Silyl Radical Activation of Alkyl Halides in Metallaphotoredox Catalysis: A Unique Pathway for Cross-Electrophile Coupling

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Supporting Information

Table of Contents

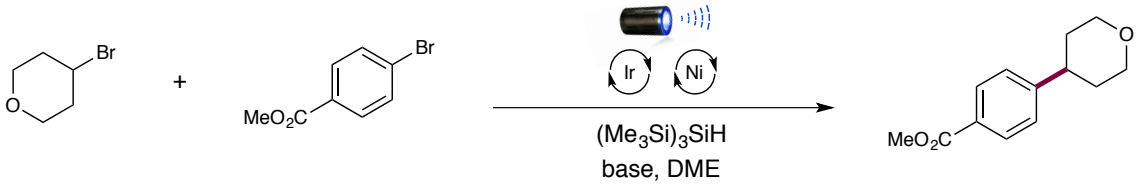
1) General Information

Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego[1]. Ir[dF(CF3)ppy]2(dtbbpy)PF6 was prepared using literature procedures[2]. Reagent grade dimethoxyethane was used for the alkyl-aryl cross-electrophile reactions. All other solvents were purified according to the method of Grubbs[3]. 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 or $KMnO_4$ stain. ^1H NMR spectra were recorded on a Bruker UltraShield Plus Avance III 500 MHz and are internally referenced to residual protic CDCl3 (δ 7.26 ppm) and $(CD_3)_2CO$ signals (δ 2.05 ppm). Data for ^1H 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 CDCl3 (77.16 ppm) or $(CD_3)_2CO$ (29.84 ppm and 206.26 ppm). ^{19}F NMR spectra were recorded on a Bruker NanoBay 300 MHz (282 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.

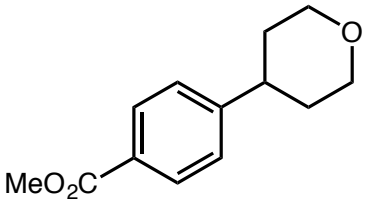
2) Procedure for Optimization Studies

To an 8 mL vial equipped with a stir bar was added photocatalyst $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.5 mg, 2.5 μmol, 0.01 equiv.), methyl 4-bromo benzoate (54 mg, 0.25 mmol, 1 equiv.), 4-bromotetrahydropyran (42 μL, 0.375 mmol, 1.5 equiv.), tris(trimethylsilyl)silane (77 μL, 0.25 mmol, 1.0 equiv), and anhydrous sodium carbonate (53 mg, 0.5 mmol, 2 equiv.). The vial was sealed and placed under nitrogen before 2mL of solvent was added. To a separate vial was added $NiCl_2$•glyme (2.8 mg, 0.013 mmol, 0.05 equiv.) and 4,4'-di-tert-butyl-2,2'-bipyridine (3.4 mg, 0.013 mmol, 0.05 equiv). The catalyst vial was sealed, purged with nitrogen then to it was added 1 mL of solvent. The precatalyst solution was sonicated or stirred for 5 minutes, after which, 0.1 mL of the solution (0.5 mol% catalyst, 1.25 μmol, 0.005 equv.) was syringed into the reaction vessel. The solution was degassed by sparging with nitrogen while stirring for 10 minutes before sealing with Parafilm. The reaction was stirred and irradiated with a 34 W blue LED lamp (7 cm away, with cooling fan to keep the reaction temperature at 25 °C) for 6 hours. The reaction was quenched by exposure to air. Mesitylene (internal standard, 35 μL, 0.250 mmol, 1.0 equiv.) was added then the reaction mixture was analyzed by ^1H NMR.

3) Procedure for Silane-Mediated Metallaphotoredox Alkyl-Aryl Cross-Electrophile Coupling



To an 8 mL vial equipped with a stir bar was added photocatalyst $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 5.0 μmol, 0.01 equiv.), methyl 4-bromo benzoate (108 mg, 0.5 mmol, 1 equiv.), 4-bromotetrahydropyran (84 μL, 0.750 mmol, 1.5 equiv.), tris(trimethylsilyl)silane (154 μL, 0.5 mmol, 1.0 equiv), and anhydrous sodium carbonate (106 mg, 1.0 mmol, 2 equiv.). The vial was sealed and placed under nitrogen before 4mL of DME was added. To a separate vial was added $NiCl_2$•glyme (1 mg, 5 μmol, 0.01 equiv.) and 4,4'-di-tert-butyl-2,2'-bipyridine (1.3 mg, 5 μmol, 0.01 equiv). The catalyst vial was sealed, purged with nitrogen then to it was added 2 mL of DME. The precatalyst solution was sonicated or stirred for 5 minutes, after which, 1 mL (0.5 mol% catalyst, 2.5 μmol, 0.005 equv.) was syringed into the reaction vessel. The solution was degassed by sparging with nitrogen while stirring for 10 minutes before sealing with Parafilm. The reaction was stirred and irradiated with a 34 W blue LED lamp (7 cm away, with cooling fan to keep the reaction temperature at 25 °C) for 6 hours. The reaction was quenched by exposure to air and concentrated *in vacuo*. Purification by column chromatography (silica gel, 0-60% EtOAc in hexanes) yielded the alkyl-aryl product.



methyl 4-(tetrahydro-2*H*-pyran-4-yl)benzoate

Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.5 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.5 mg, 2.5 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 3.0 μmol, 0.006 equiv, Na_2CO_3 (106.0

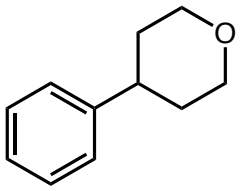
mg, 1.00 mmol, 2.0 equiv.), TTMSS (154 μL, 0.50 mmol, 1.0 equiv.), 4-bromotetrahydro-2H-pyran (84 μL, 0.75 mmol, 1.5 equiv.), methyl 4-bromobenzoate (108 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography yielded the pure product as a white solid (87 mg, 0.39 mmol, 79% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 4.15 – 4.04 (m, 2H), 3.91 (s, 3H), 3.54 (td, *J* = 11.6, 2.5 Hz, 2H), 2.82 (tt, *J* = 11.7, 4.2 Hz, 1H), 1.90 – 1.72 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ167.03, 151.08, 129.91, 128.30, 126.81, 77.28, 77.03, 76.77, 68.24, 52.06, 41.67, 33.60.

Spectroscopic data matches with previously reported data.[5]

4) Aryl Halide Scope



4-phenyltetrahydro-2*H*-pyran (1)

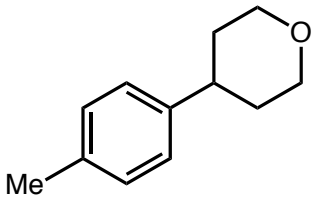
Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 5.0 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.5 mg, 2.5 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 3.0 μmol, 0.006 equiv.), Na_2CO_3 (106.0 mg, 1.00 mmol, 2.0 equiv.), tris(triethylsilyl)silane (211 μL, 0.5 mmol, 1.0 equiv.), 4-bromotetrahydro-2H-pyran (84 μL, 0.75 mmol, 1.5 equiv.), bromobenzene (52 μL, 0.5 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography yielded the pure product as a white solid (64 mg, 0.39 mmol, 79% yield).

Tris(triethylsilyl)silane was used for ease of purification. The reaction gave the same efficiency when tris(trimethylsilyl)silane was employed.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.23 (m, 3H), 4.16 – 4.02 (m, 2H), 3.54 (td, *J* = 11.6, 2.5 Hz, 2H), 2.76 (tt, *J* = 11.7, 4.2 Hz, 1H), 1.91 – 1.73 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 145.88, 128.53, 126.76, 126.75, 126.33, 77.29, 77.04, 76.79, 68.44, 41.60, 33.96.

Spectroscopic data matches with previously reported data.[6]



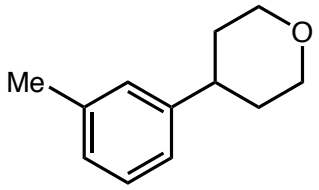
4-(*p*-tolyl)tetrahydro-2*H*-pyran (2)

Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.5 mg, 5.0 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.5 mg, 2.5 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 3.0 μmol, 0.006 equiv.), Na_2CO_3 (106.0 mg, 1.00 mmol, 2.0 equiv.), TTMSS (154 μL, 0.50 mmol, 1.0 equiv.), 4-bromotetrahydro-2H-pyran (84 μL, 0.75 mmol, 1.5 equiv.), 4-bromotoluene (86.0 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography yielded the pure product as a clear oil (72 mg, 0.41 mmol, 82% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (s, 4H), 4.08 (ddt, *J* = 11.7, 4.5, 1.1 Hz, 2H), 3.53 (td, *J* = 11.6, 2.5 Hz, 2H), 2.72 (tt, *J* = 11.7, 4.2 Hz, 1H), 2.33 (s, 3H), 1.87 – 1.69 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 142.9, 135.8, 129.2, 126.6, 68.4, 41.1, 34.0, 21.0.

Spectroscopic data matches with previously reported data.[7]



4-(*m*-tolyl)tetrahydro-2*H*-pyran (3)

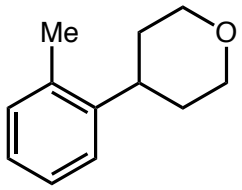
Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.5 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.5 mg, 2.5 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 3.0 μmol, 0.006 equiv, Na_2CO_3 (106.0 mg, 1.00 mmol, 2.0 equiv.), TTMSS (154 μL, 0.50 mmol, 1.0 equiv.), 4-bromotetrahydro-2H-pyran (84 μL, 0.75 mmol, 1.5 equiv.), 1-bromo-3-methylbenzene (86 mg, 61 μL, 0.5 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography yielded the pure product as a white crystalline solid (71 mg, 0.40 mmol, 80% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 1H), 7.04 (d, *J* = 8.3 Hz, 3H), 4.15 – 4.02 (m, 2H), 3.53 (td, *J* = 11.7, 2.4 Hz, 2H), 2.72 (tt, *J* = 11.8, 4.1 Hz, 1H), 2.35 (s, 3H), 1.90 – 1.71 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 145.87, 138.07, 128.43, 127.59, 127.07, 123.74, 68.47, 41.55, 21.52.

IR (film) ν_{max} 3021, 2931, 2839, 1607, 1129, 1086 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{17}O$ ($[M+H]^+$) 177.1274, found 177.1275.



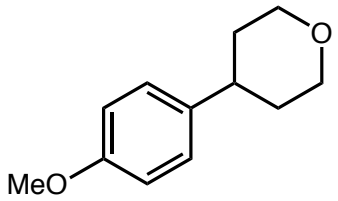
4-(*o*-tolyl)tetrahydro-2*H*-pyran (4)

Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.5 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.5 mg, 2.5 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 3.0 μmol, 0.006 equiv, Na_2CO_3 (106.0 mg, 1.00 mmol, 2.0 equizv.), TTMSS (154 μL, 0.50 mmol, 1.0 equiv.), 4-bromotetrahydro-2H-pyran (84 μL, 0.75 mmol, 1.5 equiv.), 1-bromo-2-methylbenzene (86 mg, 60 μL, 0.5 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography yielded the pure product as a white crystalline solid (74 mg, 0.42 mmol, 83% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.08 (m, 4H), 4.14 – 4.07 (m, 3H), 3.56 (td, *J* = 11.8, 2.0 Hz, 3H), 2.98 (tt, *J* = 11.9, 3.6 Hz, 1H), 2.36 (s, 3H), 1.83 (dtd, *J* = 13.5, 12.0, 4.4 Hz, 2H), 1.73 – 1.66 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.67, 135.11, 130.42, 126.37, 126.00, 125.51, 68.69, 37.37, 33.21, 19.36.

Spectroscopic data matches with previously reported data.[8]



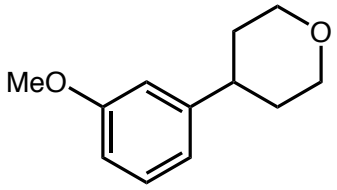
4-(4-methoxyphenyl)tetrahydro-2*H*-pyran (4)

Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.5 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.5 mg, 2.5 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 3.0 μmol, 0.006 equiv, Na_2CO_3 (106.0 mg, 1.00 mmol, 2.0 equiv.), TTMSS (154 μL, 0.50 mmol, 1.0 equiv.), 4-bromotetrahydro-2H-pyran (84 μL, 0.75 mmol, 1.5 equiv.), 4-bromoanisole (63 μL, 94.0 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography yielded the pure product as a clear oil (73 mg, 0.38 mmol, 77% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.12 – 4.03 (m, 2H), 3.80 (s, 3H), 3.52 (td, *J* = 11.4, 2.8 Hz, 2H), 2.70 (tt, *J* = 11.2, 4.6 Hz, 1H), 1.84 – 1.70 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 158.0, 138.1, 127.6, 113.9, 68.5, 55.3, 40.7, 34.2.

Spectroscopic data matches with previously reported data.[8]



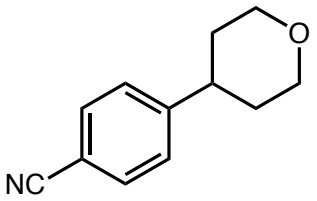
4-(3-methoxyphenyl)tetrahydro-2*H*-pyran (6)

Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.5 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.5 mg, 2.5 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 3.0 μmol, 0.006 equiv, Na_2CO_3 (106.0 mg, 1.00 mmol, 2.0 equiv.), TTMSS (154 μL, 0.50 mmol, 1.0 equiv.), 4-bromotetrahydro-2H-pyran (84 μL, 0.75 mmol, 1.5 equiv.), 3-bromoanisole (63 μL, 94.0 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography yielded the pure product as a clear oil (79 mg, 0.41 mmol, 82% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.7 Hz, 1H), 6.86 (dt, *J* = 7.7, 1.2 Hz, 1H), 6.83 – 6.77 (m, 2H), 4.14 – 4.08 (m, 2H), 3.84 (s, 3H), 3.56 (td, *J* = 11.6, 2.6 Hz, 2H), 2.77 (tt, *J* = 11.6, 4.3 Hz, 1H), 1.91 – 1.77 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7, 147.6, 129.5, 119.1, 112.8, 111.2, 68.4, 55.2, 41.6, 33.9.

Spectroscopic data matches with previously reported data.[8]



4-(tetrahydro-2H-pyran-4-yl)benzonitrile (7)

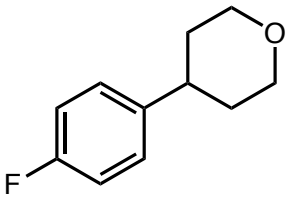
Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.5 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.5 mg, 2.5 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 3.0 μmol, 0.006 equiv, Na_2CO_3 (106.0 mg, 1.00 mmol, 2.0 equiv.), TTMSS (154 μL, 0.50 mmol, 1.0 equiv.), 4-bromotetrahydro-2H-pyran (84 μL, 0.75 mmol, 1.5 equiv.), 4-bromobenzonitrile (91 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography yielded the pure product as a white solid (68 mg, 0.365 mmol, 73% yield).

^{1}H NMR (500 MHz, Acetone-*d*6) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 4.06 – 3.93 (m, 2H), 3.49 (ddd, *J* = 11.4, 7.9, 5.1 Hz, 2H), 3.01 – 2.88 (m, 1H), 1.83 – 1.69 (m, 4H).

^{13}C NMR (126 MHz, Acetone-d_6) δ 152.70, 133.16, 128.80, 119.45, 110.82, 68.38, 42.37, 34.23.

IR (film) ν_{max} 2942, 2843, 2226, 1607, 1386, 1238, 1123, 1083, 836.93 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{14}NO$ ($[M+H]^+$) 187.09971, found 187.0996.



4-(4-fluorophenyl)tetrahydro-2*H*-pyran (8)

Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.5 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.5 mg, 2.5 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 3.0 μmol, 0.006 equiv, Na_2CO_3 (106.0 mg, 1.00 mmol, 2.0 equiv.), TTMSS (154 μL, 0.50 mmol, 1.0 equiv.), 4-bromotetrahydro-2H-pyran (84 μL, 0.75 mmol, 1.5 equiv.), 1-bromo-4fluorobenzene (55 μL, 87 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography yielded the pure product as a clear oil (66 mg, 0.36 mmol, 73% yield).

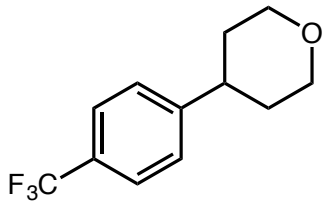
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 – 7.15 (m, 2H), 7.04 – 6.96 (m, 2H), 4.12 – 4.03 (m, 2H), 3.52 (td, J = 11.4, 3.1 Hz, 2H), 2.74 (ddd, J = 15.8, 10.4, 4.9 Hz, 1H), 1.84 – 1.70 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 161.38 (d, $J_{C,F}$ = 244.0 Hz), 141.54 (d, $J_{C,F}$ = 3.2 Hz), 128.07 (d, $J_{C,F}$ = 7.8 Hz), 115.23 (d, $J_{C,F}$ = 21.0 Hz), 68.35 , 40.87 , 34.11 .

^{19}F NMR (282 MHz, $CDCl_3$) δ -117.06.

IR (film) ν_{max} 2939, 2842, 1603, 1509, 1221, 1129, 1016 cm^{-1}.

HRMS (EI-TOF) calcd. for $C_{11}H_{13}FO$ ($[M^*]^+$) 180.0945, found 180.0952.



4-(4-(trifluoromethyl)phenyl)tetrahydro-2*H*-pyran (9)

Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.5 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.5 mg, 2.5 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 3.0 μmol, 0.006 equiv, Na_2CO_3 (106.0 mg, 1.00 mmol, 2.0 equiv.), TTMSS (154 μL, 0.50 mmol, 1.0 equiv.), 4-bromotetrahydro-2H-pyran (84 μL, 0.75 mmol, 1.5 equiv.), 1-bromo-4-(trifluoromethyl)benzene (70 μL, 113 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography yielded the pure product as a clear oil (89 mg, 0.39 mmol, 78% yield).

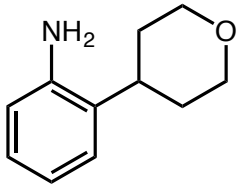
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J = 7.9 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 4.16 – 4.04 (m, 2H), 3.54 (td, J = 11.6, 2.5 Hz, 2H), 2.83 (tt, J = 11.6, 4.3 Hz, 1H), 1.92 – 1.72 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 128.7 (q, $J_{C,F}$ = 31.5 Hz), 127.1, 125.5 (q, $J_{C,F}$ = 3.8 Hz), 124.3 (q, $J_{C,F}$ = 272.2 Hz), 68.2, 41.5, 33.6.

^{19}F NMR (282 MHz, $CDCl_3$) δ -62.4.

IR (film) ν_{max} 2942, 2844, 1618, 1323, 1115, 1067 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{14}F_3O$ ($[M+H]^+$) 231.0991, found 231.0993.



2-(tetrahydro-2*H*-pyran-4-yl)aniline (10)

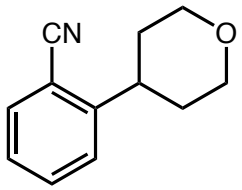
Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.5 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.5 mg, 2.5 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 3.0 μmol, 0.006 equiv, Na_2CO_3 (106.0 mg, 1.00 mmol, 2.0 equiv.), TTMSS (154 μL, 0.50 mmol, 1.0 equiv.), 4-bromotetrahydro-2H-pyran (84 μL, 0.75 mmol, 1.5 equiv.), 2-bromoaniline (86 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). The reaction was let run to 12 hours. Purification by column chromatography yielded the pure product as an orange oil (58 mg, 0.325 mmol, 65% yield).

^{1}H NMR (500 MHz, Acetone-*d*6) δ 7.04 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.91 (td, *J* = 7.6, 1.6 Hz, 1H), 6.69 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.62 (td, *J* = 7.4, 1.4 Hz, 1H), 4.51 (s, 2H), 3.96 (ddd, *J* = 11.2, 4.4, 1.7 Hz, 2H), 3.51 (td, *J* = 11.7, 2.1 Hz, 2H), 2.90 (tt, *J* = 11.7, 3.7 Hz, 1H), 1.80 – 1.72 (m, 2H), 1.72 – 1.60 (m, 2H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 146.03, 130.08, 127.30, 126.39, 118.24, 116.19, 68.85, 35.94, 33.31.

IR (film) ν_{max} 3359, 2940, 2844, 1622, 1496, 1121, 1083 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{11}H_{16}NO$ ($[M+H]^+$) 177.11536, found 177.11536.



2-(tetrahydro-2*H*-pyran-4-yl)benzonitrile (11)

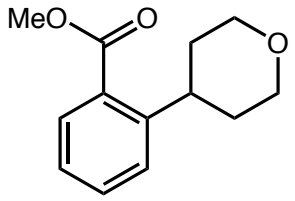
Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.5 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.5 mg, 2.5 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 3.0 μmol, 0.006 equiv, Na_2CO_3 (106.0 mg, 1.00 mmol, 2.0 equiv.), TTMSS (154 μL, 0.50 mmol, 1.0 equiv.), 4-bromotetrahydro-2H-pyran (84 μL, 0.75 mmol, 1.5 equiv.), 2-bromobenzonitrile (91 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). The reaction was let run to 12 hours. Purification by column chromatography yielded the pure product as a white solid (87 mg, 0.470 mmol, 94% yield).

^{1}H NMR (500 MHz, Acetone-d_6) δ 7.74 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.69 (td, *J* = 7.7, 1.4 Hz, 1H), 7.56 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.43 (td, *J* = 7.6, 1.2 Hz, 1H), 4.02 (ddt, *J* = 11.7, 4.5, 1.1 Hz, 2H), 3.54 (td, *J* = 11.7, 2.4 Hz, 2H), 3.25 – 3.16 (m, 1H), 1.89 – 1.73 (m, 4H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 150.05, 134.25, 133.88, 127.93, 127.77, 118.38, 112.57, 68.42, 40.95, 33.80.

IR (film) ν_{max} 2947, 2844, 2222, 1238, 1129, 1089, 760 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{14}NO$ ($[M+H]^+$) 187.09971, found 187.09939.



methyl 2-(tetrahydro-2*H*-pyran-4-yl)benzoate (12)

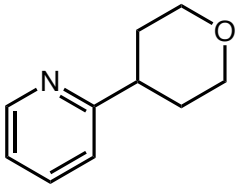
Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.5 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.5 mg, 2.5 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 3.0 μmol, 0.006 equiv, Na_2CO_3 (106.0 mg, 1.00 mmol, 2.0 equiv.), TTMSS (154 μL, 0.50 mmol, 1.0 equiv.), 4-bromotetrahydro-2H-pyran (84 μL, 0.75 mmol, 1.5 equiv.), methyl 2-bromobenzoate (70 μL, 108 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). The reaction was let run to 12 hours. Purification by column chromatography yielded the pure product as a white solid (87 mg, 0.470 mmol, 94% yield).

^{1}H NMR (500 MHz, $CDCl_3$-*d*) δ 7.80 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.52 – 7.46 (t, *J* = 7.5, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.26 (t, *J* = 8.0 Hz, 1H). δ 4.10 – 4.06 (m, 2H), 3.65 (tt, *J* = 11.6, 4.0 Hz, 1H), 3.58 (td, *J* = 11.6, 2.4 Hz, 2H), 1.90 – 1.68 (m, 5H), 4.10 – 4.04 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.58, 146.93, 132.20, 130.40, 129.80, 127.09, 126.06, 68.69, 52.23, 37.57, 34.04.

IR (film) ν_{max} 2950, 2841, 1718, 1241, 1085, 754 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{17}O_3$ ($[M+H]^+$) 220.1099, found 220.1102.



2-(tetrahydro-2*H*-pyran-4-yl)pyridine (13)

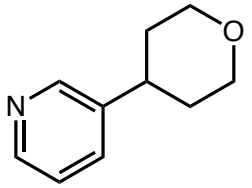
Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.5 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.5 mg, 2.5 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 3.0 μmol, 0.006 equiv, LiOH (24.0 mg, 1.00 mmol, 2.0 equiv.), TTMSS (154 μL, 0.50 mmol, 1.0 equiv.), 4-bromotetrahydro-2H-pyran (84 μL, 0.75 mmol, 1.5 equiv.), 2-bromopyridine (48 μL, 79 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography yielded the pure product as a clear oil (41 mg, 0.25 mmol, 50% yield).

^{1}H NMR (500 MHz, Acetone-d_6) δ 8.50 (ddd, *J* = 4.8, 1.9, 1.0 Hz, 1H), 7.69 (td, *J* = 7.7, 1.9 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.17 (ddd, *J* = 7.5, 4.8, 1.1 Hz, 1H), 4.00 – 3.95 (m, 2H), 3.48 (td, *J* = 11.7, 2.4 Hz, 2H), 2.93 (tt, *J* = 11.6, 4.1 Hz, 1H), 1.91 – 1.73 (m, 4H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 165.43, 150.01, 137.20, 122.18, 121.94, 68.37, 44.06, 33.23.

IR (film) ν_{max} 2943, 2842, 1589, 1472, 1433, 1237, 1127, 1087, 748 cm^{-1}.

HRMS (EI-TOF) m/z calcd. for $C_{10}H_{14}NO$ ($[M+H]^+$) 163.0997, found 163.0996.



3-(tetrahydro-2*H*-pyran-4-yl)pyridine (14)

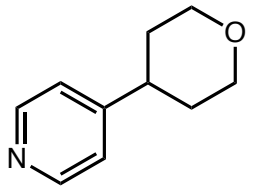
Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.5 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.5 mg, 2.5 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 3.0 μmol, 0.006 equiv, LiOH (24.0 mg, 1.00 mmol, 2.0 equiv.), TTMSS (154 μL, 0.50 mmol, 1.0 equiv.), 4-bromotetrahydro-2H-pyran (84 μL, 0.75 mmol, 1.5 equiv.), 3-bromopyridine (48 μL, 79 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography yielded the pure product as a clear oil (64 mg, 0.4 mmol, 80% yield).

^{1}H NMR (500 MHz, Acetone-d_6) δ 8.51 (s, 1H), 8.45 – 8.41 (m, 1H), 7.66 (dt, *J* = 8.1, 1.9 Hz, 1H), 7.30 (dd, *J* = 7.9, 4.7 Hz, 1H), 4.05 – 3.94 (m, 2H), 3.53 – 3.45 (m, 2H), 2.85 (ddd, *J* = 15.9, 10.6, 6.2 Hz, 1H), 1.75 (td, *J* = 9.7, 8.4, 3.7 Hz, 4H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 149.69, 148.54, 142.07, 134.62, 124.24, 68.45, 39.76, 34.38.

IR (film) ν_{max} 3414, 2940, 2843, 1575, 1425, 1238, 1126, 1085, 1019, 839 cm^{-1}.

HRMS (EI-TOF) m/z calcd. for $C_{10}H_{14}NO$ ($[M+H]^+$) 163.0997, found 163.0995.



4-(tetrahydro-2*H*-pyran-4-yl)pyridine (15)

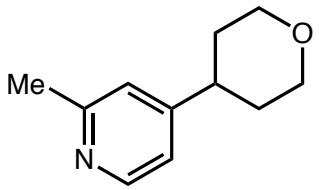
Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 10.0 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.6 mg, 5.0 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 12.0 μmol, 0.006 equiv.), LiOH (24.0 mg, 2.0 mmol, 2.0 equiv.), TTMSS (154 μL, 1.00 mmol, 1.0 equiv.), 4-bromotetrahydro-2H-pyran (84 μL, 0.75 mmol, 1.5 equiv.), 4-bromopyridine•hydrochloride (97 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography yielded the pure product as a white crystalline solid (66 mg, 0.40 mmol, 81% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 5.2 Hz, 2H), 7.14 (d, *J* = 6.1 Hz, 2H), 4.13 – 4.07 (m, 2H), 3.58 – 3.49 (m, 2H), 2.76 (tt, *J* = 10.8, 5.2 Hz, 1H), 1.86 – 1.74 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.3, 150.0, 122.2, 68.0, 40.8, 32.9.

IR (film) ν_{max} 3413, 3025, 2941, 2843, 1598, 1127 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{10}H_{14}NO$ ($[M+H]^+$) 164.1070, found 164.1070.



2-methyl-4-(tetrahydro-2*H*-pyran-4-yl)pyridine (16)

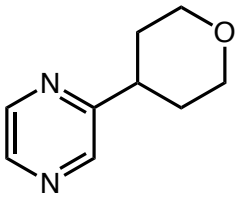
Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 5.0 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.6 mg, 2.5 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 3.0 μmol, 0.006 equiv.), quinuclidine (0.6 mg, 10.0 μmol, 0.01 equiv.), LiOH (24.0 mg, 1.0 mmol, 2.0 equiv.), TTMSS (154 μL, 1.00 mmol, 1.0 equiv.), 4-bromotetrahydro-2H-pyran (84 μL, 0.75 mmol, 1.5 equiv.), 4-bromo-2-methylpyridine (86 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography yielded the pure product as a clear oil (64 mg, 0.36 mmol, 72% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (d, *J* = 5.2 Hz, 1H), 7.00 (d, *J* = 1.6 Hz, 1H), 6.95 (dd, *J* = 5.3, 1.7 Hz, 1H), 4.08 (ddd, *J* = 11.4, 4.5, 2.0 Hz, 2H), 3.52 (td, *J* = 11.4, 3.0 Hz, 2H), 2.78 – 2.66 (m, 1H), 2.54 (s, 3H), 1.84 – 1.73 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 158.54, 154.66, 149.28, 121.68, 119.29, 68.06, 40.85, 32.97, 24.48.

IR (film) ν_{max} 3400, 2936, 2843, 1604, 1558, 1128, 1086 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{11}H_{16}NO$ ($[M+H]^+$) 177.1154, found 177.1156.



2-(tetrahydro-2*H*-pyran-4-yl)pyrazine (17)

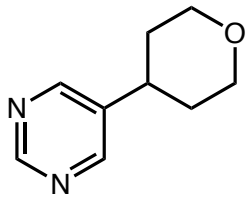
Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 10.0 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.6 mg, 5.0 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 12.0 μmol, 0.006 equiv.), LiOH (24.0 mg, 2.0 mmol, 2.0 equiv.), TTMSS (154 μL, 1.00 mmol, 1.0 equiv.), 4-bromotetrahydro-2H-pyran (84 μL, 0.75 mmol, 1.5 equiv.), 2-bromopyrazine (45 μL, 79 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography yielded the pure product as a clear oil (41 mg, 0.25 mmol, 50% yield).

^{1}H NMR (500 MHz, Acetone-d_6) δ 8.56 (d, *J* = 1.6 Hz, 1H), 8.53 (dd, *J* = 2.5, 1.5 Hz, 1H), 8.45 (d, *J* = 2.5 Hz, 1H), 4.04 – 3.96 (m, 2H), 3.51 (td, *J* = 11.7, 2.3 Hz, 2H), 3.06 (tt, *J* = 11.7, 4.1 Hz, 1H), 1.88 (dtd, *J* = 13.2, 11.9, 4.4 Hz, 2H), 1.83 – 1.77 (m, 2H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 160.67, 144.93, 144.49, 143.60, 68.16, 41.48, 32.69.

IR (film) ν_{max} 2950, 2844, 1408, 1239, 1150, 1086, 1022, 845 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_9H_{13}N_2O$ ($[M+H]^+$) 164.09496, found 164.0952.



5-(tetrahydro-2*H*-pyran-4-yl)pyrimidine (18)

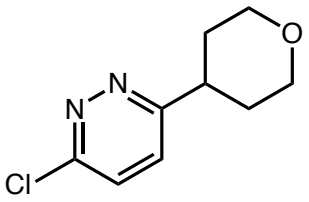
Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 10.0 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.6 mg, 5.0 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 12.0 μmol, 0.006 equiv.), LiOH (24.0 mg, 2.0 mmol, 2.0 equiv.), TTMSS (154 μL, 1.00 mmol, 1.0 equiv.), 4-bromotetrahydro-2H-pyran (84 μL, 0.75 mmol, 1.5 equiv.), 5-chloropyrimidine (57.3 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography yielded the pure product as a white crystalline solid (53 mg, 0.32 mmol, 64% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.62 (s, 2H), 4.11 (ddd, *J* = 11.5, 4.2, 1.8 Hz, 2H), 3.54 (td, *J* = 11.5, 2.8 Hz, 2H), 2.81 (tt, *J* = 11.5, 4.6 Hz, 1H), 1.92 – 1.76 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 157.2, 155.6, 138.2, 67.9, 37.1, 33.0.

IR (film) ν_{max} 3402, 2963, 2849, 1562, 1446, 1408, 1387, 1276, 1270, 1234, 1163, 1126, 1083, 1016 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_9H_{13}N_2O$ ($[M+H]^+$) 165.1022, found 165.1022.



3-chloro-6-(tetrahydro-2*H*-pyran-4-yl)pyridazine (19)

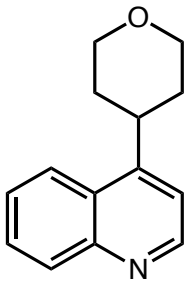
Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 10.0 μmol, 0.01 equiv.), $NiCl_2$•glyme (11 mg, 0.05 mmol, 0.1 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (15 mg, 0.055 mmol, 0.11 equiv.), LiOH (24.0 mg, 2.0 mmol, 2.0 equiv.), TTMSS (154 μL, 1.00 mmol, 1.0 equiv.), 4-bromotetrahydro-2H-pyran (84 μL, 0.75 mmol, 1.5 equiv.), 3,6-dichloropyrdazine (74 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography yielded the pure product as a white solid (53 mg, 0.265 mmol, 53% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.8 Hz, 1H), 7.34 (d, *J* = 8.8 Hz, 1H), 4.12 (dt, *J* = 11.6, 3.3 Hz, 2H), 3.62 – 3.54 (m, 2H), 3.30 – 3.18 (m, 1H), 1.96 – 1.88 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 165.13, 155.53, 128.63, 127.06, 67.89, 41.39, 32.13.

IR (film) ν_{max} 3036, 2957, 2856, 1418, 1234, 1144, 1125, 1085, 979, 871 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_9H_{12}ClN_2O$ ($[M+H]^+$) 198.0559, found 198.0561.



4-(tetrahydro-2*H*-pyran-4-yl)quinoline (20)

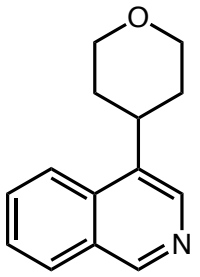
Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 10.0 μmol, 0.01 equiv.), $NiCl_2$•glyme (5.5 mg, 0.025 mmol, 0.05 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (8 mg, 0.030 mmol, 0.06 equiv.), LiOH (24.0 mg, 2.0 mmol, 2.0 equiv.), TTMSS (154 μL, 1.00 mmol, 1.0 equiv.), 4-bromotetrahydro-2H-pyran (84 μL, 0.75 mmol, 1.5 equiv.), 4-bromoquinoline (104 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography yielded the pure product as a white solid (80 mg, 0.375 mmol, 75% yield).

^{1}H NMR (300 MHz, Acetone-d_6) δ 8.87 (d, *J* = 4.6 Hz, 1H), 8.34 – 8.27 (m, 1H), 8.12 – 8.03 (m, 1H), 7.75 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 1H), 7.63 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.44 (d, *J* = 4.6 Hz, 1H), 4.07 (dt, *J* = 11.3, 3.0 Hz, 2H), 3.84 – 3.63 (m, 3H), 1.90 (tt, *J* = 5.9, 2.9 Hz, 4H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 152.11, 151.36, 149.60, 131.30, 129.61, 127.48, 127.15, 124.03, 118.57, 68.48, 36.74, 33.98.

IR (film) ν_{max} 2952, 2848, 1591, 1509, 1264, 1127, 1086, 898 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{16}NO$ ($[M+H]^+$) 213.1153, found 213.1154.



4-(tetrahydro-2*H*-pyran-4-yl)isoquinoline (21)

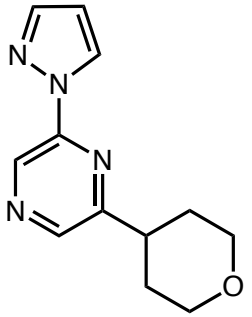
Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 10.0 μmol, 0.01 equiv.), $NiCl_2$•glyme (5.5 mg, 0.025 mmol, 0.05 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (8 mg, 0.030 mmol, 0.06 equiv.), LiOH (24.0 mg, 2.0 mmol, 2.0 equiv.), TTMSS (154 μL, 1.00 mmol, 1.0 equiv.), 4-bromotetrahydro-2H-pyran (84 μL, 0.75 mmol, 1.5 equiv.), 4-bromoisoquinoline (104 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography yielded the pure product as a white solid (83 mg, 0.390 mmol, 78% yield).

^{1}H NMR (300 MHz, Acetone-d_6) δ 9.17 (s, 1H), 8.46 (s, 1H), 8.25 (d, J = 8.6 Hz, 1H), 8.12 (d, J = 8.1 Hz, 1H), 7.81 (ddd, J = 8.5, 6.7, 1.5 Hz, 1H), 7.68 (t, J = 7.5 Hz, 1H), 4.10 – 4.01 (m, 2H), 3.75 – 3.57 (m, 3H), 2.00 – 1.85 (m, 4H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 152.05, 141.00, 135.23, 134.55, 131.12, 129.38, 129.26, 127.70, 123.11, 68.72, 35.83, 34.23.

IR (film) ν_{max} 2950, 2916, 2842, 1584, 1383, 1127, 1085, 904, 855 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{16}NO$ ($[M+H]^+$) 213.1153, found 213.1156.



2-(1*H*-pyrazol-1-yl)-6-(tetrahydro-2*H*-pyran-4-yl)pyrazine (22)

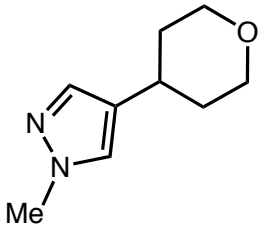
Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 10.0 μmol, 0.01 equiv.), $NiCl_2$•glyme (5.5 mg, 0.025 mmol, 0.05 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (8 mg, 0.030 mmol, 0.06 equiv.), LiOH (24.0 mg, 2.0 mmol, 2.0 equiv.), TTMSS (154 μL, 1.00 mmol, 1.0 equiv.), 4-bromotetrahydro-2H-pyran (84 μL, 0.75 mmol, 1.5 equiv.), 2-chloro-6-(1H-pyrazol-1-yl)pyrazine (90 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography yielded the pure product as a white solid (99 mg, 0.430 mmol, 86% yield).

^{1}H NMR (500 MHz, Acetone-d_6) δ 9.08 (s, 1H), 8.68 (d, J = 2.6 Hz, 1H), 8.52 (s, 1H), 7.83 (d, J = 1.6 Hz, 1H), 6.60 (dd, J = 2.6, 1.6 Hz, 1H), 4.06 – 3.98 (m, 2H), 3.54 (td, J = 11.7, 2.4 Hz, 2H), 3.14 (tt, J = 11.7, 4.1 Hz, 1H), 2.02 – 1.82 (m, 4H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 158.49, 147.58, 143.68, 141.41, 133.25, 128.13, 109.24, 68.08, 40.98, 32.47.

IR (film) ν_{max} 3161, 3117, 3076, 2957, 2844, 1532, 1454, 1400, 961 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{15}N_4O$ ($[M+H]^+$) 230.1167, found 230.1164.



1-methyl-4-(tetrahydro-2*H*-pyran-4-yl)-1*H*-pyrazole (23)

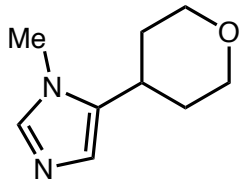
Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 10.0 μmol, 0.01 equiv.), $NiCl_2$•glyme (11 mg, 0.05 mmol, 0.1 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (15 mg, 0.055 mmol, 0.11 equiv.), LiOH (24.0 mg, 2.0 mmol, 2.0 equiv.), TTMSS (154 μL, 1.00 mmol, 1.0 equiv.), 4-bromotetrahydro-2H-pyran (84 μL, 0.75 mmol, 1.5 equiv.), 4-bromo-1-methyl-1H-pyrazole (52 μL, 80 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography (10% MeOH in DCM) yielded the pure product as a white solid (55 mg, 0.330 mmol, 66% yield).

^{1}H NMR (500 MHz, Acetone-d_6) δ 7.37 (s, 1H), 7.26 (s, 1H), 3.93 – 3.86 (m, 2H), 3.80 (s, 3H), 3.42 (td, J = 11.8, 2.1 Hz, 2H), 2.70 (tt, J = 11.7, 3.9 Hz, 1H), 1.78 (ddd, J = 13.2, 4.0, 2.0 Hz, 2H), 1.57 (dtd, J = 13.2, 11.7, 4.3 Hz, 2H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 137.19, 127.61, 127.40, 68.28, 38.78, 35.23, 32.21.

IR (film) ν_{max} 3437, 2933, 2844, 1442, 1387, 1237, 1088, 987, 826 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_9H_{15}N_2O$ ($[M+H]^+$) 166.1106, found 166.1103.



1-methyl-5-(tetrahydro-2*H*-pyran-4-yl)-1*H*-imidazole (24)

Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 10.0 μmol, 0.01 equiv.), $NiCl_2$•glyme (11 mg, 0.05 mmol, 0.1 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (15 mg, 0.055 mmol, 0.11 equiv.), LiOH (24.0 mg, 2.0 mmol, 2.0 equiv.), TTMSS (154 μL, 1.00 mmol, 1.0 equiv.), 4-bromotetrahydro-2H-pyran (84 μL, 0.75 mmol, 1.5 equiv.), 5-bromo-1-methyl-1H-imidazole (80 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography (10% MeOH in DCM) yielded the pure product as a white solid (50 mg, 0.300 mmol, 60% yield).

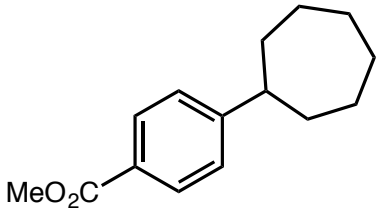
^{1}H NMR (500 MHz, Acetone-d_6) δ 7.40 (s, 1H), 6.72 (s, 1H), 3.98 – 3.90 (m, 2H), 3.64 (s, 3H), 3.48 (td, *J* = 11.8, 2.0 Hz, 2H), 2.88 (ddt, *J* = 11.8, 8.0, 3.8 Hz, 1H), 1.82 (ddd, *J* = 13.3, 3.9, 2.1 Hz, 2H), 1.62 (dtd, *J* = 13.2, 11.7, 4.2 Hz, 2H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 138.88, 137.24, 125.48, 68.18, 33.52, 31.89, 31.40.

IR (film) ν_{max} 3365, 2945, 2846, 1653, 1503, 1240, 1124, 1085, 826, 665 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_9H_{15}N_2O$ ($[M+H]^+$) 166.1106, found 166.1109.

5) Alkyl Halide Scope



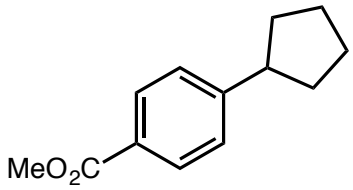
methyl 4-cycloheptylbenzoate (25)

Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 5.0 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.6 mg, 2.5 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 3.0 μmol, 0.006 equiv.), Na_2CO_3 (106.0 mg, 1.00 mmol, 2.0 equiv.), TTMSS (154 μL, 0.50 mmol, 1.0 equiv.), bromocycloheptane (103 μL, 0.75 mmol, 1.5 equiv.), methyl 4-bromobenzoate (108 mg, 0.50 mmol, 1.0 equiv.), and Toluene/DME (4/1, 5.0 mL). Purification by silica gel column chromatography (EtOAc in hexanes) followed by reverse phase chromatography (MeCN in H_2O) yielded the pure product as a clear oil (71 mg, 0.31 mmol, 62% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 3.89 (s, 3H), 2.71 (tt, *J* = 10.5, 3.6 Hz, 1H), 1.94 – 1.86 (m, 2H), 1.80 (dh, *J* = 13.3, 3.2 Hz, 2H), 1.75 – 1.50 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.21, 155.39, 129.75, 127.48, 126.72, 51.95, 47.09, 36.51, 27.88, 27.23.

Spectroscopic data matches with previously reported data.[9]



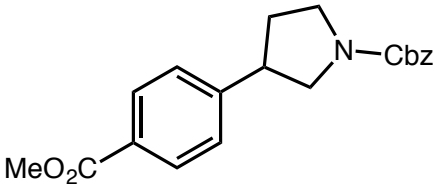
methyl 4-cyclopentylbenzoate (26)

Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 5.0 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.6 mg, 2.5 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 3.0 μmol, 0.006 equiv.), Na_2CO_3 (106.0 mg, 1.00 mmol, 2.0 equiv.), TTMSS (154 μL, 0.50 mmol, 1.0 equiv.), bromocyclopentane (76 μL, 0.75 mmol, 1.5 equiv.), methyl 4-bromobenzoate (108 mg, 0.50 mmol, 1.0 equiv.), and Toluene/DME (4/1, 5.0 mL). Purification by silica gel column chromatography (EtOAc in hexanes) followed by reverse phase chromatography (MeCN in H_2O) yielded the pure product as a clear oil (70 mg, 0.34 mmol, 68% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 3.90 (s, 3H), 3.04 (ddd, *J* = 17.2, 9.6, 7.6 Hz, 1H), 2.16 – 2.01 (m, 2H), 1.88 – 1.54 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.20, 152.22, 129.61, 127.62, 127.12, 77.28, 77.03, 76.77, 51.97, 45.99, 34.52, 25.58.

Spectroscopic data matches with previously reported data.[5]



benzyl 3-(4-(methoxycarbonyl)phenyl)pyrrolidine-1-carboxylate (27)

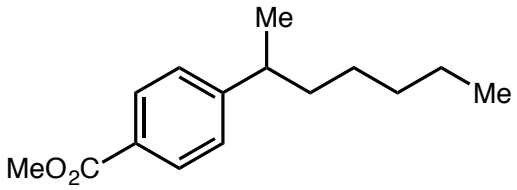
Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 10.0 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.6 mg, 5.0 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 12.0 μmol, 0.006 equiv.), Na_2CO_3 (106.0 mg, 2.0 mmol, 2.0 equiv.), TTMSS (154 μL, 1.00 mmol, 1.0 equiv.), benzyl 3-bromopyrrolidine-1-carboxylate (213 mg, 0.75 mmol, 1.5 equiv.), methyl 4-bromobenzoate (108 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography yielded the pure product as a clear oil (136 mg, 0.40 mmol, 80% yield).

^{1}H NMR (500 MHz, Acetone-d_6) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.49 – 7.44 (m, 2H), 7.37 (dd, *J* = 13.6, 7.6 Hz, 5H), 5.16 – 5.11 (m, 2H), 3.95-3.84 (m, 1H), 3.87 (s, 3H), 3.72 – 3.28 (m, 4H), 2.34 (ddt, *J* = 9.0, 6.0, 2.9 Hz, 1H), 2.17 – 2.08 (m, 1H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 167.02, 130.45, 129.62, 129.22, 128.58, 128.55, 128.26, 66.85, 53.03, 52.65, 52.26, 46.88, 46.42, 44.88, 43.95, 33.70, 32.78.

IR (film) ν_{max} 2951, 2883, 1697, 1416, 1277, 1106, 697 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{20}H_{22}NO_4$ ($[M+H]^+$) 339.1470, found 339.1468.



methyl 4-(heptan-2-yl)benzoate (28)

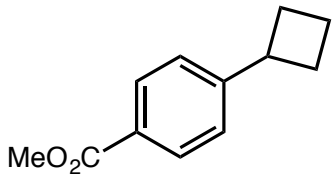
Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 5.0 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.6 mg, 2.5 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 3.0 μmol, 0.006 equiv.), Na_2CO_3 (106.0 mg, 1.00 mmol, 2.0 equiv.), TTMSS (154 μL, 0.50 mmol, 1.0 equiv.), 2-bromoheptane (118 μL, 0.75 mmol, 1.5 equiv.), methyl 4-bromobenzoate (108 mg, 0.50 mmol, 1.0 equiv.), and Toluene/DME (4/1, 5.0 mL). Purification by silica gel column chromatography (EtOAc in hexanes) followed by reverse phase chromatography (MeCN in H_2O) yielded the pure product as a clear oil (83 mg, 0.35 mmol, 71% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 3.90 (s, 3H), 2.73 (h, *J* = 7.1 Hz, 1H), 1.59 – 1.52 (m, 2H), 1.29 – 1.07 (m, 9H), 0.88 – 0.79 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.22, 153.53, 129.68, 127.76, 127.05, 77.27, 77.02, 76.77, 51.96, 40.08, 38.14, 31.87, 27.30, 22.56, 22.08, 14.06.

IR (film) ν_{max} 2956, 2926, 2856, 1721, 1610, 1434, 1274, 1106 cm^{-1}.

HRMS (ESI-TOF) calcd. for $C_{15}H_{22}O_2$ ($[M^*]^+$) 234.1614, found 234.1623.



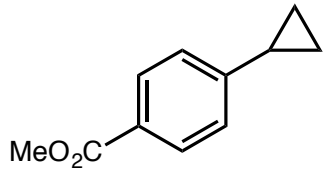
methyl 4-cyclobutylbenzoate (29)

Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 5.0 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.6 mg, 2.5 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 3.0 μmol, 0.006 equiv.), Na_2CO_3 (106.0 mg, 1.00 mmol, 2.0 equiv.), TTMSS (154 μL, 0.50 mmol, 1.0 equiv.), bromocyclobutane (70 μL, 0.75 mmol, 1.5 equiv.), methyl 4-bromobenzoate (108 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography yielded the pure product as a clear oil (58 mg, 0.31 mmol, 61% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.29 – 7.24 (m, 2H), 3.90 (s, 3H), 3.60 (p, *J* = 8.8 Hz, 1H), 2.37 (ddt, *J* = 10.6, 7.9, 3.8 Hz, 2H), 2.21 – 2.12 (m, 2H), 2.10 – 1.99 (m, 1H), 1.88 (tdd, *J* = 10.0, 5.9, 1.8 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.19, 151.68, 129.58, 127.56, 126.28, 51.98, 40.24, 29.55, 18.30.

Spectroscopic data matches with previously reported data.[5]



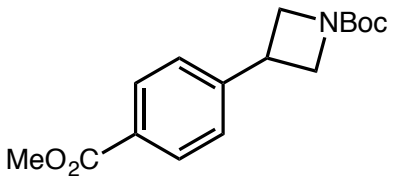
methyl 4-cyclopropylbenzoate (30)

Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 5.0 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.6 mg, 2.5 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 3.0 μmol, 0.006 equiv.), Na_2CO_3 (106.0 mg, 1.00 mmol, 2.0 equiv.), TTMSS (154 μL, 0.50 mmol, 1.0 equiv.), bromocyclopropane (60 μL, 0.75 mmol, 1.5 equiv.), methyl 4-bromobenzoate (108 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography yielded the pure product as a clear oil (29 mg, 0.16 mmol, 32% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 1.94 (tt, *J* = 8.4, 5.0 Hz, 1H), 1.08 – 1.01 (m, 2H), 0.79 – 0.74 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.15, 149.98, 129.63, 127.20, 125.32, 51.95, 15.71, 10.31.

Spectroscopic data matches with previously reported data.[10]



***tert*-butyl 3-(4-(methoxycarbonyl)phenyl)azetidine-1-carboxylate (31)**

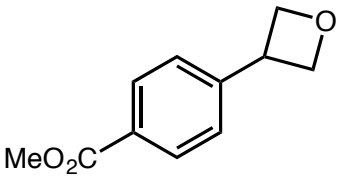
Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 10.0 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.6 mg, 5.0 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 12.0 μmol, 0.006 equiv.), Na_2CO_3 (106.0 mg, 2.0 mmol, 2.0 equiv.), TTMSS (154 μL, 1.00 mmol, 1.0 equiv.), *tert*-butyl 3-bromoazetidine-1-carboxylate (177 mg, 0.75 mmol, 1.5 equiv.), methyl 4-bromobenzoate (108 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography yielded the pure product as a clear oil (134 mg, 0.460 mmol, 92% yield).

^{1}H NMR (500 MHz, Acetone-d_6) δ 8.00 (d, J = 8.3 Hz, 2H), 7.51 (d, J = 8.3 Hz, 2H), 4.33 (s, 2H), 3.92 (d, J = 5.3 Hz, 3H), 3.88 (s, 3H), 1.44 (s, 9H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 166.99, 156.84, 149.00, 130.59, 129.69, 127.87, 79.41, 52.29, 34.13, 28.53.

IR (film) ν_{max} 2974, 2887, 1721, 1699, 1392, 1278, 1111, 770 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{14}NO_4$ ($[M+H]^+$) 235.0844, found 235.0840.



methyl 4-(oxetan-3-yl)benzoate (32)

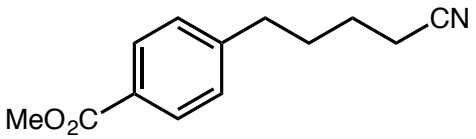
Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 5.0 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.6 mg, 2.5 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 3.0 μmol, 0.006 equiv.), Na_2CO_3 (106.0 mg, 1.00 mmol, 2.0 equiv.), TTMSS (154 μL, 0.50 mmol, 1.0 equiv.), 3-bromooxetane (63 μL, 0.75 mmol, 1.5 equiv.), methyl 4-bromobenzoate (108 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography yielded the pure product as a clear oil (69 mg, 0.36 mmol, 72% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 5.10 (dd, *J* = 8.3, 6.1 Hz, 2H), 4.77 (t, *J* = 6.3 Hz, 2H), 4.28 (tt, *J* = 8.4, 6.6 Hz, 1H), 3.92 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.84, 146.76, 130.11, 128.97, 126.83, 78.43, 52.15, 40.26.

IR (film) ν_{max} 2953, 1875, 1720, 1611, 1435, 1277 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{11}H_{13}O_3$ ($[M+H]^+$) 192.0787, found 192.0786.



methyl 4-(4-cyanobutyl)benzoate (33)

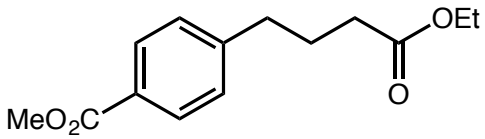
Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 5.0 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.6 mg, 2.5 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 3.0 μmol, 0.006 equiv.), Na_2CO_3 (106.0 mg, 1.00 mmol, 2.0 equiv.), TTMSS (154 μL, 0.50 mmol, 1.0 equiv.), 5-bromopentanenitrile (87 μL, 0.75 mmol, 1.5 equiv.), methyl 4-bromobenzoate (108 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography yielded the pure product as a clear oil (90 mg, 0.40 mmol, 82% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 3.91 (s, 3H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.36 (t, *J* = 7.0 Hz, 2H), 1.86 – 1.77 (m, 2H), 1.73 – 1.65 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.02, 146.65, 129.85, 128.39, 128.16, 119.46, 52.06, 29.92, 24.84, 17.10.

IR (film) ν_{max} 2951, 2868, 2246, 1716, 1610, 1434, 1276 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{15}NaNO_2$ ($[M+Na]^+$) 240.0995, found 240.0997.



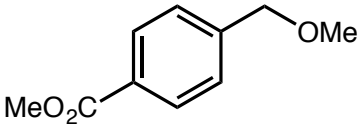
methyl 4-(4-ethoxy-4-oxobutyl)benzoate (34)

Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 5.0 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.6 mg, 2.5 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 3.0 μmol, 0.006 equiv.), Na_2CO_3 (106.0 mg, 1.00 mmol, 2.0 equiv.), TTMSS (154 μL, 0.50 mmol, 1.0 equiv.), ethyl 4-bromobutanoate (107 μL, 146 mg, 0.75 mmol, 1.5 equiv.), methyl 4-bromobenzoate (108 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography yielded the pure product as a clear oil (115 mg, 0.46 mmol, 92% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8 Hz, 2H), 4.13 (q, *J* = 7.2 Hz, 3H), 3.90 (s, 3H), 2.71 (t, *J* = 7.7 Hz, 2H), 2.32 (t, *J* = 7.5 Hz, 2H), 2.01 – 1.90 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.42, 167.24, 147.10, 129.89, 128.66, 128.14, 60.52, 52.17, 35.27, 33.68, 26.32, 14.40.

Spectroscopic data matches with previously reported data.[12]



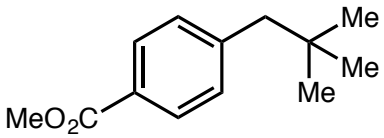
methyl 4-(methoxymethyl)benzoate (35)

Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 5.0 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.6 mg, 2.5 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 3.0 μmol, 0.006 equiv.), Na_2CO_3 (106.0 mg, 1.00 mmol, 2.0 equiv.), TTMSS (154 μL, 0.50 mmol, 1.0 equiv.), methoxymethyl chloride (57 μL, 0.75 mmol, 1.5 equiv.), methyl 4-bromobenzoate (108 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography yielded the pure product as a clear oil (52 mg, 0.29 mmol, 58% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 4.51 (s, 2H), 3.91 (s, 3H), 3.42 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.98, 143.50, 129.73, 129.36, 127.20, 77.28, 77.03, 76.77, 74.06, 58.45, 52.13.

Spectroscopic data matches with previously reported data.[11]



methyl 4-neopentylbenzoate (33)

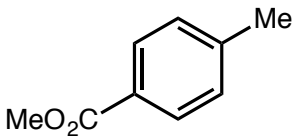
Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 5.0 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.6 mg, 2.5 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 3.0 μmol, 0.006 equiv.), Na_2CO_3 (106.0 mg, 1.00 mmol, 2.0 equiv.), TTMSS (154 μL, 0.50 mmol, 1.0 equiv.), 1-bromo-2,2-dimethylpropane (94 μL, 113 mg, 0.75 mmol, 1.5 equiv.), methyl 4-bromobenzoate (108 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography yielded the pure product as a clear oil (79 mg, 0.385 mmol, 77% yield).

^{1}H NMR (500 MHz, Acetone-d_6) δ 7.92 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 3.87 (s, 3H), 2.60 (s, 2H), 0.92 (s, 9H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 167.26, 146.15, 131.42, 129.57, 128.85, 52.16, 50.39, 32.36, 29.60.

IR (film) ν_{max} 2955, 2866, 1712, 1276, 1112, 1101, 733 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{19}O_2$ ($[M+H]^+$) 206.1306, found 206.1303.



methyl 4-methylbenzoate (37)

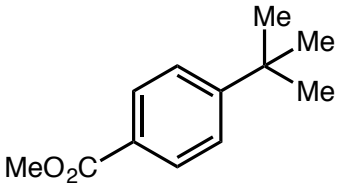
Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 5.0 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.6 mg, 2.5 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 3.0 μmol, 0.006 equiv.), Na_2CO_3 (106 mg, 1.00 mmol, 2.0 equiv.), LiBr (65.0 mg, 0.75 mmol, 1.5 equiv.), TTMSS (154 μL, 0.50 mmol, 1.0 equiv.), methyl 4-methylbenzenesulfonate (113 μL, 140 mg, 0.75 mmol, 1.5 equiv.), methyl 4-bromobenzoate (108 mg, 0.50 mmol, 1.0 equiv.), and DME (5.0 mL). Purification by column chromatography (C18 column) yielded the pure product as a clear oil (48 mg, 0.31 mmol, 62% yield).

Additionally, use of MeBr in DME afforded the product as a clear oil (56 mg, 0.375 mmol, 75% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 3.90 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.20, 143.56, 129.60, 129.08, 127.42, 51.97, 21.68.

Spectroscopic data matches with previously reported data.[13]



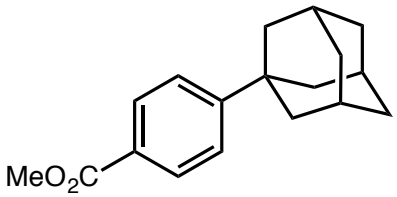
methyl 4-(*tert*-butyl)benzoate (38)

Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 5.0 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.6 mg, 2.5 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 3.0 μmol, 0.006 equiv.), Na_2CO_3 (106 mg, 1.00 mmol, 2.0 equiv.), TTMSS (213 μL, 0.75 mmol, 1.5 equiv.), 2-bromo-2-methylpropane (84 μL, 0.75 mmol, 1.5 equiv.), methyl 4-bromobenzoate (108 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxanes (5.0 mL). The reaction was allowed to run for 48 hours. Purification by column chromatography the pure product as a clear oil (39 mg, 0.26 mmol, 52% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.7 Hz, 2H), 7.45 (d, *J* = 9.0 Hz, 2H), 3.90 (s, 3H), 1.35 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.30, 156.71, 129.60, 127.52, 125.50, 51.97, 35.19, 31.31.

Spectroscopic data matches with previously reported data.[14]



methyl 4-(adamantan-1-yl)benzoate (39)

Prepared following the general procedure outlined above using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 5.0 μmol, 0.01 equiv.), $NiCl_2$•glyme (0.6 mg, 2.5 μmol, 0.005 equiv.), 4,4'-di-tert-butyl-2,2'-bipyridine (0.8 mg, 3.0 μmol, 0.006 equiv.), Na_2CO_3 (106 mg, 1.00 mmol, 2.0 equiv.), TTMSS (213 μL, 0.75 mmol, 1.5 equiv.), 1-bromoadamantane (161 mg, 0.75 mmol, 1.5 equiv.), methyl 4-bromobenzoate (108 mg, 0.50 mmol, 1.0 equiv.), and 1,4-dioxanes (5.0 mL). The reaction was allowed to run for 24 hours. Purification by column chromatography the pure product as white solide (84 mg, 0.310 mmol, 62% yield).

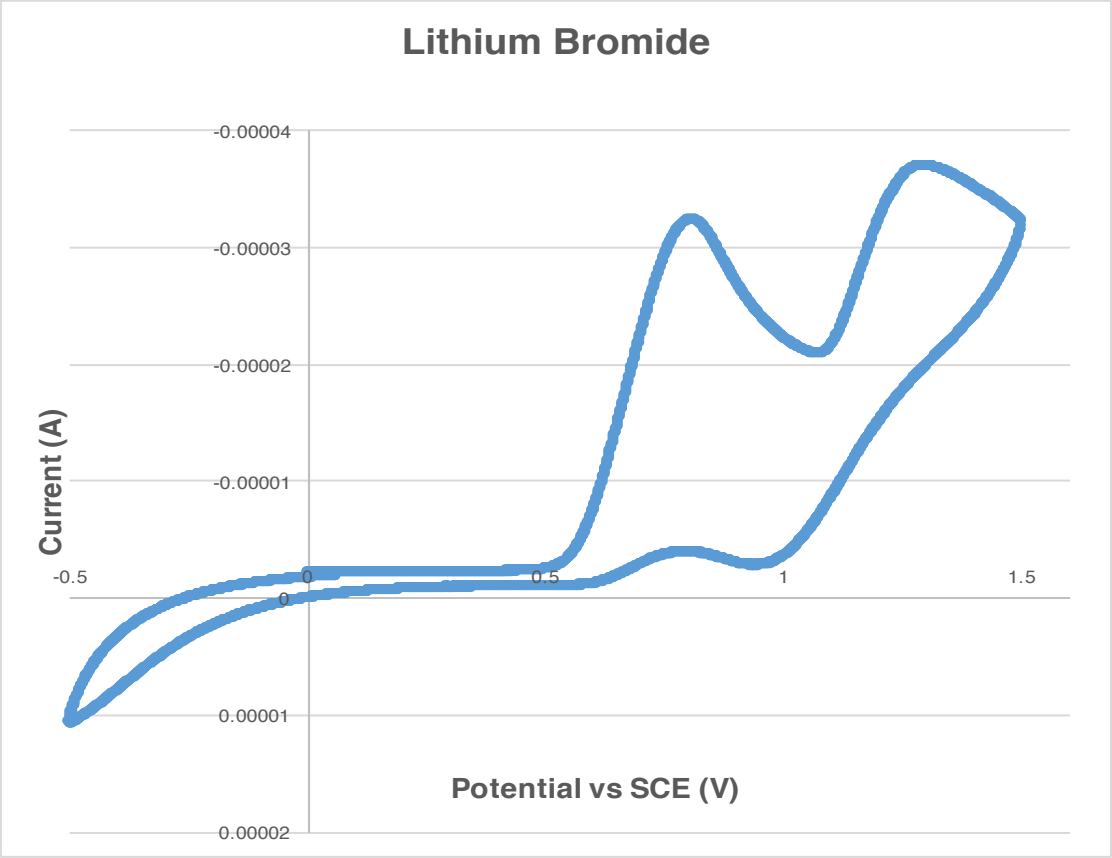
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 3.90 (s, 3H), 2.16 – 2.06 (m, 3H), 1.93 (s, 6H), 1.78 (q, *J* = 12.1 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.36, 156.79, 129.60, 127.48, 125.10, 52.11, 43.03, 36.81, 28.94.

Spectroscopic data matches with previously reported data.[15]

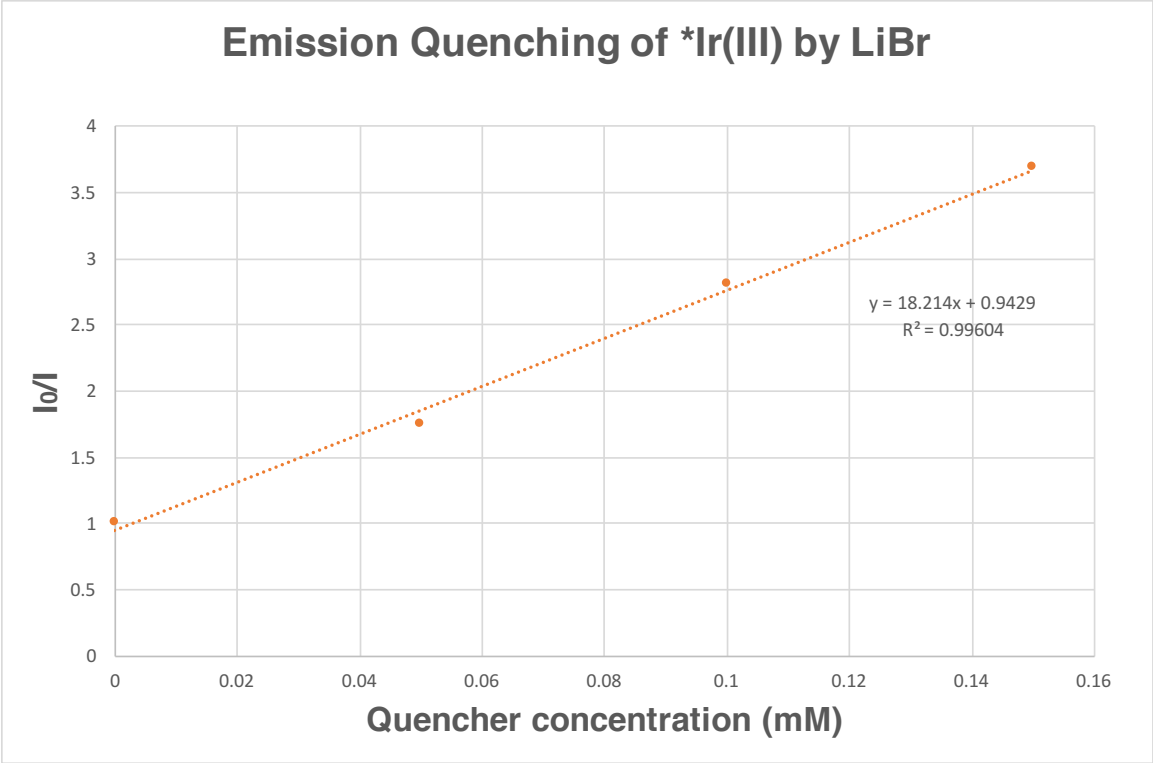
6) Cyclic Voltammetry Data

Cyclic voltammetry was performed using a CHI 1140A potentiostat, a glassy carbon working electrode, a platinum mesh counter electrode, and a Ag/AgCl reference electrode. Samples were prepared with a substrate concentration of 0.01 M in a 0.1 M tetrabutylammonium tetrafluoroborate in dimethoxyethane electrolyte solution and sparged with N_2 for 15 minutes. Data was collected with a scan rate of 0.1 V/s.



7) Stern-Volmer Fluorescence Quenching Experiments

Fluorescence quenching experiments were performed on an Agilent Cary Eclipse Fluorescence Spectrophotometer. In a typical experiment, a 2.5 μM solution of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ in DME was added to the appropriate amount of quencher in a screw-top 1.0 cm quartz cuvette. After degassing by bubbling a stream of nitrogen for 10 minutes, the emission of the sample was collected. All solutions were excited at λ = 380 nm (absorption maximum of the photocatalyst) and the emission intensity at 474 nm was observed (emission maximum). Plots were constructed according to the Stern–Volmer equation $I_0/I = 1 + kq\tau_0[Q]$.[16]



8) Procedure for Investigating Other Reductants

Reactions in Table 3 were run according to the following procedure:

To an 8 mL vial equipped with a stir bar was added the indicated photocatalyst (2.5 μmol, 0.01 equiv.), methyl 4-bromo benzoate (54 mg, 0.25 mmol, 1 equiv.), 4-bromotetrahydropyran (42 μL, 0.375 mmol, 1.5 equiv.), the indicated reductant (0.25 mmol, 1.0 equiv), and anhydrous sodium carbonate (53 mg, 0.5 mmol, 2 equiv.). The vial was sealed and placed under nitrogen before 2mL of solvent was added. To a separate vial was added $NiCl_2$•glyme (2.8 mg, 0.013 mmol, 0.05 equiv.) and 4,4'-di-tert-butyl-2,2'-bipyridine (3.4 mg, 0.013 mmol, 0.05 equiv). The catalyst vial was sealed, purged with nitrogen then to it was added 1 mL of solvent. The precatalyst solution was sonicated or stirred for 5 minutes, after which, 0.1 mL of the solution (0.5 mol% catalyst, 1.25 μmol, 0.005 equv.) was syringed into the reaction vessel. The solution was degassed by sparging with nitrogen while stirring for 10 minutes before sealing with Parafilm. The reaction was stirred and irradiated with a 34 W blue LED lamp (7 cm away, with cooling fan to keep the reaction temperature at 25 °C) for 6 hours. The reaction was quenched by exposure to air. Mesitylene (internal standard, 35 μL, 0.250 mmol, 1.0 equiv.) was added then the reaction mixture was analyzed by ^{1}H NMR.

9) References

1) Perrin, D. D. & Armarego, W. L. F. *Purification of Laboratory Chemicals* (Pergamon Press: Oxford, 1988) ed 3.

2) Lowry, M. S., Goldsmith, J. I., Slinker, J. D., Rohl, R., Pascal, R. A., Malliaras, G. G. & Bernhard, S. *Chem. Mater*. **2005**, *17*, 5712.

3) Pangborn, A. B., Giardello, M. A., Grubbs, R. H., Rosen, R. K. & Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

4) Still, W. C., Kahn, M. & Mitra, A. *J. Org. Chem*. **1978**, *43*, 2923.

5) Primer, D. N.; Karakaya, I.; Tellis, J. C.; Molander, G. A. *J. Am. Chem. Soc.* **2015**, *137*, 2195.

6) González-Bobes, F.; Fu, G. C. *J. Am. Chem. Soc.* **2006**, *128*, 5360.

7) Allwood, D. M.; Blakemore, D. C.; Brown, A. D.; Ley, S. V. *J. Org. Chem*. **2014**, *79*, 328.

8) Molander, G. A.; Traister, K. M.; O'Neill, B. T. *J. Org. Chem*. **2014**, *79*, 5771.

9) Hatakeyama, T.; Hashimoto, T.; Kondo, Y.; Fujiwara, Y.; Seike, H.; Takaya, H.; Tamada, Y.; Ono, T.; Nakamura, M. *J. Am. Chem. Soc.* **2010**, *132*, 10674.

10) Zhang, M.; Cui, X.; Chen, X.; Wang, L.; Li, J.; Wu, Y.; Hou, L.; Wu, Y. *Tetrahedron* **2012**, *68*, 900.

11) Strazzolini, P.; Runcio, A. Eur. *J. Org. Chem*. **2003**, 526.

12) Dohle, W.; Lindsay, D. M.; Knochel, P. *Org. Lett.* **2001**, *3*, 2871.

13) Behera, H.; Ramkumar, V.; Madhavan, N. *Chem. Eur. J.* **2015**, *21*, 10179.

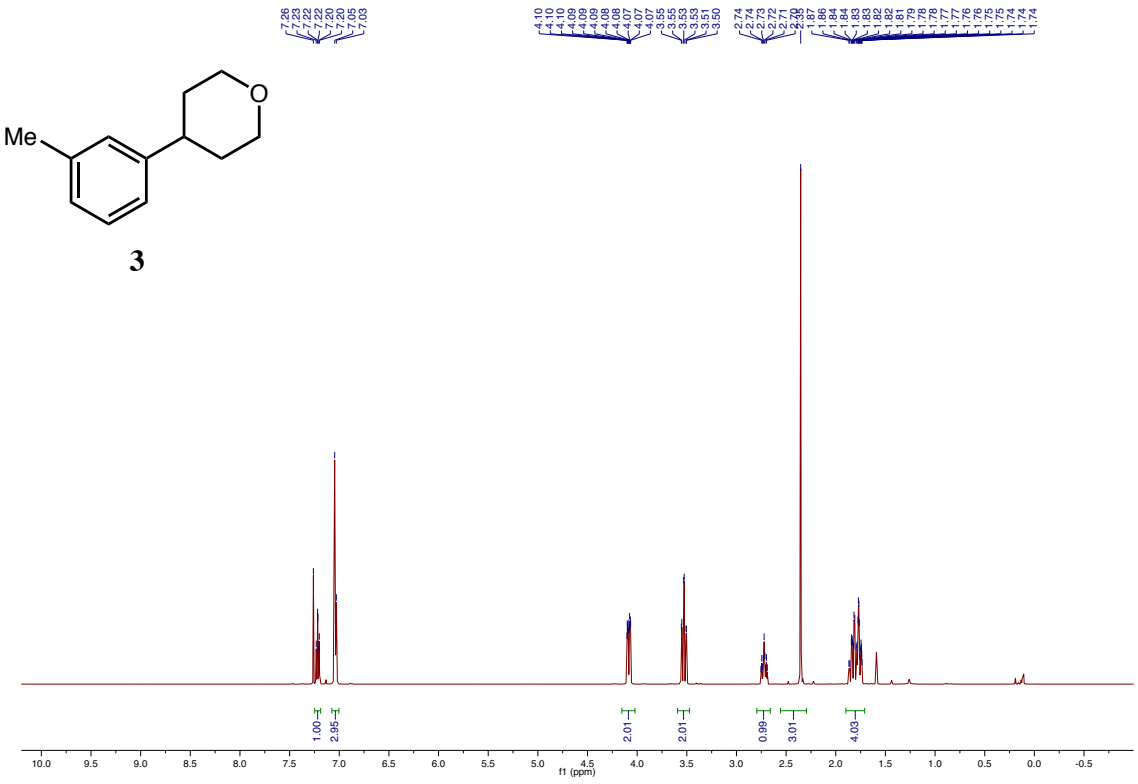
14) Bosset, C.; Coffinier, R.; Peixoto, P. A.; El Assal, M.; Miqueu, K.; Sotiropoulos, J.-M.; Pouységu, L.; Quideau, S. *Angew. Chem. Int. Ed.* **2014**, *53*, 9860.

15) Zhang, X.; Yang, C. *Adv. Synth. Catal.* **2015**, *357*, 2721.

16) N. J. Turro, *Modern Molecular Photochemistry*, Benjamin/Cummings: Menlo Park, CA, 1978

10) Spectral Data for Alkyl-Aryl Compounds

^{1}H and ^{13}C Spectra for Novel Compounds



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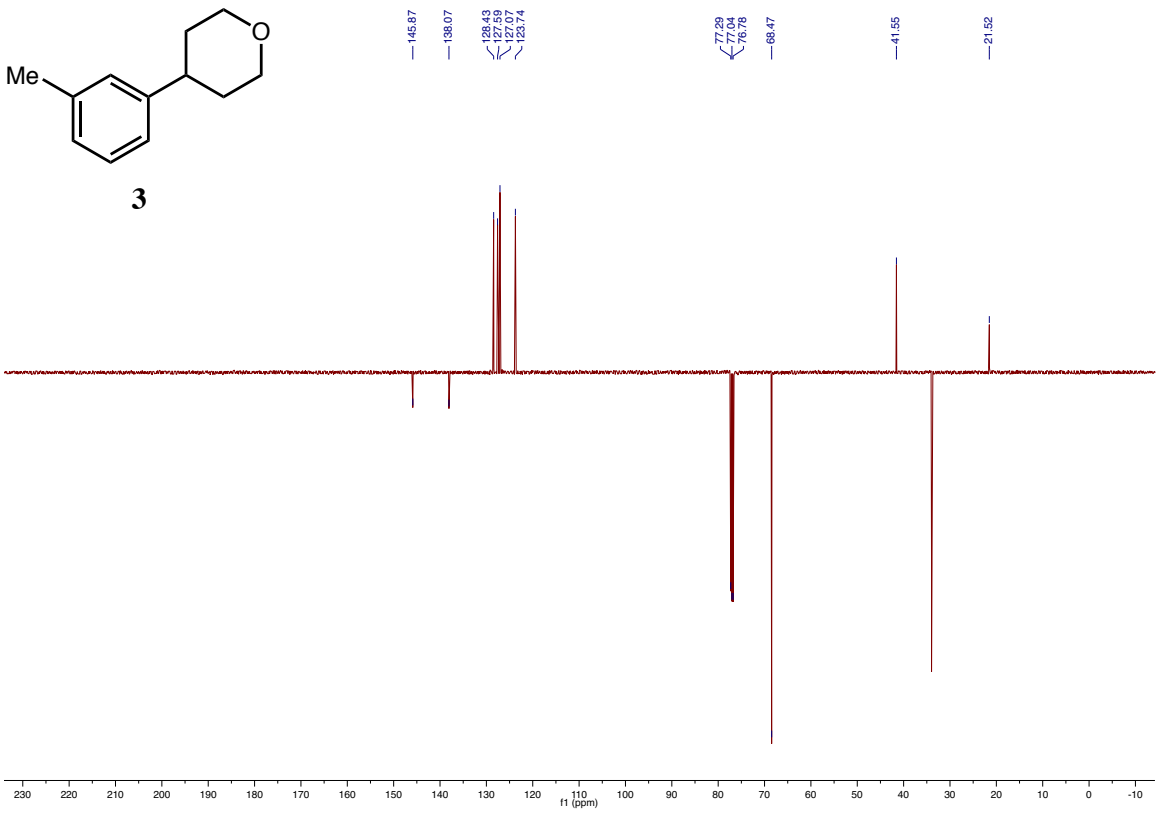
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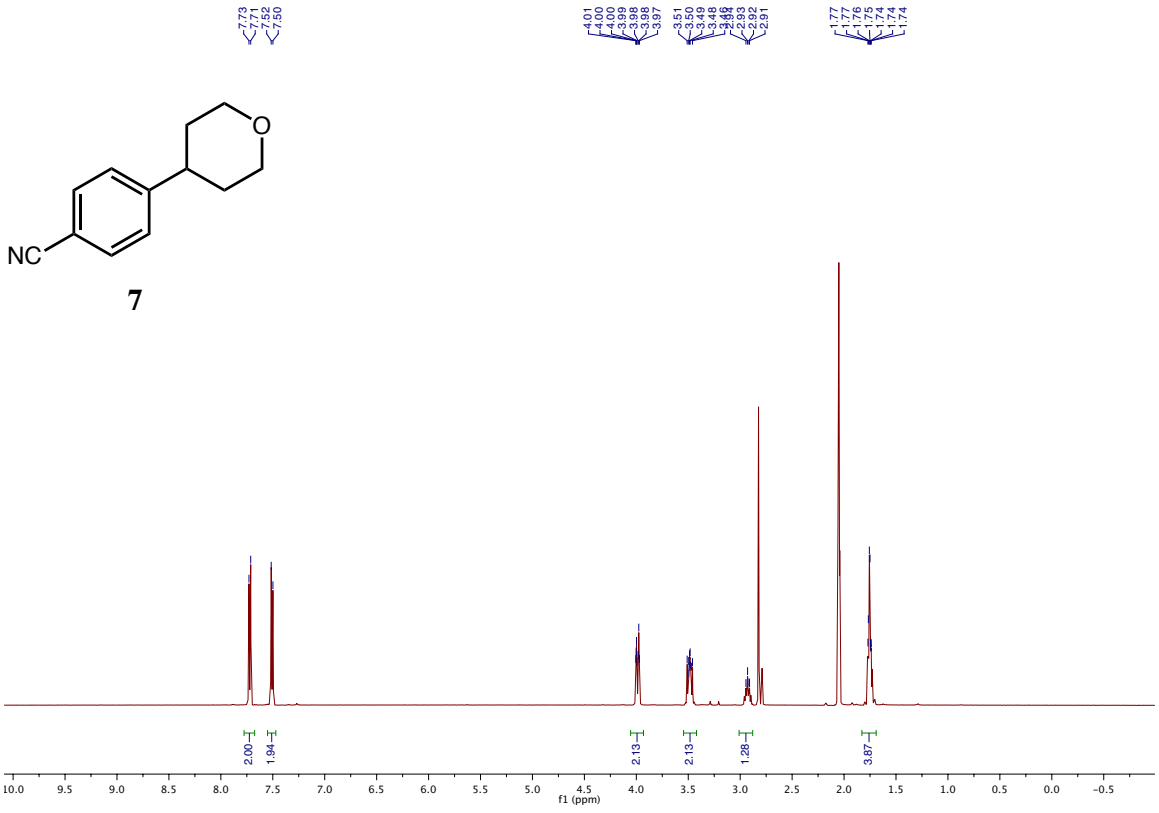
f1 (ppm)

3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7.50
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4.00
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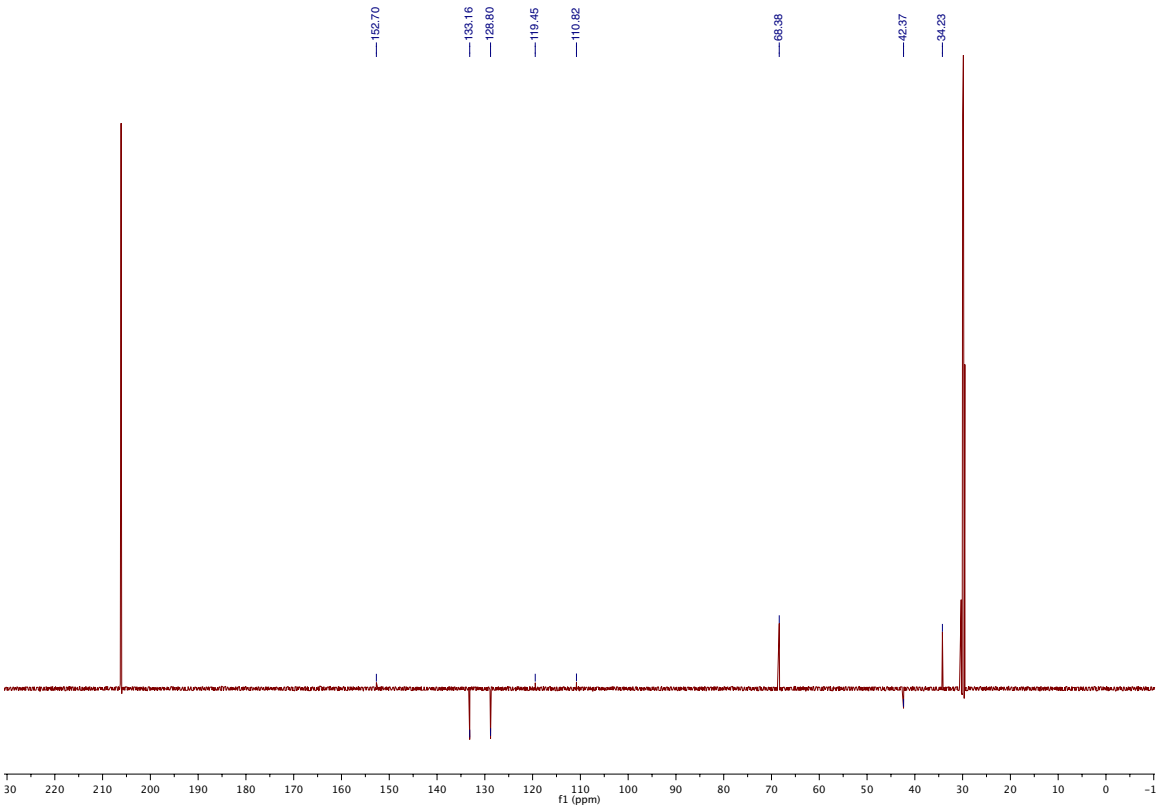
f1 (ppm)

7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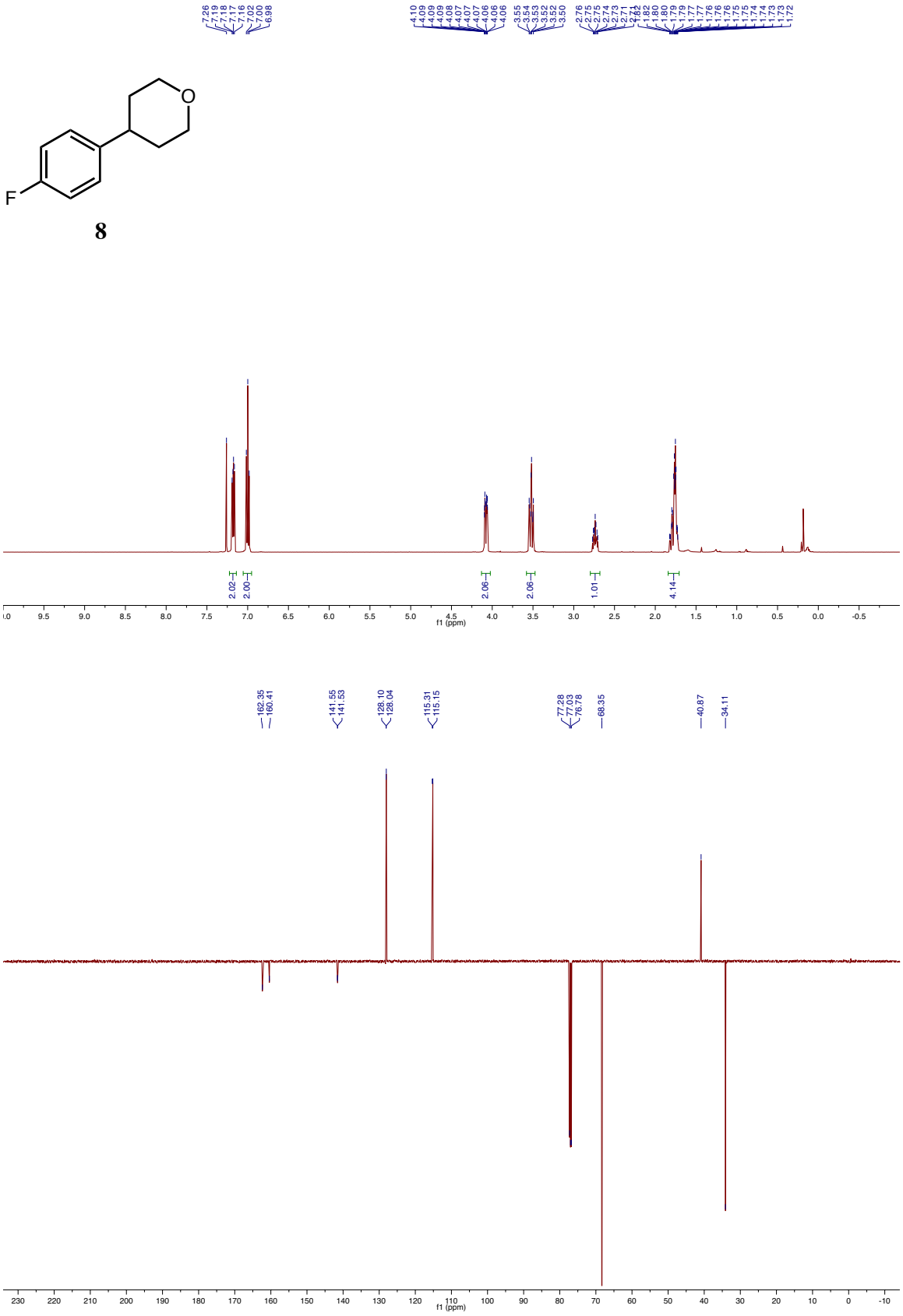
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1.76
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1.74
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1.72
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F
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2.00
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2.06
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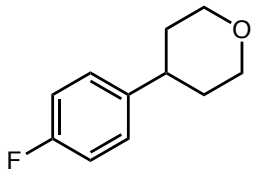
f1 (ppm)

^{19}F NMR


O
F

8

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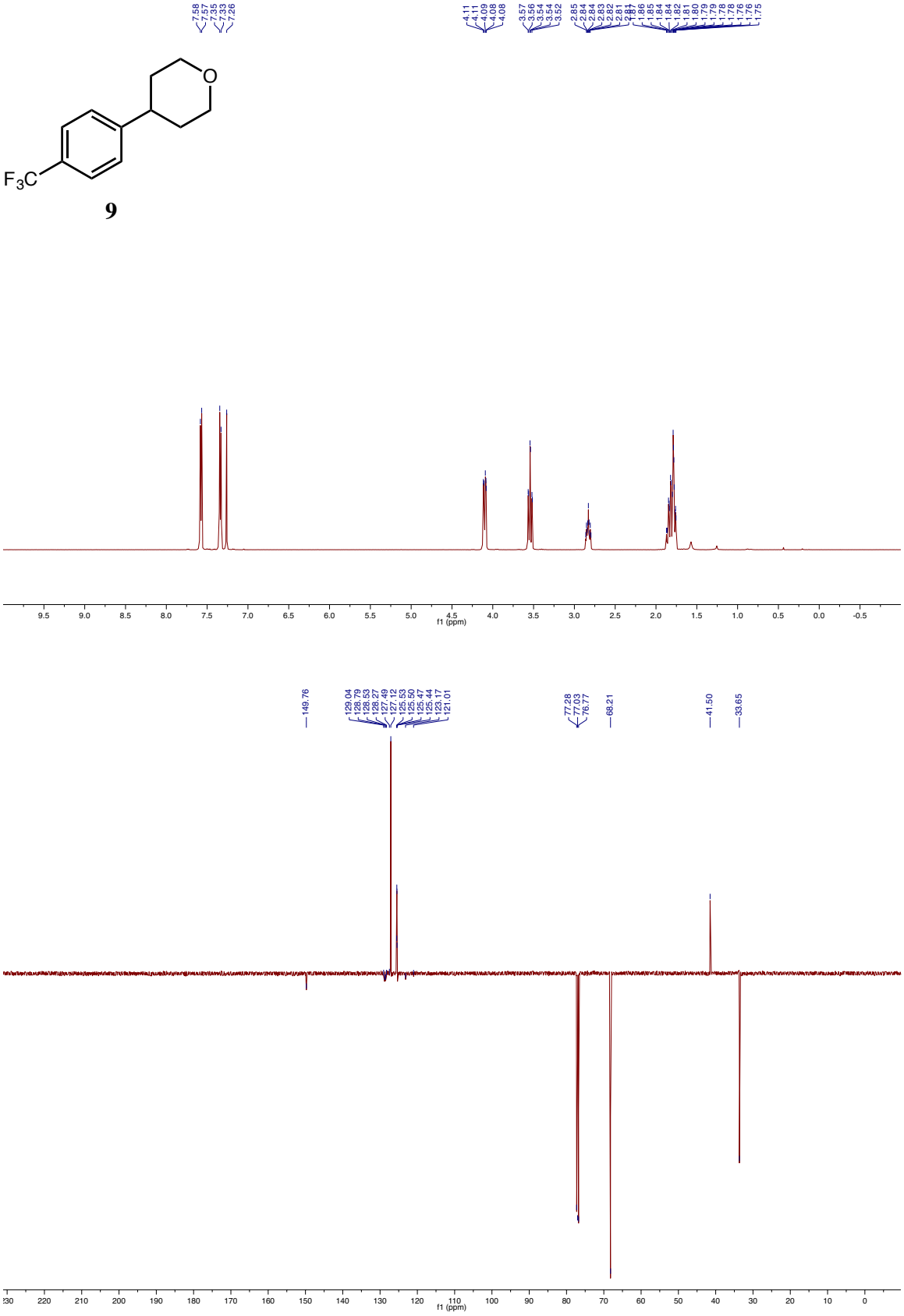
f1 (ppm)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125.47
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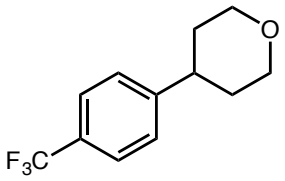
f1 (ppm)

^{19}F NMR


O
F3C

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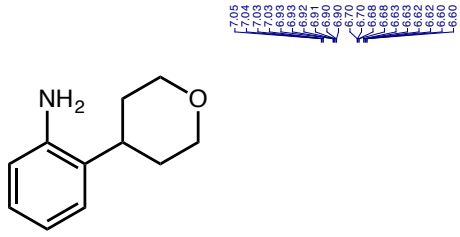
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6.62
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6.60
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3.97
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3.96
3.95
3.95
3.54
3.53
3.51
3.51
2.92
2.91
2.90
2.89
2.88
2.88
2.87
1.77
1.76
1.76
1.75
1.75
1.74
1.74
1.74
1.73
1.70
1.70
1.68
1.68
1.67
1.67
1.66
1.65
1.65
1.64
1.63
1.62
1.00
1.02
1.00
1.01
2.02
2.08
2.06
1.05
2.06
2.12
f1 (ppm)
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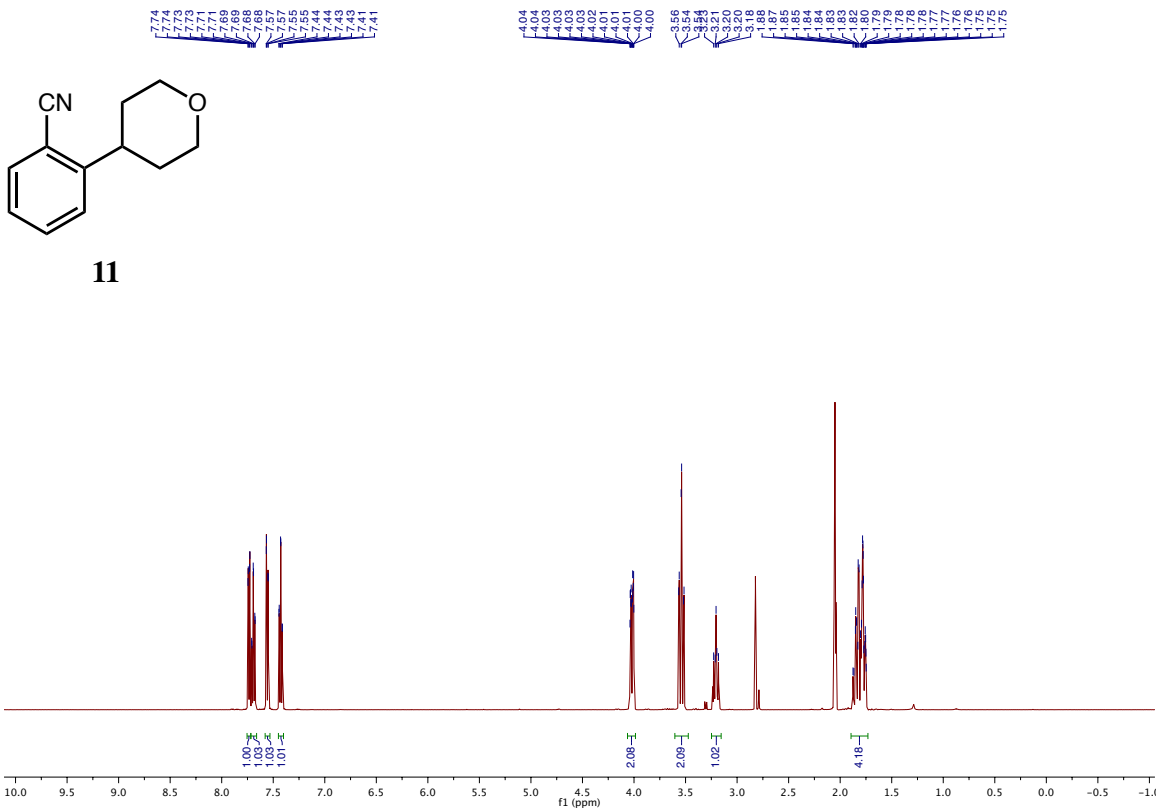
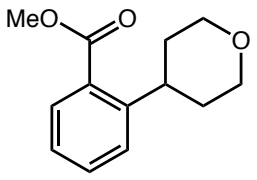
130.06
127.30
126.39
118.24
116.19
68.85
35.94
33.31
f1 (ppm)


CN
O
11
f1 (ppm)
f1 (ppm)


MeO
O
O

12

7.80
7.80
7.79
7.79
7.51
7.50
7.49
7.49
7.48
7.48
7.47
7.47
7.41
7.40
7.40
7.28
7.27
7.25
7.24
4.09
4.09
4.09
4.08
4.08
4.07
4.07
4.07
4.06
4.06
3.91
3.66
3.65
3.64
3.60
3.60
3.58
3.58
3.56
3.55
1.87
1.86
1.85
1.85
1.84
1.84
1.82
1.81
1.80
1.79
1.79
1.78
1.78
1.77
1.77
1.76
1.76
1.75
1.75
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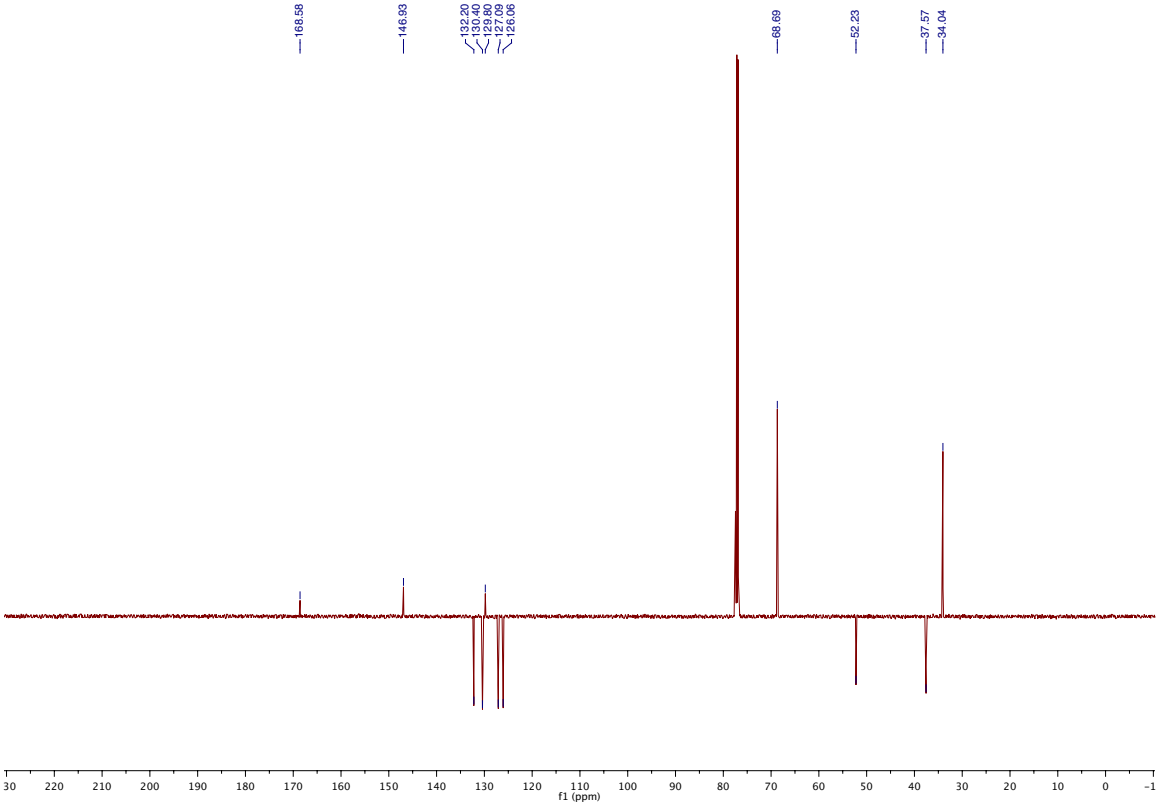
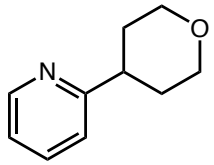
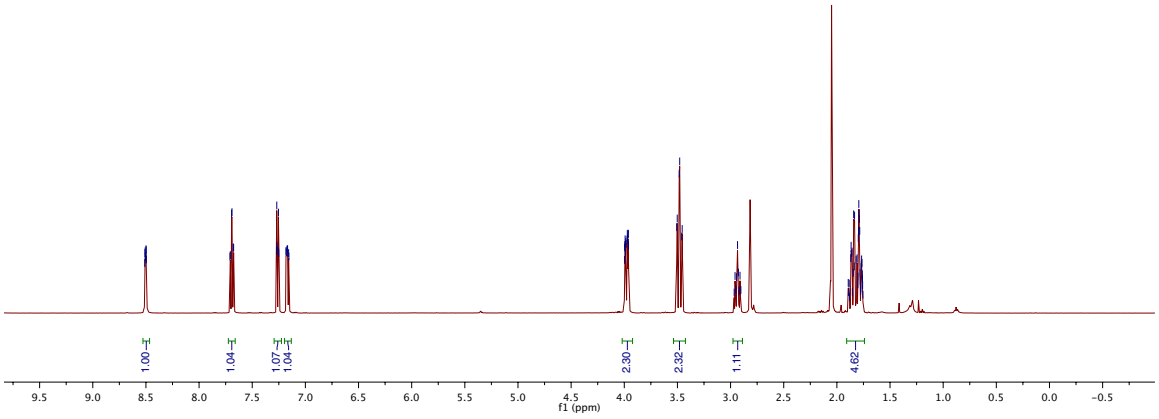
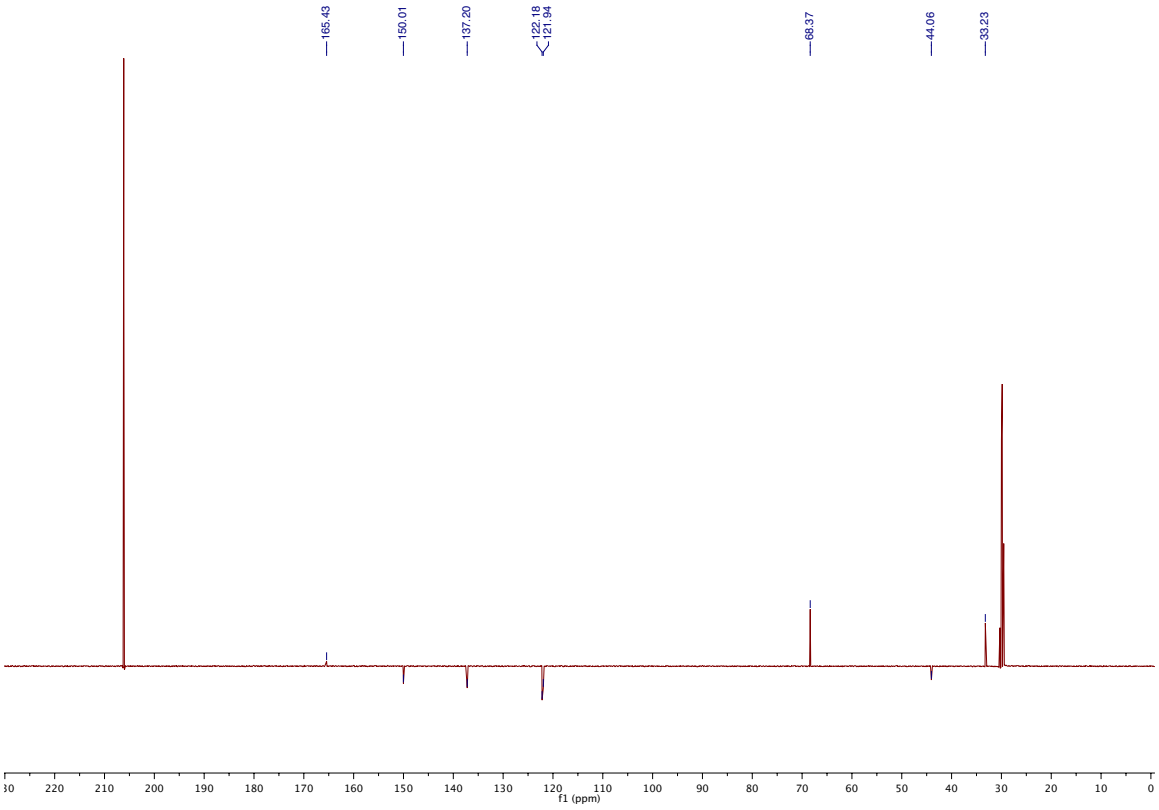
1.08
1.14
1.84
1.92
2.52
1.01
1.70
3.77
f1 (ppm)


168.58
146.93
132.20
130.40
129.80
127.09
126.06
68.69
52.23
37.57
34.04
f1 (ppm)

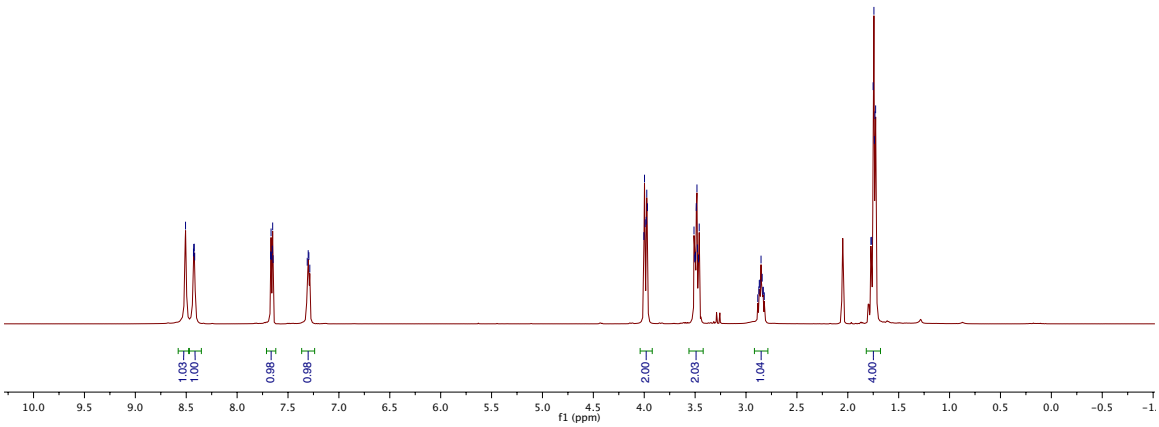

N
O

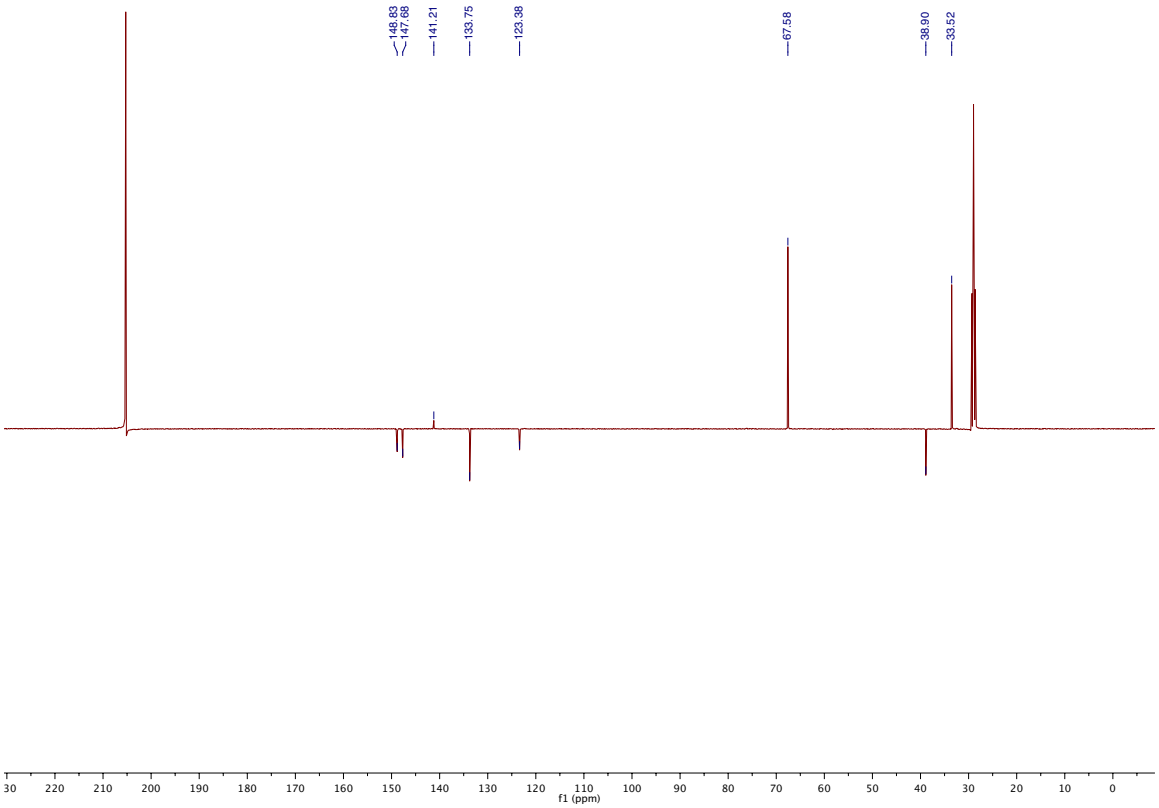
13

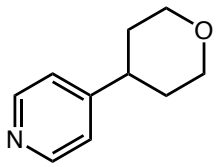

1.00
1.04
1.07
1.04
2.30
2.32
1.11
4.62
f1 (ppm)


165.43
150.01
137.20
122.18
121.94
68.37
44.06
33.23
f1 (ppm)

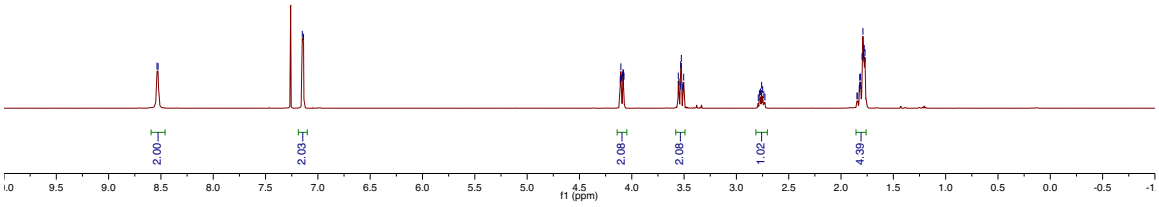
14

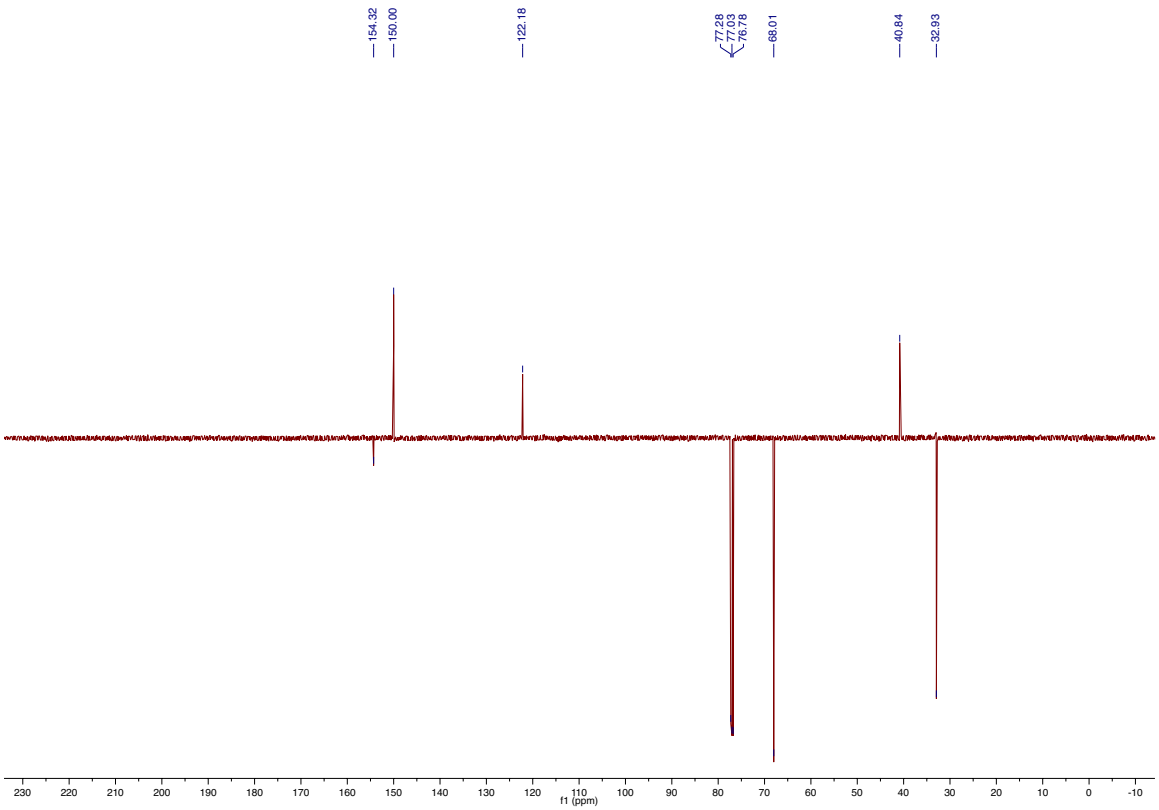


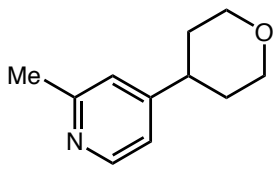




15






Me
N
O

16

8.42
8.40
7.26
7.26
7.00
7.00
6.95
6.95
6.94
6.94
4.10
4.10
4.09
4.09
4.08
4.08
4.07
4.07
3.54
3.54
3.52
3.51
3.50
3.49
2.74
2.73
2.72
2.71
2.70
2.70
2.69
1.83
1.81
1.81
1.80
1.80
1.79
1.78
1.77
1.76
1.76
1.75
1.74
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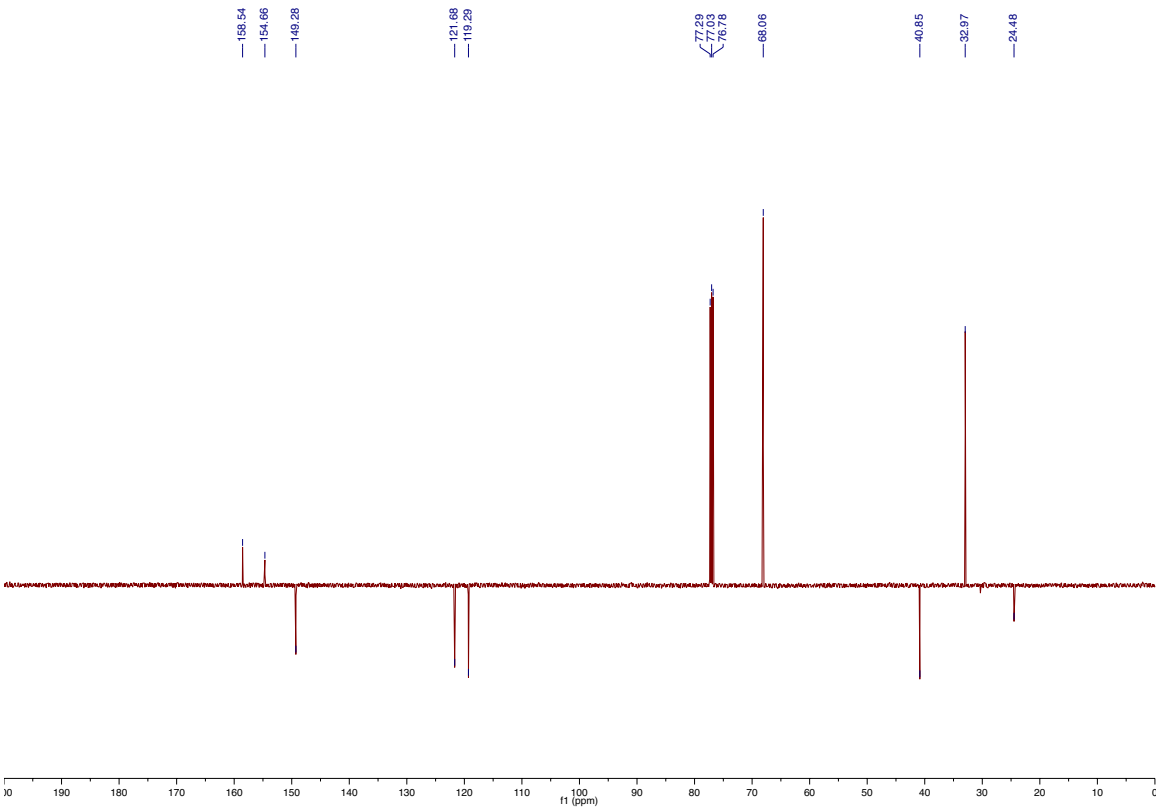
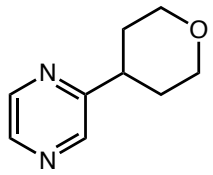
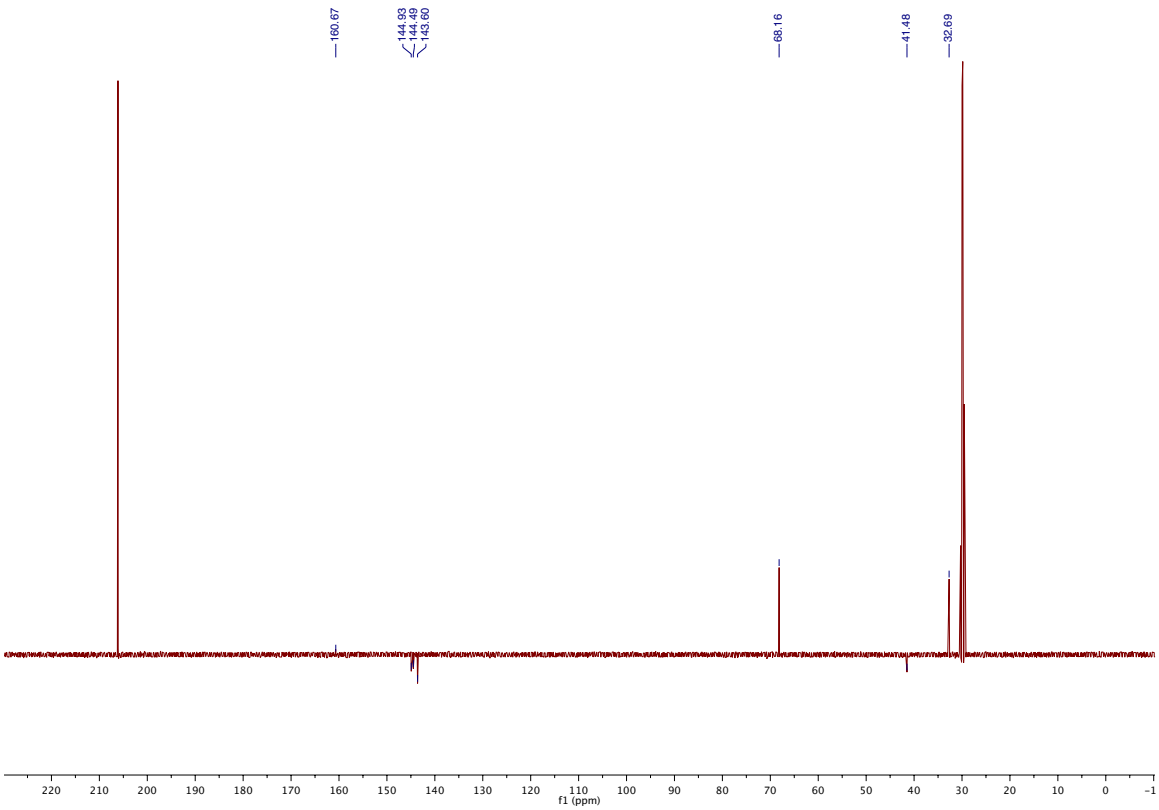
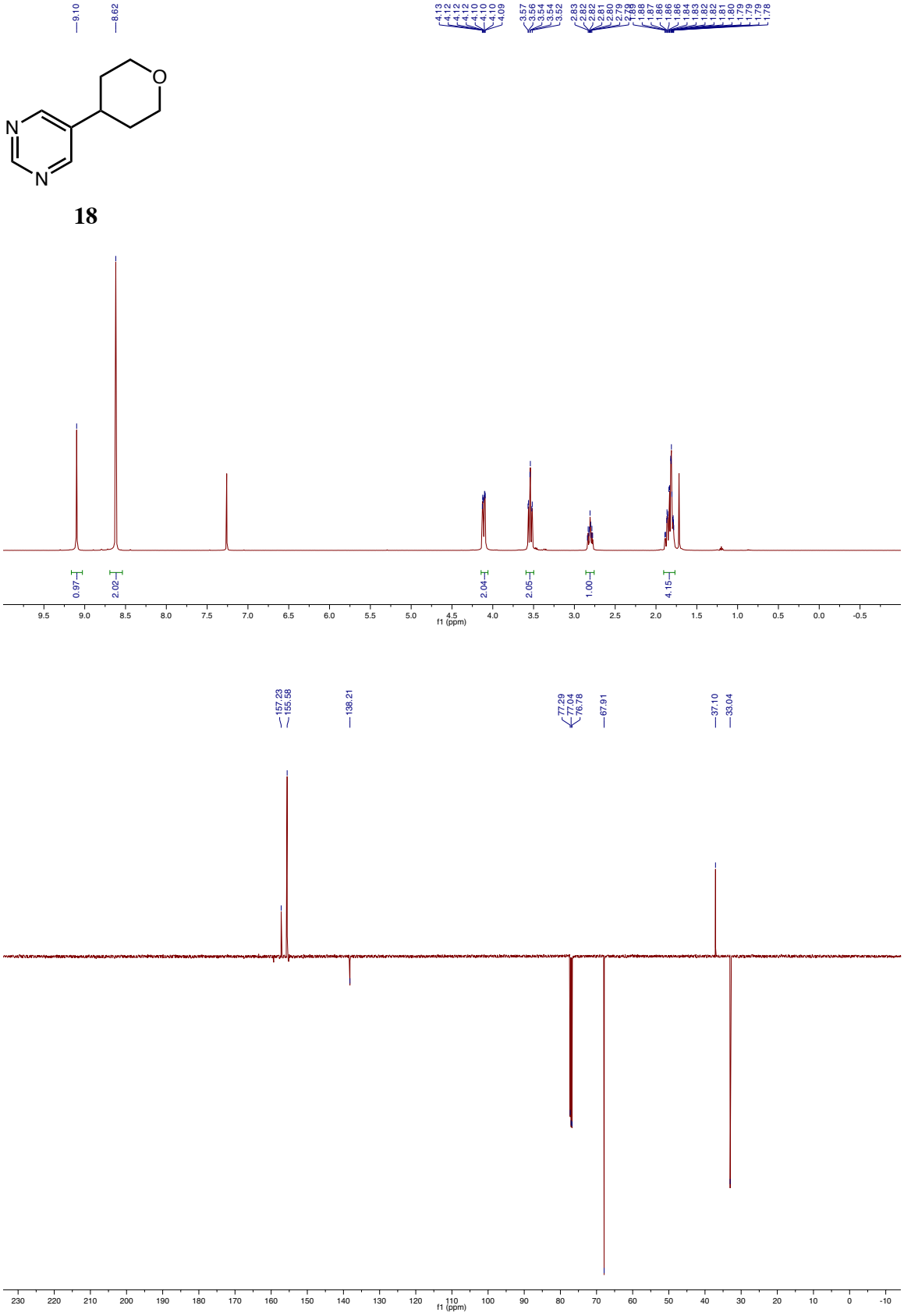
2.05
1.00
3.09
4.06
f1 (ppm)


158.54
154.66
149.28
121.68
119.29
77.29
77.03
76.78
68.06
40.85
32.97
24.48
f1 (ppm)

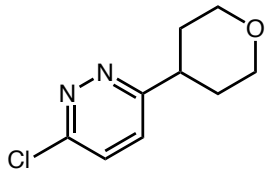


17



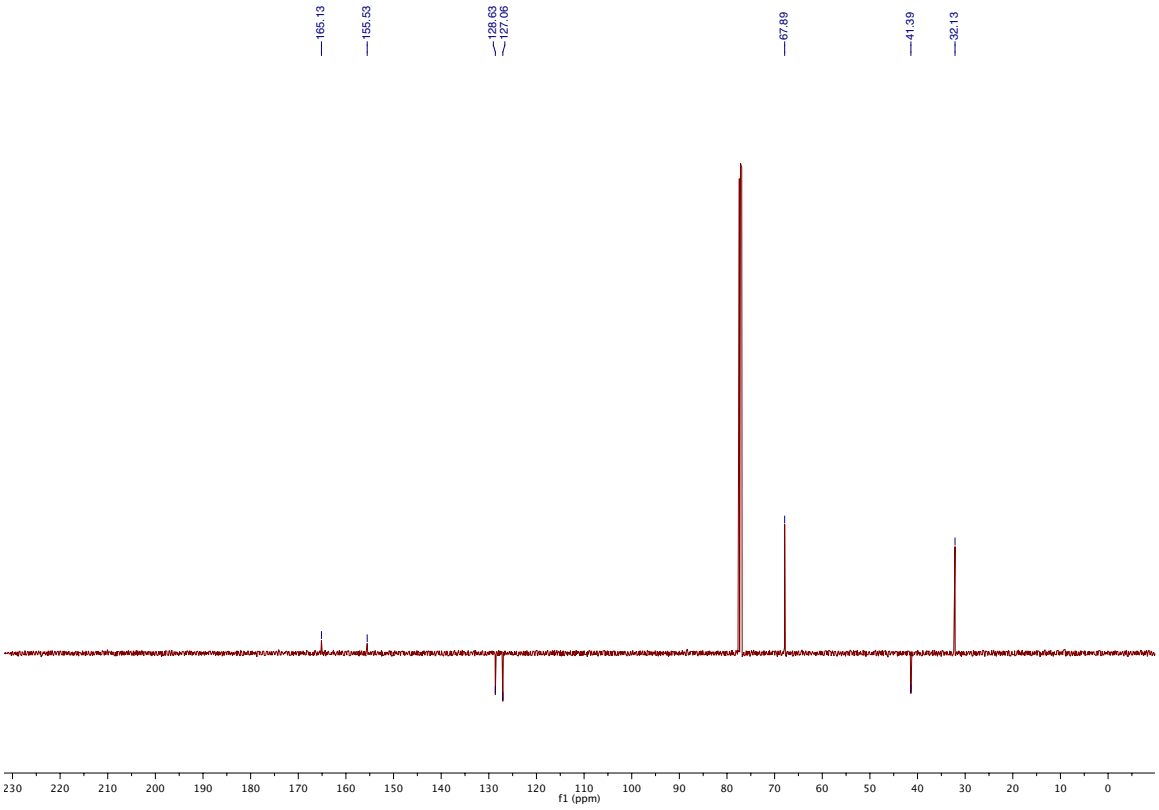

9.10
8.62
4.13
4.12
4.12
4.12
4.12
4.10
4.10
4.10
4.09
3.57
3.56
3.54
3.54
3.52
2.83
2.82
2.82
2.81
2.80
2.79
2.79
2.78
1.88
1.87
1.86
1.86
1.85
1.84
1.83
1.82
1.82
1.81
1.81
1.80
1.79
1.79
1.79
1.78
O
N
N
0.97
2.02
2.04
2.05
1.00
4.15
f1 (ppm)
157.23
155.58
138.21
77.29
77.04
76.78
67.91
37.10
33.04
f1 (ppm)

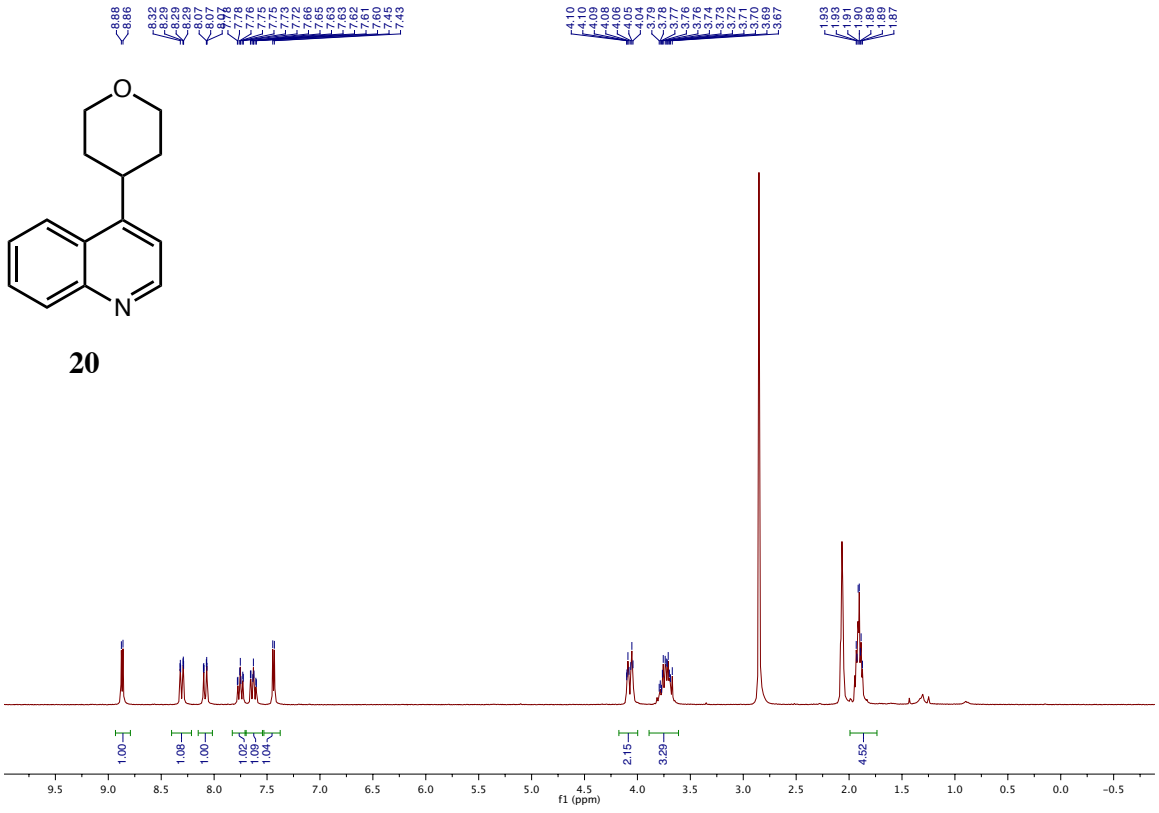
18


N
N
Cl
O

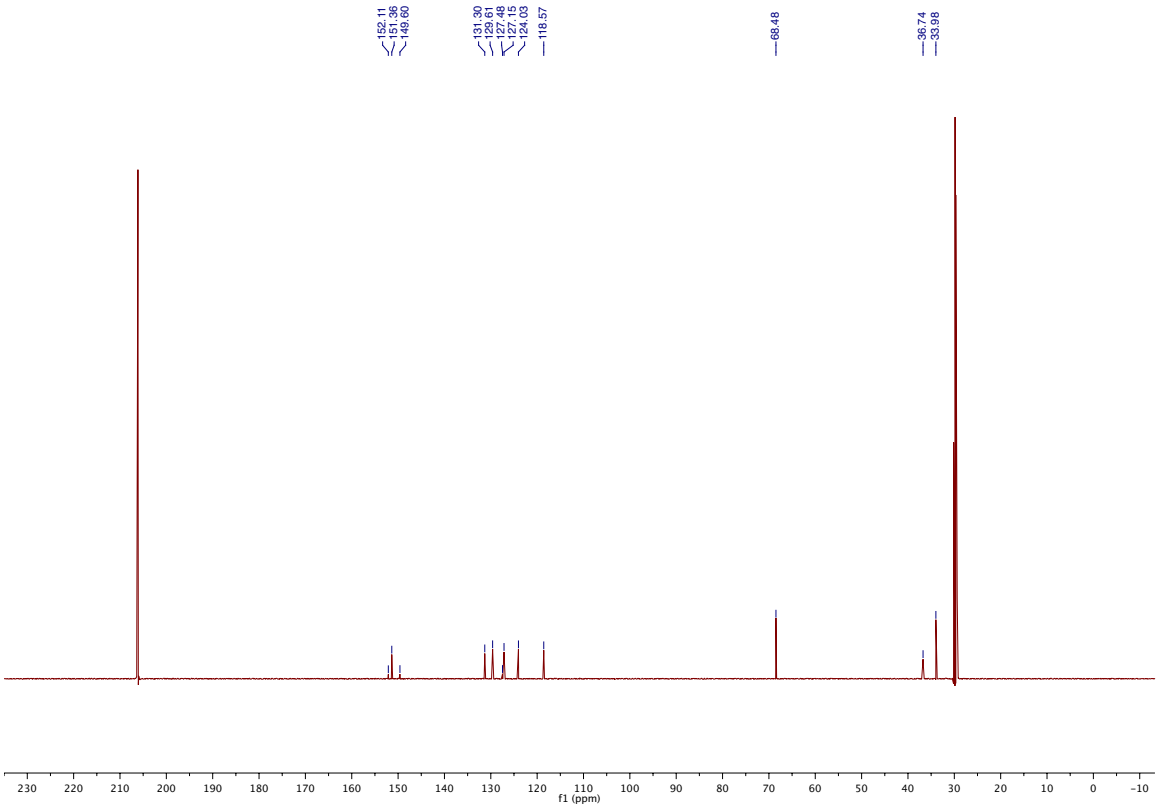
19

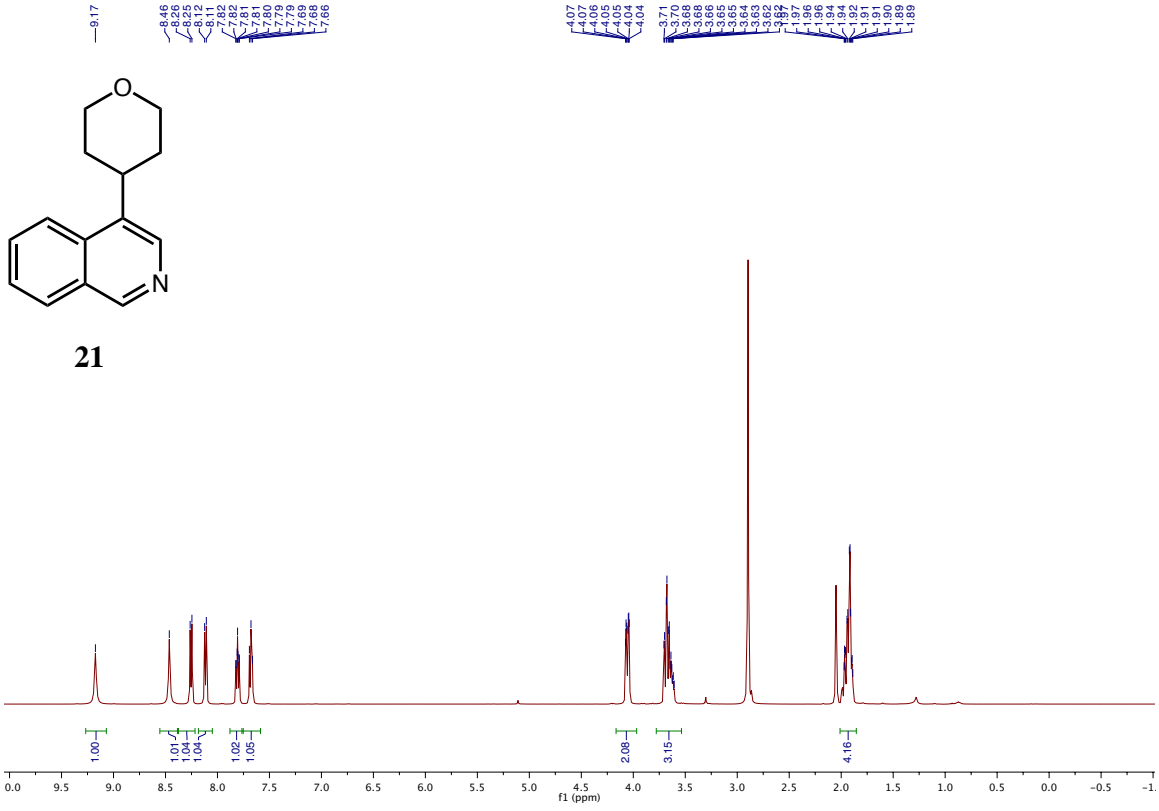
7.48
7.46
7.35
7.33
4.14
4.13
4.13
4.12
4.11
4.11
4.10
3.61
3.58
3.58
3.27
3.26
3.26
3.25
3.24
3.23
3.23
3.22
1.94
1.93
1.93
1.92
1.91
1.90
1.00
1.01
2.06
2.06
1.01
4.11
f1 (ppm)


165.13
155.53
128.63
127.06
67.89
41.39
32.13
f1 (ppm)

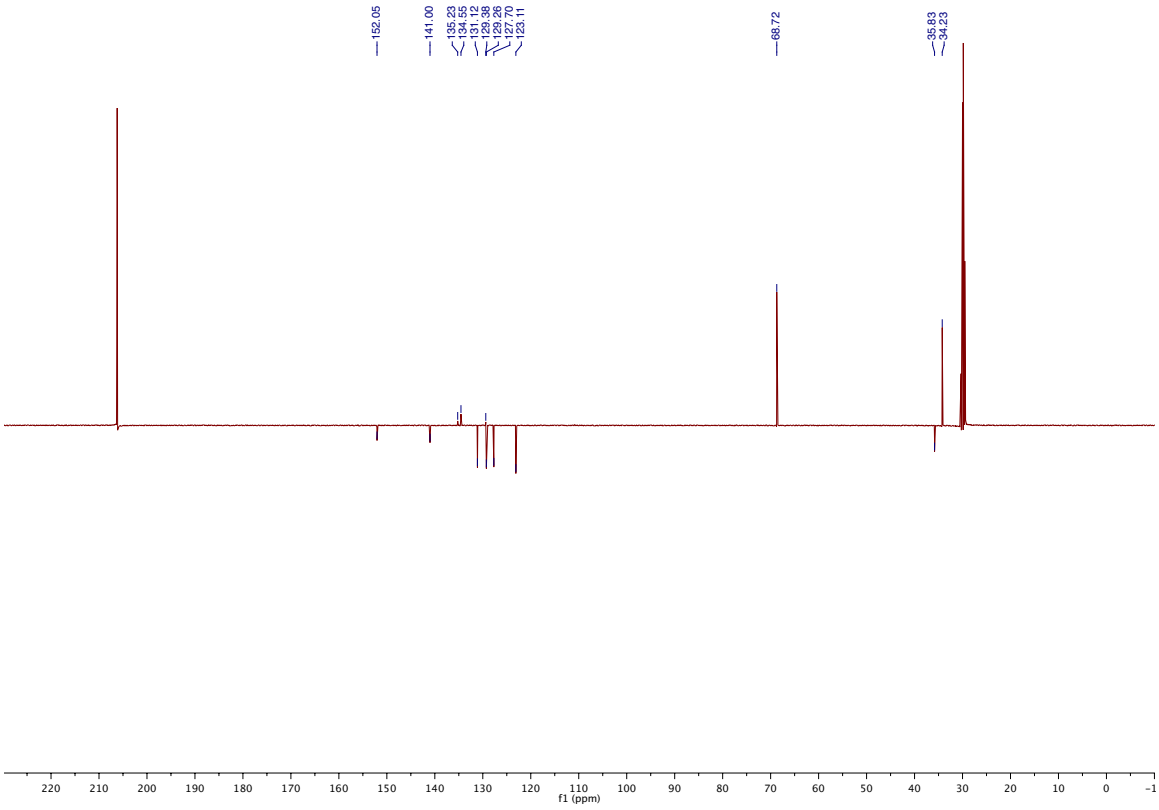

8.88
8.86
8.32
8.29
8.29
8.29
8.07
8.07
7.78
7.78
7.76
7.75
7.75
7.73
7.72
7.66
7.65
7.63
7.62
7.61
7.60
7.45
7.43
4.10
4.10
4.09
4.08
4.06
4.05
4.04
3.79
3.78
3.77
3.76
3.74
3.73
3.72
3.71
3.70
3.69
3.67
1.93
1.93
1.91
1.90
1.89
1.89
1.87
O
N
1.00
1.08
1.00
1.02
1.03
1.04
2.15
3.29
4.52
f1 (ppm)

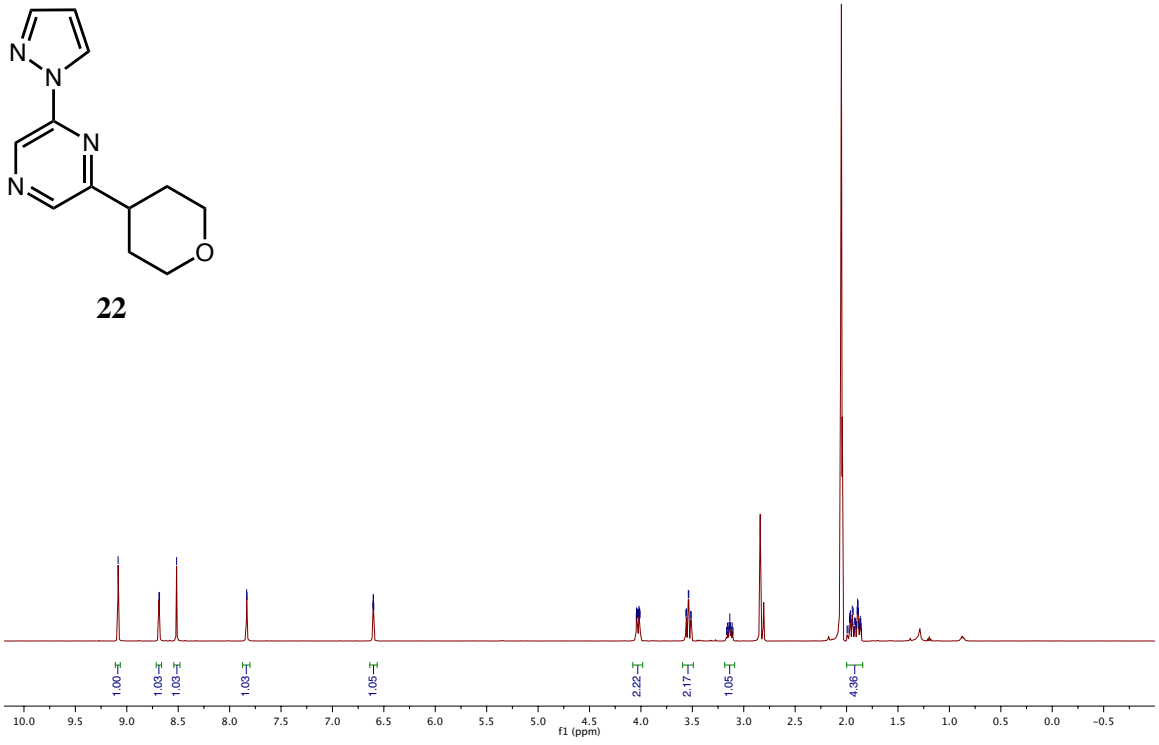
20


152.11
151.36
149.60
131.30
129.61
127.48
127.15
124.03
118.57
68.48
36.74
33.98
f1 (ppm)


9.17
8.46
8.26
8.25
8.12
8.11
7.82
7.81
7.80
7.79
7.69
7.68
7.66
4.07
4.06
4.05
4.05
4.04
3.71
3.70
3.68
3.66
3.65
3.64
3.63
3.62
1.97
1.96
1.94
1.92
1.91
1.90
1.89
O
N
1.00
1.01
1.04
1.04
1.02
1.05
2.08
3.15
4.16
f1 (ppm)

21


152.05
141.00
135.23
134.55
131.12
129.38
129.26
127.70
123.11
68.72
35.83
34.23
f1 (ppm)


9.08
8.69
8.68
8.52
7.83
7.83
6.61
6.60
6.60
6.60
4.04
4.04
4.04
4.04
4.03
4.03
4.02
4.02
4.02
4.02
4.01
4.01
3.56
3.54
3.53
3.16
3.15
3.14
3.14
3.13
3.12
2.01
2.00
1.99
1.97
1.97
1.96
1.96
1.95
1.94
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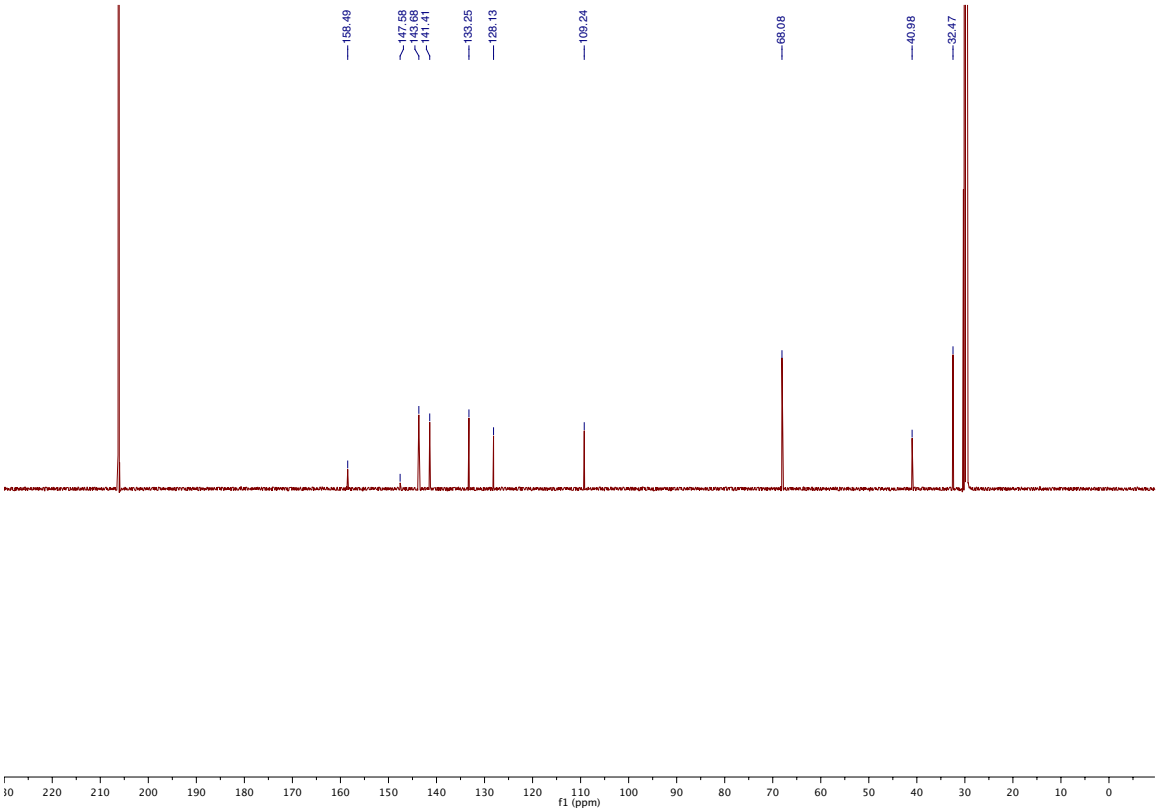
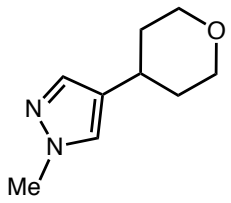
1.87
1.86
1.86
1.85
1.00
1.03
1.03
1.03
1.05
2.22
2.17
1.05
4.36
f1 (ppm)

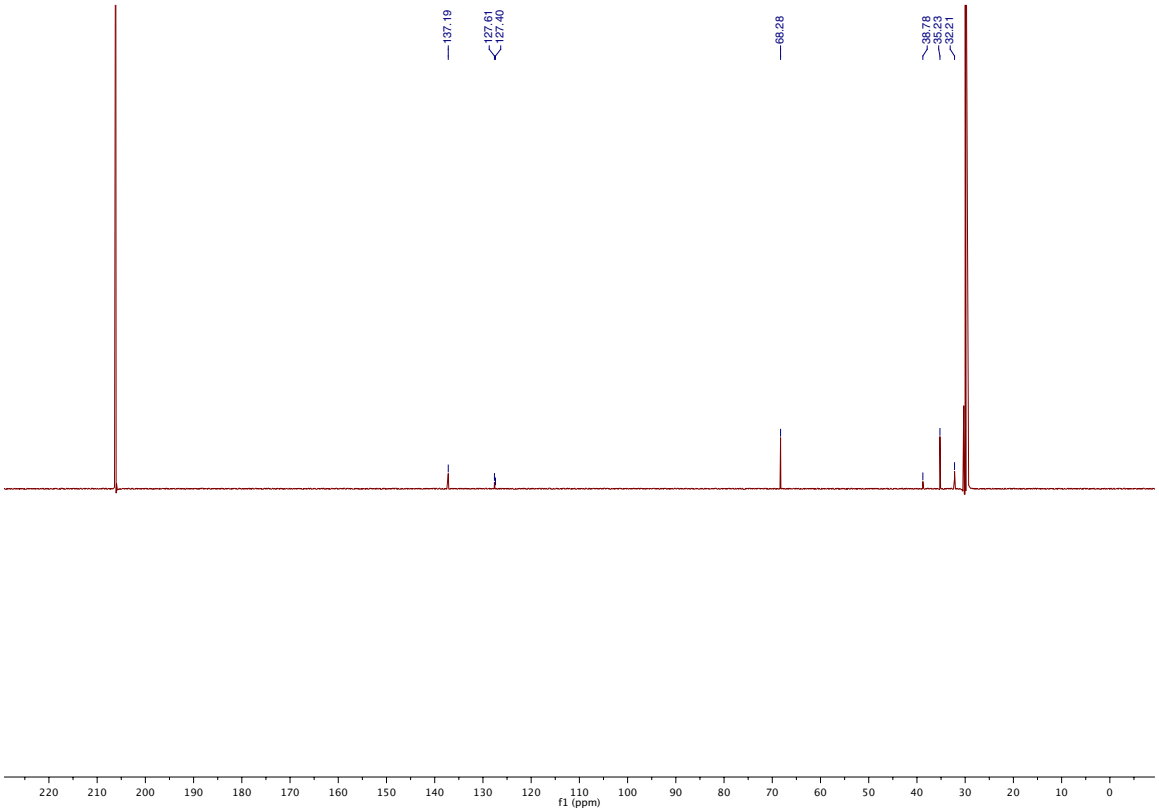
22

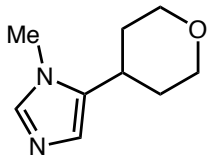

158.49
147.58
143.68
141.41
133.25
128.13
109.24
68.08
40.98
32.47
f1 (ppm)


O
N
N
Me

23

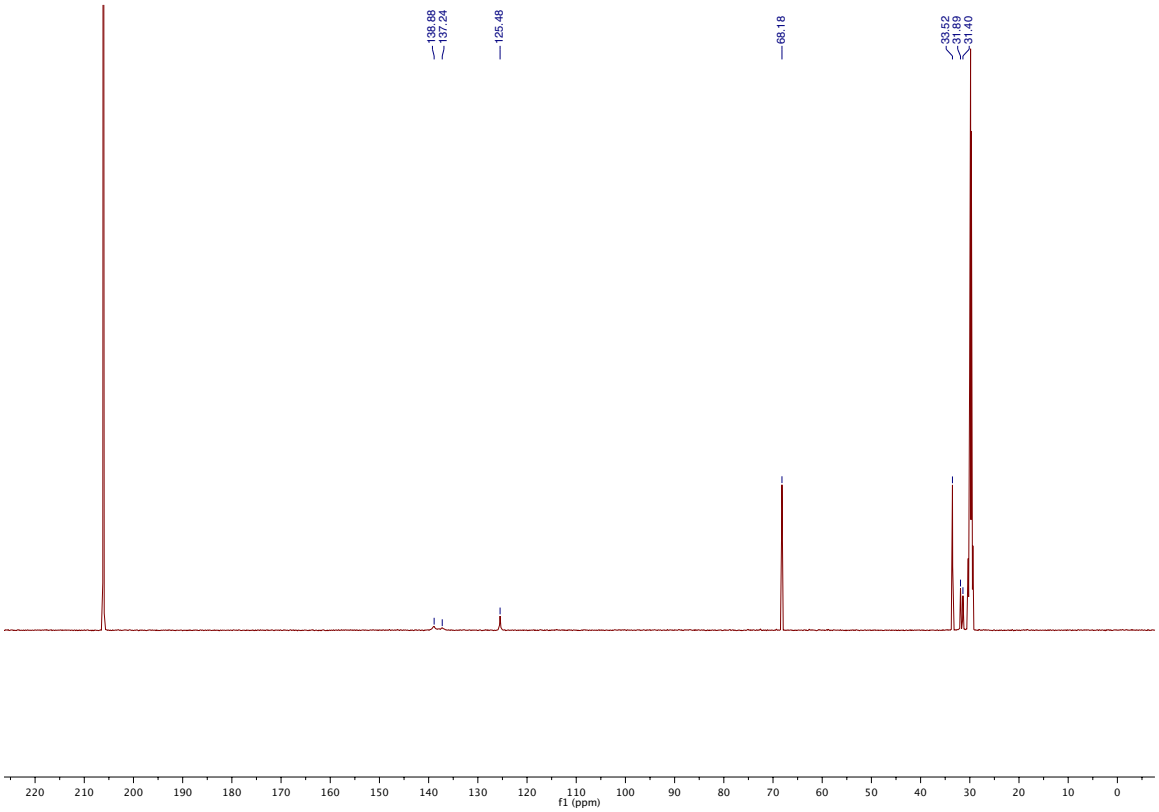
7.37
7.26
3.91
3.90
3.89
3.88
3.80
3.44
3.42
3.40
2.73
2.71
2.70
2.69
2.68
1.80
1.79
1.78
1.77
1.76
1.61
1.60
1.58
1.57
1.56
1.55
1.53
1.52
1.00
0.99
2.10
3.15
2.09
1.02
2.08
2.12
f1 (ppm)

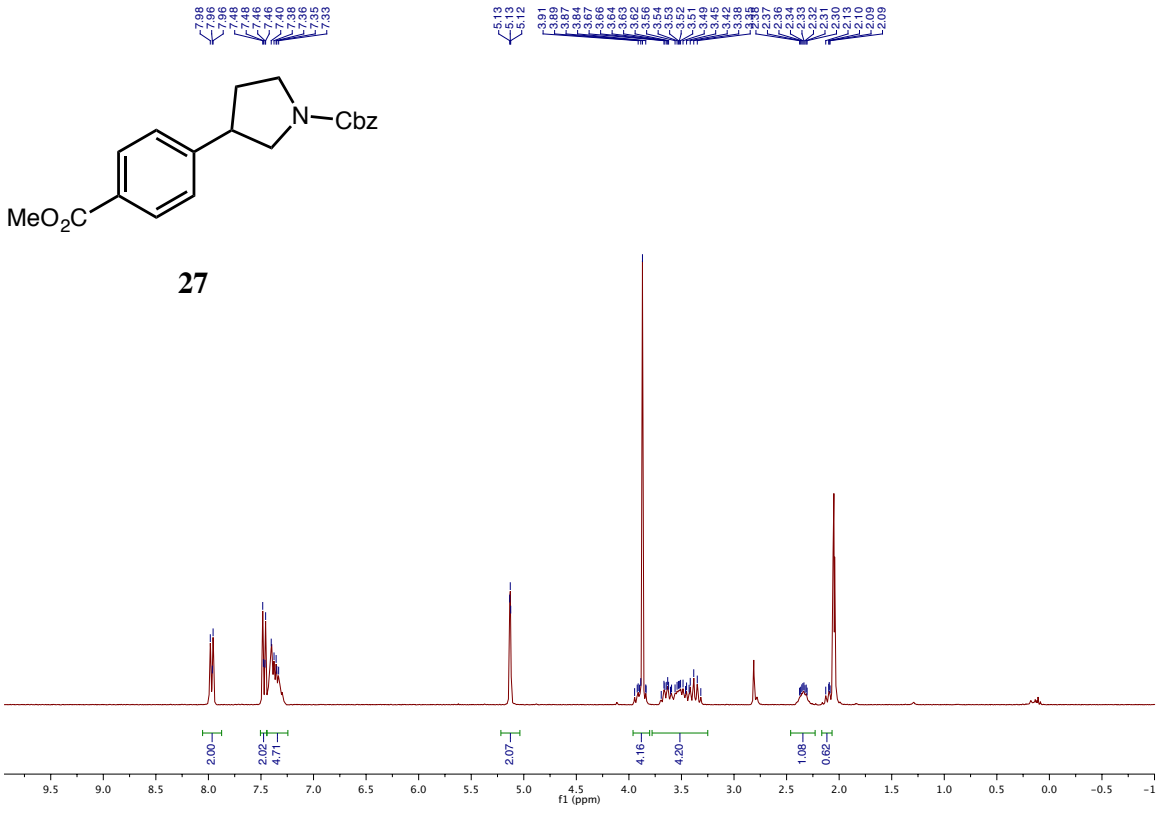

137.19
127.61
127.40
68.28
38.78
35.23
32.21
f1 (ppm)


Me
N
N
O

24

7.40
6.72
3.64
3.50
3.48
3.46
1.00
0.95
2.17
3.23
2.20
1.37
2.16
2.20
f1 (ppm)


138.88
137.24
125.48
68.18
33.52
31.89
31.40
f1 (ppm)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7.96
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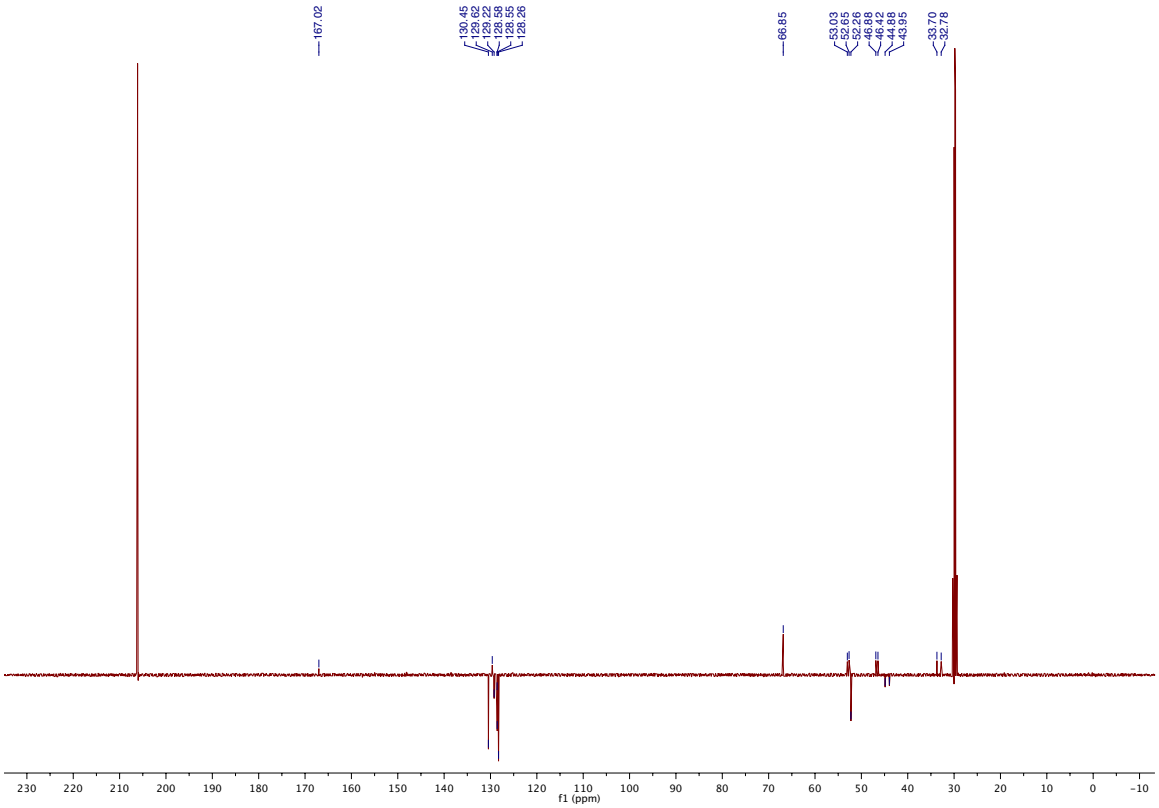
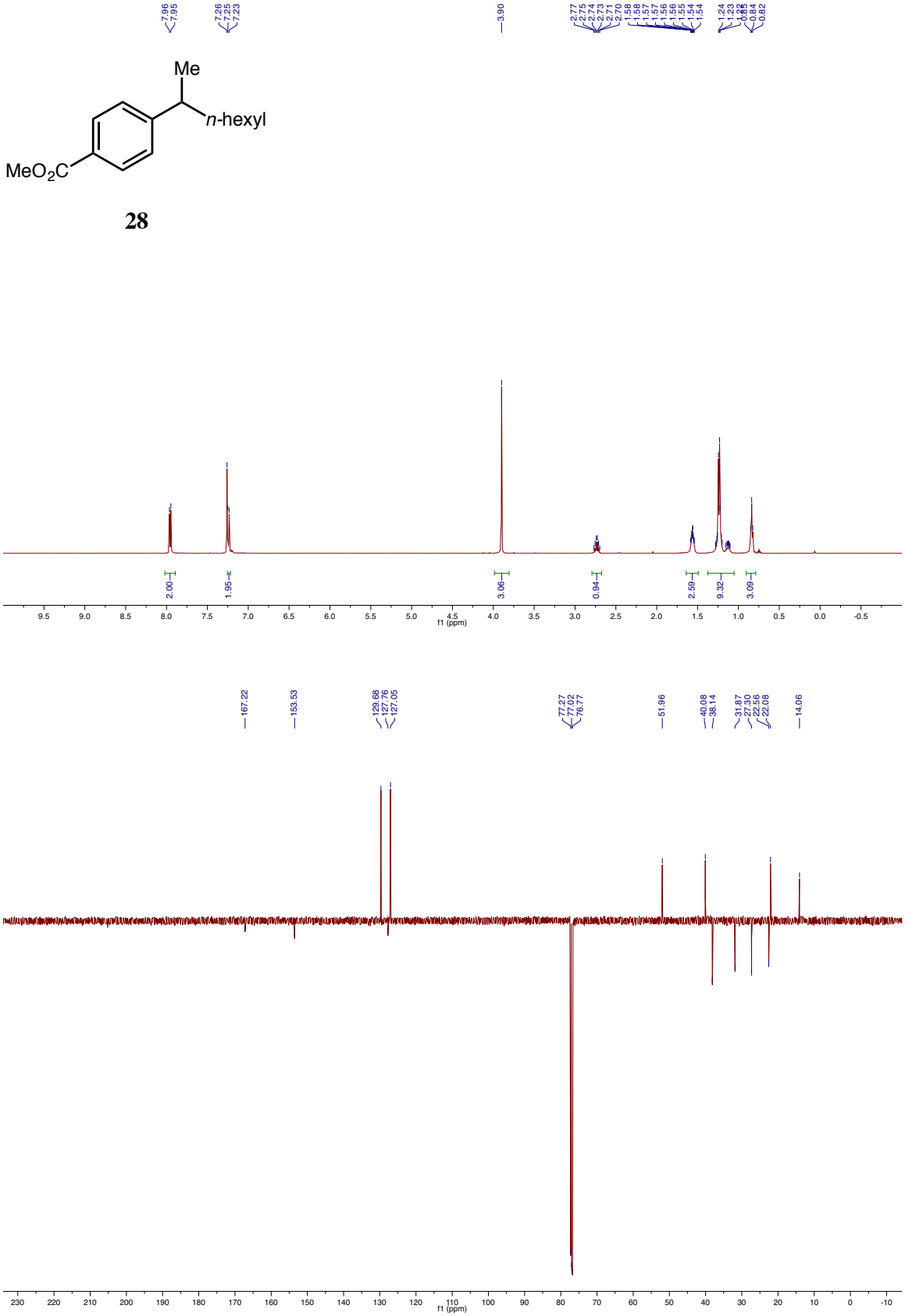
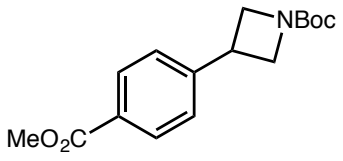
7.46
7.46
7.40
7.38
7.36
7.35
7.33
5.13
5.13
5.12
3.91
3.89
3.87
3.84
3.67
3.66
3.64
3.63
3.62
3.56
3.54
3.53
3.52
3.51
3.49
3.45
3.42
3.38
2.37
2.36
2.34
2.33
2.32
2.31
2.30
2.13
2.10
2.09
2.09
N
Cbz
MeO2C
2.00
2.02
4.71
2.07
4.16
4.20
1.08
0.62
f1 (ppm)

27


167.02
130.45
129.62
129.22
128.58
128.55
128.26
66.85
53.03
52.65
52.28
46.69
46.42
44.88
43.95
33.70
32.78
f1 (ppm)

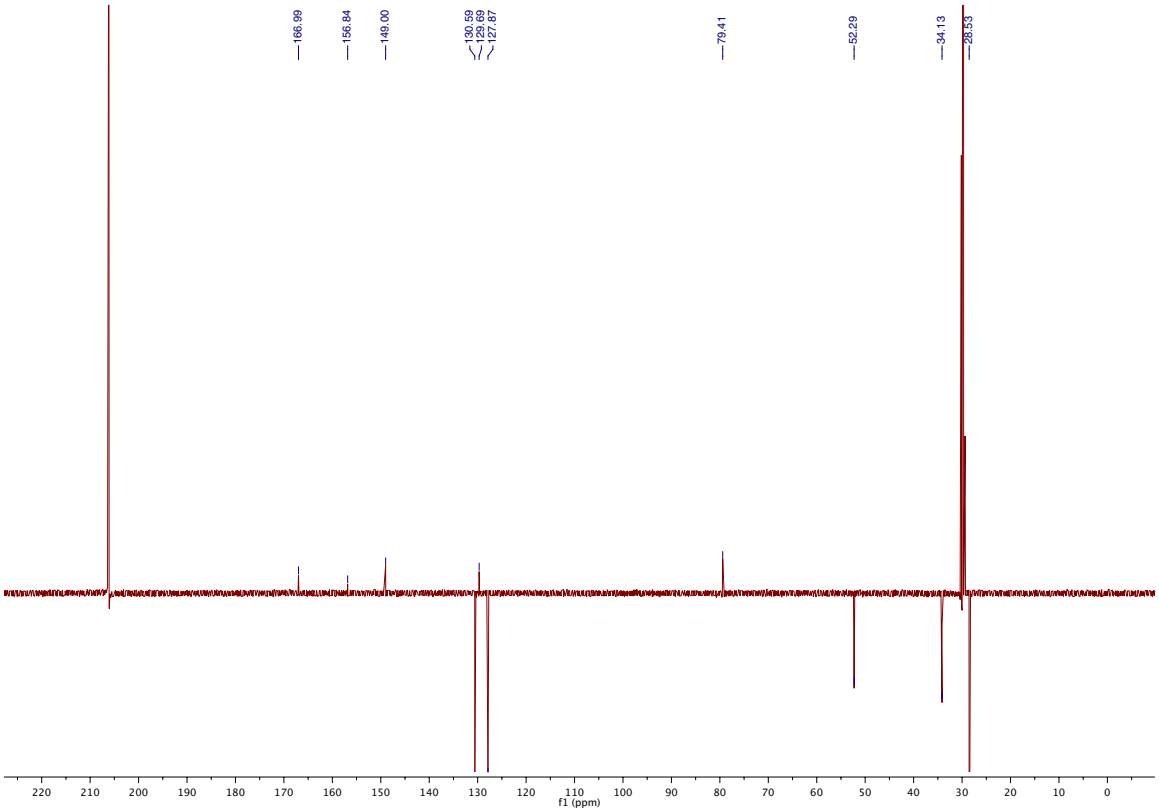

7.96
7.95
7.26
7.25
7.23
3.90
2.77
2.75
2.74
2.73
2.71
2.70
1.58
1.58
1.57
1.57
1.56
1.56
1.55
1.54
1.54
1.24
1.23
0.85
0.84
0.82
Me
n-hexyl
MeO2C
2.00
1.95
3.06
0.94
2.59
9.32
3.09
f1 (ppm)
167.22
153.53
129.68
127.76
127.05
77.27
77.02
76.77
51.96
40.08
38.14
31.87
27.30
22.56
22.08
14.06
f1 (ppm)

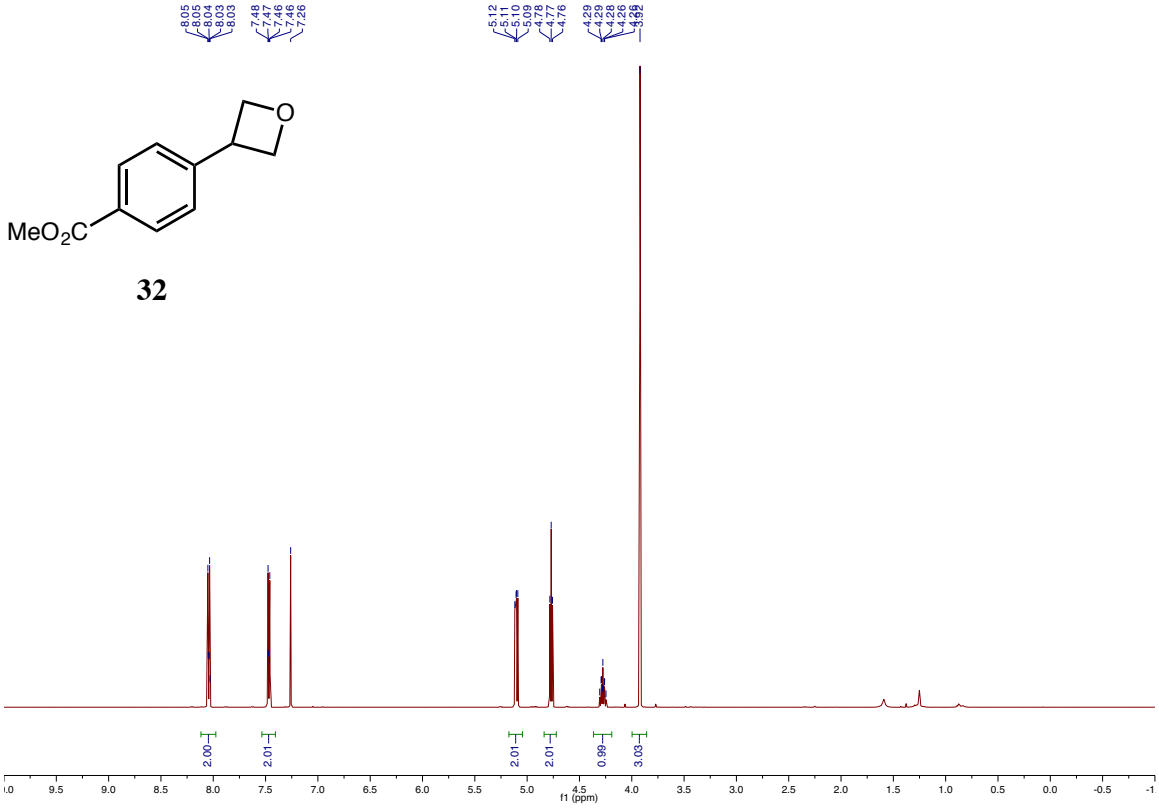
28


NBoc
MeO2C

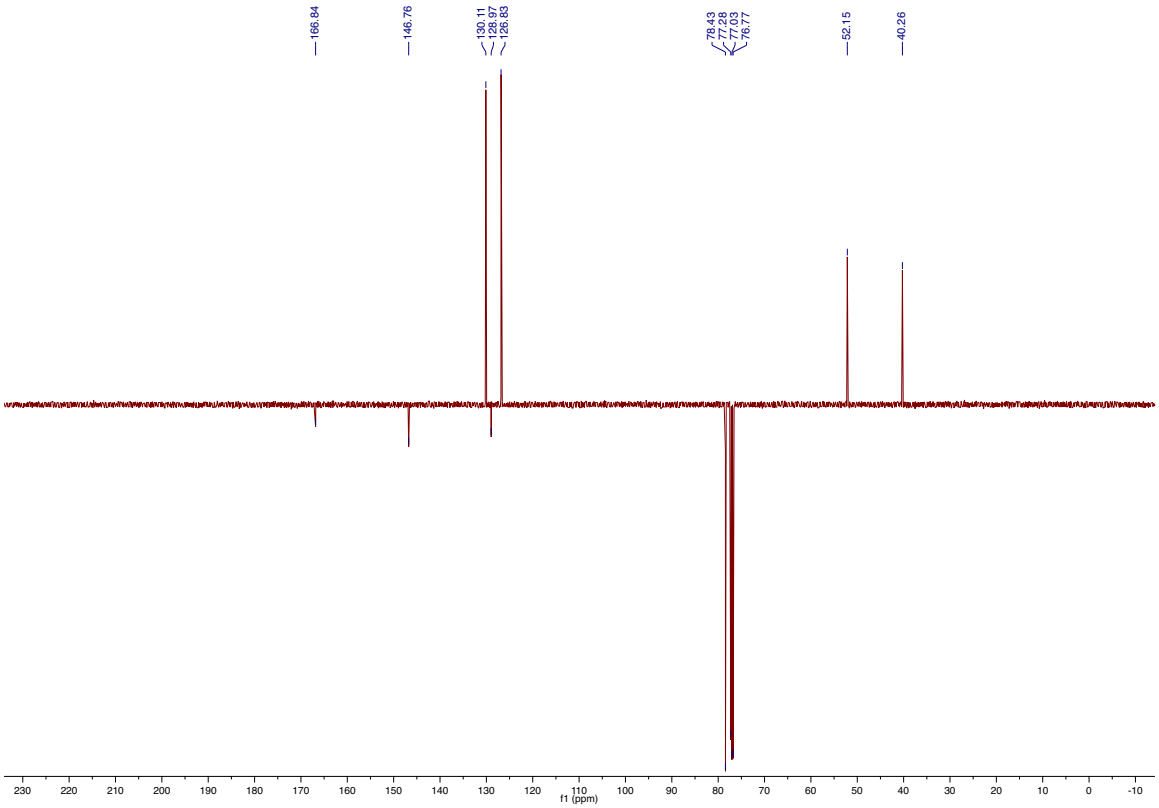
31

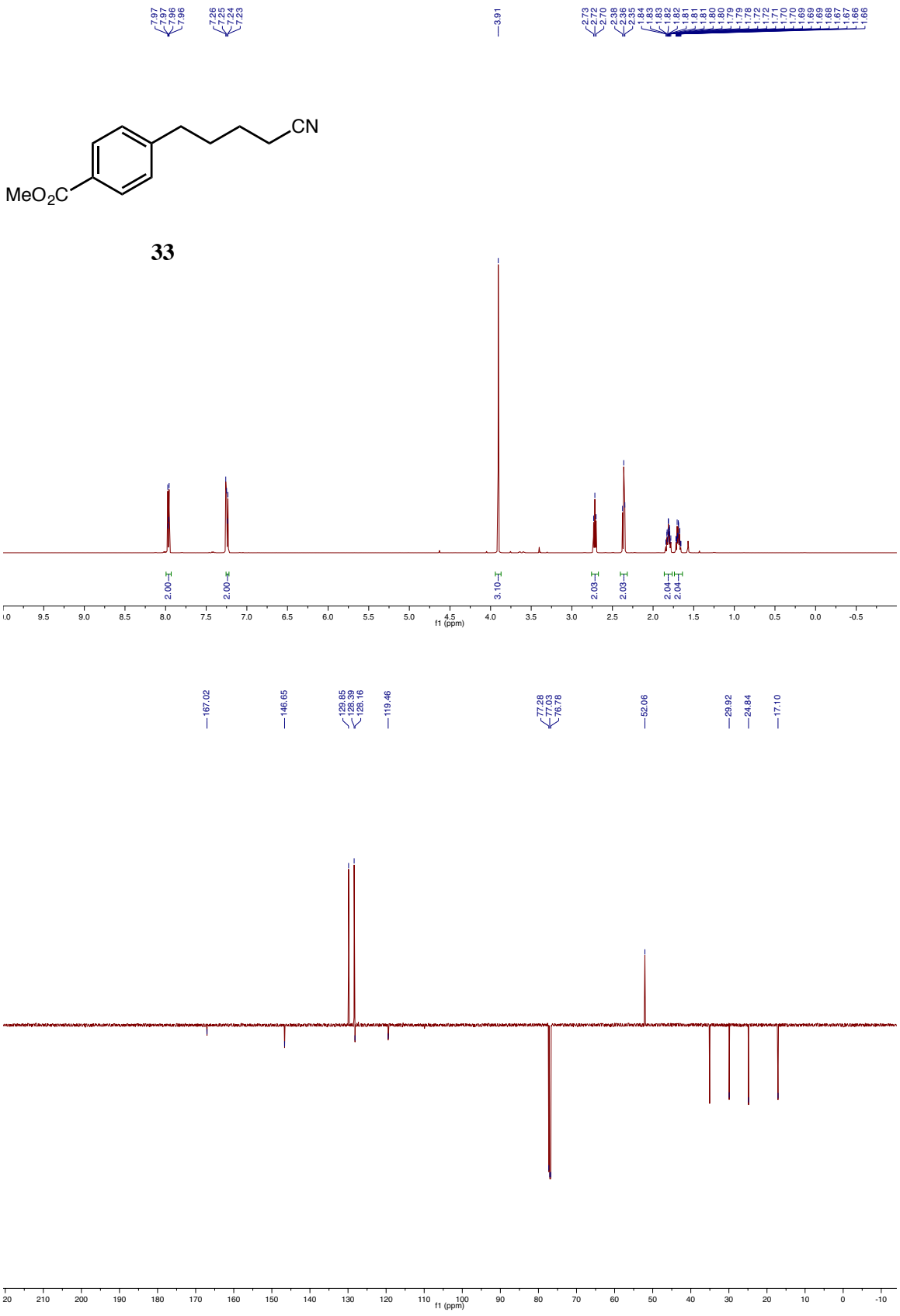
8.01
8.00
7.52
7.50
4.35
4.33
3.93
3.92
3.91
3.91
3.88
1.44
2.00
2.02
1.89
2.85
3.11
9.20
f1 (ppm)

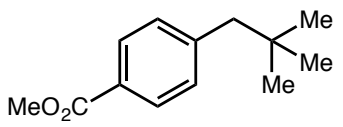

166.99
156.84
149.00
130.59
129.69
127.87
79.41
52.29
34.13
28.53
f1 (ppm)


8.05
8.05
8.04
8.03
8.03
7.48
7.47
7.47
7.46
7.26
5.12
5.11
5.10
5.09
4.78
4.77
4.76
4.29
4.29
4.28
4.26
4.26
3.82
O
MeO2C
2.00
2.01
2.01
2.01
0.99
3.03
f1 (ppm)

32

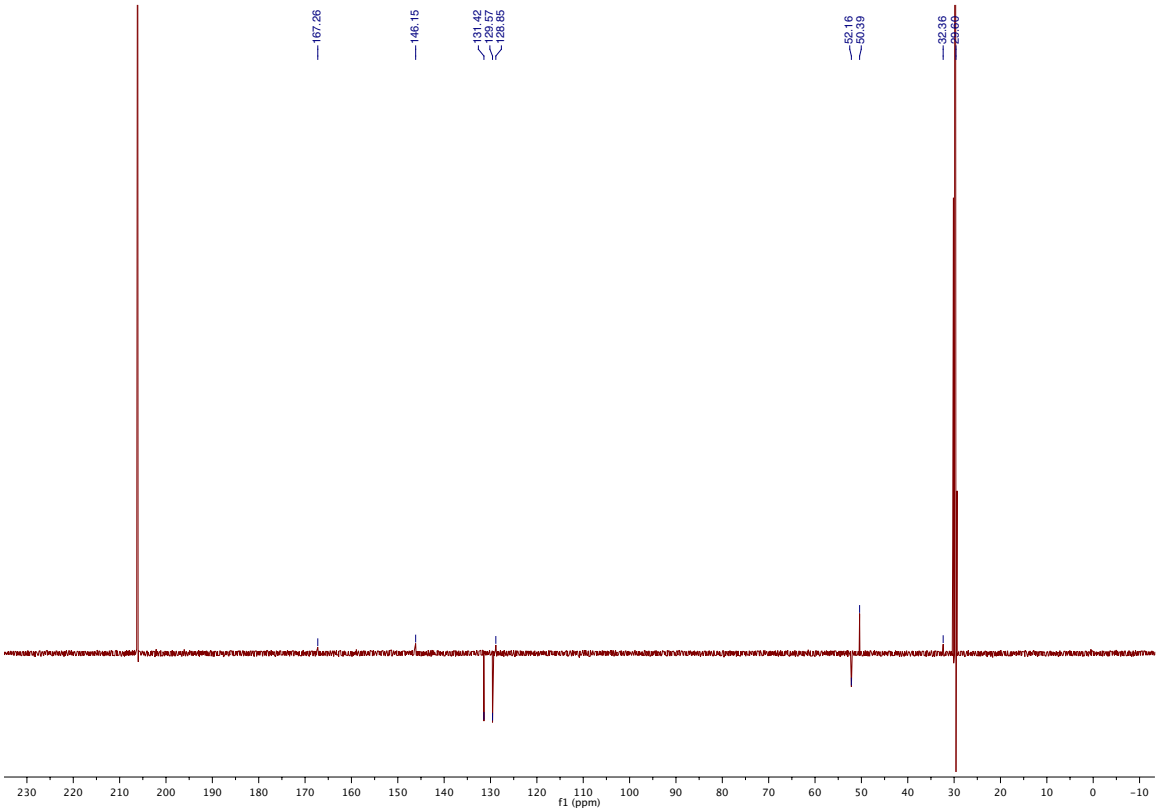

166.84
146.76
130.11
128.97
128.83
78.43
77.28
77.03
76.77
52.15
40.26
f1 (ppm)


7.97
7.97
7.96
7.96
7.26
7.25
7.24
7.23
3.91
2.73
2.72
2.70
2.38
2.36
2.35
1.84
1.83
1.82
1.82
1.81
1.81
1.81
1.80
1.80
1.79
1.79
1.78
1.72
1.72
1.71
1.71
1.70
1.70
1.69
1.69
1.68
1.67
1.67
1.66
1.66
CN
MeO2C
33
2.00
2.00
3.10
2.03
2.03
2.04
2.04
f1 (ppm)
167.02
146.65
129.85
128.39
128.16
119.46
77.28
77.03
76.78
52.06
29.92
24.84
17.10
f1 (ppm)


Me
Me
Me
MeO2C

36

7.93
7.93
7.92
7.91
7.31
7.30
7.29
7.29
3.87
2.60
0.92
2.00
2.03
3.06
2.04
9.32
f1 (ppm)


167.26
146.15
131.42
129.57
128.85
52.16
50.39
32.36
29.60
f1 (ppm)