Photocatalytic hydrotrichloromethylation of unactivated alkenes with chloroform

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1 General Information

All manipulations were carried out under an inert nitrogen atmosphere using a Schlenk line. All solvents were distilled from the appropriate drying agents under argon before use. All reagents were obtained from commercial suppliers and used without further purification. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer. The ^{1}H NMR chemical shifts were referenced to the residual solvent as determined relative to Me_4Si (δ 0 ppm). The $^{13}C\{^{1}H\}$ chemical shifts were reported in ppm relative to the carbon resonance of $CDCl_3$ (77.0 ppm). Cyclic voltammograms (CV) were collected using a VersaSTAT 3 Potentiostat Galvanostat from Princeton Applied Research. UV-vis absorption spectra and emission spectra were taken at ambient temperature using an Edinburgh FS5 spectrofluorometer. The HRMS were obtained using a hybrid quadrupole-TOF or a Q Exactive Orbitrap mass spectrometer in ESI+ mode. The Kessil PR160 series (max = 456 nm, 40 W) was used as the blue LED light source for reactions. For alkene substrates, **1a-1m**, **1o-1q**, **1w**, **1x**, and **1ak** were obtained from commercial suppliers. Alkene substrates **1n**,[1] **1r**,[2] **1s**,[3] **1t**,[4] **1u**,[5] **1v**,[6] **1ab**,[7] **1ad**,[8] **1ae**,[7] **1ah**,[9] and **1ai**,[10] was were prepared according to the literature.

2 General Procedure for Hydrotrichloromethylation

2.1 Typical Reaction Setup

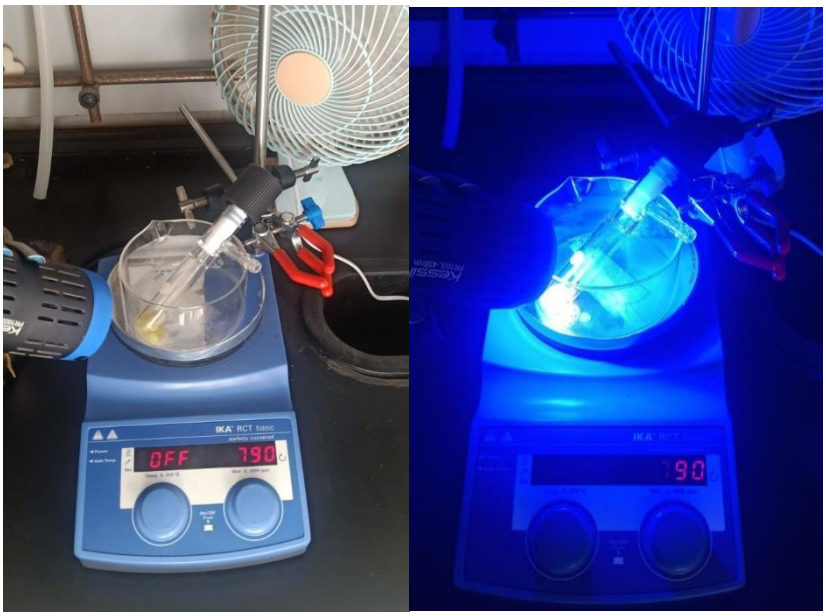


Figure S1. Reaction setup under blue LED (40 w) irradiation

2.2 Gram Synthesis Typical Reaction Setup

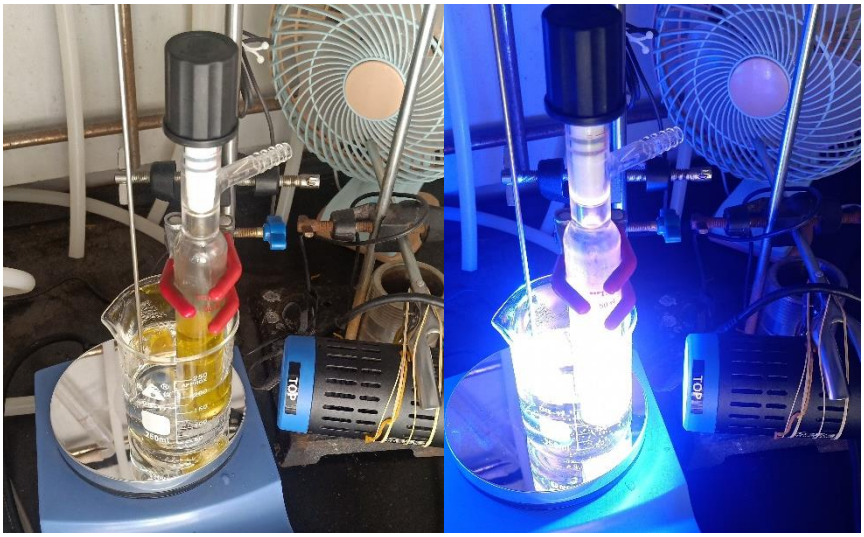
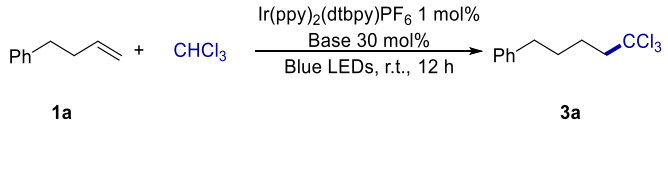


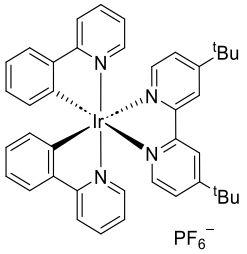
Figure S2. Reaction setup under blue LED (40 w) irradiation for gram synthesis

2.3 Reaction Optimization

Supplementary Table S1. Screening of Other Conditions[a]



1a **3a**

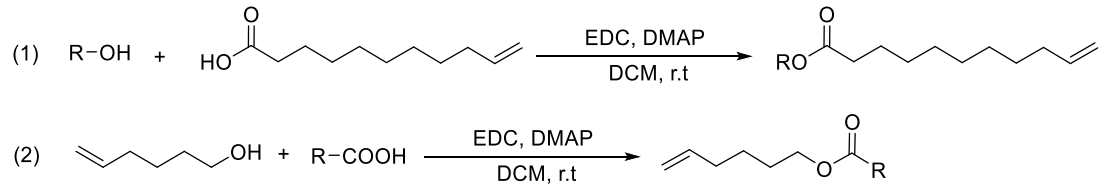


Ir(ppy)$_2$(dtbpy)PF$_6$

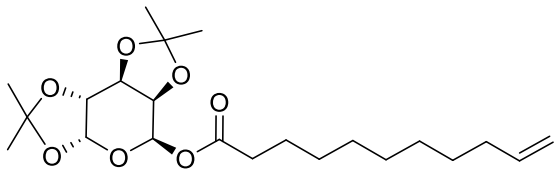
Entry	Deviation from above	Yield (%)
1	**DMAP**	**93**
2	Et_3N instead of DMAP	39
3	*i*-Pr_2NH instead of DMAP	65
4	DBU instead of DMAP	69
5	*i*-$PrNMe_2$ instead of DMAP	52
6[b]	NaH instead of DMAP	55
7[b]	*t*-BuOK instead of DMAP	78
8	1-Methylpyrrolidine instead of DMAP	31
9	*N*,*N*,*N*',*N*'-Tetramethyl-1,4-phenylenediamine instead of DMAP	trace
10	2 mL $CHCl_3$ instead of 1 mL $CHCl_3$	91
11	4 mL $CHCl_3$ instead of 1 mL $CHCl_3$	86
12	10 eq. H_2O was added	56

[a] Reaction conditions: 4-phenyl-1-butene (0.1 mmol), Ir(ppy)$_2$(dtbpy)PF_6 (1 mol%), DMAP (30 mol%) in $CHCl_3$ (0.1 M) under irradiation with 40 W, 456 nm LED light at room temperature for 12 h under argon. Yield was determined ^1H NMR using CH_2Br_2 as an internal standard. [b] with 1 eq. base.

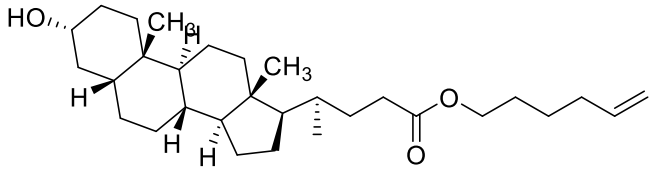
2.4 Synthesis of Alkene Substrates (1aa, 1ac, 1af, 1ag, 1aj)



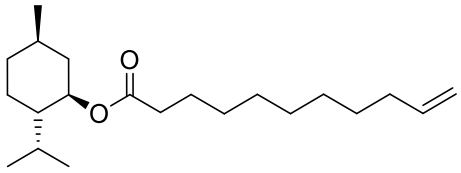
General Procedure for the Synthesis of Alkene Substrates: Alcohol (5 mmol, 1.0 equiv), carboxylic acid (5 mmol, 1.0 equiv), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) (7.5 mmol, 1.5 equiv, 1.44 g), and 4-dimethylaminopyridine (DMAP) (5 mmol, 1.0 equiv, 0.61 g) were dissolved in 20 mL DCM. The mixture was stirred under air at room temperature (26-29 °C) for 6 hours. After washing with 10 mL water and reducing the solution in vacuo, the residue was purified by chromatography on silica gel to give the alkene products (**1aa, 1ac, 1af, 1ag, 1aj**).



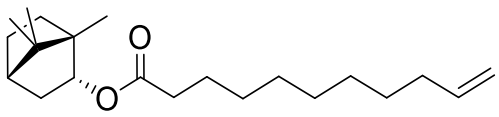
1aa: (3aR,5R,5aR,8aR,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl undec-10-enoate: colorless oil (1.71 g, 83%). Purification: 10% EtOAc/Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 5.85-5.75 (m, 1H), 5.53 (d, *J*=6.8 Hz, 1H), 5.00-4.90 (m, 2H), 4.62-4.60 (m, 1H), 4.33-4.29 (m, 2H), 4.24-4.22 (m, 1H), 4.18-4.13 (m, 1H), 4.03-3.99 (m, 1H), 2.33 (t, *J*=7.6 Hz, 2H), 2.05-2.00 (m, 2H), 1.66-1.57 (m, 2H), 1.50 (s, 3H), 1.44 (s, 3H), 1.33-1.28 (m, 14H). ^{13}C NMR (100 MHz, $CDCl_3$): 173.8, 139.2, 114.1, 109.6, 108.7, 96.3, 71.1, 70.7, 70.5, 66.0, 63.2, 34.2, 33.8, 29.3, 29.2, 29.1, 28.9, 26.02, 25.96, 25.0, 24.5. HRMS (ESI): m/z [M+H]+ calcd for $C_{22}H_{37}O_7^+$: 413.2534, found 413.2544.



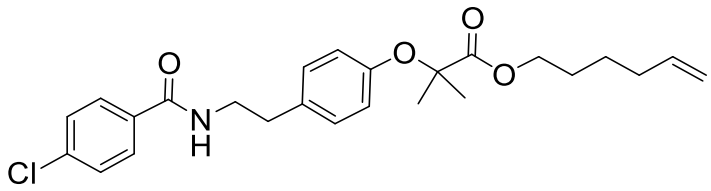
1ac: hex-5-en-1-yl (R)-4-((3R,5R,8R,9S,10S,13R,14S,17R)-3-hydroxy-10,13-dimethy-lhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate: colorless oil (1.70 g, 74%). Purification: 100% EtOAc. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 5.80-5.70 (m, 1H), 4.99-4.86 (m, 2H), 4.02 (t, *J*=6.8 Hz, 2H), 3.61-3.53 (m, 1H), 2.34-2.26 (m, 1H), 2.21-2.13 (m, 2H), 2.07-2.01 (m, 2H), 1.92 (d, *J*=12.8 Hz, 1H), 1.84-1.71 (m, 6H), 1.63-1.56 (m, 3H), 1.45-1.19 (m, 15H), 1.09-0.96 (m, 5H), 0.87 (s, 6H), 0.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 174.4, 138.3, 114.8, 74.1, 64.2, 56.5, 56.0, 42.7, 42.1, 40.4, 40.2, 36.4, 35.8, 35.4, 35.3, 34.6, 33.3, 31.3, 31.0, 30.5, 28.2, 28.1, 27.2, 26.4, 25.2, 24.2, 23.4, 20.8, 18.3, 12.0. HRMS (ESI): m/z [M+H]+ calcd for $C_{30}H_{51}O_3^+$: 459.3833, found 459.3838.



1af: (1R,2R,5R)-2-isopropyl-5-methylcyclohexyl undec-10-enoate: colorless oil (0.93 g, 58%). Purification: 10% EtOAc/Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 5.85-5.75 (m, 1H), 5.00-4.91 (m, 2H), 4.70-4.64 (m, 1H), 2.27 (t, *J*=7.2 Hz, 2H), 2.06-1.95 (m, 3H), 1.90-1.81 (m, 1H), 1.71-1.59 (m, 4H), 1.52-1.44 (m, 1H), 1.38-1.25 (m, 12H), 1.07-0.99 (m, 1H), 0.90-0.88 (m, 7H), 0.75 (d, *J*=6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 173.5, 139.2, 114.2, 73.9, 47.0, 41.0, 34.8, 34.3, 33.8, 31.4, 29.3, 29.2, 29.12, 29.06, 28.9, 26.3, 25.1, 23.4, 22.0, 20.8, 16.3. HRMS (ESI): m/z [M+H]+ calcd for $C_{21}H_{39}O_2^+$: 323.2945, found 323.2950.

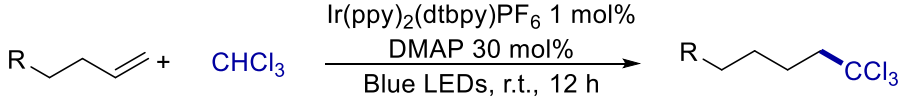


1ag: (1R,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl undec-10-enoate: colorless oil (1.23 g, 77%). Purification: 10% EtOAc/Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 5.85-5.75 (m, 1H), 5.01-4.86 (m, 3H), 2.39-2.29 (m, 3H), 2.06-2.00 (m, 2H), 1.97-1.90 (m, 1H), 1.78-1.70 (m, 1H), 1.68-1.59 (m, 3H), 1.40-1.24 (m, 12H), 0.87 (t, *J*=13.6 Hz, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): 174.2, 139.2, 114.2, 79.6, 48.7, 47.8, 44.9, 36.9, 34.7, 33.8, 29.3, 29.2, 29.14, 29.07, 28.9, 28.1, 27.1, 25.2, 19.7, 18.9, 13.5. HRMS (ESI): m/z [M+H]+ calcd for $C_{21}H_{37}O_2^+$: 321.2788, found 321.2792

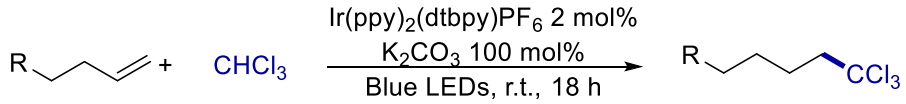


1aj: hex-5-en-1-yl 2-(4-(2-(4-chlorobenzamido)ethyl)phenoxy)-2-methylpropanoate: colorless oil (1.55 mg, 70%). Purification: 50% EtOAc/Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.61 (d, *J*=8.8 Hz, 2H), 7.37 (d, *J*=8.4 Hz, 2H), 7.08 (d, *J*=8.8 Hz, 2H), 6.80 (d, *J*=8.8 Hz, 2H), 6.08 (s, 1H), 5.78-5.67 (m, 1H), 4.95 (t, *J*=15.6 Hz, 2H), 4.16 (t, *J*=6.8 Hz, 2H), 3.68-3.63 (m, 2H), 2.85 (t, *J*=7.6 Hz, 2H), 2.04-1.98 (m, 2H), 1.67-1.59 (m, 8H), 1.40-1.32 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 174.4, 166.4, 154.2, 138.2, 137.7, 133.0, 132.3, 129.5, 128.8, 128.3, 119.4, 114.9, 79.2, 65.4, 41.2, 34.8, 33.2, 27.9, 25.4, 25.0. HRMS (ESI): m/z [M+H]+ calcd for $C_{25}H_{31}ClNO_4^+$: 444.1936, found 444.1949

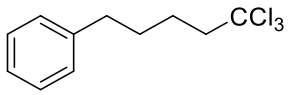
2.5 Synthesis of Trichloromethyl Compounds



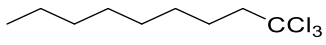
Method A: A 10 mL Schlenk tube equipped with a magnetic stir bar was charged with alkene (0.1 mmol, 1.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (0.91 mg, 0.001 mmol, 0.01 equiv.), DMAP (3.7 mg, 0.03 mmol, 0.3 equiv.), and chloroform (1 mL). The reactor was placed under a blue LED (Kessil light, 40 W, 456 nm, Spectral output can be found on: https://www.kessil.com/science/PR160L.php) and irradiated for 12 h under argon at room temperature (26-29 °C). After reducing in vacuo, the residue was purified by chromatography on silica gel to give the trichloromethyl products.



Method B: A 10 mL Schlenk tube equipped with a magnetic stir bar was charged with alkene (0.1 mmol, 1.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (1.82 mg, 0.002 mmol, 0.02 equiv.), K_2CO_3 (13.8 mg, 0.1 mmol, 1.0 equiv.), and chloroform (1 mL). The reactor was placed under a blue LED (Kessil light, 40 W, 456 nm, Spectral output can be found on: https://www.kessil.com/science/PR160L.php) and irradiated for 18 h under argon at room temperature (26-29 °C). The yield was determined by ^1H NMR using CH_2Br_2 as an internal standard.

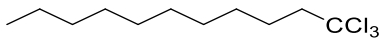


3a: (5,5,5-trichloropentyl) benzene: colorless oil (22.9 mg, 91%). Purification: 100% Petroleum ether. ^1H NMR (400 MHz, $CDCl_3$, ppm): 7.33-7.29 (m, 2H), 7.23-7.19 (m, 3H), 2.73-2.67 (m, 4H), 1.89-1.81 (m, 2H), 1.78-1.70 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 141.8, 128.44, 128.39, 126.0, 100.0, 55.0, 35.6, 30.2, 26.1. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{11}H_{13}NaCl_3^+$: 272.9975, found 272.9976.

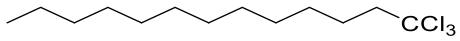


3b: 1,1,1-trichlorononane: colorless oil (20.4 mg, 88%). Purification: 100% Petroleum ether. ^1H NMR (400 MHz, $CDCl_3$, ppm): 2.67 (t, J = 8.0 Hz, 2H), 1.81-1.73 (m, 2H), 1.36-1.28 (m, 10H), 0.89 (t, J = 12.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 100.3,

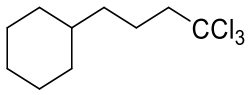
55.2, 31.8, 29.7, 29.1, 28.4, 26.4, 22.6, 14.1. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_9H_{17}NaCl_3^+$: 253.0288, found 253.0285.



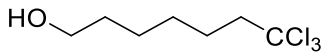
3c: 1,1,1-trichloroundecane: colorless oil (23.4 mg, 90%). Purification: 10% EtOAc/Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 2.67 (t, *J* = 8.0 Hz, 2H), 1.79-1.73 (m, 2H), 1.37-1.28 (m, 14H), 0.89 (t, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 100.3, 55.2, 31.9, 29.6, 29.5, 29.4, 29.3, 28.4, 26.4, 22.7, 14.1. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{11}H_{21}NaCl_3^+$: 281.0601, found 281.0612.



3d: 1,1,1-trichlorotridecane: colorless oil (27.0 mg, 94%). Purification: 10% EtOAc/Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 2.66 (t, *J* = 8.4 Hz, 2H), 1.81-1.73 (m, 2H), 1.39-1.27 (m, 18H), 0.89 (t, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 100.3, 55.2, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 28.4, 26.4, 22.7, 14.2. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{13}H_{26}Cl_3^+$: 287.1095, found 287.1093.

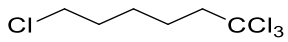


3e: (4,4,4-trichlorobutyl)cyclohexane: colorless oil (20.7 mg, 85%). Purification: 10% EtOAc/Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 2.64 (t, *J* = 8.0 Hz, 2H), 1.82-1.64 (m, 8H), 1.30-1.19 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): 100.3, 55.5, 37.4, 36.0, 33.2, 26.6, 26.3, 23.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{10}H_{18}Cl_3^+$: 243.0469, found 243.0476.

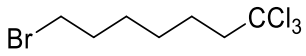


3f: 7,7,7-trichloroheptan-1-ol: colorless oil (18.9 mg, 86%). Purification: 10% EtOAc/Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.68 (t, *J* = 6.4 Hz, 2H), 2.67 (t, *J* = 8.0 Hz, 2H), 1.83-1.76 (m, 2H), 1.63-1.56 (m, 2H), 1.45-1.42 (m, 4H). ^{13}C

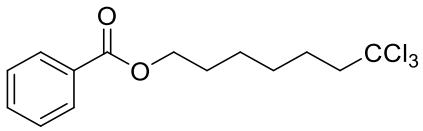
NMR (100 MHz, $CDCl_3$): 100.2, 62.8, 55.1, 32.5, 28.1, 26.4, 25.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_7H_{14}OCl_3^+$: 219.0105, found 219.0108.



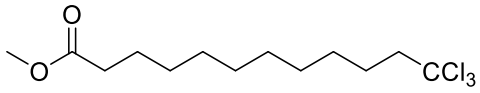
3g: 1,1,1,6-tetrachlorohexane: colorless oil (20.2 mg, 90%). Purification: 10% EtOAc/Petroleum ether. ^1H NMR (400 MHz, $CDCl_3$, ppm): 3.57 (t, J = 6.4 Hz, 2H), 2.69 (t, J = 7.6 Hz, 2H), 1.86-1.80 (m, 4H), 1.61-1.55 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 99.8, 54.9, 44.7, 32.2, 25.7, 25.6. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_6H_{11}Cl_4^+$: 222.9609, found 222.9611.



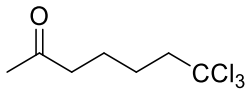
3h: 7-bromo-1,1,1-trichloroheptane: colorless oil (23.7 mg, 84%). Purification: 10% EtOAc/Petroleum ether. ^1H NMR (400 MHz, $CDCl_3$, ppm): 3.43 (t, J = 7.2 Hz, 2H), 2.68 (t, J = 8.0 Hz, 2H), 1.93-1.76 (m, 4H), 1.55-1.41 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): 100.0, 55.0, 33.7, 32.5, 27.8, 27.5, 26.2. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_7H_{12}NaCl_3Br^+$: 302.9080, found 302.9087.



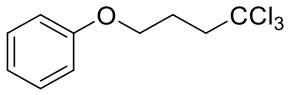
3i: 7,7,7-trichloroheptyl benzoate colorless oil (27.0 mg, 84%). Purification: 10% EtOAc/Petroleum ether. ^1H NMR (400 MHz, $CDCl_3$, ppm): 8.05 (d, J=8.4 Hz, 2H), 7.58-7.54 (m, 1H), 7.46-7.43 (m, 2H), 4.33 (t, J=9.0 Hz, 2H), 2.70-2.66 (m, 2H), 1.84-1.78 (m, 4H), 1.61-1.45 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): 166.7, 132.9, 130.4, 129.6, 128.4, 100.1, 64.8, 55.1, 28.6, 28.0, 26.3, 25.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{18}O_2Cl_3^+$: 323.0367, found 323.0369.



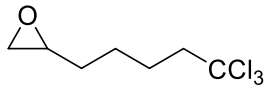
3j: methyl 12,12,12-trichlorododecanoate: colorless oil (29.2 mg, 92%). Purification: 100% DCM. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.66 (s, 3H), 2.65 (t, J = 7.6 Hz, 2H), 2.30 (t, J = 7.2 Hz, 2H), 1.77-1.72 (m, 2H), 1.68-1.59 (m, 2H), 1.38-1.25 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): 174.3, 100.3, 55.2, 51.5, 34.1, 29.34, 29.26, 29.2, 29.1, 28.3, 26.4, 24.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{13}H_{24}O_2Cl_3^+$: 317.0836, found 317.0848.



3k: 7,7,7-trichloroheptan-2-one: colorless oil (17.6 mg, 81%). Purification: 10% EtOAc/Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 2.68 (t, J = 7.2 Hz, 2H), 2.52 (t, J = 7.2 Hz, 2H), 2.16 (s, 3H), 1.81-1.66 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): 208.1, 99.8, 54.9, 43.1, 30.0, 26.0, 22.3. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_7H_{12}OCl_3^+$: 216.9948, found 216.9948.

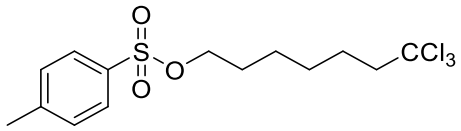


3l: (4,4,4-trichlorobutoxy)benzene: colorless oil (17.2 mg, 68%). Purification: 10% EtOAc/Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.31-7.28 (m, 2H), 6.98-6.95 (m, 1H), 6.91 (d, J = 9.2 Hz, 2H), 4.08 (t, J = 5.6 Hz, 2H), 2.93 (t, J = 7.6 Hz, 2H), 2.31-2.24 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 158.6, 129.5, 122.0, 114.5, 99.7, 66.0, 52.2, 26.7. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{10}H_{11}ONaCl_3^+$: 274.9768, found 274.9782.

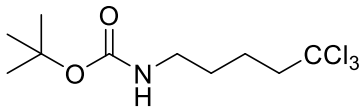


3m: 2-(5,5,5-trichloropentyl)oxirane: colorless oil (18.3 mg, 84%). Purification: 100% DCM. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 2.93 (s, 1H), 2.78 (t, J = 4.4 Hz, 1H), 2.70 (t, J = 8.4 Hz, 2H), 2.50-2.49 (m, 1H), 1.88-1.81 (m, 2H), 1.70-1.53 (m, 4H). ^{13}C NMR

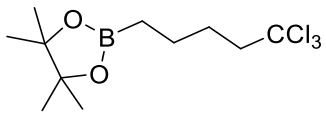
(100 MHz, $CDCl_3$): 99.9, 55.0, 52.0, 47.1, 32.2, 26.2, 24.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_7H_{12}OCl_3^+$: 216.9948, found 216.9953.



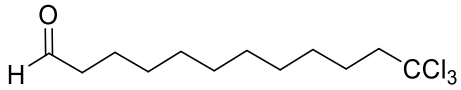
3n: 7,7,7-trichloroheptyl 4-methylbenzenesulfonate: colorless oil (26.5 mg, 71%). Purification: 10% EtOAc/Petroleum ether. ^1H NMR (400 MHz, $CDCl_3$, ppm): 7.79 (d, *J* = 7.2 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.04 (t, *J* = 6.0 Hz, 2H), 2.61 (t, *J* = 8.0 Hz, 2H), 2.45 (s, 3H), 1.76-1.64 (m, 4H), 1.44-1.32 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): 144.8, 133.1, 129.9, 127.9, 100.0, 70.3, 54.9, 28.6, 27.6, 26.2, 25.1, 21.7. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{20}Cl_3O_3S^+$: 373.0193, found 373.0192.



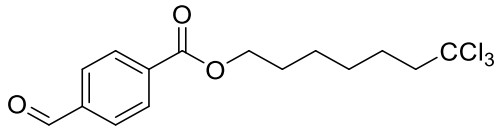
3o: tert-butyl (5,5,5-trichloropentyl) carbamate: colorless oil (25.6 mg, 88%). Purification: 10% EtOAc/Petroleum ether. ^1H NMR (400 MHz, $CDCl_3$, ppm): 4.57 (s, 1H), 3.17 (d, *J* = 4.8 Hz, 2H), 2.69 (t, *J* = 7.2 Hz, 2H), 1.84-1.76 (m, 2H), 1.63-1.55 (m, 2H), 1.44 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 156.0, 99.8, 54.7, 40.1, 29.7, 28.9, 28.4, 23.7. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{10}H_{19}NO_2Cl_3^+$: 290.0476, found 290.0475.



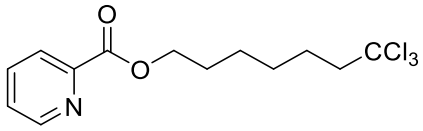
3p: 4,4,5,5-tetramethyl-2-(5,5,5-trichloropentyl)-1,3,2-dioxaborolane: colorless oil (23.8 mg, 79%). Purification: 100% DCM. ^1H NMR (400 MHz, $CDCl_3$, ppm): 2.67 (t, *J* = 6.4 Hz, 2H), 1.82-1.74 (m, 2H), 1.57-1.50 (m, 2H), 1.25 (s, 12H), 0.84 (t, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 100.3, 83.1, 55.0, 28.9, 24.8, 22.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{11}H_{21}O_2Cl_3B^+$: 301.0695, found 301.0692.



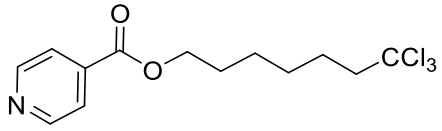
3q: 12,12,12-trichlorododecanal: colorless oil (25.3 mg, 88%). Purification: 100% DCM. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 9.76 (s, 1H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.42 (t, *J* = 7.6 Hz, 2H), 1.80-1.73 (m, 2H), 1.62 (t, *J* = 6.4 Hz, 2H), 1.38-1.25 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): 202.9, 100.3, 55.2, 43.9, 29.34, 29.32, 29.26, 29.1, 28.3, 26.4, 22.1. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{12}H_{22}OCl_3^+$: 287.0731, found 287.0732.



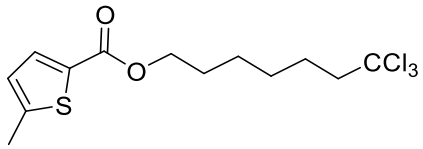
3r: 7,7,7-trichloroheptyl 4-formylbenzoate: colorless oil (27.1 mg, 77%). Purification: 10% EtOAc/Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 10.11 (s, 1H), 8.20 (d, *J* = 8.0 Hz, 2H), 7.96 (d, *J* = 7.6 Hz, 2H), 4.37 (t, *J* = 5.2 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 1.85-1.78 (m, 4H),1.57-1.48 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): 191.7, 165.6, 139.1, 135.4, 130.2, 129.6, 100.0, 65.5, 55.1, 28.5, 28.0, 26.3, 25.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{18}O_3Cl_3^+$: 351.0316, found 351.0316.



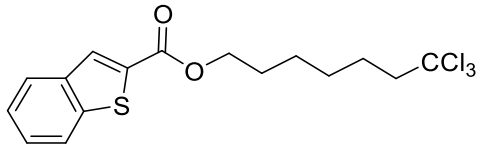
3s: 7,7,7-trichloroheptyl picolinate: colorless oil (26.0 mg, 80%). Purification: 50% EtOAc/Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.77 (d, *J* = 3.6 Hz, 1H), 8.13 (d, *J* = 7.6 Hz, 1H), 7.87-7.83 (m, 1H), 7.49-7.46 (m, 1H), 4.43 (t, *J* = 6.8 Hz, 2H), 2.67 (t, *J* = 7.6 Hz, 2H), 1.88-1.78 (m, 4H), 1.57-1.41 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): 165.3, 149.9, 148.2, 137.0, 126.9, 125.2, 100.1, 65.8, 55.1, 28.5, 28.0, 26.3, 25.7. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{13}H_{17}NO_2Cl_3^+$: 324.0319, found 324.0326.



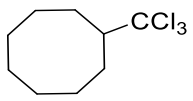
3t: 7,7,7-trichloroheptyl isonicotinate: colorless oil (27.6 mg, 85%). Purification: 50% EtOAc/Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.79 (d, J = 4.8 Hz, 2H), 7.85 (d, J = 5.2 Hz, 2H), 4.37 (t, J = 6.8 Hz, 2H), 2.68 (t, J = 8.0 Hz, 2H), 1.85-1.80 (m, 4H), 1.59-1.43(m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): 165.1, 150.6, 137.6, 122.9, 100.0, 65.7, 55.0, 28.4, 28.0, 26.3, 25.7. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{13}H_{17}NO_2Cl_3^+$: 324.0319, found 324.0331.



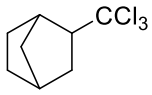
3u: 7,7,7-trichloroheptyl 5-methylthiophene-2-carboxylate: colorless oil (27.8 mg, 81%). Purification: 5% EtOAc/Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.61 (d, J = 3.2 Hz, 1H), 6.77 (d, J = 2.8 Hz, 1H), 4,27 (t, J = 6.8 Hz, 2H), 2.68 (t, J = 8.4 Hz, 2H), 2.52 (s, 3H), 1.84-1.73 (m, 4H), 1.56-1.39 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): 162.3, 147.9, 133.8, 131.2, 126.4, 100.1, 64.7, 55.1, 28.5, 28.0, 26.3, 25.8, 15.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{13}H_{18}O_2SCl_3^+$: 343.0088, found 343.0089.



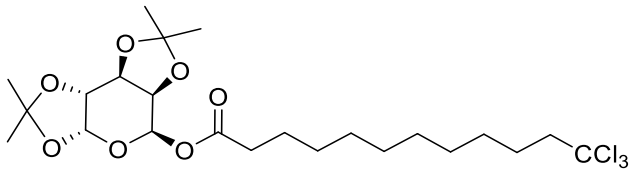
3v: 7,7,7-trichloroheptyl benzo[b]thiophene-2-carboxylate: colorless oil (25.8 mg, 68%). Purification:10% EtOAc/Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.07 (s, 1H), 7.89-7.86 (m, 2H), 7.48-7.39 (m, 2H), 4.36 (t, J = 6.8 Hz, 2H), 2.70 (t, J = 8.0 Hz, 2H), 1.86-1.79 (m, 4H), 1.54-1.45 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): 162.9, 142.2, 138.7, 134.0, 130.5, 127.0, 125.6, 124.9, 122.8, 100.1, 65.4, 55.1, 28.5, 28.0, 26.3, 25.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{18}O_2SCl_3^+$: 379.0088, found 379.0088.



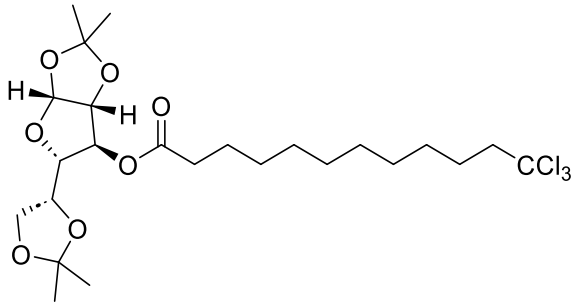
3w: (trichloromethyl)cyclooctane: colorless oil (18.1 mg, 79%). Purification: 10% EtOAc/Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 2.60 (t, *J* = 3.6 Hz, 1H), 2.16-2.12 (m, 2H), 1.84-1.77 (m, 2H), 1.66-1.53 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): 107.6, 58.3, 30.7, 26.7, 26.2. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_9H_{16}Cl_3^+$: 229.0312, found 229.0322.



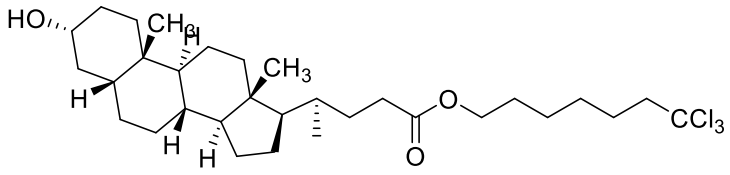
3x: 2-(trichloromethyl)bicyclo[2.2.1]heptane: colorless oil (18.8 mg, 88%). Purification: 10% EtOAc/Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 2.64 (t, *J* = 7.6 Hz, 2H), 2.36 (s, 1H), 1.92 (d, *J* = 10.4 Hz, 1H), 1.73-1.66 (m, 2H), 1.34-1.14 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): 104.1 64.2, 41.2, 37.2, 36.6, 36.2, 31.1, 27.7. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_8H_{12}Cl_3^+$: 212.9999, found 212.9997.



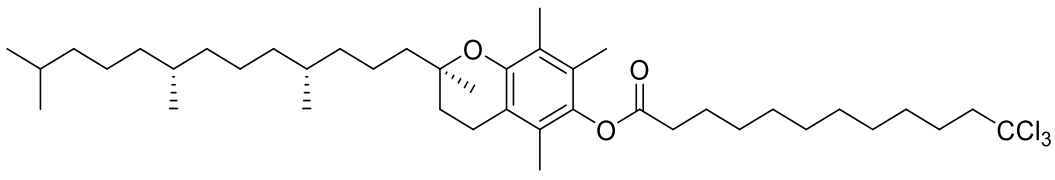
3aa:(3aR,5R,5aR,8aR,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl 12,12,12-trichlorododecanoate: colorless oil (43.6 mg, 82%). Purification: 10% EtOAc/Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 5.53 (d, *J* = 4.8 Hz, 1H), 4.60 (d, *J* = 8.4 Hz, 1H), 4.32-4.28 (m, 2H), 4.22 (d, *J* = 8.4 Hz, 1H), 4.18-4.13 (m, 1H), 4.01 (t, *J* = 6.0 Hz, 1H), 2.65 (t, *J* = 7.2 Hz, 2H), 2.33 (t, *J* = 8.0 Hz, 2H), 1.79-1.71 (m, 2H), 1.62-1.57 (m, 2H), 1.49 (s, 3H), 1.44 (s, 3H), 1.37-1.24 (m, 16H). ^{13}C NMR (100 MHz, $CDCl_3$): 173.8, 109.6, 108.7, 100.3, 96.3, 71.1, 70.7, 70.5, 66.0, 63.2, 55.2, 34.2, 29.4, 29.33, 29.26, 29.2, 29.1, 28.3, 26.4, 26.02, 25.96, 24.99, 24.95, 24.5. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{22}H_{37}O_7NaCl_3^+$: 553.1497, found 553.1516.



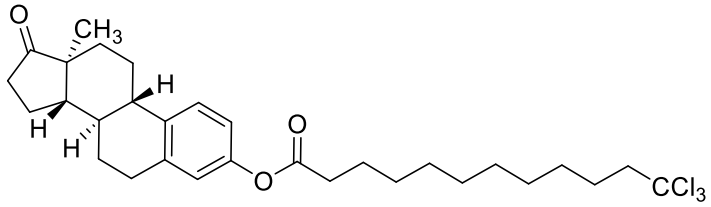
3ab:(3aR,5S,6S,6aR)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydro-furo[2,3-d][1,3]dioxol-6-yl 12,12,12-trichlorododecanoate: colorless oil (43.1 mg, 79%). Purification: 10% EtOAc/Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 5.86 (d, J = 3.6 Hz, 1H), 5.25 (s, 1H), 4.47 (d, J = 4.0 Hz, 1H), 4.20 (s, 2H), 4.09-3.99 (m, 2H), 2.66 (t, J = 8.4 Hz, 2H), 2.34 (t, J = 7.2 Hz, 2H), 1.79-1.72 (m, 2H), 1.66-1.59 (m, 3H), 1.51 (s, 3H), 1.40-1.29 (m, 20H). ^{13}C NMR (100 MHz, $CDCl_3$): 172.4, 112.3, 109.3, 105.1, 100.2, 83.4, 79.9, 75.8, 72.4, 67.3, 55.2, 34.3, 29.4, 29.3, 29.2, 29.1, 28.3, 26.83, 26.75, 26.4, 26.2, 25.3, 24.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{40}O_7Cl_3^+$: 545.1834, found 545.1846.



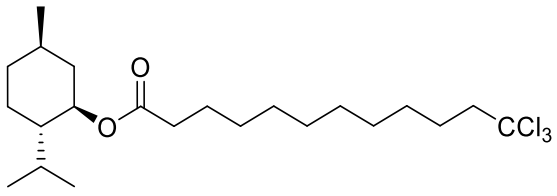
3ac:7,7,7-trichloroheptyl(R)-4-((3R,5R,8R,9S,10S,13R,14S,17R)-3-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate: colorless oil (48.0 mg, 83%). Purification: 100% EtOAc. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 4.06 (t, J = 6.4 Hz, 2H), 3.70-3.58 (m, 1H), 2.66 (t, J = 7.2 Hz, 2H), 2.41-2.14 (m, 3H), 1.81-1.04 (m, 34H), 0.90 (s, 6H), 0.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 174.4, 100.1, 71.8, 64.1, 56.5, 56.0, 55.1, 42.7, 42.1, 40.4, 40.2, 36.4, 35.8, 35.4, 34.6, 31.3, 31.0, 30.5, 28.5, 28.2, 28.0, 27.2, 26.4, 26.3, 25.7, 24.2, 23.4, 20.8, 18.3, 12.1. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{31}H_{52}O_3Cl_3^+$: 577.2977, found 577.2993.



3ad:(R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl12,12,12-trichlorododecanoate: colorless oil (52.3 mg, 73%). Purification: 5% EtOAc/ Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 2.67 (t, *J* = 8.4 Hz, 2H), 2.59 (t, *J* = 7.2 Hz, 4H), 2.09 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H), 1.81-1.76 (m, 6H), 1.56-1.51 (m, 3H), 1.42-1.23 (m, 26H), 1.16-1.06 (m, 7H), 0.86 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): 172.4, 149.4, 140.5, 126.7, 124.9, 123.0, 117.4, 100.3, 75.0, 55.2, 39.4, 37.5, 37.4, 37.3, 34.2, 32.8, 32.7, 29.38, 29.36, 29.31, 29.26, 29.24, 28.3, 28.0, 26.4, 25.2, 24.8, 24.5, 22.7, 22.6, 21.0, 20.6, 19.8, 19.7, 13.0, 12.1, 11.8. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{41}H_{69}O_3NaCl_3^+$: 737.4205, found 737.4203.

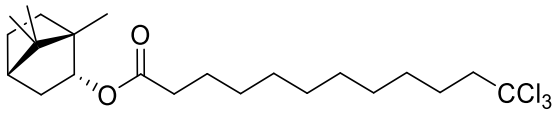


3ae:(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 12,12,12-trichlorododecanoate: colorless oil (47.3 mg, 85%). Purification: 20% EtOAc/Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.28 (d, *J* = 12.4 Hz, 1H), 6.85-6.83 (m, 2H), 2.91-2.89 (m, 2H), 2.66 (t, *J* = 8.0 Hz, 2H), 2.55-2.47 (t, *J* = 7.2 Hz, 3H), 2.42-2.39 (m, 1H), 2.31-2.25 (m, 1H), 2.19-1.95 (m, 5H), 1.80-1.62 (m, 5H), 1.57-1.25 (m, 16H), 0.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 172.6, 148.6, 138.0, 137.3, 126.4, 121.6, 118.8, 100.3, 55.2, 50.4, 48.0, 44.2, 38.0, 35.9, 34.4, 31.6, 29.41, 29.35, 29.3, 29.2, 29.1, 28.3, 26.39, 26.36, 25.8, 25.0, 21.6, 13.8. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{30}H_{41}O_3NaCl_3^+$: 577.2013, found 577.2006.

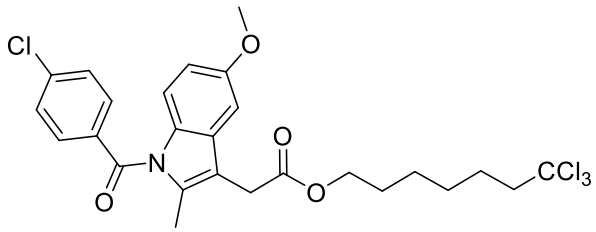


3af: (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl12,12,12-trichlorododecanoate: colorless oil (38.4 mg, 87%). Purification: 100% DCM. ^{1}H NMR (400 MHz, $CDCl_3$,

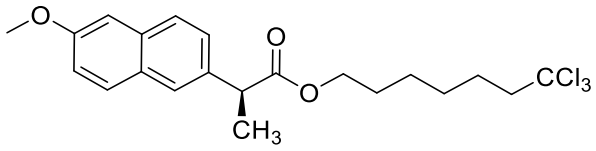
ppm): 4.70-4.64 (m, 1H), 2.66 (t, *J* = 8.0 Hz, 2H), 2.27 (t, *J* = 6.8 Hz, 2H), 1.99-1.96 (m, 1H), 1.89-1.83 (m, 1H), 1.80-1.72 (m, 2H), 1.68-1.59 (m, 5H), 1.40-1.25 (m, 16H), 0.90-0.88 (m, 6H), 0.75 (d, *J* = 9.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 173.5, 100.3, 73.9, 55.2, 47.0, 41.0, 34.8, 34.3, 31.4, 29.39, 29.36, 29.3, 29.2, 29.1, 28.3, 26.4, 26.3, 25.1, 23.4, 22.1, 20.8, 16.3. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{22}H_{39}O_2NaCl_3^+$: 463.1908, found 463.1927.



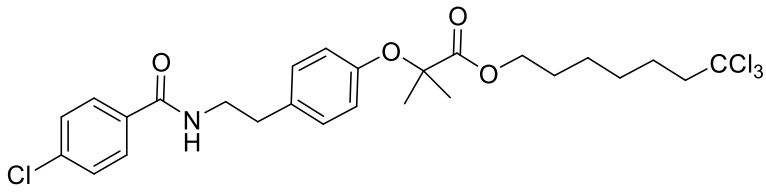
3ag:(1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 12,12,12-trichlorododecanoa -te: colorless oil (34.8 mg, 79%). Purification: 10% EtOAc/Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 4.88 (d, *J* = 7.2 Hz, 1H), 2.66 (t, *J* = 5.6 Hz, 2H), 2.30 (t, *J* = 7.6 Hz, 2H), 1.96-1.91 (m, 1H), 1.77-1.58 (m, 6H), 1.39-1.22 (m, 16H), 0.89-0.82 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 174.2, 100.3, 79.6, 55.2, 48.7, 47.8, 44.9, 36.9, 34.7, 29.39, 29.36, 29.3, 29.2, 29.1, 28.3, 28.1, 27.1, 26.4, 25.1, 19.7, 18.9, 13.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{38}O_2Cl_3^+$: 439.1932, found 439.1927.



3ah: 7,7,7-trichloroheptyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl) acetate: colorless oil (45.9 mg, 82%). Purification: 20% EtOAc/Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.66 (d, *J* = 9.2 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 6.97 (s, 1H), 6.86 (d, *J* = 9.2 Hz, 1H), 6.67 (d, *J* = 9.6 Hz, 1H), 4.11 (t, *J* = 6.8 Hz, 2H), 3.84 (s, 3H), 3.66 (s, 2H), 2.62 (t, *J* = 10.0 Hz, 2H), 2.40 (s, 3H), 1.75-1.58 (m, 4H), 1.41-1.31 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): 171.0, 168.3, 156.0, 139.3, 136.0, 133.9, 131.2, 130.8, 130.7, 129.2, 115.0, 112.7, 111.6, 101.4, 100.0, 64.9, 55.7, 55.0, 30.5, 28.5, 27.9, 26.3, 25.7, 13.4. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{28}NO_4Cl_4^+$: 558.0767, found 558.0768.

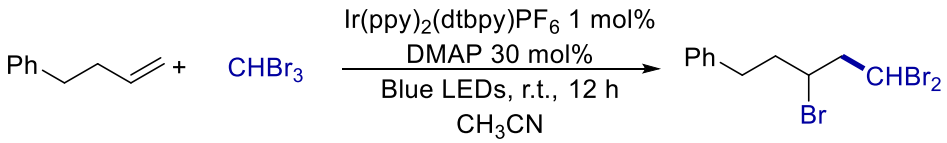


3ai: 7,7,7-trichloroheptyl (S)-2-(6-methoxynaphthalen-2-yl)propanoate: colorless oil (38.9 mg, 90%). Purification: 5% EtOAc/Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.72-7.68 (m, 3H), 7.41 (d, J = 8.0 Hz, 1H), 7.15-7.12 (m, 2H), 4.12-4.05 (m, 2H), 3.91 (s, 3H), 3.88-3.83 (m, 1H), 2.55 (t, J = 8.8 Hz, 2H), 1.68-1.63 (m, 2H), 1.58 (d, J = 6.4 Hz,3H), 1.43-1.27 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 174.7, 157.6, 135.8, 133.7, 129.2, 128.9, 127.1, 126.3, 125.9, 119.1, 105.6, 100.1, 64.6, 55.3, 54.9, 45.5, 28.4, 27.8, 26.2, 25.6, 18.4. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{21}H_{26}O_3Cl_3^+$: 431.0942, found 431.0947.



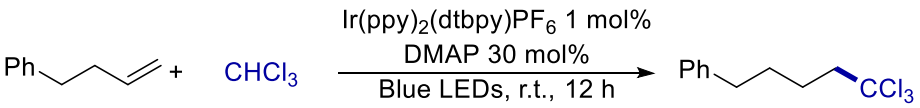
3aj:7,7,7-trichloroheptyl2-(4-(2-(4-chlorobenzamido)ethyl)phenoxy)-2-methylpropan -oate: colorless oil (37.7 mg, 67%). Purification: 50% EtOAc/Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.61 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.8 Hz, 2H), 7.08 (d, J = 7.2 Hz, 2H), 6.79 (d, J = 7.2 Hz, 2H), 6.18 (s, 1H), 4.16 (t, J = 5.6 Hz, 2H), 3.70-3.61 (m, 2H), 2.84 (t, J = 6.4 Hz, 2H), 2.62 (t, J = 7.2 Hz, 2H), 1.67-1.62 (m, 2H), 1.59 (s, 6H), 1.38-1.25 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 174.4, 166.4, 154.2, 137.6, 133.0, 132.3, 129.5, 128.8, 128.3, 119.4, 119.3, 114.9, 100.0, 79.1, 65.3, 55.0, 41.3, 34.8, 28.3, 27.9, 26.3, 25.6, 25.4, 25.0. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{32}NO_4Cl_4^+$: 562.1080, found 562.1093.

2.6 Synthesis of (3,5,5-Tribromopentyl)benzene



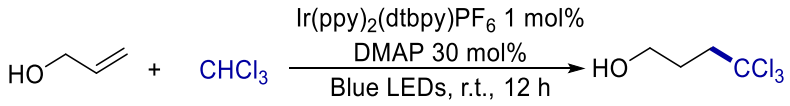
A 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 4-phenyl-1-butene (13.2 mg, 0.1 mmol, 1.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (0.91 mg, 0.001 mmol, 0.01 equiv.), DMAP (3.7 mg, 0.03 mmol, 0.3 equiv.), $CHBr_3$ (75.8 mg, 0.3 mmol, 3.0 equiv.), and CH_3CN (1 mL). The reactor was placed under a blue LED (Kessil light, 40 W, 456 nm) and irradiated for 12 h under argon at room temperature. After reducing in vacuo, the residue was purified by chromatography on silica gel to give (3,5,5-tribromopentyl)benzene (**3y**) as colorless oil (30.4 mg, 79%). ^1H NMR (400 MHz, $CDCl_3$, ppm):[11] 7.35-7.31 (m, 2H), 7.26-7.22 (m, 3H), 5.94-5.90 (dd, J_1 = 3.6 Hz, J_2 = 10.0 Hz, 1H), 4.16-4.09 (m, 1H), 2.98-2.77 (m, 4H), 2.23-2.16 (m, 2H).

3 Gram Synthesis of (5,5,5-Trichloropentyl) benzene (3a)



A 50 mL Schlenk tube equipped with a magnetic stir bar was charged with 4-phenyl-1-butene (1.0 g, 7.6 mmol, 1.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (69.2 mg, 0.076 mmol, 0.01 equiv.), DMAP (278.2 mg, 2.28 mmol, 0.3 equiv.), and chloroform (30 mL). The reactor was placed under a blue LED (Kessil light, 40 W, 456 nm) and irradiated at 28 °C under argon for 24 h. After reducing in vacuo, the residue was purified by flash column chromatography to give the (5,5,5-trichloropentyl) benzene as colorless oil (1.43 g, 75%).

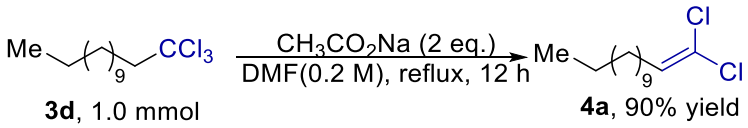
4 Gram Synthesis of the Key Intermediate in Haterumalides NA and NC



A 50 mL Schlenk tube equipped with a magnetic stir bar was charged with prop-2-en-1-ol (1.16 g, 20 mmol, 1.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (183 mg, 0.2 mmol, 0.01 equiv.), DMAP (732 mg, 6 mmol, 0.3 equiv.). and chloroform (30 mL). The reactor was placed under a blue LED (Kessil light, 40 W, 456 nm) and irradiated at 28 °C under argon for 24 h. After reducing in vacuo, the residue was purified by column chromatography on silica gel to give the 4,4,4-trichlorobutan-1-ol as colorless oil (2.83 g, 80%). Purification: 20% EtOAc/Petroleum ether. ^1H NMR (400 MHz, $CDCl_3$, ppm):[12] 3.78 (m, 2H), 2.84-2.81 (m, 2H), 2.07-2.02 (m, 2H).

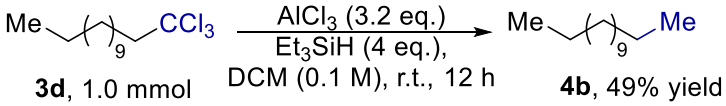
5 Derivatization of the Trichloromethyl Compounds

5.1 Synthesis of 1,1-Dichlorotridec-1-ene



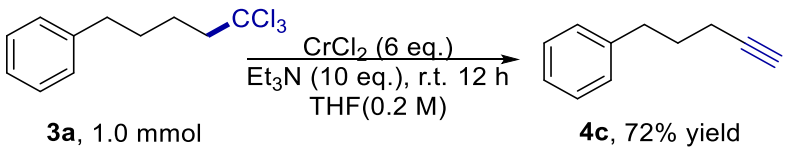
A 10 mL bottle equipped with a magnetic stir bar was charged with 1,1,1-trichlorotridecane (288 mg, 1.0 mmol, 1.0 equiv.), CH_3COONa (164 mg, 2.0 mmol, 2.0 equiv.) and DMF (2 mL). After refluxing under argon for 12 h, The mixture was reduced in a in vacuo and the residue was purified by column chromatography on silica gel to give the 1,1-dichlorotridec-1-ene as colorless oil (226 mg, 90%). Purification: 100% Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$, ppm):[13] 5.87 (t, J = 4.0 Hz, 1H), 2.20-2.16 (m, 2H), 1.27-1.31 (m, 18H), 0.91 (t, J = 4.0 Hz, 3H).

5.2 Synthesis of *n*-Tridecane



A 10 mL bottle equipped with a magnetic stir bar was charged with 1,1,1-trichlorotridecane (288 mg, 1.0 mmol, 1.0 equiv.), $AlCl_3$ (426 mg, 3.2 mmol, 3.2 equiv.), Et_3SiH (465 mg, 4.0 mmol, 4.0 equiv.) and DCM (1 mL). The mixture was reacting at 28 ºC under argon for 12 h. After reduced in vacuo, the residue was purified by column chromatography on silica gel to give the *n*-tridecane as colorless oil (90 mg, 49%). Purification: 100% Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$, ppm):[14] 1.27-1.31 (m, 22H), 0.91 (t, J = 4.0 Hz, 6H).

5.3 Synthesis of Pent-4-yn-1-ylbenzene

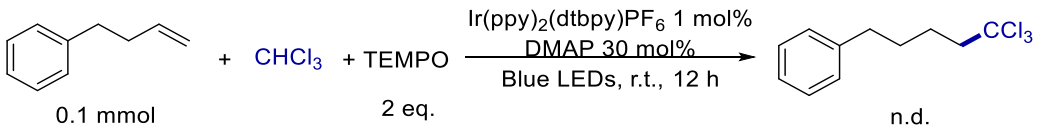


A 10 mL bottle equipped with a magnetic stir bar was charged with 1,1,1-trichlorotridecane (288 mg, 1.0 mmol, 1.0 equiv.), $CrCl_2$ (737 mg, 6.0 mmol, 6.0 equiv.),

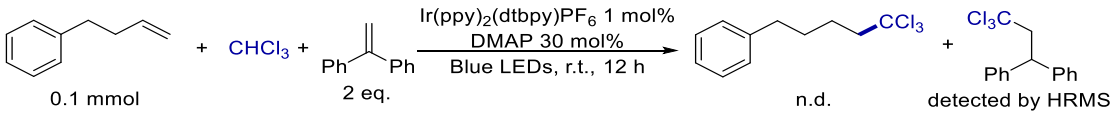
Et_3N (1.01 g, 10.0 mmol, 10.0 equiv.) and THF (2 mL). The mixture was reacting at 28 ^oC under argon for 12 h. After reduced in vacuo, the residue was purified by column chromatography on silica gel to give the 5-phenyl-1-pentyne as colorless oil (104 mg, 72%). Purification: 100% Petroleum ether. ^1H NMR (400 MHz, $CDCl_3$, ppm):[15] 7.36-7.32 (m, 2H), 7.28-7.25 (m, 3H), 2.79 (t, J = 8.0 Hz, 2H), 2.28-2.34 (m, 2H), 2.05 (t, J = 2.4 Hz, 1H), 1.94-1.87 (m, 2H).

6 Mechanism Studies

6.1 Radical Inhibition Experiment



A 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 4-phenyl-1-butene (13.2 mg, 0.1 mmol, 1.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (0.91 mg, 0.001 mmol, 0.01 equiv.), DMAP (3.7 mg, 0.03 mmol, 0.3 equiv.), TEMPO (31.2 mg, 0.2 mmol, 2.0 equiv.), and chloroform (1 mL). The reactor was placed under a blue LED (Kessil light, 40 W, 456 nm) and irradiated for 12 h under argon at room temperature. When TEMPO was added into the reaction, no corresponding products were observed according to ^1H NMR.



A 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 4-phenyl-1-butene (13.2 mg, 0.1 mmol, 1.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (0.91 mg, 0.001 mmol, 0.01 equiv.), DMAP (3.7 mg, 0.03 mmol, 0.3 equiv.), ethene-1,1-diyldibenzene (36 mg, 0.2 mmol, 2.0 equiv.) and chloroform (1 mL). The reactor was placed under a blue LED (Kessil light, 40 W, 456 nm) and irradiated for 12 h under argon at room temperature. When ethene-1,1-diyldibenzene was added into the reaction, no (5,5,5-trichloropentyl) benzene was observed according ^1H NMR. The mixture was then identified by HRMS directly. As shown in Figure S3, (3,3,3-trichloroprop-1-ene-1,1-diyl)dibenzene could be detected by HRMS. HRMS (ESI): m/z $[M+K]^+$ calcd for $C_{15}H_{13}Cl_3K^+$: 336.9714, found 336.9730.

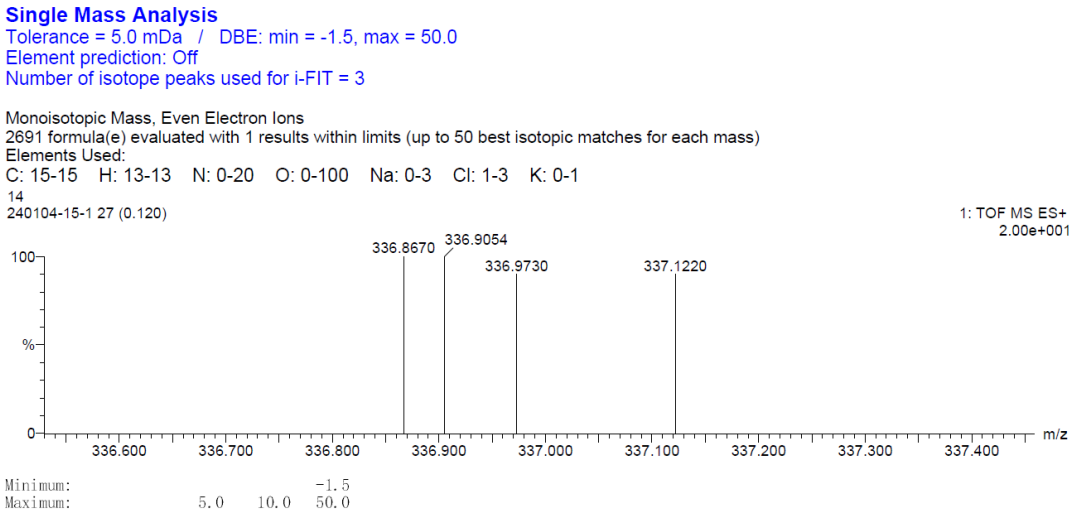
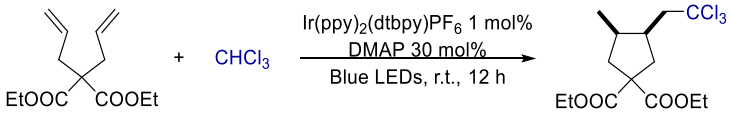


Figure S3. HRMS of (3,3,3-trichloroprop-1-ene-1,1-diyl)dibenzene

6.2 Radical Clock Experiment



A 10 mL Schlenk tube equipped with a magnetic stir bar was charged with diethyl 2,2-diallylmalonate (24.3 mg, 0.1 mmol, 1.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (0.91 mg, 0.001 mmol, 0.01 equiv.), DMAP (3.7 mg, 0.03 mmol, 0.3 equiv.), and chloroform (1 mL). The reactor was placed under a blue LED (Kessil light, 40 W, 456 nm) and irradiated for 12 h under argon at room temperature. After reducing in vacuo, the residue was purified by chromatography on silica gel to give the diethyl (3R,4R)-3-methyl-4-(2,2,2-trichloroethyl)cyclopentane-1,1-dicarboxylate as colorless oil (338 mg, 94%, d.r. = 9.3:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm):[16] 4.24-4.18 (m, 4H), 2.93-2.88 (m, 1H), 2.75-2.61 (m, 2H), 2.56-2.48 (m, 2H), 2.42-2.34 (m, 1H), 2.25 (t, J = 10.8 Hz, 1H), 2.06-2.02 (m, 1H), 1.27 (t, J = 8.0 Hz, 6H), 0.93 (d, J = 8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 172.7, 172.6, 99.7, 61.6, 58.5, 55.1, 41.2, 40.9, 38.7, 36.6, 15.3, 14.0.

6.3 Stern-Volmer Fluorescence Quenching Experiments

In a typical experiment, a solution of photocatalyst $Ir(ppy)_2(dtbbpy)PF_6$ in anhydrous MeCN (1.25×10^{-4} M) was added with an appropriate amount of quencher in a quartz

cuvette. Then the emission of the sample was collected. The emission intensity at 570 nm was collected with excited wavelength of 420 nm.

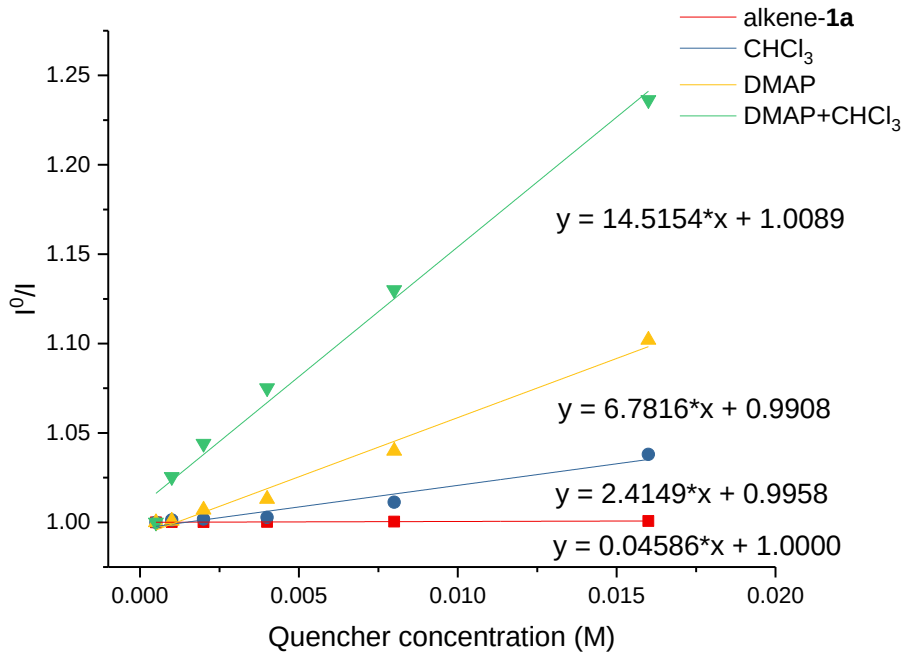
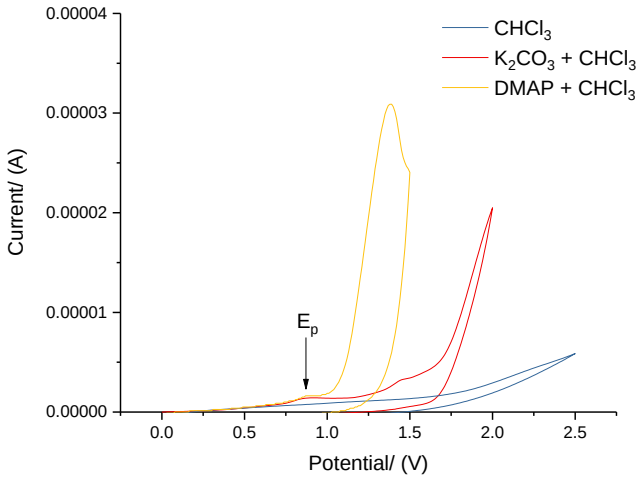


Figure S4. Stern-Volmer fluorescence quenching studies

6.4 Cyclic Voltammetry (CV) Measurements

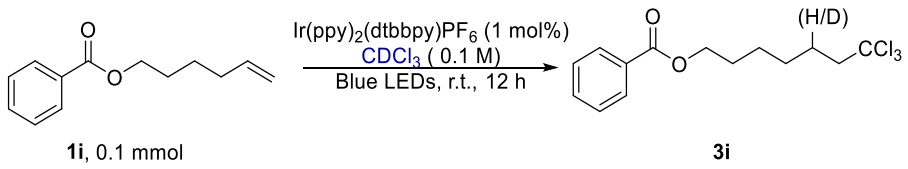
Cyclic Voltammograms were collected using a VersaSTAT 3 Potentiostat Galvanostat from Princeton Applied Research. $CHCl_3$ (0.1 M) and additives (K_2CO_3, 0.01 M or DMAP, 0.01 M) and tetrabutylammonium tetrafluoroborate 0.1 M in acetonitrile (5 mL) was used for tests. Measurements were performed using glassy carbon working electrode, platinum wire counter electrode, and 3.5 M NaCl silver-silver chloride reference electrode in a scan rate of 0.1 V/s. Ferrocene ($E_{1/2}$ = +0.42 V vs. SCE) was added at the end of the measurements as an internal standard to determine the precise potential scale. Potential values are given versus the saturated calomel electrode (SCE).



$E_{1/2}^{ox}$ (Trichloromethyl anion) = + 0.60V vs SCE in MeCN

Figure S5. The CV curves

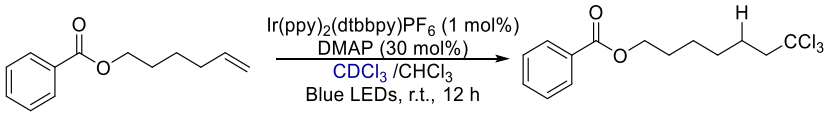
6.5 Deuterium Labeling Experiment



1i, 0.1 mmol **3i**

base:	DMAP (0.3 eq.)	K_2CO_3 (1 eq.)	KOtBu (1 eq.)
yield:	n.d	n.d	n.d

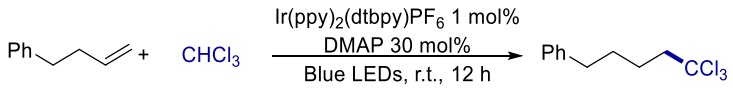
A 10 mL Schlenk tube equipped with a magnetic stir bar was charged with **1i** (20.4 mg, 0.1 mmol, 1.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (0.91 mg, 0.001 mmol, 0.01 equiv.), base, and $CDCl_3$ (1 mL). The reactor was placed under a blue LED (Kessil light, 40 W, 456 nm) and irradiated for 12 h under argon at room temperature. When $CDCl_3$ was used in this reaction, no corresponding products were observed according to ^1H NMR and GCMS.



1i, 0.1 mmol **3i** 58%.

A 10 mL Schlenk tube equipped with a magnetic stir bar was charged with **1i** (20.4 mg, 0.1 mmol, 1.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (0.91 mg, 0.001 mmol, 0.01 equiv.), DMAP (3.7 mg, 0.03 mmol, 0.3 equiv.), $CHCl_3$ (0.5 mL), and $CDCl_3$ (0.5 mL). The reactor was placed under a blue LED (Kessil light, 40 W, 456 nm) and irradiated for 12 h under argon at room temperature. After reducing in vacuo, the residue was purified by chromatography on silica gel to give 7,7,7-trichloroheptyl benzoate as colorless oil (18.7 mg, 58%). The ^1H NMR and ^2H NMR suggested no deuterated product was formed.

6.6 Light On-off Experiments



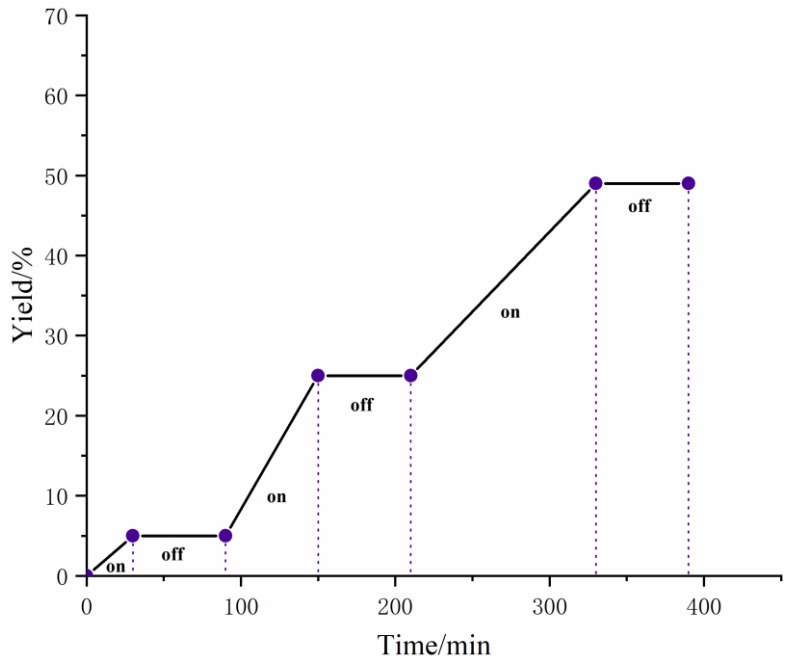


Figure S6. Light On-off Experiments

6.7 Determination of Photochemical Quantum Yields

Follow McMullen's procedure for photon flux[17]

The following solutions must be prepared ahead of time:

1. Ferrioxalate solution

A 0.15 M solution of potassium ferrioxolate was prepared by dissolving potassium

ferrioxolate ($K_3Fe(C_2O_4)_3*3H_2O$) (1.842 g, 3.75 mmol) with the 0.05 M sulfuric acid solution prepared in a 25 mL volumetric flask. Make every precaution to prepare and store the solution in the dark.

2. Developer solution

67.8 g of sodium acetate was dissolved in 500 ml of 0.5 M sulfuric acid. 5 g of 1,10-phenanthroline was added to this solution. Store in the dark.

To determine the photon flux of the Kessil lamp, 2.0 mL of the ferrioxalate solution was placed in a 10 mL Schlenk tube and irradiated at $\lambda = 456$ nm with an emission slit width of 10.0 nm. After irradiation, 10 μL aliquots of the solution were taken at different time points between 0.5 and 3 minutes of irradiation. This aliquot is immediately added to 5 mL of the developer solution and the flask is wrapped in aluminum foil. A blank sample is prepared by adding 10 μL of the ferrioxalate solution to 5 mL of developer solution. The solutions were left in the dark for one hour, eventually becoming bright red. Solutions were transferred to a separate cuvette and the absorbance spectrum of the $Fe(phen)_3^{2+}$ complex was obtained. The absorbance at 510 nm (ε = 11,100 M^{-1} cm^{-1}) was measured for each sample. The conversion was calculated using **eq 1**.

$$\text{mol } Fe^{2+} = \frac{V1 \cdot V3 \cdot \Delta A}{V2 \cdot l \cdot \varepsilon} \qquad \textbf{eq 1}$$

ΔA = the difference between the absorbance between the sample and the blank as measured at 510 nm.

l = the path length of the cuvette (1 cm)

ε = the extinction coefficient of $Fe(phen)_3^{2+}$ complex at 510 nm (11,100 M^{-1} cm^{-1})

V1 = the total volume of the irradiated solution (2 mL; 2 x 10^{-3} L)

V2 = the volume of the aliquot removed from solution (10 μL; 1 x 10^{-5} L)

V3 = the volume that aliquots are diluted with (5 mL; 5 x 10^{-3} L)

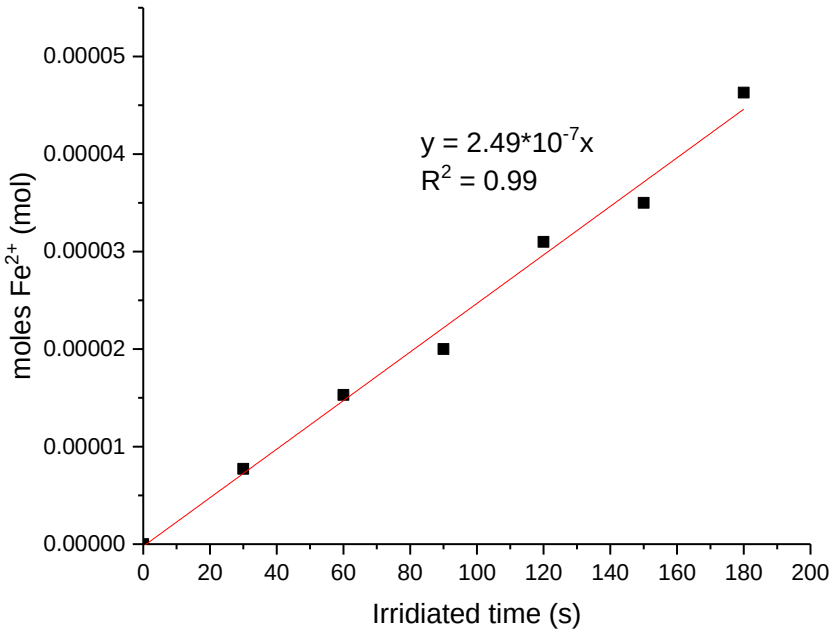


Figure S7. Compiled linear fits for the photon flux

A plot of moles Fe^{2+} as a function of time yields a linear equation with an intercept at zero. The value of the slopes collected is 2.49 x 10^{-7} mol^{-1} s^{-1}.

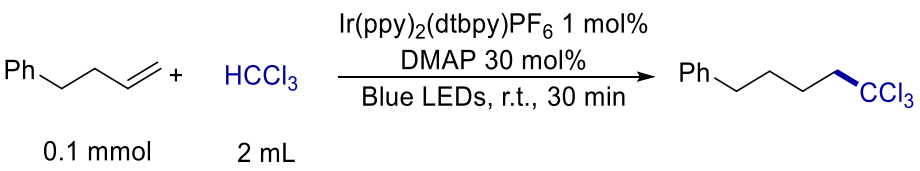
The photon flux can be calculated using **eq 2**.

$$\text{Photon flux} = \frac{\text{mol } Fe^{2+}}{\Phi \cdot t \cdot f} \qquad \textbf{eq 2}$$

The documented quantum yield of the actinometer (Φ = 0.84 at 458 nm)[18] and f is the fraction of light absorbed at λ = 456 nm (0.95, vide infra).[19] The photon flux in einsteins s^{-1}.

$$\text{Photon flux} = \frac{2.49 \times 10^{-7}}{0.84 \times 0.95} = 3.12 \times 10^{-7}$$

Determination of the reaction quantum yield.



A 10 mL Schlenk tube equipped with a magnetic stir bar was charged with alkene (0.1 mmol, 1.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (0.91 mg, 0.001 mmol, 0.01 equiv.), DMAP (3.7 mg, 0.03 mmol, 0.3 equiv.), and chloroform (2 mL). The reactor was placed under a blue LED (Kessil light, 40 W, 456 nm) and irradiated for 30 min under argon at room temperature. The solvent was removed under vacuum. The yield of product formed was determined by crude ^1H NMR based on a CH_2Br_2 standard. The quantum yield was determined using **eq 3**. Essentially, all incident light (f = 1, vide infra) is absorbed by the $Ir(ppy)_2(dtbpy)PF_6$ at the reaction conditions described above.

$$\Phi = \frac{\text{mol product}}{\text{flux} \cdot \text{t} \cdot \text{f}} \qquad \textbf{eq 3}$$

Experiment: alkene (0.1 mmol), $Ir(ppy)_2(dtbpy)PF_6$ (0.91 mg, 0.001 mmol), DMAP (0.03 mmol) in $CHCl_3$ (2.0 mL) after 1800 s yielded 6% of **3a**. $\Phi = 0.0107$.

$$\Phi = \frac{6 \times 10^{-6}}{3.12 \times 10^{-7} \times 1800 \times 1.00} = 0.0107$$

6.8 Proposed Mechanism

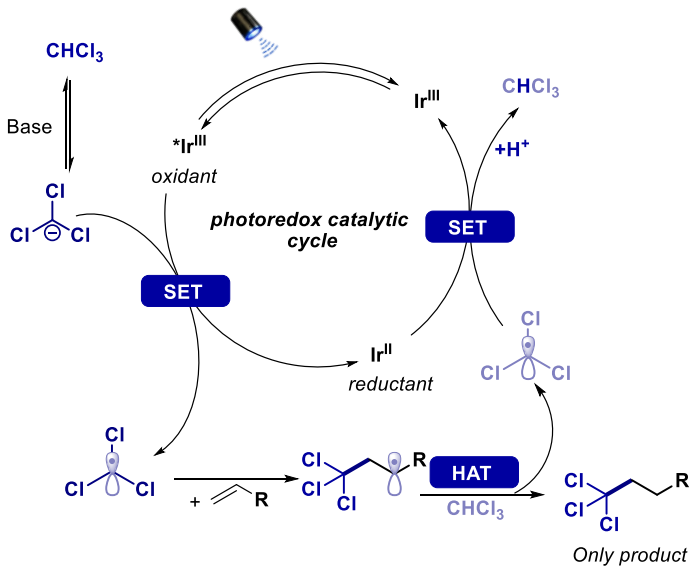


Figure S8. Proposed Catalytic Cycle

When inorganic bases sodium hydride, potassium carbonate and potassium *tert*-butoxide were employed as additives, the standard reaction consistently yielded the product in moderate to high yields. CV measurements showed identical oxidation signals in the presence of DMAP and potassium carbonate. Therefore, the process of chloroform deprotonation followed by oxidation to generate the trichloromethyl radical appears more feasible than the PCET process.

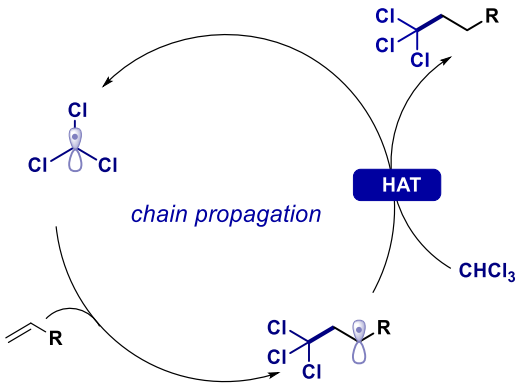


Figure S9. Chain Propagation

There was no significant yield change in the on/off light experiment and the Φ = 0.0106 <<1, the chain propagation process may not exist.

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Soc. Lond. A, 1956, **235**, 518–536.

8 NMR Spectra

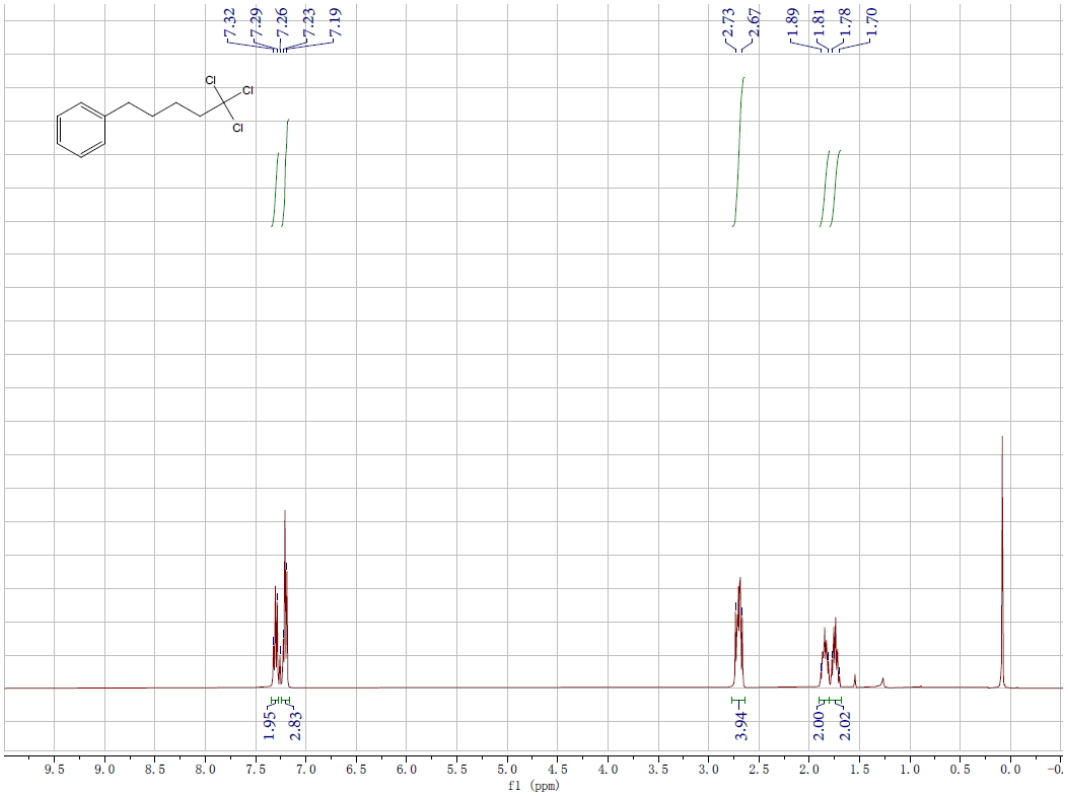

Figure S10. ^{1}H NMR Spectrum of **3a**

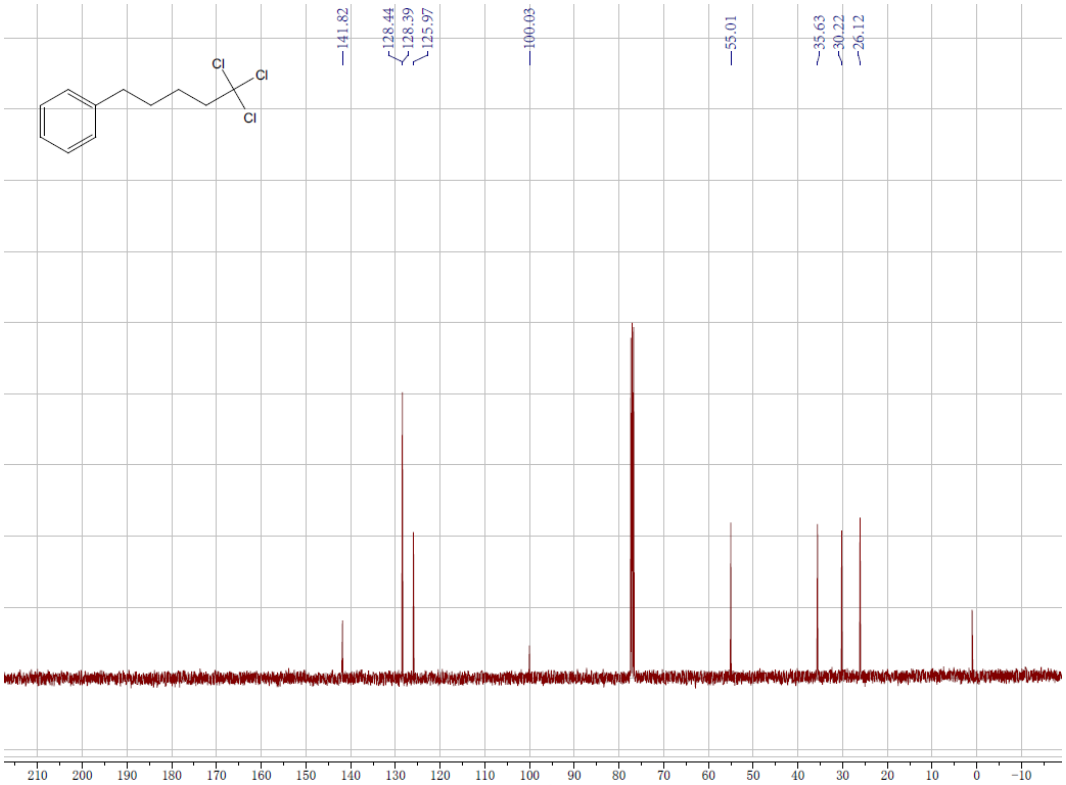

Figure S11. ^{13}C NMR Spectrum of **3a**

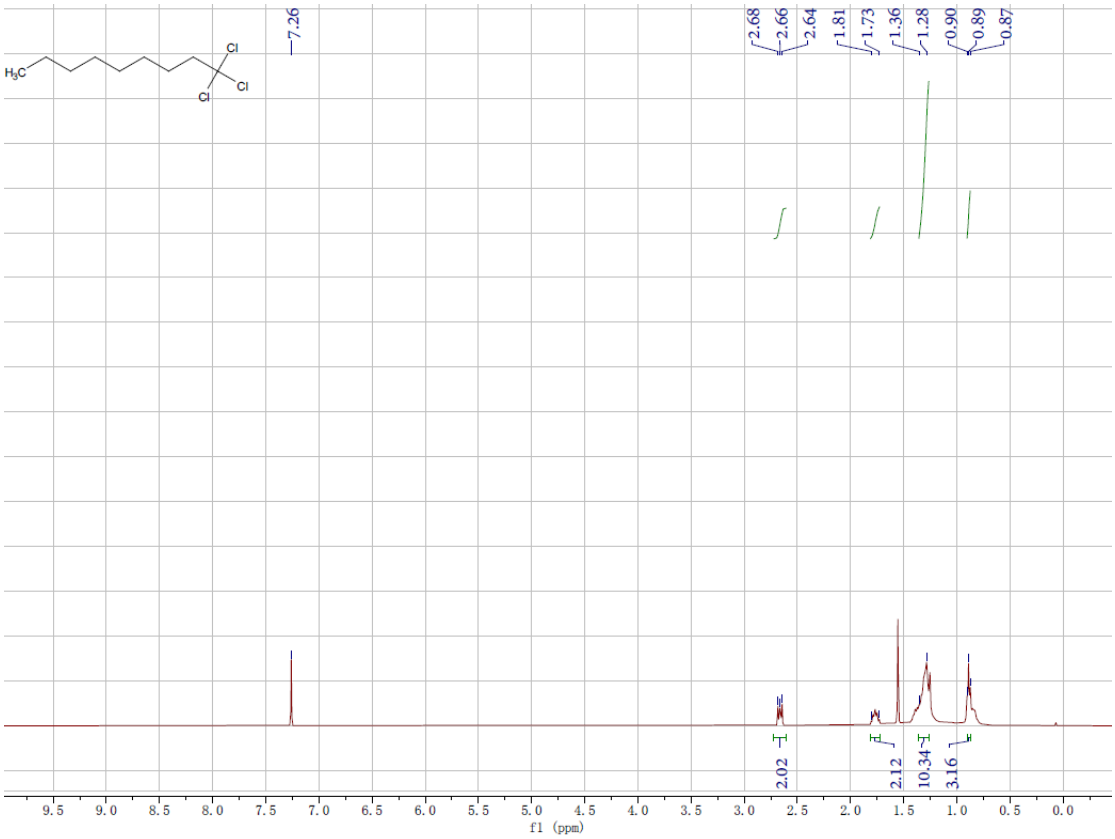

Figure S12.[1]H NMR Spectrum of **3b**

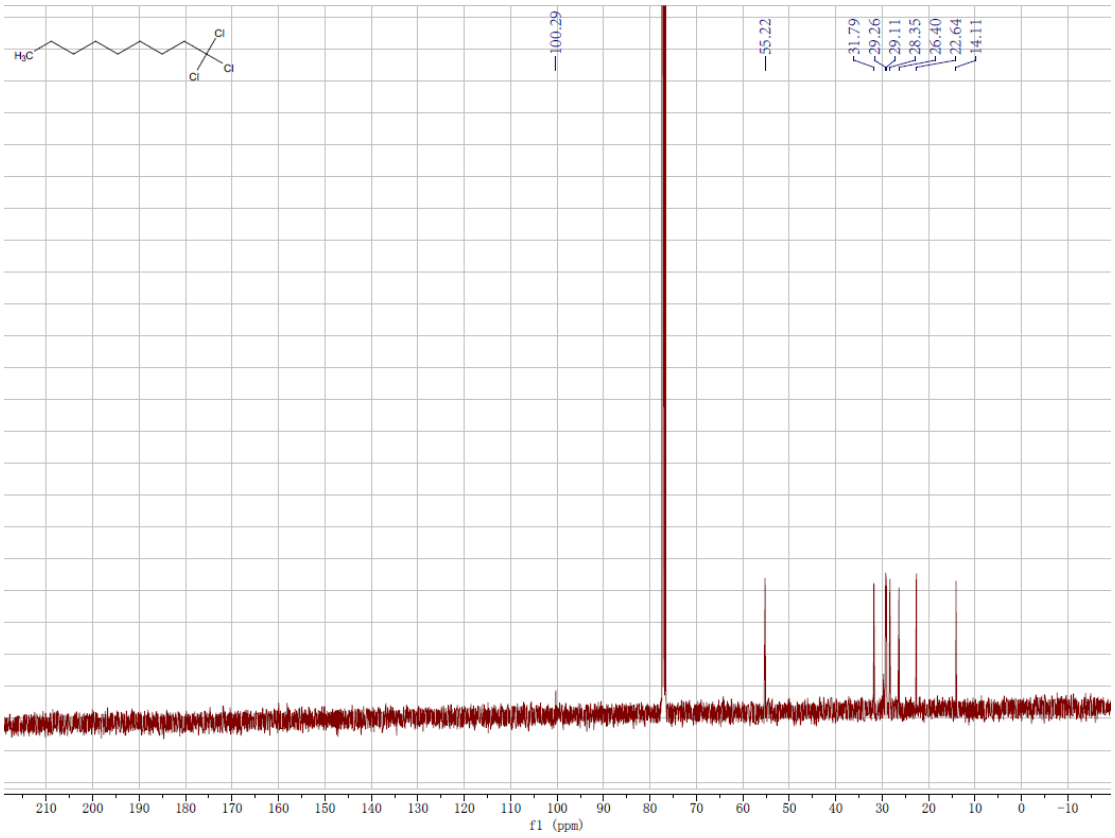

Figure S13. [13]C NMR Spectrum of **3b**

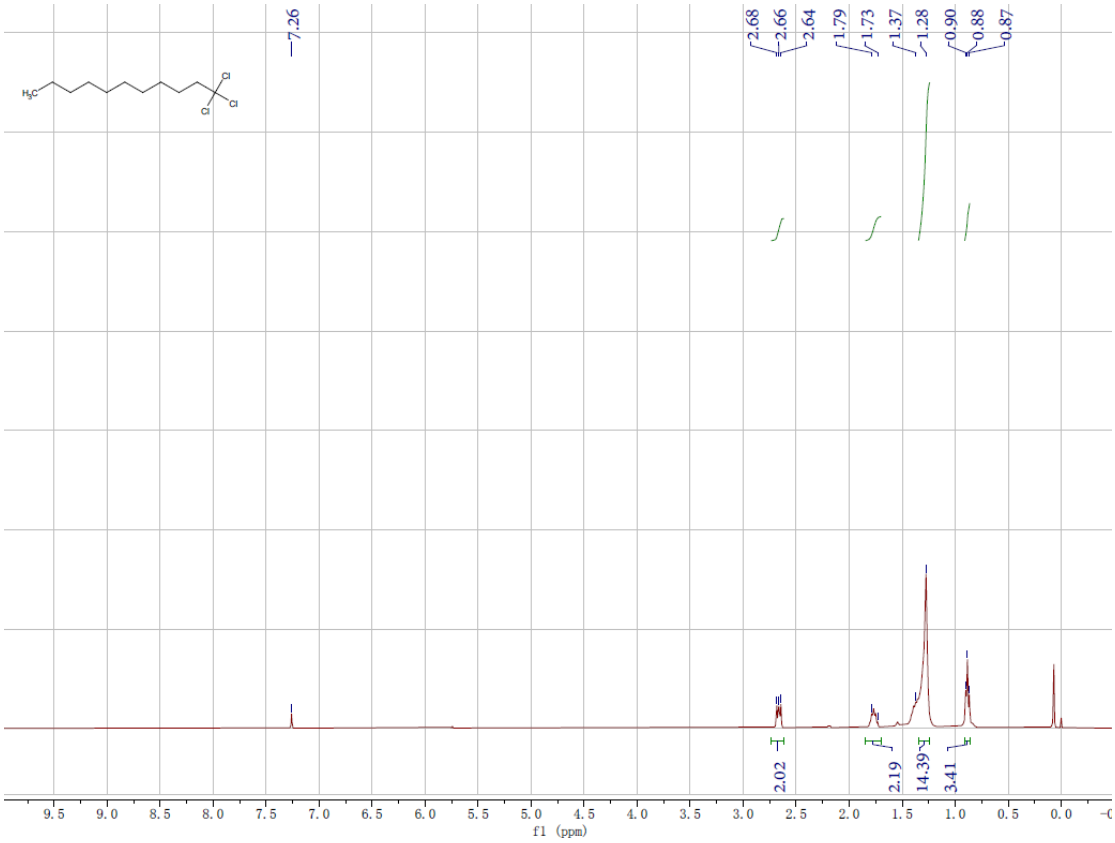

Figure S14. ^{1}H NMR Spectrum of **3c**

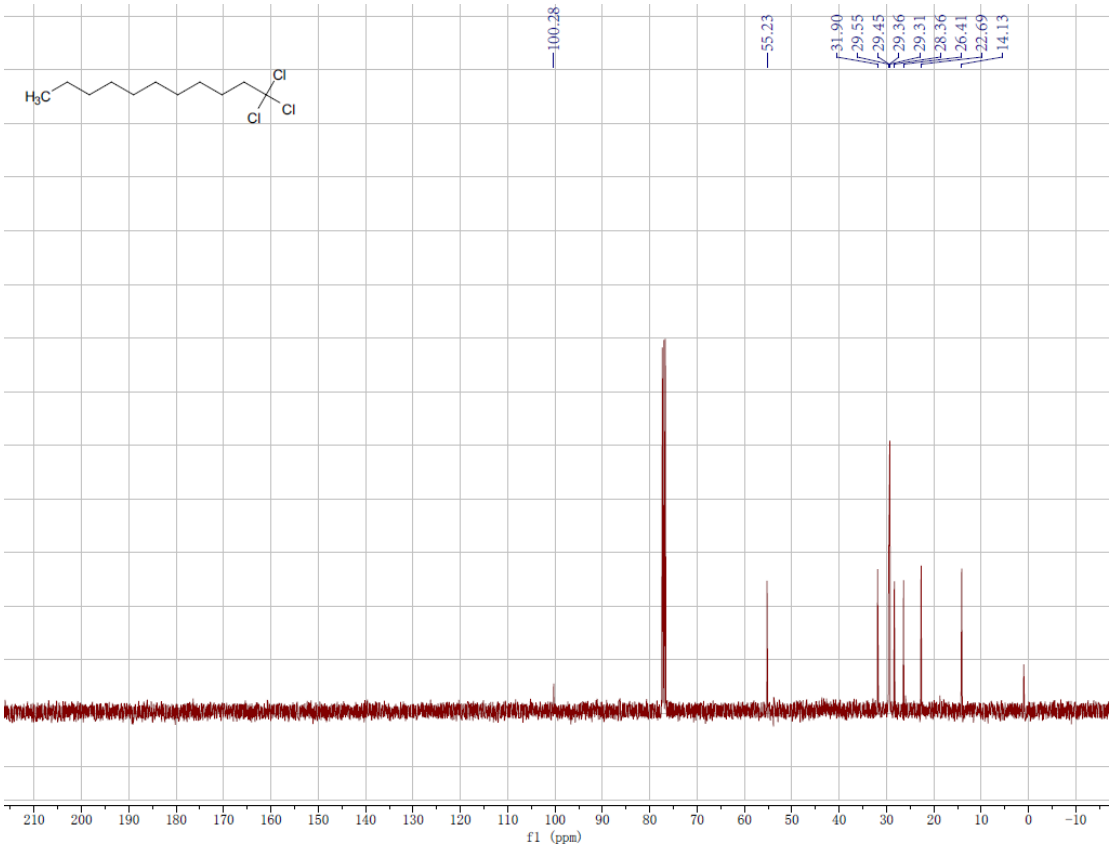

Figure S15. ^{13}C NMR Spectrum of **3c**

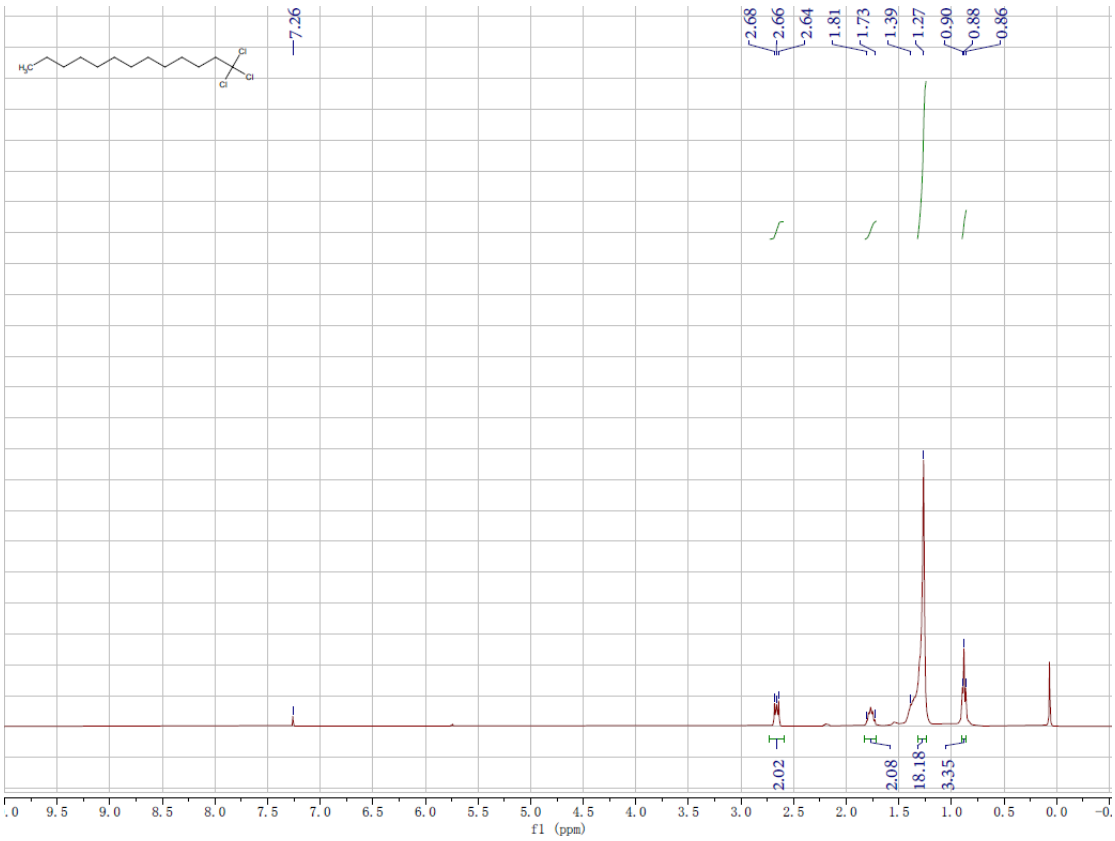

Figure S16. ^{1}H NMR Spectrum of **3d**

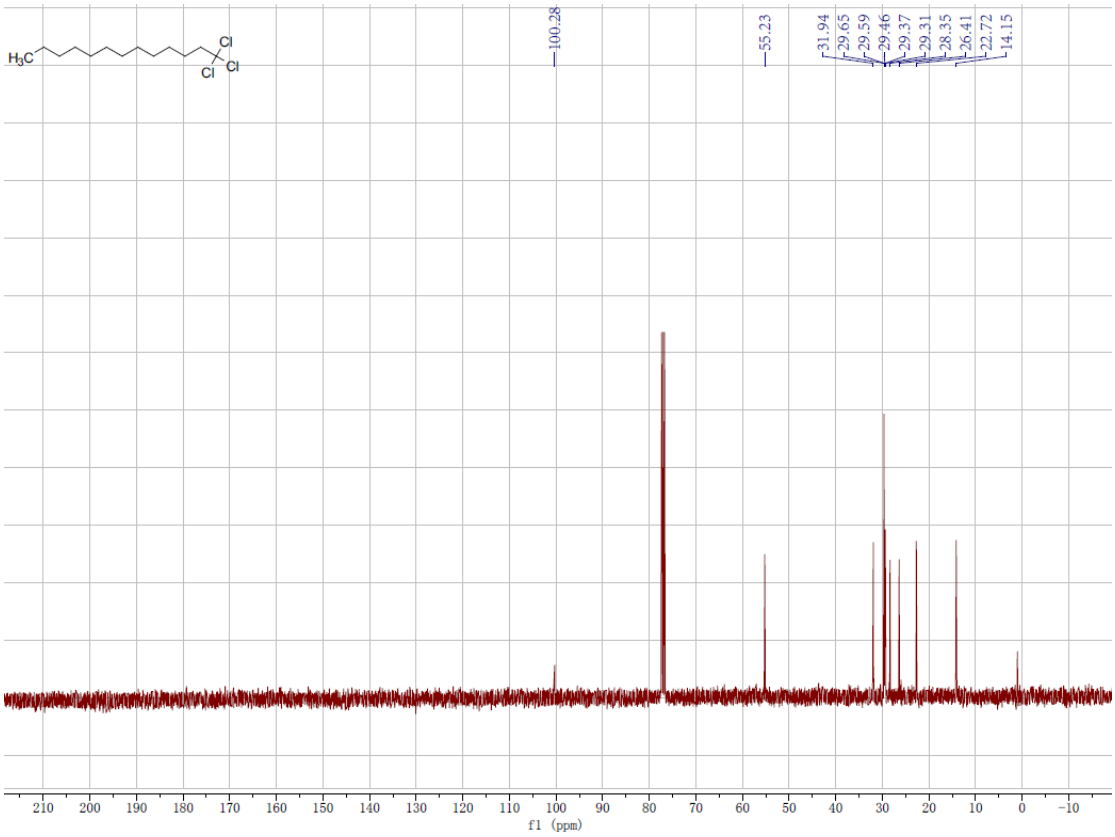

Figure S17. ^{13}C NMR Spectrum of **3d**

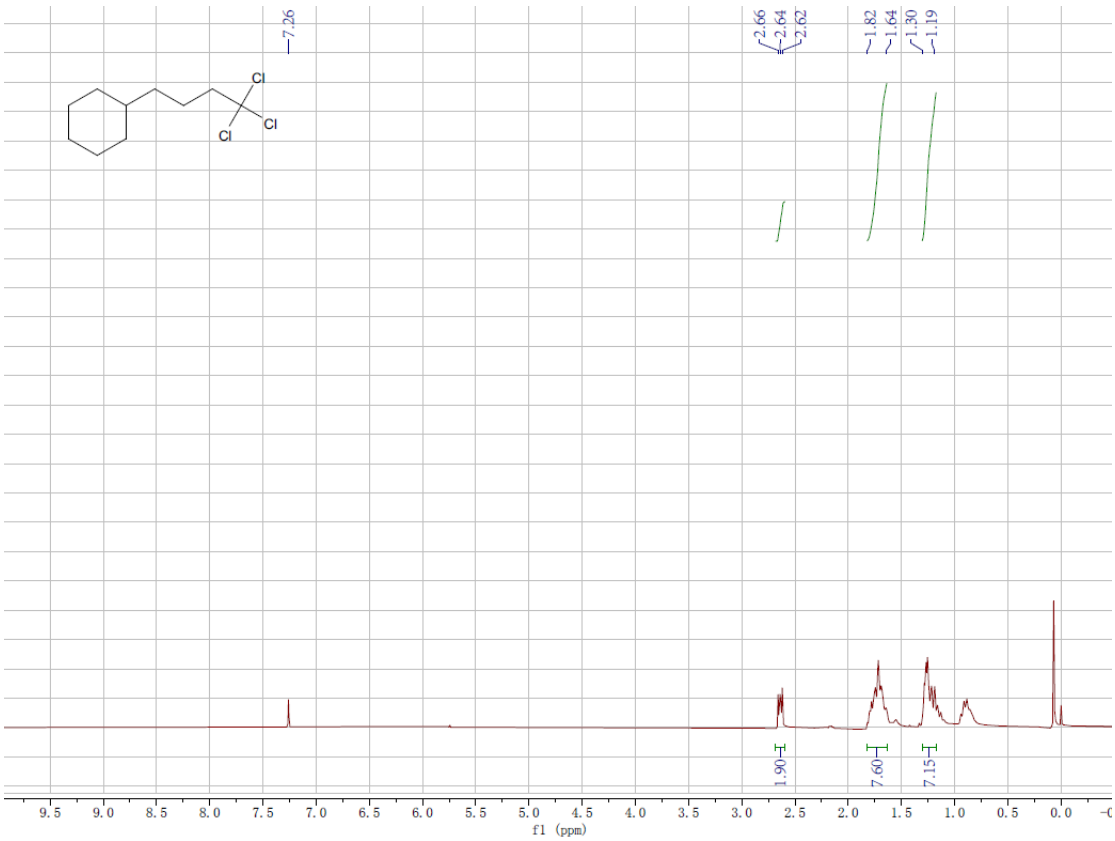

Figure S18. ^{1}H NMR Spectrum of **3e**

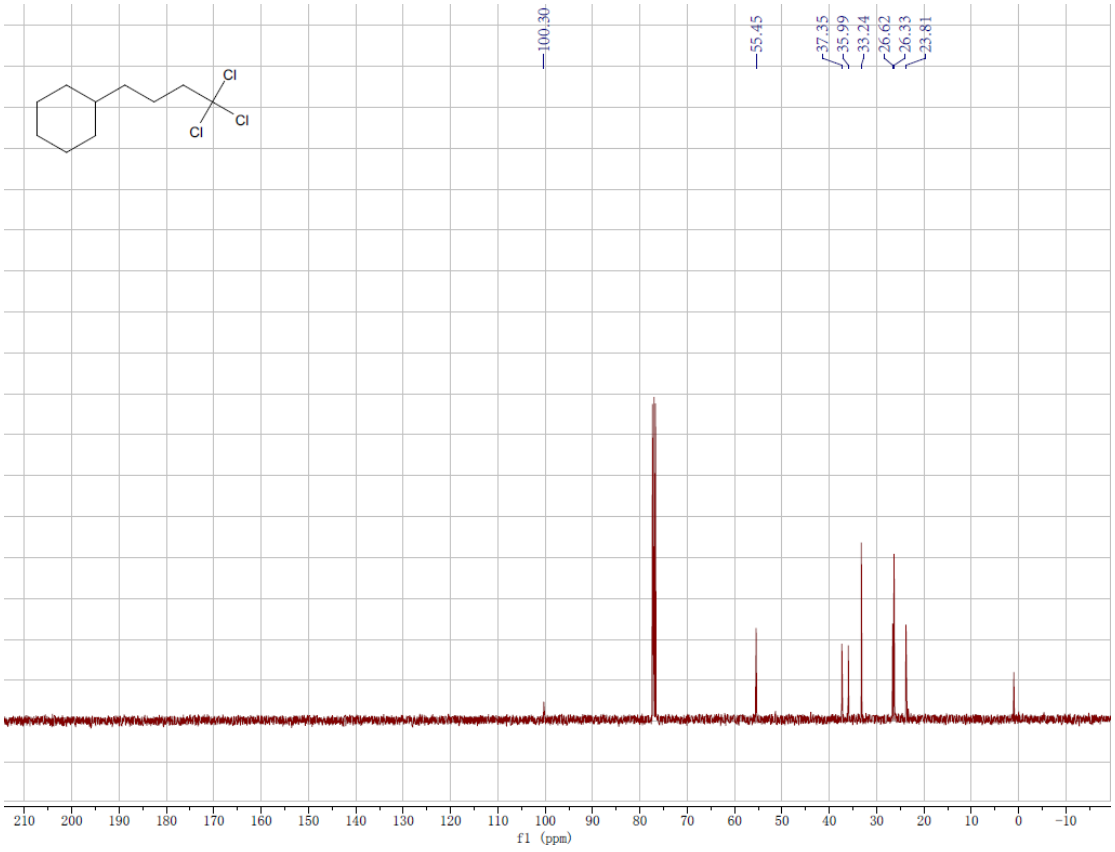

Figure S19. ^{13}C NMR Spectrum of **3e**

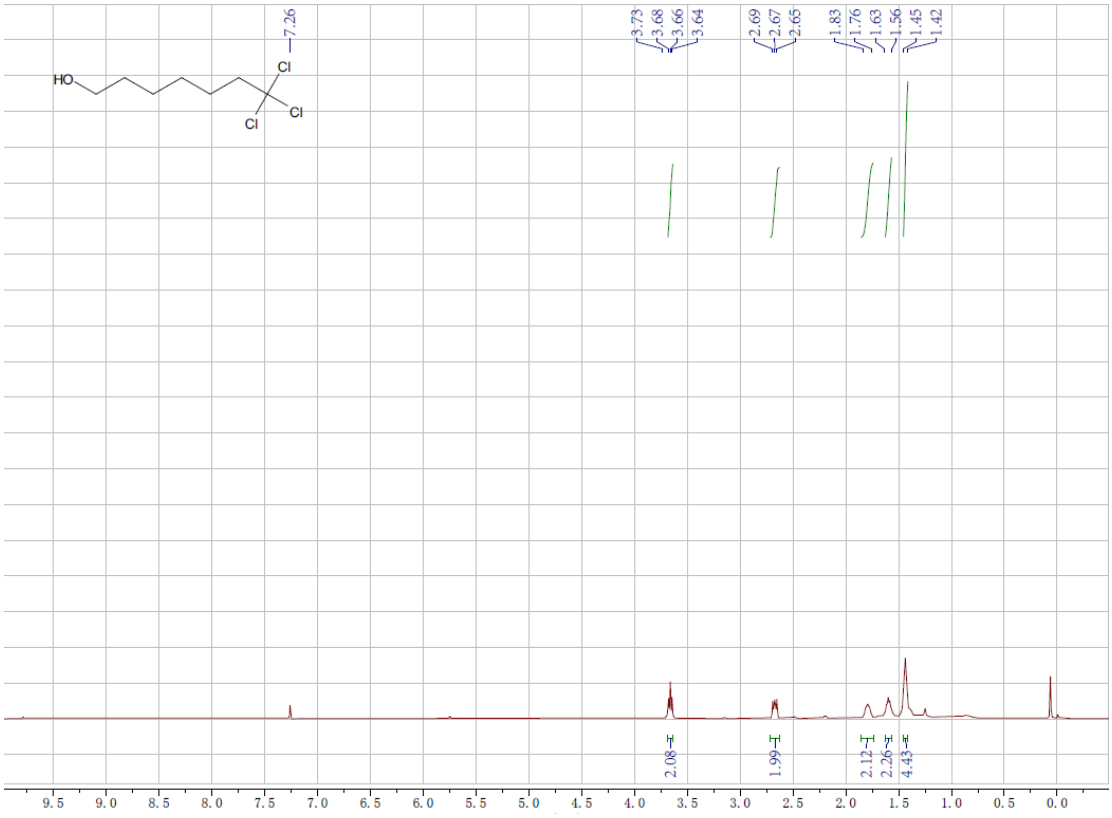

Figure S20. ^{1}H NMR Spectrum of **3f**

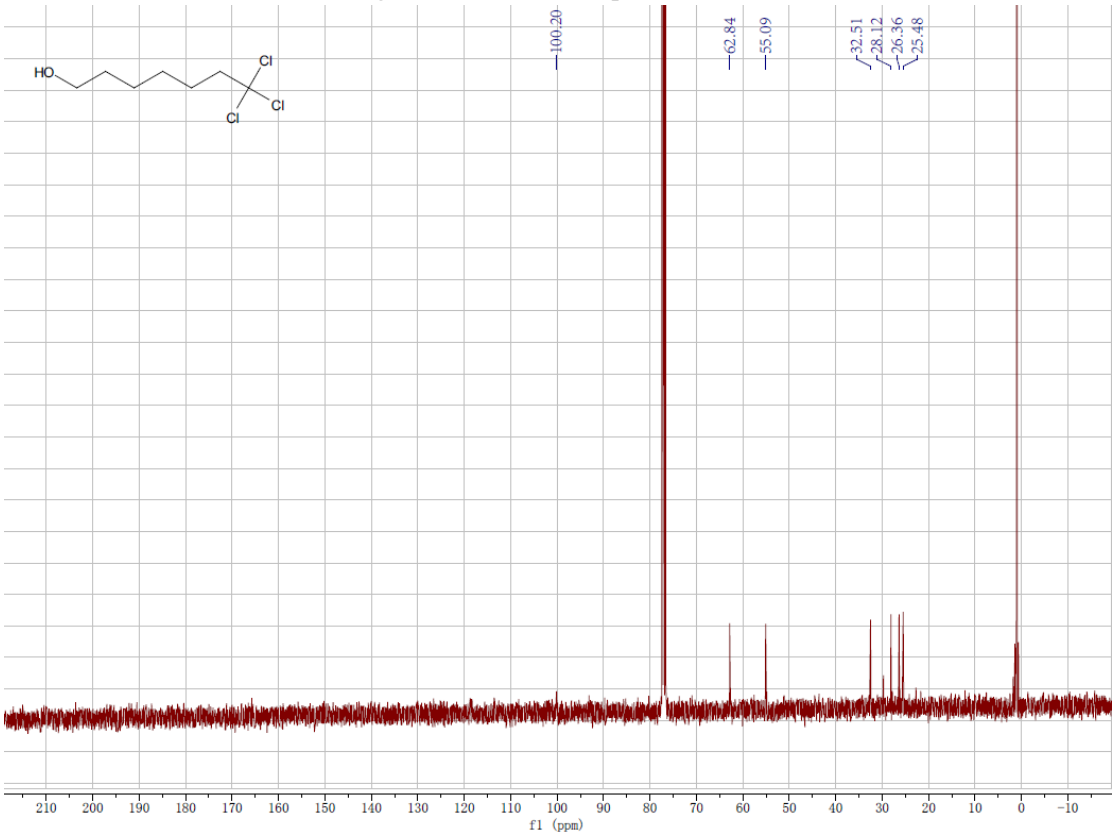

Figure S21. ^{13}C NMR Spectrum of **3f**

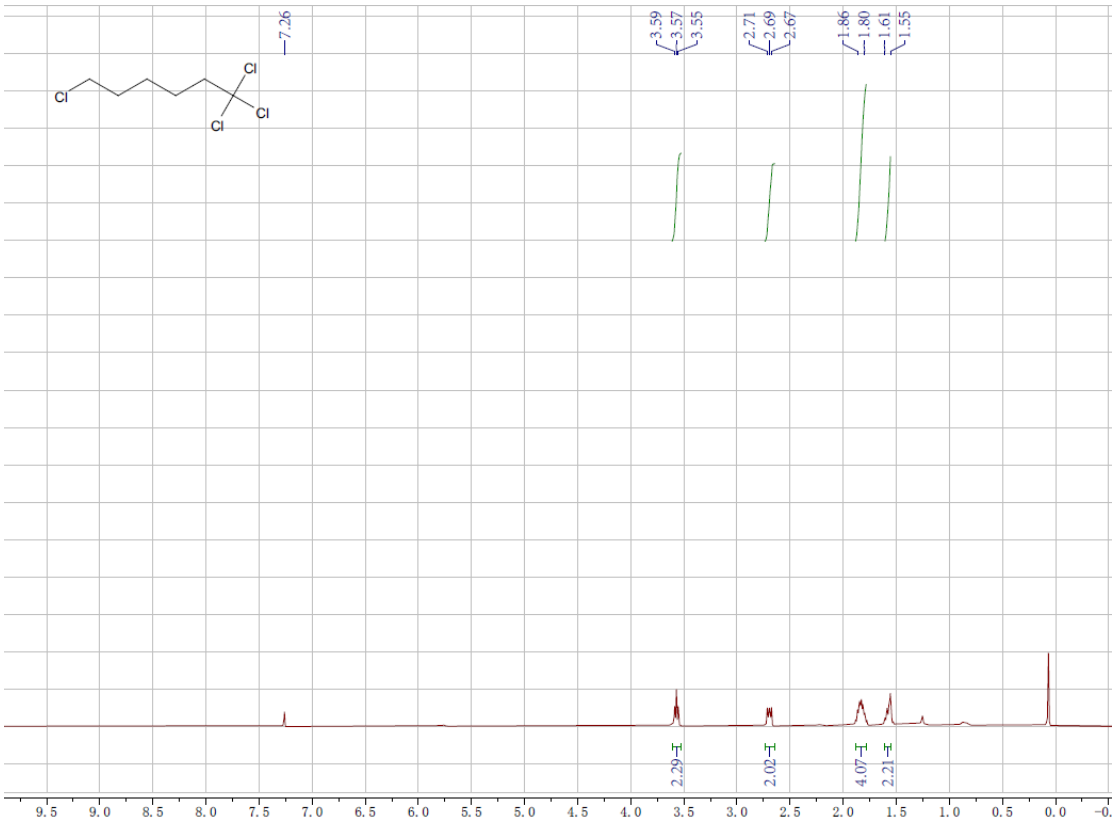

Figure S22. ^{1}H NMR Spectrum of **3g**

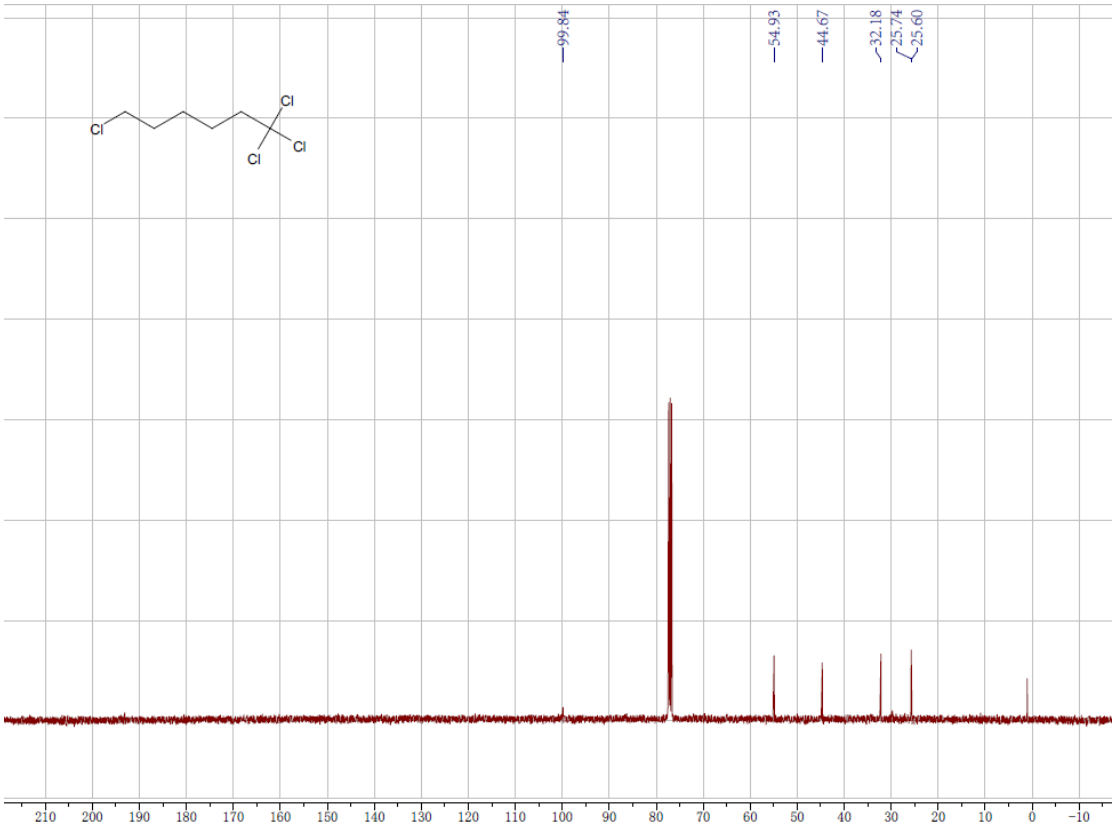

Figure S23. ^{13}C NMR Spectrum of **3g**

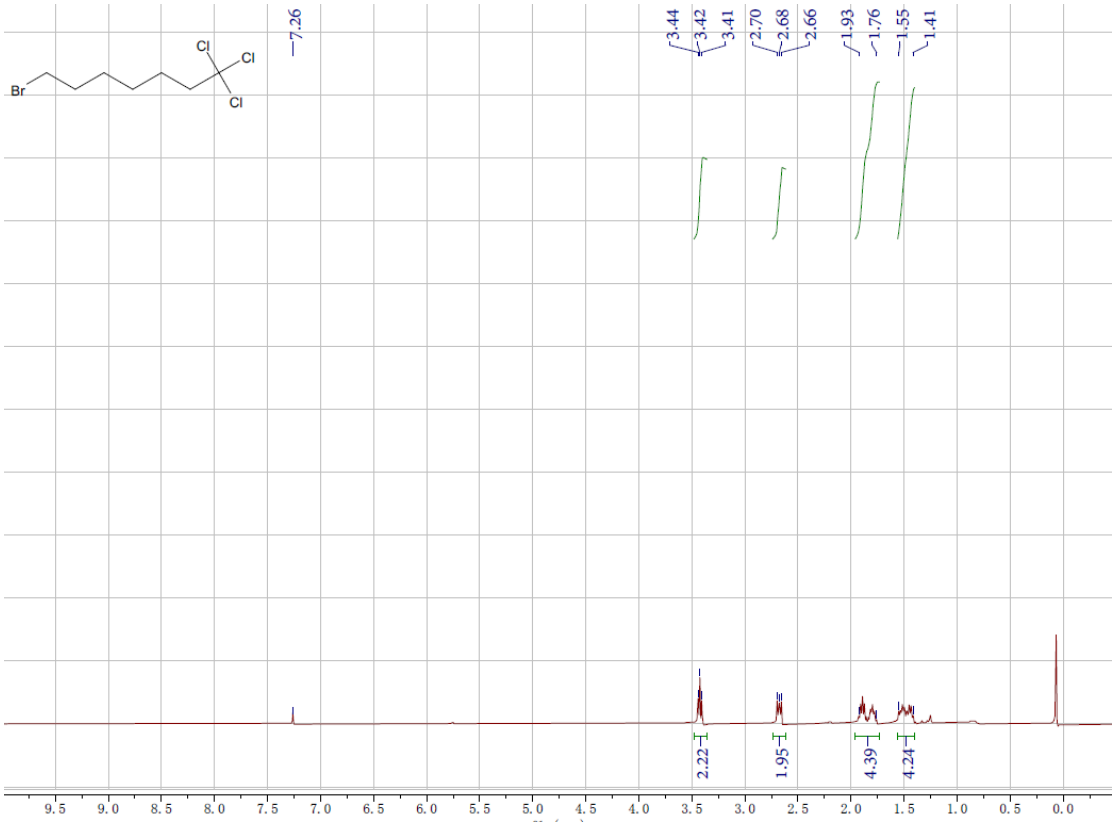

Figure S24. ^{1}H NMR Spectrum of **3h**

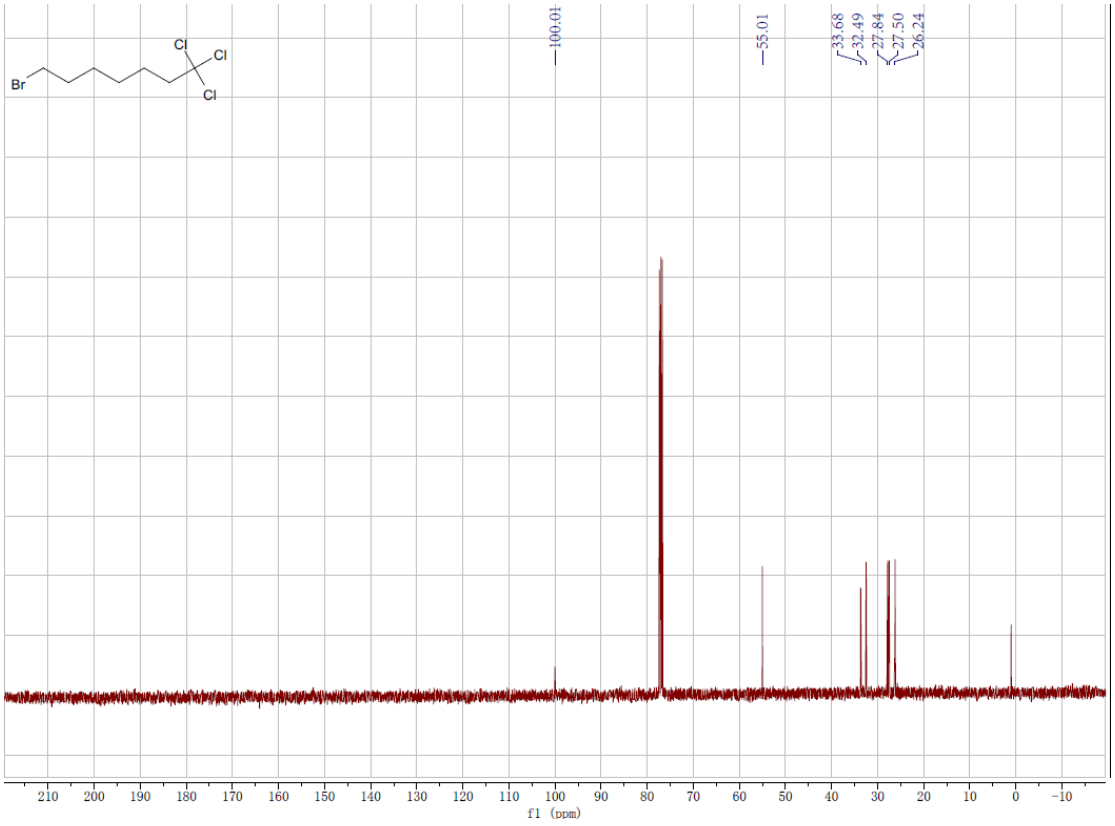

Figure S25. ^{13}C NMR Spectrum of **3h**

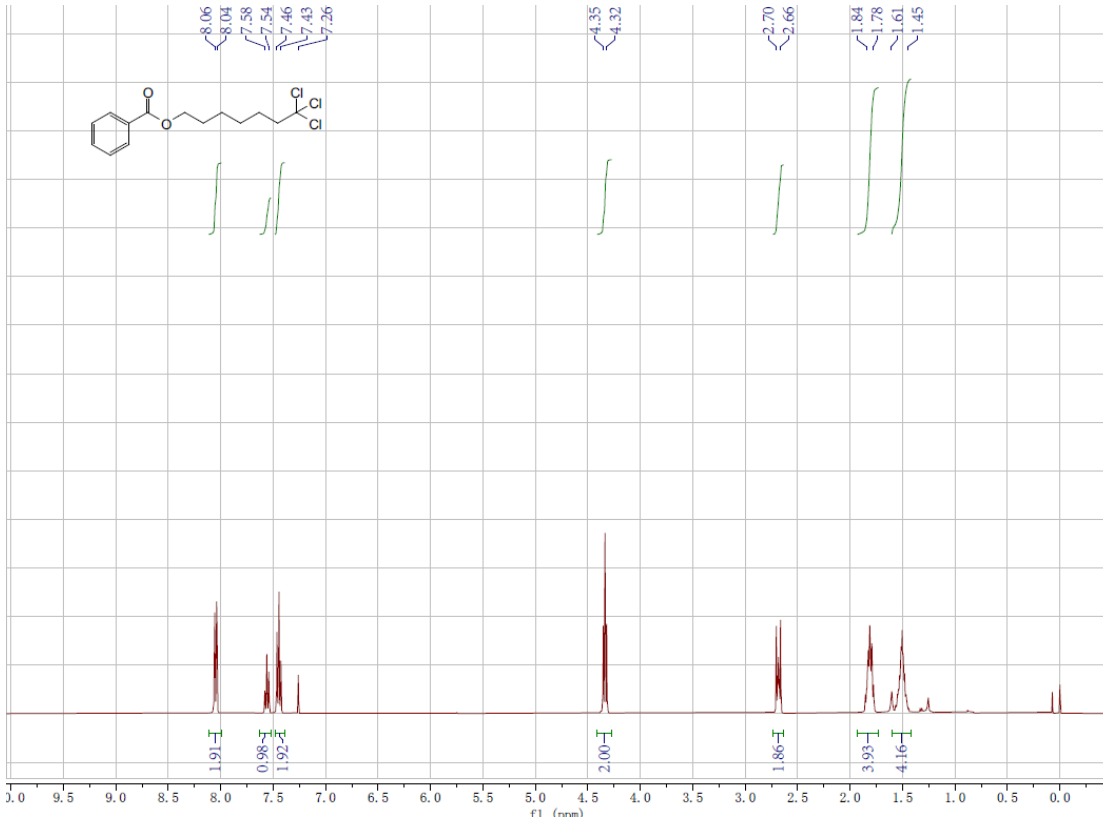

Figure S26. ^{1}H NMR Spectrum of **3i**

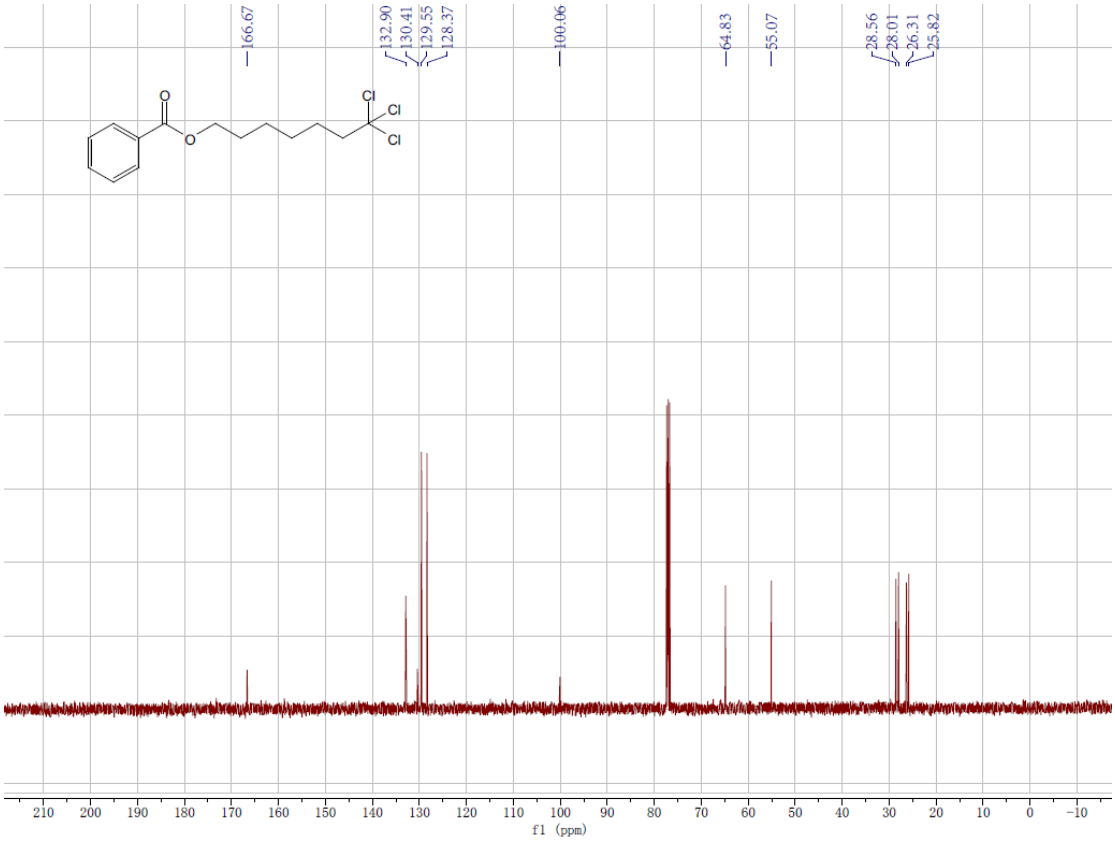

Figure S27.^{13}C NMR Spectrum of **3i**

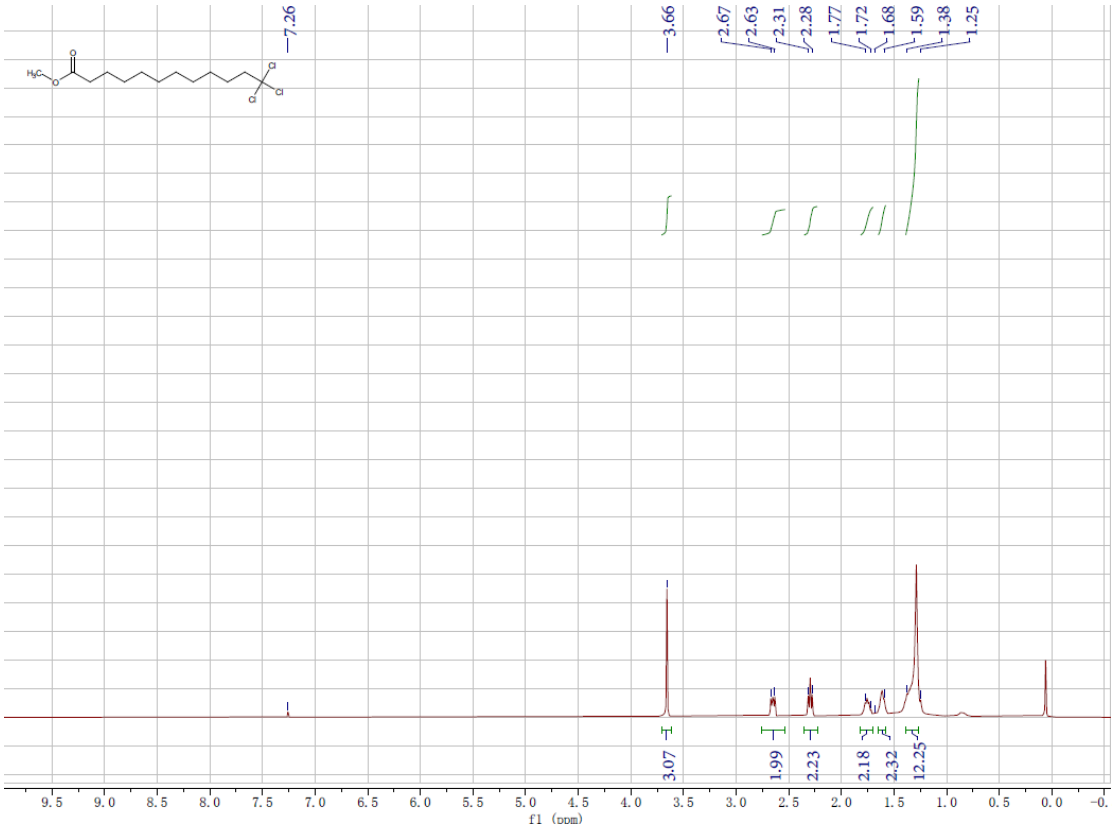

Figure S28. ^{1}H NMR Spectrum of **3j**

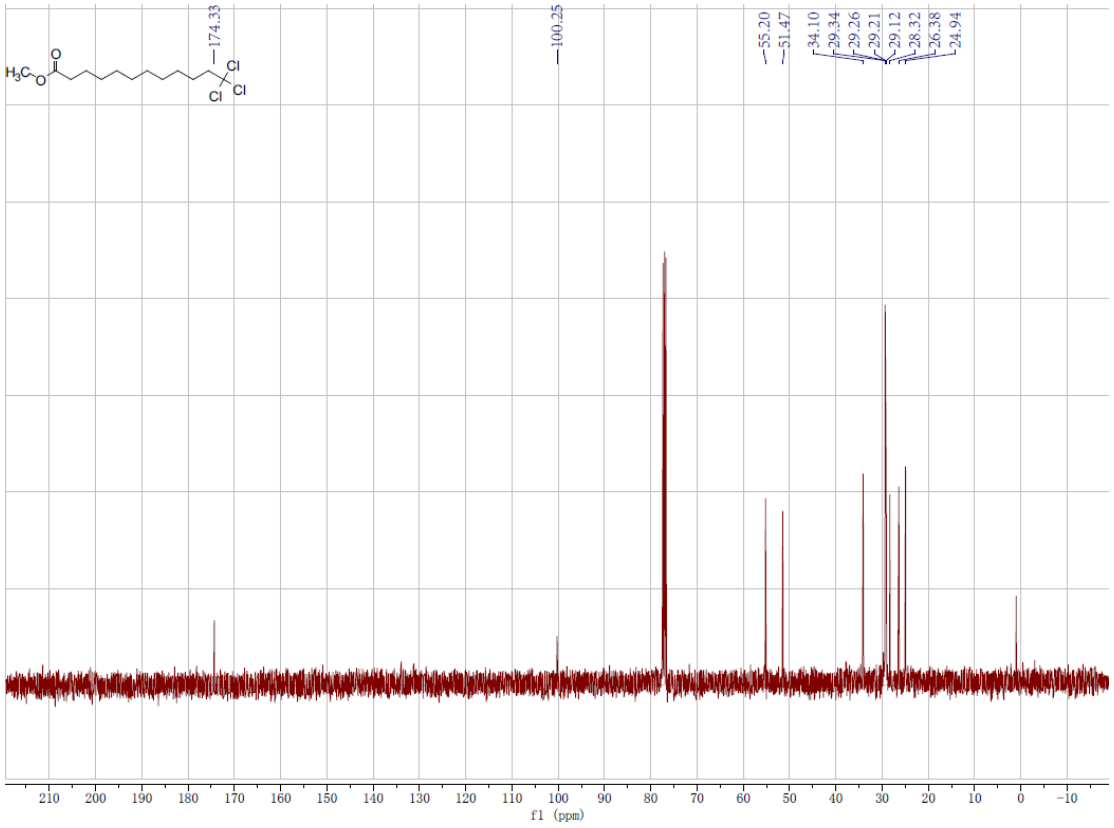

Figure S29.^{13}C NMR Spectrum of **3j**

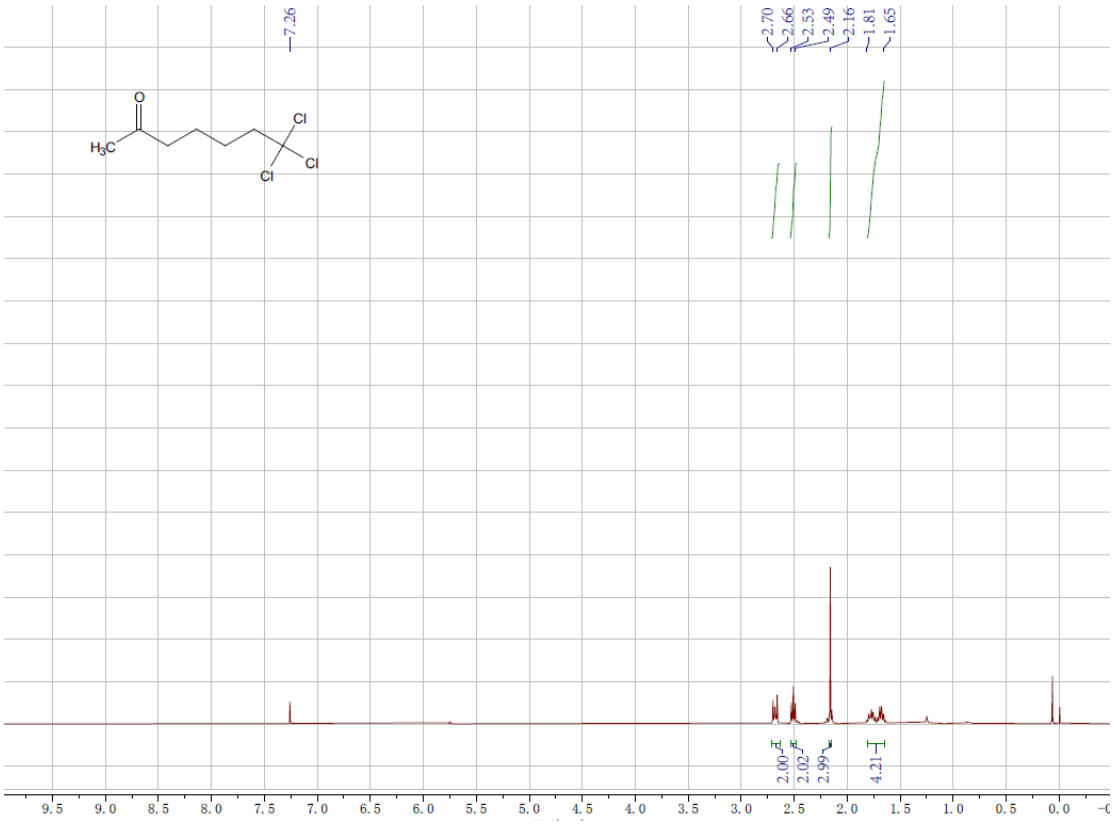

Figure S30. ^{1}H NMR Spectrum of **3k**

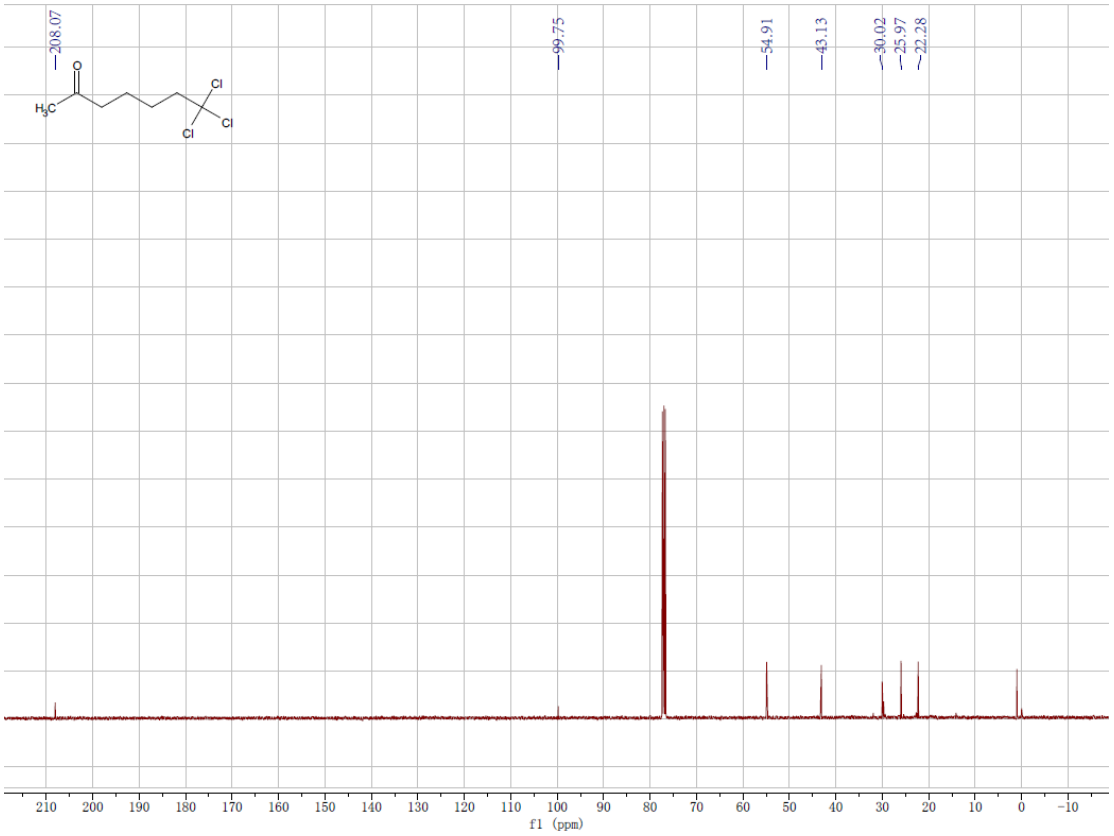

Figure S31.^{13}C NMR Spectrum of **3k**

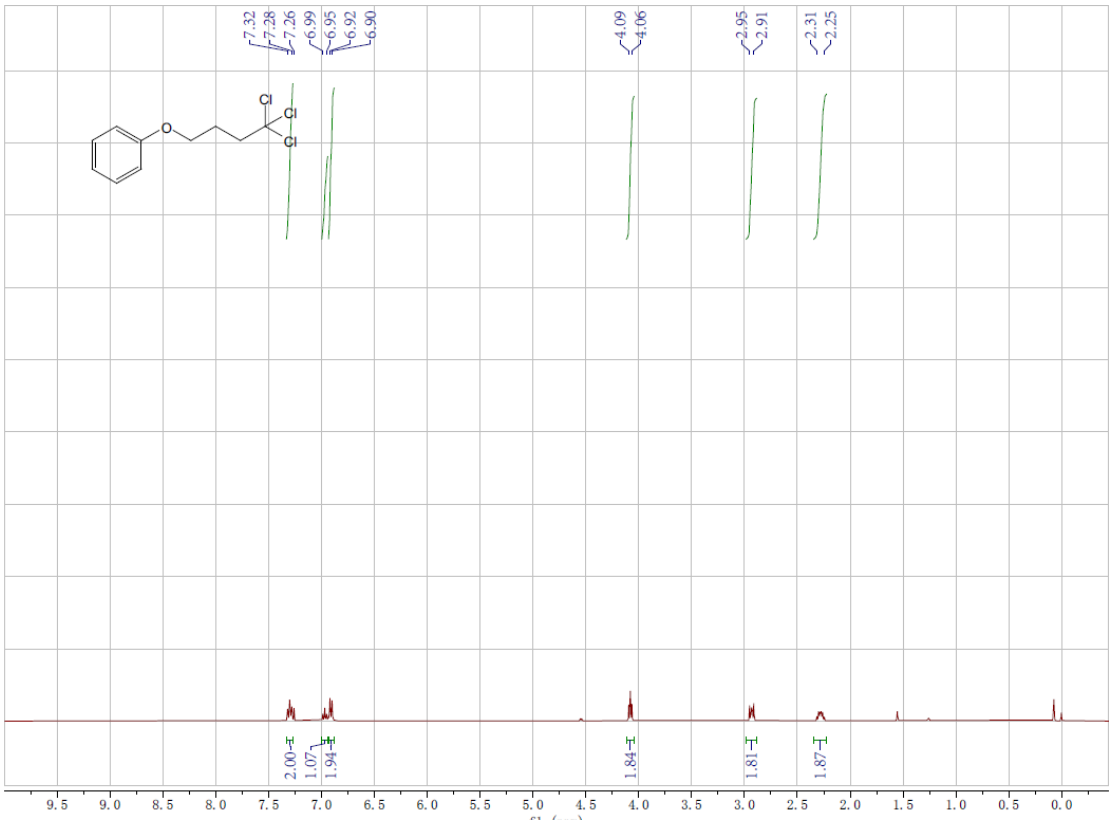

Figure S32. ^{1}H NMR Spectrum of **3l**

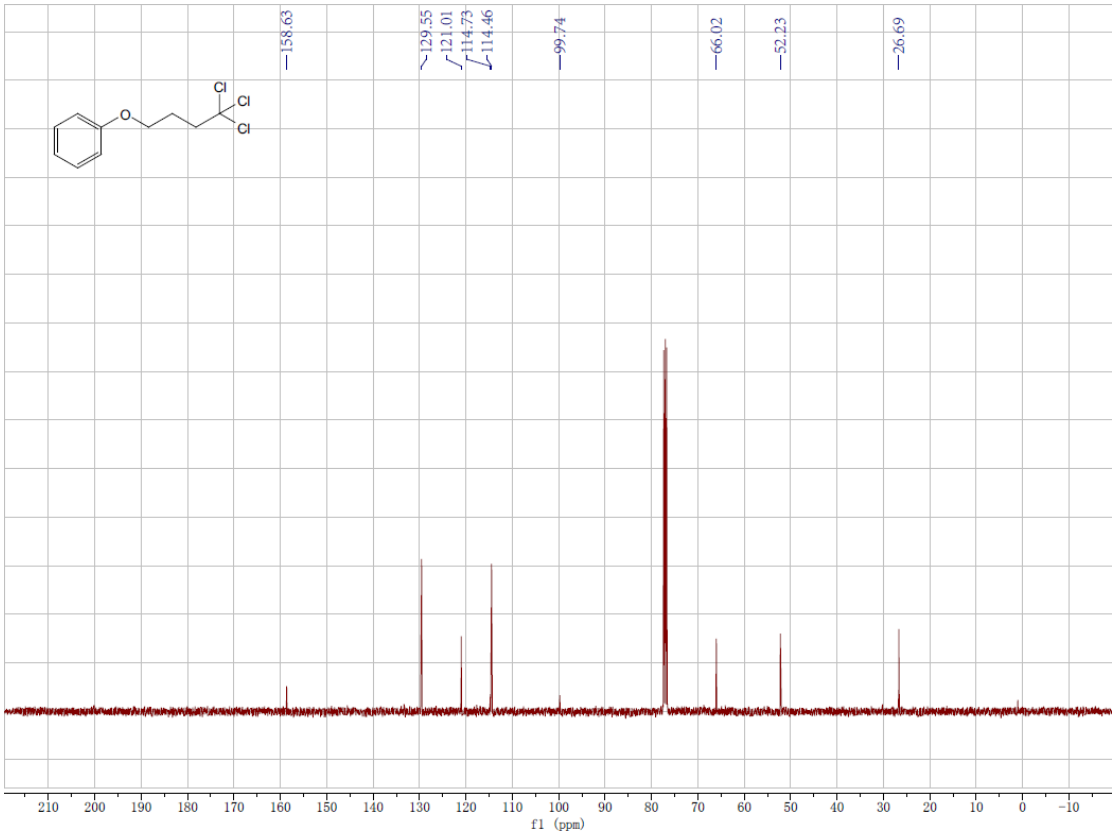

Figure S33.^{13}C NMR Spectrum of **3l**

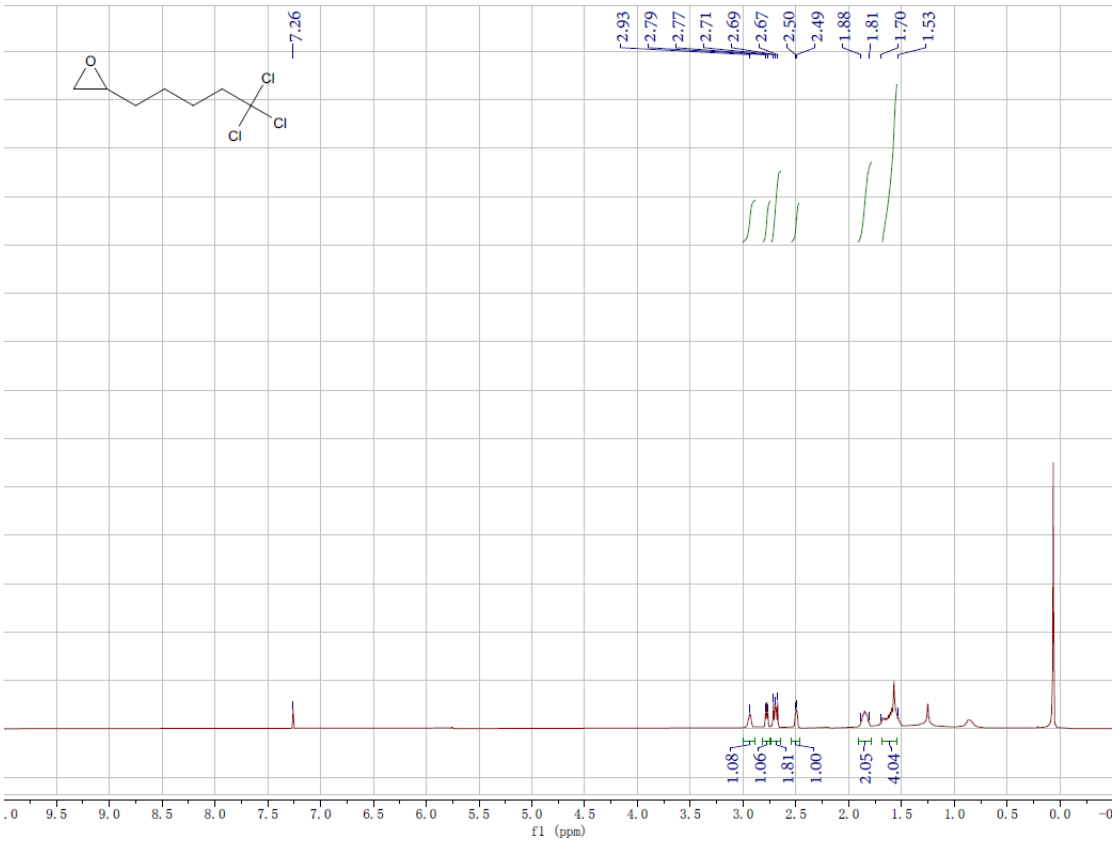

Figure S34. ^{1}H NMR Spectrum of **3m**

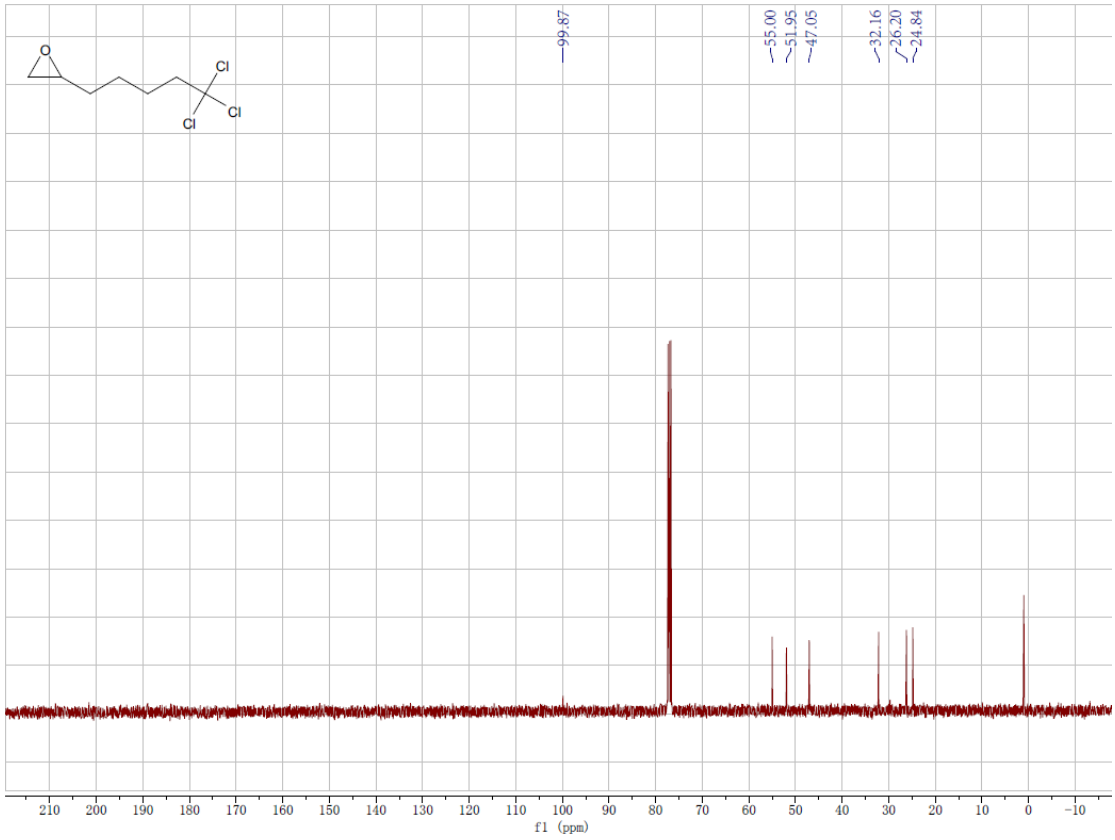

Figure S35.^{13}C NMR Spectrum of **3m**

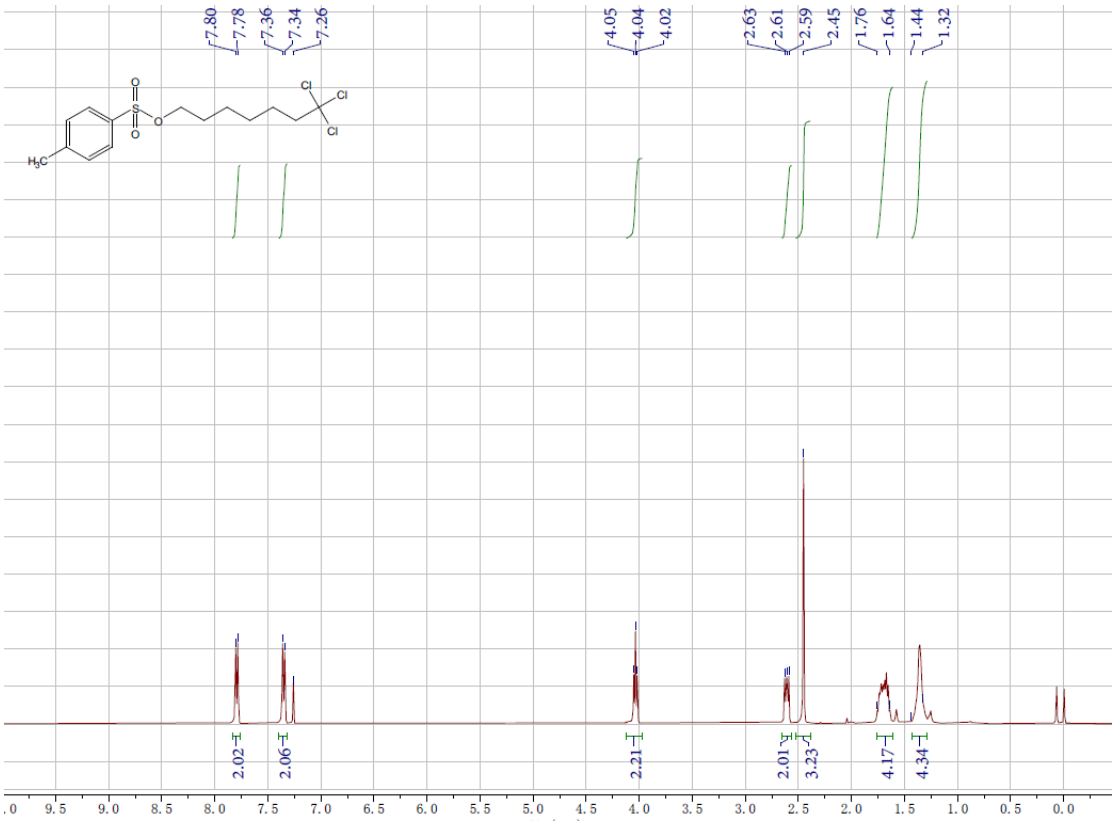

Figure S36. ^{1}H NMR Spectrum of **3n**

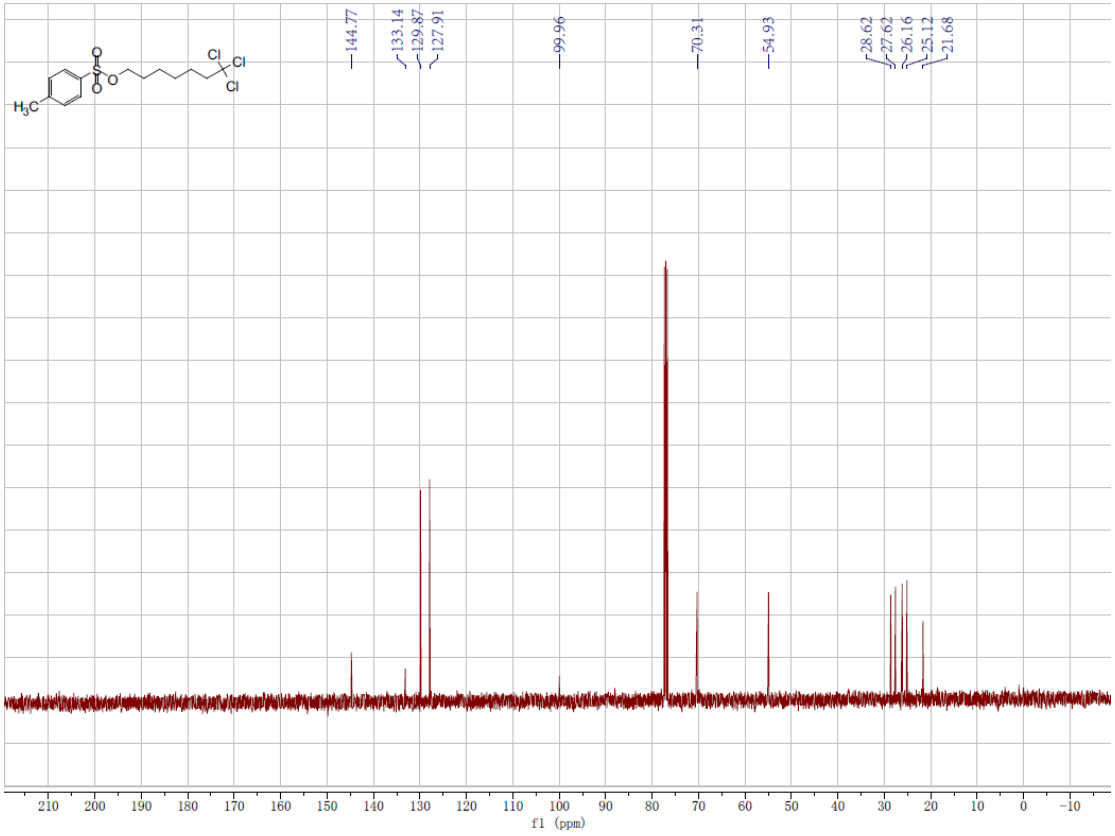

Figure S37.^{13}C NMR Spectrum of **3n**

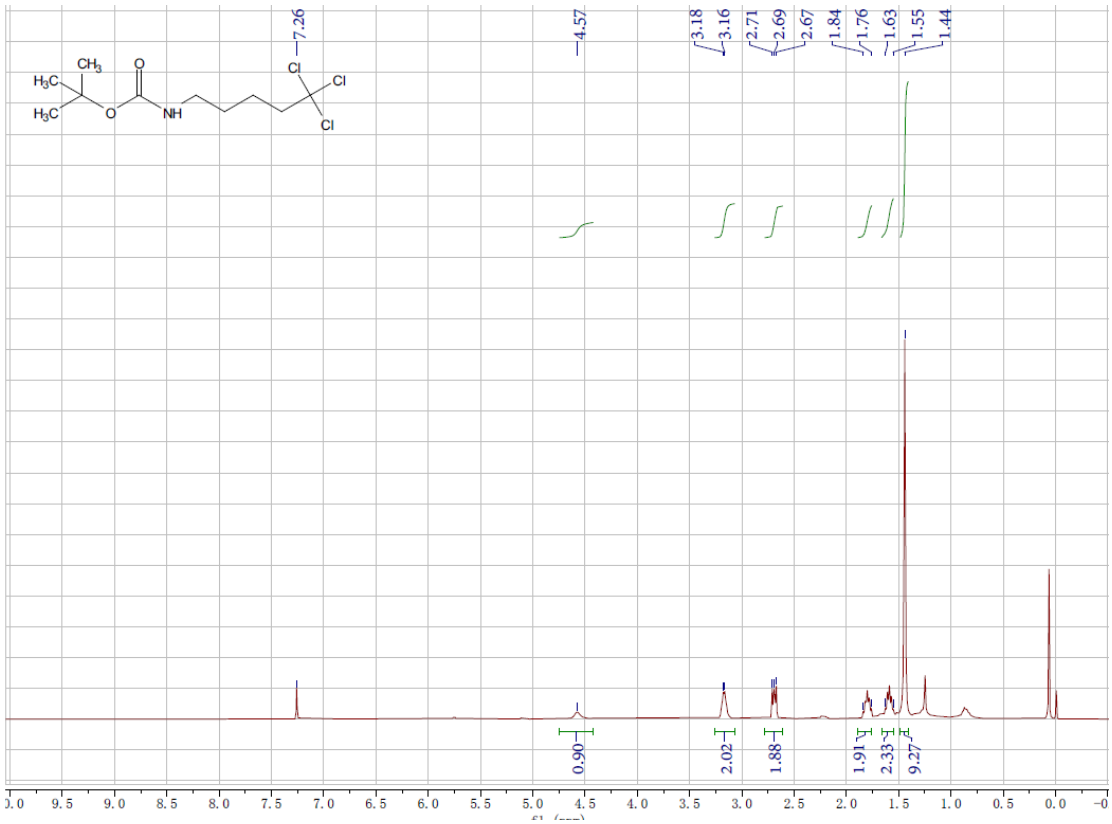

Figure S38. ^{1}H NMR Spectrum of **3o**

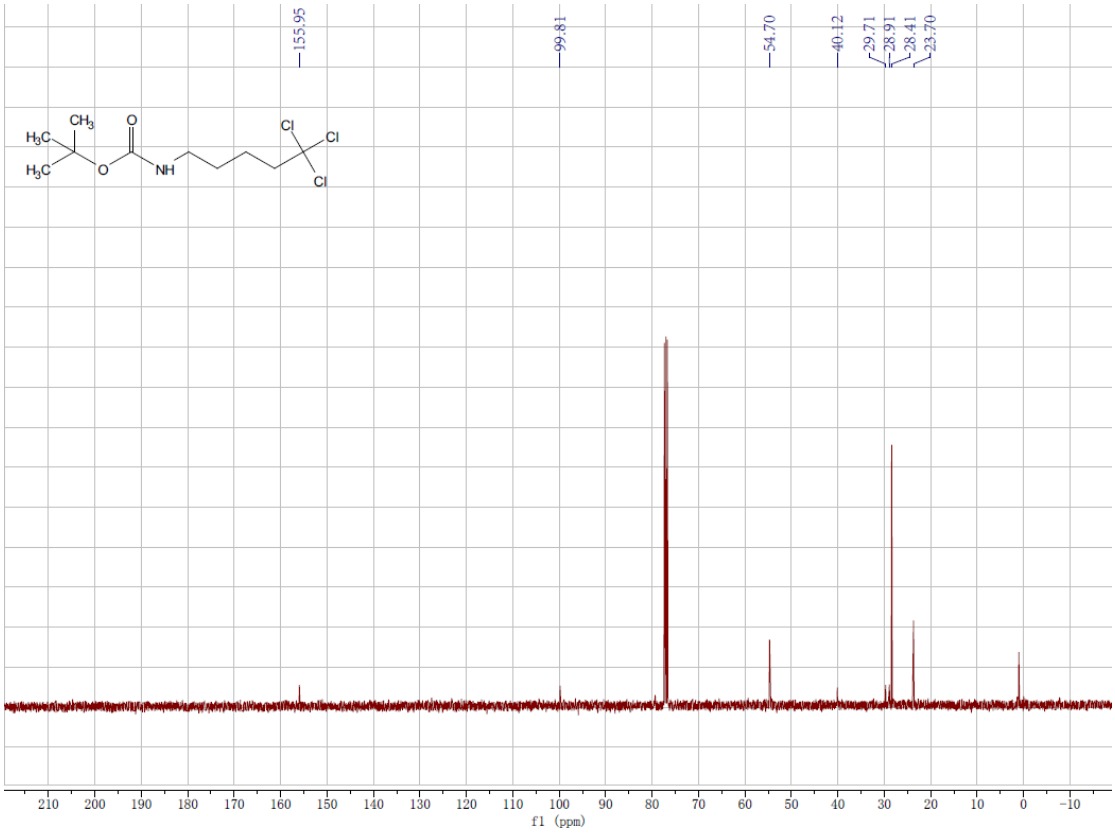

Figure S39.^{13}C NMR Spectrum of **3o**

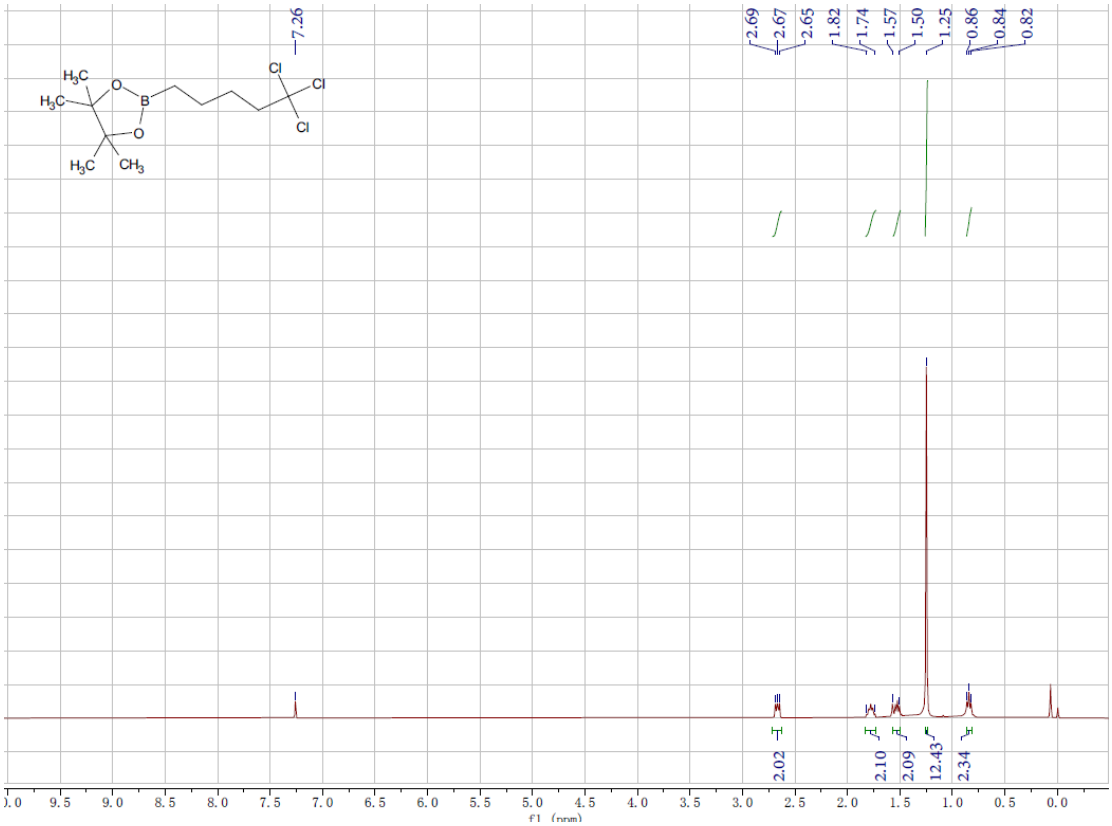

Figure S40. ^{1}H NMR Spectrum of **3p**

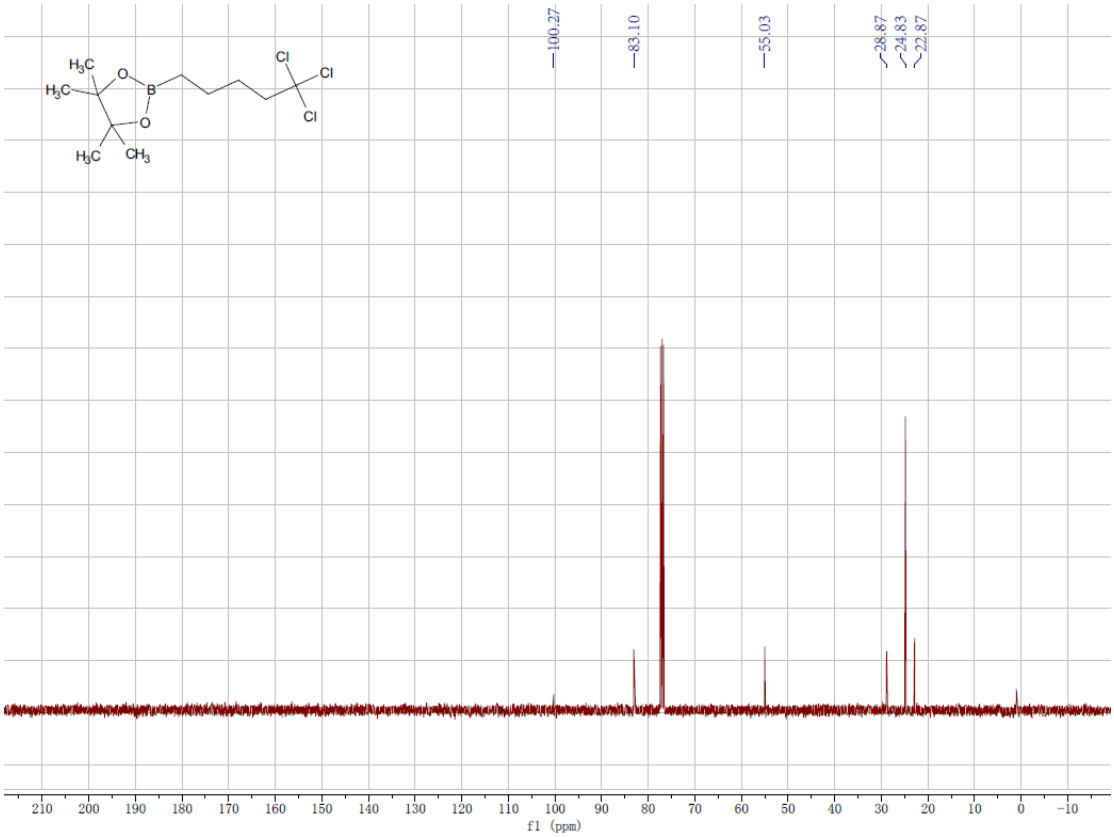

Figure S41.^{13}C NMR Spectrum of **3p**

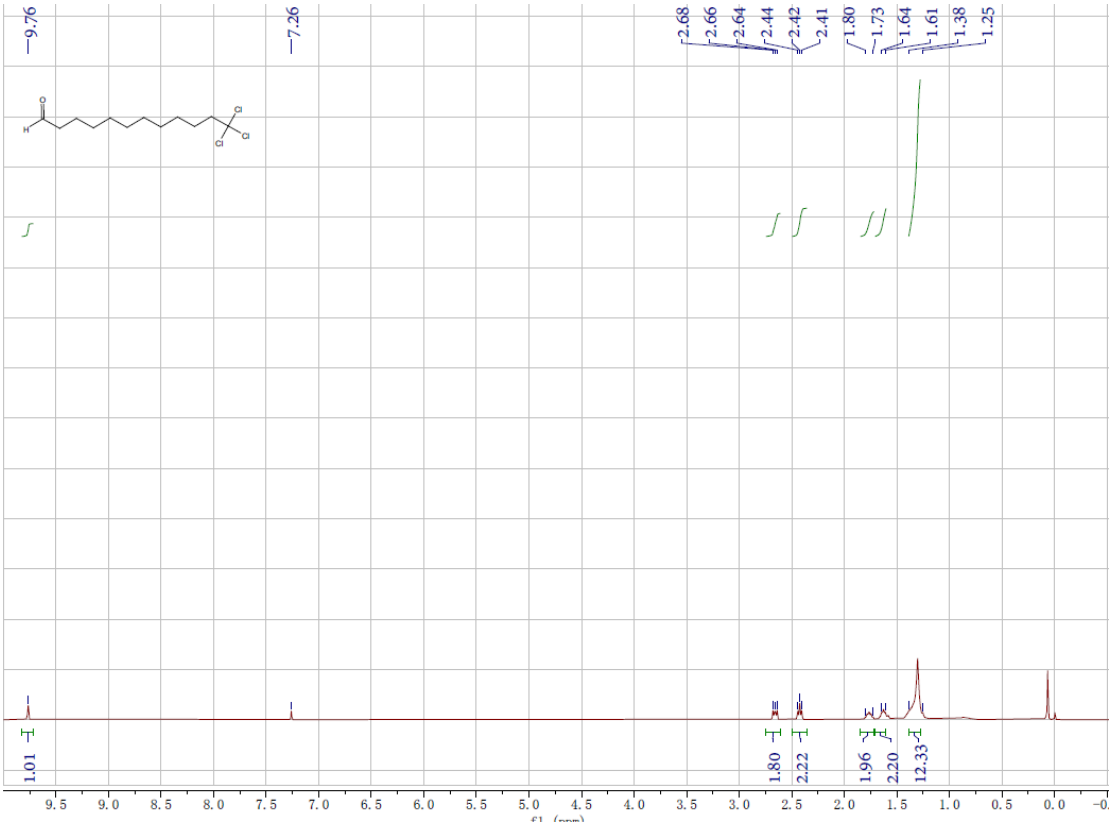

Figure S42. ^{1}H NMR Spectrum of **3q**

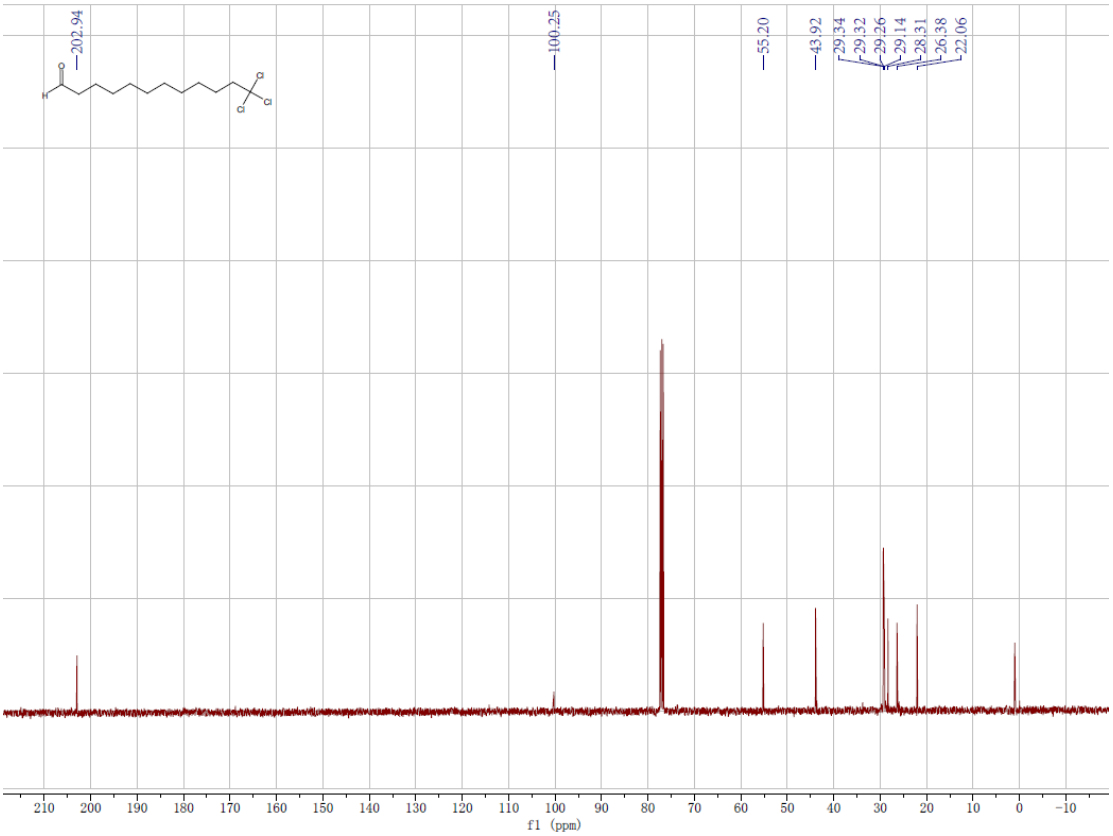

Figure S43.^{13}C NMR Spectrum of **3q**

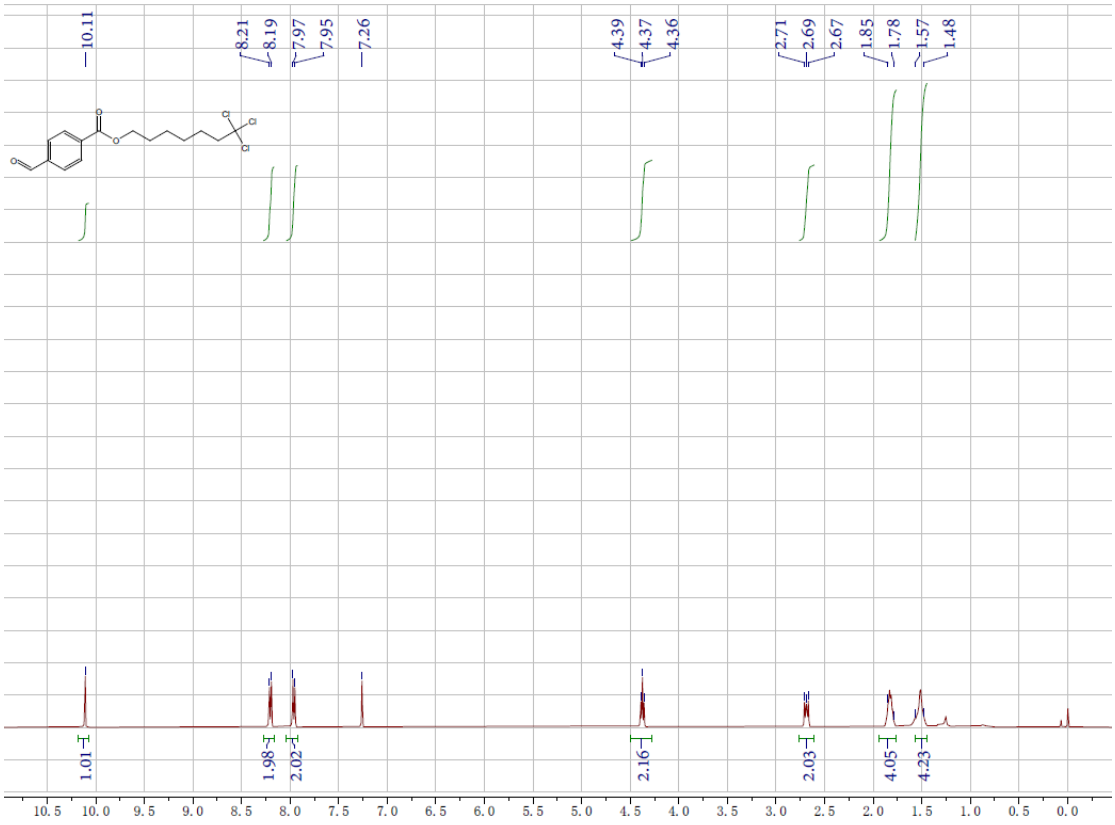

Figure S44. ^{1}H NMR Spectrum of **3r**

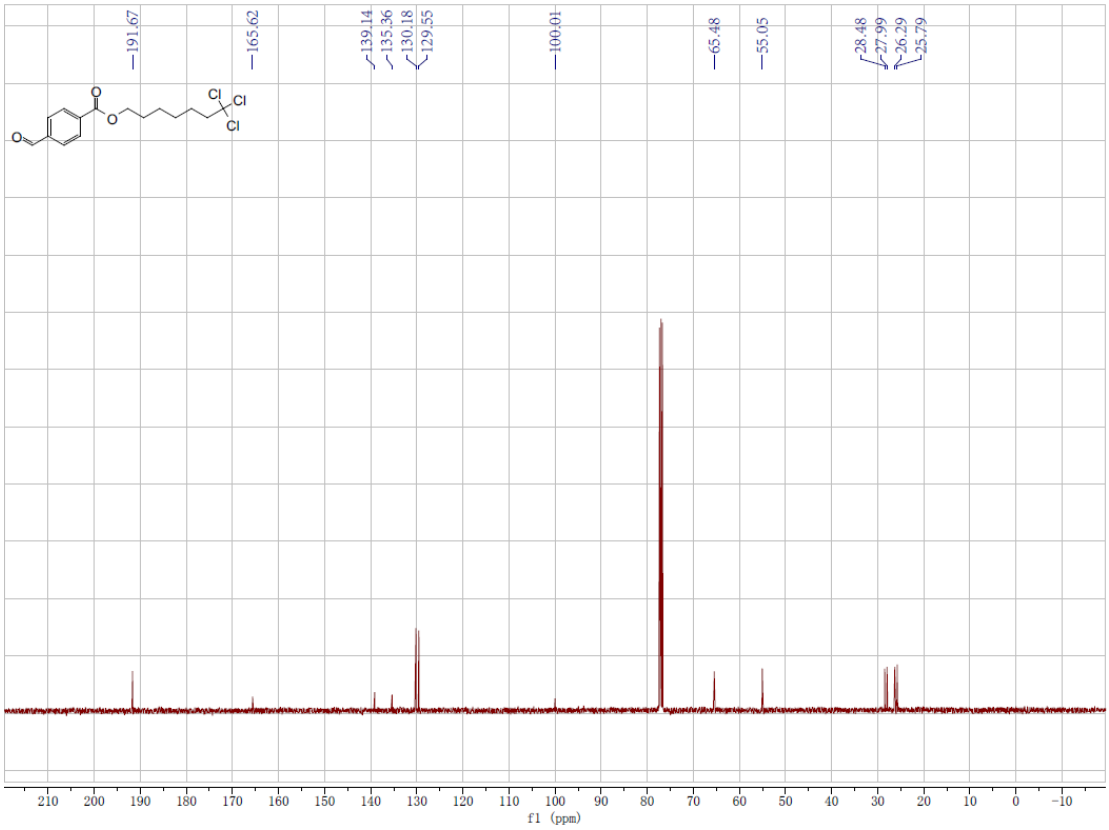

Figure S45.^{13}C NMR Spectrum of **3r**

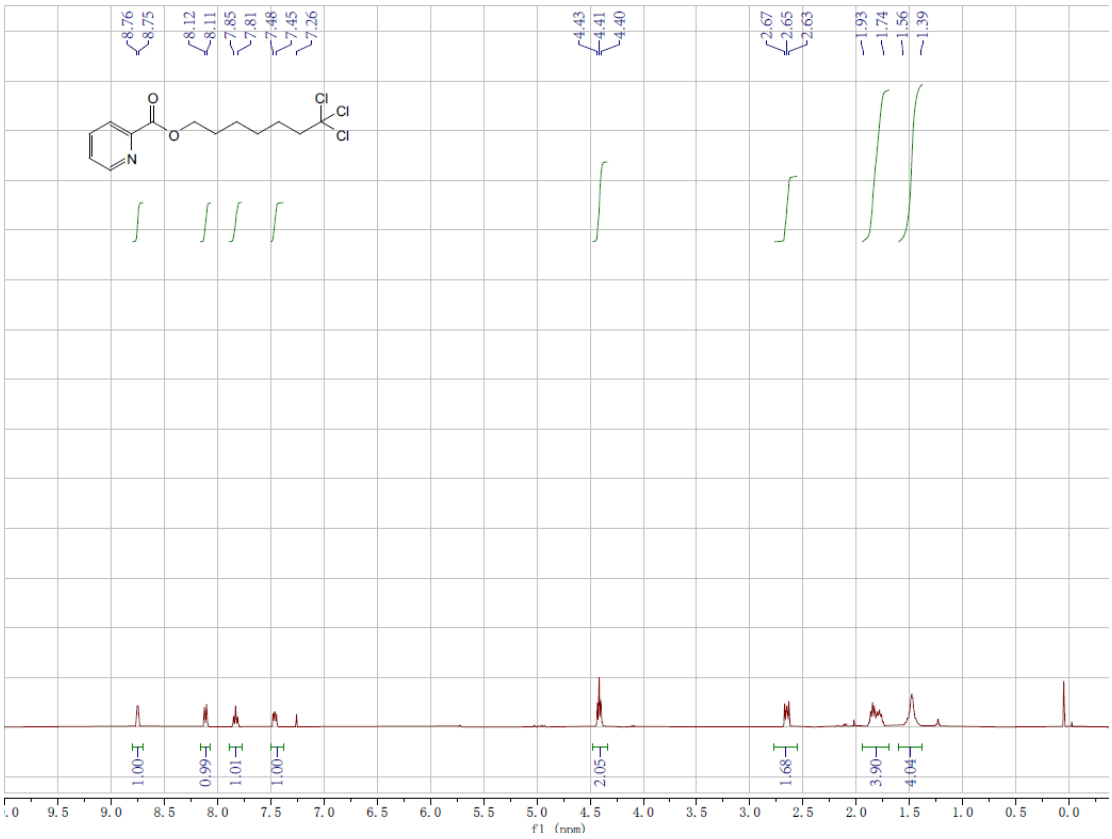

Figure S46. ^{1}H NMR Spectrum of **3s**

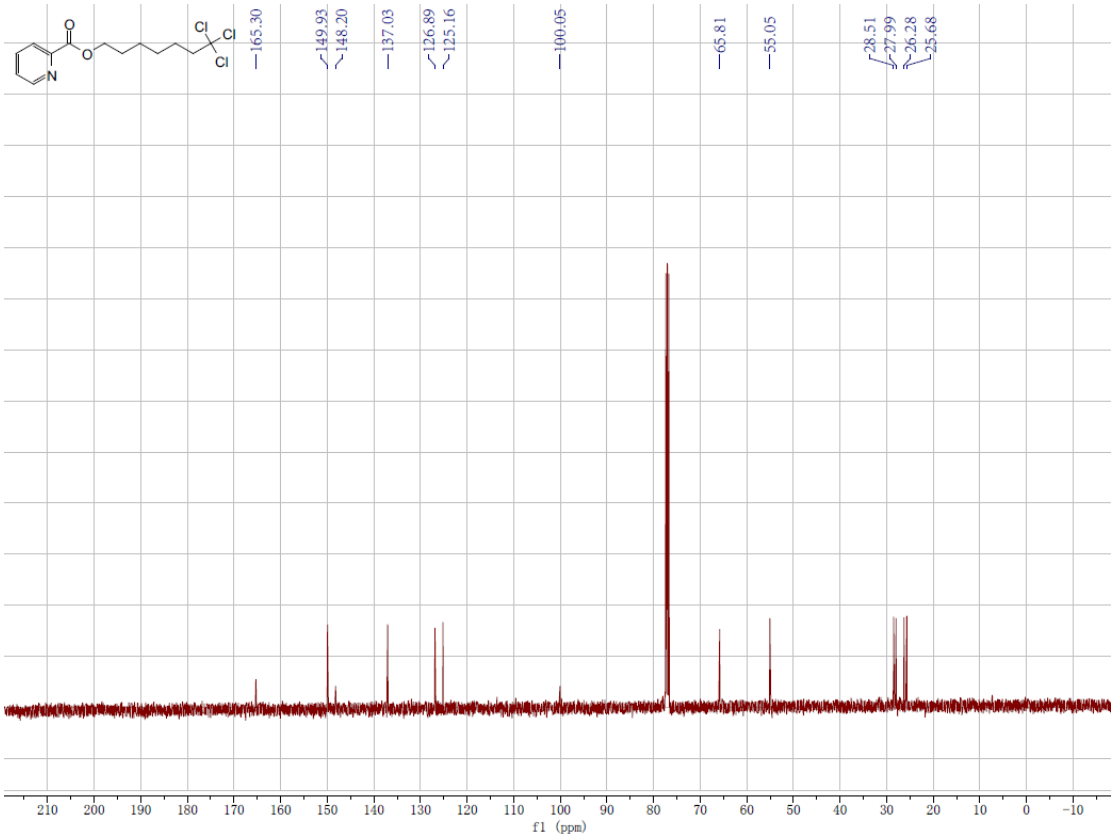

Figure S47.^{13}C NMR Spectrum of **3s**

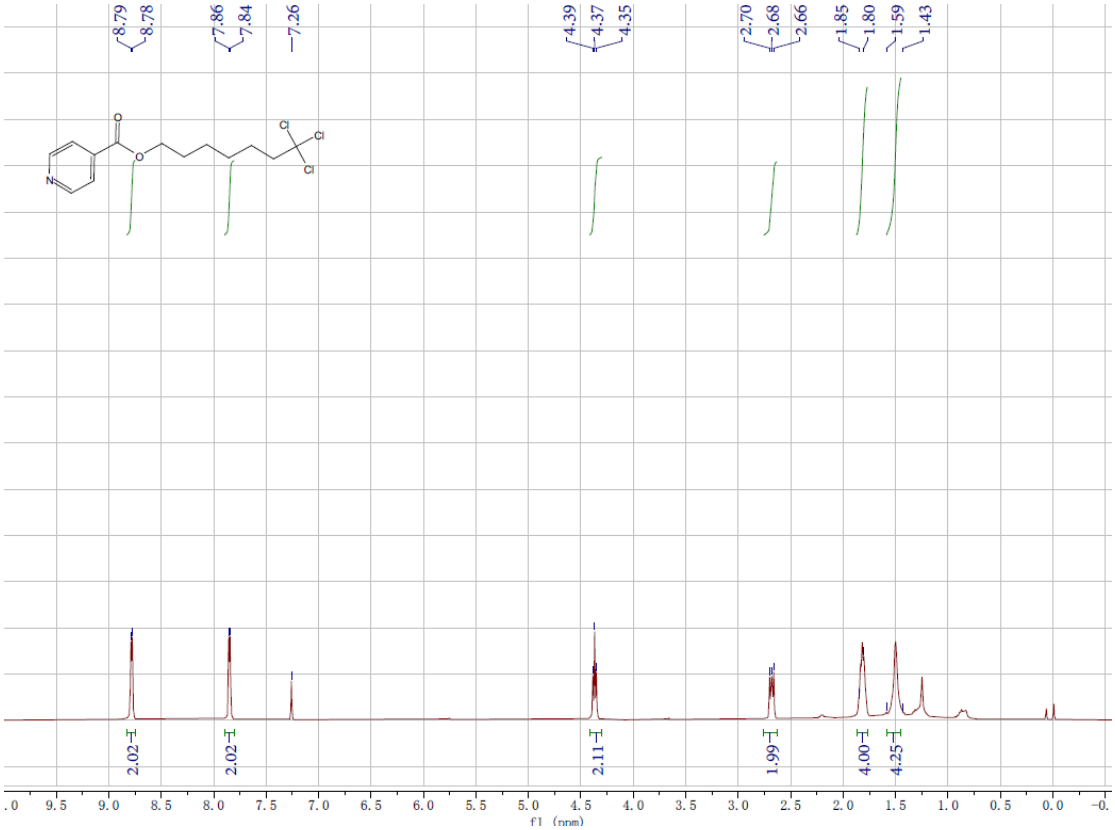

Figure S48. ^{1}H NMR Spectrum of **3t**

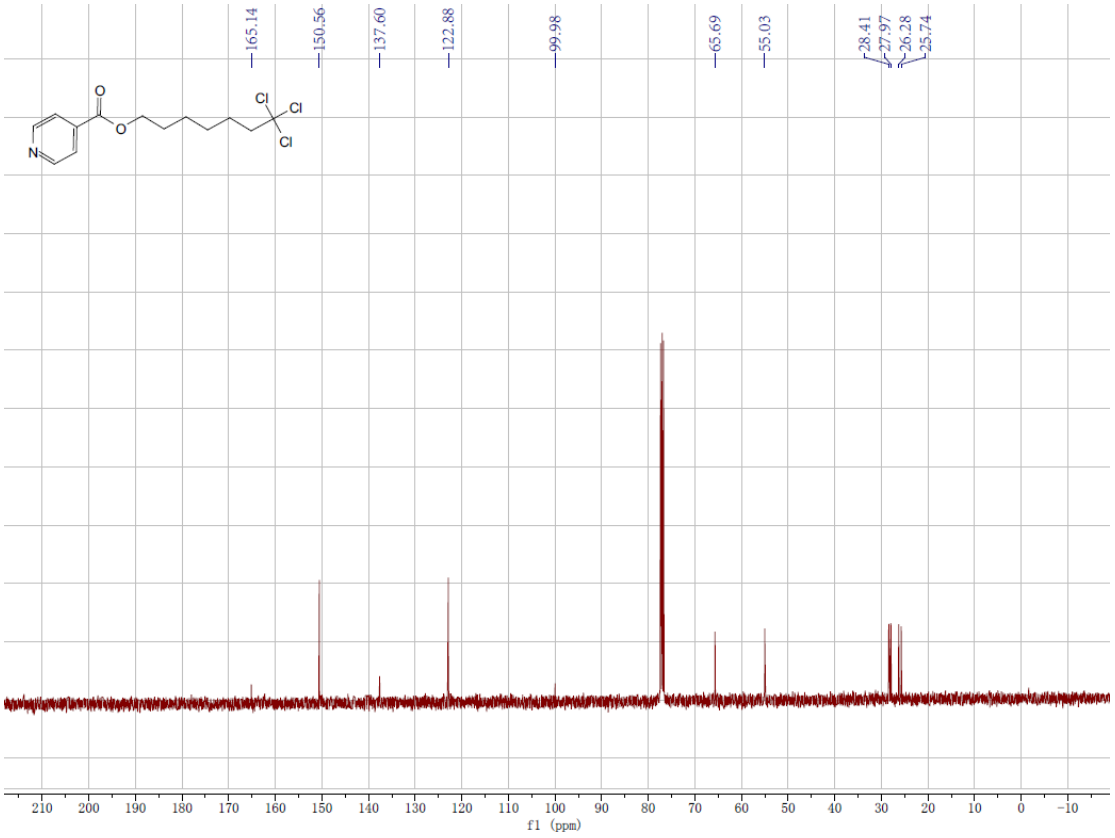

Figure S49.^{13}C NMR Spectrum of **3t**

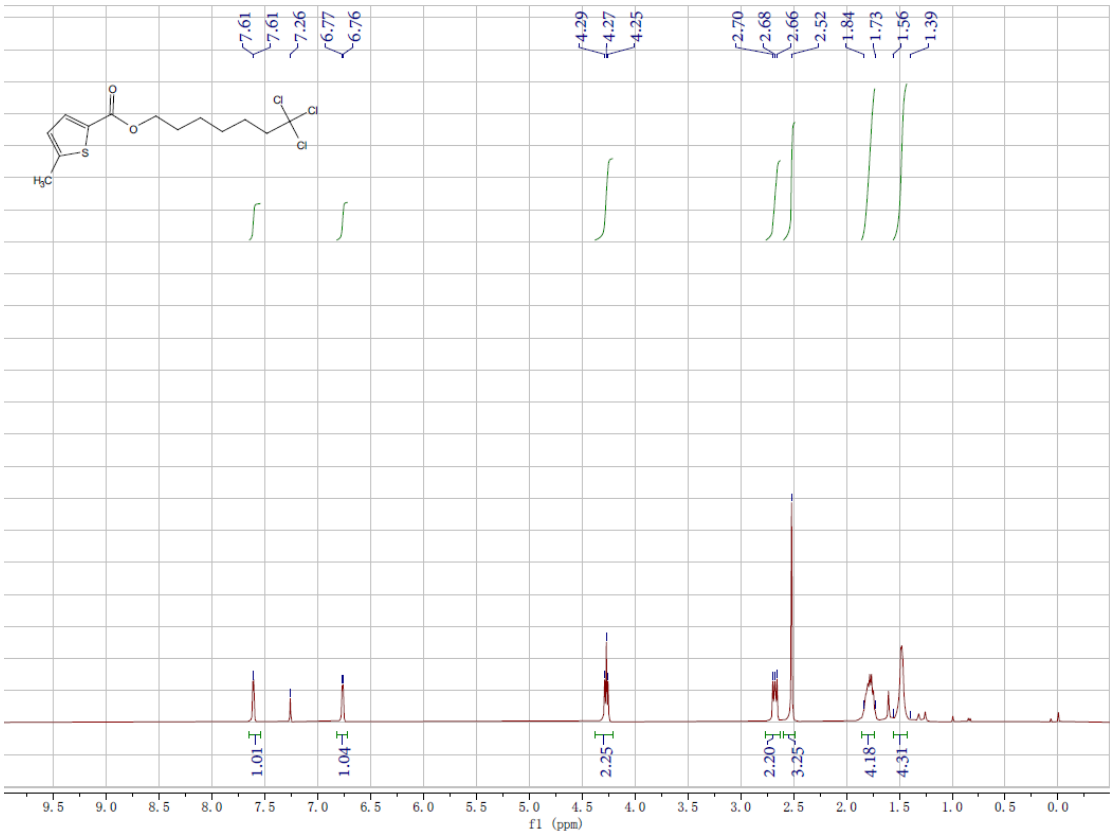

Figure S50. ^{1}H NMR Spectrum of **3u**

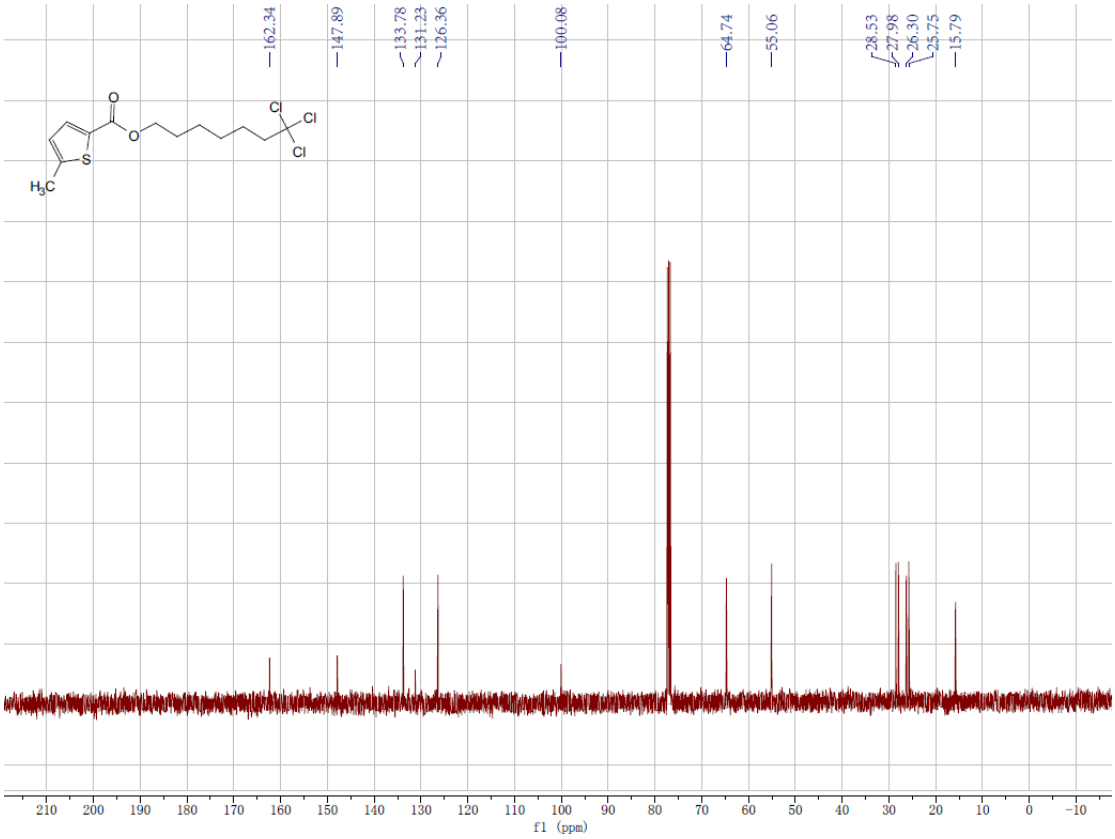

Figure S51.^{13}C NMR Spectrum of **3u**

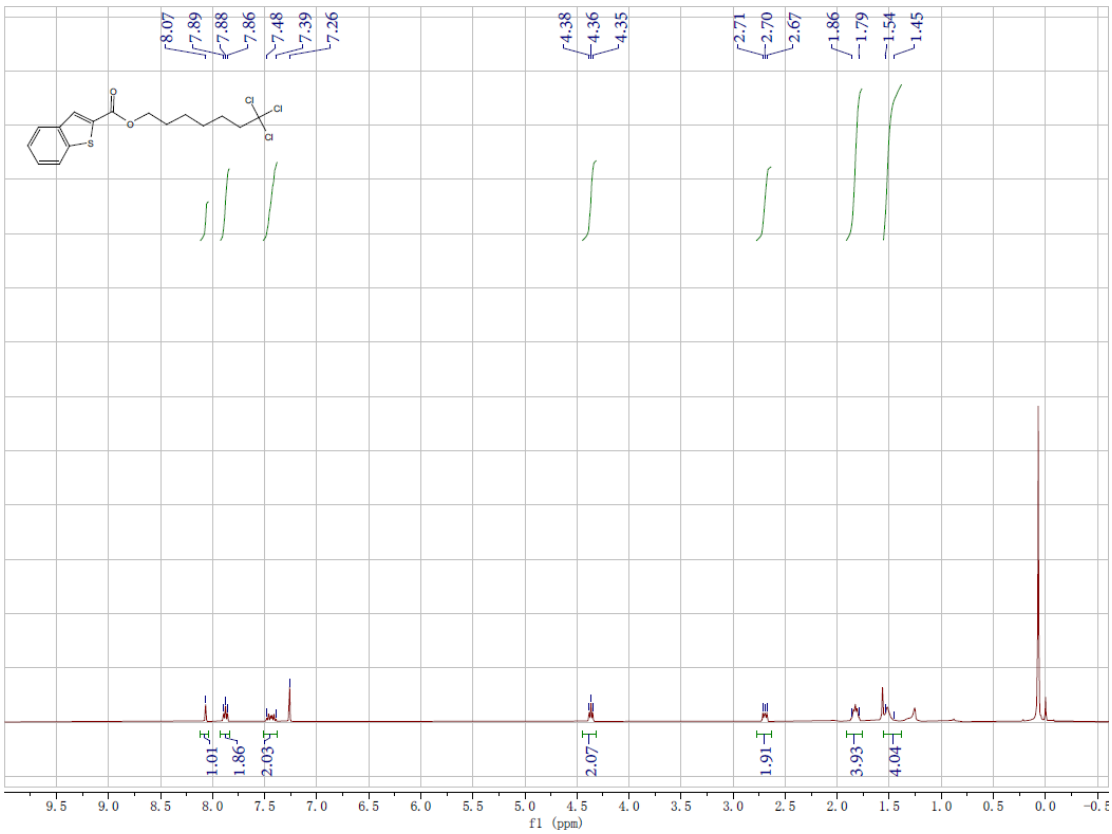

Figure S52. ^{1}H NMR Spectrum of **3v**

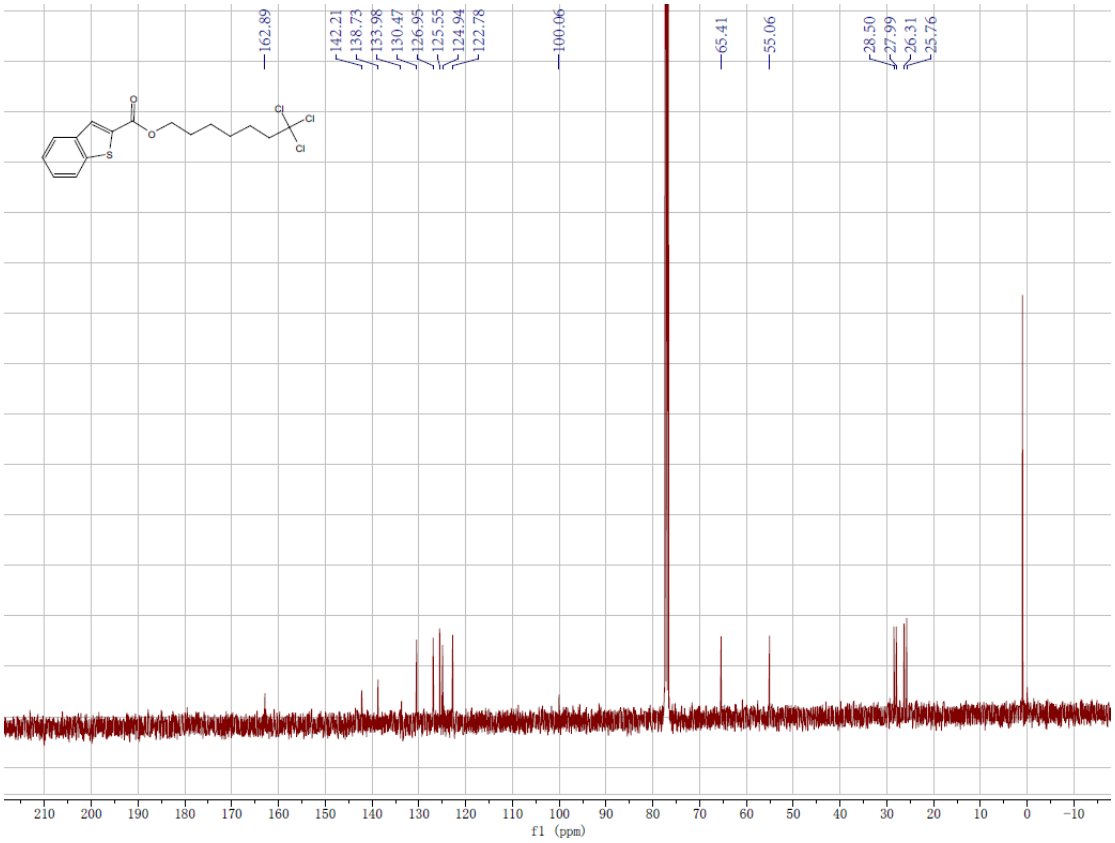

Figure S53.^{13}C NMR Spectrum of **3v**

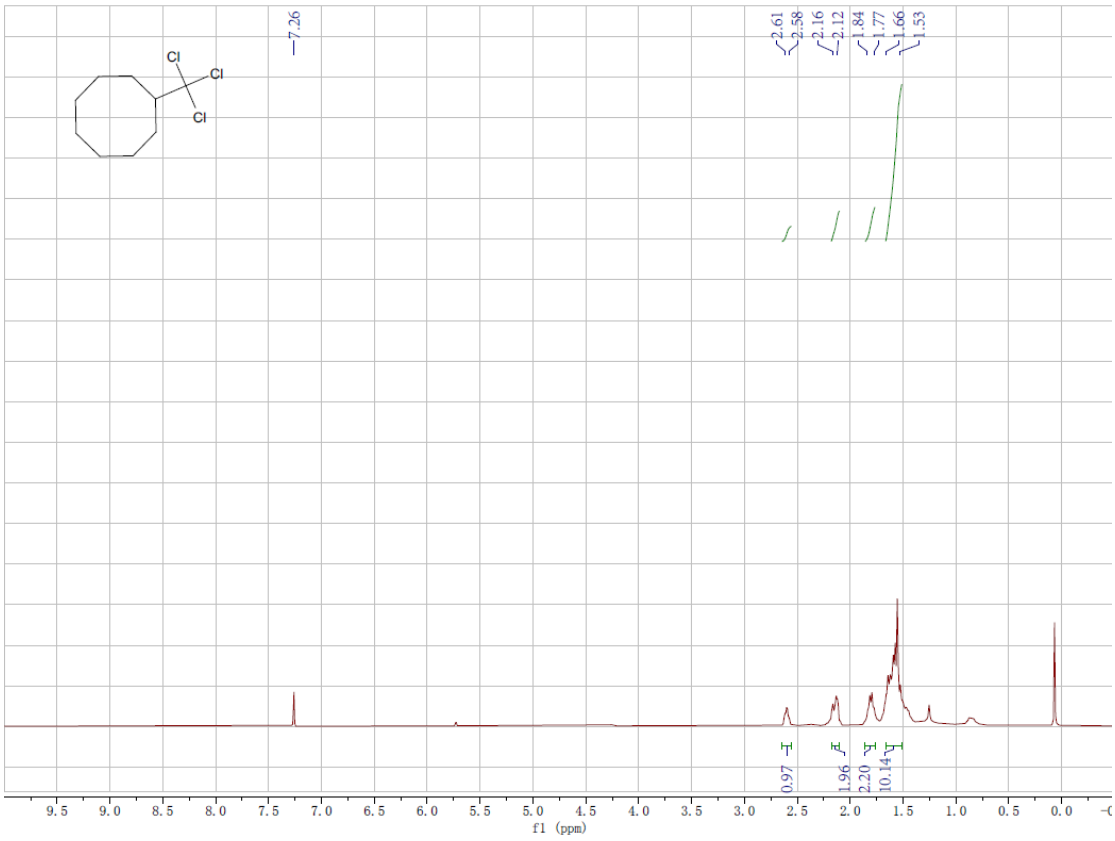

Figure S54. ^{1}H NMR Spectrum of **3w**

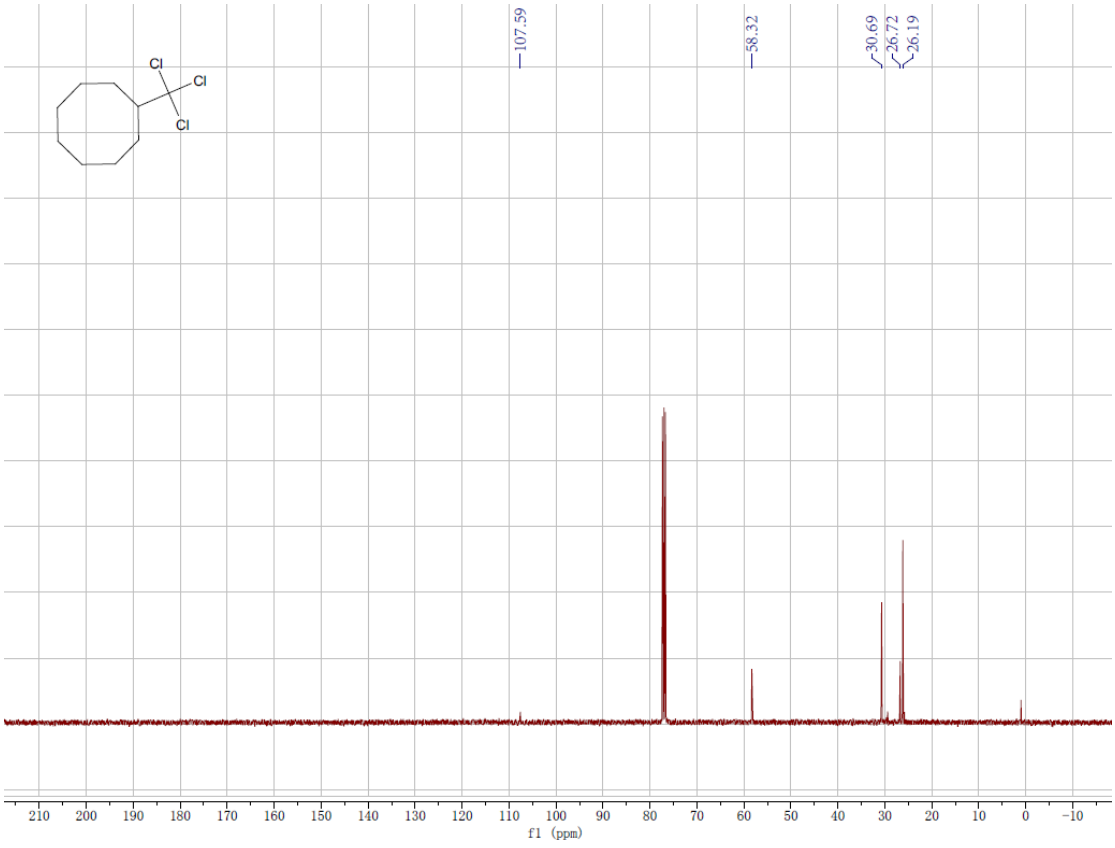

Figure S55.^{13}C NMR Spectrum of **3w**

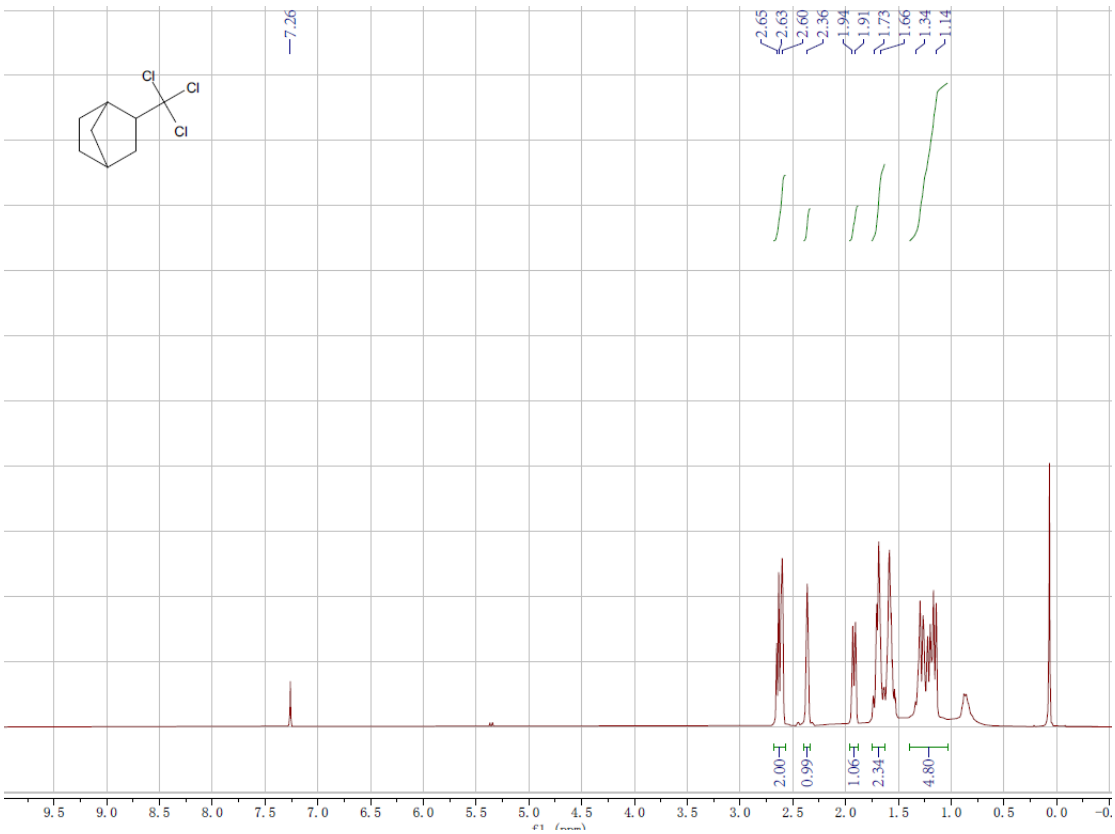

Figure S56. ^{1}H NMR Spectrum of **3x**

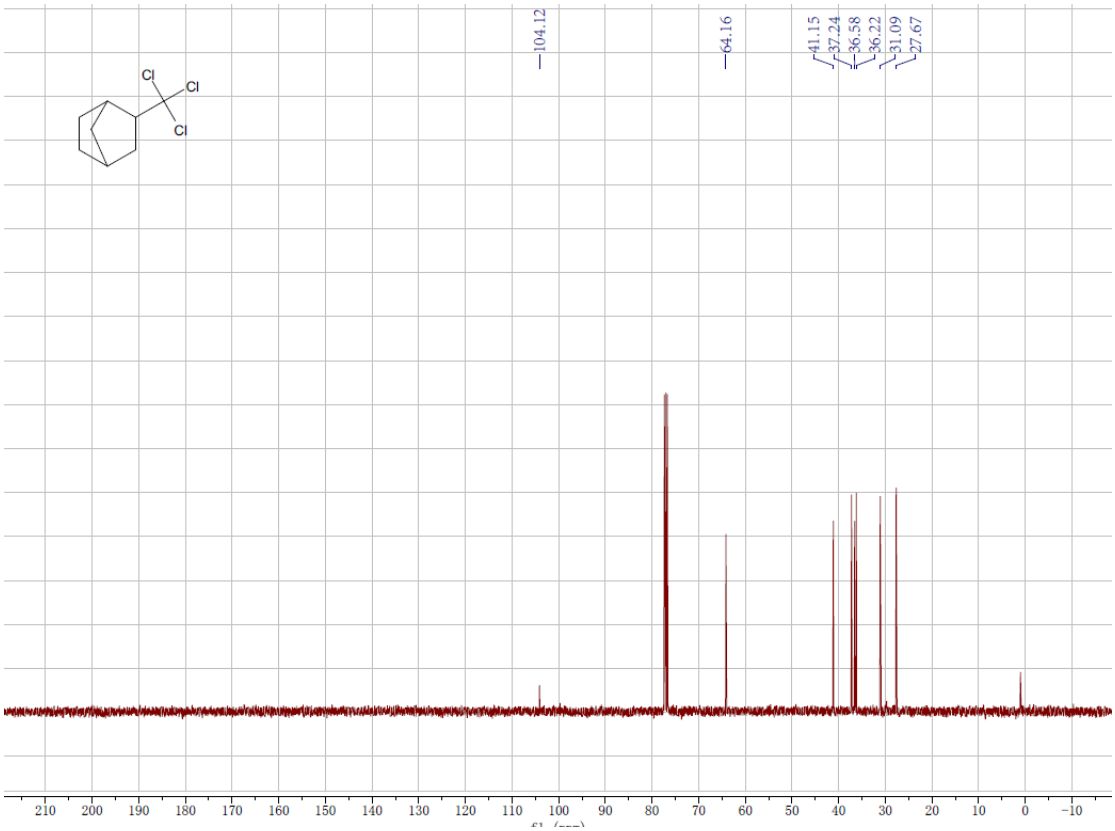

Figure S57.^{13}C NMR Spectrum of **3x**

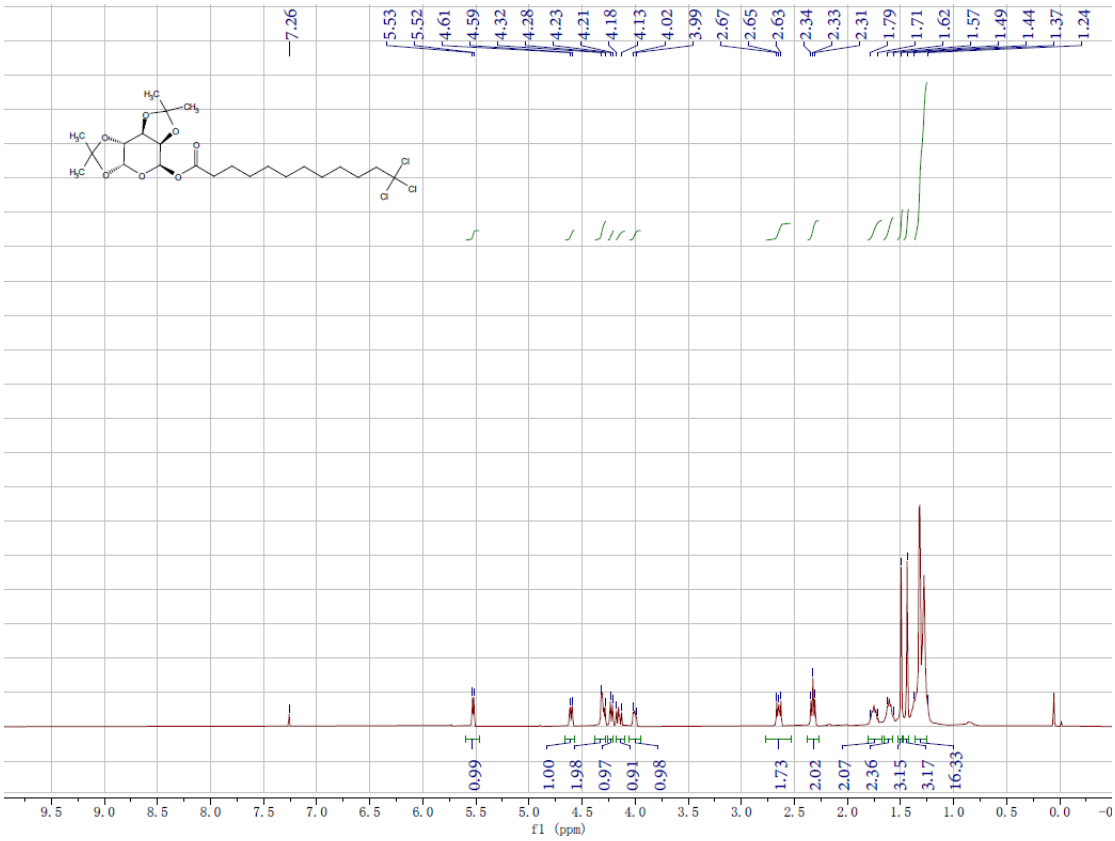

Figure S58. ^{1}H NMR Spectrum of **3aa**

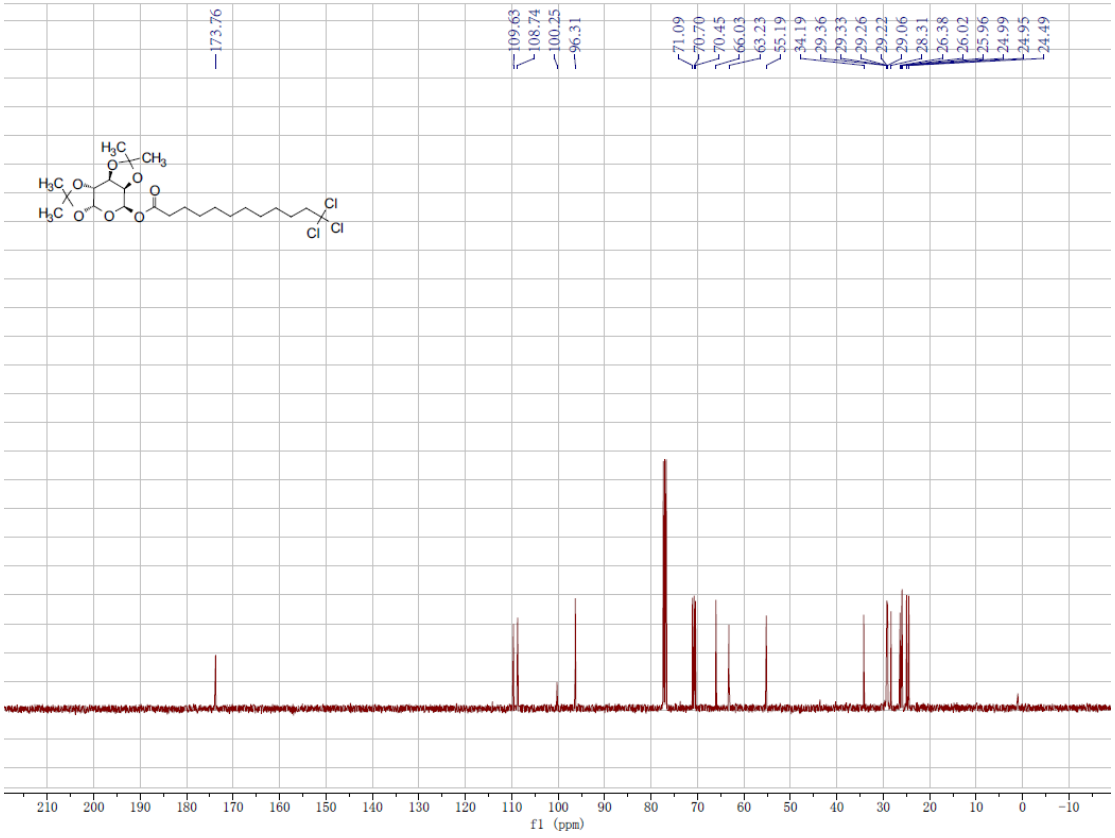

Figure S59.^{13}C NMR Spectrum of **3aa**

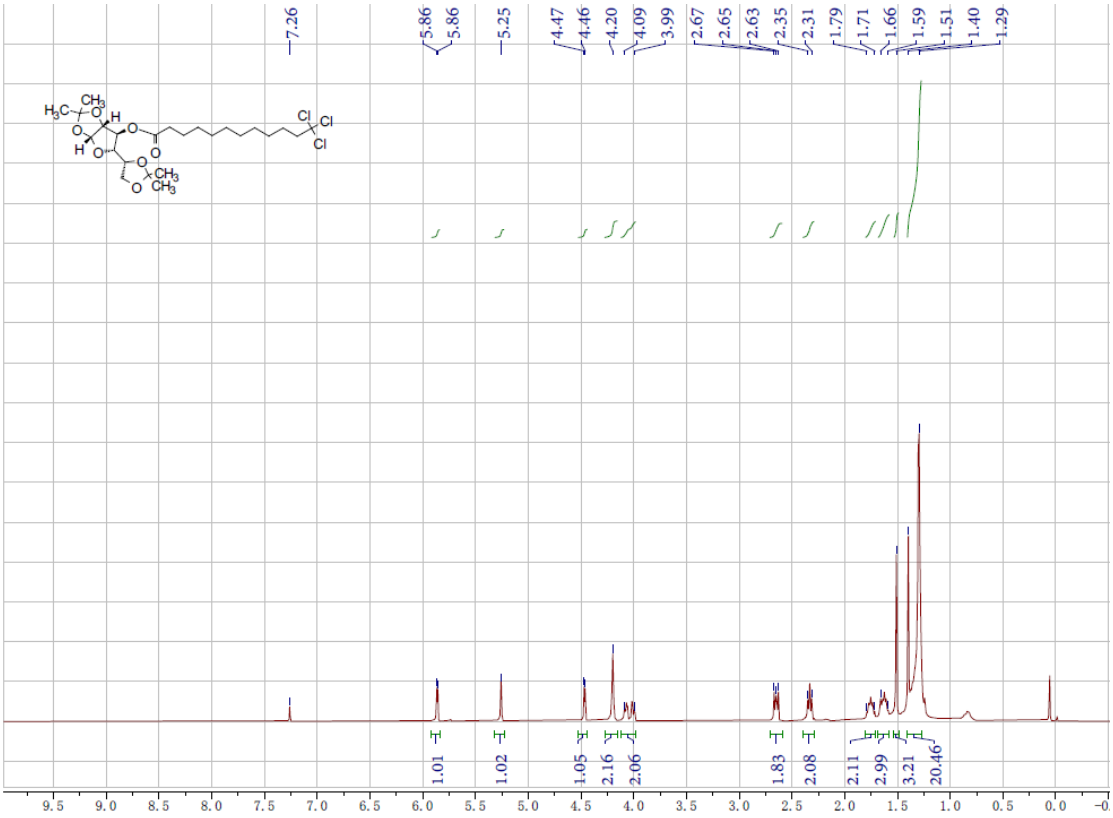

Figure S60. ^{1}H NMR Spectrum of **3ab**

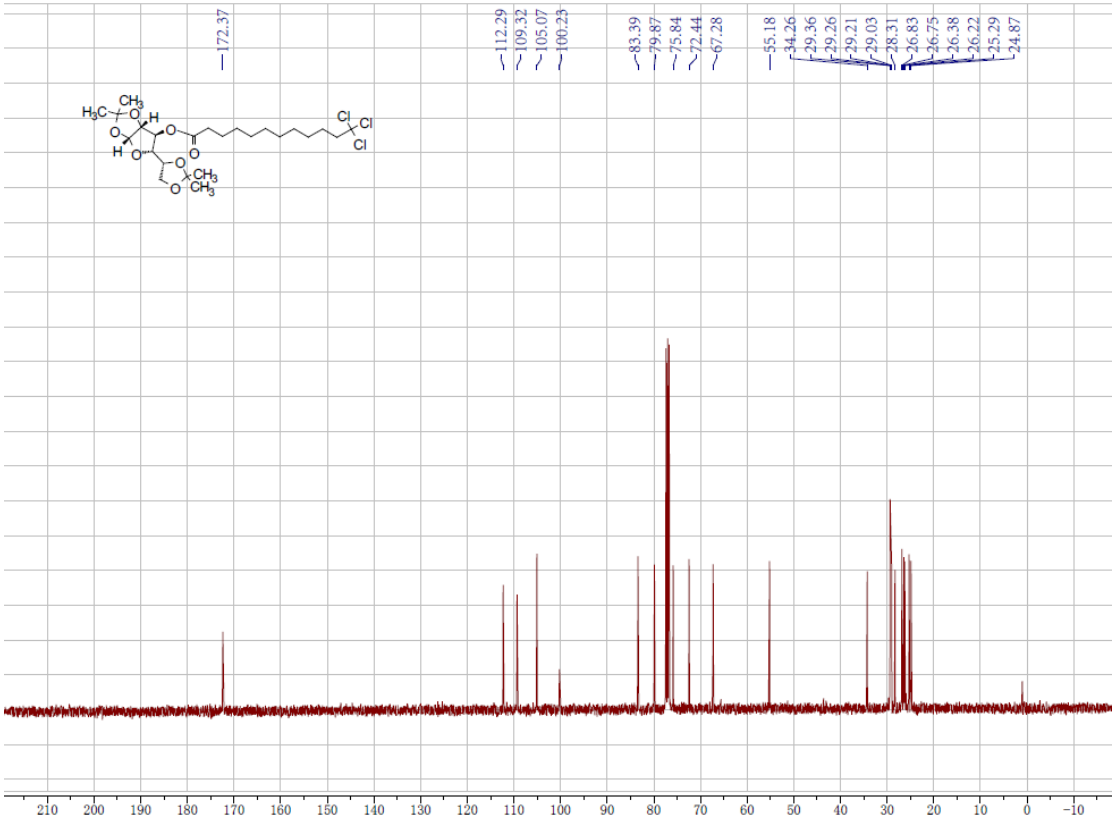

Figure S61.^{13}C NMR Spectrum of **3ab**

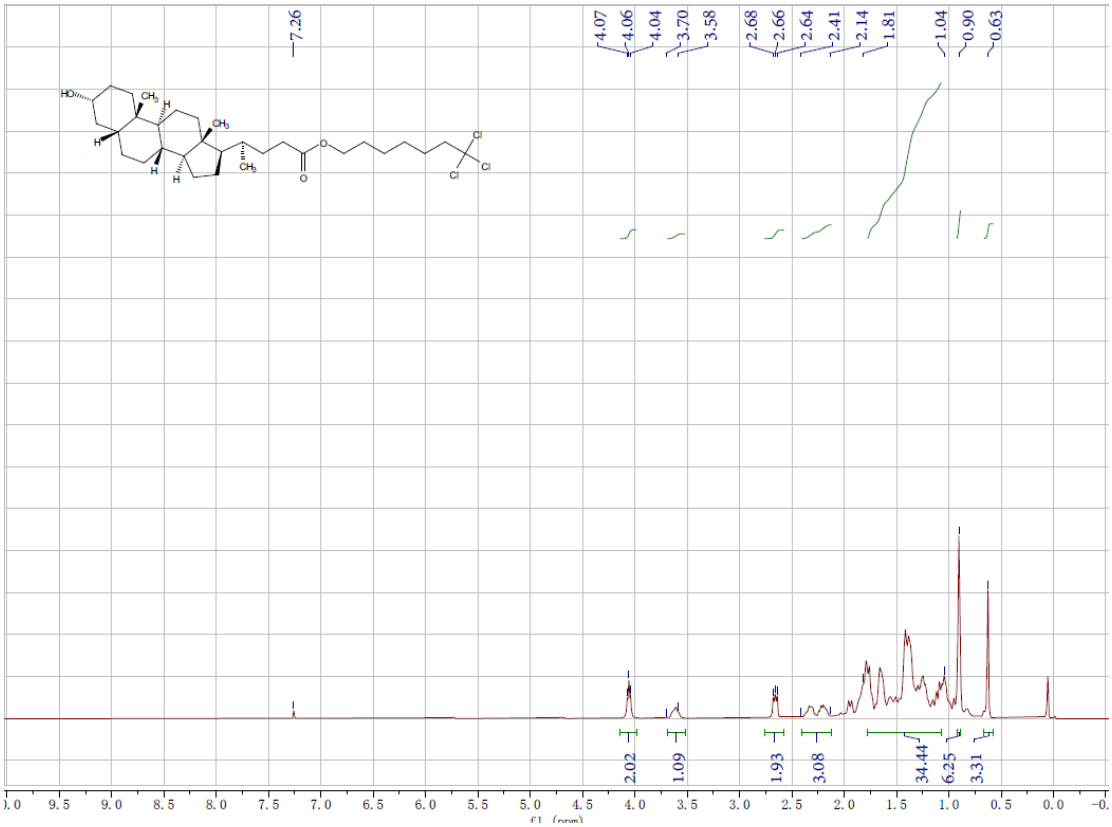

Figure S62. ^{1}H NMR Spectrum of **3ac**

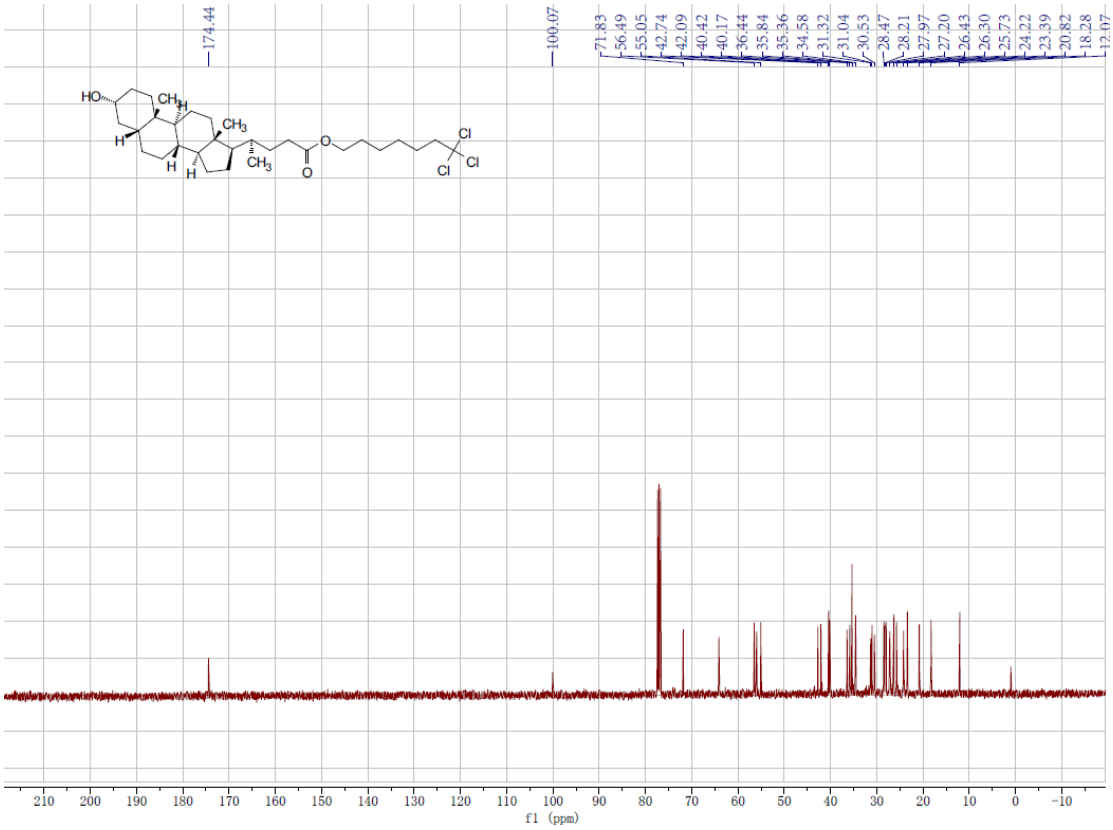

Figure S63.^{13}C NMR Spectrum of **3ac**

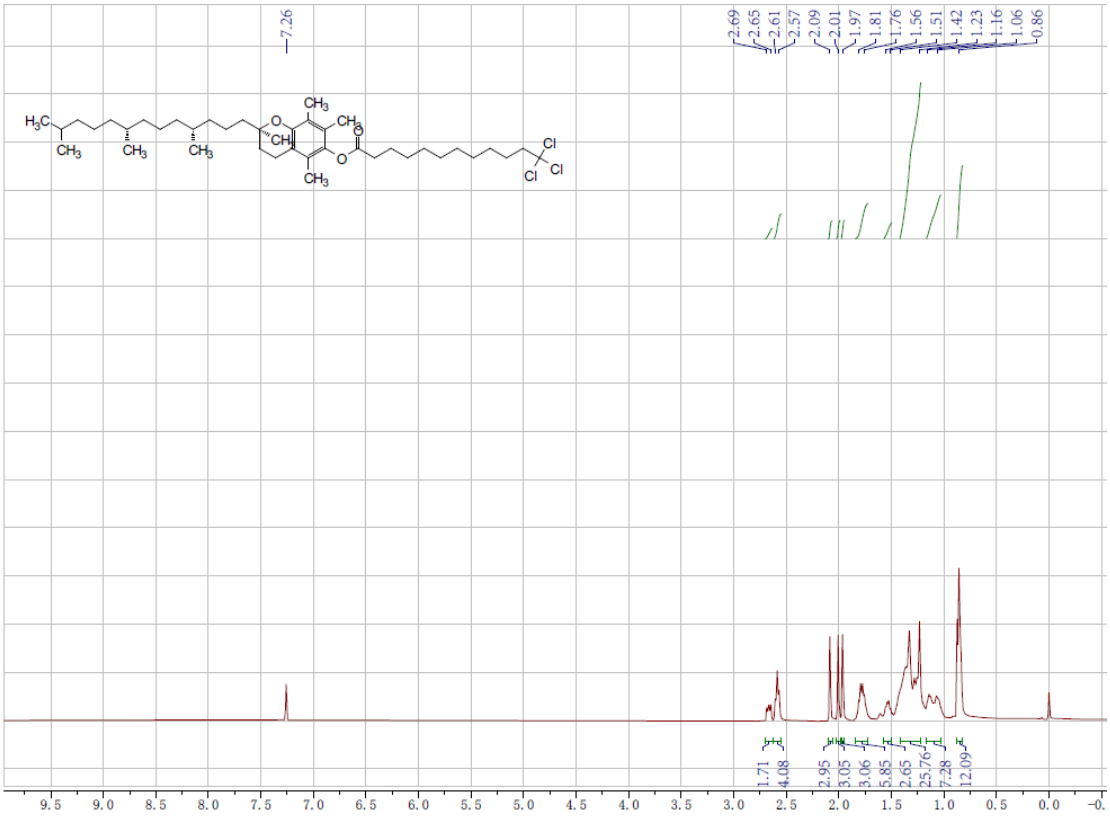

Figure S64. ^{1}H NMR Spectrum of **3ad**

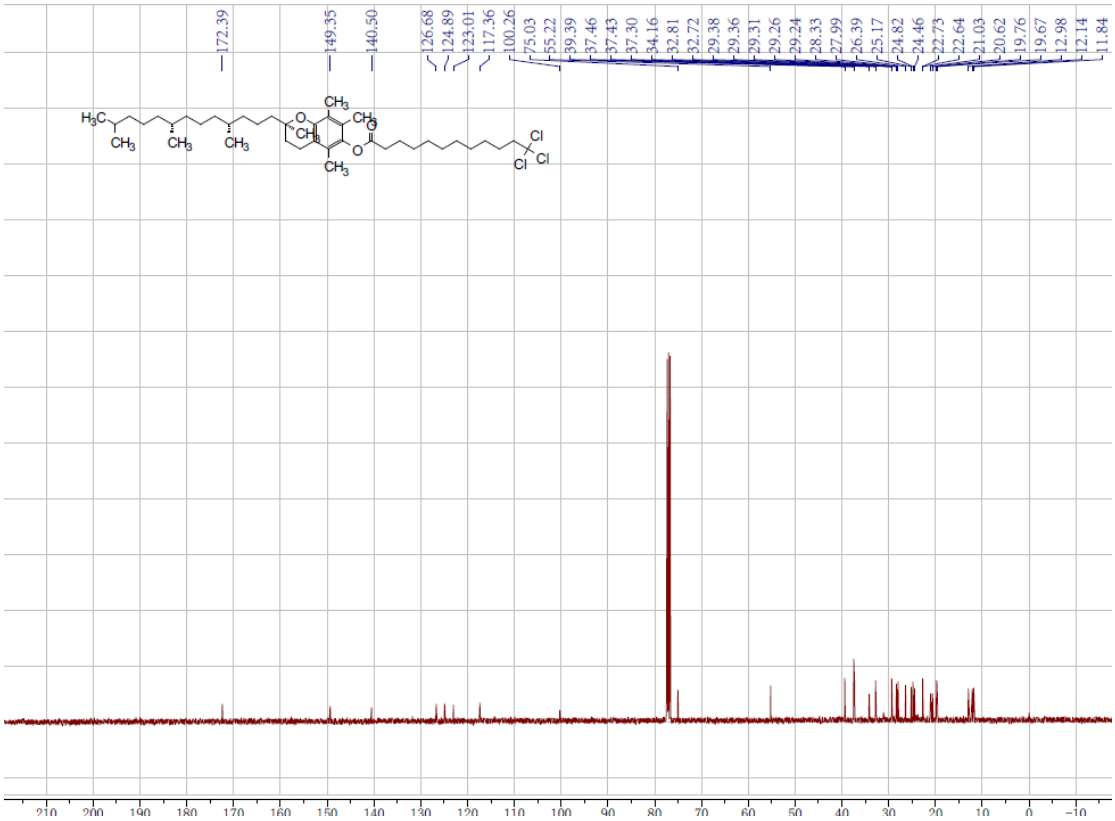

Figure S65.^{13}C NMR Spectrum of **3ad**

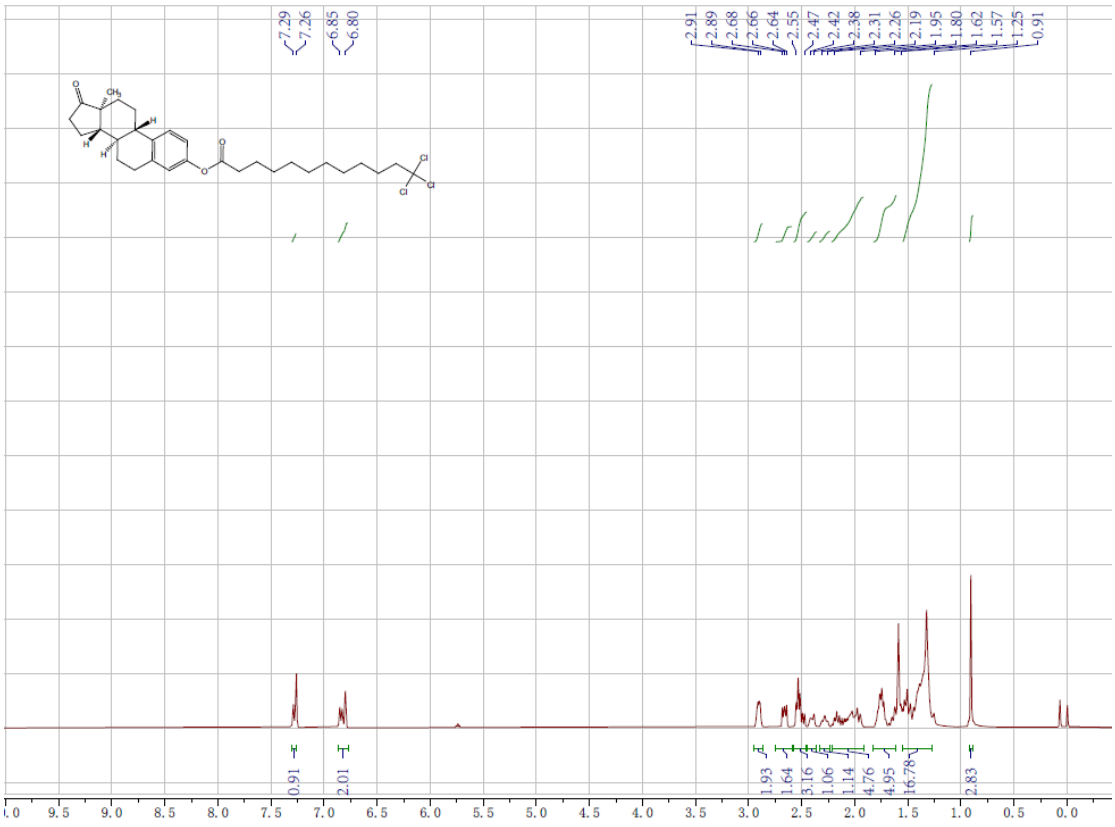

Figure S66. ^{1}H NMR Spectrum of **3ae**

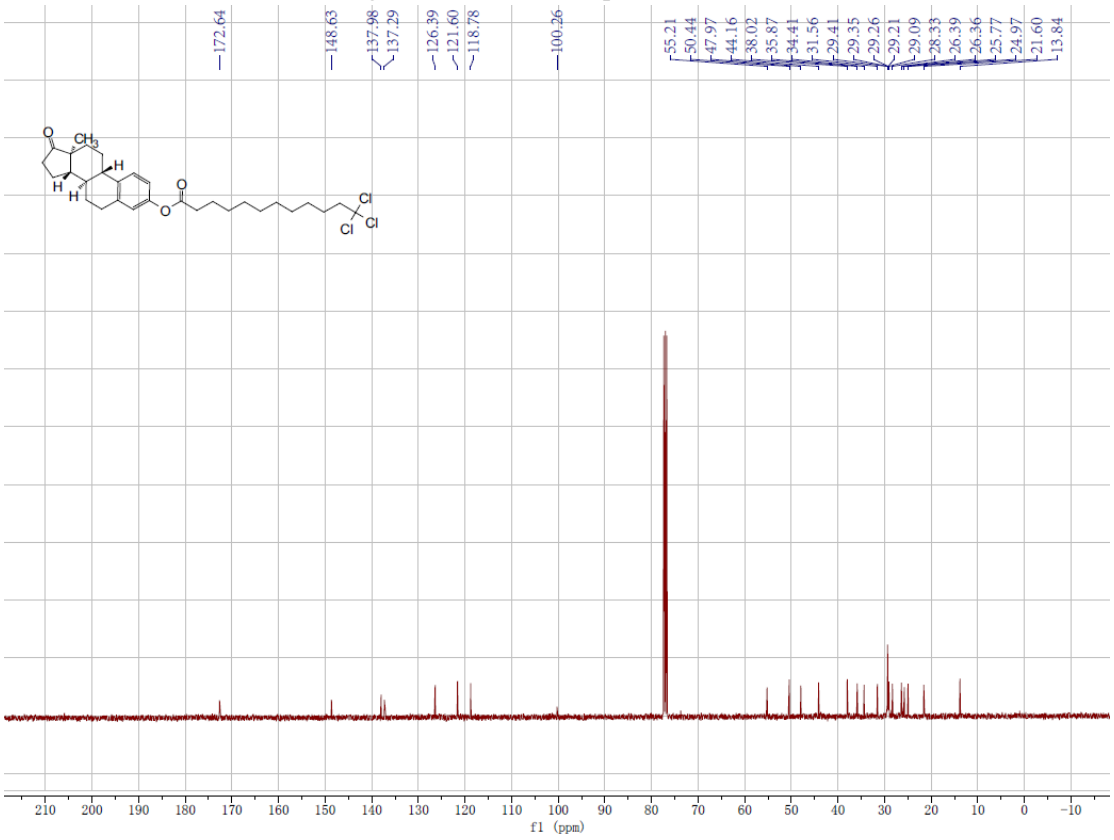

Figure S67.^{13}C NMR Spectrum of **3ae**

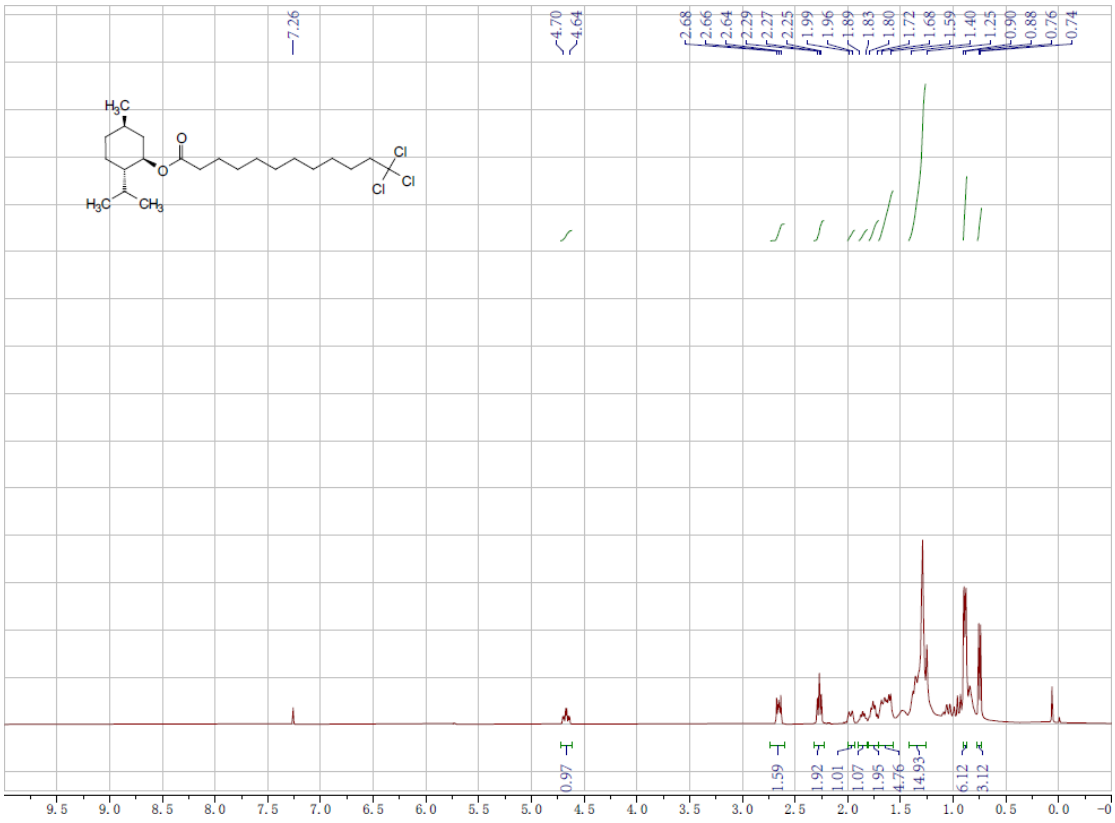

Figure S68. ^{1}H NMR Spectrum of **3af**

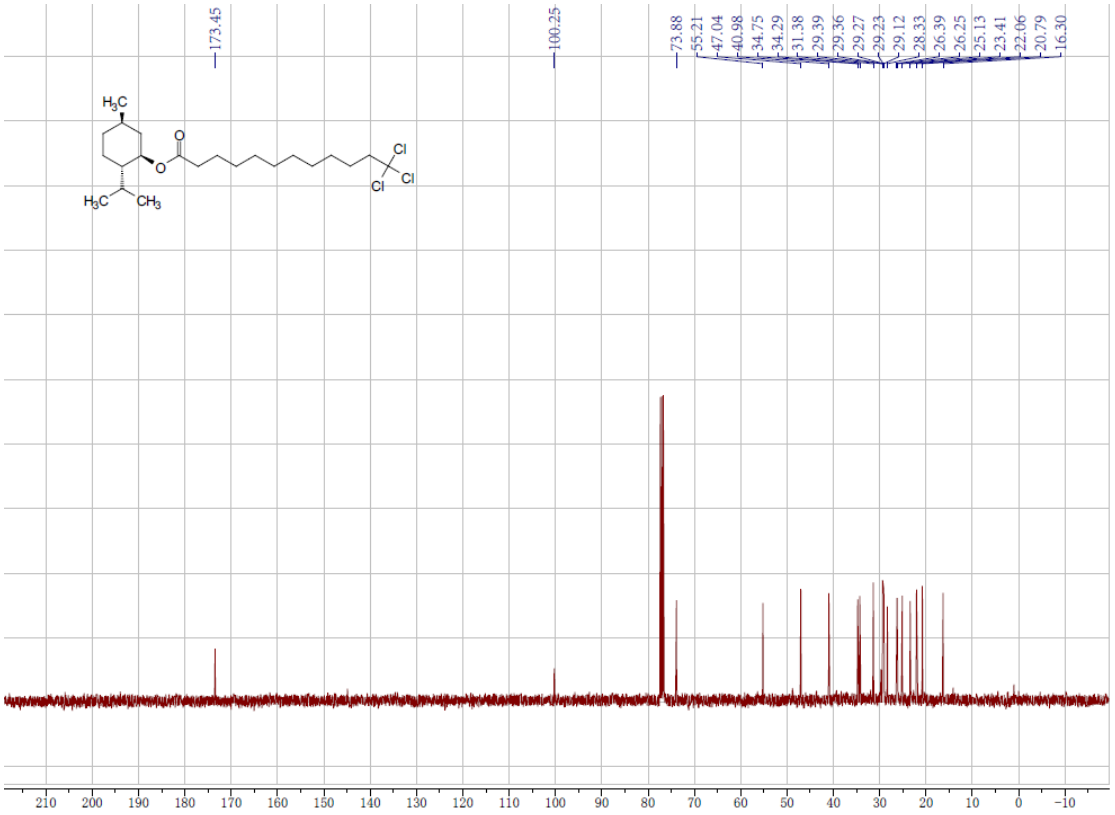

Figure S69.^{13}C NMR Spectrum of **3af**

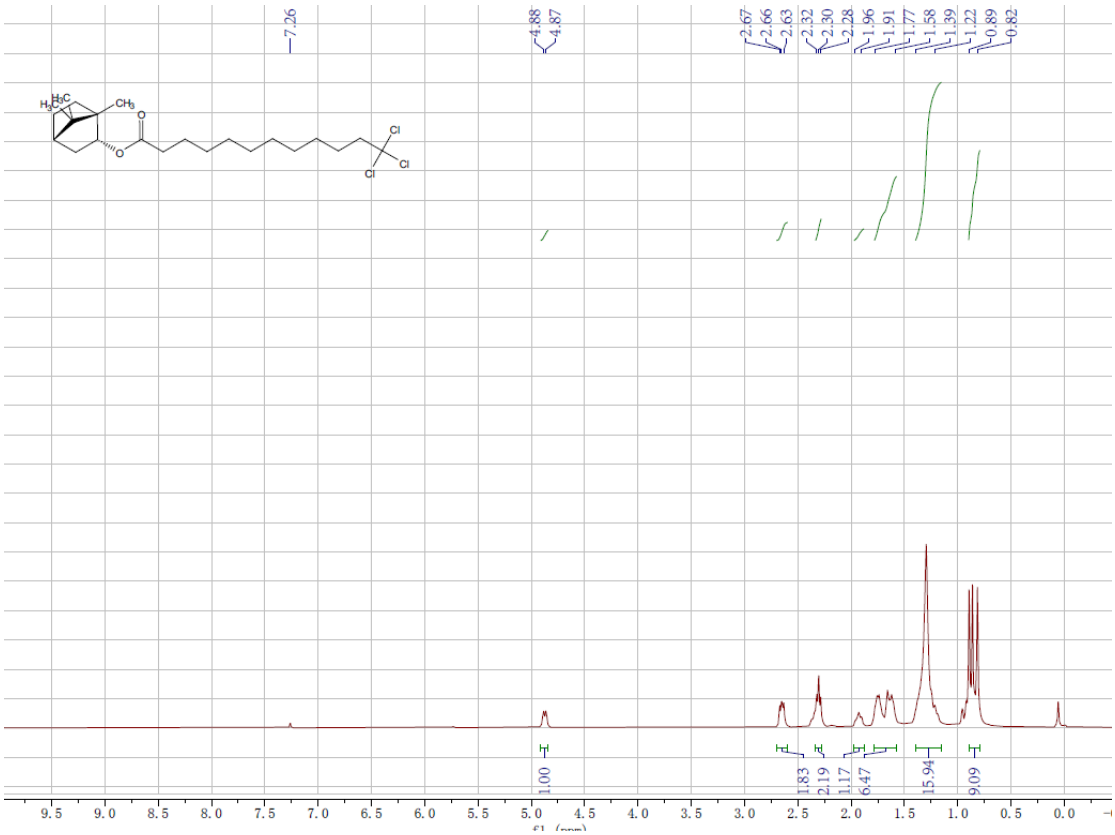

Figure S70. ^{1}H NMR Spectrum of **3ag**

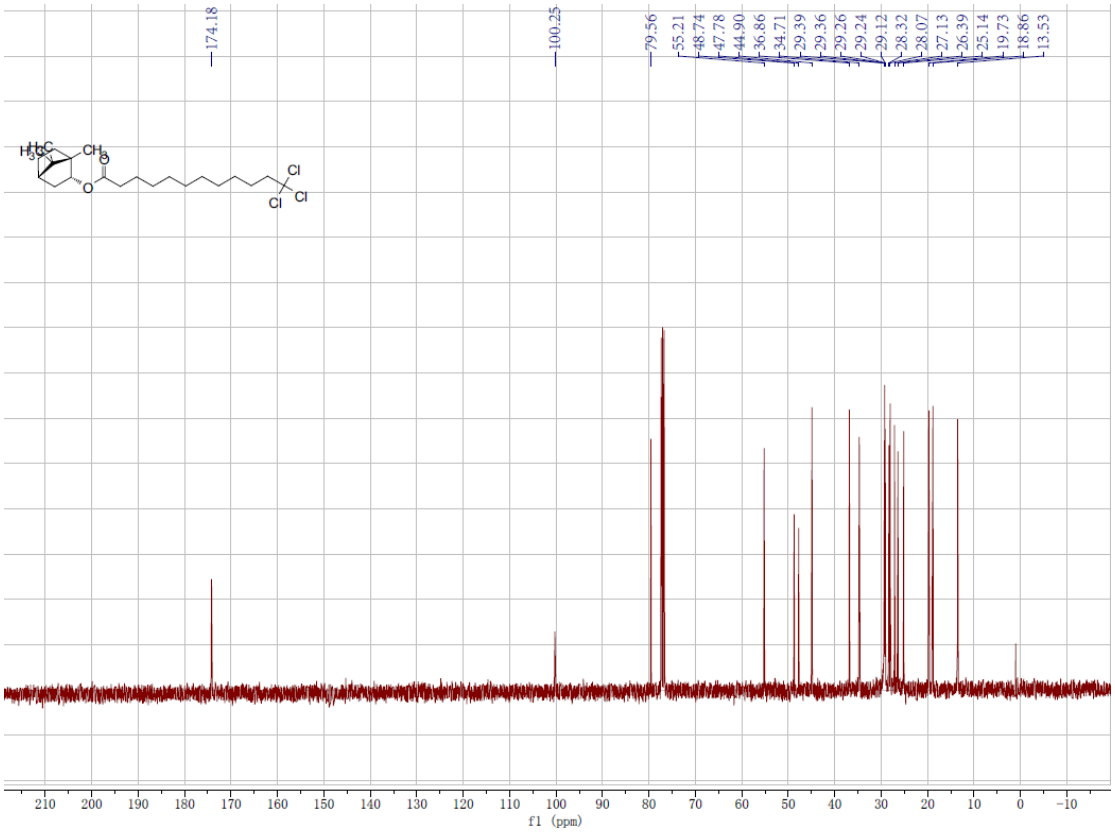

Figure S71.^{13}C NMR Spectrum of **3ag**

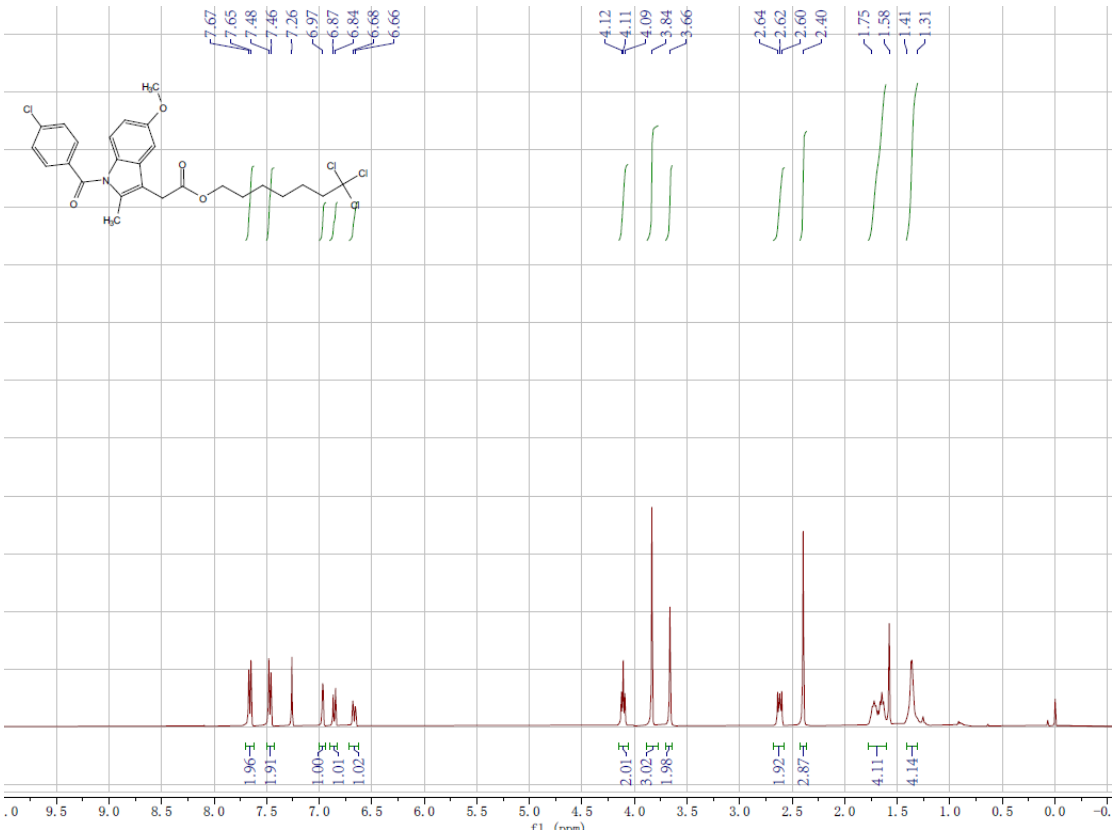

Figure S72. ^{1}H NMR Spectrum of **3ah**

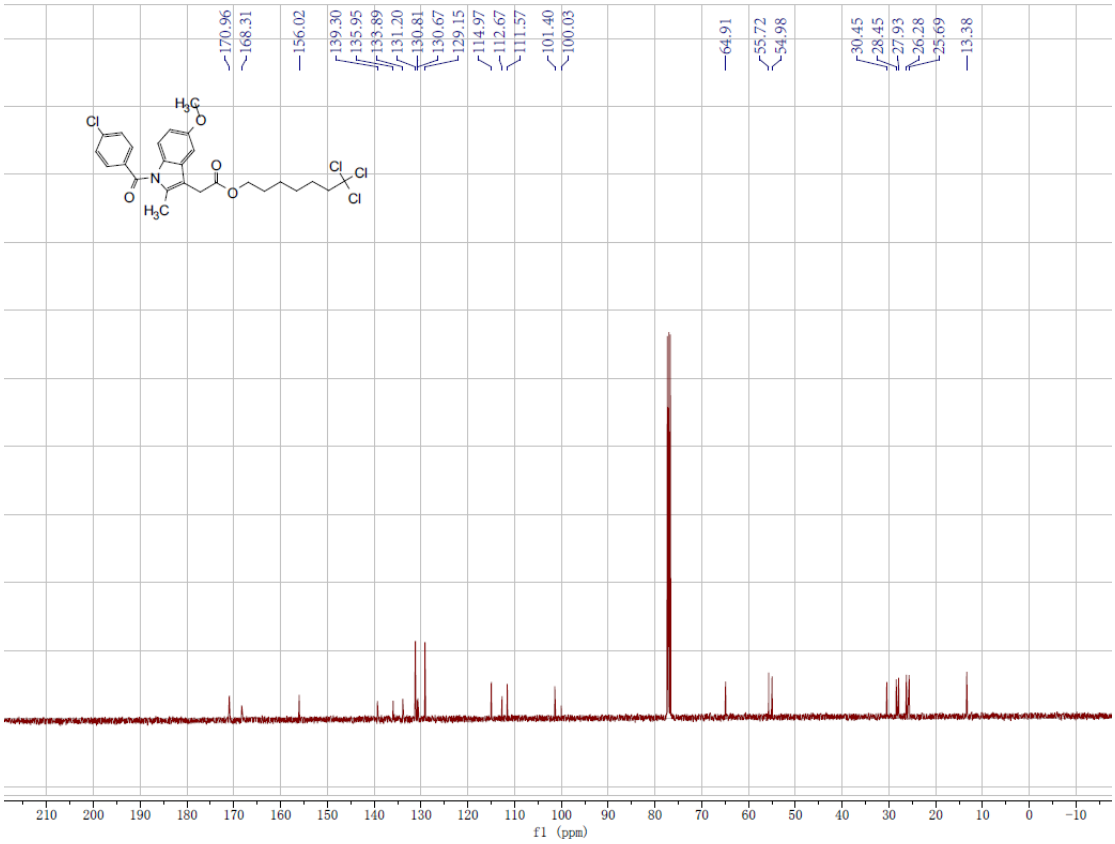

Figure S73.^{13}C NMR Spectrum of **3ah**

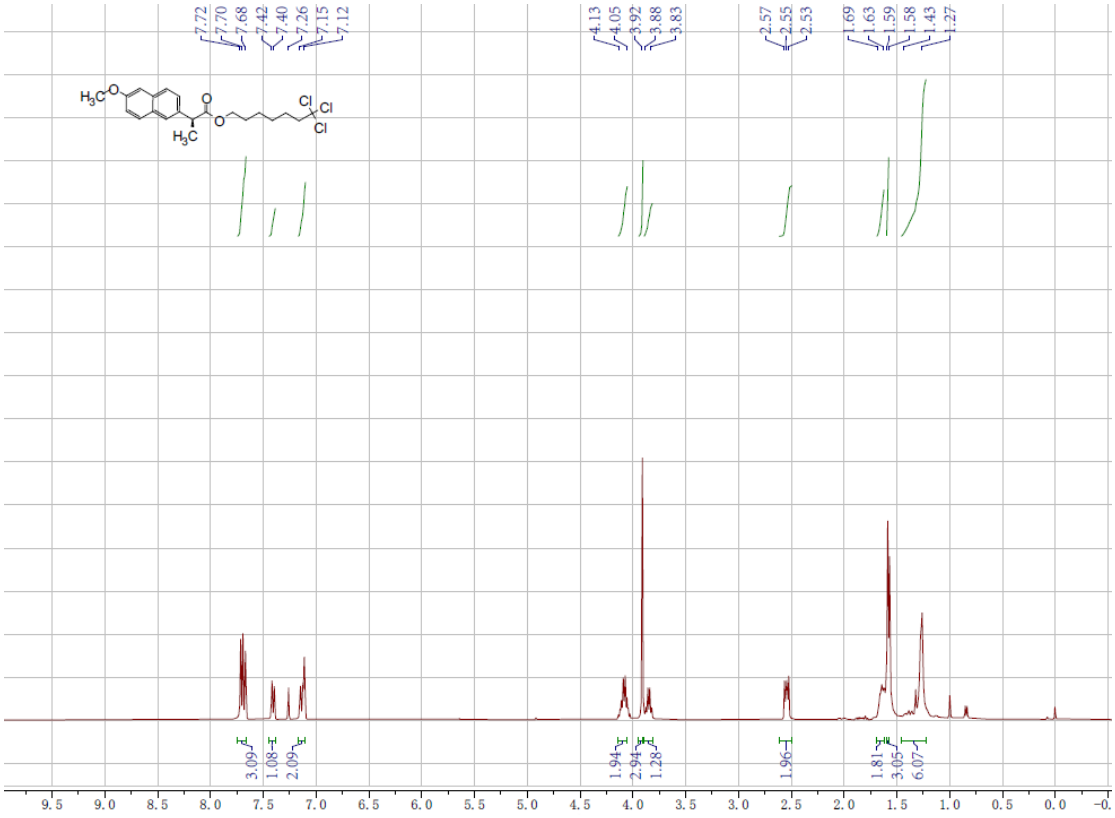

Figure S74. ^{1}H NMR Spectrum of **3ai**

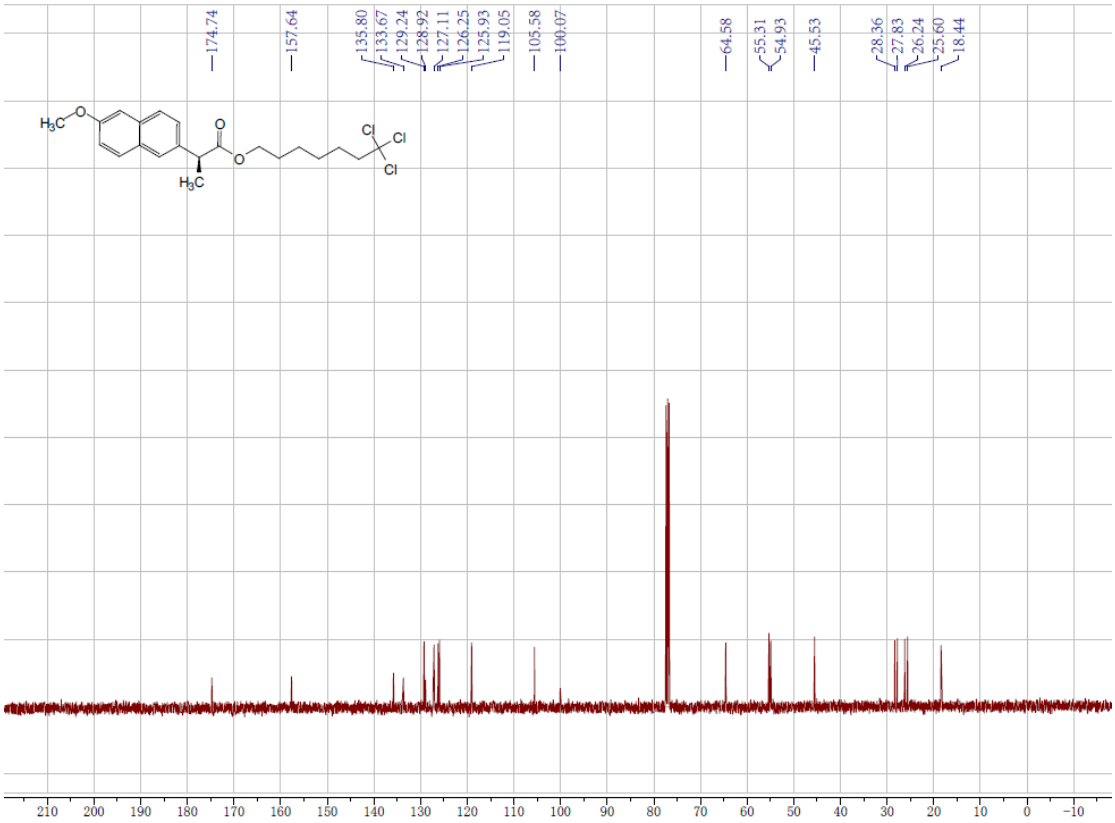

Figure S75.^{13}C NMR Spectrum of **3ai**

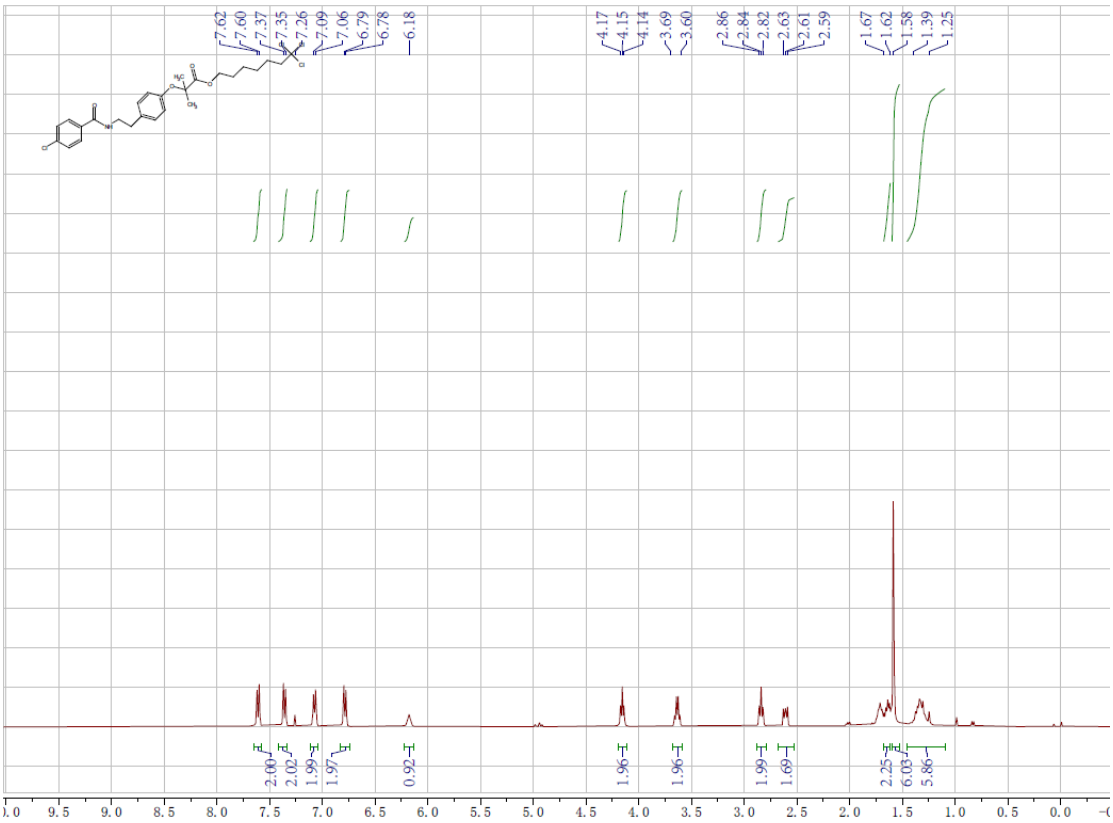

Figure S76. ^{1}H NMR Spectrum of **3aj**

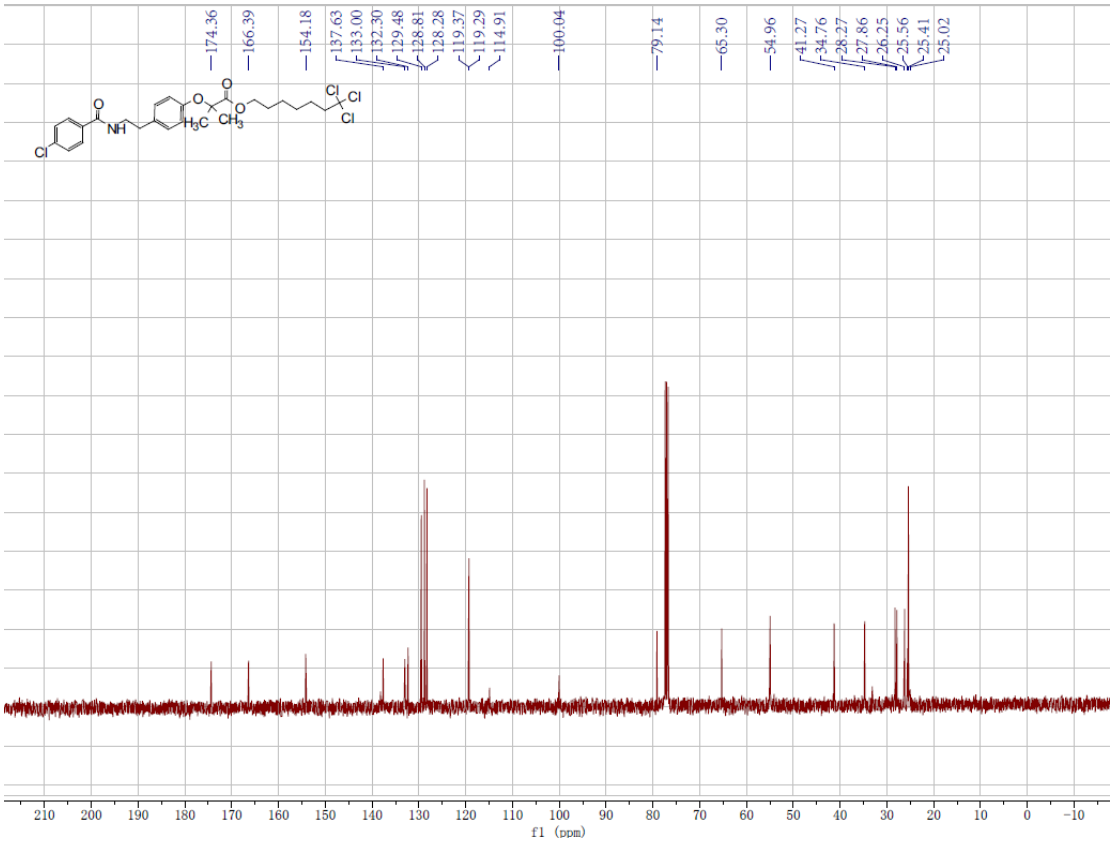

Figure S77.^{13}C NMR Spectrum of **3aj**

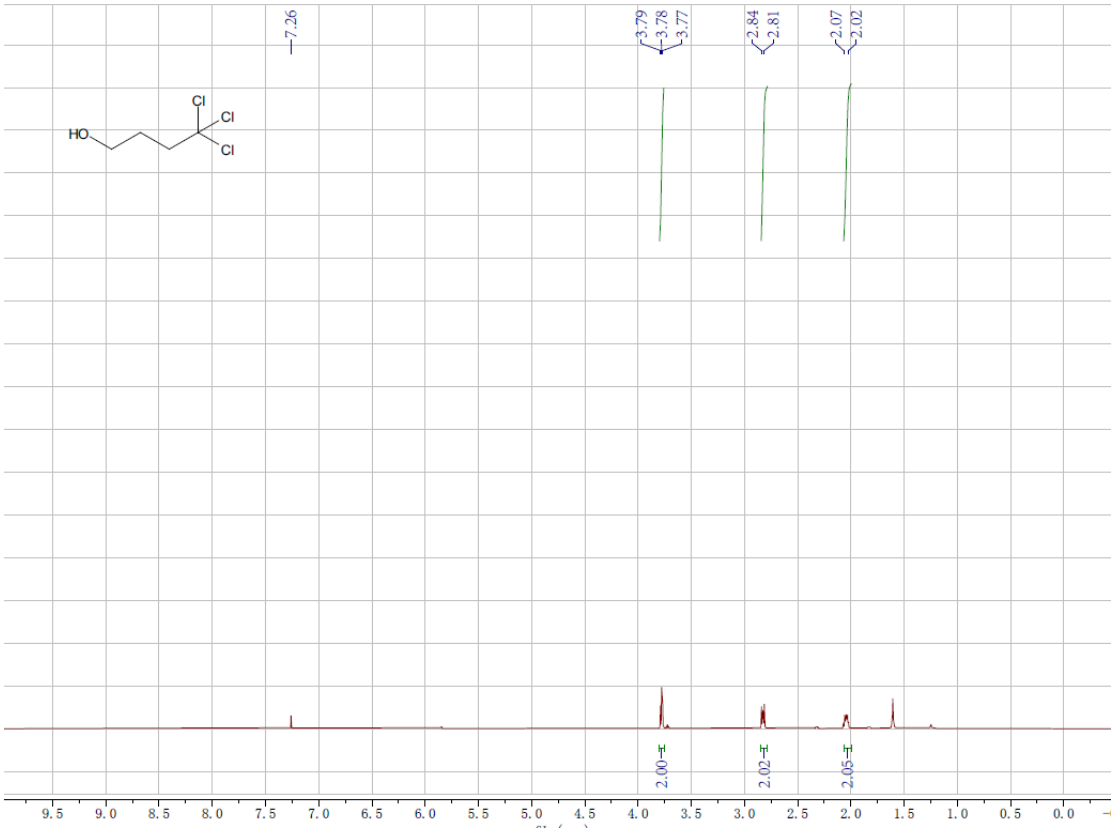

Figure S78. ^{1}H NMR Spectrum of **3ak**

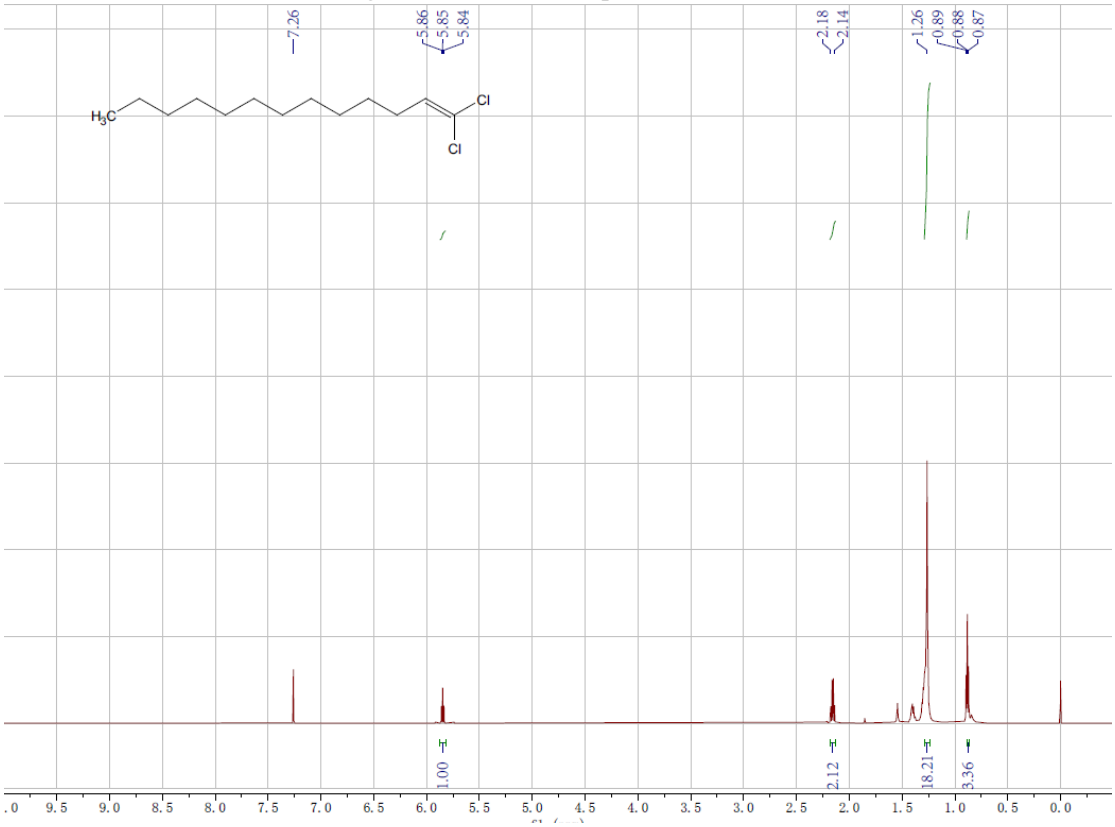

Figure S79. ^{1}H NMR Spectrum of **4a**

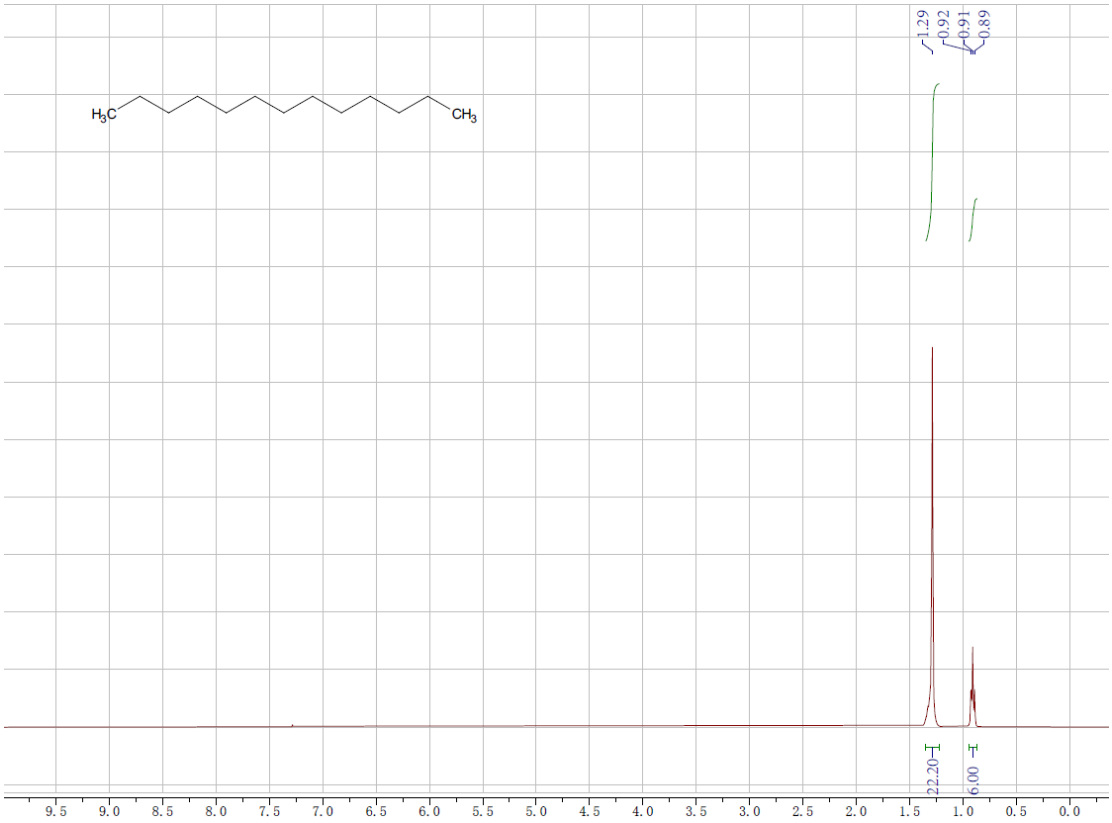

Figure S80. ^{1}H NMR Spectrum of **4b**

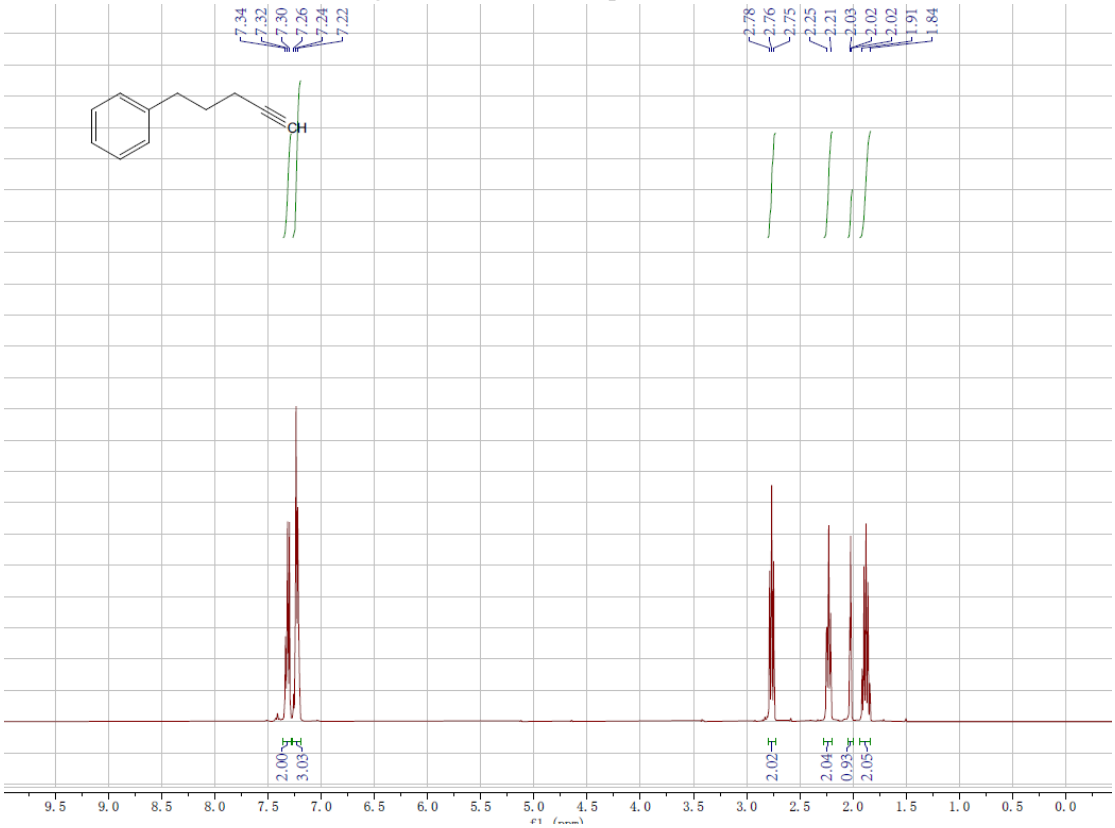

Figure S81. ^{1}H NMR Spectrum of **4c**

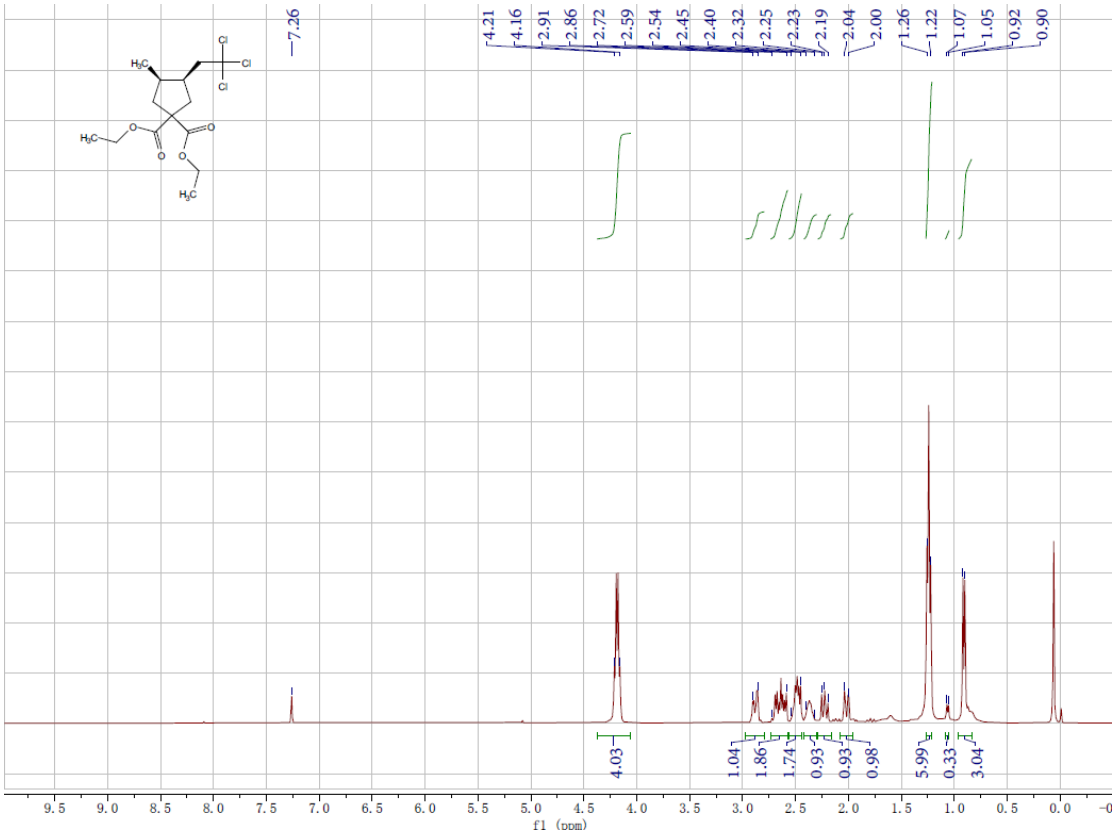

Figure S82. ^{1}H NMR Spectrum of **3z**

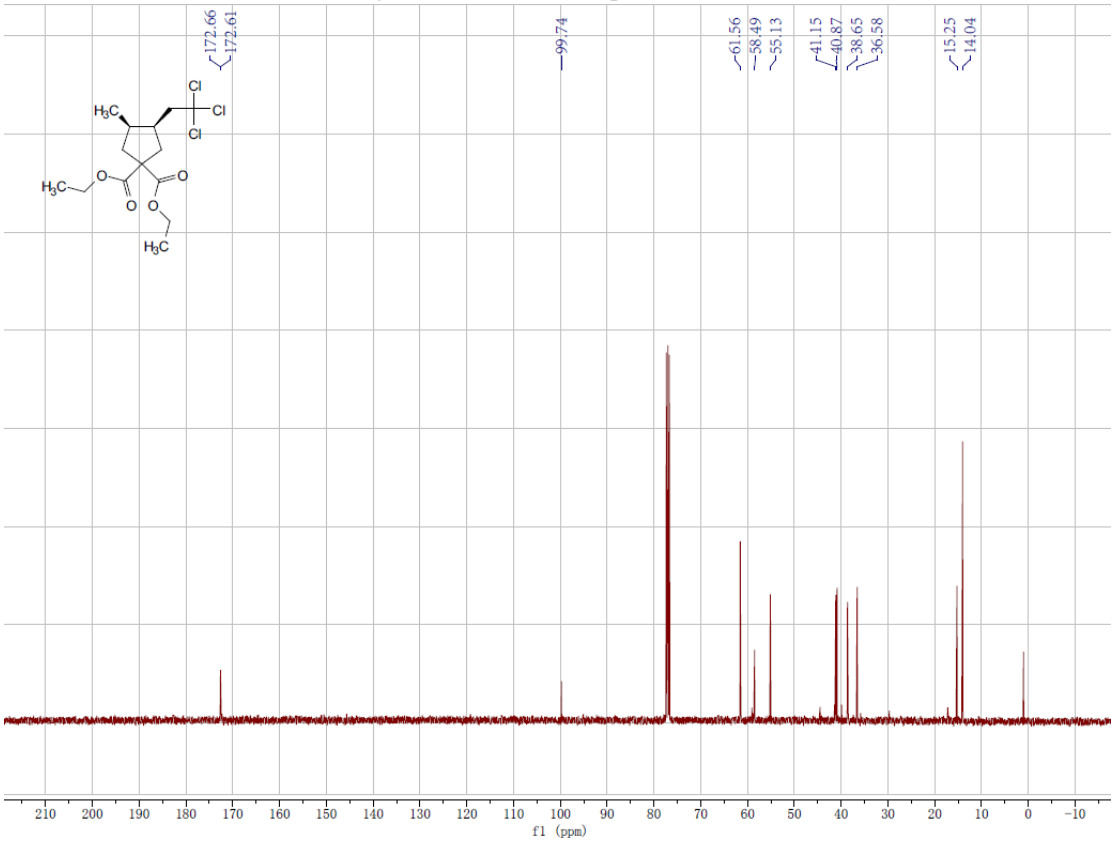

Figure S83.^{13}C NMR Spectrum of **3z**

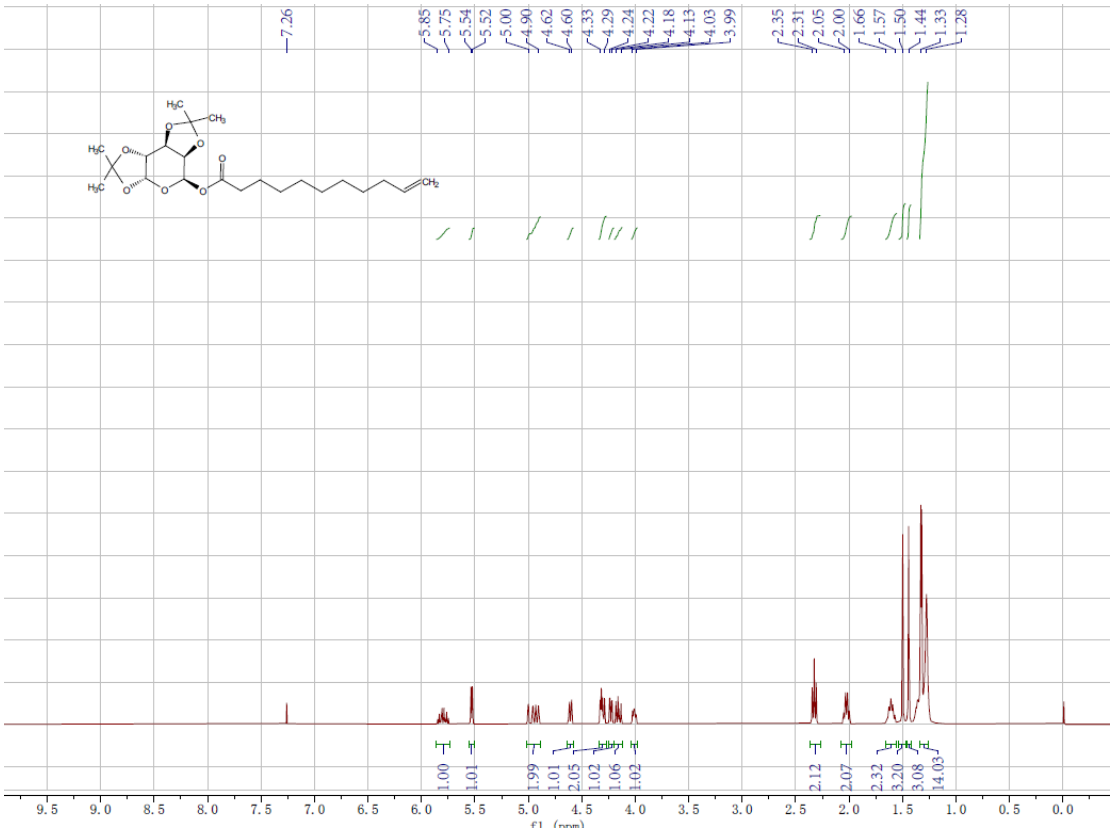

Figure S84. ^{1}H NMR Spectrum of **1aa**

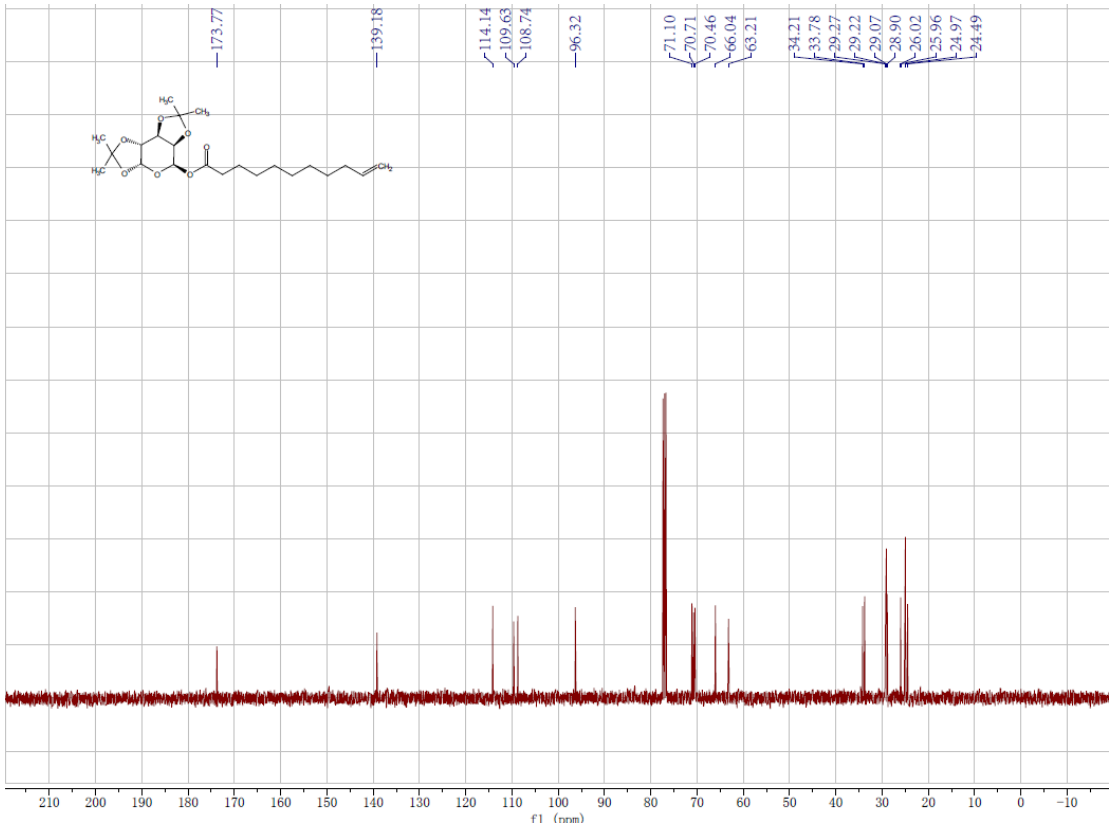

Figure S85. ^{13}C NMR Spectrum of **1aa**

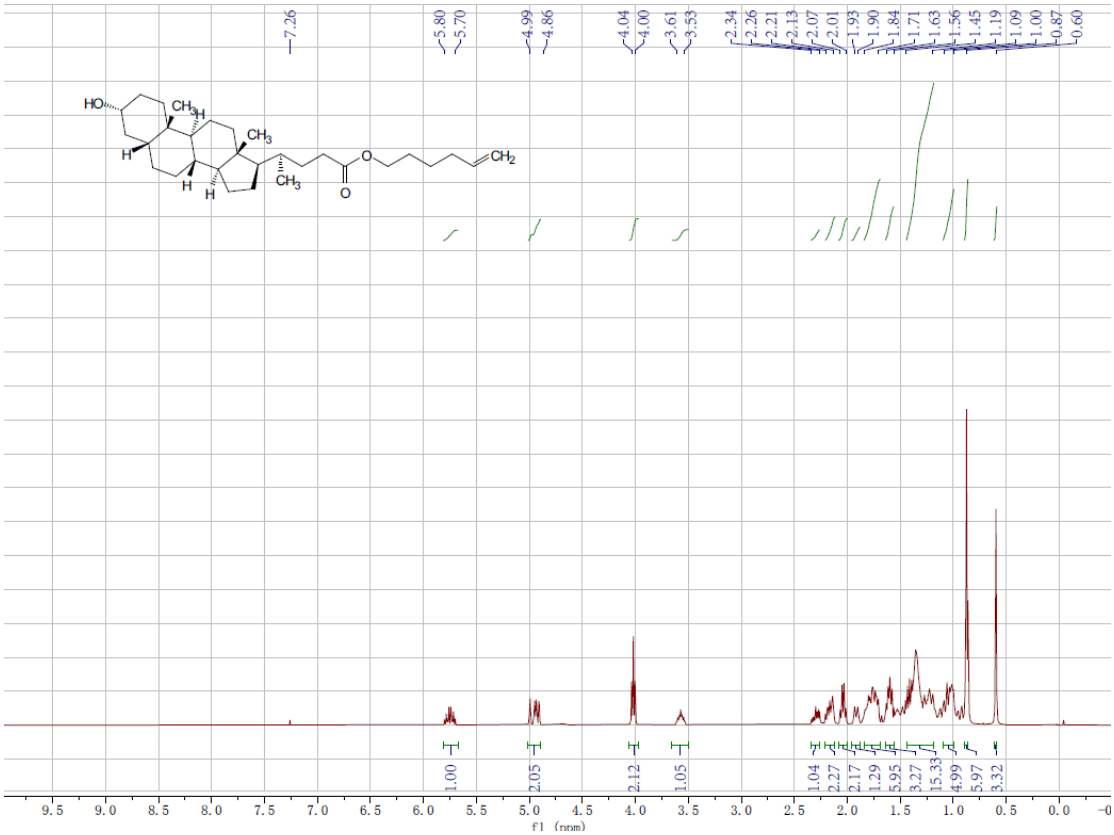

Figure S86. ^{1}H NMR Spectrum of **1ac**

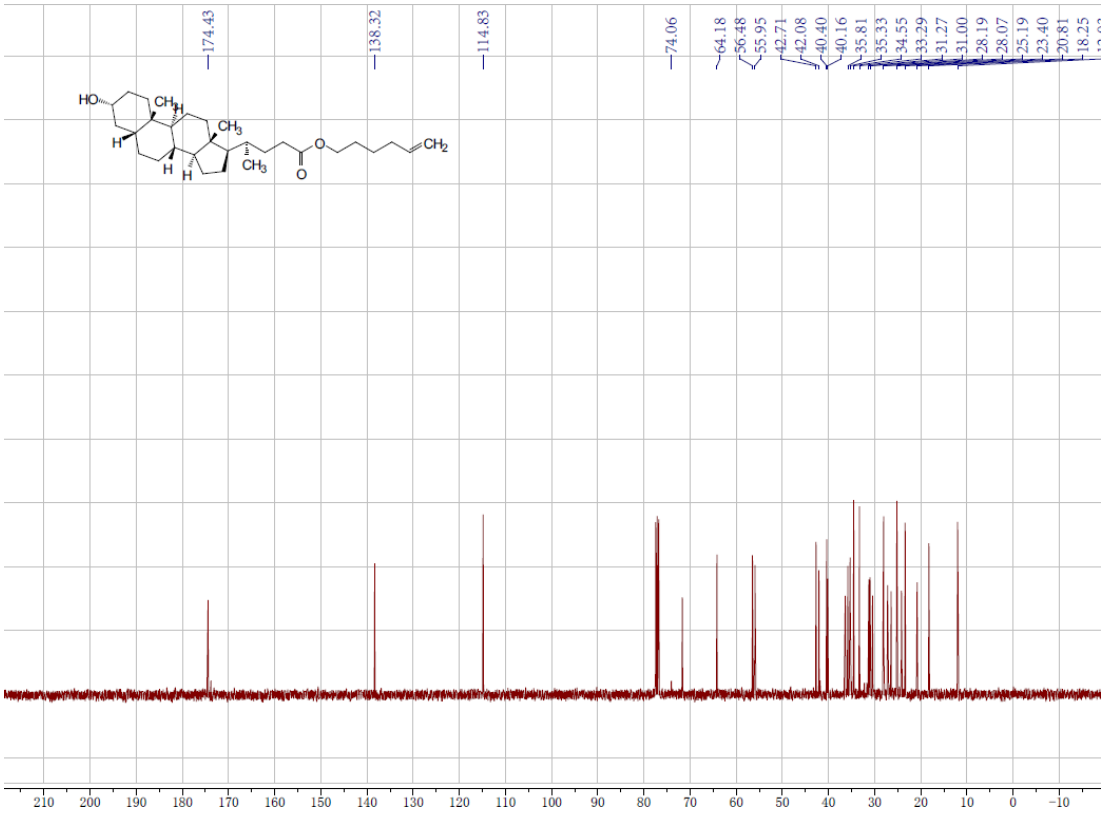

Figure S87. ^{13}C NMR Spectrum of **1ac**

Figure S88. ^{1}H NMR Spectrum of **1af**

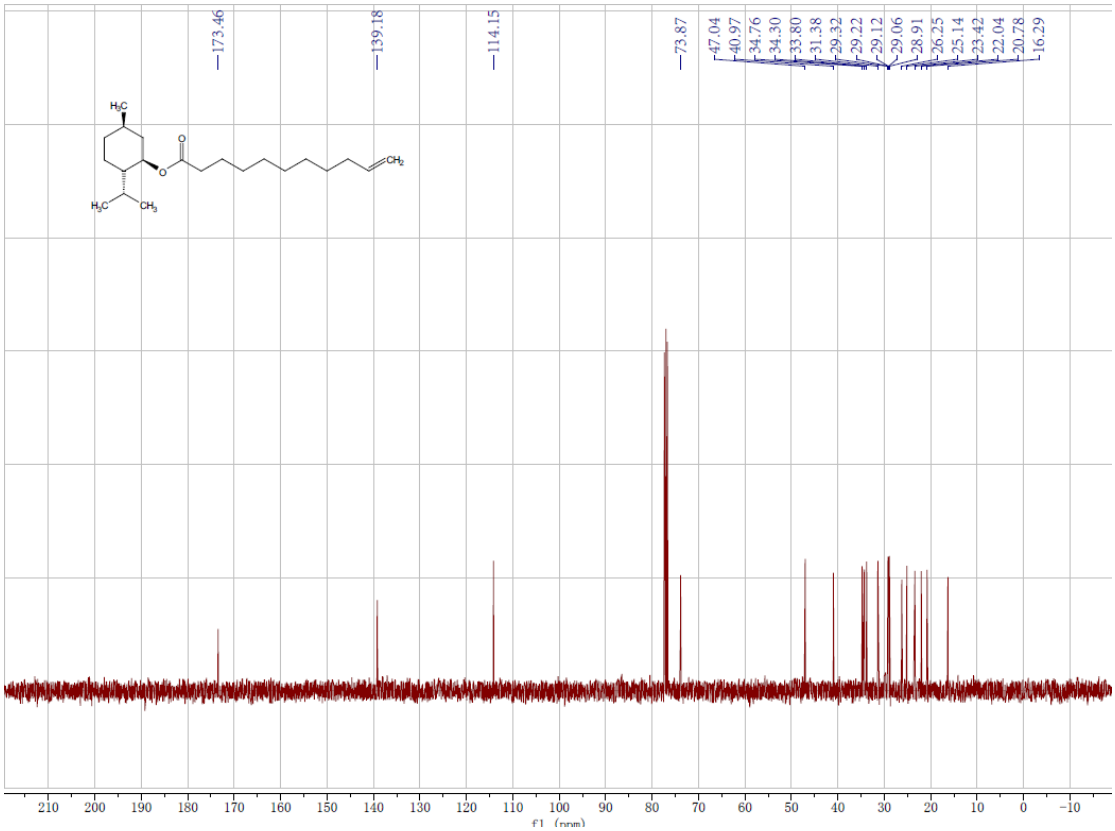

Figure S89. ^{13}C NMR Spectrum of **1af**

Figure S90. ^{1}H NMR Spectrum of **1ag**

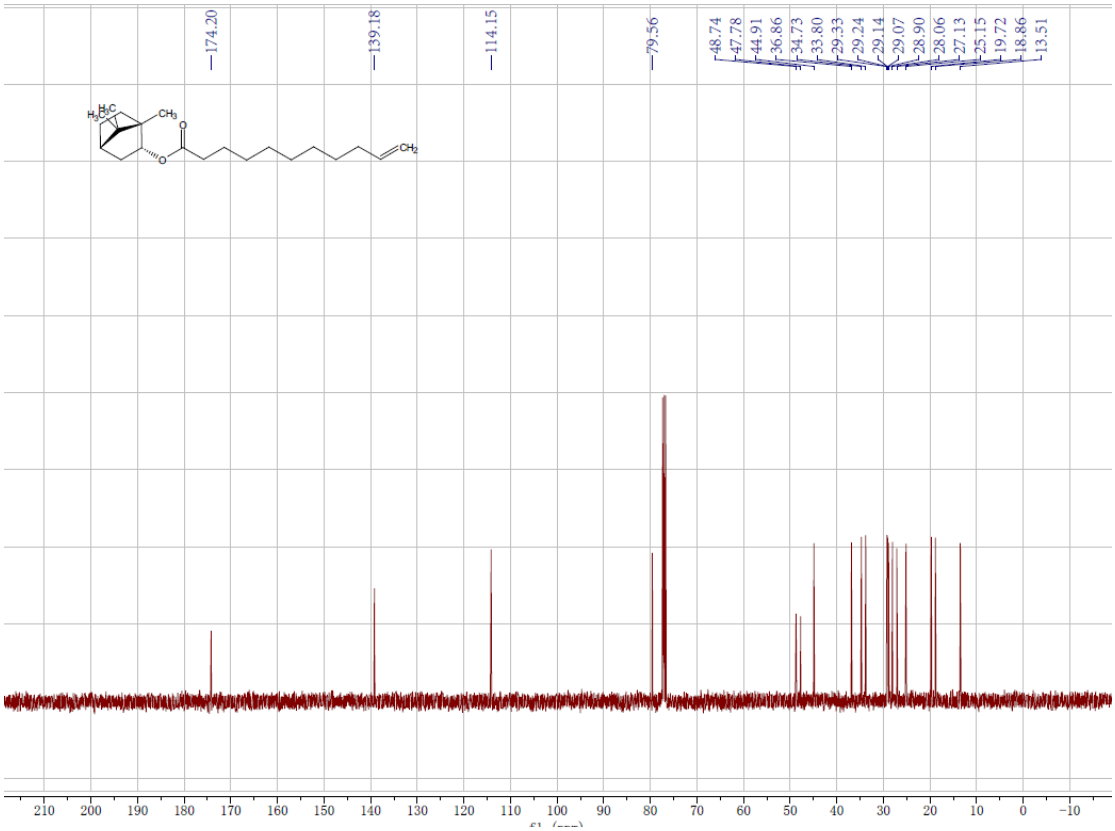

Figure S91. ^{13}C NMR Spectrum of **1ag**

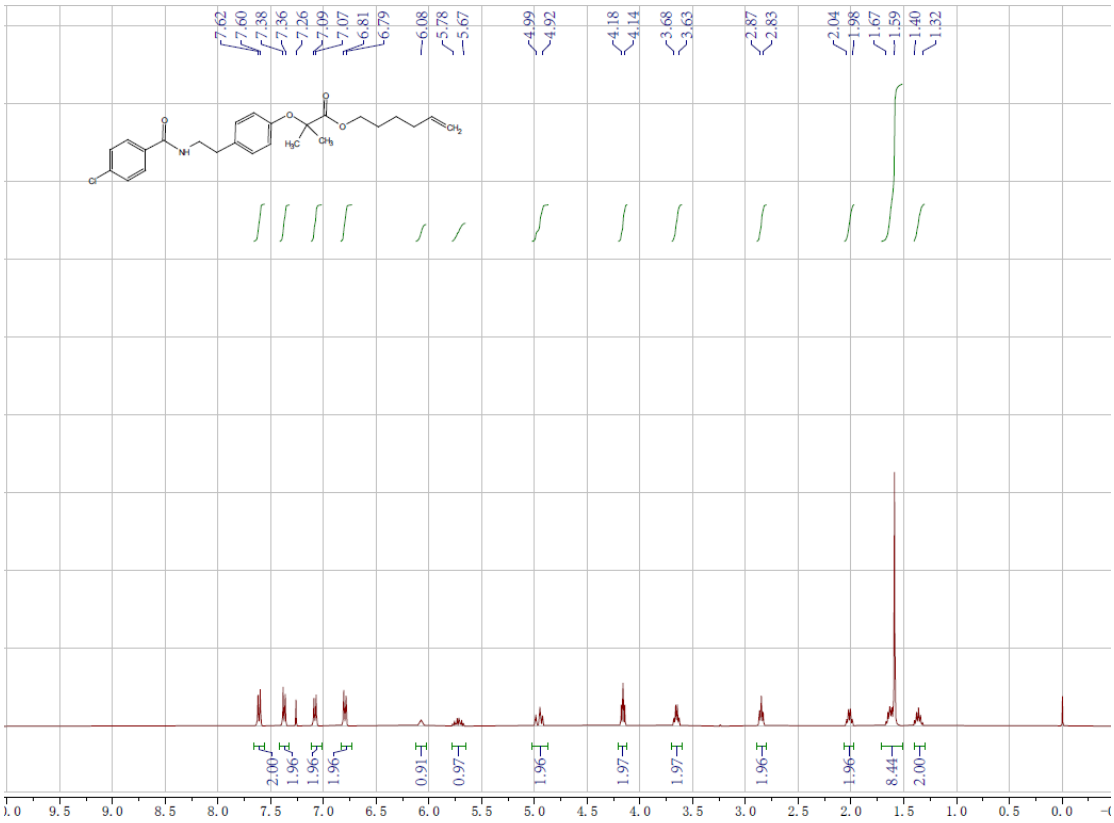

Figure S92. ^{1}H NMR Spectrum of **1aj**

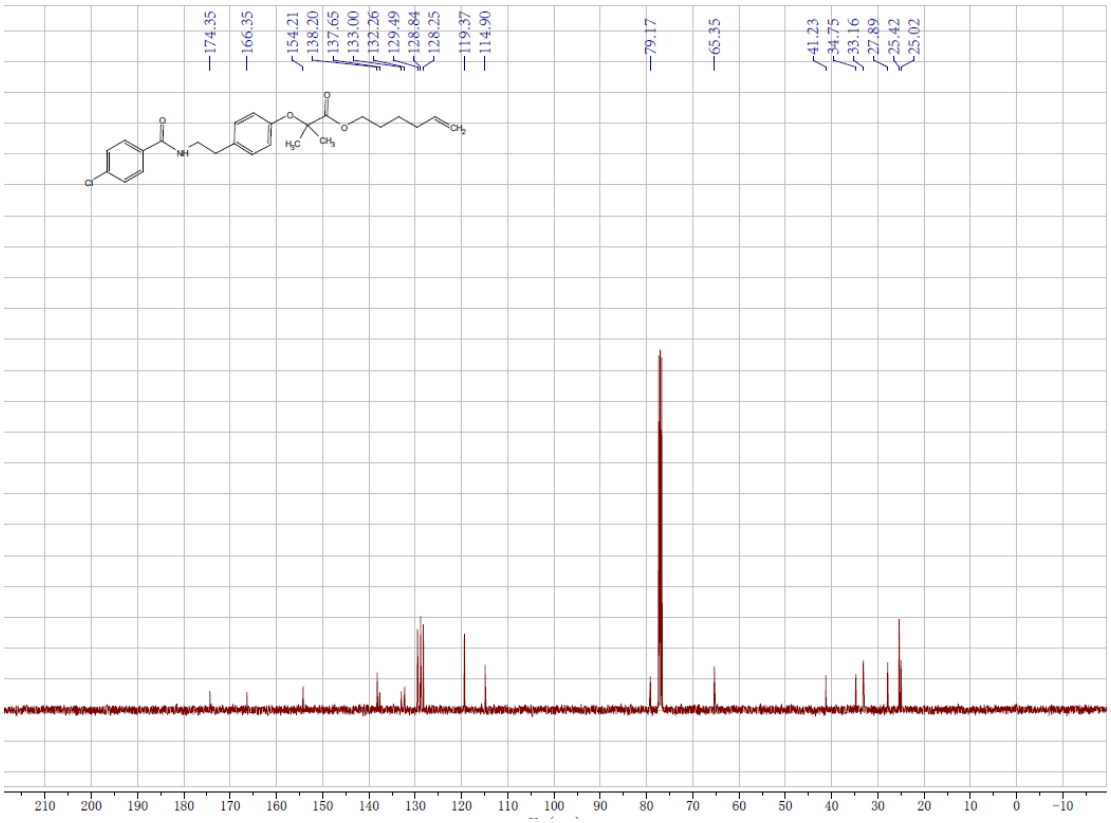

Figure S93. ^{13}C NMR Spectrum of **1aj**

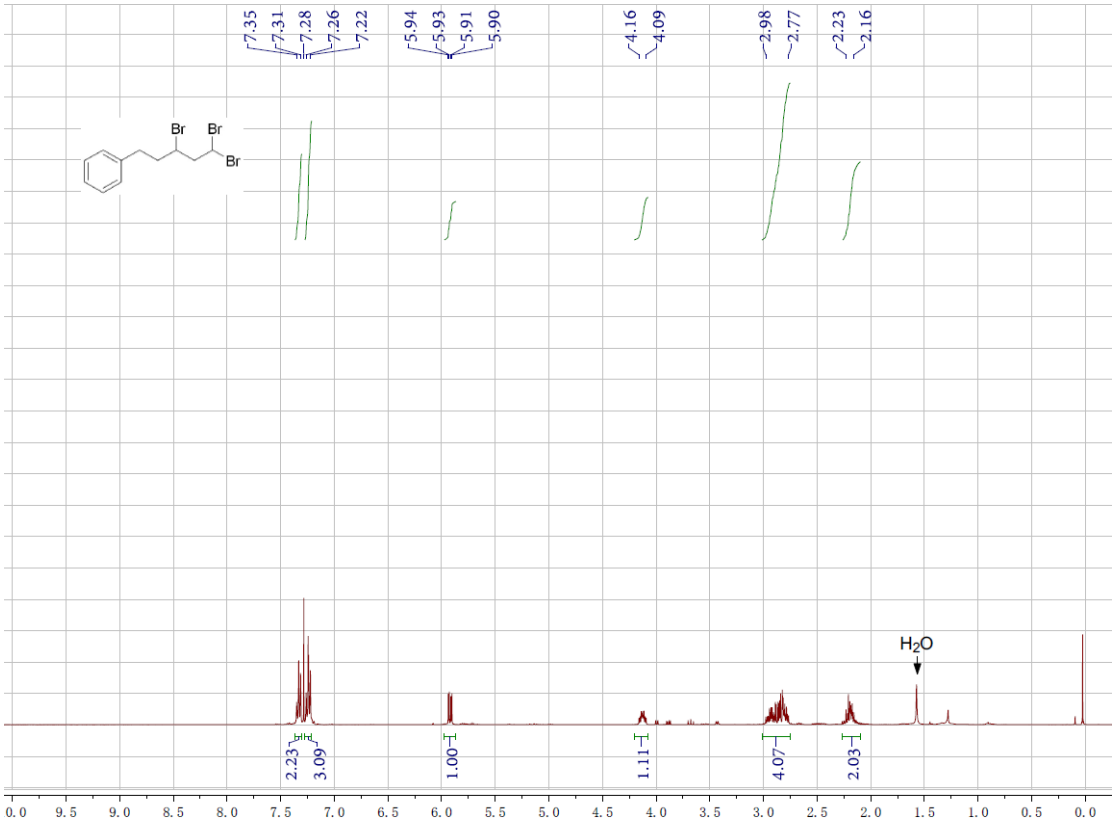

Figure S94. ^{1}H NMR Spectrum of **3y**