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SUPPLEMENTARY INFORMATION

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Decarboxylative sp^3 C–N coupling via dual copper and photoredox catalysis

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Supplementary Information

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1. General Information

Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.[1] All solvents were purified according to the method of Grubbs.[2] Ir(F-Meppy)$_2$(dtbbpy)PF_6 was prepared using literature procedures.[3] Ir(ppy)$_3$ was purchased from Sigma-Aldrich and used as received. Iodomesitylene diacetate was purchased from TCI and used as received. All of the carboxylic acids, *N*-nucleophiles, copper salts, ligands, and bases were used as received. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using a water bath. Chromatographic purification of products was accomplished using forced-flow chromatography on silica gel (Fluka, 230–400 mesh) according to the method of Still.[4] Thin-layer chromatography (TLC) was performed on Silicycle 0.25 mm silica gel F-254 plates. Visualization of the developed chromatogram was performed by fluorescence quenching, $KMnO_4$ stain, or PMA stain. ^{1}H NMR spectra were recorded on a Bruker UltraShield Plus Avance III 500 MHz and are internally referenced to residual protic $CDCl_3$ (δ 7.26 ppm). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, br = broad), coupling constant (Hz), and integration. ^{13}C NMR spectra were recorded on a Bruker UltraShield Plus Avance III 500 MHz (125 MHz) and data are reported in terms of chemical shift relative to $CDCl_3$ (77.16 ppm). ^{19}F NMR spectra were recorded on a Bruker NanoBay 300 MHz (282 MHz) and a Bruker Avance NanoBay 400 MHz (376 MHz). IR spectra were recorded on a Perkin Elmer Spectrum 100 FTIR spectrometer and are reported in wavenumbers (cm^{-1}). High Resolution Mass Spectra were obtained from the Princeton University Mass Spectral Facility.

Some abbreviations used:

CuTC: copper(I) thiophene-2-carboxylate

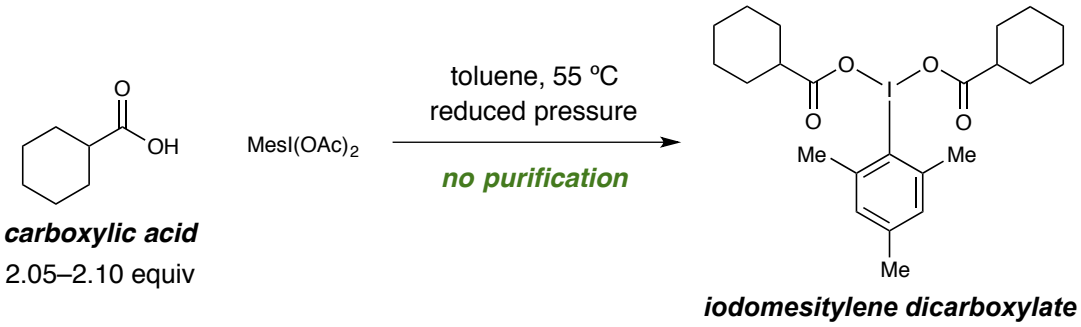
BTMG: 2-*tert*-butyl-1,1,3,3-tetramethylguanidine

BTTP: *tert*-Butylimino-tri(pyrrolidino)phosphorane

BPhen: 4,7-diphenyl-1,10-phenanthroline

dOMe-Phen: 4,7-dimethoxy-1,10-phenanthroline

2. Preparation of Iodomesitylene Dicarboxylates



carboxylic acid
2.05–2.10 equiv

iodomesitylene dicarboxylate

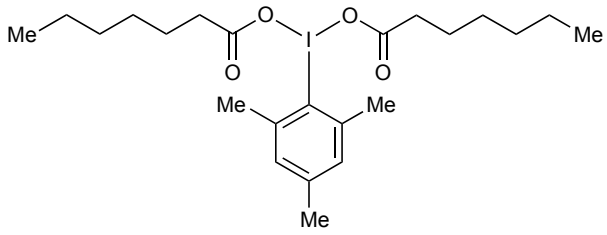
Preparation (without purifiacation):

A 500 mL round-bottom flask was charged with iodomesitylene diacetate (10 mmol), carboxylic acid (20.5–21 mmol, 2.05–2.10 equiv.), and 200 mL toluene. The flask was attached to a rotary evaporator with the water bath heated to 55 ºC and the solvent (and the generated acetic acid) was removed over a time period of ~10 min. A second 150 mL aliquot of toluene was added to the flask and the evaporation step was repeated. Repeat the evaporation step for two more times with 100 mL toluene each time.

The products are typically generated in >99% yield. After further removal of residual toluene under high-vac, these iodomesitylene dicarboxylates can be directly used in the decarboxylative sp^3 C–N coupling reactions *without purification*.

Storage:

In general, the iodomesitylene dicarboxylates synthesized can be stored in a capped vial under air at room temperature for 1–2 weeks. However, we typically stored these iodomesitylene dicarboxylates in a capped vial at a –20 ºC freezer. Under such conditions, the shelf life can be prolonged to at least 1–2 months.



Iodomesitylene diheptanoate

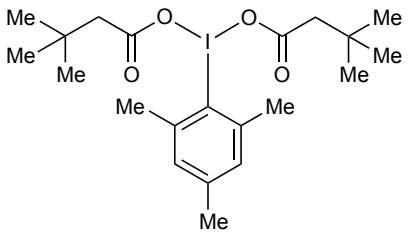
Colorless oil. Prepared following the general procedure outlined above using heptanoic acid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (s, 2H), 2.69 (s, 6H), 2.33 (s, 3H), 2.19 (t, *J* = 7.5 Hz, 4H), 1.51-1.45 (m, 4H), 1.27-1.15 (m, 12H), 0.83 (t, *J* = 7.0 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.0, 143.0, 141.3, 129.9, 128.9, 34.1, 31.5, 28.9, 26.7, 25.8, 22.6, 21.2, 14.1.

IR (film) ν_{max} 2927, 2857, 1651, 1229, 1169, 849 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{23}H_{37}INaO_4$ ($[M+Na]^+$) 527.1629, found 527.1657.



Iodomesitylene bis(3,3-dimethylbutanoate)

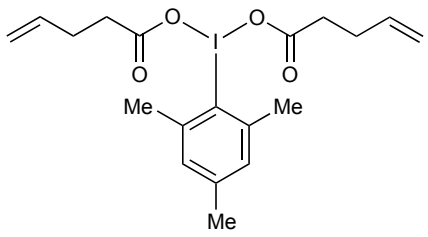
Colorless oil. Prepared following the general procedure outlined above using 3,3-dimethylbutanoic acid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (s, 2H), 2.69 (s, 6H), 2.32 (s, 3H), 2.10 (s, 4H), 0.90 (s, 18H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 177.7, 142.9, 141.2, 130.0, 128.8, 47.8, 30.7, 29.6, 26.9, 21.2.

IR (film) ν_{max} 2954, 2868, 1645, 1228, 1128, 850, 737 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{21}H_{33}INaO_4$ ($[M+Na]^+$) 499.1316, found 499.1317.



Iodomesitylene bis(pent-4-enoate)

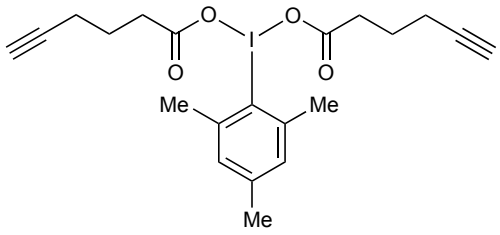
Colorless oil. Prepared following the general procedure outlined above using 4-pentenoic acid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (s, 2H), 5.73 (ddt, *J* = 16.3, 10.2, 6.2 Hz, 2H), 4.99-4.88 (m, 4H), 2.69 (s, 6H), 2.35 (s, 3H), 2.33-2.21 (m, 8H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 178.1, 143.2, 141.4, 137.1, 129.8, 129.0, 115.2, 33.3, 29.8, 26.8, 21.3.

IR (film) ν_{max} 2979, 2921, 1649, 1443, 1358, 1269, 1244, 1177, 999, 914, 851 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{19}H_{25}INaO_4$ ($[M+Na]^+$) 467.0690, found 467.0715.



Iodomesitylene bis(hex-5-ynoate)

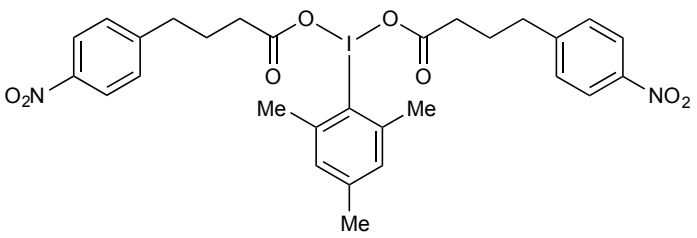
Colorless oil. Prepared following the general procedure outlined above using 5-hexynoic acid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (s, 2H), 2.70 (s, 6H), 3.26-2.32 (m, 7H), 2.14 (td, *J* = 7.0, 2.6 Hz, 4H), 1.91 (t, *J* = 2.6 Hz, 2H), 1.7-1.69 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 178.1, 143.3, 141.4, 129.8, 129.1, 83.6, 69.0, 32.7, 26.8, 24.5, 21.3, 17.9.

IR (film) ν_{max} 3292, 2938, 1731, 1651, 1450, 1375, 1318, 1301, 1232, 1157, 1035, 1000, 851 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{21}H_{25}INaO_4$ ($[M+Na]^+$) 491.0690, found 491.0684.



Iodomesitylene bis(4-(4-nitrophenyl)butanoate)

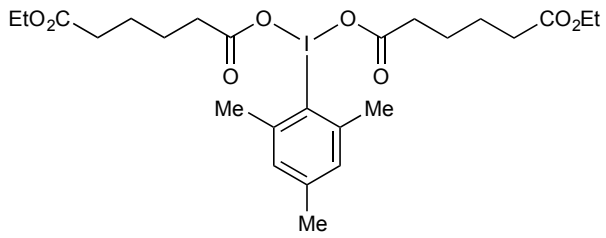
Pale yellow solid. Prepared following the general procedure outlined above using 4-(4-nitrophenyl)butanoic acid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.7 Hz, 4H), 7.24 (d, *J* = 8.7 Hz, 4H), 7.10 (s, 2H), 2.70 (s, 6H), 2.67-2.62 (m, 4H), 2.35 (s, 3H), 2.25 (t, *J* = 7.2 Hz, 4H), 1.87 (p, *J* = 7.3 Hz, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 178.1, 149.6, 146.5, 143.5, 141.4, 129.9, 129.3, 129.1, 123.7, 35.0, 33.1, 26.87, 26.85, 21.3.

IR (film) ν_{max} 2936, 2863, 1649, 1599, 1514, 1342, 1229, 850, 699 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{29}H_{31}IN_2NaO_8$ ($[M+Na]^+$) 685.1017, found 685.0999.



Iodomesitylene diethyl *O*,*O'*-diadipate

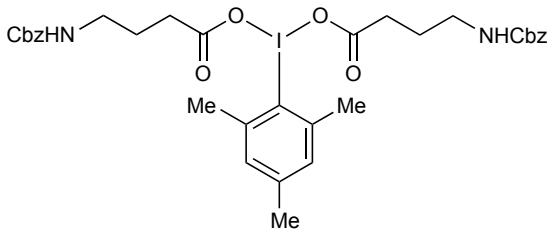
Colorless oil. Prepared following the general procedure outlined above using 6-ethoxy-6-oxohexanoic acid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (s, 2H), 4.07 (q, *J* = 7.0 Hz, 4H), 2.67 (s, 6H), 2.33 (s, 3H), 2.23-2.19 (m, 8H), 1.56-1.49 (m, 8H), 1.21 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 178.4, 173.5, 143.2, 141.4, 129.8, 129.0, 60.3, 34.0, 33.6, 26.7, 25.2, 24.5, 21.2, 14.3.

IR (film) ν_{max} 2952, 1731, 1652, 1372, 1180, 1031, 852 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{25}H_{37}INaO_8$ ($[M+Na]^+$) 615.1425, found 615.1450.



Iodomesitylene bis(4-(((benzyloxy)carbonyl)amino)butanoate)

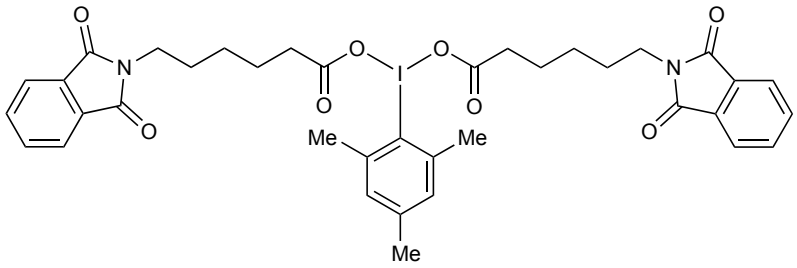
White solid. Prepared following the general procedure outlined above using 4-(((benzyloxy)carbonyl)amino)butanoic acid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.29 (m, 10H), 7.06 (s, 2H), 5.11 (brs, 2H), 5.05 (s, 4H), 3.12 (q, J = 6.5 Hz, 4H), 2.66 (s, 6H), 2.33 (s, 3H), 2.24 (t, J = 7.2 Hz, 4H), 1.71 (p, J = 6.9 Hz, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 178.2, 156.4, 143.3, 141.3, 136.6, 129.6, 129.0, 128.5, 128.1, 128.0, 66.5, 40.4, 31.1, 26.7, 25.7, 21.2.

IR (film) ν_{max} 3334, 2942, 1700, 1648, 1526, 1239, 1013, 736, 697 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{33}H_{39}IN_2NaO_8$ ($[M+Na]^+$) 741.1643, found 741.1667.



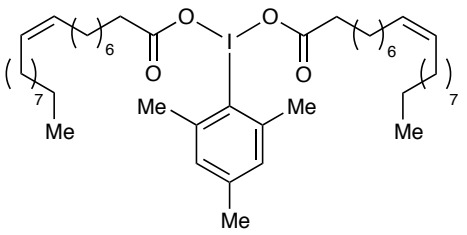
Iodomesitylene bis(6-(1,3-dioxoisoindolin-2-yl)hexanoate)

Colorless oil. Prepared following the general procedure outlined above using 6-(1,3-dioxoisoindolin-2-yl)hexanoic acid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 5.4, 3.0 Hz, 4H), 7.65 (dd, *J* = 5.4, 3.0 Hz, 4H), 7.04 (s, 2H), 3.56 (t, *J* = 7.3 Hz, 4H), 2.65 (s, 6H), 2.29 (s, 3H), 2.16 (t, *J* = 7.4 Hz, 4H), 1.56 (p, *J* = 7.5 Hz, 4H), 1.50 (p, *J* = 7.6 Hz, 4H), 1.21 (p, *J* = 7.8 Hz, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 178.4, 168.3, 143.0, 141.2, 133.8, 132.0, 129.8, 128.9, 123.1, 37.7, 33.7, 28.2, 26.6, 26.3, 25.2, 21.1.

IR (film) ν_{max} 2936, 2862, 1705, 1648, 1395, 1188, 1045, 913, 717 cm^{-1}.



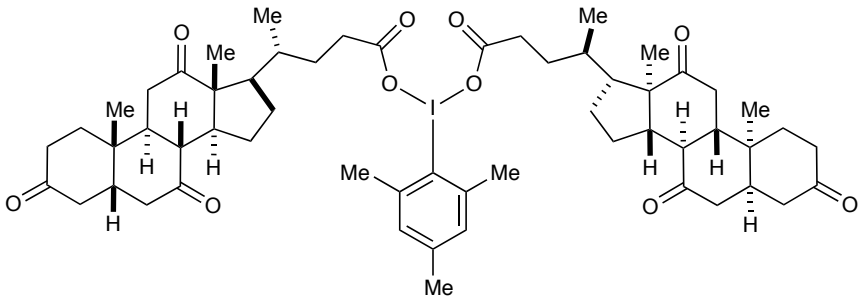
Iodomesitylene dioleate

Colorless oil. Prepared following the general procedure outlined above using oleic acid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (s, 2H), 5.38-5.27 (m, 4H), 2.70 (s, 6H), 2.34 (s, 3H), 2.20 (t, *J* = 7.5 Hz, 4H), 2.03-1.94 (m, 8H), 1.37-1.15 (m, 44H), 0.87 (t, *J* = 6.9 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.1, 143.1, 141.4, 130.3, 129.9, 129.0, 34.2, 32.0, 29.9, 29.8, 29.7, 29.5, 29.30, 29.25, 27.34, 27.33, 27.30, 26.8, 25.9, 22.8, 21.3, 14.3.

IR (film) ν_{max} 2923, 2853, 1711, 1654, 1460, 1195, 849, 723 cm^{-1}.



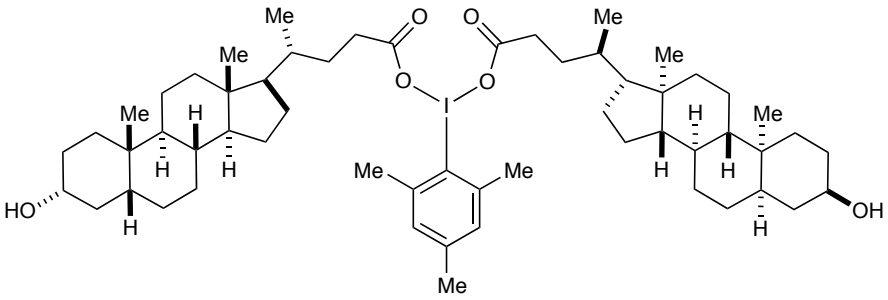
Iodomesitylene didehydrocholate

White solid. Prepared following the general procedure outlined above using dehydrocholic acid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (s, 2H), 2.91-2.76 (m, 6H), 2.67 (s, 6H), 2.35-2.05 (m, 27H), 2.03-1.87 (m, 10H), 1.37 (s, 6H), 1.27-1.13 (m, 8H), 1.00 (s, 6H), 0.73 (d, *J* = 6.4 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 212.1, 209.3, 208.9, 179.2, 143.1, 141.3, 129.7, 129.0, 56.9, 51.8, 49.0, 46.9, 45.7, 45.6, 45.0, 42.8, 38.7, 36.5, 36.1, 35.6, 35.3, 31.29, 31.26, 27.6, 26.8, 25.2, 22.0, 21.3, 18.6, 11.9.

IR (film) ν_{max} 2958, 1707, 1648, 1273, 1250, 734 cm^{-1}.



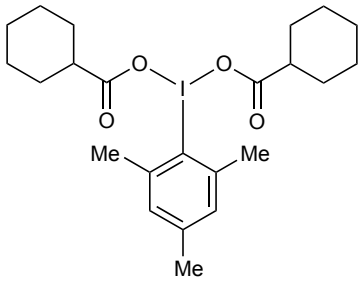
Iodomesitylene dilithocholate

White solid. Prepared following the general procedure outlined above using lithocholic acid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (s, 2H), 3.65-3.56 (m, 2H), 2.69 (s, 6H), 2.34 (s, 3H), 2.28-2.20 (m, 2H), 2.17-2.08 (m, 2H), 1.93-1.60 (m, 14H), 1.55-1.45 (m, 4H), 1.42-0.94 (m, 36H), 0.90 (s, 6H), 0.81 (d, J = 6.5 Hz, 6H), 0.57 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.5, 143.0, 141.4, 129.8, 129.0, 71.9, 56.6, 56.1, 42.8, 42.2, 40.5, 40.2, 36.5, 35.9, 35.5, 35.4, 34.7, 31.8, 31.1, 30.6, 28.2, 27.3, 26.8, 26.5, 24.3, 23.5, 21.3, 20.9, 18.3, 12.1.

IR (film) ν_{max} 3375, 2928, 2863, 1648, 1448, 1377, 1328, 1266, 1170, 1031, 736 cm^{-1}.



Iodomesitylene dicyclohexanecarboxylate

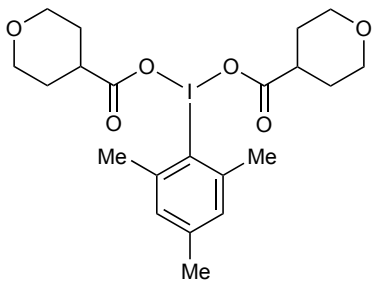
White solid. Prepared following the general procedure outlined above using cyclohexanecarboxylic acid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (s, 2H), 2.64 (s, 6H), 2.29 (s, 3H), 2.16 (tt, *J* = 11.2, 3.5 Hz, 2H), 1.73-1.68 (m, 4H), 1.64-1.47 (m, 6H), 1.31-1.24 (m, 4H), 1.18-1.01 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 181.0, 142.6, 141.1, 129.6, 128.7, 43.2, 29.6, 26.4, 25.7, 25.5, 21.0.

IR (film) ν_{max} 2927, 2853, 1738, 1644, 1448, 1367, 1174, 1132, 848, 730 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{23}H_{33}INaO_4$ ($[M+Na]^+$) 523.1316, found 523.1323.



Iodomesitylene bis(tetrahydro-2*H*-pyran-4-carboxylate)

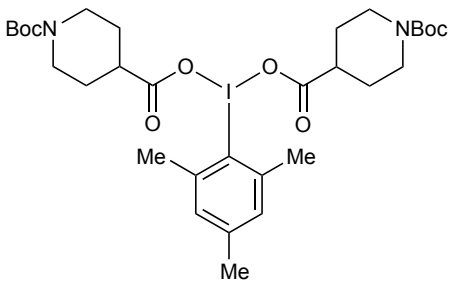
White solid. Prepared following the general procedure outlined above using tetrahydro-2*H*-pyran-4-carboxylic acid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 (s, 2H), 3.80-3.66 (m, 4H), 3.22 (td, *J* = 11.2, 2.6 Hz, 4H), 2.59 (s, 6H), 2.34 (tt, *J* = 10.4, 4.3 Hz, 2H), 2.24 (s, 3H), 1.64-1.47 (m, 8H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.0, 142.8, 140.9, 129.7, 128.7, 66.8, 39.6, 29.0, 26.3, 20.9.

IR (film) ν_{max} 2953, 2845, 1729, 1647, 1277, 1192, 1130, 1036, 866, 824 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{21}H_{29}INaO_6$ ($[M+Na]^+$) 527.0901, found 527.0925.



Iodomesitylene 1,1'-di-*tert*-butyl *O*'^{4},*O*^{4}-bis(piperidine-1,4-dicarboxylate)

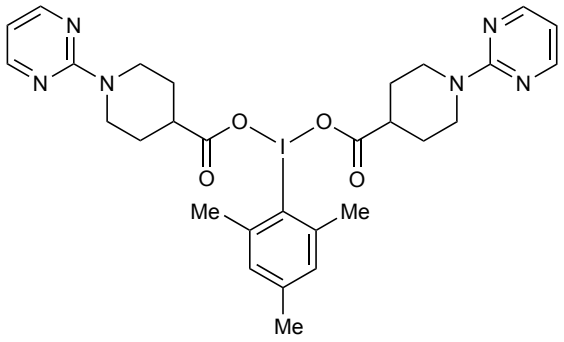
Pale yellow syrup. Prepared following the general procedure outlined above using 1-(*tert*-butoxycarbonyl)piperidine-4-carboxylic acid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 (s, 2H), 3.78 (brs, 4H), 2.65 (brs, 4H), 2.58 (s, 6H), 2.28-2.22 (m, 2H), 2.25 (s, 3H), 1.64-1.61 (m, 4H), 1.46-1.36 (m, 4H), 1.31 (s, 18H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.1, 154.4, 142.9, 140.9, 129.6, 128.8, 79.2, 43.4, 40.8, 28.3, 28.2, 26.4, 21.0.

IR (film) ν_{max} 2975, 2929, 1685, 1420, 1162, 1030, 732 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{31}H_{47}IN_2NaO_8$ ($[M+Na]^+$) 725.2269, found 725.2271.



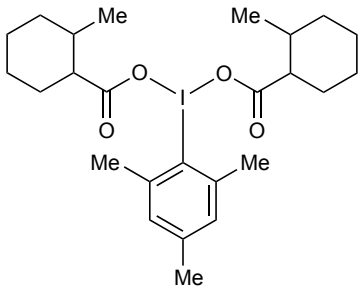
Iodomesitylene bis(1-(pyrimidin-2-yl)piperidine-4-carboxylate)

Yellow syrup. Prepared following the general procedure outlined above using 1-(pyrimidin-2-yl)piperidine-4-carboxylic acid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 4.7 Hz, 4H), 6.98 (s, 2H), 6.32 (t, *J* = 4.7 Hz, 2H), 4.42 (d, *J* = 13.5 Hz, 4H), 2.95-2.82 (m, 4H), 2.61 (s, 6H), 2.41 (tt, *J* = 10.7, 3.7 Hz, 2H), 2.24 (s, 3H), 1.80-1.71 (m, 4H), 1.56-1.46 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.3, 161.2, 157.5, 142.9, 141.0, 129.7, 128.8, 109.3, 43.1, 41.2, 28.3, 26.4, 21.0.

IR (film) ν_{max} 2938, 2855, 1725, 1584, 1445, 1360, 1174, 981, 946, 795 cm^{-1}.



Iodomesitylene bis(2-methylcyclohexane-1-carboxylate)

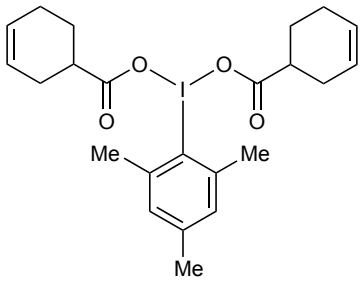
Pale yellow solid. Prepared following the general procedure outlined above using 2-methylcyclohexane-1-carboxylic acid (mixture of *trans* and *cis*).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04 (s, 2H), 2.68 (s, 6H), 2.39 (dt, *J* = 9.2, 4.2 Hz, 2H), 2.31 (s, 3H), 2.00-1.89 (m, 2H), 1.61-1.10 (m, 16H), 0.75 (d, *J* = 4.4 Hz, 3H), 0.73 (d, *J* = 4.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 180.17, 180.15, 142.8, 142.7, 141.3, 141.2, 130.1, 130.0, 128.8, 128.7, 51.7, 46.2, 34.9, 34.4, 31.8, 31.6, 30.4, 26.69, 26.66, 26.62, 25.9, 25.6, 24.7, 24.6, 21.6, 21.2, 20.7, 15.3.

IR (film) ν_{max} 2925, 2854, 1737, 1645, 1446, 1186, 911, 729 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{25}H_{37}INaO_4$ ($[M+Na]^+$) 551.1629, found 551.1650.



Iodomesitylene bis(cyclohex-3-ene-1-carboxylate)

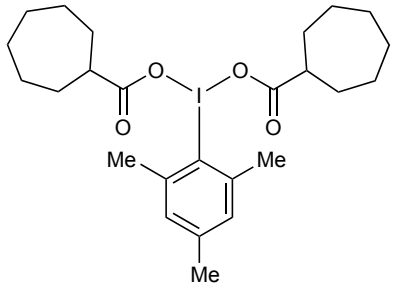
White solid. Prepared following the general procedure outlined above using cyclohex-3-ene-1-carboxylic acid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03 (s, 2H), 5.56-5.51 (m, 4H), 2.65 (s, 6H), 2.41 (ddt, *J* = 10.6, 7.6, 3.8 Hz, 2H), 2.29 (s, 3H), 2.11-2.03 (m, 4H), 1.97-1.87 (m, 4H), 1.86-1.77 (m, 2H), 1.58-1.44 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 180.6, 142.7, 141.1, 129.7, 128.7, 126.4, 125.3, 39.1, 27.9, 26.4, 25.5, 24.4, 21.0.

IR (film) ν_{max} 3024, 2921, 2840, 1704, 1647, 1300, 1222, 1170, 999, 849 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{23}H_{29}INaO_4$ ($[M+Na]^+$) 519.1003, found 519.1046.



Iodomesitylene dicycloheptanecarboxylate

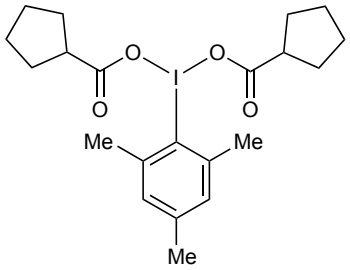
White solid. Prepared following the general procedure outlined above using cycloheptanecarboxylic acid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00 (s, 2H), 2.62 (s, 6H), 2.32 (tt, *J* = 9.2, 4.2 Hz, 2H), 2.27 (s, 3H), 1.75-1.70 (m, 4H), 1.57-1.54 (m, 4H), 1.50-1.27 (m, 16H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 181.8, 142.5, 141.0, 129.4, 128.6, 45.0, 31.3, 28.0, 26.4, 26.2, 21.0.

IR (film) ν_{max} 2920, 2855, 1646, 1454, 1191, 849, 741 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{25}H_{37}INaO_4$ ($[M+Na]^+$) 551.1629, found 551.1655.



Iodomesitylene dicyclopentanecarboxylate

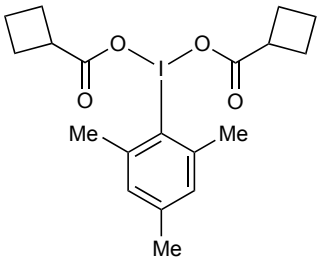
White solid. Prepared following the general procedure outlined above using cyclopentanecarboxylic acid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04 (s, 2H), 2.66 (s, 6H), 2.59 (p, *J* = 7.9 Hz, 2H), 2.30 (s, 3H), 1.75-1.53 (m, 12H), 1.47-1.42 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 181.6, 142.7, 141.2, 129.7, 128.8, 43.6, 30.5, 26.5, 25.6, 21.1.

IR (film) ν_{max} 2952, 2868, 1738, 1645, 1450, 1362, 1205, 849 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{21}H_{29}INaO_4$ ($[M+Na]^+$) 495.1003, found 495.1025.



Iodomesitylene dicyclobutanecarboxylate

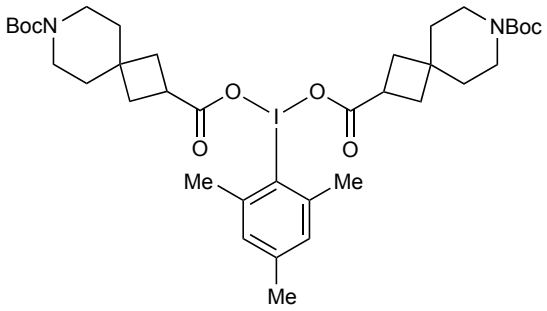
White solid. Prepared following the general procedure outlined above using cyclobutanecarboxylic acid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04 (s, 2H), 3.00 (p, *J* = 8.3 Hz, 2H), 2.67 (s, 6H), 2.31 (s, 3H), 2.17-2.01 (m, 8H), 1.89-1.73 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 180.4, 142.9, 141.3, 129.7, 128.9, 37.7, 26.6, 26.0, 21.2, 18.4.

IR (film) ν_{max} 2971, 2945, 1737, 1645, 1357, 1186, 1037, 850 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{19}H_{25}INaO_4$ ($[M+Na]^+$) 467.0690, found 467.0702.

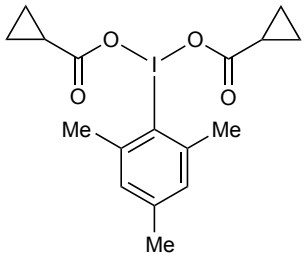


Iodomesitylene 7,7'-di-*tert*-butyl *O*'^{2},*O*^{2}-bis(7-azaspiro[3.5]nonane-2,7-dicarboxylate) White solid. Prepared following the general procedure outlined above using 7-(tert-butoxycarbonyl)-7-azaspiro[3.5]nonane-2-carboxylic acid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 (s, 2H), 3.21-3.15 (m, 4H), 3.15-3.08 (m, 4H), 2.87 (p, *J* = 8.6 Hz, 2H), 2.60 (s, 6H), 2.24 (s, 3H), 1.88-1.75 (m, 8H), 1.39-1.35 (m, 4H), 1.33 (s, 18H), 1.31-1.28 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 180.7, 155.0, 143.1, 141.3, 130.0, 129.0, 79.4, 40.7, 35.5, 34.5, 31.4, 28.5, 26.7, 21.2.

IR (film) ν_{max} 2974, 2927, 1686, 1421, 1365, 1242, 1172, 964, 731 cm^{-1}.



Iodomesitylene dicyclopropanecarboxylate

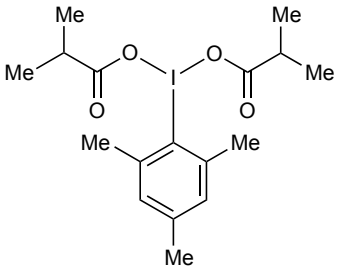
White solid. Prepared following the general procedure outlined above using cyclopropanecarboxylic acid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (s, 2H), 2.68 (s, 6H), 2.33 (s, 3H), 1.49-1.44 (m, 2H), 0.85-0.82 (m, 4H), 0.73-0.65 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.7, 143.0, 141.3, 129.8, 128.9, 26.7, 21.2, 12.1, 8.6.

IR (film) ν_{max} 3015, 2971, 1734, 1637, 1377, 1207, 1173, 1026, 940, 851 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{17}H_{21}INaO_4$ ($[M+Na]^+$) 439.0377, found 439.0392.



Iodomesitylene bis(2-methylpropanoate)

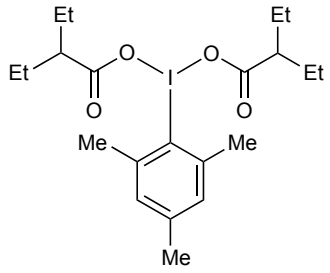
White solid. Prepared following the general procedure outlined above using isobutyric acid. 3.0 equiv of isobutyric acid was used.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (s, 2H), 2.69 (s, 6H), 2.44 (dt, *J* = 14.1, 7.0 Hz, 2H), 2.34 (s, 3H), 1.03 (d, *J* = 7.0 Hz, 12H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 182.2, 142.9, 141.3, 129.9, 128.9, 34.1, 26.6, 21.3, 19.7.

IR (film) ν_{max} 2971, 2931, 1649, 1464, 1212, 1159, 844 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{17}H_{25}INaO_4$ ($[M+Na]^+$) 443.0690, found 443.0704.



Iodomesitylene bis(2-ethylbutanoate)

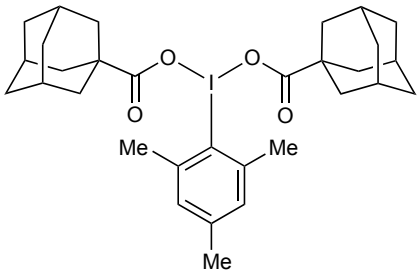
White solid. Prepared following the general procedure outlined above using 2-ethylbutanoic acid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04 (s, 2H), 2.69 (s, 6H), 2.31 (s, 3H), 2.12-2.07 (m, 2H), 1.44 (dq, *J* = 15.2, 7.5 Hz, 4H), 1.39-1.30 (m, 4H), 0.73 (t, *J* = 7.5 Hz, 12H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 181.1, 142.9, 141.3, 130.2, 128.7, 49.2, 26.6, 25.6, 21.2, 11.9.

IR (film) ν_{max} 2962, 2932, 1738, 1646, 1458, 1372, 1201, 809 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{21}H_{33}INaO_4$ ($[M+Na]^+$) 499.1316, found 499.1349.



Iodomesitylene bis(adamantane-1-carboxylate)

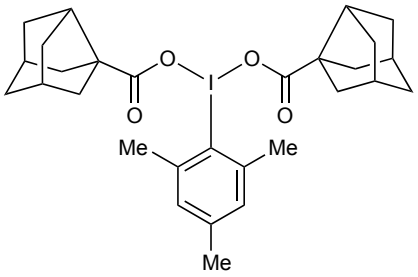
White solid. Prepared following the general procedure outlined above using 1-adamantanecarboxylic acid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (s, 2H), 2.69 (s, 6H), 2.36 (s, 3H), 1.92 (s, 6H), 1.76 (d, *J* = 2.7 Hz, 12H), 1.67-1.60 (m, 12H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 182.7, 142.4, 141.4, 129.8, 128.8, 41.3, 39.5, 36.6, 28.2, 26.5, 21.3.

IR (film) ν_{max} 2904, 2850, 1735, 1637, 1452, 1229, 1075, 907, 798, 729, 678 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{31}H_{41}INaO_4$ ($[M+Na]^+$) 627.1942, found 627.1967.



Iodomesitylene bis(3-noradamantanecarboxylate)

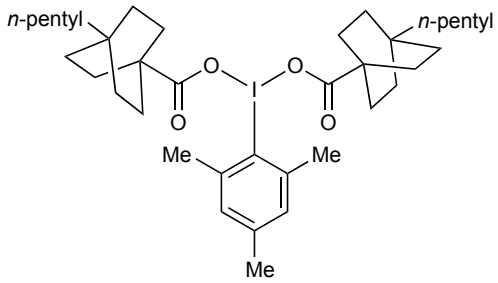
White solid. Prepared following the general procedure outlined above using 3-noradamantanecarboxylic acid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00 (s, 2H), 2.67 (s, 6H), 2.44 (t, *J* = 6.7 Hz, 2H), 2.30 (s, 3H), 2.14 (s, 4H), 1.87 (d, *J* = 10.0 Hz, 4H), 1.69-1.58 (m, 8H), 1.52-1.42 (m, 8H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 182.4, 142.4, 141.2, 130.1, 128.7, 53.6, 47.3, 44.1, 43.6, 37.4, 34.6, 26.4, 21.1.

IR (film) ν_{max} 2923, 2869, 1735, 1638, 1459, 1200, 1107, 910, 778, 729 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{29}H_{37}INaO_4$ ($[M+Na]^+$) 599.1629, found 599.1631.



Iodomesitylene bis(4-pentylbicyclo[2.2.2]octane-1-carboxylate)

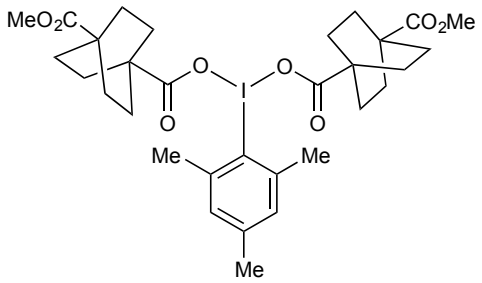
White solid. Prepared following the general procedure outlined above using 4-pentylbicyclo[2.2.2]octane-1-carboxylic acid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (s, 2H), 2.64 (s, 6H), 2.32 (s, 3H), 1.68-1.47 (m, 12H), 1.27-1.22 (m, 15H), 1.17-1.07 (m, 9H), 1.02-0.95 (m, 4H), 0.82 (t, J = 7.2 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 183.1, 142.4, 141.3, 129.9, 128.7, 41.5, 39.4, 32.8, 30.7, 30.2, 29.2, 26.5, 23.3, 22.7, 21.2, 14.1.

IR (film) ν_{max} 2921, 2858, 1740, 1645, 1455, 1377, 1231, 907, 731 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{37}H_{57}INaO_4$ ($[M+Na]^+$) 715.3194, found 715.3213.



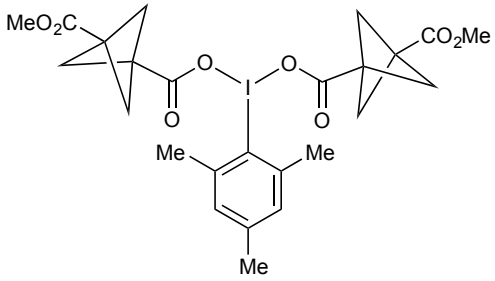
Iodomesitylene *O*'[1],*O*[1]-4,4'-dimethyl bis(bicyclo[2.2.2]octane-1,4-dicarboxylate) White solid. Prepared following the general procedure outlined above using 4-(methoxycarbonyl)bicyclo[2.2.2]octane-1-carboxylic acid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (s, 2H), 3.55 (s, 6H), 2.61 (s, 6H), 2.30 (s, 3H), 1.66 (d, J = 9.7 Hz, 12H), 1.61 (d, J = 9.4 Hz, 12H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 182.1, 177.9, 142.7, 141.2, 129.8, 128.8, 51.6, 38.9, 38.5, 28.2, 27.9, 26.4, 21.2.

IR (film) ν_{max} 2951, 2871, 1726, 1642, 1369, 1244, 1075, 854, 730 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{31}H_{41}INaO_8$ ($[M+Na]^+$) 691.1738, found 691.1746.



Iodomesitylene *O*$^{1'}$,*O*^{1}-3,3'-dimethyl bis(bicyclo[1.1.1]pentane-1,3-dicarboxylate) White solid. Prepared following the general procedure outlined above using 3-(methoxycarbonyl)bicyclo[1.1.1]pentane-1-carboxylic acid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (s, 2H), 3.64 (s, 6H), 2.67 (s, 6H), 2.36 (s, 3H), 2.17 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.2, 170.0, 143.4, 141.6, 130.1, 129.2, 53.2, 51.9, 37.7, 36.8, 26.6, 21.3.

IR (film) ν_{max} 2971, 1733, 1365, 1296, 1214, 1029 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{25}H_{29}INaO_8$ ($[M+Na]^+$) 607.0799, found 607.0802.

3. Control Experiments and Scope of Non-Photonic Protocol

3.1 Procedure for Control Experiments and Non-Photonic Protocol

All of the reactions shown in this section were performed on 0.10 mmol scale.

For control experiments and optimization studies:

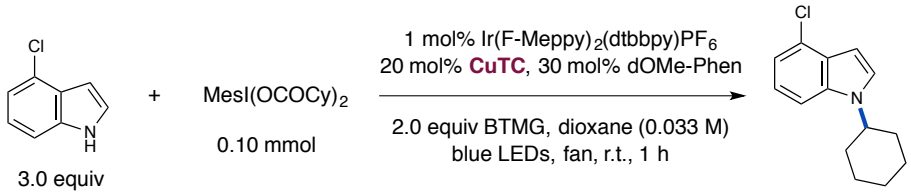
To an 8 mL vial equipped with a stir bar was added photocatalyst Ir(F-Meppy)$_2$(dtbbpy)PF$_6$, *N*-nucleophile, copper salt, ligand, and iodomesitylene dicyclohexanecarboxylate. Dioxane was added and then base was added to the mixture. Next, the solution was degassed by sparging with nitrogen for 5 minutes before sealing with parafilm. The reaction was stirred and irradiated using 34 W blue LED lamps (3 cm away, with cooling fan to keep the reaction at room temperature) for 1 hour. The reaction was quenched by exposure to air and analyzed by ^{1}H NMR after the addition of an internal standard (mesitylene).

For *non-photonic* copper-only protocol:

To an 8 mL vial equipped with a stir bar was added *N*-nucleophile, copper salt, ligand, and iodomesitylene dicarboxylate. Dioxane was added and then base was added to the mixture. Next, the solution was degassed by sparging with nitrogen for 5 minutes before sealing with parafilm. The reaction was stirred for 1 hour at room temperature. The reaction was quenched by exposure to air and analyzed by ^{1}H NMR after the addition of an internal standard (mesitylene).

If the iodomesitylene dicarboxylate is a liquid, a solution of the iodomesitylene dicarboxylate in dioxane was used instead.

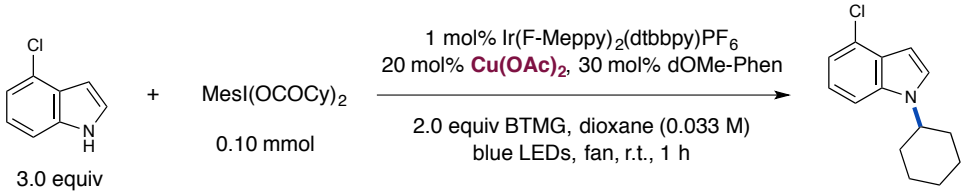
3.2 Control Experiments



Entry	Deviations from standard	Yield*
1	none	60%
2	no CuTC	<1%
3	no photocatalyst, light only	11%
4	no photocatalyst, no light	7%
5	no ligand	11%
6	no base	<1%

*Yields calculated by ^{1}H NMR with an internal standard.

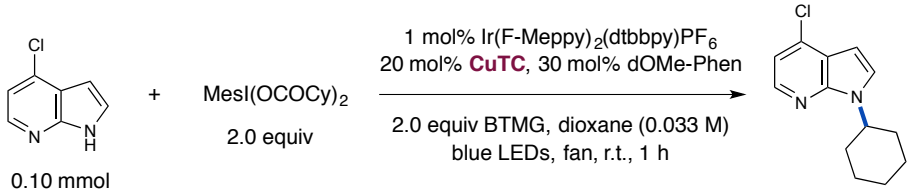
Figure S1 | Indole substrate with CuTC



Entry	*Deviations from standard*	Yield*
1	none	56%
2	no $Cu(OAc)_2$	<1%
3	no photocatalyst, light only	7%
4	no photocatalyst, no light	<1%
5	no ligand	8%
6	no base	8%

*Yields calculated by ^{1}H NMR with an internal standard.

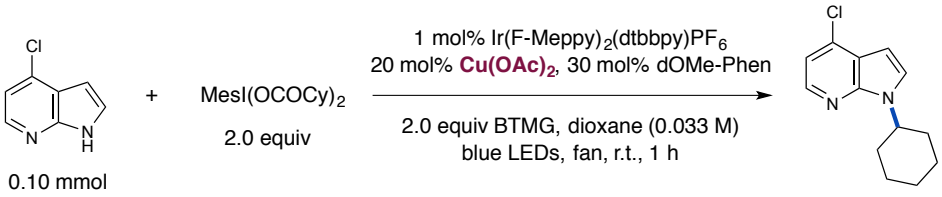
Figure S2 | Indole substrate with $Cu(OAc)_2$



Entry	Deviations from standard	Yield*
1	none	**76%**
2	no CuTC	**<1%**
3	no photocatalyst, light only	**50%**
4	no photocatalyst, no light	**47%**
5	no ligand	**6%**
6	no base	**6%**

*Yields calculated by ^{1}H NMR with an internal standard.

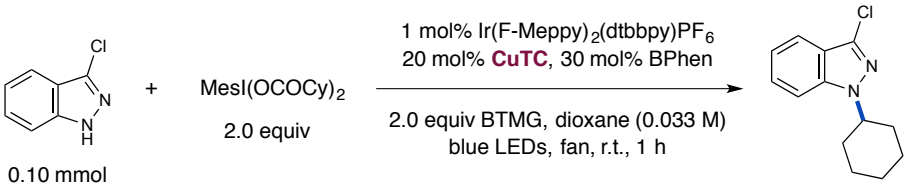
Figure S3 | Azaindole substrate with CuTC



Entry	Deviations from standard	Yield*
1	none	**67%**
2	no $Cu(OAc)_2$	**<1%**
3	no photocatalyst, light only	**11%**
4	no photocatalyst, no light	**<1%**
5	no ligand	**9%**
6	no base	**17%**

*Yields calculated by ^{1}H NMR with an internal standard.

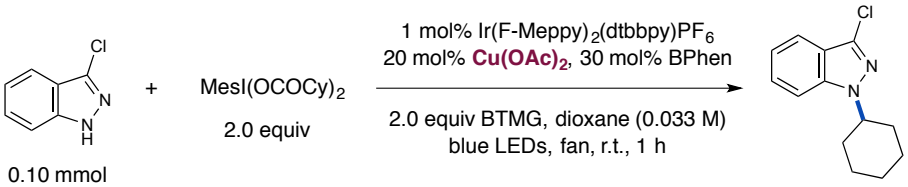
Figure S4 | Azaindole substrate with $Cu(OAc)_2$



Entry	Deviations from standard	Yield*
1	none	**90%**
2	no CuTC	**<1%**
3	no photocatalyst, light only	**86%**
4	no photocatalyst, no light	**86%**
5	no ligand	**26%**
6	no base	**86%**

*Yields calculated by ^{1}H NMR with an internal standard.

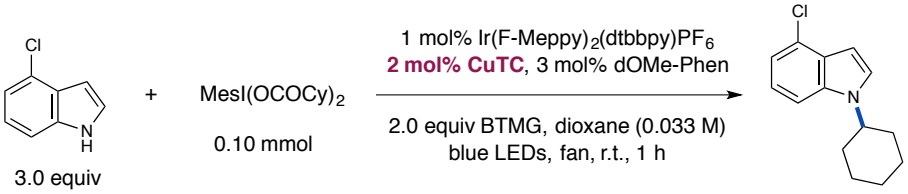
Figure S5 | Indazole substrate with CuTC



Entry	Deviations from standard	Yield*
1	none	**88%**
2	no $Cu(OAc)_2$	**<1%**
3	no photocatalyst, light only	**6%**
4	no photocatalyst, no light	**<1%**
5	no ligand	**28%**
6	no base	**84%**

*Yields calculated by ^{1}H NMR with an internal standard.

Figure S6 | Indazole substrate with $Cu(OAc)_2$



Entry	Deviations from standard	Yield*
1	none	41%
2	no photocatalyst, no light	<1%

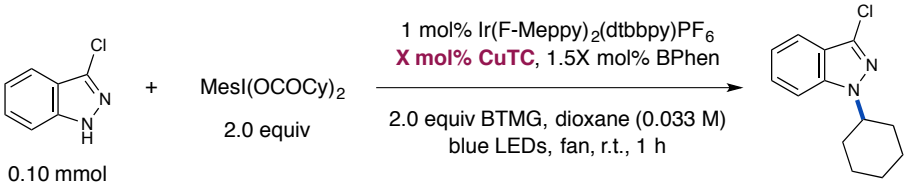
*Yields calculated by ^{1}H NMR with an internal standard.

Figure S7 | Indazole substrate with 2 mol% CuTC

Entry	Deviations from standard	Yield*
1	none	37%
2	no photocatalyst, no light	<1%

*Yields calculated by ^{1}H NMR with an internal standard.

Figure S8 | Azaindole substrate with 2 mol% CuTC

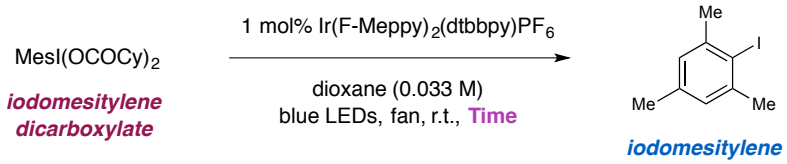


Entry	X mol% CuTC	Yield*	Yield* no photocatalyst, no light
1	20	90%	86%
2	10	88%	74%
3	5	80%	8%
4	2	64%	<1%

*Yields calculated by ^{1}H NMR with an internal standard.

Figure S9 | Indazole substrate with different copper loadings

As shown in **Figures S2**, **S4**, and **S6** (entry 3 vs. entry 4), although non-photonic conditions [with copper(II) catalyst, no photocatalyst and no light] fail to produce any product, irradiation with blue LEDs in the absence of a photocatalyst can still generate a small amount of product. These results are in consistent with a minor reaction pathway in which the photocatalyst can facilitate the homolysis of the I–O bond of iodomesitylene dicarboxylate under the irradiation with blue LEDs, presumably via an energy transfer mechanism between the the photocatalyst and the iodomesitylene dicarboxylate[5–7]. Without the photocatslyst, the degradation of iodomesitylene dicarboxylate is significantly slower but still observable after 1 hour. This is consistent with the results from the degradation experiments shown in **Figure S10.**

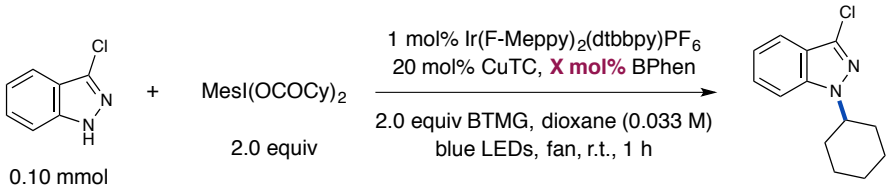


Entry	Condition	Time	Iodomesitylene dicarboxylate	Iodomesitylene
1	without photocatalyst	5 min	>95%	<1%
2	without photocatalyst	15 min	91%	4%
3	without photocatalyst	30 min	86%	6%
4	without photocatalyst	1 h	82%	11%
5	with photocatalyst	5 min	92%	5%
6	with photocatalyst	15 min	83%	11%
7	with photocatalyst	30 min	77%	18%
8	with photocatalyst	1 h	65%	26%

*Yields calculated by ^{1}H NMR with an internal standard.

Figure S10 | Light-induced degradation of iodomesitylene dicarboxylate

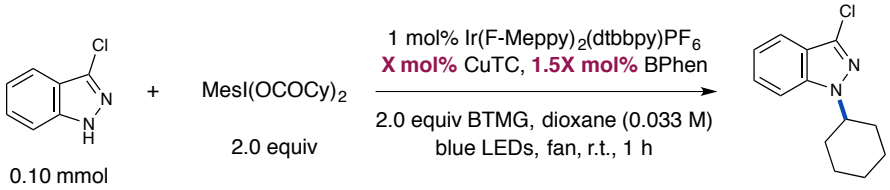
3.3 Optimization Studies



Entry	Ligand loading	Yield*
1	0 mol%	**26%**
2	20 mol%	**80%**
3	30 mol%	**90%**
4	35 mol%	**90%**

*Yields calculated by ^{1}H NMR with an internal standard.

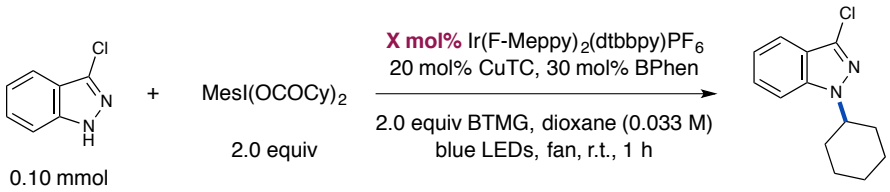
Figure S11 | Evaluation of ligand loading



Entry	Copper loading	Yield*
1	20 mol%	**90%**
2	10 mol%	**88%**
3	5 mol%	**80%**
4	2 mol%	**64%**
5	1 mol%	**52%**

*Yields calculated by ^{1}H NMR with an internal standard.

Figure S12 | Evaluation of copper loading



Entry	Photocatalyst loading	Yield*
1	1.0 mol%	**90%**
2	0.5 mol%	**86%**
3	0.2 mol%	**80%**

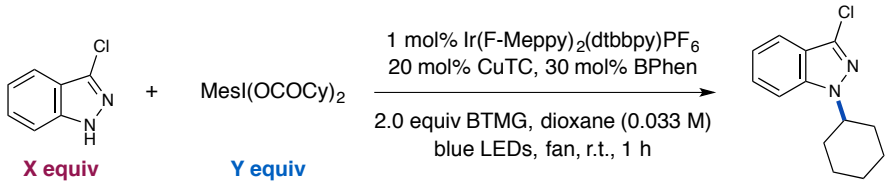
*Yields calculated by ^{1}H NMR with an internal standard.

Figure S13 | Evaluation of photocatalyst loading

Entry	Copper source	Yield*
1	CuTC	**90%**
2	CuI•0.75(Me_2S)	**80%**
3	CuI	**82%**
4	CuBr	**82%**
5	CuBr•Me_2S	**82%**
6	CuCl	**84%**
7	$CuBr_2$	**78%**
8	$CuCl_2$	**78%**
9	$Cu(OAc)_2$	**88%**
10	$Cu(acac)_2$	**76%**

*Yields calculated by ^{1}H NMR with an internal standard.

Figure S14 | Evaluation of copper source

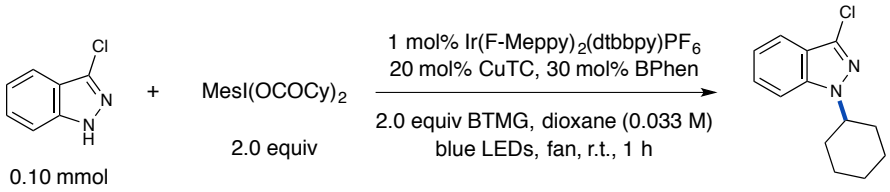


Entry	X equiv	Y equiv	Yield*
1	1.0	2.0	**90%**
2	1.0	1.5	**86%**
3	1.0	1.2	**80%**
4	1.0	1.0	**78%**
5	1.5	1.0	**78%**
6	2.0	1.0	**82%**

*Yields calculated by ^{1}H NMR with an internal standard based on the limiting reagent.

Figure S15 | Evaluation of the stoichiometry of the reactants

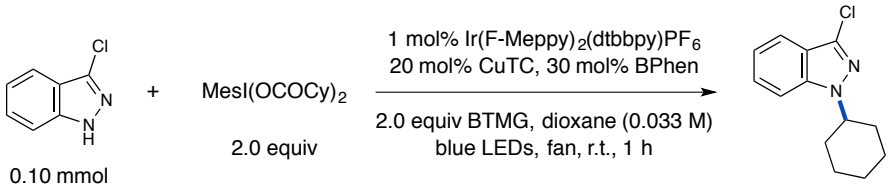
The effect of the stoichiometry of both reactants was demonstrated in **Figure S15**. For this particular *N*-nucleophile, excess amount of iodomesitylene dicarboxylate is beneficial. However, for certain other nucleophiles, using the *N*-nucleophiles in excess is beneficial. See the experimental descriptions in sections **5.3** for details. The yields of the decarboxylative coupling reactions are always calculated based on the limiting reagent employed (either the *N*-nucleophile or the iodomesitylene dicarboxylate). When *N*-nucleophiles are used in excess, after the decarboxylative C–N coupling, the remaining *N*-nucleophiles can be recovered. For two examples, see compounds **63** (page S204) and compounds **S85** (page S205).



Entry	Deviations from standard	Yield*
1	none	**90%**
2	+ 1.0 equiv. of H_2O	**80%**
3	+ 2.0 equiv. of H_2O	**78%**
4	+ 5.0 equiv. of H_2O	**72%**
5	+ 10.0 equiv. of H_2O	**58%**
6	without degassing, reaction conducted in a capped vial under air	**76%**

*Yields calculated by ^{1}H NMR with an internal standard.

Figure S16 | Evaluation of the robustness of the optimal conditions

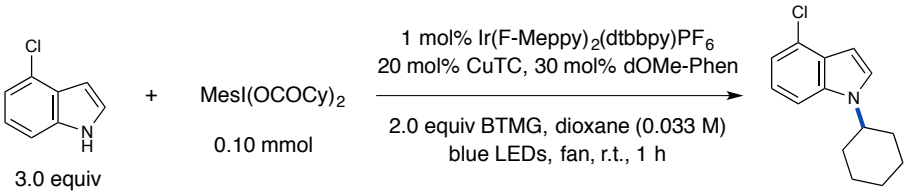


Entry	Deviations from standard	Yield*
1	none	**90%**
2	with integrated photoreactor *5 minutes*	**90%**

*Yields calculated by ^{1}H NMR with an internal standard.

Figure S17| Different light setup

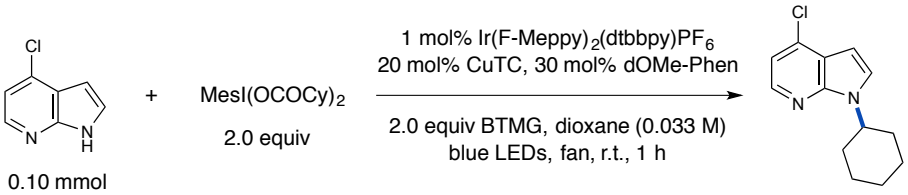
As demonstrated in **Figure S17**, performing the decarboxylative C–N coupling reaction with the assistance of the integrated photoreactor[8] gave the same efficiency compared to the standard setup. However, the reaction time can be dramatically shortened to only ***5 minutes***.



Entry	Deviations from standard	Yield*
1	none	**60%**
2	2.0 equiv PhI(OCOCy)$_2$ instead of MesI(OCOCy)$_2$	**46%**

*Yields calculated by ^{1}H NMR with an internal standard.

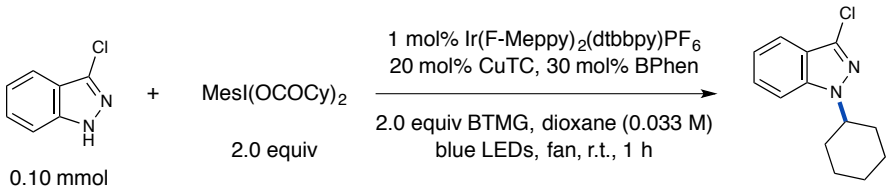
Figure S18 | Evaluation of the alkylating reagent I

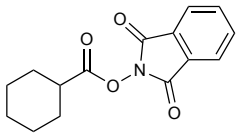


Entry	Deviations from standard	Yield*
1	none	**76%**
2	2.0 equiv PhI(OCOCy)$_2$ instead of MesI(OCOCy)$_2$	**49%**

*Yields calculated by ^{1}H NMR with an internal standard.

Figure S19| Evaluation of the alkylating reagent II

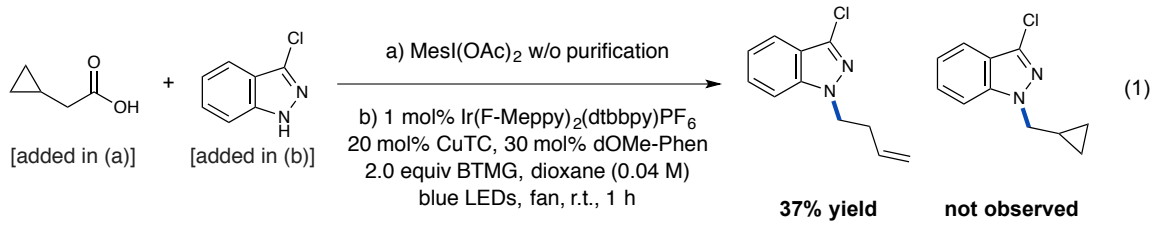


Entry	Deviations from standard	Yield*
1	none	**90%**
2	4.0 equiv CyCOOH + 2.0 equiv $MesI(OAc)_2$ formed *in situ*	**18%**
3	 2.0 equiv NHP ester instead of $MesI(OCOCy)_2$ as alkylating reagent	**<1%**

*Yields calculated by ^{1}H NMR with an internal standard.

Figure S20| Evaluation of the alkylating reagent III

As shown in **Figures S18–S20**, different alkylating reagents are surveyed for this decarboxylative C–N coupling method. Structurally related iodo*benzene* dicarboxylate gives diminished yield. In order to present a general protocol for a broad range of carboxylic acids and *N*-nucleophiles, we chose iodomesitylene dicarboxylates as the model alkylating reagents. Forming the dicarboxylates *in situ* leads to significantly lower yield. This is in consistent with the fact that $MesI(OAc)_2$ itself is a good methylating reagent (*vide infra,* see compound **13** on page S65). Additionally, the *N*-hydroxyphthalimid (NHP) ester[9,10] of the carboxylic acid did not give any C–N coupling product under our optimized conditions. Instead, acylation of the indazole was found to be the major pathway (>95% yield).



(1)

As shown in **Equation (1)** above, a primary carboxylic acid with a pendant cyclopropyl ring was employed in the decarboxylative C–N coupling reaction. The only observed C–N coupled product is the ring-opening product, which is consistent with the proposition that a primary alkyl radical was generated in the reaction.

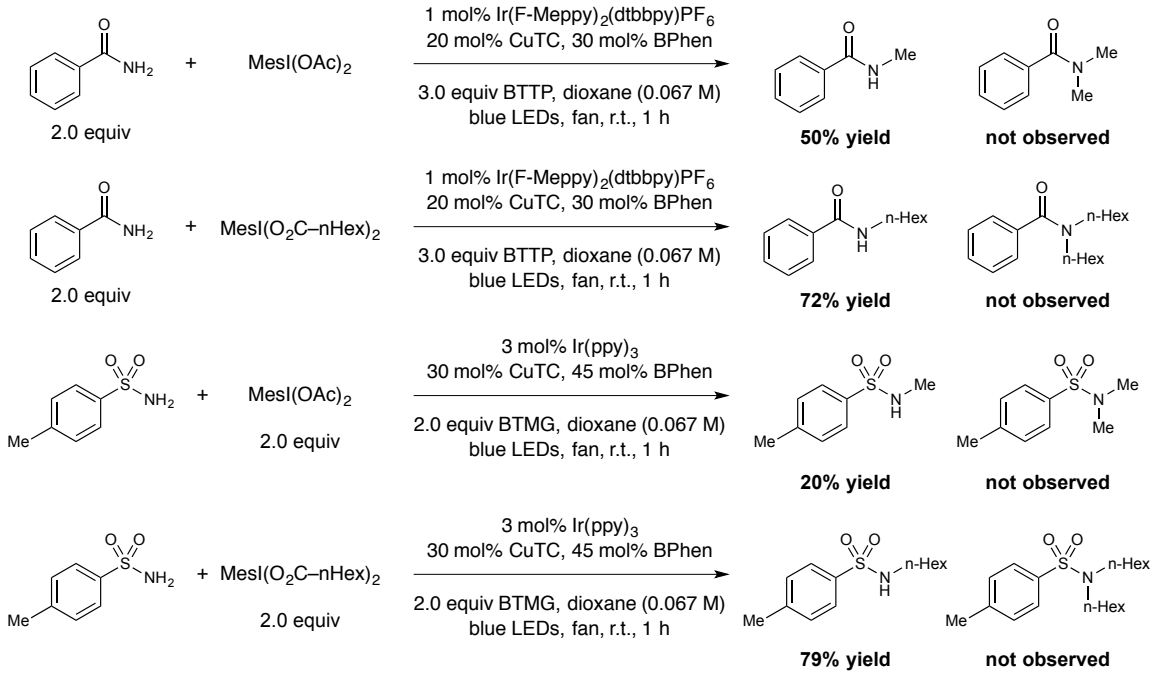


Figure S21| Amide and sulfonamide alkylation with primary alkyl acids
Yields were determined by GC analysis with an internal standard.

As shown in **Figure S21** above, two primary carboxylic acids were coupled with two nucleophiles, which have the potential to undergo dialkylations. In all cases, only monoalkylated products were observed.

3.4 Scope of Non-Photonic Protocol

General Information:

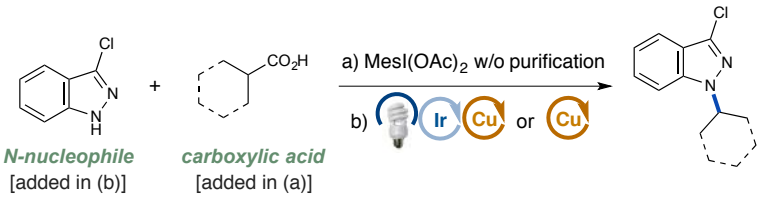
For reactions conducted using *photoredox* protocol:

See section **5.3** for experimental details. Yields were reported as isolated yields on a 0.5 mmol scale reaction unless otherwise noted.

For reactions conducted unsing *non-photonic* protocol:

Unless otherwise noted, the reaction conditions are based on the corresponding *photoredox* protocol except for the steps of adding the photocatalyst and irradiation with 34 W blue LEDs. For the experimental procedures, see section **3.1**.

All of these non-photonic reactions were conducted on 0.1 mmol scale and the yields were determined via ^{1}H-NMR studies with an internal standard unless otherwise noted.



secondary and tertiary alkyl acids

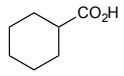
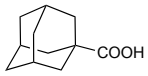
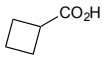
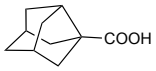
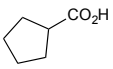
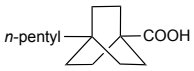
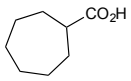
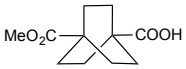
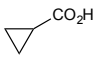
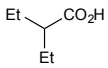
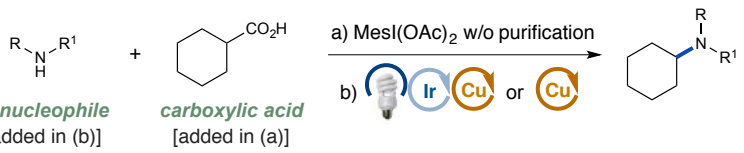
secondary acid	photoredox conditions	non-photonic conditions	tertiary acid	photoredox conditions	non-photonic conditions
	90%[a]	86%		74%	62%
	85%	80%		54%[a]	38%
	71%	56%		72%	26%[b]
	62%[a]	44%		60%	32%[c]
	44%[a]	34%		80%	20%[d]
	60%	48%			

Figure S22 | Scope of secondary and tertiary alkyl acids

[a]Yields were determined by ^{1}H-NMR studies with an internal standard on a 0.1 mmol scale reaction. [b]Reaction condition: 1 equiv indazole, 2 equiv iodomesitylene dicarboxylate, 30 mol% CuCl, 45 mol% dOMe-Phen, 2 equiv BTMG, dioxane (0.033M), r.t., 1 h. [c]Reaction condition: 1 equiv indazole, 2 equiv iodomesitylene dicarboxylate, 40 mol% CuCl, 60 mol% BPhen, 2 equiv BTMG, dioxane (0.033M), r.t., 1 h. [d]Reaction condition: 1 equiv indazole, 2 equiv iodomesitylene dicaboxylate, 40 mol% CuCl, 60 mol% BPhen, dioxane (0.033 M), r.t., 1 h.



N-nucleophiles

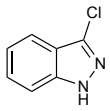
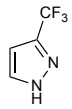
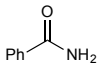
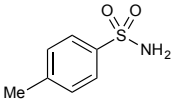
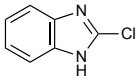
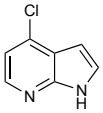
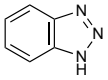
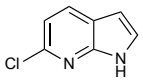
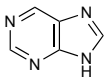
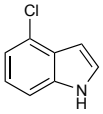
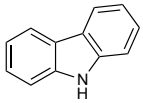
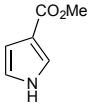
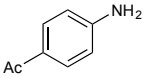
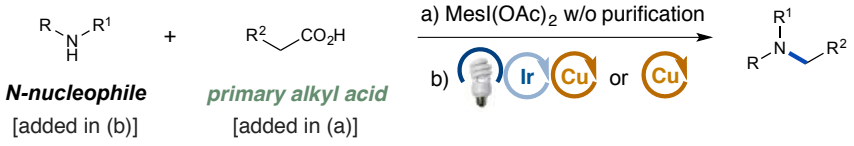
N-nucleophile	photoredox conditions	non-photonic conditions	N-nucleophile	photoredox conditions	non-photonic conditions
 indazole	90%[a]	86%	 triazole	90%	22%
 pyrazole	98%	92%	 imidazole	68%	37%
 amide	80%[b]	82%[b]	 imidazole	60%	23%
 sulfonamide	70%[b]	74%[b]	 benzimidazole	67%	19%
 azaindole	80%	47%	 benzotriazole	80%	31%
 azaindole	74%	49%	 purine	60%	17%
 indole	60%[a]	7%	 carbazole	46%	7%
 pyrrole	75%	39%	 aniline	70%	24%

Figure S23 | Scope of *N*-nucleophiles

[a]Yields were determined by ^{1}H-NMR studies with an internal standard on a 0.1 mmol scale reaction. [b]Yields were determined by GC studies with an internal standard on a 0.1 mmol scale reaction.



primary alkyl acid

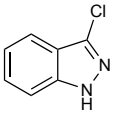
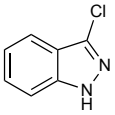
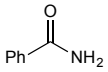
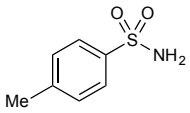
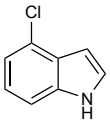
N-nucleophile	*primary alkyl acid*	***photoredox conditions***	***non-photonic conditions***
	$MeCO_2H$	**72%**[a]	**42%**
	*n*-Hex–CO_2H	**84%**	**70%**
	*n*-Hex–CO_2H	**72%**[b,c]	**52%**[b]
	*n*-Hex–CO_2H	**79%**[b,d]	**31%**[b]
	*n*-Hex–CO_2H	**56%**[a,e]	**6%**

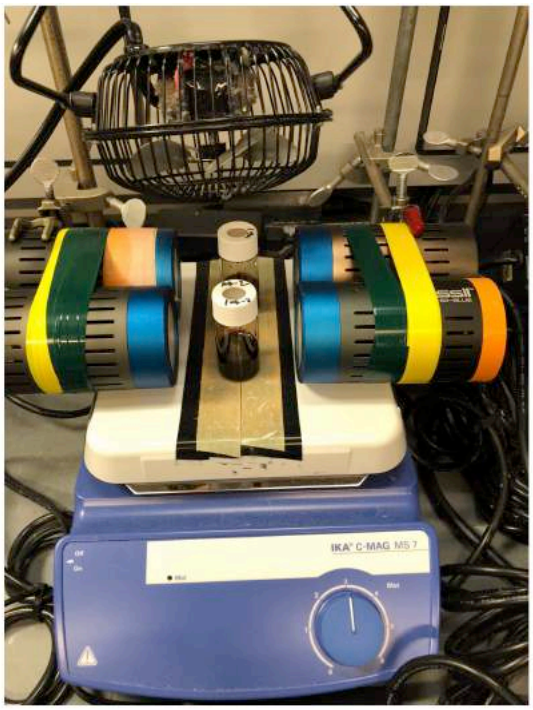
Figure S24 | Scope of primary alkyl acid

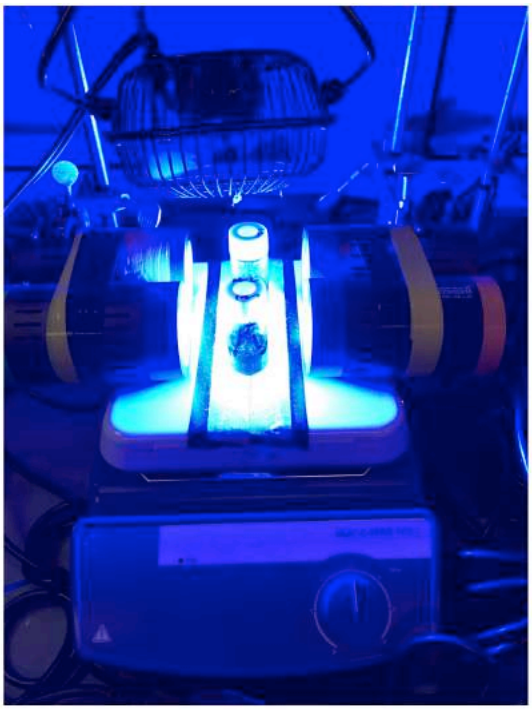
[a]Yields were determined by ^{1}H-NMR studies with an internal standard on a 0.1 mmol scale reaction. [b]Yields were determined by GC studies with an internal standard on a 0.1 mmol scale reaction. [c]Reaction condition: see compound **S64** on page S170. [d]Reaction condition: see compound **S57** on page S161. [e]Reaction condition: see compound **S23** on page S115.

4. Procedure for Decarboxylative sp^3 C–N Couplings

To a 20 mL or 40 mL vial equipped with a stir bar was added photocatalyst, *N*-nucleophile, iodomesitylene dicarboxylate, copper salt, and ligand. Dioxane was added followed by the addition of the base. The solution was sonicated for 1–3 min until it became homogeneous. Next, the solution was degassed by sparging with nitrogen for 5–10 minutes before sealing with parafilm. The reaction was stirred and irradiated using two 34 W blue LED lamps (3 cm away, with cooling fan to keep the reaction at room temperature) for 1 hour. The reaction mixture was removed from the light, cooled to ambient temperature, diluted with water (15 mL) and EtOAc (25 mL), and the aqueous layer was extracted with three portions of EtOAc (25 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography on silica gel to afford the desired decarboxylative C–N coupling product.

Note: for aniline substrates, directly mixing the *N*-nucleophile with iodomesitylene dicarboxylate neat can sometimes lead to decomposition of the nucleophiles. Therefore, a solution of aniline substrate in dioxane was used. Also, if the iodomesitylene dicarboxylate is a liquid, its solution in dioxane was used.





5. Carboxylic Acids Scope and *N*-nucleophiles Scope

5.1 Full Scope Table

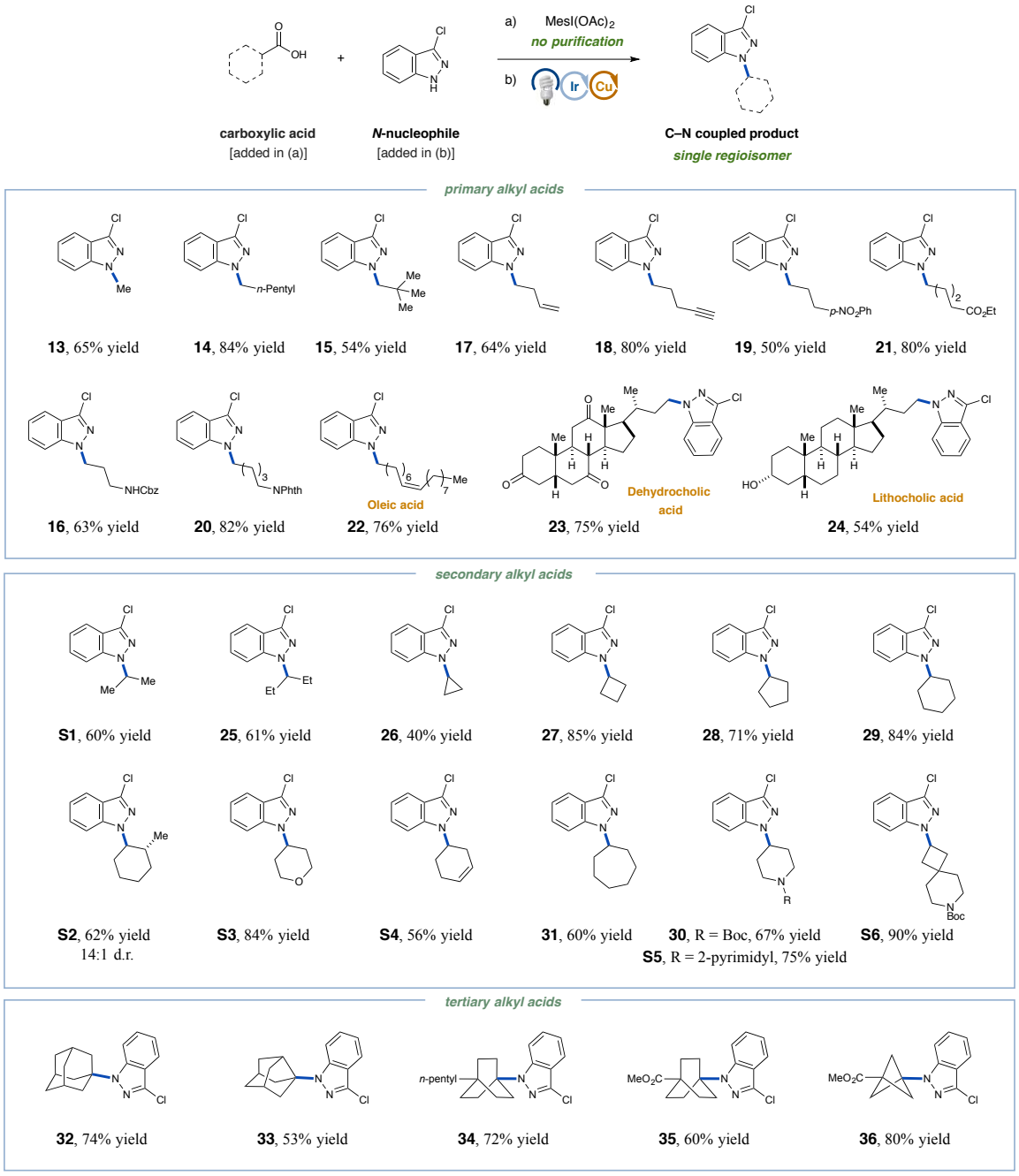


Figure S25 | Scope of carboxylic acids.

All yields are isolated yields for the decarboxylative C–N coupling step.

In all cases, only one regioisomer (>20:1 r.r.) was formed.

See **5.3** for experimental details.

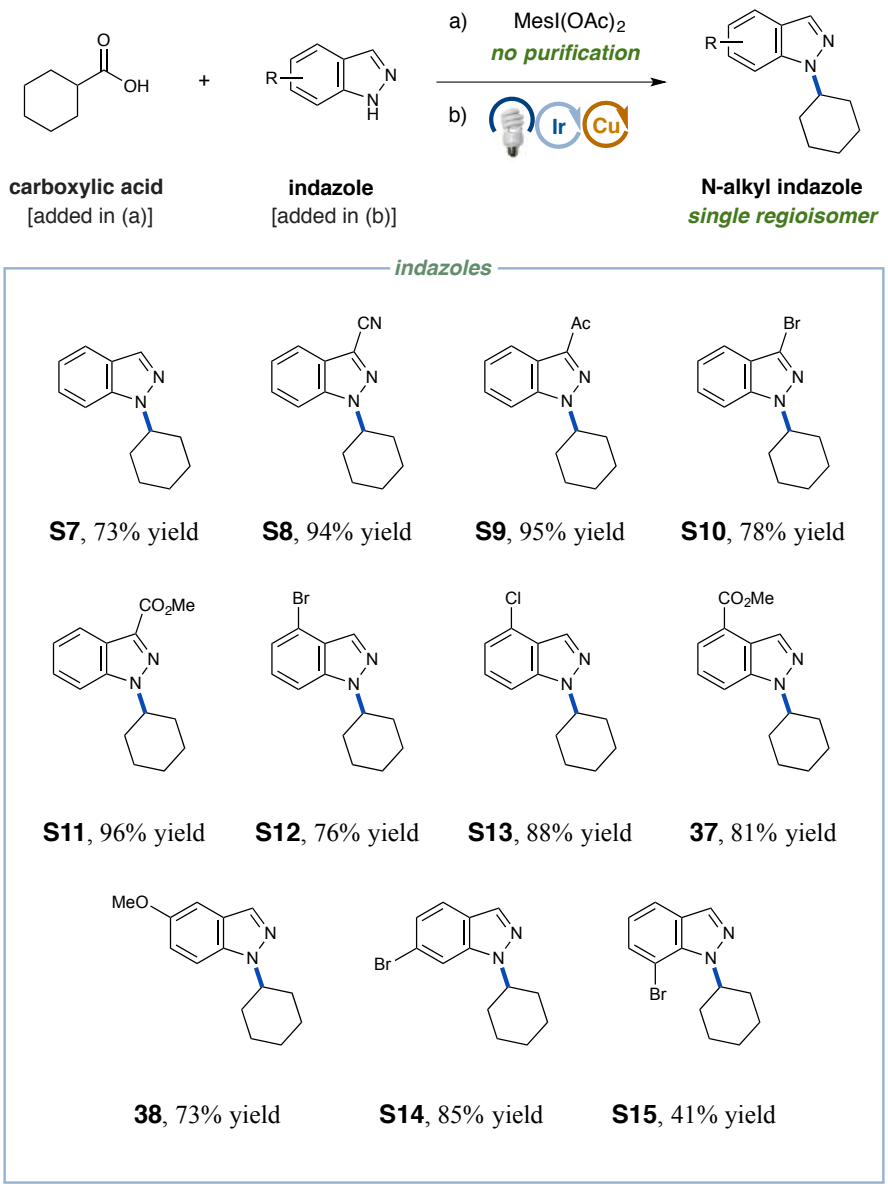


Figure S26 | Scope of indazoles.

All yields are isolated yields for the decarboxylative C–N coupling step.

In all cases, only one regioisomer (>20:1 r.r.) was formed.

See **5.3** for experimental details.

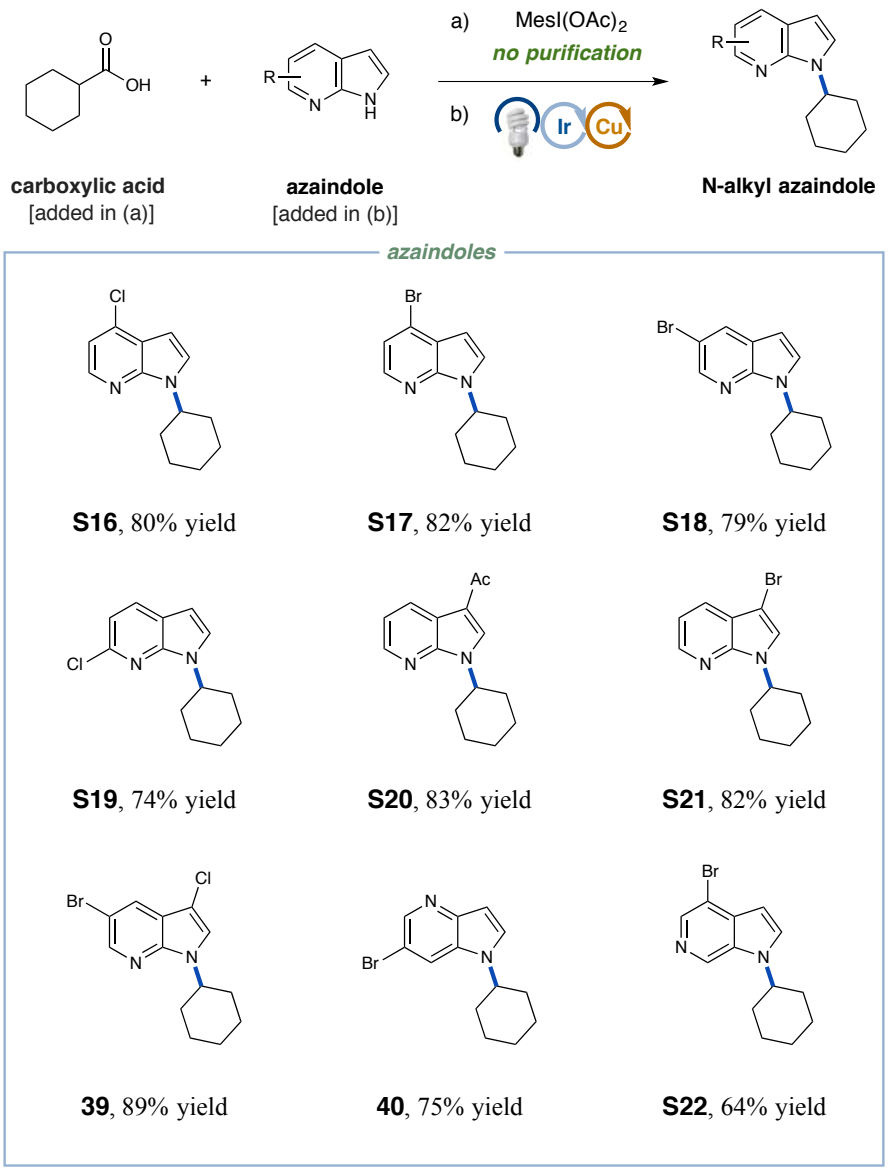


Figure S27 | Scope of azaindoles.

All yields are isolated yields for the decarboxylative C–N coupling step.

See **5.3** for experimental details.

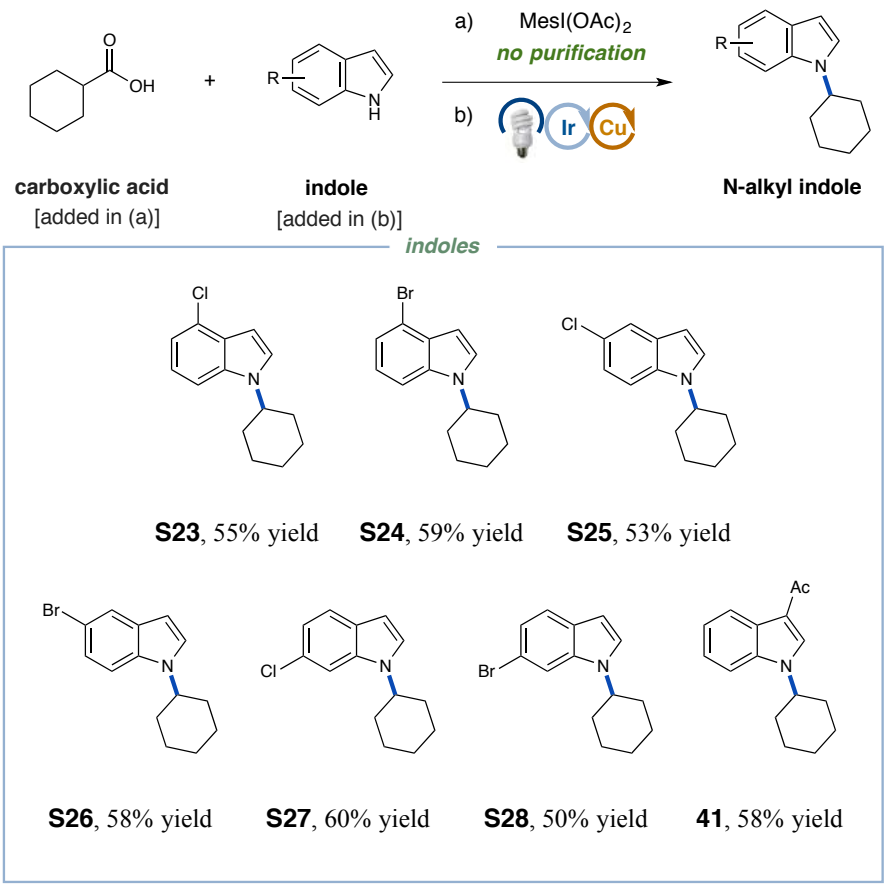


Figure S28 | Scope of indoles.

All yields are isolated yields for the decarboxylative C–N coupling step.

See **5.3** for experimental details.

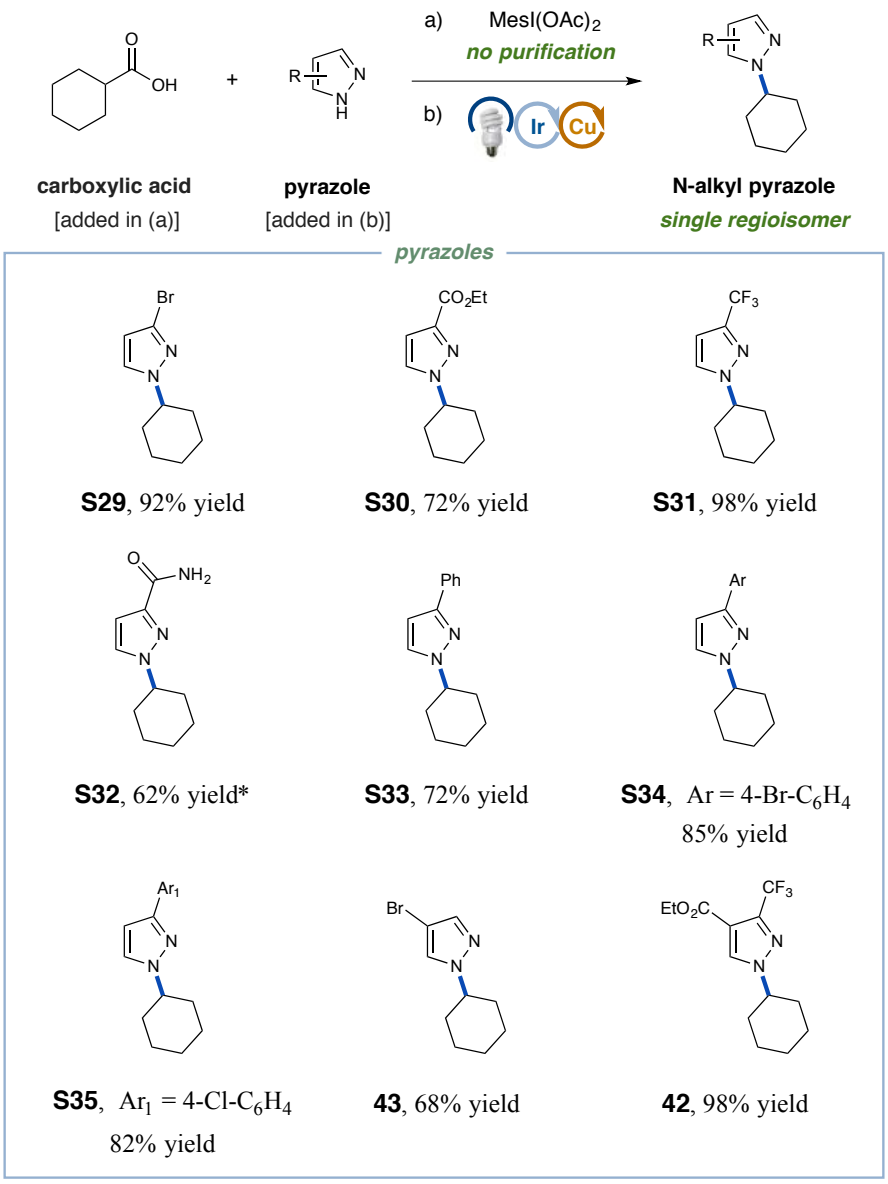


Figure S29 | Scope of pyrazoles.

All yields are isolated yields for the decarboxylative C–N coupling step.

*Alkylation only occurs at the pyrazole nitrogen.

In all cases, only one regioisomer (>20:1 r.r.) was formed.

See **5.3** for experimental details.

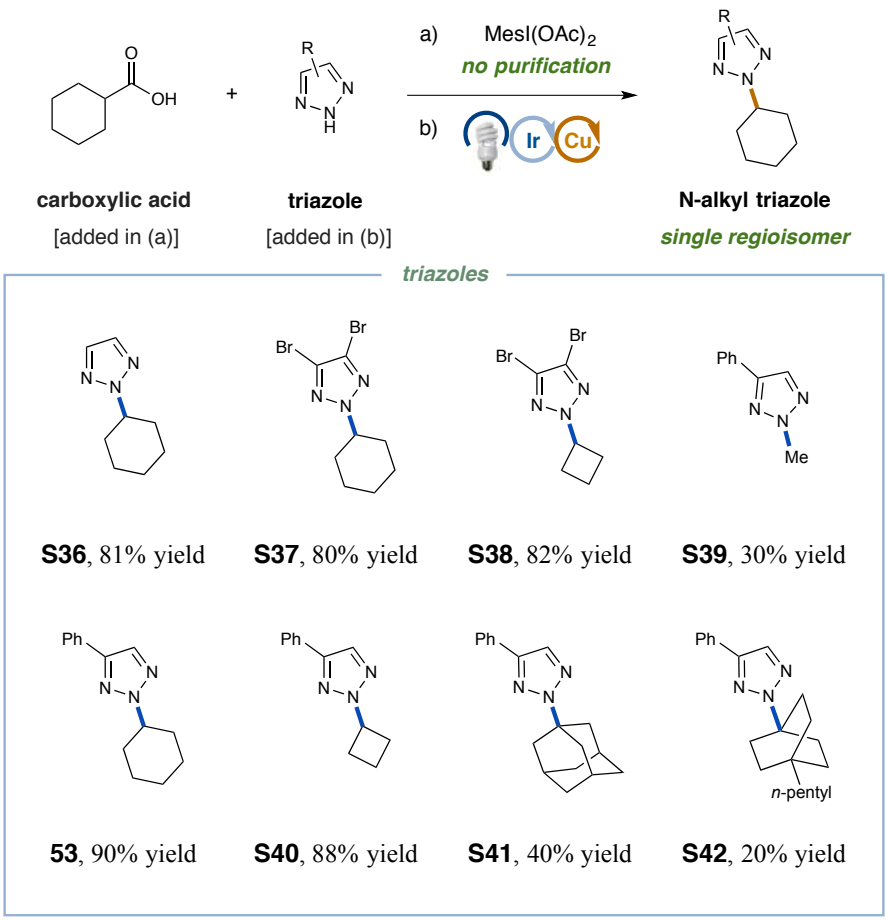


Figure S30 | Scope of triazoles.

All yields are isolated yields for the decarboxylative C–N coupling step.

In all cases, only one regioisomer (>20:1 r.r.) was formed.

See **5.3** for experimental details.

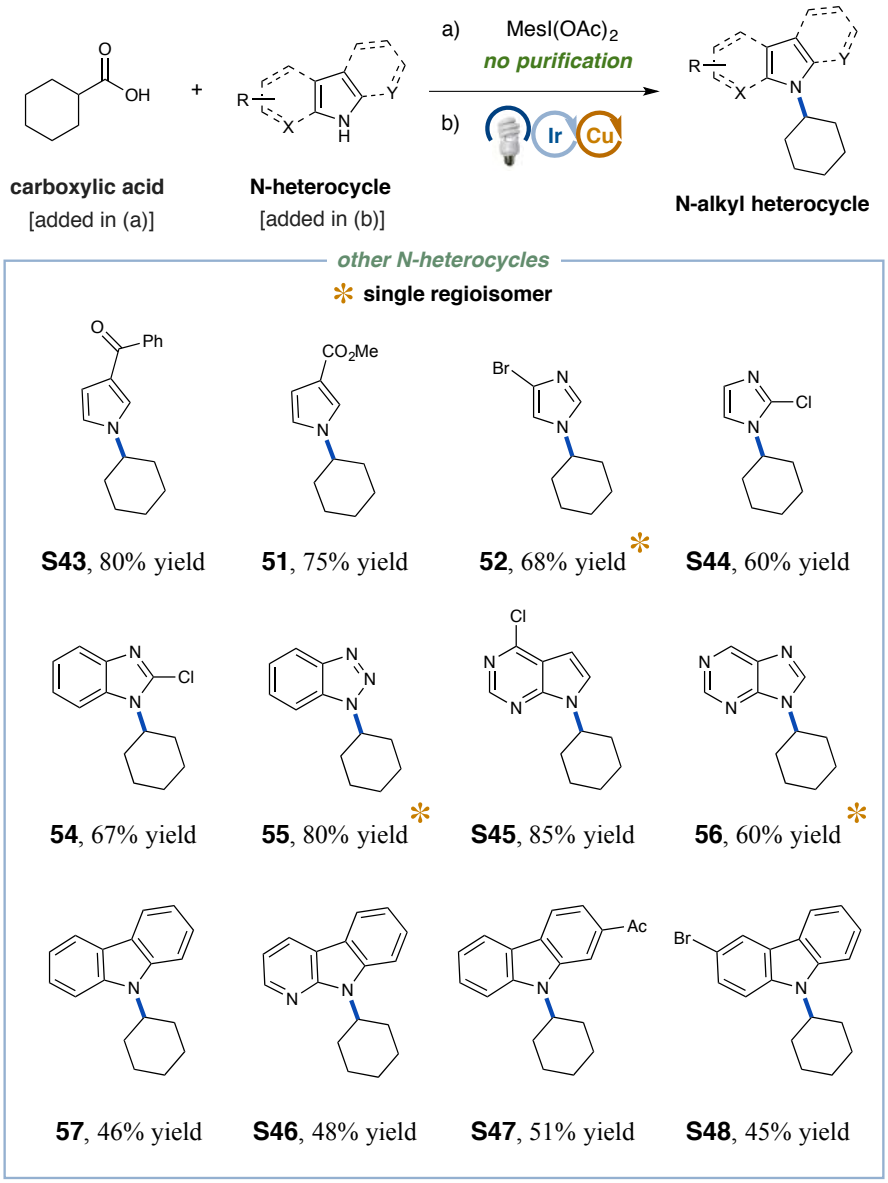


Figure S31 | Scope of other *N*-heterocycles.

All yields are isolated yields for the decarboxylative C–N coupling step.

*Only one regioisomer (>20:1 r.r.) was formed.

See **5.3** for experimental details.

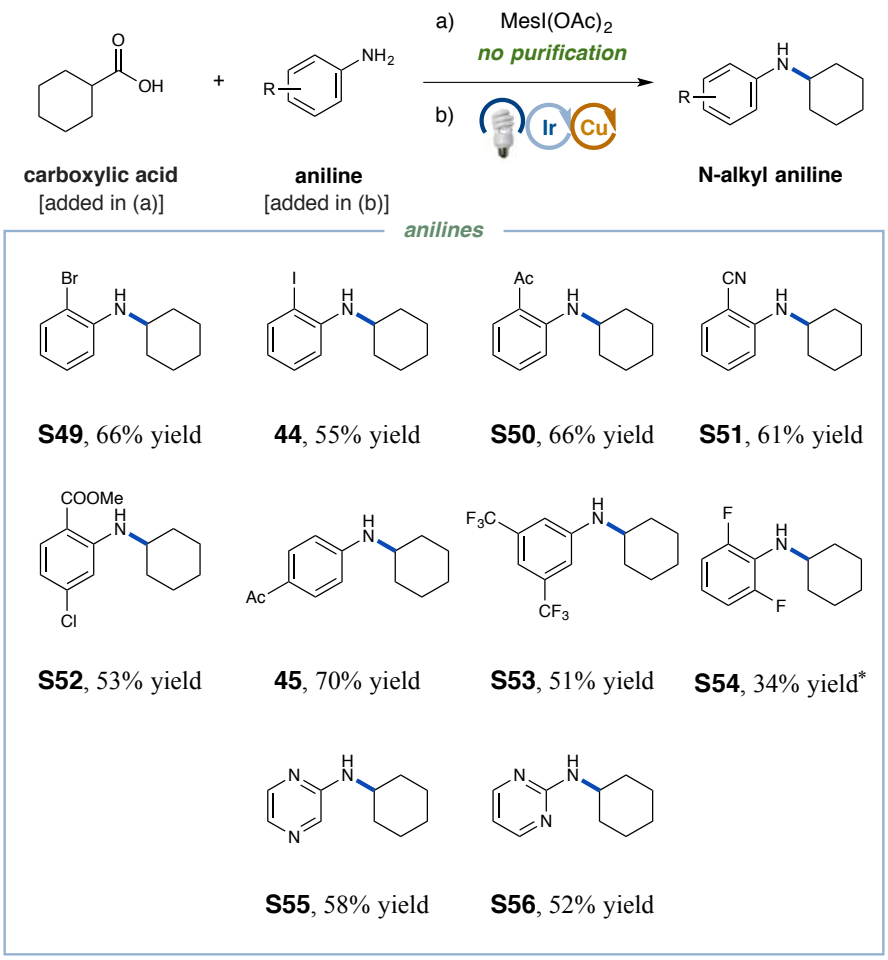


Figure S32 | Scope of anilines.

All yields are isolated yields for the decarboxylative C–N coupling step.

*Yield was calculated by ^{19}F NMR with an internal standard.

See **5.3** for experimental details.

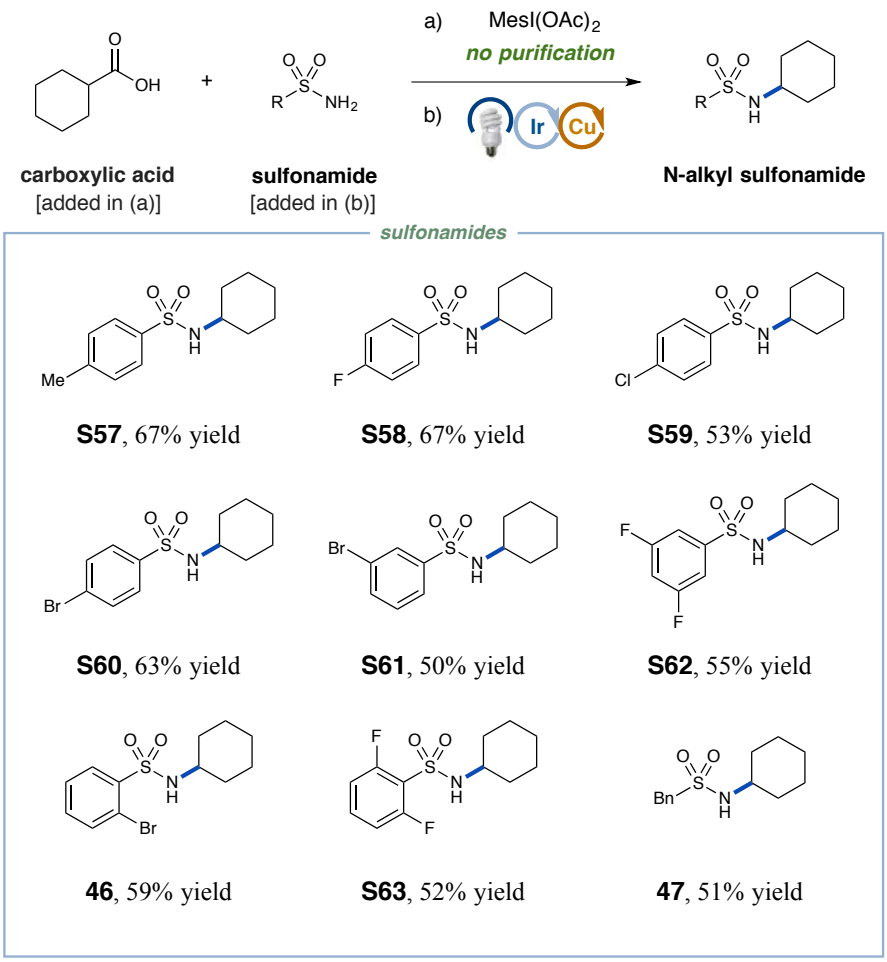


Figure S33 | Scope of sulfonamides.

All yields are isolated yields for the decarboxylative C–N coupling step.

See **5.3** for experimental details.

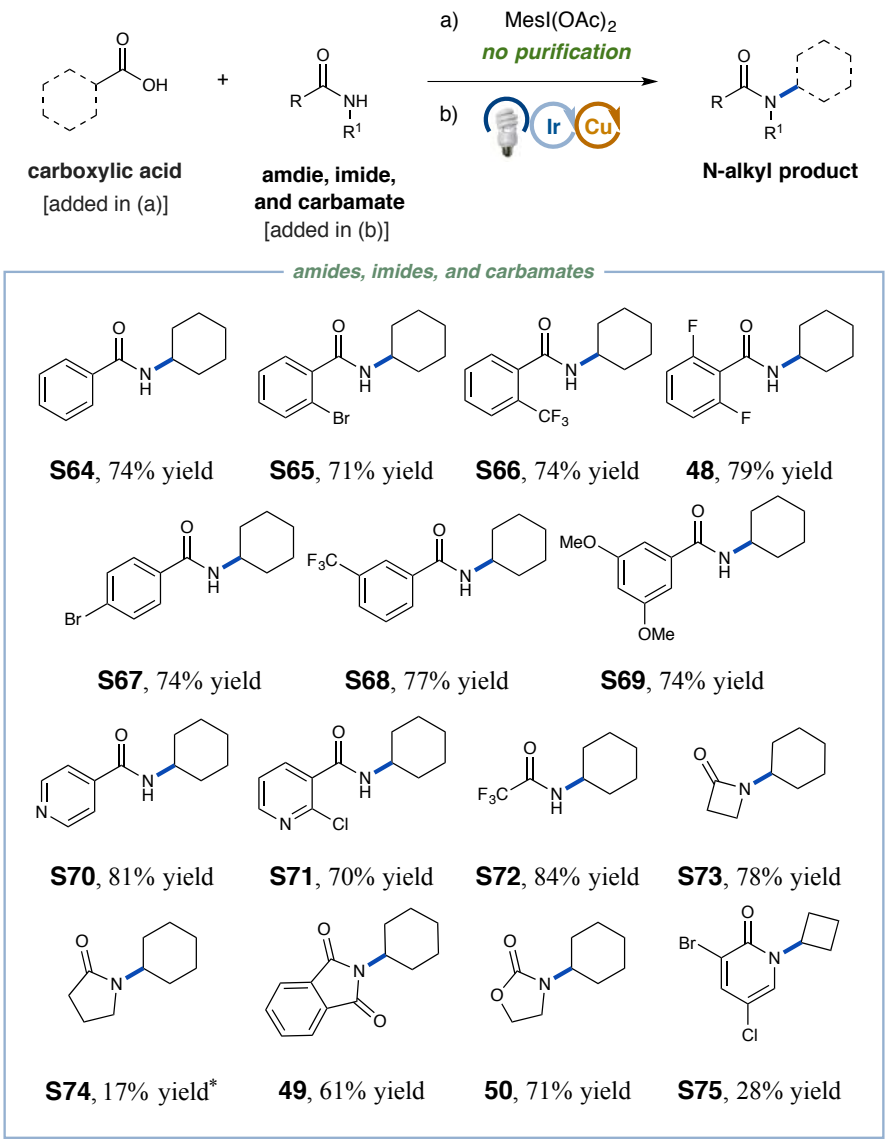


Figure S34 | Scope of amides, imides, and carbamates.

All yields are isolated yields for the decarboxylative C–N coupling step.

*Yield was calculated by GC analysis with an internal standard.

See **5.3** for experimental details.

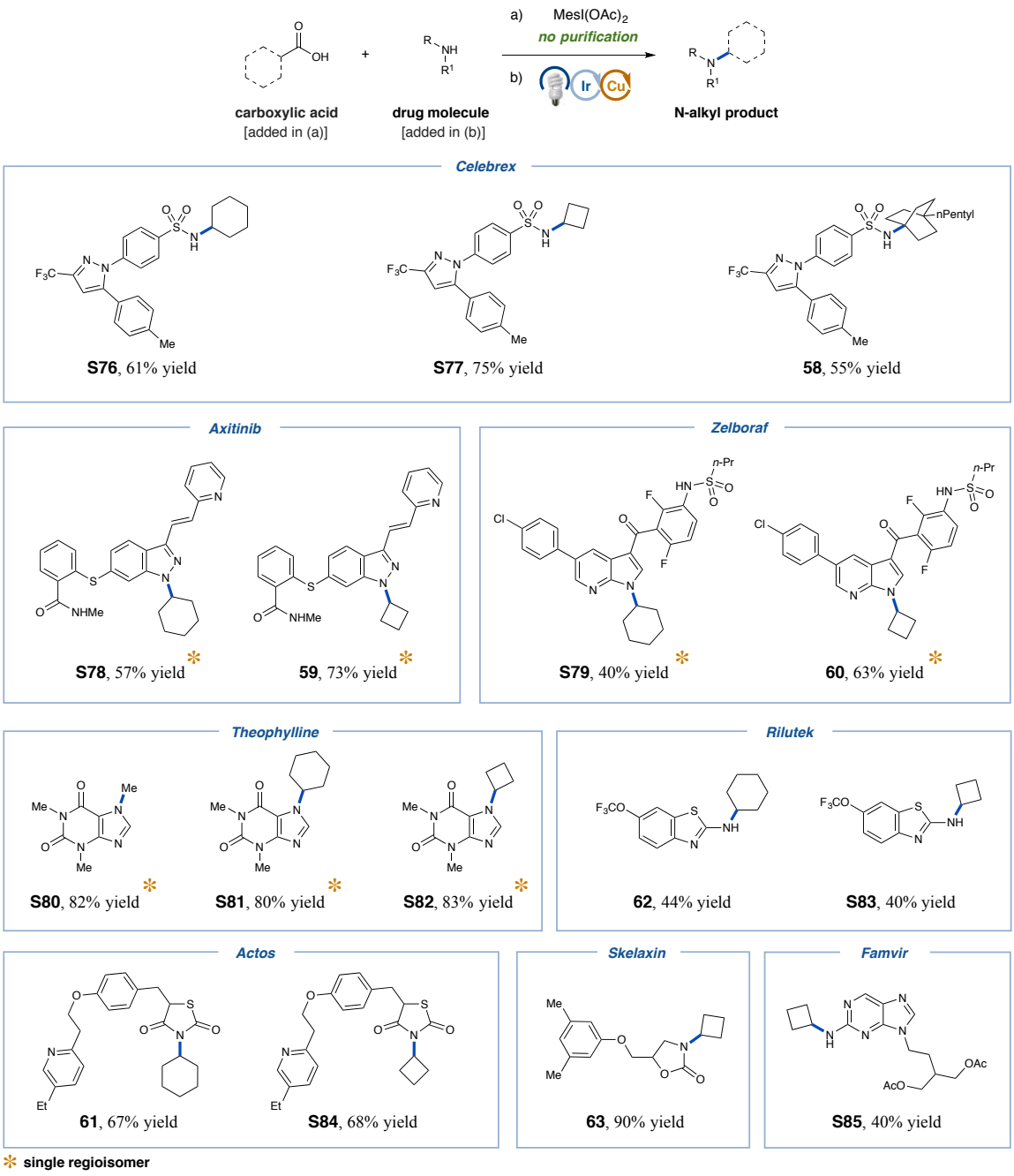
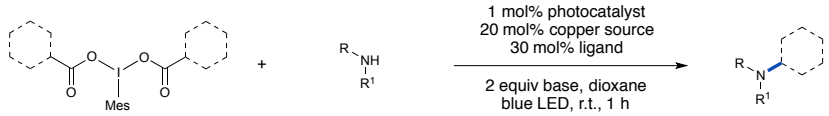


Figure S35 | Drug molecule alkylations.

All yields are isolated yields for the decarboxylative C–N coupling step.

*Only one regioisomer (>20:1 r.r.) was formed.

See **5.3** for experimental details.



Indazole

2 equiv iodomesitylene dicarboxylate
1 equiv *N*-nucleophile
1–2 mol% Ir[F-Meppy]$_2$(dtbbpy)PF$_6$
20 mol% CuTC
30 mol% BPhen or dOMe-Phen
2 equiv BTMG as base
or no extrogenous base
dioxane (0.04 M)

Azaindole

2 equiv iodomesitylene dicarboxylate
1 equiv *N*-nucleophile
1 mol% Ir[F-Meppy]$_2$(dtbbpy)PF$_6$
20 mol% CuTC
30 mol% dOMe-Phen
2 equiv BTMG as base
dioxane (0.04 M)

Indole

1 equiv iodomesitylene dicarboxylate
3 equiv *N*-nucleophile
1 mol% Ir[F-Meppy]$_2$(dtbbpy)PF$_6$
20 mol% CuTC
30 mol% dOMe-Phen
2 equiv BTMG as base
dioxane (0.04 M)

Pyrazole

2 equiv iodomesitylene dicarboxylate
1 equiv *N*-nucleophile
2 mol% Ir(ppy)$_3$
20 mol% CuTC
30 mol% BPhen
no extrogenous base
dioxane (0.04 M)

Triazole

2 equiv iodomesitylene dicarboxylate
1 equiv *N*-nucleophile
1 mol% Ir[F-Meppy]$_2$(dtbbpy)PF$_6$
20 mol% CuTC
30 mol% BPhen
no extrogenous base
dioxane (0.04 M)

Other N-heterocycle

2 equiv iodomesitylene dicarboxylate
1 equiv *N*-nucleophile
1 mol% Ir[F-Meppy]$_2$(dtbbpy)PF$_6$
20 mol% CuTC
30 mol% BPhen or dOMe-Phen
2 equiv BTMG as base
or no extrogenous base
dioxane (0.04 M)

Aniline

1 equiv iodomesitylene dicarboxylate
2 equiv *N*-nucleophile
1 mol% Ir[F-Meppy]$_2$(dtbbpy)PF$_6$
20 mol% CuTC
30 mol% BPhen
2 equiv BTTP as base
dioxane (0.07 M)

Sulfonamide

2 equiv iodomesitylene dicarboxylate
1 equiv *N*-nucleophile
3 mol% Ir(ppy)$_3$
30 mol% CuTC
45 mol% BPhen
3 equiv BTMG as base
dioxane (0.07 M)

Amide

1 equiv iodomesitylene dicarboxylate
2 equiv *N*-nucleophile
1 mol% Ir[F-Meppy]$_2$(dtbbpy)PF$_6$
20 mol% CuTC
30 mol% BPhen
3 equiv BTTP as base
dioxane (0.07 M)

Figure S36 | Summary of general reaction conditions for decarboxylative sp^3 C–N coupling

See **5.3** for experimental details.

5.2 Proof of Regioselectivity

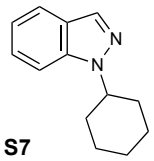
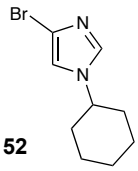
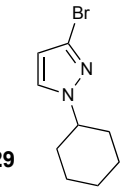
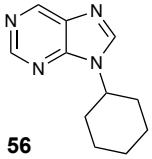
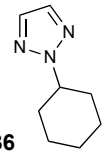
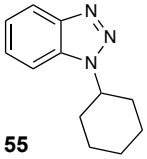
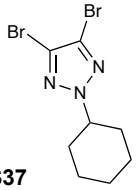
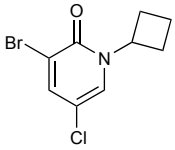
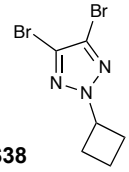
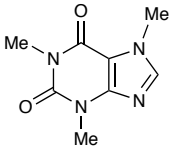
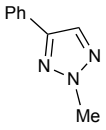
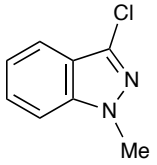
Product	Proof of Regioselectivity	Product	Proof of Regioselectivity
 **S7**	comparing to literature report	 **52**	2D NMR
 **S29**	2D NMR	 **56**	2D NMR
 **S36**	^{1}H NMR & ^{13}C NMR	 **55**	comparing to literature report
 **S37**	^{13}C NMR	 **S75**	2D NMR
 **S38**	comparing to literature report & ^{13}C NMR	 **S80**	comparing to literature report comparing to authentic sample
 **S39**	comparing to literature report		

Figure S37 | Proof of regioselectivity.

See **5.3** for experimental details. See **10** for spectra.

All the other assignments are based on analogy.

5.3 Products Characterization



3-Chloro-1-methyl-1*H*-indazole (13)

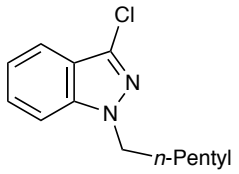
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (6.6 mg, 10 μmol, 0.02 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene diacetate (364 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (30:1 hexane/EtOAc) provided the title compound (54 mg, 65% yield, >20:1 r.r.) as a pale yellow oil. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 1H), 7.43 (ddd, *J* = 7.9, 6.8, 1.0 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.19 (ddd, *J* = 7.9, 6.9, 0.7 Hz, 1H), 4.01 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 141.3, 132.5, 127.5, 121.2, 121.1, 119.8, 109.4, 35.9.

IR (film) ν_{max} 3062, 2939, 1618, 1470, 1336, 1232, 1164, 977, 766, 741 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_8H_8ClN_2$ ($[M+H]^+$) 167.0371, found 167.0370.



3-Chloro-1-hexyl-1*H*-indazole (14)

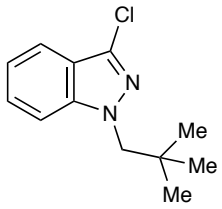
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene diheptanoate (504 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (30:1 hexane/EtOAc) provided the title compound (99 mg, 84% yield, >20:1 r.r.) as a colorless oil. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 1H), 7.46-7.33 (m, 2H), 7.19 (ddd, *J* = 7.9, 6.7, 0.9 Hz, 1H), 4.31 (t, *J* = 7.2 Hz, 2H), 1.91 (p, *J* = 7.4 Hz, 2H), 1.33-1.26 (m, 6H), 0.86 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.9, 132.5, 127.4, 121.1, 121.1, 119.9, 109.5, 49.5, 31.5, 29.9, 26.6, 22.6, 14.1.

IR (film) ν_{max} 2929, 1617, 1467, 1337, 1177, 766, 742 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{18}ClN_2$ ($[M+H]^+$) 237.1153, found 237.1155.



3-Chloro-1-neopentyl-1*H*-indazole (15)

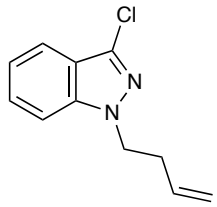
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene bis(3,3-dimethylbutanoate) (476 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (30:1 hexane/EtOAc) provided the title compound (60 mg, 54% yield, >20:1 r.r.) as a pale yellow oil. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 1H), 7.42-7.36 (m, 2H), 7.19-7.16 (m, 1H), 4.10 (s, 2H), 1.02 (s, 9H)

^{13}C NMR (125 MHz, $CDCl_3$) δ 141.9, 132.6, 127.3, 121.0, 120.9, 119.7, 110.2, 60.7, 34.4, 28.2.

IR (film) ν_{max} 2960, 2870, 1617, 1466, 1338, 1232, 1172, 986, 742 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{16}ClN_2$ ($[M+H]^+$) 223.0997, found 223.0992.



1-(But-3-en-1-yl)-3-chloro-1*H*-indazole (17)

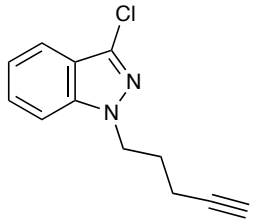
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (6.6 mg, 10 μmol, 0.02 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene bis(pent-4-enoate) (444 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (30:1 hexane/EtOAc) provided the title compound (66 mg, 64% yield, >20:1 r.r.) as a pale yellow oil. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 1H), 7.44-7.34 (m, 2H), 7.19 (ddd, *J* = 8.0, 6.7, 0.9 Hz, 1H), 5.81-5.73 (m, 1H), 5.10-5.01 (m, 2H), 4.46-4.33 (m, 2H), 2.69-2.64 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 141.0, 134.2, 132.8, 127.5, 121.2, 121.1, 119.9, 117.8, 109.5, 48.9, 34.2.

IR (film) ν_{max} 2933, 1617, 1496, 1467, 1337, 918, 765, 742 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{11}H_{12}ClN_2$ ($[M+H]^+$) 207.0684, found 207.0683.



3-Chloro-1-(pent-4-yn-1-yl)-1*H*-indazole (18)

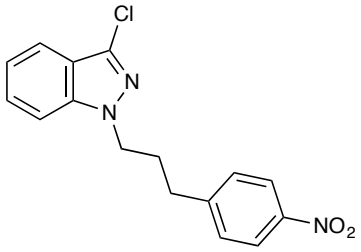
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene bis(hex-5-ynoate) (468 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (20:1 hexane/EtOAc) provided the title compound (87 mg, 80% yield, >20:1 r.r.) as a colorless oil. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 1H), 7.50-7.39 (m, 2H), 7.19 (ddd, *J* = 7.8, 6.4, 1.2 Hz, 1H), 4.45 (d, *J* = 12.9 Hz, 2H), 2.23-2.11 (m, 4H), 2.04 (t, *J* = 2.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 141.2, 133.0, 127.6, 121.3, 121.0, 119.9, 109.5, 83.0, 69.7, 47.5, 28.5, 15.9.

IR (film) ν_{max} 3299, 2939, 1617, 1467, 1337, 1172, 766, 741 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{12}ClN_2$ ($[M+H]^+$) 219.0684, found 219.0685.



3-Chloro-1-(3-(4-nitrophenyl)propyl)-1*H*-indazole (19)

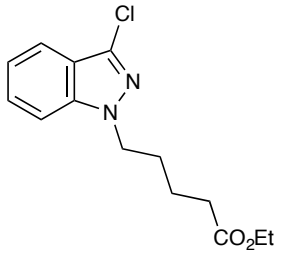
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene bis(4-(4-nitrophenyl)butanoate) (662 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (6:1 hexane/EtOAc, then 30:1 toluene/EtOAc) provided the title compound (79 mg, 50% yield, >20:1 r.r.) as a pale yellow oil. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.44-7.41 (m, 1H), 7.30-7.28 (m, 3H), 7.21 (t, *J* = 7.5 Hz, 1H), 4.35 (t, *J* = 6.7 Hz, 2H), 2.74 (t, *J* = 7.7 Hz, 2H), 2.32 (p, *J* = 6.9 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.7, 146.6, 140.9, 133.1, 129.3, 127.7, 123.8, 121.5, 121.2, 120.1, 109.2, 48.2, 32.9, 30.6.

IR (film) ν_{max} 2937, 1599, 1516, 1342, 849, 744 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{16}H_{15}ClN_3O_2$ $([M+H]^+)$ 316.0847, found 316.0845.



Ethyl 5-(3-chloro-1*H*-indazol-1-yl)pentanoate (21)

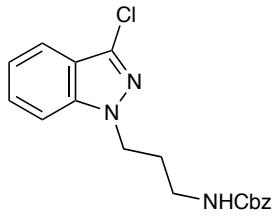
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene diethyl *O*,*O'*-diadipate (592 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (6:1 hexane/EtOAc) provided the title compound (112 mg, 80% yield, >20:1 r.r.) as a pale yellow oil. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 1H), 7.42-7.35 (m, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 4.31 (t, *J* = 7.0 Hz, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.31 (t, *J* = 7.4 Hz, 2H), 1.95 (p, *J* = 7.2 Hz, 2H), 1.63 (p, *J* = 7.5 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.2, 140.9, 132.7, 127.5, 121.2, 121.1, 119.9, 109.3, 60.5, 48.9, 33.8, 29.2, 22.2, 14.3.

IR (film) ν_{max} 2939, 2873, 1729, 1467, 1337, 1173, 1029, 765, 741 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{18}ClN_2O_2$ ($[M+H]^+$) 281.1051, found 281.1052.



Benzyl (3-(3-chloro-1*H*-indazol-1-yl)propyl)carbamate (16)

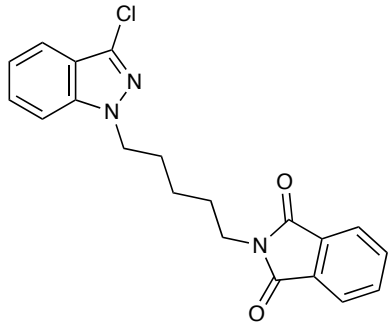
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene bis(4-(((benzyloxy)carbonyl)amino)butanoate) (719 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (2:1 hexane/EtOAc) provided the title compound (108 mg, 63% yield, >20:1 r.r.) as a pale yellow oil. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.37-7.29 (m, 6H), 7.20 (t, *J* = 7.5 Hz, 1H), 5.08 (s, 3H), 4.38 (t, *J* = 6.5 Hz, 2H), 3.19 (q, *J* = 6.0 Hz, 2H), 2.18-2.08 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 156.6, 140.8, 136.6, 133.0, 128.6, 128.2, 128.2, 127.7, 121.4, 121.2, 120.0, 109.3, 66.8, 46.4, 38.4, 29.7.

IR (film) ν_{max} 3327, 2943, 1700, 1523, 1467, 1337, 1242, 1128, 1011, 741, 697 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{18}H_{18}ClN_3NaO_2$ ($[M+Na]^+$) 366.0980, found 366.0984.



2-(5-(3-Chloro-1*H*-indazol-1-yl)pentyl)isoindoline-1,3-dione (20)

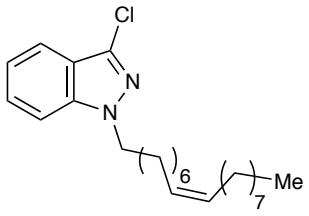
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene bis(6-(1,3-dioxoisoindolin-2-yl)hexanoate) (767 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (5:1 hexane/EtOAc) provided the title compound (150 mg, 82% yield, >20:1 r.r.) as a white solid. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.69 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.45-7.29 (m, 2H), 7.15 (t, *J* = 7.8 Hz, 1H), 4.29 (t, *J* = 7.1 Hz, 2H), 3.64 (t, *J* = 7.2 Hz, 2H), 1.95 (p, *J* = 7.3 Hz, 2H), 1.70 (p, *J* = 7.5 Hz, 2H), 1.36 (p, *J* = 7.8 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.4, 140.8, 134.0, 132.6, 132.1, 127.5, 123.3, 121.2, 121.0, 119.9, 109.4, 49.0, 37.7, 29.3, 28.2, 24.1.

IR (film) ν_{max} 2940, 2863, 1706, 1467, 1395, 1337, 1173, 1045, 743, 717 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{20}H_{19}ClN_3O_2$ ($[M+H]^+$) 368.1160, found 368.1158.



(*Z*)-3-Chloro-1-(heptadec-8-en-1-yl)-1*H*-indazole (22)

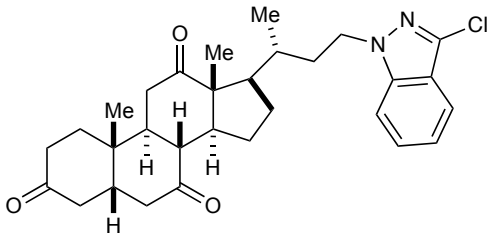
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dioleate (809 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (40:1 hexane/EtOAc) provided the title compound (148 mg, 76% yield, >20:1 r.r.) as a colorless oil. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 1H), 7.46-7.34 (m, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 5.35-5.29 (m, 2H), 4.30 (t, *J* = 7.1 Hz, 2H), 2.05-1.99 (m, 4H), 1.94-1.87 (m, 2H), 1.35-1.22 (m, 20H), 0.88 (t, *J* = 6.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.9, 132.5, 130.2, 129.8, 127.4, 121.14, 121.09, 119.9, 109.5, 49.4, 32.1, 29.94, 29.90, 29.8, 29.7, 29.5, 29.23, 29.21, 27.4, 27.3, 26.9, 22.8, 14.3.

IR (film) ν_{max} 2923, 2853, 1618, 1467, 1337, 741 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{24}H_{38}ClN_2$ ($[M+H]^+$) 389.2718, found 389.2714.



(5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-17-((*R*)-4-(3-Chloro-1*H*-indazol-1-yl)butan-2-yl)-10,13-dimethyldodecahydro-3*H*-cyclopenta[*a*]phenanthrene-3,7,12(2*H*,4*H*)-trione (23)

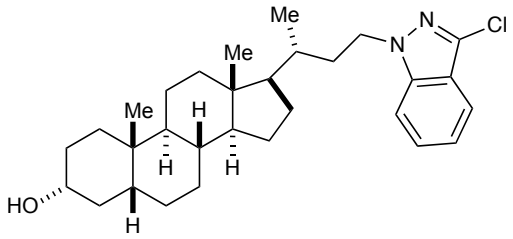
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene didehydrocholate (1.05 g, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (1:1.2 hexane/EtOAc) provided the title compound (190 mg, 75% yield, >20:1 r.r.) as a white solid. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 1H), 7.42 (ddd, *J* = 7.8, 6.8, 0.9 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.21-7.16 (m, 1H), 4.44-4.26 (m, 2H), 2.93-2.80 (m, 3H), 2.36-2.19 (m, 6H), 2.17-1.94 (m, 7H), 1.88-1.80 (m, 1H), 1.70-1.58 (m, 2H), 1.39 (s, 3H), 1.37-1.30 (m, 1H), 1.26-1.19 (m, 2H), 1.02 (s, 3H), 1.00 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 212.1, 209.2, 208.8, 140.7, 132.5, 127.5, 121.2, 121.1, 120.0, 109.4, 57.0, 51.8, 49.1, 47.3, 47.0, 45.8, 45.7, 45.1, 42.9, 38.7, 36.6, 36.1, 35.4, 35.4, 34.0, 27.9, 25.2, 22.0, 19.2, 11.9.

IR (film) ν_{max} 2952, 1709, 1466, 1338, 913, 732 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{30}H_{38}ClN_2O_3$ ($[M+H]^+$) 509.2566, found 509.2565.



(3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-17-((*R*)-4-(3-Chloro-1*H*-indazol-1-yl)butan-2-yl)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-ol (24)

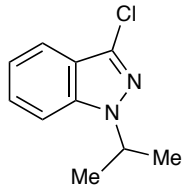
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dilithocholate (997 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (3:1 hexane/EtOAc) provided the title compound (130 mg, 54% yield, >20:1 r.r.) as a white solid. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 1H), 7.42 (ddd, *J* = 7.8, 6.8, 0.9 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.22-7.13 (m, 1H), 4.41-4.34 (m, 1H), 4.31-4.23 (m, 1H), 3.62 (dq, *J* = 10.9, 5.4, 4.6 Hz, 1H), 2.10-1.95 (m, 2H), 1.89-1.70 (m, 4H), 1.69-1.45 (m, 7H), 1.43-1.15 (m, 11H), 1.06 (d, *J* = 6.5 Hz, 3H), 1.04-0.94 (m, 2H), 0.91 (s, 3H), 0.61 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.6, 132.3, 127.4, 121.1, 119.9, 109.4, 71.9, 56.5, 56.1, 47.2, 42.9, 42.2, 40.5, 40.2, 36.5, 35.9, 35.4, 34.7, 34.0, 30.6, 28.4, 27.3, 26.5, 24.3, 23.5, 20.9, 18.9, 12.1.

IR (film) ν_{max} 3366, 2931, 2863, 1618, 1467, 1338, 909, 739 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{30}H_{44}ClN_2O$ ($[M+H]^+$) 483.3137, found 483.3135.



3-Chloro-1-isopropyl-1*H*-indazole (S1)

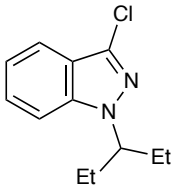
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene bis(2-methylpropanoate) (420 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (30:1 hexane/EtOAc) provided the title compound (58 mg, 60% yield, >20:1 r.r.) as a pale yellow oil. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 1H), 7.41-7.39 (m, 2H), 7.20-7.16 (m, 1H), 4.80 (p, *J* = 6.7 Hz, 1H), 1.58 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.0, 132.4, 127.2, 121.2, 119.9, 109.5, 50.9, 22.3.

IR (film) ν_{max} 2980, 2935, 1616, 1462, 1337, 1210, 977, 742 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{10}H_{12}ClN_2$ ($[M+H]^+$) 195.0684, found 195.0683.



3-Chloro-1-(pentan-3-yl)-1*H*-indazole (25)

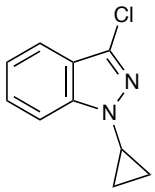
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene bis(2-ethylbutanoate) (476 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (30:1 hexane/EtOAc) provided the title compound (68 mg, 61% yield, >20:1 r.r.) as a pale yellow oil. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 1H), 7.42-7.36 (m, 2H), 7.17 (ddd, *J* = 7.9, 4.9, 2.7 Hz, 1H), 4.21 (tt, *J* = 9.6, 4.6 Hz, 1H), 2.08 (ddq, *J* = 14.7, 9.7, 7.4 Hz, 2H), 1.89 (dqd, *J* = 14.7, 7.4, 4.7 Hz, 2H), 0.73 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 142.0, 132.7, 127.2, 121.0, 120.6, 119.8, 109.5, 63.5, 28.3, 11.2.

IR (film) ν_{max} 2966, 2877, 1617, 1462, 1336, 1198, 977, 767, 740 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{16}ClN_2$ ($[M+H]^+$) 223.0997, found 223.0997.



3-Chloro-1-cyclopropyl-1*H*-indazole (26)

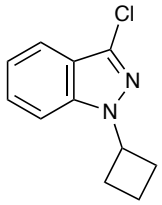
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuCl (25 mg, 0.25 mmol, 0.50 equiv.), 4,7-diphenyl-1,10-phenanthroline (116 mg, 0.35 mmol, 0.70 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclopropanecarboxylate (416 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (60:1 hexane/EtOAc) provided the title compound (38 mg, 40% yield, >20:1 r.r.) as a colorless oil. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 3.54 (tt, *J* = 7.0, 3.6 Hz, 1H), 1.25-1.22 (m, 2H), 1.17-1.13 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 142.1, 132.8, 127.6, 121.7, 121.5, 119.9, 110.2, 29.7, 6.8.

IR (film) ν_{max} 3016, 1617, 1468, 1333, 1221, 981, 767, 742 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{10}H_{10}ClN_2$ ($[M+H]^+$) 193.0527, found 193.0528.



3-Chloro-1-cyclobutyl-1*H*-indazole (27)

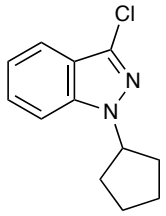
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (6.6 mg, 10 μmol, 0.02 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclobutanecarboxylate (444 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (30:1 hexane/EtOAc) provided the title compound (88 mg, 85% yield, >20:1 r.r.) as a yellow oil. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 1H), 7.40-7.35 (m, 2H), 7.22-7.10 (m, 1H), 5.01 (p, *J* = 8.7 Hz, 1H), 2.79 (pd, *J* = 9.5, 2.8 Hz, 2H), 2.66-2.38 (m, 2H), 2.01-1.77 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.3, 132.7, 127.3, 121.3, 121.2, 119.8, 109.5, 52.8, 30.1, 15.0.

IR (film) ν_{max} 2988, 2948, 1616, 1464, 1336, 1200, 1015, 968, 768, 740 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{11}H_{12}ClN_2$ ($[M+H]^+$) 207.0684, found 207.0682.



3-Chloro-1-cyclopentyl-1*H*-indazole (28)

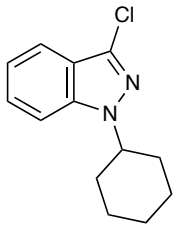
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclopentanecarboxylate (472 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (30:1 hexane/EtOAc) provided the title compound (78 mg, 71% yield, >20:1 r.r.) as a colorless oil. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 1H), 7.46-7.36 (m, 2H), 7.18 (ddd, *J* = 7.8, 6.3, 1.3 Hz, 1H), 4.93 (p, *J* = 7.4 Hz, 1H), 2.23-2.08 (m, 4H), 2.06-1.87 (m, 2H), 1.81-1.68 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.7, 132.1, 127.1, 121.2, 121.1, 119.8, 109.7, 60.0, 32.3, 24.7.

IR (film) ν_{max} 2957, 2872, 1616, 1464, 1337, 1214, 984, 767, 741 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{14}ClN_2$ ($[M+H]^+$) 221.0840, found 221.0840.



3-Chloro-1-cyclohexyl-1*H*-indazole (29)

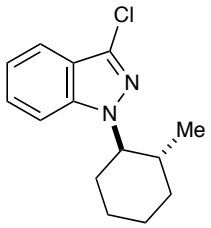
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (30:1 hexane/EtOAc) provided the title compound (99 mg, 84% yield, >20:1 r.r.) as a colorless oil. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.44-7.36 (m, 2H), 7.18 (ddd, *J* = 7.8, 6.4, 1.3 Hz, 1H), 4.43-4.26 (m, 1H), 2.09-1.99 (m, 4H), 1.98-1.94 (m, 2H), 1.78-1.74 (m, 1H), 1.51-1.41 (m, 2H), 1.37-1.29 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.1, 132.3, 127.1, 121.14, 121.05, 119.9, 109.5, 58.6, 32.7, 25.9, 25.4.

IR (film) ν_{max} 2933, 2856, 1464, 1337, 1193, 1006, 764, 741 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{16}ClN_2$ ($[M+H]^+$) 235.0997, found 235.0995.



3-Chloro-1-((2*R*)-2-methylcyclohexyl)-1*H*-indazole (S2)

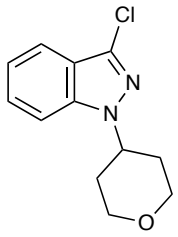
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene bis(2-methylcyclohexane-1-carboxylate) (528 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (30:1 hexane/EtOAc) provided the title compound (77 mg, 62% yield, d.r. = 14:1, >20:1 r.r.) as a yellow oil. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv). The structure of the title compound (relative sterochemistry) was further confirmed via 2D NMR (NOESY) analysis.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 1H), 7.44-7.34 (m, 2H), 7.17 (ddd, *J* = 7.8, 6.2, 1.4 Hz, 1H), 3.93 (td, *J* = 11.3, 3.9 Hz, 1H), 2.29-2.18 (m, 1H), 2.11-2.00 (m, 1H), 1.99-1.87 (m, 3H), 1.79-1.73 (m, 1H), 1.48-1.38 (m, 2H), 1.19 (qd, *J* = 12.6, 3.5 Hz, 1H), 0.62 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1, 132.5, 127.1, 121.0, 120.6, 119.8, 109.5, 64.7, 37.7, 34.8, 32.8, 26.1, 25.7, 19.2.

IR (film) ν_{max} 2928, 2856, 1616, 1465, 1337, 1192, 988, 740 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{18}ClN_2$ ($[M+H]^+$) 249.1153, found 249.1152.



3-Chloro-1-(tetrahydro-2*H*-pyran-4-yl)-1*H*-indazole (S3)

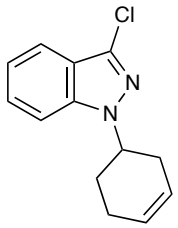
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene bis(tetrahydro-2*H*-pyran-4-carboxylate) (504 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (5:1 hexane/EtOAc) provided the title compound (99 mg, 84% yield, >20:1 r.r.) as a white solid. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 1H), 7.58-7.33 (m, 2H), 7.20 (ddd, *J* = 7.8, 6.0, 1.7 Hz, 1H), 4.59 (tt, *J* = 11.5, 4.2 Hz, 1H), 4.16 (dd, *J* = 11.4, 4.3 Hz, 2H), 3.59 (td, *J* = 12.1, 1.8 Hz, 2H), 2.39 (qd, *J* = 12.2, 4.6 Hz, 2H), 1.96 (dd, *J* = 12.9, 2.1 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.1, 132.9, 127.4, 121.42, 121.35, 120.1, 109.3, 67.3, 55.8, 32.5.

IR (film) ν_{max} 2961, 2847, 1617, 1465, 1338, 1200, 1145, 1089, 743 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{14}ClN_2O$ ($[M+H]^+$) 237.0789, found 237.0788.



3-Chloro-1-(cyclohex-3-en-1-yl)-1*H*-indazole (S4)

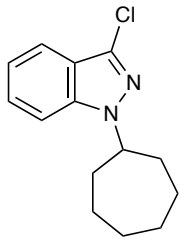
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene bis(cyclohex-3-ene-1-carboxylate) (496 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (30:1 hexane/EtOAc) provided the title compound (65 mg, 56% yield, >20:1 r.r.) as a yellow oil. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 1H), 7.47-7.37 (m, 2H), 7.23-7.15 (m, 1H), 5.82-5.70 (m, 2H), 4.70-4.56 (m, 1H), 2.82-2.73 (m, 1H), 2.49-2.38 (m, 1H), 2.36-2.26 (m, 3H), 2.12-2.03 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.3, 132.6, 127.2, 126.8, 124.9, 121.2, 121.1, 119.9, 109.4, 55.2, 31.4, 28.8, 25.7.

IR (film) ν_{max} 3028, 2920, 1616, 1465, 1336, 1226, 1190, 766, 741, 662 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{14}ClN_2$ ($[M+H]^+$) 233.0840, found 233.0841.



3-Chloro-1-cycloheptyl-1*H*-indazole (31)

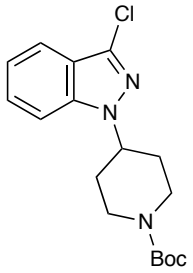
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicycloheptanecarboxylate (528 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (30:1 hexane/EtOAc) provided the title compound (75 mg, 60% yield, >20:1 r.r.) as a wax solid. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 1H), 7.43-7.37 (m, 2H), 7.17 (ddd, *J* = 7.8, 5.6, 2.1 Hz, 1H), 4.55 (td, *J* = 10.0, 5.0 Hz, 1H), 2.23-2.16 (m, 2H), 2.10-2.05 (m, 2H), 1.90-1.84 (m, 2H), 1.73-1.65 (m, 4H), 1.61-1.56 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.8, 132.2, 127.1, 121.09, 121.06, 119.9, 109.7, 61.0, 34.7, 28.0, 25.0.

IR (film) ν_{max} 2926, 2857, 1741, 1366, 1217, 740 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{18}ClN_2$ ($[M+H]^+$) 249.1153, found 249.1152.



***tert*-Butyl 4-(3-chloro-1*H*-indazol-1-yl)piperidine-1-carboxylate (30)**

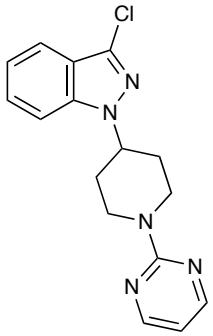
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene 1,1'-di-*tert*-butyl O^4,O^4-bis(piperidine-1,4-dicarboxylate) (703 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (5:1 hexane/EtOAc, then 6:1 to 1:0 CH_2Cl_2/hexane) provided the title compound (112 mg, 67% yield, >20:1 r.r.) as a colorless oil. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 1H), 7.46-7.38 (m, 2H), 7.20 (dt, *J* = 7.9, 3.9 Hz, 1H), 4.50 (tt, *J* = 11.5, 4.1 Hz, 1H), 4.30 (brs, 2H), 2.93 (brs, 2H), 2.31-2.12 (m, 2H), 1.99-1.97 (m, 2H), 1.48 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.6, 140.1, 132.9, 127.5, 121.5, 121.3, 120.1, 109.2, 80.0, 56.7, 43.4, 31.6, 28.6.

IR (film) ν_{max} 2974, 2863, 1686, 1421, 1365, 1240, 1159, 1013, 741 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{17}H_{22}ClN_3NaO_2$ ($[M+Na]^+$) 358.1293, found 358.1290.



3-Chloro-1-(1-(pyrimidin-2-yl)piperidin-4-yl)-1*H*-indazole (S5)

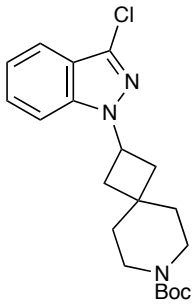
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene bis(1-(pyrimidin-2-yl)piperidine-4-carboxylate) (659 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (8:1 to 1:0 CH_2Cl_2/hexane) provided the title compound (118 mg, 75% yield, >20:1 r.r.) as a white solid. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 4.8 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.48-7.36 (m, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 6.50 (t, *J* = 4.7 Hz, 1H), 4.98 (d, *J* = 13.6 Hz, 2H), 4.65 (tt, *J* = 11.5, 4.1 Hz, 1H), 3.11 (td, *J* = 13.6, 2.4 Hz, 2H), 2.27 (qd, *J* = 12.6, 4.3 Hz, 2H), 2.17-2.03 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 161.6, 157.9, 140.2, 132.8, 127.4, 121.4, 121.3, 120.1, 110.1, 109.3, 57.1, 43.3, 31.4.

IR (film) ν_{max} 2929, 2854, 1583, 1492, 1462, 1359, 1196, 974, 765, 742 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{16}H_{17}ClN_5$ ($[M+H]^+$) 314.1167, found 314.1170.



***tert*-Butyl 2-(3-chloro-1*H*-indazol-1-yl)-7-azaspiro[3.5]nonane-7-carboxylate (S6)**

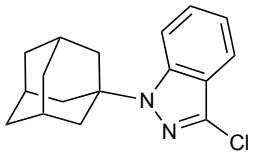
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene 7,7'-di-*tert*-butyl O'^2,O^2-bis(7-azaspiro[3.5]nonane-2,7-dicarboxylate) (783 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (5:1 hexane/EtOAc) provided the title compound (170 mg, 90% yield, >20:1 r.r.) as a colorless oil. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 1H), 7.46-7.33 (m, 2H), 7.18 (ddd, *J* = 7.9, 6.4, 1.2 Hz, 1H), 5.01 (p, *J* = 8.3 Hz, 1H), 3.47-3.41 (m, 2H), 3.39-3.31 (m, 2H), 2.61-2.50 (m, 2H), 2.47-2.43 (m, 2H), 1.71-1.68 (m, 4H), 1.46 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 155.1, 140.5, 132.9, 127.4, 121.43, 121.38, 120.0, 109.5, 79.5, 48.3, 41.4, 39.1, 36.1, 32.4, 28.6.

IR (film) ν_{max} 2976, 2929, 1685, 1417, 1243, 1147, 1001, 767, 743 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{20}H_{26}ClN_3NaO_2$ ($[M+Na]^+$) 398.1606, found 398.1605.



1-(Adamantan-1-yl)-3-chloro-1*H*-indazole (32)

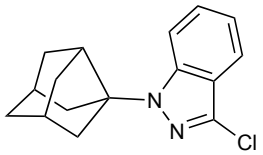
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuCl (15 mg, 0.15 mmol, 0.30 equiv.), 4,7-dimethoxy-1,10-phenanthroline (54 mg, 0.23 mmol, 0.45 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene bis(adamantane-1-carboxylate) (605 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (40:1 hexane/EtOAc) provided the title compound (106 mg, 74% yield, >20:1 r.r.) as a white solid. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.34 (ddd, *J* = 8.5, 6.9, 1.1 Hz, 1H), 7.19-7.13 (m, 1H), 2.42 (d, *J* = 2.9 Hz, 6H), 2.28 (s, 3H), 1.84-1.79 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.4, 131.4, 126.4, 122.4, 120.7, 120.1, 112.9, 61.5, 42.4, 36.4, 30.0.

IR (film) ν_{max} 2908, 2852, 1615, 1463, 1355, 1173, 1035, 740 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{17}H_{20}ClN_2$ ($[M+H]^+$) 287.1310, found 287.1309.



3-Chloro-1-(hexahydro-2,5-methanopentalen-3a(1*H*)-yl)-1*H*-indazole (33)

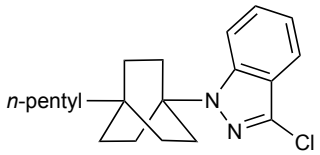
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuCl (15 mg, 0.15 mmol, 0.30 equiv.), 4,7-diphenyl-1,10-phenanthroline (75 mg, 0.23 mmol, 0.45 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene bis(3-noradamantanecarboxylate) (577 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (40:1 hexane/EtOAc) provided the title compound (72 mg, 53% yield, >20:1 r.r.) as a pale yellow solid. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.37 (ddd, *J* = 8.5, 6.9, 1.1 Hz, 1H), 7.24-7.14 (m, 1H), 3.10 (t, *J* = 6.8 Hz, 1H), 2.55-2.45 (m, 4H), 2.27 (dd, *J* = 10.0, 2.9 Hz, 2H), 2.21-2.18 (m, 2H), 1.81-1.74 (m, 3H), 1.69 (dt, *J* = 13.0, 2.4 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.8, 131.6, 126.9, 122.4, 121.0, 120.1, 111.3, 73.5, 49.6, 43.7, 43.2, 37.6, 34.8.

IR (film) ν_{max} 2928, 2868, 1615, 1462, 1338, 1322, 1211, 1177, 996, 767, 739 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{16}H_{18}ClN_2$ ($[M+H]^+$) 273.1153, found 273.1153.



3-Chloro-1-(4-pentylbicyclo[2.2.2]octan-1-yl)-1*H*-indazole (34)

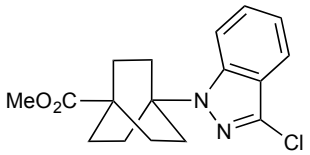
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), $Cu(OAc)_2$ (36 mg, 0.20 mmol, 0.40 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene bis(4-pentylbicyclo[2.2.2]octane-1-carboxylate) (693 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous ligand was used. Purification by flash chromatography (60:1 hexane/EtOAc) provided the title compound (119 mg, 72% yield, >20:1 r.r.) as a pale yellow oil. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.7 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.33 (ddd, *J* = 8.6, 6.9, 1.2 Hz, 1H), 7.16 (dd, *J* = 8.3, 7.2 Hz, 1H), 2.31-2.28 (m, 6H), 1.65-1.61(m, 6H), 1.37-1.30 (m, 2H), 1.27-1.21 (m, 4H), 1.18-1.15 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.7, 131.3, 126.4, 122.4, 120.7, 120.0, 112.7, 61.3, 41.1, 32.9, 31.5, 31.4, 30.6, 23.6, 22.8, 14.2.

IR (film) ν_{max} 2923, 2860, 1615, 1462, 1361, 1336, 1191, 1093, 767, 738 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{20}H_{28}ClN_2$ ($[M+H]^+$) 331.1936, found 331.1934.



Methyl 4-(3-chloro-1*H*-indazol-1-yl)bicyclo[2.2.2]octane-1-carboxylate (35)

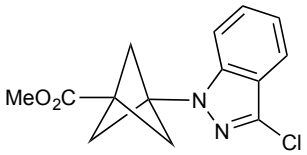
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), $Cu(OAc)_2$ (45 mg, 0.25 mmol, 0.50 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene *O*'[1],*O*[1]-4,4'-dimethyl bis(bicyclo[2.2.2]octane-1,4-dicarboxylate) (669 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous ligand was used. Purification by flash chromatography (10:1 hexane/EtOAc) provided the title compound (95 mg, 60% yield, >20:1 r.r.) as a white solid. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.5 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.35 (ddd, *J* = 8.1, 6.9, 0.9 Hz, 1H), 7.21-7.14 (m, 1H), 3.69 (s, 3H), 2.36-2.33 (m, 6H), 2.08-2.05 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 177.5, 139.7, 131.8, 126.7, 122.5, 120.9, 120.2, 112.5, 60.8, 52.0, 38.7, 30.6, 28.9.

IR (film) ν_{max} 2952, 2874, 1722, 1462, 1337, 1250, 1069, 1031, 889, 767, 739 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{17}H_{20}ClN_2O_2$ ($[M+H]^+$) 319.1208, found 319.1208.



Methyl 3-(3-chloro-1*H*-indazol-1-yl)bicyclo[1.1.1]pentane-1-carboxylate (36)

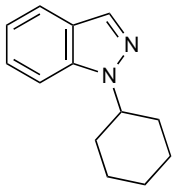
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (6.6 mg, 10 μmol, 0.02 equiv.), $Cu(acac)_2$ (65 mg, 0.25 mmol, 0.50 equiv.), 3-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene O'^1,O^1-3,3'-dimethyl bis(bicyclo[1.1.1]pentane-1,3-dicarboxylate) (584 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base and ligand were used. Purification by flash chromatography (10:1 hexane/EtOAc) provided the title compound (110 mg, 80% yield, >20:1 r.r.) as a white solid. The yield was determined based on 3-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 1H), 7.49 (d, *J* = 8.6 Hz, 1H), 7.43 (ddd, *J* = 8.5, 6.9, 0.9 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 3.76 (s, 3H), 2.75 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 140.6, 134.2, 128.1, 121.8, 121.7, 120.1, 110.1, 55.1, 52.2, 50.9, 35.4.

IR (film) ν_{max} 3003, 2925, 1729, 1519, 1333, 1207, 1122, 1016, 960, 766, 741 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{14}ClN_2O_2$ ($[M+H]^+$) 277.0738, found 277.0738.



1-Cyclohexyl-1*H*-indazole (S7)

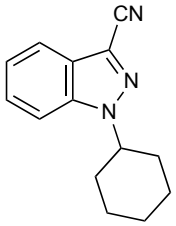
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (6.6 mg, 10 μmol, 0.02 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 1*H*-indazole (59 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (30:1 hexane/EtOAc) provided the title compound (73 mg, 73% yield, >20:1 r.r.) as a yellow oil. The yield was determined based on 1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.46 (d, *J* = 9.2 Hz, 1H), 7.36 (ddd, *J* = 8.4, 6.8, 1.0 Hz, 1H), 7.13 (ddd, *J* = 7.8, 6.9, 0.7 Hz, 1H), 4.51-4.37 (m, 1H), 2.10-1.95 (m, 6H), 1.79 (dt, *J* = 13.0, 3.2 Hz, 1H), 1.56-1.45 (m, 2H), 1.35 (dt, *J* = 12.9, 3.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6, 132.5, 125.8, 124.0, 121.1, 120.4, 109.2, 58.0, 32.6, 25.9, 25.5.

Data are consistent with those reported in the literature:

Wang, C.-S., Wu, X.-F., Dixneuf, P. H. & Soulé, J.-F. *ChemSusChem* **10**, 3075–3082 (2017).



1-Cyclohexyl-1*H*-indazole-3-carbonitrile (S8)

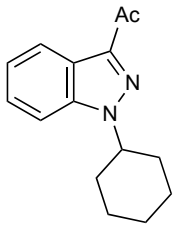
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (6.6 mg, 10 μmol, 0.02 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 1*H*-indazole-3-carbonitrile (72 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (30:1 hexane/EtOAc) provided the title compound (106 mg, 94% yield, >20:1 r.r.) as a pale yellow solid. The yield was determined based on 1*H*-indazole-3-carbonitrile as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 8.6 Hz, 1H), 7.50-7.42 (m, 1H), 7.35-7.28 (m, 1H), 4.50 (tt, *J* = 11.1, 4.3 Hz, 1H), 2.09-1.94 (m, 6H), 1.83-1.75 (m, 1H), 1.49 (qt, *J* = 13.1, 3.6 Hz, 2H), 1.35 (tt, *J* = 12.8, 3.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 127.4, 125.5, 123.5, 119.7, 117.1, 114.1, 110.3, 59.4, 32.5, 25.6, 25.3.

IR (film) ν_{max} 2934, 2858, 2231, 1465, 1351, 1211, 894, 744 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{16}N_3$ ($[M+H]^+$) 226.1339, found 226.1341.



1-(1-Cyclohexyl-1*H*-indazol-3-yl)ethan-1-one (S9)

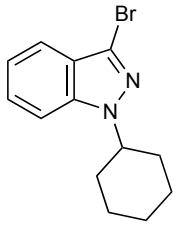
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (6.6 mg, 10 μmol, 0.02 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 1-(1*H*-indazol-3-yl)ethan-1-one (80 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (20:1 hexane/EtOAc) provided the title compound (115 mg, 95% yield, >20:1 r.r.) as a white solid. The yield was determined based on 1-(1*H*-indazol-3-yl)ethan-1-one as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.1 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.40 (ddd, *J* = 8.4, 6.9, 1.1 Hz, 1H), 7.30 (td, *J* = 7.4, 6.9, 0.8 Hz, 1H), 4.48 (tt, *J* = 10.4, 5.2 Hz, 1H), 2.71 (s, 3H), 2.13-1.94 (m, 6H), 1.80 (dt, *J* = 13.0, 3.3 Hz, 1H), 1.57-1.44 (m, 2H), 1.39 (tt, *J* = 12.8, 3.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 195.2, 142.1, 140.2, 126.4, 123.6, 123.1, 122.9, 109.5, 59.0, 32.5, 26.9, 25.8, 25.5.

IR (film) ν_{max} 2939, 2858, 1667, 1465, 1171, 933, 750 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{15}H_{19}N_2O$ ($[M+H]^+$) 243.1492, found 243.1494.



3-Bromo-1-cyclohexyl-1*H*-indazole (S10)

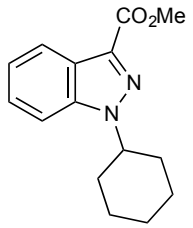
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (6.6 mg, 10 μmol, 0.02 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 3-bromo-1*H*-indazole (99 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (30:1 hexane/EtOAc) provided the title compound (109 mg, 78% yield, >20:1 r.r.) as a yellow oil. The yield was determined based on 3-bromo-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 1H), 7.45-7.36 (m, 2H), 7.19-7.16 (m, 1H), 4.45-4.23 (m, 1H), 2.07-1.92 (m, 6H), 1.75 (dt, *J* = 13.0, 3.1 Hz, 1H), 1.50-1.41 (m, 2H), 1.33 (tt, *J* = 12.9, 3.4 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.9, 127.0, 123.6, 121.2, 120.4, 119.8, 109.4, 58.7, 32.6, 25.8, 25.3.

IR (film) ν_{max} 2931, 2855, 1616, 1460, 1330, 1183, 1004, 964, 740 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{16}BrN_2$ ($[M+H]^+$) 279.0491, found 279.0490.



Methyl 1-cyclohexyl-1*H*-indazole-3-carboxylate (S11)

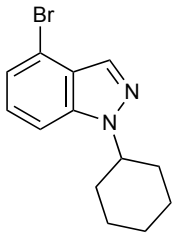
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (6.6 mg, 10 μmol, 0.02 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), methyl 1*H*-indazole-3-carboxylate (88 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (10:1 hexane/EtOAc) provided the title compound (124 mg, 96% yield, >20:1 r.r.) as a colorless oil. The yield was determined based on methyl 1*H*-indazole-3-carboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.2 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.47-7.39 (m, 1H), 7.37-7.28 (m, 1H), 4.52 (tt, *J* = 11.5, 4.4 Hz, 1H), 4.03 (s, 3H), 2.21-1.94 (m, 6H), 1.82-1.72 (m, 1H), 1.49 (qt, *J* = 13.1, 3.6 Hz, 2H), 1.37 (tt, *J* = 12.9, 3.4 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.4, 139.9, 134.4, 126.5, 124.1, 123.2, 122.4, 110.0, 59.6, 52.1, 32.4, 25.9, 25.3.

IR (film) ν_{max} 2934, 2857, 1711, 1475, 1239, 1169, 1123, 752 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{15}H_{18}N_2NaO_2$ ($[M+Na]^+$) 281.1261, found 281.1259.



4-Bromo-1-cyclohexyl-1*H*-indazole (S12)

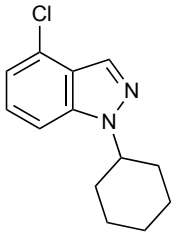
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 4-bromo-1*H*-indazole (99 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (30:1 hexane/EtOAc) provided the title compound (106 mg, 76% yield, >20:1 r.r.) as a colorless oil. The yield was determined based on 4-bromo-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.23-7.11 (m, 1H), 4.40-4.34 (m, 1H), 2.07-1.94 (m, 6H), 1.78 (dt, *J* = 13.0, 3.0 Hz, 1H), 1.54-1.43 (m, 2H), 1.35 (tt, *J* = 12.9, 3.4 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.3, 132.8, 126.7, 125.1, 123.3, 114.8, 108.4, 58.7, 32.7, 25.9, 25.5.

IR (film) ν_{max} 2932, 2855, 1610, 1561, 1419, 1166, 916, 769, 730 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{16}BrN_2$ ($[M+H]^+$) 279.0491, found 279.0493.



4-Chloro-1-cyclohexyl-1*H*-indazole (S13)

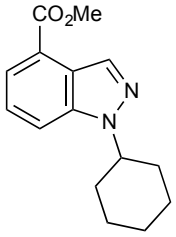
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (6.6 mg, 10 μmol, 0.02 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 4-chloro-1*H*-indazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (30:1 hexane/EtOAc) provided the title compound (103 mg, 88% yield, >20:1 r.r.) as a pale yellow oil. The yield was determined based on 4-chloro-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.31-7.26 (m, 1H), 7.11 (d, *J* = 7.3 Hz, 1H), 4.48-4.29 (m, 1H), 2.07-1.94 (m, 6H), 1.78 (dt, *J* = 13.0, 3.2 Hz, 1H), 1.54-1.44 (m, 2H), 1.36 (tt, *J* = 12.9, 3.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.7, 131.3, 126.8, 126.5, 123.3, 120.1, 107.9, 58.6, 32.7, 25.9, 25.5.

IR (film) ν_{max} 2933, 2856, 1611, 1366, 1168, 928, 771, 730 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{16}ClN_2$ ($[M+H]^+$) 235.0997, found 235.0995.



Methyl 1-cyclohexyl-1*H*-indazole-4-carboxylate (37)

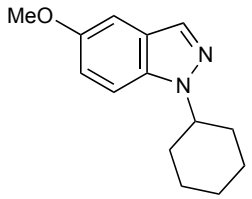
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (6.6 mg, 10 μmol, 0.02 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), methyl 1*H*-indazole-4-carboxylate (88 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (8:1 hexane/EtOAc) provided the title compound (105 mg, 81% yield, >20:1 r.r.) as a pale yellow oil. The yield was determined based on methyl 1*H*-indazole-4-carboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.41 (dd, *J* = 8.4, 7.2 Hz, 1H), 4.51-4.33 (m, 1H), 4.01 (s, 3H), 2.09-1.93 (m, 6H), 1.78 (dt, *J* = 13.0, 3.3 Hz, 1H), 1.55-1.43 (m, 2H), 1.36 (tt, *J* = 12.9, 3.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 139.2, 133.5, 125.1, 124.2, 123.0, 122.5, 114.2, 58.3, 52.2, 32.7, 25.9, 25.5.

IR (film) ν_{max} 2934, 2857, 1717, 1447, 1276, 1167, 1140, 925, 752 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{15}H_{19}N_2O_2$ ($[M+H]^+$) 259.1441, found 259.1440.



1-Cyclohexyl-5-methoxy-1*H*-indazole (38)

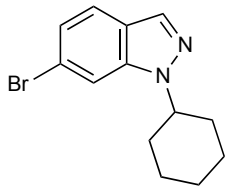
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (6.6 mg, 10 μmol, 0.02 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 5-methoxy-1*H*-indazole (74 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (20:1 hexane/EtOAc) provided the title compound (84 mg, 73% yield, >20:1 r.r.) as a yellow oil. The yield was determined based on 5-methoxy-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.35 (d, *J* = 9.0 Hz, 1H), 7.07-7.02 (m, 2H), 4.41-4.30 (m, 1H), 3.84 (s, 3H), 2.09-1.89 (m, 6H), 1.76 (dd, *J* = 9.5, 6.3 Hz, 1H), 1.47 (qt, *J* = 13.1, 3.6 Hz, 2H), 1.34 (tt, *J* = 12.8, 3.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.5, 134.8, 131.7, 124.2, 118.2, 110.2, 100.1, 58.3, 55.8, 32.7, 26.0, 25.6.

IR (film) ν_{max} 2931, 2855, 1503, 1451, 1301, 1221, 1150, 1026, 836, 802 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{19}N_2O$ ($[M+H]^+$) 231.1492, found 231.1491.



6-Bromo-1-cyclohexyl-1*H*-indazole (S14)

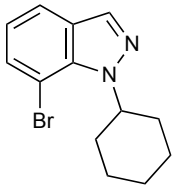
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (6.6 mg, 10 μmol, 0.02 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 6-bromo-1*H*-indazole (99 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (40:1 hexane/EtOAc) provided the title compound (119 mg, 85% yield, >20:1 r.r.) as a pale yellow oil. The yield was determined based on 6-bromo-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.63 (s, 1H), 7.56 (d, *J* = 9.0 Hz, 1H), 7.21 (dd, *J* = 8.5, 1.5 Hz, 1H), 4.32 (tt, *J* = 10.7, 5.3 Hz, 1H), 2.05-1.87 (m, 6H), 1.77 (dt, *J* = 9.8, 4.8 Hz, 1H), 1.54-1.41 (m, 2H), 1.34 (tt, *J* = 12.8, 3.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.5, 132.8, 124.0, 122.8, 122.3, 120.3, 112.1, 58.3, 32.6, 25.9, 25.5.

IR (film) ν_{max} 2932, 2855, 1608, 1462, 1180, 912, 836, 791 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{16}BrN_2$ ($[M+H]^+$) 279.0491, found 279.0490.



7-Bromo-1-cyclohexyl-1*H*-indazole (S15)

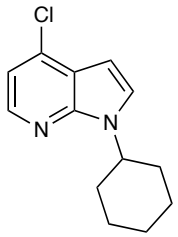
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 7-bromo-1*H*-indazole (99 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (40:1 hexane/EtOAc) provided the title compound (57 mg, 41% yield, >20:1 r.r.) as a yellow oil. The yield was determined based on 7-bromo-1*H*-indazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.53 (d, *J* = 7.3 Hz, 1H), 6.96 (t, *J* = 7.7 Hz, 1H), 5.41 (tt, *J* = 11.3, 3.3 Hz, 1H), 2.29-1.88 (m, 6H), 1.77 (d, *J* = 13.0 Hz, 1H), 1.54-1.47 (m, 2H), 1.36-1.30 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 136.2, 133.0, 131.2, 126.8, 121.5, 120.5, 102.9, 58.6, 33.6, 25.9, 25.6.

IR (film) ν_{max} 2929, 2854, 1492, 1450, 1408, 1163, 1122, 935, 824, 732 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{16}BrN_2$ ($[M+H]^+$) 279.0491, found 279.0489.



4-Chloro-1-cyclohexyl-1*H*-pyrrolo[2,3-*b*]pyridine (S16)

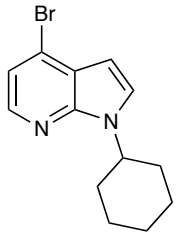
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 4-chloro-1*H*-pyrrolo[2,3-*b*]pyridine (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (10:1 hexane/EtOAc) provided the title compound (94 mg, 80% yield) as a yellow solid. The yield was determined based on 4-chloro-1*H*-pyrrolo[2,3-*b*]pyridine as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 5.1 Hz, 1H), 7.33 (d, *J* = 3.6 Hz, 1H), 7.06 (d, *J* = 5.1 Hz, 1H), 6.55 (d, *J* = 3.6 Hz, 1H), 4.76 (tt, *J* = 12.0, 3.8 Hz, 1H), 2.13-2.05 (m, 2H), 1.93-1.86 (m, 2H), 1.80-1.62 (m, 3H), 1.59-1.49 (m, 2H), 1.32-1.21 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 147.7, 142.7, 135.8, 125.5, 119.9, 115.8, 98.1, 53.5, 33.7, 25.9, 25.6.

IR (film) ν_{max} 2930, 2855, 1592, 1552, 1504, 1482, 1450, 1406, 1336, 1286, 1267, 1202, 1185, 919, 893, 840, 808, 781, 753, 715 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{16}ClN_2$ ($[M+H]^+$) 235.0997, found 235.0999.



4-Bromo-1-cyclohexyl-1*H*-pyrrolo[2,3-*b*]pyridine (S17)

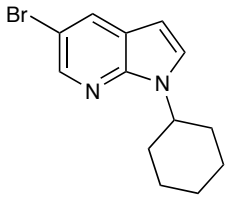
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 4-bromo-1*H*-pyrrolo[2,3-*b*]pyridine (99 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (12:1 hexane/EtOAc) provided the title compound (114 mg, 82% yield) as a yellow solid. The yield was determined based on 4-bromo-1*H*-pyrrolo[2,3-*b*]pyridine as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 5.1 Hz, 1H), 7.35 (d, *J* = 3.6 Hz, 1H), 7.23 (d, *J* = 5.1 Hz, 1H), 6.49 (d, *J* = 3.6 Hz, 1H), 4.75 (tt, *J* = 12.0, 3.8 Hz, 1H), 2.13-2.04 (m, 2H), 1.94-1.86 (m, 2H), 1.81-1.74 (m, 1H), 1.73-1.62 (m, 2H), 1.60-1.48 (m, 2H), 1.32-1.21 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 146.9, 142.6, 125.5, 125.0, 122.2, 118.9, 99.7, 53.6, 33.7, 25.9, 25.6.

IR (film) ν_{max} 2929, 2854, 1588, 1543, 1504, 1479, 1450, 1405, 1333, 1284, 1267, 1237, 1207, 1180, 906, 894, 830, 806, 751, 715 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{16}BrN_2$ ($[M+H]^+$) 279.0491, found 279.0488.



5-Bromo-1-cyclohexyl-1*H*-pyrrolo[2,3-*b*]pyridine (S18)

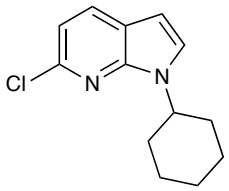
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 5-bromo-1*H*-pyrrolo[2,3-*b*]pyridine (99 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (15:1 hexane/EtOAc) provided the title compound (110 mg, 79% yield) as a yellow solid. The yield was determined based on 5-bromo-1*H*-pyrrolo[2,3-*b*]pyridine as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 1.8 Hz, 1H), 7.99 (d, *J* = 2.0 Hz, 1H), 7.31 (d, *J* = 3.5 Hz, 1H), 6.39 (d, *J* = 3.5 Hz, 1H), 4.72 (tt, *J* = 12.0, 3.7 Hz, 1H), 2.12-2.03 (m, 2H), 1.95-1.85 (m, 2H), 1.82-1.74 (m, 1H), 1.72-1.62 (m, 2H), 1.60-1.48 (m, 2H), 1.32-1.22 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 145.4, 142.9, 130.7, 126.3, 122.2, 111.4, 99.0, 53.3, 33.7, 25.9, 25.7.

IR (film) ν_{max} 2928, 2853, 1502, 1460, 1450, 1402, 1344, 1294, 1263, 1209, 1076, 995, 913, 886, 814, 754, 716 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{16}BrN_2$ ($[M+H]^+$) 279.0491, found 279.0494.



6-Chloro-1-cyclohexyl-1*H*-pyrrolo[2,3-*b*]pyridine (S19)

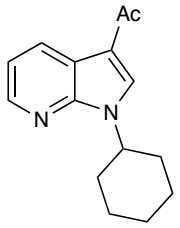
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 6-chloro-1*H*-pyrrolo[2,3-*b*]pyridine (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (16:1 hexane/EtOAc) provided the title compound (87 mg, 74% yield) as a yellow solid. The yield was determined based on 6-chloro-1*H*-pyrrolo[2,3-*b*]pyridine as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz, 1H), 7.28 (d, *J* = 3.6 Hz, 1H), 7.04 (d, *J* = 8.1 Hz, 1H), 6.44 (d, *J* = 3.6 Hz, 1H), 4.76 (tt, *J* = 12.0, 3.8 Hz, 1H), 2.10-2.01 (m, 2H), 1.92-1.84 (m, 2H), 1.81-1.74 (m, 1H), 1.71-1.60 (m, 2H), 1.60-1.48 (m, 2H), 1.32-1.21 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 146.1, 144.1, 130.9, 125.1, 119.1, 115.7, 99.8, 52.8, 33.8, 25.8, 25.6.

IR (film) ν_{max} 2929, 2855, 1596, 1556, 1503, 1450, 1422, 1404, 1299, 1261, 1207, 1116, 915, 811, 743, 716 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{16}ClN_2$ ($[M+H]^+$) 235.0997, found 235.0991.



1-(1-Cyclohexyl-1*H*-pyrrolo[2,3-*b*]pyridin-3-yl)ethan-1-one (S20)

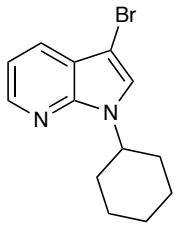
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 1-(1*H*-pyrrolo[2,3-*b*]pyridin-3-yl)ethan-1-one (80 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (3:1 hexane/EtOAc) provided the title compound (100 mg, 83% yield) as a yellow solid. The yield was determined based on 1-(1*H*-pyrrolo[2,3-*b*]pyridin-3-yl)ethan-1-one as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (dd, *J* = 7.9, 1.5 Hz, 1H), 8.34 (dd, *J* = 4.7, 1.5 Hz, 1H), 7.92 (s, 1H), 7.19 (dd, *J* = 7.9, 4.7 Hz, 1H), 4.79 (tt, *J* = 12.0, 3.7 Hz, 1H), 2.50 (s, 3H), 2.17-2.10 (m, 2H), 1.94-1.87 (m, 2H), 1.81-1.63 (m, 3H), 1.59-1.48 (m, 2H), 1.33-1.20 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 192.9, 147.7, 144.1, 131.6, 130.9, 118.9, 118.7, 115.5, 53.6, 33.6, 27.3, 25.7, 25.5.

IR (film) ν_{max} 2935, 2859, 1635, 1594, 1570, 1524, 1483, 1444, 1426, 1405, 1379, 1354, 1280, 1268, 1255, 1205, 1147, 1110, 995, 927, 894, 870, 779, 766, 742, 682 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{15}H_{19}N_2O$ ($[M+H]^+$) 243.1492, found 243.1491.



3-Bromo-1-cyclohexyl-1*H*-pyrrolo[2,3-*b*]pyridine (S21)

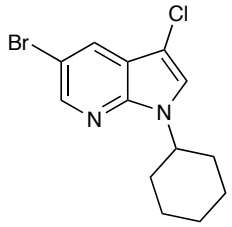
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 3-bromo-1*H*-pyrrolo[2,3-*b*]pyridine (99 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (12:1 hexane/EtOAc) provided the title compound (114 mg, 82% yield) as a light yellow oil. The yield was determined based on 3-bromo-1*H*-pyrrolo[2,3-*b*]pyridine as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, *J* = 4.6, 1.3 Hz, 1H), 7.83 (d, *J* = 7.9, 1.4 Hz, 1H), 7.32 (s, 1H), 7.10 (dd, *J* = 7.9, 4.7 Hz, 1H), 4.80 (tt, *J* = 11.9, 3.8 Hz, 1H), 2.12-2.05 (m, 2H), 1.93-1.85 (m, 2H), 1.80-1.73 (m, 1H), 1.70-1.59 (m, 2H), 1.58-1.47 (m, 2H), 1.30-1.20 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 146.1, 143.6, 127.5, 124.1, 120.0, 116.4, 87.9, 53.3, 33.8, 25.8, 25.6.

IR (film) ν_{max} 2929, 2854, 1595, 1563, 1510, 1450, 1417, 1326, 1278, 1263, 1209, 947, 789, 765, 751 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{16}BrN_2$ ($[M+H]^+$) 279.0491, found 279.0495.



5-Bromo-3-chloro-1-cyclohexyl-1*H*-pyrrolo[2,3-*b*]pyridine (39)

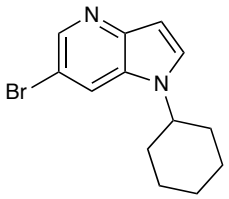
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 5-bromo-3-chloro-1*H*-pyrrolo[2,3-*b*]pyridine (116 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (16:1 hexane/EtOAc) provided the title compound (140 mg, 89% yield) as a yellow solid. The yield was determined based on 5-bromo-3-chloro-1*H*-pyrrolo[2,3-*b*]pyridine as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 2.1 Hz, 1H), 7.92 (d, *J* = 2.1 Hz, 1H), 7.18 (s, 1H), 4.63 (tt, *J* = 11.9, 3.8 Hz, 1H), 2.91-1.94 (m, 2H), 1.85-1.77 (m, 2H), 1.72-1.65 (m, 1H), 1.59-1.49 (m, 2H), 1.49-1.38 (m, 2H), 1.22-1.11 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.3, 143.9, 128.7, 123.0, 119.8, 112.0, 102.5, 53.6, 33.6, 25.8, 25.5.

IR (film) ν_{max} 2929, 2854, 1553, 1512, 1459, 1450, 1416, 1348, 1260, 1206, 1187, 1161, 1074, 1003, 972, 883, 828, 781, 767, 688 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{15}BrClN_2$ ($[M+H]^+$) 313.0102, found 313.0106.



6-Bromo-1-cyclohexyl-1*H*-pyrrolo[3,2-*b*]pyridine (40)

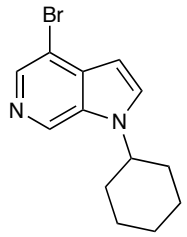
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 6-bromo-1*H*-pyrrolo[3,2-*b*]pyridine (197 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.5 mmol, 1.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (2:1 hexane/EtOAc) provided the title compound (105 mg, 75% yield) as a light yellow oil. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, *J* = 1.9 Hz, 1H), 7.82-7.79 (m, 1H), 7.40 (d, *J* = 3.4 Hz, 1H), 6.66 (d, *J* = 3.3 Hz, 1H), 4.09 (tt, *J* = 11.9, 3.7 Hz, 1H), 2.10-2.03 (m, 2H), 1.97-1.89 (m, 2H), 1.82-1.63 (m, 3H), 1.52-1.41 (m, 2H), 1.32-1.24 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 143.7, 129.2, 128.6, 119.3, 112.4, 102.4, 55.8, 33.4, 25.8, 25.5.

IR (film) ν_{max} 2931, 2855, 1501, 1451, 1410, 1283, 1267, 1214, 905, 868, 781, 764, 750, 724 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{16}BrN_2$ ($[M+H]^+$) 279.0491, found 279.0488.



4-Bromo-1-cyclohexyl-1*H*-pyrrolo[2,3-*c*]pyridine (S22)

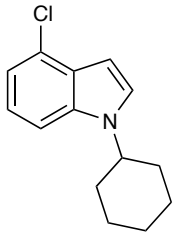
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 4-bromo-1*H*-pyrrolo[2,3-*c*]pyridine (99 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (3:1 to 2:1 hexane/EtOAc) provided the title compound (90 mg, 64% yield) as a yellow solid. The yield was determined based on 4-bromo-1*H*-pyrrolo[2,3-*c*]pyridine as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (br s, 1H), 8.35 (br s, 1H), 7.40 (d, *J* = 3.0 Hz, 1H), 6.53 (d, *J* = 3.1 Hz, 1H), 4.26 (tt, *J* = 11.9, 3.6 Hz, 1H), 2.17-2.09 (m, 2H), 1.98-1.89 (m, 2H), 1.83-1.65 (m, 3H), 1.55-1.44 (m, 2H), 1.33-1.21 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2, 133.9, 131.5, 128.6, 101.1, 56.5, 33.8, 25.8, 25.5.

IR (film) ν_{max} 2931, 2855, 1492, 1438, 1295, 1274, 1212, 1194, 1178, 894, 864, 767, 751, 725 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{16}BrN_2$ ($[M+H]^+$) 279.0491, found 279.0487.



4-Chloro-1-cyclohexyl-1*H*-indole (S23)

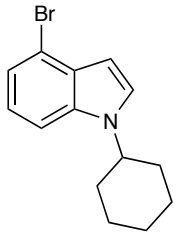
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 4-chloro-1*H*-indole (227 mg, 1.50 mmol, 3.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (10:1 hexane/DCM) provided the title compound (64 mg, 55% yield) as a white solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.37 (m, 2H), 7.25-7.22 (m, 2H), 6.75 (d, *J* = 3.1 Hz, 1H), 4.32 (tt, *J* = 11.9, 3.7 Hz, 1H), 2.30-2.22 (m, 2H), 2.12-2.03 (m, 2H), 1.98-1.90 (m, 1H), 1.88-1.77 (m, 2H), 1.68-1.57 (m, 2H), 1.48-1.37 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 136.4, 127.2, 126.2, 124.8, 121.8, 119.1, 108.2, 99.8, 55.7, 33.6, 26.0, 25.7.

IR (film) ν_{max} 2930, 2854, 1477, 1450, 1435, 1342, 1268, 1177, 904, 893, 738, 713 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{17}ClN$ ($[M+H]^+$) 234.1044, found 234.1041.



4-Bromo-1-cyclohexyl-1*H*-indole (S24)

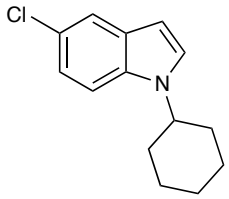
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 4-bromo-1*H*-indole (294 mg, 1.50 mmol, 3.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (10:1 hexane/DCM) provided the title compound (82 mg, 59% yield) as a white solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.3 Hz, 1H), 7.31-7.28 (m, 2H), 7.07 (t, *J* = 7.9 Hz, 1H), 6.59 (d, *J* = 3.0 Hz, 1H), 4.20 (tt, *J* = 11.8, 3.5 Hz, 1H), 2.18-2.10 (m, 2H), 2.00-1.92 (m, 2H), 1.86-1.78 (m, 1H), 1.77-1.66 (m, 2H), 1.57-1.45 (m, 2H), 1.36-1.26 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 136.0, 129.1, 124.8, 122.2, 122.1, 115.0, 108.8, 101.5, 55.7, 33.6, 26.0, 25.7.

IR (film) ν_{max} 2931, 2854, 1552, 1505, 1474, 1449, 1432, 1339, 1308, 1268, 1174, 1139, 889, 806, 737, 712 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{17}BrN$ ($[M+H]^+$) 278.0539, found 278.0536.



5-Chloro-1-cyclohexyl-1*H*-indole (S25)

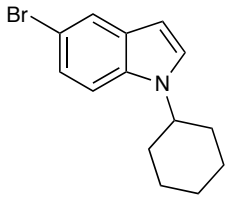
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 5-chloro-1*H*-indole (227 mg, 1.50 mmol, 3.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (10:1 hexane/DCM) provided the title compound (62 mg, 53% yield) as a yellow oil. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 2.0 Hz, 1H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.27-7.23 (m, 1H), 7.16 (dd, *J* = 8.7, 2.0 Hz, 1H), 6.46 (d, *J* = 3.2 Hz, 1H), 4.18 (tt, *J* = 11.9, 3.7 Hz, 1H), 2.17-2.10 (m, 2H), 2.00-1.92 (m, 2H), 1.85-1.77 (m, 1H), 1.70 (qd, *J* = 12.5, 3.3 Hz, 2H), 1.57-1.45 (m, 2H), 1.36-1.25 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 134.0, 129.5, 125.5, 124.9, 121.5, 120.3, 110.5, 100.8, 55.5, 33.6, 26.0, 25.7.

IR (film) ν_{max} 2932, 2855, 1465, 1451, 1331, 1269, 1209, 1063, 994, 908, 892, 866, 814, 791, 761, 752, 715, 687 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{17}ClN$ ($[M+H]^+$) 234.1044, found 234.1044.



5-Bromo-1-cyclohexyl-1*H*-indole (S26)

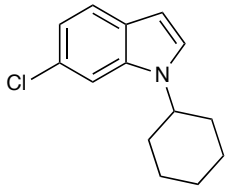
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 5-bromo-1*H*-indole (294 mg, 1.50 mmol, 3.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (10:1 hexane/DCM) provided the title compound (81 mg, 58% yield) as a white solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78-7.75 (m, 1H), 7.31-7.24 (m, 2H), 7.23 (d, *J* = 3.0 Hz, 1H), 6.46 (d, *J* = 2.9 Hz, 1H), 4.18 (tt, *J* = 11.8, 3.3 Hz, 1H), 2.17-2.09 (m, 2H), 1.99-1.91 (m, 2H), 1.86-1.78 (m, 1H), 1.75-1.64 (m, 2H), 1.56-1.45 (m, 2H), 1.36-1.25 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 134.3, 130.2, 125.3, 124.0, 123.4, 112.5, 110.0, 100.7, 55.4, 33.6, 26.0, 25.7.

Data are consistent with those reported in the literature:

Wang, C.-S., Wu, X.-F., Dixneuf, P. H. & Soulé, J.-F. *ChemSusChem* **10**, 3075–3082 (2017).



6-Chloro-1-cyclohexyl-1*H*-indole (S27)

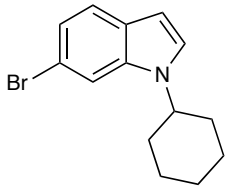
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 6-chloro-1*H*-indole (227 mg, 1.50 mmol, 3.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (10:1 hexane/DCM) provided the title compound (70 mg, 60% yield) as a white solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.4 Hz, 1H), 7.40 (s, 1H), 7.22 (d, *J* = 3.2 Hz, 1H), 7.08 (dd, *J* = 8.4, 1.7 Hz, 1H), 6.50 (d, *J* = 3.2 Hz, 1H), 4.15 (tt, *J* = 11.9, 3.7 Hz, 1H), 2.18-2.10 (m, 2H), 2.00-1.92 (m, 2H), 1.86-1.78 (m, 1H), 1.70 (qd, *J* = 12.5, 3.3 Hz, 2H), 1.57-1.45 (m, 2H), 1.36-1.25 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 136.0, 127.3, 127.1, 124.9, 121.8, 120.0, 109.6, 101.4, 55.4, 33.6, 26.0, 25.7.

IR (film) ν_{max} 2931, 2855, 1504, 1463, 1451, 1314, 1207, 1100, 903, 893, 801, 714 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{17}ClN$ ($[M+H]^+$) 234.1044, found 234.1044.



6-Bromo-1-cyclohexyl-1*H*-indole (S28)

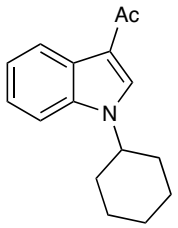
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 6-bromo-1*H*-indole (294 mg, 1.50 mmol, 3.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (10:1 hexane/DCM) provided the title compound (70 mg, 50% yield) as a white solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.22-7.17 (m, 2H), 6.48 (d, *J* = 3.1 Hz, 1H), 4.14 (tt, *J* = 11.9, 3.6 Hz, 1H), 2.16-2.08 (m, 2H), 2.00-1.90 (m, 2H), 1.85-1.77 (m, 1H), 1.75-1.63 (m, 2H), 1.57-1.44 (m, 2H), 1.35-1.23 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 136.5, 127.3, 124.8, 122.5, 122.2, 114.9, 112.6, 101.4, 55.4, 33.6, 26.0, 25.7.

IR (film) ν_{max} 2930, 2854, 1503, 1460, 1449, 1313, 1207, 891, 800, 714 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{17}BrN$ ($[M+H]^+$) 278.0539, found 278.0545.



1-(1-Cyclohexyl-1*H*-indol-3-yl)ethan-1-one (41)

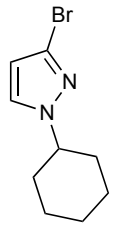
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 1-(1*H*-indol-3-yl)ethan-1-one (239 mg, 1.50 mmol, 3.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (2:1 hexane/EtOAc) provided the title compound (70 mg, 58% yield) as a yellow solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (dt, *J* = 7.1, 3.4 Hz, 1H), 7.87 (s, 1H), 7.43-7.37 (m, 1H), 7.29 (dt, *J* = 6.1, 3.5 Hz, 2H), 4.25 (tt, *J* = 11.9, 3.6 Hz, 1H), 2.54 (s, 3H), 2.23-2.16 (m, 2H), 2.02-1.94 (m, 2H), 1.87-1.80 (m, 1H), 1.78-1.68 (m, 2H), 1.59-1.47 (m, 2H), 1.37-1.26 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 193.1, 136.6, 131.5, 126.4, 123.0, 122.7, 122.6, 117.1, 110.0, 55.8, 33.5, 27.8, 25.8, 25.6.

IR (film) ν_{max} 2933, 2853, 1632, 1610, 1521, 1459, 1407, 1388, 1209, 1192, 1175, 1012, 988, 929, 739 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{16}H_{20}NO$ ($[M+H]^+$) 242.1539, found 242.1541.



3-Bromo-1-cyclohexyl-1*H*-pyrazole (S29)

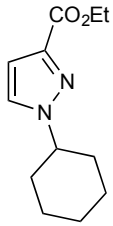
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (6.6 mg, 10 μmol, 0.02 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 3-bromo-1*H*-pyrazole (74 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (40:1 hexane/EtOAc) provided the title compound (105 mg, 92% yield, >20:1 r.r.) as a yellow oil. The yield was determined based on 3-bromo-1*H*-pyrazole as the limiting reagent (1.0 equiv). The structure of the title compound (regioselectivity) was further confirmed via 2D NMR (NOESY) analysis.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 2.3 Hz, 1H), 6.20 (d, *J* = 2.3 Hz, 1H), 4.02 (tt, *J* = 11.8, 3.8 Hz, 1H), 2.16-2.06 (m, 2H), 1.87-1.83 (m, 2H), 1.74-1.60 (m, 3H), 1.36 (qt, *J* = 13.2, 3.4 Hz, 2H), 1.22 (tt, *J* = 12.8, 3.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 128.7, 124.6, 107.7, 62.0, 33.4, 25.4, 25.3.

IR (film) ν_{max} 2933, 2857, 1494, 1386, 1359, 1302, 1046, 953, 747 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_9H_{14}BrN_2$ ($[M+H]^+$) 229.0335, found 229.0334.



Ethyl 1-cyclohexyl-1*H*-pyrazole-3-carboxylate (S30)

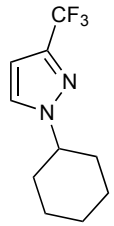
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (6.6 mg, 10 μmol, 0.02 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), ethyl 1*H*-pyrazole-3-carboxylate (70 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (8:1 to 4:1 hexane/EtOAc) provided the title compound (80 mg, 72% yield, >20:1 r.r.) as a pale yellow oil. The yield was determined based on ethyl 1*H*-pyrazole-3-carboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 2.4 Hz, 1H), 6.79 (d, *J* = 2.4 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 4.23 (tt, *J* = 11.9, 3.8 Hz, 1H), 2.23-2.13 (m, 2H), 1.96-1.85 (m, 2H), 1.76-1.64 (m, 3H), 1.48-1.38 (m, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.26 (tt, *J* = 12.9, 3.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.7, 142.9, 127.6, 108.7, 62.4, 61.0, 33.6, 25.4, 25.3, 14.6.

IR (film) ν_{max} 2935, 2858, 1717, 1453, 1374, 1227, 1214, 1153, 1027, 762 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{19}N_2O_2$ ($[M+H]^+$) 223.1441, found 223.1441.



1-Cyclohexyl-3-(trifluoromethyl)-1*H*-pyrazole (S31)

Prepared following the general procedure outlined above using $Ir(ppy)_3$ (6.6 mg, 10 μmol, 0.02 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 3-(trifluoromethyl)-1*H*-pyrazole (68 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (40:1 hexane/EtOAc) provided the title compound (107 mg, 98% yield, >20:1 r.r.) as a yellow oil. The yield was determined based on 3-(trifluoromethyl)-1*H*-pyrazole as the limiting reagent (1.0 equiv).

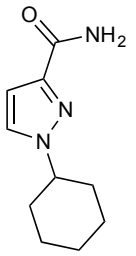
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 2.1 Hz, 1H), 6.47 (d, *J* = 2.1 Hz, 1H), 4.15 (tt, *J* = 11.8, 3.8 Hz, 1H), 2.19-2.11 (m, 2H), 1.90-1.87 (m, 2H), 1.70 (qd, *J* = 12.5, 3.4 Hz, 3H), 1.40 (qt, *J* = 13.3, 3.4 Hz, 2H), 1.26 (tt, *J* = 12.7, 3.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 141.5 (q, *J* = 37.8 Hz), 127.7, 121.5 (q, *J* = 268.2 Hz), 103.7 (q, *J* = 2.0 Hz), 62.1, 33.4, 25.2, 25.1.

^{19}F NMR (282 MHz, $CDCl_3$) δ –61.7 (s, 3F).

IR (film) ν_{max} 2938, 2861, 1490, 1368, 1274, 1234, 1120, 1056, 945, 762 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{10}H_{14}F_3N_2$ ($[M+H]^+$) 219.1104, found 219.1103.



1-Cyclohexyl-1*H*-pyrazole-3-carboxamide (S32)

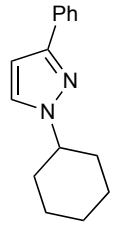
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (6.6 mg, 10 μmol, 0.02 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 1*H*-pyrazole-3-carboxamide (56 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (1:2 hexane/EtOAc) provided the title compound (60 mg, 62% yield, >20:1 r.r.) as a brown solid. The yield was determined based on 1*H*-pyrazole-3-carboxamide as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (brs, 1H), 6.77 (brs, 2H), 5.94 (brs, 1H), 4.07 (tt, *J* = 11.7, 3.4 Hz, 1H), 2.13-2.11 (m, 2H), 1.89-1.87 (m, 2H), 1.76-1.62 (m, 3H), 1.44-1.36 (m, 2H), 1.25 (tt, *J* = 12.8, 3.3 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.6, 145.3, 128.5, 106.4, 61.9, 33.5, 25.3, 25.3.

IR (film) ν_{max} 3302, 2933, 2857, 1661, 1593, 1364, 1294, 1179, 760 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{10}H_{16}N_3O$ ($[M+H]^+$) 194.1288, found 194.1287.



1-Cyclohexyl-3-phenyl-1*H*-pyrazole (S33)

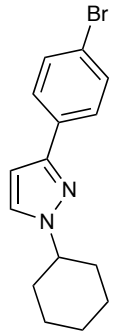
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (6.6 mg, 10 μmol, 0.02 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 3-phenyl-1*H*-pyrazole (72 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (30:1 hexane/EtOAc) provided the title compound (81 mg, 72% yield, >20:1 r.r.) as a yellow oil. The yield was determined based on 3-phenyl-1*H*-pyrazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85-7.77 (m, 2H), 7.44 (d, *J* = 2.3 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.28 (dt, *J* = 7.9, 1.5 Hz, 1H), 6.54 (d, *J* = 2.3 Hz, 1H), 4.17 (tt, *J* = 11.8, 3.8 Hz, 1H), 2.28-2.20 (m, 2H), 1.93-1.89 (m, 2H), 1.77-1.69 (m, 3H), 1.45 (qt, *J* = 13.2, 3.4 Hz, 2H), 1.29 (tt, *J* = 12.8, 3.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 150.6, 134.0, 128.7, 127.6, 127.4, 125.7, 102.3, 61.5, 33.8, 25.6, 25.6.

IR (film) ν_{max} 2932, 2856, 1498, 1454, 1358, 1224, 1074, 746, 694 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{15}H_{19}N_2$ ($[M+H]^+$) 227.1543, found 227.1542.



3-(4-Bromophenyl)-1-cyclohexyl-1*H*-pyrazole (S34)

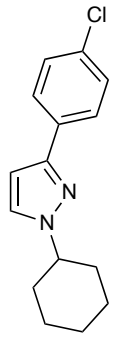
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (6.6 mg, 10 μmol, 0.02 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 3-(4-bromophenyl)-1*H*-pyrazole (112 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (30:1 hexane/EtOAc) provided the title compound (130 mg, 85% yield, >20:1 r.r.) as a pale yellow solid. The yield was determined based on 3-(4-bromophenyl)-1*H*-pyrazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 2.3 Hz, 1H), 6.50 (d, *J* = 2.3 Hz, 1H), 4.15 (tt, *J* = 11.9, 3.8 Hz, 1H), 2.27-2.14 (m, 2H), 1.92-1.89 (m, 2H), 1.72 (qd, *J* = 12.5, 3.3 Hz, 3H), 1.44 (qt, *J* = 13.2, 3.4 Hz, 2H), 1.29 (tt, *J* = 12.7, 3.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.5, 133.0, 131.7, 127.8, 127.2, 121.2, 102.3, 61.6, 33.8, 25.5, 25.5.

IR (film) ν_{max} 2933, 2856, 1492, 1223, 1009, 948, 831, 752 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{15}H_{18}BrN_2$ ($[M+H]^+$) 305.0648, found 305.0645.



3-(4-Chlorophenyl)-1-cyclohexyl-1*H*-pyrazole (S35)

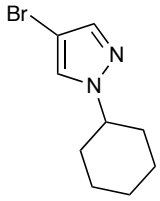
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (6.6 mg, 10 μmol, 0.02 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 3-(4-chlorophenyl)-1*H*-pyrazole (89 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (30:1 hexane/EtOAc) provided the title compound (107 mg, 82% yield, >20:1 r.r.) as a yellow solid. The yield was determined based on 3-(4-chlorophenyl)-1*H*-pyrazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 2.3 Hz, 1H), 7.35 (d, *J* = 8.6 Hz, 2H), 6.50 (d, *J* = 2.3 Hz, 1H), 4.14 (tt, *J* = 11.8, 3.8 Hz, 1H), 2.27-2.15 (m, 2H), 1.93-1.89 (m, 2H), 1.79-1.66 (m, 3H), 1.44 (qt, *J* = 13.2, 3.4 Hz, 2H), 1.28 (tt, *J* = 12.8, 3.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.5, 133.0, 132.6, 128.8, 127.8, 126.9, 102.3, 61.5, 33.7, 25.5, 25.5.

IR (film) ν_{max} 2932, 2856, 1494, 1451, 1221, 1088, 1013, 832, 750 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{15}H_{18}ClN_2$ ($[M+H]^+$) 261.1153, found 261.1151.



4-Bromo-1-cyclohexyl-1*H*-pyrazole (43)

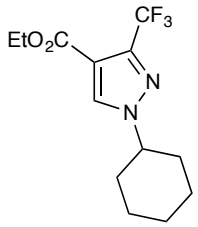
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (6.6 mg, 10 μmol, 0.02 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 4-bromo-1H-pyrazole (74 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (40:1 hexane/EtOAc) provided the title compound (78 mg, 68% yield) as a white solid. The yield was determined based on 4-bromo-1*H*-pyrazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.42 (s, 1H), 4.06 (tt, *J* = 11.7, 3.8 Hz, 1H), 2.17-2.08 (m, 2H), 1.88 (dt, *J* = 13.8, 3.3 Hz, 2H), 1.76-1.59 (m, 3H), 1.40 (qt, *J* = 13.3, 3.4 Hz, 2H), 1.24 (tt, *J* = 12.8, 3.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.1, 127.0, 92.4, 62.0, 33.5, 25.4, 25.4.

IR (film) ν_{max} 3112, 2938, 2855, 1452, 1304, 950, 852 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_9H_{14}BrN_2$ ($[M+H]^+$) 229.0335, found 229.0333.



Ethyl 1-cyclohexyl-3-(trifluoromethyl)-1*H*-pyrazole-4-carboxylate (42)

Prepared following the general procedure outlined above using $Ir(ppy)_3$ (6.6 mg, 10 μmol, 0.02 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), ethyl 3-(trifluoromethyl)-1*H*-pyrazole-4-carboxylate (104 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (10:1 hexane/EtOAc) provided the title compound (142 mg, 98% yield, >20:1 r.r.) as a pale yellow oil. The yield was determined based on ethyl 3-(trifluoromethyl)-1*H*-pyrazole-4-carboxylate as the limiting reagent (1.0 equiv).

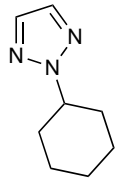
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (s, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 4.14 (tt, *J* = 11.8, 3.8 Hz, 1H), 2.21-2.12 (m, 2H), 1.95-1.86 (m, 2H), 1.78-1.62 (m, 3H), 1.45-1.35 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.25 (ddd, *J* = 16.5, 8.3, 3.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 161.2, 141.0 (q, *J* = 38.2 Hz), 133.0, 120.7 (q, *J* = 269.5 Hz), 112.7, 62.5, 60.9, 33.2, 25.2, 25.1, 14.2.

^{19}F NMR (282 MHz, $CDCl_3$) δ –62.0 (s, 3F).

IR (film) ν_{max} 2939, 2862, 1726, 1541, 1301, 1136, 1050, 775 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{18}F_3N_2O_2$ ($[M+H]^+$) 291.1315, found 291.1313.



2-Cyclohexyl-2*H*-1,2,3-triazole (S36)

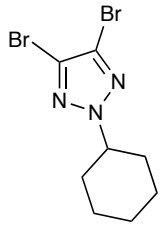
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 1*H*-1,2,3-triazole (35 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (4:1 hexane/Et_2O) provided the title compound (61 mg, 81% yield, >20:1 r.r.) as a colorless volatile oil. The yield was determined based on 1*H*-1,2,3-triazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (s, 2H), 4.47 (tt, *J* = 11.2, 3.9 Hz, 1H), 2.20-2.12 (m, 2H), 1.94-1.83 (m, 4H), 1.76-1.68 (m, 1H), 1.48-1.37 (m, 2H), 1.34-1.26 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 133.5, 64.2, 32.8, 25.4, 25.2.

IR (film) ν_{max} 2931, 2857, 1453, 1417, 1346, 969, 963, 814, 763, 751 cm^{-1}.

HRMS (EI-TOF) m/z calcd. for $C_8H_{13}N_3$ (M^+) 151.1104, found 151.1106.



4,5-Dibromo-2-cyclohexyl-2*H*-1,2,3-triazole (S37)

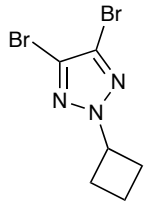
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 4,5-dibromo-1*H*-1,2,3-triazole (113 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (3:1 hexane/DCM) provided the title compound (123 mg, 80% yield, >20:1 r.r.) as a white solid. The yield was determined based on 4,5-dibromo-1*H*-1,2,3-triazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.39 (tt, *J* = 11.3, 3.8 Hz, 1H), 2.18-2.10 (m, 2H), 1.93-1.79 (m, 4H), 1.74-1.66 (m, 1H), 1.45-1.34 (m, 2H), 1.31-1.23 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 123.6, 66.2, 32.5, 25.1, 25.0.

IR (film) ν_{max} 2947, 2924, 2858, 1450, 1397, 1379, 1345, 1338, 1053, 1042, 986, 896, 890, 823, 763, 750 cm^{-1}.

HRMS (EI-TOF) m/z calcd. for $C_8H_{11}Br_2N_3$ (M^+) 306.9314, found 306.9314.



4,5-Dibromo-2-cyclobutyl-2*H*-1,2,3-triazole (S38)

Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 4,5-dibromo-1*H*-1,2,3-triazole (113 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclobutanecarboxylate (444 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (3:1 hexane/DCM) provided the title compound (115 mg, 82% yield, >20:1 r.r.) as a white solid. The yield was determined based on 4,5-dibromo-1*H*-1,2,3-triazole as the limiting reagent (1.0 equiv).

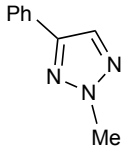
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.03 (p, *J* = 8.3 Hz, 1H), 2.72-2.61 (m, 2H), 2.54-2.45 (m, 2H), 1.97-1.80 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 124.1, 60.0, 30.2, 14.6.

IR (film) ν_{max} 3004, 2952, 1433, 1399, 1342, 1255, 1040, 987, 745 cm^{-1}.

HRMS (EI-TOF) m/z calcd. for $C_6H_7Br_2N_3$ (M^+) 278.9001, found 278.9009.

Data are consistent with those reported in the literature:
Huard, K. *et al. J. Med. Chem.* **58**, 7164–7172 (2015).



2-Methyl-4-phenyl-2*H*-1,2,3-triazole (S39)

Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 4-phenyl-1*H*-1,2,3-triazole (73 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene diacetate (364 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (10:1 to 4:1 hexane/Et_2O) provided the title compound (24 mg, 30% yield, >20:1 r.r.) as a light yellow solid. The yield was determined based on 4-phenyl-1*H*-1,2,3-triazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.80-7.75 (m, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 4.24 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 131.0, 130.5, 129.0, 128.5, 125.9, 41.9.

^{1}H NMR (500 MHz, d^6-DMSO) δ 8.22 (s, 1H), 7.83 (d, *J* = 7.3 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.39-7.33 (m, 1H), 4.19 (s, 3H).

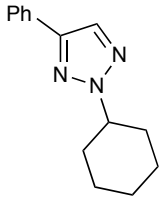
^{13}C NMR (125 MHz, d^6-DMSO) δ 146.9, 131.3, 130.1, 129.0, 128.3, 125.5, 41.6.

Data are consistent with those reported in the literature:

Abboud, J.-L. M., Foces-Foces, C., Notario, R., Trifonov, R. E., Volovodenko, A. P., Ostrovskii, V. A., Alkorta, I. & Elguero, J. *Eur. J. Org. Chem.* 3013–3024 (2001).

Röhrig, U. F. *et al. J. Med. Chem.* **55**, 5270–5290 (2012).

Kozima, S., Itano, T., Mihara, N., Sisido, K. & Isida, T. *J. Organomet. Chem.* **44**, 117–126 (1972).



2-Cyclohexyl-4-phenyl-2*H*-1,2,3-triazole (53)

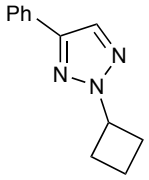
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 4-phenyl-1*H*-1,2,3-triazole (73 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (1:1 hexane/DCM) provided the title compound (102 mg, 90% yield, >20:1 r.r.) as a white solid. The yield was determined based on 4-phenyl-1*H*-1,2,3-triazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.81-7.77 (m, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 4.50 (tt, *J* = 11.4, 3.8 Hz, 1H), 2.26-2.19 (m, 2H), 2.01-1.88 (m, 4H), 1.77-1.70 (m, 1H), 1.51-1.40 (m, 2H), 1.37-1.29 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 147.0, 130.8, 130.3, 128.9, 128.2, 125.9, 64.3, 32.8, 25.3, 25.2.

IR (film) ν_{max} 2925, 2857, 1474, 1459, 1448, 1365, 1348, 1318, 989, 978, 900, 847, 822, 765, 744, 689 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{18}N_3$ ($[M+H]^+$) 228.1495, found 228.1495.



2-Cyclobutyl-4-phenyl-2*H*-1,2,3-triazole (S40)

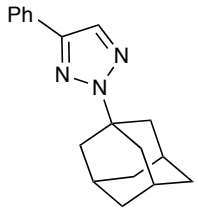
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 4-phenyl-1*H*-1,2,3-triazole (73 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclobutanecarboxylate (444 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (10:1 hexane/Et_2O) provided the title compound (88 mg, 88% yield, >20:1 r.r.) as a yellow solid. The yield was determined based on 4-phenyl-1*H*-1,2,3-triazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.80 (d, *J* = 7.3 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 5.15 (p, *J* = 8.2 Hz, 1H), 2.84-2.72 (m, 2H), 2.60-2.50 (m, 2H), 2.02-1.85 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 147.4, 130.7, 128.9, 128.4, 126.0, 58.5, 30.3, 14.9.

IR (film) ν_{max} 2991, 2949, 1474, 1459, 1374, 1320, 1303, 1255, 1084, 988, 976, 843, 767, 692 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{14}N_3$ ($[M+H]^+$) 200.1182, found 200.1183.



2-(Adamantan-1-yl)-4-phenyl-2*H*-1,2,3-triazole (S41)

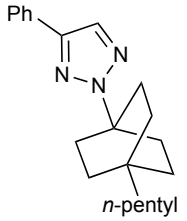
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 4-phenyl-1*H*-1,2,3-triazole (73 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene bis(adamantane-1-carboxylate) (605 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (2:1 to 1:1 hexane/DCM) provided the title compound (56 mg, 40% yield, >20:1 r.r.) as a white solid. The yield was determined based on 4-phenyl-1*H*-1,2,3-triazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.82-7.79 (m, 2H), 7.44-7.39 (m, 2H), 7.35-7.30 (m, 1H), 2.38-2.32 (m, 6H), 2.30-2.24 (m, 3H), 1.83-1.77 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 131.1, 130.0, 128.9, 128.1, 126.0, 63.0, 42.5, 36.2, 29.7.

IR (film) ν_{max} 2908, 2852, 1474, 1456, 1357, 1311, 1092, 992, 977, 967, 846, 767, 693 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{18}H_{22}N_3$ ($[M+H]^+$) 280.1808, found 280.1807.



2-(4-Pentylbicyclo[2.2.2]octan-1-yl)-4-phenyl-2*H*-1,2,3-triazole (S42)

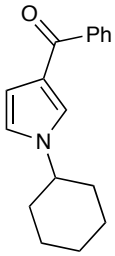
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (3.3 mg, 5.0 μmol, 0.01 equiv.), CuCl (10 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 4-phenyl-1*H*-1,2,3-triazole (73 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene bis(4-pentylbicyclo[2.2.2]octane-1-carboxylate) (693 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (1:1 hexane/DCM) provided the title compound (32 mg, 20% yield, >20:1 r.r.) as a yellow solid. The yield was determined based on 4-phenyl-1*H*-1,2,3-triazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.78 (d, *J* = 7.2 Hz, 2H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 2.27-2.19 (m, 6H), 1.66-1.59 (m, 6H), 1.33-1.14 (m, 8H), 0.90 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 146.8, 131.1, 130.1, 128.9, 128.2, 126.0, 63.1, 41.1, 32.9, 31.9, 31.4, 31.2, 23.7, 22.8, 14.3.

IR (film) ν_{max} 2952, 2924, 2859, 1459, 978, 767, 750, 692 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{21}H_{30}N_3$ ($[M+H]^+$) 324.2434, found 324.2440.



(1-Cyclohexyl-1*H*-pyrrol-3-yl)(phenyl)methanone (S43)

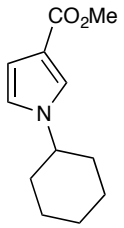
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), phenyl(1*H*-pyrrol-3-yl)methanone (171 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.5 mmol, 1.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (8:1 hexane/EtOAc) provided the title compound (101 mg, 80% yield) as a white solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.54-7.48 (m, 1H), 7.47-7.42 (m, 2H), 7.31 (t, *J* = 1.9 Hz, 1H), 6.75-6.72 (m, 1H), 6.67 (dd, *J* = 2.9, 1.7 Hz, 1H), 3.82 (tt, *J* = 11.9, 3.8 Hz, 1H), 2.14-2.07 (m, 2H), 1.93-1.85 (m, 2H), 1.77-1.70 (m, 1H), 1.67-1.57 (m, 2H), 1.45-1.33 (m, 2H), 1.27-1.19 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 190.8, 140.3, 131.2, 128.9, 128.2, 126.0, 124.0, 120.4, 110.6, 59.5, 34.5, 25.6, 25.3.

IR (film) ν_{max} 2931, 2856, 1628, 1599, 1575, 1521, 1447, 1389, 1368, 1288, 1231, 1212, 1141, 876, 720, 698, 674 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{17}H_{20}NO$ ($[M+H]^+$) 254.1539, found 254.1532.



Methyl 1-cyclohexyl-1*H*-pyrrole-3-carboxylate (51)

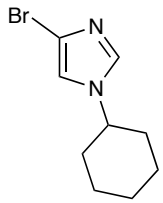
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), methyl 1*H*-pyrrole-3-carboxylate (125 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.5 mmol, 1.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (5:1 hexane/EtOAc) provided the title compound (78 mg, 75% yield) as a white solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.33 (m, 1H), 6.67-6.63 (m, 1H), 6.58-6.52 (m, 1H), 3.82-3.74 (m, 4H), 2.11-2.03 (m, 2H), 1.91-1.84 (m, 2H), 1.76-1.69 (m, 1H), 1.64-1.54 (m, 2H), 1.44-1.32 (m, 2H), 1.26-1.18 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 165.5, 123.9, 119.9, 115.1, 109.5, 59.3, 51.0, 34.5, 25.6, 25.4.

IR (film) ν_{max} 2932, 2856, 1702, 1537, 1364, 1188, 1114, 999, 761, 713 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{18}NO_2$ ($[M+H]^+$) 208.1332, found 208.1335.



4-Bromo-1-cyclohexyl-1*H*-imidazole (52)

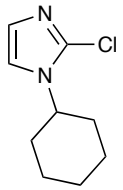
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 4-bromo-1*H*-imidazole (74 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (2:1 hexane/EtOAc) provided the title compound (78 mg, 68% yield, >20:1 r.r.) as a white solid. The yield was determined based on 4-bromo-1*H*-imidazole as the limiting reagent (1.0 equiv). The structure of the title compound (regioselectivity) was further confirmed via 2D NMR (HMBC) analysis.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 1.4 Hz, 1H), 6.90 (d, *J* = 1.5 Hz, 1H), 3.85 (tt, *J* = 11.8, 3.8 Hz, 1H), 2.10-2.02 (m, 2H), 1.91-1.83 (m, 2H), 1.75-1.68 (m, 1H), 1.62-1.51 (m, 2H), 1.43-1.31 (m, 2H), 1.26-1.16 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 135.0, 116.5, 114.8, 57.6, 34.3, 25.3, 25.1.

IR (film) ν_{max} 2932, 2856, 1475, 1451, 1234, 1112, 944, 815 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_9H_{14}BrN_2$ ($[M+H]^+$) 229.0335, found 229.0334.



2-Chloro-1-cyclohexyl-1*H*-imidazole (S44)

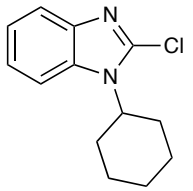
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (3.3 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 2-chloro-1*H*-imidazole (51 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (1:2 hexane/Et_2O) provided the title compound (55 mg, 60% yield) as a yellow solid. The yield was determined based on 2-chloro-1*H*-imidazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.94 (s, 2H), 4.02 (tt, J = 11.8, 3.8 Hz, 1H), 2.05-1.98 (m, 2H), 1.92-1.85 (m, 2H), 1.77-1.70 (m, 1H), 1.56-1.39 (m, 4H), 1.25-1.18 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 131.0, 128.2, 117.3, 56.1, 33.6, 25.6, 25.2.

IR (film) ν_{max} 2932, 2857, 1462, 1452, 1398, 1361, 1297, 1267, 1234, 1107, 998, 894, 746, 667 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_9H_{14}ClN_2$ ($[M+H]^+$) 185.0840, found 185.0839.



2-Chloro-1-cyclohexyl-1*H*-benzo[*d*]imidazole (54)

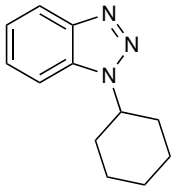
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (3.3 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 2-chloro-1*H*-benzo[*d*]imidazole (76 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (15:1 hexane/EtOAc) provided the title compound (79 mg, 67% yield) as a yellow solid. The yield was determined based on 2-chloro-1*H*-benzo[*d*]imidazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71-7.65 (m, 1H), 7.55-7.50 (m, 1H), 7.25-7.21 (m, 2H), 4.45 (tt, *J* = 12.3, 3.8 Hz, 1H), 2.27-2.17 (m, 2H), 2.01-1.91 (m, 4H), 1.85-1.77 (m, 1H), 1.53-1.41 (m, 2H), .37-1.29 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2, 140.1, 134.0, 122.6, 122.3, 119.7, 111.5, 57.3, 31.1, 26.1, 25.3.

IR (film) ν_{max} 2932, 2857, 1470, 1449, 1358, 1345, 1275, 1244, 740 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{16}ClN_2$ ($[M+H]^+$) 235.0997, found 235.0995.



1-Cyclohexyl-1*H*-benzo[*d*][1,2,3]triazole (55)

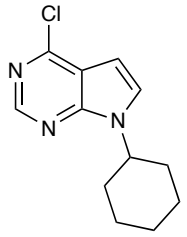
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 1*H*-benzo[*d*][1,2,3]triazole (60 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (10:1 hexane/EtOAc) provided the title compound (81 mg, 80% yield, >20:1 r.r.) as a white solid. The yield was determined based on 1*H*-benzo[*d*][1,2,3]triazole as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.48-7.43 (m, 1H), 7.37-7.33 (m, 1H), 4.70-4.62 (m, 1H), 2.21-2.15 (m, 2H), 2.05-1.97 (m, 2H), 1.86-1.79 (m, 1H), 1.59-1.24 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 146.1, 132.3, 126.9, 123.8, 120.1, 109.9, 59.2, 32.7, 25.7, 25.4.

Data are consistent with those reported in the literature:

Wang, C.-S., Wu, X.-F., Dixneuf, P. H. & Soulé, J.-F. *ChemSusChem* **10**, 3075–3082 (2017).



4-Chloro-7-cyclohexyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (S45)

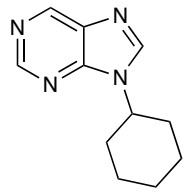
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 4-chloro-7*H*-pyrrolo[2,3-*d*]pyrimidine (77 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (10:1 hexane/EtOAc) provided the title compound (100 mg, 85% yield) as a white solid. The yield was determined based on 4-chloro-7*H*-pyrrolo[2,3-*d*]pyrimidine as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.31 (d, *J* = 3.6 Hz, 1H), 6.56 (d, *J* = 3.6 Hz, 1H), 4.67 (tt, *J* = 12.0, 3.7 Hz, 1H), 2.09-2.00 (m, 2H), 1.93-1.85 (m, 2H), 1.79-1.64 (m, 3H), 1.55-1.44 (m, 2H), 1.30-1.19 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 152.0, 150.4, 150.3, 126.4, 117.7, 99.4, 54.3, 33.4, 25.7, 25.4.

IR (film) ν_{max} 2931, 2856, 1583, 1538, 1504, 1450, 1416, 1346, 1273, 1250, 1198, 1147, 928, 894, 861, 846, 810, 755, 722 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{15}ClN_3$ ($[M+H]^+$) 236.0949, found 236.0952.



9-Cyclohexyl-9*H*-purine (56)

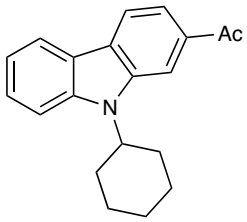
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (3.3 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 9*H*-purine (77 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (10:1 DCM/MeOH) provided the title compound (61 mg, 60% yield, >20:1 r.r.) as a white solid. The yield was determined based on 9*H*-purine as the limiting reagent (1.0 equiv). The structure of the title compound was further confirmed via 2D NMR (HMBC) analysis.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.13 (s, 1H), 8.97 (s, 1H), 8.16 (s, 1H), 4.55 (tt, *J* = 12.1, 3.8 Hz, 1H), 2.24-2.16 (m, 2H), 2.00-1.93 (m, 2H), 1.91-1.77 (m, 3H), 1.59-1.47 (m, 2H), 1.38-1.29 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 152.3, 151.1, 148.7, 143.3, 134.4, 54.6, 33.3, 25.6, 25.3.

IR (film) ν_{max} 2931, 2857, 1592, 1578, 1493, 1451, 1403, 1342, 1304, 1205, 907, 795 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{11}H_{15}N_4$ ($[M+H]^+$) 203.1291, found 203.1287.



1-(9-Cyclohexyl-9*H*-carbazol-2-yl)ethan-1-one (S47)

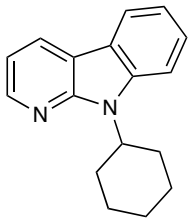
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (29 mg, 0.15 mmol, 0.30 equiv.), 4,7-diphenyl-1,10-phenanthroline (75 mg, 0.225 mmol, 0.45 equiv.), BTTP (0.31 mL, 312 mg, 1.0 mmol, 2.0 equiv.), 1-(9*H*-carbazol-2-yl)ethan-1-one (209 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (1:2 hexane/DCM) provided the title compound (74 mg, 51% yield) as a white solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 8.04 (t, *J* = 7.7 Hz, 2H), 7.71 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.44-7.38 (m, 1H), 7.18-7.12 (m, 1H), 4.49 (tt, *J* = 12.2, 3.6 Hz, 1H), 2.65 (s, 3H), 2.38-2.27 (m, 2H), 1.96-1.84 (m, 4H), 1.80-1.73 (m, 1H), 1.53-1.42 (m, 2H), 1.38-1.30 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 198.8, 141.3, 139.5, 134.2, 127.2, 126.9, 122.6, 121.3, 119.9, 119.5, 119.2, 111.1, 110.0, 55.6, 30.9, 27.2, 26.5, 25.7.

IR (film) ν_{max} 2931, 2856, 1675, 1621, 1475, 1439, 1354, 1244 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{20}H_{22}NO$ ($[M+H]^+$) 292.1696, found 292.1694.



9-Cyclohexyl-9*H*-pyrido[2,3-*b*]indole (S46)

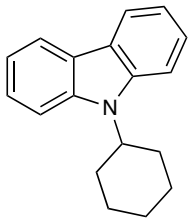
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 9*H*-pyrido[2,3-*b*]indole (168 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (10:1 hexane/Et_2O) provided the title compound (60 mg, 48% yield) as a white solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.32 (dd, *J* = 7.6, 1.6 Hz, 1H), 8.09 (d, *J* = 7.7 Hz, 1H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.52-7.46 (m, 1H), 7.30-7.24 (m, 1H), 7.15 (dd, *J* = 7.6, 4.8 Hz, 1H), 5.14-4.98 (m, 1H), 2.58-2.47 (m, 2H), 2.03-1.91 (m, 4H), 1.88-1.80 (m, 1H), 1.66-1.54 (m, 2H), 1.48-1.40 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.4, 145.7, 138.9, 127.9, 126.3, 121.1, 121.0, 119.3, 115.9, 114.8, 111.3, 53.6, 30.7, 26.4, 25.8.

IR (film) ν_{max} 2927, 2854, 1589, 1570, 1481, 1454, 1415, 1341, 1289, 1226, 1129, 1118, 773, 735 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{17}H_{19}N_2$ ($[M+H]^+$) 251.1543, found 251.1543.



9-Cyclohexyl-9*H*-carbazole (57)

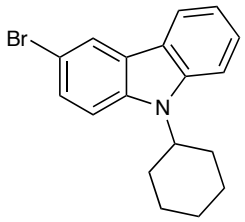
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (29 mg, 0.15 mmol, 0.30 equiv.), 4,7-diphenyl-1,10-phenanthroline (75 mg, 0.225 mmol, 0.45 equiv.), BTTP (0.31 mL, 312 mg, 1.0 mmol, 2.0 equiv.), carbazole (167 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (10:1 hexane/DCM) provided the title compound (57 mg, 46% yield) as a white solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* =7.7 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.49-7.42 (m, 2H), 7.29-7.20 (m, 2H), 4.52 (tt, *J* = 12.2, 3.8 Hz, 1H), 2.48-2.37 (m, 2H), 2.07-1.96 (m, 4H), 1.91-1.84 (m, 1H), 1.62-1.51 (m, 2H), 1.47-1.39 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.8, 125.4, 123.4, 120.4, 118.6, 110.3, 55.5, 30.8, 26.7, 25.8.

Data are consistent with those reported in the literature:

Bissember, A. C., Lundgren, R. L., Creutz, S. E., Peters, J. C. & Fu, G. C. *Angew. Chem. Int. Ed.* **52**, 5129–5133 (2013).



3-Bromo-9-cyclohexyl-9*H*-carbazole (S48)

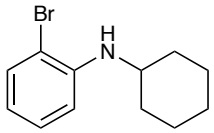
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (29 mg, 0.15 mmol, 0.30 equiv.), 4,7-diphenyl-1,10-phenanthroline (75 mg, 0.225 mmol, 0.45 equiv.), BTTP (0.31 mL, 312 mg, 1.0 mmol, 2.0 equiv.), 3-bromo-9*H*-carbazole (246 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (10:1 hexane/DCM) provided the title compound (74 mg, 45% yield) as a yellow solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 1.9 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.53-7.41 (m, 3H), 7.23 (t, *J* = 7.5 Hz, 1H), 4.46 (tt, *J* = 12.4, 3.9 Hz, 1H), 2.41-2.30 (m, 2H), 2.06-1.93 (m, 4H), 1.90-1.82 (m, 1H), 1.60-1.48 (m, 2H), 1.45-1.36 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.1, 138.4, 128.0, 126.1, 125.2, 123.1, 122.3, 120.6, 119.1, 111.8, 111.4, 110.6, 55.7, 30.8, 26.6, 25.7.

IR (film) ν_{max} 2932, 2854, 1471, 1445, 1331, 1219, 793, 743, 721 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{18}H_{19}BrN$ ($[M+H]^+$) 328.0695, found 328.0688.



2-Bromo-*N*-cyclohexylaniline (S49)

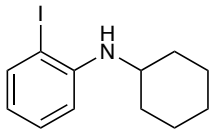
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 2-isobutyrylcyclohexanone (25 μL, 25 mg, 0.15 mmol, 0.30 equiv.), BTTP (0.31 mL, 312 mg, 1.0 mmol, 2.0 equiv.), 2-bromoaniline (172 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (10:1 hexane/DCM) provided the title compound (84 mg, 66% yield) as a colorless oil. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.7 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.66 (d, *J* = 8.1 Hz, 1H), 6.53 (t, *J* = 7.4 Hz, 1H), 4.25 (br s, 1H), 3.37-3.27 (m, 1H), 2.10-2.01 (m, 2H), 1.83-1.74 (m, 2H), 1.70-1.62 (m, 1H), 1.45-1.35 (m, 2H), 1.33-1.21 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 132.6, 128.5, 117.2, 111.9, 109.9, 51.7, 33.2, 26.0, 25.0.

Data are consistent with those reported in the literature:

Cho, D. J., Wu, C. J., S, S., Han, W.-S., Kang, S. O. & Lee, B. Y. *Organometallics.* **25**, 2133–2134 (2006).



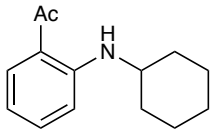
***N*-Cyclohexyl-2-iodoaniline (44)**

Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 2-isobutyrylcyclohexanone (25 μL, 25 mg, 0.15 mmol, 0.30 equiv.), BTTP (0.31 mL, 312 mg, 1.0 mmol, 2.0 equiv.), 2-iodoaniline (219 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (8:1 hexane/DCM) provided the title compound (83 mg, 55% yield) as a colorless oil. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 6.40 (t, *J* = 7.3 Hz, 1H), 4.12 (br s, 1H), 3.40-3.26 (m, 1H), 2.09-2.00 (m, 2H), 1.83-1.74 (m, 2H), 1.70-1.61 (m, 1H), 1.46-1.23 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 146.5, 139.3, 129.4, 118.1, 111.2, 85.9, 52.0, 33.1, 26.0, 24.9.

Data are consistent with those reported in the literature:
Åkerbladh, L. & Odell, L. R. *J. Org. Chem.* **81**, 2966–2973 (2016).



1-(2-(Cyclohexylamino)phenyl)ethan-1-one (S50)

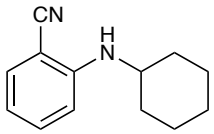
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTTP (0.31 mL, 312 mg, 1.0 mmol, 2.0 equiv.), 1-(2-aminophenyl)ethan-1-one (135 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (8:1 hexane/Et_2O) provided the title compound (72 mg, 66% yield) as a yellow solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.00 (d, *J* = 6.1 Hz, 1H), 7.73 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.35-7.28 (m, 1H), 6.73 (d, *J* = 8.6 Hz, 1H), 6.55-6.51 (m, 1H), 3.48-3.38 (m, 1H), 2.57 (s, 3H), 2.04-1.96 (m, 2H), 1.82-1.73 (m, 2H), 1.65-1.58 (m, 1H), 1.45-1.26 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 200.7, 150.4, 135.0, 133.1, 117.2, 113.4, 112.2, 50.3, 32.8, 28.1, 25.9, 24.7.

IR (film) ν_{max} 3287, 2927, 2853, 1633, 1607, 1573, 1518, 1458, 1421, 1361, 1249, 1229, 1157, 952, 744 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{20}NO$ ($[M+H]^+$) 218.1539, found 218.1538.



2-(Cyclohexylamino)benzonitrile (S51)

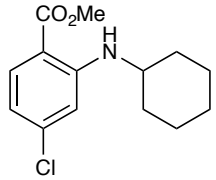
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTTP (0.31 mL, 312 mg, 1.0 mmol, 2.0 equiv.), 2-aminobenzonitrile (118 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (8:1 hexane/Et_2O) provided the title compound (61 mg, 61% yield) as a white solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.31 (m, 2H), 6.69-6.58 (m, 2H), 4.44 (d, *J* = 6.9 Hz, 1H), 3.39-3.29 (m, 1H), 2.07-1.99 (m, 2H), 1.83-1.75 (m, 2H), 1.70-1.61 (m, 1H), 1.43-1.33 (m, 2H), 1.30-1.20 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.5, 134.2, 133.0, 118.2, 116.0, 111.1, 95.5, 51.4, 33.0, 25.7, 24.9.

Data are consistent with those reported in the literature:

Dong, J., Wu, Z., Liu, Z., Liu, P. & Sun, P. *J. Org. Chem.* **80**, 12588–12593 (2015).



Methyl 4-chloro-2-(cyclohexylamino)benzoate (S52)

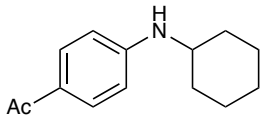
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 2-isobutyrylcyclohexanone (25 μL, 25 mg, 0.15 mmol, 0.30 equiv.), BTTP (0.31 mL, 312 mg, 1.0 mmol, 2.0 equiv.), methyl 2-amino-4-chlorobenzoate (186 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (10:1 to 5:1 hexane/DCM) provided the title compound (71 mg, 53% yield) as a white solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 6.9 Hz, 1H), 7.80 (d, *J* = 8.6 Hz, 1H), 6.65 (d, *J* = 1.8 Hz, 1H), 6.48 (dd, *J* = 8.6, 1.9 Hz, 1H), 3.83 (s, 3H), 3.39-3.30 (m, 1H), 2.05-1.95 (m, 2H), 1.81-173 (m, 2H), 1.67-1.58 (m, 1H), 1.46-1.25 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.7, 151.1, 140.9, 133.2, 114.3, 111.2, 108.1, 51.6, 50.6, 32.8, 25.9, 24.7.

IR (film) ν_{max} 3337, 2929, 2854, 1684, 1599, 1573, 1506, 1431, 1249, 1226, 1189, 1140, 1098, 913, 764 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{19}ClNO_2$ ($[M+H]^+$) 268.1099, found 268.1098.



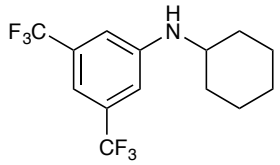
1-(4-(Cyclohexylamino)phenyl)ethan-1-one (45)

Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTTP (0.31 mL, 312 mg, 1.0 mmol, 2.0 equiv.), 1-(4-aminophenyl)ethan-1-one (135 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (1:1 hexane/Et_2O) provided the title compound (76 mg, 70% yield) as a white solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 8.8 Hz, 2H), 4.51 (br s, 1H), 3.36-3.28 (m, 1H), 2.48 (s, 3H), 2.08-2.00 (m, 2H), 1.80-1.72 (m, 2H), 1.69-1.61 (m, 1H), 1.43-1.33 (m, 2H), 1.27-1.13 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 196.4, 151.4, 131.0, 126.1, 111.6, 51.3, 33.2, 26.0, 25.8, 24.9.

Data are consistent with those reported in the literature:
Shen, Q., Ogata, T. & Hartwig, J. F. *J. Am. Chem. Soc.* **130**, 6586–6596 (2008).



***N*-Cyclohexyl-3,5-bis(trifluoromethyl)aniline (S53)**

Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTTP (0.31 mL, 312 mg, 1.0 mmol, 2.0 equiv.), 3,5-bis(trifluoromethyl)aniline (229 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (15:1 hexane/DCM) provided the title compound (79 mg, 51% yield) as a white solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

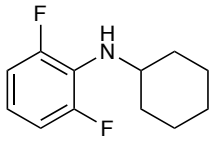
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (s, 1H), 6.89 (s, 2H), 4.00 (br s, 1H), 3.37-3.24 (m, 1H), 2.08-2.00 (m, 2H), 1.82-1.74 (m, 2H), 1.72-1.64 (m, 1H), 1.47-1.36 (m, 2H), 1.30-1.15 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 132.5 (q, J = 32.6 Hz), 123.8 (q, J = 272.6 Hz), 112.0 (m), 109.6 (m), 51.6, 33.1, 25.8, 24.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ –63.2 (s, 6F).

Data are consistent with those reported in the literature:

Jang, E. S., McMullin, C. L., Käβ, M., Meyer, K., Cundari, T. R. & Warren, T. H. *J. Am. Chem. Soc.* **136**, 10930–10940 (2014).



***N*-Cyclohexyl-2,6-difluoroaniline (S54)**

Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 2-isobutyrylcyclohexanone (25 μL, 25 mg, 0.15 mmol, 0.30 equiv.), BTTP (0.31 mL, 312 mg, 1.0 mmol, 2.0 equiv.), 2,6-difluoroaniline (129 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). The reaction provided the title compound in 34% yield, which was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv) from ^{19}F NMR analysis of the crude mixture after the addition of an internal standard. The title compound was purified by preparative TLC (10:1 hexane/Et_2O) as a light yellow oil.

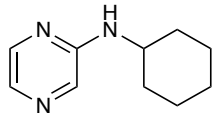
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.83-6.75 (m, 2H), 6.68-6.61 (m, 1H), 3.49-3.33 (m, 2H), 2.04-1.97 (m, 2H), 1.78-1.70 (m, 2H), 1.66-1.57 (m, 1H), 1.39-1.28 (m, 2H), 1.25-1.06 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.9 (d, J = 7.8 Hz), 153.0 (d, J = 7.8 Hz), 125.2 (t, J = 14.4 Hz), 117.7 (t, J = 9.5 Hz), 111.5 (m), 54.2, 34.6, 25.9, 25.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ –128.5 (m, 2F).

IR (film) ν_{max} 3394, 2930, 2854, 1622, 1597, 1494, 1456, 1280, 1225, 992, 704 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{16}F_2N$ ($[M+H]^+$) 212.1245, found 212.1244.



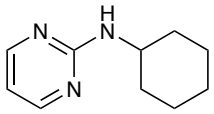
***N*-Cyclohexylpyrazin-2-amine (S55)**

Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTTP (0.31 mL, 312 mg, 1.0 mmol, 2.0 equiv.), pyrazin-2-amine (95 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (2:1 to 1:1 hexane/EtOAc) provided the title compound (51 mg, 58% yield) as a yellow solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00-7.60 (m, 3H), 4.65 (br s, 1H), 3.70-3.59 (m, 1H), 2.06-1.98 (m, 2H), 1.77-1.69 (m, 2H), 1.67-1.59 (m, 1H), 1.44-1.32 (m, 2H), 1.26-1.14 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 142.2, 132.3, 132.2, 49.8, 33.3, 25.8, 24.9.

Data are consistent with those reported in the literature:
Gandy, M. N., Raston, C. L. & Stubbs, K. A. *Org. Biomol. Chem.* **12**, 4594–4597 (2014).



***N*-Cyclohexylpyrimidin-2-amine (S56)**

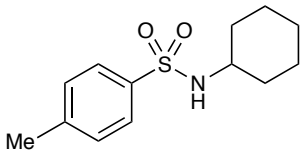
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTTP (0.31 mL, 312 mg, 1.0 mmol, 2.0 equiv.), pyrimidin-2-amine (95 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (1:1 hexane/Et_2O) provided the title compound (46 mg, 52% yield) as a white solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 4.7 Hz, 2H), 6.47 (t, *J* = 4.8 Hz, 1H), 5.13 (br s, 1H), 3.84-3.75 (m, 1H), 2.06-1.99 (m, 2H), 1.77-1.69 (m, 2H), 1.66-1.58 (m, 1H), 1.46-1.35 (m, 2H), 1.26-1.16 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 161.9, 158.2, 110.3, 49.7, 33.4, 25.9, 25.0.

Data are consistent with those reported in the literature:

Ho, L. A., Raston, C. L. & Stubbs, K. A. *Eur. J. Org. Chem.* 5957–5963 (2016).



***N*-Cyclohexyl-4-methylbenzenesulfonamide (S57)**

Prepared following the general procedure outlined above using $Ir(ppy)_3$ (10 mg, 15 μmol, 0.03 equiv.), CuTC (29 mg, 0.15 mmol, 0.30 equiv.), 4,7-diphenyl-1,10-phenanthroline (75 mg, 0.225 mmol, 0.45 equiv.), BTMG (0.32 mL, 257 mg, 1.5 mmol, 3.0 equiv.), 4-methylbenzenesulfonamide (116 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (3:1 hexane/Et_2O) provided the title compound (85 mg, 67% yield) as a white solid. The yield was determined based on 4-methylbenzenesulfonamide as the limiting reagent (1.0 equiv).

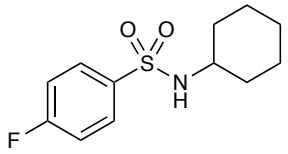
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 5.13 (d, *J* = 7.5 Hz, 1H), 3.13 (dt, *J* = 13.4, 6.5 Hz, 1H), 2.45 (s, 3H), 1.81-1.72 (m, 2H), 1.68-1.60 (m, 2H), 1.55-1.48 (m, 1H), 1.30-1.09 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.1, 138.5, 129.7, 127.0, 52.6, 33.8, 25.2, 24.7, 21.6.

Data are consistent with those reported in the literature:

Tran, B. L., Li, B., Driess, M. & Hartwig, J. F. *J. Am. Chem. Soc.* **136**, 2555–2563 (2014).

Zhang, J., Yang, C.-G. & He, C. *J. Am. Chem. Soc.* **128**, 1798–1799 (2006).



***N*-Cyclohexyl-4-fluorobenzenesulfonamide (S58)**

Prepared following the general procedure outlined above using $Ir(ppy)_3$ (10 mg, 15 μmol, 0.03 equiv.), CuTC (29 mg, 0.15 mmol, 0.30 equiv.), 4,7-diphenyl-1,10-phenanthroline (75 mg, 0.225 mmol, 0.45 equiv.), BTMG (0.32 mL, 257 mg, 1.5 mmol, 3.0 equiv.), 4-fluorobenzenesulfonamide (88 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (3:1 to 2:1 hexane/Et_2O) provided the title compound (86 mg, 67% yield) as a yellow solid. The yield was determined based on 4-fluorobenzenesulfonamide as the limiting reagent (1.0 equiv).

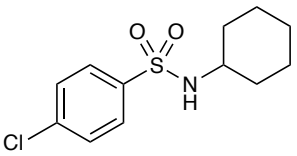
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94-7.88 (m, 2H), 7.20-7.13 (m, 2H), 5.07 (d, *J* = 7.5 Hz, 1H), 3.15-3.06 (m, 1H), 1.76-1.68 (m, 2H), 1.66-1.56 (m, 2H), 1.53-1.44 (m, 1H), 1.26-1.06 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0 (d, *J* = 254.2 Hz), 137.6, (d, *J* = 3.3 Hz), 129.7 (d, *J* = 9.2 Hz), 116.3 (d, *J* = 22.5 Hz), 55.8, 33.9, 25.2, 24.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ –105.9 (m, 1F).

IR (film) ν_{max} 3278, 2932, 2856, 1593, 1494, 1452, 1325, 1291, 1235, 1166, 1153, 1093, 1079, 884, 839, 750, 670 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{16}FNNaO_2S$ ($[M+Na]^+$) 280.0778, found 280.0778.



4-Chloro-*N*-cyclohexylbenzenesulfonamide (S59)

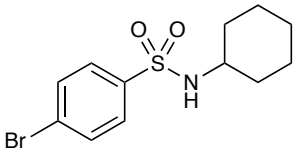
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 4-chlorobenzenesulfonamide (192 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.5 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (3:1 to 2:1 hexane/Et_2O) provided the title compound (72 mg, 53% yield) as a white solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85-7.81 (m, 2H), 7.49-7.45 (m, 2H), 4.99 (d, *J* = 7.6 Hz, 1H), 3.16-3.07 (m, 1H), 1.76-1.69 (m, 2H), 1.66-1.58 (m, 2H), 1.52-1.46 (m, 1H), 1.26-1.06 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.1, 138.9, 129.4, 128.5, 52.9, 33.9, 25.2, 24.7.

Data are consistent with those reported in the literature:

Liu, P. N., Xia, F., Zhao, Z. L., Wang, Q. W. & Ren, Y. J. *Tetrahedron Lett.* **52**, 6113–6117 (2011).



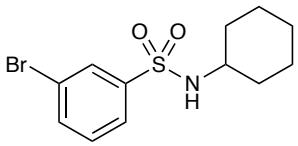
4-Bromo-*N*-cyclohexylbenzenesulfonamide (S60)

Prepared following the general procedure outlined above using $Ir(ppy)_3$ (10 mg, 15 μmol, 0.03 equiv.), CuTC (29 mg, 0.15 mmol, 0.30 equiv.), 4,7-diphenyl-1,10-phenanthroline (75 mg, 0.225 mmol, 0.45 equiv.), BTMG (0.32 mL, 257 mg, 1.5 mmol, 3.0 equiv.), 4-bromobenzenesulfonamide (118 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (3:1 to 2:1 hexane/Et_2O) provided the title compound (100 mg, 63% yield) as a yellow solid. The yield was determined based on 4-bromobenzenesulfonamide as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 5.06 (d, *J* = 7.6 Hz, 1H), 3.16-3.06 (m, 1H), 1.76-1.68 (m, 2H), 1.66-1.58 (m, 2H), 1.53-1.45 (m, 1H), 1.26-1.06 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.7, 132.4, 128.6, 127.4, 52.8, 33.9, 25.2, 24.7.

Data are consistent with those reported in the literature:
Veisi, H., Ghorbani-Vaghei, R., Hemmati, S. & Mahmoodi, J. *Synlett* 2315–2320 (2010).



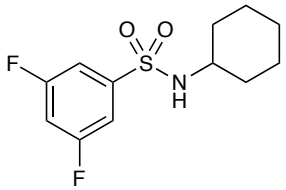
3-Bromo-*N*-cyclohexylbenzenesulfonamide (S61)

Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 3-bromobenzenesulfonamide (236 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.5 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (2:1 hexane/Et_2O) provided the title compound (80 mg, 50% yield) as a white solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (t, *J* = 1.8 Hz, 1H), 7.82 (ddd, *J* = 7.9, 1.6, 1.0 Hz, 1H), 7.68 (ddd, *J* = 8.0, 1.8, 0.9 Hz, 1H), 7.38 (t, *J* = 7.9 Hz, 1H), 5.04 (d, *J* = 7.6 Hz, 1H), 3.19-3.10 (m, 1H), 1.78-1.70 (m, 2H), 1.67-1.59 (m, 2H), 1.54-1.46 (m, 1H), 1.27-1.05 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 135.5, 130.7, 129.9, 125.5, 123.0, 52.9, 33.9, 25.2, 24.7.

Data are consistent with those reported in the literature:
Procopiou, P. A. *et al. J. Med. Chem.* **52**, 2280–2288 (2009).



***N*-Cyclohexyl-3,5-difluorobenzenesulfonamide (S62)**

Prepared following the general procedure outlined above using $Ir(ppy)_3$ (10 mg, 15 μmol, 0.03 equiv.), CuTC (29 mg, 0.15 mmol, 0.30 equiv.), 4,7-diphenyl-1,10-phenanthroline (75 mg, 0.225 mmol, 0.45 equiv.), BTMG (0.32 mL, 257 mg, 1.5 mmol, 3.0 equiv.), 3,5-difluorobenzenesulfonamide (97 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (4:1 to 3:1 hexane/Et_2O) provided the title compound (76 mg, 55% yield) as a yellow solid. The yield was determined based on 3,5-difluorobenzenesulfonamide as the limiting reagent (1.0 equiv).

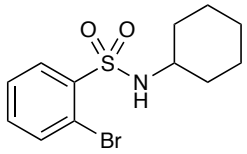
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.40 (m, 2H), 7.03-6.98 (m, 1H), 4.96 (d, *J* = 7.7 Hz, 1H), 3.23-3.12 (m, 1H), 1.80-1.73 (m, 2H), 1.68-1.61 (m, 2H), 1.56-1.49 (m, 1H), 1.30-1.08 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9 (d, *J* = 11.6 Hz), 161.9 (d, *J* = 11.6 Hz), 145.1 (t, *J* = 8.2 Hz), 110.5 (m), 108.2 (t, *J* = 25.1 Hz), 53.2, 34.0, 25.1, 24.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ –105.8 (m, 2F).

IR (film) ν_{max} 3283, 2932, 2857, 1606, 1439, 1332, 1297, 1159, 1126, 1077, 988, 863, 672 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{15}F_2NNaO_2S$ ($[M+Na]^+$) 298.0684, found 298.0679.



2-Bromo-*N*-cyclohexylbenzenesulfonamide (46)

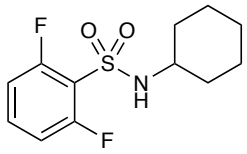
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (10 mg, 15 μmol, 0.03 equiv.), CuTC (29 mg, 0.15 mmol, 0.30 equiv.), 4,7-diphenyl-1,10-phenanthroline (75 mg, 0.225 mmol, 0.45 equiv.), BTMG (0.32 mL, 257 mg, 1.5 mmol, 3.0 equiv.), 2-bromobenzenesulfonamide (118 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (5:1 to 3:1 hexane/Et_2O) provided the title compound (94 mg, 59% yield) as a yellow solid. The yield was determined based on 2-bromobenzenesulfonamide as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17-8.11 (m, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.1 Hz, 1H), 5.15 (d, *J* = 7.2 Hz, 1H), 3.16-3.06 (m, 1H), 1.76-1.67 (m, 2H), 1.65-1.55 (m, 2H), 1.52-1.44 (m, 1H), 1.26-1.10 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.2, 135.1, 133.6, 131.2, 127.9, 119.8, 53.1, 33.6, 25.2, 24.6.

IR (film) ν_{max} 3304, 2930, 2855, 1448, 1427, 1328, 1161, 1127, 1076, 1028, 884, 760, 732, 706, 651 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{16}BrNNaO_2S$ ($[M+Na]^+$) 339.9977, found 339.9973.



***N*-Cyclohexyl-2,6-difluorobenzenesulfonamide (S63)**

Prepared following the general procedure outlined above using $Ir(ppy)_3$ (10 mg, 15 μmol, 0.03 equiv.), CuTC (29 mg, 0.15 mmol, 0.30 equiv.), 4,7-diphenyl-1,10-phenanthroline (75 mg, 0.225 mmol, 0.45 equiv.), BTMG (0.32 mL, 257 mg, 1.5 mmol, 3.0 equiv.), 2,6-difluorobenzenesulfonamide (97 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (4:1 to 3:1 hexane/Et_2O) provided the title compound (71 mg, 52% yield) as a yellow solid. The yield was determined based on 2,6-difluorobenzenesulfonamide as the limiting reagent (1.0 equiv).

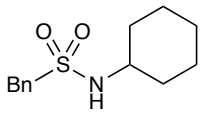
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53-7.46 (m, 1H), 7.01 (t, *J* = 8.6 Hz, 2H), 5.03 (d, *J* = 7.5 Hz, 1H), 3.39-3.29 (m, 1H), 1.85-1.77 (m, 2H), 1.68-1.60 (m, 2H), 1.56-1.48 (m, 1H), 1.30-1.17 (m, 4H), 1.16-1.09 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5 (d, *J* = 4.0 Hz), 158.4 (d, *J* = 4.0 Hz), 134.2 (t, *J* = 11.1 Hz), 119.7 (t, *J* = 15.8 Hz), 113.2 (dd, *J* = 23.3, 3.8 Hz), 53.3, 33.7, 25.2, 24.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ –107.9 (m, 2F).

IR (film) ν_{max} 3300, 2932, 2857, 1612, 1587, 1467, 1452, 1342, 1236, 1167, 1107, 1076, 1001, 886, 790, 769 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{15}F_2NNaO_2S$ ($[M+Na]^+$) 298.0684, found 298.0685.



***N*-Cyclohexyl-1-phenylmethanesulfonamide (47)**

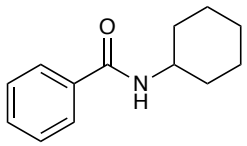
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), phenylmethanesulfonamide (171 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.5 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (2:1 hexane/Et_2O) provided the title compound (64 mg, 51% yield) as a white solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.35 (m, 5H), 4.23 (s, 2H), 4.11 (d, *J* = 7.5 Hz, 1H), 3.15-3.06 (m, 1H), 1.95-1.86 (m, 2H), 1.72-1.63 (m, 2H), 1.59-1.51 (m, 1H), 1.28-1.09 (m, 5H) .

^{13}C NMR (125 MHz, $CDCl_3$) δ 130.8, 129.7, 128.80, 128.76, 60.1, 53.4, 34.7, 25.2, 24.9.

Data are consistent with those reported in the literature:

Day, J. J., Neill, D. L., Xu, S. & Xian, M. *Org. Lett.* **19**, 3819–3822 (2017).



***N*-Cyclohexylbenzamide (S64)**

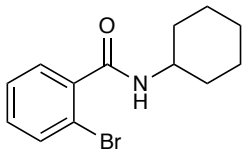
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTTP (0.46 mL, 469 mg, 1.5 mmol, 3.0 equiv.), benzamide (121 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (3:1 hexane/EtOAc) provided the title compound (75 mg, 74% yield) as a white solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76-7.72 (m, 2H), 7.46-7.41 (m, 1H), 7.39-7.34 (m, 2H), 6.26 (d, *J* = 6.6 Hz, 1H), 3.93 (dtt, *J* = 11.8, 8.0, 4.0 Hz, 1H), 2.02-1.94 (m, 2H), 1.76-1.68 (m, 2H), 1.65-1.57 (m, 1H), 1.42-1.31 (m, 2H), 1.27-1.11 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7, 135.1, 131.2, 128.5, 126.9, 48.8, 33.2, 25.6, 25.0.

Data are consistent with those reported in the literature:

Jiang, H., Liu, B., Li, Y., Wang, A. & Huang, H. *Org. Lett.* **13**, 1028–1031 (2011).



2-Bromo-*N*-cyclohexylbenzamide (S65)

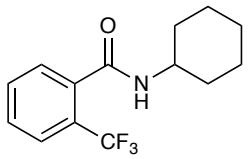
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTTP (0.46 mL, 469 mg, 1.5 mmol, 3.0 equiv.), 2-bromobenzamide (200 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (4:1 hexane/EtOAc) provided the title compound (100 mg, 71% yield) as a white solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58-7.54 (m, 1H), 7.50 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.34 (td, *J* = 7.5, 1.0 Hz, 1H), 7.25 (td, *J* = 7.8, 1.7 Hz, 1H), 5.91 (br s, 1H), 4.04-3.95 (m, 1H), 2.09-2.00 (m, 2H), 1.79-1.70 (m, 2H), 1.68-1.60 (m, 1H), 1.48-1.37 (m, 2H), 1.32-1.16 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 138.3, 133.3, 131.1, 129.6, 127.6, 119.3, 49.0, 33.0, 25.6, 24.9.

Data are consistent with those reported in the literature:

Nandi, J., Ovian, J. M., Kelly, C. B. & Leadbeater, N. E. *Org. Biomol. Chem.* **15**, 8295–8301 (2017).



***N*-Cyclohexyl-2-(trifluoromethyl)benzamide (S66)**

Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTTP (0.46 mL, 469 mg, 1.5 mmol, 3.0 equiv.), 2-(trifluoromethyl)benzamide (189 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (5:1 hexane/EtOAc) provided the title compound (100 mg, 74% yield) as a white solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

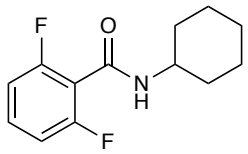
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.5 Hz, 1H), 7.58-7.53 (m, 1H), 7.53-7.47 (m, 2H), 5.71 (br s, 1H), 4.00-3.91 (m, 1H), 2.05-1.97 (m, 2H), 1.76-1.69 (m, 2H), 1.67-1.59 (m, 1H), 1.45-1.34 (m, 2H), 1.25-1.13 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 136.5 (q, *J* = 2.1 Hz), 132.1, 129.7, 128.8, 127.1 (q, *J* = 31.7 Hz), 126.3 (q, *J* = 5.0 Hz), 123.8 (q, *J* = 273.7 Hz), 49.0, 32.8, 25.6, 24.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ –58.7 (s, 3F).

Data are consistent with those reported in the literature:

Basavanag, U. M. V., Santos, A. D., Kaim, L. E., Gámez-Montaño, R. & Grimaud, L. *Angew. Chem. Int. Ed.* **52**, 7194–7197 (2013).



***N*-Cyclohexyl-2,6-difluorobenzamide (48)**

Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTTP (0.46 mL, 469 mg, 1.5 mmol, 3.0 equiv.), 2,6-difluorobenzamide (157 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (4:1 hexane/EtOAc) provided the title compound (95 mg, 79% yield) as a white solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

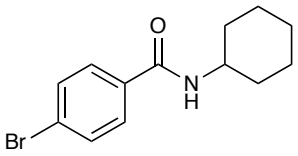
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (tt, *J* = 8.4, 6.3 Hz, 1H), 6.94-6.87 (m, 2H), 5.86 (br s, 1H), 3.99 (tdt, *J* = 12.1, 8.1, 3.9 Hz, 1H), 2.06-1.97 (m, 2H), 1.77-1.69 (m, 2H), 1.66-1.58 (m, 1H), 1.46-1.35 (m, 2H), 1.28-1.15 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 161.0 (d, *J* = 7.1 Hz), 159.5, 159.0 (d, *J* = 7.1 Hz), 131.5 (t, *J* = 10.2 Hz), 114.9 (t, *J* = 20.5 Hz), 112.1 (d, *J* = 4.7 Hz), 119.3 (d, *J* = 4.7 Hz), 49.0, 33.0, 25.6, 24.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ –112.6 (m, 2F).

IR (film) ν_{max} 3243, 2929, 2856, 1636, 1625, 1588, 1557, 1464, 1450, 1333, 1234, 1005, 791 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{16}F_2NO$ ($[M+H]^+$) 240.1195, found 240.1191.



4-Bromo-*N*-cyclohexylbenzamide (S67)

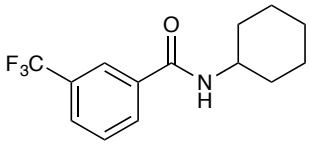
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTTP (0.46 mL, 469 mg, 1.5 mmol, 3.0 equiv.), 4-bromobenzamide (200 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (5:1 hexane/EtOAc) provided the title compound (105 mg, 74% yield) as a white solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63-7.59 (m, 2H), 7.56-7.52 (m, 2H), 6.00 (d, *J* = 6.5 Hz, 1H), 3.94 (dtt, *J* = 11.6, 8.0, 4.0 Hz, 1H), 2.05-1.97 (m, 2H), 1.78-1.70 (m, 2H), 1.69-1.61 (m, 1H), 1.46-1.35 (m, 2H), 1.27-1.15 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 134.0, 131.8, 128.6, 126.0, 49.0, 33.3, 25.7, 25.0.

Data are consistent with those reported in the literature:

Pelletier, G., Bechara, W. S. & Charetts, A. B. *J. Am. Chem. Soc.* **132**, 12817–12819 (2010).



***N*-Cyclohexyl-3-(trifluoromethyl)benzamide (S68)**

Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTTP (0.46 mL, 469 mg, 1.5 mmol, 3.0 equiv.), 3-(trifluoromethyl)benzamide (189 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (5:1 hexane/EtOAc) provided the title compound (104 mg, 77% yield) as a white solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

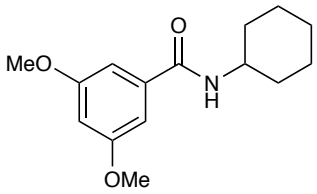
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 6.18 (d, *J* = 6.6 Hz, 1H), 3.96 (dtt, *J* = 11.6, 8.0, 4.0 Hz, 1H), 2.06-1.98 (m, 2H), 1.80-1.71 (m, 2H), 1.69-1.61 (m, 1H), 1.46-1.34 (m, 2H), 1.30-1.14 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 165.3, 136.0, 131.1 (q, *J* = 32.8 Hz), 130.3, 129.2, 127.9 (q, *J* = 3.6 Hz), 124.0 (q, *J* = 3.8 Hz), 123.8 (q, *J* = 272.4 Hz), 49.2, 33.3, 25.6, 25.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ –62.7 (s, 3F).

Data are consistent with those reported in the literature:

Wang, Y., Wu, Z., Li, Q., Zhu, B. & Yu, L. *Catal. Sci. Technol.* **7**, 3747–3757 (2017).



***N*-Cyclohexyl-3,5-dimethoxybenzamide (S69)**

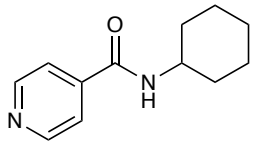
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTTP (0.46 mL, 469 mg, 1.5 mmol, 3.0 equiv.), 3,5-dimethoxybenzamide (181 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (3:1 hexane/EtOAc) provided the title compound (97 mg, 74% yield) as a white solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.86 (d, *J* = 2.3 Hz, 2H), 6.54 (t, *J* = 2.3 Hz, 1H), 5.98 (d, *J* = 7.3 Hz, 1H), 3.98-3.89 (m, 1H), 3.81 (s, 6H), 2.04-1.96 (m, 2H), 1.78-1.70 (m, 2H), 1.67-1.60 (m, 1H), 1.46-1.35 (m, 2H), 1.27-1.15 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6, 160.9, 137.5, 104.9, 103.3, 55.7, 48.8, 33.3, 25.7, 25.0.

Data are consistent with those reported in the literature:

Tran, B. L., Li, B., Driess, M. & Hartwig, J. F. *J. Am. Chem. Soc.* **136**, 2555–2563 (2014).



***N*-Cyclohexylisonicotinamide (S70)**

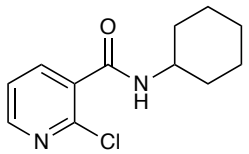
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTTP (0.46 mL, 469 mg, 1.5 mmol, 3.0 equiv.), isonicotinamide (122 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (1:3 hexane/EtOAc with 5% Et_3N) provided the title compound (83 mg, 81% yield) as a yellow solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68-8.63 (m, 2H), 7.58-7.56 (m, 2H), 6.41 (d, *J* = 6.8 Hz, 1H), 3.92 (dtt, *J* = 11.6, 8.0, 4.0 Hz, 1H), 2.02-1.94 (m, 2H), 1.77-1.68 (m, 2H), 1.67-1.58 (m, 1H), 1.43-1.31 (m, 2H), 1.27-1.11 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 150.5, 142.2, 121.0, 49.2, 33.1, 25.5, 25.0.

Data are consistent with those reported in the literature:

Rao, S. N., Mohan, D. C. & Adimurthy, S. *RSC Adv.* **5**, 95313–95317 (2015).



2-Chloro-*N*-cyclohexylnicotinamide (S71)

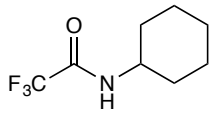
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTTP (0.46 mL, 469 mg, 1.5 mmol, 3.0 equiv.), 2-chloronicotinamide (157 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (1:1.5 hexane/EtOAc) provided the title compound (84 mg, 70% yield) as a yellow solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (dd, *J* = 4.7, 2.0 Hz, 1H), 8.03 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.31 (dd, *J* = 7.6, 4.8 Hz, 1H), 6.38 (br s, 1H), 4.03-3.93 (m, 1H), 2.05-1.97 (m, 2H), 1.78-1.69 (m, 2H), 1.67-1.58 (m, 1H), 1.47-1.36 (m, 2H), 1.33-1.18 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8, 150.8, 147.2, 139.7, 131.8, 122.8, 49.3, 32.8, 25.6, 24.8.

IR (film) ν_{max} 3262, 2930, 2855, 1638, 1582, 1543, 1450, 1398, 1330, 1171, 1066, 857, 814, 735 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{16}ClN_2O$ ($[M+H]^+$) 239.0946, found 239.0946.



***N*-Cyclohexyl-2,2,2-trifluoroacetamide (S72)**

Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 2,2,2-trifluoroacetamide (113 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (10:1 hexane/EtOAc) provided the title compound (82 mg, 84% yield) as a white solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

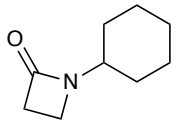
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.29 (br s, 1H), 3.79 (dtq, *J* = 11.6, 8.2, 3.9 Hz, 1H), 2.00-1.90 (m, 2H), 1.79-1.70 (m, 2H), 1.68-1.60 (m, 1H), 1.42-1.31 (m, 2H), 1.28-1.13 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 156.4 (q, *J* = 36.5 Hz), 116.0 (q, *J* = 288.1 Hz), 49.4, 32.5, 25.3, 24.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ –76.1 (s, 3F).

IR (film) ν_{max} 3309, 2935, 2861, 1691, 1555, 1452, 1265, 1162, 737, 725, 704 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_8H_{13}F_3NO$ ($[M+H]^+$) 196.0944, found 196.0940.



1-Cyclohexylazetidin-2-one (S73)

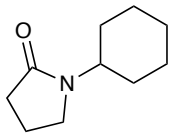
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTTP (0.46 mL, 469 mg, 1.5 mmol, 3.0 equiv.), azetidin-2-one (71 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (1:1 hexane/EtOAc) provided the title compound (60 mg, 78% yield) as a light yellow oil. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.50 (tt, *J* = 11.2, 3.8 Hz, 1H), 3.17 (t, *J* = 4.0 Hz, 2H), 2.81 (t, *J* = 4.0 Hz, 2H), 1.86-1.79 (m, 2H), 1.76-1.69 (m, 2H), 1.63-1.56 (m, 1H), 1.38-1.21 (m, 4H), 1.15-1.04 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 51.0, 36.2, 35.5, 30.8, 25.4, 25.0.

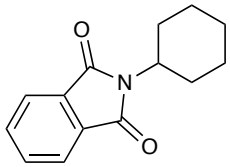
Data are consistent with those reported in the literature:

Willcox, D., Chappell, B. G. N., Hogg, K. F., Calleja, J., Smalley, A. P. & Gaunt, M. J. *Science* **354**, 851–857 (2016).



1-Cyclohexylpyrrolidin-2-one (S74)

Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTTP (0.46 mL, 469 mg, 1.5 mmol, 3.0 equiv.), pyrrolidin-2-one (85 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). The reaction provided the title compound in 17% yield. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv) from a calibrated GC assay after the addition of an internal standard. Authentic sample was purchased from Sigma-Aldrich.



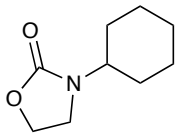
2-Cyclohexylisoindoline-1,3-dione (49)

Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), phthalimide (200 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (1:1 hexane/DCM) provided the title compound (70 mg, 61% yield) as a white solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82-7.77 (m, 2H), 7.70-7.65 (m, 2H), 4.10 (tt, *J* = 12.4, 3.9 Hz, 1H), 2.25-2.14 (m, 2H), 1.89-1.81 (m, 2H), 1.75-1.64 (m, 3H), 1.41-1.21 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.6, 133.8, 132.2, 123.1, 51.0, 30.0, 26.1, 25.2.

Data are consistent with those reported in the literature:
Worlikar, S. A. & Larock, R. C. *J. Org. Chem.* **73**, 7175–7180 (2008).



3-Cyclohexyloxazolidin-2-one (50)

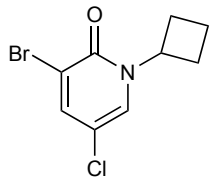
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTTP (0.46 mL, 469 mg, 1.5 mmol, 3.0 equiv.), oxazolidin-2-one (87 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (1:1 hexane/EtOAc) provided the title compound (60 mg, 71% yield) as a yellow oil. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.28 (dd, *J* = 8.7, 7.4 Hz, 2H), 3.69-3.61 (m, 1H), 3.49 (dd, *J* = 8.7, 7.4 Hz, 2H), 1.83-1.72 (m, 4H), 1.68-1.60 (m, 1H), 1.40-1.27 (m, 4H), 1.12-1.01 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 157.9, 62.1, 52.5, 40.6, 30.3, 25.42, 25.39.

Data are consistent with those reported in the literature:

Tran, B. L., Li, B., Driess, M. & Hartwig, J. F. *J. Am. Chem. Soc.* **136**, 2555–2563 (2014).



3-Bromo-5-chloro-1-cyclobutylpyridin-2(1*H*)-one (S75)

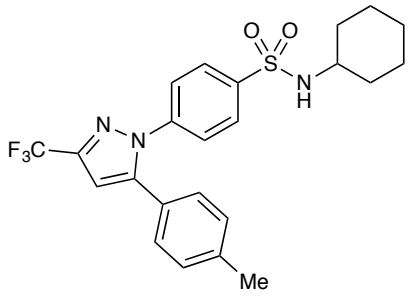
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuCl (9.9 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.3 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), 3-bromo-5-chloropyridin-2(1*H*)-one (104 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclobutanecarboxylate (444 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (3:1 hexane/EtOAc, then 10:1 toluene/EtOAc) provided the title compound (37 mg, 28% yield, >20:1 r.r.) as a pale yellow oil. The yield was determined based on 3-bromo-5-chloropyridin-2(1*H*)-one as the limiting reagent (1.0 equiv). The structure of the title compound (regioselectivity, *N*-alkylation v.s. *O*-alkylation) was further confirmed via 2D NMR (NOESY) analysis.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 2.7 Hz, 1H), 7.43 (d, *J* = 2.6 Hz, 1H), 5.06-4.99 (m, 1H), 2.59-2.46 (m, 2H), 2.22-2.14 (m, 2H), 1.90-1.87 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 157.6, 141.4, 131.1, 117.2, 111.5, 53.6, 29.9, 14.8.

IR (film) ν_{max} 2986, 2949, 1654, 1593, 1513, 1257, 859, 742 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_9H_{10}BrClNO$ ($[M+H]^+$) 261.9629, found 261.9627.



_N_-Cyclohexyl-4-(5-(_p_-tolyl)-3-(trifluoromethyl)-1_H_-pyrazol-1-yl)benzenesulfonamide (S76)

Prepared following the general procedure outlined above using $Ir(ppy)_3$ (10 mg, 15 μmol, 0.03 equiv.), CuTC (29 mg, 0.15 mmol, 0.30 equiv.), 4,7-diphenyl-1,10-phenanthroline (75 mg, 0.225 mmol, 0.45 equiv.), BTMG (0.32 mL, 257 mg, 1.5 mmol, 3.0 equiv.), Celecoxib (191 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (3:1 to 2:1 hexane/Et_2O) provided the title compound (141 mg, 61% yield) as a yellow solid. The yield was determined based on Celecoxib as the limiting reagent (1.0 equiv).

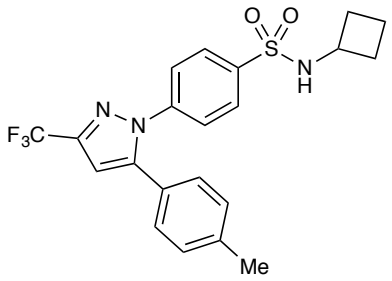
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90-7.84 (m, 2H), 7.48-7.43 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.74 (s, 1H), 4.74 (d, *J* = 7.7 Hz, 1H), 3.17-3.08 (m, 1H), 2.37 (s, 3H), 1.76-1.69 (m, 2H), 1.67-1.59 (m, 2H), 1.56-1.48 (m, 1H), 1.27-1.08 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 145.4, 144.1 (q, *J* = 38.5 Hz), 142.3, 141.1, 139.9, 129.8, 128.8, 128.0, 125.78, 125.73, 121.2 (q, *J* = 269.2 Hz), 106.3 (d, *J* = 1.8 Hz), 52.9, 34.0, 25.2, 24.7, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ –62.4 (s, 3F).

IR (film) ν_{max} 3279, 2933, 2857, 1598, 1499, 1472, 1450, 1409, 1374, 1329, 1270, 1235, 1158, 1132, 1095, 1079, 975, 842, 825, 807, 759, 742 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{23}H_{25}F_3N_3O_2S$ ($[M+H]^+$) 464.1614, found 464.1607.



***N*-Cyclobutyl-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide (S77)**

Prepared following the general procedure outlined above using $Ir(ppy)_3$ (10 mg, 15 μmol, 0.03 equiv.), CuTC (29 mg, 0.15 mmol, 0.30 equiv.), 4,7-diphenyl-1,10-phenanthroline (75 mg, 0.225 mmol, 0.45 equiv.), BTMG (0.32 mL, 257 mg, 1.5 mmol, 3.0 equiv.), Celecoxib (191 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclobutanecarboxylate (444 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (3:1 hexane/Et_2O) provided the title compound (163 mg, 75% yield) as a yellow solid. The yield was determined based on Celecoxib as the limiting reagent (1.0 equiv).

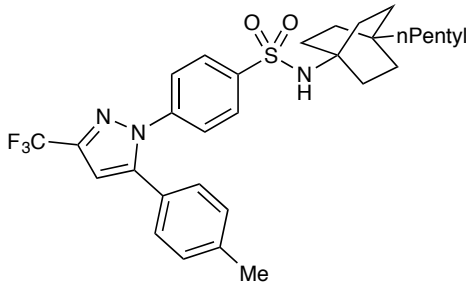
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87-7.82 (m, 2H), 7.48-7.43 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.74 (s, 1H), 5.02 (d, *J* = 9.0 Hz, 1H), 3.84-3.74 (m, 1H), 2.37 (s, 3H), 2.15-2.06 (m, 2H), 1.82-1.71 (m, 2H), 1.68-1.52 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 145.4, 144.2 (q, *J* = 38.5 Hz), 142.5, 140.5, 139.9, 129.8, 128.8, 128.1, 125.79, 125.72, 121.1 (q, *J* = 269.1 Hz), 48.3, 31.8, 21.4, 15.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ –62.4 (s, 3F).

IR (film) ν_{max} 3271, 2945, 1598, 1499, 1472, 1448, 1409, 1374, 1340, 1271, 1235, 1159, 1132, 1094, 973, 908, 843, 825, 807, 760, 742 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{21}H_{21}F_3N_3O_2S$ ($[M+H]^+$) 436.1301, found 436.1305.



***N*-(4-Pentylbicyclo[2.2.2]octan-1-yl)-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide (58)**

Prepared following the general procedure outlined above using $Ir(ppy)_3$ (10 mg, 15 μmol, 0.03 equiv.), CuTC (29 mg, 0.15 mmol, 0.30 equiv.), 4,7-diphenyl-1,10-phenanthroline (75 mg, 0.225 mmol, 0.45 equiv.), BTMG (0.32 mL, 257 mg, 1.5 mmol, 3.0 equiv.), Celecoxib (191 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene bis(4-pentylbicyclo[2.2.2]octane-1-carboxylate) (693 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (3:1 hexane/Et_2O) provided the title compound (154 mg, 55% yield) as a yellow solid. The yield was determined based on Celecoxib as the limiting reagent (1.0 equiv).

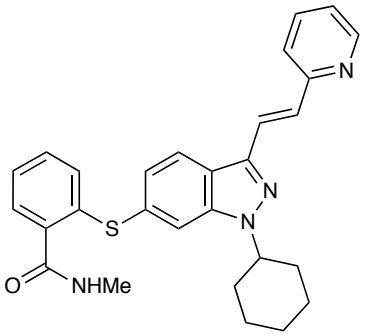
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.7 Hz, 2H), 7.43 (d, *J* = 8.7 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.74 (s, 1H), 4.81 (s, 1H), 2.37 (s, 3H), 1.68-1.60 (m, 6H), 1.39-1.32 (m, 6H), 1.29-1.21 (m, 3H), 1.20-1.07 (m, 4H), 1.01-0.97 (m, 1H), 0.84 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 145.4, 144.1, 143.4, 142.1, 139.8, 129.8, 128.8, 128.1, 125.8, 125.6, 121.2 (q, *J* = 269.1 Hz), 106.2, 55.3, 41.0, 32.8, 32.3, 31.2, 30.0, 23.4, 22.7, 21.4, 14.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ –62.4 (s, 3F).

IR (film) ν_{max} 3268, 2925, 2861, 1499, 1471, 1375, 1335, 1272, 1236, 1158, 1135, 1096, 976, 843, 825, 806, 760, 743 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{30}H_{37}F_3N_3O_2S$ ($[M+H]^+$) 560.2553, found 560.2557.



(*E*)-2-((1-Cyclohexyl-3-(2-(pyridin-2-yl)vinyl)-1*H*-indazol-6-yl)thio)-*N*-methylbenzamide (S78)

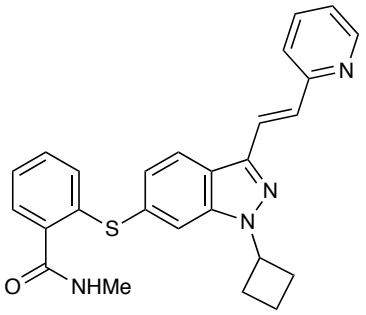
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (6.6 mg, 10 μmol, 0.02 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), Axitinib (193 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (1:1 to 2:1 hexane/EtOAc with 1% Et_3N) provided the title compound (134 mg, 57% yield, >20:1 r.r.) as a pale yellow foam. The yield was determined based on Axitinib as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (d, *J* = 5.6 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 16.4 Hz, 1H), 7.70 (td, *J* = 7.8, 1.6 Hz, 1H), 7.62-7.56 (m, 2H), 7.53-7.50 (m, 2H), 7.25-7.15 (m, 4H), 7.11-7.07 (m, 1H), 6.47-6.34 (m, 1H), 4.38-4.31 (m, 1H), 2.96 (d, *J* = 4.9 Hz, 3H), 2.08-1.91 (m, 6H), 1.767-1.75 (m, 1H), 1.50-1.41 (m, 2H), 1.33 (ddd, *J* = 16.3, 8.3, 3.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.7, 155.8, 149.6, 141.4, 140.6, 136.8, 136.1, 135.8, 132.0, 130.8, 130.7, 129.5, 128.5, 126.5, 125.9, 124.1, 122.2, 122.12, 122.08, 121.7, 114.3, 58.6, 32.6, 26.9, 25.8, 25.4.

IR (film) ν_{max} 3290, 2933, 2856, 2238, 1737, 1639, 1433, 1313, 907, 730 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{28}H_{29}N_4OS$ ($[M+H]^+$) 469.2057, found 469.2058.



(*E*)-2-((1-Cyclobutyl-3-(2-(pyridin-2-yl)vinyl)-1*H*-indazol-6-yl)thio)-*N*-methylbenzamide (59)

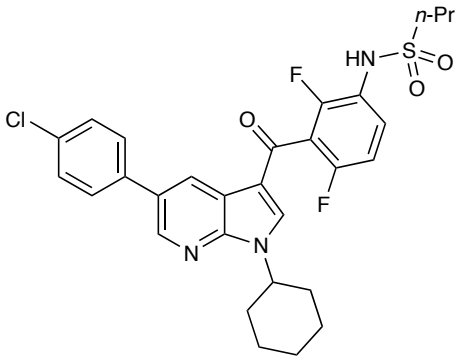
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (6.6 mg, 10 μmol, 0.02 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), Axitinib (193 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclobutanecarboxylate (444 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (1:1 CH_2Cl_2/EtOAc with 1% Et_3N) provided the title compound (161 mg, 73% yield, >20:1 r.r.) as a brown solid. The yield was determined based on Axitinib as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.2 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 16.4 Hz, 1H), 7.65 (td, *J* = 7.7, 1.5 Hz, 1H), 7.57 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.55-7.50 (m, 2H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.25-7.18 (m, 2H), 7.18-7.08 (m, 3H), 6.61-6.44 (m, 1H), 4.97 (p, *J* = 8.3 Hz, 1H), 2.94 (d, *J* = 4.9 Hz, 3H), 2.84-2.70 (m, 2H), 2.50-2.45 (m, 2H), 2.00-1.80 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.7, 155.7, 149.6, 141.7, 140.8, 136.7, 136.1, 135.6, 132.5, 131.1, 130.8, 129.8, 128.5, 126.7, 125.6, 123.8, 122.2, 122.1, 121.9, 121.8, 113.8, 52.7, 29.9, 26.8, 15.1.

IR (film) ν_{max} 3284, 3058, 2947, 2237, 1738, 1640, 1434, 1314, 909, 731 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{26}H_{25}N_4OS$ ($[M+H]^+$) 441.1744, found 441.1739.



***N*-(3-(5-(4-Chlorophenyl)-1-cyclohexyl-1*H*-pyrrolo[2,3-*b*]pyridine-3-carbonyl)-2,4-difluorophenyl)propane-1-sulfonamide (S79)**

Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), Vemurafenib (245 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (3:1 hexane/EtOAc) provided the title compound (114 mg, 40% yield) as a yellow solid. The yield was determined based on Vemurafenib as the limiting reagent (1.0 equiv).

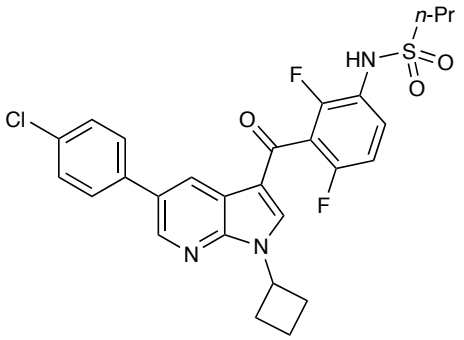
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.62 (d, *J* = 2.2 Hz, 1H), 7.71-7.63 (m, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.48-7.42 (m, 2H), 7.07-7.01 (m, 1H), 6.89 (s, 1H), 4.81 (tt, *J* = 12.0, 3.7 Hz, 1H), 3.15-3.05 (m, 2H), 2.21-2.13 (m, 2H), 1.96-1.85 (m, 4H), 1.82-1.75 (m, 1H), 1.73-1.63 (m, 2H), 1.61-1.50 (m, 2H), 1.32-1.24 (m, 1H), 1.03 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 180.3, 156.6 (dd, *J* = 250.3, 6.9 Hz), 151.43 (dd, *J* = 249.0, 7.9 Hz), 147.8, 143.9, 137.2, 135.7, 133.9, 132.1, 129.3, 129.1, 128.8, 128.0 (m), 125.8 (d, *J* = 9.1 Hz), 121.8 (dd, *J* = 13.1, 3.3 Hz), 119.0, 118.6 (m), 115.7, 112.7 (dd, *J* = 22.9, 3.0 Hz), 54.6, 33.5, 25.7, 25.4, 17.3, 13.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ –115.0 (m, 1F), –125.8 (d, *J* = 8.5 Hz, 1F).

IR (film) ν_{max} 3234, 2929, 2856, 1630, 1522, 1484, 1466, 1454, 1434, 1402, 1331, 1296, 1267, 1248, 1210, 1186, 1148, 1092, 1013, 995, 971, 897, 824, 736 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{29}H_{29}ClF_2N_3O_3S$ ($[M+H]^+$) 572.1581, found 572.1578.



***N*-(3-(5-(4-Chlorophenyl)-1-cyclobutyl-1*H*-pyrrolo[2,3-*b*]pyridine-3-carbonyl)-2,4-difluorophenyl)propane-1-sulfonamide (60)**

Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-dimethoxy-1,10-phenanthroline (36 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), Vemurafenib (245 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclobutanecarboxylate (444 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (3:1 hexane/EtOAc) provided the title compound (171 mg, 63% yield) as a white solid. The yield was determined based on Vemurafenib as the limiting reagent (1.0 equiv).

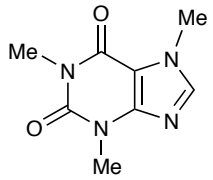
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.61 (d, *J* = 2.2 Hz, 1H), 7.76 (s, 1H), 7.71-7.64 (m, 1H), 7.62- 7.55 (m, 2H), 7.48-7.41 (m, 2H), 7.10-7.03 (m, 1H), 6.75 (s, 1H), 5.40-5.29 (m, 1H), 3.15-3.09 (m, 2H), 2.65-2.57 (m, 2H), 2.52-2.41 (m, 2H), 2.00-1.84 (m, 4H), 1.04 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 180.3, 156.6 (dd, *J* = 250.3, 7.1 Hz), 151.4 (dd, *J* = 249.0, 8.0 Hz), 148.0, 144.1, 137.2, 135.9, 133.9, 131.2, 129.3, 129.1, 128.9, 128.1 (m), 125.8 (d, *J* = 9.2 Hz), 121.8 (dd, *J* = 13.1, 3.8 Hz), 119.1, 118.6 (dd, *J* = 24.2, 21.6 Hz), 115.8, 112.7 (dd, *J* = 22.9, 3.8 Hz), 54.6, 49.5, 30.9, 17.4, 15.2, 13.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ –115.0 (m, 1F), –125.9 (d, *J* = 8.5 Hz, 1F).

IR (film) ν_{max} 3237, 2975, 2878, 1630, 1522, 1485, 1468, 1434, 1405, 1329, 1300, 1248, 1209, 1150, 1092, 1021, 1013, 970, 899, 829, 737 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{27}H_{25}ClF_2N_3O_3S$ ($[M+H]^+$) 544.1268, found 544.1265.



1,3,7-Trimethyl-3,7-dihydro-1*H*-purine-2,6-dione (S80)

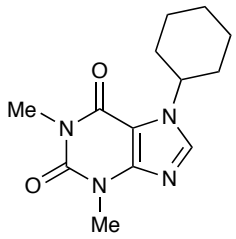
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (3.3 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), theophylline (90 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene diacetate (364 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (19:1 DCM/MeOH) provided the title compound (80 mg, 82% yield, >20:1 r.r.) as a white solid. The yield was determined based on theophylline as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (s, 1H), 3.98 (s, 3H), 3.57 (s, 3H), 3.40 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 155.6, 151.8, 148.8, 141.5, 107.7, 33.7, 29.9, 28.1.

Data are consistent with those reported in the literature:
Yanuka, Y. & Bergmann, F. *Tetrahedron* **42**, 5991–6002 (1986).

Data are also consistent with an authentic sample purchased from Sigma-Aldrich.



7-Cyclohexyl-1,3-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione (S81)

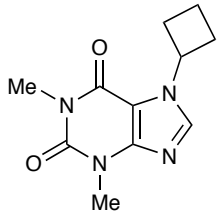
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (3.3 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), theophylline (90 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (1:2 hexane/EtOAc) provided the title compound (105 mg, 80% yield, >20:1 r.r.) as a white solid. The yield was determined based on theophylline as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (s, 1H), 4.63 (tt, *J* = 12.0, 3.7 Hz, 1H), 3.58 (s, 3H), 3.40 (s, 3H), 2.24-2.16 (m, 2H), 1.95-1.87 (m, 2H), 1.80-1.63 (m, 3H), 1.54-1.43 (m, 2H), 1.31-1.23 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 155.2, 151.7, 149.1, 138.3, 106.9, 57.2, 33.9, 29.9, 28.2, 25.6, 25.3.

IR (film) ν_{max} 3113, 2944, 2854, 1694, 1653, 1546, 1452, 1425, 1351, 1304, 1252, 1233, 1202, 1029, 997, 974, 760, 750, 740 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{19}N_4O_2$ ($[M+H]^+$) 263.1503, found 263.1496.



7-Cyclobutyl-1,3-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione (S82)

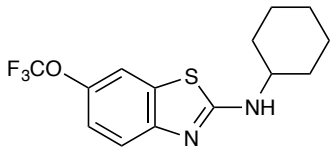
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (3.3 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), theophylline (90 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclobutanecarboxylate (444 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (1:3 hexane/EtOAc) provided the title compound (97 mg, 83% yield, >20:1 r.r.) as a yellow solid. The yield was determined based on theophylline as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (s, 1H), 5.18-5.09 (m, 1H), 3.57 (s, 3H), 3.40 (s, 3H), 2.62-2.54 (m, 2H), 2.48-2.38 (m, 2H), 1.98-1.87 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 155.1, 151.8, 149.3, 138.8, 107.2, 51.4, 30.8, 29.9, 28.2, 14.9.

IR (film) ν_{max} 3111, 2927, 1700, 1650, 1599, 1541, 1470, 1455, 1429, 1409, 1277, 1237, 1201, 1037, 996, 973, 760, 744, 728 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{11}H_{15}N_4O_2$ ($[M+H]^+$) 235.1190, found 235.1183.



***N*-Cyclohexyl-6-(trifluoromethoxy)benzo[*d*]thiazol-2-amine (62)**

Prepared following the general procedure outlined above using Ir(F-Meppy)$_2$(dtbbpy)PF$_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTTP (0.31 mL, 312 mg, 1.0 mmol, 2.0 equiv.), Riluzole (234 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (12:1 hexane/EtOAc) provided the title compound (70 mg, 44% yield) as a white solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

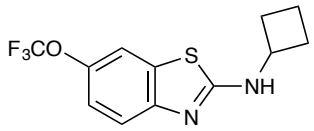
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.38 (d, *J* = 1.9 Hz, 1H), 7.31-7.23 (m, 3H), 2.94-2.86 (m, 1H), 1.93-1.85 (m, 2H), 1.80-1.72 (m, 2H), 1.65-1.57 (m, 1H), 1.39-1.19 (m, 5H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 144.1 (d, *J* = 2.0 Hz), 138.8, 129.8, 123.7, 120.6, 120.5 (q, *J* = 257.6 Hz), 115.4, 110.2, 49.3, 33.5, 26.1, 25.5.

^{19}F NMR (376 MHz, CDCl$_3$) δ –58.4 (s, 3F).

IR (film) ν_{max} 3213, 2931, 2855, 2241, 1493, 1388, 1250, 1215, 1190, 1164 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{16}F_3N_2OS$ ($[M+H]^+$) 317.0930, found 317.0935.



_N_-Cyclobutyl-6-(trifluoromethoxy)benzo[_d_]thiazol-2-amine (S83)

Prepared following the general procedure outlined above using Ir(F-Meppy)$_2$(dtbbpy)PF$_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTTP (0.31 mL, 312 mg, 1.0 mmol, 2.0 equiv.), Riluzole (234 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclobutanecarboxylate (222 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (12:1 hexane/EtOAc) provided the title compound (58 mg, 40% yield) as a white solid. The yield was determined based on iodomesitylene dicyclobutanecarboxylate as the limiting reagent (1.0 equiv).

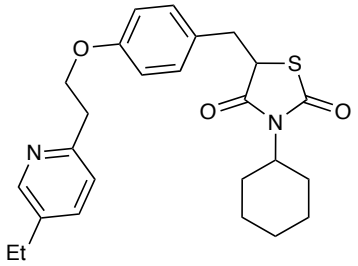
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.31-7.19 (m, 3H), 7.08 (br s, 1H), 3.62 (p, J = 8.0 Hz, 1H), 2.32-2.23 (m, 2H), 2.03-1.81 (m, 4H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 144.3 (d, J = 1.9 Hz), 138.1, 128.8, 123.5, 121.2, 120.5 (q, J = 257.6 Hz), 115.6, 110.1, 42.8, 30.7, 18.5.

^{19}F NMR (376 MHz, CDCl$_3$) δ –58.4 (s, 3F).

IR (film) ν_{max} 3206, 2940, 2241, 1494, 1390, 1253, 1217, 1192, 1164 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{12}F_3N_2OS$ ([M+H]$^+$) 289.0617, found 289.0621.



3-Cyclohexyl-5-(4-(2-(5-ethylpyridin-2-yl)ethoxy)benzyl)thiazolidine-2,4-dione (61)

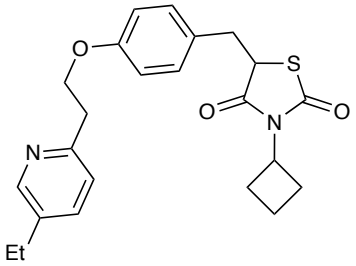
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), Pioglitazone (535 mg, 1.5 mmol, 3.0 equiv.), iodomesitylene dicyclohexanecarboxylate (250 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (2:1 hexane/EtOAc) provided the title compound (146 mg, 67% yield) as a white solid. The yield was determined based on iodomesitylene dicyclohexanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, *J* = 1.9 Hz, 1H), 7.44 (dd, *J* = 7.9, 2.3 Hz, 1H), 7.17 (d, *J* = 7.9 Hz, 1H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.85-6.79 (m, 2H), 4.33-4.27 (m, 3H), 4.01 (tt, *J* = 12.3, 3.8 Hz, 1H), 3.34 (dd, *J* = 14.1, 3.9 Hz, 1H), 3.21 (t, *J* = 6.7 Hz, 2H), 3.07 (dd, *J* = 14.1, 8.7 Hz, 1H), 2.62 (q, *J* = 7.6 Hz, 2H), 2.15-2.01 (m, 2H), 1.83-1.75 (m, 2H), 1.65-1.58 (m, 1H), 1.52-1.43 (m, 2H), 1.32-1.14 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.3, 171.3, 158.3, 155.7, 149.1, 137.2, 135.9, 130.6, 127.7, 123.4, 114.8, 67.4, 55.1, 50.8, 38.0, 37.7, 28.6, 28.5, 26.0, 25.8, 25.0, 15.5.

IR (film) ν_{max} 2929, 2857, 1747, 1675, 1611, 1511, 1488, 1357, 1330, 1245, 1178, 1125, 1028, 824 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{25}H_{31}N_2O_3S$ ($[M+H]^+$) 439.2050, found 439.2046.



3-Cyclobutyl-5-(4-(2-(5-ethylpyridin-2-yl)ethoxy)benzyl)thiazolidine-2,4-dione (S84)

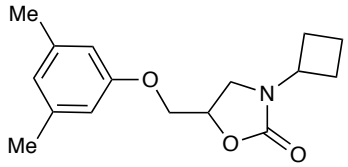
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTMG (0.21 mL, 171 mg, 1.0 mmol, 2.0 equiv.), Pioglitazone (535 mg, 1.5 mmol, 3.0 equiv.), iodomesitylene dicyclobutanecarboxylate (222 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). Purification by flash chromatography (2:1 hexane/EtOAc) provided the title compound (140 mg, 68% yield) as a yellow oil. The yield was determined based on iodomesitylene dicyclobutanecarboxylate as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, *J* = 2.0 Hz, 1H), 7.44 (dd, *J* = 7.9, 2.3 Hz, 1H), 7.17 (d, *J* = 7.9 Hz, 1H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.85-6.79 (m, 2H), 4.68-4.56 (m, 1H), 4.33-4.26 (m, 3H), 3.39 (dd, *J* = 14.1, 3.8 Hz, 1H), 3.20 (t, *J* = 6.7 Hz, 2H), 3.02 (dd, *J* = 14.1, 9.2 Hz, 1H), 2.84-2.70 (m, 2H), 2.61 (q, *J* = 7.6 Hz, 2H), 2.14-2.05 (m, 2H), 1.90-1.77 (m, 1H), 1.75-1.63 (m, 1H), 1.23 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.4, 171.4, 158.3, 155.7, 149.1, 137.1, 135.9, 130.4, 127.8, 123.4, 114.8, 67.4, 51.0, 48.2, 38.1, 37.7, 26.7, 26.5, 25.8, 15.5, 15.1.

IR (film) ν_{max} 2958, 2873, 1747, 1676, 1611, 1511, 1488, 1397, 1343, 1301, 1242, 1177, 1114, 1065, 1027, 823 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{23}H_{27}N_2O_3S$ ($[M+H]^+$) 411.1737, found 411.1737.



3-Cyclobutyl-5-((3,5-dimethylphenoxy)methyl)oxazolidin-2-one (63)

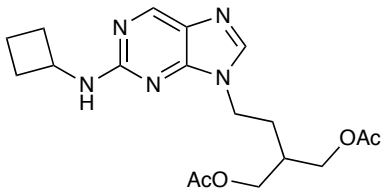
Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), BTTP (0.46 mL, 469 mg, 1.5 mmol, 3.0 equiv.), Metaxalone (221 mg, 1.0 mmol, 2.0 equiv.), iodomesitylene dicyclobutanecarboxylate (222 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (3:1 to 2:1 hexane/EtOAc) provided the title compound (124 mg, 90% yield) as a white solid. The yield was determined based on iodomesitylene dicyclobutanecarboxylate as the limiting reagent (1.0 equiv). The remaining Metaxalone can be recovered after the reaction (120 mg, 0.54 mmol, 1.08 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.63 (s, 1H), 6.52 (s, 2H), 4.80 (dtd, *J* = 10.1, 5.7, 4.5 Hz, 1H), 4.41 (p, *J* = 8.8 Hz, 1H), 4.14-4.01 (m, 2H), 3.75 (t, *J* = 8.8 Hz, 1H), 3.58 (dd, *J* = 8.7, 5.8 Hz, 1H), 2.28 (s, 6H), 2.21-2.14 (m, 4H), 1.73-1.65 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 158.2, 156.6, 139.5, 123.4, 112.3, 70.9, 68.1, 48.2, 43.6, 27.43, 27.36, 21.5, 14.9.

IR (film) ν_{max} 2943, 1738, 1613, 1593, 1480, 1428, 1322, 1295, 1255, 1172, 1157, 1068, 991, 831, 760, 696, 689 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{16}H_{22}NO_3$ ($[M+H]^+$) 276.1594, found 276.1591.



2-(2-(2-(Cyclobutylamino)-9*H*-purin-9-yl)ethyl)propane-1,3-diyl diacetate (S85)

Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuTC (29 mg, 0.15 mmol, 0.30 equiv.), 4,7-diphenyl-1,10-phenanthroline (75 mg, 0.23 mmol, 0.45 equiv.), BTTP (0.46 mL, 469 mg, 1.5 mmol, 3.0 equiv.), Famciclovir (402 mg, 1.25 mmol, 2.5 equiv.), iodomesitylene dicyclobutanecarboxylate (222 mg, 0.5 mmol, 1.0 equiv.), and 1,4-dioxane (7.5 mL). Purification by flash chromatography (40:1 CH_2Cl_2/MeOH) provided the title compound (75 mg, 40% yield) as a pale yellow oil. The yield was determined based on iodomesitylene dicyclobutanecarboxylate as the limiting reagent (1.0 equiv). The remaining Famciclovir can be recovered after the reaction (257 mg, 0.80 mmol, 1.6 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.69 (s, 1H), 5.49 (brs, 1H), 4.44 (h, *J* = 7.9 Hz, 1H), 4.18 (t, *J* = 7.2 Hz, 2H), 4.15-4.07 (m, 4H), 2.47-2.35 (m, 2H), 2.03 (s, 6H), 1.99-1.86 (m, 5H), 1.78-1.72 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 158.9, 153.3, 149.9, 141.6, 127.6, 63.7, 47.0, 40.7, 34.9, 31.5, 28.8, 20.9, 15.2.

IR (film) ν_{max} 3260, 2958, 1733, 1612, 1417, 1225, 1036, 796 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{18}H_{26}N_5O_4$ ($[M+H]^+$) 376.1979, found 376.1983.

5.3 Additional Examples

These reactions were performed on 0.1 mmol scale and the yields were determined by ^{1}H NMR with an internal standard. All of these conditions are unoptimized.

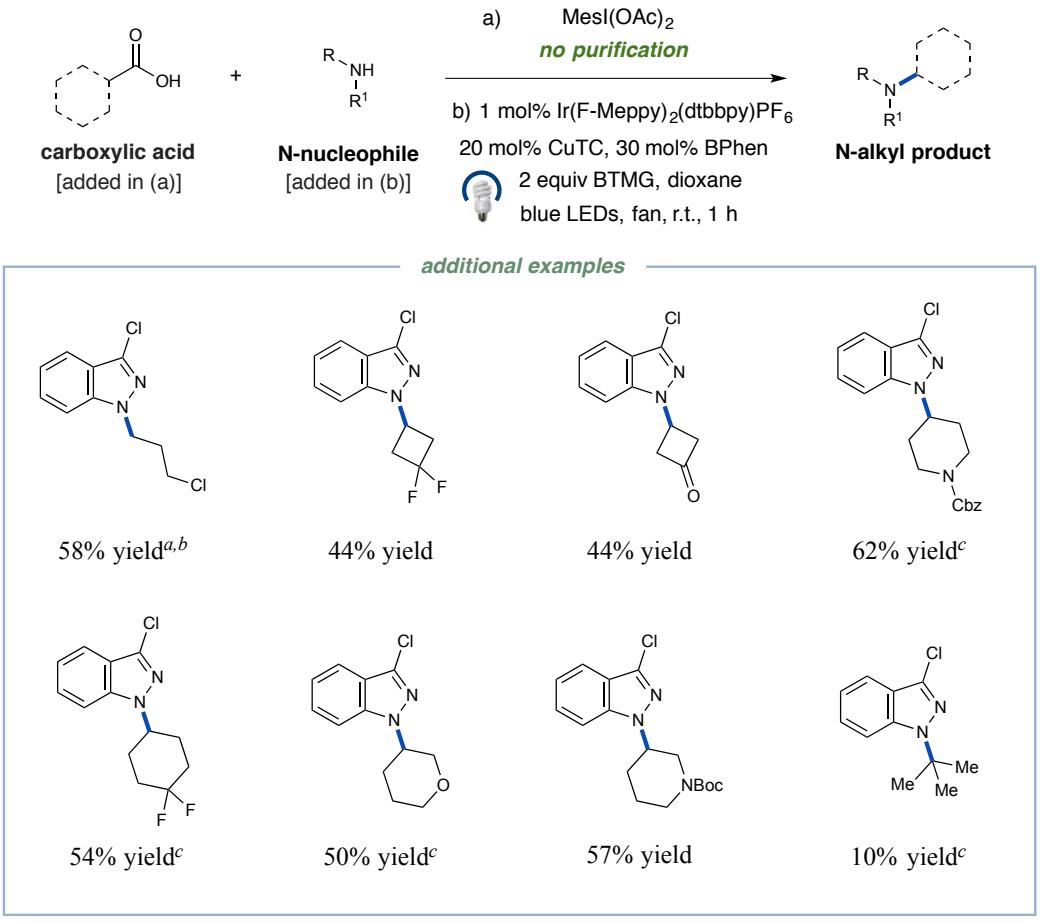
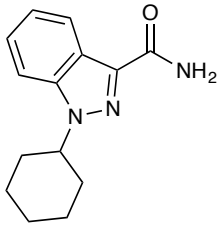


Figure S38 | Additional Examples.

General reaction conditions: 1.0 equiv *N*-nucleophile, 2.0 equiv iodomesitylene dicarboxylate, 1 mol% photocatalyst, 20 mol% CuTC, 30 mol% BPhen, 2 equiv BTMG, in dioxane (0.033 M). All yields were determined by ^{1}H NMR with an internal standard for the decarboxylative C–N coupling step. [a]1 mol% $Ir(ppy)_3$ as photocatalyst. [b]No exogenous base was used. [c]30 mol% dOMe-Phen as ligand.

6. Sequential C–N Couplings



1-Cyclohexyl-1*H*-indazole-3-carboxamide (65)

Prepared following the general procedure outlined above using $Ir(ppy)_3$ (6.6 mg, 10 μmol, 0.02 equiv.), CuTC (19 mg, 0.10 mmol, 0.20 equiv.), 4,7-diphenyl-1,10-phenanthroline (50 mg, 0.15 mmol, 0.30 equiv.), 1*H*-indazole-3-carboxamide (81 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (500 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (12 mL). No extrogenous base was used. Purification by flash chromatography (1.5:1 hexane/EtOAc) provided the title compound (107 mg, 88% yield, >20:1 r.r.) as a brown solid. The yield was determined based on 1*H*-indazole-3-carboxamide as the limiting reagent (1.0 equiv).

For gram scale:

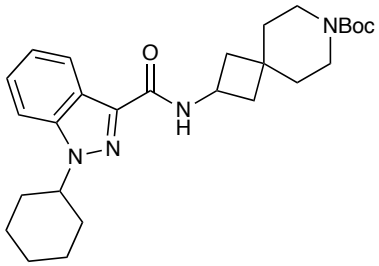
Prepared following the general procedure outlined above using $Ir(ppy)_3$ (98 mg, 0.15 mmol, 0.02 equiv.), CuTC (142 mg, 0.75 mmol, 0.10 equiv.), 4,7-diphenyl-1,10-phenanthroline (371 mg, 1.12 mmol, 0.15 equiv.), 1*H*-indazole-3-carboxamide (1.20 g, 7.45 mmol, 1.0 equiv.), iodomesitylene dicyclohexanecarboxylate (5.59 g, 11.2 mmol, 1.5 equiv.), and 1,4-dioxane (150 mL). No extrogenous base was used. Purification by flash chromatography (1.5:1 hexane/EtOAc) provided the title compound (1.45 g, 80% yield, >20:1 r.r.) as a brown solid. The yield was determined based on 1*H*-indazole-3-carboxamide as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.2 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.38 (t, *J* = 6.8 Hz, 1H), 7.26 (t, *J* = 7.7 Hz, 1H), 6.98 (brs, 1H), 6.12 (brs, 1H), 4.43 (tt, *J* = 11.2, 4.2 Hz, 1H), 2.09-1.91 (m, 6H), 1.79-1.76 (m, 1H), 1.48 (qt, *J* = 13.2, 3.7 Hz, 2H), 1.33 (tt, *J* = 12.7, 3.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 165.2, 140.2, 136.3, 126.3, 123.0, 122.8, 122.7, 109.4, 58.5, 32.6, 25.7, 25.4.

IR (film) ν_{max} 3420, 3176, 2932, 2857, 1649, 1598, 1476, 1308, 1189, 750 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{18}N_3O$ ($[M+H]^+$) 244.1444, found 244.1444.



***tert*-Butyl 2-(1-cyclohexyl-1*H*-indazole-3-carboxamido)-7-azaspiro[3.5]nonane-7-carboxylate (66)**

Prepared following the general procedure outlined above using $Ir(F\text{-}Meppy)_2(dtbbpy)PF_6$ (4.9 mg, 5.0 μmol, 0.01 equiv.), CuCl (20 mg, 0.20 mmol, 0.40 equiv.), 4,7-diphenyl-1,10-phenanthroline (100 mg, 0.30 mmol, 0.60 equiv.), BTTP (0.46 mL, 469 mg, 1.5 mmol, 3.0 equiv.), 1-cyclohexyl-1*H*-indazole-3-carboxamide (122 mg, 0.50 mmol, 1.0 equiv.), iodomesitylene 7,7'-di-*tert*-butyl O'^2,O^2-bis(7-azaspiro[3.5]nonane-2,7-dicarboxylate) (783 mg, 1.0 mmol, 2.0 equiv.), and 1,4-dioxane (8 mL). Purification by flash chromatography (3:1 to 1.5:1 hexane/EtOAc) provided the title compound (118 mg, 51% yield) as a pale yellow oil. The yield was determined based on 1-cyclohexyl-1*H*-indazole-3-carboxamide as the limiting reagent (1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.2 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 7.7 Hz, 1H), 4.61 (h, *J* = 8.2 Hz, 1H), 4.41 (tt, *J* = 10.0, 4.9 Hz, 1H), 3.44-3.34 (m, 2H), 3.30-3.23 (m, 2H), 2.42-2.38 (m, 2H), 2.06-1.91 (m, 6H), 1.84-1.74 (m, 3H), 1.64-1.59 (m, 2H), 1.56-1.45 (m, 4H), 1.44 (s, 9H), 1.33 (ddd, *J* = 16.1, 8.1, 3.2 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.3, 155.0, 140.1, 136.8, 126.4, 122.94, 122.93, 122.6, 109.4, 79.4, 58.6, 40.4, 39.6, 39.4, 35.7, 32.6, 28.52, 28.49, 25.7, 25.4.

IR (film) ν_{max} 3325, 2929, 2857, 2243, 1672, 1529, 1421, 1243, 1173, 910, 727 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{27}H_{39}N_4O_3$ ($[M+H]^+$) 467.3017, found 467.3020.

7. Comparison with Nucleophilic Substitution

7.1 Experimental Procedures

All of the reactions shown in this section were performed on 0.10 mmol scale.

For decarboxylative sp^3 C–N coupling:

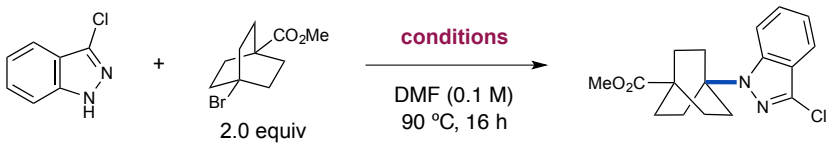
To an 8 mL vial equipped with a stir bar was added photocatalyst Ir(F-Meppy)$_2$(dtbbpy)PF_6, *N*-nucleophile, iodomesitylene dicarboxylate, copper salt, and ligand. Dioxane (3.0 mL) was added and followed by the addition of the base. The solution was sonicated for 1–3 min until it became homogeneous. Next, the solution was degassed by sparging with nitrogen for 5 minutes before sealing with parafilm. The reaction was stirred and irradiated using 34 W blue LED lamps (3 cm away, with cooling fan to keep the reaction at room temperature) or with the integreated photoreactor[8] for the indicated period of time. The reaction was quenched by exposure to air and analyzed by ^{1}H NMR after the addition of an internal standard (mesitylene).

For the stoichiometry of reagents used for these reactions, see **5.3** (Products Characterization) for details.

For S_N2/S_N1 nucleophillic substitution:

To an 8 mL vial equipped with a stir bar was added 3-chloro-1*H*-indazole (1.0 equiv.), base (2.0 equiv.), and anhydrous DMF (0.1 M). The mixture was stirred at r.t. for 15 min. Then alkyl bromide (2.0 equiv.) was added and the mixture was heated at 90 ^{o}C for the indicated period of time (16 hours or 40 hours). After cooling to room temperature, the reaction was analyzed by ^{1}H NMR after the addition of an internal standard (mesitylene).

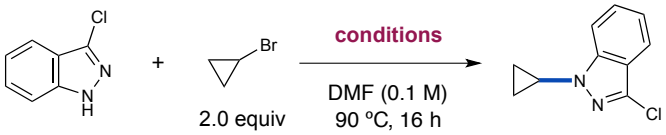
7.2 Results



Entry	Conditions	Yield[a]
1	2.0 equiv K_2CO_3	**<1%**
2	2.0 equiv K_2CO_3 + 10 mol% NaI	**<1%**
3	2.0 equiv Cs_2CO_3	**<1%**
4	2.0 equiv BTMG	**<1%**
5	2.0 equiv BTTP	**<1%**
6	2.0 equiv NaH	**<1%**
7	2.0 equiv Ag_2O[b]	**<1%**

[a]Yields calculated by ^{1}H NMR with an internal standard.
[b]With 3Å molecular sieves in DCM (0.1 M), r.t.

Figure S39 | Nucleophillic substitution with a tertiary alkyl bromide.



Entry	Conditions	Yield[a]
1	2.0 equiv K_2CO_3	**<1%**
2	2.0 equiv K_2CO_3 + 10 mol% NaI	**<1%**
3	2.0 equiv Cs_2CO_3	**<1%**
4	2.0 equiv BTMG	**<1%**
5	2.0 equiv BTTP	**<1%**
6	2.0 equiv NaH	**<1%**
7	2.0 equiv Ag_2O[b]	**<1%**

[a]Yields calculated by ^{1}H NMR with an internal standard.
[b]With 3Å molecular sieves in DCM (0.1 M), r.t.

Figure S40 | Nucleophillic substitution with bromocyclopropane.

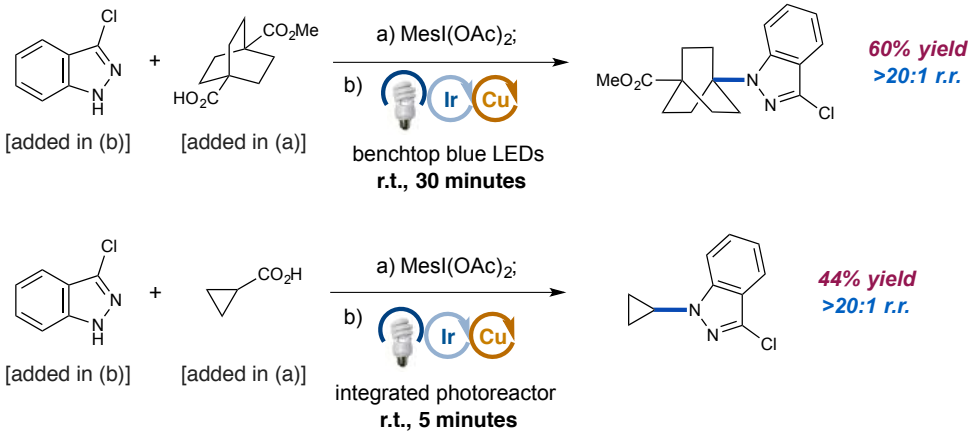


Figure S41 | Decarboxylative sp^3 C–N coupling with a tertiary acid and cyclopropanecarboxylic acid.

As shown in **Figure S39** and **Figure S40**, under a variety of commonly-used nucleophillic substitution conditions, alkylations with a tertirary alkyl bromide and bromocyclopropane are completely unsuccessful in both cases. As a comparison and shown in **Figure S41**, this new sp^3 C–N coupling can deliver the desired *N*-alkylated products in good yield.

7.3 Additional Examples for Comparisons

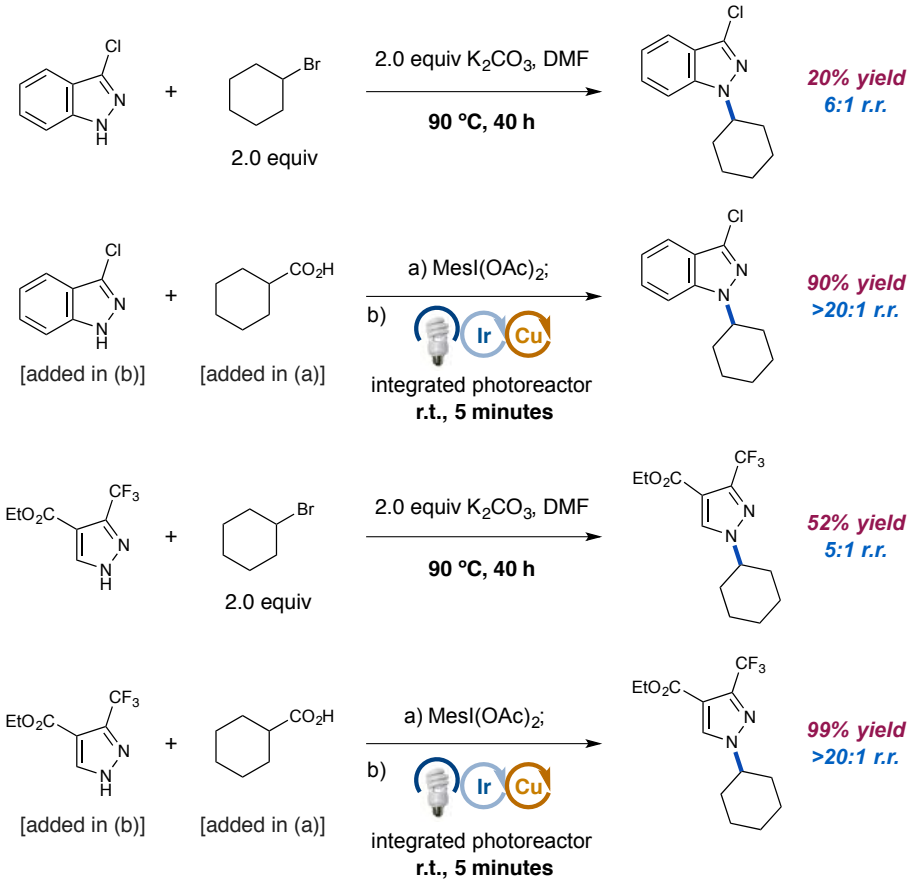
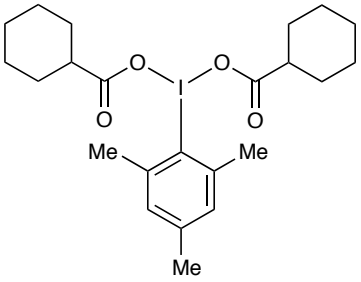


Figure S42 | Comparing decarboxylative sp^3 C–N couplings with nucleophilic substitutions.

8. Cyclic Voltammetry Data

Cyclic voltammetry was performed on a CH Instruments Electrochemical Analyzer (CHI600E). A 0.005 M CH_3CN solution of the iodomesitylene dicyclohexanecarboxylate was prepared with 0.10 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte and the solution was sparged with N_2 for 15 minutes. The cyclic voltammogram was obtained using a glassy carbon working electrode, a Pt counter electrode, and a saturated calomel reference electrode (SCE). Data was collected with a scan rate of 0.5 V/s.



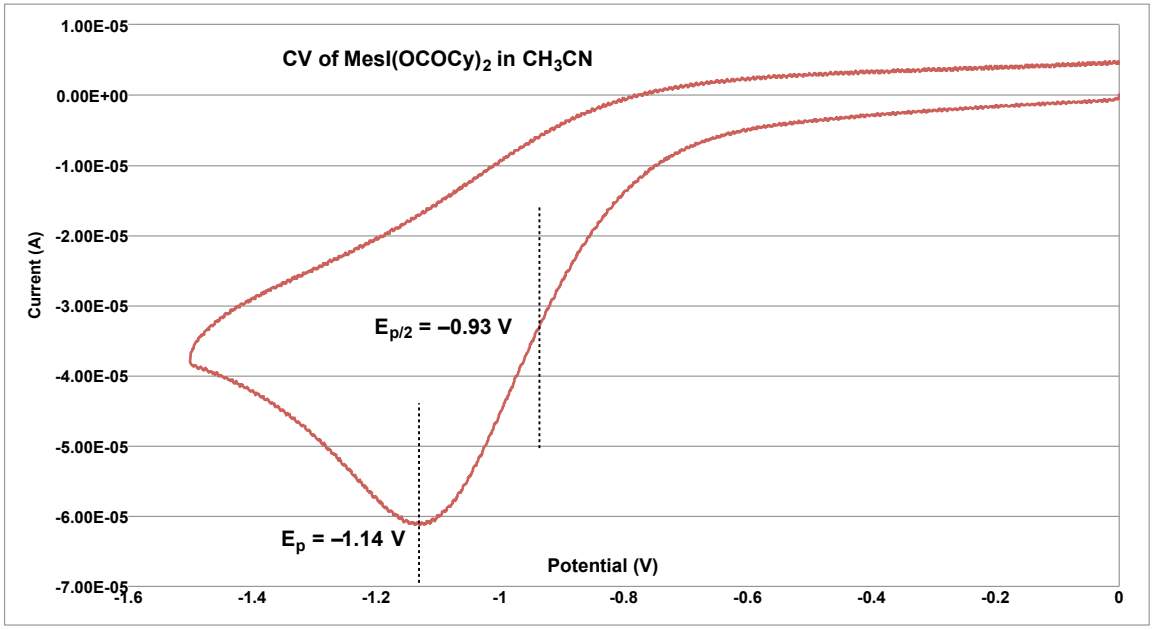


Figure S43| Cyclic voltammogram of the iodomesitylene dicyclohexanecarboxylate shows an irreversible reduction event at –1.14 V vs. SCE in CH_3CN.

9. References

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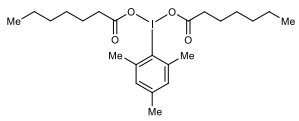
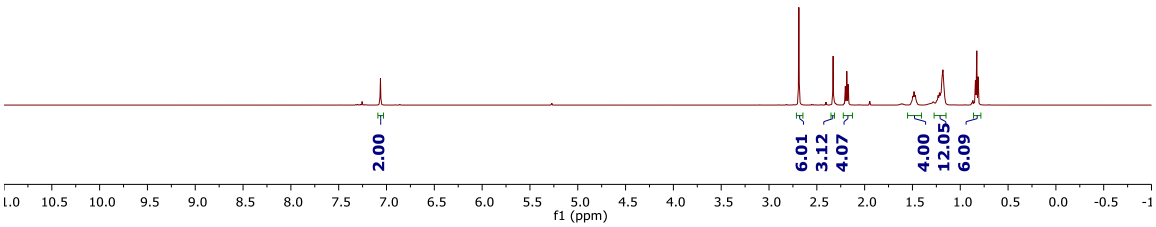
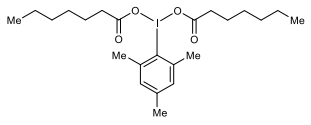
10. Spectral Data

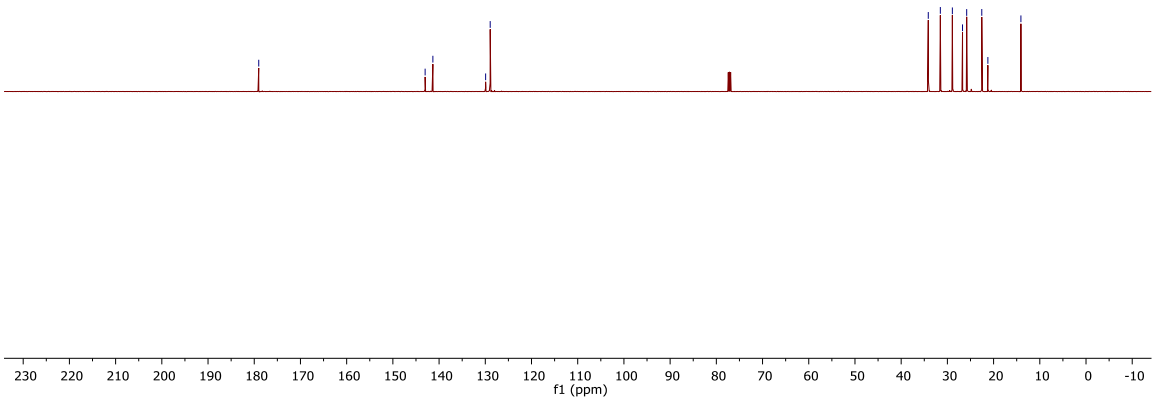


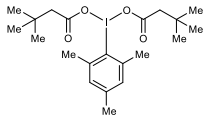
^{1}H NMR (500 MHz, $CDCl_3$)



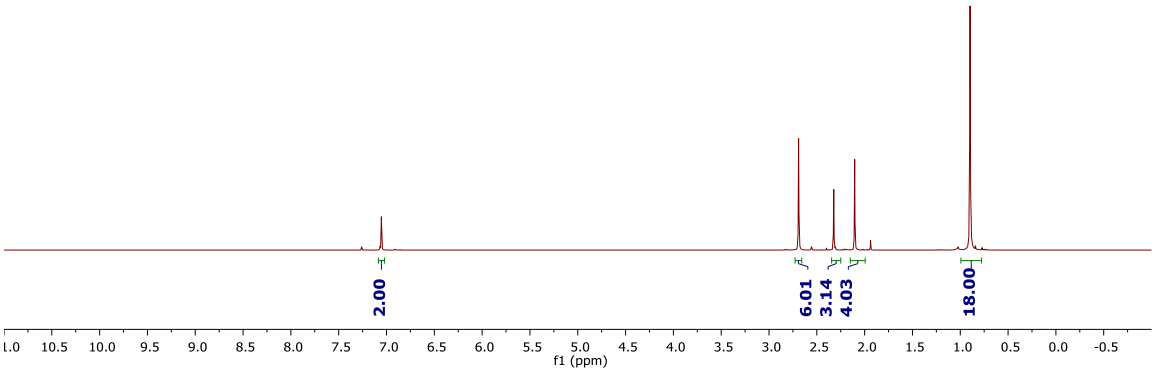


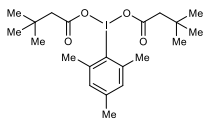
^{13}C NMR (125 MHz, $CDCl_3$)



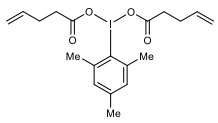


^{1}H NMR (500 MHz, $CDCl_3$)

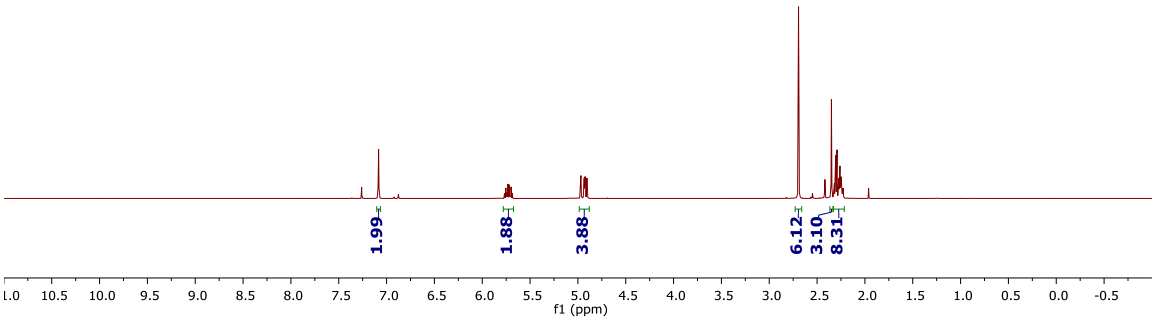


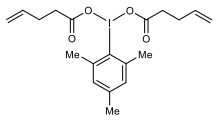


^{13}C NMR (125 MHz, $CDCl_3$)

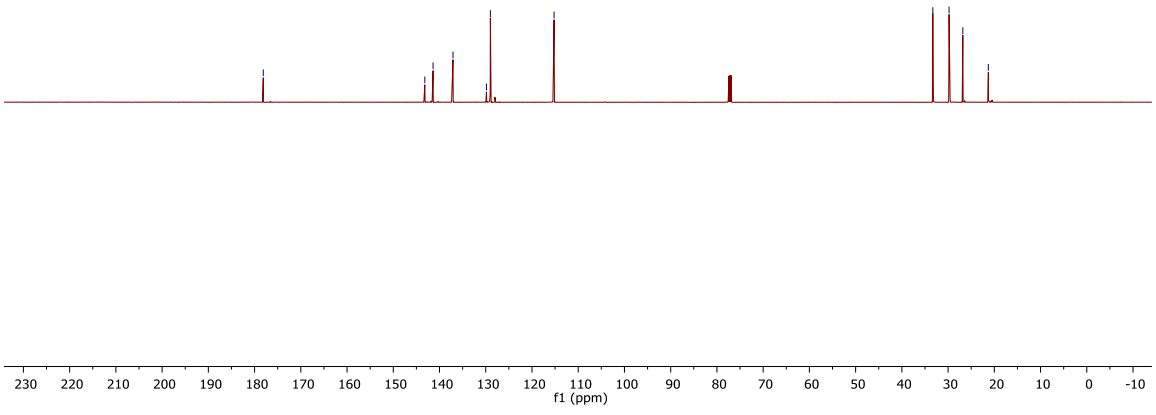


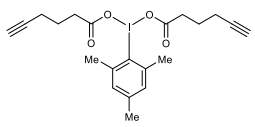
^{1}H NMR (500 MHz, $CDCl_3$)



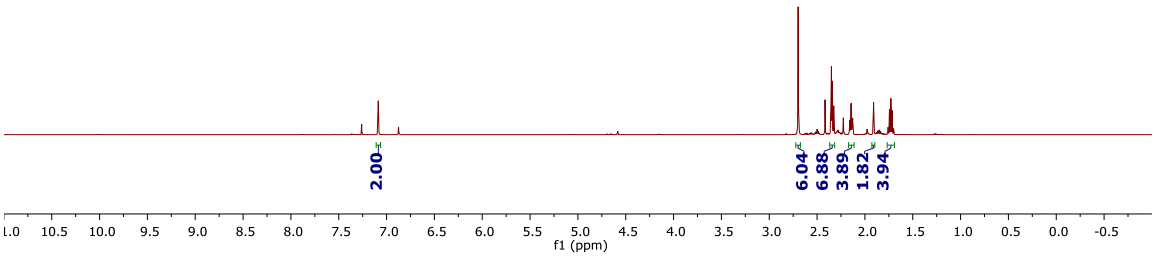


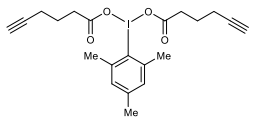
^{13}C NMR (125 MHz, $CDCl_3$)



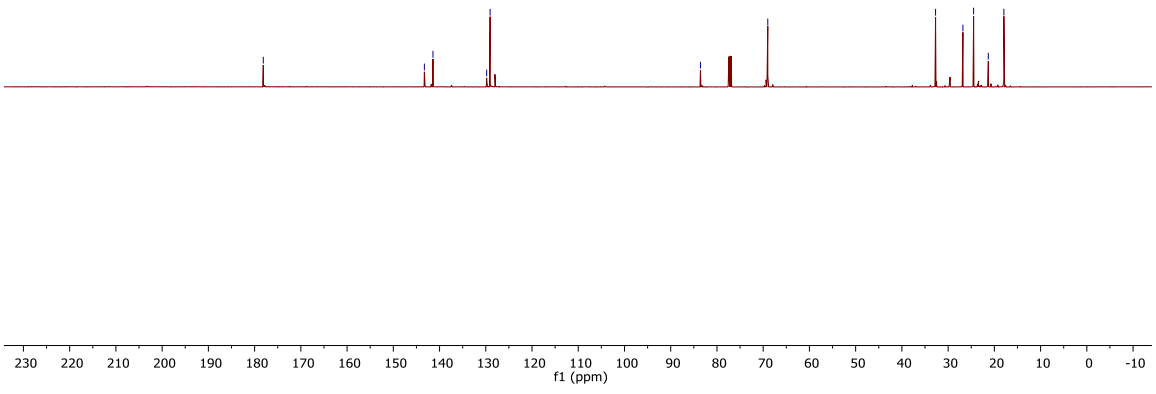


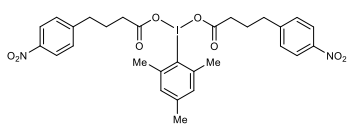
^{1}H NMR (500 MHz, $CDCl_3$)



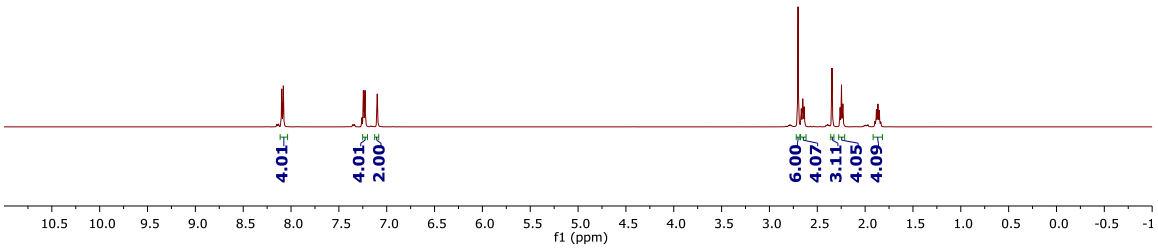


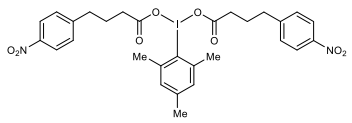
^{13}C NMR (125 MHz, $CDCl_3$)



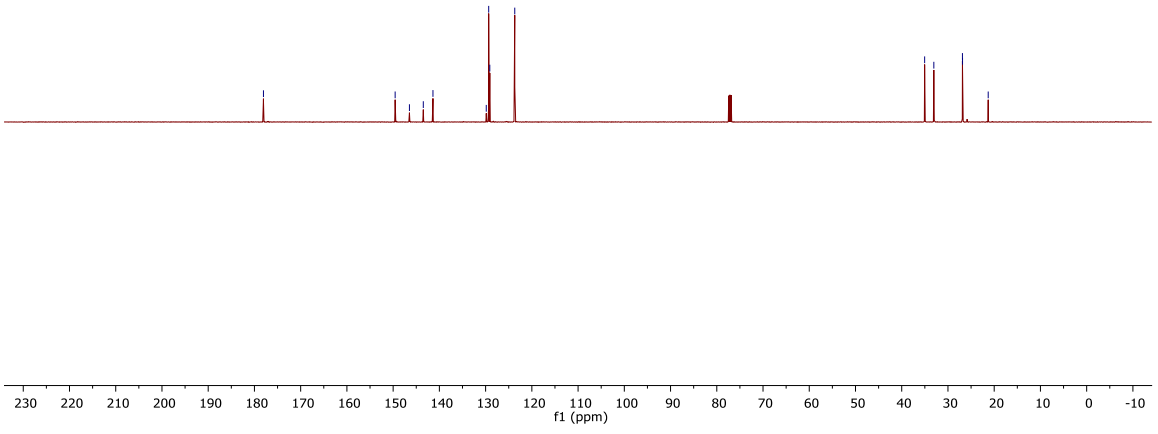


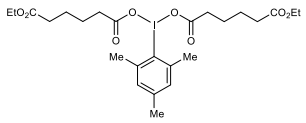
^{1}H NMR (500 MHz, $CDCl_3$)



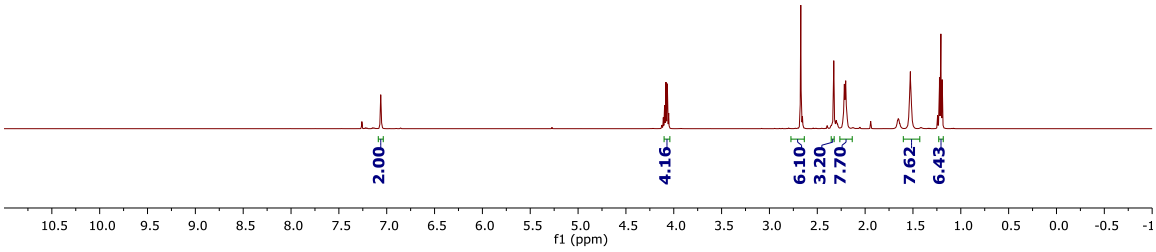


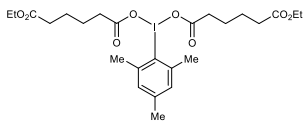
^{13}C NMR (125 MHz, $CDCl_3$)



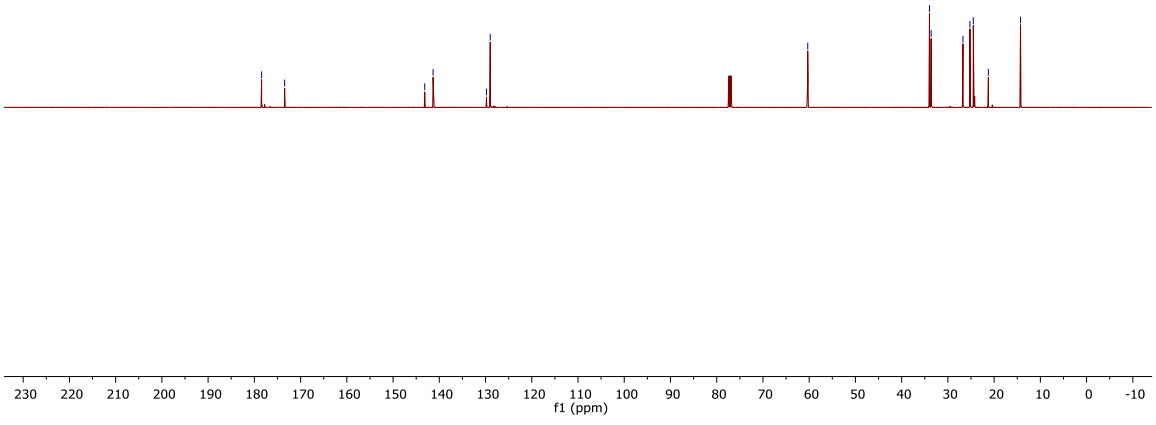


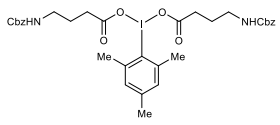
^{1}H NMR (500 MHz, $CDCl_3$)



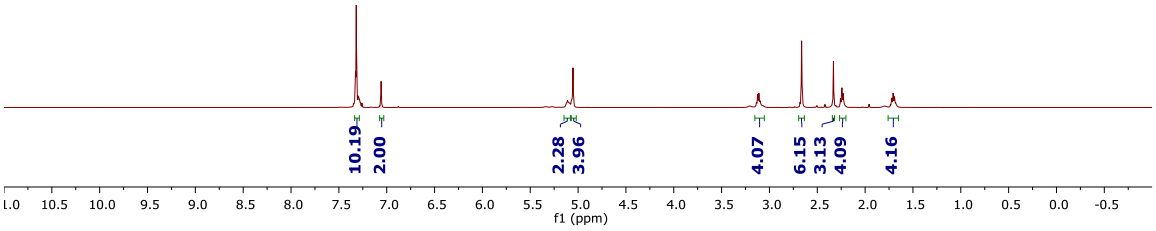


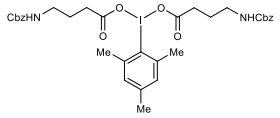
^{13}C NMR (125 MHz, $CDCl_3$)



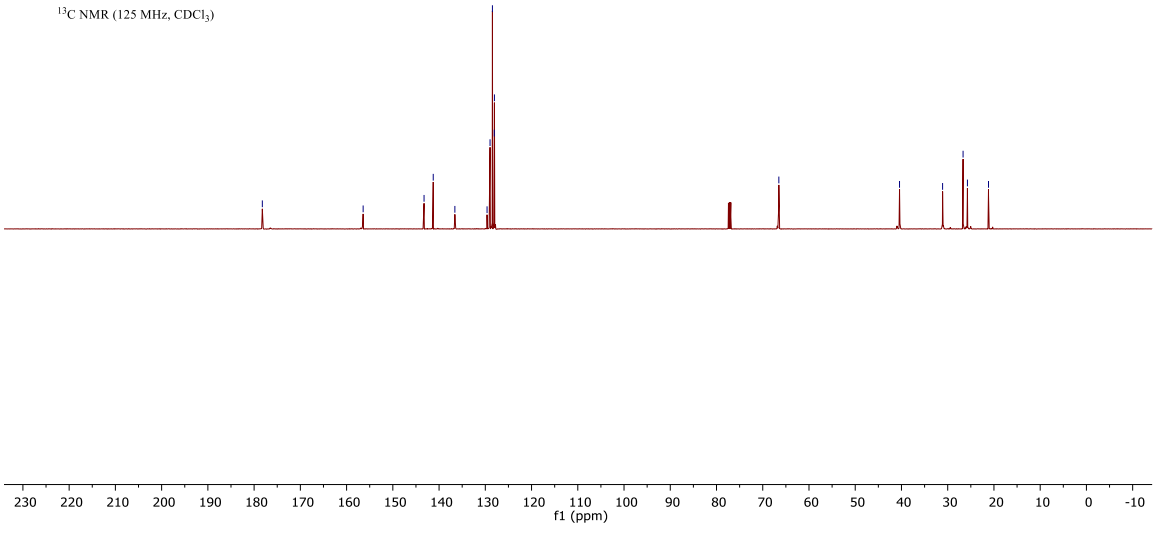


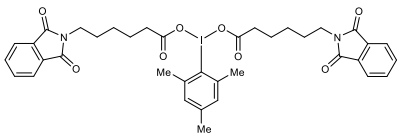
^{1}H NMR (500 MHz, $CDCl_3$)



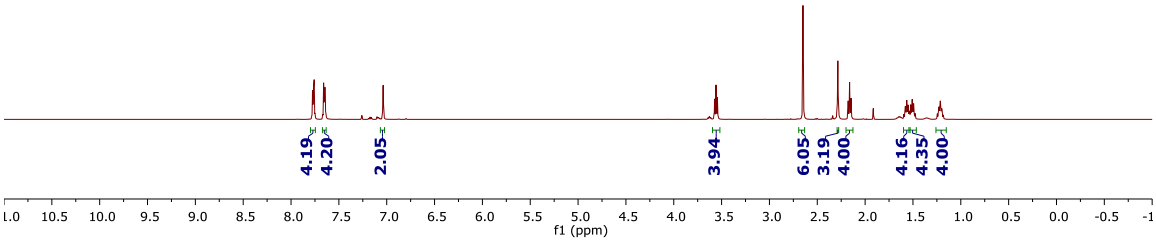


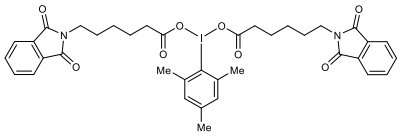
^{13}C NMR (125 MHz, $CDCl_3$)



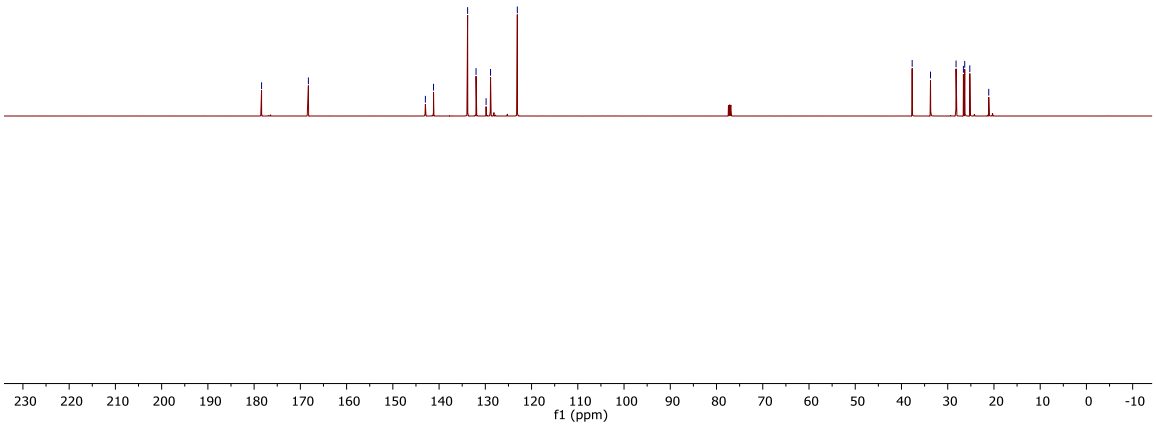


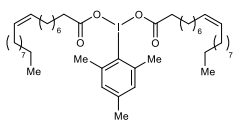
^{1}H NMR (500 MHz, $CDCl_3$)



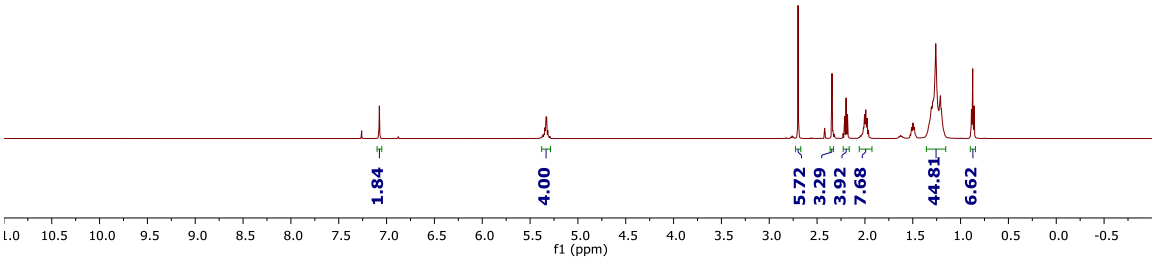


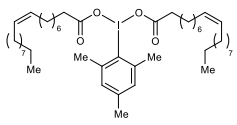
^{13}C NMR (125 MHz, $CDCl_3$)



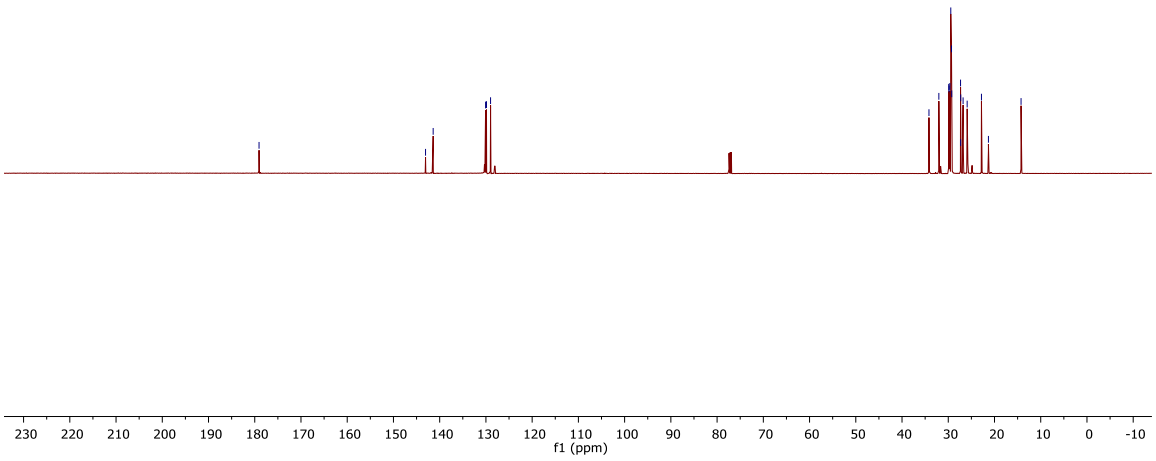


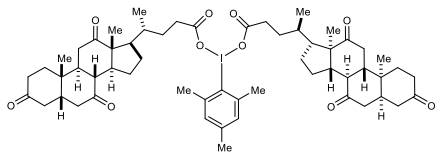
^{1}H NMR (500 MHz, $CDCl_3$)



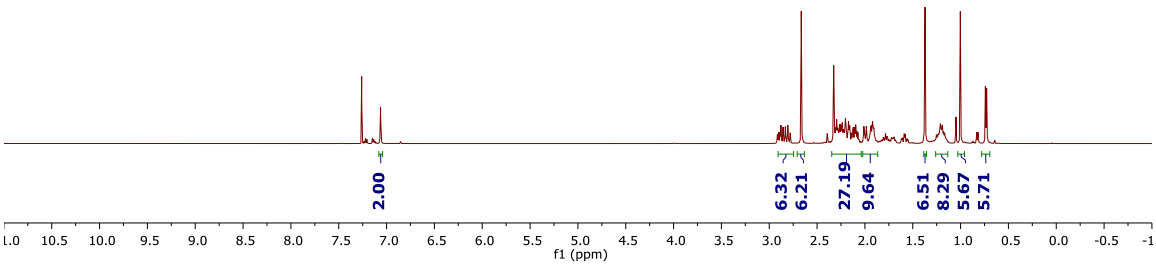


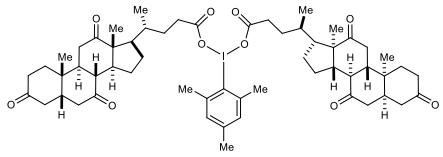
^{13}C NMR (125 MHz, $CDCl_3$)



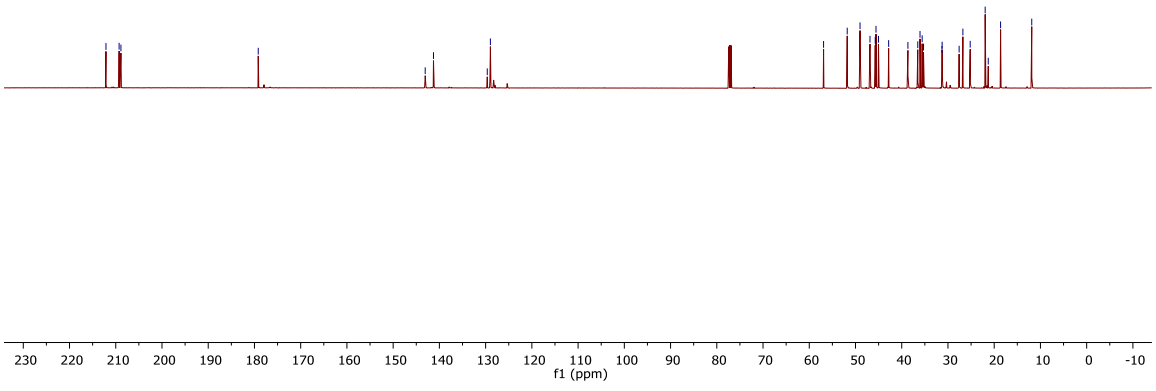


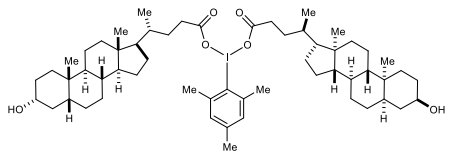
^{1}H NMR (500 MHz, $CDCl_3$)



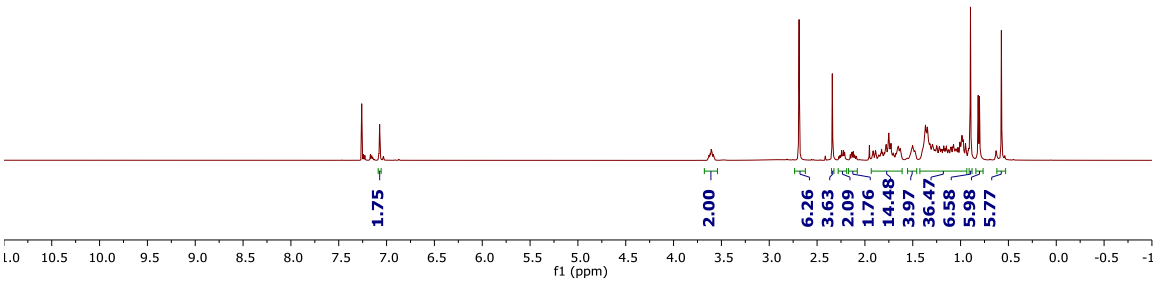


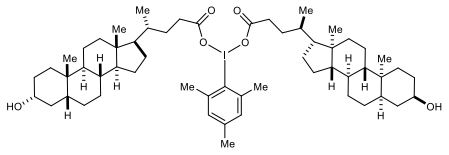
^{13}C NMR (125 MHz, $CDCl_3$)



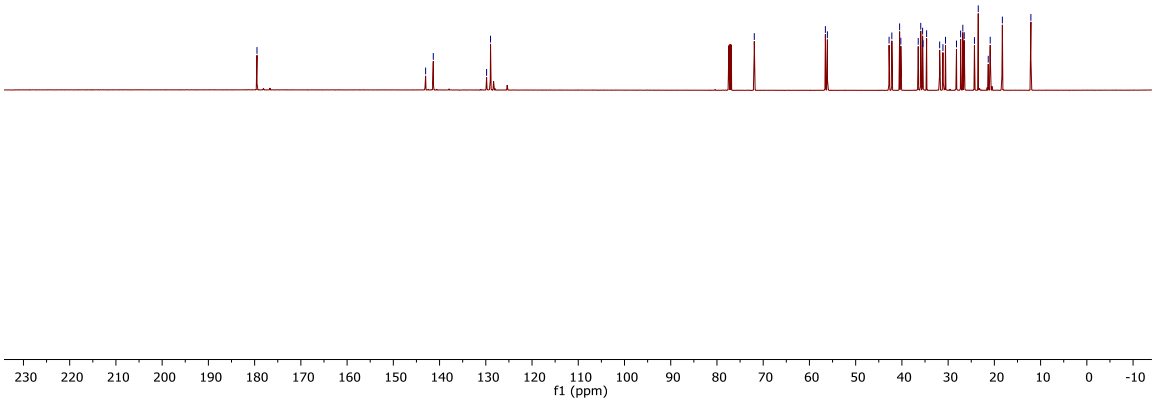


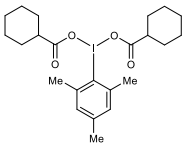
^{1}H NMR (500 MHz, $CDCl_3$)



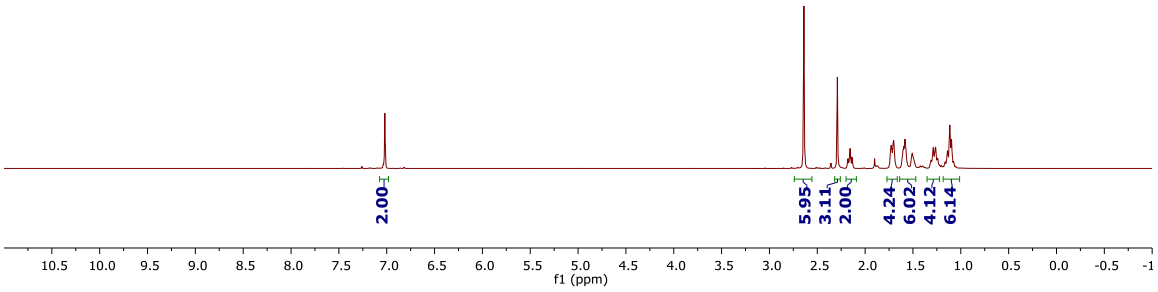


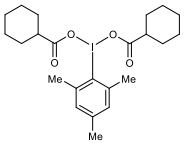
^{13}C NMR (125 MHz, $CDCl_3$)



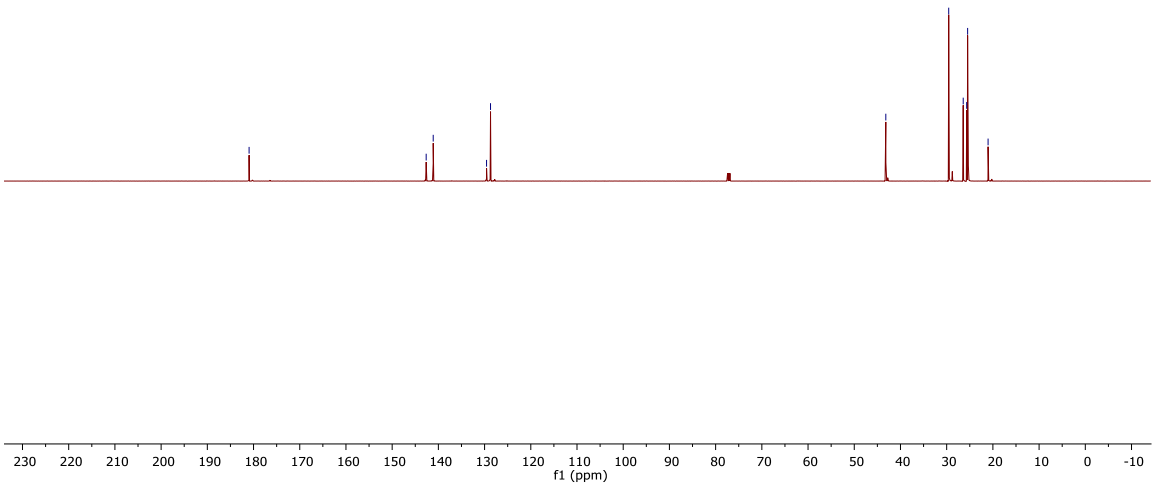


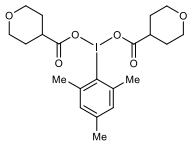
^{1}H NMR (500 MHz, $CDCl_3$)



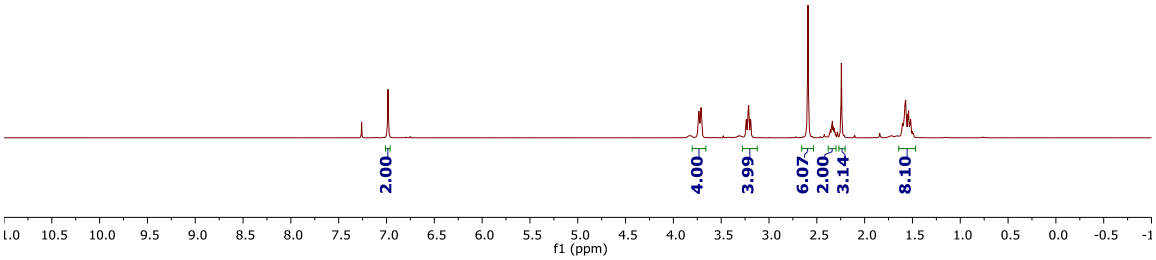


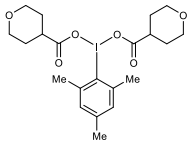
^{13}C NMR (125 MHz, $CDCl_3$)



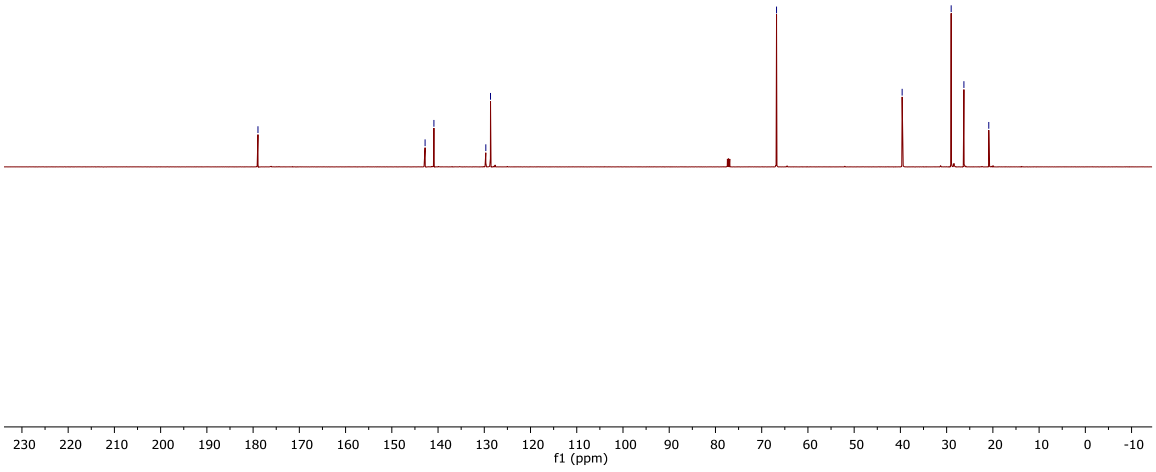


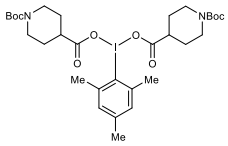
^{1}H NMR (500 MHz, $CDCl_3$)



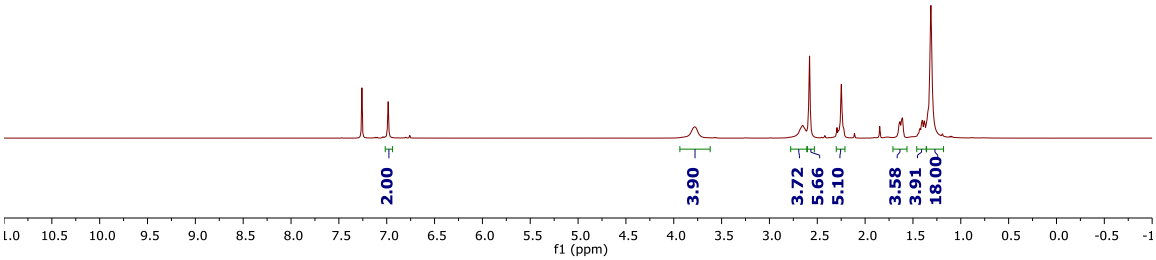


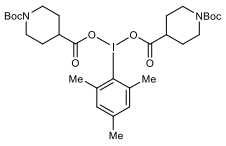
^{13}C NMR (125 MHz, $CDCl_3$)



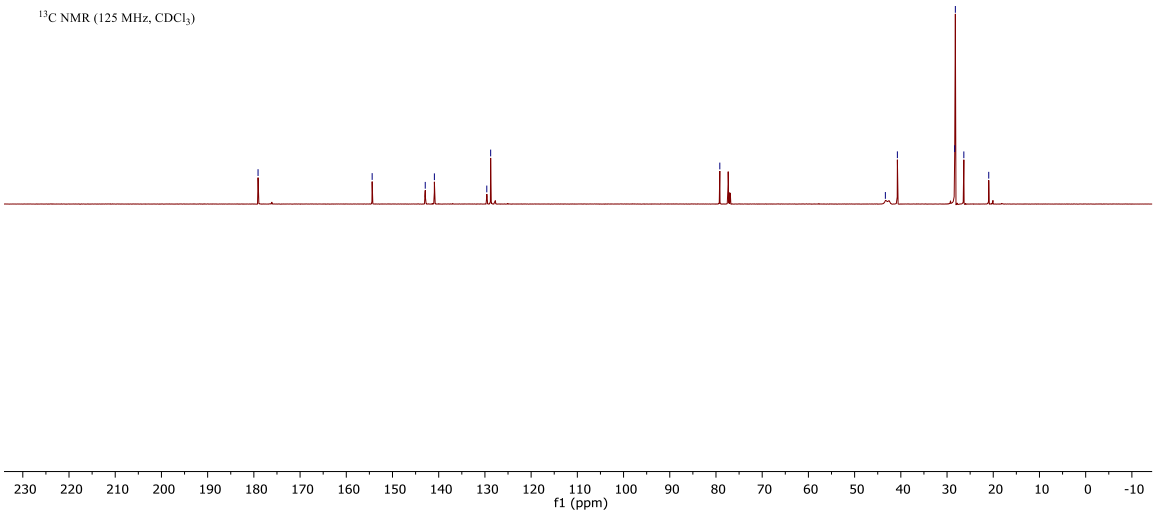


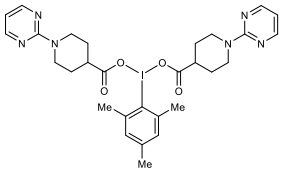
^{1}H NMR (500 MHz, $CDCl_3$)



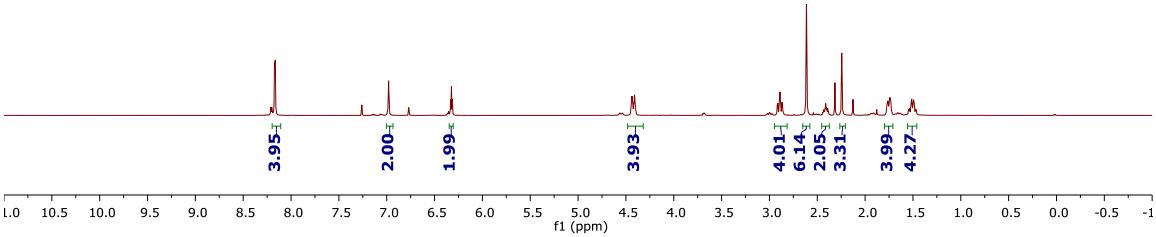


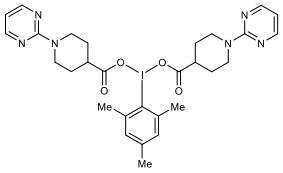
^{13}C NMR (125 MHz, $CDCl_3$)



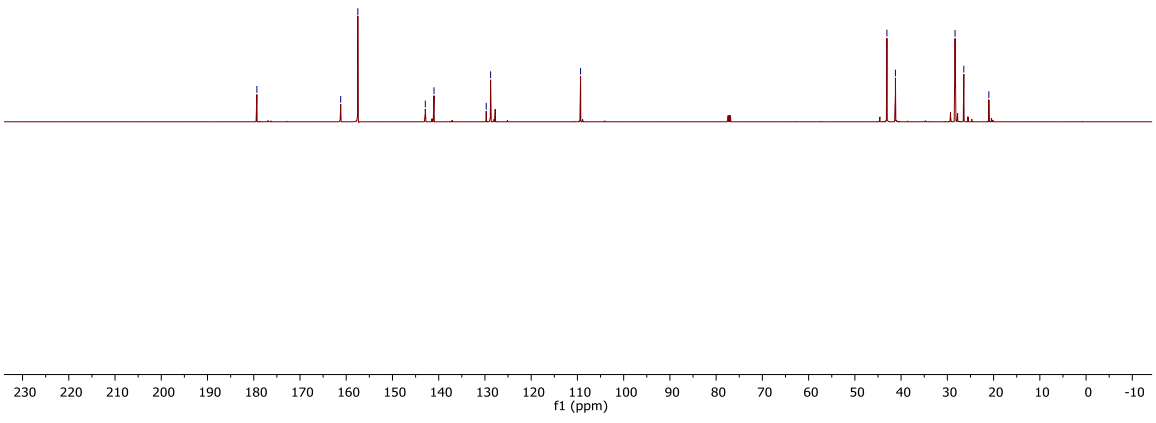


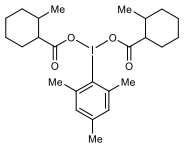
^{1}H NMR (500 MHz, $CDCl_3$)



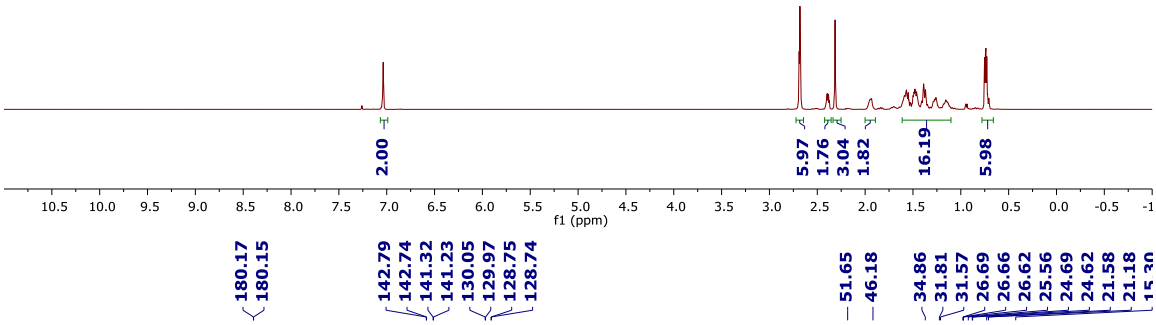


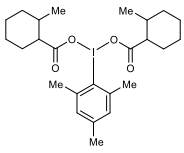
^{13}C NMR (125 MHz, $CDCl_3$)



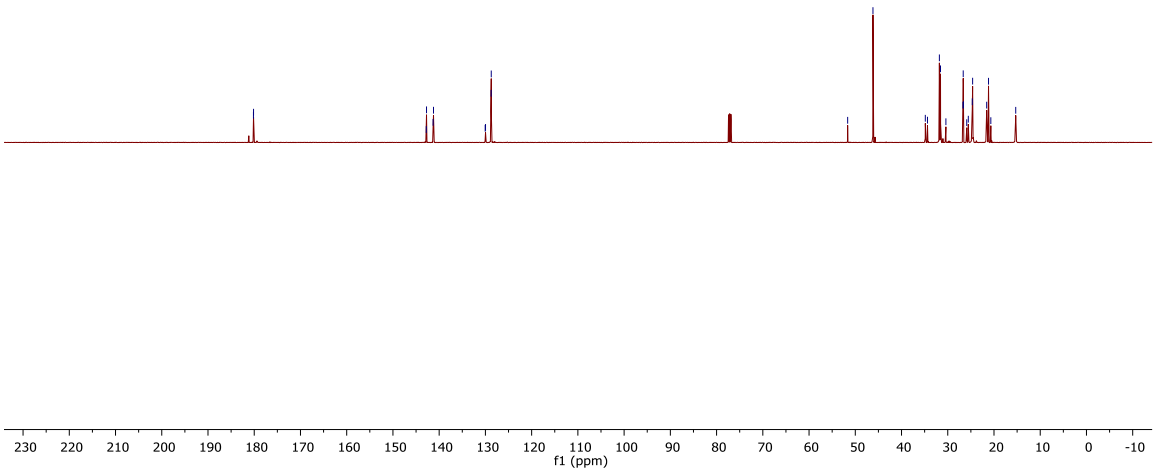


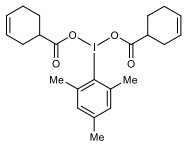
^{1}H NMR (500 MHz, $CDCl_3$)



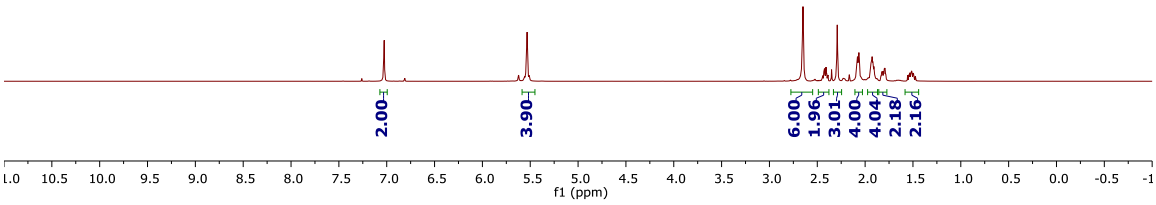


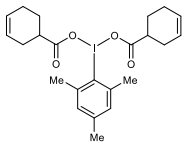
^{13}C NMR (125 MHz, $CDCl_3$)



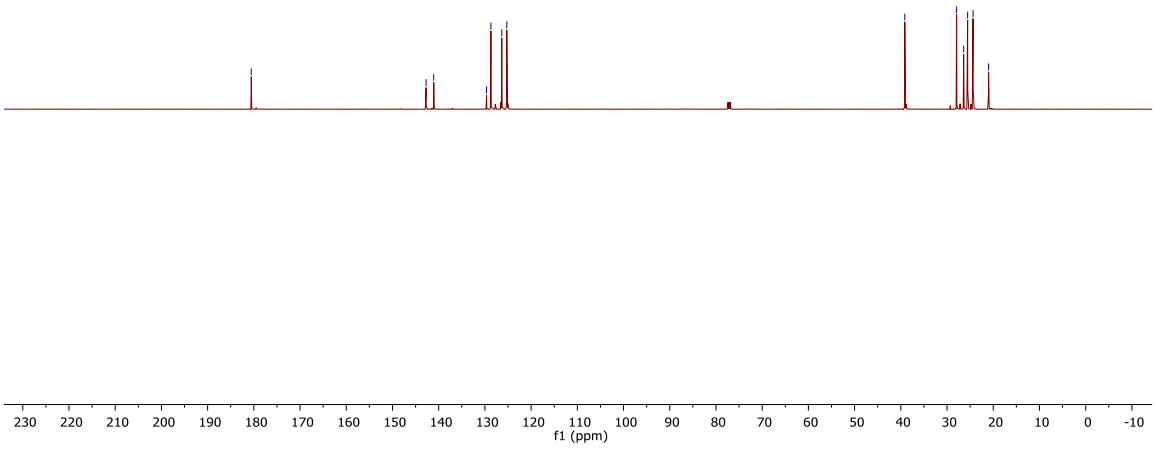


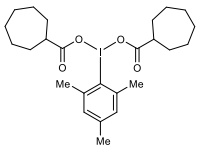
^{1}H NMR (500 MHz, $CDCl_3$)



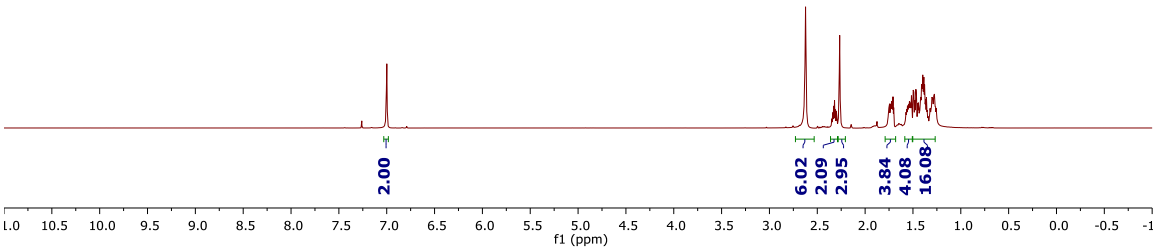


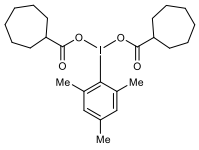
^{13}C NMR (125 MHz, $CDCl_3$)



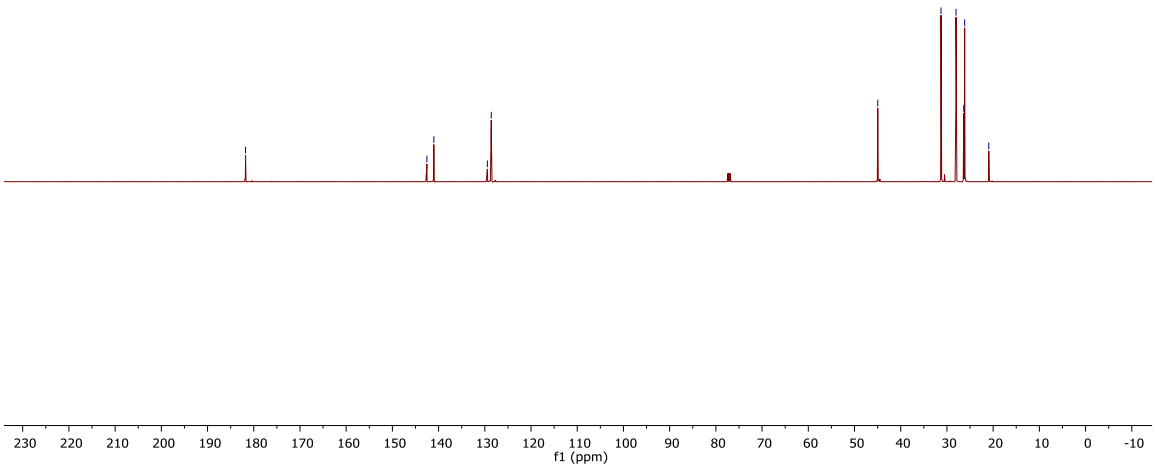


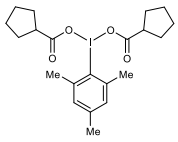
^{1}H NMR (500 MHz, $CDCl_3$)



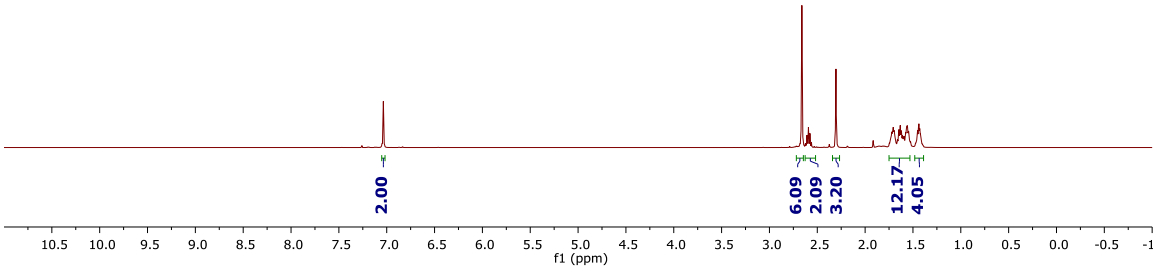


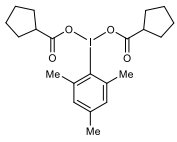
^{13}C NMR (125 MHz, $CDCl_3$)



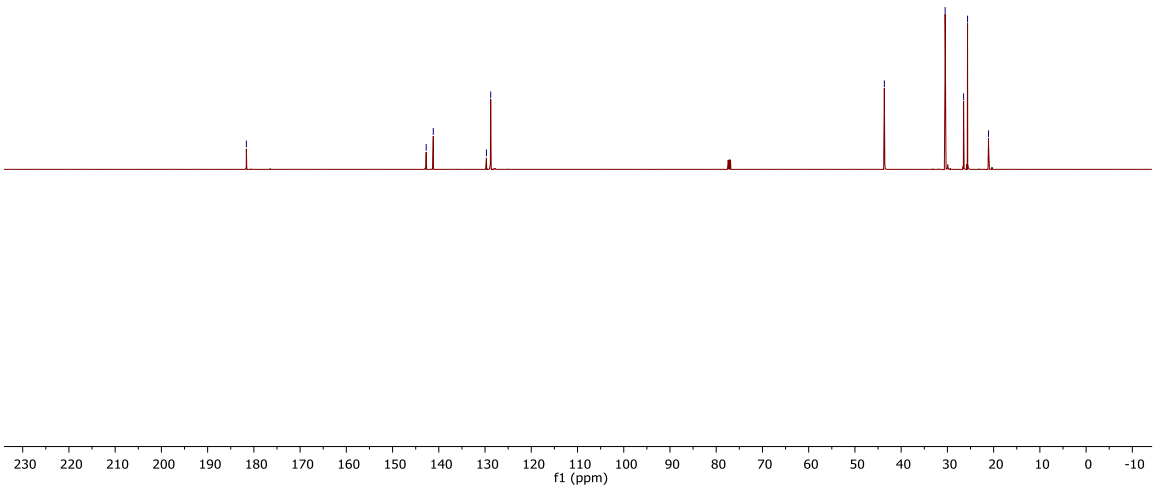


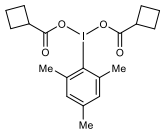
^{1}H NMR (500 MHz, $CDCl_3$)



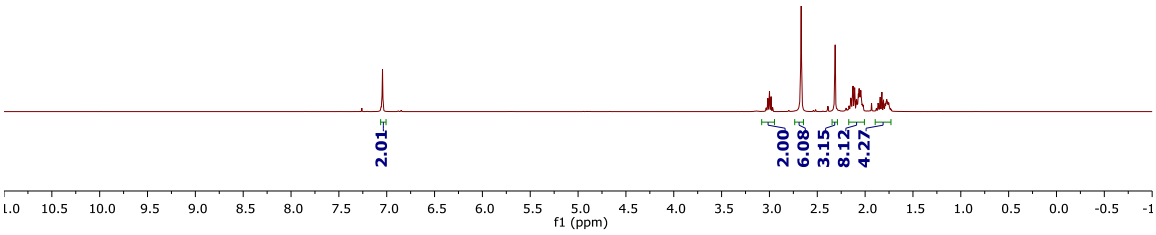


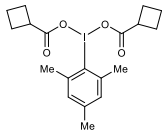
^{13}C NMR (125 MHz, $CDCl_3$)



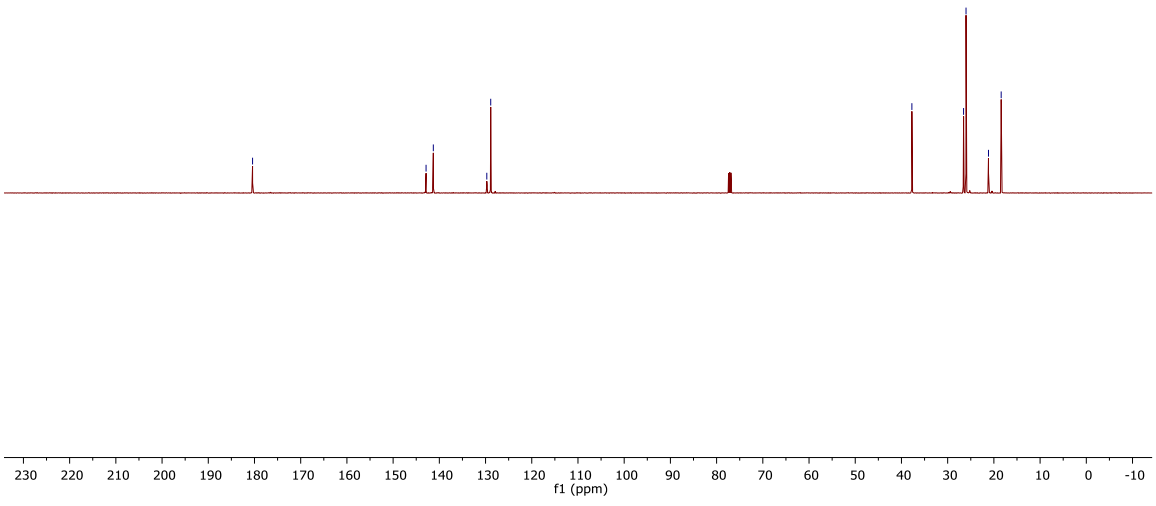


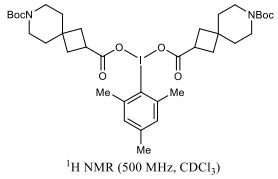
^{1}H NMR (500 MHz, $CDCl_3$)



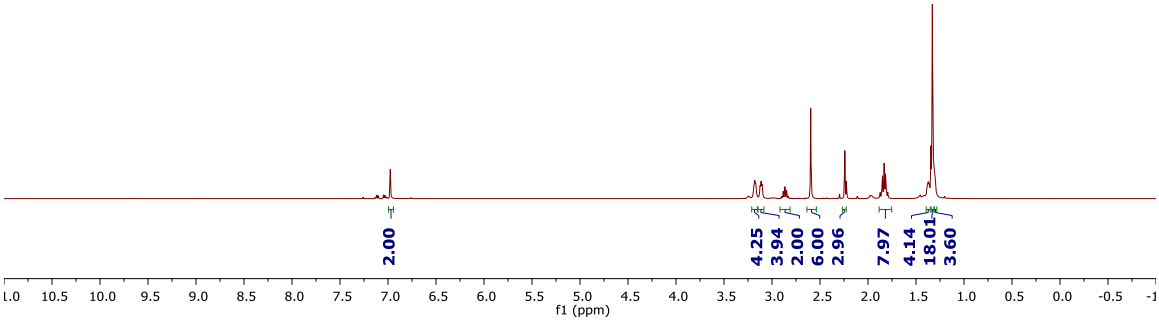


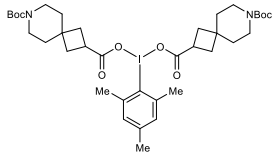
^{13}C NMR (125 MHz, $CDCl_3$)



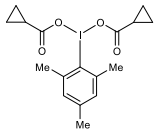


^{1}H NMR (500 MHz, $CDCl_3$)

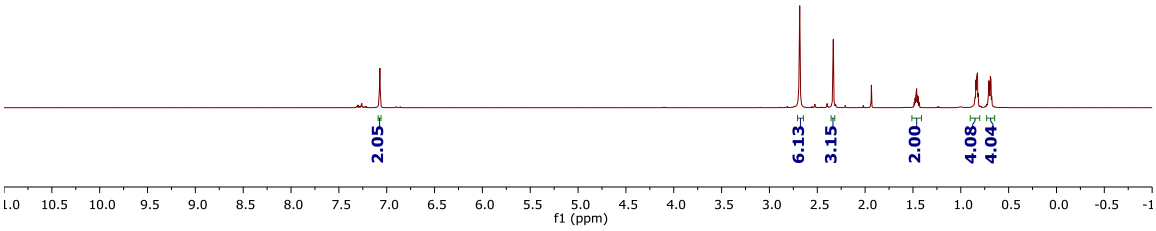


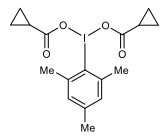


^{13}C NMR (125 MHz, $CDCl_3$)

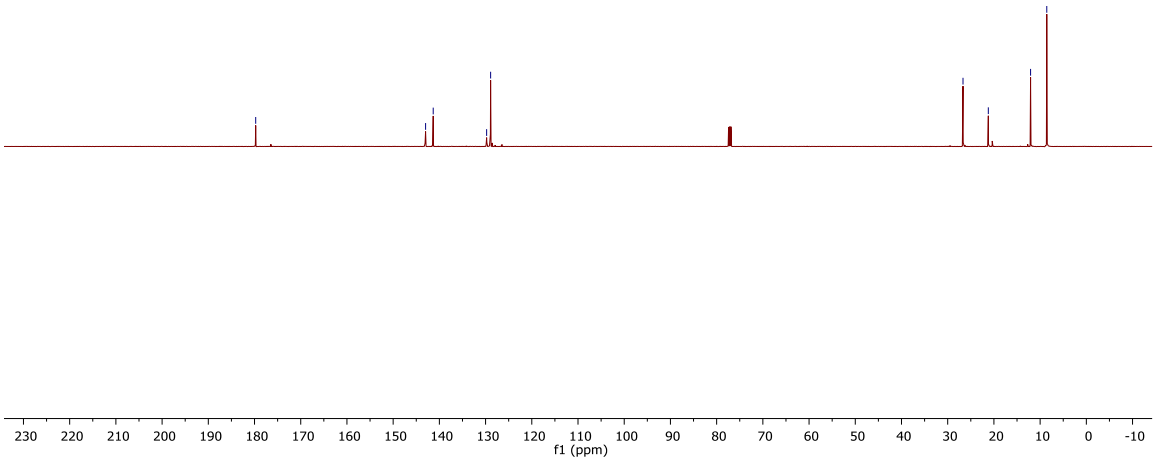


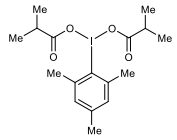
^{1}H NMR (500 MHz, $CDCl_3$)



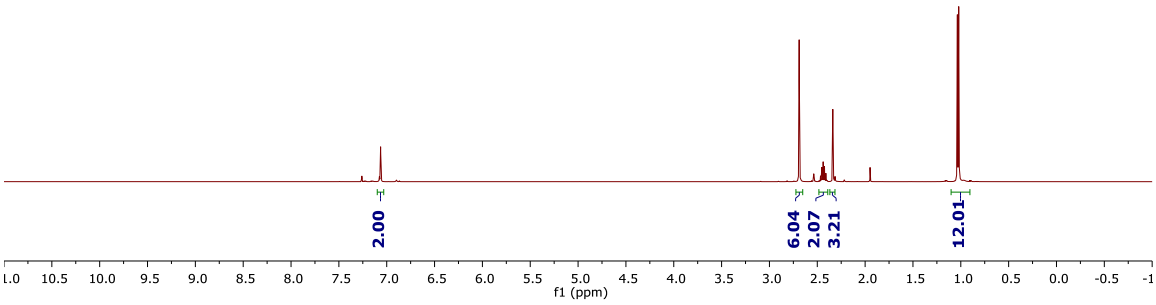


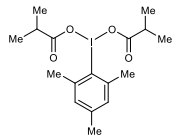
^{13}C NMR (125 MHz, $CDCl_3$)



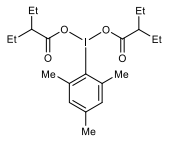


^{1}H NMR (500 MHz, $CDCl_3$)

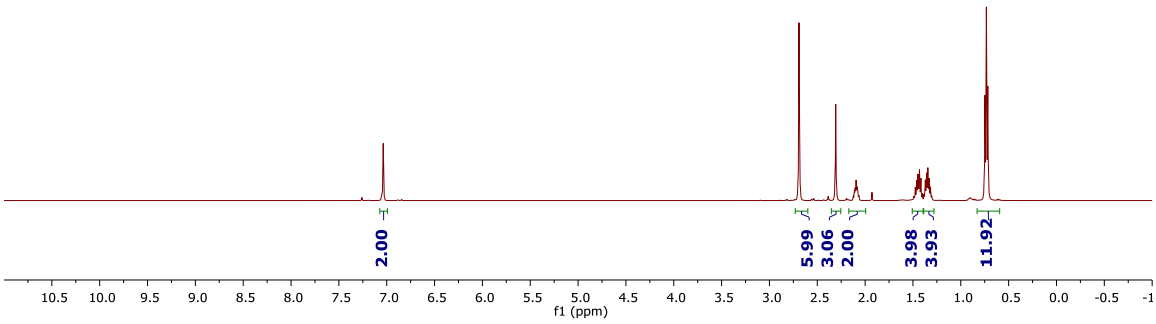


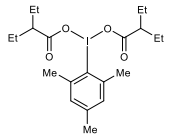


^{13}C NMR (125 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)





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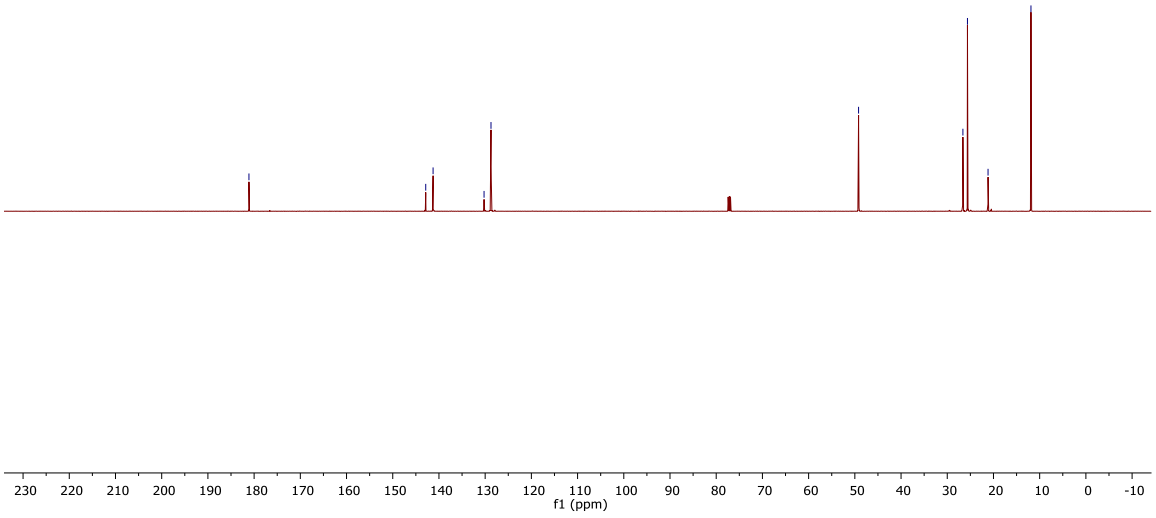
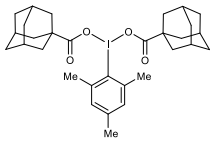
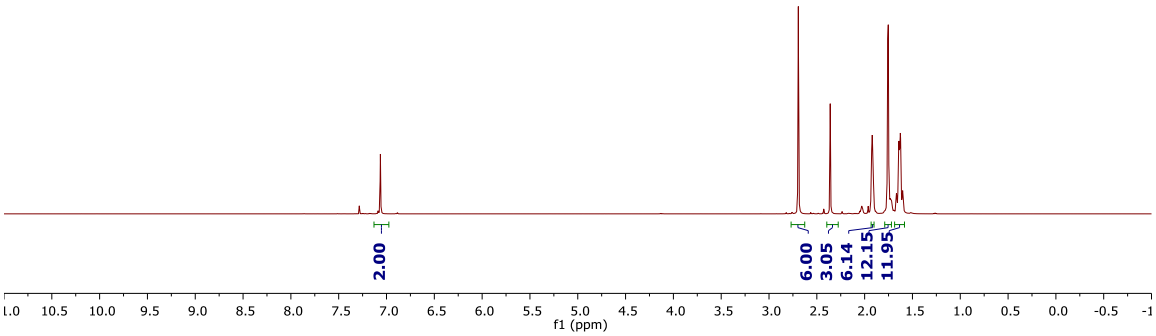
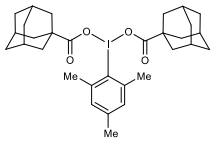


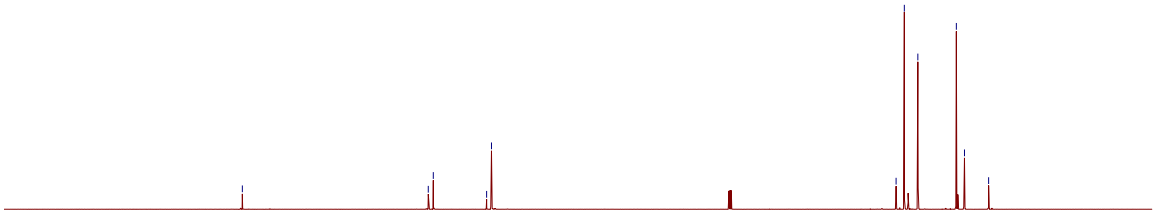


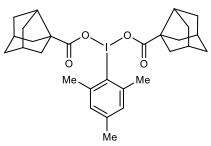
^{1}H NMR (500 MHz, $CDCl_3$)



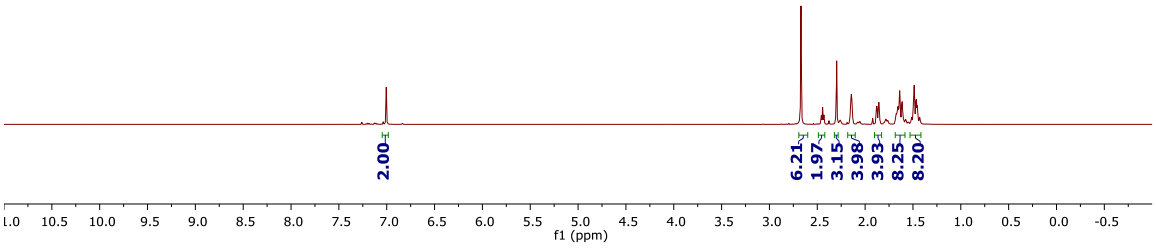


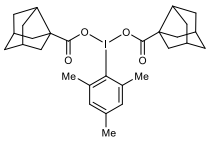
^{13}C NMR (125 MHz, $CDCl_3$)



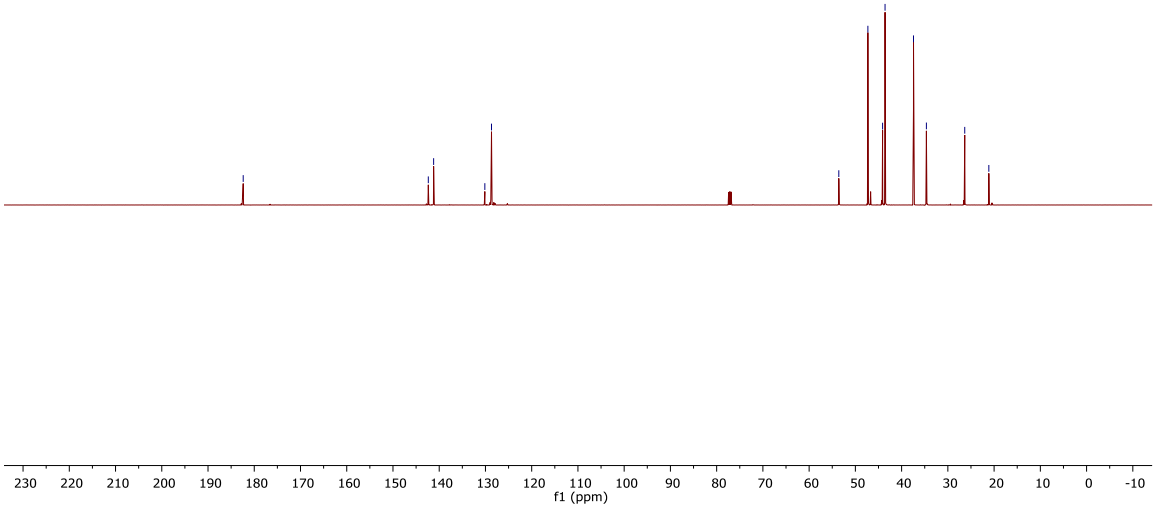


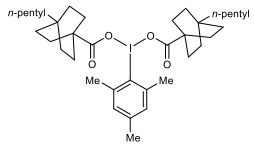
^{1}H NMR (500 MHz, $CDCl_3$)



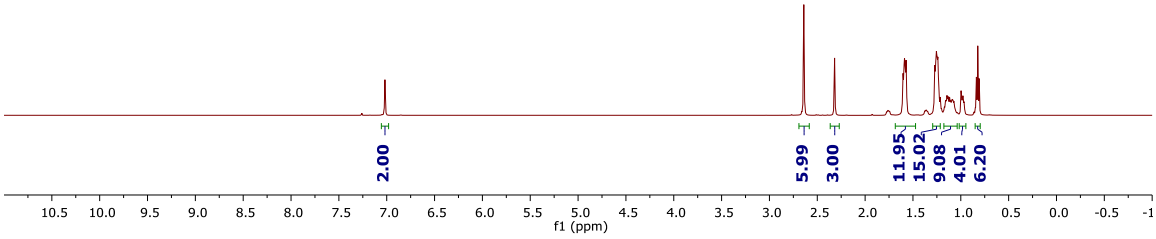


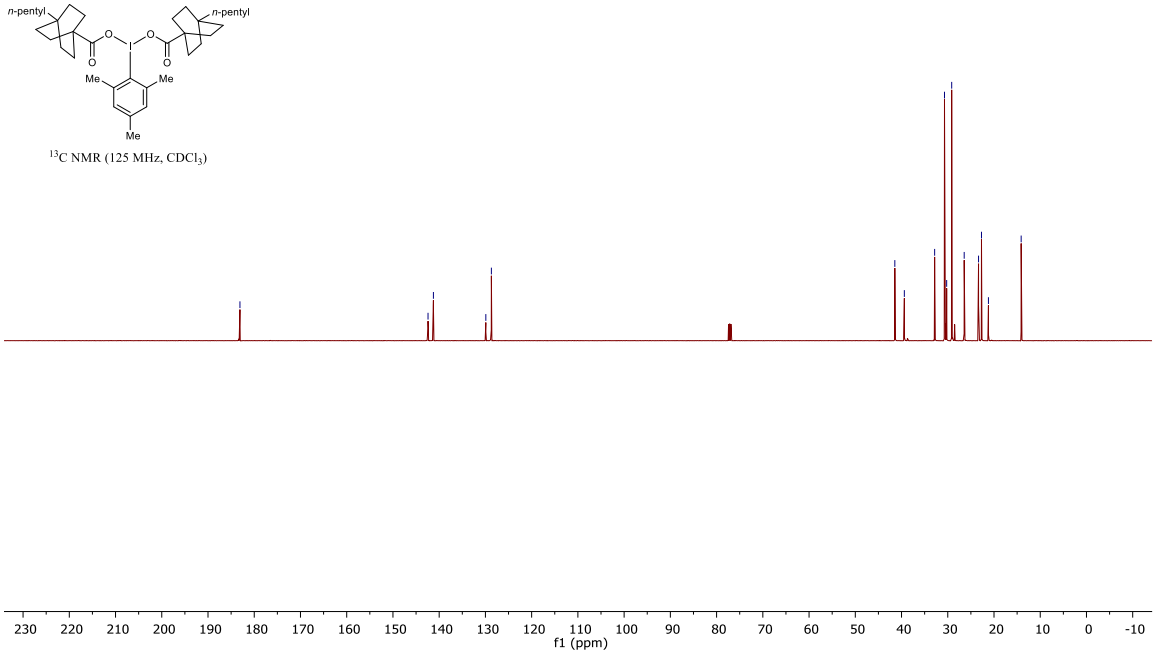
^{13}C NMR (125 MHz, $CDCl_3$)



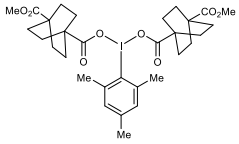


^{1}H NMR (500 MHz, $CDCl_3$)

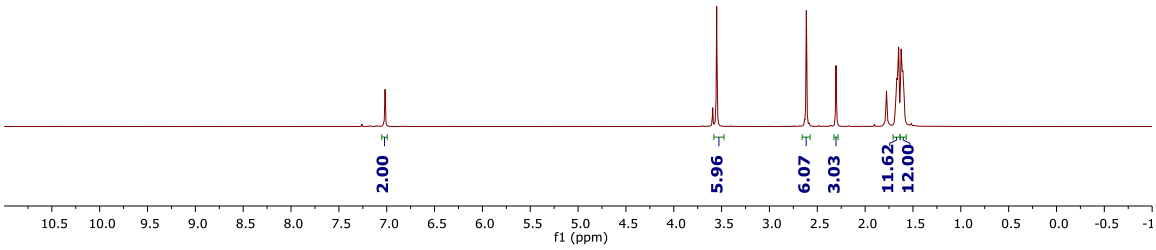


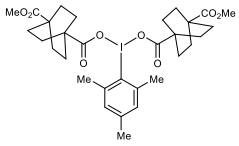


^{13}C NMR (125 MHz, $CDCl_3$)

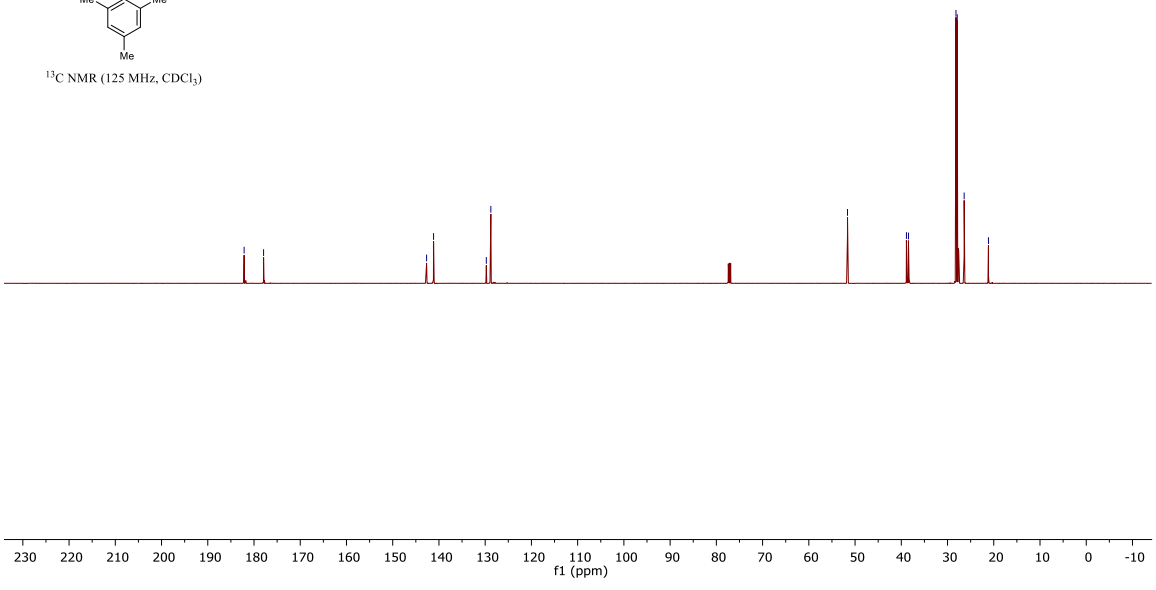


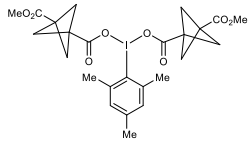
^{1}H NMR (500 MHz, $CDCl_3$)



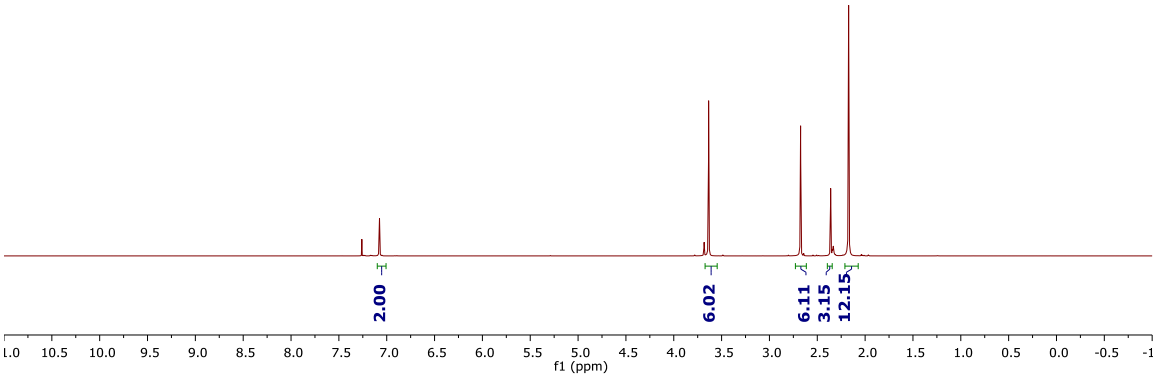


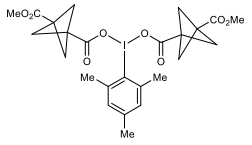
^{13}C NMR (125 MHz, $CDCl_3$)



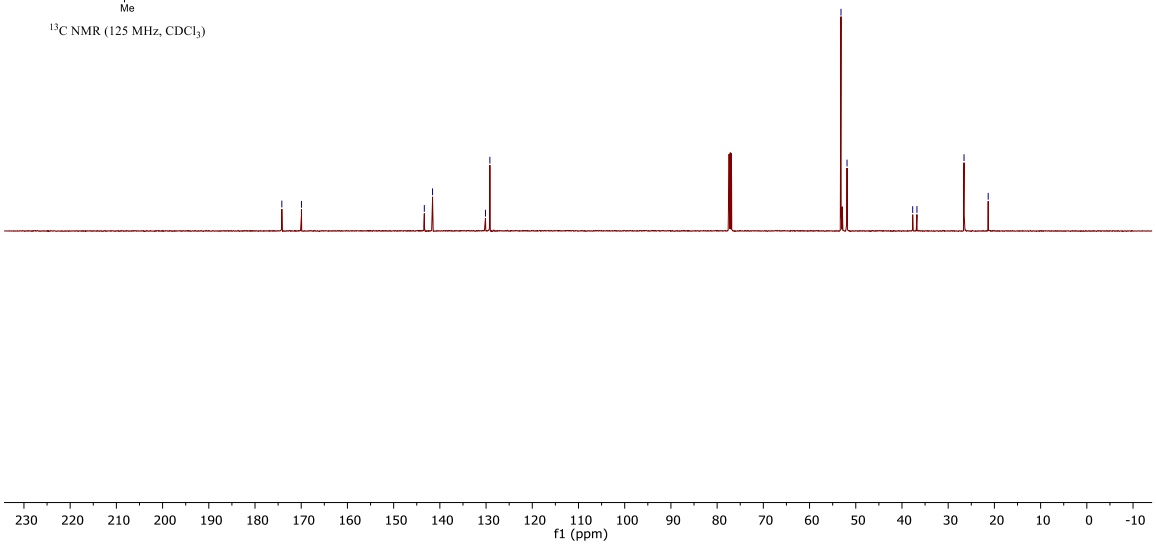


^{1}H NMR (500 MHz, $CDCl_3$)

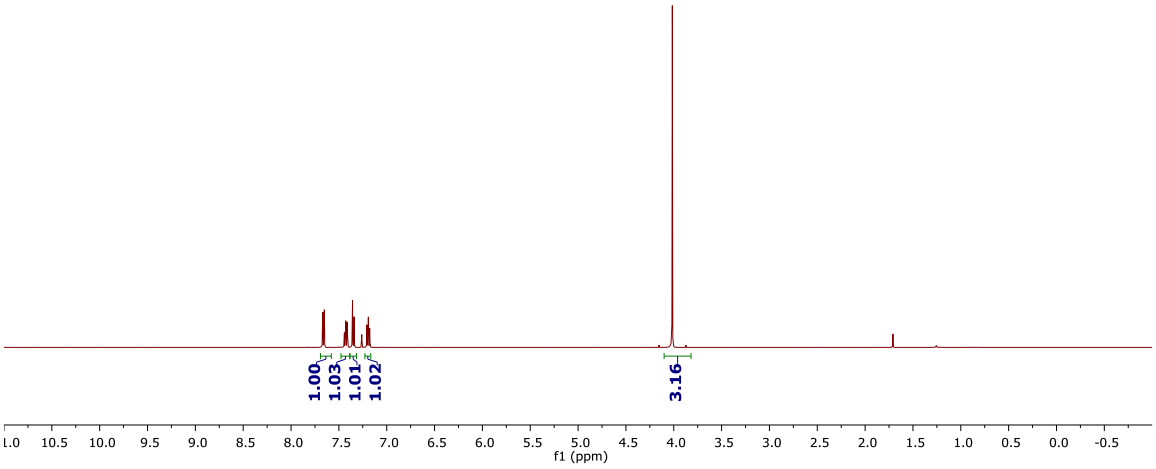




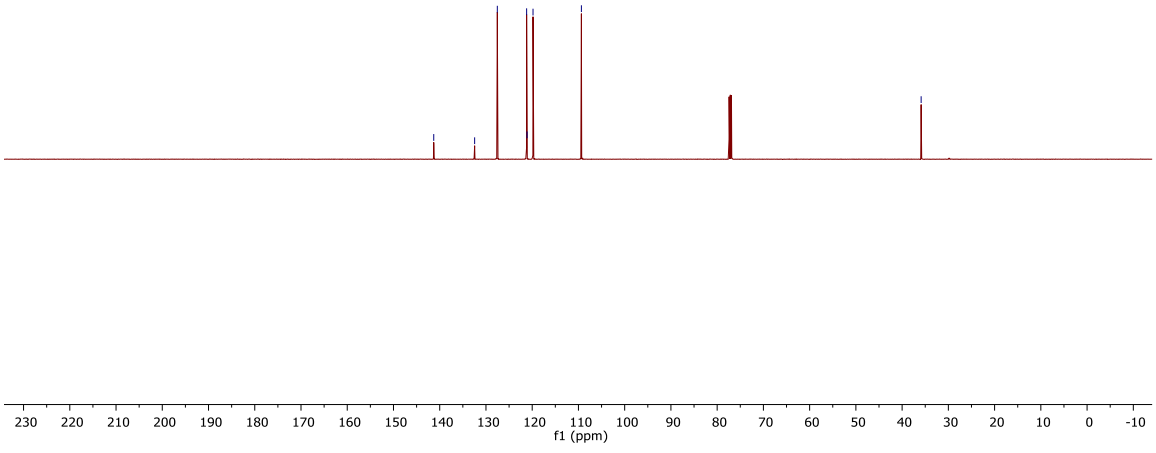
^{13}C NMR (125 MHz, $CDCl_3$)

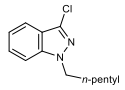


^{1}H NMR (500 MHz, $CDCl_3$)

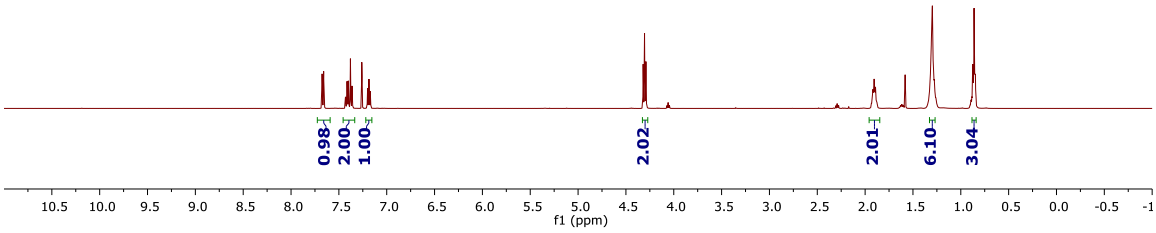


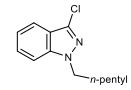
^{13}C NMR (125 MHz, $CDCl_3$)



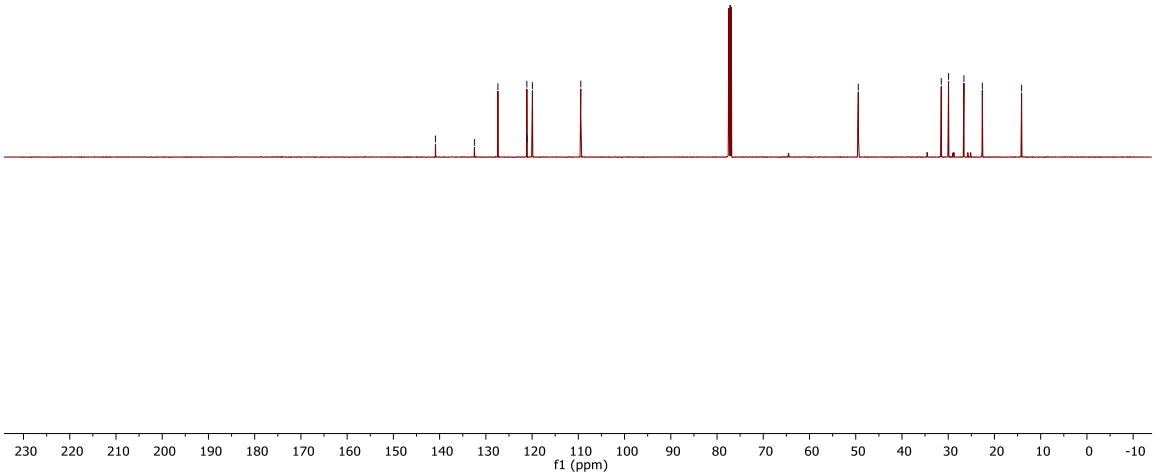


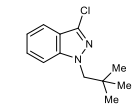
^{1}H NMR (500 MHz, $CDCl_3$)



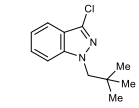


^{13}C NMR (125 MHz, $CDCl_3$)





^{1}H NMR (500 MHz, $CDCl_3$)



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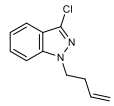

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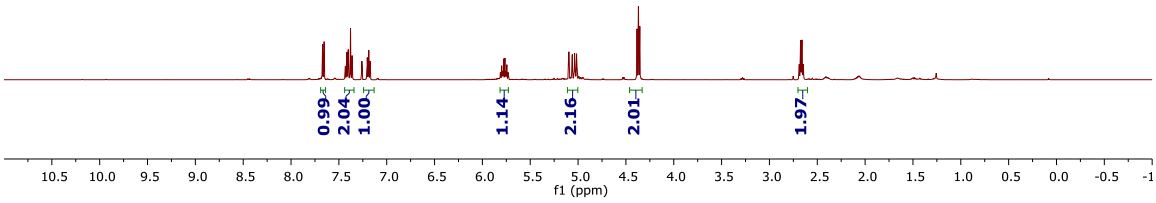
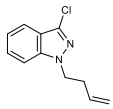
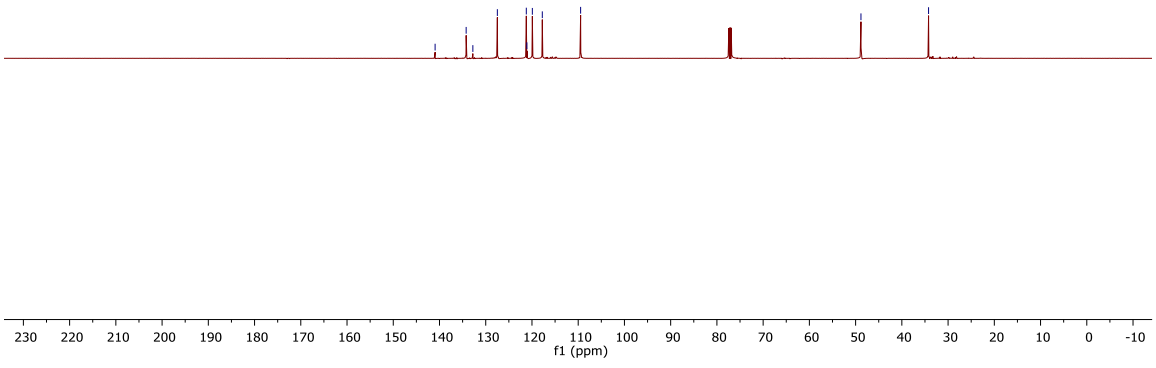
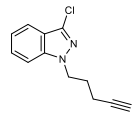




^{13}C NMR (125 MHz, $CDCl_3$)





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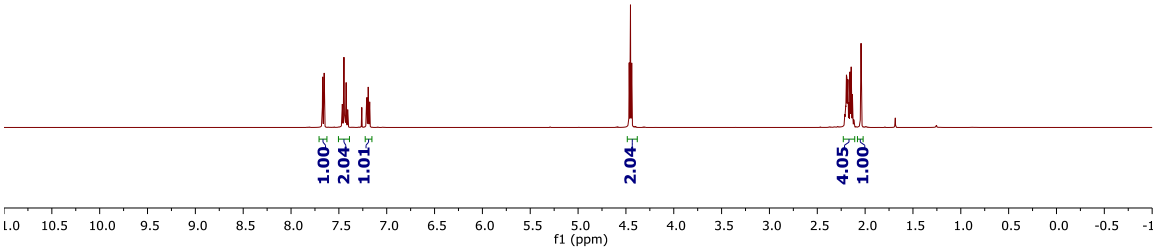
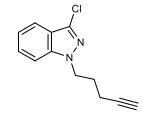
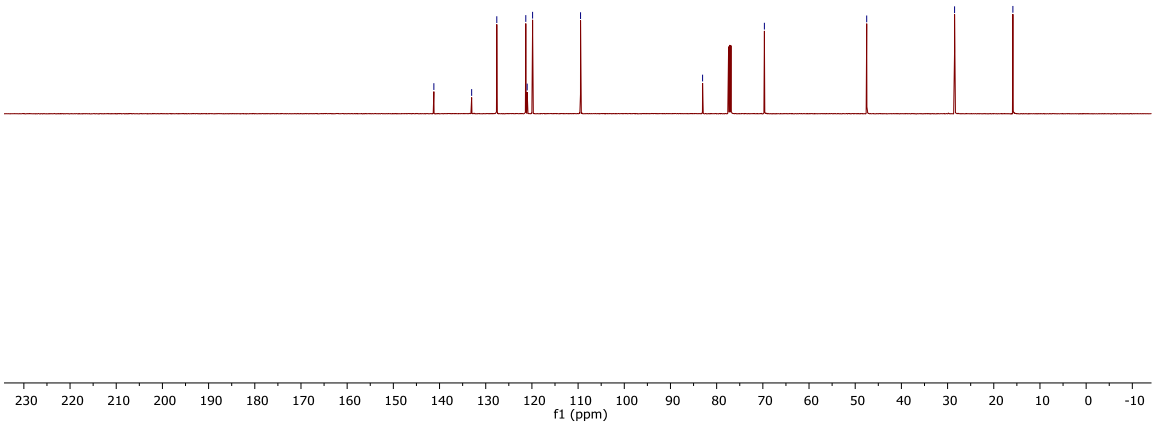
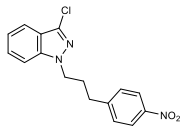




^{13}C NMR (125 MHz, $CDCl_3$)





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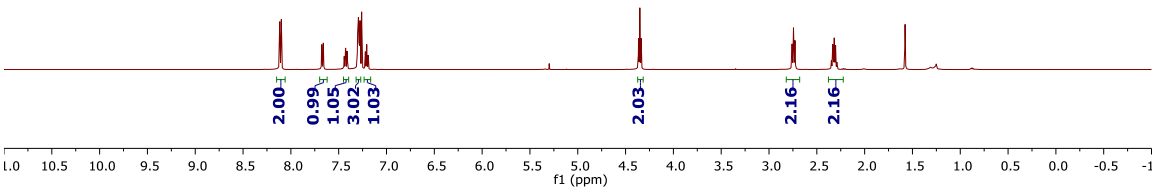
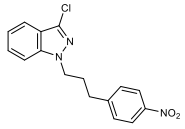
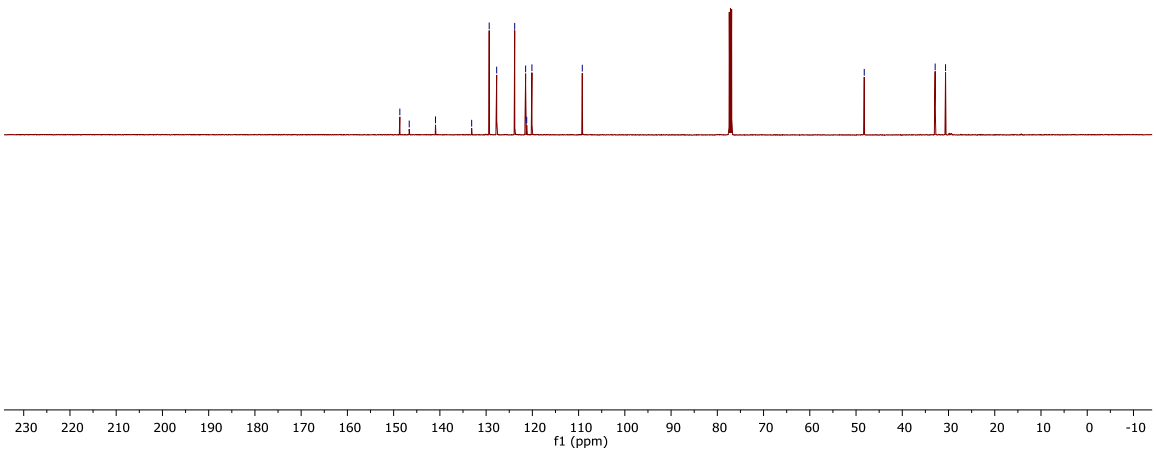
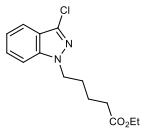




^{13}C NMR (125 MHz, $CDCl_3$)





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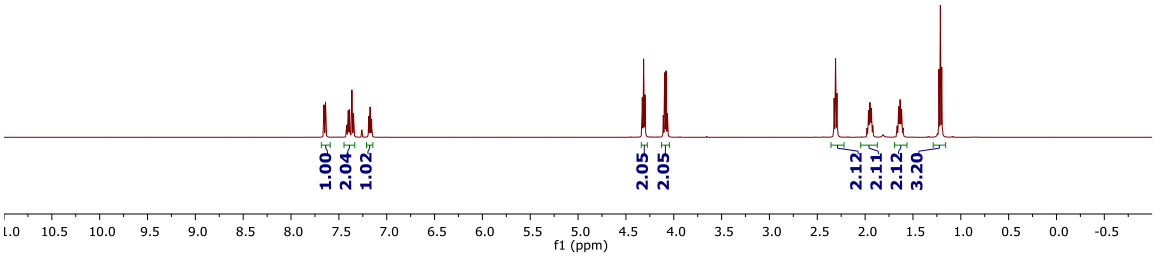
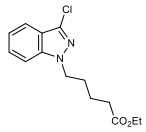
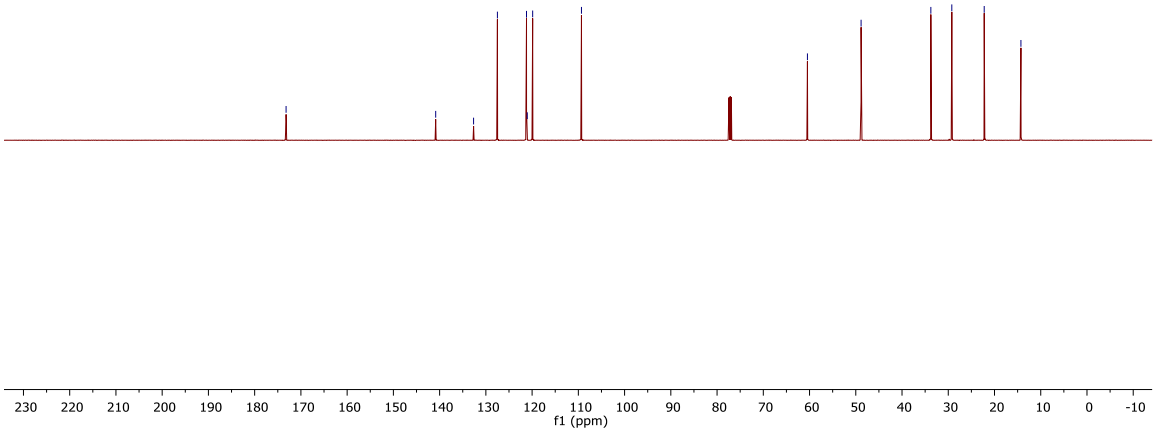
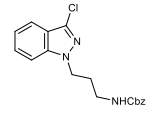


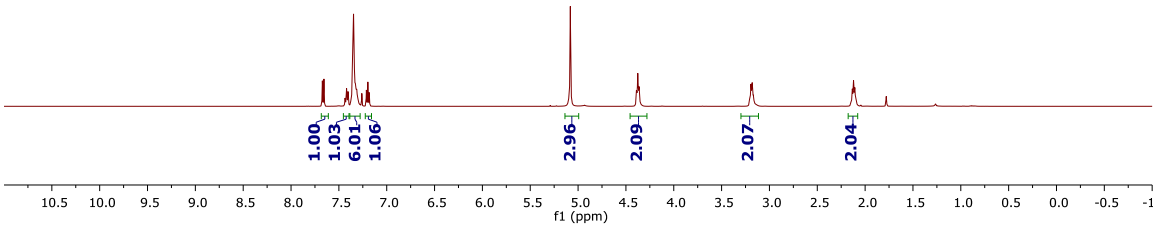


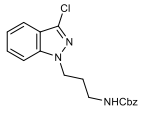
^{13}C NMR (125 MHz, $CDCl_3$)



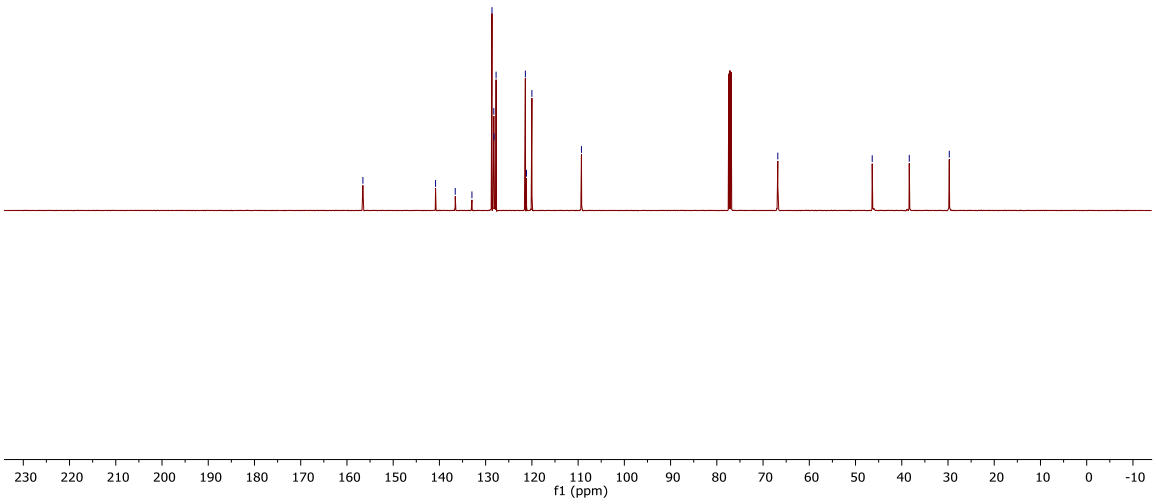


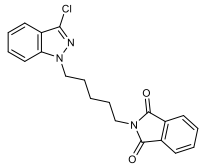
^{1}H NMR (500 MHz, $CDCl_3$)





^{13}C NMR (125 MHz, $CDCl_3$)





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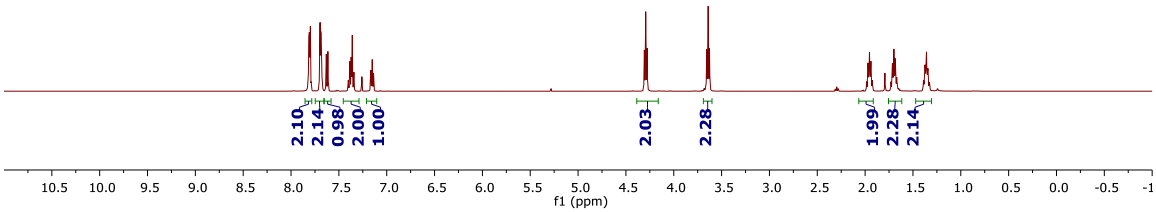
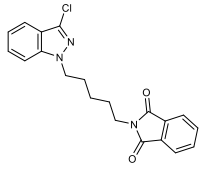
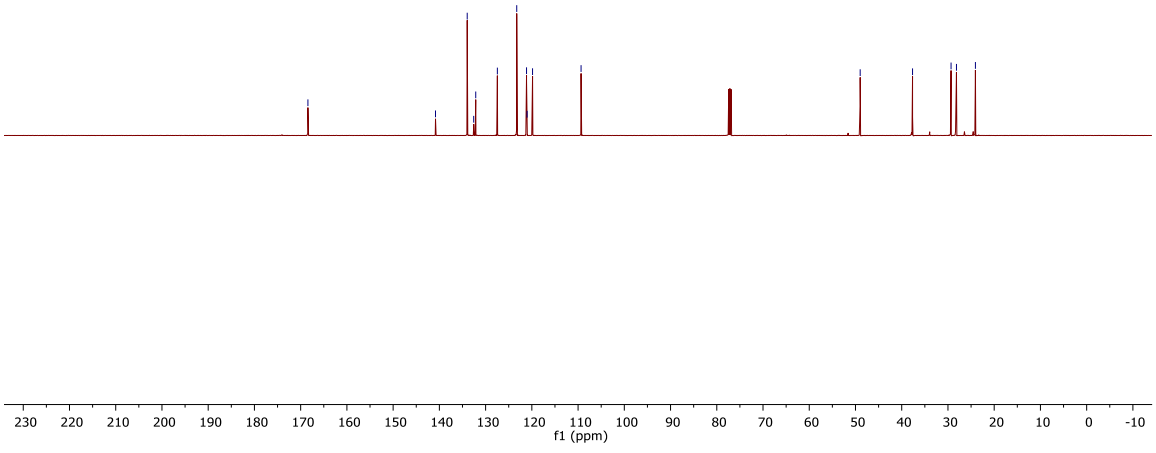
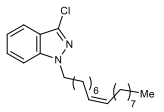


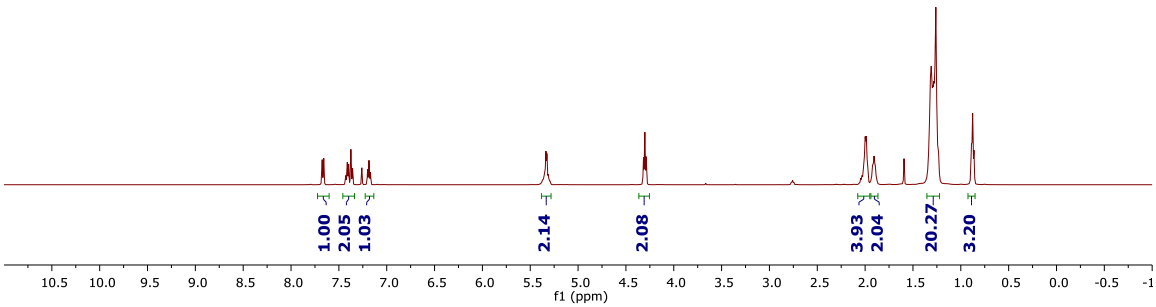


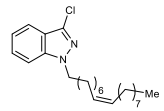
^{13}C NMR (125 MHz, $CDCl_3$)



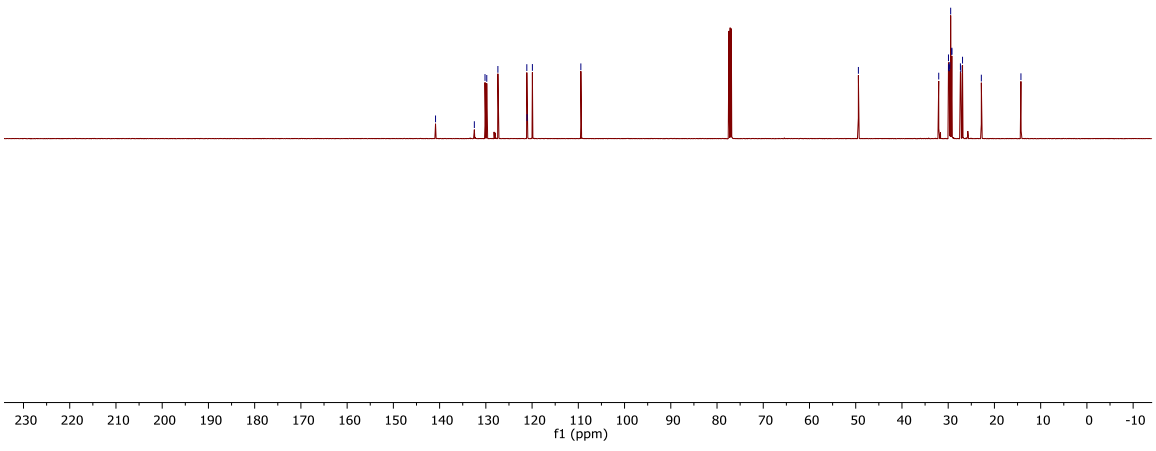


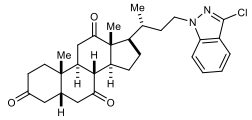
^{1}H NMR (500 MHz, $CDCl_3$)



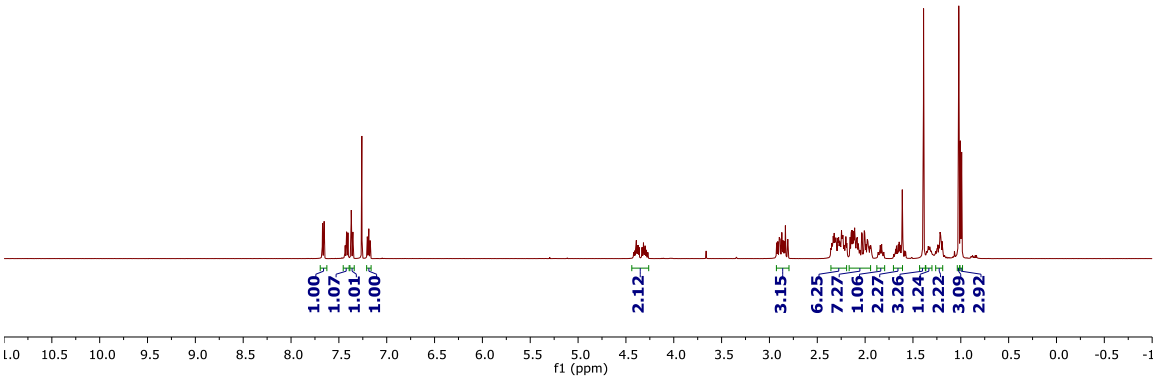


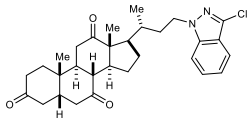
^{13}C NMR (125 MHz, $CDCl_3$)



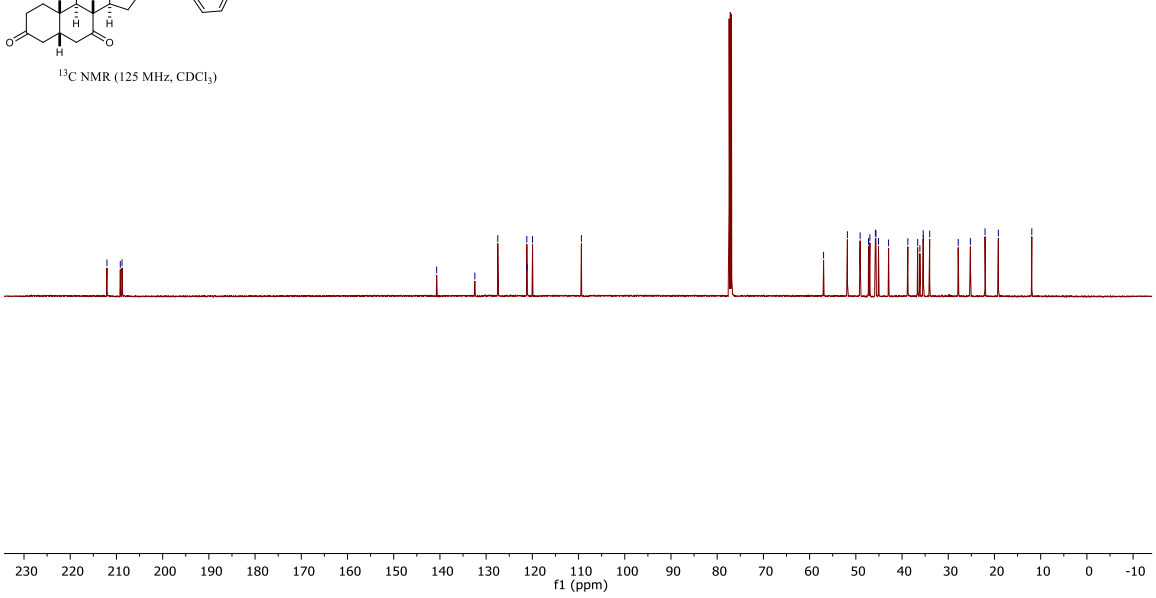


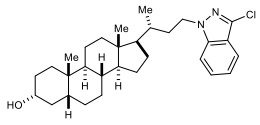
^{1}H NMR (500 MHz, $CDCl_3$)



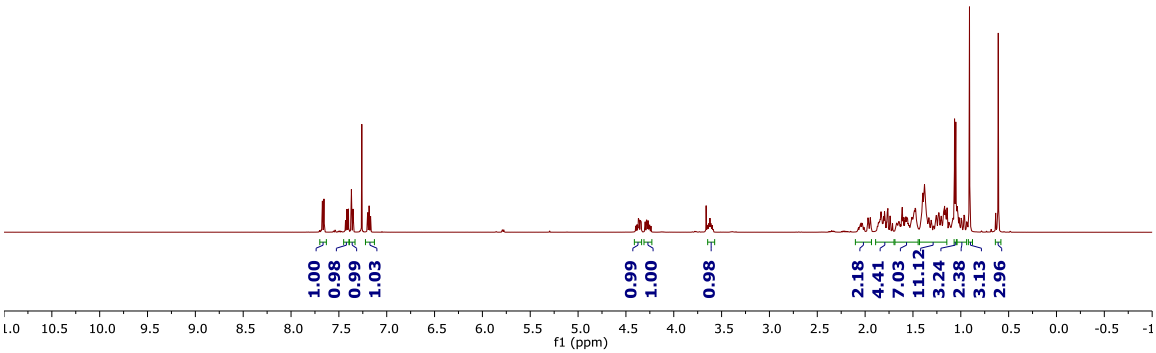


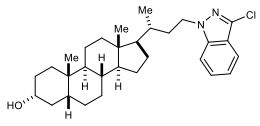
^{13}C NMR (125 MHz, $CDCl_3$)



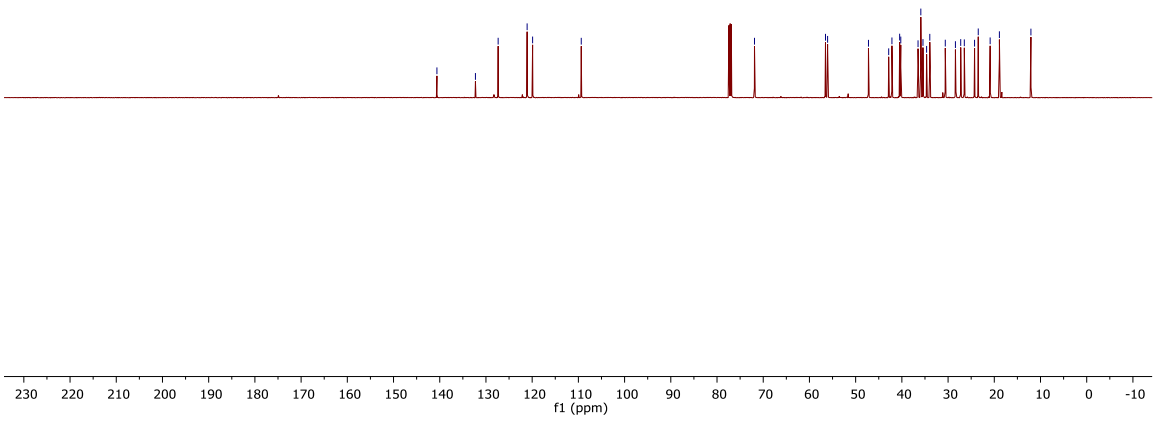


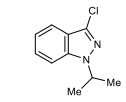
^{1}H NMR (500 MHz, $CDCl_3$)



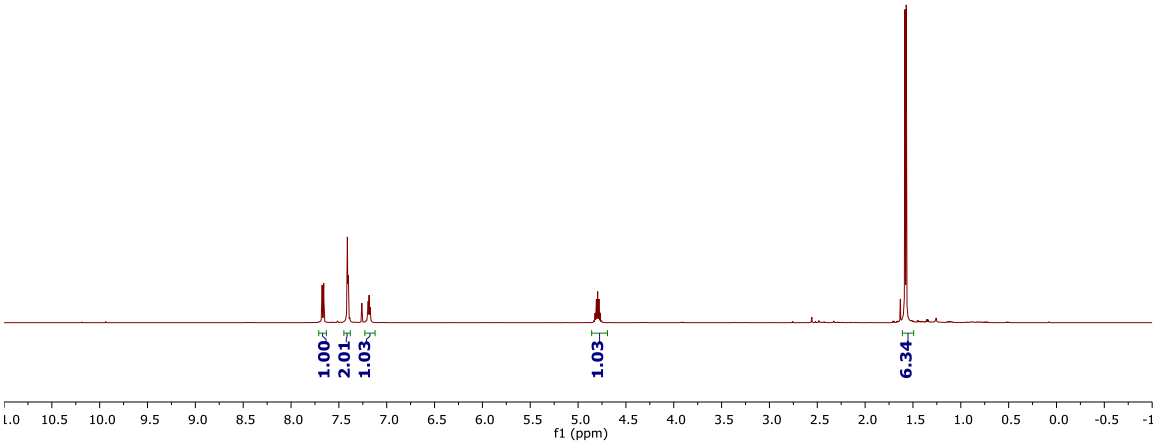


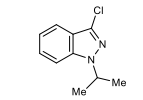
^{13}C NMR (125 MHz, $CDCl_3$)



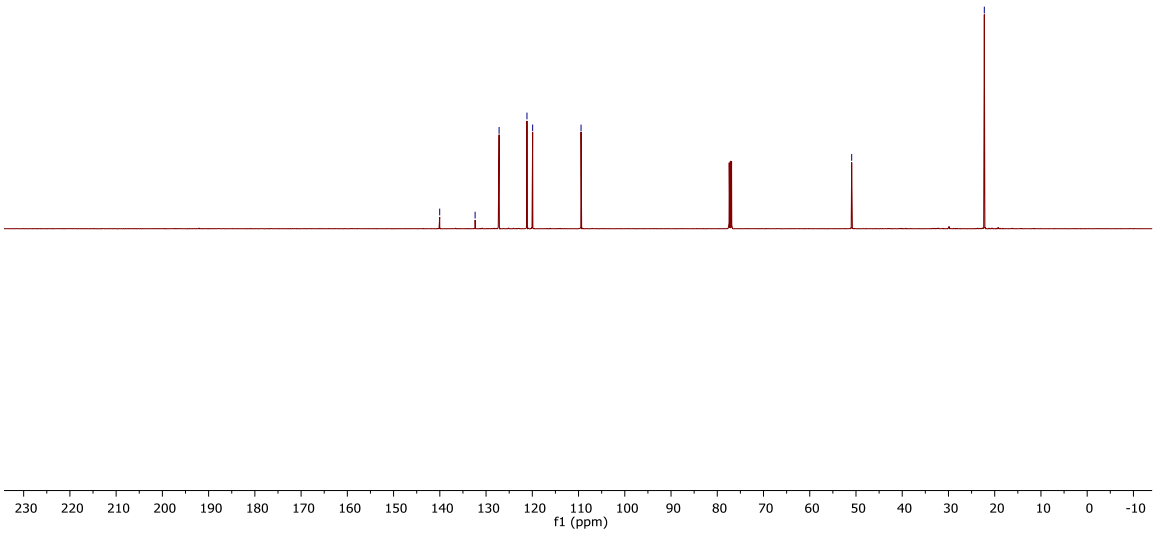


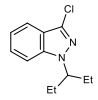
^{1}H NMR (500 MHz, $CDCl_3$)



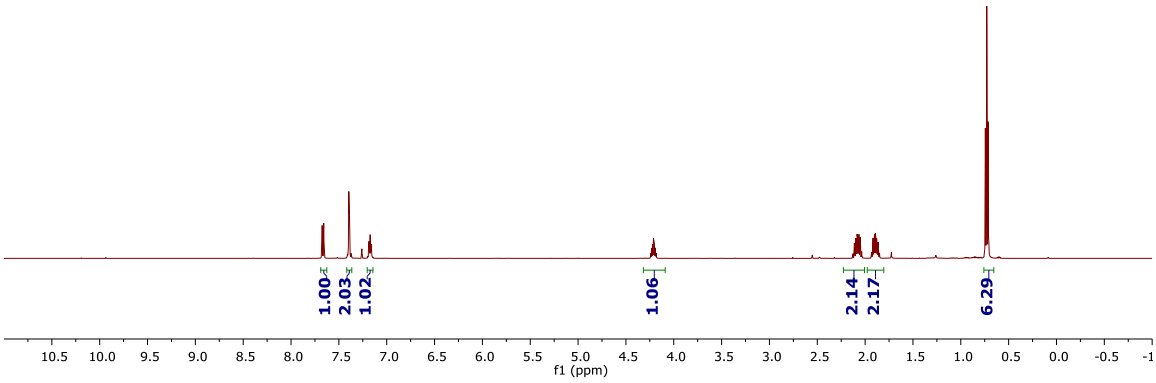


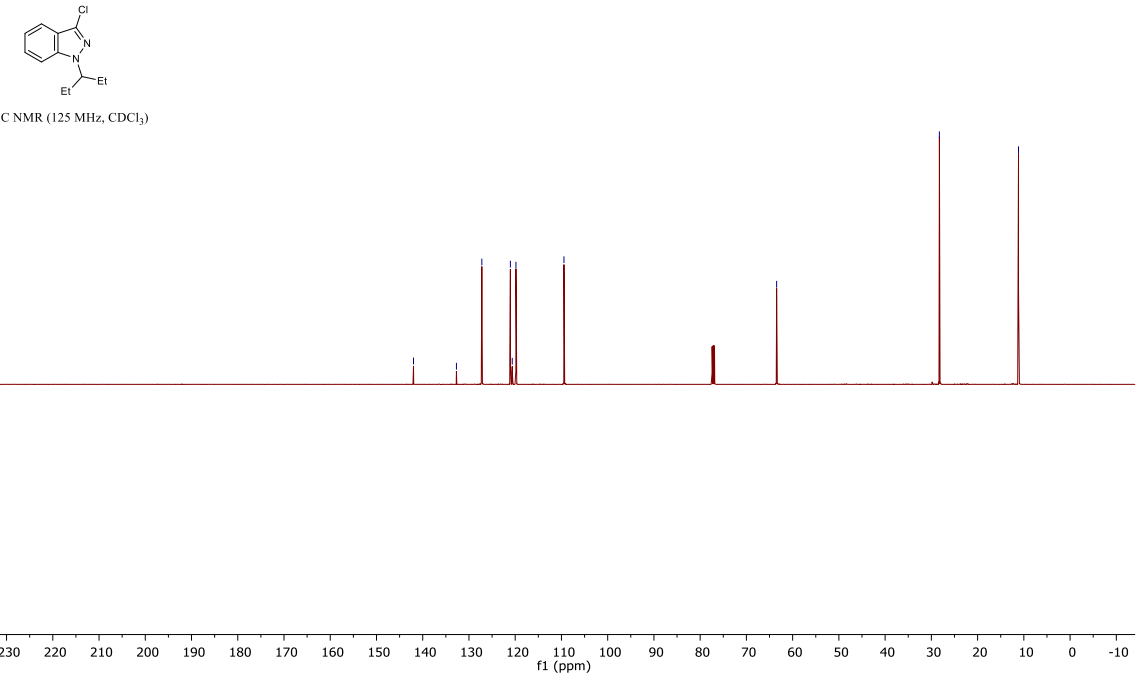
^{13}C NMR (125 MHz, $CDCl_3$)



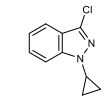


^{1}H NMR (500 MHz, $CDCl_3$)

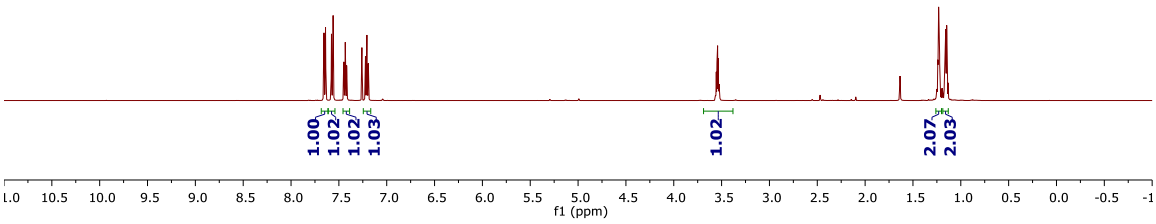


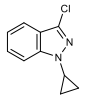


^{13}C NMR (125 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)





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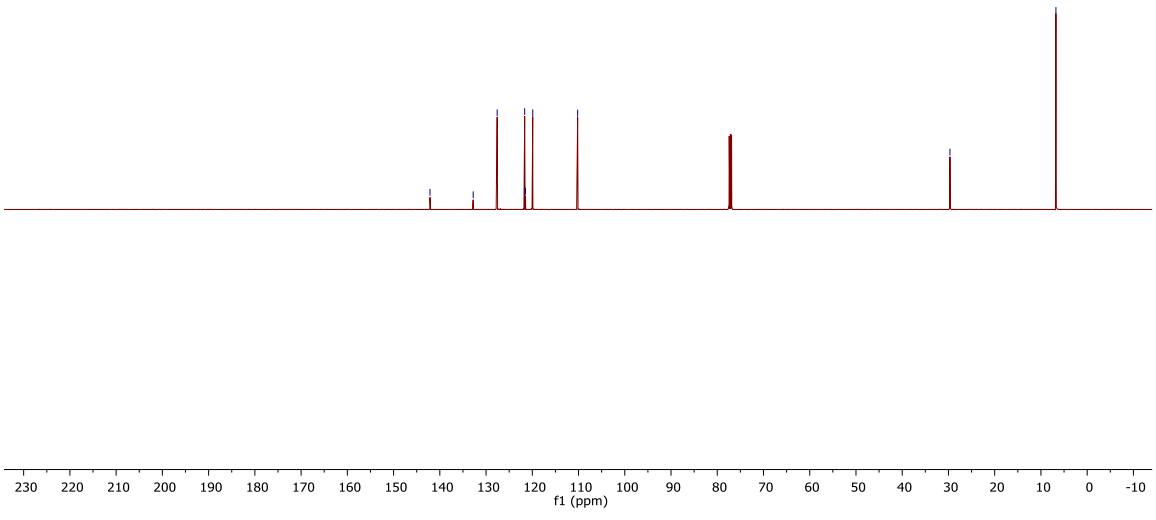

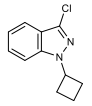

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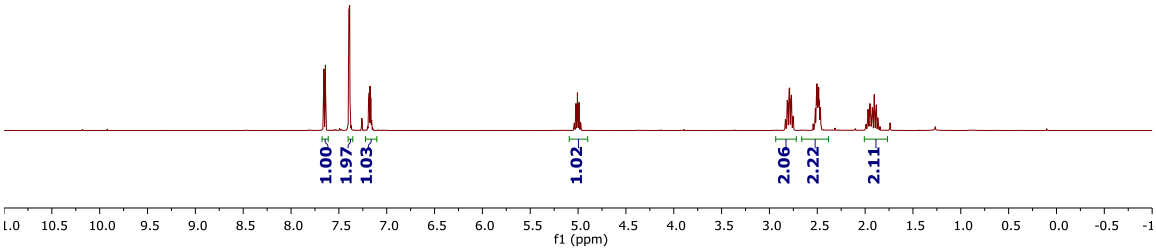
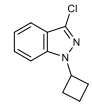
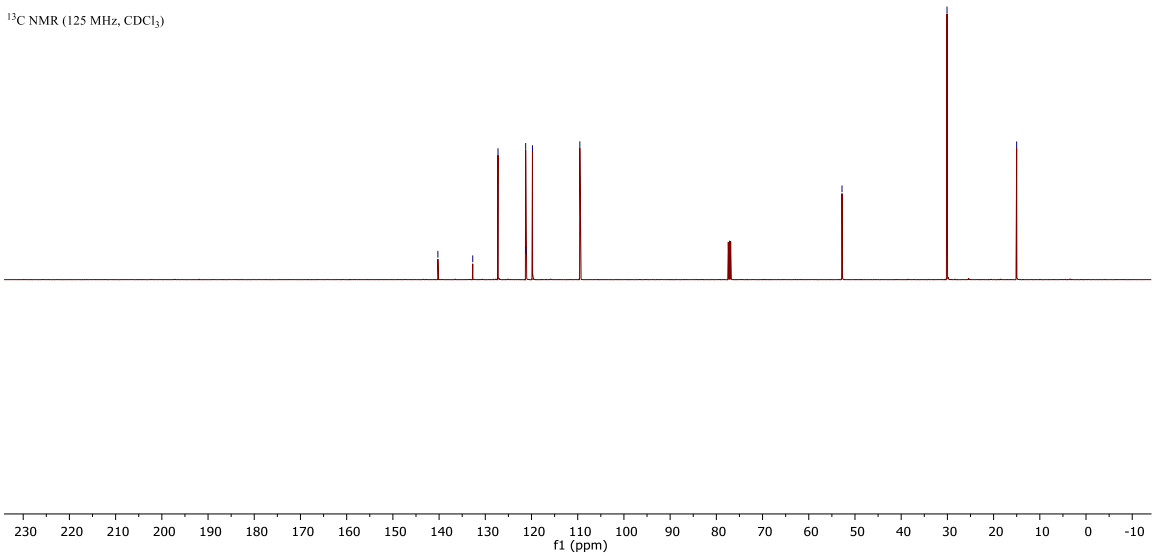
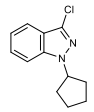


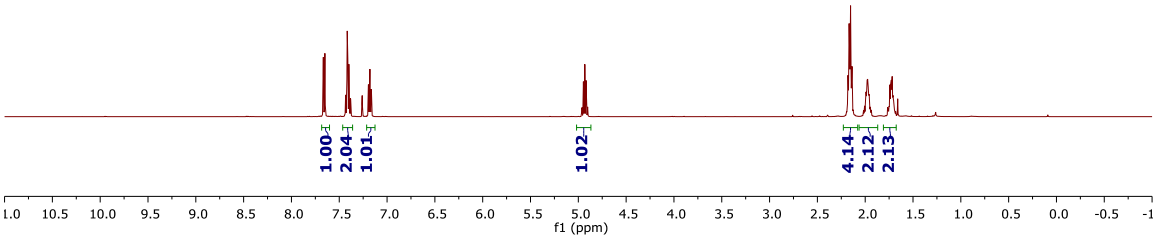


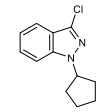
^{13}C NMR (125 MHz, $CDCl_3$)



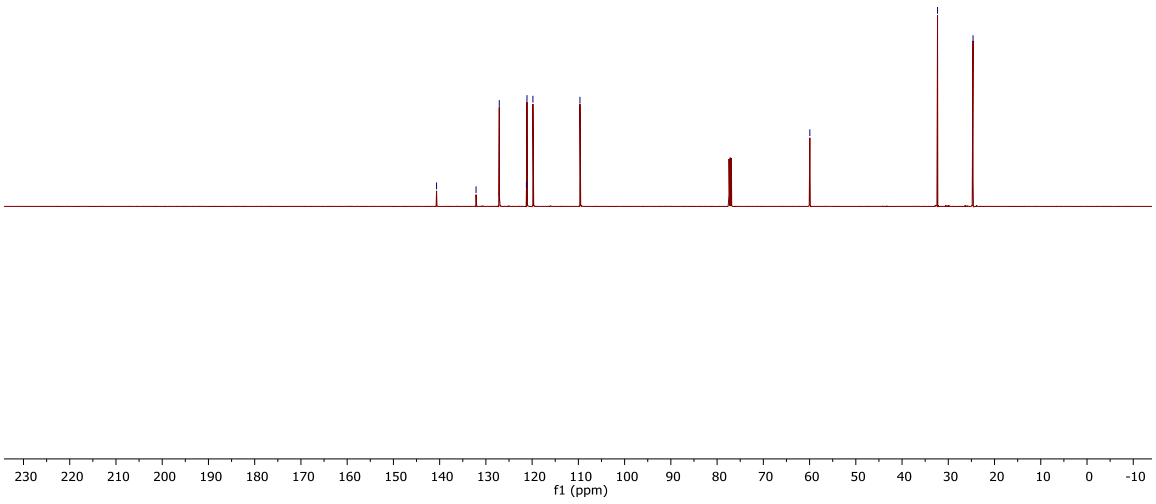


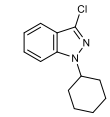
^{1}H NMR (500 MHz, $CDCl_3$)



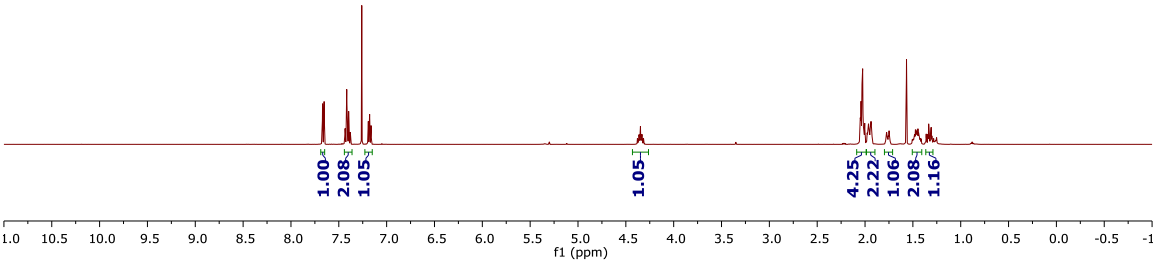


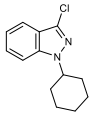
^{13}C NMR (125 MHz, $CDCl_3$)



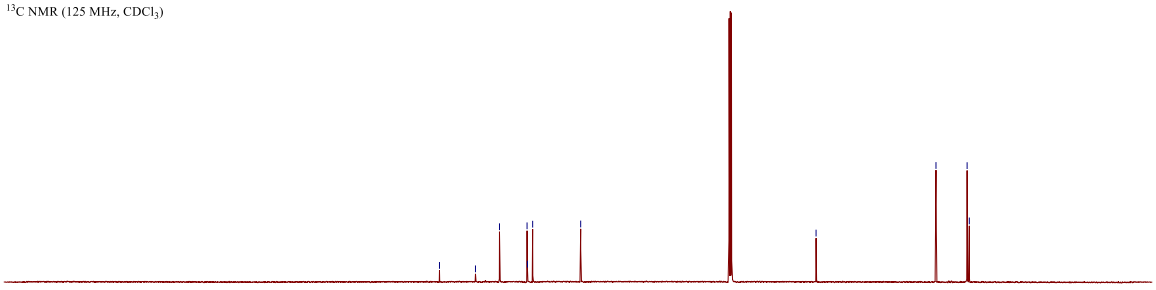


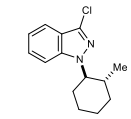
^{1}H NMR (500 MHz, $CDCl_3$)





^{13}C NMR (125 MHz, $CDCl_3$)





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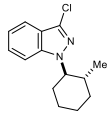

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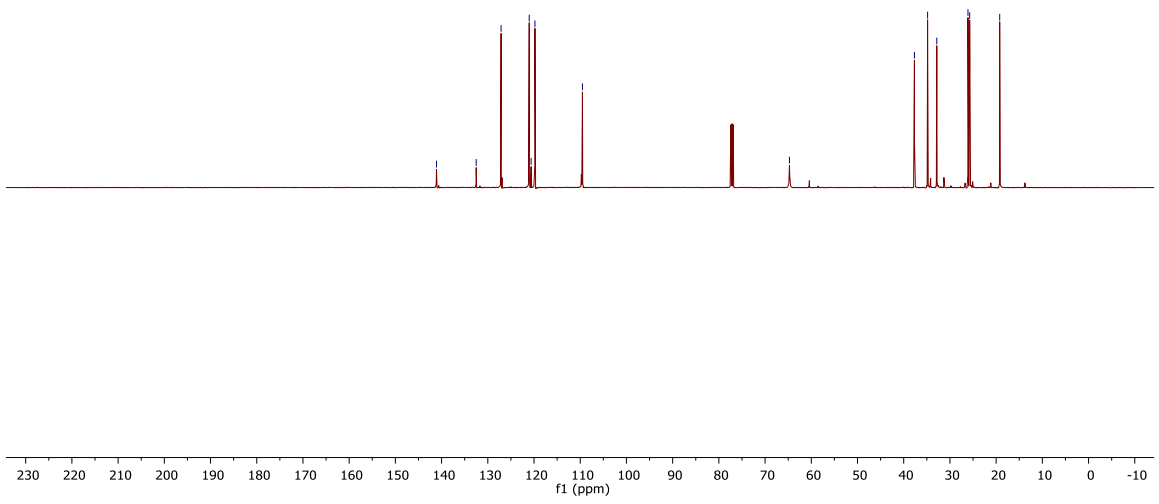
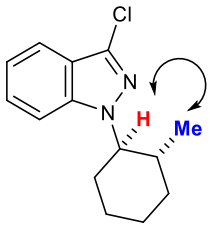
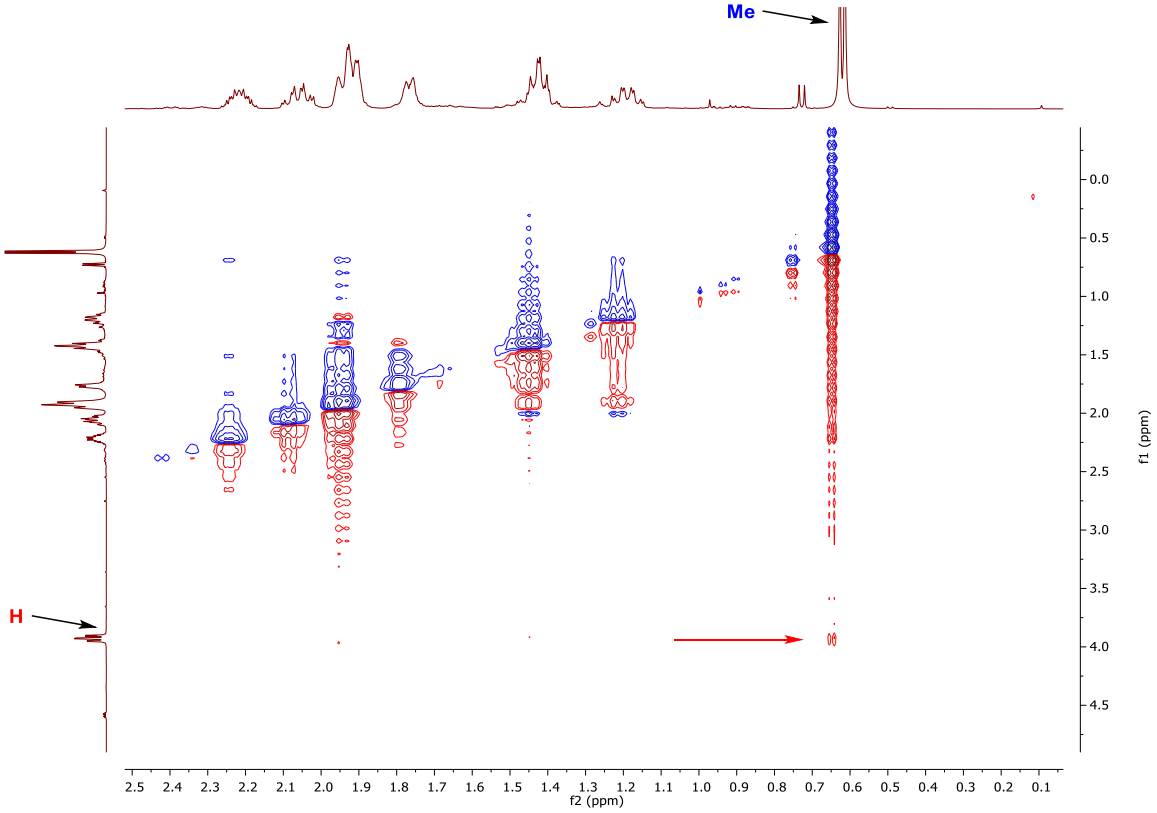
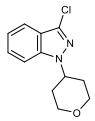




NOESY, $CDCl_3$





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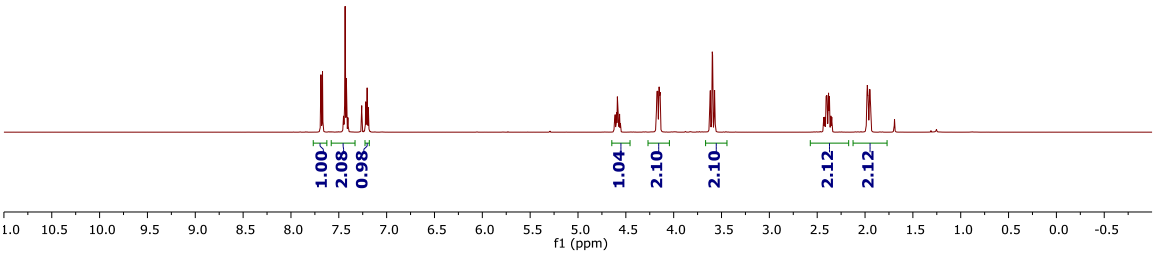
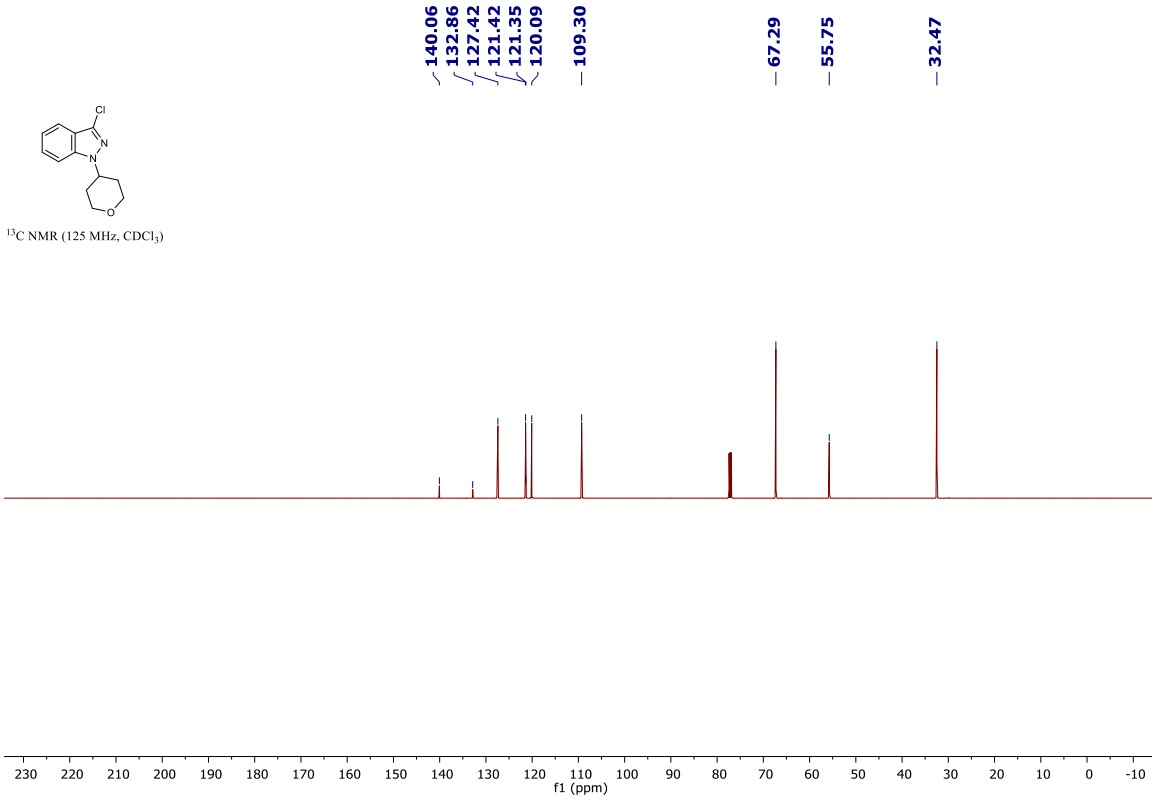
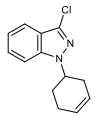




^{13}C NMR (125 MHz, $CDCl_3$)



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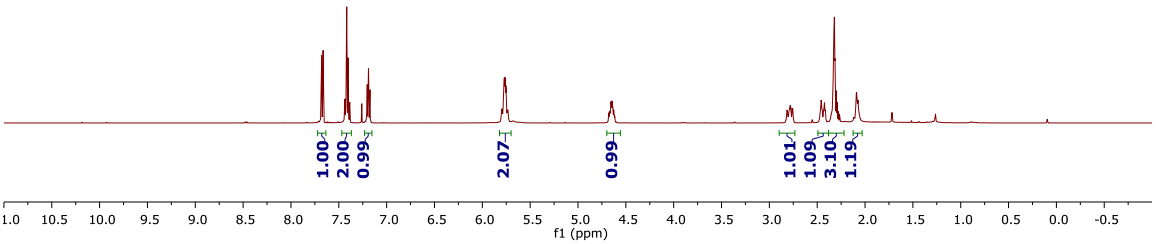
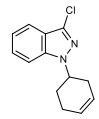
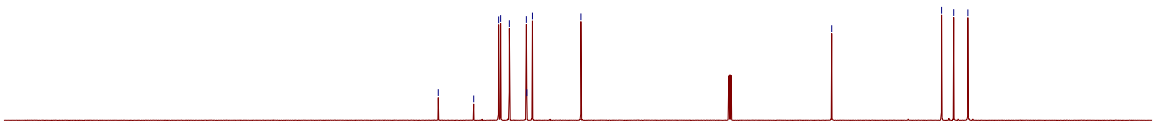
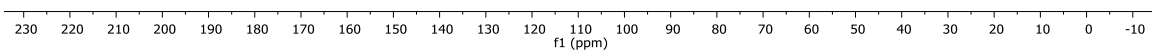
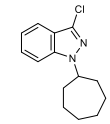




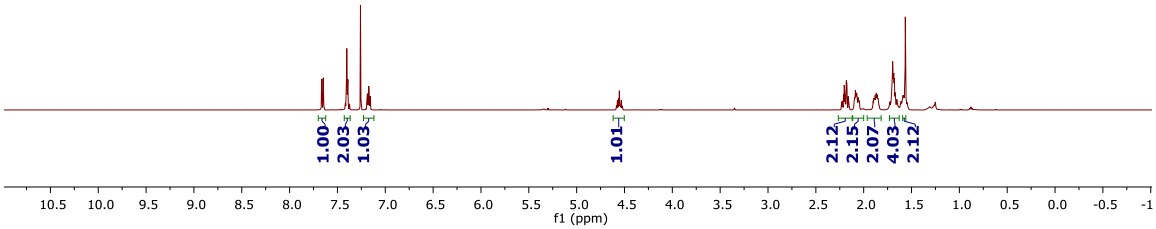
^{13}C NMR (125 MHz, $CDCl_3$)

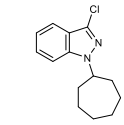




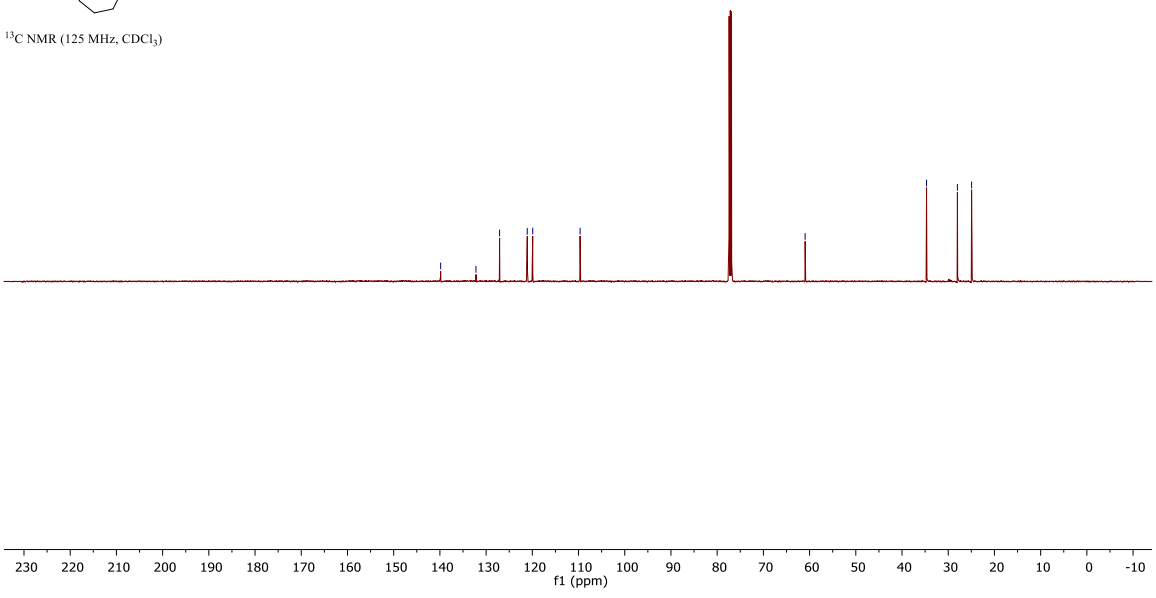


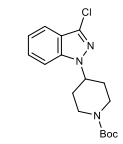
^{1}H NMR (500 MHz, $CDCl_3$)



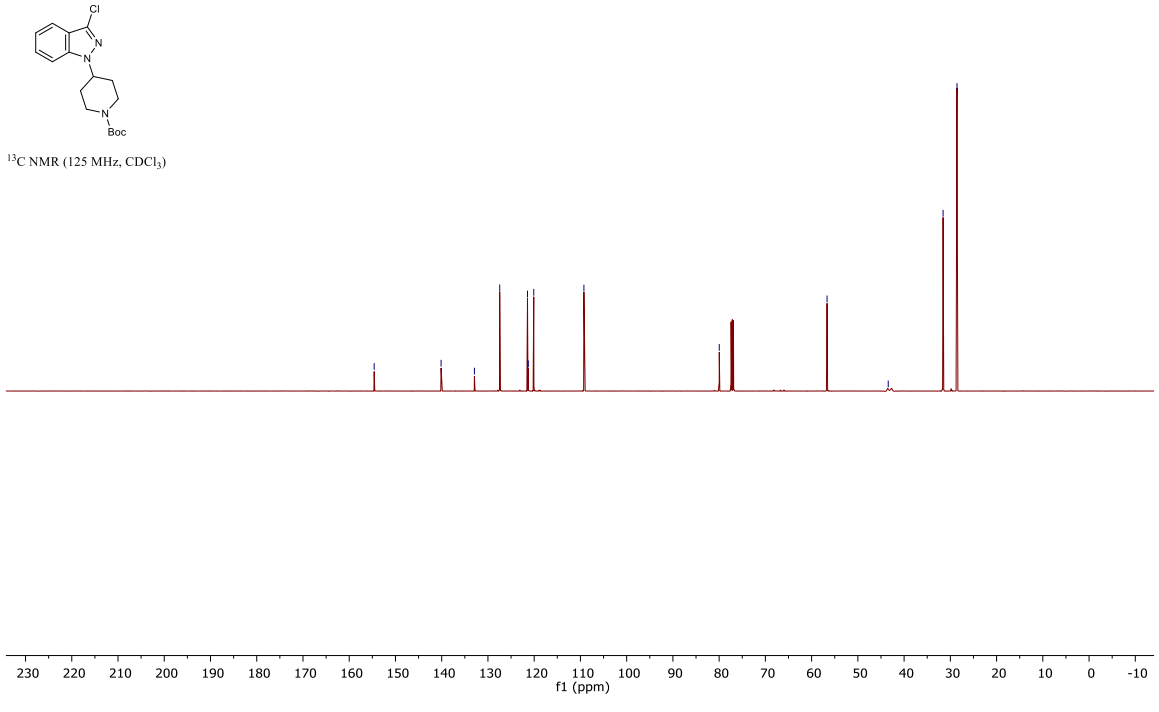


^{13}C NMR (125 MHz, $CDCl_3$)

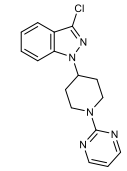




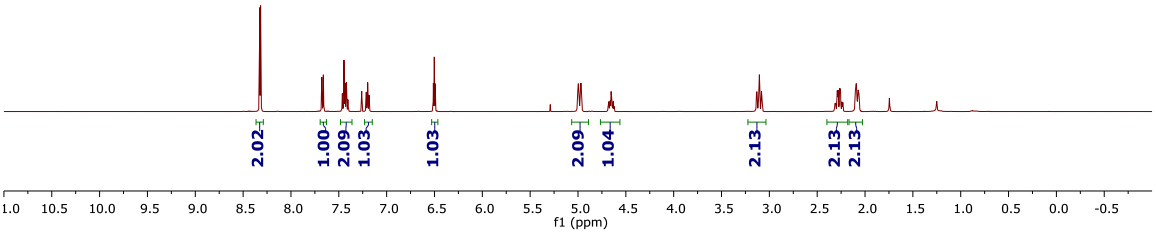
^{1}H NMR (500 MHz, $CDCl_3$)

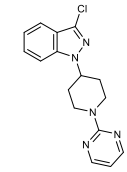


^{13}C NMR (125 MHz, $CDCl_3$)

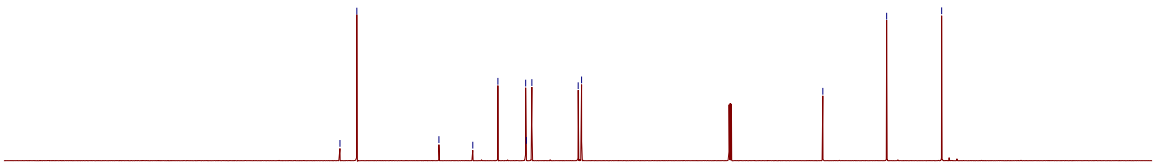


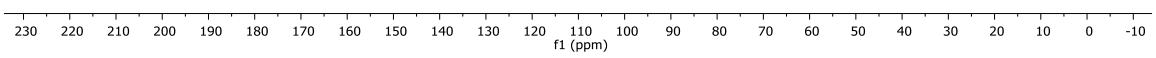
^{1}H NMR (500 MHz, $CDCl_3$)

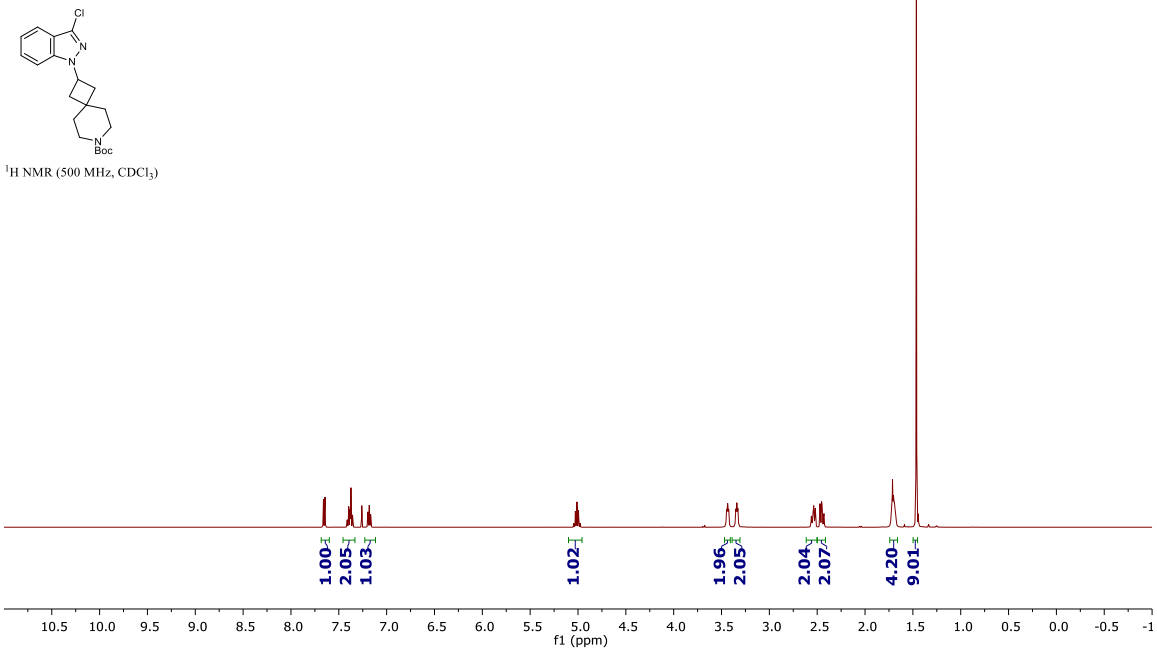




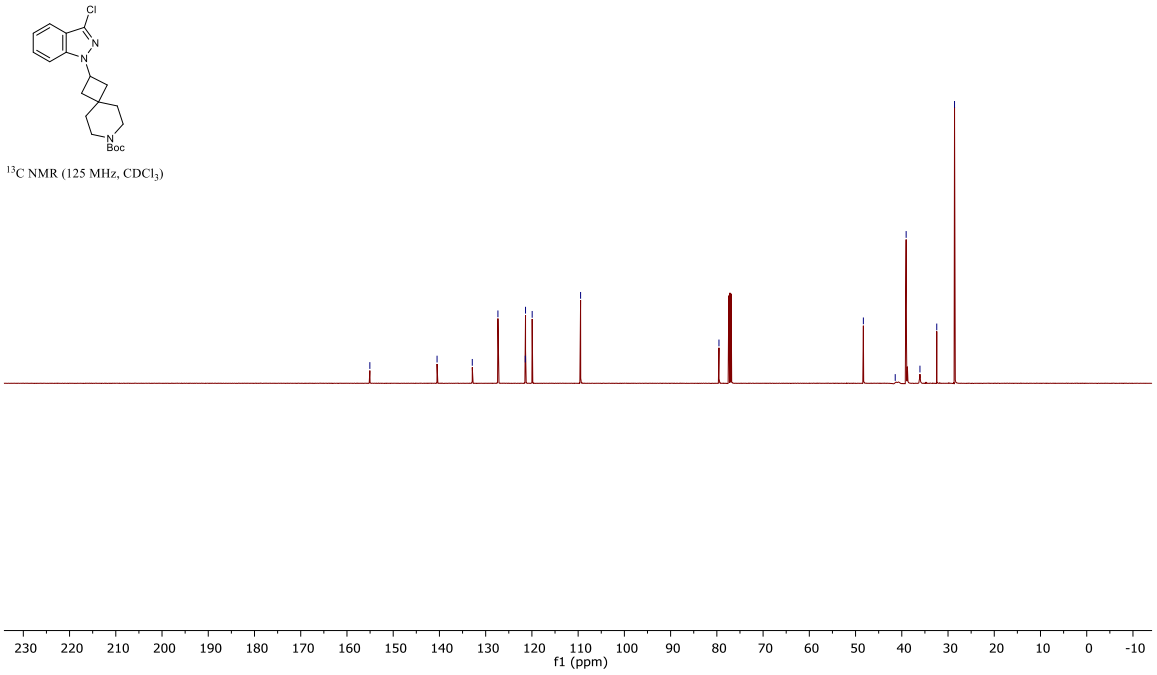
^{13}C NMR (125 MHz, $CDCl_3$)



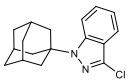




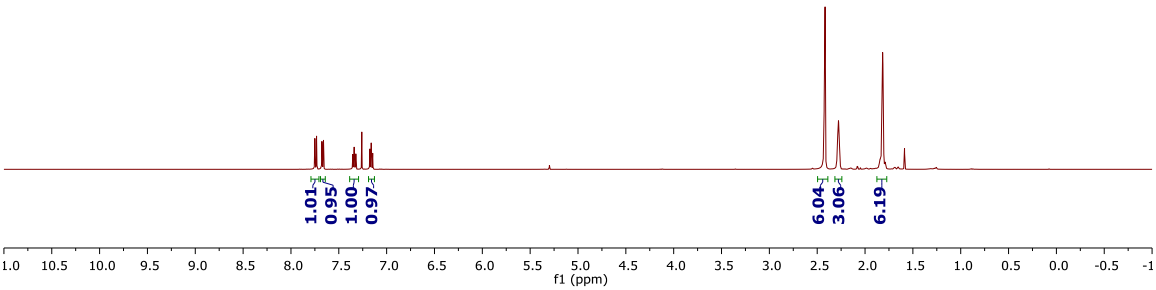
^{1}H NMR (500 MHz, $CDCl_3$)

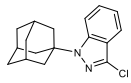


^{13}C NMR (125 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)





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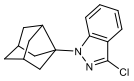

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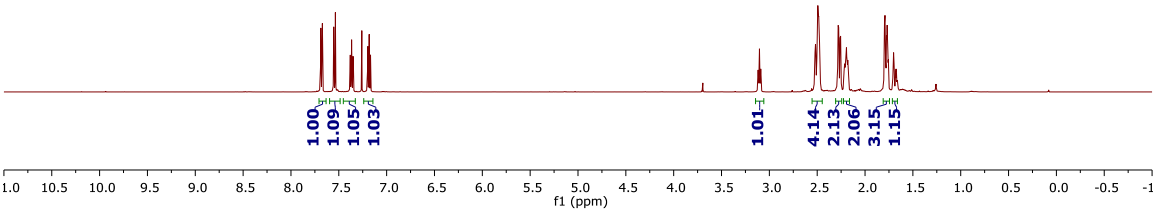

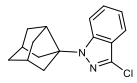

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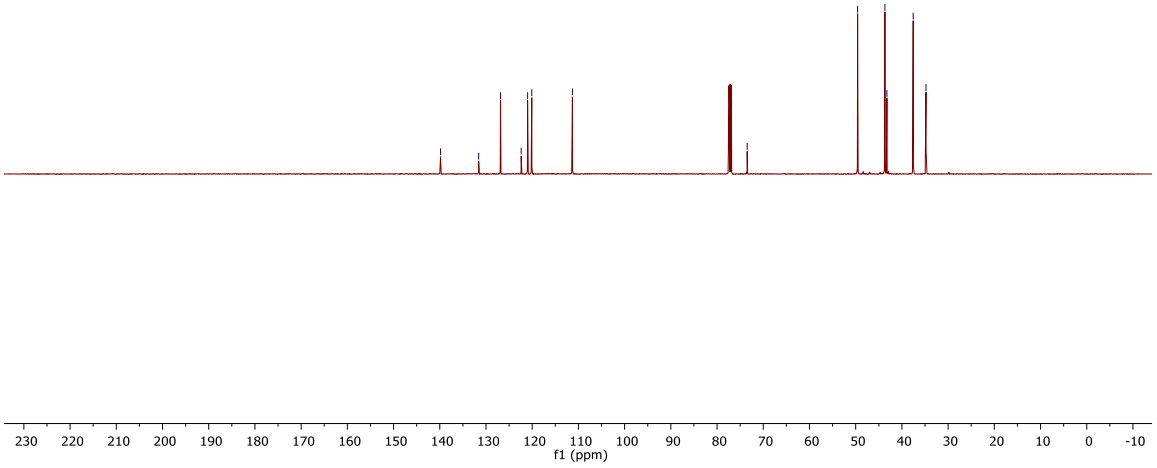

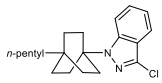

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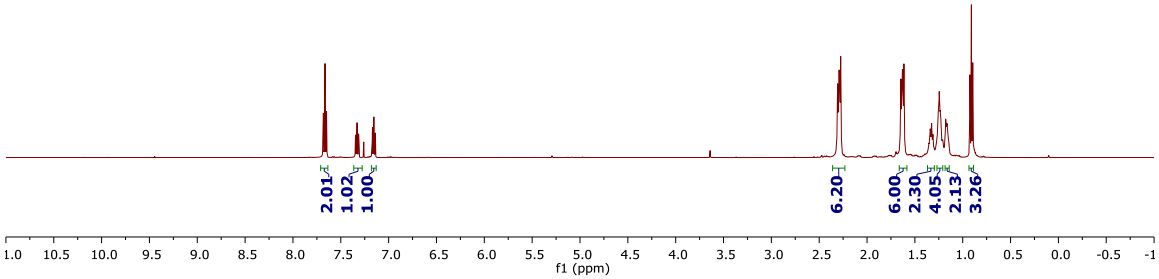
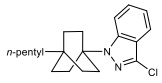
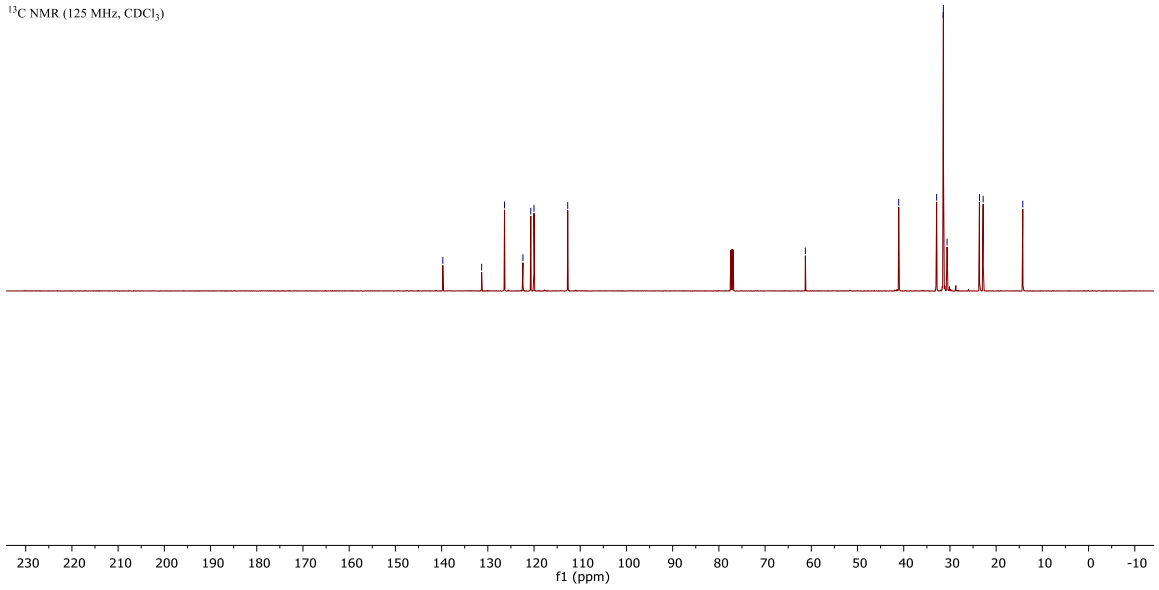
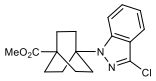




^{13}C NMR (125 MHz, $CDCl_3$)





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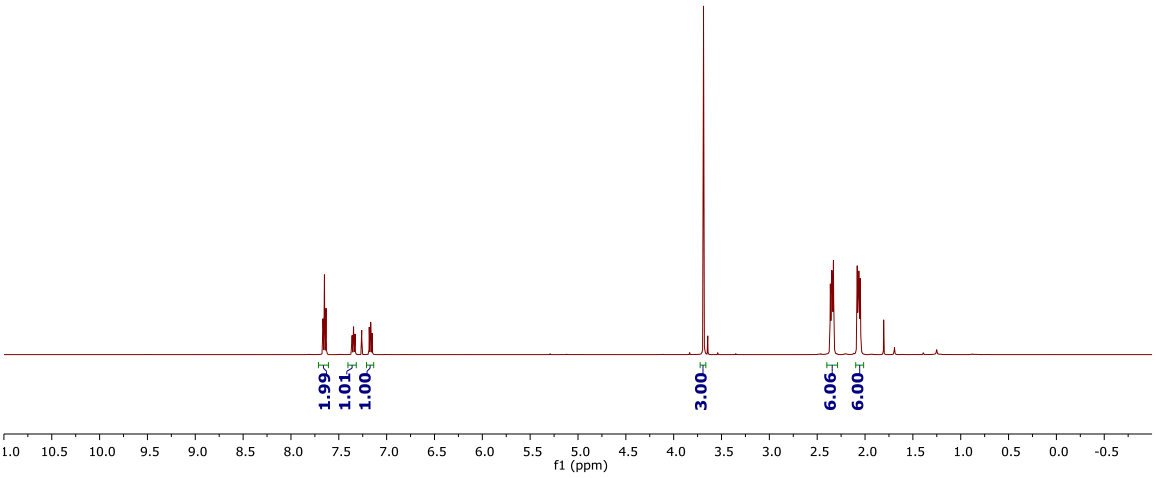
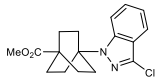
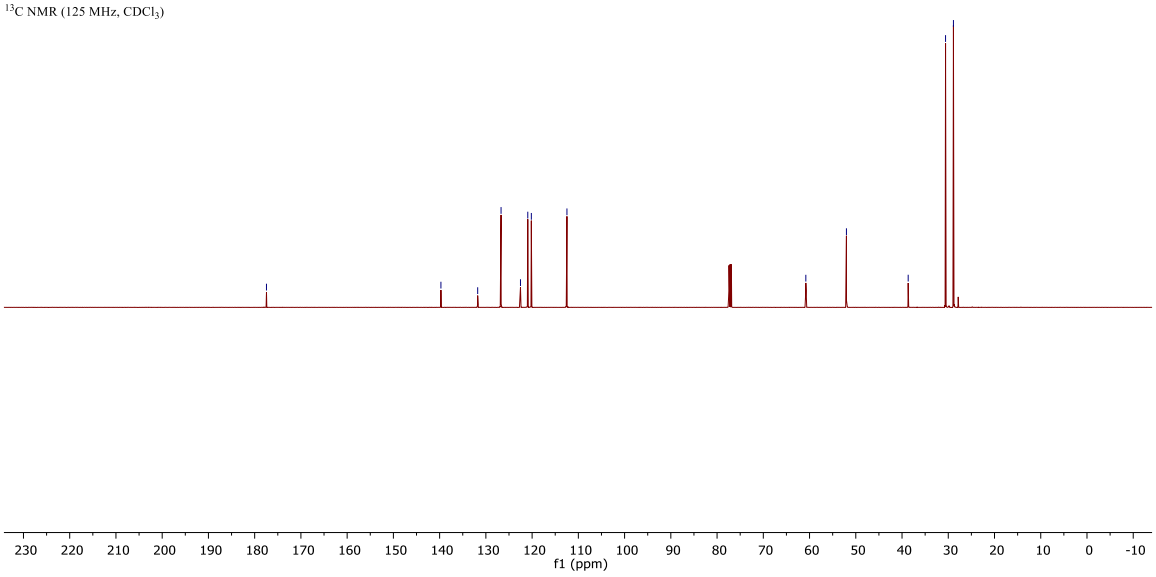
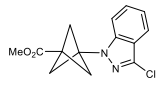


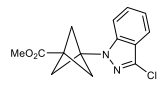


^{13}C NMR (125 MHz, $CDCl_3$)





^{1}H NMR (500 MHz, $CDCl_3$)



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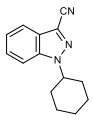

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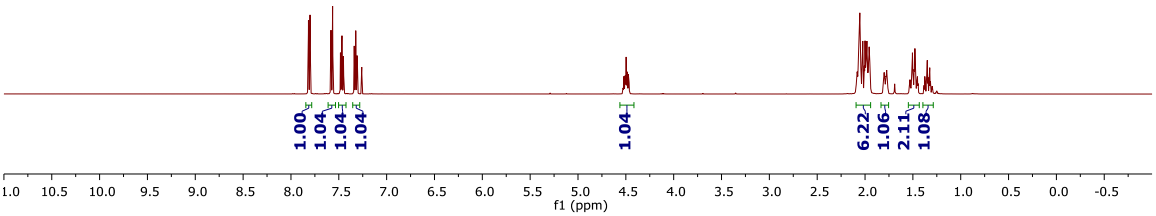

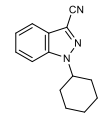

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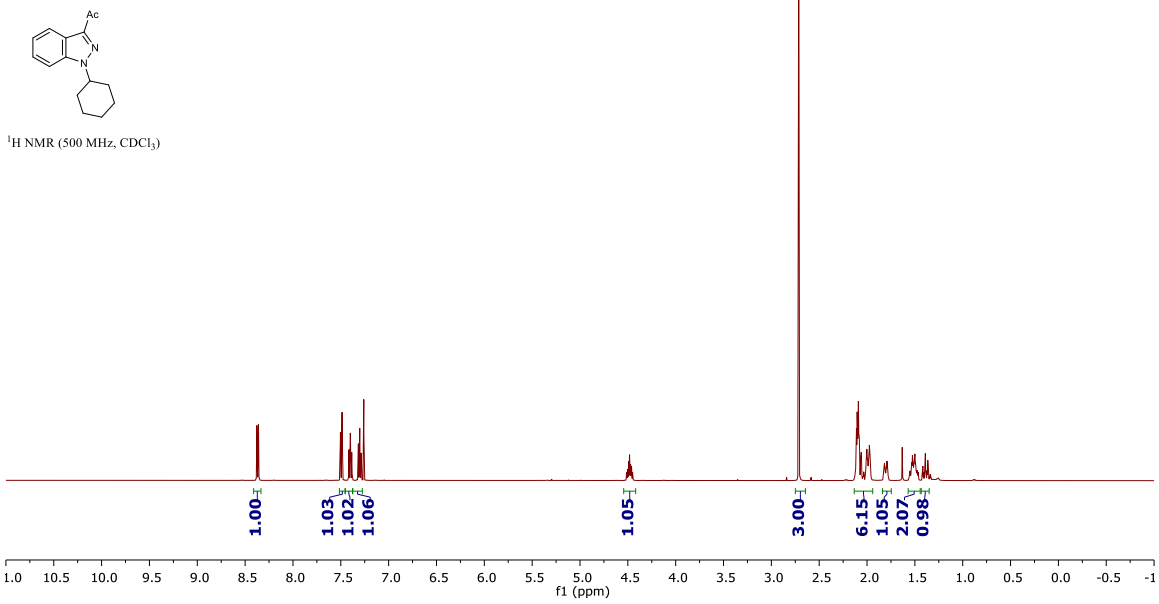

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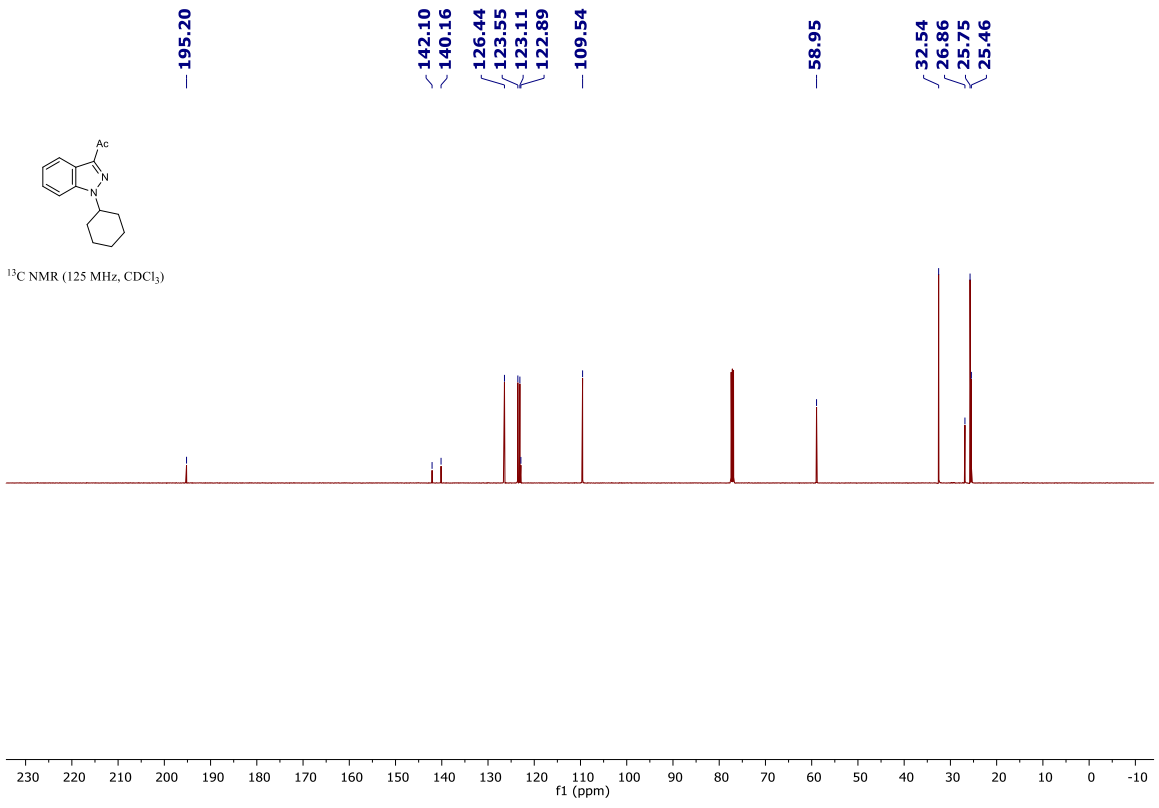

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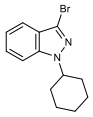

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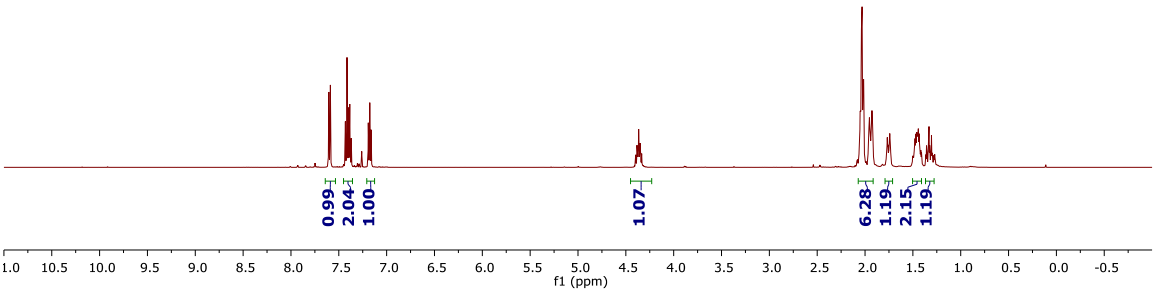

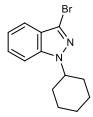

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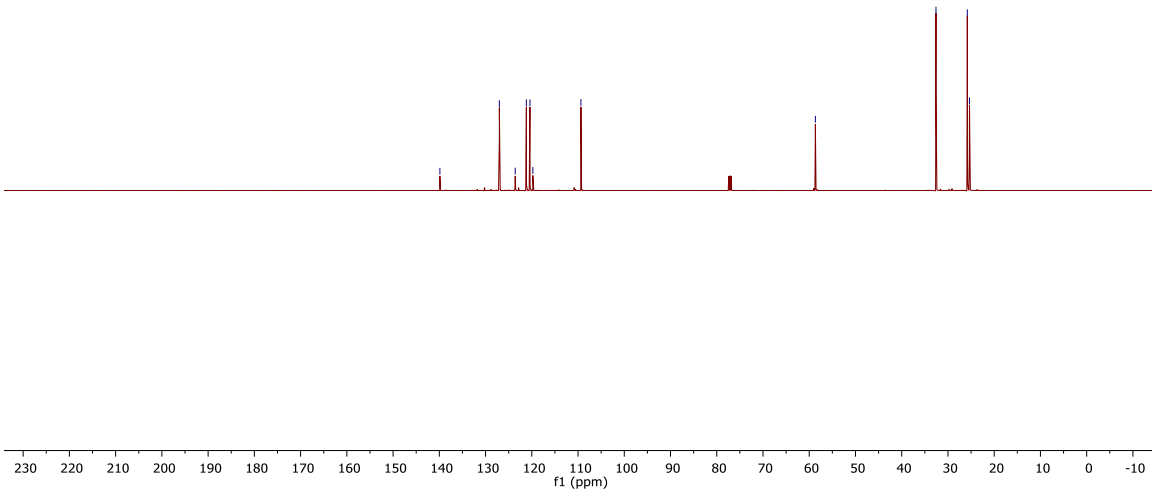
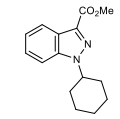
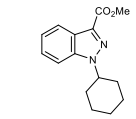




^{1}H NMR (500 MHz, $CDCl_3$)



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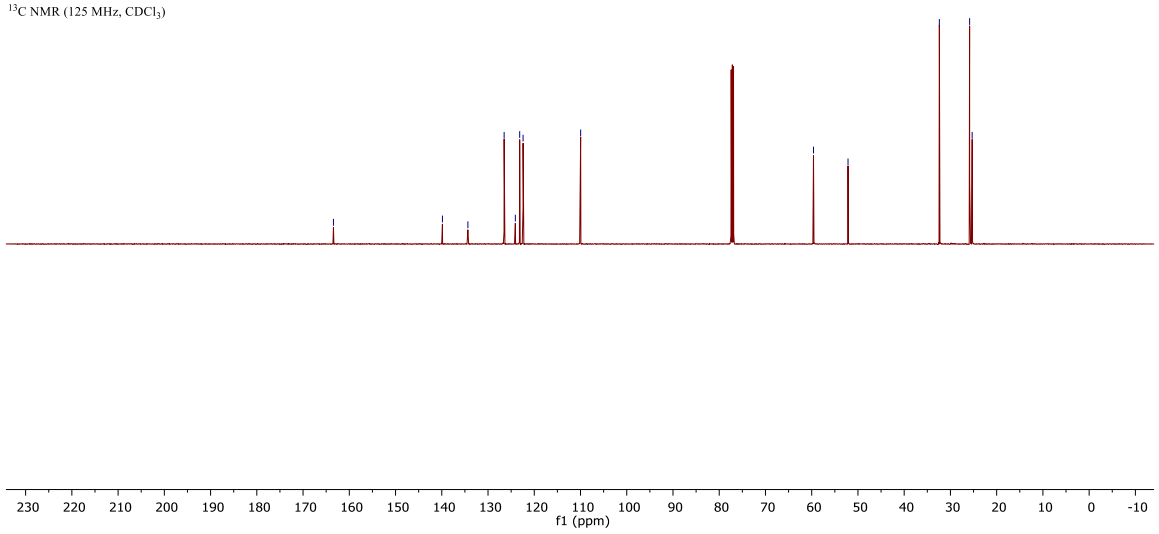

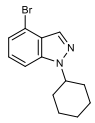

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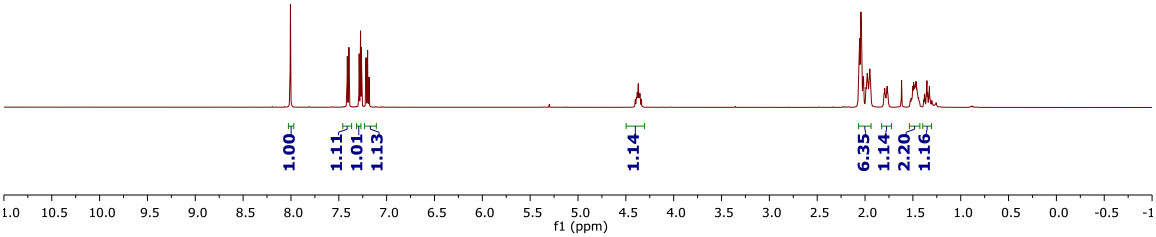
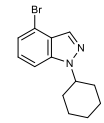
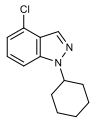
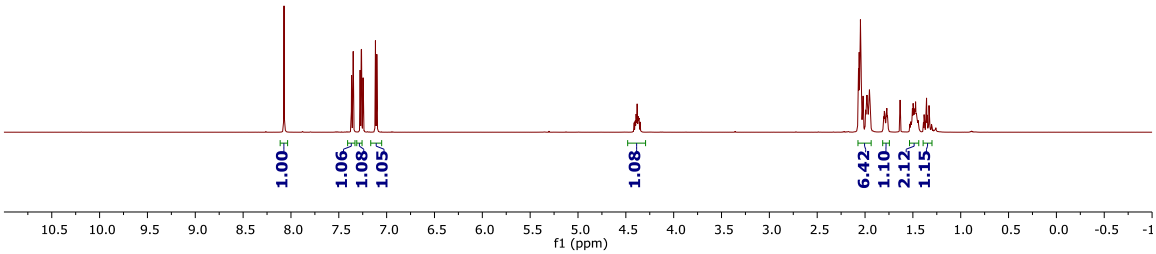


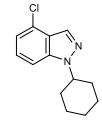


^{13}C NMR (125 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)





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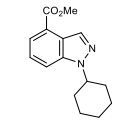
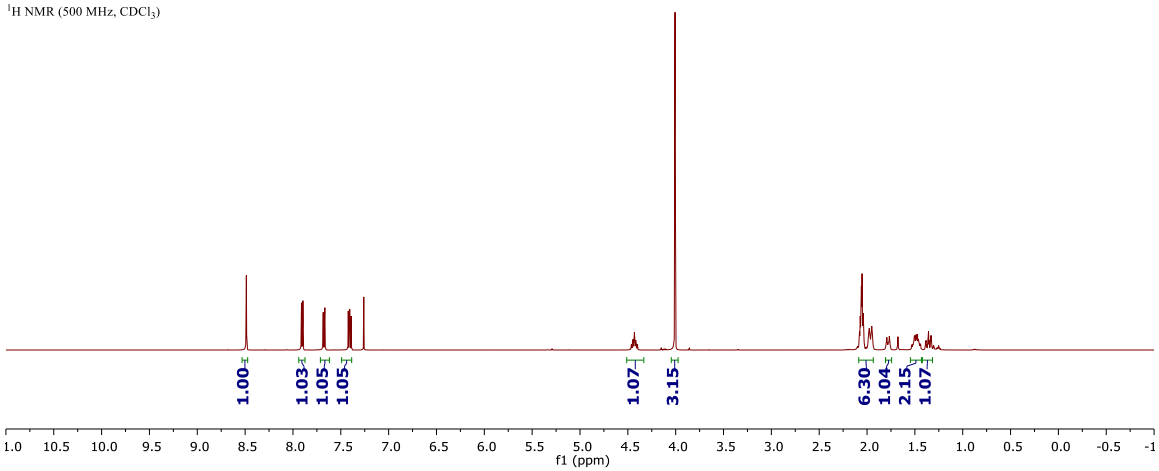


^{1}H NMR (500 MHz, $CDCl_3$)



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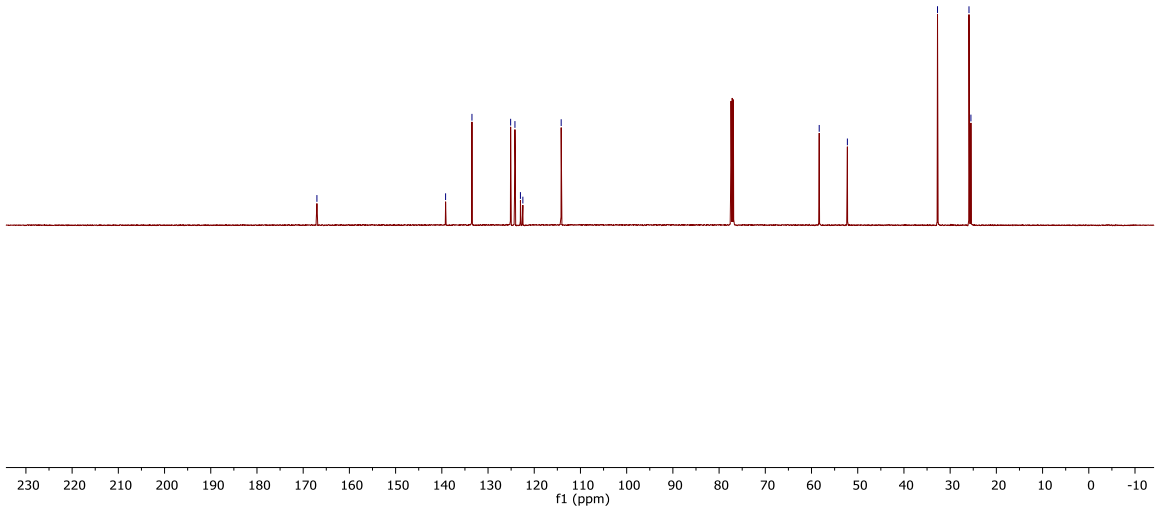
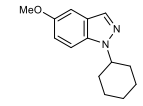
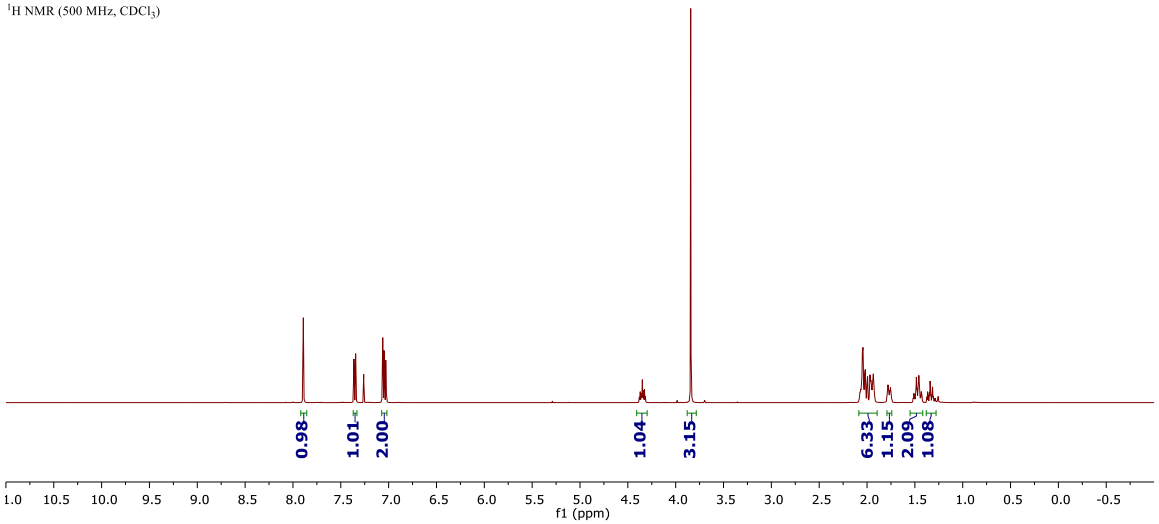
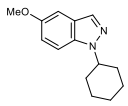


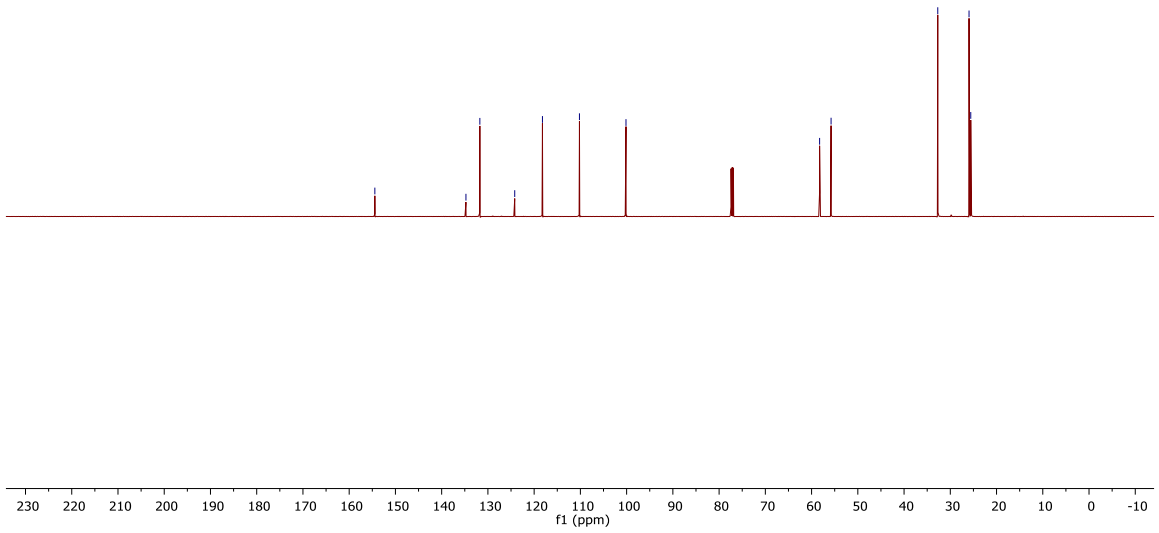


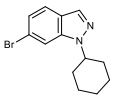
^{1}H NMR (500 MHz, $CDCl_3$)



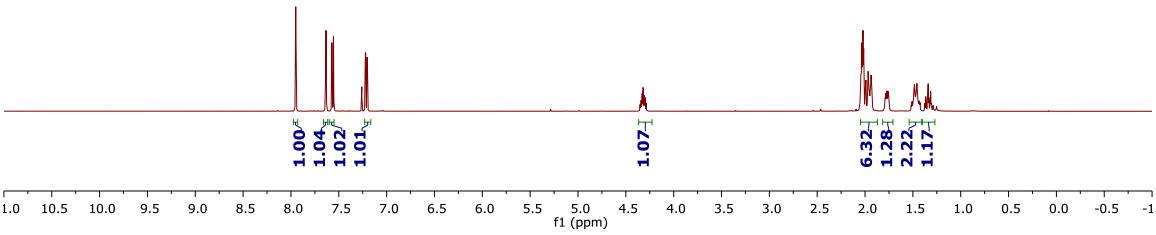


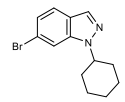
^{13}C NMR (125 MHz, $CDCl_3$)



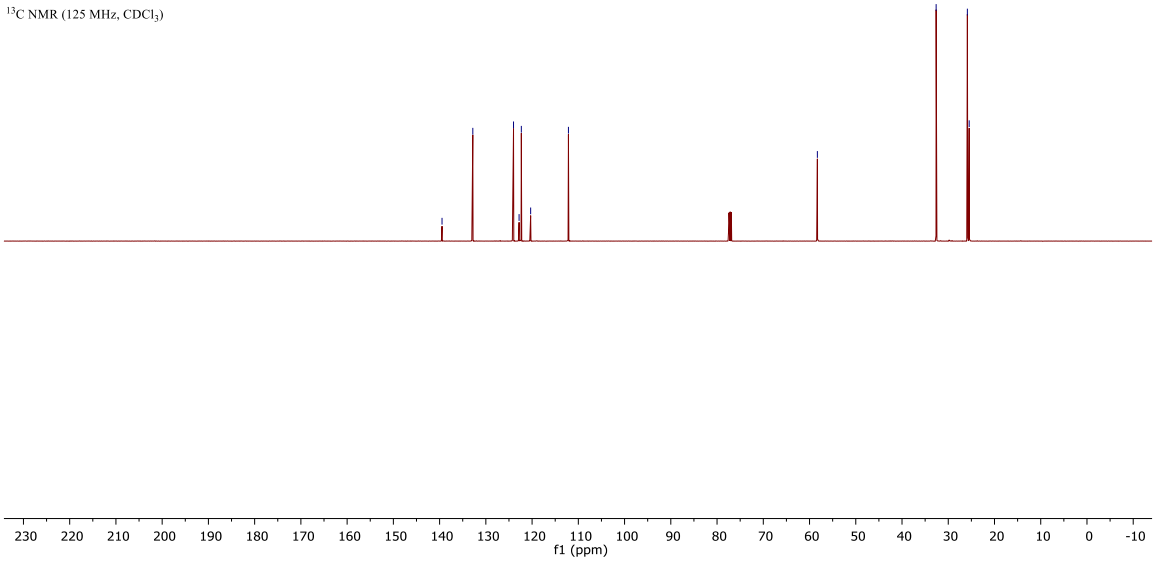


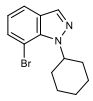
^{1}H NMR (500 MHz, $CDCl_3$)



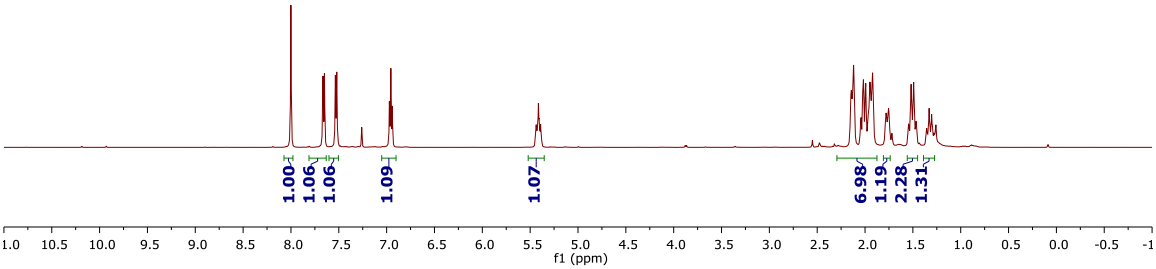


^{13}C NMR (125 MHz, $CDCl_3$)

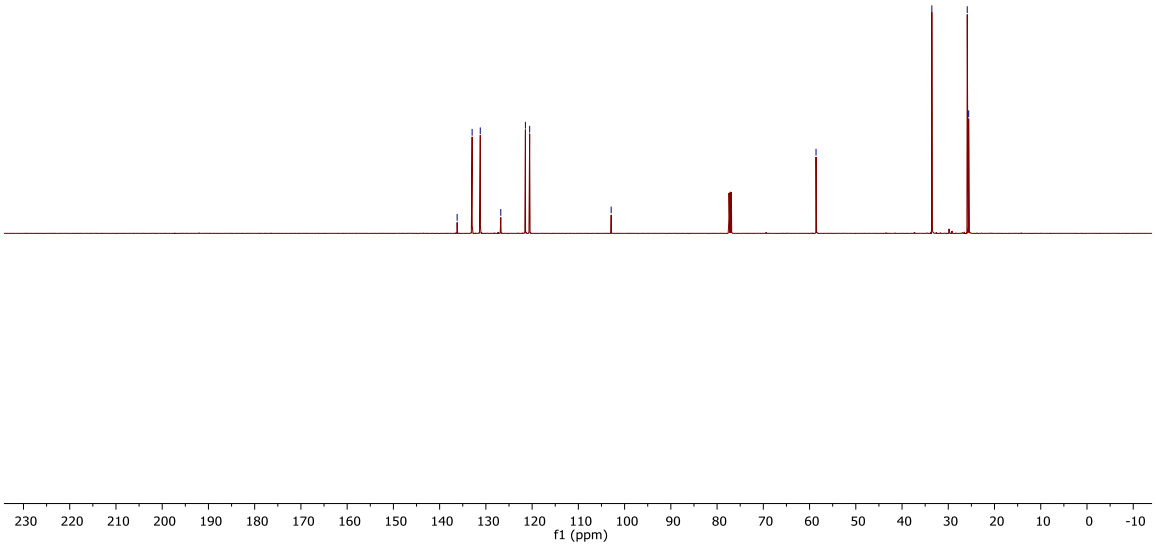


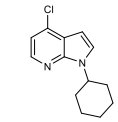


^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)





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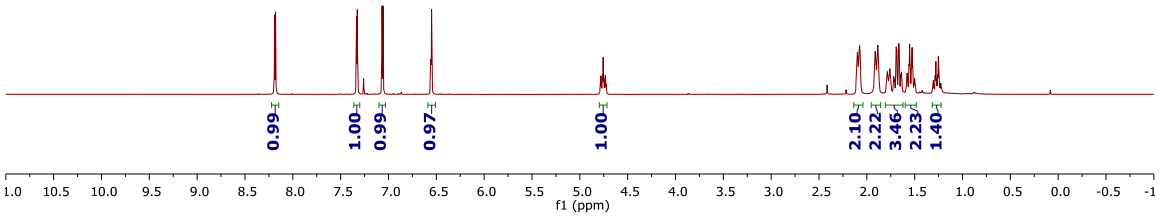
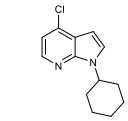
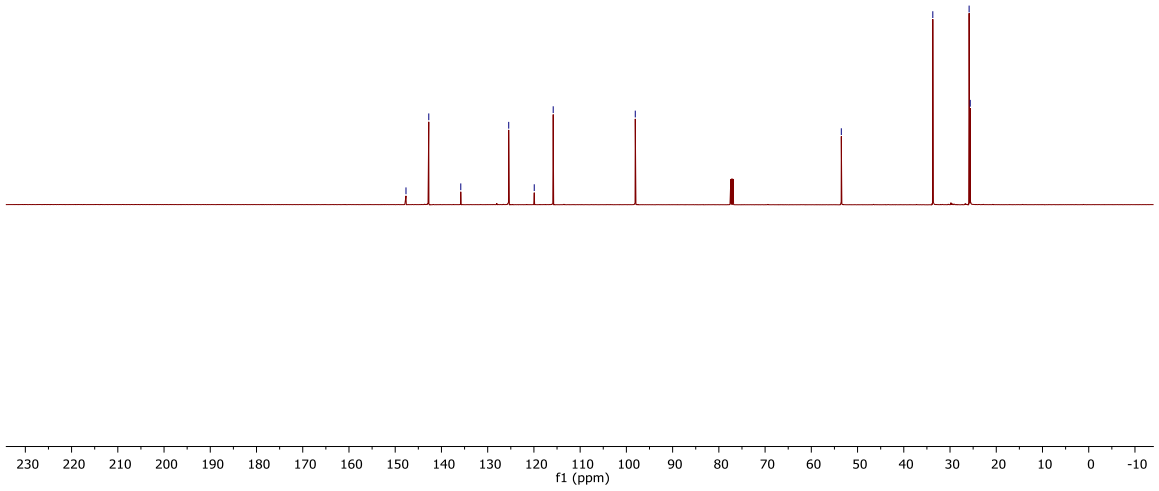
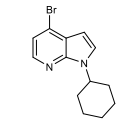




^{13}C NMR (125 MHz, $CDCl_3$)





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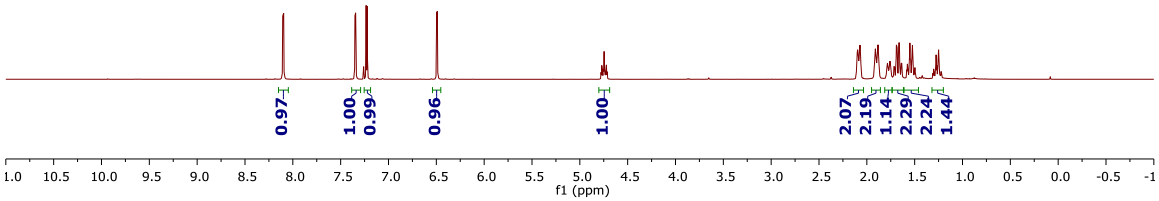
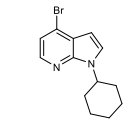
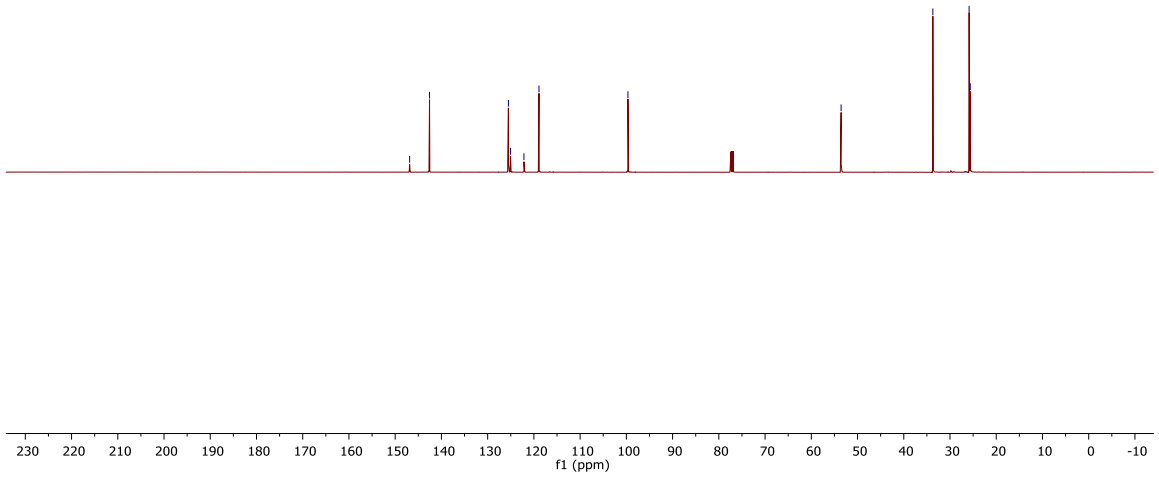
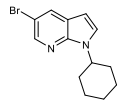


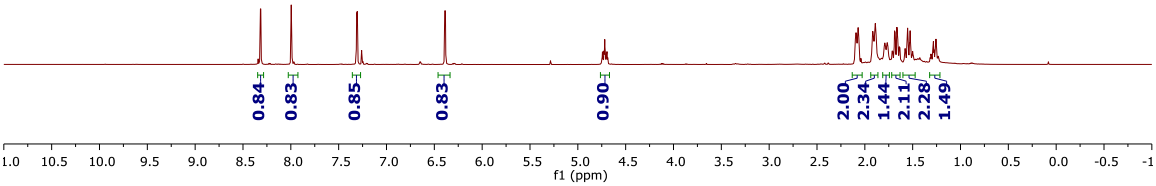


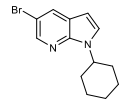
^{13}C NMR (125 MHz, $CDCl_3$)



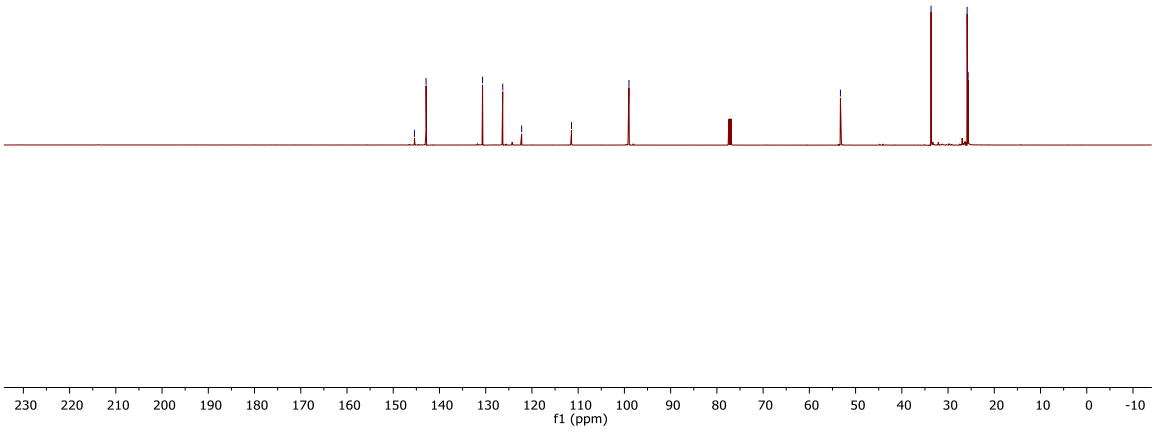


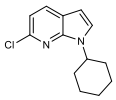
^{1}H NMR (500 MHz, $CDCl_3$)



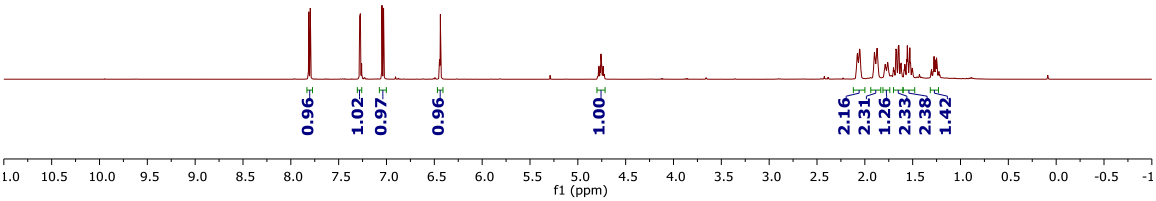


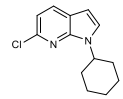
^{13}C NMR (125 MHz, $CDCl_3$)



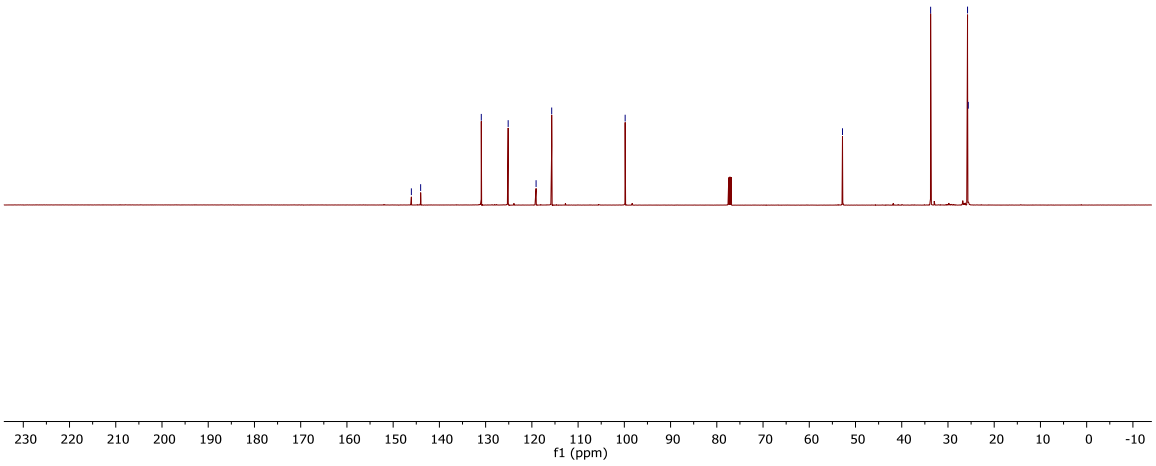


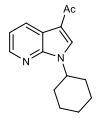
^{1}H NMR (500 MHz, $CDCl_3$)





^{13}C NMR (125 MHz, $CDCl_3$)





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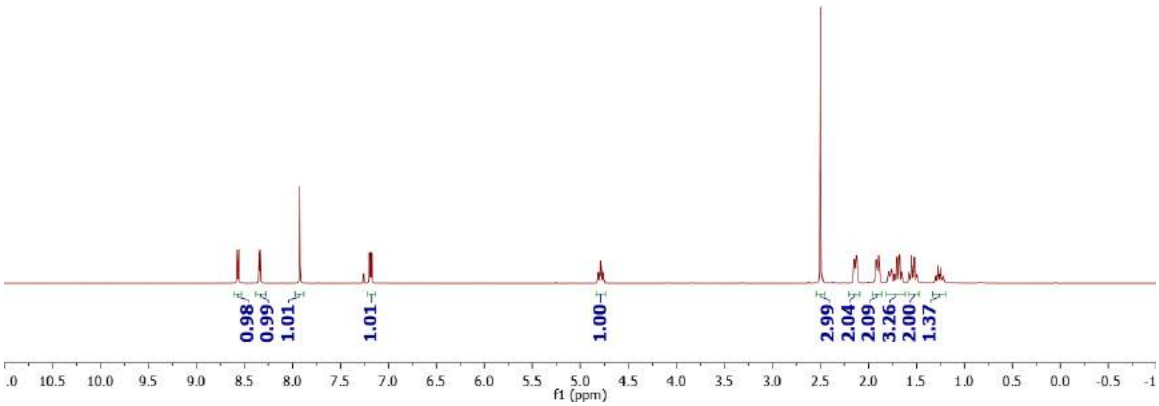

192.89
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118.66
115.47
53.61
33.60
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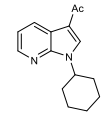
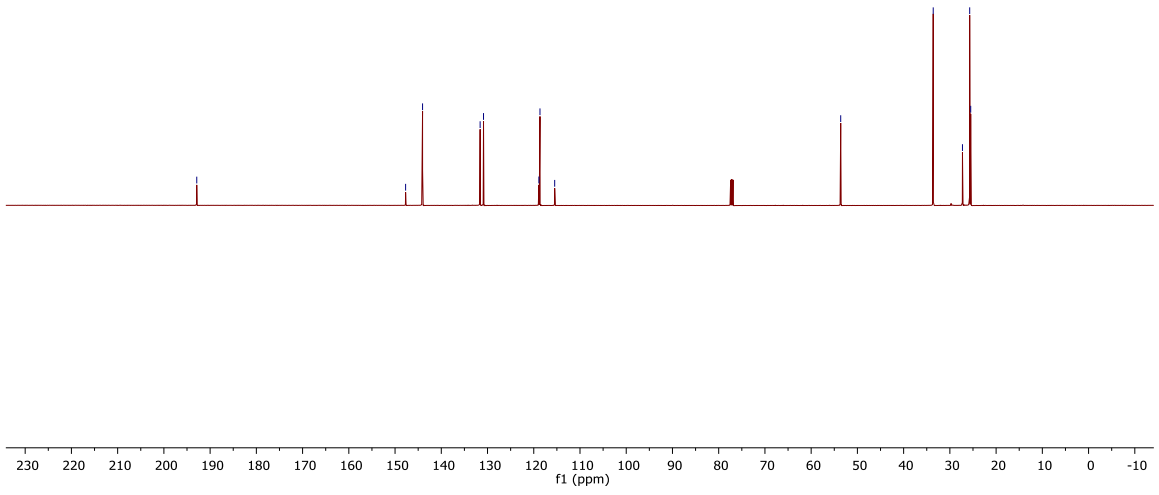
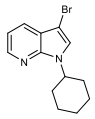
25.71
25.49



^{13}C NMR (125 MHz, $CDCl_3$)





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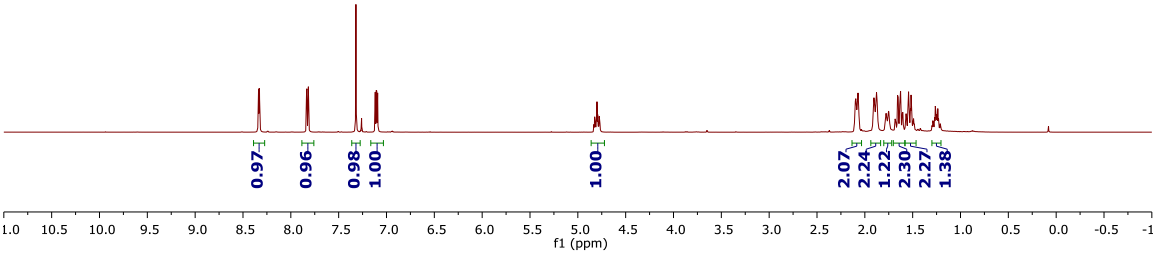
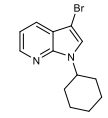
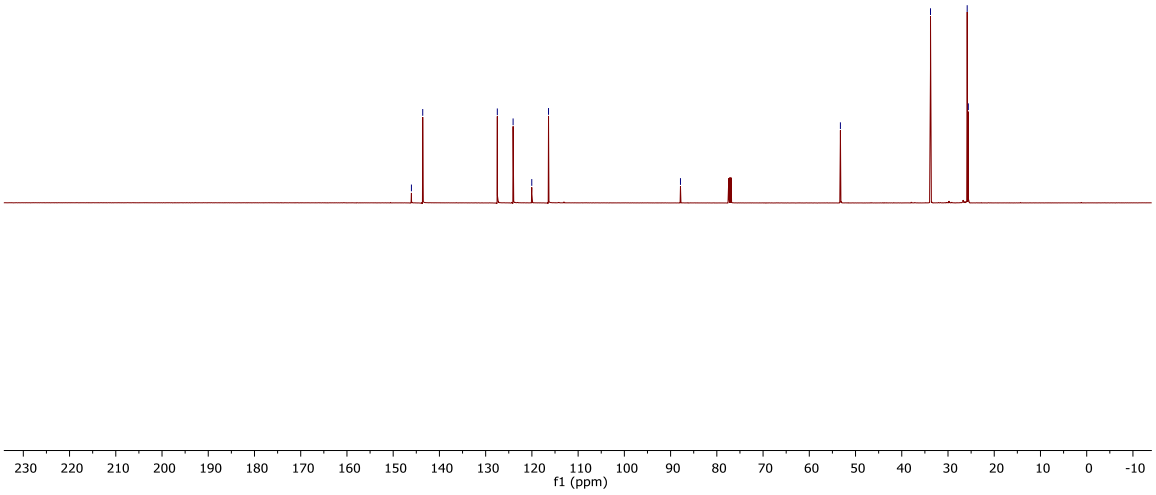
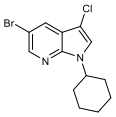




^{13}C NMR (125 MHz, $CDCl_3$)





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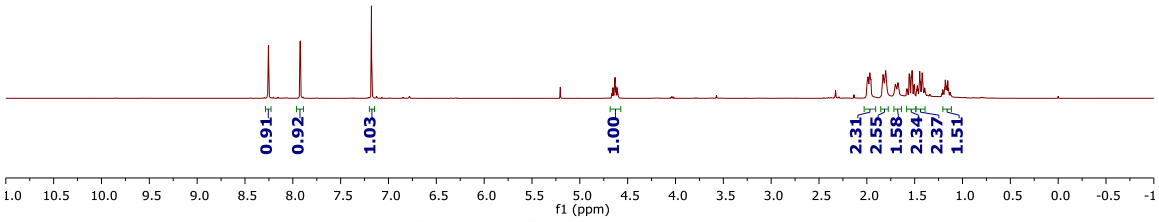

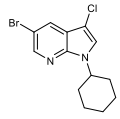

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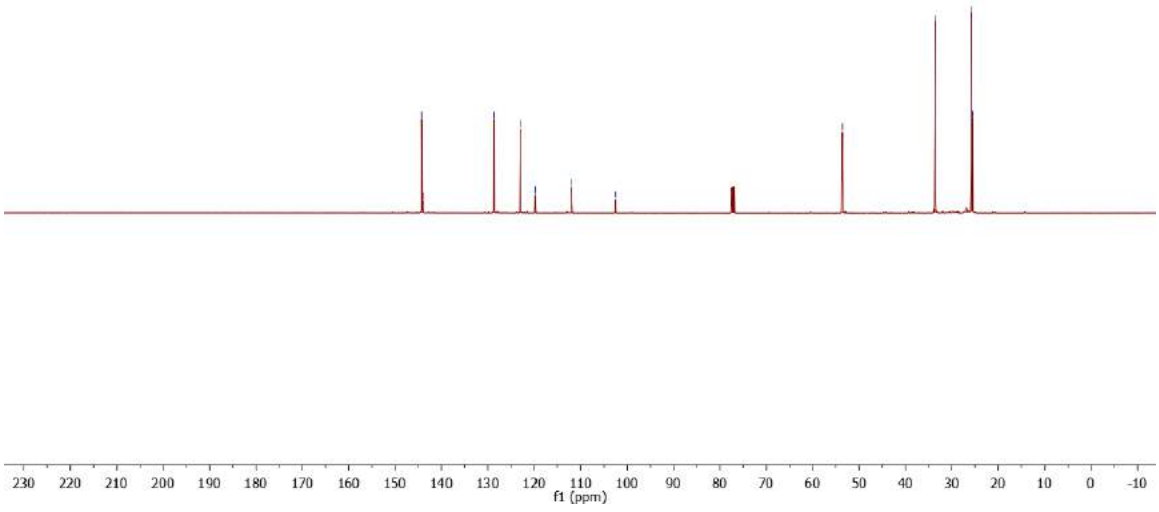

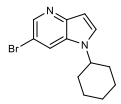

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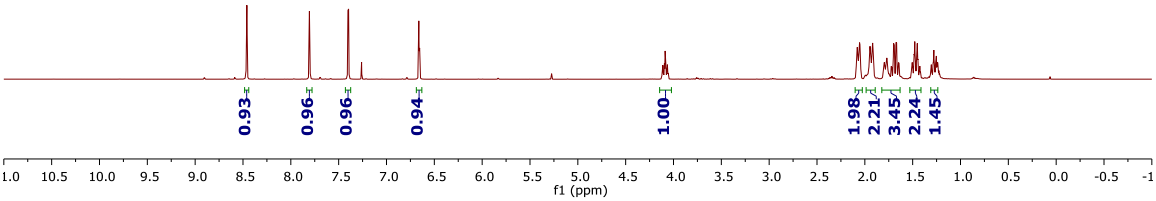

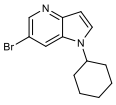

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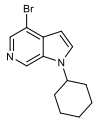

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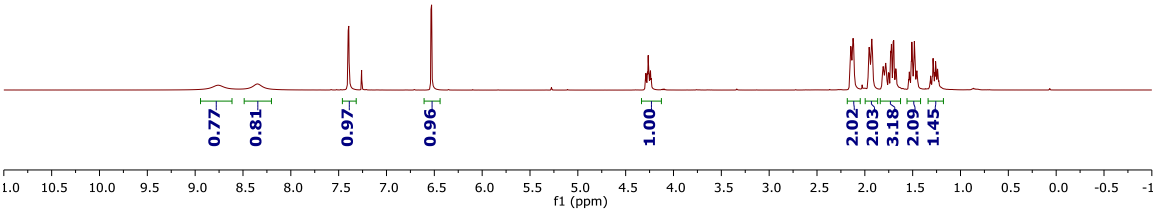

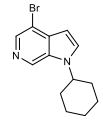

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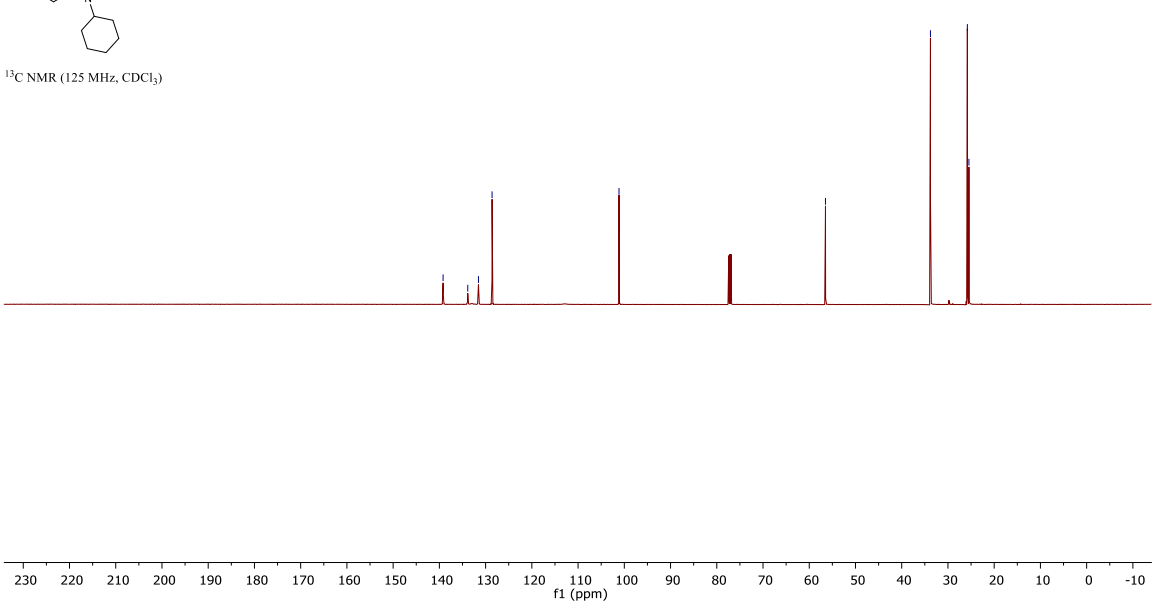
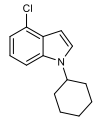
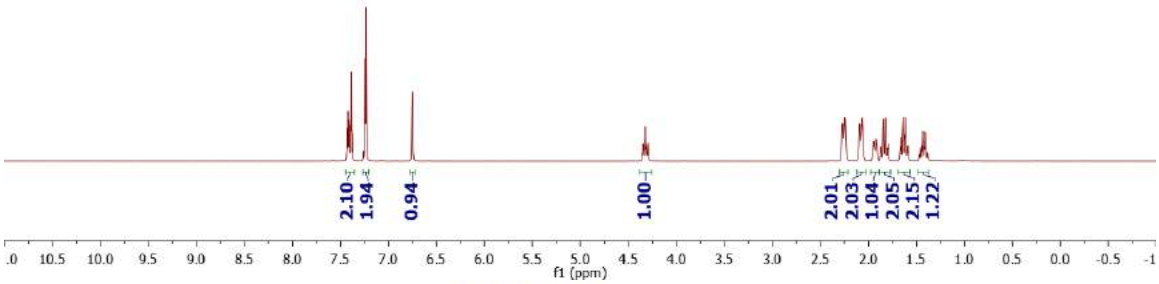
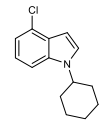


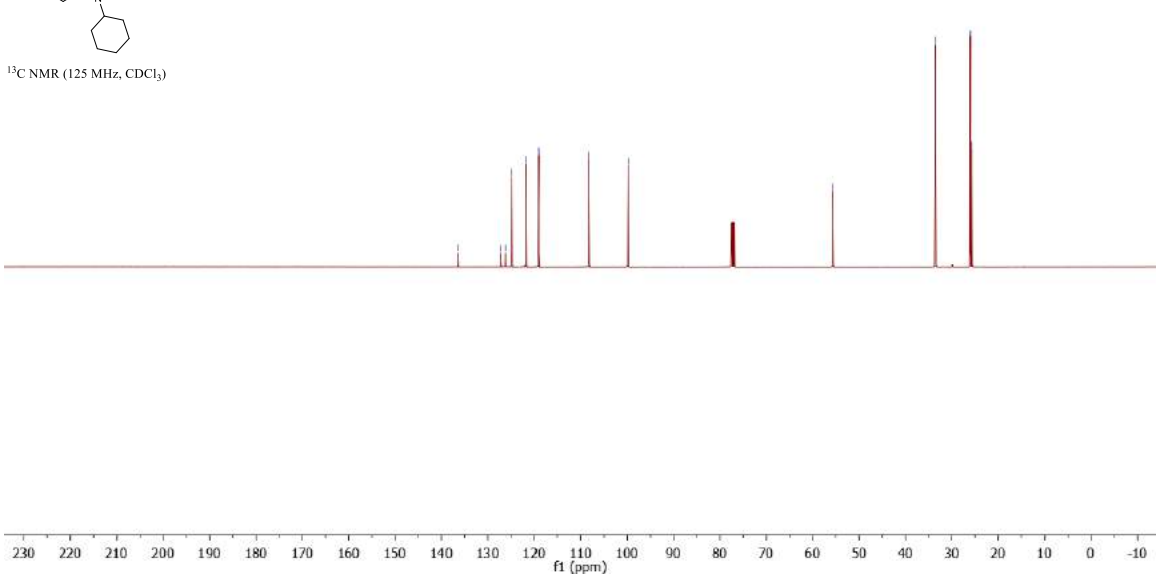


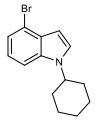
^{1}H NMR (500 MHz, $CDCl_3$)



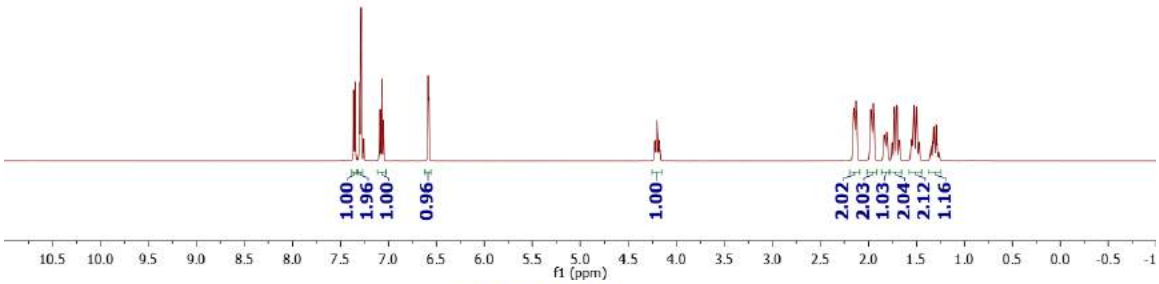


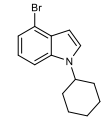
^{13}C NMR (125 MHz, $CDCl_3$)



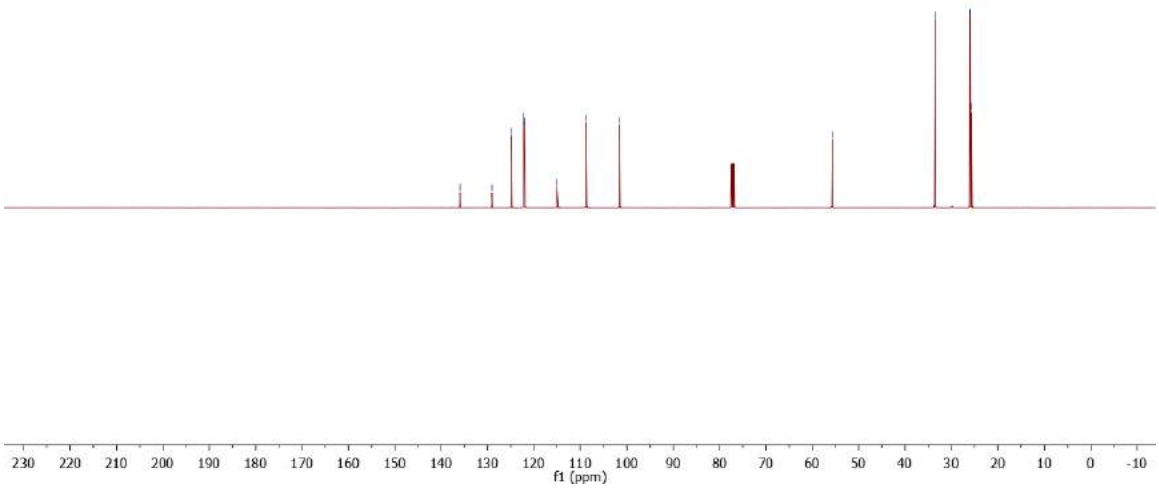


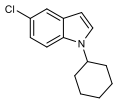
^{1}H NMR (500 MHz, $CDCl_3$)



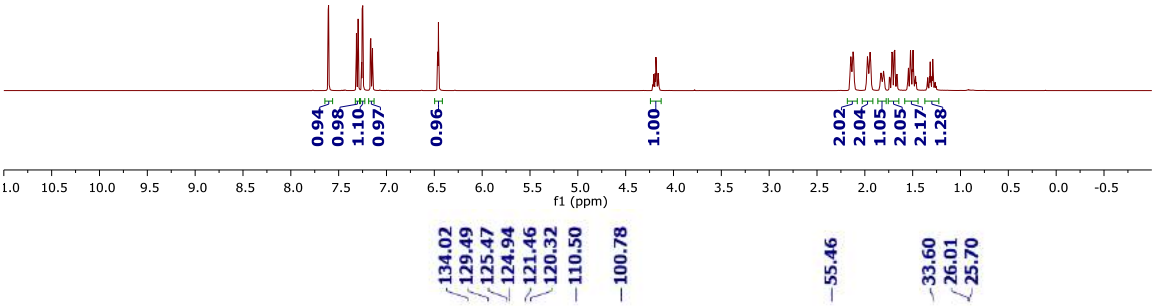


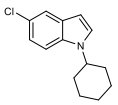
^{13}C NMR (125 MHz, $CDCl_3$)



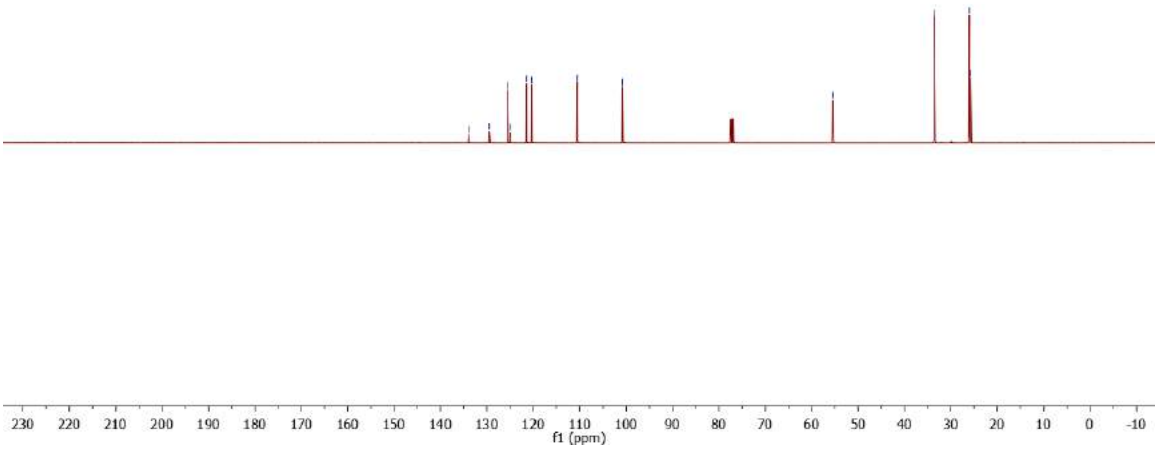


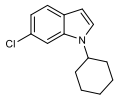
^{1}H NMR (500 MHz, $CDCl_3$)



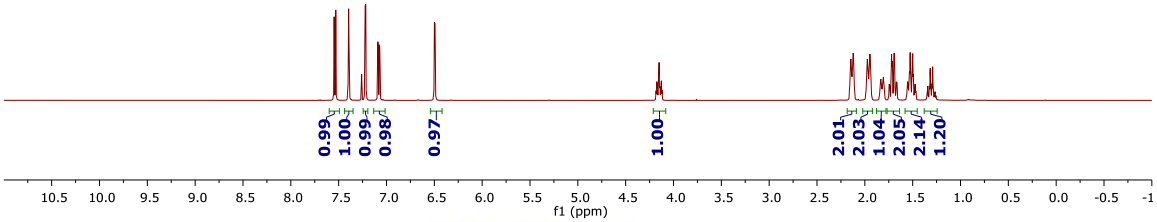


^{13}C NMR (125 MHz, $CDCl_3$)

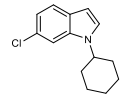




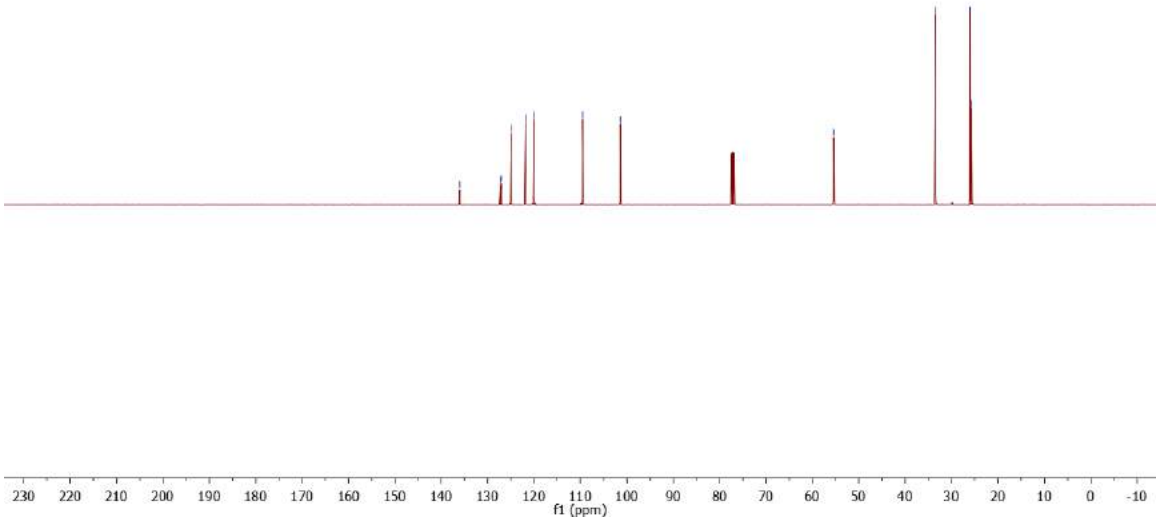
^{1}H NMR (500 MHz, $CDCl_3$)

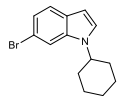


136.03
127.28
127.05
124.92
121.83
120.00
109.59
101.36
55.43
33.57
26.02
25.69

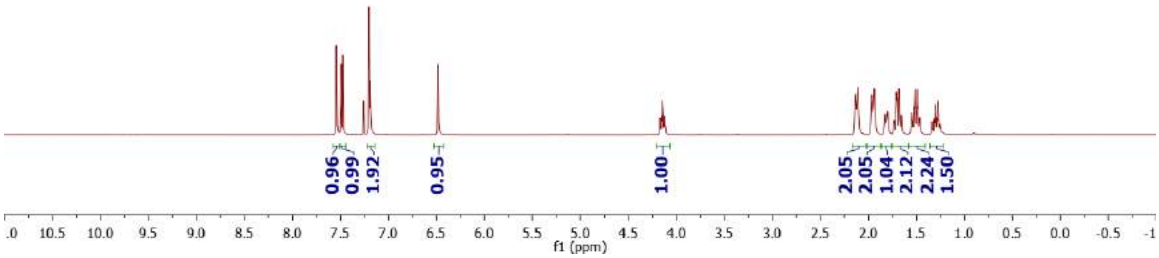


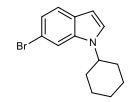
^{13}C NMR (125 MHz, $CDCl_3$)



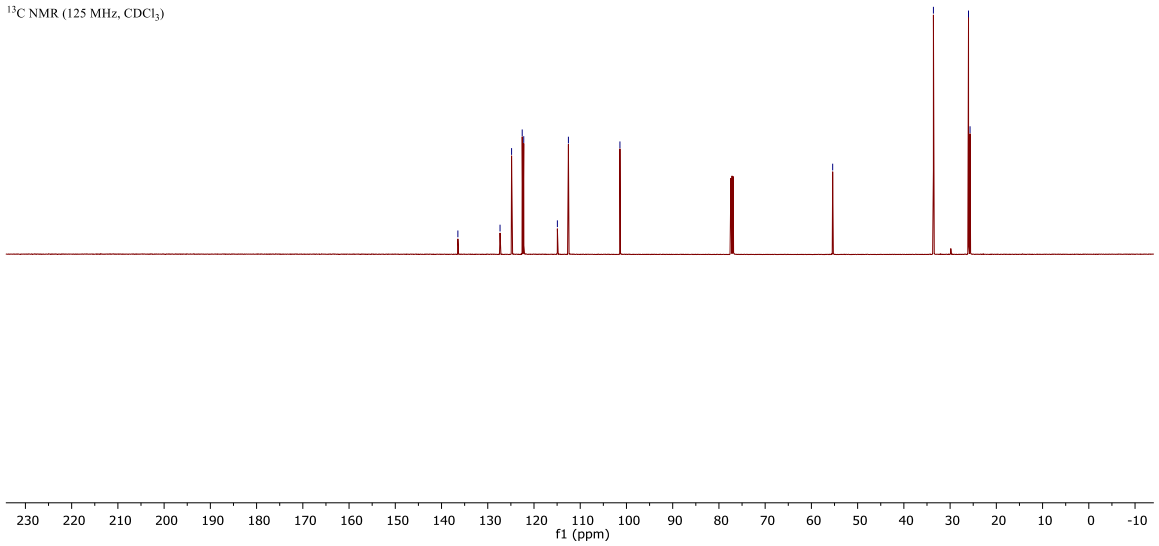


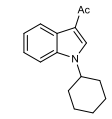
^{1}H NMR (500 MHz, $CDCl_3$)



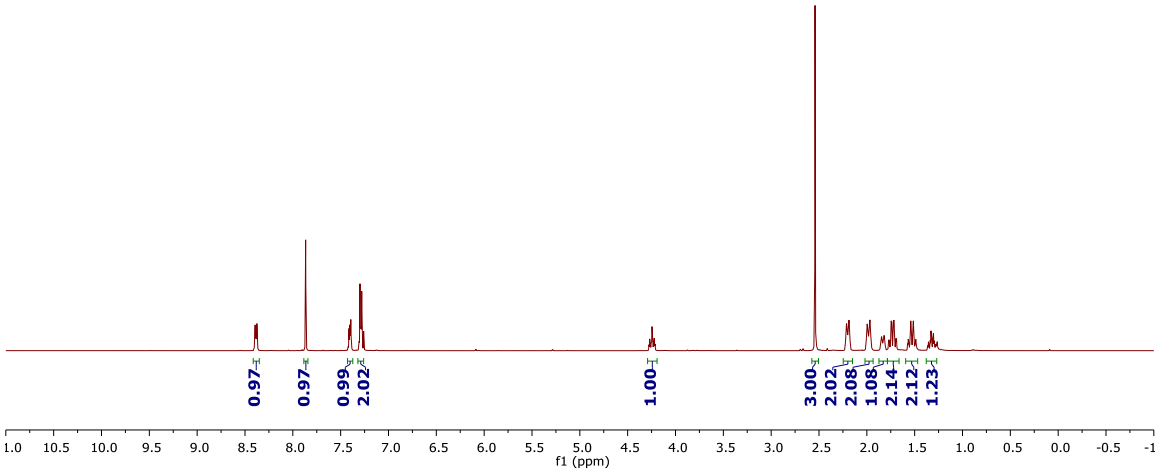


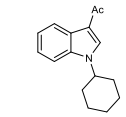
^{13}C NMR (125 MHz, $CDCl_3$)



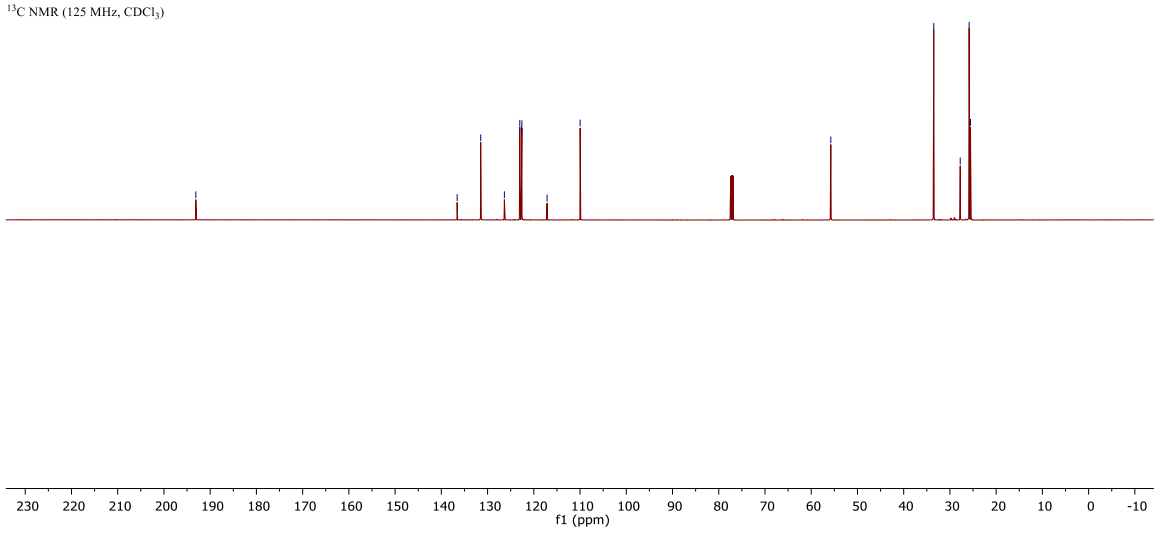


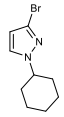
^{1}H NMR (500 MHz, $CDCl_3$)



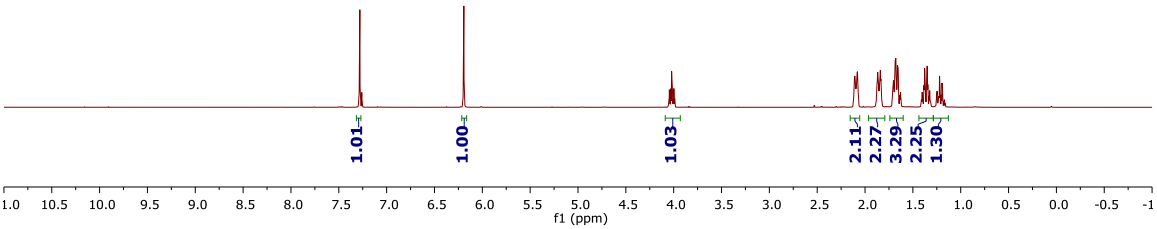


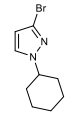
^{13}C NMR (125 MHz, $CDCl_3$)



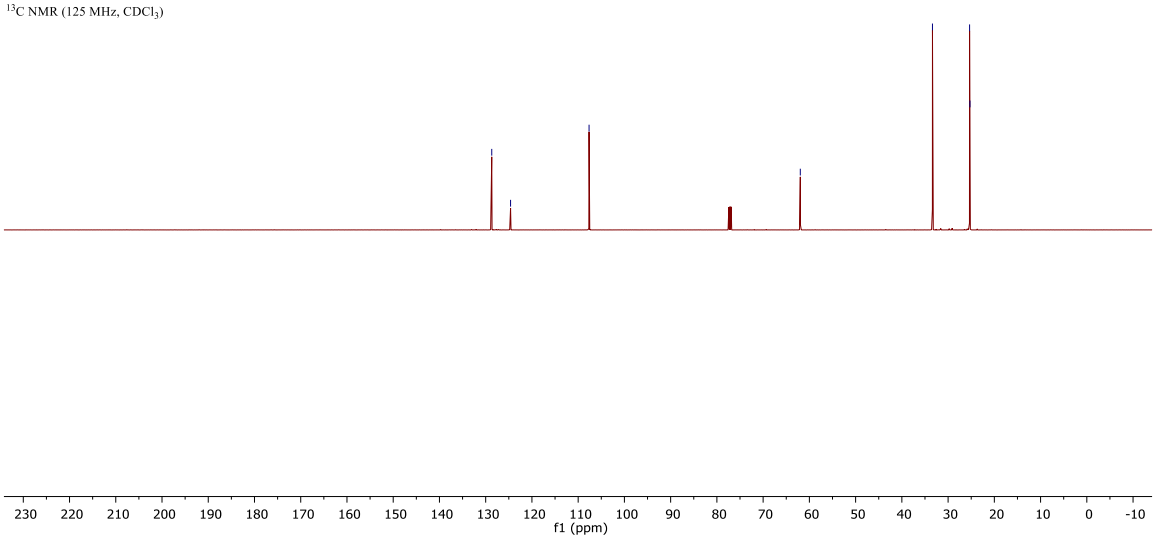


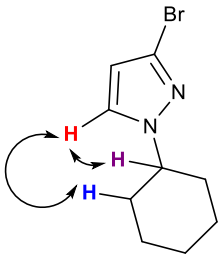
^{1}H NMR (500 MHz, $CDCl_3$)



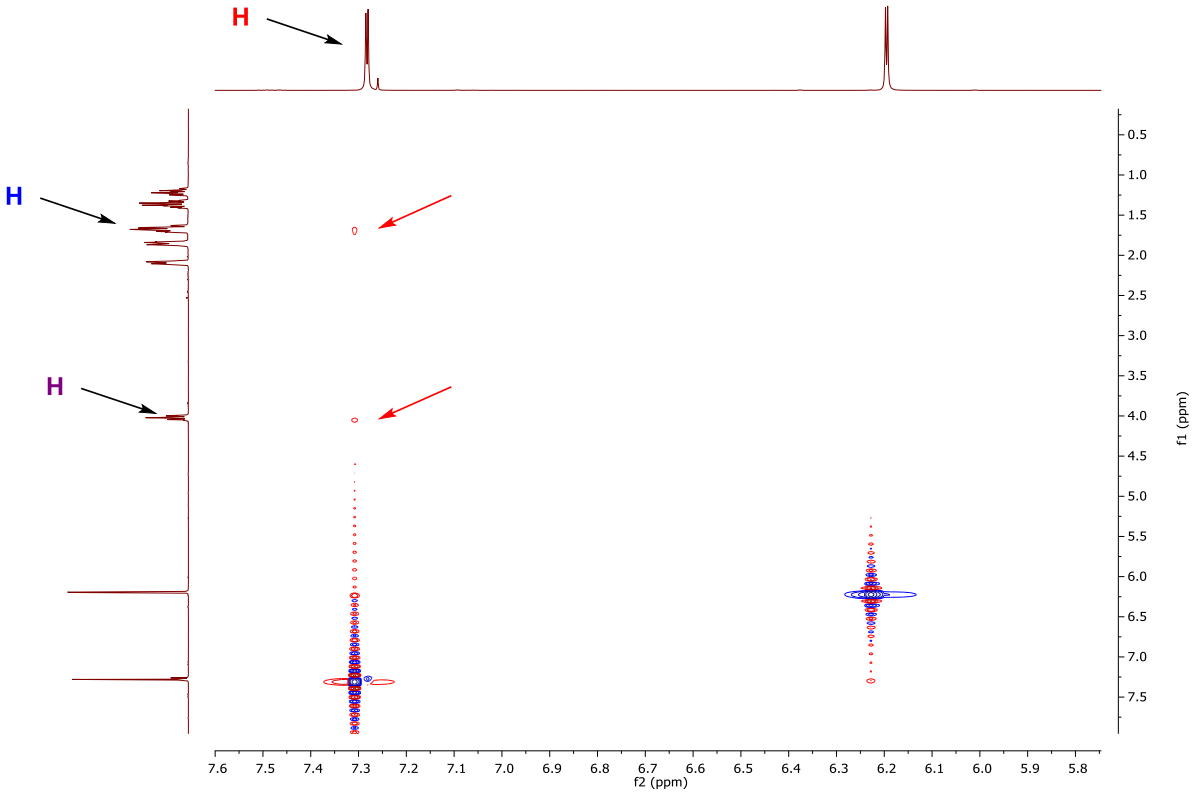


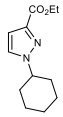
^{13}C NMR (125 MHz, $CDCl_3$)



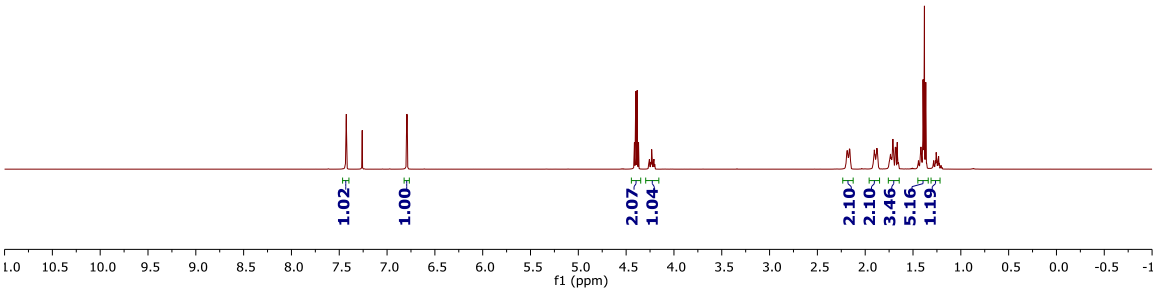

Br
N
N
H
H
H

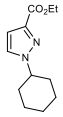
NOESY, $CDCl_3$


H
H
H
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8
f2 (ppm)
0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5
f1 (ppm)

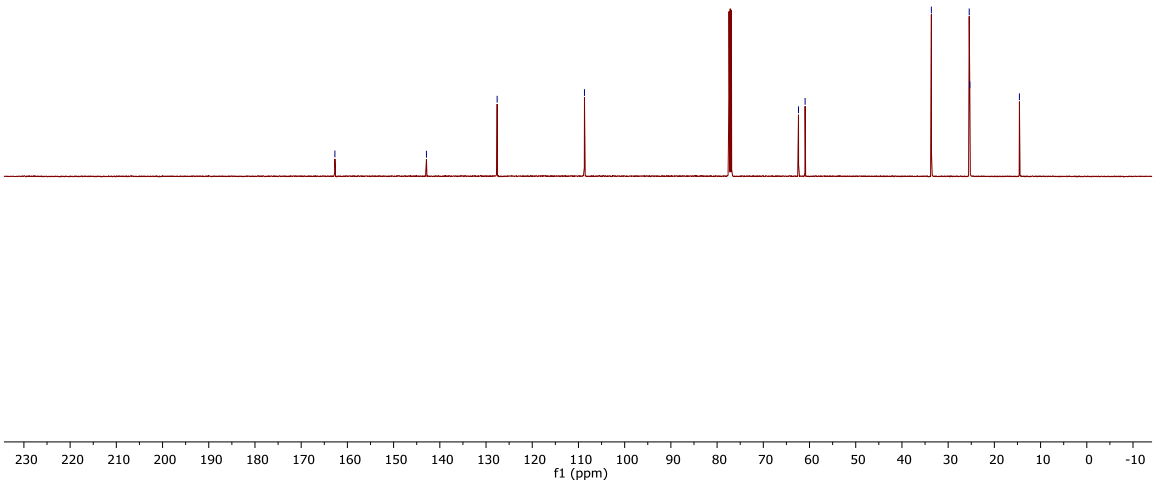


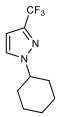
^{1}H NMR (500 MHz, $CDCl_3$)



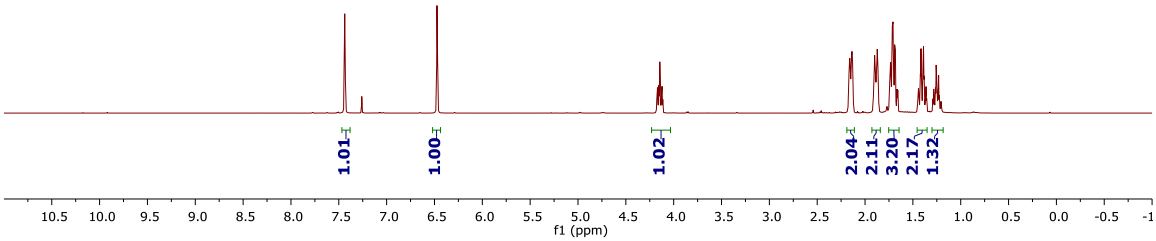


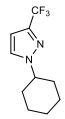
^{13}C NMR (125 MHz, $CDCl_3$)



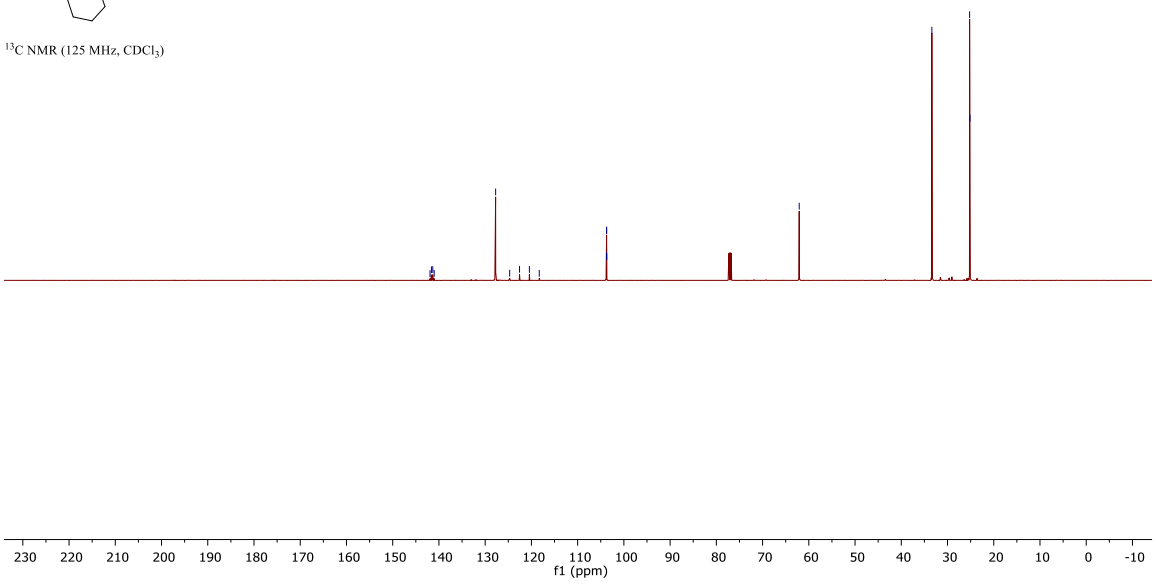


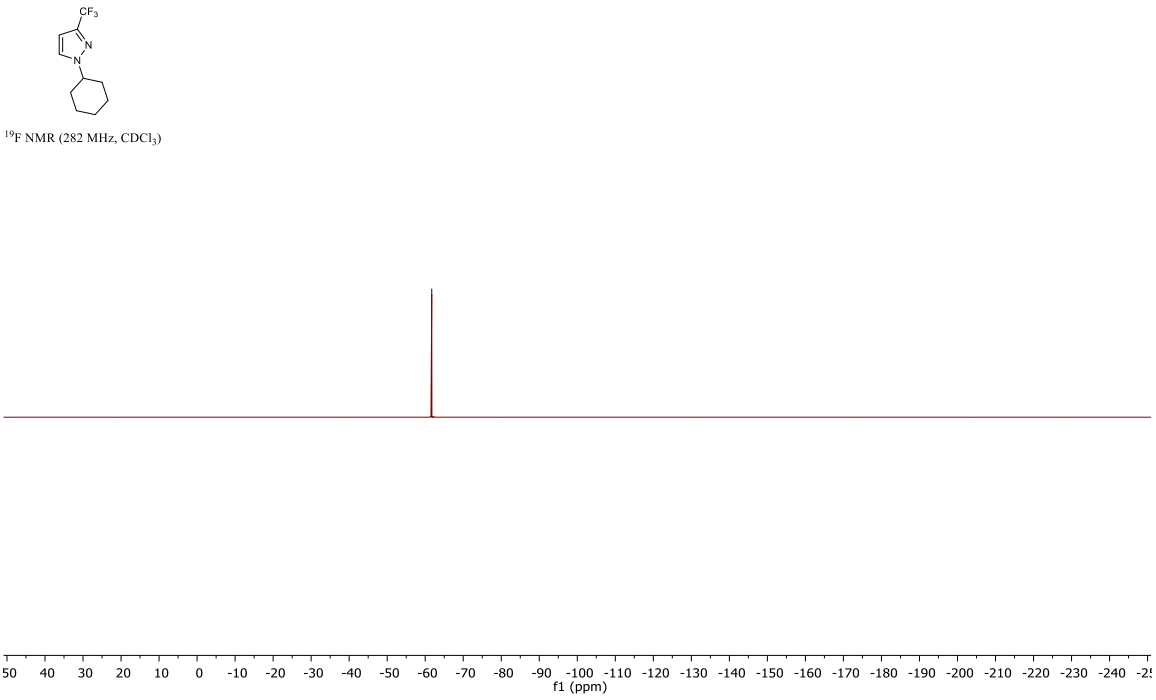
^{1}H NMR (500 MHz, $CDCl_3$)



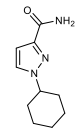


^{13}C NMR (125 MHz, $CDCl_3$)

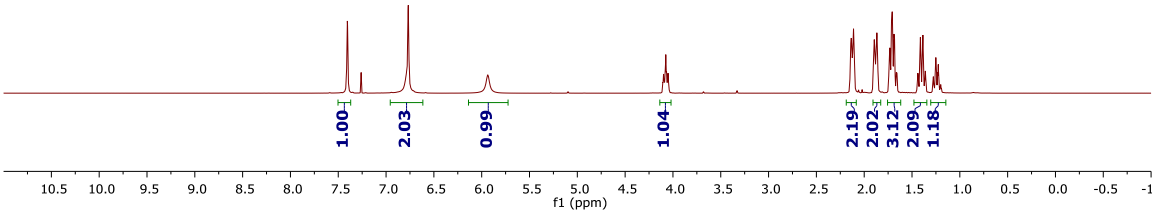


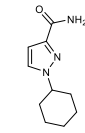


^{19}F NMR (282 MHz, $CDCl_3$)

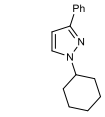


^{1}H NMR (500 MHz, $CDCl_3$)

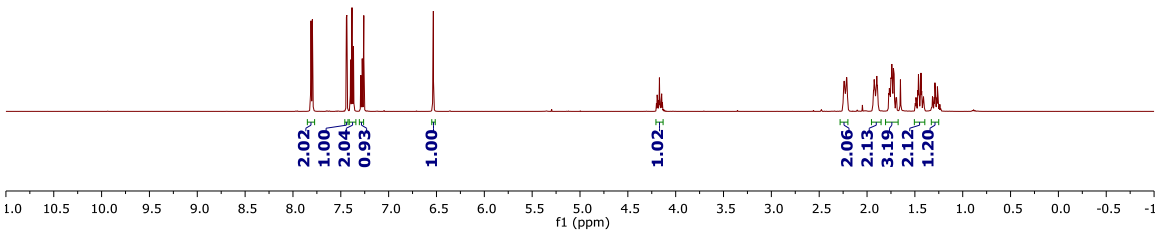


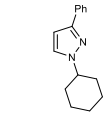


^{13}C NMR (125 MHz, $CDCl_3$)

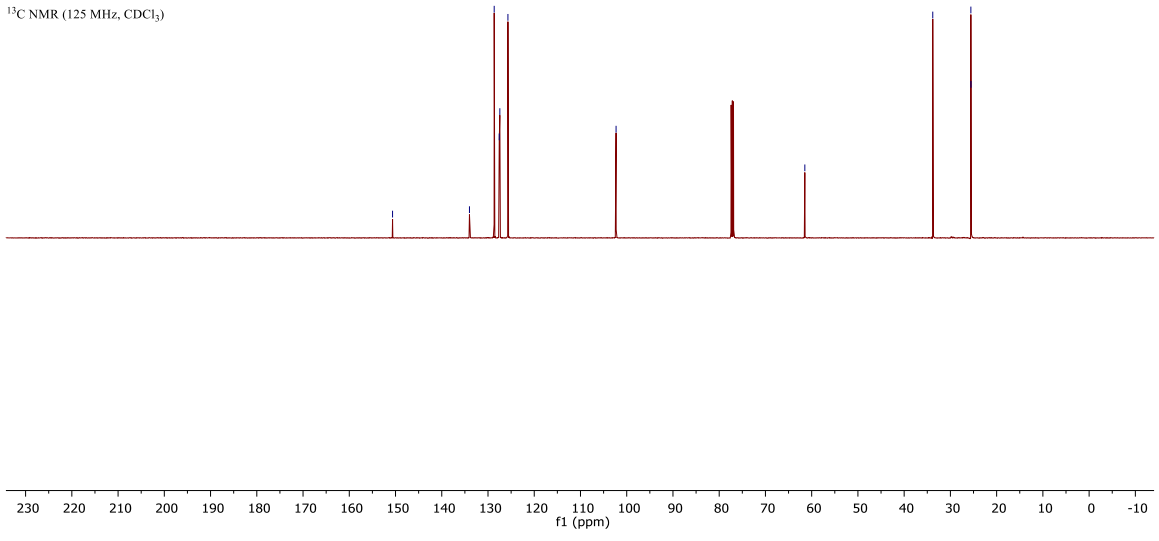


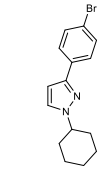
^{1}H NMR (500 MHz, $CDCl_3$)



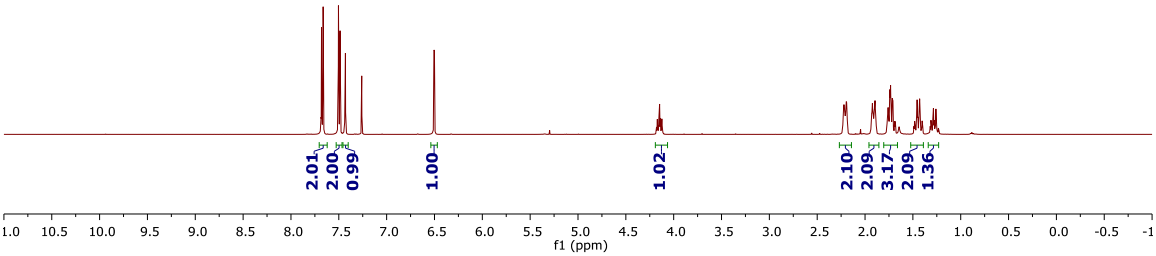


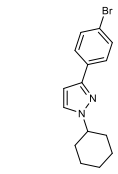
^{13}C NMR (125 MHz, $CDCl_3$)



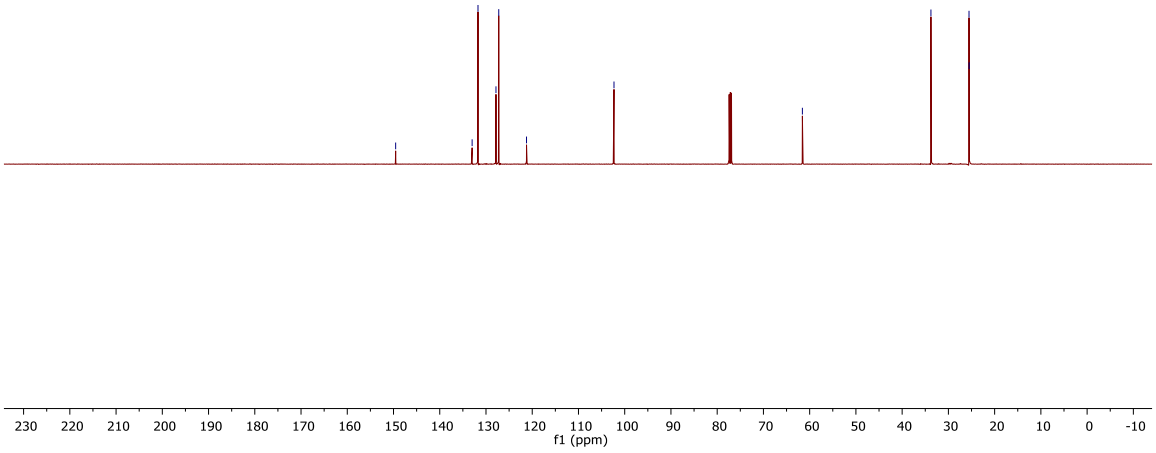


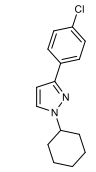
^{1}H NMR (500 MHz, $CDCl_3$)



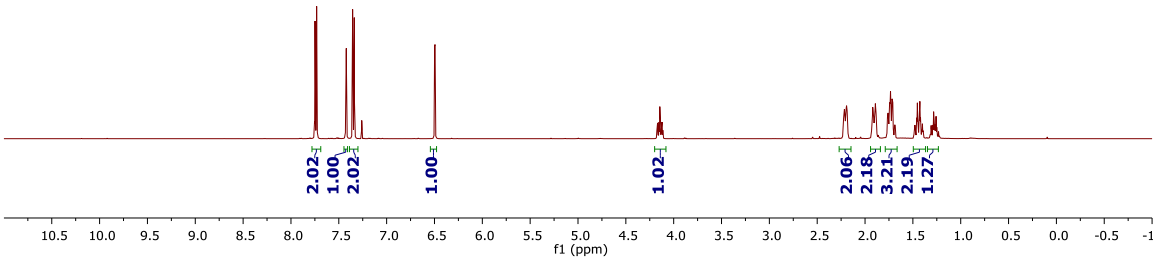


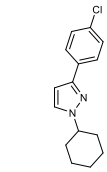
^{13}C NMR (125 MHz, $CDCl_3$)



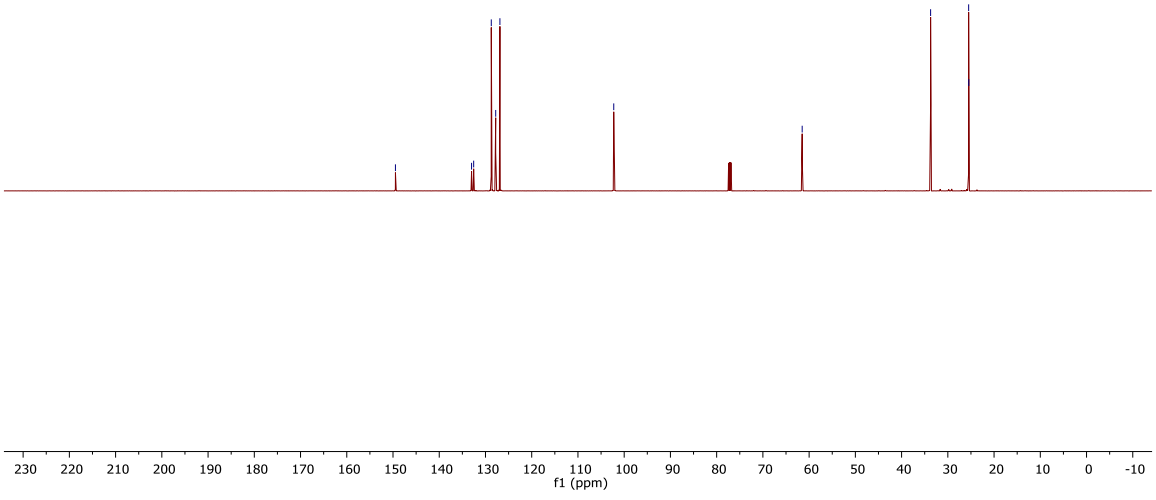


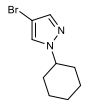
^{1}H NMR (500 MHz, $CDCl_3$)



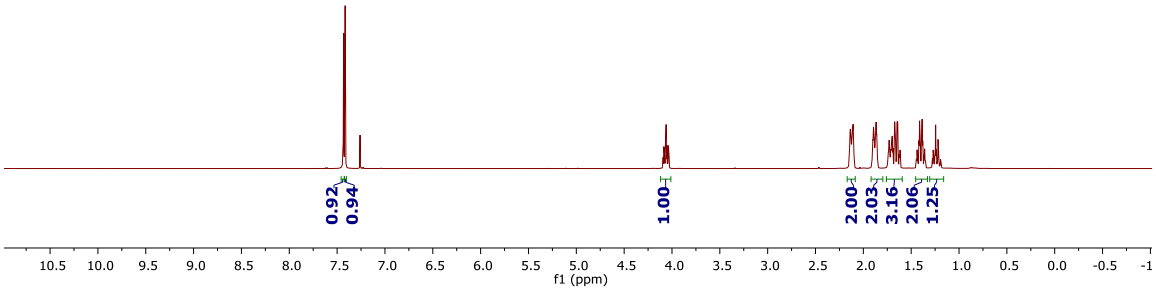


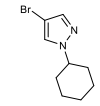
^{13}C NMR (125 MHz, $CDCl_3$)



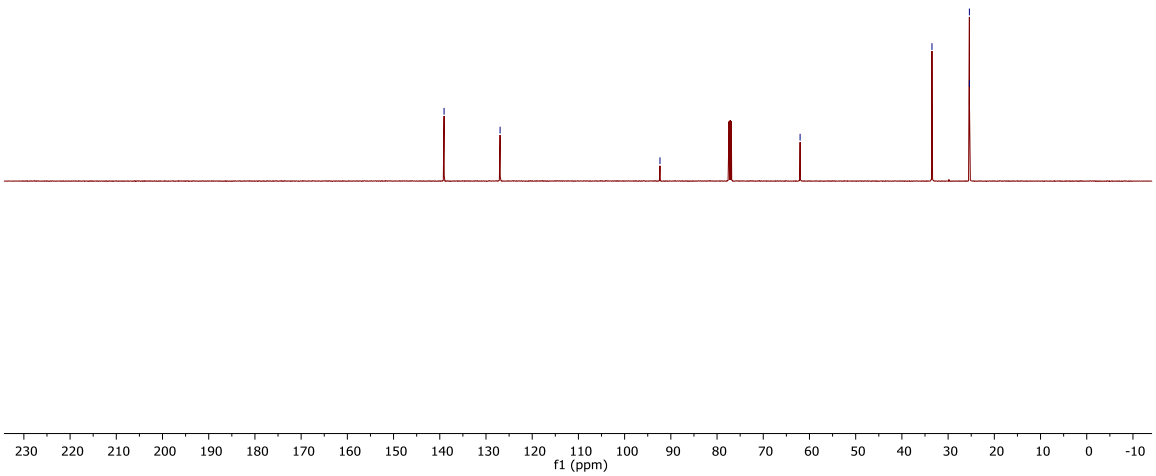


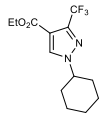
^{1}H NMR (500 MHz, $CDCl_3$)



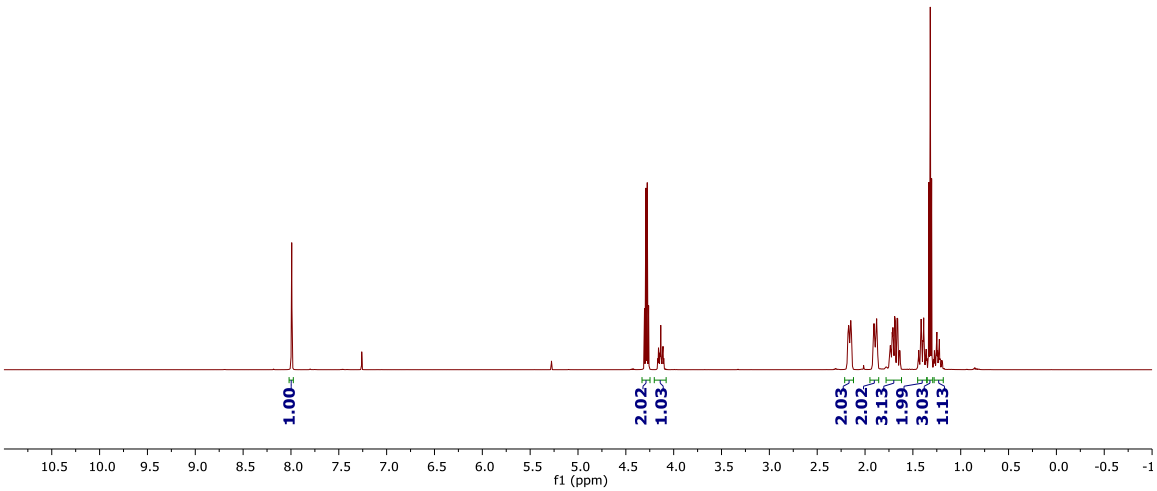


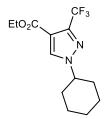
^{13}C NMR (125 MHz, $CDCl_3$)



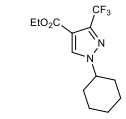


^{1}H NMR (500 MHz, $CDCl_3$)



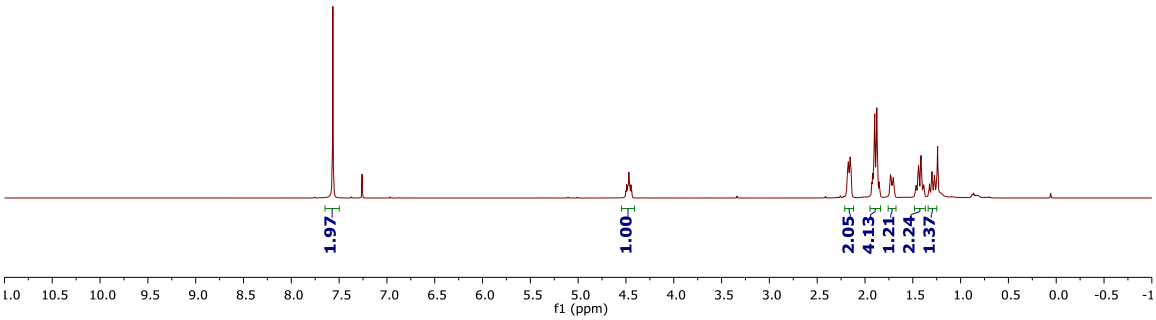


^{13}C NMR (125 MHz, $CDCl_3$)

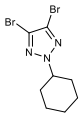


^{19}F NMR (282 MHz, $CDCl_3$)

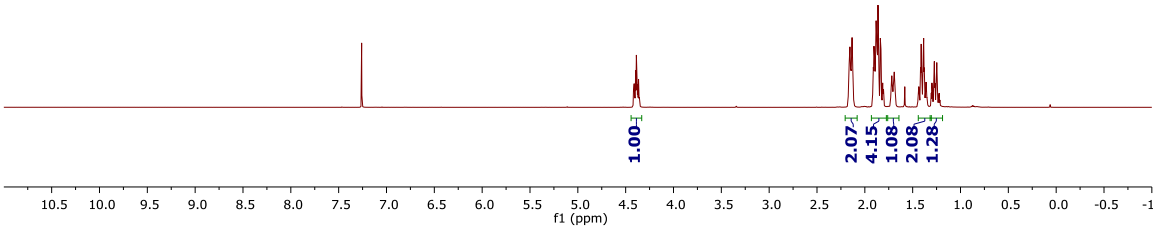
^{1}H NMR (500 MHz, $CDCl_3$)

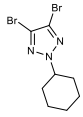


^{13}C NMR (125 MHz, $CDCl_3$)

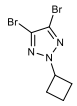


^{1}H NMR (500 MHz, $CDCl_3$)

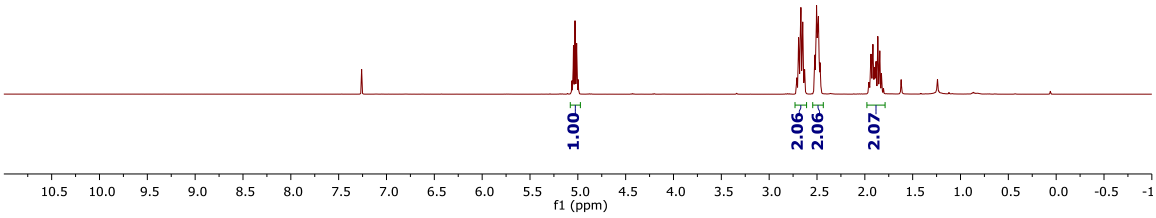


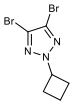


^{13}C NMR (125 MHz, $CDCl_3$)

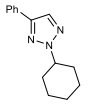


^{1}H NMR (500 MHz, $CDCl_3$)

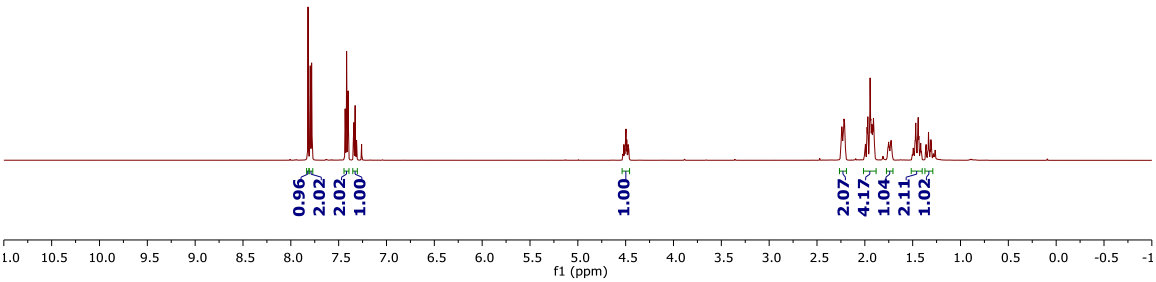


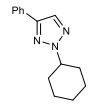


^{13}C NMR (125 MHz, $CDCl_3$)

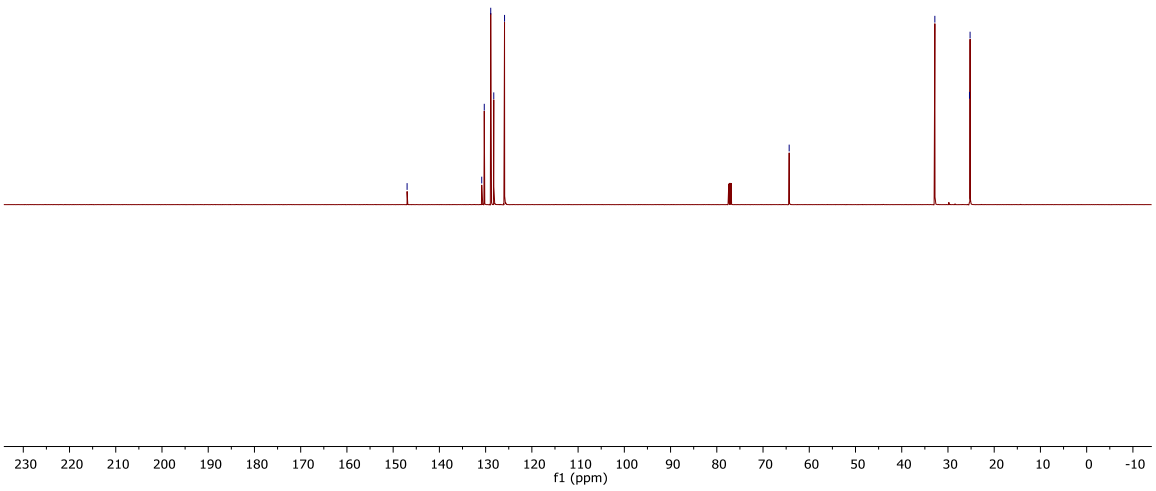


^{1}H NMR (500 MHz, $CDCl_3$)

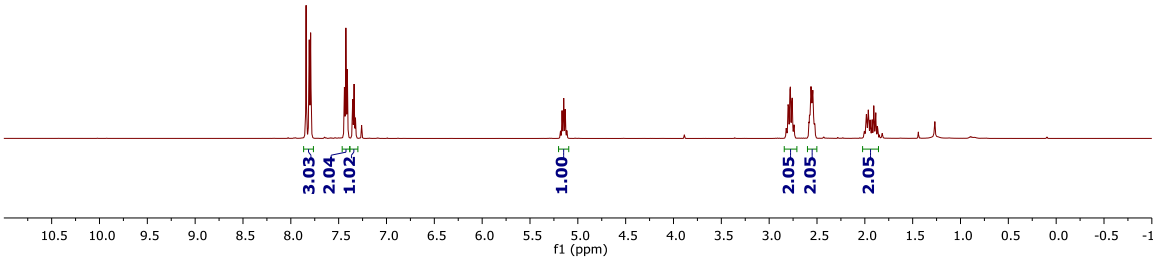




^{13}C NMR (125 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)



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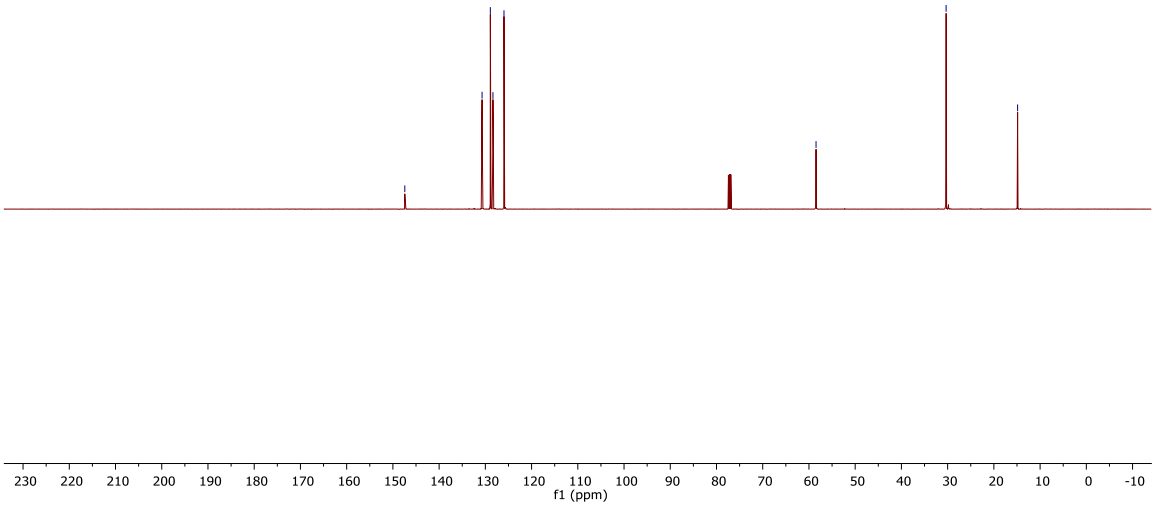

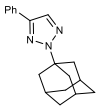

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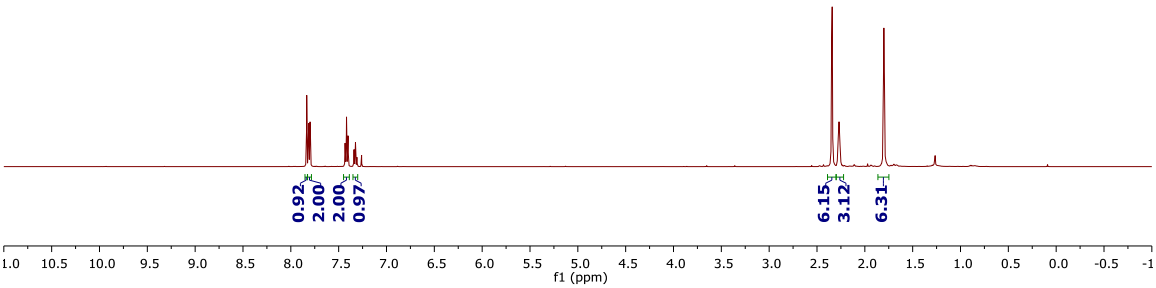
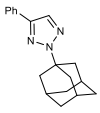
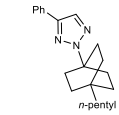
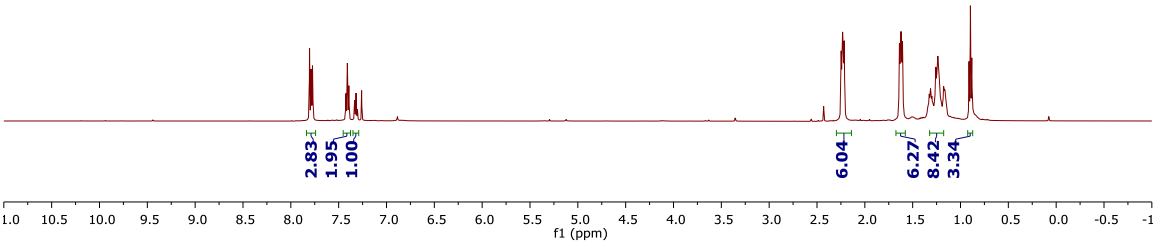


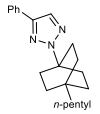


^{13}C NMR (125 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)





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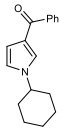

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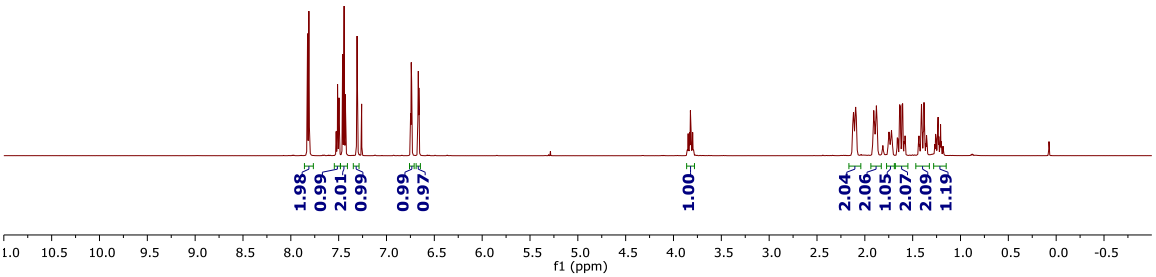
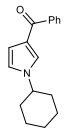
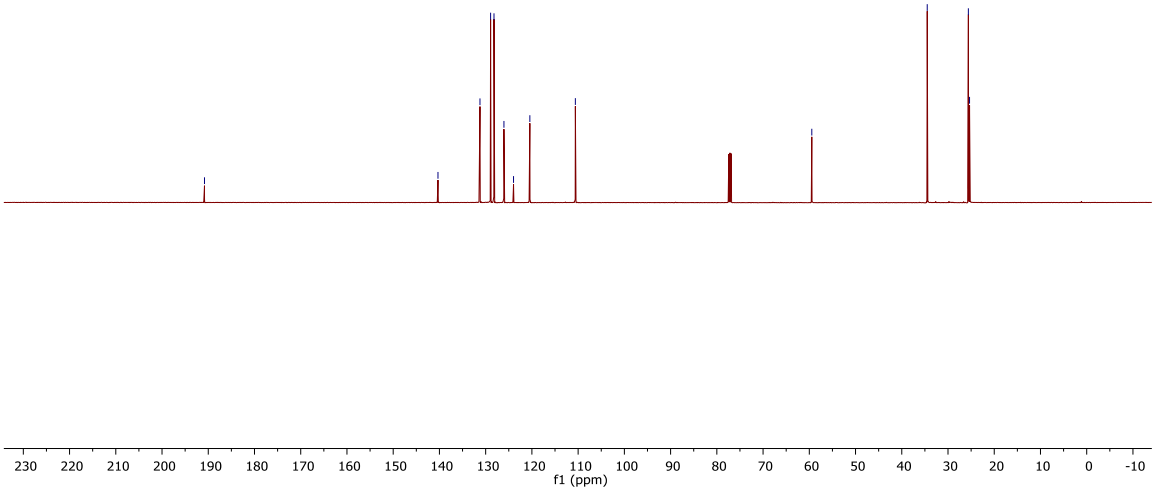
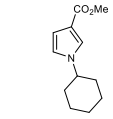


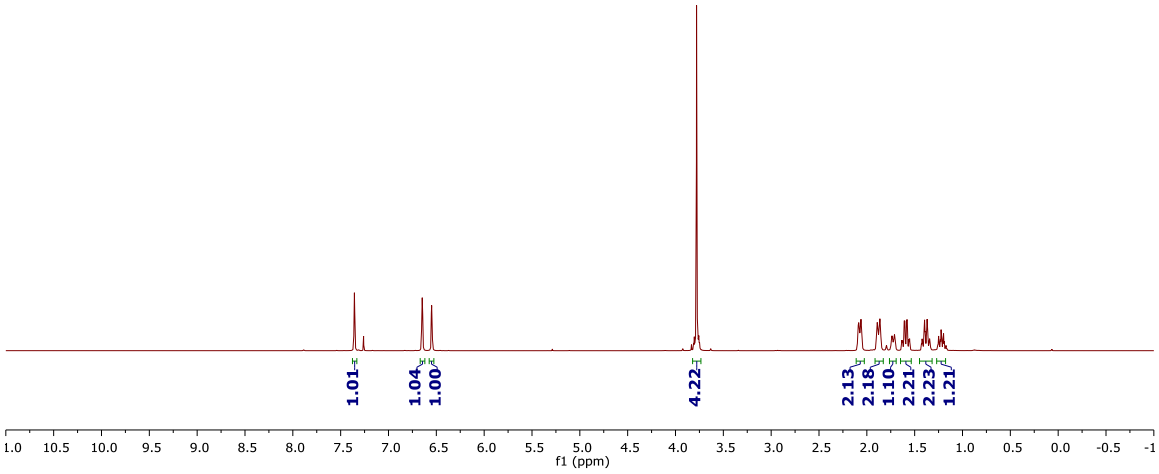


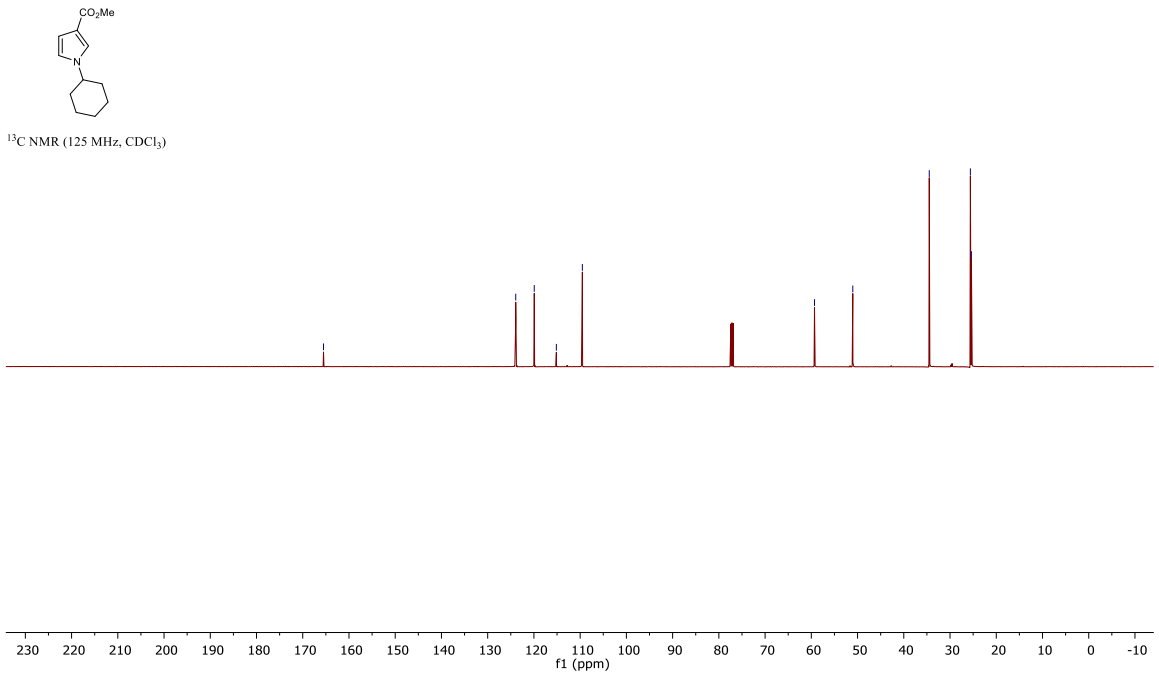
^{13}C NMR (125 MHz, $CDCl_3$)



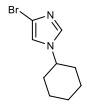


^{1}H NMR (500 MHz, $CDCl_3$)

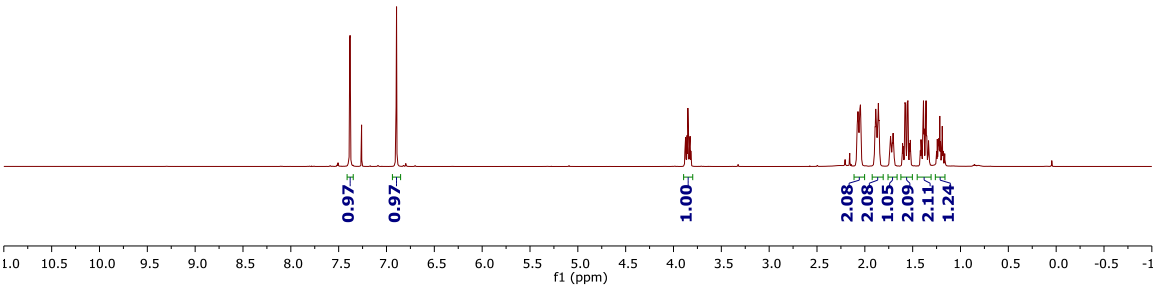


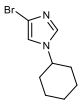


^{13}C NMR (125 MHz, $CDCl_3$)

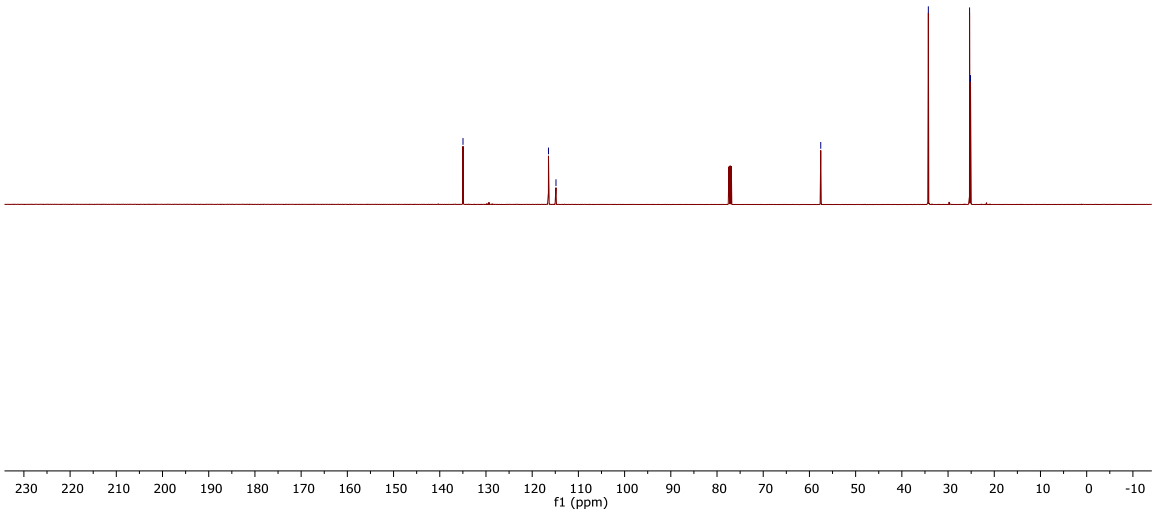


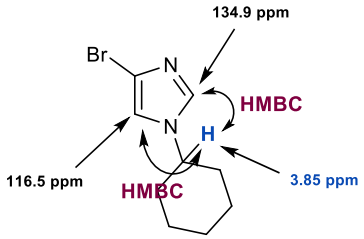
^{1}H NMR (500 MHz, $CDCl_3$)





^{13}C NMR (125 MHz, $CDCl_3$)

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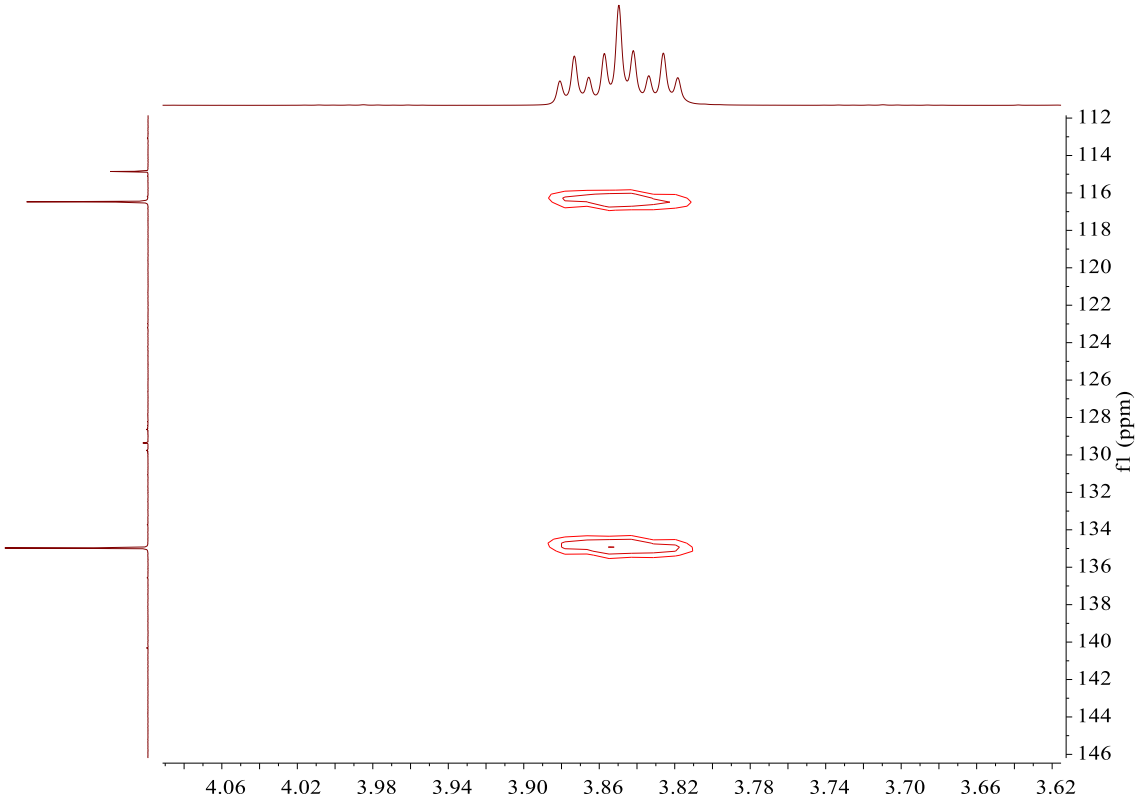
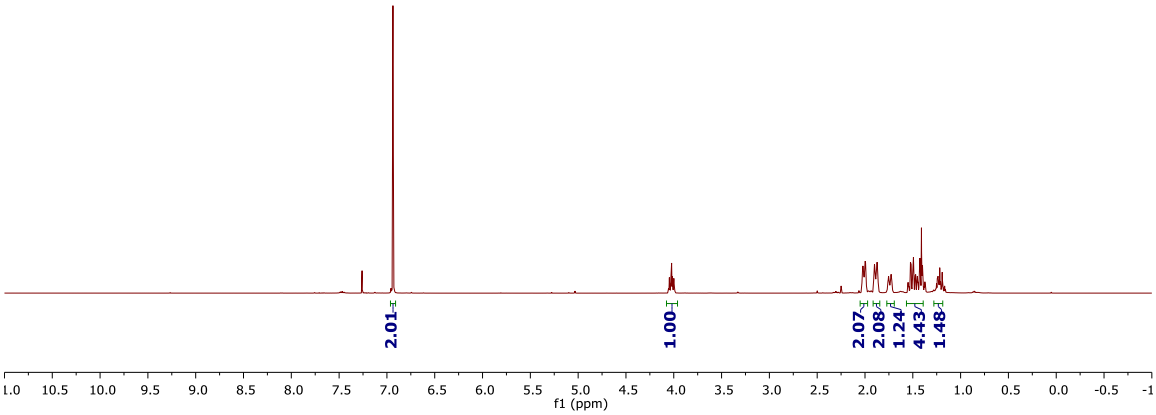
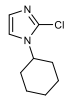
Br
N
N
HMBC
H
116.5 ppm
HMBC
3.85 ppm

HMBC, $CDCl_3$

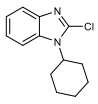

112
114
116
118
120
122
124
126
128
130
132
134
136
138
140
142
144
146
f1 (ppm)
4.06
4.02
3.98
3.94
3.90
3.86
3.82
3.78
3.74
3.70
3.66
3.62

^{1}H NMR (500 MHz, $CDCl_3$)

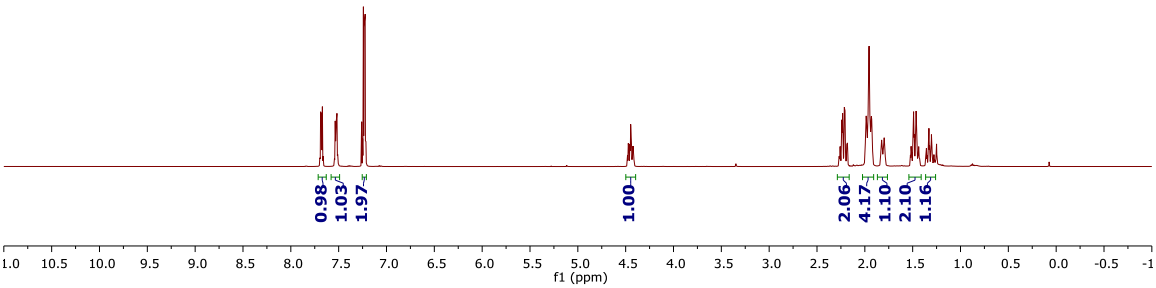


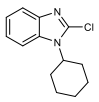


^{13}C NMR (125 MHz, $CDCl_3$)

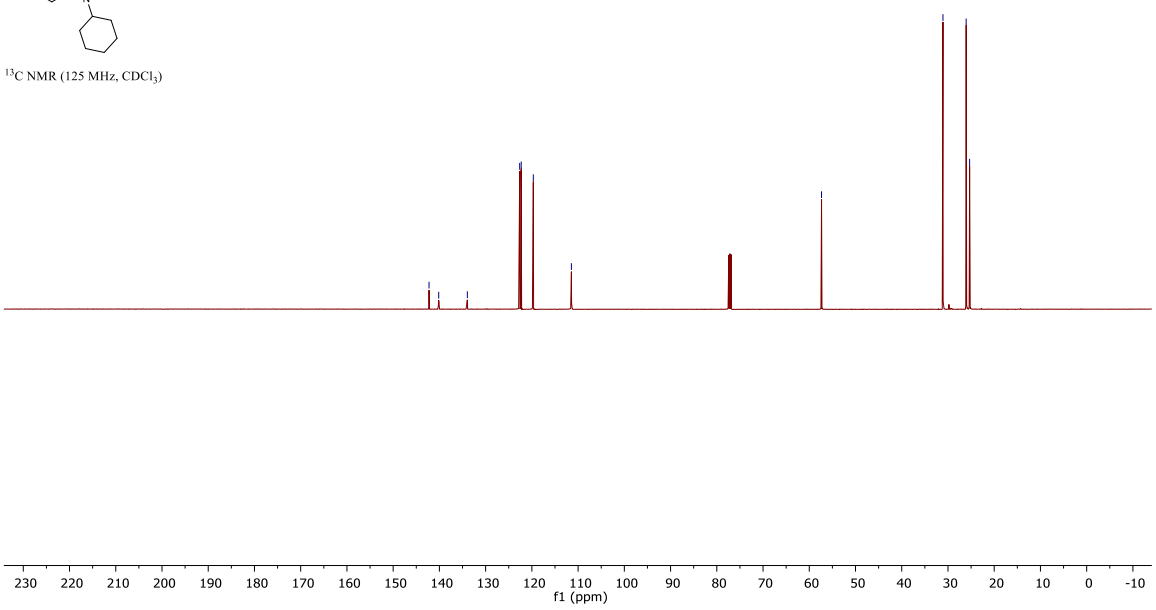


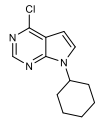
^{1}H NMR (500 MHz, $CDCl_3$)



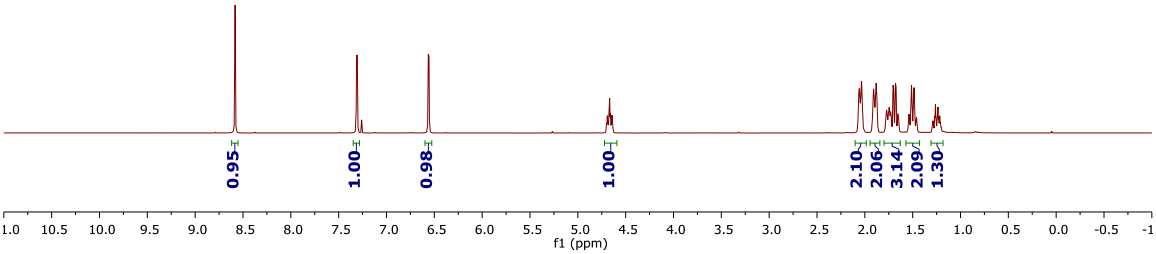


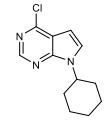
^{13}C NMR (125 MHz, $CDCl_3$)



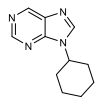


^{1}H NMR (500 MHz, $CDCl_3$)

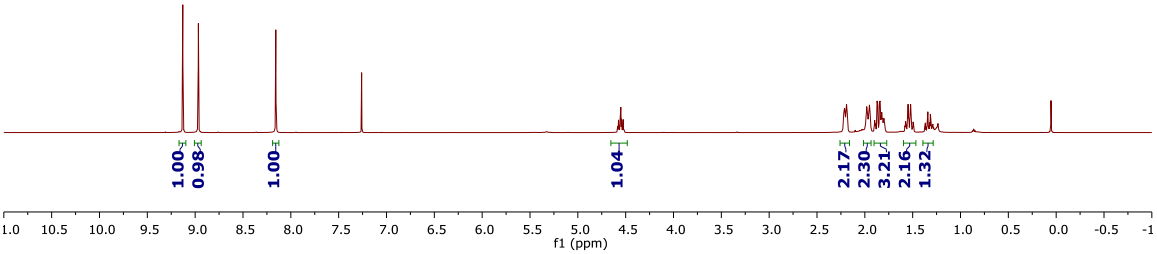


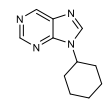


^{13}C NMR (125 MHz, $CDCl_3$)

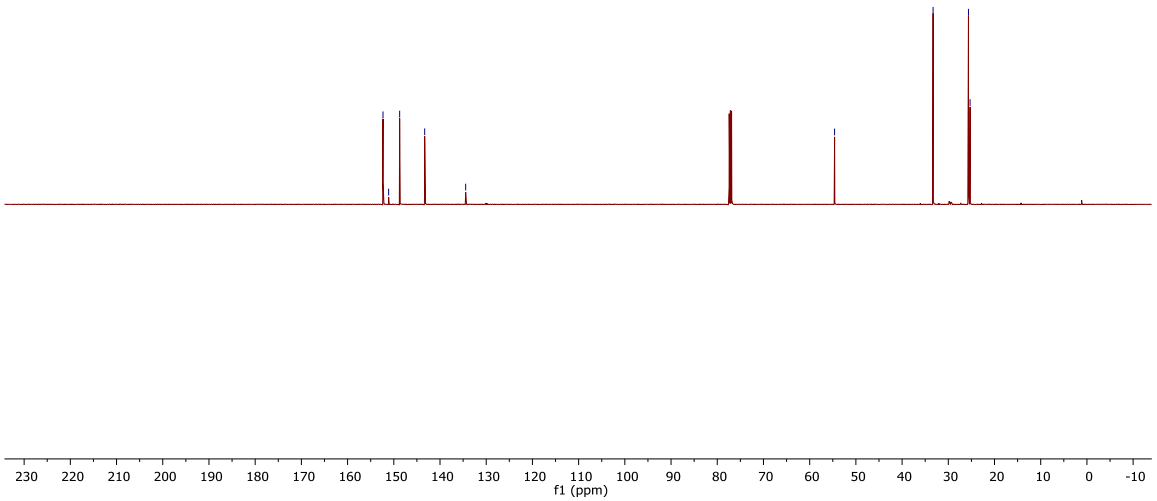


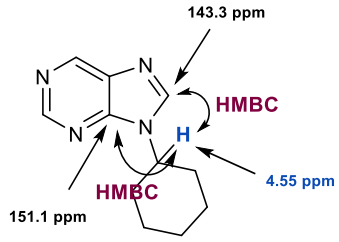
^{1}H NMR (500 MHz, $CDCl_3$)





^{13}C NMR (125 MHz, $CDCl_3$)

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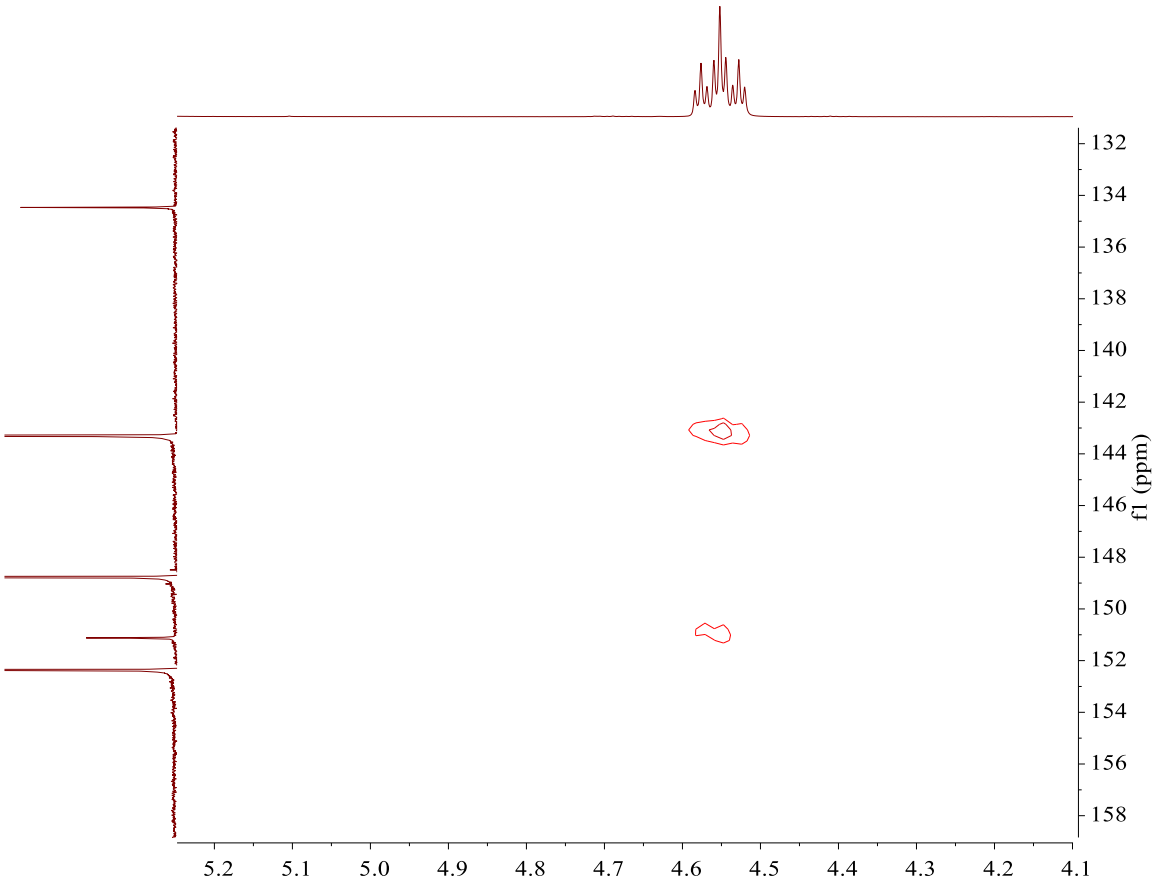
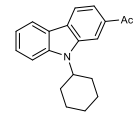
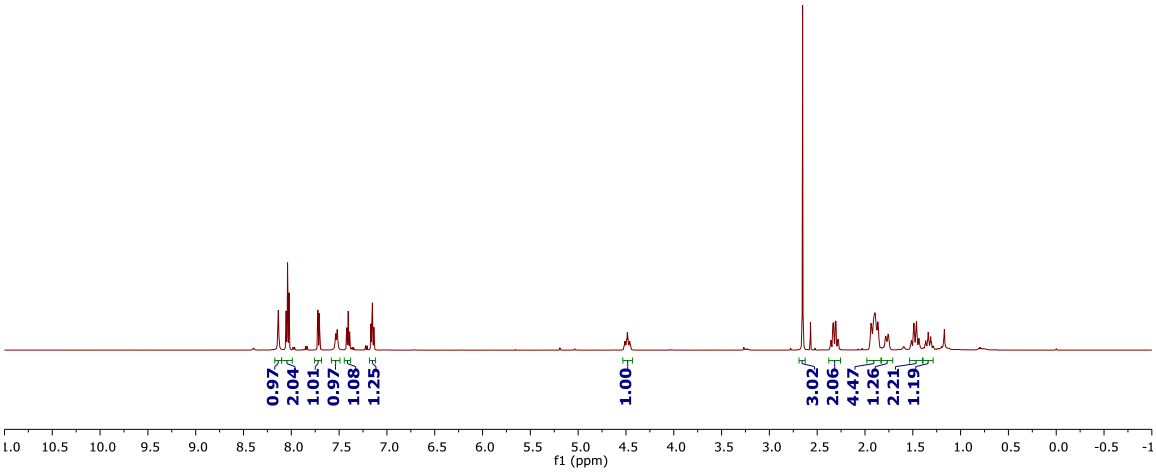
HMBC
H
4.55 ppm
HMBC
151.1 ppm

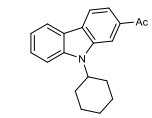
HMBC, $CDCl_3$


132
134
136
138
140
142
144
146
148
150
152
154
156
158
f1 (ppm)
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1

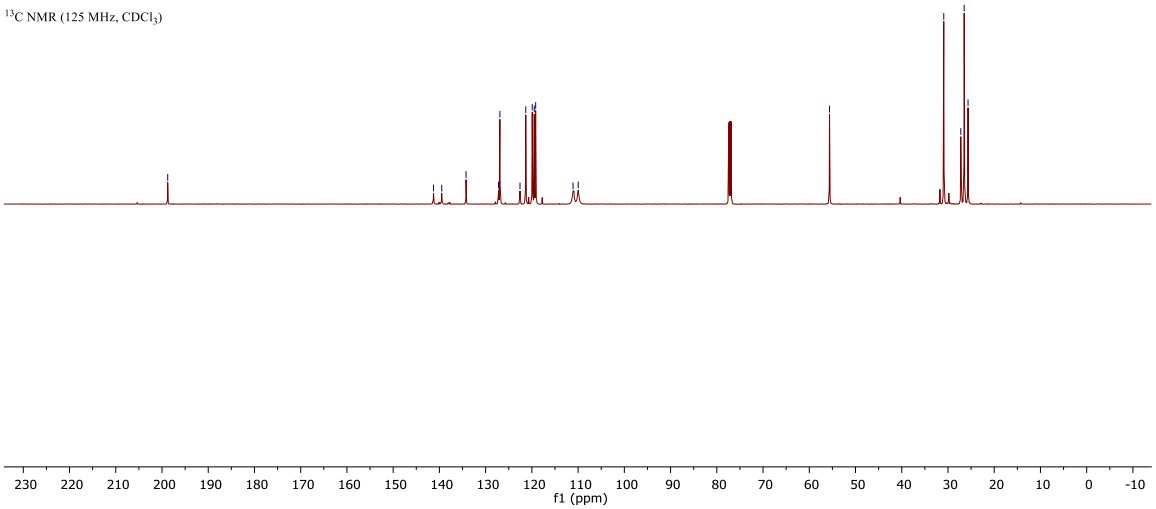


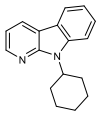
^{1}H NMR (500 MHz, $CDCl_3$)



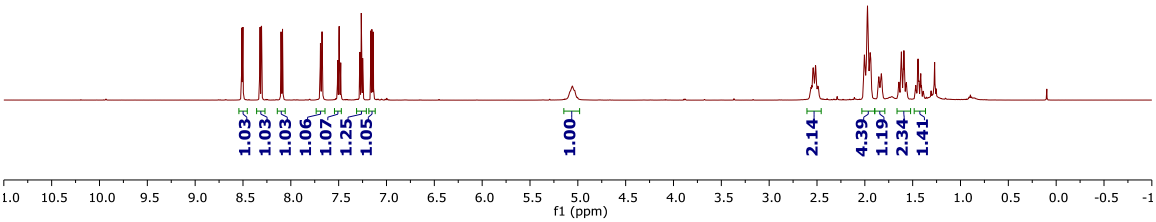


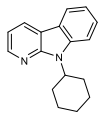
^{13}C NMR (125 MHz, $CDCl_3$)



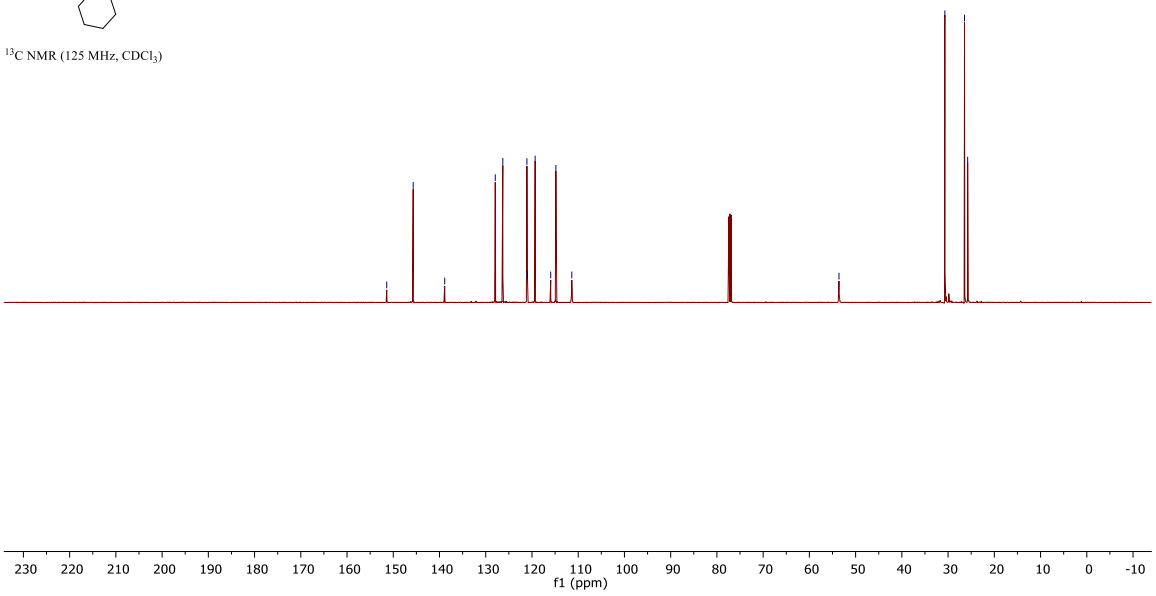


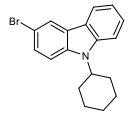
^{1}H NMR (500 MHz, $CDCl_3$)



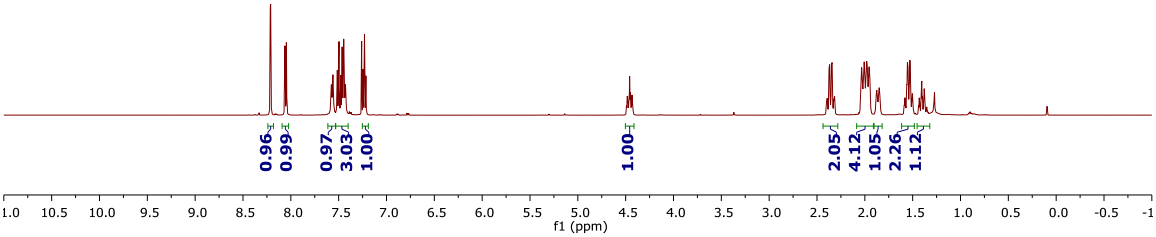


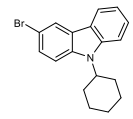
^{13}C NMR (125 MHz, $CDCl_3$)



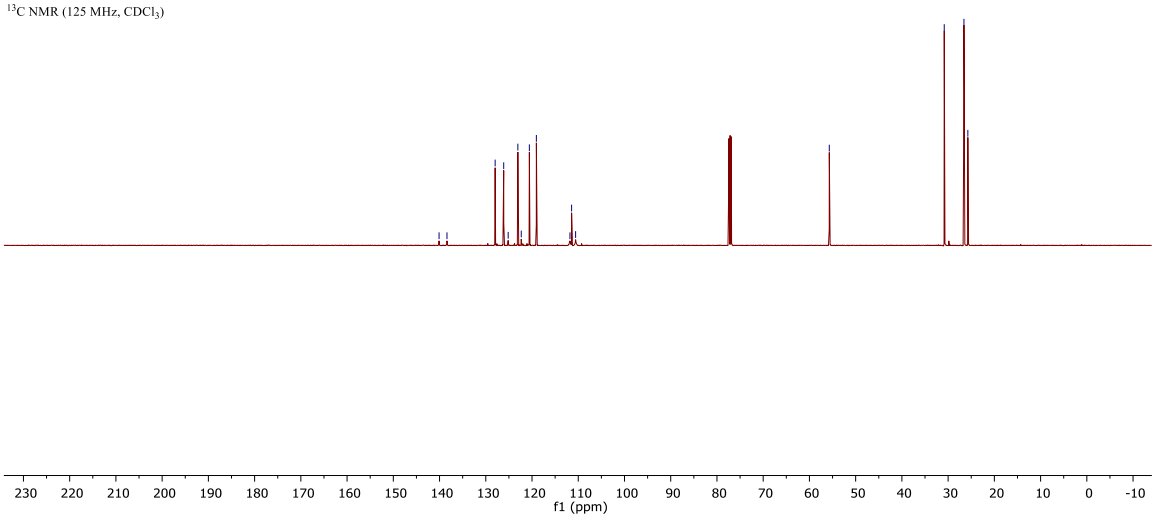


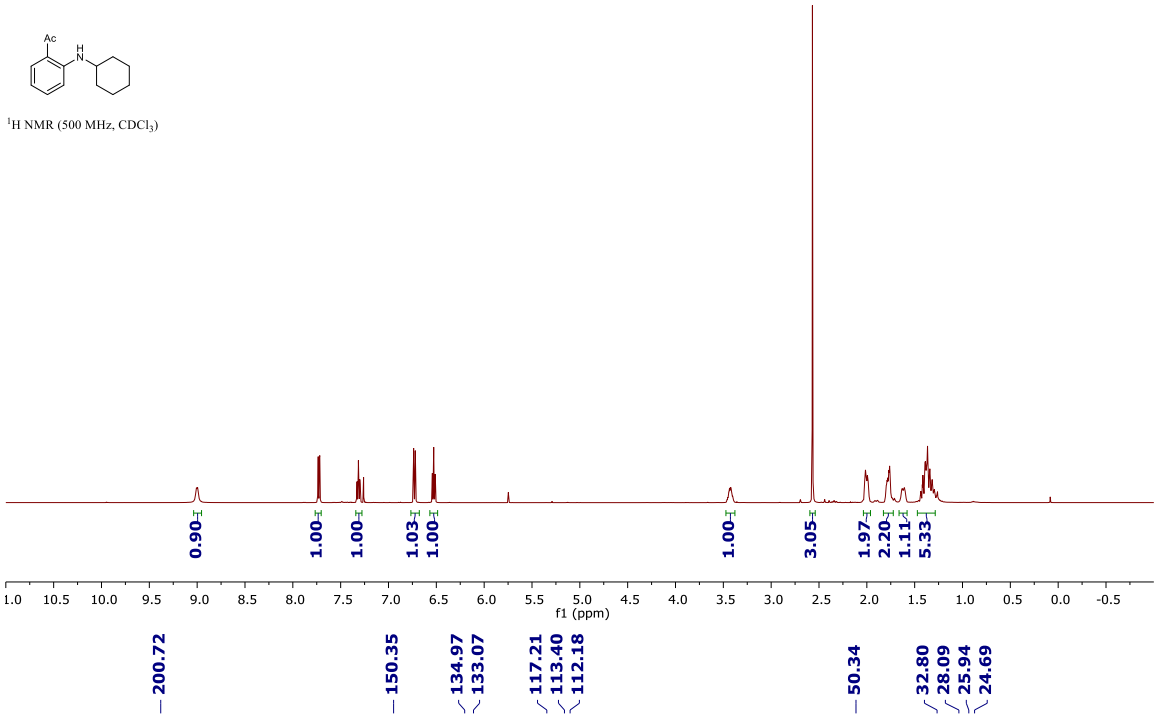
^{1}H NMR (500 MHz, $CDCl_3$)





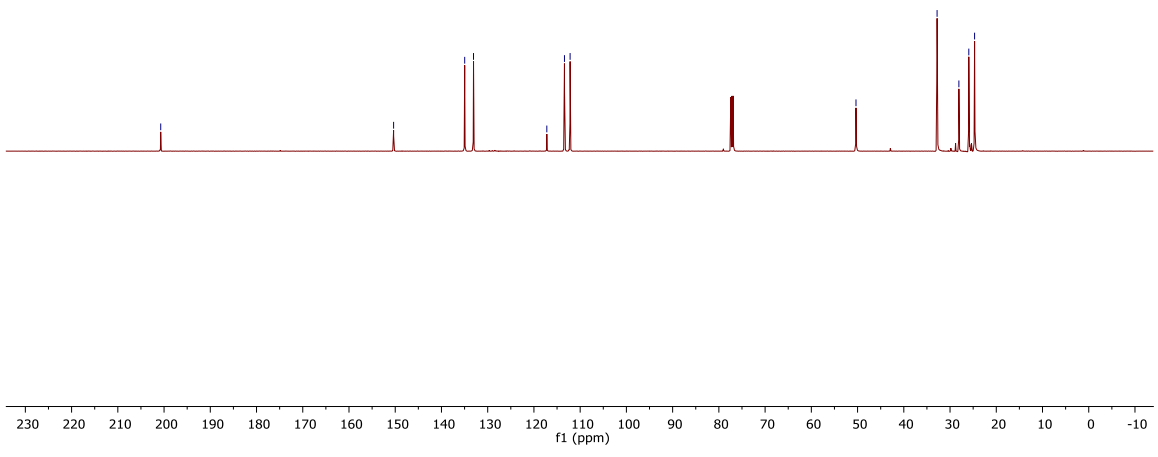
^{13}C NMR (125 MHz, $CDCl_3$)

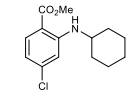




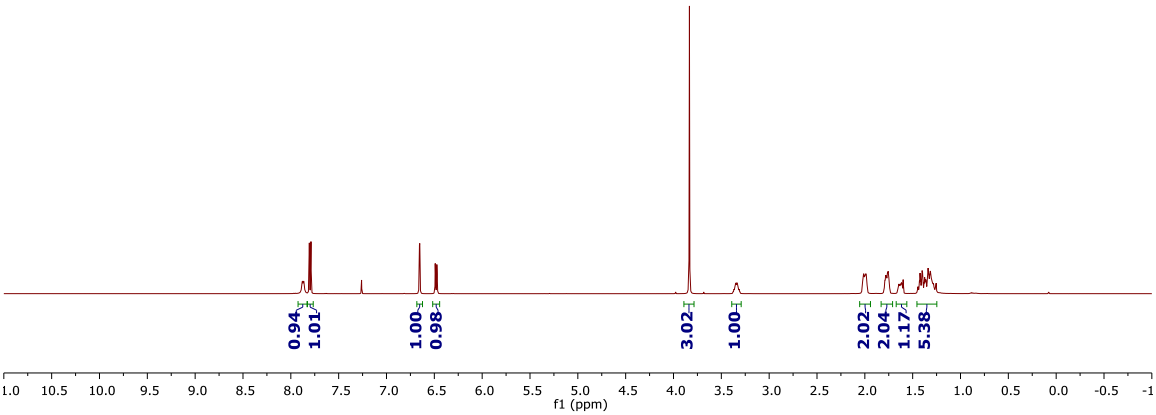
^{1}H NMR (500 MHz, $CDCl_3$)

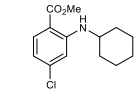
^{13}C NMR (125 MHz, $CDCl_3$)



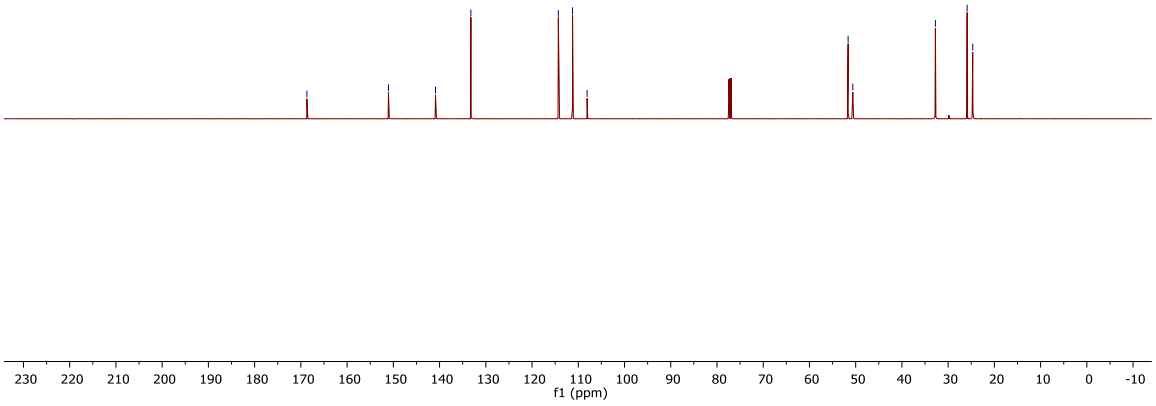


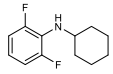
^{1}H NMR (500 MHz, $CDCl_3$)



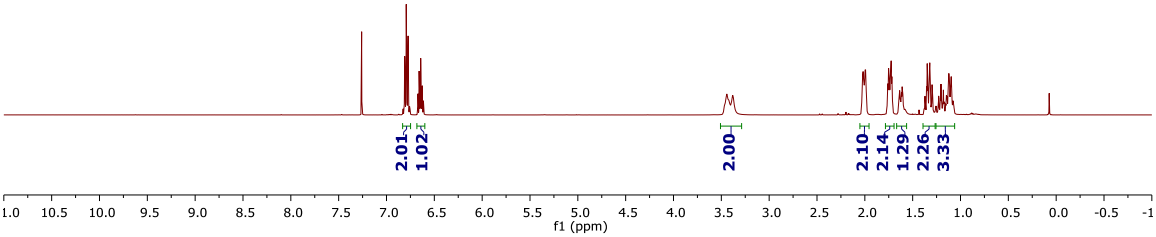


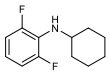
^{13}C NMR (125 MHz, $CDCl_3$)



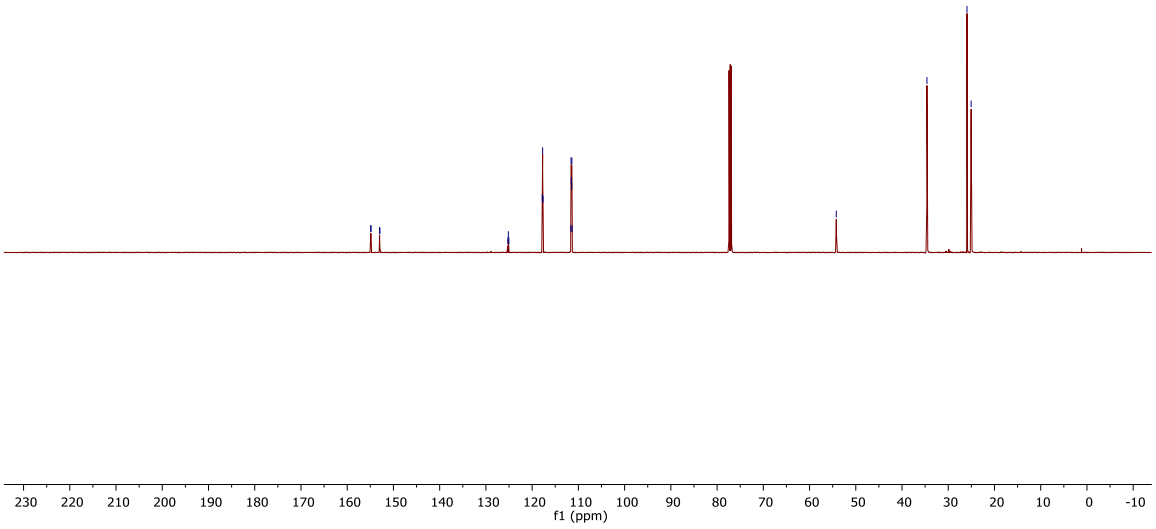


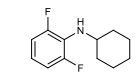
^{1}H NMR (500 MHz, $CDCl_3$)



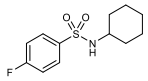


^{13}C NMR (125 MHz, $CDCl_3$)

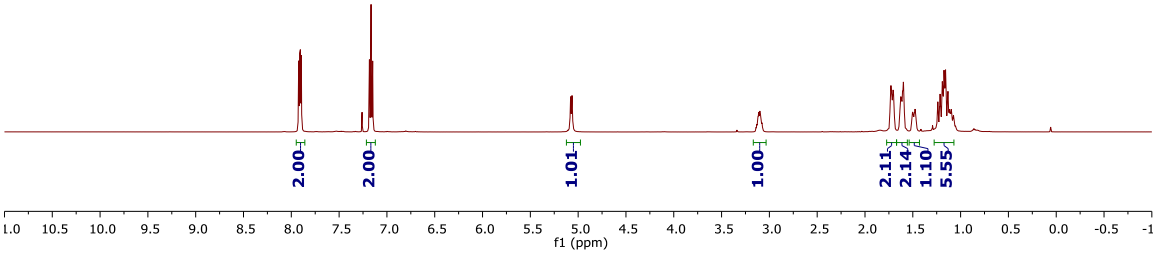


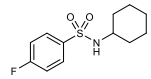


^{19}F NMR (376 MHz, $CDCl_3$)

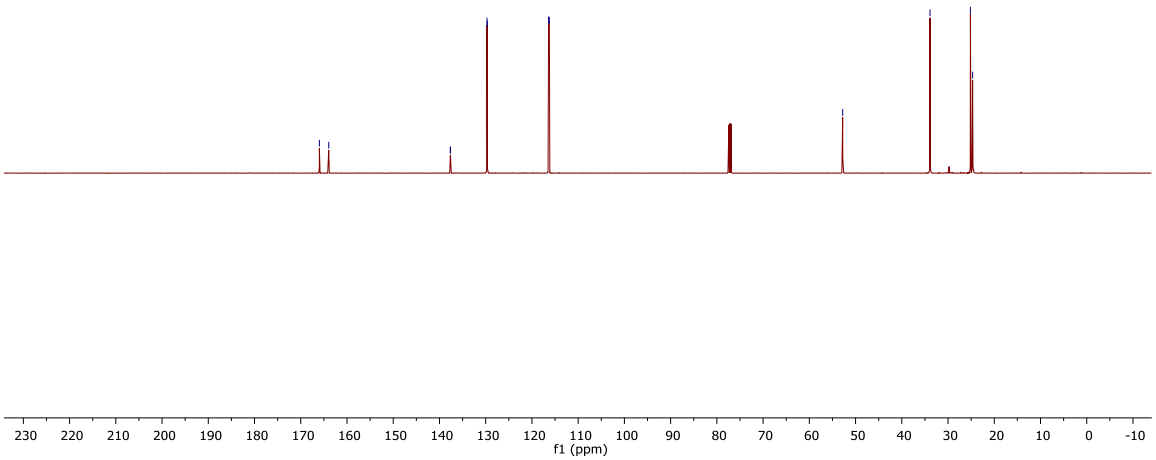


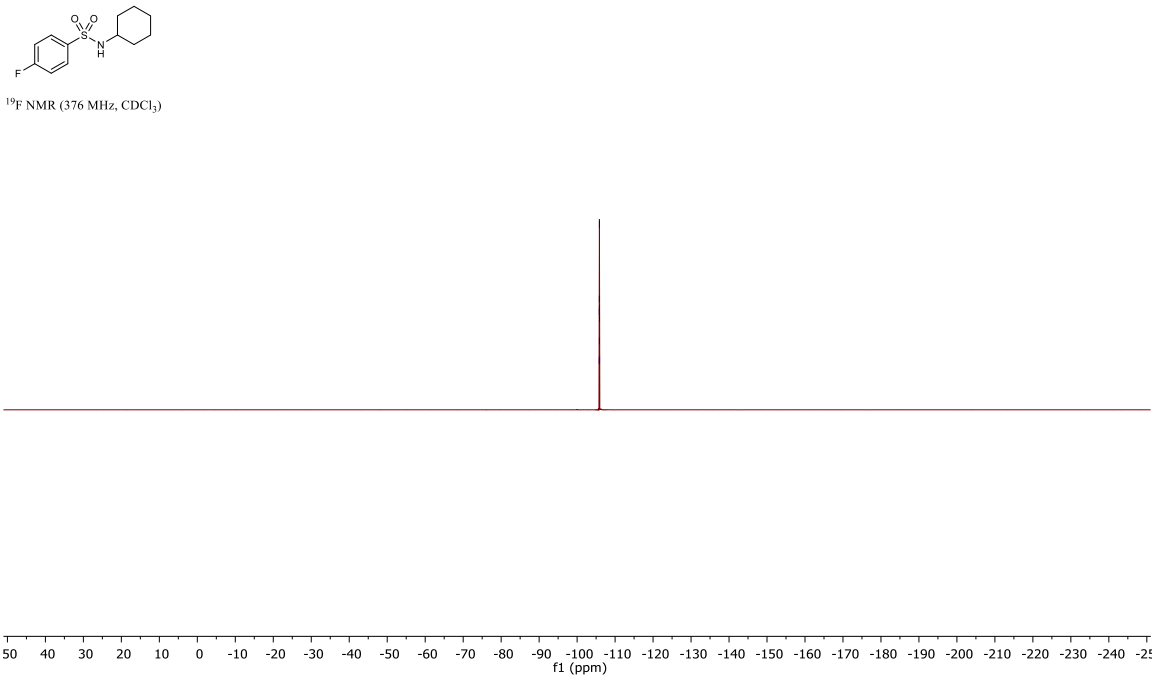
^{1}H NMR (500 MHz, $CDCl_3$)



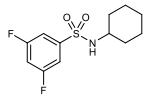


^{13}C NMR (125 MHz, $CDCl_3$)

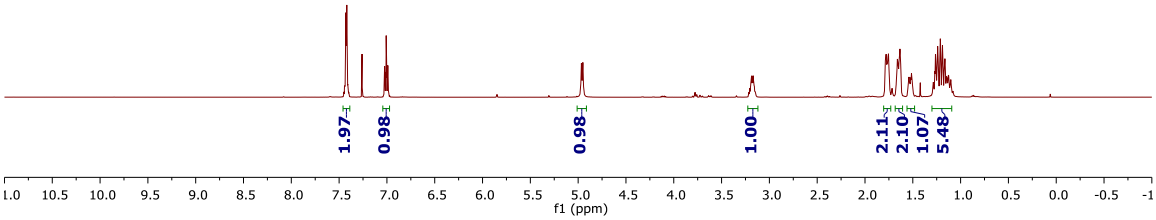


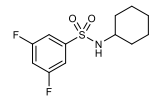


^{19}F NMR (376 MHz, $CDCl_3$)

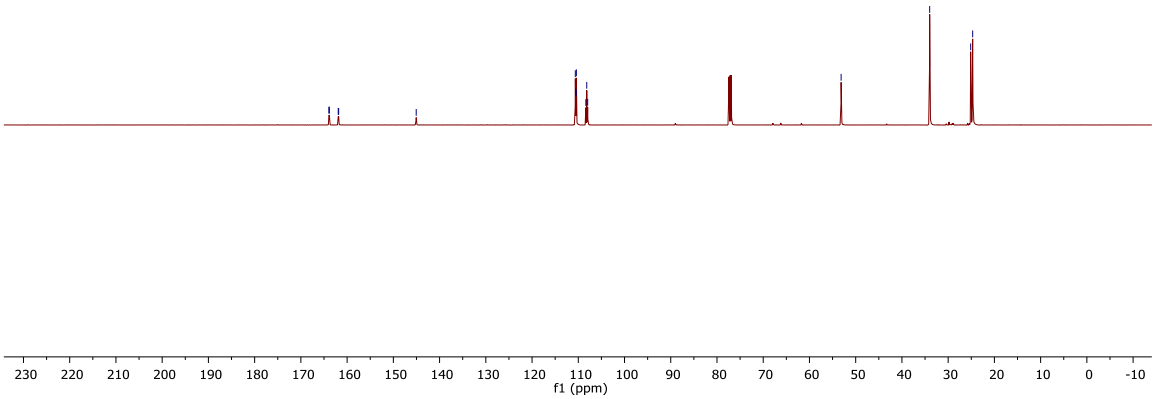


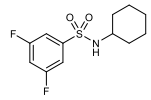
^{1}H NMR (500 MHz, $CDCl_3$)



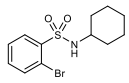


^{13}C NMR (125 MHz, $CDCl_3$)

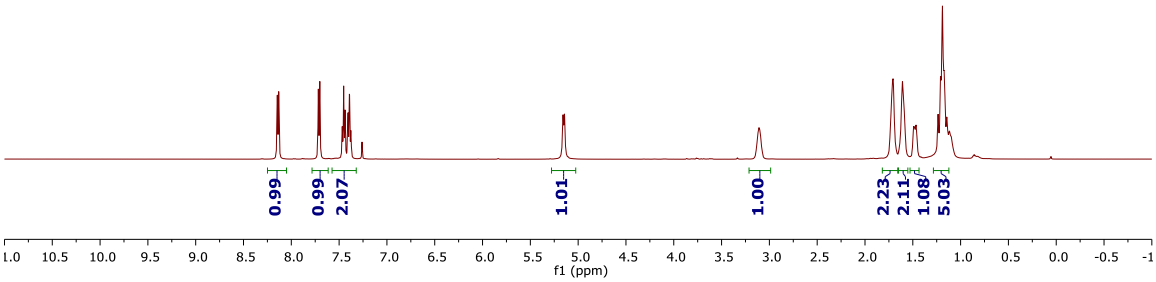


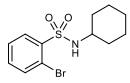


^{19}F NMR (376 MHz, $CDCl_3$)

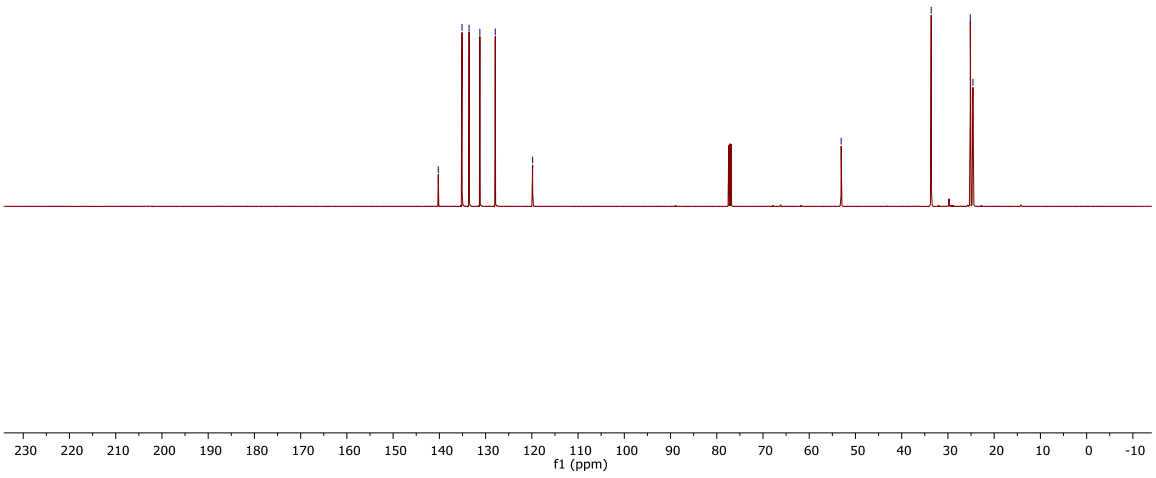


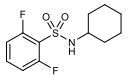
^{1}H NMR (500 MHz, $CDCl_3$)



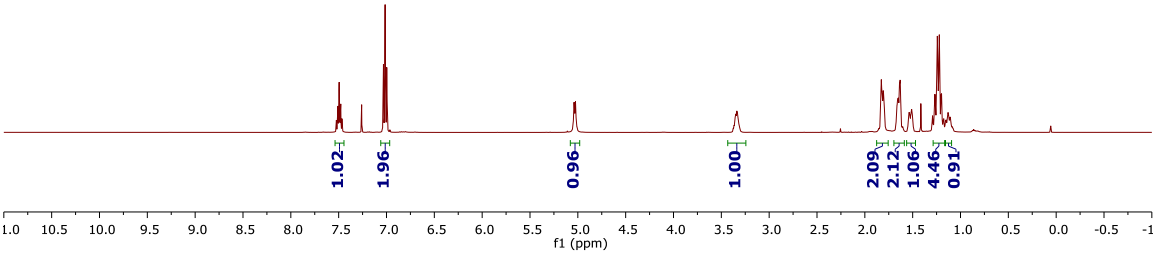


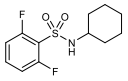
^{13}C NMR (125 MHz, $CDCl_3$)



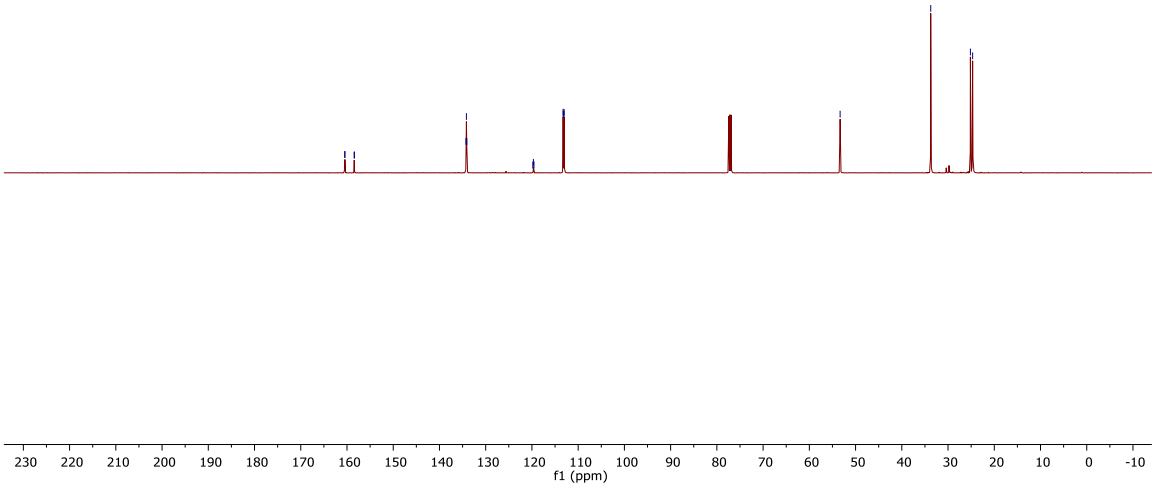


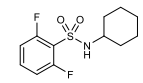
^{1}H NMR (500 MHz, $CDCl_3$)



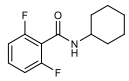


^{13}C NMR (125 MHz, $CDCl_3$)

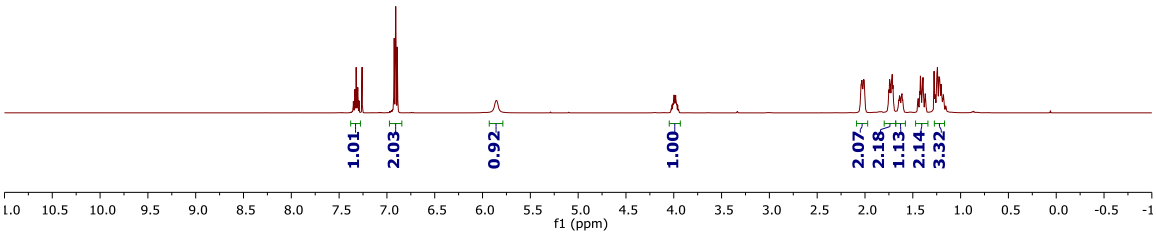


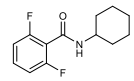


^{19}F NMR (376 MHz, $CDCl_3$)

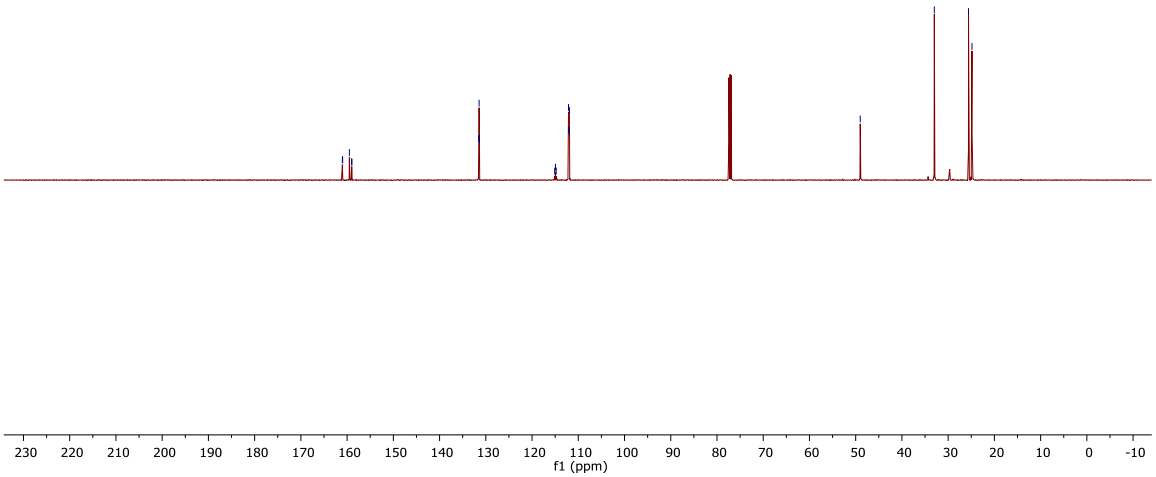


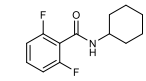
^{1}H NMR (500 MHz, $CDCl_3$)



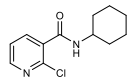


^{13}C NMR (125 MHz, $CDCl_3$)

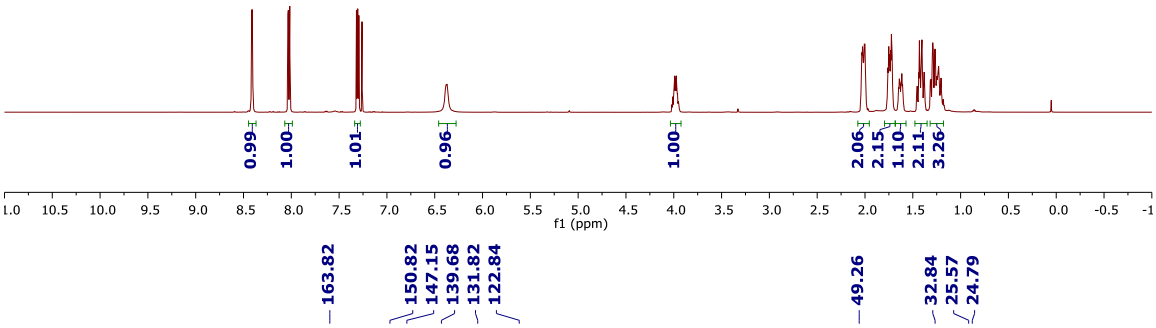


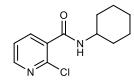


^{19}F NMR (376 MHz, $CDCl_3$)

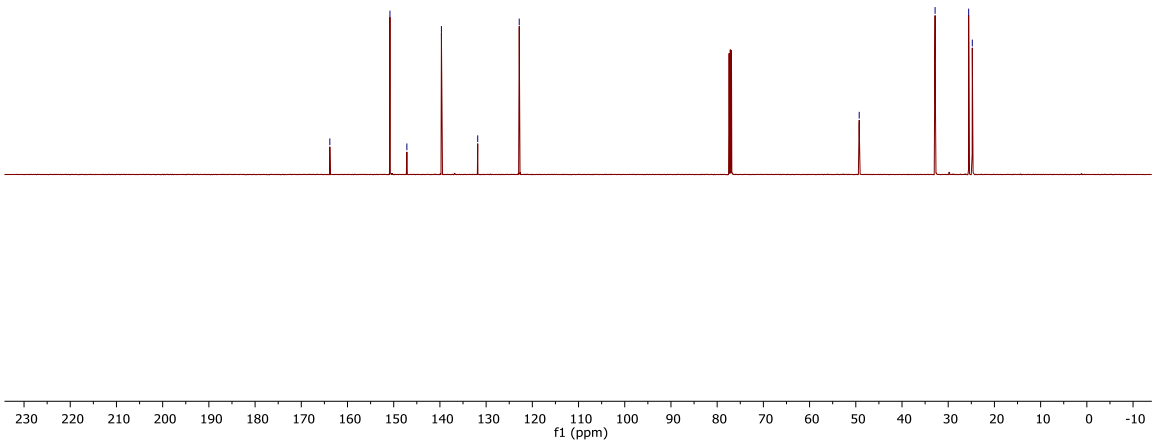


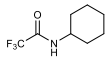
^{1}H NMR (500 MHz, $CDCl_3$)



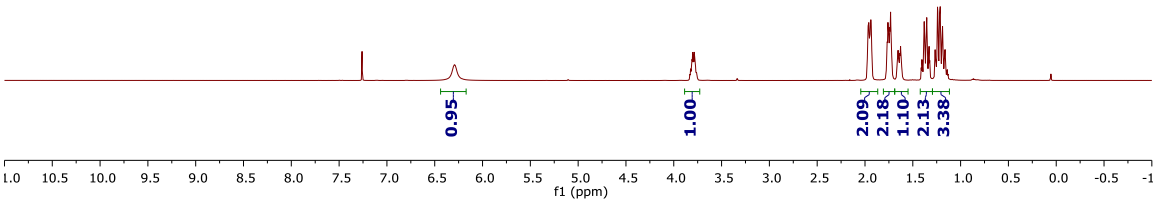


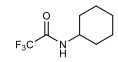
^{13}C NMR (125 MHz, $CDCl_3$)



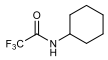


^{1}H NMR (500 MHz, $CDCl_3$)

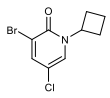




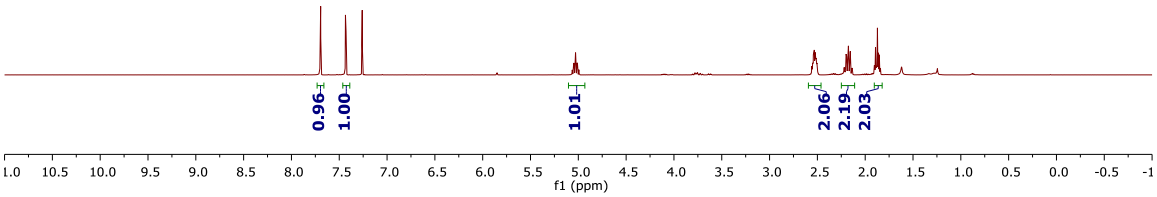
^{13}C NMR (125 MHz, $CDCl_3$)



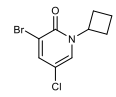
^{19}F NMR (376 MHz, $CDCl_3$)



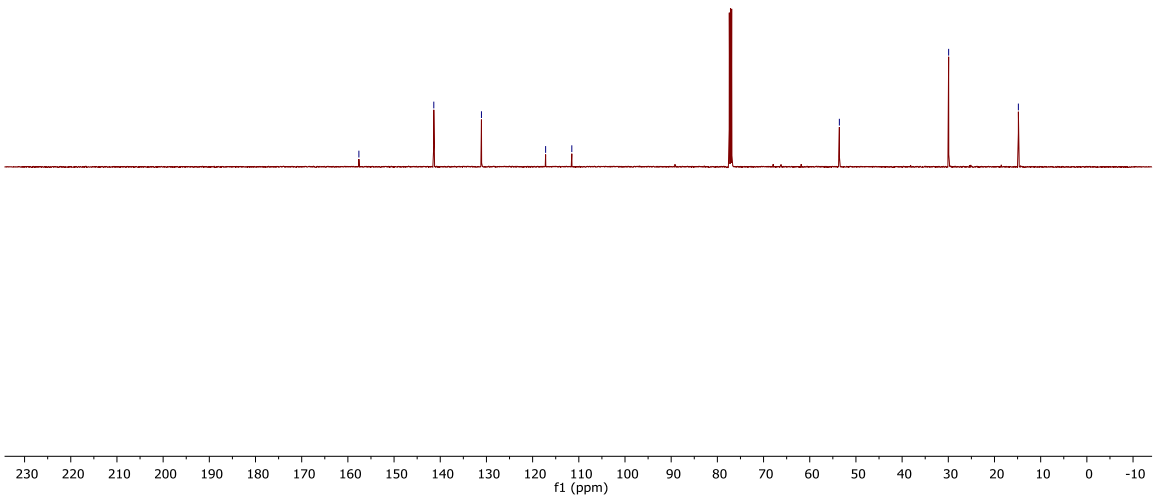
^{1}H NMR (500 MHz, $CDCl_3$)

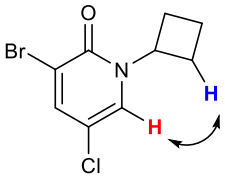


157.62
141.40
131.08
117.19
111.51
53.59
29.93
14.83

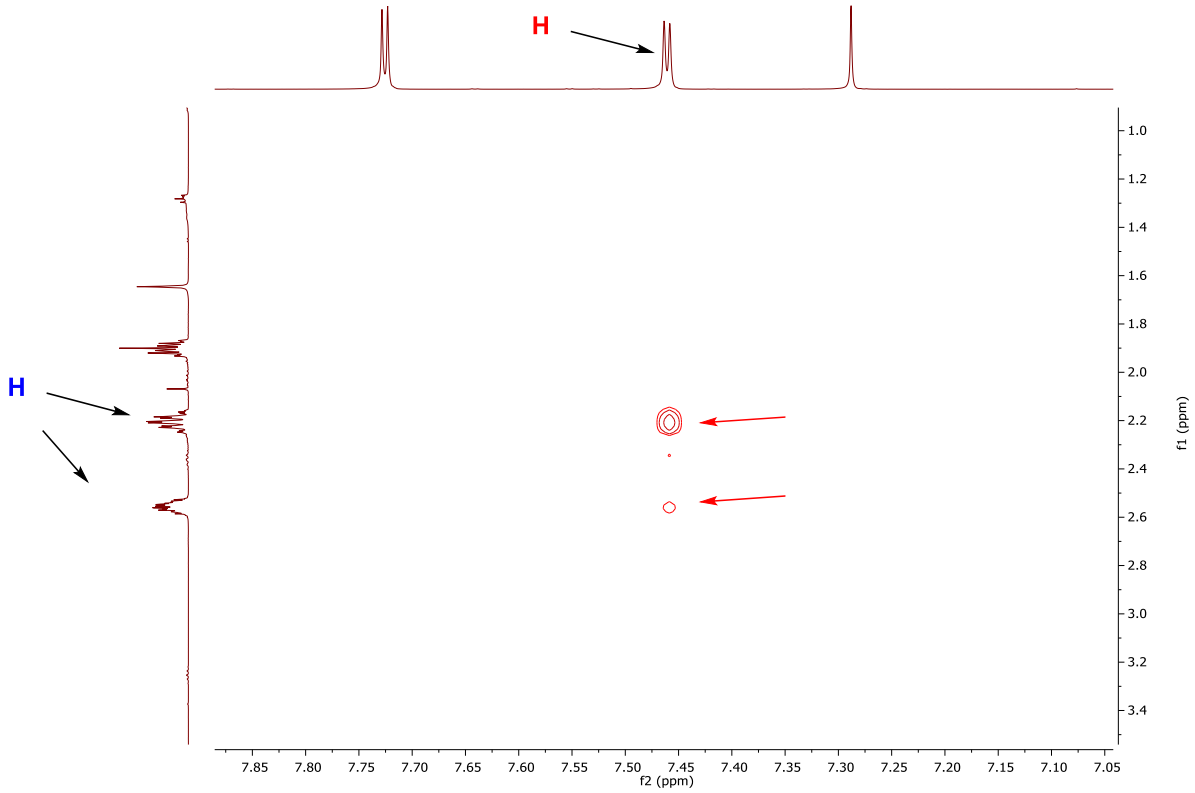


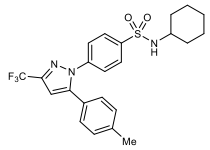
^{13}C NMR (125 MHz, $CDCl_3$)



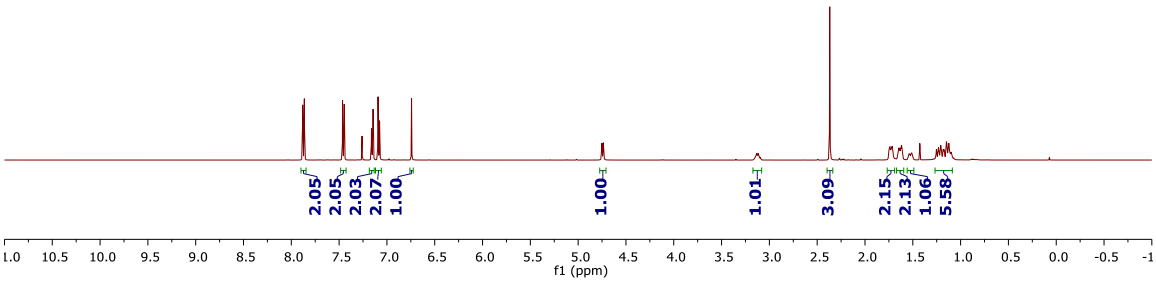

O
Br
N
H
H
Cl

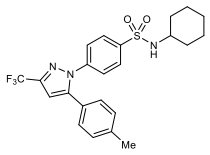
NOESY, $CDCl_3$


H
H
7.85
7.80
7.75
7.70
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
7.05
f2 (ppm)
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
f1 (ppm)

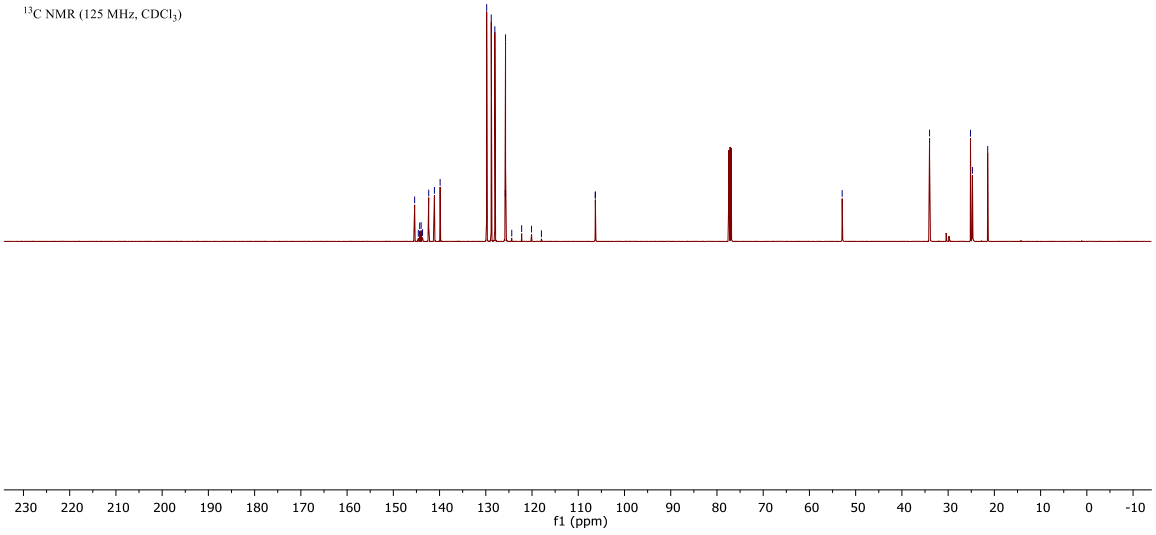


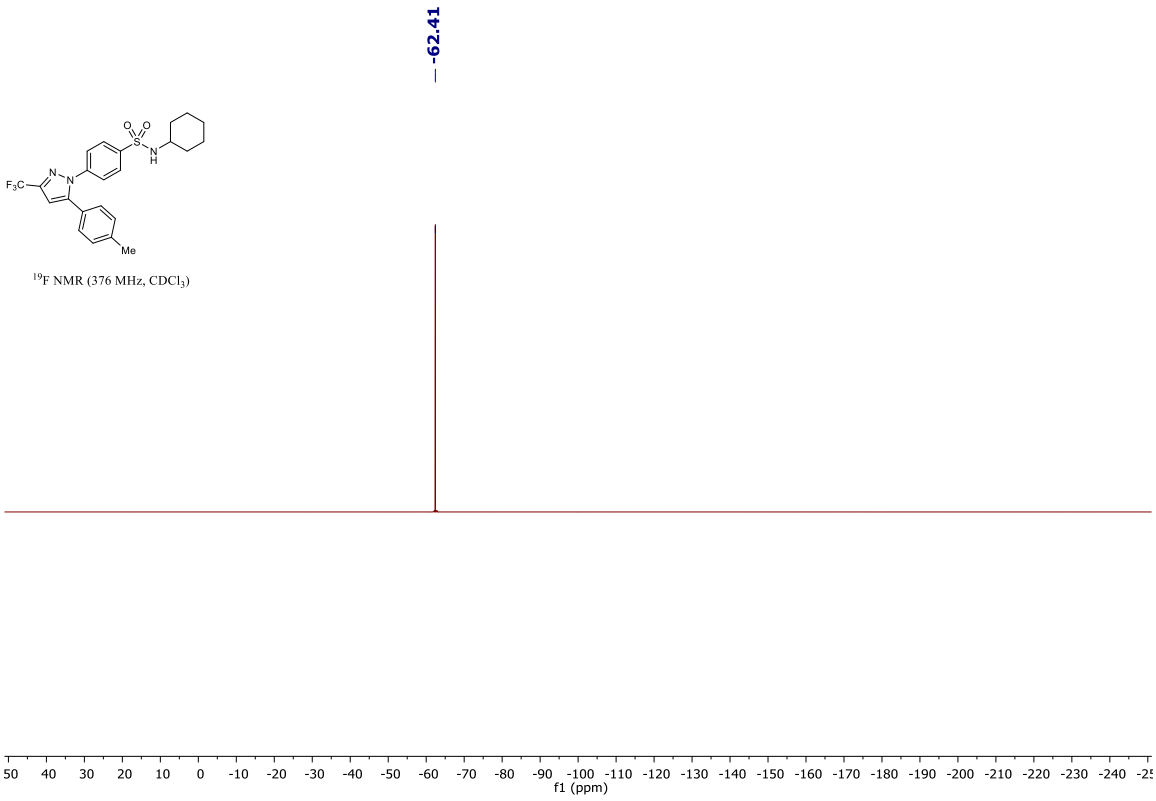
^{1}H NMR (500 MHz, $CDCl_3$)



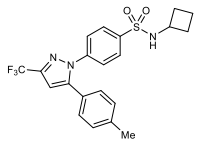


^{13}C NMR (125 MHz, $CDCl_3$)

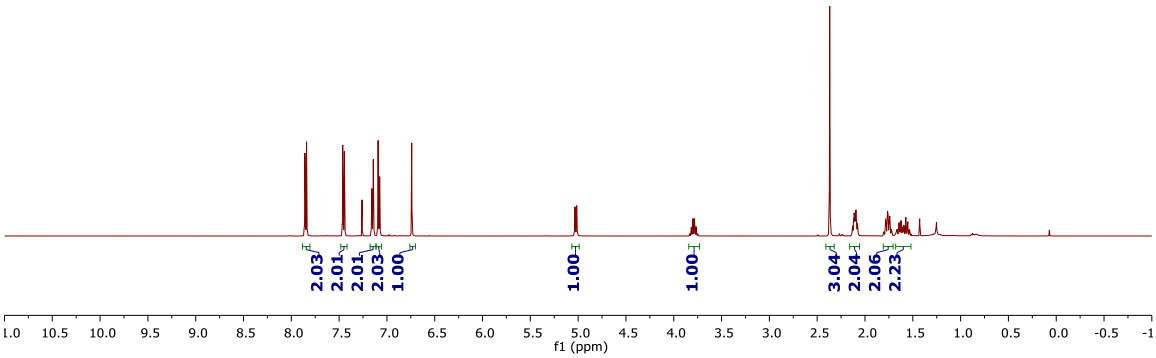


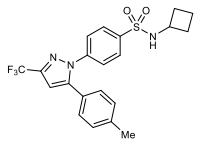


^{19}F NMR (376 MHz, $CDCl_3$)

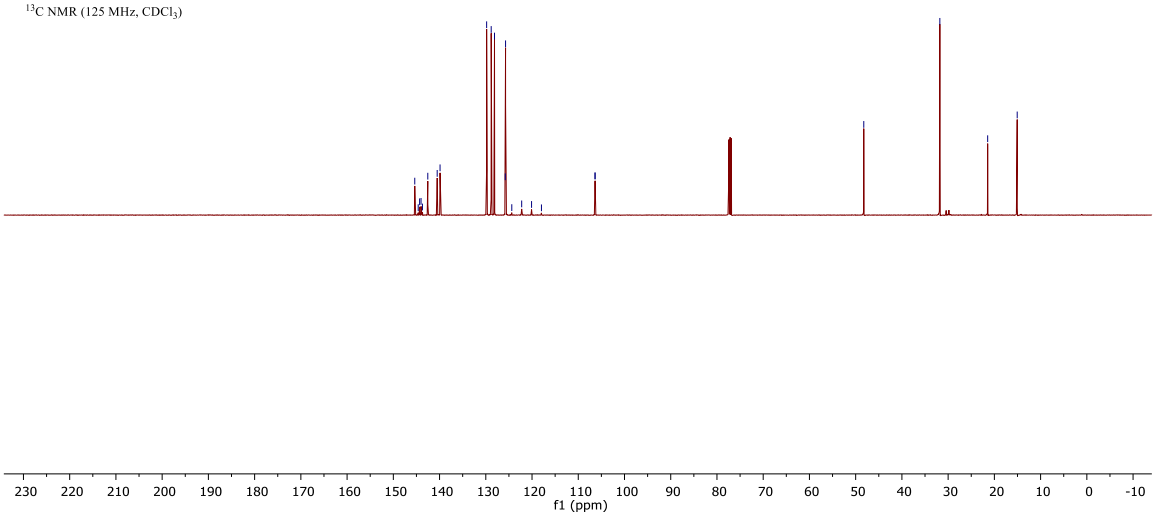


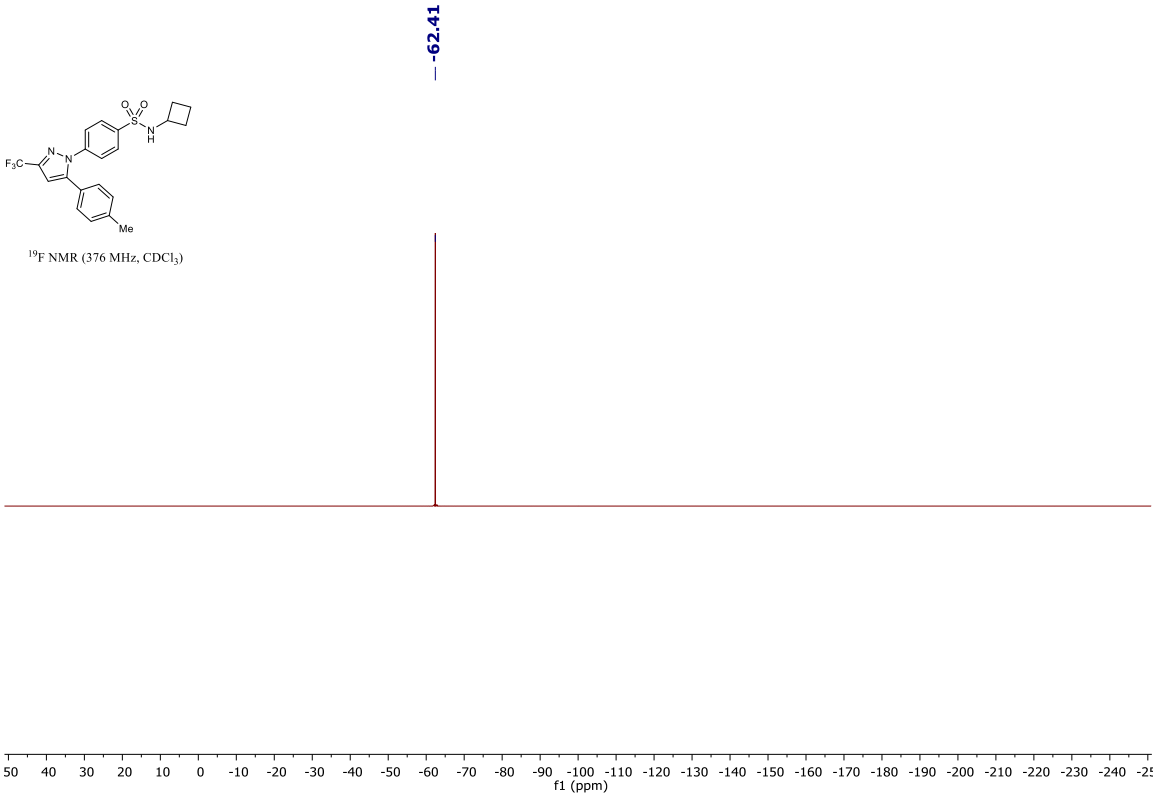
^{1}H NMR (500 MHz, $CDCl_3$)



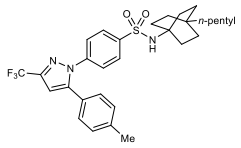


^{13}C NMR (125 MHz, $CDCl_3$)

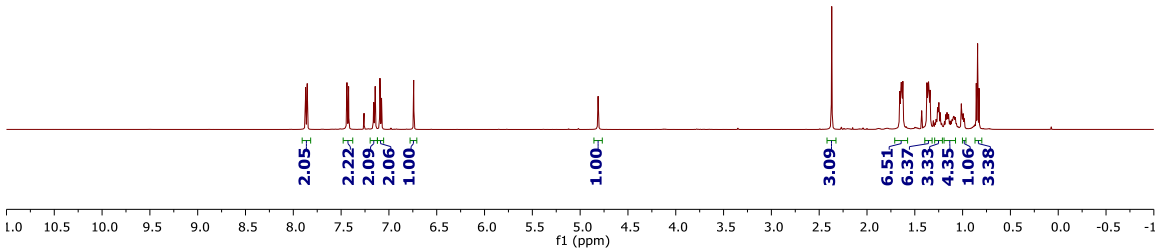


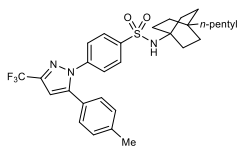


^{19}F NMR (376 MHz, $CDCl_3$)

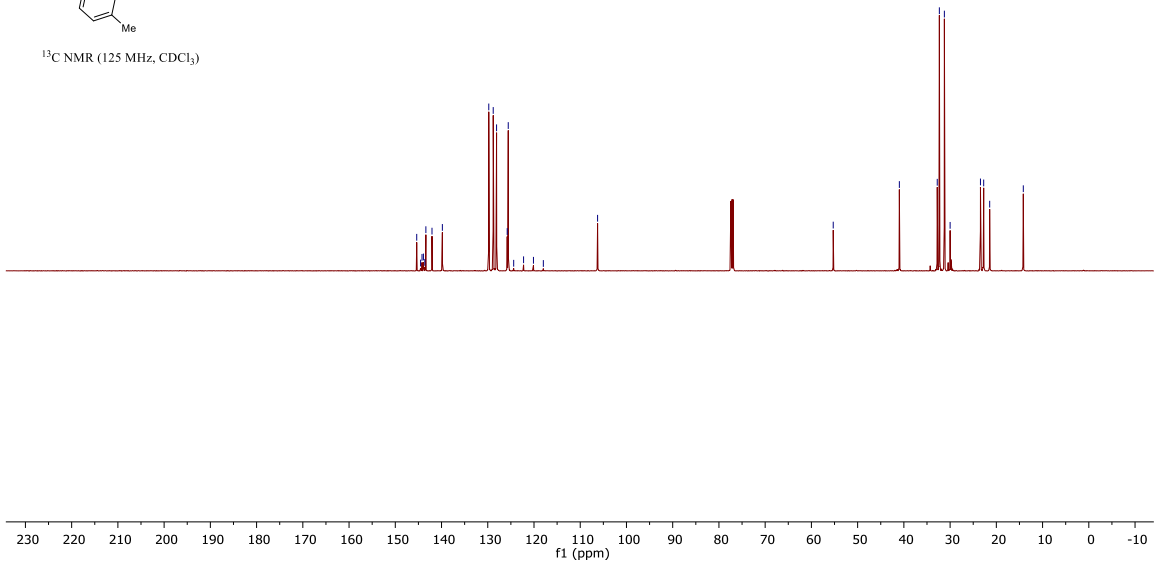


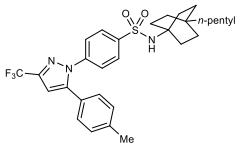
^{1}H NMR (500 MHz, $CDCl_3$)



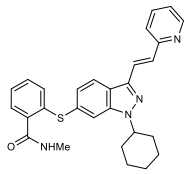


^{13}C NMR (125 MHz, $CDCl_3$)

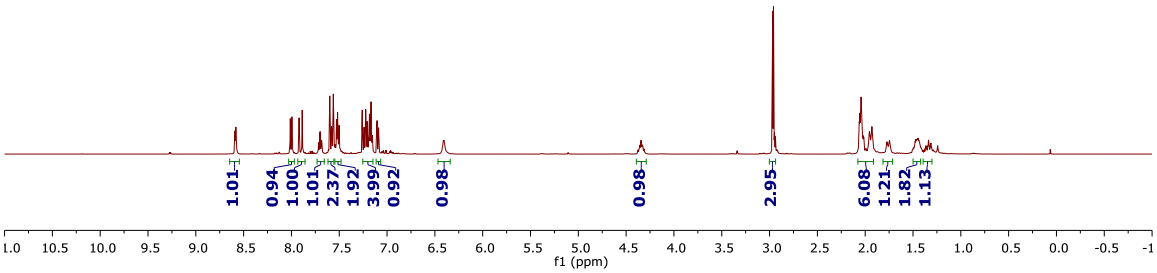


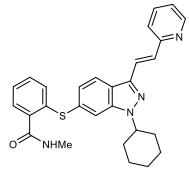


^{19}F NMR (376 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)





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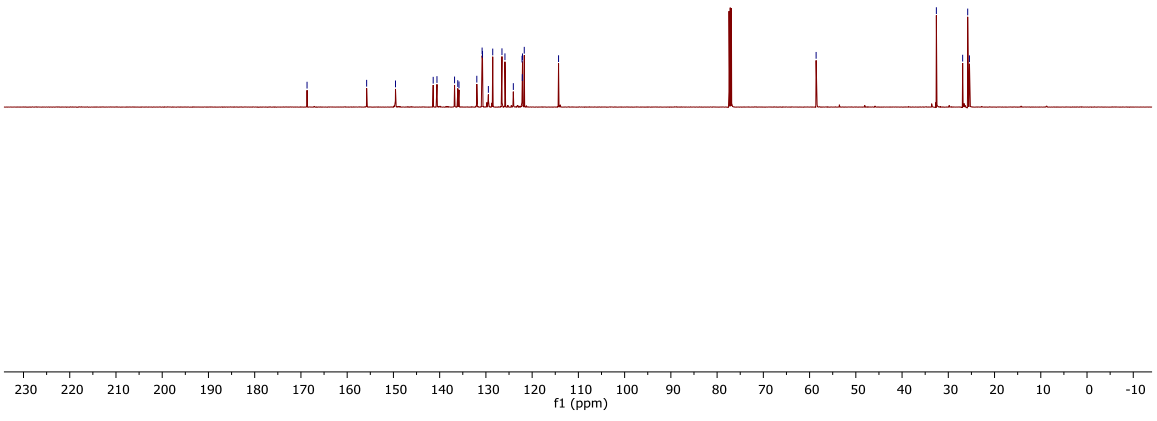
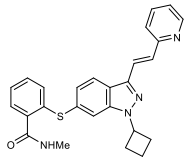
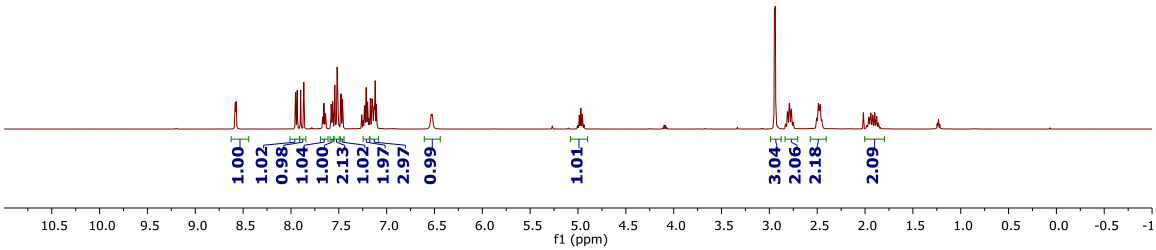
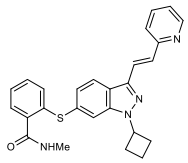


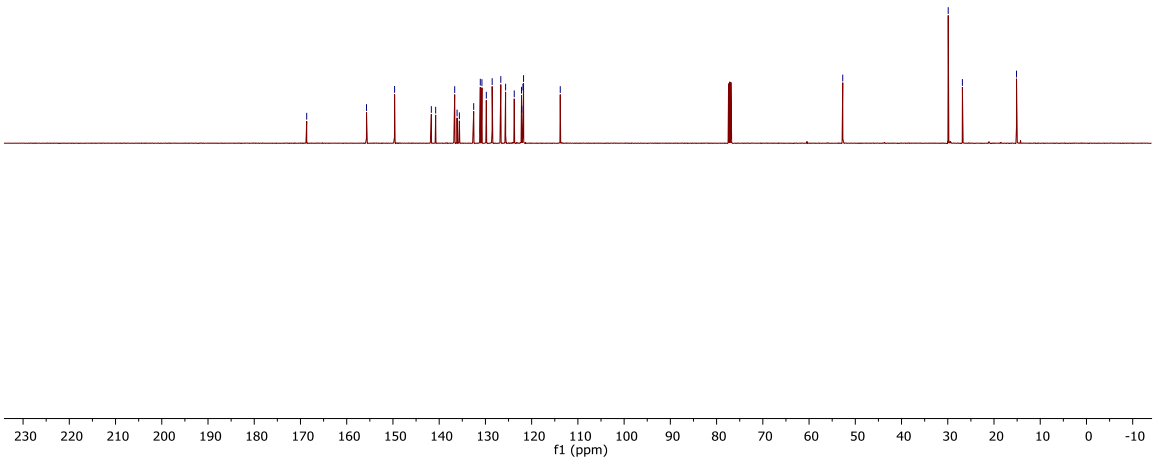


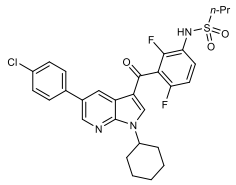
^{1}H NMR (500 MHz, $CDCl_3$)



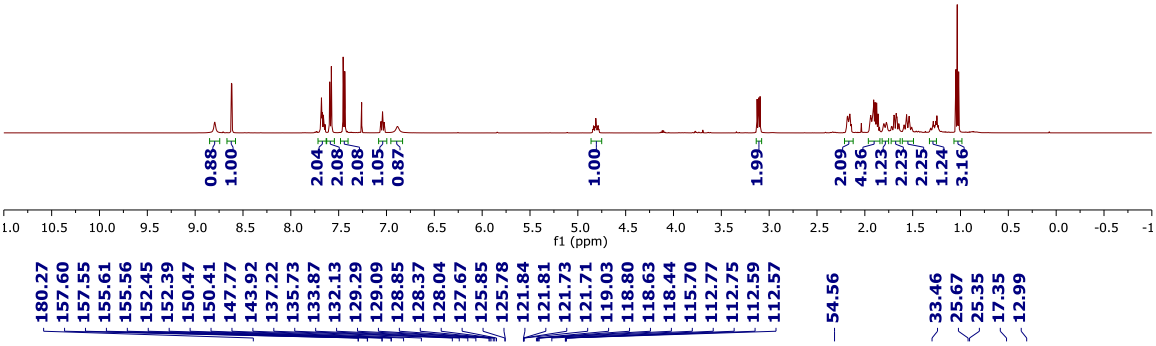


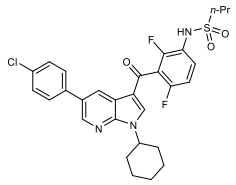
^{13}C NMR (125 MHz, $CDCl_3$)



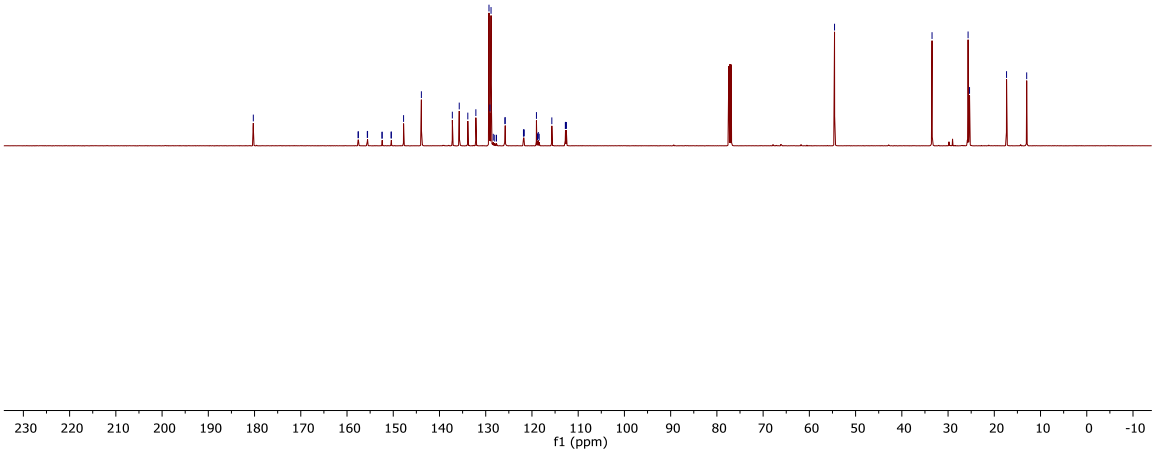


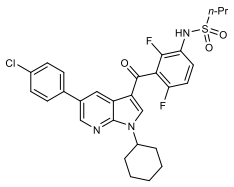
^{1}H NMR (500 MHz, $CDCl_3$)



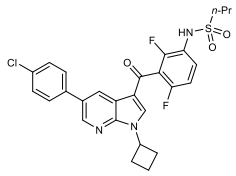


^{13}C NMR (125 MHz, $CDCl_3$)

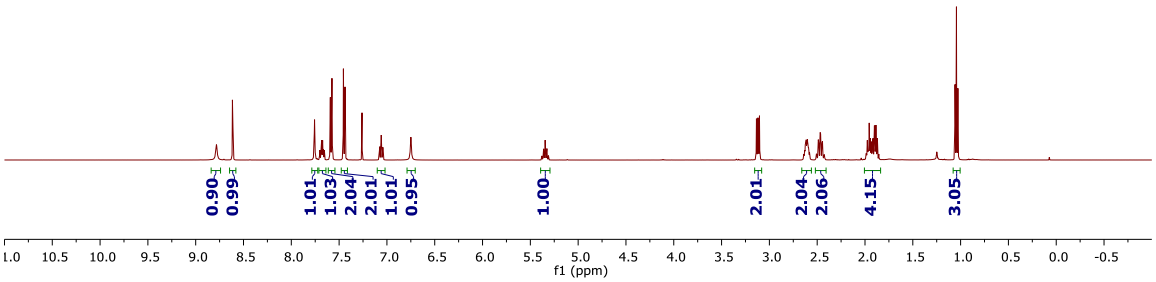


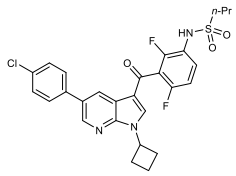


^{19}F NMR (376 MHz, $CDCl_3$)

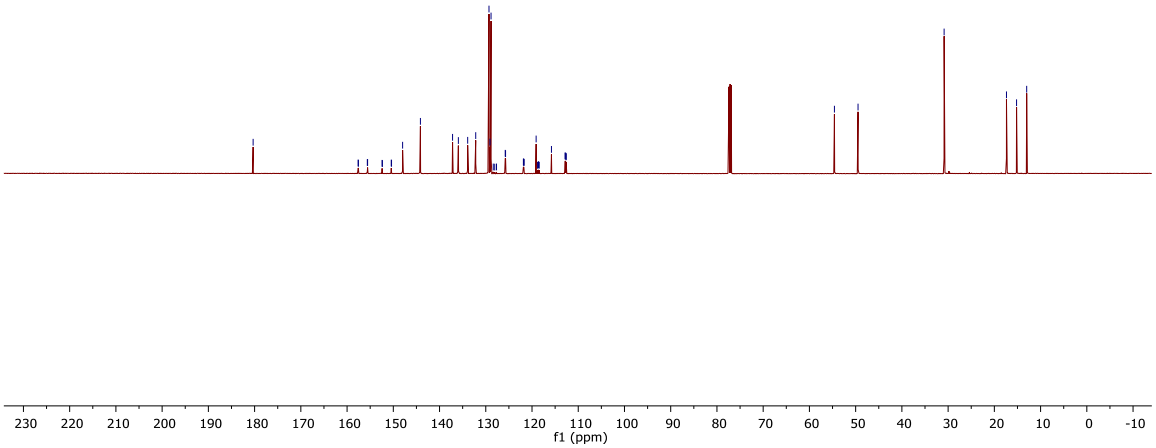


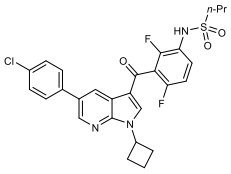
^{1}H NMR (500 MHz, $CDCl_3$)



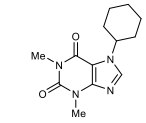


^{13}C NMR (125 MHz, $CDCl_3$)

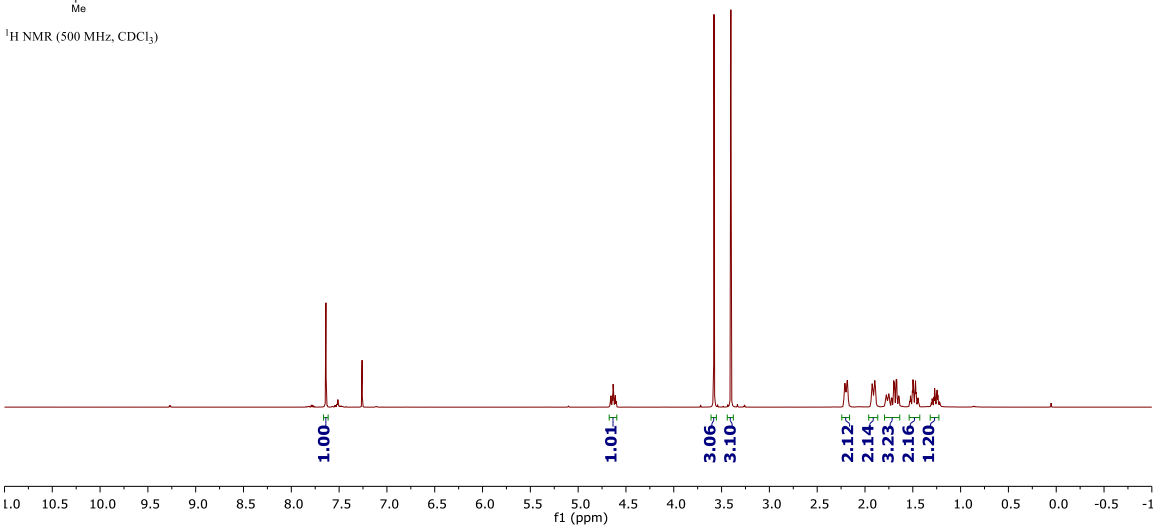




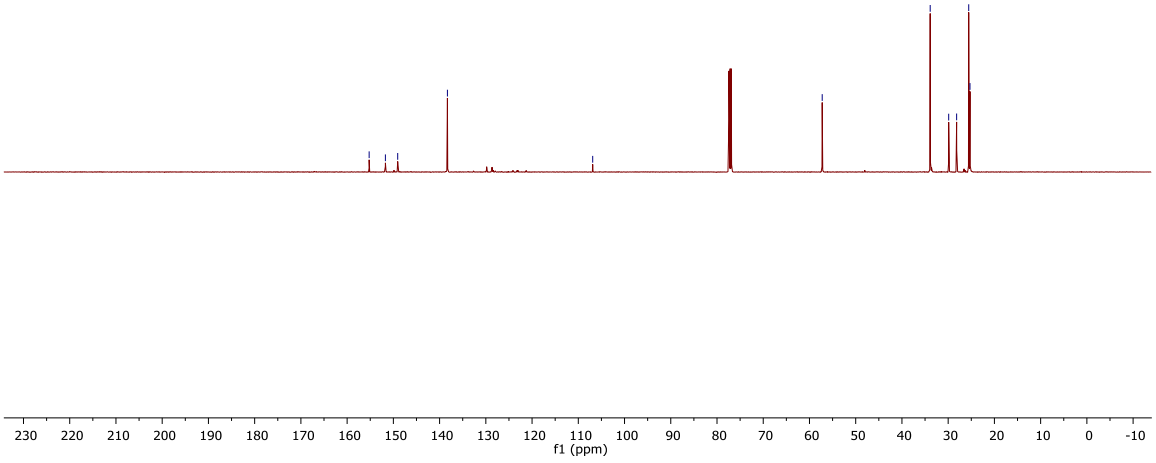
^{19}F NMR (376 MHz, $CDCl_3$)

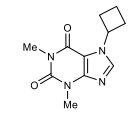


^{1}H NMR (500 MHz, $CDCl_3$)

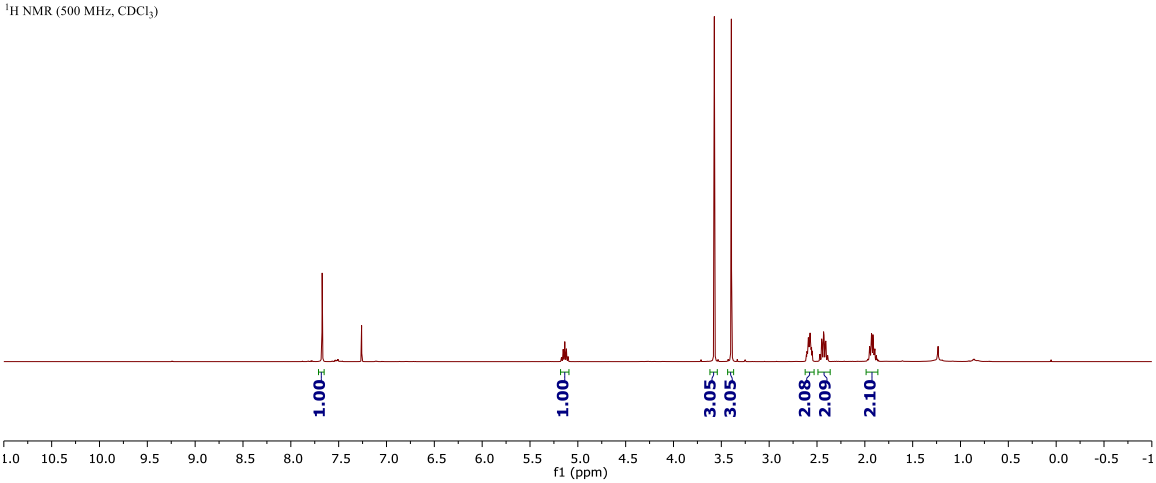


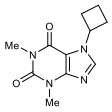
^{13}C NMR (125 MHz, $CDCl_3$)



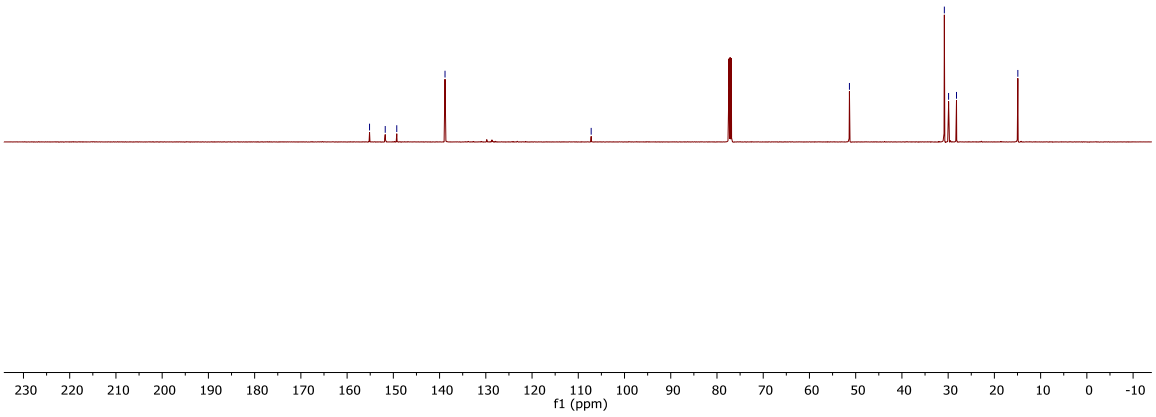


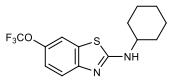
^{1}H NMR (500 MHz, $CDCl_3$)



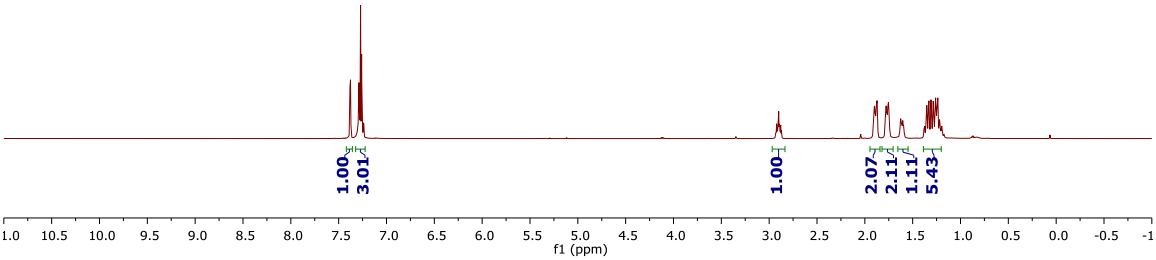


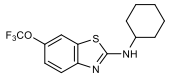
^{13}C NMR (125 MHz, $CDCl_3$)



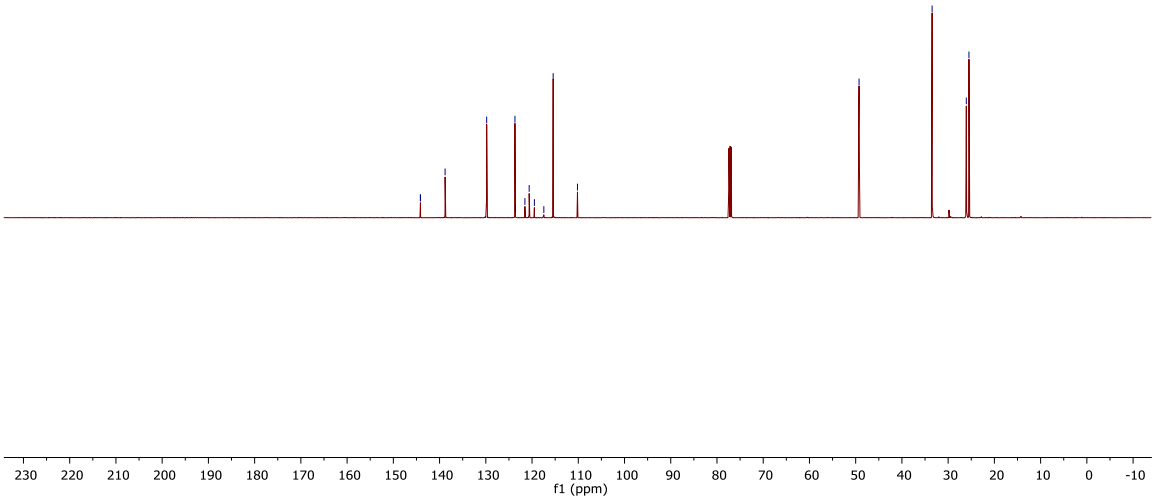


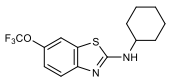
^{1}H NMR (500 MHz, $CDCl_3$)



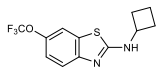


^{13}C NMR (125 MHz, $CDCl_3$)

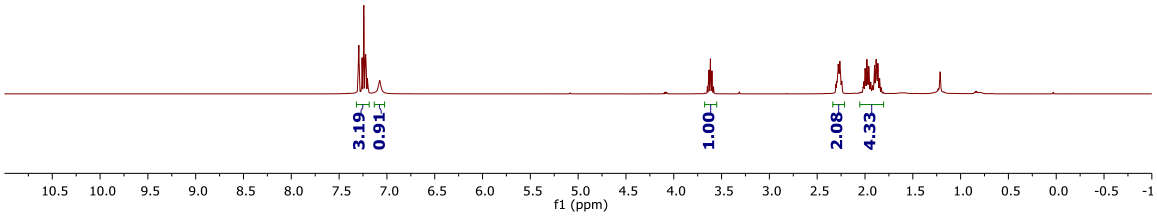


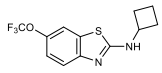


^{19}F NMR (376 MHz, $CDCl_3$)

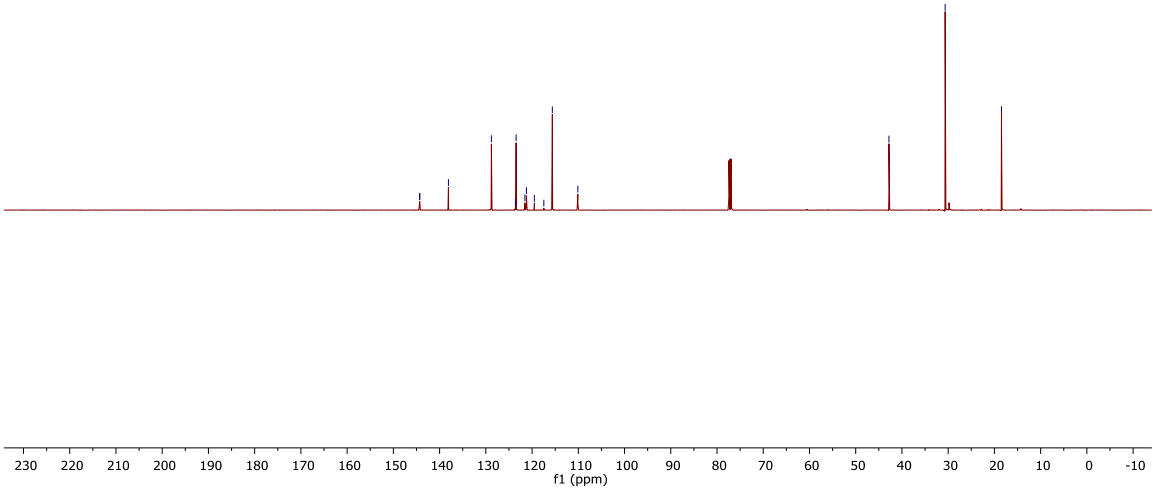


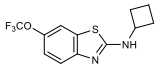
^{1}H NMR (500 MHz, $CDCl_3$)



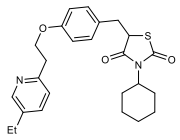


^{13}C NMR (125 MHz, $CDCl_3$)

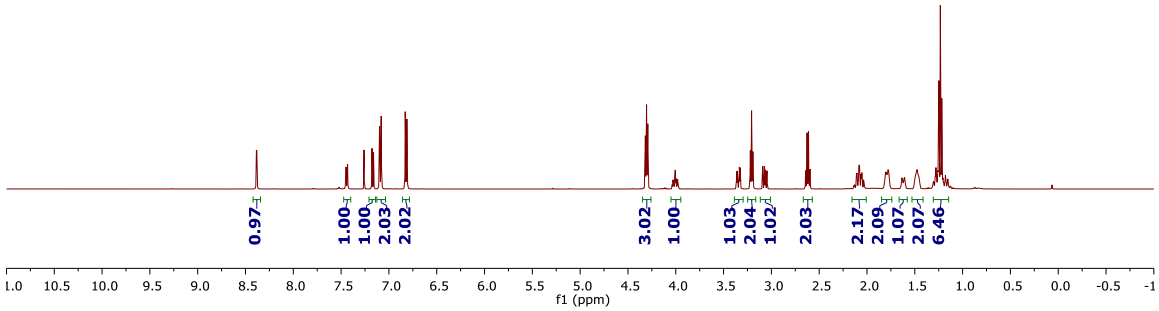


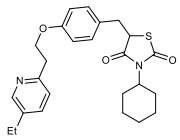


^{19}F NMR (376 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)





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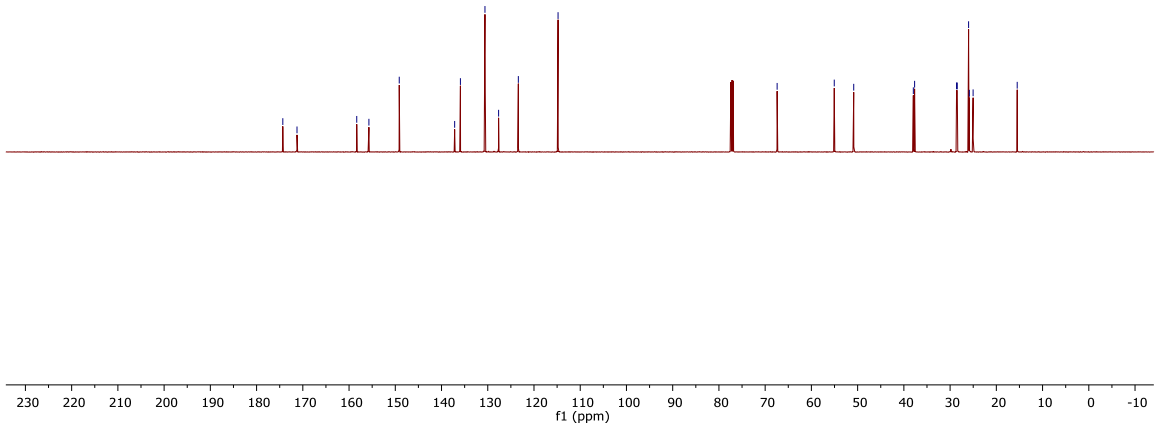
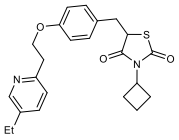
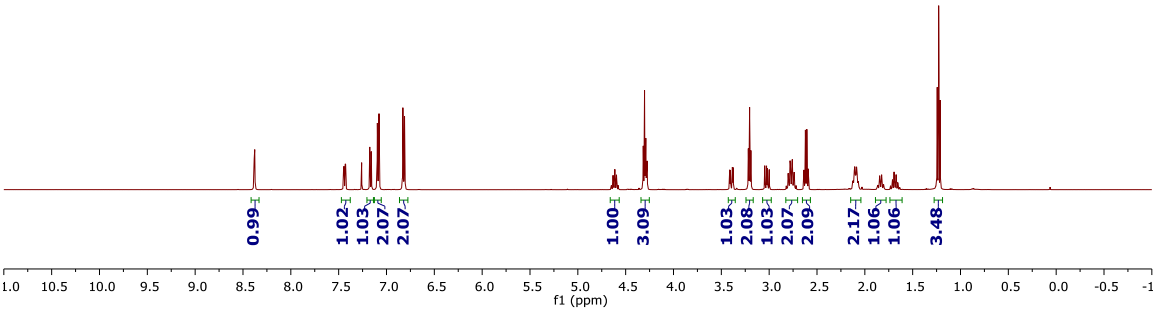
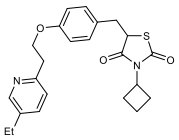


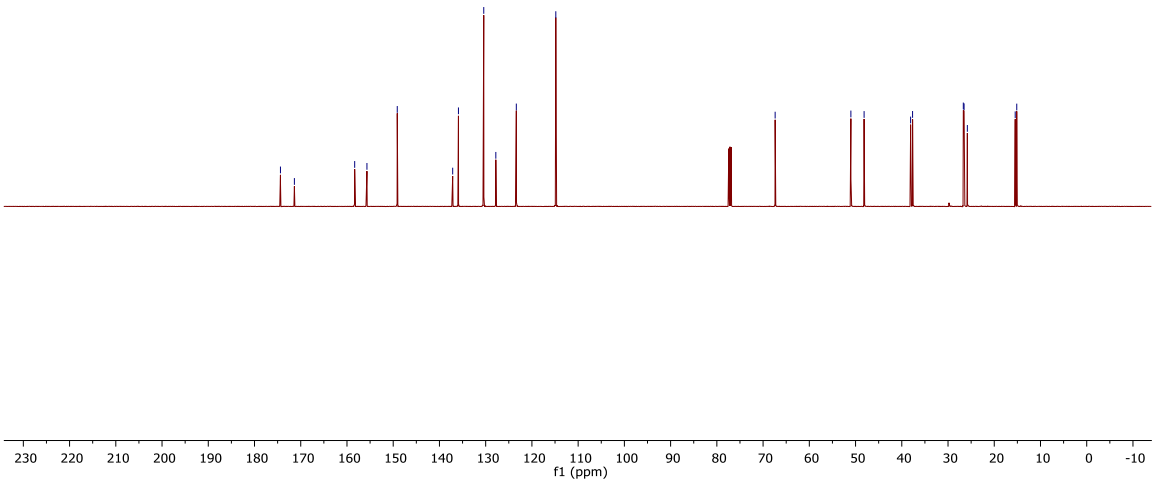


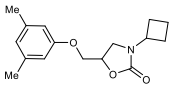
^{1}H NMR (500 MHz, $CDCl_3$)



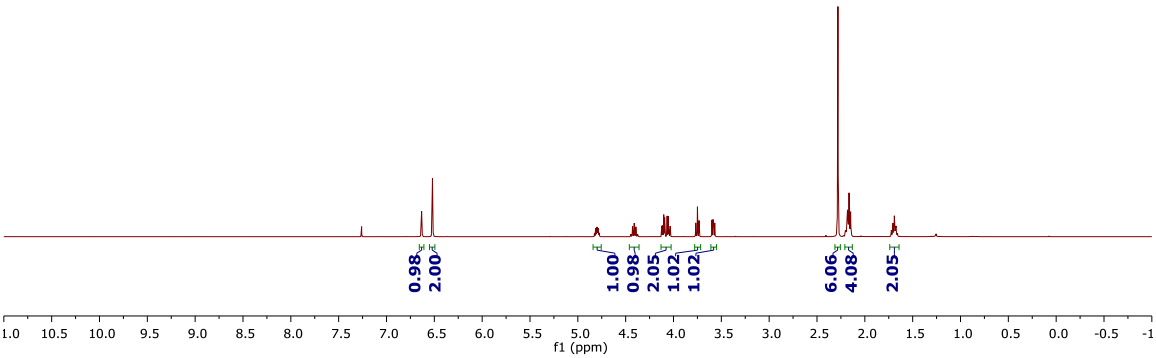


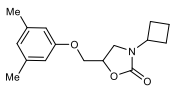
^{13}C NMR (125 MHz, $CDCl_3$)



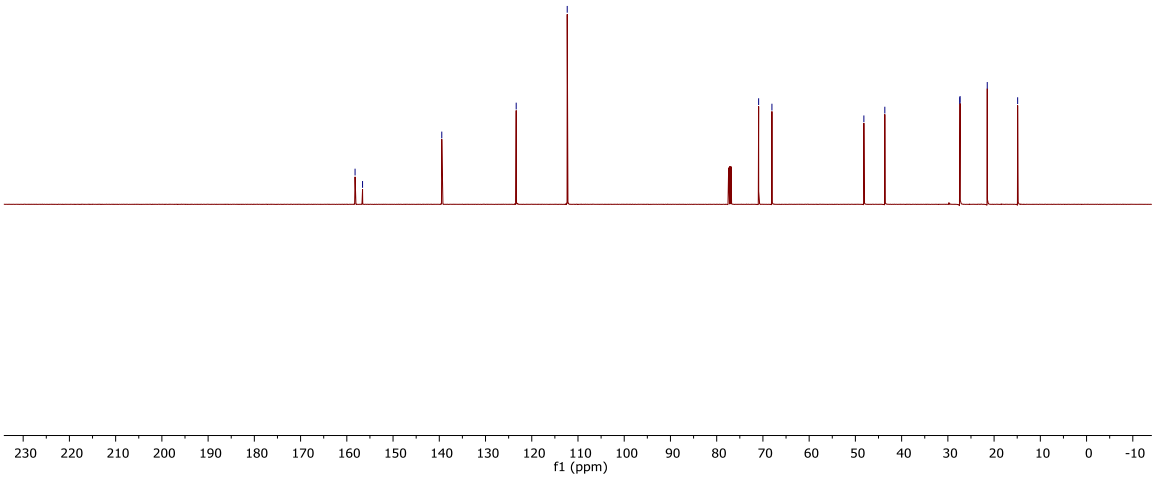


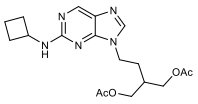
^{1}H NMR (500 MHz, $CDCl_3$)



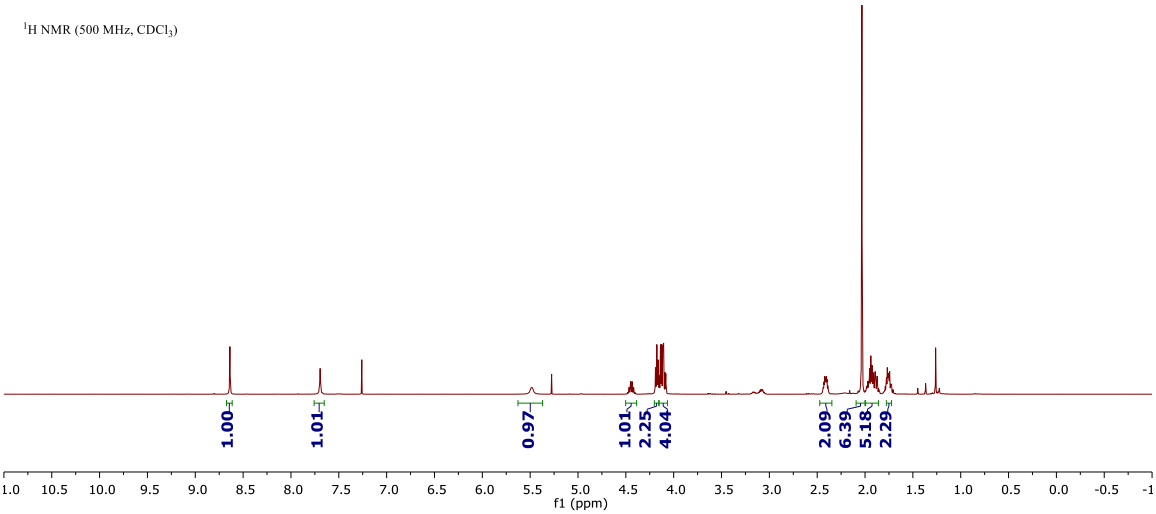


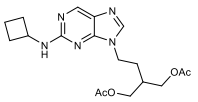
^{13}C NMR (125 MHz, $CDCl_3$)



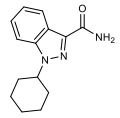


^{1}H NMR (500 MHz, $CDCl_3$)





^{13}C NMR (125 MHz, $CDCl_3$)



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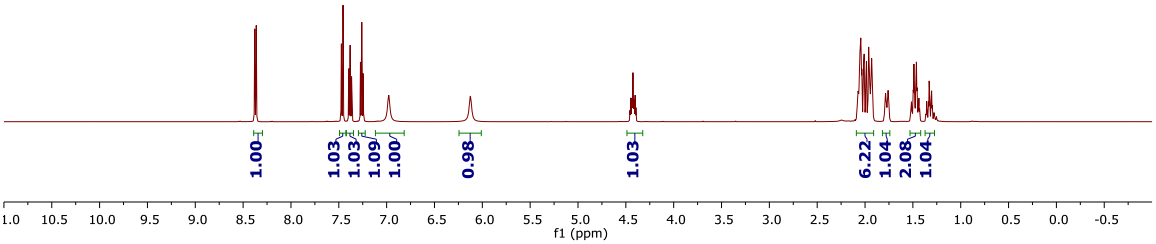

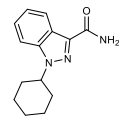

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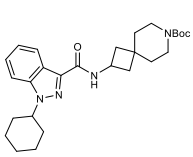
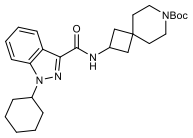


^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)