

## Oxidative Radical Addition–Chlorination of Alkenes to access 1,1-Dichloroalkanes from Simple Reagents

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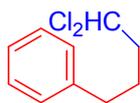
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**General Information.** All the reactions were carried out at 70 °C for 12 h in a round-bottom flask equipped with a magnetic stir bar. Unless otherwise stated, all reagents and solvents were purchased from commercial suppliers and used without further purification. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a 400 MHz spectrometer in solutions of CDCl<sub>3</sub> using tetramethylsilane as the internal standard; δ values are given in ppm, and coupling constants (*J*) in Hz. GC-MS was obtained using electron ionization (EI).

**Typical procedure: 1-(4,4-dichlorobutyl)benzene (Table 2, entry 1, 3aa).** A mixture of allylbenzene (**1a**) (118 mg, 1.0 mmol), CHCl<sub>3</sub> (0.5 mL), TBHP (129 mg, 1.0 mmol, 70% in water), and Et<sub>3</sub>N (1.0 mL) was added successively in a round-bottom flask, and the resulting solution was stirred for 12 h at 70 °C. The mixture was purified by column chromatography on silica gel to afford product **2a** with PE as the eluent.

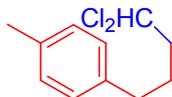
**1-(4,4-dichlorobutyl)benzene (Table 2, entry 1, 3aa)**



Yield: 77% (155 mg); a pale yellow oily liquid; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 Hz) δ 7.34 (t, *J* = 7.6 Hz, 2H), 7.24 (m, 3H), 5.77 (t, *J* = 6.0 Hz, 1H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.45 (m, 2H), 1.92 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 Hz) δ 141.1, 128.5, 128.3, 126.1, 73.4, 42.9, 34.7, 37.5; GC-MS *m/z* (% rel inten.): 202.02 (M<sup>+</sup>, 13), 91.04 (100); Anal. Calcd for C<sub>10</sub>H<sub>12</sub>Cl<sub>2</sub>: C, 59.13; H, 5.96. Found: C,

59.30; H, 5.88.

**1-(4,4-dichlorobutyl)-4-methylbenzene (Table 2, entry 2, 3ba)**



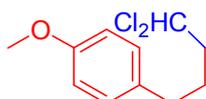
Yield: 71% (153 mg); a pale yellow oily liquid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 Hz)  $\delta$  7.12 (d,  $J$  = 8.0 Hz, 2H), 7.08 (d,  $J$  = 8.0 Hz, 2H), 5.75 (t,  $J$  = 6.0 Hz, 1H), 2.65 (t,  $J$  = 7.6 Hz, 2H), 2.34 (s, 3H), 2.22 (m, 2H), 1.88 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 Hz)  $\delta$  138.0, 135.6, 129.1, 128.2, 73.4, 42.9, 34.2, 27.6, 21.0; GC-MS  $m/z$  (% rel inten.): 216.04 ( $\text{M}^+$ , 98), 105.06 (100); Anal. Calcd for  $\text{C}_{11}\text{H}_{14}\text{Cl}_2$ : C, 60.85; H, 6.50. Found: C, 60.68; H, 6.61.

**1-(4,4-dichlorobutyl)-2-methylbenzene (Table 2, entry 3, 3ca)**



Yield: 75% (162 mg); a pale yellow oily liquid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 Hz)  $\delta$  7.23 (m, 1H), 7.17 (m, 4H), 5.79 (t,  $J$  = 6.0 Hz, 1H), 2.69 (t,  $J$  = 8.0 Hz, 2H), 2.35 (s, 3H), 2.29 (m, 2H), 1.88 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 Hz)  $\delta$  139.4, 135.8, 130.3, 128.7, 126.2, 126.0, 73.4, 43.3, 32.1, 26.4, 19.3; GC-MS  $m/z$  (% rel inten.): 216.03 ( $\text{M}^+$ , 83), 105.04 (100); Anal. Calcd for  $\text{C}_{11}\text{H}_{14}\text{Cl}_2$ : C, 60.85; H, 6.50. Found: C, 60.73; H, 6.58.

**1-(4,4-dichlorobutyl)-4-methoxybenzene (Table 2, entry 4, 3da)**



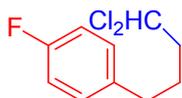
Yield: 80% (185 mg); a pale yellow oily liquid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 Hz)  $\delta$  7.10 (d,  $J$  = 8.8 Hz, 2H), 6.86 (d,  $J$  = 8.8 Hz, 2H), 5.76 (t,  $J$  = 6.0 Hz, 1H), 3.81 (s, 3H), 2.63 (t,  $J$  = 7.6 Hz, 2H), 2.20 (m, 2H), 1.87 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 Hz)  $\delta$  158.0, 133.2, 129.2, 113.9, 73.4, 55.2, 42.9, 33.8, 27.7; GC-MS  $m/z$  (% rel inten.): 232.05 ( $\text{M}^+$ , 85), 121.07 (100); Anal. Calcd for  $\text{C}_{11}\text{H}_{14}\text{Cl}_2\text{O}$ : C, 56.67; H, 6.05. Found: C, 56.59; H, 6.17.

**1-(4,4-dichlorobutyl)-2-methoxybenzene (Table 2, entry 5, 3ea)**



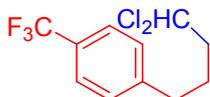
Yield: 78% (180 mg); a pale yellow oily liquid;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 Hz)  $\delta$  7.23 (m, 1H), 7.14 (d,  $J = 7.6$  Hz, 1H), 6.92 (m, 1H), 6.88 (d,  $J = 7.6$  Hz, 1H), 5.75 (t,  $J = 6.0$  Hz, 1H), 3.85 (s, 3H), 2.69 (t,  $J = 7.6$  Hz, 2H), 2.23 (m, 2H), 1.88 (m, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 Hz)  $\delta$  157.4, 129.8, 129.6, 127.3, 120.4, 110.3, 73.6, 55.2, 43.1, 28.8, 26.2; GC-MS  $m/z$  (% rel inten.): 232.04 ( $\text{M}^+$ , 19), 121.06 (100); Anal. Calcd for  $\text{C}_{11}\text{H}_{14}\text{Cl}_2\text{O}$ : C, 56.67; H, 6.05. Found: C, 56.79; H, 6.13.

**1-(4,4-dichlorobutyl)-3-fluorobenzene (Table 2, entry 6, 3fa)**



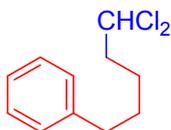
Yield: 88% (193 mg); a pale yellow oily liquid;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 Hz)  $\delta$  7.13 (m, 2H), 6.99 (m, 2H), 5.76 (t,  $J = 6.0$  Hz, 1H), 2.66 (t,  $J = 7.6$  Hz, 2H), 2.22 (m, 2H), 1.89 (m, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 Hz)  $\delta$  161.6 (d,  $^1J_{\text{C-F}} = 242.4$  Hz), 136.7 (d,  $^4J_{\text{C-F}} = 3.3$  Hz), 129.6 (d,  $^3J_{\text{C-F}} = 7.7$  Hz), 115.2 (d,  $^2J_{\text{C-F}} = 21.0$  Hz), 73.3, 42.8, 33.9, 27.5; GC-MS  $m/z$  (% rel inten.): 220.02 ( $\text{M}^+$ , 100); Anal. Calcd for  $\text{C}_{10}\text{H}_{11}\text{Cl}_2\text{F}$ : C, 54.32; H, 5.01. Found: C, 54.50; H, 5.10.

**1-(4,4-dichlorobutyl)-3-(trifluoromethyl)benzene (Table 2, entry 7, 3ga)**



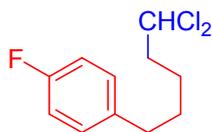
Yield: 82% (216 mg); a pale yellow oily liquid;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 Hz)  $\delta$  7.57 (d,  $J = 8.0$  Hz, 2H), 7.31 (d,  $J = 8.0$  Hz, 2H), 5.78 (t,  $J = 6.0$  Hz, 1H), 2.75 (t,  $J = 7.6$  Hz, 2H), 2.23 (t,  $J = 7.6$  Hz, 2H), 1.93 (m, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 Hz)  $\delta$  145.2, 128.6, 125.4, 122.9, 73.1, 42.7, 34.5, 27.1; GC-MS  $m/z$  (% rel inten.): 270.01 ( $\text{M}^+$ , 11), 159.03 (100); Anal. Calcd for  $\text{C}_{11}\text{H}_{11}\text{Cl}_2\text{F}_3$ : C, 48.73; H, 4.09. Found: C, 48.66; H, 4.21.

**1-(5,5-dichloropentyl)benzene (Table 2, entry 8, 3ha)**



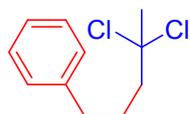
Yield: 79% (170 mg); a pale yellow oily liquid;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 Hz)  $\delta$  7.34 (t,  $J = 7.6$  Hz, 2H), 7.26 (m, 3H), 5.77 (t,  $J = 6.0$  Hz, 1H), 2.69 (t,  $J = 7.6$  Hz, 2H), 2.78 (m, 2H), 1.74 (m, 2H), 1.63 (m, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 Hz)  $\delta$  141.9, 128.42, 128.40, 125.9, 73.5, 43.5, 35.6, 30.4, 25.6; GC-MS  $m/z$  (% rel inten.): 216.05 ( $\text{M}^+$ , 68), 91.02 (100); Anal. Calcd for  $\text{C}_{11}\text{H}_{14}\text{Cl}_2$ : C, 60.85; H, 6.50. Found: C, 60.97; H, 6.57.

**1-(5,5-dichloropentyl)-3-fluorobenzene (Table 2, entry 9, 3ia)**



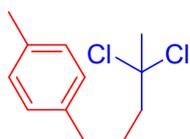
Yield: 86% (201 mg); a pale yellow oily liquid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 Hz)  $\delta$  7.12 (m, 2H), 6.98 (m, 2H), 5.75 (t,  $J = 6.0$  Hz, 1H), 2.62 (t,  $J = 7.6$  Hz, 2H), 2.22 (m, 2H), 1.63 (m, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 Hz)  $\delta$  161.7 (d,  $^1J_{\text{C-F}} = 241.9$  Hz), 137.4 (d,  $^4J_{\text{C-F}} = 3.6$  Hz), 129.6 (d,  $^3J_{\text{C-F}} = 7.7$  Hz), 114.9 (d,  $^2J_{\text{C-F}} = 20.9$  Hz), 73.4, 43.4, 34.8, 30.4, 25.4; GC-MS  $m/z$  (% rel inten.): 234.03 ( $\text{M}^+$ , 13), 109.04 (100); Anal. Calcd for  $\text{C}_{11}\text{H}_{13}\text{Cl}_2\text{F}$ : C, 56.19; H, 5.57. Found: C, 56.08; H, 5.70.

**1-(4,4-dichloropentyl)benzene (Table 2, entry 10, 3ab)**



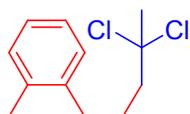
Yield: 77% (166 mg); a pale yellow oily liquid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 Hz)  $\delta$  7.32 (t,  $J = 7.6$  Hz, 2H), 7.23 (m, 3H), 2.71 (t,  $J = 7.6$  Hz, 2H), 2.25 (m, 2H), 2.14 (s, 3H), 2.04 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 Hz)  $\delta$  141.3, 128.4, 128.3, 126.0, 90.5, 49.1, 37.3, 35.0, 27.2; GC-MS  $m/z$  (% rel inten.): 216.05 ( $\text{M}^+$ , 37), 91.03 (100); Anal. Calcd for  $\text{C}_{11}\text{H}_{14}\text{Cl}_2$ : C, 60.85; H, 6.50. Found: C, 60.94; H, 6.66.

**1-(4,4-dichloropentyl)-4-methylbenzene (Table 2, entry 11, 3bb)**



Yield: 81% (186 mg); a pale yellow oily liquid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 Hz)  $\delta$  7.1 (m, 4H), 2.69 (t,  $J = 7.6$  Hz, 2H), 2.34 (s, 3H), 2.24 (m, 2H), 2.14 (s, 3H), 2.00 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 Hz)  $\delta$  138.2, 135.5, 129.1, 128.2, 90.6, 49.1, 37.3, 34.6, 27.3, 21.0; GC-MS  $m/z$  (% rel inten.): 230.03 ( $\text{M}^+$ , 12), 105.06 (100); Anal. Calcd for  $\text{C}_{12}\text{H}_{16}\text{Cl}_2$ : C, 62.35; H, 6.98. Found: C, 62.23; H, 6.89.

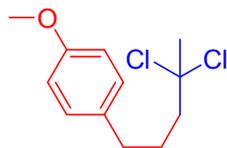
**1-(4,4-dichloropentyl)-2-methylbenzene (Table 2, entry 12, 3cb)**



Yield: 80% (184 mg); a pale yellow oily liquid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 Hz)  $\delta$  7.16 (m, 4H), 2.69 (t,  $J = 7.6$  Hz, 2H), 2.34 (s, 3H), 2.29 (m, 2H), 2.16 (s, 3H), 1.99 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 Hz)

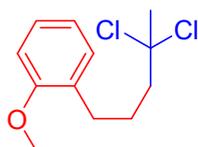
$\delta$  139.6, 135.8, 130.2, 128.7, 126.1, 126.0, 90.5, 49.4, 37.3, 32.4, 26.1, 19.3; GC–MS  $m/z$  (% rel inten.): 230.07 ( $M^+$ , 12), 105.07 (100); Anal. Calcd for  $C_{12}H_{16}Cl_2$ : C, 62.35; H, 6.98. Found: C, 62.39; H, 7.09.

**1-(4,4-dichloropentyl)-4-methoxybenzene (Table 2, entry 13, 3db)**



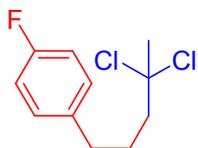
Yield: 78% (192 mg); a pale yellow oily liquid;  $^1H$  NMR ( $CDCl_3$ , 400 Hz)  $\delta$  7.11 (d,  $J$  = 8.8 Hz, 2H), 6.85 (d,  $J$  = 8.8 Hz, 2H), 3.80 (s, 3H), 2.64 (t,  $J$  = 7.6 Hz, 2H), 2.23 (m, 2H), 2.13 (m, 3H), 1.98 (m, 2H);  $^{13}C$  NMR ( $CDCl_3$ , 100 Hz)  $\delta$  157.9, 133.4, 129.2, 113.8, 90.6, 55.2, 49.1, 37.3, 34.1, 27.5; GC–MS  $m/z$  (% rel inten.): 246.06 ( $M^+$ , 48), 121.05 (100); Anal. Calcd for  $C_{12}H_{16}Cl_2O$ : C, 58.31; H, 6.52. Found: C, 58.44; H, 6.46.

**1-(4,4-dichloropentyl)-2-methoxybenzene (Table 2, entry 14, 3eb)**



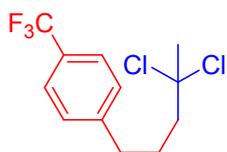
Yield: 73% (179 mg); a pale yellow oily liquid;  $^1H$  NMR ( $CDCl_3$ , 400 Hz)  $\delta$  7.17 (m, 2H), 6.88 (m, 2H), 3.84 (s, 3H), 2.70 (t,  $J$  = 7.6 Hz, 2H), 2.27 (m, 2H), 2.14 (s, 3H), 1.98 (m, 2H);  $^{13}C$  NMR ( $CDCl_3$ , 100 Hz)  $\delta$  157.4, 129.8, 129.7, 127.2, 120.4, 110.3, 90.8, 55.2, 49.4, 37.2, 29.4, 25.8; GC–MS  $m/z$  (% rel inten.): 246.04 ( $M^+$ , 36), 121.06 (100); Anal. Calcd for  $C_{12}H_{16}Cl_2O$ : C, 58.31; H, 6.52. Found: C, 58.36; H, 6.58.

**1-(4,4-dichloropentyl)-4-fluorobenzene (Table 2, entry 15, 3fb)**



Yield: 87% (203 mg); a pale yellow oily liquid;  $^1H$  NMR ( $CDCl_3$ , 400 Hz)  $\delta$  7.16 (m, 2H), 6.99 (m, 2H), 2.67 (t,  $J$  = 7.6 Hz, 2H), 2.22 (m, 2H), 2.14 (s, 3H), 2.01 (m, 2H);  $^{13}C$  NMR ( $CDCl_3$ , 100 Hz)  $\delta$  161.4 (d,  $^1J_{C-F}$  = 242.3 Hz), 136.9 (d,  $^4J_{C-F}$  = 3.2 Hz), 129.6 (d,  $^3J_{C-F}$  = 7.8 Hz), 115.1 (d,  $^2J_{C-F}$  = 20.8 Hz), 90.4, 49.0, 37.4, 34.2, 27.3; GC–MS  $m/z$  (% rel inten.): 234.04 ( $M^+$ , 57), 122.98 (100); Anal. Calcd for  $C_{11}H_{13}Cl_2F$ : C, 56.19; H, 5.57. Found: C, 56.22; H, 5.69.

**1-(4,4-dichloropentyl)-4-(trifluoromethyl)benzene (Table 2, entry 16, 3gb)**



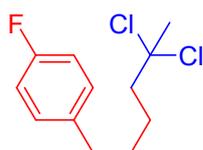
Yield: 77% (218 mg); a pale yellow oily liquid;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 Hz)  $\delta$  7.57 (d,  $J = 8.0$  Hz, 2H), 7.33 (d,  $J = 8.0$  Hz, 2H), 2.76 (t,  $J = 7.6$  Hz, 2H), 2.23 (t,  $J = 7.6$  Hz, 2H), 2.15 (s, 3H), 2.05 (m, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 Hz)  $\delta$  145.4, 128.6, 128.3, 125.4, 90.2, 48.9, 37.4, 34.8, 26.9; GC-MS  $m/z$  (% rel inten.): 284.01 ( $\text{M}^+$ , 66), 159.02 (100); Anal. Calcd for  $\text{C}_{12}\text{H}_{13}\text{Cl}_2\text{F}_3$ : C, 50.55; H, 4.60. Found: C, 50.71; H, 4.55.

**1-(5,5-dichlorohexyl)benzene (Table 2, entry 17, 3hb)**



Yield: 81% (186 mg); a pale yellow oily liquid;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 Hz)  $\delta$  7.32 (t,  $J = 7.6$  Hz, 2H), 7.22 (m, 3H), 2.69 (t,  $J = 7.6$  Hz, 2H), 2.27 (m, 2H), 2.16 (s, 3H), 1.73 (m, 4H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 Hz)  $\delta$  142.1, 128.3, 125.8, 90.7, 49.6, 37.3, 35.7, 30.8, 25.4; GC-MS  $m/z$  (% rel inten.): 230.05 ( $\text{M}^+$ , 39), 91.01 (100); Anal. Calcd for  $\text{C}_{12}\text{H}_{16}\text{Cl}_2$ : C, 62.35; H, 6.98. Found: C, 62.48; H, 7.09.

**1-(5,5-dichlorohexyl)-4-fluorobenzene (Table 2, entry 18, 3ib)**



Yield: 90% (223 mg); a pale yellow oily liquid;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 Hz)  $\delta$  7.14 (m, 2H), 6.98 (m, 2H), 2.64 (t,  $J = 7.6$  Hz, 2H), 2.23 (m, 2H), 2.15 (s, 3H), 1.69 (m, 4H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 Hz)  $\delta$  161.2 (d,  $^1J_{\text{C-F}} = 241.9$  Hz), 137.6 (d,  $^4J_{\text{C-F}} = 3.2$  Hz), 129.6 (d,  $^3J_{\text{C-F}} = 7.8$  Hz), 115.0 (d,  $^2J_{\text{C-F}} = 20.9$  Hz), 90.6, 49.5, 37.3, 34.8, 30.9, 25.2; GC-MS  $m/z$  (% rel inten.): 248.01 ( $\text{M}^+$ , 62), 109.02 (100); Anal. Calcd for  $\text{C}_{12}\text{H}_{15}\text{Cl}_2\text{F}$ : C, 57.85; H, 6.07. Found: C, 57.92; H, 6.22.

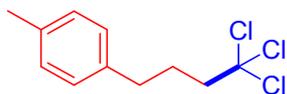
**1-(4,4,4-trichlorobutyl)benzene (Table 2, entry 19, 3ac)**



Yield: 65% (152 mg); a pale yellow oily liquid;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 Hz)  $\delta$  7.32 (t,  $J = 7.6$  Hz,

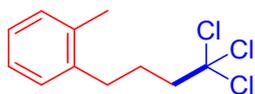
2H), 7.24 (m, 3H), 2.72 (m, 4H), 2.15 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 Hz)  $\delta$  140.7, 128.5, 128.3, 126.2, 99.9, 54.5, 34.3, 27.9; GC–MS  $m/z$  (% rel inten.): 236.01 ( $\text{M}^+$ , 41), 91.02 (100); Anal. Calcd for  $\text{C}_{10}\text{H}_{11}\text{Cl}_3$ : C, 50.56; H, 4.67. Found: C, 50.40; H, 4.58.

**1-(4,4,4-trichlorobutyl)-4-methylbenzene (Table 2, entry 20, 3bc)**



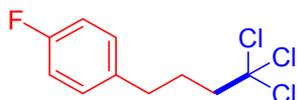
Yield: 67% (167 mg); a pale yellow oily liquid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 Hz)  $\delta$  7.12 (m, 4H), 2.67 (m, 4H), 2.34 (s, 3H), 2.12 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 Hz)  $\delta$  137.6, 135.7, 129.2, 128.2, 99.6, 54.5, 33.9, 27.9, 21.0; GC–MS  $m/z$  (% rel inten.): 250.01 ( $\text{M}^+$ , 55), 105.04 (100); Anal. Calcd for  $\text{C}_{11}\text{H}_{13}\text{Cl}_3$ : C, 52.52; H, 5.21. Found: C, 52.59; H, 5.33.

**1-(4,4,4-trichlorobutyl)-2-methylbenzene (Table 2, entry 21, 3cc)**



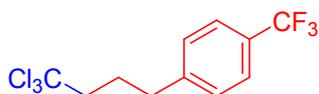
Yield: 65% (162 mg); a pale yellow oily liquid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 Hz)  $\delta$  7.17 (m, 4H), 2.75 (m, 4H), 2.34 (s, 3H), 2.10 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 Hz)  $\delta$  139.0, 135.6, 130.3, 128.7, 126.3, 126.1, 99.6, 54.7, 31.7, 26.7, 19.3; GC–MS  $m/z$  (% rel inten.): 250.00 ( $\text{M}^+$ , 39), 105.03 (100); Anal. Calcd for  $\text{C}_{11}\text{H}_{13}\text{Cl}_3$ : C, 52.52; H, 5.21. Found: C, 52.66; H, 5.18.

**1-(4,4,4-trichlorobutyl)-4-fluorobenzene (Table 2, entry 22, 3fc)**



Yield: 74% (187 mg); a pale yellow oily liquid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 Hz)  $\delta$  7.16 (m, 2H), 7.00 (m, 2H), 2.71 (m, 4H), 2.1 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 Hz)  $\delta$  161.8 (d,  $^1J_{\text{C-F}} = 241.6$  Hz), 136.3 (d,  $^4J_{\text{C-F}} = 3.0$  Hz), 129.6 (d,  $^3J_{\text{C-F}} = 7.8$  Hz), 115.3 (d,  $^2J_{\text{C-F}} = 21.1$  Hz), 99.6, 54.4, 33.5, 28.0; GC–MS  $m/z$  (% rel inten.): 254.00 ( $\text{M}^+$ , 53), 109.04 (100); Anal. Calcd for  $\text{C}_{10}\text{H}_{10}\text{Cl}_3\text{F}$ : C, 47.00; H, 3.94. Found: C, 47.05; H, 3.99.

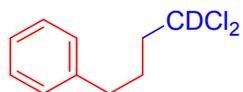
**1-(4,4,4-trichlorobutyl)-4-(trifluoromethyl)benzene (Table 2, entry 23, 3gc)**



Yield: 79% (272 mg); a pale yellow oily liquid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 Hz)  $\delta$  7.58 (d,  $J = 8.0$  Hz, 2H), 7.33 (d,  $J = 7.6$  Hz, 2H), 2.81 (t,  $J = 7.6$  Hz, 2H), 2.71 (m, 4H), 2.13 (m, 2H);  $^{13}\text{C}$  NMR

(CDCl<sub>3</sub>, 100 Hz)  $\delta$  144.8, 128.9, 128.6, 126.7, 125.5, 99.6, 54.3, 34.1, 27.5; GC–MS  $m/z$  (% rel inten.): 304.01 (M<sup>+</sup>, 61), 172.96 (100); Anal. Calcd for C<sub>11</sub>H<sub>10</sub>Cl<sub>3</sub>F<sub>3</sub>: C, 43.24; H, 3.30. Found: C, 43.38; H, 3.39.

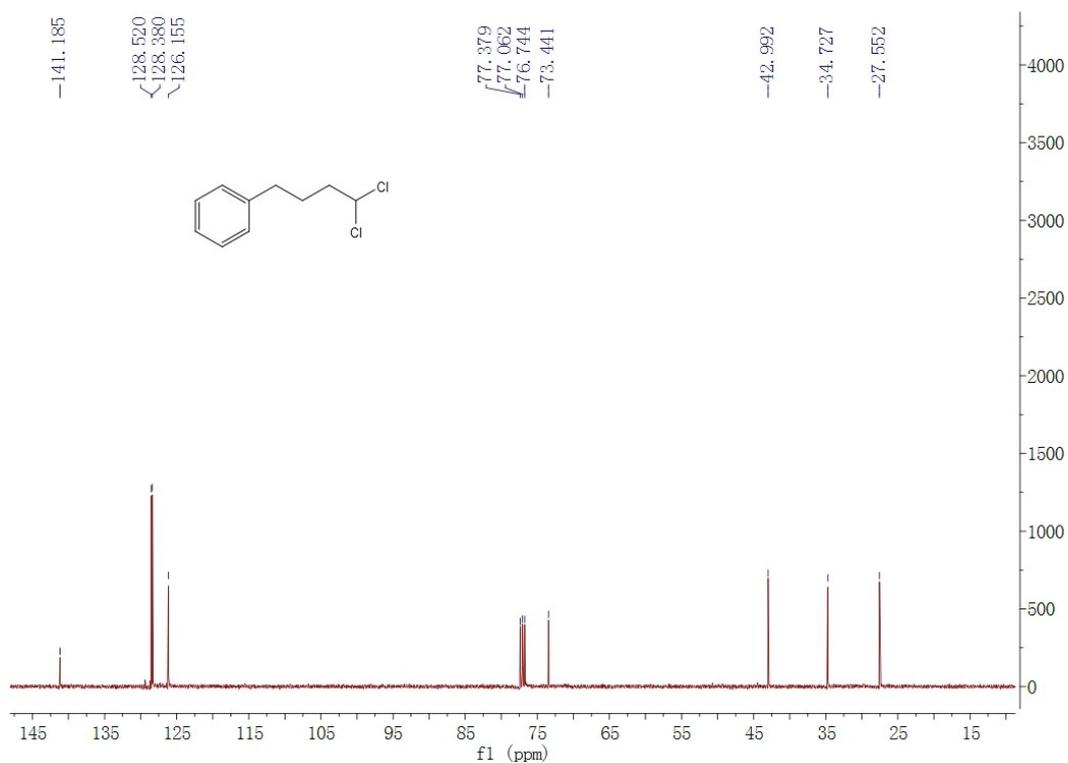
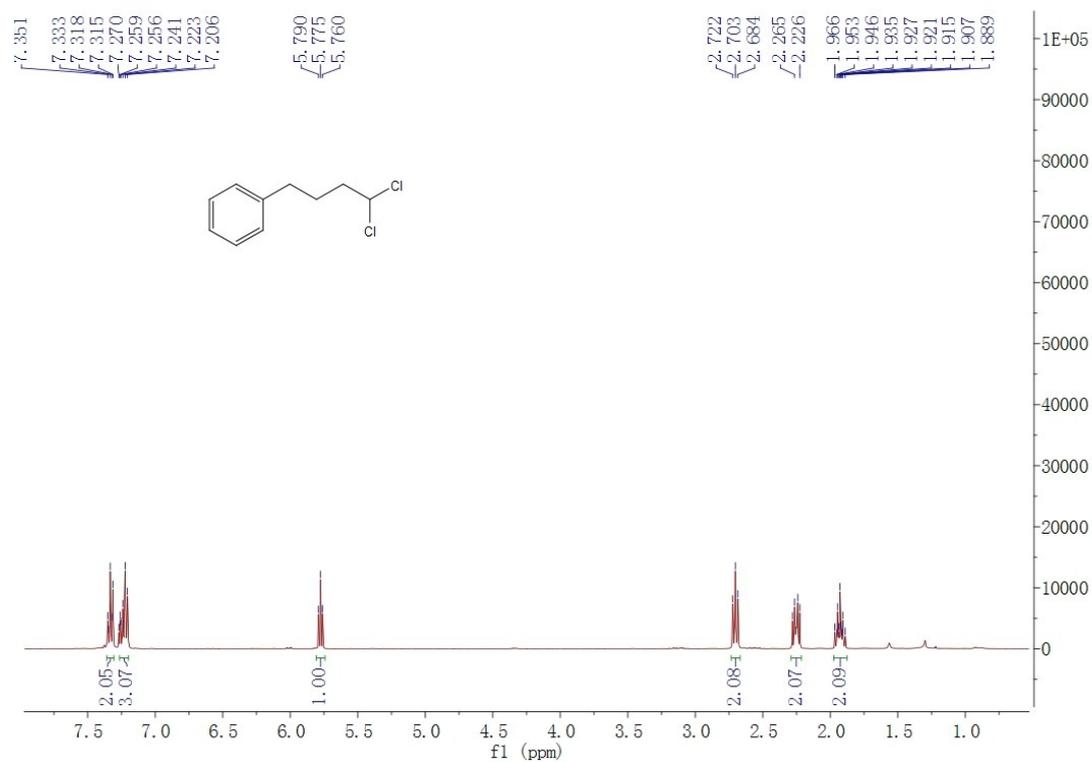
**1-(4,4,4-trichlorobutyl)benzene (Scheme 3, 4)**



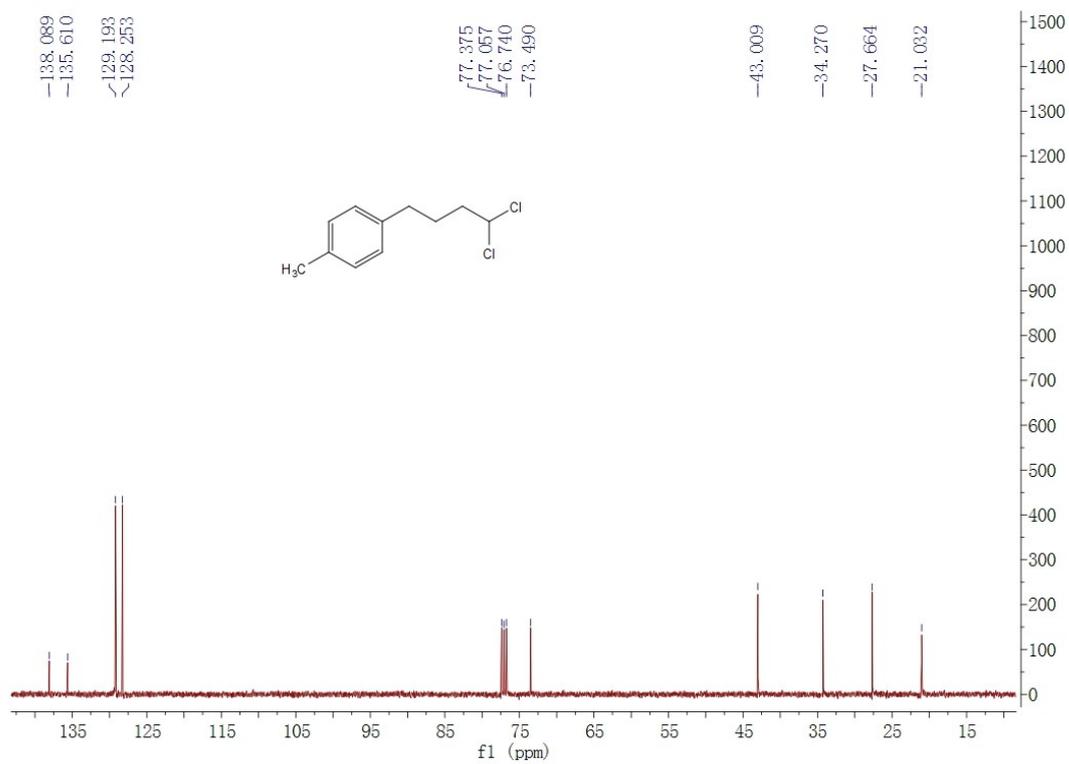
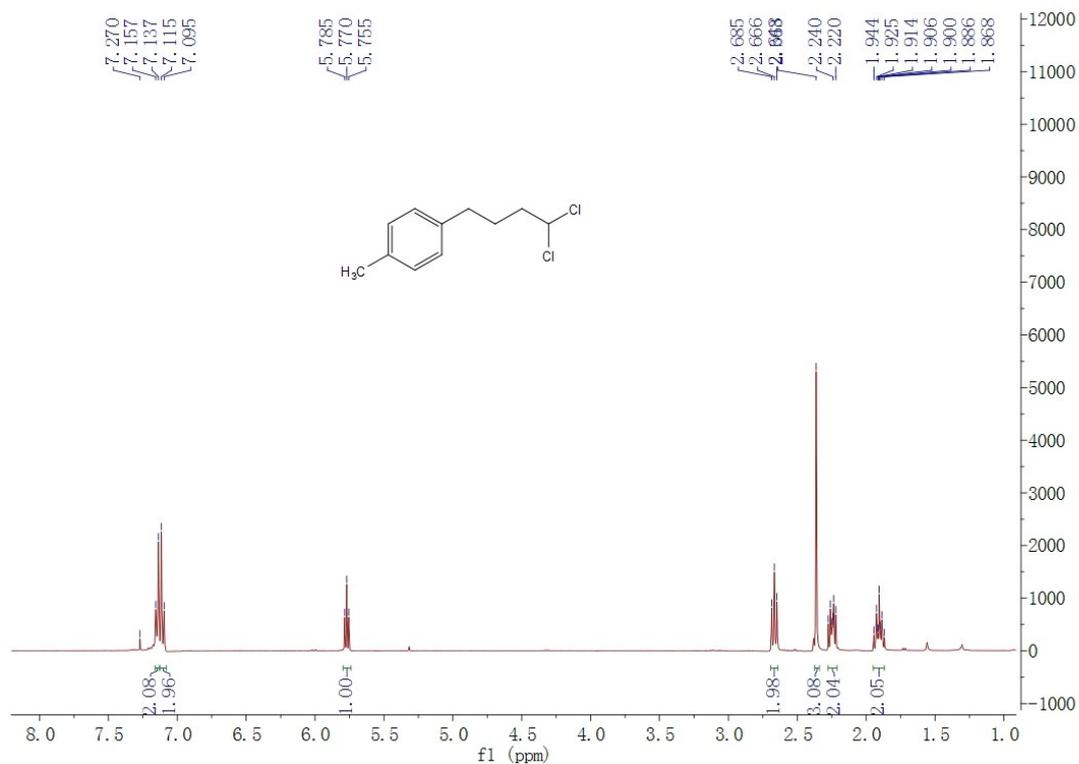
Yield: 77% (156 mg); a pale yellow oily liquid; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 Hz)  $\delta$  7.32 (t,  $J$  = 7.6 Hz, 2H), 7.22 (m, 3H), 2.69 (t,  $J$  = 7.6 Hz, 2H), 2.24 (t,  $J$  = 8.4 Hz, 2H), 1.92 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 Hz)  $\delta$  141.1, 128.5, 128.3, 126.1, 42.8, 34.7, 27.4; GC–MS  $m/z$  (% rel inten.): 203.04 (M<sup>+</sup>, 15), 91.00 (100); Anal. Calcd for C<sub>10</sub>H<sub>11</sub>DCl<sub>2</sub>: C, 58.84; H, 6.42. Found: C, 58.92; H, 6.37.

# NMR Spectra

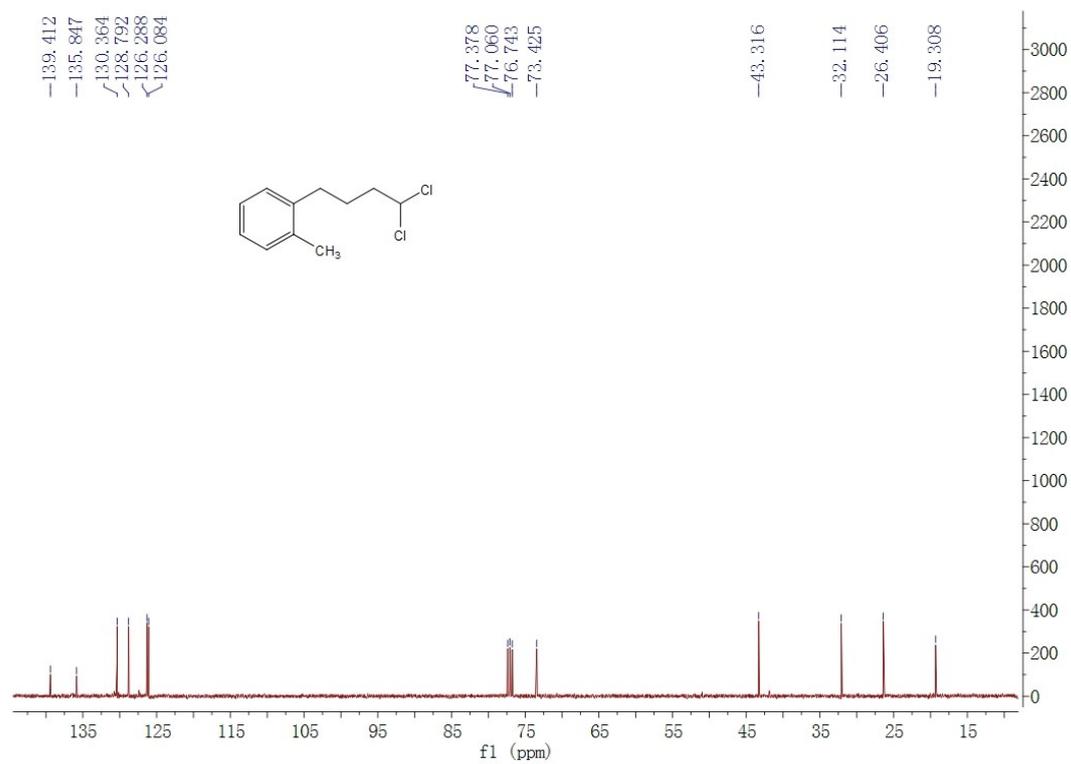
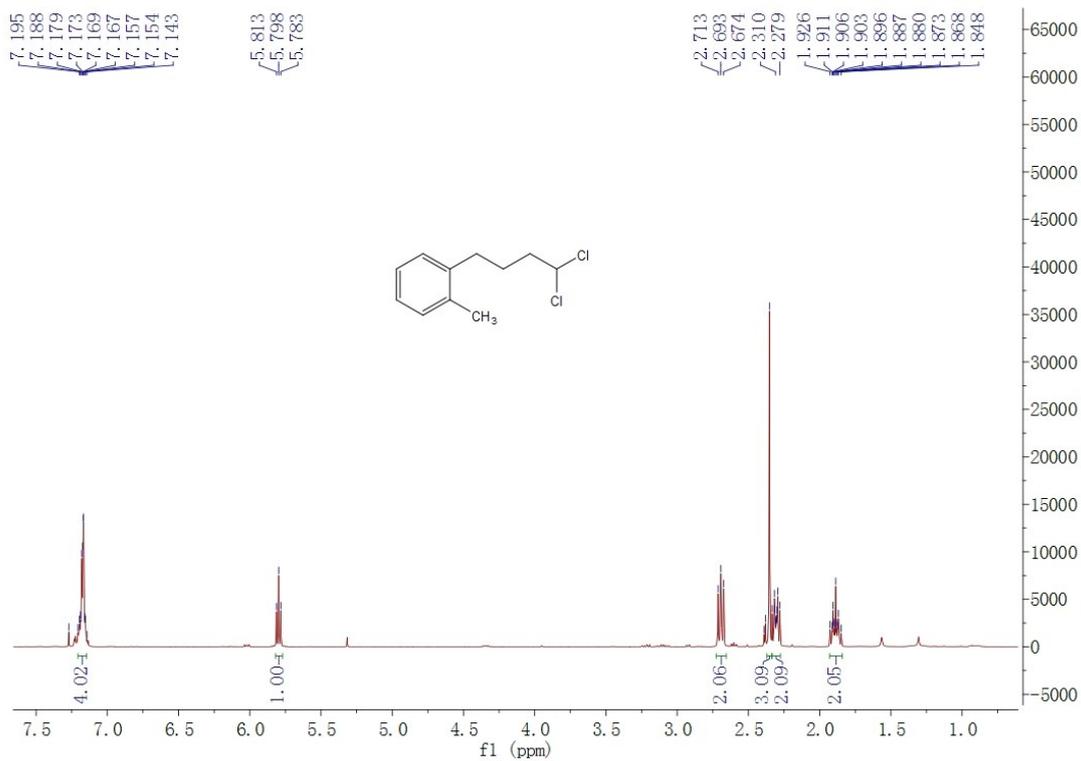
## 1-(4,4-dichlorobutyl)benzene (Table 2, entry 1, 3aa)



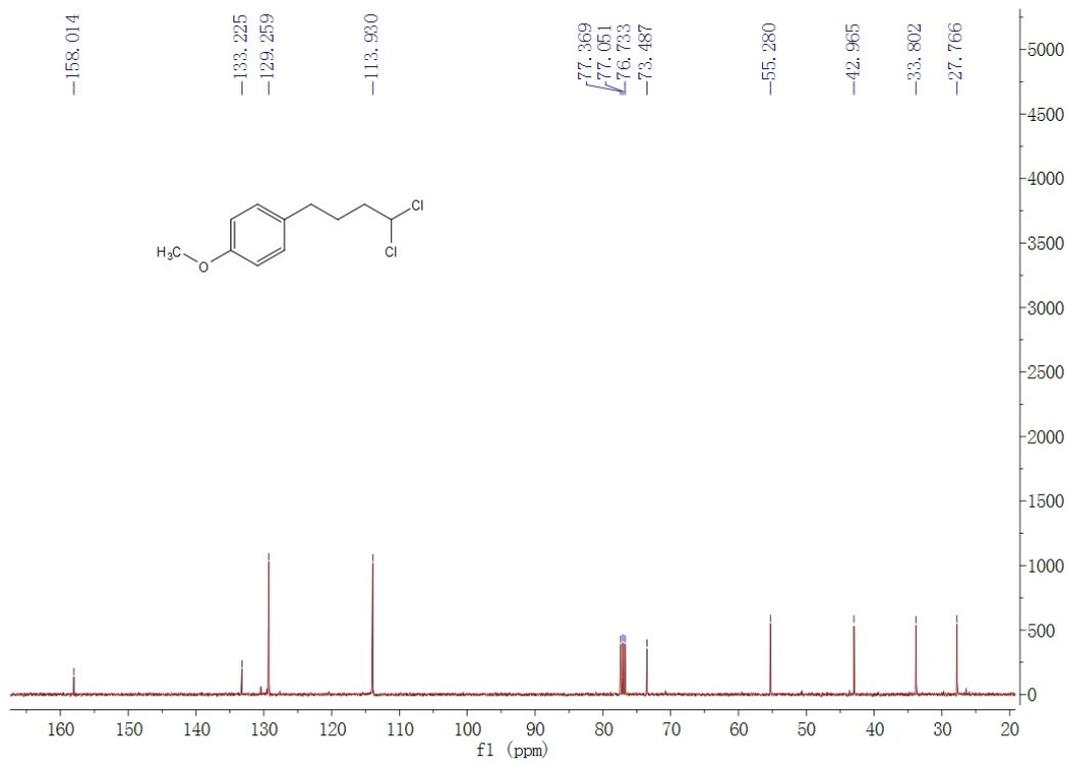
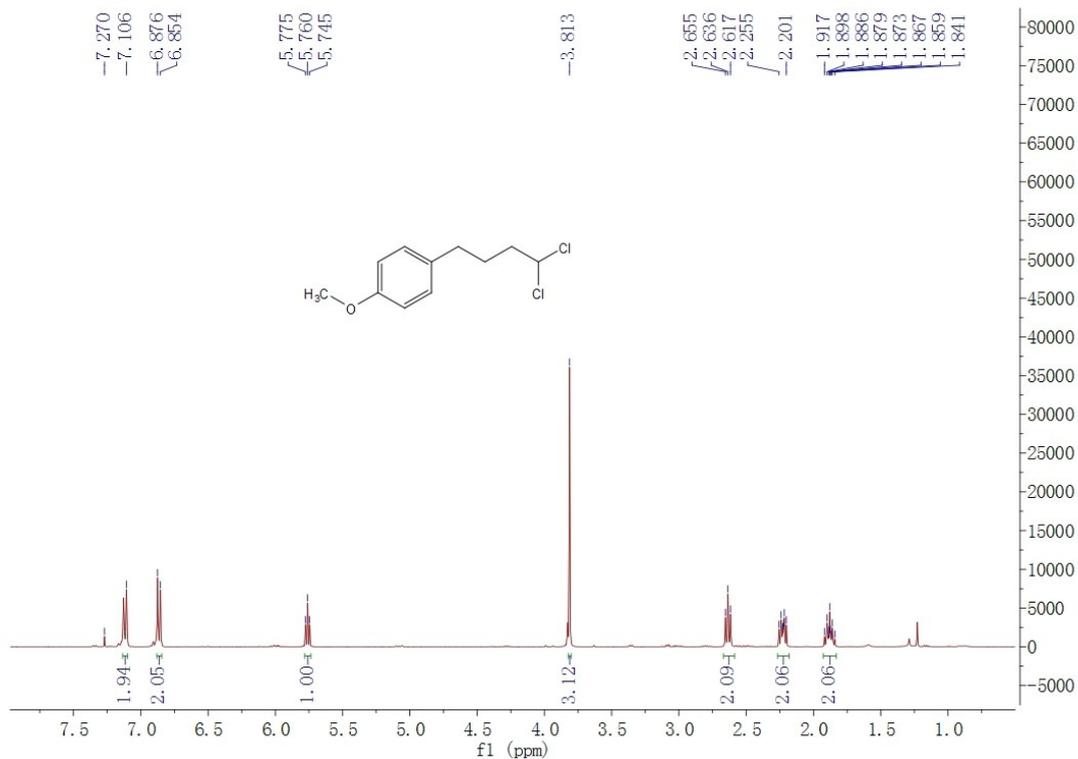
1-(4,4-dichlorobutyl)-4-methylbenzene (Table 2, entry 2, 3ba)



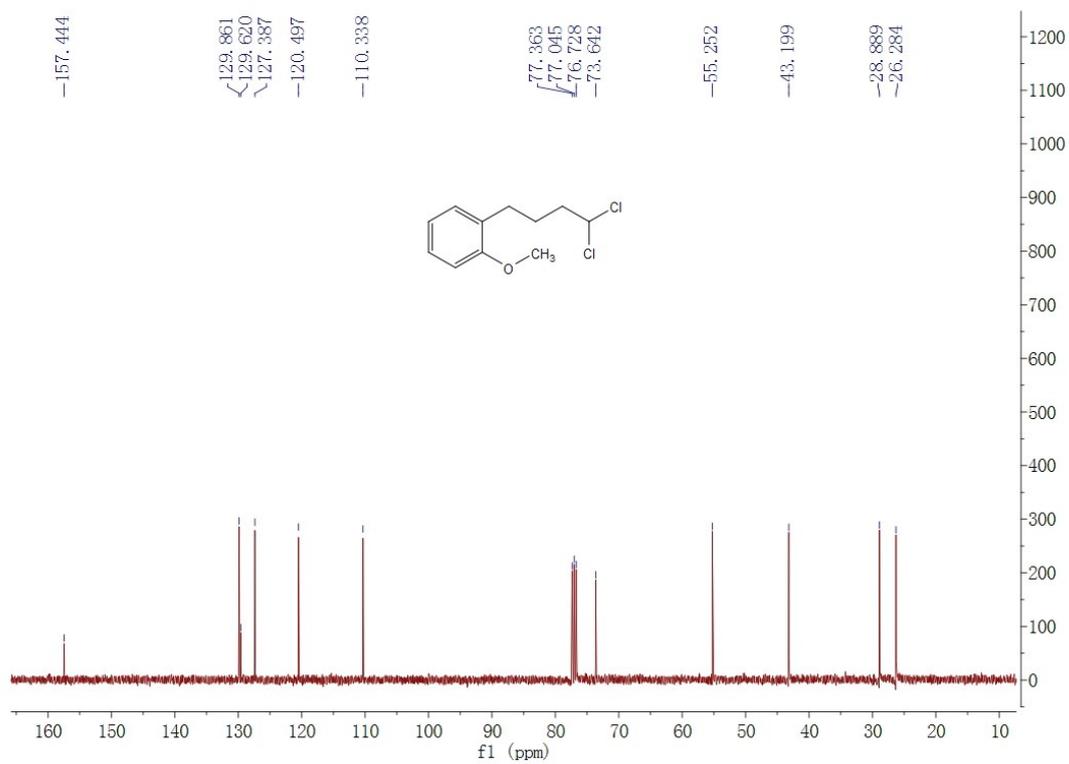
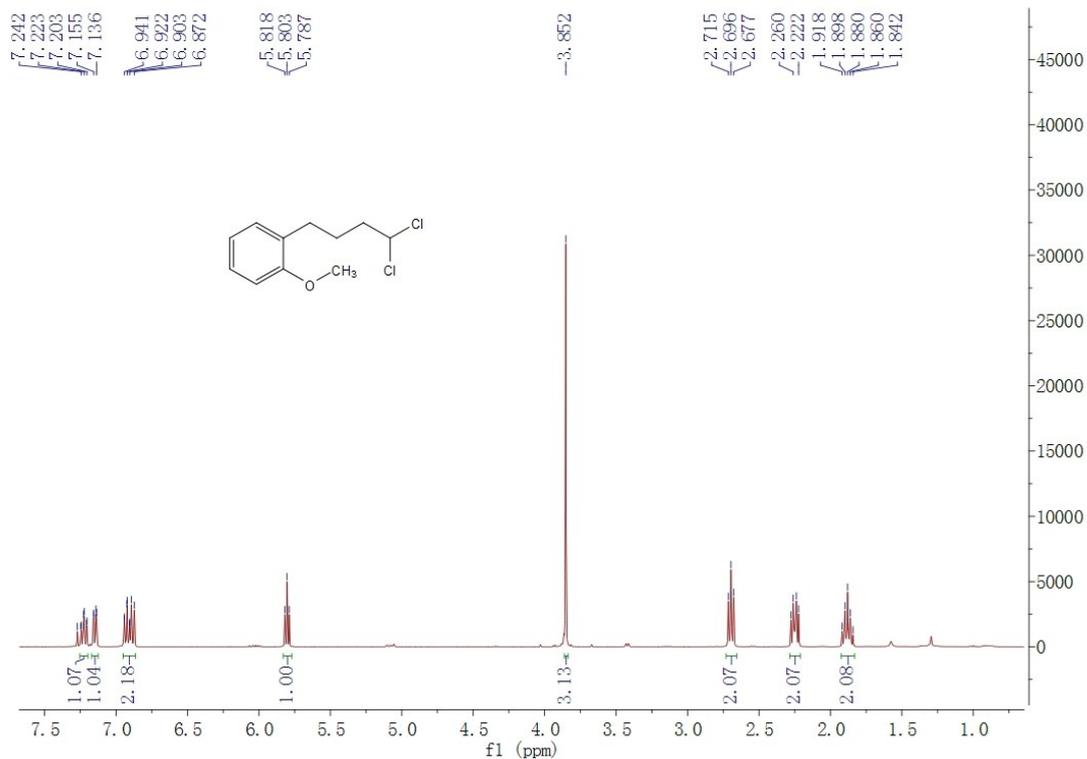
### 1-(4,4-dichlorobutyl)-2-methylbenzene (Table 2, entry 3, 3ca)



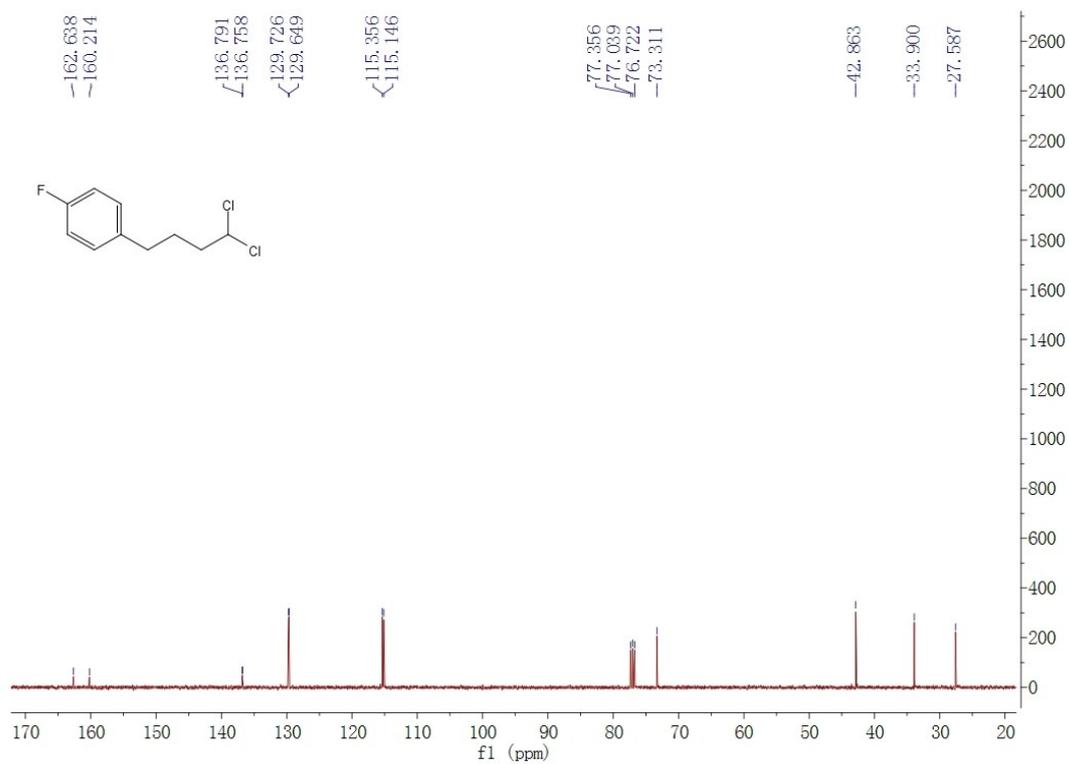
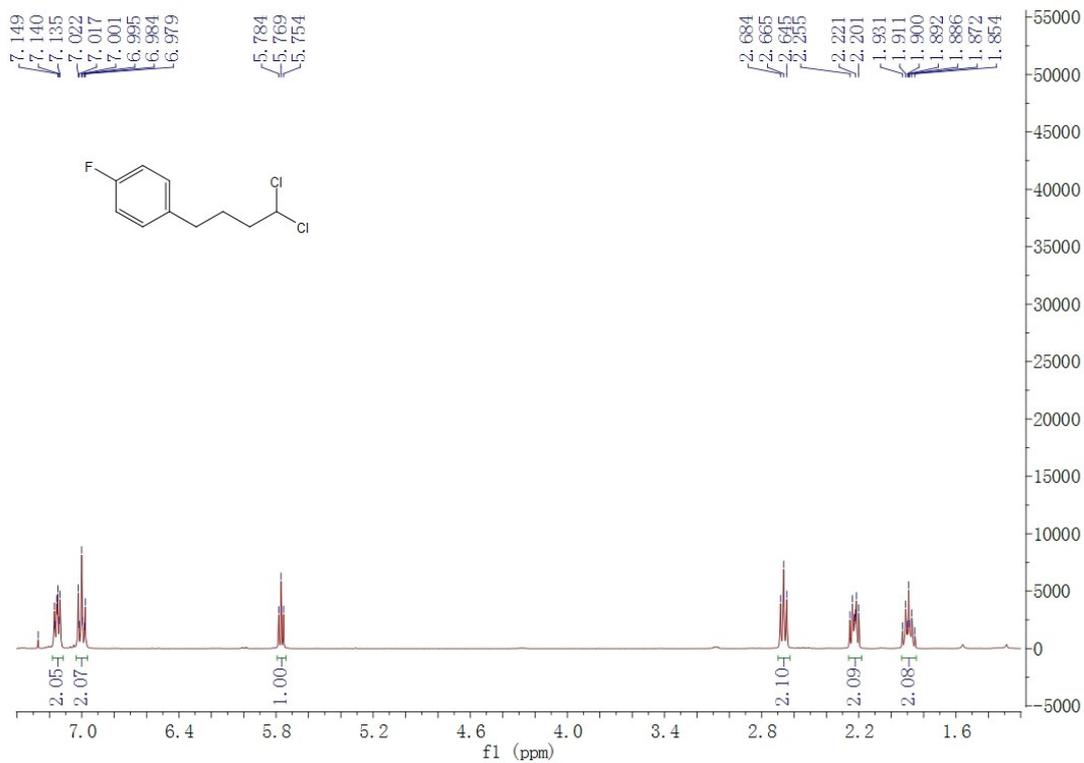
### 1-(4,4-dichlorobutyl)-4-methoxybenzene (Table 2, entry 4, 3da)



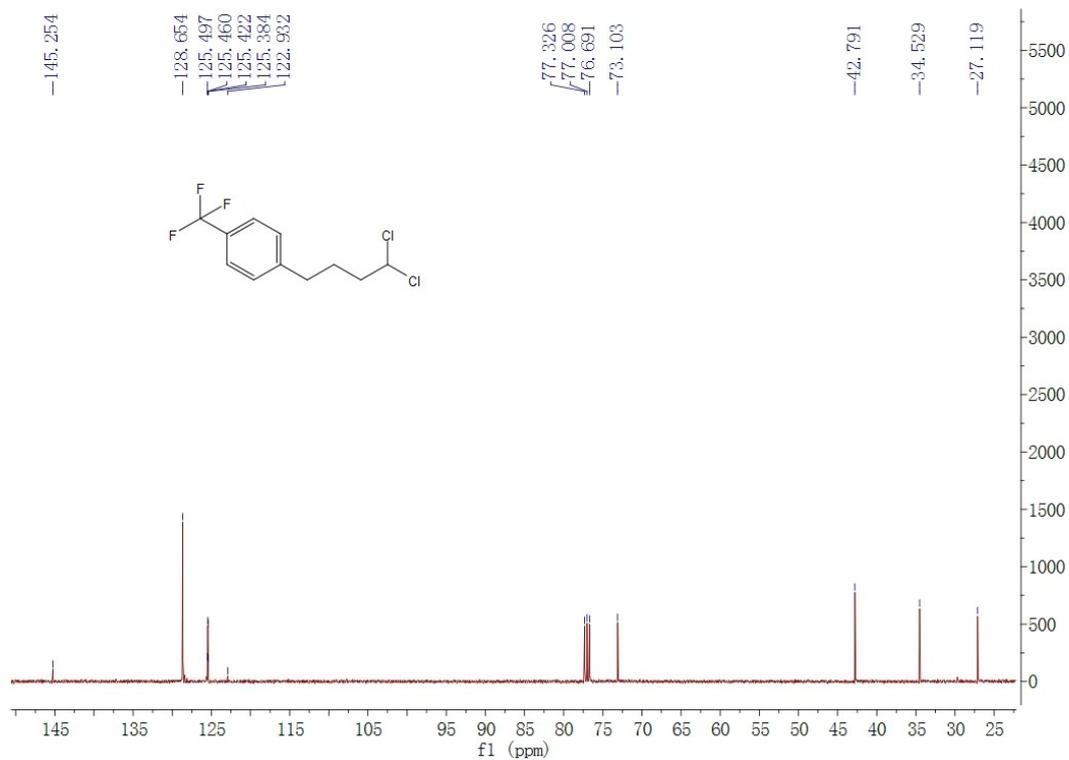
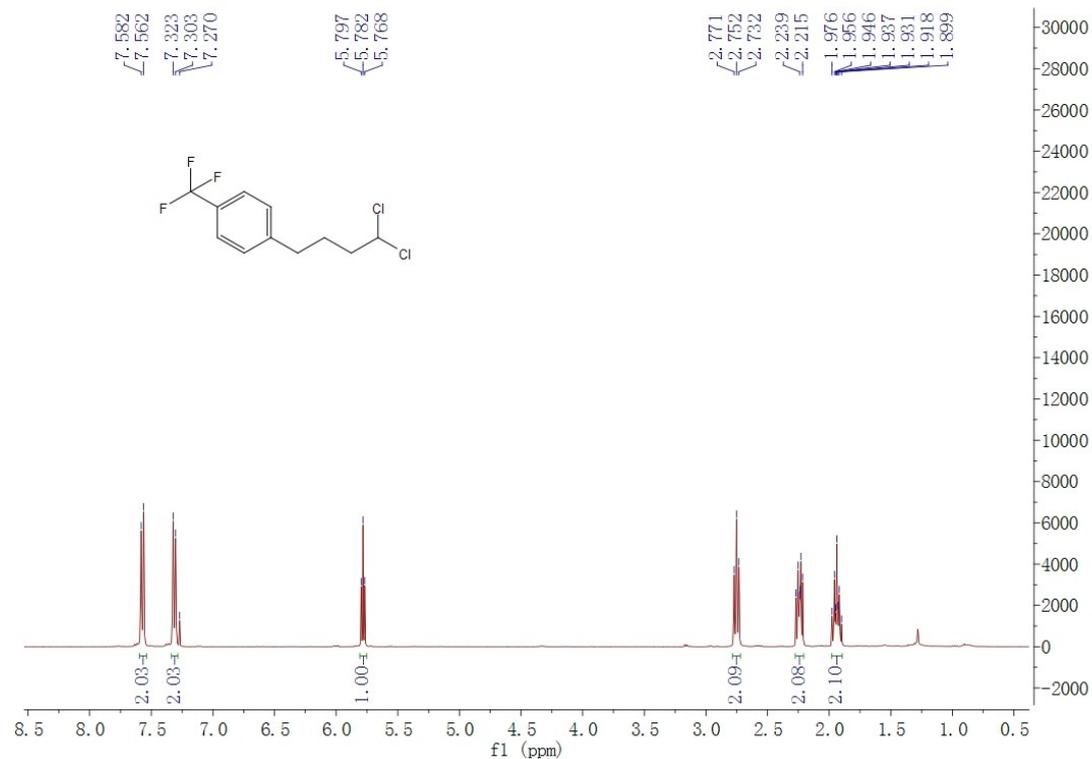
### 1-(4,4-dichlorobutyl)-2-methoxybenzene (Table 2, entry 5, 3ea)



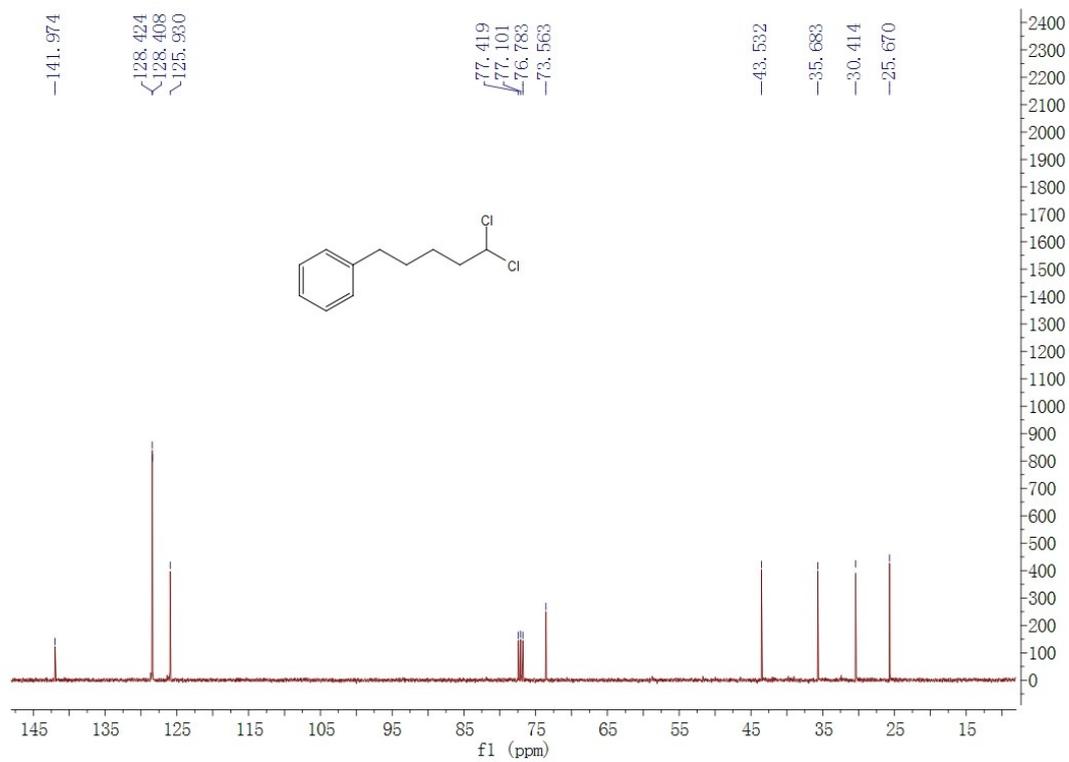
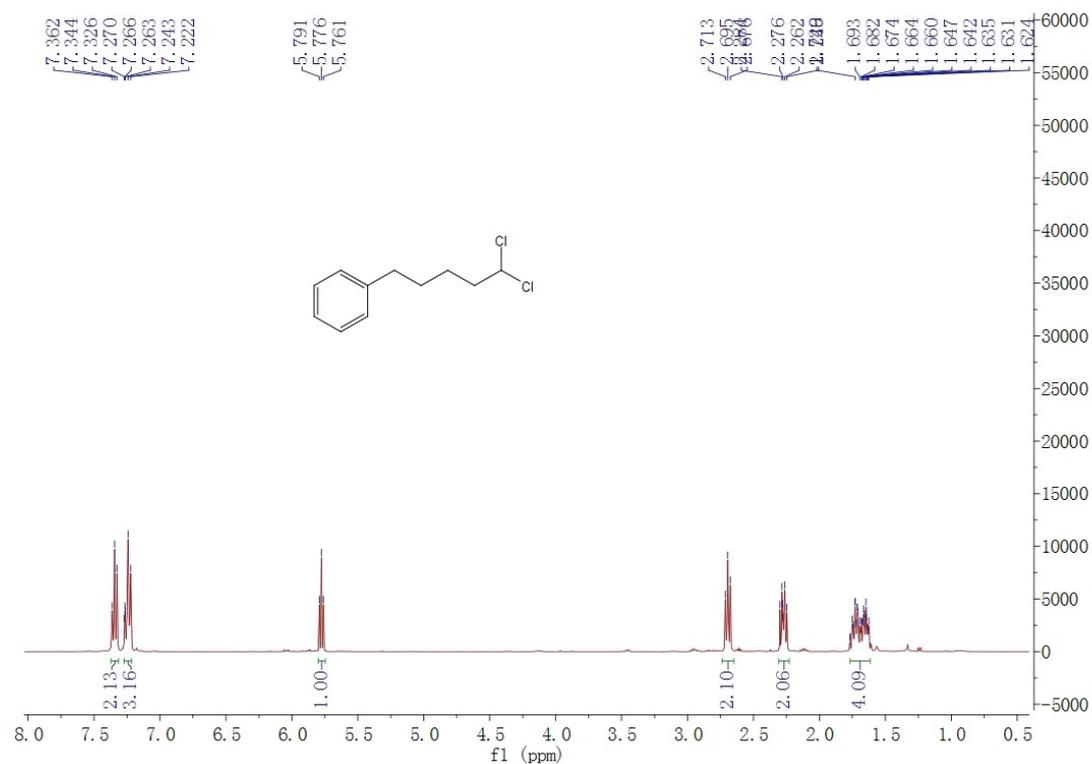
**1-(4,4-dichlorobutyl)-3-fluorobenzene (Table 2, entry 6, 3fa)**



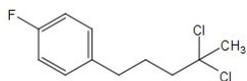
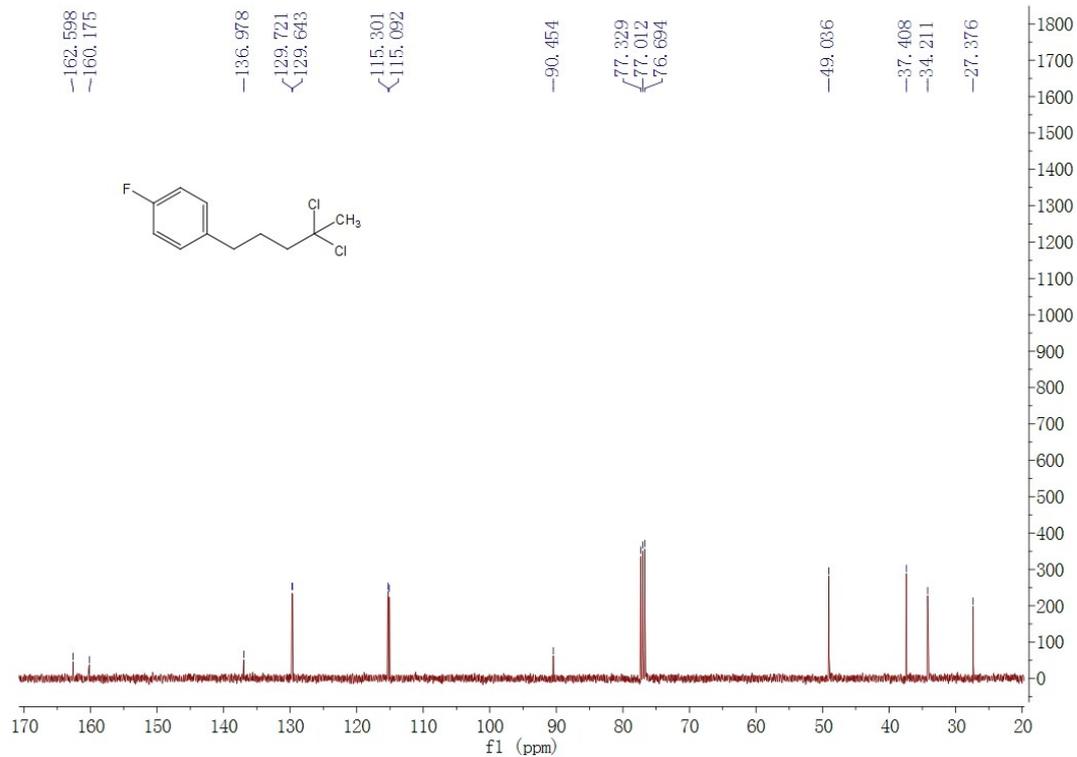
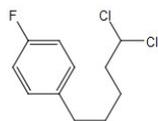
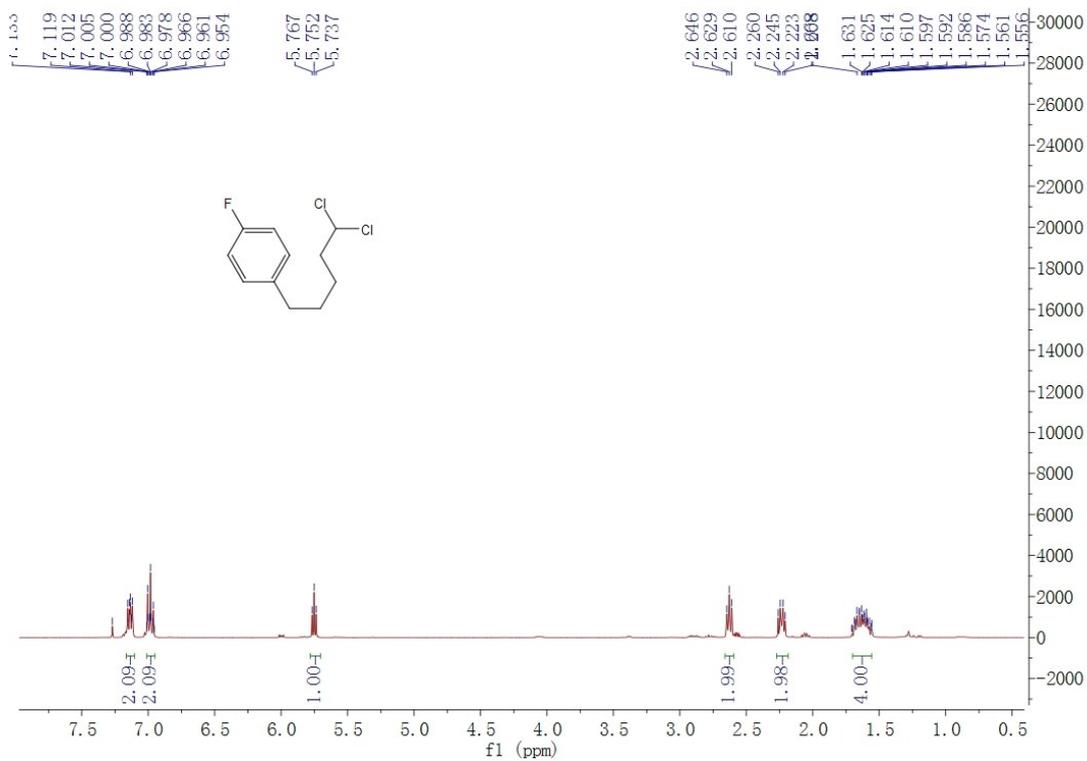
**1-(4,4-dichlorobutyl)-3-(trifluoromethyl)benzene (Table 2, entry 7, 3ga)**



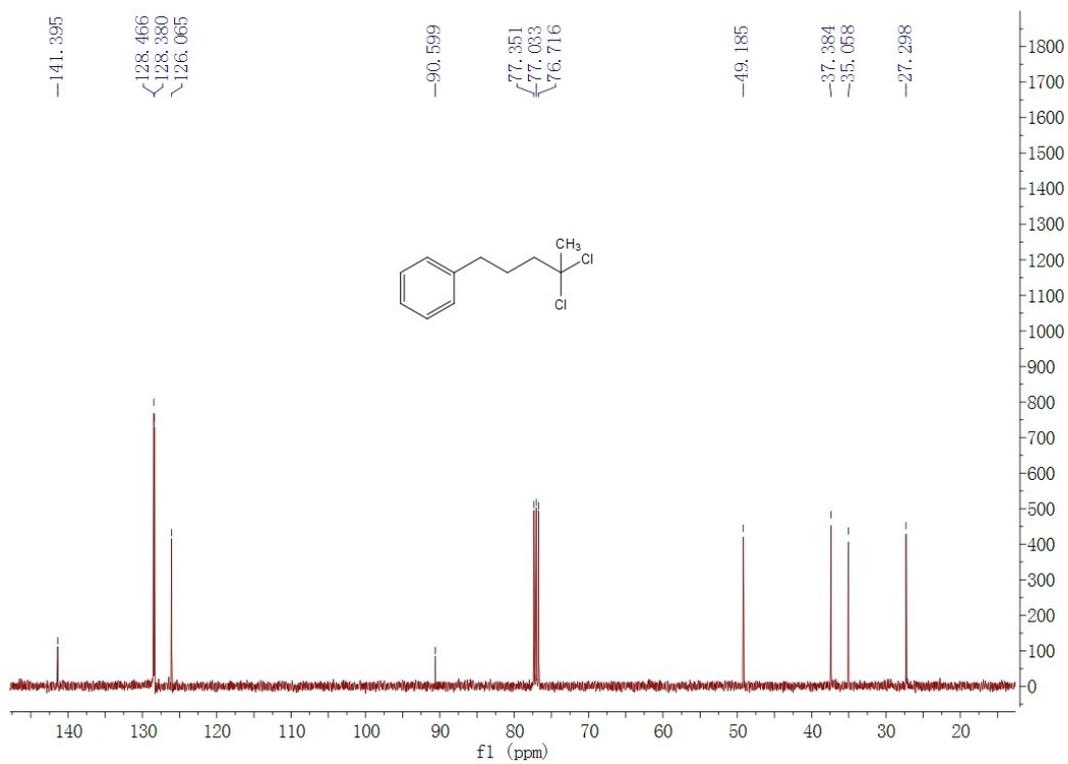
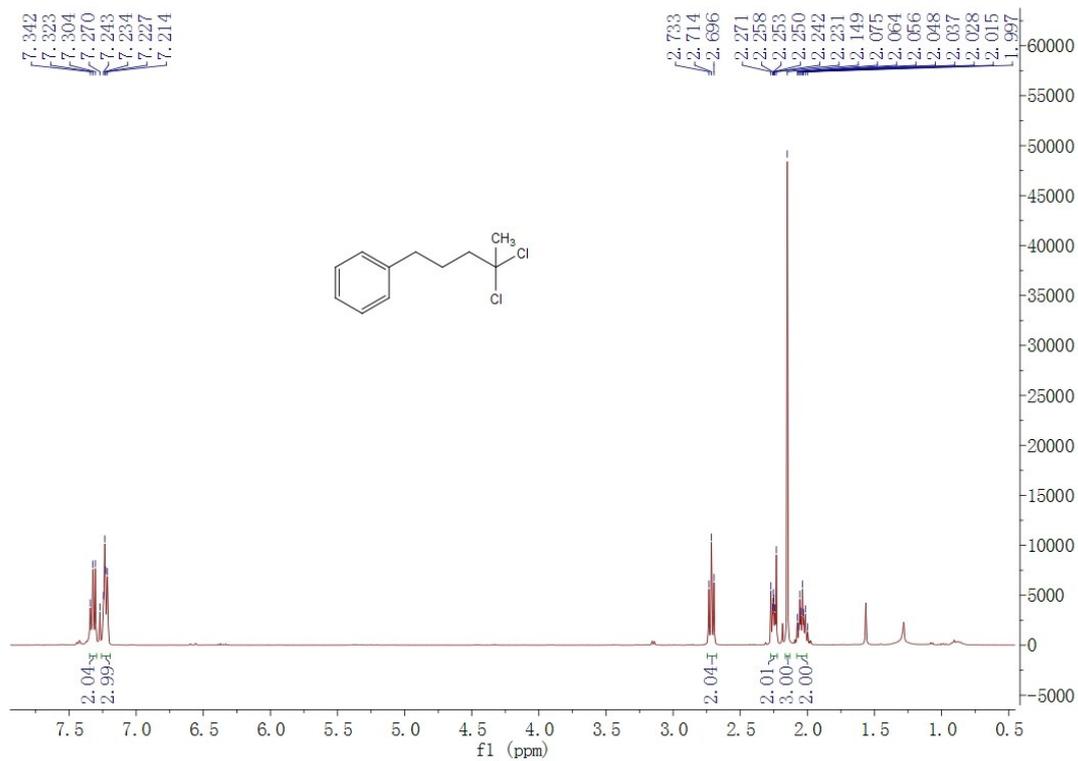
1-(5,5-dichloropentyl)benzene (Table 2, entry 8, 3ha)



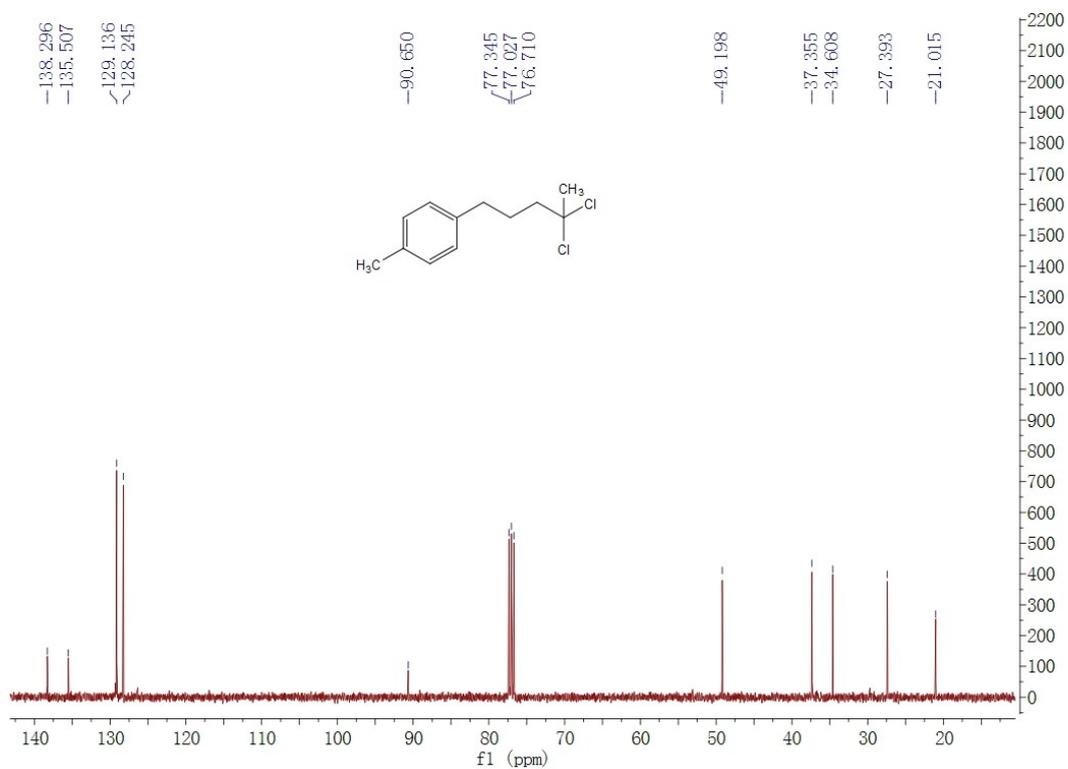
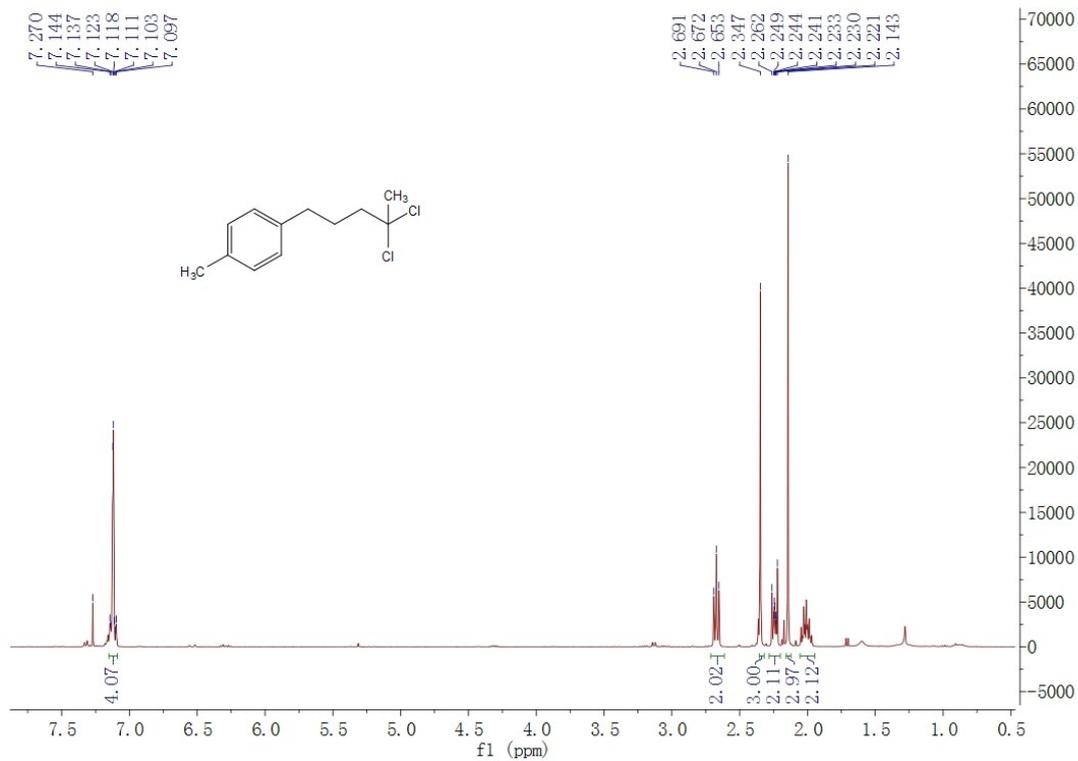
**1-(5,5-dichloropentyl)-3-fluorobenzene (Table 2, entry 9, 3ia)**



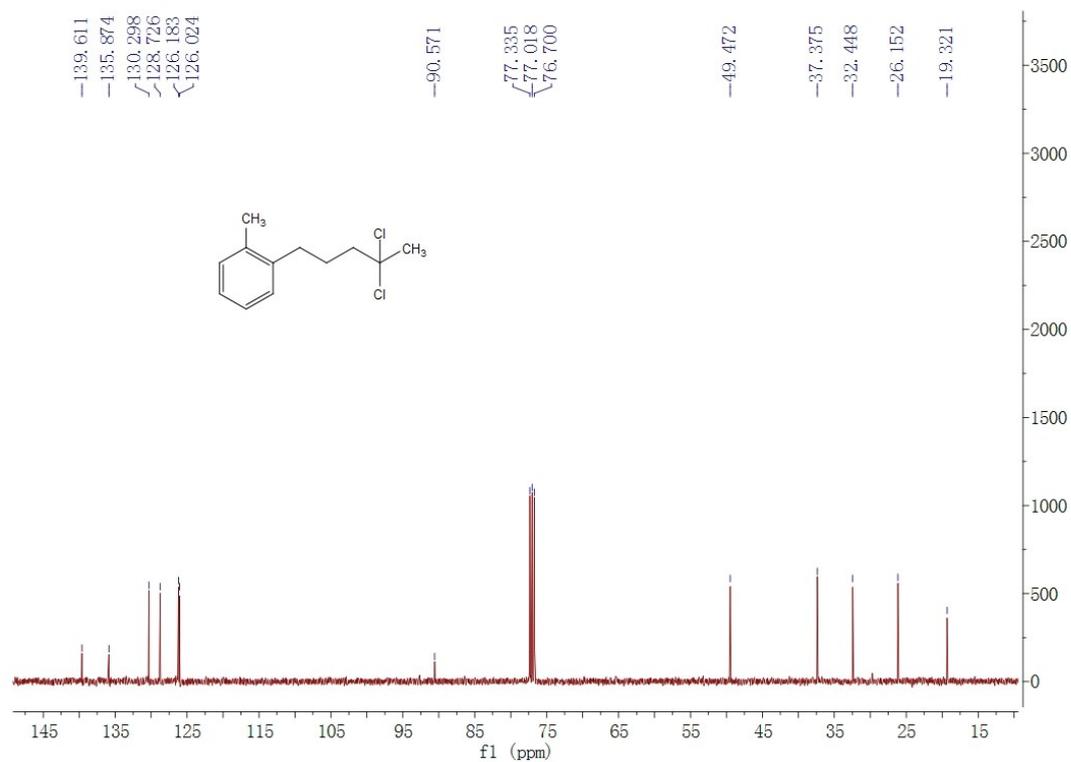
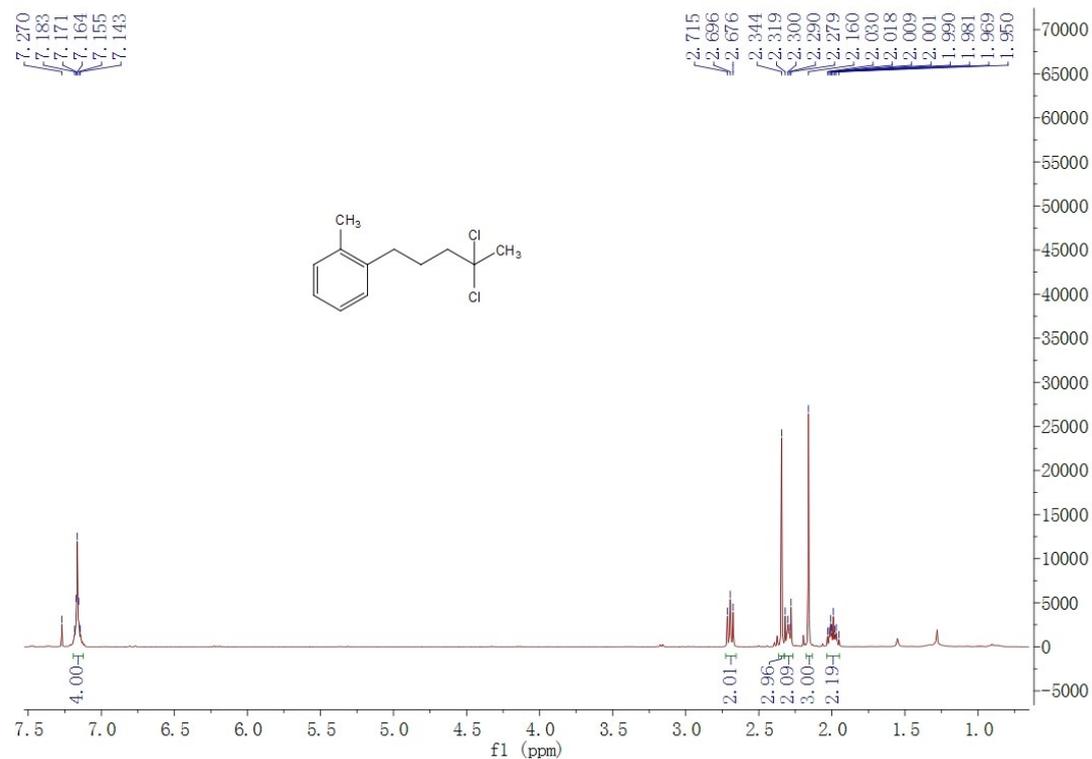
### 1-(4,4-dichloropentyl)benzene (Table 2, entry 10, 3ab)



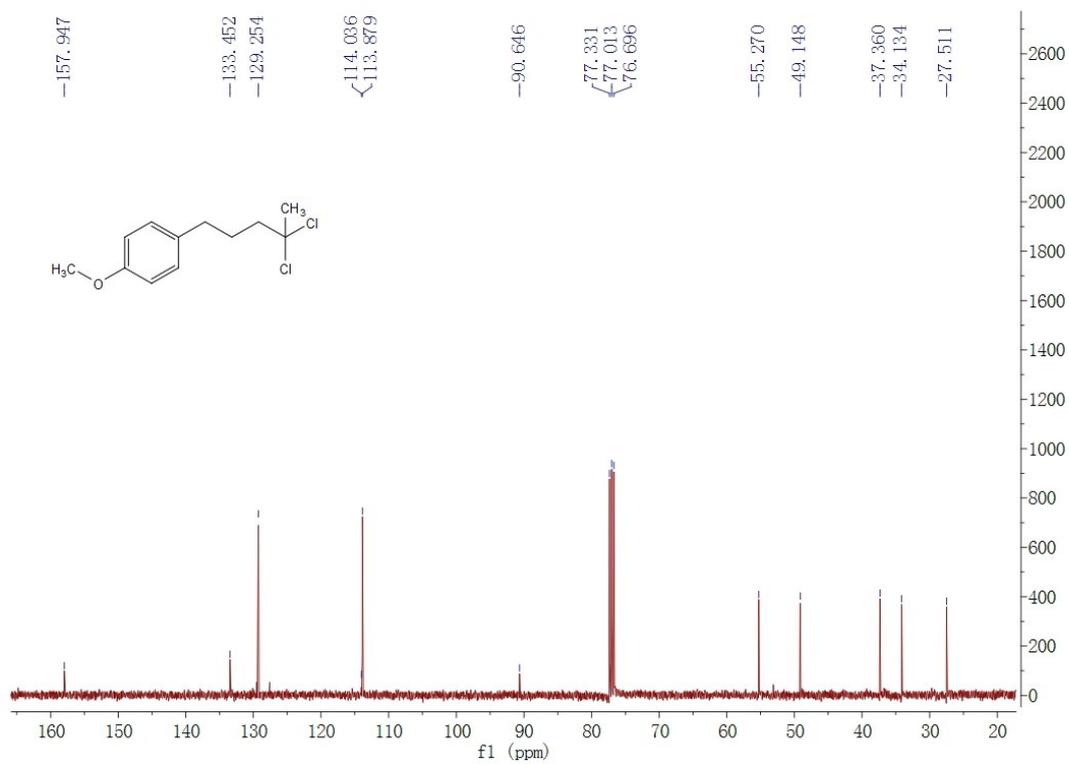
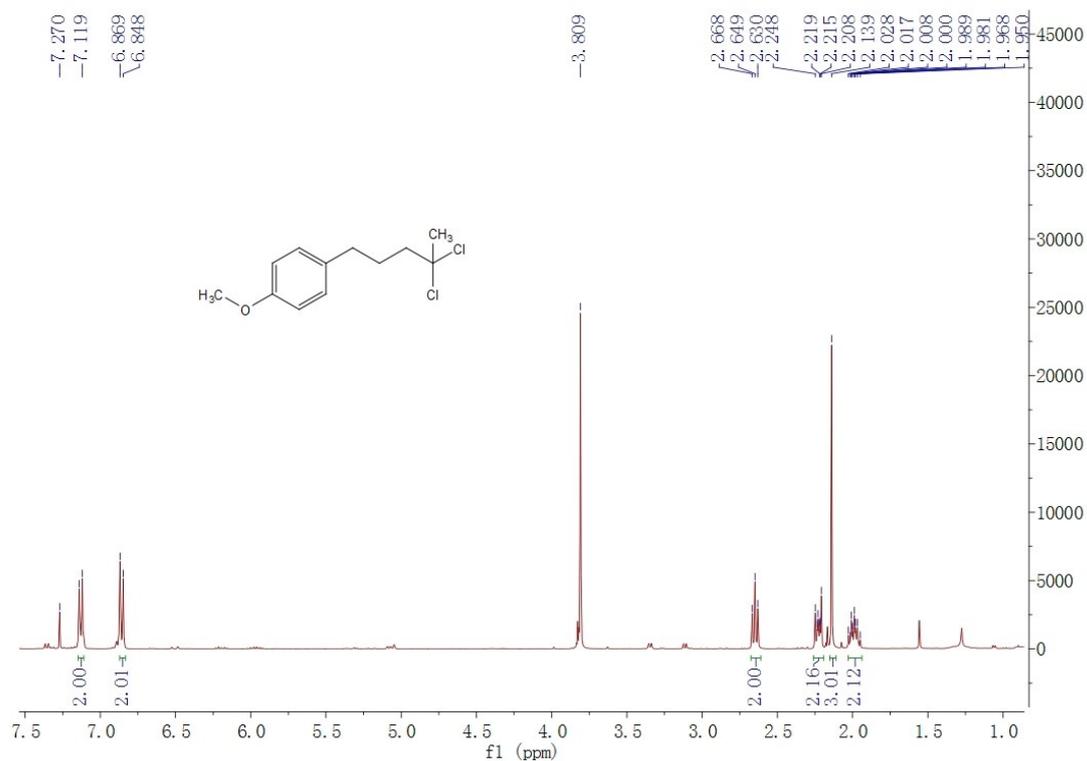
1-(4,4-dichloropentyl)-4-methylbenzene (Table 2, entry 11, 3bb)



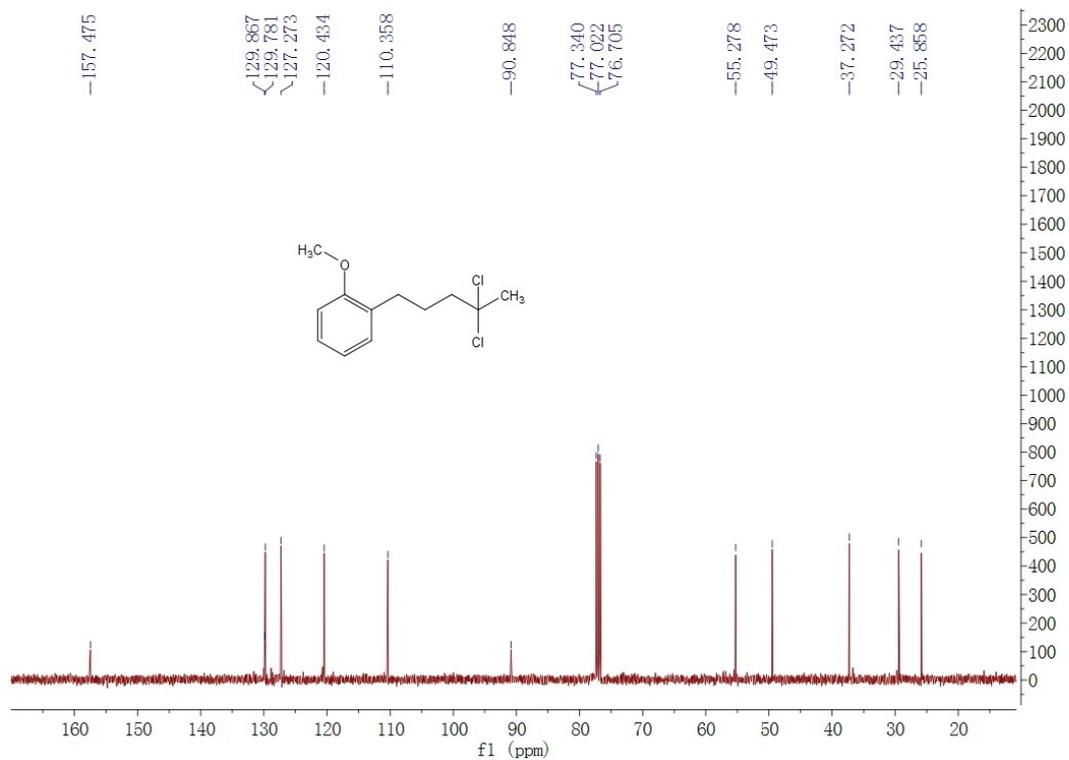
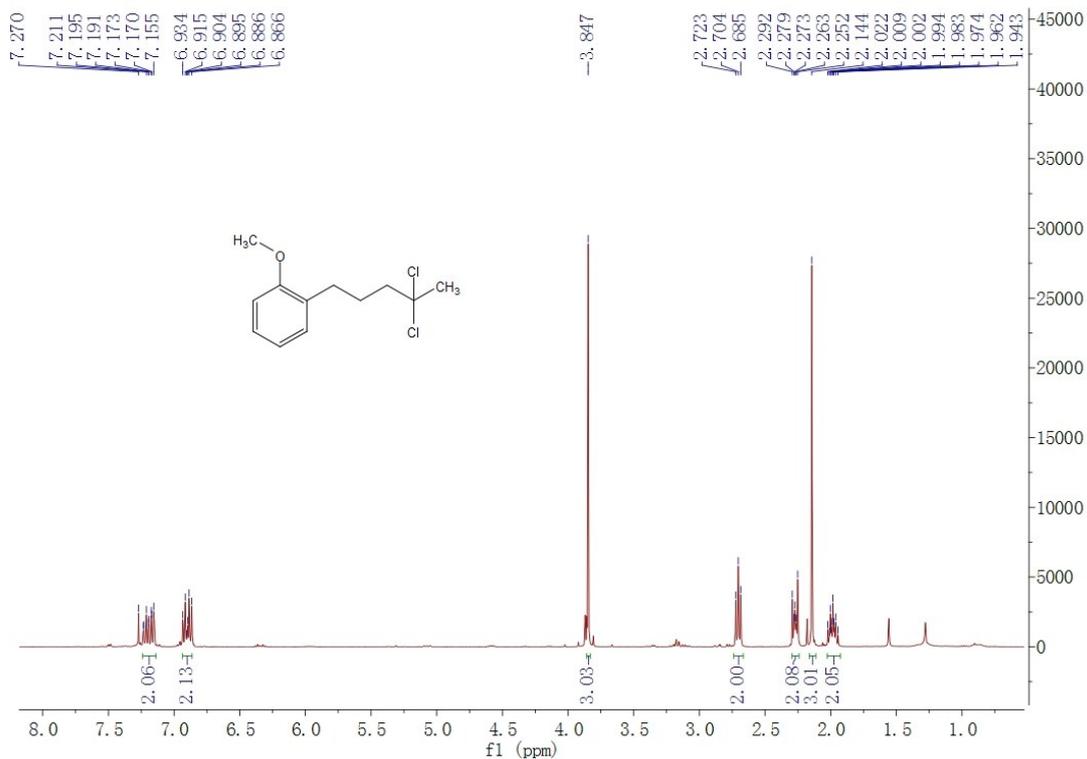
### 1-(4,4-dichloropentyl)-2-methylbenzene (Table 2, entry 12, 3cb)



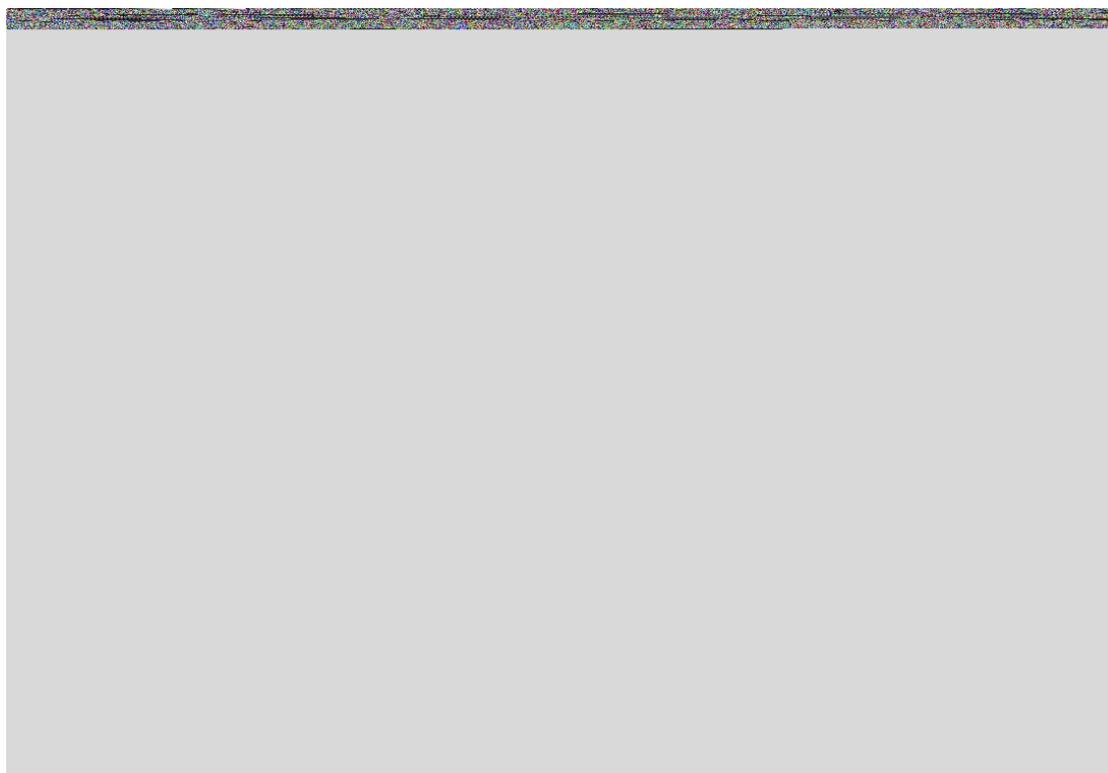
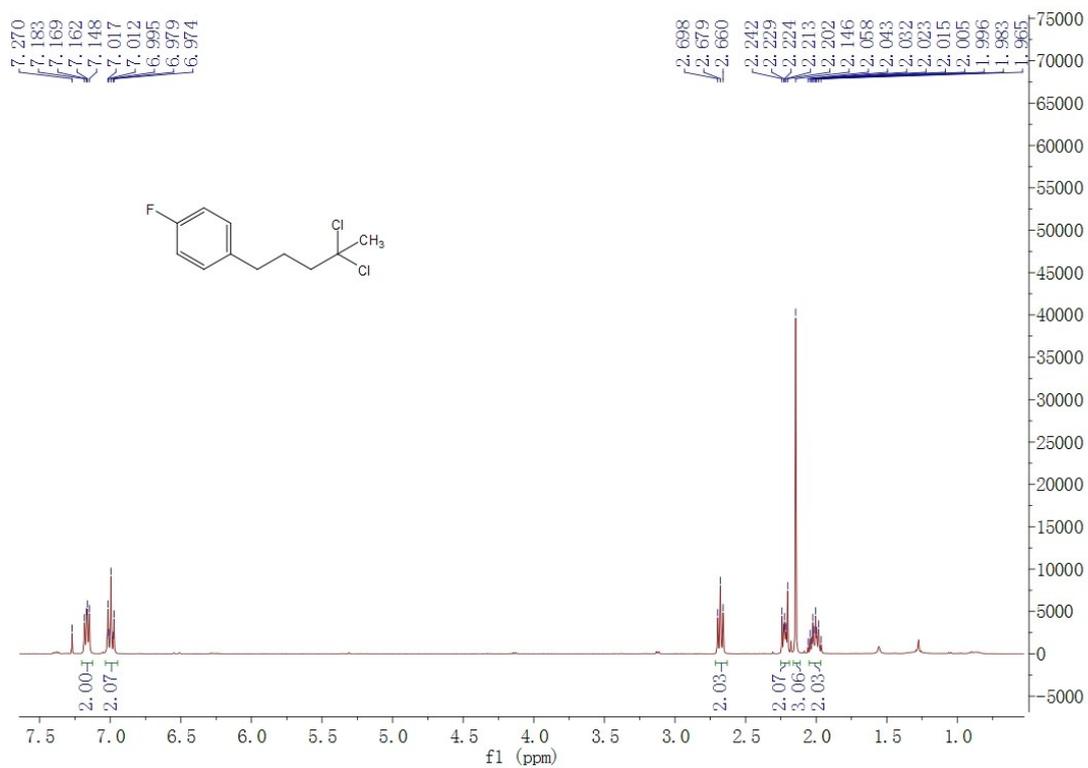
1-(4,4-dichloropentyl)-4-methoxybenzene (Table 2, entry 13, 3db)



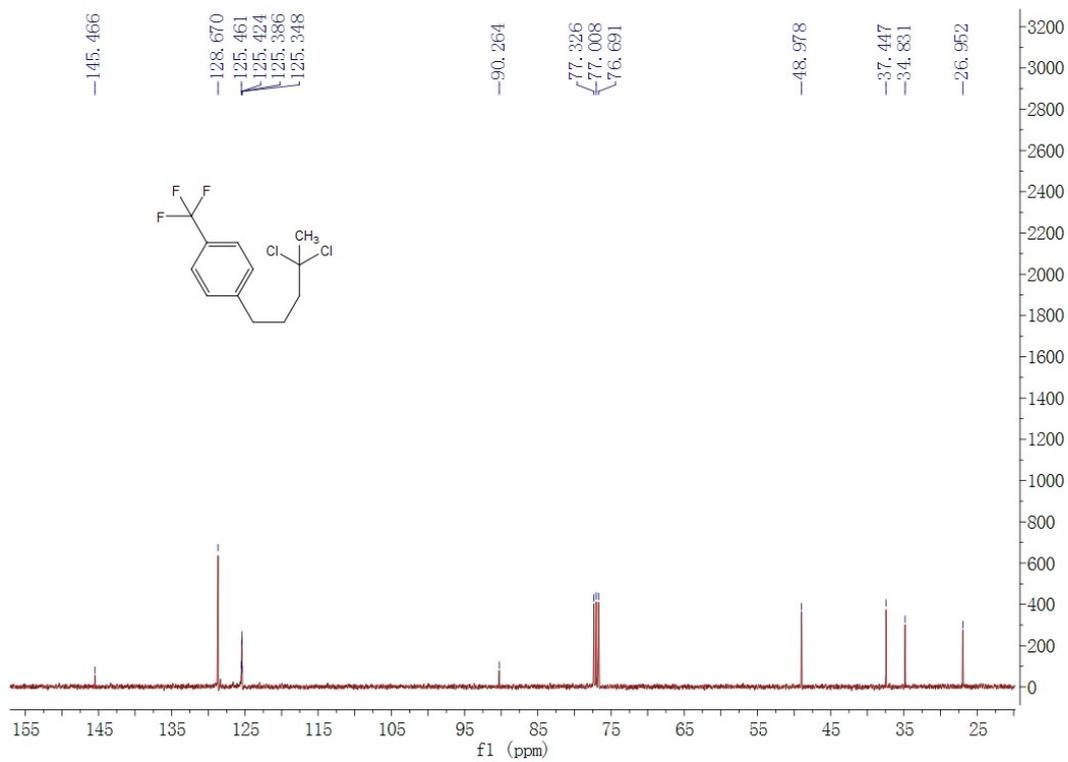
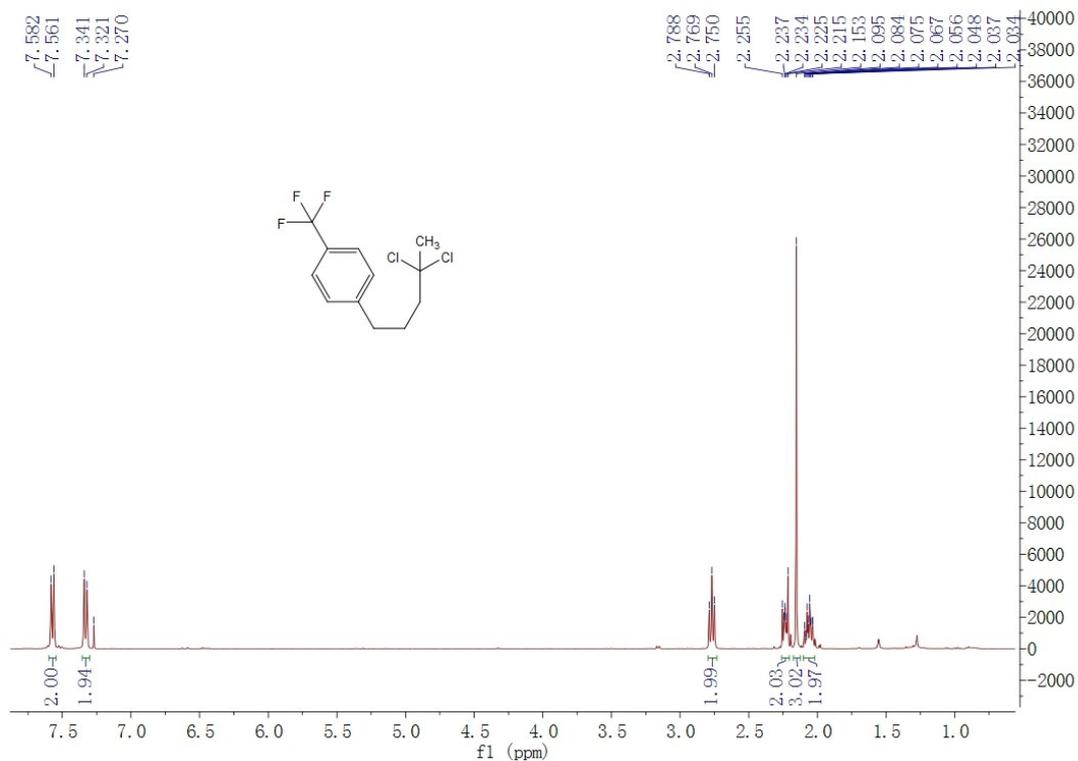
**1-(4,4-dichloropentyl)-2-methoxybenzene (Table 2, entry 14, 3eb)**



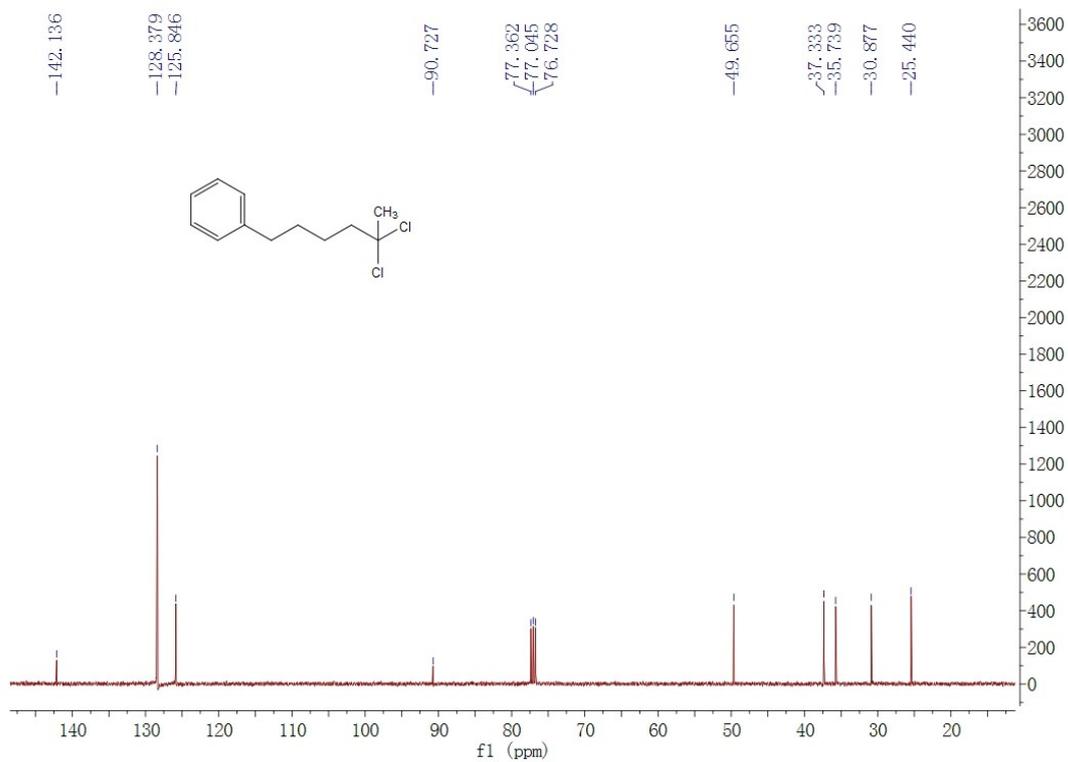
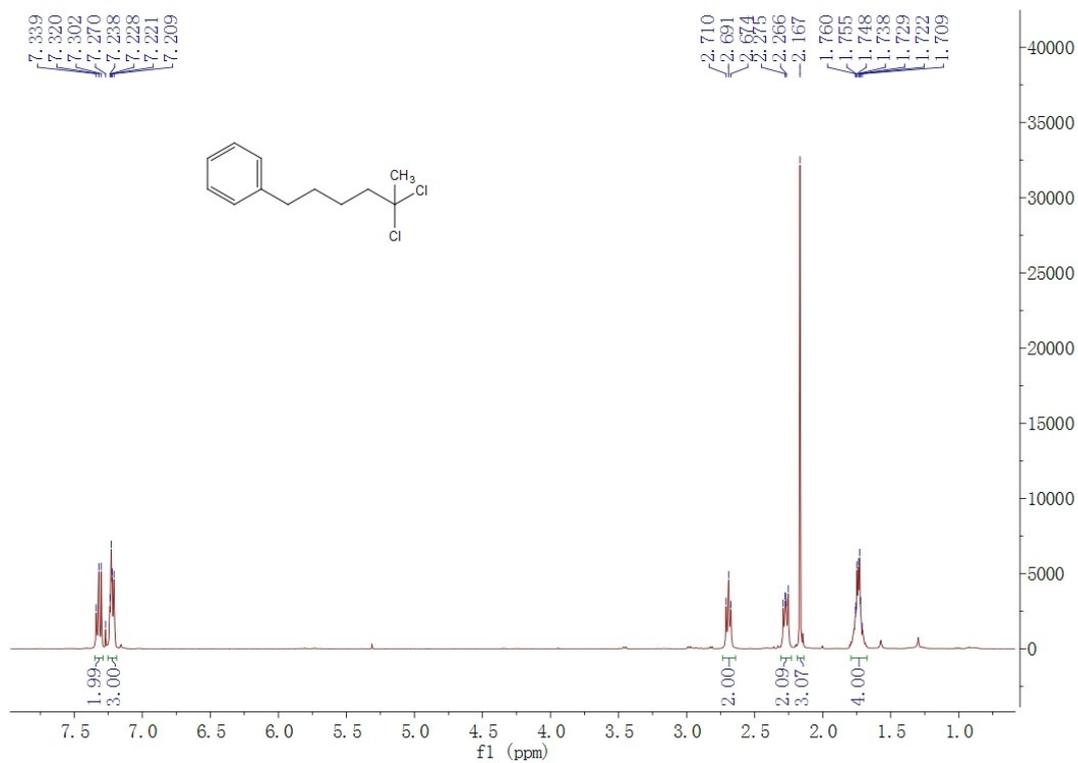
1-(4,4-dichloropentyl)-4-fluorobenzene (Table 2, entry 15, 3fb)



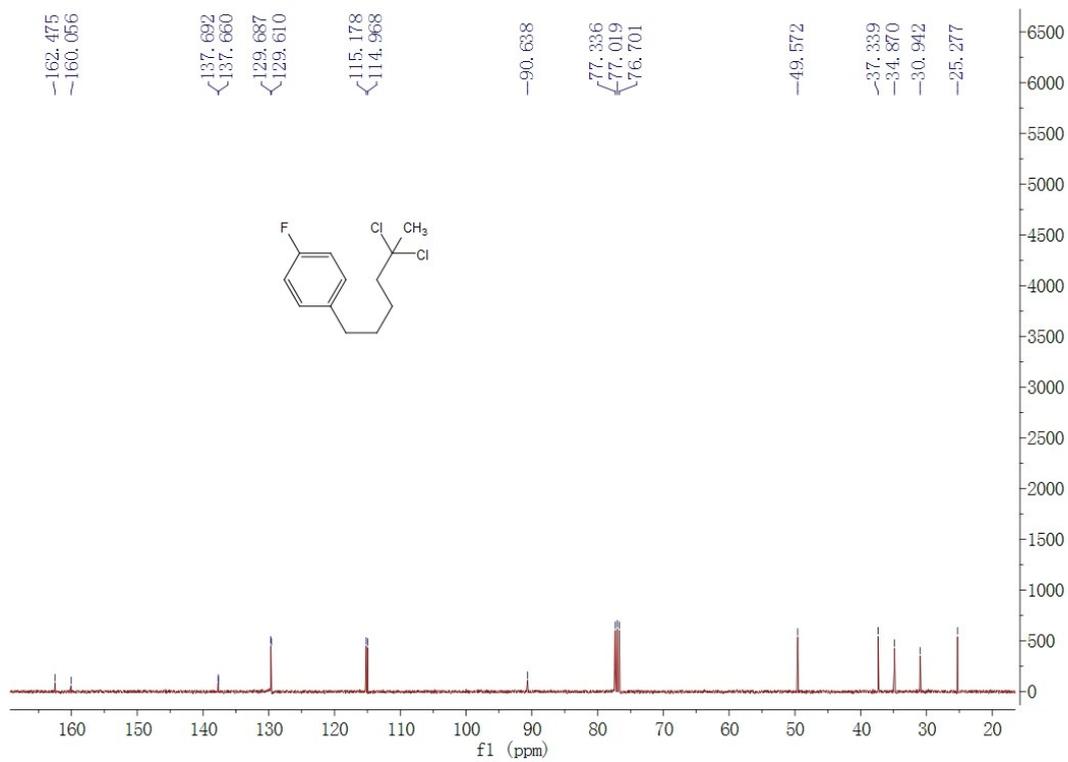
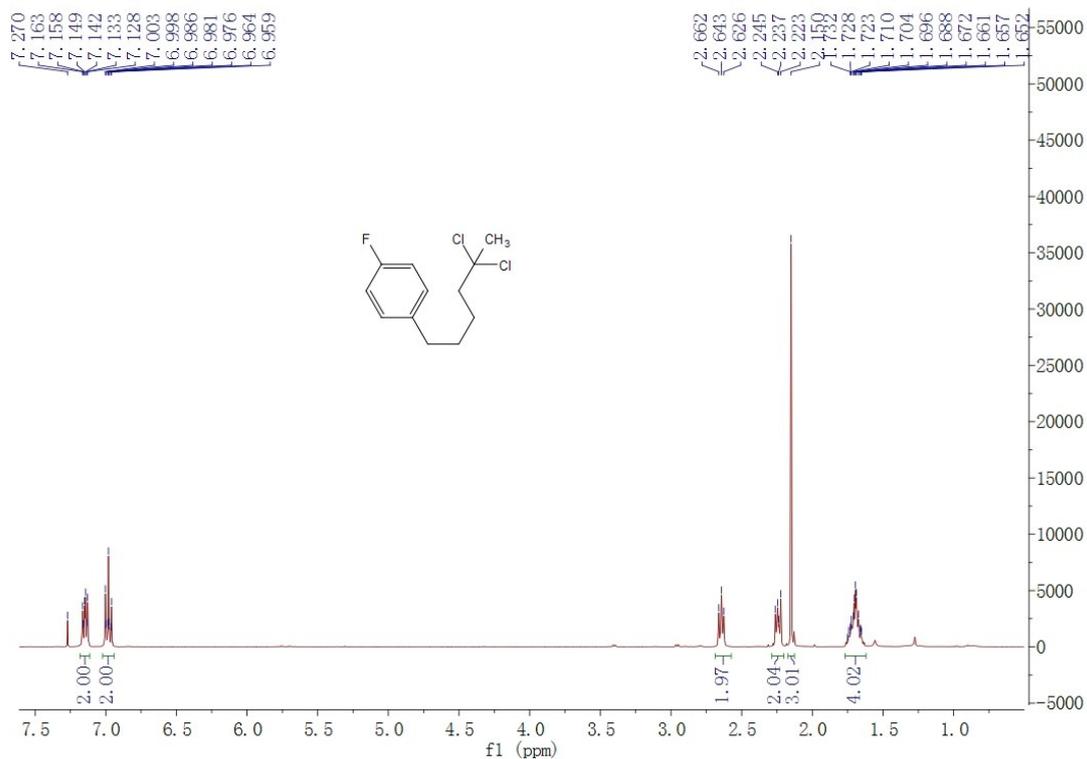
1-(4,4-dichloropentyl)-4-(trifluoromethyl)benzene (Table 2, entry 16, 3gb)



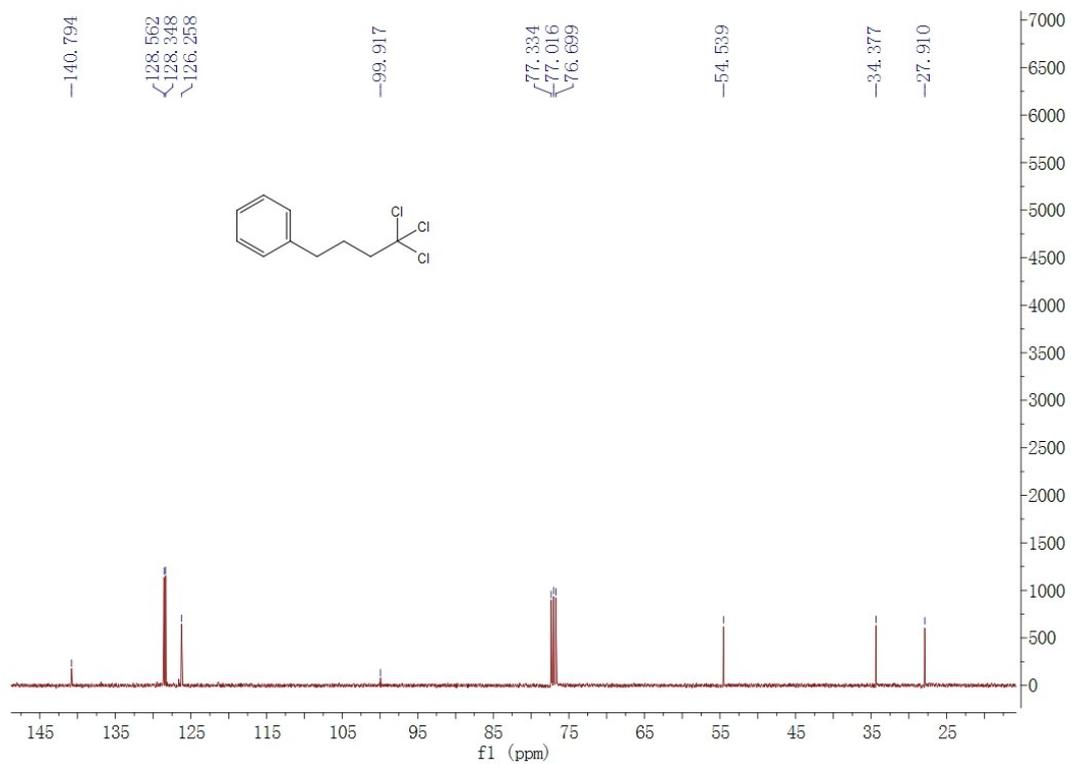
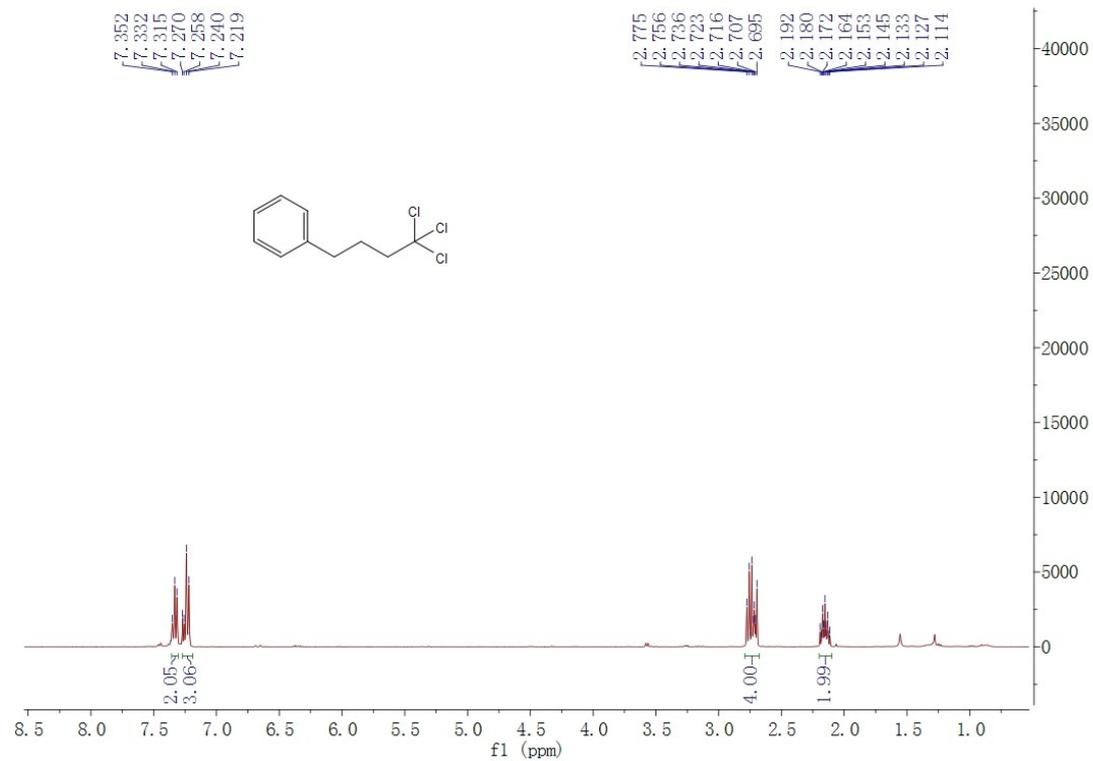
1-(5,5-dichlorohexyl)benzene (Table 2, entry 17, 3hb)



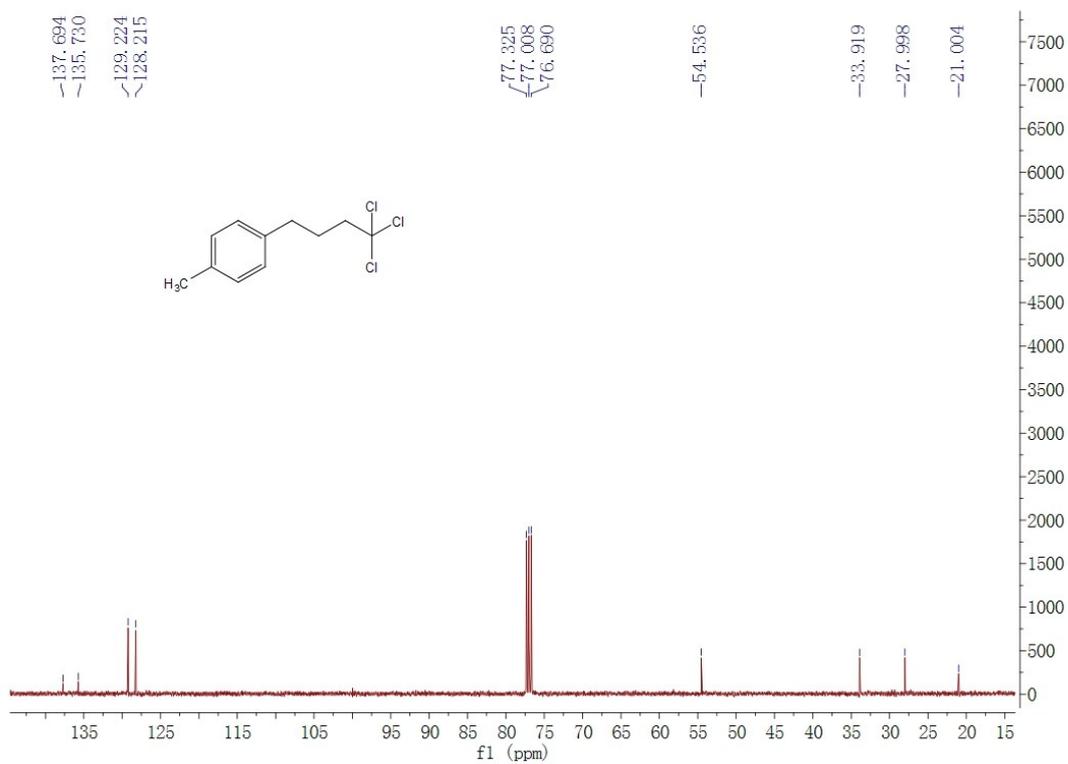
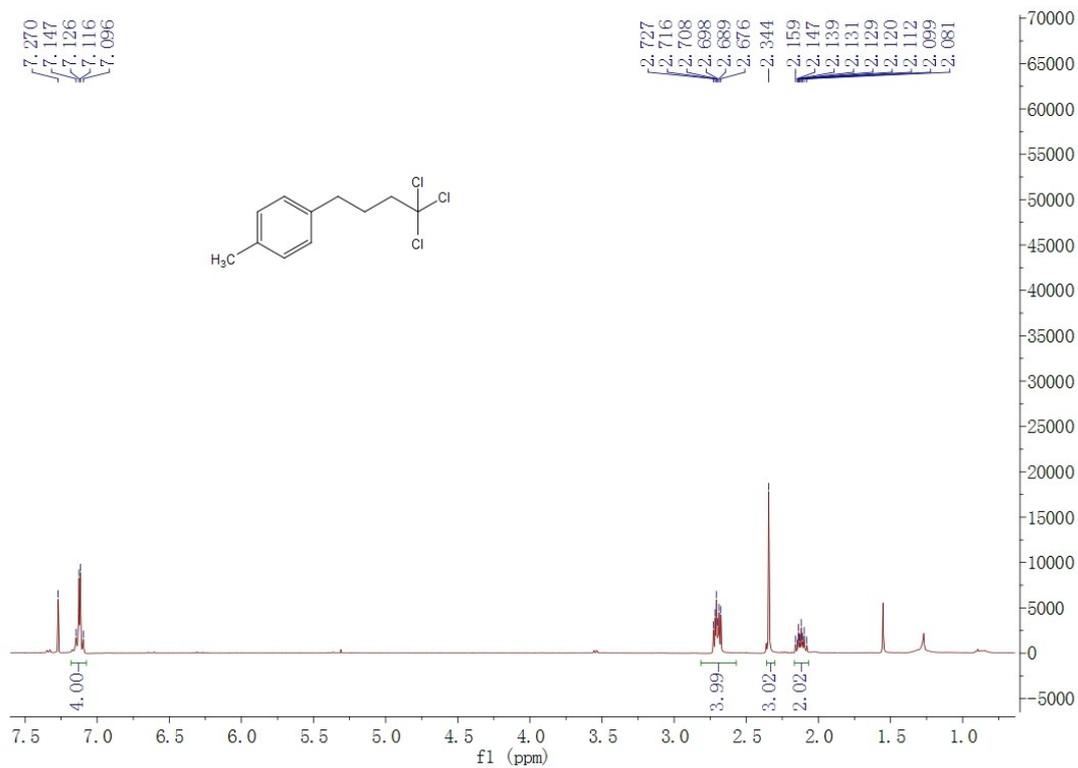
**1-(5,5-dichlorohexyl)-4-fluorobenzene (Table 2, entry 18, 3ib)**



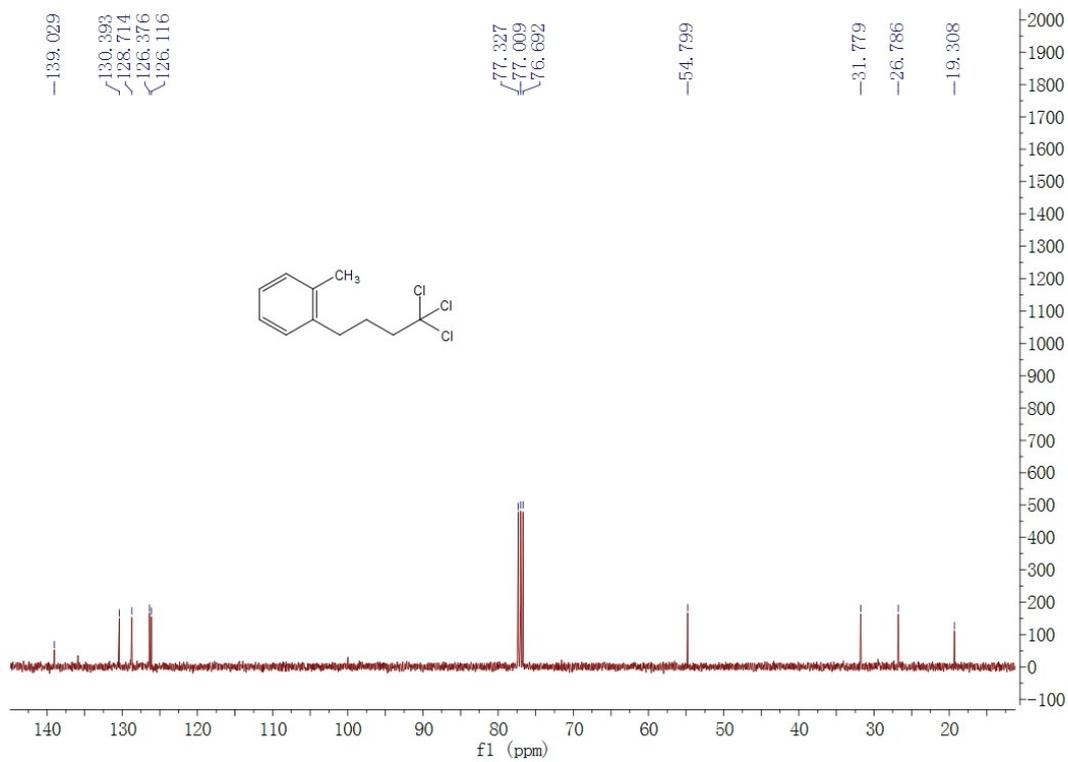
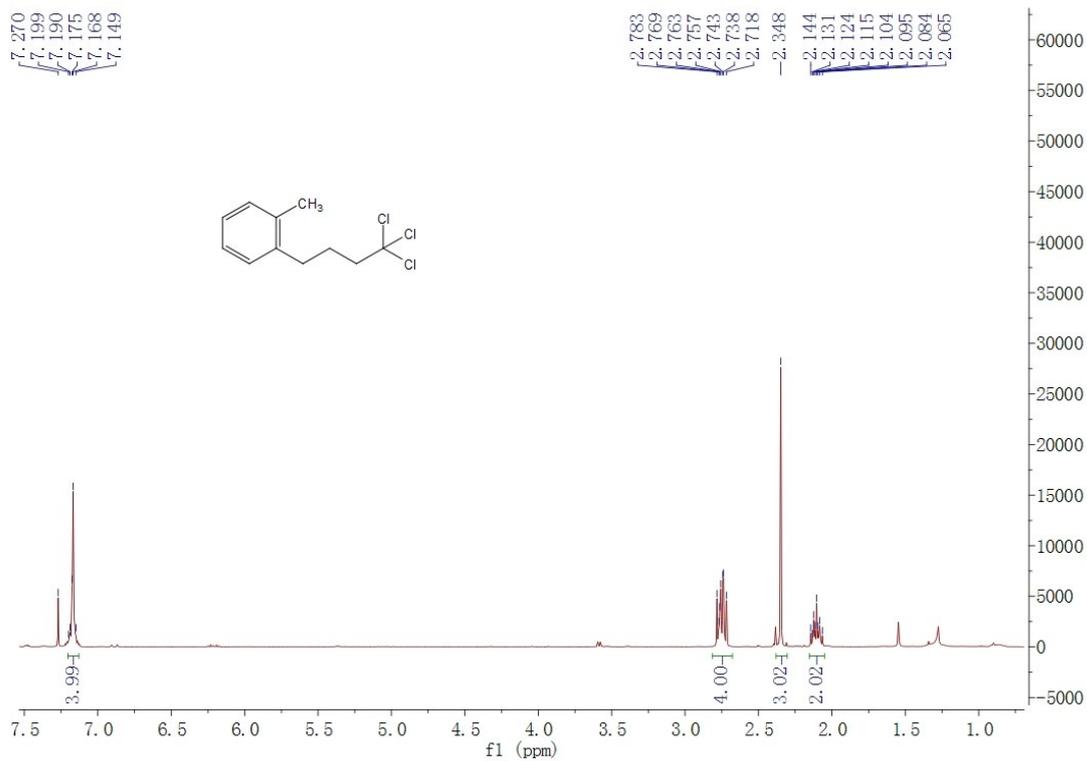
# 1-(4,4,4-trichlorobutyl)benzene (Scheme 2, 3ac)



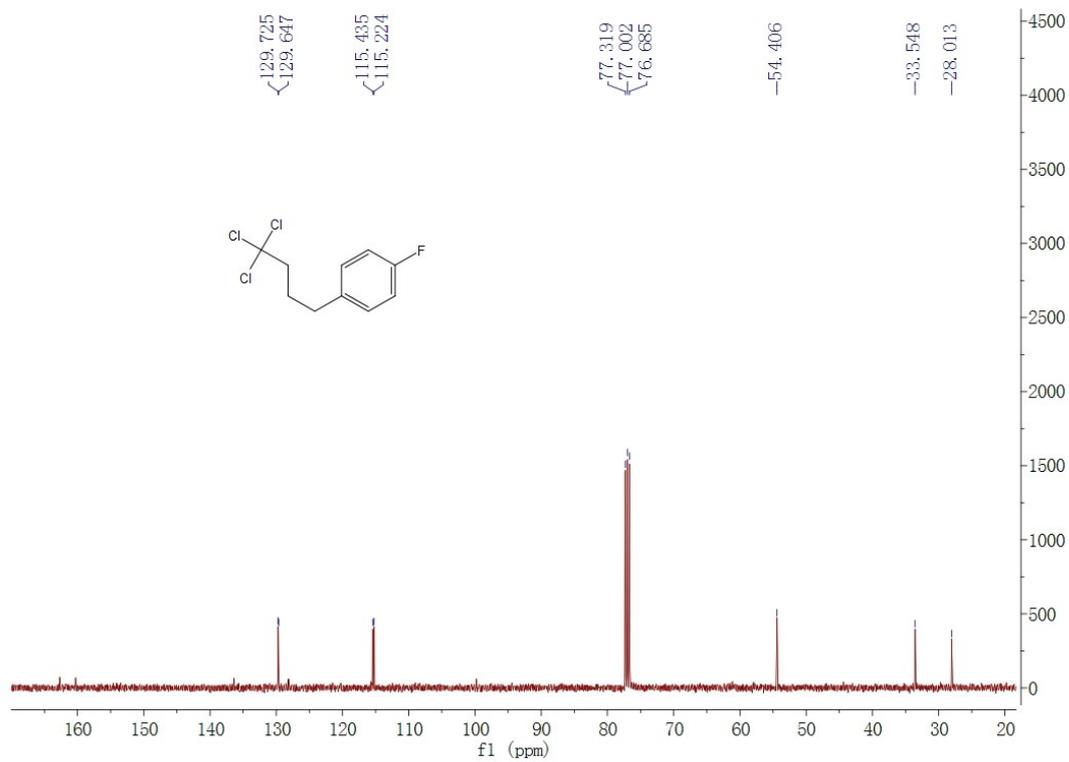
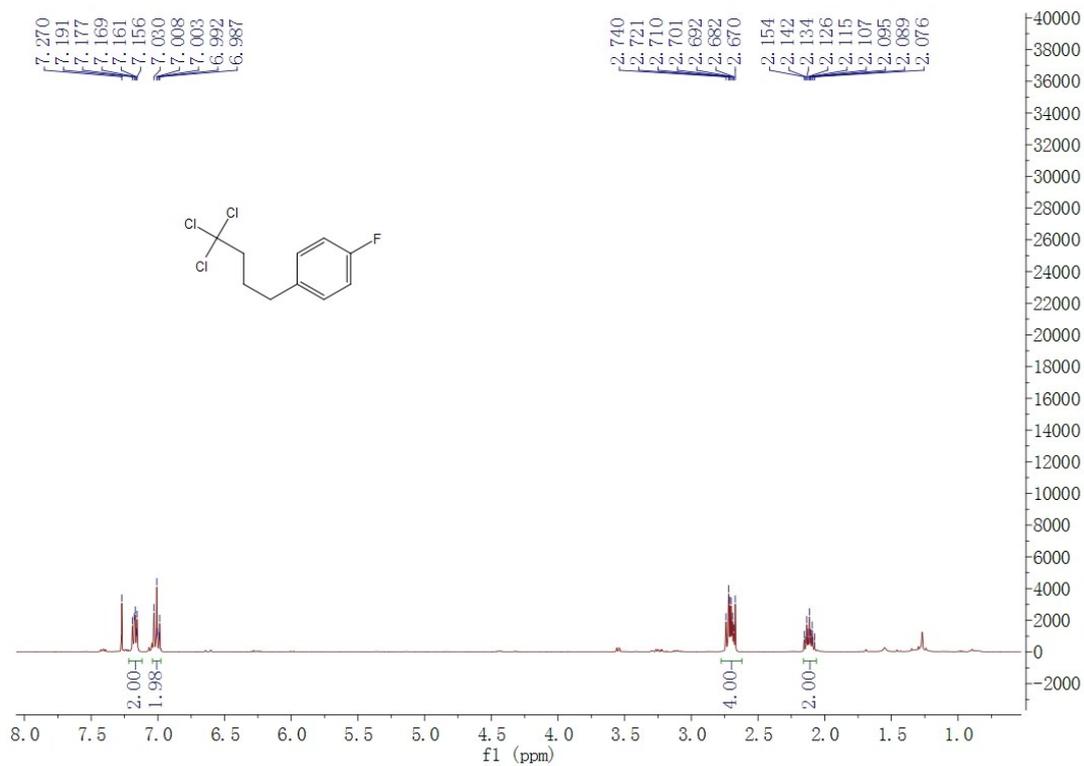
1-(4,4,4-trichlorobutyl)-4-methylbenzene (Scheme 2, 3bc)



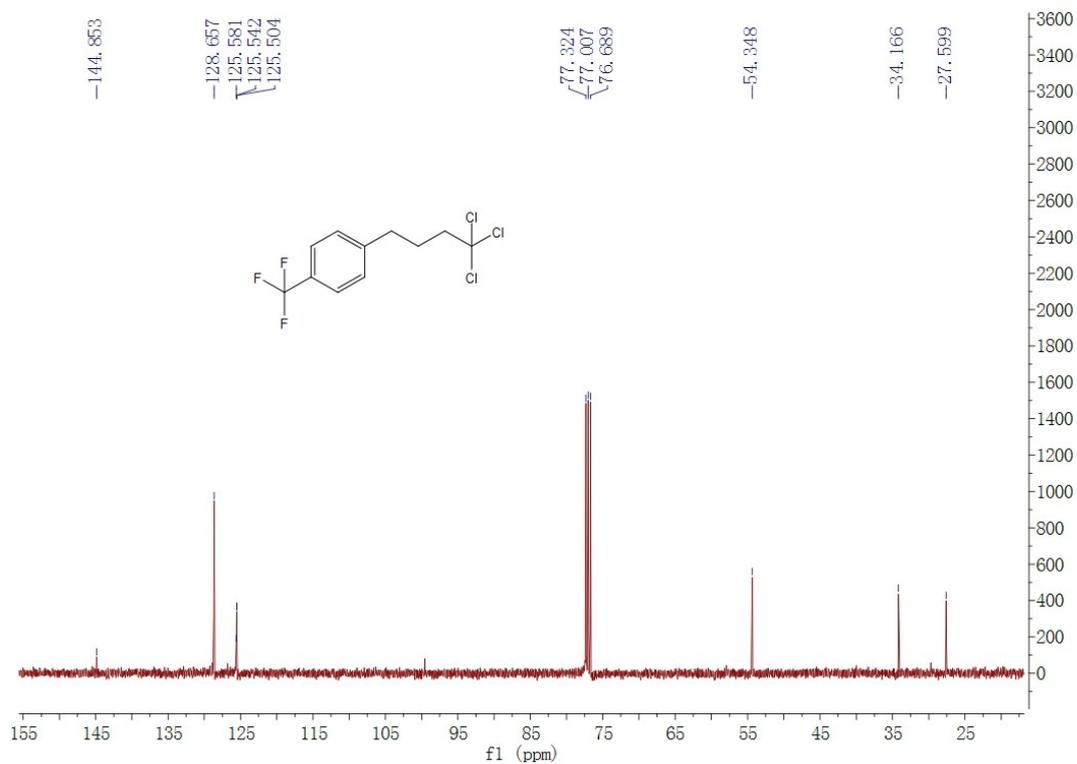
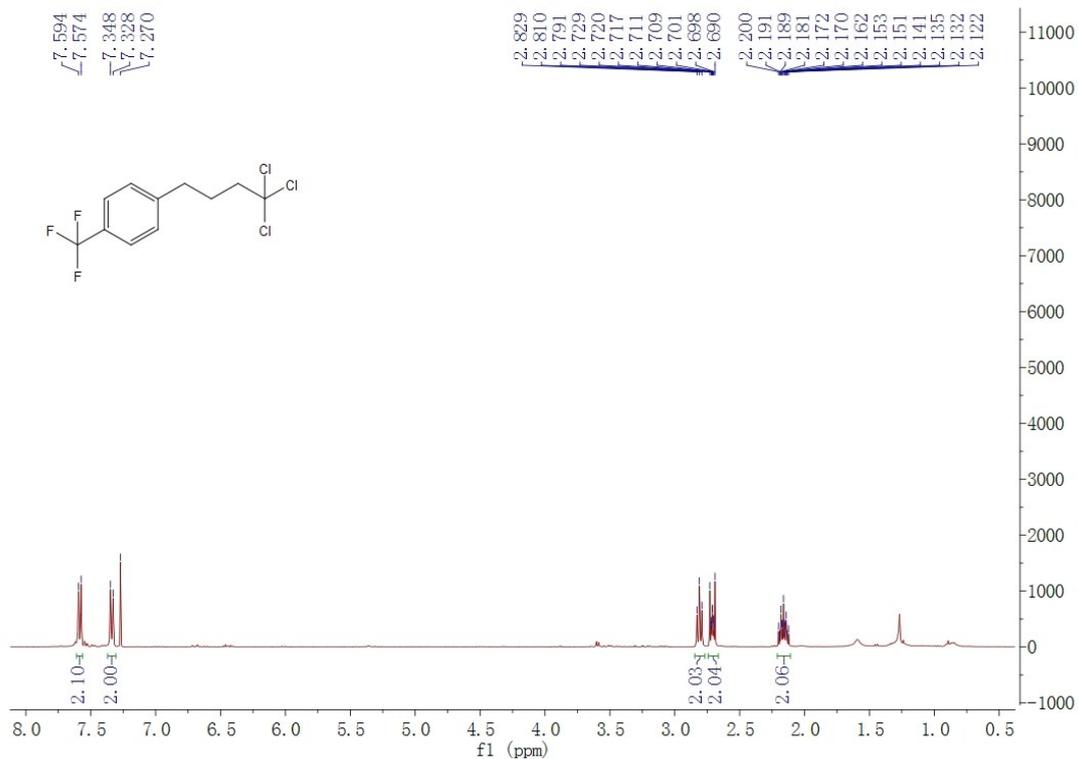
**1-(4,4,4-trichlorobutyl)-2-methylbenzene (Scheme 2, 3cc)**



# 1-(4,4,4-trichlorobutyl)-4-fluorobenzene (Scheme 2, 3fc)



1-(4,4,4-trichlorobutyl)-4-(trifluoromethyl)benzene (Table 2, entry 23, 3gc)



# 1-(4,4,4-trichlorobutyl)benzene (Scheme 3, 4)

