Supplementary Information

Radical-Mediated Alkoxypolyhaloalkylation of Styrenes with Polyhaloalkanes and Alcohols via C(sp^3)-H Bond Cleavage

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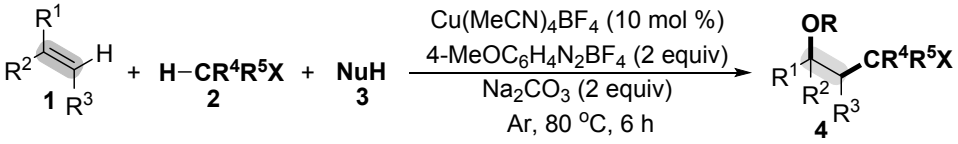
(A) Typical experimental procedure

(a) General

The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solvent on a NMR spectrometer using TMS as internal standard. HRMS was measured on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. Melting points are uncorrected.

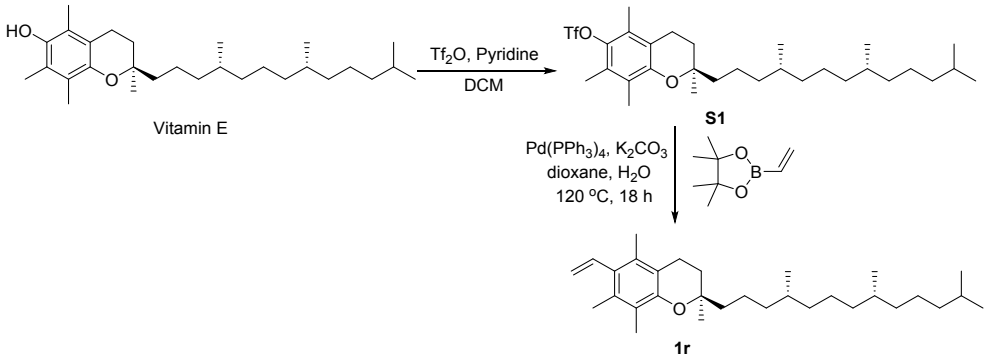
(b) General procedure for the synthesis of 4.



To a Schlenk tube were added $Cu(MeCN)_4BF_4$ (0.02 mmol, 10 mol%), 4-$MeOC_6H_4N_2BF_4$ (0.4 mmol, 2 equiv), Na_2CO_3 (0.4 mmol, 2 equiv), alkene **1** (0.2 mmol), nucleophiles **3** (0.6 mmol), Poylhaloalkanes **2** (2 mL), the tube was then charged with argon. The mixture was stirred at 60-80 ^{o}C until complete consumption of starting material as monitored by TLC and/or GC-MS analysis (about 6 h). After the reaction was finished, the combined organic phases concentrated, and the resulting residue was purified by silica gel column chromatography (petroleum/ethyl acetate) to afford the desired product **4**.

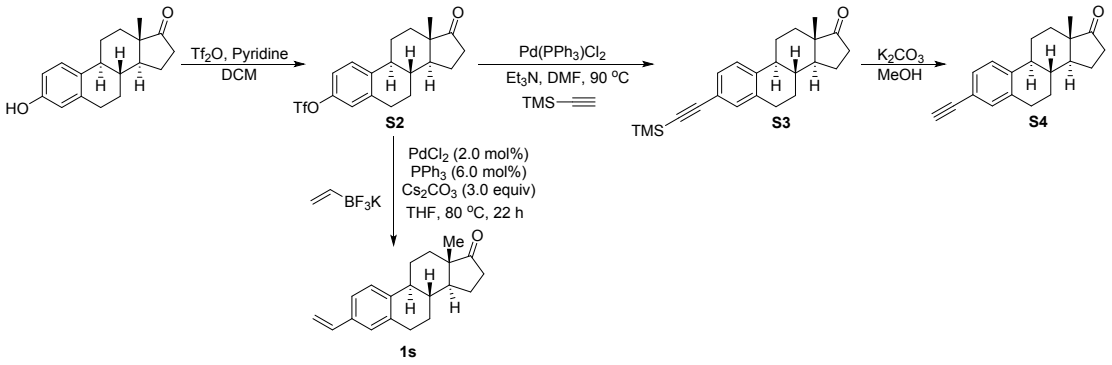
(B) General procedure for the synthesis of the starting materials

Synthesis of 1z



Under nitrogen atmosphere, to a 50 mL flamed dried round bottom charged with Vitamin E (4300 mg, 10.0 mmol, 1.0 equiv) was added DCM (30.0 mL) and pyridine (1580 mg, 1.6 mL, 20.0 mmol, 2.0 equiv). The resulting mixture was cooled to 0°C in an ice/water bath. Tf_2O (3390 mg, 2.1 mL, 15.0 mmol, 1.5 equiv) was added dropwise over ca. 5 minutes. The reaction mixture was warmed to room temperature and stirred for 5 hours. The resulting reaction was then quenched by water (15 mL). The layers were separated, and the aqueous layer was extracted with DCM (3 × 20 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel, to afford the **S1**.

Under nitrogen atmosphere, to a 25 mL flamed dried round bottom charged with **S1** (562 mg, 1 mmol, 1.0 equiv), 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane (308 mg, 2.0 mmol, 2.0 equiv), $Pd(PPh_3)_4$ (139 mg, 0.12 mmol, 0.12 equiv), and K_2CO_3(414 mg, 3 mmol, 3equiv), was added dioxane-water (4:1) mixture at 120 °C for 18 h. The reaction mixture was then diluted with water, and the aqueous layer was extracted with ethyl acetate (3 × 10 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated in vacuo. Chromatography of the residue on silica gel provided the corresponding product **1r**.



Synthesis of S2

3-(Trifluoromethanesulfonyl)estrone (**S2**) was synthesized according to the reported procedure. Under nitrogen atmosphere, to a 50 mL flamed dried round bottom charged with Estrone (2700 mg, 10.0 mmol, 1.0 equiv) was added DCM (30.0 mL) and pyridine (1580 mg, 1.60 mL, 20.0 mmol, 2.0 equiv). The resulting mixture was cooled to 0°C in an ice/water bath. Tf_2O (3390 mg, 2.10 mL, 15.0 mmol, 1.5 equiv) was added dropwise over ca. 5 minutes. The reaction mixture was warmed to room temperature and stirred for 5 hours. The resulting brown reaction was then quenched by water (15 mL). The layers were separated, and the aqueous layer was extracted with DCM (3 × 20 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel, to afford the **S2** as a white solid.

Under nitrogen atmosphere, to a 25 mL flamed dried round bottom charged with **S2** (1 mmol, 1.0 equiv), Potassium Vinyltrifluoroborate (308 mg, 2.0 mmol, 2.0 equiv), $PdCl_2$ (3.5 mg, 0.02 mmol, 0.02 equiv), PPh_3 (15.7 mg, 0.06 mmol, 0.06 equiv), and Cs_2CO_3 (975 mg, 3 mmol, 3.0 equiv), was added THF at 80 °C for 22 h. The reaction mixture was then diluted with water, and the aqueous layer was extracted with ethyl acetate (3 × 10 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated in vacuo. Chromatography of the residue on silica gel provided the corresponding product **1s**.

Synthesis of S3

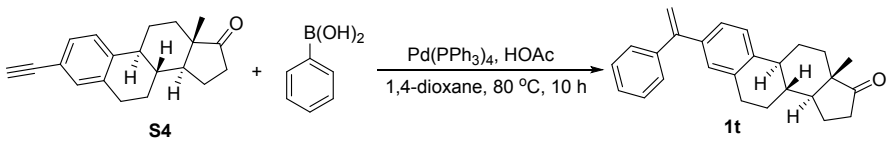
A mixture of **S2** (1610 mg, 4.0 mmol, 1.00 equiv), ethynyltrimethylsilane (0.85 mL, 6.0 mmol,1.5 equiv), Et_3N (3.0 mL), and $Pd(PPh_3)_2Cl_2$ (84 mg, 0.12 mmol, 0.03 equiv)

in 15 mL DMF was stirred at 90 °C for 4 h under nitrogen. The reaction mixture was then diluted with water, extracted with 1:1 petroleum ether/ether, washed with water until neutral, and dried (Na_2SO_4), after filtration the filtrate was evaporated. Chromatography of the residue on silica gel provided the corresponding product **S3**.

Synthesis of S4

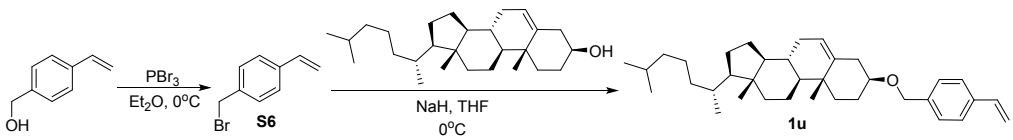
To **S3** (1160 mg, 3.30 mmol, 1.00 equiv) a solution of K_2CO_3 (520 mg, 4.95 mmol, 1.5equiv) in 10 mL MeOH was added and the mixture was stirred at room temperature, until TLC analysis showed that **S3** was completely consumed. The reaction mixture was filtered through a short plug of silica gel. The filtration was concentrated and then purified by flash chromatography to give the corresponding product **S4**.

Synthesis of 1t



Under nitrogen atmosphere, to a 25 mL flamed dried round bottom charged with **S4** (278 mg, 1 mmol, 1.0 equiv), Arylboronic acid (2.0 mmol, 2.0 equiv), and $Pd(PPh_3)_4$ (33 mg, 0.03 mmol, 0.03 equiv) was added 1,4-dioxane (8.0 mL) and HOAc (0.10-0.15 equiv), then stirred at 80 °C for 10 h. The reaction mixture was then diluted with water, and the aqueous layer was extracted with ethyl acetate (3 × 10 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated in vacuo. Chromatography of the residue on silica gel provided the corresponding product **1t**.

Synthesis of 1u



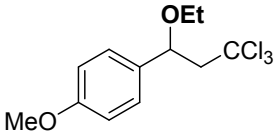
PBr_3 (940 mg, 0.35 equiv) was slowly added to a solution of the corresponding alcohol (1340 mg, 10 mmol, 1.0 equiv) in Et_2O (20 mL) at 0°C , and the mixture was stirred for 2 h at 0°C. After the reaction was completed, the mixture was quenched

with aqueous sodium bicarbonate slowly. The organic layer was extracted with Et_2O, washed with aqueous sodium bicarbonate and brine. The combined organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure to give the target product **S6** which was used without further purification.

Under nitrogen atmosphere, to a 25 mL flamed dried round bottom charged with 1N (196 mg, 1 mmol, 1.0 equiv), Cholesterol (772 mg, 2.0 mmol, 2.0 equiv), and THF (15 ml), NaH (36 mg, 1.5 mmol, 1.5 equiv) was added slowly at 0 ^oC for 12 h. The reaction mixture was then diluted with water, and the aqueous layer was extracted with ethyl acetate (3 10 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel, to afford the **1u** as a white solid.

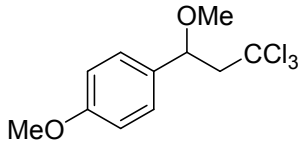
(C) Analytical data

Methoxy-4-(3,3,3-trichloro-1-ethoxypropyl)benzene (4aaa):



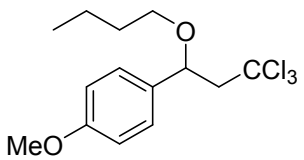
Yield: 70%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 4.68-4.66 (m, 1H), 3.81 (s, 3H), 3.40-3.38 (m, 2H), 3.29-3.25 (m, 1H), 2.97-2.93 (m, 1H), 1.18 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4, 133.4, 127.7, 114.0, 97.6, 78.7, 64.3, 62.1, 55.3, 15.2; LRMS (EI, 70eV) *m/z* (%): 298 (M^++2, 4), 296 (M^+, 4), 165 (100), 137 (61), 109 (24); HRMS *m/z* (ESI) calcd for $C_{12}H_{16}O_2Cl_3$ ($[M+H]^+$) 297.0210, found 297.0217.

1-Methoxy-4-(3,3,3-trichloro-1-methoxypropyl)benzene (4aab)



Yield: 82%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.26 (m, 2H), 6.92-6.90 (m, 2H), 4.56-4.54 (m, 1H), 3.82 (s, 3H), 3.29-3.25 (m, 1H), 3.23 (s, 3H), 2.99-2.96 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 132.6, 127.9, 127.8, 114.1, 114.0, 97.4, 80.6, 62.1, 56.4, 55.3; LRMS (EI, 70eV) *m/z* (%): 284 (M^+ + 2, 3), 282 (3), 151 (100), 135 (16), 108 (6); HRMS *m/z* (ESI) calcd for $C_{11}H_{14}O_2Cl_3$ ($[M+H]^+$) 283.0054, found 283.0058.

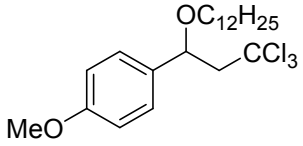
1-(1-Butoxy-3,3,3-trichloropropyl)-4-methoxybenzene (4aac)



Yield: 65%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 4.66-4.64 (m, 1H), 3.81 (s, 3H), 3.32-3.29 (m, 2H), 3.28-3.23 (m, 1H), 2.96-2.92 (m, 1H), 1.55-1.51 (m, 2H), 1.40-1.32 (m, 2H), 0.87 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ

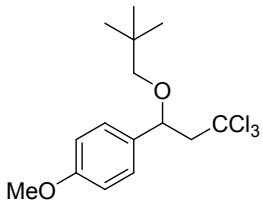
159.3, 133.4, 127.8, 114.0, 97.6, 78.9, 68.6, 62.2, 55.3, 31.8, 19.4, 13.8; LRMS (EI, 70eV) *m/z* (%): 326 (M^+ + 2, 2), 324 (2), 193 (52), 137 (100), 109 (17); HRMS *m/z* (ESI) calcd for $C_{14}H_{20}O_2Cl_3$ ($[M+H]^+$) 325.0523, found 325.0522.

1-Methoxy-4-(3,3,3-trichloro-1-(dodecyloxy)propyl)benzene (4aad)



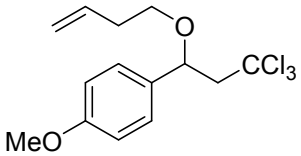
Yield: 54%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 4.65-4.63 (m, 1H), 3.82 (s, 3H), 3.31-3.29 (m, 2H), 3.28-3.25 (m, 1H), 2.96-2.92 (m, 1H), 1.55-1.52 (m, 2H), 1.30-1.24 (m, 18H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 133.4, 127.8, 114.0, 97.6, 79.0, 69.0, 62.2, 55.3, 31.9, 29.7, 29.6 (3H), 29.4, 29.3, 29.2, 26.2, 22.7, 14.1; LRMS (EI, 70eV) *m/z* (%): 438 (M^+ + 2, 2), 436 (2), 305 (56), 137 (100), 109 (7); HRMS *m/z* (ESI) calcd for $C_{22}H_{36}O_2Cl_3$ ($[M+H]^+$) 437.1775, found 437.1779.

1-Methoxy-4-(3,3,3-trichloro-1-(neopentyloxy)propyl)benzene (4aae)



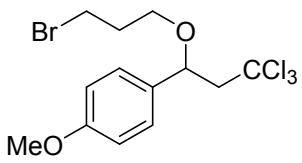
Yield: 56%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 4.63-4.61 (m, 1H), 3.81 (s, 3H), 3.30-3.25 (m, 1H), 2.94 (s, 2H), 2.93-2.90 (m, 1H), 0.89 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 133.5, 127.7, 114.0, 97.6, 79.2, 79.1, 62.4, 55.2, 31.9, 26.8; LRMS (EI, 70eV) *m/z* (%): 340 (M^+ + 2, 3), 338 (3), 207 (38), 155 (28), 137 (100); HRMS *m/z* (ESI) calcd for $C_{15}H_{22}O_2Cl_3$ ($[M+H]^+$) 339.0680, found 339.0685.

1-(1-(But-3-en-1-yloxy)-3,3,3-trichloropropyl)-4-methoxybenzene (4aaf)



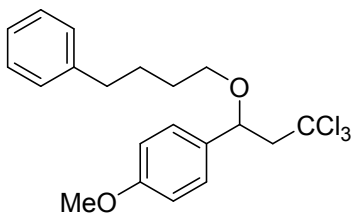
Yield: 53%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.26 (m, 2H), 6.91-6.89 (m, 2H), 5.82-5.77 (m, 1H), 5.06-4.99 (m, 2H), 4.68-4.66 (m, 1H), 3.82 (s, 3H), 3.38-3.35 (m, 2H), 3.30-3.26 (m, 1H), 2.97-2.93 (m, 1H), 2.32-2.30 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4, 135.3, 133.2, 127.8, 116.2, 114.1, 97.5, 79.1, 68.3, 62.1, 55.3, 34.2; LRMS (EI, 70eV) *m/z* (%): 324 (M^+ + 2, 5), 322 (5), 191 (100), 161 (30), 137 (49); HRMS *m/z* (ESI) calcd for $C_{14}H_{18}O_2Cl_3$ ($[M+H]^+$) 323.0367, found 323.0371.

1-(1-(3-Bromopropoxy)-3,3,3-trichloropropyl)-4-methoxybenzene (4aag)



Yield: 51%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.0 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 4.68-4.67 (m, 1H), 3.82 (s, 3H), 3.55-3.50 (m, 2H), 3.43 (t, *J* = 6.0 Hz, 2H), 3.28-3.24 (m, 1H), 2.96-2.93 (m, 1H), 2.09-2.04 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 132.8, 127.8, 114.2, 97.4, 79.2, 66.1, 62.0, 55.3, 32.9, 30.7; LRMS (EI, 70eV) *m/z* (%): 392 (M^+ + 4, 2), 390 (M^+ + 2, 4), 388(2), 257 (68), 137 (100), 109(30); HRMS *m/z* (ESI) calcd for $C_{13}H_{17}O_2Cl_3Br$ ($[M+H]^+$) 388.9472, found 388.9473.

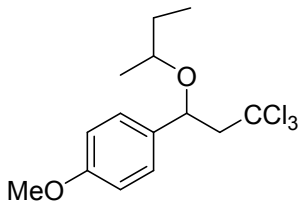
1-Methoxy-4-(3,3,3-trichloro-1-(4-phenylbutoxy)propyl)benzene (4aah)



Yield: 67%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25-7.21 (m, 4H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 4.65-4.63 (m, 1H), 3.79 (s, 3H), 3.32 (t, *J* = 6.5 Hz, 2H), 3.29-3.24 (m, 1H), 2.96-2.92 (m, 1H), 2.57 (t, *J* = 7.5 Hz, 2H), 1.69-1.64 (m, 2H), 1.61-1.56 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ

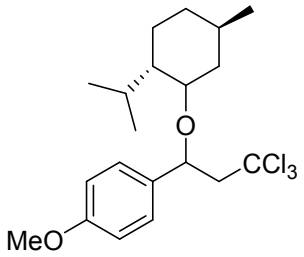
159.4, 142.4, 133.3, 128.4, 128.2, 127.8, 125.6, 114.0, 97.6, 79.0, 68.6, 62.1, 55.2, 35.6, 29.3, 28.0; LRMS (EI, 70eV) *m/z* (%): 402 (M^+ + 2, 1), 400 (1), 253 (17), 137 (82), 91 (100); HRMS *m/z* (ESI) calcd for $C_{20}H_{24}O_2Cl_3$ ($[M+H]^+$) 401.0836, found 401.0840.

1-(1-(Sec-butoxy)-3,3,3-trichloropropyl)-4-methoxybenzene (4aai)



Yield: 77%, Yellow oil; 1H NMR (500 MHz, CDCl3) δ 7.28-7.25 (m, 2H), 6.91-6.88 (m, 2H), 4.64-4.62 (m, 1H), 3.81 (s, 3H), 3.30 – 3.25 (m, 1H), 3.08-3.06 (m, 2H), 2.96-2.92 (m, 1H), 1.86-1.80 (m, 1H), 0.91-0.86 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 133.4, 127.8, 114.0, 97.6, 79.1, 75.7, 62.3, 55.3, 28.6, 19.5(2H); LRMS (EI, 70eV) *m/z* (%): 326 (M^+ + 2, 4), 324 (4), 253 (5), 193 (37), 137 (100); HRMS *m/z* (ESI) calcd for $C_{14}H_{20}O_2Cl_3$ ($[M+H]^+$) 325.0523, found 325.0521.

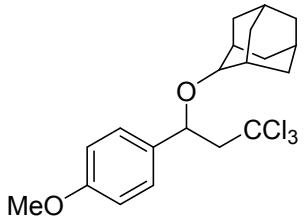
1-Methoxy-4-(3,3,3-trichloro-1-(((2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)propyl)benzene (4aaj)



Yield: 44%, Yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.28-7.26 (m, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 4.88-4.86 (m, 1H), 3.81 (s, 3H), 3.33-3.29 (m, 1H), 3.04-3.00 (m, 1H), 2.92-2.87 (m, 1H), 2.24-2.21 (m, 2H), 1.55-1.52 (m, 1H), 1.21-1.17 (m, 2H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.88 (s, 1H), 0.84 (d, *J* = 7.0 Hz, 3H), 0.81-0.76 (m, 2H), 0.26 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4, 133.3, 128.9, 113.8, 97.6, 74.3, 74.2, 61.9, 55.3, 48.4, 39.4, 34.5, 31.4, 24.8, 22.8, 22.5, 21.3,

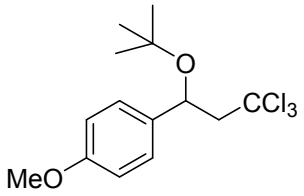
15.5; LRMS (EI, 70eV) *m/z* (%): 408 (M^+ + 2, 2), 406 (2), 275 (17), 253 (10), 137 (100); HRMS *m/z* (ESI) calcd for $C_{20}H_{30}O_2Cl_3$ ($[M+H]^+$) 407.1306, found 407.1302.

(1r,3r,5r,7r)-2-(3,3,3-Trichloro-1-(4-methoxyphenyl)propoxy)adamantane (4aak)



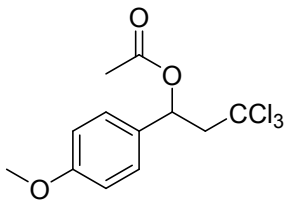
Yield: 56%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 2H), 4.88-4.87 (m, 1H), 3.81 (s, 3H), 3.35 (s, 1H), 3.33-3.29 (m, 1H), 2.97-2.93 (m, 1H), 2.23 (d, *J* = 12.0 Hz, 1H), 2.11-2.08 (m, 2H), 1.77-1.66 (m, 9H), 1.40 (d, *J* = 12.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2, 134.1, 128.0, 113.9, 97.6, 79.5, 76.0, 62.5, 55.2, 37.6, 36.7, 36.4, 33.3, 31.6, 31.5, 30.4, 27.4 (2C); LRMS (EI, 70eV) *m/z* (%): 404 (M^+ + 2, 3), 402 (3), 271 (63), 155 (32), 135 (100); HRMS *m/z* (ESI) calcd for $C_{20}H_{26}O_2Cl_3$ ($[M+H]^+$) 403.0993, found 403.0997.

1-(1-(*Tert*-butoxy)-3,3,3-trichloropropyl)-4-methoxybenzene (4aal)



Yield: 37%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 5.00-4.98 (m, 1H), 3.80 (s, 3H), 3.22-3.17 (m, 1H), 2.88-2.84 (m, 1H), 1.13 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 137.0, 127.6, 113.8, 97.5, 75.2, 72.1, 63.1, 55.3, 28.9; LRMS (EI, 70eV) *m/z* (%): 326 (M^+ + 2, 6), 324 (6), 193 (24), 137 (100), 109 (35); HRMS *m/z* (ESI) calcd for $C_{14}H_{20}O_2Cl_3$ ($[M+H]^+$) 325.0523, found 325.0524.

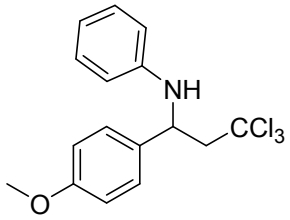
3,3,3-Trichloro-1-(4-methoxyphenyl)propyl acetate (4aam):



Yield: 66%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 9.0 Hz, 2H), 6.26-6.24 (m, 1H), 3.80 (s, 3H), 3.46-3.41 (m, 1H), 3.11-3.07 (m, 1H), 2.07

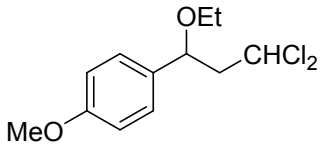
(s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.6, 159.7, 131.4, 127.9, 114.1, 96.5, 72.2, 59.7, 55.3, 21.2; LRMS (EI, 70eV) *m/z* (%): 312 (M^+ + 2, 6), 310 (6), 215 (12), 179 (18), 137 (100); HRMS *m/z* (ESI) calcd for $C_{12}H_{14}O_3Cl_3$ ($[M+H]^+$) 311.0003, found 311.0008.

***N*-(3,3,3-trichloro-1-(4-methoxyphenyl)propyl)aniline (4aan):**



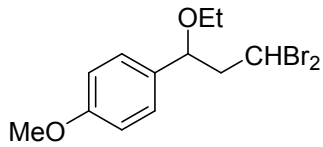
Yield: 31%, Yellow oil;^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.5 Hz, 2H), 7.12 (t, *J* = 7.5 Hz, 2H), 6.89 (d, *J* = 9.0 Hz, 2H), 6.70 (t, *J* = 7.5 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 2H), 4.86-4.84 (m, 1H), 4.31 (s, 1H), 3.79 (s, 3H), 3.24-3.14 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 146.5, 134.4, 129.2, 127.5, 118.0, 114.4, 113.6, 97.4, 61.6, 56.4, 55.3; LRMS (EI, 70eV) *m/z* (%): 345 (M^+ + 2, 16), 343 (16), 212 (100), 197 (21), 168 (27); HRMS *m/z* (ESI) calcd for $C_{16}H_{17}NOCl_3$ ($[M+H]^+$) 344.0370, found 344.0373.

1-(3,3-Dichloro-1-ethoxypropyl)-4-methoxybenzene (4aba)



Yield: 70%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 5.91-5.88 (m, 1H), 4.44-4.42 (m, 1H), 3.81 (s, 3H), 3.39-3.27 (m, 2H), 2.66-2.61 (m, 1H), 2.39-2.33 (m, 1H), 1.15 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4, 132.6, 127.7, 114.0, 77.9, 70.9, 64.0, 55.3, 52.0, 15.2; LRMS (EI, 70eV) *m/z* (%): 264 (M^+ + 2, 6), 262 (6), 165 (100), 137 (48), 109 (21); HRMS *m/z* (ESI) calcd for $C_{12}H_{17}O_2Cl_2$ ($[M+H]^+$) 263.0600, found 263.0599.p

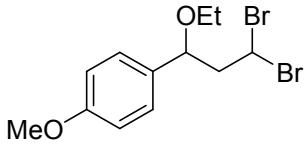
1-(3,3-Dibromo-1-ethoxypropyl)-4-methoxybenzene (4afa:4afa' = 1:9)



Yield: 74%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ

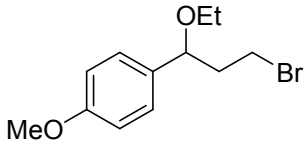
7.23 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 5.81-5.79 (m, 1H), 4.41-4.39 (m, 1H), 3.80 (s, 3H), 3.41-3.31 (m, 2H), 2.84-2.79 (m, 1H), 2.58-2.52 (m, 1H), 1.16 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4, 132.5, 127.8, 127.7,114.0, 81.0, 79.2, 66.3, 64.3, 64.0, 55.2, 53.7, 43.0, 15.2; LRMS (EI, 70eV) *m/z* (%): 354 (M^+ + 4, 1), 352 (M^+ + 2, 3), 350 (1), 165 (100), 137 (48), 109 (22); HRMS *m/z* (ESI) calcd for $C_{12}H_{17}O_2Br_2$ ($[M+H]^+$) 350.9590, found 350.9587.

1-(3,3-Dibromo-1-ethoxypropyl)-4-methoxybenzene (4afa')



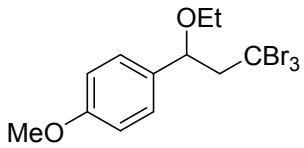
Yield: 34%, White oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 5.81-5.79 (m, 1H), 4.42-4.39 (m, 1H), 3.81 (s, 3H), 3.40 – 3.28 (m, 2H), 2.85-2.79 (m, 1H), 2.58-2.53 (m, 1H), 1.16 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4, 132.5, 127.7, 114.0, 79.2, 64.1, 55.3, 53.7, 43.0, 15.2; LRMS (EI, 70eV) *m/z* (%): 352 (M^+ + 2, 1), 350 (1), 165 (100), 137 (49), 109 (23); HRMS *m/z* (ESI) calcd for $C_{12}H_{17}O_2Br_2$ ($[M+H]^+$) 350.9590, found 350.9595.

1-(3-Bromo-1-ethoxypropyl)-4-methoxybenzene (4aga')



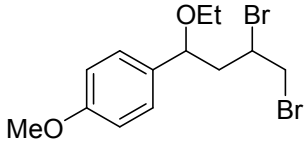
Yield: 34%, White oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 9,0 Hz, 2H), 4.42-4.39 (m, 1H), 3.81 (s, 3H), 3.42-3.39 (m, 1H), 3.37-3.30 (m, 1H), 3.36 – 3.28 (m, 2H), 2.34-2.27 (m, 1H), 2.08-2.04 (m, 1H), 1.17 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2, 133.7, 127.7, 127.3, 113.9, 78.9, 64.0, 55.2, 41.1, 30.5, 15.3; LRMS (EI, 70eV) *m/z* (%): 274 (M^+ + 2, 3), 272 (3), 165 (100), 137 (62), 109 (28); HRMS *m/z* (ESI) calcd for $C_{12}H_{18}O_2Br$ ($[M+H]^+$) 273.0485, found 273.0489.

1-Methoxy-4-(3,3,3-tribromo-1-ethoxypropyl)benzene (4afa)



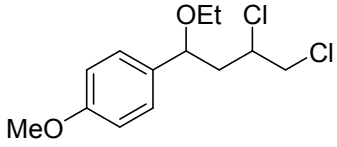
Yield: 77%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 4.59-4.57 (m, 1H), 3.81 (s, 3H), 3.64-3.60 (m, 1H), 3.43-3.40 (m, 2H), 3.35-3.31 (m, 1H), 1.20 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 133.3 127.8, 114.0, 81.0, 66.3, 64.3, 55.3, 37.2, 15.3; LRMS (EI, 70eV) *m/z* (%): 432 (M^+ + 4, 3), 430 (M^+ + 2, 3), 428 (1), 165 (100), 137 (48), 109 (22); HRMS *m/z* (ESI) calcd for $C_{12}H_{16}O_2Br_3$ ($[M+H]^+$) 428.8695, found 428.8691.

1-(3,4-Dibromo-1-ethoxybutyl)-4-methoxybenzene (4aia)



Yield: 41%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26-7.23 (m, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 4.58 (d, *J* = 8.5 Hz, 1H), 3.81 (s, 3H), 3.36-3.33 (m, 2H), 2.91-2.86 (m, 1H), 2.79-2.76 (m, 1H), 2.62 (s, 3H), 1.16 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2, 133.8, 127.6, 114.0, 80.5, 66.9, 64.0, 60.5, 55.3, 41.7, 15.3; LRMS (EI, 70eV) *m/z* (%): 368 (M^+ + 4, 1), 366 (M^+ + 2, 3), 364 (1), 165 (100), 137 (48), 109 (18); HRMS *m/z* (ESI) calcd for $C_{13}H_{18}O_2Br_2$ ($[M+H]^+$) 364.9746, found 364.9749.

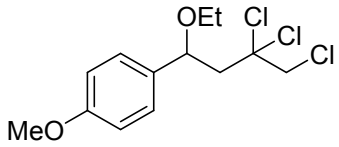
1-(3,4-Dichloro-1-ethoxybutyl)-4-methoxybenzene (4aja)



Yield: 58%, White oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 4.52-4.50 (m, 1H), 3.81 (s, 3H), 3.78-3.70 (m, 2H), 3.44-3.41 (m, 1H), 3.34-3.30 (m, 2H), 2.31-2.27 (m, 1H), 1.84-1.81 (m, 1H), 1.17 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2, 134.0, 128.0, 127.5, 127.3, 114.0, 113.9, 113.7, 77.5, 64.2, 63.8, 58.5,

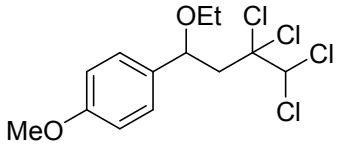
58.1, 55.3, 55.2, 49.1, 48.6, 44.6, 43.1, 15.3, 15.2; LRMS (EI, 70eV) *m/z* (%): 278 (M^+ + 2, 3), 276 (5), 165 (100), 137 (55), 109 (24); HRMS *m/z* (ESI) calcd for $C_{13}H_{19}O_2Cl_2$ ($[M+H]^+$) 277.0757, found 277.00761.

1-Methoxy-4-(3,4,4-trichloro-1-ethoxybutyl)benzene (4aka)



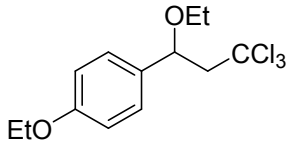
Yield: 67%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26-7.23 (m, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 4.63-4.60 (m, 1H), 4.29 (d, *J* = 12.0 Hz, 1H), 4.11 (d, *J* = 12.0 Hz, 1H), 3.81 (s, 3H), 3.37-3.26 (m, 2H), 2.95-2.91 (m, 1H), 2.52-2.49 (m, 1H), 1.16 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4, 133.1, 127.7, 114.0, 89.8, 78.6, 63.9, 55.3, 54.8, 52.1, 15.1; LRMS (EI, 70eV) *m/z* (%): 312 (M^+ + 2, 3), 310 (3), 165 (100), 137 (51), 109 (32); HRMS *m/z* (ESI) calcd for $C_{13}H_{18}O_2Cl_3$ ($[M+H]^+$) 311.0367, found 311.0363.

1-Methoxy-4-(3,3,4,4-tetrachloro-1-ethoxybutyl)benzene (4ala)



Yield: 74%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 6.0 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 6.47 (s, 1H), 4.70-4.67 (m, 1H), 3.81 (s, 3H), 3.37-3.26 (m, 2H), 3.11-3.08 (m, 1H), 2.58-2.55 (m, 1H), 1.17 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 132.5, 127.8, 114.1, 93.1, 78.5, 78.3, 64.0, 55.3, 52.0, 15.1; LRMS (EI, 70eV) *m/z* (%):346 (M^+ + 2, 3), 344 (2), 165 (100), 137 (51), 109 (22); HRMS *m/z* (ESI) calcd for $C_{13}H_{17}O_2Cl_4$ ($[M+H]^+$) 344.9977, found 344.9982.

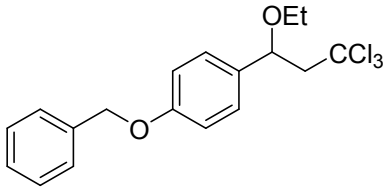
1-Ethoxy-4-(3,3,3-trichloro-1-ethoxypropyl)benzene (4baa)



Yield: 77%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27-7.25 (m, 2H), 6.90-6.88 (m, 2H), 4.67-4.65 (m, 1H), 4.05-

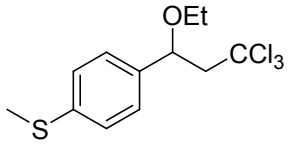
4.01 (m, 2H), 3.40-3.37 (m, 2H), 3.29-3.25 (m, 1H), 2.97-2.93 (m, 1H), 1.42 (t, *J* = 7.0 Hz, 3H), 1.18 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.8, 133.2, 127.7, 114.5, 97.6, 78.8, 64.2, 63.4, 62.1, 15.2, 14.8; LRMS (EI, 70eV) *m/z* (%): 312 (M^+ + 2, 20), 310 (20), 179 (100), 151 (80), 123 (74); HRMS *m/z* (ESI) calcd for $C_{13}H_{18}O_2Cl_3$ ($[M+H]^+$) 311.0367, found 311.0371.

1-(Benzyloxy)-4-(3,3,3-trichloro-1-ethoxypropyl)benzene (4caa)



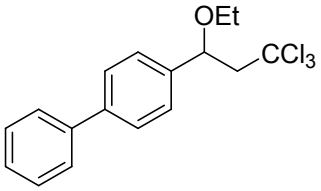
Yield: 85%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.0 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 9.0 Hz, 2H), 5.06 (s, 2H), 4.68-4.66 (m, 1H), 3.40-3.38 (m, 2H), 3.29-3.24 (m, 1H), 2.96-2.93 (m, 1H), 1.18 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.6, 136.8, 133.6, 128.6, 128.0, 127.8, 127.5, 114.9, 97.5, 78.7, 70.0, 64.3, 62.1, 15.2; LRMS (EI, 70eV) *m/z* (%): 374 (M^+ + 2, 3), 372 (3), 285 (17), 241 (73), 91 (100); HRMS *m/z* (ESI) calcd for $C_{18}H_{20}O_2Cl_3$ ($[M+H]^+$) 373.0523, found 373.0524.

Methyl(4-(3,3,3-trichloro-1-ethoxypropyl)phenyl)sulfane (4daa)



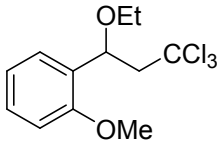
Yield: 51%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.24 (m, 4H), 4.69-4.67 (m, 1H), 3.42-3.38 (m, 2H), 3.29-3.24 (m, 1H), 2.96-2.92 (m, 1H), 2.49 (s, 3H), 1.19 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.3, 138.1, 127.0, 126.6, 97.4, 78.8, 64.5, 62.0, 15.7, 15.2; LRMS (EI, 70eV) *m/z* (%): 314 (M^+ + 2, 5), 312 (5), 181 (100), 153 (50), 109 (21); HRMS *m/z* (ESI) calcd for $C_{12}H_{16}OSCl_3$ ($[M+H]^+$) 312.9982, found 312.9979.

4-(3,3,3-Trichloro-1-ethoxypropyl)-1,1'-biphenyl (4eaa)



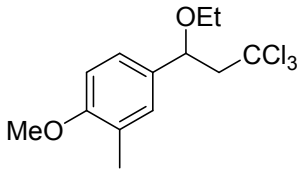
Yield: 52%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61-7.58 (m, 4H), 7.46-7.43 (m, 4H), 7.35 (t, *J* = 7.5 Hz, 1H), 4.79-4.77 (m, 1H), 3.48-3.44 (m, 2H), 3.34-3.29 (m, 1H), 3.02-2.99 (m, 1H), 1.22 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.0, 140.6, 140.4, 128.8, 127.4 (2H), 127.1, 127.0, 97.5, 79.0, 64.6, 62.2, 15.2; LRMS (EI, 70eV) *m/z* (%): 344 (M^+ + 2, 4), 342 (4), 211 (100), 183 (42), 155 (29); HRMS *m/z* (ESI) calcd for $C_{17}H_{18}OCl_3$ ($[M+H]^+$) 343.0418, found 348.0414.

1-Methoxy-2-(3,3,3-trichloro-1-ethoxypropyl)benzene (4gaa)



Yield: 68%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 5.14 (d, *J* = 7.0 Hz, 1H), 3.85 (s, 3H), 3.47-3.44 (m, 2H), 3.12-3.08 (m, 1H), 2.98-2.95 (m, 1H), 1.22 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.5, 129.3, 128.8, 126.7, 120.7, 110.4, 98.0, 73.8, 64.8, 60.3, 55.2, 15.3; LRMS (EI, 70eV) *m/z* (%): 298(M^+ + 2, 12), 296 (12), 166 (35), 137 (88), 107 (100); HRMS *m/z* (ESI) calcd for $C_{12}H_{17}O_2Cl_3$ ($[M+H]^+$) 297.0210, found 297.0209.

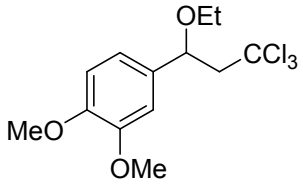
1-Methoxy-2-methyl-4-(3,3,3-trichloro-1-ethoxypropyl)benzene (4haa)



Yield: 68%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 – 7.12 (m, 2H), 6.81 (d, *J* = 8.5 Hz, 1H), 4.65-4.63 (m, 1H), 3.83 (s, 3H), 3.42-3.36 (m, 2H), 3.29-3.24 (m, 1H), 2.97-2.93 (m, 1H), 2.23 (s, 3H), 1.19 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.5, 132.8, 128.8, 127.0, 125.0, 109.7, 97.6, 78.8, 64.2, 62.2, 55.3, 16.3, 15.2;

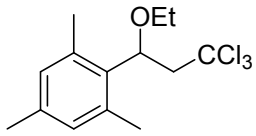
LRMS (EI, 70eV) *m/z* (%): 312 (M^+ + 2, 9), 310 (9), 197 (100), 151 (97), 123 (90); HRMS *m/z* (ESI) calcd for $C_{13}H_{18}OCl_3$ ($[M+H]^+$) 311.0367, found 311.0370.

1,2-Dimethoxy-4-(3,3,3-trichloro-1-ethoxypropyl)benzene (4iaa)



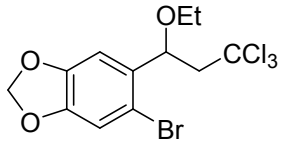
Yield: 67%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (t, *J* = 8.0 Hz, 1H), 7.03-7.01 (m, 1H), 6.89-6.87 (m, 1H), 5.12-5.10 (m, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.44 (m, 2H), 3.22 (m, 1H), 3.00 (m, 1H), 1.20 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.6, 146.4, 134.8, 124.2, 118.8, 111.8, 97.8, 73.9, 64.7, 60.8, 60.7, 55.7, 15.2; LRMS (EI, 70eV) *m/z* (%): 328 (M^+ + 2, 30), 326 (30), 196 (68), 167 (100), 139 (97); HRMS *m/z* (ESI) calcd for $C_{13}H_{18}O_3Cl_3$ ($[M+H]^+$) 327.0316, found 327.0311.

1,3,5-Trimethyl-2-(3,3,3-trichloro-1-ethoxypropyl)benzene (4jaa)



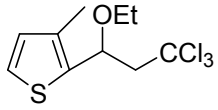
Yield: 56%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.86 (s, 1H), 6.81 (s, 1H), 5.16-5.14 (m, 1H), 3.55-3.51 (m, 1H), 3.39-3.31 (m, 2H), 3.00-2.97 (m, 1H), 2.46 (s, 3H), 2.41 (s, 3H), 2.26 (s, 3H), 1.16 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.2 (2H), 136.2, 133.7, 131.2, 129.0, 98.4, 75.3, 63.9, 60.1, 20.8 (2H), 20.4, 15.3; LRMS (EI, 70eV) *m/z* (%): 310 (M^+ + 2, 9), 308 (9), 177 (100), 149 (69), 121 (74); HRMS *m/z* (ESI) calcd for $C_{14}H_{20}OCl_3$ ($[M+H]^+$) 309.0574, found 309.0570.

5-(3,3,3-Trichloro-1-ethoxypropyl)benzo[d][1,3]dioxole (4kaa)



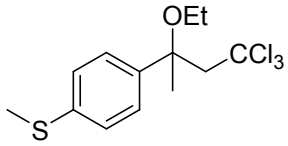
Yield: 77%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00 (d, *J* = 12.0 Hz, 2H), 6.00 (d, *J* = 8.5 Hz, 2H), 5.14-5.12 (m, 1H), 3.44-3.41 (m, 2H), 3.09-3.04 (m, 1H), 2.93-2.90 (m, 1H), 1.20 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.1 (2H), 133.6, 112.9, 112.6, 107.5, 101.9, 97.1, 77.7, 64.7, 60.1, 15.2; LRMS (EI, 70eV) *m/z* (%): 392 (M^+ + 4, 9), 390 (M^+ + 2, 18), 388 (9), 257 (100), 229 (86), 122 (90); HRMS *m/z* (ESI) calcd for $C_{12}H_{13}O_3BrCl_3$ ($[M+H]^+$) 388.9108, found 388.9105.

3-Methyl-2-(3,3,3-trichloro-1-ethoxypropyl)thiophene (4laa):



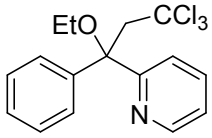
Yield: 57%, Yellow oil; 1H NMR (500 MHz, CDCl3) δ 7.19 (d, *J* = 5.0 Hz, 1H), 6.79 (d, *J* = 5.0 Hz, 1H), 5.05-5.03 (m, 1H), 3.52-3.41 (m, 2H), 3.36-3.32 (m, 1H), 3.04-3.01 (m, 1H), 2.26 (s, 3H), 1.19 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.7, 134.4, 130.0, 124.0, 97.1, 73.1, 64.4, 61.8, 15.1, 13.9; LRMS (EI, 70eV) *m/z* (%): 288 (M^+ + 2, 6), 286 (6), 155 (70), 127 (100), 99 (35); HRMS *m/z* (ESI) calcd for $C_{10}H_{14}SOCl_3$ ($[M+H]^+$) 286.9825, found 286.9828.

Methyl(4-(4,4,4-trichloro-2-ethoxybutan-2-yl)phenyl)sulfane (4naa):



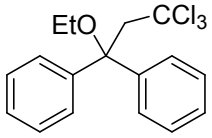
Yield: 66%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 3.39-3.36 (M, 1H), 3.30-3.17 (m, 2H), 3.11-3.08 (m, 1H), 2.49 (s, 3H), 1.86 (s, 3H), 1.16 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.8, 137.7, 127.0, 126.1, 96.2, 78.4, 64.9, 57.2, 22.1, 15.5, 15.5; LRMS (EI, 70eV) *m/z* (%): 328 (M^+ + 2, 3), 326 (3), 195 (100), 167 (34), 151 (27); HRMS *m/z* (ESI) calcd for $C_{13}H_{18}OSCl_3$ ($[M+H]^+$) 327.0138, found 327.0841.

2-(3,3,3-Trichloro-1-ethoxy-1-phenylpropyl)pyridine (4oaa):



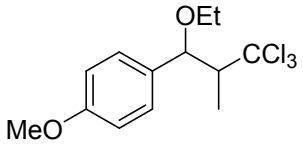
Yield: 46%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51-8.50 (m, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 6.5 Hz, 1H), 4.22-4.10 (m, 2H), 3.50 – 3.44 (m, 1H), 3.29-3.23 (m, 1H), 1.24 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3, 147.8, 142.9, 136.6, 128.0, 127.2, 127.0, 122.2, 122.1, 96.9, 82.9, 58.5, 54.2, 15.0; LRMS (EI, 70eV) *m/z* (%): 345 (M^+ + 2, 2), 343 (2), 227 (100), 182 (50), 105 (75); HRMS *m/z* (ESI) calcd for $C_{16}H_{17}ONCl_3$ ($[M+H]^+$) 344.0370, found 344.0373.

(3,3,3-Trichloro-1-ethoxypropane-1,1-diyl)dibenzene (4paa):



Yield: 65%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.0 Hz, 4H), 7.29 (t, *J* = 7.5 Hz, 4H), 7.22 (t, *J* = 7.0 Hz, 2H), 3.86 (s, 2H), 3.28-3.24 (m, 2H), 1.19 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 127.9, 127.4, 127.2, 96.5, 81.5, 58.1, 55.6, 15.0; LRMS (EI, 70eV) *m/z* (%): 344 (M^+ + 2, 4), 342 (4), 211 (93), 183 (36), 105 (100); HRMS *m/z* (ESI) calcd for $C_{17}H_{18}OCl_3$ ($[M+H]^+$) 343.0418, found 342.0414.

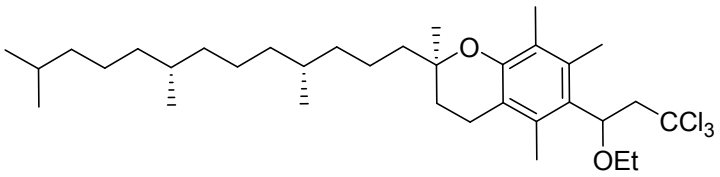
1-Methoxy-4-(3,3,3-trichloro-1-ethoxy-2-methylpropyl)benzene (4qaa):



Yield: 67%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 5.06 (s, 1H), 3.81 (s, 3H), 3.50-3.38 (m, 2H), 2.63-2.59 (m, 1H), 1.28 (d, *J* = 6.5 Hz, 3H), 1.19 (t, *J*

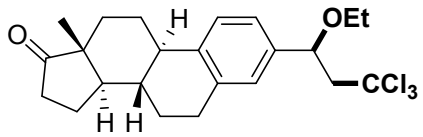
= 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9, 133.6, 127.1, 113.8, 104.6, 79.3, 65.1, 61.4, 55.3, 15.3, 9.9; LRMS (EI, 70eV) *m/z* (%): 312 (M^+ + 2, 4), 310 (4), 165 (67), 137 (100), 109 (45); HRMS *m/z* (ESI) calcd for $C_{13}H_{18}O_2Cl_3$ ($[M+H]^+$) 311.0367, found 311.0363.

(R)-2,5,7,8-Tetramethyl-6-((R)-3,3,3-trichloro-1-ethoxypropyl)-2-((4R,8R)-4,8,12-trimethyltridecyl)chromane (4raa) :



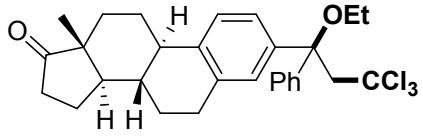
Yield: 58%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.29-5.25 (m, 1H), 3.57-3.52 (m, 1H), 3.39-3.32 (m, 2H), 3.04-3.01 (m, 1H), 2.62-2.59 (m, 2H), 2.37-2.34 (m, 3H), 2.32-2.28 (m, 3H), 2.13-2.10 (m, 3H), 1.85-1.75 (m, 2H), 1.58-1.50 (m, 4H), 1.40-1.34 (m, 4H), 1.28-1.23 (m, 11H), 1.16-1.13 (m, 6H), 0.87-0.84 (m, 14H); 13C NMR (125 MHz, $CDCl_3$) δ 151.1, 134.6, 133.5, 133.4, 132.2, 127.8, 124.0, 121.8, 118.6, 116.3, 98.7, 75.6, 75.5, 75.0, 74.8, 63.6, 61.2, 61.0, 40.3, 39.4, 37.5, 37.4, 37.3, 32.8, 32.7, 31.4, 31.3, 28.0, 24.8, 24.4, 24.0, 23.8, 23.7, 22.7, 22.6, 21.4, 21.0, 20.7, 19.8, 19.7, 16.6, 16.2, 15.7, 15.4, 15.3, 15.2, 12.3, 11.6.; HRMS *m/z* (ESI) calcd for $C_{34}H_{58}O_2Cl_3$ ($[M+H]^+$) 603.3497, found 603.3497.

13-Methyl-2-(3,3,3-trichloro-1-ethoxypropyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[*a*]phenanthren-17-one (4saa):



Yield: 64%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.5 Hz, 1H), 7.14 (s, 1H), 7.08 (s, 1H), 4.67 (d, *J* = 6.0 Hz, 1H), 3.44-3.40 (m, 2H), 3.28-3.23 (m, 1H), 2.96-2.93 (m, 3H), 2.54-2.49 (m, 1H), 2.44-2.42 (m, 1H), 2.33-2.31 (m, 1H), 2.19-2.13 (m, 1H), 2.10-2.03 (m, 2H), 1.99-1.97 (m, 1H), 1.68-1.62 (m, 2H), 1.56-1.45 (m, 4H), 1.20 (t, *J* = 6.5 Hz, 3H), 0.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 220.9, 139.5, 138.8, 136.9 (2C), 126.9 (2C), 125.7 (2C), 123.8 (2C), 97.7, 79.0, 78.9, 64.6, 62.2, 50.5, 47.9, 44.4, 38.1, 35.8, 31.6, 29.4, 26.4, 25.7, 21.6, 15.2, 13.8; HRMS *m/z* (ESI) calcd for $C_{23}H_{30}O_2Cl_3$ ($[M+H]^+$) 443.1306, found 443.1308.

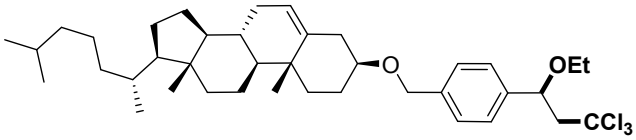
13-Methyl-2-(3,3,3-trichloro-1-ethoxy-1-phenylpropyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (4taa):



Yield: 72%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 2H), 7.29-7.27 (m, 2H), 7.22-7.20 (m, 1H), 7.19-7.17 (m, 1H), 7.07-7.04 (m, 1H), 3.88-3.76 (m, 2H), 3.33-3.26 (m, 2H), 3.21-3.17 (m, 1H), 2.87-2.85 (m, 2H), 2.53-2.47 (m, 1H), 2.40-2.47 (m, 1H), 2.29-2.25 (m, 1H), 2.17-2.10 (m, 1H), 2.02-1.99 (m, 1H), 1.96-1.94 (m, 1H), 1.66-1.64 (m, 2H), 1.49-1.46 (m, 2H), 1.27-1.25 (m, 2H), 1.21-1.18 (m, 3H), 0.91 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 220.8, 143.8 (2C), 141.4, 141.3, 138.7, 138.6, 135.9, 131.7, 128.0, 127.7, 127.6 (2C), 127.5, 127.4, 127.1, 127.0 (2C), 127.6(2C), 125.0, 124.9 (2C), 124.8 (2C), 124.2, 124.1, 96.7, 82.4, 81.5, 81.4, 60.4, 59.3, 58.0, 55.8 (2C), 50.5, 47.9, 44.3, 38.0 (2C), 35.8, 31.6, 29.5, 29.5, 26.5, 25.54 (s), 21.5, 21.0, 15.4, 15.0, 14.2, 13.9, 13.8; HRMS *m/z* (ESI) calcd for

$C_{29}H_{34}O_2Cl_3$ ([M+H]$^+$) 519.1619, found 519.1616.

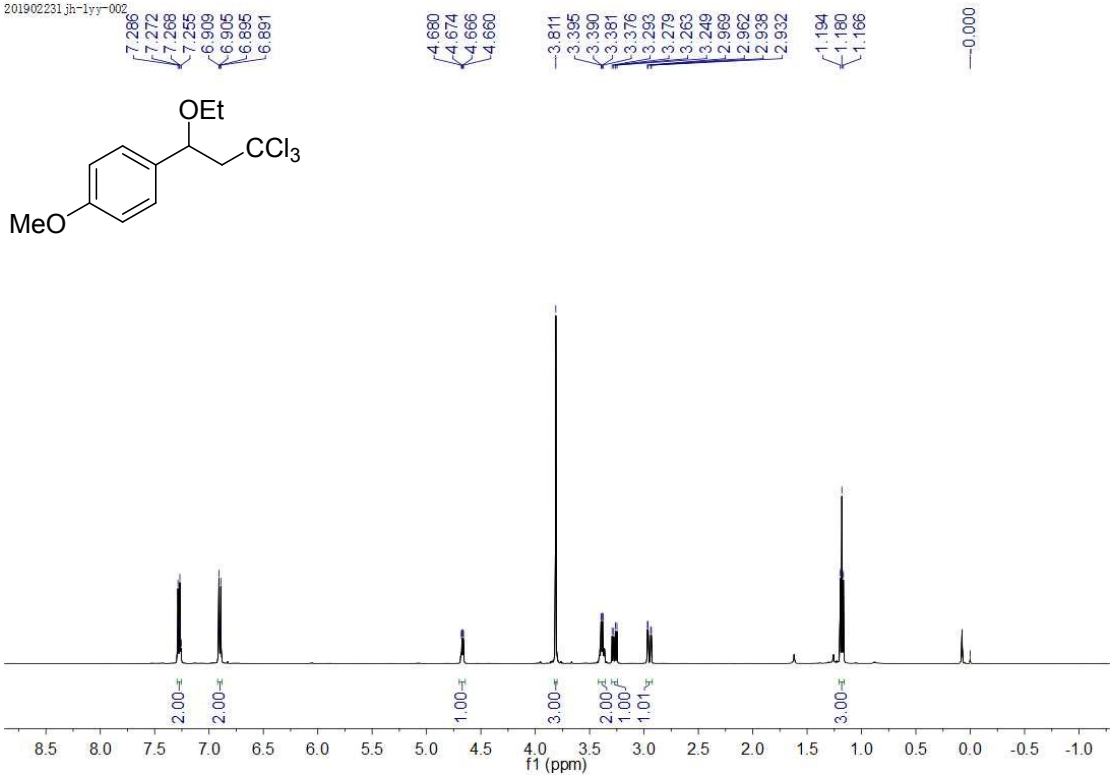
(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-3-((4-((S)-3,3,3-trichloro-1-ethoxypropyl)benzyl)oxy)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[*a*]phenanthrene (4uaa):

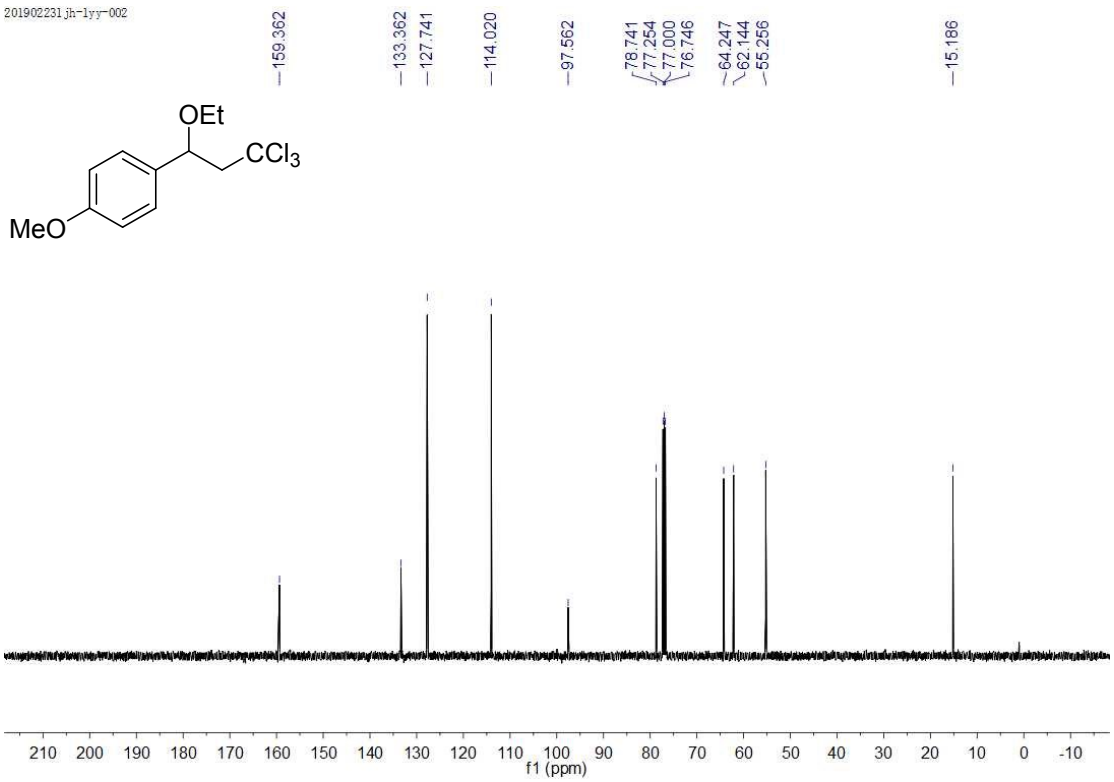


Yield: 53%, Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.32 (m, 4H), 5.36-5.35 (m, 1H), 4.72-4.71 (m, 1H), 4.55 (s, 2H), 3.42-3.38 (m, 2H), 3.28-3.24 (m, 2H), 2.95-2.92 (m, 1H), 2.44-2.42 (m, 1H), 2.31-2.26 (m, 1H), 2.02-1.96 (m, 3H), 1.89-1.79 (m, 2H), 1.61-1.44 (m, 8H), 1.35-1.33 (m, 4H), 1.26 (d, *J* = 7.0 Hz, 2H), 1.18 (d, *J* = 6.9 Hz, 3H), 1.12-1.04 (m, 5H), 1.02 (s, 3H), 1.00-0.95 (m, 2H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.87-0.86 (m, 6H), 0.68 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.9, 140.5, 138.9, 128.0 (2C), 126.5, 121.6, 97.5, 79.0, 78.8, 69.6, 64.5, 62.2, 56.8, 56.1, 50.2, 42.3, 39.8, 39.5, 39.1, 37.2, 36.9, 36.2, 35.8, 31.9 (2C), 28.4, 28.2, 28.0, 24.3, 23.8, 22.8, 22.6, 21.0, 19.4, 18.7, 15.2, 11.8; HRMS *m/z* (ESI) calcd for $C_{39}H_{60}O_2Cl_3$ ([M+H]$^+$) 665.3653, found 665.3650.

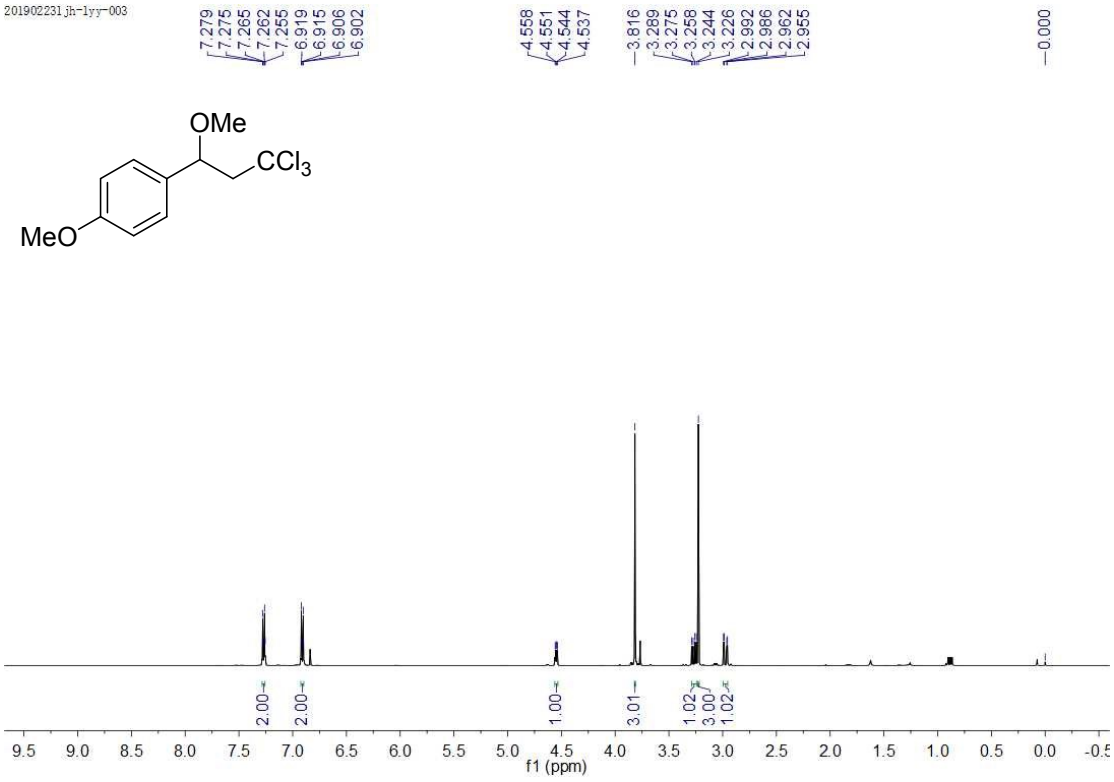
(E) Spectra

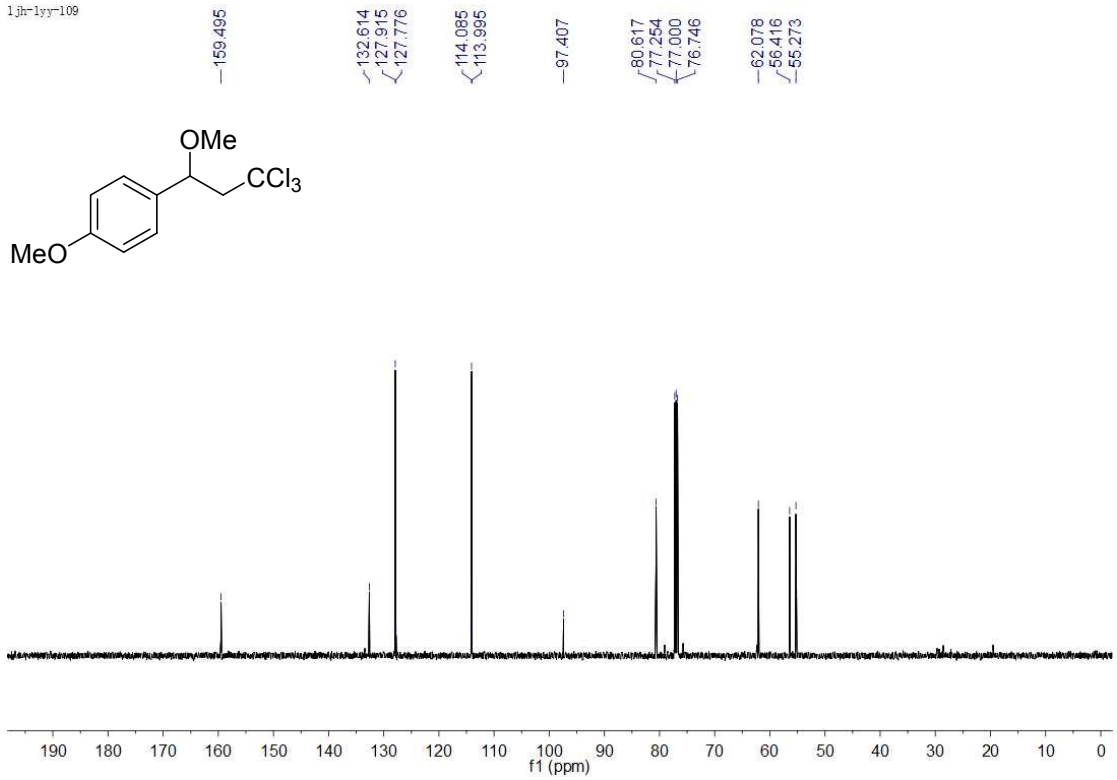
1-Methoxy-4-(3,3,3-trichloro-1-ethoxypropyl)benzene (4aaa)



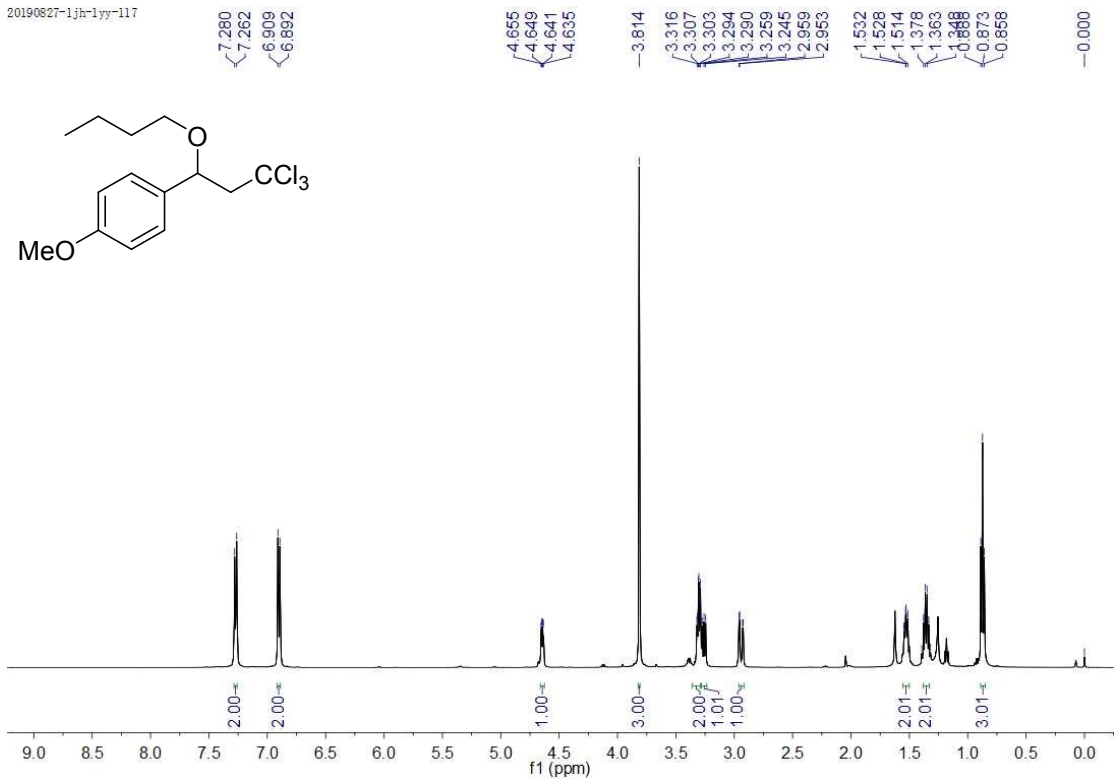


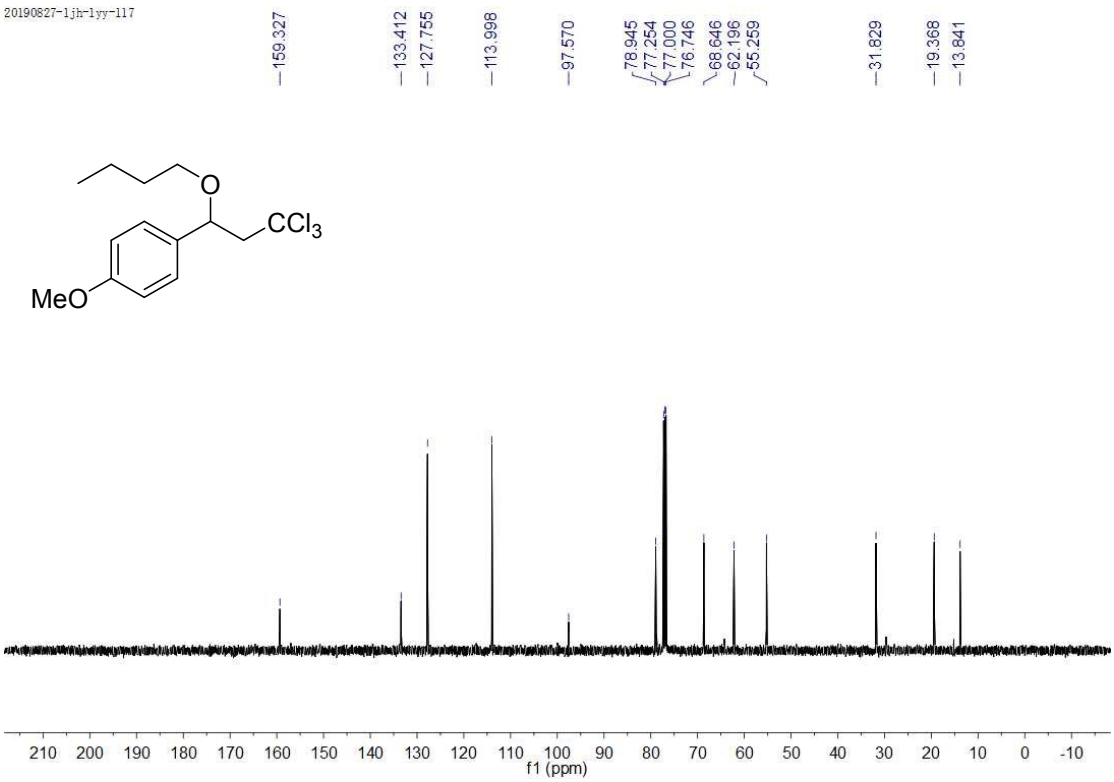
1-Methoxy-4-(3,3,3-trichloro-1-methoxypropyl)benzene (4aab)



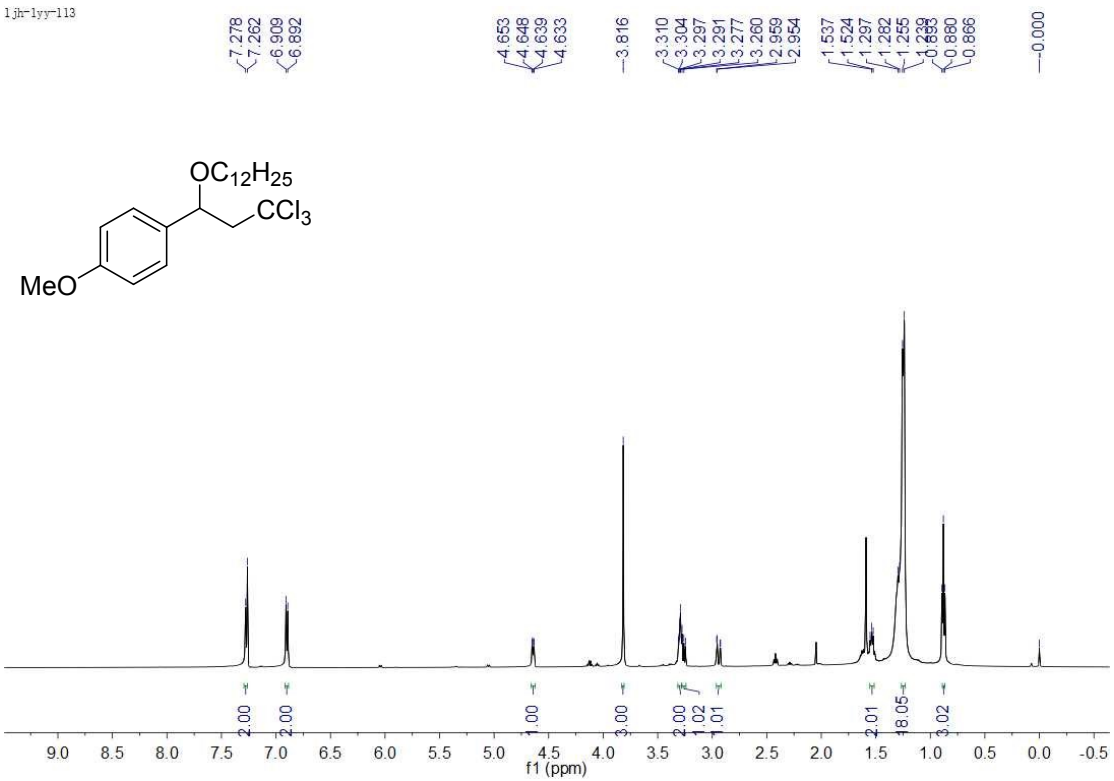


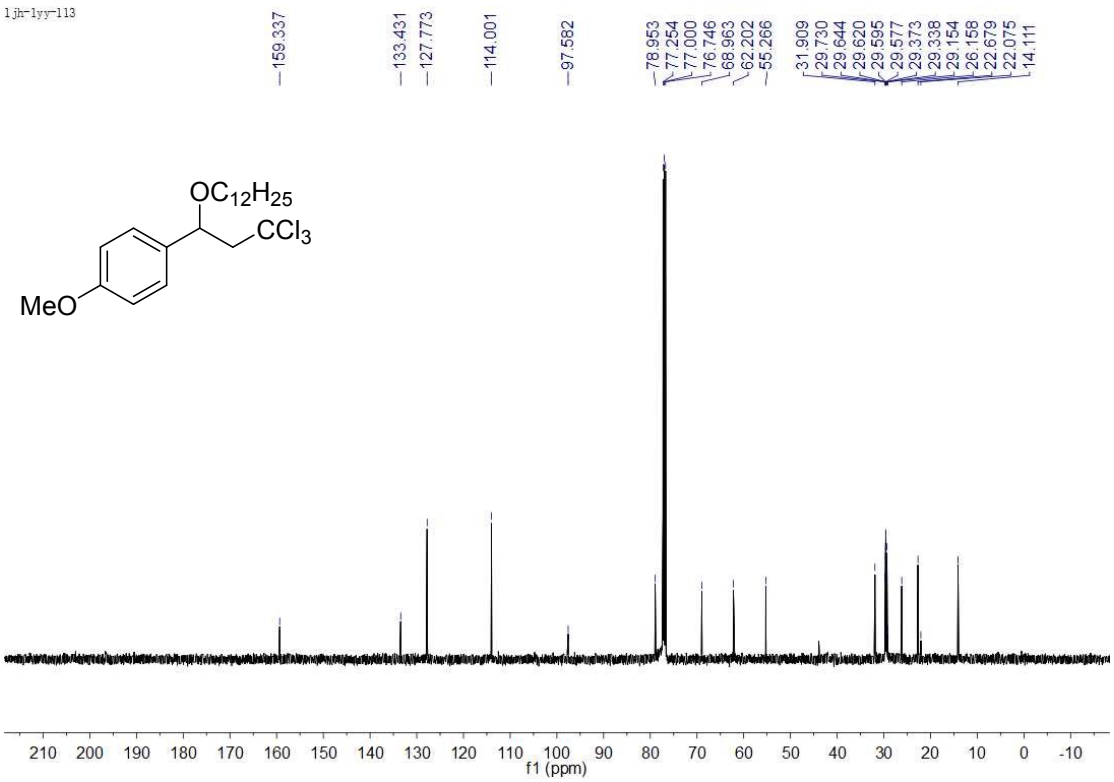
1-(1-Butoxy-3,3,3-trichloropropyl)-4-methoxybenzene (4aac)



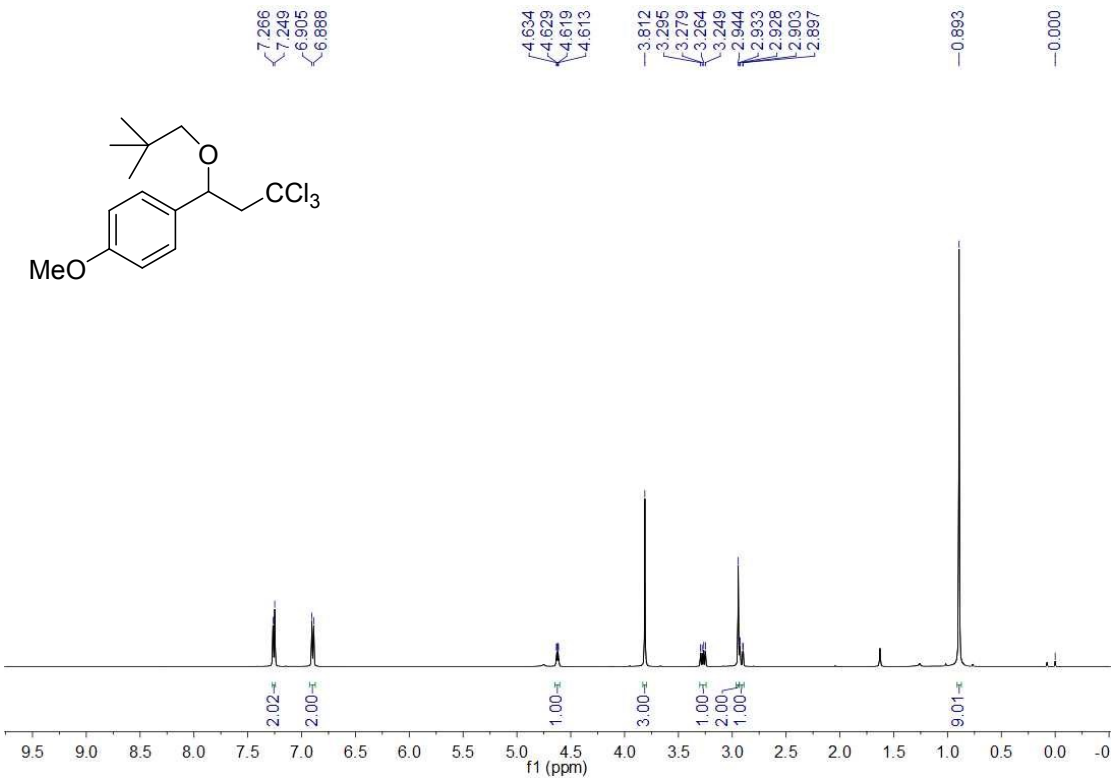


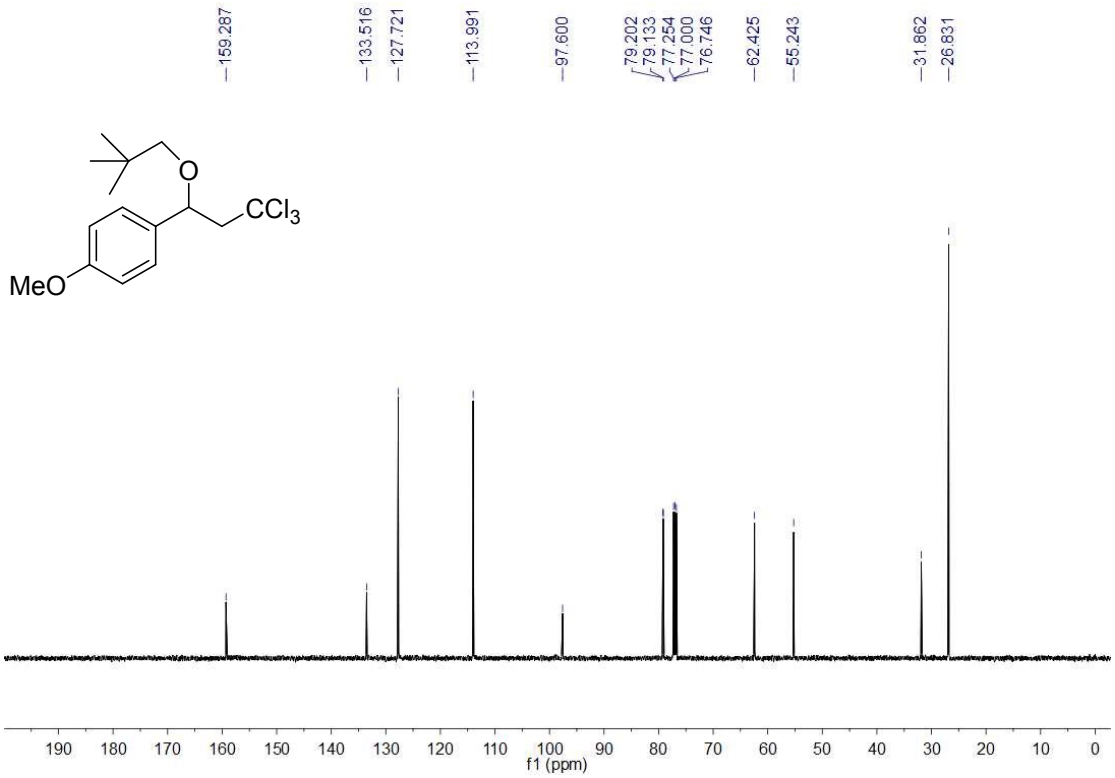
1-Methoxy-4-(3,3,3-trichloro-1-(dodecyloxy)propyl)benzene (4aad）



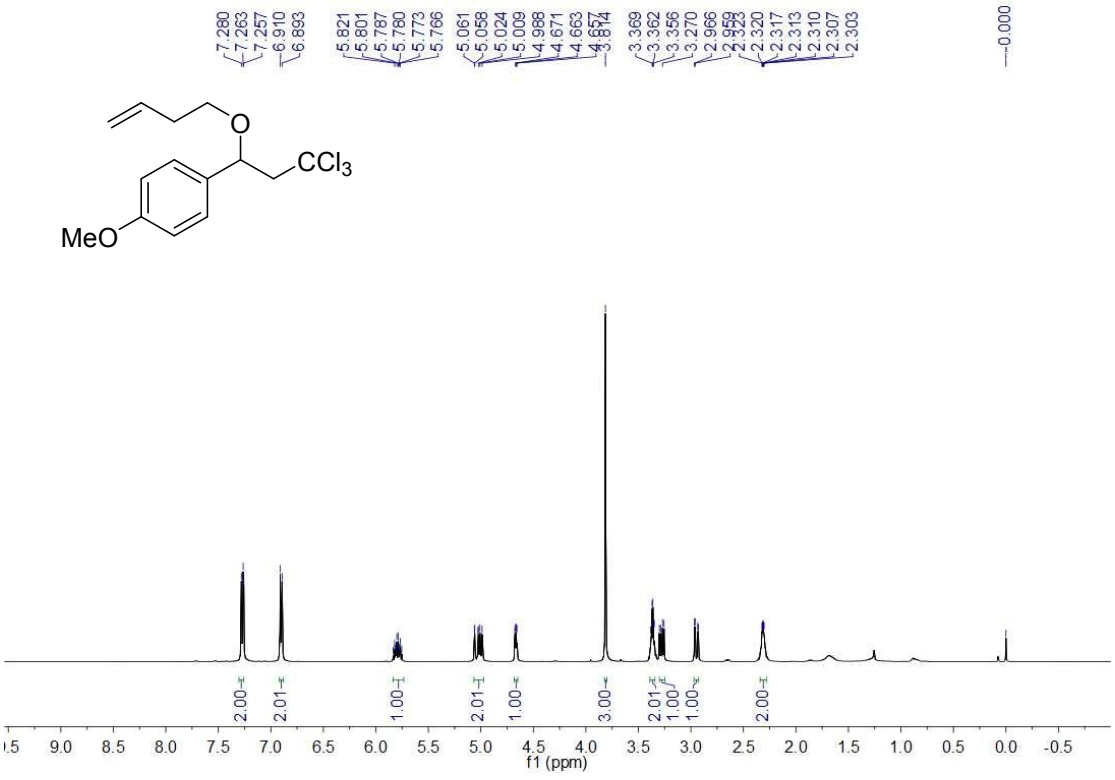


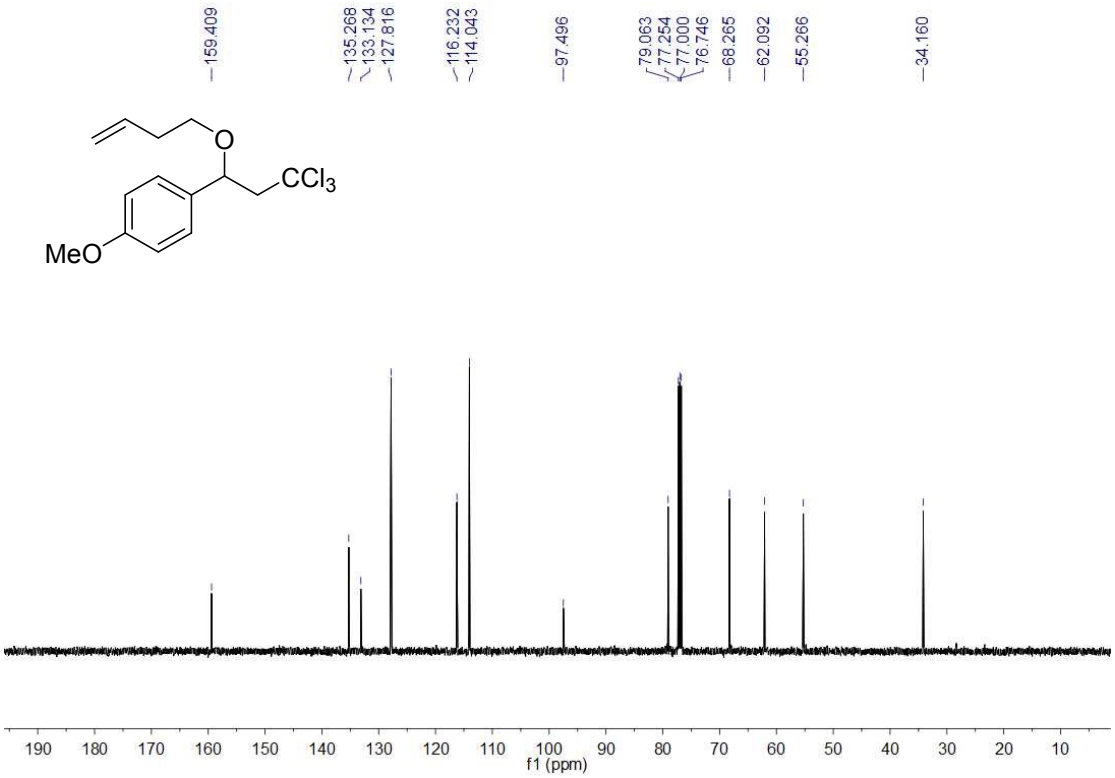
1-Methoxy-4-(3,3,3-trichloro-1-(neopentyloxy)propyl)benzene (4aae)



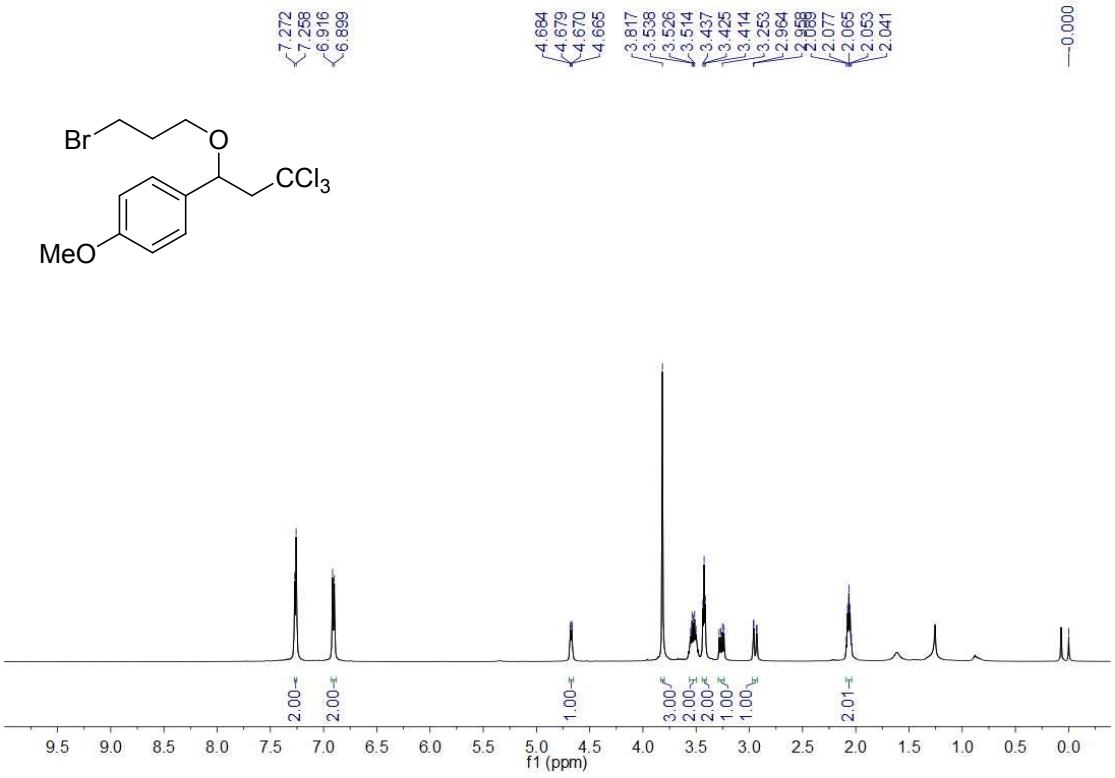


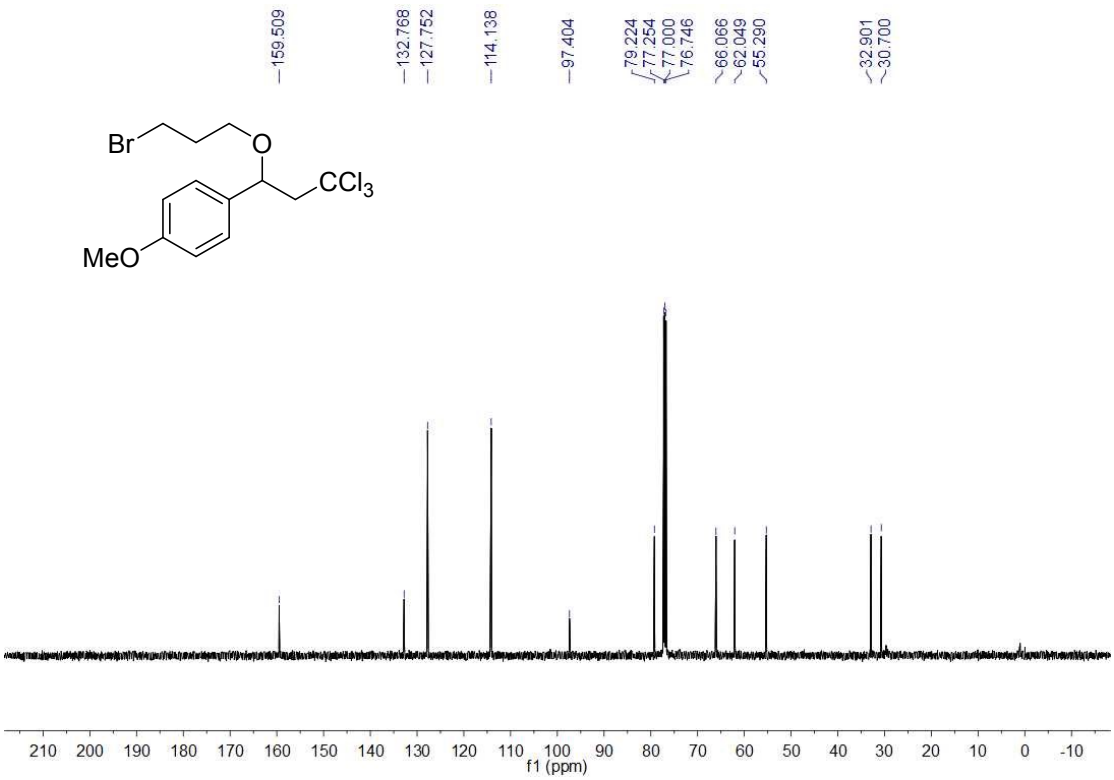
1-(1-(But-3-en-1-yloxy)-3,3,3-trichloropropyl)-4-methoxybenzene (4aaf)



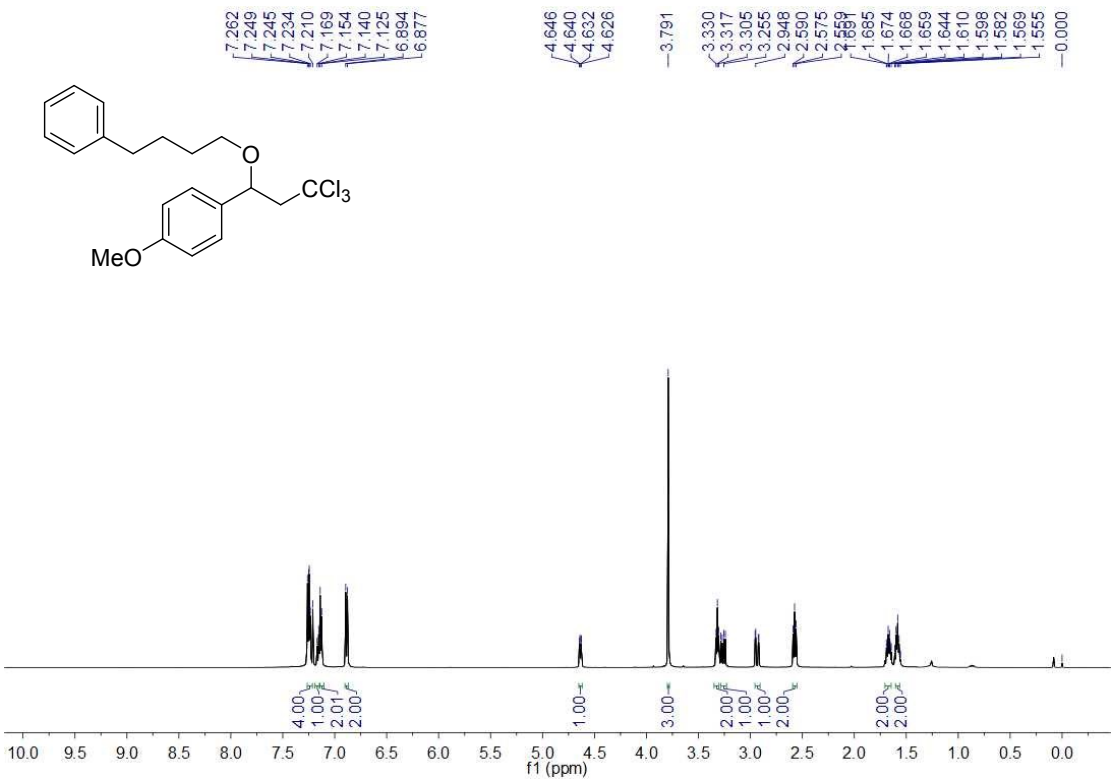


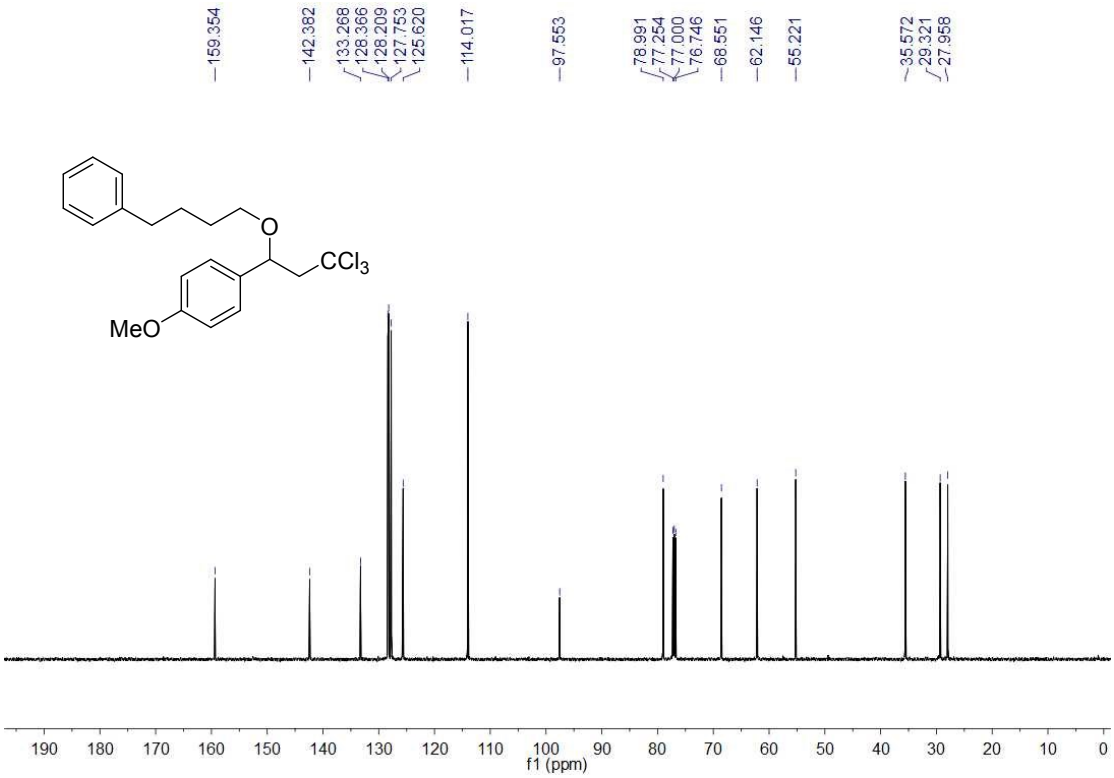
1-(1-(3-Bromopropoxy)-3,3,3-trichloropropyl)-4-methoxybenzene (4aag)



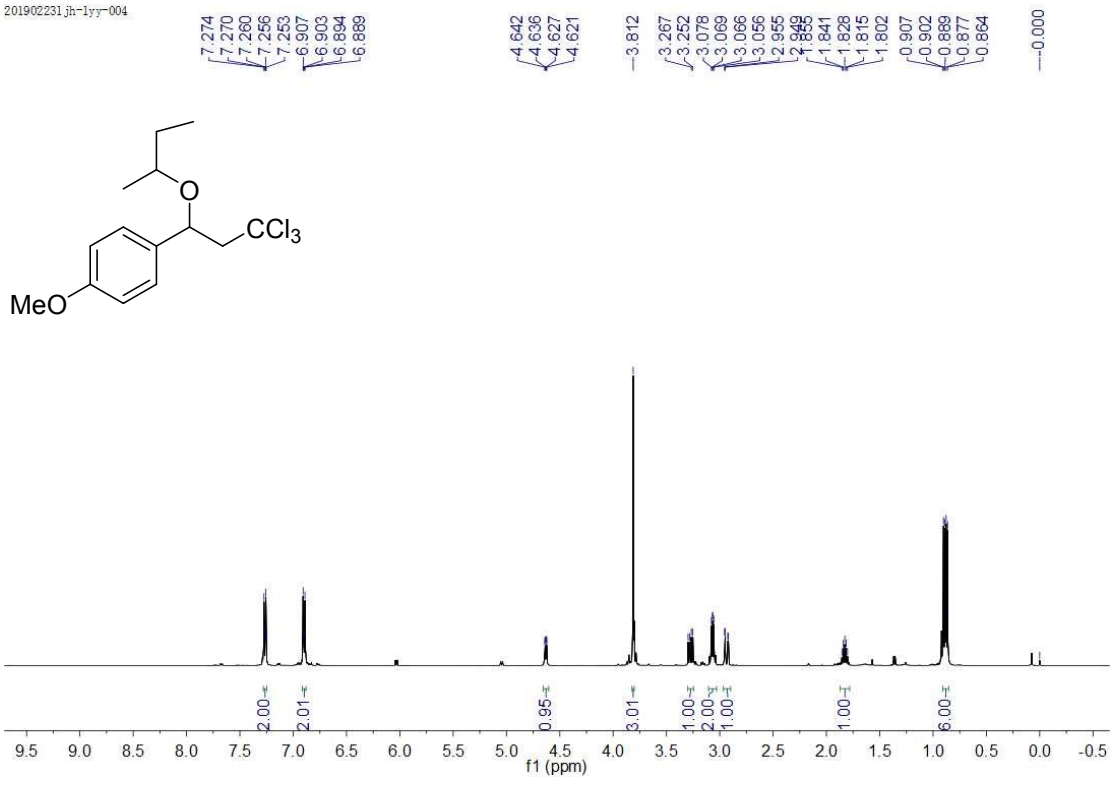


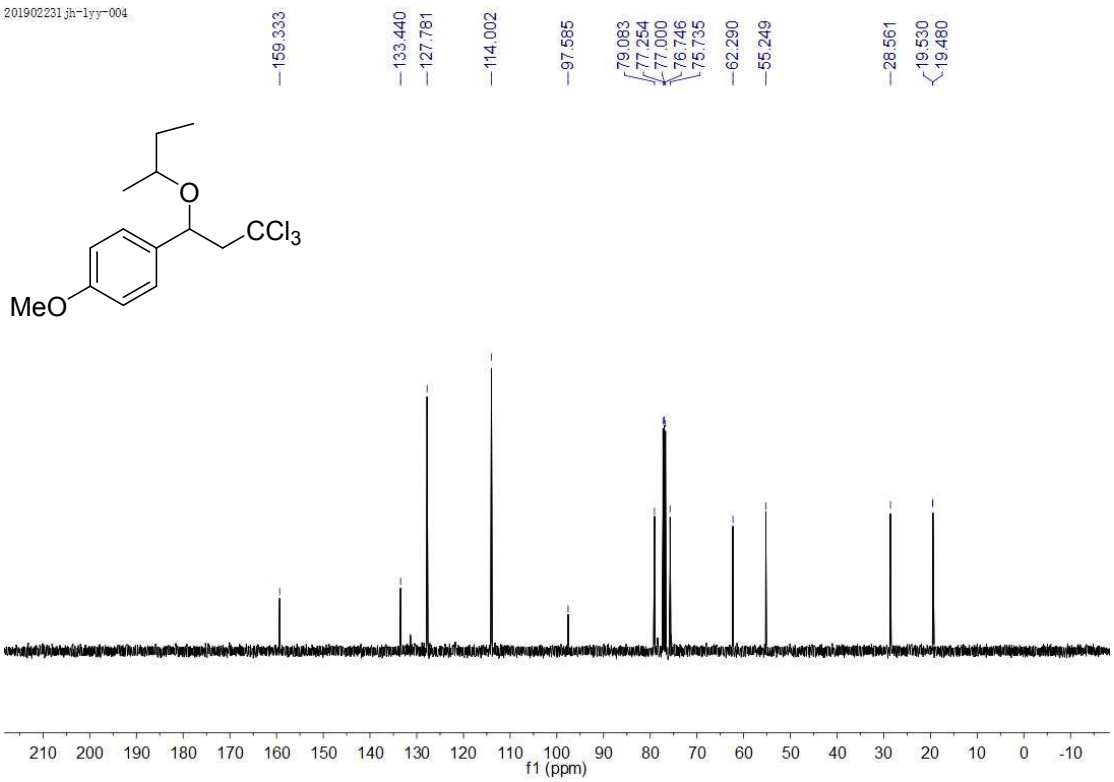
1-Methoxy-4-(3,3,3-trichloro-1-(4-phenylbutoxy)propyl)benzene (4aah)



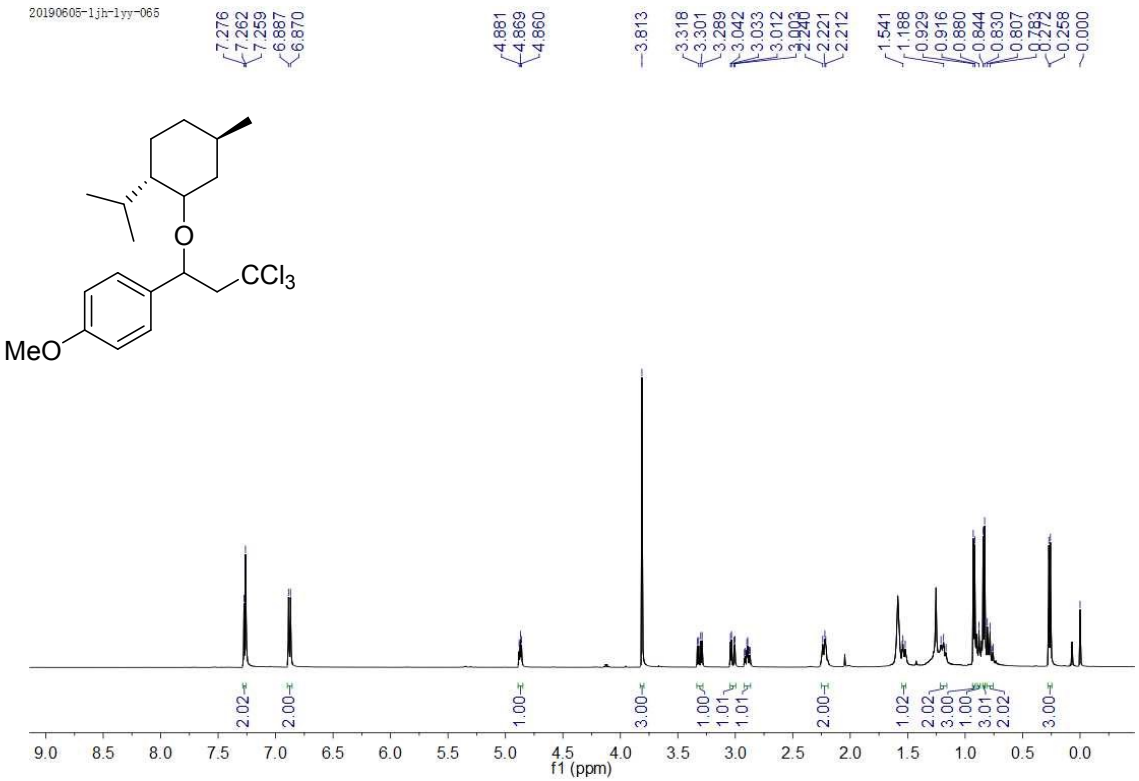


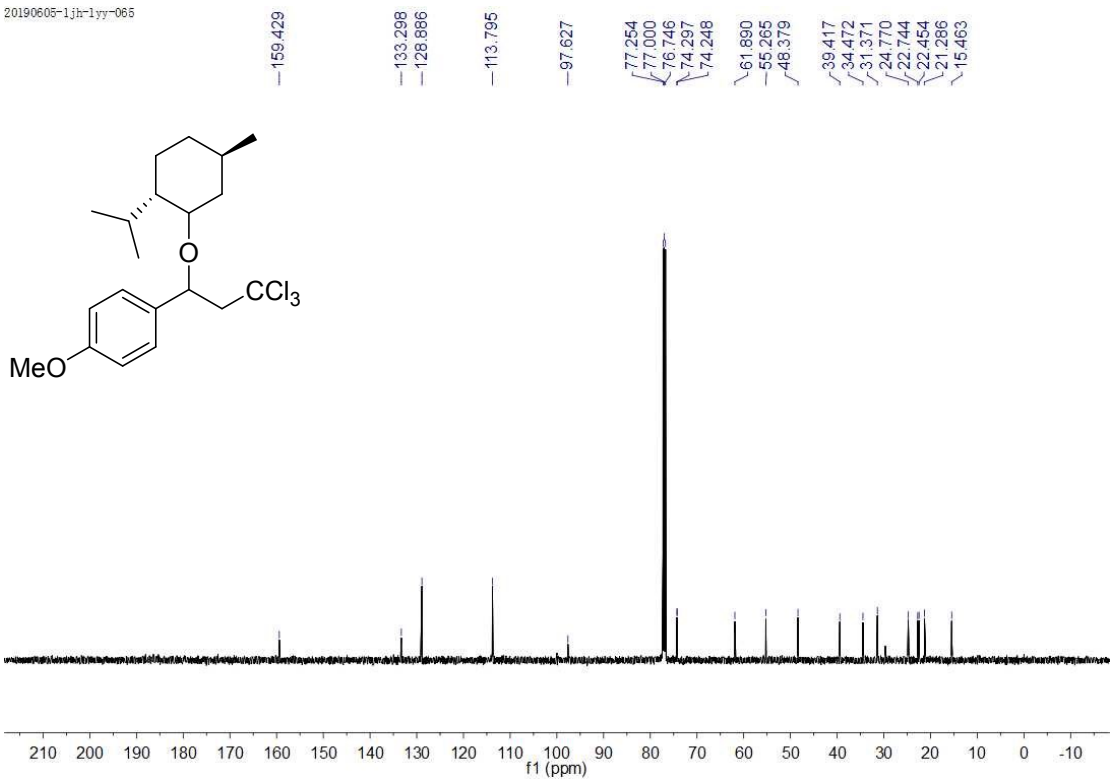
1-(1-(Sec-butoxy)-3,3,3-trichloropropyl)-4-methoxybenzene (4aai)



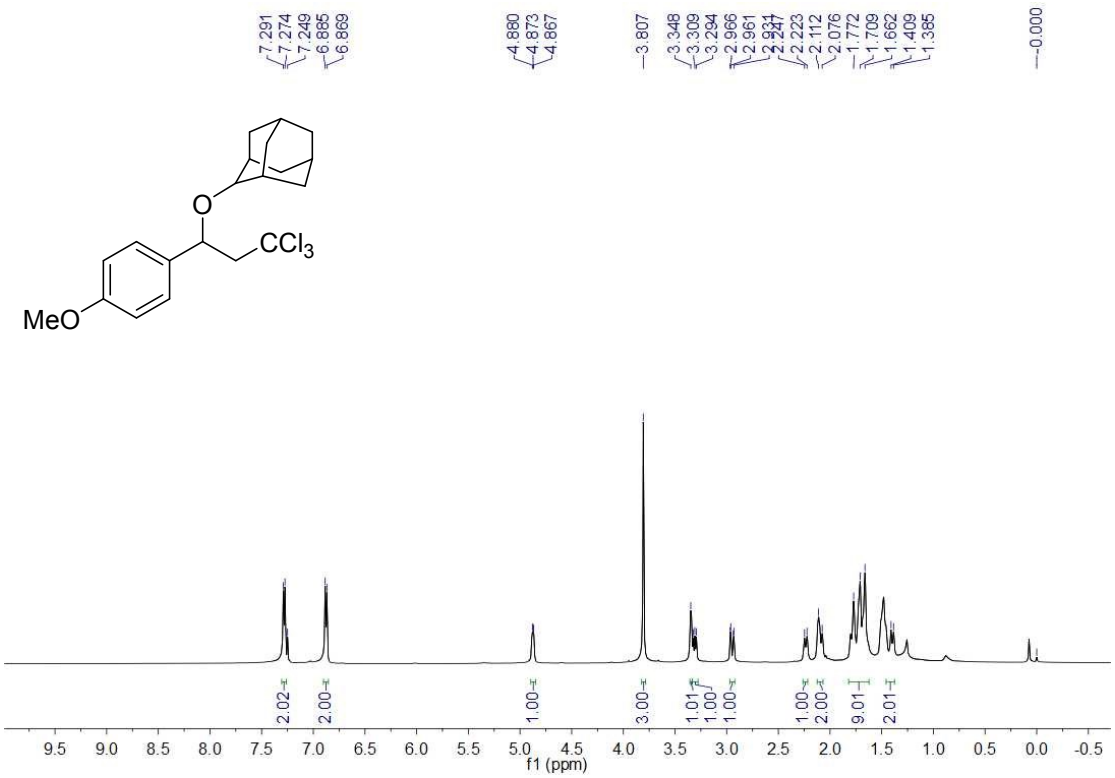


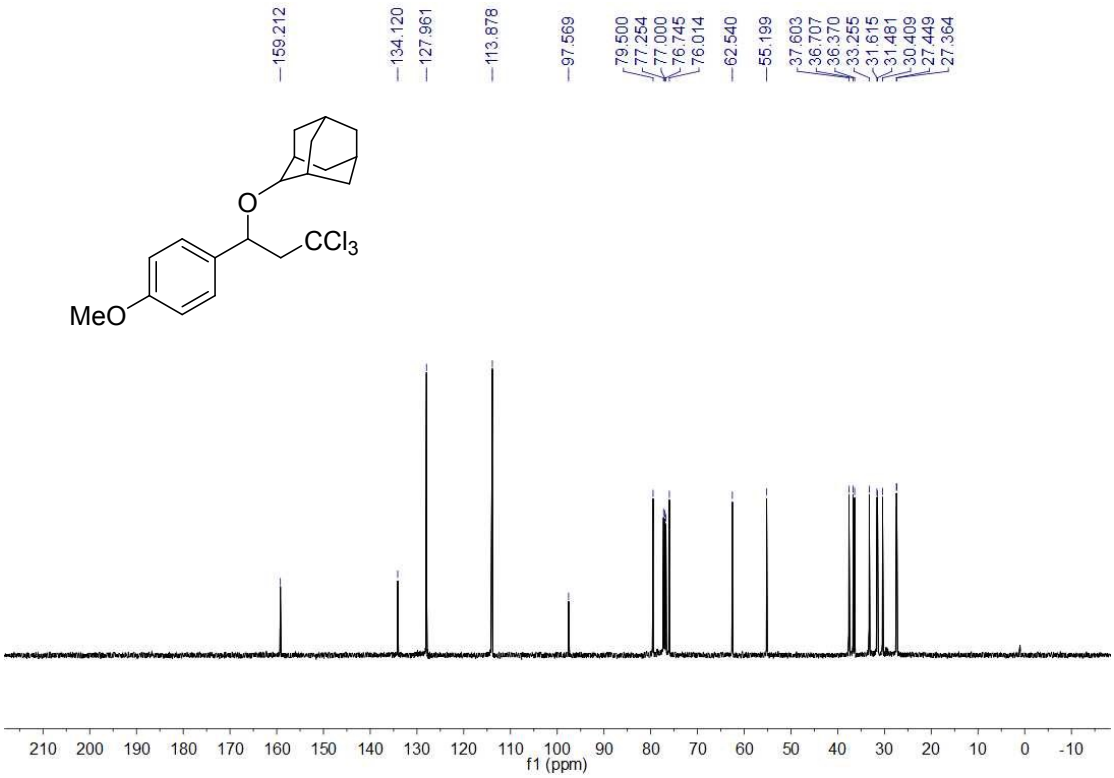
1-Methoxy-4-(3,3,3-trichloro-1-(((2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)propyl)benzene (4aaj)



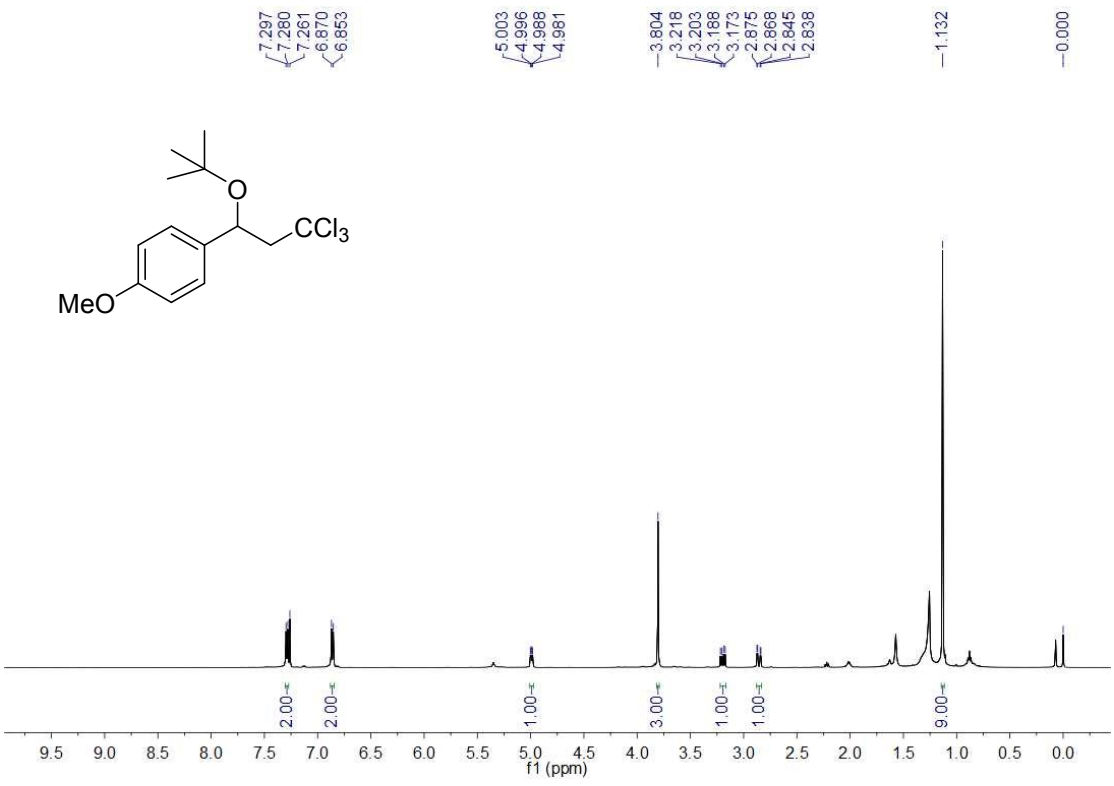


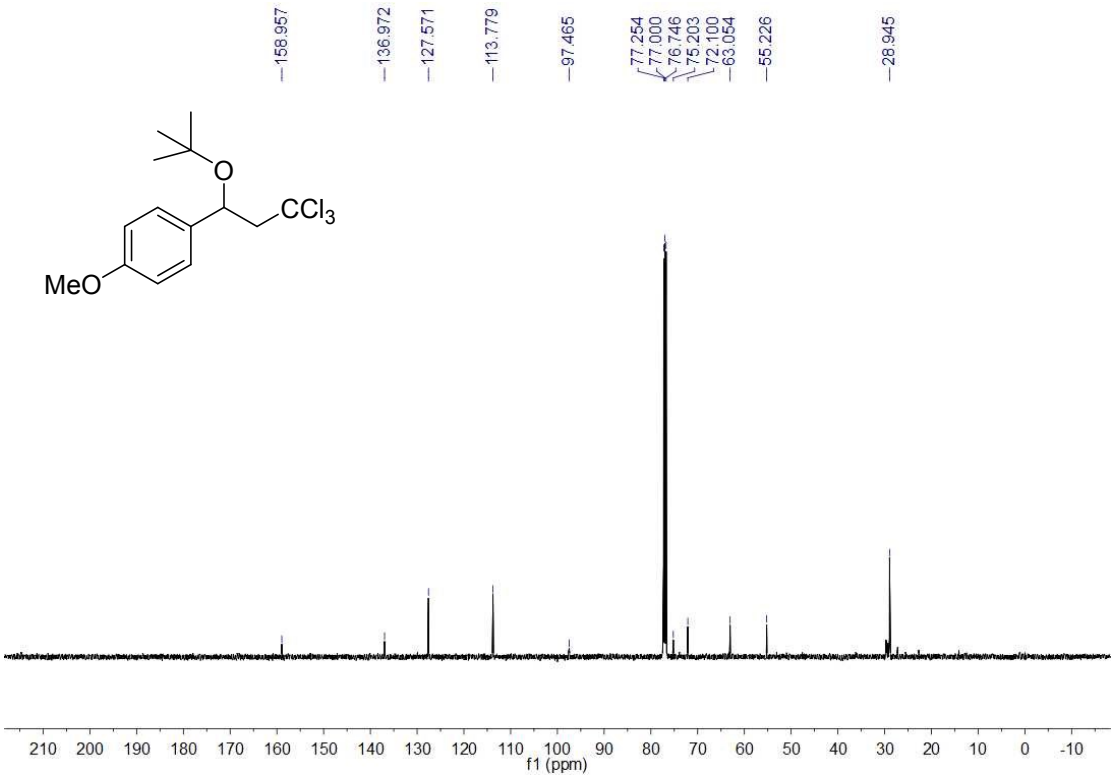
(1r,3r,5r,7r)-2-(3,3,3-trichloro-1-(4-methoxyphenyl)propoxy)adamantane (4aak)



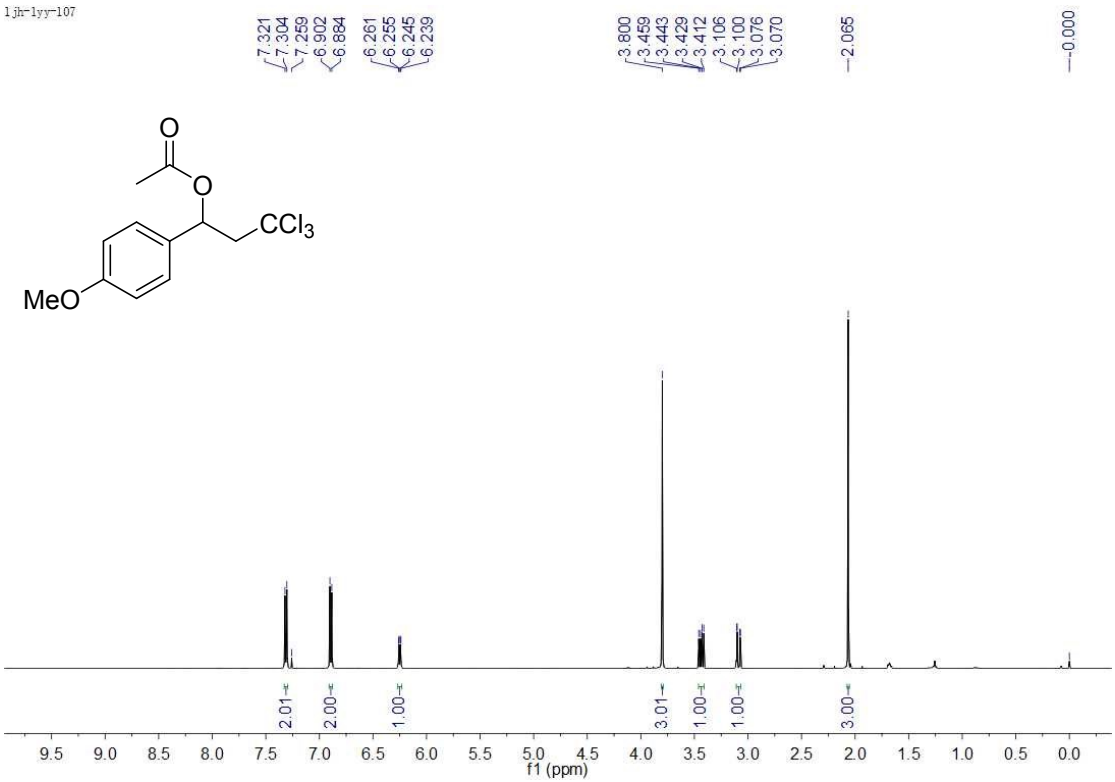


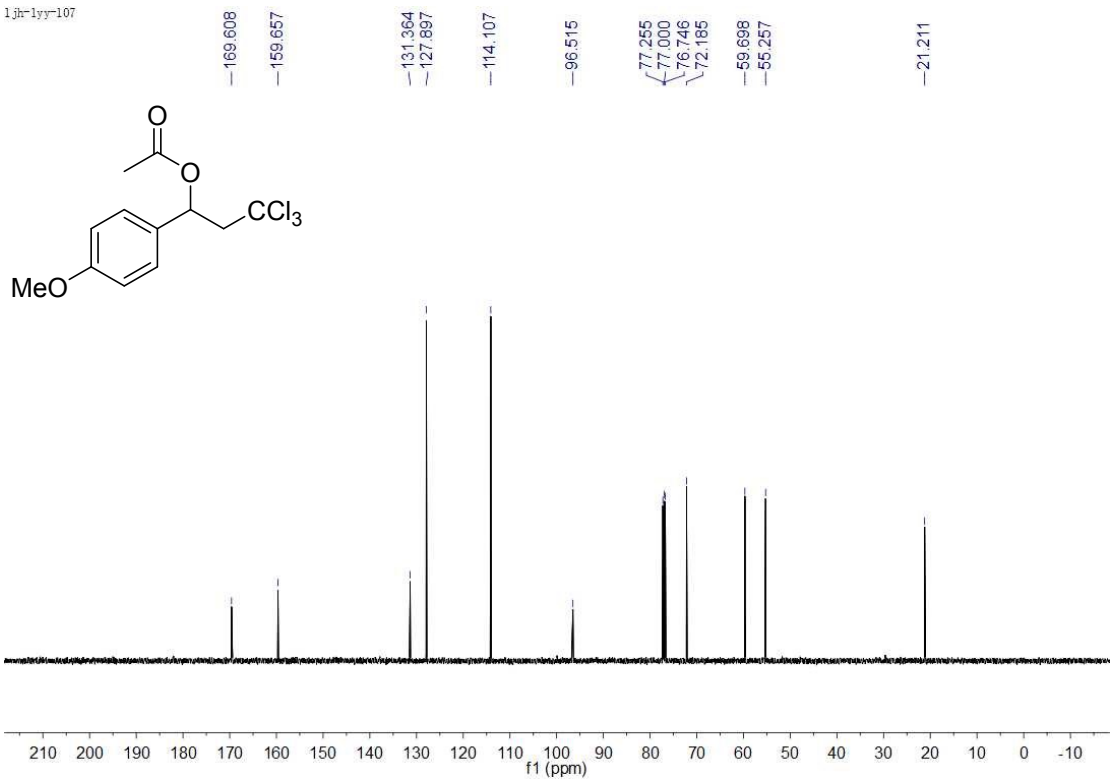
1-(1-(*Tert*-butoxy)-3,3,3-trichloropropyl)-4-methoxybenzene (4aal)



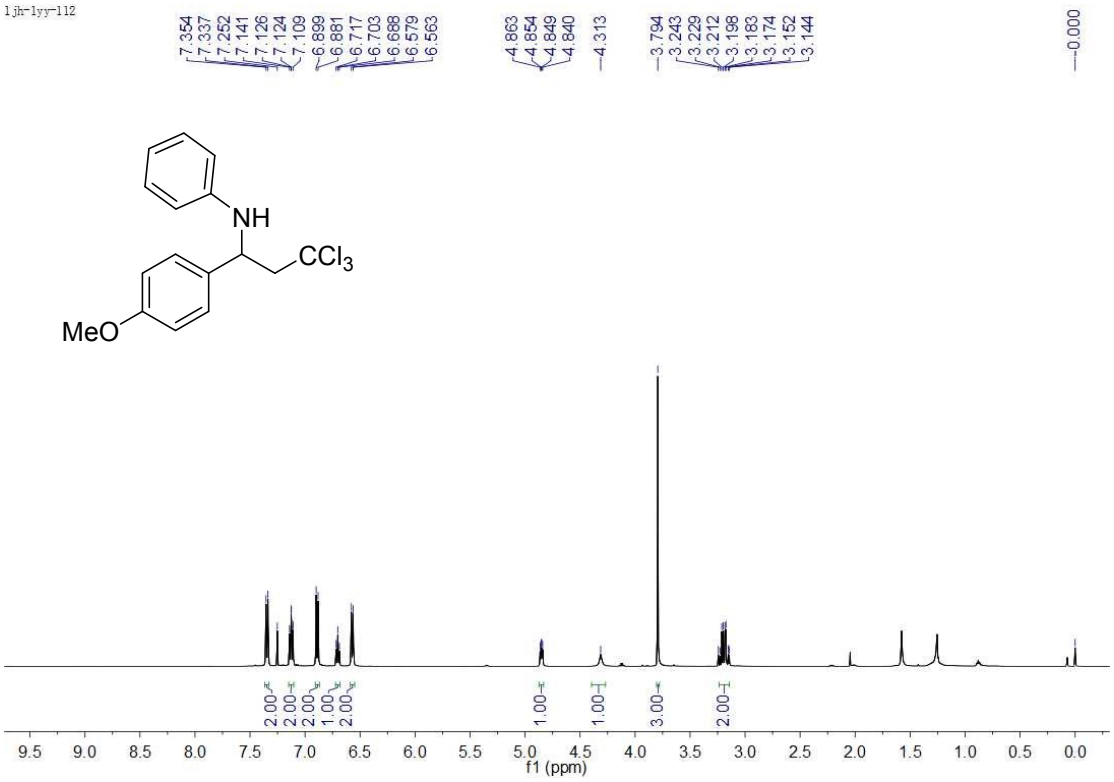


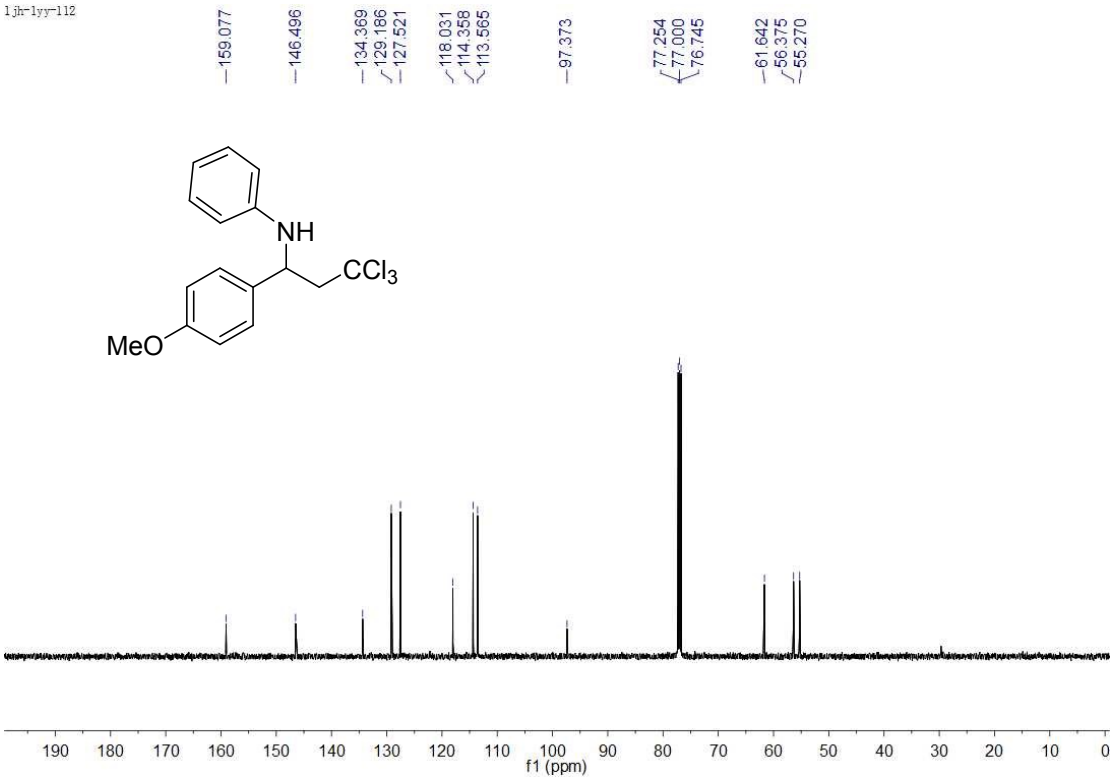
3,3,3-trichloro-1-(4-methoxyphenyl)propyl acetate (4aam)



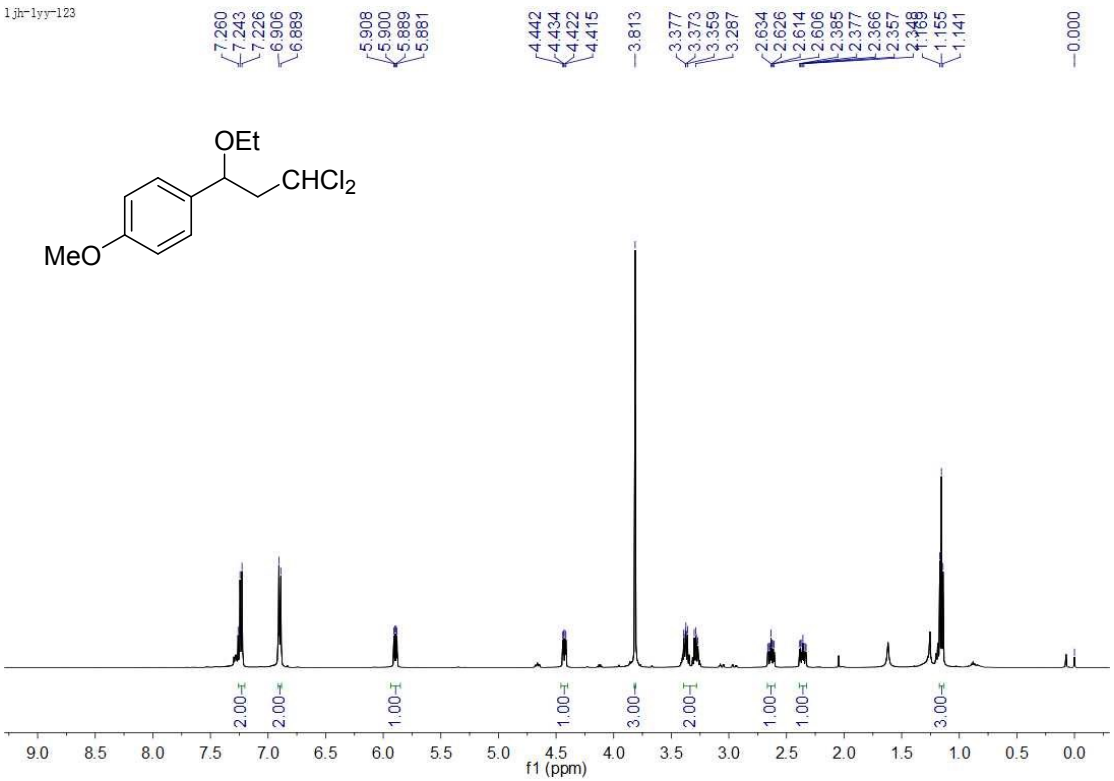


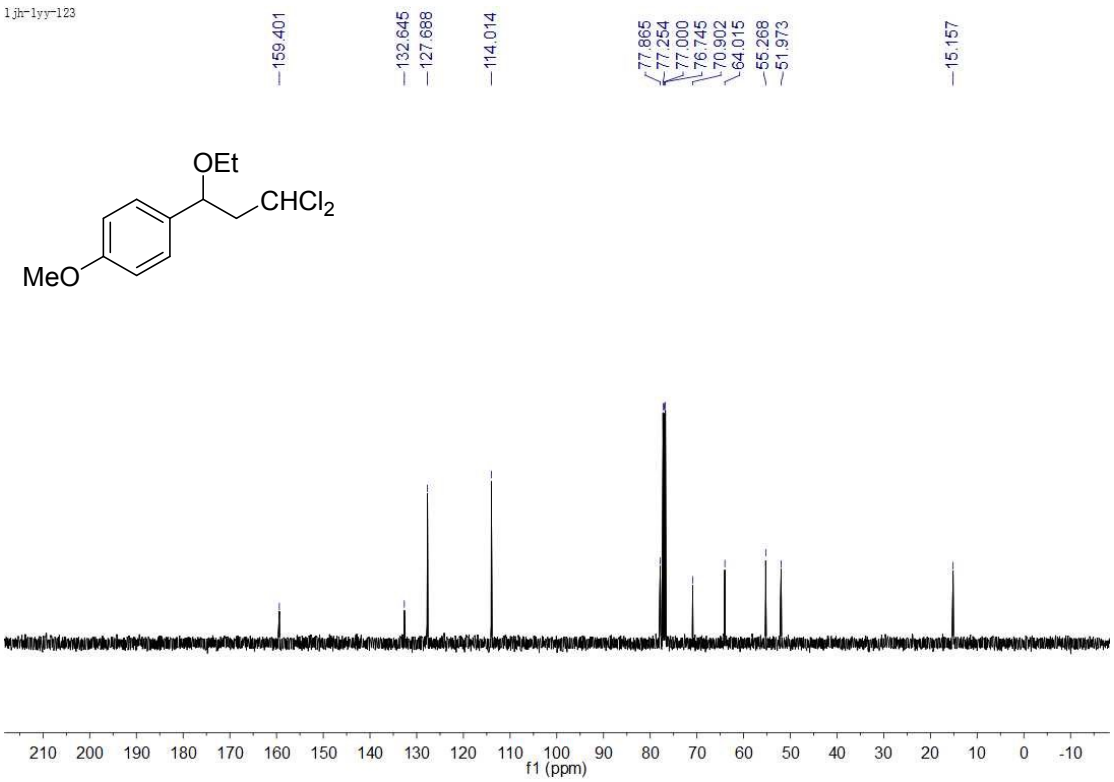
N-(3,3,3-trichloro-1-(4-methoxyphenyl)propyl)aniline (4aan)



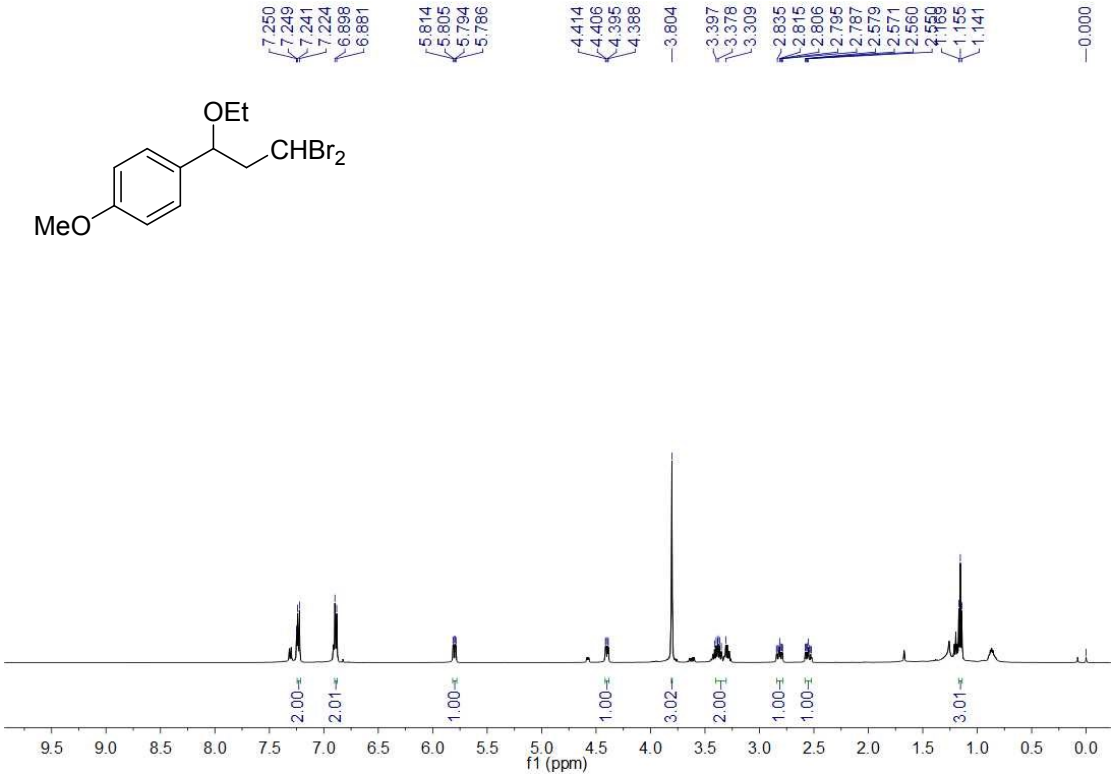


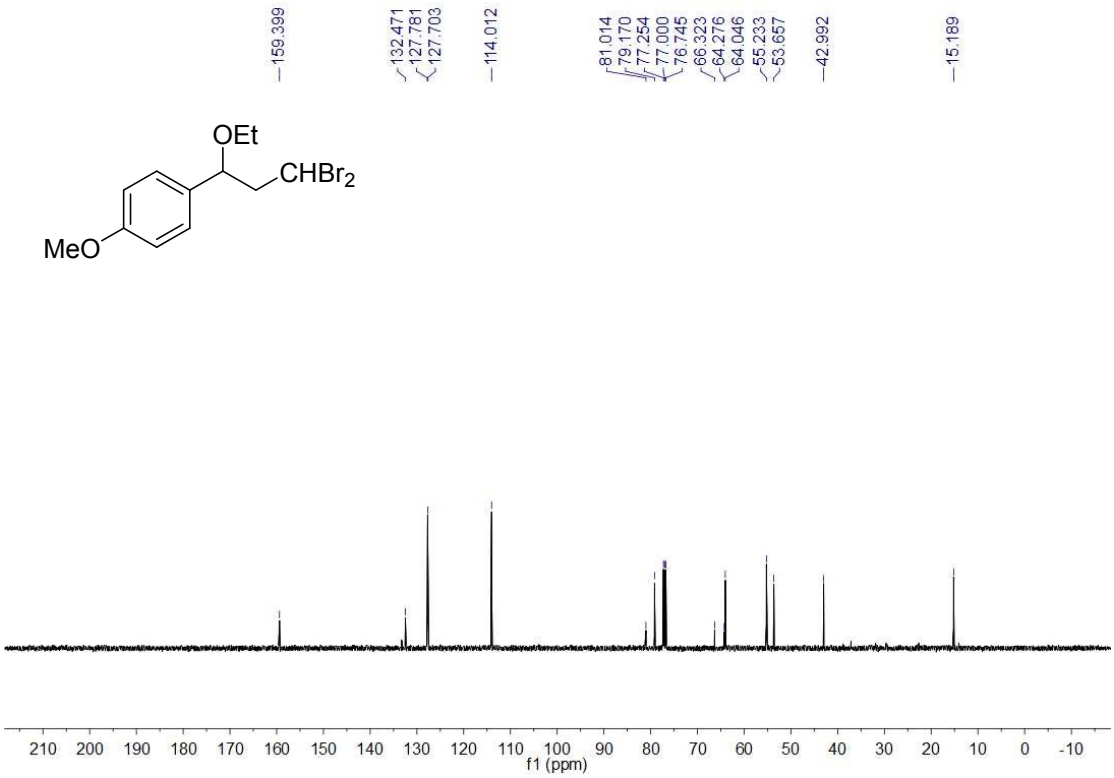
1-(3,3-Dichloro-1-ethoxypropyl)-4-methoxybenzene (4aba)



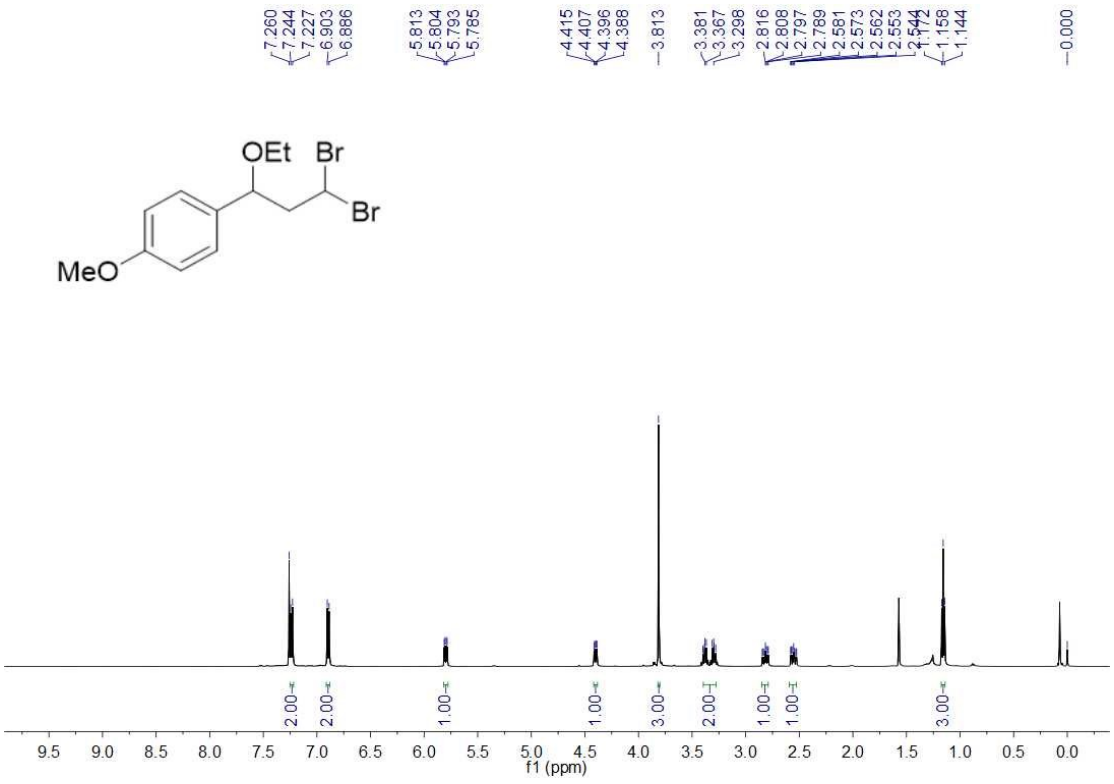


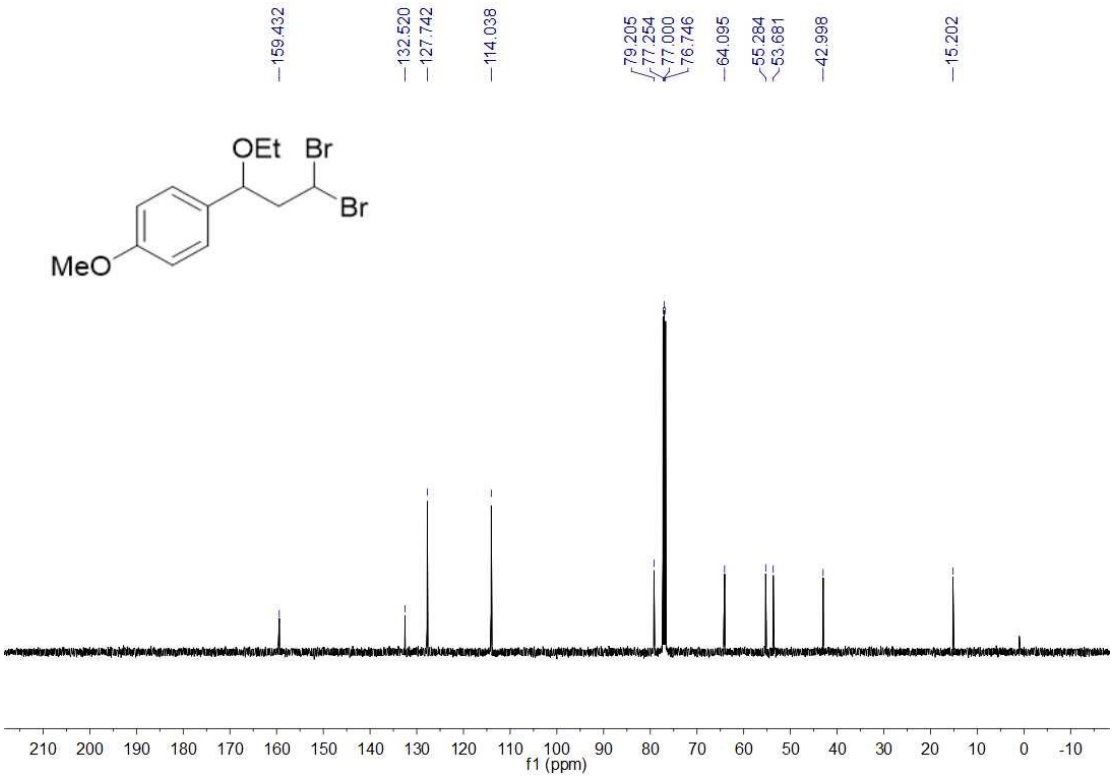
1-(3,3-Dibromo-1-ethoxypropyl)-4-methoxybenzene (4afa:4afa' = 1:9)



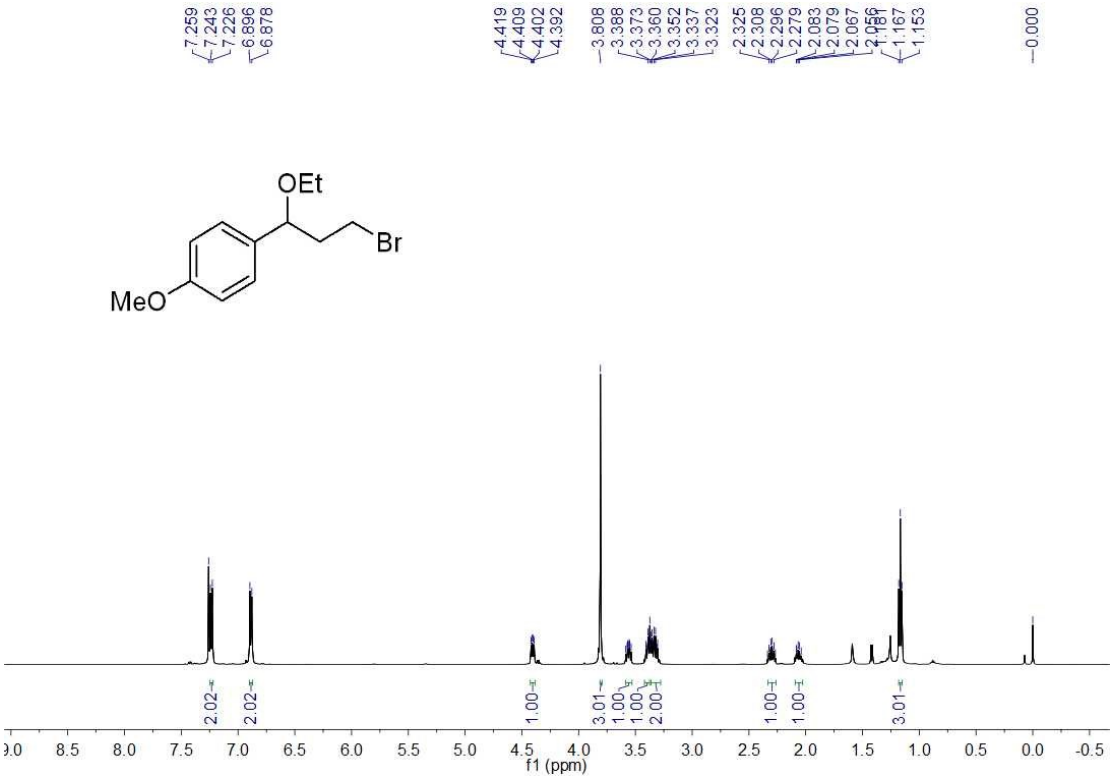


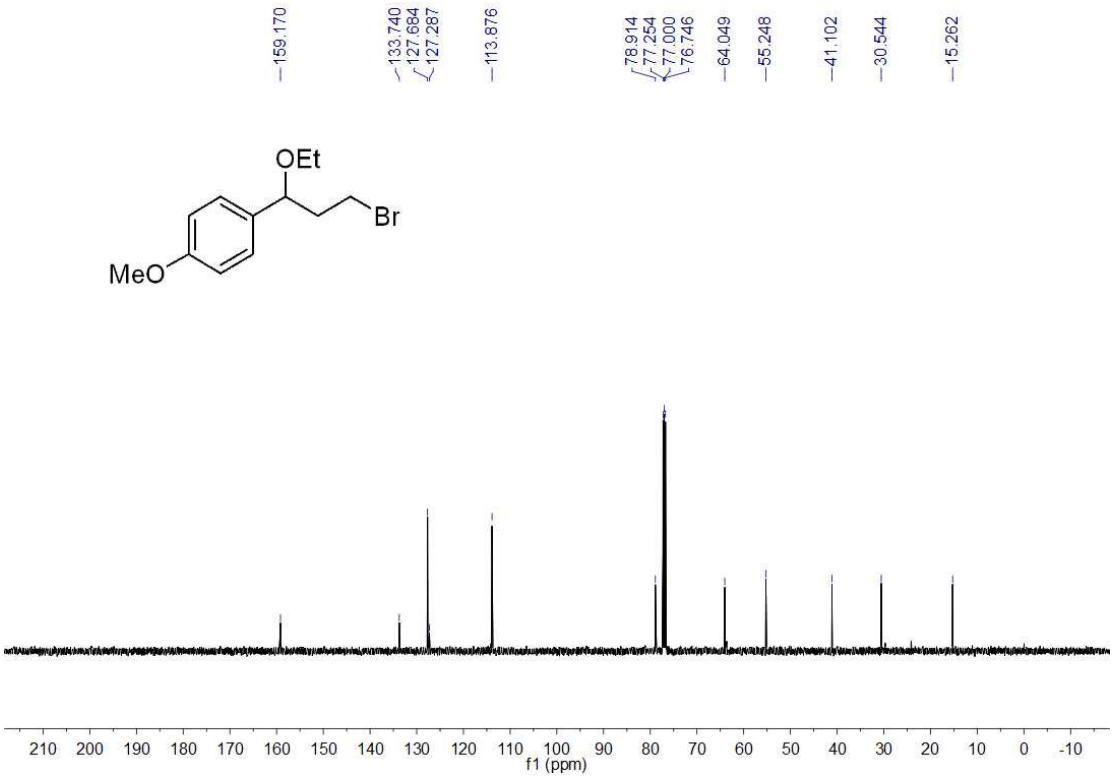
1-(3,3-dibromo-1-ethoxypropyl)-4-methoxybenzene (4afa)



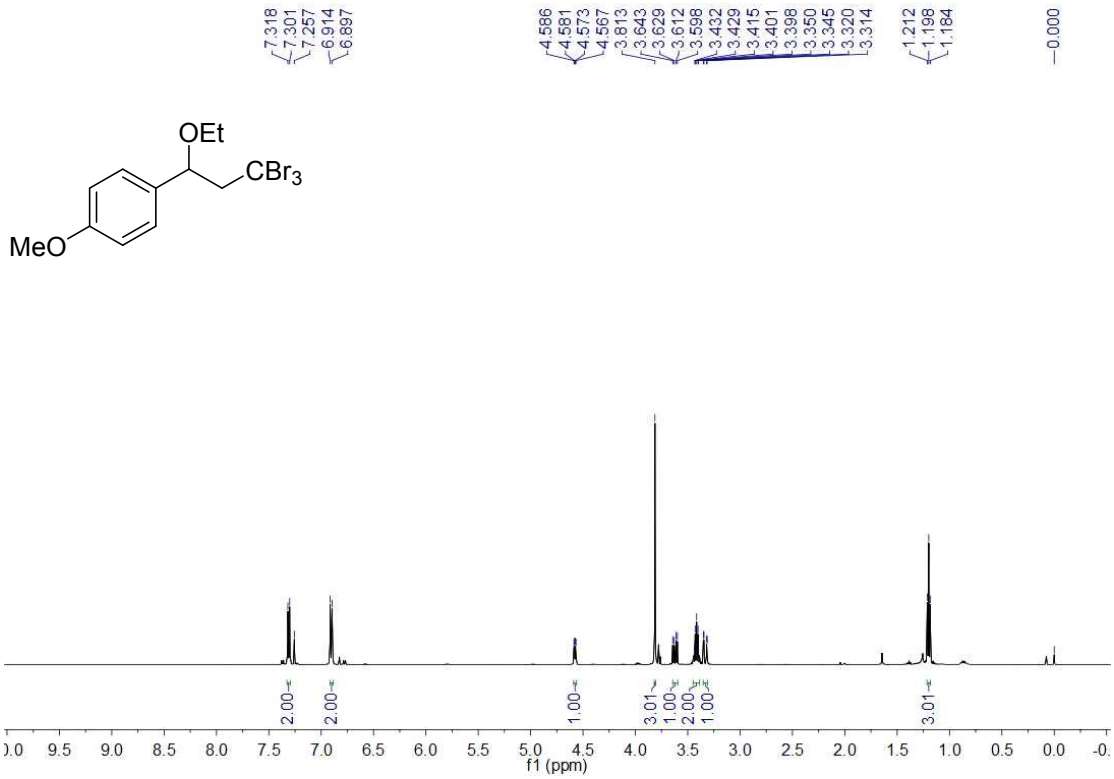


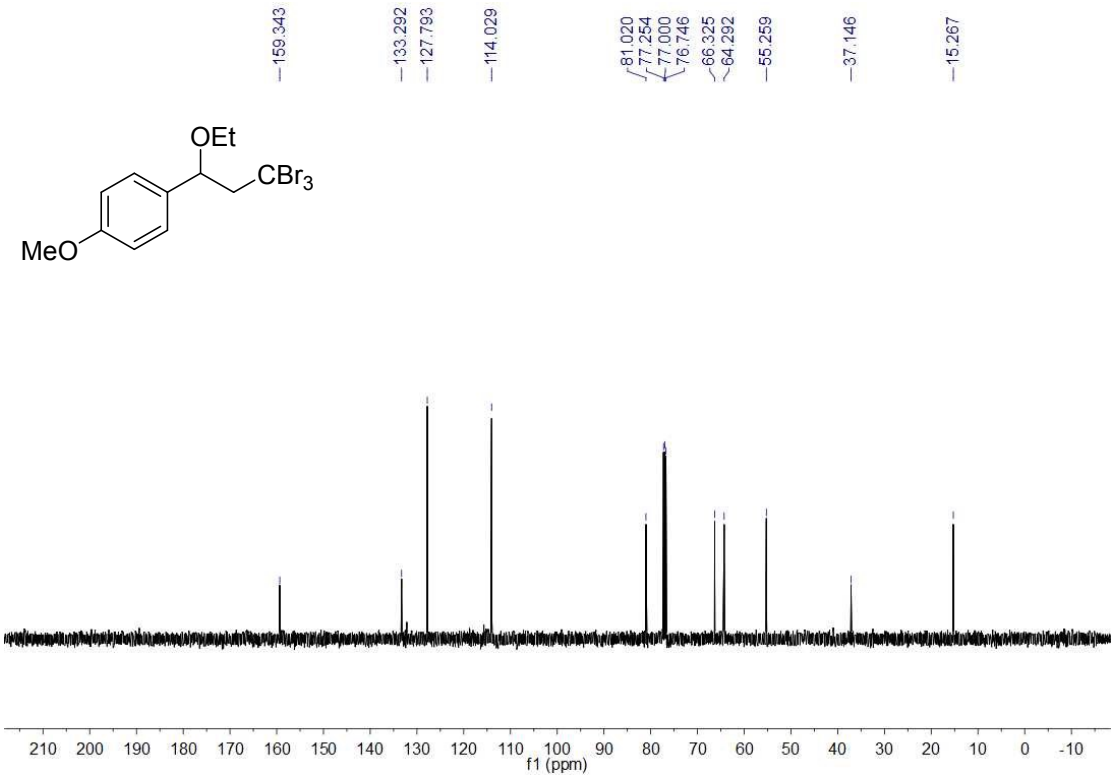
1-(3-bromo-1-ethoxypropyl)-4-methoxybenzene (4aga')



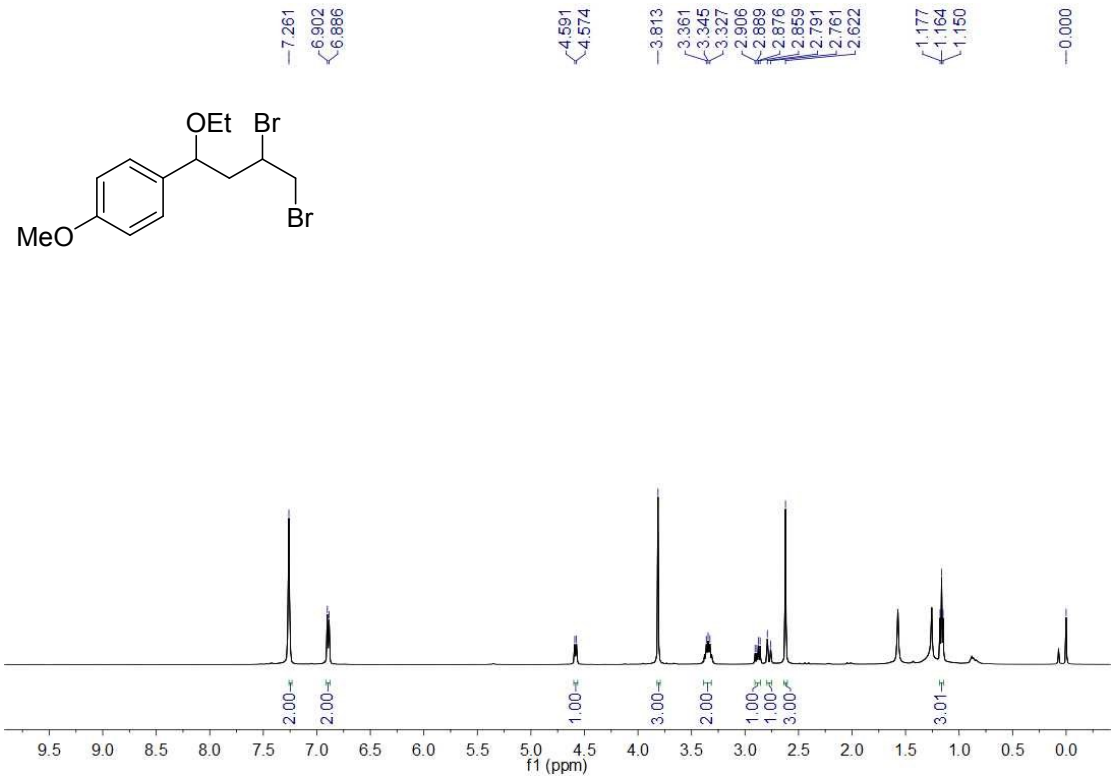


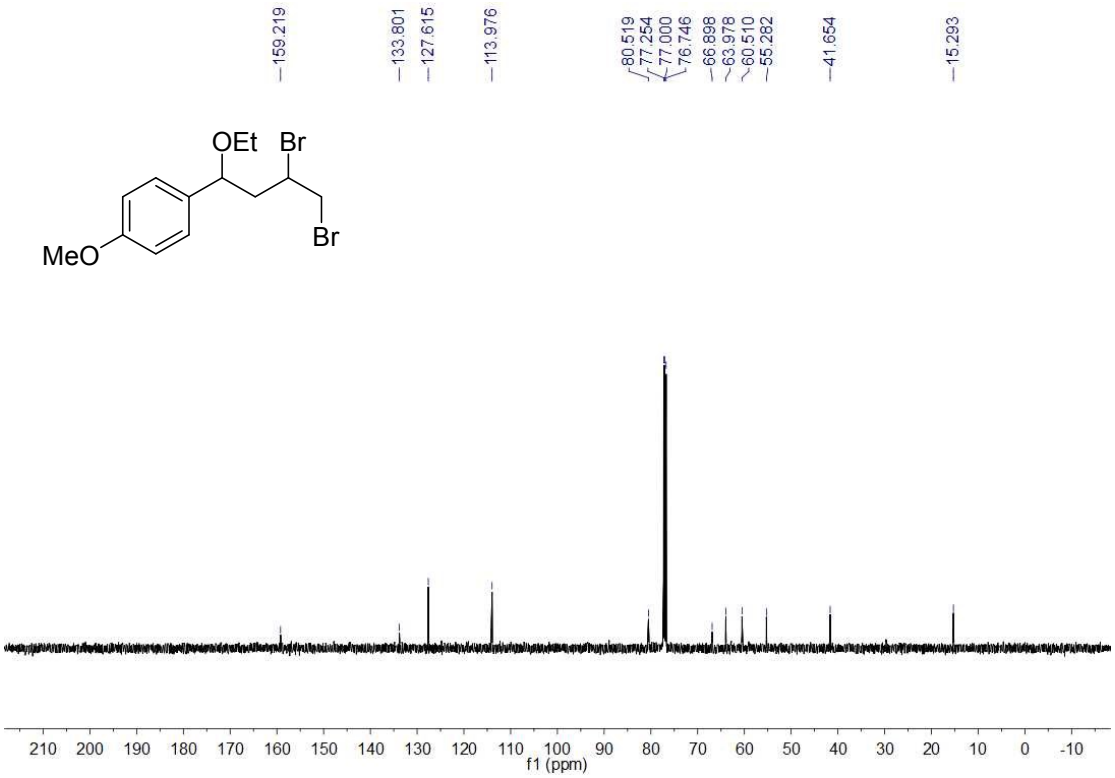
1-Methoxy-4-(3,3,3-tribromo-1-ethoxypropyl)benzene (4afa)



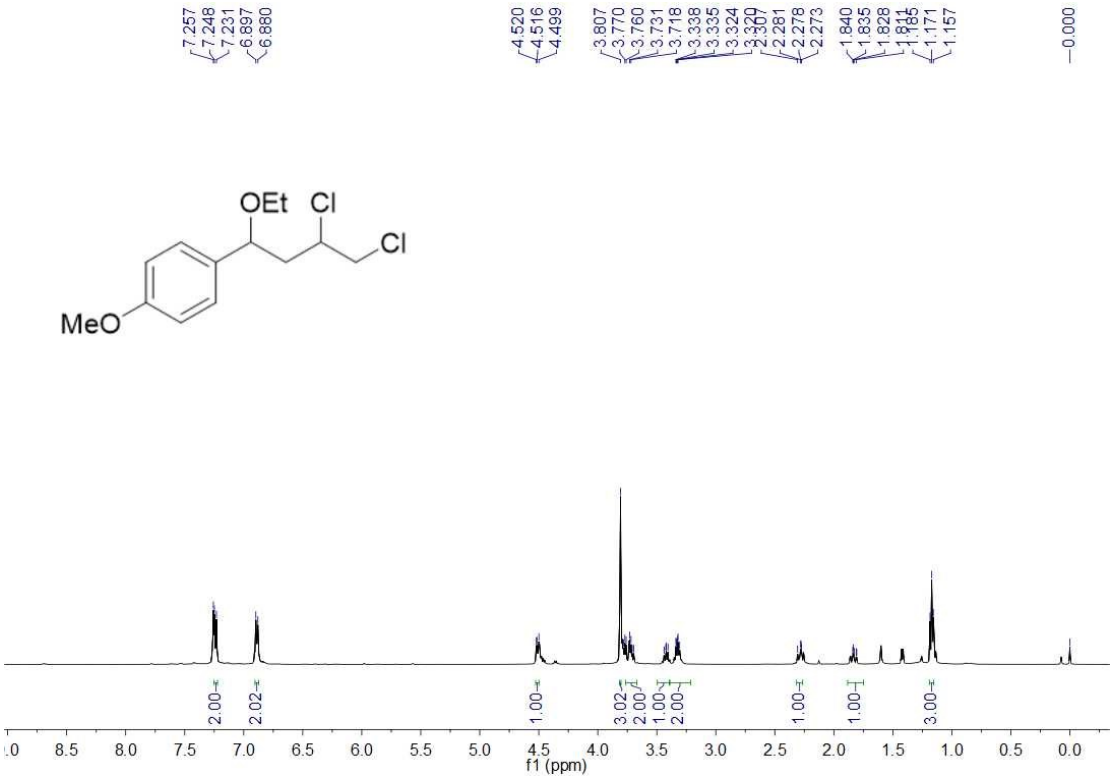


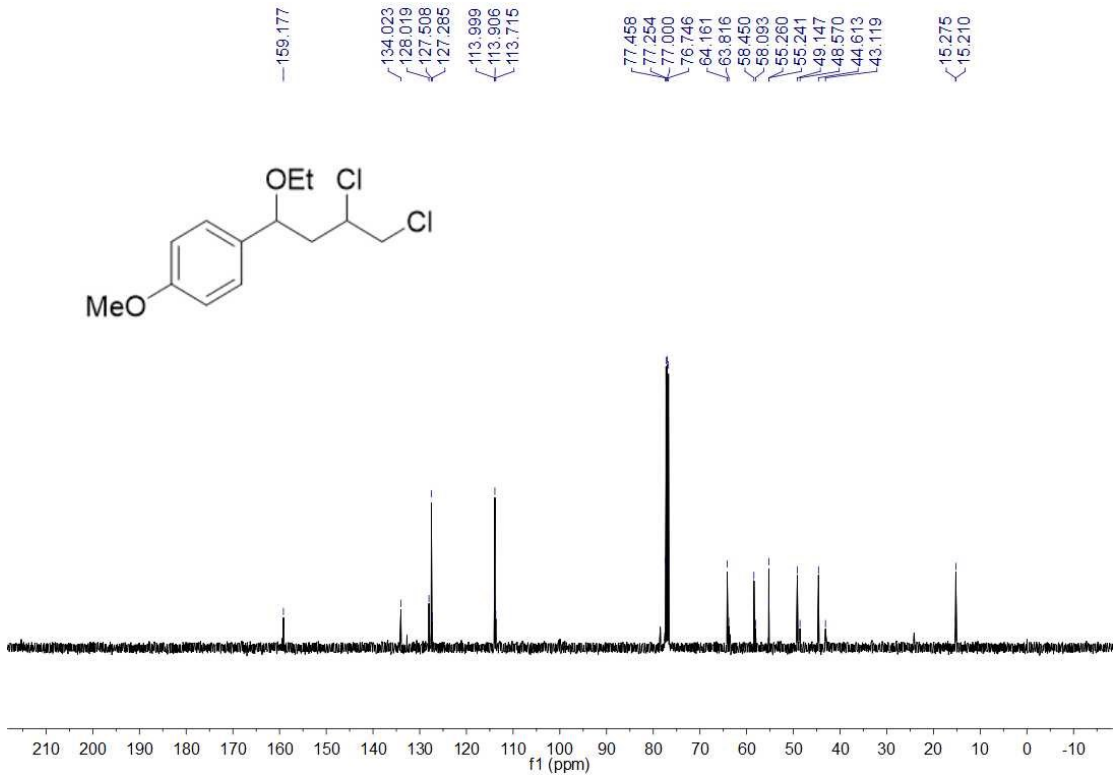
1-(3,4-Dibromo-1-ethoxybutyl)-4-methoxybenzene (4aia)



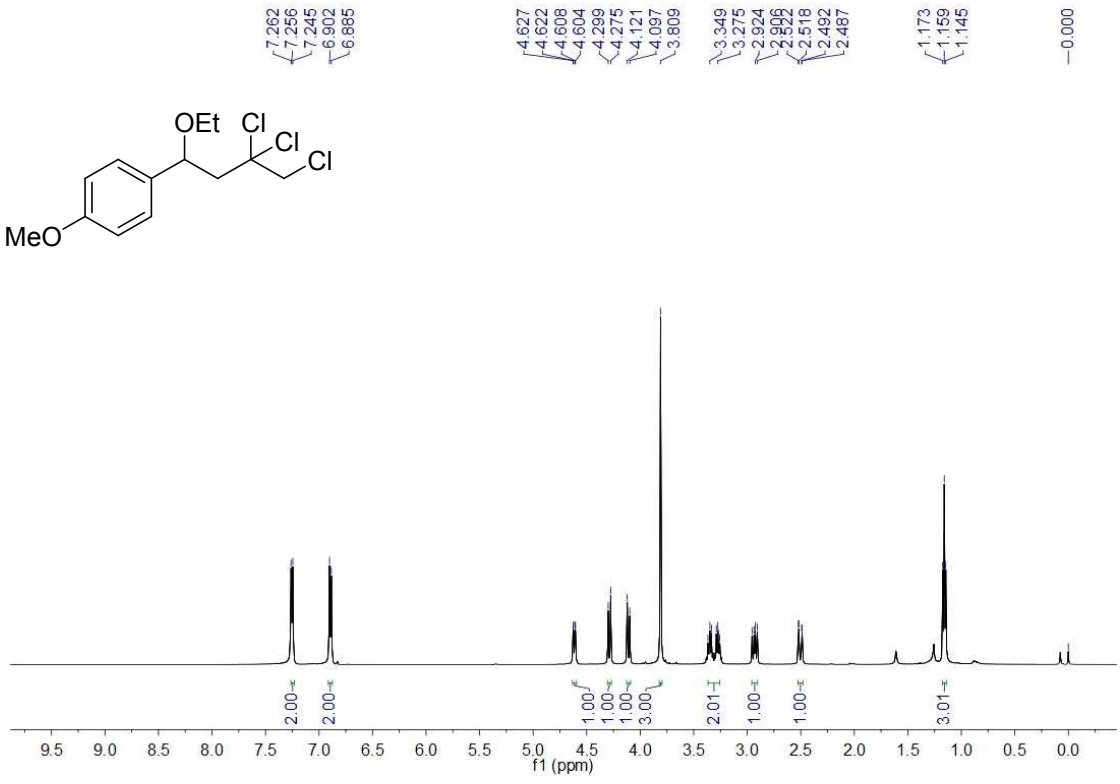


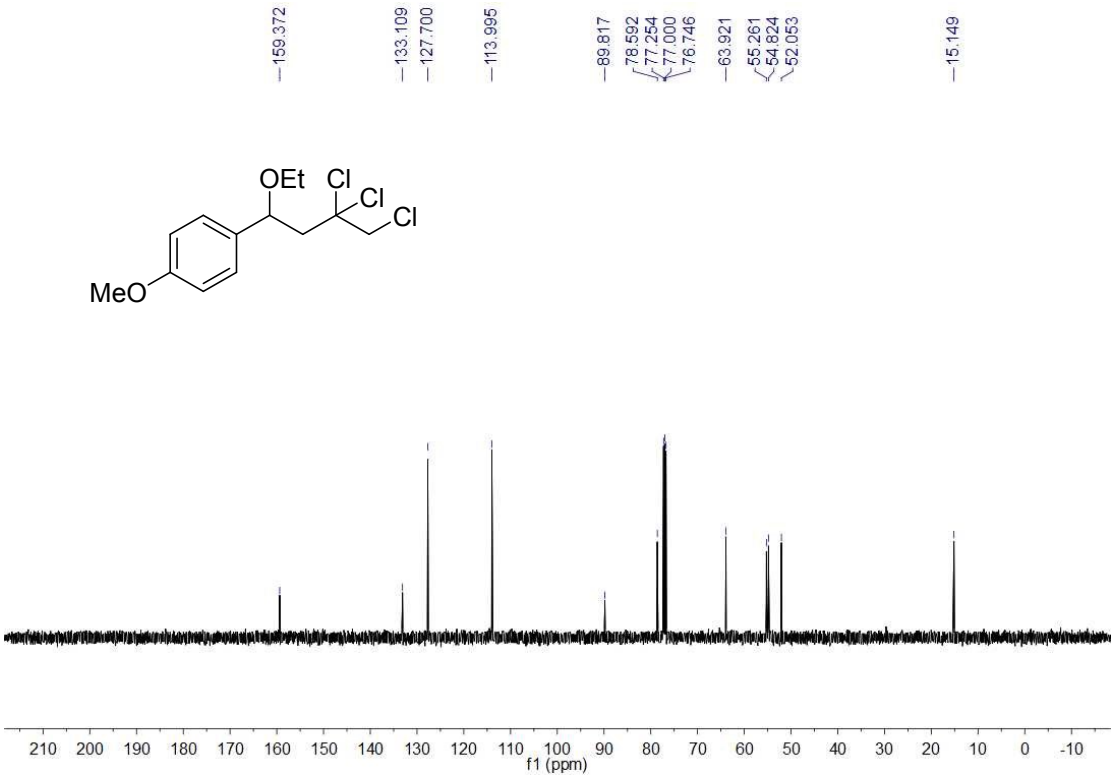
1-(3,4-Dichloro-1-ethoxybutyl)-4-methoxybenzene (4aja)



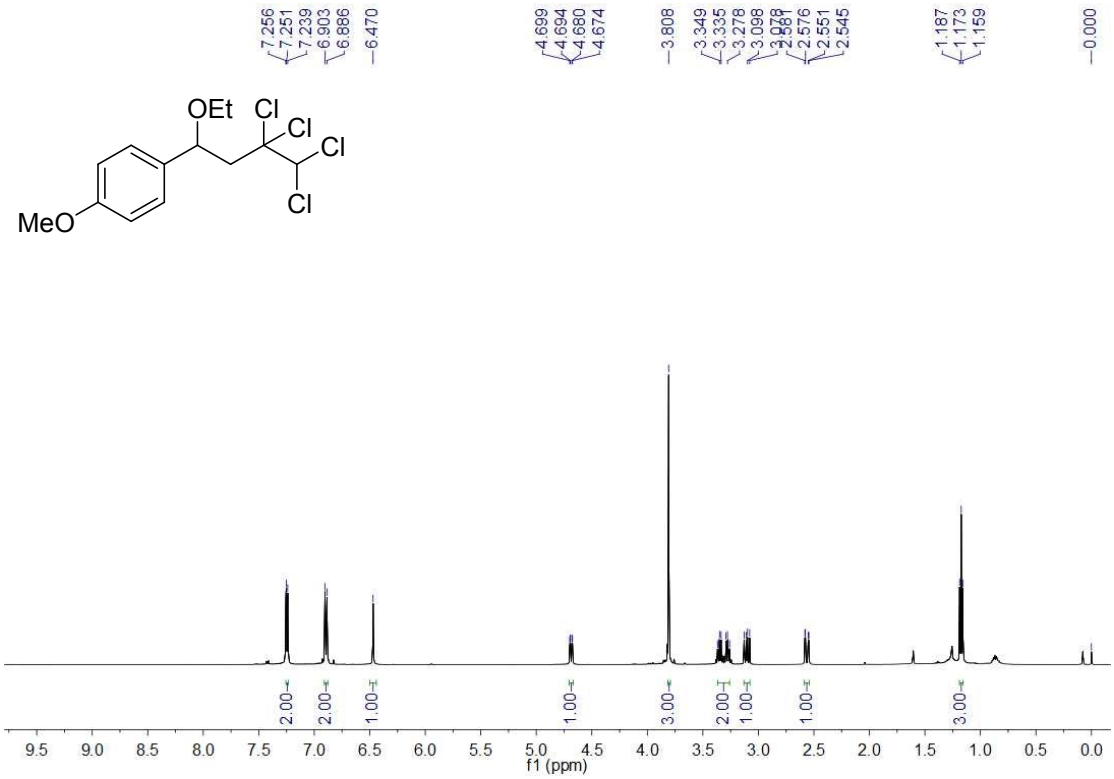


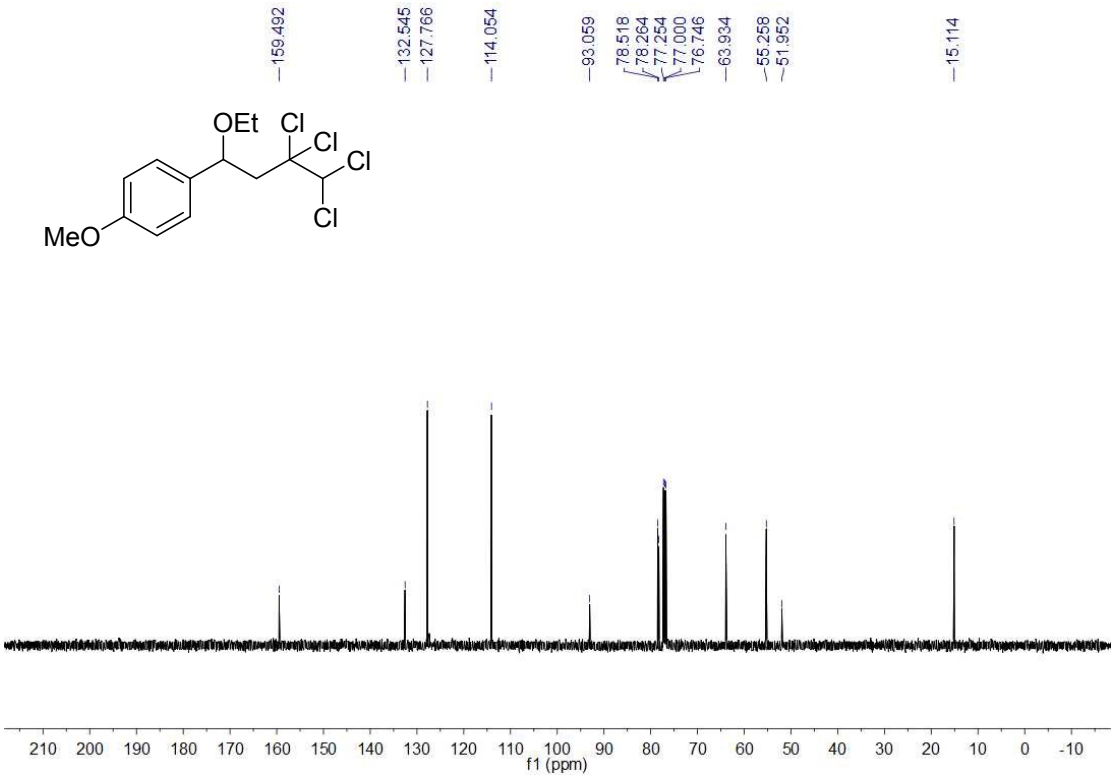
1-Methoxy-4-(3,4,4-trichloro-1-ethoxybutyl)benzene (4aka)



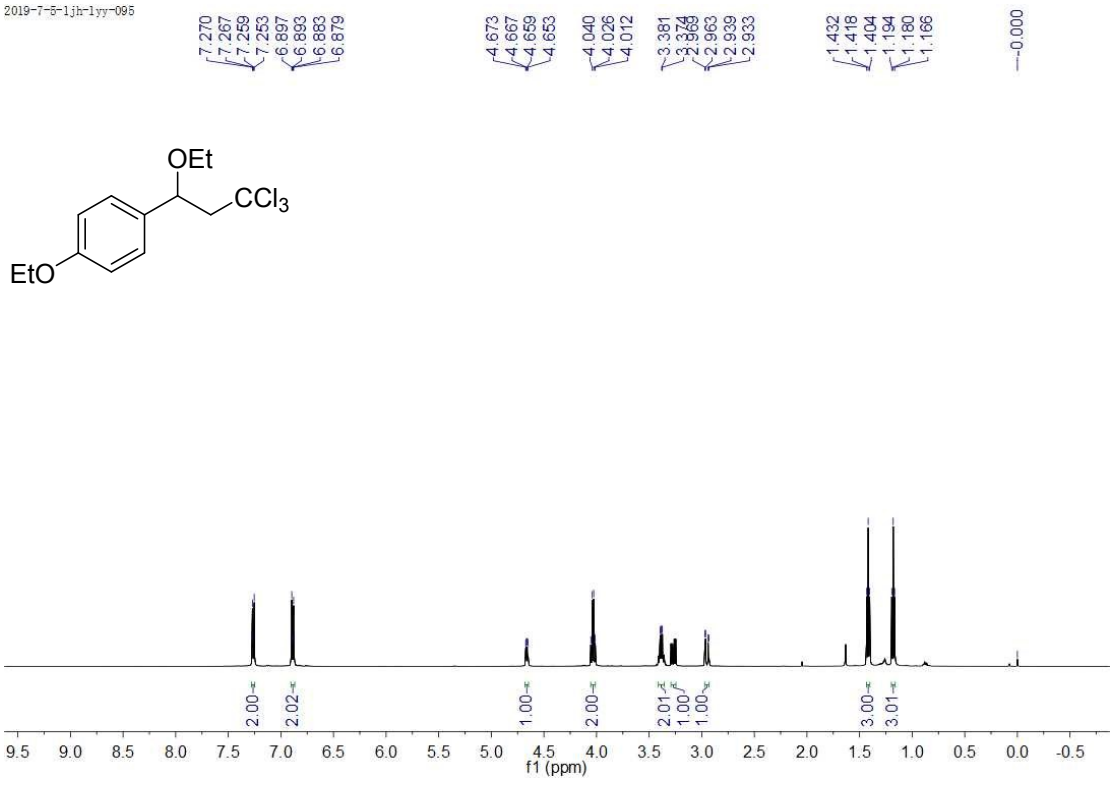


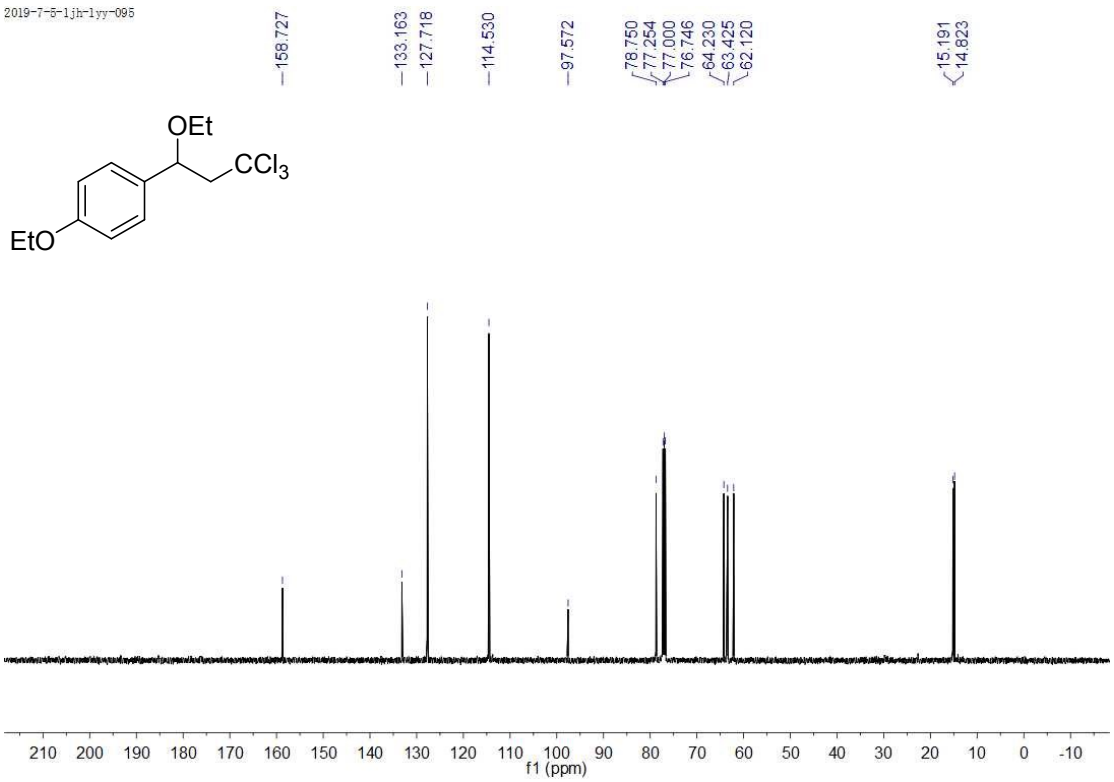
1-Methoxy-4-(3,3,4,4-tetrachloro-1-ethoxybutyl)benzene (4ala)



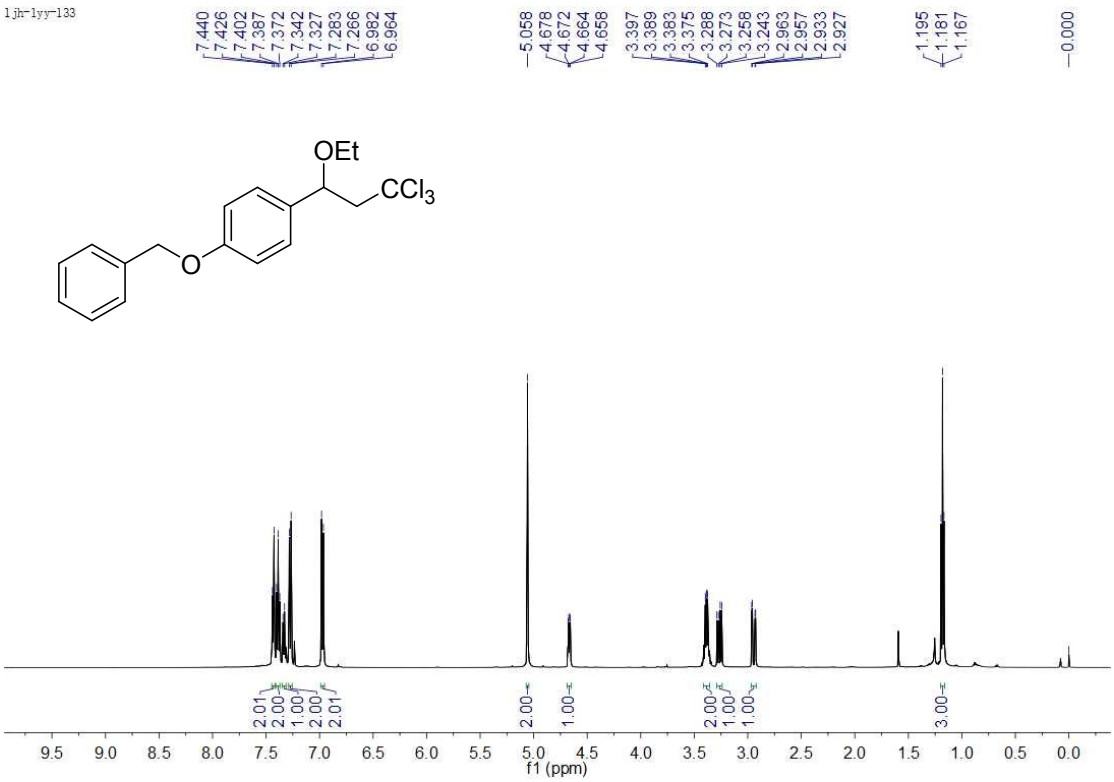


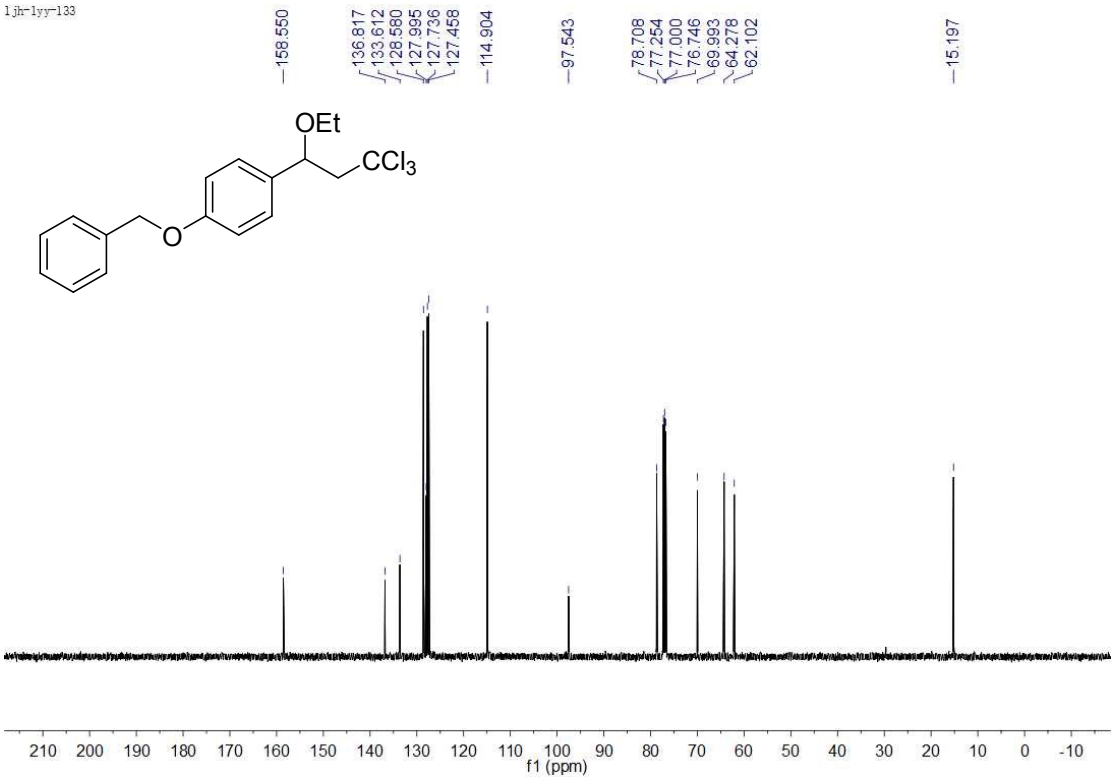
1-Ethoxy-4-(3,3,3-trichloro-1-ethoxypropyl)benzene (4baa)



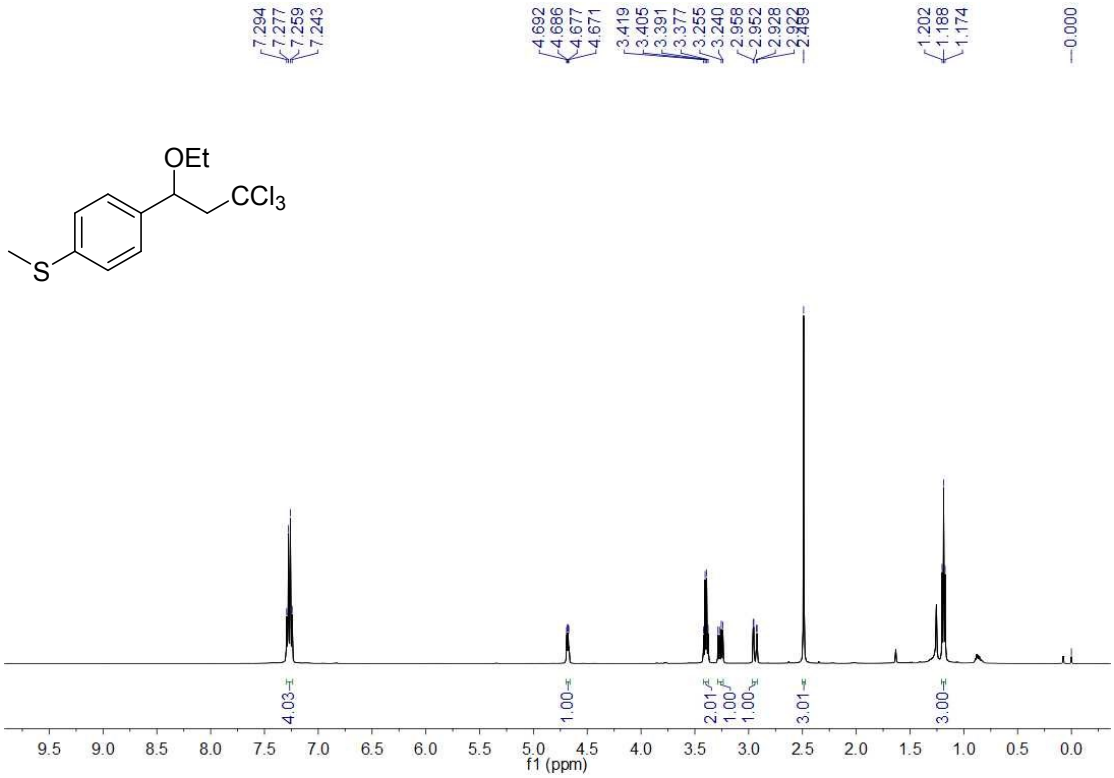


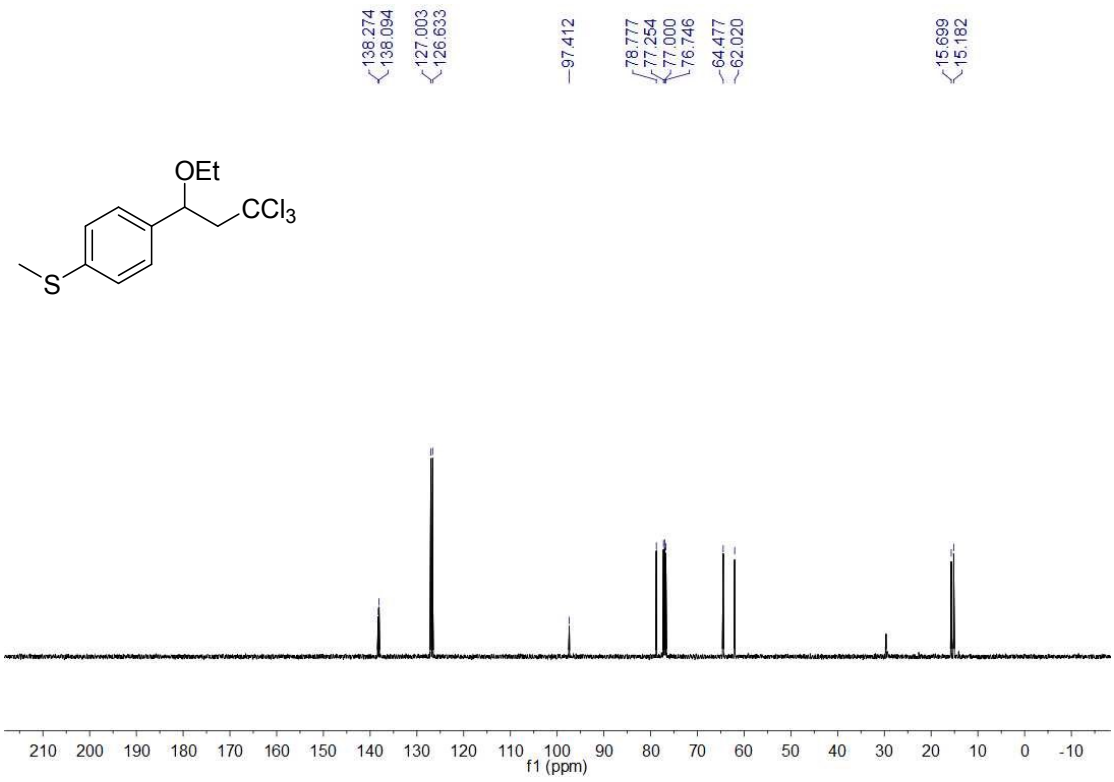
1-(Benzyloxy)-4-(3,3,3-trichloro-1-ethoxypropyl)benzene (4caa)



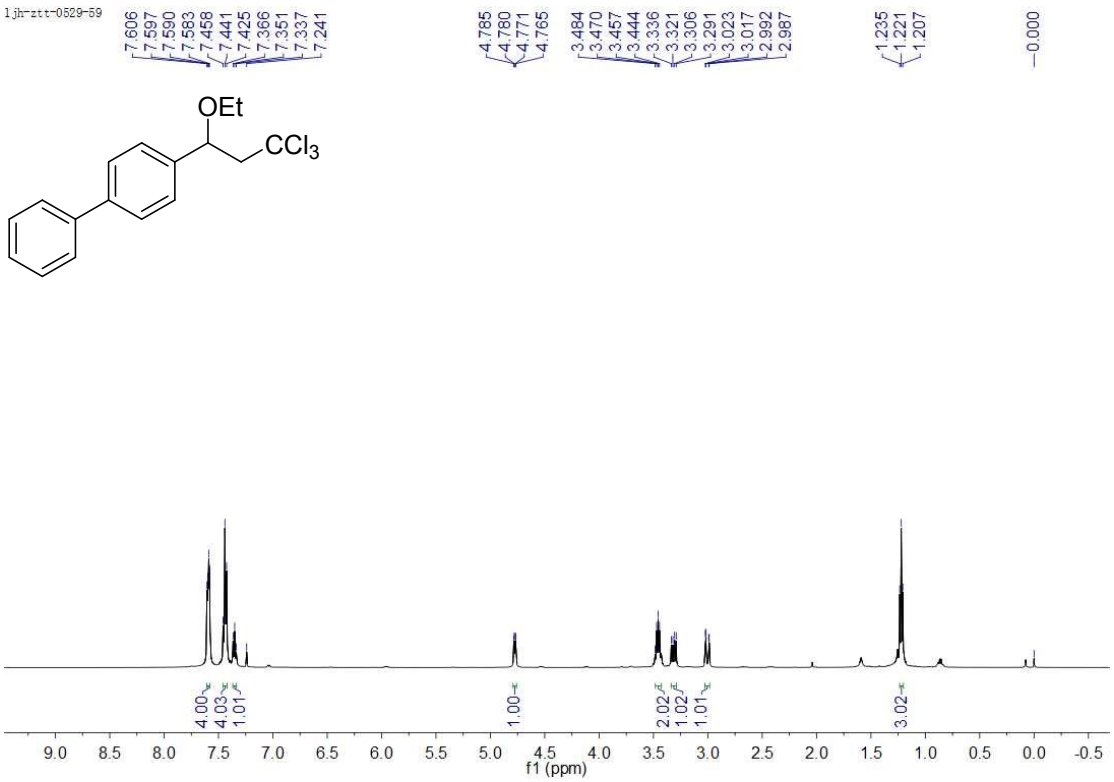


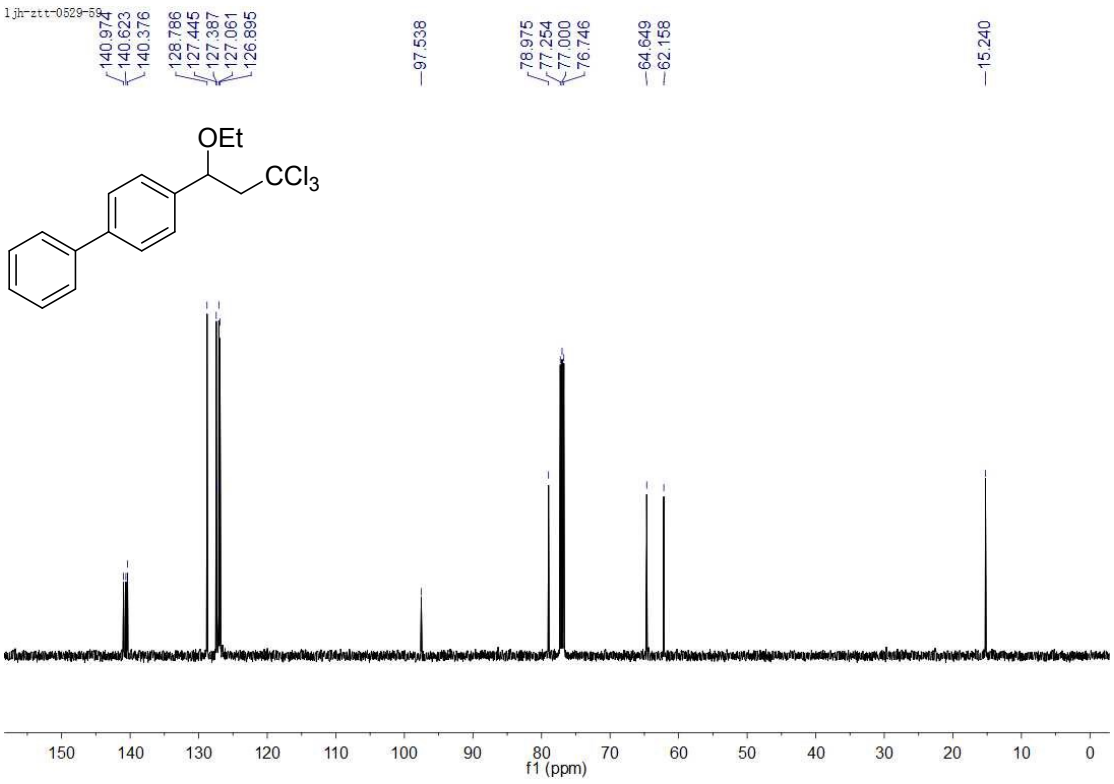
Methyl(4-(3,3,3-trichloro-1-ethoxypropyl)phenyl)sulfane (4daa)



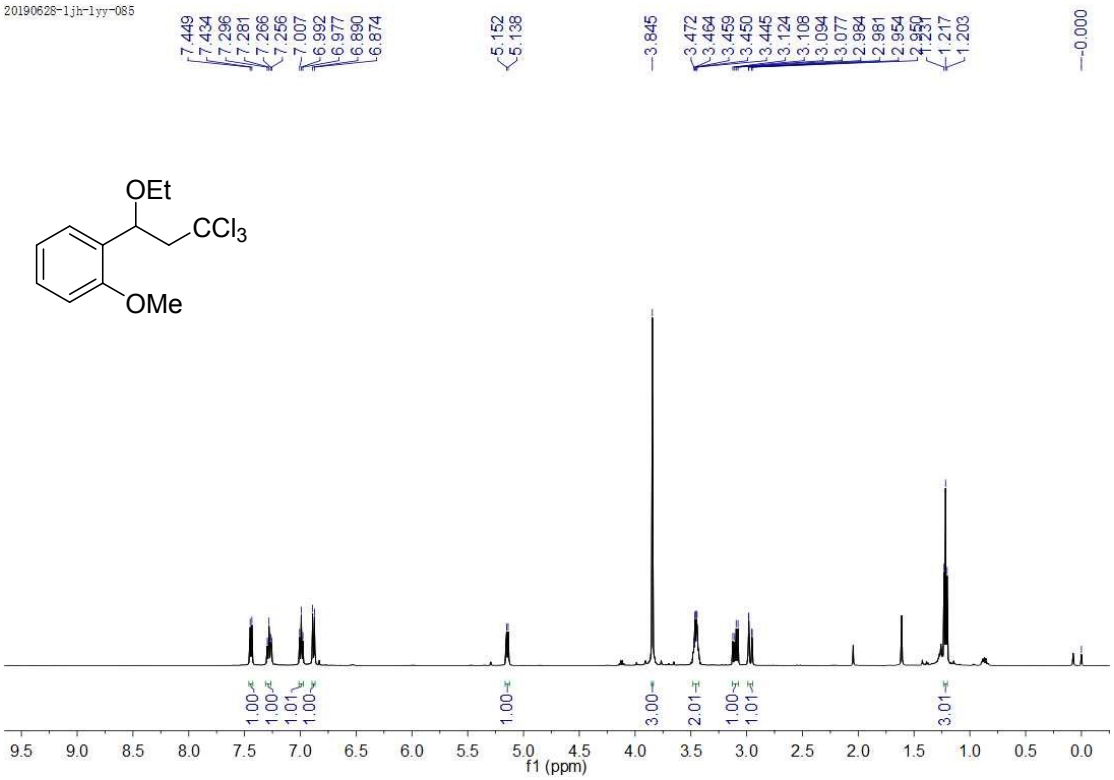


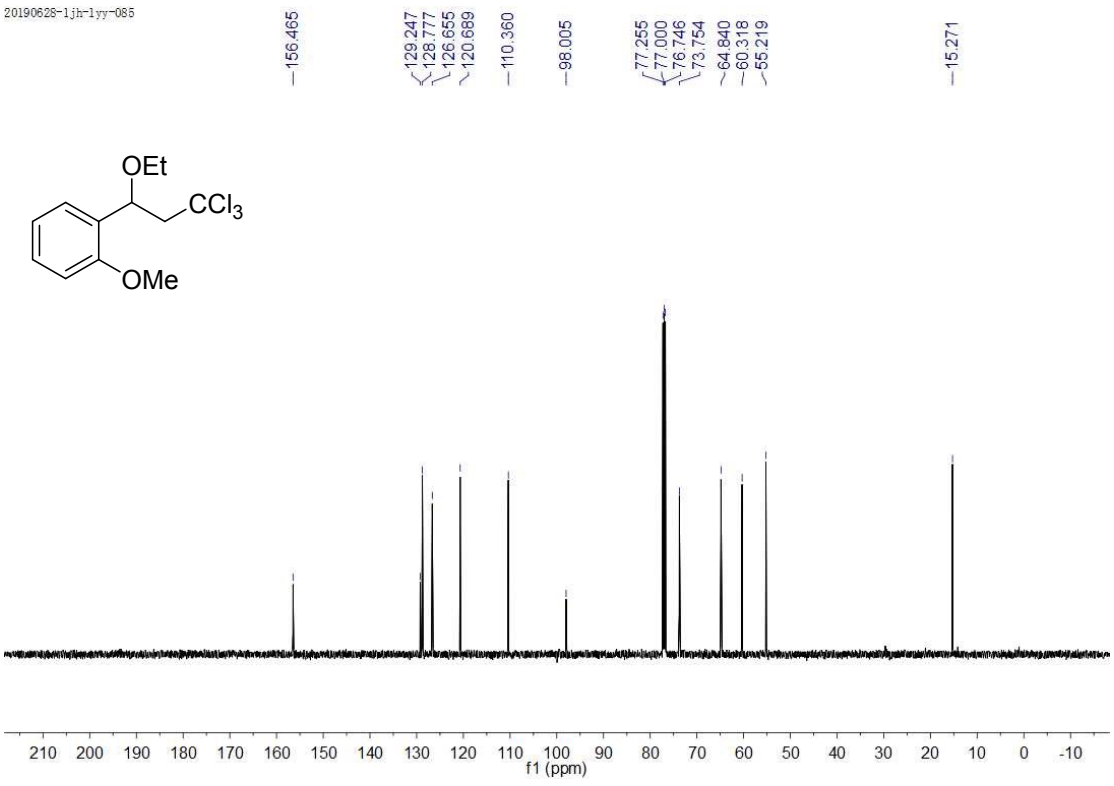
4-(3,3,3-Trichloro-1-ethoxypropyl)-1,1'-biphenyl (4eaa)



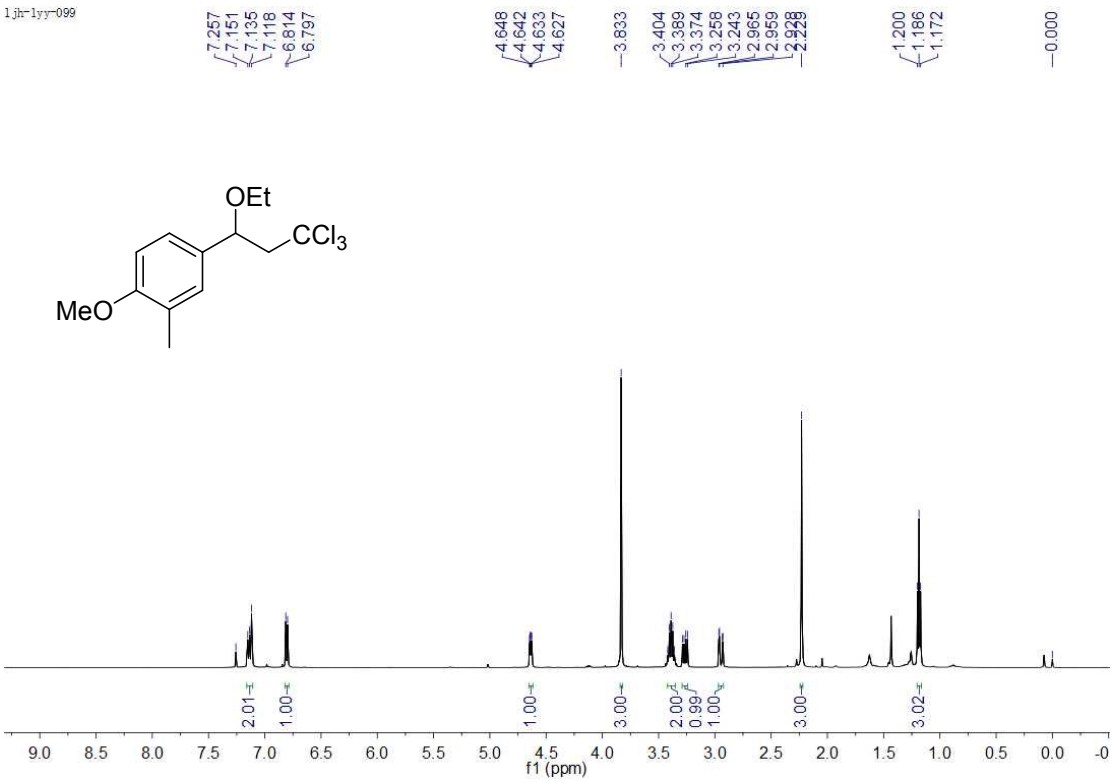


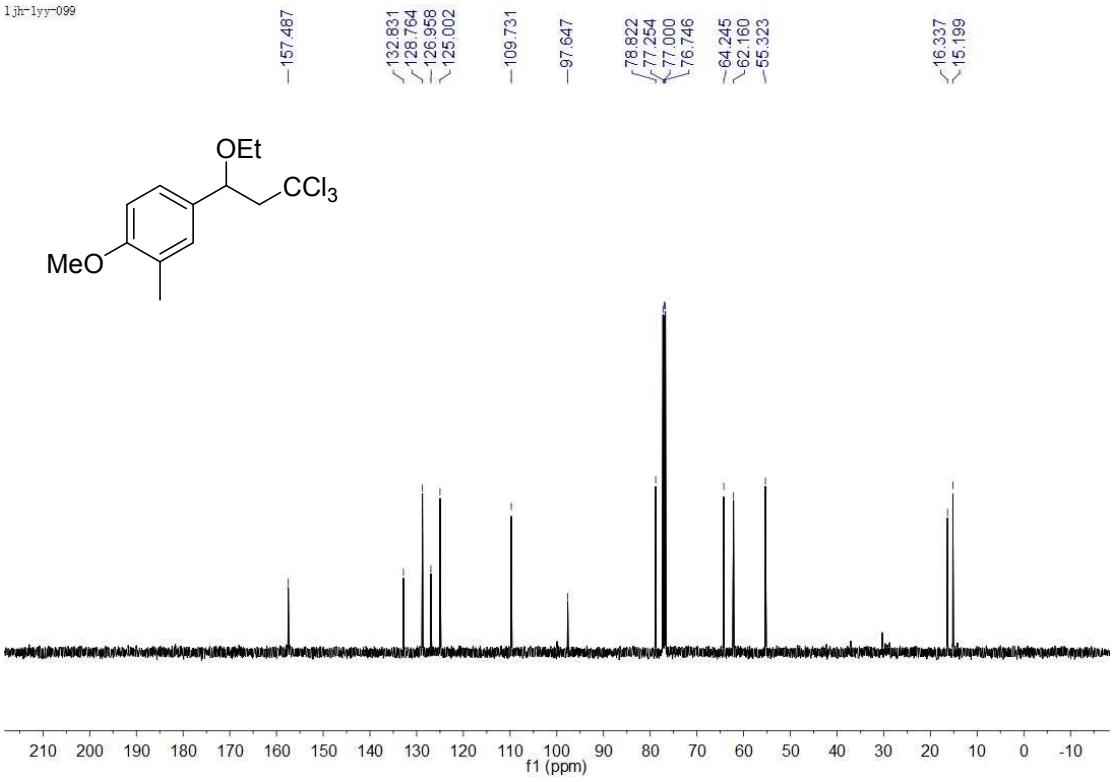
1-Methoxy-2-(3,3,3-trichloro-1-ethoxypropyl)benzene (4gaa)



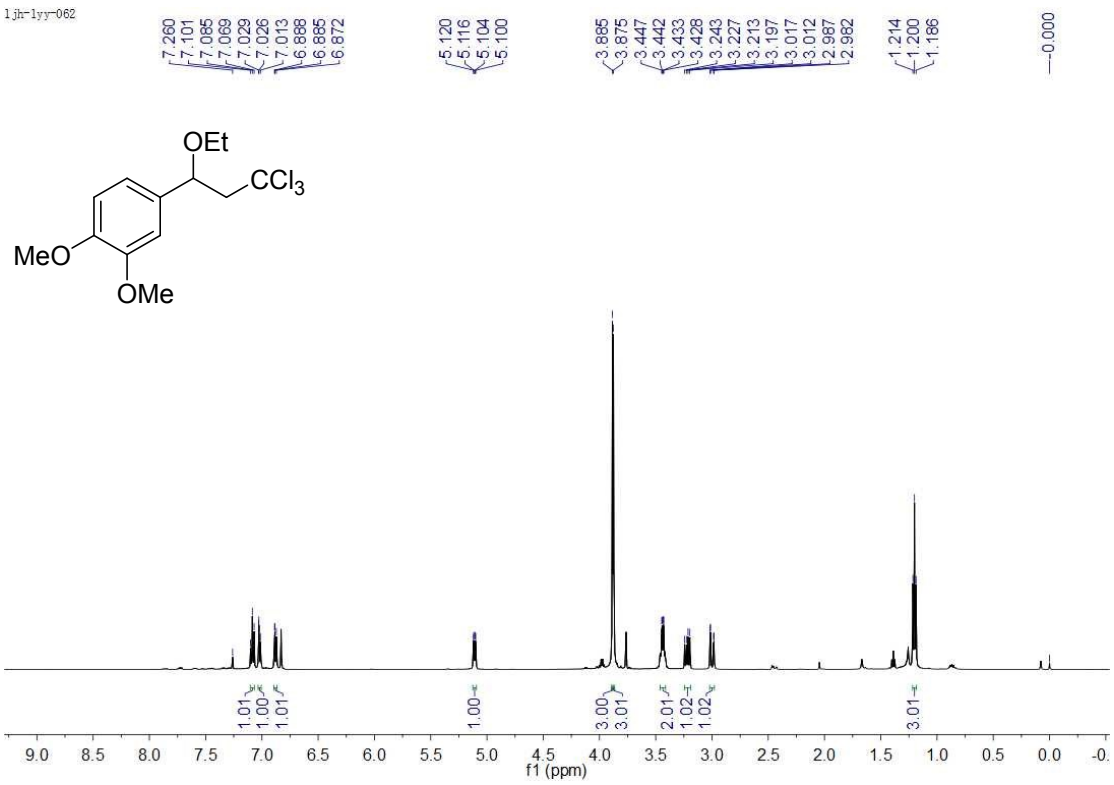


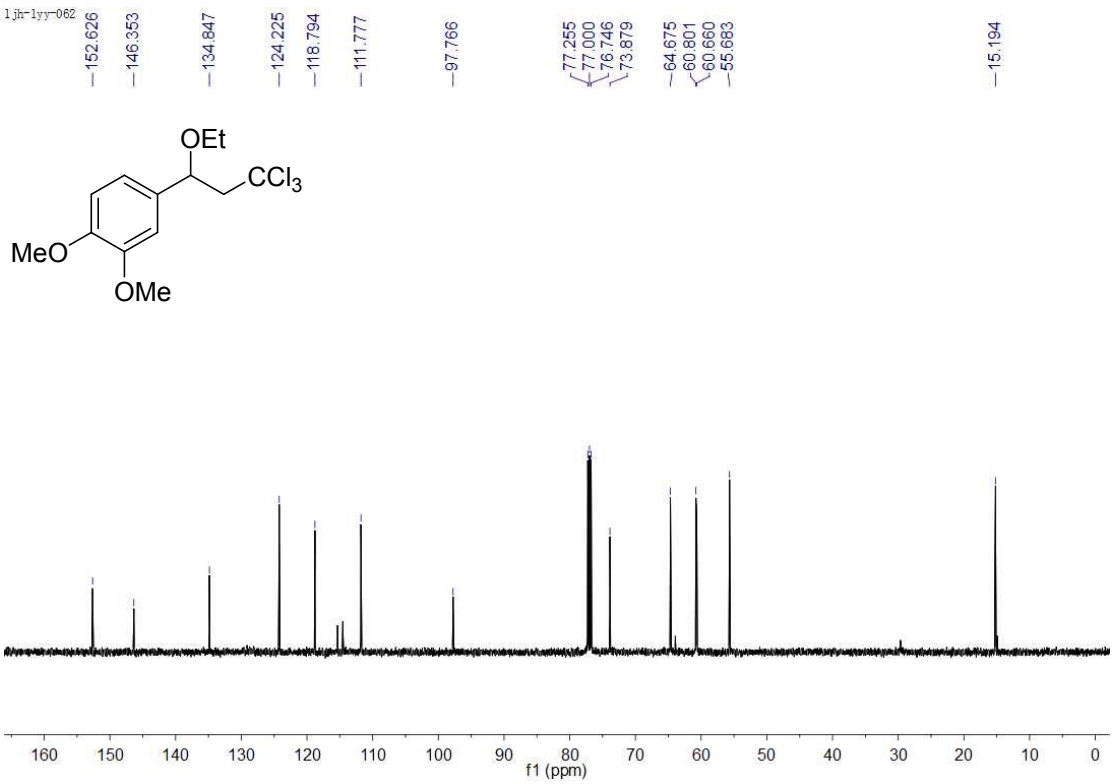
1-Methoxy-2-methyl-4-(3,3,3-trichloro-1-ethoxypropyl)benzene (4haa)



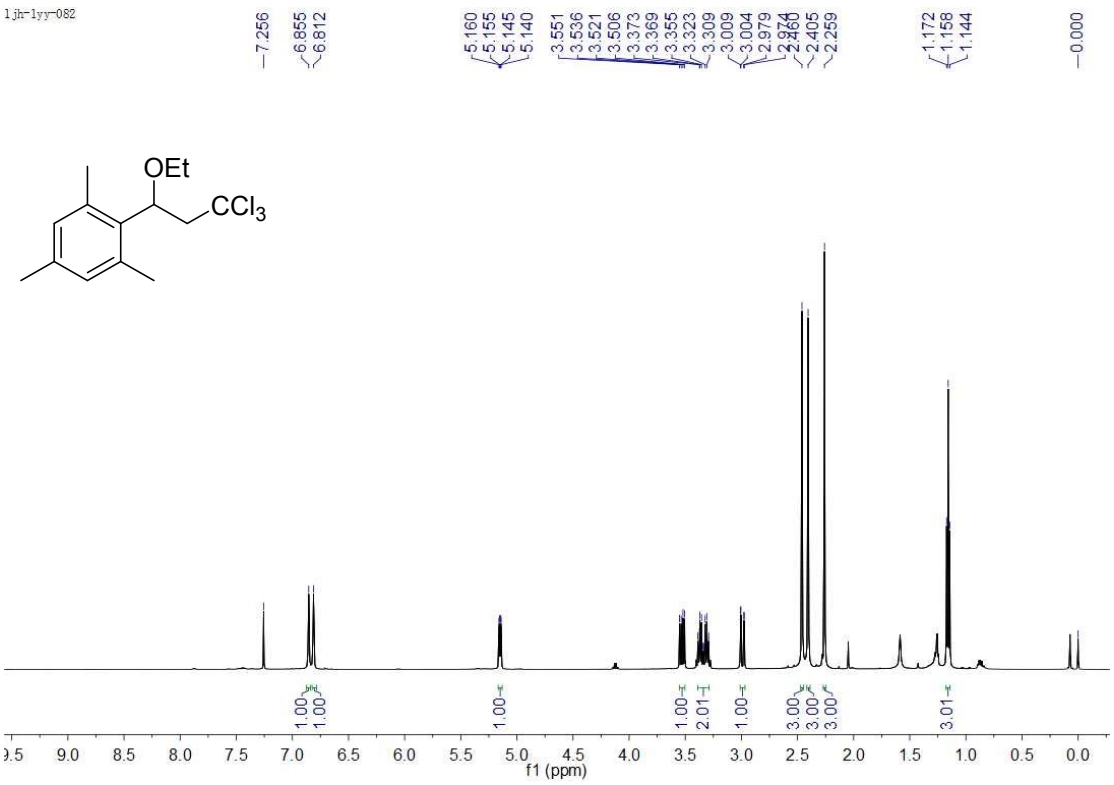


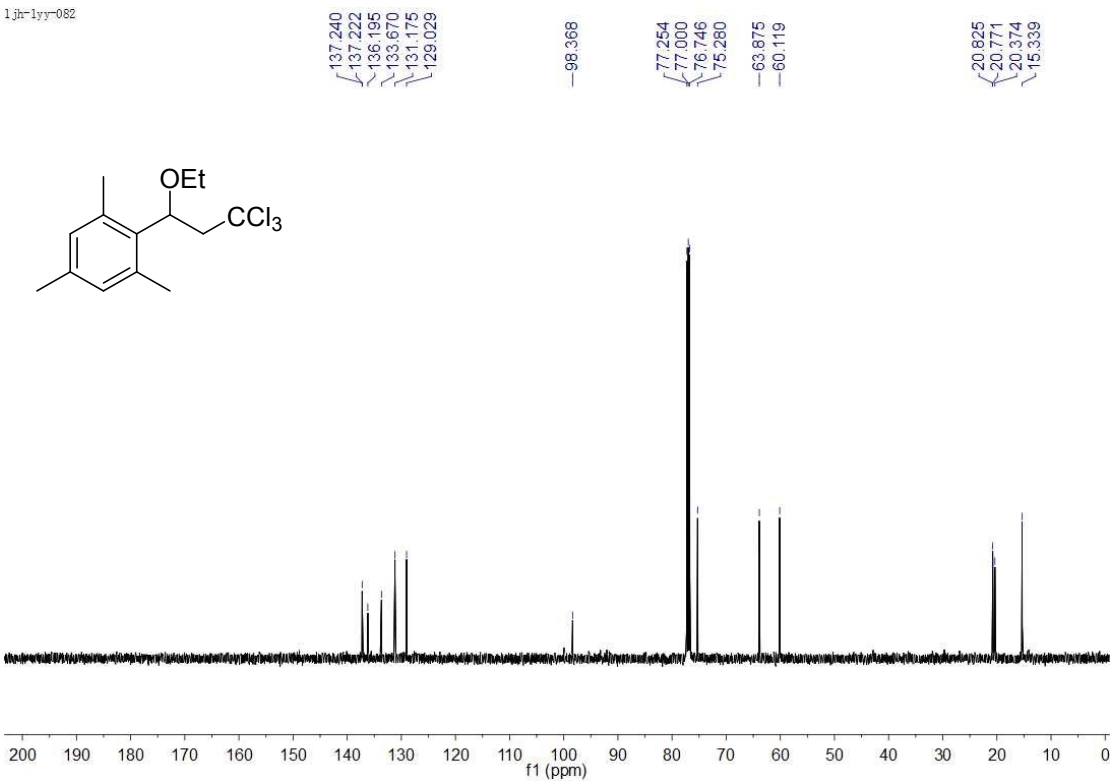
1,2-Dimethoxy-4-(3,3,3-trichloro-1-ethoxypropyl)benzene (4iaa)



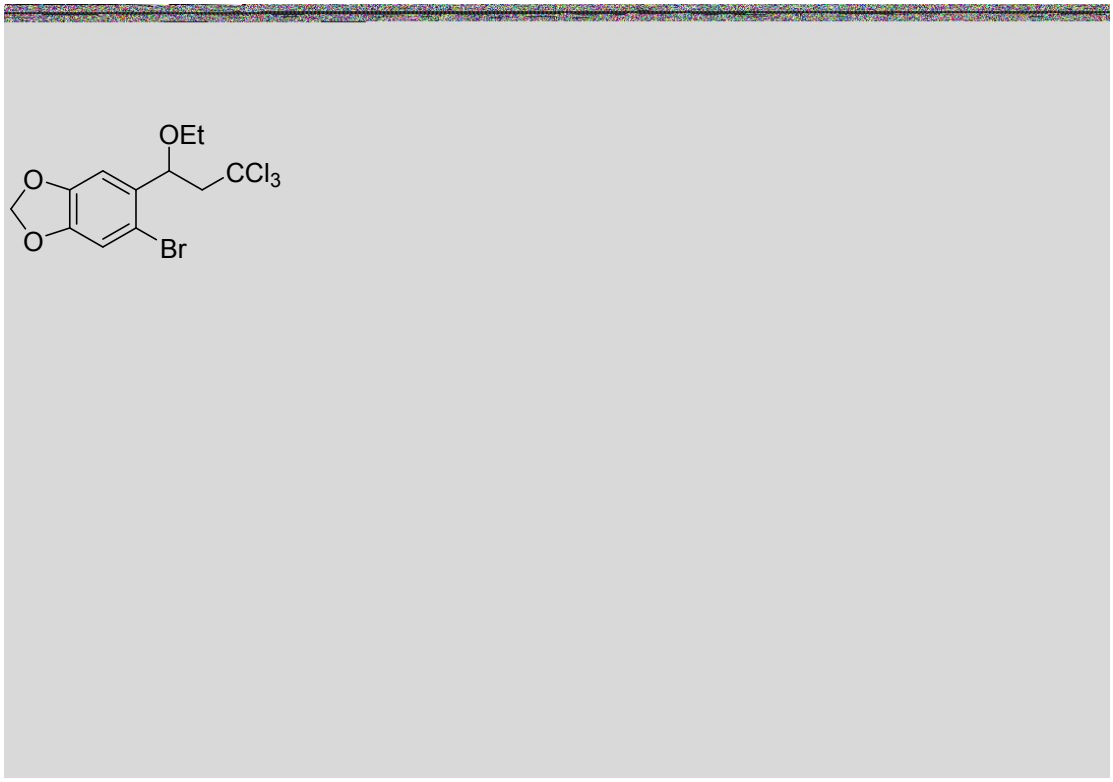


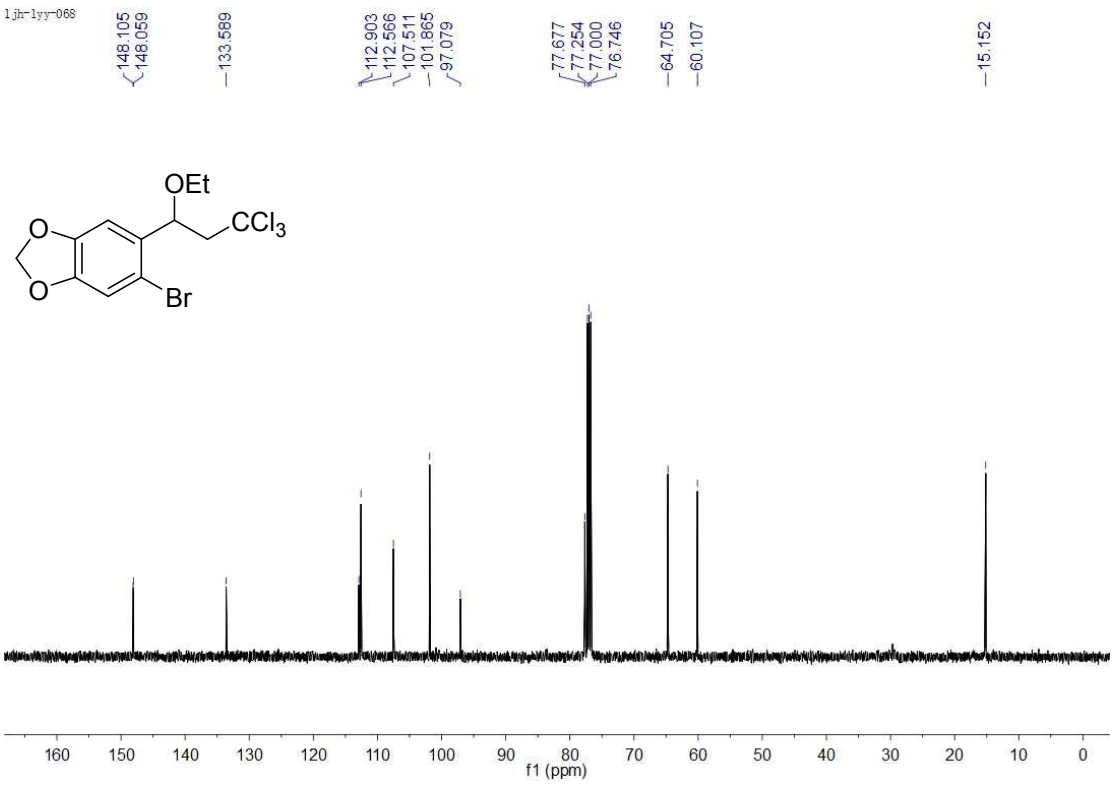
1,3,5-Trimethyl-2-(3,3,3-trichloro-1-ethoxypropyl)benzene (4jaa)



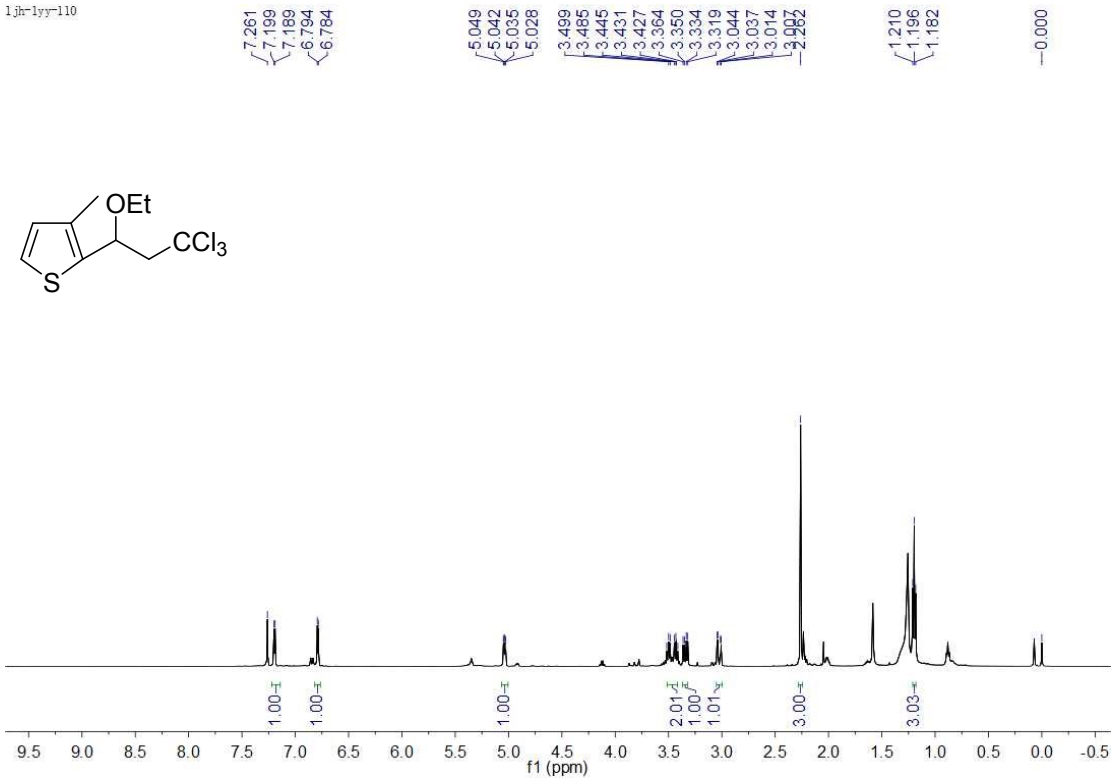


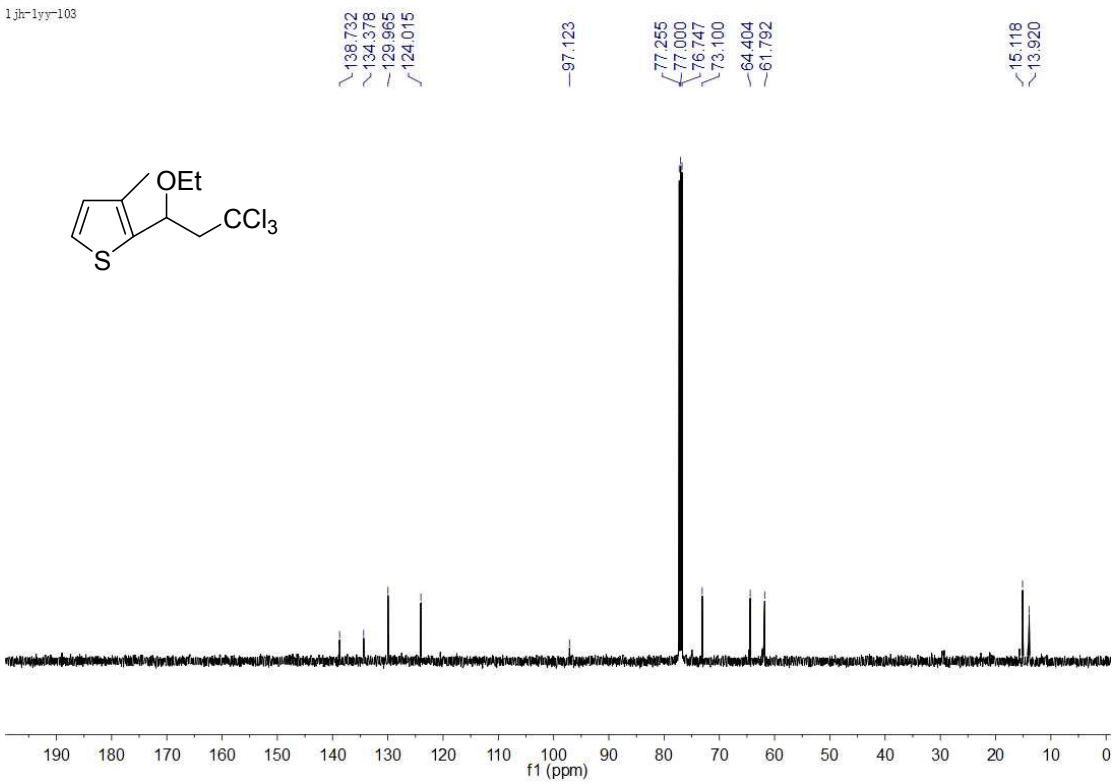
5-(3,3,3-Trichloro-1-ethoxypropyl)benzo[*d*][1,3]dioxole (4kaa)



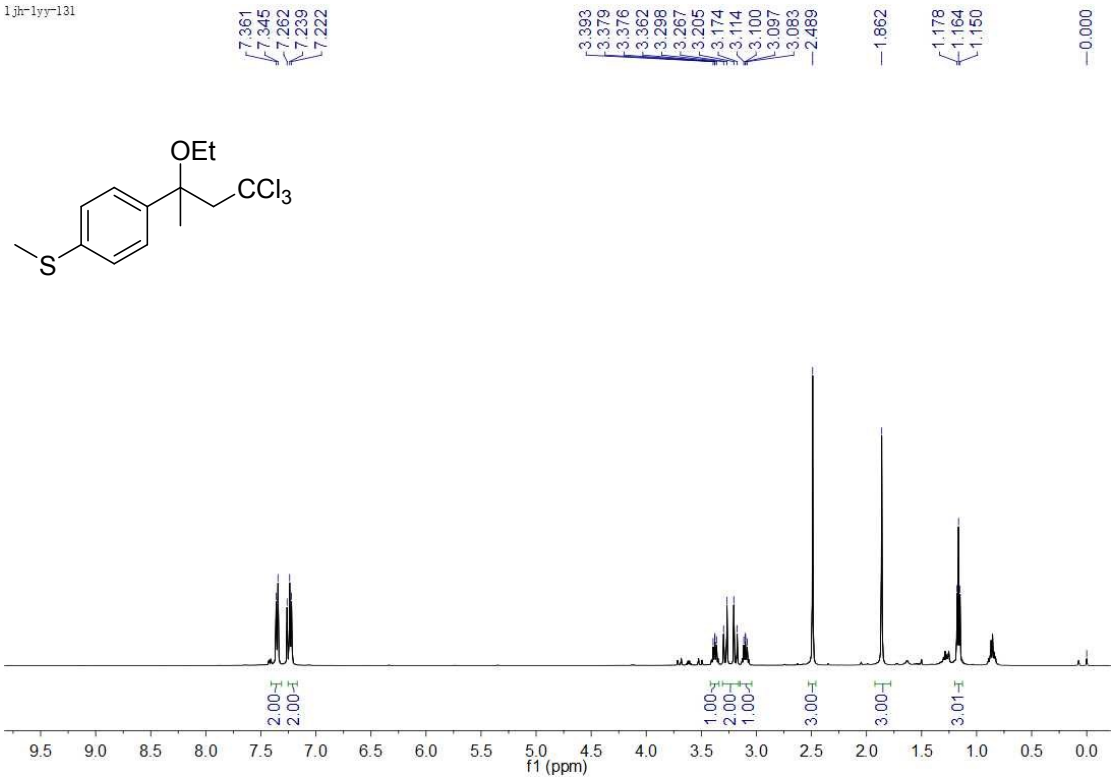


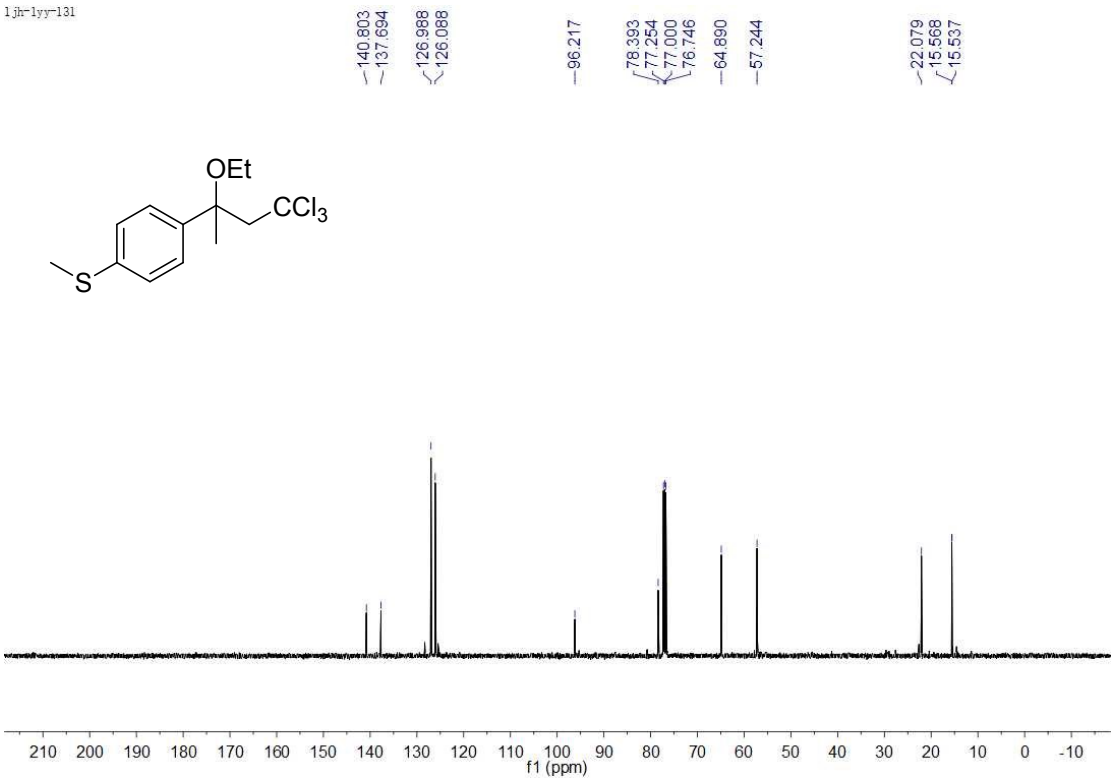
3-Methyl-2-(3,3,3-trichloro-1-ethoxypropyl)thiophene (4laa)



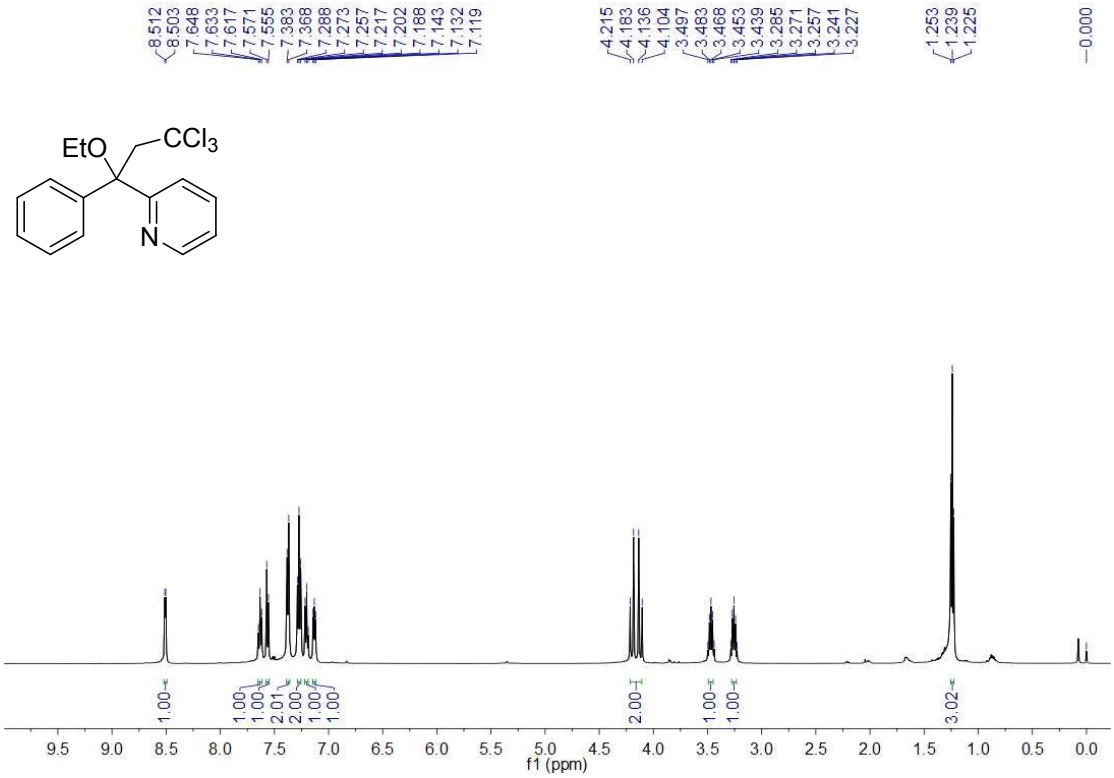


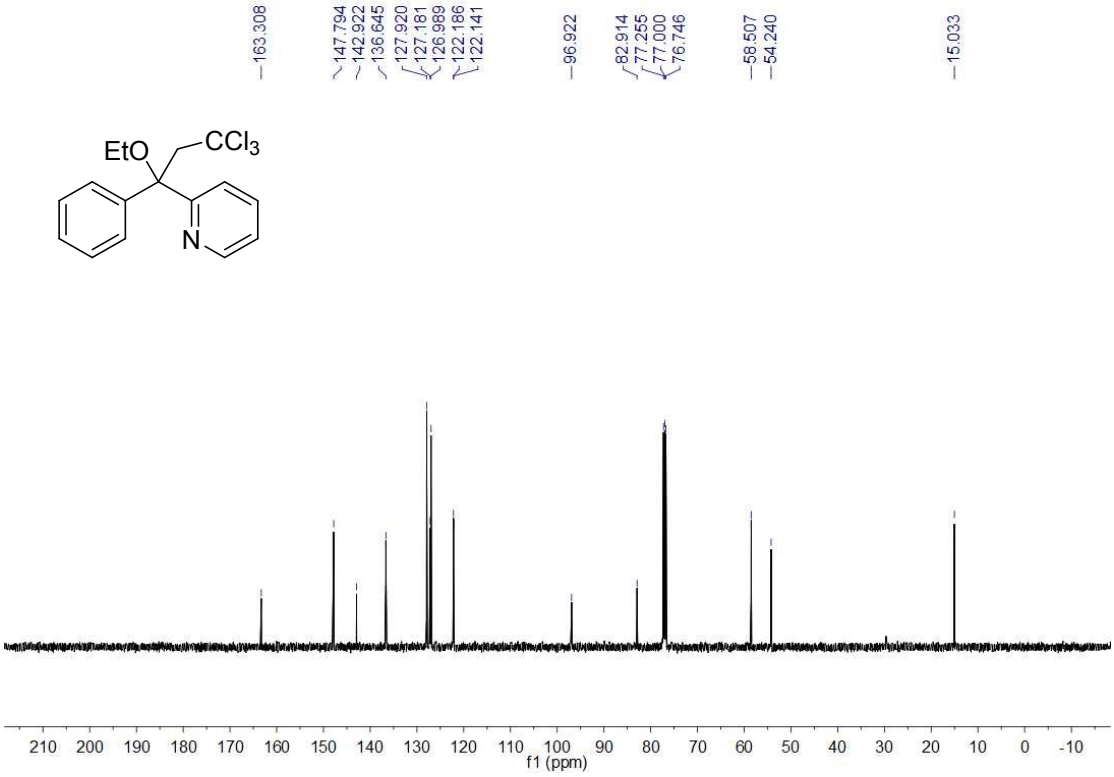
Methyl(4-(4,4,4-trichloro-2-ethoxybutan-2-yl)phenyl)sulfane (4naa)



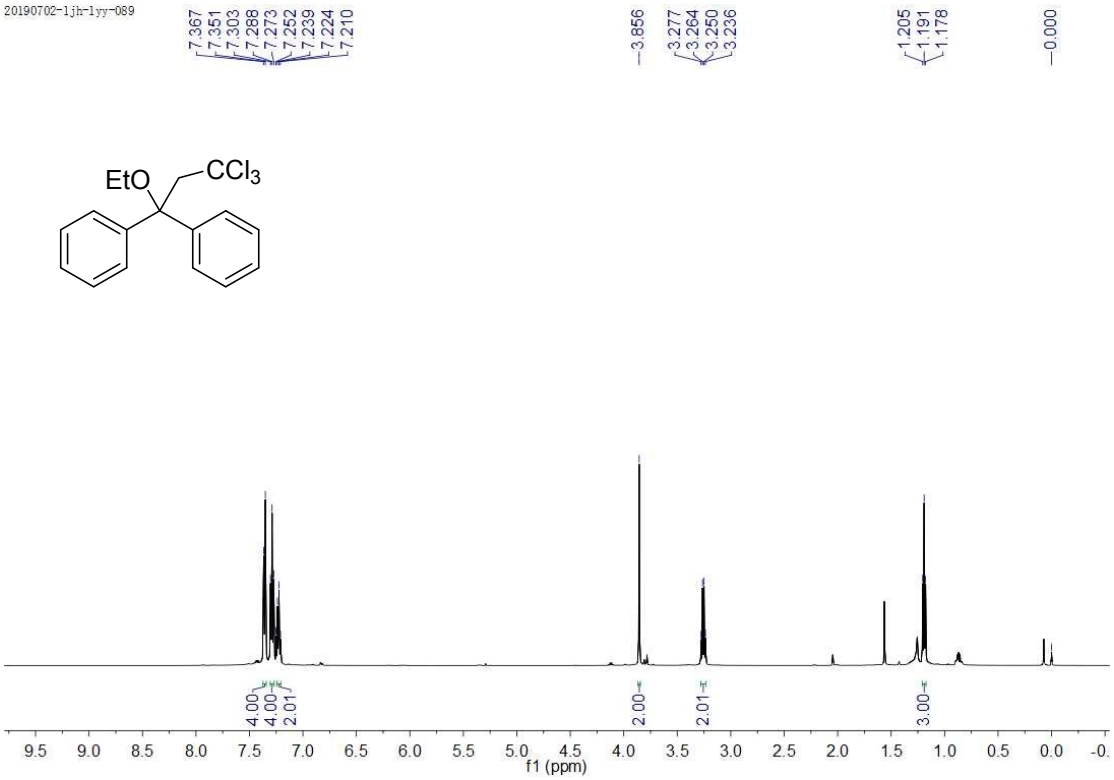


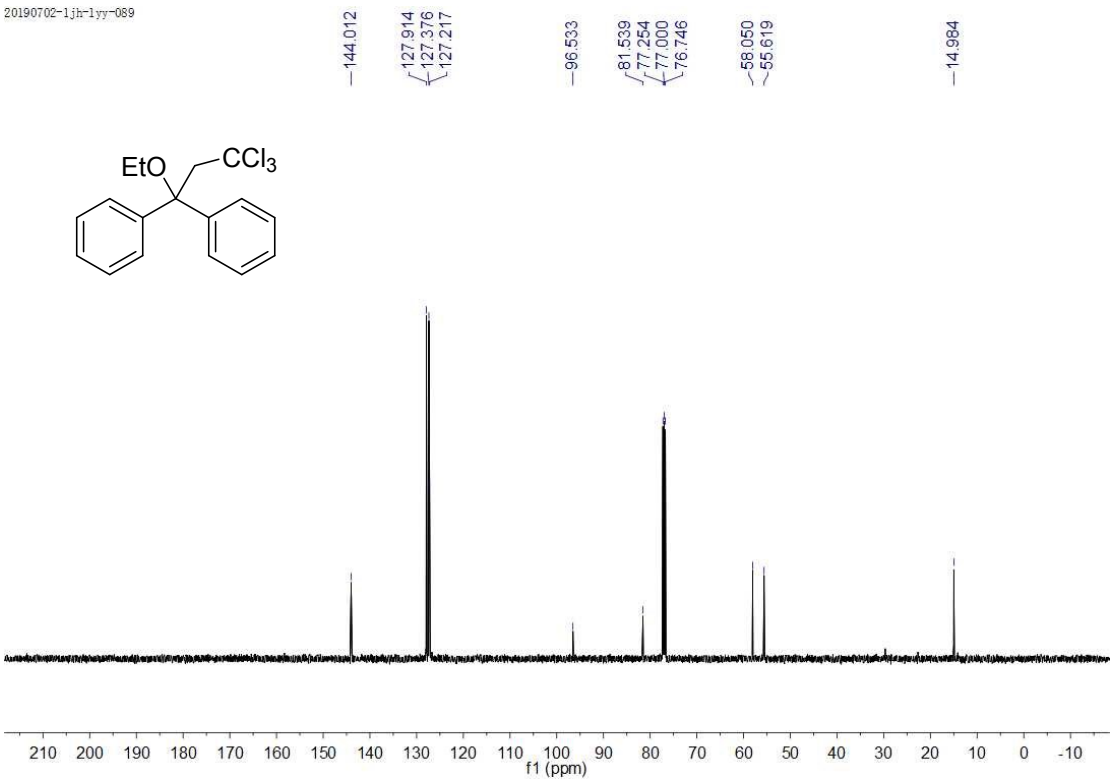
2-(3,3,3-Trichloro-1-ethoxy-1-phenylpropyl)pyridine (4oaa)



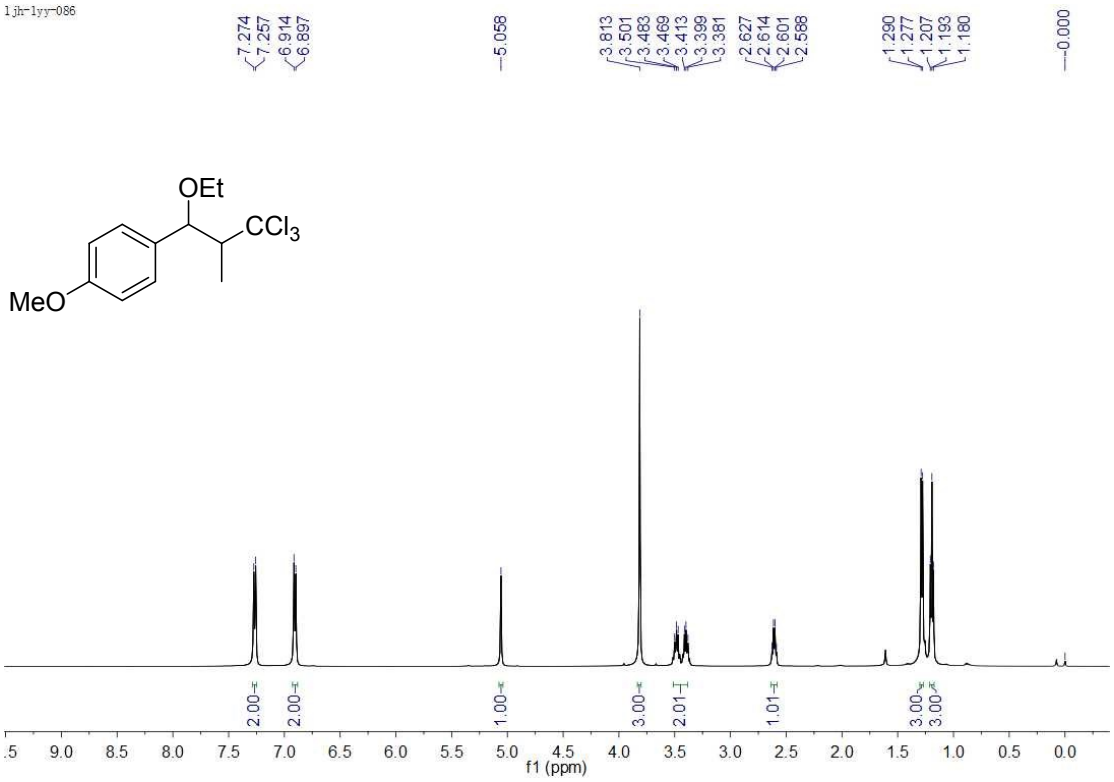


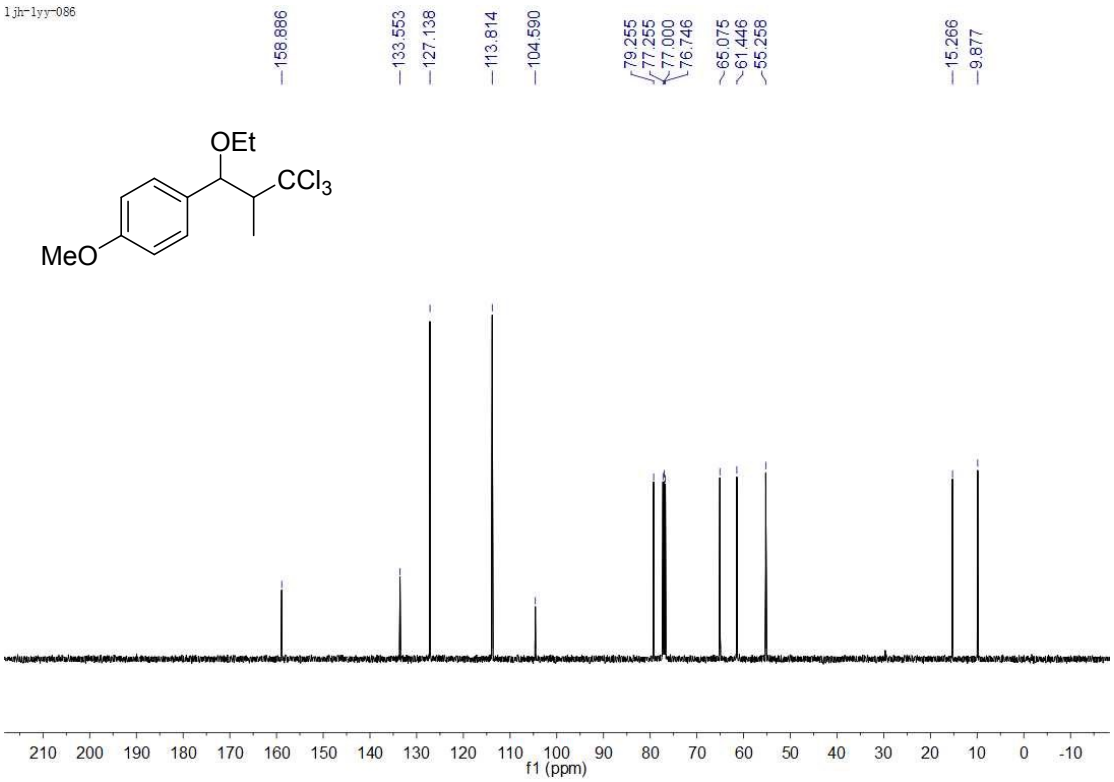
(3,3,3-Trichloro-1-ethoxypropane-1,1-diyl)dibenzene (4paa)



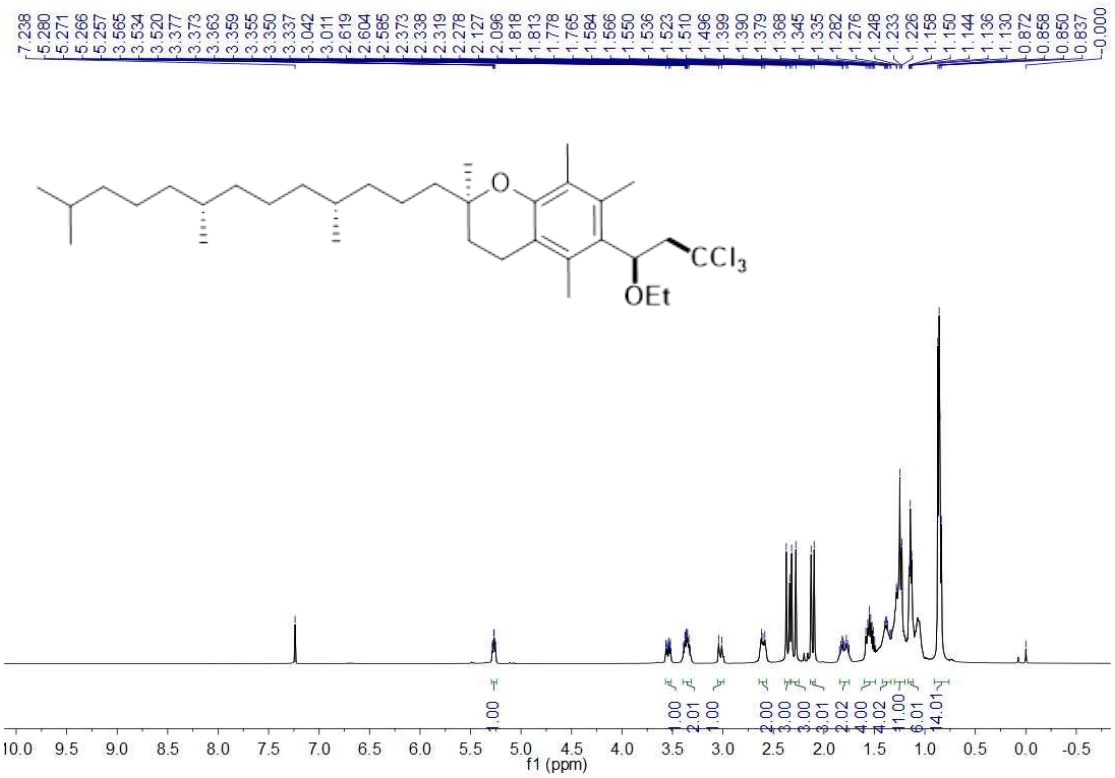


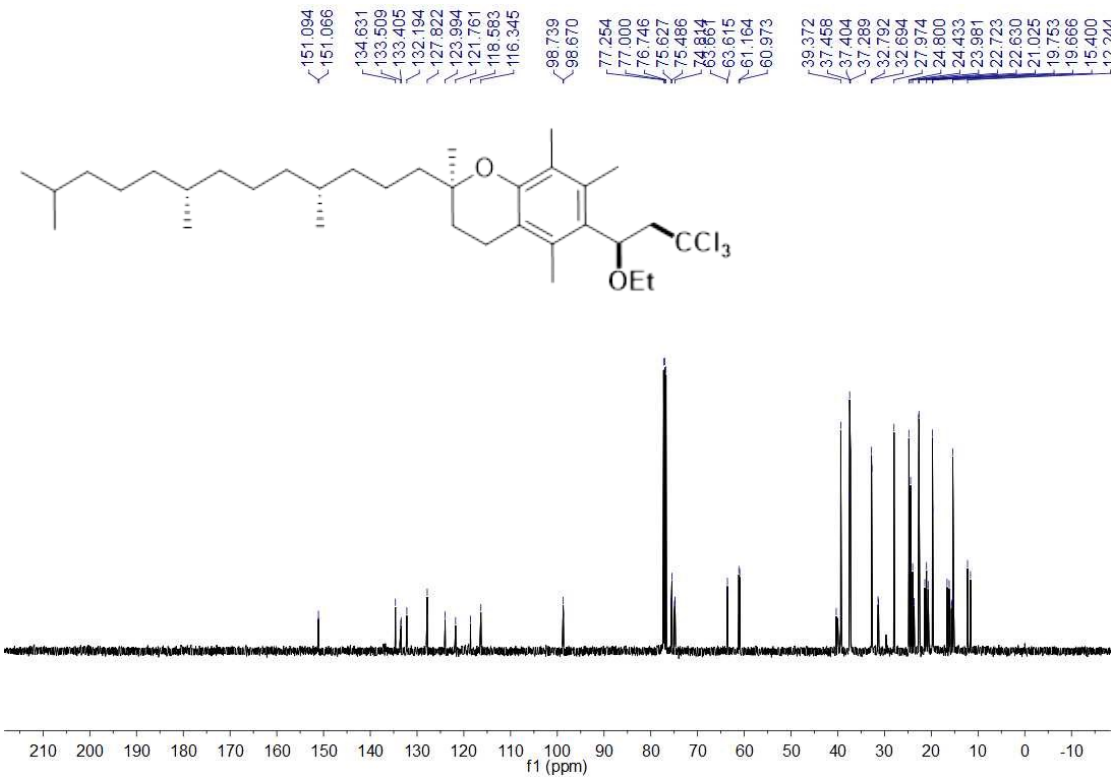
1-Methoxy-4-(3,3,3-trichloro-1-ethoxy-2-methylpropyl)benzene (4qaa)



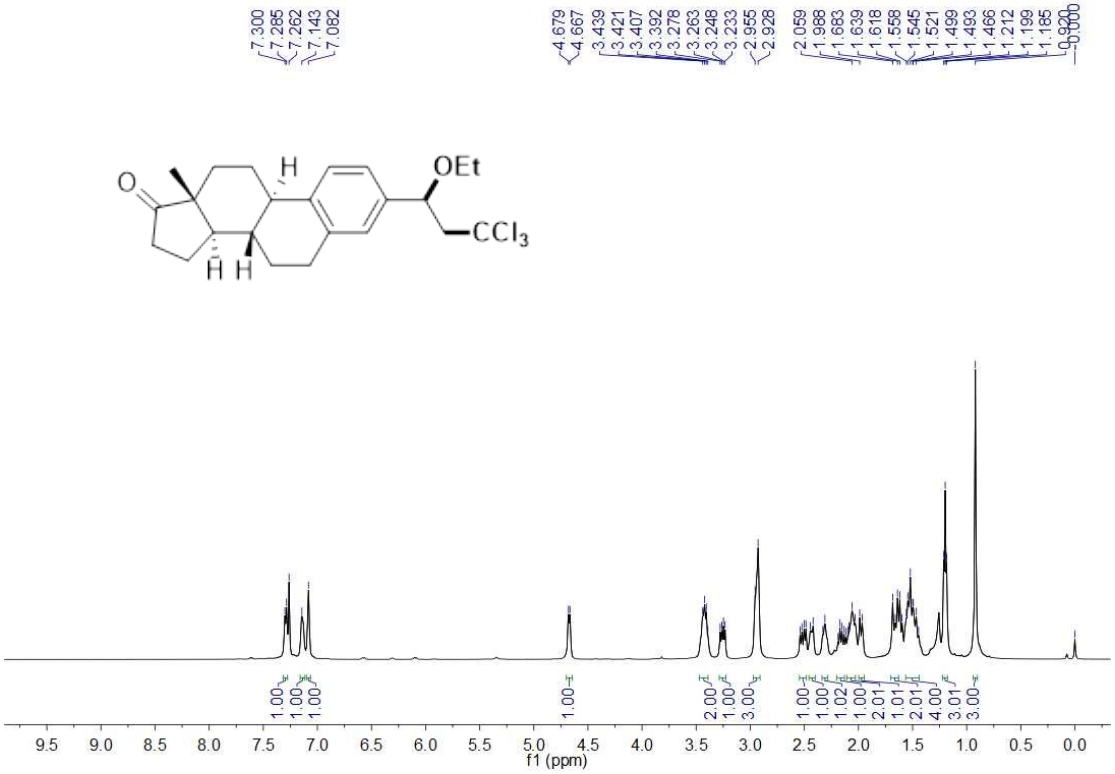


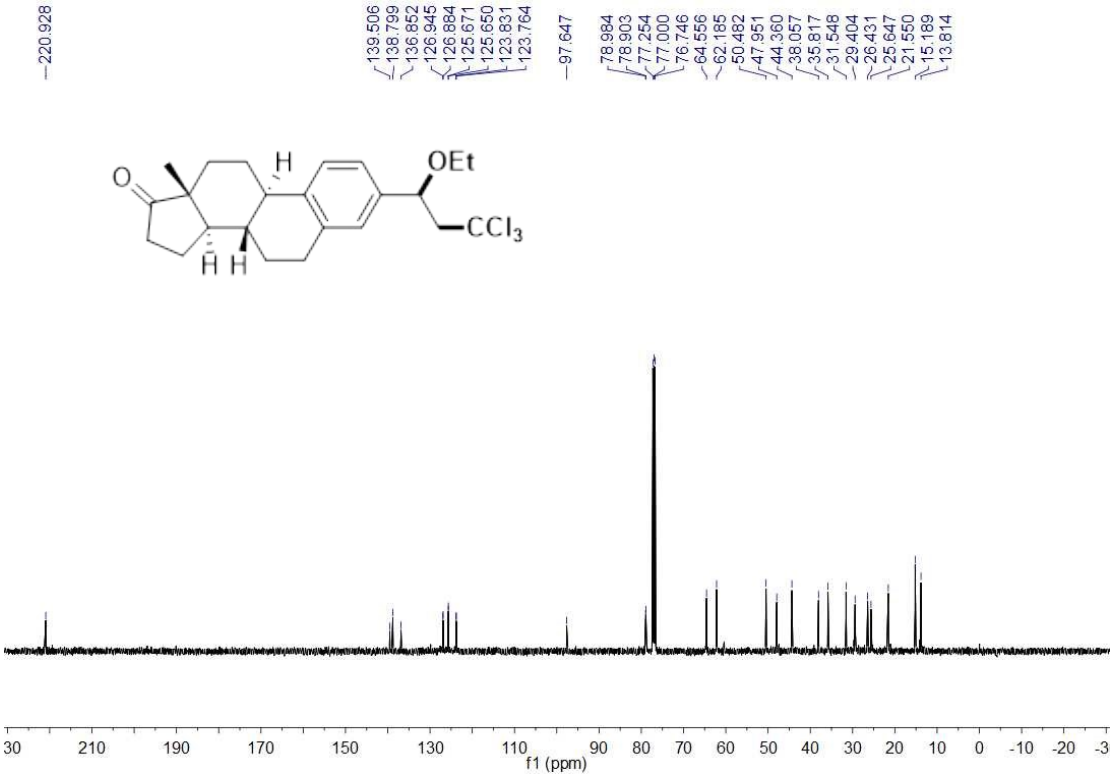
(R)-2,5,7,8-tetramethyl-6-((R)-3,3,3-trichloro-1-ethoxypropyl)-2-((4R,8R)-4,8,12-trimethyltridecyl)chromane (4raa)



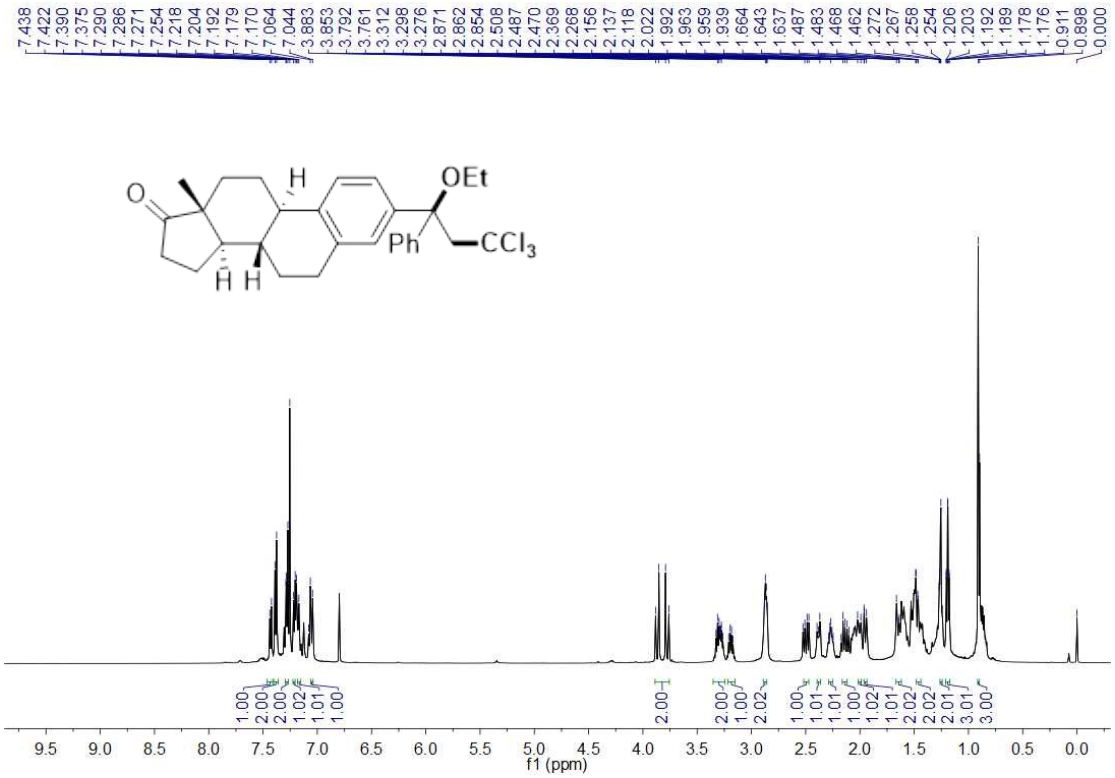


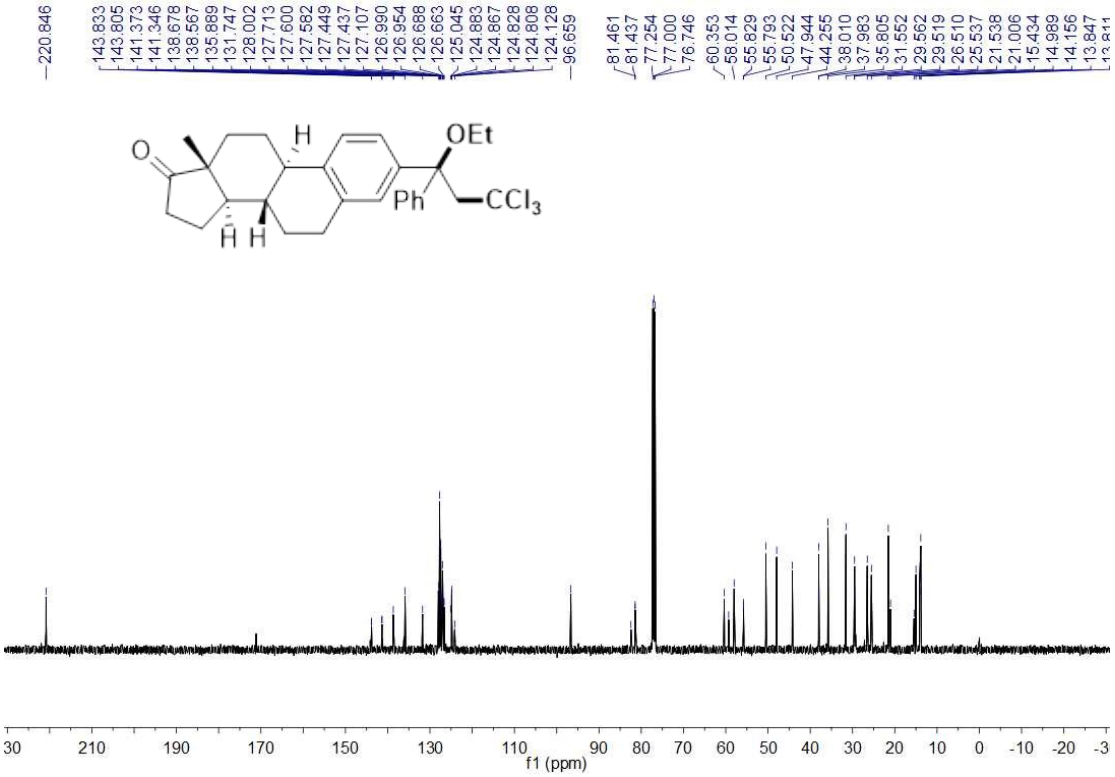
13-Methyl-2-(3,3,3-trichloro-1-ethoxypropyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (4saa)





13-Methyl-2-(3,3,3-trichloro-1-ethoxy-1-phenylpropyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (4taa)





(3S,8S,9S,10R,13R,14S,17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)-3-((4-((S)-3,3,3-trichloro-1-ethoxypropyl)benzyl)oxy)-

2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[*a*]phenanthrene (4uaa)