

# Supporting Information

## **Aromatic *ortho*-Benzylation Reveals an Unexpected Reductant**

*Andrew Martins and Mark Lautens\**

*Davenport Research Laboratories, Department of Chemistry, University of Toronto,*

*80 St. George St., Toronto, Ontario, M5S 3H6 Canada.*

mlautens@chem.utoronto.ca

### Table of Contents

General Information.....	S2
General Procedure.....	S3
Experimental Data.....	S4
Representative Spectra (in numerical order).....	S12

## General Information

The following includes general experimental procedures, specific details for representative reactions, isolation, and spectroscopic data for new compounds. All of the reactions listed in the main publication were performed in capped 2.5–5 mL microwave reaction vials from Personal Chemistry. Melting points were recorded using a Fisher-Johns melting point apparatus and are uncorrected.  $^1\text{H}$ ,  $^2\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR spectra were obtained using either Varian Mercury 300 MHz or Varian Unity 400 MHz spectrometers.  $^1\text{H}$  spectra were referenced to tetramethylsilane (TMS, 0 ppm) or solvent carbons and  $^{13}\text{C}$  spectra were referenced to solvent carbons (77.23 ppm for  $\text{CDCl}_3$ ).  $^2\text{H}$  spectra were referenced to deuterated methylene chloride (5.23 ppm for  $\text{CD}_2\text{Cl}_2$ ), and  $^{19}\text{F}$  spectra were unreferenced. IR spectra were obtained using a Perkin Elmer Spectrum 1000 FT-IR spectrometer on NaCl plates. High-resolution mass spectra were obtained using a VG 70-250S (double focusing) mass spectrometer at 70 eV for electron impact ionization or a Sciex QStar operating at a spray voltage of 5500 V for electrospray ionization. Dimethoxyethane (DME) was distilled under  $\text{N}_{2(\text{g})}$  over  $\text{CaH}_2$  prior to use. Neutral silica (Silia-P, 40–63  $\mu\text{m}$ , Silicycle, Québec, Canada) for flash chromatography was used as received. All reagents, metal catalysts and ligands were purchased from Sigma-Aldrich, VWR International, or Strem Chemical Company and used as received unless otherwise noted.

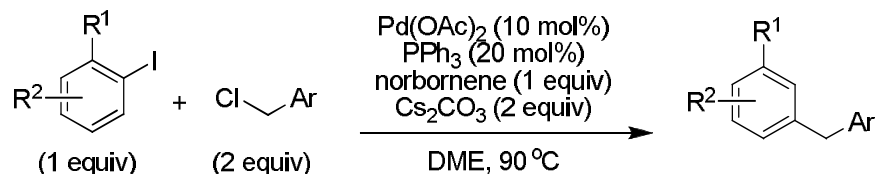
### Abbreviations:

$\text{Et}_2\text{O}$ : Diethyl Ether  
 $\text{EtOAc}$ : Ethyl Acetate  
br: broad (IR)  
w: weak (IR)

RT: Room Temperature  
h: hours  
s: strong (IR)  
m: moderate (IR)

## General Procedure

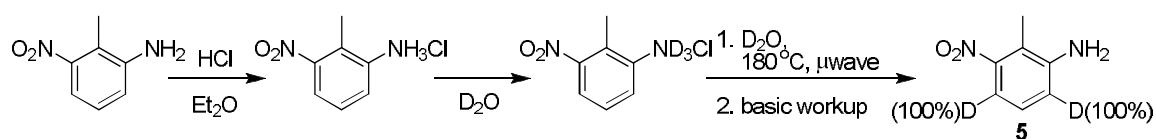
General Procedure for the synthesis of diarylmethanes:



In a 2.5–5 mL microwave reaction vial with a magnetic stir bar, aryl iodide (1 equiv, 0.2 mmol), benzyl chloride (2 equiv, 0.4 mmol), Pd(OAc)<sub>2</sub> (10 mol%, 0.02 mmol), PPh<sub>3</sub> (20 mol%, 0.04 mmol), Cs<sub>2</sub>CO<sub>3</sub> (2 equiv, 0.4 mmol), and norbornene (2 equiv, 0.6 mmol) were added (Note: if all reagents were solids, they were combined in the reaction vial; however, if any reagents were liquids, they were added to the reaction vial prior to the addition of solid reagents). DME (2 mL, 0.1 M of aryl iodide relative to the solvent volume) was added, and the vial capped and sealed. The vial was then flushed with N<sub>2(g)</sub> for 5 minutes and then transferred to a pre-heated oil bath at 90 °C and stirred until the reaction was complete (typically 12–24 h). The vial was then removed from the oil bath, cooled to RT, and H<sub>2</sub>O (3 mL) added. The mixture was then washed with Et<sub>2</sub>O (3 × 5 mL), and the combined organic extracts dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The crude product was then purified by column chromatography on silica gel to afford product.

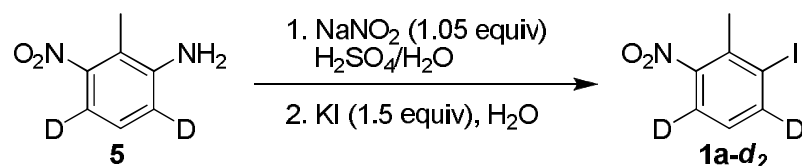
## Experimental Data

### 4,6-dideutero-2-methyl-3-nitroaniline (**5**)



2-methyl-3-nitroaniline (500 mg, 3.29 mmol) was dissolved in 20 mL Et<sub>2</sub>O, and 10 drops of conc. HCl were added, causing the solution to become a white precipitate. The precipitate was then filtered off, rinsing with Et<sub>2</sub>O, and dried under reduced pressure (0.2 torr) to give a white solid. The solid was then dissolved in 10 mL D<sub>2</sub>O and stirred for 1 day. The solution was concentrated *in vacuo*, and dried under reduced pressure (0.2 torr). The resultant solid was then dissolved/suspended in 20 mL D<sub>2</sub>O, transferred to a 25 mL microwave reaction vial, and heated to 180 °C under microwave irradiation for 30 minutes to give a yellow solution. The mixture was then transferred to a separatory funnel and 20 mL 5N NaOH was added. The mixture was extracted with 50 mL EtOAc which was washed with another 20 mL 5N NaOH, dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to give **5** as a flaky yellow solid (mp = 84–85 °C). Isolated yield: 433 mg (85 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.25 (s, 3H), 3.89 (br s, 2H), 7.10 (s, 1H); <sup>2</sup>H NMR (61 MHz, CHCl<sub>3</sub>) δ 6.93 (s, 1D), 7.25 (s, 1D); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 12.5, 113.6 (1:1:1 t, *J*=25.7 Hz), 115.8, 118.1 (1:1:1 t, *J*=24.3 Hz), 126.4, 146.2, 151.5; IR thin film, ν (cm<sup>-1</sup>) 759 (w), 915 (w), 1358 (m), 1516 (s), 3411 (m); HRMS (EI) Calc'd for C<sub>6</sub>H<sub>6</sub>D<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: 154.0711 (M<sup>+</sup>), found 154.0712.

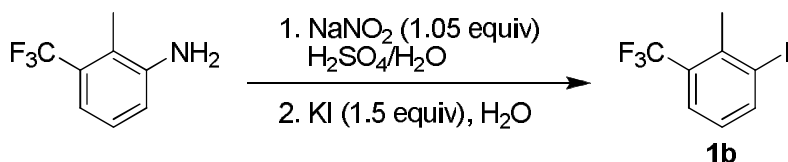
### 4,6-dideutero-1-iodo-2-methyl-3-nitrobenzene (**1a-d<sub>2</sub>**)



4,6-dideutero-2-Methyl-3-nitroaniline **5** (336 mg, 2.18 mmol) was suspended in 5 mL H<sub>2</sub>O, and a mixture of 0.5 mL conc. H<sub>2</sub>SO<sub>4</sub> in 5 mL H<sub>2</sub>O was added. The mixture was cooled to 0 °C in an ice bath, and a solution of NaNO<sub>2</sub> (158 mg, 2.29 mmol) in 5 mL H<sub>2</sub>O was added dropwise *via* addition funnel over 10 min, and stirred for 1 h. To this mixture was added dropwise a solution of KI (543 mg, 3.27 mmol) in 5 mL H<sub>2</sub>O *via* addition funnel over 10 min, and the mixture allowed to warm to RT and stirred overnight. The reaction mixture was extracted with 2 x 15 mL CH<sub>2</sub>Cl<sub>2</sub>, and the combined organic phases washed with 20 mL sat. Na<sub>2</sub>SO<sub>3</sub>. The organic phase was then dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The crude product was then purified by flash chromatography on silica gel (R<sub>f</sub> 0.51 in 5 % Et<sub>2</sub>O/hexane) using 5 % Et<sub>2</sub>O/hexane to afford **1a-d<sub>2</sub>** as a pale yellow oil which slowly solidifies to a pale yellow solid (mp = 30–32 °C). Isolated yield: 513 mg (89 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.60 (s, 3H), 7.04 (br s, 1H); <sup>2</sup>H NMR (61 MHz, CHCl<sub>3</sub>) δ 7.75 (s, 1D), 8.08 (s, 1D); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 24.9, 103.3, 123.7(1:1:1 t, *J*=26.5 Hz), 127.7, 135.0, 142.8 (1:1:1 t, *J*=25.7 Hz), 150.3; IR thin

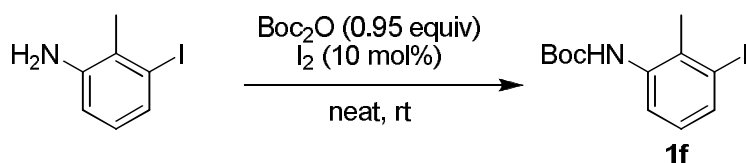
film,  $\nu$  ( $\text{cm}^{-1}$ ) 692 (m), 857 (m), 1015 (m), 1088 (w), 1350 (s), 1519 (s), 2361 (s); HRMS (EI) Calc'd for  $\text{C}_7\text{H}_4\text{D}_2\text{NO}_2$ : 264.9569 ( $\text{M}^+$ ), found 264.9562.

1-iodo-2-methyl-3-(trifluoromethyl)benzene (**1b**)



2-Methyl-3-(trifluoromethyl)aniline (1.75 g, 10.0 mmol) was suspended in 10 mL  $\text{H}_2\text{O}$ , and a mixture of 2 mL conc.  $\text{H}_2\text{SO}_4$  in 10 mL  $\text{H}_2\text{O}$  was added. The mixture was cooled to  $0^\circ\text{C}$  in an ice bath, and a solution of  $\text{NaNO}_2$  (724 mg, 10.5 mmol) in 10 mL  $\text{H}_2\text{O}$  was added dropwise *via* addition funnel over 10 min, and stirred for 1 h. To this mixture was added dropwise a solution of KI (2.49 g, 15.0 mmol) in 10 mL  $\text{H}_2\text{O}$  *via* addition funnel over 10 min, and the mixture allowed to warm to RT and stirred overnight. The reaction mixture was extracted with 3 x 50 mL  $\text{Et}_2\text{O}$ , and the combined organic phases washed with 25 mL sat.  $\text{NaHSO}_3$ . The organic phase was then dried with  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated *in vacuo*. The crude product was then purified by flash chromatography on silica gel ( $R_f$  0.72 in hexane) using hexane to afford **1b** as a pale orange oil. Isolated yield: 2.405 g (84 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.58 (s, 3 H), 6.95 (t,  $J=7.9$  Hz, 1H), 7.62 (d,  $J=7.8$  Hz, 1H), 8.01 (d,  $J=8.0$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  25.6, 104.6, 124.0 (q,  $J=274.3$  Hz), 126.2 (app qn,  $J=5.9$  Hz), 127.3 (d,  $J=2.2$  Hz), 129.9 (q,  $J=29.7$  Hz), 139.9 (q,  $J=1.5$  Hz), 143.1;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -61.6; IR neat,  $\nu$  ( $\text{cm}^{-1}$ ) 677 (s), 716 (m), 788 (m), 1005 (w), 1052 (s), 1124 (s), 1172 (s), 1221 (m), 1308 (s), 1438 (m); HRMS (EI) Calc'd for  $\text{C}_8\text{H}_6\text{F}_3\text{I}$ : 285.9466 ( $\text{M}^+$ ), found 285.9465.

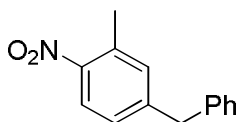
*tert*-butyl (3-iodo-2-methylphenyl)carbamate (**1f**)



3-iodo-2-methylaniline (1.00 g, 4.29 mmol) and  $\text{Boc}_2\text{O}$  (890 mg, 4.08 mmol) were combined and stirred, followed by the addition of  $\text{I}_2$  (108 mg, 0.43 mmol). The mixture was stirred for 6 h, eventually becoming a solid mass. MeOH (10 mL) was added to facilitate stirring, and the mixture stirred an additional 2 d. The mixture was then concentrated *in vacuo*, and taken up in 10 mL EtOAc, which was then washed with 10 mL 10 %  $\text{Na}_2\text{S}_2\text{O}_8$ . The organic phase was then dried with  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated *in vacuo*. The crude mixture was purified by flash chromatography on silica gel ( $R_f$  0.68 in 20 % EtOAc/hexane) using 20 % EtOAc/hexane to afford **1f** as a pale gray solid (mp =  $94\text{--}96^\circ\text{C}$ ). Isolated yield: 1.00 g (74 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.52 (s, 9H), 2.41 (s, 3H), 6.28 (br s, 1H), 6.88 (t,  $J=8.0$  Hz, 1H), 7.60 (dd,  $J=7.8, 1.2$  Hz, 1H), 7.71 (br d,  $J=8.2$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  23.4, 28.3, 80.8, 101.8, 122.2, 128.0, 135.1, 136.3, 153.0; IR thin film,  $\nu$  ( $\text{cm}^{-1}$ ) 774 (w), 1165 (w), 1244 (w), 1362 (w), 1428 (m), 1505 (m), 1558 (m), 1698 (s), 3358 (s); Elemental Anal. Calc'd for

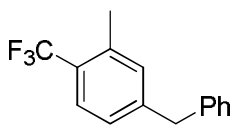
$C_{12}H_{16}NO_2I$ : C: 43.26 % (found 43.25 %), H: 4.84 % (found 4.86 %), N: 4.20 % (found 4.44 %).

4-benzyl-2-methyl-1-nitrobenzene (**3a**)



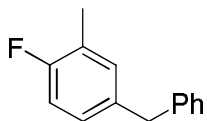
Following the general procedure 2-iodo-6-nitrotoluene **1a** (53 mg, 0.20 mmol) and benzyl chloride **2a** (46  $\mu$ L, 0.40 mmol) were reacted at 90 °C for 14 h. The crude mixture was purified by flash chromatography on silica gel ( $R_f$  0.54 in 5 % Et<sub>2</sub>O/pentane) using 3 % to 5 % Et<sub>2</sub>O/pentane to afford **3a** as a yellow oil. Isolated yield: 39 mg (86 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  2.56 (s, 3H), 4.00 (s, 2H), 7.09–7.18 (m, 4H), 7.20–7.26 (m, 1H), 7.28–7.33 (m, 2H), 7.91 (dd,  $J$ =9.1, 2.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  20.7, 41.5, 125.1, 126.6, 127.3, 128.7, 128.9, 133.1, 134.0, 139.4, 147.0, 147.4; IR neat,  $\nu$  (cm<sup>-1</sup>) 701 (m), 723 (m), 1029 (w), 1075 (w), 1341 (m), 1508 (m), 1585 (m), 1609 (m), 3027 (w); HRMS (EI) Calc'd for C<sub>14</sub>H<sub>13</sub>NO<sub>2</sub>: 227.0946 (M<sup>+</sup>), found 227.0947.

4-benzyl-2-methyl-1-(trifluoromethyl)benzene (**3b**)



Following the general procedure 1-iodo-2-methyl-3-(trifluoromethyl)benzene **1b** (57 mg, 0.20 mmol) and benzyl chloride **2a** (46  $\mu$ L, 0.40 mmol) were reacted at 90 °C for 14 h. The crude mixture was purified by flash chromatography on silica gel ( $R_f$  0.30 in pentane) using pentane to afford **3b** as a clear, colourless oil. Isolated yield: 28 mg (56 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  2.43 (q,  $J$ =1.8 Hz, 3H), 3.97 (s, 2H), 7.07 (d,  $J$ =8.8 Hz, 1H), 7.09 (br s, 1H), 7.15–7.19 (m, 2H), 7.19–7.24 (m, 1H), 7.27–7.32 (m, 2H), 7.50 (d,  $J$ =7.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  19.5 (q,  $J$ =1.7 Hz), 41.8, 120.9, 123.6, 126.2 (q,  $J$ =5.1 Hz), 126.4, 126.6, 128.8, 129.1, 132.6, 137.0, 140.3, 145.2; <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)  $\delta$  -61.7 (br s); IR neat,  $\nu$  (cm<sup>-1</sup>) 698 (m), 721 (m), 1042 (s), 1123 (br s), 1158 (m), 1176 (m), 1318 (s), 1452 (m), 1616 (m), 3028 (m); HRMS (EI) Calc'd for C<sub>15</sub>H<sub>13</sub>F<sub>3</sub>: 250.0969 (M<sup>+</sup>), found 250.0972.

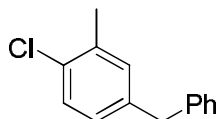
4-benzyl-1-fluoro-2-methylbenzene (**3c**)



Following the general procedure 2-fluoro-6-iodotoluene **1c** (47 mg, 0.20 mmol) and benzyl chloride **2a** (46  $\mu$ L, 0.40 mmol) were reacted at 90 °C for 14 h. The crude mixture was purified by flash chromatography on silica gel ( $R_f$  0.24 in pentane) using pentane to afford **3c** as a clear, colourless oil. Isolated yield: 31 mg (77 %). <sup>1</sup>H NMR (400 MHz,

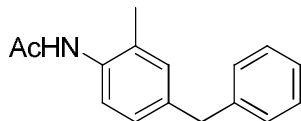
CDCl<sub>3</sub>)  $\delta$  2.22 (d,  $J=1.9$  Hz, 3H), 3.90 (s, 2H), 6.87–6.92 (m, 1H), 6.92–6.95 (m, 1H), 6.96–7.00 (m, 1H), 7.14–7.18 (m, 2H), 7.18–7.22 (m, 1H), 7.25–7.30 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  14.5 (d,  $J=3.7$  Hz), 41.1, 114.8 (d,  $J=22.1$  Hz), 124.6 (d,  $J=16.9$  Hz), 126.1, 127.5 (d,  $J=7.4$  Hz), 128.5, 128.8, 131.8 (d,  $J=5.1$  Hz), 136.4 (d,  $J=4.4$  Hz), 141.1, 159.9 (d,  $J=242.7$  Hz); <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)  $\delta$  -122.24 – -122.12 (m); IR neat,  $\nu$  (cm<sup>-1</sup>) 696 (s), 722 (s), 775 (m), 881 (w), 1118 (s), 1208 (s), 1247 (s), 1500 (s), 1602 (m), 2922 (m); HRMS (EI) Calc'd for C<sub>14</sub>H<sub>13</sub>F: 200.1001 (M<sup>+</sup>), found 200.1001.

#### 4-benzyl-1-chloro-2-methylbenzene (**3d**)

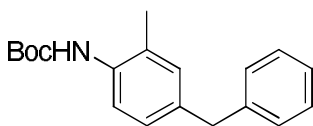


Following the general procedure 2-chloro-6-iodotoluene **1d** (50 mg, 0.20 mmol) and benzyl chloride **2a** (46  $\mu$ L, 0.40 mmol) were reacted at 90 °C for 18 h. The crude mixture was purified by flash chromatography on silica gel ( $R_f$  0.25 in pentane, CAN stain) using pentane to afford **3d** as a clear, colourless oil. Isolated yield: 29 mg (67 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  2.32 (s, 3H), 3.90 (s, 2H), 6.93 (ddd,  $J=8.1, 2.2, 0.6$  Hz, 1H), 7.04 (d,  $J=1.6$  Hz, 1H), 7.14–7.17 (m, 2H), 7.17–7.21 (m, 1H), 7.21–7.24 (m, 1H), 7.25–7.30 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  20.0, 41.2, 126.2, 127.6, 128.5, 128.8, 129.0, 131.5, 132.0, 135.9, 139.6, 140.7; IR neat,  $\nu$  (cm<sup>-1</sup>) 696 (s), 723 (s), 797 (m), 830 (m), 1045 (s), 1162 (w), 1452 (m), 1482 (s), 1598 (m), 2921 (m); HRMS (EI) Calc'd for C<sub>14</sub>H<sub>13</sub>Cl: 216.0706 (M<sup>+</sup>), found 216.0710.

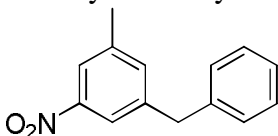
#### N-(4-benzyl-2-methylphenyl)acetamide (**3e**)



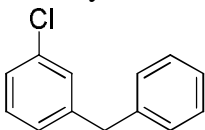
Following the general procedure N-(3-iodo-2-methylphenyl)acetamide **1e** (55 mg, 0.20 mmol) and benzyl chloride **2a** (46  $\mu$ L, 0.40 mmol) were reacted at 90 °C for 18 h. The crude mixture was purified by flash chromatography on silica gel ( $R_f$  0.13 in 50 % EtOAc/pentane) using 50 % to 60 % EtOAc/pentane to afford **3e** as a crystalline, off-white solid (mp = 106–108 °C). Isolated yield: 36 mg (75 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  2.14 (s, 3H), 2.17 (s, 3H), 3.89 (s, 2H), 6.97–7.02 (m, 2H), 7.11 (br s, 1H), 7.17 (app t,  $J=8.7$  Hz, 3H), 7.27 (app t,  $J=7.3$  Hz, 2H), 7.55 (d,  $J=7.8$  Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  17.7, 24.0, 41.3, 123.9, 126.0, 127.1, 128.4, 128.8, 130.0, 130.9, 133.6, 138.2, 141.0, 168.4; IR thin film,  $\nu$  (cm<sup>-1</sup>) 694 (m), 793 (w), 1122 (w), 1298 (m), 1368 (m), 1533 (s), 1653 (s), 3272 (br, s); HRMS (EI) Calc'd for C<sub>16</sub>H<sub>17</sub>NO: 239.1310 (M<sup>+</sup>), found 239.1310.

tert-butyl (4-benzyl-2-methylphenyl)carbamate (**3f**)

Following the general procedure tert-butyl (3-iodo-2-methylphenyl)carbamate **1f** (67 mg, 0.20 mmol) and benzyl chloride **2a** (46  $\mu$ L, 0.40 mmol) were reacted at 90 °C for 16 h. The crude mixture was purified by flash chromatography on silica gel ( $R_f$  0.65 in 10 % EtOAc/pentane) using 10 % EtOAc/pentane to afford **3f** as a viscous colourless oil which slowly solidifies to a white solid (mp = 63–64 °C). Isolated yield: 42 mg (71 %).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.51 (s, 9H), 2.19 (s, 3H), 3.89 (s, 2H), 6.19 (br s, 1H), 6.96 (s, 1H), 7.02 (dd,  $J=8.2, 1.8$  Hz, 1H), 7.14–7.21 (m, 3H), 7.23–7.30 (m, 2H), 7.67 (d,  $J=8.2$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  17.7, 28.3, 41.3, 80.3, 121.4, 125.9, 127.2, 128.4, 128.8, 130.8, 134.3, 136.5, 141.3, 153.2; IR thin film,  $\nu$  ( $\text{cm}^{-1}$ ) 723 (m), 1024 (m), 1049 (m), 1160 (s), 1237 (m), 1366 (m), 1451 (m), 1522 (s), 1718 (s), 2975 (m), 3329 (br, m); HRMS (EI) Calc'd for  $\text{C}_{19}\text{H}_{23}\text{NO}_2$ : 297.1729 ( $\text{M}^+$ ), found 297.1724.

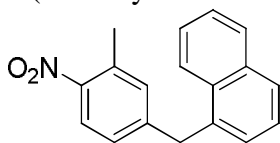
1-benzyl-3-methyl-5-nitrobenzene (**3g**)

Following the general procedure 2-iodo-5-nitrotoluene **1g** (53 mg, 0.20 mmol) and benzyl chloride **2a** (46  $\mu$ L, 0.40 mmol) were reacted at 90 °C for 14 h. The crude mixture was purified by flash chromatography on silica gel ( $R_f$  0.58 in 5 %  $\text{Et}_2\text{O}$ /pentane) using 3 % to 4 %  $\text{Et}_2\text{O}$ /pentane to afford **3g** as a pale yellow oil, slowly solidifying to a white solid (mp = 42–43 °C). Isolated yield: 33 mg (73 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.40 (s, 3H), 4.02 (s, 2H), 7.16–7.20 (m, 2H), 7.21–7.26 (m, 1H), 7.29–7.33 (m, 3H), 7.85–7.87 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  21.2, 41.5, 121.0, 121.8, 126.6, 128.7, 128.8, 135.8, 139.5, 139.8, 142.8, 148.4; IR thin film,  $\nu$  ( $\text{cm}^{-1}$ ) 683 (m), 704 (s), 746 (m), 780 (m), 816 (w), 878 (m), 914 (m), 1028 (m), 1101 (m), 1346 (s), 1446 (s), 1492 (s), 1534 (s), 3061 (s); HRMS (EI) Calc'd for  $\text{C}_{14}\text{H}_{13}\text{NO}_2$ : 227.0946 ( $\text{M}^+$ ), found 227.0950.

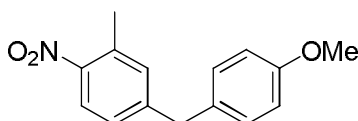
1-benzyl-3-chlorobenzene (**3h**)

Following the general procedure 2-chloro-1-iodobenzene **1h** (24  $\mu$ L, 0.2 mmol) and benzyl chloride **2a** (46  $\mu$ L, 0.40 mmol) were reacted at 90 °C for 12 h. The crude mixture was purified by flash chromatography on silica gel ( $R_f$  0.32 in pentane) using pentane to afford **3h** as a clear, colourless oil. Isolated yield: 14 mg (34 %). The spectroscopic properties of **3h** were identical to those previously reported in the literature.

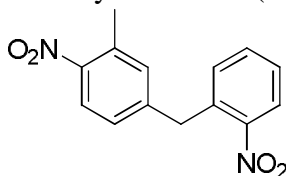


1-(3-methyl-4-nitrobenzyl)naphthalene (**3i**)

Following the general procedure 2-iodo-6-nitrotoluene **1a** (53 mg, 0.20 mmol) and 1-(chloromethyl)naphthalene **2b** (78 mg, 0.40 mmol based upon 90 % purity of the material) were reacted at 90 °C for 18 h. The crude mixture was purified by flash chromatography on silica gel ( $R_f$  0.32 in 5 % Et<sub>2</sub>O/pentane) using 5 % Et<sub>2</sub>O/pentane to afford **3i** as a viscous, clear colourless oil. Isolated yield: 33 mg (60 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  2.53 (s, 3H), 4.45 (s, 2H), 7.09–7.12 (m, 1H), 7.13–7.15 (m, 1H), 7.29 (dd,  $J$ =6.9, 1.1 Hz, 1H), 7.42–7.50 (m, 3H), 7.80 (d,  $J$ =8.2 Hz, 1H), 7.84–7.90 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  20.7, 38.7, 123.8, 125.1, 125.5, 125.8, 126.3, 127.0, 127.6, 127.8, 128.8, 131.8, 132.8, 134.0, 134.9, 146.7; IR neat,  $\nu$  (cm<sup>-1</sup>) 779 (m), 1017 (w), 1076 (w), 1166 (w), 1227 (w), 1340 (s), 1507 (s), 1576 (m), 1609 (m); HRMS (EI) Calc'd for C<sub>18</sub>H<sub>15</sub>NO<sub>2</sub>: 277.1103 (M<sup>+</sup>), found 277.1108.

4-(4-methoxybenzyl)-2-methyl-1-nitrobenzene (**3j**)

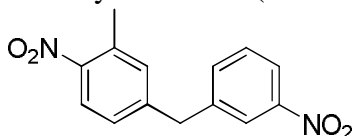
Following the general procedure 2-iodo-6-nitrotoluene **1a** (53 mg, 0.20 mmol) and 1-(chloromethyl)-4-methoxybenzene **2c** (63 mg, 0.40 mmol) were reacted at 90 °C for 16 h. The crude mixture was purified by flash chromatography on silica gel ( $R_f$  0.25 in 5 % Et<sub>2</sub>O/pentane) using 5 % Et<sub>2</sub>O/pentane to afford **3j** as a clear, colourless oil. Isolated yield: 41 mg (80 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  2.56 (s, 3H), 3.79 (s, 3H), 3.94 (s, 2H), 6.83–6.87 (m, 2H), 7.06–7.10 (m, 2H), 7.10–7.13 (m, 2H), 7.91 (d,  $J$ =8.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  20.7, 40.6, 55.2, 114.1, 125.0, 127.1, 129.9, 131.4, 133.0, 134.0, 147.5, 158.3; IR neat,  $\nu$  (cm<sup>-1</sup>) 739 (m), 818 (m), 1036 (m), 1105 (m), 1177 (m), 1244 (m), 1340 (m), 1499 (s), 1585 (m), 1609 (m); HRMS (EI) Calc'd for C<sub>15</sub>H<sub>15</sub>NO<sub>3</sub>: 257.1052 (M<sup>+</sup>), found 257.1056.

2-methyl-1-nitro-4-(2-nitrobenzyl)benzene (**3k**)

Following the general procedure 2-iodo-6-nitrotoluene **1a** (53 mg, 0.20 mmol) and 1-(chloromethyl)-2-nitrobenzene **2d** (69 mg, 0.40 mmol) were reacted at 90 °C for 14 h. The crude mixture was purified by flash chromatography on silica gel ( $R_f$  0.36 in 20 % Et<sub>2</sub>O/pentane) using 10 % to 20 % Et<sub>2</sub>O/pentane to afford **3k** as a pale yellow oil. Isolated yield: 29 mg (53 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  2.57 (s, 3H), 4.35 (s, 2H), 7.07–7.13

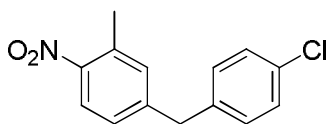
(m, 2H), 7.31 (d,  $J=7.6$  Hz, 1H), 7.46 (td,  $J=7.8, 1.2$  Hz, 1H), 7.59 (td,  $J=7.5, 1.3$  Hz, 1H), 7.92 (d,  $J=8.2$  Hz, 1H), 8.01 (dd,  $J=8.1, 1.3$  Hz, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  20.7, 38.3, 125.2 (2C), 127.2, 128.2, 132.6, 133.1, 133.4, 134.0, 134.1, 144.6; IR neat,  $\nu$  ( $\text{cm}^{-1}$ ) 724 (s), 747 (m), 838 (s), 859 (m), 1164 (m), 1342 (s), 1508 (s), 1586 (s), 1609 (s), 1701 (m); HRMS (EI) Calc'd for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4$ : 272.0797 ( $\text{M}^+$ ), found 272.0790.

#### 2-methyl-1-nitro-4-(3-nitrobenzyl)benzene (**3l**)



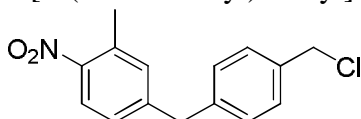
Following the general procedure 2-iodo-6-nitrotoluene **1a** (53 mg, 0.20 mmol) and 1-(chloromethyl)-3-nitrobenzene **2e** (69 mg, 0.40 mmol) were reacted at 90 °C for 14 h. The crude mixture was purified by flash chromatography on silica gel ( $R_f$  0.15 in 20 %  $\text{Et}_2\text{O}$ /pentane) using 15 % to 20 %  $\text{Et}_2\text{O}$ /pentane to afford **3l** as an off-white solid (mp = 83–84 °C). Isolated yield: 41 mg (75 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.59 (s, 3H), 4.12 (s, 2H), 7.14–7.17 (m, 2H), 7.50–7.52 (m, 2H), 7.94–7.97 (m, 1H), 8.05–8.07 (m, 1H), 8.09–8.14 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  20.6, 41.0, 121.9, 123.7, 125.4, 127.3, 129.7, 133.1, 134.4, 135.0, 141.4, 145.0, 147.8; IR thin film,  $\nu$  ( $\text{cm}^{-1}$ ) 704 (m), 725 (m), 746 (w), 802 (w), 839 (m), 891 (w), 1155 (w), 1231 (w), 1338 (s), 1444 (m), 1518 (s), 1585 (m), 1612 (m); HRMS (EI) Calc'd for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4$ : 272.0797 ( $\text{M}^+$ ), found 272.0804.

#### 4-(4-chlorobenzyl)-2-methyl-1-nitrobenzene (**3m**)



Following the general procedure 2-iodo-6-nitrotoluene **1a** (53 mg, 0.20 mmol) and 1-chloro-4-(chloromethyl)benzene **2f** (64 mg, 0.40 mmol) were reacted at 90 °C for 18 h. The crude mixture was purified by flash chromatography on silica gel ( $R_f$  0.42 in 5 %  $\text{Et}_2\text{O}$ /pentane) using 5 %  $\text{Et}_2\text{O}$ /pentane to afford **3m** as a clear, colourless oil. Isolated yield: 36 mg (69 %).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  2.57 (s, 3H), 3.97 (s, 2H), 7.07–7.13 (m, 4H), 7.25–7.30 (m, 2H), 7.92 (d,  $J=9.1$  Hz, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  20.6, 40.8, 125.1, 127.2, 128.8, 130.2, 132.5, 133.0, 134.1, 137.8, 146.3, 147.5; IR neat,  $\nu$  ( $\text{cm}^{-1}$ ) 739 (m), 801 (m), 823 (m), 839 (m), 1015 (m), 1090 (m), 1340 (br s), 1507 (s), 1585 (m), 1610 (m); HRMS (EI) Calc'd for  $\text{C}_{14}\text{H}_{12}\text{ClNO}_2$ : 261.0557 ( $\text{M}^+$ ), found 261.0562.

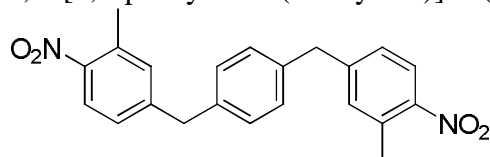
#### 4-[4-(chloromethyl)benzyl]-2-methyl-1-nitrobenzene (**3n**)



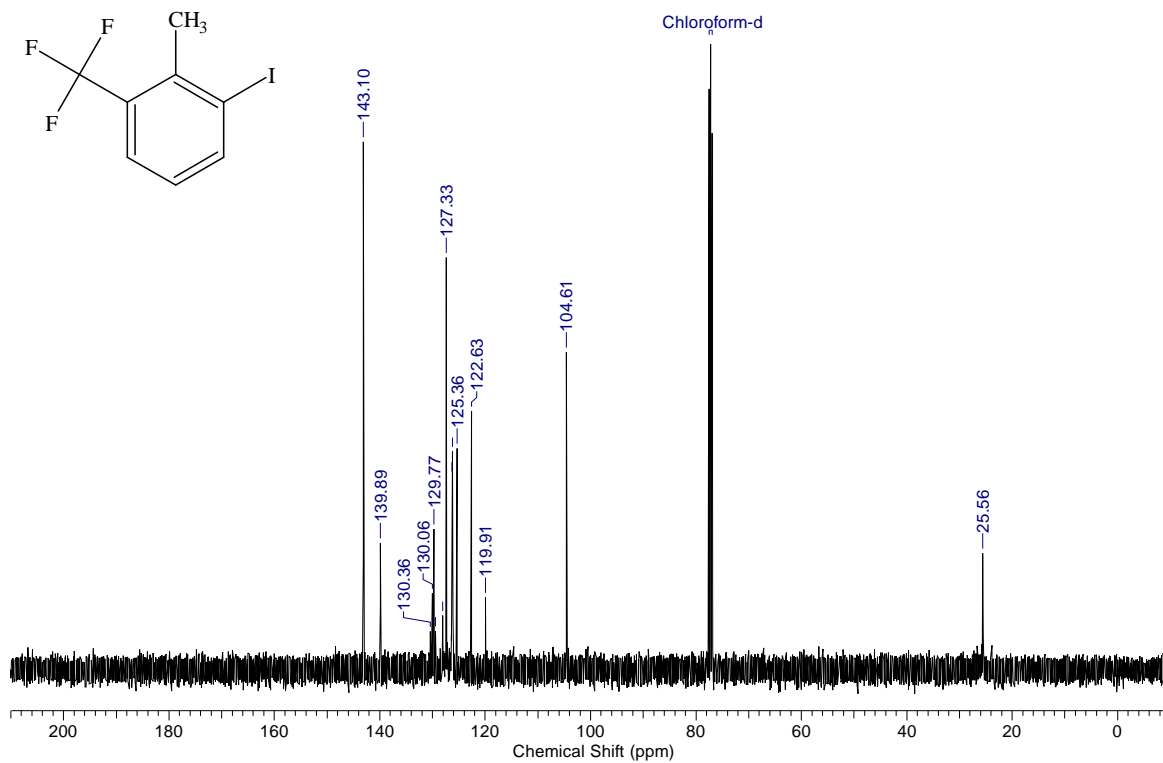
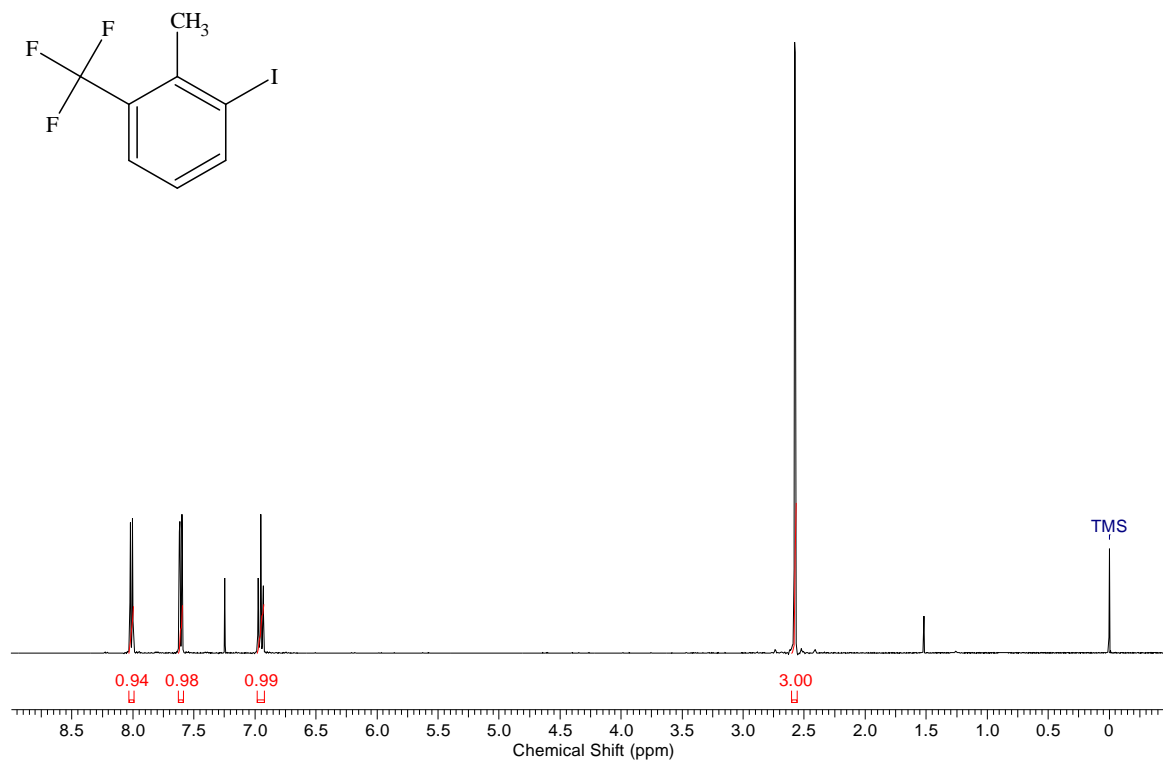
Following the general procedure 2-iodo-6-nitrotoluene **1a** (53 mg, 0.20 mmol) and 1,4-bis(chloromethyl)benzene **2g** (70 mg, 0.40 mmol) were reacted at 90 °C for 18 h. The

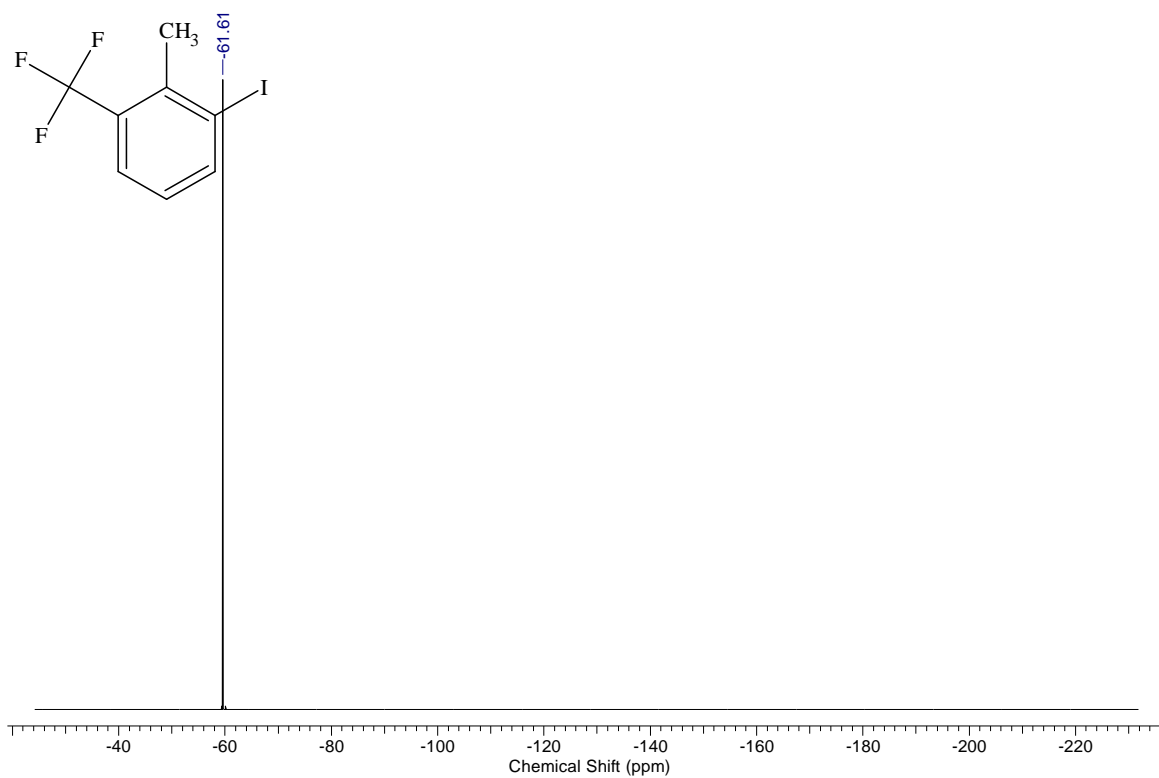
crude mixture was purified by flash chromatography on silica gel ( $R_f$  0.25 in 5 % Et<sub>2</sub>O/pentane) using 5 % to 7 % Et<sub>2</sub>O/pentane to afford **3n** as a viscous, colourless oil. Isolated yield: 20 mg (36 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  2.57 (s, 3H), 3.96 (s, 0.45 H, rotamer), 3.97 (s, 0.15 H, rotamer), 4.00 (s, 1.40 H, rotamer), 4.44 (s, 0.45 H, rotamer), 4.45 (s, 0.05 H, rotamer), 4.57 (s, 1.50 H, rotamer), 7.07–7.18 (m, 4H), 7.30–7.36 (m, 2H), 7.92 (d,  $J$ =9.1 Hz, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  5.6 (rotamer), 20.9, 41.4, 46.2, 125.4, 127.5, 129.0, 129.3, 129.4, 129.5, 129.6, 133.4, 134.3, 136.2, 139.9, 146.8; IR neat,  $\nu$  (cm<sup>-1</sup>) 714 (m), 747 (m), 830 (m), 1109 (m), 1153 (m), 1228 (m), 1261 (m), 1342 (s), 1439 (m), 1508 (s), 1585 (m), 1607 (m), 2921 (s); HRMS (EI) Calc'd for C<sub>15</sub>H<sub>14</sub>ClNO<sub>2</sub>: 275.0713 (M<sup>+</sup>), found 275.0712.

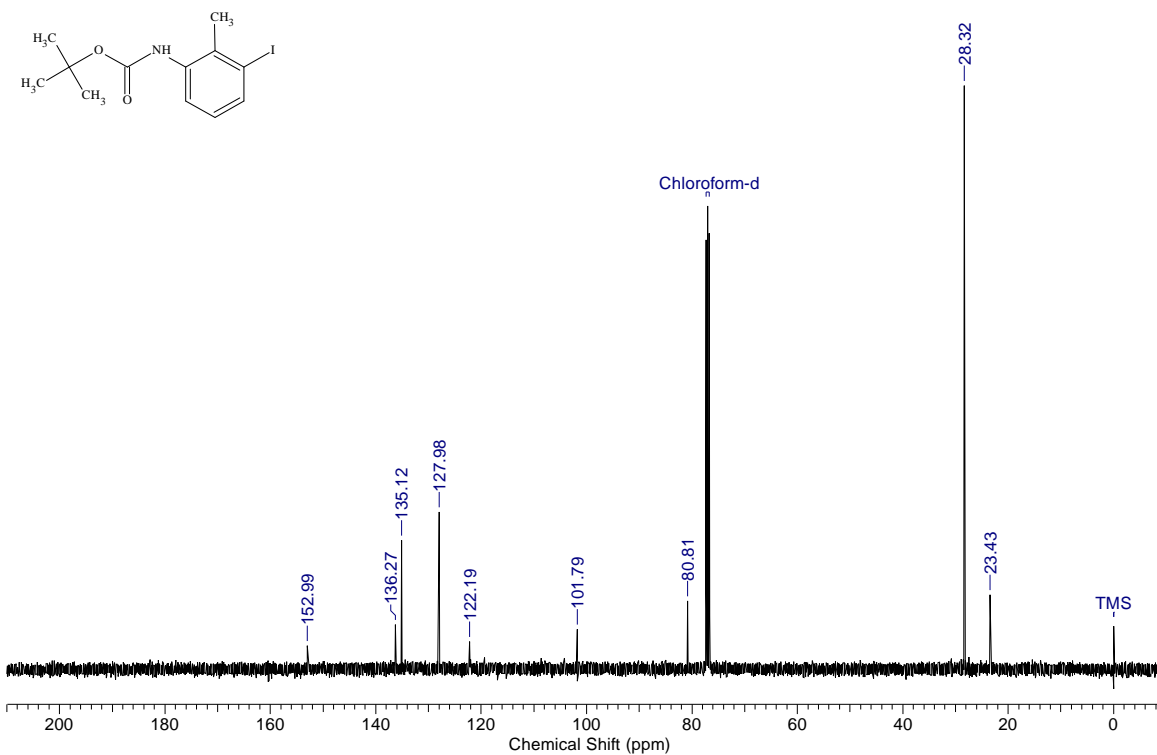
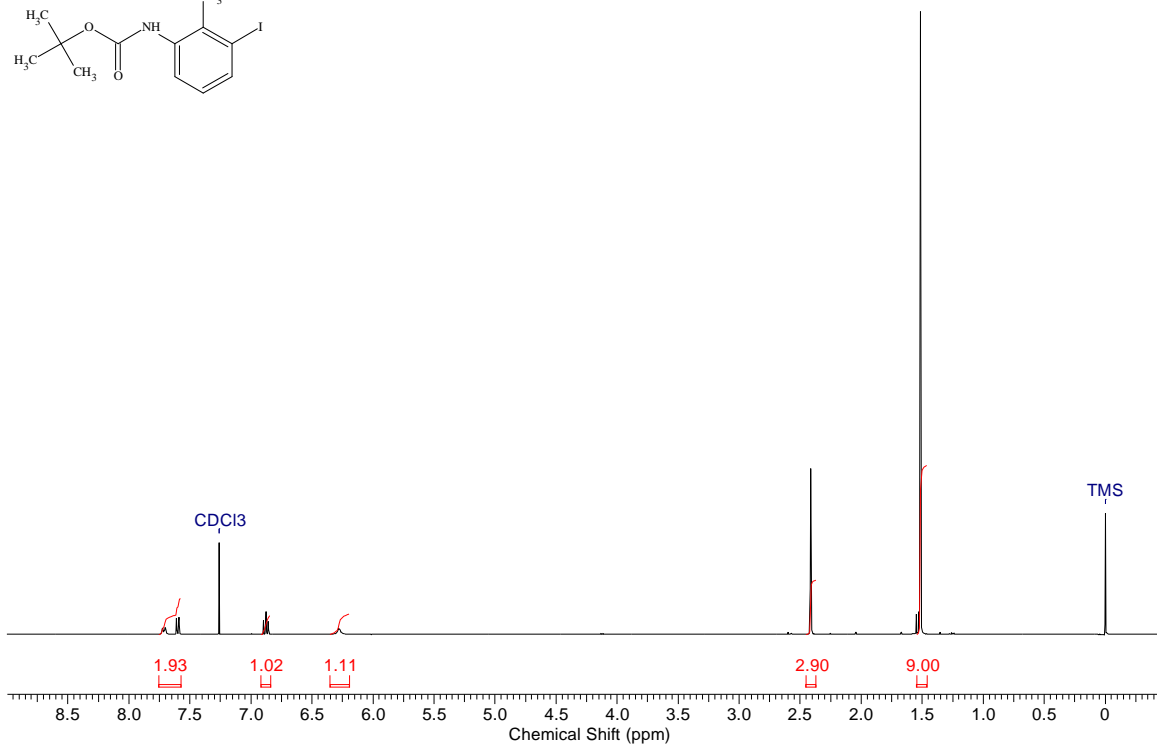
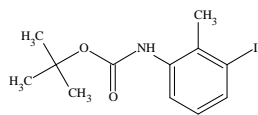
1,1'-[1,4-phenylenedi(methylene)]bis(3-methyl-4-nitrobenzene) (**3o**)



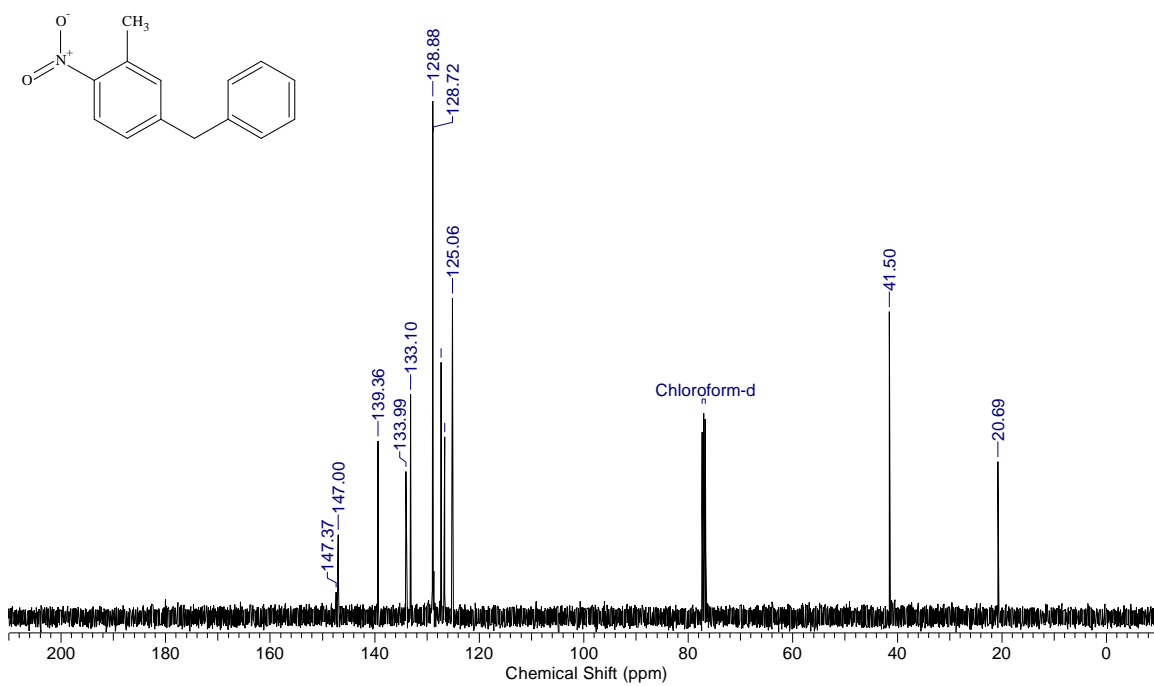
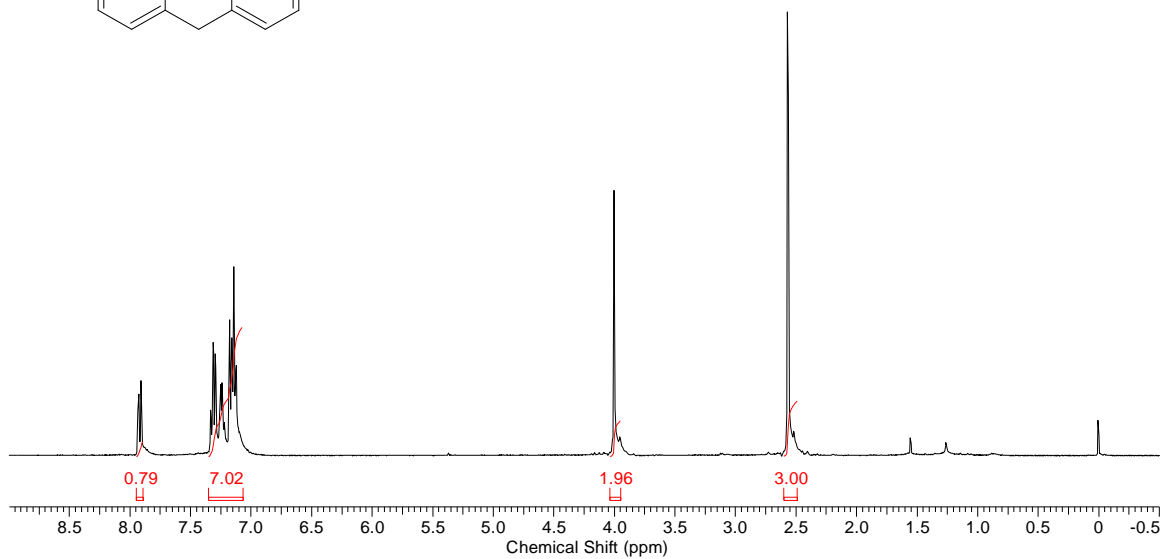
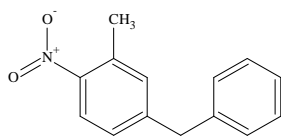
Following the general procedure 2-iodo-6-nitrotoluene **1a** (53 mg, 0.20 mmol) and 1,4-bis(chloromethyl)benzene **2g** (35 mg, 0.20 mmol) were reacted at 90 °C for 18 h. The crude mixture was purified by flash chromatography on silica gel using 10 % to 20 % Et<sub>2</sub>O/pentane to afford **3n** ( $R_f$  0.47 in 10 % Et<sub>2</sub>O/pentane) as a clear, colourless oil and **3o** ( $R_f$  0.25 in 10 % Et<sub>2</sub>O/pentane) as a crystalline white solid (mp = 182 – 183 °C). Isolated yield: **3n**, 9 mg (16 %); **3o**, 13 mg (34 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  2.57 (s, 6H), 3.98 (s, 4H), 7.11 (s, 4H), 7.12–7.13 (m, 1H), 7.13–7.15 (m, 3H), 7.92 (d,  $J$ =8.8 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  20.7, 41.1, 125.1, 127.3, 129.2, 133.1, 134.0, 137.8, 146.8; IR thin film,  $\nu$  (cm<sup>-1</sup>) 729 (m), 829 (m), 896 (w), 1338 (m), 1508 (s), 1607 (m); HRMS (EI) Calc'd for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>: 376.1423 (M<sup>+</sup>), found 376.1422.

**Representative Spectra (in numerical order):****Compound 1b**

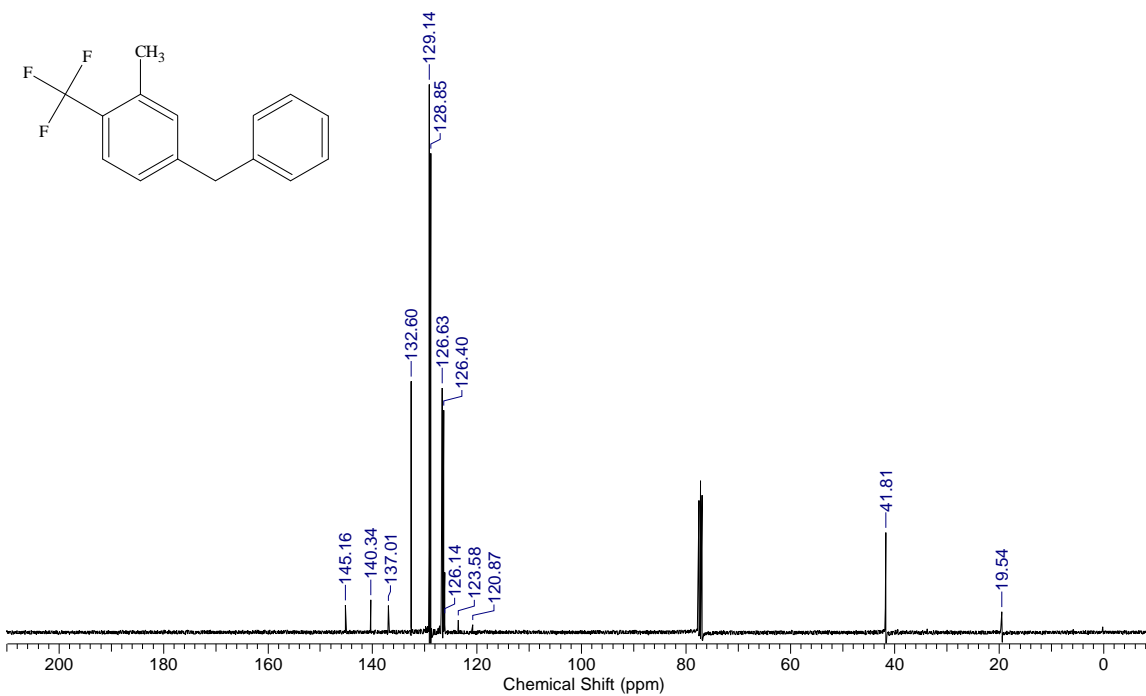
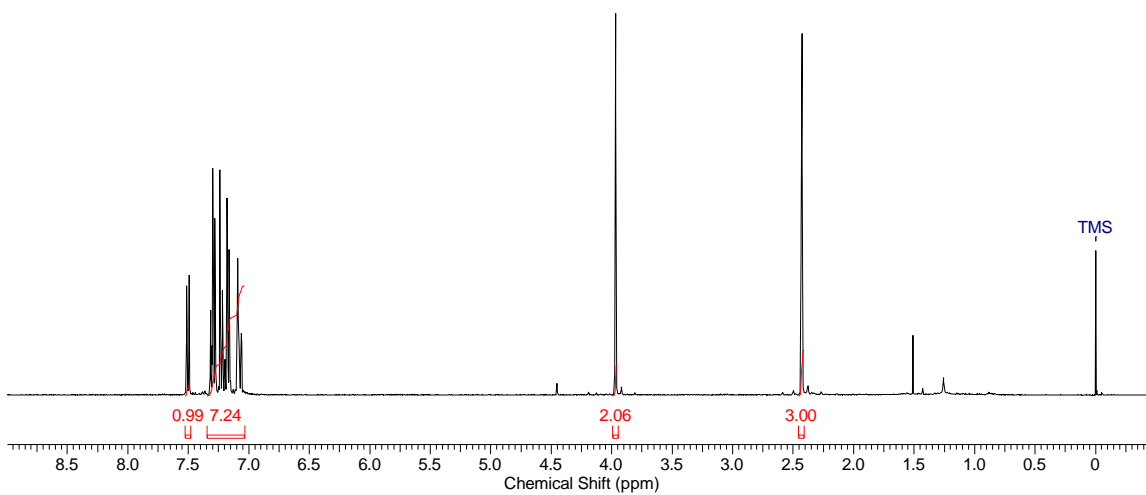
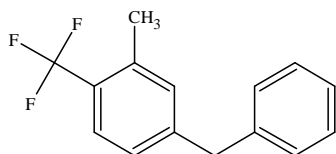


Compound **1f**

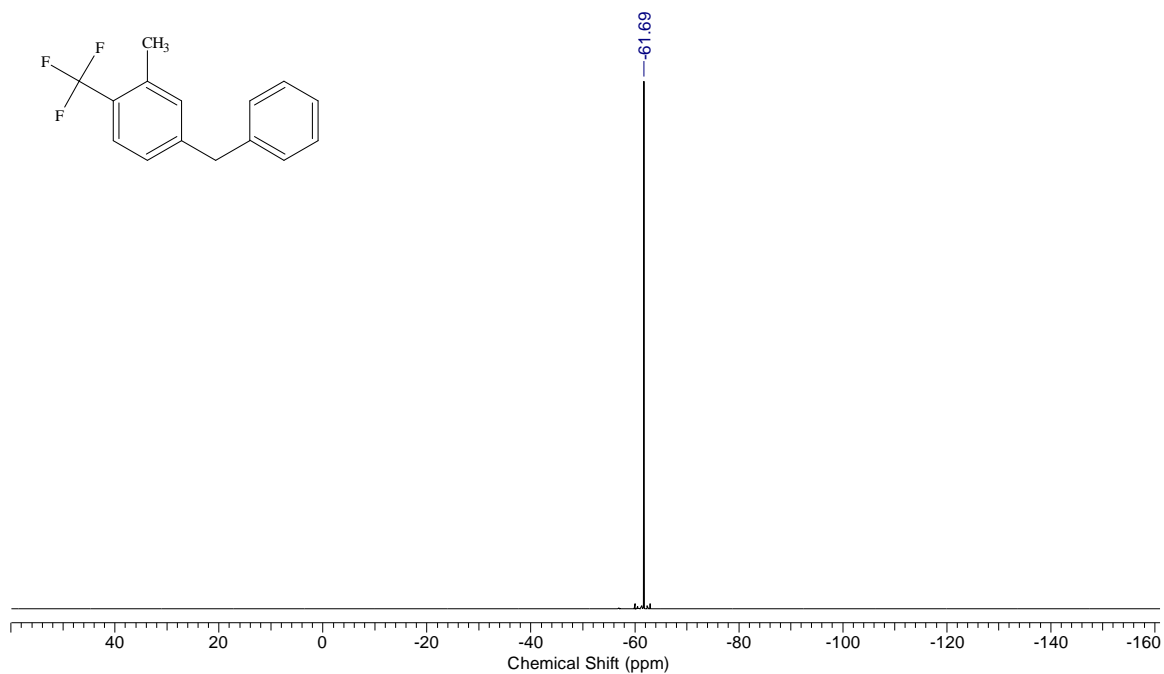
## Compound 3a



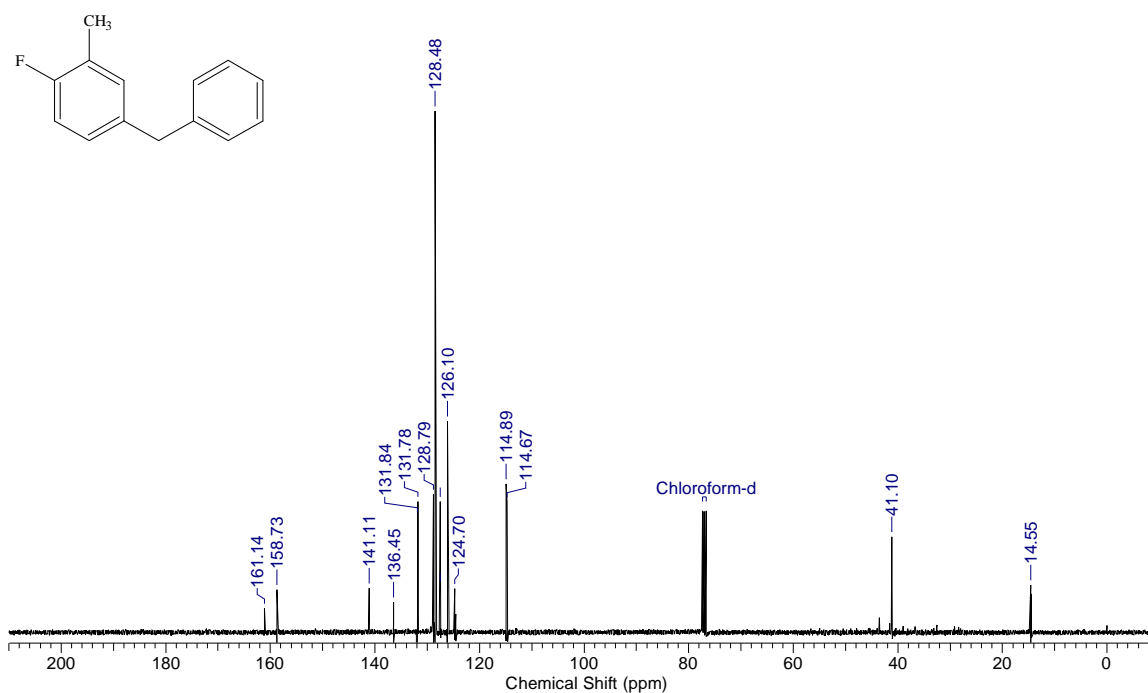
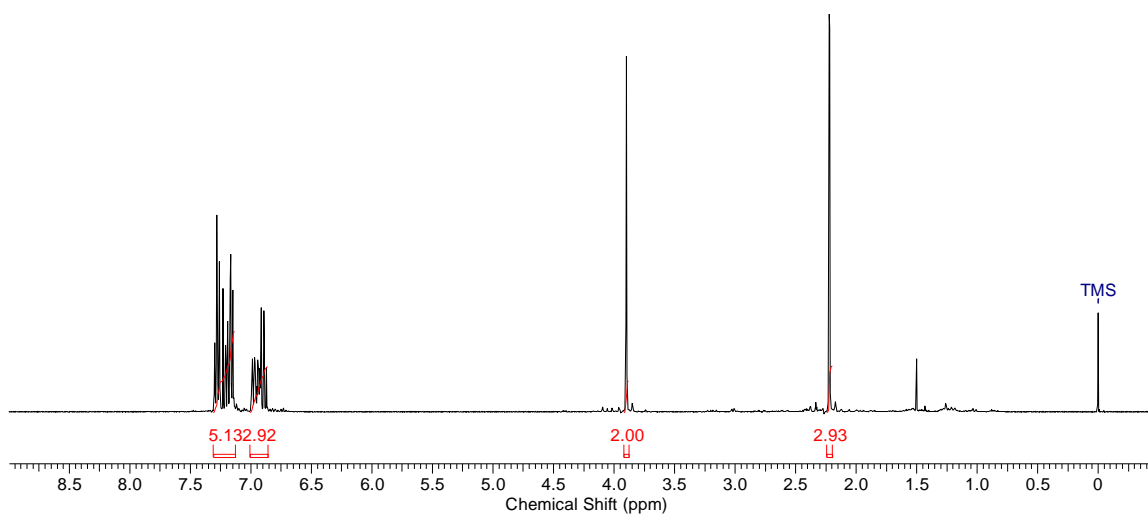
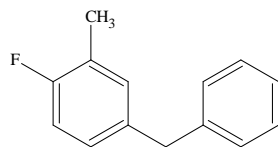
## Compound 3b

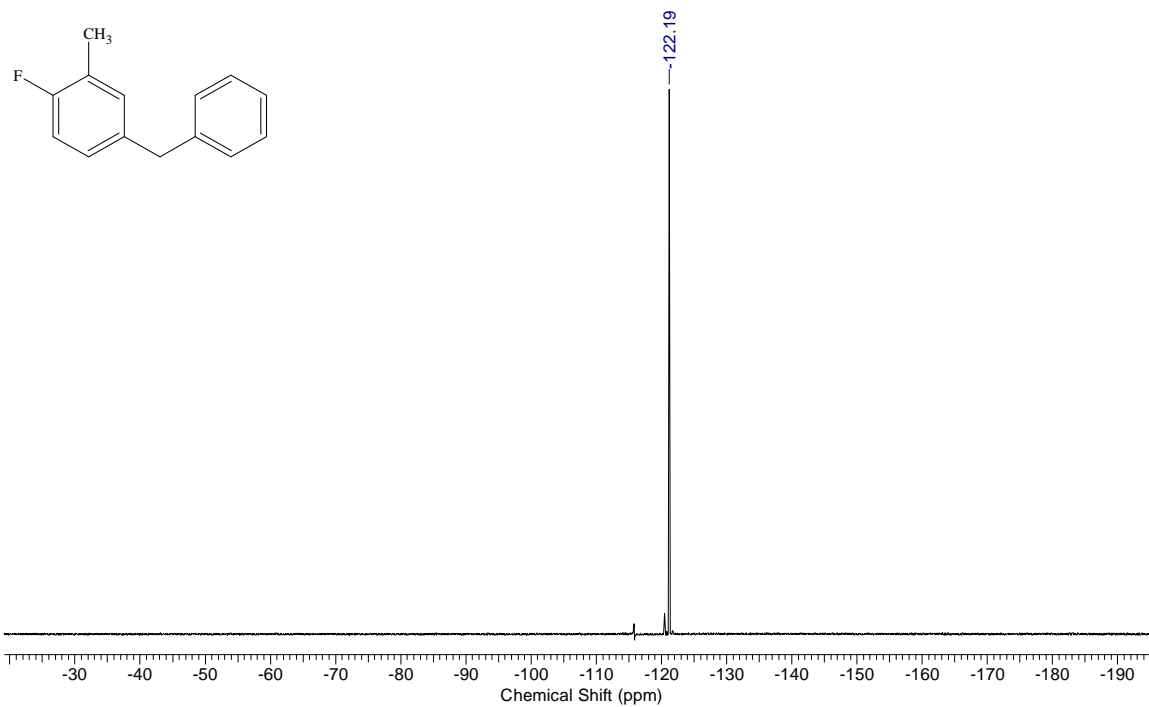


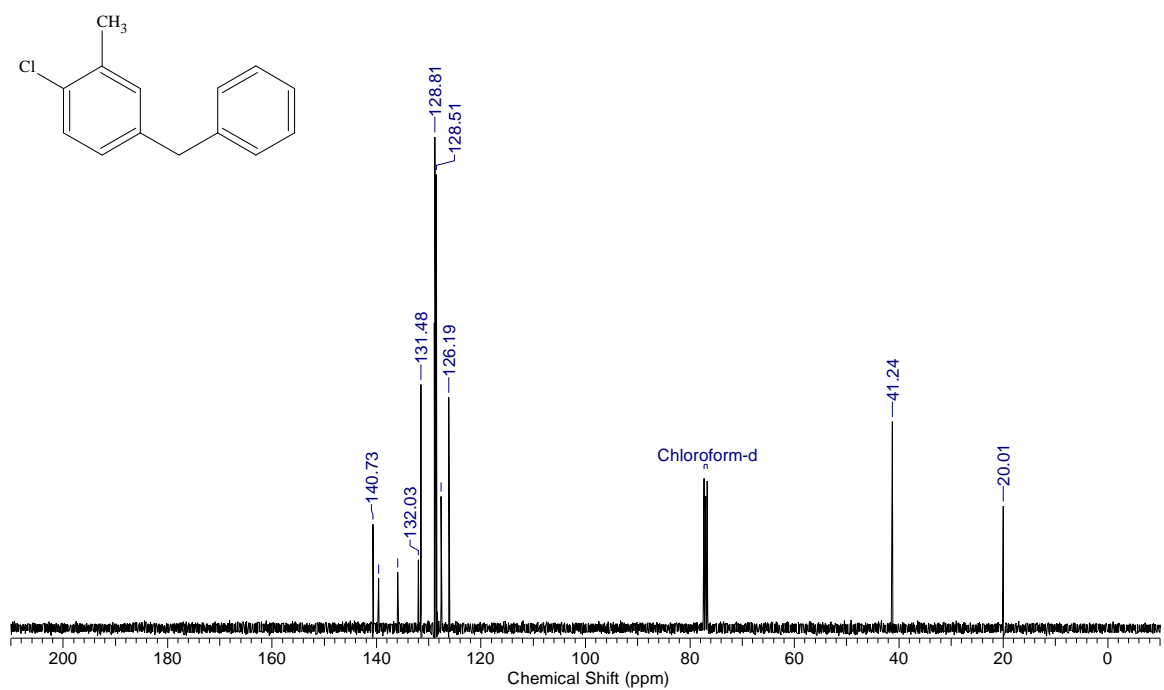
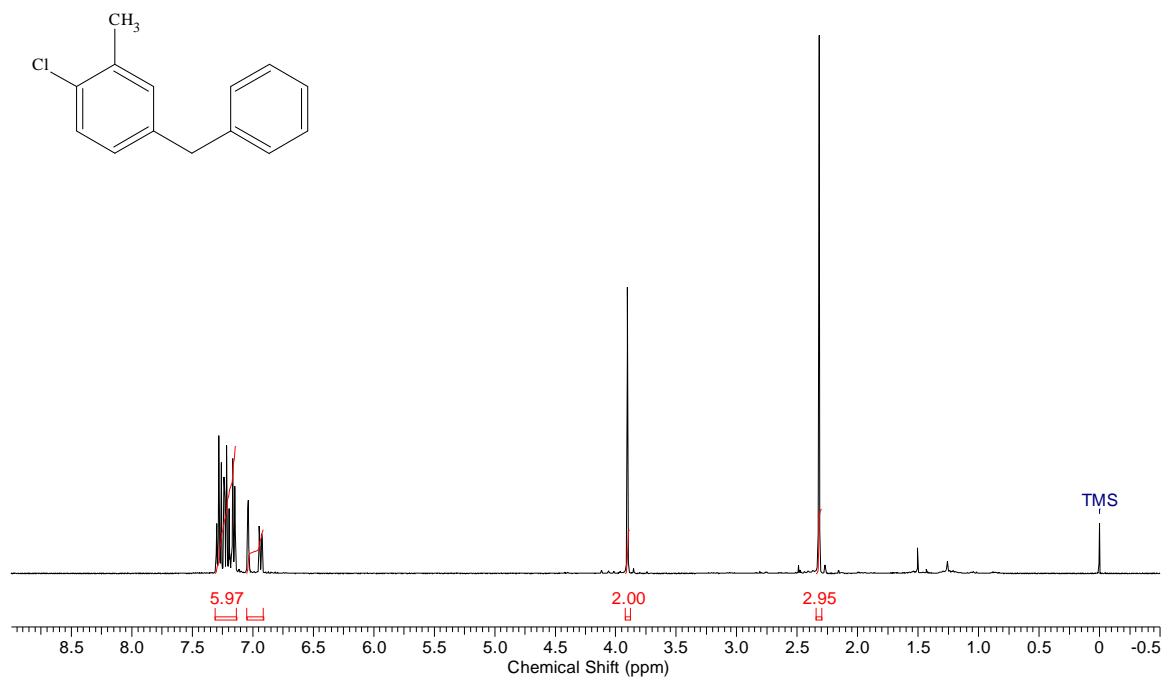


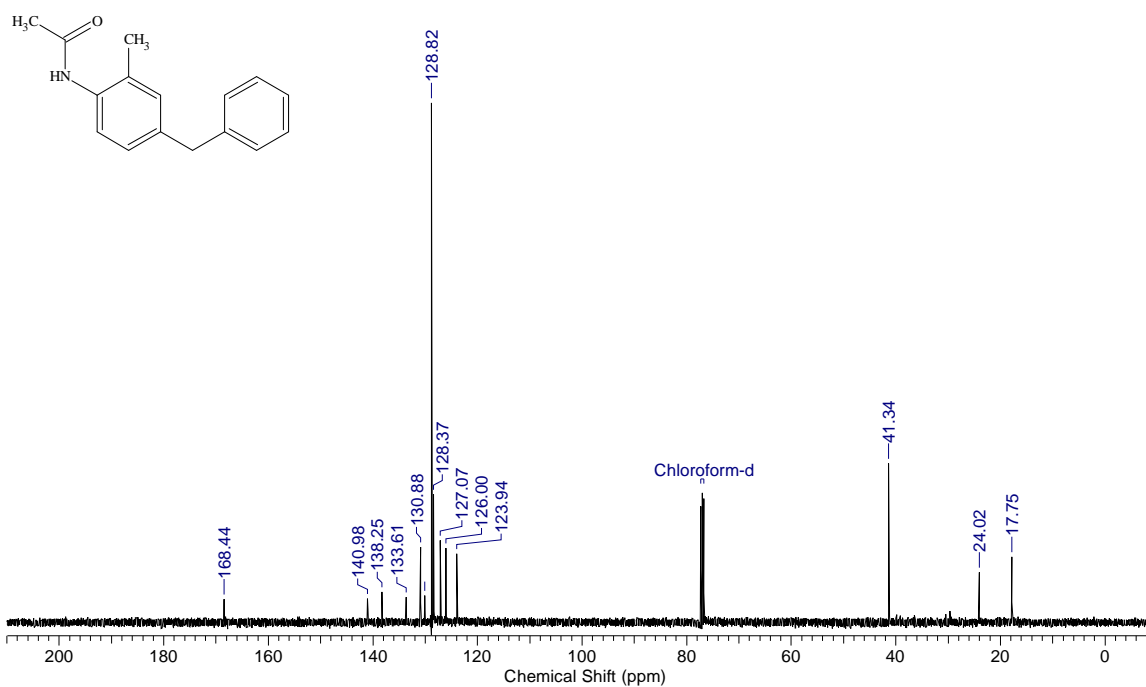
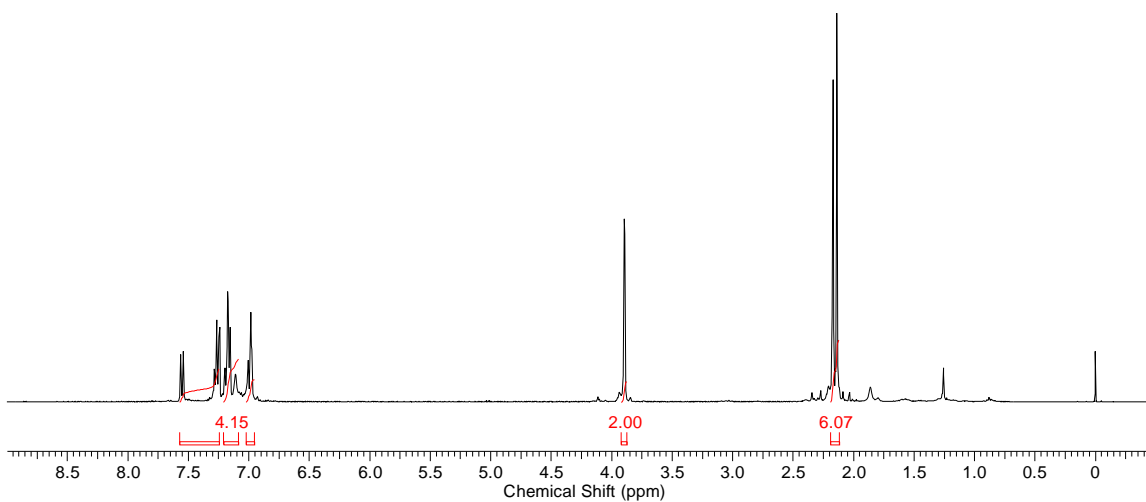
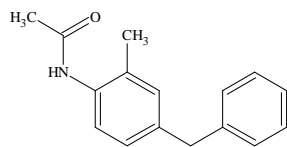


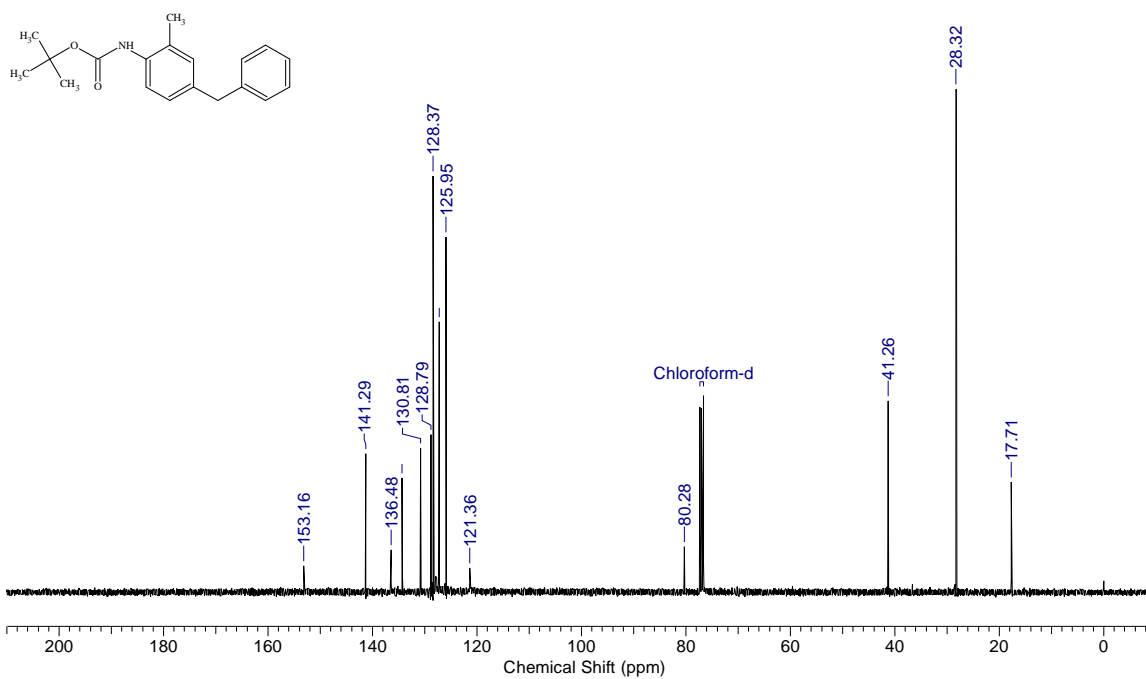
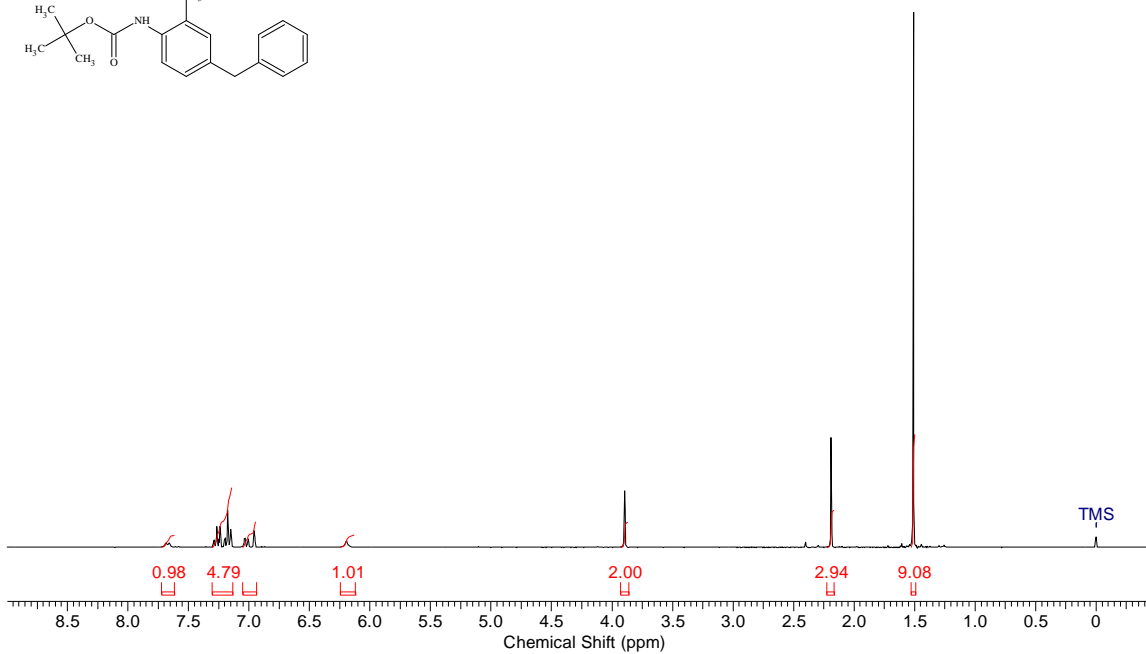
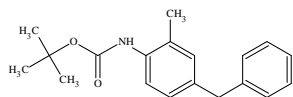
## Compound 3c

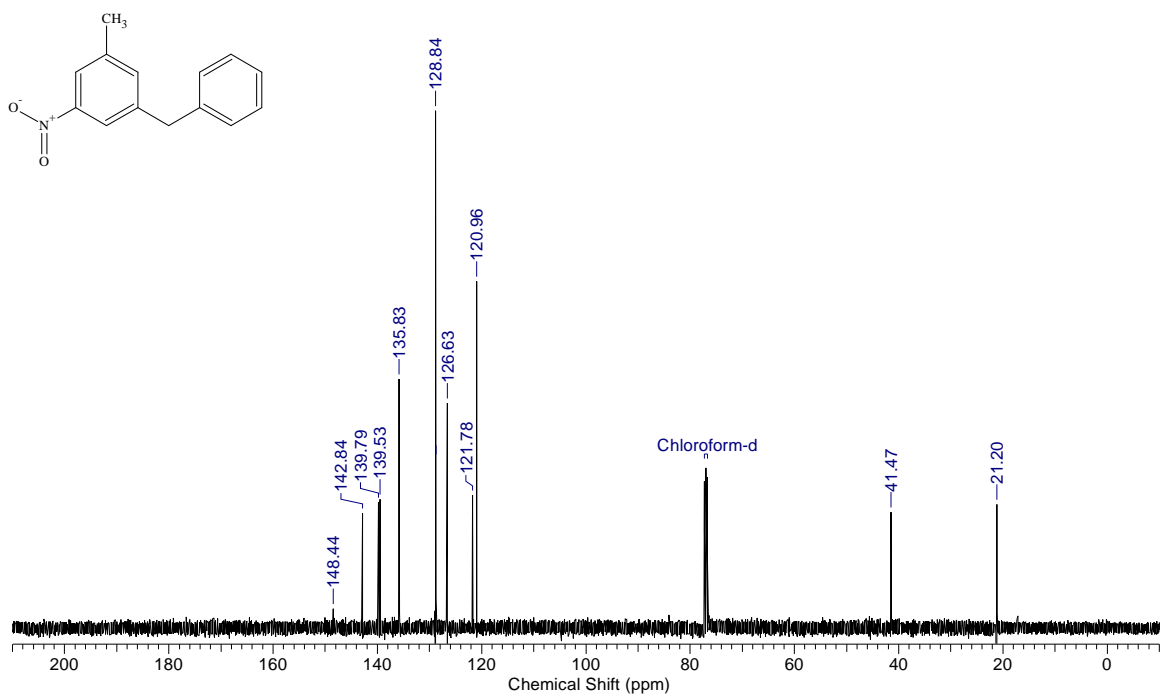
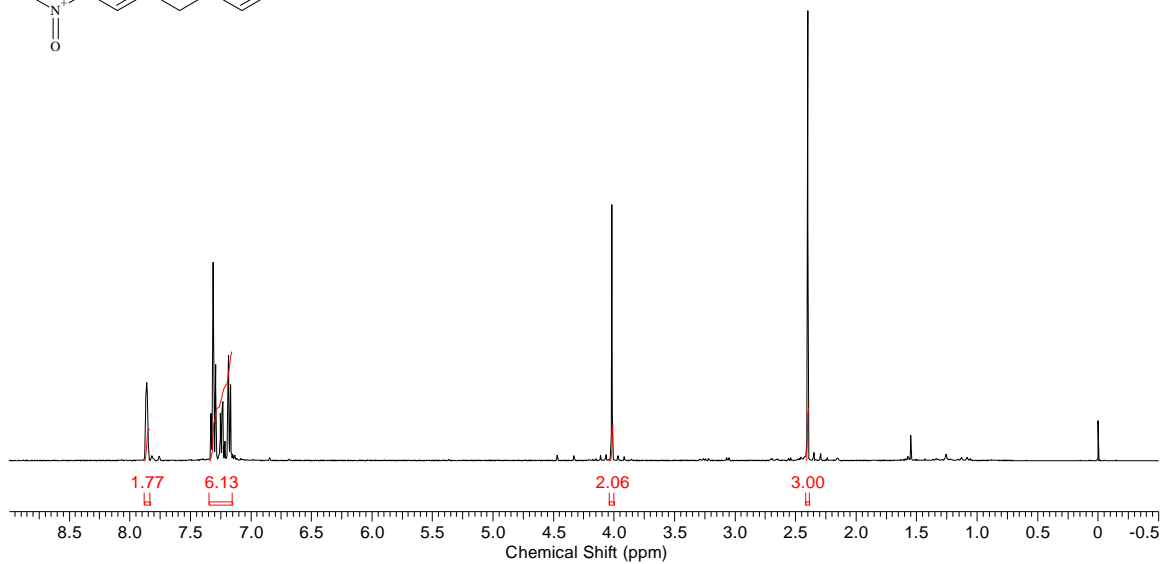
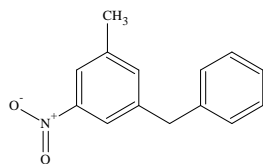


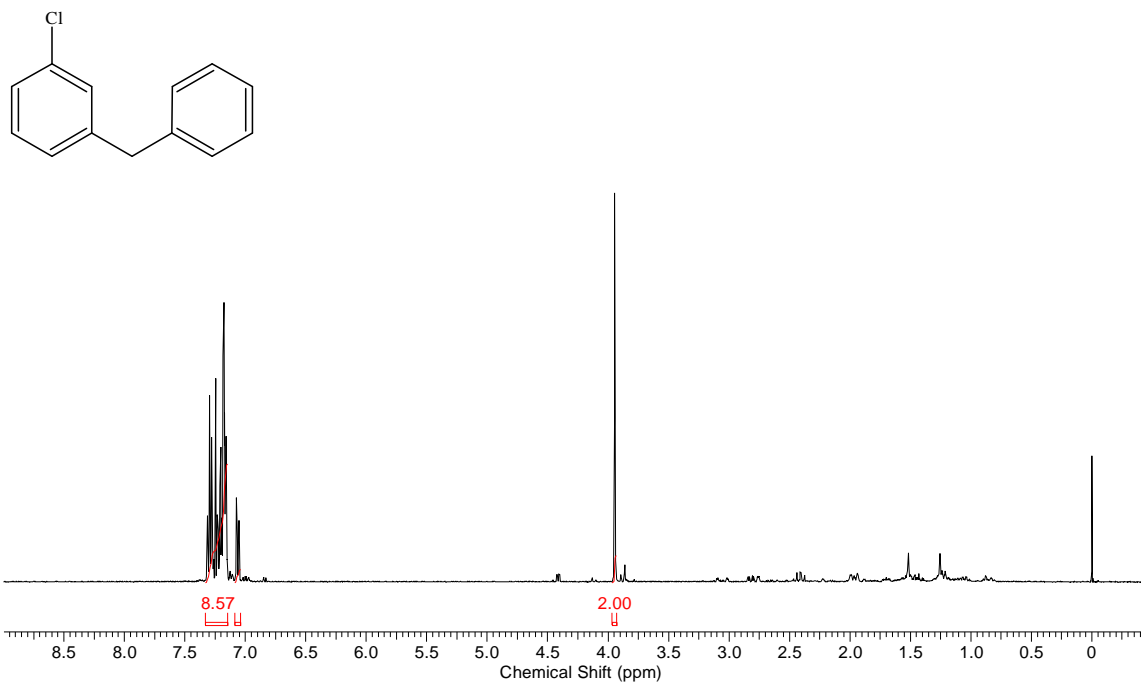


Compound **3d**

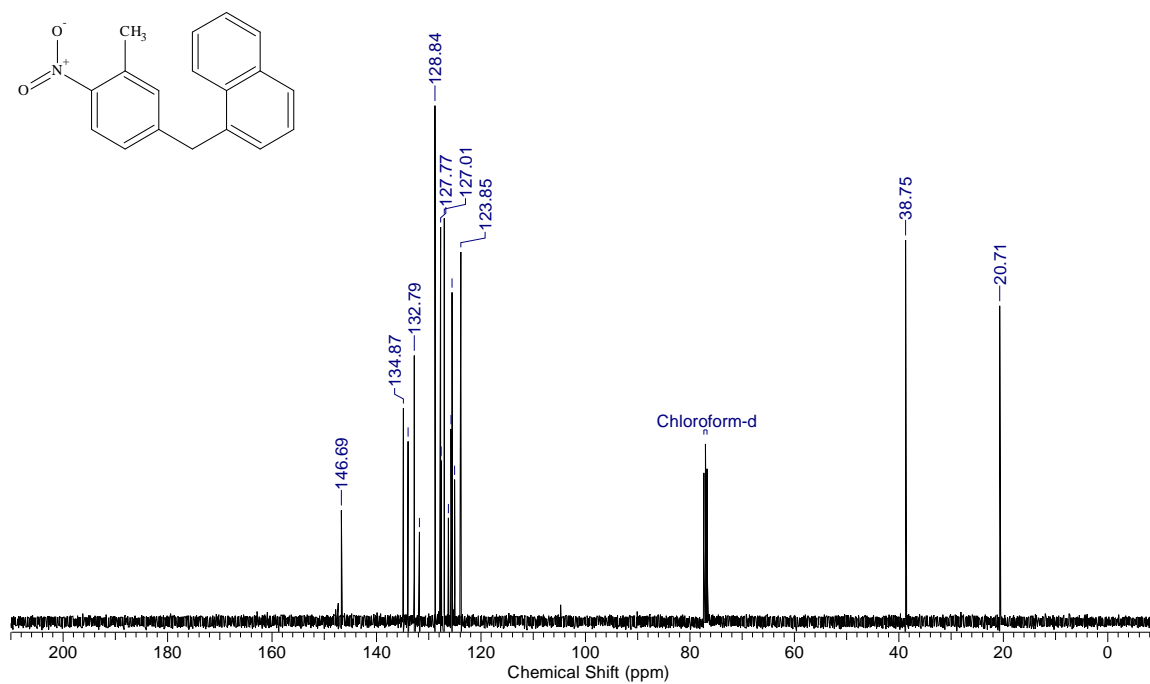
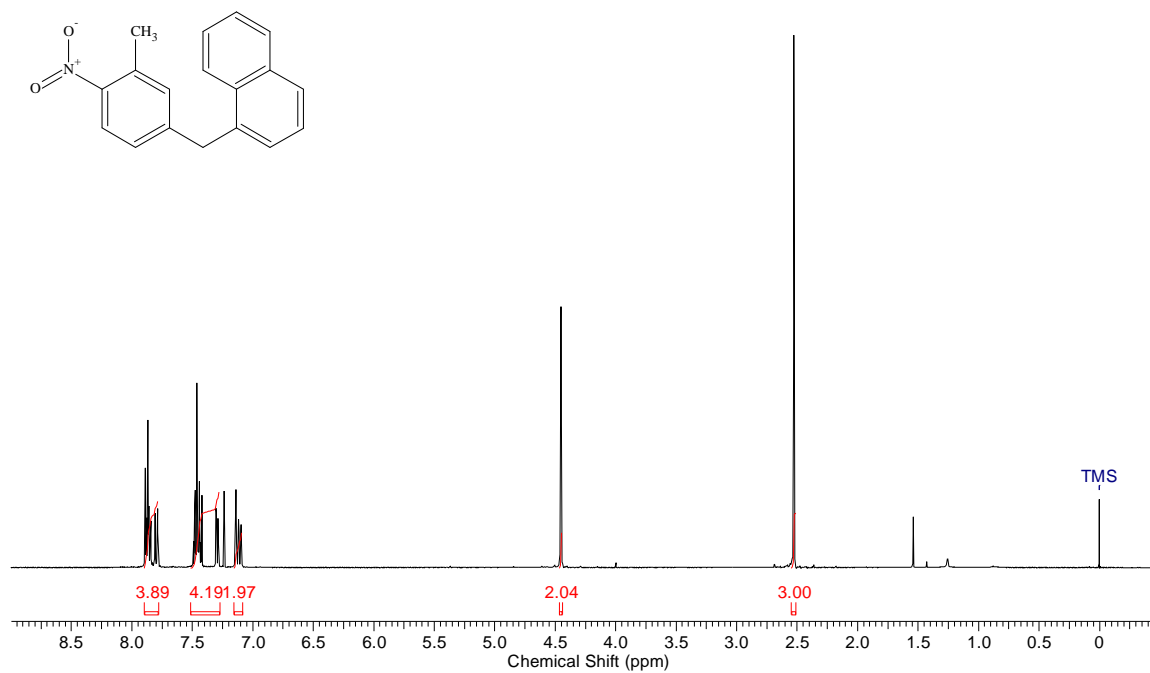
Compound **3e**

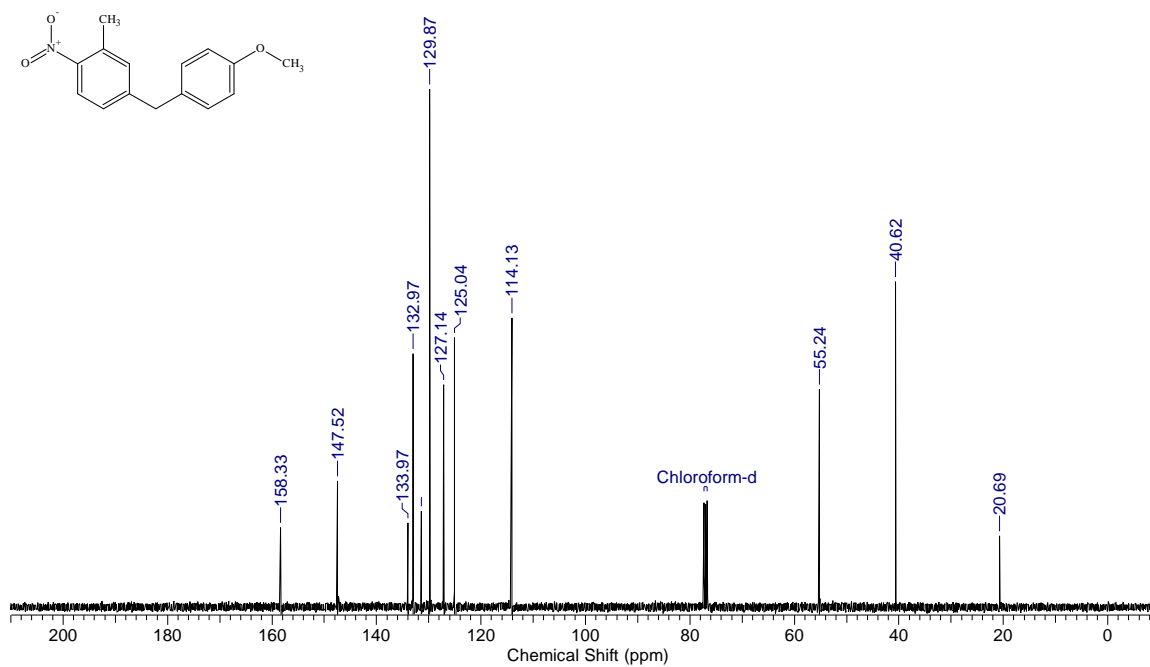
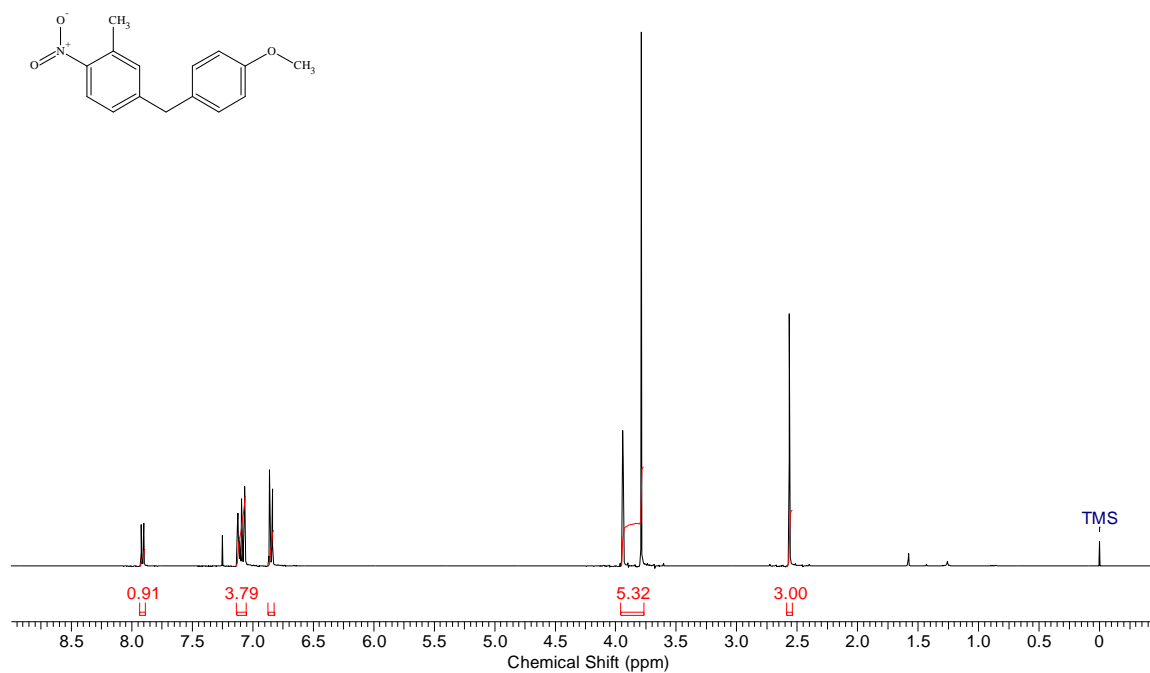
Compound **3f**

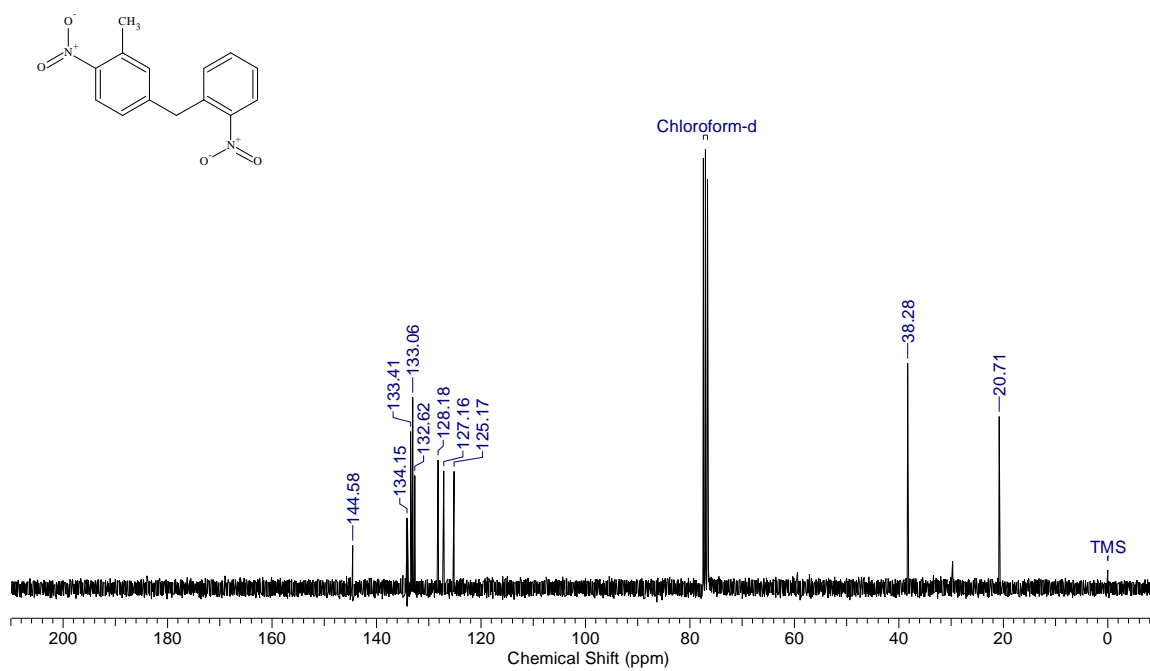
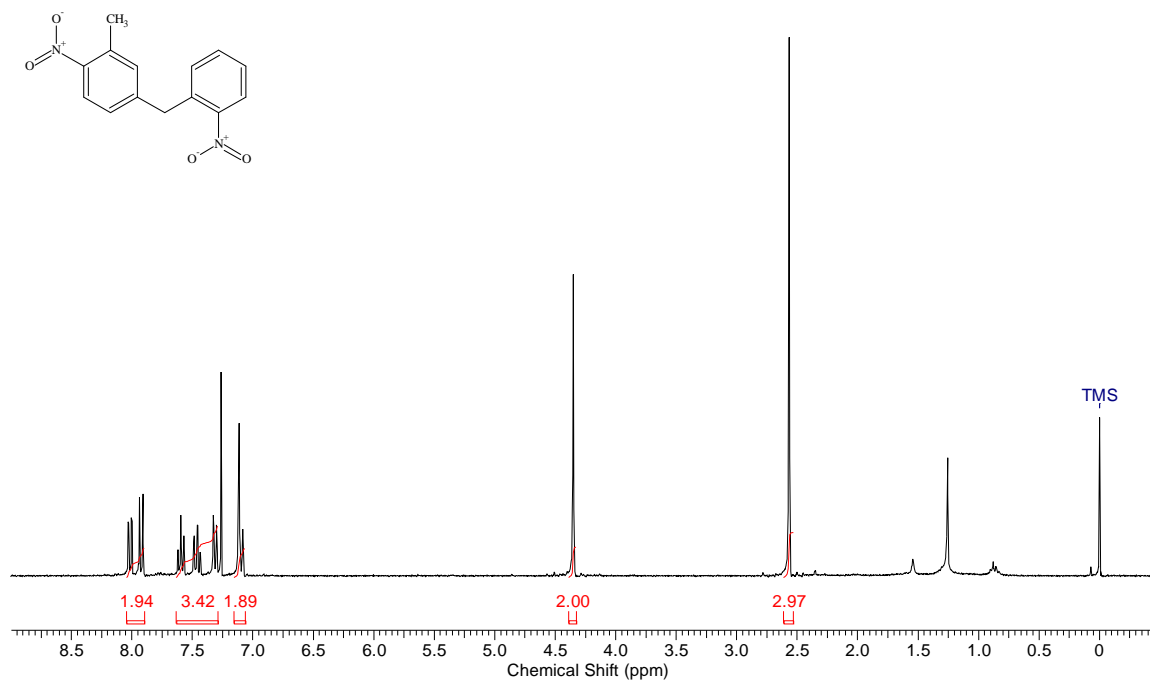
Compound **3g**

Compound **3h**

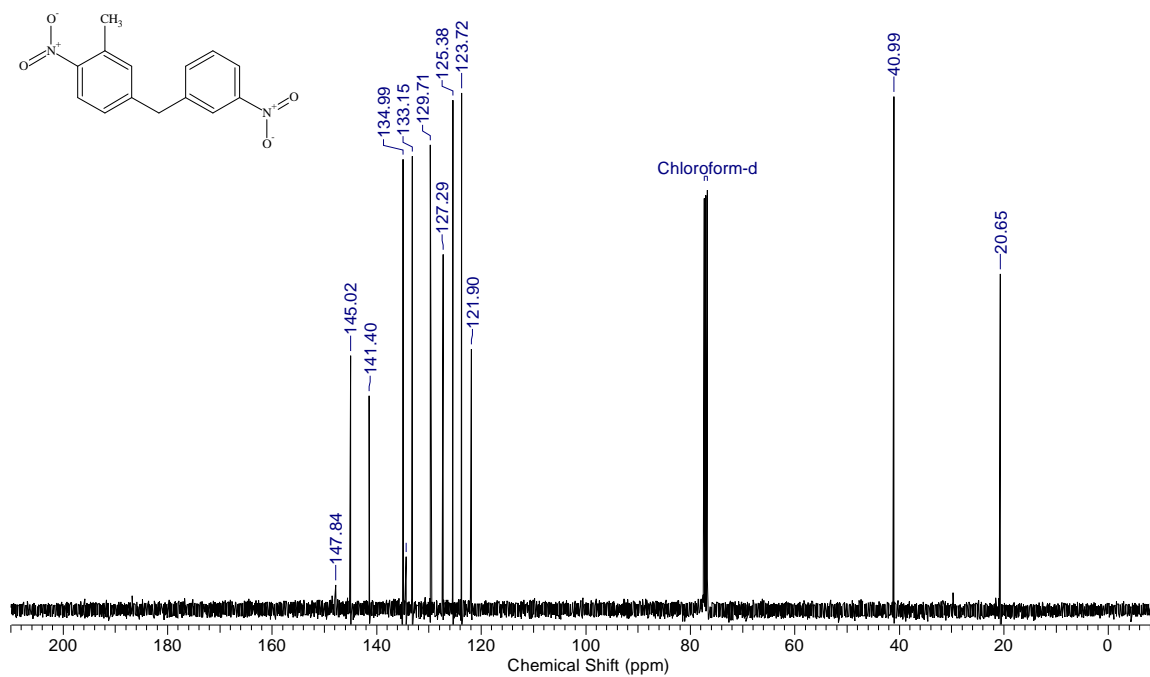
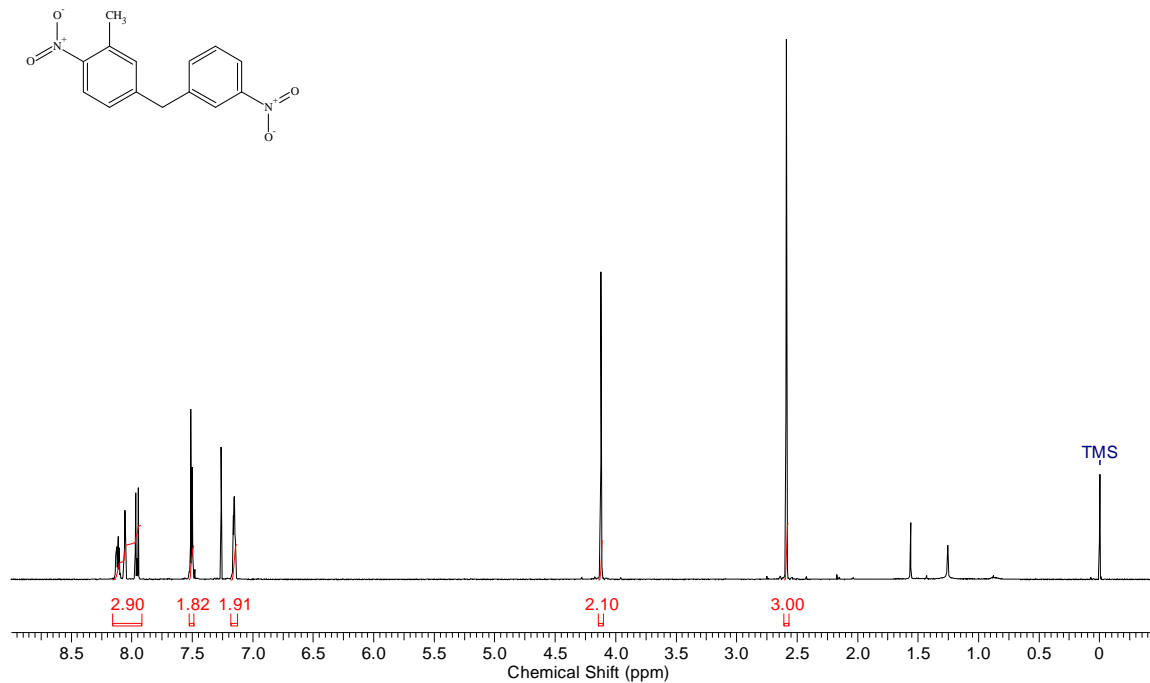


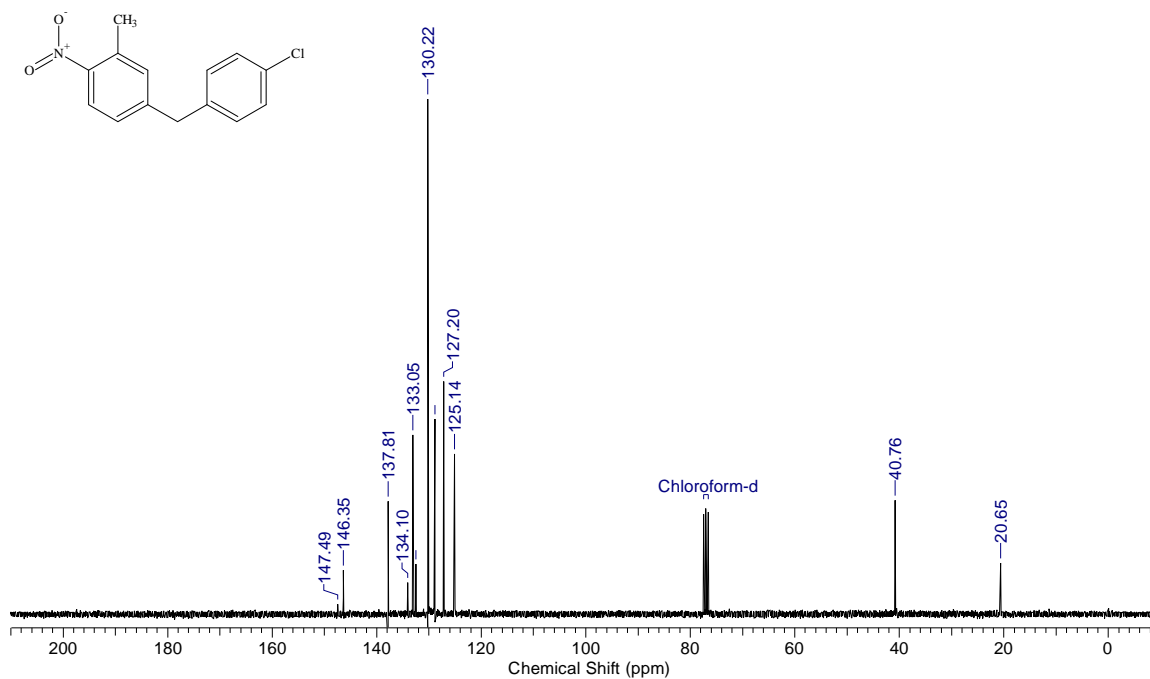
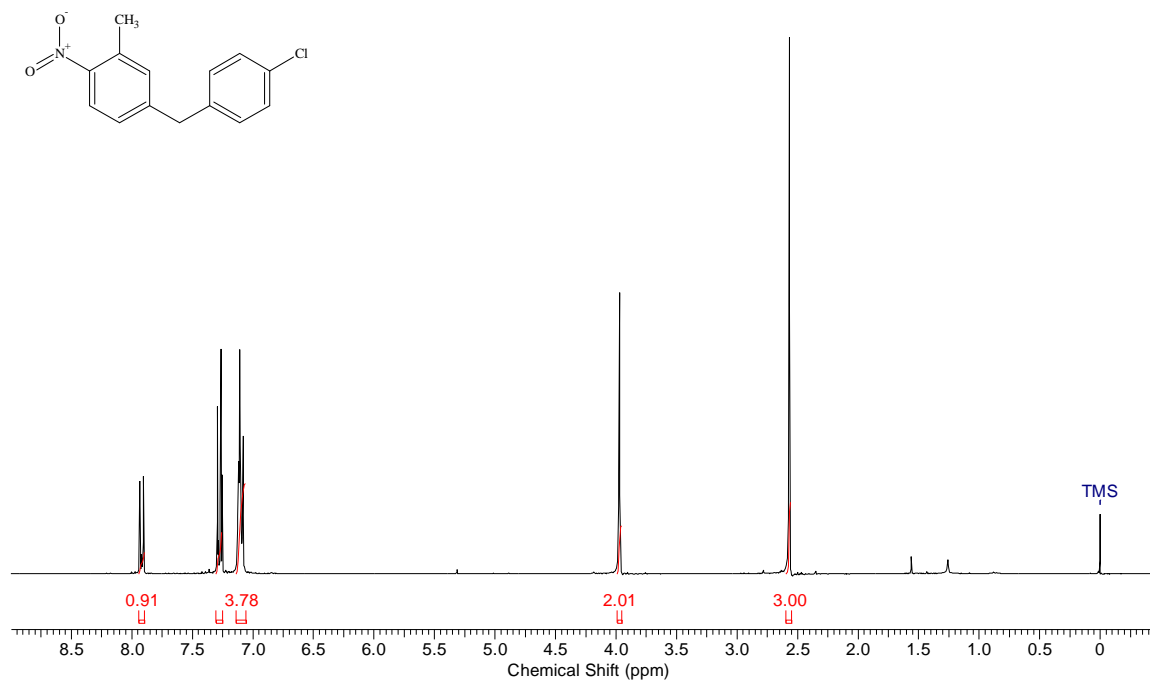
Compound **3i**

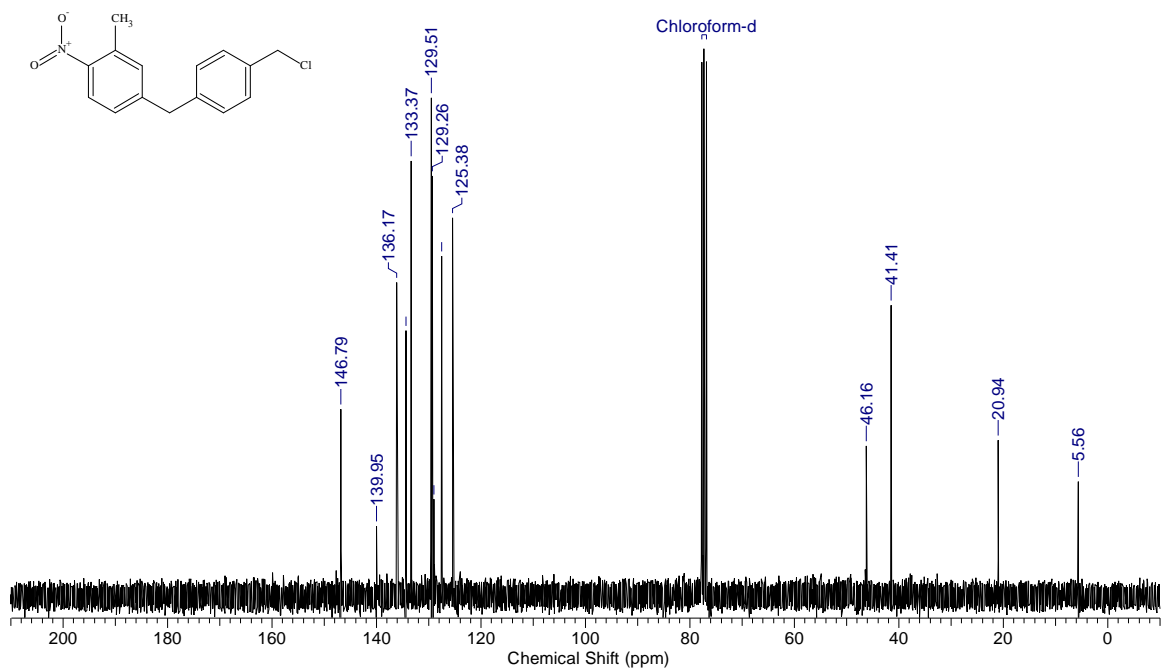
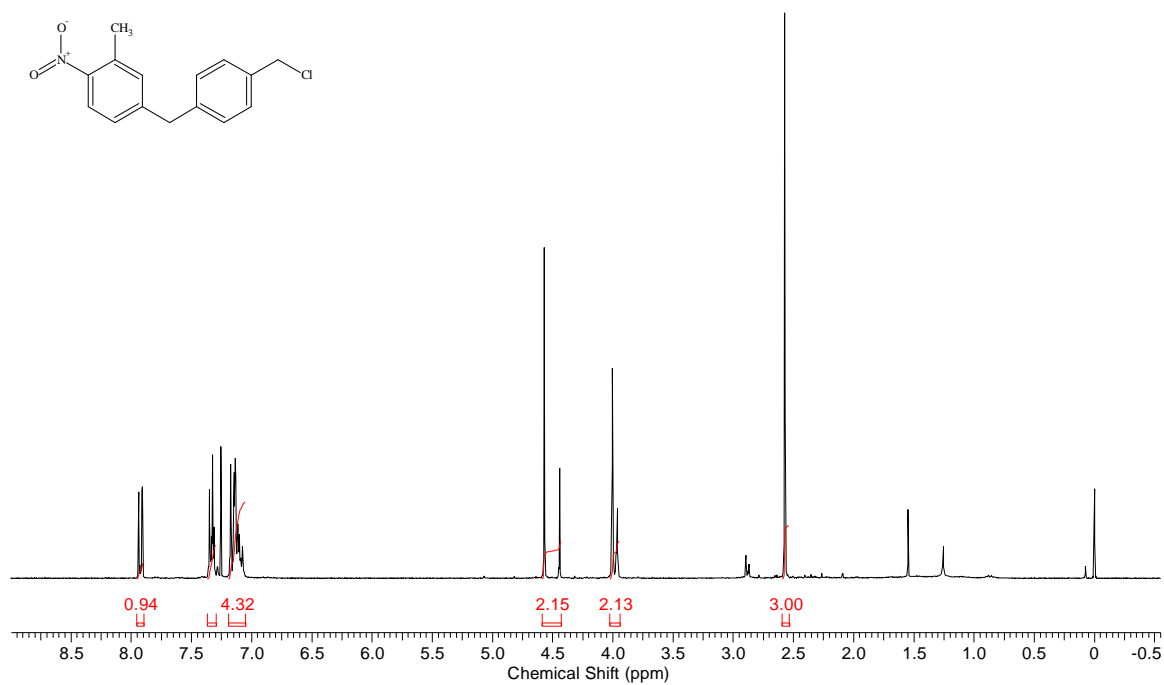
Compound **3j**

Compound **3k**

## Compound 3l



Compound **3m**

Compound **3n**

## Compound 3o

