Supporting Information

Difunctionalization of unactivated olefins via selective electrochemical chlorosulfuration or chlorosulfoxidation

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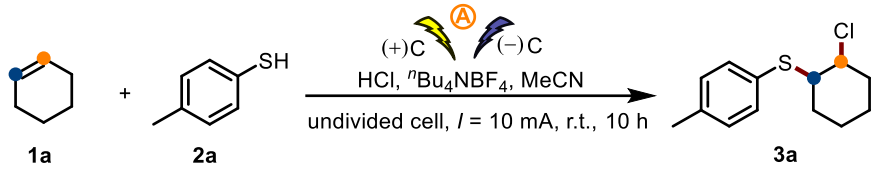
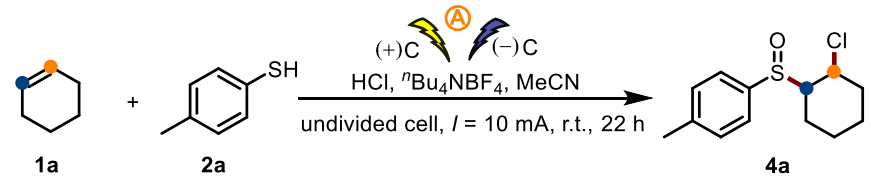
1. General Information

Unless otherwise noted, reagents were purchased from commercial sources and were used as received. ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance 400 Ultrashield NMR spectrometers. Chemical shifts (δ) were given in parts per million (ppm) and were measured downfield from internal tetramethylsilane. High-resolution mass spectrometry (HRMS) data were obtained on an FTICR-MS instrument (Ionspec 7.0 T). The melting points were determined on an X-4 microscope melting point apparatus and are uncorrected. Conversion was monitored by thin layer chromatography (TLC). Flash column chromatography was performed over silica gel (100-200 mesh).

2. General procedure for the electrolysis

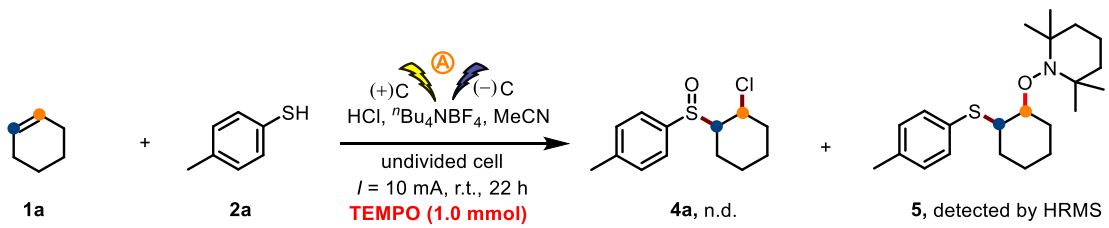


An oven-dried 10 mL undivided cell equipped with two graphite sheet electrodes (10 mm × 10 mm × 3 mm) was charged with cyclohexene (50.0 μL, 0.5 mmol, 1.0 equiv.), *p*-toluenethiol (124.2 mg, 1.0 mmol, 2.0 equiv.), concentrated HCl (219.0 μL, 1.0 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (329.3 mg, 1.0 mmol, 2.0 equiv.), and CH_3CN (5 mL). The stirred solution was electrolyzed at a current of 10.0 mA for 10 h at room temperature. The reaction mixture was concentrated in vacuo, and the residue was purified by column chromatography on silica gel to afford the desired product (petroleum ether/ethyl acetate).



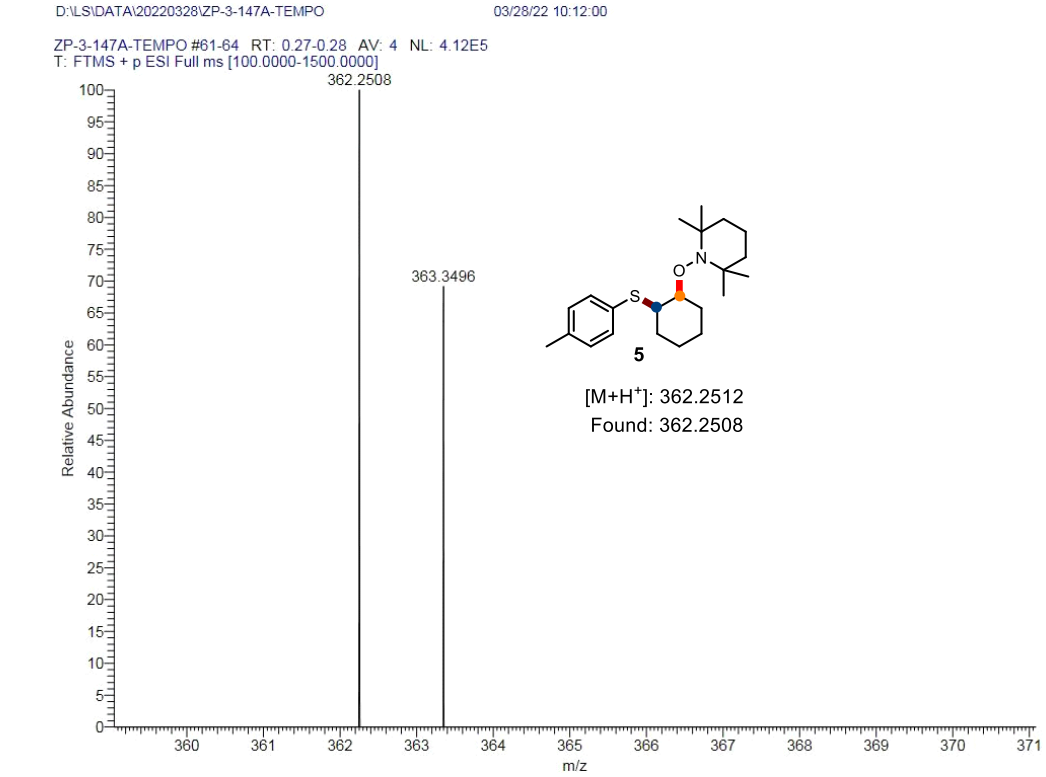
An oven-dried 10 mL undivided cell equipped with two graphite sheet electrodes (10 mm × 10 mm × 3 mm) was charged with cyclohexene (50.0 μL, 0.5 mmol, 1.0 equiv.), *p*-toluenethiol (124.2 mg, 1.0 mmol, 2.0 equiv.), concentrated HCl (219.0 μL, 1.0 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (329.3 mg, 1.0 mmol, 2.0 equiv.), and CH_3CN (5 mL). The stirred solution was electrolyzed at a current of 10.0 mA for 22 h at room temperature. The reaction mixture was concentrated in vacuo, and the residue was purified by column chromatography on silica gel to afford the desired product (petroleum ether/ethyl acetate). The target chlorosulfoxides were obtained as a pair of diastereoisomers since two stereogenic centers were generated. Some compounds show one point on TLC, so we give one spectrum of their isomers, while some compounds could be separated by TLC, and we give two spectrums of their isomers.

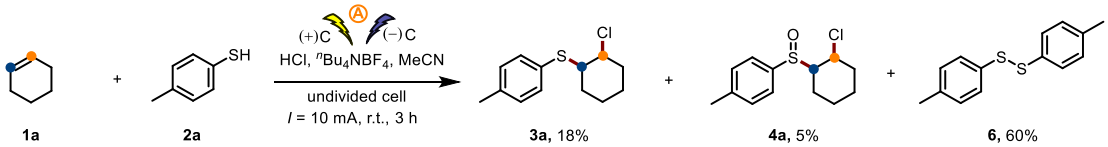
3. Mechanistic Studies



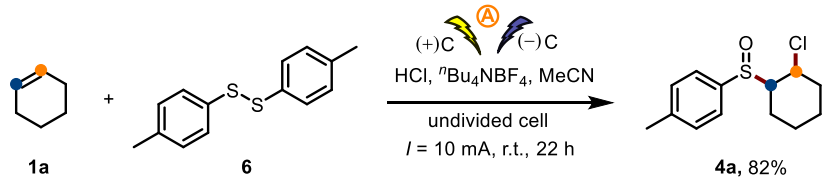
To a 10 mL oven-dried undivided bottle was added cyclohexene (50.0 μL, 0.5 mmol, 1.0 equiv.), *p*-toluenethiol (124.2 mg, 1.0 mmol, 2.0 equiv.), concentrated HCl (219.0 μL, 1.0 mmol, 2.0 equiv.),

$^{n}Bu_4NBF_4$ (329.3 mg, 1.0 mmol, 2.0 equiv.), TEMPO (156.3 mg, 1.0 mmol, 2.0 equiv.) and MeCN (5 mL). The stirred solution was electrolyzed at a current of 10.0 mA for 22 h at room temperature. The reaction was completely suppressed. The radical trapping product **5** can be observed by HR-MS (positive mode ESI).

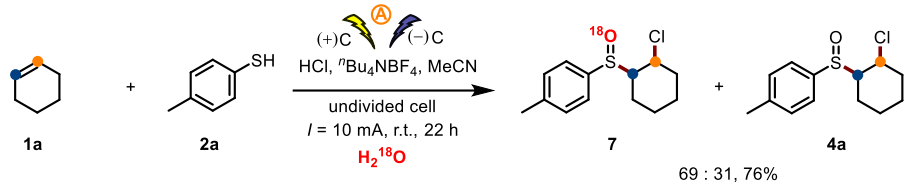




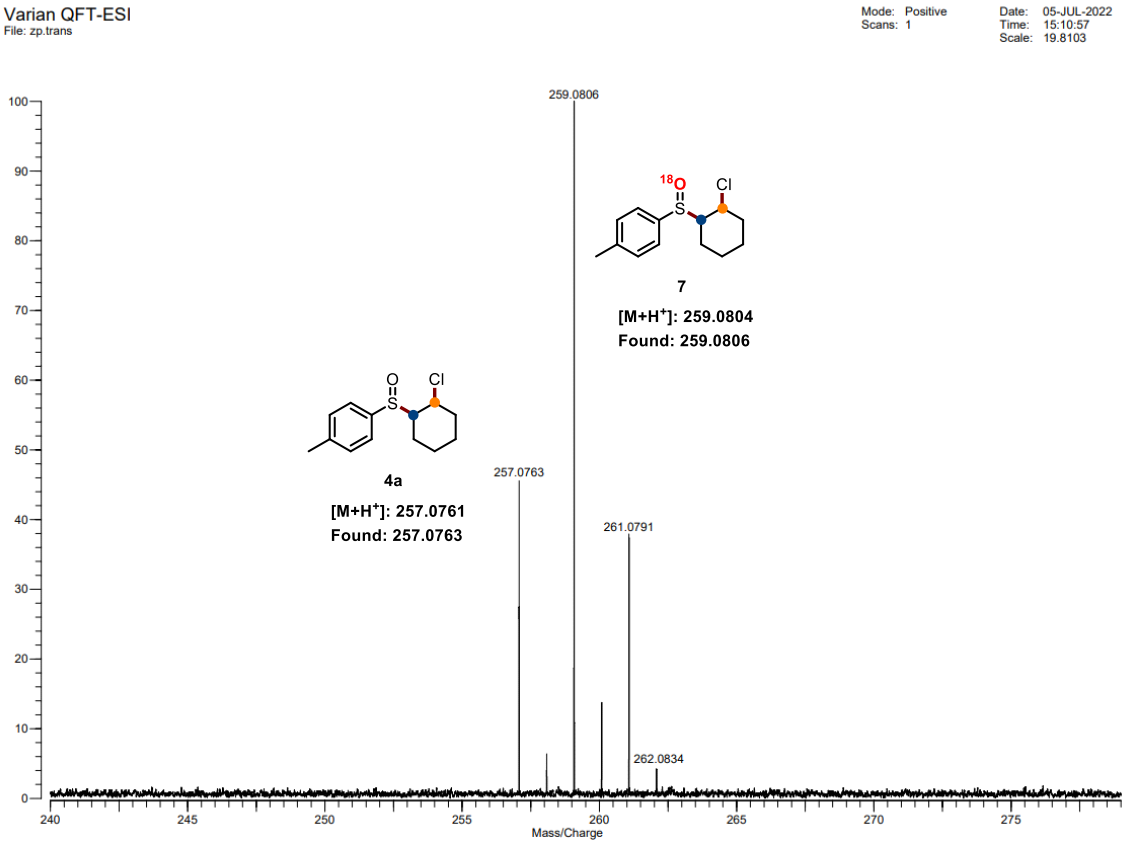
To a 10 mL oven-dried undivided bottle was added cyclohexene (50.0 μL, 0.5 mmol, 1.0 equiv.), *p*-toluenethiol (124.2 mg, 1.0 mmol, 2.0 equiv.), concentrated HCl (219.0 μL, 1.0 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (329.3 mg, 1.0 mmol, 2.0 equiv.), and MeCN (5 mL). The stirred solution was electrolyzed at a current of 10.0 mA for 3 h at room temperature. 1,2-di-*p*-tolyldisulfane **6** can be obtained in 60% isolated yield.



To a 10 mL oven-dried undivided bottle was added cyclohexene (50.0 μL, 0.5 mmol, 1.0 equiv.), 1,2-di-p-tolyldisulfane (246.4 mg, 1.0 mmol, 2.0 equiv.), concentrated HCl (219.0 μL, 1.0 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (329.3 mg, 1.0 mmol, 2.0 equiv.), and MeCN (5 mL). The stirred solution was electrolyzed at a current of 10.0 mA for 22 h at room temperature. The desired product **4a** can be obtained in 82% isolated yield.

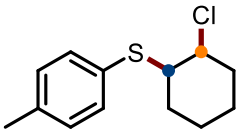


To a 10 mL oven-dried undivided bottle was added cyclohexene (50.0 μL, 0.5 mmol, 1.0 equiv.), *p*-toluenethiol (124.2 mg, 1.0 mmol, 2.0 equiv.), concentrated HCl (219.0 μL, 1.0 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (329.3 mg, 1.0 mmol, 2.0 equiv.), $H_2{}^{18}O$ (1.0 g) and MeCN (5 mL). The stirred solution was electrolyzed at a current of 10.0 mA for 22 h at room temperature. The desired product **4a** and compound **7** can be obtained in 69:31.



4. Characterization Data for Electrolysis Products

((*trans*)-2-chlorocyclohexyl)(p-tolyl)sulfane (3a)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether) to give **3a** as a colorless oil (89.1 mg, 74% yield).

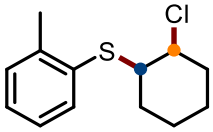
Rf = 0.5 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 7.8 Hz, 2H), 7.12 (d, J = 7.7 Hz, 2H), 4.06 – 3.92 (m, 1H), 3.28 – 3.18 (m, 1H), 2.34 (s, 3H), 2.28 – 2.15 (m, 2H), 1.79 – 1.71 (m, 2H), 1.69 – 1.63 (m, 1H), 1.57 – 1.52 (m, 1H), 1.44 – 1.34 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 134.6, 133.6, 129.8, 62.2, 56.7, 33.8, 32.6, 26.2, 24.3, 21.1.

HRMS (ESI): Calcd for $C_{13}H_{18}ClS^+$ $[M+H]^+$: 241.0812; found: 241.0810.

((*trans*)-2-chlorocyclohexyl)(o-tolyl)sulfane (3b)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether) to give **3b** as a colorless oil (77.1 mg, 64% yield).

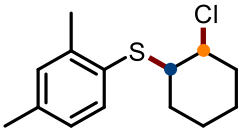
Rf = 0.5 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 6.9 Hz, 1H), 7.21 (t, J = 5.9 Hz, 1H), 7.18 – 7.13 (m, 2H), 3.49 – 3.39 (m, 1H), 2.93 – 2.81 (m, 2H), 2.46 (s, 3H), 2.17 – 2.07 (m, 2H), 1.76 – 1.65 (m, 2H), 1.41 – 1.29 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 133.1, 133.0, 130.5, 127.5, 126.5, 72.8, 56.3, 33.9, 32.7, 26.1, 24.3, 21.2.

HRMS (ESI): Calcd for $C_{13}H_{18}ClS^+$ $[M+H]^+$: 241.0812; found: 241.0812.

((*trans*)-2-chlorocyclohexyl)(2,4-dimethylphenyl)sulfane (3c)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether) to give **3c** as a colorless oil (95.6 mg, 75% yield).

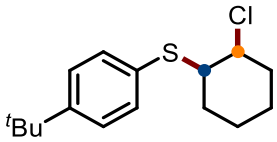
Rf = 0.5 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.0 Hz, 1H), 7.03 (d, J = 8.0 Hz, 1H), 6.96 (d, J = 7.0 Hz, 1H), 4.07 (s, 1H), 3.25 (s, 1H), 2.42 (s, 3H), 2.29 (s, 3H), 2.22 – 2.12 (m, 1H), 1.80 – 1.56 (m, 5H), 1.42 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 137.8, 134.5, 133.8, 131.4, 127.3, 62.3, 56.8, 33.9, 32.6, 26.1, 24.3, 21.0, 20.9.

HRMS (ESI): Calcd for $C_{14}H_{20}ClS^+$ $[M+H]^+$: 255.0969; found: 255.0970.

(4-(tert-butyl)phenyl)((*trans*)-2-chlorocyclohexyl)sulfane (3d)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether) to give **3d** as a colorless oil (69.3 mg, 49% yield).

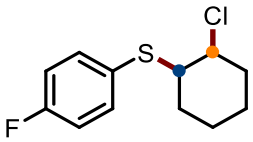
Rf = 0.4 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.5 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 3.31 (td, J = 10.0, 4.3 Hz, 1H), 2.77 – 2.68 (m, 1H), 2.16 – 2.06 (m, 2H), 1.76 – 1.65 (m, 2H), 1.31 (s, 9H), 1.28 – 1.22 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 133.9, 132.9, 128.7, 126.0, 72.0, 56.7, 34.6, 33.8, 32.7, 31.3, 26.2, 24.3.

HRMS (ESI): Calcd for $C_{16}H_{24}ClS^+$ $[M+H]^+$: 283.1282; found: 283.1283.

((*trans*)-2-chlorocyclohexyl)(4-fluorophenyl)sulfane (3e)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether) to give **3e** as a colorless oil (80.8 mg, 66% yield).

Rf = 0.5 (Petroleum ether);

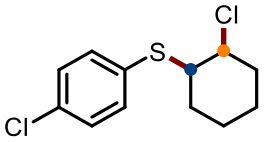
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.39 (m, 2H), 7.07 – 6.92 (m, 2H), 3.92 (d, J = 3.2 Hz, 1H), 3.24 – 3.02 (m, 1H), 2.42 – 2.24 (m, 1H), 2.24 – 2.06 (m, 1H), 1.80 – 1.61 (m, 3H), 1.58 – 1.48 (m, 1H), 1.43 – 1.31 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, J = 246.7 Hz), 136.0 (d, J = 8.2 Hz), 128.5, 116.1 (d, J = 21.7 Hz), 62.1, 54.0, 33.9, 30.6, 23.7, 23.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.37 (s).

HRMS (ESI): Calcd for $C_{12}H_{15}ClFS^+$ $[M+H]^+$: 245.0562; found: 245.0565.

((*trans*)-2-chlorocyclohexyl)(4-chlorophenyl)sulfane (3f)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether) to give **3f** as a colorless oil (81.0 mg, 62% yield).

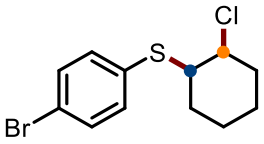
Rf = 0.5 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.34 (m, 2H), 7.31 – 7.25 (m, 2H), 3.94 (s, 1H), 3.24 (s, 1H), 2.38 – 2.27 (m, 1H), 2.25 – 2.14 (m, 1H), 1.75 (d, J = 5.4 Hz, 2H), 1.65 (d, J = 2.9 Hz, 1H), 1.54 (d, J = 5.4 Hz, 1H), 1.39 (d, J = 3.1 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 134.3, 133.8, 132.3, 129.2, 62.1, 53.5, 33.8, 30.5, 23.7, 23.1.

HRMS (ESI): Calcd for $C_{12}H_{15}Cl_2S^+$ $[M+H]^+$: 261.0266; found: 261.0266.

(4-bromophenyl)((*trans*)-2-chlorocyclohexyl)sulfane (3g)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether) to give **3g** as a colorless oil (76.4 mg, 50% yield).

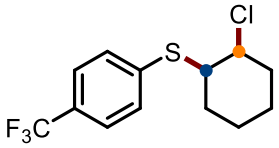
Rf = 0.5 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.5 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 3.95 (td, J = 7.3, 3.8 Hz, 1H), 3.26 (td, J = 7.4, 4.3 Hz, 1H), 2.37 – 2.29 (m, 1H), 2.24 – 2.16 (m, 1H), 1.77 (m, 2H), 1.69 – 1.62 (m, 1H), 1.57 (s, 1H), 1.44 – 1.36 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4, 133.0, 132.1, 121.8, 62.1, 53.3, 33.8, 30.5, 23.6, 23.2.

HRMS (ESI): Calcd for $C_{12}H_{15}BrClS^+$ $[M+H]^+$: 304.9761; found: 304.9762.

((*trans*)-2-chlorocyclohexyl)(4-(trifluoromethyl)phenyl)sulfane (3h)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether) to give **3h** as a colorless oil (75.2 mg, 51% yield).

Rf = 0.6 (Petroleum ether);

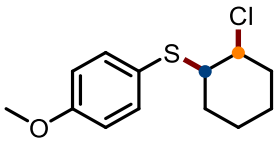
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.3 Hz, 2H), 7.49 (d, J = 7.0 Hz, 2H), 4.03 (s, 1H), 3.45 (s, 1H), 2.38 – 2.24 (m, 2H), 1.79 (d, J = 4.8 Hz, 2H), 1.72 – 1.57 (m, 2H), 1.44 (d, J = 5.1 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 130.8, 125.9 – 125.8 (q, J = 270.0 Hz), 122.7, 61.9, 52.2, 33.5, 30.2, 23.5, 22.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.55 (s).

HRMS (ESI): Calcd for $C_{13}H_{15}ClF_3S^+$ $[M+H]^+$: 295.0530; found: 295.0524.

((*trans*)-2-chlorocyclohexyl)(4-methoxyphenyl)sulfane (3i)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether) to give **3i** as a colorless oil (81.2 mg, 64% yield).

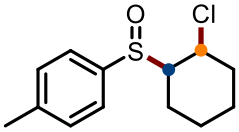
Rf = 0.3 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 2H), 6.89 – 6.83 (m, 2H), 3.91 (td, J = 7.3, 3.9 Hz, 1H), 3.81 (s, 3H), 3.09 (td, J = 7.6, 4.3 Hz, 1H), 2.40 – 2.30 (m, 1H), 2.20 – 2.12 (m, 1H), 1.77 – 1.63 (m, 3H), 1.56 – 1.47 (m, 1H), 1.42 – 1.31 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 136.3, 123.5, 114.6, 62.3, 55.4, 54.1, 33.9, 30.6, 23.7, 23.4.

HRMS (ESI): Calcd for $C_{13}H_{18}ClOS^+$ $[M+H]^+$: 257.0761; found: 257.0759.

1-((2-chlorocyclohexyl)sulfinyl)-4-methylbenzene (4a)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether /EtOAc = 10:1) to give **4a** as a white solid (104.0 mg, 81% yield, dr = 1.2:1).

Diastereoisomer 1

Rf = 0.3 (Petroleum ether /EtOAc = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.8 Hz, 2H), 7.33 (d, J = 7.7 Hz, 2H), 4.19 (td, J = 10.8, 4.2 Hz, 1H), 2.51 (td, J = 11.3, 3.8 Hz, 1H), 2.42 (s, 3H), 1.83 – 1.57 (m, 5H), 1.33 (d, J = 13.4 Hz, 2H), 1.21 – 1.10 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 138.2, 129.8, 124.3, 70.4, 58.2, 37.3, 25.3, 24.0, 21.4, 20.4.

HRMS (ESI): Calcd for $C_{13}H_{18}ClOS^+$ $[M+H]^+$: 257.0761; found: 257.0761.

Diastereoisomer 2

M. p. = 82-83 °C;

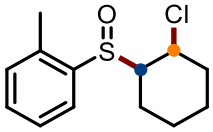
Rf = 0.2 (Petroleum ether /EtOAc = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 7.9 Hz, 2H), 3.70 – 3.58 (m, 1H), 3.17 (td, J = 9.6, 3.6 Hz, 1H), 2.43 (s, 3H), 2.36 – 2.30 (m, 1H), 2.28 – 2.20 (m, 1H), 1.82 – 1.71 (m, 3H), 1.38 – 1.28 (m, 1H), 1.23 – 1.12 (m, 1H), 0.91 – 0.80 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 135.9, 129.7, 125.7, 68.1, 57.7, 36.1, 24.4, 23.7, 21.5, 21.4.

HRMS (ESI): Calcd for $C_{13}H_{18}ClOS^+$ $[M+H]^+$: 257.0761; found: 257.0763.

1-((S)-((2-chlorocyclohexyl)sulfinyl)-2-methylbenzene (4b)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether /EtOAc = 10:1) to give **4b** as a yellow oil (89.9 mg, 70% yield, dr = 1:1).

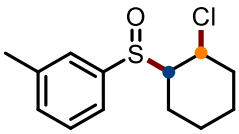
Rf = 0.2 (Petroleum ether /EtOAc = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 4.0 Hz, 0.5H), 7.78 (d, J = 6.8 Hz, 0.5H), 7.41 (t, J = 6.6 Hz, 2H), 7.23 (s, 1H), 4.45 (d, J = 4.1 Hz, 0.5H), 4.23 (td, J = 11.1, 4.2 Hz, 0.5H), 3.16 (d, J = 5.2 Hz, 0.5H), 2.60 (td, J = 11.5, 3.8 Hz, 0.5H), 2.48 (s, 1.5H), 2.39 (s, 1.5H), 2.35 – 2.27 (m, 0.5H), 2.24 – 2.15 (m, 0.5H), 1.96 – 1.88 (m, 0.5H), 1.85 – 1.66 (m, 3.5H), 1.50 – 1.47 (m, 1H), 1.40 – 1.30 (m, 1H), 1.28 – 1.17 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 139.1, 136.9, 134.3, 131.4, 130.9, 130.8, 130.6, 127.1, 126.4, 125.6, 125.3, 68.7, 66.6, 58.6, 56.7, 37.6, 33.0, 25.4, 24.1, 23.2, 22.5, 21.7, 20.2, 19.2, 18.2.

HRMS (ESI): Calcd for $C_{13}H_{18}ClOS^+$ $[M+H]^+$: 257.0761; found: 257.0759.

1-((2-chlorocyclohexyl)sulfinyl)-3-methylbenzene (4c)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether /EtOAc = 10:1) to give **4c** as a white solid (80.9 mg, 63% yield, dr = 2:1).

Diastereoisomer 1

Rf = 0.3 (Petroleum ether /EtOAc = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (t, J = 7.6 Hz, 1H), 7.36 (s, 1H), 7.34 – 7.26 (m, 2H), 4.20 (td, J = 11.0, 4.5 Hz, 1H), 2.54 (td, J = 11.4, 4.1 Hz, 1H), 2.43 (s, 3H), 2.41 (s, 1H), 1.80 – 1.72 (m, 3H), 1.70 – 1.61 (m, 1H), 1.38 – 1.30 (m, 2H), 1.23 – 1.13 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 139.3, 131.4, 128.9, 124.6, 121.3, 70.4, 58.2, 37.4, 25.3, 24.0, 21.5, 20.5.

HRMS (ESI): Calcd for $C_{13}H_{18}ClOS^+$ $[M+H]^+$: 257.0761; found: 257.0763.

Diastereoisomer 2

M. p. = 65-66 °C;

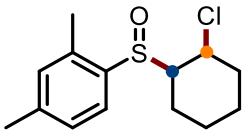
Rf = 0.2 (Petroleum ether /EtOAc = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.46 (d, J = 7.7 Hz, 1H), 7.41 (t, J = 7.5 Hz, 1H), 7.34 (d, J = 7.3 Hz, 1H), 3.69 (td, J = 9.2, 4.0 Hz, 1H), 3.18 (td, J = 9.6, 3.7 Hz, 1H), 2.44 (s, 3H), 2.37 – 2.30 (m, 1H), 2.29 – 2.22 (m, 1H), 1.83 – 1.72 (m, 3H), 1.39 – 1.29 (m, 1H), 1.26 – 1.17 (m, 1H), 0.92 – 0.82 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 139.0, 132.4, 128.8, 125.8, 122.8, 68.1, 57.6, 36.0, 24.3, 23.7, 21.5, 21.5.

HRMS (ESI): Calcd for $C_{13}H_{18}ClOS^+$ $[M+H]^+$: 257.0761; found: 257.0760.

1-((2-chlorocyclohexyl)sulfinyl)-2,4-dimethylbenzene (4d)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether /EtOAc = 5:1) to give **4d** as a yellow oil (119.2 mg, 88% yield, dr = 1.5:1).

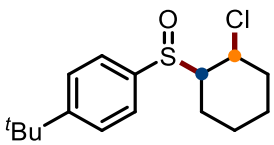
Rf = 0.2 (Petroleum ether /EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.1 Hz, 0.6H), 7.60 (d, J = 8.0 Hz, 0.4H), 7.16 (d, J = 8.0 Hz, 1H), 7.00 (s, 1H), 4.43 – 4.37 (m, 0.6H), 4.17 (td, J = 11.2, 4.5 Hz, 0.4H), 3.12 – 3.06 (m, 0.6H), 2.57 – 2.48 (m, 0.4H), 2.39 (s, 2H), 2.32 (s, 3H), 2.29 (s, 1H), 2.27 – 2.21 (m, 0.6H), 2.17 – 2.08 (m, 0.6H), 1.90 – 1.81 (m, 0.6H), 1.79 – 1.68 (m, 1.6H), 1.67 – 1.58 (m, 1H), 1.50 – 1.38 (m, 1.4H), 1.37 – 1.24 (m, 0.8H), 1.21 – 1.07 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 140.8, 137.3, 136.9, 135.8, 134.0, 131.7, 131.5, 128.0, 127.2, 125.6, 125.3, 68.8, 66.6, 58.6, 56.8, 37.5, 32.9, 25.4, 24.0, 23.1, 22.2, 21.6, 21.3, 21.2, 20.2, 19.0, 18.1.

HRMS (ESI): Calcd for $C_{14}H_{20}ClOS^+$ $[M+H]^+$: 271.0918; found: 271.0918.

1-(tert-butyl)-4-((2-chlorocyclohexyl)sulfinyl)benzene (4e)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was

purified by flash column chromatography (silica gel, petroleum ether /EtOAc = 10:1) to give **4e** as a colorless oil (115.1 mg, 77% yield, dr > 10:1).

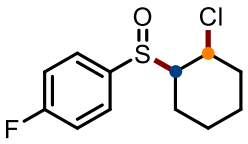
Rf = 0.2 (Petroleum ether /EtOAc = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 3.31 (td, *J* = 9.9, 4.5 Hz, 1H), 3.05 (s, 1H), 2.76 – 2.67 (m, 1H), 2.16 – 2.06 (m, 2H), 1.73 – 1.65 (m, 2H), 1.36 – 1.33 (m, 1H), 1.31 (s, 9H), 1.28 – 1.22 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 133.9, 128.8, 126.0, 72.0, 56.7, 34.6, 33.8, 32.7, 31.3, 26.2, 24.3.

HRMS (ESI): Calcd for $C_{16}H_{24}ClOS^+$ $[M+H]^+$: 299.1231; found: 299.1229.

1-((2-chlorocyclohexyl)sulfinyl)-4-fluorobenzene (4f)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether /EtOAc = 10:1) to give **4f** as a colorless oil (91.3 mg, 70% yield, dr > 10:1).

Rf = 0.2 (Petroleum ether /EtOAc = 10:1);

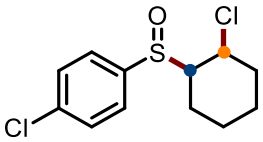
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 2H), 7.05 – 6.98 (m, 2H), 3.28 (td, *J* = 10.1, 4.4 Hz, 1H), 2.96 (s, 1H), 2.67 (td, *J* = 10.2, 3.7 Hz, 1H), 2.17 – 2.03 (m, 2H), 1.75 – 1.66 (m, 2H), 1.35 – 1.23 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1 (d, *J* = 246.7 Hz), 136.7 (d, *J* = 8.2 Hz), 127.1, 116.2 (d, *J* = 21.6 Hz), 71.7, 56.9, 33.8, 32.5, 26.2, 24.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.19 (s).

HRMS (ESI): Calcd for $C_{12}H_{15}ClFOS^+$ $[M+H]^+$: 261.0511; found: 261.0511.

1-chloro-4-((2-chlorocyclohexyl)sulfinyl)benzene (4g)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether /EtOAc = 10:1) to give **4g** as a yellow solid (101.2 mg, 73% yield, dr > 10:1).

M. p. = 78-79 °C;

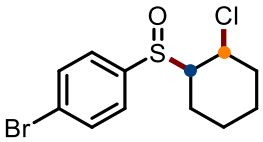
Rf = 0.2 (Petroleum ether /EtOAc = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 3.53 (td, *J* = 9.7, 4.1 Hz, 1H), 3.21 (td, *J* = 10.2, 3.6 Hz, 1H), 2.41 – 2.31 (m, 1H), 2.30 – 2.19 (m, 1H), 1.84 – 1.74 (m, 3H), 1.36 – 1.30 (m, 1H), 1.20 – 1.14 (m, 1H), 0.88 – 0.80 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 137.6, 129.3, 127.1, 68.2, 57.5, 36.5, 29.7, 24.6, 23.8, 21.5.

HRMS (ESI): Calcd for $C_{12}H_{15}Cl_2OS^+$ $[M+H]^+$: 277.0215; found: 277.0215.

1-bromo-4-((2-chlorocyclohexyl)sulfinyl)benzene (4h)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether /EtOAc = 10:1) to give **4h** as a yellow solid (114.2 mg, 71% yield, dr > 10:1).

M. p. = 65-66 °C;

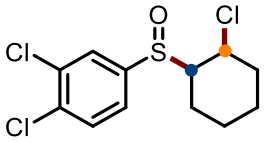
Rf = 0.2 (Petroleum ether /EtOAc = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.9 Hz, 2H), 7.57 (d, J = 7.9 Hz, 2H), 3.61 – 3.46 (m, 1H), 3.21 (t, J = 8.4 Hz, 1H), 2.35 (d, J = 12.0 Hz, 1H), 2.25 (d, J = 10.2 Hz, 1H), 1.85 – 1.73 (m, 3H), 1.36 – 1.30 (m, 1H), 1.21 – 1.15 (m, 1H), 0.86 – 0.80 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 132.2, 127.2, 126.1, 68.2, 57.5, 36.5, 24.7, 23.8, 21.5.

HRMS (ESI): Calcd for $C_{12}H_{15}BrClOS^+$ $[M+H]^+$: 320.9710; found: 320.9711.

1,2-dichloro-4-((2-chlorocyclohexyl)sulfinyl)benzene (4i)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether /EtOAc = 5:1) to give **4i** as a white solid (129.3 mg, 83% yield, dr = 1:1).

Diastereoisomer 1

Rf = 0.4 (Petroleum ether /EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 1.8 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.40 – 7.34 (m, 1H), 4.24 – 4.13 (m, 1H), 2.61 – 2.51 (m, 1H), 2.50 – 2.38 (m, 1H), 1.83 – 1.76 (m, 2H), 1.75 – 1.61 (m, 2H), 1.36 – 1.29 (m, 2H), 1.22 – 1.16 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 135.1, 134.1, 131.1, 126.3, 123.4, 70.7, 57.9, 37.4, 25.3, 24.0, 20.6.

HRMS (ESI): Calcd for $C_{12}H_{14}Cl_3OS^+$ $[M+H]^+$: 310.9825; found: 310.9826.

Diastereoisomer 2

M. p. = 105-106 °C;

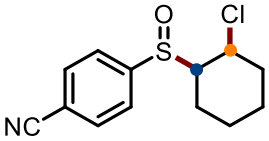
Rf = 0.3 (Petroleum ether /EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.63 (d, J = 8.3, 1.7 Hz, 1H), 7.52 (d, J = 8.3 Hz, 1H), 3.57 – 3.48 (m, 1H), 3.28 – 3.19 (m, 1H), 2.38 (d, J = 12.4 Hz, 1H), 2.32 – 2.23 (m, 1H), 1.86 – 1.75 (m, 3H), 1.39 – 1.29 (m, 1H), 1.27 – 1.16 (m, 1H), 0.86 – 0.76 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 136.1, 134.1, 131.0, 127.5, 124.8, 68.4, 57.4, 36.7, 24.7, 23.9, 21.7.

HRMS (ESI): Calcd for $C_{12}H_{14}Cl_3OS^+$ $[M+H]^+$: 310.9825; found: 310.9827.

4-((2-chlorocyclohexyl)sulfinyl)benzonitrile (4j)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether /EtOAc = 5:1) to give **4j** as a yellow solid (53.5 mg, 45% yield, dr = 2.5:1).

Diastereoisomer 1

M. p. = 106-107 °C;

Rf = 0.1 (Petroleum ether /EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 4.20 (td, *J* = 11.3, 4.5 Hz, 1H), 2.60 (td, *J* = 11.7, 3.9 Hz, 1H), 2.50 – 2.41 (m, 1H), 1.81 – 1.76 (m, 2H), 1.73 (s, 1H), 1.71 – 1.64 (m, 1H), 1.39 – 1.28 (m, 1H), 1.26 – 1.14 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 132.7, 125.2, 117.8, 114.5, 70.9, 57.9, 37.4, 25.3, 24.0, 20.8.

HRMS (ESI): Calcd for $C_{13}H_{15}ClNOS^+$ $[M+H]^+$: 268.0557; found: 268.0558.

Diastereoisomer 2

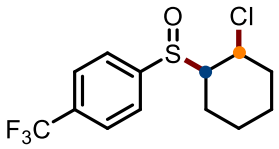
Rf = 0.1 (Petroleum ether /EtOAc = 3:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 4H), 3.50 (td, *J* = 10.0, 4.2 Hz, 1H), 3.27 (td, *J* = 10.6, 3.6 Hz, 1H), 2.45 – 2.35 (m, 1H), 2.33 – 2.23 (m, 1H), 1.87 – 1.74 (m, 3H), 1.39 – 1.29 (m, 1H), 1.22 – 1.10 (m, 1H), 0.83 – 0.69 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 132.5, 126.4, 117.7, 115.3, 68.6, 57.2, 36.8, 24.8, 23.9, 22.1.

HRMS (ESI): Calcd for $C_{13}H_{15}ClNOS^+$ $[M+H]^+$: 268.0557; found: 268.0557.

1-((2-chlorocyclohexyl)sulfinyl)-4-(trifluoromethyl)benzene (4k)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether /EtOAc = 10:1) to give **4k** as a white solid (63.7 mg, 41% yield, dr > 10:1).

M. p. = 103-104 °C;

Rf = 0.3 (Petroleum ether /EtOAc = 10:1);

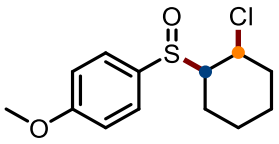
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 4H), 3.46 – 3.37 (m, 1H), 3.01 – 2.91 (m, 1H), 2.19 – 2.10 (m, 2H), 1.80 – 1.69 (m, 2H), 1.43 – 1.34 (m, 2H), 1.33 – 1.27 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 131.6, 125.7, 72.7, 56.0, 34.0, 32.8, 26.0, 24.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.58 (s).

HRMS (ESI): Calcd for $C_{13}H_{15}ClF_3OS^+$ $[M+H]^+$: 311.0479; found: 311.0480.

1-((2-chlorocyclohexyl)sulfinyl)-4-methoxybenzene (4l)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether /EtOAc = 5:1) to give **4l** as a yellow oil (94.1 mg, 69% yield, dr = 1:1).

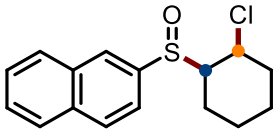
Rf = 0.2 (Petroleum ether /EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.8 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 2H), 4.18 (td, *J* = 10.9, 4.4 Hz, 0.5H), 3.87 (d, *J* = 5.0 Hz, 3H), 3.62 (td, *J* = 9.2, 4.0 Hz, 0.5H), 3.17 (td, *J* = 9.6, 3.7 Hz, 0.5H), 2.49 (td, *J* = 11.2, 4.1 Hz, 0.5H), 2.44 – 2.37 (m, 0.5H), 2.36 – 2.29 (m, 0.5H), 2.28 – 2.20 (m, 0.5H), 1.86 – 1.70 (m, 3.5H), 1.70 – 1.64 (m, 0.5H), 1.42 – 1.29 (m, 2H), 1.23 – 1.13 (m, 1H), 0.92 – 0.81 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 161.7, 132.1, 129.9, 127.5, 125.9, 114.7, 114.5, 70.4, 68.1, 58.2, 57.82, 55.5, 37.3, 36.0, 29.7, 25.2, 24.3, 24.0, 23.7, 21.3, 20.3.

HRMS (ESI): Calcd for $C_{13}H_{18}ClO_2S^+$ $[M+H]^+$: 273.0711; found: 273.0709.

2-((2-chlorocyclohexyl)sulfinyl)naphthalene (4m)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether /EtOAc = 10:1) to give **4m** as a white solid (57.1 mg, 39% yield, dr = 1:1).

M. p. = 104-105 °C;

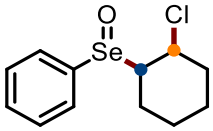
Rf = 0.2 (Petroleum ether /EtOAc = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 8.2 Hz, 0.5H), 8.16 (s, 0.5H), 8.03 – 7.90 (m, 3H), 7.87 (d, J = 8.6 Hz, 0.5H), 7.73 – 7.64 (m, 1H), 7.62 – 7.59 (m, 1H), 7.51 – 7.47 (m, 0.5H), 4.33 – 4.22 (m, 1H), 3.21 (td, J = 11.5, 4.1 Hz, 0.5H), 2.68 (td, J = 11.2, 4.2 Hz, 0.5H), 2.50 – 2.42 (m, 1H), 1.79 – 1.72 (m, 3H), 1.38 – 1.26 (m, 3H), 1.19 – 1.11 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 136.7, 135.5, 134.2, 132.9, 130.6, 129.2, 128.6, 128.4, 128.3, 128.2, 128.1, 127.7, 127.4, 125.1, 124.0, 122.2, 120.0, 70.1, 66.3, 58.2, 58.0, 37.5, 37.4, 25.4, 24.1, 24.0, 21.6, 20.6.

HRMS (ESI): Calcd for $C_{16}H_{18}ClOS^+$ $[M+H]^+$: 293.0761; found: 293.0760.

((-2-chlorocyclohexyl)seleninyl)benzene (4n)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether /EtOAc = 5:1) to give **4n** as a yellow oil (30.4 mg, 21% yield, dr > 20:1).

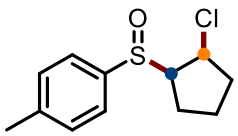
Rf = 0.3 (Petroleum ether /EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 2H), 7.34 – 7.26 (m, 3H), 3.33 (td, J = 10.1, 4.3 Hz, 1H), 2.95 – 2.85 (m, 2H), 2.23 – 2.10 (m, 2H), 1.77 – 1.68 (m, 1H), 1.63 (d, J = 9.6 Hz, 1H), 1.48 – 1.38 (m, 1H), 1.38 – 1.30 (m, 1H), 1.29 – 1.21 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 129.0, 128.2, 126.6, 77.4, 77.1, 76.7, 72.3, 53.6, 33.9, 33.4, 26.9, 24.5.

HRMS (ESI): Calcd for $C_{12}H_{16}ClOSe^+$ $[M+H]^+$: 291.0049; found: 291.0234.

1-((2-chlorocyclopentyl)sulfinyl)-4-methylbenzene (4o)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether /EtOAc = 5:1) to give **4o** as a yellow oil (88.6 mg, 73% yield, dr = 1.5:1).

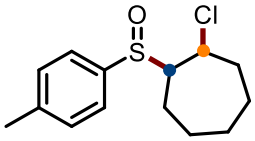
Rf = 0.3 (Petroleum ether /EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.1 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.36 – 7.30 (m, 2H), 4.66 – 4.61 (m, 0.4H), 4.55 – 4.48 (m, 0.6H), 3.39 – 3.31 (m, 0.4H), 3.22 – 3.12 (m, 0.6H), 2.42 (d, *J* = 5.1 Hz, 3H), 2.23 – 2.13 (m, 1.4H), 2.11 – 2.04 (m, 0.6H), 2.01 – 1.91 (m, 1.6H), 1.90 – 1.81 (m, 1.4H), 1.80 – 1.73 (m, 0.6H), 1.63 – 1.52 (m, 0.6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 141.4, 139.0, 138.7, 130.0, 129.9, 124.6, 124.0, 72.9, 72.5, 59.6, 57.9, 37.6, 37.3, 26.6, 23.9, 22.8, 21.5, 21.4, 20.6.

HRMS (ESI): Calcd for $C_{12}H_{16}ClOS^+$ $[M+H]^+$: 243.0605; found: 243.0605.

1-chloro-2-(p-tolylsulfinyl)cycloheptane (4p)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether /EtOAc = 10:1) to give **4p** as a colorless oil (86.7 mg, 64 % yield, dr = 1:1).

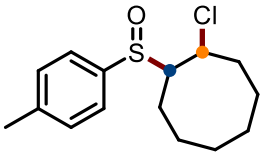
Rf = 0.3 (Petroleum ether /EtOAc = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.1 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.35 – 7.30 (m, 2H), 4.65 – 4.58 (m, 0.5H), 4.03 – 3.97 (m, 0.5H), 3.27 – 3.20 (m, 0.5H), 2.78 (td, *J* = 9.4, 3.0 Hz, 0.5H), 2.42 (s, 3H), 2.36 – 2.27 (m, 0.5H), 2.22 – 2.14 (m, 1H), 2.14 – 2.01 (m, 1H), 1.76 – 1.62 (m, 4H), 1.59 – 1.34 (m, 3H), 1.22 – 1.06 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 141.1, 139.1, 136.6, 129.9, 129.7, 125.4, 124.3, 74.8, 71.9, 61.4, 59.1, 37.4, 37.0, 28.8, 28.5, 27.1, 26.8, 23.0, 22.8, 22.5, 21.9, 21.5, 21.4.

HRMS (ESI): Calcd for $C_{14}H_{20}ClOS^+$ $[M+H]^+$: 271.0918; found: 271.0915.

1-chloro-2-(p-tolylsulfinyl)cyclooctane (4q)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether /EtOAc = 10:1) to give **4q** as a yellow oil(76.9 mg, 54% yield, dr = 1.5:1).

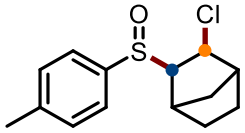
Rf = 0.2 (Petroleum ether /EtOAc = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.1 Hz, 1.2H), 7.45 (d, *J* = 8.1 Hz, 0.8H), 7.35 – 7.29 (m, 2H), 4.60 – 4.52 (m, 0.4H), 3.65 – 3.58 (m, 0.6H), 3.53 – 3.44 (m, 0.6H), 2.86 – 2.78 (m, 0.4H), 2.52 – 2.45 (m, 0.6H), 2.41 (s, 3H), 2.29 – 2.20 (m, 0.4H), 2.18 – 2.09 (m, 0.6H), 2.08 – 2.02 (m, 0.6H), 2.00 – 1.89 (m, 2H), 1.87 – 1.79 (m, 0.6H), 1.73 – 1.65 (m, 1.2H), 1.62 – 1.47 (m, 3.4H), 1.43 – 1.34 (m, 1.6H), 1.31 – 1.22 (m, 1H), 0.89 – 0.75 (m, 0.8H), 0.61 – 0.50 (m, 0.4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 140.8, 139.2, 135.3, 129.8, 129.6, 125.8, 124.0, 72.4, 68.8, 61.4, 60.9, 32.4, 31.8, 29.5, 29.4, 26.3, 26.0, 25.3, 24.5, 22.6, 22.0, 21.5, 21.4, 21.1, 20.6.

HRMS (ESI): Calcd for $C_{15}H_{22}ClOS^+$ $[M+H]^+$: 285.1074; found: 285.1072.

2-chloro-3-(p-tolylsulfinyl)bicyclo[2.2.1]heptane (4r)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether /EtOAc = 5:1) to give **4r** as a white solid (68.5 mg, 51 % yield, dr > 10:1).

M. p. = 99-100 °C;

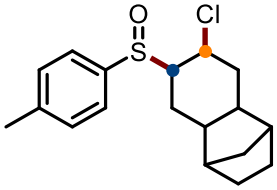
Rf = 0.2 (Petroleum ether /EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 4.53 (d, *J* = 4.2 Hz, 1H), 2.85 (d, *J* = 4.1 Hz, 1H), 2.72 – 2.67 (m, 1H), 2.61 – 2.53 (m, 1H), 2.43 (s, 3H), 2.25 – 2.19 (m, 1H), 2.11 (d, *J* = 10.9 Hz, 1H), 1.84 – 1.75 (m, 2H), 1.66 (d, *J* = 11.0 Hz, 2H), 1.60 (s, 1H), 1.36 – 1.32 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 137.4, 129.0, 128.7, 70.2, 51.7, 45.8, 36.9, 23.6, 21.5, 21.1.

HRMS (ESI): Calcd for $C_{14}H_{18}ClOS^+$ $[M+H]^+$: 269.0761; found: 269.0761.

6-chloro-7-(p-tolylsulfinyl)decahydro-1,4-methanonaphthalene (4s)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether /EtOAc = 10:1) to give **4s** as a white solid (82.3 mg, 51% yield, dr = 1.5:1).

M. p. = 88-89 °C;

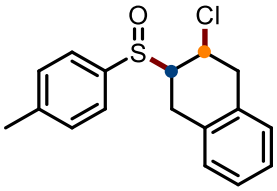
Rf = 0.4 (Petroleum ether /EtOAc = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.1 Hz, 0.6H), 7.52 (d, *J* = 8.1 Hz, 1.4H), 7.32 (d, *J* = 7.8 Hz, 2H), 4.64 (s, 0.4H), 4.40 – 4.29 (m, 0.6H), 3.21 – 3.11 (m, 0.6H), 2.58 – 2.49 (m, 0.4H), 2.43 (d, *J* = 8.7 Hz, 3H), 2.31 – 2.21 (m, 0.4H), 2.13 – 1.97 (m, 2.6H), 1.90 (d, *J* = 15.3 Hz, 2H), 1.79 – 1.71 (m, 1H), 1.67 (d, *J* = 9.8 Hz, 1H), 1.58 – 1.48 (m, 3.6H), 1.27 – 1.18 (m, 2.4H), 1.09 – 1.00 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 138.9, 129.8, 129.2, 127.6, 124.4, 68.1, 59.7, 49.0, 45.3, 42.0, 42.0, 41.9, 41.6, 37.6, 37.5, 37.4, 35.7, 34.2, 33.0, 32.6, 32.0, 30.6, 29.2, 29.1, 28.6, 27.7, 21.6, 21.5.

HRMS (ESI): Calcd for $C_{18}H_{24}ClOS^+$ $[M+H]^+$: 323.1231; found: 323.1228.

2-chloro-3-(p-tolylsulfinyl)-1,2,3,4-tetrahydronaphthalene (4t)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether /EtOAc = 10:1) to give **4t** as a white solid (85.4 mg, 56% yield, dr = 1.1:1).

Diastereoisomer 1

M. p. = 93-94 °C;

Rf = 0.4 (Petroleum ether /EtOAc = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.1 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.17 – 7.11 (m, 2H), 7.10 – 7.06 (m, 1H), 7.05 – 7.01 (m, 1H), 4.49 (td, J = 10.0, 5.3 Hz, 1H), 3.55 – 3.46 (m, 1H), 3.41 – 3.31 (m, 1H), 3.30 – 3.21 (m, 1H), 3.06 (td, J = 10.1, 6.0 Hz, 1H), 2.53 – 2.48 (m, 1H), 2.47 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 138.0, 132.8, 132.6, 130.1, 129.0, 128.2, 126.9, 126.5, 124.3, 66.8, 55.1, 39.8, 23.6, 21.5.

HRMS (ESI): Calcd for $C_{17}H_{18}ClOS^+$ $[M+H]^+$: 305.0761; found: 305.0760.

Diastereoisomer 2

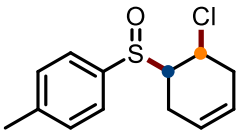
Rf = 0.3 (Petroleum ether /EtOAc = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 7.4 Hz, 2H), 7.36 (d, J = 7.1 Hz, 2H), 7.20 – 7.13 (m, 2H), 7.12 – 7.08 (m, 1H), 7.07 – 7.02 (m, 1H), 4.61 (d, J = 4.4 Hz, 1H), 3.60 (d, J = 17.2 Hz, 1H), 3.51 (d, J = 5.1 Hz, 1H), 3.36 (d, J = 17.4 Hz, 1H), 3.29 – 3.19 (m, 1H), 2.54 – 2.46 (m, 1H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 132.3, 131.9, 130.1, 129.0, 128.6, 126.9, 126.8, 125.7, 54.0, 36.9, 25.3, 21.6.

HRMS (ESI): Calcd for $C_{17}H_{18}ClOS^+$ $[M+H]^+$: 305.0761; found: 305.0759.

1-((6-chlorocyclohex-3-en-1-yl)sulfinyl)-4-methylbenzene (4u)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether /EtOAc = 10:1) to give **4u** as a yellow solid (52.2 mg, 41% yield, dr > 10:1).

M. p. = 62-63 °C;

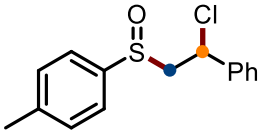
Rf = 0.2 (Petroleum ether /EtOAc = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 5.66 (s, 2H), 4.46 – 4.39 (m, 1H), 3.38 – 3.31 (m, 1H), 2.99 – 2.89 (m, 1H), 2.65 – 2.52 (m, 2H), 2.43 (s, 3H), 1.79 – 1.72 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 137.5, 130.0, 125.8, 123.7, 123.5, 65.0, 53.6, 32.8, 21.5, 21.2.

HRMS (ESI): Calcd for $C_{13}H_{16}ClOS^+$ $[M+H]^+$: 255.0605; found: 255.0605.

1-((2-chloro-2-phenylethyl)sulfinyl)-4-methylbenzene (4v)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether /EtOAc = 10:1) to give **4v** as a colorless oil (87.8 mg, 63% yield).

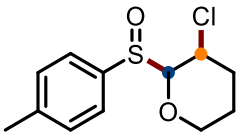
Rf = 0.5 (Petroleum ether /EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 6H), 7.31 – 7.27 (m, 1H), 7.13 (d, J = 8.0 Hz, 2H), 4.71 – 4.64 (m, 1H), 3.30 – 3.22 (m, 1H), 3.07 – 2.98 (m, 1H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 137.2, 131.1, 130.0, 128.6, 127.9, 125.9, 71.5, 44.9, 21.1.

HRMS (ESI): Calcd for $C_{15}H_{16}ClOS^+$ $[M+H]^+$: 279.0605; found: 279.0613.

2-chloro-3-((p-tolylsulfinyl)tetrahydro-2H-pyran (4w)



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether /EtOAc = 5:1) to give **4w** as a white solid (41.4 mg, 32% yield).

M. p. = 82-83 °C;

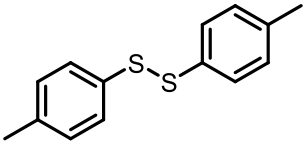
Rf = 0.5 (Petroleum ether /EtOAc = 4:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.2 Hz, 2H), 7.61 (s, 1H), 7.31 (d, J = 8.0 Hz, 2H), 4.04 – 4.00 (m, 2H), 2.43 (s, 3H), 2.17 (t, J = 6.1 Hz, 2H), 1.87 (M, 2H), 1.57 (s, 1H), 1.29 (M, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 137.7, 129.7, 127.5, 115.4, 66.5, 29.7, 21.6, 20.8, 18.9.

HRMS (ESI): Calcd for $C_{12}H_{16}ClO_2S^+$ $[M+H]^+$: 259.0554; found: 259.0555.

1,2-di-*p*-tolyldisulfane (6)



On 0.5 mmol scale. Electrolysis was conducted following the mechanistic studies procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether) to give **6** as a white solid (73.9 mg, 60% yield).

Rf = 0.8 (Petroleum ether)

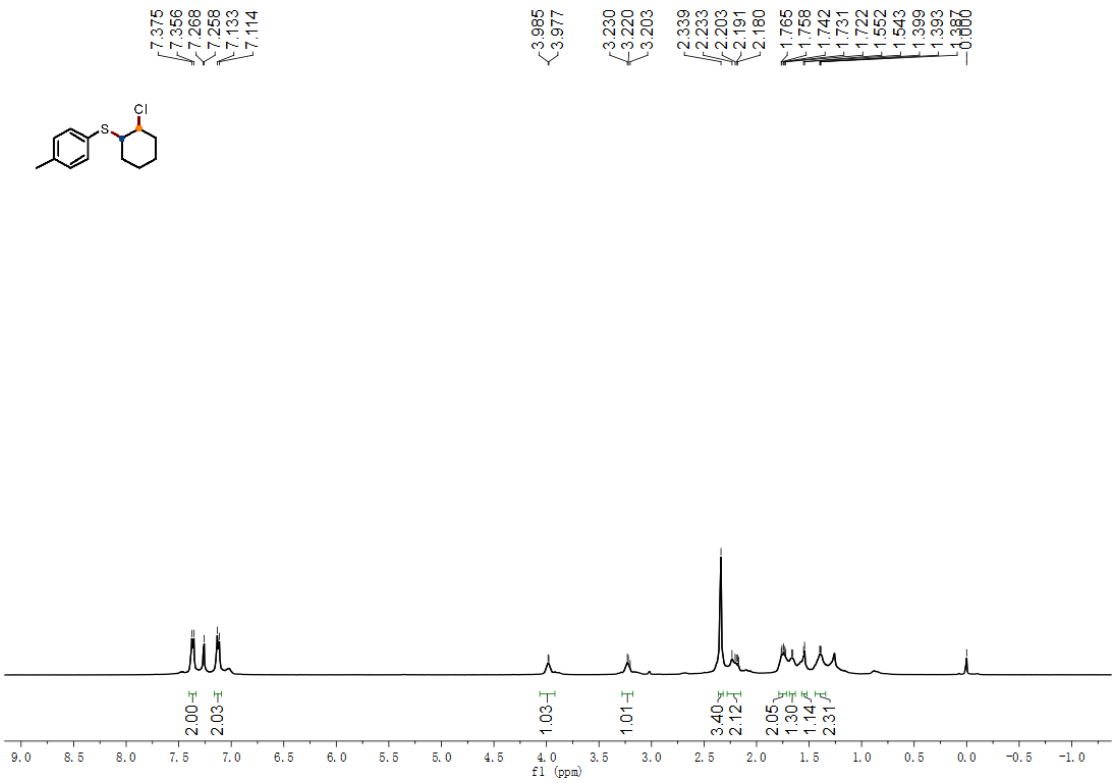
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 6.5 Hz, 2H), 7.09 (d, J = 7.0 Hz, 2H), 2.30 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 133.9, 129.8, 128.6, 21.11.

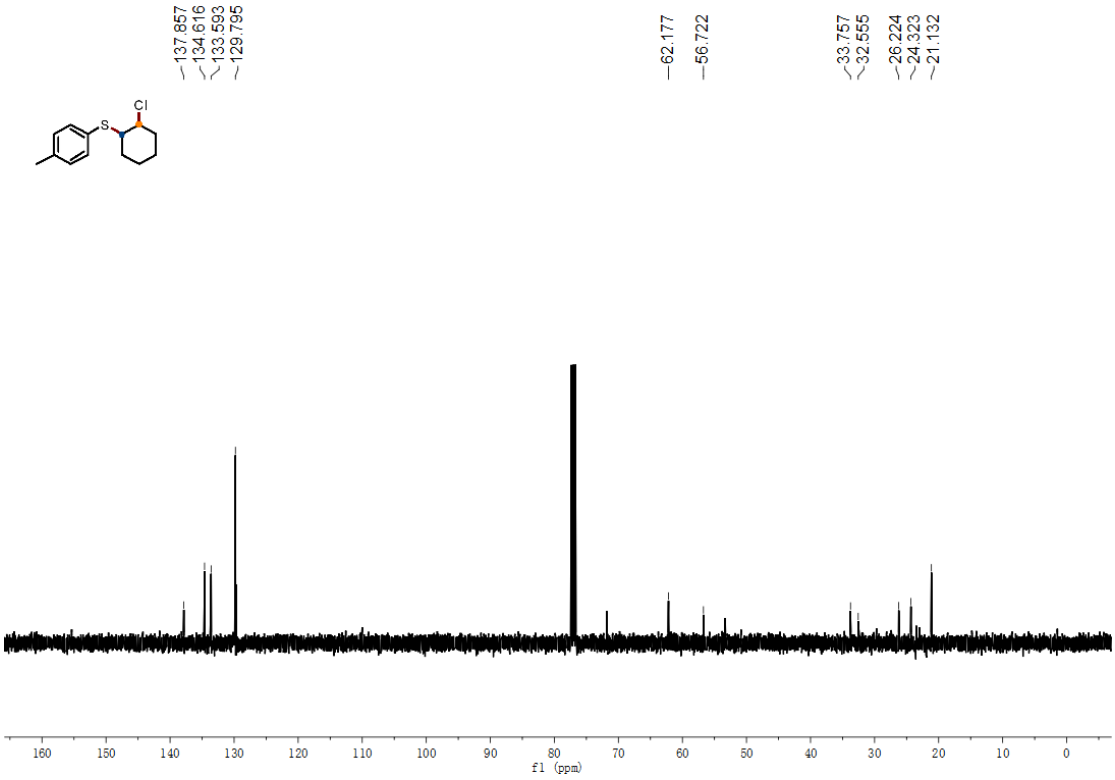
The analytic data is consistent with those reported in the literature. [1]

5. Spectra of prepared compounds

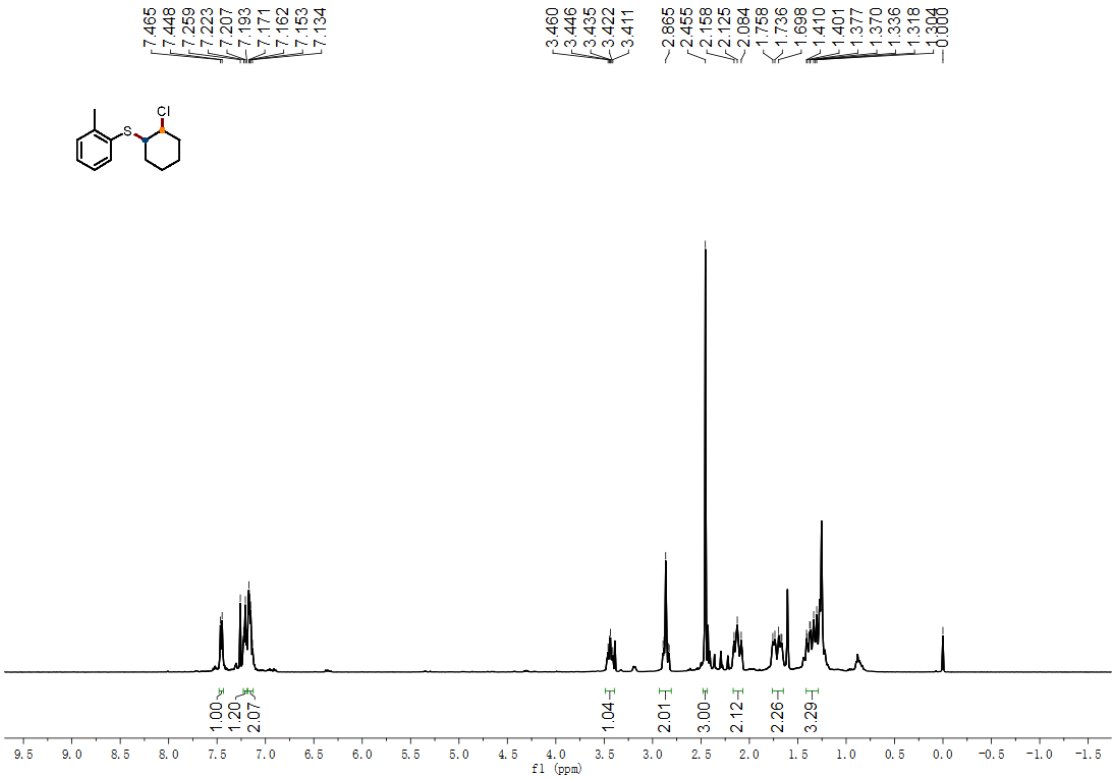
^{1}H NMR spectrum of compound **3a**



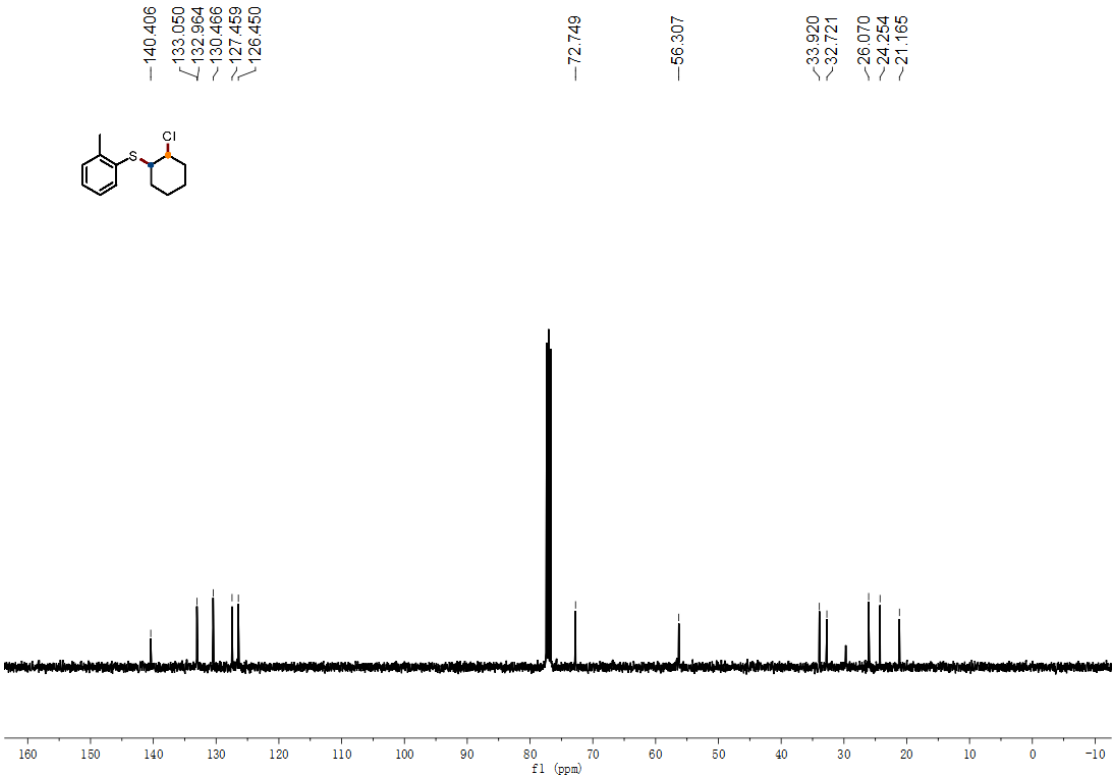
^{13}C NMR spectrum of compound **3a**



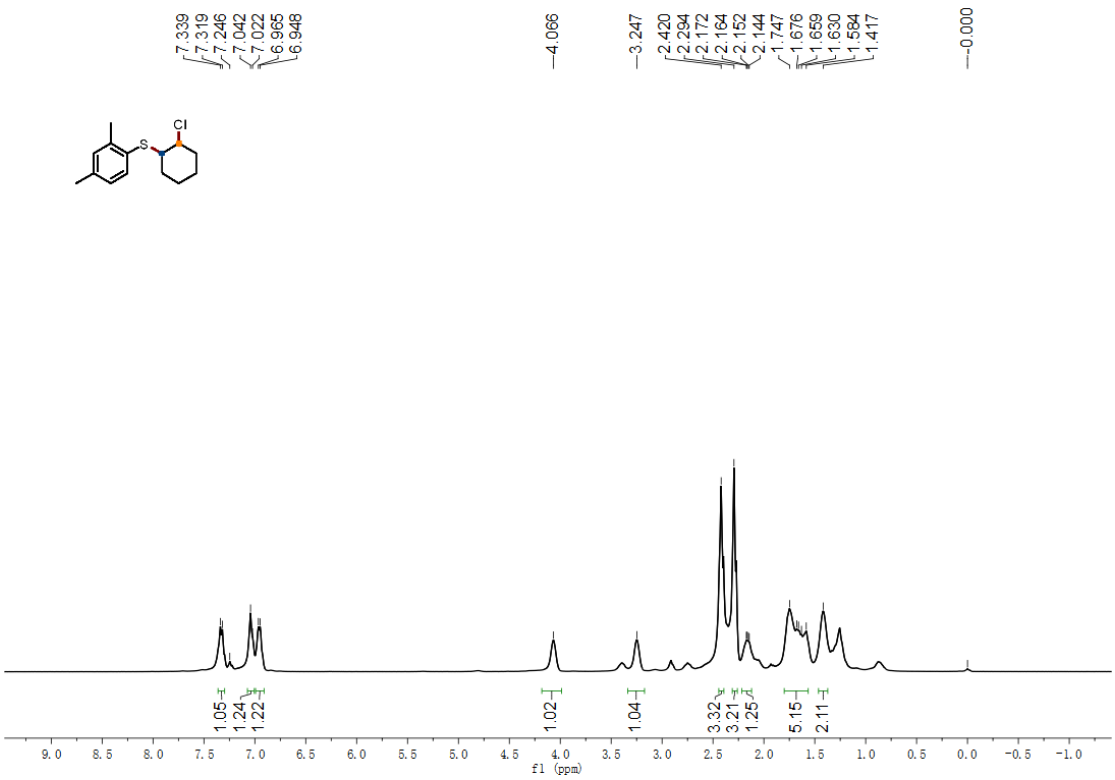
^{1}H NMR spectrum of compound **3b**



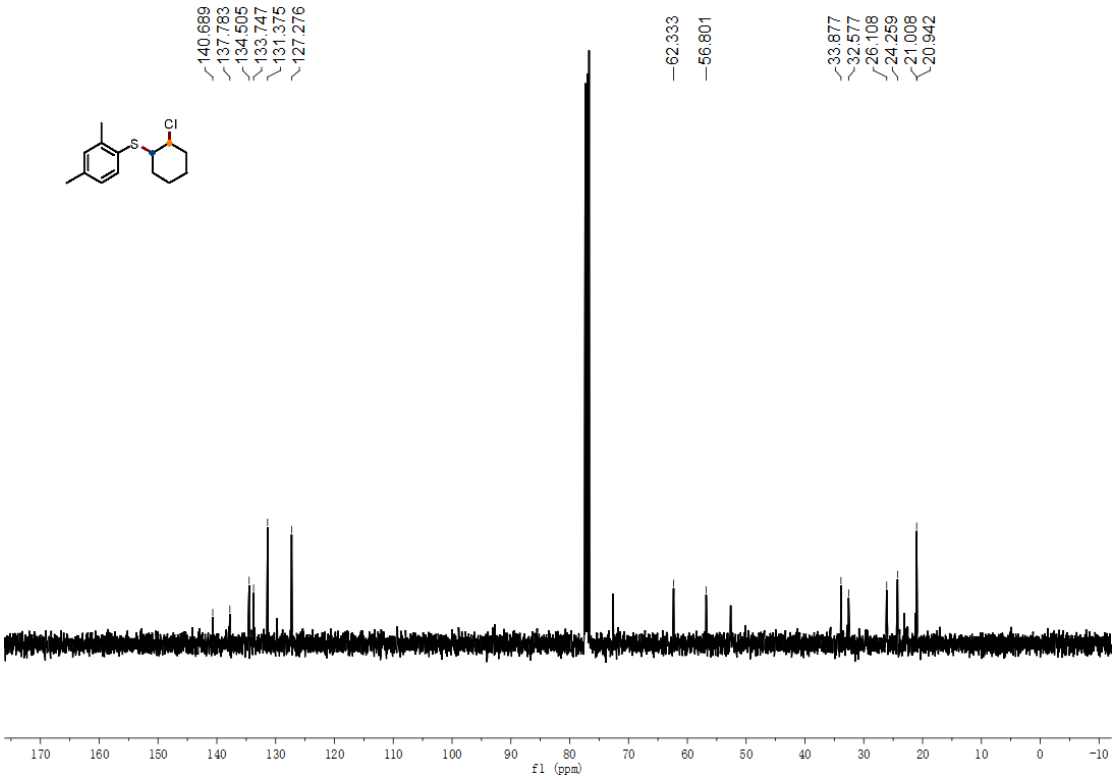
^{13}C NMR spectrum of compound **3b**



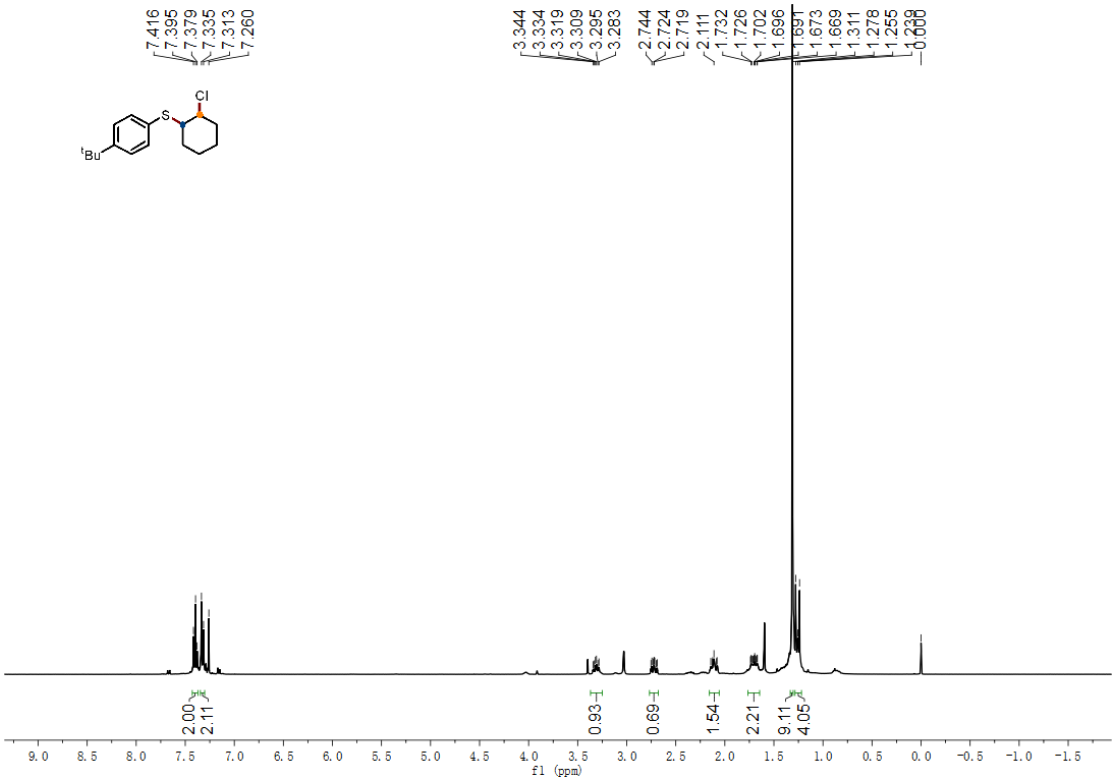
^{1}H NMR spectrum of compound **3c**



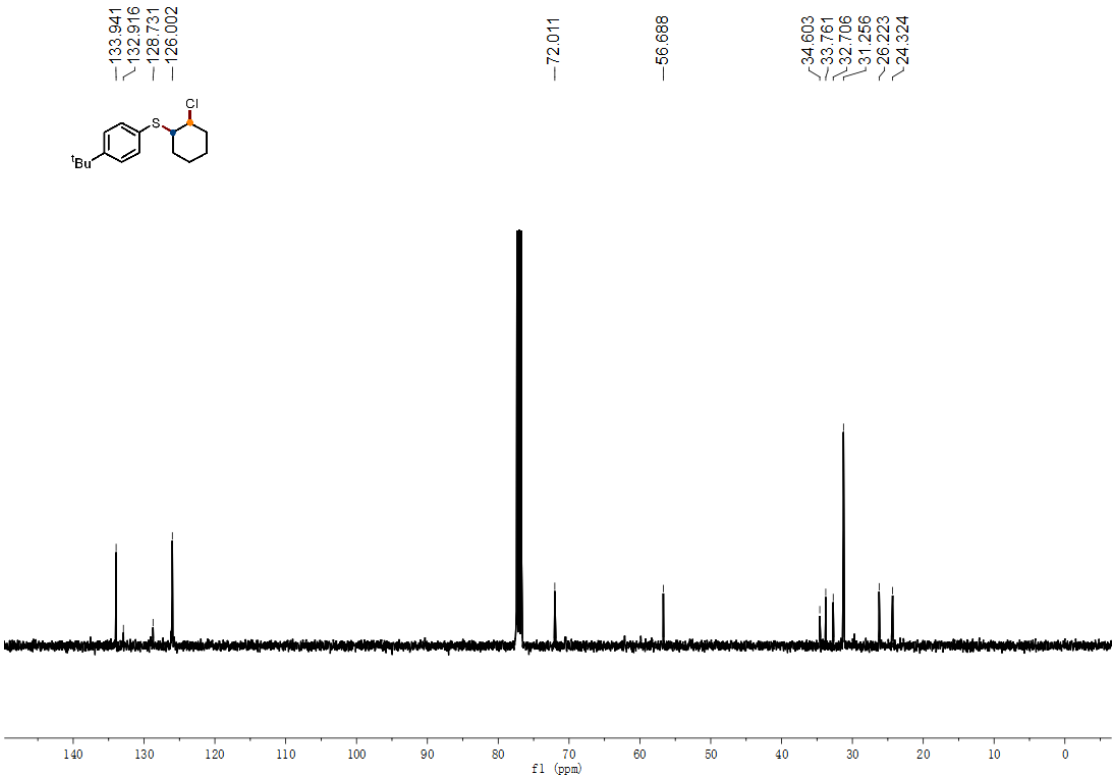
^{13}C NMR spectrum of compound **3c**



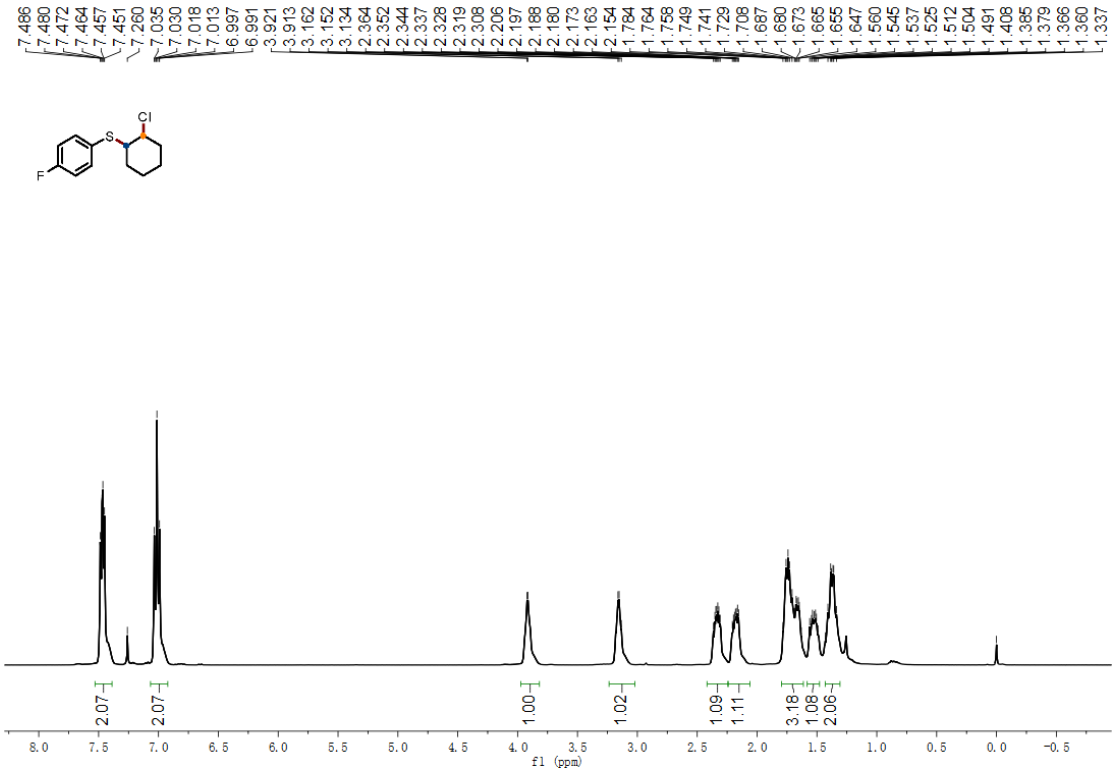
^{1}H NMR spectrum of compound **3d**



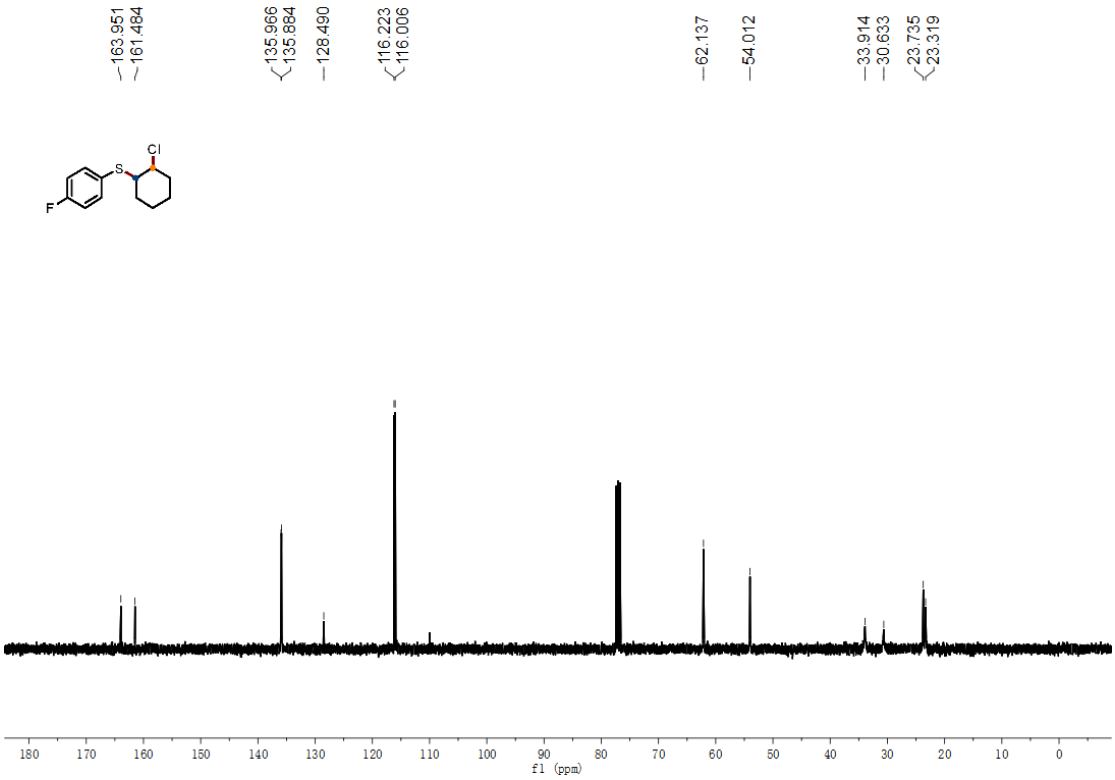
^{13}C NMR spectrum of compound **3d**



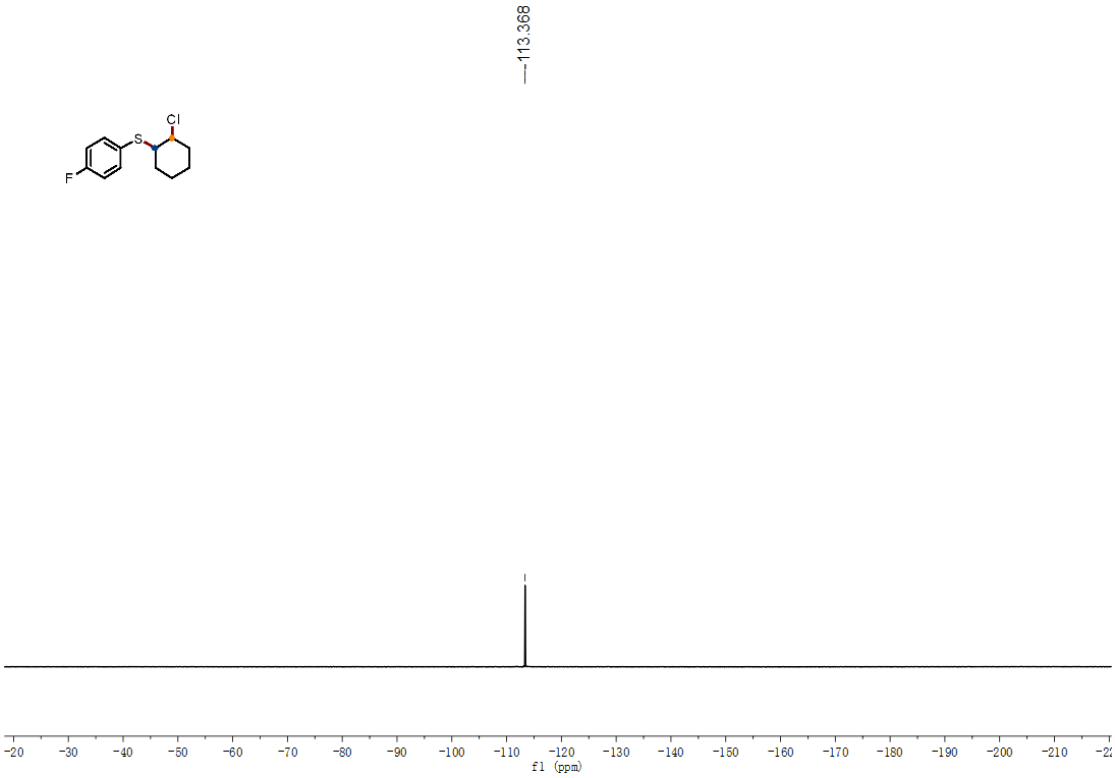
^{1}H NMR spectrum of compound **3e**



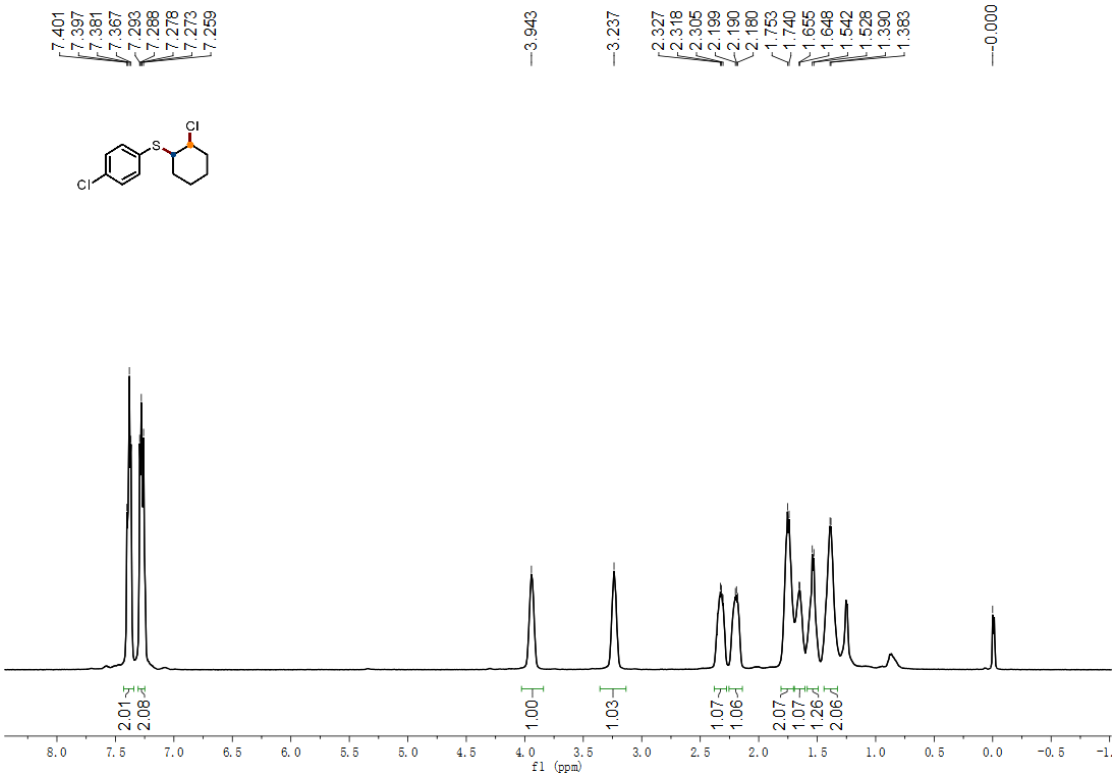
^{13}C NMR spectrum of compound **3e**



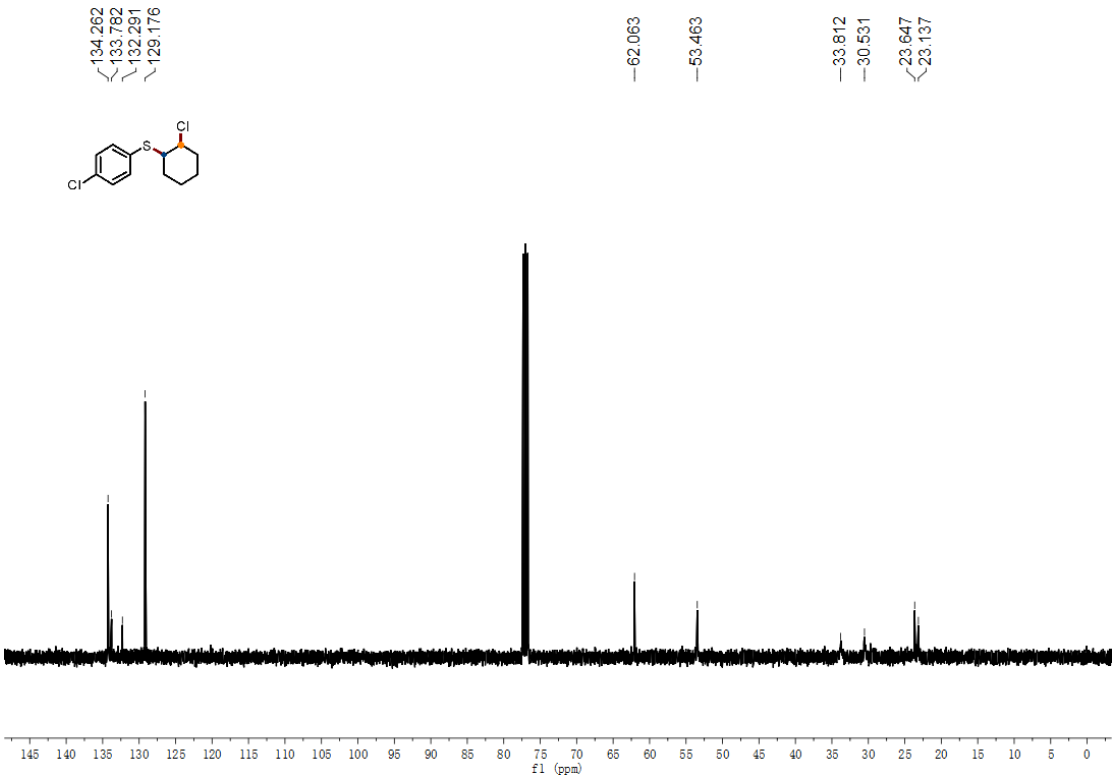
^{19}F NMR spectrum of compound **3e**



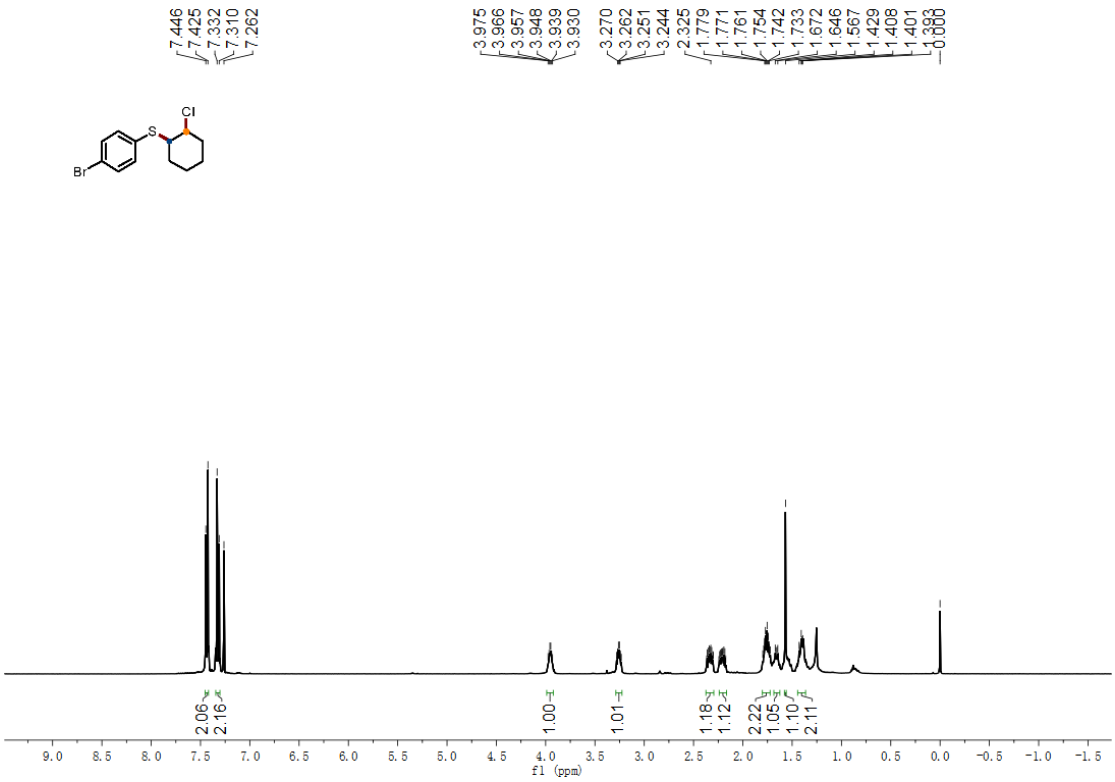
^{1}H NMR spectrum of compound **3f**



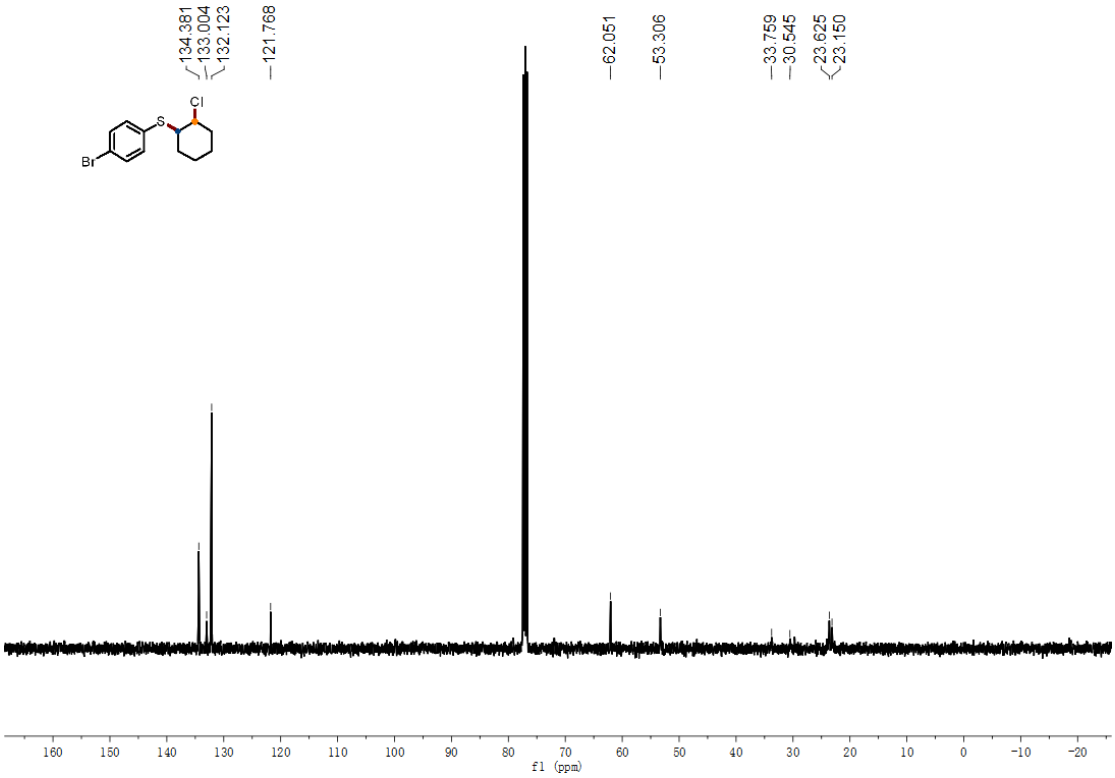
^{13}C NMR spectrum of compound **3f**



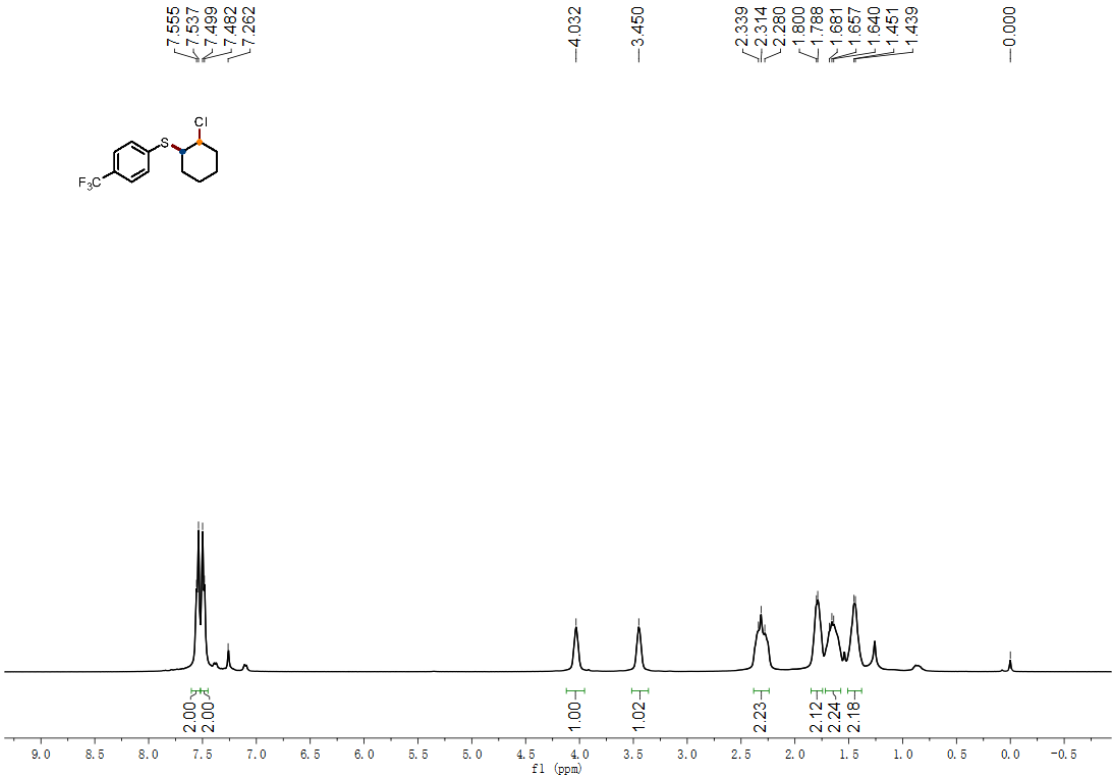
^{1}H NMR spectrum of compound **3g**



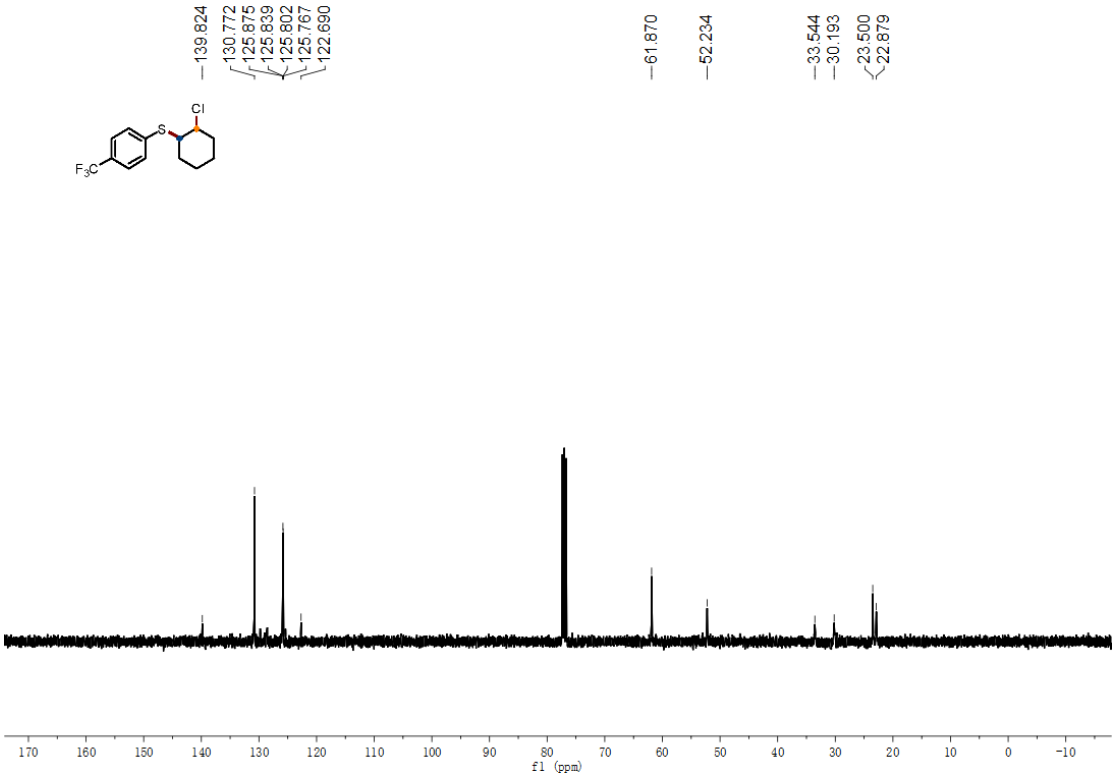
^{13}C NMR spectrum of compound **3g**



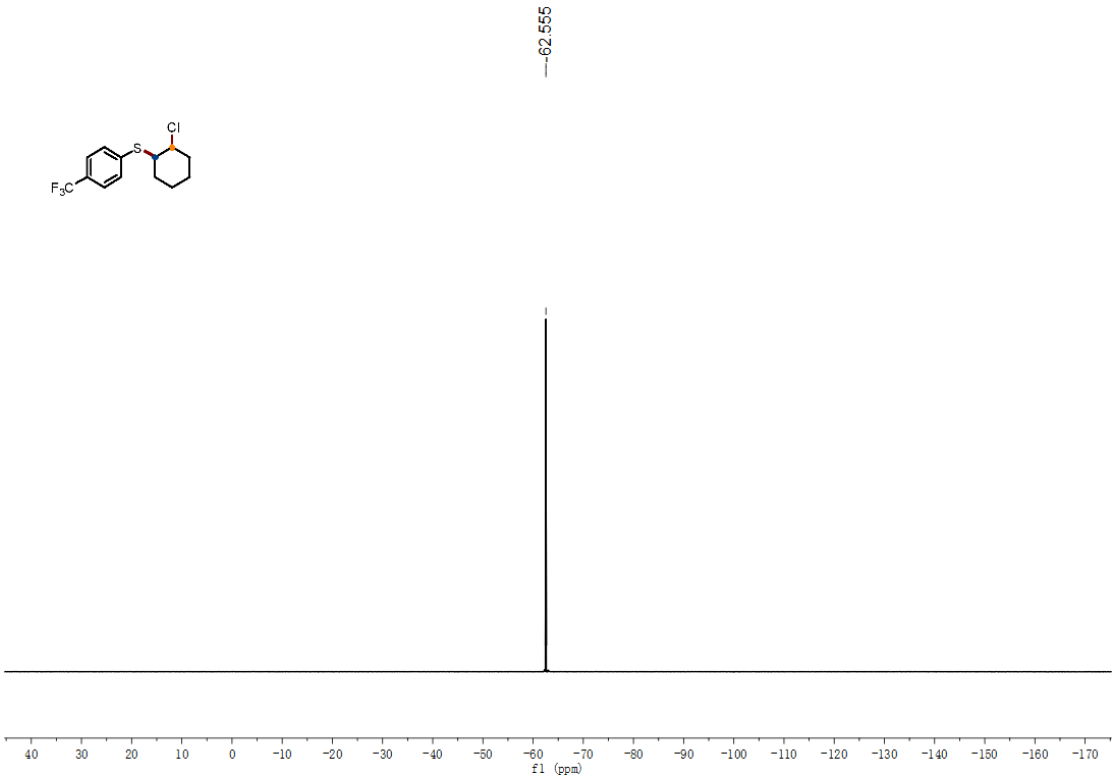
^{1}H NMR spectrum of compound **3h**



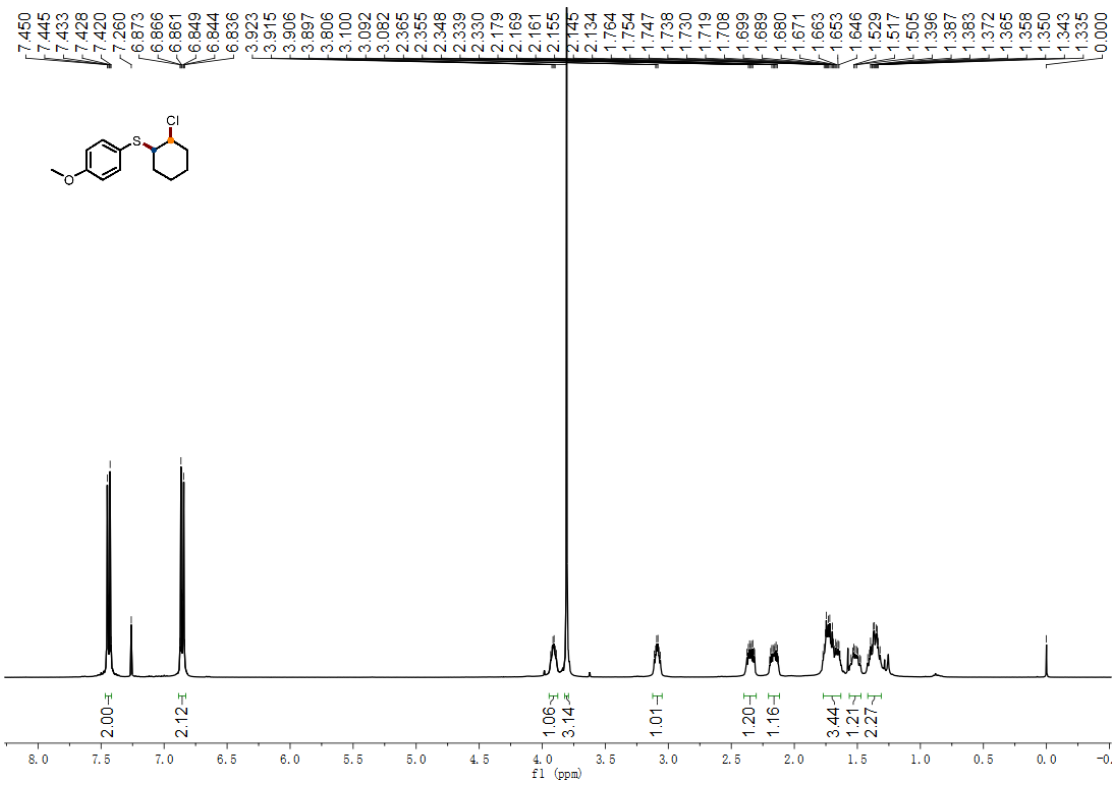
^{13}C NMR spectrum of compound **3h**



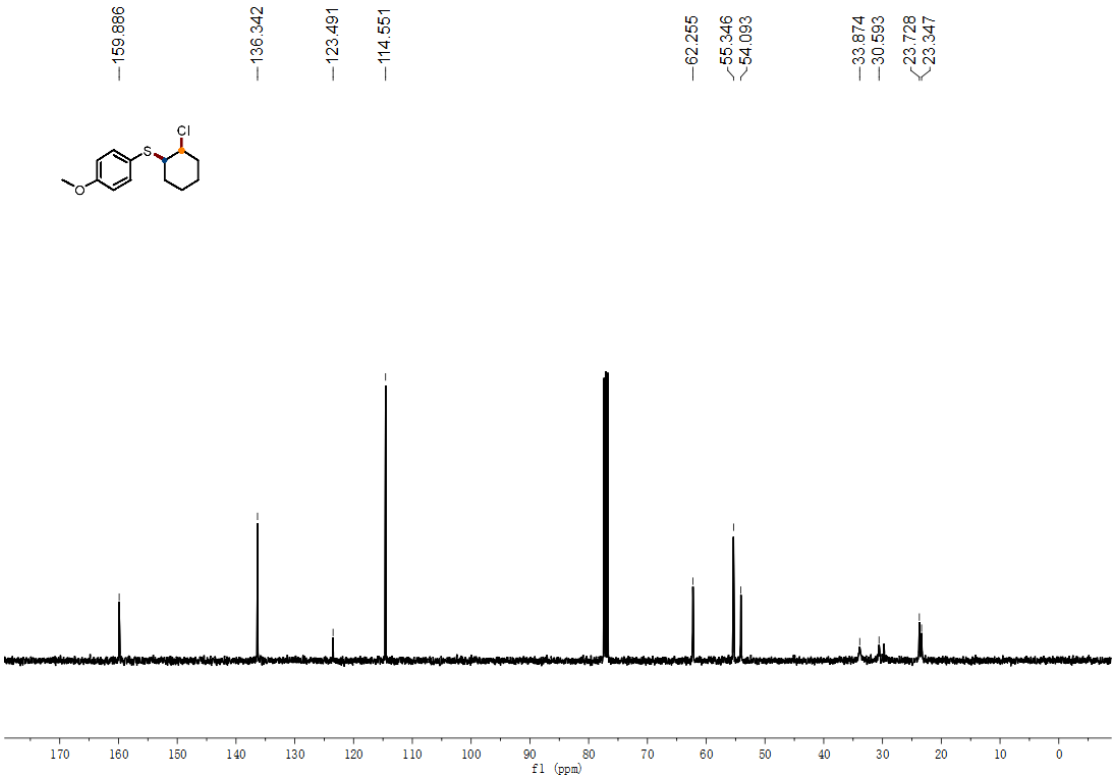
^{19}F NMR spectrum of compound **3h**



^{1}H NMR spectrum of compound **3i**

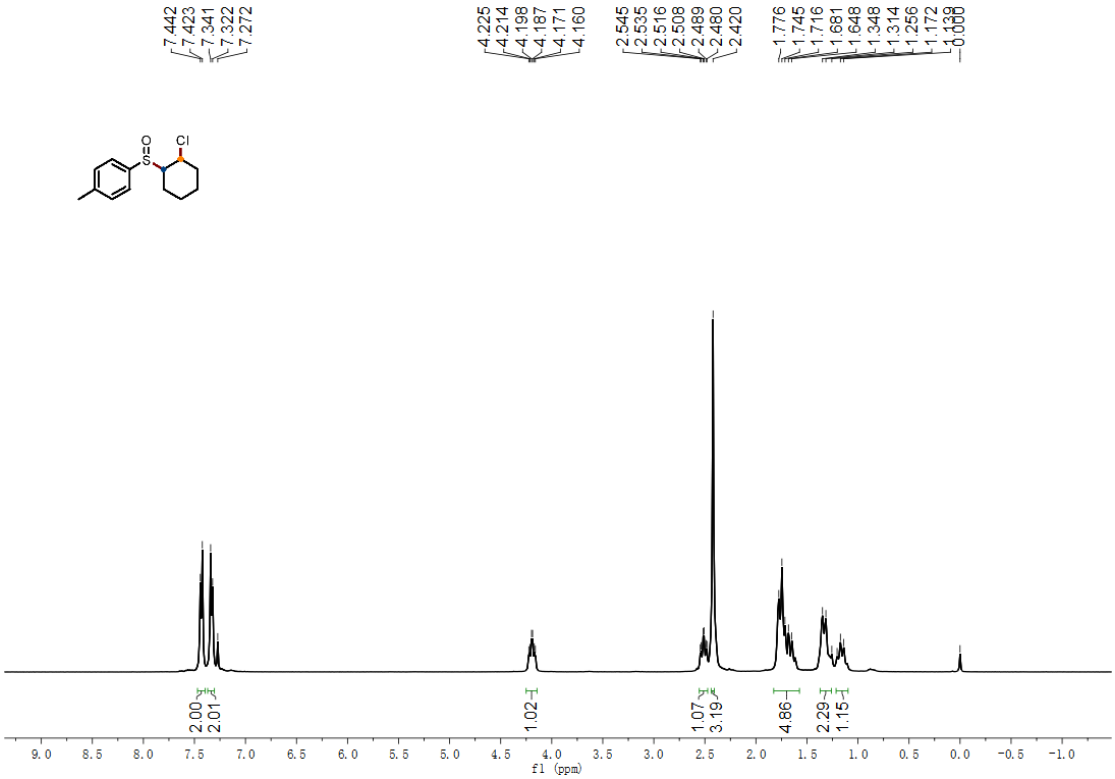


^{13}C NMR spectrum of compound **3i**

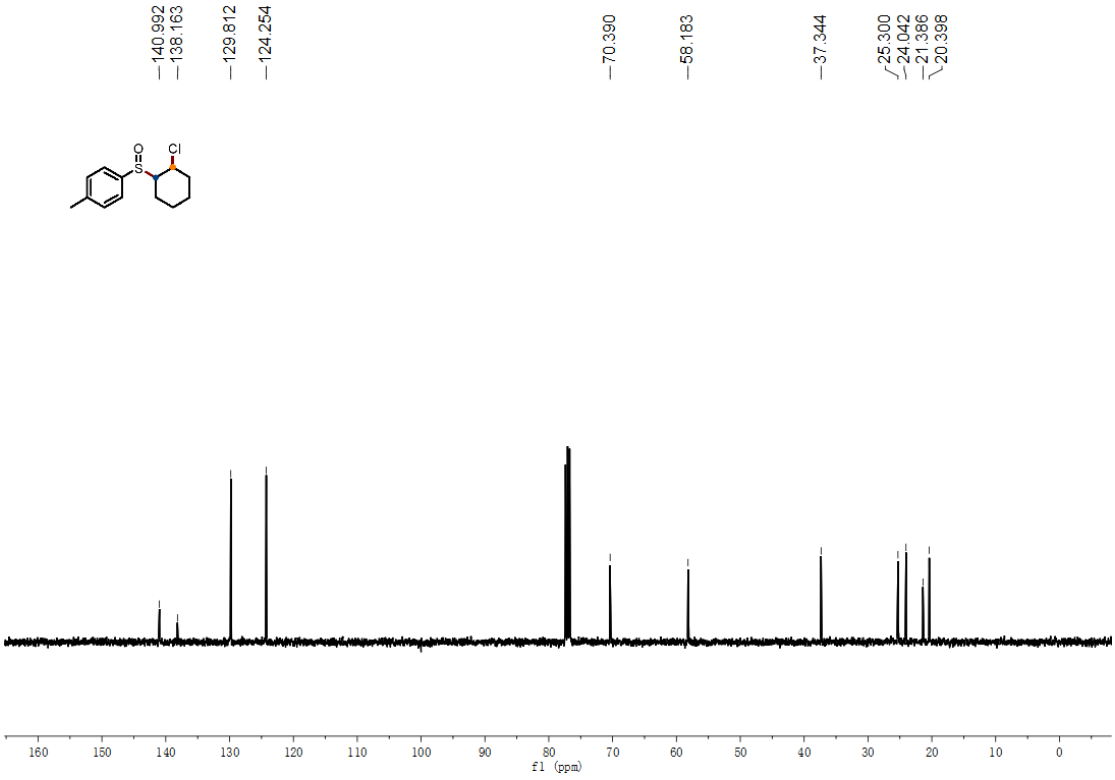


Diastereoisomer 1

^{1}H NMR spectrum of compound **4a**

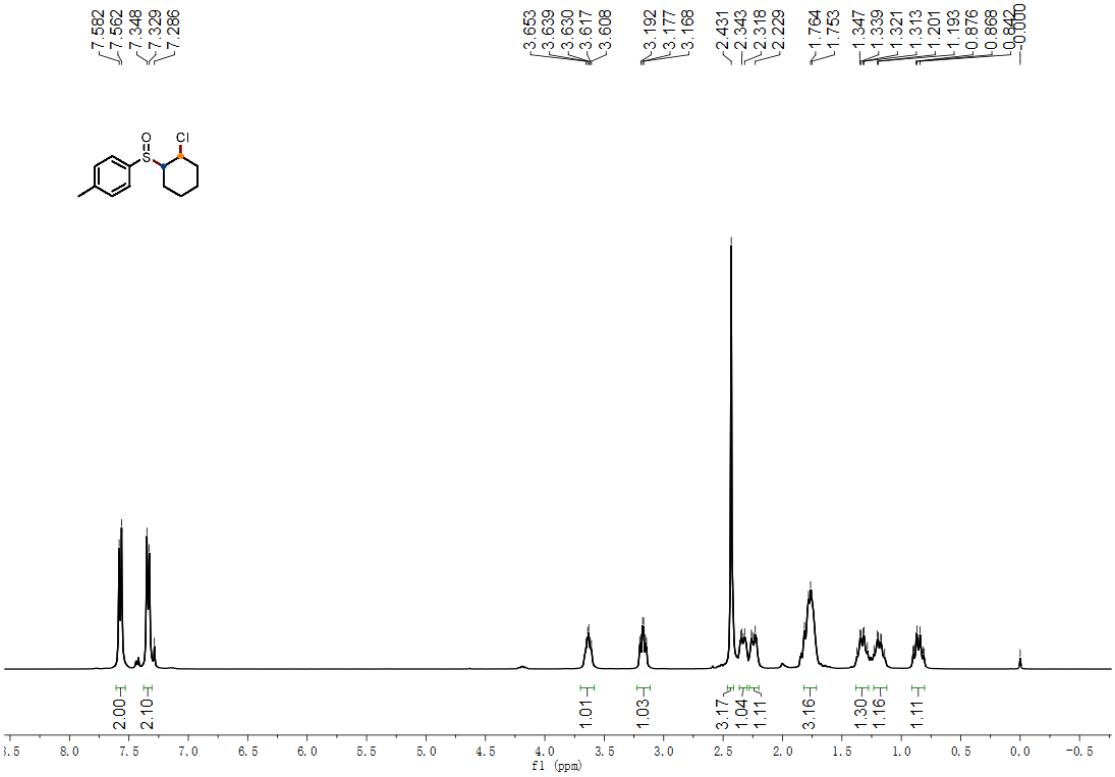


^{13}C NMR spectrum of compound **4a**

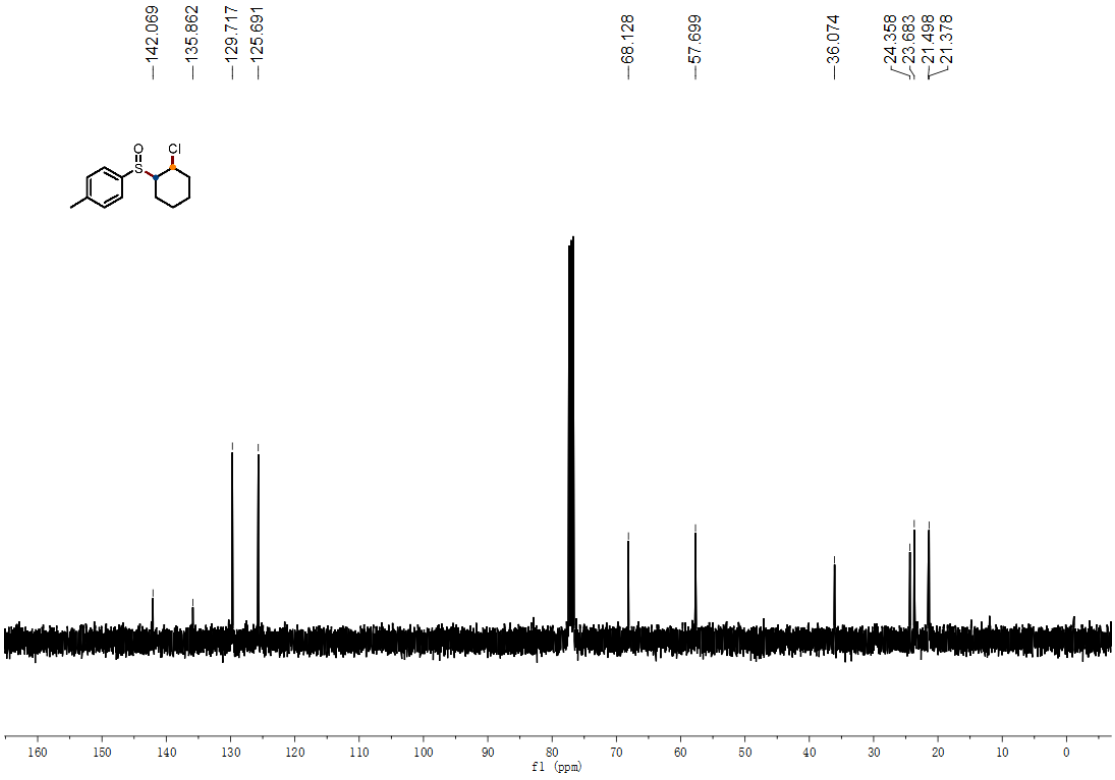


Diastereoisomer 2

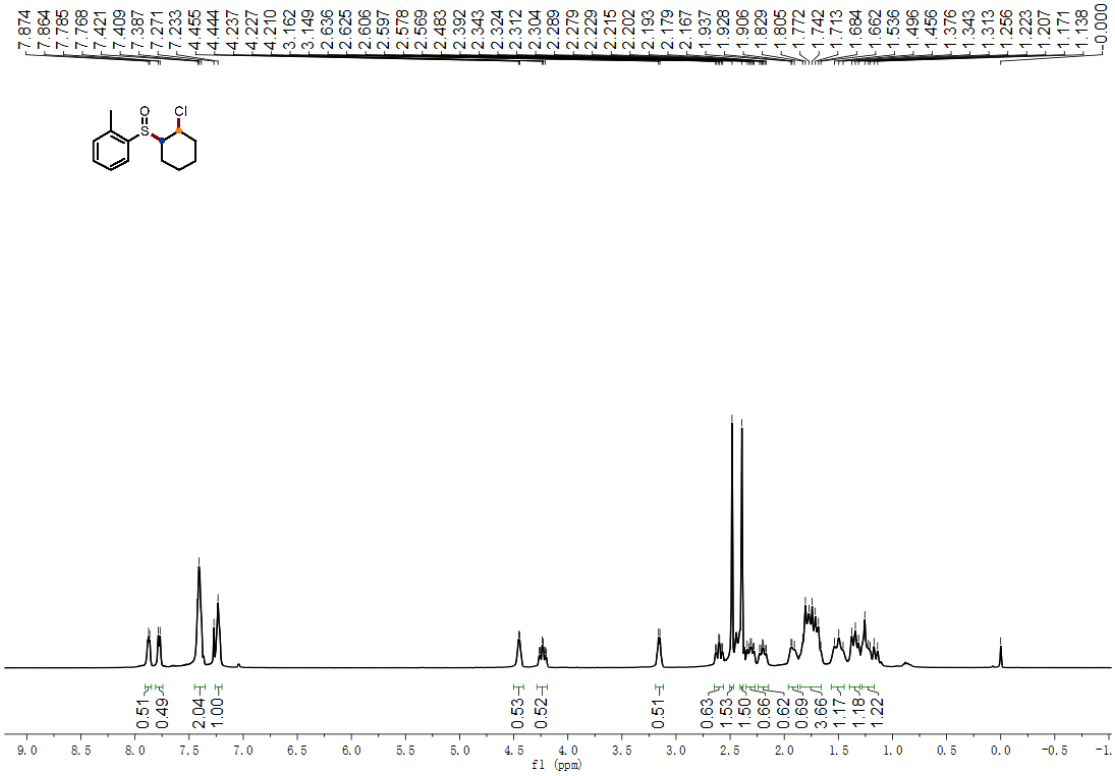
^{1}H NMR spectrum of compound **4a**



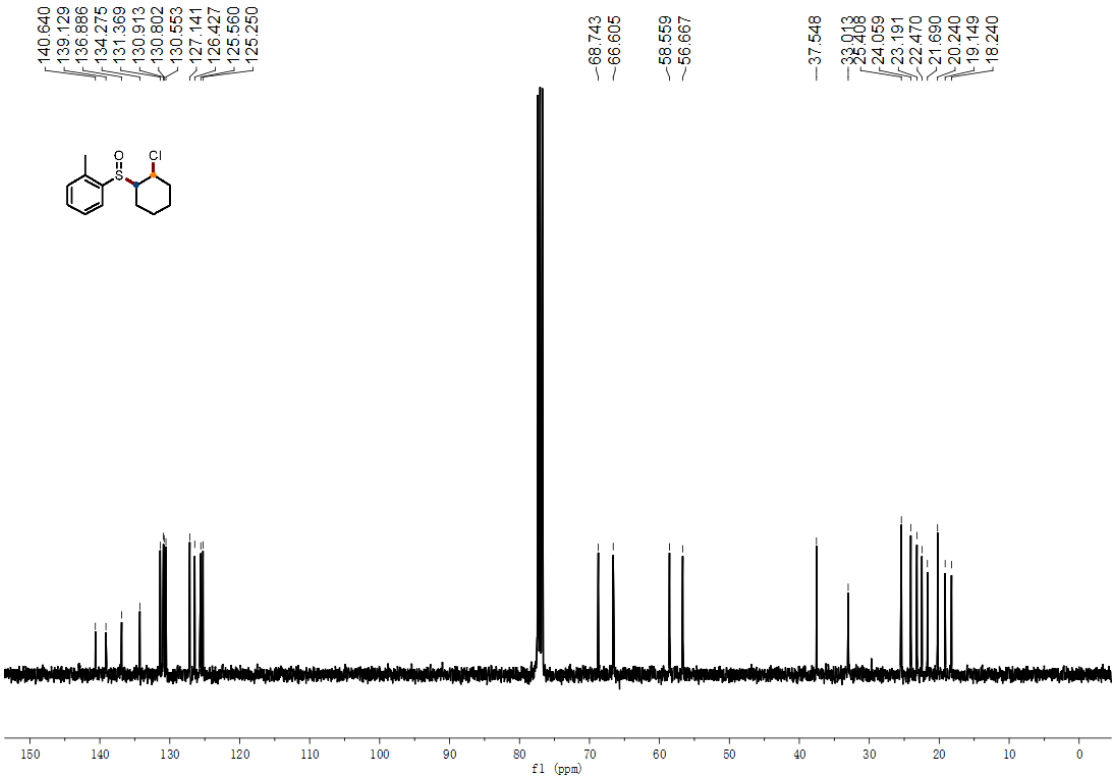
^{13}C NMR spectrum of compound **4a**



^{1}H NMR spectrum of compound **4b**

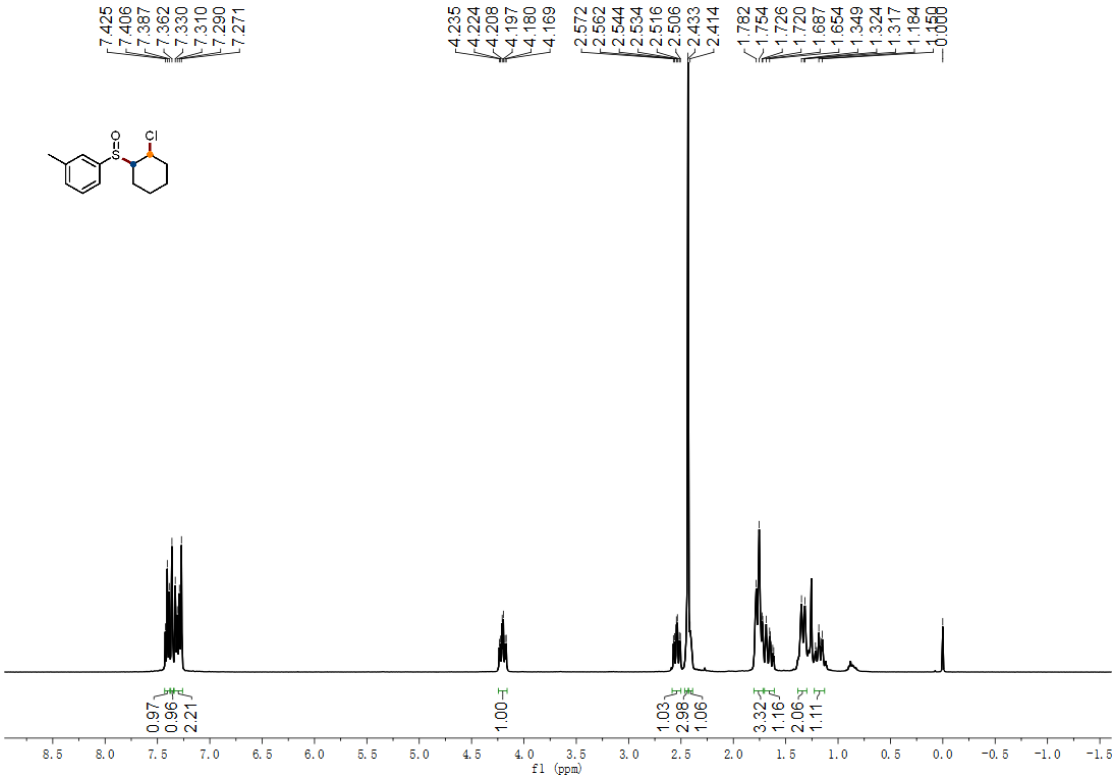


^{13}C NMR spectrum of compound **4b**

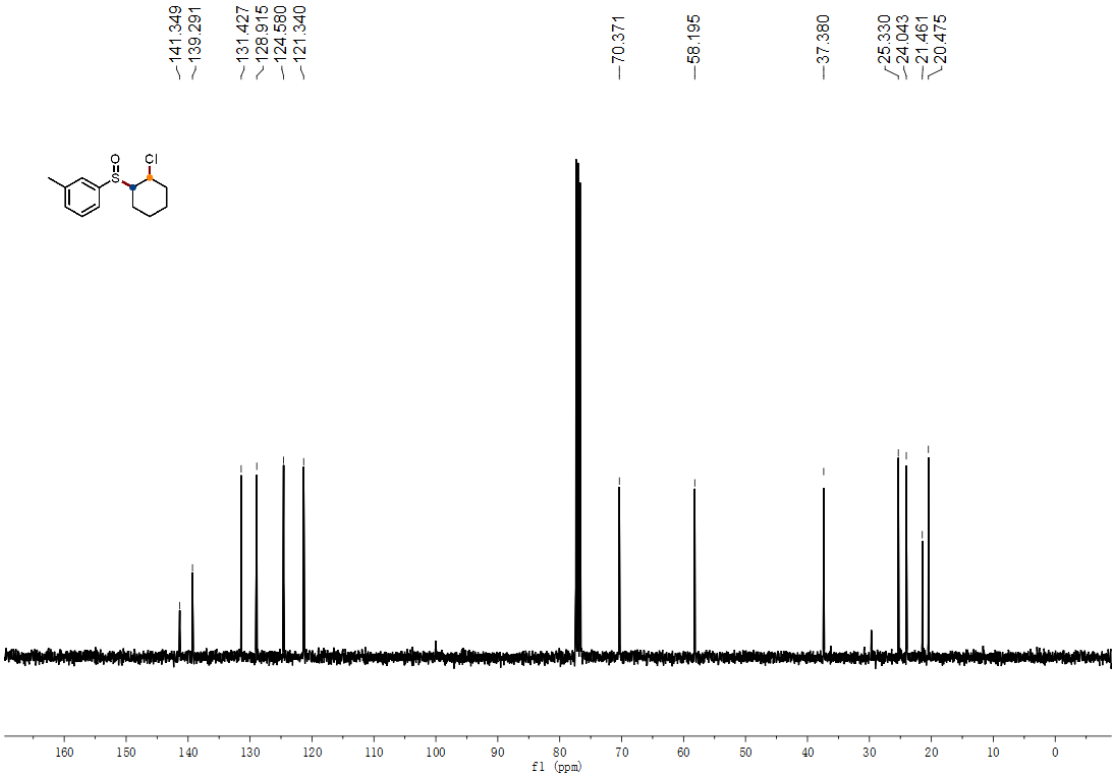


Diastereoisomer 1

^{1}H NMR spectrum of compound **4c**

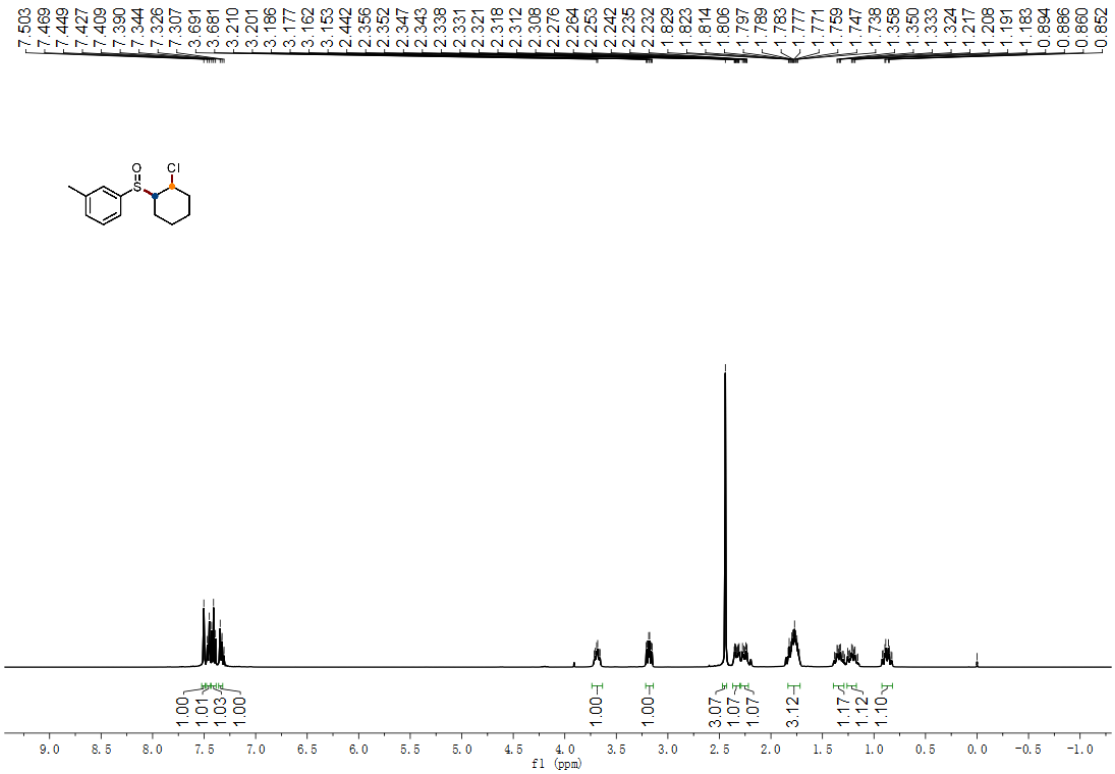


^{13}C NMR spectrum of compound **4c**

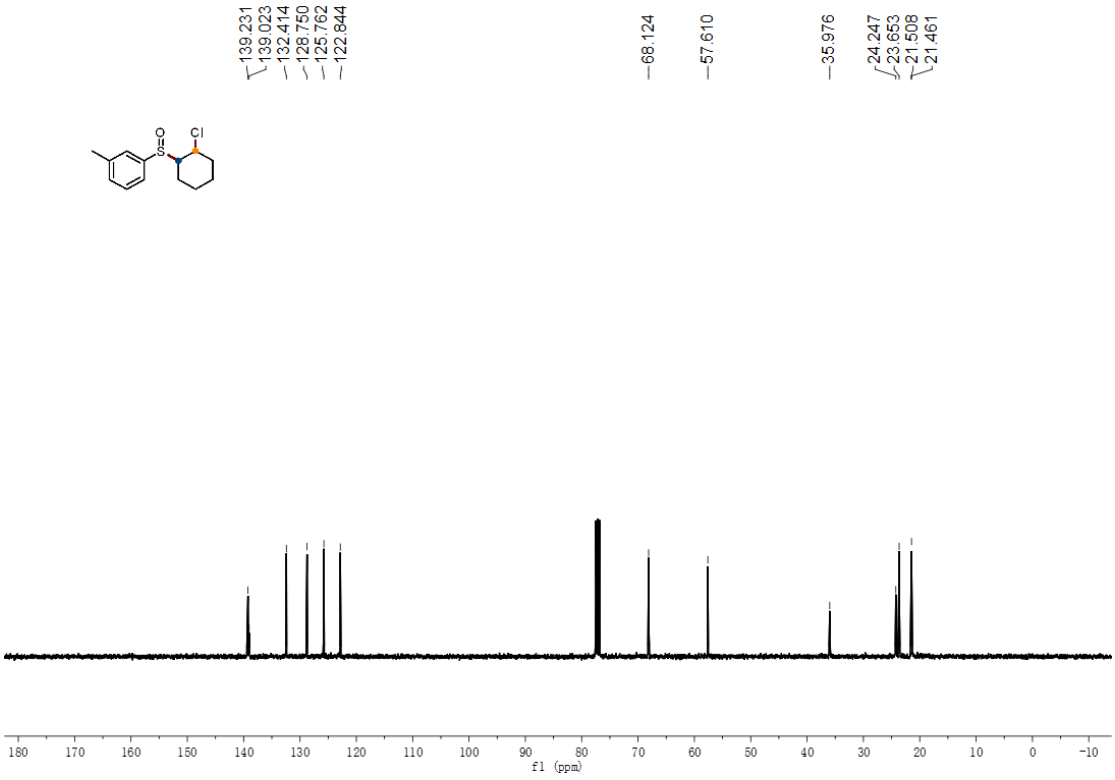


Diastereoisomer 2

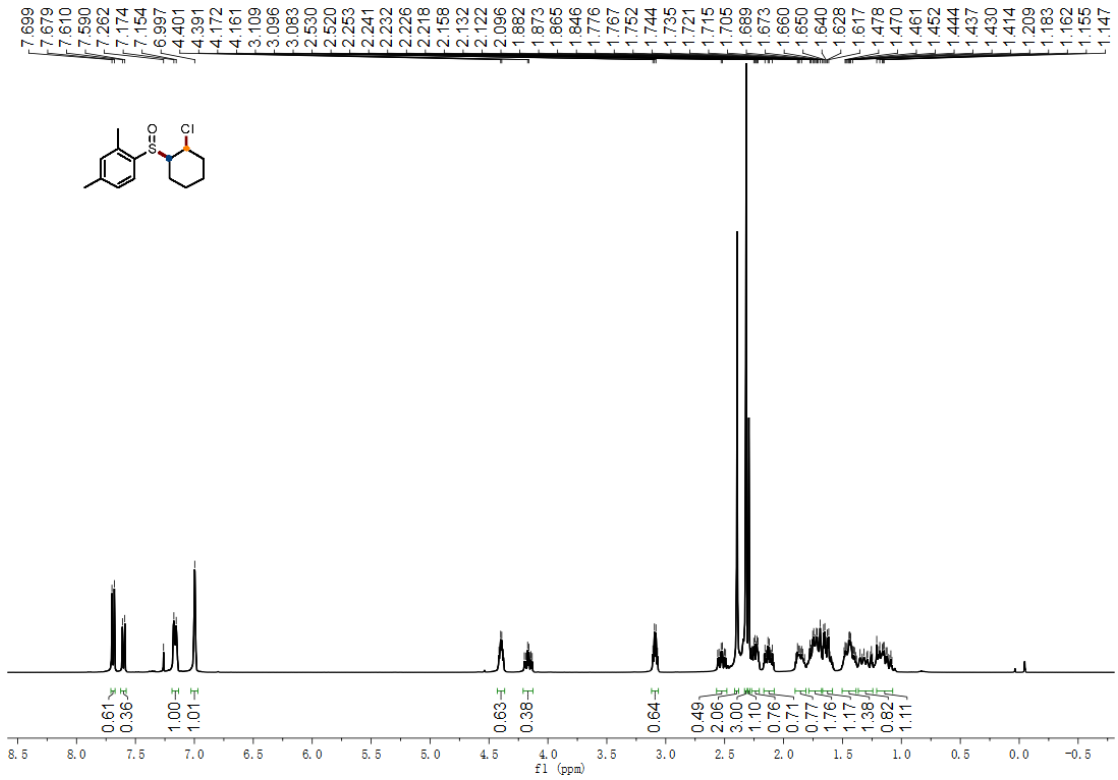
^{1}H NMR spectrum of compound **4c**



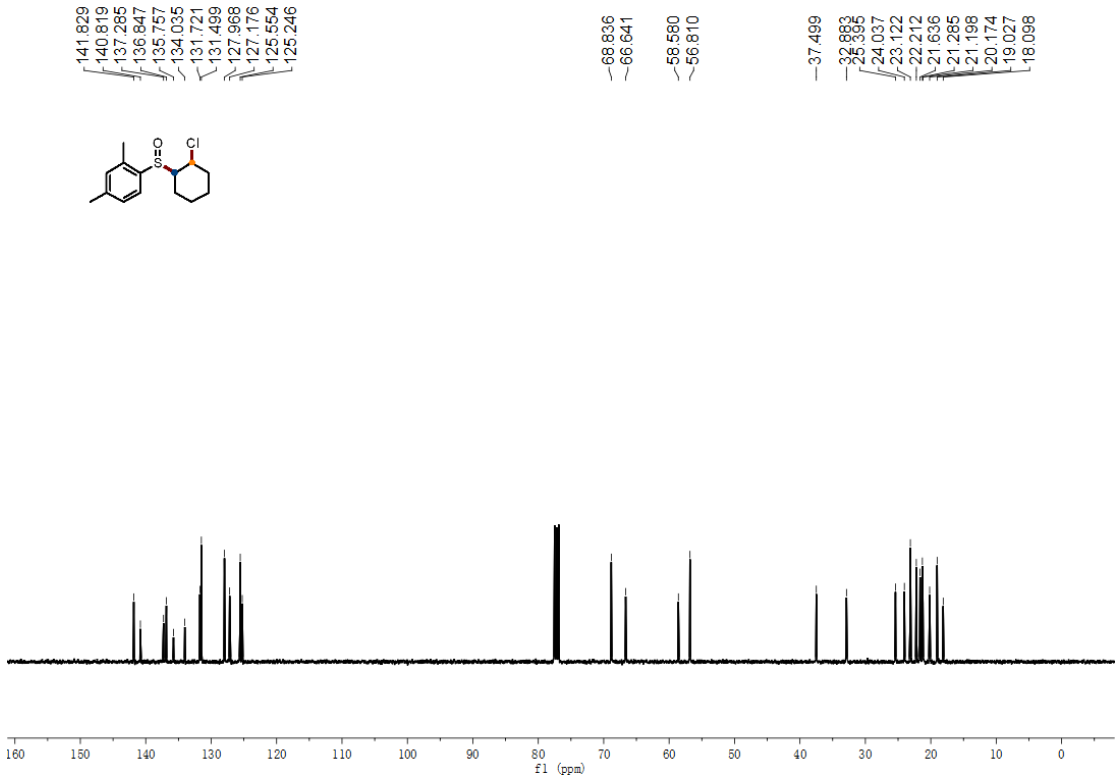
^{13}C NMR spectrum of compound **4c**



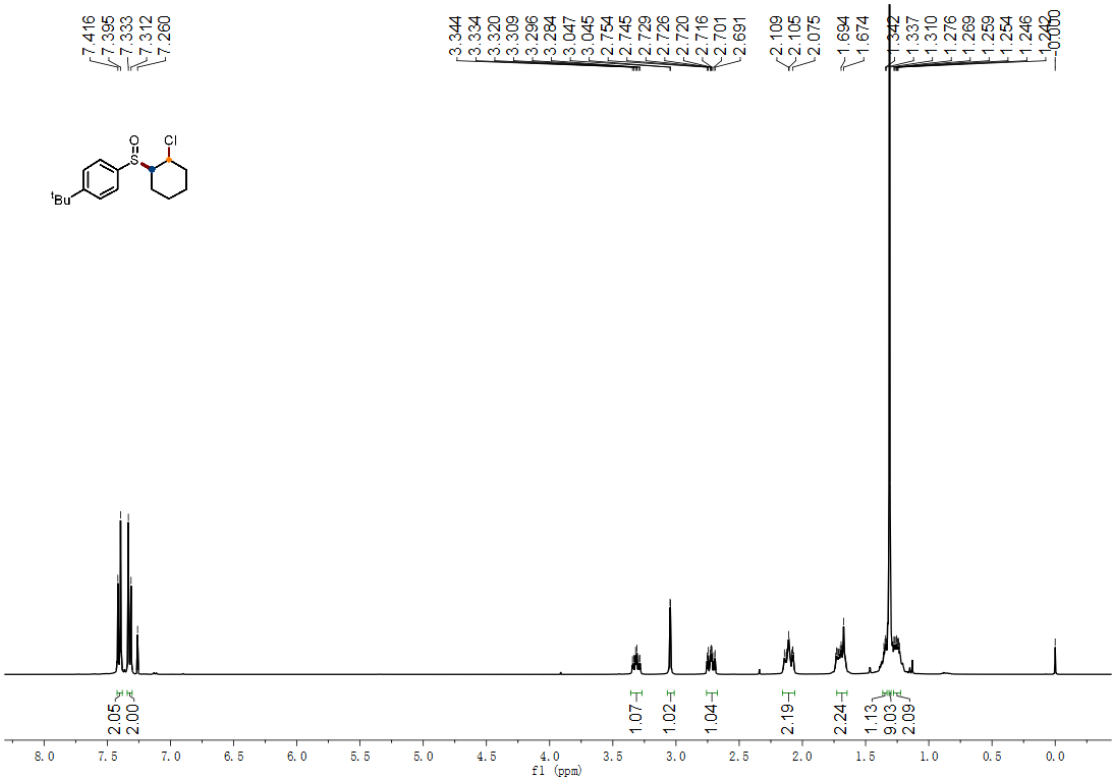
^{1}H NMR spectrum of compound **4d**



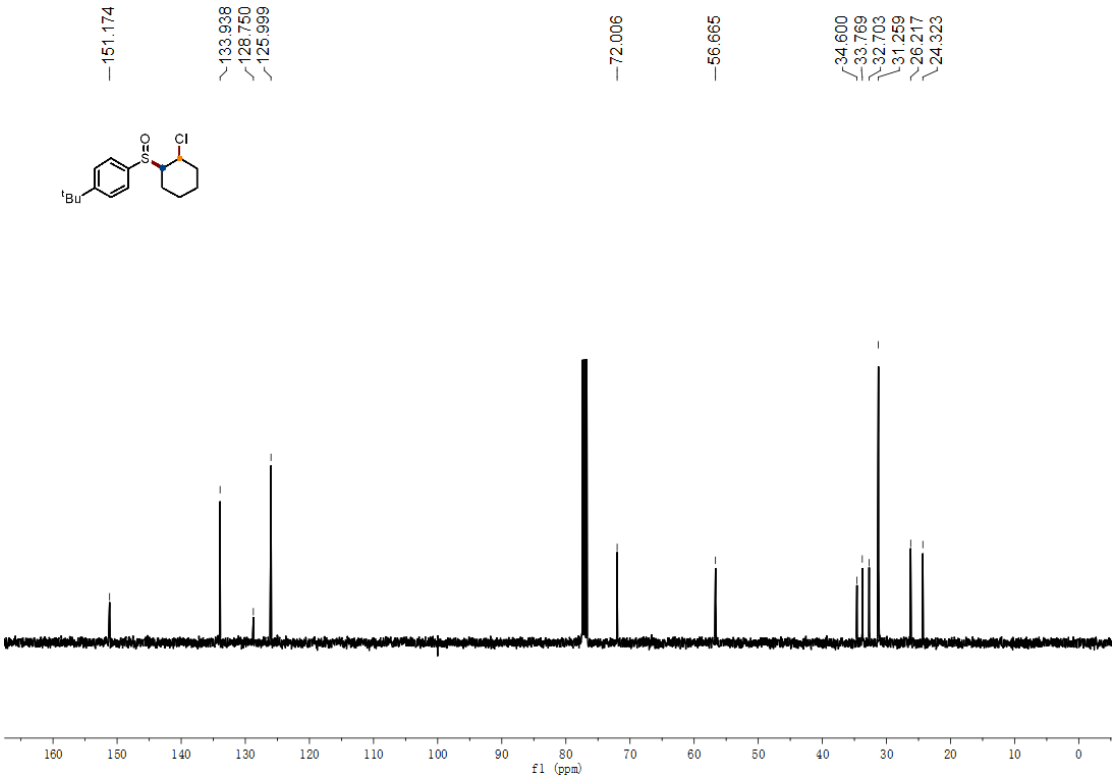
^{13}C NMR spectrum of compound **4d**



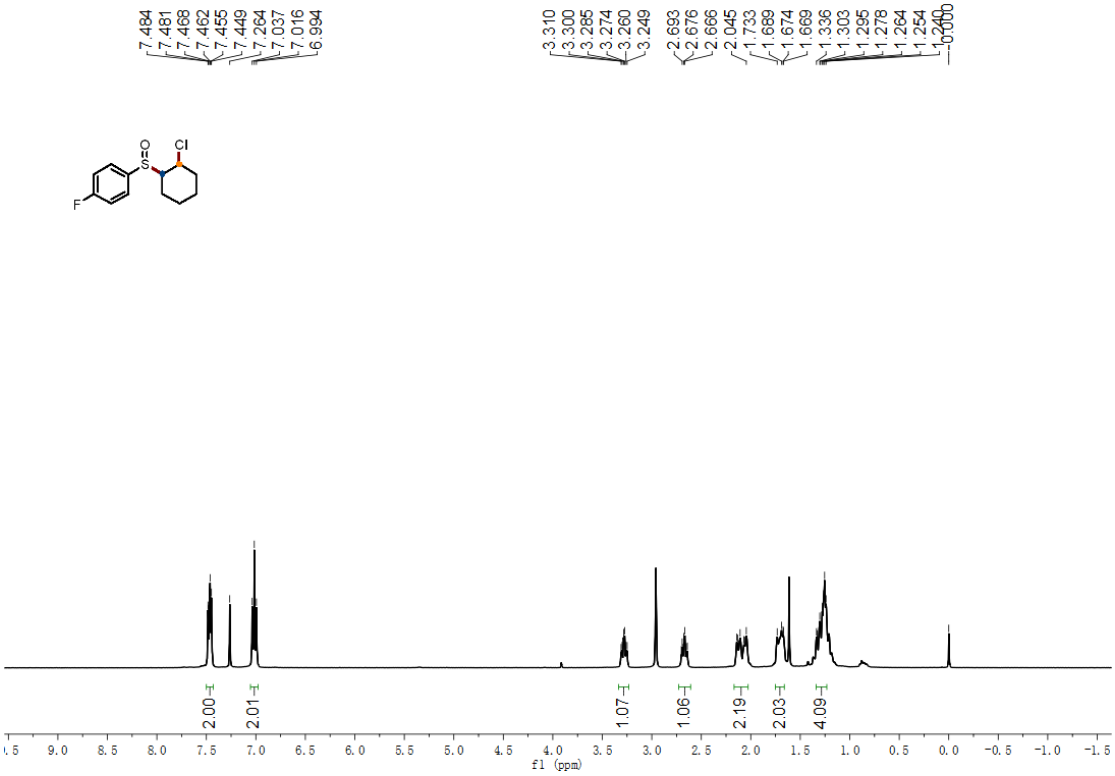
^{1}H NMR spectrum of compound **4e**



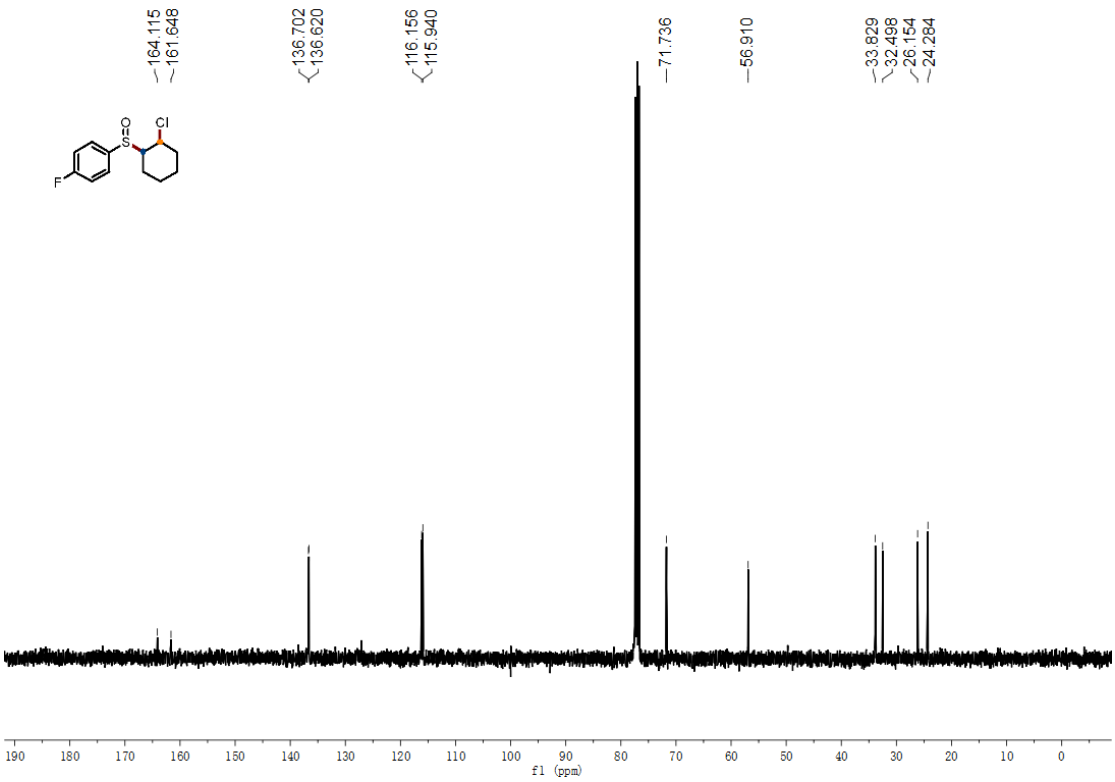
^{13}C NMR spectrum of compound **4e**



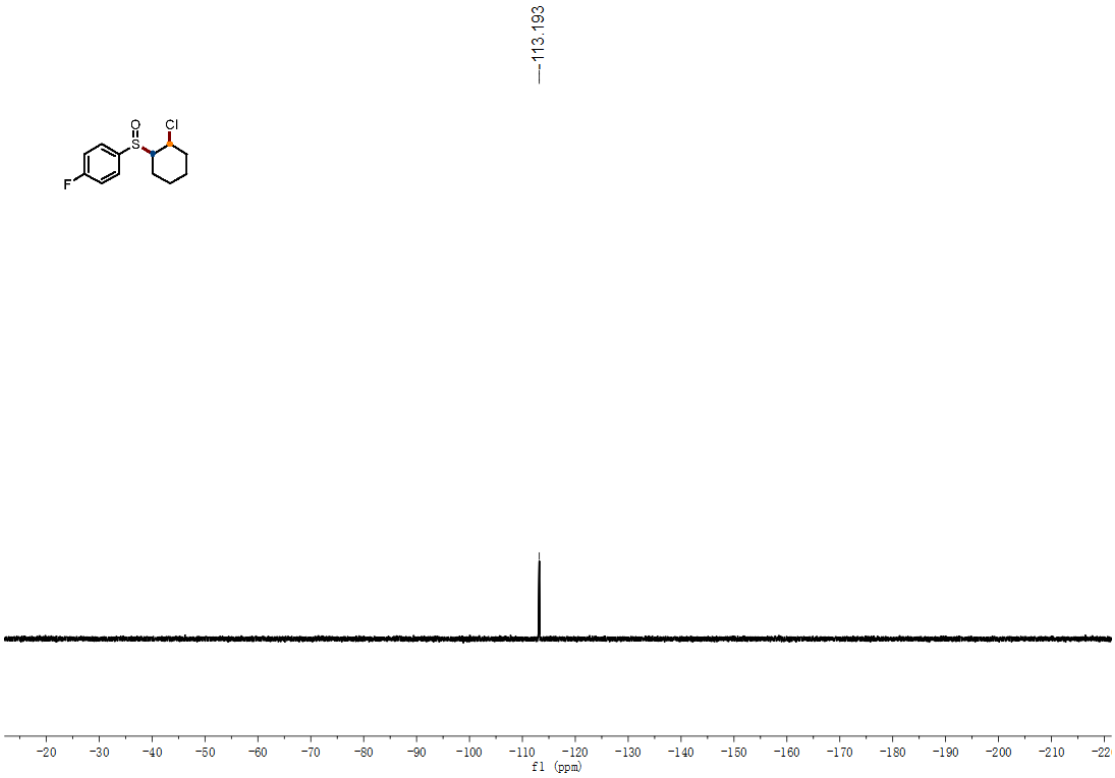
^{1}H NMR spectrum of compound **4f**



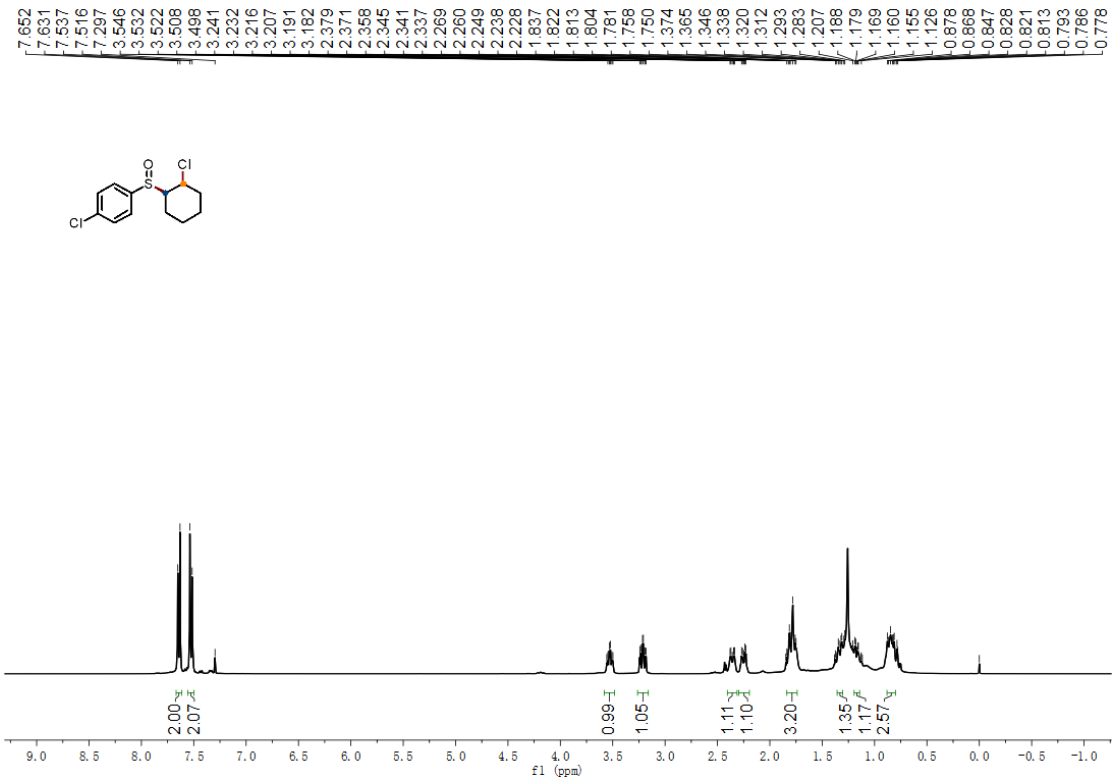
^{13}C NMR spectrum of compound **4f**



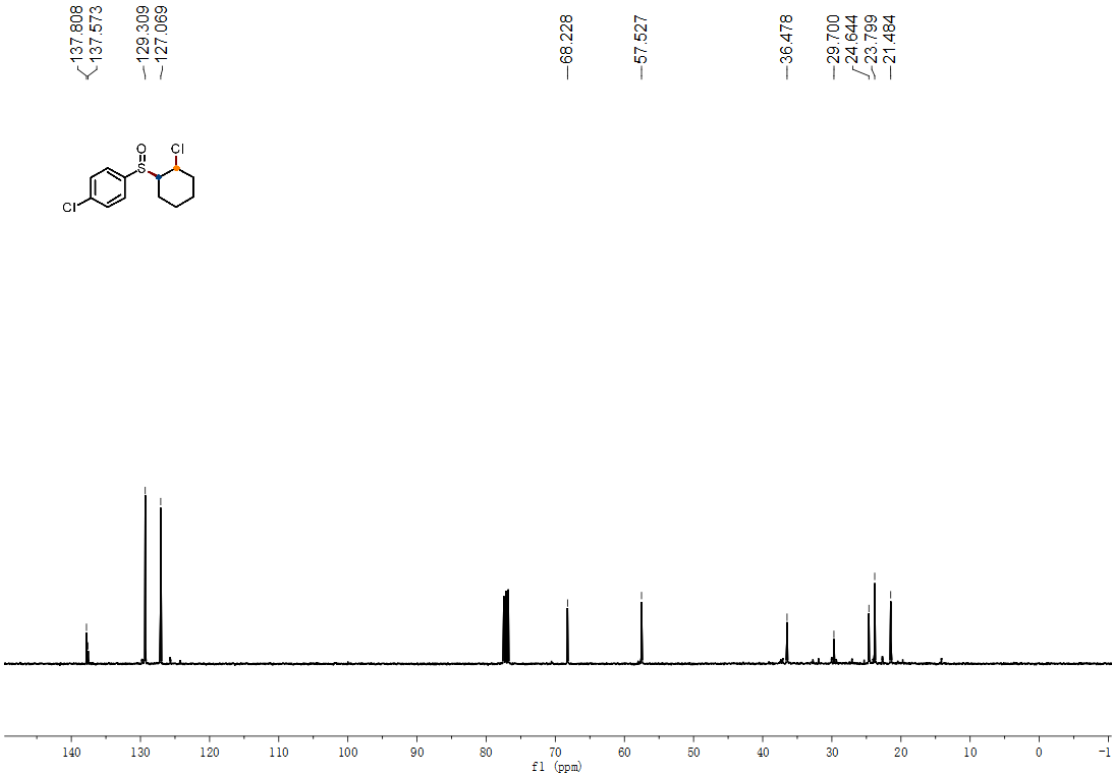
^{19}F NMR spectrum of compound **4f**



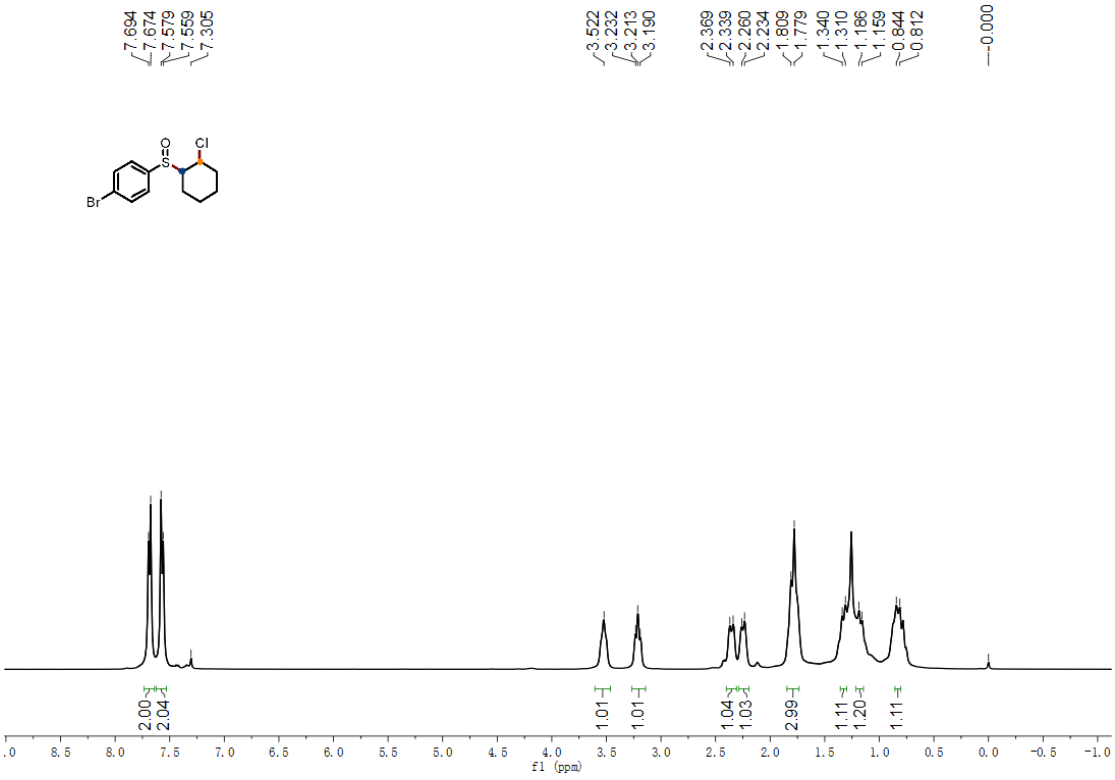
^{1}H NMR spectrum of compound **4g**



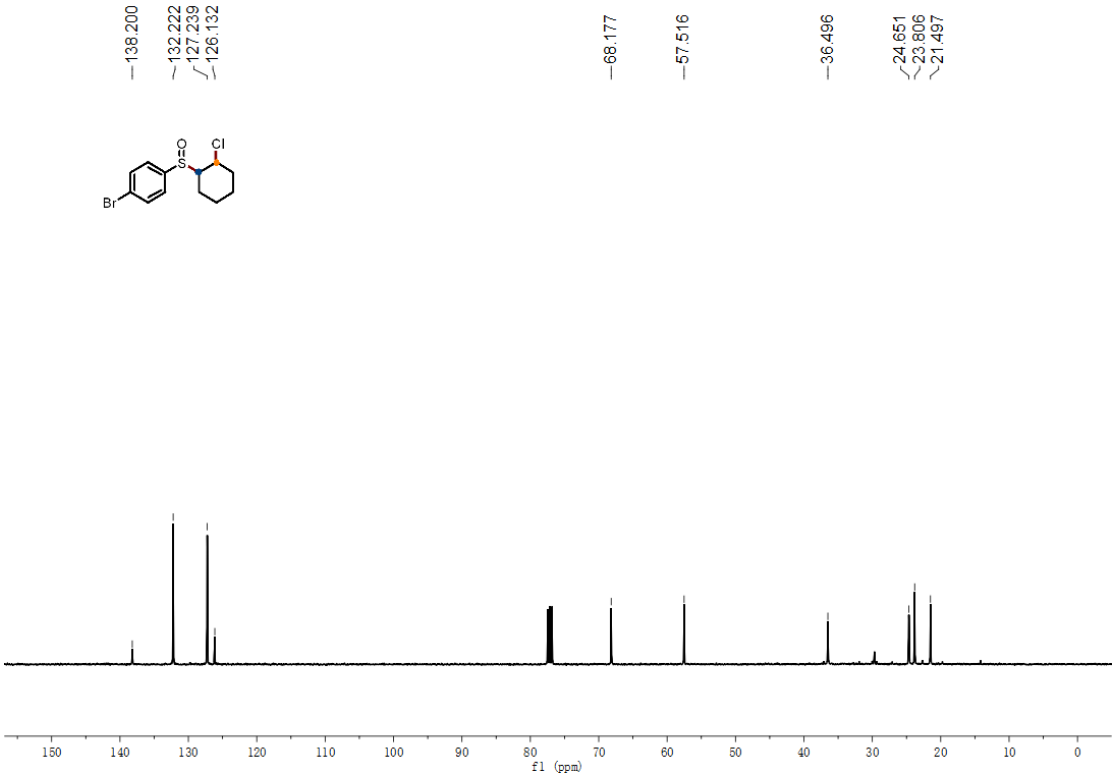
^{13}C NMR spectrum of compound **4g**



^{1}H NMR spectrum of compound **4h**

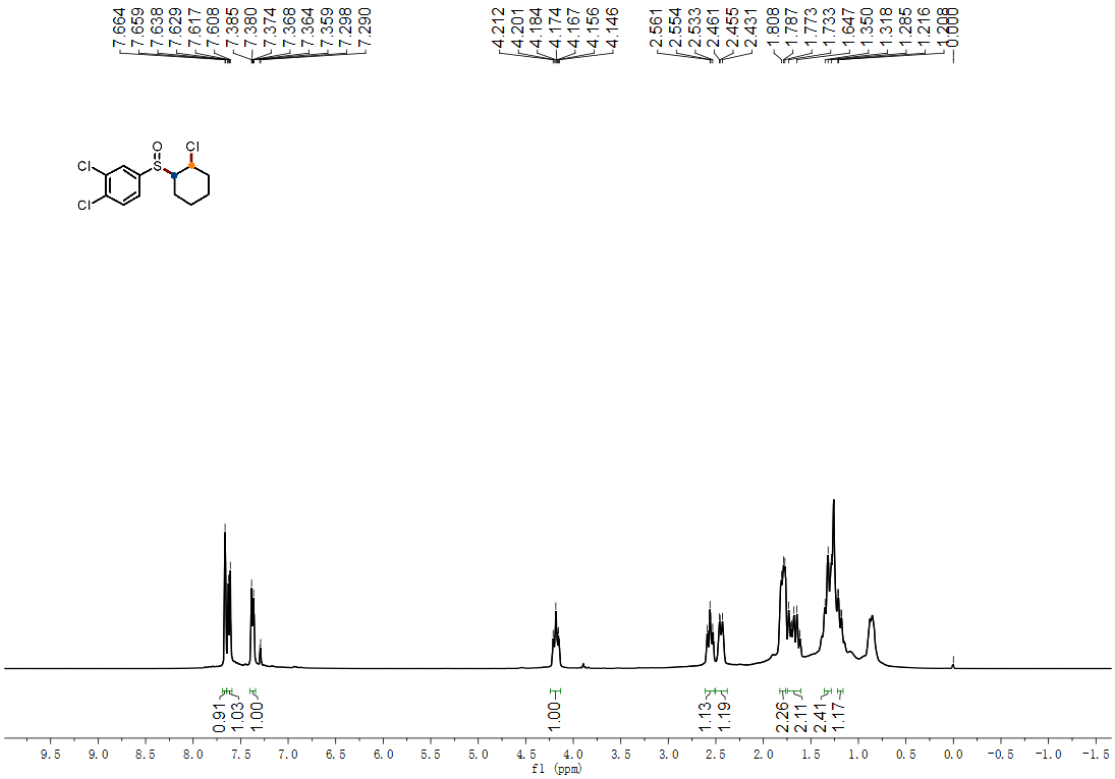


^{13}C NMR spectrum of compound **4h**

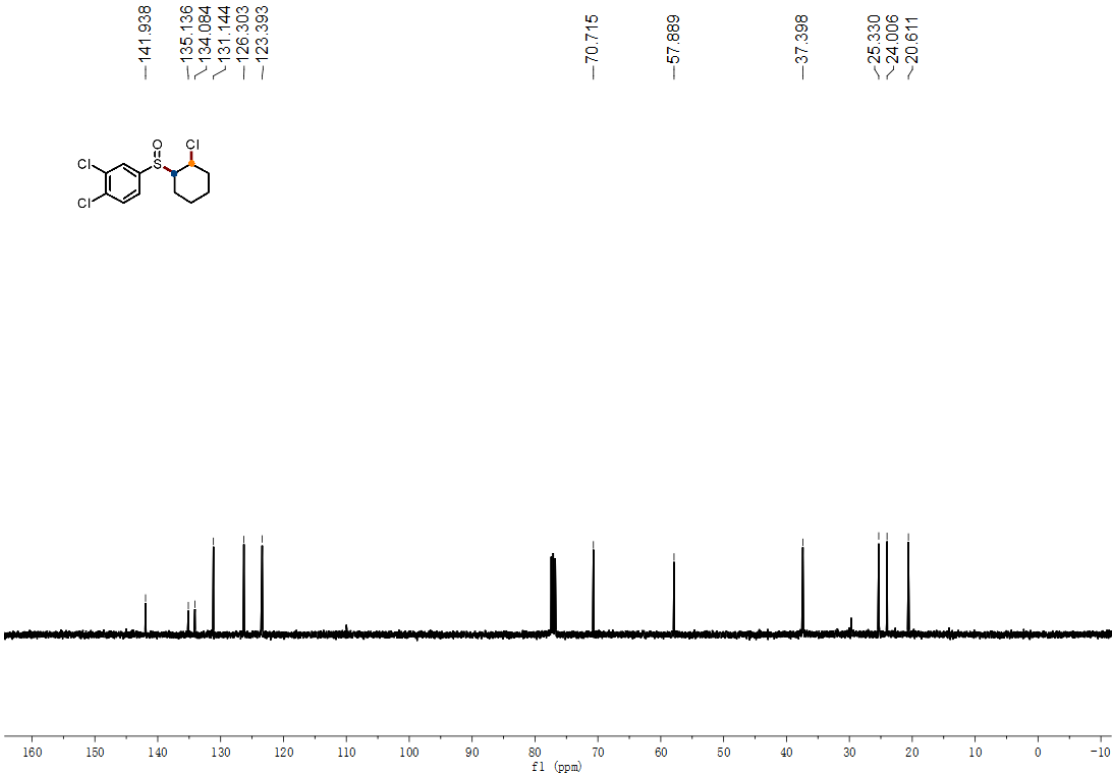


Diastereoisomer 1

^{1}H NMR spectrum of compound **4i**

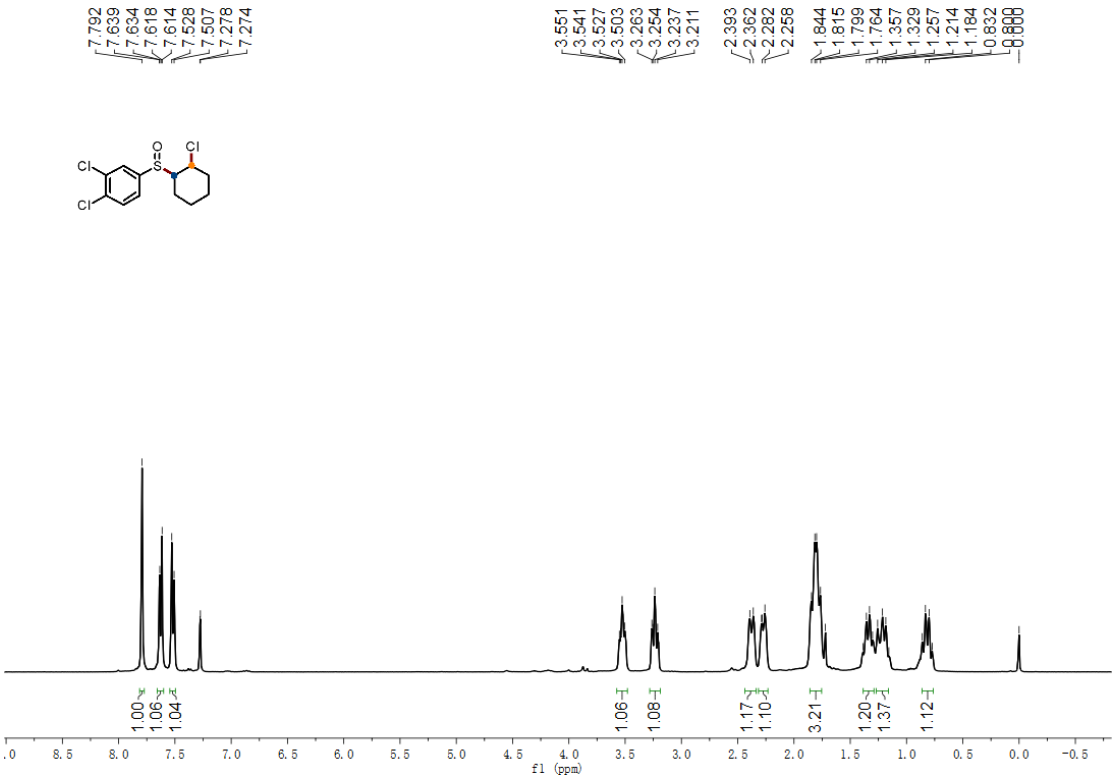


^{13}C NMR spectrum of compound **4i**

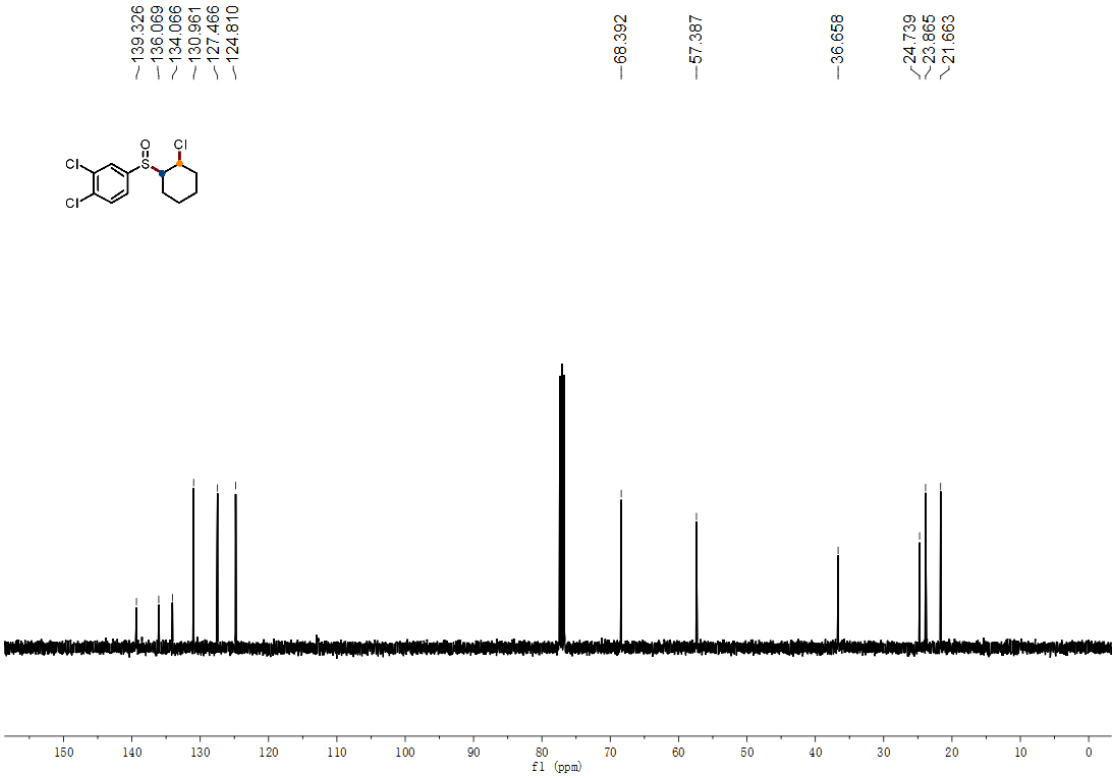


Diastereoisomer 2

^{1}H NMR spectrum of compound **4i**

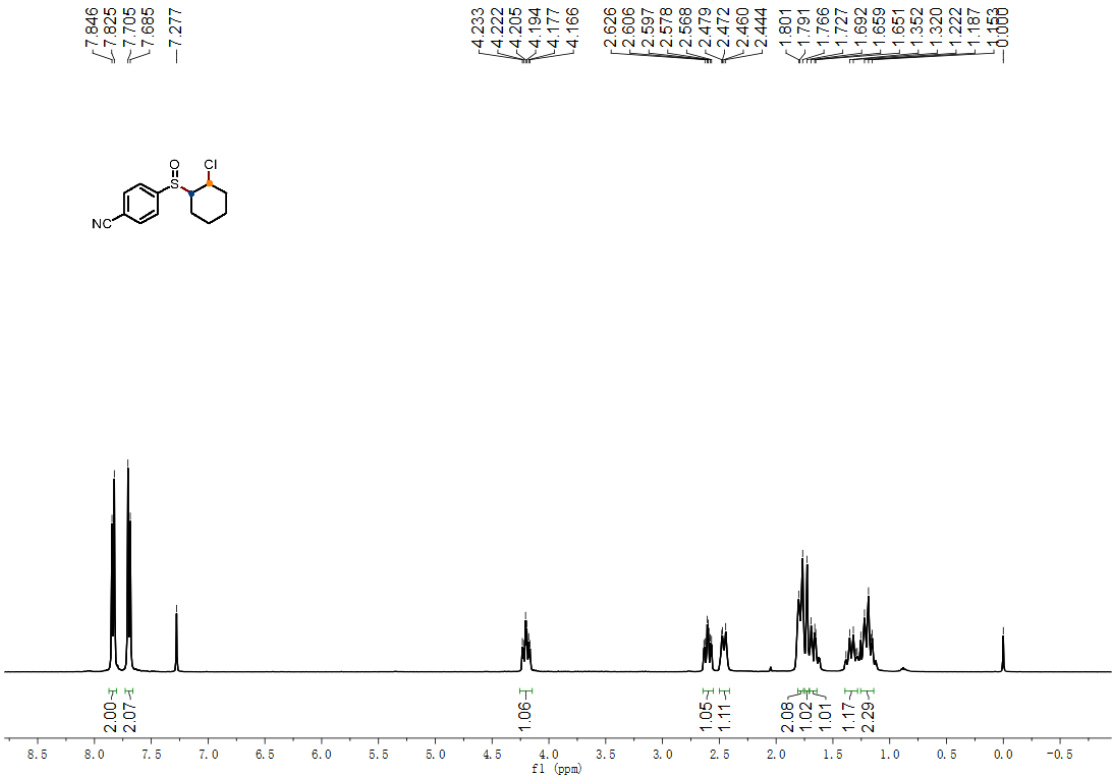


^{13}C NMR spectrum of compound **4i**

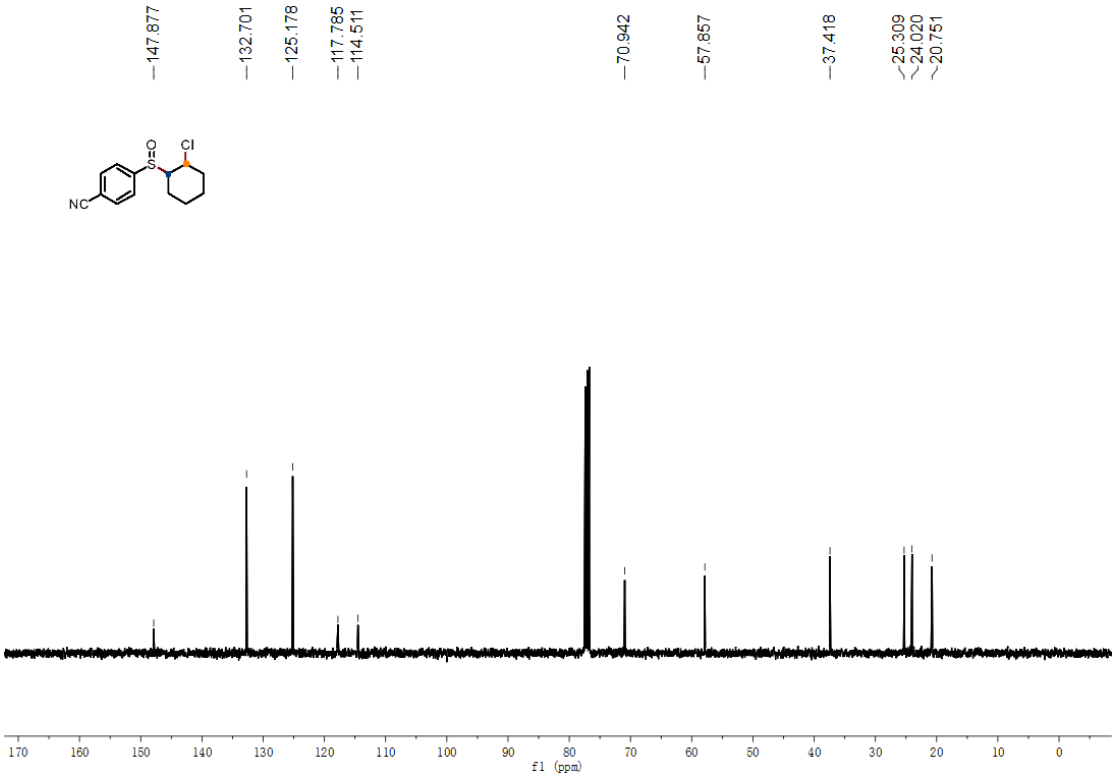


Diastereoisomer 1

^{1}H NMR spectrum of compound **4j**

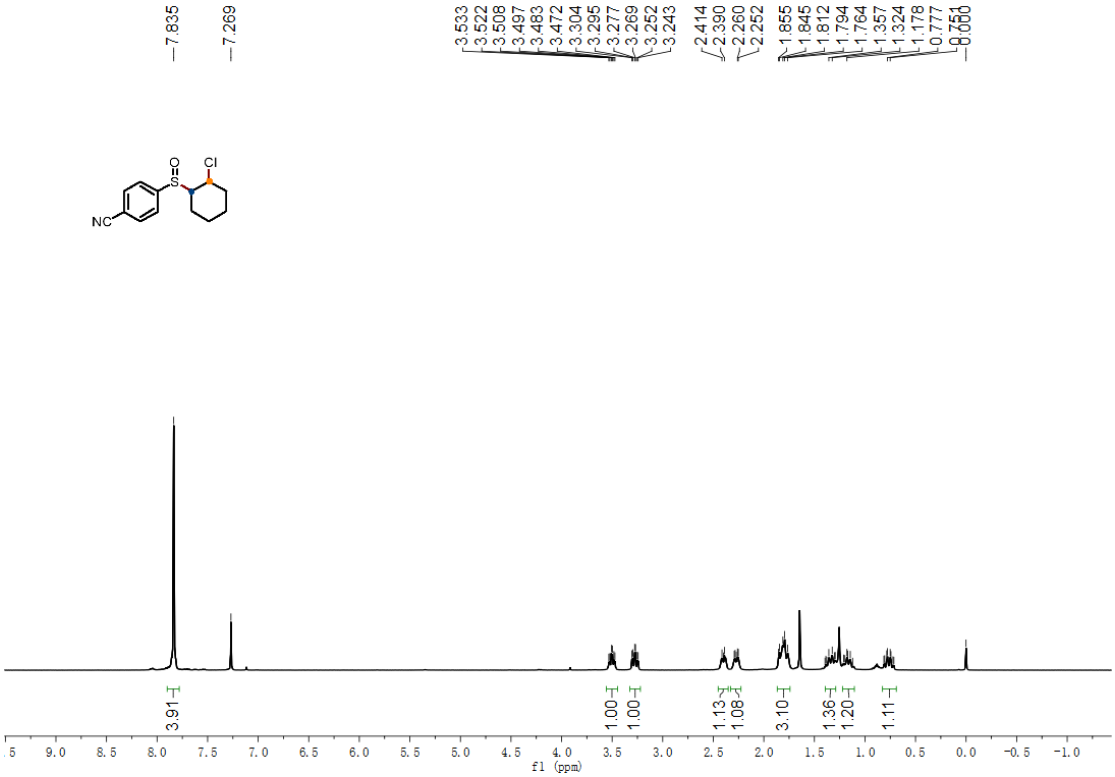


^{13}C NMR spectrum of compound **4j**

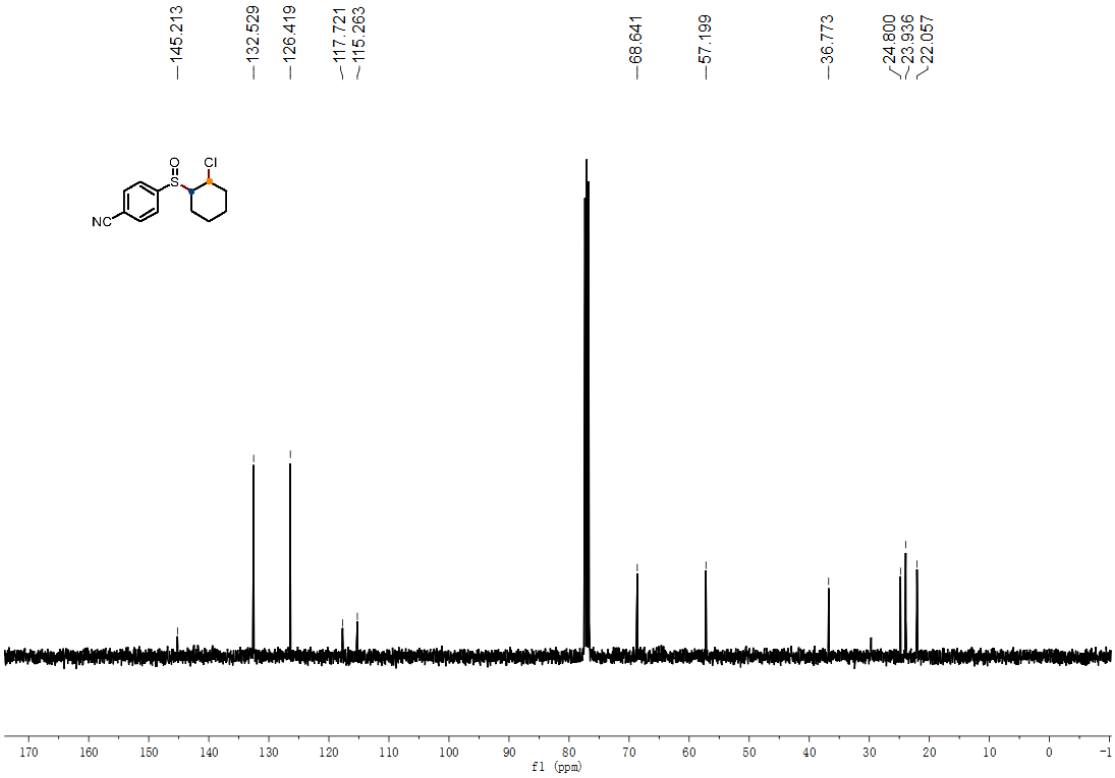


Diastereoisomer 2

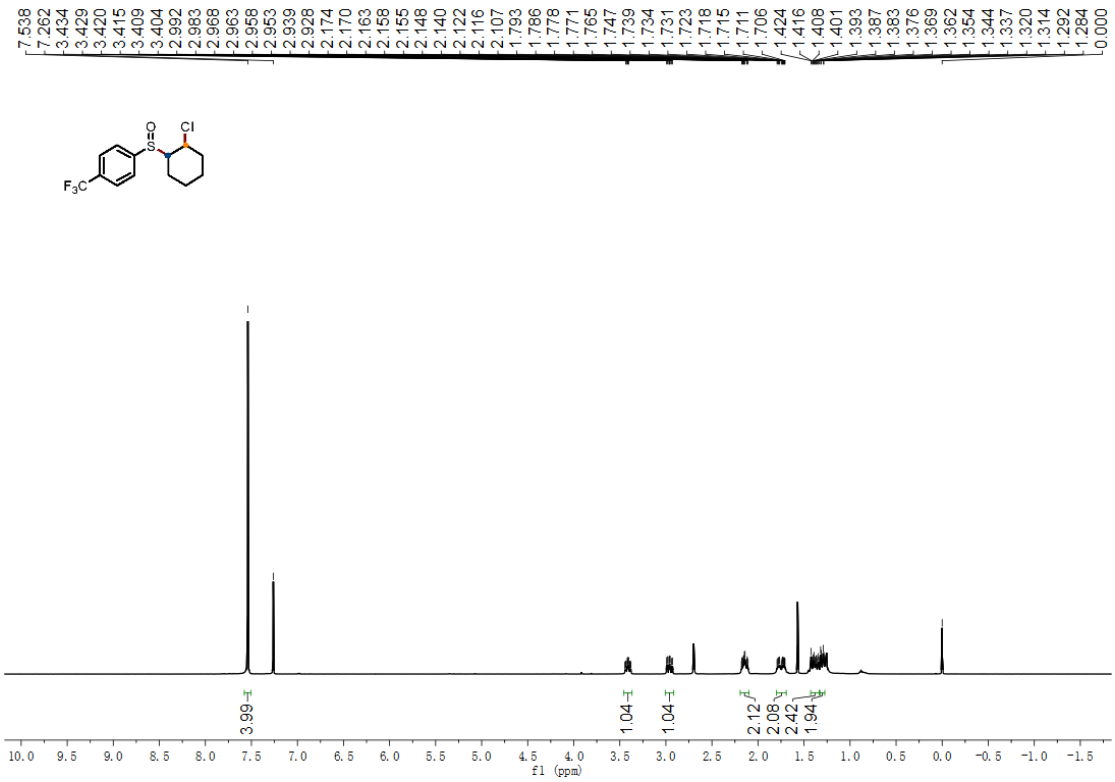
^{1}H NMR spectrum of compound **4j**



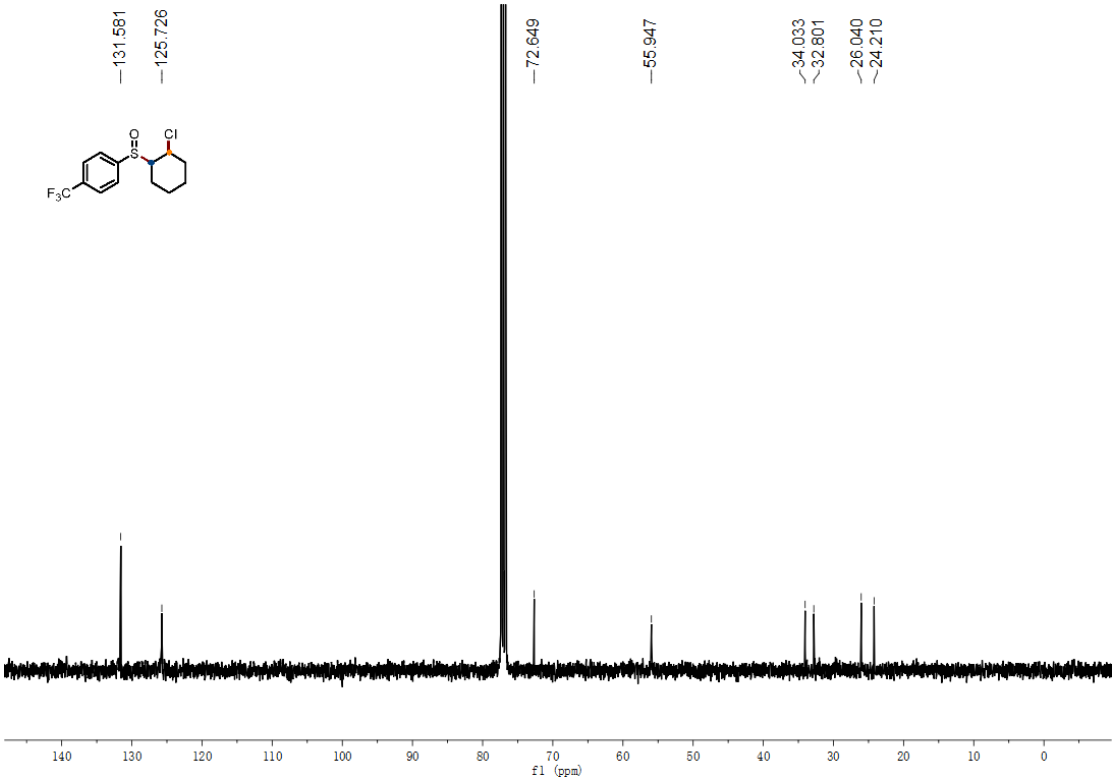
^{13}C NMR spectrum of compound **4j**



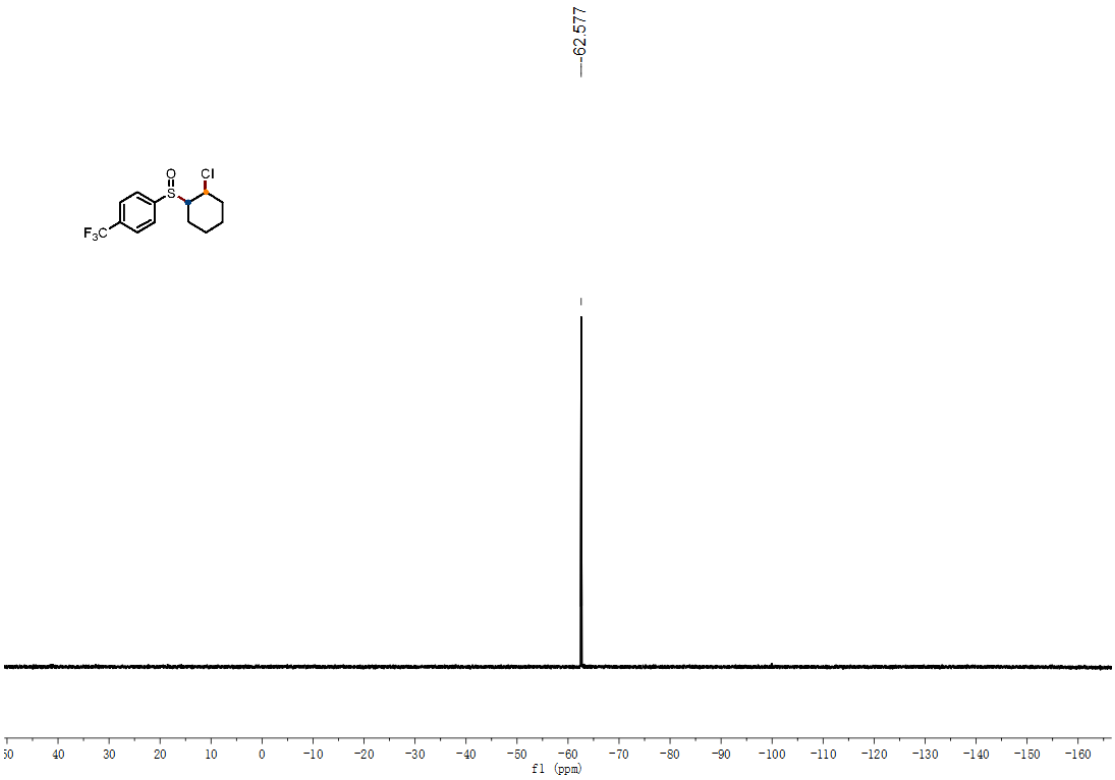
^{1}H NMR spectrum of compound **4k**



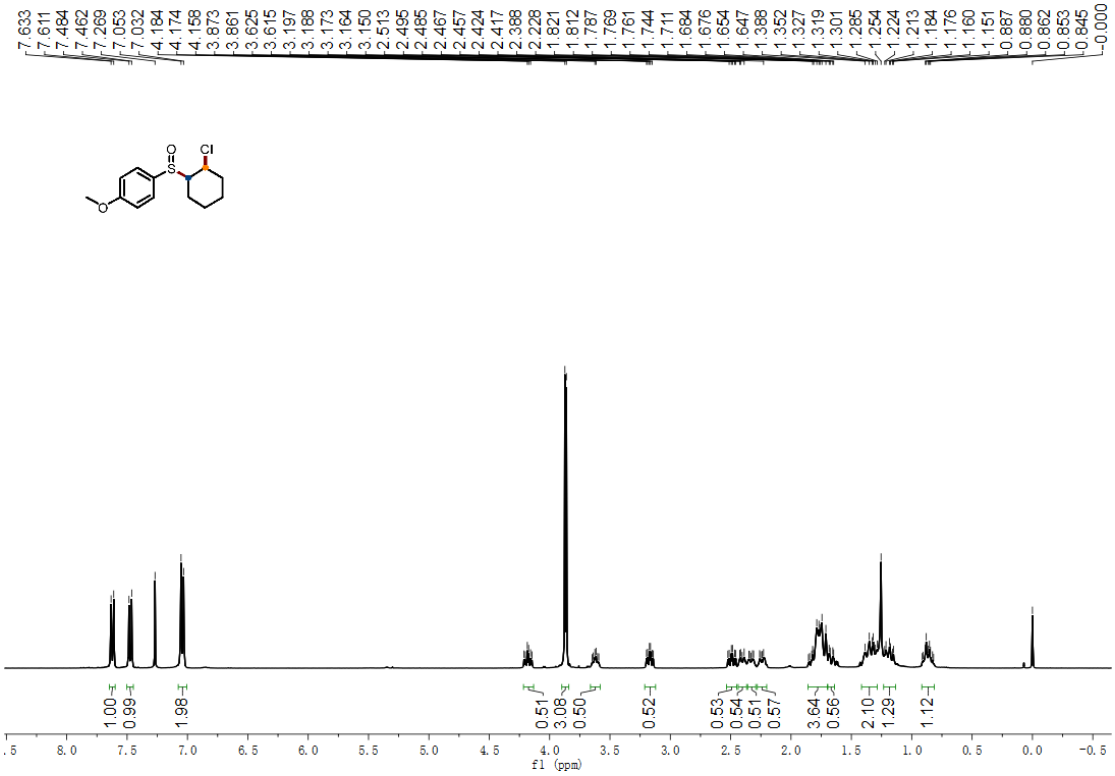
^{13}C NMR spectrum of compound **4k**



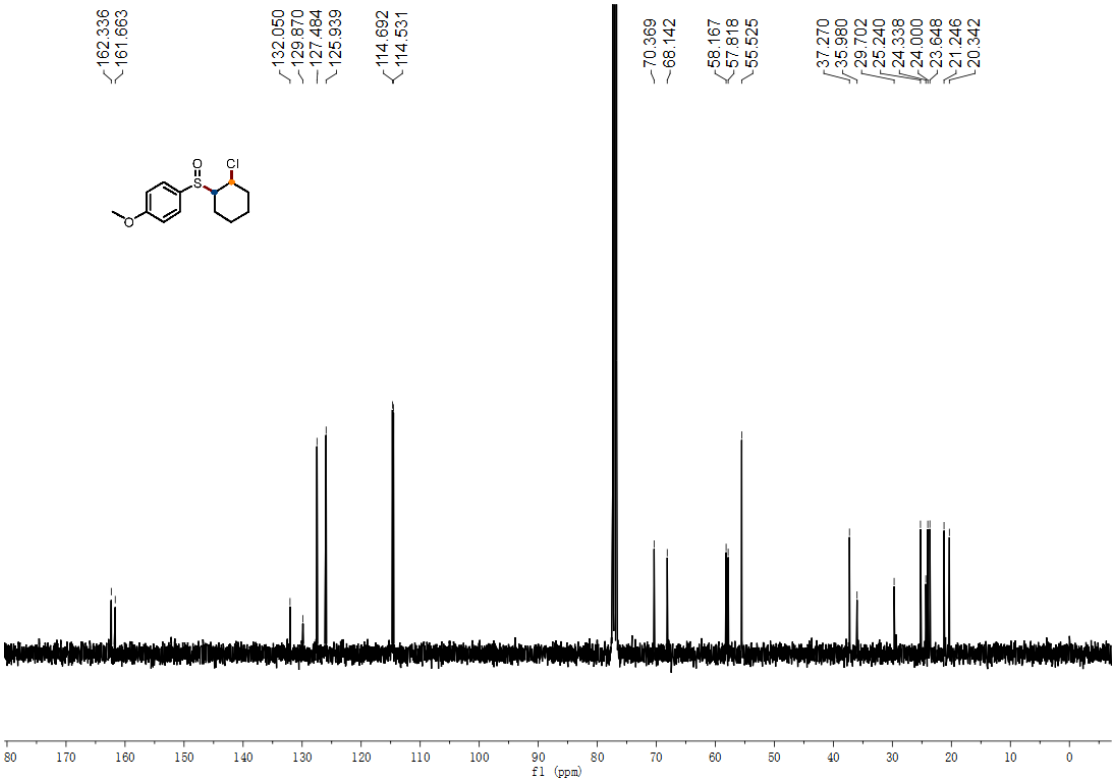
^{19}F NMR spectrum of compound **4k**



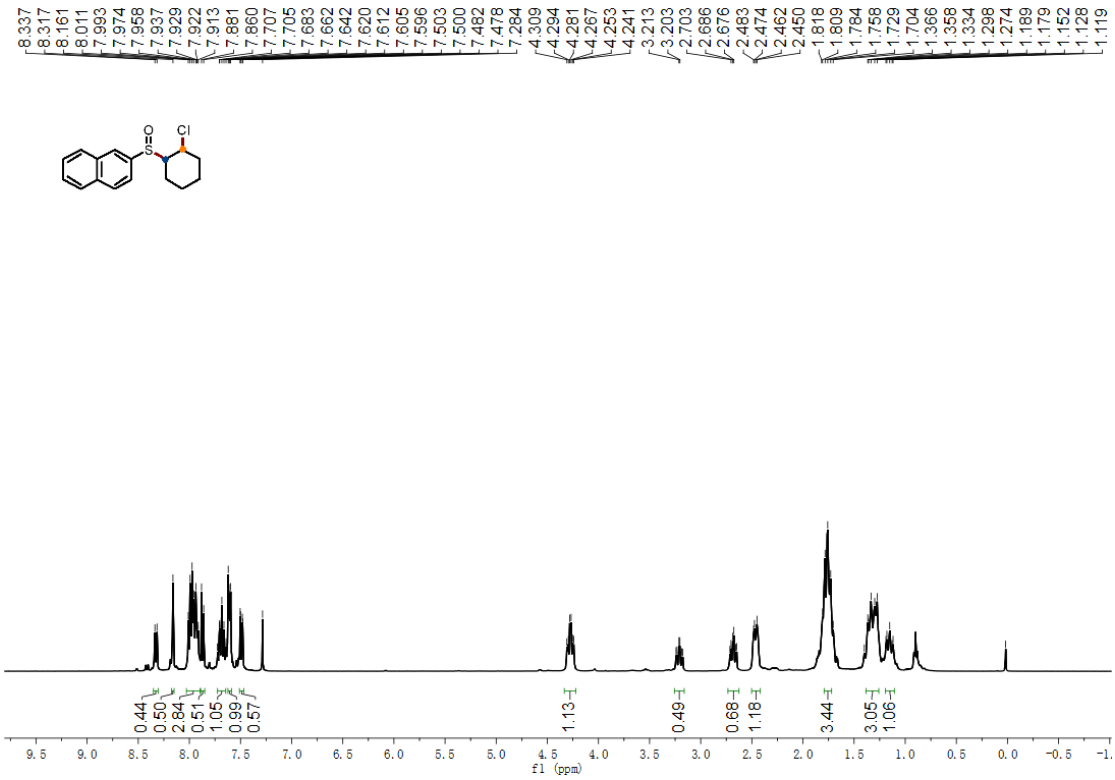
^{1}H NMR spectrum of compound **4l**



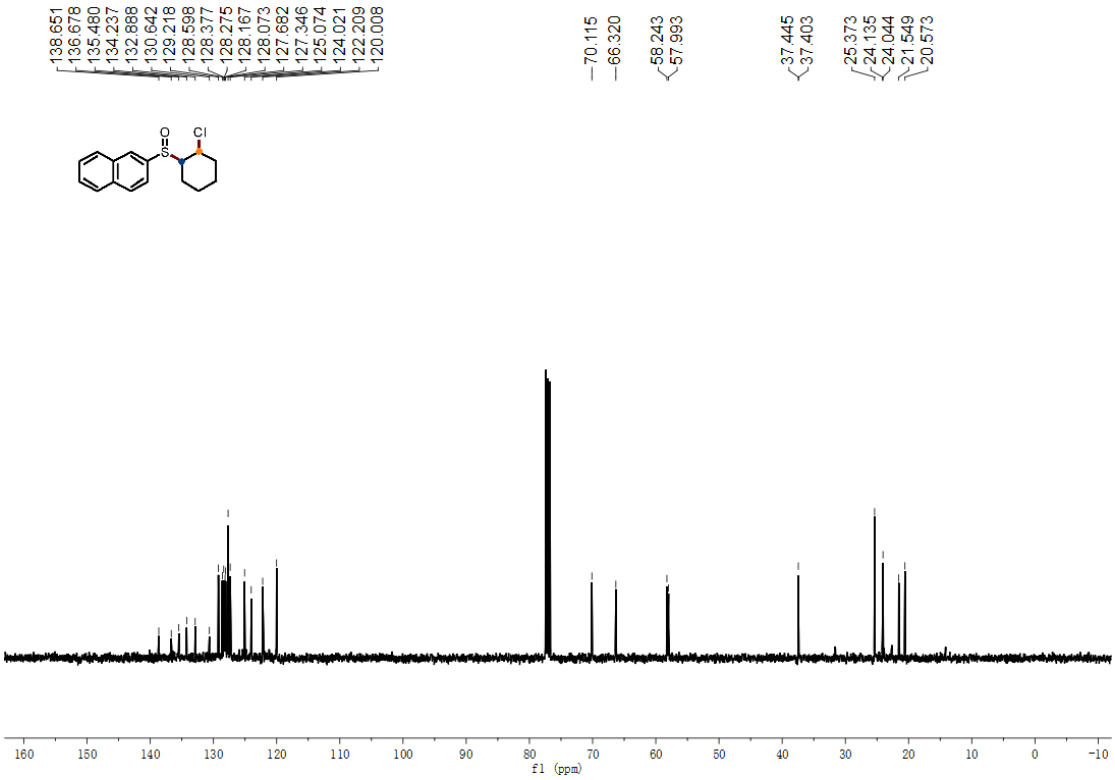
^{13}C NMR spectrum of compound **4l**



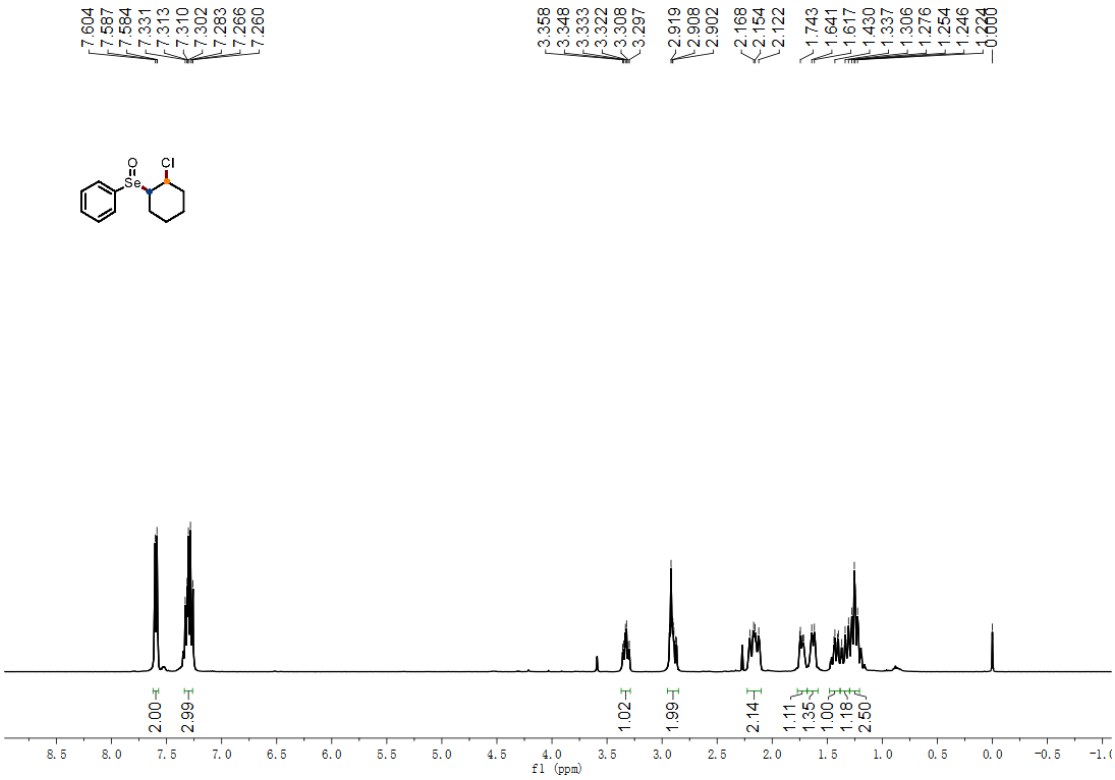
^{1}H NMR spectrum of compound **4m**



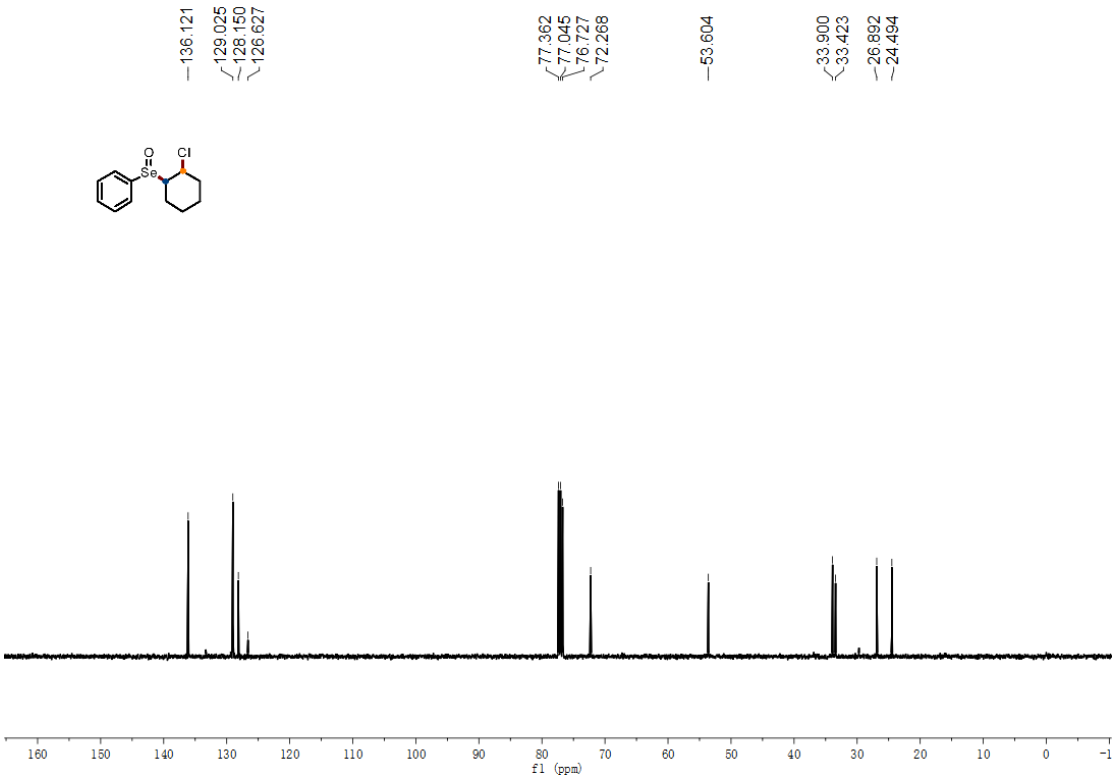
^{13}C NMR spectrum of compound **4m**



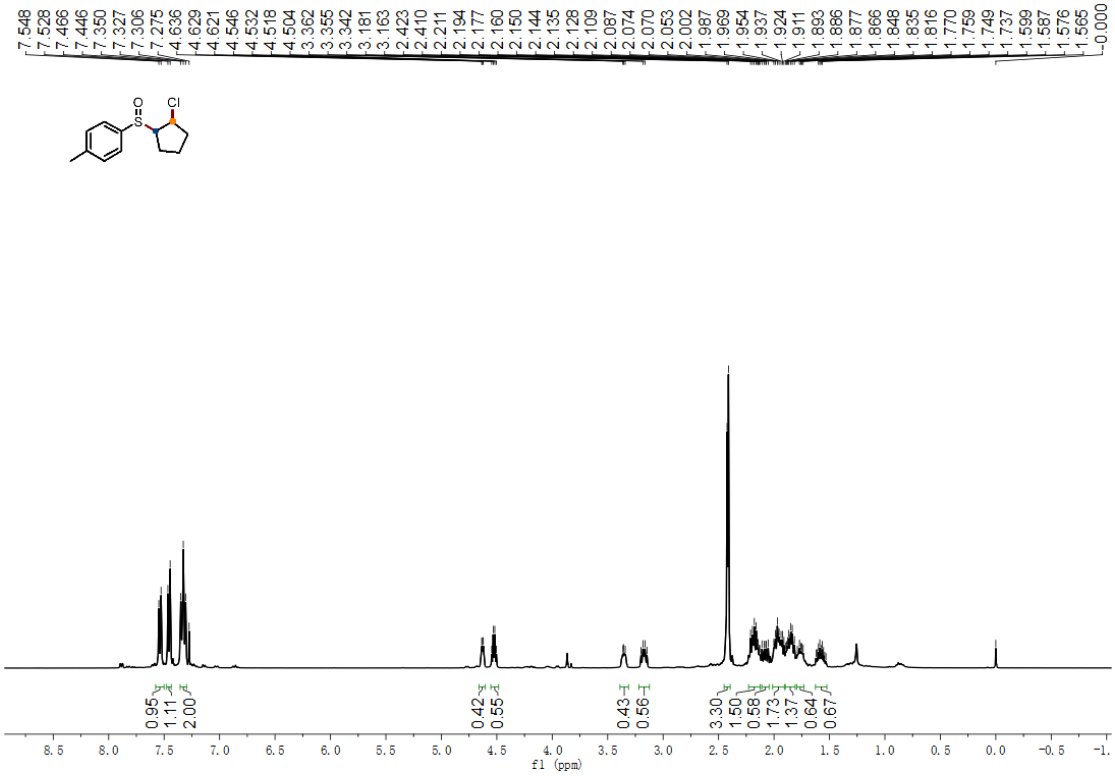
^{1}H NMR spectrum of compound **4n**



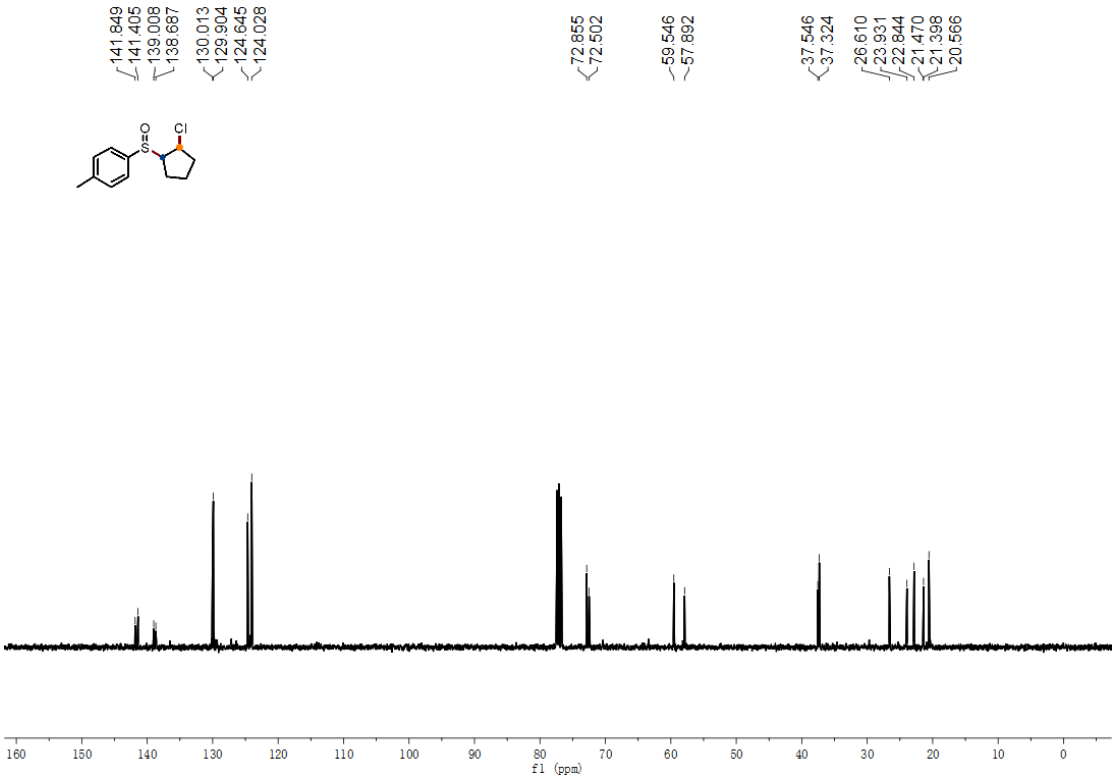
^{13}C NMR spectrum of compound **4n**



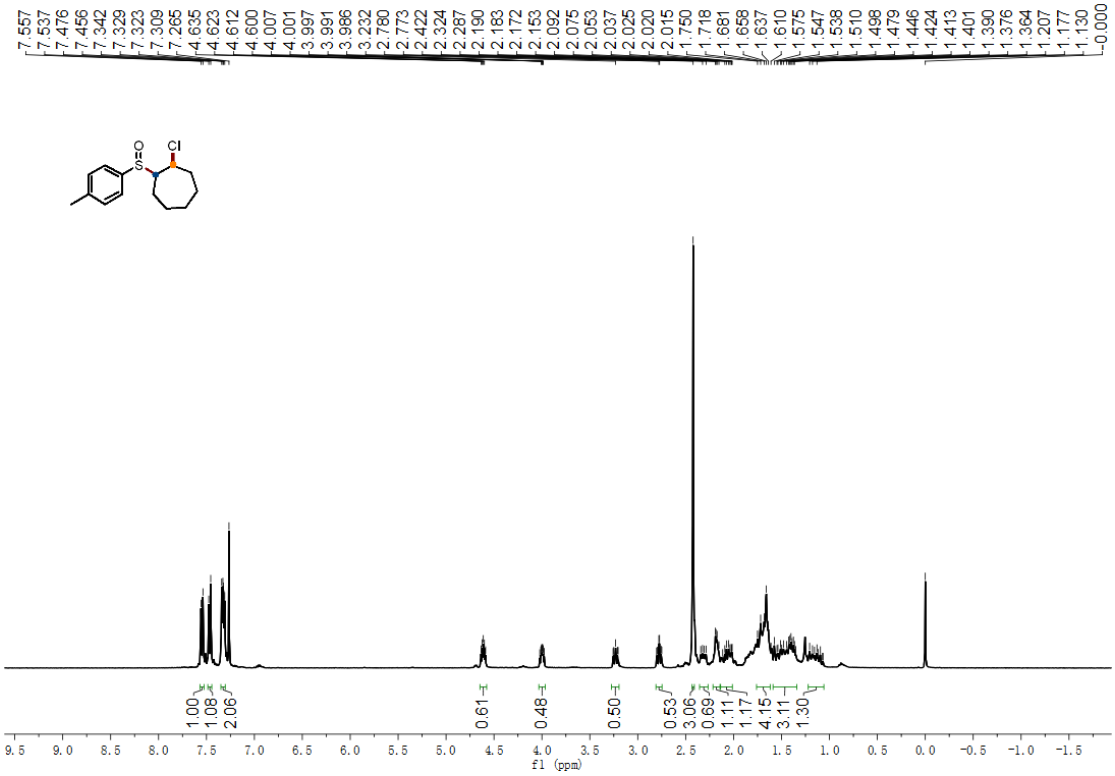
^{1}H NMR spectrum of compound **4o**



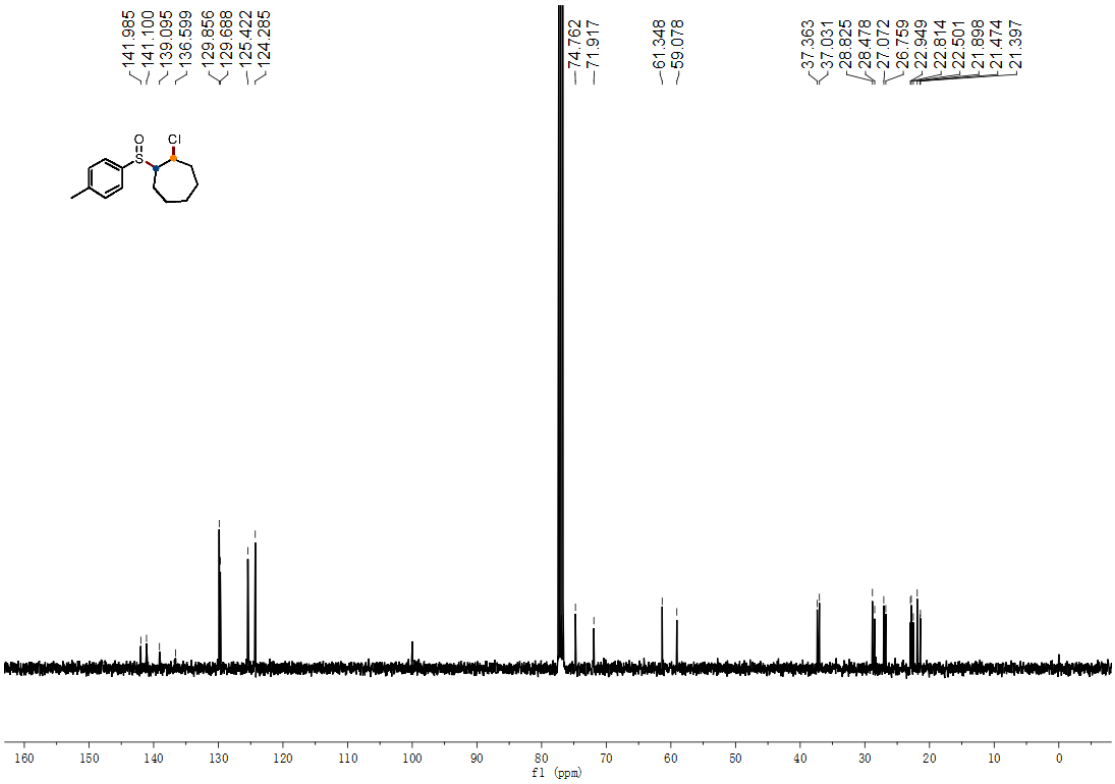
^{13}C NMR spectrum of compound **4o**



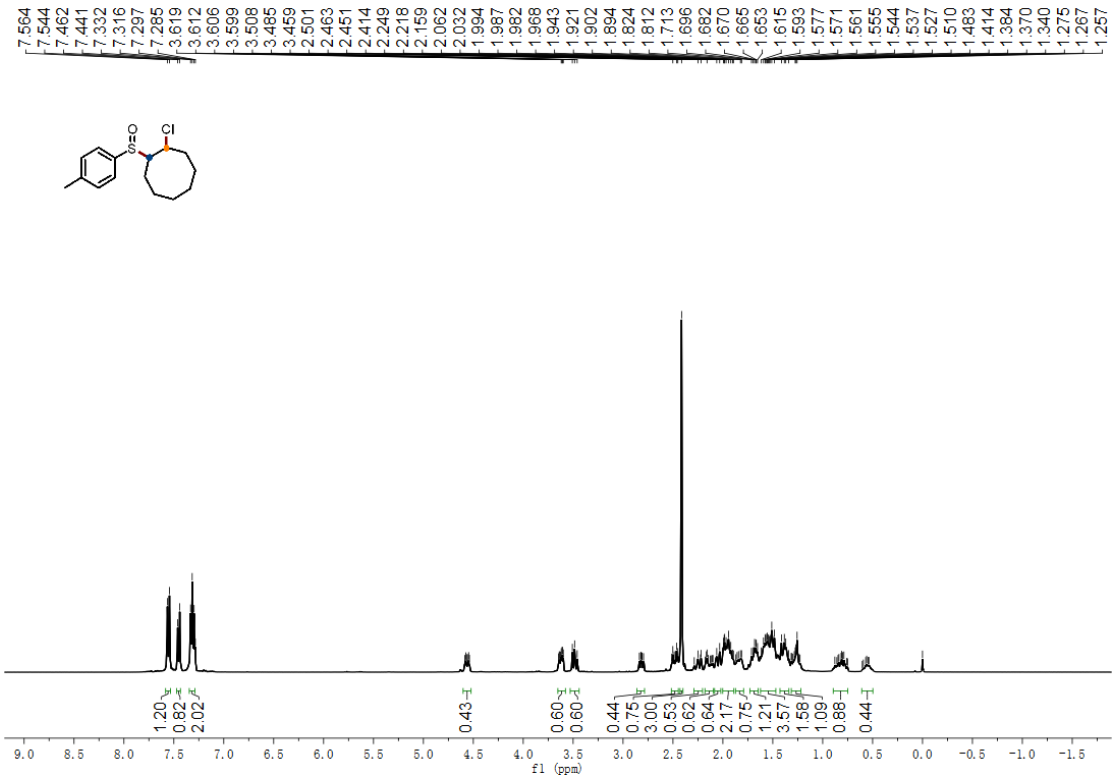
^{1}H NMR spectrum of compound **4p**



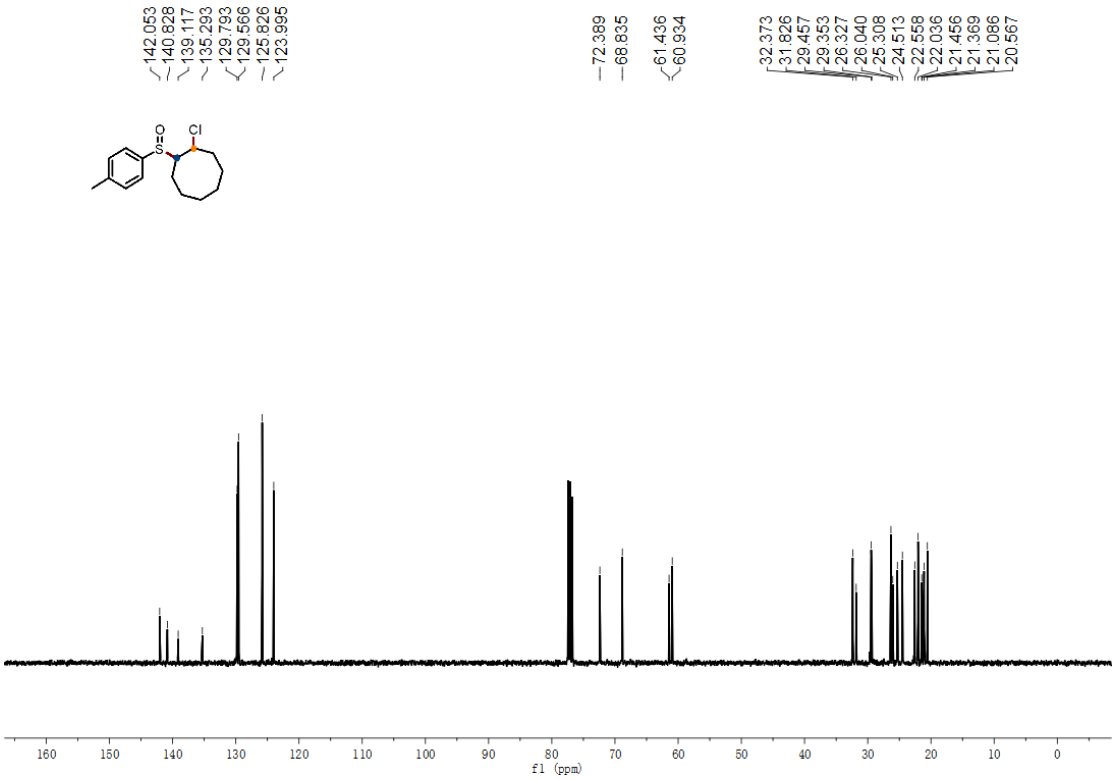
^{13}C NMR spectrum of compound **4p**



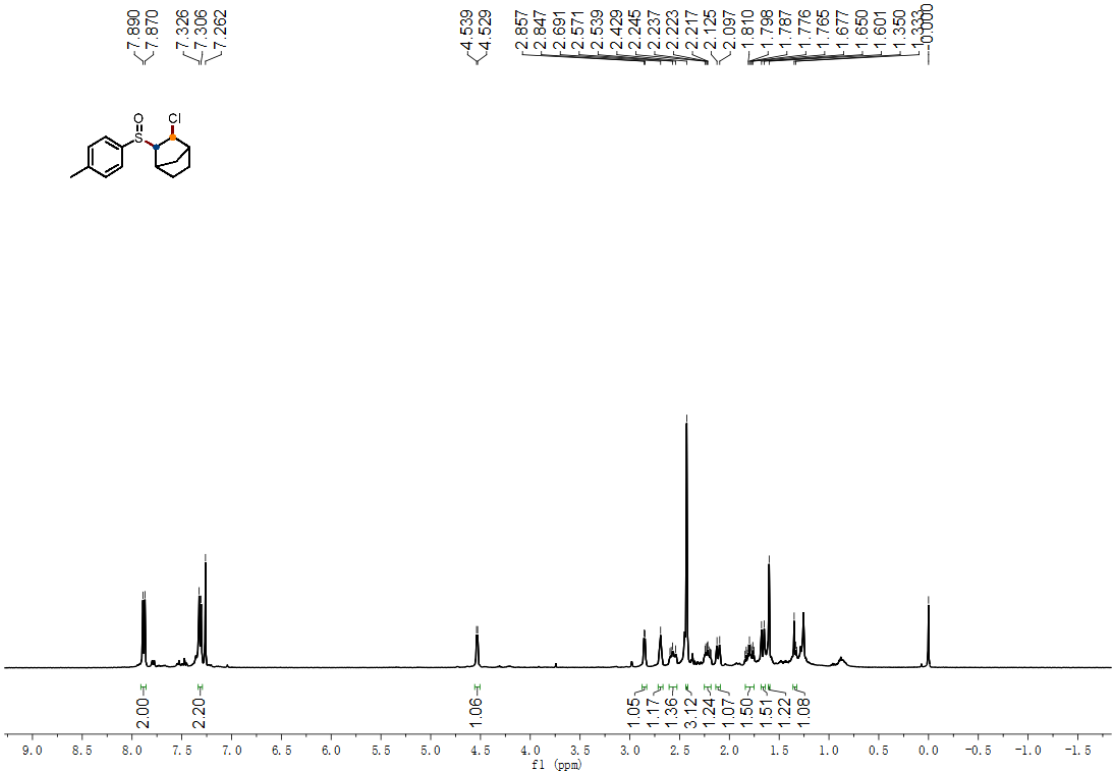
^{1}H NMR spectrum of compound **4q**



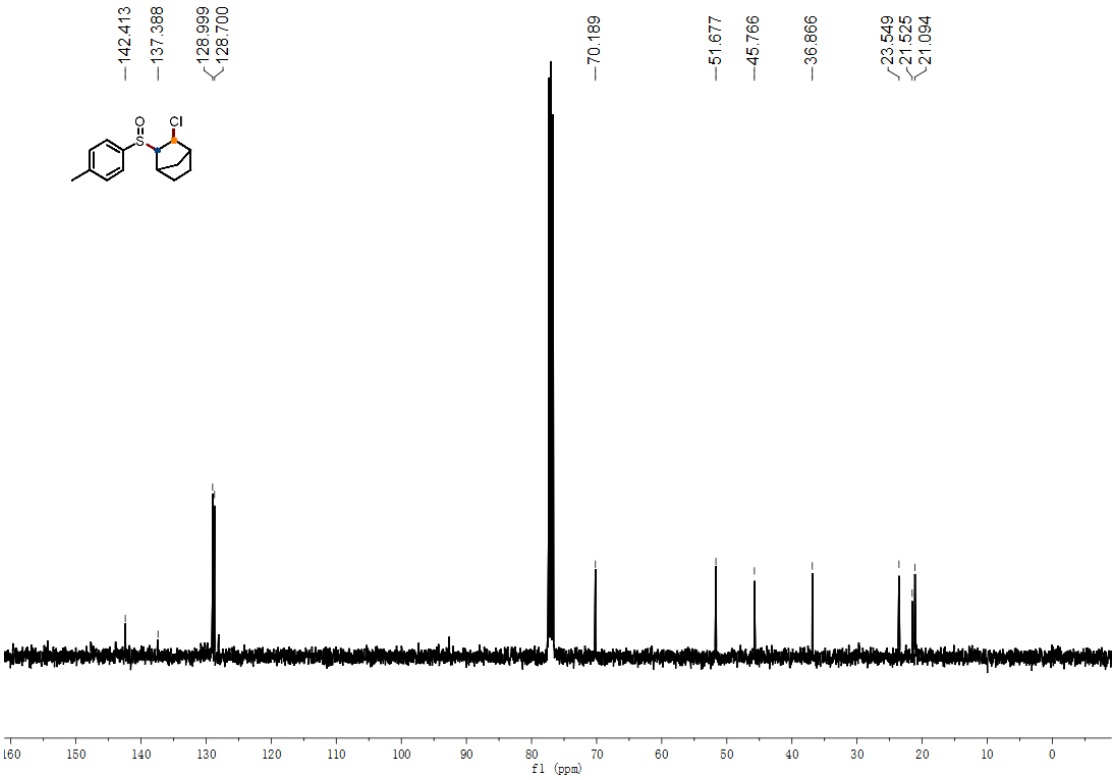
^{13}C NMR spectrum of compound **4q**



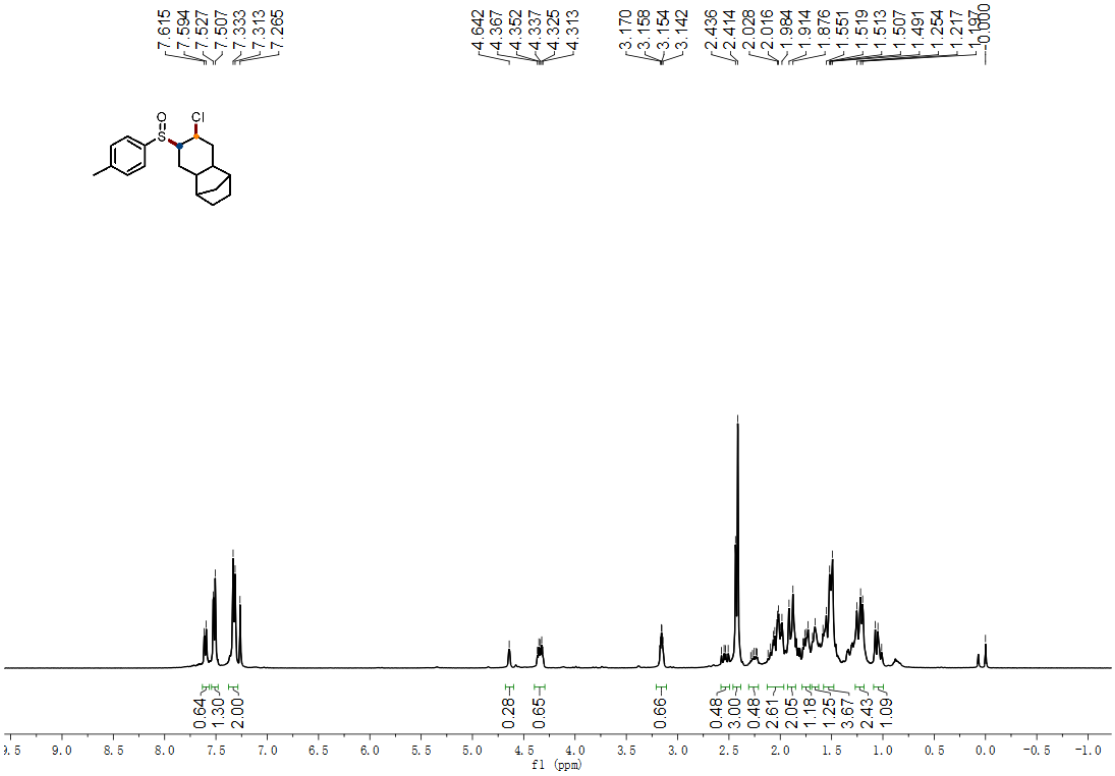
^{1}H NMR spectrum of compound **4r**



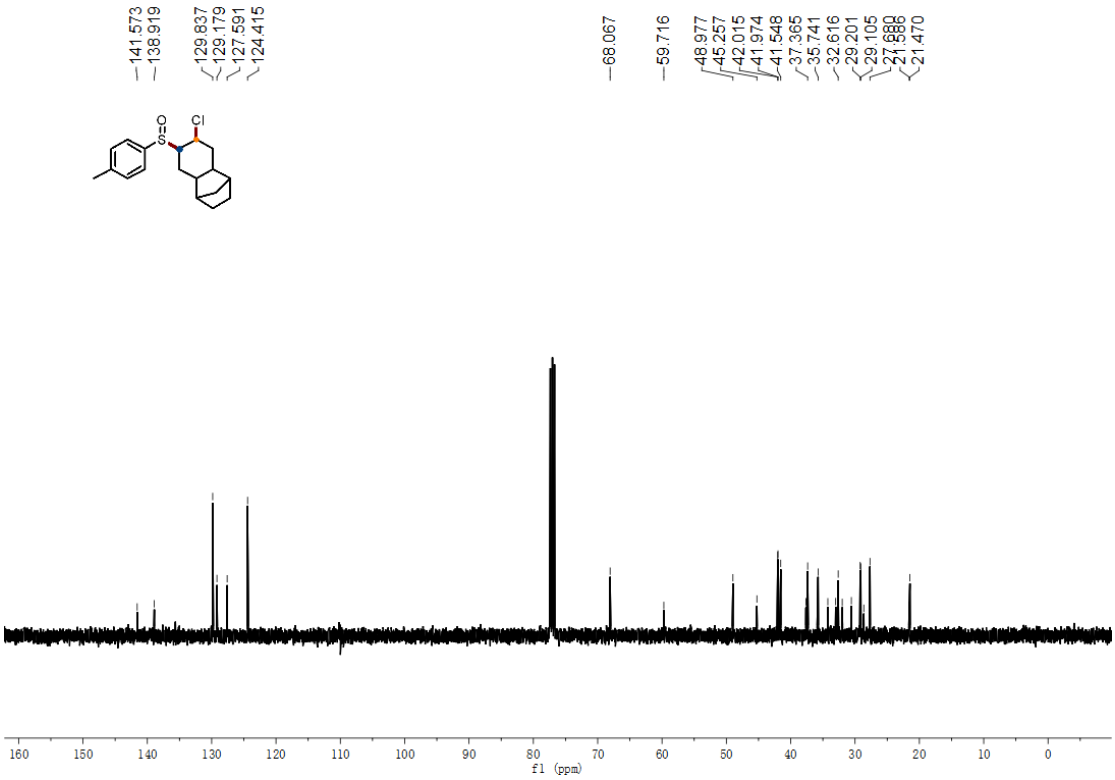
^{13}C NMR spectrum of compound **4r**



^{1}H NMR spectrum of compound **4s**

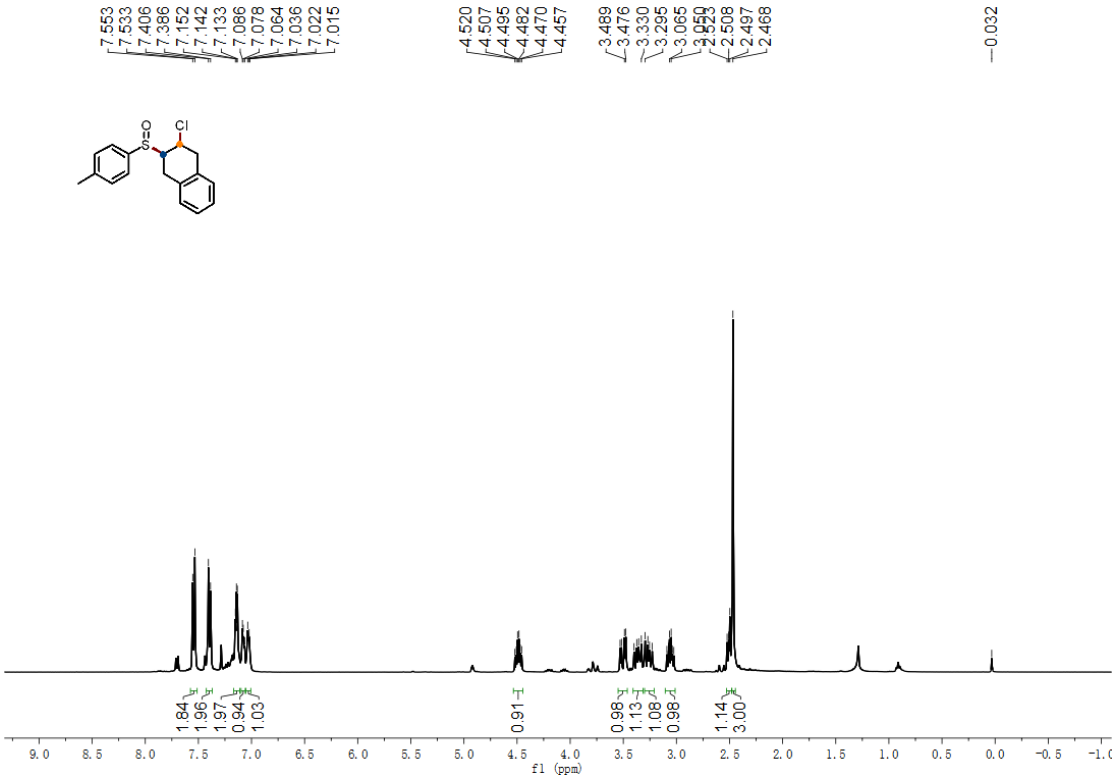


^{13}C NMR spectrum of compound **4s**

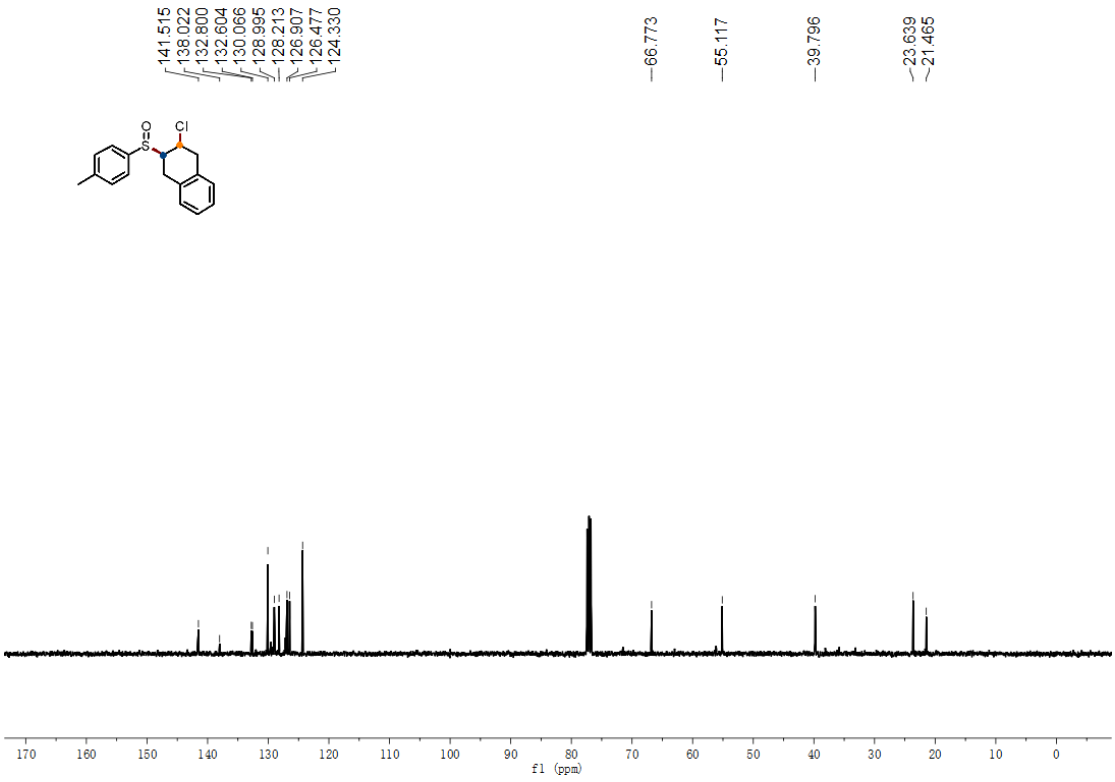


Diastereoisomer 1

^{1}H NMR spectrum of compound **4t**

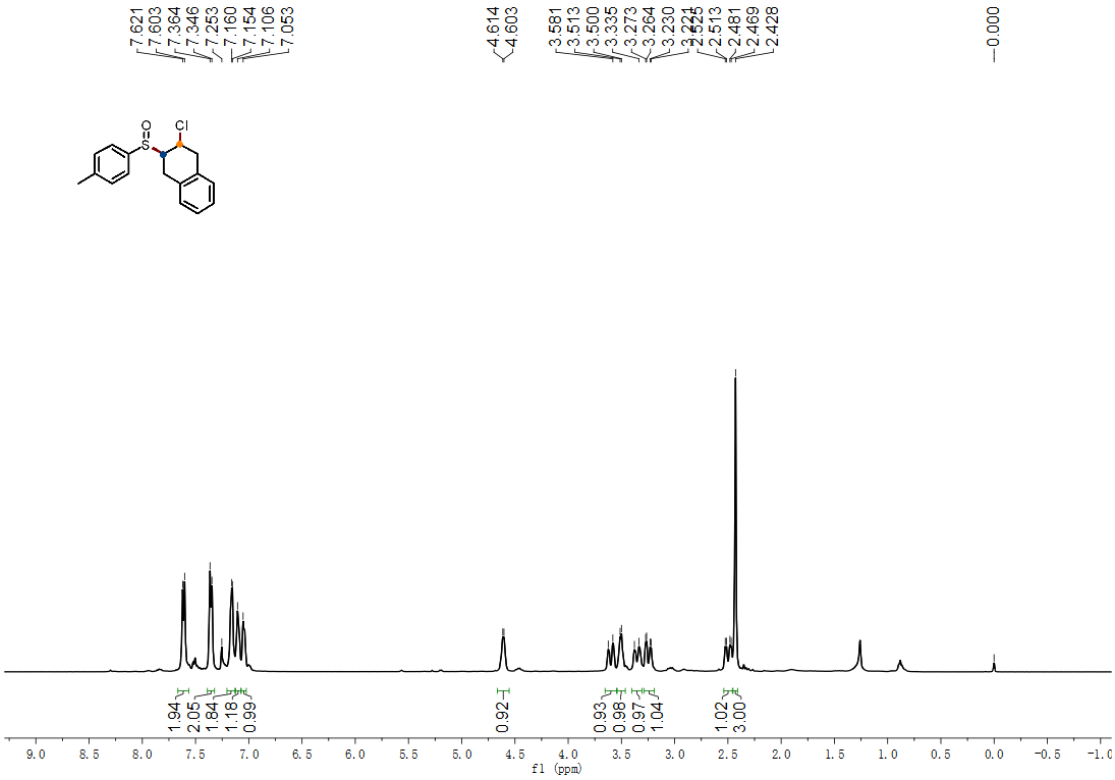


^{13}C NMR spectrum of compound **4t**

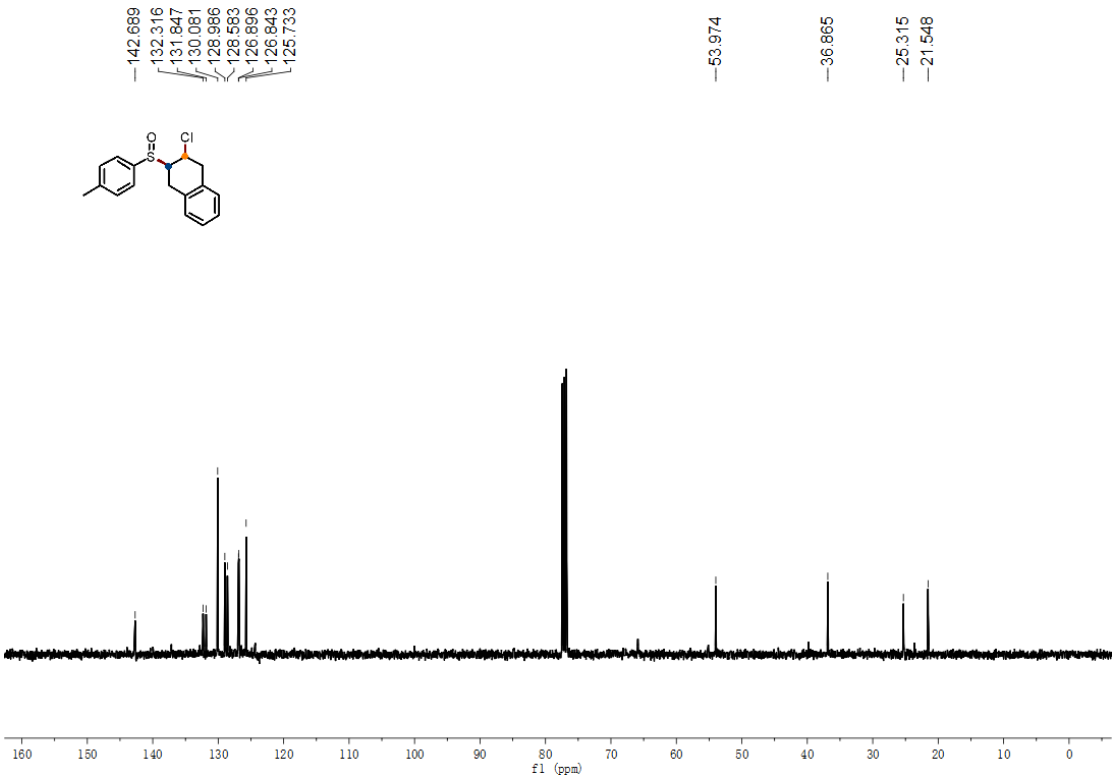


Diastereoisomer 2

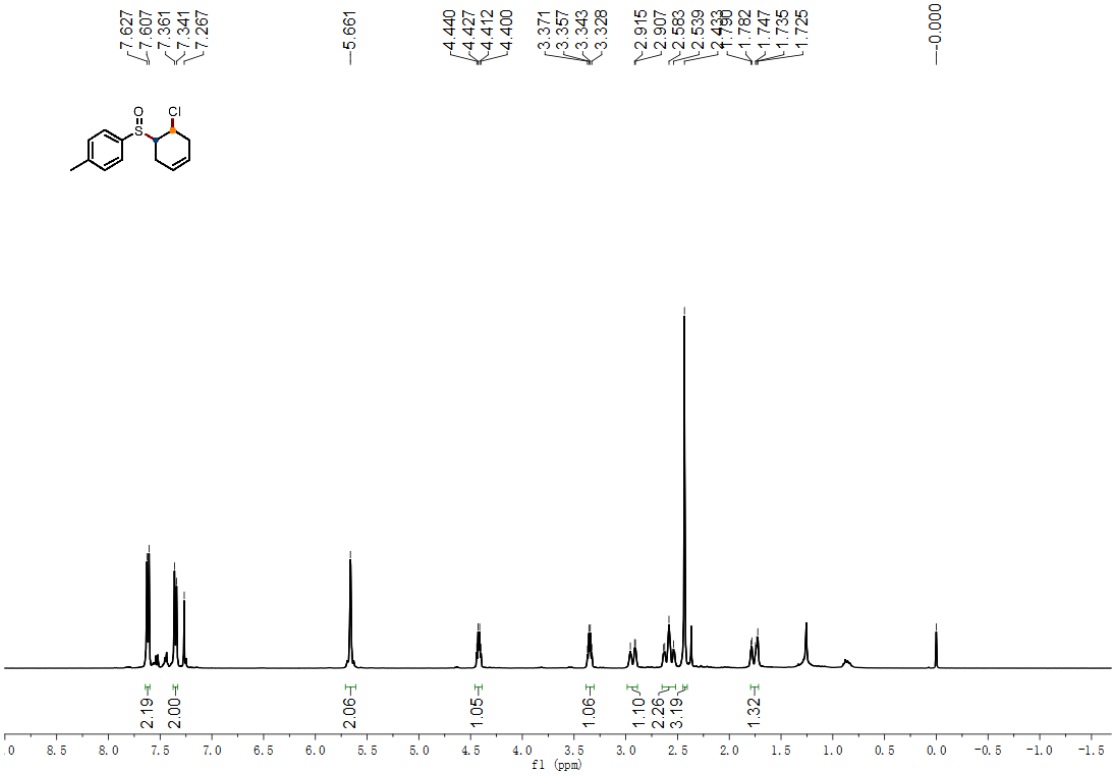
^{1}H NMR spectrum of compound **4t**



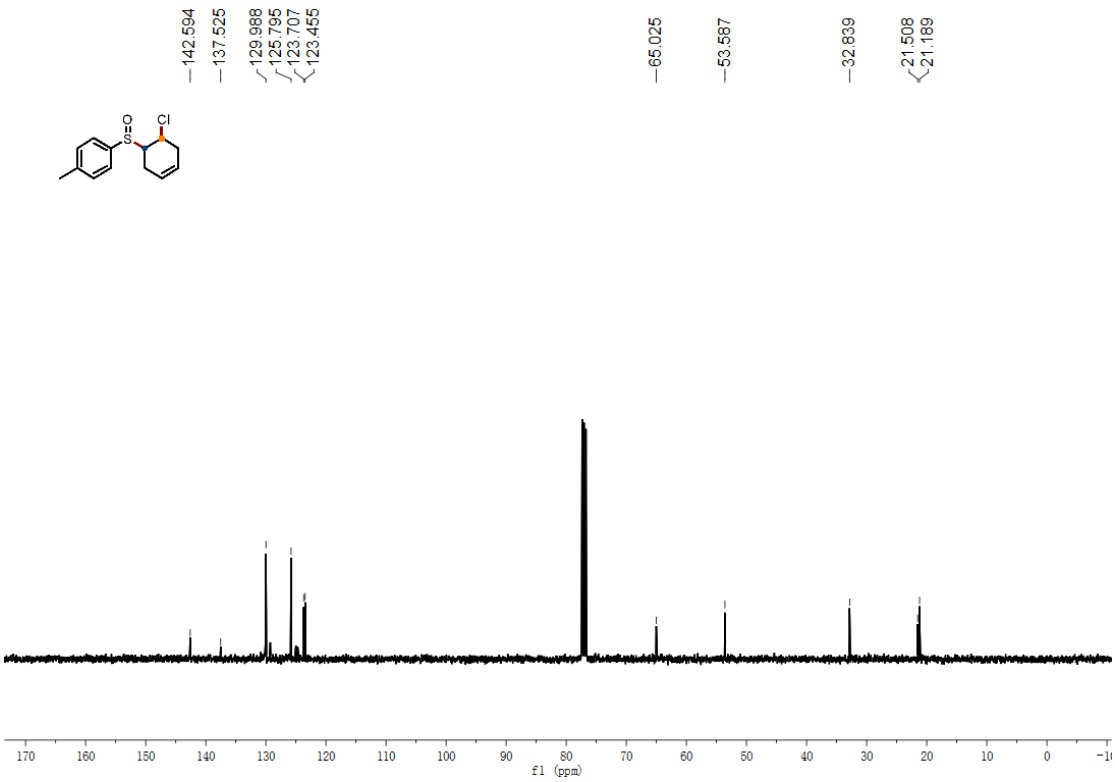
^{13}C NMR spectrum of compound **4t**



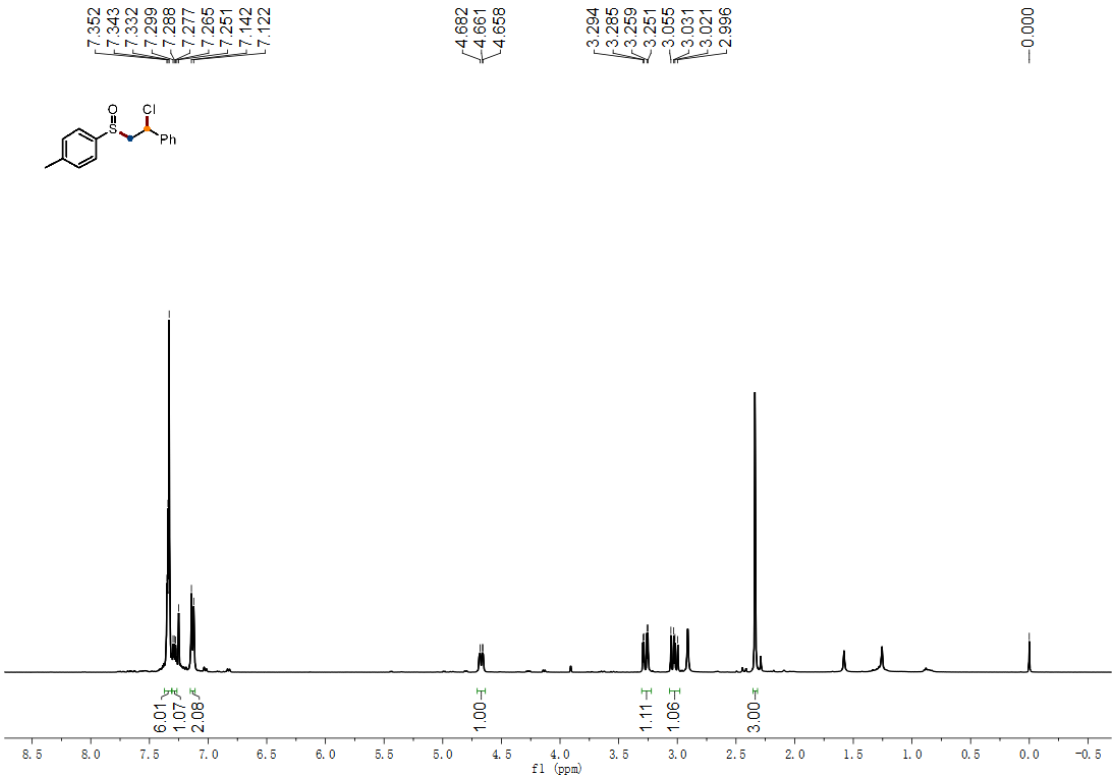
^{1}H NMR spectrum of compound **4u**



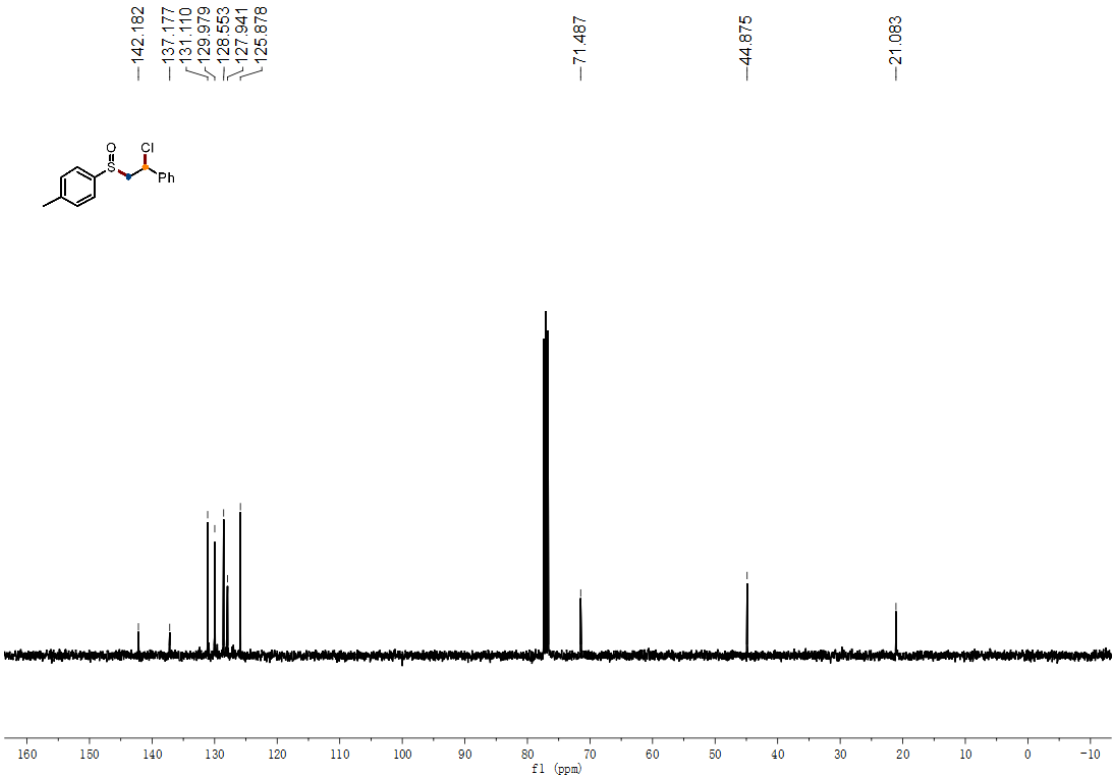
^{13}C NMR spectrum of compound **4u**



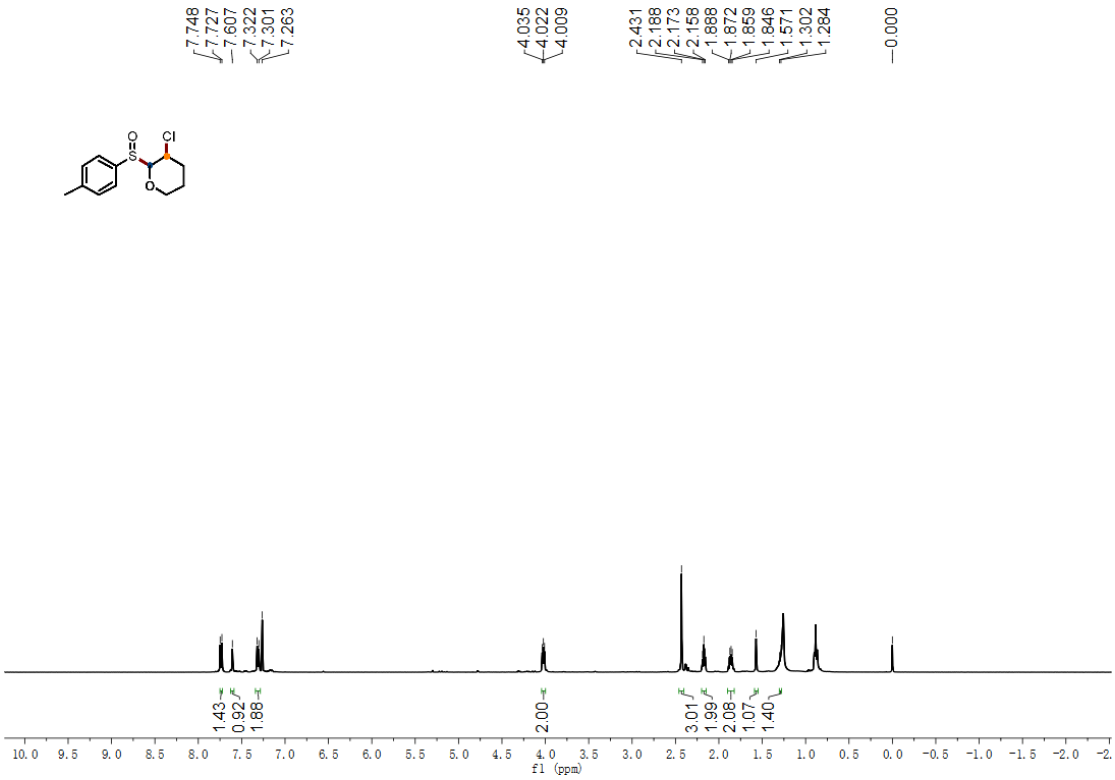
^{1}H NMR spectrum of compound **4v**



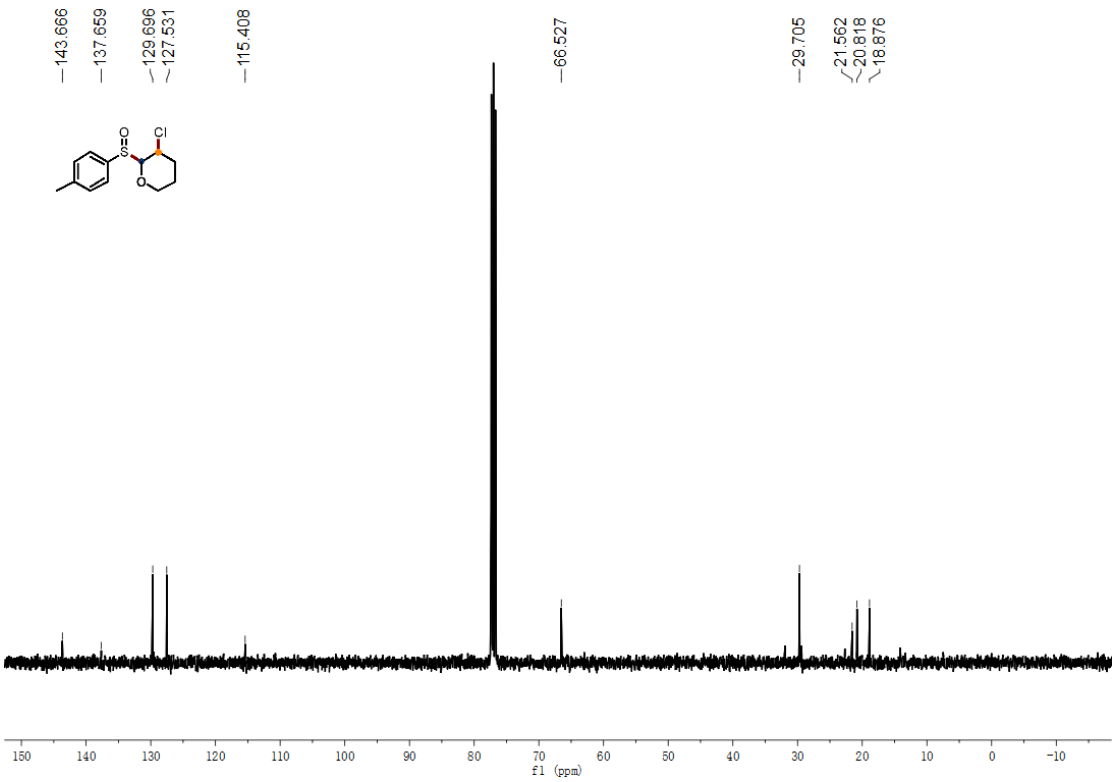
^{13}C NMR spectrum of compound **4v**



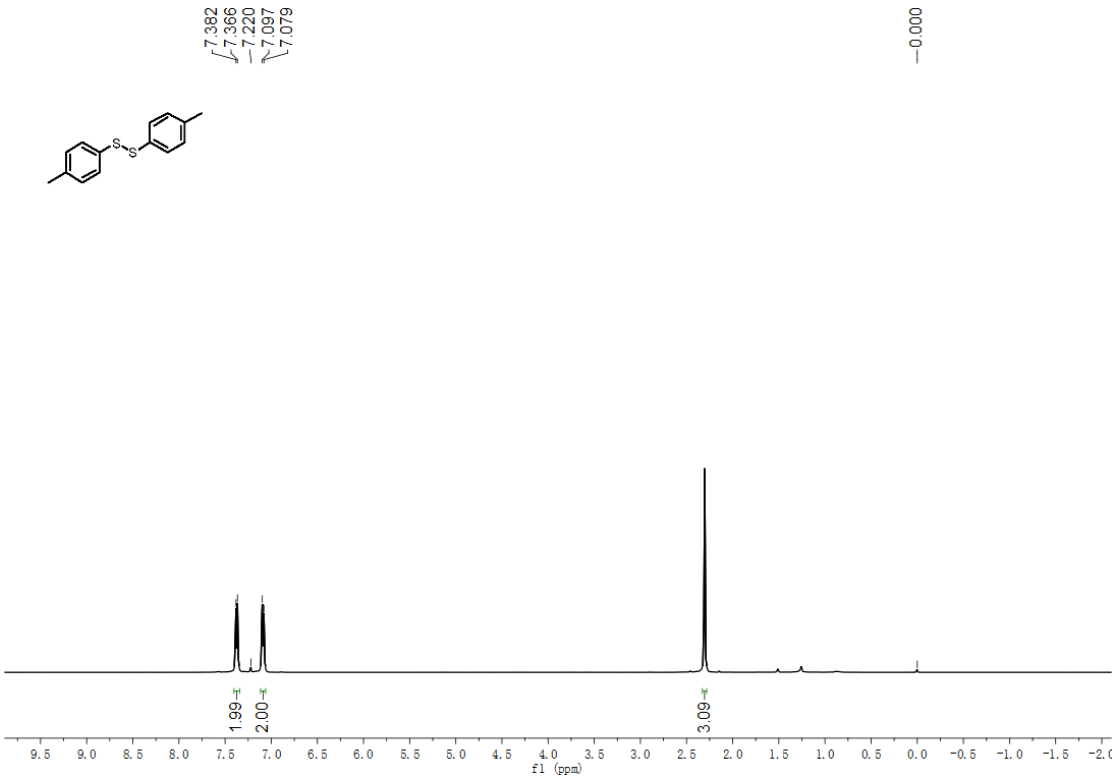
^{1}H NMR spectrum of compound **4w**



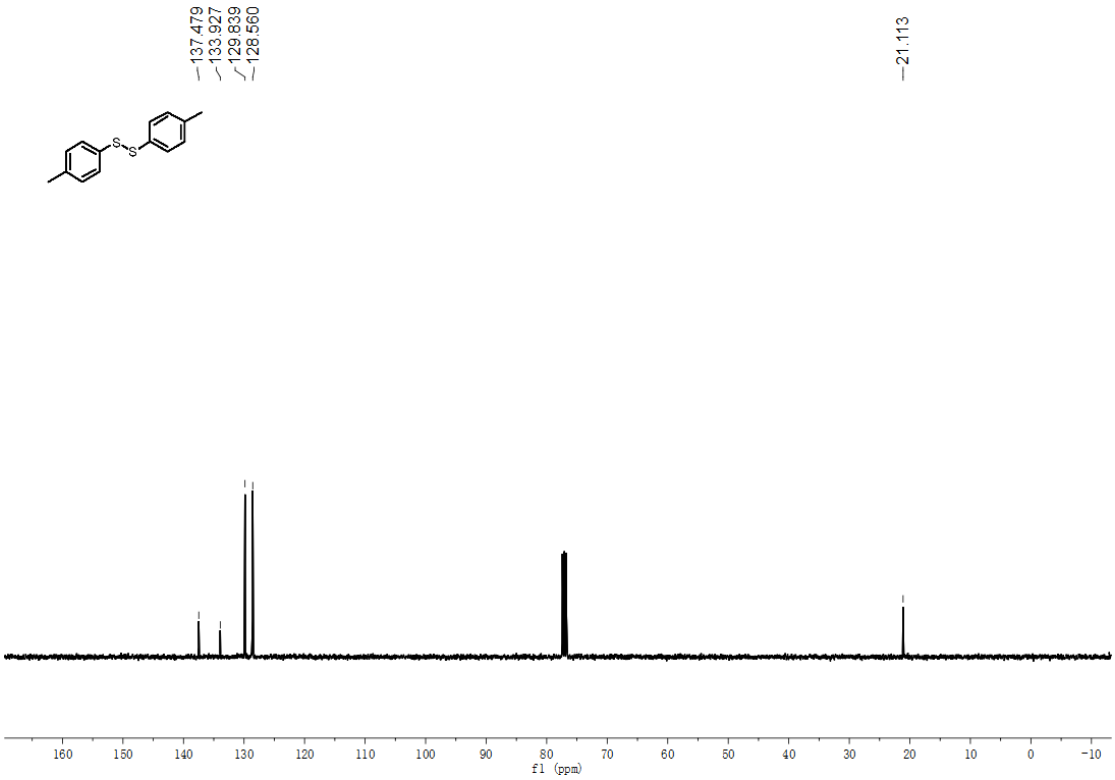
^{13}C NMR spectrum of compound **4w**



^{1}H NMR spectrum of compound **6**



^{13}C NMR spectrum of compound **6**



6. Reference:

1. S. Liu, Z. Qi, Z. Zhang and B. Qian, *Org. Lett.* **2019**, *21*, 7722-7725.