Supporting Information for

Cyanation of Arenes via Iridium-Catalyzed Borylation

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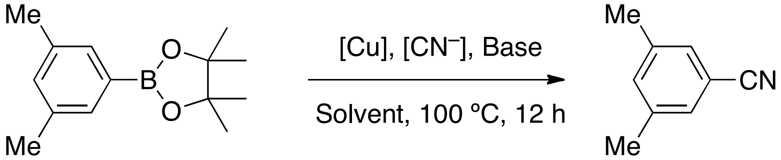
General Experimental Details

All borylation reactions were conducted under a nitrogen atmosphere in an Innovative Technologies drybox. The cyanation reactions were conducted under an atmosphere of air in 20 mL vials sealed with Teflon-lined caps. All other reactions were conducted under a nitrogen atmosphere unless otherwise noted. Borylation reactions were performed using THF that was degassed by purging with argon for 45 min and then dried with a solvent purification system using a 1 m column containing activated alumina. For the conversion of arylboronic acids and esters to aryl nitriles, distilled water and ACS reagent grade methanol was used as received. $[Ir(cod)OMe]_2$ was obtained from Johnson-Matthey and used as received. 4,4'-di-*tert*-butylbipyridine was obtained from Sigma-Aldrich Chemicals and used as received. B_2pin_2 was obtained from Allychem and used as received. Arenes were purchased from Sigma-Aldrich and used as received. Arylboronic acids were purchased from Sigma-Aldrich or Combi-Blocks and used as received. $Cu(NO_3)_2•3H_2O$ (99.5%) was purchased from Strem chemicals. $Zn(CN)_2$ (98%) and CsF were purchased from Sigma-Aldrich and used as received. $LiAlH_4$, DIBAL-H, NaN_3, KOH, *t*-BuOH, MeMgBr, and $ZnBr_2$ were purchased from Sigma-Aldrich and were used as received. The methoxymethyl-protected phenols were prepared by reaction of meta-cresol or 2,6-dimethylphenol with NaH and chloromethyl methyl ether in THF by a known procedure.[1]

Flash column chromatography was performed on Silicylce Siala-P silica gel or on a Teledyne Isco CombiFlash Rf automated chromatography system with 4 g RediSep Rf Gold normal-phase silica columns. Products were visualized on TLC plates by UV (254 nm) or by staining with $KMnO_4$. GC-MS data were obtained on an Agilent 6890-N GC system containing an Alltech EC-1 capillary column and an Agilent 5973 mass selective detector. NMR spectra were acquired on a 400 MHz Varian Unity instrument or on 500 MHz Varian Unity or Inova instruments at the University of Illinois VOICE NMR facility. Chemical shifts are reported in ppm relative to a residual solvent peak ($CDCl_3$ = 7.26 ppm for ^1H and 77.23 ppm for ^{13}C; $(CD_3)_2CO$ = 2.05 for ^1H and 29.8 for ^{13}C). Elemental analyses were conducted by the University of Illinois at Urbana-Champaign Microanalysis Laboratory or Robertson Microlit Laboratories (Madison, NJ, USA).

Table 3. Effect of Reaction Conditions on Yields

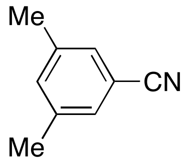


Entry	[Cu]	[CN⁻]	Base	Solvent	Yield (%)[1]
1	$Cu(OAc)_2$	$Zn(CN)_2$	KOH	$MeOH/H_2O$	8
2	$Cu(OAc)_2$	$Zn(CN)_2$	CsF	$MeOH/H_2O$	0
3	$Cu(OAc)_2$	$Zn(CN)_2$	KOH	DMF/H_2O	33
4	CuCN	$Zn(CN)_2$	CsF	$MeOH/H_2O$	0
5	CuBr	$Zn(CN)_2$	CsF	$MeOH/H_2O$	0
6	$CuSO_4$	$Zn(CN)_2$	KOH	DMF/H_2O	32
7	$Cu(NO_3)_2$	$Zn(CN)_2$	CsF	$MeOH/H_2O$	64
8	$Cu(NO_3)_2$	$K_4[Fe(CN)_6]$	CsF	$MeOH/H_2O$	<5
9	$Cu(NO_3)_2$	$(CH_3)_2C(OH)CN$	CsF	$MeOH/H_2O$	67
10	$Cu(NO_3)_2$	CuCN	CsF	$MeOH/H_2O$	0
11	$Cu(NO_3)_2$	Tosyl Cyanide	CsF	$MeOH/H_2O$	0
12	$Cu(NO_3)_2$	NaCN	CsF	$MeOH/H_2O$	<5
13	$Cu(NO_3)_2$	$Zn(CN)_2$	KOH	$MeOH/H_2O$	60
14	$Cu(NO_3)_2$	$Zn(CN)_2$	K_3PO_4	$MeOH/H_2O$	22
15	$Cu(NO_3)_2$	$Zn(CN)_2$	K_2CO_3	$MeOH/H_2O$	56
16	$Cu(NO_3)_2$	$Zn(CN)_2$	KF	$MeOH/H_2O$	41
17	$Cu(NO_3)_2$	$Zn(CN)_2$	No Base	$MeOH/H_2O$	0
18	$Cu(NO_3)_2$	$Zn(CN)_2$	CsF	DMF/H_2O	55
19	$Cu(NO_3)_2$	$Zn(CN)_2$	CsF	$DMSO/H_2O$	53
20	$Cu(NO_3)_2$	$Zn(CN)_2$	CsF	MeOH	54
21	$Cu(NO_3)_2$	$Zn(CN)_2$	CsF	t-BuOH/H_2O	43

[1] General Conditions: 0.10 mmol arylboronate ester, 1.5 equiv [Cu], 3 equiv [CN⁻], 1 equiv base, 0.5 mL solvent, 100 ºC, 12 h. Yield determined by GC analysis with dodecane as internal standard. See S-5 for general procedure.

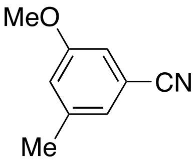
For the one-pot method, it was found that 2 equiv of copper-source was required to achieve full conversion. Also, reactions with $Zn(CN)_2$ as the cyanide source produced the benzonitrile product in higher yield (68%) than $(CH_3)_2C(OH)CN$ on 0.50 mmol scale.

General Procedure for One-pot Generation of Benzonitriles *via* C–H Borylation. In a nitrogen-filled glove box, arene (0.50 mmol), B_2pin_2 (95.3 mg, 0.375 mmol), and a stock solution of precatalyst and ligand in THF (1.0 mL) were combined in a 20 mL vial. The stock solution contained 0.33 mg $[Ir(cod)(OMe)]_2$ (0.50 μmol) 0.27 mg dtbpy (1.0 μmol) per 1 mL THF . The reaction mixture was heated in a sealed vessel at 80 °C for 16 h. The red solution was then cooled to room temperature, and the volatile materials were evaporated under reduced pressure for 2 h. The residue was then dissolved in 2.5 mL MeOH and $Cu(NO_3)_2{\bullet}3H_2O$ (242 mg, 1.00 mmol), $Zn(CN)_2$ (176 mg, 1.50 mmol), and CsF (76.0 mg, 0.500 mmol) were added to the reaction vessel followed by H_2O (1.0 mL). The reaction vessel was sealed with a Teflon-lined cap, and the green suspension was stirred vigorously at 100 ºC for 3-6 h. Reaction progress was monitored by GC-MS. After this time, the reaction mixture was cooled to room temperature. A saturated solution of NH_4Cl (4 mL) was added, and the product was extracted with EtOAc (4 x 15 mL). The organic layers were combined, washed with brine, dried with Na_2SO_4 (anhydrous), filtered, and concentrated under vacuum. The crude product was purified by column chromatography on silica gel with a gradient of 100:0 to 95:5 hexanes:EtOAc. Alternate elutents are described for individual examples.

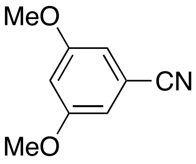


3,5-dimethylbenzonitrile.[2] Prepared according to the general procedure from *m*-xylene (61 μL, 0.50 mmol) with a catalyst loading of $[Ir(cod)OMe]_2$ (1.7 mg, 2.5 μmol), and dtbpy (1.3 mg, 5.0 μmol) for the borylation reaction and a reaction time of 5 h for the cyanation of the resulting arylboronate ester. The crude mixture was purified by flash column chromatography (100:0 to 95:5 hexanes:EtOAc) to give the nitrile product as a white solid in 60% yield

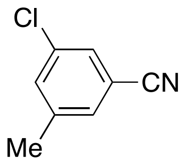
(40. mg, 0.30 mmol). ^{1}H NMR ($CDCl_3$) : δ 7.23 (s, 2H), 7.18 (s, 1H), 2.31 (s, 6H); ^{13}C NMR : δ 139.0, 134.5, 129.6, 119.1, 112.0, 21.0.



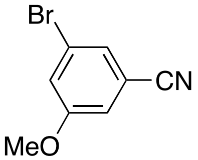
3-methoxy-5-methylbenzonitrile. Prepared according to the general procedure from 3-methylanisole (63 μL, 0.50 mmol) with a catalyst loading of [Ir(cod)OMe]$_2$ (0.33 mg, 0.50 μmol), and dtbpy (0.27 mg, 1.0 μmol) for the borylation reaction and a reaction time of 6 h for the cyanation of the resulting arylboronate ester. The crude mixture was purified by flash column chromatography (100:0 to 95:5 hexanes:EtOAc) to give the nitrile product as a white solid in 55% yield (40.3 mg, 0.273 mmol). ^{1}H NMR ($CDCl_3$) : δ 7.05 (s, 1H), 6.94 (s, 1H), 6.93 (s,1H), 3.80 (s, 3H), 2.35 (s, 3H). ^{13}C NMR : δ 151.9, 141.1, 125.3, 120.5, 119.1, 114.1, 113.0, 55.4, 25.2. Anal Calc'd for C_9H_9NO : C, 73.45; H, 6.16; N, 9.52 Found : C, 73.37; H, 6.44; N, 9.17.



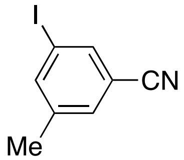
3,5-dimethoxybenzonitrile.[3] Prepared according to the general procedure from 1,3-dimethoxybenzene (66 μL, 0.50 mmol) with a catalyst loading of [Ir(cod)OMe]$_2$ (0.33 mg, 0.50 μmol), and dtbpy (0.27 mg, 1.0 μmol) for the borylation reaction and a reaction time of 6 h for the cyanation of the resulting arylboronate ester. The crude mixture was purified by flash column chromatography (100:0 to 95:5 hexanes:EtOAc) to give the nitrile product as a white solid in 53% yield (43.2 mg, 0.264 mmol). ^{1}H NMR ($CDCl_3$) : δ 6.76 (d, J = 2.5 Hz, 2H), 6.65 (t, J = 2.5 Hz, 1H), 3.81 (s, 6H); ^{13}C NMR ($CDCl_3$) : 161.3, 119.1, 113.7, 110.2, 106.0, 59.0.



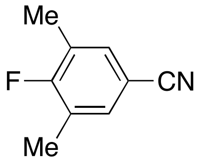
3-chloro-5-methylbenzonitrile.[4] Prepared according to the general procedure from 1-chloro-3-methylbenzene (59 μL, 0.50 mmol) with a catalyst loading of $[Ir(cod)OMe]_2$ (0.33 mg, 0.50 μmol), and dtbpy (0.27 mg, 1.0 μmol) for the borylation reaction and a reaction time of 6 h for the cyanation of the resulting arylboronate ester. The crude mixture was purified by flash column chromatography (100:0 to 95:5 hexanes:EtOAc) to give the nitrile product as a white solid in 63% yield (47.9 mg, 0.316 mmol). ^{1}H NMR ($CDCl_3$) : δ 7.45 (s, 1H), 7.41 (s, 1H), 7.36 (s, 1H), 2.31 (s, 3H); ^{13}C NMR : δ 141.5, 135.3, 134.3, 131.2, 129.4, 118.0, 112.0, 21.35.



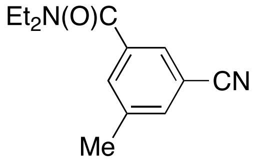
3-bromo-5-methoxybenzonitrile. Prepared according to the general procedure from 1-bromo-3-methoxybenzene (64 μL, 0.50 mmol) with a catalyst loading of $[Ir(cod)OMe]_2$ (0.33 mg, 0.50 μmol), and dtbpy (0.27 mg, 1.0 μmol) for the borylation reaction and a reaction time of 6 h for the cyanation of the resulting arylboronate ester. The crude mixture was purified by flash column chromatography (100:0 to 95:5 hexanes:EtOAc) to give the nitrile product as a white solid in 67% yield (71.3 mg, 0.336 mmol). ^{1}H NMR ($CDCl_3$) : δ 7.36 (t, *J* = 2.4 Hz, 1H), 7.28 (t, *J* = 2.4 Hz, 1H), 7.09 (dd, *J* = 1.2 Hz, 1H) 3.83 (s, 3H) ^{13}C NMR : δ 160.6, 127.3, 123.8, 122.7, 117.6, 116.7, 114.8, 56.3. Anal Calc'd for C_8H_6BrNO : C, 45.31; H, 2.85; N, 6.61 Found : C, 45.15; H, 2.72; N, 6.47.



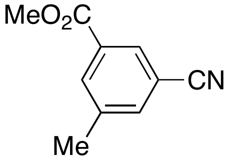
3-iodo-5-methylbenzonitrile. Prepared according to the general procedure from 3-iodotoluene (64 μL, 0.50 mmol) with a catalyst loading of $[Ir(cod)OMe]_2$ (5.0 mg, 7.5 μmol), and dtbpy (4.0 mg, 15 μmol) for the borylation reaction and a reaction time of 4 h for the cyanation of the resulting arylboronate ester. The crude mixture was purified by flash column chromatography (100:0 to 95:5 hexanes:EtOAc) to give the nitrile product as a white solid in 57% yield (69.0 mg, 0.284 mmol). ^{1}H NMR ($CDCl_3$) : δ 7.28 (2 overlapping peaks, 2H), 6.93 (s, 1H), 1.85 (s, 3H). ^{13}C NMR : δ 142.9, 141.7, 137.9, 132.2, 118.2, 114.8, 94.0, 21.3. Anal Calc'd for C_8H_6IN : C, 39.53; H, 2.49; N, 5.76 Found : C, 39.52; H, 2.22; N, 5.64.



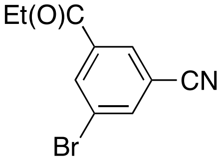
4-fluoro-3,5-dimethylbenzonitrile. Prepared according to the general procedure from 2,6-dimethylfluorobenzene (67 μL, 0.50 mmol) with a catalyst loading of [Ir(cod)OMe]$_2$ (0.33 mg, 0.5 μmol) and dtbpy (0.27 mg, 1.0 μmol) for the borylation reaction and a reaction time of 3 h for the cyanation of the resulting arylboronate ester. The crude mixture was purified by flash column chromatography (100:0 to 95:5 hexanes:EtOAc) to give the nitrile product as a white solid in 61% yield (45.8 mg, 0.305 mmol). ^{1}H NMR ($CDCl_3$) : δ 7.35 (d, 2 H, *J* = 4 Hz, 1H), 2.30 (d, 2 H, *J* = 4 Hz, 1H). ^{13}C NMR ($CDCl_3$) : δ 133.3, 127.2, 118.8, 108.0, 14.3. ^{19}F NMR ($CDCl_3$) : δ -111.7. Anal Calc'd for C_9H_8FN : C, 72.47; H, 5.41; N, 9.39. Found : C, 72.12; H, 5.20; N, 9.27.



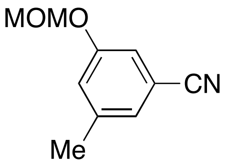
3-cyano-5-methyl-N,N-diethylbenzamide. Prepared according to the general procedure from *N,N*-diethyl-*m*-toluamide (96 μL, 0.50 mmol) with a catalyst loading of [Ir(cod)OMe]$_2$ (5.0 mg, 7.5 μmol), and dtbpy (4.0 mg, 15 μmol) for the borylation reaction and a reaction time of 4 h for the cyanation of the resulting arylboronate ester. The crude mixture was purified by flash column chromatography (100:0 to 90:10 hexanes:*i*-PrOH) to give the nitrile product as a colorless oil in 66% yield (71.0 mg, 0.328 mmol). ^{1}H NMR ($CDCl_3$) : δ 7.49 (s, 1H), 7.45 (s, 1H), 7.41 (s, 1H), 3.54 (br s, 2H), 3.21 (br s, 2H), 2.42 (s, 3H), 1.23 (br s, 3H), 1.10 (br s, 3H). ^{13}C NMR ($CDCl_3$) : δ 169.2, 140.2, 138.6, 133.3, 131.7, 127.1, 118.5, 112.7, 43.6, 39.7, 21.4, 14.4, 13.0. HRMS Calc'd : 216.12627. Found : 216.12500.



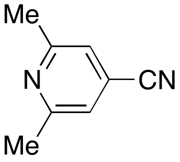
5-methyl-3-cyanomethylbenzoate. Prepared according to the general procedure from methyl-*m*-toluate (71 µL, 0.50 mmol) with a catalyst loading of $[Ir(cod)OMe]_2$ (0.33 mg, 0.5 µmol) and dtbpy (0.27 mg, 1.0 µmol) for the borylation reaction and a reaction time of 6 h for the cyanation of the resulting arylboronate ester. The crude mixture was purified by flash column chromatography (100:0 to 90:10 hexanes:EtOAc) to give the nitrile product as a white solid in 66% yield (57.1 mg, 0.326 mmol). ^1H NMR ($CDCl_3$) : δ 8.12 (s, 1H), 8.07 (s, 1H), 7.63 (s, 1H), 3.94 (s, 3H), 2.47 (s, 3H); ^{13}C NMR : δ 156.6, 140.2, 136.7, 134.8, 131.6, 130.8, 118.4, 113.0, 53.0, 21.4. Anal Calc'd for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00 Found : C, 68.58; H, 5.12; N, 8.01.



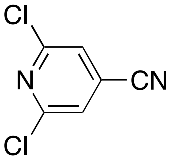
3-bromo-5-propionylbenzonitrile. Prepared according to the general procedure from 1-(3-bromophenyl)propan-1-one (106 mg, 0.500 mmol) with a catalyst loading of $[Ir(cod)OMe]_2$ (0.33 mg, 0.5 µmol) and dtbpy (0.27 mg, 1.0 µmol) for the borylation reaction and a reaction time of 3 h for the cyanation of the resulting arylboronate ester. The crude mixture was purified by flash column chromatography (100:0 to 95:5 hexanes:EtOAc) to give the nitrile product as a white solid in 62% yield (74.2 mg, 0.312 mmol). ^1H NMR ($CDCl_3$) : δ 8.29, 8.15, 7.95, 2.99 (q, *J* = 7 Hz, 2H), 1.25 (t, *J* = 7 Hz, 3H). ^{13}C NMR : δ 197.7, 139.3, 138.4, 135.5, 130.4, 123.9, 116.8, 115.0, 32.4, 8.1. Anal Calc'd for $C_{10}H_8BrNO$: C, 50.45; H, 3.39; N, 5.88. Found : C, 50.71; H, 3.25; N, 5.80.



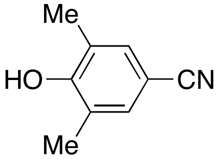
3-methoxymethyl-5-methylbenzonitrile. Prepared according to the general procedure from 1-(methoxymethoxy)-3-methylbenzene (76 mg, 0.50 mmol) with a catalyst loading of $[Ir(cod)OMe]_2$ (5.0 mg, 7.5 µmol), and dtbpy (4.0 mg, 15 µmol) for the borylation reaction and a reaction time of 3 h for the cyanation of the resulting arylboronate ester. The crude mixture was purified by flash column chromatography (100:0 to 95:5 hexanes:EtOAc) to give the nitrile product as a colorless oil in 51% yield (44.1 mg, 0.249 mmol). ^{1}H NMR ($CDCl_3$) : δ 7.12 (s, 1H), 7.10 (s, 1H), 7.07 (s, 1H), 5.16 (s, 2H), 3.47 (s, 3H), 2.35 (s, 3H). ^{13}C NMR : δ 157.5, 141.1, 126.4, 122.1, 119.0, 117.0, 113.1, 94.6, 56.4, 21.5. Anal Calc'd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.90. Found : C, 67.78; H, 6.25; N, 7.68.



4-cyano-2,6-lutidine.[5] Prepared according to the general procedure from 2,6-lutidine (58 µL, 0.50 mmol) with a catalyst loading of $[Ir(cod)OMe]_2$ (9.9 mg, 15 µmol), and dtbpy (8.1 mg, 30. µmol) for the borylation reaction and a reaction time of 4 h for the cyanation of the resulting arylboronate ester. The crude mixture was purified by flash column chromatography (100:0 to 95:5 $CDCl_3$:*i*-PrOH) to give the nitrile product as a white solid in 61% yield (40.1 mg, 0.304 mmol). ^{1}H NMR ($CDCl_3$) : δ 7.20 (s, 2H), 2.59 (s, 6H); ^{13}C NMR : δ 159.7, 122.0, 121.0, 117.2, 24.7.



2,6-dichloro-4-cyanopyridine. Prepared according to the general procedure from 2,6-dichloropyridine (74 mg, 0.50 mmol) with a catalyst loading of $[Ir(cod)OMe]_2$ (9.9 mg, 15 µmol), and dtbpy (8.1 mg, 30. µmol) for the borylation reaction and a reaction time of 3 h for the cyanation of the resulting arylboronate ester. The crude mixture was purified by flash column chromatography (100:0 to 90:10 hexanes:EtOAc) to give the nitrile product as a white solid in 60% yield (49.9 mg, 0.289 mmol). ^{1}H NMR ($CDCl_3$) : δ 7.52 (s, 2H); ^{13}C NMR ($CDCl_3$) : δ 152.4, 125.1, 125.0, 114.5. Anal Calc'd for $C_6H_2Cl_2N_2$: C, 41.66; H, 1.17; N, 16.19. Found : C, 41.53; H, 1.13; N, 15.94.



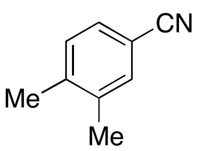
4-hydroxy-3,5-dimethylbenzonitrile. Prepared according to the general procedure from 1-(methoxymethoxy)-2,6-dimethylbenzene (83 mg, 0.50 mmol) with a catalyst loading of $[Ir(cod)OMe]_2$ (5.0 mg, 7.5 μmol), and dtbpy (4.0 mg, 15 μmol) for the borylation reaction and a reaction time of 4 h for the cyanation of the resulting arylboronate ester. The crude mixture was purified by flash column chromatography (100:0 to 95:5 hexanes:EtOAc) to give the nitrile product as a white solid in 58% yield (42.7 mg, 0.290 mmol). The methoxymethyl protecting group was cleaved under the standard reaction conditions. The protecting group was not cleaved when the protected hydroxyl group was located meta to the cyano substitutent (Table 1, Entry 11). ^{1}H NMR ($CDCl_3$) : δ 7.29 (s, 2H), 5.16 (br s, 1H), 2.26 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 156.3, 133.1, 124.4, 119.5, 106.3, 15.7. Anal Calc'd for C_9H_9NO : C, 73.45; H, 6.16; N, 9.52. Found : C, 73.60; H, 6.19; N, 9.24.

Procedure for the Cyanation of 3-Chlorotoluene on a 10.0 mmol Scale.

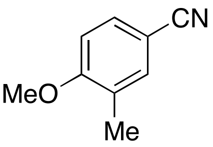
In a nitrogen-filled glove box, 3-chlorotoluene (1.18 mL, 10.0 mmol), B_2pin_2 (1.91 g, 7.50 mmol), $[Ir(cod)(OMe)]_2$ (6.6 mg, 0.10 mmol) dtbpy (5.4 mg, 0.20 mmol) were combined in a 20 mL vial containing a stirbar and dissolved in 15 mL THF. The reaction was sealed with a Teflon-lined cap and was heated at 80 °C for 16 h. The red solution was then cooled to room temperature, and the volatile materials were evaporated under reduced pressure for 2 h. The residue was then dissolved in 20 mL MeOH and transferred to a 250 mL flask with a Teflon-stopper. The vial was rinsed with MeOH (2 x 15 mL) and the rinses were transferred to the flask. $Cu(NO_3)_2 \cdot 3H_2O$ (4.83 g, 20.0 mmol), $Zn(CN)_2$ (3.52 g, 30.0 mmol), and CsF (1.52 g, 10.0 mmol) were added to the reaction flask followed by H_2O (20 mL). The reaction vessel was sealed with a Teflon-stopper, and the green suspension was stirred vigorously at 100 ºC for 5 h. Reaction progress was monitored by GC-MS. After this time, the reaction mixture was cooled to room temperature. A saturated solution of NH_4Cl (40 mL) was added, and the product was extracted with EtOAc (5 x 50 mL). The organic layers were combined, washed with brine, dried with Na_2SO_4 (anhydrous), filtered, and concentrated under vacuum. The crude product was purified by column chromatography on silica gel with a gradient of 100:0 to 95:5 hexanes:EtOAc to give the white nitrile product in 59% yield (0.890 g,.5.86 mmol).

General Procedure for the Cyanation of Arylboronic Acids.

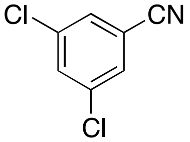
In a 20 mL vial containing a stirbar, the arylboronic acid was dissolved in 2.5 mL MeOH. $Cu(NO_3)_2 \cdot 3H_2O$ (242 mg, 1.00 mmol), $Zn(CN)_2$ (176 mg, 1.50 mmol), and CsF (76.0 mg, 0.500 mmol) were added to the reaction vial, followed by H_2O (1.0 mL). The reaction was sealed with a Teflon-lined cap under an atmosphere of air and heated to 80 ºC for 2 h. After heating, the reaction mixture was cooled to room temperature. A saturated solution of NH_4Cl (4 mL) was added, and the product was extracted with EtOAc (4 x 15 mL). The organic layers were combined, washed with brine, dried with Na_2SO_4 (anhydrous), filtered, and concentrated under vacuum. The product was then purified by column chromatography on silica gel eluting with a mixture of 5% EtOAc: 95% hexanes. Alternate elutents used are described for individual examples.



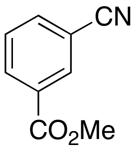
3,4-dimethylbenzonitrile.[6] Prepared according to the general procedure with 3,4-dimethylphenylboronic acid (85 mg, 0.50 mmol). The crude mixture was purified by flash column chromatography (100:0 to 95:5 hexanes:EtOAc) to give the nitrile product as a white solid in 68% yield (44.5 mg, 0.339 mmol). ^{1}H NMR (CDCl$_3$) : δ 7.42 (s, 1H), 7.40 (d, 1H, J = 8.0 Hz), 7.22 (d, 1H, J = 8.0 Hz), 2.33 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (CDCl$_3$) : δ 142.9, 138.1, 131.2, 130.1, 129.9, 119.4, 109.6, 20.5, 19.3.



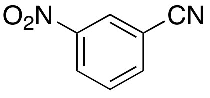
4-methoxy-3-methylbenzonitrile. Prepared according to the general procedure with 4-methoxy-3-methylphenylboronic acid (83 mg, 0.50 mmol. The crude mixture was purified by flash column chromatography (100:0 to 95:5 hexanes:EtOAc) to give the nitrile product as a white solid in 70% yield (51.6 mg, 0.350 mmol). ^{1}H NMR (CDCl$_3$) : δ 7.49 (d, 1H, J = 8.8 Hz), 7.40 (s, 1H), 6.85 (d, 1H, J = 8.8 Hz), 3.88 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (CDCl$_3$) : δ 161.8, 134.1, 132.3, 128.4, 120.0, 110.7, 103.6, 55.7, 16.2. Anal Calc'd for C_9H_9NO : C, 73.45; H, 6.16; N, 9.62. Found : C, 73.18; H, 6.01; N, 9.36.



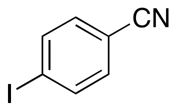
3,5-dichlorobenzonitrile. Prepared according to the general procedure with 3,5-dichlorophenylboronic acid (95 mg, 0.50 mmol). The crude mixture was purified by flash column chromatography (100:0 to 95:5 hexanes:EtOAc) to give the nitrile product as a white solid in 69% yield (59.0 mg, 0.343 mmol). ^{1}H NMR (CDCl$_3$) : δ 7.59 (s, 1H), 7.53 (s, 2H). ^{13}C NMR (CDCl$_3$) : δ 136.4, 133.6, 130.5, 116.4, 115.2. Anal Calc'd for $C_7H_3Cl_2N$: C, 48.88; H, 1.76; N, 8.14. Found : C, 48.60; H, 1.53; N, 7.92.



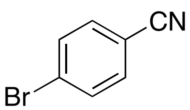
Methyl-3-cyanobenzoate. Prepared according to the general procedure with 3-(methoxycarbonyl)phenylboronic acid (90. mg, 0.50 mmol) The crude mixture was purified by flash column chromatography (100:0 to 90:10 hexanes:EtOAc) to give the nitrile product as a white solid in 68% yield (54.6 mg, 0.339 mmol).^{1}H NMR ($CDCl_3$) : δ 8.28 (s, 1H), 8.23 (d, 1H, *J* = 7.6 Hz), 7.81 (d, 1H, *J* = 7.6 Hz), 7.55 (t, 1H, *J* = 7.6 Hz), 3.92 (s, 3H). ^{13}C NMR ($CDCl_3$) : δ 165.3, 136.2, 133.9, 133.5, 131.6, 129.7, 118.1, 113.1, 52.9. Anal Calc'd for $C_9H_7NO_2$: C, 67.07; H, 4.38; N, 8.69. Found : C, 67.10; H, 4.16; N, 8.51.



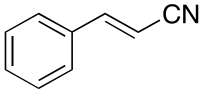
3-nitrobenzonitrile.[7] Prepared according to the general procedure with 3-nitrophenylboronic acid (83.5 mg, 0.500 mmol). The crude mixture was purified by flash column chromatography (100:0 to 90:10 hexanes:EtOAc) to give the nitrile product as a white solid in 67% yield (49.9 mg, 0.337 mmol).^{1}H NMR ($CDCl_3$) : δ 8.54 (s, 1H), 8.48 (d, 1H, *J* = 8.0 Hz), 8.00 (d, 1H, *J* = 8.0 Hz), 7.75 (t, 1H, *J* = 8.0 Hz) ^{13}C NMR ($CDCl_3$) : δ 148.6, 137.9, 131.0, 127.9, 127.6, 116.9, 114.5.



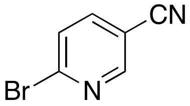
4-iodobenzonitrile.[8] Prepared according to the general procedure with 4-iodophenylboronic acid (124 mg, 0.500 mmol). The crude mixture was purified by flash column chromatography (100:0 to 95:5 hexanes:EtOAc) to give the nitrile product as a white solid in 62% yield (70.7 mg, 0.309 mmol). ^{1}H NMR ($CDCl_3$) : δ 7.85 (dd, *J* = 1.6 Hz, 8.4 Hz, 2H), 7.37 (dd, *J* = 1.6 Hz, 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$) : δ139.0, 131.4, 118.5, 111.9, 100.6.



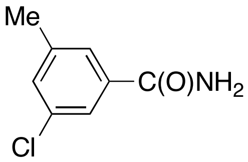
4-bromobenzonitrile.[9] Prepared according to the general procedure with 4-bromophenylboronic acid (100. mg, 0.500 mmol). The crude mixture was purified by flash column chromatography (100:0 to 95:5 hexanes:EtOAc) to give the nitrile product as a white solid in 58% yield (52.7 mg, 0.290 mmol).^{1}H NMR ($CDCl_3$) : δ 7.64 (dd, *J* = 2.0 Hz, 6.8 Hz, 2H), (7.53, dd, *J* = 2.0 Hz, 6.8 Hz, 2H). ^{13}C NMR ($CDCl_3$) : δ 133.8, 132.8, 128.3, 118.6, 111.7.



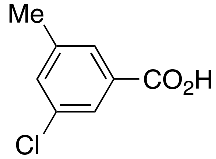
3-phenylacrylonitrile.[10] Prepared according to the general procedure with *trans*-styrenylboronic acid (74.0 mg, 0.500 mmol). Purified by flash column chromatography (100:0 to 95:5 hexanes:EtOAc) to give the nitrile product as a colorless oil in 65% yield (42.0 mg, 0.326 mmol). ^{1}H NMR ($CDCl_3$) : δ 7.43-7.46 (m, 6H), 5.88 (d, 1H, *J* = 17 Hz). ^{13}C NMR ($CDCl_3$) : δ 135.1, 146.9, 141.1, 129.0, 116.0, 109.5.



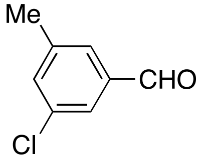
2-bromo-5-cyanopyridine.[11] Prepared according to the general procedure with 2-bromopyridine-5-boronic acid (101 mg, 0.500 mmol). The crude mixture was purified by flash column chromatography (100:0 to 85:15 hexanes:EtOAc) to give the nitrile product as a white solid in 61% yield (55.5 mg, 0.303 mmol).^{1}H NMR ($CDCl_3$) : δ 8.66 (d, 1H, *J* = 2.5 Hz), 7.80 (dd, 1H, *J* = 2.5, 8.5 Hz), 7.66 (d, 1H, *J* = 8.5 Hz) ^{13}C NMR ($CDCl_3$) : δ 135.1, 146.9, 141.1, 129.0, 116.0, 109.5.



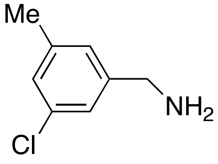
Synthesis of 3-chloro-5-methylbenzamide. The hydrolysis of 3-chloro-5-methylbenzonitrile was performed by a modified literature procedure.[12] In a vial containing a stirbar, 3-chloro-5-methylbenzonitrile (76 mg, 0.50 mmol) was dissolved in *t*-BuOH (10. mL). Solid KOH (420 mg, 7.5 mmol) was added, and the reaction was sealed under an atmosphere of air. The reaction was heated at 60 ºC for 4 h. After full conversion occurred, as determined by GC-MS, H_2O (10 mL) was added, and the solution was extracted with EtOAc (3 x 25 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered, and concentrated under vacuum. The product was purified by column chromatography on silica gel, eluting with a mixture of 5% *i*-PrOH in $CHCl_3$ to yield a white solid in 94% yield (79.9 mg, 0.471 mmol). ^{1}H NMR ($CDCl_3$) : δ 7.58 (s, 1H), 7.50 (s, 1H), 7.31 (s, 1H), 6.27 (br s, 2H), 2.38 (s, 3H). ^{13}C NMR : δ 168.9, 140.7, 135.9, 134.9, 132.8, 126.6, 124.9, 21.4. Anal Calc'd for C_8H_8ClNO : C, 56.65; H, 4.75; N, 8.26. Found : C, 56.64; H, 4.82; N, 8.20.



Synthesis of 3-Chloro-5-methylbenzoic Acid. The hydrolysis of 3-chloro-5-methylbenzonitrile (76 mg, 0.50 mmol) was performed by a modified literature procedure.[13] In a 10 mL round bottom flask containing a stirbar, 3-chloro-5-methylbenzonitrile and AcOH (1 mL) was added to form a homogenous solution. H_2O (1 mL) and H_2SO_4 (1 mL) were added to create a heterogenous solution. A reflux condenser was attached to the flask and the reaction was heated to 120 °C for 1 h. The reaction was then refluxed for 5 h. After cooling to room temperature, NaOH (2M) was added dropwise at 0 °C until pH=14. The suspension was diluted with H_2O until all the solids dissolved. The solution was then washed with EtOAc (2 x 20 mL). HCl (concentrated) was added dropwise until the pH=1. The suspension was then extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with brine, dried with $MgSO_4$, filtered, and concentrated. The resulting waxy, white solid was azeotroped with heptane (3x) to yield a white solid in 94% yield (80.0 mg, 0.469 mmol). ^{1}H NMR ($CDCl_3$) : δ 7.89 (s, 1H), 7.81 (s, 1H), 7.41 (s, 1H), 2.41 (s, 3H). ^{13}C NMR ($CDCl_3$) : δ 171.4, 140.4, 134.8, 134.7, 130.0, 127.7, 21.4. Anal Calc'd for $C_8H_7ClO_2$: C, 56.32; H, 4.14; N, 0.00. Found C, 56.09; H, 4.01; N, <0.02.

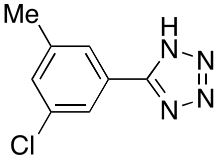


Synthesis of 3-Chloro-5-methylbenzaldehyde. The partial reduction of 3-chloro-5-methylbenzonitrile was conducted by a modified literature procedure.[14] To a stirred solution of 3-chloro-5-methylbenzonitrile (76 mg, 0.50 mmol) in hexanes at 0 ºC under an atmosphere of nitrogen, diisopropylaluminum hydride in hexanes (1.2 mL, 1.2 mmol, 2.5 equiv, 1M) was added dropwise. The solution was allowed to warm to room temperature and stirred for 5 h. HCl (10%) was then added to the light yellow solution. The reaction was stirred for 30 min at room temperature. The reaction was extracted with Et_2O (3 x 20 mL). The combined organic layers were washed with $NaHCO_3$ (sat'd) and brine, dried with $MgSO_4$ (anhydrous), filtered, and concentrated. The crude product was purified by column chromatography (0:100 to 5:95 EtOAc:hexanes) to afford a colorless liquid in 68% yield (53 mg, 0.34 mmol). ^{1}H NMR ($CDCl_3$) : δ 9.93 (s, 1H), 7.64 (s, 1H), 7.56 (s, 1H), 7.41 (s,1H), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$) : δ 191.3, 141.1, 137.9, 135.3, 135.2, 128.8, 126.9, 21.3. Anal Calc'd for C_8H_7ClO : C, 62.15; H, 4.56; N, 0. Found : C, 62.13; H, 4.76; N, 0.22.



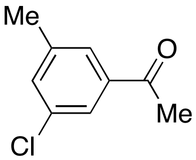
Synthesis of 3-Chloro-5-methylbenzyl Amine. The reduction of 3-chloro-5-methylbenzonitrile was conducted by a modified literature procedure.[15] In a nitrogen-filled glovebox, $LiAlH_4$ (57 mg, 1.5 mmol) and dry Et_2O (2 mL) (-35 °C) were added to a vial containing a stirbar. A solution of 3-chloro-5-methylbenzonitrile (76 mg, 0.50 mmol) in 2 mL Et_2O (-35 °C) was then added dropwise to the stirred suspension of $LiAlH_4$. The reaction was sealed and allowed to warm to room temperature. The grey suspension was stirred for 5 h. The reaction was cooled to 0 °C, and H_2O (0.2 mL) was added, followed by NaOH (0.2 mL, 2M) and H_2O

(0.2 mL). The suspension was filtered and washed with Et_2O (50 mL). The solution was washed with brine, dried with $MgSO_4$ (anhydrous), filtered, and concentrated under vacuum. The product was purified by flash column chromatography (2 : 2 : 96 MeOH : Et_3N : DCM) to yield a colorless oil in 86% yield (67.0 mg, 0.431 mmol). ^{1}H NMR ($CDCl_3$) : δ 7.09 (s, 1H), 7.03 (s, 1H), 6.99 (s, 1H), 3.79 (s, 2H), 2.31 (s, 3H), 1.41 (s, 2H). ^{13}C NMR ($CDCl_3$) : δ 145.3, 140.2, 134.3, 127.7, 126.3, 124.5, 46.2, 21.4. Anal Calc'd for $C_8H_{10}ClN$: C, 61.74; H, 6.48; N, 9.00. Found : C, 61.47; H, 5.67; N, 8.69.



Synthesis of 5-(3-chloro-5-methylphenyl)-1*H*-tetrazole. 3-chloro-5-methylbenzonitrile was converted to the corresponding tetrazole by a modified literature procedure.[16] In a 10 mL round bottom flask containing a stirbar, 3-chloro-5-methylbenzonitrile (76 mg, 0.50 mmol), $ZnBr_2$ (110 mg, 0.50 mmol), and NaN_3 (39 mg, 0.60 mmol) were added. H_2O (1.5 mL) and *i*-PrOH (0.5 mL) were added to form a white suspension. A reflux condenser was placed on the flask, and the reaction was heated at 100 ºC for 30 h until full conversion of the benzonitrile was observed by GC-MS. HCl (3N, 1.5 mL) and EtOAc (5mL) were added until a homogenous solution was formed with a pH = 1. The organic layer was separated, and the aqueous layer was extracted with EtOAc (2 x 20 mL). The organic layers were concentrated under vacuum. NaOH (0.25 N, 10 mL) was added, and the mixture was stirred for 30 min. The suspension was filtered and washed with NaOH (0.25 N, 20 mL). HCl (3N, 2 mL) was added and the product precipitated. The suspension was filtered, washed with HCl (3N, 2 x 4 mL), and water (2 x 10 mL). The product was then dried under vacuum and azeotroped with heptane (3 x 4 mL). A white solid was obtained in 65% yield (63 mg, 0.32 mmol). ^{1}H NMR ($(CD_3)CO$) : δ 7.89 (s, 1H), 7.87 (s, 1H), 7.40

(s, 1H), 2.41 (s, 3H). ^{13}C NMR (($(CD_3)CO$) : δ 196.9, 142.4, 135.2, 132.1, 127.7, 127.0, 124.7, 21.0. Anal Calc'd for $C_8H_{10}ClN_4$: C, 49.37; H, 3.63; N, 28.79. Found : C, 49.07; H, 3.43; N, 28.53.



Synthesis of 3-Chloro-5-methylacetophenone. 3-Chloro-5-methylacetophenone was prepared by a modified literature procedure.[17] To a 10 mL round bottom flask containing a stirbar, was added 3-chloro-5-methylbenzonitrile (76 mg, 0.50 mmol). The nitrile was dissolved in dry Et_2O (3 mL). The flask was sealed with a septum and purged with N_2. A solution of MeMgBr (3M, 0.50 mL, 1.5 mmol) was added dropwise. The septum was replaced with a reflux condenser, and the solution was refluxed for 48 h to yield a light yellow solution. After cooling to room temperature, the reaction was added to a mixture of Et_2O (6 mL), ice water (5 mL), and HCl (10%, 5 mL). After mixing, the aqueous layer was transferred to a round bottom flask and refluxed for one hour. After cooling to room temperature, the mixture was extracted with Et_2O (4 x 10 mL). The combined organic layers were washed with $NaHCO_3$ (sat'd) and brine, dried with $MgSO_4$ (anhydrous), filtered, and concentrated under vacuum. The product was purified by flash column chromatography to yield a colorless oil in 68% yield (56.8 mg, 0.338 mmol). ^{1}H NMR ($CDCl_3$) : δ 7.72 (s, 1H), 7.64 (s, 1H), 7.36 (s, 1H), 2.58 (s, 3H), 2.41 (s, 3H). ^{13}C NMR ($CDCl_3$) : δ 197.3, 140.6, 138.8, 135.7, 133.8, 127.4, 125.9, 27.0, 21.4. Anal Calc'd for C_9H_9ClO : C, 64.11; H, 5.38, N, 0.00. Found : C, 64.36; H, 5.41; N, <0.02.

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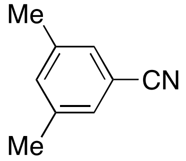
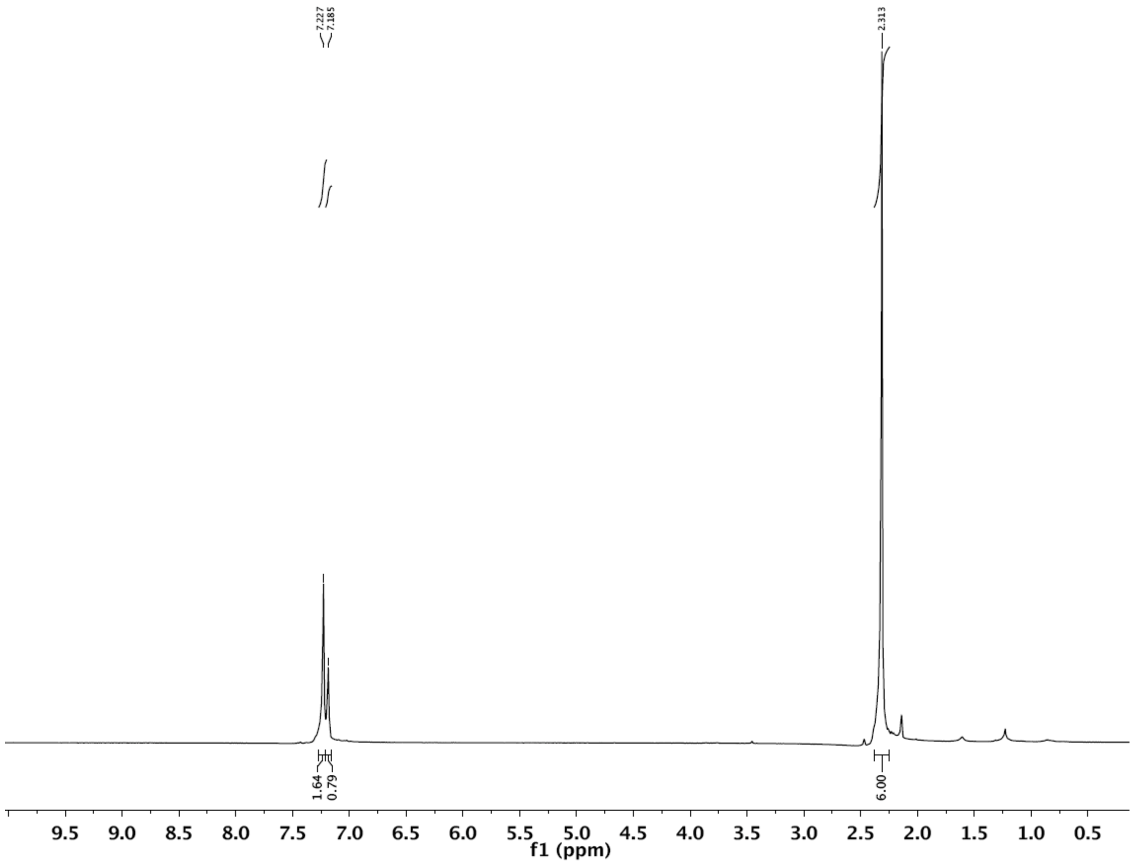
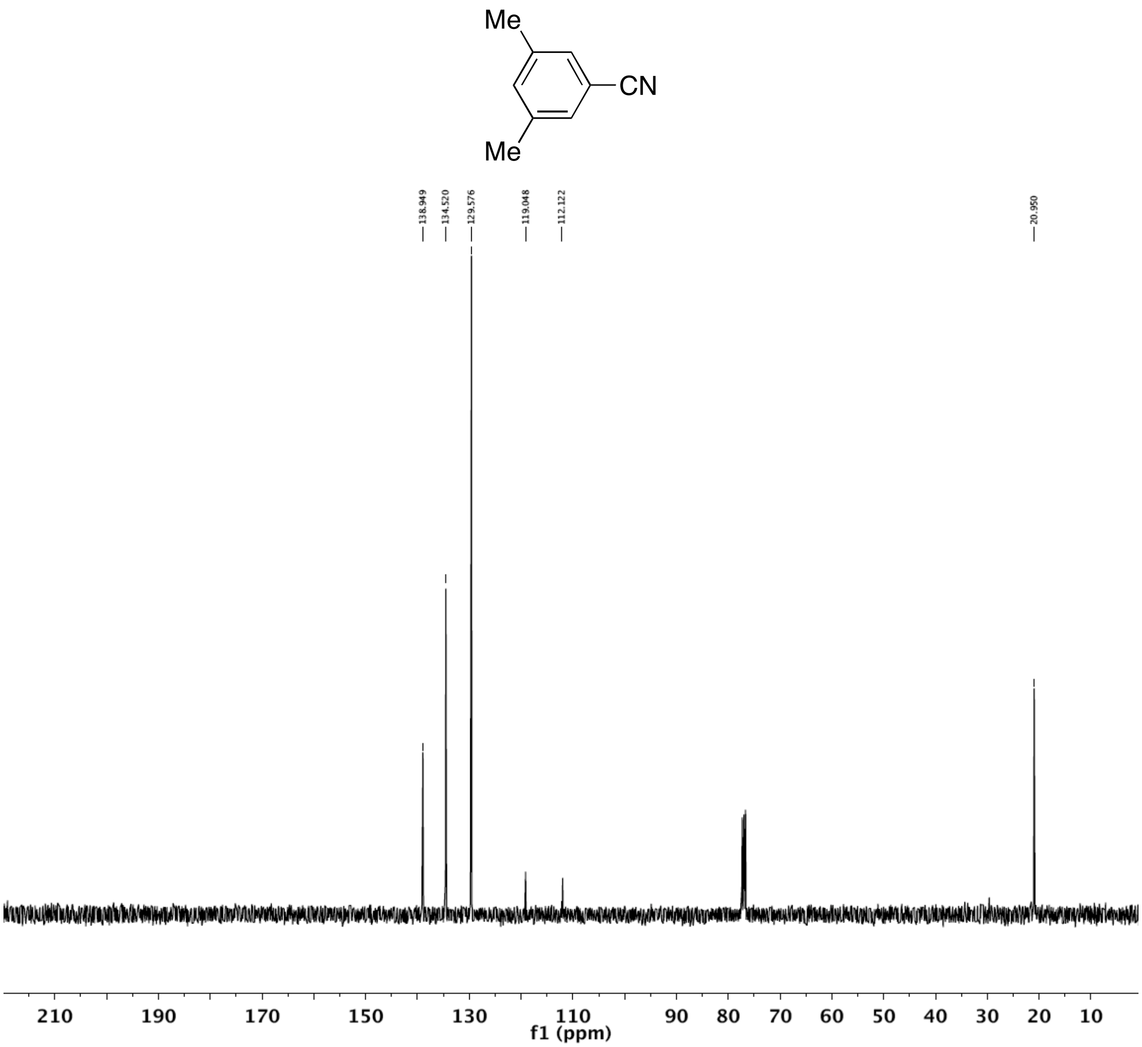
^{1}H NMR and ^{13}C NMR Spectral Data of Cyanation Products



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CN
Me
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129.576
119.048
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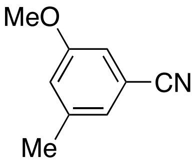
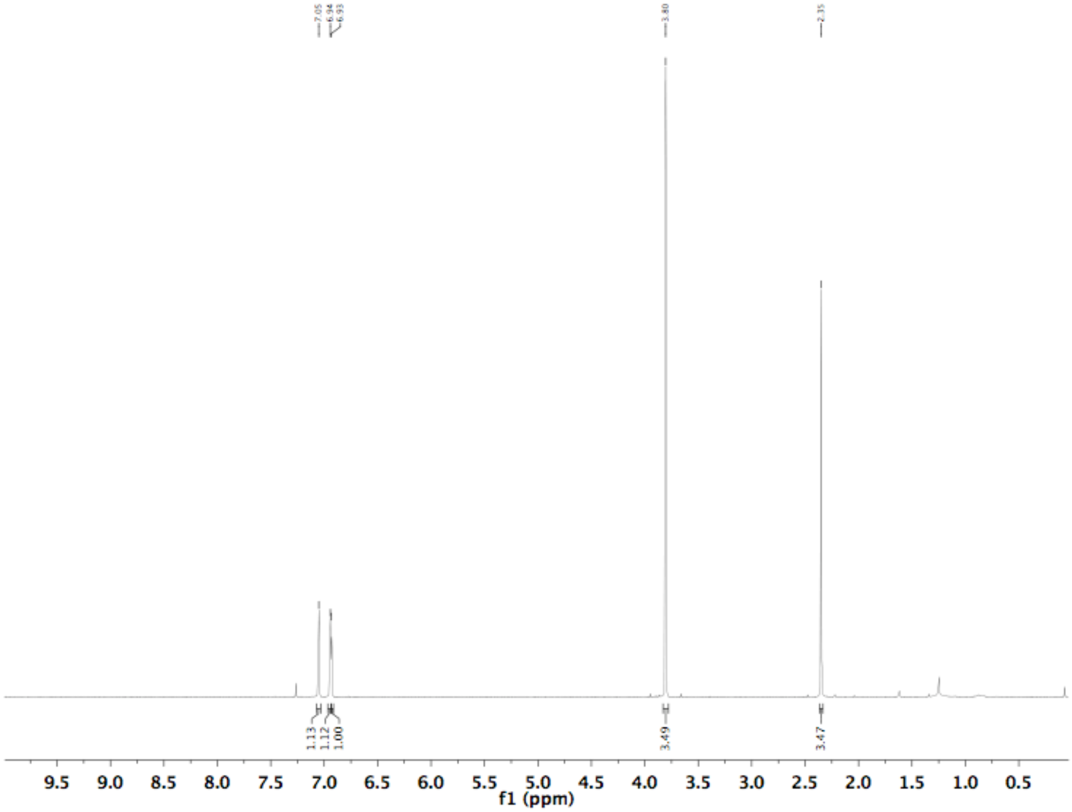
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)


MeO
CN
Me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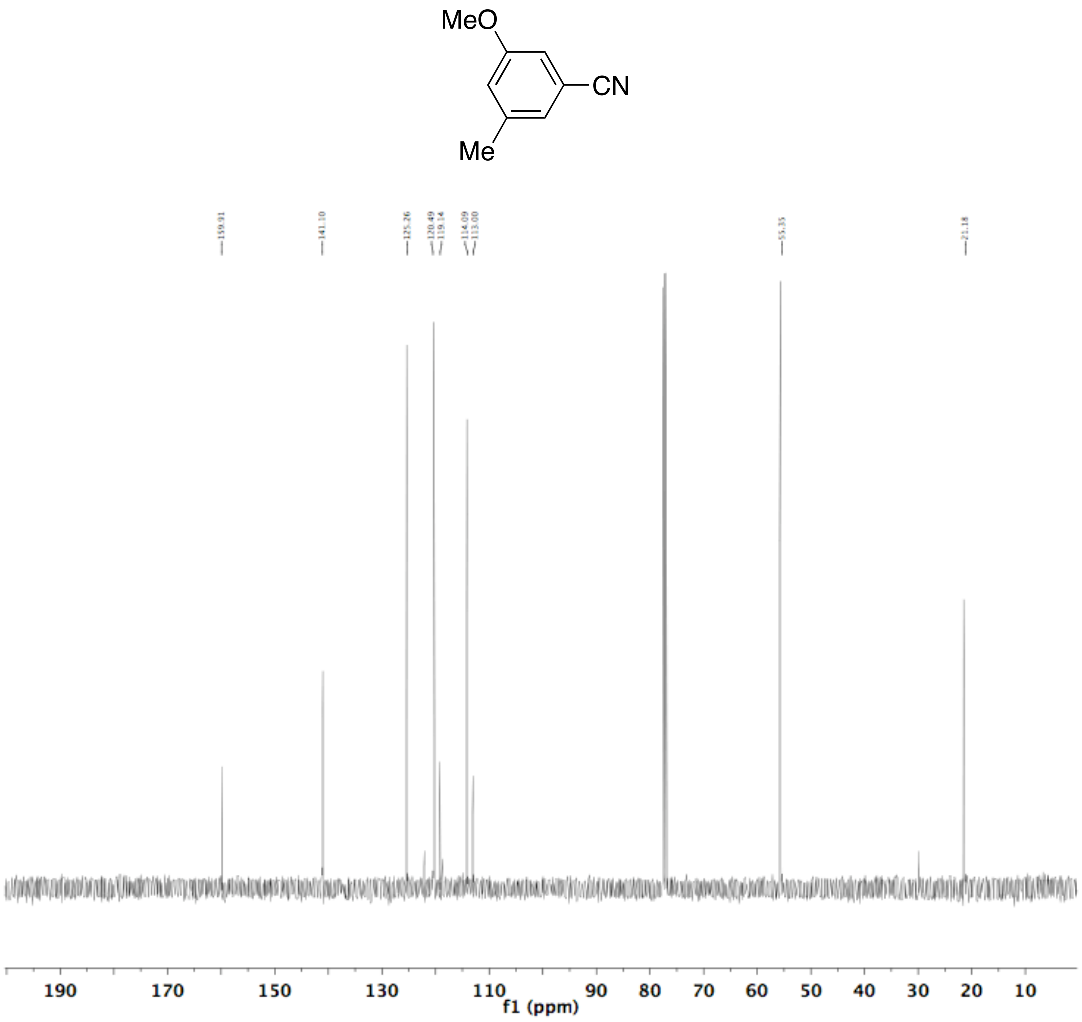
6.94
6.93
3.80
2.35
1.13
1.12
1.00
3.49
3.47
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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CN
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120.49
119.14
114.09
113.00
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150
130
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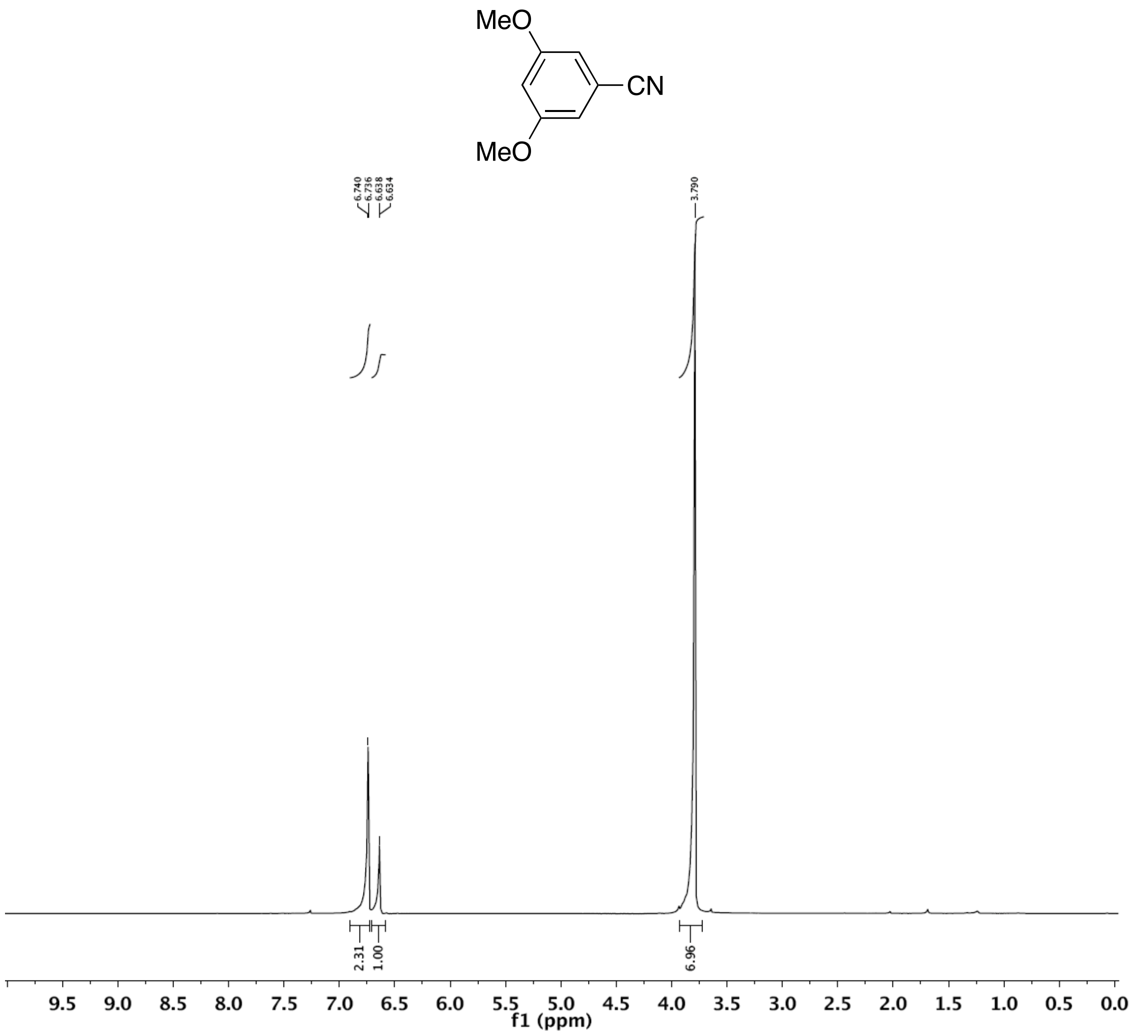
f1 (ppm)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CN
MeO
6.740
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6.634
3.790
2.31
1.00
6.96
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
2.0
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1.0
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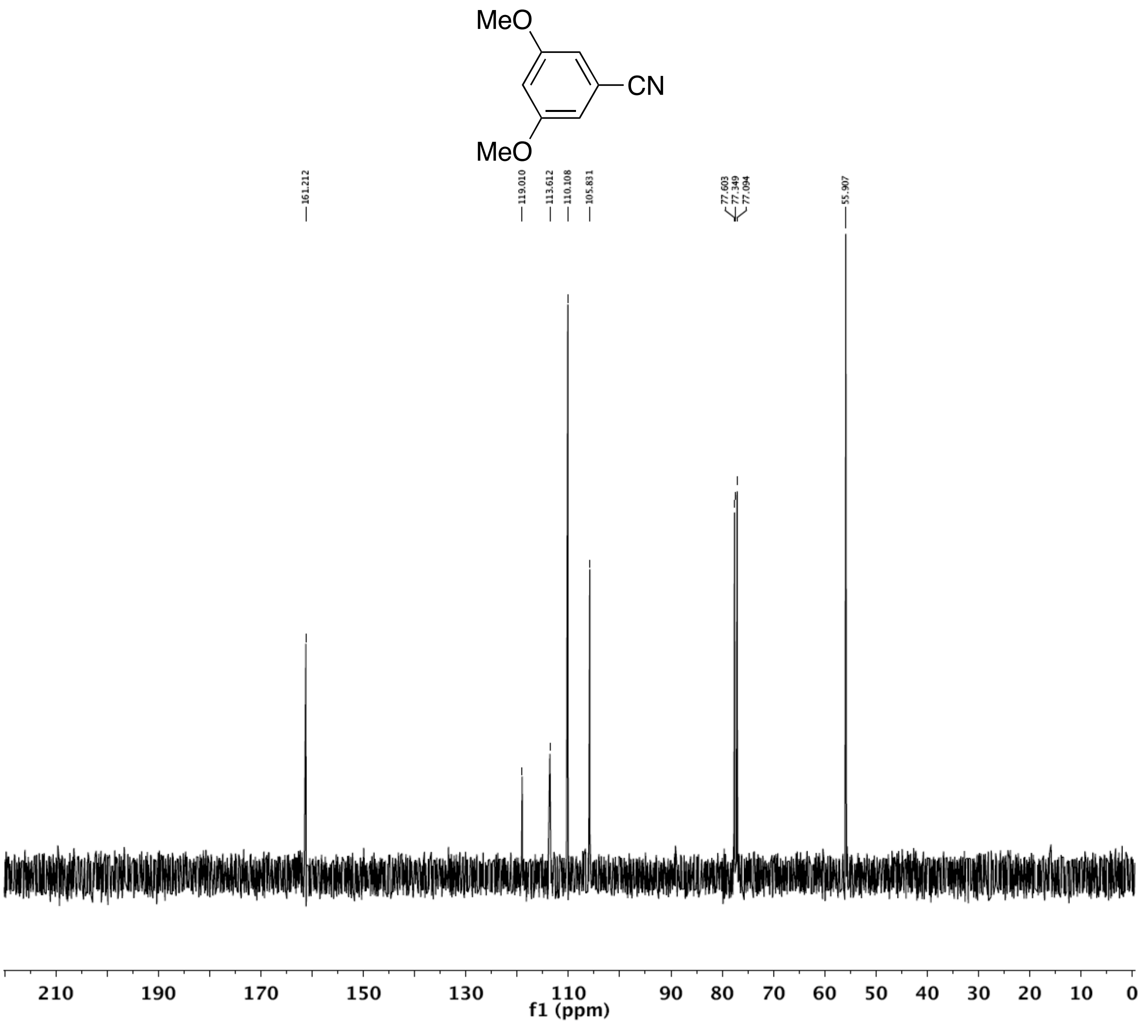
0.0
f1 (ppm)



MeO
CN
MeO
161.212
119.010
113.612
110.108
105.831
77.603
77.349
77.094
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210
190
170
150
130
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50
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30
20
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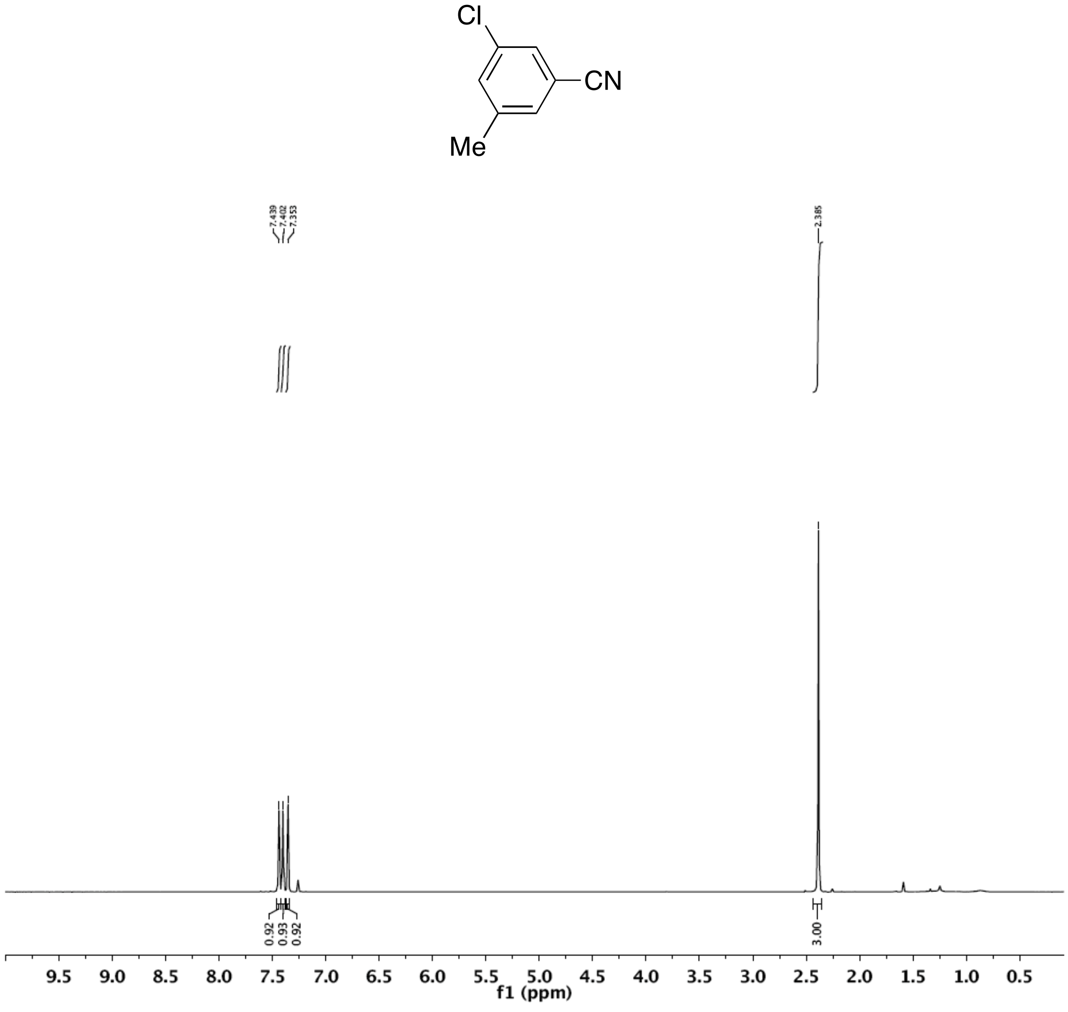
0
f1 (ppm)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7.353
2.385
0.92
0.93
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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3.0
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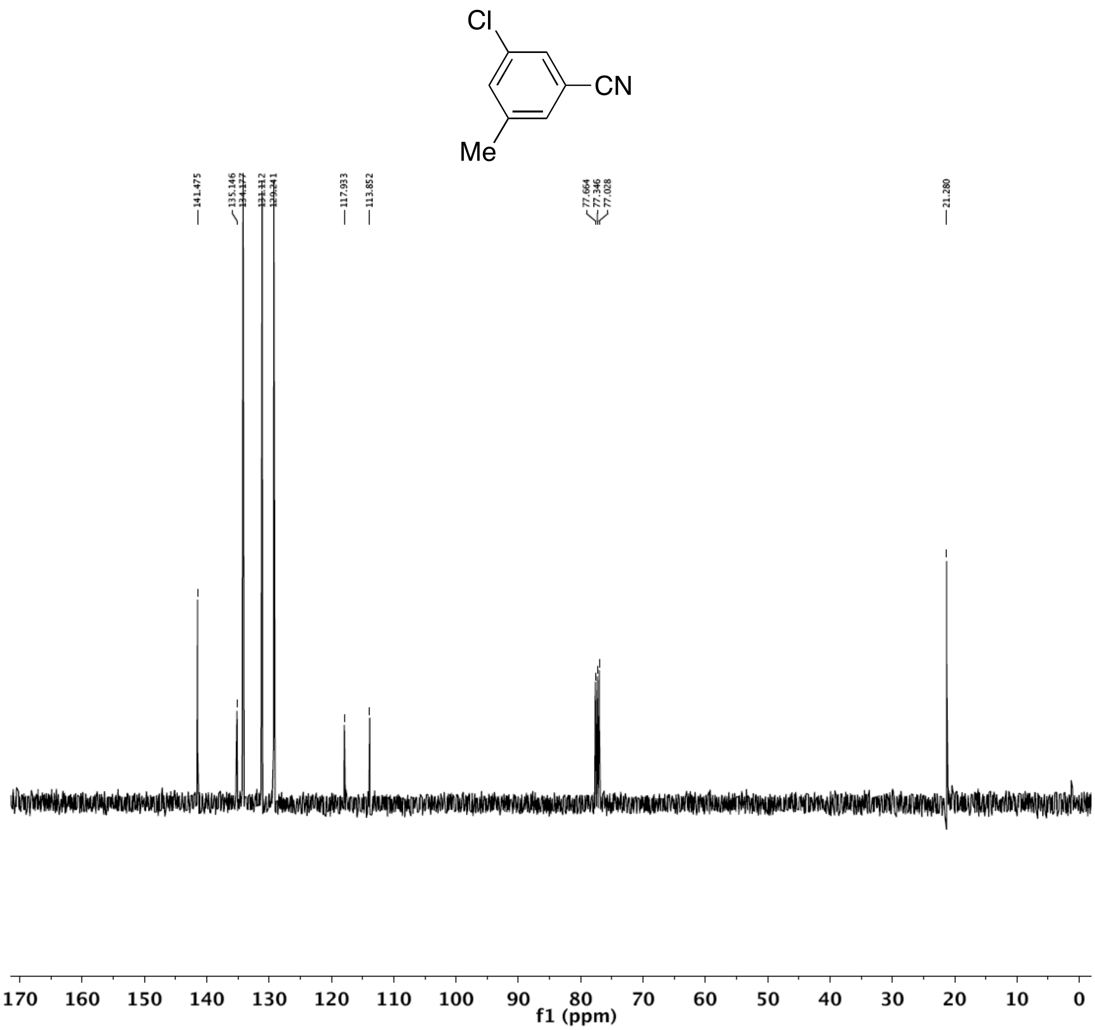
1.0
0.5
f1 (ppm)


Cl
CN
Me
141.475
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134.177
131.112
129.241
117.933
113.852
77.664
77.346
77.028
21.280
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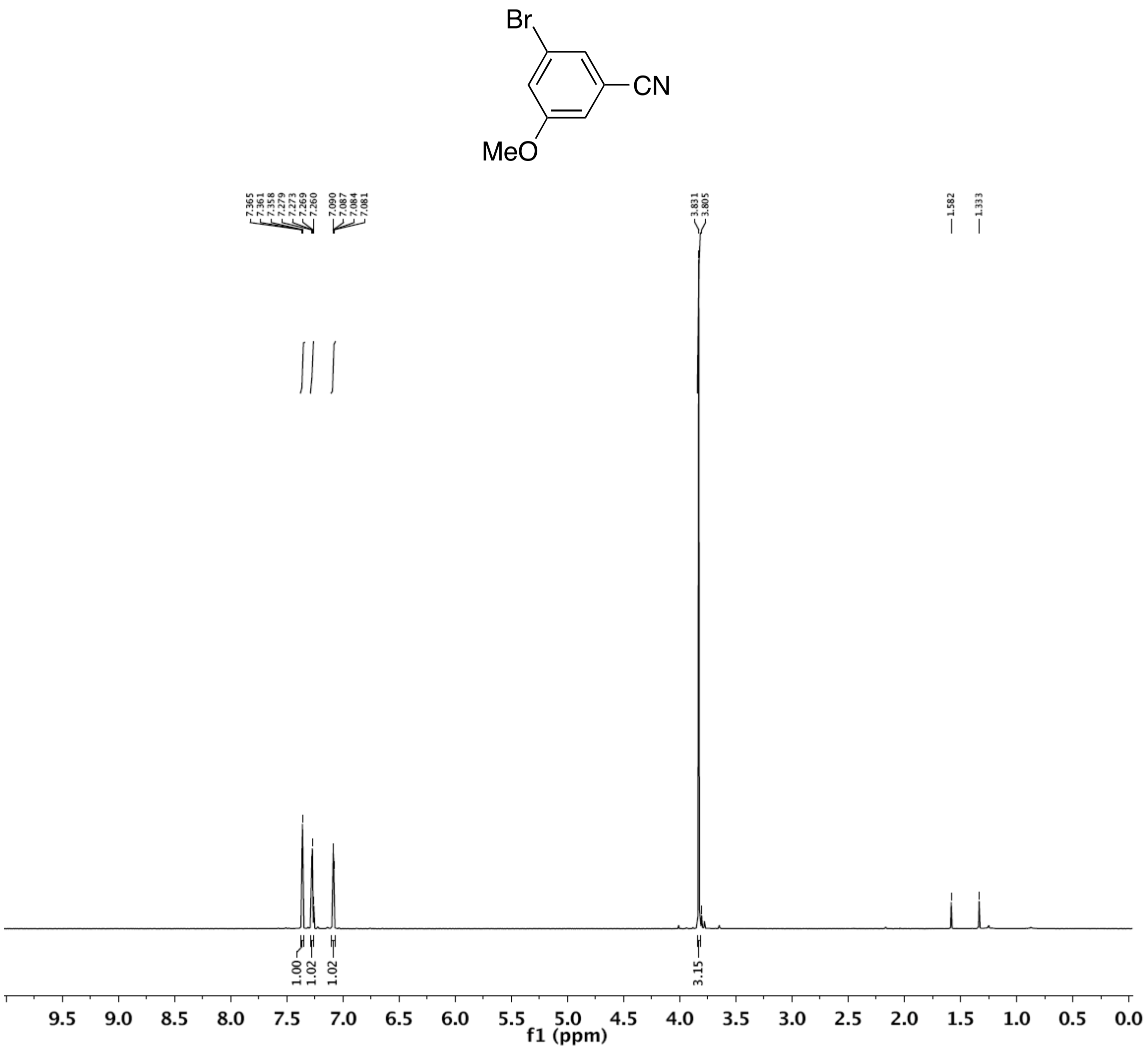
10
0
f1 (ppm)


Br
CN
MeO
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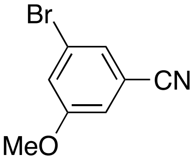
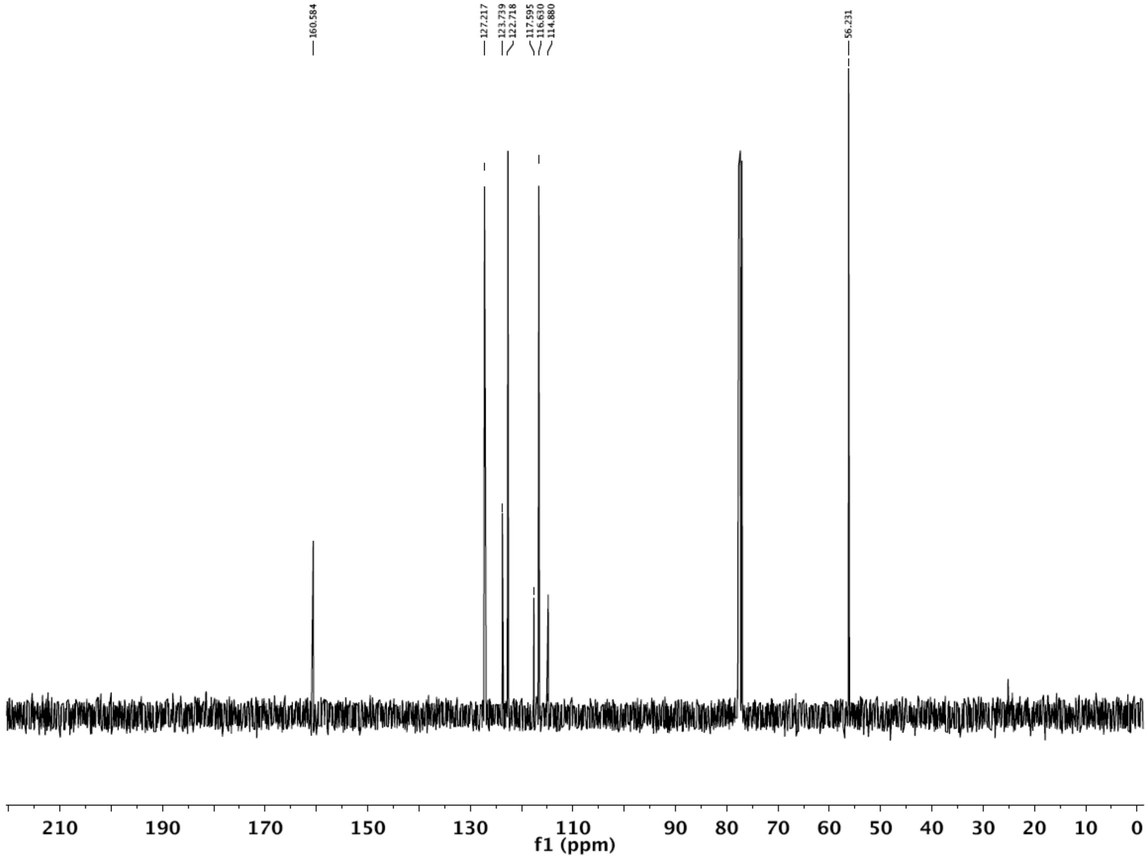
7.361
7.358
7.279
7.273
7.269
7.260
7.090
7.087
7.084
7.081
3.831
3.805
1.582
1.333
1.00
1.02
1.02
3.15
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Br
CN
MeO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127.217
123.739
122.718
117.595
116.630
114.880
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170
150
130
110
90
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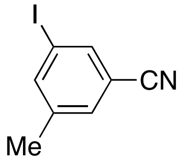
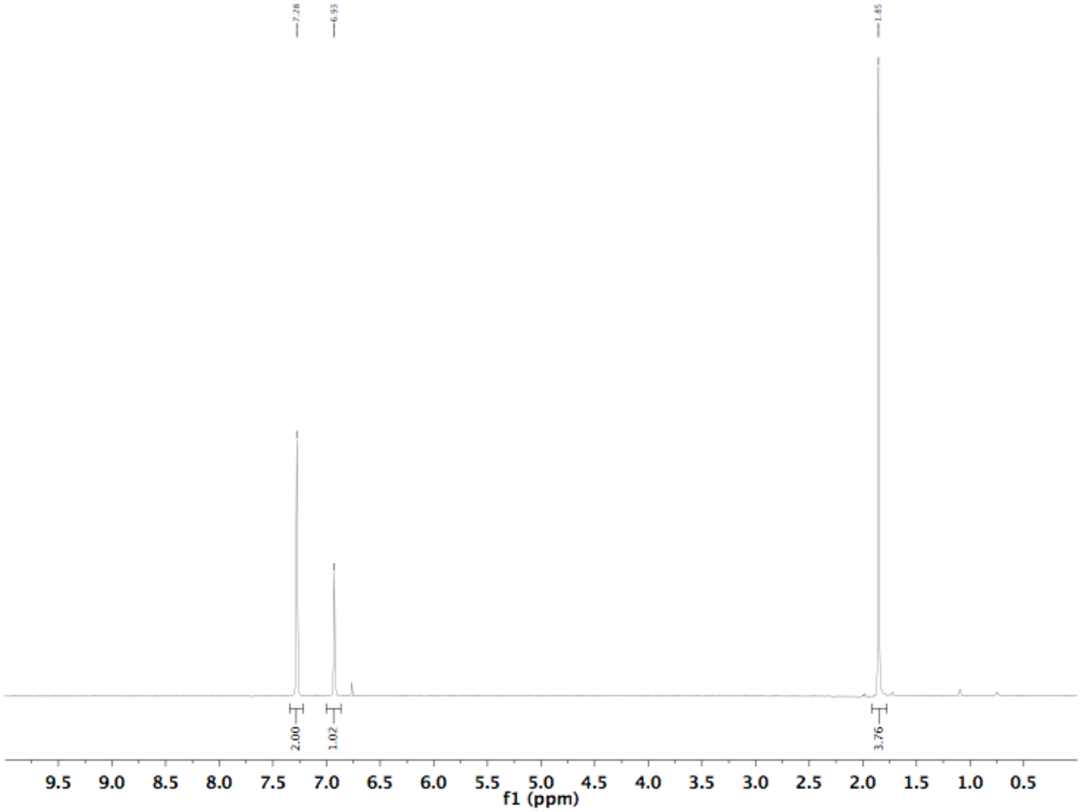
70
60
50
40
30
20
10
0
f1 (ppm)


I
CN
Me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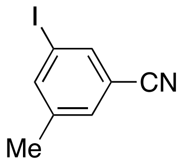
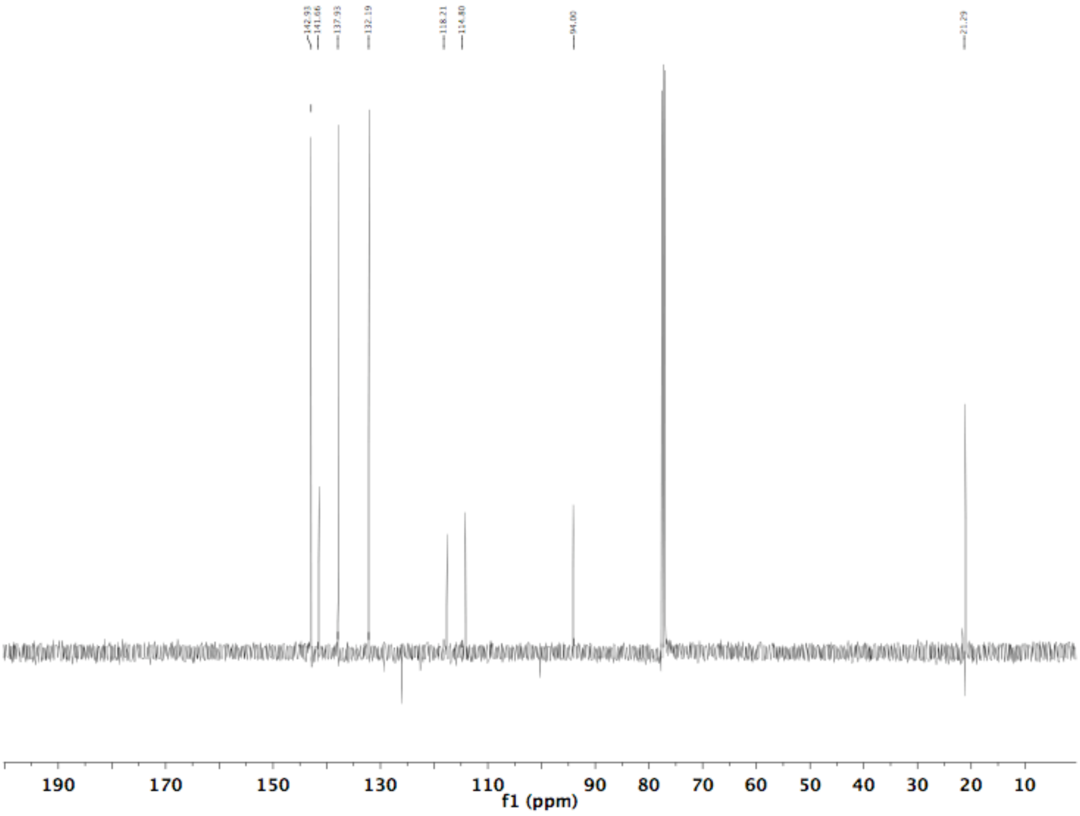
6.93
1.85
2.00
1.02
3.76
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


I
CN
Me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141.66
137.93
132.19
118.21
114.80
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21.29
190
170
150
130
110
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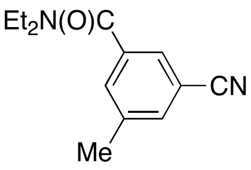
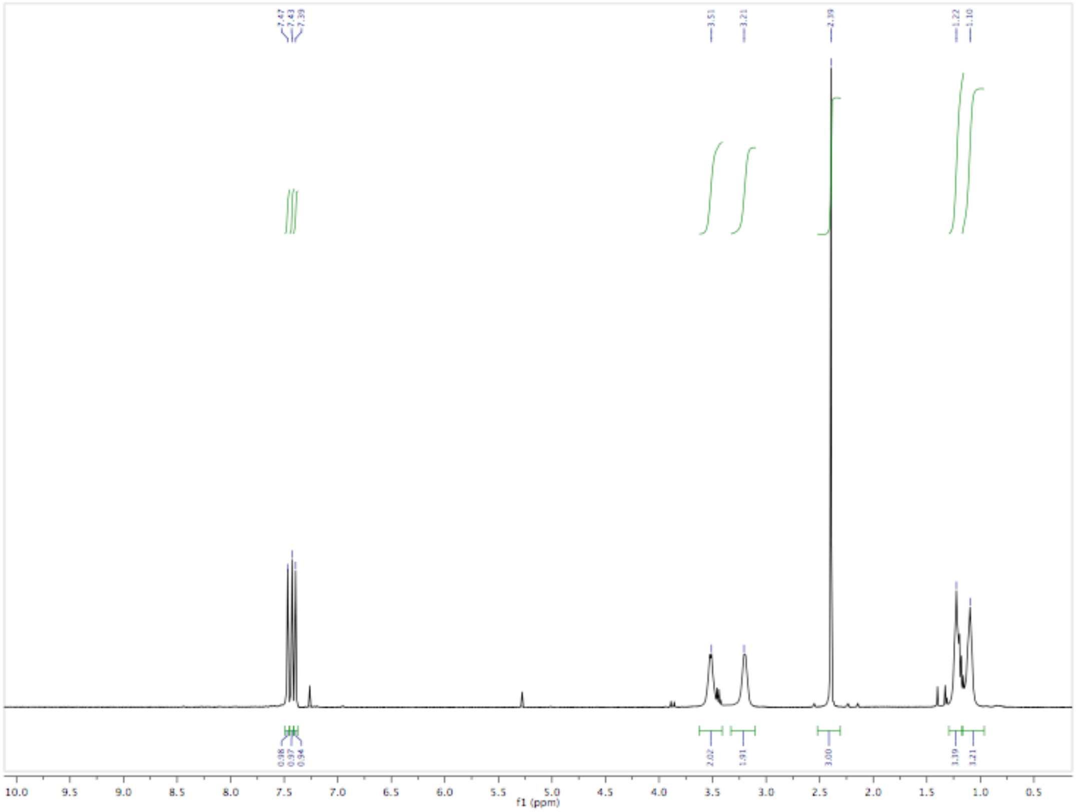
40
30
20
10
f1 (ppm)


Et$_2$N(O)C
CN
Me


7.47
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7.39
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3.21
2.39
1.22
1.10
0.98
0.97
0.94
2.02
1.91
3.00
3.19
3.21
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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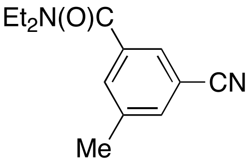
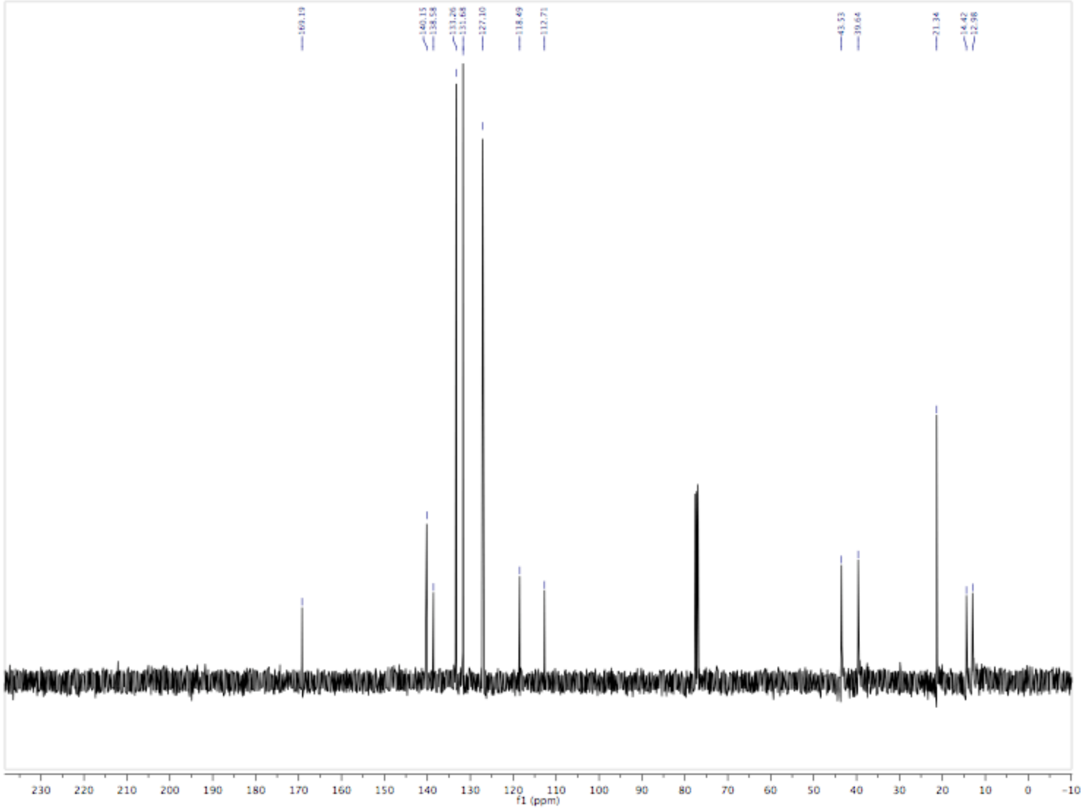
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


Et2N(O)C
CN
Me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138.58
133.26
131.68
127.10
118.49
112.71
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39.64
21.34
14.42
12.98
230
220
210
200
190
180
170
160
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120
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100
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80
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40
30
20
10
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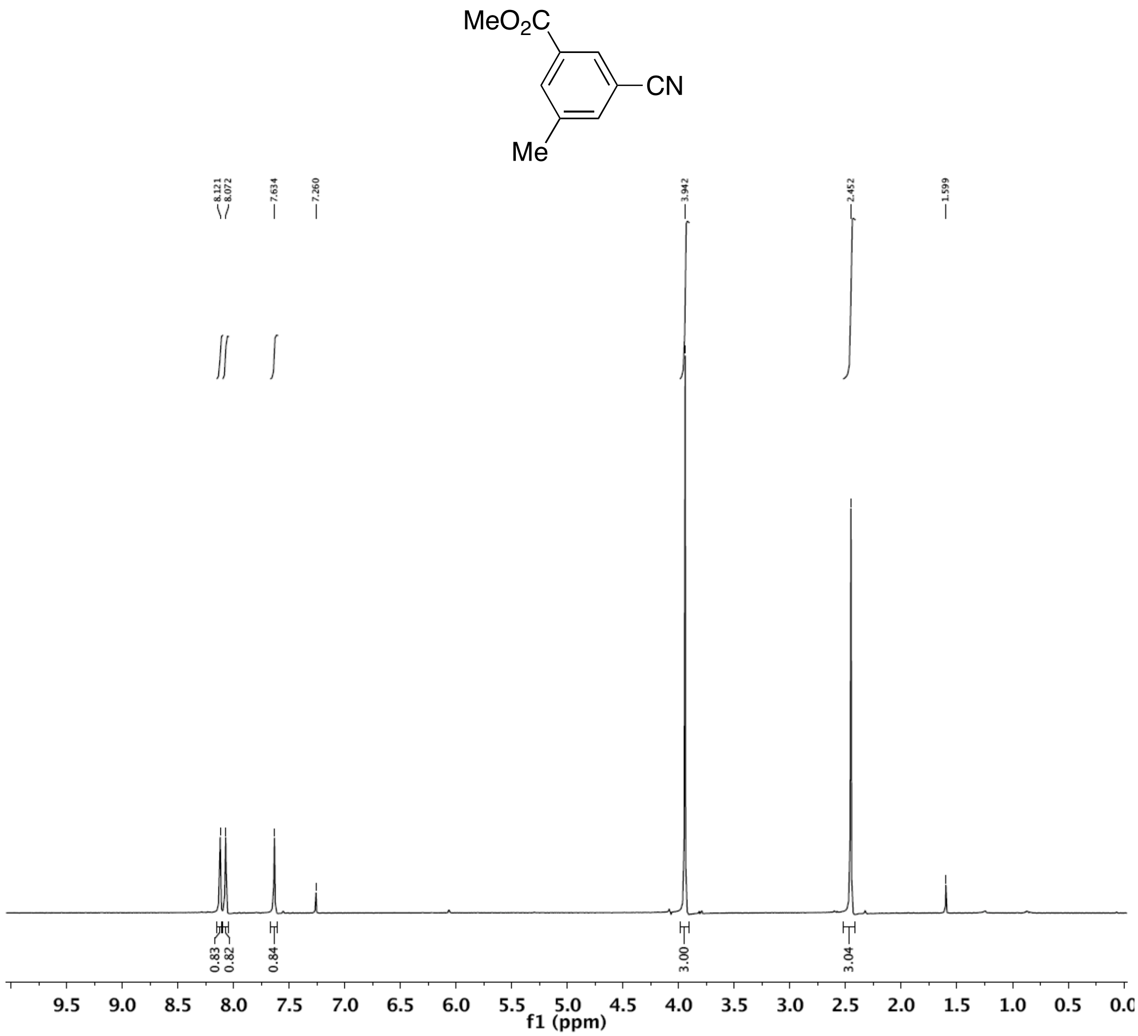
f1 (ppm)


MeO2C
CN
Me
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7.260
3.942
2.452
1.599
0.83
0.82
0.84
3.00
3.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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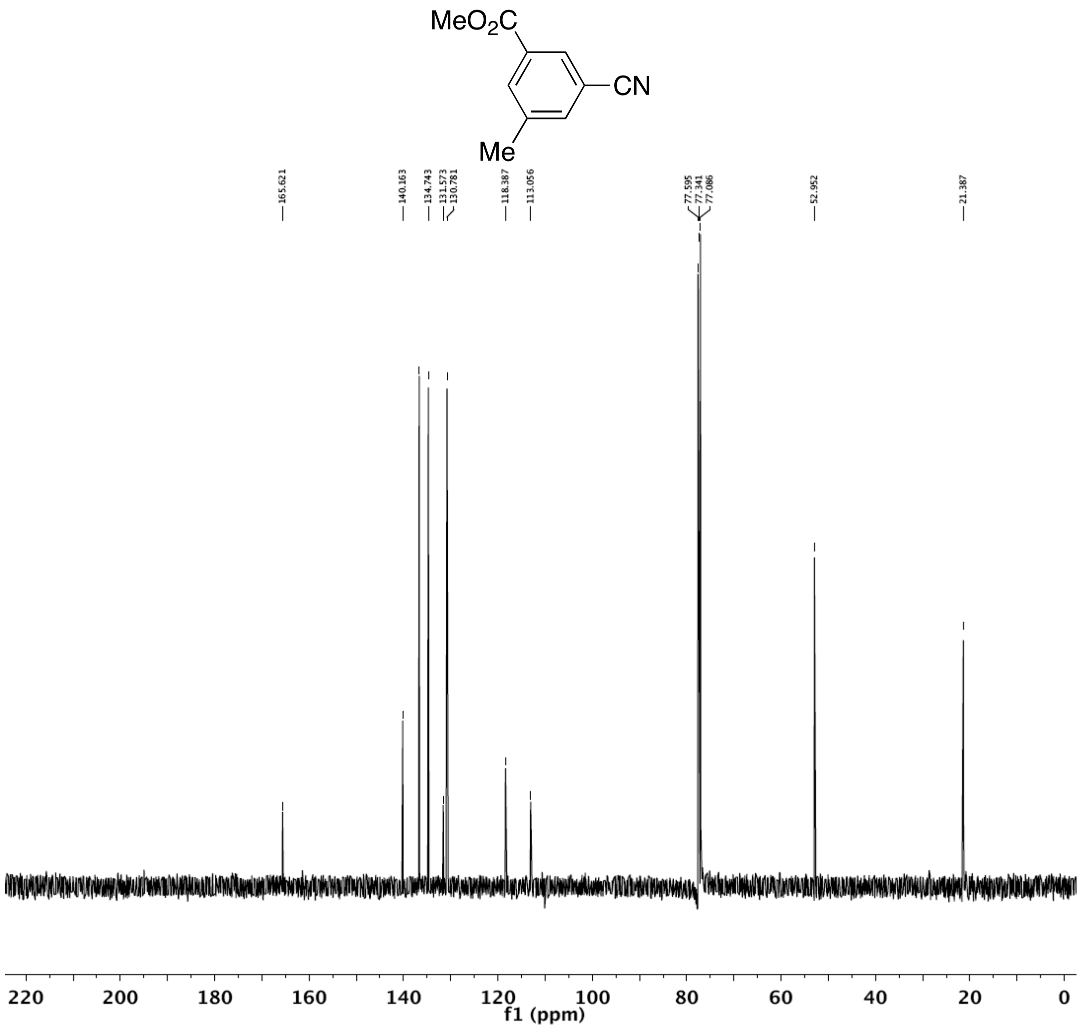
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


MeO2C
CN
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113.056
77.595
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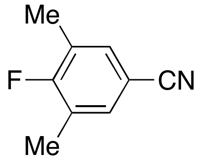
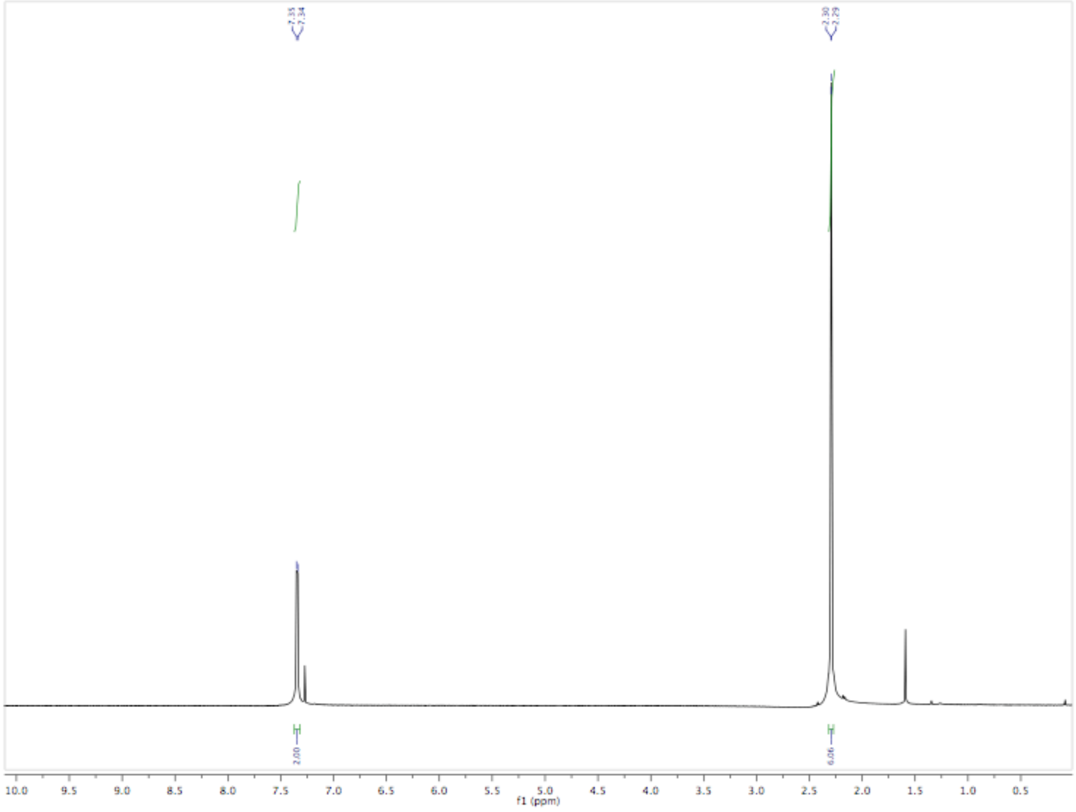
f1 (ppm)


Me
F
CN
Me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9.0
8.5
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7.5
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6.5
6.0
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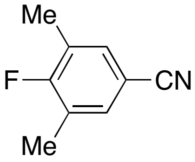
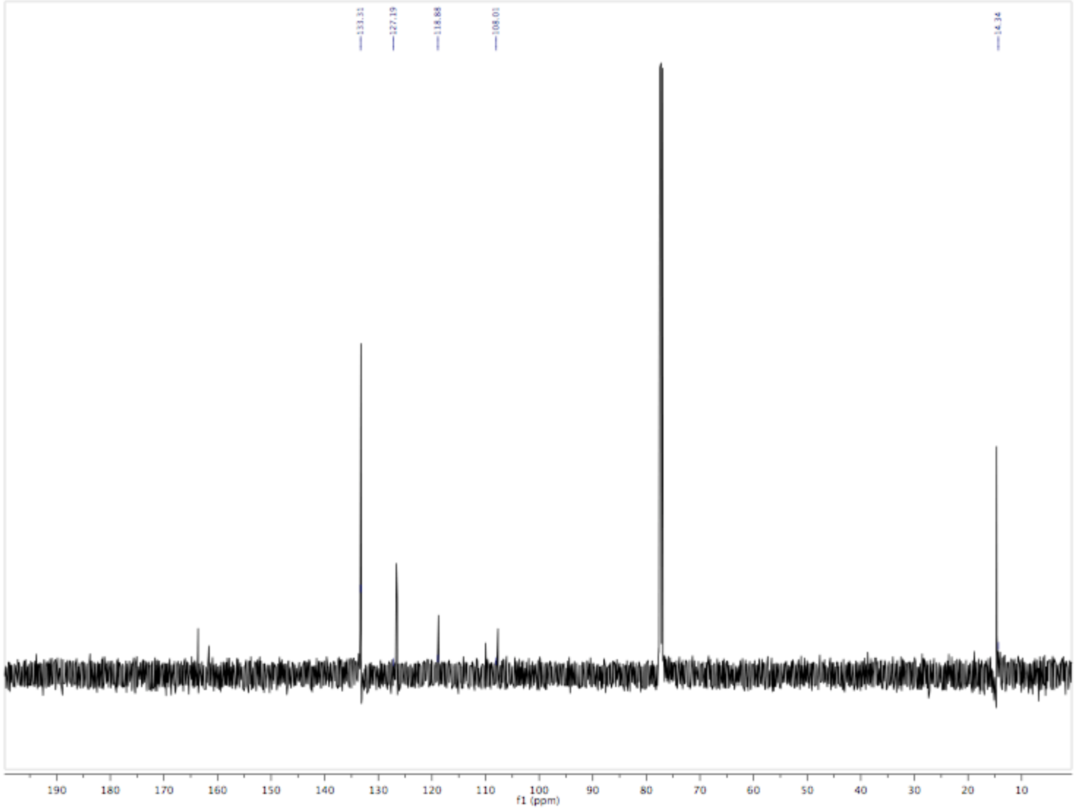
1.5
1.0
0.5
f1 (ppm)


Me
F
CN
Me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127.19
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108.01
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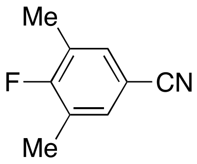
f1 (ppm)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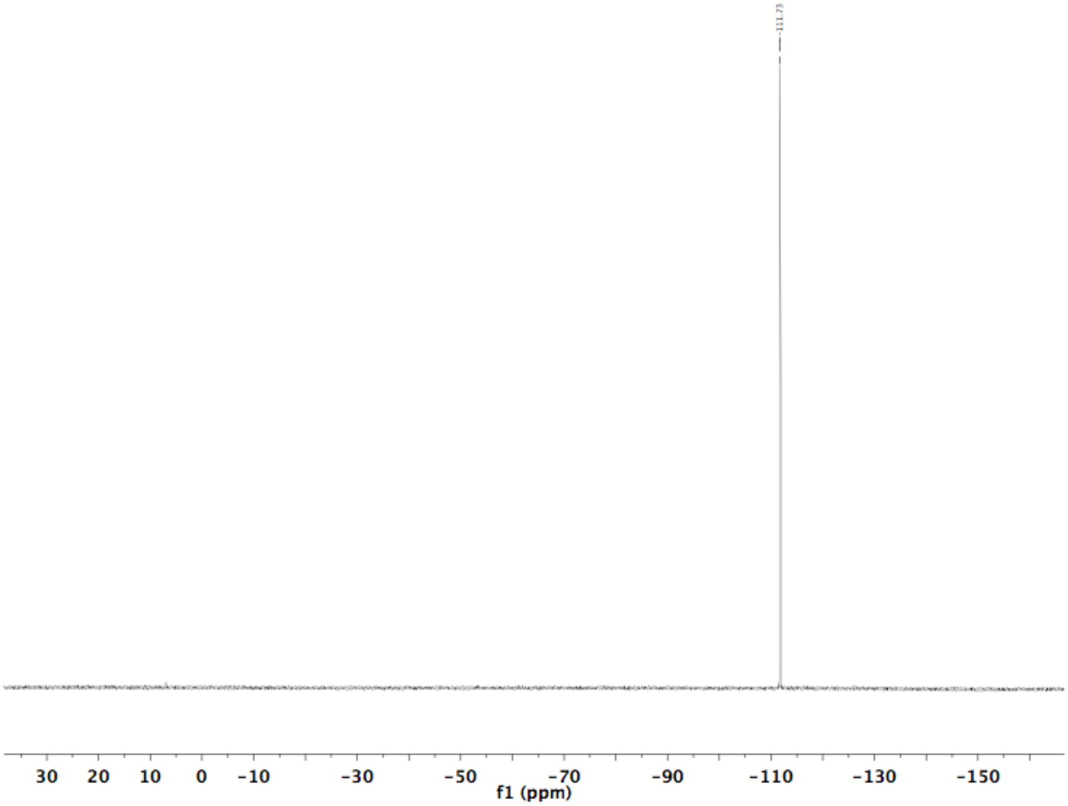
F
CN
Me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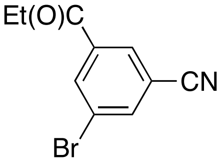
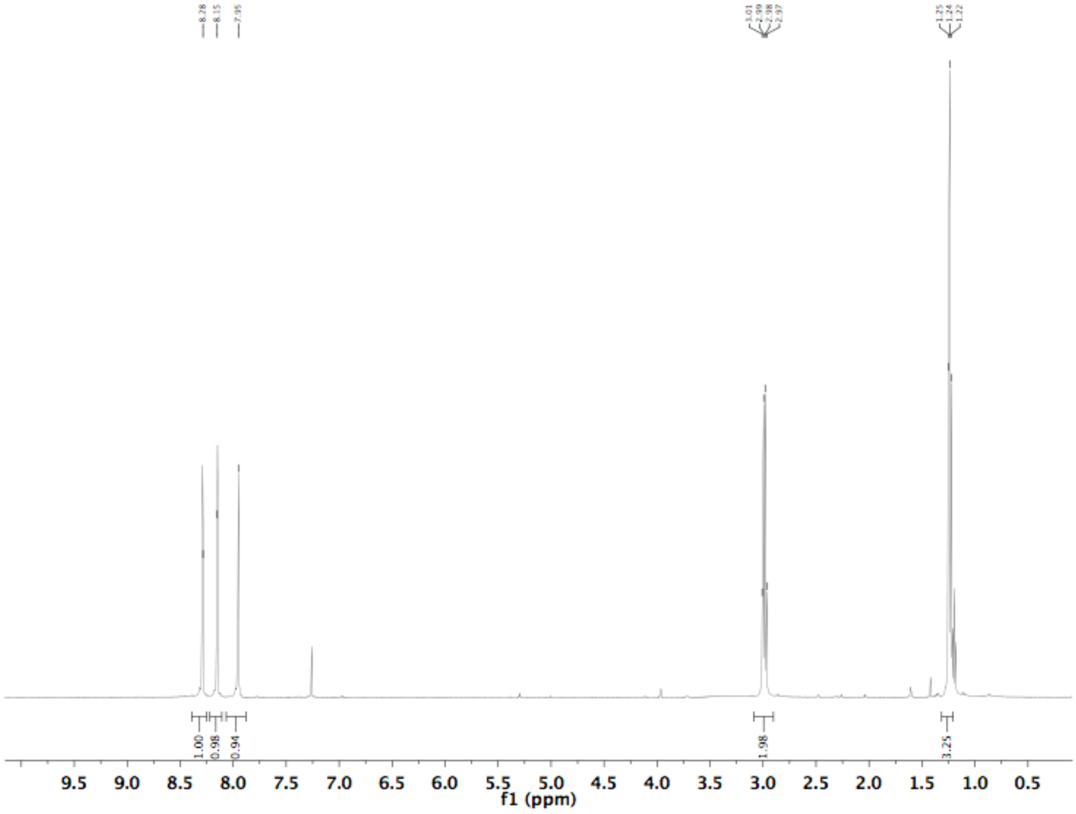
f1 (ppm)


Et(O)C
CN
Br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2.98
2.97
1.25
1.24
1.22
1.00
0.98
0.94
1.98
3.25
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
3.5
3.0
2.5
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1.5
1.0
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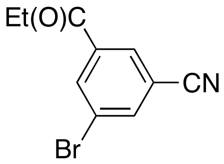
f1 (ppm)


Et(O)C
CN
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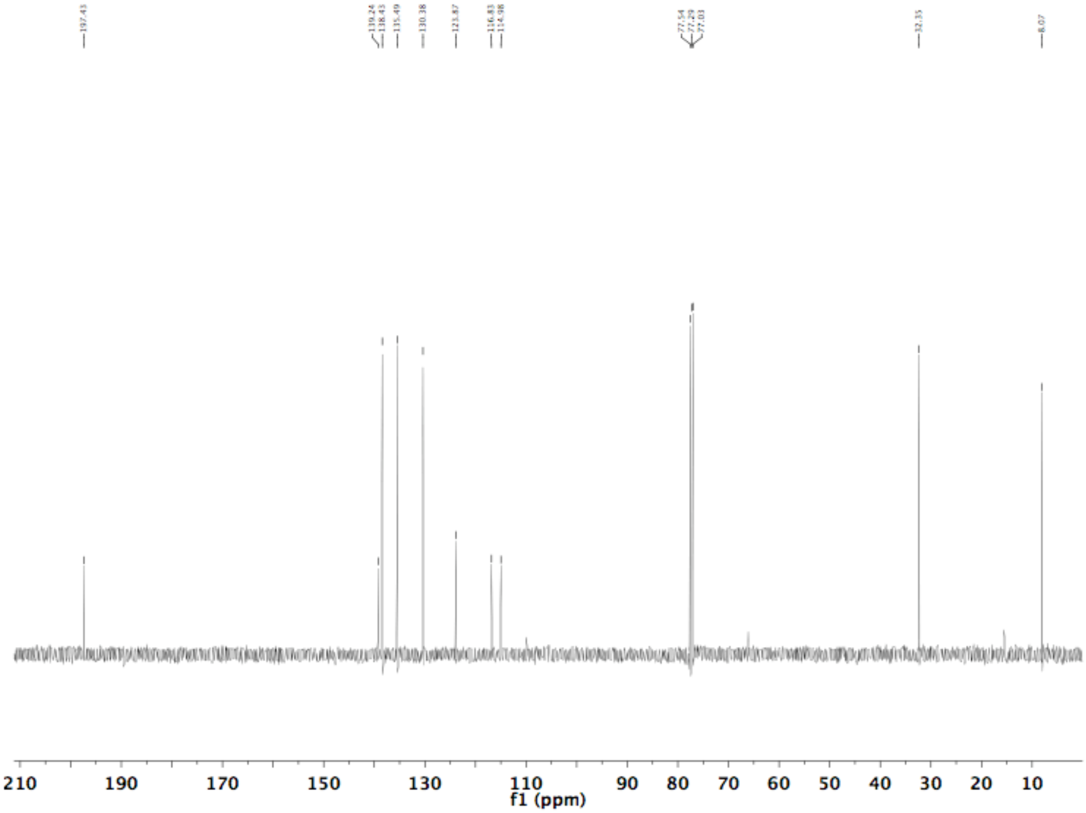
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114.98
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77.29
77.03
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190
170
150
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110
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20
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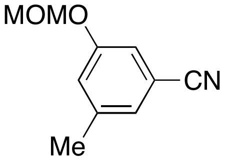
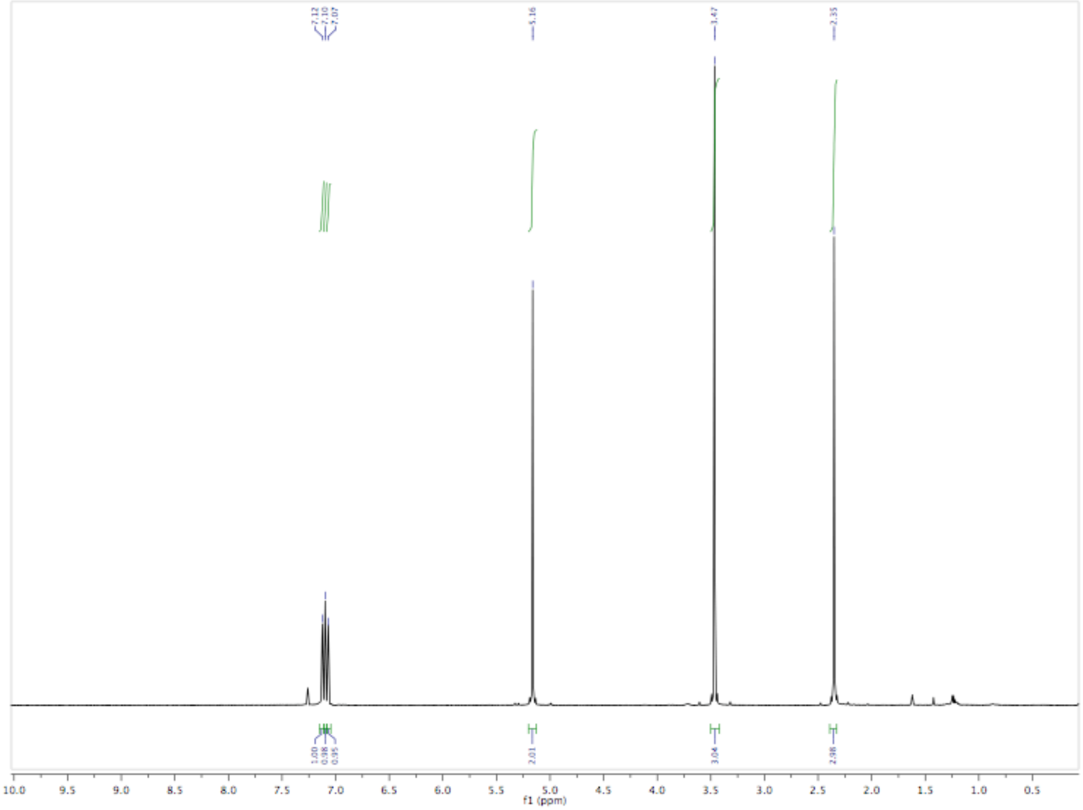
f1 (ppm)


MOMO
CN
Me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0.95
2.01
3.04
2.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
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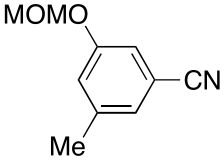
f1 (ppm)


MOMO
CN
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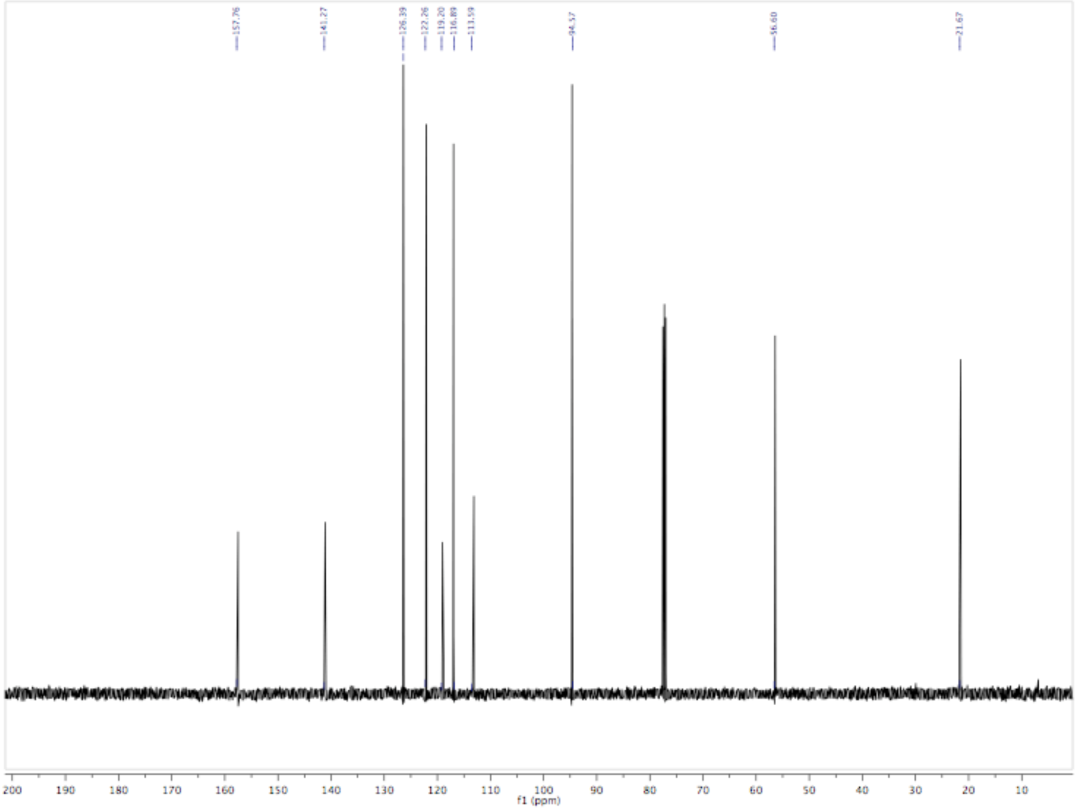
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122.26
119.20
116.89
113.59
94.57
56.60
21.67
200
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150
140
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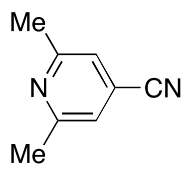
20
10
f1 (ppm)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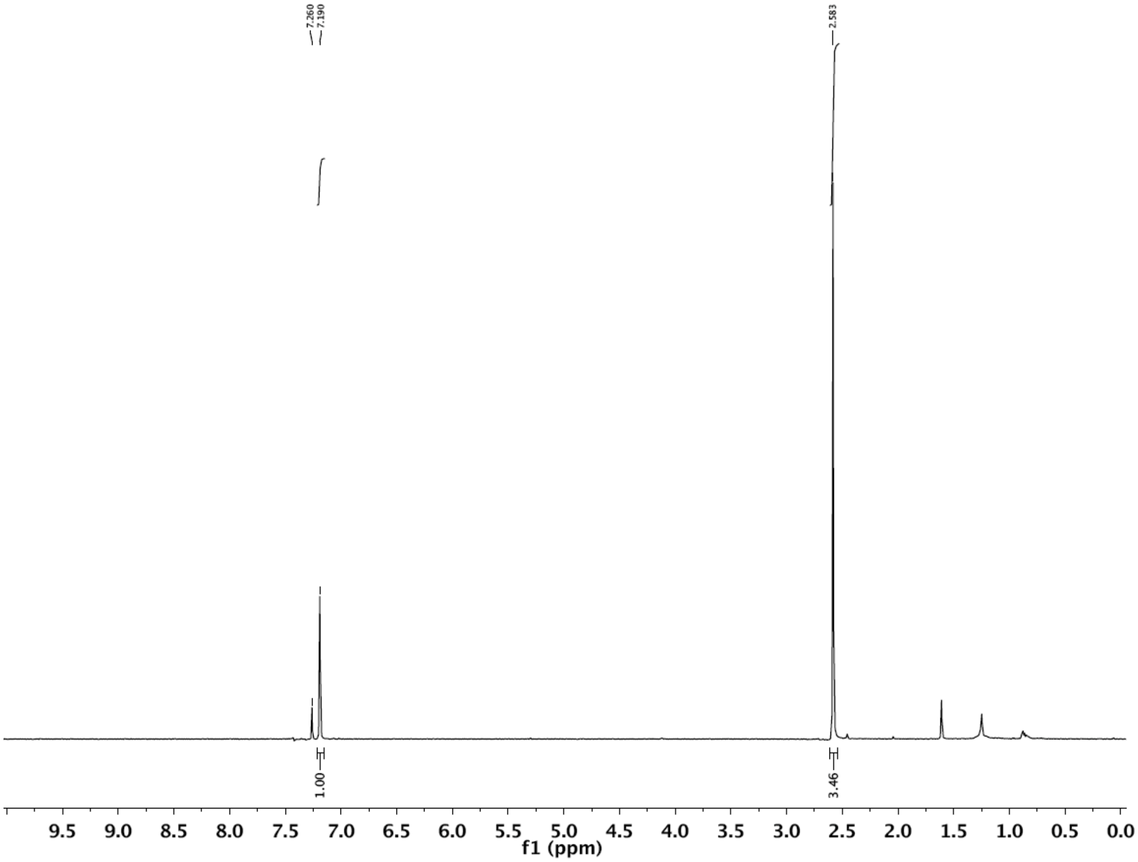
Me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6.0
5.5
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2.5
2.0
1.5
1.0
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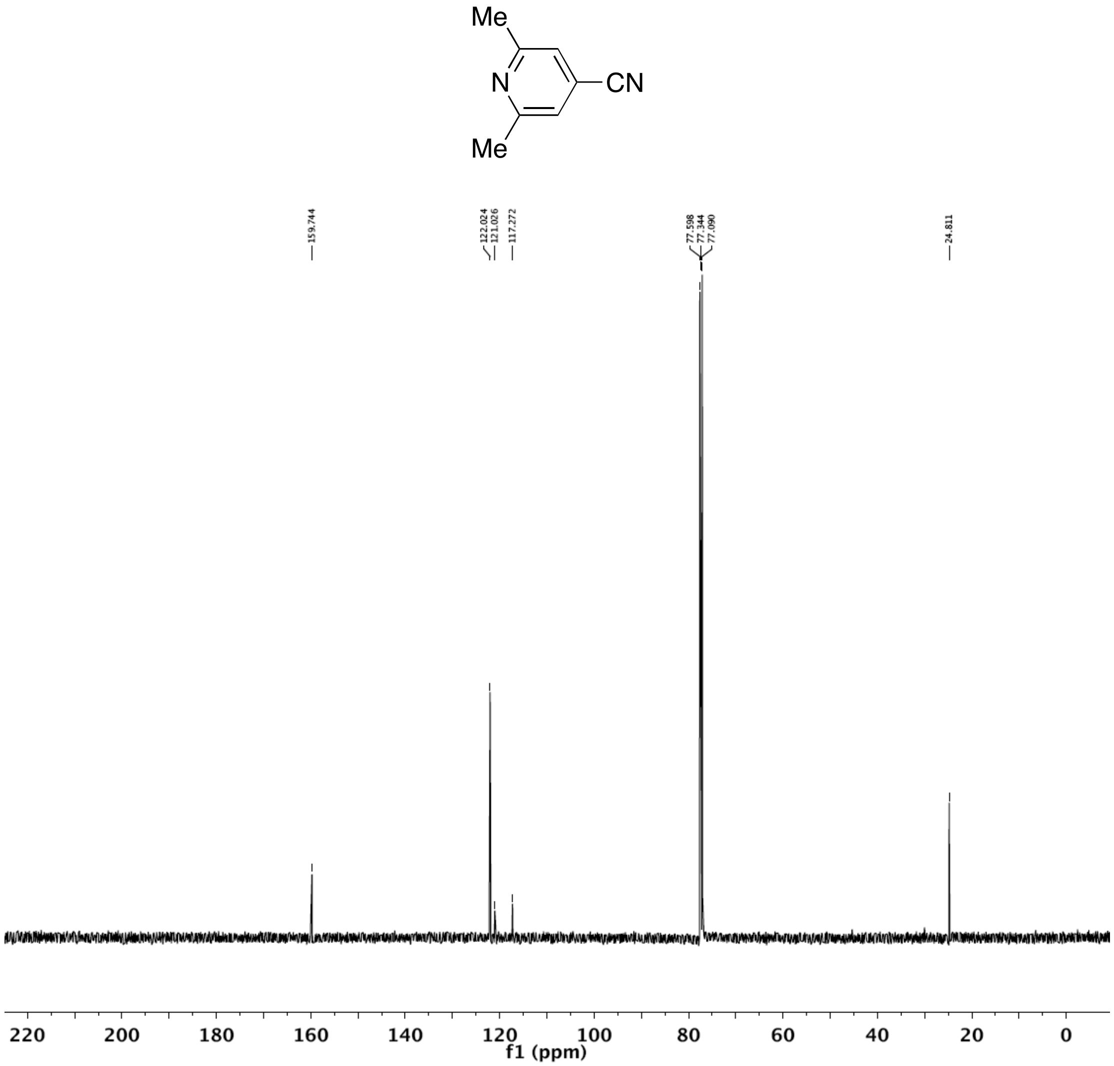
0.0
f1 (ppm)


Me
N
CN
Me
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117.272
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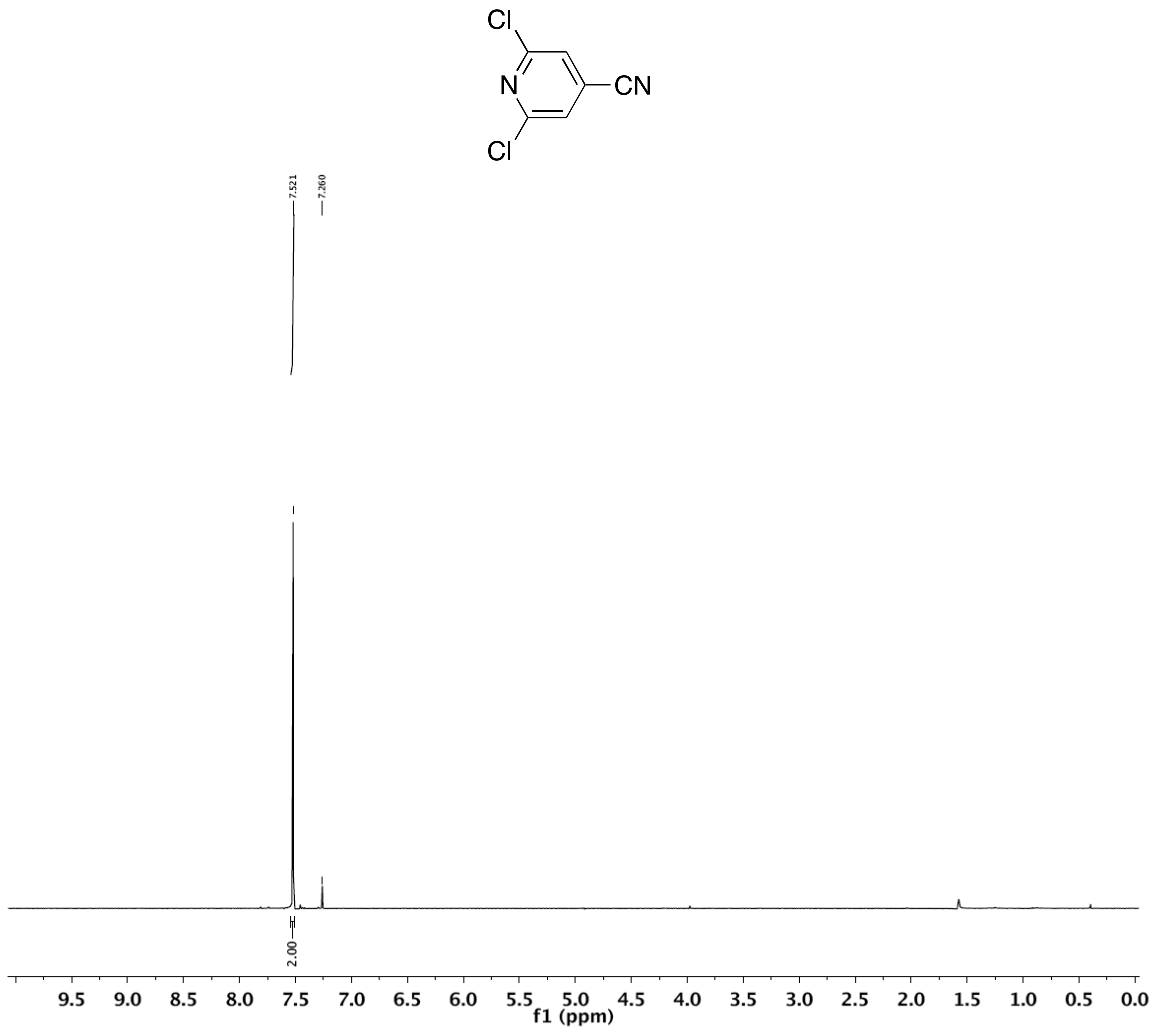
f1 (ppm)


Cl
N
CN
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2.00
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8.5
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7.5
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6.5
6.0
5.5
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1.0
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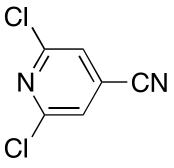
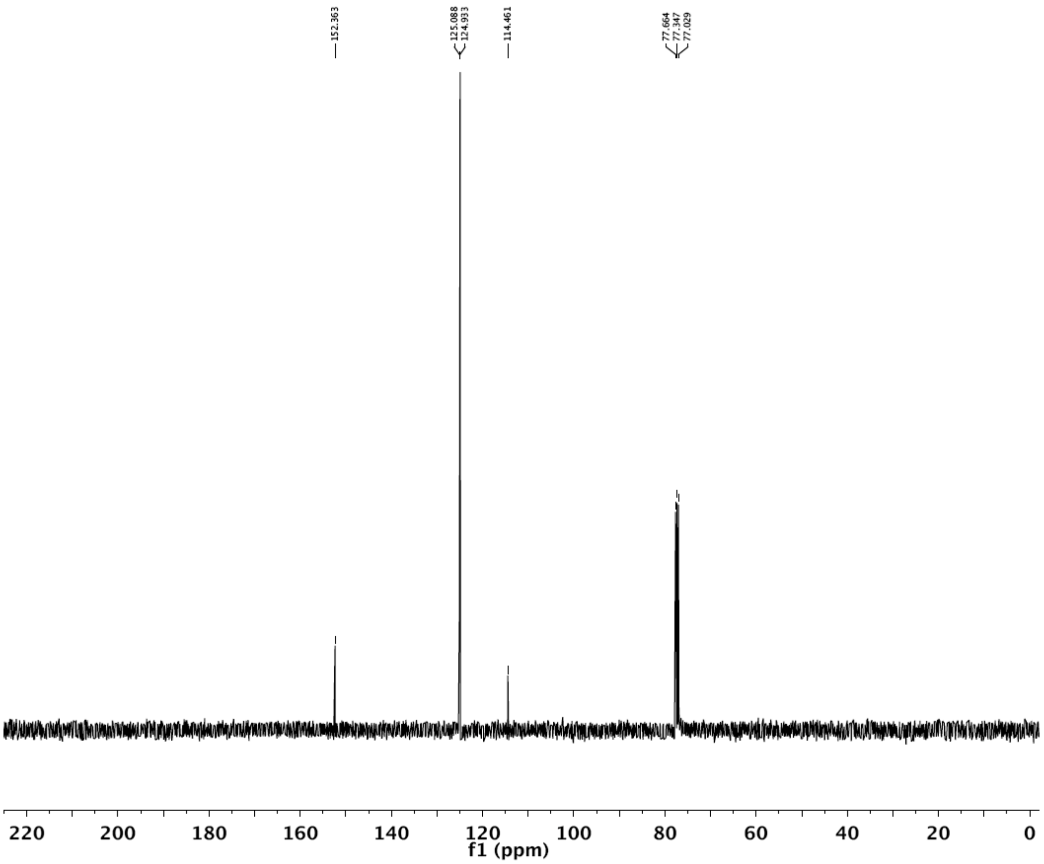
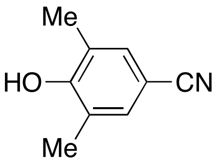
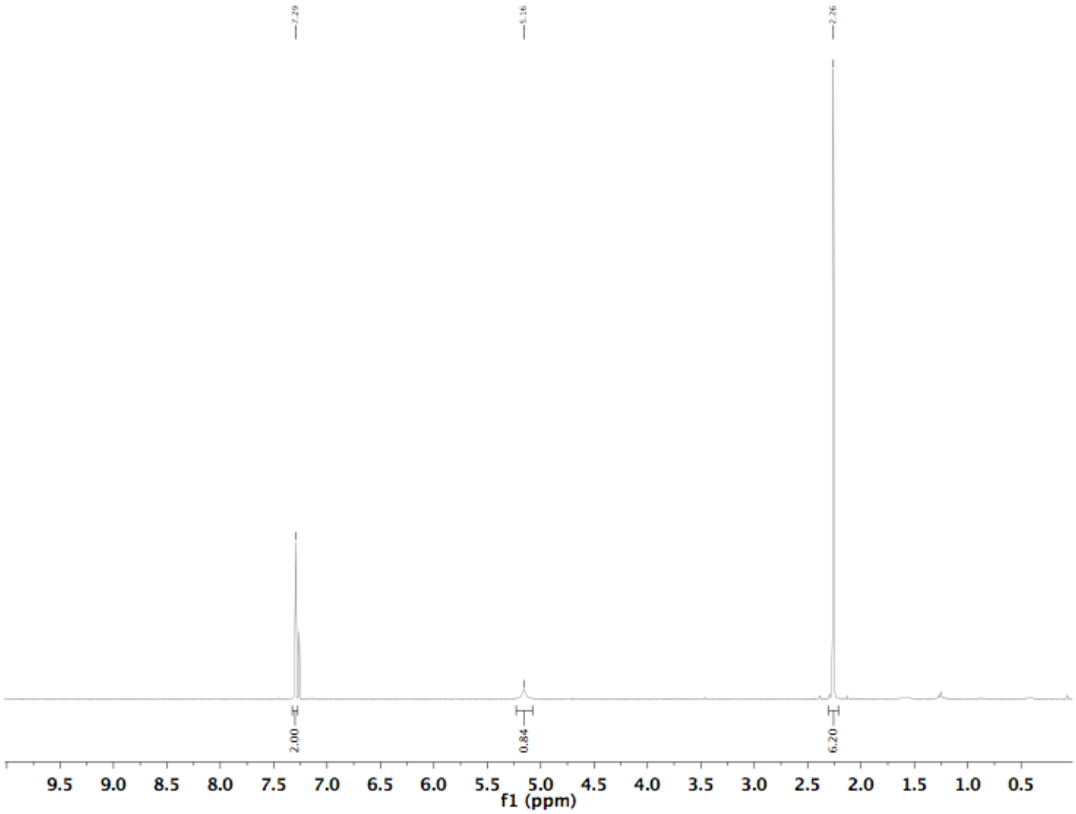
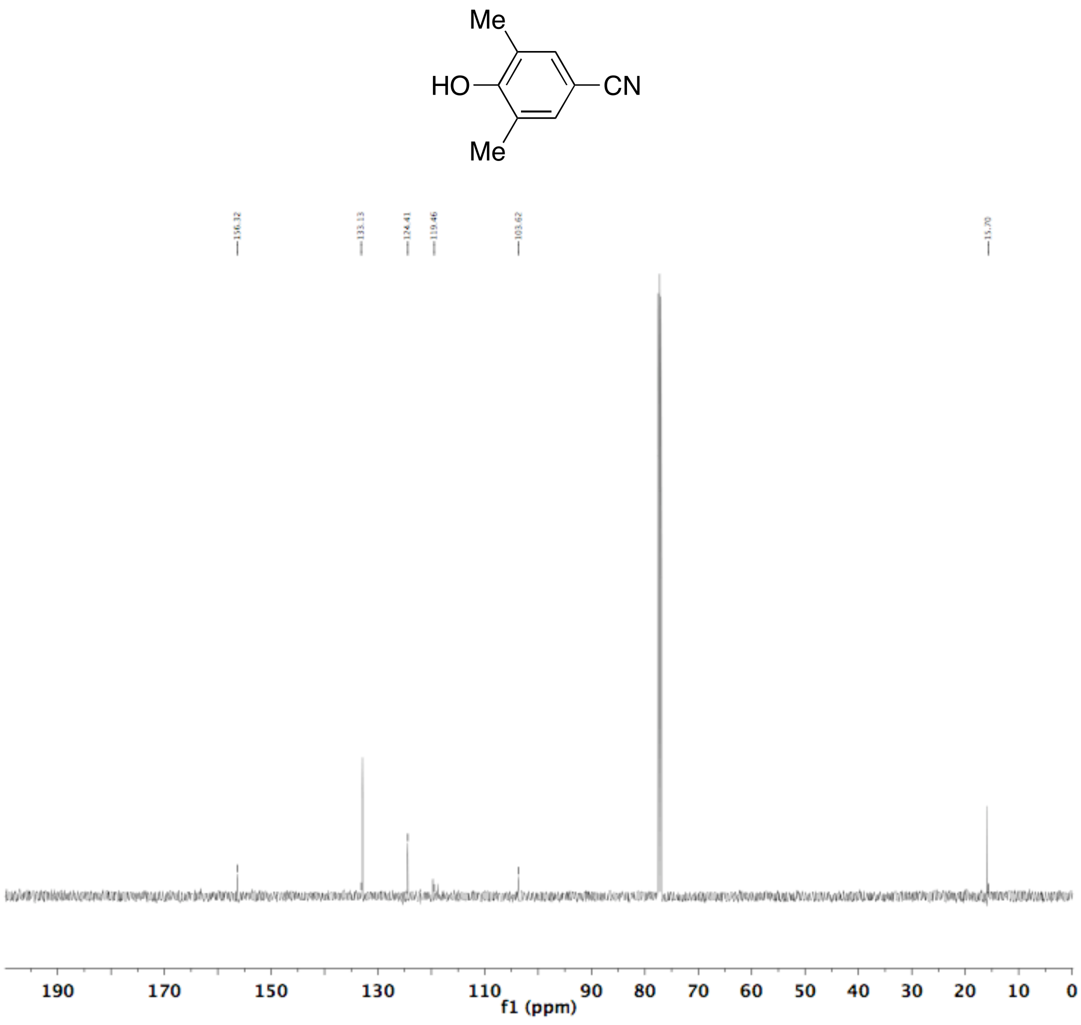
0.0
f1 (ppm)

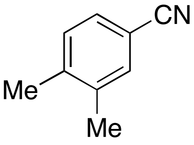

Cl
N
CN
Cl

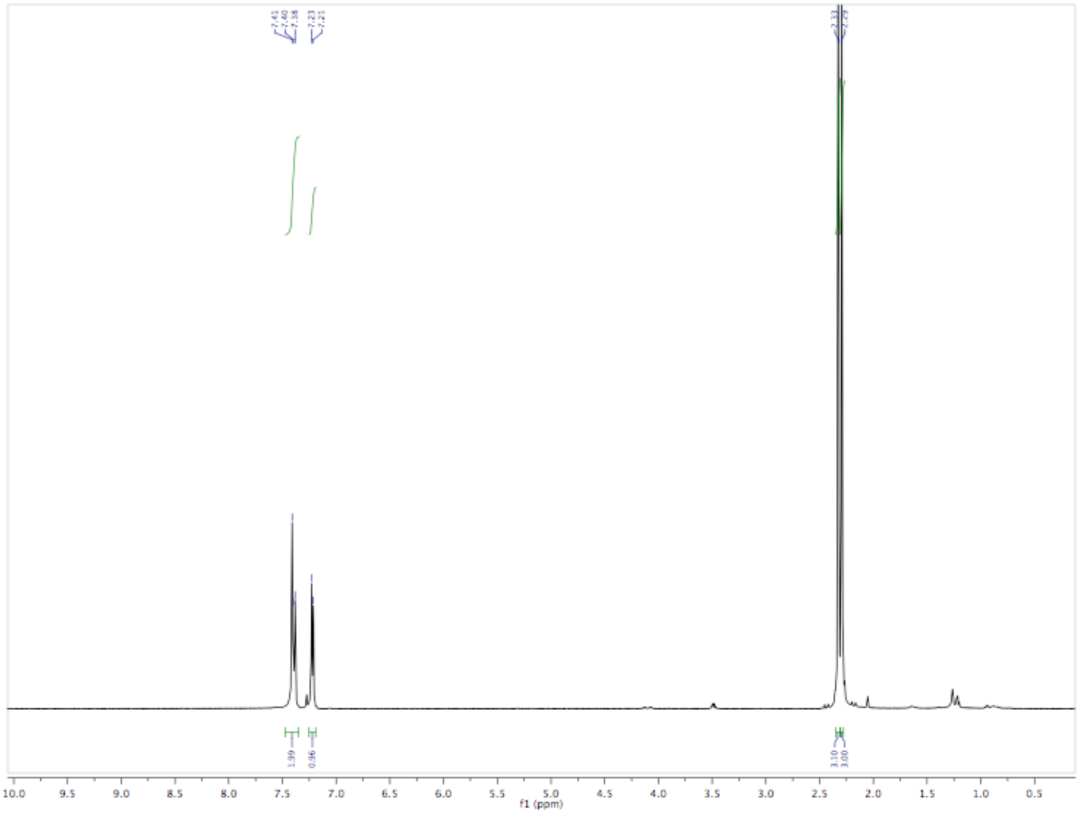

152.363
125.088
124.933
114.461
77.664
77.347
77.029
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

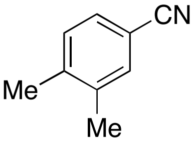

Me
HO
CN
Me

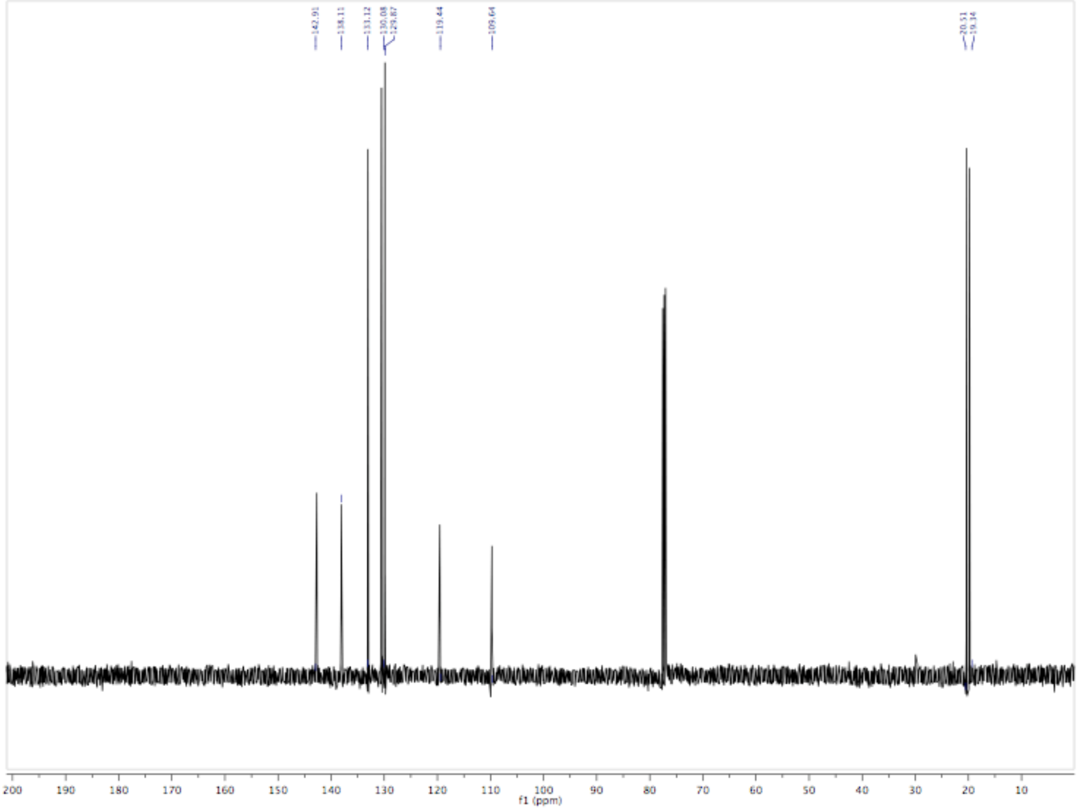

7.29
5.16
2.26
2.00
0.84
6.20
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

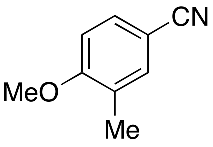

Me
HO
CN
Me
156.32
133.13
124.41
119.46
103.62
15.70
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

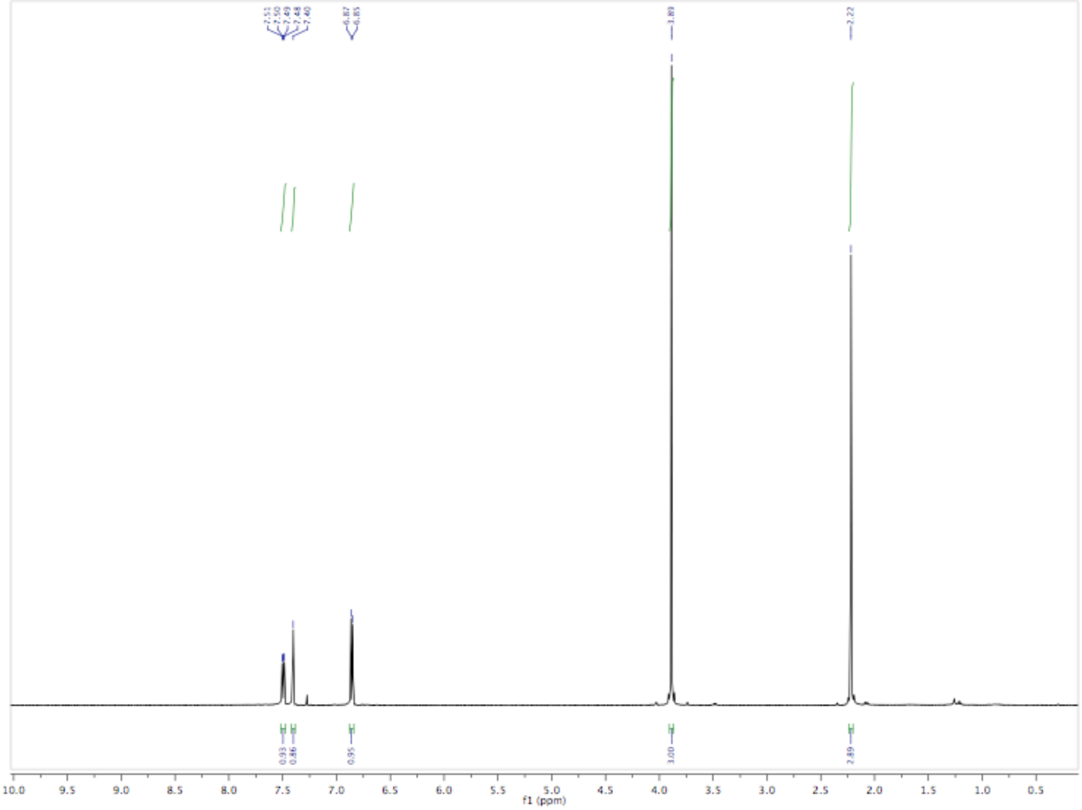

CN
Me
Me

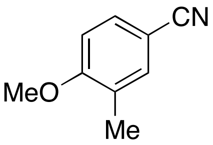

7.41
7.40
7.38
7.23
7.21
2.33
2.29
1.99
0.96
3.10
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

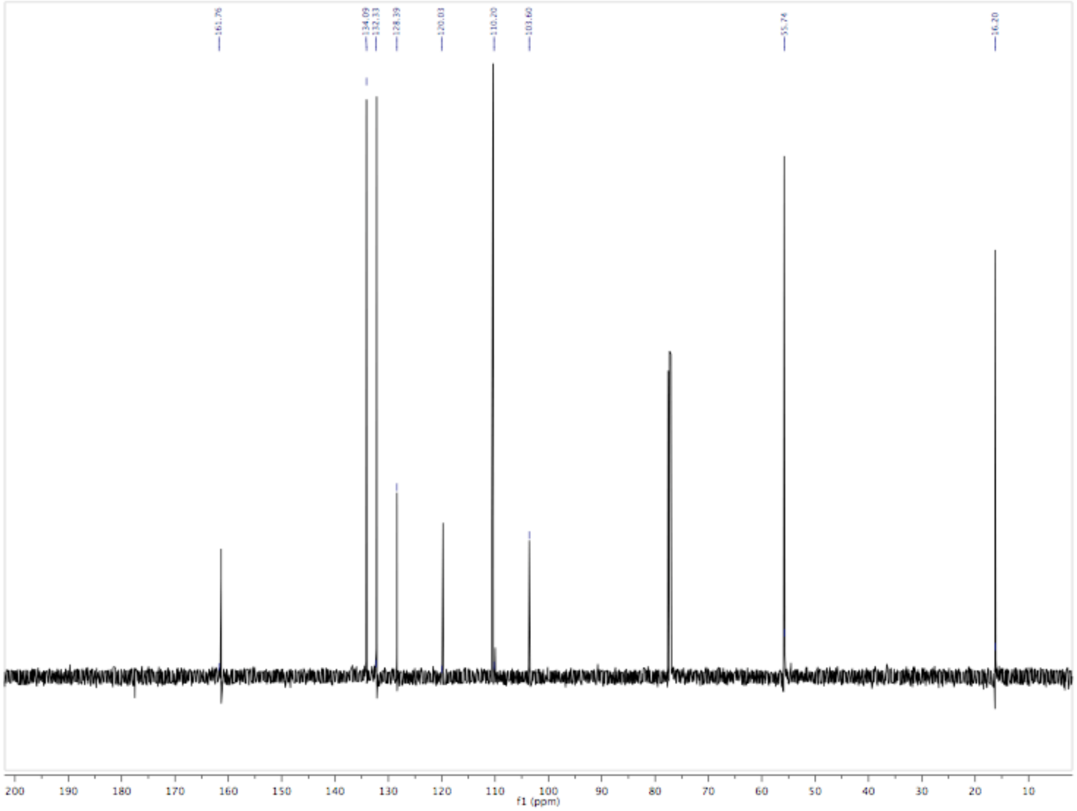

CN
Me
Me

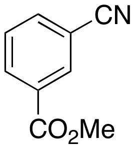

142.91
138.11
133.12
130.08
129.87
119.44
109.64
20.51
19.34
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

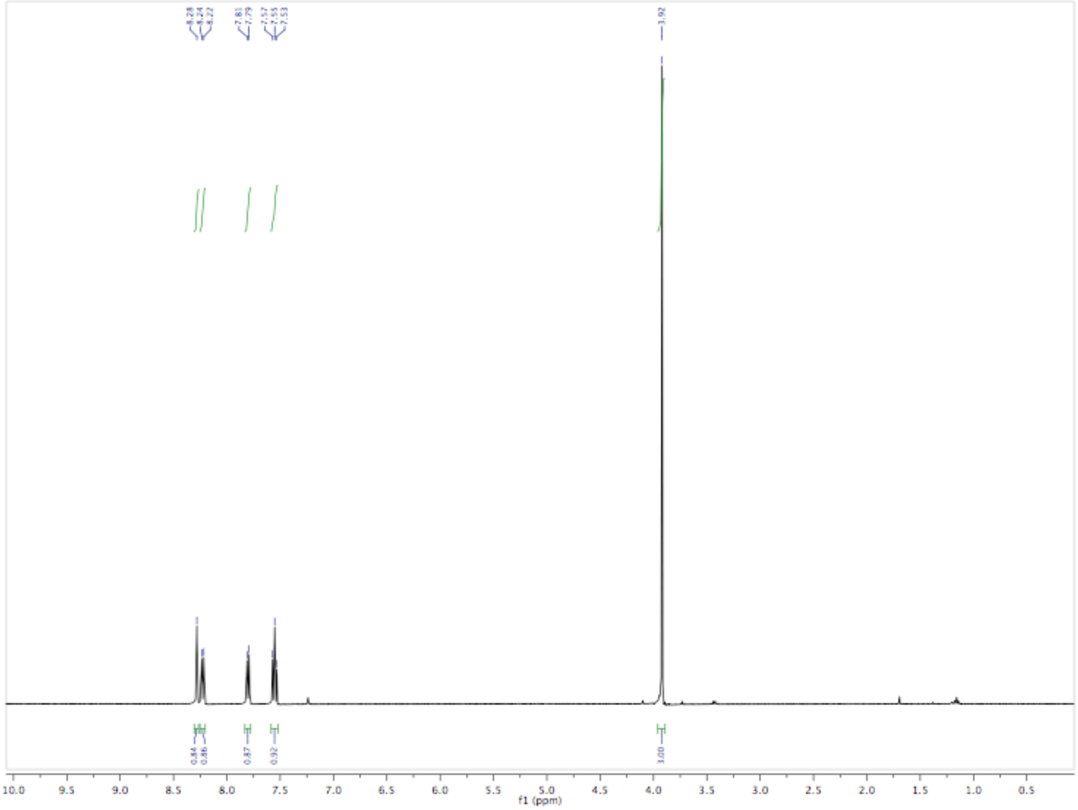

CN
MeO
Me

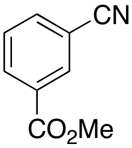

7.51
7.50
7.49
7.48
7.40
6.87
6.85
3.89
2.22
0.93
0.86
0.95
3.00
2.89
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

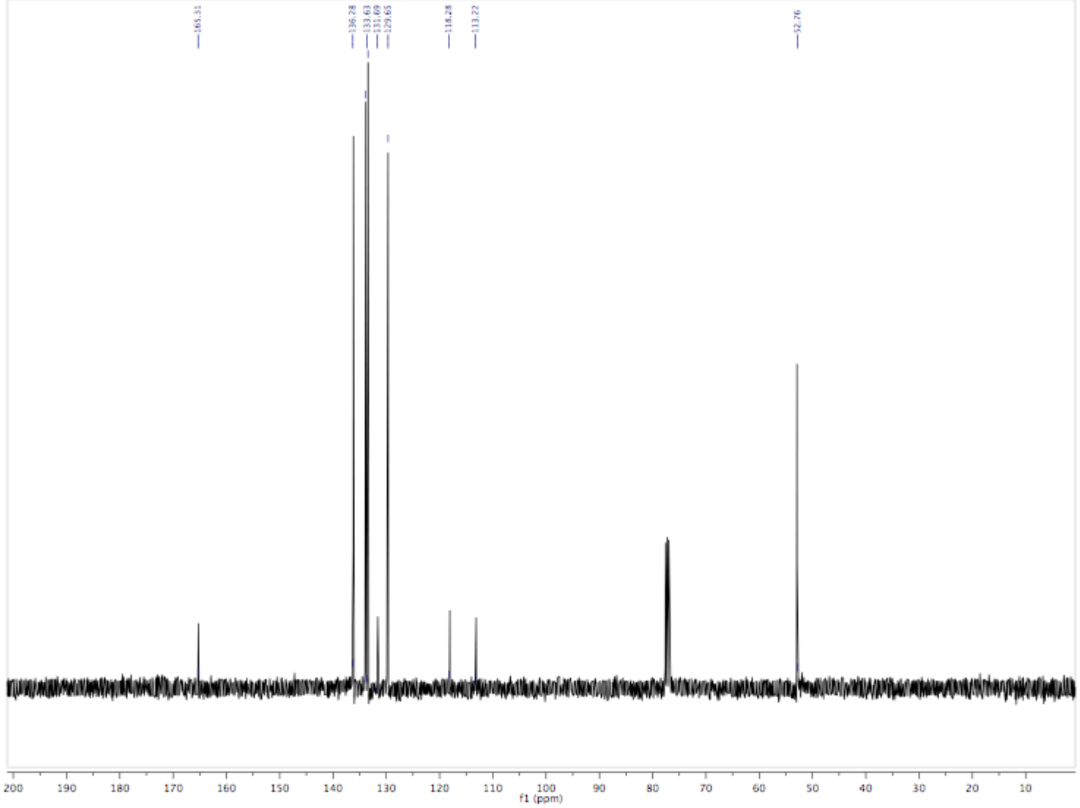

CN
MeO
Me

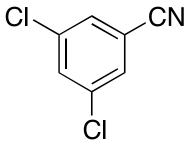

161.76
134.09
132.33
128.39
120.03
110.20
103.60
55.74
16.20
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

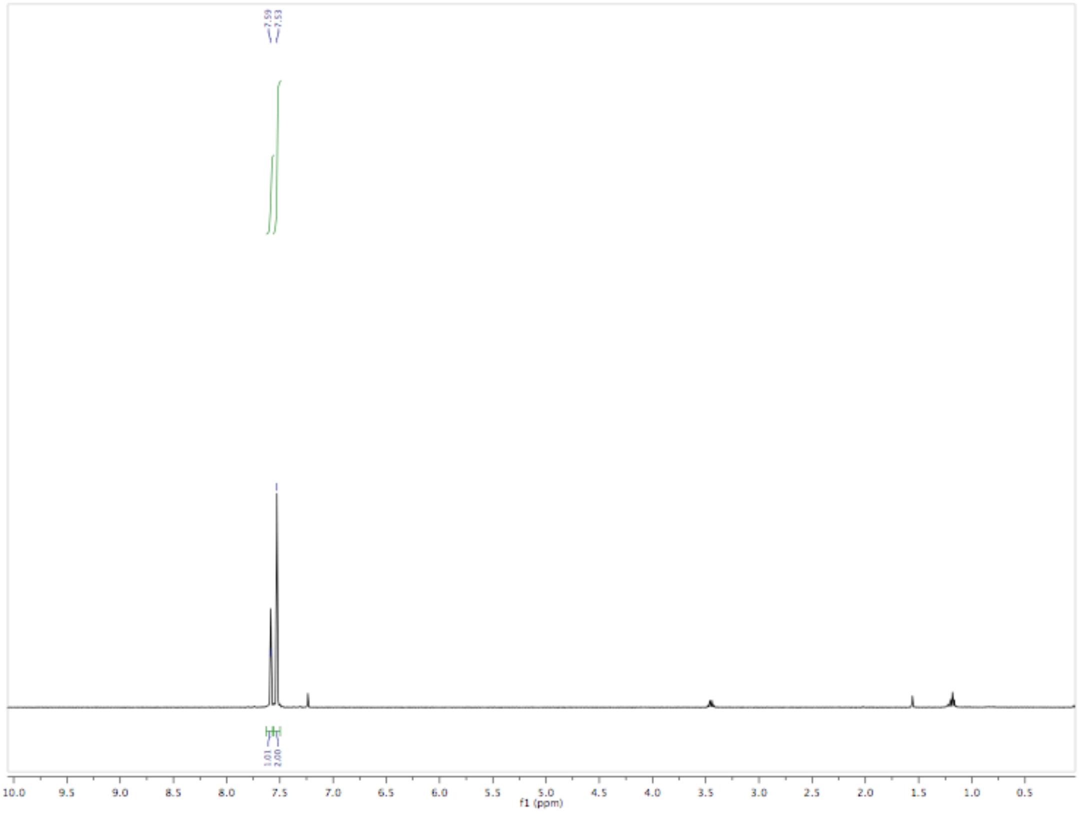

CN
CO$_2$Me

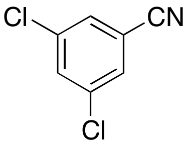

8.28
8.24
8.22
7.81
7.79
7.57
7.55
7.53
3.92
0.84
0.86
0.87
0.92
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

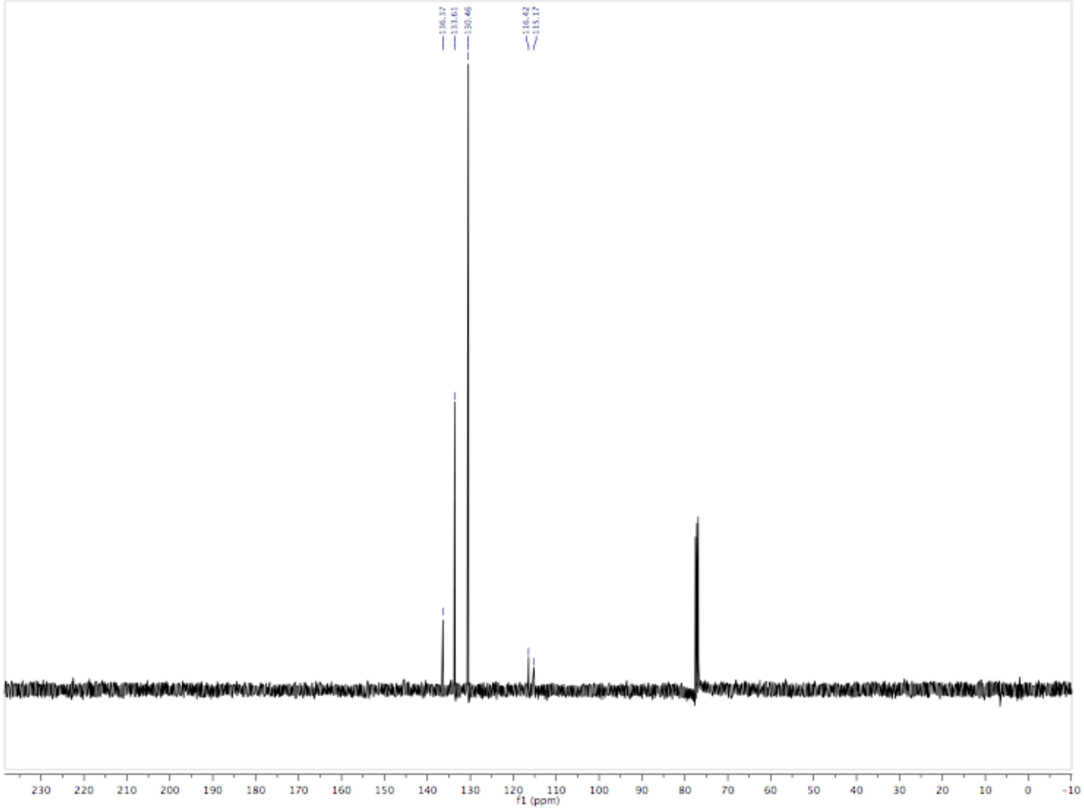

CN
CO2Me

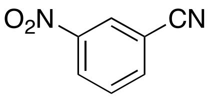

165.31
136.28
133.63
131.69
129.65
118.28
113.22
52.76
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Cl
CN
Cl

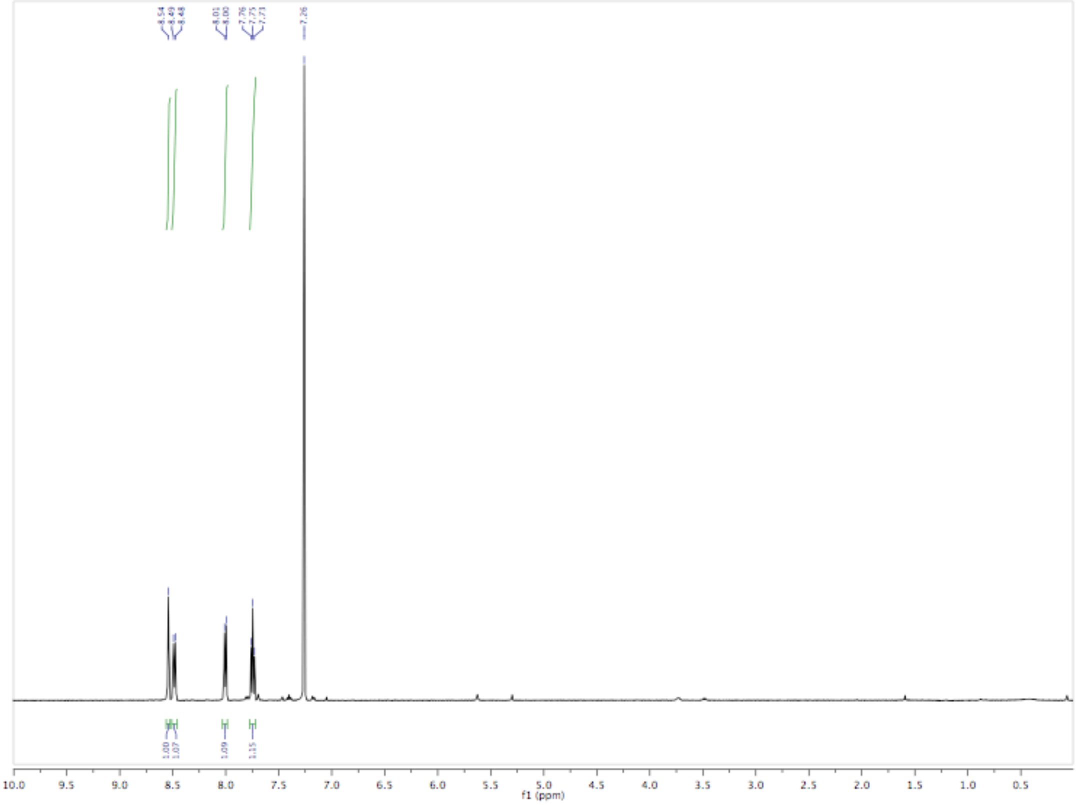

7.59
7.53
1.01
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


Cl
CN
Cl

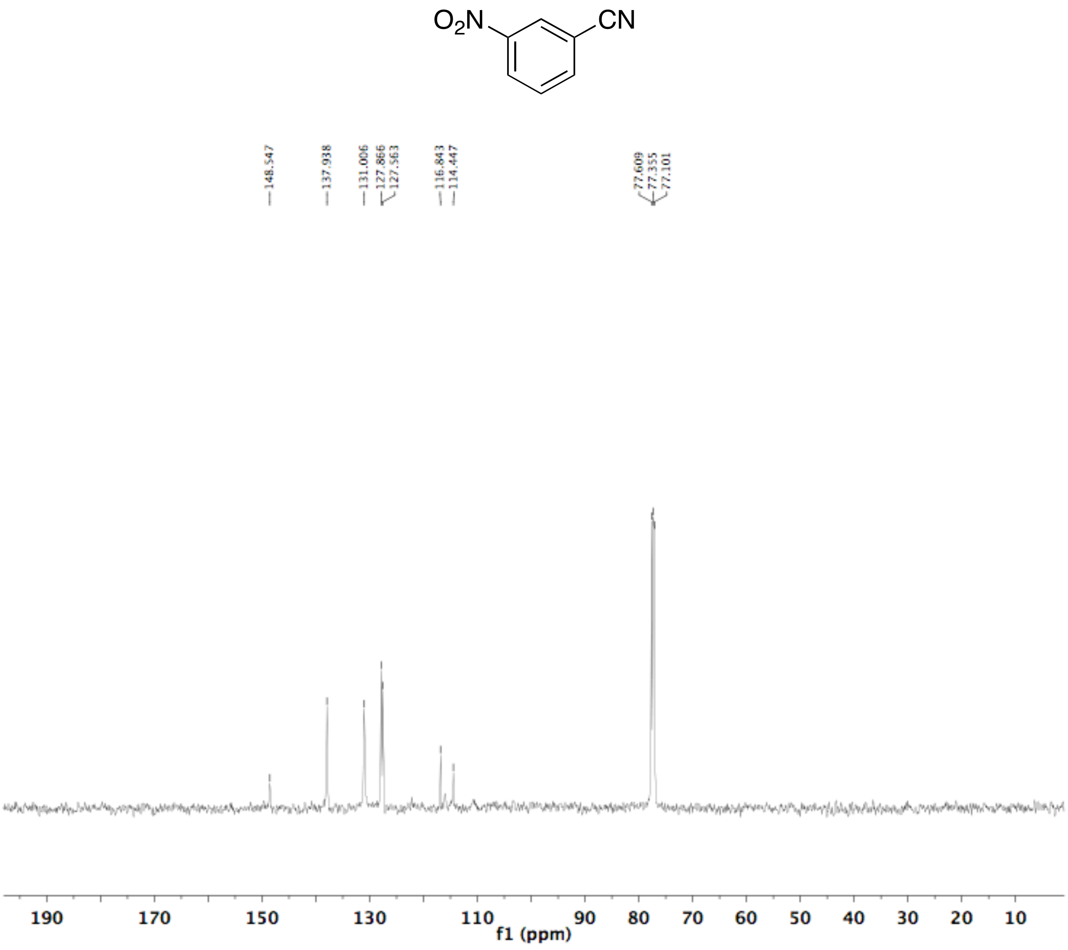

136.37
133.61
130.46
116.42
115.17
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

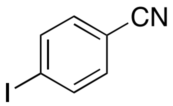


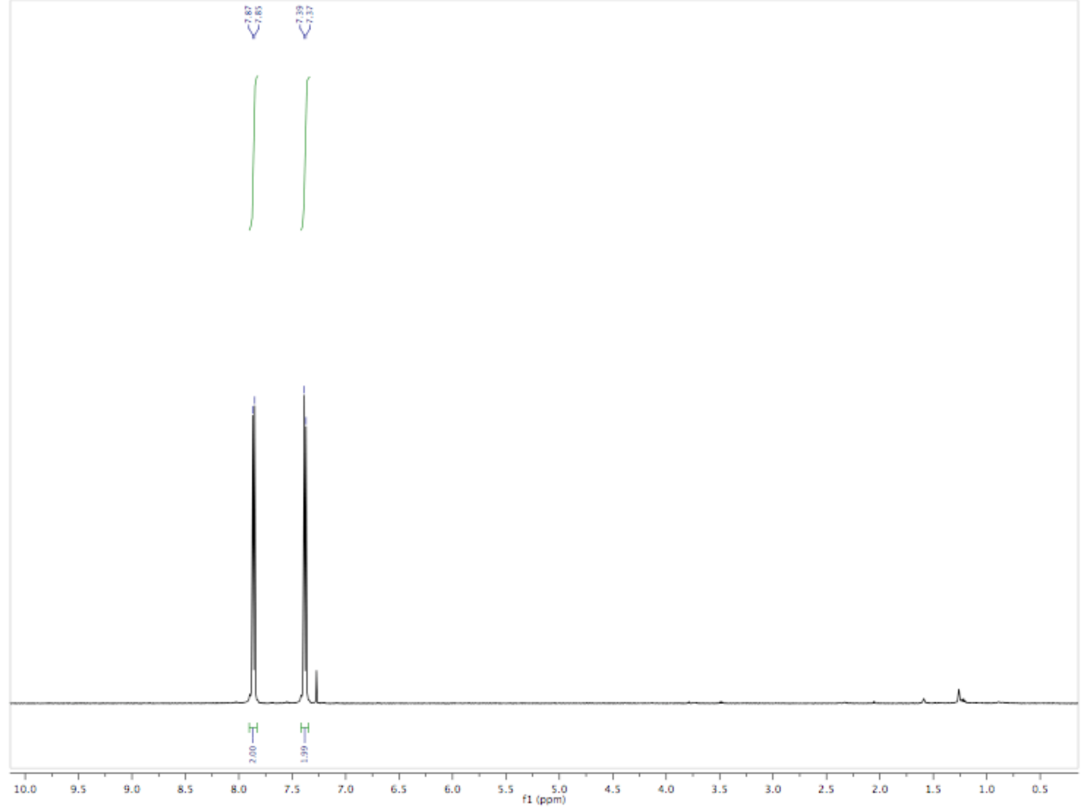
O2N
CN

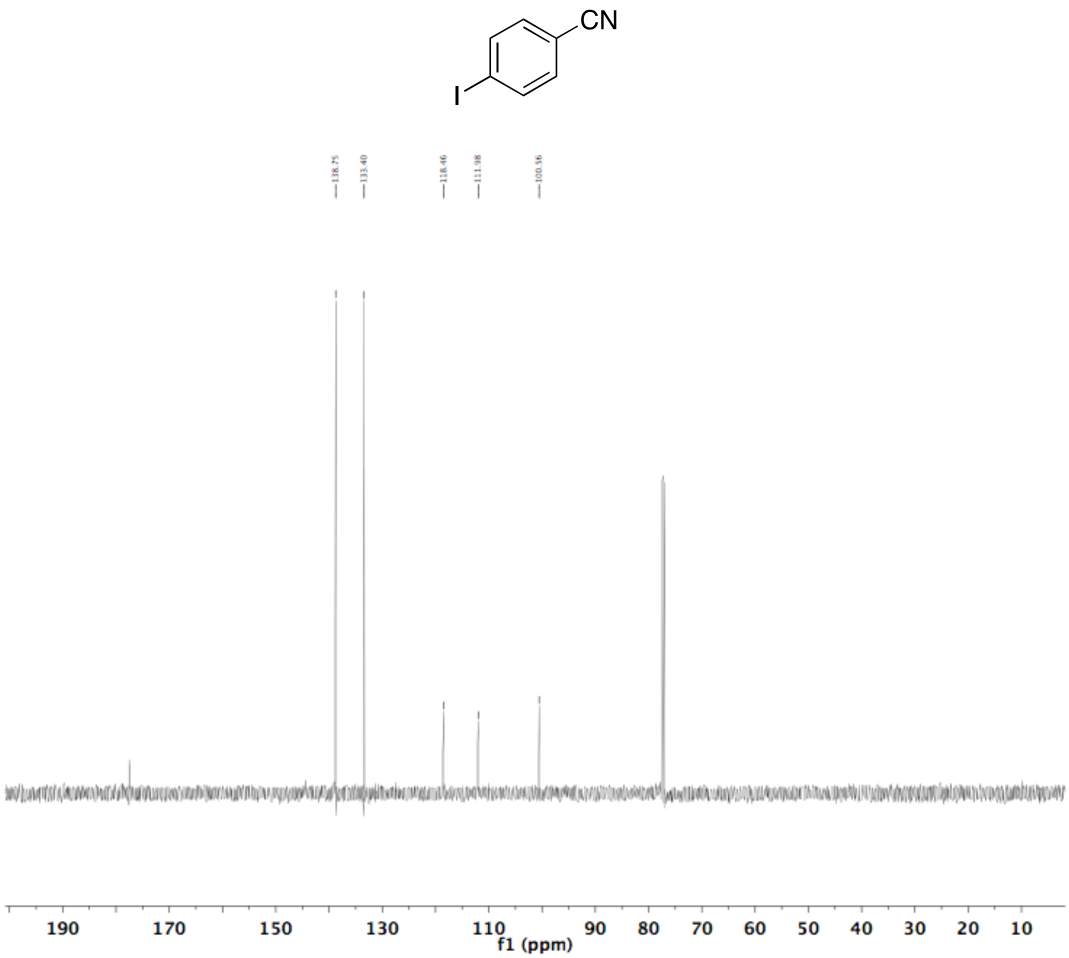


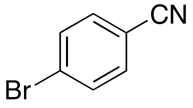
8.54
8.49
8.48
8.01
8.00
7.76
7.75
7.73
7.26
1.00
1.07
1.09
1.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

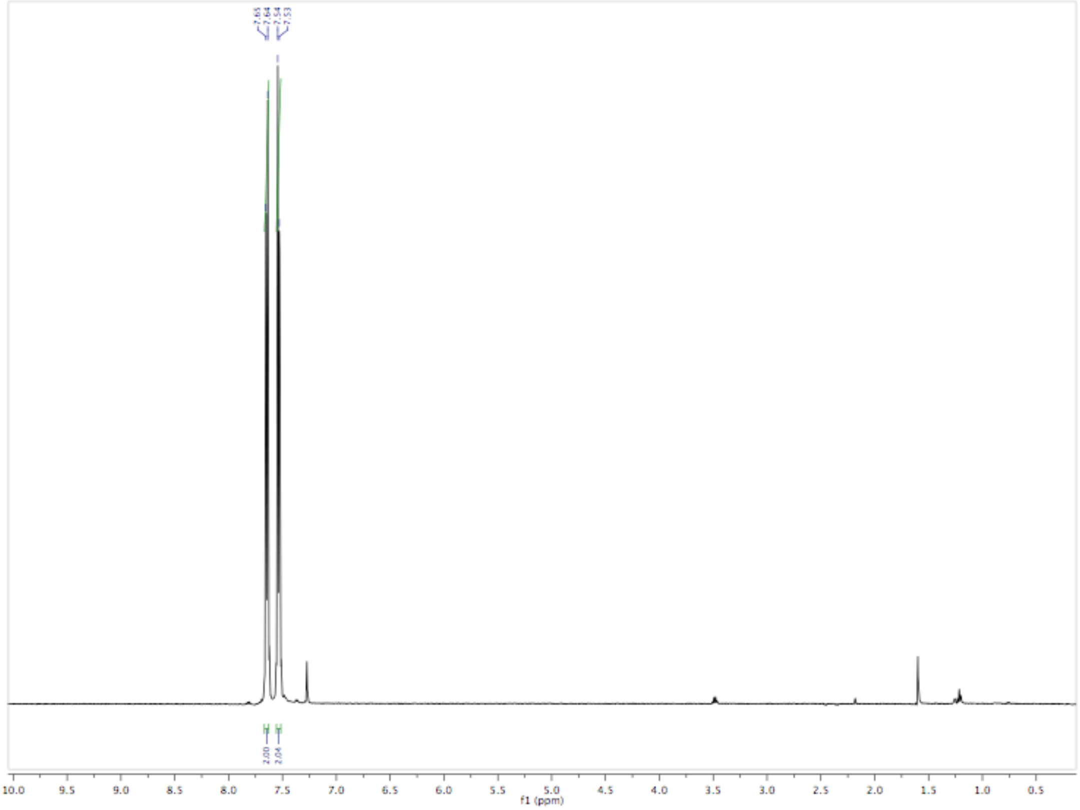

O2N
CN
148.547
137.938
131.006
127.866
127.563
116.843
114.447
77.609
77.355
77.101
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)

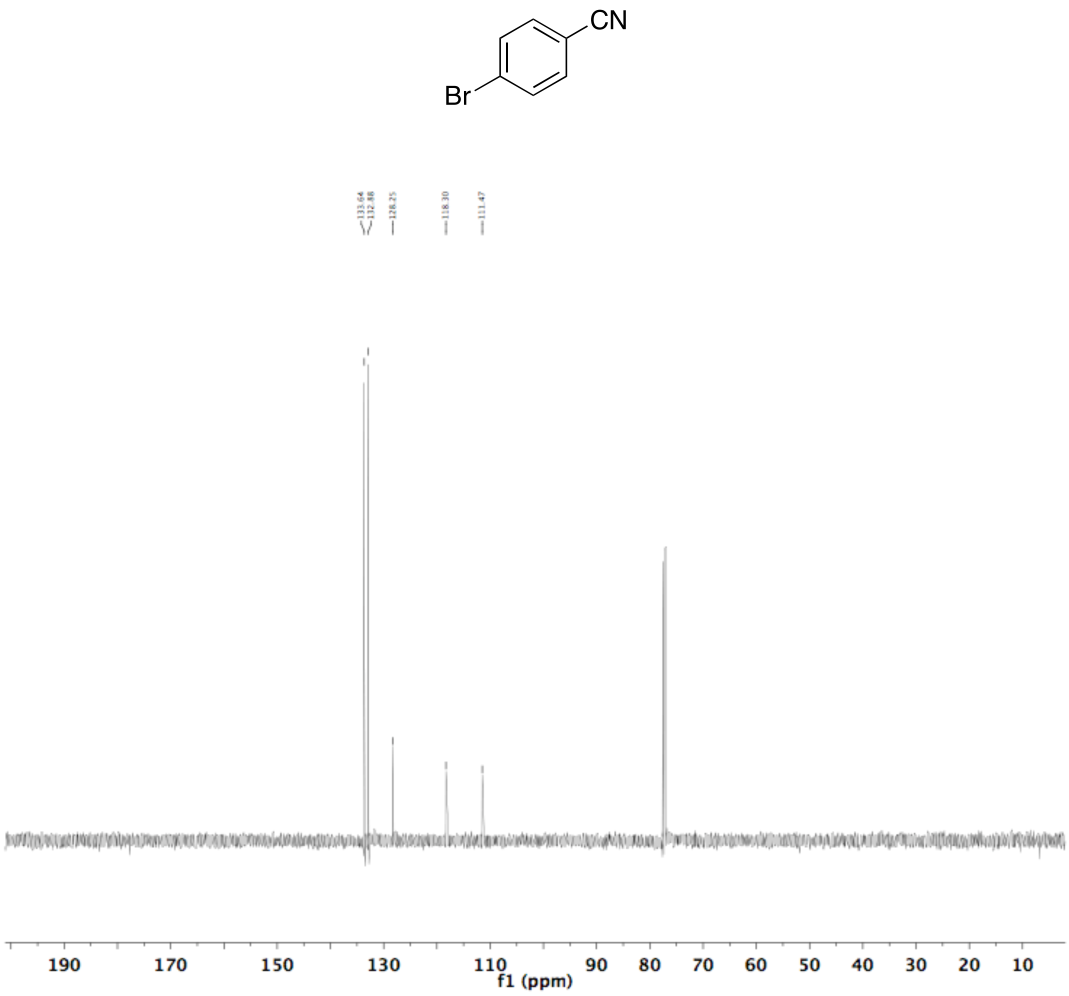

CN
I

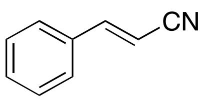

7.87
7.85
7.39
7.37
2.00
1.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

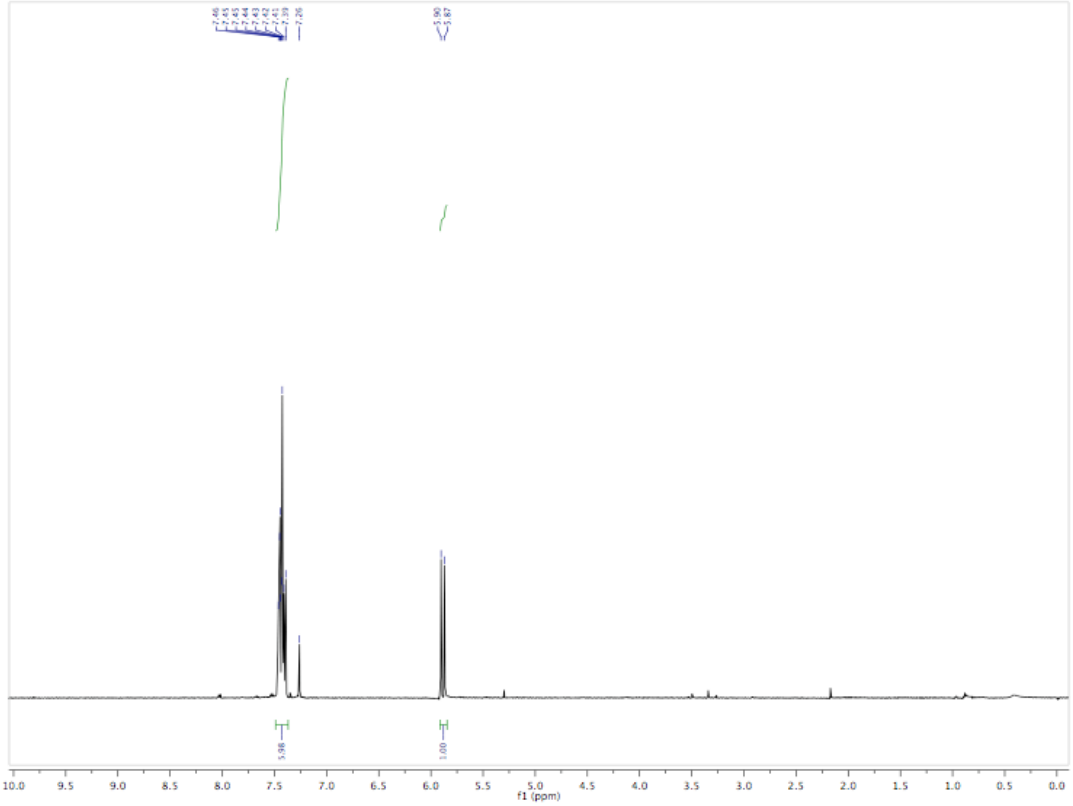

CN
I
138.75
133.40
118.46
111.98
100.56
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)

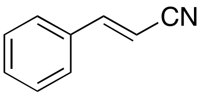

CN
Br

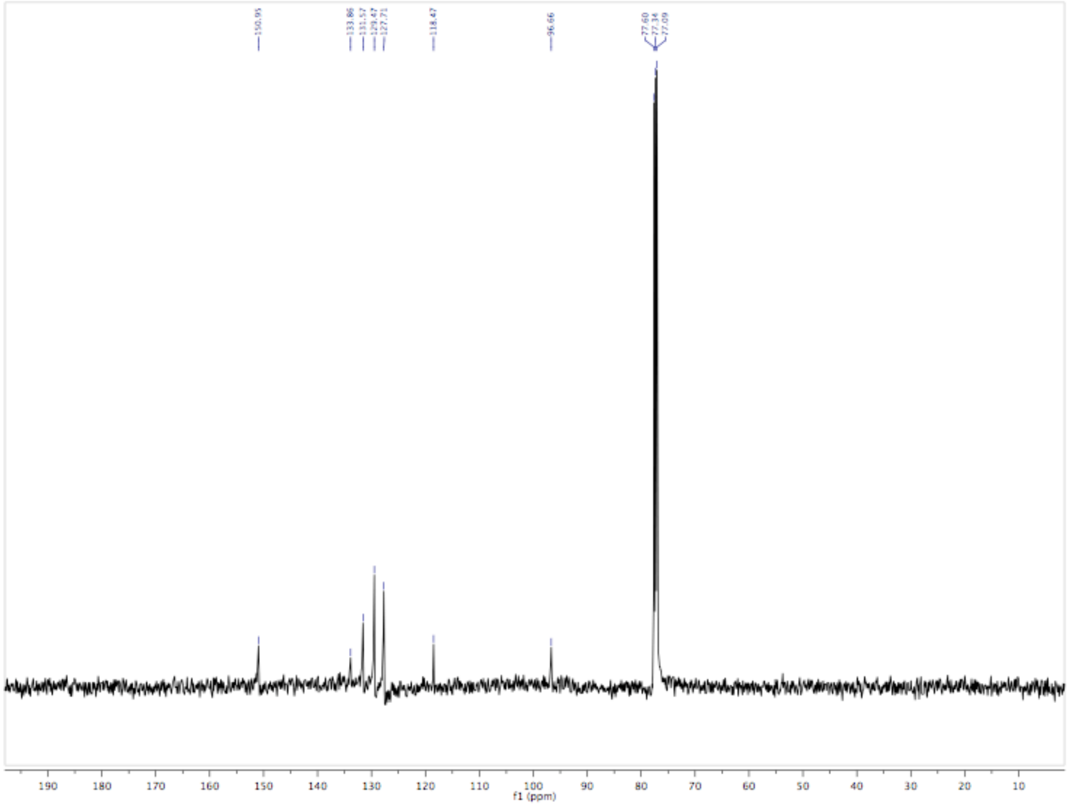

7.65
7.64
7.54
7.53
2.00
2.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

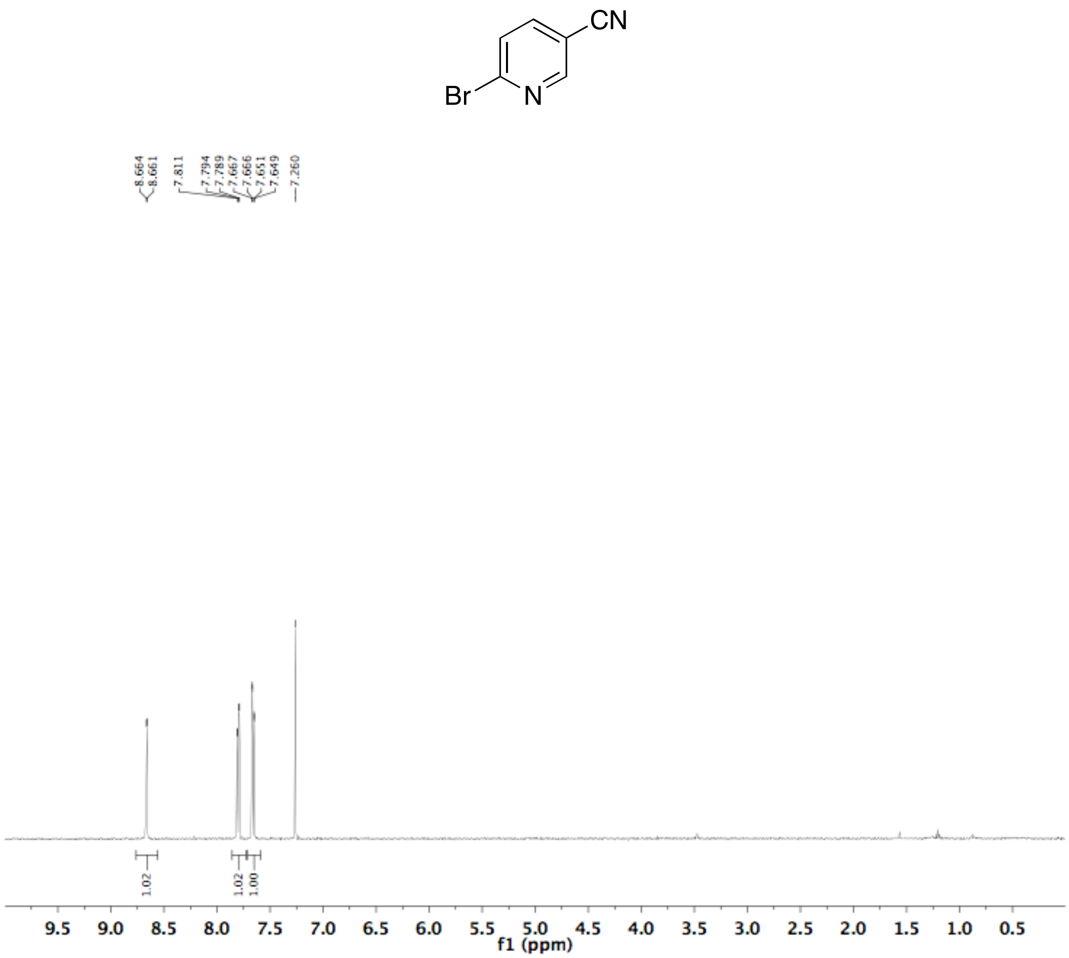

CN
Br
133.64
132.86
128.25
118.30
111.47
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)

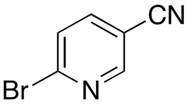

CN

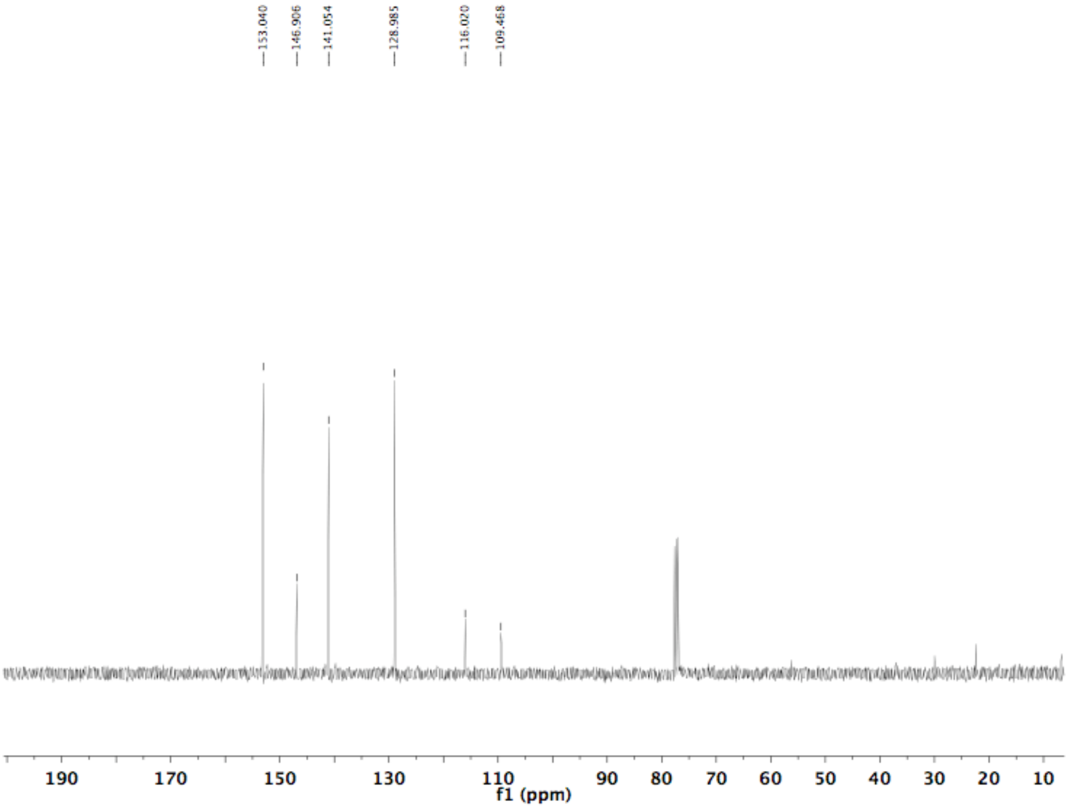

7.46
7.45
7.45
7.44
7.43
7.42
7.41
7.39
7.26
5.90
5.87
5.98
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


CN


150.95
133.86
131.57
129.47
127.71
118.47
96.66
77.60
77.34
77.09
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


CN
Br
N
8.664
8.661
7.811
7.794
7.789
7.667
7.666
7.651
7.649
7.260
1.02
1.02
1.00
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)


CN
Br
N


153.040
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141.054
128.985
116.020
109.468
190
170
150
130
110
90
80
70
60
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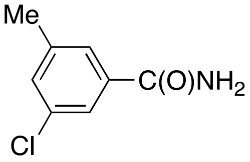
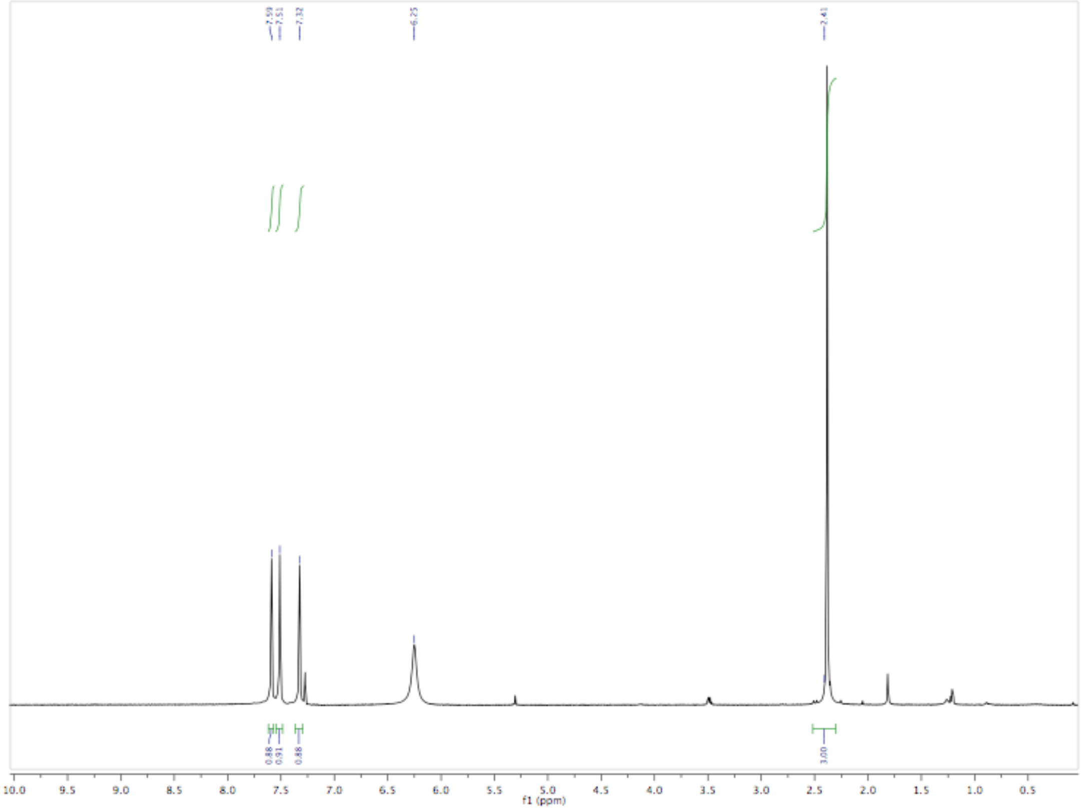
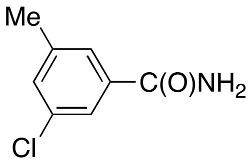
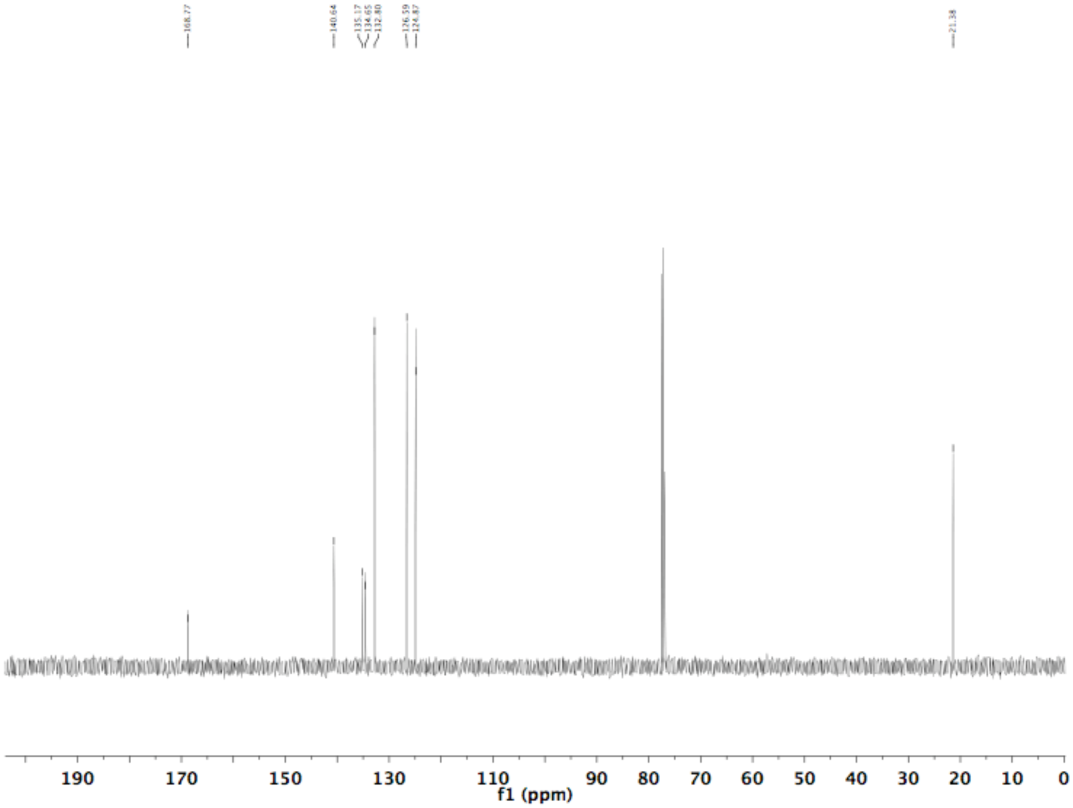
40
30
20
10
f1 (ppm)


Me
C(O)NH2
Cl


7.59
7.51
7.32
6.25
2.41
0.88
0.91
0.88
3.00
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
f1 (ppm)


Me
C(O)NH$_2$
Cl


168.77
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135.17
134.65
132.80
126.59
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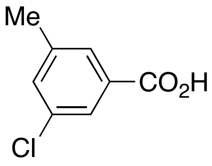
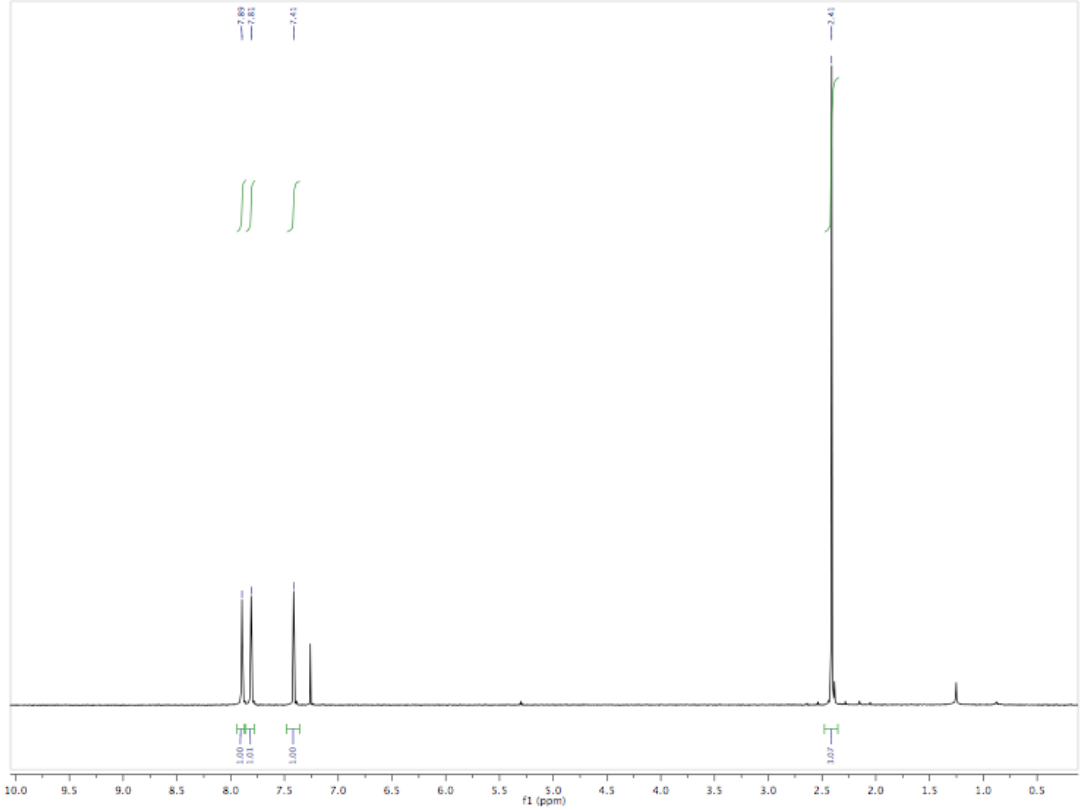
21.38
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
CO2H
Cl


7.89
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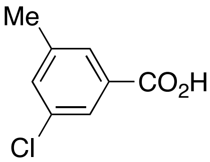
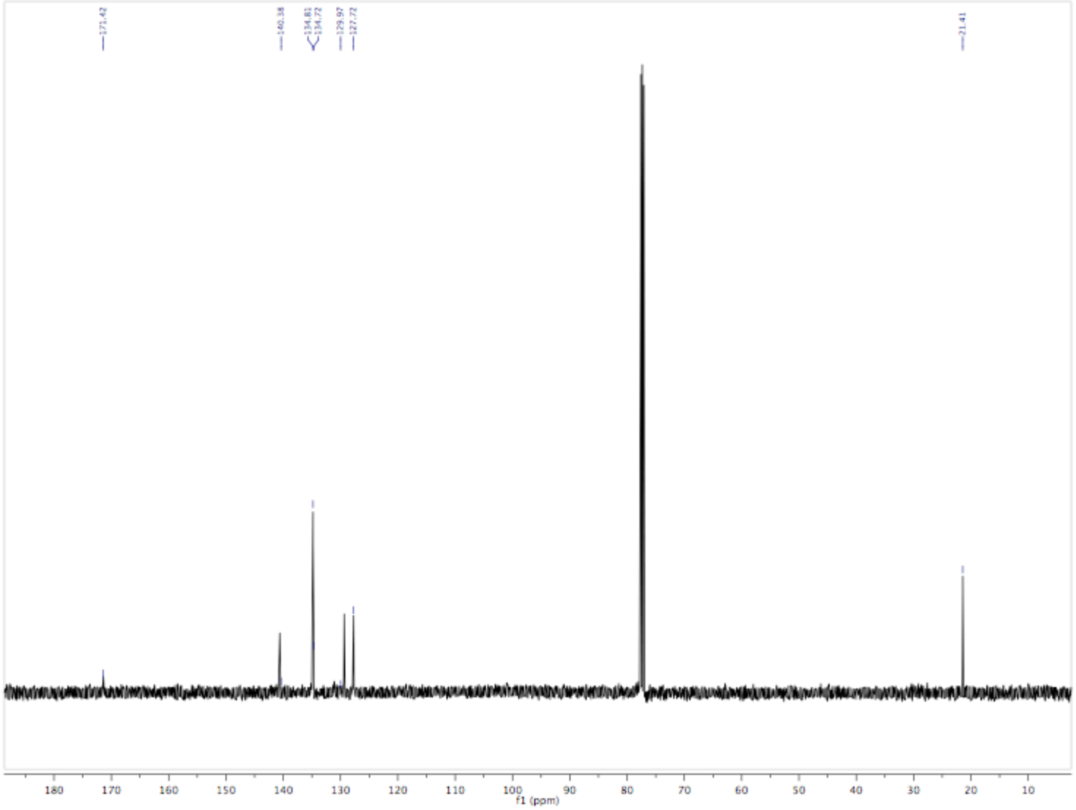
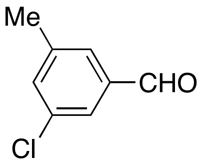
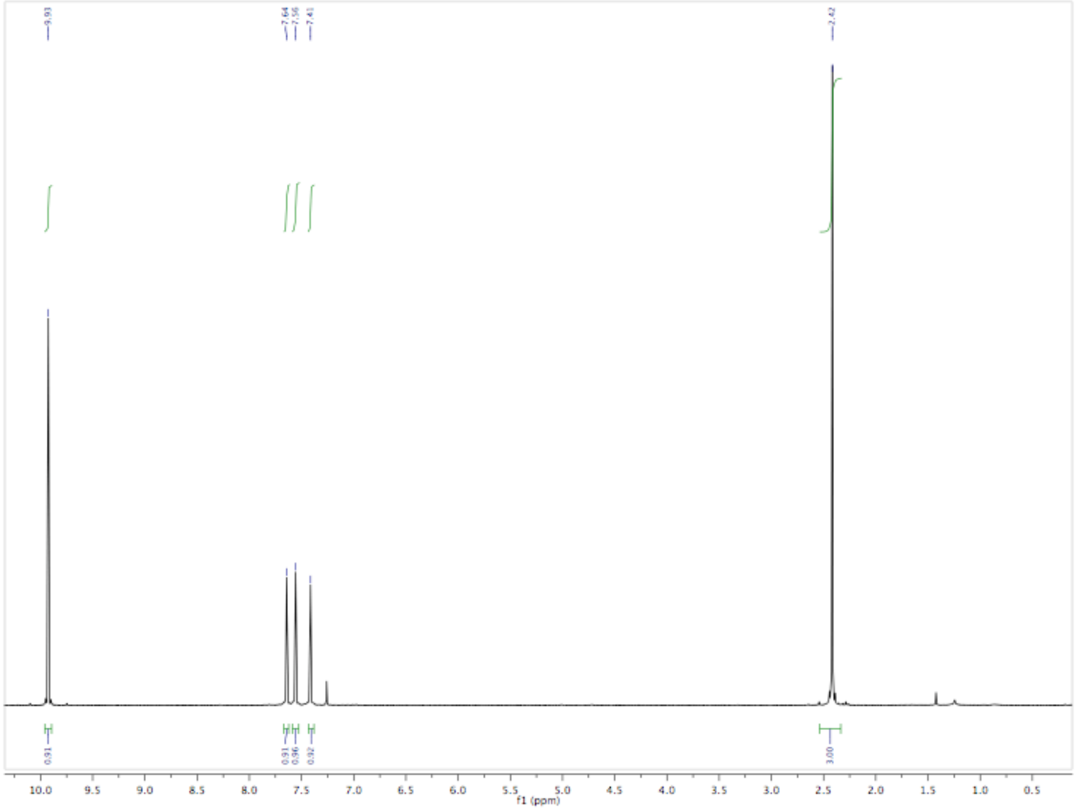
7.41
2.41
1.00
1.01
1.00
3.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


Me
CO2H
Cl


171.42
140.38
134.81
134.72
129.97
127.72
21.41
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Me
CHO
Cl


9.93
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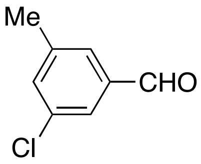
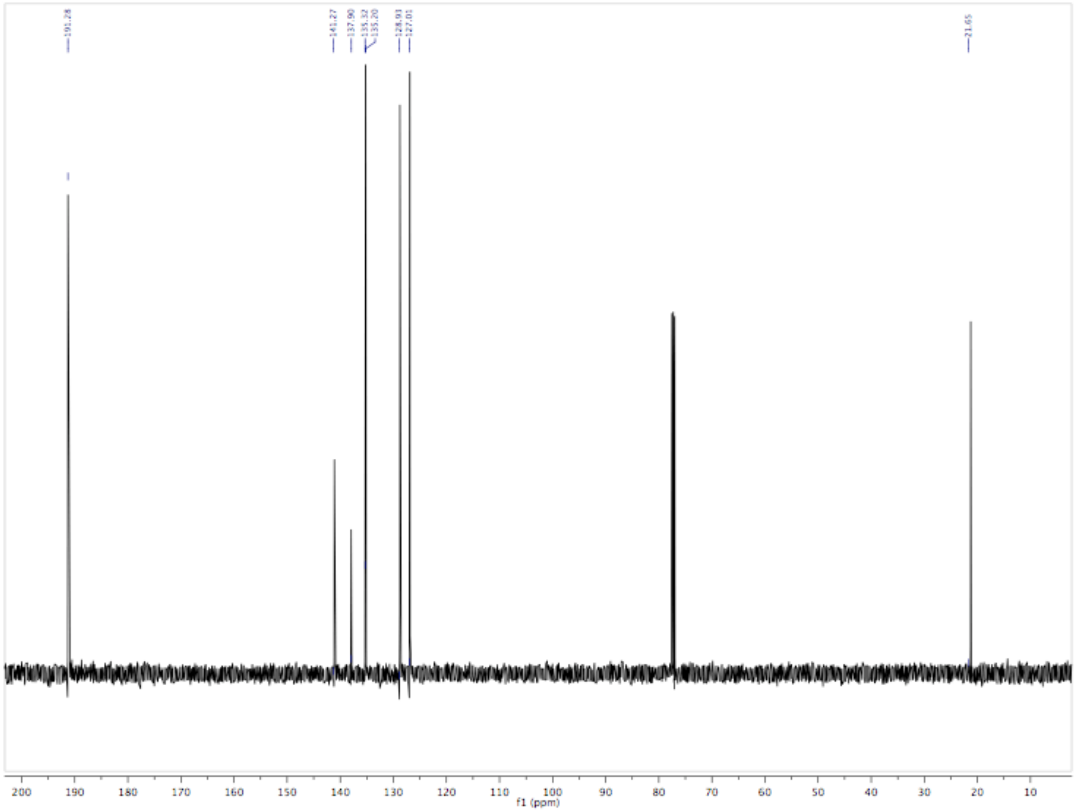
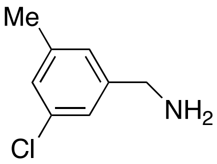
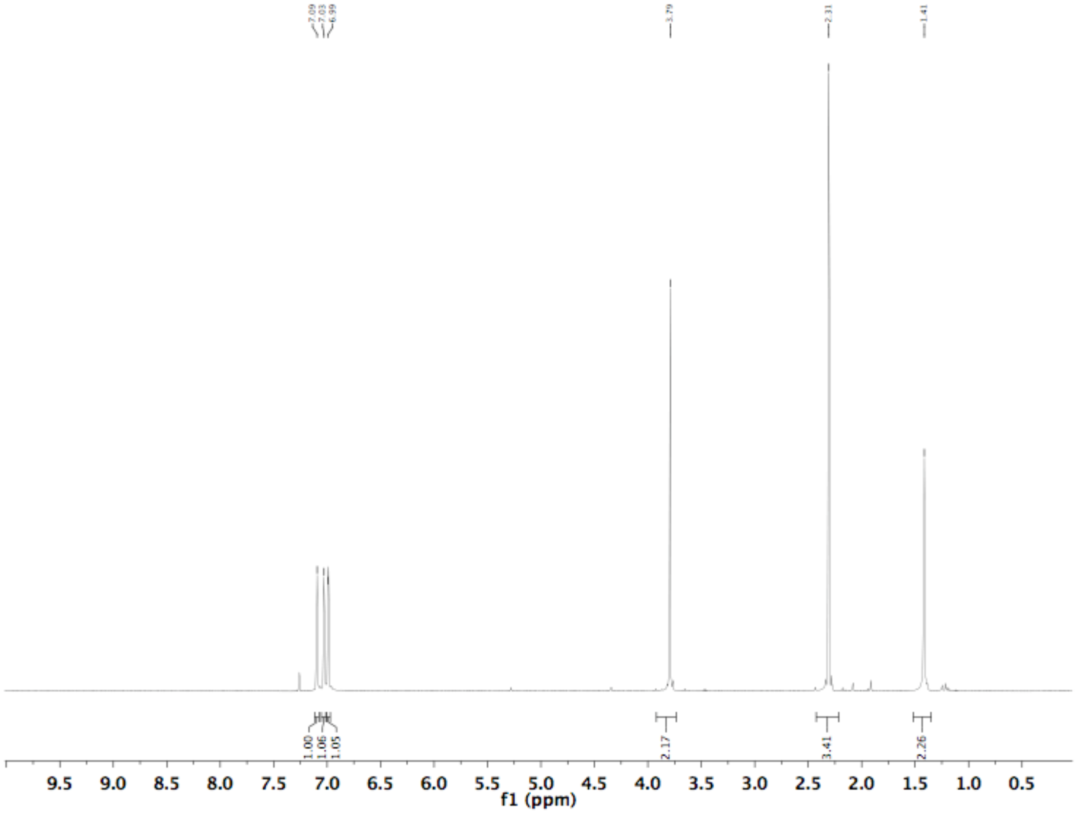
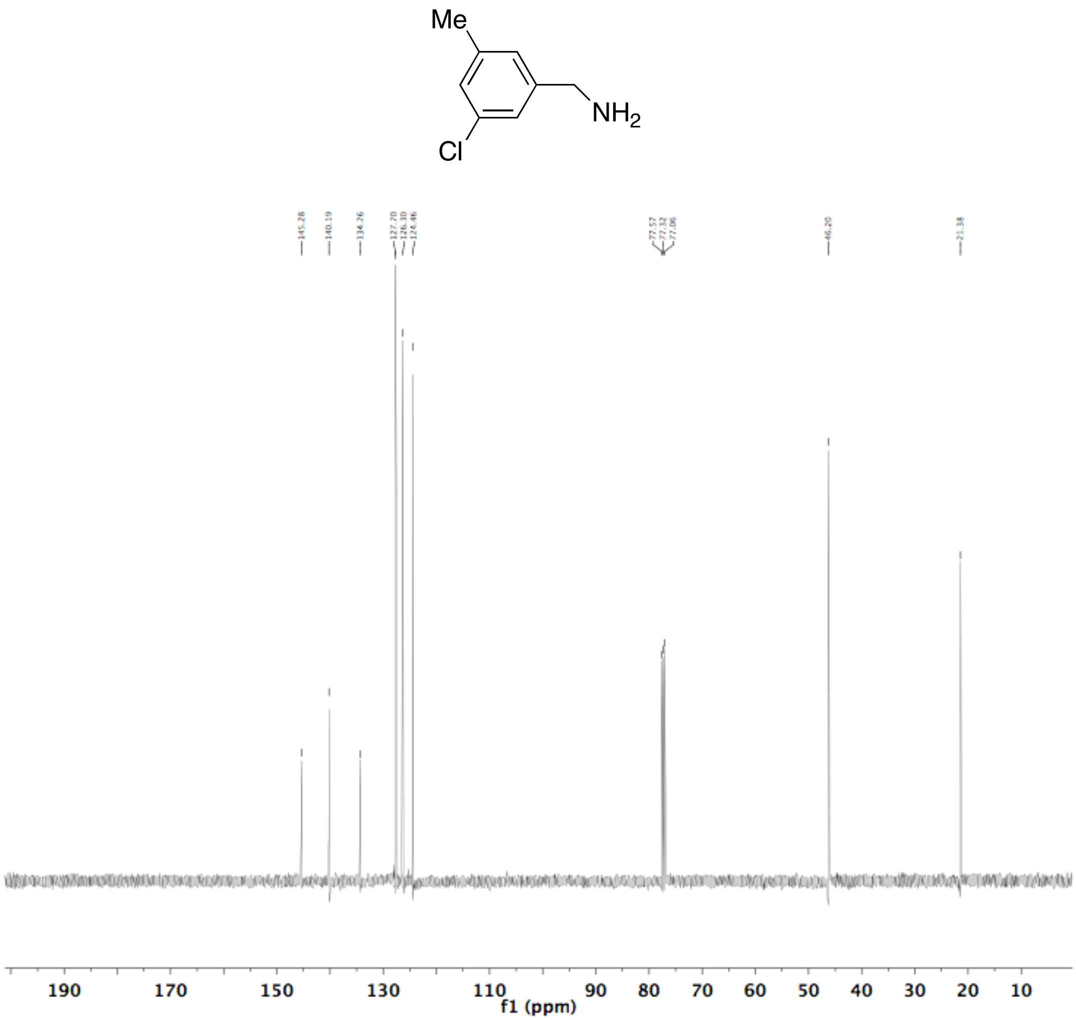
7.56
7.41
2.42
0.91
0.91
0.96
0.92
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

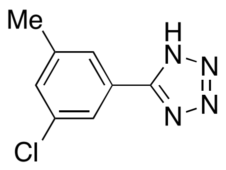

Me
CHO
Cl

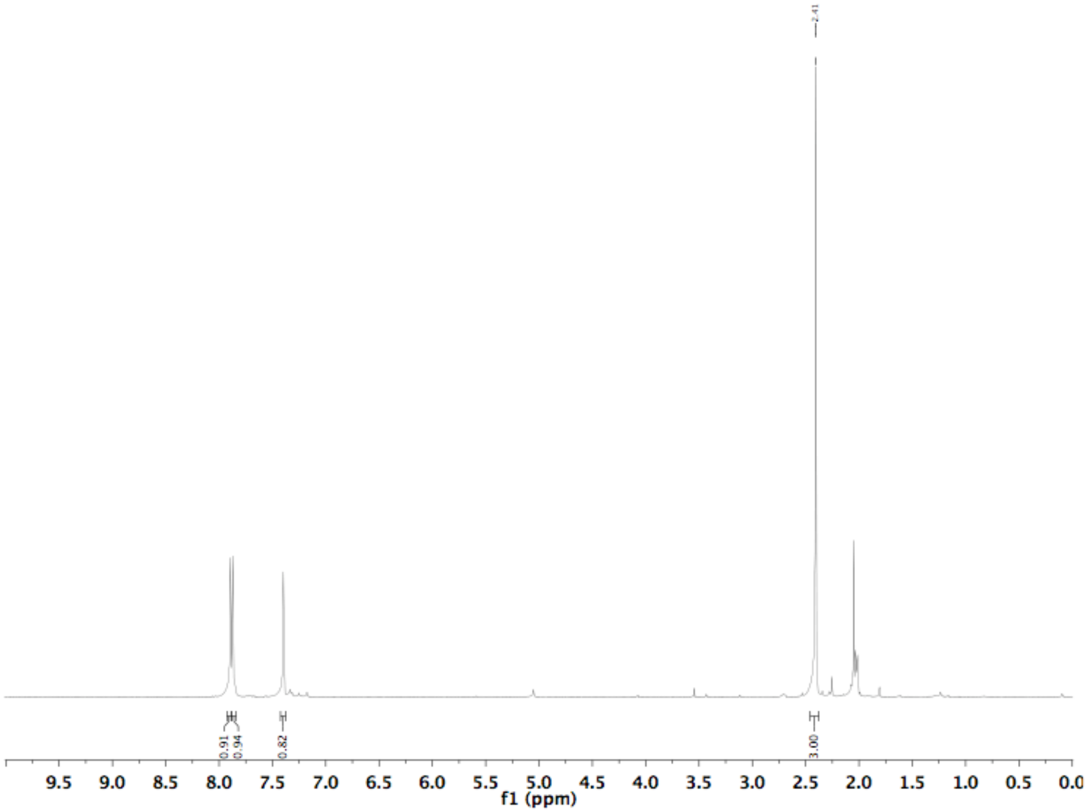

191.28
141.27
137.90
135.32
135.20
128.93
127.01
21.65
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

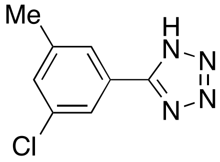

Me
NH2
Cl

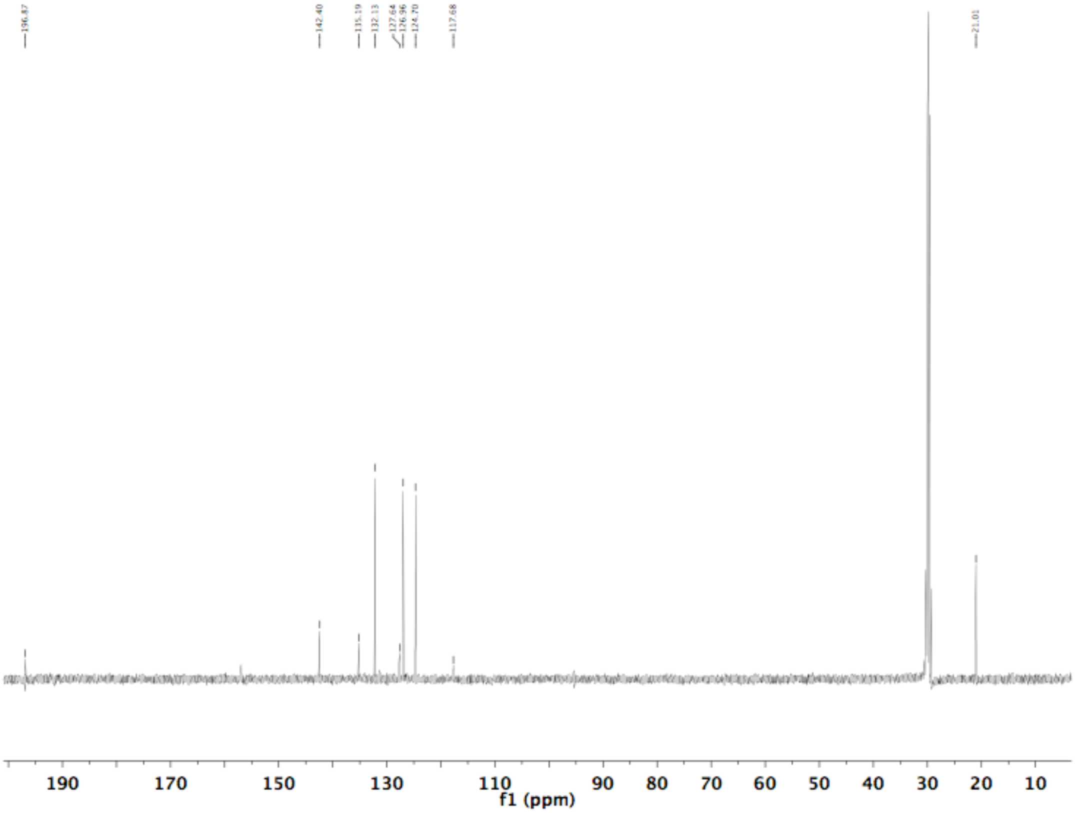

7.09
7.03
6.99
3.79
2.31
1.41
1.00
1.06
1.05
2.17
3.41
2.26
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

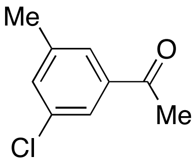

Me
NH$_2$
Cl
145.28
140.19
134.26
127.20
126.30
124.46
77.57
77.32
77.06
46.20
21.38
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)

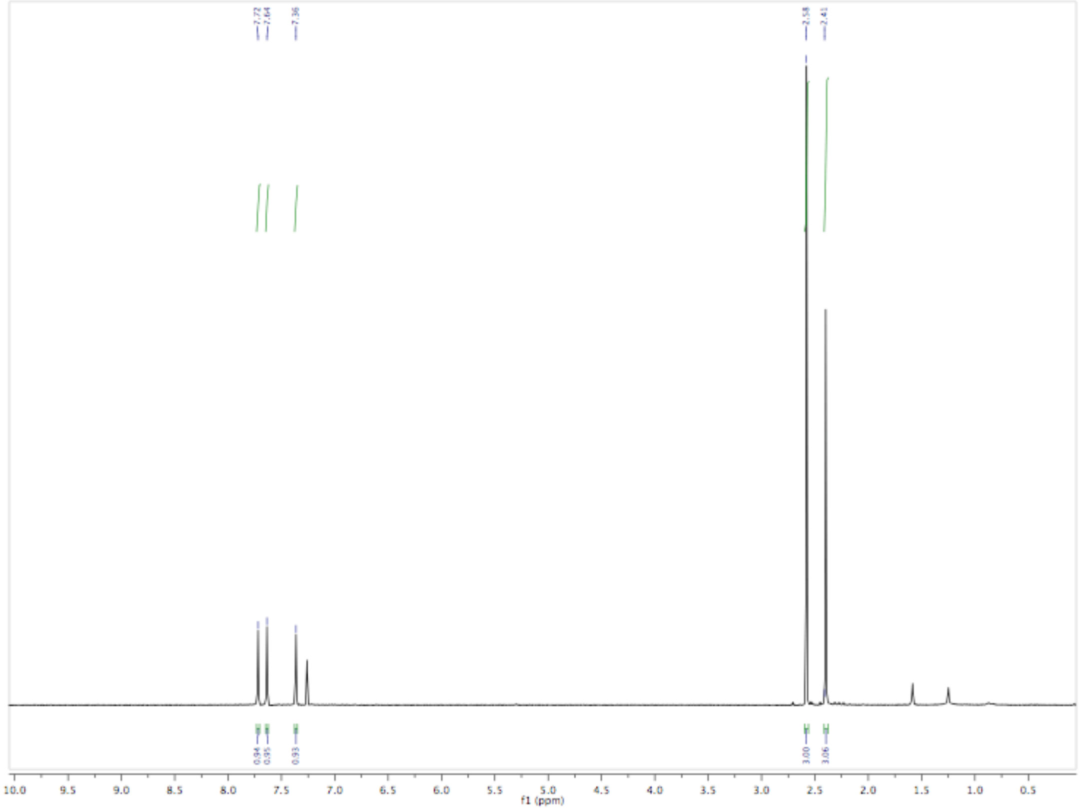

Me
H
N
N
N
N
Cl

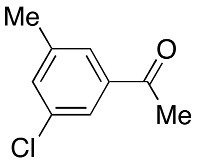

2.41
0.91
0.94
0.82
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

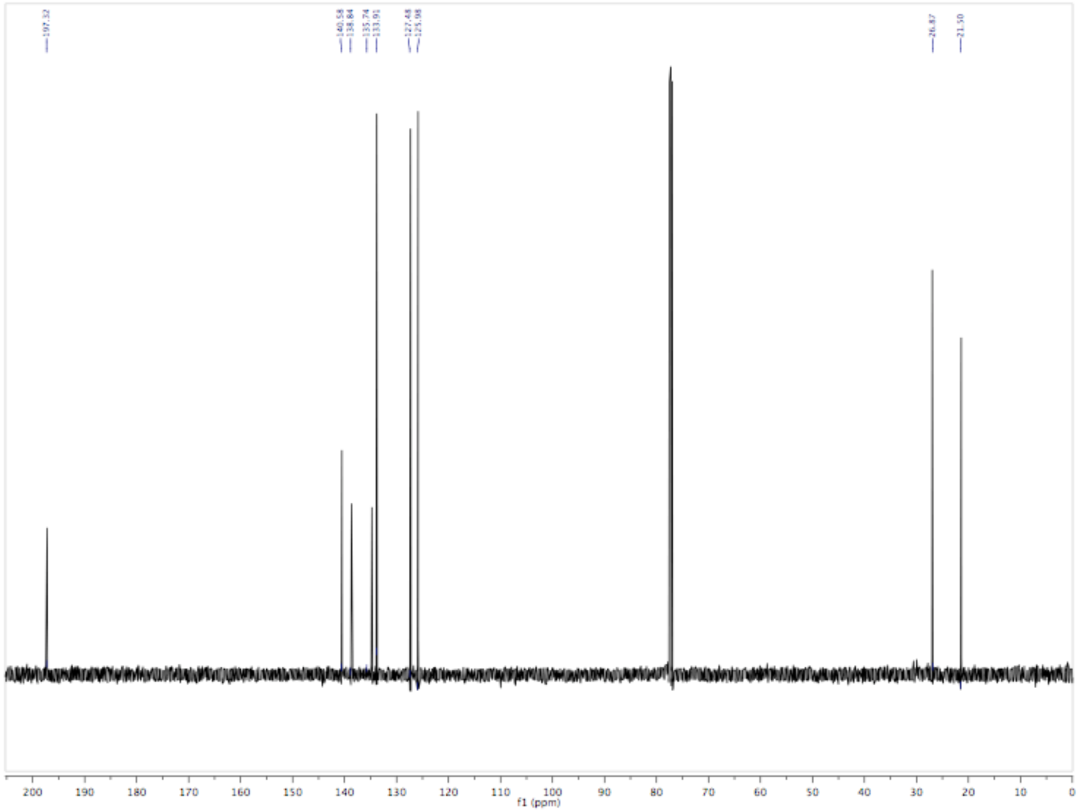

Me
H
N
N
N
N
Cl


196.87
142.40
135.19
132.13
127.64
126.96
124.70
117.68
21.01
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)


Me
O
Me
Cl


7.72
7.64
7.36
2.58
2.41
0.94
0.95
0.93
3.00
3.06
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
f1 (ppm)


Me
O
Me
Cl


197.32
140.58
138.84
135.74
133.91
127.48
125.98
26.87
21.50
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)