Electronic Supplementary Material (ESI) for Green Chemistry.

Visible Light-Mediated Polychlorination of Alkenes via Dichloromethyl Radical Generated by Chloroform and Chlorides

Chunying Wu[†], Xin Hui[†], Dan Zhang, Minghui Zhang, Yunbo Zhu* and Sicen Wang

School of Pharmacy, Health Science Center, Xi'an Jiaotong University, 76 Yanta West Road, Xi'an, Shaanxi 710061, P.R. China

Supporting Information

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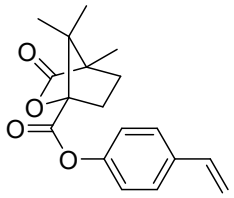
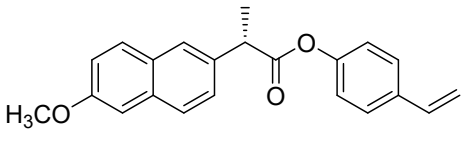
General information and Materials: All solvents were purified according to the reported method.[1] If no special indicated, commercial reagents were used without further purification. Column chromatographic purification of all products was conducted using 200-300 dry mesh silica gel. ^{1}H and ^{13}C NMR spectra were measured on a JEOL JNM-ECZ400S/L1 and AVANCE III HD 600 spectrometers, NMR (400 and 600 MHz for ^{1}H NMR, 101 and 151 MHz for ^{13}C NMR). Tetramethylsilane (TMS) served as the internal standard for ^{1}H NMR, and $CDCl_3$ served as the internal standard for ^{13}C NMR. Infrared spectra were collected on a Bruker VERTEX70 as a thin film, and selected maximum absorbance were reported in wavenumbers. Mass spectra were performed on GCMS-QP2010 ultra (EI Source). High-resolution mass spectra (HRSM) were obtained on a Waters I-Class VION IMS QTof and are reported as m/z (relative intensity).

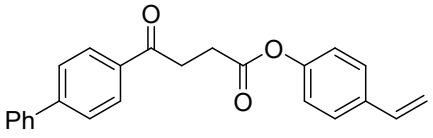
Procedure for Synthesis of Pharmaceuticals-derived Olefins



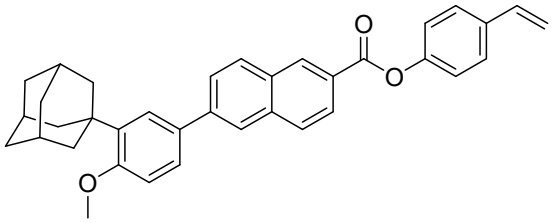
I
from (1*S*)-(-)-camphanic acid



III
from (*S*)-(+) naproxen



II
from fenbufen



IV
from adapalene

These compounds were prepared following reported literature procedure.[2] To a solution of 4-vinylphenol (2.5 mmol) and acid (2.5 mmol) in CH_2Cl_2 (25 mL), DMAP (10 mol%) and EDCI•HCl (6.25 mmol) was added. The mixture was stirred at room temperature under N_2 until the reaction was complete by TLC monitoring. The mixture was diluted with water (10 mL) and the CH_2Cl_2 layer was separated, dried over anhydrous Na_2SO_4 and concentrated. The crude mixture was purified by column chromatography to deliver the target products.

Compound **I:** 76% yield, white powder. The NMR data was coincident with the report in the literature.[2] **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.46-7.42 (m, 2H), 7.12-7.07 (m, 2H), 6.71 (dd, *J* = 17.6, 10.9, 1H), 5.73 (dd, *J* = 17.6, 0.7, 1H), 5.27 (dd, *J* = 11.0, 0.5, 1H), 2.57 (ddd, *J* = 13.5, 10.8, 4.3, 1H), 2.20 (ddd, *J* = 13.6, 9.4, 4.6, 1H), 2.00 (ddd, *J* = 13.2, 10.8, 4.6, 1H), 1.77 (ddd, *J* = 13.4, 9.4, 4.3, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 178.0, 166.2, 149.5, 136.1, 135.8, 127.4, 121.5, 114.7, 91.0, 55.0, 54.9, 30.9, 29.1, 17.0, 9.9. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{18}H_{20}O_4$ $[M+H]^+$ 301.1434; found 301.1415.

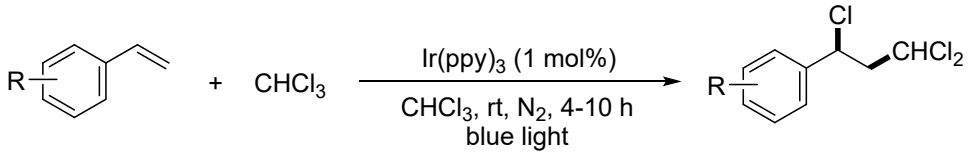
New compound **II:** 72% yield, white powder. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.10-8.05 (m, 2H), 7.72-7.67 (m, 2H), 7.64-7.60 (m, 2H), 7.51-7.43 (m, 2H), 7.45-7.37 (m, 3H), 7.10-7.05 (m, 2H), 6.69 (dd, *J* = 17.6, 10.9, 1H), 5.69 (dd, *J* = 17.6, 0.7, 1H), 5.23 (dd, *J* = 10.9, 0.7, 1H), 3.46 (t, *J* = 6.5, 2H), 3.03 (t, *J* = 6.5, 2H). **^{13}C NMR** (101

MHz, $CDCl_3$) δ = 197.3, 171.5, 150.3, 145.8, 139.6, 135.9, 135.2, 135.1, 128.9, 128.6, 128.2, 127.1, 127.1, 121.6, 113.9, 33.39, 28.41. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{24}H_{20}O_3$ $[M+H]^+$ 357.1485; found 357.1463.

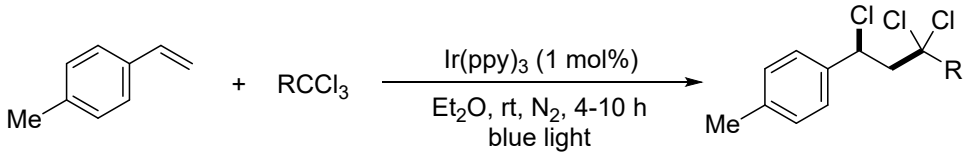
New compound **III:** 73% yield, light yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.80-7.70 (m, 3H), 7.50 (dd, *J* = 8.5, 1.7, 1H), 7.38-7.32 (m, 2H), 7.20-7.12 (m, 2H), 6.98-6.92 (m, 2H), 6.66 (dd, *J* = 17.6, 10.9, 1H), 5.67 (d, *J* = 17.6, 1H), 5.21 (d, *J* = 10.9, 1H), 4.09 (q, *J* = 7.1, 1H), 3.92 (s, 3H), 1.69 (d, *J* = 7.1, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 173.3, 157.9, 150.5, 136.0, 135.4, 135.3, 134.0, 129.5, 129.1, 127.5, 127.2, 126.3, 126.3, 121.6, 119.3, 114.1, 105.7, 55.46, 45.72, 18.67. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{22}H_{20}O_3$ $[M+Li]^+$ 339.1567; found 339.1585.

New compound **IV:** 52% yield, white powder. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.78 (s, 1H), 8.19 (d, *J* = 8.4, 1H), 8.06-7.93 (m, 3H), 7.82 (d, *J* = 8.3, 1H), 7.62 (s, 1H), 7.55 (d, *J* = 8.2, 1H), 7.49 (d, *J* = 8.2, 2H), 7.24 (d, *J* = 8.1, 2H), 7.00 (d, *J* = 8.4, 1H), 6.73 (dd, *J* = 11.2, 6.2, 1H), 5.74 (d, *J* = 17.6, 1H), 5.27 (d, *J* = 10.8, 1H), 3.90 (s, 3H), 2.19 (s, 6H), 2.11 (s, 3H), 1.81 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 165.5, 159.1, 150.7, 141.9, 139.1, 136.4, 136.1, 135.5, 132.5, 131.8, 131.3, 129.9, 128.6, 127.4, 126.8, 126.3, 126.1, 125.9, 124.9, 122.0, 114.1, 112.2, 55.3, 40.7, 37.3, 37.2, 29.2. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{36}H_{34}O_3$ $[M+H]^+$ 515.2581; found 515.2588.

General Procedure of the Catalytic Reactions



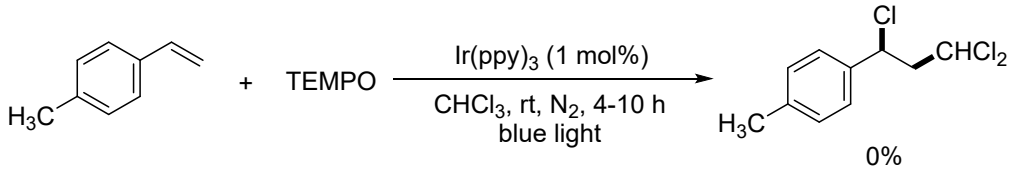
General procedure A: To a 10 mL of Schlenk tube was added *fac*-Tris(2-phenylpyridine)iridium [$Ir(ppy)_3$] (2.62 mg, 1 mol%), the tube was evacuated and backfilled with N_2 (3 times), then alkenes **1** (0.4 mmol, 1.0 equiv), $CHCl_3$ (1 mL) were added subsequently. The Schlenk tube was then sealed with a Teflon lined cap. After stirring in room temperature under blue LED for 4-10 h until completion as indicated by TLC or NMR analysis, the reaction mixture was diluted with EtOAc or CH_2Cl_2 and filtered through a pad of Celite. The filtrate was concentrated under vacuum and purified rapidly by flash column chromatography on silica gel to give the desired product.



General procedure B: To a 10 mL of Schlenk tube was added *fac*-tris(2-phenylpyridine)iridium [$Ir(ppy)_3$] (2.62 mg) under air atmosphere, the tube was evacuated and backfilled with N_2(3 times), then 4-methylphenylene (0.4 mmol, 1.0 equiv), $RCCl_3$ (5.0 equiv), ether (0.2 M) were added subsequently. The Schlenk tube was then sealed with a Teflon lined cap. After stirring in room temperature under blue LED for 4-10 h until completion as indicated by TLC or NMR analysis, the reaction mixture was diluted with EtOAc or CH_2Cl_2 and filtered through a pad of Celite. The filtrate was concentrated under vacuum and purified rapidly by flash column chromatography on silica gel to give the desired product.

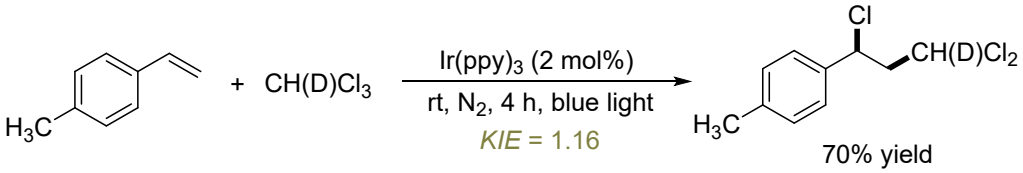
Mechanistic Studies

1. Radical trapping experiment



To a 10 mL of Schlenk tube was added *fac*-Tris(2-phenylpyridine)iridium [$Ir(ppy)_3$] (2.62 mg, 1 mol%), the tube was evacuated and backfilled with N_2 (3 times), TEMPO (3 equiv.), then 4-methylphenylene (0.4 mmol, 1.0 equiv), $CHCl_3$ (1 mL) were added subsequently. The Schlenk tube was then sealed with a Teflon lined cap. After stirring in room temperature under blue LED for 4 h, the reaction mixture was diluted with EtOAc or CH_2Cl_2 and filtered through a pad of Celite. The filtrate was concentrated under vacuum. No product can be detected by ^{1}HNMR.

2. Kinetic isotope effect



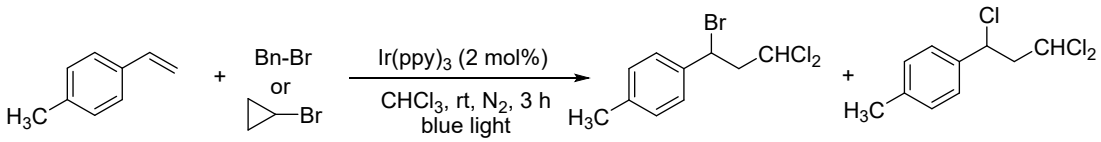
To a 10 mL of Schlenk tube was added *fac*-Tris(2-phenylpyridine)iridium [$Ir(ppy)_3$] (2.62 mg, 1 mol%), the tube was evacuated and backfilled with N_2 (3 times), then 4-methylphenylene (0.4 mmol, 1.0 equiv), $CHCl_3$ (0.5 mL), $CDCl_3$ (0.5 mL) were added subsequently. The Schlenk tube was then sealed with a Teflon lined cap. After stirring in room temperature under blue LED for 4 h, the reaction mixture was diluted with EtOAc or CH_2Cl_2 and filtered through a pad of Celite. The filtrate was concentrated under vacuum. The two products can be detected by ^{1}HNMR to determine the KIE value.

3. Light on-off experiment

To a 10 mL of Schlenk tube was added *fac*-Tris(2-phenylpyridine)iridium [$Ir(ppy)_3$] (2.62 mg, 1 mol%), the tube was evacuated and backfilled with N_2 (3 times), then 4-methoxyphenylene (0.4 mmol, 1.0 equiv), $CHCl_3$ (1.0 mL) were added subsequently. The Schlenk tube was then sealed with a Teflon lined cap. Seven reactions were setup

in parallel under blue LED. After 0.5 h, the light was turned off, one reaction was analyzed by ^{1}H NMR to determine the yield (CH_3NO_2 as internal standard), the remaining six were kept stirring for another 0.5 h without irradiation. The experiments were cycled as above.

4. Radical propagation experiment



To a 10 mL of Schlenk tube was added *fac*-Tris(2-phenylpyridine)iridium [$Ir(ppy)_3$] (2.62 mg, 2 mol%), the tube was evacuated and backfilled with N_2 (3 times), then 4-methylphenylene (0.2 mmol, 1.0 equiv), BnBr or C_3H_5Br (0.2 mmol, 1.0 equiv), $CHCl_3$ (1.0 mL) were added subsequently. The Schlenk tube was then sealed with a Teflon lined cap. After stirring in room temperature under blue LED for 3 h, the reaction mixture was diluted with EtOAc and filtered through a pad of Celite. The filtrate was concentrated under vacuum. The products were analyzed by ^{1}HNMR and GC-MS.

5. Quantum Yield Measurements

The photon flux of the spectrophotometer was determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate in 30 mL of 0.05 M H_2SO_4. A buffered solution of phenanthroline was prepared by dissolving 50 mg of phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H_2SO_4. Both solutions were stored in the dark. To determine the photon flux of the spectrophotometer, 3.0 mL of the ferrioxalate solution was placed in a schlenk tube with 10 cm away from light source and irradiated for 30 seconds at blue light (λ = 450 nm). After irradiation, 0.525 mL of the phenanthroline solution was added to the tube. The solution was allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured.

$$\text{mol } Fe^{2+} = \frac{V \bullet \Delta A}{l \bullet \varepsilon} \quad (1)$$

$$\text{photon flux} = \frac{\text{mol } Fe^{2+}}{\Phi \bullet t \bullet f} \quad (2)$$

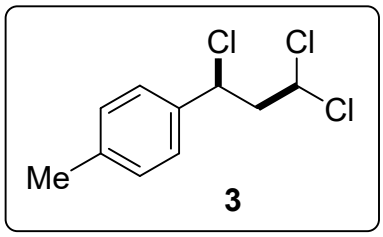
$$f = 1 - 10^{-A} \quad (3)$$

Where V is the total volume (0.003525 L) after complexation with phenanthroline, ΔA (0.059484) is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.0 cm), ε is the molar absorptivity at 510 nm (11,100 L mol^{-1} cm^{-1}), the quantum yield (Φ) for Fe^{2+} at 450 nm is about 0.95, t is the time (30.0 s), and f (0.998) is the fraction of light absorbed at λ = 450 nm.

The photon flux was determined to be $6.64 \bullet 10^{-10}$ einstein s^{-1} .

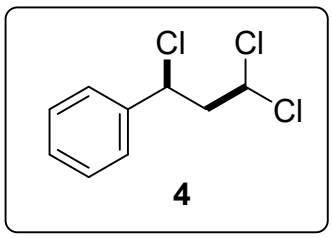
Model reaction was setup following general procedure. The tube was placed 10 cm away from the light source and was irradiated for 20 min under 450 nm without stirring. Then, the solution was passed through a silica plug. The yield of product formed ($8.38 \bullet 10^{-6}$ mol) was determined by ^1H NMR based on a CH_3NO_2 internal standard. The quantum yield (Φ = 10.5) was determined using the eq 2.

Characterization of Products



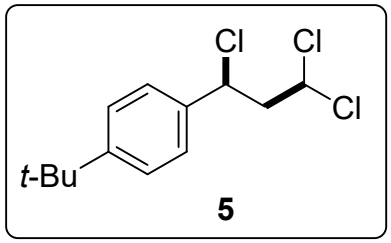
3

New compound **3**: Prepared according to the general procedure A and obtained as colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.28 (d, *J* = 8.2, 2H), 7.19 (d, *J* = 8.0, 2H), 5.78 (dd, *J* = 8.2, 5.1, 1H), 5.05 (dd, *J* = 9.4, 5.1, 1H), 2.97 (ddd, *J* = 14.5, 9.4, 5.1, 1H), 2.77 (ddd, *J* = 14.6, 8.2, 5.1, 1H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 139.2, 136.6, 129.8, 127.0, 70.5, 59.5, 52.8, 21.3. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2924, 1513, 1424, 1241, 1022, 934, 847, 817, 787, 727, 637, 519. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{10}H_{11}Cl_3$ $[M+K]^+$ 274.9558; found 274.9556.



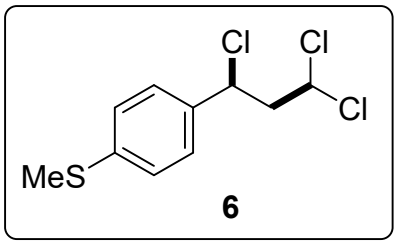
4

Known compound **4**: Prepared according to the general procedure A and obtained as colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). The data was coincident with the report in the literature[3]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.42-7.34 (m, 5H), 5.81 (dd, *J* = 8.4, 4.9, 1H), 5.08 (dd, *J* = 9.5, 5.0, 1H), 2.98 (ddd, *J* = 14.5, 9.5, 4.9, 1H), 2.79 (ddd, *J* = 14.7, 8.3, 5.0, 1H). **^{13}C NMR** (101 MHz, CDCl3) δ 139.5, 129.2, 127.1, 70.5, 59.5, 52.85. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2924, 1452, 1243, 1020, 932, 754, 694, 646, 528. **HRMS (LCMS-ESI)** m/z: calcd. for $C_9H_9C_{l3}$ $[M+Na]^+$ 244.9662; found 244.9663.



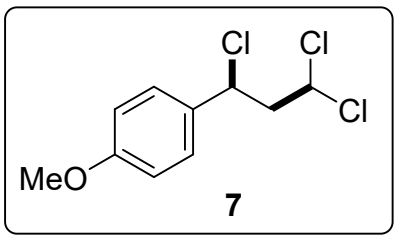
5

New compound **5**: Prepared according to the general procedure A and obtained as colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.40 (d, *J* = 8.5, 2H), 7.32 (d, *J* = 8.4, 2H), 5.80 (dd, *J* = 8.3, 5.0, 1H), 5.07 (dd, *J* = 9.4, 5.1, 1H), 2.98 (ddd, *J* = 14.5, 9.4, 5.0, 1H), 2.79 (ddd, *J* = 14.7, 8.3, 5.1, 1H), 1.32 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 152.4, 136.5, 126.8, 126.1, 70.6, 59.4, 52.8, 34.8, 31.4. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2960, 1241, 1020, 934, 833, 755, 684, 635, 568. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{13}H_{17}Cl_3$ $[M+H]^+$ 279.0469; found 269.0483.



6

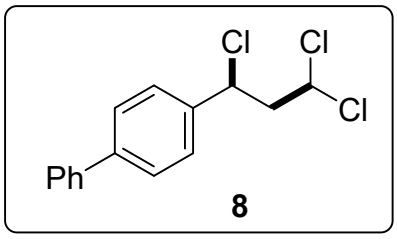
New compound **6**: Prepared according to the general procedure A and obtained as colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.30-7.24 (m, 4H), 5.91-5.87 (m, 1H), 4.93-4.89 (m, 1H), 2.67-2.62 (m, 1H), 2.49 (s, 3H), 2.46-2.41 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 139.6, 138.8, 126.9, 126.4, 71.1, 70.8, 52.4, 15.9. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2919, 1490, 1415, 1249, 1054, 1003, 817, 751, 543. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{10}H_{11}SCl_3$ $[M+H]^+$ 268.9720; found 268.9723.



7

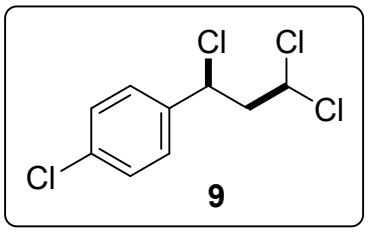
New compound **7**: Prepared according to the general procedure A and obtained as colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.32 (d, *J* = 8.6, 2H), 6.90 (d, *J* = 8.7, 2H), 5.78 (dd, *J* = 8.1, 5.1, 1H), 5.06 (dd, *J* = 9.3, 5.2, 1H), 3.81 (s, 3H), 2.98 (ddd, *J* = 14.5, 9.3, 5.1, 1H), 2.77 (ddd, *J* = 14.6, 8.1, 5.2, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 160.1, 131.5, 128.4, 114.4, 70.5, 59.4, 55.5, 52.7. **FT-IR** (thin film) ν_{max} (cm^{-1})

2927, 2103, 1603, 1510, 1246, 1174, 1029, 827, 730, 540. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{10}H_{11}OCl_3$ $[M+Na]^+$ 274.9768; found 274.9774.



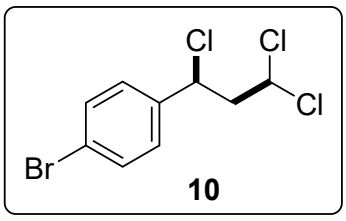
8

New compound **8**: Prepared according to the general procedure A and obtained as colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.62-7.57 (m, 4H), 7.48-7.43 (m, 4H), 7.39-7.35 (m, 1H), 5.84 (dd, *J* = 8.3, 5.0, 1H), 5.13 (dd, *J* = 9.5, 5.0, 1H), 3.02 (ddd, *J* = 14.6, 9.5, 5.0, 1H), 2.83 (ddd, *J* = 14.6, 8.3, 5.0, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 142.2, 140.3, 138.4, 129.0, 127.9, 127.6, 127.3, 70.5, 59.3, 52.8. **FT-IR** (thin film) ν_{max} (cm^{-1}) 3031, 2923, 1485, 1242, 1012, 933, 841, 762, 724, 690, 642, 562, 561. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{15}H_{13}Cl_3$ $[M+Li]^+$ 305.0237; found 305.0259.



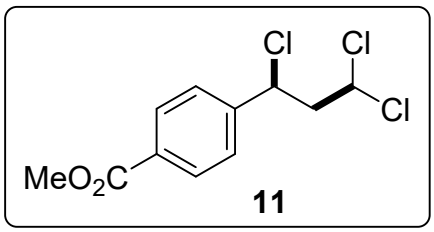
9

Known compound **9**: Prepared according to the general procedure A and obtained as a pale yellow oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). The data was coincident with the report in the literature[4]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.38-7.33 (m, 4H), 5.80 (dd, *J* = 8.4, 4.8, 1H), 5.05 (dd, *J* = 9.6, 4.9, 1H), 2.94 (ddd, *J* = 14.5, 9.6, 4.8, 1H), 2.75 (ddd, *J* =14.7, 8.4, 4.9, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 138.1, 135.1, 129.4, 128.5, 70.2, 58.7, 52.7. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2922, 1489, 1240, 1091, 1016, 935, 820, 759, 679, 531. **HRMS (LCMS-ESI)** m/z: calcd. for $C_9H_8Cl_4$ $[M-Cl]^+$ 220.9692; found 220.9681.



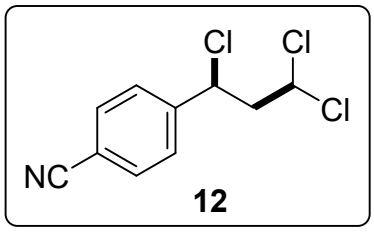
10

New compound **10**: Prepared according to the general procedure A and obtained as a pale yellow oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.52 (d, *J* = 8.5, 2H), 7.28 (d, *J* = 8.5, 2H), 5.80 (dd, *J* = 8.4, 4.8, 1H), 5.04 (dd, *J* = 9.6, 4.9, 1H), 2.93 (ddd, *J* = 14.5, 9.6, 4.9, 1H), 2.75 (ddd, *J* = 14.7, 8.4, 4.9, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 138.6, 132.3, 128.8, 123.2, 70.2, 58.7, 52.7. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2921, 1485, 1241, 1072, 1012, 936, 816, 755, 717, 663, 529. **HRMS (LCMS-ESI)** m/z: calcd. for $C_9H_8BrCl_3$ $[M+Na]^+$ 322.8767; found 322.8748.



11

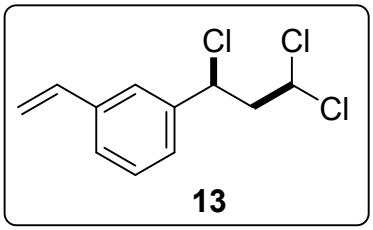
New compound **11**: Prepared according to the general procedure A and obtained as a colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.06 (d, *J* = 8.5, 2H), 7.49 (d, *J* = 8.3, 2H), 5.83 (dd, *J* = 8.6, 4.7, 1H), 5.12 (dd, *J* = 9.7, 4.7, 1H), 3.93 (s, 3H), 2.96 (ddd, *J* = 14.5, 9.7, 4.7, 1H), 2.77 (ddd, *J* = 14.7, 8.6, 4.7, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 166.5, 144.2, 130.9, 130.4, 127.2, 70.2, 58.7, 52.6, 52.5. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2953, 1721, 1429, 1277, 1186, 1108, 1018, 856, 761, 707, 666. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{11}H_{11}O_2Cl_3$ $[M+NH_4]^+$ 298.0163; found 298.0166.



12

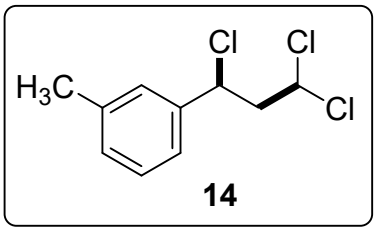
New compound **12**: Prepared according to the general procedure A and obtained as a colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.71 (d, *J* = 8.3, 2H), 7.54 (d, *J* = 8.4, 2H), 5.85 (dd, *J* = 8.8, 4.4, 1H), 5.11 (dd, *J* = 9.9, 4.5, 1H), 2.93 (ddd, *J* = 14.5, 9.9, 4.4, 1H), 2.75 (ddd, *J* = 14.7, 8.8, 4.5, 1H). **^{13}C NMR** (101 MHz, CDCl3) δ = 144.5, 133.0, 128.0, 118.2, 113.1, 69.9, 58.3, 52.3. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2922, 2230, 1414,

1242, 1018, 936, 839, 774, 705, 638, 560. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{10}H_8NCl_3$ $[M+Na]^+$ 269.9615; found 269.9617.



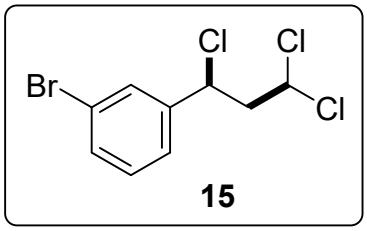
13

New compound **13**: Prepared according to the general procedure A and obtained as a colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.43-7.38 (m, 2H), 7.37-7.33 (m, 3H), 7.30-7.26 (m, 1H), 6.72 (dd, *J* = 17.6, 10.9, 1H), 5.84-5.77 (m, 2H), 5.34-5.30 (m, 1H), 5.07 (dd, *J* = 9.5, 4.9, 1H), 2.98 (ddd, *J* = 14.5, 9.6, 4.9, 1H), 2.79 (ddd, *J* = 14.7, 8.4, 4.9, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 139.8, 138.5, 136.2, 129.4, 126.9, 126.4, 125.0, 115.2, 70.4, 59.5, 52.8. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2921, 2857, 1454, 1241, 984, 909, 790, 700. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{11}H_{11}Cl_3$ $[M-Cl]^+$ 213.0238; found 213.0239.



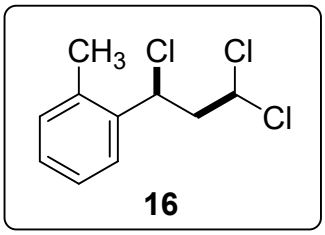
14

New compound **14**: Prepared according to the general procedure A and obtained as a colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.29-7.15 (m, 4H), 5.81 (dd, *J* = 8.3, 4.9, 1H), 5.04 (dd, *J* = 9.5, 5.0, 1H), 3.01-2.93 (m, 1H), 2.81-2.74 (m, 1H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, CDCl3) δ = 139.4, 139.0, 130.0, 129.0, 127.8, 124.2, 70.5, 59.6, 52.8, 21.5. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2919, 2857, 1457, 1083, 1025, 785, 729, 702. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{10}H_{11}Cl_3$ $[M+NH_4]^+$ 254.0265; found 254.0264.



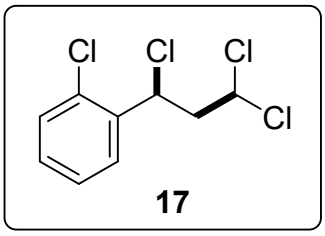
15

New compound **15**: Prepared according to the general procedure A and obtained as a pale yellow oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.57-7.25 (m, 5H), 5.83 (dd, *J* = 8.6, 4.7, 1H), 5.02 (dd, *J* = 9.7, 4.7, 1H), 2.97-2.89 (m, 1H), 2.79-2.72 (m, 1H). **^{13}C NMR** (101 MHz, CDCl3) δ = 141.7, 132.3, 130.7, 130.3, 125.8, 123.1, 70.2, 58.5, 52.7. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2921, 1574, 1469, 1425, 1242, 1073, 878, 772, 693. **HRMS (LCMS-ESI)** m/z: calcd. for $C_9H_8BrCl_3$ $[M+H]^+$ 300.8948; found 300.8949.



16

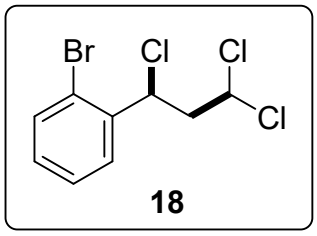
New compound **16**: Prepared according to the general procedure A and obtained as a colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.47-7.17 (m, 4H), 5.81 (dd, *J* = 8.4, 4.9, 1H), 5.08 (dd, *J* = 9.5, 5.0, 1H), 2.98 (ddd, *J* = 14.5, 9.5, 4.9, 1H), 2.79 (ddd, *J* = 14.7, 8.3, 5.0, 1H), 2.42 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.6, 135.5, 131.0, 128.9, 127.0, 126.6, 70.7, 55.8, 52.0, 19.2. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2926, 1457, 1237, 1023, 932, 752, 730, 689, 642. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{10}H_{11}Cl_3$ $[M-Cl]^+$ 201.0238; found 201.0252.



17

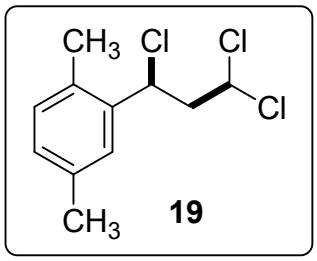
New compound **17**: Prepared according to the general procedure A and obtained as a pale yellow oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.61-7.27 (m, 6H), 5.97 (dd, *J* = 8.9,

4.3, 1H), 5.64 (dd, *J* = 9.7, 4.3, 1H), 2.90-2.77 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 137.1, 132.7, 130.1, 130.1, 128.6, 127.8, 77.5, 77.2, 76.8, 70.4, 55.8, 51.8. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2920, 1461, 1246, 1035, 755, 695. **HRMS (LCMS-ESI)** m/z: calcd. for $C_9H_8Cl_4$ $[M-Cl]^+$ 220.9692; found 220.9693.



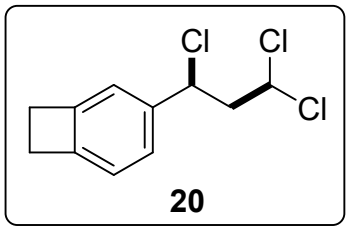
18

New compound **18**: Prepared according to the general procedure A and obtained as a colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.61-7.57 (m, 2H), 7.41-7.31 (m, 1H), 7.23-7.19 (m, 1H), 6.00-5.97 (m, 1H), 5.64-5.59 (m, 1H), 2.82 (dd, *J* = 7.7, 5.9, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 138.7, 133.3, 130.4, 128.8, 128.4, 122.8, 70.3, 58.4, 51.9. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2919, 1458, 1244, 1021, 934, 852, 755, 718, 675, 594. **HRMS (LCMS-ESI)** m/z: calcd. for $C_9H_8BrCl_3$ $[M+H]^+$ 300.8948; found 300.8949.



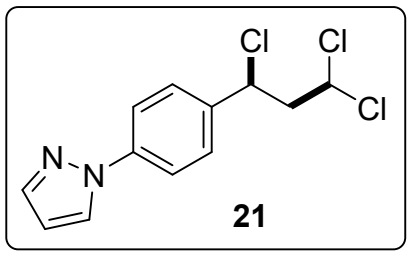
19

New compound **19**: Prepared according to the general procedure A and obtained as a colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.09-7.02 (m, 3H), 5.94-5.90 (m, 1H), 5.35-5.32 (m, 1H), 3.02-2.96 (m, 1H), 2.79-2.74 (m, 1H), 2.37 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 137.3, 136.6, 132.3, 130.9, 129.7, 127.2, 70.9, 56.0, 52.0, 21.2, 18.7. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2922, 1500, 1454, 1299, 1029, 930, 807, 741, 684, 650. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{11}H_{13}Cl_3$ $[M-Cl]^+$ 215.0394; found 215.0386.



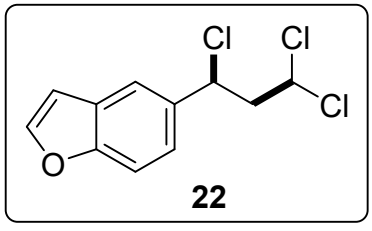
20

New compound **20**: Prepared according to the general procedure A and obtained as a colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.25-7.19 (m, 1H), 7.11 (s, 1H), 7.06-7.03 (m, 1H), 5.77 (dd, *J* = 8.1, 5.2, 1H), 5.04 (dd, *J* = 9.2, 5.3, 1H), 3.18 (s, 4H), 2.98 (ddd, *J* = 14.5, 9.2, 5.2, 1H), 2.78 (ddd, *J* = 14.6, 8.1, 5.3, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 147.1, 146.7, 138.1, 126.0, 123.1, 121.3, 70.6, 60.5, 53.1, 29.6, 29.5. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2926, 1426, 1239, 1074, 1020, 920, 891, 823, 745, 708, 648. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{11}H_{11}Cl_3$ $[M-Cl]^+$ 213.0238; found 213.0234.



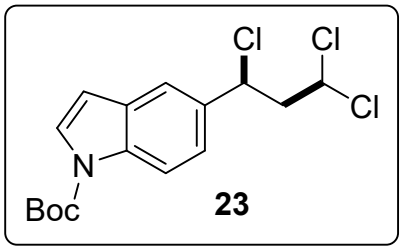
21

New compound **21**: Prepared according to the general procedure A and obtained as a colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.94 (d, *J* = 2.5, 1H), 7.74-7.71 (s, 3H), 7.51-7.47 (m, 2H), 6.48 (t, *J* = 2.2, 1H), 5.83 (dd, *J* = 8.4, 4.9, 1H), 5.12 (dd, *J* = 9.5, 5.0, 1H), 2.99 (ddd, *J* = 14.6, 9.6, 4.9, 1H), 2.84-2.76 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 141.6, 140.6, 137.5, 128.4, 126.9, 119.6, 108.2, 70.3, 58.9, 52.7. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2923, 1609, 1522, 1396, 1333, 1245, 1198, 1117, 1035, 932, 840, 746, 669, 545. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{12}H_{11}Cl_3N_2$ $[M+H]^+$ 289.0061; found 289.0049.



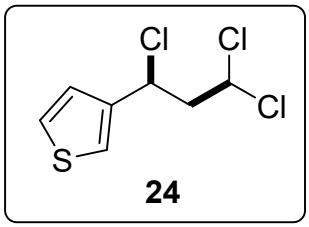
22

New compound **22**: Prepared according to the general procedure A and obtained as a colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.63 (dd, *J* = 17.0, 1.9, 2H), 7.50 (d, *J* = 8.5, 1H), 7.30 (dd, *J* = 8.5, 1.8, 1H), 6.77 (dd, *J* = 2.1, 0.8, 1H), 5.90 (dd, *J* = 8.9, 4.4, 1H), 5.05 (dd, *J* = 9.3, 4.0, 1H), 2.72 (ddd, *J* = 13.9, 9.3, 4.4, 1H), 2.50 (ddd, *J* = 14.4, 8.9, 4.0, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 154.9, 146.0, 137.6, 127.9, 122.3, 118.7, 111.8, 106.7, 71.7, 71.0, 52.8. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2922, 1458, 1258, 1119, 1037, 883, 813, 734, 661, 567. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{11}H_9Cl_3O$ $[M+Na]^+$ 284.9611; found 284.9611.



23

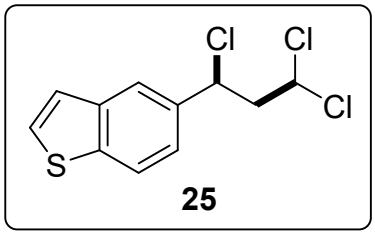
New compound **23**: Prepared according to the general procedure A and obtained as a colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.13 (d, *J* = 8.4, 1H), 7.59 (dd, *J* = 19.5, 2.6, 2H), 7.30 (dd, *J* = 8.6, 1.7, 1H), 6.56 (d, *J* = 3.7, 1H), 5.89 (dd, *J* = 8.8, 4.5, 1H), 5.04 (dd, *J* = 9.2, 4.0, 1H), 2.73 (ddd, *J* = 14.1, 9.3, 4.5, 1H), 2.51 (ddd, *J* = 14.4, 8.8, 4.1, 1H), 1.67 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 149.8, 137.3, 135.2, 130.9, 126.9, 122.1, 118.3, 115.6, 107.3, 84.1, 71.7, 71.0, 52.8, 28.3. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2972, 2924, 1728, 1465, 1359, 1255, 1158, 1077, 1027, 823, 731. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{16}H_{18}Cl_3NO_2$ $[M+Li]^+$ 368.0558; found 368.0575.



24

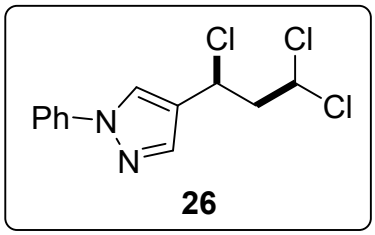
New compound **24**: Prepared according to the general procedure A and obtained as a colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.37 (dd, *J* = 5.1, 3.0, 1H), 7.33-7.30 (m,

1H), 7.14 (dd, *J* = 5.0, 1.3, 1H), 5.84 (dd, *J* = 8.4, 4.9, 1H), 5.21 (dd, *J* = 9.5, 4.9, 1H), 2.97 (ddd, *J* = 14.4, 9.5, 4.9, 1H), 2.84 (ddd, *J* = 14.7, 8.4, 4.9, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 140.4, 127.5, 126.1, 123.3, 70.3, 54.6, 52.3. **FT-IR** (thin film) ν_{max} (cm^{-1}) 3106, 1418, 1236, 1155, 1079, 1021, 931, 835, 777, 677, 653. **HRMS (LCMS-ESI)** m/z: calcd. for $C_7H_7Cl_3S$ $[M+H]^+$ 228.9407; found 228.9420.



25

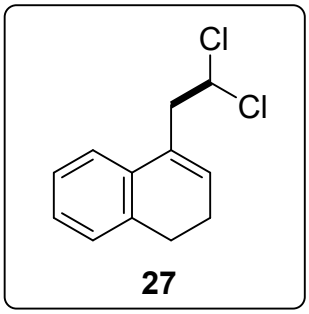
New compound **25**: Prepared according to the general procedure A and obtained as a colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.90 (d, *J* = 8.4, 1H), 7.84 (d, *J* = 1.7, 1H), 7.51 (d, *J* = 5.5, 1H), 7.39 (dd, *J* = 8.4, 1.8, 1H), 7.35 (d, *J* = 5.5, 1H), 5.80 (dd, *J* = 8.1, 5.2, 1H), 5.21 (dd, *J* = 9.3, 5.3, 1H), 3.06 (ddd, *J* = 14.6, 9.3, 5.2, 1H), 2.86 (ddd, *J* = 14.6, 8.1, 5.3, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 140.4, 139.9, 135.7, 128.0, 123.9, 123.4, 123.1, 122.3, 70.5, 59.8, 53.0. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2925, 1426, 1328, 1241, 1089, 1052, 1021, 904, 794, 723, 702, 488. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{11}H_9Cl_3S$ $[M+Na]^+$ 300.9383; found 300.9360.



26

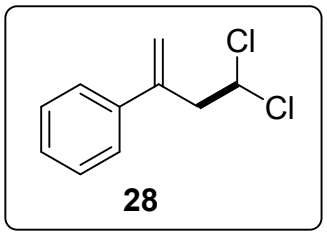
New compound **26**: Prepared according to the general procedure A and obtained as a colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.93 (s, 1H), 7.72 (s, 1H), 7.69-7.64 (m, 2H), 7.50-7.43 (m, 2H), 7.34-7.29 (m, 1H), 5.96 (dd, *J* = 9.1, 4.2, 1H), 5.07 (dd, *J* = 9.5, 3.8, 1H), 2.76 (ddd, *J* = 14.0, 9.6, 4.2, 1H), 2.57 (ddd, *J* = 14.3, 9.1, 3.9, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 139.8, 139.3, 129.7, 127.2, 125.5, 123.4, 119.4, 70.3, 52.3, 51.1. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2922, 2852, 1599, 1564, 1501, 1406, 1240,

1020, 954, 805, 756, 721, 684. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{12}H_{11}Cl_3N_2$ $[M+H]^+$ 289.0061; found 289.0045.



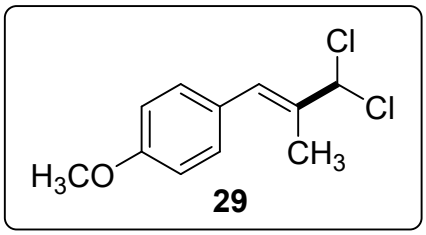
27

Known compound **27**: Prepared according to the general procedure A and obtained as a colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). The data was coincident with the report in the literature[5]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.20-7.12 (m, 4H), 6.06 (t, *J* = 4.6, 1H), 5.84 (t, *J* = 6.6, 1H), 3.34 (dd, *J* = 6.6, 1.0, 2H), 2.78-2.74 (m, 2H), 2.32-2.27 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 137.0, 133.4, 131.2, 130.8, 128.2, 127.4, 126.7, 122.0, 71.8, 47.6, 28.1, 23.2. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2924, 1440, 950, 781, 745, 663. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{12}H_{12}Cl_2$ $[M+NH_4]^+$ 244.0654; found 244.0653.



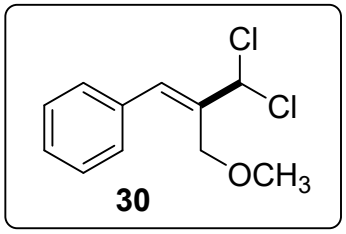
28

Known compound **28**: Prepared according to the general procedure A and obtained as a colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). The data was coincident with the report in the literature[6]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.38-7.35 (m, 4H), 7.35-7.30 (m, 1H), 5.65 (t, *J* = 6.7, 1H), 5.44 (d, *J* = 0.9, 1H), 5.26 (q, *J* = 1.1, 1H), 3.40 (dd, *J* = 6.7, 1.0, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 142.8, 139.2, 128.9, 128.3, 126.4, 117.8, 71.3, 50.0. **FT-IR** (thin film) ν_{max} (cm^{-1}) 3085, 2925, 1494, 1442, 1267, 1218, 1031, 942, 907, 783, 701, 666. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{10}H_{10}Cl_2$ $[M+Li]^+$ 207.0314; found 207.0310.



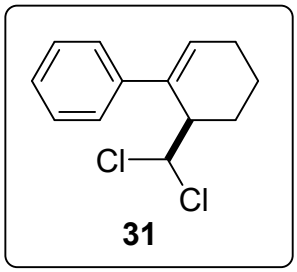
29

New compound **29**: Prepared according to the general procedure A and obtained as a colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.26-7.22 (m, 2H), 6.90-6.85 (m, 2H), 6.37 (dd, *J* = 11.5, 1.8, 1H), 5.70 (dq, *J* = 11.6, 7.2, 1H), 3.80 (s, 3H), 1.89 (dd, *J* = 7.2, 1.8, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.2, 130.4, 130.1, 129.4, 125.2, 113.6, 55.4, 14.7. **FT-IR** (thin film) ν_{max} (cm^{-1}) 3013, 2935, 2836, 1606, 1508, 1460, 1244, 1174, 1033, 837, 615, 527. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{11}H_{12}Cl_2O$ $[M+H]^+$ 231.0338; found 231.0329.



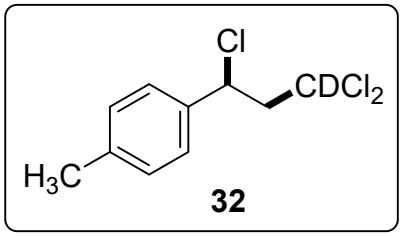
30

New compound **30**: Prepared according to the general procedure A and obtained as a colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.39-7.31 (m, 2H), 7.29-7.23 (m, 1H), 7.23-7.19 (m, 2H), 6.61 (d, *J* =11.9, 1H), 5.89-5.80 (m, 1H), 4.20 (dd, *J* = 6.3, 1.8, 2H), 3.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 136.8, 131.7, 129.1, 128.9, 128.4, 127.3, 69.4, 58.3. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2924, 2816, 1493, 1449, 1192, 1099, 959, 915, 771, 696. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{11}H_{12}Cl_2O$ $[M-Cl]^+$ 195.0577; found 195.0561.



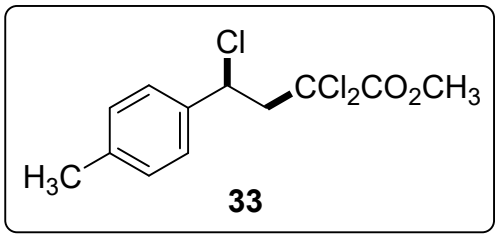
31

New compound **31**: Prepared according to the general procedure A and obtained as a colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.36-7.31 (m, 2H), 7.29-7.26 (m, 1H), 7.25-7.21 (m, 2H), 6.04 -5.98 (m, 1H), 5.81 (d, *J* = 2.8, 1H), 3.43-3.39 (m, 1H), 2.24-2.16 (m, 3H), 2.13-2.04 (m, 1H), 2.03-1.96 (m, 1H), 1.68-1.57 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 141.2, 137.2, 131.8, 128.7, 127.3, 126.8, 46.7, 25.9, 22.4, 20.7. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2929, 1491, 1445, 1274, 907, 786, 750, 696, 543. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{13}H_{14}Cl_2$ $[M+NH_4]^+$ 258.0811; found 258.0815.



32

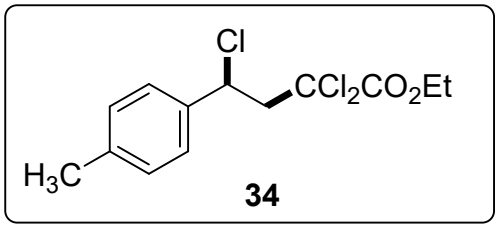
New compound **32**: Prepared according to the general procedure A and obtained as a colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.28 (d, *J* = 8.2, 2H), 7.19 (d, *J* = 7.9, 2H), 5.05 (dd, *J* = 9.4, 5.1, 1H), 2.97 (dd, *J* = 14.7, 9.4, 1H), 2.77 (dd, *J* = 14.7, 5.1, 1H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 139.2, 136.6, 129.8, 127.0, 70.6, 70.3, 70.0, 59.5, 52.7, 21.3. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2922, 1512, 1451, 1196, 1046, 984, 918, 814, 771, 714, 634, 529. **MS** (EI) *m/z*: 236.8 (M^+). **HRMS (LCMS-ESI)** m/z: calcd. for $C_{10}H_{10}DCl_3$ $[M+Na]^+$ 259.9881; found 259.9891.



33

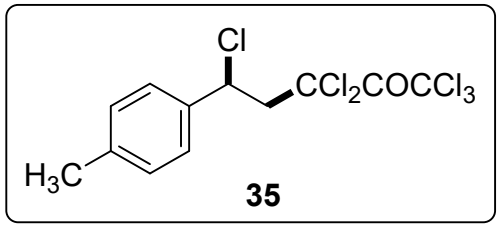
New compound **33**: Prepared according to the general procedure B and obtained as a colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.28 (d, *J* = 8.2, 2H), 7.17 (d, *J* = 7.9, 2H), 5.20 (dd, *J* = 7.5, 6.1, 1H), 3.68 (s, 3H), 3.44 (dd, *J* = 14.9, 7.6, 1H), 3.20 (dd, *J* = 14.9, 6.1, 1H), 2.35 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 165.7, 139.1, 136.7, 129.5, 127.5, 82.3, 58.6, 54.52, 54.17, 21.32. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2924,

1757, 1437, 1251, 1195, 1009, 818, 693, 522. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{12}H_{13}Cl_3O_2$ $[M\text{-}Cl]^+$ 259.0293; found 259.0265.



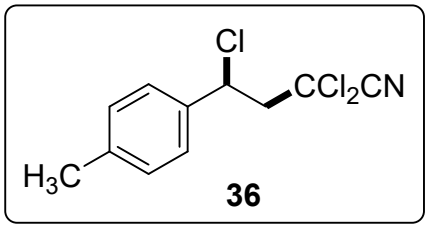
34

New compound **34**: Prepared according to the general procedure B and obtained as a colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.29 (d, *J* = 8.2, 2H), 7.16 (d, *J* = 8.0, 2H), 5.20 (dd, *J* = 7.5, 6.1, 1H), 4.18-4.03 (m, 2H), 3.44 (dd, *J* = 14.9, 7.6, 1H), 3.19 (dd, *J* = 14.9, 6.0, 1H), 2.34 (s, 3H), 1.29 (t, J=7.2, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 165.1, 139.0, 136.9, 129.5, 127.4, 82.5, 64.2, 58.7, 54.0, 21.3, 13.8. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2983, 2929, 1752, 1301, 1249, 1195, 1089, 1026, 860, 817, 693, 525. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{13}H_{15}Cl_3O_2$ $[M+Na]^+$ 331.0030; found 331.0030.



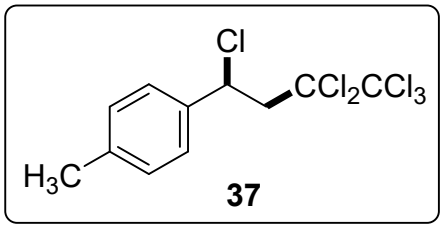
35

New compound **35**: Prepared according to the general procedure B and obtained as a colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.33-7.29 (m, 2H), 7.18 (d, *J* = 7.9, 2H), 5.23 (dd, *J* = 7.8, 5.0, 1H), 3.69 (dd, *J* = 15.3, 7.8, 1H), 3.28 (dd, *J* = 15.3, 5.0, 1H), 2.35 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 180.4, 139.1, 137.2, 129.7, 127.3, 92.0, 81.6, 58.1, 55.0, 21.4. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2925, 1751, 1189, 1129, 1023, 966, 815, 636. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{12}H_{10}Cl_6O$ $[M\text{-}Cl]^+$ 344.9174; found 344.9186.



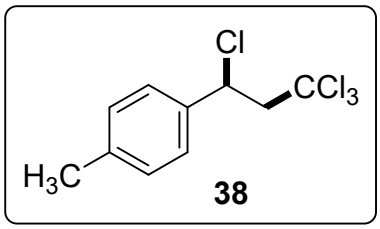
36

New compound **36**: Prepared according to the general procedure B and obtained as a yellow oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.35-7.29 (m, 2H), 7.24-7.19 (m, 2H), 5.19 (t, *J* = 6.7, 1H), 3.35 (dd, *J* = 15.1, 7.0, 1H), 3.20 (dd, *J* = 15.1, 6.5, 1H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 139.8, 135.8, 129.9, 127.3, 114.6, 66.2, 57.6, 56.0, 21.4. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2926, 1799, 1513, 1422, 1212, 992, 803, 732, 621, 525, 498. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{11}H_{10}Cl_3N$ $[M+H]^+$ 261.9952; found 261.9956.



37

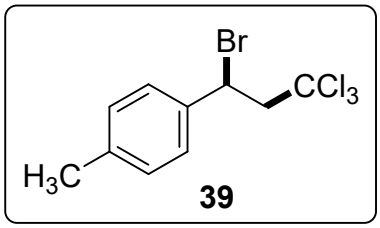
New compound **37**: Prepared according to the general procedure B and obtained as a colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.35 (d, *J* = 8.1, 2H), 7.18 (d, *J* = 8.0, 2H), 5.44-5.38 (m, 1H), 3.53-3.40 (m, 2H), 2.35 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 138.9, 138.2, 129.7, 127.4, 105.1, 96.9, 59.06, 50.80, 21.36. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2923, 1512, 1427, 1115, 987, 810, 772, 734, 681, 571, 524. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{11}H_{10}Cl_6$ $[M-Cl]^+$ 316.9225; found 316.9230.



38

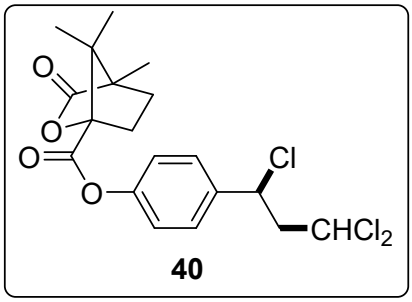
Known compound **38**: Prepared according to the general procedure B and obtained as a colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). The data was coincident with the report in the literature[7]. **^{1}H NMR**

(400 MHz, $CDCl_3$) δ = 7.31 (d, *J* = 8.1, 2H), 7.17 (d, *J* = 7.9, 2H), 5.27 (dd, *J* = 6.4, 5.5, 1H), 3.65-3.48 (m, 2H), 2.35 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 139.0, 137.6, 129.7, 127.4, 96.4, 62.8, 58.4, 21.3. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2923, 1611, 1513, 1421, 1201, 967, 802, 691, 575, 515. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{10}H_{10}Cl_4$ $[M-Cl]^+$ 234.9848; found 234.9862.



39

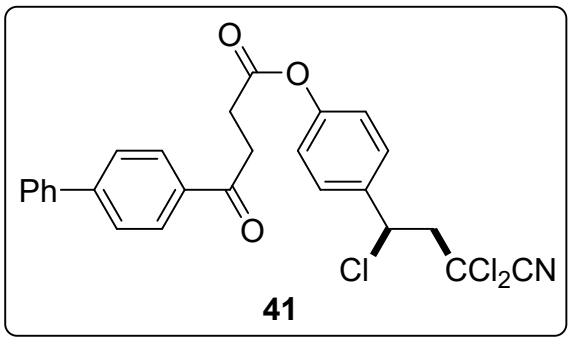
Known compound **39**: Prepared according to the general procedure B and obtained as a colorless oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). The data was coincident with the report in the literature[8]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.33 (d, *J* = 8.1, 2H), 7.16 (d, *J* = 7.9, 2H), 5.37 (t, *J* = 6.3, 1H), 3.74 (d, *J* = 6.3, 2H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 139.1, 138.0, 129.7, 127.8, 96.7, 62.7, 47.9, 21.4. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2919, 1319, 1210, 1167, 1060, 1020, 964, 825, 782, 726, 688, 551. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{10}H_{10}BrCl_3$ $[M+H]^+$ 314.9104; found 314.9109.



40

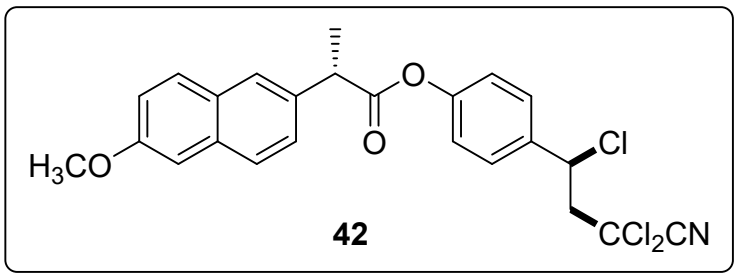
New compound **40**: Prepared according to the general procedure A and obtained as a pale yellow oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.46 (d, *J* = 8.6, 2H), 7.17 (d, *J* = 8.6, 2H), 5.82 (dd, *J* = 8.5, 4.8, 1H), 5.09 (dd, *J* = 9.6, 4.8, 1H), 2.96 (ddd, *J* = 14.5, 9.6, 4.8, 1H), 2.77 (ddd, *J* = 14.7, 8.5, 4.9, 1H), 2.60-2.54 (m, 1H), 2.23-2.18 (m, 1H), 2.03-1.98 (m, 1H), 1.77-1.80 (m, 1H), 1.17 (s, 3H), 1.15 (s, 3H), 1.10 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 177.8, 166.0, 150.2, 137.7, 128.5, 122.0, 90.8, 70.2,

58.6, 55.0, 54.9, 52.7, 30.9, 29.0, 17.0, 9.8. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2968, 1784, 1506, 1310, 1260, 1203, 1165, 1096, 1046, 923, 867, 796, 729, 652, 537. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{19}H_{21}O_4Cl_3$ $[M+Na]^+$ 441.0398; found 441.0381.



41

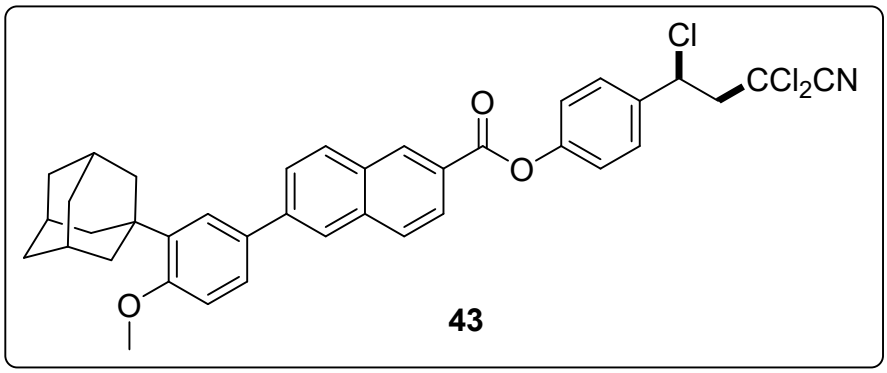
New compound **41**: Prepared according to the general procedure B and obtained as a pale yellow solid after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.11-8.06 (m, 2H), 7.74-7.69 (m, 2H), 7.66-7.61 (m, 2H), 7.51-7.40 (m, 5H), 7.21-7.17 (m, 2H), 5.22 (dd, *J* = 7.1, 6.2, 1H), 3.47 (t, *J* = 6.4, 2H), 3.35 (dd, *J* = 15.1, 7.3, 1H), 3.18 (dd, *J* = 15.1, 6.0, 1H), 3.04 (t, *J* = 6.4, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 197.5, 171.5, 151.6, 146.2, 139.9, 136.3, 135.2, 129.1, 128.8, 128.6, 128.4, 127.5, 127.4, 122.5, 114.6, 66.1, 56.9, 56.1, 33.6, 28.6. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{26}H_{20}NO_3Cl_3$ $[M+Na]^+$ 522.0401; found 522.0405.



42

New compound **42**: Prepared according to the general procedure B and obtained as a yellow oil after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.77-7.70 (m, 3H), 7.47 (dd, *J* = 8.5, 1.7, 1H), 7.39-7.33 (m, 2H), 7.19 -7.10 (m, 2H), 7.07-6.99 (m, 2H), 5.18-5.13 (m, 1H), 4.13-4.03 (m, 1H), 3.90 (s), 3.29 (dd, *J* = 15.1, 7.3), 3.11 (ddd, *J* = 15.1, 6.1, 1.4), 1.68 (d, *J* = 7.1). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 173.0, 157.9, 151.6, 136.2, 135.0, 134.0, 129.4, 129.1, 128.5, 127.6, 126.3, 126.1, 122.3, 119.3, 114.6, 105.7, 66.00, 56.82,

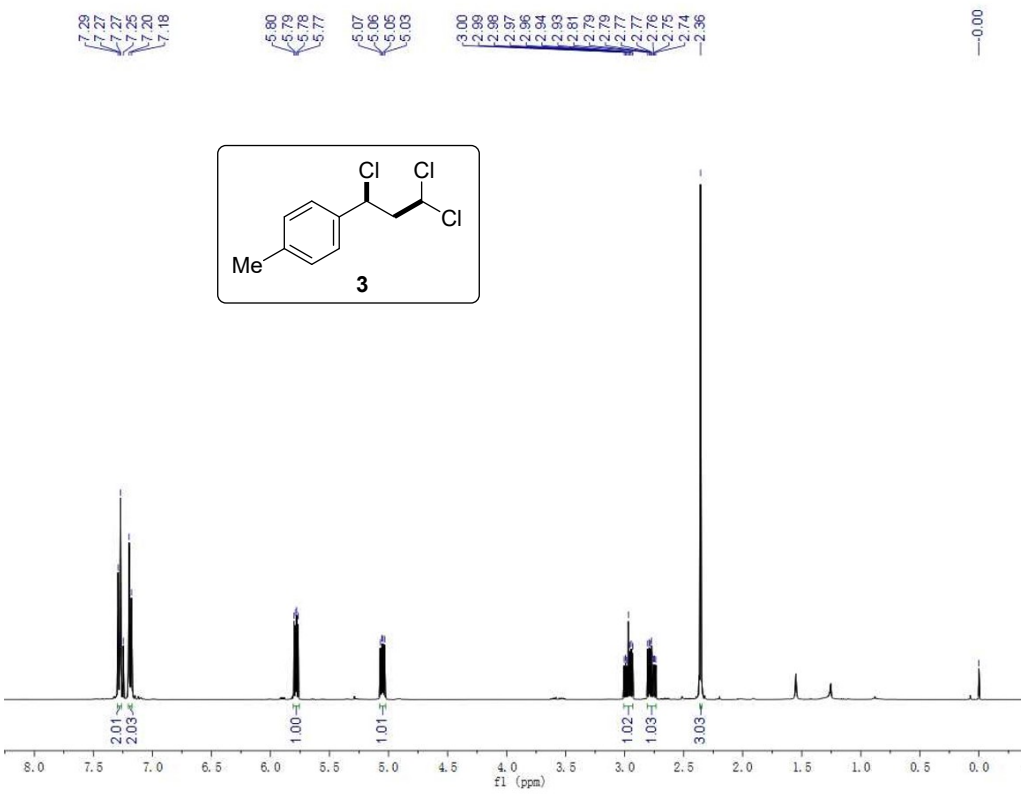
55.9, 55.4, 45.6, 18.6. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2927, 1755, 1676, 1602, 1501, 1205, 1161, 1126, 1071, 1029, 991, 845, 730, 688, 619, 535. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{24}H_{20}NO_3Cl_3$ $[M+H]^+$ 476.0582; found 476.0573.

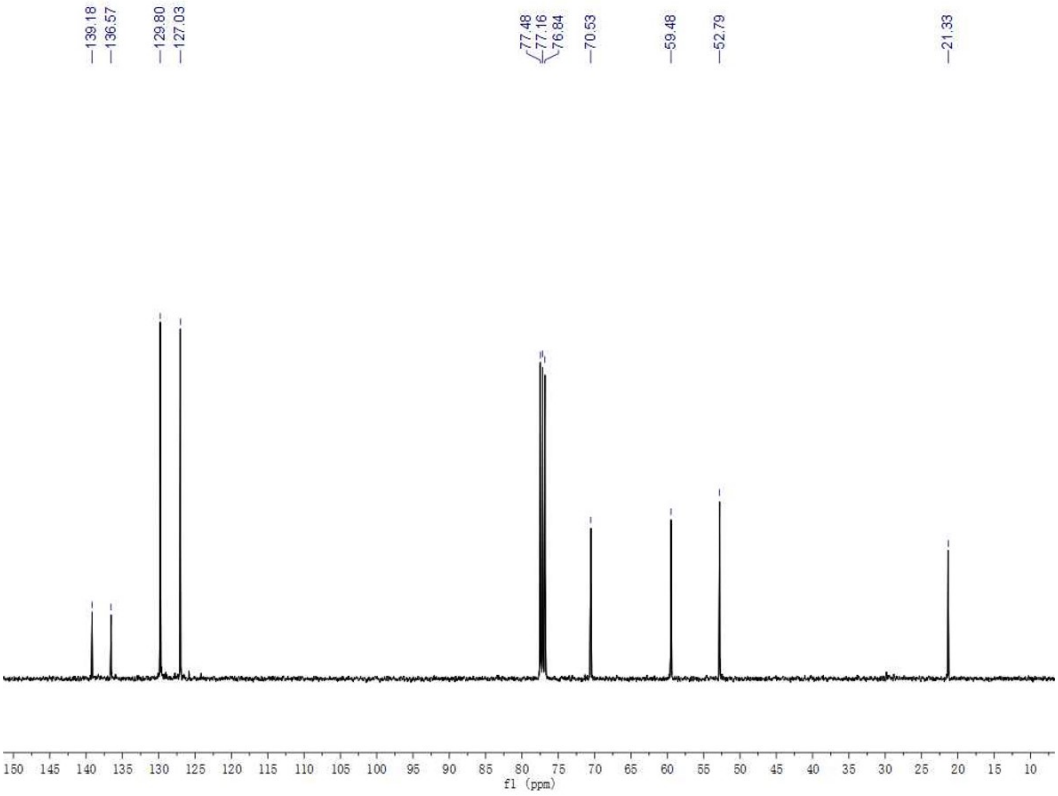


43

New compound **43**: Prepared according to the general procedure B and obtained as a white solid after purification by flash chromatography (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.78 (s, 1H), 8.20-8.17 (m, 1H), 8.07-7.95 (m, 3H), 7.84 (dd, *J* = 8.5, 1.8, 1H), 7.62 (d, *J* = 2.3, 1H), 7.58-7.53 (m, 3H), 7.36-7.33 (m, 2H), 7.01 (d, *J* = 8.5, 1H), 5.30-5.25 (m, 1H), 3.91 (s, 3H), 3.39 (dd, *J* = 15.1, 7.3, 1H), 3.24 (dd, *J* = 15.1, 6.1, 1H), 2.19 (d, *J* = 2.5, 6H), 2.11 (s, 3H), 1.81 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 165.3, 159.2, 152.0, 142.1, 139.2, 136.5, 136.4, 132.5, 132.0, 131.3, 130.0, 128.7, 128.7, 126.9, 126.2, 125.9, 125.9, 124.9, 122.8, 114.6, 112.3, 66.1, 60.6, 57.0, 56.1, 55.3, 40.8, 37.4, 37.3, 29.8, 29.2. **FT-IR** (thin film) ν_{max} (cm^{-1}) 2917, 1731, 1634, 1519, 1437, 1206, 1174, 1067, 809. **HRMS (LCMS-ESI)** m/z: calcd. for $C_{38}H_{34}NO_3Cl_3$ $[M+Na]^+$ 680.1497; found 680.1440.

NMR Spectra


7.29
7.27
7.27
7.25
7.20
7.18
5.80
5.79
5.78
5.77
5.07
5.06
5.05
5.03
3.00
2.99
2.98
2.97
2.96
2.94
2.93
2.81
2.79
2.79
2.77
2.77
2.76
2.75
2.74
2.36
0.00
Cl
Cl
Cl
Me
3
2.01
2.03
1.00
1.01
1.02
1.03
3.03
f1 (ppm)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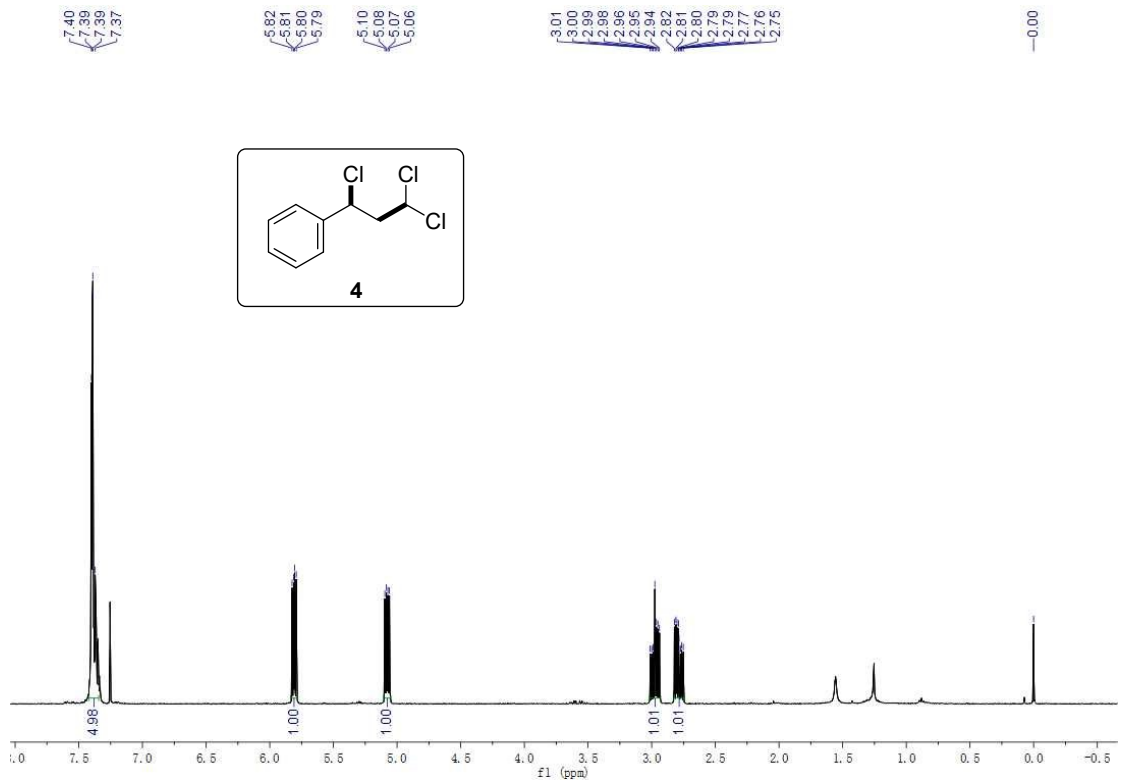
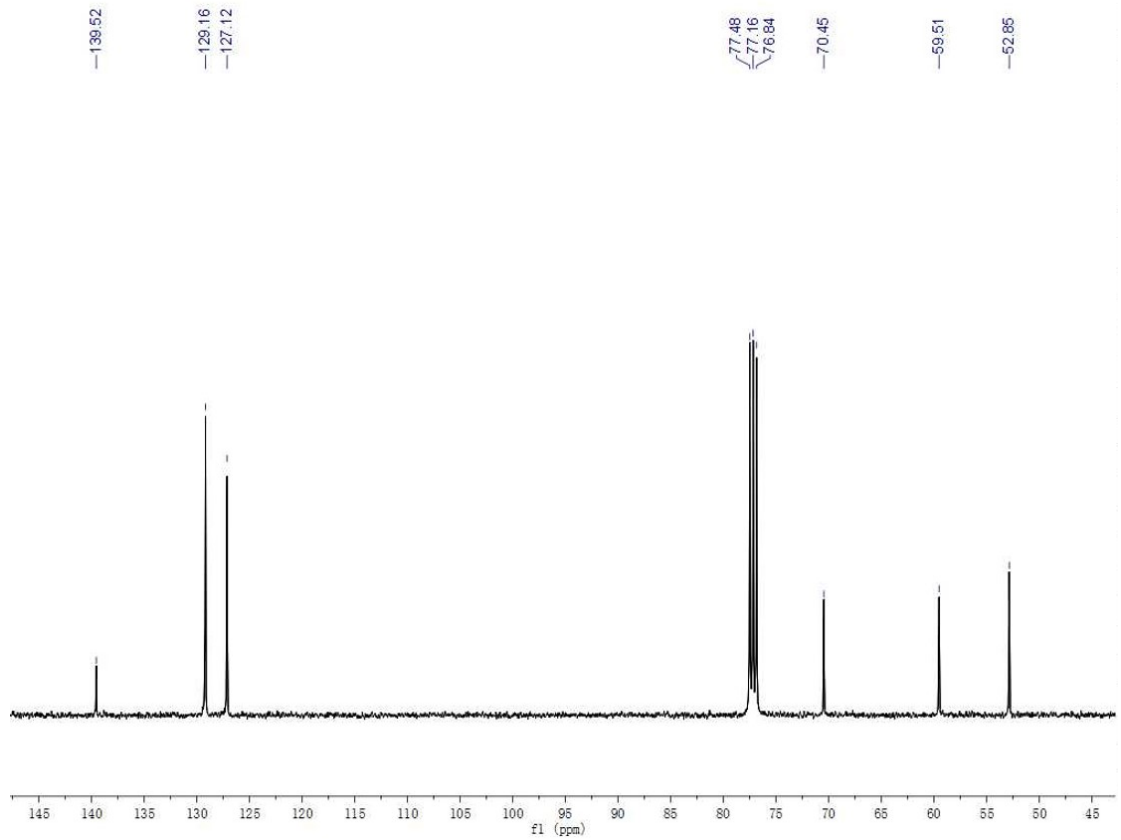
136.57
129.80
127.03
77.48
77.16
76.84
70.53
59.48
52.79
21.33
f1 (ppm)


7.40
7.39
7.39
7.37
5.82
5.81
5.80
5.79
5.10
5.08
5.07
5.06
3.01
3.00
2.99
2.98
2.96
2.95
2.94
2.82
2.81
2.80
2.79
2.79
2.77
2.76
2.75
0.00
Cl
Cl
Cl
4
4.98
1.00
1.00
1.01
1.01
f1 (ppm)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76.84
70.45
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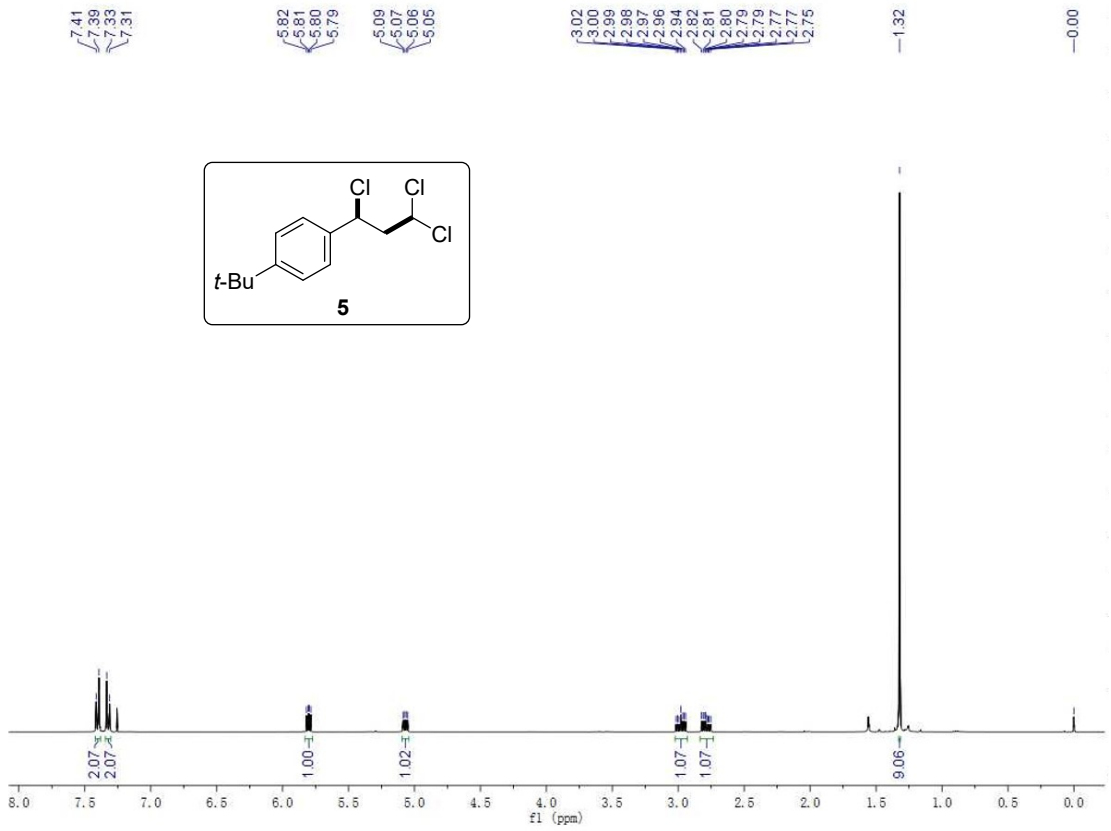
52.85
f1 (ppm)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7.39
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5.79
5.09
5.07
5.06
5.05
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3.00
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2.98
2.97
2.96
2.94
2.82
2.81
2.80
2.79
2.79
2.77
2.77
2.75
1.32
0.00
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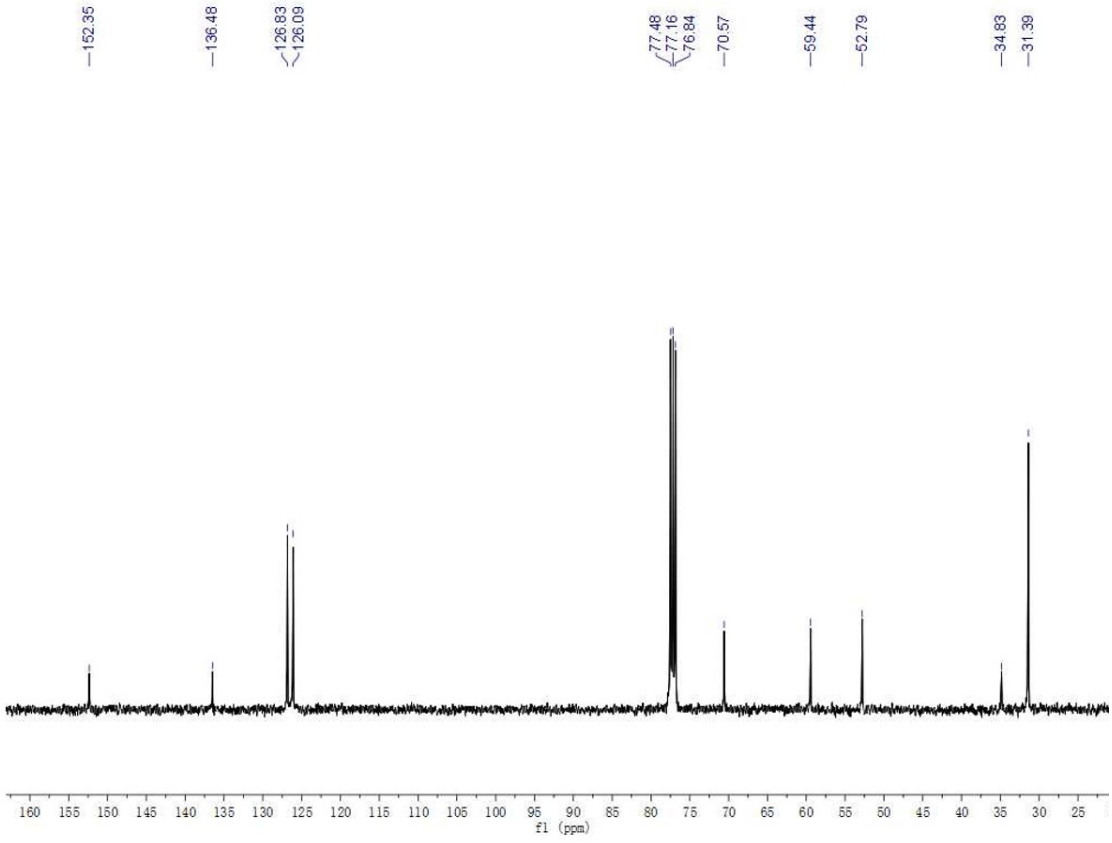
Cl
Cl
t-Bu
5
2.07
2.07
1.00
1.02
1.07
1.07
9.06
f1 (ppm)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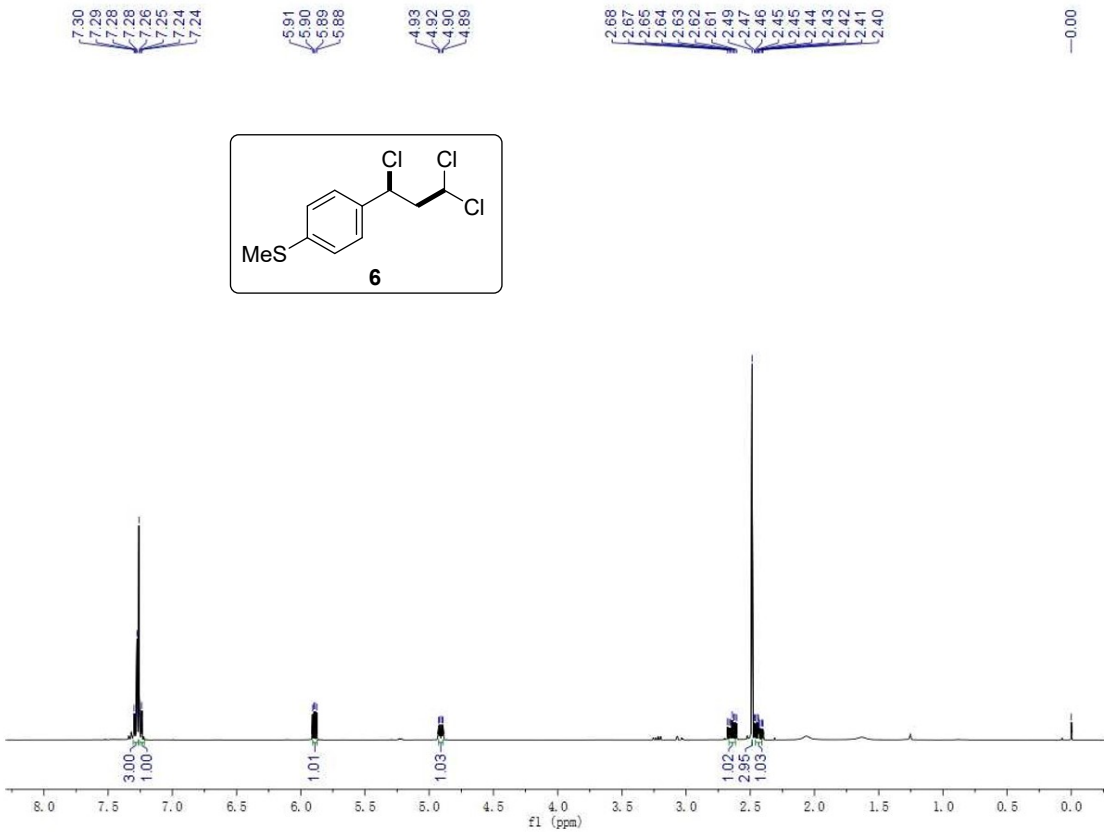
77.16
76.84
70.57
59.44
52.79
34.83
31.39
f1 (ppm)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7.28
7.28
7.26
7.25
7.24
7.24
5.91
5.90
5.89
5.88
4.93
4.92
4.90
4.89
2.68
2.67
2.65
2.64
2.63
2.62
2.61
2.49
2.47
2.46
2.45
2.45
2.44
2.43
2.42
2.41
2.40
0.00
Cl
Cl
Cl
MeS
6
3.00
1.00
1.01
1.03
1.02
2.95
1.03
f1 (ppm)
139.56
138.84
126.91
126.44
77.48
77.16
76.84
71.09
70.82
52.36
15.89
f1 (ppm)


7.33
7.31
7.25
6.91
6.89
5.79
5.78
5.77
5.76
5.08
5.06
5.05
5.04
3.81
3.01
3.00
2.99
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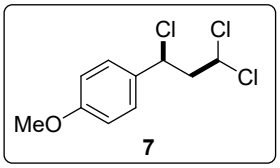
2.77
2.77
2.76
2.75
2.74
0.00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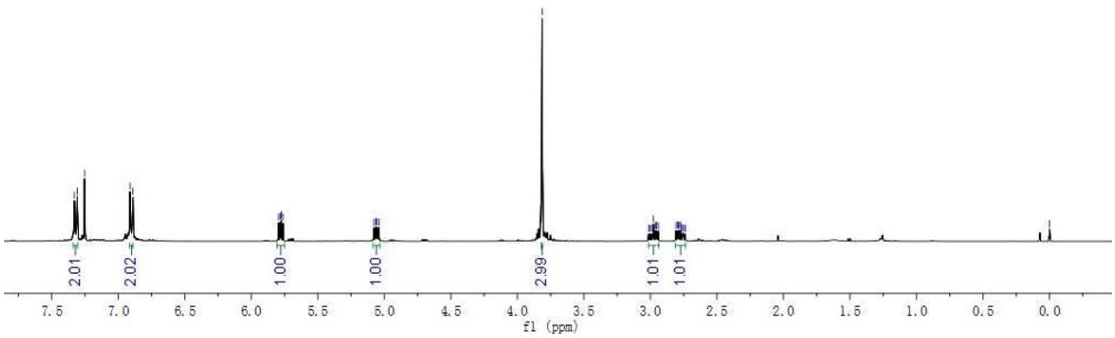
Cl
Cl
MeO

7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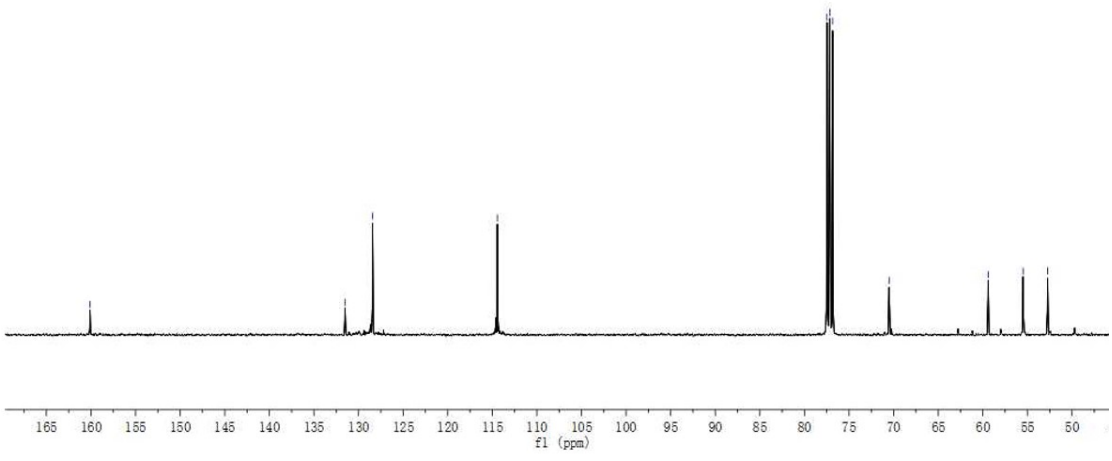
2.02
1.00
1.00
2.99
1.01
1.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


160.11
131.52
128.42
114.43
77.48
77.16
76.84
70.51
59.41
55.49
52.74


165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
f1 (ppm)


7.62
7.61
7.60
7.60
7.59
7.59
7.57
7.48
7.47
7.47
7.46
7.45
7.45
7.44
7.43
7.39
7.39
7.39
7.38
7.37
7.36
7.35
7.35
7.35
7.25
5.86
5.84
5.84
5.82
5.15
5.14
5.12
5.11
3.05
3.04
3.03
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2.85
2.84
2.83
2.81
2.81
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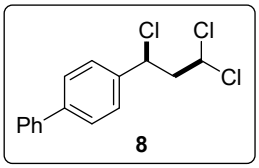
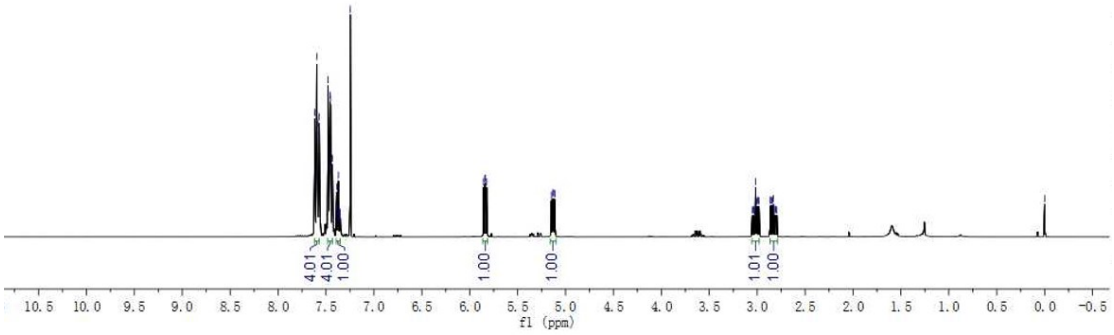
0.00


Cl
Cl
Cl
Ph

8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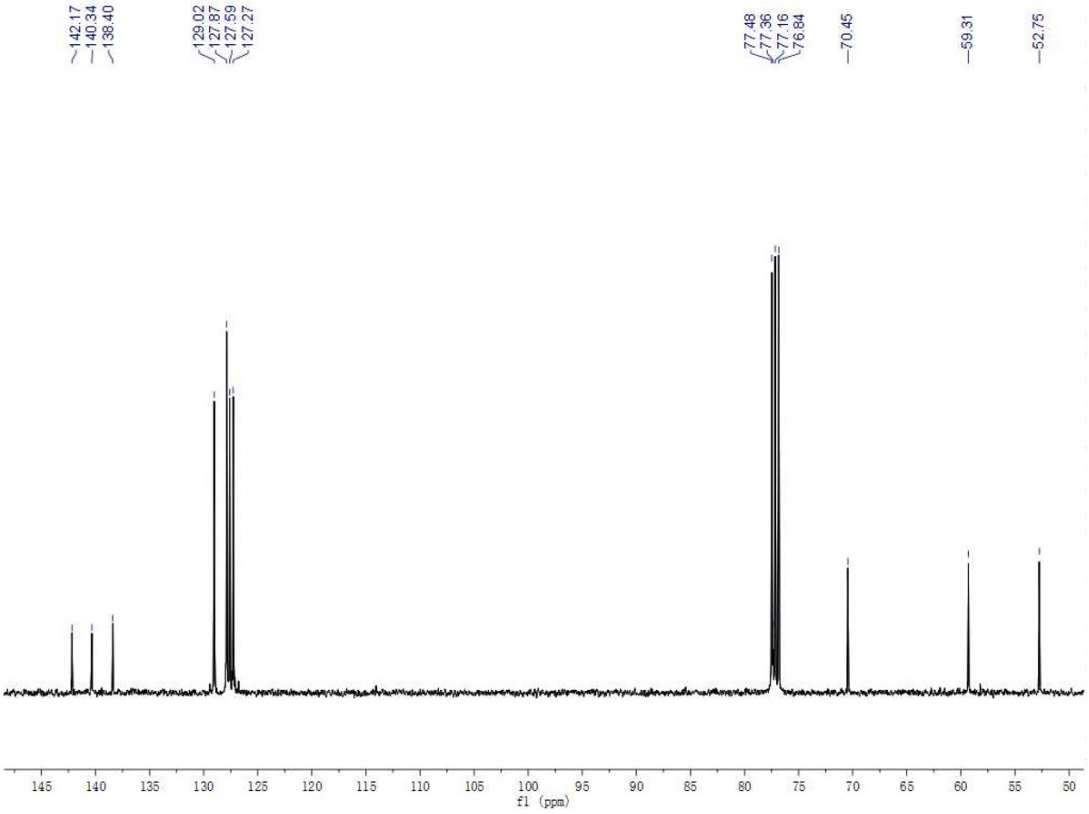
4.01
1.00
1.00
1.00
1.01
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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138.40
129.02
127.87
127.59
127.27
77.48
77.36
77.16
76.84
70.45
59.31
52.75
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50
f1 (ppm)


7.38
7.38
7.37
7.36
7.36
7.35
7.34
7.33
7.26
5.82
5.81
5.80
5.78
5.07
5.06
5.04
5.03
2.98
2.96
2.95
2.94
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2.92
2.90
2.78
2.77
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2.75
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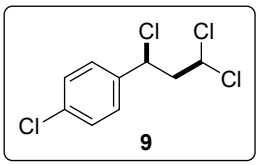
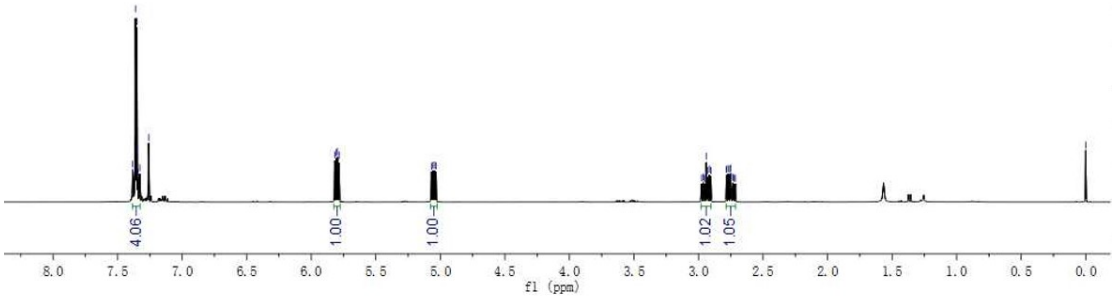

Cl
Cl
Cl
Cl

9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1.00
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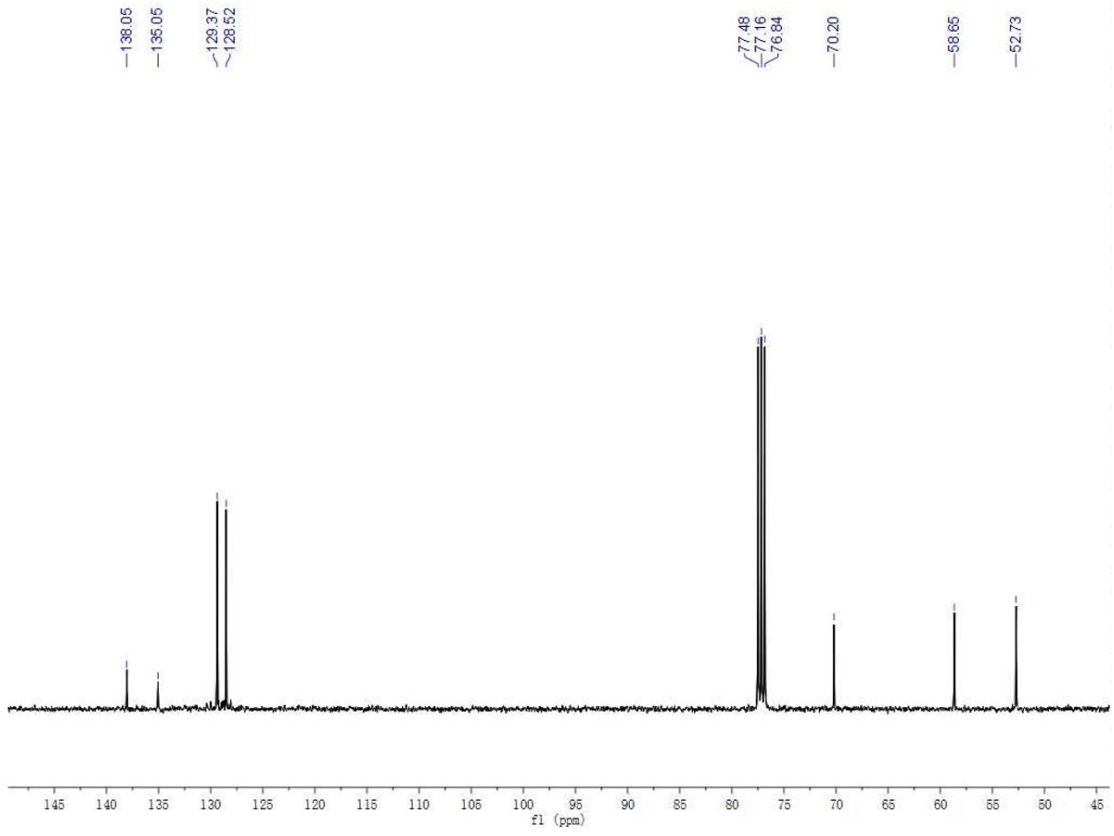
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


138.05
135.05
129.37
128.52
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77.16
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58.65
52.73
145
140
135
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110
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100
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90
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80
75
70
65
60
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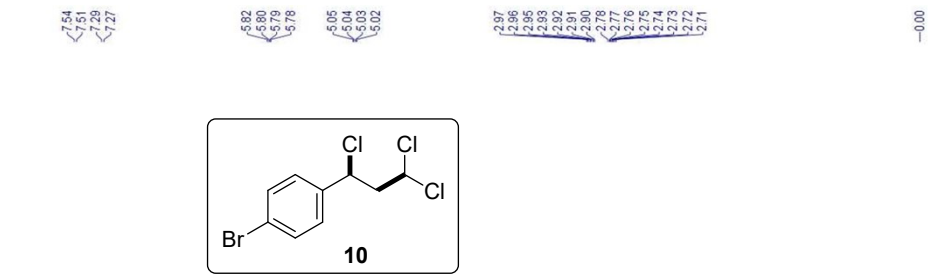
50
45
f1 (ppm)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5.02
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2.90
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2.75
2.74
2.73
2.72
2.71
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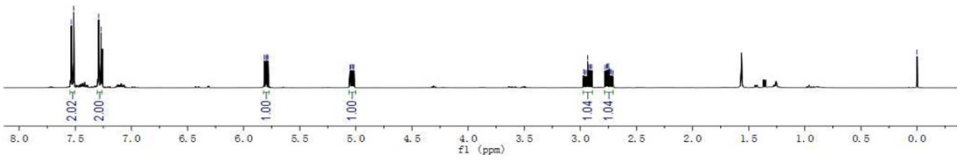
Cl
Cl
Cl
Br
10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1.04
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6.0
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5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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f1 (ppm)


138.56
132.34
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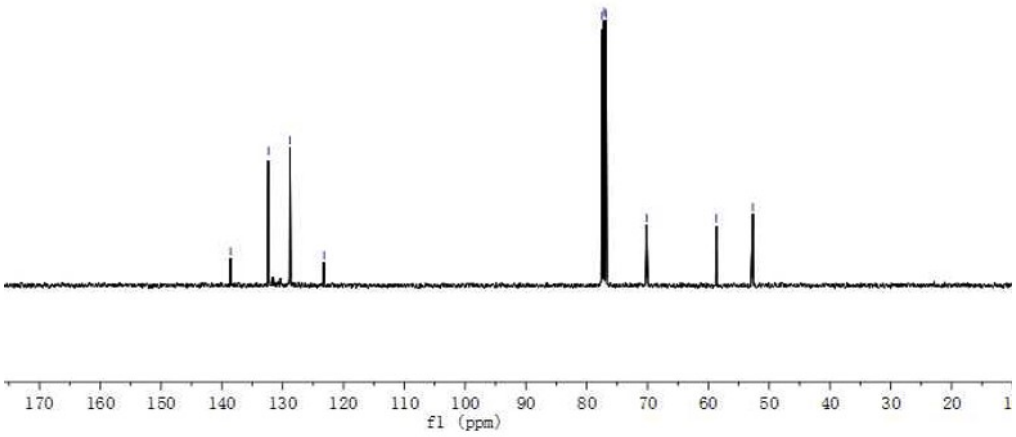
123.19
77.48
77.16
76.84
70.17
58.68
52.67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120
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100
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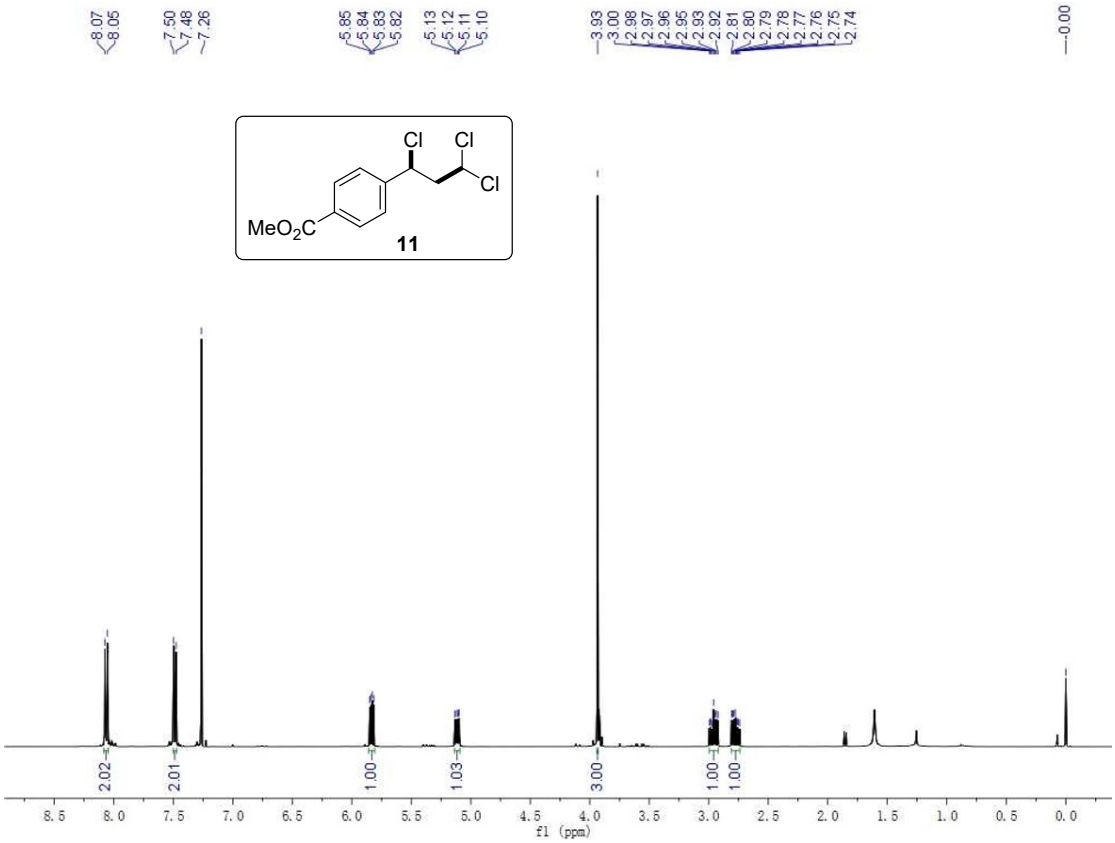
80
70
60
50
40
30
20
1
f1 (ppm)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2.96
2.95
2.93
2.92
2.81
2.80
2.79
2.78
2.77
2.76
2.75
2.74
0.00
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Cl
Cl
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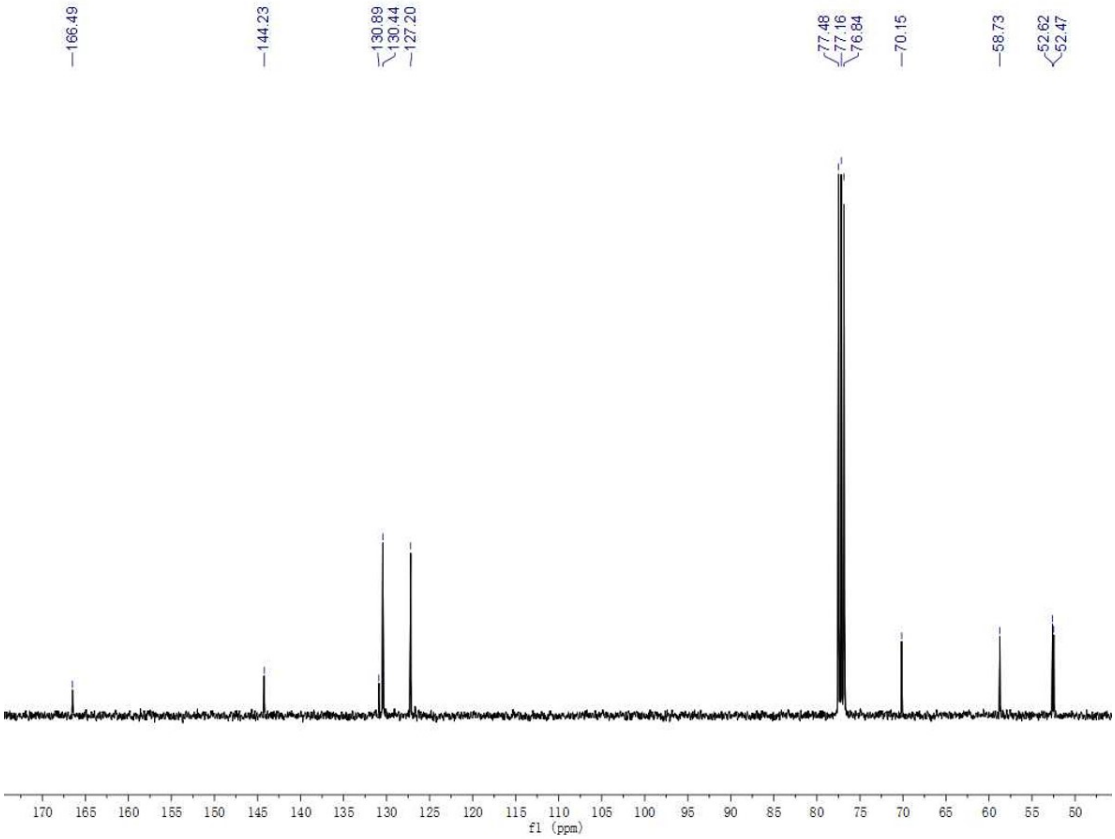
11
2.02
2.01
1.00
1.03
3.00
1.00
1.00
f1 (ppm)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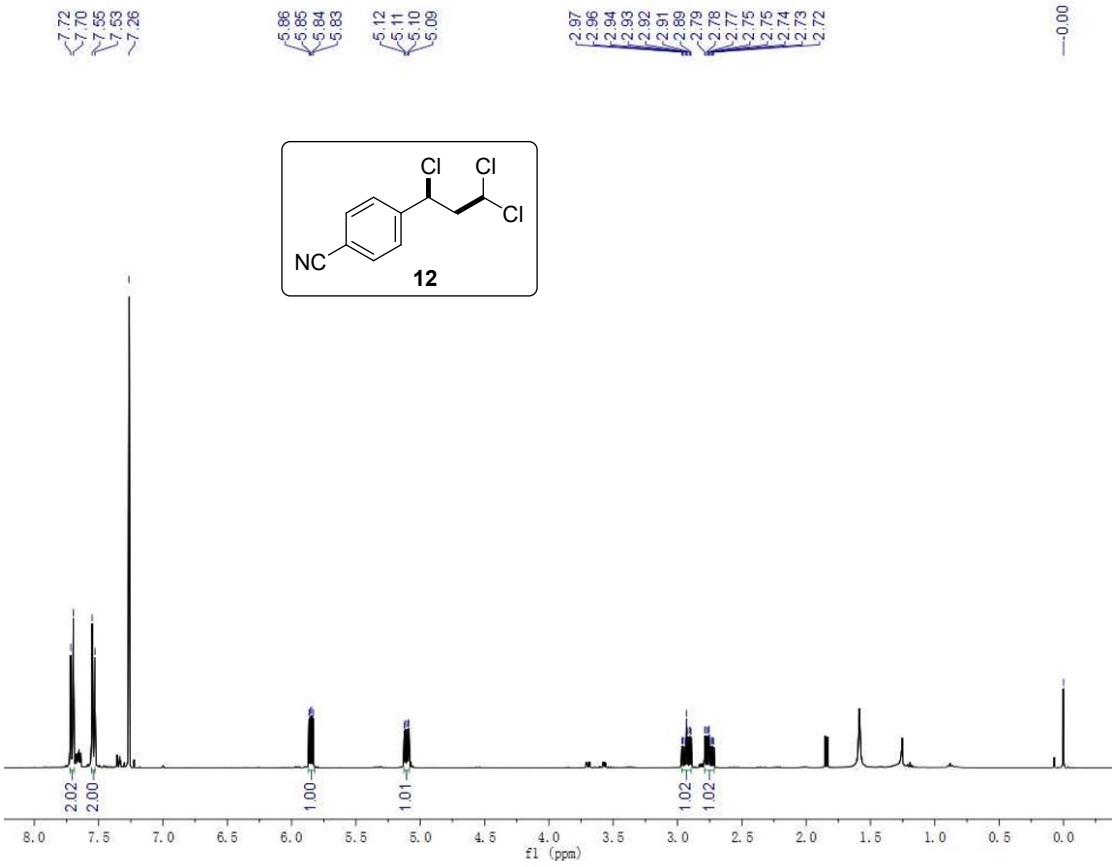
76.84
70.15
58.73
52.62
52.47
f1 (ppm)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5.10
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2.97
2.96
2.94
2.93
2.92
2.91
2.89
2.79
2.78
2.77
2.75
2.75
2.74
2.73
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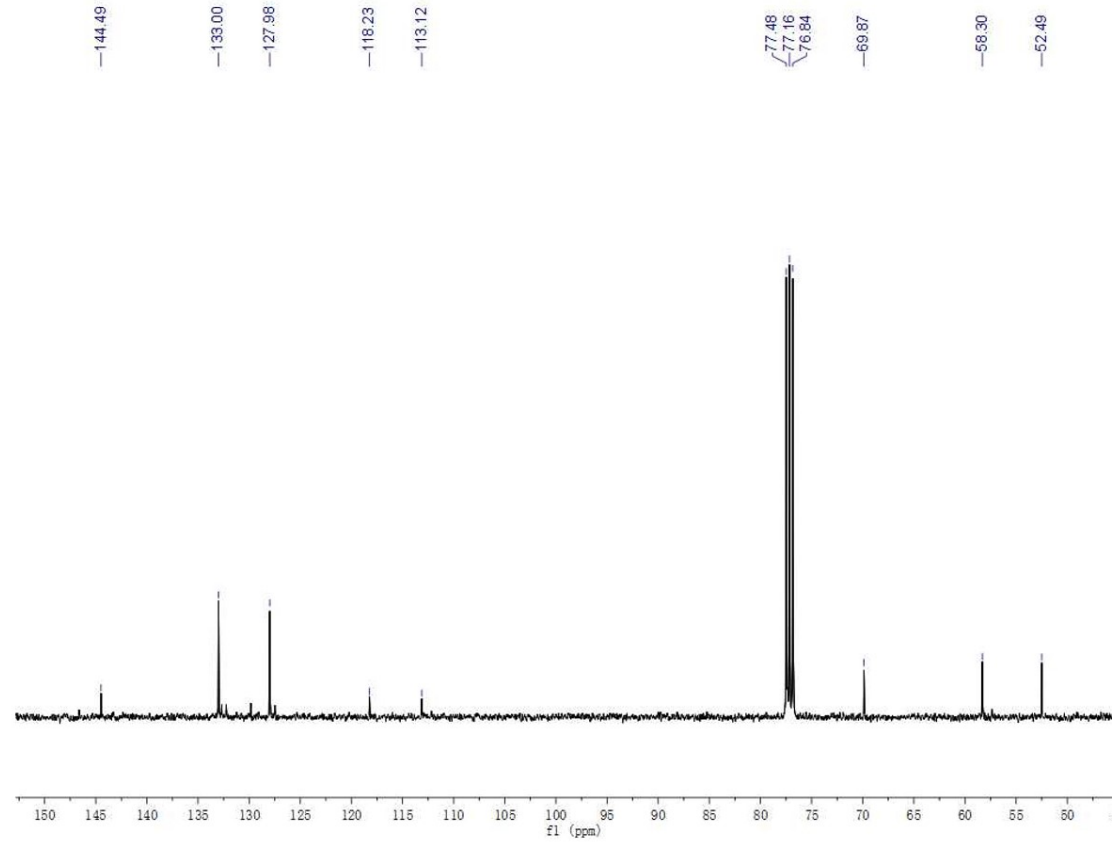
Cl
Cl
NC
12
2.02
2.00
1.00
1.01
1.02
1.02
f1 (ppm)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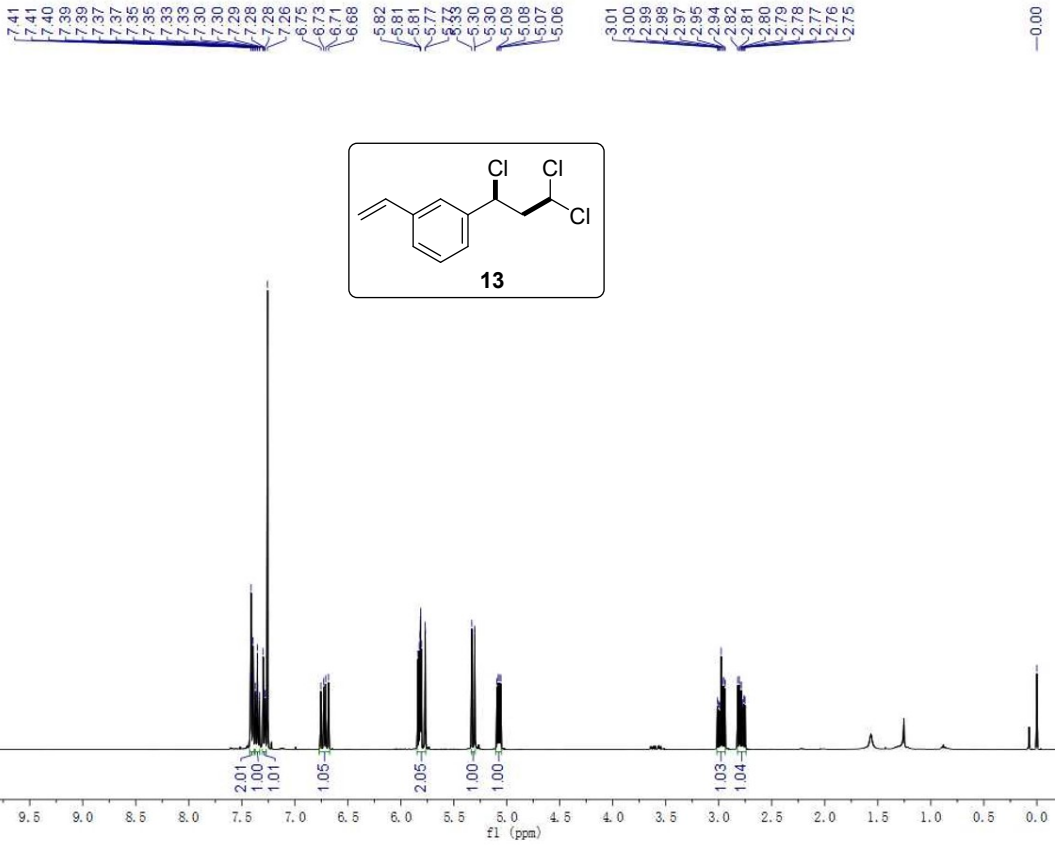
77.48
77.16
76.84
69.87
58.30
52.49
f1 (ppm)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7.30
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5.81
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5.06
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3.00
2.99
2.98
2.97
2.95
2.94
2.82
2.81
2.80
2.79
2.78
2.77
2.76
2.75
0.00
Cl
Cl
Cl
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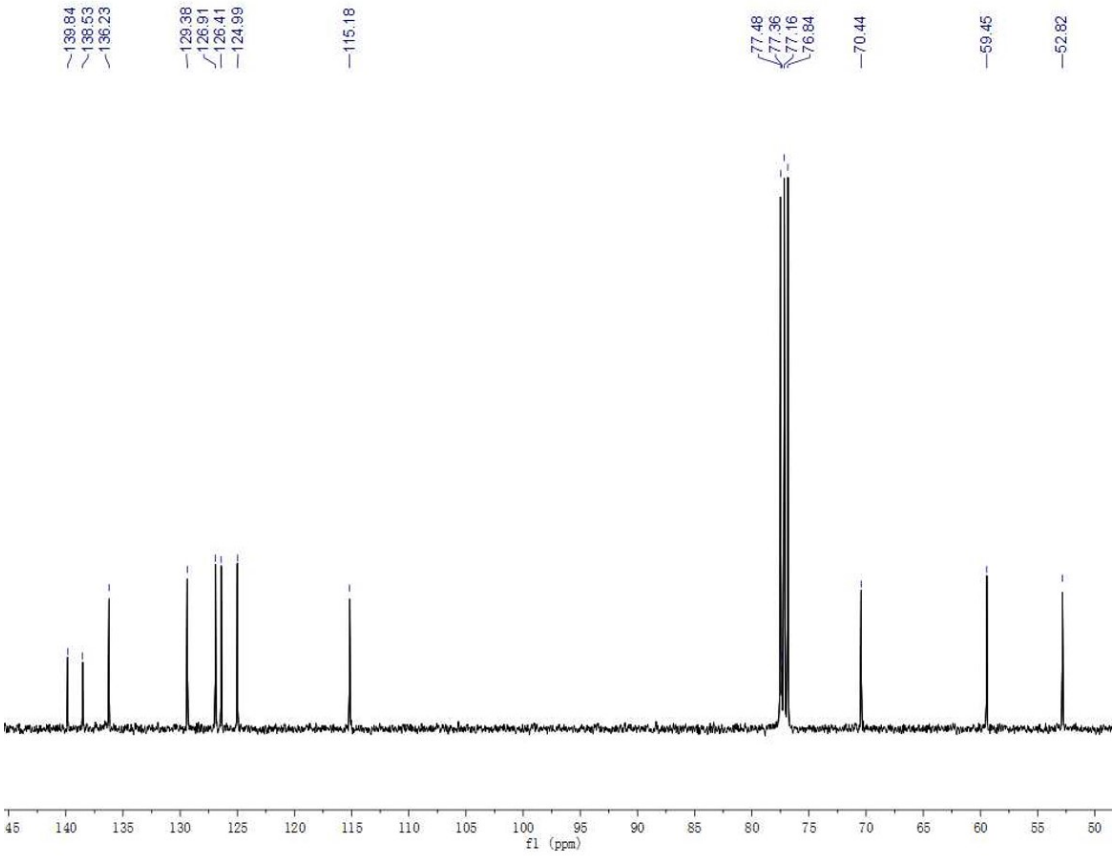
1.00
1.01
1.05
2.05
1.00
1.00
1.03
1.04
f1 (ppm)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126.91
126.41
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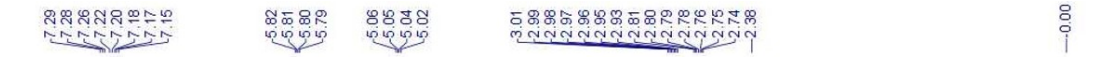
115.18
77.48
77.36
77.16
76.84
70.44
59.45
52.82
f1 (ppm)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7.28
7.26
7.22
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7.18
7.17
7.15
5.82
5.81
5.80
5.79
5.06
5.05
5.04
5.02
3.01
2.99
2.98
2.97
2.96
2.95
2.93
2.81
2.80
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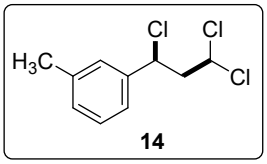
2.78
2.76
2.75
2.74
2.38
0.00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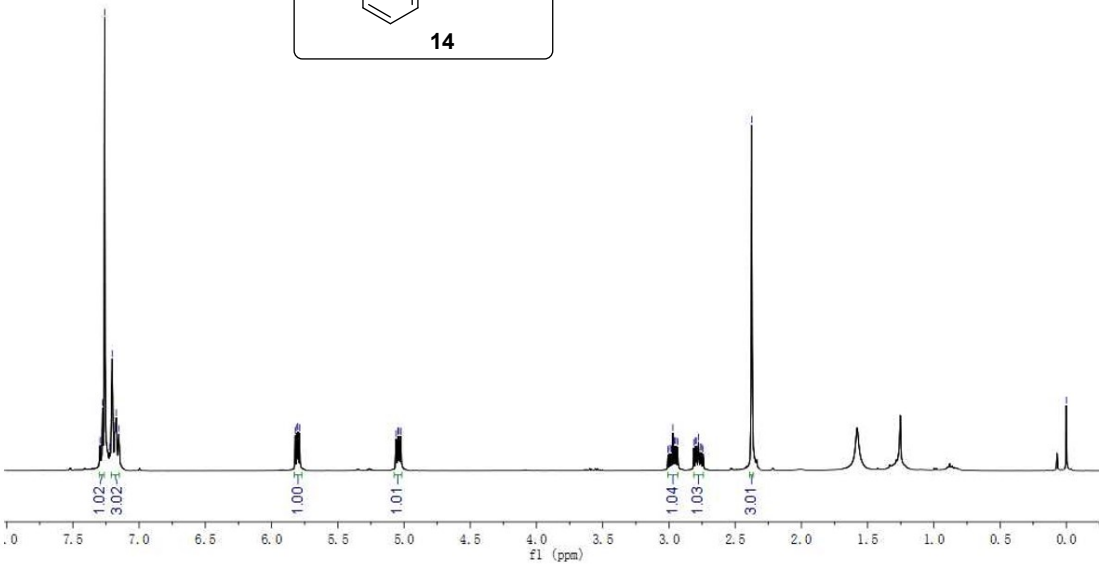
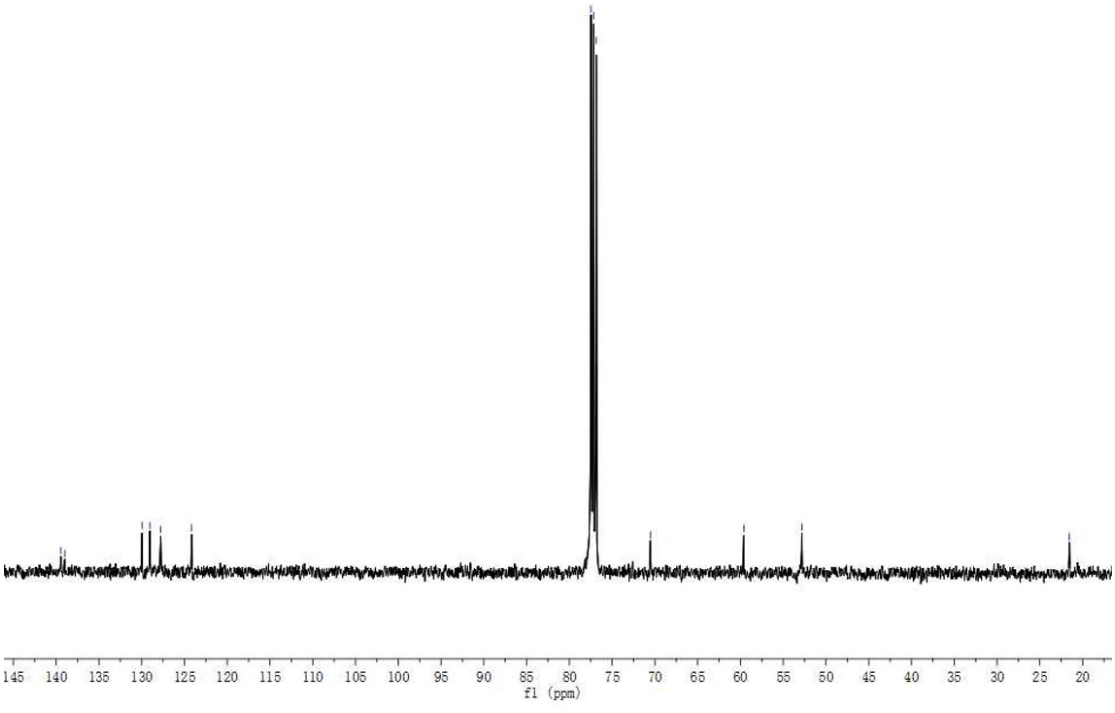
Cl
H3C
Cl

14


1.02
3.02
1.00
1.01
1.04
1.03
3.01
f1 (ppm)


139.44
138.99
129.96
129.04
127.77
124.16
77.48
77.16
76.84
70.52
59.61
52.82
21.54


f1 (ppm)


7.57
7.56
7.56
7.50
7.50
7.50
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7.48
7.48
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7.34
7.33
7.32
7.29
7.27
7.26
5.84
5.83
5.82
5.81
5.04
5.03
5.02
5.01
2.97
2.96
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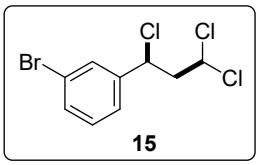
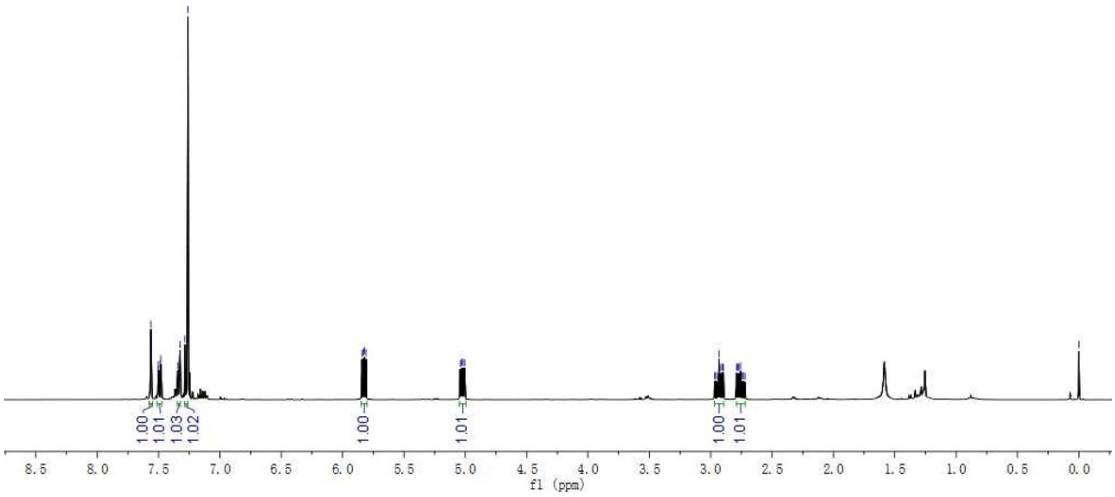
2.76
2.75
2.74
2.73
2.72
0.00


Cl
Cl
Br
Cl

15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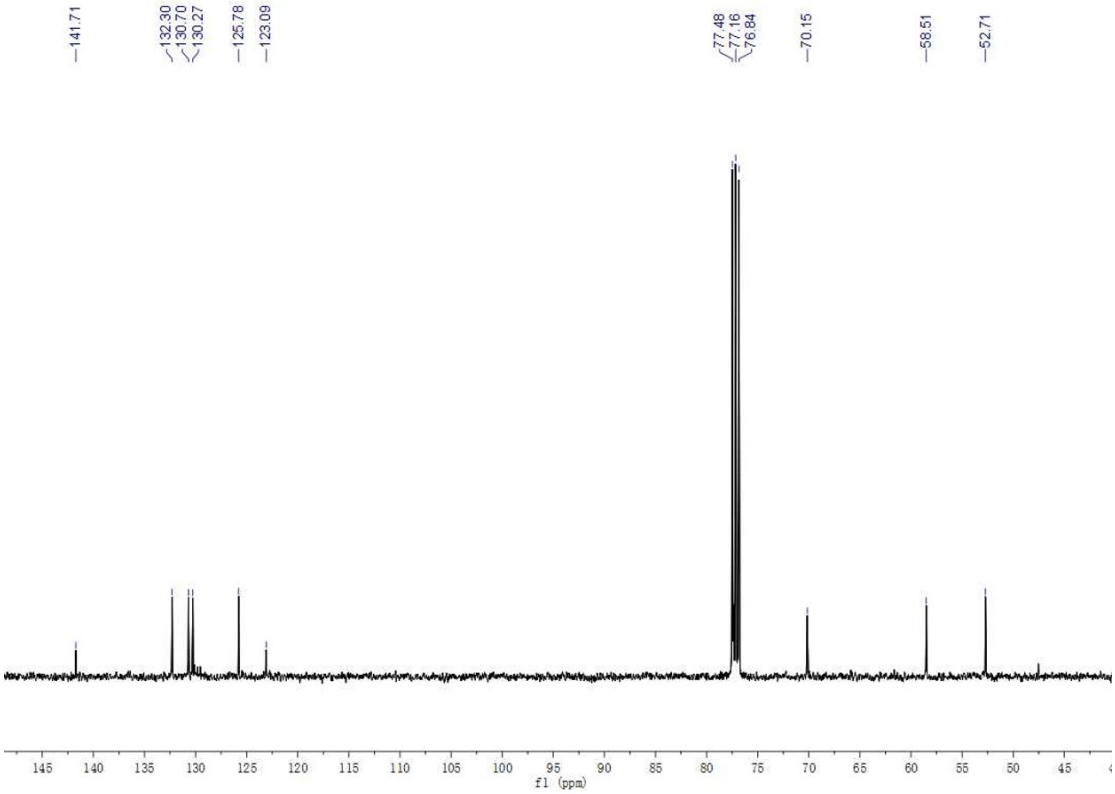
1.02
1.00
1.01
1.00
1.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


141.71
132.30
130.70
130.27
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123.09
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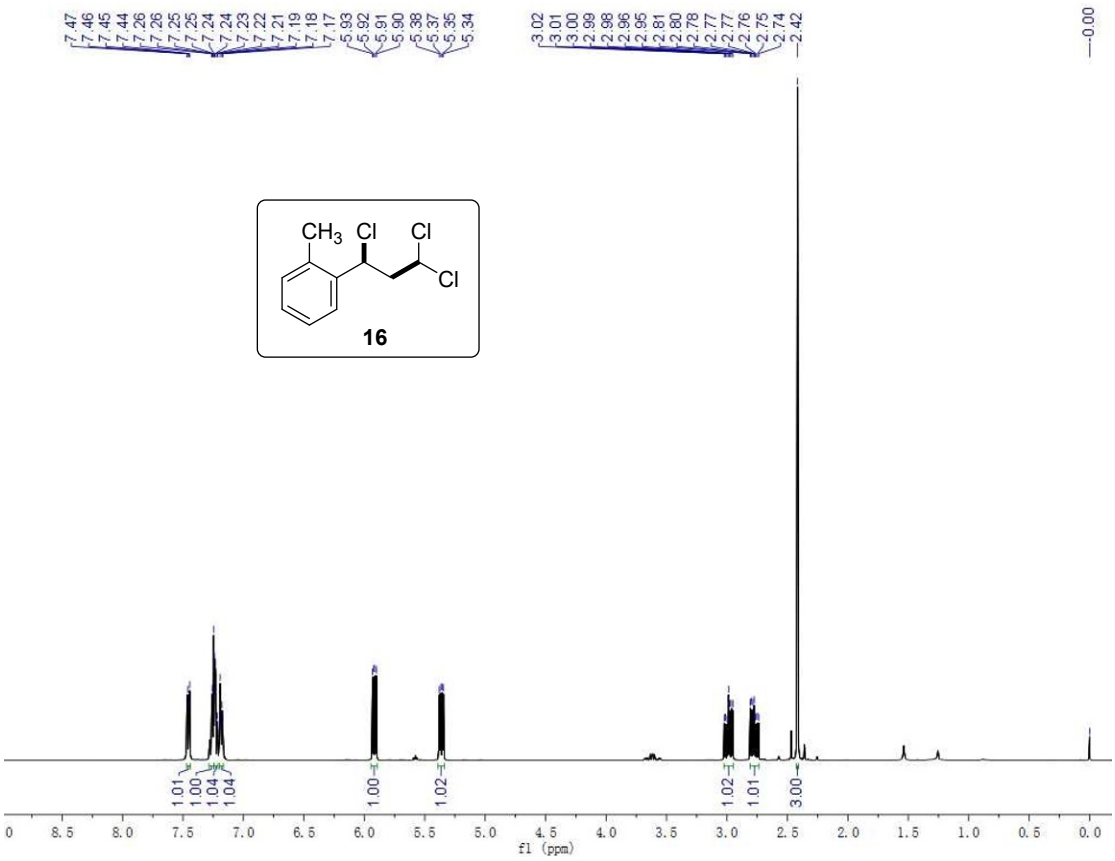
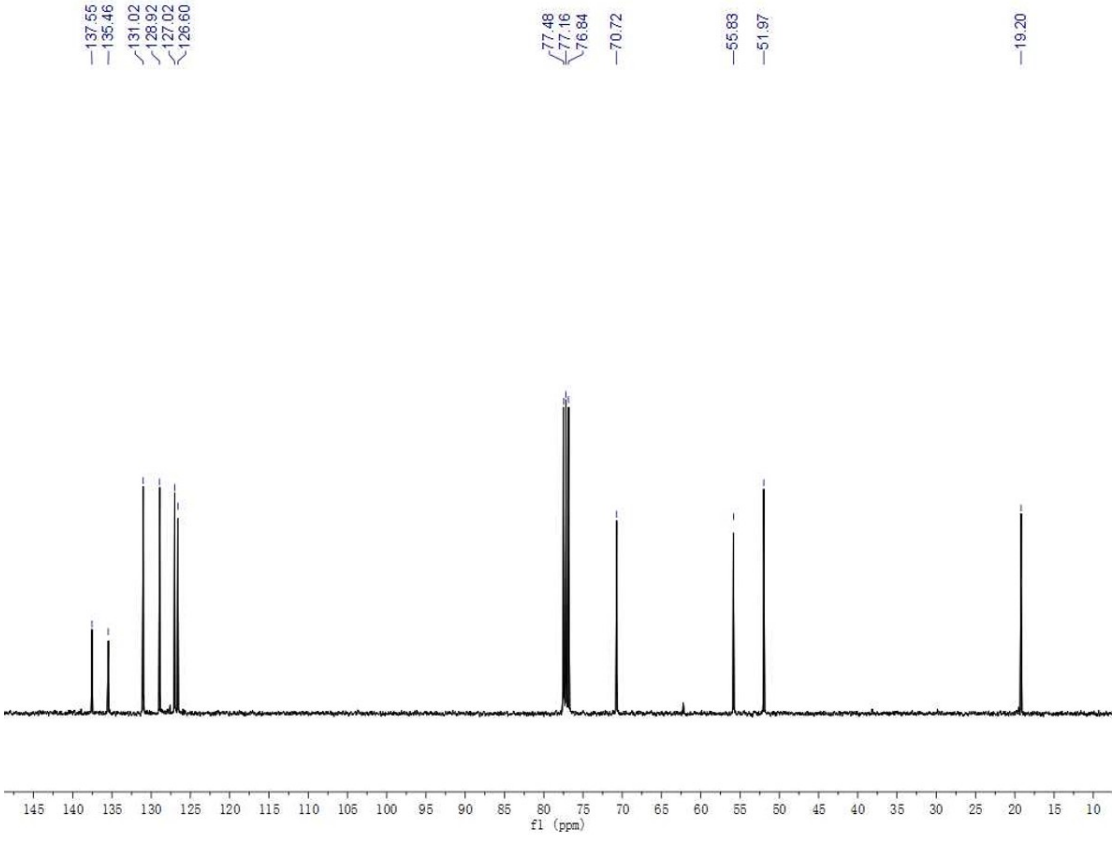
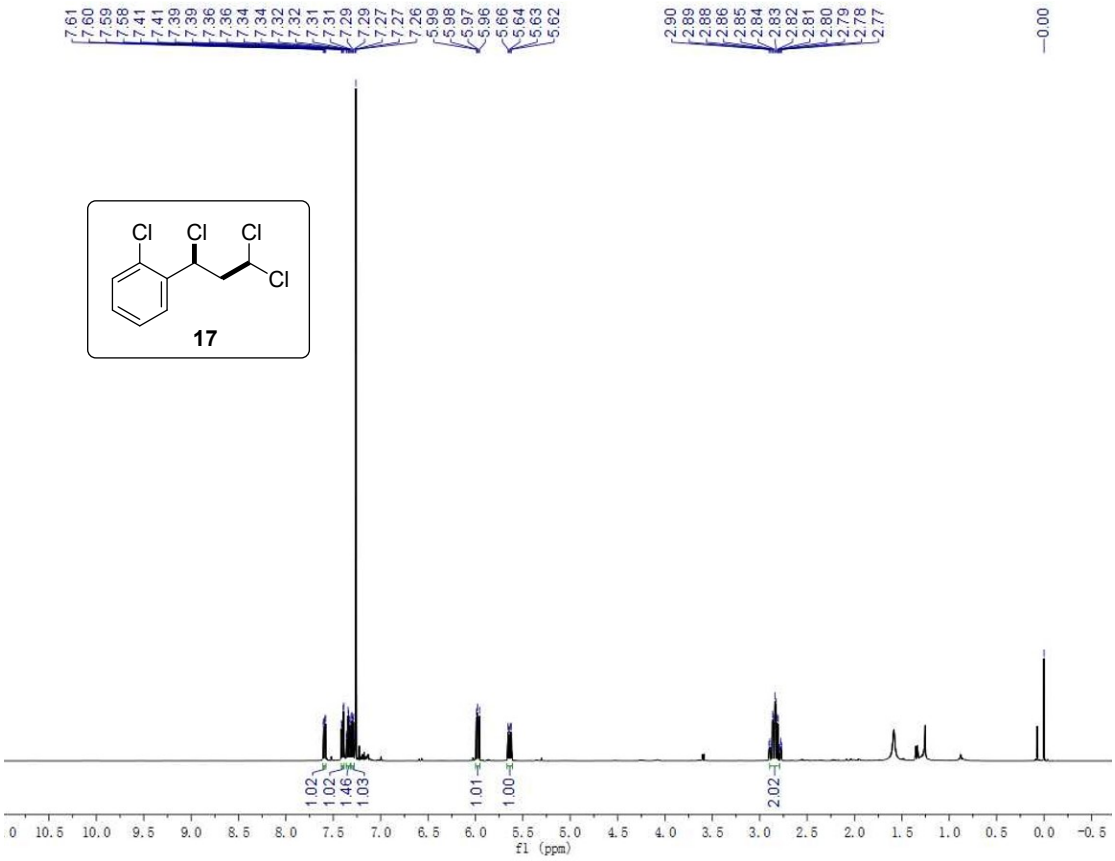
77.16
76.84
70.15
58.51
52.71
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
f1 (ppm)


7.47
7.46
7.45
7.44
7.26
7.26
7.25
7.25
7.24
7.24
7.23
7.22
7.21
7.19
7.18
7.17
5.93
5.92
5.91
5.90
5.38
5.37
5.35
5.34
3.02
3.01
3.00
2.99
2.98
2.96
2.95
2.81
2.80
2.78
2.77
2.77
2.76
2.75
2.74
2.42
0.00
CH3 Cl Cl
Cl
16
1.01
1.00
1.04
1.04
1.00
1.02
1.02
1.01
3.00
f1 (ppm)


137.55
135.46
131.02
128.92
127.02
126.60
77.48
77.16
76.84
70.72
55.83
51.97
19.20
f1 (ppm)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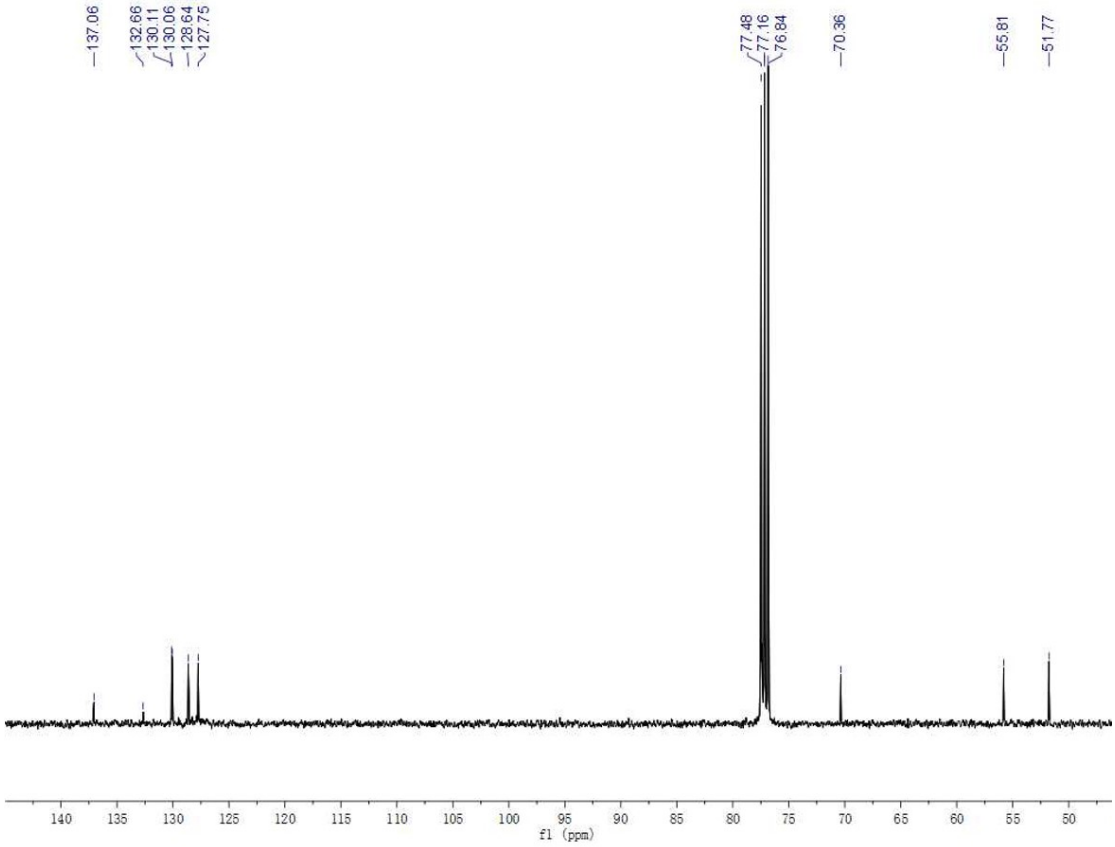
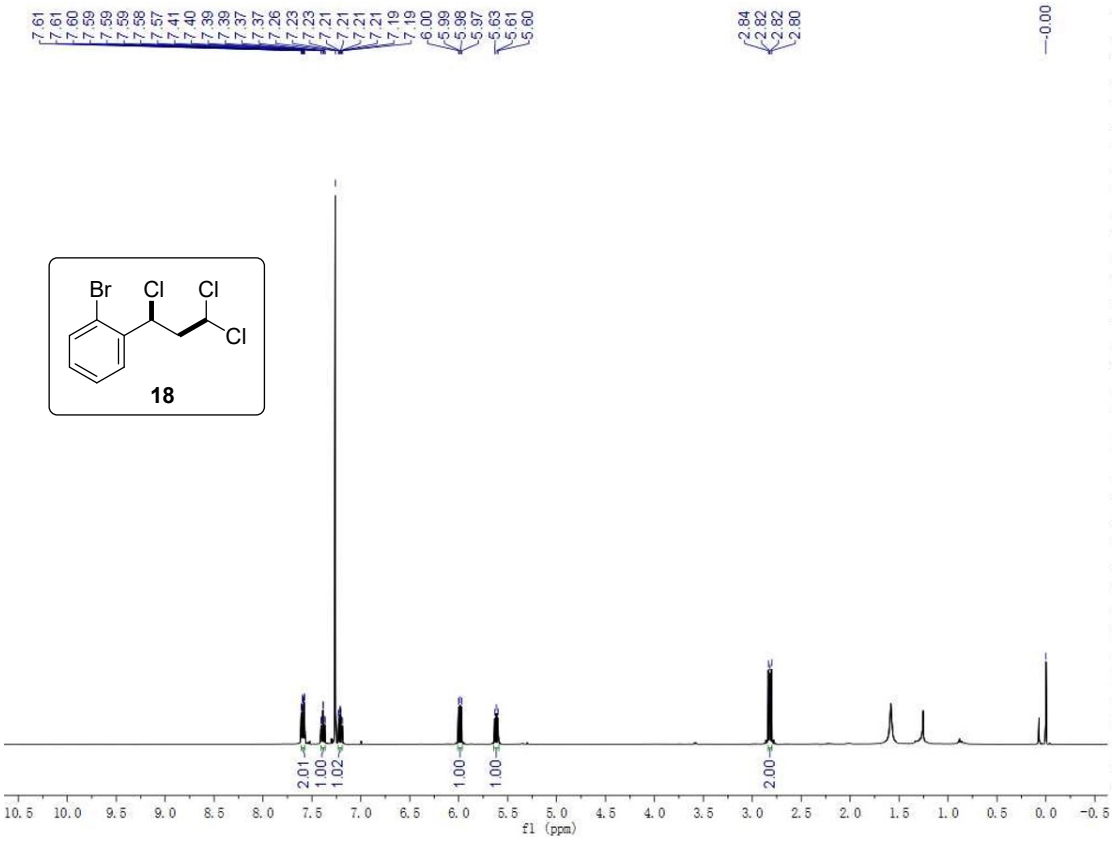
7.41
7.39
7.39
7.36
7.36
7.34
7.34
7.32
7.32
7.31
7.31
7.29
7.29
7.27
7.27
7.26
5.99
5.98
5.97
5.96
5.66
5.64
5.63
5.62
2.90
2.89
2.88
2.86
2.85
2.84
2.83
2.82
2.81
2.80
2.79
2.78
2.77
0.00
Cl
Cl
Cl
Cl
17
1.02
1.02
1.46
1.03
1.01
1.00
2.02
f1 (ppm)


137.06
132.66
130.11
130.06
128.64
127.75
77.48
77.16
76.84
70.36
55.81
51.77
f1 (ppm)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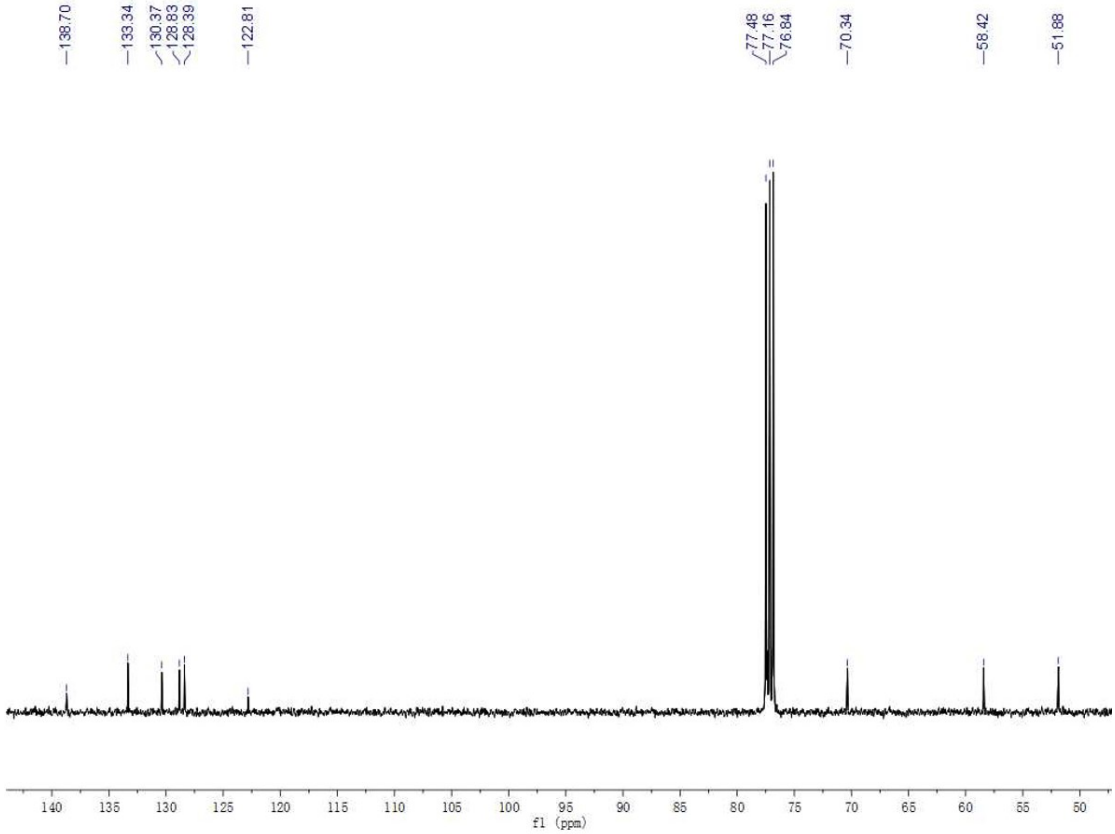
7.61
7.60
7.59
7.59
7.59
7.58
7.57
7.41
7.40
7.39
7.39
7.37
7.37
7.26
7.23
7.23
7.21
7.21
7.21
7.21
7.19
7.19
6.00
5.99
5.98
5.97
5.63
5.61
5.60
2.84
2.82
2.82
2.80
0.00
Br
Cl
Cl
Cl
18
2.01
1.00
1.02
1.00
1.00
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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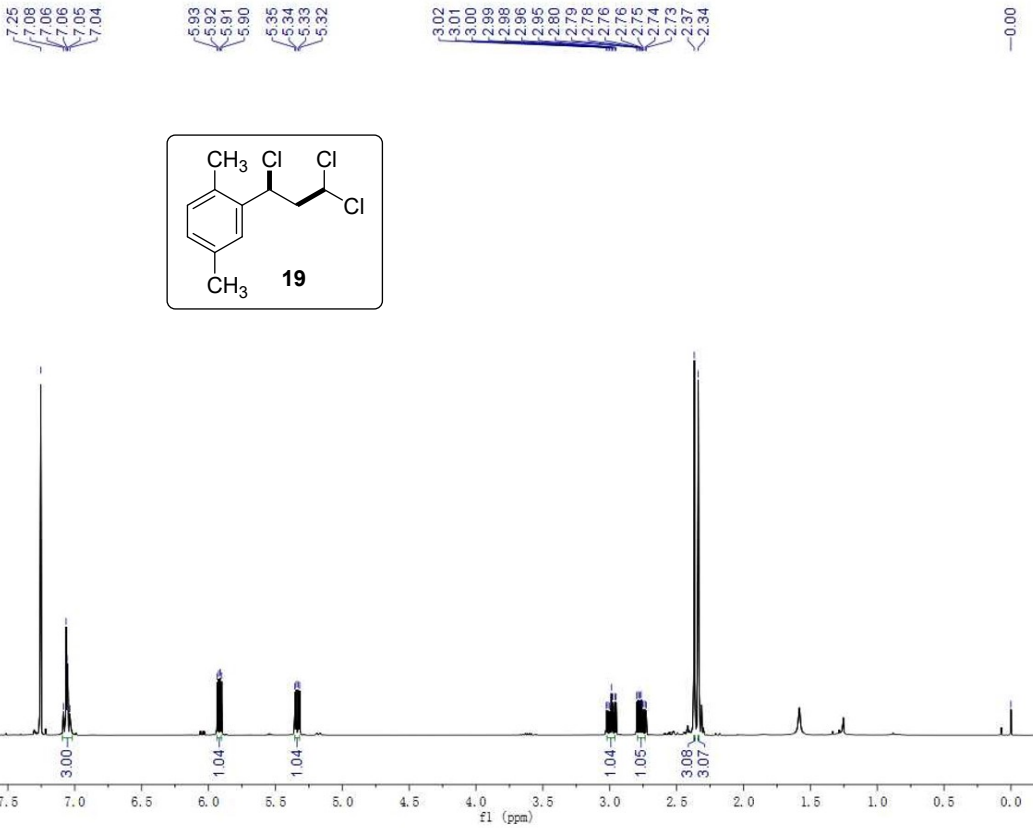
133.34
130.37
128.83
128.39
122.81
77.48
77.16
76.84
70.34
58.42
51.88
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50
f1 (ppm)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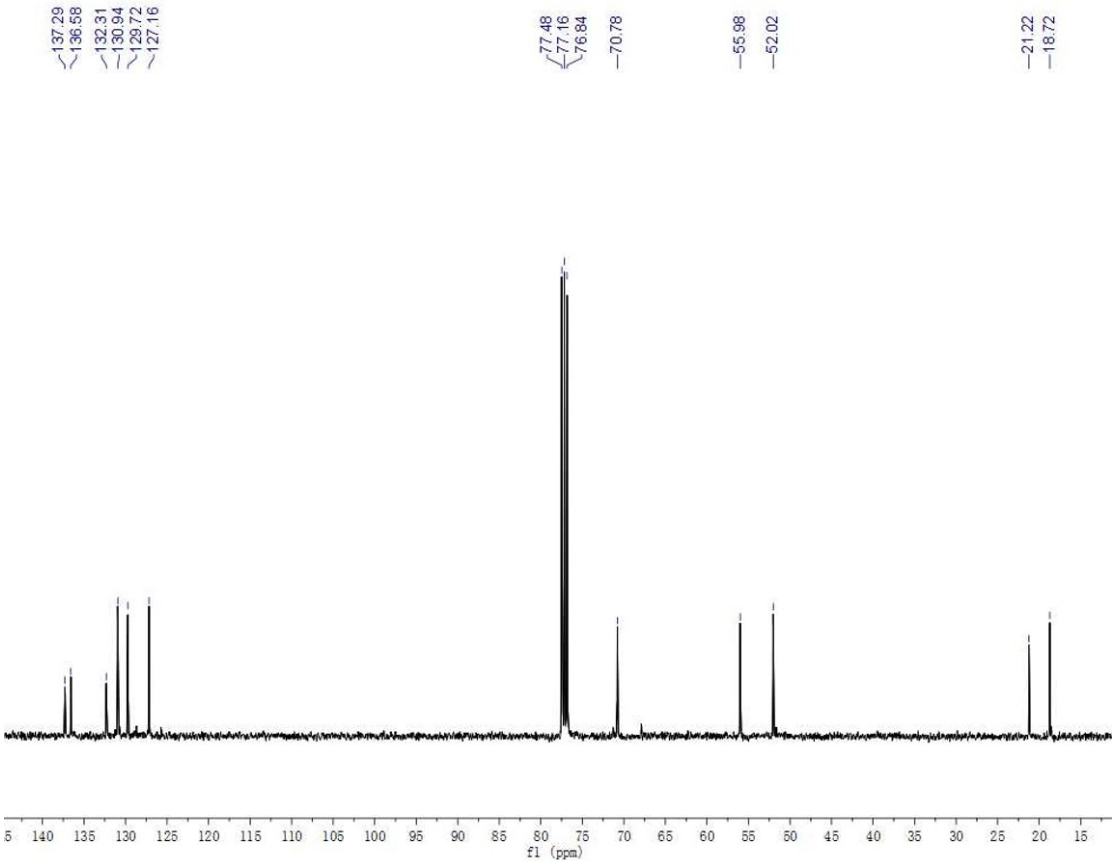
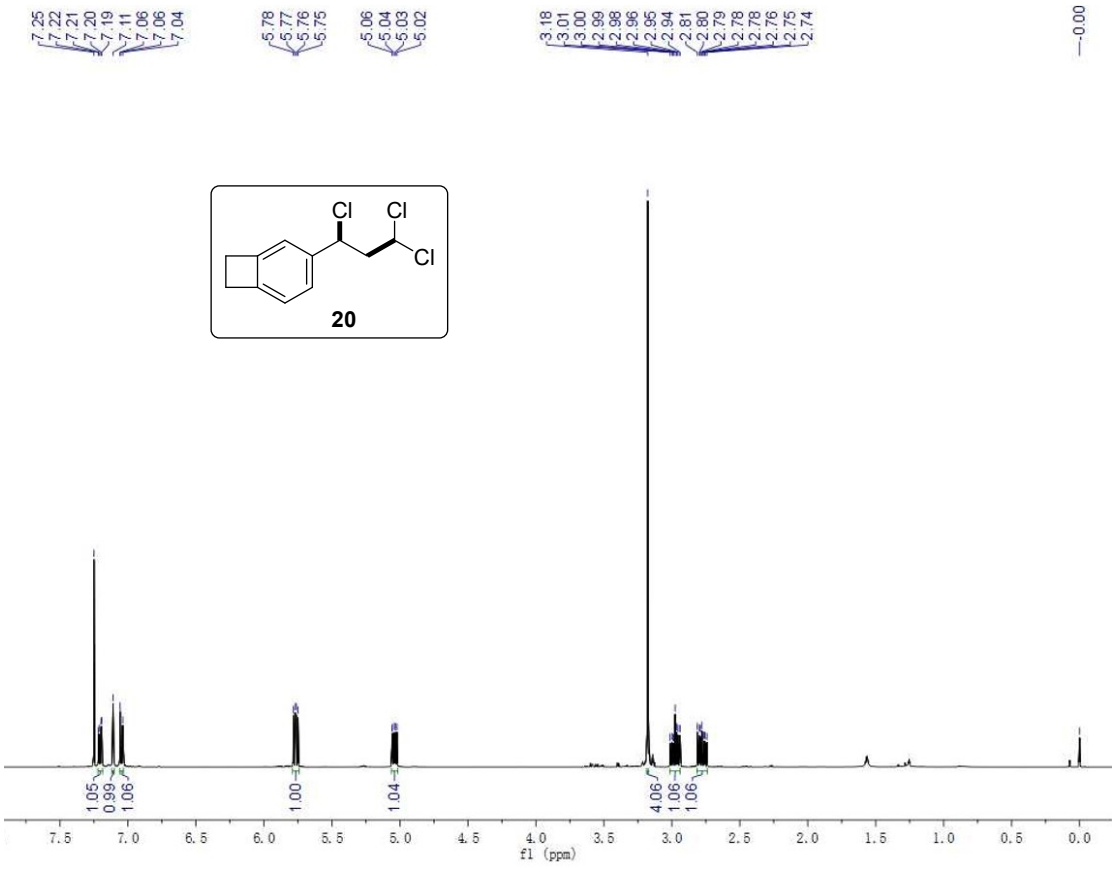
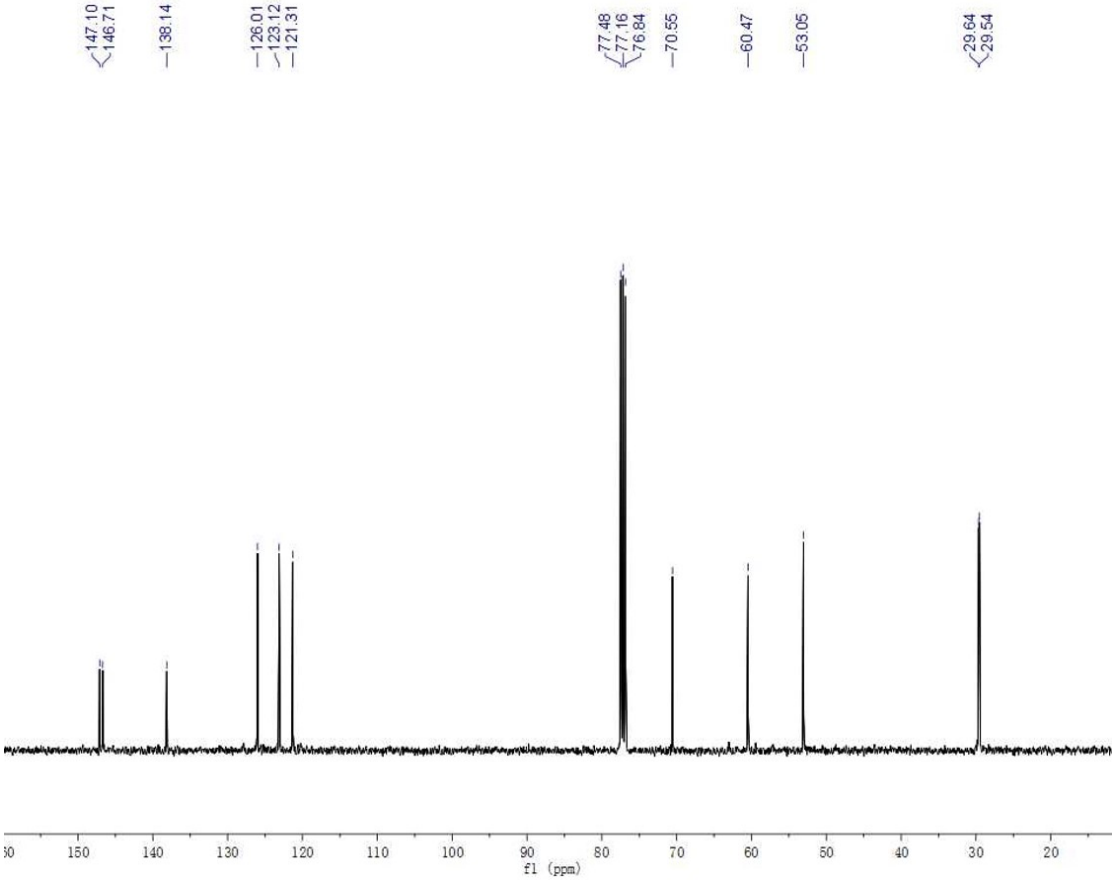
7.08
7.06
7.06
7.05
7.04
5.93
5.92
5.91
5.90
5.35
5.34
5.33
5.32
3.02
3.01
3.00
2.99
2.98
2.96
2.95
2.80
2.79
2.78
2.76
2.76
2.75
2.74
2.73
2.37
2.34
0.00
CH3
Cl
Cl
Cl
CH3
19
3.00
1.04
1.04
1.04
1.05
3.08
3.07
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


137.29
136.58
132.31
130.94
129.72
127.16
77.48
77.16
76.84
70.78
55.98
52.02
21.22
18.72
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
f1 (ppm)


7.25
7.22
7.21
7.20
7.19
7.11
7.06
7.06
7.04
5.78
5.77
5.76
5.75
5.06
5.04
5.03
5.02
3.18
3.01
3.00
2.99
2.98
2.96
2.95
2.94
2.81
2.80
2.79
2.78
2.78
2.76
2.75
2.74
0.00
Cl
Cl
Cl
20
1.05
0.99
1.06
1.00
1.04
4.06
1.06
1.06
f1 (ppm)


147.10
146.71
138.14
126.01
123.12
121.31
77.48
77.16
76.84
70.55
60.47
53.05
29.64
29.54
f1 (ppm)


7.94
7.93
7.74
7.72
7.72
7.71
7.50
7.49
7.48
7.48
7.26
6.49
6.49
6.48
5.84
5.83
5.82
5.81
5.13
5.12
5.11
5.10
3.03
3.02
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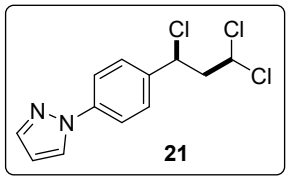
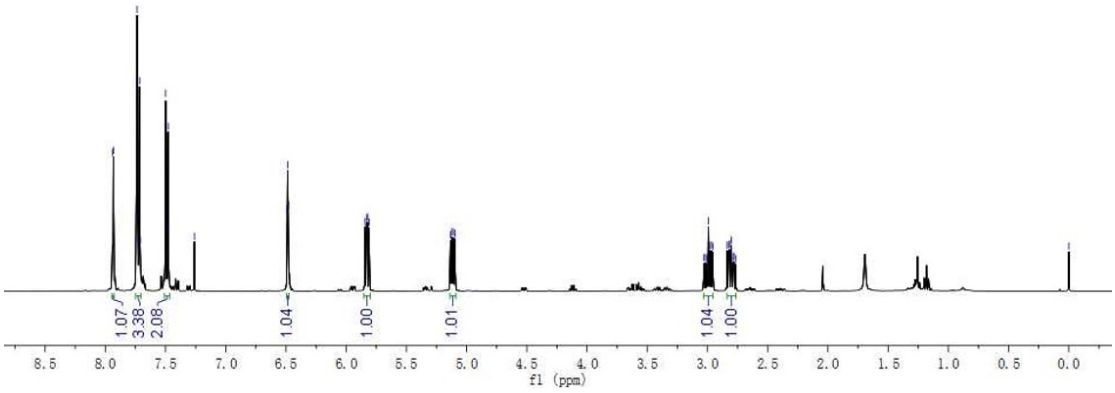
2.80
2.80
2.79
2.78
2.77
0.00


Cl
Cl
Cl
N
N

21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3.38
2.08
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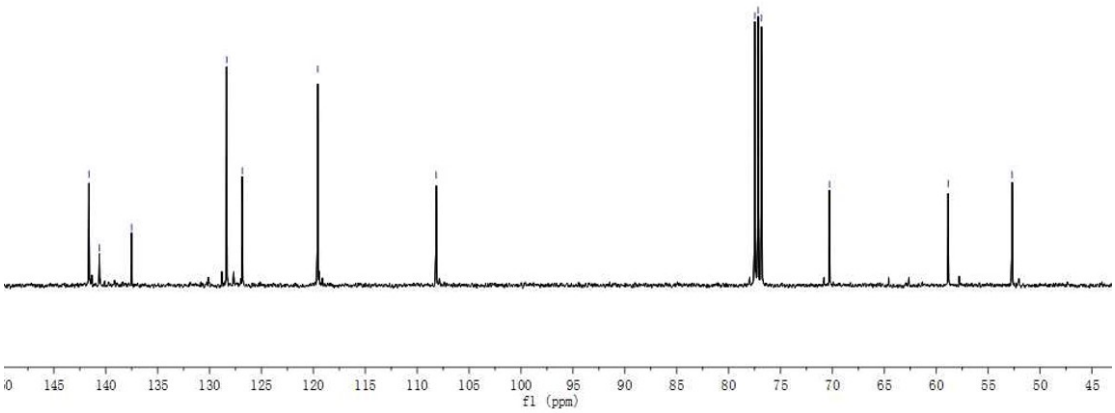
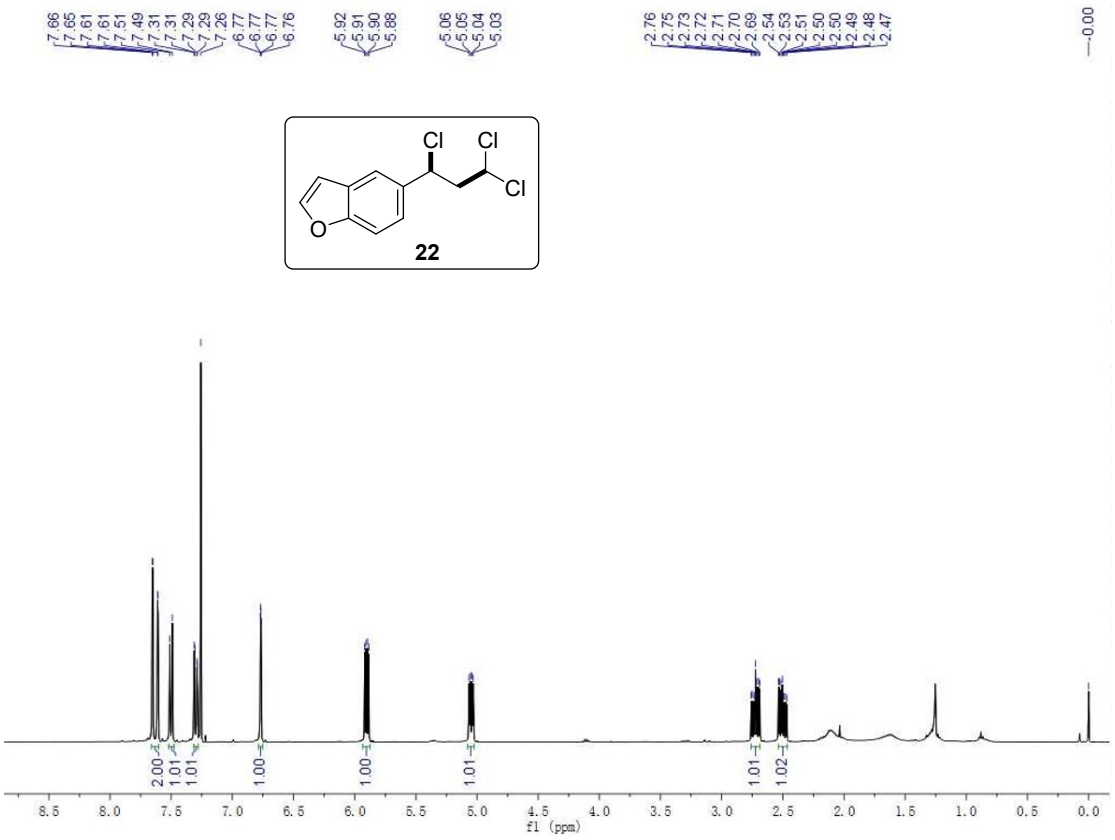
1.00
1.01
1.04
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


141.62
140.60
137.50
128.35
126.85
119.58
108.17
77.48
77.16
76.84
70.29
58.85
52.70


145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
f1 (ppm)


7.66
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7.31
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7.29
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6.77
6.77
6.77
6.76
5.92
5.91
5.90
5.88
5.06
5.05
5.04
5.03
2.76
2.75
2.73
2.72
2.71
2.70
2.69
2.54
2.53
2.51
2.50
2.50
2.49
2.48
2.47
0.00
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Cl
O
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2.00
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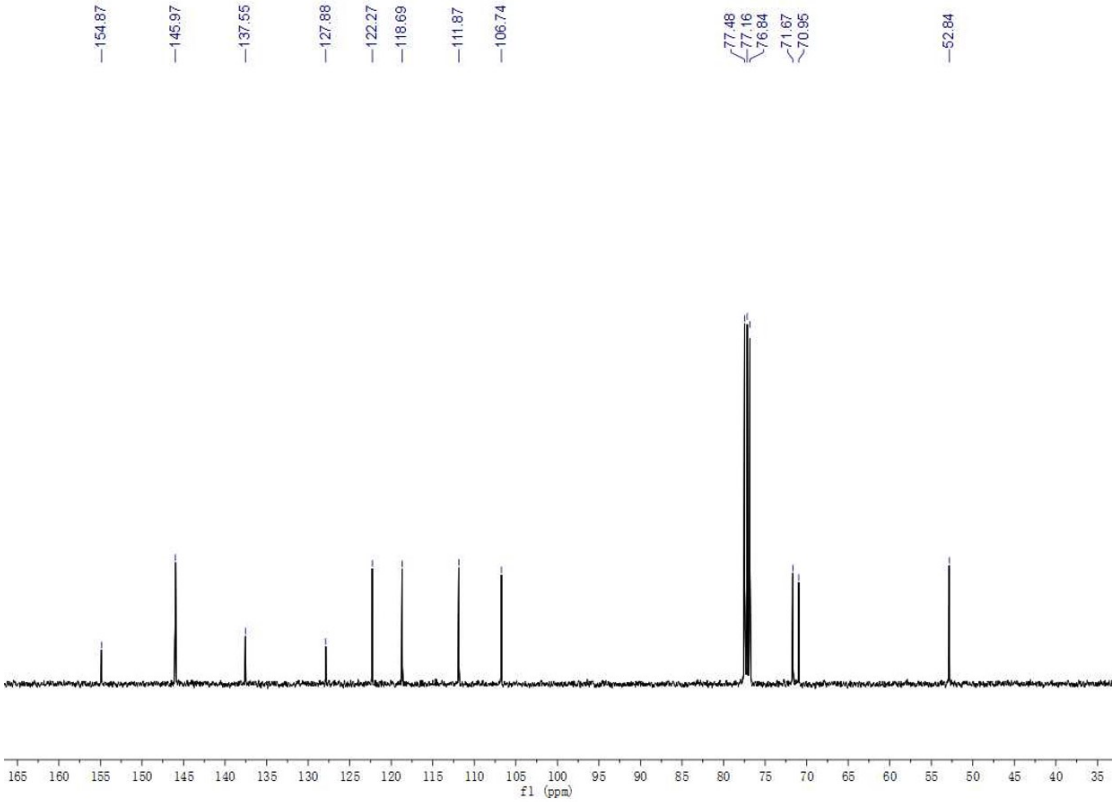
1.01
1.00
1.00
1.01
1.01
1.02
f1 (ppm)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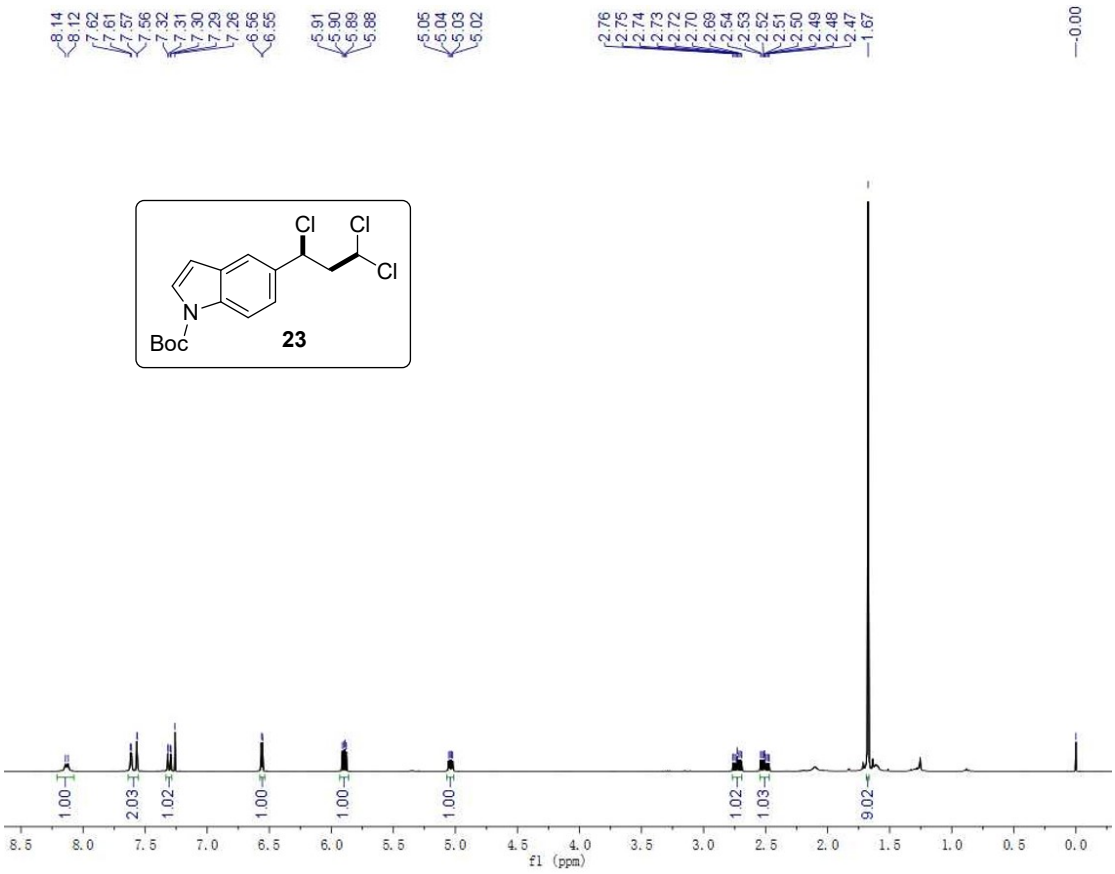
111.87
106.74
77.48
77.16
76.84
71.67
70.95
52.84
f1 (ppm)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8.12
7.62
7.61
7.57
7.56
7.32
7.31
7.30
7.29
7.26
6.56
6.55
5.91
5.90
5.89
5.88
5.05
5.04
5.03
5.02
2.76
2.75
2.74
2.73
2.72
2.70
2.69
2.54
2.53
2.52
2.51
2.50
2.49
2.48
2.47
1.67
0.00
Cl
Cl
Cl
N
Boc
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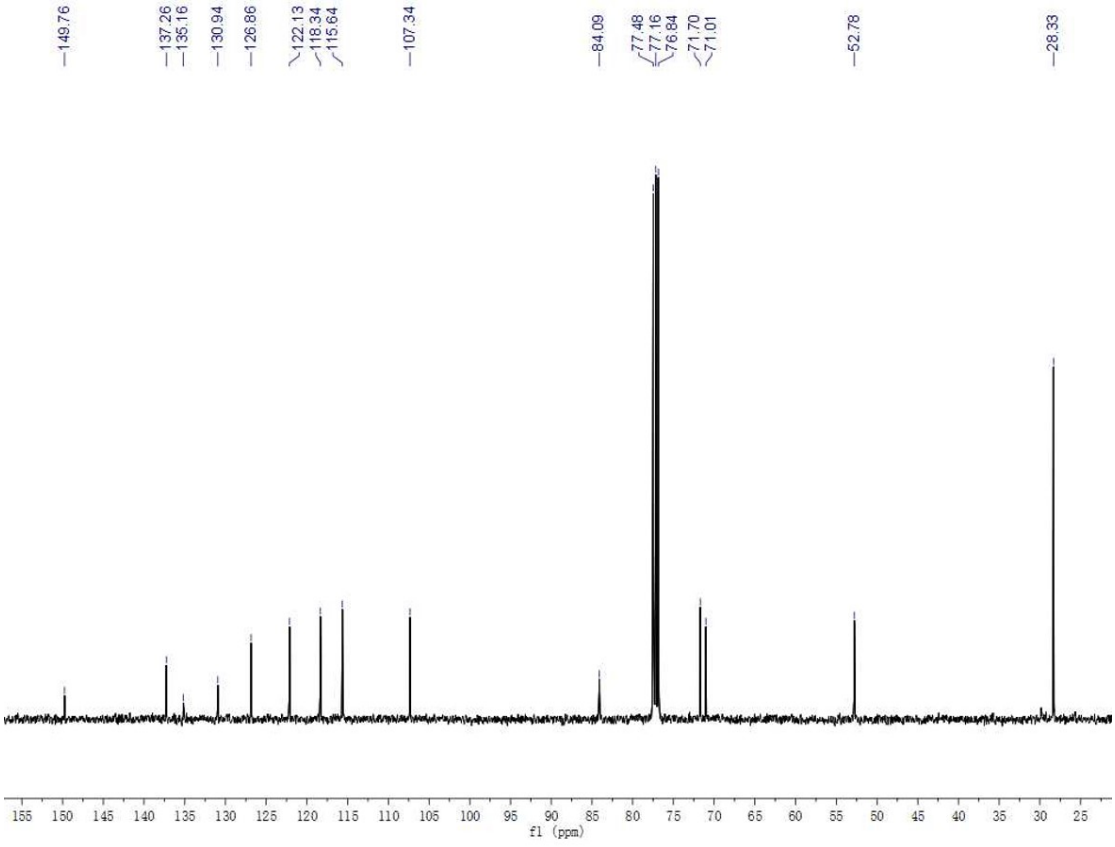
2.03
1.02
1.00
1.00
1.00
1.02
1.03
9.02
f1 (ppm)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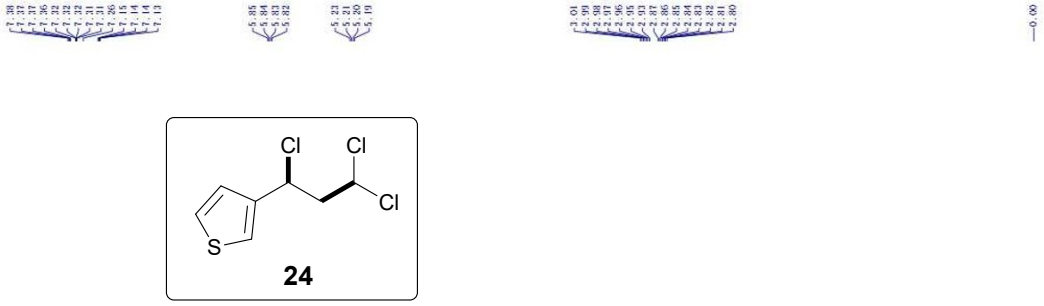
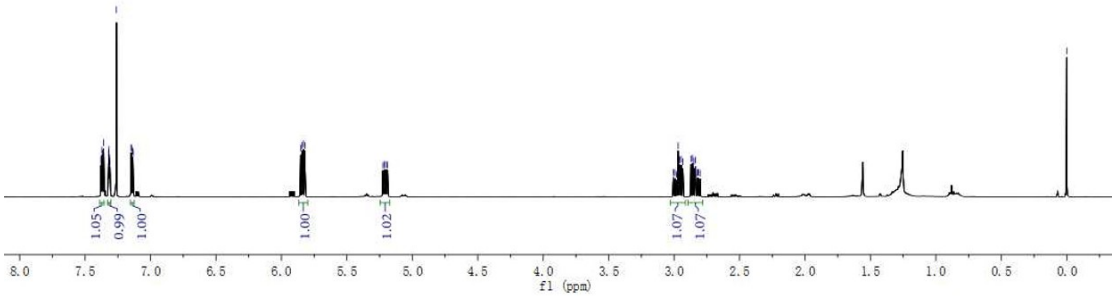
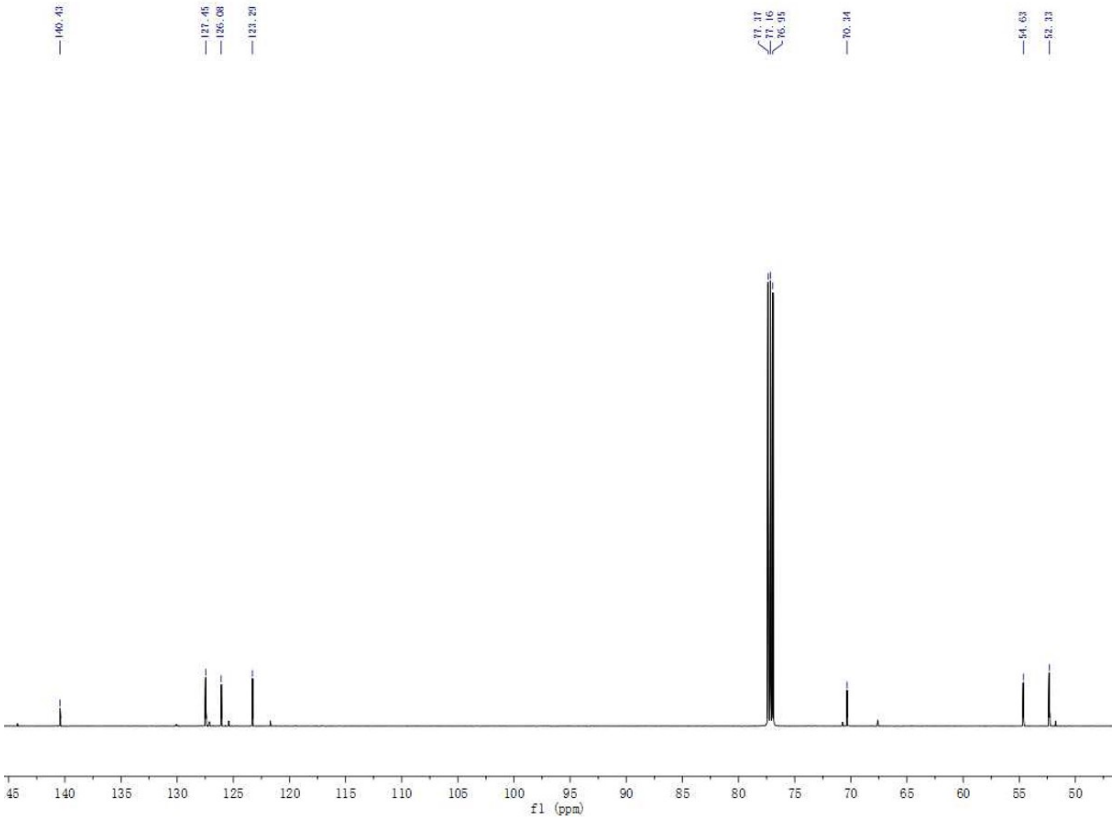
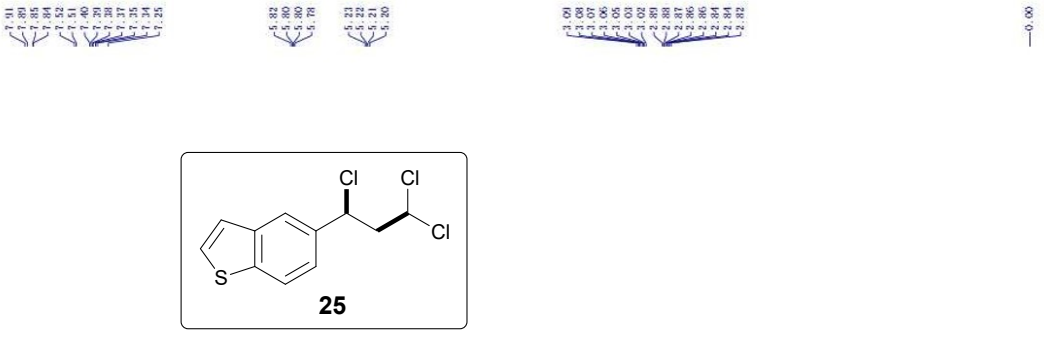
126.86
122.13
118.34
115.64
107.34
84.09
77.48
77.16
76.84
71.70
71.01
52.78
28.33
f1 (ppm)

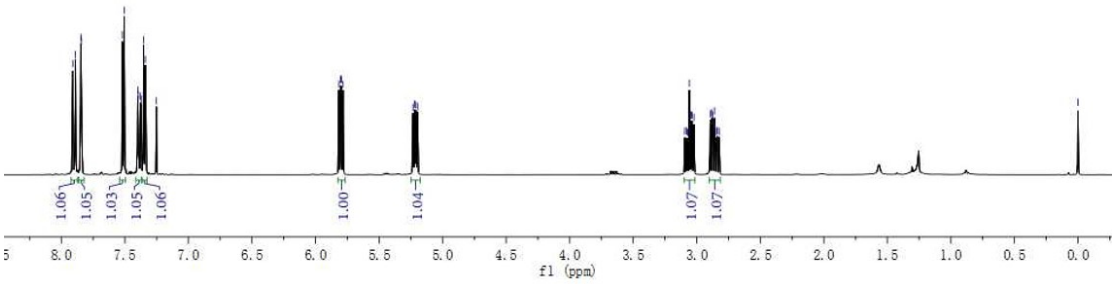


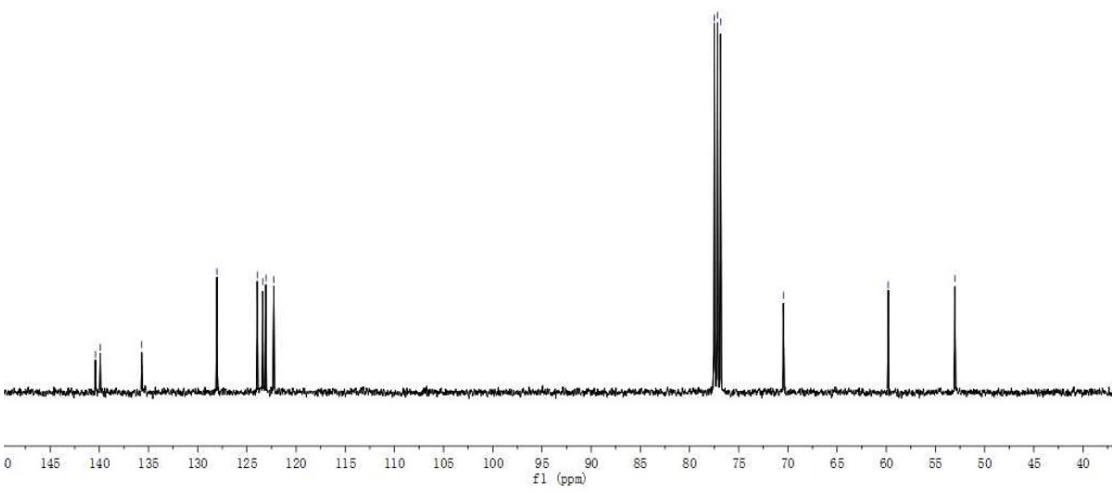
24

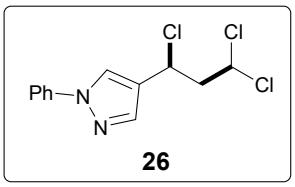




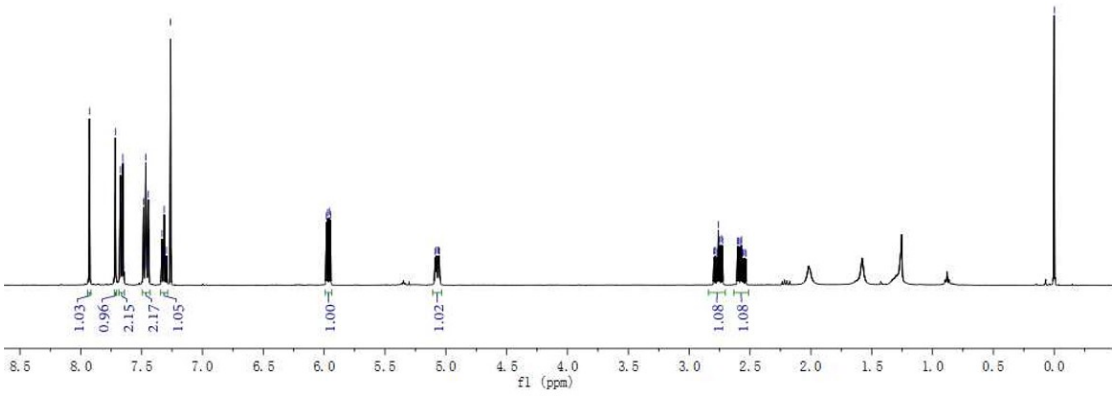

Cl
Cl
Cl
S
25

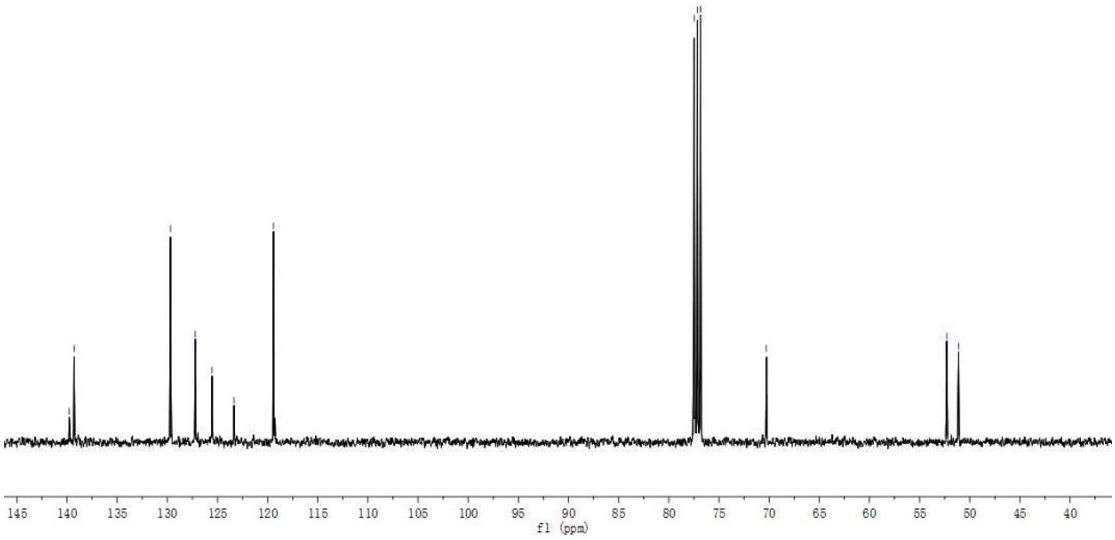

1.06
1.05
1.03
1.05
1.06
1.00
1.04
1.07
1.07
f1 (ppm)


f1 (ppm)

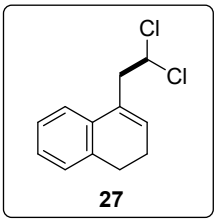


26

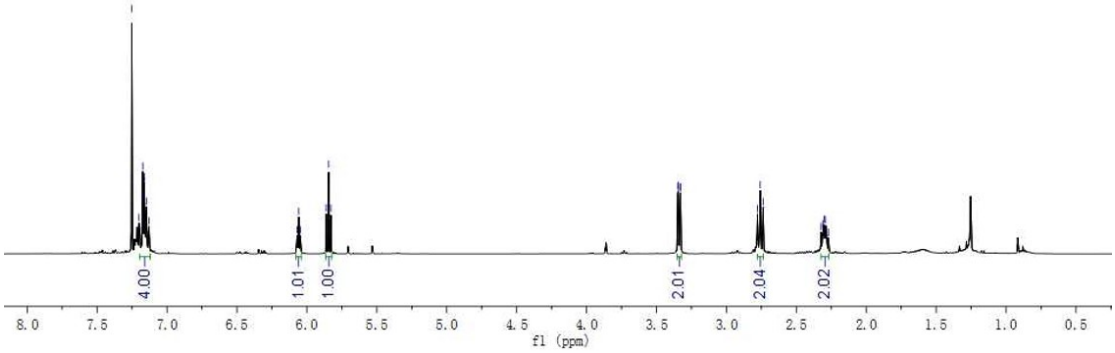




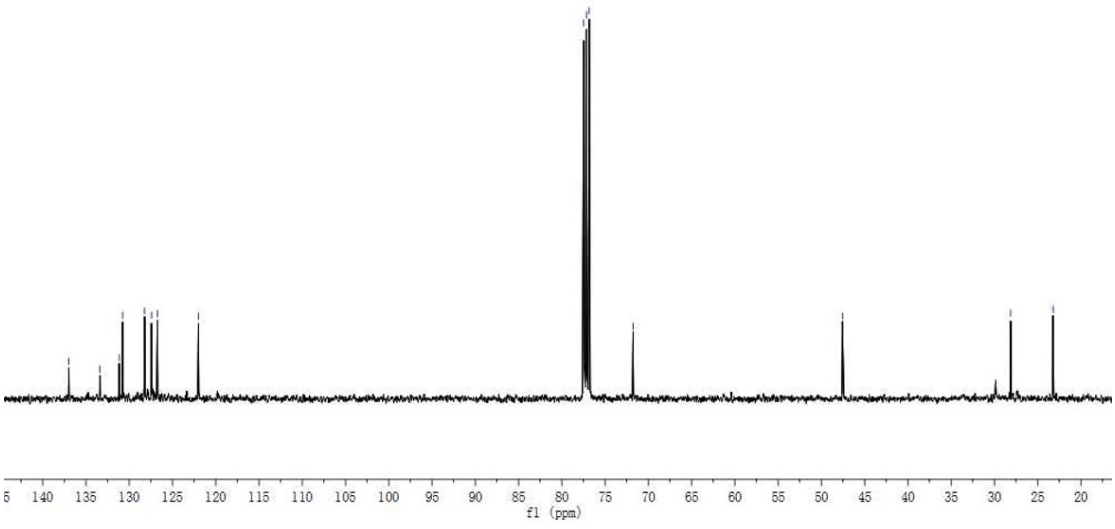

7.25
7.20
7.19
7.18
7.17
7.17
7.16
7.16
7.15
7.13
6.07
6.06
6.05
5.86
5.84
5.83
3.35
3.34
3.33
3.33
2.78
2.76
2.74
2.32
2.31
2.31
2.30
2.29
2.28
2.27

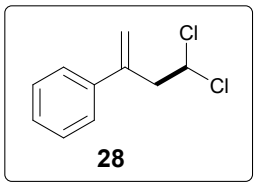

Cl
Cl

27

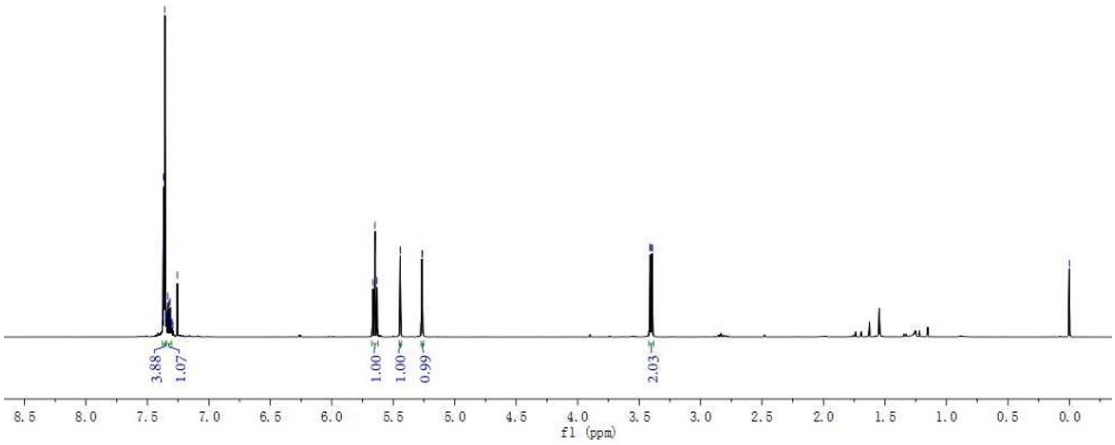

4.00
1.01
1.00
2.01
2.04
2.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

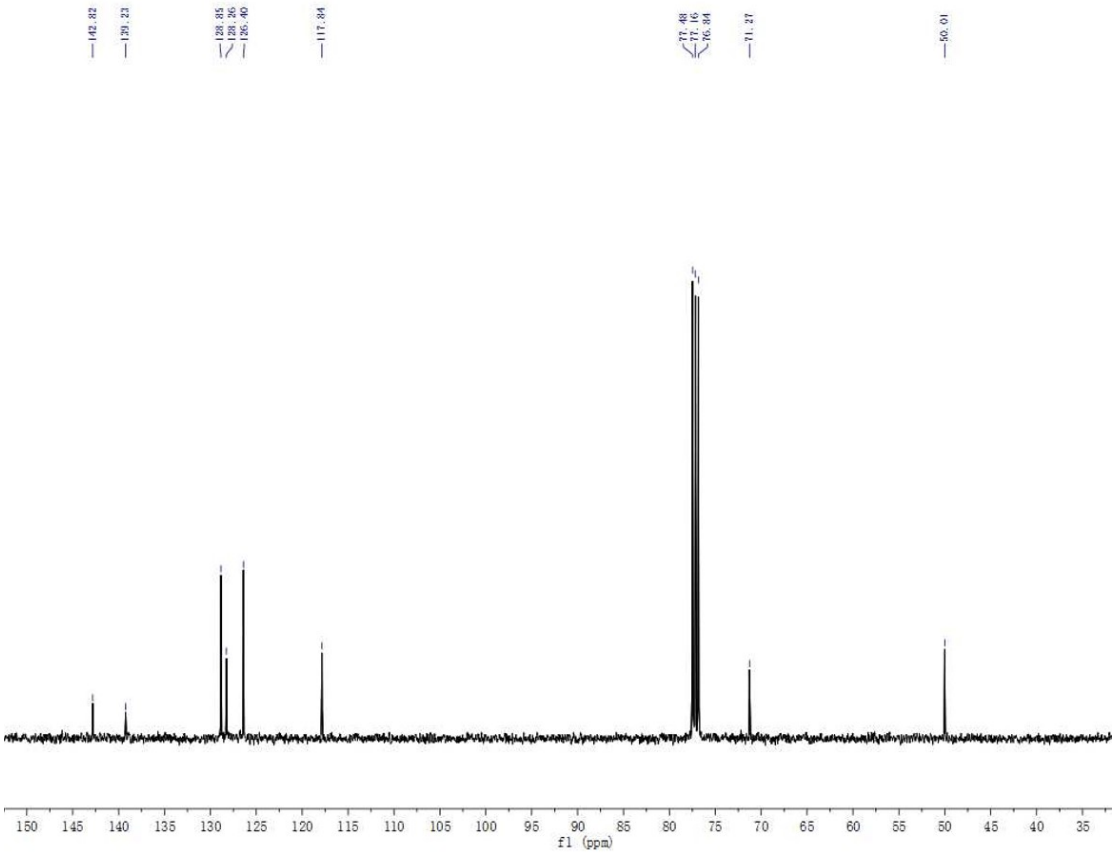

136.98
133.38
131.15
130.76
128.22
127.42
126.74
122.00
77.48
77.16
76.84
71.76
47.56
28.12
23.22

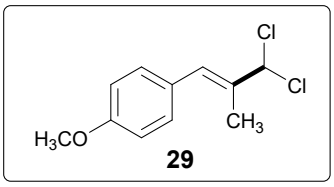

140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
f1 (ppm)


Cl
Cl

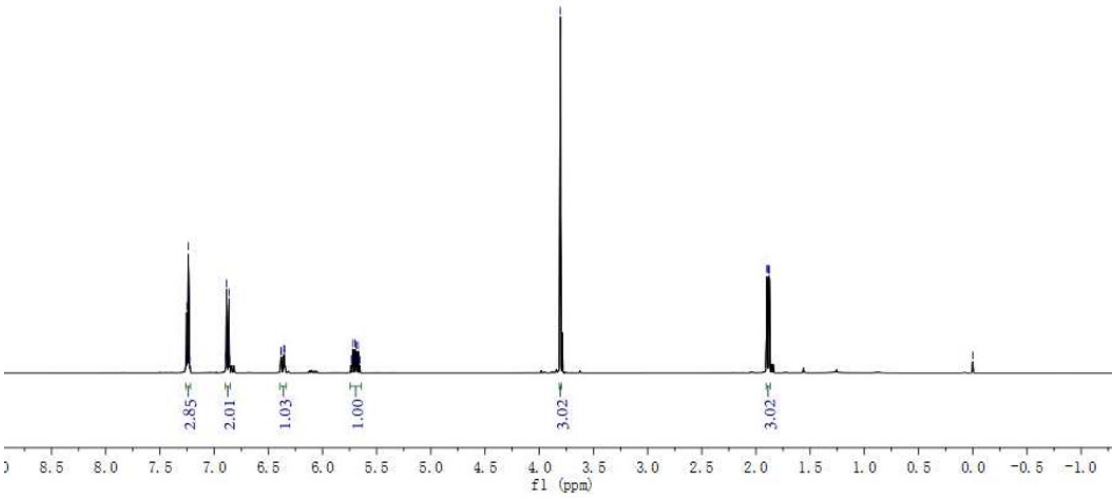
28

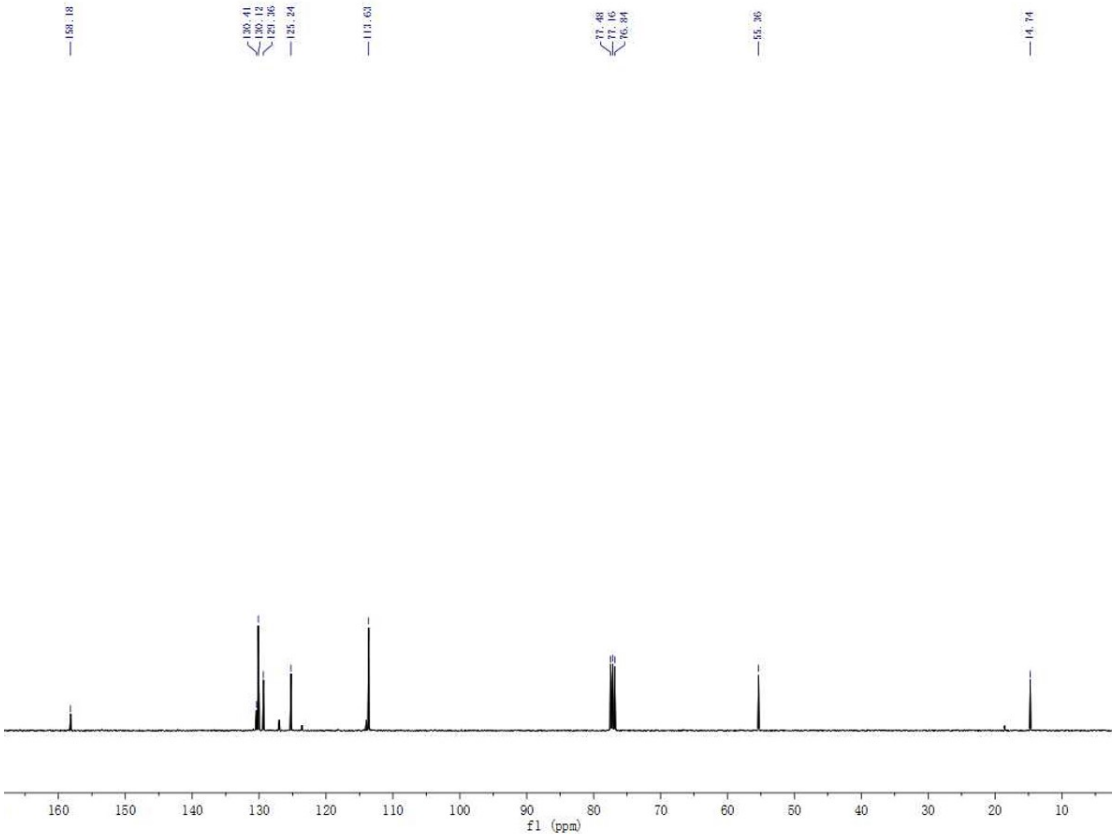

3.88
1.07
1.00
1.00
0.99
2.03
f1 (ppm)

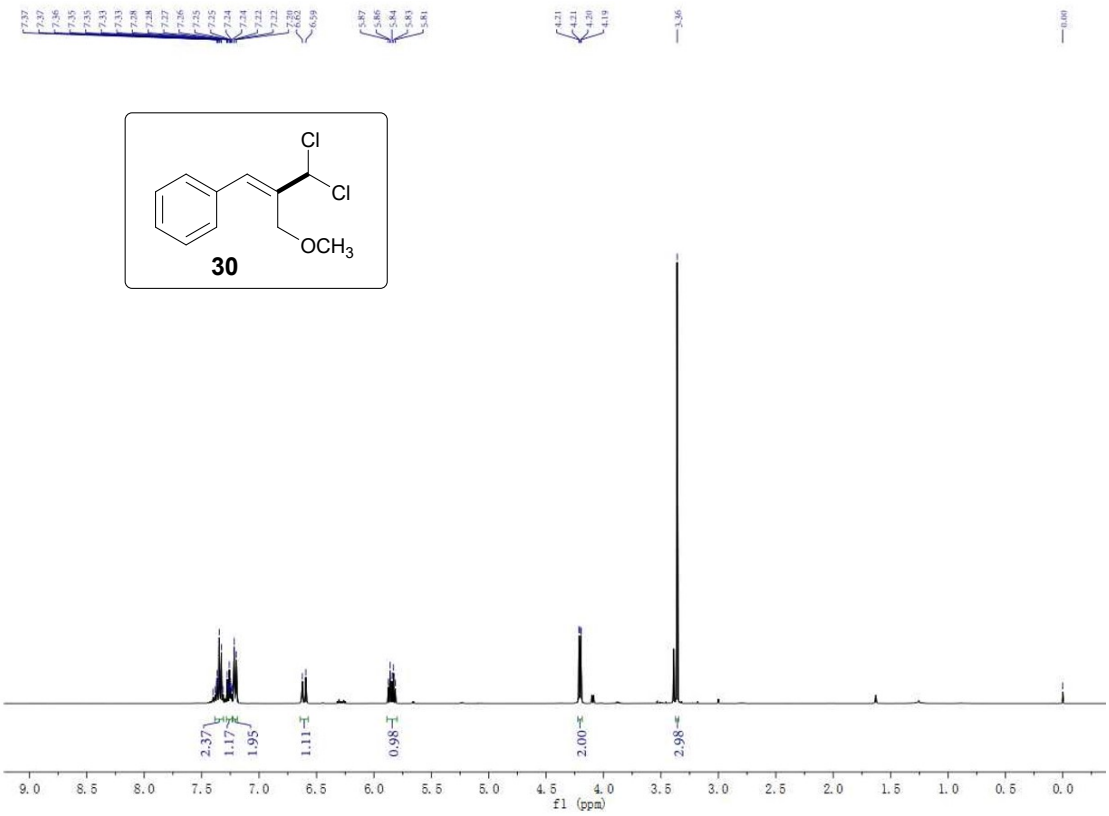

142.82
129.23
128.85
128.26
126.40
117.84
77.48
77.16
76.84
71.27
50.01
f1 (ppm)

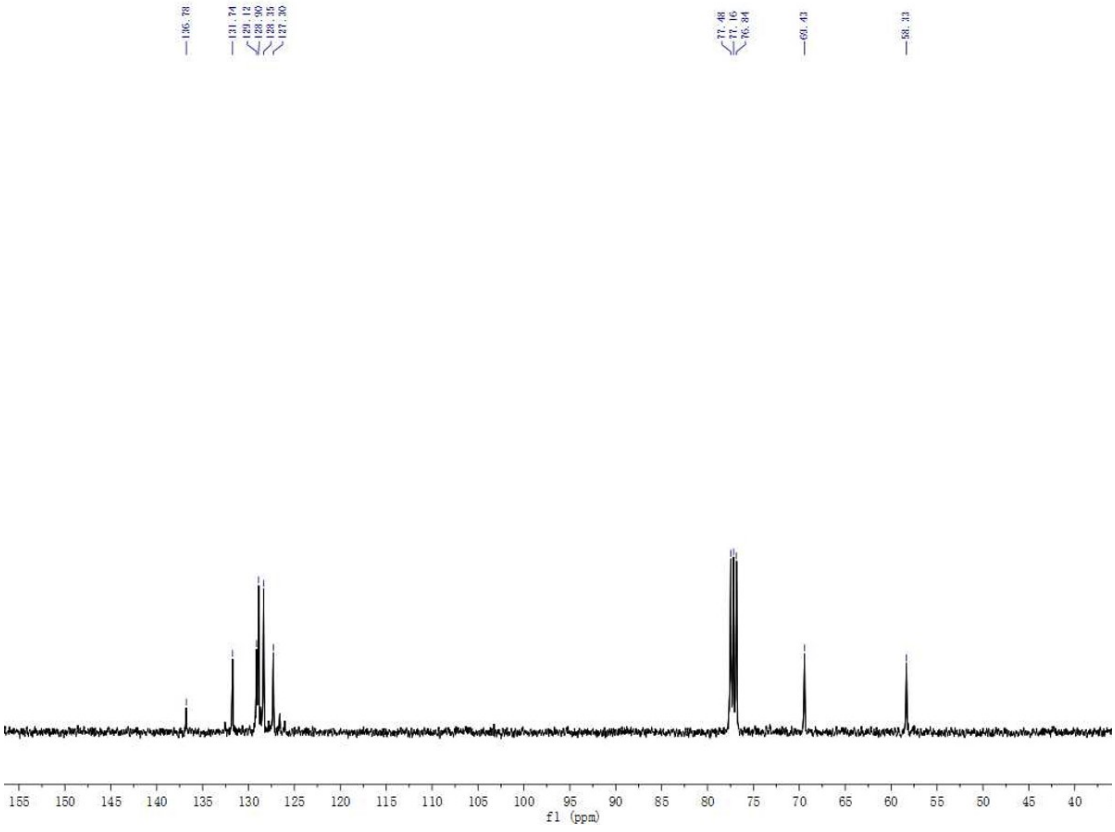


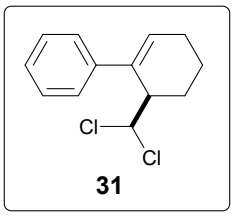
29



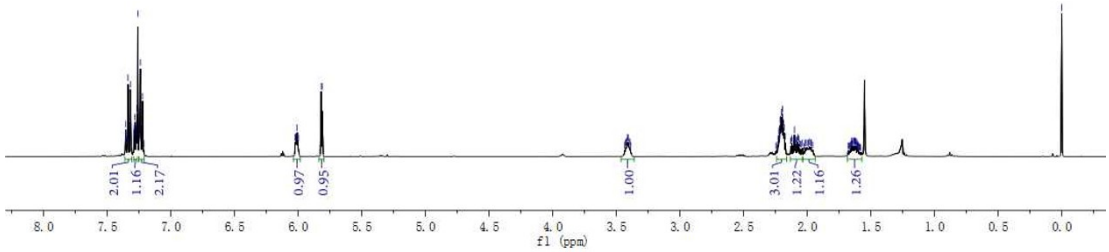


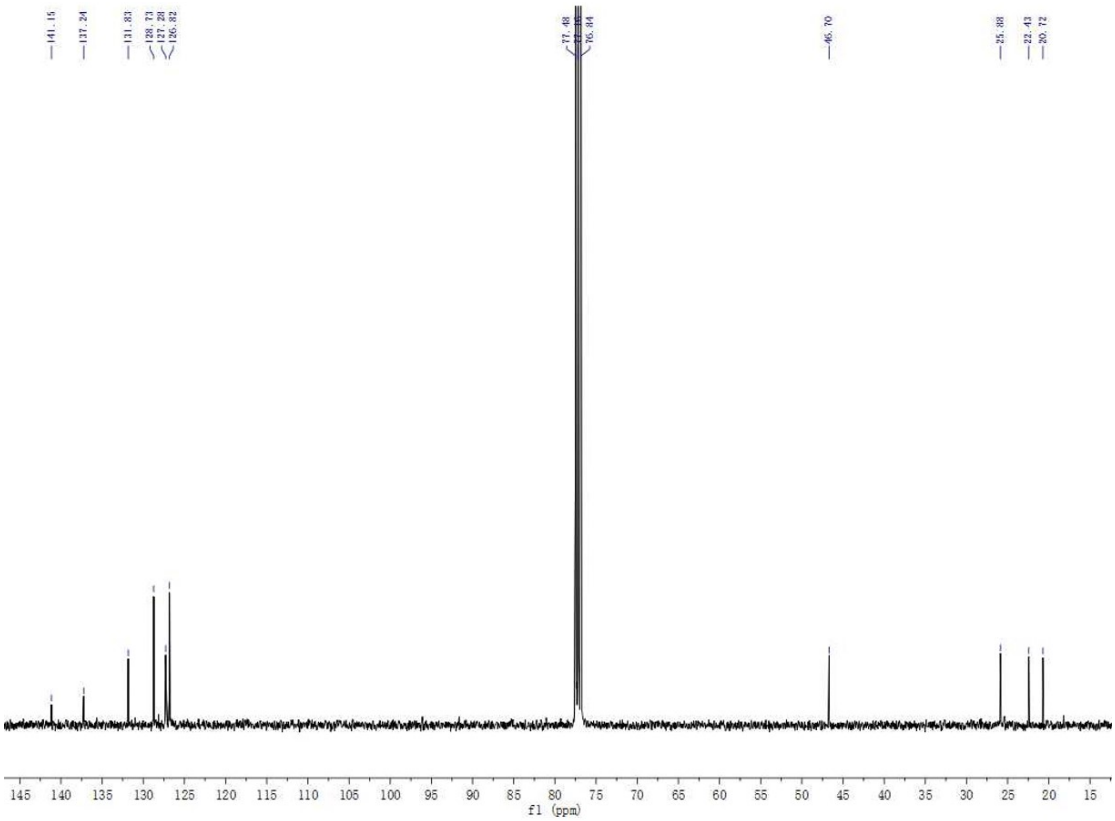

Cl
Cl
OCH3
30
2.37
1.17
1.95
1.11
0.98
2.00
2.98
f1 (ppm)

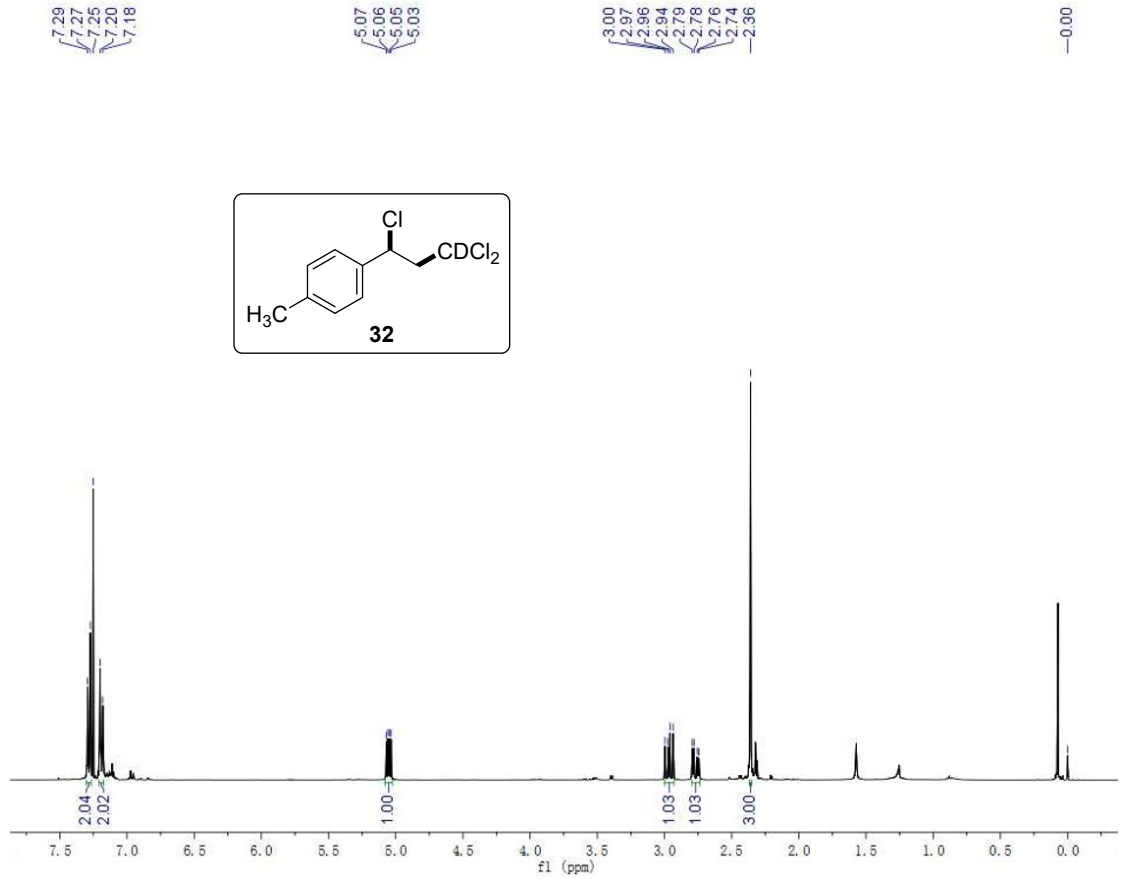

f1 (ppm)

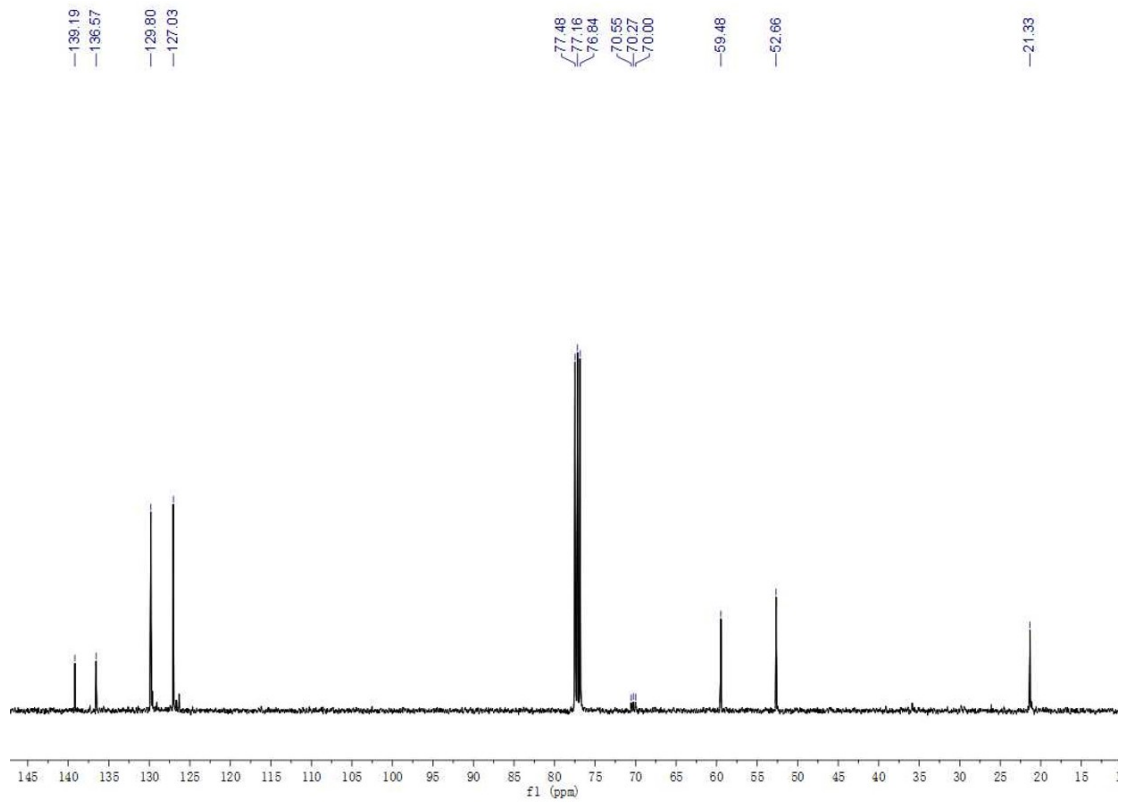

Cl
Cl

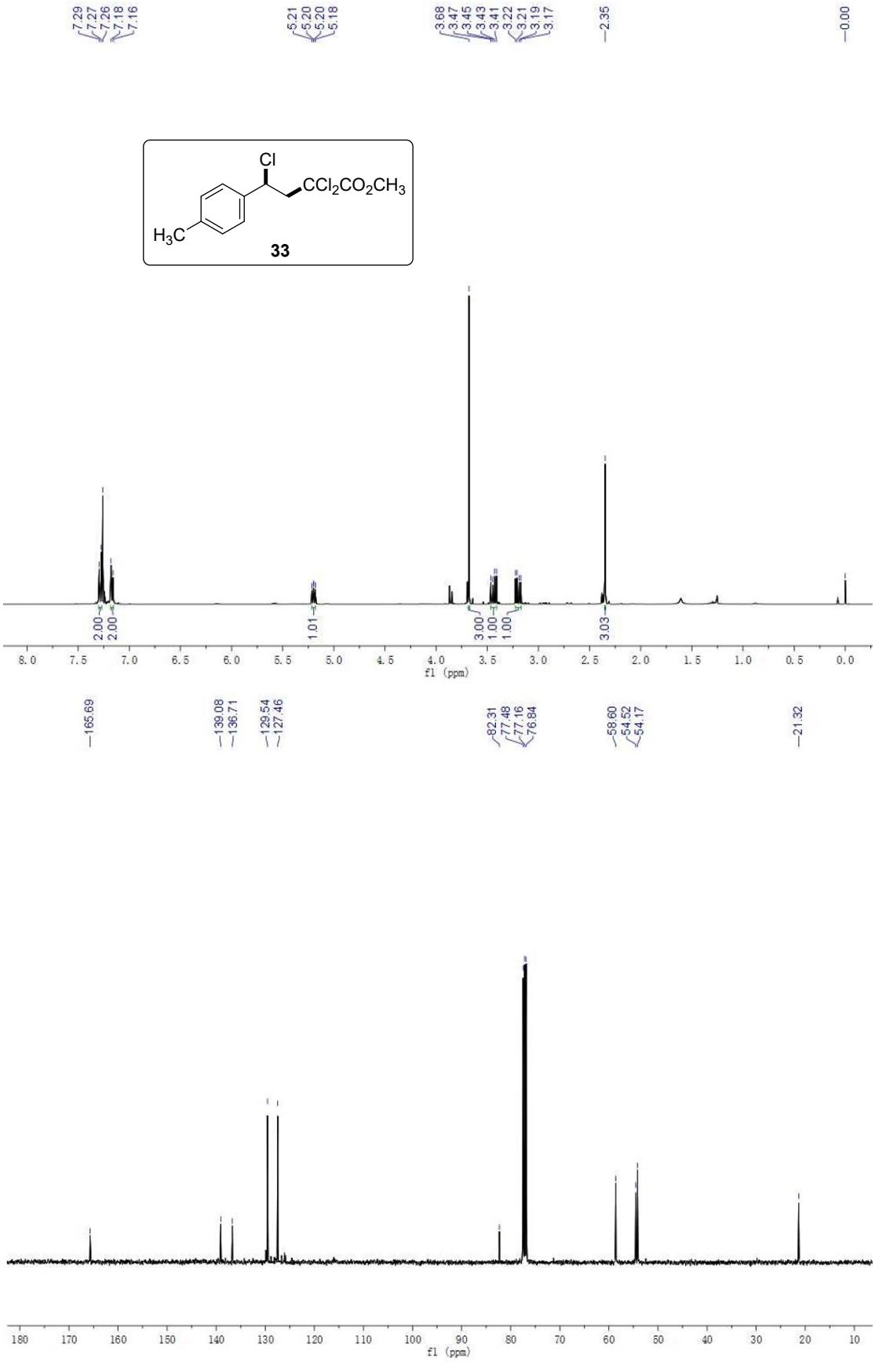
31

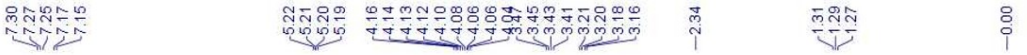

2.01
1.16
2.17
0.97
0.95
1.00
3.01
1.22
1.16
1.26
f1 (ppm)

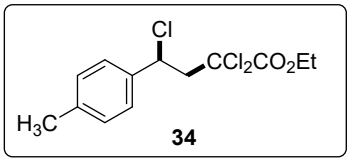

141.15
137.24
131.83
128.73
127.28
126.82
77.48
77.16
76.84
46.70
25.88
22.43
20.72
f1 (ppm)


7.29
7.27
7.25
7.20
7.18
5.07
5.06
5.05
5.03
3.00
2.97
2.96
2.94
2.79
2.78
2.76
2.74
2.36
0.00
Cl
CDCl2
H3C
32
2.04
2.02
1.00
1.03
1.03
3.00
f1 (ppm)

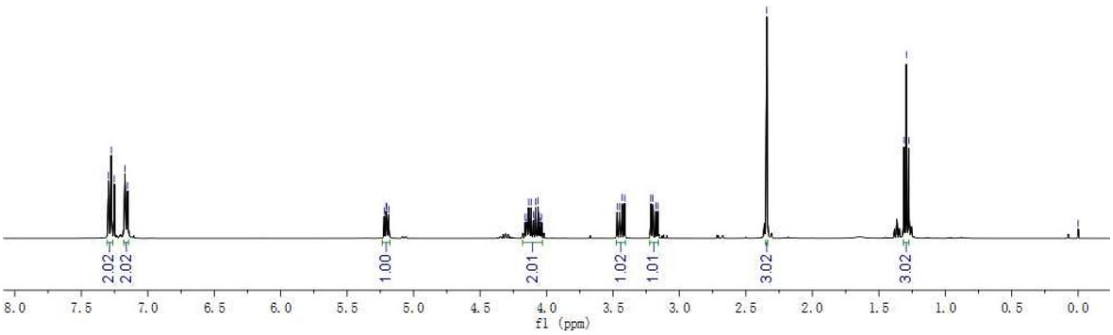

139.19
136.57
129.80
127.03
77.48
77.16
76.84
70.55
70.27
70.00
59.48
52.66
21.33
f1 (ppm)


7.29
7.27
7.26
7.18
7.16
5.21
5.20
5.20
5.18
3.68
3.47
3.45
3.43
3.41
3.22
3.21
3.19
3.17
2.35
0.00
Cl
CCl2CO2CH3
H3C
33
2.00
2.00
1.01
3.00
1.00
1.00
3.03
f1 (ppm)
165.69
139.08
136.71
129.54
127.46
82.31
77.48
77.16
76.84
58.60
54.52
54.17
21.32
f1 (ppm)

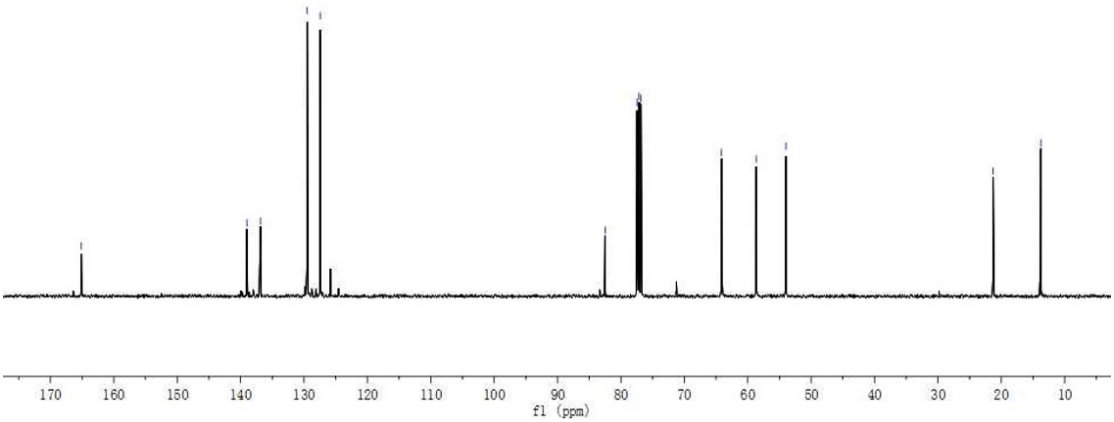

7.30
7.27
7.25
7.17
7.15
5.22
5.21
5.20
5.19
4.16
4.14
4.13
4.12
4.10
4.08
4.06
4.06
4.04
3.47
3.45
3.43
3.41
3.21
3.20
3.18
3.16
2.34
1.31
1.29
1.27
0.00

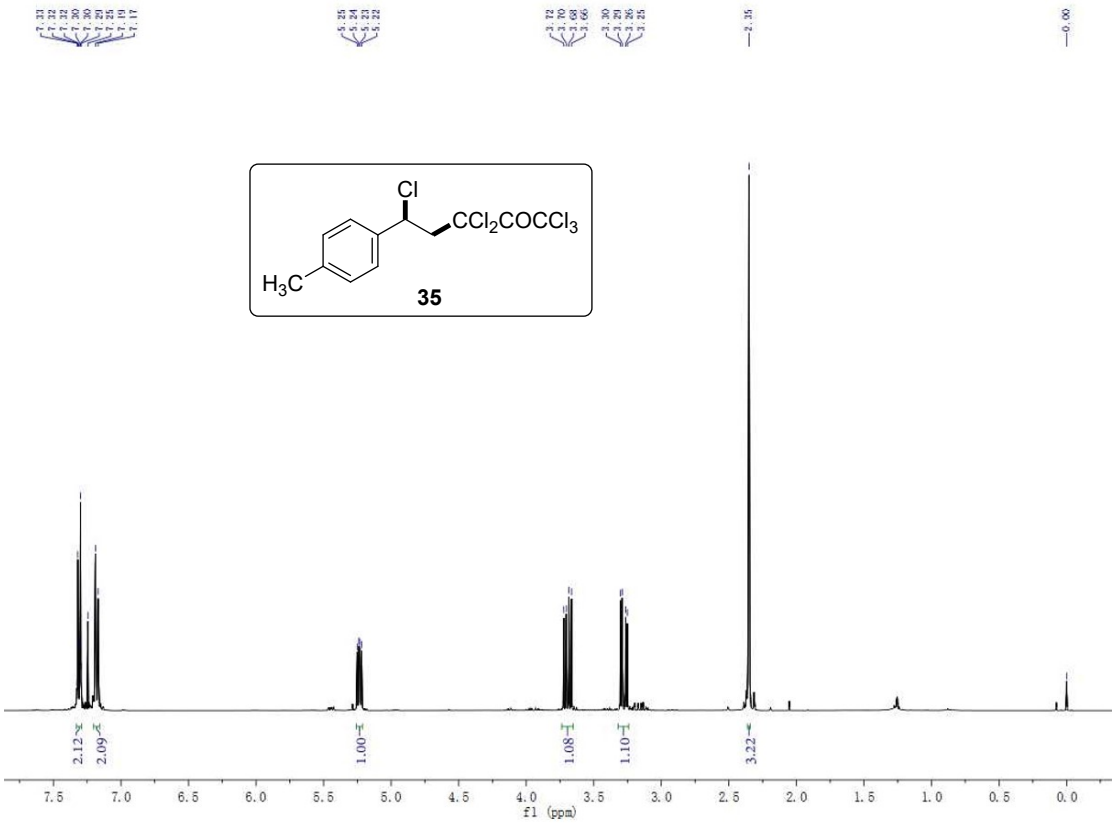

Cl
CCl2CO2Et
H3C

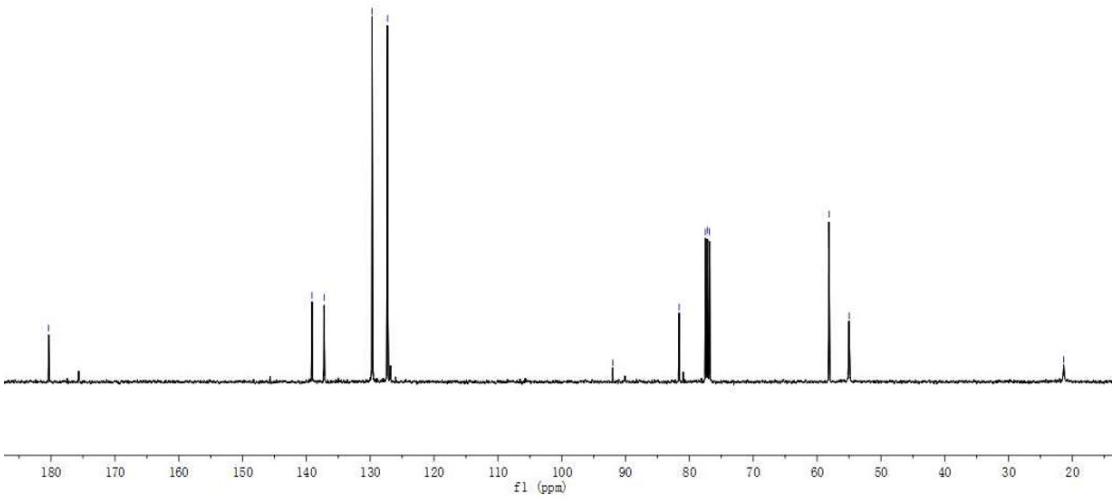
34

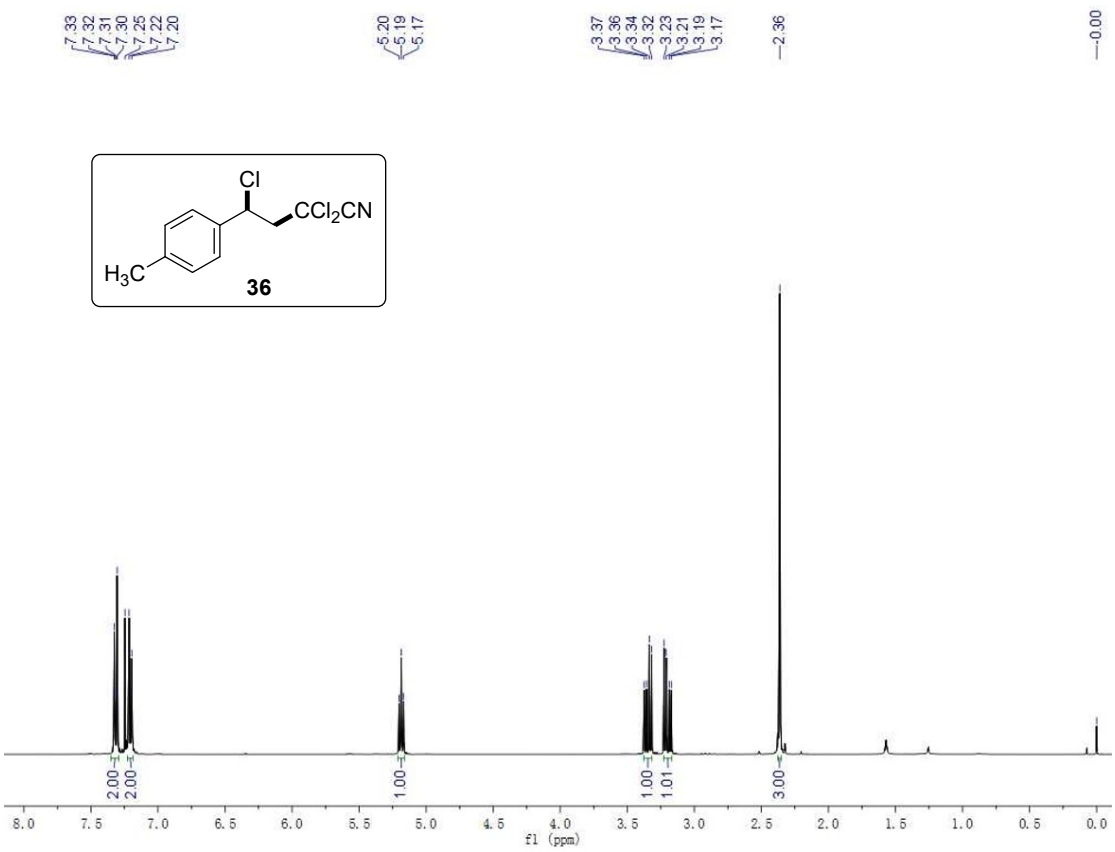

2.02
2.02
1.00
2.01
1.02
1.01
3.02
3.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

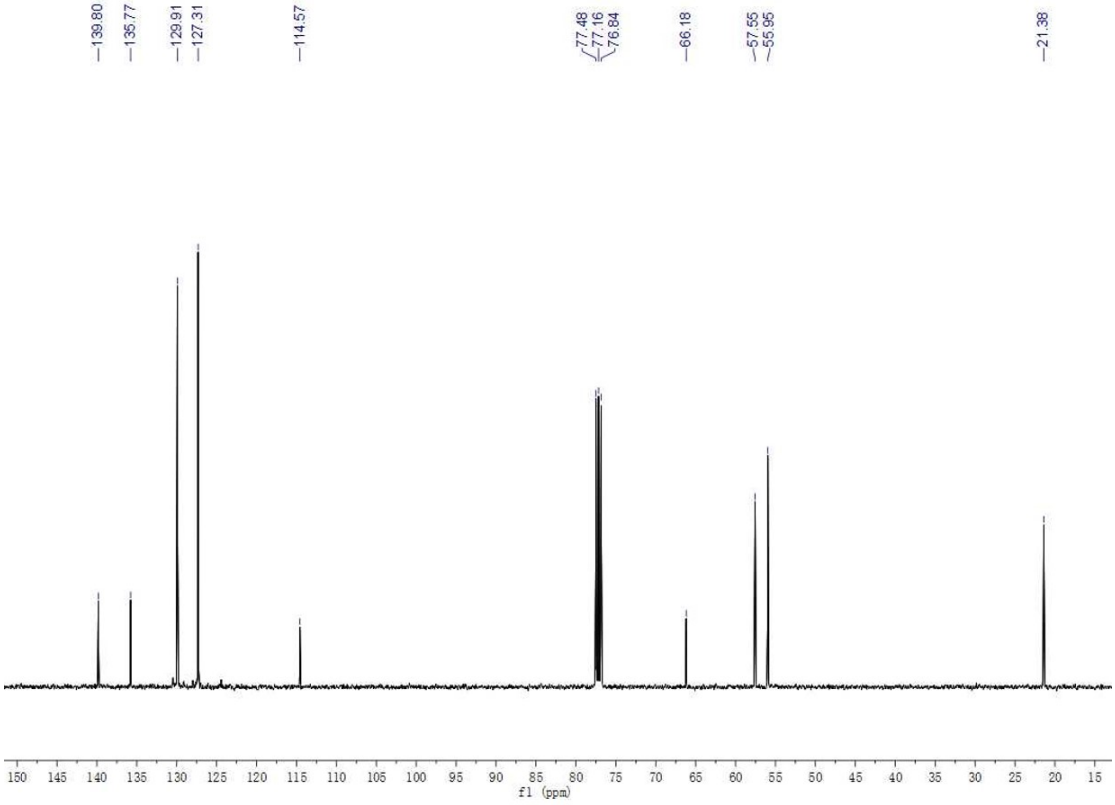

165.13
139.01
136.86
129.49
127.43
82.51
77.48
77.16
76.84
64.15
58.66
53.98
21.29
13.77


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Cl
CCl2COCCl3
H3C
35
2.12
2.09
1.00
1.08
1.10
3.22
f1 (ppm)


f1 (ppm)


7.33
7.32
7.31
7.30
7.25
7.22
7.20
5.20
5.19
5.17
3.37
3.36
3.34
3.32
3.23
3.21
3.19
3.17
2.36
0.00
Cl
CCl2CN
H3C
36
2.00
2.00
1.00
1.00
1.01
3.00
f1 (ppm)


139.80
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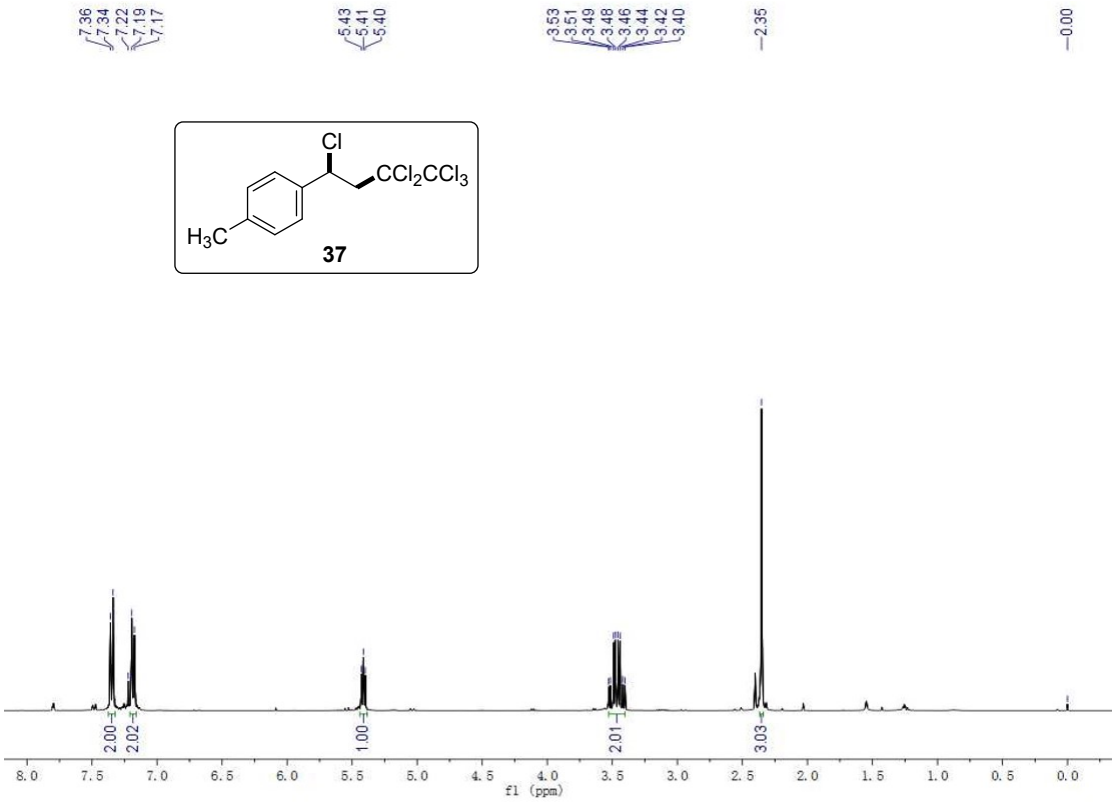
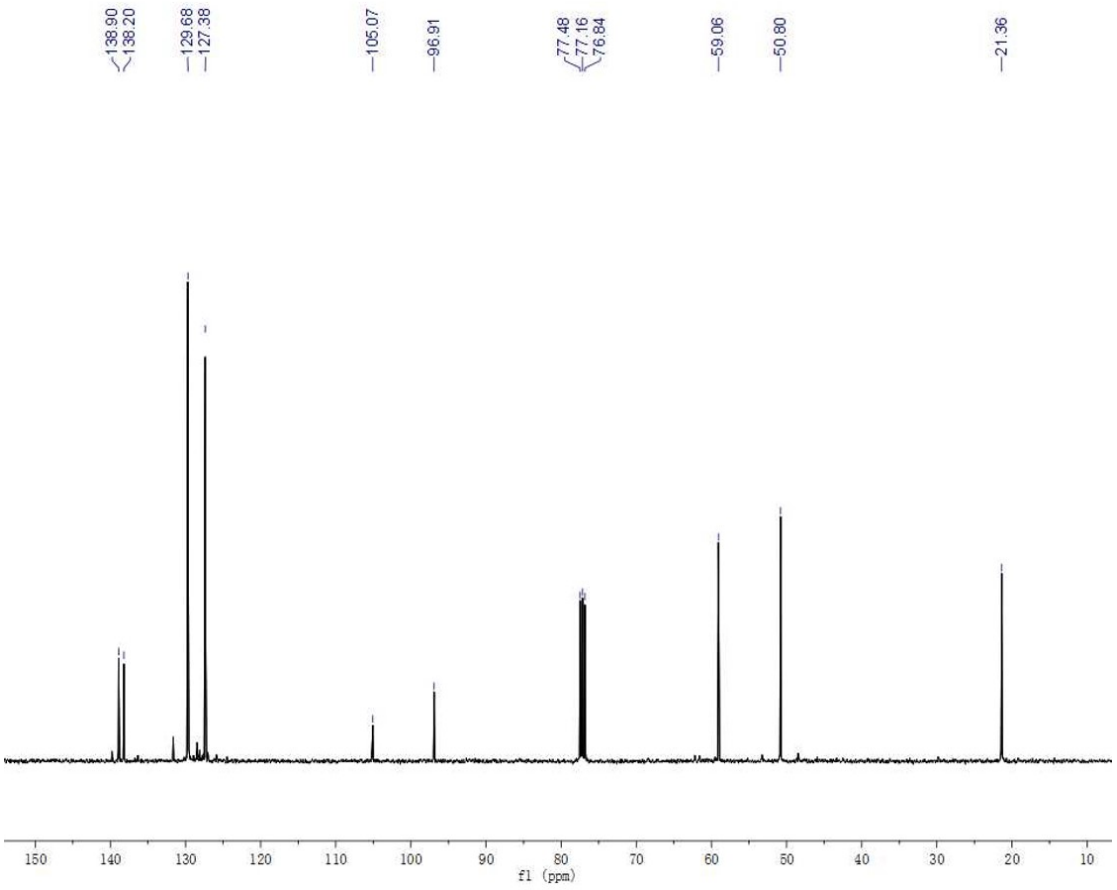
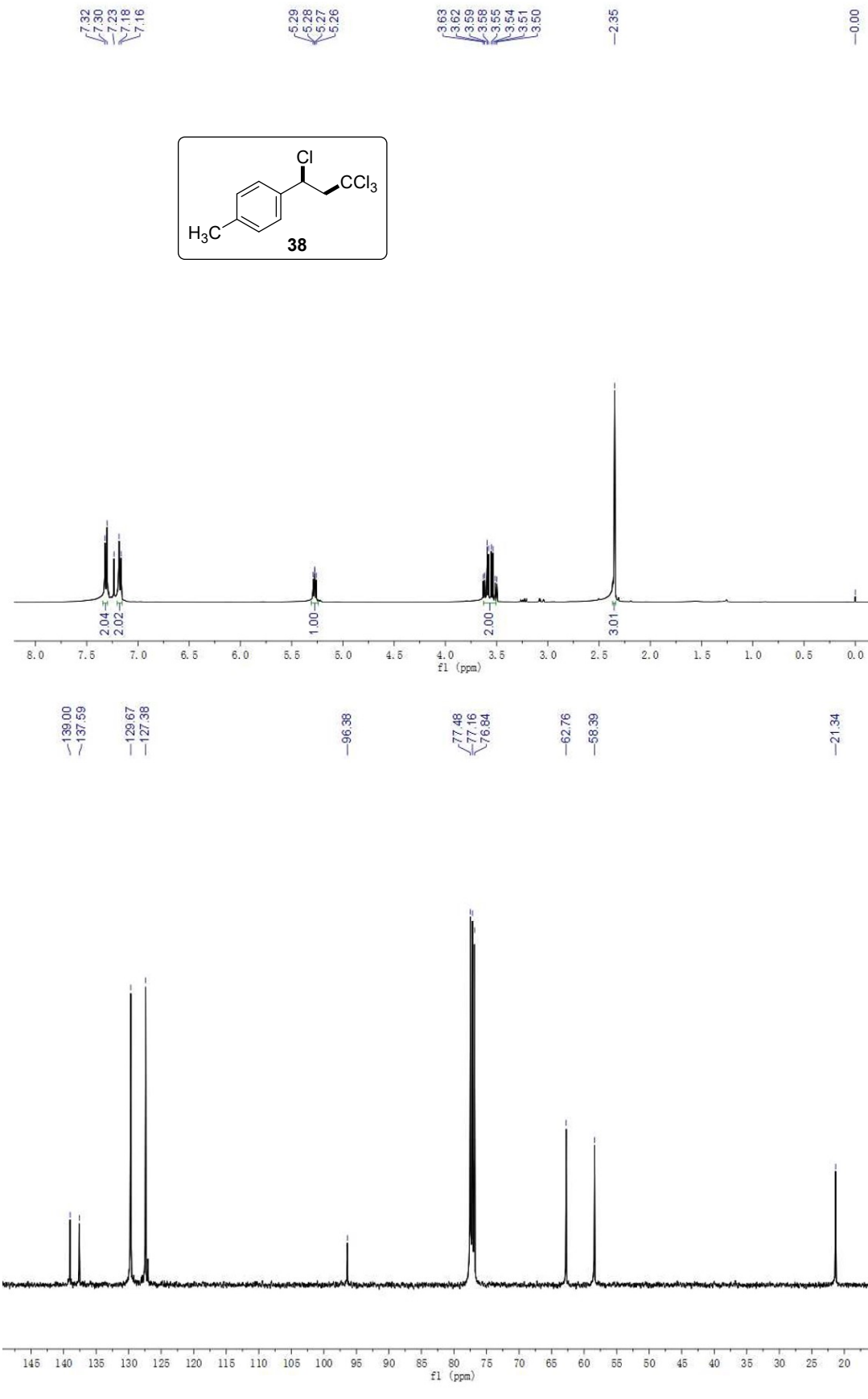
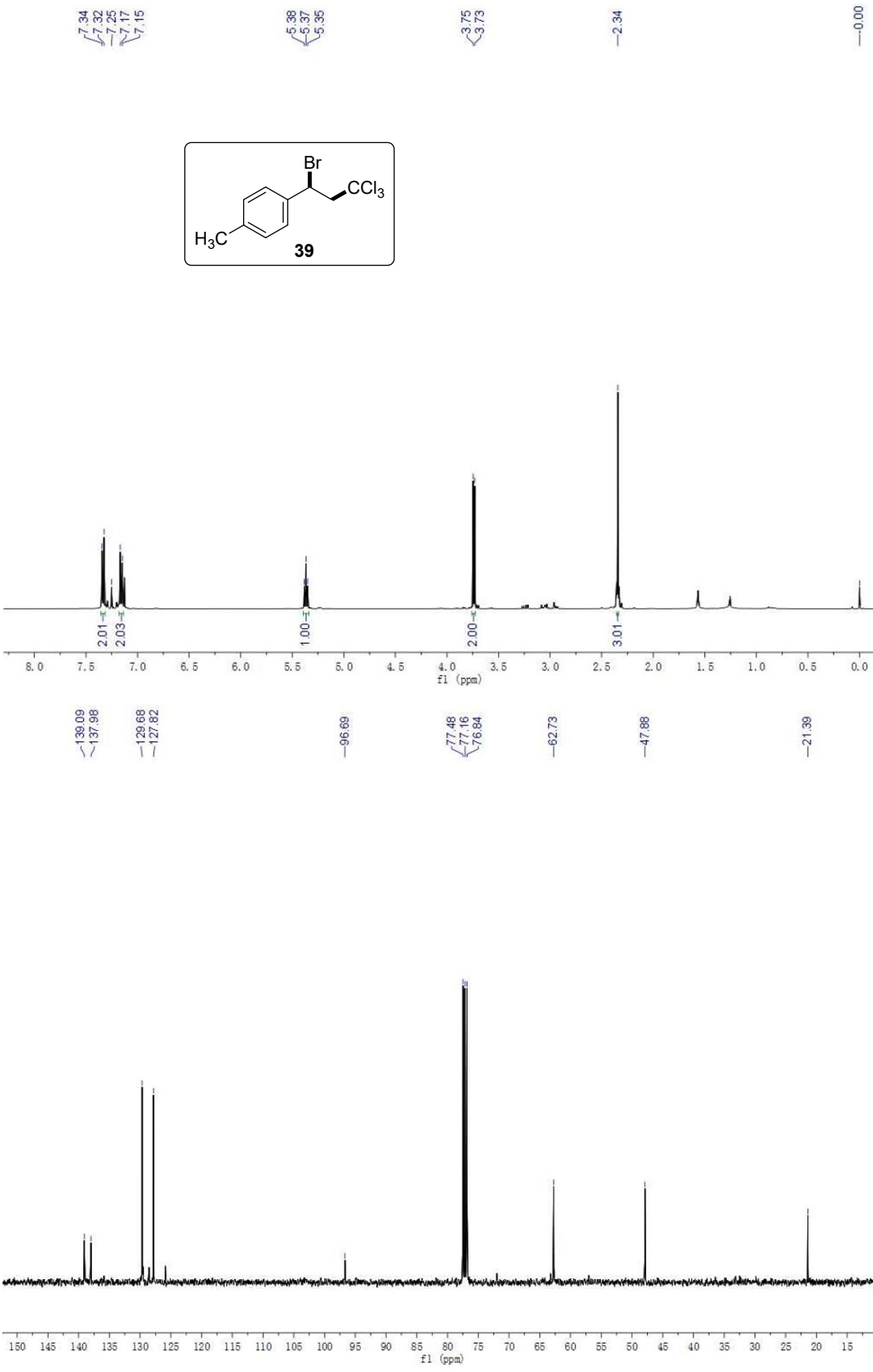
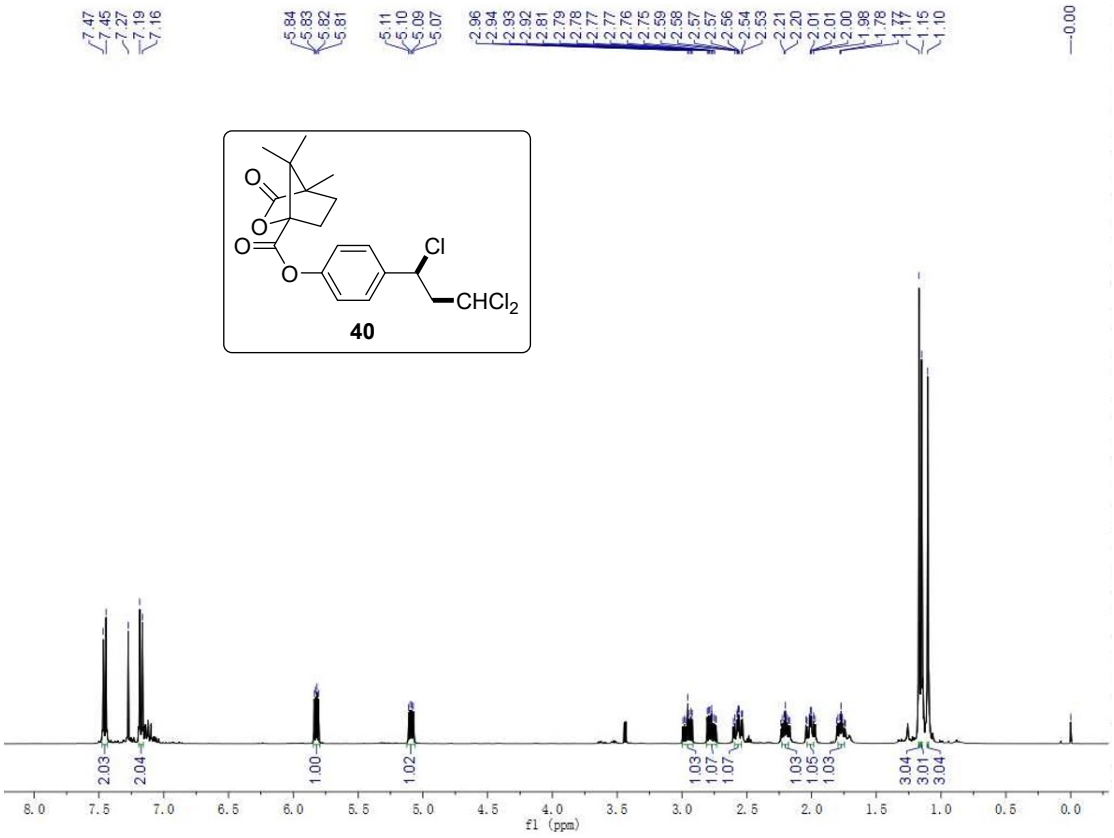
129.91
127.31
114.57
77.48
77.16
76.84
66.18
57.55
55.95
21.38
f1 (ppm)

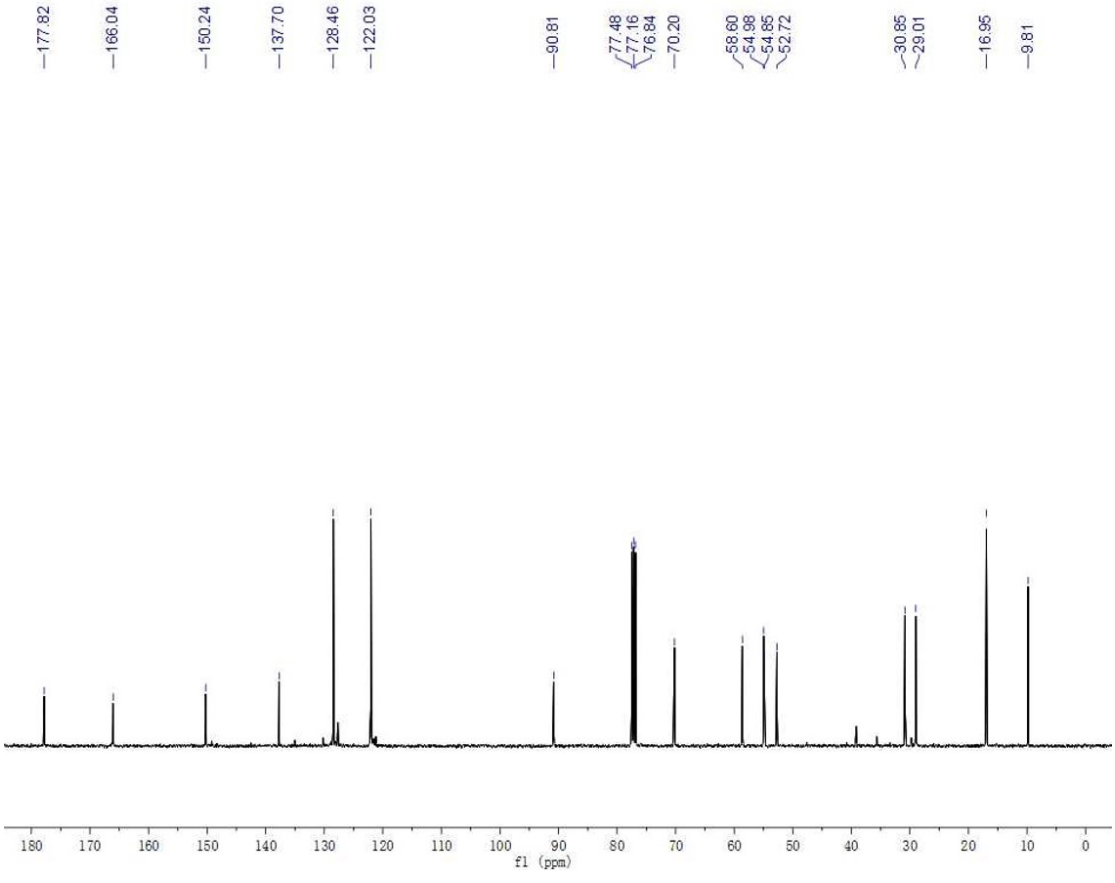

7.36
7.34
7.22
7.19
7.17
5.43
5.41
5.40
3.53
3.51
3.49
3.48
3.46
3.44
3.42
3.40
2.35
0.00
Cl
CCl2CCl3
H3C
37
2.00
2.02
1.00
2.01
3.03
f1 (ppm)

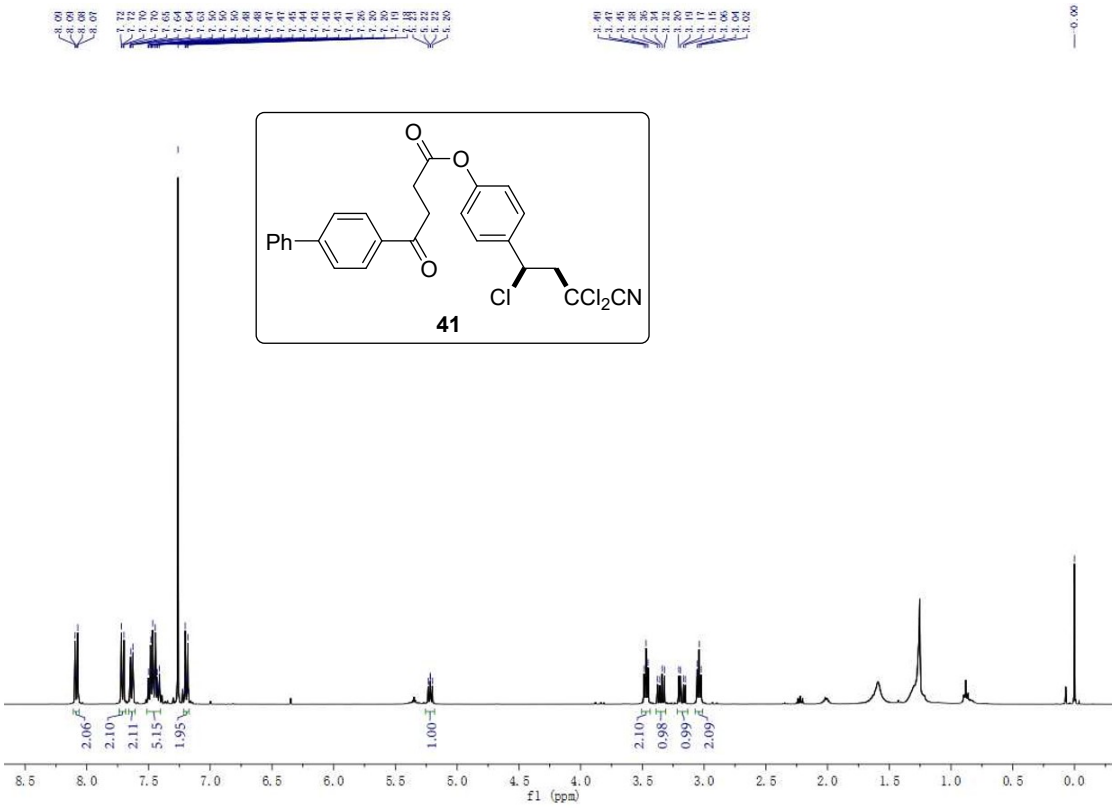

138.90
138.20
129.68
127.38
105.07
96.91
77.48
77.16
76.84
59.06
50.80
21.36
f1 (ppm)

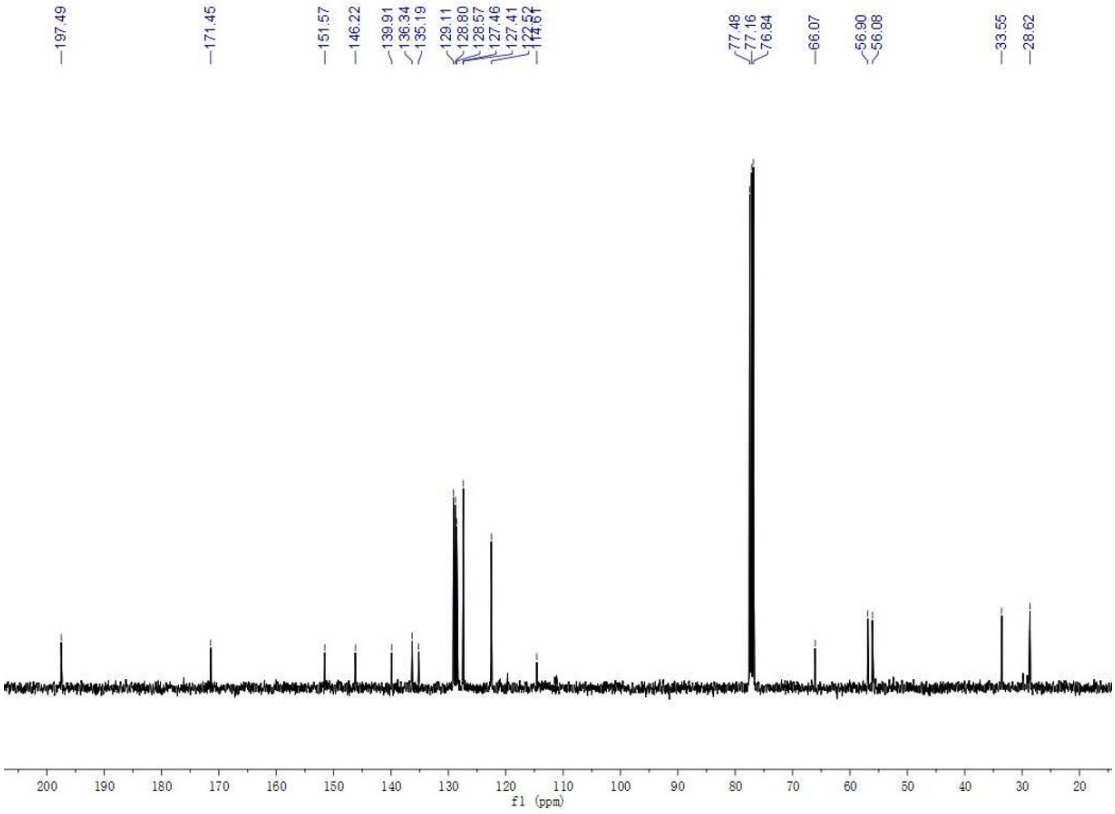

7.32
7.30
7.23
7.18
7.16
5.29
5.28
5.27
5.26
3.63
3.62
3.59
3.58
3.55
3.54
3.51
3.50
2.35
0.00
Cl
CCl3
H3C
38
2.04
2.02
1.00
2.00
3.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
139.00
137.59
129.67
127.38
96.38
77.48
77.16
76.84
62.76
58.39
21.34
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
f1 (ppm)

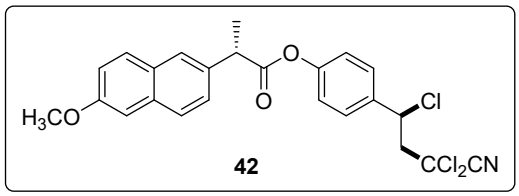

7.34
7.32
7.25
7.17
7.15
5.38
5.37
5.35
3.75
3.73
2.34
0.00
Br
CCl3
H3C
39
2.01
2.03
1.00
2.00
3.01
f1 (ppm)
139.09
137.98
129.68
127.82
96.69
77.48
77.16
76.84
62.73
47.88
21.39
f1 (ppm)


7.47
7.45
7.27
7.19
7.16
5.84
5.83
5.82
5.81
5.11
5.10
5.09
5.07
2.96
2.94
2.93
2.92
2.81
2.79
2.78
2.77
2.76
2.75
2.59
2.58
2.57
2.57
2.56
2.54
2.53
2.21
2.20
2.01
2.01
2.00
1.98
1.78
1.77
1.77
1.15
1.10
0.00
O
O
O
O
Cl
CHCl2
40
2.03
2.04
1.00
1.02
1.03
1.07
1.07
1.03
1.05
1.03
3.04
3.01
3.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


177.82
166.04
150.24
137.70
128.46
122.03
90.81
77.48
77.16
76.84
70.20
58.60
54.98
54.85
52.72
30.85
29.01
16.95
9.81
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

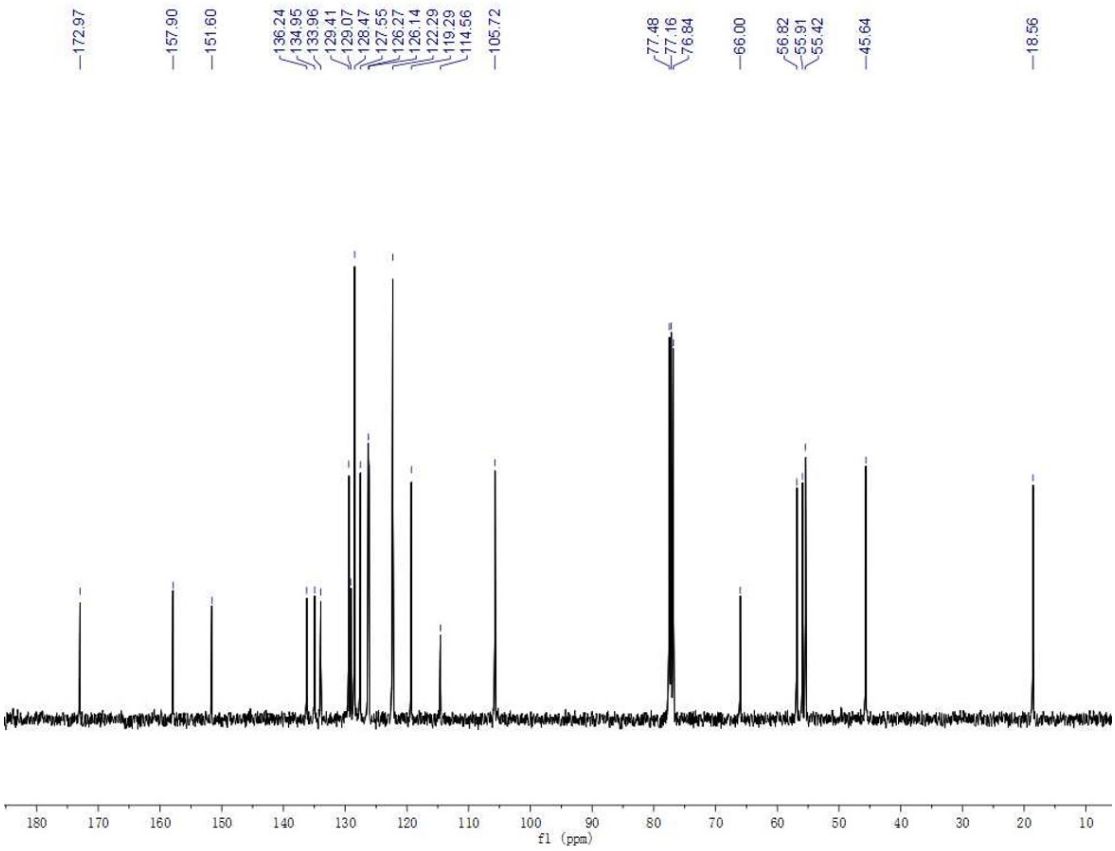

Ph
O
O
O
Cl
CCl2CN
41
f1 (ppm)

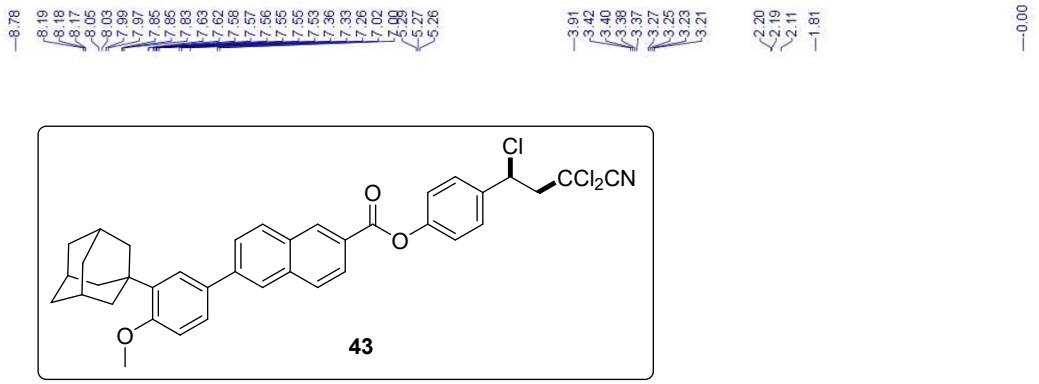

f1 (ppm)


H3CO
O
O
Cl
CCl2CN

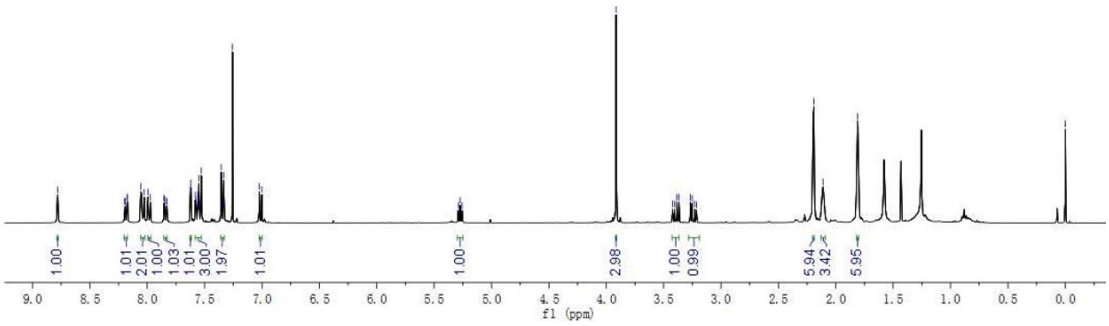
42

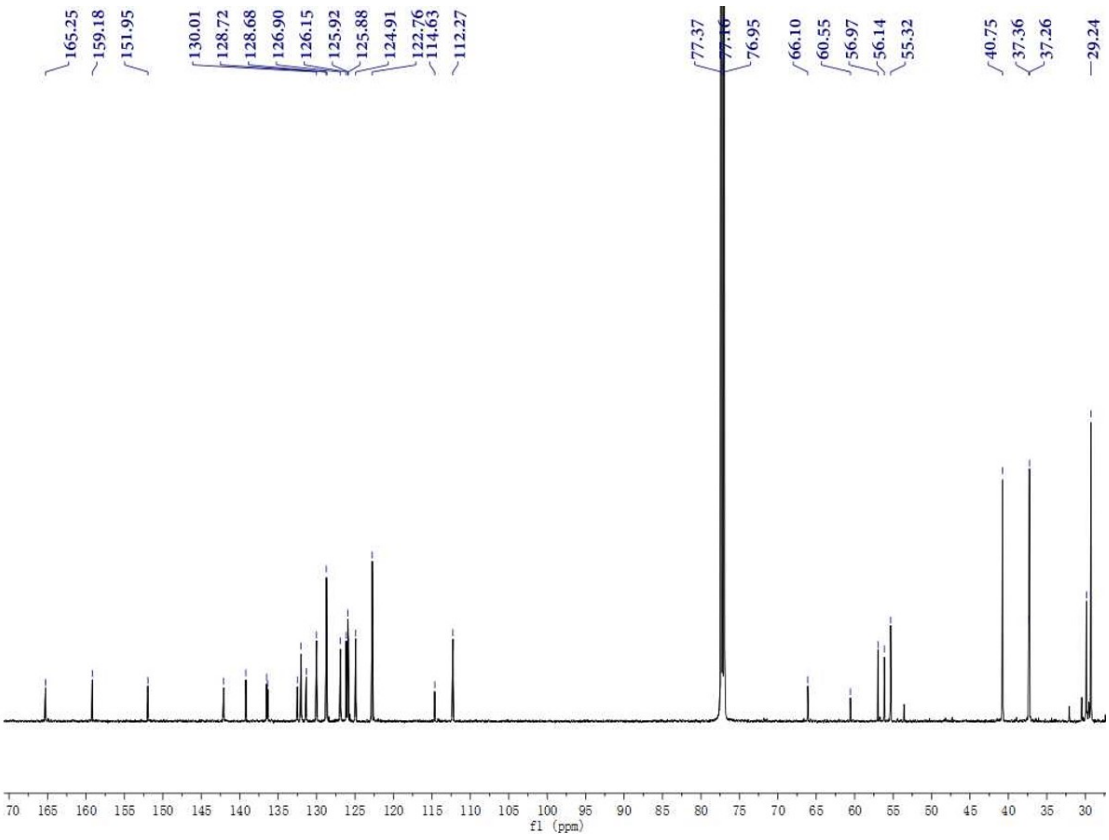
2.93
1.13
1.87
2.17
1.85
0.78
1.23
2.94
1.00
0.88
2.90
f1 (ppm)


172.97
157.90
151.60
136.24
134.95
133.96
129.41
129.07
128.47
127.55
126.27
126.14
122.29
119.29
114.56
105.72
77.48
77.16
76.84
66.00
56.82
55.91
55.42
45.64
18.56
f1 (ppm)



43





Reference

1 W. L. F. Armarego and C. L. L. Chai, Purification of Laboratory Chemicals, Bulterworth-Heinemann, Oxford, UK, 7th edition, 2013.

2 T. Patra, M. Das, C. G. Daniliuc and F. Glorius, *Nature Catalysis*, 2021, **4**, 54-61.

3 Z. Liu, J. Xu, W. Ruan, C. Fu, H.-J. Zhang and T.-B. Wen, *Dalton Trans*., 2013, **42**, 11976-11980.

4 K. Thommes, B. Içli, R. Scopelliti and K. Severin, *Chem. Eur. J*., 2007, **13**, 6899-6907.

5 Y.-X. Zhang, R.-X. Jin, H. Yan and X.-S. Wang, *Org. Lett*., 2018, **20**, 7283-7287.

6 Y. Bao, G.-Y. Wang, Y.-X. Zhang, K.-J. Bian and X.-S. Wang, *Chem. Sci*., 2018, **9**, 2986-2990.

7 H. Nishiyama, H. Ikeda, T. Saito, B. Kriegel, H. Tsurugi, J. Arnold and K. Mashima, *J. Am. Chem. Soc*., 2017, **139**, 6494-6505.

8 B. Chen, C. Fang, P. Liu and J. M. Ready, *Angew. Chem. Int. Ed.,* 2017, **56**, 8780-8784