Alcohols as Latent Coupling Fragments for Metallaphotoredox Catalysis: sp^3-sp^2 Cross-Coupling of Oxalates with Aryl Halides

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Supporting Information

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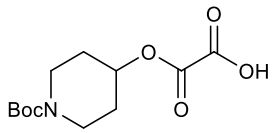
1) General Information

Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.[1] $Ir[dFppy]_2(dtbbpy)PF_6$ was prepared using literature procedures.[2] Anhydrous THP, 1,4-dioxane and DMSO were purchased from Sigma-Aldrich or Acros and used as received. Cesium hydrogencarbonate (note: hygroscopic) was dried in oven for 48 h. 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 $CDCl_3$ (δ 7.26 ppm), $(CD_3)_2SO$ signals (δ 2.50 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 $CDCl_3$ (77.16 ppm), $(CD_3)_2SO$ signals (δ 39.52 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) Preparation of Oxalates from Alcohols



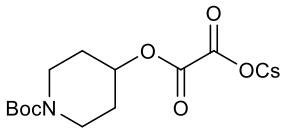
2-((1-(*tert*-Butoxycarbonyl)piperidin-4-yl)oxy)-2-oxoacetic acid. A round-bottom flask was charged with *tert*-butyl 4-hydroxypiperidine-1-carboxylate (10 g, 49.7 mmol 1.0 equiv) followed by the addition of Et_2O (250 mL) and dichloromethane (80 mL). The solution was cooled to 0 ^oC. Next, oxalyl chloride (8.41 mL, 99.0 mmol, 2.0 equiv) was added dropwise. The homogeneous reaction mixture was allowed to warm to ambient temperature and stir for 18 h. The reaction was cooled to 0 ^oC and quenched by slow addition of H_2O (100 mL). After stirring for 1 h at ambient temperature, the resulting mixture was transferred to a separatory funnel, and the aqueous layer mixture was extracted with three portions of Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure affording the title compound as a white solid (13.4 g, 49.0 mmol, 99% yield). All the oxalates were used without further purification.

^{1}H NMR (500 MHz, Acetone-d_6) δ 5.09 (tt, J = 7.8, 3.6 Hz, 1H), 3.73 (dt, J = 12.6, 4.7 Hz, 2H), 3.28 (brs, 2H), 1.96-1.92 (m, 2H), 1.68-1.62 (m, 2H), 1.44 (s, 9H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 159.15, 158.74, 155.01, 79.70, 73.41, 30.94, 28.48.

IR (film) ν_{max} 3106, 2971, 2931, 1766, 1747, 1647, 1481, 1435, 1371, 1250, 1171, 1143, 1019, 853, 708 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{19}H_{19}NNaO_6$ ($[M+Na]^+$) 296.1105, found 296.1106.

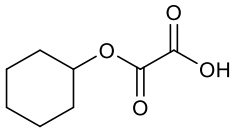


Cesium 2-((1-(*tert*-butoxycarbonyl)piperidin-4-yl)oxy)-2-oxoacetate. A round-bottom flask was charged with 2-((1-(*tert*-butoxycarbonyl)piperidin-4-yl)oxy)-2-oxoacetic acid (300 mg, 1.10 mmol 1.0 equiv) followed by the addition of THF (2 mL) and H_2O (10 mL). To this solution, cesium carbonate (179 mg, 0.55 mmol, 1.0 equiv) was added dropwise. The mixture was stirred vigorously for 30 min at room temperature, then concentrated under reduced pressure affording the title compound as a white solid (439 mg, 1.08 mmol, 99% yield).

^{1}H NMR (500 MHz, DMSO-d_6) δ 4.73 (tt, J = 8.4, 3.8 Hz, 1H), 3.75-3.55 (m, 2H), 3.36 (brs, 2H), 3.08 (brs, 2H), 1.78-1.74 (m, 2H), 1.38 (s, 9H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 166.80, 162.58, 153.90, 78.75, 67.90, 30.39 (br), 28.08.

IR (film) ν_{max} 3444, 2973, 2854, 1714, 1687, 1634, 1419, 1207, 1178, 1020, 766 cm^{-1}.



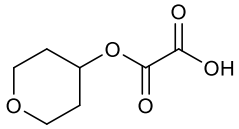
2-(Cyclohexyloxy)-2-oxoacetic acid. A round-bottom flask was charged with cyclohexanol (5.0 mL, 47.9 mmol 1.0 equiv) followed by the addition of Et_2O (250 mL) . The solution was cooled to 0 ^oC. Next, oxalyl chloride (8.11 mL, 96 mmol, 2.0 equiv) was added dropwise. The homogeneous reaction mixture was allowed to warm to ambient temperature and stir for 18 h. The reaction was cooled to 0 ^oC and quenched by slow addition of H_2O (100 mL). After stirring for 1 h at ambient temperature, the resulting mixture was transferred to a separatory funnel, and the aqueous layer mixture was extracted with three portions of Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure affording the title compound as a colorless oil (7.59 g, 44.1 mmol, 92% yield).

^{1}H NMR (500 MHz, Acetone-d_6) δ 4.88 (tt, J = 8.9, 3.8 Hz, 1H), 1.92-1.89 (m, 2H), 1.80-1.72 (m, 2H), 1.62-1.48 (m, 3H), 1.47-1.36 (m, 2H), 1.37-1.23 (m, 1H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 159.36, 158.83, 75.83, 31.67, 25.68, 23.99.

IR (film) ν_{max} 3166, 2983, 2862, 1761, 1730, 1452, 1251, 1179, 1152, 1119, 1006, 893, 705 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_8H_{12}NaO_4$ ($[M+Na]^+$) 195.0628, found 195.0630.



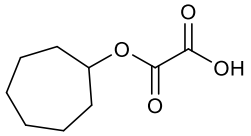
2-Oxo-2-((tetrahydro-2*H*-pyran-4-yl)oxy)acetic acid. A round-bottom flask was charged with tetrahydro-2*H*-pyran-4-ol (3.0 mL g, 31.5 mmol 1.0 equiv) followed by the addition of Et_2O (200 mL) . The solution was cooled to 0 ^oC. Next, oxalyl chloride (5.32 mL, 62.9 mmol, 2.0 equiv) was added dropwise. The homogeneous reaction mixture was allowed to warm to ambient temperature and stir for 18 h. The reaction was cooled to 0 ^oC and quenched by slow addition of H_2O (90 mL). After stirring for 1 h at ambient temperature, the resulting mixture was transferred to a separatory funnel, and the aqueous layer mixture was extracted with three portions of Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure affording the title compound as a white solid (4.96 g, 28.5 mmol, 91% yield).

^{1}H NMR (500 MHz, Acetone-d_6) δ 5.08 (dp, *J* = 8.6, 4.3 Hz, 1H), 3.88 (dt, *J* = 11.6, 4.4 Hz, 2H), 3.62-3.48 (m, 2H), 2.03-1.90 (m, 2H), 1.73-1.66 (m, 2H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 159.22, 158.79, 72.84, 65.42, 32.18.

IR (film) ν_{max} 3458, 2965, 2863, 1734, 1299, 1191, 1007, 863, 723 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_7H_{10}NaO_5$ ($[M+Na]^+$) 197.0420, found 197.0418.



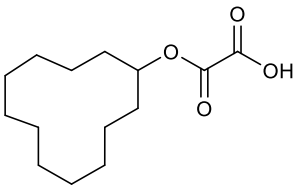
2-(Cycloheptyloxy)-2-oxoacetic acid. A round-bottom flask was charged with cycloheptanol (3.0 mL, 24.9 mmol 1.0 equiv) followed by the addition of Et_2O (200 mL) . The solution was cooled to 0 ^oC. Next, oxalyl chloride (4.22 mL, 49.8 mmol, 2.0 equiv) was added dropwise. The homogeneous reaction mixture was allowed to warm to ambient temperature and stir for 18 h. The reaction was cooled to 0 ^oC and quenched by slow addition of H_2O (90 mL). After stirring for 1 h at ambient temperature, the resulting mixture was transferred to a separatory funnel, and the aqueous layer mixture was extracted with three portions of Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure affording the title compound as a colorless oil (4.5 g, 24.2 mmol, 97% yield).

^{1}H NMR (500 MHz, Acetone-d_6) δ 5.05 (tt, J = 8.2, 4.5 Hz, 1H), 2.03-1.88 (m, 2H), 1.81-1.63 (m, 4H), 1.61-1.57 (m, 4H), 1.52-1.46 (m, 2H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 159.47, 158.83, 78.41, 33.92, 28.77, 23.20.

IR (film) ν_{max} 3500, 2929, 2861, 1728, 1461, 1448, 1184, 1166, 955, 711 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_9H_{14}NaO_4$ ($[M+Na]^+$) 209.0784, found 209.0783.



2-(Cyclododecyloxy)-2-oxoacetic acid. A round-bottom flask was charged with cyclododecanol (5.0 g, 27.1 mmol 1.0 equiv) followed by the addition of Et_2O (200 mL) .

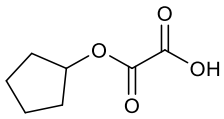
The solution was cooled to 0 ^{o}C. Next, oxalyl chloride (4.59 mL, 54.3 mmol, 2.0 equiv) was added dropwise. The homogeneous reaction mixture was allowed to warm to ambient temperature and stir for 18 h. The reaction was cooled to 0 ^{o}C and quenched by slow addition of H_2O (90 mL). After stirring for 1 h at ambient temperature, the resulting mixture was transferred to a separatory funnel, and the aqueous layer mixture was extracted with three portions of Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure affording the title compound as a white solid (6.8 g, 26.5 mmol, 98% yield).

^{1}H NMR (500 MHz, Acetone-d_6) δ 5.17-5.12 (m, 1H), 1.82 (dq, *J* = 13.1, 6.5 Hz, 2H), 1.69-1.54 (m, 2H), 1.54-1.31 (m, 18H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 159.50, 159.35, 75.54, 29.60, 24.58, 24.40, 24.07, 23.85, 21.49.

IR (film) ν_{max} 3515, 2931, 2863, 1733, 1471, 1446, 1195, 1151, 718 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{24}NaO_4$ ([M+Na]$^{+}$) 279.1567, found 279.1562.



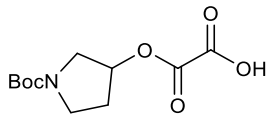
2-(Cyclopentyloxy)-2-oxoacetic acid. A round-bottom flask was charged with cyclopentanol (4.0 mL, 44.1 mmol 1.0 equiv) followed by the addition of Et_2O (200 mL) . The solution was cooled to 0 ^{o}C. Next, oxalyl chloride (7.46 mL, 88 mmol, 2.0 equiv) was added dropwise. The homogeneous reaction mixture was allowed to warm to ambient temperature and stir for 18 h. The reaction was cooled to 0 ^{o}C and quenched by slow addition of H_2O (90 mL). After stirring for 1 h at ambient temperature, the resulting mixture was transferred to a separatory funnel, and the aqueous layer mixture was extracted with three portions of Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure affording the title compound as a colorless oil (6.5 g, 41.1 mmol, 93% yield).

^{1}H NMR (500 MHz, Acetone-d_6) δ 5.33-5.23 (m, 1H), 1.99-1.87 (m, 2H), 1.82-1.69 (m, 4H), 1.66-1.61 (m, 2H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 159.53, 159.41, 80.52, 33.12, 24.32.

IR (film) ν_{max} 3512, 2963, 2876, 1726, 1195, 1157, 947, 835, 714 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_7H_{10}NaO_4$ ($[M+Na]^+$) 181.0471, found 181.0471.



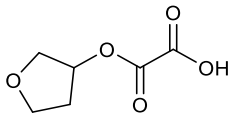
2-((1-(*tert*-Butoxycarbonyl)pyrrolidin-3-yl)oxy)-2-oxoacetic acid. A round-bottom flask was charged with *tert*-butyl 3-hydroxypyrrolidine-1-carboxylate (4.0 g, 21.4 mmol 1.0 equiv) followed by the addition of Et_2O (200 mL) . The solution was cooled to 0 ^oC. Next, oxalyl chloride (3.62 mL, 42.7 mmol, 2.0 equiv) was added dropwise. The homogeneous reaction mixture was allowed to warm to ambient temperature and stir for 18 h. The reaction was cooled to 0 ^oC and quenched by slow addition of H_2O (90 mL). After stirring for 1 h at ambient temperature, the resulting mixture was transferred to a separatory funnel, and the aqueous layer mixture was extracted with three portions of Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure affording the title compound as a colorless oil (5.1 g, 19.7 mmol, 92% yield, rotameric).

^{1}H NMR (500 MHz, Acetone-d_6) δ 5.45 (brs, 1H), 3.69-3.56 (m, 1H), 3.54-3.49 (m, 2H), 3.43-3.35 (m, 1H), 2.30-2.09 (m, 2H), 1.44 (s, 9H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 159.09, 158.96, 154.66, 154.53, 79.50, 77.53, 76.67, 52.22, 51.95, 44.64, 44.34, 31.87, 31.05, 28.59.

IR (film) ν_{max} 3396, 2978, 1740, 1666, 1425, 1368, 1167, 1128, 876 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{11}H_{17}NNaO_6$ ($[M+Na]^+$) 282.0948, found 282.0945.



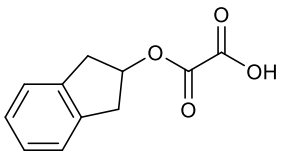
2-Oxo-2-((tetrahydrofuran-3-yl)oxy)acetic acid. A round-bottom flask was charged with tetrahydrofuran-3-ol (1.2 mL, 14.9 mmol 1.0 equiv) followed by the addition of Et_2O (100 mL) . The solution was cooled to 0 ^oC. Next, oxalyl chloride (2.51 mL, 29.7 mmol, 2.0 equiv) was added dropwise. The homogeneous reaction mixture was allowed to warm to ambient temperature and stir for 18 h. The reaction was cooled to 0 ^oC and quenched by slow addition of H_2O (40 mL). After stirring for 1 h at ambient temperature, the resulting mixture was transferred to a separatory funnel, and the aqueous layer mixture was extracted with three portions of Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure affording the title compound as a pale yellow oil (1.7 g, 10.6 mmol, 72% yield).

^{1}H NMR (500 MHz, Acetone-d_6) δ 5.46-5.42 (m, 1H), 3.94-3.75 (m, 4H), 2.28 (td, J = 14.6, 8.2 Hz, 1H), 2.10-2.05 (m, 1H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 159.16, 158.92, 78.35, 72.99, 67.25, 33.12.

IR (film) ν_{max} 3469, 2881, 1733, 1185, 1105, 1078, 967, 894, 718 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_6H_8NaO_5$ ($[M+Na]^+$) 183.0264, found 183.0260.



2-((2,3-Dihydro-1*H*-inden-2-yl)oxy)-2-oxoacetic acid. A round-bottom flask was charged with 2,3-dihydro-1*H*-inden-2-ol (4.0 g, 29.8 mmol 1.0 equiv) followed by the addition of Et_2O (200 mL) . The solution was cooled to 0 ^oC. Next, oxalyl chloride (5.05

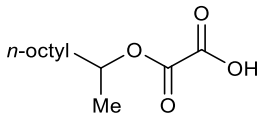
mL, 59.6 mmol, 2.0 equiv) was added dropwise. The homogeneous reaction mixture was allowed to warm to ambient temperature and stir for 18 h. The reaction was cooled to 0 ^{o}C and quenched by slow addition of H_2O (80 mL). After stirring for 1 h at ambient temperature, the resulting mixture was transferred to a separatory funnel, and the aqueous layer mixture was extracted with three portions of Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure affording the title compound as a brown solid (6.1 g, 29.6 mmol, 99% yield).

^{1}H NMR (500 MHz, Acetone-d_6) δ 7.27 (dd, *J* = 5.2, 3.6 Hz, 2H), 7.19 (dd, *J* = 5.6, 3.2 Hz, 2H), 5.68-5.65 (m, 1H), 3.40 (dd, *J* = 17.3, 6.3 Hz, 2H), 3.09 (dd, *J* = 17.2, 2.3 Hz, 2H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 158.99, 158.77, 140.66, 127.30, 125.08, 78.52, 39.59.

IR (film) ν_{max} 3472, 2963, 2909, 1752, 1729, 1223, 1206, 1186, 1002, 952, 751, 733, 714, 703 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{11}H_{10}NaO_4$ ([M+Na]$^{+}$) 229.0471, found 229.0474.



2-(Decan-2-yloxy)-2-oxoacetic acid. A round-bottom flask was charged with decan-2-ol (6.0 mL, 31.3 mmol 1.0 equiv) followed by the addition of Et_2O (200 mL) . The solution was cooled to 0 ^{o}C. Next, oxalyl chloride (5.31 mL, 62.7 mmol, 2.0 equiv) was added dropwise. The homogeneous reaction mixture was allowed to warm to ambient temperature and stir for 18 h. The reaction was cooled to 0 ^{o}C and quenched by slow addition of H_2O (90 mL). After stirring for 1 h at ambient temperature, the resulting mixture was transferred to a separatory funnel, and the aqueous layer mixture was extracted with three portions of Et_2O. The combined organic layers were washed with

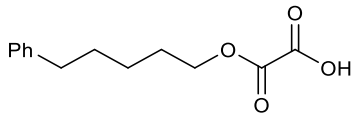
brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure affording the title compound as a colorless oil (6.9 g, 30.0 mmol, 96% yield).

^{1}H NMR (500 MHz, Acetone-d_6) δ 5.06-5.00 (m, 1H), 1.74-1.56 (m, 2H), 1.40-1.29 (m, 15H), 0.87 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 159.62, 159.37, 74.80, 36.36, 32.66, 30.26, 30.14, 30.03, 26.03, 23.39, 19.98, 14.43.

IR (film) ν_{max} 3567, 2926, 2856, 1735, 1462, 1381, 1191, 1120, 731 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{22}NaO_4$ ($[M+Na]^+$) 253.1410, found 253.1410.



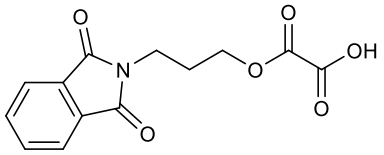
2-Oxo-2-((5-phenylpentyl)oxy)acetic acid. A round-bottom flask was charged with 5-phenylpentan-1-ol (2.0 mL, 11.9 mmol 1.0 equiv) followed by the addition of Et_2O (100 mL) . The solution was cooled to 0 ^oC. Next, oxalyl chloride (2.0 mL, 23.8 mmol, 2.0 equiv) was added dropwise. The homogeneous reaction mixture was allowed to warm to ambient temperature and stir for 18 h. The reaction was cooled to 0 ^oC and quenched by slow addition of H_2O (60 mL). After stirring for 1 h at ambient temperature, the resulting mixture was transferred to a separatory funnel, and the aqueous layer mixture was extracted with three portions of Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure affording the title compound as a pale yellow oil (2.55 g, 10.8 mmol, 91% yield).

^{1}H NMR (500 MHz, Acetone-d_6) δ 7.26 (t, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 7.4 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 4.27 (t, *J* = 6.6 Hz, 2H), 2.63 (t, *J* = 7.7 Hz, 2H), 1.76 (dt, *J* = 14.4, 6.8 Hz, 2H), 1.71-1.64 (m, 2H), 1.48-1.42 (m, 2H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 159.66, 159.33, 143.29, 129.20, 129.09, 126.48, 67.06, 36.31, 31.88, 28.88, 26.12.

IR (film) ν_{max} 3120, 2936, 2859, 1737, 1454, 1374, 1228, 1169, 1040, 946, 746 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{16}NaO_4$ ([M+Na]$^+$) 259.0941, found 259.0937.



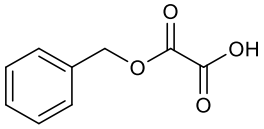
2-(3-(1,3-Dioxoisoindolin-2-yl)propoxy)-2-oxoacetic acid. A round-bottom flask was charged with 2-(3-hydroxypropyl)isoindoline-1,3-dione (1.5 g, 7.31 mmol 1.0 equiv) followed by the addition of Et_2O (100 mL) . The solution was cooled to 0 ^oC. Next, oxalyl chloride (1.24 mL, 14.6 mmol, 2.0 equiv) was added dropwise. The homogeneous reaction mixture was allowed to warm to ambient temperature and stir for 18 h. The reaction was cooled to 0 ^oC and quenched by slow addition of H_2O (50 mL). After stirring for 1 h at ambient temperature, the resulting mixture was transferred to a separatory funnel, and the aqueous layer mixture was extracted with three portions of Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure affording the title compound as a white solid (1.83 g, 6.60 mmol, 90% yield).

^{1}H NMR (500 MHz, Acetone-d_6) δ 7.94-7.77 (m, 4H), 4.35 (t, *J* = 6.3 Hz, 2H), 3.82 (t, *J* = 6.6 Hz, 2H), 2.17-2.12 (m, 2H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 168.91, 159.36, 158.94, 134.97, 133.26, 123.76, 65.19, 35.55, 28.21.

IR (film) ν_{max} 3441, 2952, 2008, 1768, 1744, 1686, 1652, 1608, 1398, 1326, 1298, 1216, 1059, 924, 803, 725 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{11}NNaO_6$ ($[M+Na]^+$) 300.0479, found 300.0476.



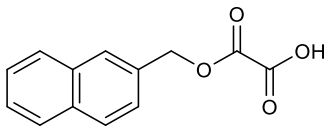
2-(Benzyloxy)-2-oxoacetic acid. A round-bottom flask was charged with benzyl alcohol (1.0 mL, 9.66 mmol 1.0 equiv) followed by the addition of Et_2O (100 mL) . The solution was cooled to 0 ^oC. Next, oxalyl chloride (1.64 mL, 19.3 mmol, 2.0 equiv) was added dropwise. The homogeneous reaction mixture was allowed to warm to ambient temperature and stir for 18 h. The reaction was cooled to 0 ^oC and quenched by slow addition of H_2O (50 mL). After stirring for 1 h at ambient temperature, the resulting mixture was transferred to a separatory funnel, and the aqueous layer mixture was extracted with three portions of Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure affording the title compound as a colorless oil (1.62 g, 8.99 mmol, 93% yield).

^{1}H NMR (500 MHz, Acetone-d_6) δ 7.49-7.45 (m, 2H), 7.44-7.35 (m, 3H), 5.32 (s, 2H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 159.42, 159.13, 136.10, 129.53, 129.51, 68.68.

IR (film) ν_{max} 3450, 2944, 1758, 1698, 1498, 1454, 1385, 1179, 906, 696 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_9H_8NaO_4$ ($[M+Na]^+$) 203.0315, found 203.0310.



2-(Naphthalen-2-ylmethoxy)-2-oxoacetic acid. A round-bottom flask was charged with 2-naphthalenemethanol (1.45 g, 9.17 mmol 1.0 equiv) followed by the addition of Et_2O (50 mL) . The solution was cooled to 0 ^oC. Next, oxalyl chloride (1.55 mL, 18.3 mmol, 2.0 equiv) was added dropwise. The homogeneous reaction mixture was allowed to warm to ambient temperature and stir for 18 h. The reaction was cooled to 0 ^oC and quenched

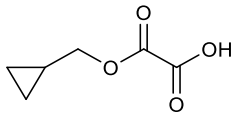
by slow addition of H_2O (30 mL). After stirring for 1 h at ambient temperature, the resulting mixture was transferred to a separatory funnel, and the aqueous layer mixture was extracted with three portions of Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure affording the title compound as a white solid (2.05 g, 8.90 mmol, 97% yield).

^{1}H NMR (500 MHz, Acetone-d_6) δ 8.00 (s, 1H), 7.97-7.91 (m, 3H), 7.59 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.56-7.53 (m, 2H), 5.50 (s, 2H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 159.48, 159.15, 134.36, 134.25, 133.64, 129.36, 128.98, 128.78, 128.68, 127.48, 127.42, 127.08, 68.85.

IR (film) ν_{max} 3414, 2944, 2576, 1764 1728, 1601, 1508, 1458, 1356, 1205, 1179, 941, 901, 863, 833, 754, 741, 709 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{10}NaO_4$ ($[M+Na]^+$) 253.0471, found 253.0466.



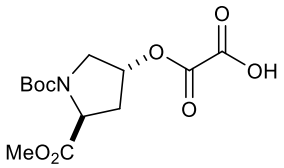
2-(Cyclopropylmethoxy)-2-oxoacetic acid. A round-bottom flask was charged with cyclopropylmethanol (1.0 mL, 12.3 mmol 1.0 equiv) followed by the addition of Et_2O (100 mL) . The solution was cooled to 0 ^oC. Next, oxalyl chloride (2.10 mL, 24.7 mmol, 2.0 equiv) was added dropwise. The homogeneous reaction mixture was allowed to warm to ambient temperature and stir for 18 h. The reaction was cooled to 0 ^oC and quenched by slow addition of H_2O (40 mL). After stirring for 1 h at ambient temperature, the resulting mixture was transferred to a separatory funnel, and the aqueous layer mixture was extracted with three portions of Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure affording the title compound as a pale yellow oil (1.6 g, 11.1 mmol, 90% yield).

^{1}H NMR (500 MHz, Acetone-d_6) δ 4.11 (dd, *J* = 7.4, 4.2 Hz, 2H), 1.30-1.11 (m, 1H), 0.72-0.50 (m, 2H), 0.37 (q, *J* = 5.2, 4.4 Hz, 2H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 159.67, 159.33, 159.11, 72.03, 71.89, 10.24, 3.77, 3.74.

IR (film) ν_{max} 3169, 3011, 2959, 1760, 1733, 1309, 1288, 1191, 1158, 1024, 943, 832, 701 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_6H_8NaO_4$ ([M+Na]$^+$) 167.0315, found 167.0316.



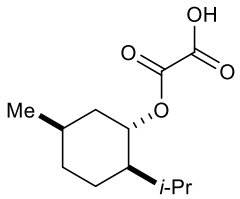
2-(((3*R*,5*S*)-1-(*tert*-Butoxycarbonyl)-5-(methoxycarbonyl)pyrrolidin-3-yl)oxy)-2-oxoacetic acid. A round-bottom flask was charged with 1-(*tert*-butyl) 2-methyl (2*S*,4*R*)-4-hydroxypyrrolidine-1,2-dicarboxylate (2.0 g, 8.15 mmol 1.0 equiv) followed by the addition of Et_2O (100 mL) . The solution was cooled to 0 ^{o}C. Next, oxalyl chloride (2.07 mL, 24.5 mmol, 2.0 equiv) was added dropwise. The homogeneous reaction mixture was allowed to warm to ambient temperature and stir for 18 h. The reaction was cooled to 0 ^{o}C and quenched by slow addition of H_2O (40 mL). After stirring for 1 h at ambient temperature, the resulting mixture was transferred to a separatory funnel, and the aqueous layer mixture was extracted with three portions of Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure affording the title compound as a white solid (2.4 g, 7.56 mmol, 93% yield, rotameric).

^{1}H NMR (500 MHz, Acetone-d_6) δ 5.48 (brs, 1H), 4.39 (q, *J* = 8.0 Hz, 1H), 3.80-3.62 (m, 5H), 2.65-2.49 (m, 1H), 2.37-2.27 (m, 1H), 1.44&1.39 (9H, s).

^{13}C NMR (125 MHz, Acetone-d_6) δ 173.60, 173.15, 158.82, 158.79, 158.59, 158.57, 154.57, 153.89, 80.47, 76.28, 75.61, 58.55, 58.31, 52.68, 52.46, 52.34, 36.79, 35.84, 28.50, 28.37.

IR (film) ν_{max} 3469, 2979, 1742, 1691, 1404, 1368, 1159, 1133, 1060 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{19}NNaO_8$ ([M+Na]$^+$) 340.1003, found 340.1003.



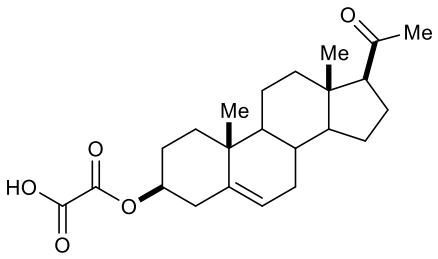
2-(((1*S*,2*R*,5*R*)-2-Isopropyl-5-methylcyclohexyl)oxy)-2-oxoacetic acid. A round-bottom flask was charged with (+)-isomenthol (2.0 g, 12.8 mmol 1.0 equiv) followed by the addition of Et_2O (100 mL) . The solution was cooled to 0 ^oC. Next, oxalyl chloride (2.17 mL, 25.6 mmol, 2.0 equiv) was added dropwise. The homogeneous reaction mixture was allowed to warm to ambient temperature and stir for 18 h. The reaction was cooled to 0 ^oC and quenched by slow addition of H_2O (40 mL). After stirring for 1 h at ambient temperature, the resulting mixture was transferred to a separatory funnel, and the aqueous layer mixture was extracted with three portions of Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure affording the title compound as a colorless oil (2.75 g, 12.1 mmol, 94% yield).

^{1}H NMR (500 MHz, Acetone-d_6) δ 5.17 (td, J = 6.8, 3.5 Hz, 1H), 2.00-1.88 (m, 1H), 1.82 (dq, J = 13.6, 6.8 Hz, 1H), 1.72-1.43 (m, 6H), 1.33-1.24 (m, 1H), 0.96 (d, J = 3.3 Hz, 3H), 0.95 (d, J = 3.5 Hz, 3H), 0.88 (d, J = 6.8 Hz, 3H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 159.51, 159.04, 75.05, 46.25, 35.94, 30.24, 28.14, 26.81, 21.25, 20.91, 20.46.

IR (film) ν_{max} 3475, 2957, 2873, 1734, 1457, 1370, 1204, 1140, 926 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{20}NaO_4$ ($[M+Na]^+$) 251.1254, found 251.1252.



2-(((3*S*,10*R*,13*S*,17*S*)-17-Acetyl-10,13-dimethyl 2,3,4,7,8,9,10,11,12,13,14,15,16, 17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl)oxy)-2-oxoacetic acid. A round-bottom flask was charged with pregnenolone (3.0 g, 9.48 mmol 1.0 equiv) followed by the addition of Et_2O (100 mL) . The solution was cooled to 0 ^oC. Next, oxalyl chloride (1.60 mL, 19.0 mmol, 2.0 equiv) was added dropwise. The homogeneous reaction mixture was allowed to warm to ambient temperature and stir for 18 h. The reaction was cooled to 0 ^oC and quenched by slow addition of H_2O (40 mL). After stirring for 1 h at ambient temperature, the resulting mixture was transferred to a separatory funnel, and the aqueous layer mixture was extracted with three portions of Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure affording the title compound as a white solid (3.6 g, 9.27 mmol, 98% yield).

^{1}H NMR (500 MHz, Acetone-d_6) δ 5.44 (brs, 1H), 4.70 (tt, *J* = 10.9, 5.6 Hz, 1H), 2.61 (t, *J* = 9.1 Hz, 1H), 2.48-2.38 (m, 2H), 2.19-2.09 (m, 3H), 2.08 (s, 3H), 2.03-1.91 (m, 3H), 1.82-1.58 (m, 5H), 1.57-1.50 (m, 3H), 1.29-1.17 (m, 3H), 1.08 (s, 3H), 0.62 (s, 3H).

^{13}C NMR (125 MHz, Acetone-d_6) δ 208.38, 159.41, 158.99, 140.21, 123.64, 77.25, 63.98, 57.53, 50.89, 44.39, 39.43, 38.40, 37.71, 37.41, 32.66, 32.54, 31.54, 28.16, 25.14, 23.43, 21.82, 19.65, 13.53.

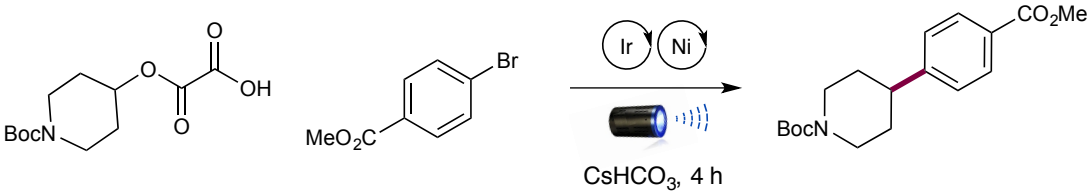
IR (film) ν_{max} 2945, 2893, 2856, 1760, 1735, 1669, 1363, 1281, 1179, 945, 720 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{23}H_{33}O_5$ ($[M+H]^+$) 389.2323, found 389.2320.

3) Procedure for Optimization Studies

To an oven-dried 8 mL vial equipped with a stir bar was added photocatalyst $Ir[dFppy]_2(dtbbpy)PF_6$ (1.1 mg, 1.1 μmol, 0.01 equiv.), methyl 4-bromobenzoate (23 mg, 0.11 mmol, 1.0 equiv.), 2-((1-(*tert*-butoxycarbonyl)piperidin-4-yl)oxy)-2-oxoacetic acid (38 mg, 0.14 mmol, 1.3 equiv.) and anhydrous cesium hydrogencarbonate (31 mg, 0.16 mmol, 1.5 equiv.). The vial was sealed and placed under nitrogen before 2 mL of solvent was added. To a separate vial was added $NiBr_2$•glyme (1.6 mg, 5.3 μmmol, 0.05 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (1.4 mg, 5.3 μmmol, 0.05 equiv). The pre-catalyst vial was sealed, purged with nitrogen, dissolved in 1 ml of solvent and then sonicated until it became homogeneous. Subsequently, the catalyst was syringed into the reaction vessel and the solution was degassed by sparging with nitrogen while stirring for 15 minutes before sealing with parafilm. The reaction was stirred and irradiated using 34 W blue LED lamps (7 cm away, with cooling fan to keep the reaction temperature at 25 °C; 3 cm away without cooling fan to heated the reaction to approximately 50 °C; 1 cm away without cooling fan to heated the reaction to approximately 70 °C) for 4 hours. The reaction was quenched by exposure to air. 1,3-Benzodioxole (internal standard, 11 μL, 0.11 mmol, 1.0 equiv.) was added then the reaction mixture was analyzed by ^1H NMR.

4) Procedure for Cross-Coupling of Oxalates with Aryl Halides



To an oven-dried 40 mL vial equipped with a stir bar was added photocatalyst $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), methyl 4-bromobenzoate (86 mg, 0.40 mmol, 1.0 equiv.), 2-((1-(*tert*-butoxycarbonyl)piperidin-4-yl)oxy)-2-oxoacetic acid (142 mg, 0.52 mmol, 1.3 equiv.) and anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.). The vial was sealed and placed under nitrogen before THP (6 mL) and DMSO (2 mL) was added. To a separate vial was added $NiBr_2$•glyme (6.2 mg, 20 μmol, 0.05 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.4 mg, 20 μmol, 0.05 equiv.). The pre-catalyst vial was sealed, purged with nitrogen, dissolved in THP (4 mL) and then sonicated until it became homogeneous. Subsequently, the catalyst was syringed into the reaction vessel and the solution was degassed by sparging with nitrogen while stirring for 15 minutes before sealing with parafilm. The reaction mixture was preheated to 70 ^{o}C. Then the reaction was stirred and irradiated using 34 W blue LED lamps (1 cm away without cooling fan to heated the reaction to approximately 70 °C, see figure S1) for 4 hours. The reaction mixture was removed from the light, cooled to ambient temperature, diluted with water and EtOAc, and the aqueous layer was extracted with three portions of EtOAc. 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 alkyl-aryl product.

Reaction Setup A:

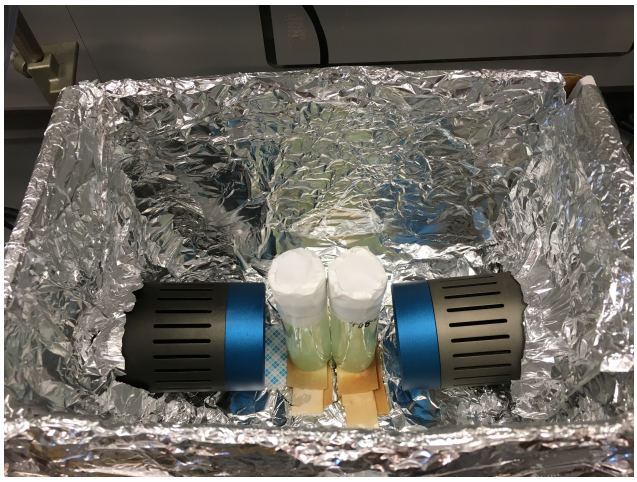


Figure S1. Two 34 W Kessil KSH150B Blue LED Grow Light 150 are positioned 1 cm away from the vials on both sides of the box covered with aluminum foil. Note: a lid is placed on top of the box after LED lamps are turned on. Reaction temperature is approximately 70 °C.

Reaction Setup B:

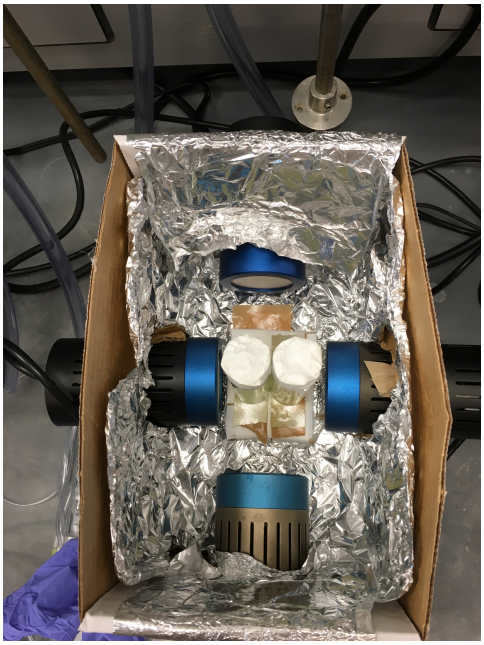


Figure S2. Top view. Four 34 W Kessil KSH150B Blue LED Grow Light 150 are positioned on all four sides of the box covered with aluminum foil.

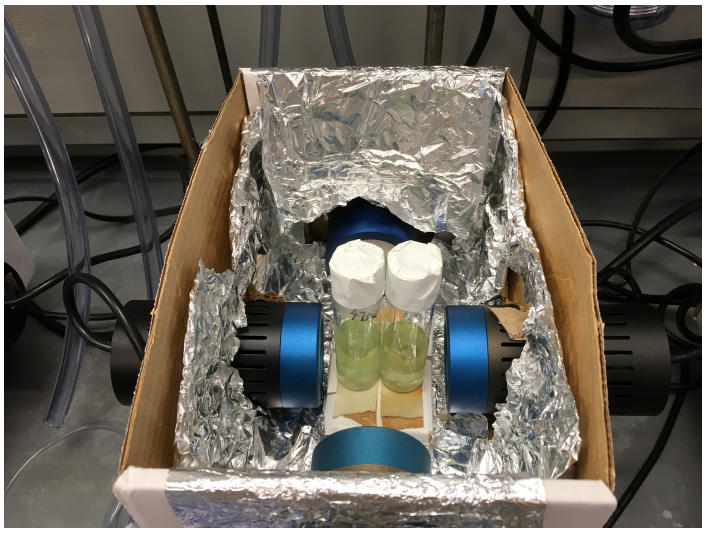
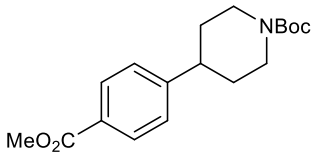


Figure S3. Four 34 W Kessil KSH150B Blue LED Grow Light 150 are positioned on all four sides of the box covered with aluminum foil. Lamps on the left and right are positioned 1 cm away from the vials and lamps on the front and back are positioned 7 cm away from the vials. Note: a lid is placed on top of the box after LED lamps are turned on. Reaction temperature is approximately 80 °C.

5) Experimental Data



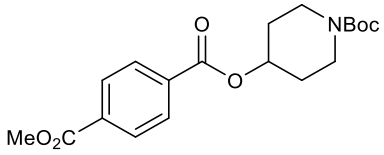
***tert*-Butyl 4-(4-(methoxycarbonyl)phenyl)piperidine-1-carboxylate (13)**

Prepared following the general procedure outlined above (reaction setup A) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (6.2 mg, 20 μmol, 0.05 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.4 mg, 20 μmol, 0.05 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-((1-(*tert*-butoxycarbonyl)piperidin-4-yl)oxy)-2-oxoacetic acid (142 mg, 0.52 mmol, 1.3 equiv.), methyl 4-bromobenzoate (86 mg, 0.40 mmol, 1.0 equiv.), THP (10.0 mL) and DMSO (2.0 mL). Purification by column chromatography (10-15% EtOAc/hexanes) provided the title compound (79 mg, 0.25 mmol, 62% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 4.25 (d, *J* = 12.1 Hz, 2H), 3.89 (s, 3H), 2.79 (t, *J* = 12.3 Hz, 2H), 2.69 (t, *J* = 12.1 Hz, 1H), 1.81 (d, *J* = 12.5 Hz, 2H), 1.66-1.58 (m, 2H), 1.47 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.09, 154.89, 151.15, 129.99, 128.42, 126.94, 79.65, 52.13, 44.33 (br), 42.91, 32.99, 28.59.

Spectroscopic data matches with previously reported data.[5]



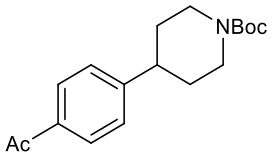
(ester by-product)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (brs, 4H), 5.21 (tt, *J* = 7.7, 3.7 Hz, 1H), 3.95 (s, 3H), 3.75 (brs, 2H), 3.41-3.29 (m, 2H), 2.03-1.92 (m, 2H), 1.83-1.73 (m, 2H), 1.48 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.40, 165.13, 154.89, 134.31, 134.12, 129.71, 129.68, 79.94, 70.98, 52.63, 43.77 (br), 30.76 (br), 28.58.

IR (film) ν_{max} 2930, 2862, 1720, 1694, 1423, 1366, 1272, 1239, 1170, 1116, 1104, 1019, 731 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{19}H_{25}NNaO_6$ ($[M+Na]^+$) 386.1574, found 386.1576.



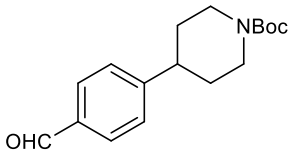
***tert*-Butyl 4-(4-acetylphenyl)piperidine-1-carboxylate (14)**

Prepared following the general procedure outlined above (reaction setup A) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (6.2 mg, 20 μmol, 0.05 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.4 mg, 20 μmol, 0.05 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-((1-(*tert*-butoxycarbonyl)piperidin-4-yl)oxy)-2-oxoacetic acid (142 mg, 0.52 mmol, 1.3 equiv.), 4-bromoacetophenone (80 mg, 0.40 mmol, 1.0 equiv.), THP (10.0 mL) and DMSO (2.0 mL). Purification by column chromatography (10-15% EtOAc/hexanes) provided the title compound (76 mg, 0.25 mmol, 63% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 4.25 (d, *J* = 12.5 Hz, 2H), 2.80 (t, *J* = 12.7 Hz, 2H), 2.70 (tt, *J* = 11.9, 3.1 Hz, 1H), 2.57 (s, 3H), 1.81 (d, *J* = 12.8 Hz, 2H), 1.66-1.58 (m, 2H), 1.47 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 197.82, 154.87, 151.40, 135.59, 128.80, 127.11, 79.65, 44.30 (br), 42.88, 32.94, 28.57, 26.68.

Spectroscopic data matches with previously reported data.[6]



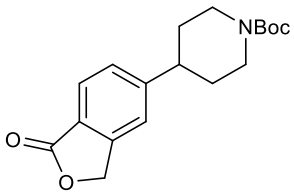
***tert*-Butyl 4-(4-formylphenyl)piperidine-1-carboxylate (15)**

Prepared following the general procedure outlined above (reaction setup B) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (6.2 mg, 20 μmol, 0.05 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.4 mg, 20 μmol, 0.05 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-((1-(*tert*-butoxycarbonyl)piperidin-4-yl)oxy)-2-oxoacetic acid (142 mg, 0.52 mmol, 1.3 equiv.), 4-bromobenzaldehyde (74 mg, 0.40 mmol, 1.0 equiv.), dioxane (10.0 mL) and DMSO (2.0 mL). Purification by column chromatography (10-20% EtOAc/hexanes) provided the title compound (71 mg, 0.24 mmol, 61% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 4.26 (d, *J* = 12.9 Hz, 2H), 2.81 (t, *J* = 12.1 Hz, 2H), 2.73 (tt, *J* = 12.2, 3.4 Hz, 1H). , 1.83 (d, *J* = 13.2 Hz, 2H), 1.68-1.60 (m, 2H), 1.48 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 192.03, 154.89, 153.01, 135.04, 130.25, 127.64, 79.74, 44.30 (br), 43.15, 32.93, 28.59.

Spectroscopic data matches with previously reported data.[7]



***tert*-Butyl 4-(1-oxo-1,3-dihydroisobenzofuran-5-yl)piperidine-1-carboxylate (16)**

Prepared following the general procedure outlined above (reaction setup A) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (6.2 mg, 20 μmol, 0.05 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.4 mg, 20 μmol, 0.05 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-((1-(*tert*-

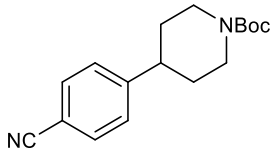
butoxycarbonyl)piperidin-4-yl)oxy)-2-oxoacetic acid (142 mg, 0.52 mmol, 1.3 equiv.), 5-bromoisobenzofuran-1(3*H*)-one (85 mg, 0.40 mmol, 1.0 equiv.), dioxane (10.0 mL) and DMSO (2.0 mL). Purification by column chromatography (30-50% EtOAc/hexanes) provided the title compound (72 mg, 0.23 mmol, 56% yield) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.31 (s, 1H), 5.29 (s, 2H), 4.27 (brs, 2H), 2.85-2.76 (m, 3H), 1.85 (d, *J* = 13.0 Hz, 2H), 1.69-1.62 (m, 2H), 1.48 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 171.09, 154.88, 152.99, 147.39, 128.43, 126.07, 124.25, 120.29, 79.85, 69.66, 46.94 (br), 43.39, 33.18, 28.61.

IR (film) ν_{max} 2929, 2856, 1765, 1685, 1423, 1165, 1045, 1016, 775 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{18}H_{23}NNaO_4$ ($[M+Na]^+$) 340.1519, found 340.1521.



***tert*-Butyl 4-(4-cyanophenyl)piperidine-1-carboxylate (17)**

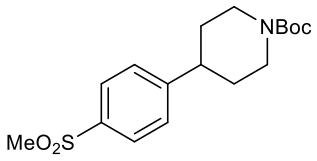
Prepared following the general procedure outlined above (reaction setup A) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (6.2 mg, 20 μmol, 0.05 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.4 mg, 20 μmol, 0.05 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-((1-(*tert*-butoxycarbonyl)piperidin-4-yl)oxy)-2-oxoacetic acid (142 mg, 0.52 mmol, 1.3 equiv.), 4-bromobenzonitrile (73 mg, 0.40 mmol, 1.0 equiv.), dioxane (10.0 mL) and DMSO (2.0 mL). Purification by column chromatography (5-10% EtOAc/toluene) provided the title compound (69 mg, 0.24 mmol, 60% yield) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 4.27 (brs, 2H), 2.80 (t, *J* = 12.5 Hz, 2H), 2.71 (tt, *J* = 12.2, 3.5 Hz, 1H), 1.81 (d, *J* = 13.1 Hz,

2H), 1.64-1.56 (m, 2H), 1.48 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.88, 151.26, 132.56, 127.78, 119.08, 110.39, 79.83, 44.18 (br), 43.04, 32.87, 28.60.

Spectroscopic data matches with previously reported data.[8]



***tert*-Butyl 4-(4-(methylsulfonyl)phenyl)piperidine-1-carboxylate (18)**

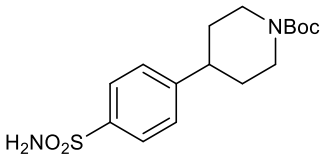
Prepared following the general procedure outlined above (reaction setup B) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (6.2 mg, 20 μmol, 0.05 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.4 mg, 20 μmol, 0.05 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-((1-(*tert*-butoxycarbonyl)piperidin-4-yl)oxy)-2-oxoacetic acid (142 mg, 0.52 mmol, 1.3 equiv.), 1-bromo-4-(methylsulfonyl)benzene (94 mg, 0.40 mmol, 1.0 equiv.), dioxane (10.0 mL) and DMSO (2.0 mL). Purification by column chromatography (15-25% EtOAc/toluene) provided the title compound (95 mg, 0.28 mmol, 70% yield) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.3 Hz, 2H), 4.28 (d, J = 12.3 Hz, 2H), 3.05 (s, 3H), 2.86-2.69 (m, 3H), 1.83 (d, J = 13.3 Hz, 2H), 1.65 (td, J = 12.7, 4.2 Hz, 2H), 1.48 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.89, 152.27, 138.71, 127.98, 127.86, 79.85, 44.70, 44.27 (br), 42.95, 32.98, 28.62.

IR (film) ν_{max} 2925, 2854, 1684, 1598, 1421, 1365, 1305, 1232, 1149, 1126, 1014, 957, 766 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{17}H_{25}NNaO_4S$ ($[M+Na]^+$) 362.1397, found 362.1399.



***tert*-Butyl 4-(4-sulfamoylphenyl)piperidine-1-carboxylate (19)**

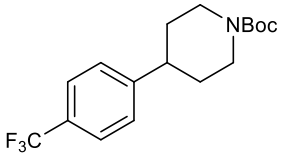
Prepared following the general procedure outlined above (reaction setup B) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (6.2 mg, 20 μmol, 0.05 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.4 mg, 20 μmol, 0.05 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-((1-(*tert*-butoxycarbonyl)piperidin-4-yl)oxy)-2-oxoacetic acid (142 mg, 0.52 mmol, 1.3 equiv.), 4-bromobenzenesulfonamide (94 mg, 0.40 mmol, 1.0 equiv.), THP (10.0 mL) and DMSO (2.0 mL). Purification by column chromatography (50-60% EtOAc/hexanes) provided the title compound (86 mg, 0.25 mmol, 63% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 4.91 (brs, 2H), 4.26 (d, *J* = 12.8 Hz, 2H), 2.80 (t, *J* = 12.4 Hz, 2H), 2.73 (tt, *J* = 12.1, 3.4 Hz, 1H), 1.82 (d, *J* = 13.2 Hz, 2H), 1.65-1.59 (m, 2H), 1.48 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.90, 151.26, 140.04, 127.74, 126.92, 79.84, 42.85, 33.00, 28.61.

IR (film) ν_{max} 3248, 2928, 2854, 1665, 1429, 1322, 1235, 1158, 1128, 1013, 734 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{16}H_{24}N_2NaO_4S$ ($[M+Na]^+$) 363.1349, found 363.1346.



***tert*-Butyl 4-(4-(trifluoromethyl)phenyl)piperidine-1-carboxylate (20)**

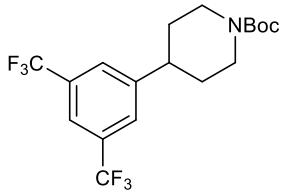
Prepared following the general procedure outlined above (reaction setup A) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (6.2 mg, 20 μmol,

0.05 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.4 mg, 20 μmol, 0.05 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-((1-(*tert*-butoxycarbonyl)piperidin-4-yl)oxy)-2-oxoacetic acid (142 mg, 0.52 mmol, 1.3 equiv.), 1-bromo-4-(trifluoromethyl)benzene (90 mg, 0.40 mmol, 1.0 equiv.), dioxane (10.0 mL) and DMSO (2.0 mL). Purification by column chromatography (5-15% EtOAc/hexanes) provided the title compound (86 mg, 0.26 mmol, 65% yield) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 4.26 (d, J = 13.1 Hz, 2H), 2.81 (t, J = 13.9 Hz, 2H), 2.71 (tt, J = 12.2, 3.5 Hz, 1H), 1.82 (d, J = 13.3 Hz, 2H), 1.66-1.58 (m, 2H), 1.48 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.92, 149.85 (q, $J_{C,F}$ = 1.4 Hz), 128.80 (q, $J_{C,F}$ = 32.4 Hz), 127.27, 125.59 (q, $J_{C,F}$ = 4.0 Hz), 124.36 (q, $J_{C,F}$ = 271.8 Hz), 79.72, 44.33 (br), 42.78, 33.06, 28.60.

Spectroscopic data matches with previously reported data.[7]



***tert*-Butyl 4-(3,5-bis(trifluoromethyl)phenyl)piperidine-1-carboxylate (21)**

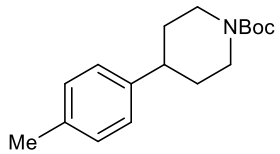
Prepared following the general procedure outlined above (reaction setup A) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (6.2 mg, 20 μmol, 0.05 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.4 mg, 20 μmol, 0.05 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-((1-(*tert*-butoxycarbonyl)piperidin-4-yl)oxy)-2-oxoacetic acid (142 mg, 0.52 mmol, 1.3 equiv.), 1,3-bis(trifluoromethyl)-5-bromobenzene (117 mg, 0.40 mmol, 1.0 equiv.), THP (10.0 mL) and DMSO (2.0 mL). Purification by column chromatography (5-10% EtOAc/hexanes) provided the title compound (91 mg, 0.23 mmol, 57% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.65 (s, 2H), 4.30 (brs, 2H), 2.83-2.75 (m, 3H), 1.87 (d, J = 12.9 Hz, 2H), 1.70-1.62 (m, 2H), 1.49 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.82, 148.20, 131.90 (q, $J_{C,F}$ = 33.1 Hz), 127.22 (q, $J_{C,F}$ = 3.5 Hz), 123.50 (q, $J_{C,F}$ = 272.7 Hz), 120.64 (quintet, $J_{C,F}$ = 4.1 Hz), 79.94, 42.67, 33.00, 28.60.
^{19}F NMR (282 MHz, $CDCl_3$) δ -62.83.

IR (film) ν_{max} 2934, 2857, 1692, 1425, 1365, 1277, 1169, 1131, 932, 894, 683 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{18}H_{21}F_6NNaO_2$ ($[M+Na]^+$) 420.1369, found 420.1366.



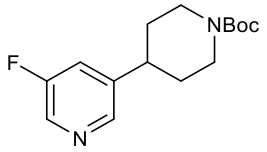
***tert*-Butyl 4-(*p*-tolyl)piperidine-1-carboxylate (22)**
Prepared following the general procedure outlined above (reaction setup A) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (12.3 mg, 40 μmol, 0.10 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (10.8 mg, 40 μmol, 0.10 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-((1-(*tert*-butoxycarbonyl)piperidin-4-yl)oxy)-2-oxoacetic acid (142 mg, 0.52 mmol, 1.3 equiv.), 1-bromo-4-methylbenzene (68 mg, 0.40 mmol, 1.0 equiv.), dioxane (8.0 mL) and DMSO (2.0 mL). Purification by column chromatography (0-5% EtOAc/toluene) provided the title compound (46 mg, 0.17 mmol, 42% yield) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H), 4.24 (brs, 2H), 2.79 (brs, 2H), 2.60 (tt, J = 12.1, 3.2 Hz, 1H), 2.32 (s, 3H), 1.80 (d, J = 12.9 Hz, 2H), 1.67-1.58 (m, 2H), 1.48 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 155.03, 142.99, 136.00, 129.32, 126.78, 79.55, 42.45,

33.47, 28.64, 21.14.

Spectroscopic data matches with previously reported data.[7]



***tert*-Butyl 4-(5-fluoropyridin-3-yl)piperidine-1-carboxylate (23)**

Prepared following the general procedure outlined above (reaction setup A) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (12.3 mg, 40 μmol, 0.10 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (10.8 mg, 40 μmol, 0.10 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-((1-(*tert*-butoxycarbonyl)piperidin-4-yl)oxy)-2-oxoacetic acid (142 mg, 0.52 mmol, 1.3 equiv.), 3-bromo-5-fluoropyridine (70 mg, 0.40 mmol, 1.0 equiv.), THP (10.0 mL) and DMSO (2.0 mL). Purification by column chromatography (40-60% EtOAc/hexanes) provided the title compound (64 mg, 0.23 mmol, 57% yield) as a yellow oil.

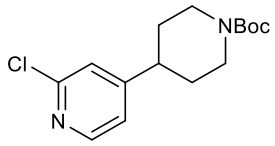
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, J = 2.6 Hz, 1H), 8.31 (s, 1H), 7.26 (d, J = 9.5 Hz, 1H), 4.26 (brs, 2H), 2.80-2.68 (m, 3H), 1.84 (d, J = 12.8 Hz, 2H), 1.64-1.55 (m, 2H), 1.47 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.81 (d, $J_{C,F}$ = 256.9 Hz), 154.81, 144.41 (d, $J_{C,F}$ = 4.1 Hz), 143.15 (d, $J_{C,F}$ = 3.5 Hz), 135.93 (d, $J_{C,F}$ = 23.8 Hz), 121.43 (d, $J_{C,F}$ = 18.0 Hz), 79.88, 46.91 (br), 39.90, 32.83, 28.57.

^{19}F NMR (282 MHz, $CDCl_3$) δ -126.48.

IR (film) ν_{max} 2931, 2856, 1688, 1600, 1579, 1427, 1366, 1240, 1163, 1025, 960, 881, 764, 709 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{15}H_{22}FN_2O_2$ ($[M+H]^+$) 281.1660, found 281.1661.



***tert*-Butyl 4-(2-chloropyridin-4-yl)piperidine-1-carboxylate (24)**

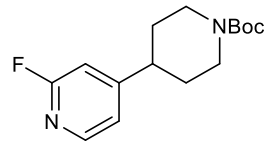
Prepared following the general procedure outlined above (reaction setup A) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (6.2 mg, 20 μmol, 0.05 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.4 mg, 20 μmol, 0.05 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-((1-(*tert*-butoxycarbonyl)piperidin-4-yl)oxy)-2-oxoacetic acid (142 mg, 0.52 mmol, 1.3 equiv.), 2-chloro-4-bromopyridine (77 mg, 0.40 mmol, 1.0 equiv.), THP (10.0 mL) and DMSO (2.0 mL). Purification by column chromatography (20-30% EtOAc/hexanes) provided the title compound (66 mg, 0.22 mmol, 56% yield) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 5.2 Hz, 1H), 7.15 (s, 1H), 7.04 (dd, *J* = 5.1, 1.1 Hz, 1H), 4.24 (brs, 2H), 2.78 (brs, 2H), 2.64 (tt, *J* = 12.2, 3.5 Hz, 1H), 1.81 (d, *J* = 12.9 Hz, 2H), 1.61-1.53 (m, 2H), 1.46 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 157.85, 154.74, 151.92, 149.86, 122.79, 121.17, 79.85, 41.95, 32.22, 28.54.

IR (film) ν_{max} 2927, 2854, 1686, 1591, 1543, 1421, 1364, 1232, 1162, 1116, 1087, 1020, 910, 768, 738 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{15}H_{22}ClN_2O_2$ ($[M+H]^+$) 297.1364, found 297.1364.



***tert*-Butyl 4-(2-fluoropyridin-4-yl)piperidine-1-carboxylate (25)**

Prepared following the general procedure outlined above (reaction setup A) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (6.2 mg, 20 μmol,

0.05 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.4 mg, 20 μmol, 0.05 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-((1-(*tert*-butoxycarbonyl)piperidin-4-yl)oxy)-2-oxoacetic acid (142 mg, 0.52 mmol, 1.3 equiv.), 4-bromo-2-fluoropyridine (71 mg, 0.40 mmol, 1.0 equiv.), THP (10.0 mL) and DMSO (2.0 mL). Purification by column chromatography (20-40% EtOAc/hexanes) provided the title compound (69 mg, 0.25 mmol, 62% yield) as a yellow oil.

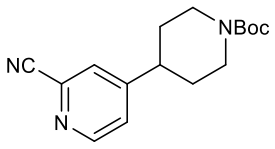
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, J = 5.2 Hz, 1H), 7.00 (d, J = 5.1 Hz, 1H), 6.73 (s, 1H), 4.23 (brs, 2H), 2.78 (t, J = 12.3 Hz, 2H), 2.68 (tt, J = 12.1, 3.3 Hz, 1H), 1.82 (d, J = 13.0 Hz, 2H), 1.64-1.53 (m, 2H), 1.45 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.25 (d, $J_{C,F}$ = 238.5 Hz), 160.54 (d, $J_{C,F}$ = 7.9 Hz), 154.76, 147.73 (d, $J_{C,F}$ = 15.5 Hz), 120.13 (d, $J_{C,F}$= 4.3 Hz), 107.67 (d, $J_{C,F}$ = 37.1 Hz), 79.83, 43.82 (br), 42.00, 32.24, 28.53.

^{19}F NMR (282 MHz, $CDCl_3$) δ -68.38.

IR (film) ν_{max} 2930, 2857, 1688, 1610, 1567, 1415, 1366, 1278, 1244, 1165, 1124, 1023, 952, 871, 772 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{15}H_{22}FN_2O_2$ ($[M+H]^+$) 281.1660, found 281.1658.



***tert*-Butyl 4-(2-cyanopyridin-4-yl)piperidine-1-carboxylate (26)**

Prepared following the general procedure outlined above (reaction setup A) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (6.2 mg, 20 μmol, 0.05 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.4 mg, 20 μmol, 0.05 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-((1-(*tert*-butoxycarbonyl)piperidin-4-yl)oxy)-2-oxoacetic acid (142 mg, 0.52 mmol, 1.3 equiv.), 4-

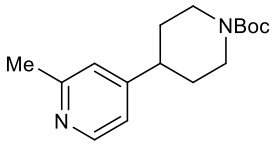
bromo-2-cyanopyridine (73 mg, 0.40 mmol, 1.0 equiv.), THP (10.0 mL) and DMSO (2.0 mL). Purification by column chromatography (40-50% EtOAc/hexanes) provided the title compound (61 mg, 0.21 mmol, 53% yield) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (d, *J* = 5.1 Hz, 1H), 7.54 (s, 1H), 7.35-7.34 (m, 1H), 4.27 (d, *J* = 12.1 Hz, 2H), 2.80 (t, *J* = 12.7 Hz, 2H), 2.72 (tt, *J* = 8.9, 5.2 Hz, 1H), 1.84 (d, *J* = 12.9 Hz, 2H), 1.64-1.55 (m, 2H), 1.47 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 156.11, 154.71, 151.33, 134.29, 127.35, 125.52, 117.40, 80.01, 43.89 (br), 41.89, 32.15, 28.55.

IR (film) ν_{max} 2927, 2855, 2237, 1684, 1596, 1420, 1365, 1241, 1162, 1123, 1021, 931, 867, 769 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{16}H_{22}N_3O_2$ ($[M+H]^+$) 288.1707, found 288.1710.



***tert*-Butyl 4-(2-methylpyridin-4-yl)piperidine-1-carboxylate (27)**

Prepared following the general procedure outlined above (reaction setup B) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (6.2 mg, 20 μmol, 0.05 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.4 mg, 20 μmol, 0.05 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-((1-(*tert*-butoxycarbonyl)piperidin-4-yl)oxy)-2-oxoacetic acid (142 mg, 0.52 mmol, 1.3 equiv.), 4-bromo-2-methylpyridine (69 mg, 0.40 mmol, 1.0 equiv.), THP (10.0 mL) and DMSO (2.0 mL). Purification by column chromatography (200% EtOAc/hexanes) provided the title compound (68 mg, 0.25 mmol, 62% yield) as a yellow oil.

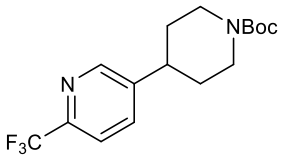
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, *J* = 5.2 Hz, 1H), 7.00 (s, 1H), 6.94 (d, *J* = 5.2 Hz, 1H), 4.23 (brs, 2H), 2.78 (brs, 2H), 2.60 (tt, *J* = 12.1, 3.4 Hz, 1H), 2.53 (s, 3H), 1.79 (d, *J*

= 12.8 Hz, 2H), 1.66-1.52 (m, 2H), 1.46 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 158.29, 155.39, 154.82, 148.80, 122.07, 119.65, 79.73, 42.14, 32.36, 28.56, 24.25.

IR (film) ν_{max} 2926, 2854, 1687, 1605, 1420, 1365, 1240, 1163, 1122, 1024, 934, 840, 769 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{16}H_{25}N_2O_2$ ($[M+H]^+$) 277.1911, found 277.1908.



***tert*-Butyl 4-(6-(trifluoromethyl)pyridin-3-yl)piperidine-1-carboxylate (28)**

Prepared following the general procedure outlined above (reaction setup A) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (6.2 mg, 20 μmol, 0.05 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.4 mg, 20 μmol, 0.05 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-((1-(*tert*-butoxycarbonyl)piperidin-4-yl)oxy)-2-oxoacetic acid (142 mg, 0.52 mmol, 1.3 equiv.), 5-bromo-2(trifluoromethyl)pyridine (90 mg, 0.40 mmol, 1.0 equiv.), THP (10.0 mL) and DMSO (2.0 mL). Purification by column chromatography (20-30% EtOAc/hexanes) provided the title compound (80 mg, 0.24 mmol, 61% yield) as a yellow oil.

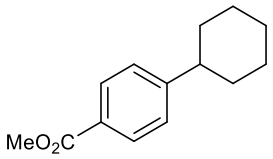
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, J = 1.6 Hz, 1H), 7.67 (dd, J = 8.1, 1.9 Hz, 1H), 7.62 (d, J = 8.1 Hz, 1H), 4.26 (brs, 2H), 2.84-2.74 (m, 3H), 1.84 (d, J = 13.2 Hz, 2H), 1.67-1.59 (m, 2H), 1.46 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.81, 149.26, 146.54 (q, $J_{C,F}$ = 34.8 Hz), 144.25 (q, $J_{C,F}$ = 1.0 Hz), 135.41, 121.70 (q, $J_{C,F}$ = 273.8 Hz), 120.48 (q, $J_{C,F}$ = 2.9 Hz), 79.89, 44.26 (br), 40.25, 32.74, 28.55.

^{19}F NMR (282 MHz, $CDCl_3$) δ -67.76.

IR (film) ν_{max} 2932, 2856, 1686, 1423, 1336, 1234, 1164, 1133, 1086, 1014, 850, 767, 685 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{16}H_{22}F_3N_2O_2$ ($[M+H]^+$) 331.1628, found 331.1628.



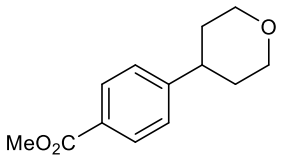
Methyl 4-cyclohexylbenzoate (29)

Prepared following the general procedure outlined above (reaction setup A) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (12.3 mg, 40 μmol, 0.10 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (10.8 mg, 40 μmol, 0.10 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-(cyclohexyloxy)-2-oxoacetic acid (90 mg, 0.52 mmol, 1.3 equiv.), methyl 4-bromobenzoate (86 mg, 0.40 mmol, 1.0 equiv.), dioxane (8.0 mL) and DMSO (2.0 mL). Purification by column chromatography (0-5% EtOAc/hexanes) provided the title compound (39 mg, 0.18 mmol, 45% yield) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 3H), 2.62-2.49 (m, 1H), 1.92-1.81 (m, 4H), 1.78-1.74 (m, 1H), 1.47-1.35 (m, 4H), 1.31-1.27 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.35, 153.62, 129.82, 127.86, 127.01, 52.11, 44.84, 34.29, 26.89, 26.19.

Spectroscopic data matches with previously reported data.[5]



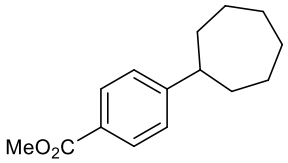
Methyl 4-(tetrahydro-2*H*-pyran-4-yl)benzoate (30)

Prepared following the general procedure outlined above (reaction setup A) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (6.2 mg, 20 μmol, 0.05 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.4 mg, 20 μmol, 0.05 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-oxo-2-((tetrahydro-2*H*-pyran-4-yl)oxy)acetic acid (91 mg, 0.52 mmol, 1.3 equiv.), methyl 4-bromobenzoate (86 mg, 0.40 mmol, 1.0 equiv.), dioxane (10.0 mL) and DMSO (2.0 mL). Purification by column chromatography (10-15% EtOAc/hexanes) provided the title compound (47 mg, 0.21 mmol, 53% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 7.7 Hz, 2H), 4.09 (d, *J* = 8.2 Hz, 2H), 3.91 (s, 3H), 3.54 (t, *J* = 11.4 Hz, 2H), 2.84-2.80 (m, 1H), 1.86-1.71 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.16, 151.22, 130.05, 128.44, 126.94, 68.37, 52.19, 41.81, 33.73.

Spectroscopic data matches with previously reported data.[5]



Methyl 4-cycloheptylbenzoate (31)

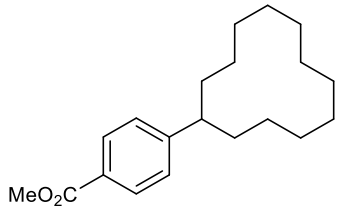
Prepared following the general procedure outlined above (reaction setup B) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (6.2 mg, 20 μmol, 0.05 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.4 mg, 20 μmol, 0.05 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-(cycloheptyloxy)-2-

oxoacetic acid (97 mg, 0.52 mmol, 1.3 equiv.), methyl 4-bromobenzoate (86 mg, 0.40 mmol, 1.0 equiv.), dioxane (8.0 mL) and DMSO (2.0 mL). Purification by column chromatography (0-5% EtOAc/hexanes) followed by reverse phase chromatography (MeCN in H_2O) provided the title compound (78 mg, 0.24 mmol, 61% yield) as a a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 3.0 Hz, 2H), 3.92 (s, 3H), 2.74 (tt, *J* = 10.5, 3.5 Hz, 1H), 1.96-1.87 (m, 2H), 1.87-1.80 (m, 2H), 1.78-1.62 (m, 6H), 1.58-1.53 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.35, 155.52, 129.88, 127.61, 126.85, 52.08, 47.22, 36.64, 28.01, 27.36.

Spectroscopic data matches with previously reported data.[9]



Methyl 4-cyclododecylbenzoate (32)

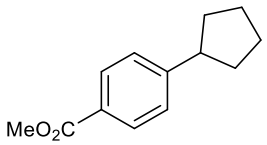
Prepared following the general procedure outlined above (reaction setup A) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (12.3 mg, 40 μmol, 0.10 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (10.8 mg, 40 μmol, 0.10 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-(cyclododecyloxy)-2-oxoacetic acid (133 mg, 0.52 mmol, 1.3 equiv.), methyl 4-bromobenzoate (86 mg, 0.40 mmol, 1.0 equiv.), dioxane (8.0 mL) and DMSO (2.0 mL). Purification by column chromatography (0-10% EtOAc/hexanes) provided the title compound (75 mg, 0.25 mmol, 62% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.90 (s, 3H), 2.84-2.79 (m, 1H), 1.86-1.77 (m, 2H), 1.52-1.26 (m, 20H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.37, 153.41, 129.70, 127.82, 52.10, 40.05, 31.47, 24.04, 23.94, 23.56, 23.34, 22.74.

IR (film) ν_{max} 2932, 2861, 1723, 1610, 1470, 1435, 1277, 1180, 1111, 1102, 772, 708 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{20}H_{31}O_2$ ($[M+H]^+$) 303.2319, found 303.2317.



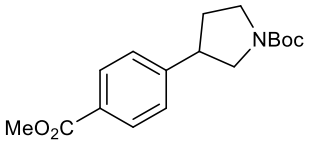
Methyl 4-cyclopentylbenzoate (33)

Prepared following the general procedure outlined above (reaction setup A) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (6.2 mg, 20 μmol, 0.05 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.4 mg, 20 μmol, 0.05 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-(cyclopentyloxy)-2-oxoacetic acid (82 mg, 0.52 mmol, 1.3 equiv.), methyl 4-bromobenzoate (86 mg, 0.40 mmol, 1.0 equiv.), dioxane (10.0 mL) and DMSO (2.5 mL). Purification by column chromatography (0-5% EtOAc/hexanes) followed by reverse phase chromatography (MeCN in H_2O) provided the title compound (51 mg, 0.25 mmol, 62% yield) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 3.90 (s, 3H), 3.09-2.96 (m, 1H), 2.12-2.06 (m, 2H), 1.86-1.77 (m, 2H), 1.74-1.68 (m, 2H), 1.64-1.59 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.34, 152.35, 129.74, 127.74, 127.26, 52.10, 46.12, 34.65, 25.71.

Spectroscopic data matches with previously reported data.[5]



(±)-*tert*-Butyl 3-(4-(methoxycarbonyl)phenyl)pyrrolidine-1-carboxylate (34)

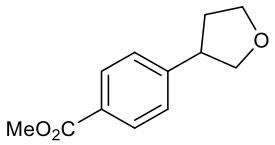
Prepared following the general procedure outlined above (reaction setup A) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (12.3 mg, 40 μmol, 0.10 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (10.8 mg, 40 μmol, 0.10 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-((1-(*tert*-butoxycarbonyl)pyrrolidin-3-yl)oxy)-2-oxoacetic acid (135 mg, 0.52 mmol, 1.3 equiv.), methyl 4-bromobenzoate (86 mg, 0.40 mmol, 1.0 equiv.), dioxane (12.0 mL) and DMSO (2.4 mL). Purification by column chromatography (15-25% EtOAc/hexanes) provided the title compound (78 mg, 0.26 mmol, 64% yield, rotameric) as a colorless oil.

1H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.90 (s, 3H), 3.85 (t, *J* = 7.3 Hz, 0.5H), 3.80-3.77 (m, 0.5H), 3.64 (t, *J* = 8.5 Hz, 0.5H), 3.55 (t, *J* = 8.2 Hz, 0.5H), 3.47-3.25 (m, 3H), 2.33-2.21 (m, 1H), 2.06-1.92 (m, 1H), 1.47&1.46 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.95, 154.55, 154.52, 147.01, 146.93, 130.00, 128.81, 128.77, 127.20, 79.49, 79.45, 52.32, 52.18, 51.66, 45.92, 45.64, 44.33, 43.40, 33.30, 32.42, 28.63.

IR (film) ν_{max} 2975, 2878, 1722, 1693, 1402, 1279, 1169, 1111, 770 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{17}H_{24}NO_4$ ($[M+H]^+$) 306.1700, found 306.1691.



(±)-Methyl 4-(tetrahydrofuran-3-yl)benzoate (35)

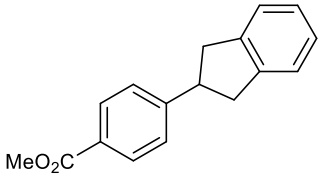
Prepared following the general procedure outlined above (reaction setup B) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (12.3 mg, 40 μmol, 0.10 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (10.8 mg, 40 μmol, 0.10 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-oxo-2-((tetrahydrofuran-3-yl)oxy)acetic acid (83 mg, 0.52 mmol, 1.3 equiv.), methyl 4-bromobenzoate (86 mg, 0.40 mmol, 1.0 equiv.), THP (12.0 mL) and DMSO (2.0 mL). Purification by column chromatography (15-25% EtOAc/hexanes) provided the title compound (43 mg, 0.21 mmol, 52% yield) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 4.14 (t, *J* = 8.0 Hz, 1H), 4.08 (td, *J* = 8.4, 4.7 Hz, 1H), 3.93 (t, *J* = 7.7 Hz, 1H), 3.91 (s, 3H), 3.77-3.74 (m, 1H), 3.49-3.43 (m, 1H), 2.45-2.35 (m, 1H), 2.05-1.97 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.08, 148.54, 130.06, 128.58, 127.40, 74.58, 68.63, 52.21, 45.12, 34.75.

IR (film) ν_{max} 2951, 2861, 1720, 1611, 1435, 1278, 1182, 1110, 770, 707 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{15}O_3$ ($[M+H]^+$) 207.1016, found 207.1011.



Methyl 4-(2,3-dihydro-1*H*-inden-2-yl)benzoate (36)

Prepared following the general procedure outlined above (reaction setup A) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (6.2 mg, 20 μmol,

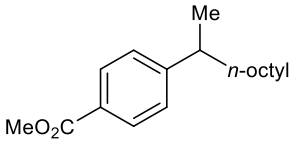
0.05 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.4 mg, 20 μmol, 0.05 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-((2,3-dihydro-1*H*-inden-2-yl)oxy)-2-oxoacetic acid (107 mg, 0.52 mmol, 1.3 equiv.), methyl 4-bromobenzoate (86 mg, 0.40 mmol, 1.0 equiv.), dioxane (10.0 mL) and DMSO (2.0 mL). Purification by column chromatography (0-10% EtOAc/hexanes) provided the title compound (79 mg, 0.31 mmol, 78% yield) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.26-7.24 (m, 2H), 7.22-7.18 (m, 2H), 3.91 (s, 3H), 3.78-3.71 (m, 1H), 3.38 (dd, *J* = 15.4, 8.3 Hz, 2H), 3.09 (dd, *J* = 15.5, 8.6 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.21, 151.14, 142.67, 129.96, 128.28, 127.22, 126.75, 124.50, 52.17, 45.48, 40.87.

IR (film) ν_{max} 2946, 2845, 1721, 1611, 1435, 1278, 1208, 744 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{17}H_{17}O_2$ ($[M+H]^+$) 253.1223, found 253.1226.



(±)-Methyl 4-(decan-2-yl)benzoate (37)

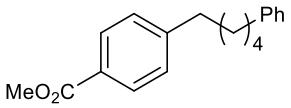
Prepared following the general procedure outlined above (reaction setup A) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (6.2 mg, 20 μmol, 0.05 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.4 mg, 20 μmol, 0.05 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-(decan-2-yloxy)-2-oxoacetic acid (120 mg, 0.52 mmol, 1.3 equiv.), methyl 4-bromobenzoate (86 mg, 0.40 mmol, 1.0 equiv.), dioxane (10.0 mL) and DMSO (2.5 mL). Purification by column chromatography (0-5% EtOAc/hexanes) provided the title compound (70 mg, 0.25 mmol, 63% yield) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 3.90 (s, 3H), 2.77-2.70 (m, 1H), 1.60-1.51 (m, 2H), 1.30-1.18 (m, 15H), 0.86 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.35, 153.67, 129.82, 127.89, 127.18, 52.10, 40.22, 38.32, 32.01, 29.81, 29.64, 29.42, 27.77, 22.80, 22.22, 14.26.

IR (film) ν_{max} 2925, 2855, 1725, 1611, 1435, 1277, 1180, 1111, 775, 708 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{18}H_{29}O_2$ ($[M+H]^+$) 277.2162, found 277.2164.



Methyl 4-(5-phenylpentyl)benzoate (38)

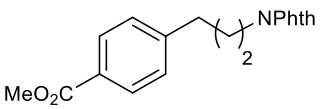
Prepared following the general procedure outlined above (reaction setup B) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (6.2 mg, 20 μmol, 0.05 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.4 mg, 20 μmol, 0.05 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-oxo-2-((5-phenylpentyl)oxy)acetic acid (123 mg, 0.52 mmol, 1.3 equiv.), methyl 4-bromobenzoate (86 mg, 0.40 mmol, 1.0 equiv.), dioxane (8.0 mL) and DMSO (2.0 mL). Purification by column chromatography (0-5% EtOAc/hexanes) provided the title compound (47 mg, 0.15 mmol, 37% yield) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.30-7.27 (m, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.20-7.15 (m, 3H), 3.90 (s, 3H), 2.65 (t, *J* = 7.8 Hz, 2H), 2.60 (t, *J* = 7.8 Hz, 2H), 1.70-1.62 (m, 4H), 1.43-1.35 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.34, 148.46, 142.76, 129.78, 128.57, 128.52, 128.40, 127.79, 125.79, 52.12, 36.05, 35.98, 31.45, 31.16, 29.00.

IR (film) ν_{max} 2930, 2856, 1720, 1610, 1435, 1276, 1178, 1107, 1020, 748, 699 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{19}H_{23}O_2$ ($[M+H]^+$) 283.1693, found 283.1692.



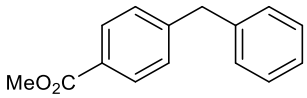
Methyl 4-(3-(1,3-dioxoisoindolin-2-yl)propyl)benzoate (39)

Prepared following the general procedure outlined above (reaction setup A) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (6.2 mg, 20 μmol, 0.05 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.4 mg, 20 μmol, 0.05 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-(3-(1,3-dioxoisoindolin-2-yl)propoxy)-2-oxoacetic acid (144 mg, 0.52 mmol, 1.3 equiv.), methyl 4-bromobenzoate (86 mg, 0.40 mmol, 1.0 equiv.), dioxane (10.0 mL) and DMSO (2.0 mL). Purification by column chromatography (25-40% EtOAc/hexanes) provided the title compound (65 mg, 0.20 mmol, 50% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.82 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.70 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 3.88 (s, 3H), 3.76 (d, *J* = 7.1 Hz, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.09-2.03 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.53, 167.17, 146.64, 134.07, 132.18, 129.89, 128.47, 128.08, 123.35, 52.12, 37.80, 33.37, 29.62.

Spectroscopic data matches with previously reported data.[10]



Methyl 4-benzylbenzoate (40)

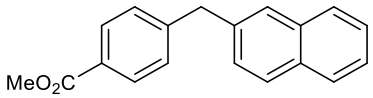
Prepared following the general procedure outlined above (the reaction vial was placed 7 cm away from the blue LED lamp, with cooling fan) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (6.2 mg, 20 μmol, 0.05 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.4 mg, 20 μmol, 0.05 equiv.), anhydrous cesium

hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-(benzyloxy)-2-oxoacetic acid (94 mg, 0.52 mmol, 1.3 equiv.), methyl 4-bromobenzoate (86 mg, 0.40 mmol, 1.0 equiv.), dioxane (12.0 mL). The reaction was allowed to run for 15 hours. Purification by column chromatography (0-5% EtOAc/hexanes) provided the title compound (86 mg, 0.38 mmol, 95% yield) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.27-7.20 (m, 3H), 7.18 (d, *J* = 7.3 Hz, 2H), 4.03 (s, 2H), 3.90 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.21, 146.65, 140.25, 129.96, 129.08, 128.74, 128.22, 126.51, 52.17, 42.06.

Spectroscopic data matches with previously reported data.[11]



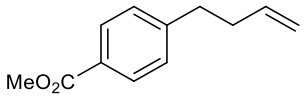
Methyl 4-(naphthalen-2-ylmethyl)benzoate (41)

Prepared following the general procedure outlined above (the reaction vial was placed 3 cm away from the blue LED lamp, without cooling fan) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (6.2 mg, 20 μmol, 0.05 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.4 mg, 20 μmol, 0.05 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-(naphthalen-2-ylmethoxy)-2-oxoacetic acid (120 mg, 0.52 mmol, 1.3 equiv.), methyl 4-bromobenzoate (86 mg, 0.40 mmol, 1.0 equiv.), dioxane (16.0 mL). The reaction was allowed to run for 15 hours. Purification by column chromatography (10-20% EtOAc/hexanes) provided the title compound (101 mg, 0.36 mmol, 91% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.65 (s, 1H), 7.50-7.45 (m, 2H), 7.31 (t, *J* = 7.2 Hz, 3H), 4.20 (s, 2H), 3.92 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.13, 146.45, 137.67, 133.66, 132.24, 129.94, 129.14, 128.37, 128.26, 127.74, 127.64, 127.52, 127.35, 126.23, 125.65, 52.11, 42.15.

Spectroscopic data matches with previously reported data.[12]



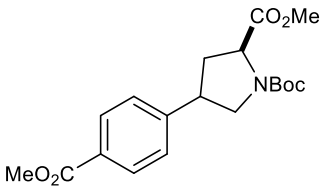
Methyl 4-(but-3-en-1-yl)benzoate (42)

Prepared following the general procedure outlined above (reaction setup A) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (6.2 mg, 20 μmol, 0.05 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.4 mg, 20 μmol, 0.05 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-(cyclopropylmethoxy)-2-oxoacetic acid (75 mg, 0.52 mmol, 1.3 equiv.), methyl 4-bromobenzoate (86 mg, 0.40 mmol, 1.0 equiv.), dioxane (10.0 mL) and DMSO (2.0 mL). Purification by column chromatography (0-5% EtOAc/hexanes) provided the title compound (31 mg, 0.16 mmol, 41% yield) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 5.83 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.01 (dd, *J* = 23.2, 13.7 Hz, 2H), 3.90 (s, 3H), 2.76 (d, *J* = 7.5 Hz, 2H), 2.39 (q, *J* = 7.2 Hz, 2H).

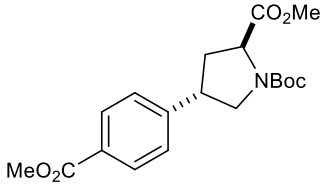
^{13}C NMR (125 MHz, $CDCl_3$) δ 167.30, 147.49, 137.63, 129.80, 128.64, 127.98, 115.50, 52.14, 35.51, 35.22.

Spectroscopic data matches with previously reported data.[13]



1-(*tert*-Butyl) 2-methyl (2*S*)-4-(4-(methoxycarbonyl)phenyl)pyrrolidine-1,2-dicarboxylate (43)

Prepared following the general procedure outlined above (reaction setup A) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (12.3 mg, 40 μmol, 0.10 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (10.8 mg, 40 μmol, 0.10 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-(((3*R*,5*S*)-1-(*tert*-butoxycarbonyl)-5-(methoxycarbonyl)pyrrolidin-3-yl)oxy)-2-oxoacetic acid (165 mg, 0.52 mmol, 1.3 equiv.), methyl 4-bromobenzoate (86 mg, 0.40 mmol, 1.0 equiv.), dioxane (15.0 mL) and DMSO (3.0 mL). Purification by column chromatography (20-30% EtOAc/hexanes) provided the title compound (83 mg, 0.23 mmol, 57% yield, 7:1 dr) as a colorless oil.



(Major diastereomer)

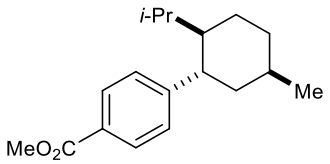
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 7.1 Hz, 2H), 4.51 (t, *J* = 5.7 Hz, 0.4H)&4.39 (t, *J* = 5.6 Hz, 0.6H), 4.04 (dd, *J* = 10.3, 8.0 Hz, 0.6H)&3.97 (dd, *J* = 10.2, 8.2 Hz, 0.4H), 3.88 (s, 3H), 3.75&3.73 (s, 3H), 3.66-3.52 (m, 1H), 3.46-3.33 (m, 1H), 2.42-2.26 (m, 2H), 1.45&1.41 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.36, 173.16, 166.82, 154.22, 153.59, 145.79, 145.72, 130.08, 129.06, 129.04, 127.20, 127.16, 80.36, 80.33, 59.15, 58.86, 52.81, 52.41, 52.26, 52.18, 42.52, 41.55, 37.69, 36.69, 28.49, 28.36.

IR (film) ν_{max} 2975, 2954, 1747, 1720, 1696, 1613, 1435, 1394, 1366, 1278, 1179, 1157,

1110, 1019, 892, 770, 706 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{19}H_{25}NNaO_6$ ($[M+Na]^+$) 386.1574, found 386.1578.



Methyl 4-((1*S*,2*R*,5*R*)-2-isopropyl-5-methylcyclohexyl)benzoate (44)

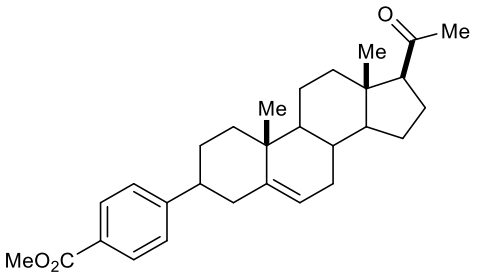
Prepared following the general procedure outlined above (reaction setup A) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (18.5 mg, 60 μmol, 0.15 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (16.1 mg, 60 μmol, 0.15 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-(((1*S*,2*R*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)-2-oxoacetic acid (119 mg, 0.52 mmol, 1.3 equiv.), methyl 4-bromobenzoate (86 mg, 0.40 mmol, 1.0 equiv.), dioxane (8.0 mL) and DMSO (2.0 mL). Purification by column chromatography (0-5% EtOAc/hexanes) provided the title compound (47 mg, 0.17 mmol, 43% yield, single isomer) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 3.89 (s, 3H), 2.71 (td, *J* = 11.9, 3.4 Hz, 1H), 2.10-2.02 (m, 1H), 1.70 (td, *J* = 12.8, 4.6 Hz, 1H), 1.65-1.56 (m, 3H), 1.54-1.47 (m, 2H), 1.40-1.33 (m, 2H), 1.06 (d, *J* = 7.2 Hz, 3H), 0.79 (d, *J* = 7.0 Hz, 3H), 0.69 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.21, 152.51, 129.72, 127.68, 51.95, 48.06, 42.03, 41.74, 31.70, 27.91, 27.76, 21.32, 18.47, 17.94, 15.50.

IR (film) ν_{max} 2956, 2928, 1723, 1609, 1435, 1277, 1180, 1112, 1101, 1019, 764 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{18}H_{27}O_2$ ($[M+H]^+$) 275.2006, found 275.2003.



Methyl 4-((10*R*,13*S*,17*S*)-17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16, 17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl)benzoate (45)

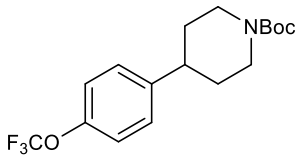
Prepared following the general procedure outlined above (reaction setup A) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (12.3 mg, 40 μmol, 0.10 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (10.8 mg, 40 μmol, 0.10 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-(((3*S*,10*R*,13*S*,17*S*)-17-acetyl-10,13-dimethyl 2,3,4,7,8,9,10,11,12,13,14,15,16, 17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl)oxy)-2-oxoacetic acid (202 mg, 0.52 mmol, 1.3 equiv.), methyl 4-bromobenzoate (86 mg, 0.40 mmol, 1.0 equiv.), dioxane (10.0 mL) and DMSO (2.0 mL). Purification by column chromatography (0-10% EtOAc/hexanes) provided the title compound (85 mg, 0.20 mmol, 51% yield, 1.3:1 dr) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 1.6H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 1.6H), 5.46 (brs, 1H), 5.35 (brs, 0.8H), 3.90 (s, 2.3H), 3.89 (s, 3H), 3.15 (brs, 1H), 2.82-2.77 (m, 1H), 2.60-2.33 (m, 5H), 2.22-2.16 (m, 3H), 2.13 (s, 2.3H), 2.11 (s, 3H), 2.09-1.96 (m, 5H), 1.82-1.64 (m, 8H), 1.60-1.35 (m, 9H), 1.32-1.15 (m, 6H), 1.08 (s, 5.3H), 0.65 (s, 2.3H), 0.63 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 209.75, 209.72, 167.37, 167.25, 152.43, 152.23, 142.53, 141.10, 129.87, 129.27, 128.42, 128.09, 127.35, 126.91, 121.74, 120.32, 63.86, 63.83, 57.11, 57.08, 52.12, 52.07, 50.43, 49.81, 45.97, 44.15, 44.14, 40.33, 39.83, 39.01, 38.93, 38.68, 37.36, 37.05, 35.39, 33.13, 31.97, 31.94, 31.92, 31.87, 31.72, 31.70, 29.87, 28.41, 24.63, 24.57, 22.96, 22.94, 21.09, 20.82, 19.83, 19.73, 13.39.

IR (film) ν_{max} 2934, 2850, 1720, 1703, 1610, 1434, 1277, 1185, 1108, 1019, 708 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{29}H_{38}NaO_3$ ($[M+Na]^+$) 457.2713, found 457.2711.



***tert*-Butyl 4-(4-(trifluoromethoxy)phenyl)piperidine-1-carboxylate**

Prepared following the general procedure outlined above (reaction setup A) using $Ir[dFppy]_2(dtbbpy)PF_6$ (4.0 mg, 4.0 μmol, 0.01 equiv.), $NiBr_2$•glyme (12.3 mg, 40 μmol, 0.10 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (10.8 mg, 40 μmol, 0.10 equiv.), anhydrous cesium hydrogencarbonate (116 mg, 0.60 mmol, 1.5 equiv.), 2-((1-(*tert*-butoxycarbonyl)piperidin-4-yl)oxy)-2-oxoacetic acid (142 mg, 0.52 mmol, 1.3 equiv.), 1-bromo-4-(trifluoromethoxy)benzene (96 mg, 0.40 mmol, 1.0 equiv.), THP (10.0 mL) and DMSO (2.5 mL). Purification by column chromatography (5-10% EtOAc/hexanes) provided the title compound (77 mg, 0.22 mmol, 56% yield) as a white solid.

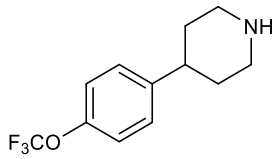
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, J = 8.6 Hz, 2H), 7.15 (d, J = 8.2 Hz, 2H), 4.24 (br, 2H), 2.80 (t, J = 12.4 Hz, 2H), 2.66 (tt, J = 12.2, 3.5 Hz, 1H), 1.81 (d, J = 13.1 Hz, 2H), 1.63-1.50 (m, 2H), 1.48 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.96, 147.75 (q, $J_{C,F}$ = 2.0 Hz), 144.59, 128.15, 121.19, 120.63 (q, $J_{C,F}$ = 256.7 Hz), 79.70, 44.41 (br), 42.27, 33.32, 28.62.

^{19}F NMR (282 MHz, $CDCl_3$) δ -57.91.

IR (film) ν_{max} 2927, 2855, 1691, 1509, 1423, 1366, 1256, 1223, 1159, 1015, 770 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{17}H_{22}F_3NNaO$ ($[M+Na]^+$) 368.1444, found 368.1444.



4-(4-(Trifluoromethoxy)phenyl)piperidine

To a solution of *tert*-butyl 4-(4-(trifluoromethoxy)phenyl)piperidine-1-carboxylate (80 mg, 0.23 mmol, 1.0 equiv.) in anhydrous DCM (4 ml) was added trifluoroacetic acid (0.60 mL, 8.1 mmol, 35.0 equiv.) in 0 °C and the reaction was stirred at room temperature for 8 h. After the reaction was finished, the mixture was evaporated and the residue was redissolved with EA. The solution was washed with saturated $NaHCO_3$ to the aqueous layer pH = 8.0. Organic layer was separated, washed with brine and evaporated to dryness to afford the title compound (56 mg, 0.23 mmol, 99% yield) as a brown solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, J = 8.6 Hz, 2H), 7.14 (d, J = 8.2 Hz, 2H), 6.84 (brs, 1H), 3.42 (d, J = 12.0 Hz, 2H), 2.88 (t, J = 8.8 Hz, 2H), 2.80-2.64 (m, 1H), 1.98-1.87 (m, 4H).

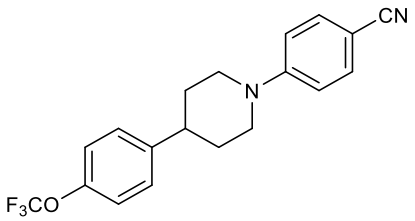
^{13}C NMR (125 MHz, $CDCl_3$) δ 147.89 (q, $J_{C,F}$ = 2.0 Hz), 143.72, 128.13, 121.24, 120.55 (q, $J_{C,F}$ = 256.9 Hz), 45.67, 41.19, 31.99.

^{19}F NMR (282 MHz, $CDCl_3$) δ -57.94.

IR (film) ν_{max} 3397, 2926, 2853, 1510, 1255, 1216, 1156, 1014, 837, 807 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{15}F_3NO$ ($[M+H]^+$) 246.1100, found 246.1098.

Spectroscopic data matches with previously reported data.[14]



4-(4-(4-(Trifluoromethoxy)phenyl)piperidin-1-yl)benzonitrile (46)

To a solution of 4-bromobenzonitrile (42 mg, 0.23 mmol, 1.0 equiv.), 4-(4-(trifluoromethoxy)phenyl)piperidine (85 mg, 0.35 mmol, 1.5 equiv), and DABCO (46 mg, 0.41 mmol, 1.8 equiv) in DMA (0.8 mL) was added photocatalyst **1** (0.056 mg, 0.0002 equiv) as a solution in DMA (10 μL). A solution of $NiBr_2$•glyme (3.5 mg, 0.012 mmol, 0.05 equiv) in DMA (0.3 mL), which had been sonicated for 5 min, was then added. The vial was placed under an atmosphere of nitrogen, cooled to –78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED, and irradiated. The reaction vial was heated to approximately 55 °C by the blue LED without fan cooling. After 48 h, the reaction mixture was purified directly by flash column chromatography (10-25% EtOAc/hexanes) to give the title compound (57 mg, 0.16 mmol, 73% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 9.4 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 7.16 (d, *J* = 9.1 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 3.99 (d, *J* = 12.8 Hz, 2H), 2.98 (t, *J* = 12.1 Hz, 2H), 2.77 (t, *J* = 12.1 Hz, 1H), 1.96 (d, *J* = 12.8 Hz, 2H), 1.82-1.75 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 153.42, 147.87 (d, $J_{C,F}$ = 2.0 Hz), 144.09, 133.72, 128.13, 121.27, 120.61 (q, $J_{C,F}$ = 257.0 Hz), 120.29, 114.56, 99.92, 48.38, 41.99, 32.81.

^{19}F NMR (282 MHz, $CDCl_3$) δ -57.91.

IR (film) ν_{max} 2925, 2853, 2221, 2210, 1605, 1511, 1256, 1178, 1009, 817 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{19}H_{18}F_3N_2O$ ($[M+H]^+$) 347.1366, found 347.1363.

6) Cyclic Voltammetry Data

Cyclic voltammetry was performed on a CH Instruments Electrochemical Analyzer (CHI600E). A 0.005 M CH_3CN solution of the cesium oxalate derivative of *N*-Boc-4-hydroxypiperidine was prepared with 0.1 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 0.1 V/s.

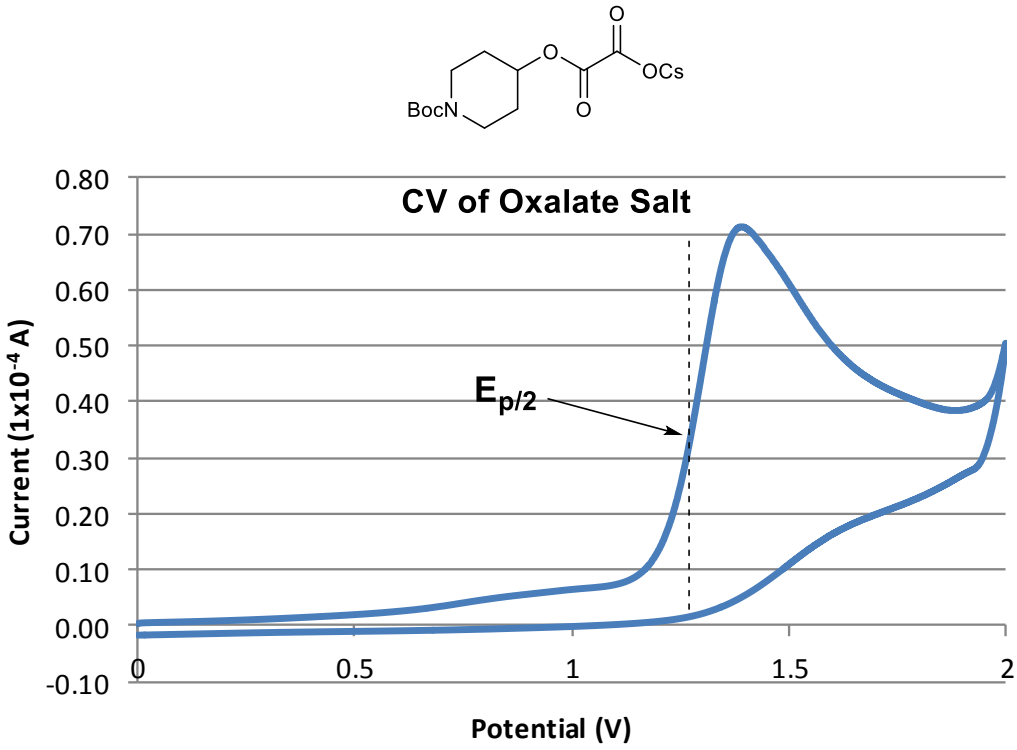


Figure S4. Cyclic voltammogram of the cesium oxalate derivative of *N*-Boc-4-hydroxypiperidine shows an irreversible oxidation event at +1.26 V ($E_{p/2}$) vs. SCE in CH_3CN.[15]

7) References

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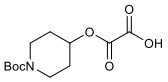
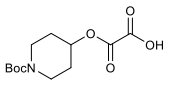
8) Spectral Data



^{1}H NMR (500 MHz, Acetone-d_6)



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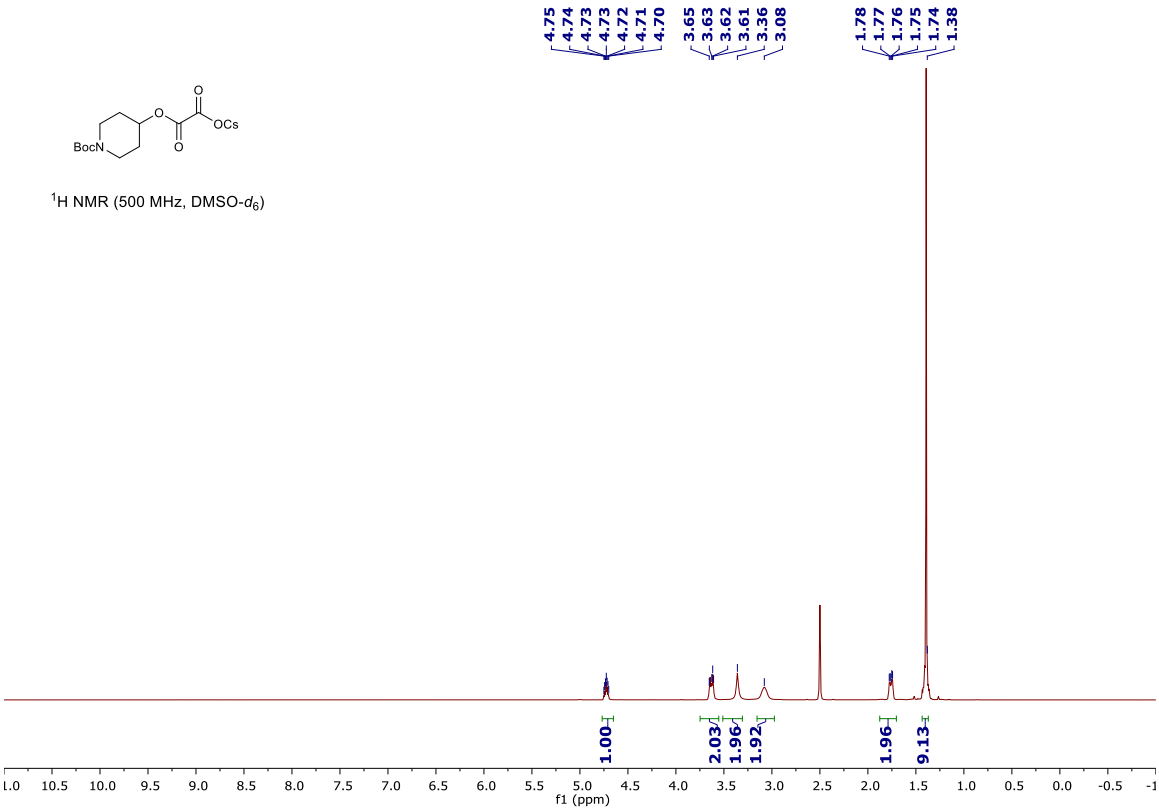

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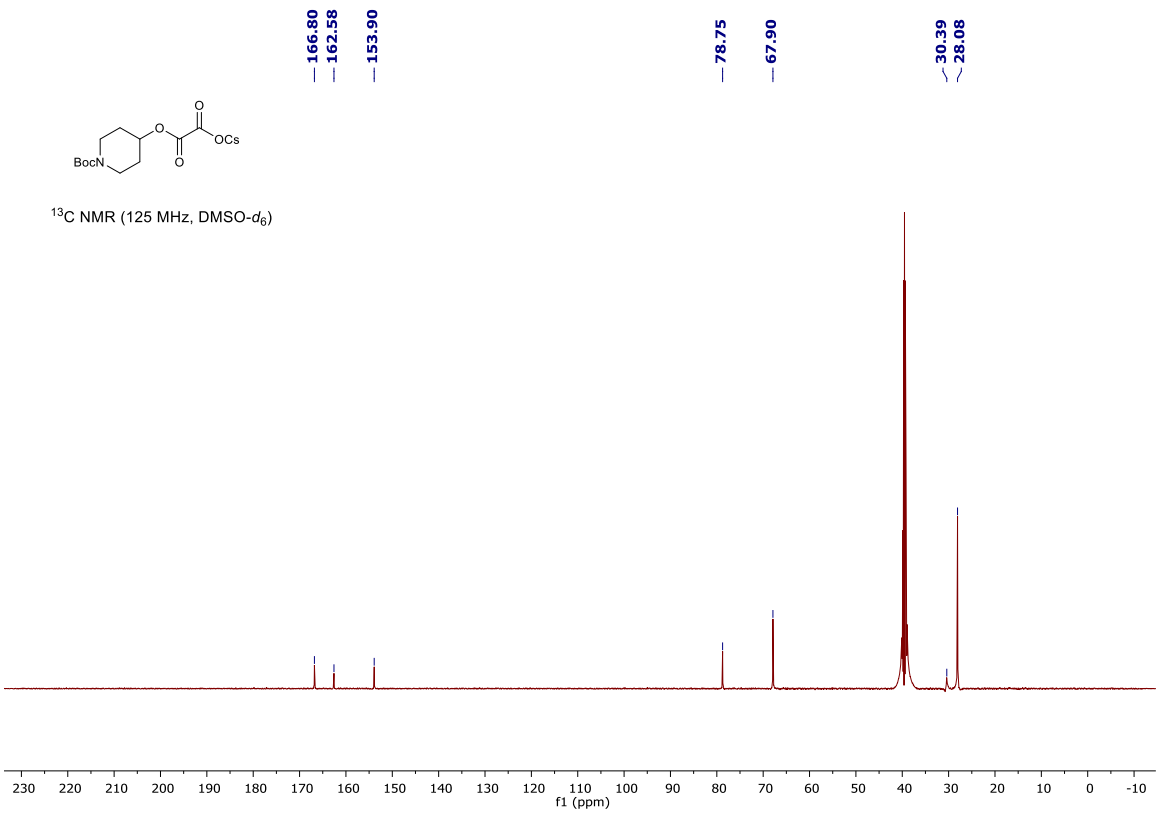

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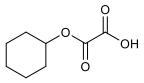

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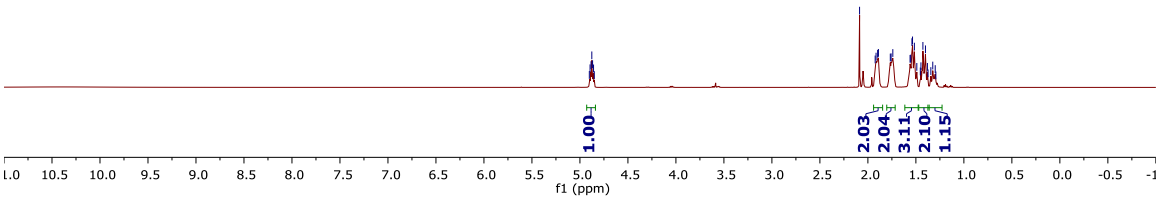

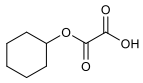

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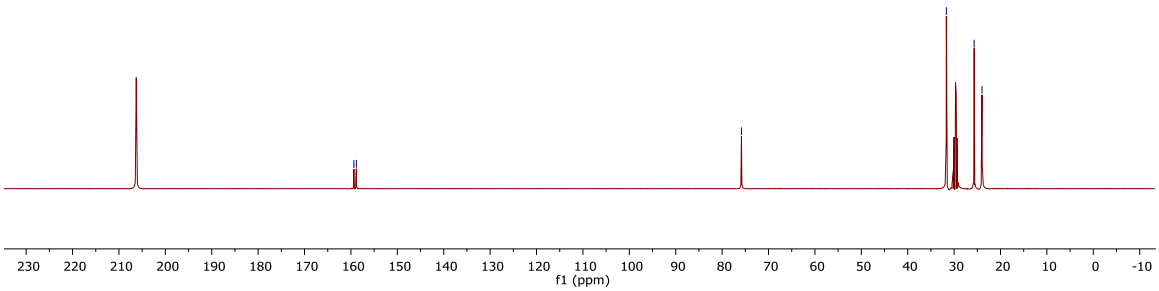

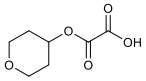

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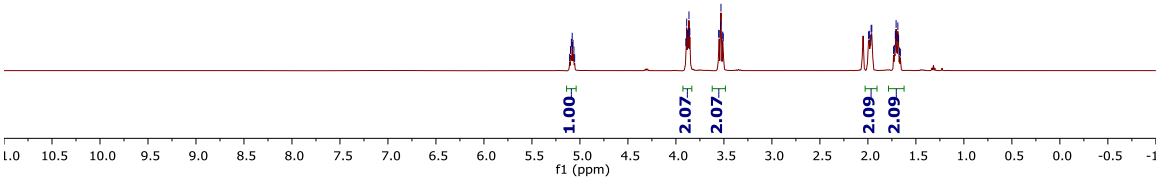

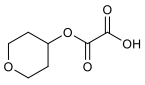

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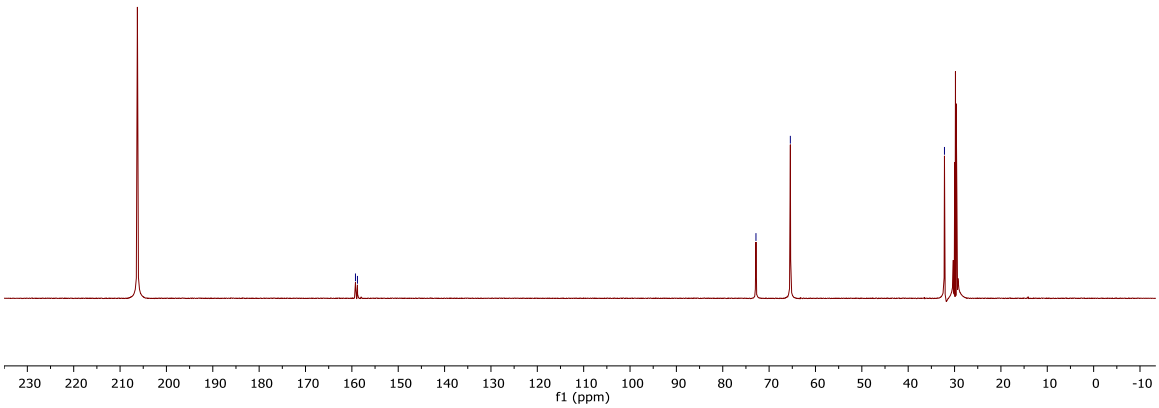

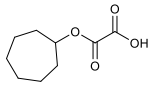

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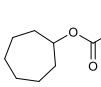

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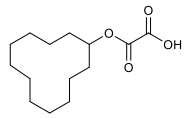

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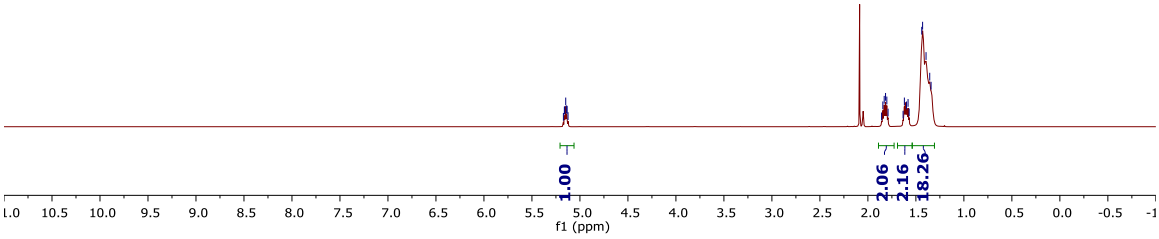

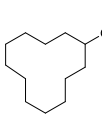

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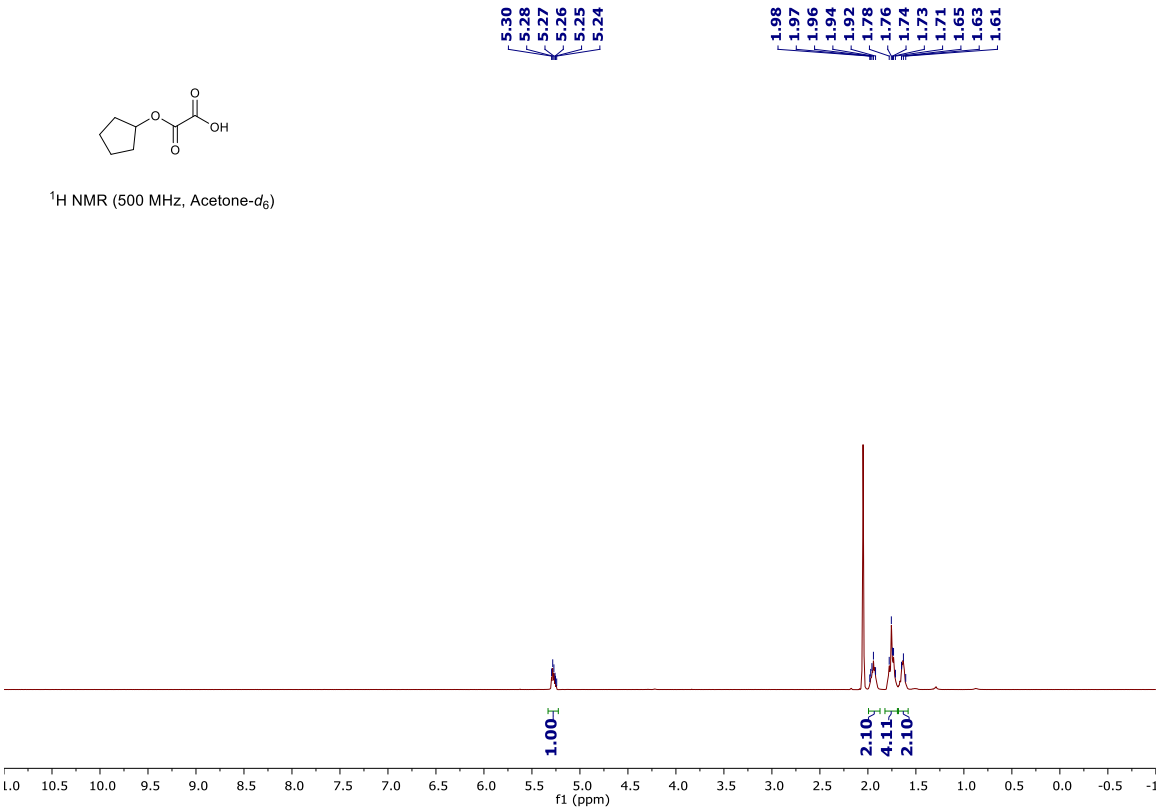

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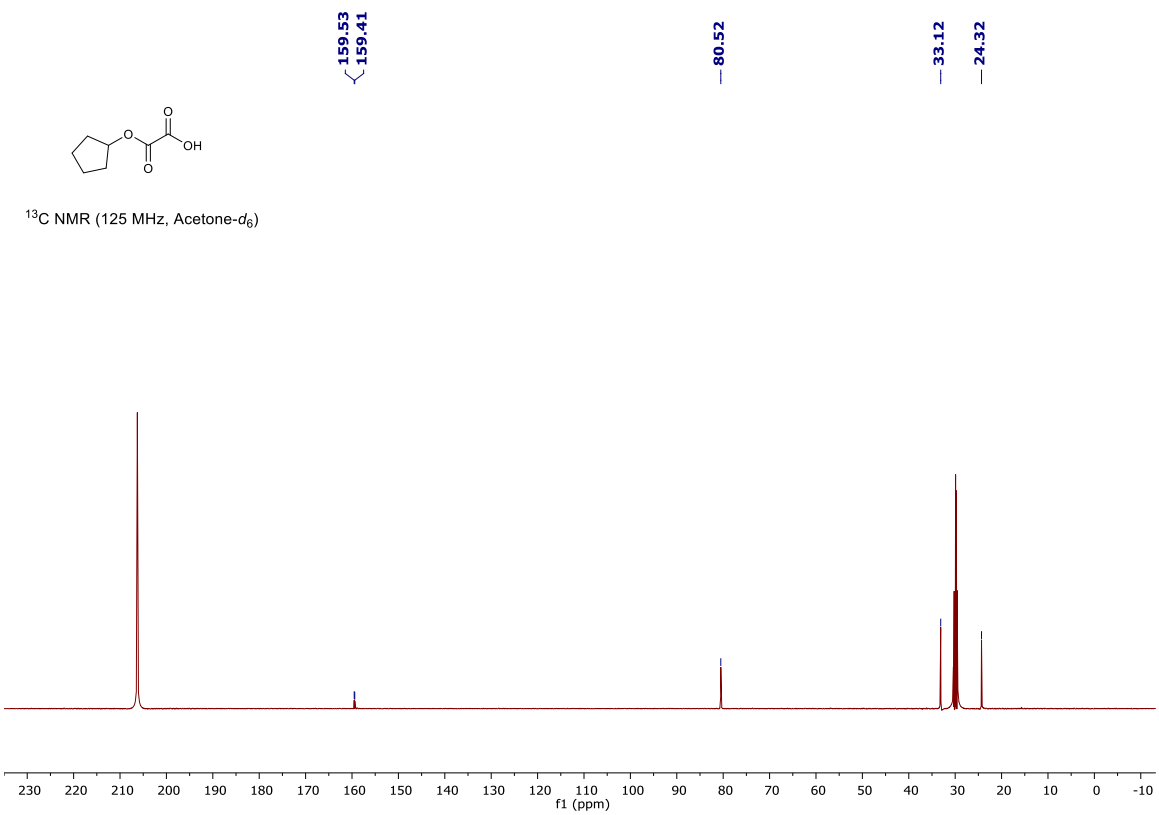

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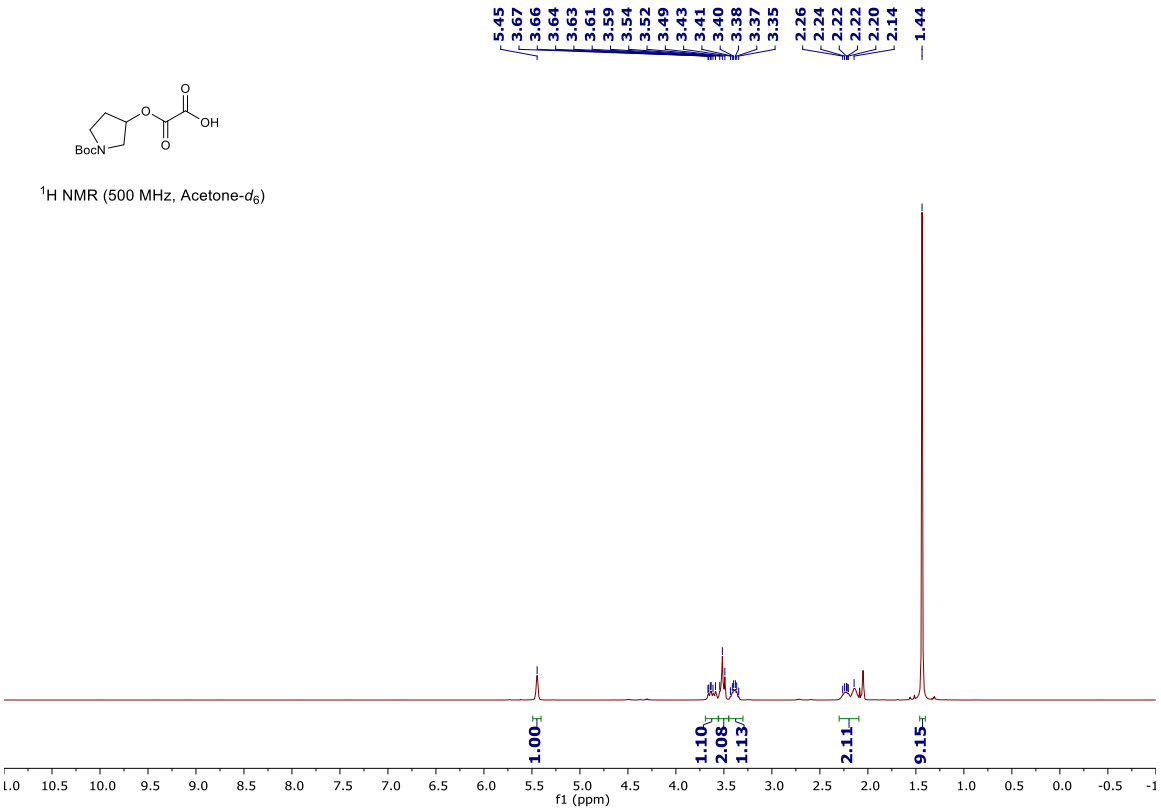

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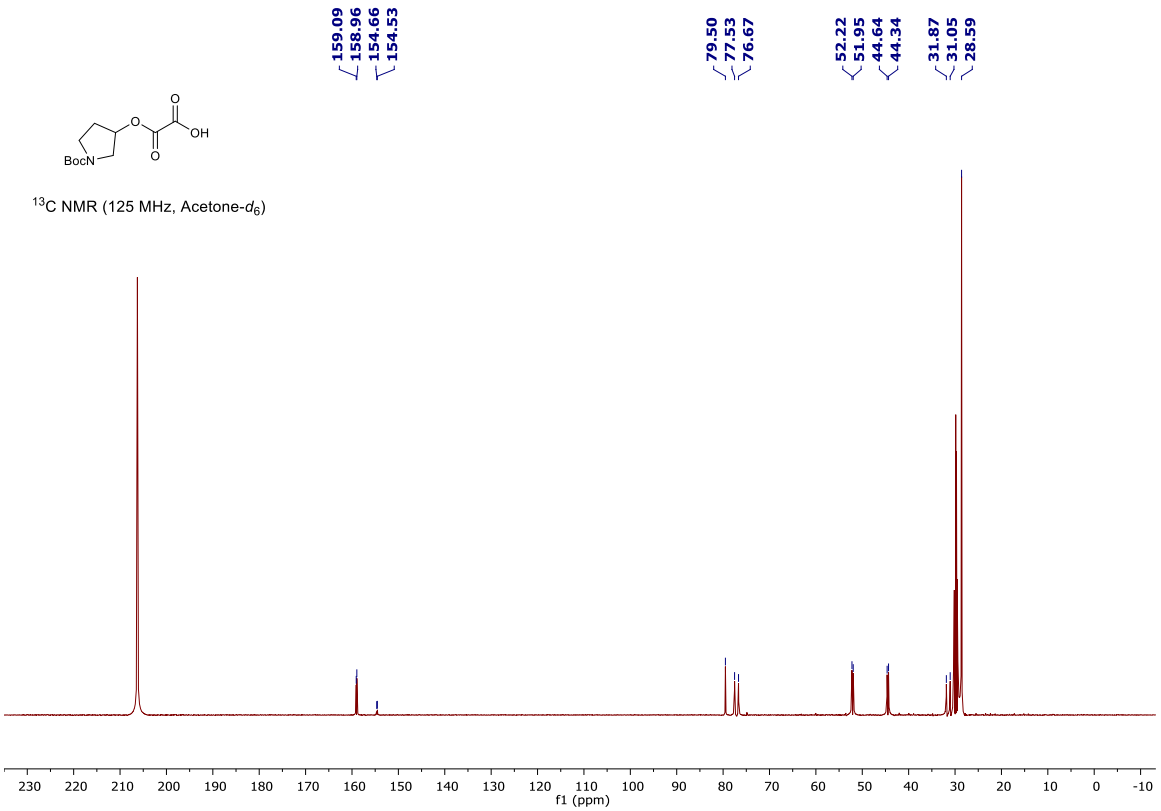

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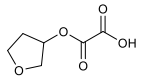

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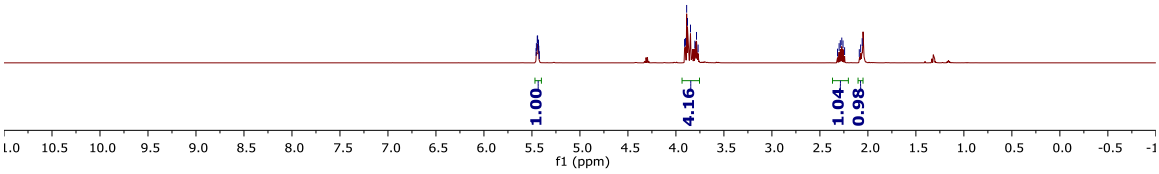

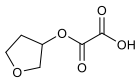

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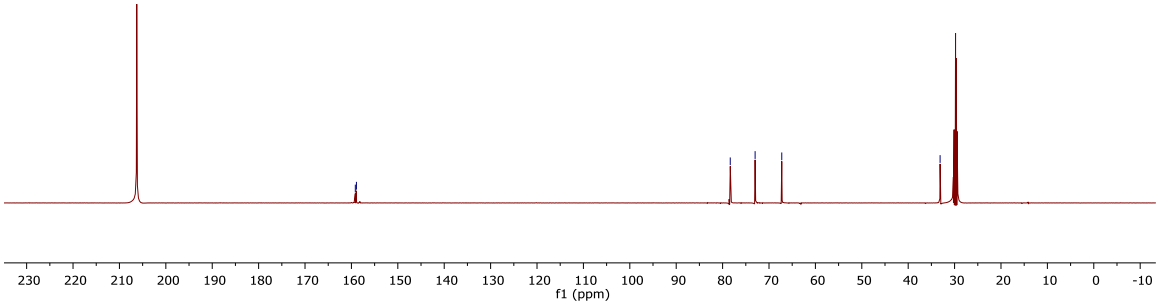

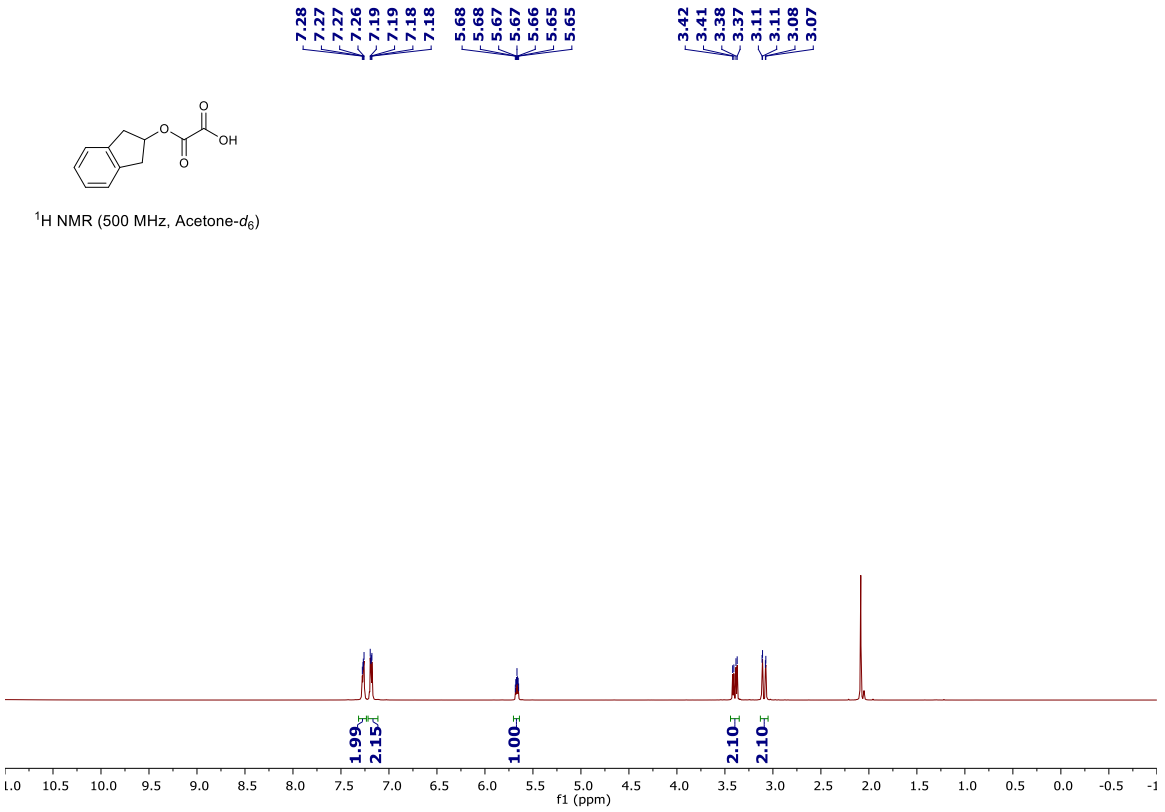

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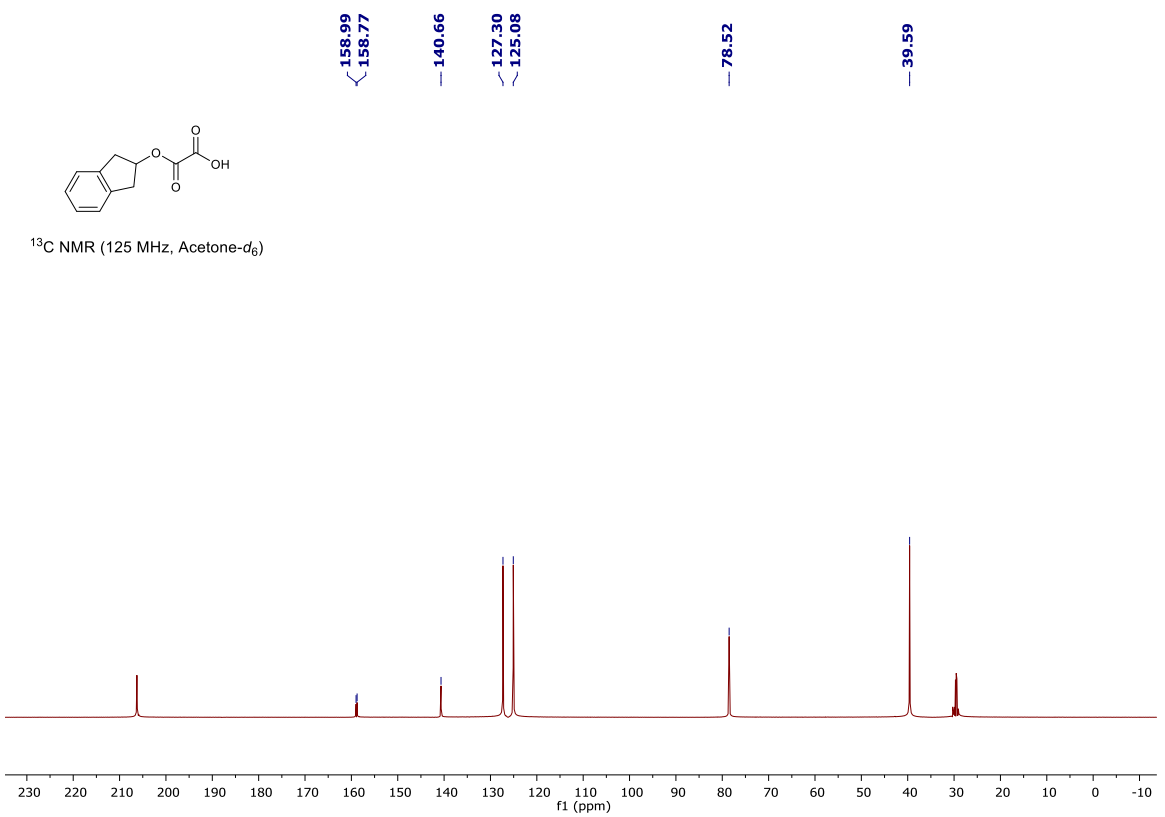

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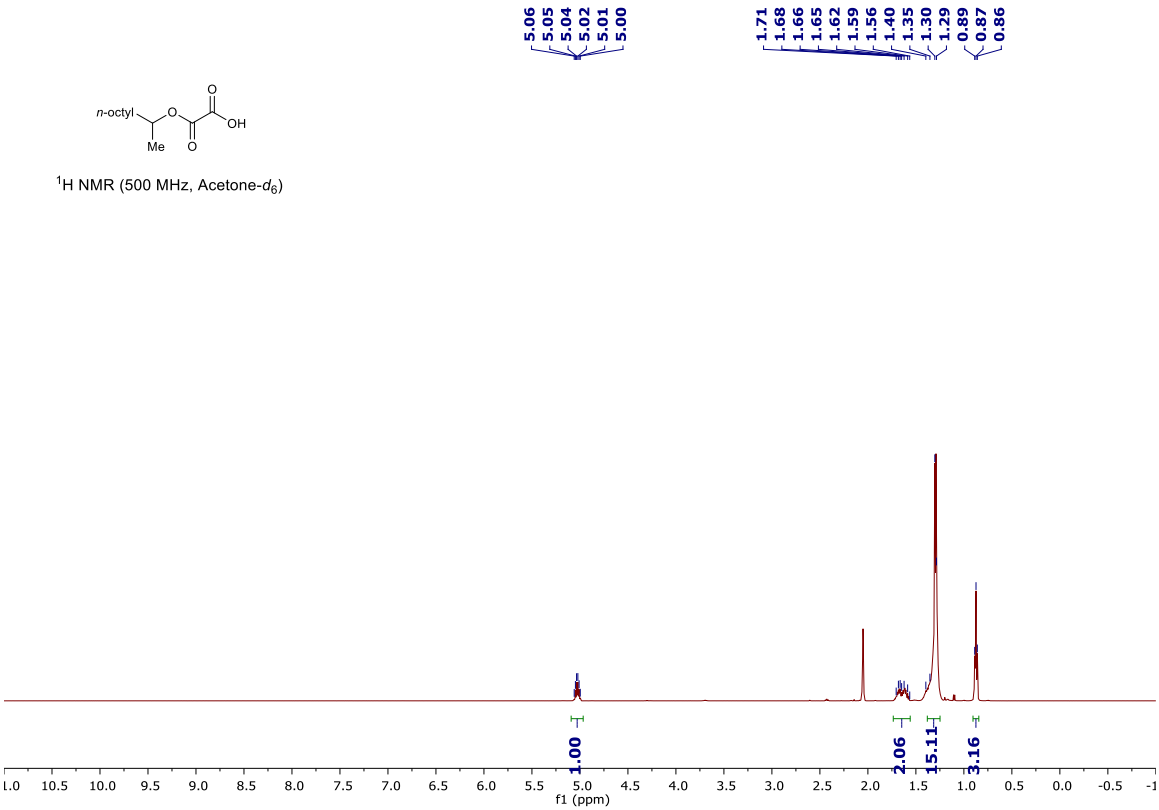

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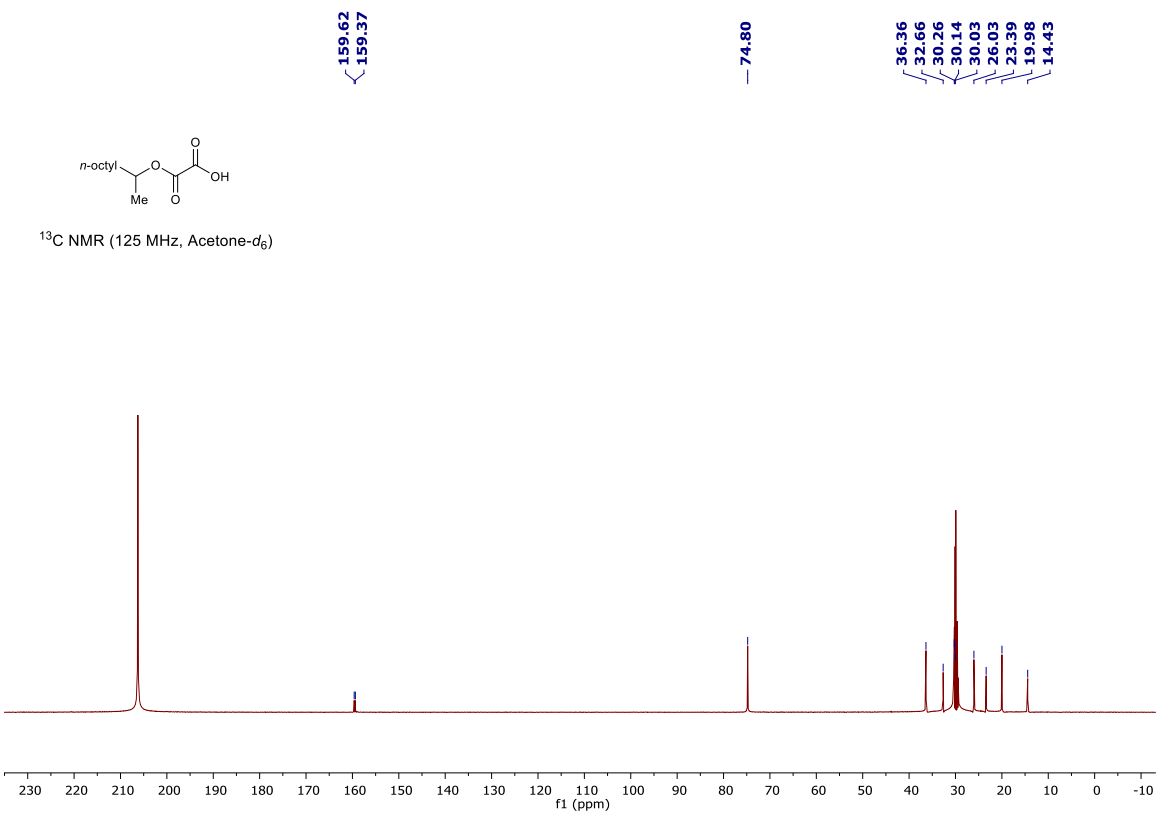

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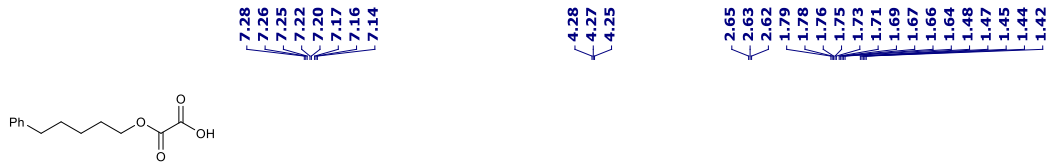

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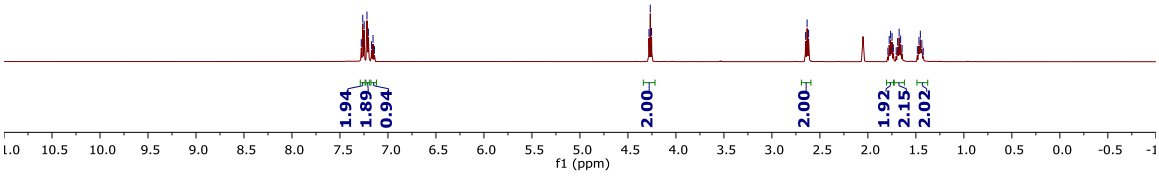

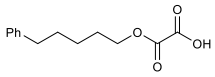

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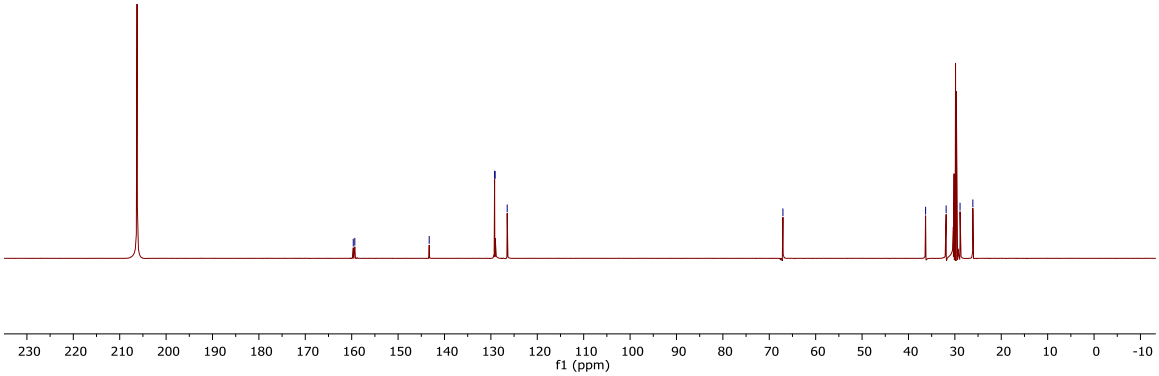

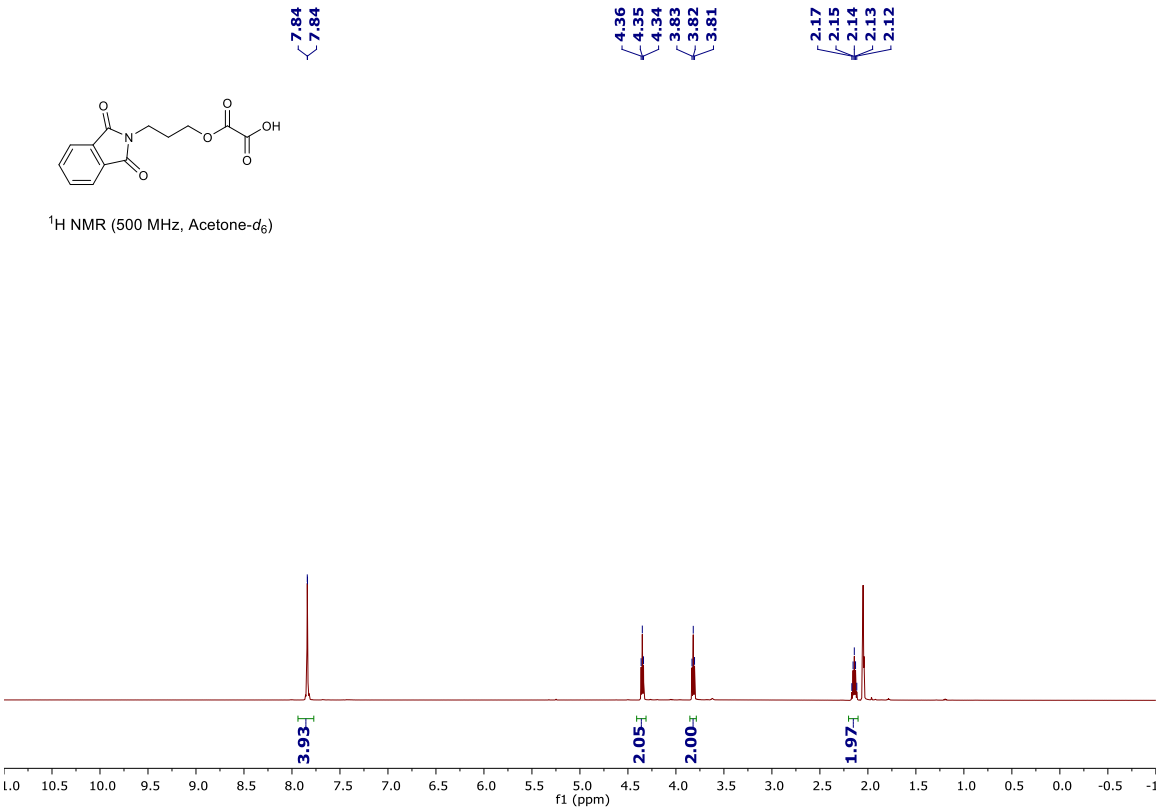

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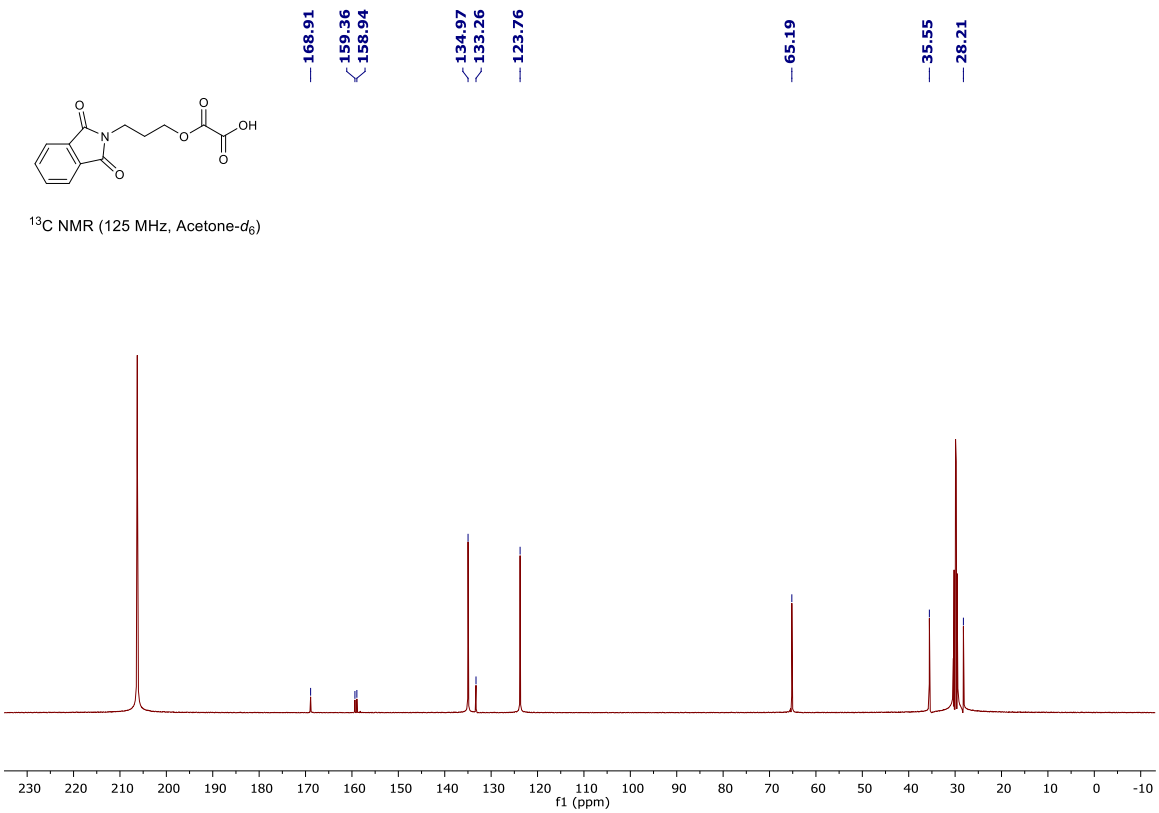

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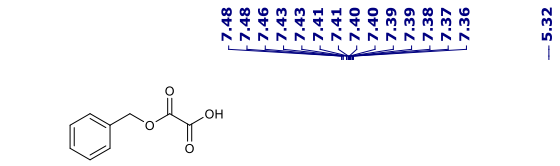

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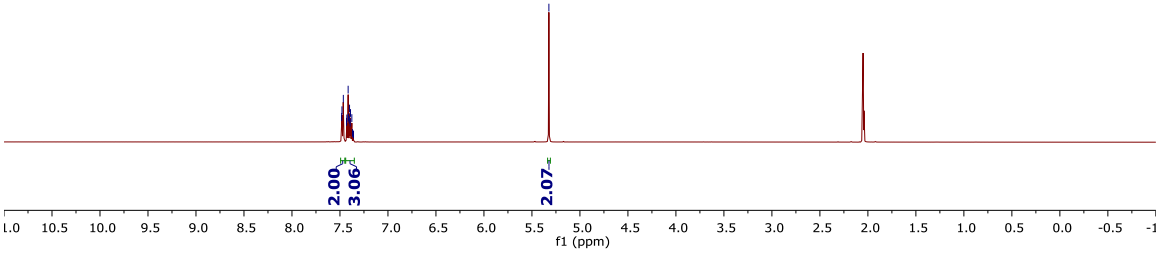

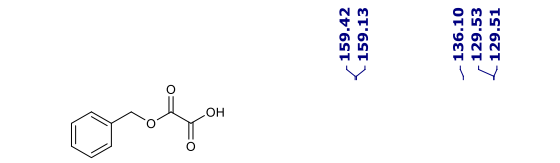

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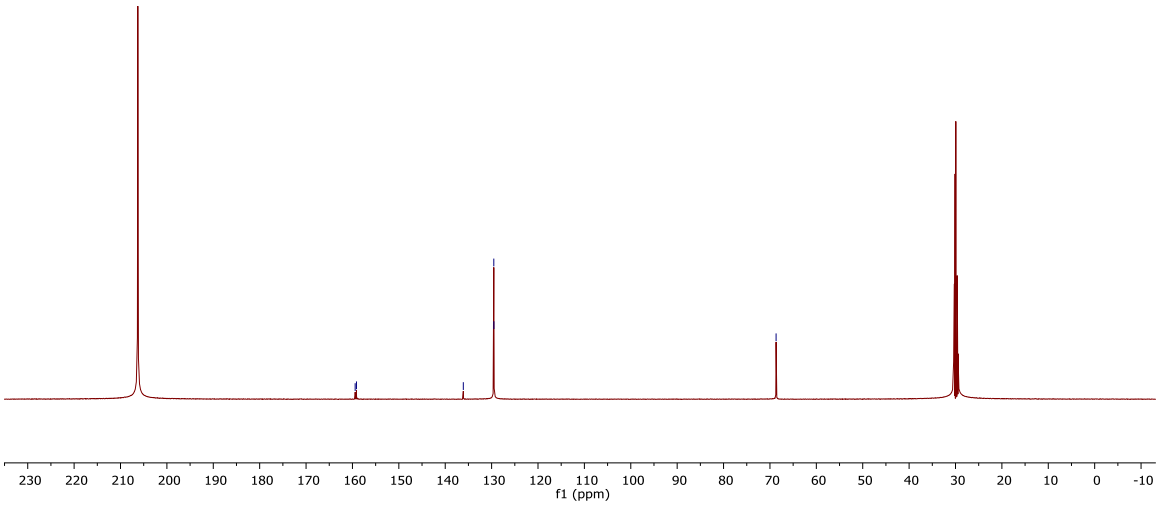

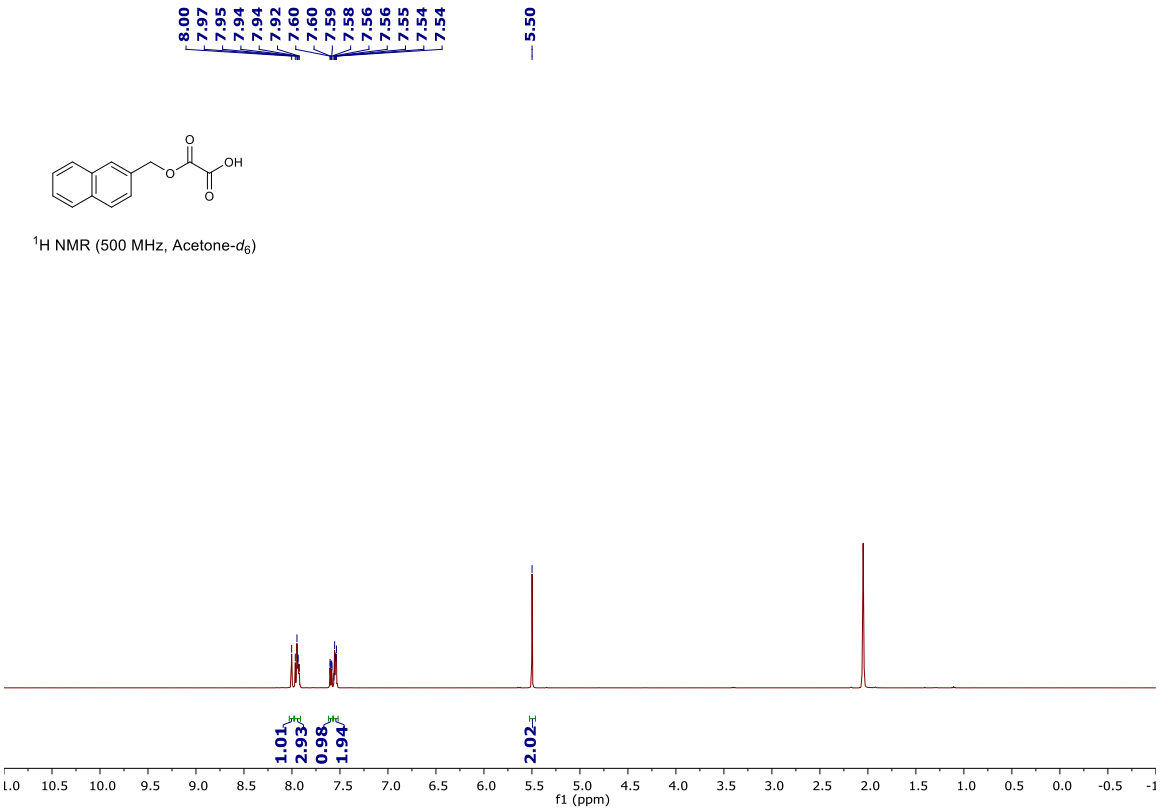

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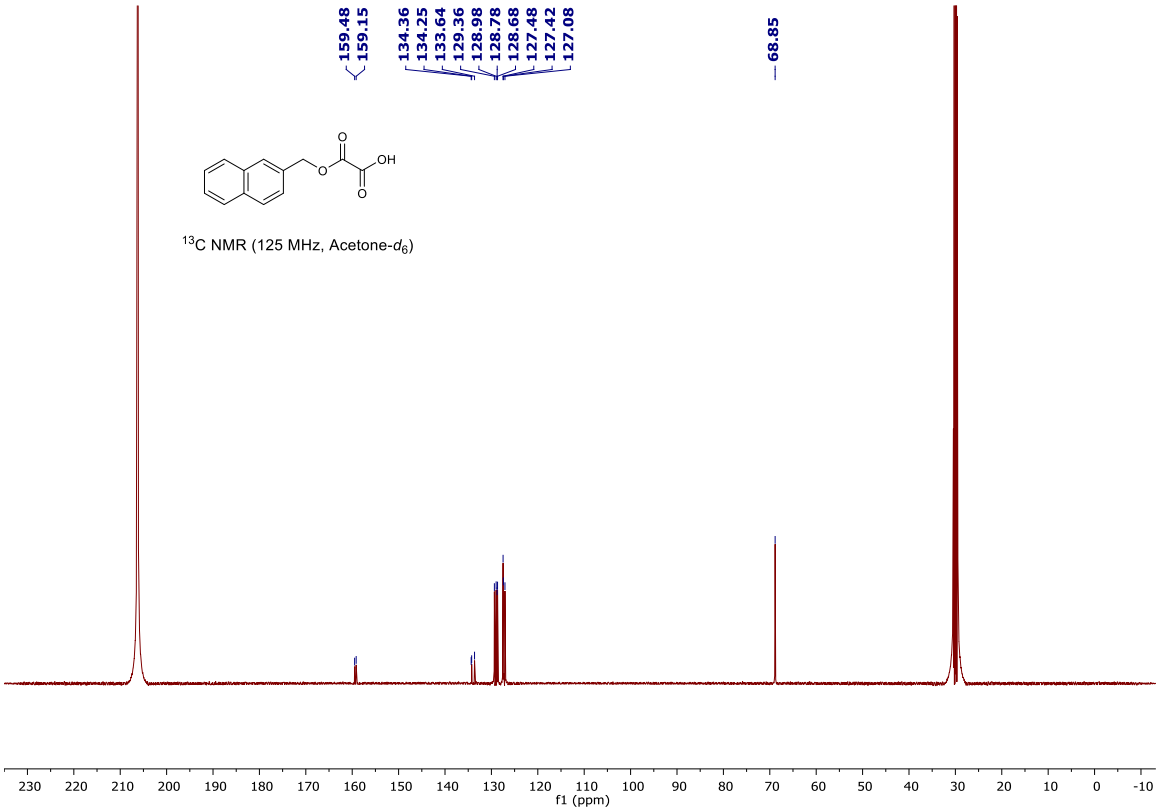

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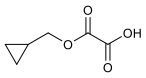
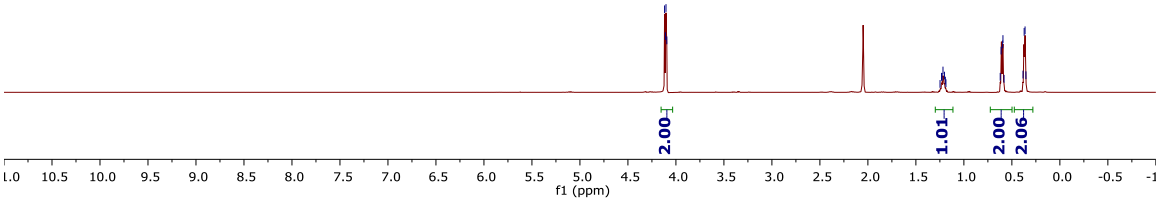
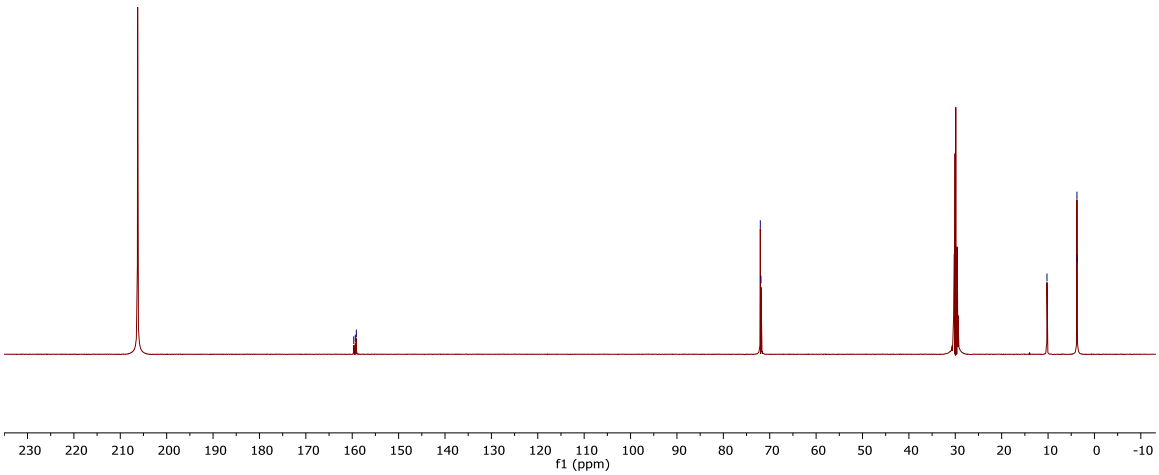
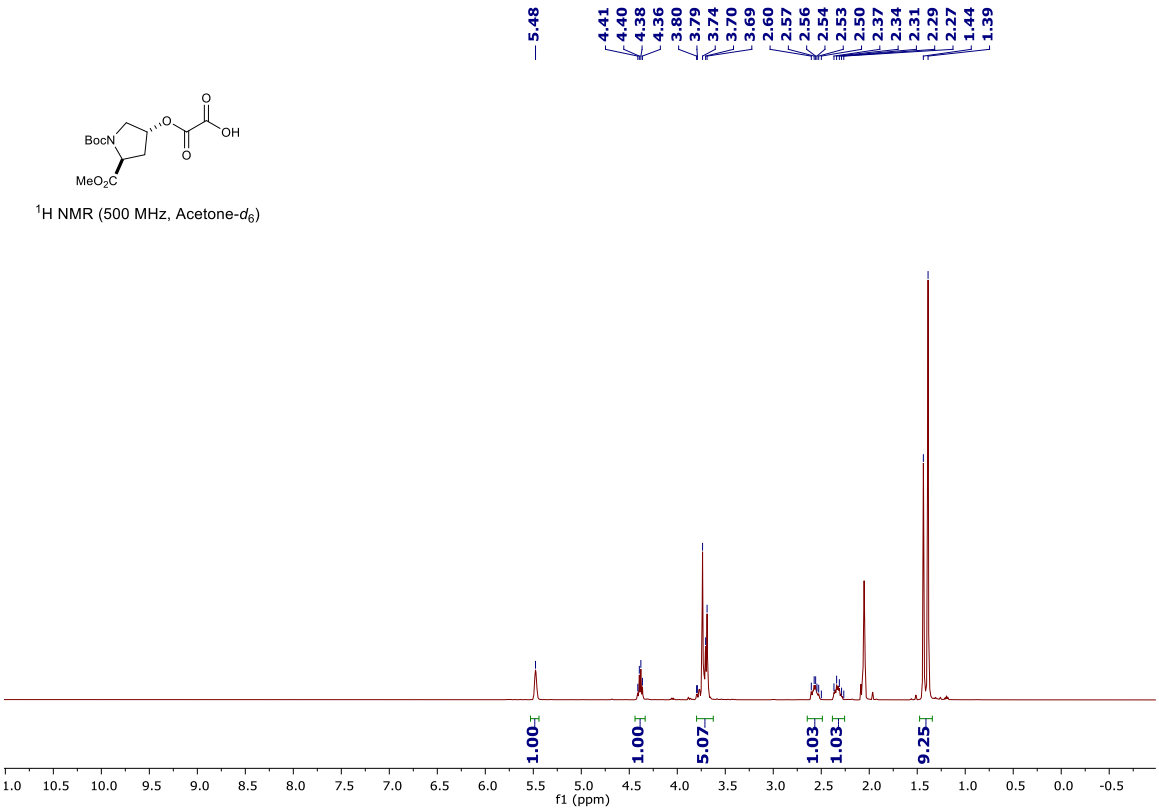


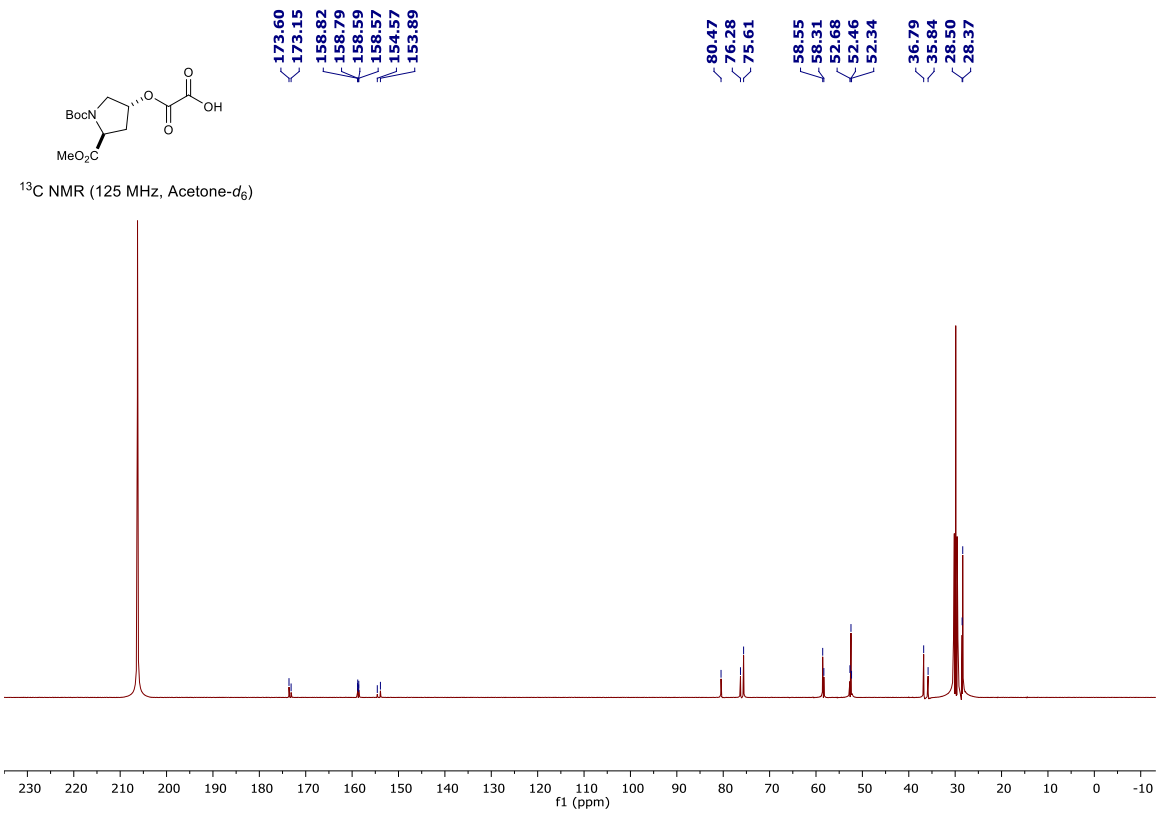
^{1}H NMR (500 MHz, Acetone-d_6)

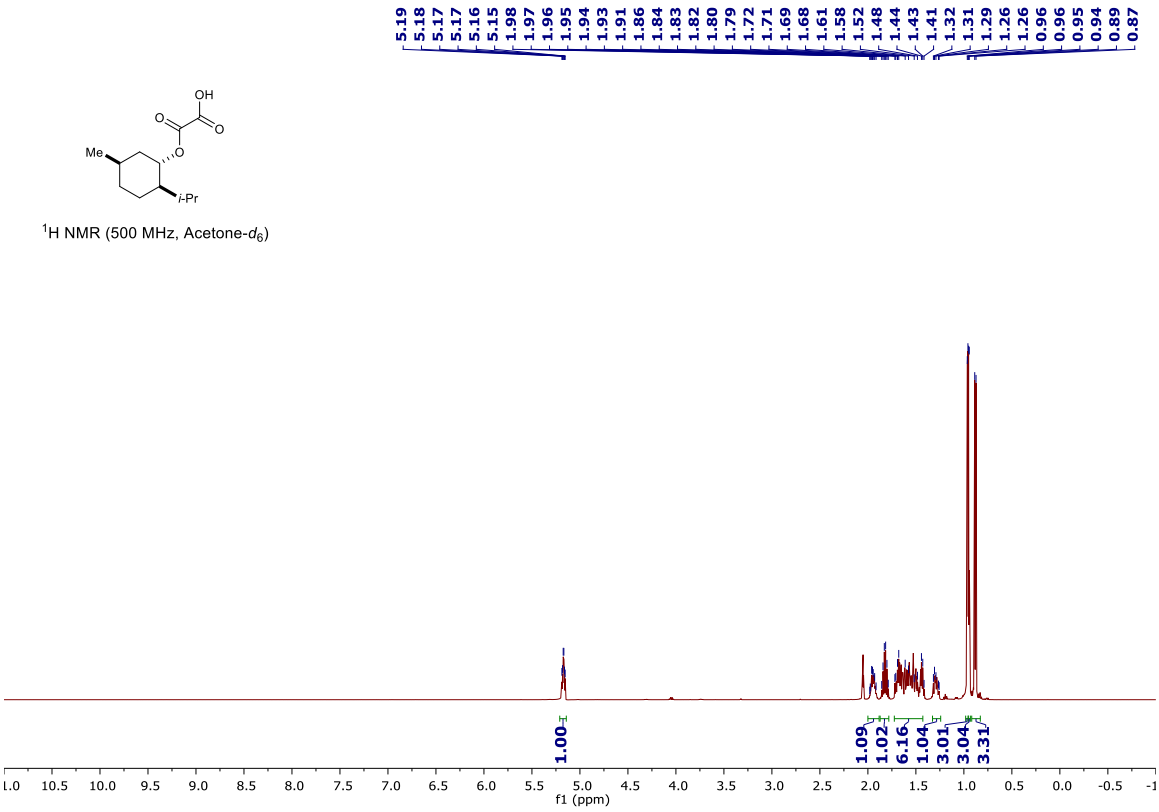


^{13}C NMR (125 MHz, Acetone-d_6)

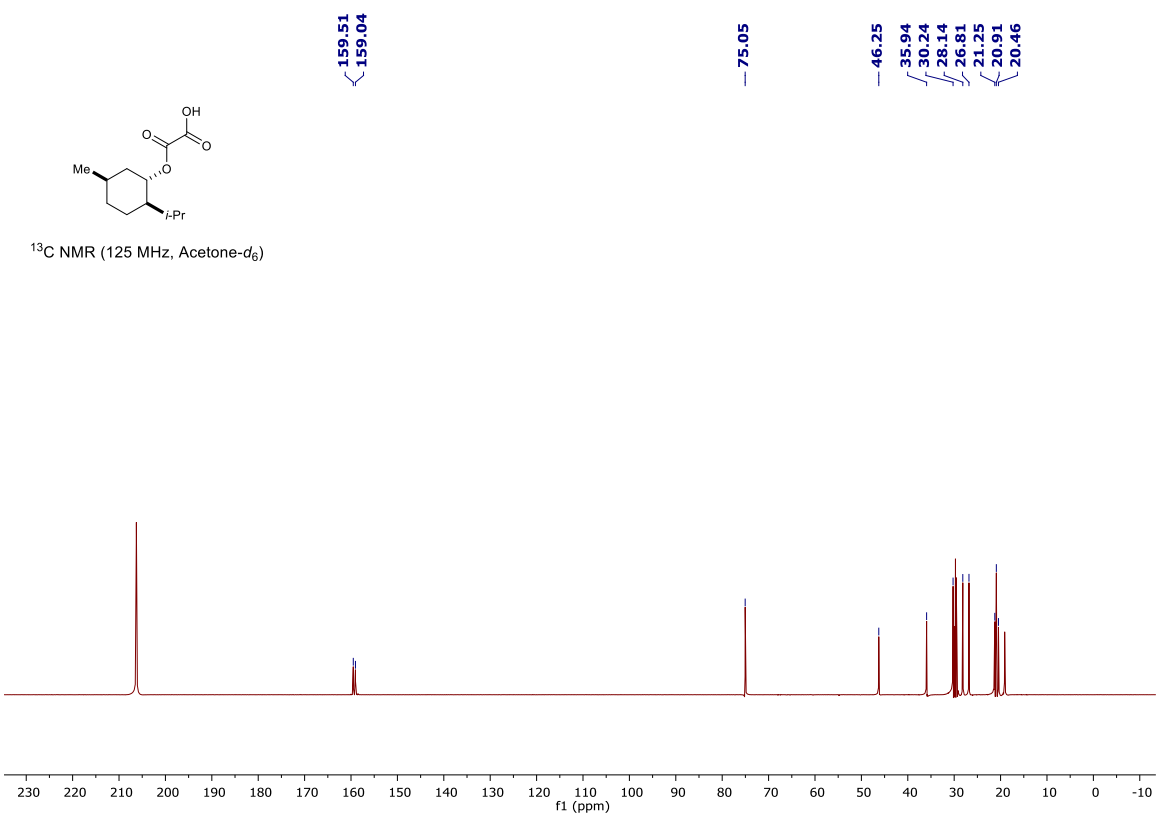



5.48
4.41
4.40
4.38
4.36
3.80
3.79
3.74
3.70
3.69
2.60
2.57
2.56
2.54
2.53
2.50
2.37
2.34
2.31
2.29
2.27
1.44
1.39
BocN
O
OH
MeO2C
1H NMR (500 MHz, Acetone-d6)
1.00
1.00
5.07
1.03
1.03
9.25
f1 (ppm)

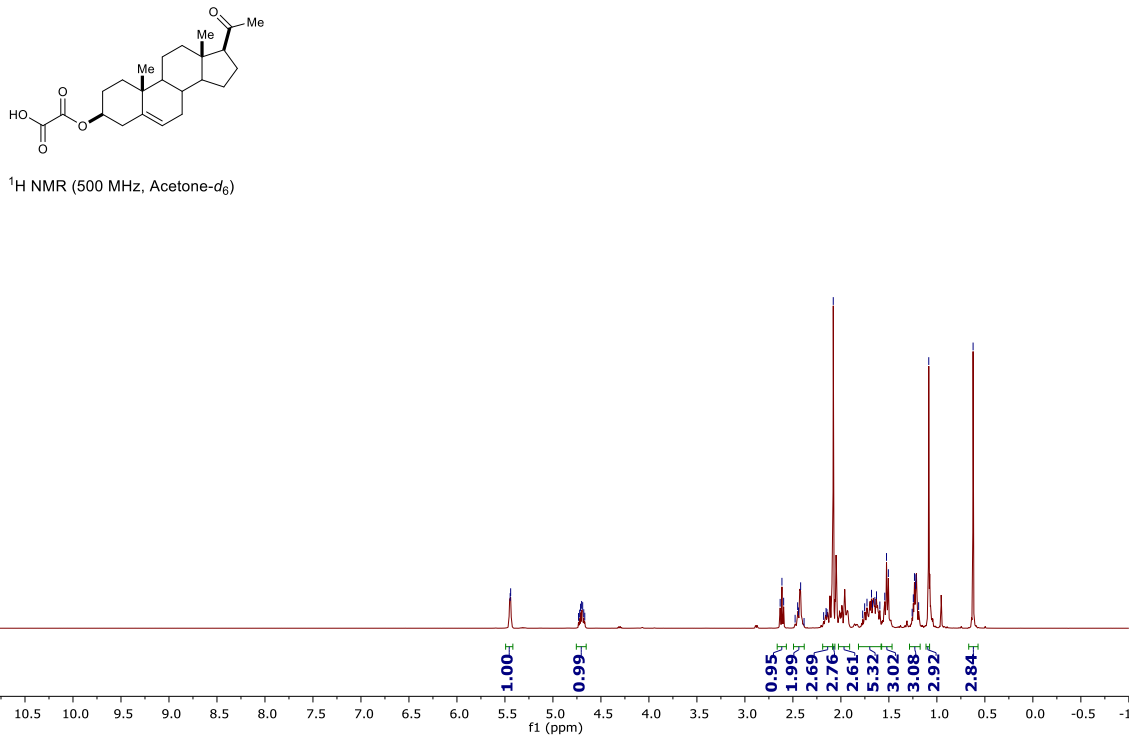

173.60
173.15
158.82
158.79
158.59
158.57
154.57
153.89
80.47
76.28
75.61
58.55
58.31
52.68
52.46
52.34
36.79
35.84
28.50
28.37
BocN
O
OH
MeO2C
13C NMR (125 MHz, Acetone-d6)
f1 (ppm)



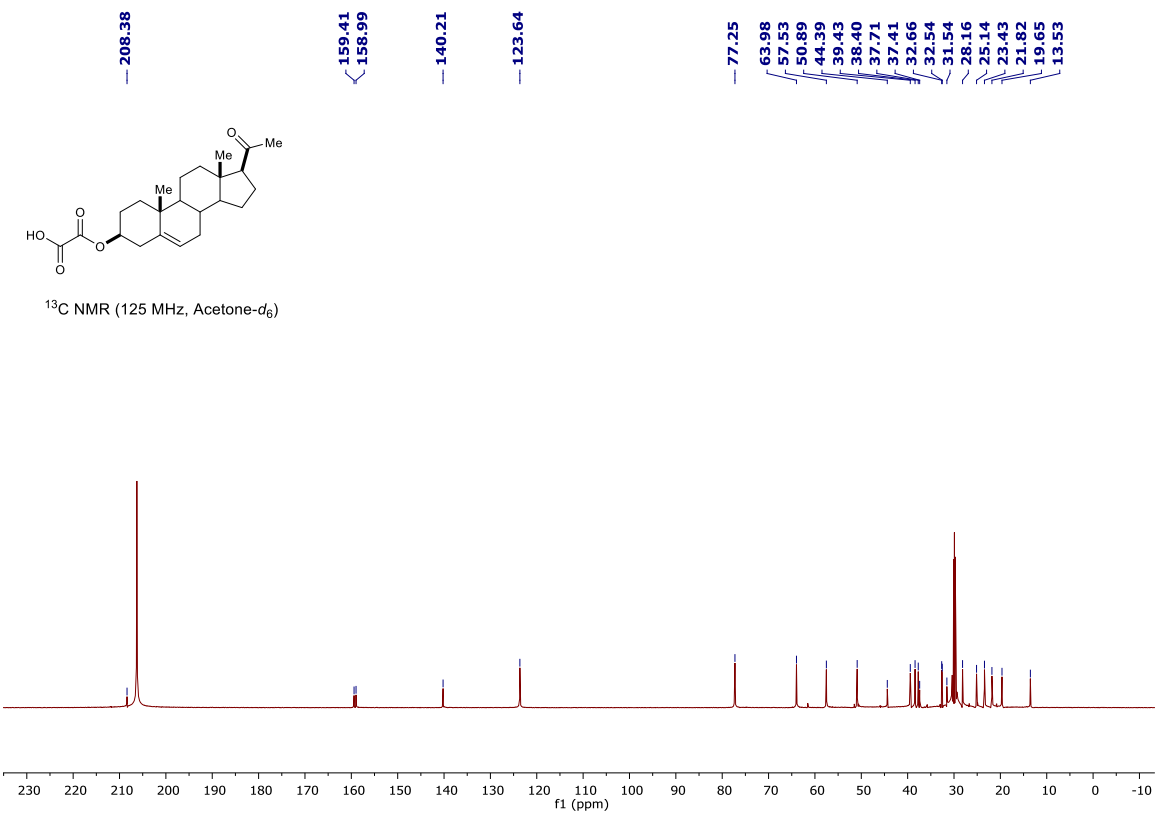
^{1}H NMR (500 MHz, Acetone-d_6)



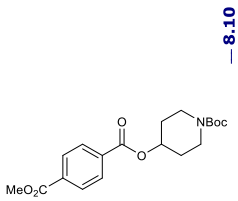
^{13}C NMR (125 MHz, Acetone-d_6)



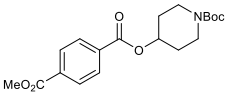
^{1}H NMR (500 MHz, Acetone-d_6)



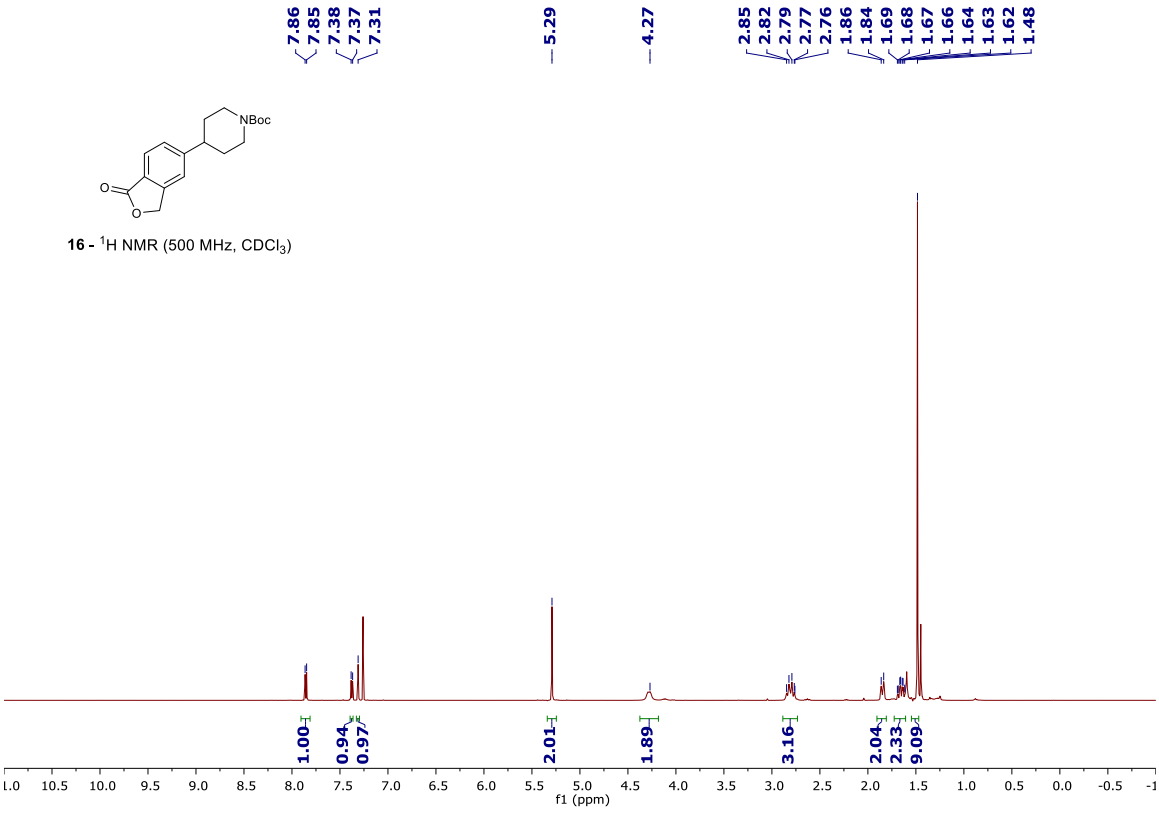
^{13}C NMR (125 MHz, Acetone-d_6)



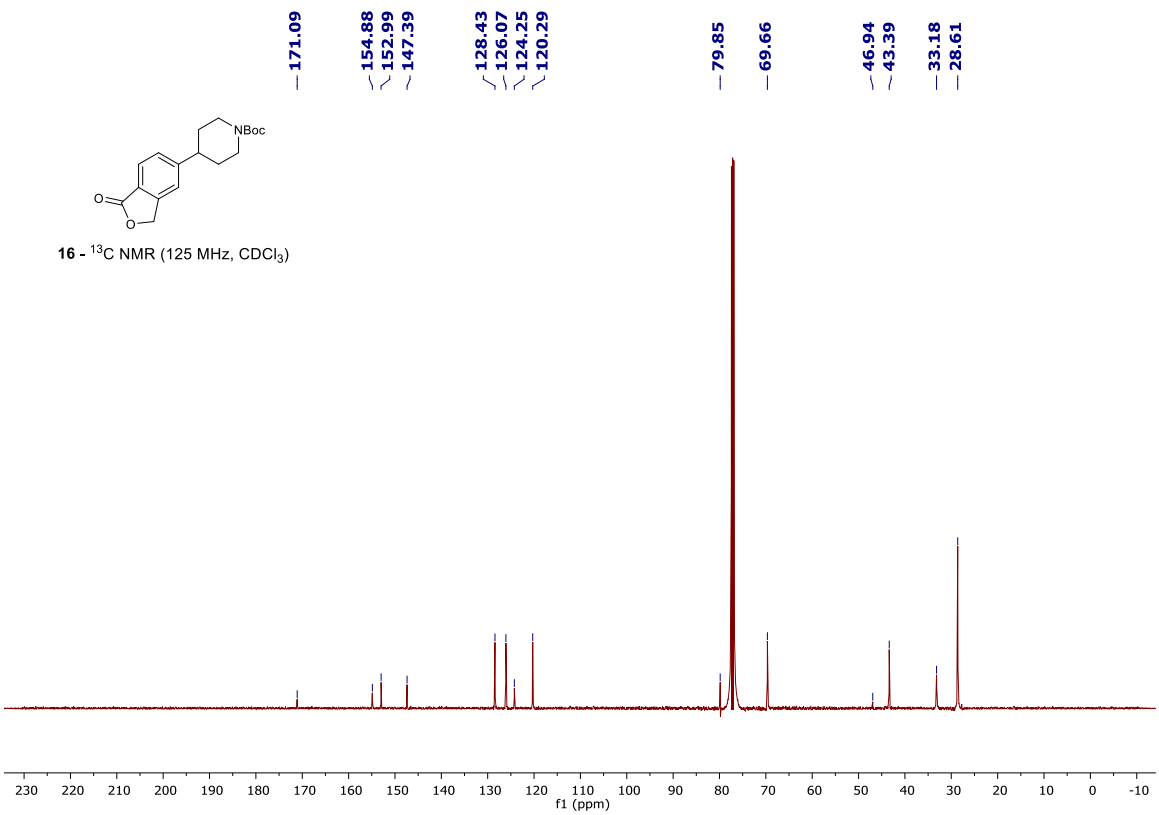
^{1}H NMR (500 MHz, $CDCl_3$)



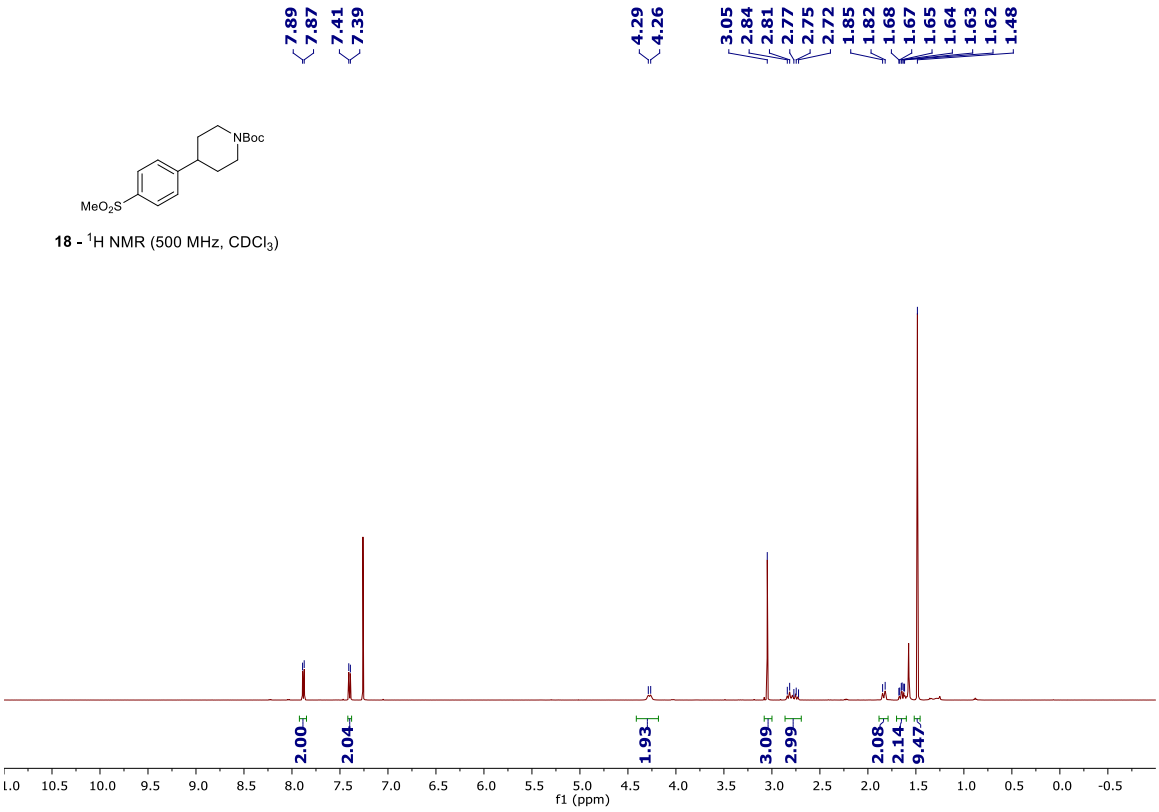
^{13}C NMR (125 MHz, $CDCl_3$)



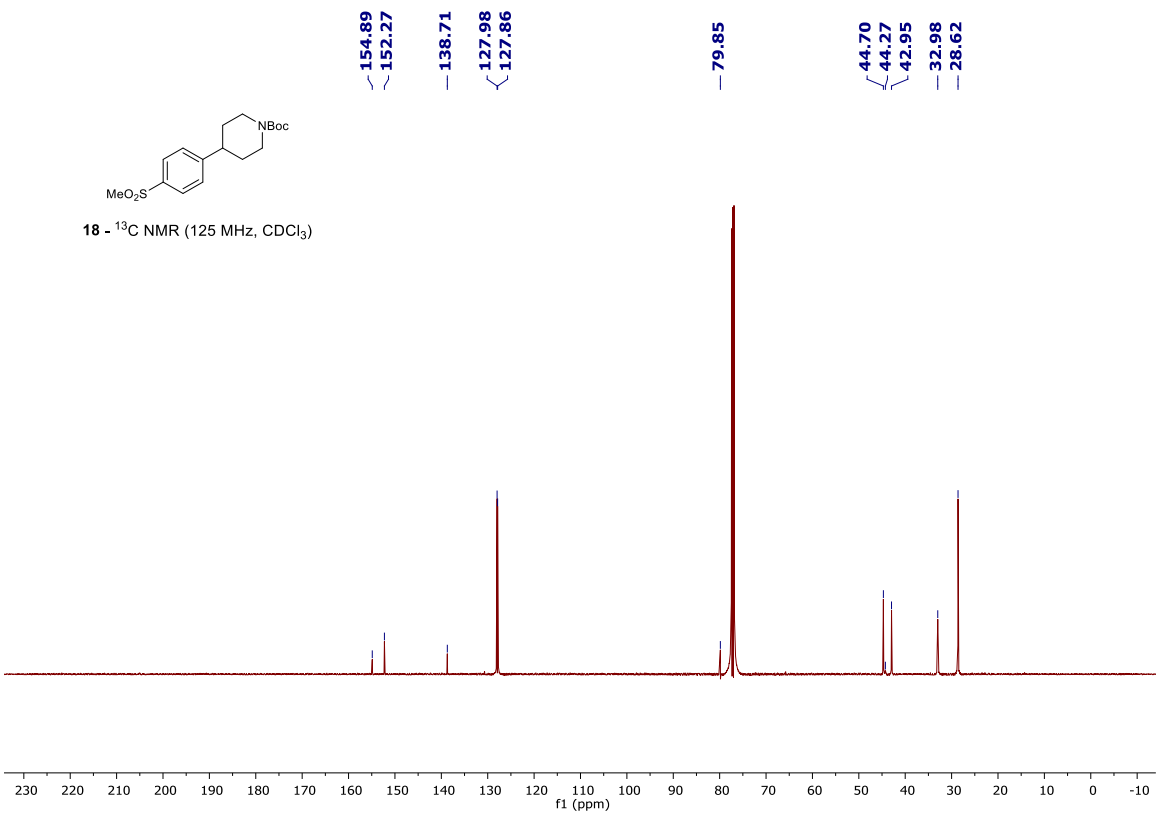
16 - ^{1}H NMR (500 MHz, $CDCl_3$)



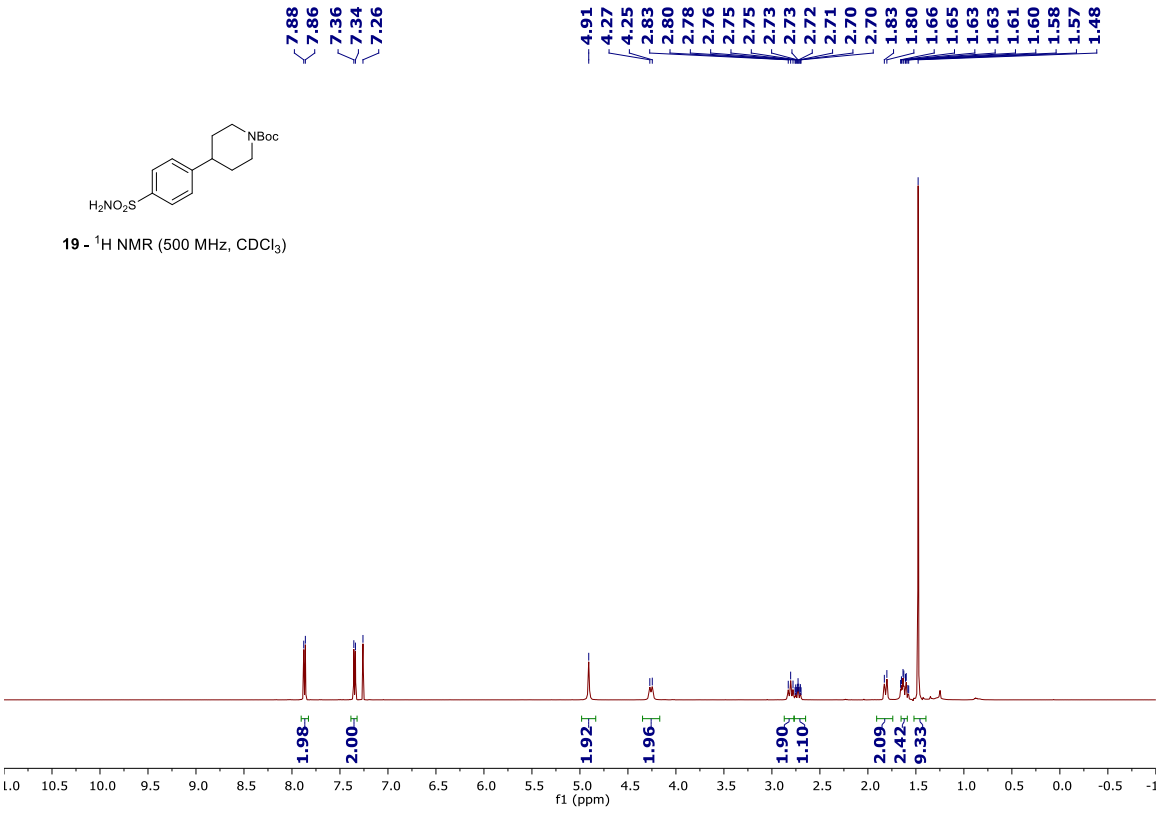
16 - ^{13}C NMR (125 MHz, $CDCl_3$)



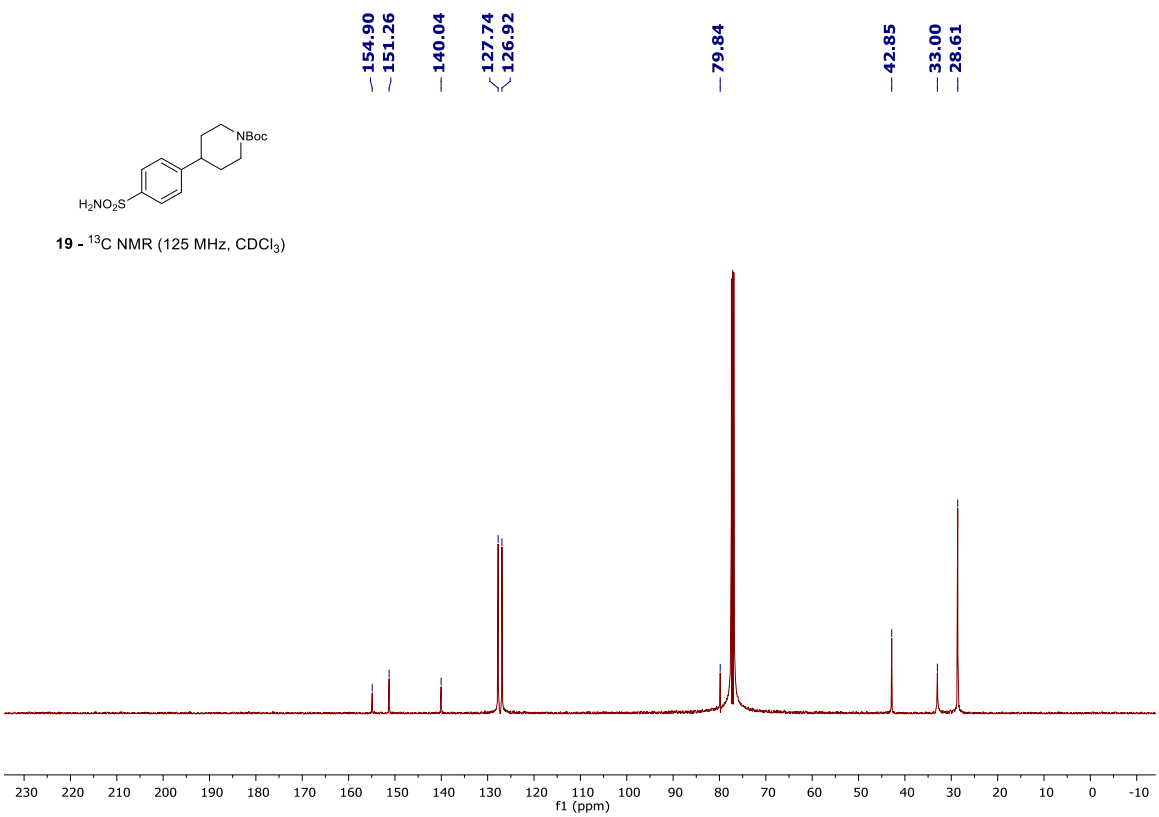
18 - ^{1}H NMR (500 MHz, $CDCl_3$)



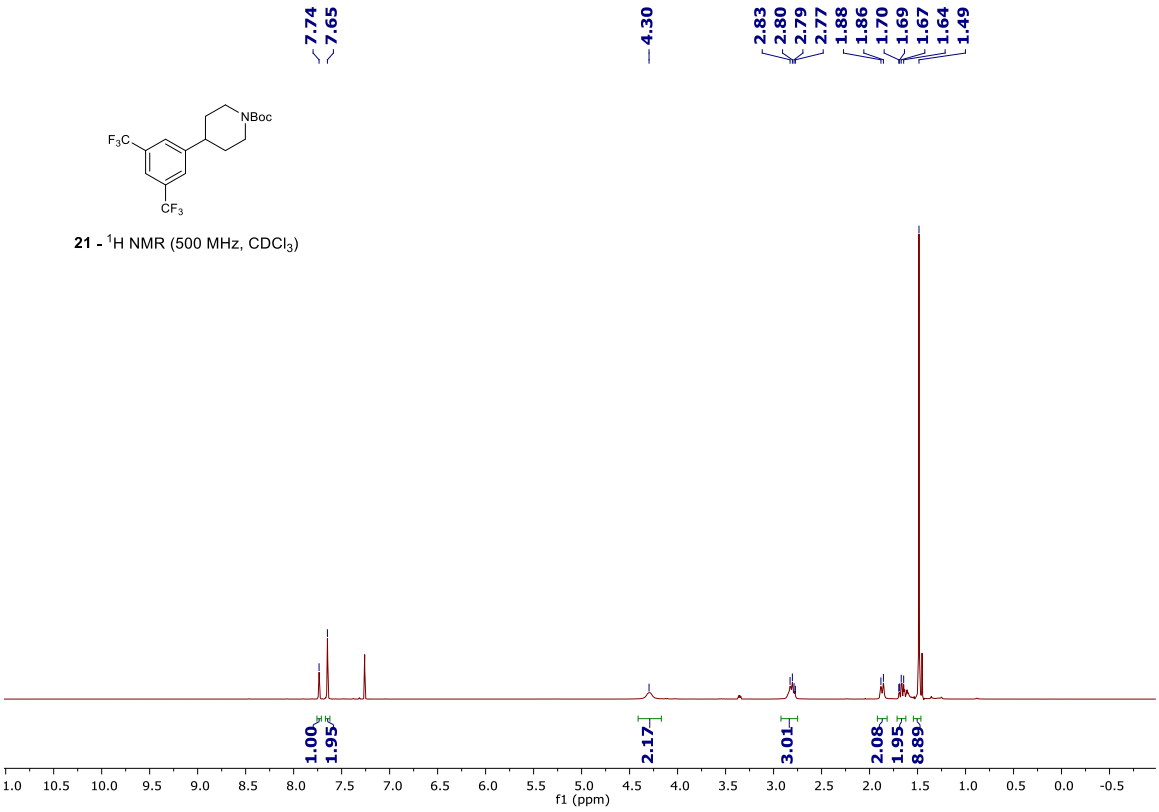
18 - ^{13}C NMR (125 MHz, $CDCl_3$)



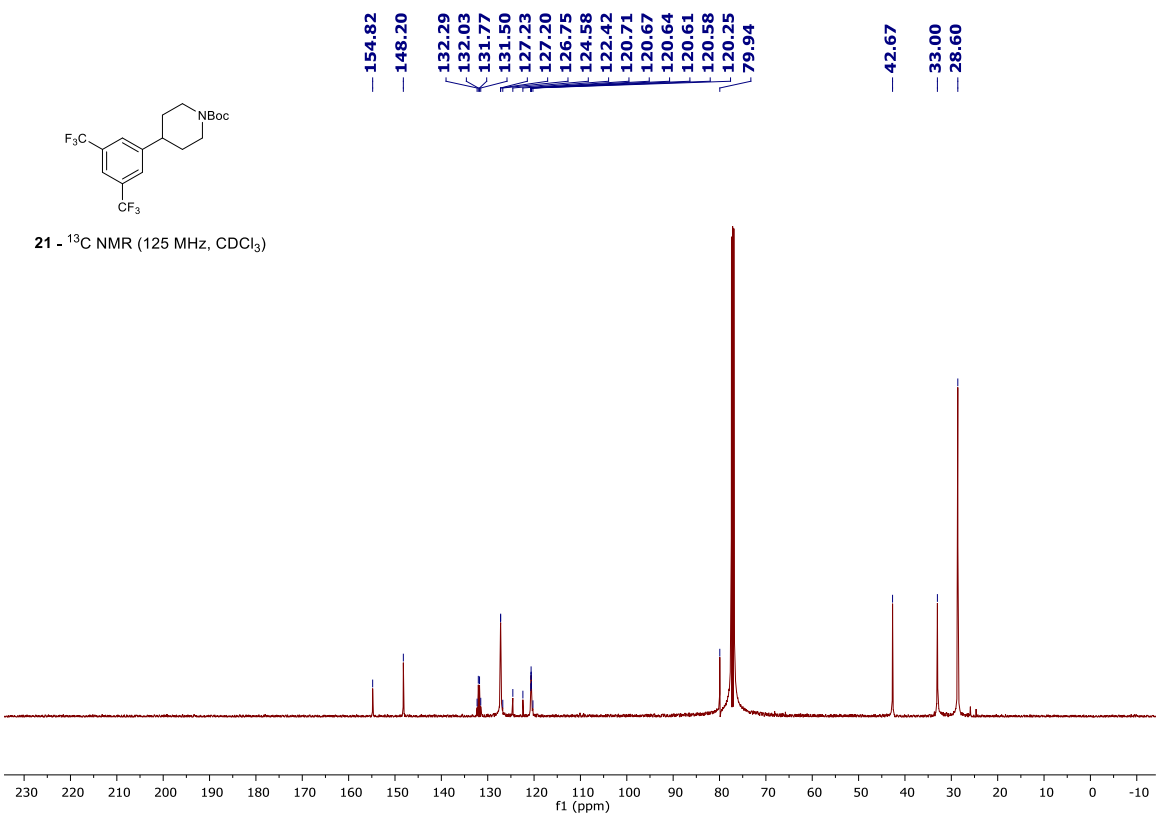
19 - ^{1}H NMR (500 MHz, $CDCl_3$)



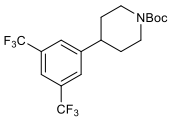
19 - ^{13}C NMR (125 MHz, $CDCl_3$)



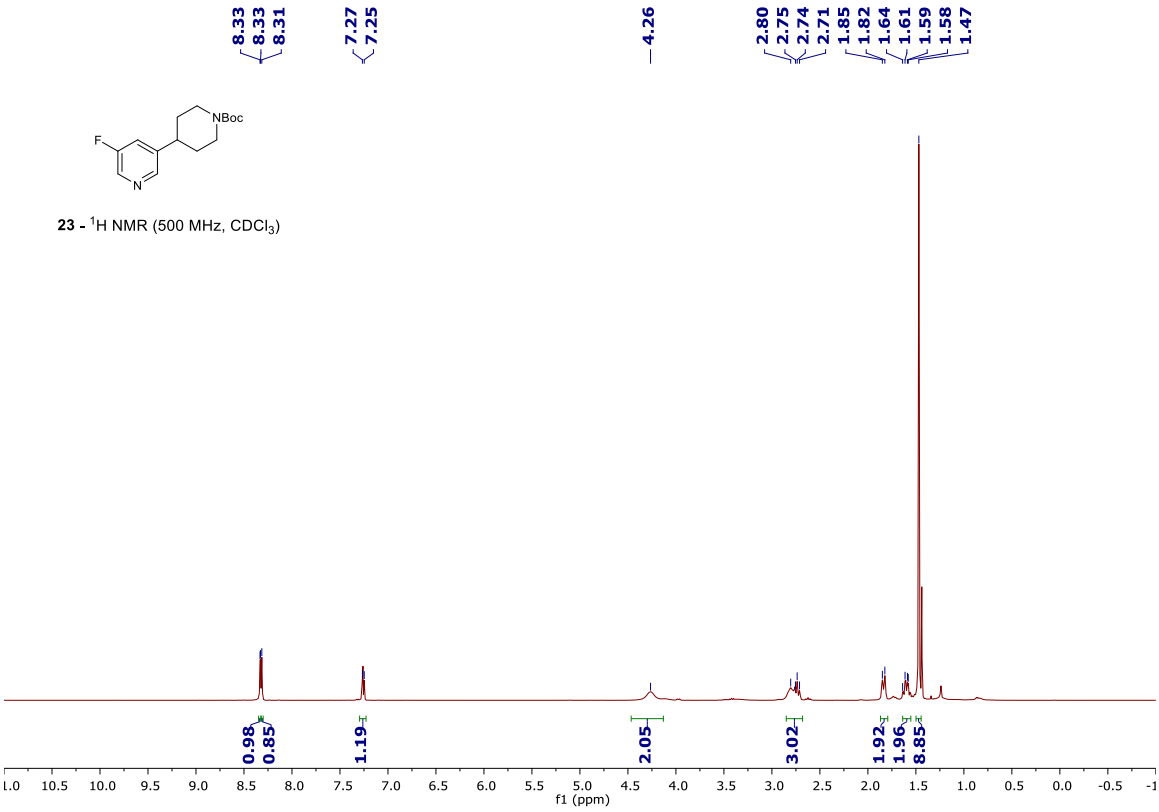
21 - ^{1}H NMR (500 MHz, $CDCl_3$)



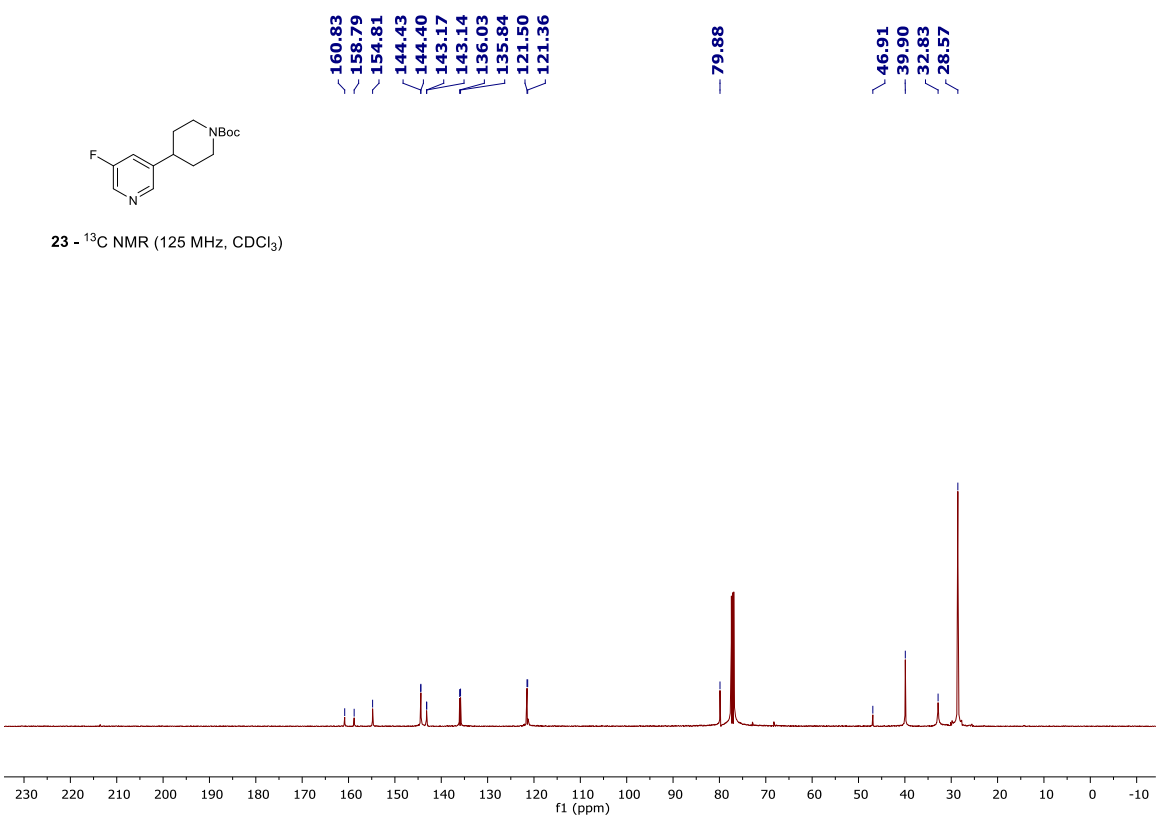
21 - ^{13}C NMR (125 MHz, $CDCl_3$)



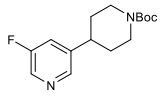
21 - ^{19}F NMR (282 MHz, $CDCl_3$)



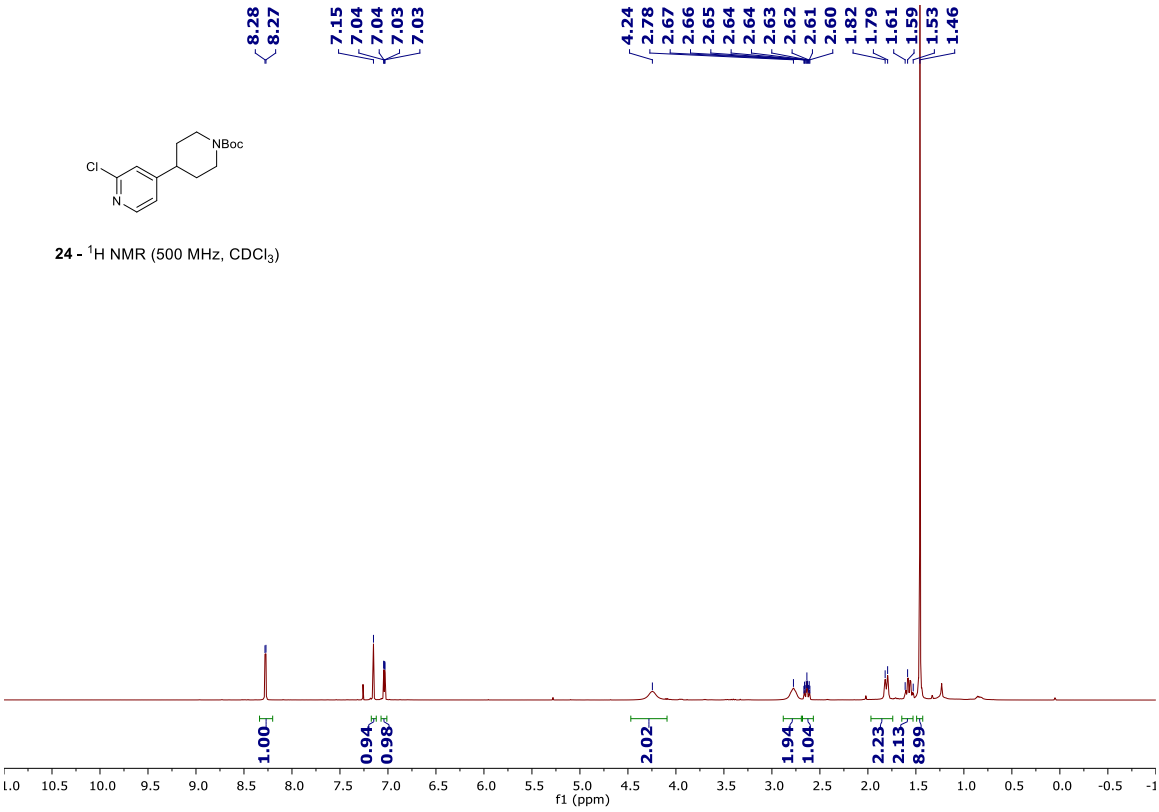
23 - ^{1}H NMR (500 MHz, $CDCl_3$)



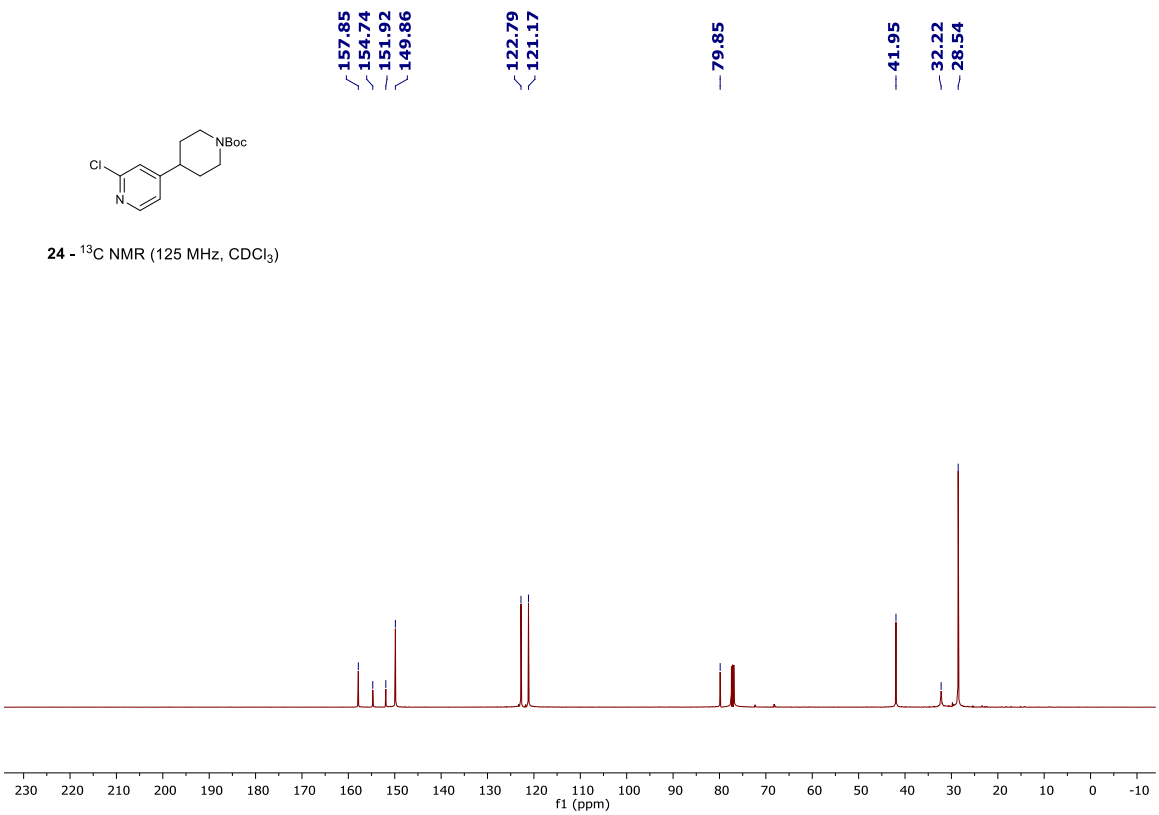
23 - ^{13}C NMR (125 MHz, $CDCl_3$)



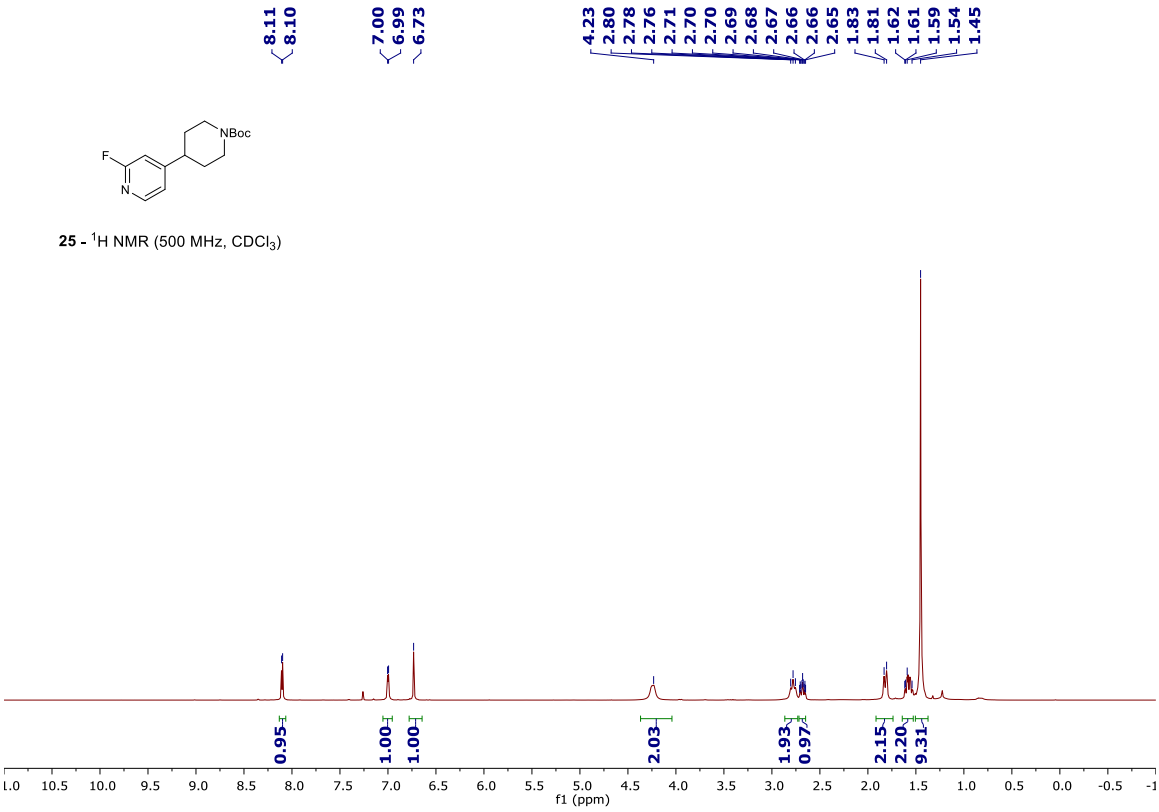
23 - ^{19}F NMR (282 MHz, $CDCl_3$)



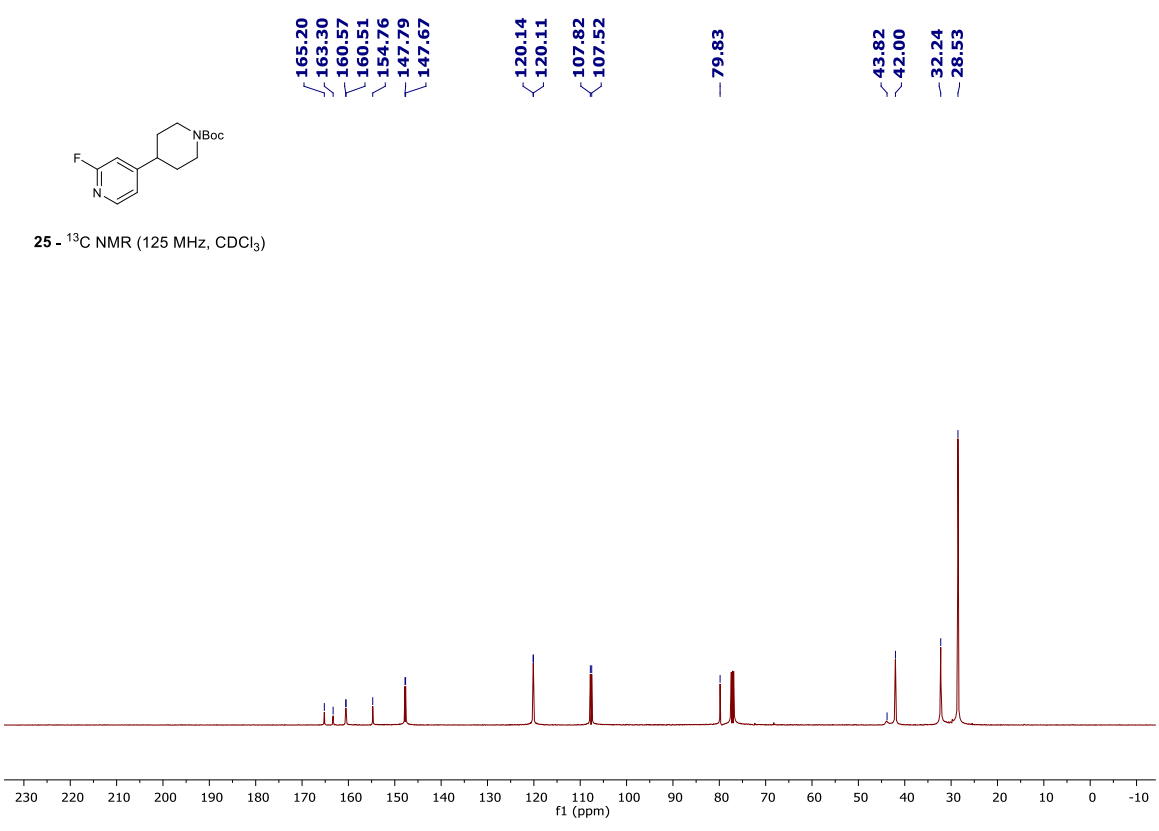
24 - ^{1}H NMR (500 MHz, $CDCl_3$)



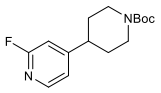
24 - ^{13}C NMR (125 MHz, $CDCl_3$)



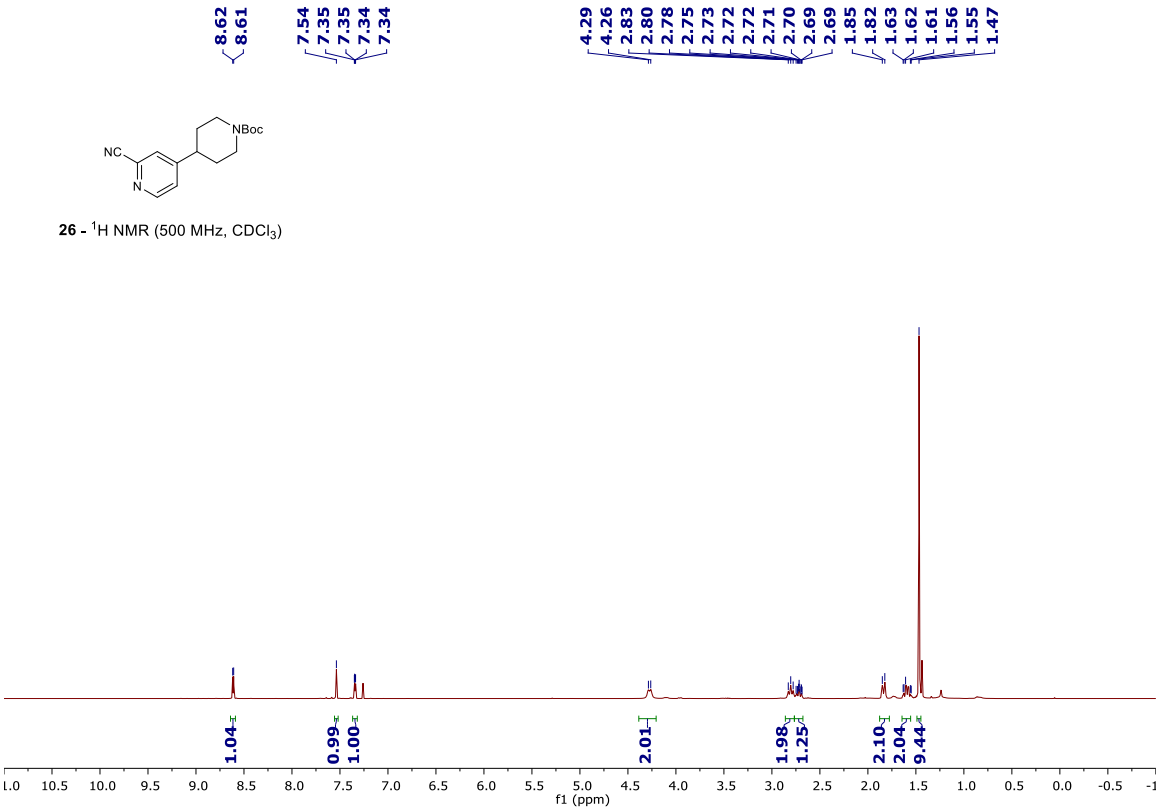
25 - ^{1}H NMR (500 MHz, $CDCl_3$)



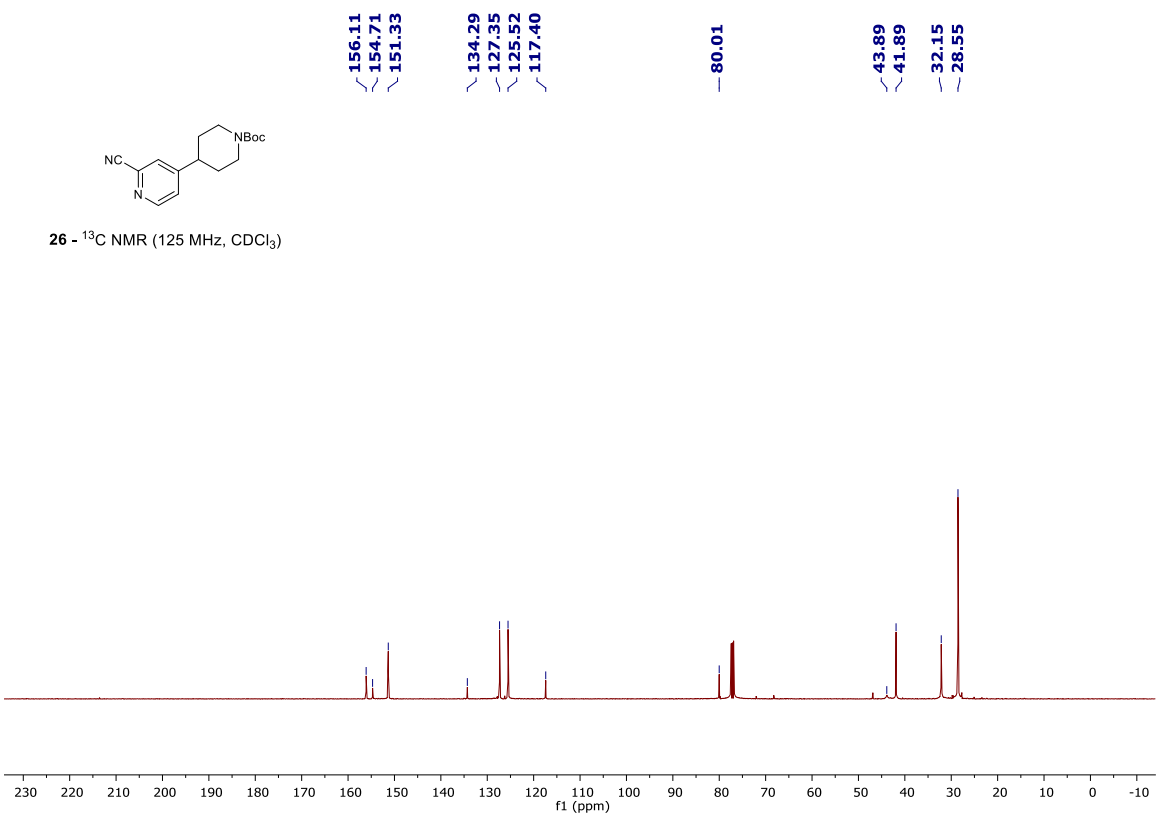
25 - ^{13}C NMR (125 MHz, $CDCl_3$)



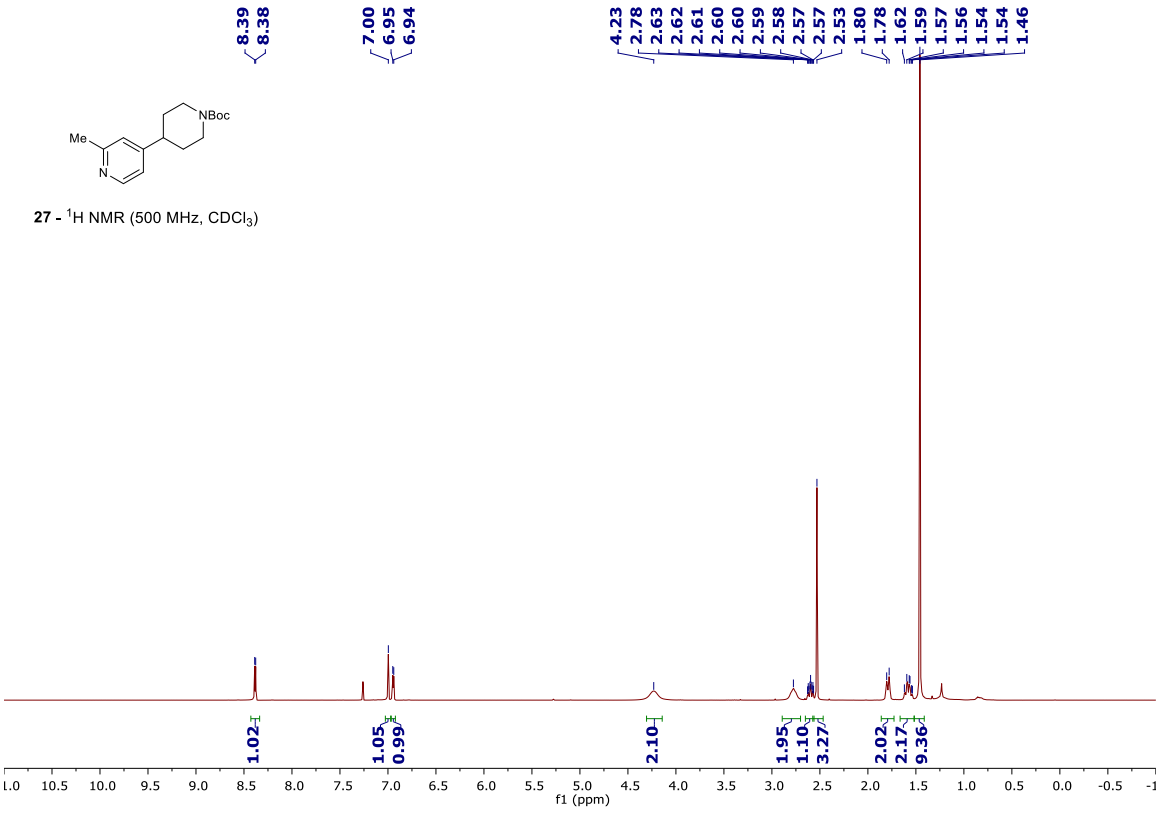
25 - ^{19}F NMR (282 MHz, $CDCl_3$)



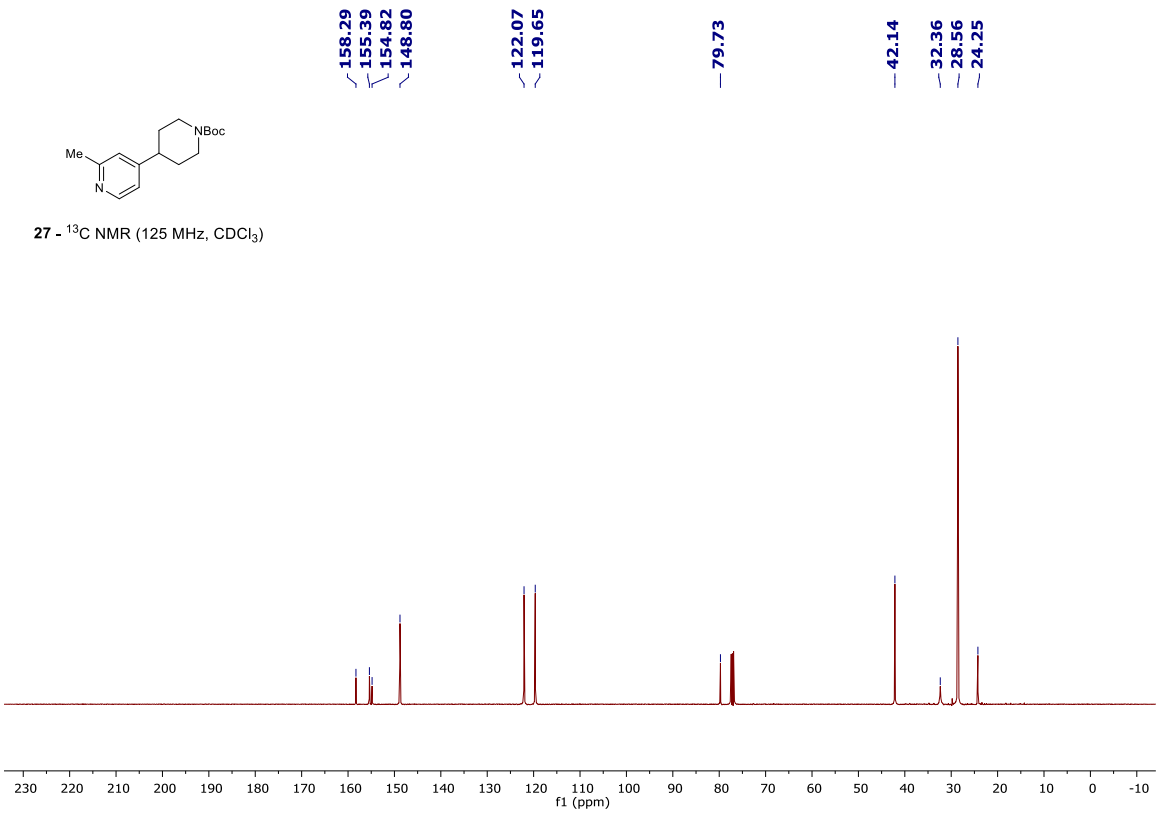
26 - ^{1}H NMR (500 MHz, $CDCl_3$)



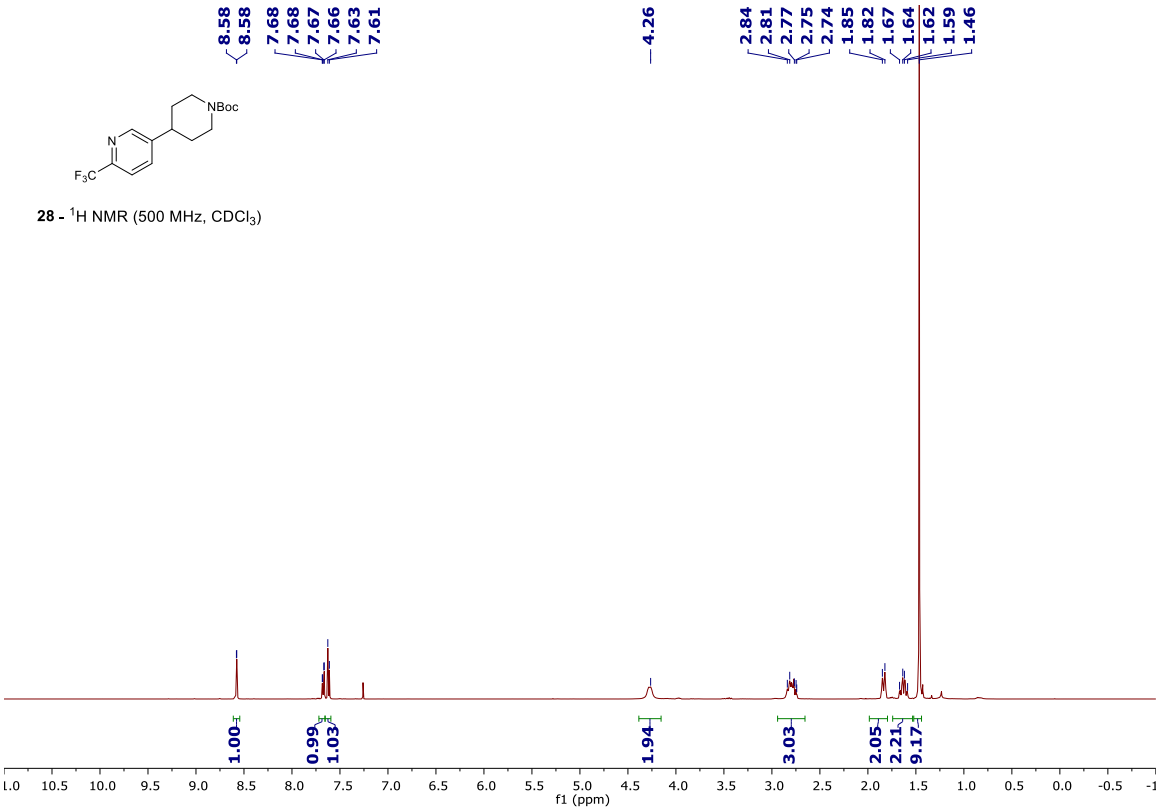
26 - ^{13}C NMR (125 MHz, $CDCl_3$)



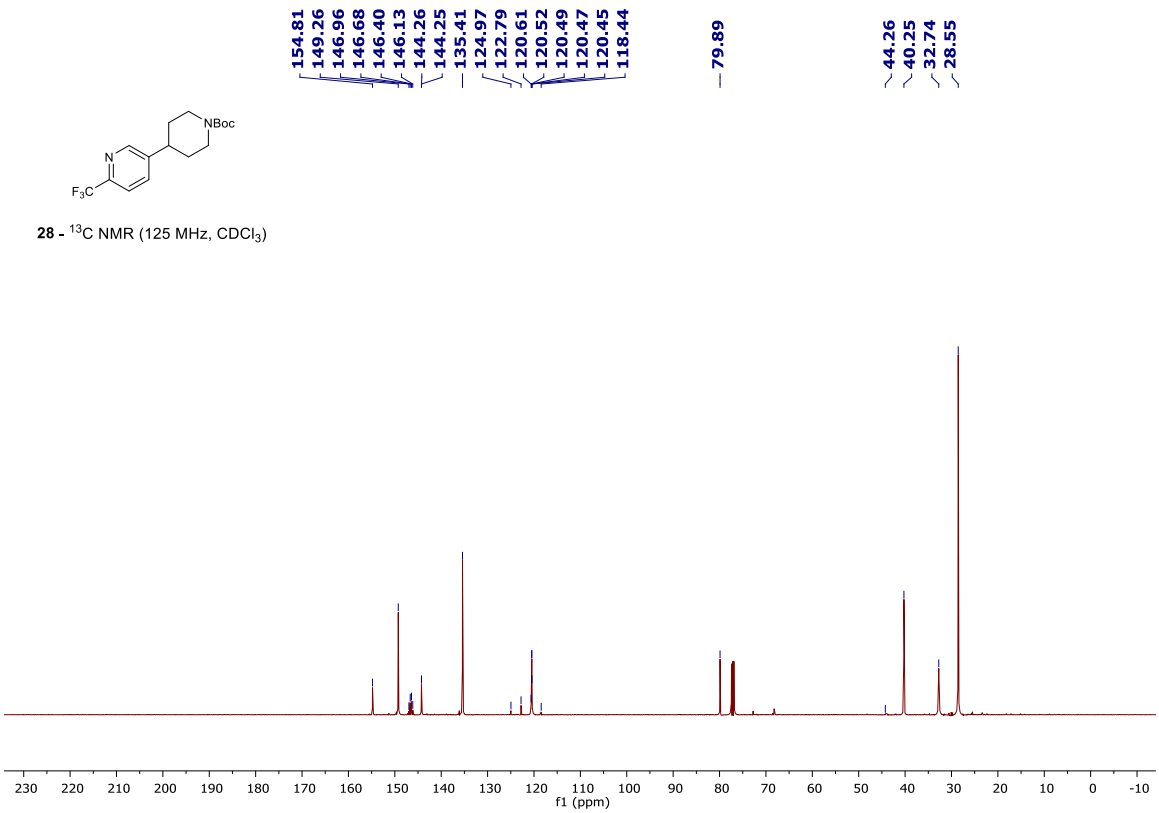
27 - ^{1}H NMR (500 MHz, $CDCl_3$)



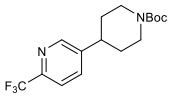
27 - ^{13}C NMR (125 MHz, $CDCl_3$)



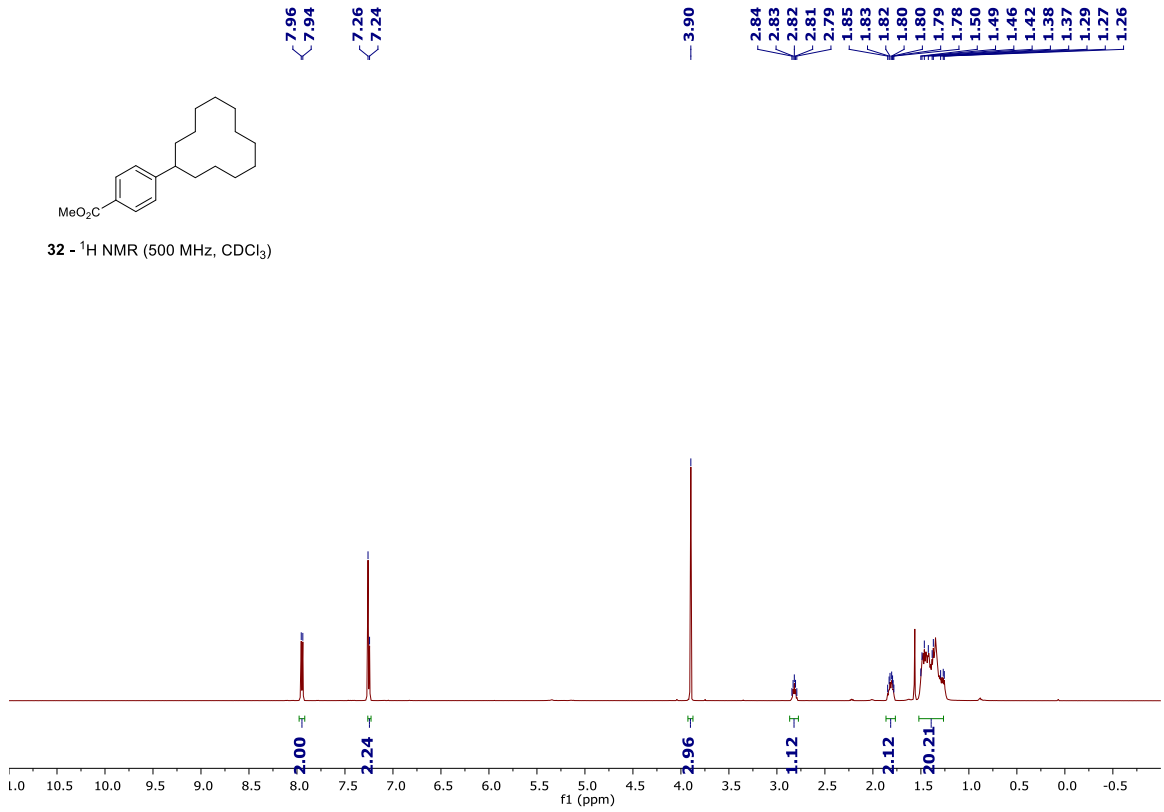
28 - ^{1}H NMR (500 MHz, $CDCl_3$)



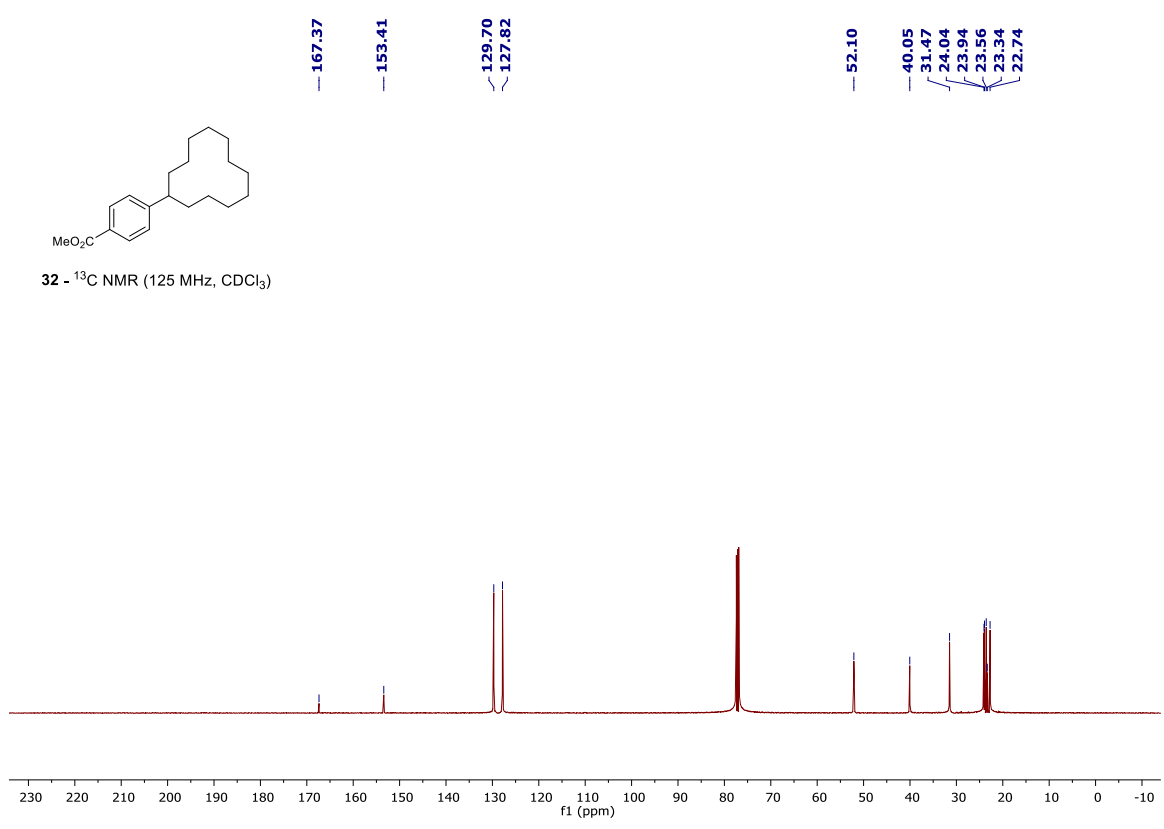
28 - ^{13}C NMR (125 MHz, $CDCl_3$)



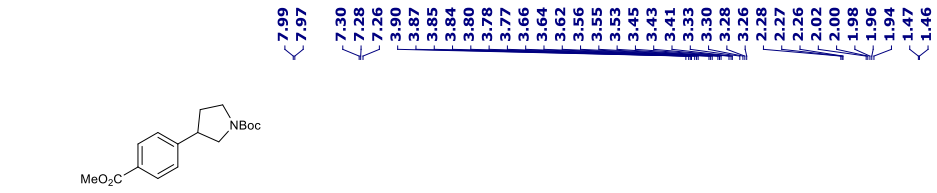
28 - ^{19}F NMR (282 MHz, $CDCl_3$)



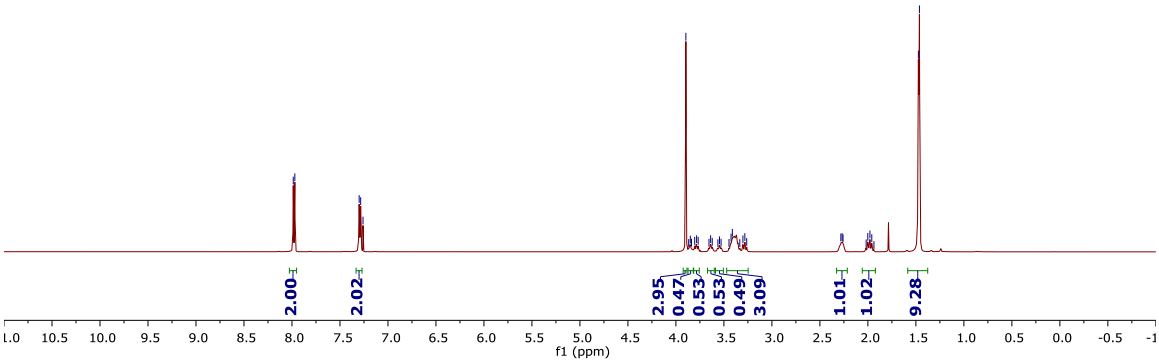
32 - ^{1}H NMR (500 MHz, $CDCl_3$)

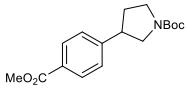


32 - ^{13}C NMR (125 MHz, $CDCl_3$)

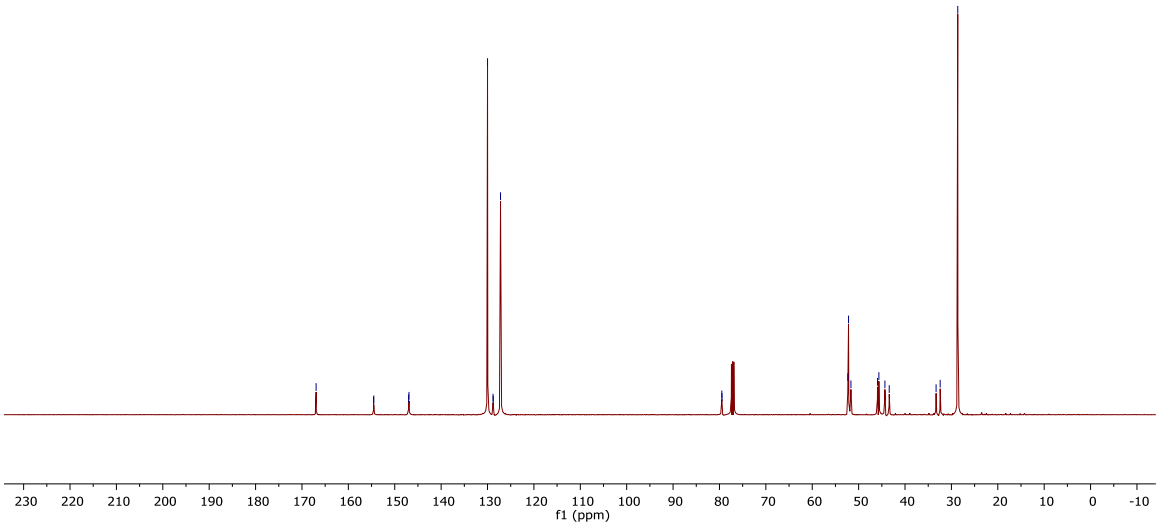


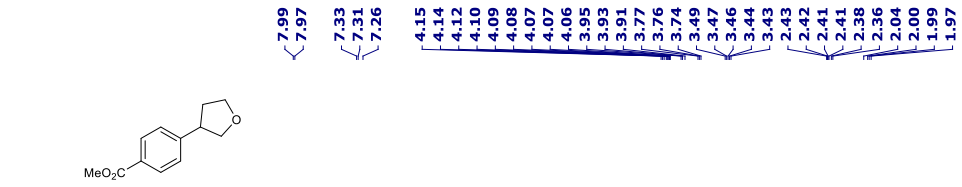
(±)-34 - ^{1}H NMR (500 MHz, $CDCl_3$)



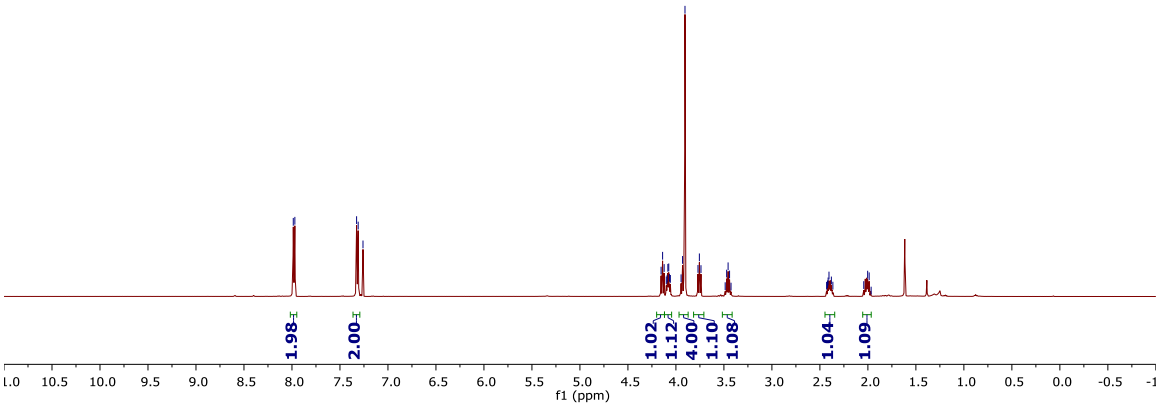


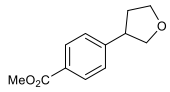
(±)-34 - ^{13}C NMR (125 MHz, $CDCl_3$)



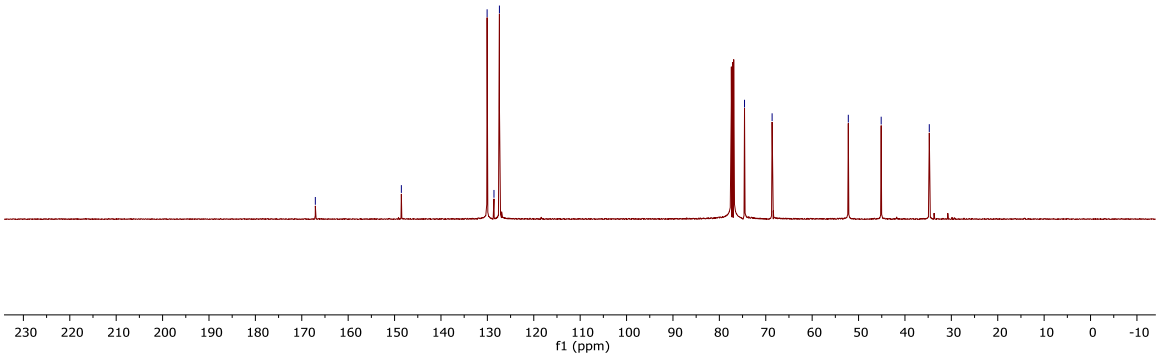


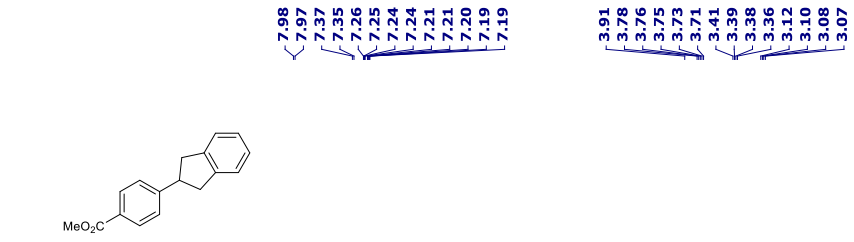
(±)-35 - ^{1}H NMR (500 MHz, $CDCl_3$)



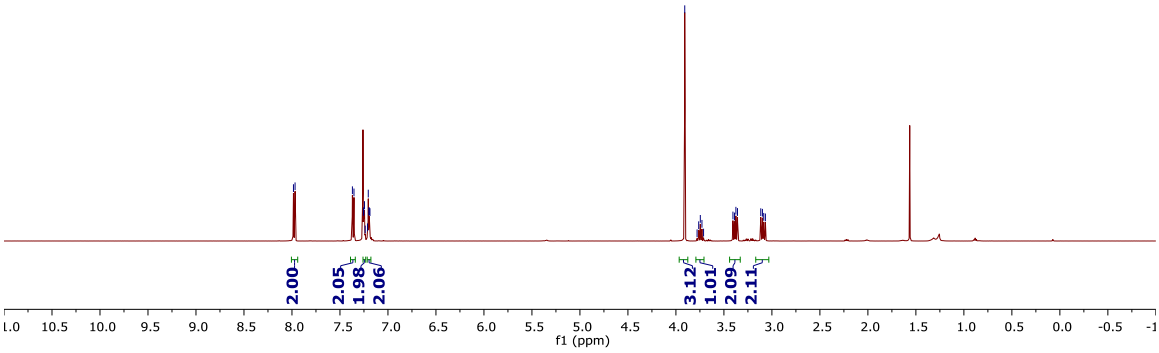


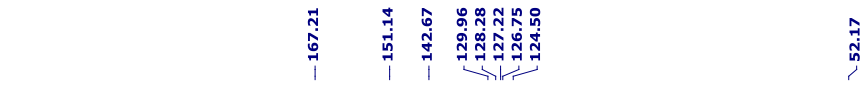
(±)-35 - ^{13}C NMR (125 MHz, $CDCl_3$)



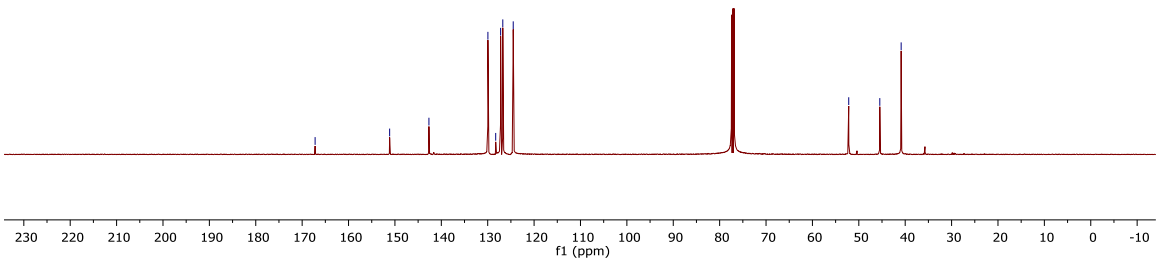


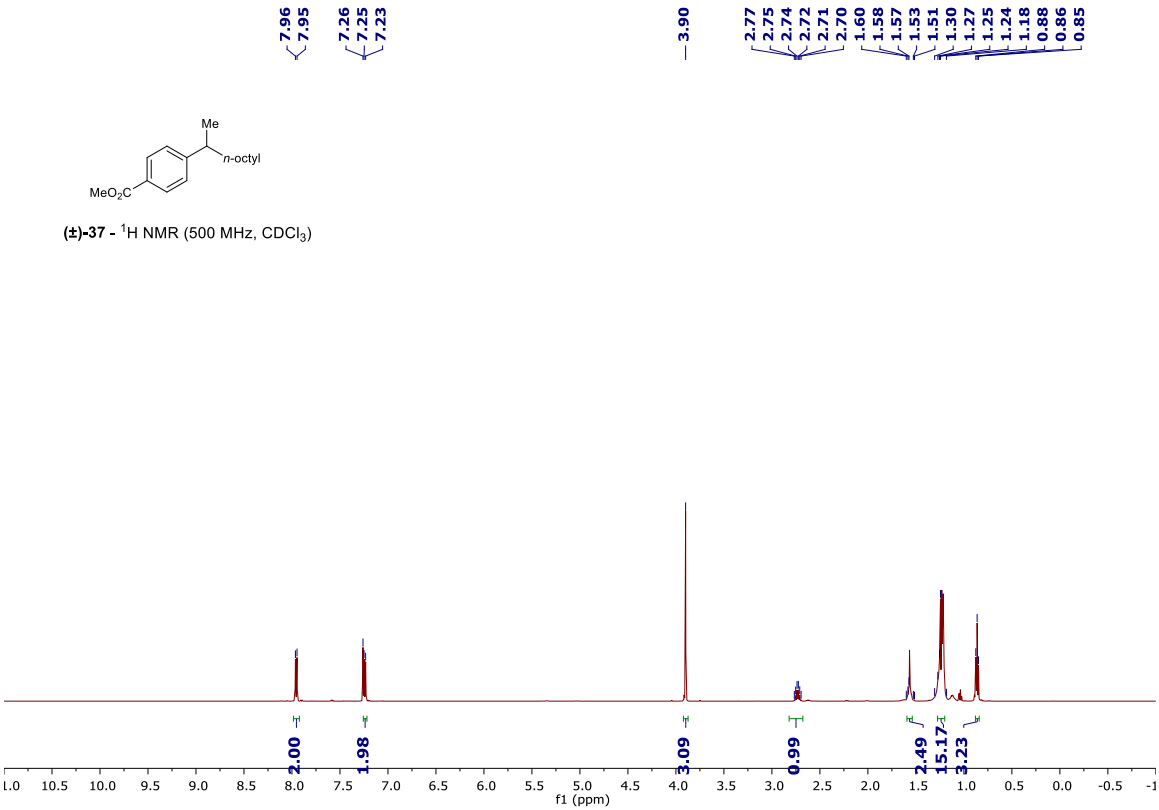
36 - ^{1}H NMR (500 MHz, $CDCl_3$)



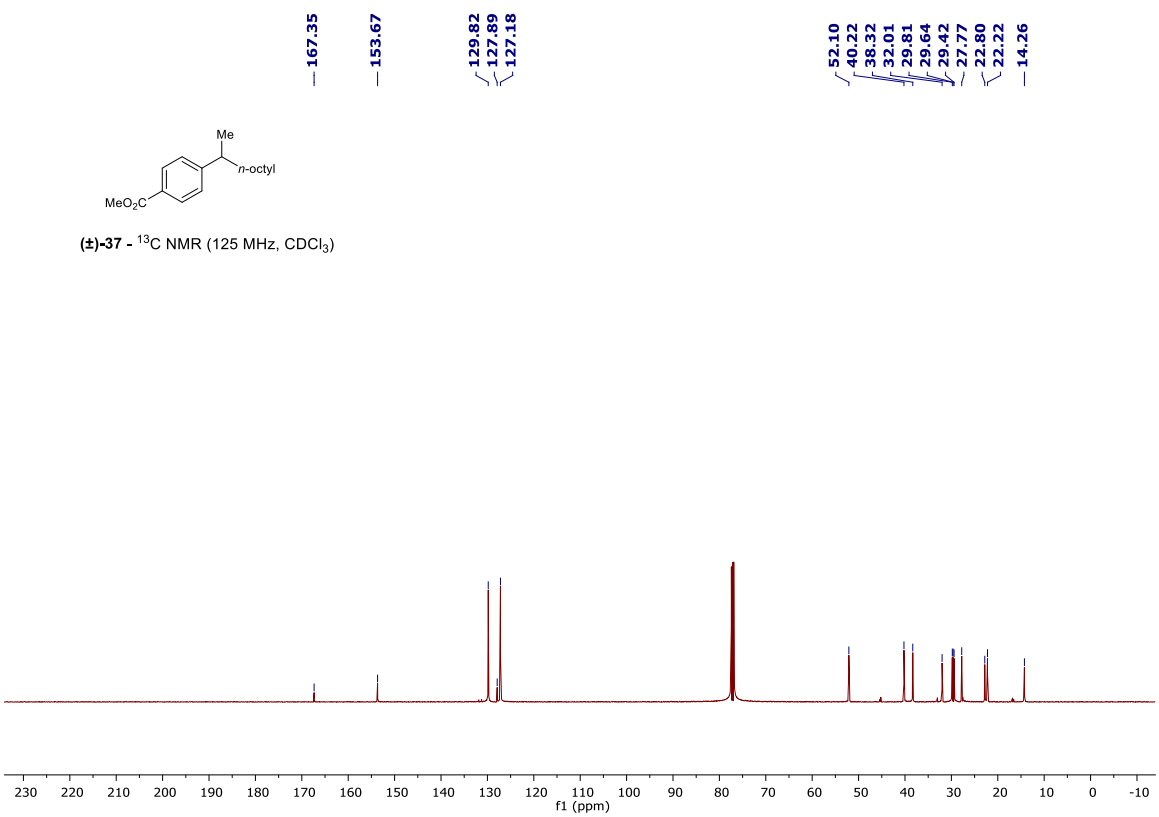


36 - ^{13}C NMR (125 MHz, $CDCl_3$)



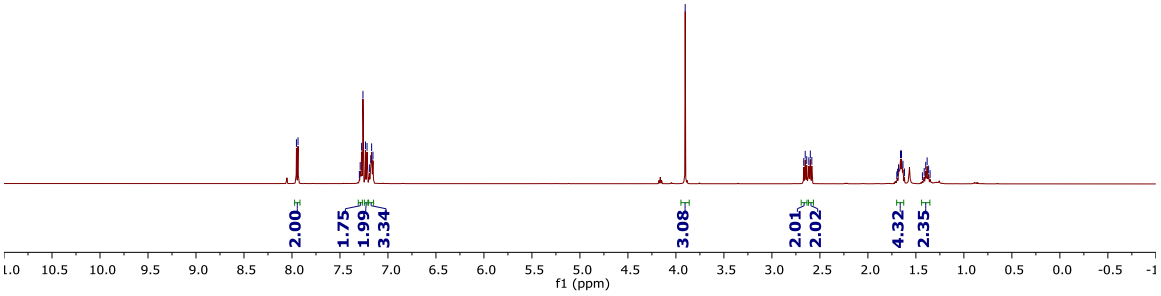


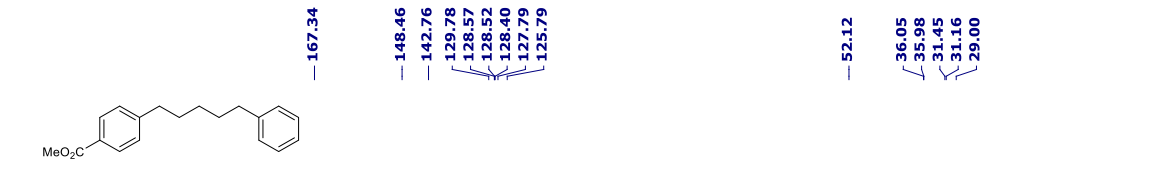
(±)-37 - ^{1}H NMR (500 MHz, $CDCl_3$)



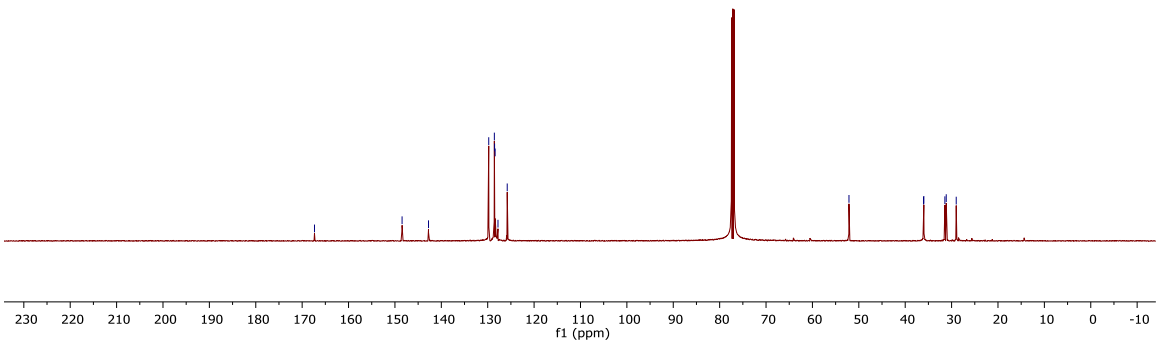
(±)-37 - ^{13}C NMR (125 MHz, $CDCl_3$)

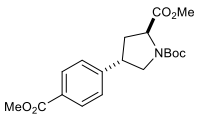
38 - ^{1}H NMR (500 MHz, $CDCl_3$)



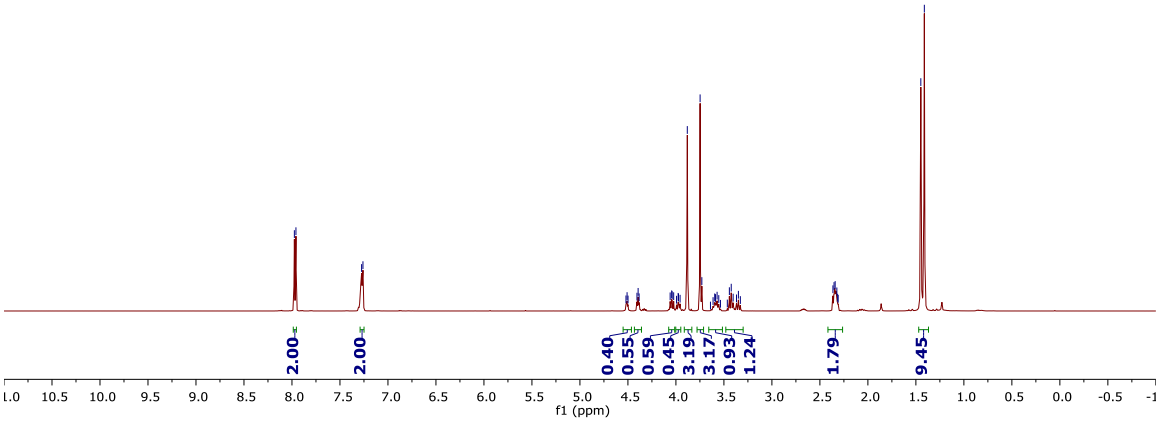


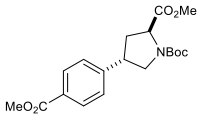
38 - ^{13}C NMR (125 MHz, $CDCl_3$)



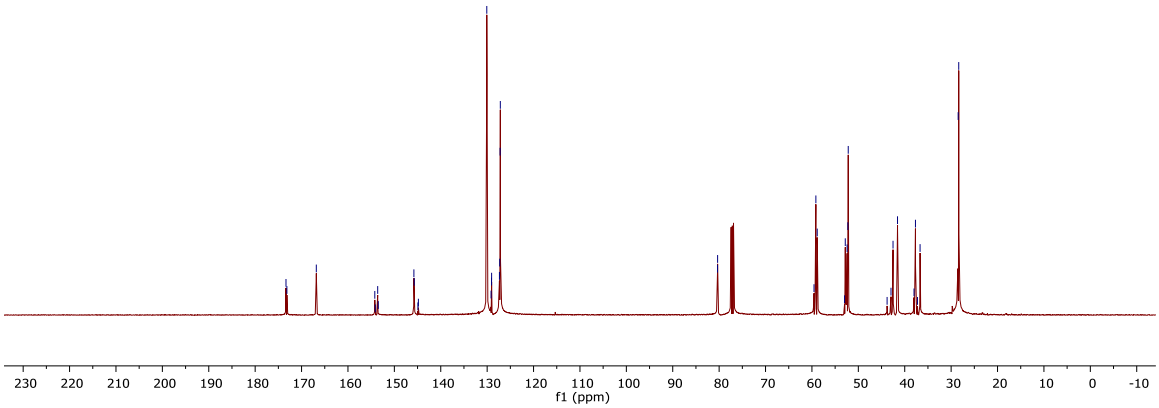


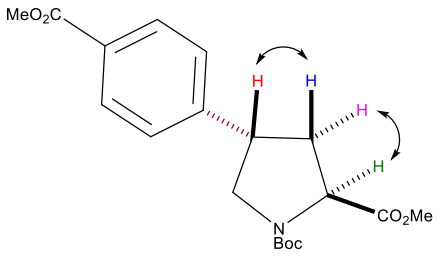
43 - ^{1}H NMR (500 MHz, $CDCl_3$), d.r. 7:1



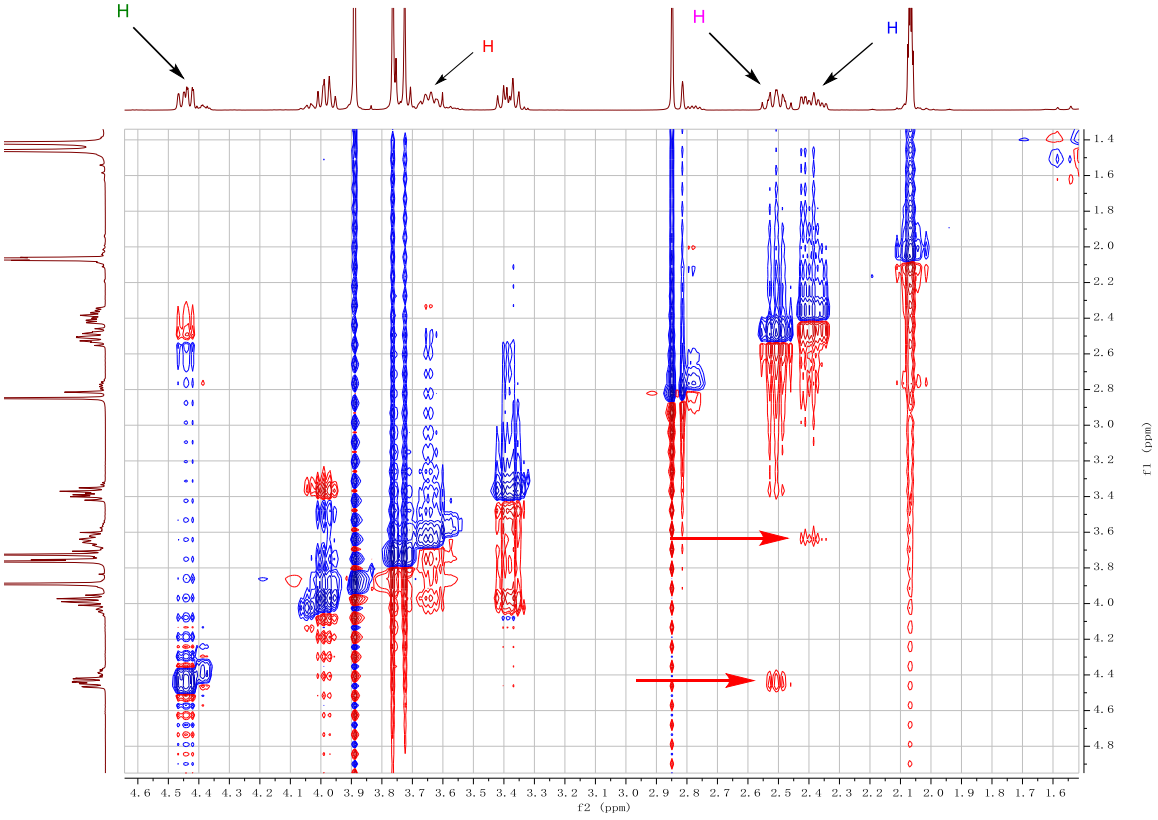


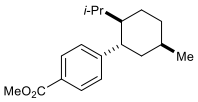
43 - ^{13}C NMR (125 MHz, $CDCl_3$), d.r. 7:1



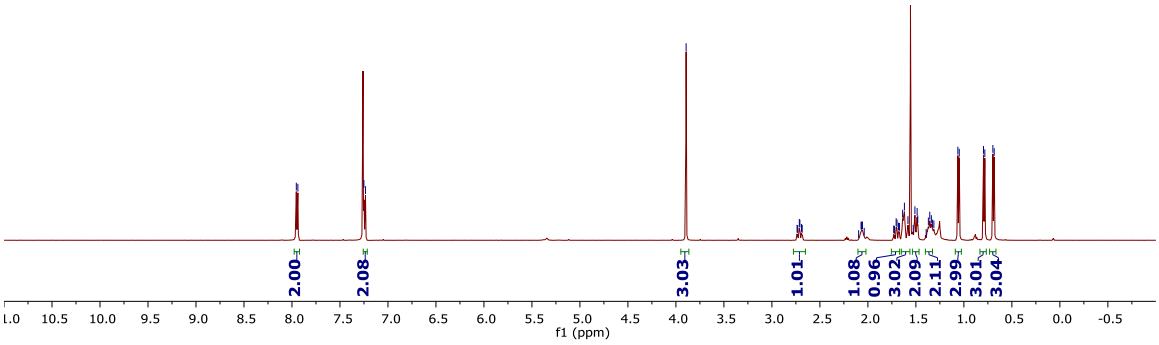


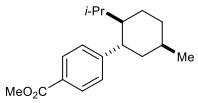
43 - NOESY, Acetone-d_6



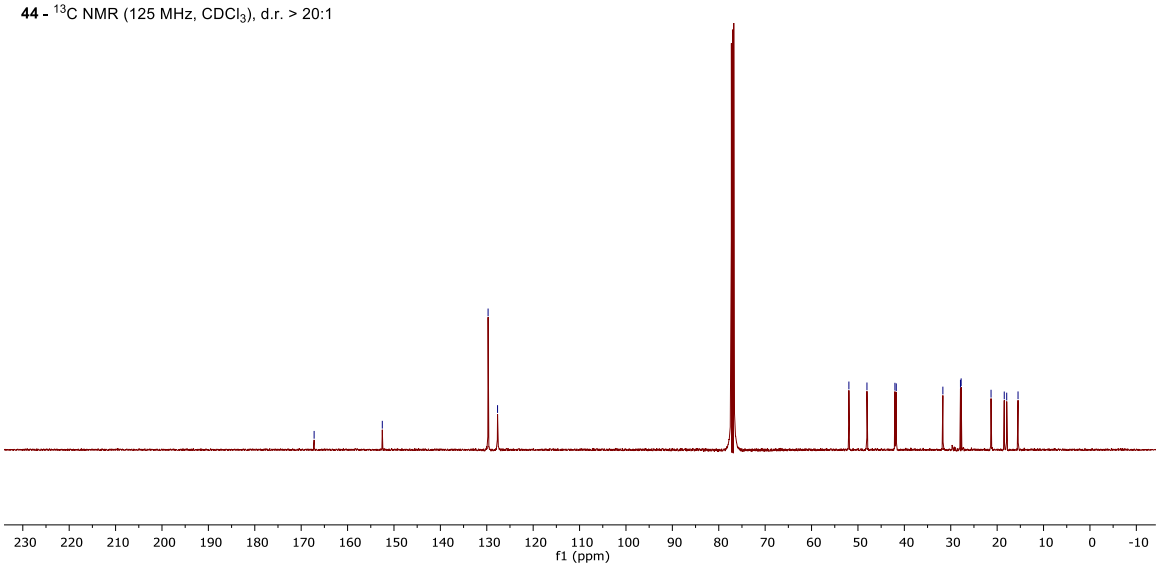


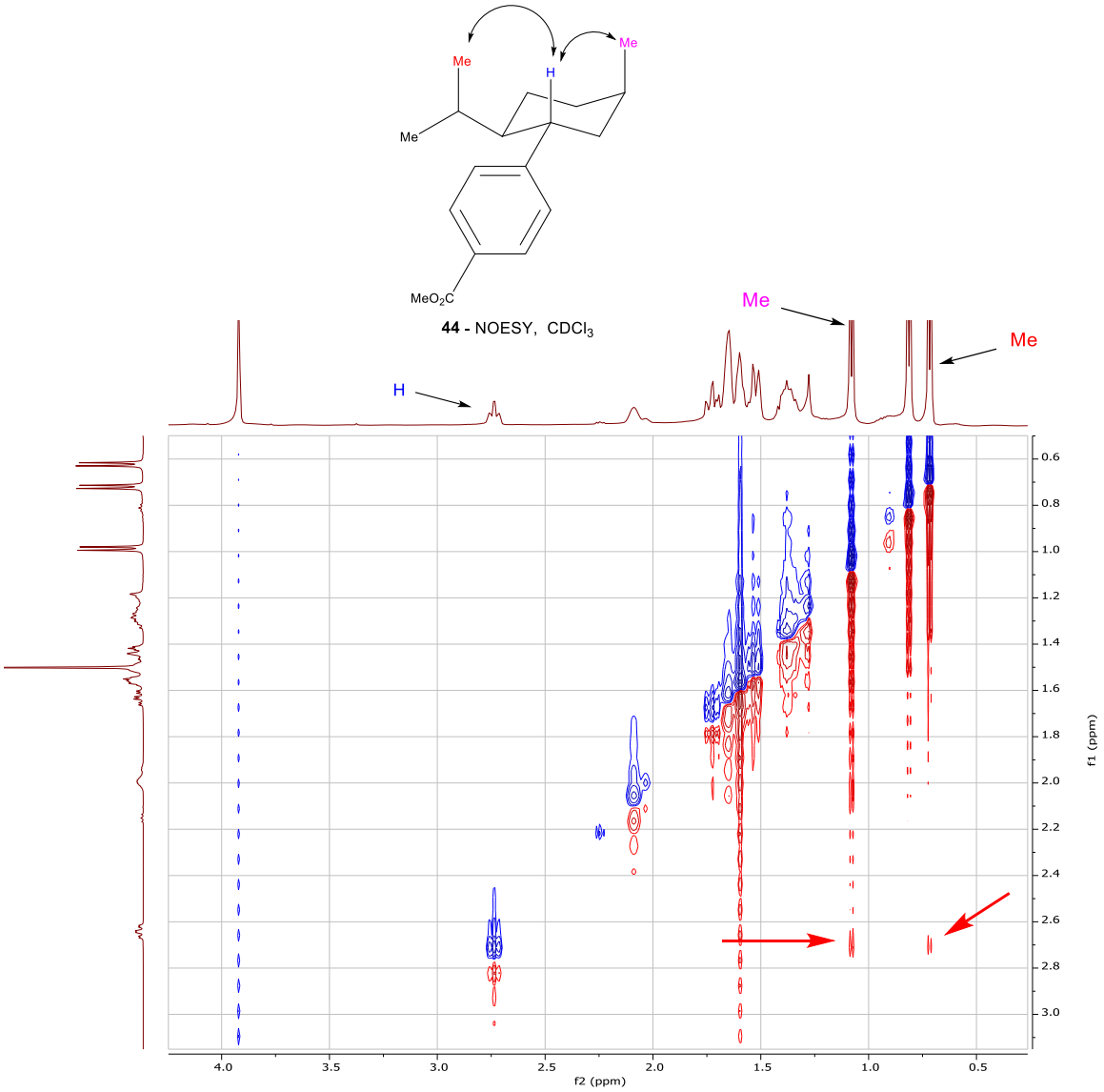
44 - ^{1}H NMR (500 MHz, $CDCl_3$), d.r. > 20:1



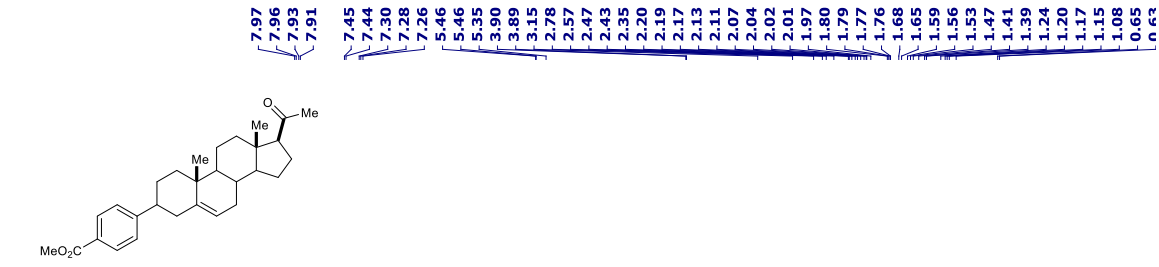


44 - ^{13}C NMR (125 MHz, $CDCl_3$), d.r. > 20:1

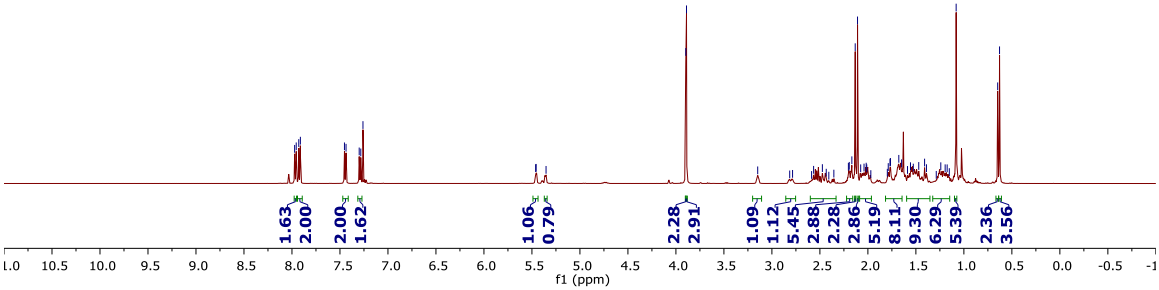


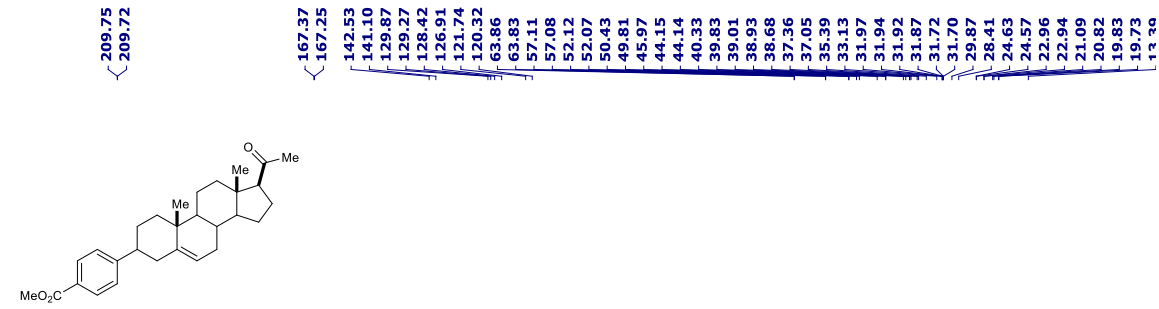


44 - NOESY, $CDCl_3$

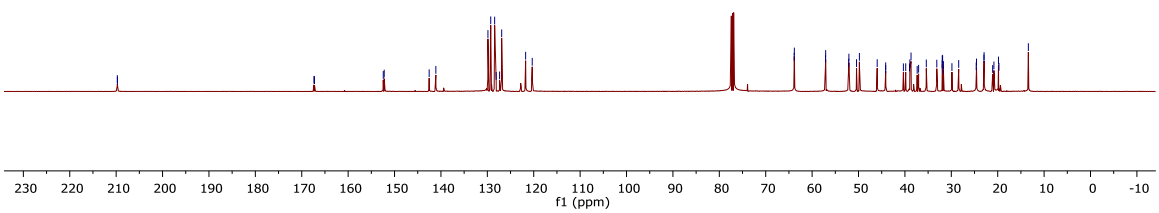


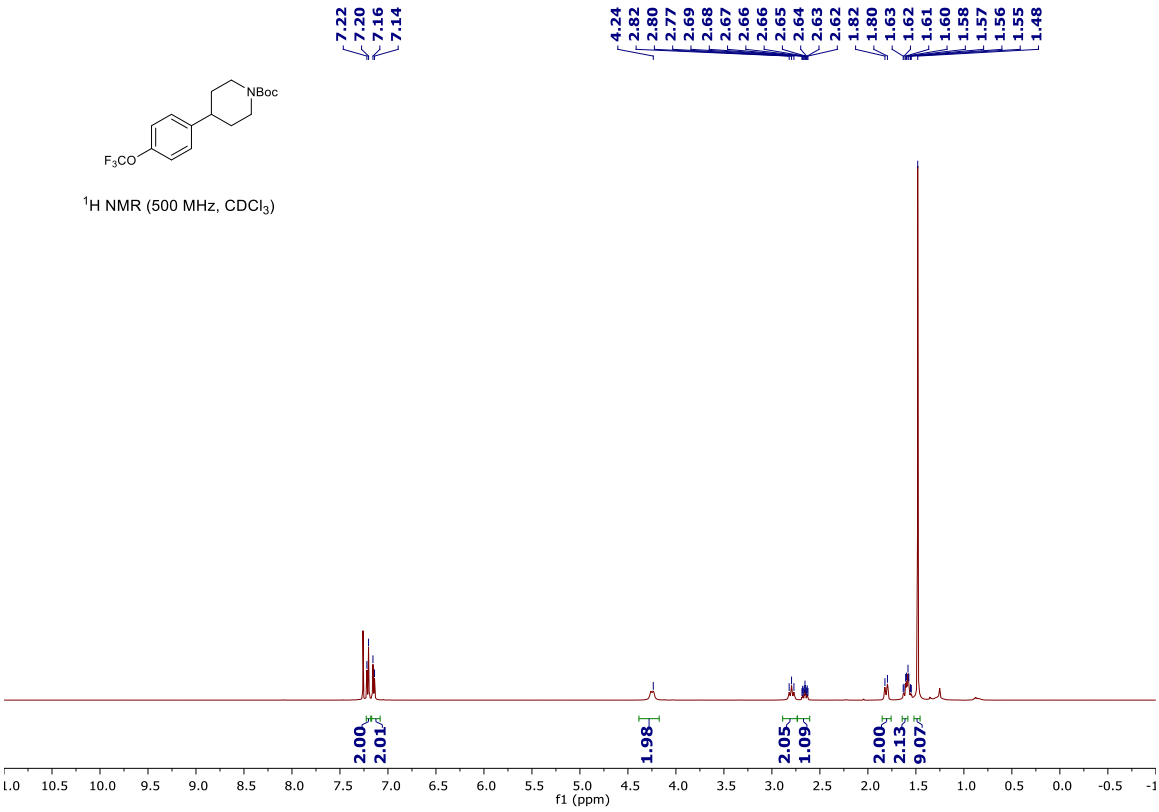
45 - ^{1}H NMR (500 MHz, $CDCl_3$), d.r. 1.3:1



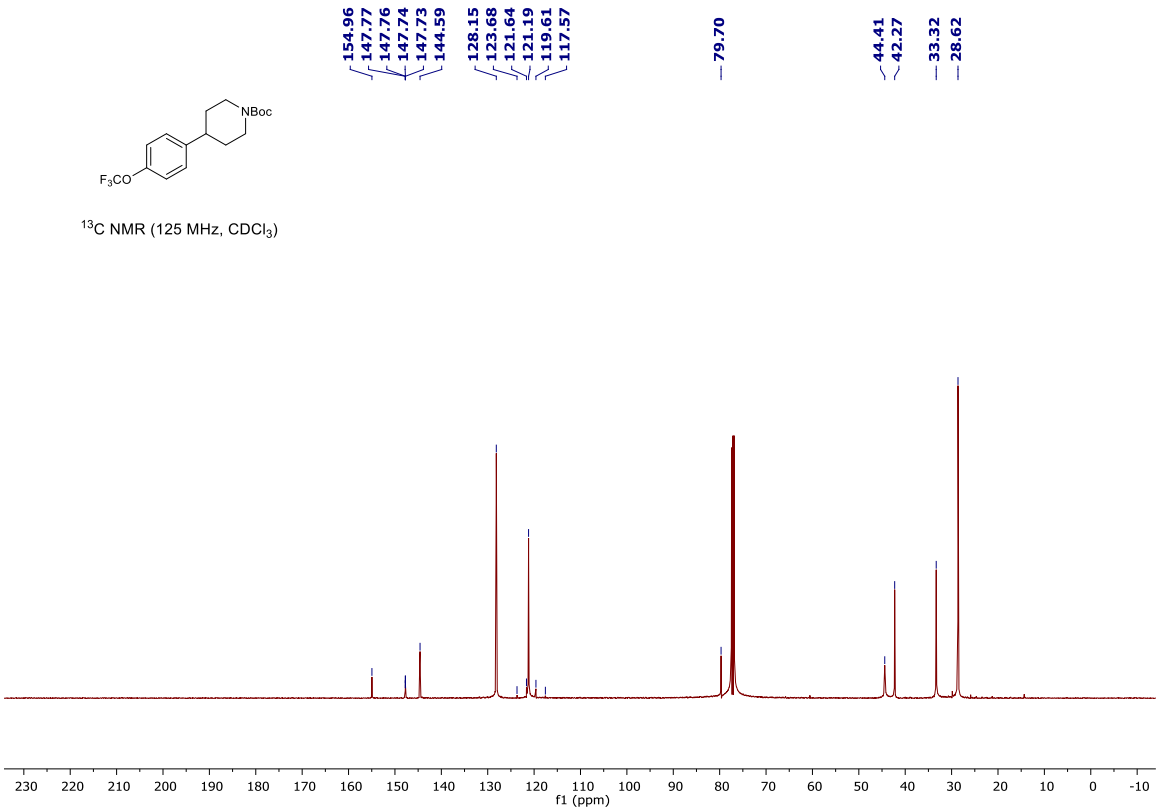


45 - ^{13}C NMR (125 MHz, $CDCl_3$), d.r. 1.3:1

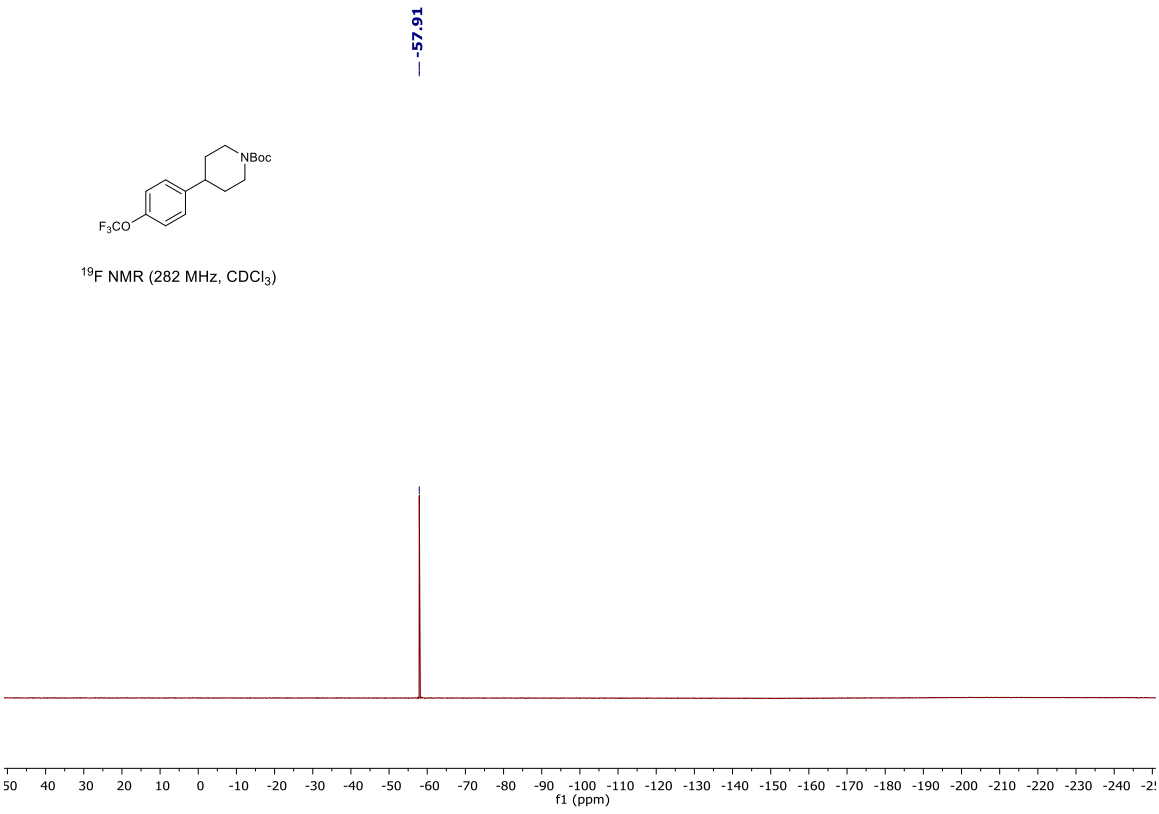




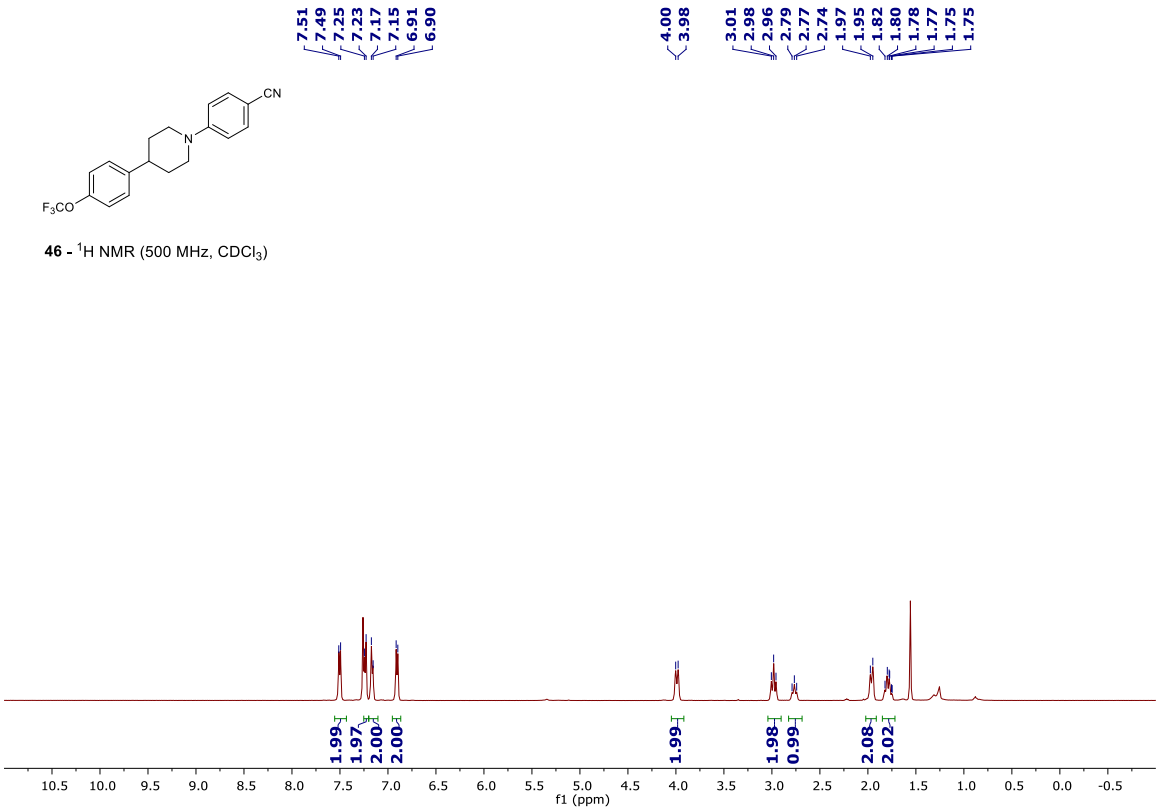
^{1}H NMR (500 MHz, $CDCl_3$)



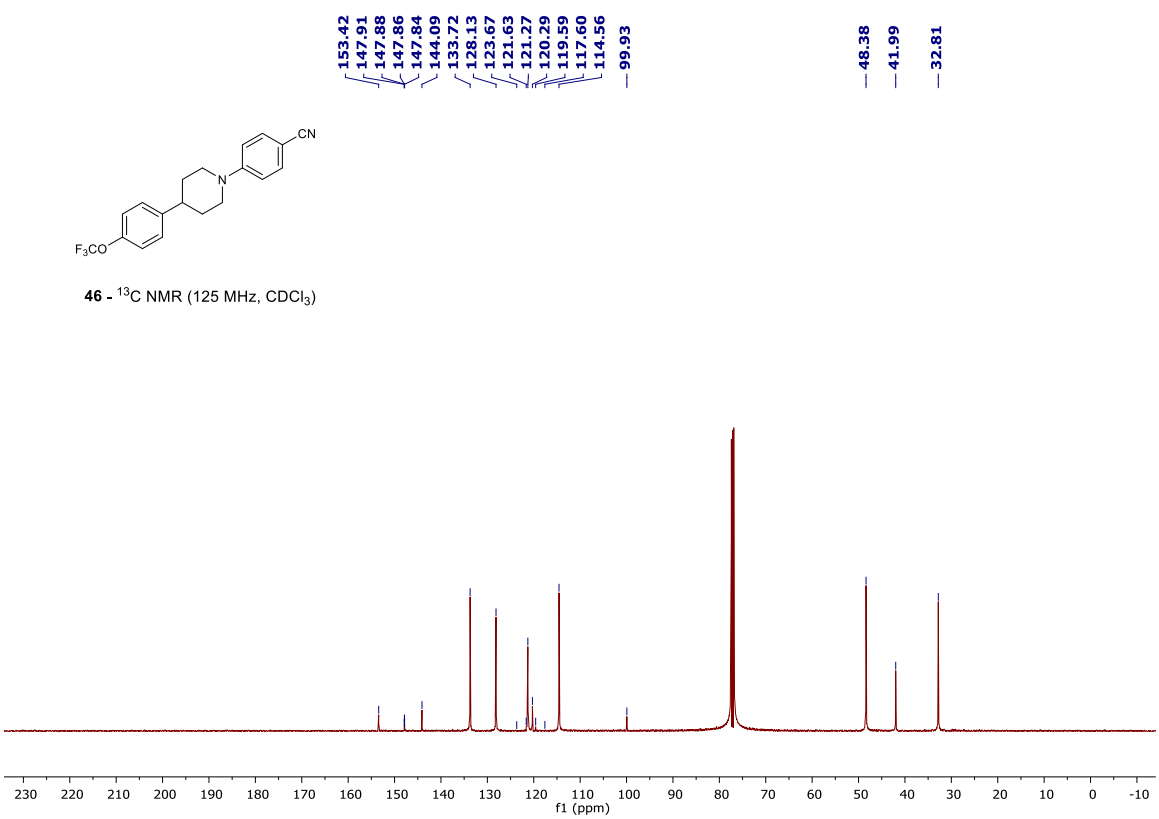
^{13}C NMR (125 MHz, $CDCl_3$)



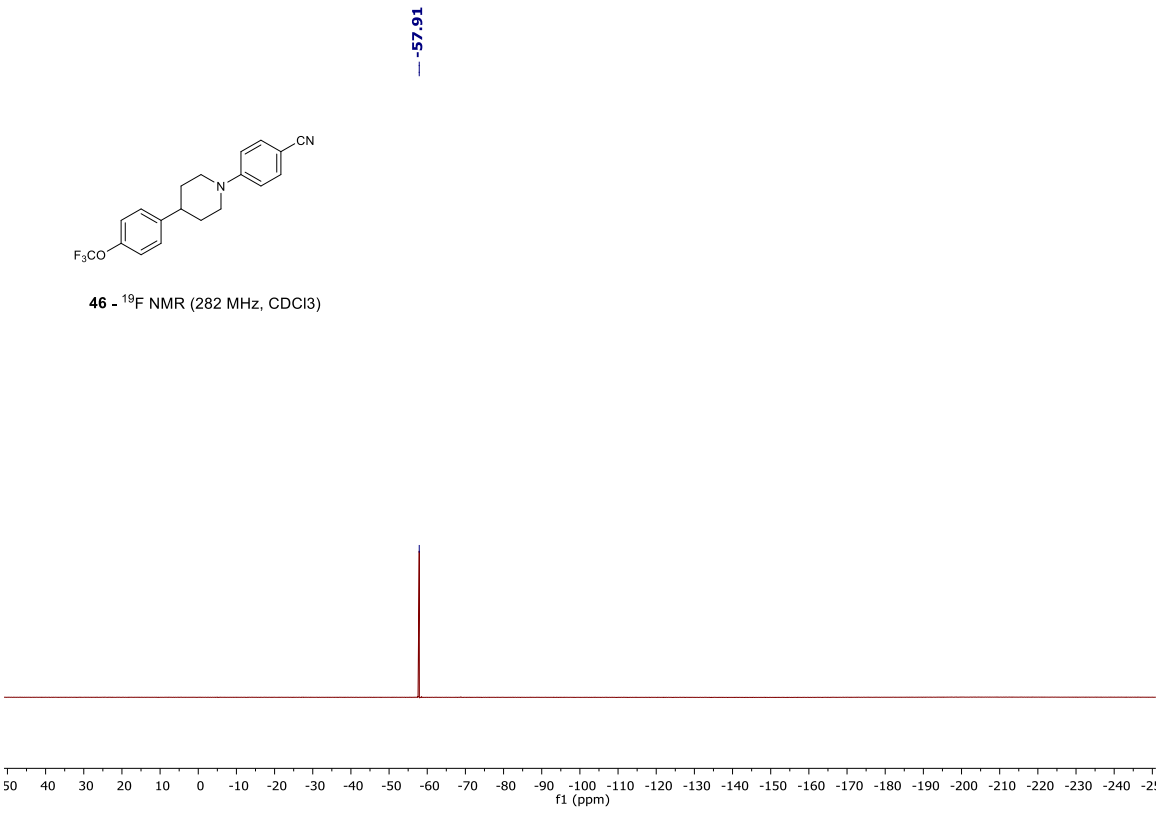
^{19}F NMR (282 MHz, $CDCl_3$)



46 - ^{1}H NMR (500 MHz, $CDCl_3$)



46 - ^{13}C NMR (125 MHz, $CDCl_3$)



46 - ^{19}F NMR (282 MHz, CDCl3)