Supplementary Information for

Switching on Elusive Organometallic Mechanisms with Photoredox Catalysis

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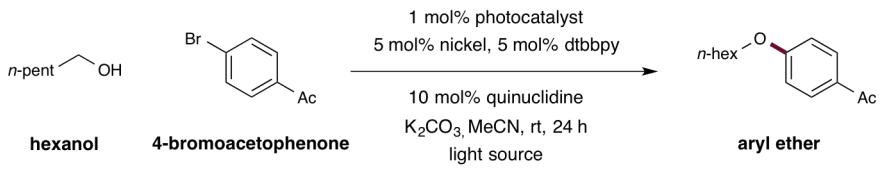
I. General Information.

Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego[1]. $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ was prepared using literature procedures[2]. Reagent grade acetonitrile was used for the direct aryl etherification reactions. All other solvents were purified according to the method of Grubbs[3]. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using a water bath. Chromatographic purification of products was accomplished using forced-flow chromatography on silica gel (Fluka, 230–400 mesh) according to the method of Still[4]. Thin-layer chromatography (TLC) was performed on Silicycle 0.25 mm silica gel F-254 plates. Visualization of the developed chromatogram was performed by fluorescence quenching or $KMnO_4$ stain. ^1H NMR spectra were recorded on a Bruker UltraShield Plus Avance III 500 MHz unless otherwise noted and are internally referenced to residual protio $CDCl_3$ signals (7.26 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). ^{19}F NMR spectra were recorded on a Bruker NanoBay 300 MHz (282 MHz). ^{31}P NMR spectra were recorded on a Bruker UltraShield Plus Avance III 500 MHz (203 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. Optical rotations were measured on a Jasco P-1010 polarimeter with $[a]_D$ values reported in degrees; concentration (c) is in g/100 mL.

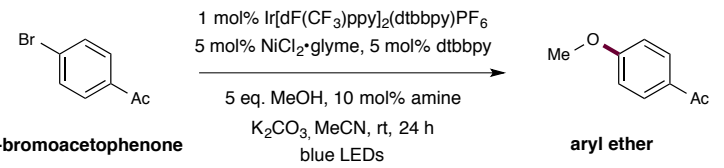
II. Optimization Tables and Control Experiments



hexanol **4-bromoacetophenone** **aryl ether**

entry	photocatalyst	nickel source	light source	yield
1	None	$Ni(COD)_2$	blue LEDs	0%
2[a]	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	$Ni(COD)_2$	blue LEDs	8%
3	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	$Ni(COD)_2$	blue LEDs	86%
4	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	$NiBr_2$•diglyme	blue LEDs	89%
5	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	$NiCl_2$•glyme	blue LEDs	91%
6[a]	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	$NiCl_2$•glyme	blue LEDs	0%
7	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	None	blue LEDs	0%
8[b]	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	$NiCl_2$•glyme	blue LEDs	0%
9	None	$NiCl_2$•glyme	blue LEDs	0%
10	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	$NiCl_2$•glyme	None	0%
11	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	$NiCl_2$•glyme	26W CFL	86%

Figure S1. Optimization and control experiments in the photoredox–nickel catalyzed C–O coupling. Yields determined by ^{1}H NMR analysis using 1,3-benzodioxole as internal standard. Reactions performed using 1.5 equiv. hexanol on 0.25 mmol scale. [a]Reaction performed in the absence of quinuclidine. [b]Reaction performed in the absence of 4,4'-di-*tert*-butyl-2,2'-dipyridyl.

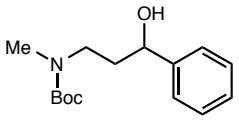


4-bromoacetophenone **aryl ether**

entry	amine base/reductant	yield
1	Ph_3N	0%
2	DMAP	1%
3	*i*-Pr_2NEt	29%
4	DABCO	34%
5	Cy_2NEt	44%
6	Et_3N	54%
7	quinuclidine	90%

Figure S2. Evaluation of amine reductants/bases in the photoredox-nickel catalyzed C–O coupling. Yields determined by ^{1}H NMR analysis using 1,3-benzodioxole as internal standard. Reactions performed using 5.0 equiv. methanol on 0.25 mmol scale.

III. Substrate Synthesis



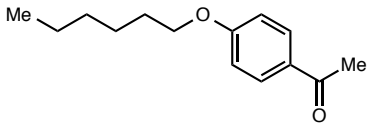
***tert*-Butyl (3-hydroxy-3-phenylpropyl)(methyl)carbamate:** To a 50 mL round bottom flask containing 3-methylamino-1-phenylpropan-1-ol (1.65 g, 10.0 mmol, 1.0 equivs.) in CH_2Cl_2 at 0 °C was added di-*tert*-butyl dicarbonate (2.18 g, 10.0 mmol, 1.0 equivs.). The solution was stirred for 10 min at 0 °C, then warmed to room temperature and stirred for 2 hours. The reaction mixture was then concentrated *in vacuo* and dissolved in diethyl ether (200 mL). The solution was added to a separatory funnel and washed with 1 M aq. HCl (100 mL). The organic phase was washed with brine (100 mL), dried (Na_2SO_4), and then concentrated *in vacuo* to afford a colorless oil (2.57 g, 97% yield, 9.7 mmol). δ_H (500 MHz, $CDCl_3$) 7.41–7.22 (m, 5H), 4.72–4.52 (m, 1H), 4.32 (s, 1H), 3.98–3.87 (m, 1H), 3.08–2.97 (m, 1H), 2.87 (s, 3H), 2.00–1.68 (m, 2H), 1.47 (s, 9H); δ_C (125 MHz, $CDCl_3$) 157.4, 144.3, 128.5, 127.2, 125.8, 80.3, 70.1, 45.3, 37.4, 34.4, 28.5.

Data are consistent with those reported in the literature[5].

IV. General Procedure for the etherification reaction

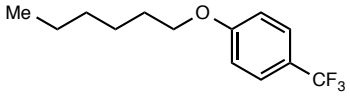
To an 8 mL vial containing a solution of the arene (1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.) and potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs) in acetonitrile (2.0 mL) was added a solution of $NiCl_2$•DME (11.0 mg, 0.050 mmol, 0.05 equivs.) and 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.) in acetonitrile (4.0 mL). The vial was placed under an atmosphere of nitrogen, then the alcohol (1.00 – 3.00 mmol, 1.0 – 3.0 equivs.) was added. The reaction mixture was then cooled to –78 °C and degassed via vacuum evacuation (5 min), backfilled with nitrogen, and then warmed to room temperature. This process was repeated three times, then the vial was sealed with parafilm, placed 1 cm away from three blue LED strips, and irradiated with blue LEDs under fan cooling (to maintain at room temperature). After 24 hours, the reaction mixture was diluted with ethyl acetate (10 mL) then poured into a separatory funnel containing water (10 mL). The aqueous phase was separated and extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were washed with brine (10 mL), dried (Na_2SO_4), and then concentrated *in vacuo*. Purification of the crude material by flash column chromatography on silica gel using the indicated solvent system afforded the desired aryl ether product.

V. Experimental Data



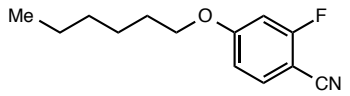
1-(4-(Hexyloxy)phenyl)ethan-1-one 9: Prepared according to the general procedure using 4-bromoacetophenone (199 mg, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$•DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), hexanol (188 µL, 1.50 mmol, 1.5 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 19:1) to give the *title compound* (199 mg, 91%, 0.905 mmol) as a colorless crystalline solid; IR ν_{max}/cm^{-1} 2931, 2860, 1675, 1599, 1575, 1509, 1357, 1249, 1170, 1019, 955, 833; δ_H (500 MHz, $CDCl_3$) 7.94 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 4.04 (t, J = 6.5 Hz, 2H), 2.57 (s, 3H), 1.82 (tt, J = 7.2, 6.5 Hz, 2H), 1.48 (tt, J = 8.3, 7.3 Hz, 2H), 1.42−1.32 (m, 4H), 0.93 (t, J = 6.9 Hz, 3H); δ_C (125 MHz, $CDCl_3$) 196.8, 163.1, 130.6, 130.1, 114.1, 68.3, 31.6, 29.1, 26.4, 25.7, 22.6, 14.0; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{21}O_2$) requires m/z 221.1536, found m/z 221.1537.

NMR spectroscopic data are consistent with those reported in the literature[6].

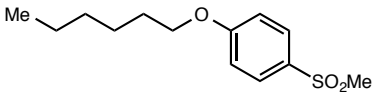


1-(Hexyloxy)-4-(trifluoromethyl)benzene 10: Prepared according to the general procedure using 1-bromo-4-(trifluoromethyl)benzene (140 µL, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$•DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), hexanol (188 µL, 1.50 mmol, 1.5 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 19:1) to give the *title compound* (221 mg, 90%, 0.899 mmol) as a colorless oil; IR ν_{max}/cm^{-1} 2933, 2866, 1616, 1520, 1325, 1255, 1159, 1108, 1067, 834; δ_H (500 MHz, $CDCl_3$) 7.55 (d, J = 8.6 Hz, 2H), 6.97 (d, J = 8.6 Hz, 2H), 4.01 (t, J = 6.6 Hz, 2H), 1.82 (tt, J = 6.9, 6.6 Hz, 2H), 1.49 (tt, J = 8.2, 7.2 Hz, 2H), 1.41−1.34 (m, 4H),

0.94 (t, J = 7.0 Hz, 3H); δ_C (125 MHz, $CDCl_3$) 161.6, 126.8 (q, J = 3.8 Hz), 124.5 (q, J = 271.1 Hz), 122.6 (q, J = 32.6 Hz), 114.4, 68.3, 31.6, 29.1, 25.7, 22.6, 14.0; δ_F (282 MHz, $CDCl_3$) –61.4 (s, 3F); HRMS (EI) exact mass calculated for $[M]^+$ ($C_{13}H_{17}F_3O$) requires m/z 246.1226, found m/z 246.1224.

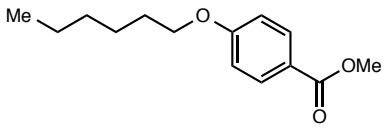


2-Fluoro-4-(hexyloxy)benzonitrile 11: Prepared according to the general procedure using 4-bromo-2-fluorobenzonitrile (200 mg, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$•DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), hexanol (188 µL, 1.50 mmol, 1.5 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 9:1) to give the *title compound* (202 mg, 91%, 0.913 mmol) as a colorless oil; IR ν_{max}/cm^{-1} 2932, 2860, 2230, 1620, 1572, 1505, 1299, 1171, 1114, 1100; δ_H (500 MHz, $CDCl_3$) 7.52 (dd, J = 8.7, 7.5 Hz, 1H), 6.77 (dd, J = 8.7, 2.4 Hz, 1H), 6.71 (dd, J = 11.1, 2.3 Hz, 1H), 4.01 (t, J = 6.5 Hz, 2H), 1.82 (tt, J = 9.3, 6.6 Hz, 2H), 1.47 (tt, J = 7.3, 7.0 Hz, 2H), 1.40−1.32 (m, 4H), 0.93 (t, J = 7.2 Hz, 3H); δ_C (125 MHz, $CDCl_3$) 164.7 (d, J = 257.6 Hz), 164.4 (d, J = 11.0 Hz), 134.2 (d, J = 2.4 Hz), 114.5, 111.7 (d, J = 2.8 Hz), 102.6 (d, J = 22.8 Hz), 92.7 (d, J = 15.7 Hz), 69.1, 31.5, 28.8, 25.6, 22.6, 14.0; δ_F (282 MHz, $CDCl_3$) –104.3 (dd, J = 11.2, 7.3 Hz, 1F); HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{17}FNO$) requires m/z 222.1289, found m/z 222.1292.



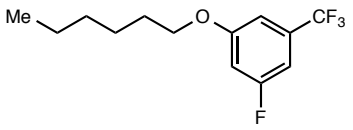
1-(Hexyloxy)-4-(methylsulfonyl)benzene 12: Prepared according to the general procedure using 1-bromo-4-(methylsulfonyl)benzene (235 mg, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$•DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), hexanol (188 µL, 1.50 mmol, 1.5 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 9:1) to give the

title compound (239 mg, 93%, 0.933 mmol) as a white solid; IR ν_{max}/cm^{-1} 2923, 2854, 1594, 1577, 1499, 1313, 1293, 1256, 1139, 1092, 967; δ_H (500 MHz, $CDCl_3$) 7.85 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 4.02 (t, *J* = 6.5 Hz, 2H), 3.02 (s, 3H), 1.80 (tt, *J* = 8.8, 6.6 Hz, 2H), 1.50−1.42 (m, 2H), 1.38−1.30 (m, 4H), 0.91 (t, *J* = 6.9 Hz, 3H); δ_C (125 MHz, $CDCl_3$) 163.5, 132.1, 129.6, 115.0, 68.7, 45.0, 31.6, 29.1, 25.7, 22.7, 14.2; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{21}O_3S$) requires m/z 257.1206, found m/z 257.1205.

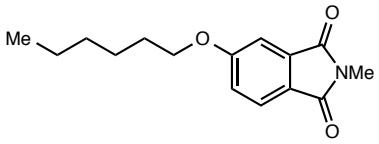


Methyl 4-(hexyloxy)benzoate 13: Prepared according to the general procedure using methyl 4-bromobenzoate (215 mg, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$•DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), hexanol (188 µL, 1.50 mmol, 1.5 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 40:1) to give the *title compound* (209 mg, 88%, 0.884 mmol) as a waxy white solid; IR ν_{max}/cm^{-1} 2946, 2870, 1711, 1605, 1510, 1437, 1276, 1247, 1165, 1106, 1025, 843, 768, 693; δ_H (500 MHz, $CDCl_3$) 7.98 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 4.00 (t, *J* = 6.6 Hz, 2H), 3.88 (s, 3H), 1.79 (m, 2H), 1.51–1.41 (m, 2H), 1.38–1.30 (m, 4H), 0.98–0.82 (m, 3H); δ_C (125 MHz, $CDCl_3$) 167.1, 163.1, 131.7, 122.4, 114.2, 68.3, 52.0, 31.7, 29.2, 25.8, 22.7, 14.2; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{21}O_3$) requires m/z 237.1485, found m/z 237.1483.

Reversal of stoichiometry: Prepared according to the general procedure using methyl 4-bromobenzoate (323 mg, 1.50 mmol, 1.5 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$•DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), hexanol (126 µL, 1.00 mmol, 1.0 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 40:1) to give the *title compound* (200 mg, 85%, 0.846 mmol) as a waxy white solid.

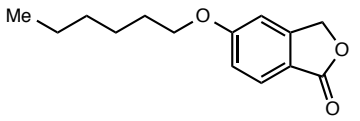


1-Fluoro-3-(hexyloxy)-5-(trifluoromethyl)benzene 14: Prepared according to the general procedure using 1-bromo-3-fluoro-5-(trifluoromethyl)benzene (161 μL, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$•DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), hexanol (188 μL, 1.50 mmol, 1.5 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 19:1) to give the *title compound* (254 mg, 96%, 0.962 mmol) as a colorless oil; IR ν_{max}/cm^{-1} 2934, 2862, 1602, 1457, 1355, 1316, 1171, 1128, 1039, 848; δ_H (500 MHz, $CDCl_3$) 6.93 (t, J = 2.2 Hz, 1H), 6.90 (dt, J = 8.2, 2.2 Hz, 1H), 6.76 (dt, J = 10.4, 2.2 Hz, 1H), 3.97 (t, J = 6.5 Hz, 2H), 1.79 (tt, J = 14.7, 6.6 Hz, 2H), 1.50−1.42 (m, 2H), 1.38−1.31 (m, 4H), 0.91 (t, J = 7.0 Hz, 3H); δ_C (125 MHz, $CDCl_3$) 163.5 (d, J = 247.2 Hz), 161.0 (d, J = 11.1 Hz), 132.9 (dd, J = 33.3, 10.2 Hz), 123.5 (dd, J = 272.5, 3.8 Hz), 107.8 (q, J = 3.6 Hz), 105.5 (d, J = 24.3 Hz), 104.8 (dq, J = 24.9, 3.8 Hz), 68.9, 31.6, 29.1, 25.8, 22.7, 14.2; δ_F (282 MHz, $CDCl_3$) –63.0 (s, 3F), –109.4 (dd, J = 9.2, 9.2 Hz, 1F); HRMS (EI) exact mass calculated for $[M]^+$ ($C_{13}H_{16}F_4O$) requires m/z 264.1132, found m/z 264.1135.

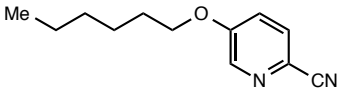


5-(Hexyloxy)-2-methylisoindoline-1,3-dione 15: Prepared according to the general procedure using 5-bromo-2-methylisoindoline-1,3-dione (240 mg, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$•DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), hexanol (188 μL, 1.50 mmol, 1.5 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 9:1) to give the *title compound* (240 mg, 92%, 0.919 mmol) as a white solid; IR ν_{max}/cm^{-1} 2955, 2931, 2867, 1756, 1713, 1621, 1490, 1454, 1380, 1296, 1236, 1010; δ_H (500 MHz, $CDCl_3$) 7.73 (d, J = 8.2 Hz, 1H), 7.30 (d, J = 2.3 Hz, 1H), 7.12 (dd, J = 8.2, 2.3 Hz, 1H), 4.06 (t, J = 6.6 Hz, 2H), 3.15 (s, 3H), 1.81

(tt, *J* = 7.8, 6.9 Hz, 2H), 1.52−1.43 (m, 2H), 1.39−1.31 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H); δ_C (125 MHz, $CDCl_3$) 168.6, 168.5, 164.3, 134.9, 125.0, 123.9, 120.1, 108.6, 69.1, 31.6, 29.0, 25.7, 24.0, 22.7, 14.1; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{20}NO_3$) requires m/z 262.1438, found m/z 262.1438.

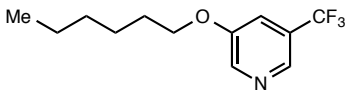


5-(Hexyloxy)isobenzofuran-1(3*H*)-one 16: Prepared according to the general procedure using 5-bromoisobenzofuran-1(3*H*)-one (213 mg, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$•DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), hexanol (188 µL, 1.50 mmol, 1.5 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 9:1) to give the *title compound* (188 mg, 80%, 0.801 mmol) as a white solid; IR ν_{max}/cm^{-1} 2925, 2868, 1746, 1607, 1464, 1267, 1094, 1045, 992; δ_H (500 MHz, $CDCl_3$) 7.81 (d, *J* = 8.5 Hz, 1H), 7.02 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.90 (d, *J* = 2.2 Hz, 1H), 5.24 (s, 2H), 4.04 (t, *J* = 6.4 Hz, 2H), 1.82 (tt, *J* = 7.6, 6.6 Hz, 2H), 1.51−1.43 (m, 2H), 1.38−1.32 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H); δ_C (125 MHz, $CDCl_3$) 171.1, 164.5, 149.5, 127.4, 117.9, 117.0, 106.5, 69.2, 68.9, 31.6, 29.1, 25.8, 22.7, 14.2; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{19}O_3$) requires m/z 235.1329, found m/z 235.1330.

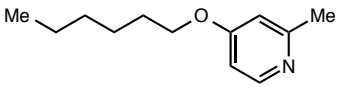


5-(Hexyloxy)picolinonitrile 17: Prepared according to the general procedure using 5-bromopicolinonitrile (183 mg, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$•DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), hexanol (188 µL, 1.50 mmol, 1.5 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 9:1) to give the *title compound* (180 mg, 88%, 0.880 mmol) as a colorless oil; IR ν_{max}/cm^{-1} 2932, 2860, 2232, 1581, 1569,

1461, 1307, 1276, 1251, 1010, 837; δ_H (500 MHz, $CDCl_3$) 8.35 (d, J = 3.0 Hz, 1H), 7.63 (d, J = 8.7 Hz, 1H), 7.21 (dd, J = 8.7, 3.0 Hz, 1H), 4.05 (t, J = 6.5 Hz, 2H), 1.82 (tt, J = 8.2, 6.6 Hz, 2H), 1.50−1.42 (m, 2H), 1.38−1.30 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H); δ_C (125 MHz, $CDCl_3$) 157.6, 140.5, 129.7, 125.1, 120.3, 117.7, 69.1, 31.6, 28.9, 25.6, 22.7, 14.1; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{17}N_2O$) requires m/z 205.1335, found m/z 205.1335.

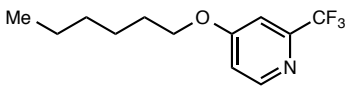


3-(Hexyloxy)-5-(trifluoromethyl)pyridine 18: Prepared according to the general procedure using 3-bromo-5-(trifluoromethyl)pyridine (226 mg, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$•DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), hexanol (188 µL, 1.50 mmol, 1.5 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 4:1) to give the *title compound* (167 mg, 67%, 0.674 mmol) as a colorless oil; IR ν_{max}/cm^{-1} 2933, 2862, 1599, 1464, 1439, 1333, 1129, 1081, 1017, 877; δ_H (500 MHz, $CDCl_3$) 8.47 (d, J = 2.4 Hz, 2H), 7.36 (t, J = 2.4 Hz, 1H), 4.04 (t, J = 6.5 Hz, 2H), 1.82 (tt, J = 8.4, 6.7 Hz, 2H), 1.51−1.44 (m, 2H), 1.38−1.32 (m, 4H), 0.91 (t, J = 7.0 Hz, 3H); δ_C (125 MHz, $CDCl_3$) 155.1, 141.9, 138.4 (q, J = 4.3 Hz), 127.2 (q, J = 32.7 Hz), 123.5 (q, J = 272.8 Hz), 117.5 (q, J = 3.6 Hz), 69.0, 31.6, 29.1, 25.7, 22.7, 14.1; δ_F (282 MHz, $CDCl_3$) –62.4 (s, 3F); HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{17}F_3NO$) requires m/z 248.1257, found m/z 248.1261.

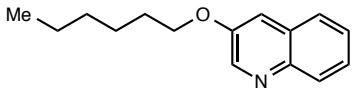


4-(Hexyloxy)-2-methylpyridine 19: Prepared according to the general procedure using 4-bromo-2-methylpyridine (119 µL, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$•DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), hexanol (188 µL, 1.50 mmol, 1.5 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude

material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 3:1) to give the *title compound* (177 mg, 91%, 0.913 mmol) as a yellow oil; IR ν_{max}/cm^{-1} 2929, 2859, 1596, 1568, 1468, 1306, 1283, 1173, 1026, 827; δ_H (500 MHz, $CDCl_3$) 8.28 (d, *J* = 5.8 Hz, 1H), 6.65 (d, *J* = 2.5 Hz, 1H), 6.61 (dd, *J* = 5.8, 2.5 Hz, 1H), 3.97 (t, *J* = 6.6 Hz, 2H), 2.48 (s, 3H), 1.77 (tt, *J* = 8.0, 6.7 Hz, 2H), 1.47−1.39 (m, 2H), 1.37−1.29 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H); δ_C (125 MHz, $CDCl_3$) 165.6, 160.0, 150.3, 109.5, 107.7, 67.9, 31.6, 29.0, 25.7, 24.7, 22.7, 14.1; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{20}NO$) requires m/z 194.1539, found m/z 194.1542.

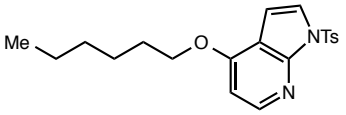


4-(Hexyloxy)-2-(trifluoromethyl)pyridine 20: Prepared according to the general procedure using 4-bromo-2-(trifluoromethyl)pyridine (226 mg, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$•DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), hexanol (188 μL, 1.50 mmol, 1.5 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 9:1) to give the *title compound* (203 mg, 82%, 0.822 mmol) as a colorless oil; IR ν_{max}/cm^{-1} 2934, 2862, 1603, 1446, 1329, 1178, 1137, 1070, 1015; δ_H (500 MHz, $CDCl_3$) 8.52 (d, *J* = 5.7 Hz, 1H), 7.17 (d, *J* = 2.5 Hz, 1H), 6.94 (dd, *J* = 5.7, 2.5 Hz, 1H), 4.06 (t, *J* = 6.5 Hz, 2H), 1.82 (tt, *J* = 8.5, 6.6 Hz, 2H), 1.51−1.43 (m, 2H), 1.38−1.32 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H); δ_C (125 MHz, $CDCl_3$) 166.3, 151.5, 149.8 (q, *J* = 34.3 Hz), 121.6 (q, *J* = 274.5 Hz), 112.3, 107.9 (q, *J* = 2.9 Hz), 68.8, 31.6, 28.8, 25.7, 22.7, 14.1; δ_F (282 MHz, $CDCl_3$) –68.3 (s, 3F); HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{17}F_3NO$) requires m/z 248.1257, found m/z 248.1255.

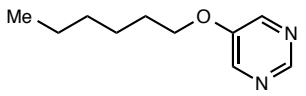


4-(Hexyloxy)quinoline 21: Prepared according to the general procedure using 3-bromoquinoline (208 mg, 136 μL, 1.00 mmol, 1.0 equivs.), quinuclidine (22.2 mg, 0.200 mmol, 0.2 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$•DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate

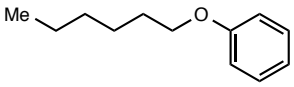
(138 mg, 1.00 mmol, 1.0 equivs.), hexanol (377 µL, 3.00 mmol, 3.0 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 19:1 to 9:1) to give the *title compound* (137 mg, 60%, 0.597 mmol) as a colorless oil; IR ν_{max}/cm^{-1} 2929, 2860, 1603, 1426, 1379, 1346, 1274, 1211, 1181, 1140, 1015, 848, 780, 748; δ_H (500 MHz, $CDCl_3$) 8.68 (d, *J* = 2.8 Hz, 1H), 8.04 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.71 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.54 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.50 (ddd, *J* = 8.1, 6.9, 1.4 Hz, 1H), 7.36 (d, *J* = 2.8 Hz, 1H), 4.08 (t, *J* = 6.5 Hz, 2H), 1.91–1.83 (m, 2H), 1.56–1.48 (m, 2H), 1.42–1.31 (m, 4H), 0.93–0.87 (m, 3H); δ_C (125 MHz, $CDCl_3$) 152.7, 145.0, 143.5, 129.3, 129.0, 127.1, 126.8, 126.6, 113.0, 68.5, 31.7, 29.2, 25.9, 22.8, 14.2; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{20}NO$) requires m/z 230.15394, found m/z 230.15374.



4-(Hexyloxy)-1-tosyl-7-azaindole 22: Prepared according to the general procedure using 4-bromo 4-bromo-1-tusyl-7-azaindole (351 mg, 1.00 mmol, 1.0 equivs.), quinuclidine (22.2 mg, 0.200 mmol, 0.2 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.010 equivs.), $NiCl_2$•DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.050 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), hexanol (377 µL, 3.00 mmol, 3.0 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 4:1) to give the *title compound* (329 mg, 88%, 0.883 mmol) as a white solid; IR ν_{max}/cm^{-1} 2953, 2918, 2855, 1597, 1575, 1490, 1369, 1294, 1175, 1159, 1147, 1060, 804, 741, 678, 655; δ_H (500 MHz, $CDCl_3$) 8.27 (d, *J* = 5.6 Hz, 1H), 8.04 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 4.0 Hz, 1H), 7.25 (d, *J* = 8.3 Hz, 2H), 6.66 (d, *J* = 4.0 Hz, 1H), 6.59 (d, *J* = 5.6 Hz, 1H), 4.09 (t, *J* = 6.5 Hz, 2H), 2.36 (s, 3H), 1.86–1.79 (m, 2H), 1.50–1.42 (m, 2H), 1.37–1.30 (m, 4H), 0.93–0.87 (m, 3H). δ_C (125 MHz, $CDCl_3$) 159.5, 149.1, 147.1, 145.1, 135.7, 129.7, 128.1, 124.1, 113.2, 102.9, 101.6, 68.6, 31.6, 29.0, 25.8, 22.7, 21.8, 14.2; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{20}H_{25}N_2O_3S$) requires m/z 373.1580, found m/z 373.1582.

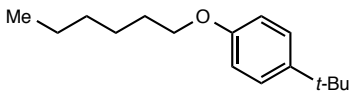


5-(Hexyloxy)pyrimidine 23: Prepared according to the general procedure using 5-bromopyrimidine (159 mg, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$•DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), hexanol (377 µL, 3.00 mmol, 3.0 equivs.) and acetonitrile (4.0 mL). Differed from general procedure by performing reaction at 50 °C (no fan cooling). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 3:1) to give the *title compound* (136 mg, 75%, 0.753 mmol) as a colorless oil; IR ν_{max}/cm^{-1} 2930, 2860, 1558, 1416, 1272, 1181, 1007, 885, 721; δ_H (500 MHz, $CDCl_3$) 8.82 (s, 1H), 8.39 (s, 2H), 4.05 (t, J = 6.5 Hz, 2H), 1.81 (tt, J = 7.6, 6.6 Hz, 2H), 1.50−1.42 (m, 2H), 1.38−1.30 (m, 4H), 0.90 (t, J = 7.0 Hz, 3H); δ_C (125 MHz, $CDCl_3$) 153.2, 151.4, 143.7, 68.9, 31.6, 29.1, 25.6, 22.7, 14.1; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{10}H_{17}N_2O$) requires m/z 181.1335, found m/z 181.1334.

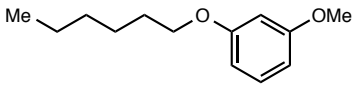


(Hexyloxy)benzene 24: Prepared according to the general procedure using bromobenzene (157 mg, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$·DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), hexanol (377 µL, 3.0 mmol, 3.0 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Pentane) to give the *title compound* (122 mg, 68%, 0.684 mmol) as a colorless oil; δH (500 MHz, $CDCl_3$) 7.30−7.25 (m, 2H), 6.95−6.88 (m, 3H), 3.95 (t, J = 6.6 Hz, 2H), 1.82−1.74 (m, 2H), 1.50−1.41 (m, 2H), 1.38−1.30 (m, 4H), 0.91 (t, J = 7.0 Hz, 3H); δ_C (125 MHz, $CDCl_3$) 159.3, 129.5, 120.6, 114.6, 68.0, 31.8, 29.4, 25.9, 22.8, 14.2.

Data are consistent with those reported in the literature[7].

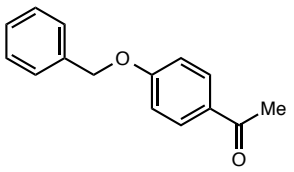


1-(*tert*-Butyl)-4-(hexyloxy)benzene 25: Prepared according to the general procedure using 1-bromo-4-(*tert*-butyl)benzene (173 µL, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$•DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), hexanol (377 µL, 3.00 mmol, 3.0 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 9:1) to give the *title compound* (181 mg, 77%, 0.773 mmol) as a colorless oil; IR ν_{max}/cm^{-1} 2956, 2865, 1513, 1467, 1244, 1183, 827; δ_H (500 MHz, $CDCl_3$) 7.30 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 3.94 (t, J = 6.6 Hz, 2H), 1.78 (tt, J = 8.1, 6.5 Hz, 2H), 1.50−1.43 (m, 2H), 1.38−1.31 (m, 4H), 1.31 (s, 9H), 0.91 (t, J = 7.0 Hz, 3H); δ_C (125 MHz, $CDCl_3$) 157.0, 143.2, 126.3, 114.0, 68.1, 34.2, 31.8, 31.7, 29.5, 25.9, 22.8, 14.2; HRMS (EI) exact mass calculated for $[M]^+$ ($C_{16}H_{26}O$) requires m/z 234.1978, found m/z 234.1980.



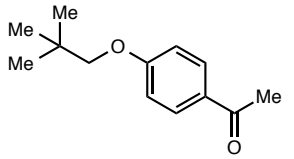
1-(Hexyloxy)-3-methoxybenzene 26: Prepared according to the general procedure using 1-bromo-3-methoxybenzene (187 mg, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$·DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), hexanol (377 µL, 3.00 mmol, 3.0 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 99:1) to give the *title compound* (166 mg, 80%, 0.797 mmol) as a colorless oil; δ_H (500 MHz, $CDCl_3$) 7.17 (t, J = 8.2 Hz, 1H), 6.52–6.48 (m, 2H), 6.46 (t, J = 2.3 Hz, 1H), 3.94 (t, J = 6.6 Hz, 2H), 3.79 (s, 3H), 1.81–1.72 (m, 2H), 1.51–1.41 (m, 2H), 1.39–1.29 (m, 4H), 0.94–0.87 (t, J = 7.0 Hz, 3H); δ_C (125 MHz, $CDCl_3$) 160.9, 160.5, 130.0, 106.8, 106.2, 101.1, 68.1, 55.4, 31.7, 29.4, 25.9, 22.8, 14.2.

Data are consistent with those reported in the literature[8].

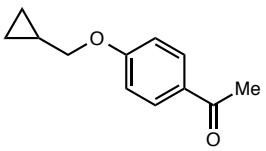


1-(4-(Benzyloxy)phenyl)ethan-1-one 27: Prepared according to the general procedure using 4-bromoacetophenone (199 mg, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$·DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), benzyl alcohol (155 µL, 1.50 mmol, 1.5 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 19:1) to give the *title compound* (186 mg, 82%, 0.822 mmol) as a colorless crystalline solid; δ_H (500 MHz, $CDCl_3$) 7.94 (d, J = 8.9 Hz, 2H), 7.45–7.38 (m, 3H), 7.37–7.33 (m, 2H), 7.01 (d, J = 8.9 Hz, 2H), 5.14 (s, 2H), 2.56 (s, 3H); δ_C (125 MHz, $CDCl_3$) 196.9, 162.8, 136.3, 130.7, 130.7, 128.8, 128.4, 127.6, 114.7, 70.3, 26.5.

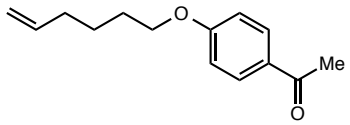
Data are consistent with those reported in the literature[9].



1-(4-(Neopentyloxy)phenyl)ethan-1-one 28: Prepared according to the general procedure using 4-bromoacetophenone (199 mg, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$·DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), neopentyl alcohol (162 µL, 1.50 mmol, 1.5 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 19:1 → 9:1) to give the *title compound* (184 mg, 89%, 0.892 mmol) as a colorless crystalline solid; IR ν_{max}/cm^{-1} 2958, 1667, 1600, 1575, 1274, 1246, 1176, 1014, 955, 838, 811; δ_H (500 MHz, $CDCl_3$) 7.92 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 3.65 (s, 2H), 2.55 (s, 3H), 1.05 (s, 9H); δ_C (125 MHz, $CDCl_3$) 197.0, 163.7, 130.7, 130.2, 114.3, 78.1, 32.0, 26.7, 26.5; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{19}O_2$) requires m/z 207.1380, found m/z 207.1381.

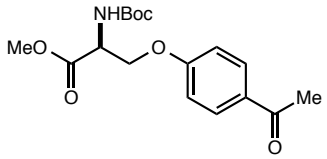


1-(4-(Cyclopropylmethoxy)phenyl)ethan-1-one 29: Prepared according to the general procedure using 4-bromoacetophenone (199 mg, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$·DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), cyclopropanemethanol (122 µL, 1.50 mmol, 1.5 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 19:1) to give the *title compound* (156 mg, 82%, 0.820 mmol) as a colorless crystalline solid; IR ν_{max}/cm^{-1} 1666, 1599, 1575, 1510, 1423, 1355, 1244, 1186, 1171, 1023, 1002, 962, 848, 806; δ_H (500 MHz, $CDCl_3$) 7.92 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 3.87 (d, *J* = 7.0 Hz, 2H), 2.55 (s, 3H), 1.34–1.22 (m, 1H), 0.71–0.63 (m, 2H), 0.39–0.34 (m, 2H); δ_C (125 MHz, $CDCl_3$) 197.0, 163.1, 130.7, 130.3, 114.3, 73.1, 26.5, 10.2, 3.4; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{15}O_2$) requires m/z 191.1067, found m/z 191.1067.

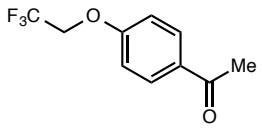


1-(4-(Hex-5-en-1-yloxy)phenyl)ethan-1-one 30: Prepared according to the general procedure using 4-bromoacetophenone (199 mg, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$·DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), hexen-1-ol (180 µL, 1.50 mmol, 1.5 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked-up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 19:1) to give the *title compound* (167 mg, 77%, 0.765 mmol) as a colorless oil; IR ν_{max}/cm^{-1} 1674, 1599, 1509, 1357, 1248, 1170, 833; δ_H (500 MHz, $CDCl_3$) 7.92 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 5.82 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.04 (ddt, *J* = 16.9, 2.1, 1.7 Hz, 1H), 4.98 (ddt, *J* = 10.2, 2.1, 1.2 Hz, 1H), 4.02 (t, *J* = 6.5 Hz, 2H), 2.55 (s, 3H), 2.17–2.10 (m, 2H), 1.86–1.78 (m, 2H), 1.58 (tt, *J* = 9.9, 6.5 Hz, 2H); δ_C (125

MHz, $CDCl_3$) 196.9, 163.2, 138.5, 130.7, 130.3, 115.0, 114.2, 68.1, 33.5, 28.7, 26.5, 25.4; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{19}O_2$) requires m/z 219.1380, found m/z 219.1378.



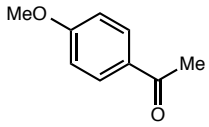
Methyl 3-(4-acetylphenoxy)-2-((tert-butoxycarbonyl)amino)propanoate 31: Prepared according to the general procedure using 4-bromoacetophenone (199 mg, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$·DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), *N*-(*tert*-butoxycarbonyl)-L-serine methyl ester (329 mg, 1.50 mmol, 1.5 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 4:1 → 2:1) to give the *title compound* (262 mg, 78%, 0.777 mmol) as a colorless oil; $[\alpha]_D^{21}$ = +57.0 (*c* 1.00, $CHCl_3$); IR ν_{max}/cm^{-1} 3348 (br), 2977, 1750, 1710, 1675, 1600, 1505, 1358, 1243, 1161, 1058, 1033, 834; δ_H (500 MHz, $CDCl_3$) 7.93 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 5.48 (d, *J* = 8.5 Hz, 1H), 4.73–4.66 (m, 1H), 4.45 (dd, *J* = 9.3, 3.0 Hz, 1H), 4.28 (dd, *J* = 9.3, 3.2 Hz, 1H), 3.78 (s, 3H), 2.56 (s, 3H), 1.46 (s, 9H); δ_C (125 MHz, $CDCl_3$) 196.8, 170.4, 162.1, 155.4, 131.1, 130.7, 114.4, 80.6, 68.6, 53.5, 53.0, 28.4, 26.6; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{17}H_{23}NNaO_6$) requires m/z 360.1418, found m/z 360.1418.



1-(4-(2,2,2-Trifluoroethoxy)phenyl)ethanone 32: Prepared according to the general procedure using 4-bromoacetophenone (199 mg, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$·DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), trifluoroethanol (108 μL, 1.50 mmol, 1.5 equivs.) and acetonitrile/2-Me-THF (9:1, 4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc

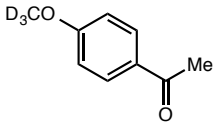
– 9:1) to give the *title compound* (168 mg, 77%, 0.770 mmol) as a colorless crystalline solid; δ_H (500 MHz, $CDCl_3$) 7.97 (d, J = 8.9 Hz, 2H), 6.99 (d, J = 8.9 Hz, 2H), 4.42 (q, J = 8.0 Hz, 2H), 2.58 (s, 3H); δ_C (125 MHz, $CDCl_3$) 196.7, 160.9, 132.0, 130.8, 123.2 (q, J = 277.9 Hz), 114.6, 65.7 (q, J = 36.1 Hz), 26.6; δ_F (282 MHz, $CDCl_3$) –73.8 (t, J = 8.0 Hz).

Data are consistent with those reported in the literature[10].



1-(4-Methoxyphenyl)ethan-1-one 33: Prepared according to the general procedure using 4-bromoacetophenone (199 mg, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$·DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), methanol (61.0 µL, 1.50 mmol, 1.5 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 19:1 → 9:1) to give the *title compound* (130 mg, 87%, 0.866 mmol) as a colorless crystalline solid; δ_H (500 MHz, $CDCl_3$) 7.94 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 3.87 (s, 3H), 2.55 (s, 3H); δ_C (125 MHz, $CDCl_3$) 196.9, 163.6, 130.7, 130.5, 113.8, 55.6, 26.5.

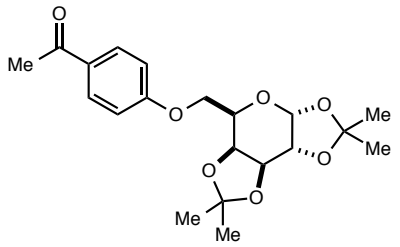
Data are consistent with those reported in the literature[11].



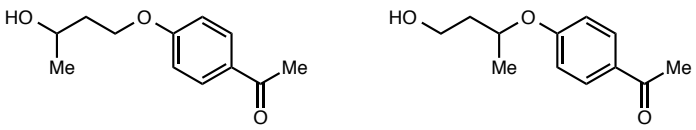
1-(4-Methoxy-d_3-phenyl)ethan-1-one 34: Prepared according to the general procedure using 4-bromoacetophenone (199 mg, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$·DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), d_4-methanol (61.0 µL, 1.50 mmol, 1.5 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the

crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 19:1 → 9:1) to give the *title compound* (124 mg, 81%, 0.809 mmol) as a colorless crystalline solid; δ_H (500 MHz, $CDCl_3$) 7.94 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 2.56 (s, 3H); δ_C (125 MHz, $CDCl_3$) 196.9, 163.6, 130.7, 130.5, 113.8, 26.5 (signal for $–OCD_3$ group not observed).

Under these conditions, some deuterium is incorporated into the methyl ketone. Data are consistent with those reported in the literature[11].



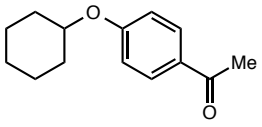
1-(4-(((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-Tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methoxy)phenyl)ethan-1-one 35: Prepared according to the general procedure using 4-bromoacetophenone (199 mg, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$·DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), 1,2:3,4-di-*O*-isopropylidene-*D*-galactopyranose (390 mg, 1.50 mmol, 1.5 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 9:1 → 4:1) to give the *title compound* (310 mg, 82%, 0.819 mmol) as a colorless oil; $[\alpha]_D^{21}$ = –102.2 (*c* 1.00, $CHCl_3$); IR ν_{max}/cm^{-1} 1676, 1599, 1253, 1210, 1168, 1114, 1066, 1001, 834, 730; δ_H (500 MHz, $CDCl_3$) 7.92 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 5.58 (d, *J* = 5.0 Hz, 1H), 4.66 (dd, *J* = 7.9, 2.4 Hz, 1H), 4.38–4.35 (m, 2H), 4.26–4.16 (m, 3H), 2.55 (s, 3H), 1.53 (s, 3H), 1.47 (s, 3H), 1.36 (s, 3H), 1.35 (s, 3H); δ_C (125 MHz, $CDCl_3$) 197.0, 162.7, 130.7, 130.6, 114.5, 109.7, 109.0, 96.5, 71.1, 70.8, 70.7, 67.0, 66.3, 26.5, 26.2, 26.1, 25.1, 24.6; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{20}H_{27}O_7$) requires m/z 379.1753, found m/z 379.1751.



1-(4-(3-Hydroxybutoxy)phenyl)ethan-1-one and 1-(4-((4-hydroxybutan-2-yl)oxy)phenyl)ethan-1-one 36: Prepared according to the general procedure using 4-bromoacetophenone (199 mg, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$·DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), 1,3-butanediol (269 µL, 3.00 mmol, 3.0 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 2:1 → 1:1) to give an inseparable mixture of the *title compounds* (148 mg, 71%, 0.711 mmol, 5.8:1) as a pale yellow oil; IR ν_{max}/cm^{-1} 3409 (br), 1667, 1598, 1574, 1359, 1249, 1171, 957, 833; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{17}O_3$) requires m/z 209.1172, found m/z 209.1172.

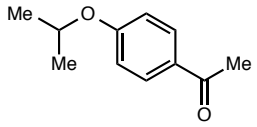
1-(4-(3-Hydroxybutoxy)phenyl)ethan-1-one (Major): δ_H (500 MHz, $CDCl_3$) 7.93 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 4.23 (ddd, *J* = 9.5, 7.2, 5.3 Hz, 1H), 4.19–4.13 (m, 1H), 4.14–4.07 (m, 1H), 2.56 (s, 3H), 2.02–1.86 (m, 2H), 1.29 (d, *J* = 6.3 Hz, 3H); δ_C (125 MHz, $CDCl_3$) 197.0, 162.8, 130.7, 130.5, 114.3, 65.9, 65.8, 38.1, 26.5, 24.0.

1-(4-((4-Hydroxybutan-2-yl)oxy)phenyl)ethan-1-one (Minor): δ_H (500 MHz, $CDCl_3$) 7.92 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 4.78–4.69 (m, 1H), 3.87–3.77 (m, 2H), 2.55 (s, 3H), 2.04–1.86 (m, 2H), 1.37 (d, *J* = 6.1 Hz, 3H); δ_C (125 MHz, $CDCl_3$) 196.9, 162.1, 130.8, 130.3, 115.3, 71.9, 59.6, 39.1, 26.5, 17.8.



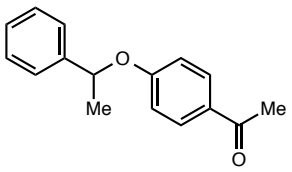
1-(4-(Cyclohexyloxy)phenyl)ethan-1-one 37: Prepared according to the general procedure using 4-bromoacetophenone (199 mg, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$•DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), cyclohexanol (317 µL, 3.00 mmol, 3.0 equivs.) and acetonitrile (4.0

mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 9:1) to give the *title compound* (188 mg, 86%, 0.860 mmol) as a colorless oil; IR ν_{max}/cm^{-1} 2928, 2854, 1660, 1601, 1573, 1505, 1358, 1277, 1247, 1175, 839; δ_H (500 MHz, $CDCl_3$) 7.91 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.35 (tt, *J* = 8.9, 4.3 Hz, 1H), 2.55 (s, 3H), 2.03–1.96 (m, 2H), 1.85–1.78 (m, 2H), 1.63–1.51 (m, 3H), 1.44–1.31 (m, 3H); δ_C (125 MHz, $CDCl_3$) 196.9, 162.1, 130.8, 130.0, 115.3, 75.6, 31.7, 26.5, 25.6, 23.8; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{19}O_2$) requires m/z 219.1380, found m/z 219.1381.



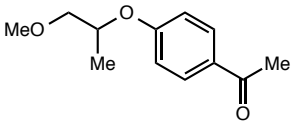
1-(4-Isopropoxyphenyl)ethanone 38: Prepared according to the general procedure using 4-bromoacetophenone (199 mg, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2{\cdot}DME$ (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), isopropanol (230 µL, 3.00 mmol, 3.0 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 19:1) to give the *title compound* (146 mg, 82%, 0.819 mmol) as an off-white crystalline solid; IR ν_{max}/cm^{-1} 1669, 1593, 1504, 1361, 1251, 1120, 1104, 948, 828; δ_H (500 MHz, $CDCl_3$) 7.91 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 4.64 (h, *J* = 6.0 Hz, 1H), 2.54 (s, 3H), 1.36 (d, *J* = 6.0 Hz, 6H); δ_C (125 MHz, $CDCl_3$) 196.9, 162.1, 130.8, 130.0, 115.2, 70.2, 26.5, 22.0; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{11}H_{15}O_2$) requires m/z 179.1067, found m/z 179.1066.

NMR Spectroscopic data are consistent with those reported in the literature[12].



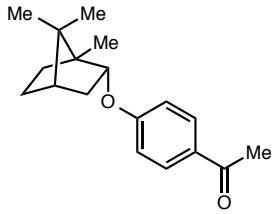
1-(4-(1-Phenylethoxy)phenyl)ethanone 39: Prepared according to the general procedure using 4-bromoacetophenone (199 mg, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$·DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), α-methylbenzyl alcohol (363 μL, 3.00 mmol, 3.0 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 19:1) to give the *title compound* (191 mg, 80%, 0.795 mmol) as a colorless crystalline solid; IR ν_{max}/cm^{-1} 1677, 1599, 1578, 1507, 1418, 1356, 1272, 1239, 1178, 1170, 1063, 926, 841, 805, 765, 705; δ_H (500 MHz, $CDCl_3$) 7.84 (d, J = 8.9 Hz, 2H), 7.37–7.31 (m, 4H), 7.29–7.24 (m, 1H), 6.88 (d, J = 8.9 Hz, 2H), 5.39 (q, J = 6.5 Hz, 1H), 2.50 (s, 3H), 1.67 (d, J = 6.5 Hz, 3H); δ_C (125 MHz, $CDCl_3$) 196.9, 162.0, 142.5, 130.6, 130.3, 128.9, 127.9, 125.6, 115.6, 76.4, 26.4, 24.6; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{16}H_{17}O_2$) requires m/z 241.1223, found m/z 241.1222.

NMR Spectroscopic data are consistent with those reported in the literature[13].

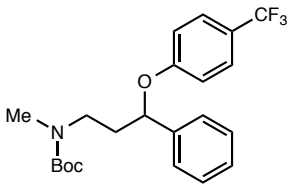


1-(4-((1-Methoxypropan-2-yl)oxy)phenyl)ethan-1-one 40: Prepared according to the general procedure using 4-bromoacetophenone (199 mg, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$·DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), 1-methoxy-2-propanol (293 μL, 3.00 mmol, 3.0 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 4:1) to give the *title compound* (172 mg, 83%, 0.826 mmol) as a colorless oil; IR ν_{max}/cm^{-1} 1673, 1597, 1506, 1358, 1247, 1172, 1108, 956, 834; δ_H (500 MHz, $CDCl_3$) 7.91 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 4.64 (qdd, J = 6.3, 6.0, 4.2 Hz, 1H), 3.59 (dd, J = 10.3, 6.0 Hz, 1H), 3.50 (dd, J = 10.3, 4.2 Hz,

1H), 3.40 (s, 3H), 2.54 (s, 3H), 1.33 (d, J = 6.3 Hz, 3H); δ_C (125 MHz, $CDCl_3$) 196.9, 162.1, 130.7, 130.4, 115.4, 75.8, 73.2, 59.5, 26.5, 16.8; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{17}O_3$) requires m/z 209.1172, found m/z 209.1171.



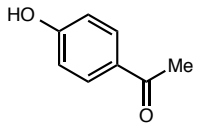
1-(4-(((2*R*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl)oxy)phenyl)ethanone 41: Prepared according to the general procedure using 4-bromoacetophenone (199 mg, 1.00 mmol, 1.0 equivs.), quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$.DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), (–)-borneol (463 mg, 3.00 mmol, 3.0 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/Et_2O – 19:1 → 9:1) to give the *title compound* (201 mg, 74%, 0.738 mmol) as a colorless crystalline solid; $[\alpha]_D^{21}$ = –112.2 (*c* 1.00, $CHCl_3$). IR ν_{max}/cm^{-1} 2953, 1667, 1600, 1574, 1275, 1252, 1178, 1021, 837; δ_H (500 MHz, $CDCl_3$) 7.91 (d, J = 8.9 Hz, 2H), 6.86 (d, J = 8.9 Hz, 2H), 4.39 (ddd, J = 9.5, 3.4, 1.8 Hz, 1H), 2.55 (s, 3H), 2.45–2.35 (m, 1H), 2.22 (ddd, J = 13.3, 9.6, 4.2 Hz, 1H), 1.82–1.72 (m, 2H), 1.41–1.32 (m, 1H), 1.30–1.21 (m, 1H), 1.09 (dd, J = 13.4, 3.3 Hz, 1H) 0.96 (s, 3H), 0.93 (s, 3H), 0.93 (s, 3H); δ_C (125 MHz, $CDCl_3$) 196.9, 163.3, 130.7, 129.9, 115.2, 83.4, 49.7, 47.8, 45.2, 36.9, 28.0, 26.9, 26.5, 19.8, 19.1, 13.9; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{18}H_{25}O_2$) requires m/z 273.1849, found m/z 273.1850.



***tert*-Butyl methyl(3-phenyl-3-(4-(trifluoromethyl)phenoxy)propyl)carbamate 42:** Prepared according to the general procedure using 1-bromo-4-(trifluoromethyl)benzene (140 μL, 1.00 mmol, 1.0 equivs.),

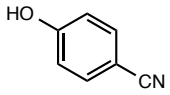
quinuclidine (11.1 mg, 0.100 mmol, 0.1 equivs.), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$•DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), *tert*-butyl (3-hydroxy-3-phenylpropyl)(methyl)carbamate (796 mg, 3.00 mmol, 3.0 equivs.) and acetonitrile (4.0 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 9:1) to give the *title compound* (335 mg, 82%, 0.818 mmol) as a colorless oil; IR ν_{max}/cm^{-1} 2977, 2931, 1691, 1614, 1323, 1246, 1154, 1109, 1067, 834; δ_H (500 MHz, $CDCl_3$) 7.42 (d, J = 8.5 Hz, 2H), 7.36–7.25 (m, 5H), 6.88 (d, J = 8.6 Hz, 2H), 5.21–5.11 (m, 1H), 3.57–3.24 (m, 2H), 2.85 (s, 3H), 2.27–2.00 (m, 2H), 1.41 (br s, 3H), 1.36 (br s, 6H); δ_C (125 MHz, $CDCl_3$) 160.5, 155.9, 140.9, 129.0, 128.1, 126.9 (q, J = 4.0 Hz), 125.8, 124.5 (q, J = 271.2 Hz), 123.0 (q, J = 34.0 Hz) 115.8, 79.6, 77.7, 45.9, 37.3, 34.6, 28.5; δ_F (282 MHz, $CDCl_3$) –61.6 (s, 3F); HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{22}H_{26}F_3NNaO_3$) requires m/z 432.1757, found m/z 432.1755.

Data are consistent with those reported in the literature[5].



4-Hydroxyacetophenone 43: Prepared according to the general procedure using 4-bromoacetophenone (199 mg, 1.00 mmol, 1.0 equivs.), quinuclidine (111 mg, 1.00 mmol, 1.0 equivs.), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$·DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), water (90.0 µL, 5.00 mmol, 5.0 equivs.) and acetonitrile/DMPU (4:1, 3.6 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 4:1 → 2:1) to give the *title compound* (92 mg, 68%, 0.676 mmol) as a colorless crystalline solid; δ_H (500 MHz, $CDCl_3$) 7.91 (d, J = 8.7 Hz, 2H), 6.90 (d, J = 8.7 Hz, 2H), 2.57 (s, 3H); δ_C (125 MHz, $CDCl_3$) 198.2, 161.0, 131.3, 130.0, 115.6, 26.5.

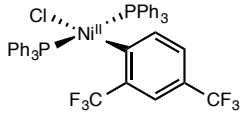
Data are consistent with those reported in the literature[14].



4-Hydroxybenzonitrile 44: Prepared according to the general procedure using 4-bromobenzonitrile (182 mg, 1.00 mmol, 1.00 equivs.), quinuclidine (111 mg, 1.00 mmol, 1.0 equivs.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 0.010 mmol, 0.01 equivs.), $NiCl_2$·DME (11.0 mg, 0.050 mmol, 0.05 equivs.), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 0.05 mmol, 0.05 equivs.), potassium carbonate (138 mg, 1.00 mmol, 1.0 equivs.), water (90.0 μL, 5.00 mmol, 5.0 equivs.) and acetonitrile/2-MeTHF (4:1, 3.6 mL). After 24 hours, the reaction mixture was worked up as outlined in the general procedure, then the crude material was purified by flash column chromatography (SiO_2, Hexanes/EtOAc – 4:1) to give the *title compound* (74 mg, 62%, 0.621 mmol) as a colorless crystalline solid; δ_H (500 MHz, $CDCl_3$) 7.56 (d, J = 8.7 Hz, 2H), 6.90 (d, J = 8.7 Hz, 2H); δ_C (125 MHz, $CDCl_3$) 159.9, 134.5, 119.3, 116.5, 103.7.

Data are consistent with those reported in the literature[15].

VI. General Procedures for Ni(II) Complex Synthesis



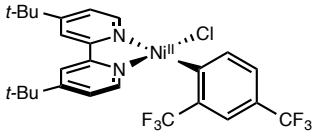
$(PPh_3)_2$Ni(2,4-bis(CF_3)phenyl)Cl:

Preparation of the Grignard reagent 2,4-bis(trifluoromethyl)phenylMgBr: Magnesium (1.09 g, 45.0 mmol, 3.0 equiv.) was flame dried in a 25 mL three-necked round-bottom flask and cooled to rt. A small iodine crystal and anhydrous THF (7.0 mL) were added. The middle neck was fitted with a greased reflux condenser and the flask was purged/backfilled with N_2 three times before 2,4-bis(trifluoromethyl)bromobenzene (4.40 g, 15.0 mmol, 1.0 equiv.) was added dropwise as a solution in anhydrous THF (3.0 mL). At the beginning of the addition, a color change was observed from brown to clear to gray to black; after the reaction initiated, drops were added so as to maintain a gentle reflux. After the addition was complete, the mixture was stirred 2 h, then titrated as described in the next section.

Titration of the Grignard reagent: Procedure adapted from the method of Love and Jones[16]. Salicylaldehyde phenylhydrazone (~25 mg, ~0.118 mmol) was dissolved in anhydrous THF (2.0 mL). The freshly prepared solution of 2,4-bis(trifluoromethyl)phenylMgBr was added until a color change was observed from yellow to dark orange and additional drops did not cause further color change, signifying the endpoint. The average of three titrations indicated a concentration of 0.413 M (83% yield, 12.4 mmol).

Addition of the Grignard reagent: Procedure adapted from the method of Jamison et al.[17]. $(PPh_3)_2NiCl_2$ (5.27 g, 8.06 mmol, 1.0 equiv., prepared by the method of Jamison et al.[17]) was dissolved in CH_2Cl_2 (73 mL, 0.11 M) and cooled to 0 °C. The resulting solution was stirred for 5 minutes, over which time it became red in color. Freshly prepared 2,4-bis(trifluoromethyl)phenylMgBr (0.413 M in THF, 19.5 mL, 8.06 mmol, 1.0 equiv.) was then added dropwise, causing a color change from red to brown-yellow just before the addition was complete. The solution was stirred at 0 °C for 15 min. before being concentrated by rotary evaporation. Residual solvent was removed under high vacuum to provide a green foam. Methanol was added to this residue and the mixture was sonicated, producing a bright yellow suspension. This suspension was filtered and the resulting solid was washed with cold Et_2O. Removal of residual solvent under high vacuum afforded the *title compound* (5.70 g, 85%, 6.86 mmol) as a pale golden yellow solid. IR ν_{max}/cm^{-1} 3054, 1819, 1602, 1483, 1436, 1340, 1268, 1237, 1156, 1118, 1089, 1023, 828, 745, 692; δ_H (500 MHz, C_6D_6) Two rotamers apparent. Major rotamer: 7.81–7.69 (m, 12H), 7.49 (d, J = 8.1

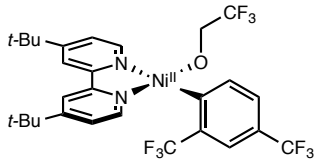
Hz, 1H), 7.04 (s, 1H), 7.02–6.93 (m, 18H), 6.22 (dd, *J* = 8.1, 1.9 Hz, 1H). Minor rotamer diagnostic peaks: 7.47 (d, 1H), 6.23 (d, 1H); δ_H (500 MHz, acetone-d_6) Two rotamers apparent. Major rotamer: 7.67 (d, *J* = 8.2 Hz, 1H), 7.64–7.58 (m, 12H), 7.41 (dd, J = 7.4 Hz, 7.4 Hz, 6H), 7.33 (dd, *J* = 7.4 Hz, 7.4 Hz, 12H), 6.79 (s, 1H), 6.59 (d, *J* = 8.2 Hz, 1H). Minor rotamer diagnostic peak: 6.60 (d, *J* = 9.0 Hz, 1H); δ_C (125 MHz, C_6D_6) Minor rotamer also apparent. 167.2 (t, *J* = 33.1 Hz), 139.8 (t, *J* = 4.2 Hz), 135.8 (qt, *J* = 29.3, 2.4 Hz), 135.5 (t, *J* = 5.3 Hz), 132.1 (t, *J* = 22.3 Hz), 130.8, 128.7 (t, *J* = 4.9 Hz), 125.7 (q, *J* = 273.2 Hz), 125.3 (q, *J* = 270.8 Hz), 125.1 (qt, *J* = 32.2, 2.3 Hz), 124.0, 122.8 (m); δ_F (282 MHz, C_6D_6) Two rotamers apparent. Major rotamer: –58.67 (dd, *J* = 5.2 Hz, 5.2 Hz), –62.06 (dd, *J* = 2.5 Hz, 2.5 Hz). Minor rotamer: –58.90 (dd, *J* = 5.4 Hz, 5.4 Hz), –62.01 (dd, *J* = 2.5 Hz, 2.5 Hz); δ_F (282 MHz, acetone-d_6) Two rotamers apparent. Major rotamer: –59.08 (dd, *J* = 5.1 Hz, 5.1 Hz), –62.94 (dd, *J* = 2.5 Hz); Minor rotamer: –59.30 (dd, *J* = 5.2 Hz, 5.2 Hz), –62.90 (dd, *J* = 2.5 Hz, 2.5 Hz), δ_P (203 MHz, C_6D_6) Two rotamers apparent. Major rotamer: 20.92–20.70 (m, 2 P). Minor rotamer: 19.77–19.62 (m, 2P); δ_P (203 MHz, acetone-d_6) Two rotamers apparent. Major rotamer: 25.55–25.25 (m, 2P). Minor rotamer: 24.68–24.38 (m, 2P).



(dtbbpy)Ni(2,4-bis(CF_3)phenyl)Cl. A flame-dried 100 mL round-bottom flask was charged with $(PPh_3)_2$Ni(2,4-bis(CF_3)phenyl)Cl (500 mg, 0.601 mmol, 1 equiv.) and 4,4'-di-tert-butyl-2,2'-bipyridine (169 mg, 0.631 mmol, 1.05 equiv.). Et_2O (30.0 mL, 0.020 M) was added and the mixture was stirred at rt for 4 days. The reaction mixture was filtered through a fritted funnel and the resulting solid was washed with pentane. Residual solvent was removed by high vacuum to afford the *title compound* (259 mg, 75%, 0.449 mmol) as an orange solid. IR ν_{max}/cm^{-1} 2959, 1617, 1604, 1414, 1342, 1265, 1121, 1105, 1025, 901, 826, 745, 689, 656; δ_H (500 MHz, C_6D_6) Two rotamers apparent. Major rotamer: 9.54 (br s, 1H), 8.65 (d, *J* = 8.1 Hz, 1H), 8.00 (s, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.11 (br s, 2H), 6.87 (br s, 1H), 6.51 (br s, 1H), 5.95 (br s, 1H), 0.89 (s, 9H), 0.78 (s, 9H). Minor rotamer diagnostic peaks: 9.31 (br s, 1H), 6.94 (br s, 1H), 6.59 (br s, 1H); δ_H (500 MHz, acetone-d_6) Two rotamers apparent. Major rotamer: 9.21 (br s, 1H), 8.47 (s, 2H), 8.40 (d, J = 8.3 Hz, 1H), 7.72 (br s, 1H), 7.54 (s, 1H), 7.42 (br s, 1H), 7.38 (d, *J* = 8.3 Hz, 1H), 6.90 (br s, 1H), 1.43 (s, 9H), 1.37 (s, 9H). Minor rotamer diagnostic peaks: 8.95 (s, 1H), 6.98 (s, 1H); δ_C (125 MHz, acetone-d_6) Two rotamers apparent. Major rotamer: 164.6, 164.3, 160.1 (br q, *J* = 2.5 Hz), 156.0, 153.3, 150.8, 150.5, 139.5, 135.9 (q, *J* = 29.8 Hz), 124.8 (q, *J* = 272.9 Hz), 124.7 (q, *J* = 270.6 Hz), 124.5 (q, *J* = 32.4 Hz), 123.7, 123.4, 122.6 (br q, *J* = 2.4 Hz), 120.6–120.4 (m), 119.3, 118.6, 35.4,

29.5, 29.3. Minor rotamer diagnostic peaks: 160.9 (br q, J = 2.7 Hz), 151.2, 149.0, 138.8, 135.8 (q, J = 29.8 Hz), 124.6 (q, J = 32.3 Hz), 123.2, 120.5–120.2 (m), 118.5; δ_F (282 MHz, C_6D_6) Two rotamers apparent. Major rotamer: –57.63 (s, 3F), –61.58 (s, 3F). Minor rotamer: –57.75 (s, 3F), –61.59 (s, 3F); δ_F (282 MHz, acetone-d_6) Two rotamers apparent. Major rotamer: –58.58 (s, 3F), –62.54 (s, 3F), –58.72 (s, 3F), –62.56 (s, 3F); HRMS (ESI) exact mass calculated for $[M–Cl]^+$ ($C_{26}H_{27}F_6N_2{}^{58}Ni$) requires m/z 539.1426, found m/z 539.1427; exact mass calculated for $[M–Cl+CH_3CN]^+$ ($C_{28}H_{30}F_6N_3{}^{58}Ni$) requires m/z 580.1692, found m/z 539.1692.

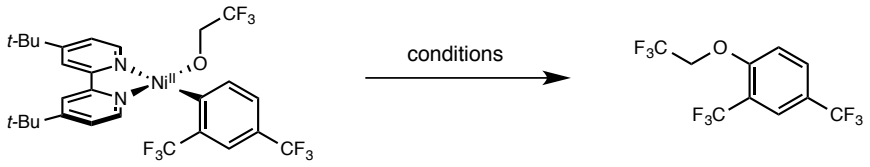
Sodium trifluoroethoxide ($NaOCH_2CF_3$). A flame-dried 250 mL round-bottom flask was charged with 2,2,2-trifluoroethanol (15.0 ml, 205 mmol, 25.0 equiv., dried over $CaSO_4$ and $NaHCO_3$ for 3 h). Sodium (189 mg, 8.22 mmol, 1.00 equiv.) was added in small portions and allowed to dissolve. After dissolution was complete, the mixture was allowed to stir for 15 min, then concentrated *in vacuo*. The residue was placed under high vacuum for several days to remove residual solvent, affording the *title compound* (0.95 g, 7.79 mmol, 95% yield) as a white solid. This bulk material was stored in a glovebox, but small portions were removed just before use and weighed out in air.



(dtbbpy)Ni(2,4-bis(CF_3)phenyl)(OCH_2CF_3) 45. An oven-dried 8 mL vial was charged with sodium trifluoroethoxide (3.60 mg, 0.030 mmol, 1.00 equiv.) and CD_3CN (591 µL, 0.050 M). (dtbbpy)Ni(2,4-bis(CF_3)phenyl)Cl (17.0 mg, 0.030 mmol, 1.00 equiv.) was added and the resulting red mixture was stirred for 1 h at rt before being filtered. ^{1}H NMR analysis indicated 74% yield vs. 1,3-benzodioxole as internal standard. IR ν_{max}/cm^{-1} 2968, 1604, 1413, 1341, 1266, 1113, 1063, 1026, 834, 689; δ_H (500 MHz, CD_3CN) 8.66 (d, J = 7.7 Hz, 1H), 8.54 (d, J = 5.9 Hz, 1H), 8.12 (d, J = 1.9 Hz, 1H), 8.04 (d, J = 2.2 Hz, 1H), 7.70 (s, 1H), 7.66 (dd, J = 5.9, 1.9 Hz, 1H), 7.50 (d, J = 7.7 Hz, 1H), 7.08 (dd, J = 6.2, 2.2 Hz, 1H), 6.94 (d, J = 6.2 Hz, 1H), 2.63 (dq, J = 12.4, 10.0 Hz, 1H), 2.54 (dq, J = 12.4, 10.0 Hz, 1H), 1.42 (s, 9H), 1.31 (s, 9H). δ_C (125 MHz, CD_3CN) 171.0 (br q, J = 3.2 Hz), 165.6, 164.5, 156.9, 153.4, 152.8, 147.2, 139.5, 137.5 (q, J = 29.5 Hz), 127.2 (q, J = 281.3 Hz), 126.3 (q, J = 32.4 Hz), 126.1 (q, J = 272.3 Hz), 125.7 (q, J = 270.7 Hz), 124.5 (br m), 124.1, 123.8, 121.9–121.5 (m), 120.0, 118.9, 67.3 (q, J = 30.4 Hz), 36.4, 36.2, 30.5, 30.2; δ_F (282 MHz, CD_3CN) –60.49 (s, 3F), –62.64 (s, 3F), –77.09 (t, J = 9.9 Hz);

HRMS (ESI) exact mass calculated for [M–$HOCH_2CF_3$] ($C_{26}H_{27}F_6N_2{}^{58}Ni$) requires m/z 539.14319, found m/z 539.14342; exact mass calculated for [M–$HOCH_2CF_3$+CH_3CN] ($C_{28}H_{30}F_6N_3{}^{58}Ni$) requires m/z 580.1697, found m/z 539.1695.

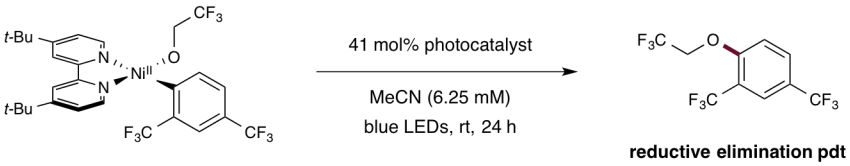
VII. Reductive Elimination Study of Ni(II) Complex 45



Standard reaction conditions: An 8 mL vial was charged with (dtbbpy)Ni(2,4-bis(CF_3)phenyl)(OCH_2CF_3) (150 µL, 0.037 M, 5.55 µmol, 1.00 equiv.), Ir[dF(CF_3)ppy]$_2$(dtbbpy) (2.5 mg, 2.25 µmol, 0.41 equiv.), and 1.05 mL CD_3CN. The mixture was sparged with N_2 for 30 seconds before the reaction was sealed, placed next to blue LED strips, and stirred for 24 h with cooling by fan. The reaction was then removed from the light and analyzed by ^{1}H NMR vs. 1,3-benzodioxole as an internal standard (see section XII for crude NMR spectrum).

Reaction without photocatalyst: An 8 mL vial was charged with (dtbbpy)Ni(2,4-bis(CF_3)phenyl)(OCH_2CF_3) (150 µL, 0.037 M, 5.55 µmol, 1.00 equiv.) and 1.05 mL CD_3CN. The mixture was sparged with N_2 for 30 seconds before the reaction was sealed, placed next to blue LED strips, and stirred for 24 h with cooling by fan. The reaction was then removed from the light and analyzed by ^{1}H NMR vs. 1,3-benzodioxole as an internal standard (see section XII for crude NMR spectrum).

Reaction without light: An 8 mL amber vial was charged with (dtbbpy)Ni(2,4-bis(CF_3)phenyl)(OCH_2CF_3) (150 µL, 0.037 M, 5.55 µmol, 1.00 equiv.), Ir[dF(CF_3)ppy]$_2$(dtbbpy) (2.5 mg, 2.25 µmol, 0.41 equiv.), and 1.05 mL CD_3CN. The mixture was sparged with N_2 for 30 seconds before the reaction was sealed, covered with foil, and stirred for 24 h in the dark. The reaction was then analyzed by ^{1}H NMR vs. 1,3-benzodioxole as an internal standard (see section XII for crude NMR spectrum).

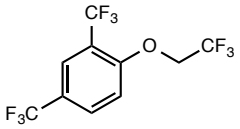


Ni(II) complex 45

reductive elimination pdt aryl ether 46

entry	conditions	remaining **45**	yield **46**
1	as shown	0%	59%
2	no photocatalyst	76%	0%
3	no light	76%	0%

Figure S3. Reductive elimination studies of Ni complex **45**. Yields determined by ^{1}H NMR analysis using 1,3-benzodioxole as internal standard. Reactions performed on 5.55 μmol scale.



1-(2,2,2-Trifluoroethoxy)-2,4-bis(trifluoromethyl)benzene 46. Authentic product was prepared by the method of Vuluga et al.[18]. IR ν_{max}/cm^{-1} 2956, 1629, 1514, 1347, 1279, 1265, 1167, 1124, 1067, 916, 824, 685, 664; δ_H (500 MHz, CD_3CN) 8.01–7.89 (m, 2H), 7.34 (d, J = 9.4 Hz, 1H), 4.73 (q, J = 8.2 Hz, 2H); δ_C (125 MHz, CD_3CN) 158.5 (br q), 132.4 (q, J = 3.5 Hz), 126.1–125.7 (m), 124.7 (q, J = 270.9 Hz), 124.5 (q, J = 32.8 Hz), 124.3 (q, J = 276.7 Hz), 123.8 (q, J = 271.8 Hz), 120.1 (q, J = 32.2), 115.5, 66.9 (q, J = 36.0 Hz); δ_F (282 MHz, CD_3CN) –62.61 (s, 3F), –63.46 (s, 3F), –74.91 (t, J = 8.3 Hz, 3F); HRMS (EI) exact mass calculated for $[M]^+$ ($C_{10}H_5F_9O$) requires m/z 312.0191, found m/z 312.0190.

VIII. Cyclic Voltammetry

Cyclic Voltammetry was performed on a CH Instruments Electrochemical Analyzer (CHI600E). A 0.0054 M CH_3CN solution of Ni(II) complex **45** was prepared with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte and sparged with N_2 for 10 minutes. The cyclic voltammogram was obtained using a glassy carbon working electrode, a Pt counter electrode, and a saturated calomel reference electrode. Scan rate = 0.1 V/s.

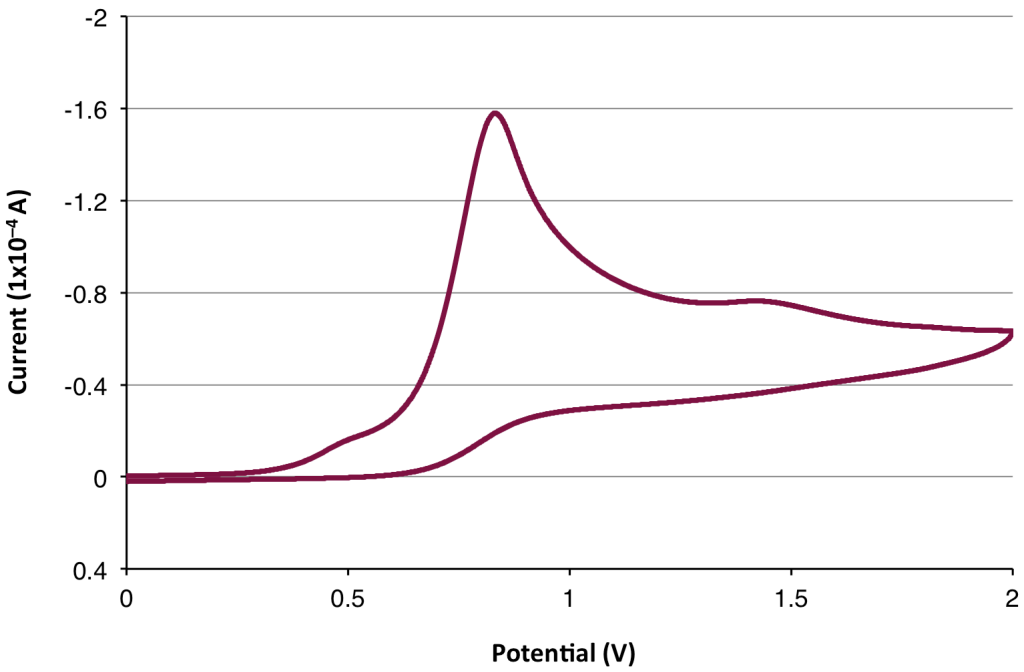


Figure S4. Cyclic voltammogram of Ni(II) complex **45** shows an irreversible oxidation potential at +0.83 V vs. SCE in CH_3CN, which corresponds to the Ni^{III}/Ni^{II} couple, generating Ni(III) complex **47**. There is a minor potential peak at around +0.5 V vs. SCE, which is indicative of the Ni^{III}/Ni^{II} couple of (dtbbpy)Ni(aryl)(OH), a minor byproduct in the formation of complex **45**.

IX. UV–Vis Spectroscopy Data

UV–Vis spectroscopy was performed on an Agilent 8453 Spectrophotometer. In a typical experiment, a solution of Ni complex **45** in CH_3CN was added to a screw-top 1.0 cm quartz cuvette. After degassing by bubbling a stream of nitrogen for 10 minutes, the absorption spectrum of the sample was collected from 300 to 800 nm.

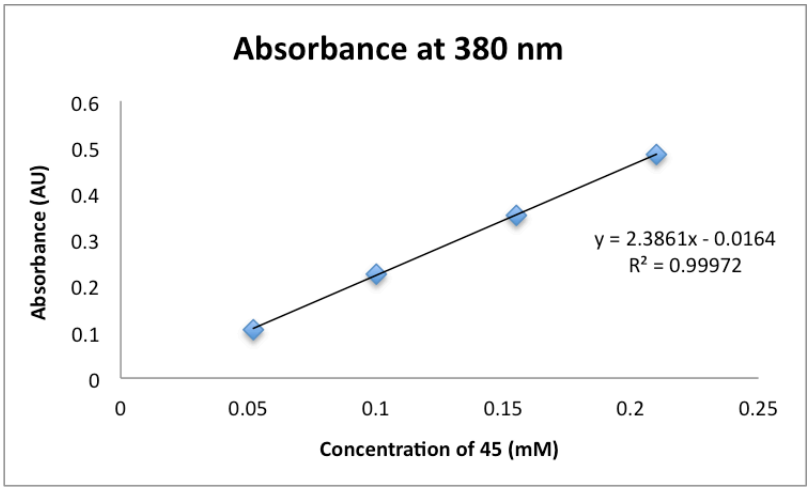


Figure S5. The absorbance of Ni complex **45** at 380 nm over concentrations from 0.05–0.20 mM. A linear relationship between concentration and absorbance is observed.

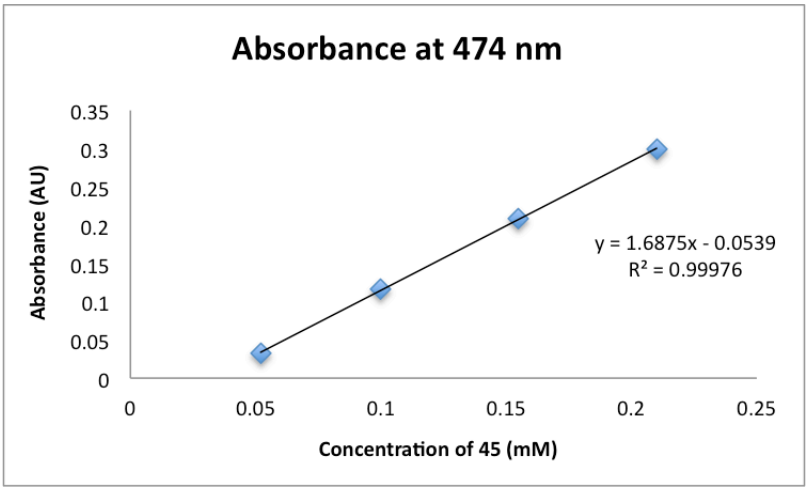


Figure S6. The absorbance of Ni complex **45** at 474 nm over concentrations from 0.05–0.20 mM. A linear relationship between concentration and absorbance is observed.

X. Stern–Volmer Fluorescence Quenching Experiments

Fluorescence quenching experiments were performed on an Agilent Cary Eclipse Fluorescence Spectrophotometer. In a typical experiment, a 2.5 μM solution of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ in CH_3CN was added to the appropriate amount of quencher in a screw-top 1.0 cm quartz cuvette. After degassing by bubbling a stream of nitrogen for 10 minutes, the emission of the sample was collected. All solutions were excited at λ = 380 nm (absorption maximum of the photocatalyst) and the emission intensity at 474 nm was observed (emission maximum).

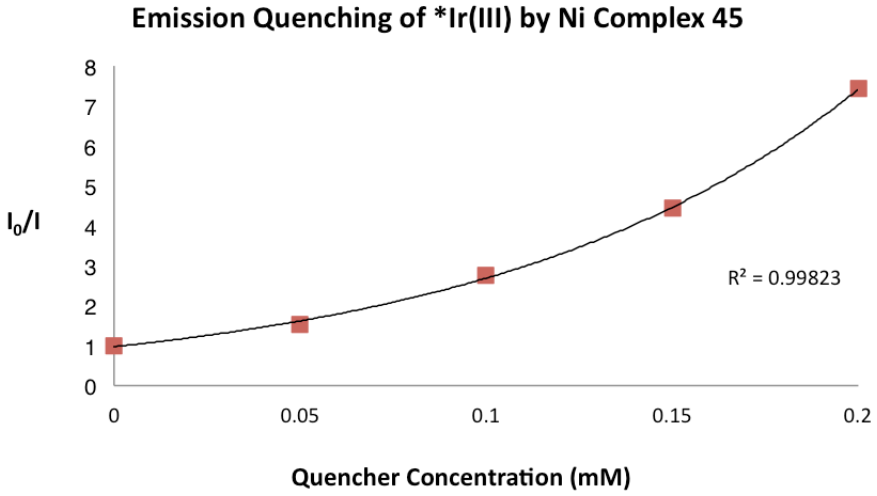


Figure S7. $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ emission quenching by Ni complex **45**. Non-linear quenching is observed.

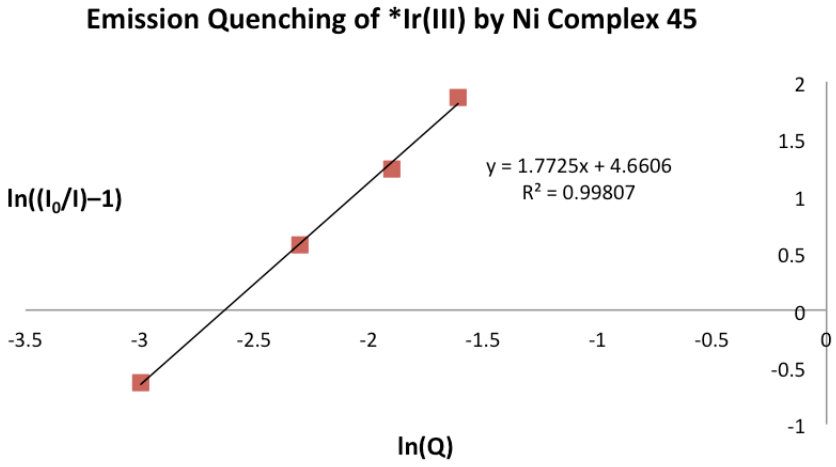


Figure S8. Log plot of emission quenching of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ by Ni complex **45**. Linear correlation represents exponential trend in emission quenching.

As highlighted in Figure S6, we observe non-linear quenching of $*Ir^{III}$ in the presence of Ni complex **45**. The diminished intensity of $*Ir^{III}$ emission is attributed to several factors. Firstly, UV–Vis spectroscopy data has shown that Ni complex **45** absorbs at the excitation wavelength (380 nm) and at the emission wavelength of $*Ir^{III}$ (474 nm). As demonstrated in Figures S4 and S5, the absorbance by **45** at these wavelengths is linear. Taking into consideration these data, we conclude that the trend observed in Figure S6 is due to the additive effects of absorbance by Ni complex **45** and non-linear emission quenching by Ni complex **45**. The origin of this non-linearity may be due to multiple quenching pathways, although we cannot rule out additional factors that may influence the emission intensity.

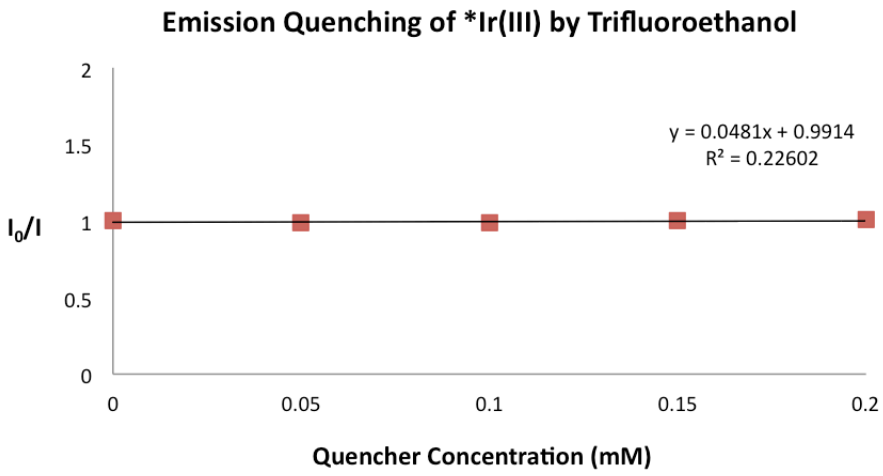


Figure S9. $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ emission quenching by trifluoroethanol.

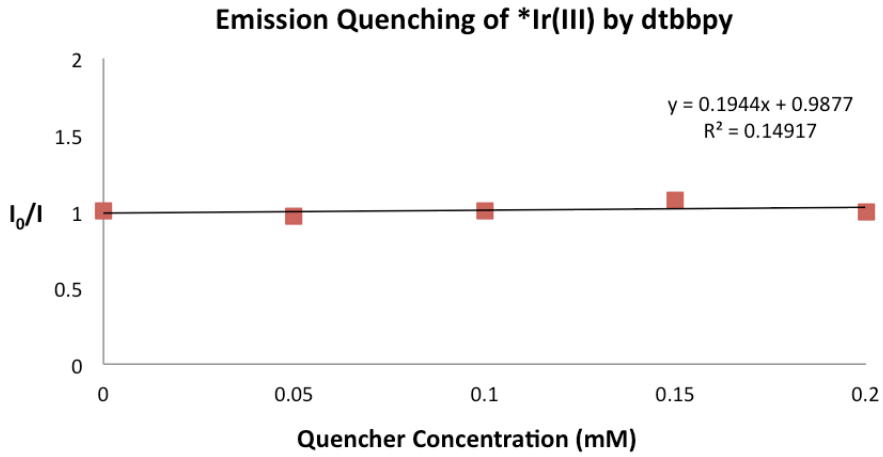


Figure S10. Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ emission quenching by 4,4'-di-tert-butyl-2,2'-bipyridine.

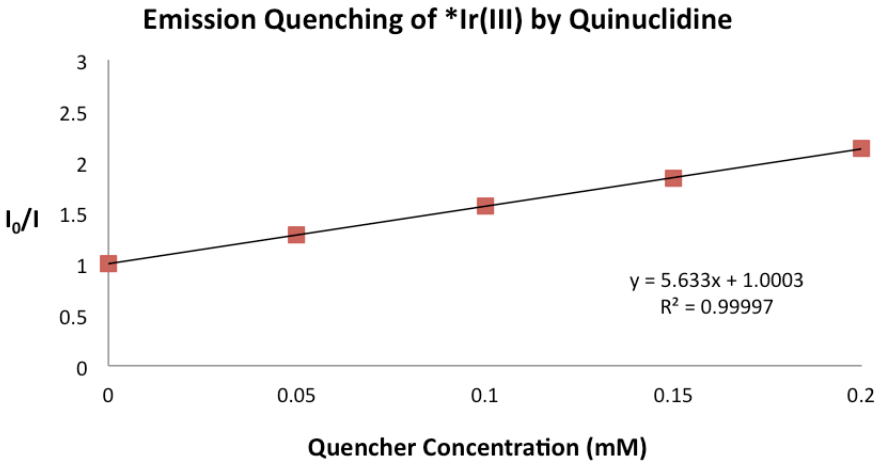


Figure S11. Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ emission quenching by quinuclidine.

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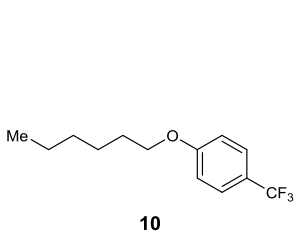
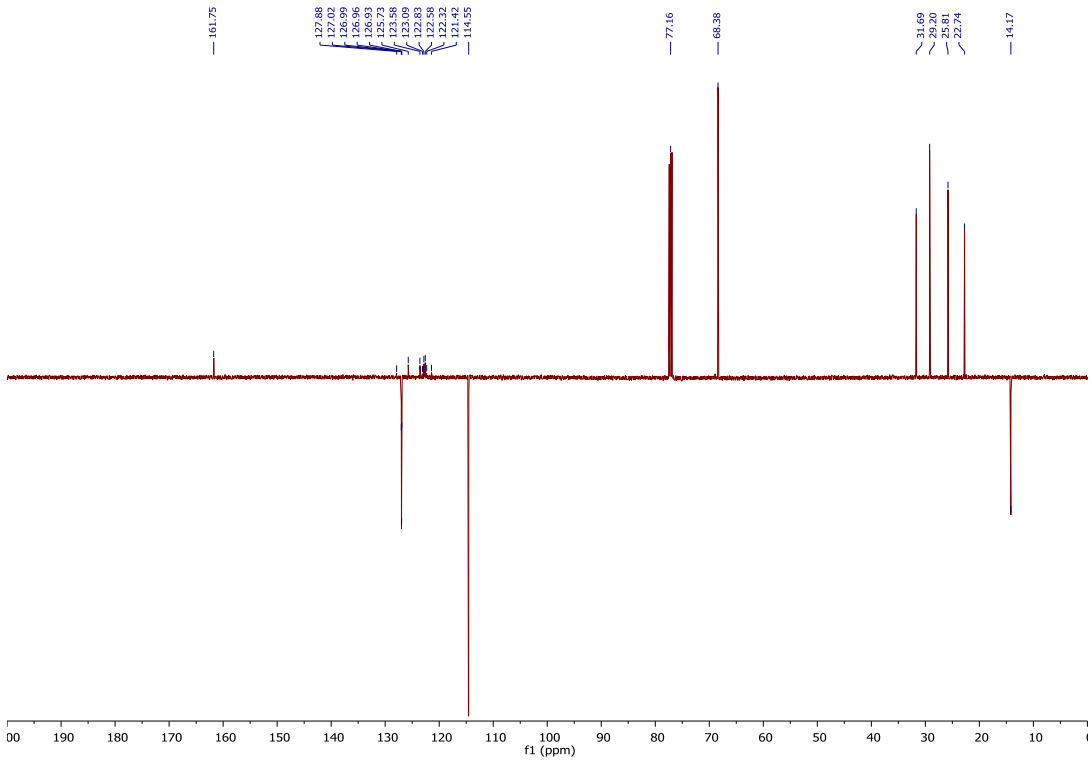
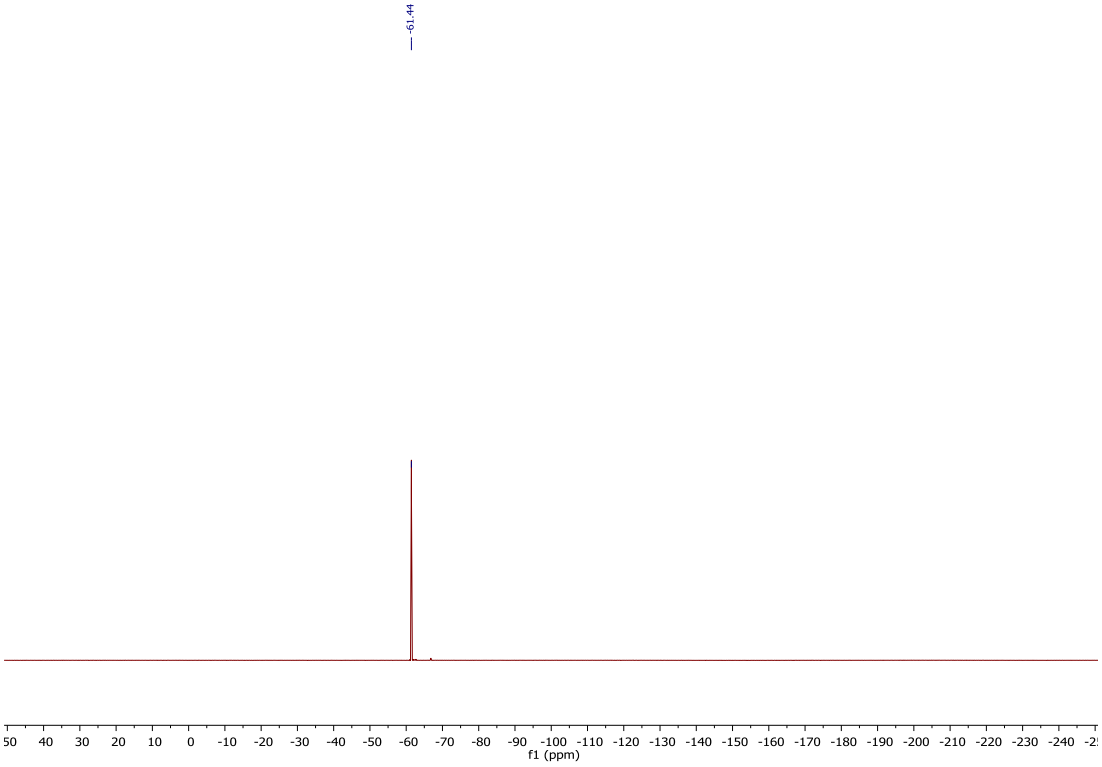
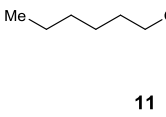
XII. NMR Spectral Data for Novel Compounds



10

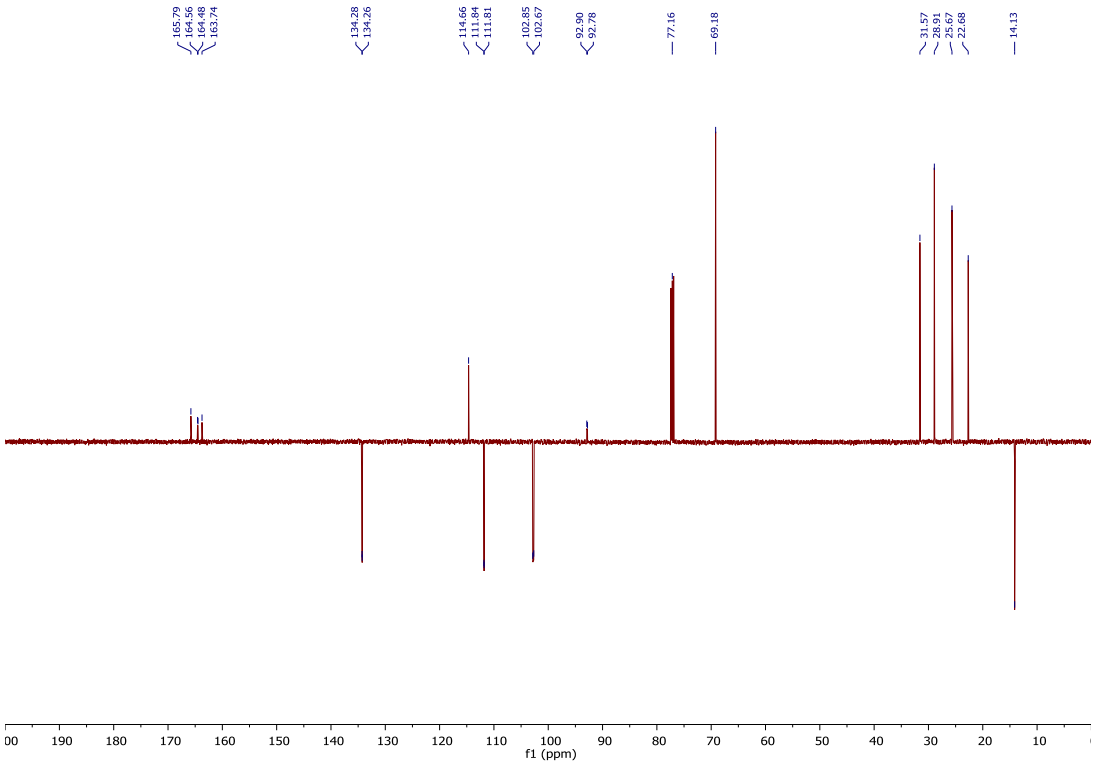


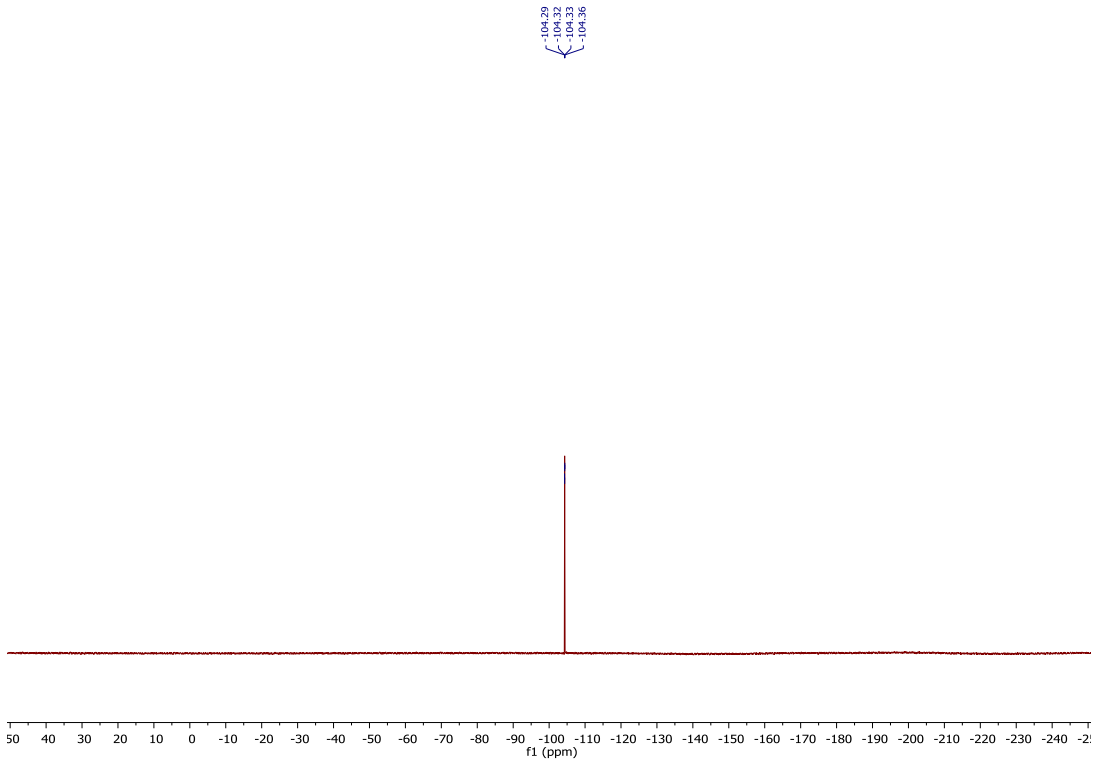

-61.44
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

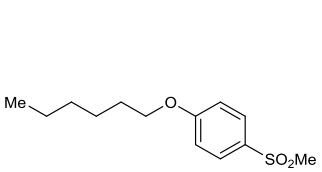

Me
O
F
CN

11

7.26
1.00
1.01
1.02
2.03
2.03
2.04
4.09
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

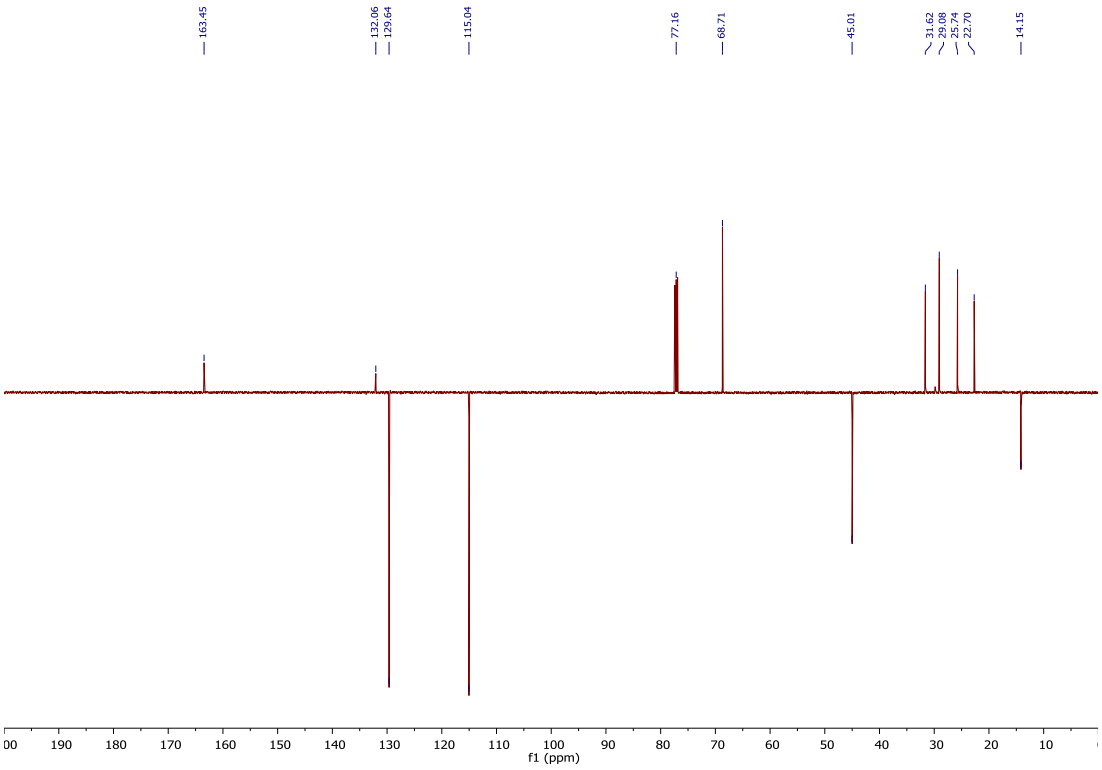

165.79
164.56
164.48
163.74
134.28
134.26
114.66
111.84
111.81
102.85
102.67
92.90
92.78
77.16
69.18
31.57
28.91
25.67
22.68
14.13
f1 (ppm)

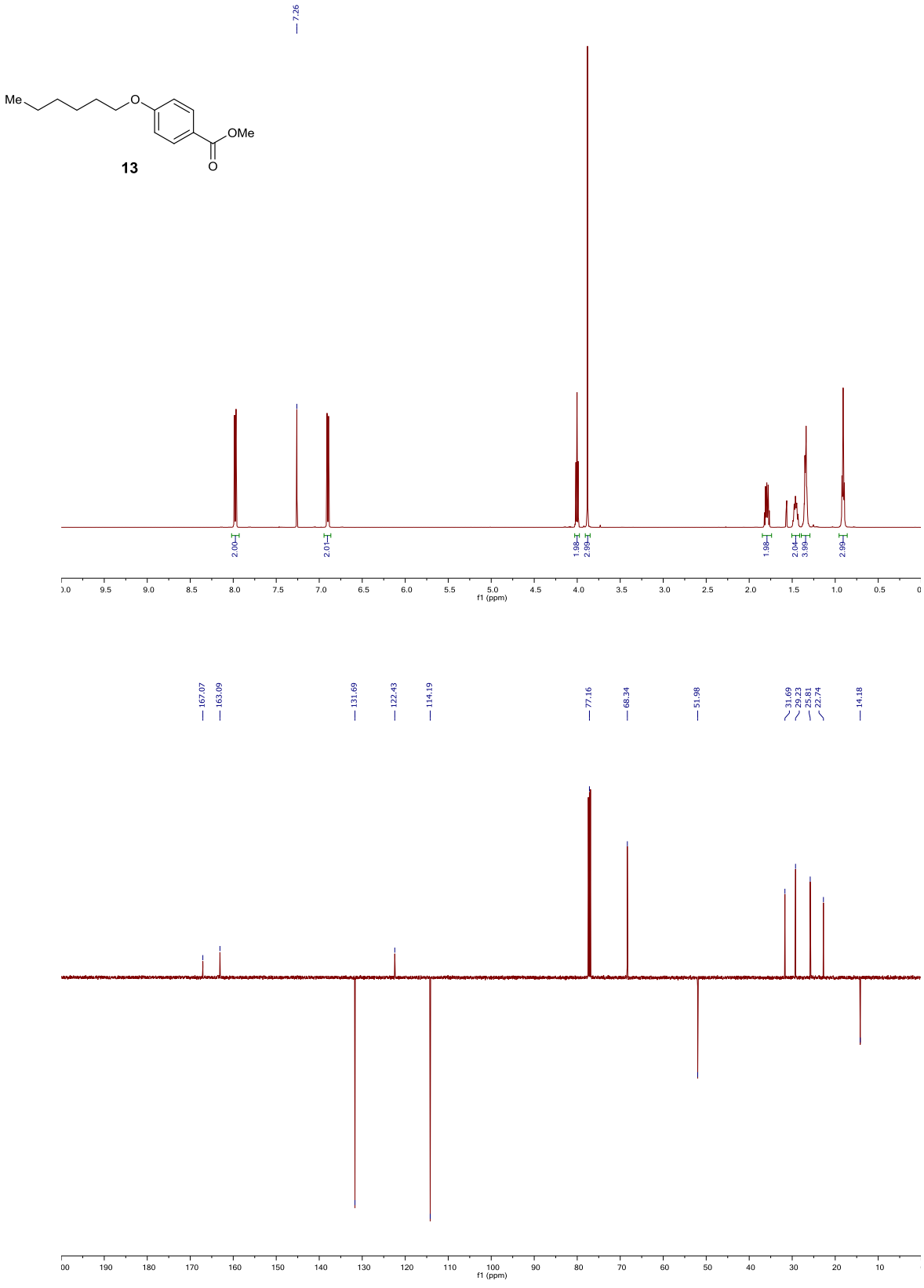

-104.29
-104.32
-104.33
-104.36
f1 (ppm)

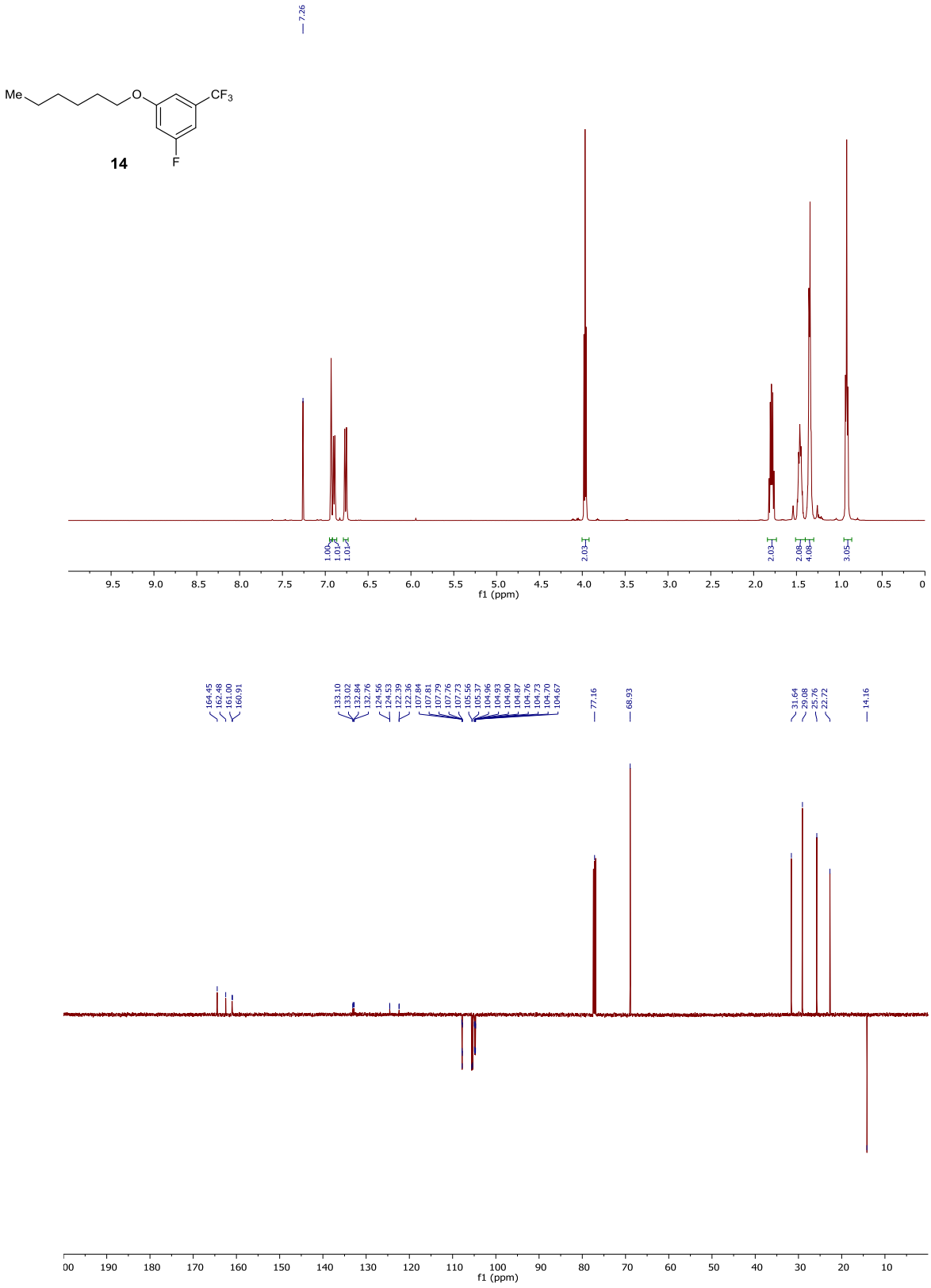

Me
O
SO2Me

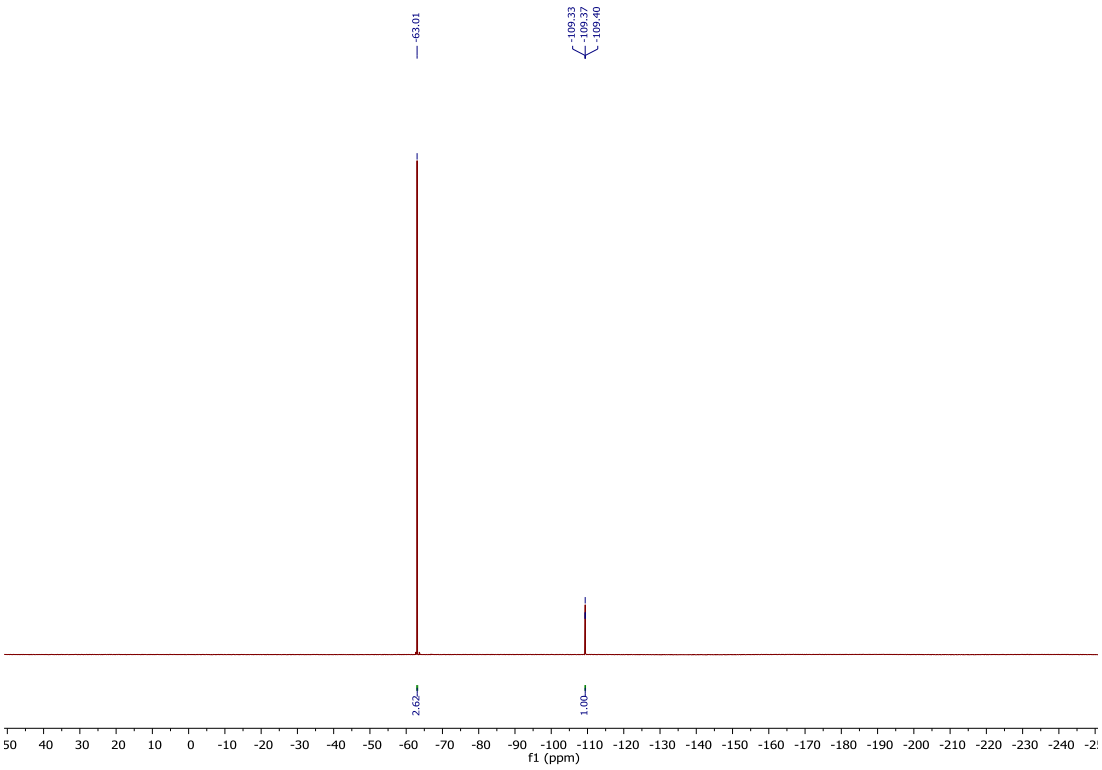
12

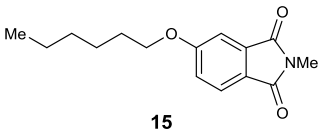
7.26
2.00
2.02
2.01
3.02
2.01
2.05
4.14
3.07
f1 (ppm)


163.45
132.06
129.64
115.04
77.16
68.71
45.01
31.62
29.08
25.74
22.70
14.15
f1 (ppm)


Me
O
OMe
O
13
7.26
2.00
2.01
1.98
2.99
1.98
2.04
3.99
2.99
f1 (ppm)
167.07
163.09
131.69
122.43
114.19
77.16
68.34
51.98
31.69
29.23
25.81
22.74
14.18
f1 (ppm)

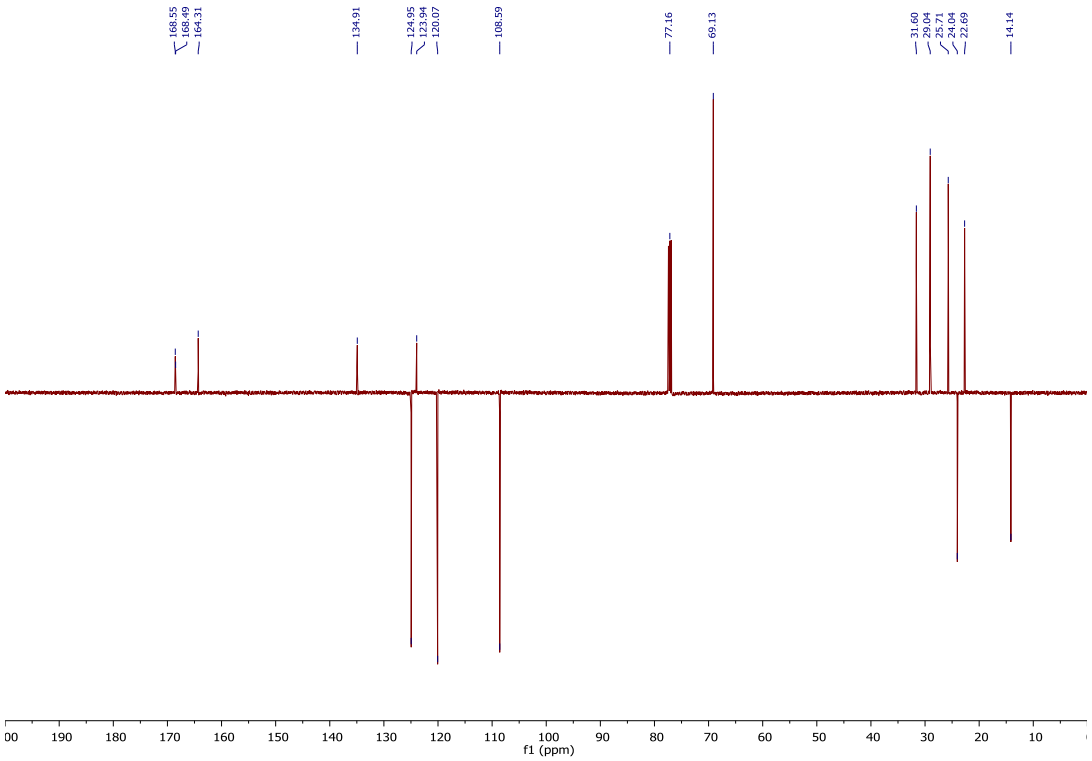

Me
O
CF3
F
14
7.26
1.00
1.03
1.01
2.03
2.03
2.08
4.08
3.05
f1 (ppm)
164.45
162.48
161.00
160.91
133.10
133.02
132.84
132.76
124.56
124.53
122.39
122.36
107.84
107.81
107.79
107.76
107.73
105.56
105.37
104.96
104.93
104.90
104.87
104.76
104.73
104.70
104.67
77.16
68.93
31.64
29.08
25.76
22.72
14.16
f1 (ppm)

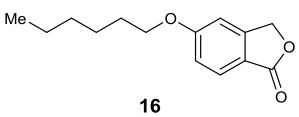

-63.01
-109.33
-109.37
-109.40
2.62
1.00
f1 (ppm)


Me
O
O
NMe
O

15

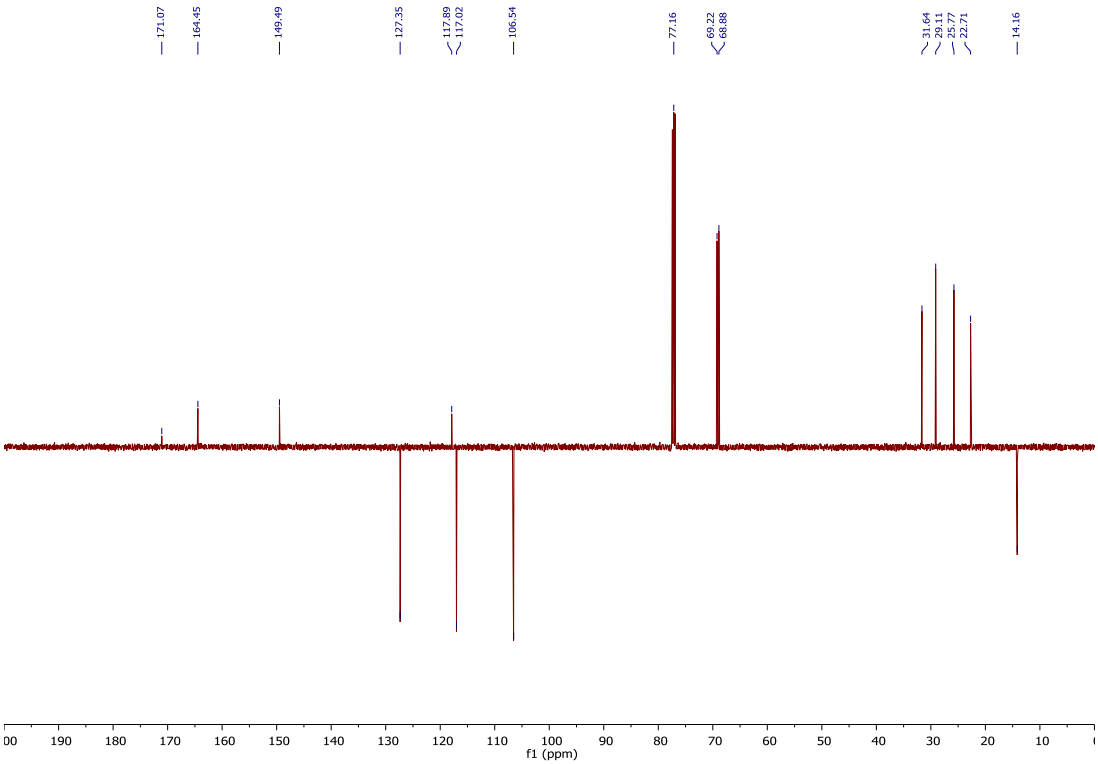
7.26
1.00
1.00
1.01
2.02
3.01
2.00
2.01
4.02
3.00
f1 (ppm)

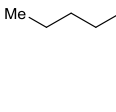

168.55
168.49
164.31
134.91
124.95
123.94
120.07
108.59
77.16
69.13
31.60
29.04
25.71
24.04
22.69
14.14
f1 (ppm)


Me
O
O
O

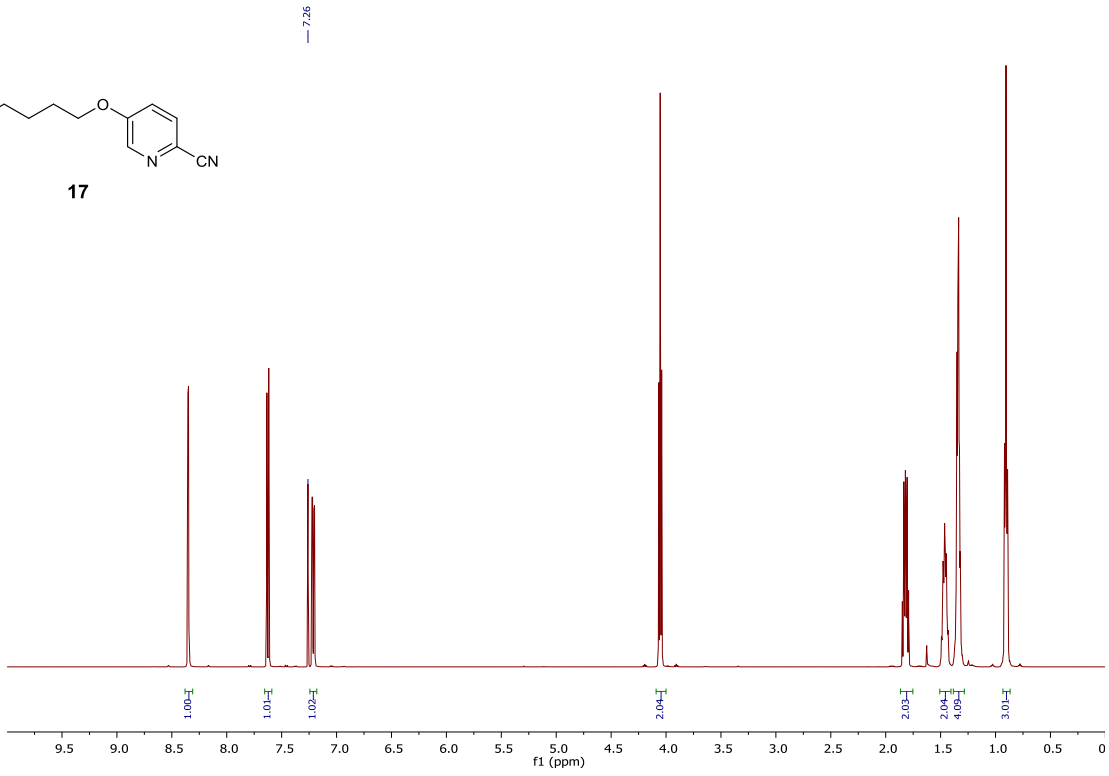
16

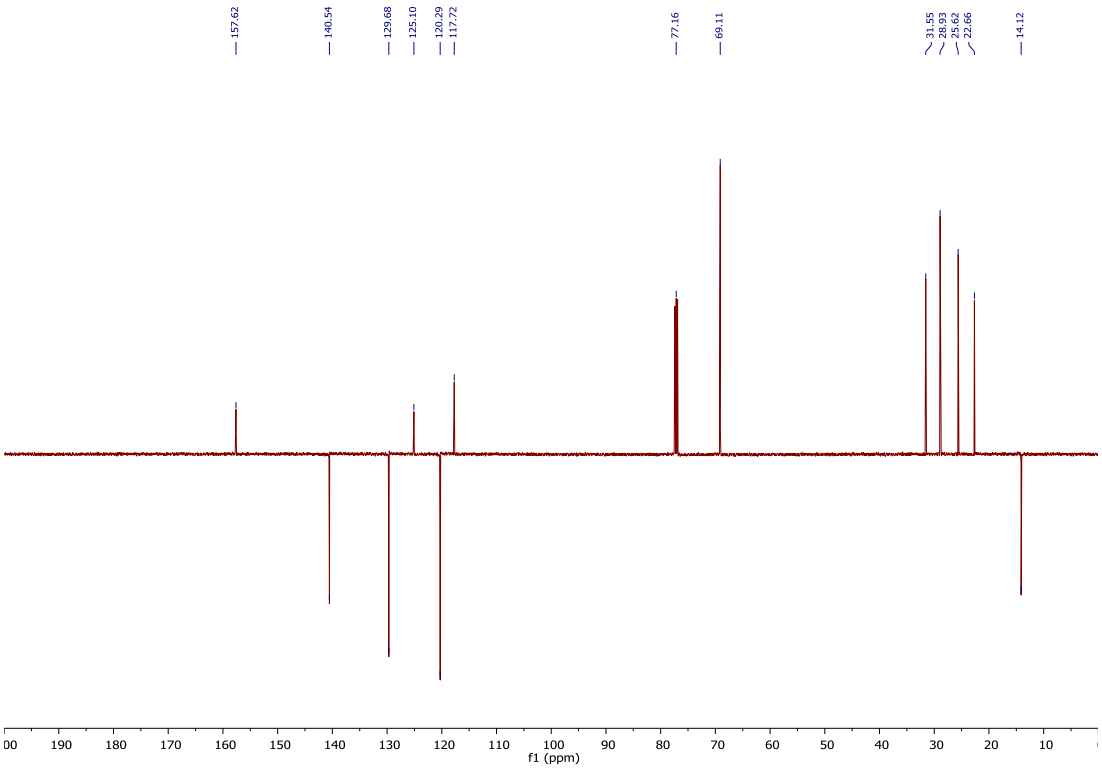
7.26
1.00
1.00
1.00
2.01
2.01
2.00
2.01
4.03
3.03
f1 (ppm)

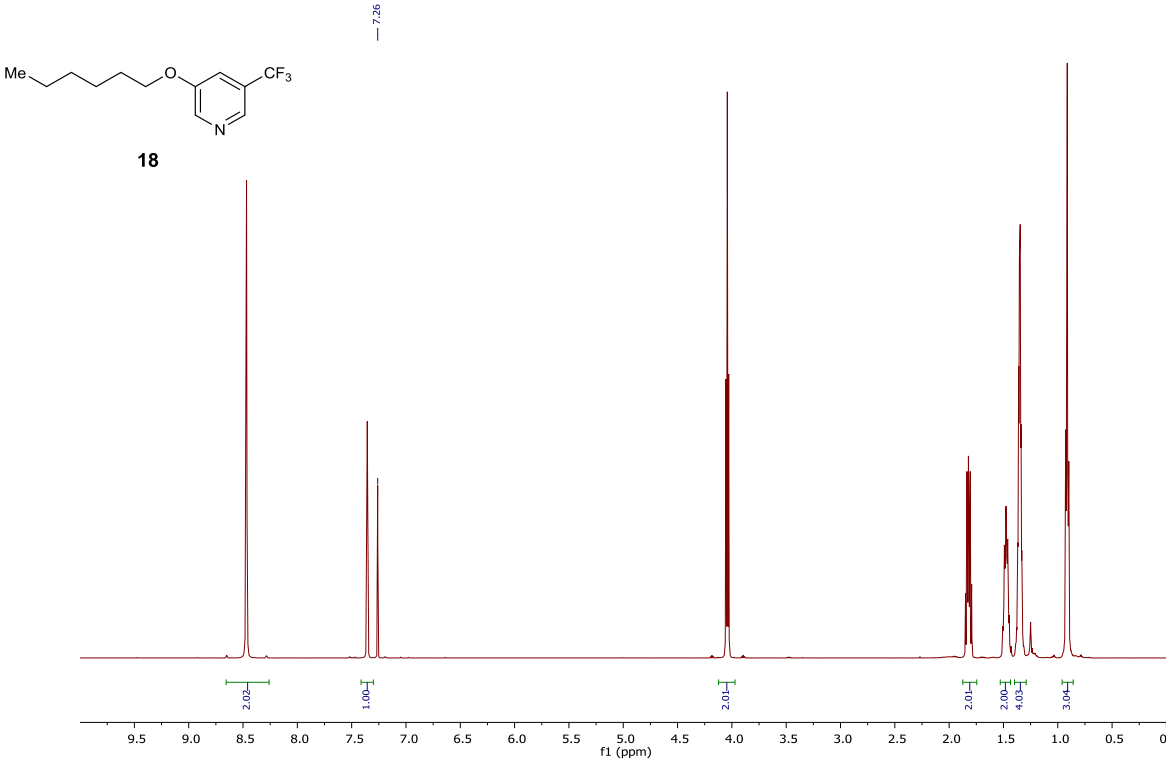

171.07
164.45
149.49
127.35
117.89
117.02
106.54
77.16
69.22
68.88
31.64
29.11
25.77
22.71
14.16
f1 (ppm)

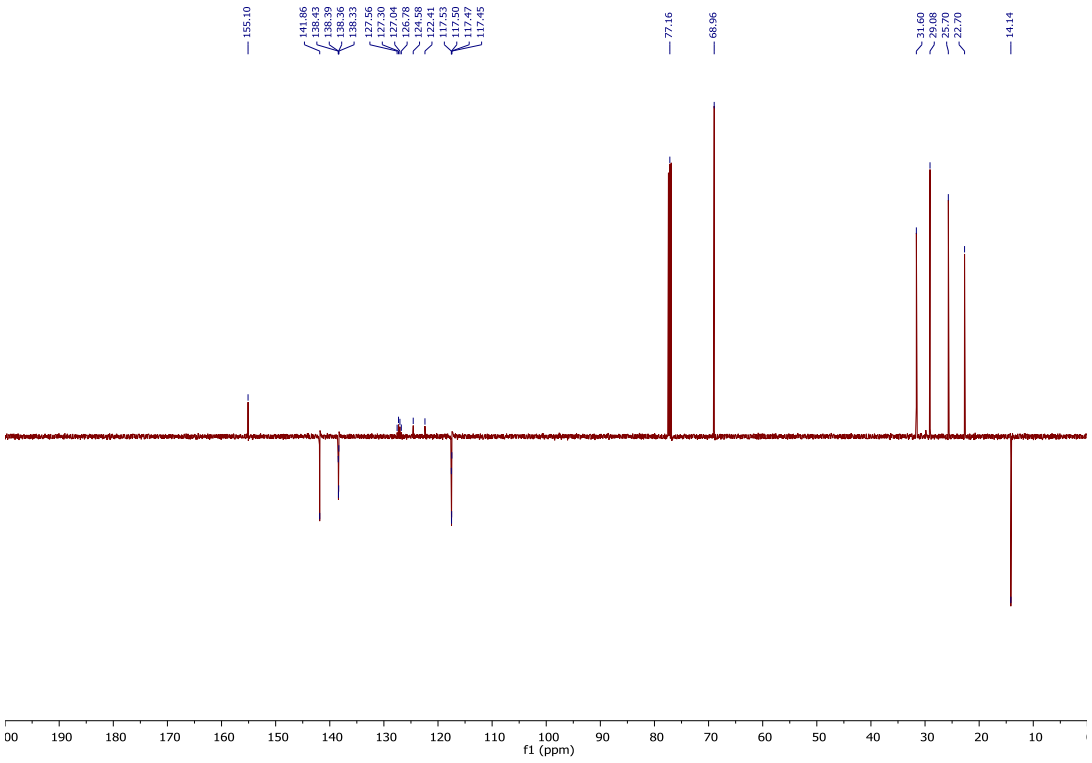

Me
O
N
CN

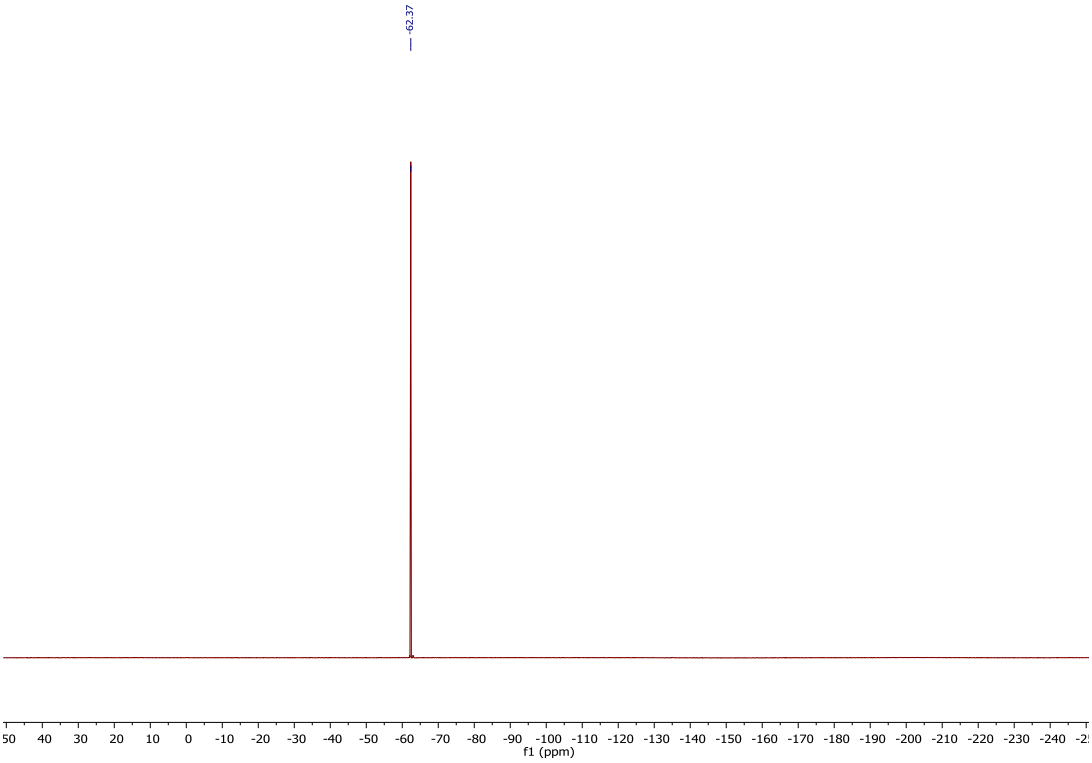
17

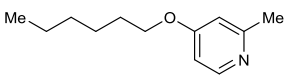

7.26
1.00
1.01
1.02
2.04
2.03
2.04
4.09
3.01
f1 (ppm)


157.62
140.54
129.68
125.10
120.29
117.72
77.16
69.11
31.55
28.93
25.62
22.66
14.12
f1 (ppm)


7.26
Me
O
CF3
N
18
2.02
1.00
2.01
2.01
2.00
4.03
3.04
f1 (ppm)

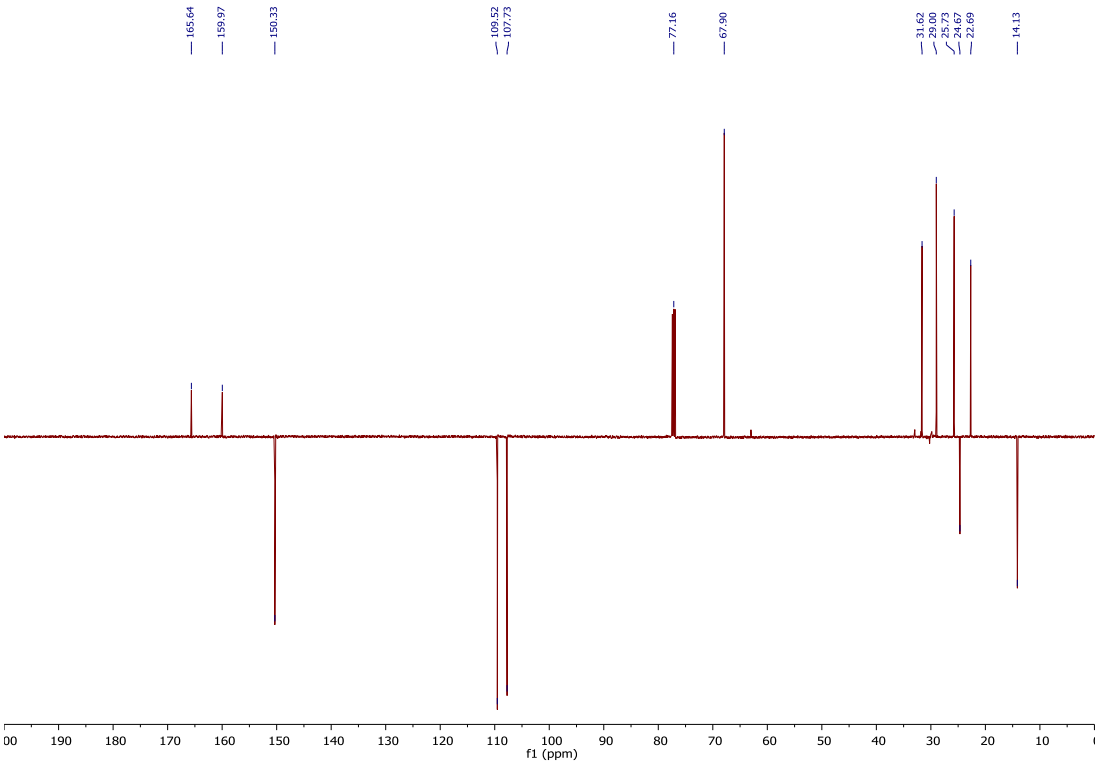

155.10
141.86
138.43
138.39
138.36
138.33
127.56
127.30
127.04
126.78
124.58
123.41
117.53
117.50
117.47
117.45
77.16
68.96
31.60
29.08
25.70
22.70
14.14
f1 (ppm)

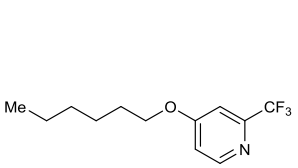

-62.37
f1 (ppm)


Me
O
Me
N

19

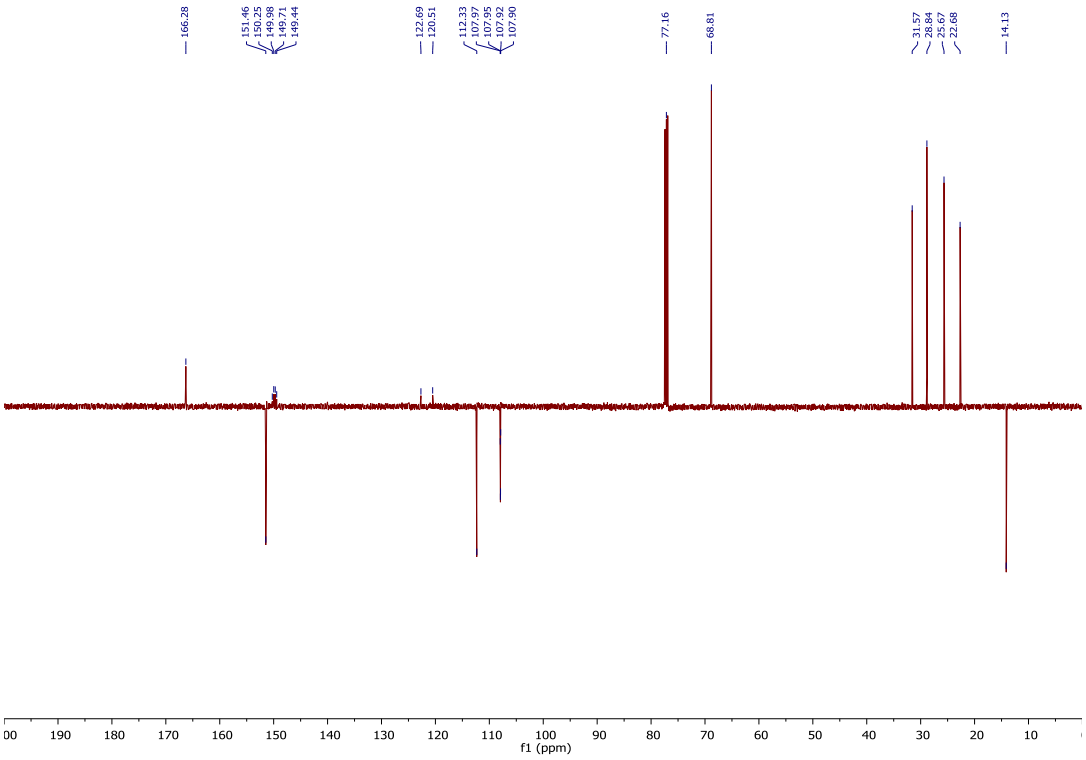
7.26
1.00
1.00
1.02
2.00
3.01
1.99
2.09
4.23
3.02
f1 (ppm)


165.64
159.97
150.33
109.52
107.73
77.16
67.90
31.62
29.00
25.73
24.67
22.69
14.13
f1 (ppm)


Me
O
CF3
N

20

7.26
1.00
1.01
1.01
2.02
2.03
2.01
4.03
3.00
f1 (ppm)


166.28
151.46
150.25
149.98
149.71
149.44
122.69
120.51
112.33
107.97
107.95
107.92
107.90
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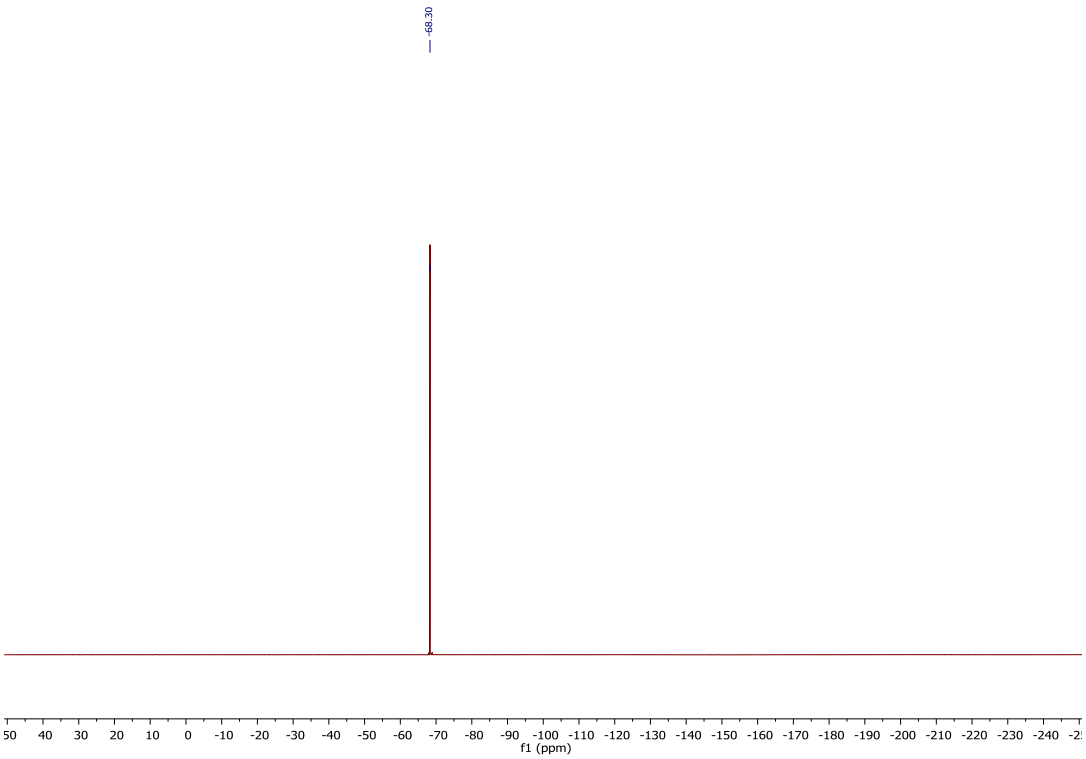
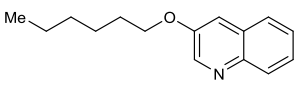
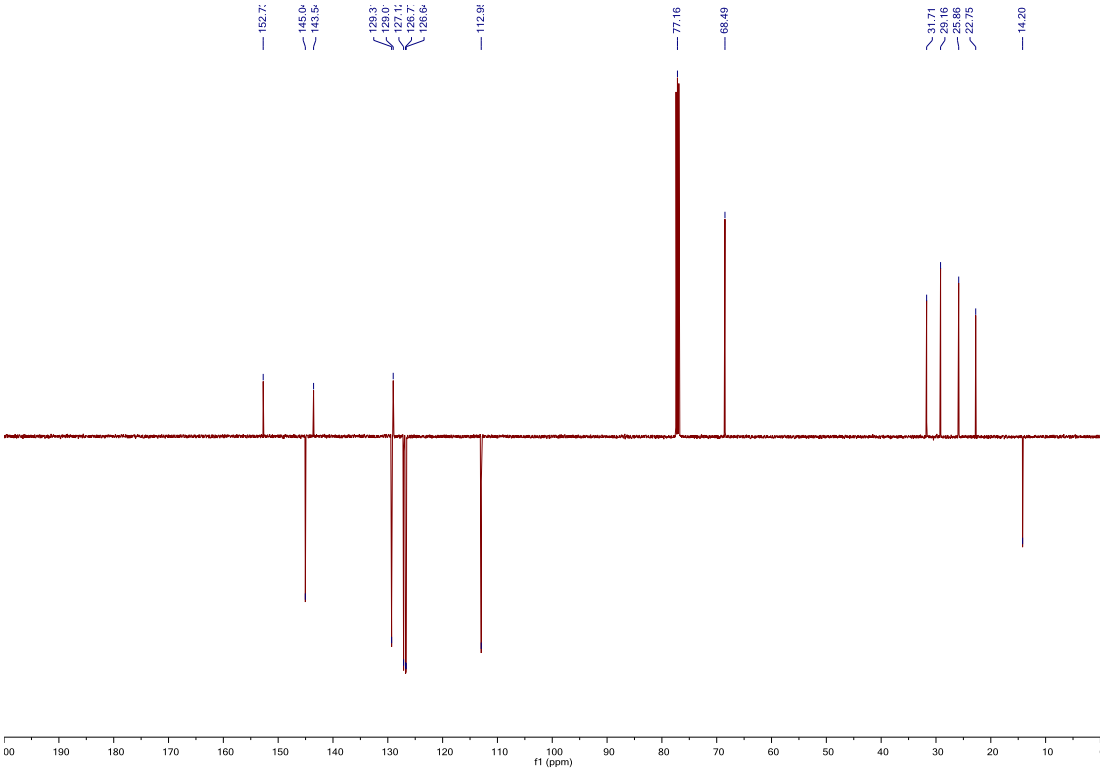
31.57
28.84
25.67
22.68
14.13
f1 (ppm)

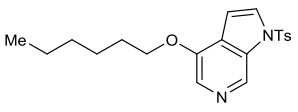

-68.30
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)


Me
O
N

21

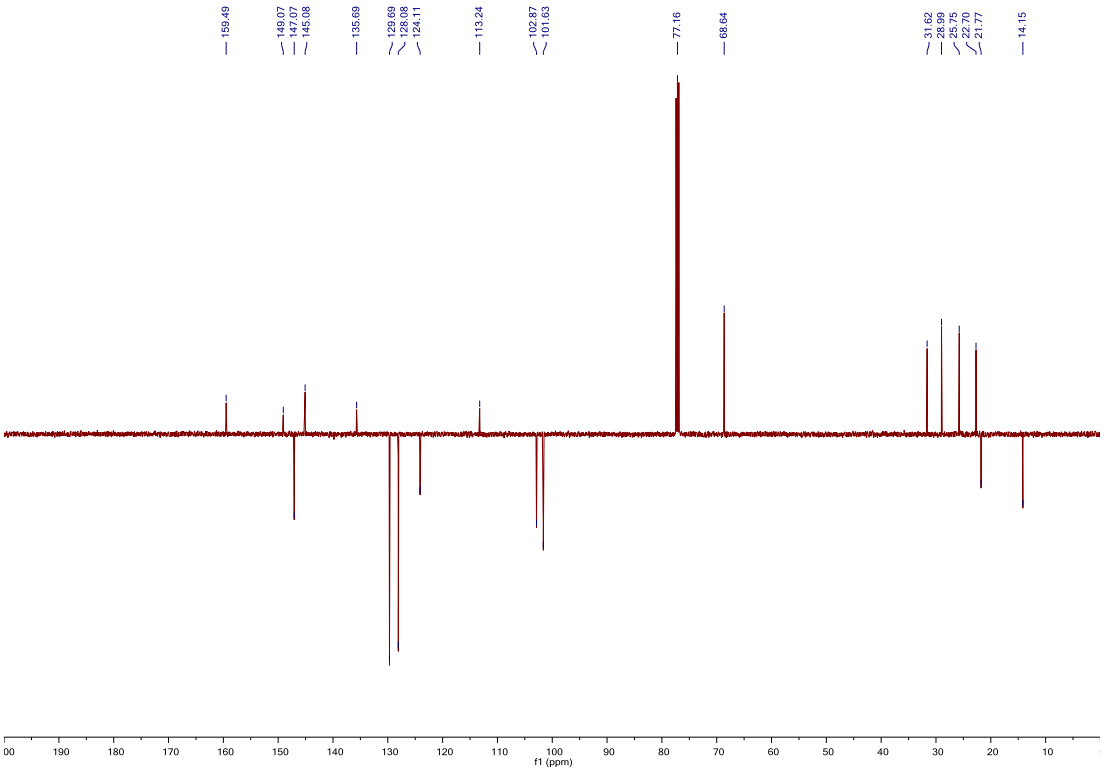
7.26
0.99
1.00
1.02
1.03
1.02
1.02
2.03
2.02
2.04
4.07
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

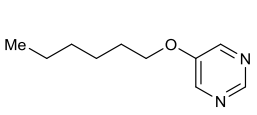

152.7
145.0
143.5
129.3
129.0
127.1
126.7
126.6
112.9
77.16
68.49
31.71
29.16
25.86
22.75
14.20
f1 (ppm)


Me
O
NTs
N

22

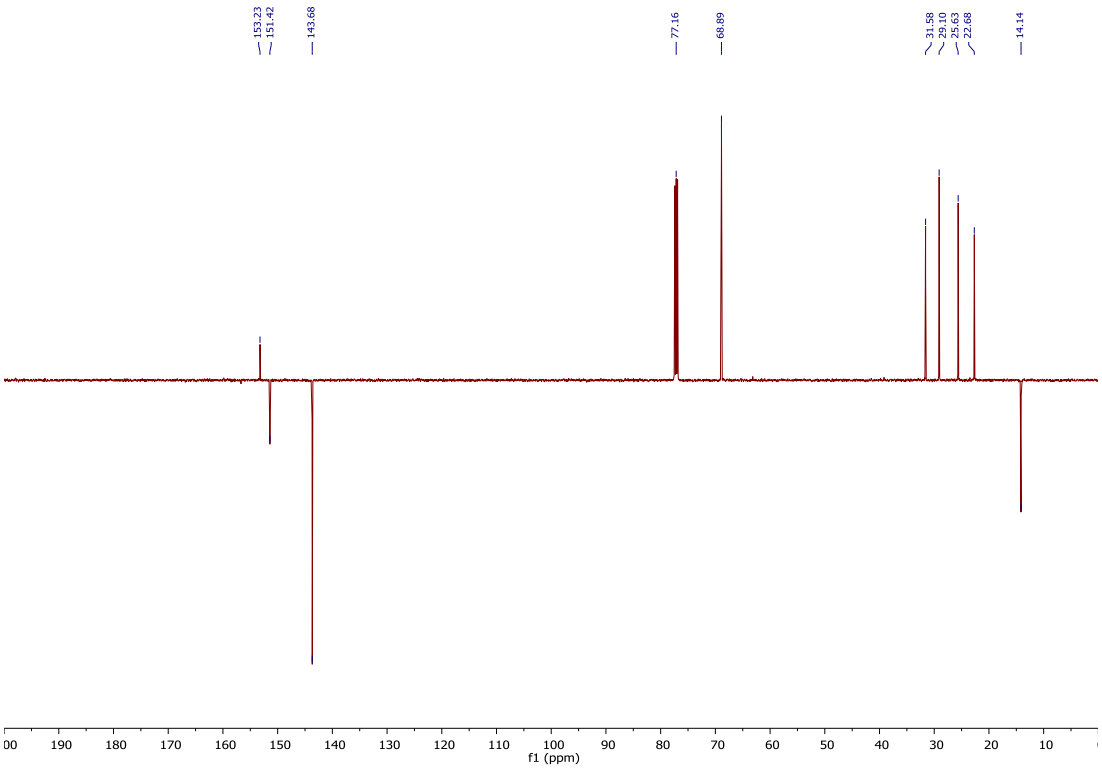
7.26
1.00
2.01
1.00
2.02
1.00
1.00
2.00
3.03
1.99
2.01
4.05
3.03
f1 (ppm)

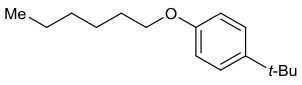

159.49
149.07
147.07
145.08
135.69
129.69
128.08
124.11
113.24
102.87
101.63
77.16
68.64
31.62
28.99
25.75
22.70
21.77
14.15
f1 (ppm)


Me
O
N
N

23

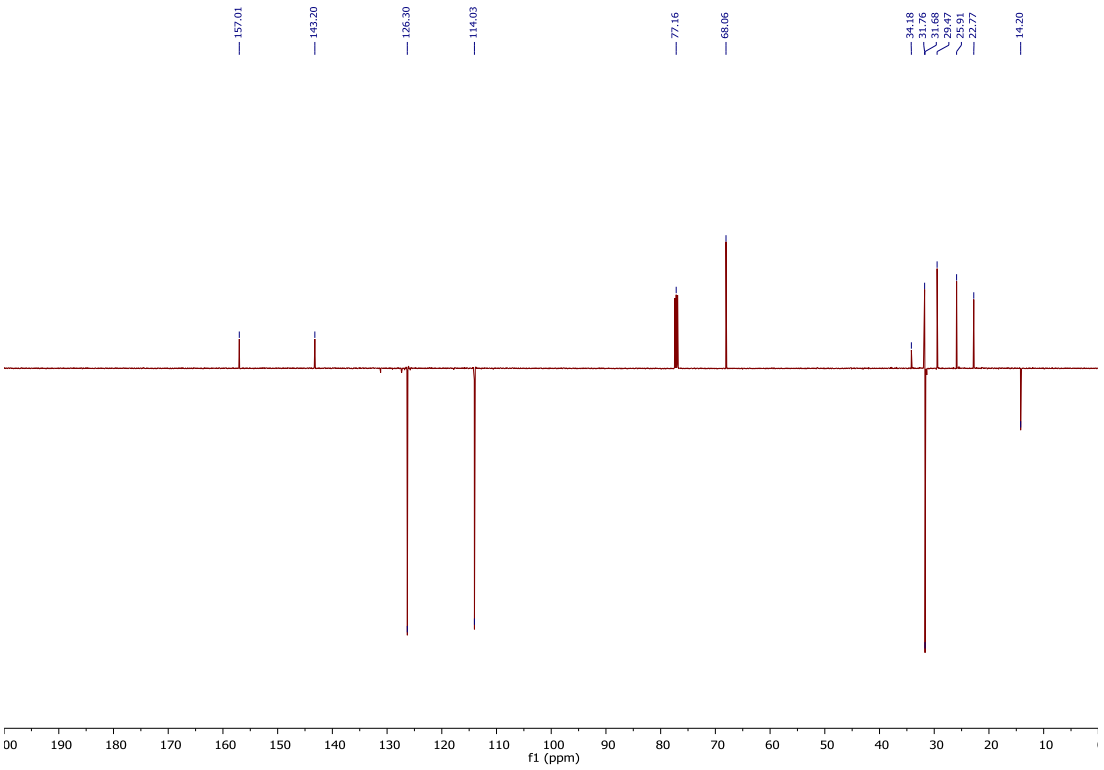
7.26
0.97
2.00
2.01
1.99
2.05
4.16
3.06
f1 (ppm)

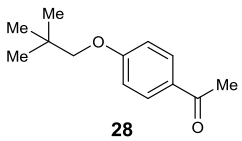

153.23
151.42
143.68
77.16
68.89
31.58
29.10
25.63
22.68
14.14
f1 (ppm)


Me
O
t-Bu

25

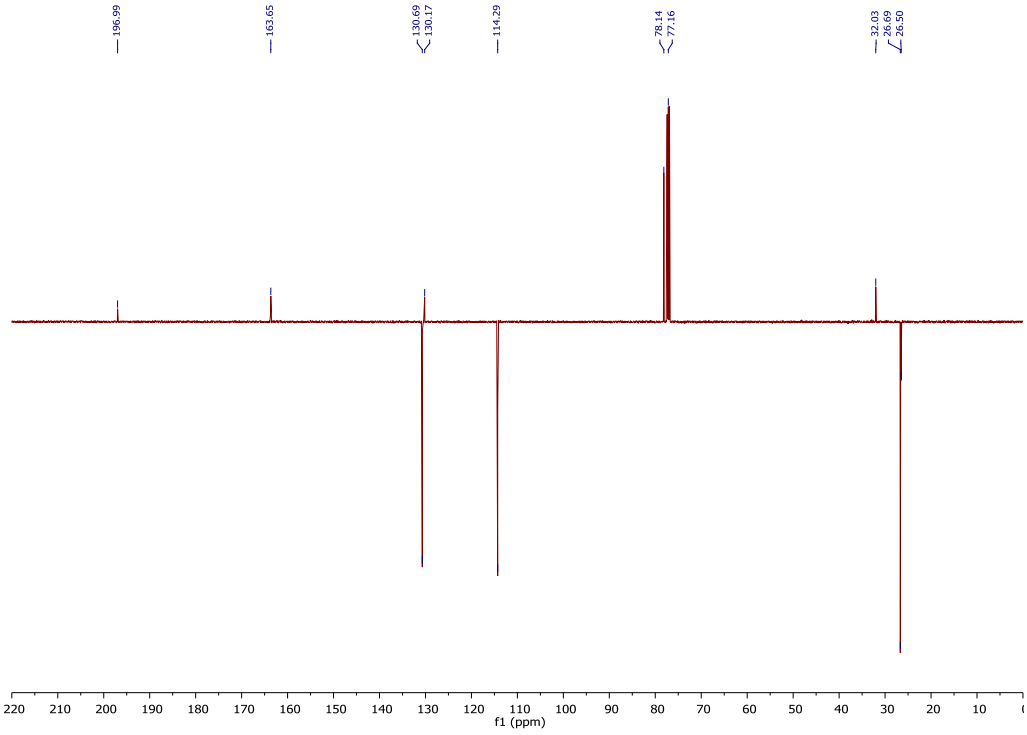
7.26
2.00
2.00
2.01
2.01
2.04
4.14
9.21
3.01
f1 (ppm)

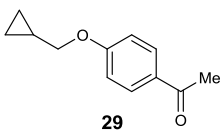

157.01
143.20
126.30
114.03
77.16
68.06
34.18
31.76
31.68
29.47
25.91
22.77
14.20
f1 (ppm)


Me
Me
Me
O
Me
O

28

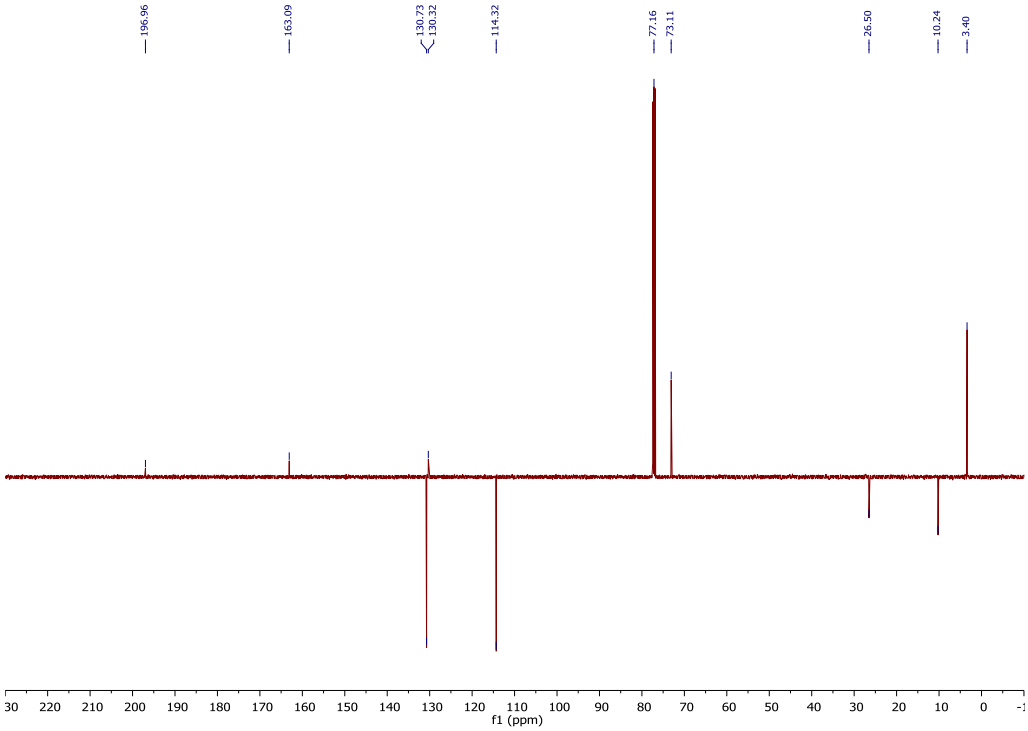
7.26
2.00
2.00
2.00
3.00
9.00
f1 (ppm)

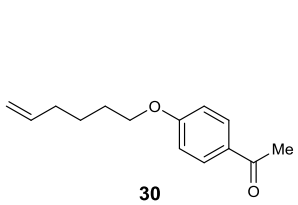

196.99
163.65
130.69
130.17
114.29
78.14
77.16
32.03
26.69
26.50
f1 (ppm)


O
Me
O

29

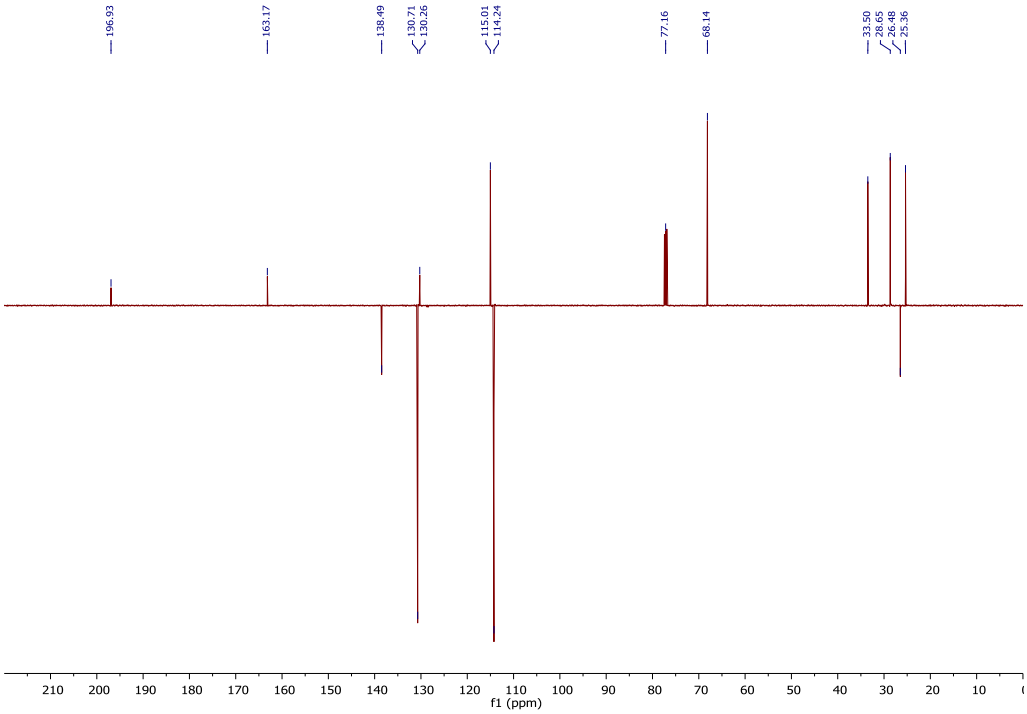
7.26
2.00
2.00
1.99
3.01
1.03
1.98
1.98
f1 (ppm)

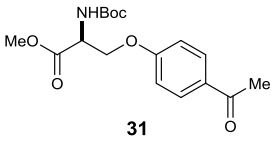

196.96
163.09
130.73
130.32
114.32
77.16
73.11
26.50
10.24
3.40
f1 (ppm)


O
Me
O

30

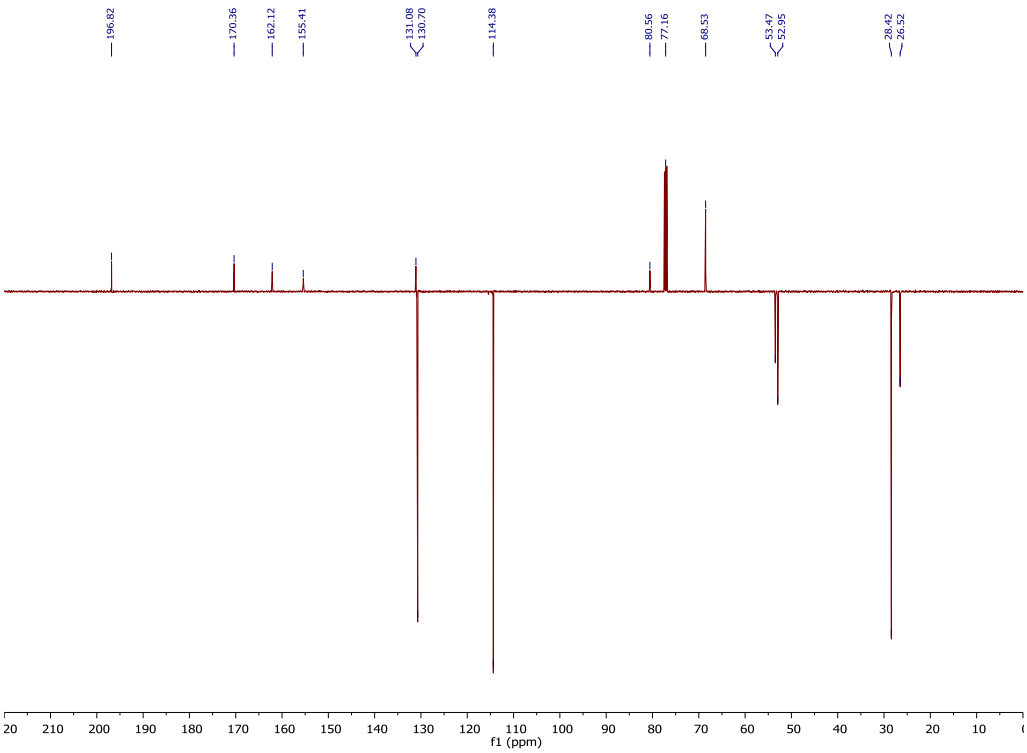
7.26
2.02
2.01
0.96
1.93
2.00
3.01
1.97
1.97
1.97
f1 (ppm)

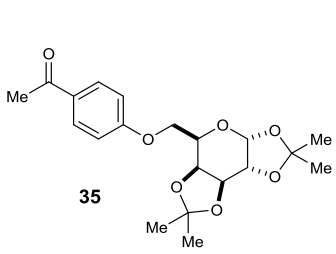

196.93
163.17
138.49
130.71
130.26
115.01
114.24
77.16
68.14
33.50
28.65
26.48
25.36
f1 (ppm)


NHBoc
MeO
O
O
O
Me
O

31

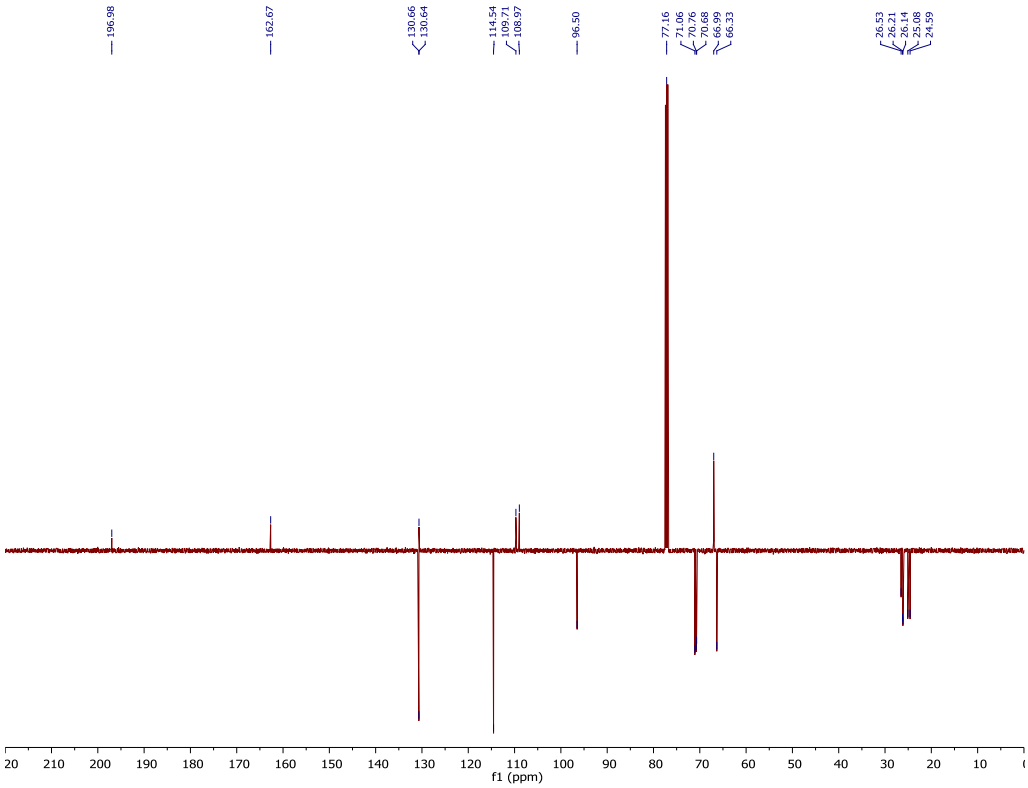
7.26
2.01
2.00
0.82
0.89
1.00
0.99
2.97
3.01
8.97
f1 (ppm)

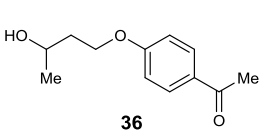

196.82
170.36
162.12
155.41
131.08
130.70
114.38
80.56
77.16
68.53
53.47
52.95
28.42
26.52
f1 (ppm)


Me
O
O
O
O
O
Me
Me
O
Me
Me

35

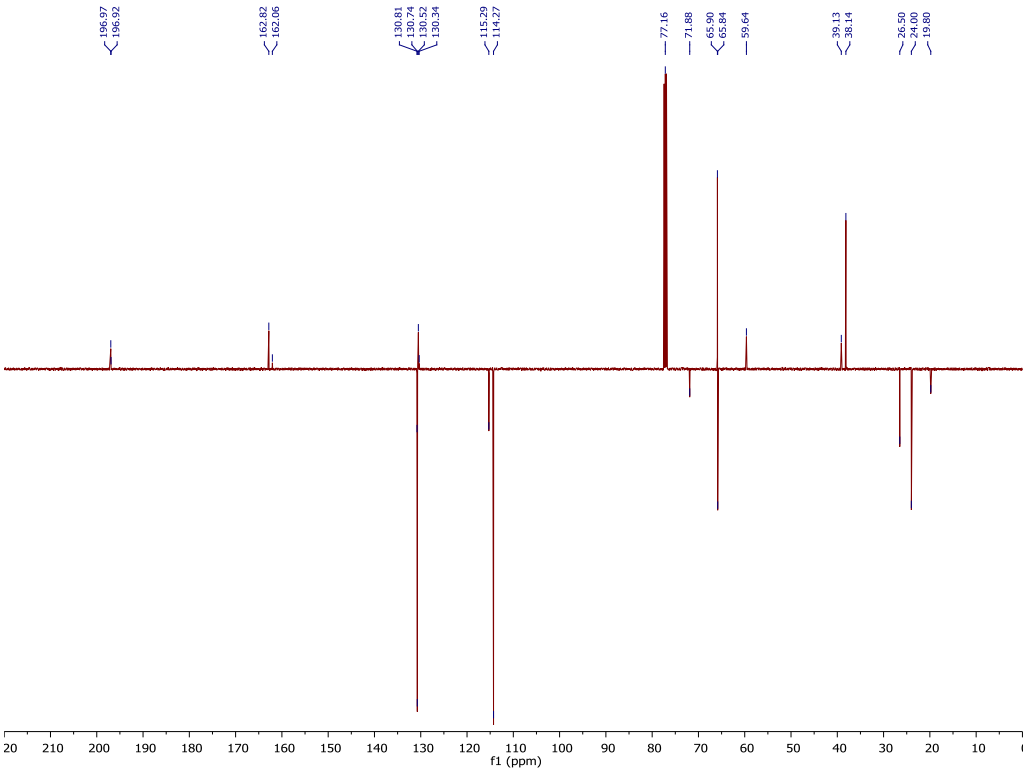
7.26
2.00
2.00
0.99
1.01
2.02
3.02
3.05
2.94
2.94
2.76
2.93
f1 (ppm)

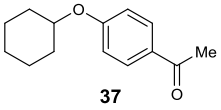

196.98
162.67
130.66
130.64
114.54
109.71
108.97
96.50
77.16
71.06
70.76
70.68
66.99
66.33
26.53
26.21
25.14
25.08
24.59
f1 (ppm)


HO
Me
O
Me
O

36

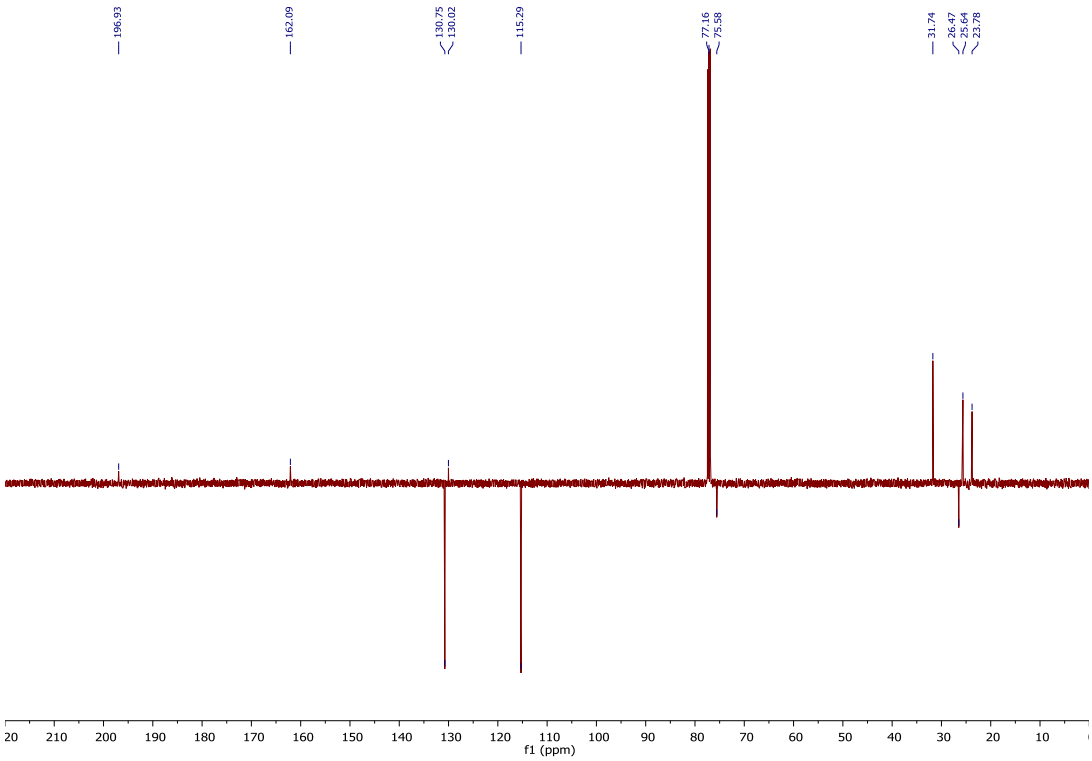
7.26
2.00
2.00
0.15
2.57
0.29
2.99
1.95
0.44
2.57
f1 (ppm)

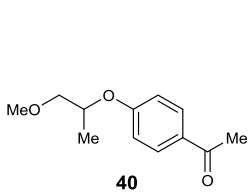

196.97
196.92
162.82
162.06
130.81
130.74
130.52
130.34
115.29
114.27
77.16
71.88
65.90
65.84
59.64
39.13
38.14
26.50
24.00
19.80
f1 (ppm)


O
Me
O

37

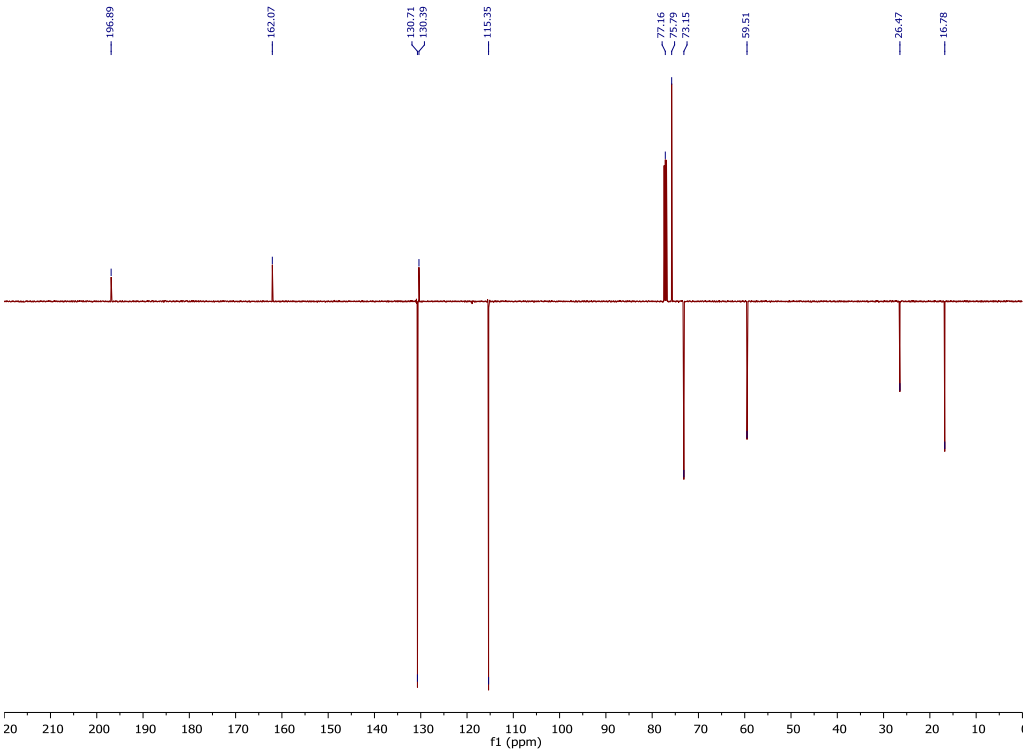
7.26
2.00
2.00
1.00
3.00
1.98
1.98
3.49
2.97
f1 (ppm)

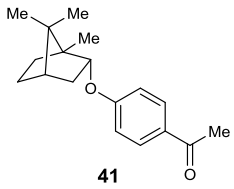

196.93
162.09
130.75
130.02
115.29
77.16
75.58
31.74
26.47
25.64
23.78
f1 (ppm)


MeO
O
Me
Me
O

40

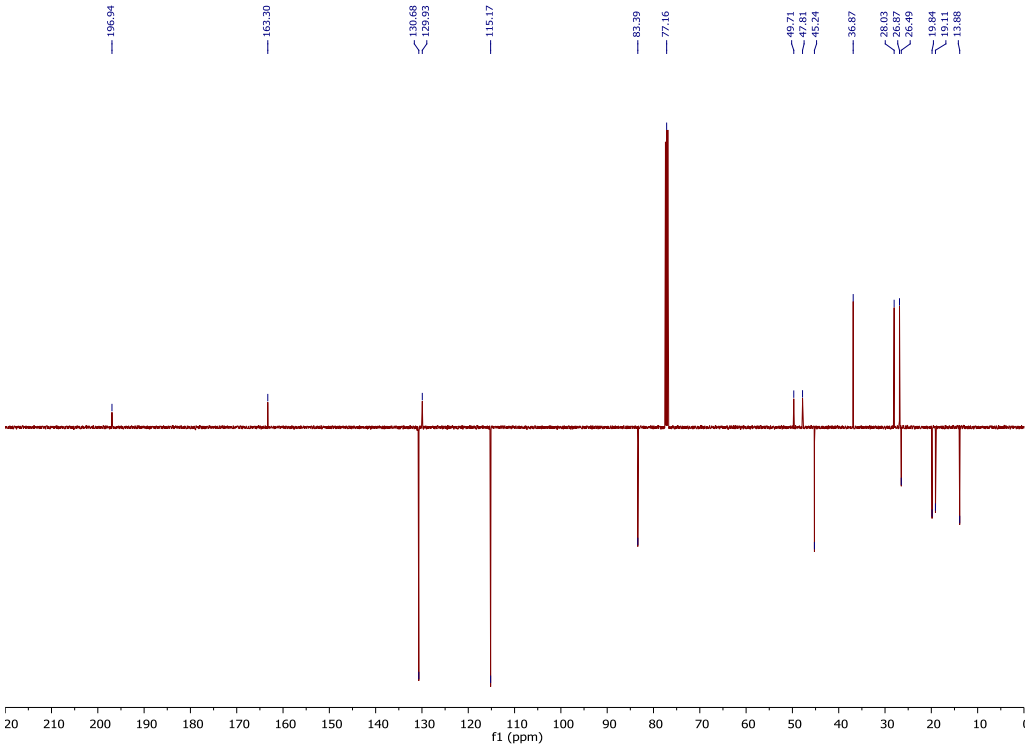
7.26
1.99
2.00
1.00
0.99
0.99
2.97
2.99
3.00
f1 (ppm)

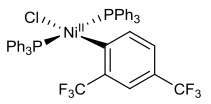

196.89
162.07
130.71
130.39
115.35
77.16
75.79
73.15
59.51
26.47
16.78
f1 (ppm)


Me
Me
Me
O
Me
O

41

7.26
2.00
2.00
1.00
2.98
1.02
1.00
2.01
1.02
1.16
1.02
9.07
f1 (ppm)



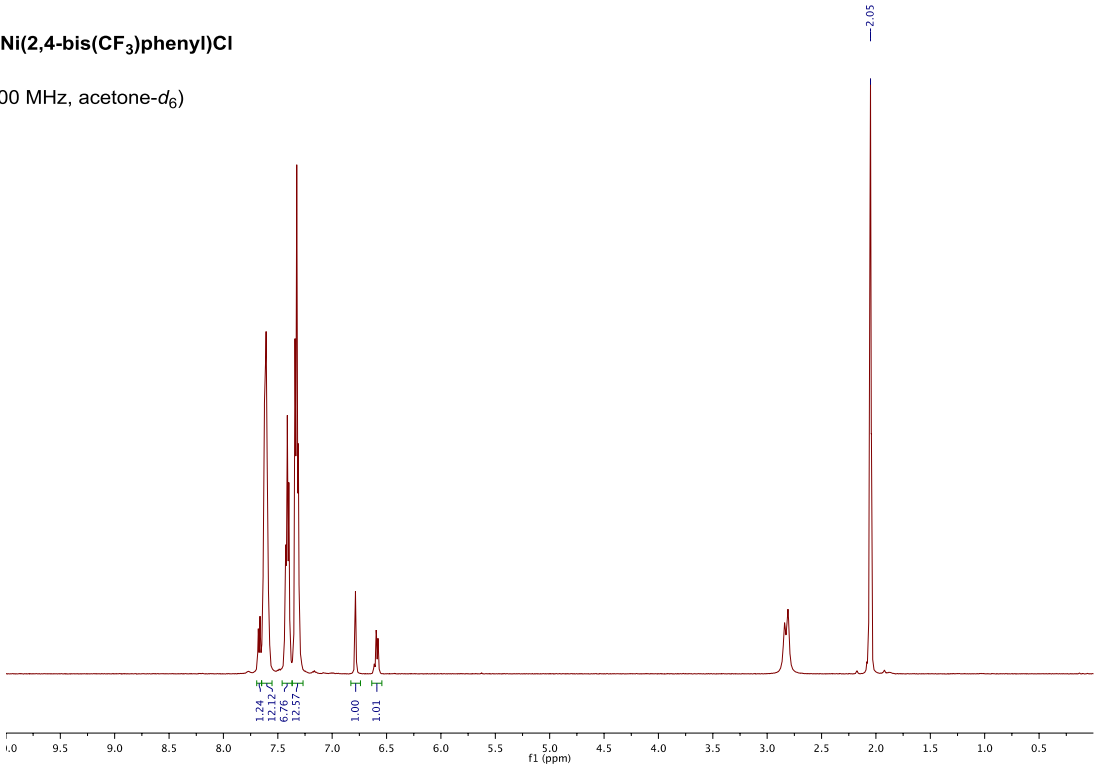


$(PPh_3)_2Ni(2,4\text{-bis}(CF_3)phenyl)Cl$

(500 MHz, C_6D_6)

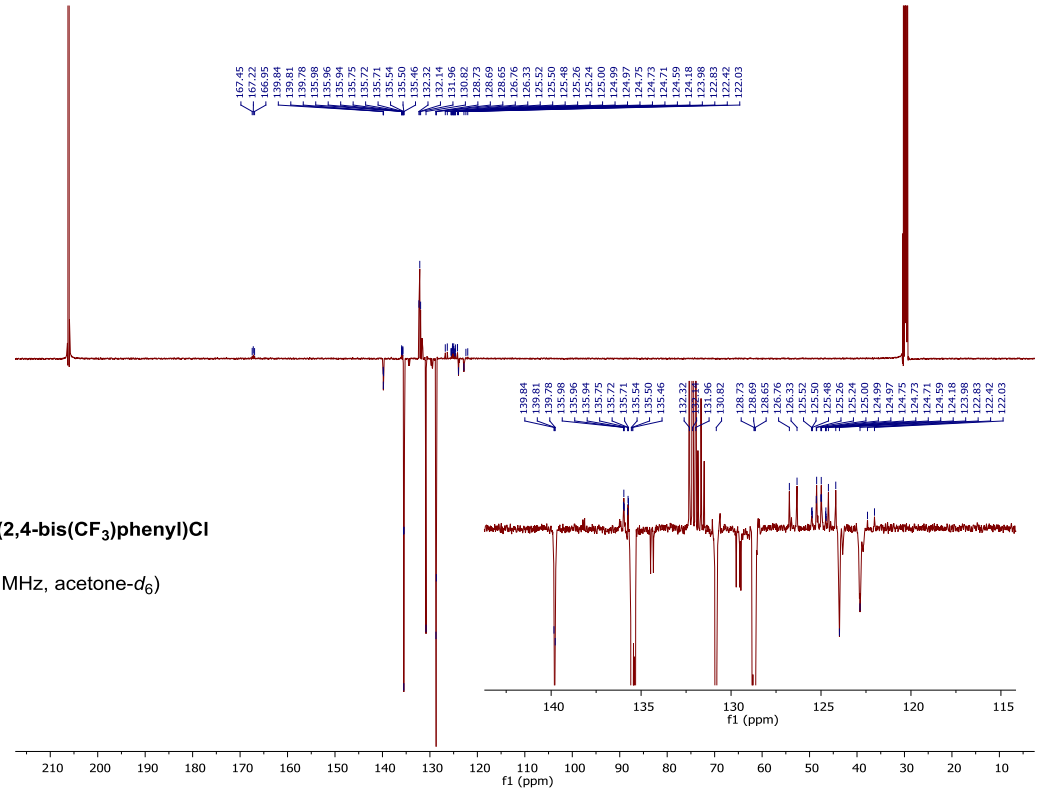
$(PPh_3)_2Ni(2,4\text{-bis}(CF_3)phenyl)Cl$

(500 MHz, acetone-d_6)



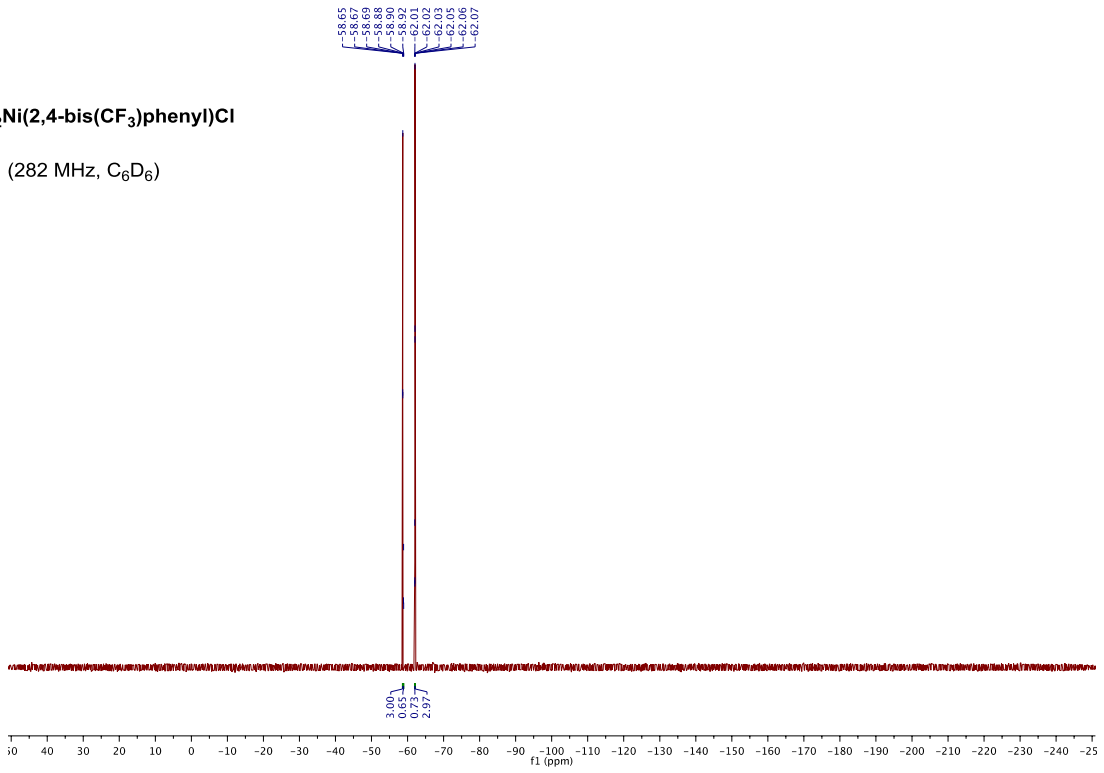
$(PPh_3)_2Ni(2,4\text{-bis}(CF_3)phenyl)Cl$

(125 MHz, acetone-d_6)



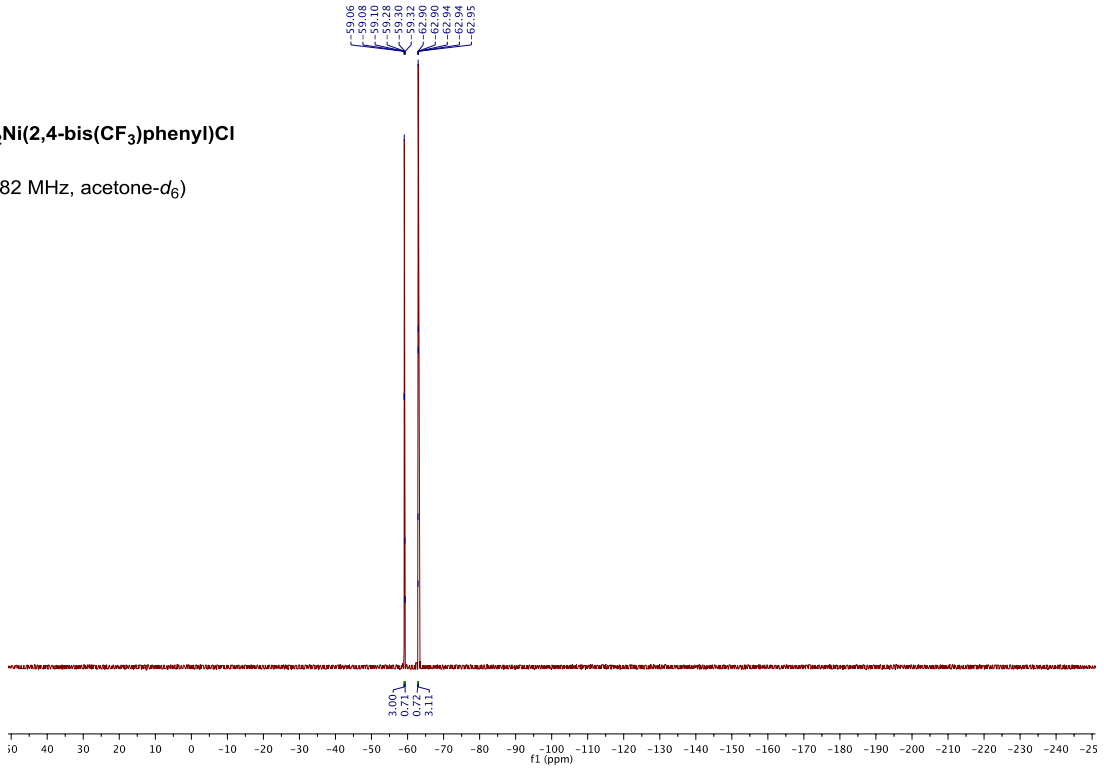
$(PPh_3)_2Ni(2,4\text{-bis}(CF_3)phenyl)Cl$

(282 MHz, C_6D_6)



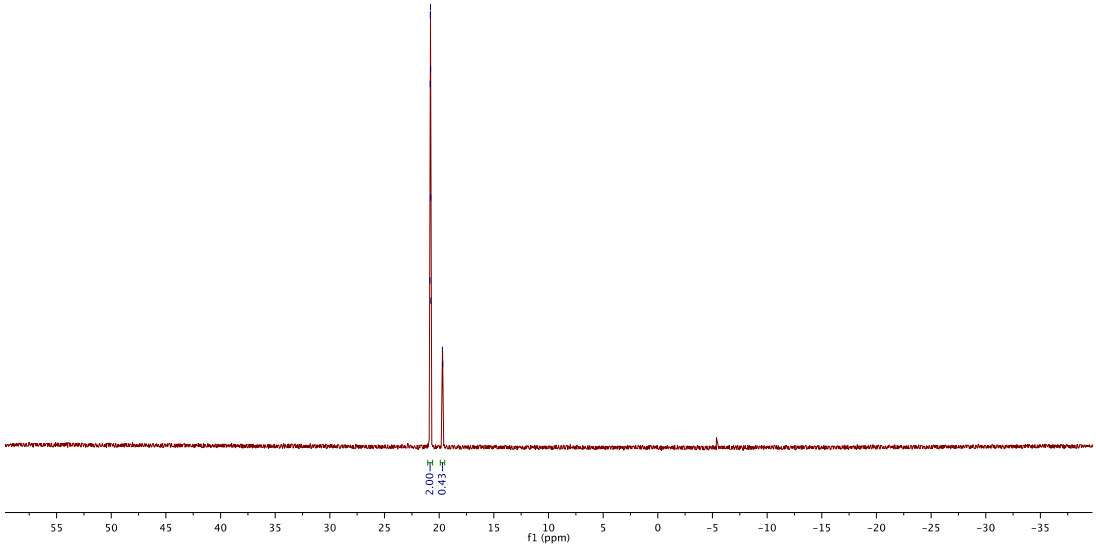
$(PPh_3)_2Ni(2,4\text{-bis}(CF_3)phenyl)Cl$

(282 MHz, acetone-d_6)



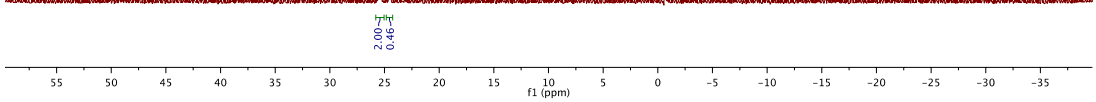
$(PPh_3)_2Ni(2,4\text{-bis}(CF_3)phenyl)Cl$

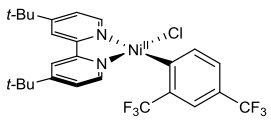
(203 MHz, C_6D_6)



$(PPh_3)_2Ni(2,4\text{-bis}(CF_3)phenyl)Cl$

(203 MHz, acetone-d_6)



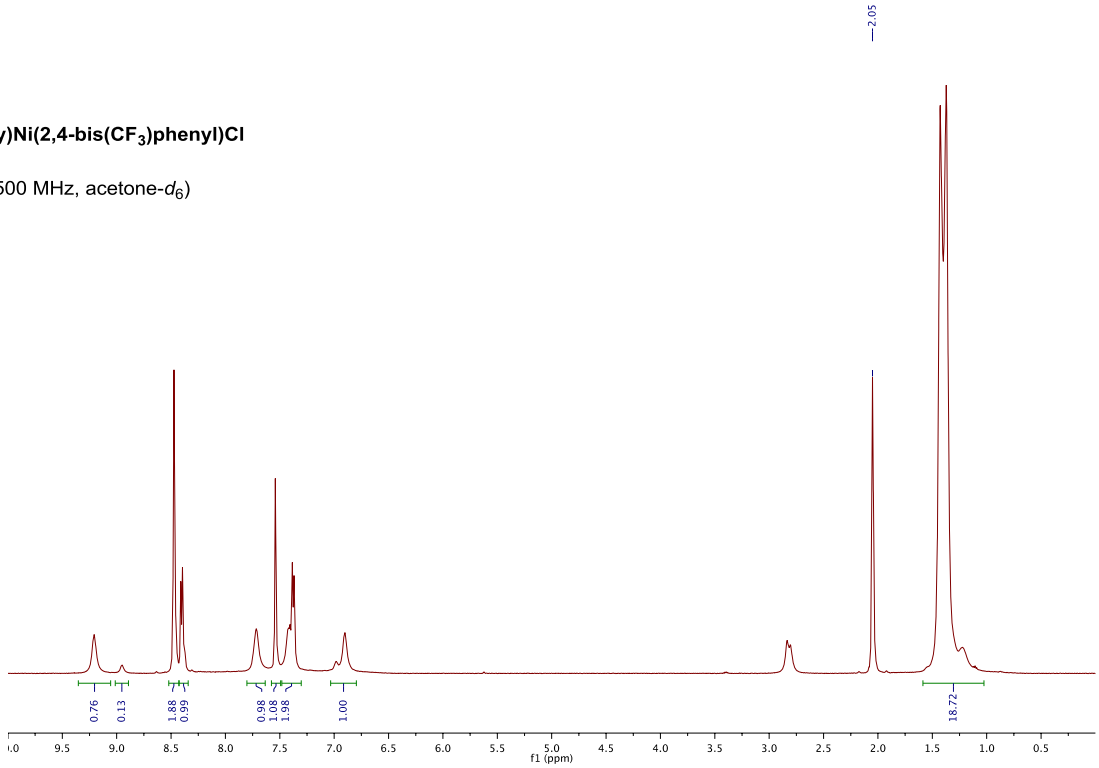


(dtbbpy)Ni(2,4-bis(CF_3)phenyl)Cl

(500 MHz, C_6D_6)

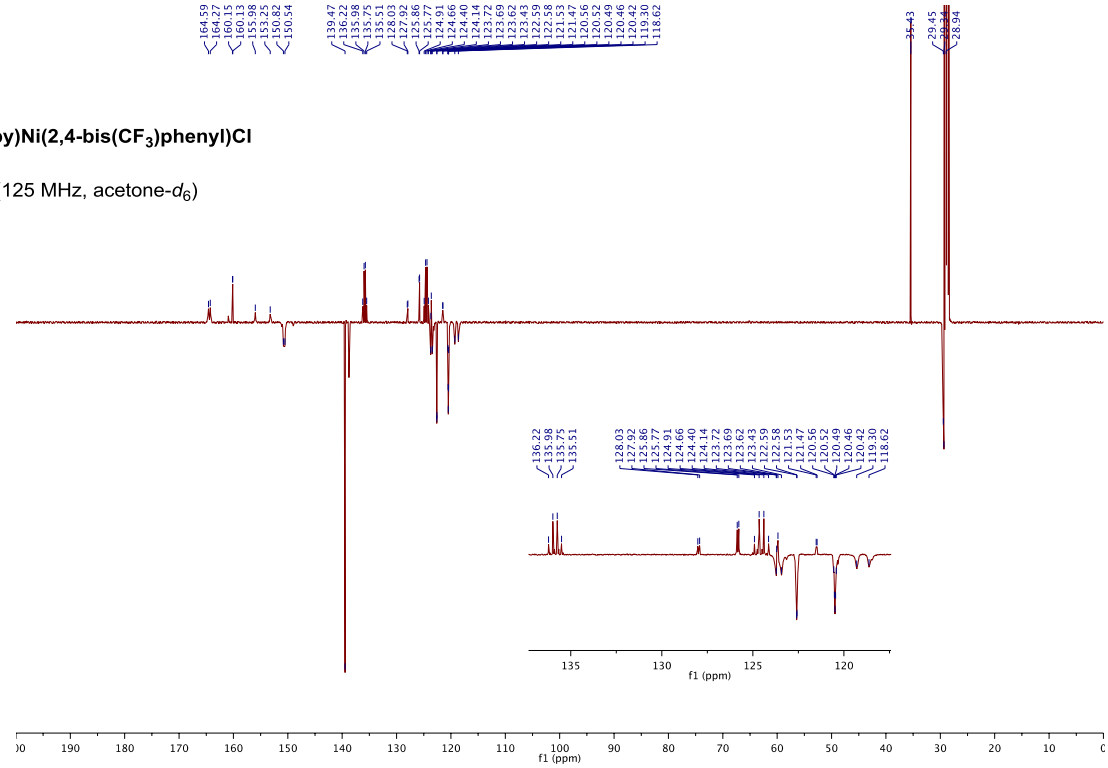
(dtbbpy)Ni(2,4-bis(CF_3)phenyl)Cl

(500 MHz, acetone-d_6)



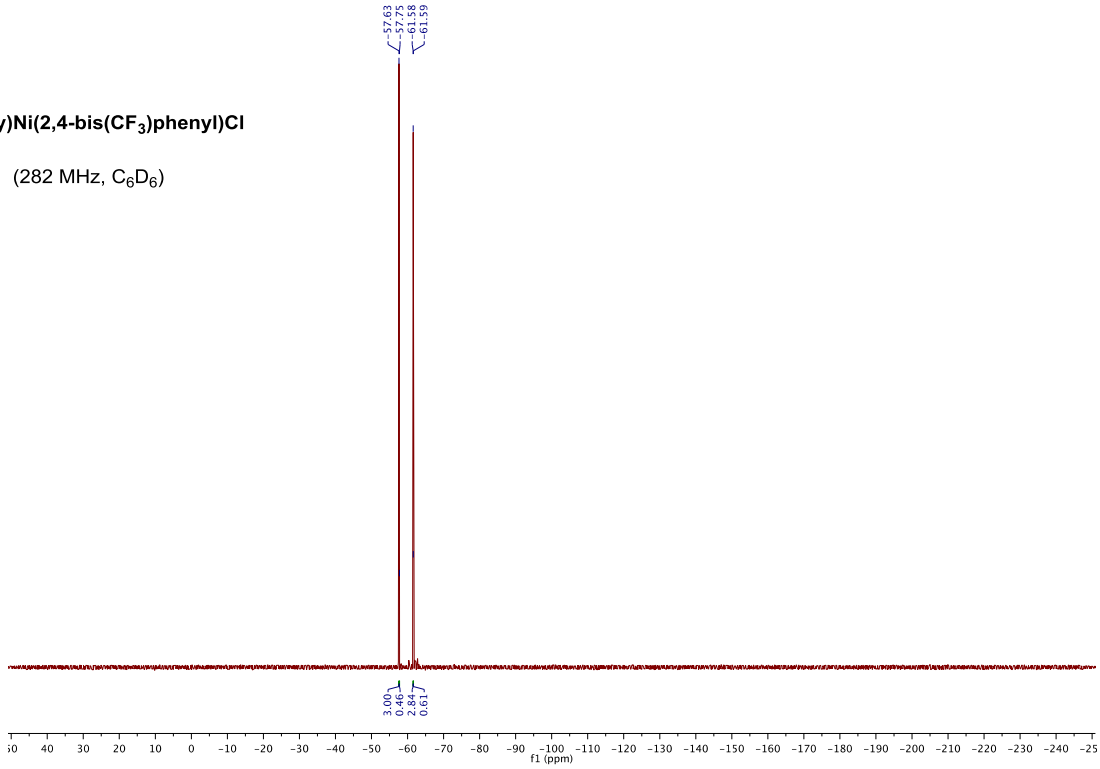
(dtbbpy)Ni(2,4-bis(CF_3)phenyl)Cl

(125 MHz, acetone-d_6)



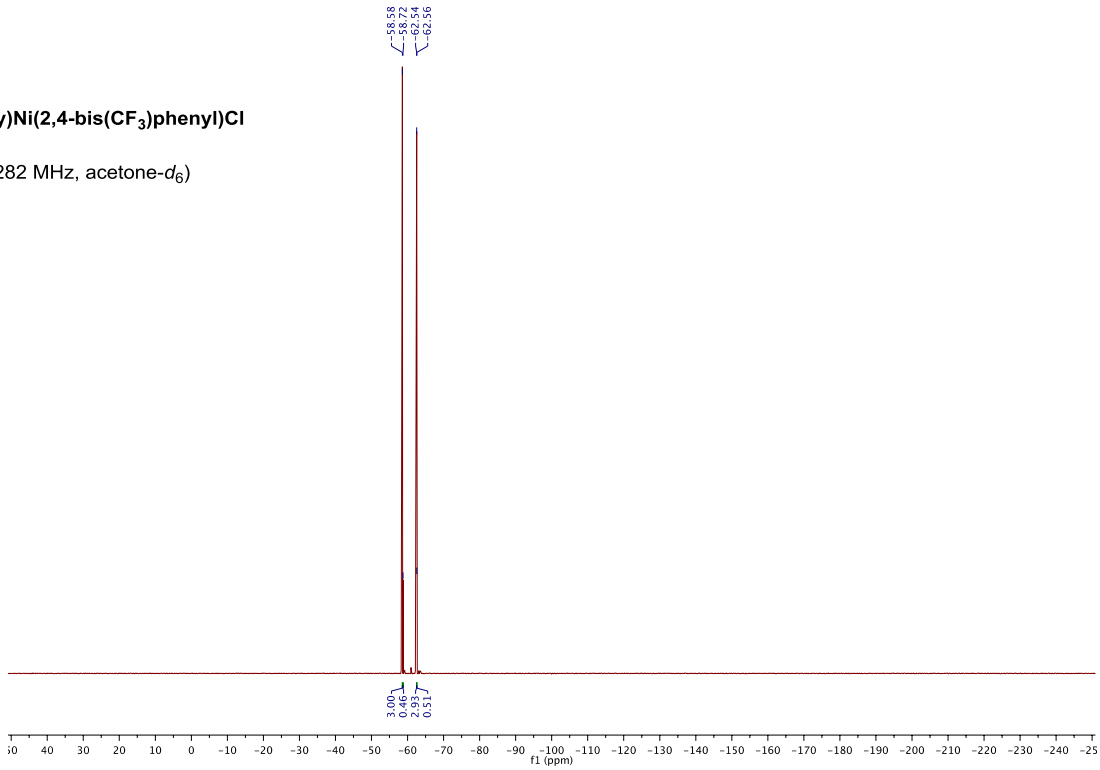
(dtbbpy)Ni(2,4-bis(CF_3)phenyl)Cl

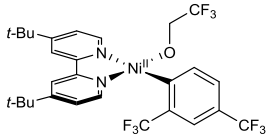
(282 MHz, C_6D_6)



(dtbbpy)Ni(2,4-bis(CF_3)phenyl)Cl

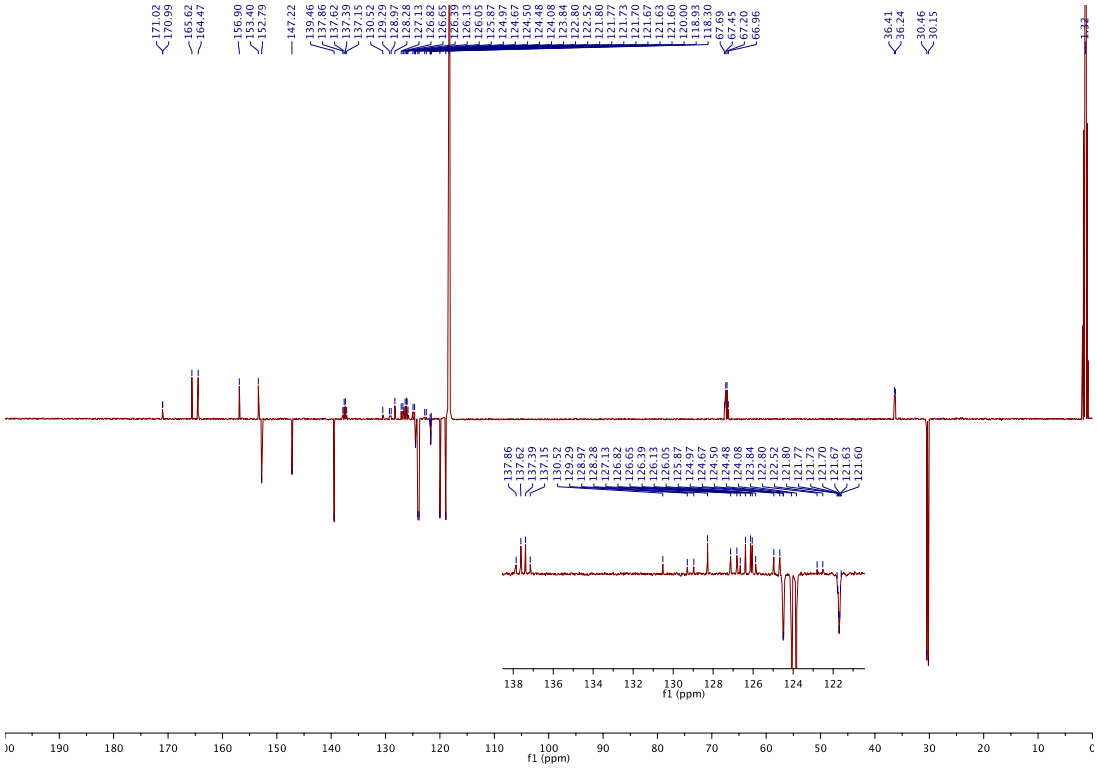
(282 MHz, acetone-d_6)

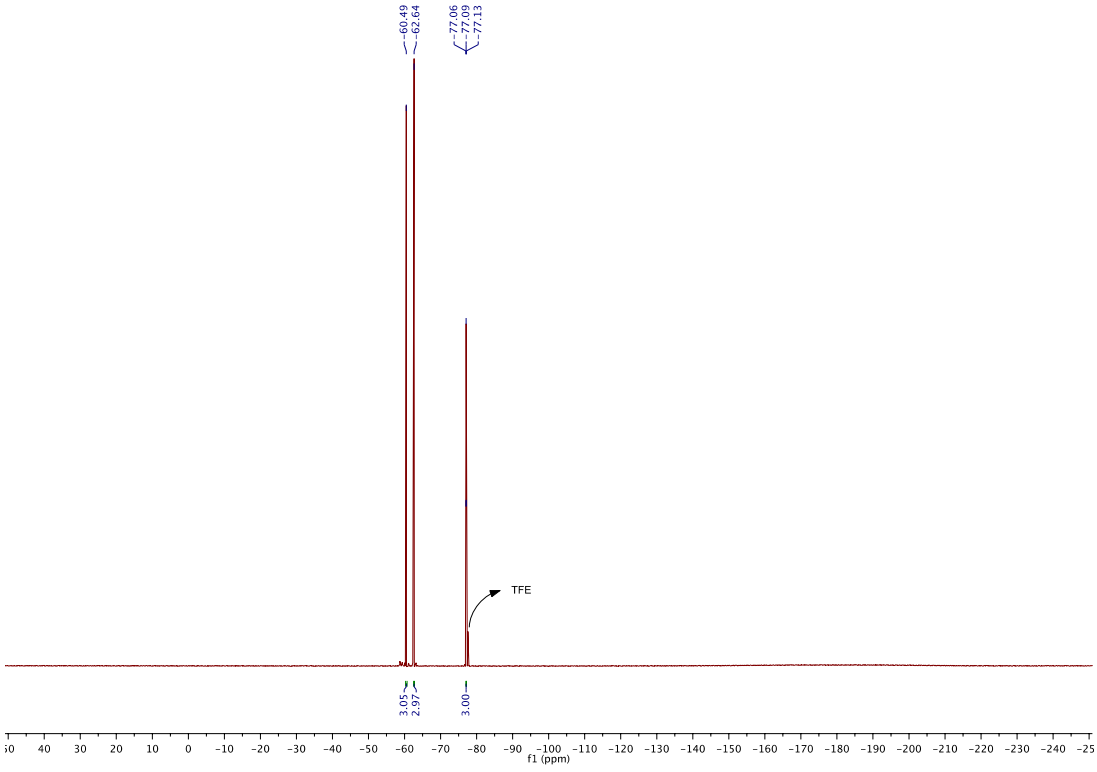


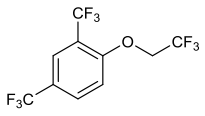


(dtbbpy)Ni(2,4-bis(CF_3)phenyl)(OCH_2CF_3) 45

(500 MHz, CD_3CN)

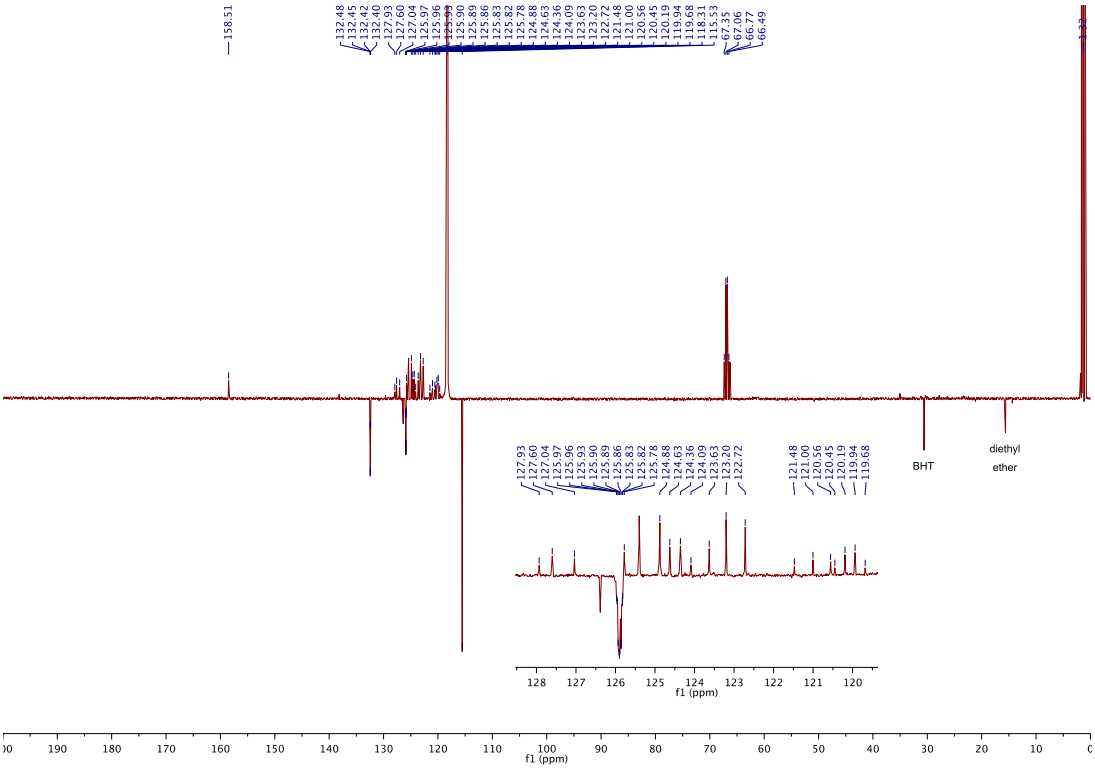

171.02
170.99
165.62
164.47
156.90
155.40
152.79
147.22
139.46
137.86
137.62
137.39
137.15
130.52
129.29
128.97
128.28
127.13
126.82
126.65
126.39
126.13
126.05
125.87
124.97
124.67
124.50
124.48
124.08
123.84
122.80
122.52
121.80
121.77
121.73
121.70
121.67
121.63
121.60
120.00
118.93
118.30
67.69
67.45
67.20
66.96
36.41
36.24
30.46
30.15
1.32
f1 (ppm)

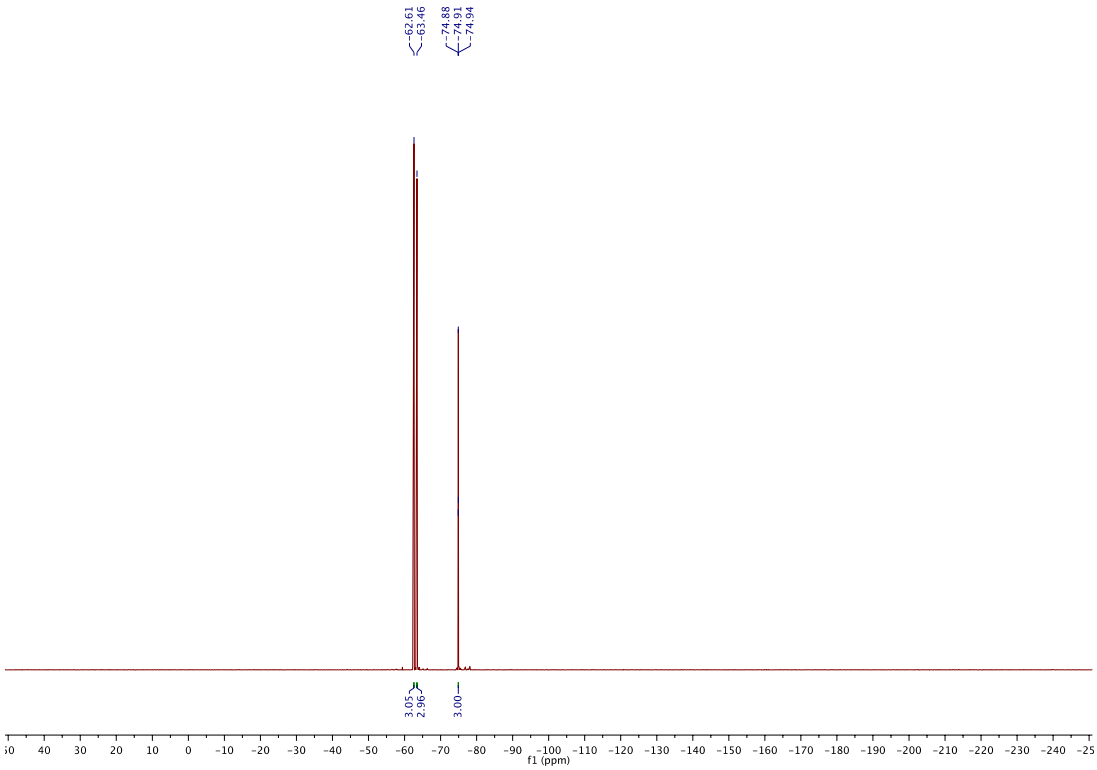

60.49
62.64
77.06
77.09
77.13
TFE
3.05
2.97
3.00
f1 (ppm)



46

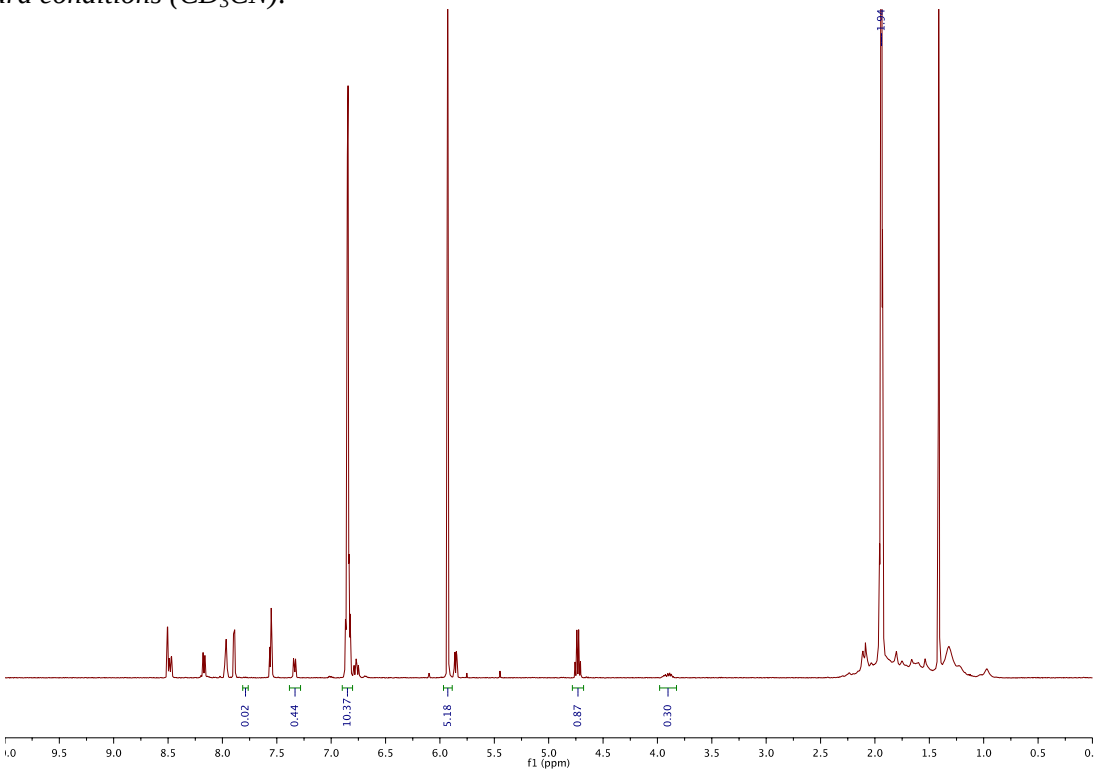
(500 MHz, CD_3CN)



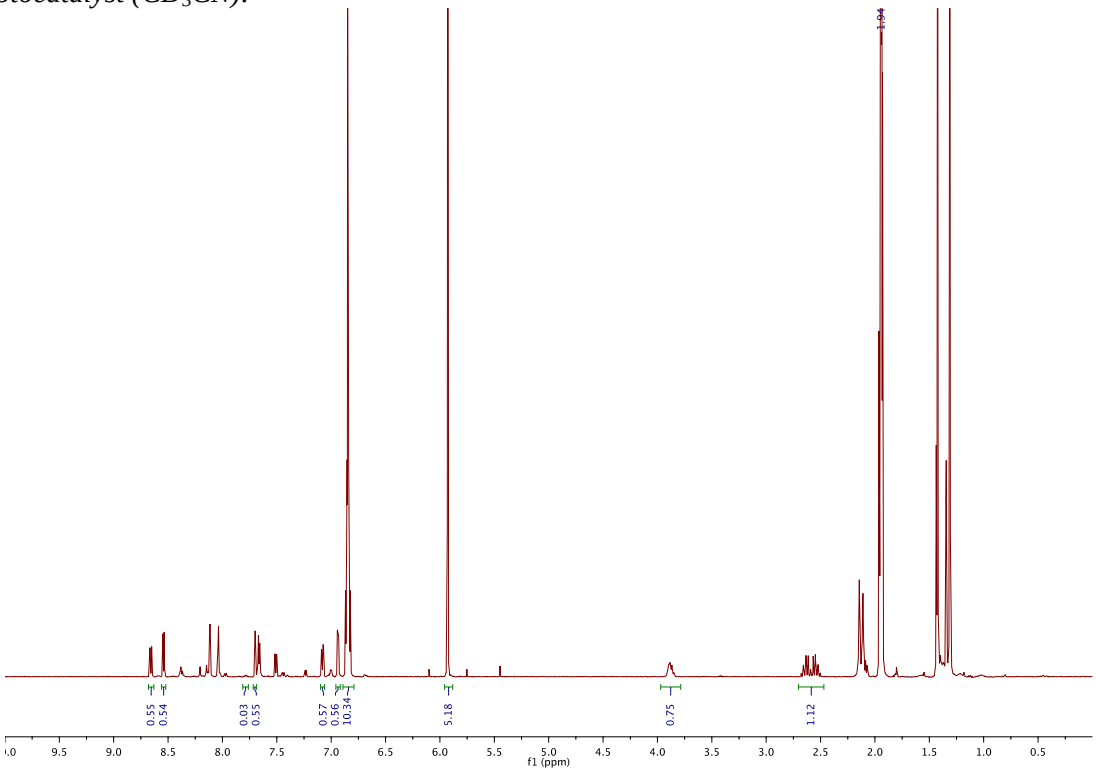


Reductive Elimination Studies

Standard conditions (CD_3CN):



No photocatalyst (CD_3CN):



No light (CD_3CN):