Supporting Information

A General Strategy for the Organocatalytic Activation of C-H Bonds via Photoredox Catalysis: The Direct Arylation of Benzylic Ethers

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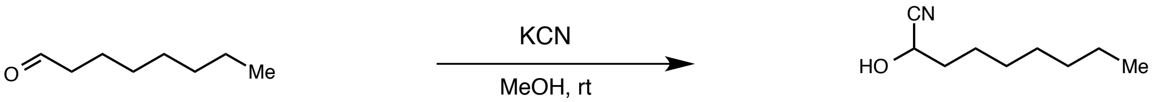
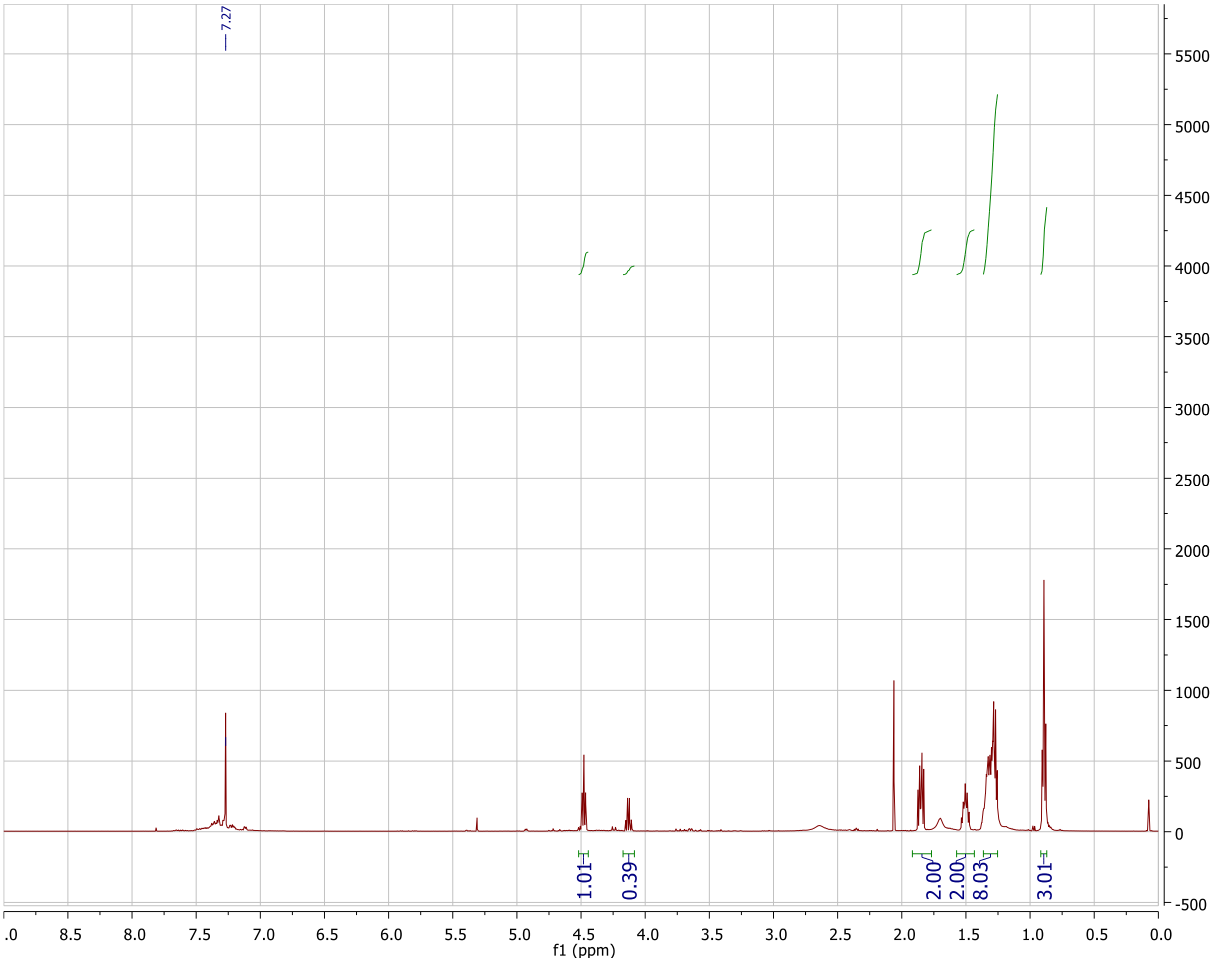
General Information. Commercial reagents were purchased from Sigma Aldrich and purified prior to use following the guidelines of Perrin and Armarego.[1] All aldehydes were distilled prior to use. All solvents were purified by passage through columns of activated alumina. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using an acetone-dry ice bath. Chromatographic purification of products was accomplished using forced-flow chromatography according to the method of Still[3] on ICN 60 32-64 mesh silica gel 63. Thin-layer chromatography (TLC) was performed on Silicycle 250 mm silica gel F-254 plates. Visualization of the developed plates was performed by fluorescence quenching, potassium permanganate, or ceric ammonium molybdate stain. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 500 (500 and 125 MHz), and are internally referenced to residual protio solvent signals (for $CDCl_3$, δ 7.27 and 77.0 ppm, respectively). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad), integration, coupling constant (Hz). ^{13}C spectra were reported in terms of chemical shifts in ppm and no special nomenclature is used for equivalent carbons. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in terms of wavenumber of absorption (cm^{-1}). High Resolution Mass spectra were obtained from the Princeton University Mass Spectral Facility. All benzyl ethers were used from commercial suppliers or prepared using standard literature procedures. All cyano aromatics were used from commercial suppliers or prepared using standard literature procedures.

Studies of aldehyde as cyanide scavenger:

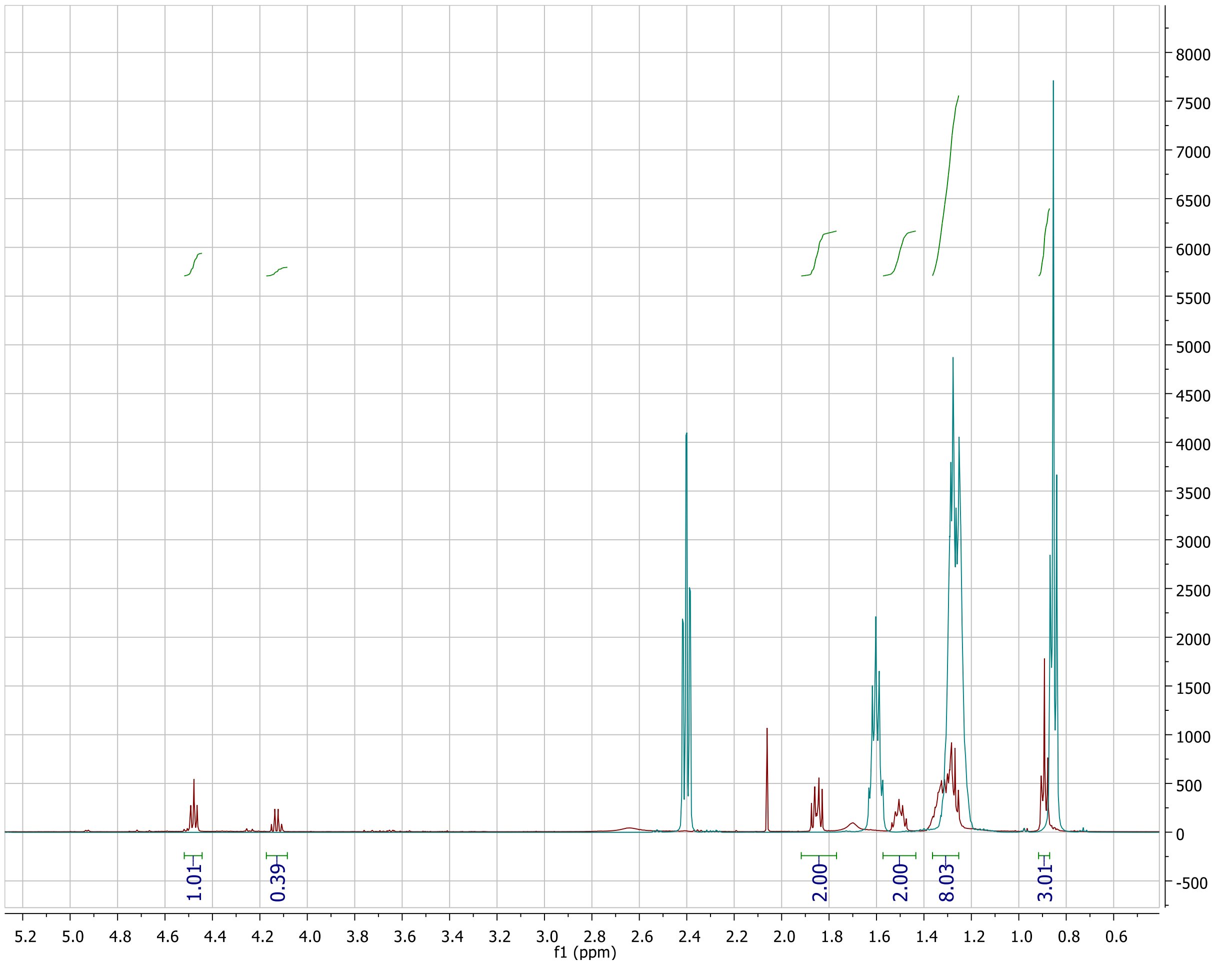
Synthesis of 2-hydroxynonanenitrile:



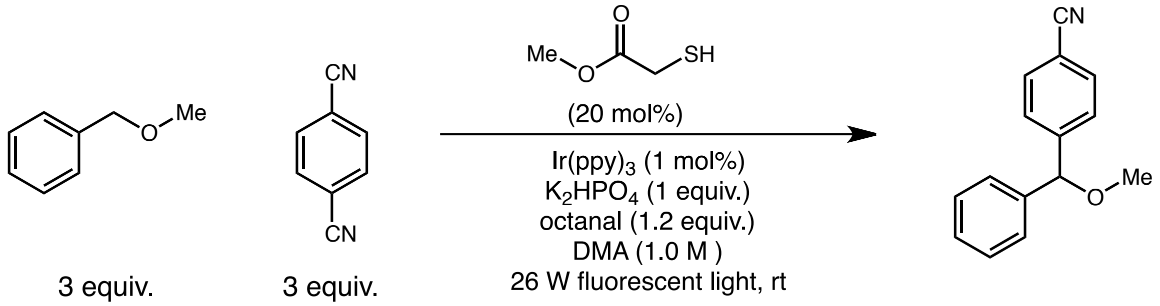
A 8 mL vial equipped with a Teflon septum and magnetic stir bar was charged with KCN (80.0 mg, 1.23 mmol, 1.5 equiv.). The vial was purged with a stream of nitrogen and 2.0 mL of MeOH was added via syringe, followed by freshly distilled octanal (128.0 μL, 0.82 mmol, 1.0 equiv.). After 24 h, the reaction mixture was diluted with EtOAc and organic layer was washed with sat. aqueous $NaHCO_3$, brine, dried (Na_2SO_4), and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel using 20% Et_2O in hexane afforded the desired cyanohydrin product.



Superimposed spectra of 2-hydroxynonanenitrile and octanal:

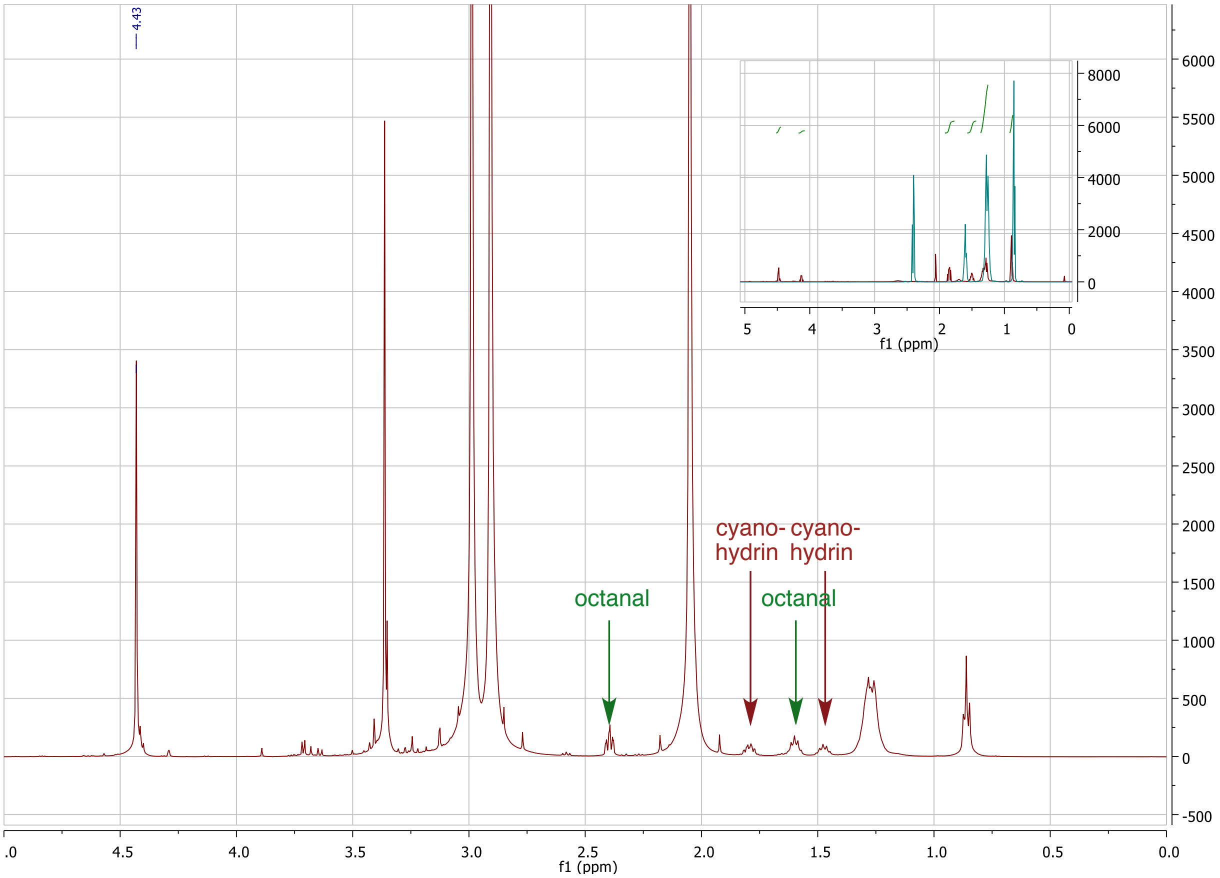


* Superimposed spectra of octanal (green) and 2-hydroxynonanenitrile (red)

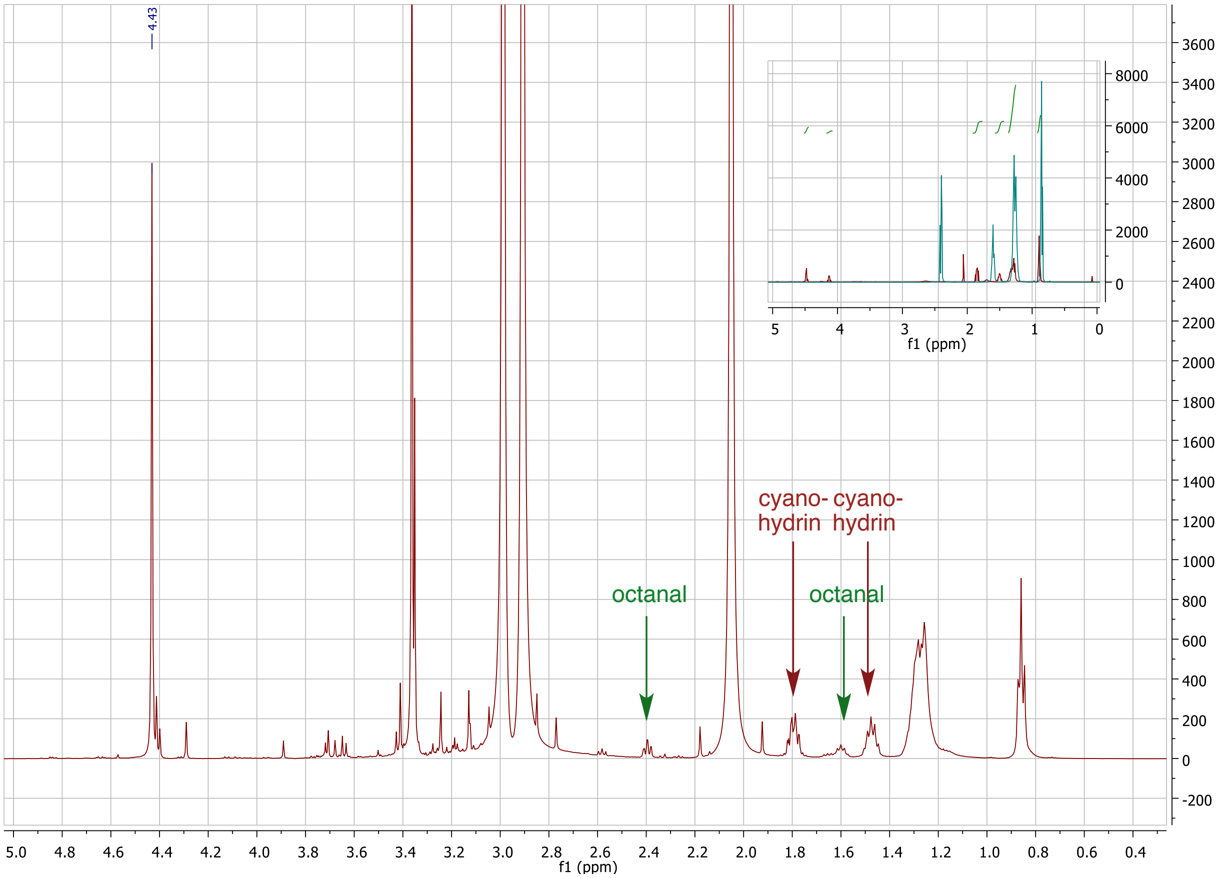


A 8 mL vial equipped with a Teflon septum and magnetic stir bar was charged with tris[2-phenylpyridinato-C^2,*N*]iridium(III) (4.8 mg, 7.5 μmol, 0.01 equiv.), the corresponding aromatic nitrile (0.75 mmol, 1.0 equiv.), the corresponding benzyl ether (2.25 mmol, 3.0 equiv.) and K$_2$HPO$_4$ (131.0 mg, 0.75 mmol, 1.0 equiv.). The vial was purged with a stream of nitrogen and 0.75 mL of DMA was added via syringe, followed by freshly distilled octanal (0.14 mL, 0.90 mmol, 1.2 equiv.) and methyl 2-mercaptoacetate (13.0 μL, 0.15 mmol, 0.2 equiv.). The reaction mixture was then cooled to –78 ºC and degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times. After the reaction was thoroughly degassed, the vial was placed approximately 2 cm from a 26 W fluorescent lamp. After the indicated time, the reaction mixture was diluted with $CDCl_3$ and the crude reaction analyzed by ^{1}H-NMR.

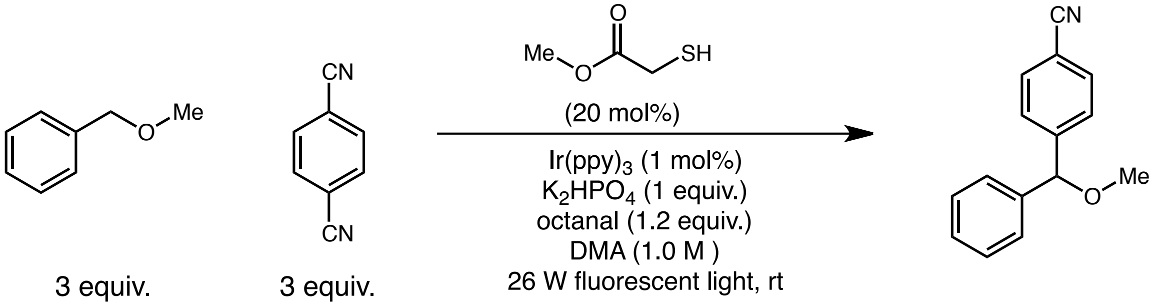
Crude reaction mixture after 2h:



Crude reaction mixture after 6h:



Optimization Studies :



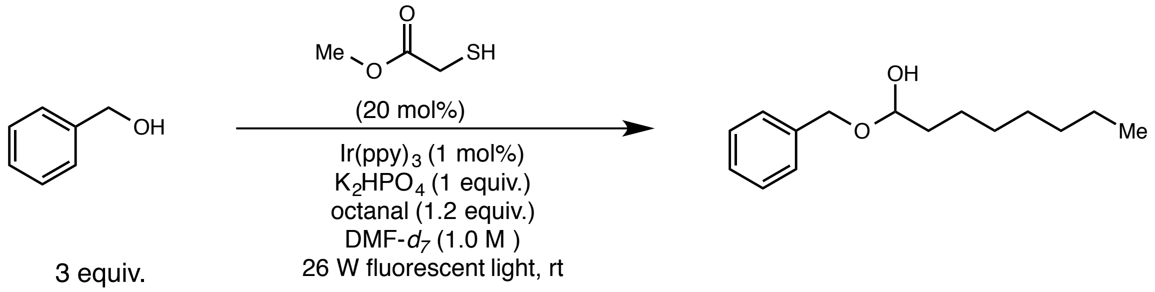
Conditions	Product %
Ir(ppy)$_3$, no light	0%
no photocatalyst	0%
no thiol	0%
As shown	77%

Benzyl methyl ether	Product %
5 equiv.	79%
4 equiv.	80%
3 equiv.	77%
2 equiv.	68%
1 equiv.	42%

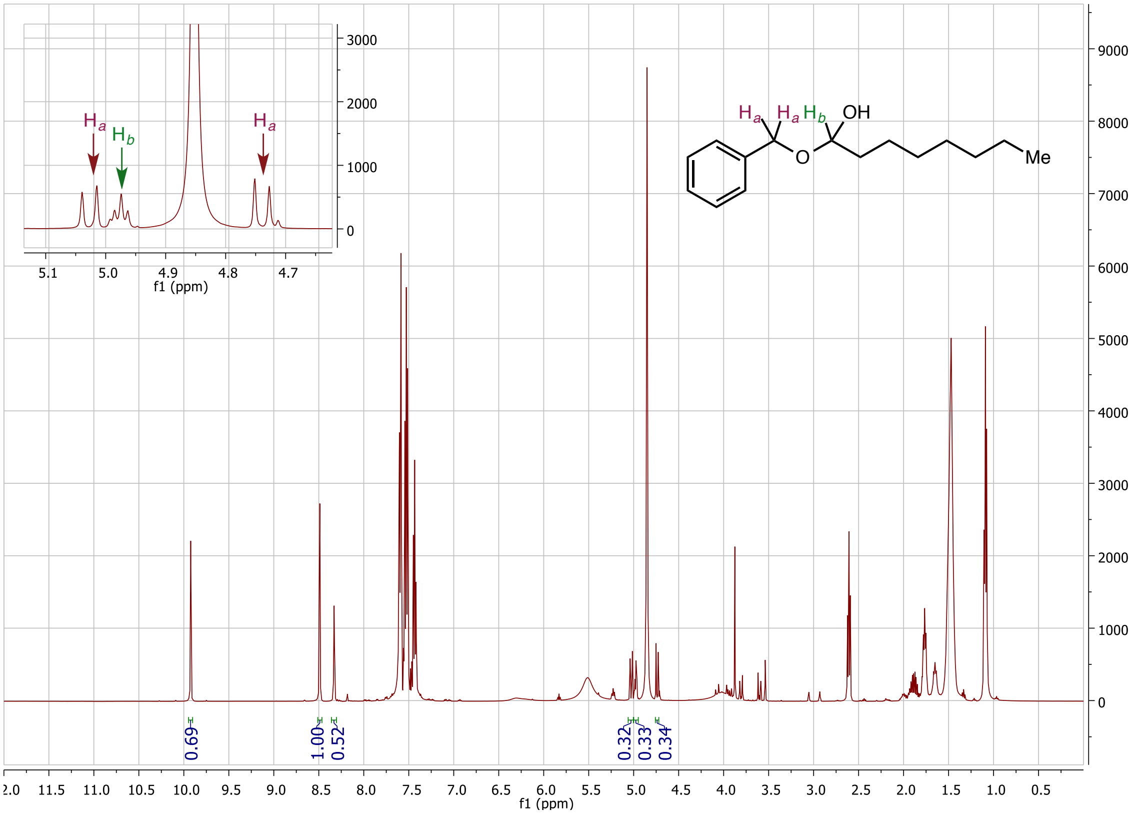
Table S1. Optimization Studies

* % Yields calculated by ^{1}H-NMR with 1-bromo-3,5-bis(trifluoromethyl)benzene

Studies of benzyl alcohol hemiacetal formation:



A 8 mL vial equipped with a Teflon septum and magnetic stir bar was charged with tris[2-phenylpyridinato-*C*^{2},*N*]iridium(III) (4.8 mg, 7.5 μmol, 0.01 equiv.), benzyl alcohol (2.25 mmol, 3.0 equiv.) and K_2HPO_4 (131.0 mg, 0.75 mmol, 1.0 equiv.). The vial was purged with a stream of nitrogen and 0.75 mL of DMA was added via syringe, followed by freshly distilled octanal (0.14 mL, 0.90 mmol, 1.2 equiv.) and methyl 2-mercaptoacetate (13.0 µL, 0.15 mmol, 0.2 equiv.). The reaction mixture was then cooled to –78 ºC and degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times. After the reaction was thoroughly degassed, the vial was placed approximately 2 cm from a 26 W fluorescent lamp. After 2 h, the reaction mixture was transferred to a NMR tube and the crude reaction mixture analyzed by ^{1}H-NMR.

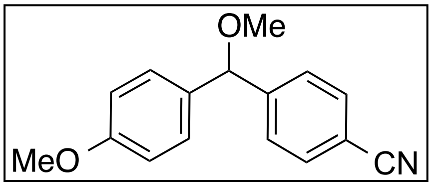


Conditions	Hemiacetal
as shown	33%

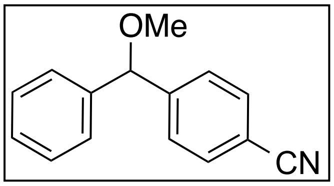
Table S2. Hemiacetal Formation Studies

* % Yields calculated by ^{1}H-NMR with 1-bromo-3,5-bis(trifluoromethyl)benzene

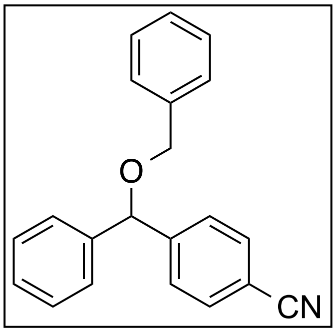
General Procedure for the C-H arylation of Benzyl ethers: A 8 mL vial equipped with a Teflon septum and magnetic stir bar was charged with tris[2-phenylpyridinato-C^2,*N*]iridium(III) (4.8 mg, 7.5 μmol, 0.01 equiv.), the corresponding aromatic nitrile (0.75 mmol, 1.0 equiv.), the corresponding benzyl ether (2.25 mmol, 3.0 equiv.) and K_2HPO_4 (131.0 mg, 0.75 mmol, 1.0 equiv.). The vial was purged with a stream of nitrogen and 0.75 mL of DMA was added via syringe, followed by freshly distilled octanal (0.14 mL, 0.90 mmol, 1.2 equiv.) and methyl 2-mercaptoacetate (13.0 μL, 0.15 mmol, 0.2 equiv.). The reaction mixture was then cooled to –78 ºC and degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times. After the reaction was thoroughly degassed, the vial was placed approximately 2 cm from a 26 W fluorescent lamp. After 24 h, the reaction mixture was diluted with water, extracted with EtOAc (3 x 5 mL), combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired C-H arylated benzyl ether product.



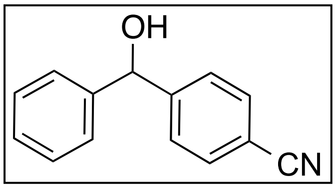
4-(methoxy(4-methoxyphenyl)methyl)benzonitrile (Table 2.1): Prepared according to the general procedure using 4.8 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (7.5 mmol, 0.01 equiv), 96 mg of terephthalonitrile (0.75 mmol, 1.00 equiv), 342 mg of 4-methoxybenzyl methyl ether (2.25 mmol, 3.00 equiv), 131 mg of K_2HPO_4 (0.75 mmol, 1.00 equiv), 141 μL of octanal (0.90 mmol, 1.2 equiv), 13.0 μL of methyl 2-mercaptoacetate (0.15 mmol, 0.2 equiv.) 0.75 mL of DMA. After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the title compound as a clear oil (155 mg, 0.61 mmol, 82%). IR (film) 2935, 2229, 1611, 1512, 1247, 1173, 1092, 805, 829, 728 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H, Ar**H**), 7.46 (d, *J* = 8.2 Hz, 2H, Ar**H**), 7.21 (d, *J* = 8.6 Hz, 2H, Ar**H**), 6.88 (d, *J* = 8.7 Hz, 2H, Ar**H**), 5.23 (s, 1H, ArC**H**Ar), 3.80 (s, 3H, ArOC**H₃**), 3.37 (s, 3H, ArCHOC**H₃**); ^{13}C NMR (125 MHz, CDCl$_3$) δ 159.36, 147.90, 132.19, 128.38, 127.16, 118.89, 114.03, 113.14, 110.93, 84.11, 56.90, 55.26; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{16}H_{16}NO_2$) requires *m/z* 254.11756, found *m/z* 254.11751.



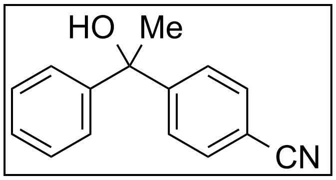
4-(Methoxy(phenyl)methyl)benzonitrile (Table 2.2): Prepared according to the general procedure using 4.8 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (7.5 μmol, 0.01 equiv), 96 mg of terephthalonitrile (0.75 mmol, 1.00 equiv), 275 mg of benzyl methyl ether (2.25 mmol, 3.00 equiv), 131 mg of K_2HPO_4 (0.75 mmol, 1.00 equiv), 141 μL of octanal (0.90 mmol, 1.2 equiv), 13.0 μL of methyl 2-mercaptoacetate (0.15 mmol, 0.2 equiv.) 0.75 mL of DMA. After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the title compound as a clear oil (129 mg, 0.58 mmol, 77%). IR (film) 2933, 2228, 1739, 1609, 1454, 1193, 1095, 804, 700 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H, Ar**H**), 7.48 (d, *J* = 8.3 Hz, 2H, Ar**H**), 7.37–7.30 (m, 5 H, Ar**H**), 5.27 (s, 1H, ArC**H**Ar), 3.39 (s, 3H, OC**H$_3$**); ^{13}C NMR (125 MHz, CDCl$_3$) δ 147.58, 140. 60, 132.24, 128.71, 128.12, 127.26, 126.99, 84.58, 57.08; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{14}NO$) requires *m/z* 224.10699, found *m/z* 224.10702.



4-((Benzyloxy)(phenyl)methyl)benzonitrile (Table 2.3): Prepared according to the general procedure using 4.8 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (7.5 μmol, 0.01 equiv), 96 mg of terephthalonitrile (0.75 mmol, 1.00 equiv), 446 mg of dibenzyl ether (2.25 mmol, 3.00 equiv), 131 mg of K_2HPO_4 (0.75 mmol, 1.00 equiv), 141 μL of octanal (0.90 mmol, 1.2 equiv), 13.0 μL of methyl 2-mercaptoacetate (0.15 mmol, 0.2 equiv.) 0.75 mL of DMA. After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the title compound as a clear oil (180 mg, 0.60 mmol, 80%). IR (film) 3032, 2864, 2230, 1495, 1454, 1276, 1085, 906, 714, 700 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H, Ar**H**), 7.51 (d, *J* = 8.1 Hz, 2H, Ar**H**), 7.41–7.30 (m, 10 H, Ar**H**), 5.47 (s, 1H, ArC**H**Ar), 4.58 (d, *J* = 11.9 Hz, 1H, OHC**H**Ar), 4.51 (d, *J* = 11.9 Hz, 1H, OHC**H**Ar)); ^{13}C NMR (125 MHz, CDCl$_3$) δ 147.64, 140.61, 137.64, 132.22, 128.75, 128.46, 128.16, 127.81, 127.71, 127.43, 127.21, 118.85, 111.07, 81.59, 70.60; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{21}H_{18}NO$) requires *m/z* 300.13829, found *m/z* 300.13831.

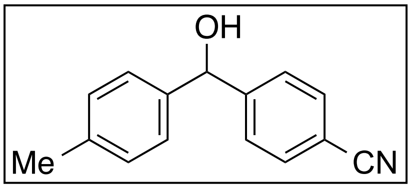


4-(hydroxy(phenyl)methyl)benzonitrile (Table 2.4): Prepared according to the general procedure using 4.8 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (7.5 μmol, 0.01 equiv), 96 mg of terephthalonitrile (0.75 mmol, 1.00 equiv), 243 mg of benzyl alcohol (2.25 mmol, 3.00 equiv), 131 mg of K_2HPO_4 (0.75 mmol, 1.00 equiv), 141 μL of octanal (0.90 mmol, 1.2 equiv), 13.0 μL of methyl 2-mercaptoacetate (0.15 mmol, 0.2 equiv.) 0.75 mL of DMA. After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (silica gel: 20% ethyl acetate in hexanes) to afford the title compound as a clear oil (121 mg, 0.58 mmol, 77%). IR (film) 3425, 2230, 1608, 1493, 1454, 1261, 1189, 1042, 906 737 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz, 2H Ar**H**), 7.51 (d, *J* = 8.2 Hz, 2H, Ar**H**), 7.39-7.28 (m, 5H, Ar**H**), 5.87 (s, 1H, ArC**H**Ar), 2.38 (bs, 1H, O**H**); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.70, 142.72, 132.25, 128.86, 128.29, 126.92, 126.63, 118.82, 111.08, 75.60; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{12}NO$) requires *m/z* 210.09134, found *m/z* 210.09137.

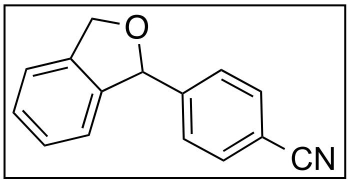


4-(1-hydroxy-1-phenylethyl)benzonitrile (Table 2.5): Prepared according to the general procedure using 4.8 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (7.5 μmol, 0.01 equiv), 96 mg of terephthalonitrile (0.75 mmol, 1.00 equiv), 275 mg of 1-phenylethan-1-ol (2.25 mmol, 3.00 equiv), 131 mg of K_2HPO_4 (0.75 mmol, 1.00 equiv), 141 μL of octanal (0.90 mmol, 1.2 equiv), 13.0 μL of methyl 2-mercaptoacetate (0.15 mmol, 0.2

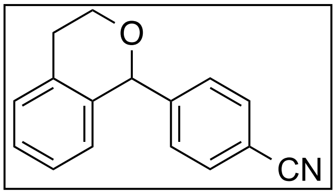
equiv.) 0.75 mL of DMA. After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (silica gel: 20% ethyl acetate in hexanes) to afford the title compound as a clear oil (125 mg, 0.56 mmol, 74%). IR (film) 3456, 2982, 2230, 1606, 1493, 1447, 1276, 1191, 1069, 907, 847, 753, 721 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.61 (d, *J* = 8.3 Hz, 2H Ar**H**), 7.54 (d, *J* = 8.3 Hz, 2H, Ar**H**), 7.40 (d, *J* = 7.6 Hz, 2H, Ar**H**), 7.35 (t, *J* = 7.6 Hz, 2H, Ar**H**), 7.29 (t, *J* = 7.3 Hz, 1H, Ar**H**), 2.26 (bs, 1H, O**H**), 1.97 (s, 3H, C**H₃**); ^{13}C NMR (125 MHz, CDCl$_3$) δ 153.21, 146.51, 132.01, 128.51, 127.62, 126.47, 125.77, 118.88, 110.57, 75.93, 30.53; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{14}NO$) requires *m/z* 224.10699, found *m/z* 224.10694.



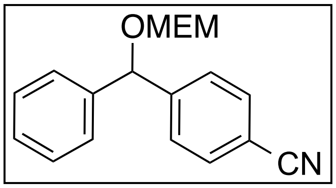
4-(1-hydroxy-1-phenylethyl)benzonitrile (Table 2.6): Prepared according to the general procedure using 4.8 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (7.5 μmol, 0.01 equiv), 96 mg of terephthalonitrile (0.75 mmol, 1.00 equiv), 275 mg of 4-methylbenzyl alcohol (2.25 mmol, 3.00 equiv), 131 mg of K_2HPO_4 (0.75 mmol, 1.00 equiv), 141 μL of octanal (0.90 mmol, 1.2 equiv), 13.0 μL of methyl 2-mercaptoacetate (0.15 mmol, 0.2 equiv.) 0.75 mL of DMA. After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (silica gel: 20% ethyl acetate in hexanes) to afford the title compound as a clear oil (121 mg, 0.54 mmol, 72%). IR (film) 3426, 2924, 2229, 1608, 1514, 1409, 1190, 1040, 818, 769 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.63 (d, *J* = 7.8 Hz, 2H Ar**H**), 7.52 (d, *J* = 7.6 Hz, 2H, Ar**H**), 7.23 (d, *J* = 7.6 Hz, 2H, Ar**H**), 7.17 (d, *J* = 7.4 Hz, 2H, Ar**H**), 5.85 (s, 1H, ArC**H**Ar), 2.35 (s, 3H, C**H$_3$**), 2.29 (bs, 1H, O**H**); ^{13}C NMR (125 MHz, CDCl$_3$) δ 148.91, 139.90, 138.19, 132.22, 129.54, 126.86, 126.62, 118.87, 110.99, 75.47, 21.14; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{14}NO$) requires *m/z* 224.10699, found *m/z* 224.10690.



4-(1,3-dihydroisobenzofuran-1-yl)benzonitrile (Table 2.7): Prepared according to the general procedure using 4.8 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (7.5 μmol, 0.01 equiv), 96 mg of terephthalonitrile (0.75 mmol, 1.00 equiv), 270 mg of phthalan (2.25 mmol, 3.00 equiv), 131 mg of K_2HPO_4 (0.75 mmol, 1.00 equiv), 141 μL of octanal (0.90 mmol, 1.2 equiv), 13.0 μL of methyl 2-mercaptoacetate (0.15 mmol, 0.2 equiv.), 0.75 mL of DMA. After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the title compound as a clear oil (118 mg, 0.53 mmol, 71%). IR (film) 2861, 2229, 1772, 1681, 1606, 1461, 1285, 1044, 904, 817, 730 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.66 (d, *J* = 8.1 Hz, 2H Ar**H**), 7.48 (d, *J* = 8.1 Hz, 2H, Ar**H**), 7.36-7.30 (m, 2H, Ar**H**), 7.30-7.23 (m, 1H Ar**H**), 7.03 (d, *J* = 7.5 Hz, 1H, Ar**H**), 6.21 (s, 1H, ArC**H**Ar), 5.38 (dd, *J* = 12.2, 2.3 Hz, 1H ArHC**H**O), 5.26 (d, *J* = 12.2, 1H, ArHC**H**O); ^{13}C NMR (125 MHz, CDCl$_3$) δ 147.51, 140.71, 138.69, 132.47, 128.13, 127.75, 127.30, 121.95, 121.19, 118.77, 111.74, 85.27, 73.68; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{12}NO$) requires *m/z* 222.09134, found *m/z* 222.09126.

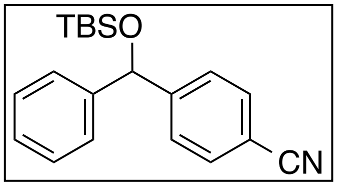


4-(isochroman-1-yl)benzonitrile (Table 2.8): Prepared according to the general procedure using 4.8 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (7.5 μmol, 0.01 equiv), 96 mg of terephthalonitrile (0.75 mmol, 1.00 equiv), 302 mg of isochroman (2.25 mmol, 3.00 equiv), 131 mg of K_2HPO_4 (0.75 mmol, 1.00 equiv), 141 μL of octanal (0.90 mmol, 1.2 equiv), 13.0 μL of methyl 2-mercaptoacetate (0.15 mmol, 0.2 equiv.), 0.75 mL of DMA. After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the title compound as a clear oil (124 mg, 0.53 mmol, 70%). IR (film) 2928, 2858, 2229, 1606, 1608, 1492, 1453, 1276, 1112, 1096, 1060, 908, 744 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 2H Ar**H**), 7.45 (d, *J* = 8.0 Hz, 2H, Ar**H**), 7.24-7.18 (m, 2H, Ar**H**), 7.11 dd, *J* = 10.8, 4.5 Hz, 1H Ar**H**), 6.69 (d, *J* = 7.8 Hz, 1H, Ar**H**), 5.78 (s, 1H, ArC**H**Ar), 4.23-4.15 (m, 1H, CH_2HC**H**O), 3.95 (td, *J* = 10.5, 3.8 Hz, 1H, CH_2HC**H**O), 3.22-3.11 (m, 1H, CH_2HC**H**Ar), 2.84 (dt, *J* = 16.4, 3.5 Hz, 1H, CH_2HC**H**Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.29, 135.85, 133.67, 132.27, 129.45, 129.02, 127. 07, 126.49, 126.15, 118.73, 111.86, 78.79, 64.09, 28.56; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{16}H_{14}NO$) requires *m/z* 236.10699, found *m/z* 236.10686.

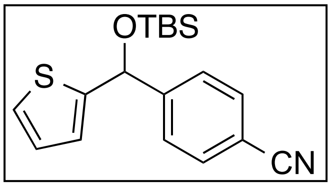


4-(((2-methoxyethoxy)methoxy)(phenyl)methyl)-benzonitrile (Table 2.9): Prepared according to the general procedure using 4.8 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (7.5 μmol, 0.01 equiv), 96 mg of terephthalonitrile (0.75 mmol, 1.00

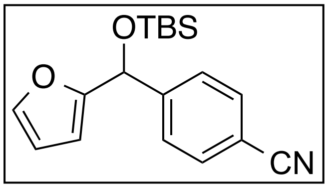
equiv), 442 mg of (((2-methoxyethoxy)methoxy)methyl)benzene (2.25 mmol, 3.00 equiv), 131 mg of K_2HPO_4 (0.75 mmol, 1.00 equiv), 141 μL of octanal (0.90 mmol, 1.2 equiv), 13.0 μL of methyl 2-mercaptoacetate (0.15 mmol, 0.2 equiv.), 0.75 mL of DMA. After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the title compound as a clear oil (140 mg, 0.47 mmol, 62%). IR (film) 2926, 2887, 2228, 1738, 1609, 1493, 1454, 1409, 1268, 1105, 1028, 805, 732, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.1 Hz, 2H Ar**H**), 7.49 (d, *J* = 8.2 Hz, 2H, Ar**H**), 7.38-7.28 (m, 5H, Ar**H**), 5.81 (s, 1H, ArC**H**Ar), 4.79 (q, *J* = 7.0 Hz, 2H, OC**H**$_2$O), 3.76-3.68 (m, 2H, OC**H**$_2$CH$_2$), 3.50 (t, *J* = 4.6 Hz, 2H, OC**H**$_2$CH$_2$), 3.36 (s, 1H, OC**H**$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.37, 140.40, 132.21, 128.67, 128.11, 127.56, 127.32, 118.49, 126.15, 118.80, 111.13, 93.20, 78.17, 71.58, 67.29, 59.02; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{20}H_{26}NOSi$) requires *m/z* 298.14428, found *m/z* 298.14432.



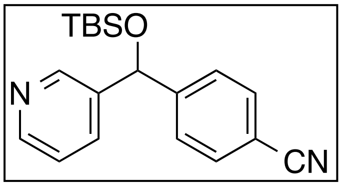
4-(((*tert*-butyldimethylsilyl)oxy)(phenyl)methyl)-benzonitrile (Table 2.10): Prepared according to the general procedure using 4.8 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (7.5 mmol, 0.01 equiv), 96 mg of terephthalonitrile (0.75 mmol, 1.00 equiv), 500 mg of (benzyloxy)(*tert*-butyl)dimethylsilane (2.25 mmol, 3.00 equiv), 131 mg of K_2HPO_4 (0.75 mmol, 1.00 equiv), 141 μL of octanal (0.90 mmol, 1.2 equiv), 13.0 μL of methyl 2-mercaptoacetate (0.15 mmol, 0.2 equiv.), 0.75 mL of DMA. After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the title compound as a clear oil (181 mg, 0.56 mmol, 74%). IR (film) 2930, 2957, 2229, 1738, 1608, 1472, 1255, 1089, 843, 778, 699 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.3 Hz, 2H Ar**H**), 7.49 (d, *J* = 8.1 Hz, 2H, Ar**H**), 7.35-7.29 (m, 4H, Ar**H**), 7.27-7.23 (m, 1H, Ar**H**), 5.77 (s, 1H, ArC**H**Ar), 0.92 (s, 9H, SiC(C**H**$_3$)$_3$), 0.01 (s, 3H, SiC**H**$_3$), -0.04 (s, 3H, SiC**H**$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.51, 143.78, 132.14, 128.49, 127.59, 126.67, 126.27, 76.12, 25.75, 18.24, -4.82, -4.96; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{20}H_{26}NOSi$) requires *m/z* 324.17782, found *m/z* 324.17750.



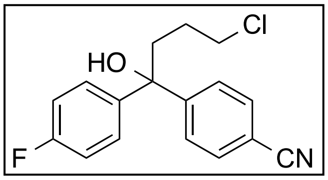
4-(((*tert*-butyldimethylsilyl)oxy)(thiophen-2-yl)methyl)-benzonitrile (Table 2.11): Prepared according to the general procedure using 4.8 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (7.5 mmol, 0.01 equiv), 96 mg of terephthalonitrile (0.75 mmol, 1.00 equiv), 514 mg of *tert*-butyldimethyl(thiophen-2-ylmethoxy)silane (2.25 mmol, 3.00 equiv.), 131 mg of K_2HPO_4 (0.75 mmol, 1.00 equiv), 141 mL of octanal (0.90 mmol, 1.2 equiv), 13.0 mL of methyl 2-mercaptoacetate (0.15 mmol, 0.2 equiv.), 0.75 mL of DMA. After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the title compound as a clear oil (181 mg, 0.55 mmol, 73%). IR (film) 2955, 2230, 1608, 1472, 1254, 1078, 907, 863, 779, 733 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H Ar**H**), 7.54 (d, *J* = 8.2 Hz, 2H, Ar**H**), 7.24 (dd, *J* = 5.1, 1.1 Hz, 1H, Ar**H**), 6.91 (dd, *J* = 5.0, 3.5 Hz, 1H, Ar**H**), 6.81 (d, *J* = 3.5 Hz, 1H, Ar**H**), 6.02 (s, 1H, ArC**H**Ar), 0.93 (s, 9H, SiC(C**H**$_3$)$_3$), 0.04 (s, 3H, SiC**H**$_3$), 0.02 (s, 3H, SiC**H**$_3$); ^{13}C NMR (125 MHz, CDCl$_3$) δ 149.59, 148.52, 132.24, 126.62, 126.48, 125.33, 123.98, 118.87, 111.14, 72.37, 25.67, 18.24, -4.97, -5.03; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{18}H_{24}NOSSi$) requires *m/z* 330.13424, found *m/z* 330.13397.



4-(((*tert*-butyldimethylsilyl)oxy)(furan-2-yl)methyl)-benzonitrile (Table 2.12): Prepared according to the general procedure using 4.8 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (7.5 mmol, 0.01 equiv.), 96 mg of terephthalonitrile (0.75 mmol, 1.00 equiv.), 478 mg of *tert*-butyl(furan-2-ylmethoxy)dimethylsilane (2.25 mmol, 3.00 equiv.), 158 mg of Na$_2$CO$_3$ (0.75 mmol, 2.00 equiv), 141 mL of octanal (0.90 mmol, 1.2 equiv.), 13.0 mL of methyl 2-mercaptoacetate (0.15 mmol, 0.2 equiv.), 0.75 mL of DMA. After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the title compound as a clear oil (150 mg, 0.48 mmol, 64%). IR (film) 2955, 2230, 1472, 1253, 1079, 1230, 905, 839, 780, 730 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.64 (d, *J* = 8.0 Hz, 2H Ar**H**), 7.54 (d, *J* = 8.1 Hz, 2H, Ar**H**), 7.35 (s, 1H Ar**H**), 6.35-6.23 (m, 1H Ar**H**), 6.12 (d, *J* = 3.1 Hz, 1H, Ar**H**), 5.82 (s, 1H, ArC**H**Ar), 0.92 (s, 9H, SiC(C**H**$_3$)$_3$), -0.08 (s, 3H, SiC**H**$_3$), 0.01 (s, 3H, SiC**H**$_3$); ^{13}C NMR (125 MHz, CDCl$_3$) δ 155.34, 147.32, 142.47, 132.09, 126.87, 118.92, 111.18, 110.20, 107.28, 69.86, 25.70, 18.27, -5.10, -5.17; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{18}H_{24}NO_2Si$) requires *m/z* 314.15708, found *m/z* 314.15697.

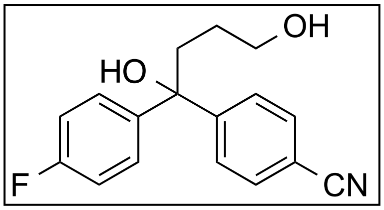


4-(((*tert*-butyldimethylsilyl)oxy)(pyridin-3-yl)methyl)benzonitrile (Table 2.13): Prepared according to the general procedure using 4.8 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (7.5 mmol, 0.01 equiv.), 96 mg of terephthalonitrile (0.75 mmol, 1.00 equiv.), 503 mg of 3-(((*tert*-butyldimethylsilyl)oxy)methyl)pyridine (2.25 mmol, 3.00 equiv.), 131 mg of K_2HPO_4 (0.75 mmol, 1.00 equiv.), 141 mL of octanal (0.90 mmol, 1.2 equiv.), 13.0 mL of methyl 2-mercaptoacetate (0.15 mmol, 0.2 equiv.), 0.75 mL of DMA. After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (silica gel: 20% ethyl acetate in hexanes) to afford the title compound as a clear oil (149 mg, 0.46 mmol, 61%). IR (film) 2955, 2930, 1608, 1472, 1426, 1253, 1086, 904, 862, 729 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.61 (d, *J* = 2.0 Hz, 1H, Ar**H**), 8.52 (dd, *J* = 4.8, 1.5 Hz, 1H, Ar**H**), 7.60-7.65 (m, 3H, Ar**H**), 7.49 (d, *J* = 8.3 Hz, 2H, Ar**H**), 7.26 (dd, *J* = 8.1, 5.0 Hz, 1H, Ar**H**), 5.81 (s, 1H, ArC**H**Ar), 0.92 (s, 9H, SiC(C**H**$_3$)$_3$), 0.02 (s, 3H, SiC**H**$_3$), -0.01 (s, 3H, SiC**H**$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.29, 149.15, 147.84, 139.21, 133.83, 132.38, 126.63, 123.59, 118.70, 111.23, 74.05, 25.68, 18.19, -4.83, -4.91; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{19}H_{25}N_2OSi$) requires *m/z* 325.17307, found *m/z* 325.17288.

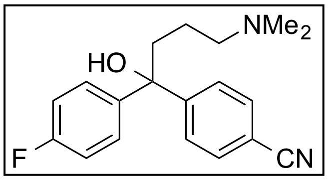


4-(4-chloro-1-(4-fluorophenyl)-1-hydroxybutyl)-benzonitrile (Table 2.14): Prepared according to the general procedure using 4.8 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (7.5 mmol, 0.01 equiv.), 96 mg of terephthalonitrile (0.75 mmol, 1.00

equiv.), 456 mg of 4-chloro-1-(4-fluorophenyl)butan-1-ol (2.25 mmol, 3.00 equiv.), 131 mg of K_2HPO_4 (0.75 mmol, 1.00 equiv.), 141 mL of octanal (0.90 mmol, 1.2 equiv.), 13.0 mL of methyl 2-mercaptoacetate (0.15 mmol, 0.2 equiv.), 0.75 mL of DMA. After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the title compound as a clear oil (161 mg, 0.53 mmol, 70%). IR (film) IR (film) 3392, 2945, 2254, 1605, 1509, 1224, 904, 837, 726 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.6 Hz, 2H Ar**H**), 7.53 (d, *J* = 8.5 Hz, 2H, Ar**H**), 7.42-7.34 (m, 2H, Ar**H**), 7.03 (t, *J* = 8.7 Hz, 2H, Ar**H**), 3.58 (t, *J* = 6.2 Hz, 2H, $C\mathbf{H_2}Cl$), 2.63 (s, 1H, O**H**), 2.52-2.39 (m, 2H, $C\mathbf{CH_2}CH_2$), 1.93-1.62 (m, 2H, $CH_2C\mathbf{H_2}CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.99 (d, *J* = 246 Hz), 151.42, 141.42 (d, *J* = 3.3 Hz), 132.16, 127.70 (d, *J* = 8.6 Hz), 126.62, 118.67, 115.46 (d, *J* = 21.6 Hz), 110.91, 76.75, 45.22, 38.91, 26.75; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{17}H_{16}ClFNO$) requires *m/z* 304.08990, found *m/z* 304.08978.

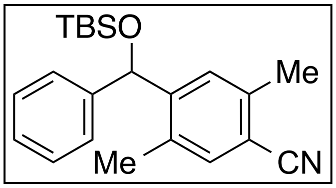


4-(1-(4-fluorophenyl)-1,4-dihydroxybutyl)benzonitrile (Table 2.15): Prepared according to the general procedure using 4.8 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (7.5 mmol, 0.01 equiv.), 96 mg of terephthalonitrile (0.75 mmol, 1.00 equiv.), 414 mg of 1-(4-fluorophenyl)butane-1,4-diol (2.25 mmol, 3.00 equiv.), 262 mg of K_2HPO_4 (0.75 mmol, 2.00 equiv.), 176 mL of octanal (1.125 mmol, 1.5 equiv.), 13.0 mL of methyl 2-mercaptoacetate (0.15 mmol, 0.2 equiv.), 0.75 mL of DMA. After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the title compound as a clear oil (156 mg, 0.54 mmol, 72%). IR (film) 3436, 2945, 2254, 2232,1680, 1600, 1508, 1276, 1232, 904, 725 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.60 (d, *J* = 8.4 Hz, 2H Ar**H**), 7.55 (d, *J* = 8.3 Hz, 2H, Ar**H**), 7.40 (dd, *J* = 8.7, 5.4 Hz, 2H, Ar**H**), 7.01 (t, *J* = 8.6 Hz, 2H, Ar**H**), 3.72 (t, *J* = 5.7 Hz, 2H, C**H$_2$**OH), 2.55-2.36 (m, 2H, CC**H$_2$**CH$_2$), 1.72-1.49 (m, 3H, CH$_2$C**H$_2$**CH$_2$ + O**H**); ^{13}C NMR (125 MHz, CDCl$_3$) δ 161.78 (d, *J* = 321 Hz), 152.42, 141.95 (d, *J* = 3.2 Hz), 132.04, 127.77 (d, *J* = 8.5 Hz), 126.76, 118.84, 115.21 (d, *J* = 21.5 Hz), 110.50, 76.75, 62.90, 39.23, 26.57; HRMS (ESI) exact mass calculated for [M+H]$^+$ ($C_{17}H_{17}NO_2$) requires *m/z* 286.12443, found *m/z* 286.12441.



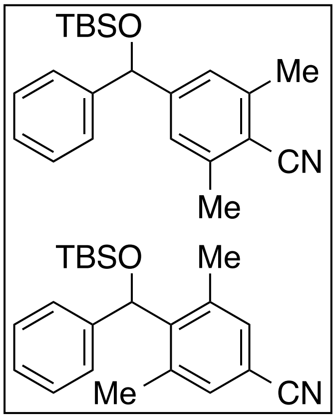
4-(4-(dimethylamino)-1-(4-fluorophenyl)-1-hydroxybutyl)benzonitrile (Table 2.16): Prepared according to the general procedure using 4.8 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (7.5 mmol, 0.01 equiv.), 96 mg of terephthalonitrile (0.75 mmol, 1.00 equiv.), 475 mg of 4-(dimethylamino)-1-(4-fluorophenyl)butan-1-ol (2.25 mmol, 3.00 equiv.), 131 mg of K$_2$HPO$_4$ (0.75 mmol, 1.00 equiv.), 141 mL of octanal (0.90 mmol, 1.2 equiv.), 13.0 mL of methyl 2-mercaptoacetate (0.15 mmol, 0.2 equiv.), 0.75 mL of DMA. After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the title compound as a clear oil (176 mg, 0.56 mmol, 75%). IR (film) 3600, 2953, 2225, 1604, 1225, 1160, 1016, 904, 832, 727 cm^{-1}; ^{1}H

NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.5 Hz, 2H Ar**H**), 7.58 (d, *J* = 8.5 Hz, 2H, Ar**H**), 7.47-7.42 (m, 2H, Ar**H**), 6.99 (t, *J* = 8.7 Hz, 2H, Ar**H**), 2.54-2.30 (m, 5H, C$\mathbf{H_2}$$CH_2C\mathbf{H_2}$N + O**H**), 2.12 (s, 6H, N(C$\mathbf{H_3}$)$_2$), 1.66-1.52 (m, 2H, CH_2C$\mathbf{H_2}$$CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.49 (d, *J* = 244 Hz), 154.12, 142.98, 142.98 (d *J* = 3.1 Hz), 131.92, 127.75 (d, *J* = 8.5 Hz), 126.80, 119.07, 114.93 (d, *J* = 21.4 Hz), 109.99, 75.70, 59.65, 44.55, 42.02, 22.36; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{19}H_{22}FN_2O$) requires *m/z* 313.17107, found *m/z* 313.17119.



4-(((*tert*-butyldimethylsilyl)oxy)(phenyl)methyl)-2,5-dimethylbenzonitrile (Table 3.1): Prepared according to the general procedure using 4.8 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (7.5 mmol, 0.01 equiv.), 117 mg of 2,5-dimethylterephthalonitrile (0.75 mmol, 1.00 equiv.), 500 mg of (benzyloxy)(*tert*-butyl)dimethylsilane (2.25 mmol, 3.00 equiv.), 131 mg of K_2HPO_4 (0.75 mmol, 1.00 equiv.), 141 mL of octanal (0.90 mmol, 1.2 equiv.), 13.0 mL of methyl 2-mercaptoacetate (0.15 mmol, 0.2 equiv.), 0.75 mL of DMA. After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the title compound as a clear oil (141 mg, 0.40 mmol, 53%). IR (film) 2930, 2858, 2225, 1463, 1254, 1093, 907, 837, 778, 731 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (s, 1H, Ar**H**), 7.38-7.23 (m, 6H, Ar**H**), 5.87 (s, 1H, ArC**H**Ar), 2.56 (s, 3H, ArC$\mathbf{H_3}$), 2.21 (s, 3H, ArC$\mathbf{H_3}$), 0.93 (s, 9H, SiC(C$\mathbf{H_3}$)$_3$), 0.01 (s, 3H, SiC$\mathbf{H_3}$), -0.01 (s, 3H, SiC$\mathbf{H_3}$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.82, 142.57, 139.34, 134.16, 132.88, 128.57, 128.28, 127.34, 126.77, 118.39, 111.08, 73.84, 25.75, 20.23, 18.87, 18.24, -4.85, -4.87;

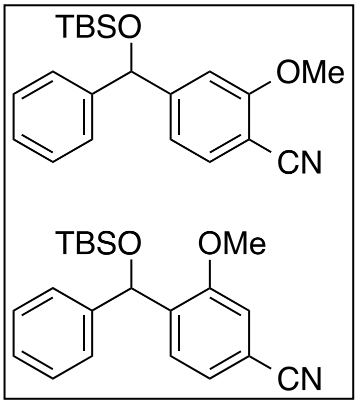
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{22}H_{30}NOSi$) requires *m/z* 352.20912, found *m/z* 352.20916.



4-(((*tert*-butyldimethylsilyl)oxy)(phenyl)methyl)-2,6-dimethylbenzonitrile and 4-(((*tert*-butyldimethylsilyl)oxy)(phenyl)methyl)-3,5-dimethylbenzonitrile (Table 3.2): Prepared according to the general procedure using 4.8 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (7.5 mmol, 0.01 equiv.), 117 mg of 2-methoxyterephthalonitrile (0.75 mmol, 1.00 equiv.), 500 mg of (benzyloxy)(*tert*-butyl)dimethylsilane (2.25 mmol, 3.00 equiv.), 131 mg of K_2HPO_4 (0.75 mmol, 1.00 equiv.), 141 mL of octanal (0.90 mmol, 1.2 equiv.), 13.0 mL of methyl 2-mercaptoacetate (0.15 mmol, 0.2 equiv.), 0.75 mL of DMA. After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Analysis of the crude reaction mixture by ^{1}H NMR in $CDCl_3$ determined that the regioisomer ratio was 2:1. Purification of the crude reaction mixture by flash chromatography (silica gel: 5% ethyl acetate in hexanes) afforded 4-(((tert-butyldimethylsilyl)oxy)(phenyl)methyl)-2,6-dimethylbenzonitrile (127 mg, 0.36 mmol, 48%) and 4-(((tert-butyldimethylsilyl)oxy)-(phenyl)methyl)-3,5-dimethylbenzonitrile (63 mg, 0.18 mmol, 24%) as colorless oils.
4-(((tert-butyldimethylsilyl)oxy)(phenyl)methyl)-2,6-dimethylbenzonitrile: IR (film) 2958, 2219, 1607, 1472, 1254, 1095, 908, 862, 732 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.29 (m, 2H, Ar**H**), 7.26-7.22 (m, 1H, Ar**H**), 7.14 (s, 1H, Ar**H**), 5.68 (s, 1H, ArC**H**Ar), 2.50 (s, 6H, 2 × ArC**H**$_3$), 0.92 (s, 9H, SiC(C**H**$_3$)$_3$), 0.00 (s, 3H, SiC**H**$_3$), -0.04 (s, 3H,

SiC**H**$_3$); ^{13}C NMR (125 MHz, CDCl$_3$) δ 149.64, 144.06, 142.14, 128.40, 127.41, 126.17, 124.89, 117.46, 111.73, 76.10, 25.76, 20.92, 18.27, -4.83, -4.92; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{22}H_{30}NOSi$) requires *m/z* 352.20916, found *m/z* 352.20919.

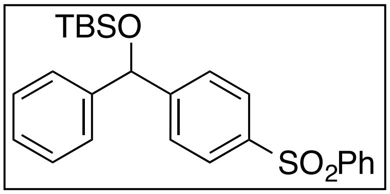
4-(((tert-butyldimethylsilyl)oxy)(phenyl)methyl)-3,5-dimethylbenzonitrile: IR (film) 2955, 2225, 1471, 1251, 1066, 903, 778, 724 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.33-7.28 (m, 4H, Ar**H**), 7.26-7.22 (m, 1H, Ar**H**), 7.22-7.19 (m, 2H, Ar**H**), 6.27 (s, 1H, ArC**H**Ar), 2.32 (bs, 6H, 2 × ArC**H**$_3$), 0.95 (s, 9H, SiC(C**H**$_3$)$_3$), 0.15 (s, 3H, SiC**H**$_3$), -0.17 (s, 3H, SiC**H**$_3$); ^{13}C NMR (125 MHz, CDCl$_3$) δ 145.73, 142.56, 128.17 (2C), 126.74, 125.08 (2C), 119.01, 110.97, 71.05, 25.80, 20.50, 18.29, -4.80, -5.05; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{22}H_{30}NOSi$) requires *m/z* 352.20912, found *m/z* 352.20906.



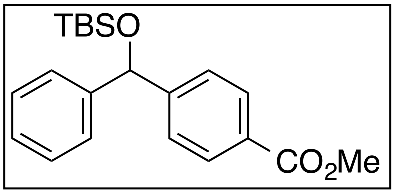
4-(((*tert*-butyldimethylsilyl)oxy)(phenyl)methyl)-2-methoxybenzonitrile and 4-(((*tert*-butyldimethylsilyl)oxy)(phenyl)methyl)-3-methoxybenzonitrile (Table 3.3): Prepared according to the general procedure using 4.8 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (7.5 mmol, 0.01 equiv.), 96 mg of 2-methoxyterephthalonitrile (0.75 mmol, 1.00 equiv.), 500 mg of (benzyloxy)(*tert*-butyl)dimethylsilane (2.25 mmol, 3.00 equiv.), 131 mg of K_2HPO_4 (0.75 mmol, 1.00 equiv.), 141 mL of octanal (0.90 mmol, 1.2 equiv.), 13.0 mL of methyl 2-mercaptoacetate (0.15 mmol, 0.2 equiv.), 0.75 mL of DMA. After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Analysis of the crude reaction mixture by ^{1}H NMR in $CDCl_3$ determined that the regioisomer ratio was 2:1. Purification of the crude reaction mixture by flash chromatography (silica gel: 5% ethyl acetate in hexanes) afforded 4-(((tert-butyldimethylsilyl)oxy)(phenyl)methyl)-3-methoxybenzonitrile (95 mg, 0.27 mmol, 36%) and 4-(((tert-butyldimethylsilyl)oxy)-(phenyl)methyl)-2-methoxybenzonitrile (50 mg, 0.14 mmol, 18%) as colorless oils.

4-(((tert-butyldimethylsilyl)oxy)(phenyl)methyl)-3-methoxybenzonitrile: IR (film) 2955, 2226, 1608, 1463, 1412, 1261, 1093, 904, 729 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.9 Hz, 1H, Ar**H**), 7.29-7.26 (m, 3H, Ar**H**), 7.24-7.20 (m, 2H, Ar**H**), 7.07 (s, 1H, Ar**H**), 6.90 (dd, *J* = 7.9, 0.7 Hz, 1H, Ar**H**), 5.69 (s, 1H, ArC**H**Ar), 3.87 (s, 3H, ArO**Me**), 0.88 (s, 9H, SiC(C**H**$_3$)$_3$), -0.01 (s, 3H, SiC**H**$_3$), -0.09 (s, 3H, SiC**H**$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.33, 152.57, 143.65, 133.46, 128.48, 127.64, 126.29, 118.56, 116.65, 108.50, 99.97, 76.13, 55.86, 25.73, 18.24, -4.81, -4.97; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{21}H_{28}NO_2Si$) requires *m/z* 354.18838, found *m/z* 354.18829.

4-(((tert-butyldimethylsilyl)oxy)(phenyl)methyl)-2-methoxybenzonitrile: IR (film) 2956, 2231, 1574, 1462, 1407, 1260, 1066, 905, 741 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.9 Hz, 1H, Ar**H**), 7.36 (d, *J* = 7.3 Hz, 2H, Ar**H**), 7.31-7.25 (m, 3H, Ar**H**), 7.20 (t, *J* = 7.3 Hz, 1H, Ar**H**), 7.03 (d, *J* = 1.1 Hz, 1H, Ar**H**), 6.12 (s, 1H, ArC**H**Ar), 3.85 (s, 3H, ArO**Me**), 0.90 (s, 9H, SiC(C**H**$_3$)$_3$), -0.02 (s, 3H, SiC**H**$_3$), -0.05 (s, 3H, SiC**H**$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.29, 143.66, 139.64, 128.04, 127.44, 127.11, 126.32, 125.02, 119.08, 113.24, 111.18, 69.70, 55.61, 25.75, 18.19, -4.94, -5.06; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{21}H_{28}NO_2Si$) requires *m/z* 354.18838, found *m/z* 354.18861.

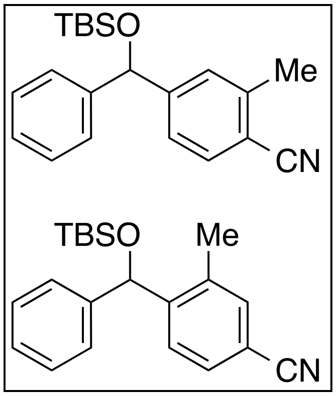


***tert*-butyldimethyl(phenyl(4- (phenylsulfonyl)-phenyl)methoxy)silane (Table 3.4)**: Prepared according to the general procedure using 4.8 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (7.5 mmol, 0.01 equiv.), 547 mg of 4-(phenylsulfonyl)benzonitrile (0.75 mmol, 1.00 equiv.), 500 mg of (benzyloxy)(*tert*-butyl)dimethylsilane (2.25 mmol, 3.00 equiv.), 131 mg of K_2HPO_4 (0.75 mmol, 1.00 equiv.), 141 mL of octanal (0.90 mmol, 1.2 equiv.), 13.0 mL of methyl 2-mercaptoacetate (0.15 mmol, 0.2 equiv.), 0.75 mL of DMA. After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the title compound as a clear oil (232 mg, 0.53 mmol, 71%). IR (film) 2955, 2857, 2255, 1595, 1447, 1318, 1258, 1156, 1090, 903, 723 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 2H Ar**H**), 7.84 (d, *J* = 8.5 Hz, 2H, Ar**H**), 7.56-7.45 (m, 5H, Ar**H**), 7.30-7.24 (m, 4H, Ar**H**), 7.23-7.18 (m, 1H, Ar**H**), 5.73 (s, 1H, ArC**H**Ar), 0.88 (s, 9H, $SiC(C\mathbf{H}_3)_3$), -0.03 (s, 3H, $SiC\mathbf{H}_3$), -0.09 (s, 3H, $SiC\mathbf{H}_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.91, 143.83, 141.52, 139.84, 133.10, 129.21, 128.43, 127.68, 127.63, 127.54, 126.73, 126.29, 76.05, 25.73, 18.22, -4.83, -4.98; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{25}H_{31}O_3SSi$) requires *m/z* 439.17632, found *m/z* 439.17599.



Methyl 4-(((*tert*-butyldimethylsilyl)oxy)-(phenyl)methyl)benzoate (Table 3.5): Prepared according to the general procedure using 4.8 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (7.5 mmol, 0.01 equiv.), 121 mg of methyl 4-

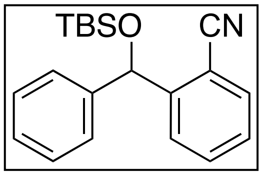
cyanobenzoate (0.75 mmol, 1.00 equiv.), 500 mg of (benzyloxy)(*tert*-butyl)dimethylsilane (2.25 mmol, 3.00 equiv.), 393 mg of K_2HPO_4 (0.75 mmol, 3.00 equiv), 141 mL of octanal (0.90 mmol, 1.2 equiv.), 13.0 mL of methyl 2-mercaptoacetate (0.15 mmol, 0.2 equiv.), 0.75 mL of DMA. After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the title compound as a clear oil (146 mg, 0.41 mmol, 55%). IR (film) 2954, 2858, 2256, 1721, 1612, 1436, 1279, 1190, 1090, 908, 837, 778, 732 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1 Hz, 2H Ar**H**), 7.45 (d, *J* = 8.2 Hz, 2H, Ar**H**), 7.34 (d, *J* = 7.6 Hz, 2H Ar**H**), 7.30 (t, *J* = 7.6 Hz, 2H, Ar**H**), 7.23 (t, *J* = 7.1 Hz, 1H, Ar**H**), 5.79 (s, 1H, ArC**H**Ar), 3.90 (s, 3H, $ArCO_2C\mathbf{H}_3$), 0.92 (s, 9H, $SiC(C\mathbf{H}_3)_3$), -0.01 (s, 3H, $SiC\mathbf{H}_3$), -0.02 (s, 3H, $SiC\mathbf{H}_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.00, 150.34, 144.37, 129.60, 128.73, 128.31, 127.25, 126.24, 126.09, 52.04, 25.77, 18.26, -4.86, -4.90; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{21}H_{29}O_3Si$) requires *m/z* 357.18805, found *m/z* 357.18774.



4-(((*tert*-butyldimethylsilyl)oxy)(phenyl)methyl)-2-methylbenzonitrile and 4-(((*tert*-butyldimethylsilyl)oxy)-(phenyl)methyl)-3-methylbenzonitrile (Table 3.6): Prepared according to the general procedure using 4.8 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (7.5 mmol, 0.01 equiv.), 107 mg of 2-methylterephthalonitrile (0.75 mmol, 1.00 equiv.), 500 mg of (benzyloxy)(*tert*-butyl)dimethylsilane (2.25 mmol, 3.00 equiv.), 79 mg of Na_2CO_3 (0.75 mmol, 1.00 equiv.), 141 mL of octanal (0.90 mmol, 1.2 equiv.), 13.0 mL of methyl 2-mercaptoacetate (0.15 mmol, 0.2 equiv.), 0.75 mL of DMA. After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Analysis of the crude reaction mixture by ^{1}H NMR in $CDCl_3$ determined that the regioisomer ratio was 1.4:1. Purification of the crude reaction mixture by flash chromatography (silica gel: 5% ethyl acetate in hexanes) afforded a mixture of the title compounds as a clear oil (176 mg, 0.52 mmol, 69%, 1.4:1 r.r.).

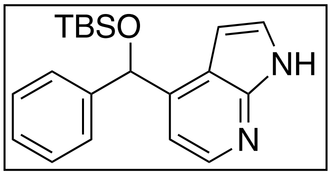
4-(((tert-butyldimethylsilyl)oxy)(phenyl)methyl)-2-methylbenzonitrile: IR (film) 2955, 2930, 2858, 2228, 1736, 1609, 1472, 1259, 1089, 1068, 905, 864, 837, 734 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.6 Hz, 1H, Ar**H**), 7.34-7.22 (m, 7H, Ar**H**), 5.73 (s, 1H, ArC**H**Ar), 2.52 (s, 3H, ArC**H**$_3$), 0.92 (s, 9H, SiC(C**H**$_3$)$_3$), 0.01 (s, 2H, SiC**H**$_3$), -0.04 (s, 3H, SiC**H**$_3$); HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{21}H_{28}NOSi$) requires *m/z* 338.19368, found *m/z* 338.19347.

4-(((tert-butyldimethylsilyl)oxy)(phenyl)methyl)-4-methylbenzonitrile: IR (film) 2955, 2930, 2858, 2228, 1736, 1609, 1472, 1259, 1089, 1068, 905, 864, 837, 734 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 1H, Ar**H**), 7.56 (s, 1H,Ar**H**), 7.38 (s, 1H,Ar**H**), 7.34-7.20 (m, 5H, Ar**H**), 5.788 (s, 1H, ArC**H**Ar), 2.24 (s, 3H, ArC**H**$_3$), 0.90 (s, 9H, SiC(C**H**$_3$)$_3$), -0.02 (s, 2H, SiC**H**$_3$), -0.03 (s, 3H, SiC**H**$_3$); HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{21}H_{28}NOSi$) requires *m/z* 338.19368, found *m/z* 338.19347.



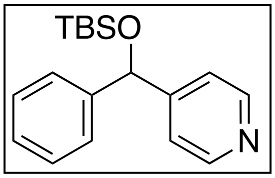
2-(((*tert*-butyldimethylsilyl)oxy)(phenyl)methyl)benzonitrile (Table 3.7): Prepared according to the general procedure using 4.8 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (7.5 mmol, 0.01

equiv.), 96 mg of phthalonitrile (0.75 mmol, 1.00 equiv.), 500 mg of (benzyloxy)(*tert*-butyl)dimethylsilane (2.25 mmol, 3.00 equiv.), 131 mg of K_2HPO_4 (0.75 mmol, 1.00 equiv.), 141 mL of octanal (0.90 mmol, 1.2 equiv.), 13.0 mL of methyl 2-mercaptoacetate (0.15 mmol, 0.2 equiv.), 0.75 mL of DMA. After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the title compound as a clear oil (100 mg, 0.31 mmol, 41%). IR (film) 2955, 2859, 2255, 1471, 1252, 1107, 1069, 903, 725 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.81-7.73 (m, 1H, Ar**H**), 7.62-7.55 (m, 2H, Ar**H**), 7.47 (d, *J* = 7.3 Hz, 2H, Ar**H**), 7.31 (t, *J* = 7.6 Hz, 3H, Ar**H**), 7.26 – 7.21 (m, 1H, Ar**H**), 6.14 (s, 1H, ArC**H**Ar), 0.91 (m, 9H, SiC(C**H**$_3$)$_3$), 0.01 (s, 3H, SiC**H**$_3$), 0.01 (s, 3H, SiC**H**$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.06, 143.22, 133.13, 132.56, 128.36, 127.50, 127.52, 127.13, 126.15, 117.95, 109.80, 74.17, 25.73, 18.19, -4.94, -4.99; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{20}H_{26}NOSi$) requires *m/z* 324.17782, found *m/z* 324.17781.



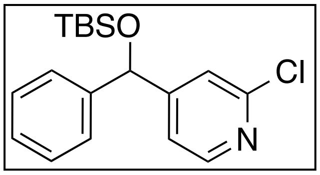
4-(((*tert*-butyldimethylsilyl)oxy)(phenyl)methyl)-1*H*-pyrrolo[2,3-*b*]pyridine (Table 3.8): Prepared according to the general procedure using 4.8 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (7.5 mmol, 0.01 equiv.), 107 mg of 1*H*-pyrrolo[2,3-*b*]pyridine-4-carbonitrile (0.75 mmol, 1.00 equiv.), 500 mg of (benzyloxy)(*tert*-butyl)dimethylsilane (2.25 mmol, 3.00 equiv.), 131 mg of K_2HPO_4 (0.75 mmol, 1.00 equiv.), 141 mL of octanal (0.90 mmol, 1.2 equiv.), 13.0 mL of methyl 2-mercaptoacetate (0.15 mmol, 0.2

equiv.), 0.375 mL of DMA, 0.375 mL of DMSO. After 48 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (silica gel: 20% ethyl acetate in hexanes) to afford the title compound as a clear oil (186 mg, 0.55 mmol, 73%). IR (film) 2955, 2857, 2254, 1591, 1472, 1252, 1100, 904, 724 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 9.95 (bs, 1H, N**H**), 8.31 (d, *J* = 5.0 Hz, 1H Ar**H**), 7.45 (d, *J* = 7.4 Hz, 2H, Ar**H**), 7.31-7.26 (m, 3H Ar**H**), 7.21 (t, *J* = 7.3 Hz, 1H, Ar**H**), 7.23 (t, *J* = 7.1 Hz, 1H, Ar**H**), 6.56 (d, *J* = 2.1 Hz, 1H, Ar**H**), 6.10 (s, 1H, ArC**H**Ar), 0.93 (s, 9H, SiC(C**H**$_3$)$_3$), -0.01 (s, 3H, SiC**H**$_3$), -0.02 (s, 3H, SiC**H**$_3$); ^{13}C NMR (125 MHz, CDCl$_3$) δ 148.85, 146.21, 143.76, 142.97, 128.20, 127.24, 126.26, 124.48, 117.41, 112.84, 100.01, 74.93, 25.80, 18.30, -4.92, -4.95; HRMS (ESI) exact mass calculated for [M+H]$^+$ ($C_{20}H_{27}N_2OSi$) requires *m/z* 339.18872, found *m/z* 339.18873.

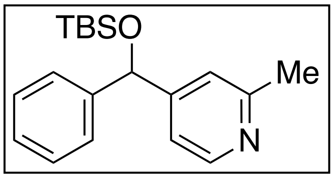


4-(((*tert*-butyldimethylsilyl)oxy)(phenyl)methyl)pyridine (Table 3.9): Prepared according to the general procedure using 4.8 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (7.5 mmol, 0.01 equiv.), 78 mg of isonicotinonitrile (0.75 mmol, 1.00 equiv.), 500 mg of (benzyloxy)(*tert*-butyl)dimethylsilane (2.25 mmol, 3.00 equiv.), 131 mg of K_2HPO_4 (0.75 mmol, 1.00 equiv.), 141 mL of octanal (0.90 mmol, 1.2 equiv.), 13.0 mL of methyl 2-mercaptoacetate (0.15 mmol, 0.2 equiv.), 0.75 mL of DMA. After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (silica gel: 20% ethyl acetate in hexanes) to afford the title compound as a clear oil (171 mg, 0.57 mmol, 76%). IR (film) 2955, 2858, 1597, 1472, 1412, 1252, 1191, 1090, 1067, 906, 837, 779, 842, 729 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.52 (d, *J*

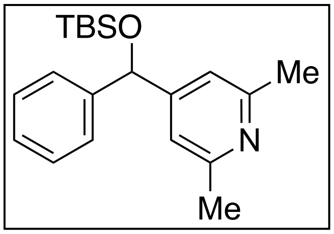
= 6.1 Hz, 2H Ar**H**), 7.35-7.29 (m, *J* = 7.4 Hz, 6H, Ar**H**), 7.27-7.24 (m, 1H Ar**H**), 5.70 (s, 1H, ArC**H**Ar), 0.93 (s, 9H, SiC(C**H**$_3$)$_3$), 0.04 (s, 3H, SiC**H**$_3$), -0.05 (s, 3H, SiC**H**$_3$); ^{13}C NMR (125 MHz, CDCl$_3$) δ 153.83, 149.67, 143.52, 128.45, 127.63, 126.38, 120.93, 75.54, 25.74, 18.24, -4.83, -4.99; HRMS (ESI) exact mass calculated for [M+H]$^+$ ($C_{18}H_{26}NOSi$) requires *m/z* 300.17782, found *m/z* 300.17784.



4-(((*tert*-butyldimethylsilyl)oxy)(phenyl)methyl)-2-chloropyridine (Table 3.10): Prepared according to the general procedure using 4.8 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (7.5 mmol, 0.01 equiv.), 104 mg of 2-chloroisonicotinonitrile (0.75 mmol, 1.00 equiv), 500 mg of (benzyloxy)(*tert*-butyl)dimethylsilane (2.25 mmol, 3.00 equiv.), 131 mg of K_2HPO_4 (0.75 mmol, 1.00 equiv.), 141 mL of octanal (0.90 mmol, 1.2 equiv.), 13.0 mL of methyl 2-mercaptoacetate (0.15 mmol, 0.2 equiv.), 0.75 mL of DMA. After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (silica gel: 20% ethyl acetate in hexanes) to afford the title compound as a clear oil (127 mg, 0.38 mmol, 51%). IR (film) 2955, 2858, 1590, 1550, 1463, 1379, 1256, 1095, 904, 862, 779, 724 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.28 (d, *J* = 5.1 Hz, 1H Ar**H**), 7.37-7.27 (m, 6H Ar**H**), 7.21 (d, *J* = 5.1 Hz, 1H, Ar**H**), 5.67 (s, 1H, ArC**H**Ar), 0.92 (s, 9H, SiC(C**H**$_3$)$_3$), 0.05 (s, 3H, SiC**H**$_3$), -0.06 (s, 3H, SiC**H**$_3$); ^{13}C NMR (125 MHz, CDCl$_3$) δ 157.41, 151.56, 149.51, 142.84, 128.65, 127.99, 126.41, 121.31, 119.80, 75.29, 25.72, 18.22, -4.81, -5.02; HRMS (ESI) exact mass calculated for [M+H]$^+$ ($C_{18}H_{25}ClNOSi$) requires *m/z* 334.13940, found *m/z* 334.13935.

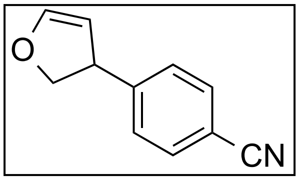


4-(((*tert*-butyldimethylsilyl)oxy)(phenyl)methyl)-2-methylpyridine (Table 3.11): Prepared according to the general procedure using 4.8 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (7.5 mmol, 0.01 equiv.), 89 mg of 2-methylisonicotinonitrile (0.75 mmol, 1.00 equiv.), 500 mg of (benzyloxy)(*tert*-butyl)dimethylsilane (2.25 mmol, 3.00 equiv.), 131 mg of K_2HPO_4 (0.75 mmol, 1.00 equiv.), 141 mL of octanal (0.90 mmol, 1.2 equiv.), 13.0 mL of methyl 2-mercaptoacetate (0.15 mmol, 0.2 equiv.), 0.75 mL of DMA. After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (silica gel: 20% ethyl acetate in hexanes) to afford the title compound as a clear oil (204 mg, 0.65 mmol, 86%). IR (film) 2955, 2858, 1601, 1472, 1405, 1253, 1154, 1093, 907, 864, 778, 732 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (d, *J* = 5.1 Hz, 1H Ar**H**), 7.38-7.31 (m, 4H Ar**H**), 7.30-7.25 (m, 1H, Ar**H**), 7.17-7.12 (m, 2H, Ar**H**), 5.68 (s, 1H, ArC**H**Ar), 0.94 (s, 9H, SiC(C**H**$_3$)$_3$), 0.05 (s, 3H, SiC**H**$_3$), -0.02 (s, 3H, SiC**H**$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.20, 154.18, 148.99, 143.68, 128.41, 127.55, 126.34, 120.40, 118.14, 75.62, 25.75, 24.51, 18.26, -4.83, -4.97; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{19}H_{27}NOSi$) requires *m/z* 314.19347, found *m/z* 314.19325.



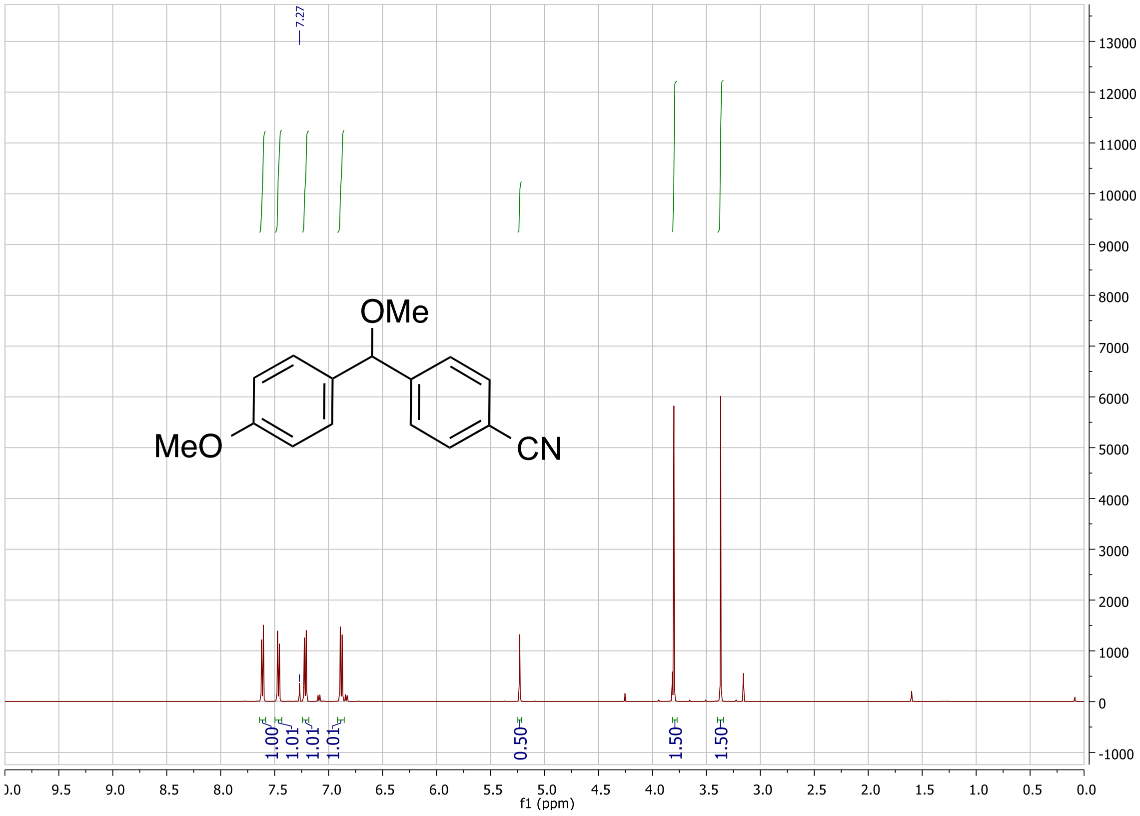
4-(((*tert*-butyldimethylsilyl)oxy)(phenyl)methyl)-2,6-dimethylpyridine (Table 3.12): Prepared according to the general procedure using 4.8 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (7.5 mmol, 0.01 equiv.), 99 mg of 2,6-dimethylisonicotinonitrile (0.75 mmol, 1.00 equiv.), 500 mg of (benzyloxy)(*tert*-

butyl)dimethylsilane (2.25 mmol, 3.00 equiv.), 131 mg of K_2HPO_4 (0.75 mmol, 1.00 equiv.), 141 mL of octanal (0.90 mmol, 1.2 equiv.), 13.0 mL of methyl 2-mercaptoacetate (0.15 mmol, 0.2 equiv.), 0.375 mL of DMA, 0.375 mL of DMSO. After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (silica gel: 20% ethyl acetate in hexanes) to afford the title compound as a clear oil (197 mg, 0.60 mmol, 80%). IR (film) 2955, 2858, 1741, 1606, 1572, 1454, 1254, 1097, 907, 838, 778, 731 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.31 (m, 4H Ar**H**), 7.29-7.25 (m, 1H Ar**H**), 6.99 (s, 2H Ar**H**), 5.65 (s, 1H, ArC**H**Ar), 2.51 (s, 6H, 2×ArC**H**$_3$), 0.94 (s, 9H, SiC(C**H**$_3$)$_3$), 0.04 (s, 3H, SiC**H**$_3$), -0.02 (s, 3H, SiC**H**$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.53, 154.48, 143.84, 128.37, 127.46, 126.30, 117.56, 75.66, 25.77, 24.48, 18.28, -4.84, -4.94; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{18}H_{25}ClNOSi$) requires *m/z* 328.20912, found *m/z* 328.20889.



4-(2,3-dihydrofuran-3-yl)benzonitrile (Figure 6): Prepared according to the general procedure using 4.8 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (7.5 μmol, 0.01 equiv.), 96 mg of terephthalonitrile (0.75 mmol, 1.00 equiv.), 263 mg of 2,5-dihydrofuran (3.75 mmol, 5.00 equiv.), 131 mg of K_2HPO_4 (0.75 mmol, 1.00 equiv.), 141 μL of octanal (0.90 mmol, 1.2 equiv.), 13.0 μL of methyl 2-mercaptoacetate (0.15 mmol, 0.2 equiv.), 0.75 mL of DMA. After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the title compound as a clear oil (106 mg, 0.62 mmol, 82%). IR (film) 2230, 1609, 1140, 1063, 904, 725 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ

7.62 (d, *J* = 8.1 Hz, 2H Ar**H**), 7.35 (d, *J* = 8.1 Hz, 2H, Ar**H**), 6.58 (s, 1H, C**H**=CH), 5.08 (s, 1H, C**H**=CH), 4.82-4.60 (m, 1H, OC**H**H), 4.31-4.07 (m, 2H, OC**H**H, C**H**Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.63, 147.53, 132.49, 128.10, 118.87, 110.63, 103.68, 77.05, 48.02; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{11}H_{10}NO$) requires *m/z* 172.07569, found *m/z* 172.07644.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11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
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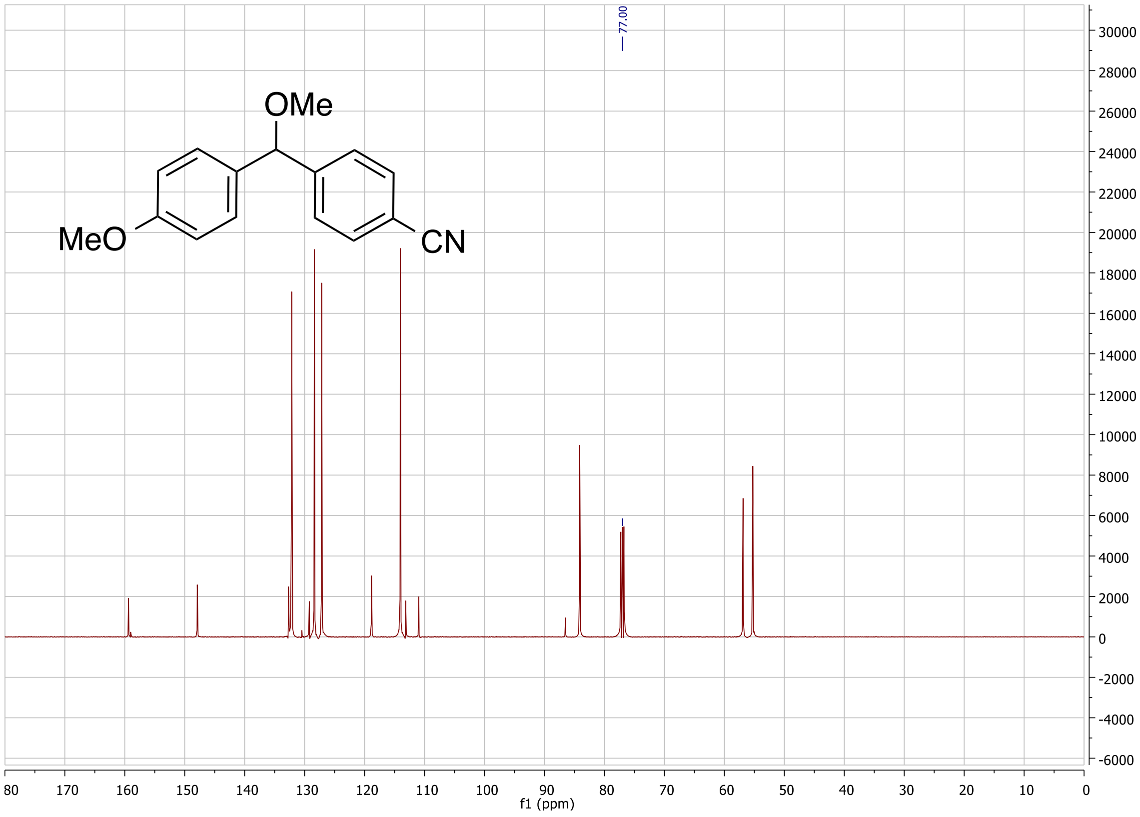
f1 (ppm)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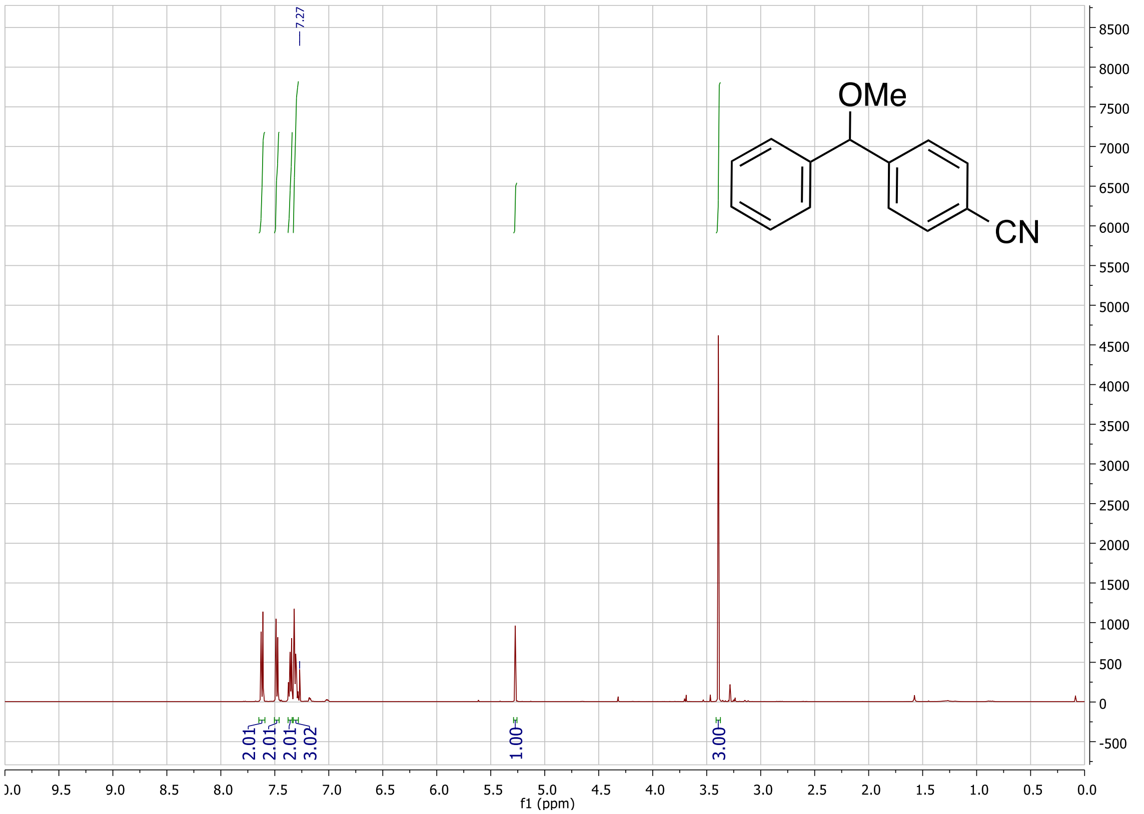
f1 (ppm)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5000
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3500
3000
2500
2000
1500
1000
500
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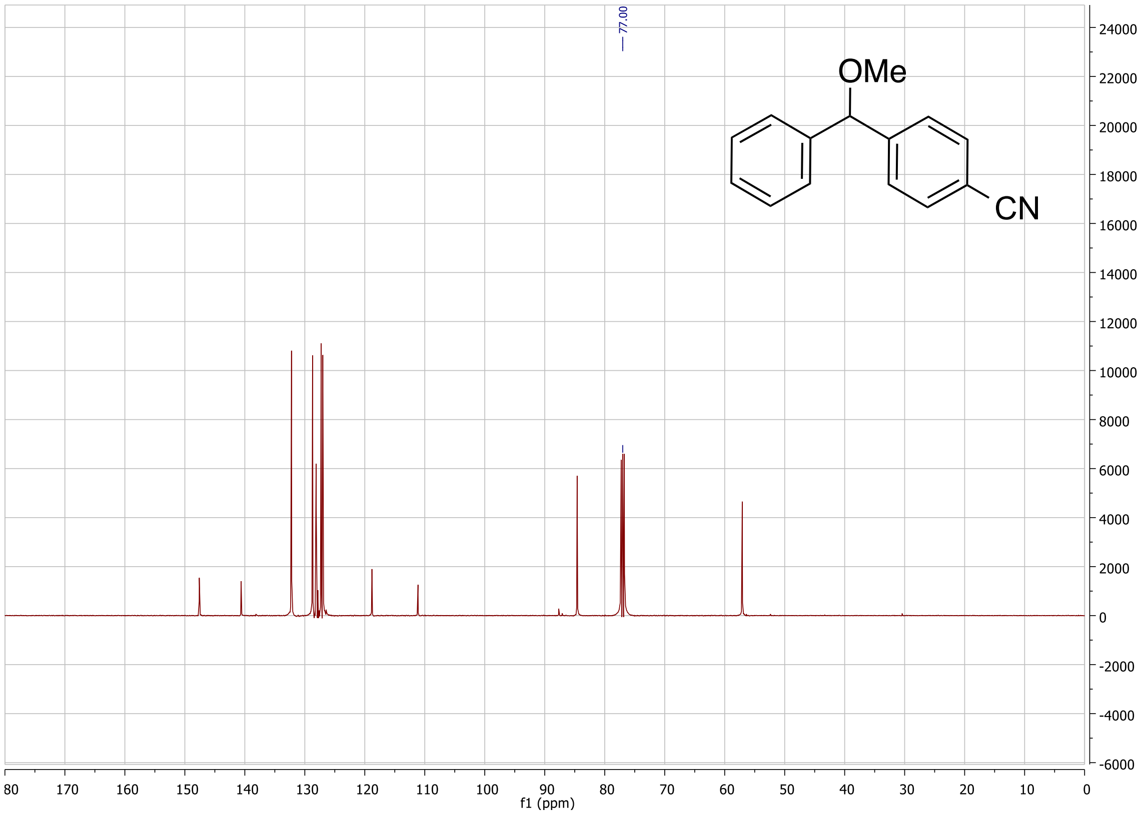
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-6000
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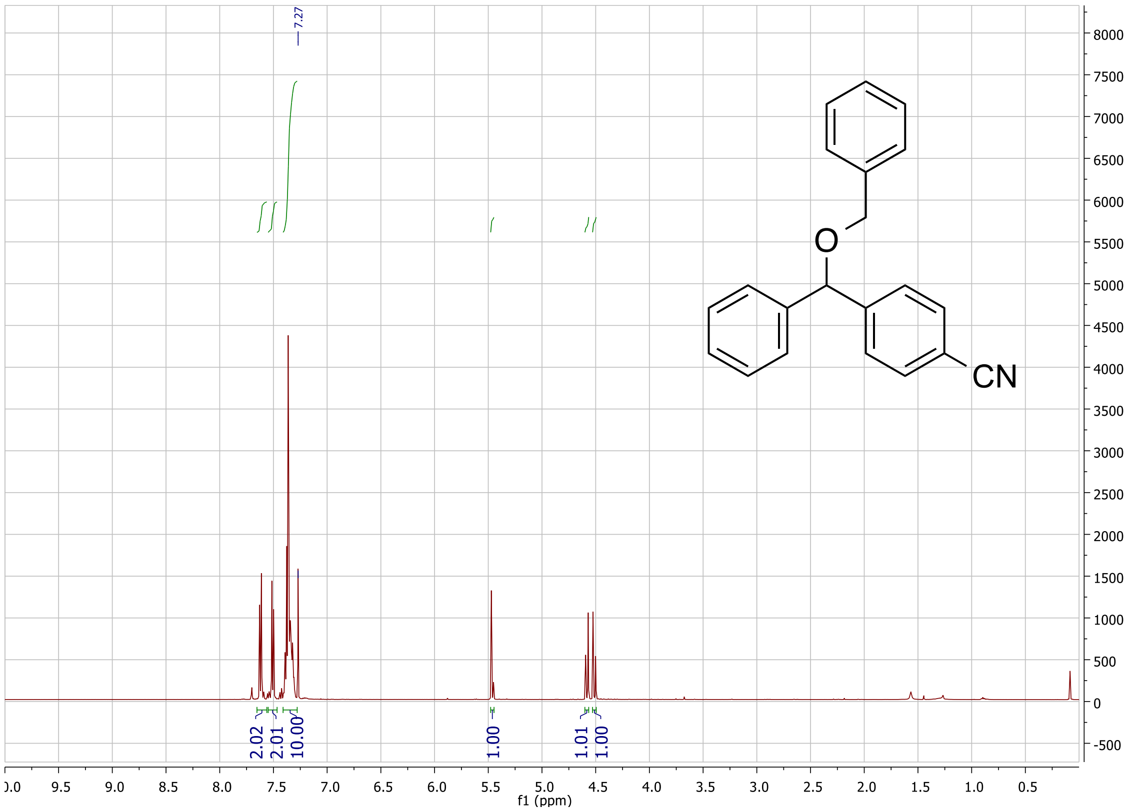
f1 (ppm)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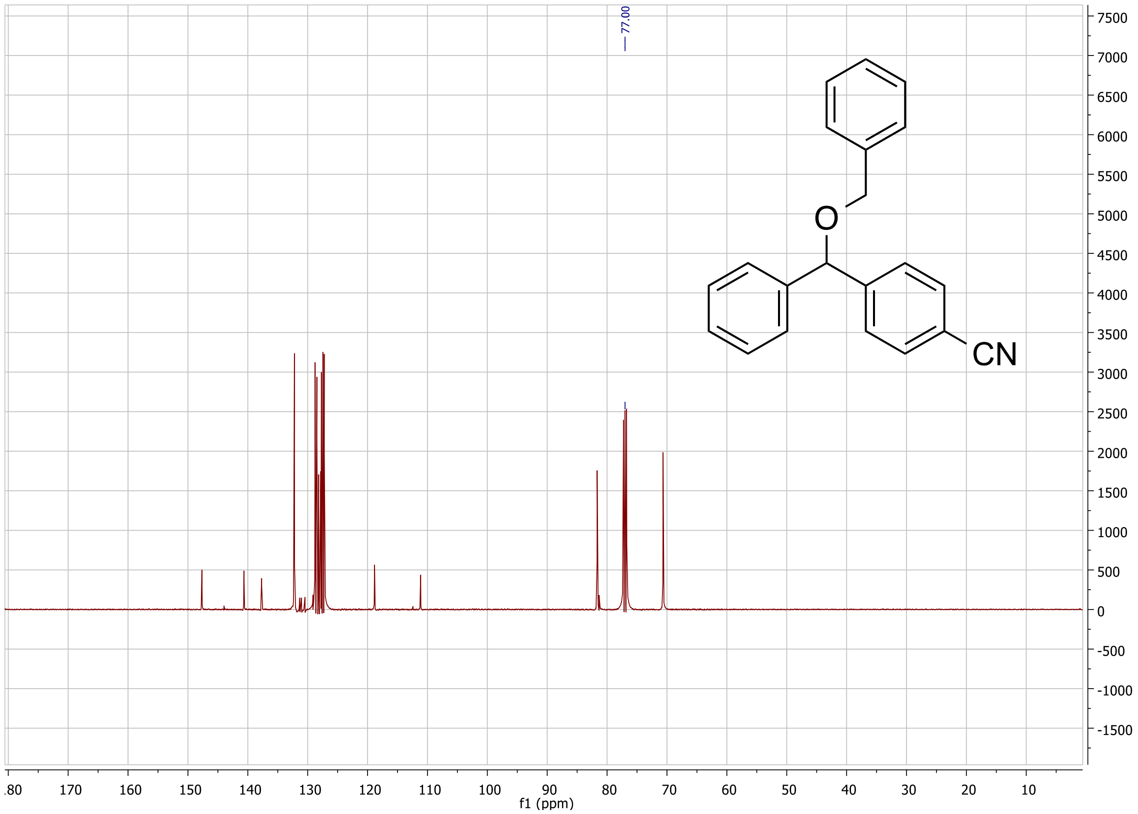
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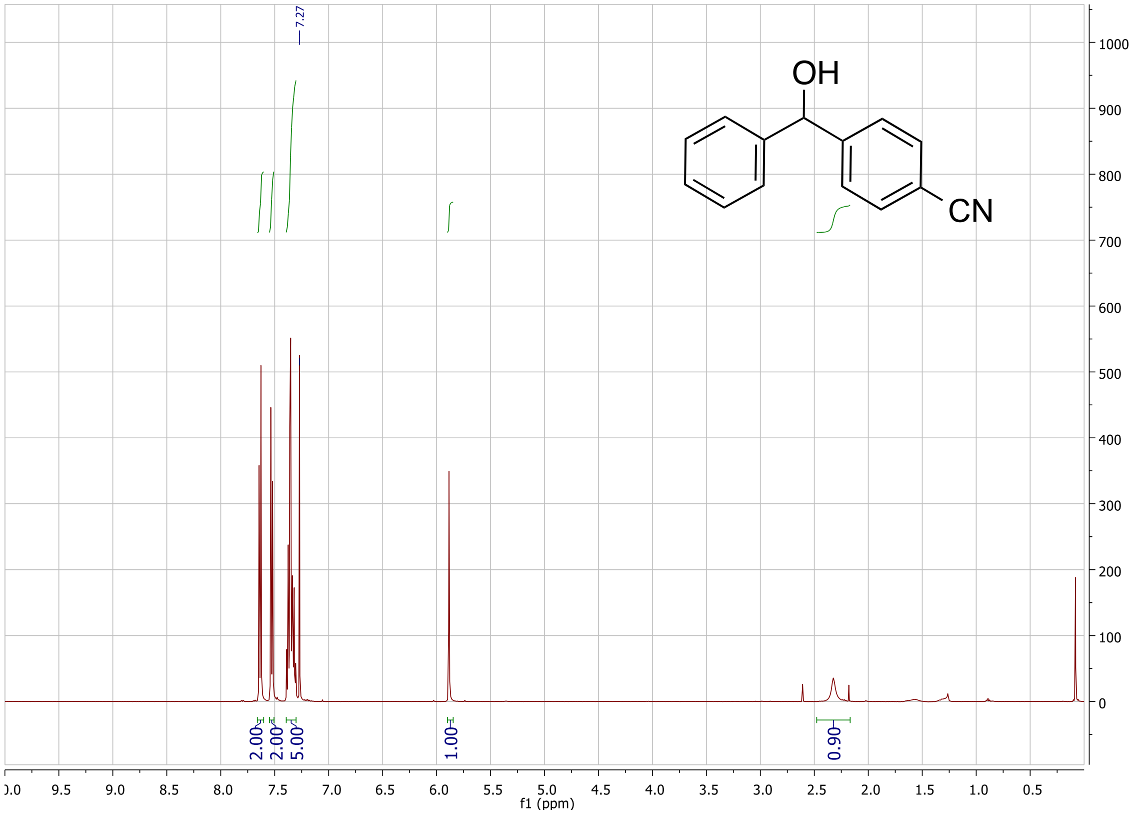
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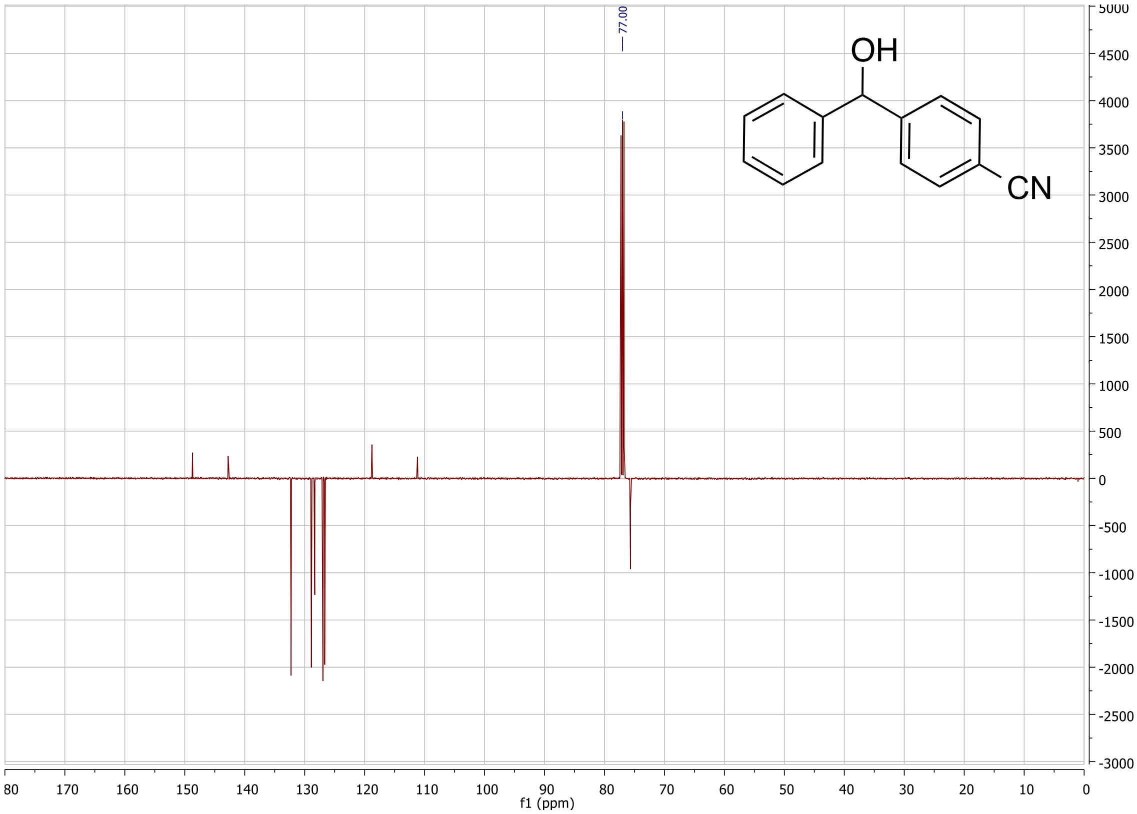
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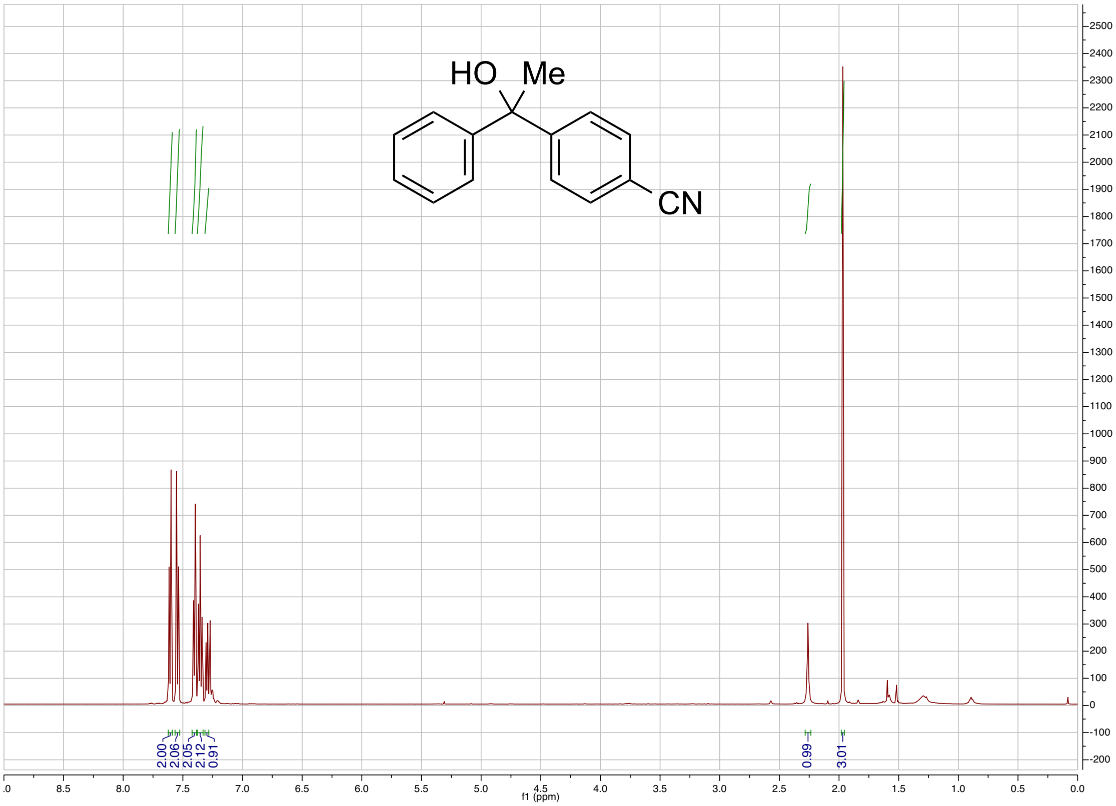
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3.0
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1600
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700
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500
400
300
200
100
0
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-200


HO
Me
CN
f1 (ppm)
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170
160
150
140
130
120
110
100
90
80
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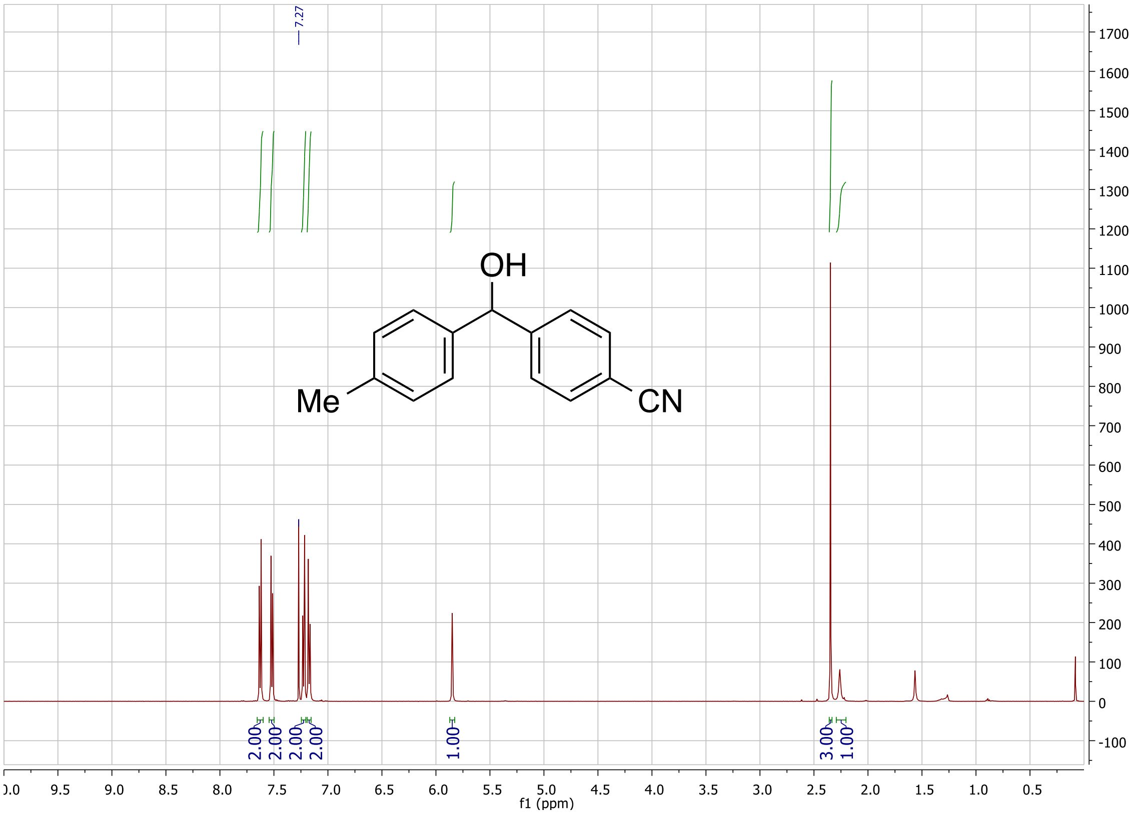
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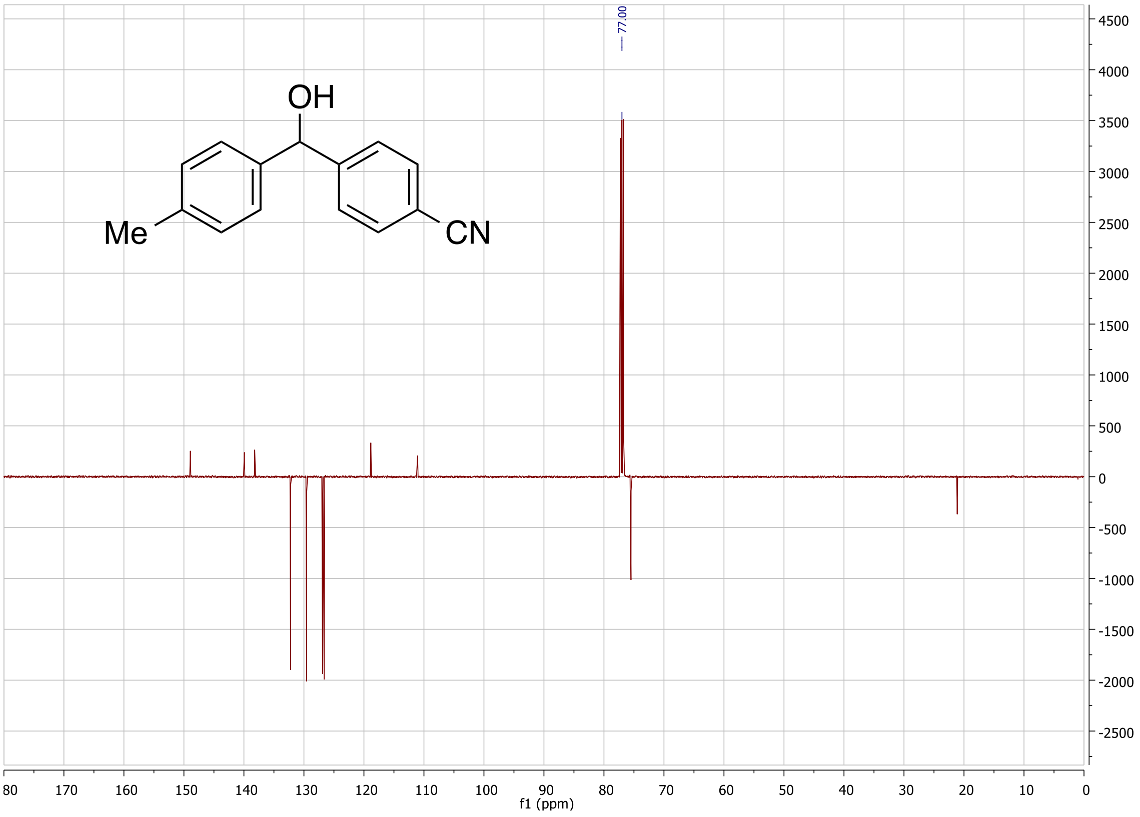
f1 (ppm)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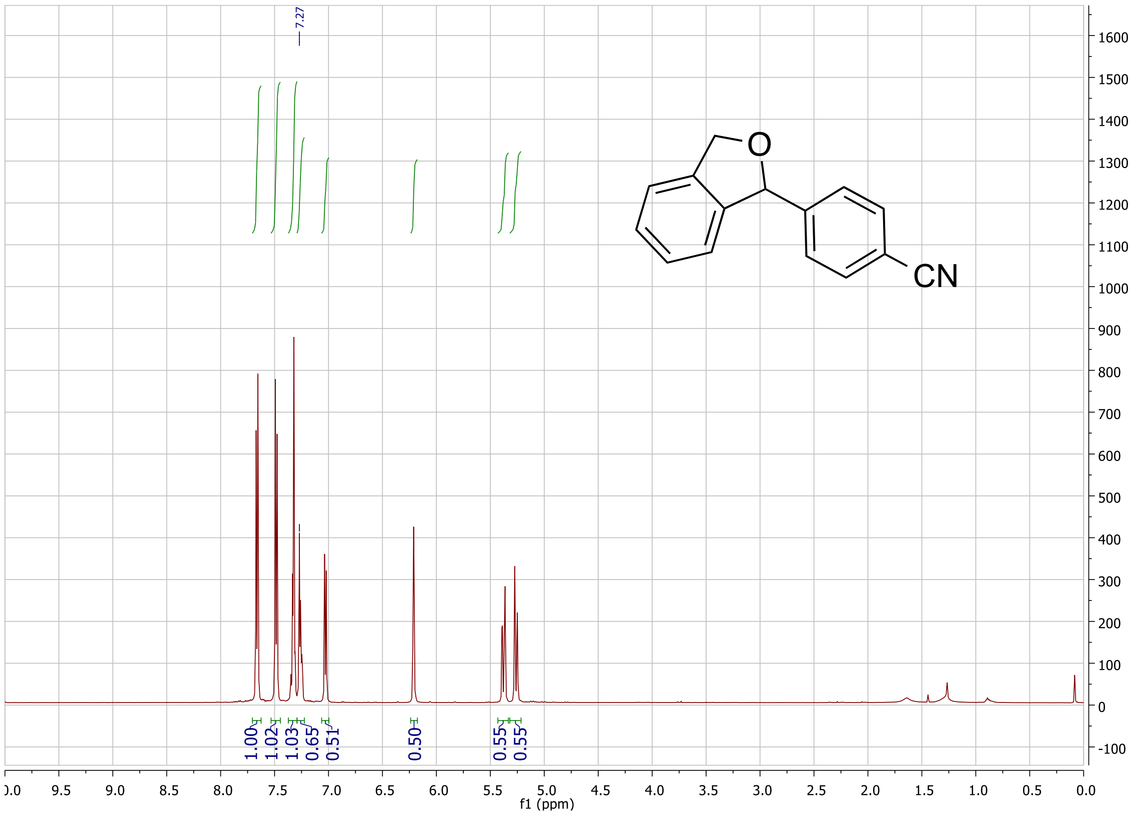
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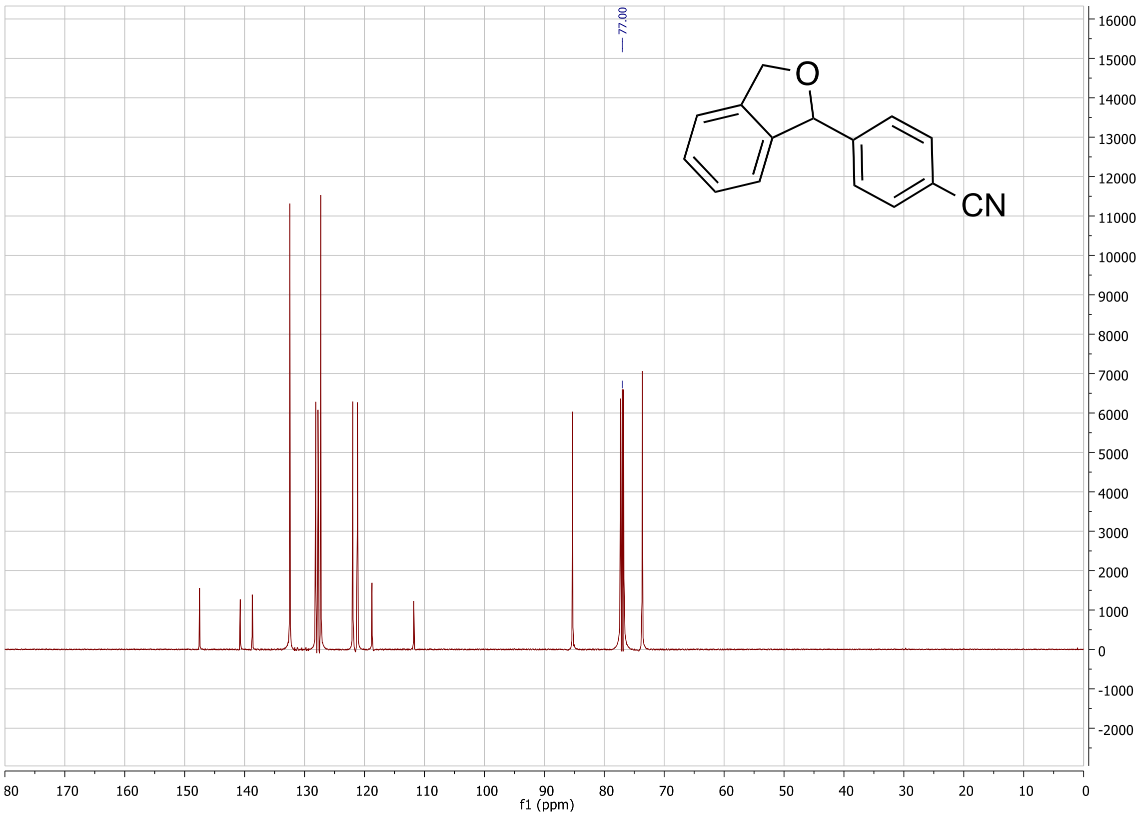
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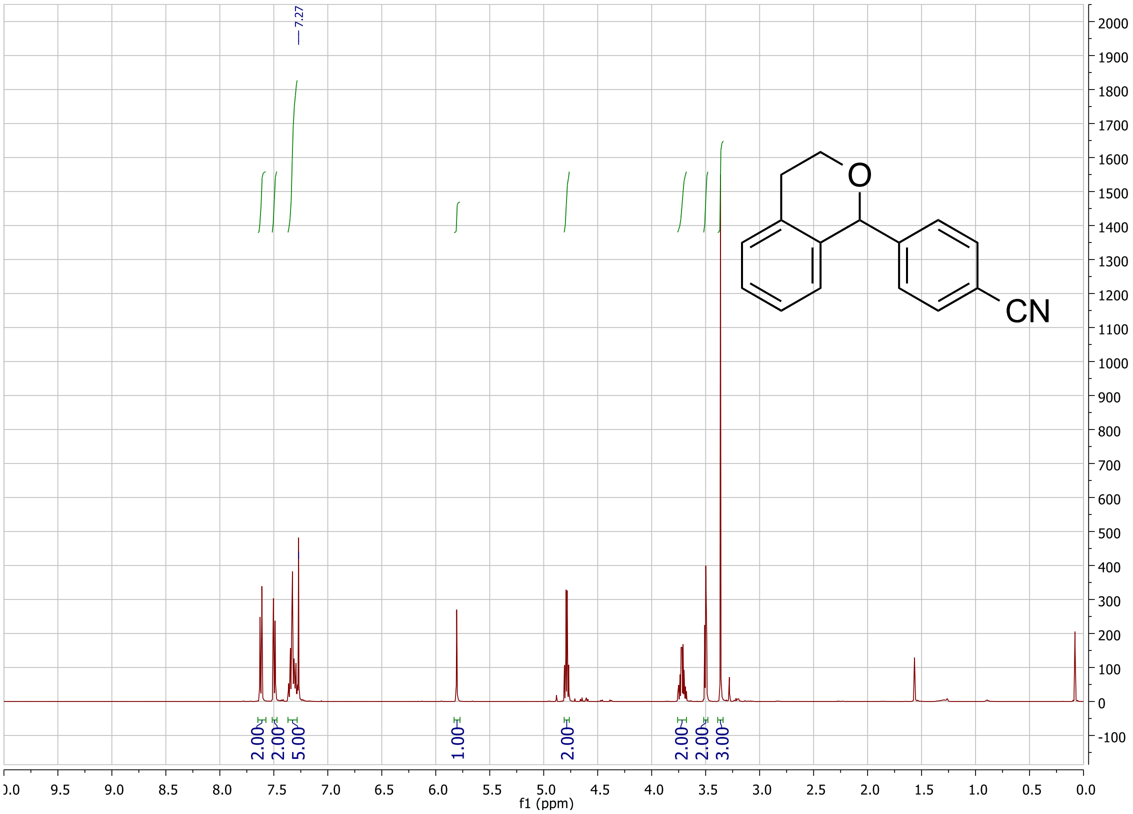
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1100
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800
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300
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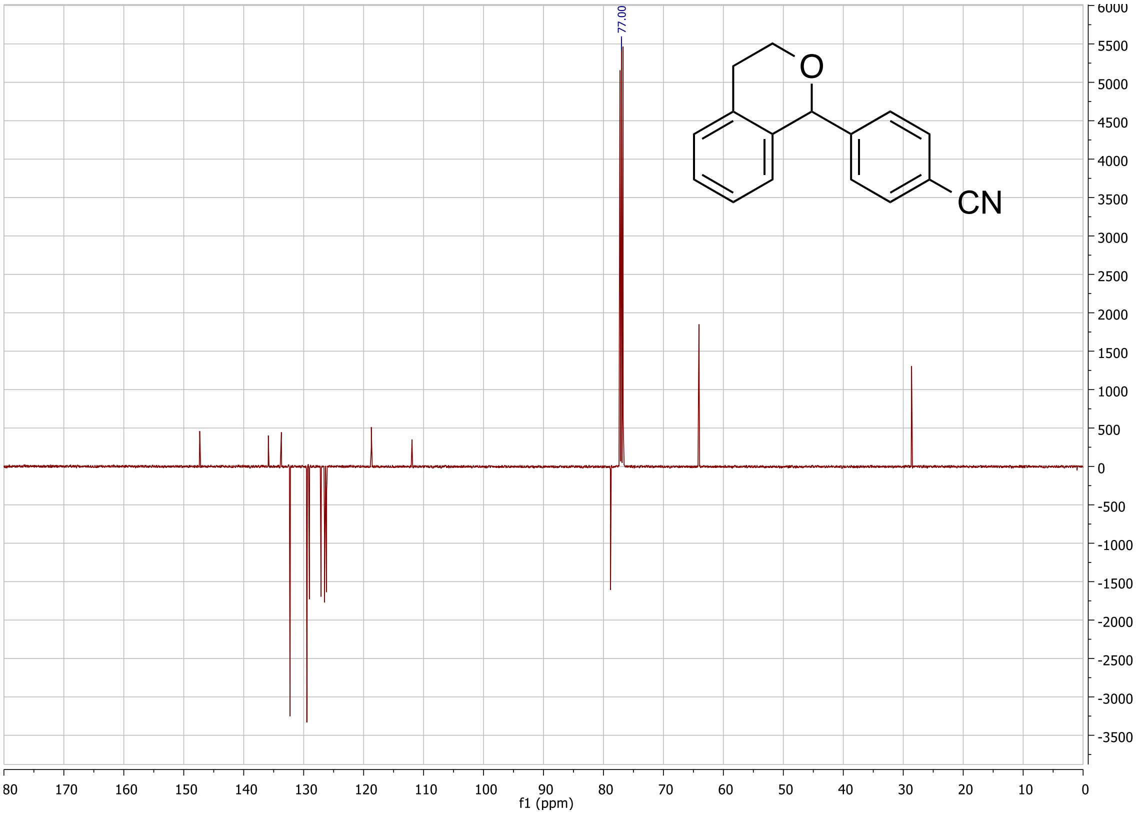
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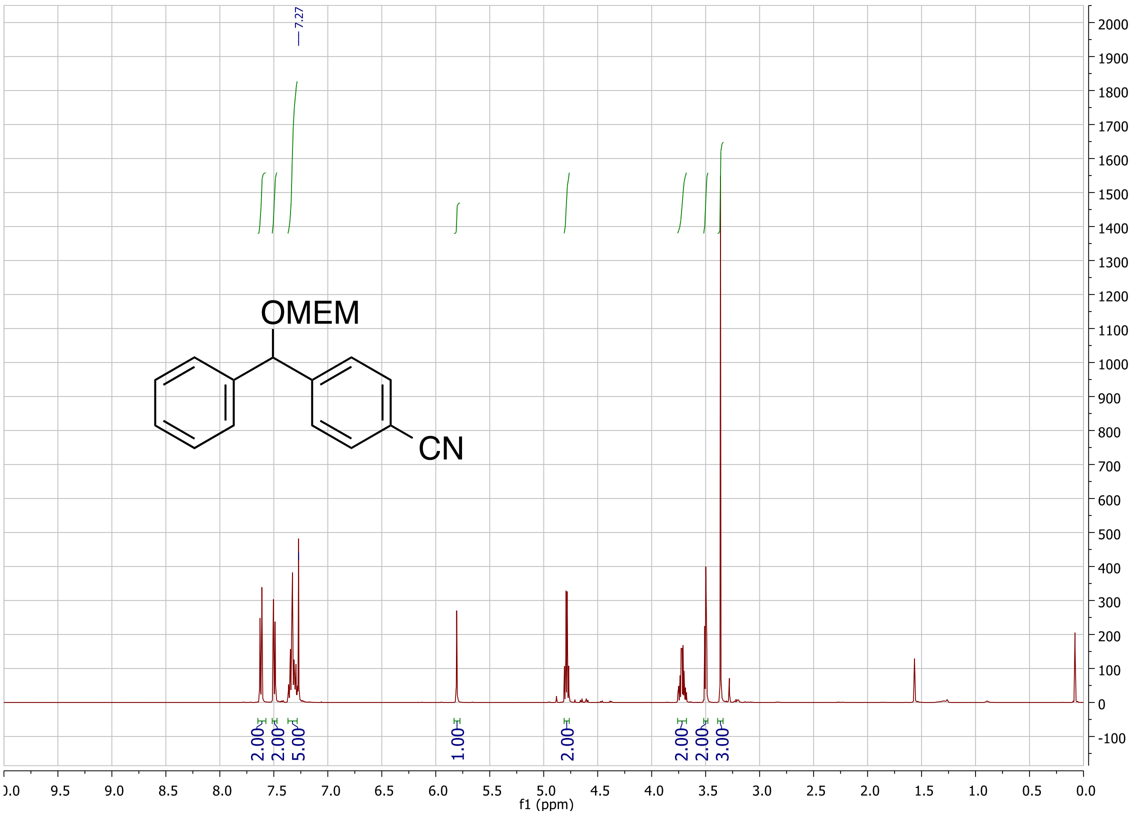
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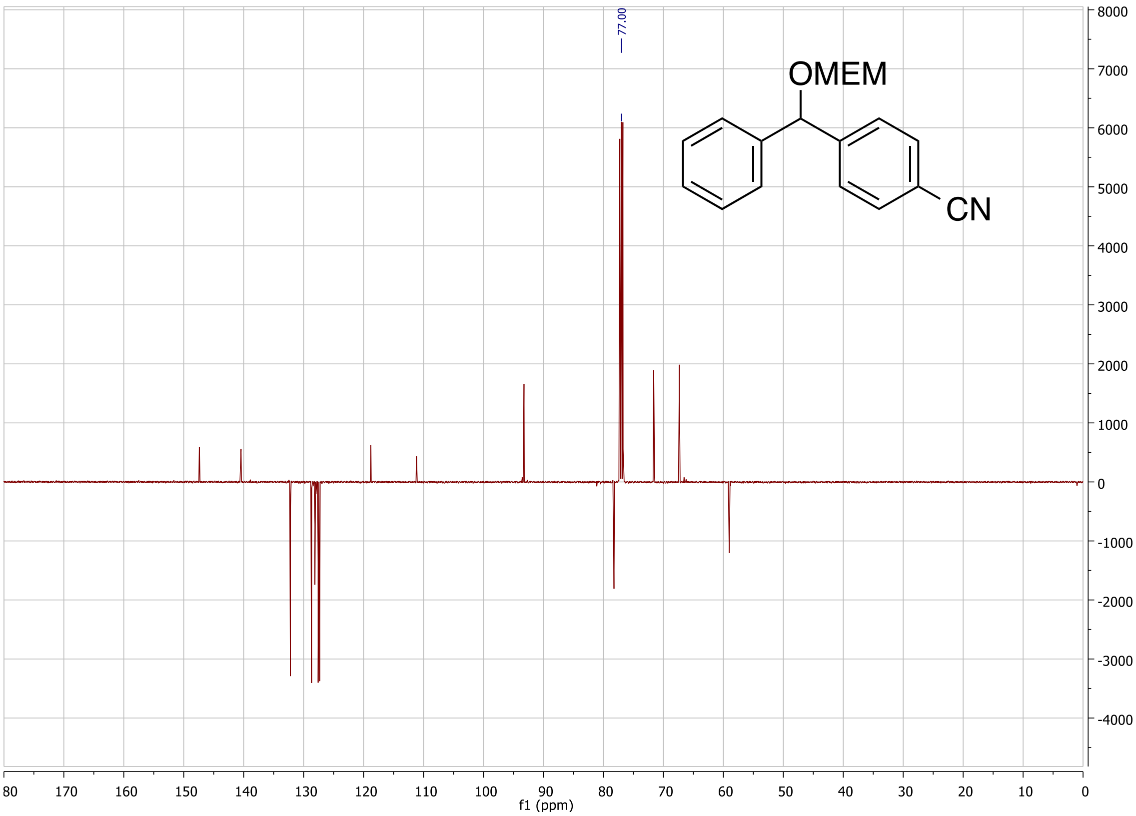
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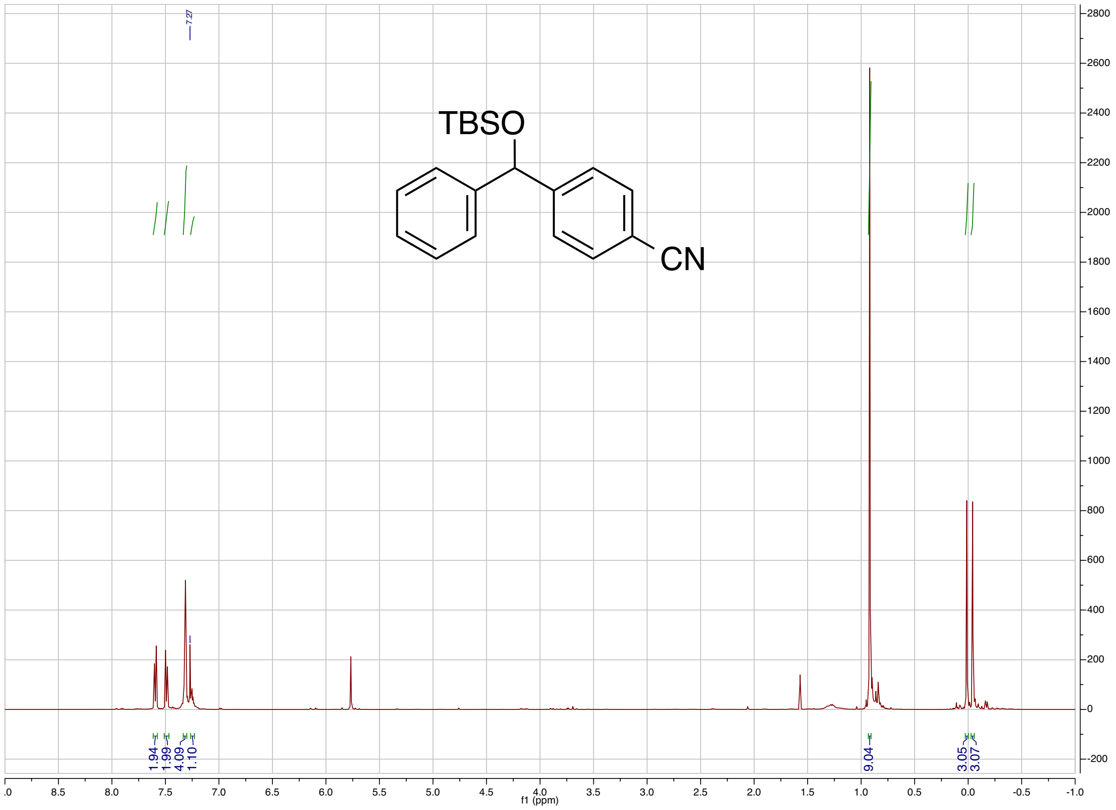
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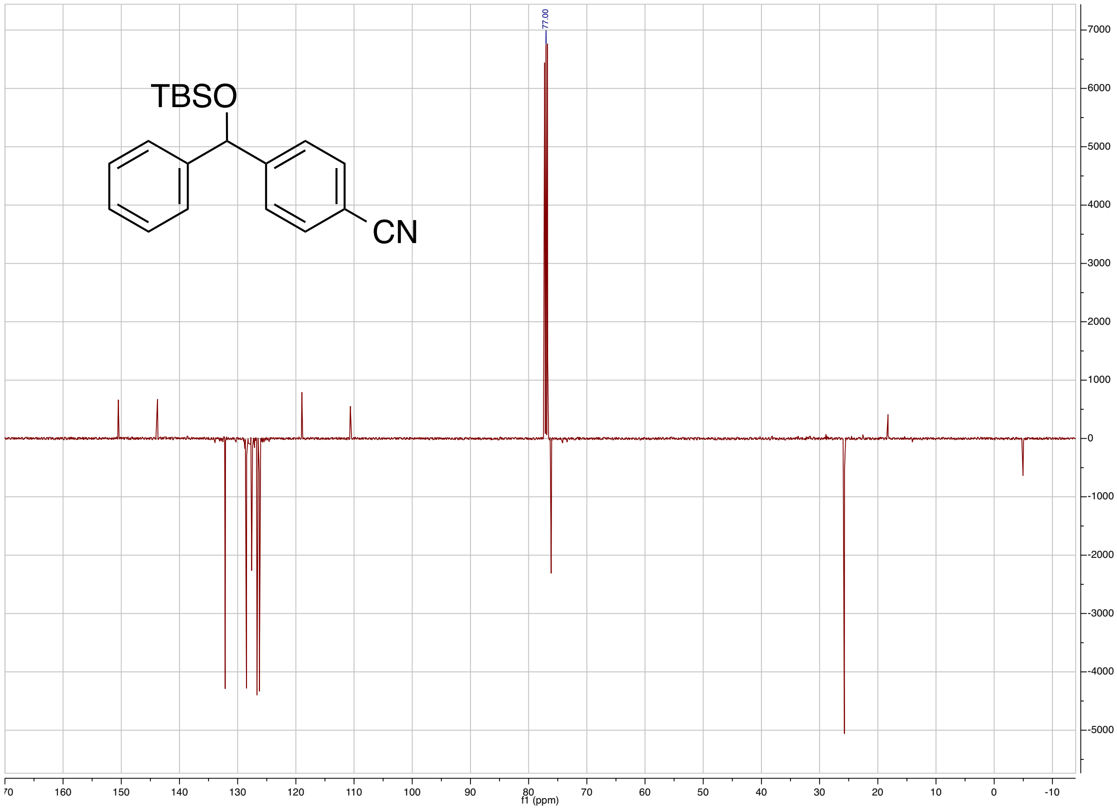
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f1 (ppm)
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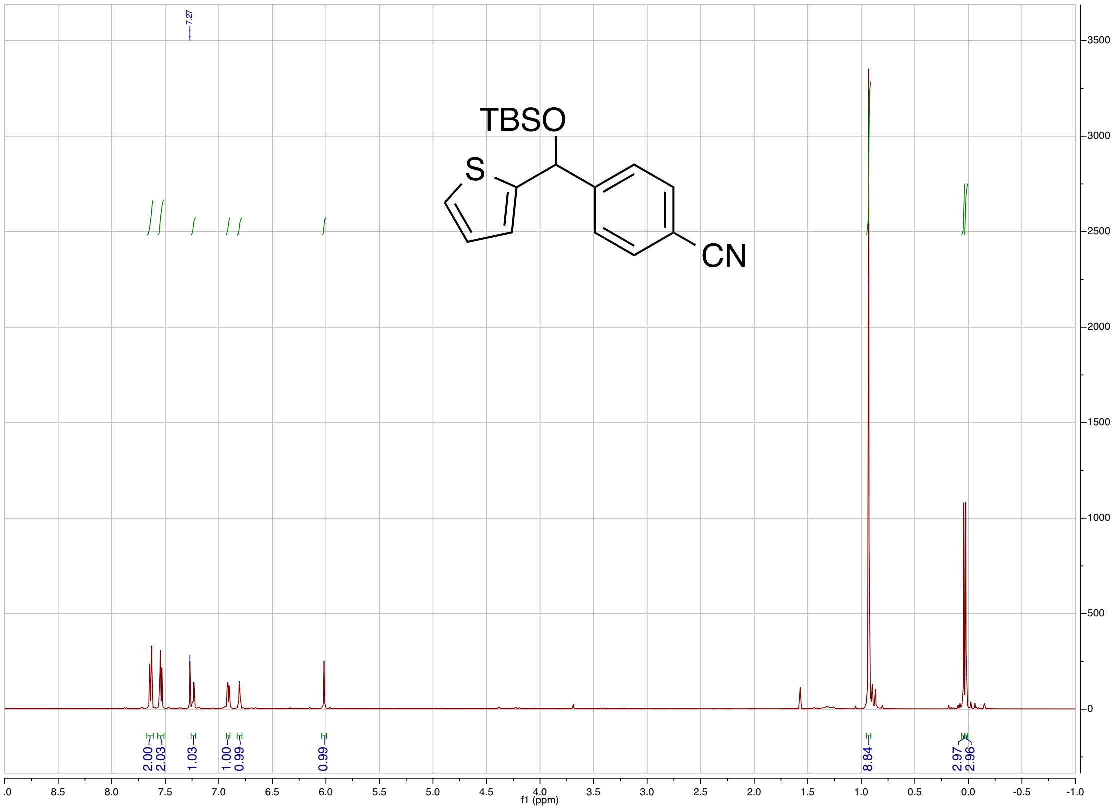
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4.5
4.0
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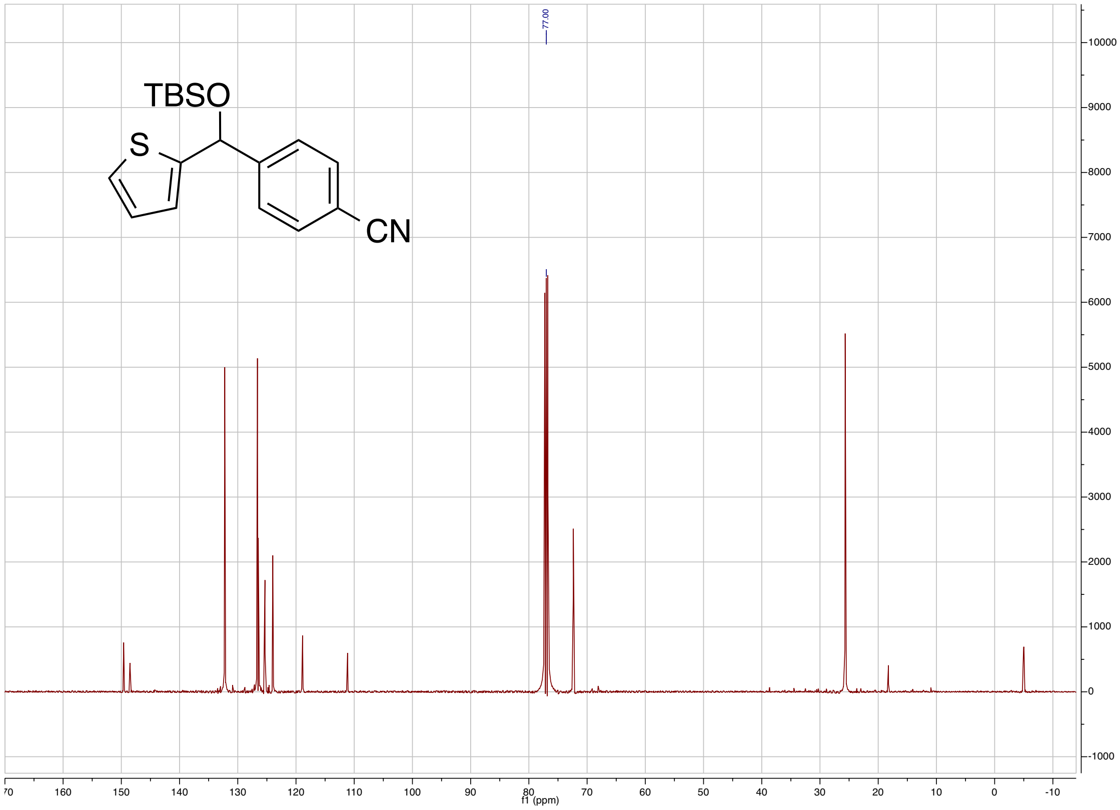
f1 (ppm)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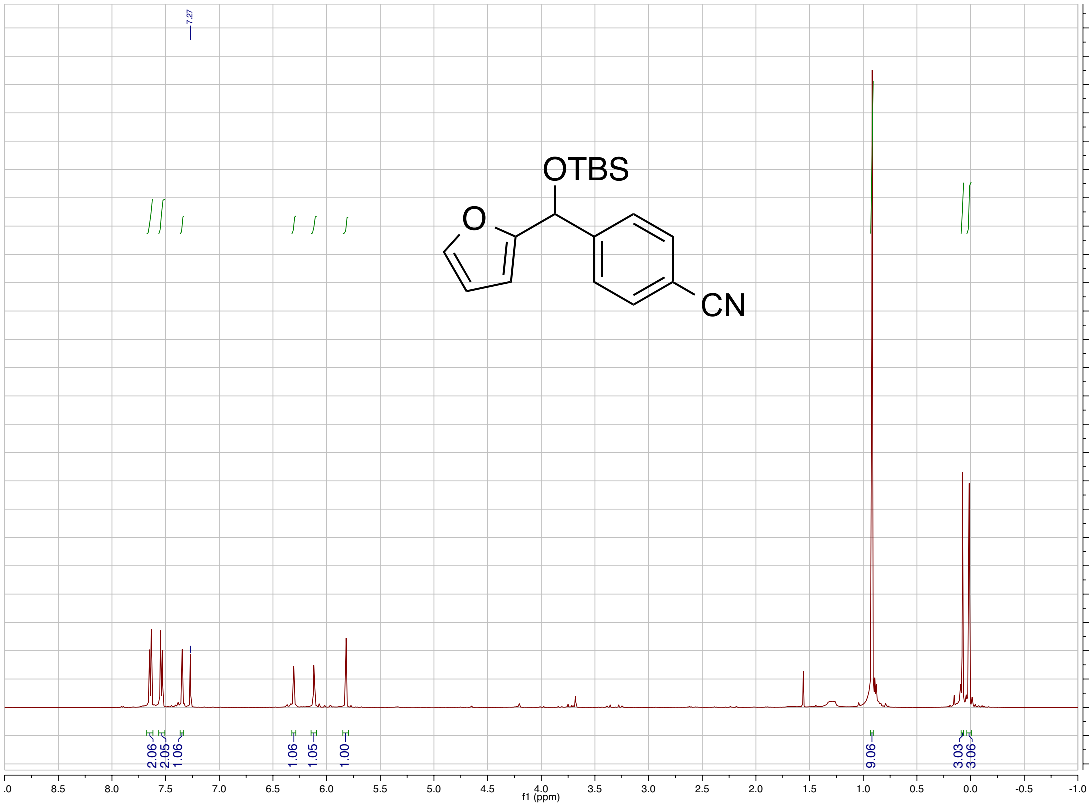
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8.0
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7.0
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6.0
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3.0
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2.0
1.5
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-0.5
-1.0
f1 (ppm)
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2300
2200
2100
2000
1900
1800
1700
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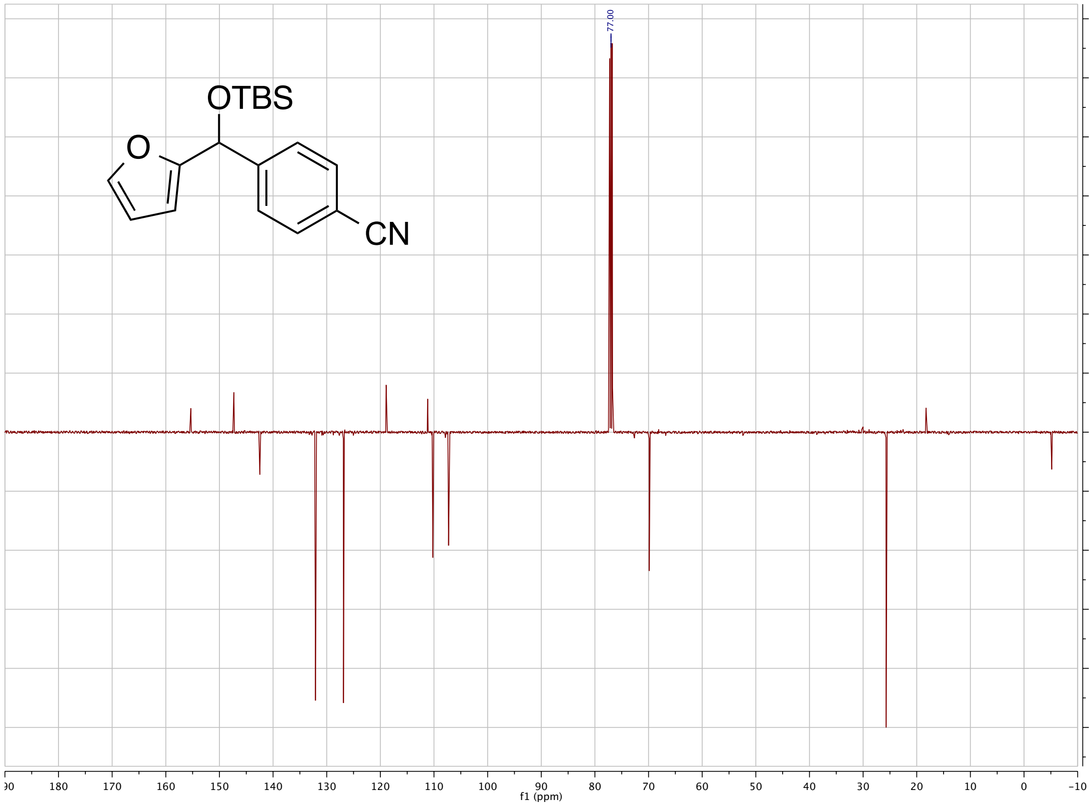
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20
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1000
0
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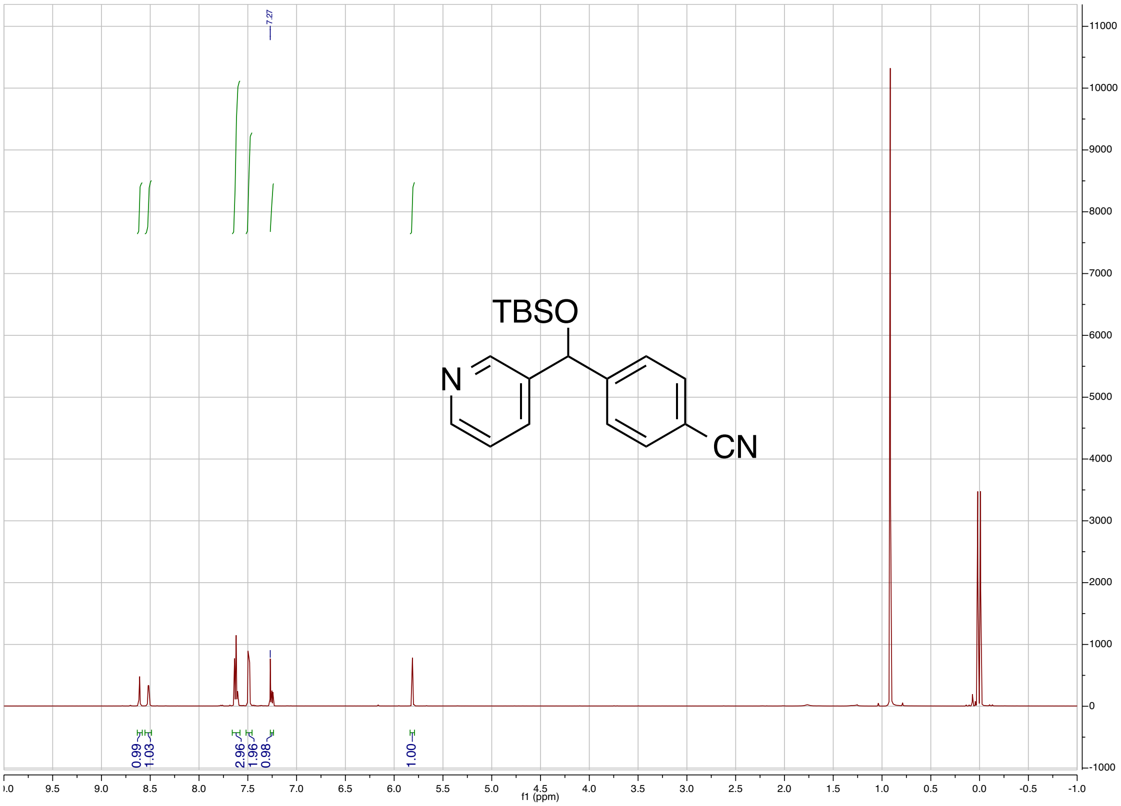
−3000
−4000
−5000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8.0
7.5
7.0
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)
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10000
9000
8000
7000
6000
5000
4000
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2000
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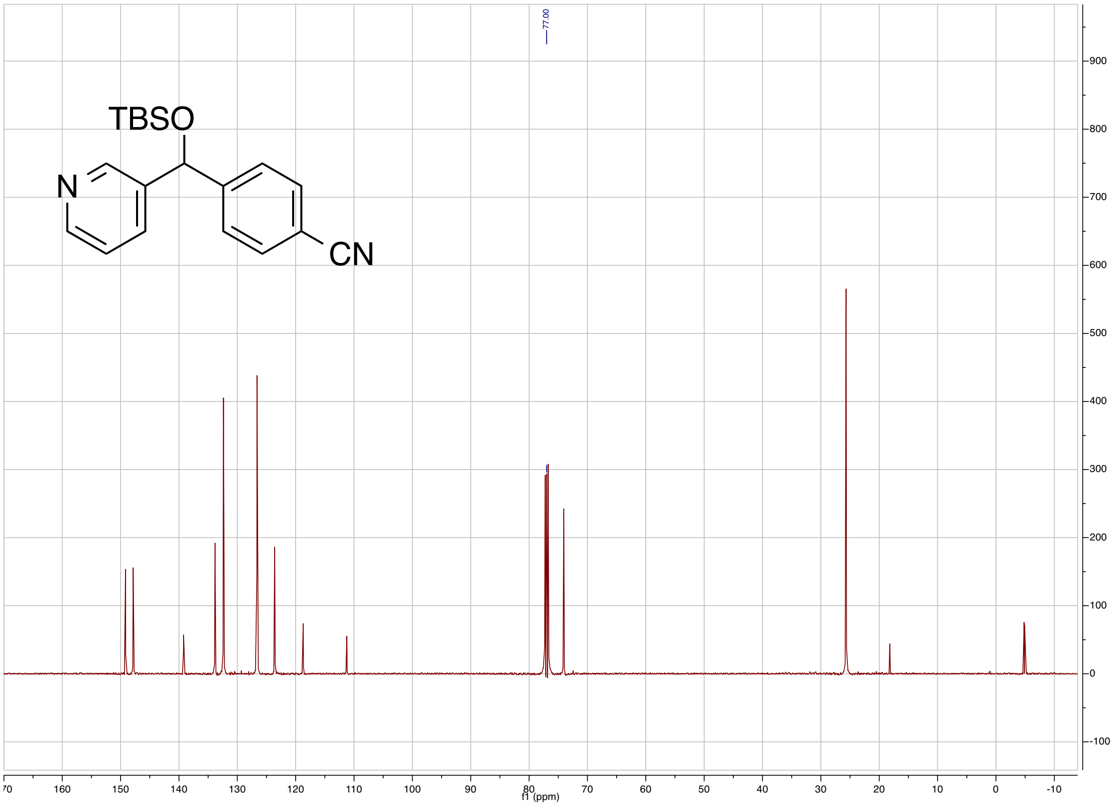
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CN
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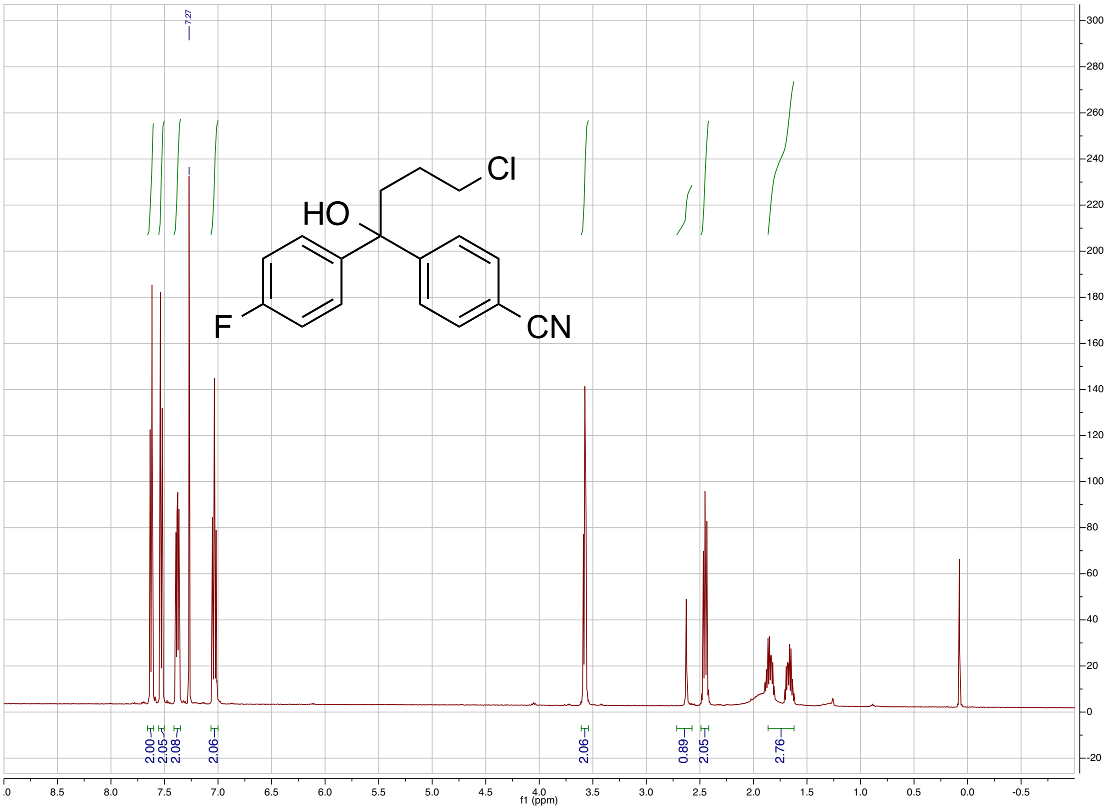
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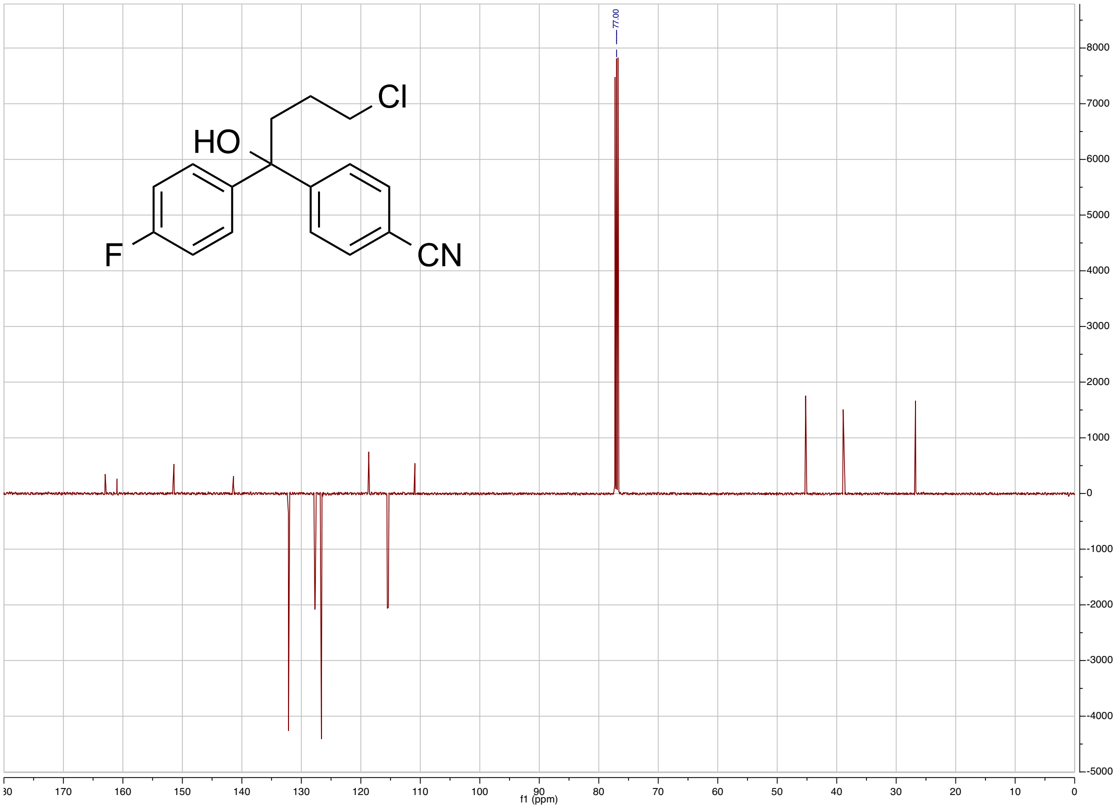
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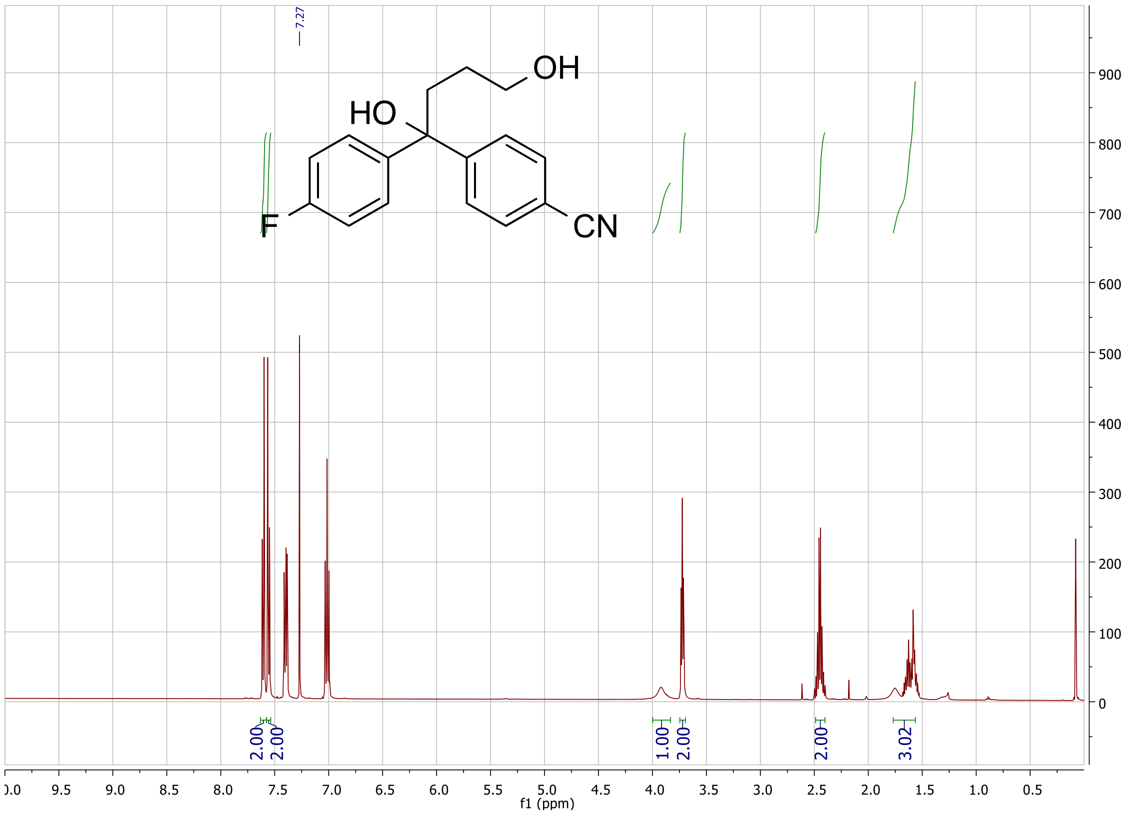
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CN
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2.00
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500
400
300
200
100
0
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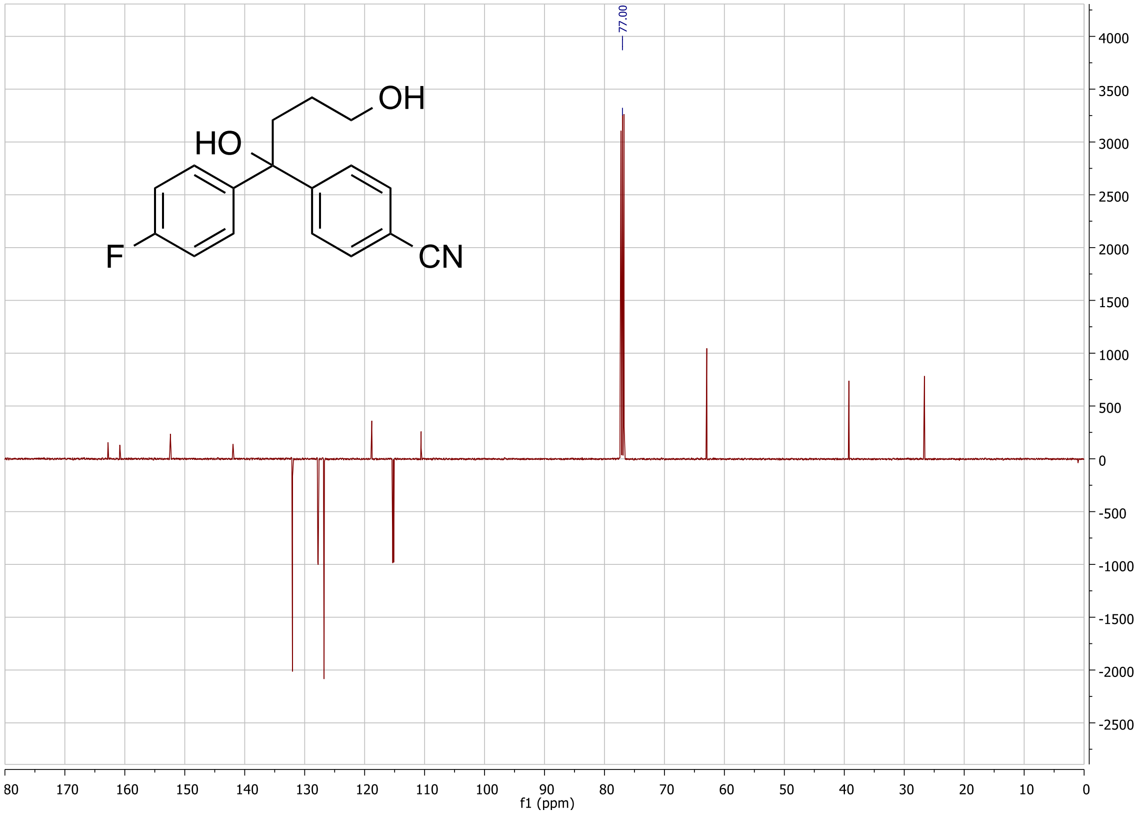
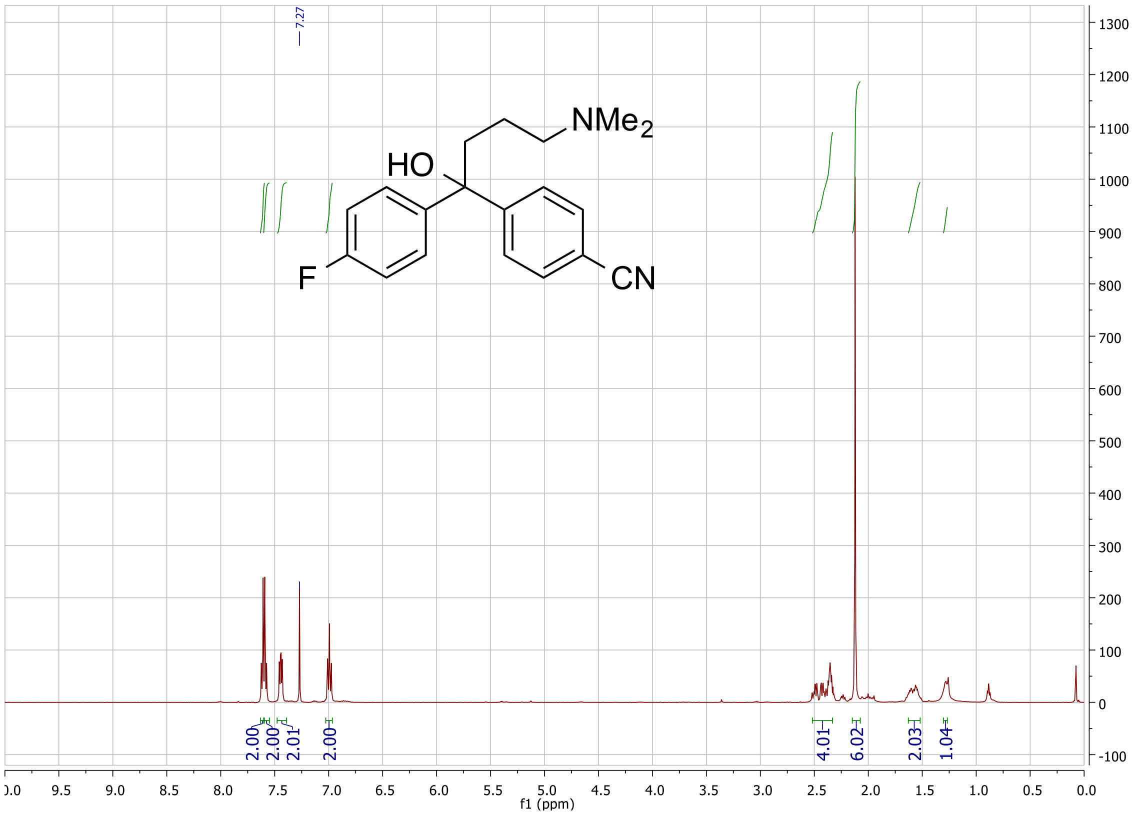
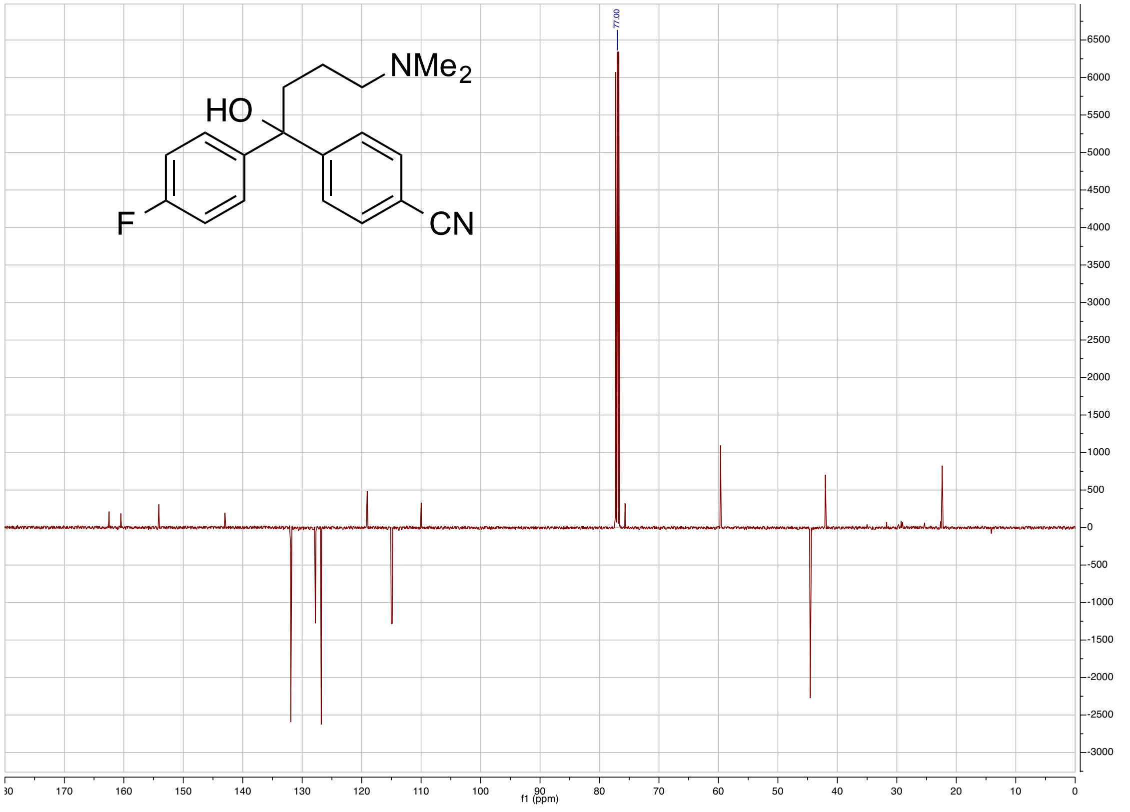
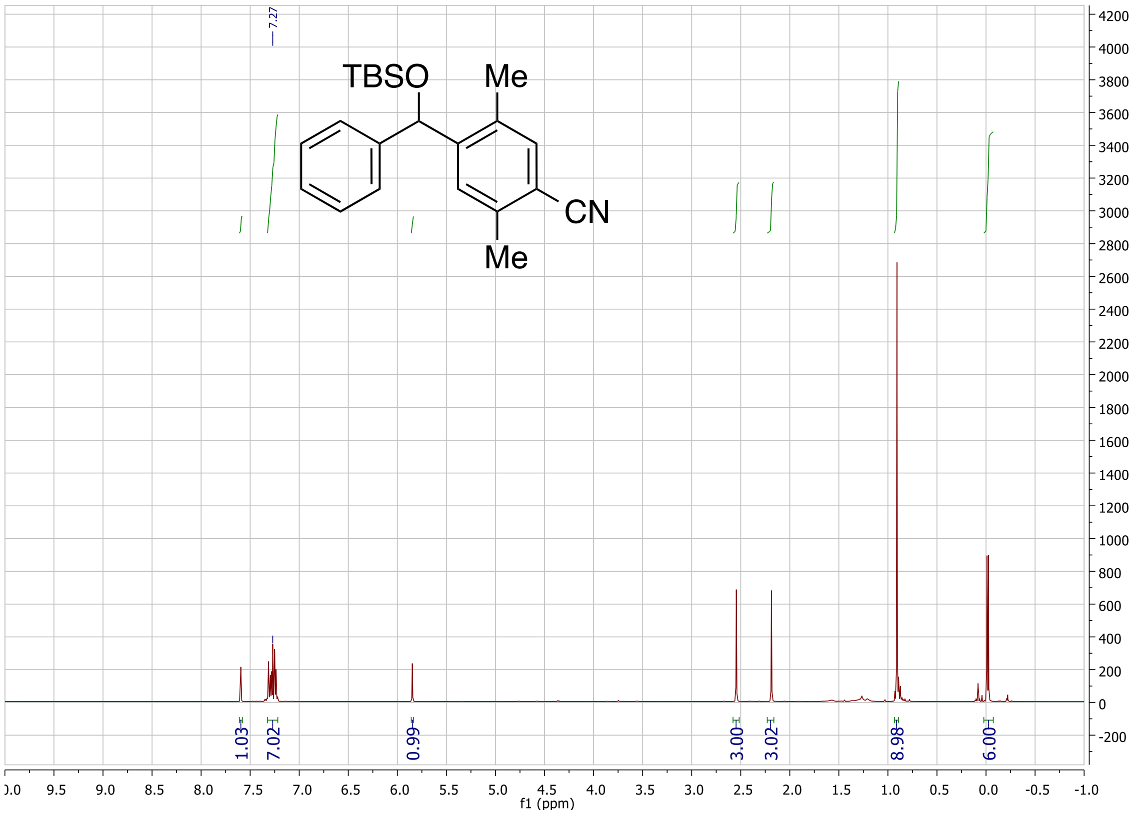
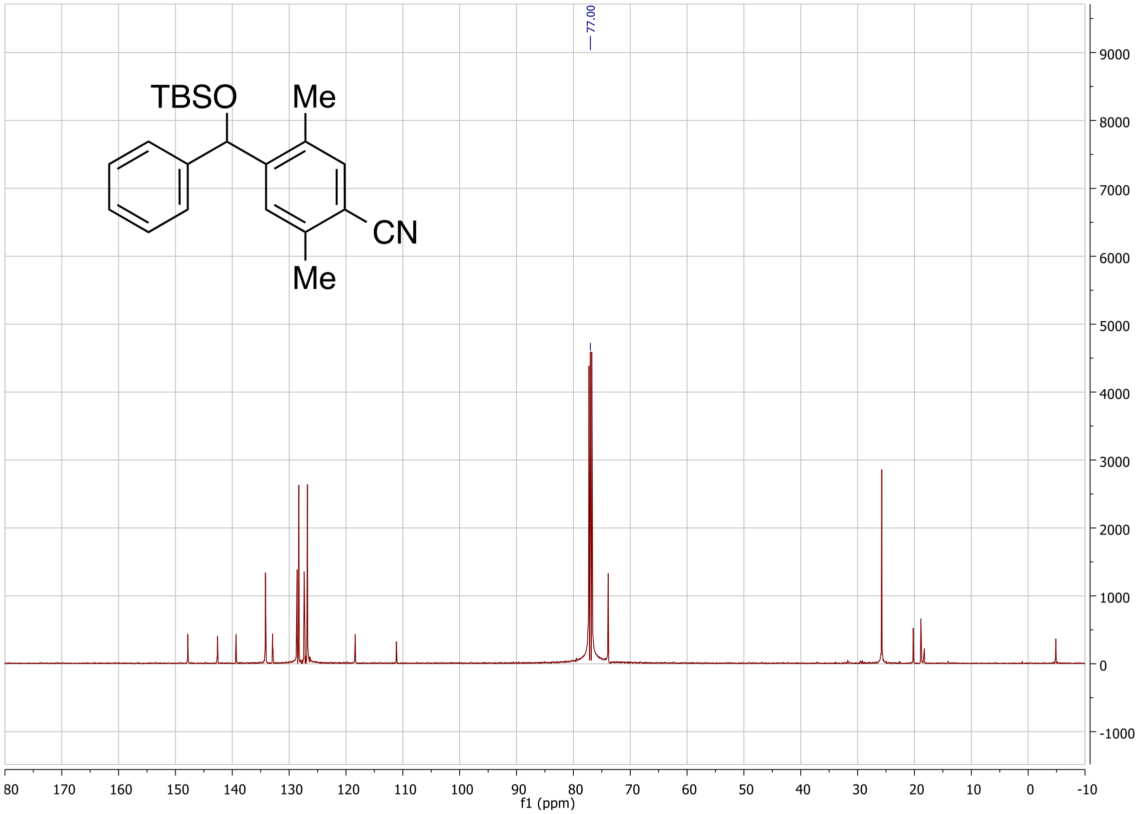
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

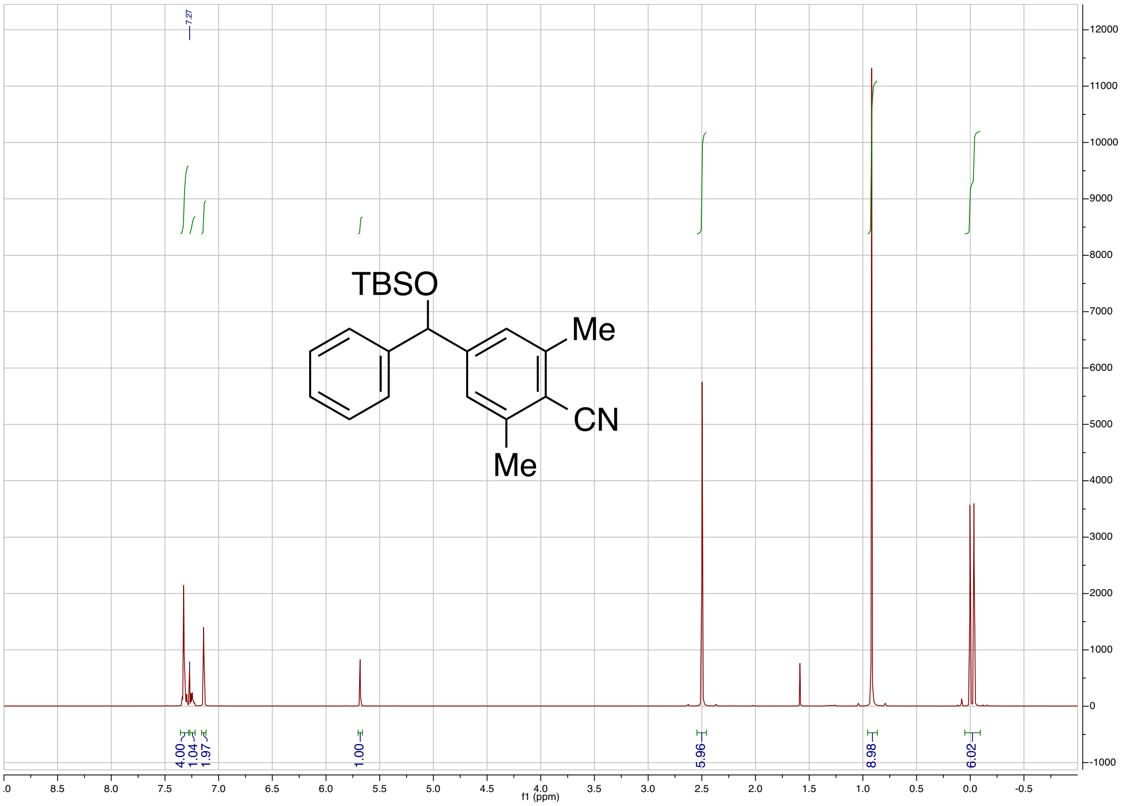

77.00
OH
HO
F
CN
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
-1500
-2000
-2500
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

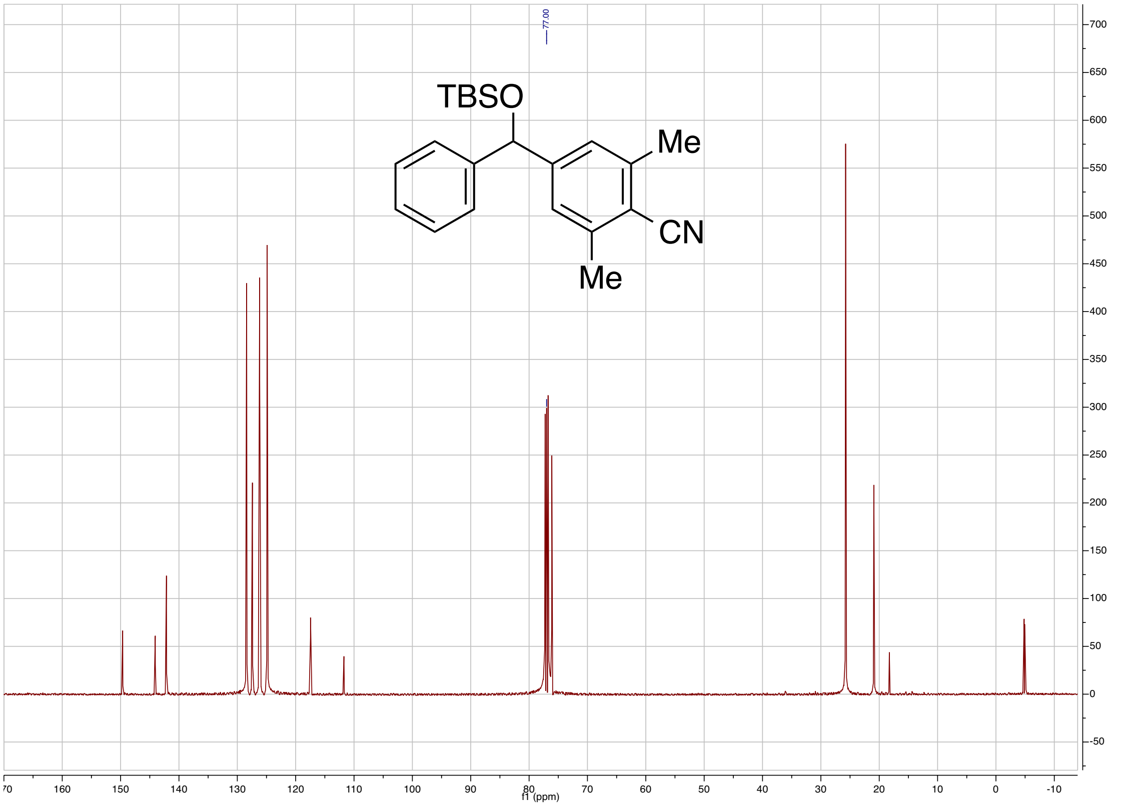

7.27
HO
NMe2
F
CN
2.00
2.00
2.01
2.00
4.01
6.02
2.03
1.04
f1 (ppm)
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

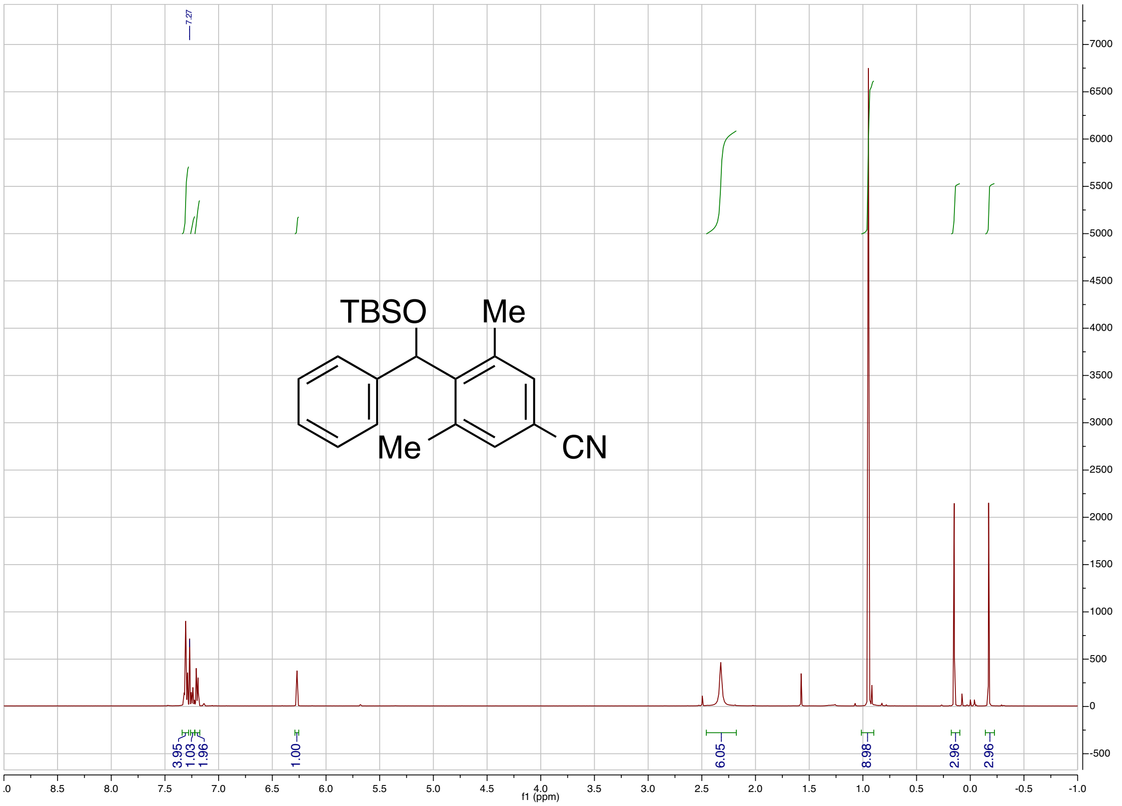

77.00
HO
NMe2
F
CN
f1 (ppm)
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
-1500
-2000
-2500
-3000

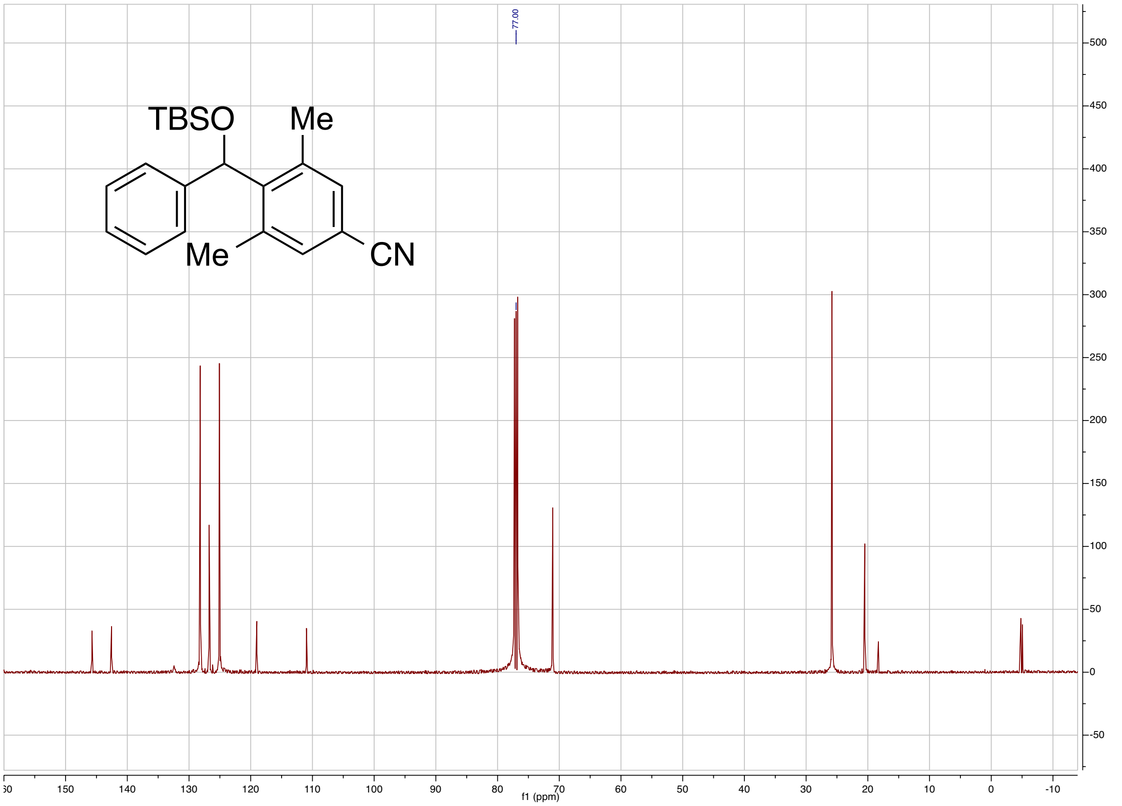

7.27
TBSO
Me
CN
Me
1.03
7.02
0.99
3.00
3.02
8.98
6.00
f1 (ppm)

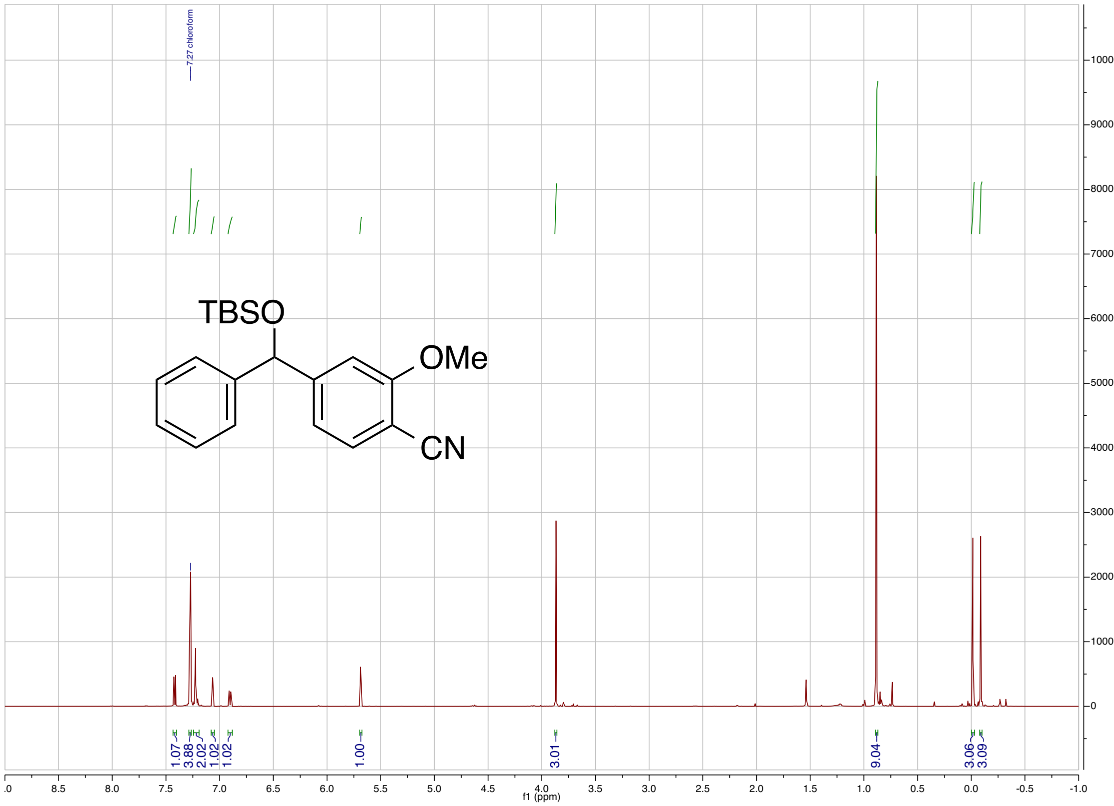

77.00
TBSO
Me
CN
Me
f1 (ppm)

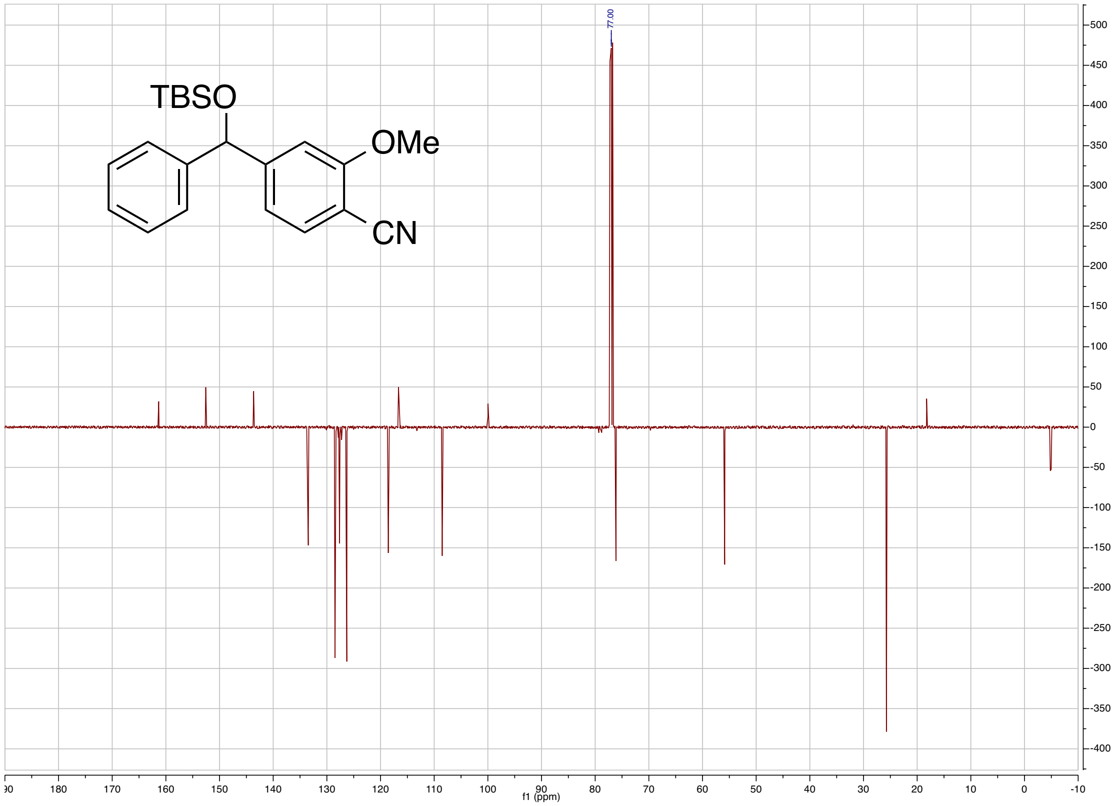

7.27
TBSO
Me
CN
Me
4.00
1.04
1.97
1.00
5.96
8.98
6.02
f1 (ppm)

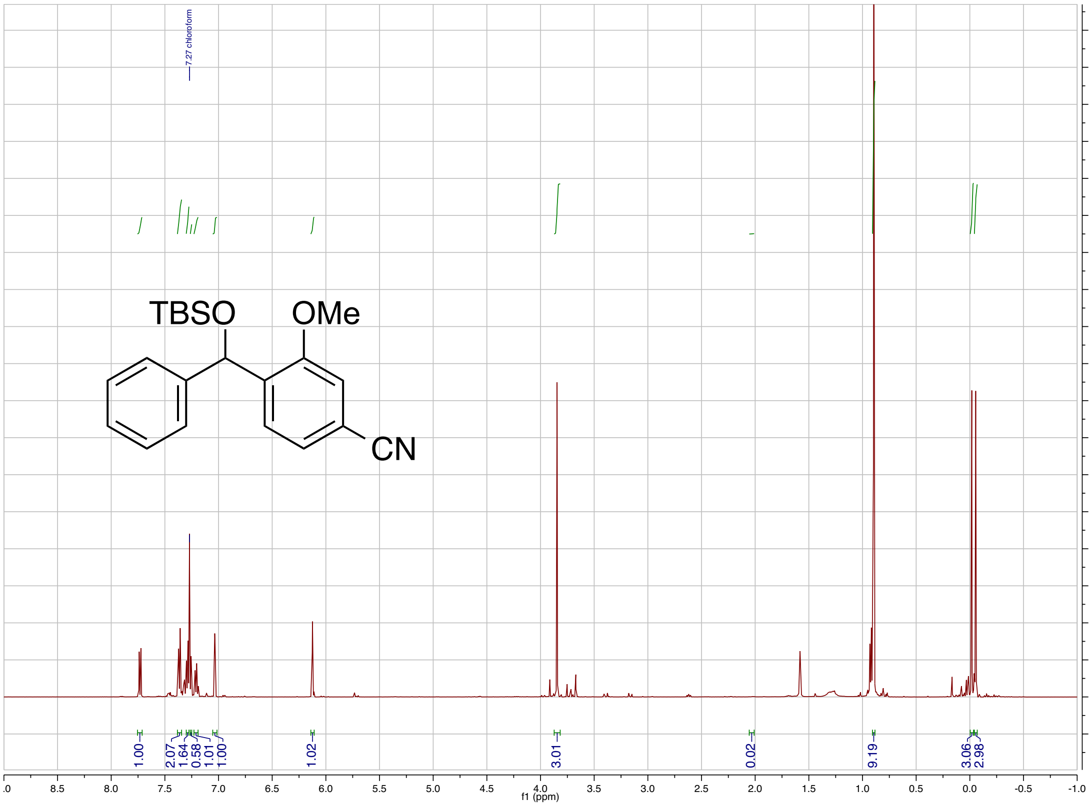

77.00
TBSO
Me
CN
Me
f1 (ppm)

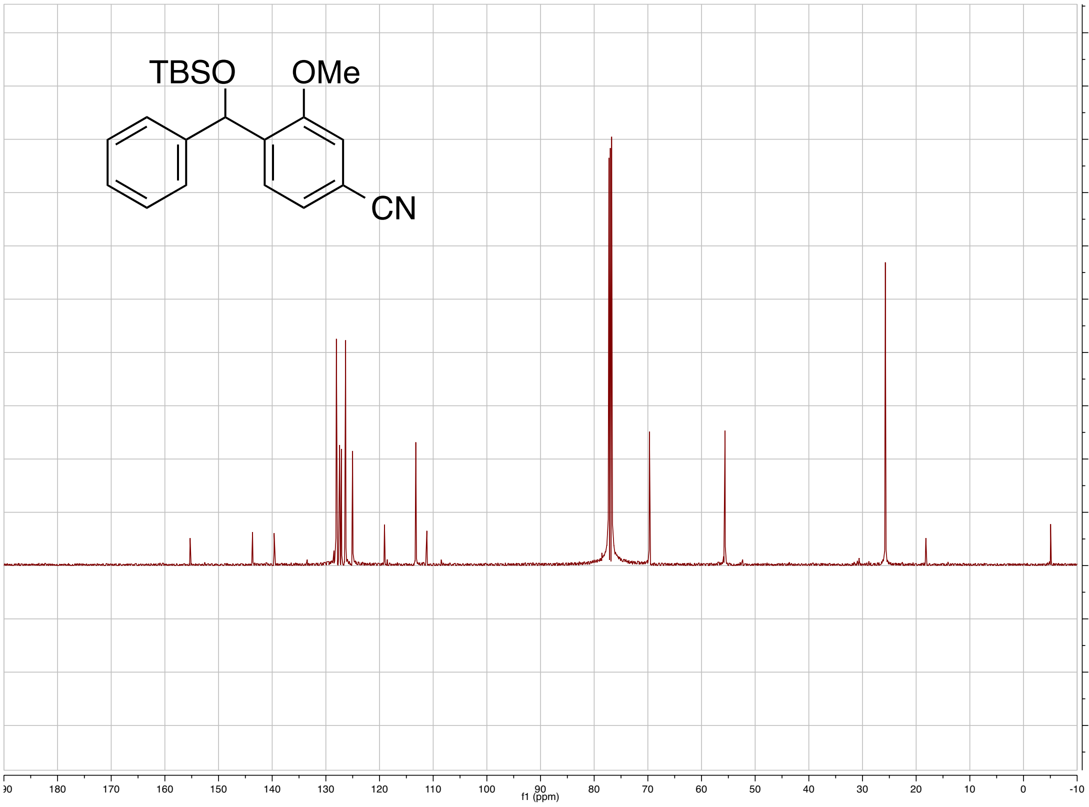

7.27
TBSO
Me
Me
CN
3.95
1.03
1.96
1.00
6.05
8.98
2.96
2.96
f1 (ppm)
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

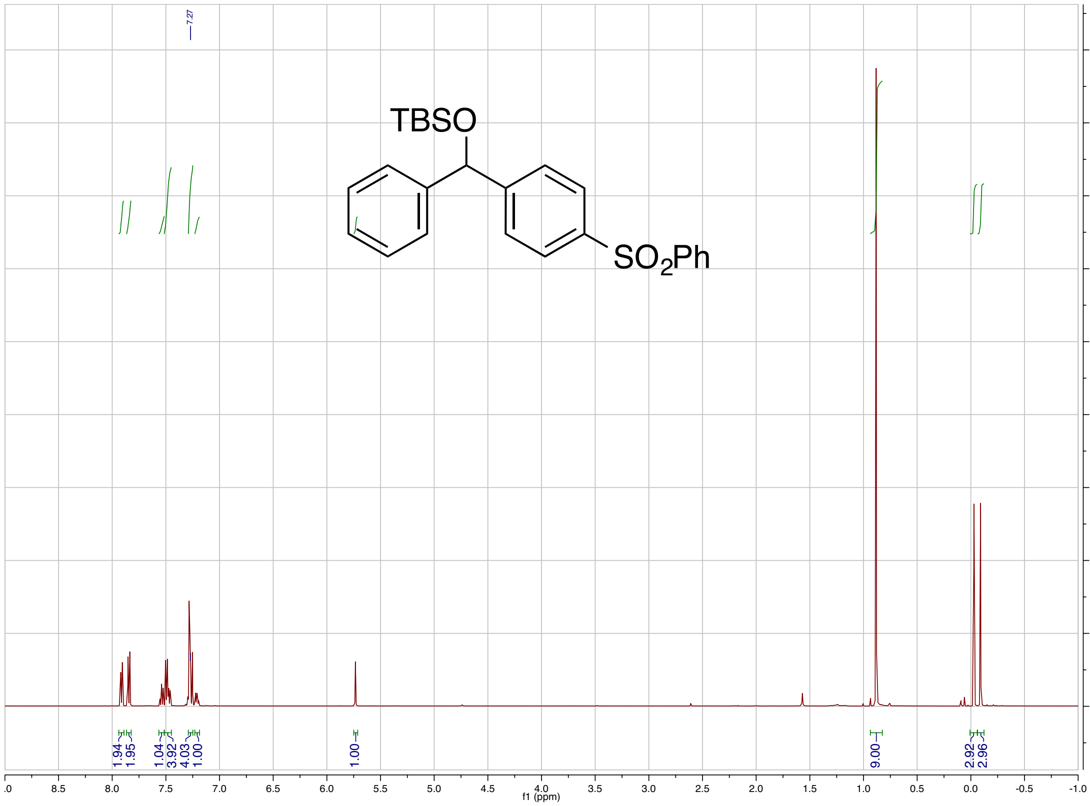

77.00
TBSO
Me
Me
CN
f1 (ppm)
500
450
400
350
300
250
200
150
100
50
0
-50
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

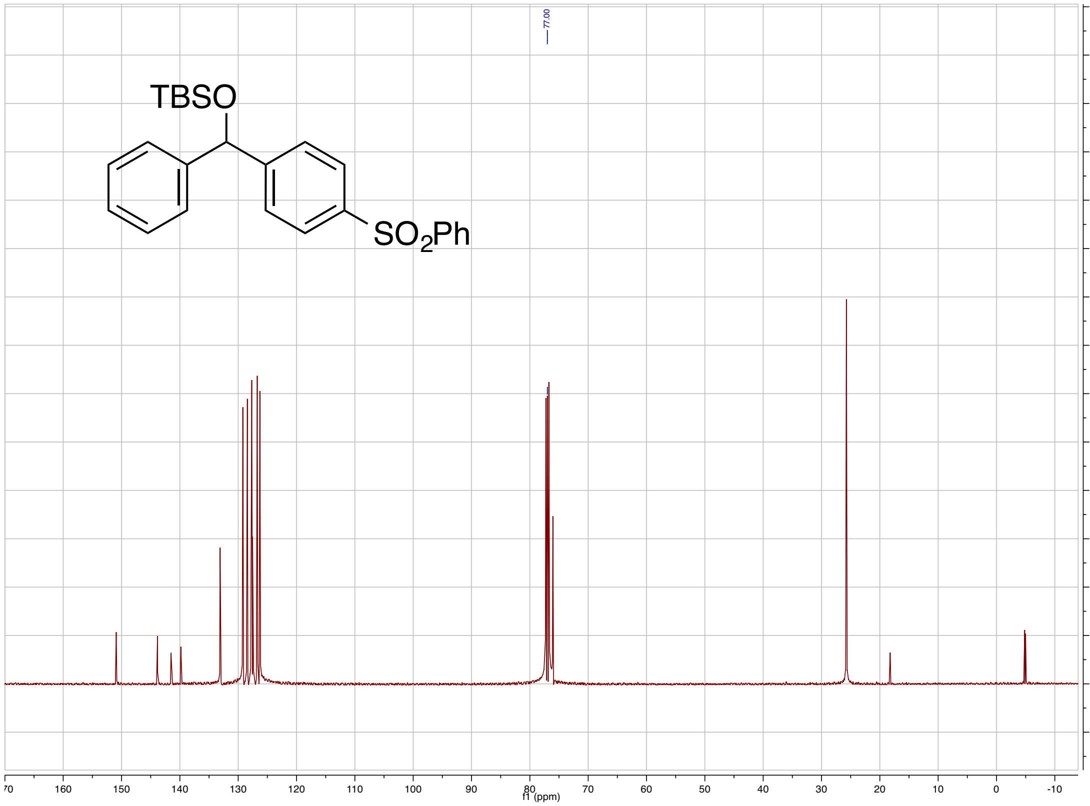

7.27 chloroform
TBSO
OMe
CN
1.07
3.88
2.02
1.02
1.02
1.00
3.01
9.04
3.06
3.09
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

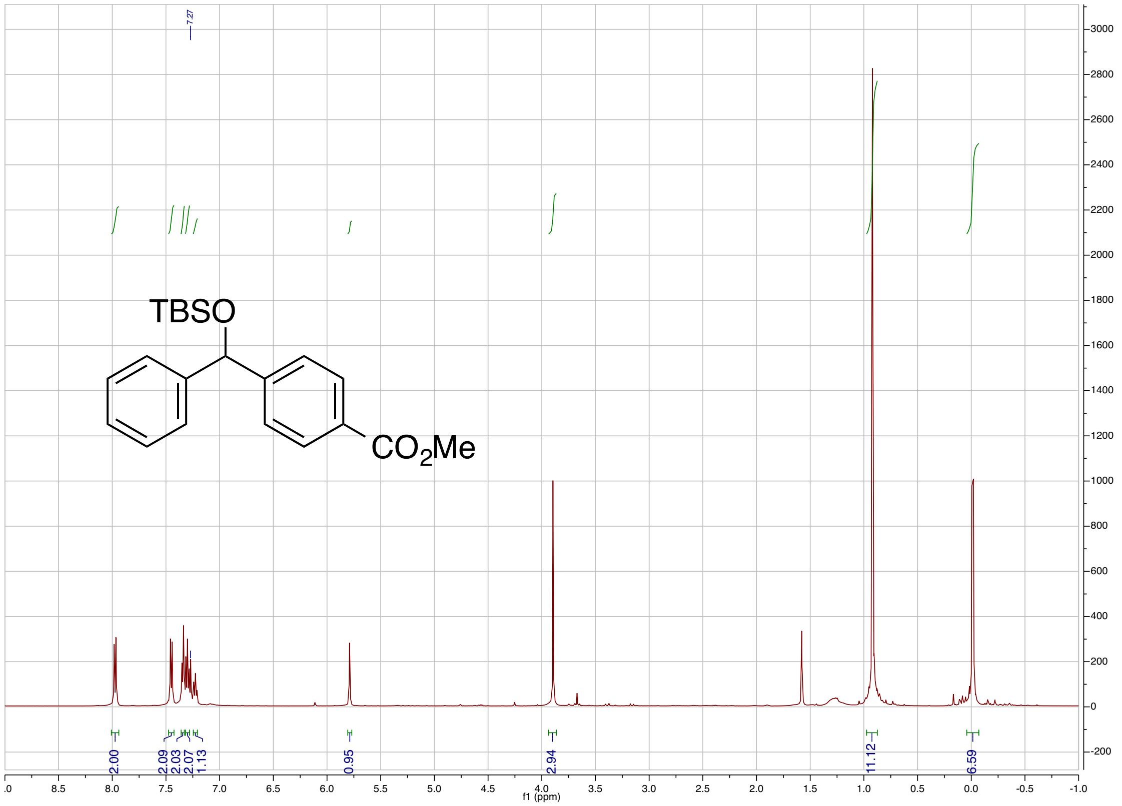

77.00
TBSO
OMe
CN
500
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

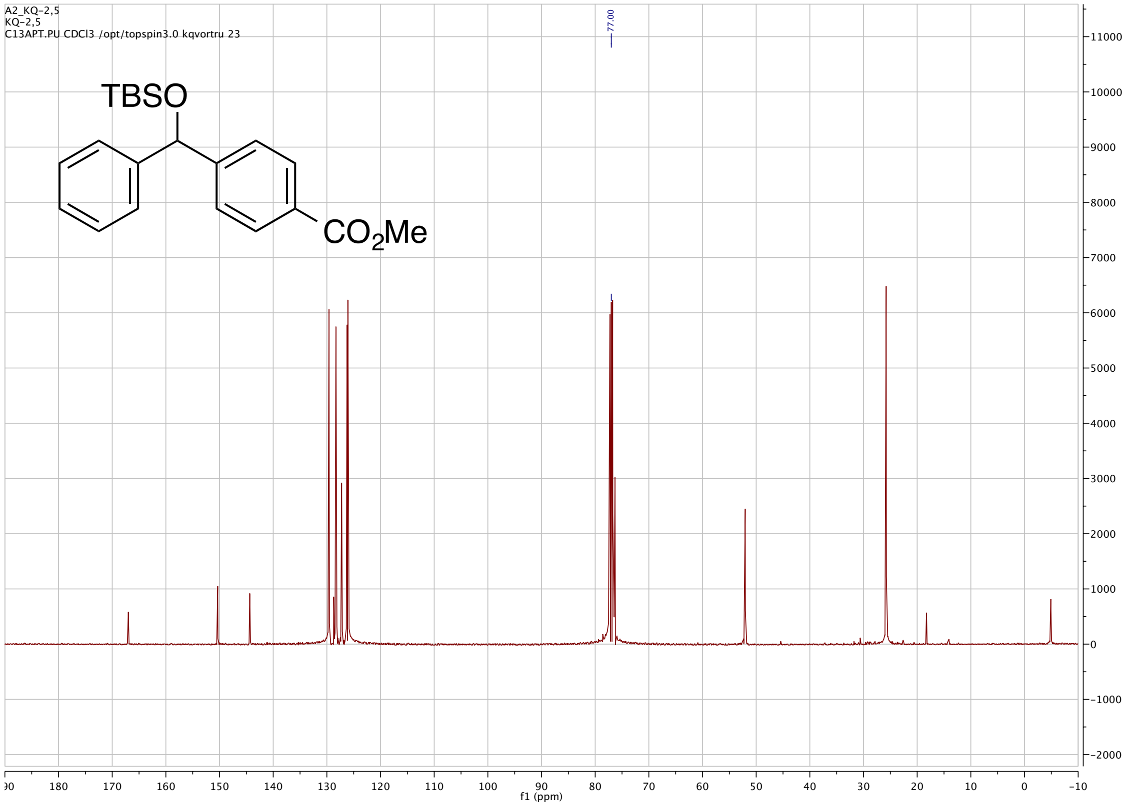

7.27 chloroform
TBSO
OMe
CN
1.00
2.07
1.64
0.58
1.01
1.00
1.02
3.01
0.02
9.19
3.06
2.98
f1 (ppm)
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

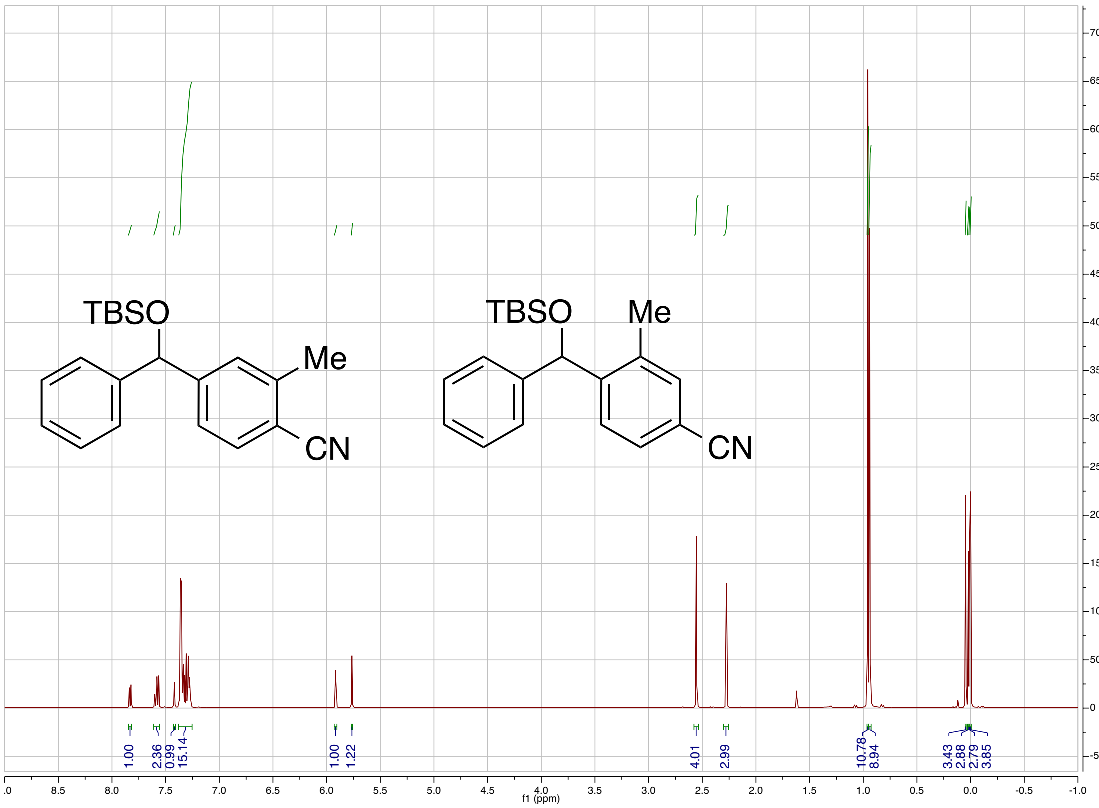

TBSO
OMe
CN
f1 (ppm)
500
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

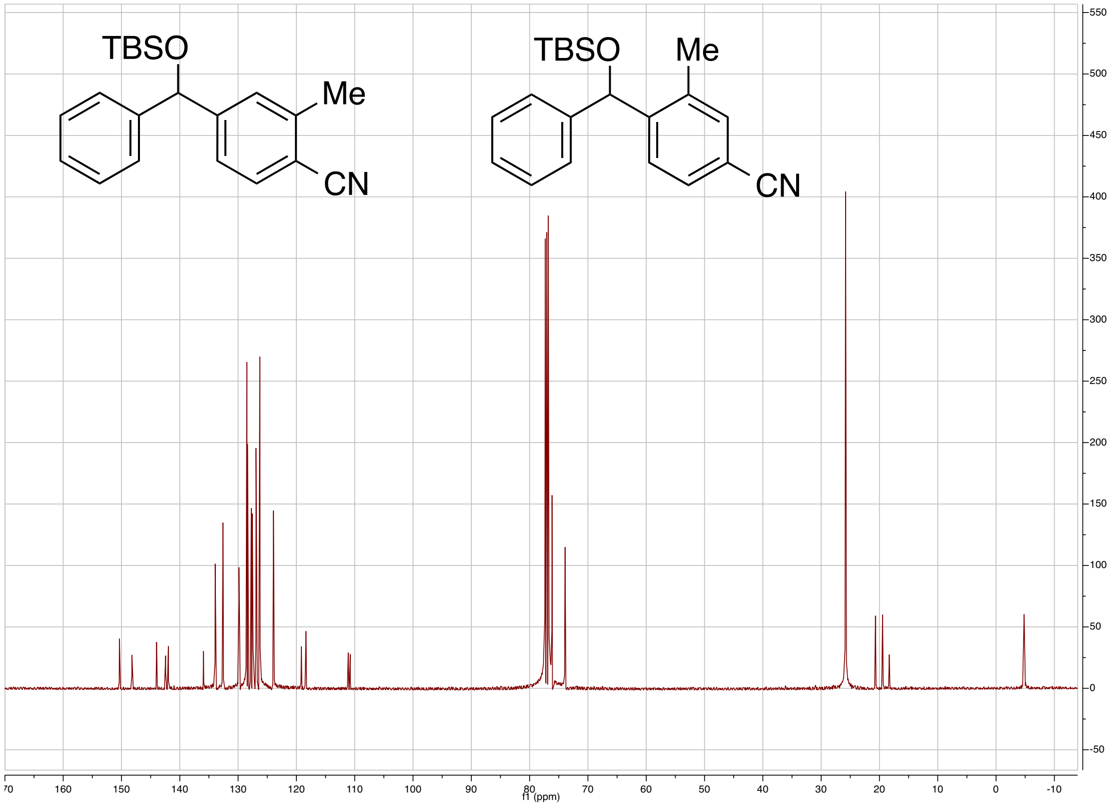

7.27
TBSO
SO2Ph
1.94
1.95
1.04
3.92
4.03
1.00
1.00
9.00
2.92
2.96
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

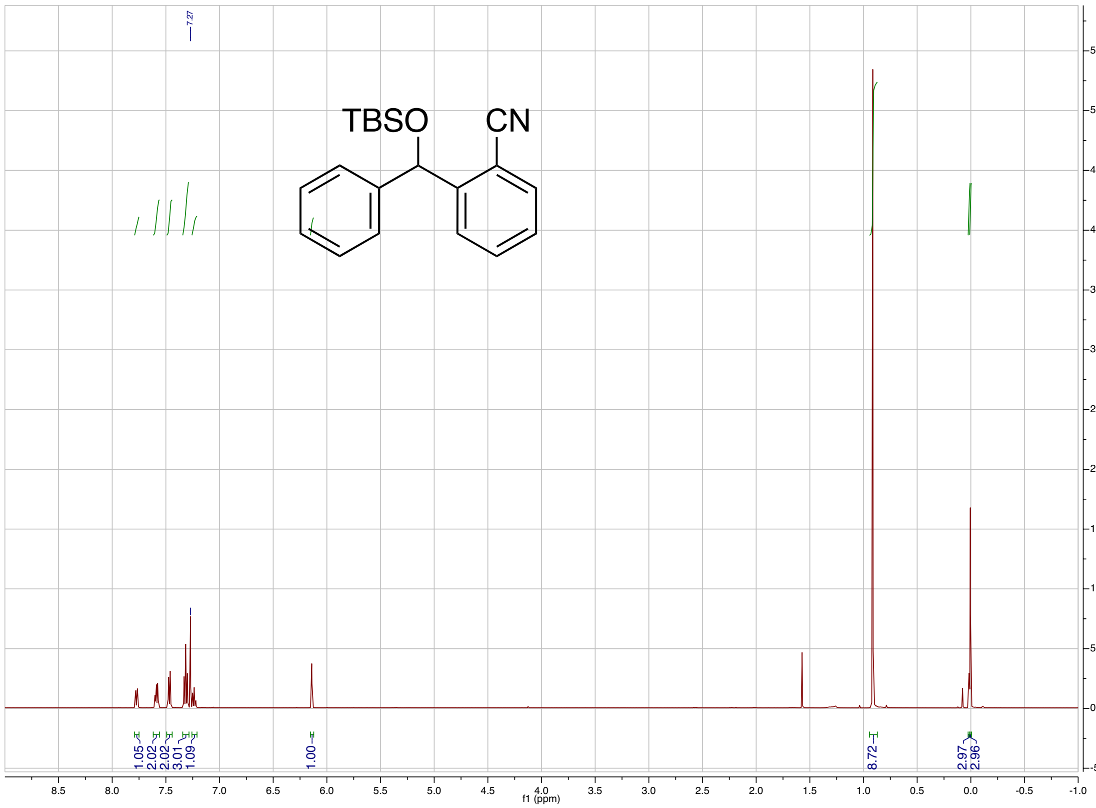

77.00
TBSO
SO2Ph
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

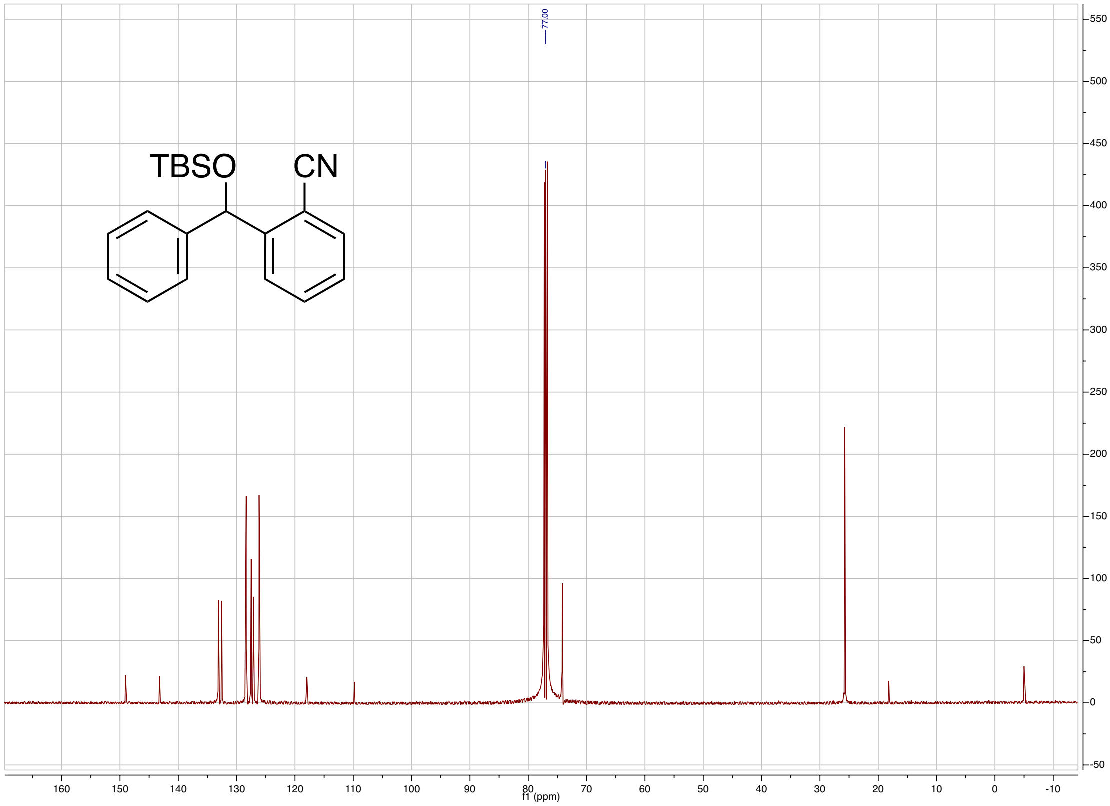

7.27
TBSO
CO2Me
2.00
2.09
2.03
2.07
1.13
0.95
2.94
11.12
6.59
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

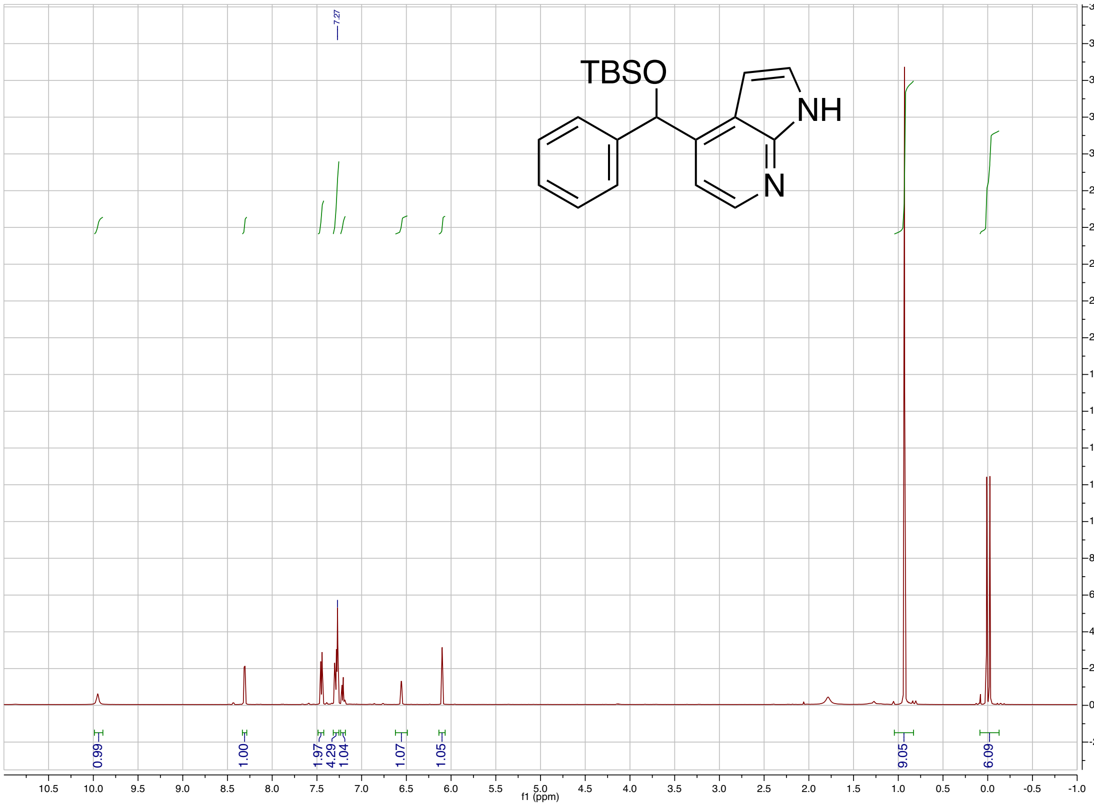

A2_KQ-2,5
KQ-2,5
C13APT.PU CDCl3 /opt/topspin3.0 kqvortru 23
77.00
TBSO
CO2Me
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000

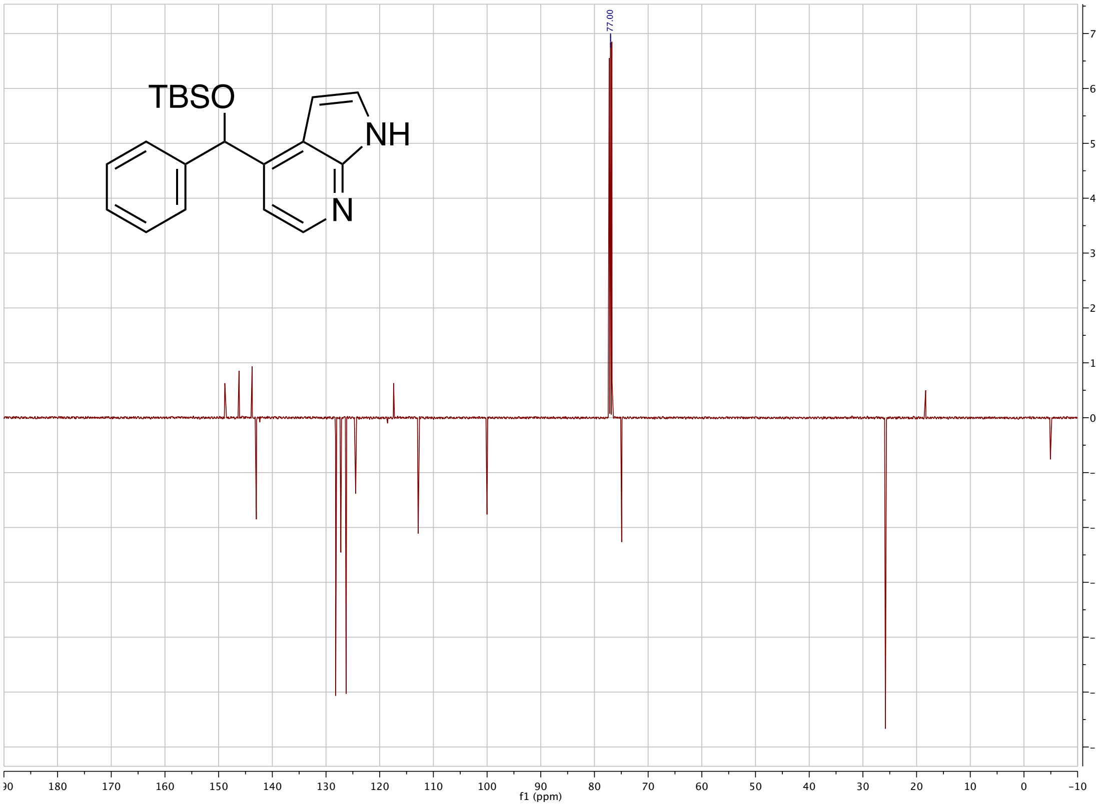

TBSO
Me
CN
TBSO
Me
CN
1.00
2.36
0.99
15.14
1.00
1.22
4.01
2.99
10.78
8.94
3.43
2.88
2.79
3.85
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

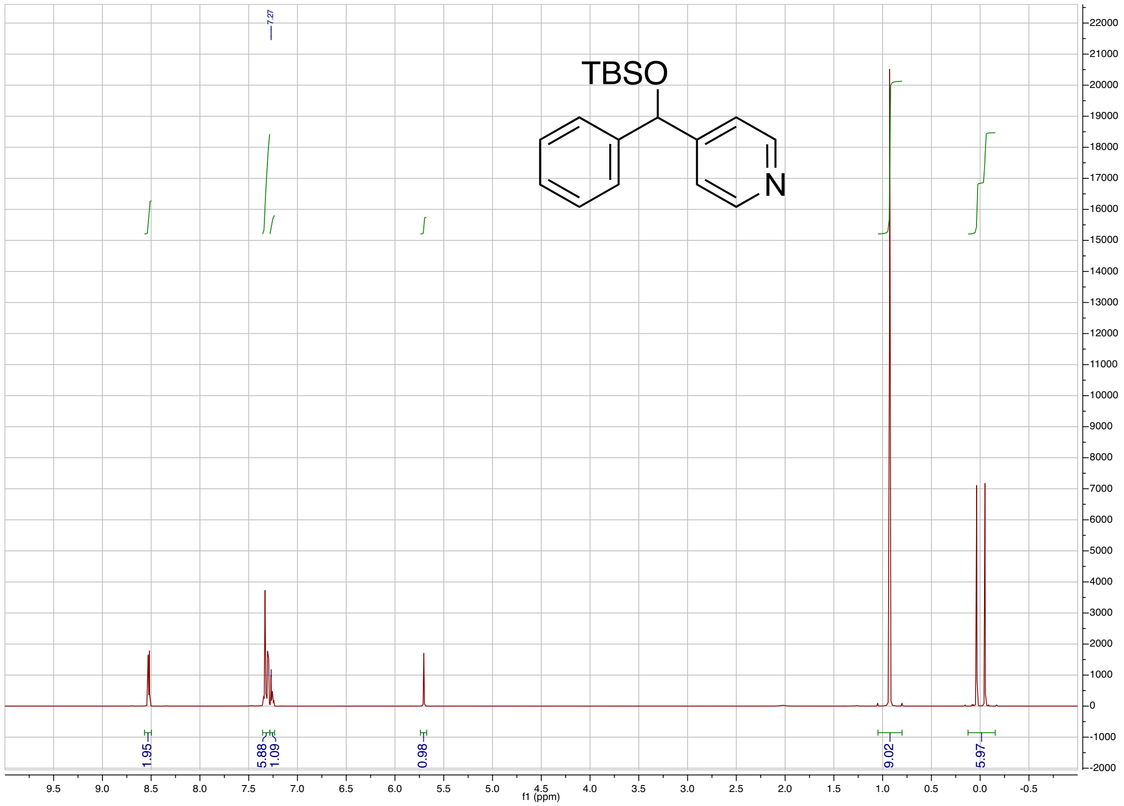

TBSO
Me
CN
TBSO
Me
CN
550
500
450
400
350
300
250
200
150
100
50
0
-50
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

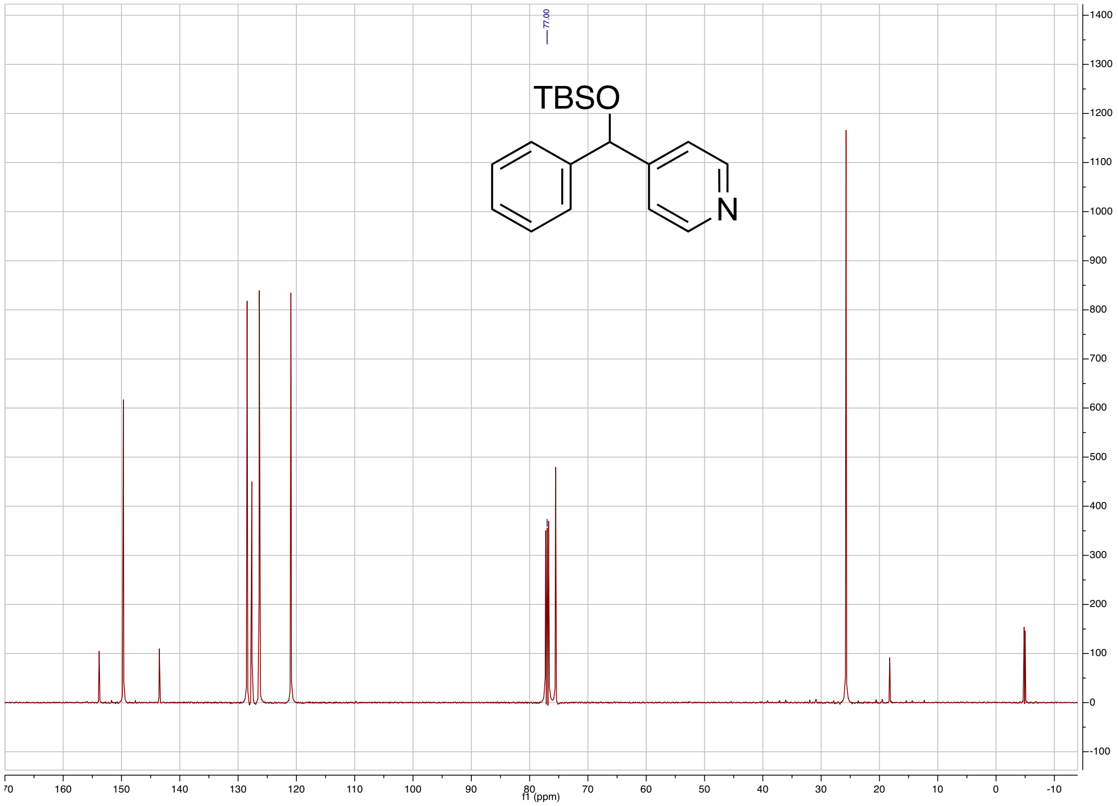

7.27
TBSO
CN
1.05
2.02
2.02
3.01
1.09
1.00
8.72
2.97
2.96
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

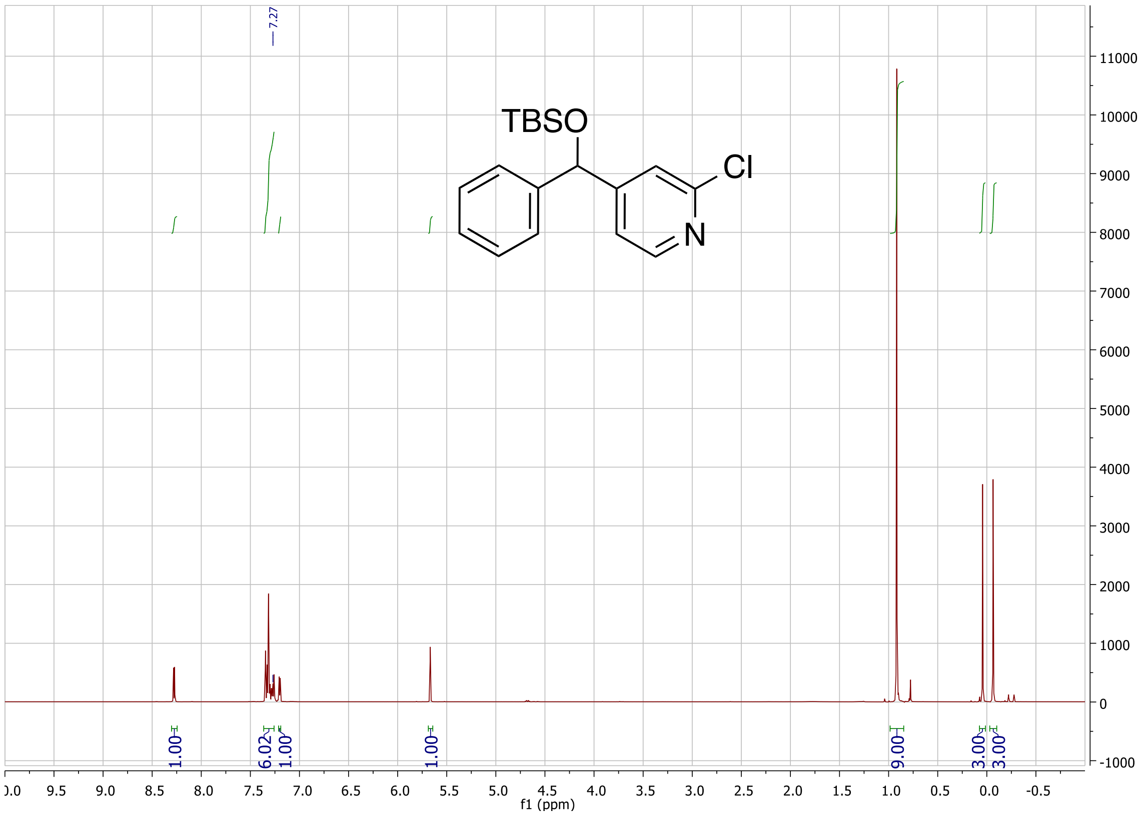

77.00
TBSO
CN
550
500
450
400
350
300
250
200
150
100
50
0
-50
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

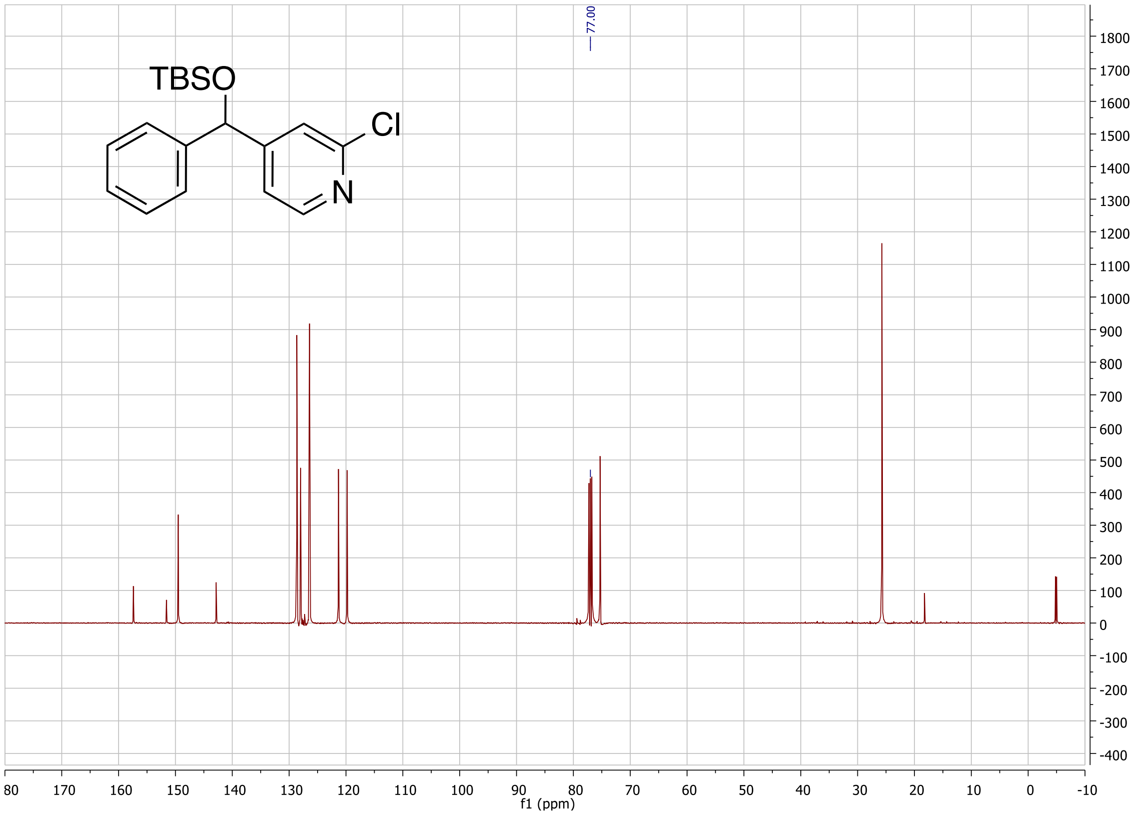

7.27
TBSO
NH
N
0.99
1.00
1.97
4.29
1.04
1.07
1.05
9.05
6.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200

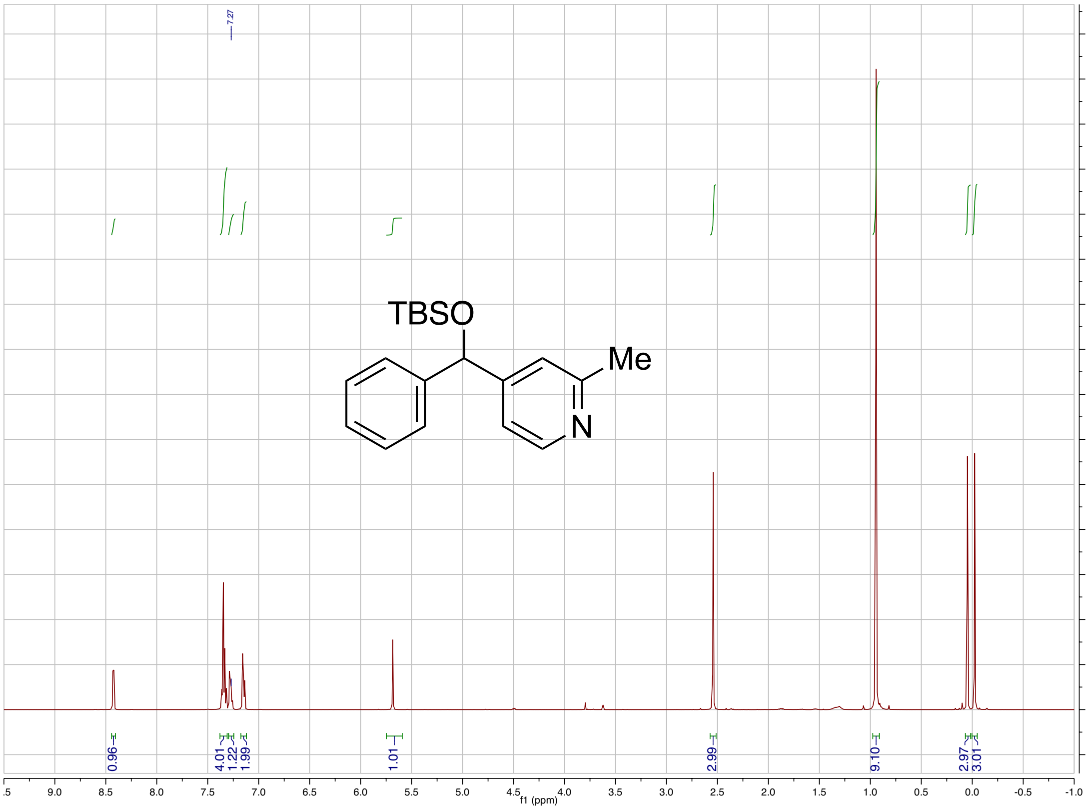

77.00
TBSO
NH
N
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)
7000 6000 5000 4000 3000 2000 1000 0 −1000 −2000 −3000 −4000 −5000 −6000

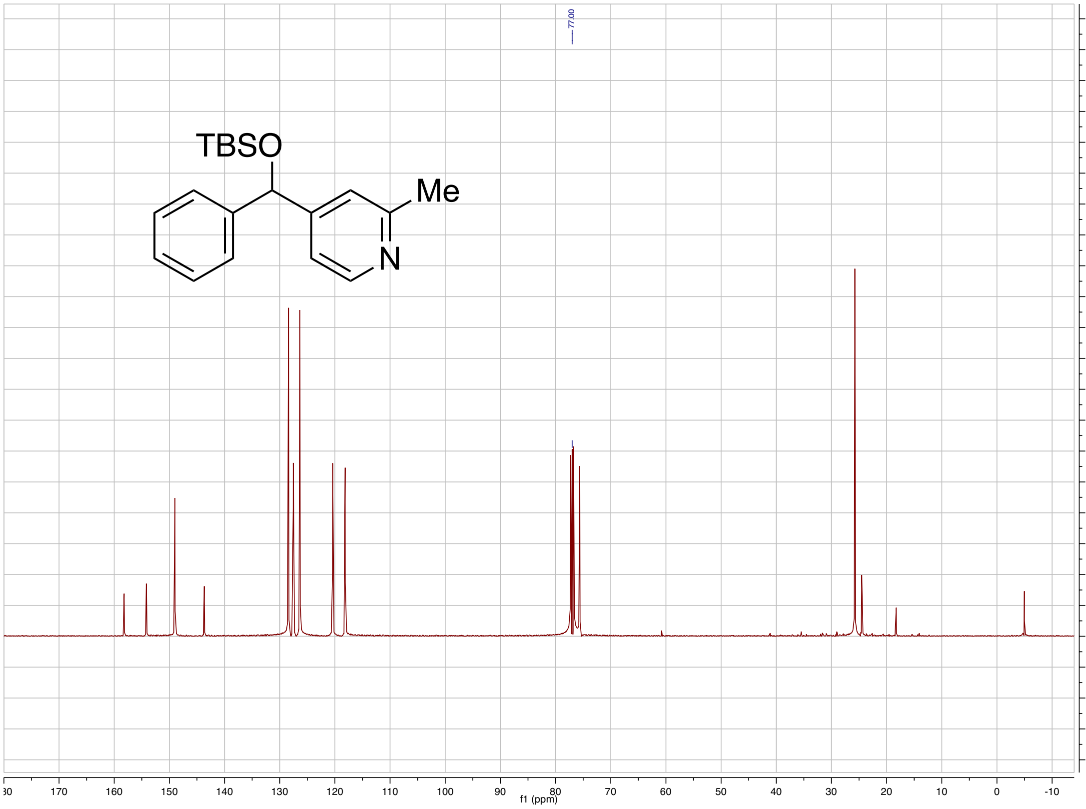

7.27
TBSO
N
1.95
5.88
1.09
0.98
9.02
5.97
f1 (ppm)

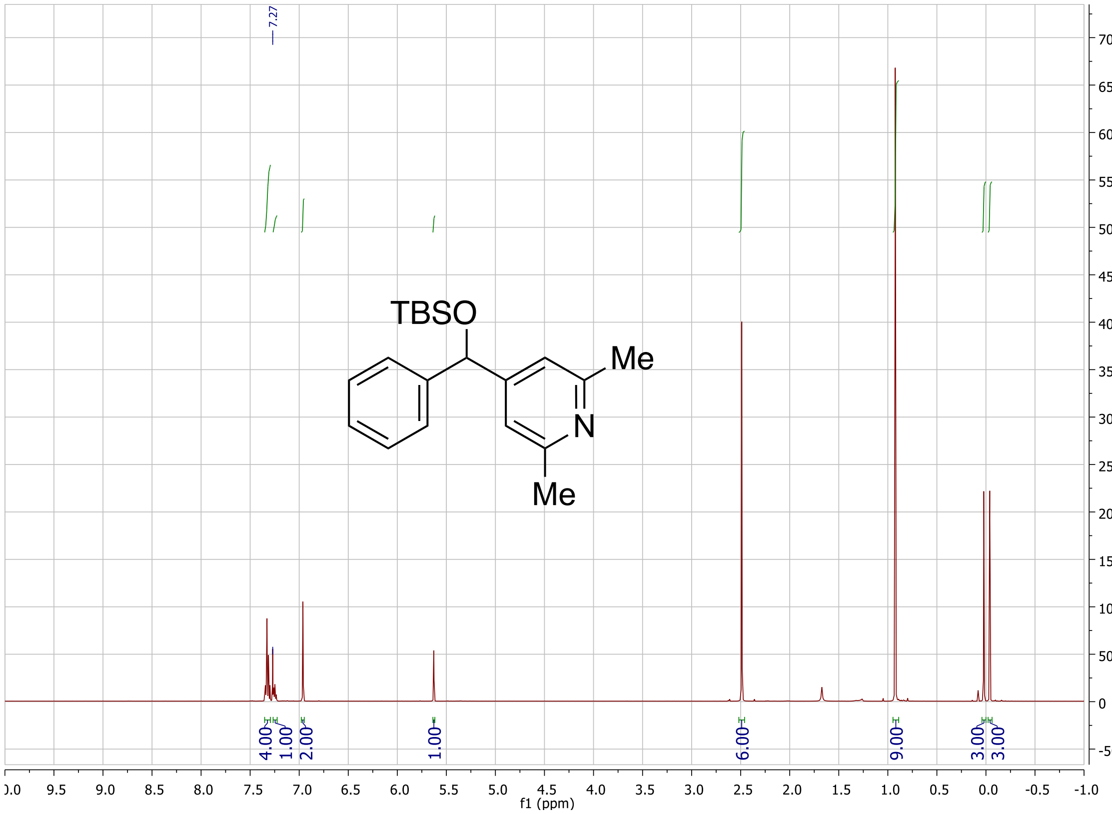

77.00
TBSO
N
f1 (ppm)

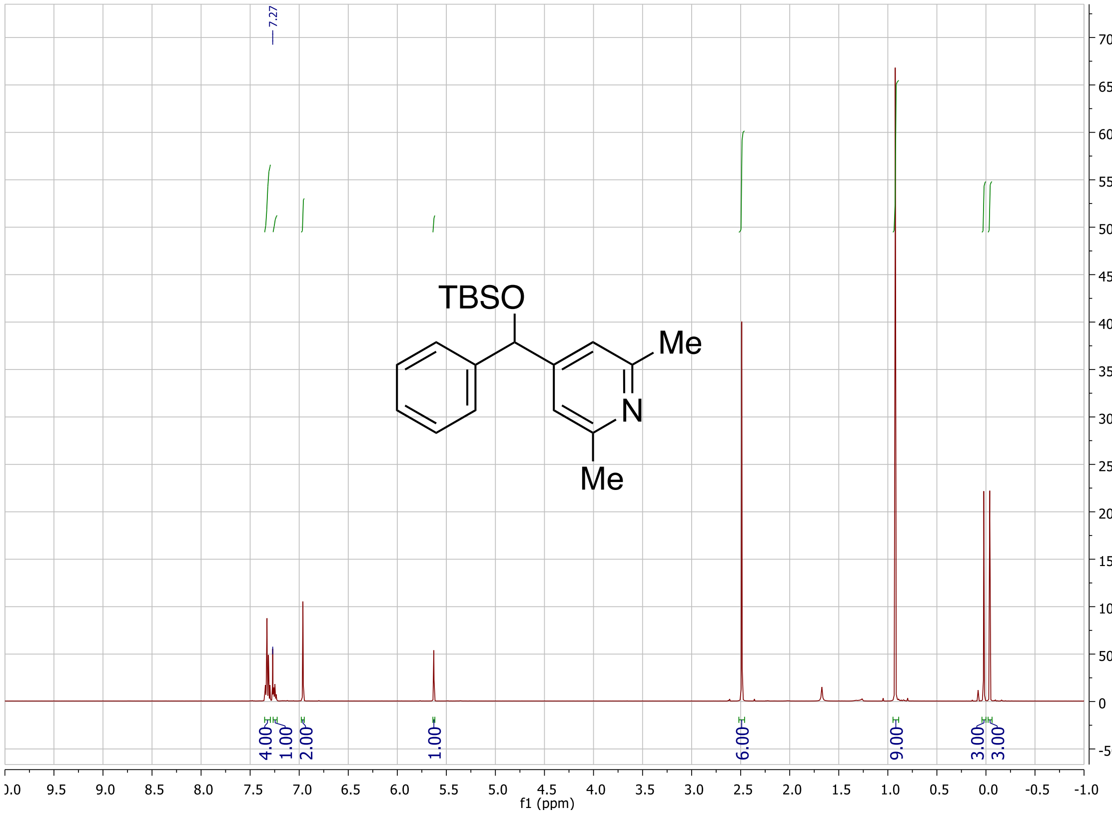

7.27
TBSO
Cl
N
1.00
6.02
1.00
1.00
9.00
3.00
3.00
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

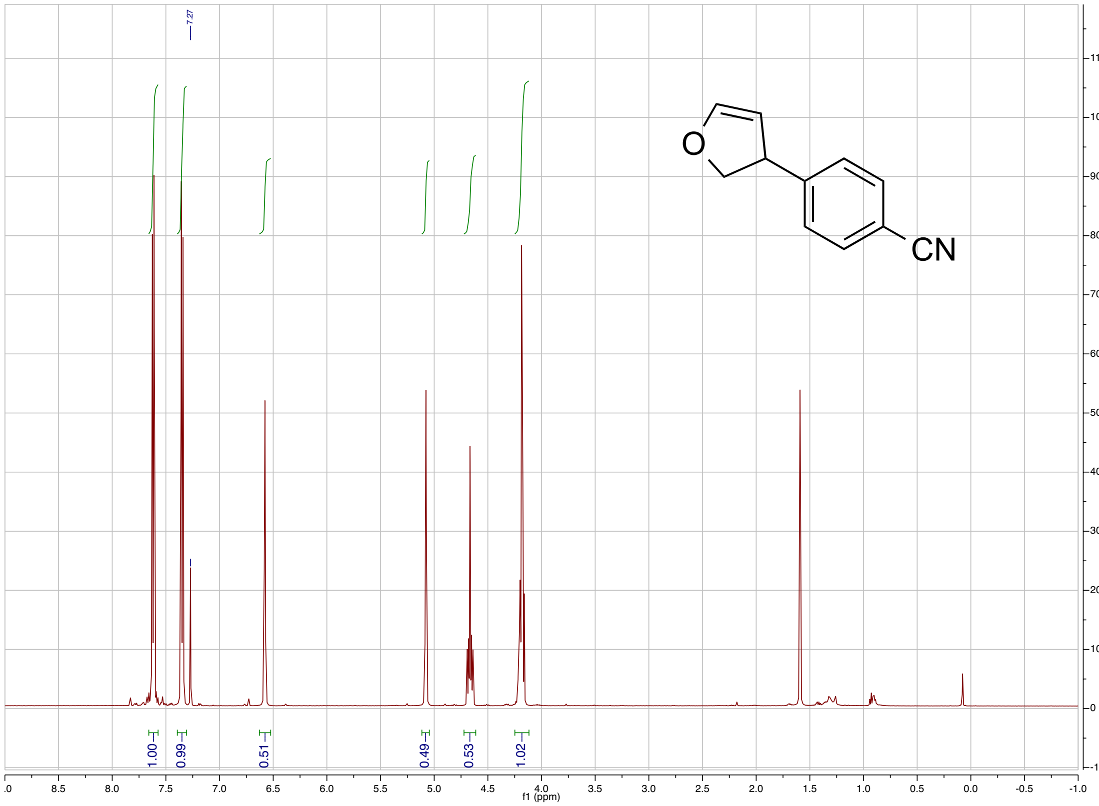

77.00
TBSO
Cl
N
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
-300
-400
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

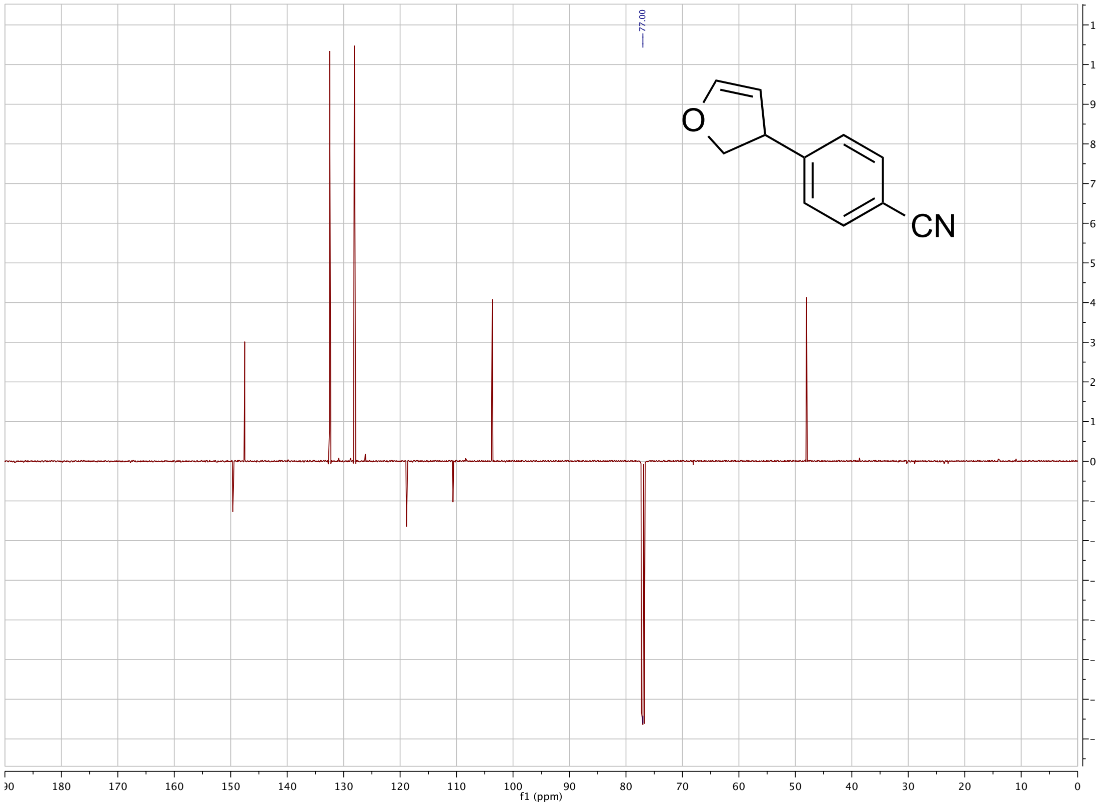

7.27
TBSO
Me
N
0.96
4.01
1.22
1.99
1.01
2.99
9.10
2.97
3.01
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500


77.00
TBSO
Me
N
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
-4000


7.27
TBSO
Me
N
Me
4.00
1.00
2.00
1.00
6.00
9.00
3.00
3.00
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10.0
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
0.0
-0.5
-1.0
f1 (ppm)


7.27
TBSO
Me
N
Me
4.00
1.00
2.00
1.00
6.00
9.00
3.00
3.00
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10.0
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
0.0
-0.5
-1.0
f1 (ppm)


7.27
1.00
0.99
0.51
0.49
0.53
1.02
f1 (ppm)
O
CN
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
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
0.0
-0.5
-1.0


77.00
f1 (ppm)
O
CN
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10000
9000
8000
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6000
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3000
2000
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-4000
-5000
-6000
-7000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0