Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information

Electrochemical β-chlorosulfoxidation of alkenes

Yi Yu,† Yi-Min Jiang,† Xiao-Bin Zhu, Yong-Ying Lin, Yaofeng Yuan and Ke-Yin Ye*

Key Laboratory of Molecule Synthesis and Function Discovery (Fujian Province University), College of Chemistry, Fuzhou University, Fuzhou 350108, P. R. China.

† These authors contributed equally to this work.

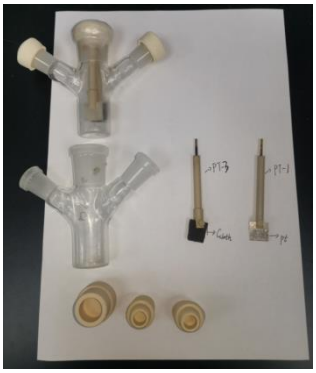
E-mail: kyye@fzu.edu.cn

Table of Contents

1. General Information

All reactions were performed under an atmosphere of nitrogen using standard undivided three-necked glassware, unless otherwise indicated. All commercial reagents were used without further purification, unless otherwise noted. Reactions were monitored by thin layer chromatography (TLC) analysis. TLC plates were viewed under UV light. Yields refer to products isolated after purification by column chromatography, unless otherwise stated. Proton nuclear magnetic resonance (^{1}H NMR) spectra, carbon nuclear magnetic resonance (^{13}C NMR) spectra and fluorine nuclear magnetic resonance (^{19}F NMR) were recorded on Bruker AV-400 (400 MHz), JEOL-500 (500 MHz) and JEOL-600 (600 MHz) spectrometers. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances. IR spectra were obtained from Thermo Scientific NICOLET 380 FT-IR. HRMS were obtained on an Exactive Plus LC-MS (ESI) mass spectrometer with the use of quadrupole analyzer. Cyclic voltammetry data were measured with a CHI 760E potentiostat (Chinstruments). All chemcials were purchased from *TCI Shanghai* or *Energy Chemical* and used as received.

Electrolysis experiments were performed using MESTEK DC power supply. Electrode clips (PT-1 or PT-3) and platinum plate (99.99%, 15*15*0.3 mm or 30*30*0.1 mm) was purchased from Gaoss Union. The carbon cloth (CeTech WOS1002) was cut into 15 x 15 x 0.1 mm pieces before use, and was clamped between electrode clips.

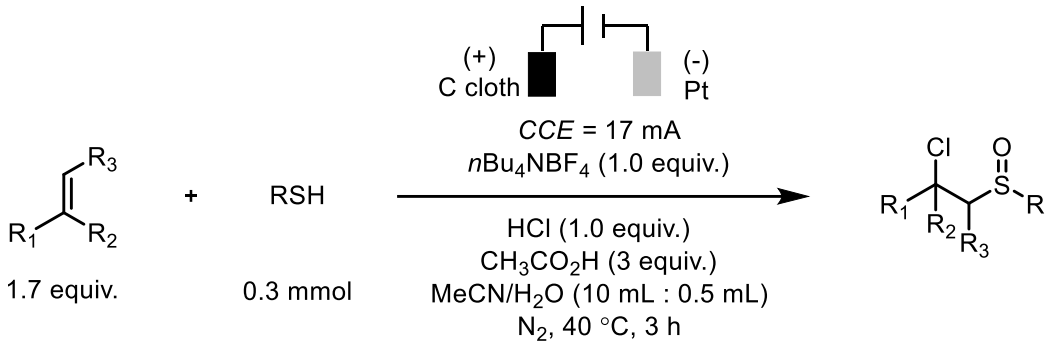


2. General Procedures

General procedure for the preparation of substituted olefins:[1]

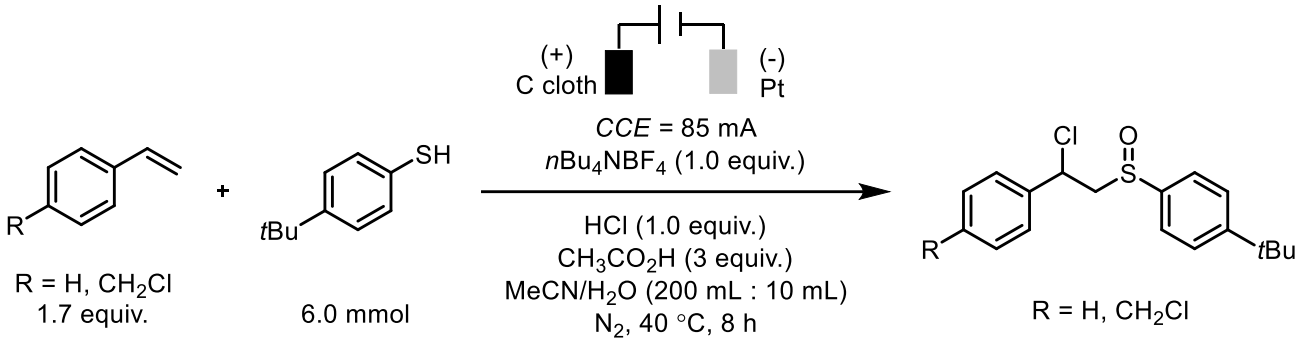
An oven-dried round-bottom flask was charged with CH_3PPh_3Br (1.5 equiv.) or $CH_3CH_2PPh_3Br$ (1.5 equiv.) and THF (carbonyl substrate concentration = 0.2 M). ^{t}BuOK (1.5 equiv.) was added to the suspension at 0 ℃. The resulting mixture was allowed to warm up to room temperature and stirred for 1 h. The yellow suspension was cooled to 0 ℃ again followed by portion-wise addition of the carbonyl substrate (1 equiv.). Subsequently, the mixture was further stirred at room temperature for 1-12 hours. After the completion of the reaction, the solvent was removed by evaporation, the resulting mixture was diluted with water (30 mL) and extracted with dichloromethane (3 x 20 mL), and the combined organic layer was dried with anhydrous Na_2SO_4. Concentration in vacuo followed by silica gel column purification with petroleum ether/ethyl acetate eluent gave the desired product in yields ranging from 50-95%.

Method A: General procedure for the electrochemical β-chlorosulfoxidation of alkenes (constant current electrolysis)



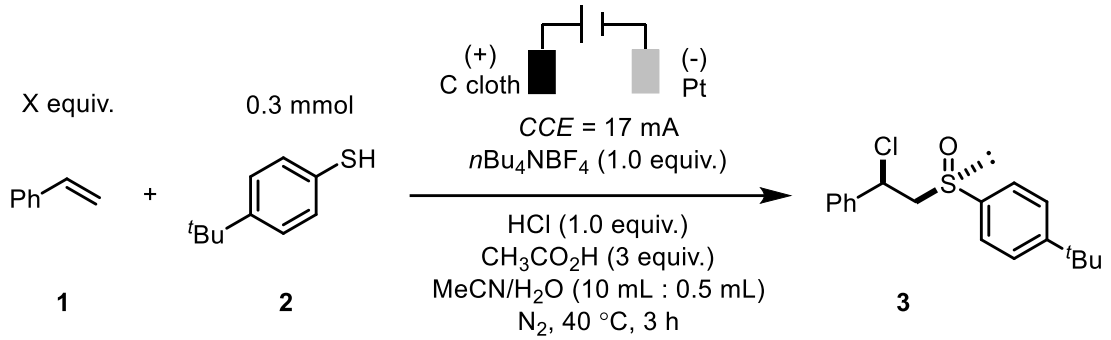
In an undivided three-necked glassware (25 mL) equipped with a stirring bar, nBu$_4$NBF$_4$ (1.0 equiv.) were added. The glassware was equipped with carbon cloth (15 mm × 15 mm × 0.1 mm) as the anode and platinum plate (15 mm × 15 mm × 0.3 mm) as the cathode. Under the protection of N_2, thiophenol (0.3 mmol), olefin substrates (1.7 equiv.), 1 M HCl in water (0.3 mL), water (0.2 mL), CH_3COOH (3.0 equiv.), and MeCN (10.0 mL) were injected respectively into the glassware via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 17 mA at 40 ℃ for 3 h. After completion, the resultant reaction mixture was concentrated in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product.

Method B: Scale-up synthesis



In an undivided three-necked glassware (250 mL) equipped with a stirring bar, nBu$_4$NBF$_4$ (1.0 equiv.) were added. The glassware was equipped with carbon cloth (30 mm × 30 mm × 0.1 mm) as the anode and platinum plate (30 mm × 30 mm × 0.1 mm) as the cathode. Under the protection of N_2, 4-tert-butylbenzenethiol (6.0 mmol), olefin substrates (1.7 equiv.), 1 M HCl in water (6.0 mL), water (4.0 mL), CH_3COOH (3.0 equiv.), and MeCN (200.0 mL) were injected respectively into the glassware via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 85 mA at 40 ° C for 8 h. After completion, the resultant reaction mixture was concentrated in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product.

3. Screening of the amount of styrene [a]

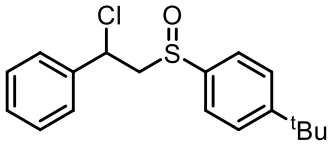


Entry	X equiv.	Yield (%)
1	1.7	83(80)[b]
2	1.5	62
3	1.2	21
4	1.0	18

[a] Reaction conditions: **1** (X equiv.), **2** (0.3 mmol, 1.0 equiv.), $^{n}Bu_4NBF_4$ (1.0 equiv.), HCl (1.0 equiv., 1.0 M), HOAc (3.0 equiv.), MeCN/H_2O = 10:0.5, carbon cloth anode, platinum cathode, undivided cell, constant current = 17 mA, 40 ℃, 3 h, yields were determined by ^1H NMR with 1,3,5-trimethoxybenzene as the internal standard; [b] Isolated yield.

The reaction proceeded a little bit less efficiently with a smaller amount of olefin (1.5 equiv.). However, further reducing the amount of olefin to 1.2 or 1.0 equiv. dramatically depressed the anticipated reactivity. Concomitantly, we observed some polymerization side products of olefin during the electrolysis. This is indeed a drawback of the current method and is the challenge we aim to address in the ongoing research project in our group.

4 Characterization of Products

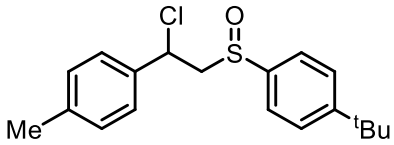


1-(Tert-butyl)-4-((2-chloro-2-phenylethyl)sulfinyl)benzene (3)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 7:1) to give 76.7 mg (80% yield, dr = 1.6:1) of **3** as yellow oil.

Followed **Method B**, the desired pure product was purified using silica gel chromatography (PE:EA = 7:1) to give 1.19 g (62% yield) of **3.**

IR (neat, cm^{-1}): 3059(w), 2960(m), 2869(w), 1394(m), 1364(w), 1046(s), 831(m), 766(w), 697(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.60 – 7.50 (m, 11H), 7.46 (d, *J* = 7.1 Hz, 3.4H), 7.44 – 7.36 (m, 6H), 7.35 – 7.28 (m, 3H), 5.43 (dd, *J* = 10.9, 3.2 Hz, 1H, minor diastereoisomer), 5.18 (dd, *J* = 9.4, 6.1 Hz, 1.6H, major diastereoisomer), 3.68 (dd, *J* = 12.8, 6.0 Hz, 1.6H, major diastereoisomer), 3.39 – 3.23 (m, 3.6H), 1.34 (s, 14.4H, major diastereoisomer), 1.32 (s, 9H, minor diastereoisomer). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.3, 155.0, 140.0, 139.8, 139.2, 138.5, 129.2, 129.0, 128.91, 128.86, 127.3, 126.9, 126.5, 126.4, 123.9, 123.7, 67.7, 67.0, 56.3, 56.2, 35.0, 34.9, 31.1. HRMS (ESI) calculated for $C_{18}H_{22}ClOS^+$ $[M+H]^+$: 321.1074; found: 321.1081.

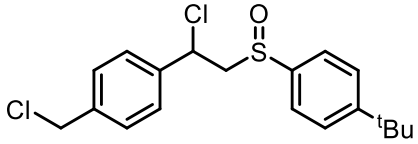


1-(Tert-butyl)-4-((2-chloro-2-(p-tolyl)ethyl)sulfinyl)benzene (4)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 7:1) to give 50.7 mg (51% yield, dr = 1.4:1) of **4** as yellow solid.

IR (neat, cm^{-1}): 3027(w), 2961(m), 2869(w), 1047(s), 825(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.60 – 7.50 (m, 10.5H), 7.35 (d, *J* = 8.0 Hz, 2.5H), 7.27 (d, *J* = 8.5 Hz, 1.5H), 7.22 (d, *J* = 7.9 Hz, 2.5H), 7.14 (d, *J* = 7.9 Hz, 2.2H), 5.39 (dd, *J* = 10.8, 3.5 Hz, 1H, minor diastereoisomer), 5.16 (dd, *J* = 9.5, 6.0 Hz, 1.4H, major diastereoisomer), 3.67 (dd, *J* = 12.8, 6.0 Hz, 1.4H, major diastereoisomer), 3.38 – 3.24 (m, 3.4H), 2.37 (s, 4.2H, major diastereoisomer), 2.32 (s, 3H, minor diastereoisomer), 1.34 (s, 12.6H, major diastereoisomer), 1.33 (s, 9H, minor diastereoisomer). ^{13}C NMR (126 MHz,

Chloroform-*d*) δ 155.3, 155.1, 140.1, 140.0, 139.3, 139.0, 136.3, 135.6, 129.7, 129.6, 127.2, 126.9, 126.51, 126.46, 124.0, 123.8, 67.7, 67.1, 56.3, 56.2, 35.03, 34.99, 31.2, 21.2, 21.1. HRMS (ESI) calculated for $C_{19}H_{24}ClOS^+$ $[M+H]^+$: 335.1231; found: 335.1236.

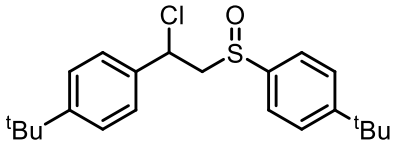


1-(Tert-butyl)-4-((2-chloro-2-(4-(chloromethyl)phenyl)ethyl)sulfinyl)benzene (5)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 5:1) to give 81.5 mg (74% yield, dr = 1.5:1) of **5** as white solid.

Followed **Method B**, the desired pure product was purified using silica gel chromatography (PE:EA = 5:1) to give 1.43 g (68% yield) of **5**.

IR (neat, cm^{-1}): 3052(w), 2962(m), 2869(w), 1047(m), 832(m), 733(s). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.59 – 7.51 (m, 10H), 7.45 (q, *J* = 8.3 Hz, 6H), 7.37 (q, *J* = 8.3 Hz, 4H), 5.42 (dd, *J* = 10.9, 3.3 Hz, 1H, minor diastereoisomer), 5.19 (dd, *J* = 9.5, 5.9 Hz, 1.5H, major diastereoisomer), 4.59 (s, 3H, major diastereoisomer), 4.54 (s, 2H, minor diastereoisomer), 3.66 (dd, *J* = 12.9, 5.9 Hz, 1.5H, major diastereoisomer), 3.35 – 3.22 (m, 3.5H, major diastereoisomer), 1.34 (s, 13.5H, major diastereoisomer), 1.32 (s, 9H, minor diastereoisomer). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.4, 155.1, 139.9, 139.7, 139.3, 138.7, 138.5, 138.2, 129.2, 129.1, 127.7, 127.4, 126.52, 126.46, 123.9, 123.7, 67.6, 66.8, 55.73, 55.71, 45.44, 45.37, 35.0, 34.9, 31.1. HRMS (ESI) calculated for $C_{19}H_{23}Cl_2OS^+$ $[M+H]^+$: 369.0841; found: 369.0854.

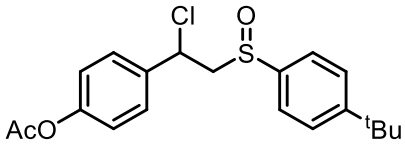


1-(Tert-butyl)-4-((2-(4-(tert-butyl)phenyl)-2-chloroethyl)sulfinyl)benzene (6)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 7:1) to give 59.5 mg (53% yield, dr = 1.5:1) of **6** as colorless oil.

IR (neat, cm^{-1}): 3056(w), 2960(s), 2869(m), 1396(m), 1364(w), 1047(s), 833(s). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.61 – 7.51 (m, 10H), 7.44 – 7.31 (m, 10H), 5.41 (dd, *J* = 10.9, 3.5 Hz, 1H, minor diastereoisomer), 5.15 (dd, *J* = 9.1, 6.3 Hz, 1.5H, major diastereoisomer), 3.69 (dd, *J* = 12.9, 6.3 Hz,

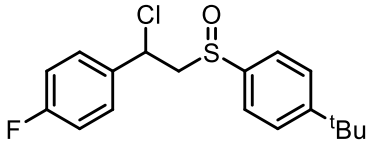
1.5H, major diastereoisomer), 3.35 – 3.23 (m, 3.5H), 1.35 (s, 13.5H, major diastereoisomer), 1.33 (s, 13.5H, major diastereoisomer), 1.33 (s, 9H, minor diastereoisomer), 1.29 (s, 9H, minor diastereoisomer). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.3, 155.1, 152.4, 152.2, 140.3, 140.0, 136.2, 135.5, 127.0, 126.7, 126.52, 126.48, 126.0, 125.9, 124.0, 123.8, 68.1, 67.0, 56.24, 56.19, 35.1, 35.0, 34.7, 34.6, 31.23, 31.19, 31.17, 31.16. HRMS (ESI) calculated for $C_{22}H_{30}ClOS^+$ $[M+H]^+$: 377.1700; found: 377.1710.



4-(2-((4-(Tert-butyl)phenyl)sulfinyl)-1-chloroethyl)phenyl acetate (7)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 80.4 mg (71% yield, dr = 1.5:1) of **7** as yellow oil.

IR (neat, cm^{-1}): 3062(w), 2963(w), 2869(w), 1765(m), 1200(s), 1048(m), 832(w). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59 – 7.50 (m, 10H), 7.47 (d, *J* = 8.6 Hz, 3H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.14 (d, *J* = 8.6 Hz, 3H), 7.05 (d, *J* = 8.6 Hz, 2H), 5.43 (dd, *J* = 10.9, 3.4 Hz, 1H, minor diastereoisomer), 5.17 (dd, *J* = 9.3, 6.1 Hz, 1.5H, major diastereoisomer), 3.66 (dd, *J* = 12.9, 6.0 Hz, 1.5H, major diastereoisomer), 3.38 – 3.21 (m, 3.5H), 2.30 (s, 4.5H, major diastereoisomer), 2.27 (s, 3H, minor diastereoisomer), 1.33 (s, 13.5H, major diastereoisomer), 1.32 (s, 9H, minor diastereoisomer). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.1, 155.4, 155.1, 151.0, 150.8, 139.9, 139.7, 136.7, 136.0, 128.5, 128.1, 126.53, 126.47, 123.9, 123.7, 122.14, 122.06, 67.7, 66.9, 55.6, 55.5, 35.00, 34.95, 31.1, 21.1, 21.0. HRMS (ESI) calculated for $C_{20}H_{24}ClO_3S^+$ $[M+H]^+$: 379.1129; found: 379.1144.

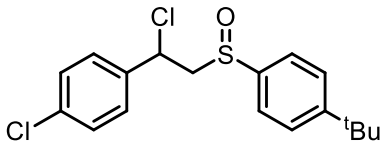


1-(Tert-butyl)-4-((2-chloro-2-(4-fluorophenyl)ethyl)sulfinyl)benzene (8)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 7:1) to give 75.1 mg (74% yield, dr = 1.5:1) of **8** as white solid.

IR (neat, cm^{-1}): 3058(w), 2962(m), 2870(w), 1230(s), 1047(s), 835(s). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59 – 7.49 (m, 10H), 7.45 (dd, *J* = 8.6, 5.2 Hz, 3H), 7.36 (dd, *J* = 8.7, 5.2 Hz, 2H),

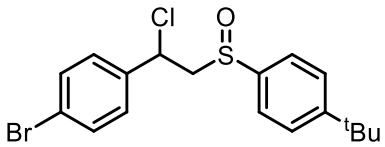
7.09 (t, *J* = 8.6 Hz, 3H), 7.00 (t, *J* = 8.6 Hz, 2H), 5.42 (dd, *J* = 10.8, 3.5 Hz, 1H, minor diastereoisomer), 5.19 (dd, *J* = 9.8, 5.8 Hz, 1.5H, major diastereoisomer), 3.65 (dd, *J* = 12.9, 5.8 Hz, 1.5H, major diastereoisomer), 3.37 – 3.21 (m, 3.5H), 1.34 (s, 13.5H, major diastereoisomer), 1.32 (s, 9H, minor diastereoisomer). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.9 (d, *J* = 248.9 Hz), 162.7 (d, *J* = 248.7 Hz), 155.4, 155.1, 139.8, 139.6, 135.1 (d, *J* = 3.5 Hz), 134.4 (d, *J* = 3.2 Hz), 129.2 (d, *J* = 8.4 Hz), 128.9 (d, *J* = 8.5 Hz), 126.6, 126.5, 123.9, 123.7, 116.0 (d, *J* = 23.4 Hz), 115.9 (d, *J* = 23.5 Hz), 67.5, 67.0, 55.5, 55.4, 35.02, 34.97, 31.1. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -111.5 (tt, *J* = 8.4, 4.6 Hz), -111.9 (tt, *J* = 8.3, 4.6 Hz). HRMS (ESI) calculated for $C_{18}H_{21}ClFOS^+$ $[M+H]^+$: 339.0980; found: 339.0990.



1-(Tert-butyl)-4-((2-chloro-2-(4-chlorophenyl)ethyl)sulfinyl)benzene (9)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 7:1) to give 76.2 mg (71% yield, dr = 1.5:1) of **9** as yellow solid.

IR (neat, cm^{-1}): 3055(w), 2961(m), 2869(w), 1046(s), 829(s). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.57 – 7.49 (m, 10H), 7.43 – 7.36 (m, 6H), 7.36 – 7.24 (m, 4H), 5.40 (dd, *J* = 10.7, 3.5 Hz, 1H, minor diastereoisomer), 5.18 (dd, *J* = 9.7, 5.7 Hz, 1.5H, major diastereoisomer), 3.64 (dd, *J* = 12.9, 5.7 Hz, 1.5H, major diastereoisomer), 3.39 – 3.19 (m, 3.5H), 1.34 (s, 13.5H, major diastereoisomer), 1.32 (s, 9H, minor diastereoisomer). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.5, 155.1, 139.7, 139.6, 137.7, 137.0, 135.1, 134.8, 129.2, 129.1, 128.7, 128.4, 126.6, 126.5, 123.9, 123.7, 67.2, 66.8, 55.4, 55.3, 35.03, 34.97, 31.1. HRMS (ESI) calculated for $C_{18}H_{21}Cl_2OS^+$ $[M+H]^+$: 355.0685; found: 355.0697.

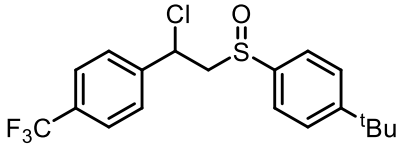


1-Bromo-4-(2-((4-(tert-butyl)phenyl)sulfinyl)-1-chloroethyl)benzene (10)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 7:1) to give 76.1 mg (63% yield, dr = 1.7:1) of **10** as white solid.

IR (neat, cm^{-1}): 3053(w), 2961(m), 2869(w), 1045(s), 827(s). ^{1}H NMR (500 MHz, Chloroform-*d*) δ

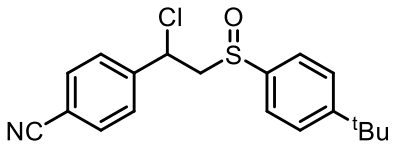
7.54 (q, *J* = 4.2 Hz, 14H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 3.3H), 7.25 (d, *J* = 9.1 Hz, 2.3H), 5.39 (dd, *J* = 10.7, 3.5 Hz, 1H, minor diastereoisomer), 5.17 (dd, *J* = 9.8, 5.7 Hz, 1.7H, major diastereoisomer), 3.64 (dd, *J* = 12.9, 5.7 Hz, 1.7H, major diastereoisomer), 3.36 – 3.21 (m, 3.7H), 1.34 (s, 15.3H, major diastereoisomer), 1.33 (s, 9H, minor diastereoisomer). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.5, 155.2, 139.8, 139.7, 138.3, 137.6, 132.2, 132.0, 129.0, 128.7, 126.6, 126.5, 123.9, 123.7, 123.3, 122.9, 67.2, 66.8, 55.5, 55.4, 35.04, 34.99, 31.1. HRMS (ESI) calculated for $C_{18}H_{21}BrClOS^+$ $[M+H]^+$: 401.0159; found: 401.0166.



1-(Tert-butyl)-4-((2-chloro-2-(4-(trifluoromethyl)phenyl)ethyl)sulfinyl)benzene (11)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 7:1) to give 73.1 mg (63% yield, dr = 1.2:1) of **11** as colorless oil.

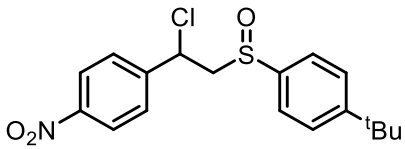
IR (neat, cm^{-1}): 3056(w), 2963(m), 2870(w), 1323(s), 1049(m), 835(m). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.68 (d, 2.3H), 7.63 – 7.57 (m, 5.3H), 7.57 – 7.54 (m, 6H), 7.52 (dt, *J* = 8.0, 1.5 Hz, 4H), 5.48 (dd, *J* = 10.9, 3.4 Hz, 1H, minor diastereoisomer), 5.25 (dd, *J* = 9.7, 5.7 Hz, 1.2H, major diastereoisomer), 3.67 (dd, *J* = 12.9, 5.7 Hz, 1.2H, major diastereoisomer), 3.37 – 3.22 (m, 3.2H), 1.34 (s, 10.8H, major diastereoisomer), 1.32 (s, 9H, minor diastereoisomer). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.6, 155.3, 143.0 (q, *J* = 1.3 Hz), 142.4 (q, *J* = 1.3 Hz), 139.7, 139.6, 131.3 (q, *J* = 33.7 Hz), 131.1 (q, *J* = 32.7 Hz), 127.9, 127.5, 126.6, 126.5, 126.1 (q, *J* = 3.8 Hz), 125.9 (q, *J* = 3.8 Hz), 123.9, 123.70 (q, *J* = 272.3 Hz), 123.67, 123.6 (q, *J* = 272.4 Hz), 67.3, 66.6, 55.2, 35.1, 35.0, 31.1, 31.1. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -62.6, -62.7. HRMS (ESI) calculated for $C_{19}H_{21}ClF_3OS^+$ $[M+H]^+$: 389.0948; found: 389.0960.



4-(2-((4-(Tert-butyl)phenyl)sulfinyl)-1-chloroethyl)benzonitrile (12)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 57.6 mg (56% yield, dr = 1.1:1) of **12** as colorless oil.

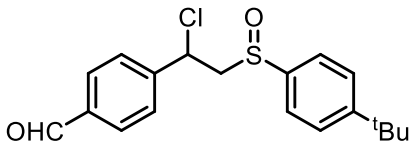
IR (neat, cm^{-1}): 3054(w), 2962(m), 2870(w), 2229(m), 1046(s), 833(s). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.75 – 7.70 (m, 2H), 7.64 – 7.59 (m, 4H), 7.57 – 7.49 (m, 10H), 5.46 (dd, *J* = 10.7, 3.5 Hz, 1H), 5.23 (dd, *J* = 9.8, 5.6 Hz, 1H), 3.64 (dd, *J* = 13.0, 5.6 Hz, 1H), 3.34 – 3.18 (m, 3H), 1.34 (s, 9H), 1.32 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.7, 155.3, 144.1, 143.5, 139.5, 139.4, 132.8, 132.7, 128.2, 127.9, 126.7, 126.6, 123.9, 123.6, 118.1, 118.0, 113.1, 112.8, 66.9, 66.2, 55.0, 35.1, 35.0, 31.1. HRMS (ESI) calculated for $C_{19}H_{21}ClNOS^+$ $[M+H]^+$: 346.1027; found: 346.1038.



1-(Tert-butyl)-4-((2-chloro-2-(4-nitrophenyl)ethyl)sulfinyl)benzene (13)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 5:1) to give 29.7 mg (27% yield, dr = 1.5:1) of **13** as yellow oil.

IR (neat, cm^{-1}): 3067(w), 2960(m), 2866(w), 1523(s), 1347(s), 1046(m), 855(m), 829(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 8.28 (d, *J* = 8.7 Hz, 3H), 8.18 (d, *J* = 8.7 Hz, 2H), 7.68 (d, *J* = 8.7 Hz, 3H), 7.62 – 7.49 (m, 12H), 5.52 (dd, *J* = 10.6, 3.5 Hz, 1H, minor diastereoisomer), 5.29 (dd, *J* = 9.8, 5.6 Hz, 1.5H, major diastereoisomer), 3.67 (dd, *J* = 13.0, 5.6 Hz, 1.5H, major diastereoisomer), 3.39 – 3.23 (m, 3.5H), 1.34 (s, 13.5H, major diastereoisomer), 1.31 (s, 9H, minor diastereoisomer). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.7, 155.4, 148.2, 147.9, 146.0, 145.4, 139.4, 139.3, 128.5, 128.2, 126.7, 126.6, 124.3, 124.1, 123.9, 123.7, 66.8, 66.2, 54.7, 54.6, 35.1, 35.0, 31.13, 31.12. HRMS (ESI) calculated for $C_{18}H_{21}ClNO_3S^+$ $[M+H]^+$: 366.0925; found: 366.0937.

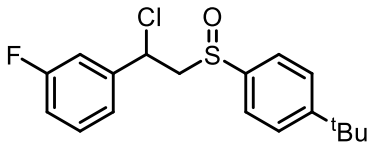


4-(2-((4-(tert-butyl)phenyl)sulfinyl)-1-chloroethyl)benzaldehyde (14)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 65.1 mg (62% yield, dr = 1.5:1) of **14** as colorless oil.

IR (neat, cm^{-1}): 3054(w), 2961(m), 2868(w), 1700(s), 1045(s), 832(s). ^1H NMR (500 MHz,

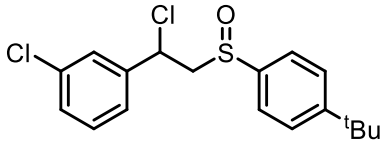
Chloroform-*d*) δ 10.03 (s, 1.5H, major diastereoisomer), 9.98 (s, 1H, minor diastereoisomer), 7.93 (d, *J* = 8.2 Hz, 3H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.1 Hz, 3H), 7.61 – 7.46 (m, 12H), 5.50 (dd, *J* = 10.4, 3.8 Hz, 1H, minor diastereoisomer), 5.24 (dd, *J* = 9.5, 5.8 Hz, 1.5H, major diastereoisomer), 3.69 (dd, *J* = 13.0, 5.8 Hz, 1.5H, major diastereoisomer), 3.37 – 3.27 (m, 3.5H), 1.33 (s, 13.5H, major diastereoisomer), 1.30 (s, 9H, minor diastereoisomer). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 191.4, 191.3, 155.6, 155.3, 145.4, 144.8, 139.4, 139.2, 136.8, 136.5, 130.3, 130.2, 128.1, 127.8, 126.62, 126.55, 124.0, 123.7, 67.0, 66.3, 55.31, 55.27, 35.03, 34.97, 31.1. HRMS (ESI) calculated for $C_{19}H_{22}ClO_2S^+$ $[M+H]^+$: 349.1024; found: 349.1036.



1-(2-((4-(tert-butyl)phenyl)sulfinyl)-1-chloroethyl)-3-fluorobenzene (15)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 7:1) to give 67.4 mg (66% yield, dr = 1.3:1) of **15** as colorless oil.

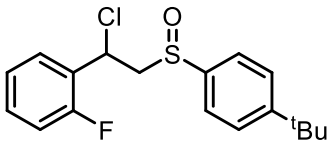
IR (neat, cm^{-1}): 3058(w), 2962(m), 2870(w), 1262(m), 1046(s), 832(m), 773(s), 692(m). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59 – 7.51 (m, 9.5H), 7.38 (td, *J* = 8.0, 5.8 Hz, 1.3H), 7.30 (td, *J* = 8.0, 5.8 Hz, 1H), 7.27 – 7.24 (m, 1H), 7.20 – 7.15 (m, 2.3H), 7.13 – 7.05 (m, 2.3H), 6.99 (tdd, *J* = 8.4, 2.5, 0.9 Hz, 1H), 5.41 (dd, *J* = 10.6, 3.6 Hz, 1H, minor diastereoisomer), 5.17 (dd, *J* = 9.6, 5.9 Hz, 1.3H, major diastereoisomer), 3.64 (dd, *J* = 12.9, 5.9 Hz, 1.3H, major diastereoisomer), 3.34 – 3.22 (m, 3.3H), 1.34 (s, 11.7H, major diastereoisomer), 1.32 (s, 9H, minor diastereoisomer). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.9 (d, *J* = 247.8 Hz), 162.8 (d, *J* = 247.8 Hz), 155.5, 155.2, 141.6 (d, *J* = 7.3 Hz), 141.0 (d, *J* = 7.3 Hz), 139.8, 139.7, 130.7 (d, *J* = 8.2 Hz), 130.5 (d, *J* = 8.3 Hz), 126.6, 126.5, 123.9, 123.7, 123.2 (d, *J* = 3.0 Hz), 122.7 (d, *J* = 3.0 Hz), 116.3 (d, *J* = 21.1 Hz), 116.0 (d, *J* = 21.1 Hz), 114.4 (d, *J* = 22.6 Hz), 114.1 (d, *J* = 22.8 Hz), 67.5, 66.8, 55.4 (d, *J* = 1.5 Hz), 55.3 (d, *J* = 1.5 Hz), 35.1, 35.0, 31.14, 31.13. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -111.1 (q, *J* = 8.7 Hz), -111.4 (q, *J* = 8.8 Hz). HRMS (ESI) calculated for $C_{18}H_{21}ClFOS^+$ $[M+H]^+$: 339.0980; found: 339.0992.



1-(2-((4-(Tert-butyl)phenyl)sulfinyl)-1-chloroethyl)-3-chlorobenzene (16)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 7:1) to give 75.4 mg (71% yield, dr = 1.5:1) of **16** as colorless oil.

IR (neat, cm^{-1}): 3057(w), 2961(m), 2869(w), 1045(s), 831(m), 790(m), 691(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.62 – 7.50 (m, 10.5H), 7.46 (s, 1.5H), 7.37 (d, *J* = 15.3 Hz, 5.5H), 7.27 (d, *J* = 1.2 Hz, 2.5H), 5.40 (dd, *J* = 10.8, 3.4 Hz, 1H, minor diastereoisomer), 5.15 (dd, *J* = 9.5, 5.9 Hz, 1.5H, major diastereoisomer), 3.65 (dd, *J* = 12.9, 5.9 Hz, 1.5H, major diastereoisomer), 3.35 – 3.22 (m, 3.5H), 1.35 (s, 13.5H, major diastereoisomer), 1.33 (s, 9H, minor diastereoisomer). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.4, 155.1, 141.1, 140.5, 139.7, 139.6, 134.9, 134.7, 130.3, 130.2, 129.4, 129.1, 127.4, 127.2, 126.6, 126.5, 125.6, 125.2, 123.9, 123.7, 67.3, 66.6, 55.3, 55.2, 35.01, 34.96, 31.1. HRMS (ESI) calculated for $C_{18}H_{21}Cl_2OS^+$ $[M+H]^+$: 355.0685; found: 355.0696.



1-(2-((4-(Tert-butyl)phenyl)sulfinyl)-1-chloroethyl)-2-fluorobenzene (17)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 7:1) to give 71.6 mg (70% yield, dr = 1.5:1) of **17** as colorless oil.

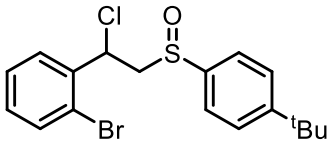
Diastereoisomer 1:

IR (neat, cm^{-1}): 3059(w), 2961(m), 2869(w), 1235(m), 1047(s), 832(m), 760(s). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.44 – 7.40 (m, 1H), 7.30 (ddd, *J* = 13.3, 5.5, 2.7 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.06 – 7.01 (m, 1H), 5.66 (dd, *J* = 10.7, 3.7 Hz, 1H), 3.47 (dd, *J* = 13.3, 10.8 Hz, 1H), 3.33 (dd, *J* = 13.4, 3.7 Hz, 1H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.8 (d, *J* = 250.2 Hz), 155.1, 139.9, 130.8 (d, *J* = 8.5 Hz), 128.9 (d, *J* = 3.1 Hz), 126.5, 126.3 (d, *J* = 12.5 Hz), 124.6 (d, *J* = 3.7 Hz), 123.8, 116.1 (d, *J* = 21.5 Hz), 65.8 (d, *J* = 1.6 Hz), 50.2 (d, *J* = 3.2 Hz), 35.0, 31.2. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -115.4 (dt, *J* = 11.8, 6.4 Hz). HRMS (ESI) calculated for $C_{18}H_{21}ClFOS^+$ $[M+H]^+$: 339.0980; found: 339.0993.

Diastereoisomer 2:

IR (neat, cm^{-1}): 3058(w), 2961(m), 2869(w), 1235(m), 1049(s), 832(m), 758(s). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.57 (q, *J* = 8.6 Hz, 4H), 7.48 (td, *J* = 7.6, 1.4 Hz, 1H), 7.41 – 7.33 (m, 1H), 7.20 (t,

J = 7.3 Hz, 1H), 7.14 – 7.06 (m, 1H), 5.36 (dd, *J* = 8.7, 6.8 Hz, 1H), 3.67 (dd, *J* = 13.0, 6.6 Hz, 1H), 3.49 (dd, *J* = 13.0, 8.9 Hz, 1H), 1.34 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.1 (d, *J* = 250.1 Hz), 155.4, 139.7, 131.1 (d, *J* = 8.5 Hz), 129.3 (d, *J* = 3.1 Hz), 126.5, 125.6 (d, *J* = 12.2 Hz), 124.8 (d, *J* = 3.6 Hz), 124.0, 116.3 (d, *J* = 21.5 Hz), 65.2 (d, *J* = 2.0 Hz), 50.5 (d, *J* = 3.1 Hz), 35.0, 31.1. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -115.5 (dt, *J* = 11.2, 6.2 Hz). HRMS (ESI) calculated for $C_{18}H_{21}ClFOS^+$ $[M+H]^+$: 339.0980; found: 339.0992.



1-Bromo-2-(2-((4-(tert-butyl)phenyl)sulfinyl)-1-chloroethyl)benzene (18)

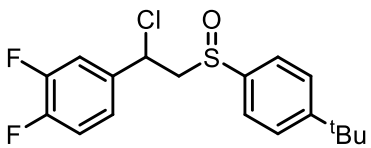
Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 7:1) to give 84.2 mg (70% yield, dr = 1:1) of **18** as colorless oil.

Diastereoisomer 1:

IR (neat, cm^{-1}): 3060(w), 2960(m), 2868(w), 1047(s), 831(m), 759(m). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.61 – 7.58 (m, 2H), 7.58 – 7.54 (m, 2H), 7.54 – 7.51 (m, 2H), 7.34 – 7.29 (m, 1H), 7.16 (td, *J* = 7.8, 1.6 Hz, 1H), 5.89 (dd, *J* = 10.7, 3.5 Hz, 1H), 3.36 (dd, *J* = 13.4, 3.5 Hz, 1H), 3.27 (dd, *J* = 13.3, 10.8 Hz, 1H), 1.32 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.1, 140.1, 138.0, 133.3, 130.2, 128.8, 128.1, 126.5, 123.8, 122.8, 66.3, 55.1, 35.0, 31.1. HRMS (ESI) calculated for $C_{18}H_{21}BrClOS^+$ $[M+H]^+$: 401.0159; found: 401.0169.

Diastereoisomer 2:

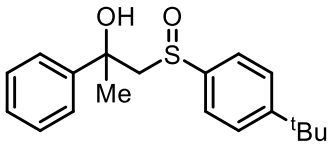
IR (neat, cm^{-1}): 3060(w), 2960(m), 2868(w), 1050(s), 832(m), 747(m). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.64 – 7.55 (m, 3H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.21 – 7.14 (m, 1H), 5.32 (dd, *J* = 8.7, 5.9 Hz, 1H), 3.66 (dd, *J* = 13.1, 8.8 Hz, 1H), 3.32 (dd, *J* = 13.1, 5.9 Hz, 1H), 1.35 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.7, 139.5, 137.6, 133.2, 130.4, 128.9, 128.3, 126.6, 124.3, 122.6, 65.8, 55.2, 35.1, 31.2. HRMS (ESI) calculated for $C_{18}H_{21}BrClOS^+$ $[M+H]^+$: 401.0159; found: 401.0168.



4-(2-((4-(Tert-butyl)phenyl)sulfinyl)-1-chloroethyl)-1,2-difluorobenzene (19)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 7:1) to give 61.7 mg (58% yield, dr = 1.5:1) of **19** as yellow oil.

IR (neat, cm^{-1}): 3054(w), 2962(m), 2869(w), 1283(s), 1048(s), 872(w), 830(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.61 – 7.49 (m, 10H), 7.31 (td, *J* = 7.9, 7.4, 4.2 Hz, 1.5H), 7.25 – 7.16 (m, 4H), 7.14 – 7.06 (m, 2H), 5.39 (dd, *J* = 10.6, 3.6 Hz, 1H, minor diastereoisomer), 5.17 (dd, *J* = 9.9, 5.6 Hz, 1.5H, major diastereoisomer), 3.62 (dd, *J* = 12.9, 5.6 Hz, 1.5H, major diastereoisomer), 3.36 – 3.19 (m, 3.5H), 1.34 (s, 13.5H, major diastereoisomer), 1.32 (s, 9H, minor diastereoisomer). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.6, 155.2, 151.8 – 151.0 (m), 149.8 – 149.1 (m), 139.6, 139.5, 136.3 – 136.2 (m), 135.7 – 135.4 (m), 126.6, 126.5, 123.9, 123.8 (dd, *J* = 6.6, 3.6 Hz), 123.7, 123.3 (dd, *J* = 6.5, 3.7 Hz), 117.8 (d, *J* = 17.6 Hz), 117.7 (d, *J* = 17.6 Hz), 116.5 (d, *J* = 18.2 Hz), 116.3 (d, *J* = 18.3 Hz), 67.1, 66.7, 54.9, 54.8, 35.04, 34.98, 31.1. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -135.2 – -135.3 (m), -135.5 – -135.6 (m), -135.8 (ddt, *J* = 21.2, 13.9, 6.6 Hz), -136.3 (dp, *J* = 21.5, 7.2, 6.3 Hz). HRMS (ESI) calculated for $C_{18}H_{20}ClF_2OS^+$ $[M+H]^+$: 357.0886; found: 357.0874.



1-((4-(Tert-butyl)phenyl)sulfinyl)-2-phenylpropan-2-ol (20)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 5:1) to give 68.1 mg (72% yield, dr = 1.4:1) of **20** as colorless oil.

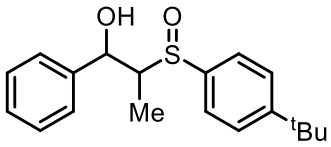
Diastereoisomer 1:

IR (neat, cm^{-1}): 3369(br), 3059(w), 2961(m), 2868(w), 1057(m), 832(m), 768(m), 702(s). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.56 – 7.48 (m, 4H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 5.00 (s, 1H), 3.15 (d, *J* = 13.4 Hz, 1H), 2.98 (d, *J* = 13.4 Hz, 1H), 2.00 (s, 3H), 1.31 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.1, 146.5, 139.8, 128.3, 127.2, 126.5, 124.5, 123.8, 74.3, 67.7, 35.0, 31.1, 28.5. HRMS (ESI) calculated for $C_{19}H_{25}O_2S^+$ $[M+H]^+$: 317.1570; found: 317.1579.

Diastereoisomer 2:

IR (neat, cm^{-1}): 3369(br), 3058(w), 2961(m), 2868(w), 1060(m), 831(m), 767(m), 702(s). ^1H NMR

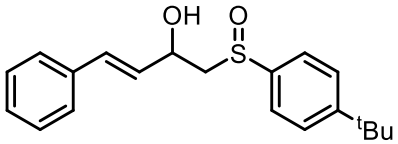
(500 MHz, Chloroform-*d*) δ 7.59 – 7.55 (m, 2H), 7.53 (s, 4H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 5.19 (s, 1H), 3.30 (d, *J* = 13.2 Hz, 1H), 3.16 (d, *J* = 13.2 Hz, 1H), 1.61 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.2, 145.4, 140.3, 128.6, 127.3, 126.5, 125.1, 123.8, 75.0, 67.8, 35.0, 32.0, 31.2. HRMS (ESI) calculated for $C_{19}H_{25}O_2S^+$ $[M+H]^+$: 317.1570; found: 317.1580.



2-((4-(Tert-butyl)phenyl)sulfinyl)-1-phenylpropan-1-ol (21)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 42.2 mg (44% yield, >20:1 dr) of **21** as white solid.

IR (neat, cm^{-1}): 3325(br), 3060(w), 2961(m), 2870(w), 1021(s), 831(m), 738(m), 701(s). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.42 – 7.33 (m, 4H), 7.30 – 7.26 (m, 1H), 5.50 (d, *J* = 2.3 Hz, 1H), 3.60 (s, 1H), 2.80 (qd, *J* = 6.9, 2.9 Hz, 1H), 1.33 (s, 9H), 0.97 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 154.6, 141.3, 137.6, 128.4, 127.7, 126.2, 125.8, 124.1, 73.8, 64.4, 35.0, 31.2, 3.2. HRMS (ESI) calculated for $C_{19}H_{25}O_2S^+$ $[M+H]^+$: 317.1570; found: 317.1579.

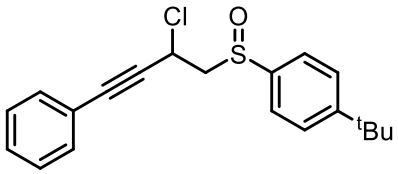


(E)-1-((4-(tert-butyl)phenyl)sulfinyl)-4-phenylbut-3-en-2-ol (22)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 70.2 mg (71% yield, dr = 2.3:1) of **22** as white solid.

IR (neat, cm^{-1}): 3325(br), 3057(w), 2960(m), 2869(w), 1079(m), 970(s), 830(m), 738(m), 693(m). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.62 – 7.57 (m, 6.6H), 7.57 – 7.51 (m, 6.6H), 7.37 – 7.33 (m, 5.5H), 7.32 – 7.26 (m, 8H), 7.25 – 7.21 (m, 3H), 6.68 (t, *J* = 15.5 Hz, 3.3H), 6.19 (ddd, *J* = 19.7, 15.9, 6.1 Hz, 3.3H), 4.97 – 4.90 (m, 3.3H), 3.18 (dd, *J* = 13.1, 8.8 Hz, 2.3H, major diastereoisomer), 3.09 (dd, *J* = 13.4, 10.0 Hz, 1H, minor diastereoisomer), 2.94 (dd, *J* = 13.1, 3.6 Hz, 2.3H, major diastereoisomer), 2.89 (dd, *J* = 13.4, 2.2 Hz, 1H, minor diastereoisomer), 1.34 (s, 9H, minor diastereoisomer), 1.33 (s, 20.7H, major diastereoisomer). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.1, 154.8, 140.1, 139.4,

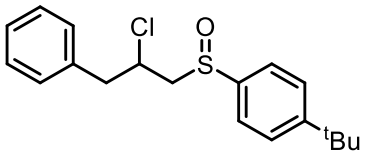
136.2, 136.1, 131.3, 131.0, 129.3, 129.1, 128.51, 128.49, 127.9, 127.8, 126.54, 126.47, 126.4, 123.9, 123.8, 69.3, 67.2, 62.5, 62.1, 36.0, 35.0, 31.1, 31.1. HRMS (ESI) calculated for $C_{20}H_{25}O_2S^+$ $[M+H]^+$: 329.1570; found: 329.1582.



1-(Tert-butyl)-4-((2-chloro-4-phenylbut-3-yn-1-yl)sulfinyl)benzene (23)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 5:1) to give 49.6 mg (48% yield, dr = 1.2:1) of **23** as yellow oil.

IR (neat, cm^{-1}): 3057(w), 2960(m), 2868(w), 2233(w), 1048(s), 831(m), 757(s), 691(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.67 – 7.60 (m, 4H), 7.60 – 7.54 (m, 5H), 7.53 – 7.47 (m, 2.2H), 7.41 – 7.29 (m, 8.6H), 5.21 (dd, *J* = 9.8, 4.3 Hz, 1H, minor diastereoisomer), 5.12 (dd, *J* = 9.8, 5.4 Hz, 1.2H, major diastereoisomer), 3.51 (dd, *J* = 12.6, 5.4 Hz, 1.2H, major diastereoisomer), 3.45 (dd, *J* = 13.3, 4.3 Hz, 1H, minor diastereoisomer), 3.31 (td, *J* = 12.7, 9.9 Hz, 2.2H), 1.35 (s, 10.8H, major diastereoisomer), 1.33 (s, 9H, minor diastereoisomer). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.5, 155.3, 139.7, 139.4, 132.0, 131.8, 129.3, 129.2, 128.4, 128.3, 126.62, 126.58, 123.92, 123.87, 121.4, 121.3, 88.7, 87.8, 84.6, 84.4, 66.2, 65.8, 43.0, 42.6, 35.1, 35.0, 31.2, 31.1. HRMS (ESI) calculated for $C_{20}H_{22}ClOS^+$ $[M+H]^+$: 345.1074; found: 345.1089.

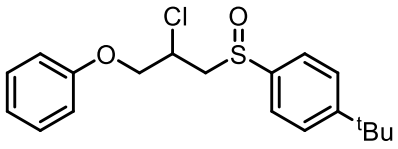


1-(Tert-butyl)-4-((2-chloro-3-phenylpropyl)sulfinyl)benzene (24)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 7:1) to give 46.6 mg (46% yield, dr = 1.3:1) of **24** as yellow oil.

IR (neat, cm^{-1}): 3060(w), 3028(w), 2960(m), 2868(w), 1044(s), 832(m), 748(m), 700(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.65 – 7.53 (m, 9.2H), 7.32 – 7.18 (m, 7.2H), 7.12 (d, *J* = 7.7 Hz, 4.3H), 3.99 (dd, *J* = 11.8, 5.7 Hz, 1H, minor diastereoisomer), 3.71 – 3.62 (m, 1.3H, major diastereoisomer), 3.52 (dd, *J* = 11.8, 4.2 Hz, 1H, minor diastereoisomer), 3.36 (dd, *J* = 12.1, 3.9 Hz, 1.3H, major diastereoisomer), 3.22 – 3.10 (m, 2.3H), 3.08 – 2.93 (m, 3.6H), 2.86 (dd, *J* = 14.0, 6.1 Hz, 1H, minor

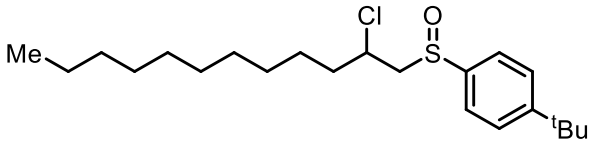
diastereoisomer), 1.36 (s, 9H, minor diastereoisomer), 1.35 (s, 11.7H, major diastereoisomer). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.5, 155.2, 137.9, 137.5, 136.83, 136.77, 129.09, 129.08, 128.78, 128.77, 126.99, 126.9, 126.42, 126.40, 125.2, 124.7, 68.6, 67.9, 41.2, 41.0, 35.1, 35.0, 31.2, 30.3. HRMS (ESI) calculated for $C_{19}H_{24}ClOS^+$ $[M+H]^+$: 335.1231; found: 335.1242.



1-(tert-butyl)-4-((2-chloro-3-phenoxypropyl)sulfinyl)benzene (25)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 6:1) to give 46.6 mg (46% yield, dr = 1.1:1) of **25** as colorless oil.

IR (neat, cm^{-1}): 3060(w), 2960(m), 2870(w), 1236(s), 1045(s), 831(m), 751(s), 691(m). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.66 – 7.51 (m, 8.7H), 7.31 – 7.26 (m, 4H), 6.99 (q, *J* = 7.2 Hz, 2H), 6.89 – 6.79 (m, 4.2H), 4.48 (dd, *J* = 10.4, 5.9 Hz, 1.1H, major diastereoisomer), 4.35 – 4.28 (m, 2.1H), 4.22 (dd, *J* = 10.5, 4.5 Hz, 1H, minor diastereoisomer), 4.05 (dd, *J* = 11.5, 9.1 Hz, 1H, minor diastereoisomer), 3.92 (ddd, *J* = 11.7, 7.3, 4.7 Hz, 2.1H), 3.66 (dd, *J* = 11.5, 7.8 Hz, 1.1H, major diastereoisomer), 3.41 (dq, *J* = 7.6, 5.4 Hz, 1.1H, major diastereoisomer), 3.33 – 3.27 (m, 1H, minor diastereoisomer), 1.36 (s, 9.9H, major diastereoisomer), 1.35 (s, 9H, minor diastereoisomer). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.72, 157.69, 155.6, 155.5, 137.6, 137.0, 129.51, 129.49, 126.49, 126.46, 124.8, 124.7, 121.6, 121.5, 114.53, 114.50, 66.0, 65.6, 62.6, 62.0, 38.99, 38.98, 35.1, 31.1. HRMS (ESI) calculated for $C_{19}H_{24}ClO_2S^+$ $[M+H]^+$: 351.1180; found: 351.1192.

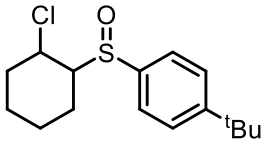


1-(Tert-butyl)-4-((2-chlorododecyl)sulfinyl)benzene (26)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 46.6 mg (46% yield, dr = 1.2:1) of **26** as colorless oil.

IR (neat, cm^{-1}): 3056(w), 2955(m), 2923(s), 2855(m), 1045(s), 832(m), 725(w). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 7.5 Hz, 6.8H), 4.07 – 3.99 (m, 1H, minor diastereoisomer), 3.94 (dd, *J* = 11.6, 6.8 Hz, 1.2H, major diastereoisomer), 3.66 (dd, *J* = 11.7, 3.9 Hz,

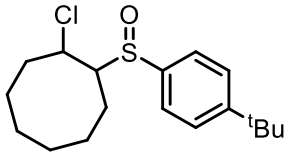
1.2H, major diastereoisomer), 3.38 (dd, *J* = 13.2, 6.2 Hz, 1H, minor diastereoisomer), 3.01 (dd, *J* = 13.1, 7.5 Hz, 1H, minor diastereoisomer), 2.84 – 2.74 (m, 1.2H, major diastereoisomer), 2.02 (ddt, *J* = 14.2, 9.6, 4.7 Hz, 1H), 1.88 – 1.68 (m, 3H), 1.67 – 1.49 (m, 2.6H), 1.49 – 1.37 (m, 4.5H), 1.34 (s, 19.8H), 1.24 (d, *J* = 11.0 Hz, 28.5H), 0.87 (t, *J* = 6.8 Hz, 6.6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.23, 155.16, 139.8, 137.9, 126.5, 126.3, 124.9, 124.0, 65.8, 65.6, 56.2, 41.3, 37.3, 35.02, 35.01, 31.9, 31.8, 31.2, 29.51, 29.50, 29.47, 29.42, 29.36, 29.3, 29.24, 29.20, 29.18, 26.4, 26.0, 25.3, 22.6, 14.1. HRMS (ESI) calculated for $C_{22}H_{38}ClOS^+$ $[M+H]^+$: 385.2326; found: 385.2340.



1-(tert-butyl)-4-((2-chlorocyclohexyl)sulfinyl)benzene (27)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 47.0 mg (52% yield, dr = 2.4:1) of **27** as colorless oil.

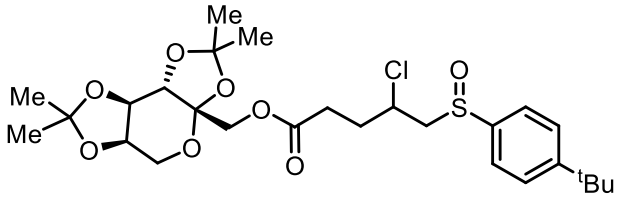
IR (neat, cm^{-1}): 3055(w), 2944(s), 2865(m), 1043(s), 833(m). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 – 7.57 (m, 2.8H), 7.53 (ddd, *J* = 8.5, 3.8, 1.9 Hz, 4.8H), 7.47 – 7.42 (m, 2H), 4.19 (td, *J* = 11.0, 4.4 Hz, 1H, minor diastereoisomer), 3.69 (td, *J* = 8.9, 3.9 Hz, 1.4H, major diastereoisomer), 3.18 (td, *J* = 9.5, 3.7 Hz, 1.4H, major diastereoisomer), 2.53 (td, *J* = 11.6, 4.2 Hz, 1H, minor diastereoisomer), 2.45 – 2.37 (m, 1H, minor diastereoisomer), 2.37 – 2.29 (m, 1.4H, major diastereoisomer), 2.29 – 2.20 (m, 1.4H, major diastereoisomer), 1.86 – 1.61 (m, 9.6H), 1.38 – 1.36 (m, 1H, minor diastereoisomer), 1.34 (s, 12.6H, major diastereoisomer), 1.34 (s, 9H, minor diastereoisomer), 1.23 – 1.11 (m, 2.8H, major diastereoisomer), 0.94 – 0.83 (m, 2H, minor diastereoisomer). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.1, 154.1, 138.0, 135.9, 126.1, 126.0, 125.5, 124.1, 70.2, 68.1, 58.2, 57.6, 37.3, 35.8, 35.0, 34.9, 31.2, 31.2, 25.2, 24.1, 24.0, 23.6, 21.3, 20.4. HRMS (ESI) calculated for $C_{16}H_{24}ClOS^+$ $[M+H]^+$: 299.1231; found: 299.1231.



1-((4-(tert-butyl)phenyl)sulfinyl)-2-chlorocyclooctane (28)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 39.5 mg (40% yield, dr = 3.6:1) of **28** as white solid.

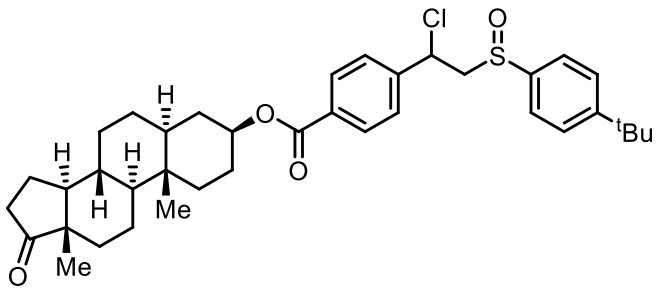
IR (neat, cm^{-1}): 3057(w), 2927(s), 2867(m), 1046(s), 833(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.60 – 7.56 (m, 2H), 7.52 – 7.49 (m, 2H), 3.64 (ddd, *J* = 11.1, 5.4, 3.0 Hz, 1H), 3.54 – 3.47 (m, 1H), 2.50 (dtd, *J* = 15.1, 5.2, 1.1 Hz, 1H), 2.12 – 2.04 (m, 1H), 2.01 – 1.89 (m, 2H), 1.88 – 1.80 (m, 1H), 1.75 – 1.62 (m, 3H), 1.57 – 1.43 (m, 3H), 1.34 (s, 9H), 0.87 – 0.77 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.1, 135.2, 125.9, 125.7, 68.7, 61.0, 35.0, 32.3, 31.2, 29.5, 26.3, 24.5, 22.0, 20.6. HRMS (ESI) calculated for $C_{18}H_{28}ClOS^+$ $[M+H]^+$: 327.1544; found: 327.1544.



((3aS,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl 5-((4-(tert-butyl)phenyl)sulfinyl)-4-chloropentanoate (29)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 112.1 mg (67% yield, dr = 1.4:1) of **29** as yellow oil.

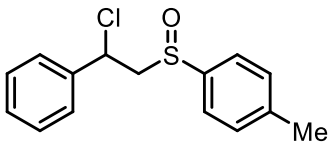
IR (neat, cm^{-1}): 3058(w), 2965(w), 2875(w), 1742(m), 1049(m), 907(s), 836(m). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.54 (s, 9.6H), 4.58 (dd, *J* = 7.7, 2.4 Hz, 2.4H), 4.44 – 4.34 (m, 2.4H), 4.29 – 4.19 (m, 4.8H), 4.01 (td, *J* = 11.2, 6.8 Hz, 2.4H), 3.94 – 3.84 (m, 4.8H), 3.74 (dd, *J* = 13.0, 4.4 Hz, 2.4H), 3.64 (dt, *J* = 11.8, 3.7 Hz, 1H), 3.40 (dd, *J* = 11.8, 6.3 Hz, 1H), 3.04 – 2.88 (m, 2.4H), 2.64 – 2.51 (m, 2.6H), 2.48 (t, *J* = 7.4 Hz, 2.2H), 2.24 – 2.10 (m, 2.4H), 2.10 – 1.95 (m, 2.4H), 1.51 (s, 7H), 1.46 (d, *J* = 3.3 Hz, 7.2H), 1.37 (t, *J* = 8.8 Hz, 7.8H), 1.33 (d, *J* = 2.5 Hz, 28.8H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.52, 171.51, 171.45, 155.33, 155.32, 155.27, 137.38, 137.35, 137.2, 137.1, 126.50, 126.46, 126.3, 124.84, 124.79, 124.68, 124.67, 123.66, 109.1, 108.71, 108.70, 108.69, 101.3, 70.7, 70.58, 70.56, 70.5, 70.0, 65.64, 65.62, 65.56, 64.92, 64.85, 64.03, 63.96, 61.21, 41.9, 41.8, 40.92, 40.89, 35.02, 35.00, 31.3, 31.2, 31.1, 30.7, 26.4, 25.9, 25.2, 24.0, 21.3, 21.0, 20.9. HRMS (ESI) calculated for $C_{27}H_{40}ClO_8S^+$ $[M+H]^+$: 559.2127; found: 559.2118.



(3S,5S,8R,9S,10S,13S,14S)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta [a]phenanthren-3-yl 4-(2-((4-(tert-butyl)phenyl)sulfinyl)-1-chloroethyl)benzoate (30)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 101.7 mg (54% yield, dr = 1.3:1) of **30** as white solid.

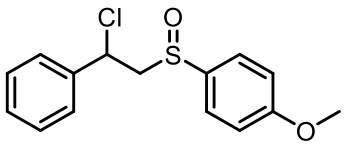
IR (neat, cm^{-1}): 3053(w), 2935(m), 2859(w), 1733(m), 1712(s), 1273(s), 1050(m), 830(w). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 8.2 Hz, 2.6H), 7.98 (d, *J* = 8.2 Hz, 2H), 7.52 (q, *J* = 8.6, 7.1 Hz, 12H), 7.43 (d, *J* = 8.2 Hz, 1.8H), 5.45 (dd, *J* = 10.6, 3.4 Hz, 1H, minor diastereoisomer), 5.22 (dd, *J* = 9.6, 5.8 Hz, 1.3H, major diastereoisomer), 4.93 (ddq, *J* = 16.6, 11.4, 4.8 Hz, 2.3H), 3.66 (dd, *J* = 12.9, 5.7 Hz, 1.3H, major diastereoisomer), 3.40 – 3.22 (m, 3.3H), 2.43 (dd, *J* = 19.2, 8.7 Hz, 2.3H), 2.24 (tdd, *J* = 20.8, 14.2, 7.3 Hz, 1H), 2.06 (dt, *J* = 18.6, 9.0 Hz, 2.3H), 2.00 – 1.86 (m, 4.6H), 1.84 – 1.64 (m, 14H), 1.52 (qd, *J* = 18.6, 18.0, 6.8 Hz, 9H), 1.37 – 1.26 (m, 29.2H), 1.18 – 0.92 (m, 6H), 0.94 – 0.85 (m, 14.4H), 0.80 – 0.69 (m, 2.3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 221.2, 165.3, 165.2, 155.4, 155.1, 143.6, 143.0, 139.7, 139.6, 131.6, 131.3, 130.2, 130.1, 127.3, 127.0, 126.6, 126.5, 123.9, 123.7, 74.4, 74.3, 67.1, 66.7, 55.5, 55.4, 54.22, 54.21, 51.3, 47.7, 44.62, 44.60, 36.7, 36.6, 35.8, 35.63, 35.61, 35.01, 34.95, 33.93, 33.91, 31.44, 31.1, 30.7, 28.2, 27.42, 27.4, 21.7, 20.4, 13.8, 12.22, 12.21. HRMS (ESI) calculated for $C_{38}H_{50}ClO_4S^+$ $[M+H]^+$: 637.3113; found: 637.3142.



1-((2-Chloro-2-phenylethyl)sulfinyl)-4-methylbenzene (31)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 7:1) to give 53.3 mg (64% yield, dr = 1.5:1) of **31** as a colorless oil.

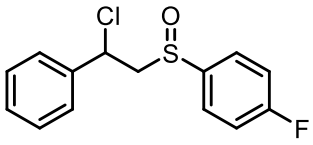
IR (neat, cm^{-1}): 3035(w), 2922(w), 2864(w), 1453(m), 1399(w), 1045(s). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.54 (dd, *J* = 12.4, 8.2 Hz, 5H), 7.48 – 7.37 (m, 9.5H), 7.37 – 7.28 (m, 8H), 5.41 (dd, *J* = 10.9, 3.4 Hz, 1H, minor diastereoisomer), 5.13 (dd, *J* = 9.1, 6.4 Hz, 1.5H, major diastereoisomer), 3.67 (dd, *J* = 12.9, 6.3 Hz, 1.5H, major diastereoisomer), 3.36 – 3.23 (m, 3.5H), 2.43 (s, 4.5H, major diastereoisomer), 2.40 (s, 3H, minor diastereoisomer). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.2, 142.0, 140.2, 140.00, 139.2, 138.6, 130.2, 130.1, 129.3, 129.1, 128.98, 128.95, 127.3, 127.00, 124.2, 124.00, 68.0, 67.2, 56.3, 56.2, 21.5, 21.4. HRMS (ESI) calculated for $C_{15}H_{16}ClOS^{+}$ $[M+H]^{+}$: 279.0605; found: 279.0605.



1-((2-Chloro-2-phenylethyl)sulfinyl)-4-methoxybenzene (32)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 4:1) to give 50.6 mg (57% yield, dr = 1.5:1) of **32** as yellow oil.

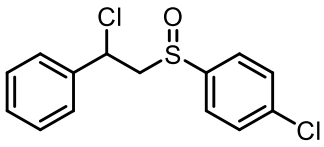
IR (neat, cm^{-1}): 3062(w), 2924(w), 2849(w), 1252(s), 1026(s), 831(m), 734(w), 699(m). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59 (tt, *J* = 7.0, 2.3 Hz, 5H), 7.46 – 7.31 (m, 12.5H), 7.05 – 7.00 (m, 5H), 5.39 (dd, *J* = 10.1, 4.3 Hz, 1H, minor diastereoisomer), 5.08 (dd, *J* = 8.7, 6.6 Hz, 1.5H, major diastereoisomer), 3.86 (s, 4.5H, major diastereoisomer), 3.84 (s, 3H, minor diastereoisomer), 3.69 (dd, *J* = 12.9, 6.6 Hz, 1.5H, major diastereoisomer), 3.35 – 3.22 (m, 3.5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.4, 162.3, 139.2, 138.6, 134.2, 133.9, 129.2, 129.01, 128.97, 128.9, 127.2, 127.0, 126.2, 126.0, 114.99, 114.97, 68.0, 67.1, 56.29, 56.25, 55.54, 55.53. HRMS (ESI) calculated for $C_{15}H_{16}ClO_2S^{+}$ $[M+H]^{+}$: 295.0554; found: 295.0561.



1-((2-Chloro-2-phenylethyl)sulfinyl)-4-fluorobenzene (33)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 7:1) to give 63.5 mg (75% yield, dr = 1.5:1) of **33** as a colorless oil.

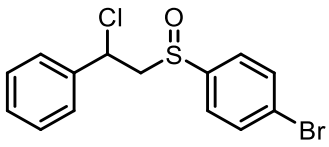
IR (neat, cm^{-1}): 3063(w), 2923(w), 2855(w), 1225(s), 1044(s), 833(s), 731(m), 698(s). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.65 (dddt, *J* = 11.3, 7.7, 4.5, 2.3 Hz, 5H), 7.49 – 7.29 (m, 12H), 7.28 – 7.19 (m, 5.5H), 5.42 (dd, *J* = 11.1, 3.2 Hz, 1H, minor diastereoisomer), 5.15 (dd, *J* = 9.0, 6.3 Hz, 1.5H, major diastereoisomer), 3.67 (dd, *J* = 12.9, 6.3 Hz, 1.5H, major diastereoisomer), 3.38 – 3.22 (m, 3.5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.6 (d, *J* = 252.5 Hz), 164.5 (d, *J* = 252.2 Hz), 139.0, 138.8 (d, *J* = 3.1 Hz), 138.6 (d, *J* = 3.1 Hz), 138.4, 129.4, 129.10, 129.07, 129.0, 127.2, 126.9, 126.5 (d, *J* = 9.0 Hz), 126.2 (d, *J* = 8.9 Hz), 116.9 (d, *J* = 22.6 Hz), 116.8 (d, *J* = 22.6 Hz), 68.0, 67.2, 56.1, 56.0. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -107.2 (tt, *J* = 8.7, 4.5 Hz), -107.7 (tt, *J* = 8.9, 4.7 Hz). HRMS (ESI) calculated for $C_{14}H_{13}ClFOS^{+}$ $[M+H]^{+}$: 283.0354; found: 283.0359.



1-Chloro-4-((2-chloro-2-phenylethyl)sulfinyl)benzene (34)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 7:1) to give 55.6 mg (62% yield, dr = 1.5:1) of **34** as a white solid.

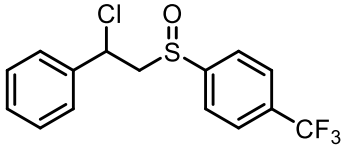
IR (neat, cm^{-1}): 3060(w), 2923(w), 2853(w), 1045(s), 822(m), 738(m), 697(m). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.62 – 7.56 (m, 5H), 7.53 – 7.47 (m, 5H), 7.46 (dd, *J* = 8.2, 1.6 Hz, 2.5H), 7.44 – 7.41 (m, 2.5H), 7.41 – 7.36 (m, 4.3H), 7.37 – 7.29 (m, 3.2H), 5.42 (dd, *J* = 11.1, 3.2 Hz, 1H, minor diastereoisomer), 5.16 (dd, *J* = 9.1, 6.2 Hz, 1.5H, major diastereoisomer), 3.65 (dd, *J* = 12.9, 6.2 Hz, 1.5H, major diastereoisomer) , 3.42 – 3.20 (m, 3.5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.9, 141.6, 138.9, 138.3, 137.9, 137.6, 129.8, 129.7, 129.4, 129.13, 129.10, 129.0, 127.3, 126.9, 125.5, 125.3, 67.9, 67.1, 56.0, 55.9. HRMS (ESI) calculated for $C_{14}H_{13}Cl_2OS^{+}$ $[M+H]^{+}$: 299.0059; found: 299.0059.



1-Bromo-4-((2-chloro-2-phenylethyl)sulfinyl)benzene (35)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 7:1) to give 84.8 mg (82% yield, dr = 2.3:1) of **35** as colorless oil.

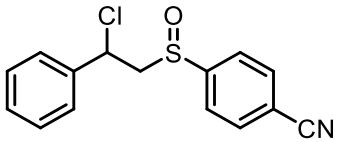
IR (neat, cm^{-1}): 3060(w), 2923(w), 2854(w), 1046(s), 818(m), 724(m), 698(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.66 (ddt, *J* = 12.3, 8.9, 2.3 Hz, 6.7H), 7.51 (ddt, *J* = 10.9, 9.0, 2.2 Hz, 7H), 7.48 – 7.32 (m, 16H), 5.42 (dd, *J* = 11.1, 3.2 Hz, 1H, minor diastereoisomer), 5.16 (dd, *J* = 9.2, 6.2 Hz, 2.3H, major diastereoisomer), 3.65 (dd, *J* = 12.9, 6.2 Hz, 2.3H, major diastereoisomer), 3.38 – 3.21 (m, 4.3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.6, 142.4, 138.9, 138.4, 132.71, 132.65, 129.4, 129.12, 129.09, 129.0, 127.3, 126.9, 126.1, 125.8, 125.6, 125.4, 67.9, 67.1, 56.0, 55.9. HRMS (ESI) calculated for $C_{14}H_{13}BrClOS^+$ $[M+H]^+$: 342.9554; found: 342.9562.



1-((2-Chloro-2-phenylethyl)sulfinyl)-4-(trifluoromethyl)benzene (36)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 7:1) to give 73.7 mg (74% yield, dr = 1.5:1) of **36** as white solid.

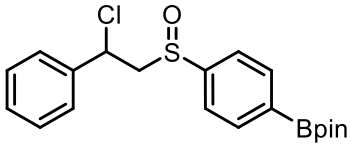
IR (neat, cm^{-1}): 3061(w), 2924(w), 2856(w), 1127(s), 1054(s), 837(m), 767(w), 698(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.82 – 7.73 (m, 10H), 7.50 – 7.46 (m, 3.1H), 7.46 – 7.36 (m, 6.7H), 7.36 – 7.31 (m, 2.7H), 5.45 (dd, *J* = 11.1, 3.2 Hz, 1H, minor diastereoisomer), 5.23 (dd, *J* = 9.4, 6.0 Hz, 1.5H, major diastereoisomer), 3.66 (dd, *J* = 12.9, 6.0 Hz, 1.5H, major diastereoisomer), 3.44 – 3.33 (m, 2.5H), 3.26 (dd, *J* = 13.4, 3.2 Hz, 1H, minor diastereoisomer). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 147.9, 147.7, 138.7, 138.2, 133.5 (q, *J* = 33.0 Hz), 133.3 (q, *J* = 32.8 Hz), 129.5, 129.16, 129.15, 129.0, 127.3, 126.9, 126.4 (dq, *J* = 7.5, 3.7 Hz), 124.5, 124.3, 123.3(q, *J* = 272.8 Hz), 67.6, 67.0, 55.9, 55.7. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -62.76, -62.79. HRMS (ESI) calculated for $C_{15}H_{13}ClF_3OS^+$ $[M+H]^+$: 333.0322; found: 333.0329.



4-((2-Chloro-2-phenylethyl)sulfinyl)benzonitrile (37)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 4:1) to give 37.0 mg (43% yield, dr = 1.5:1) of **37** as colorless oil.

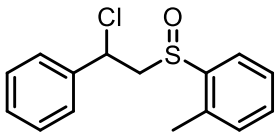
IR (neat, cm^{-1}): 3061(w), 2923(w), 2855(w), 2230(m), 1048(s), 833(m), 732(m), 700(s). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.87 – 7.70 (m, 10.5H), 7.50 – 7.29 (m, 12H), 5.44 (dd, *J* = 11.1, 3.1 Hz, 1H, minor diastereoisomer), 5.24 (dd, *J* = 9.2, 6.0 Hz, 1.5H, major diastereoisomer), 3.64 (dd, *J* = 13.0, 6.0 Hz, 1.5H, major diastereoisomer), 3.44 – 3.33 (m, 2.5H), 3.24 (dd, *J* = 13.3, 3.1 Hz, 1H, minor diastereoisomer). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 149.2, 148.9, 138.6, 138.1, 133.01, 132.97, 129.5, 129.21, 129.20, 129.0, 127.2, 126.9, 124.7, 124.6, 117.5, 115.2, 115.0, 67.5, 66.7, 55.8, 55.5. HRMS (ESI) calculated for $C_{15}H_{13}ClNOS^+$ $[M+H]^+$: 290.0401; found: 290.0409.



2-(4-((2-Chloro-2-phenylethyl)sulfinyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 4:1) to give 50.8 mg (43% yield, dr = 1.6:1) of **38** as colorless oil.

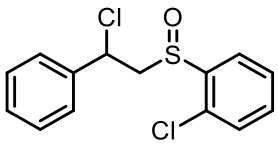
IR (neat, cm^{-1}): 3037(w), 2927(w), 2864(w), 1358(s), 1073(m), 855(m), 729(m), 653(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.98 – 7.90 (m, 6H), 7.67 – 7.58 (m, 5.4H), 7.48 – 7.32 (m, 12H), 5.42 (dd, *J* = 11.2, 3.1 Hz, 1H, minor diastereoisomer), 5.15 (dd, *J* = 9.2, 6.2 Hz, 1.6H, major diastereoisomer), 3.65 (dd, *J* = 12.9, 6.2 Hz, 1.6H, major diastereoisomer), 3.37 – 3.28 (m, 2.6H), 3.24 (dd, *J* = 13.4, 3.2 Hz, 1H, minor diastereoisomer), 1.35 (s, 19.2H, major diastereoisomer), 1.34 (s, 12H, minor diastereoisomer). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 146.4, 146.1, 139.0, 138.5, 135.62, 135.61, 129.3, 129.1, 129.0, 128.9, 127.3, 126.9, 126.3, 125.6, 123.1, 122.9, 84.3, 84.2, 67.8, 67.0, 56.1, 56.1, 24.83, 24.81. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.1. HRMS (ESI) calculated for $C_{20}H_{25}BClO_3S^+$ $[M+H]^+$: 391.1300; found: 391.1309.



1-((2-Chloro-2-phenylethyl)sulfinyl)-2-methylbenzene (39)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 7:1) to give 60.0 mg (72% yield, dr = 1.6:1) of **39** as white solid.

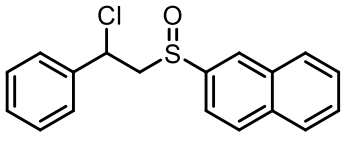
IR (neat, cm^{-1}): 3058(w), 2923(w), 2856(w), 1065(s), 759(m), 731(m), 699(m). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96 – 7.87 (m, 2.7H), 7.54 – 7.48 (m, 3.4H), 7.41 (dt, *J* = 19.4, 7.0 Hz, 11.4H), 7.37 – 7.28 (m, 3.4H), 7.20 (dd, *J* = 13.9, 7.2 Hz, 2.6H), 5.50 (dd, *J* = 11.6, 2.4 Hz, 1H, minor diastereoisomer), 5.31 (dd, *J* = 10.3, 5.2 Hz, 1.6H, major diastereoisomer), 3.49 (dd, *J* = 13.0, 5.2 Hz, 1.6H, major diastereoisomer), 3.39 (ddd, *J* = 13.5, 10.9, 9.2 Hz, 2.6H), 3.10 (dd, *J* = 13.5, 2.5 Hz, 1H, minor diastereoisomer), 2.44 (s, 3H, minor diastereoisomer), 2.18 (s, 4.8H, major diastereoisomer). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.61, 141.59, 139.2, 138.6, 134.4, 134.3, 131.1, 131.0, 130.80, 130.78, 129.3, 129.1, 129.0, 128.9, 127.5, 127.4, 127.3, 126.9, 123.6, 123.4, 66.5, 65.8, 56.5, 56.3, 18.1, 17.9. HRMS (ESI) calculated for $C_{15}H_{16}ClOS^{+}$ $[M+H]^{+}$: 279.0605; found: 279.0611.



1-Chloro-2-((2-chloro-2-phenylethyl)sulfinyl)benzene (40)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 7:1) to give 56.8 mg (63% yield, dr = 1.5:1) of **40** as white solid.

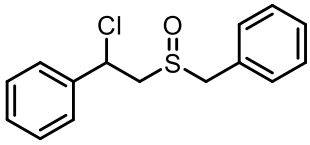
IR (neat, cm^{-1}): 3062(w), 2924(w), 2854(w), 1062(s), 760(m), 730(s), 698(m). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 (dd, *J* = 7.8, 1.5 Hz, 1.5H), 7.87 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.58 – 7.49 (m, 5H), 7.47 – 7.36 (m, 12H), 7.36 – 7.28 (m, 3H), 5.49 (dd, *J* = 11.3, 3.0 Hz, 1H, minor diastereoisomer), 5.42 (dd, *J* = 10.3, 5.2 Hz, 1.5H, major diastereoisomer), 3.82 (ddd, *J* = 13.3, 10.8, 8.2 Hz, 2.5H), 3.51 – 3.40 (m, 1.5H, major diastereoisomer), 3.10 (dd, *J* = 13.3, 3.0 Hz, 1H, minor diastereoisomer). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.3, 139.1, 138.3, 132.3, 132.2, 129.9, 129.83, 129.81, 129.7, 129.4, 129.03, 128.99, 128.9, 128.2, 128.1, 127.5, 127.0, 125.9, 125.7, 64.6, 63.9, 56.1, 55.8. HRMS (ESI) calculated for $C_{14}H_{13}Cl_2OS^{+}$ $[M+H]^{+}$: 299.0059; found: 299.0066.



2-((2-Chloro-2-phenylethyl)sulfinyl)naphthalene (41)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 7:1) to give 49.8 mg (53% yield, dr = 1.5:1) of **41** as a yellow solid.

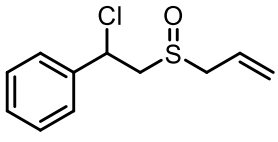
IR (neat, cm^{-1}): 3055(w), 2923(w), 2854(w), 1044(s), 746(s), 698(m). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 18.4 Hz, 2.5H), 7.99 (dd, *J* = 12.7, 8.6 Hz, 2.5H), 7.96 – 7.86 (m, 5H), 7.68 – 7.54 (m, 7.5H), 7.54 – 7.45 (m, 3H), 7.45 – 7.37 (m, 6.5H), 7.36 – 7.28 (m, 3H), 5.48 (dd, *J* = 11.1, 3.1 Hz, 1H, minor diastereoisomer), 5.21 (dd, *J* = 9.1, 6.2 Hz, 1.5H, major diastereoisomer), 3.75 (dd, *J* = 12.9, 6.2 Hz, 1.5H, major diastereoisomer), 3.61 – 3.10 (m, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 140.4, 140.2, 139.1, 138.5, 134.7, 134.6, 132.9, 132.8, 129.8, 129.7, 129.3, 129.1, 129.0, 128.9, 128.6, 128.4, 128.10, 128.06, 127.9, 127.5, 127.4, 127.3, 127.0, 125.0, 124.6, 119.6, 119.5, 67.7, 66.9, 56.24, 56.20. HRMS (ESI) calculated for $C_{18}H_{16}ClOS^{+}$ $[M+H]^{+}$: 315.0605; found: 315.0610.



(2-(Benzylsulfinyl)-1-chloroethyl)benzene (42)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 5:1) to give 49.5 mg (60% yield, dr = 1.4:1) of **42** as a white solid.

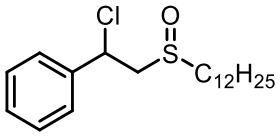
IR (neat, cm^{-1}): 3032(w), 2922(w), 2854(w), 1037(s), 766(m), 697(s). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43 – 7.32 (m, 19H), 7.32 – 7.20 (m, 5H), 5.35 (dd, *J* = 11.3, 3.0 Hz, 1H, minor diastereoisomer), 5.28 (dd, *J* = 10.1, 5.4 Hz, 1.4H, major diastereoisomer), 4.13 – 3.95 (m, 4.8H), 3.39 (dd, J = 12.8, 5.4 Hz, 1.4H, major diastereoisomer), 3.33 – 3.18 (m, 2.4H), 3.07 (dd, J = 13.2, 3.0 Hz, 1H, minor diastereoisomer). ^{13}C NMR (126 MHz, Chloroform-d) δ 139.4, 138.5, 130.02, 130.00, 129.21, 129.16, 129.09, 129.05, 129.02, 128.99, 128.96, 128.61, 128.59, 127.2, 126.9, 61.11, 60.3, 58.72, 58.71, 56.0, 55.9. HRMS (ESI) calculated for $C_{15}H_{16}ClOS^{+}$ $[M+H]^{+}$: 279.0605; found: 279.0612.



(2-(Allylsulfinyl)-1-chloroethyl)benzene (43)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 39.6 mg (58% yield, dr = 1.4:1) of **43** as white solid.

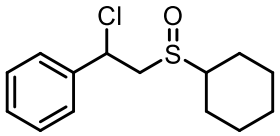
IR (neat, cm^{-1}): 3063(w), 3032(w), 2922(w), 2854(w), 1635(w), 1034(s), 931(m), 767(m), 699(s). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.48 – 7.34 (m, 5H), 5.96 – 5.81 (m, 1H), 5.46 (d, *J* = 10.2 Hz, 1H), 5.43 – 5.32 (m, 2H), 3.53 (ddt, *J* = 27.8, 14.9, 8.0 Hz, 2H), 3.42 (dd, *J* = 13.0, 7.6 Hz, 0.6H), 3.32 (dt, *J* = 12.8, 10.7 Hz, 1H), 3.17 (dd, *J* = 13.2, 2.9 Hz, 0.4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.5, 138.6, 129.30, 129.1, 129.0, 127.3, 126.9, 125.2, 125.1, 124.21, 124.16, 61.1, 60.3, 56.3, 56.2, 56.00, 55.96. HRMS (ESI) calculated for $C_{11}H_{14}ClOS^+$ $[M+H]^+$: 229.0448; found: 229.0454.



(1-Chloro-2-(dodecylsulfinyl)ethyl)benzene (44)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 5:1) to give 41.5 mg (39% yield, dr = 2:1) of **44** as white solid.

IR (neat, cm^{-1}): 3053(w), 2923(s), 2853(m), 1033(m), 733(s), 701(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.49 – 7.45 (m, 2H), 7.39 (dddd, *J* = 12.6, 10.0, 5.4, 1.4 Hz, 3H), 5.36 (dd, *J* = 10.4, 5.1 Hz, 1H), 3.50 (dd, *J* = 12.7, 5.1 Hz, 1H), 3.29 (dd, *J* = 12.6, 10.4 Hz, 1H), 2.76 (ddd, *J* = 13.0, 9.2, 5.7 Hz, 1H), 2.62 (ddd, *J* = 12.9, 9.3, 6.9 Hz, 1H), 1.71 (q, *J* = 7.6, 7.1 Hz, 2H), 1.37 (ddd, *J* = 18.5, 9.8, 5.8 Hz, 2H), 1.34 – 1.21 (m, 16H), 0.87 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 138.7, 129.3, 129.0, 127.3, 61.9, 55.9, 53.0, 31.9, 29.56, 29.55, 29.46, 29.29, 29.27, 29.1, 28.7, 22.7, 22.4, 14.1. HRMS (ESI) calculated for $C_{20}H_{34}ClOS^+$ $[M+H]^+$: 357.2013; found: 3357.2022.



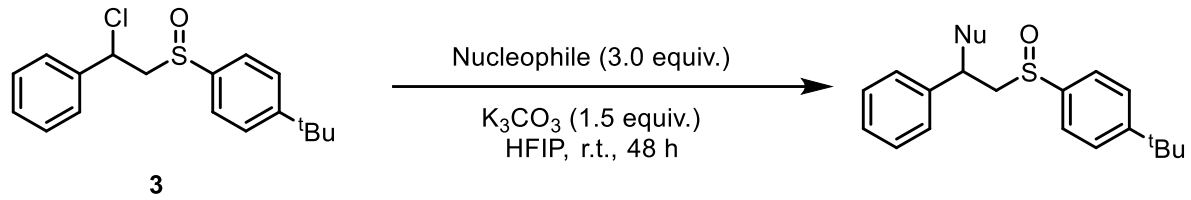
(1-Chloro-2-(cyclohexylsulfinyl)ethyl)benzene (45)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 39.7 mg (49% yield, dr = 1:1) of **45** as white solid.

IR (neat, cm^{-1}): 3033(w), 2929(s), 2855(m), 1038(s), 767(m), 698(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 7.1 Hz, 2H), 7.41 – 7.32 (m, 3H), 5.41 (dd, *J* = 11.4, 2.5 Hz, 1H), 3.28 (dd, *J* = 13.1, 11.5 Hz, 1H), 3.12 (dd, *J* = 13.1, 2.6 Hz, 1H), 2.60 (tt, *J* = 11.6, 3.4 Hz, 1H), 2.13 (d, *J* = 12.7 Hz, 1H), 1.97 – 1.81 (m, 3H), 1.76 – 1.64 (m, 2H), 1.49 (dqd, *J* = 25.1, 13.4, 12.7, 3.9 Hz, 2H),

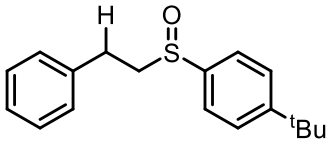
1.31 – 1.23 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.8, 128.98, 128.96, 126.9, 59.8, 59.5, 56.3, 26.2, 25.5, 25.3, 25.11. HRMS (ESI) calculated for $C_{14}H_{20}ClOS^+$ $[M+H]^+$: 271.0918; found: 271.0924.

5 Derivatizations of Compound 3



3

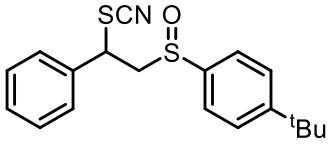
In an oven-dried Schleck tube (10 mL) equipped with a stirring bar, compound **3** (0.1 mmol, 32.1 mg), K_2CO_3 (1.5 equiv.) were added. Under the protection of N_2, Nucleophile (3.0 equiv.), HFIP (0.1 M) were injected respectively into the tube via syringes. The reaction mixture was stirred at room temperature for 48 h. After completion, the reaction mixture was concentrated in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product.



1-(Tert-butyl)-4-(phenethylsulfinyl)benzene (46)

Reaction with Et_3SiH (48 μL). The desired pure product was purified using silica gel chromatography (PE:EA = 2:1) to give 15.2 mg (53% yield) of **46** as white solid.

IR (neat, cm^{-1}): 3061(w), 3027(w), 2960(s), 2925(m), 2868(m), 1047(s), 833(m), 753(m), 701(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.58 – 7.51 (m, 4H), 7.30 – 7.25 (m, 2H), 7.23 – 7.16 (m, 3H), 3.12 – 3.00 (m, 3H), 2.99 – 2.89 (m, 1H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.6, 140.3, 138.8, 128.6, 128.5, 126.6, 126.2, 123.8, 58.3, 34.9, 31.2, 28.3. HRMS (ESI) calculated for $C_{18}H_{23}OS^+$ $[M+H]^+$: 287.1464; found: 287.1452.

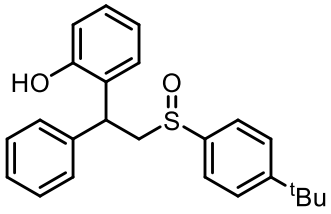


1-(Tert-butyl)-4-((2-phenyl-2-thiocyanatoethyl)sulfinyl)benzene (48)

Reaction with KSCN (29 mg). The desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 19.9 mg (58% yield, dr = 1.8:1) of **48** as white solid.

IR (neat, cm^{-1}): 3061(w), 2960(s), 2925(s), 2868(m), 2152(m), 1048(s), 831(m), 717(m), 697(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.59 – 7.51 (m, 11H), 7.51 – 7.44 (m, 9H), 7.37 – 7.29 (m, 5.2H),

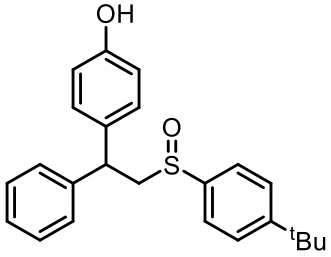
4.90 (dd, *J* = 11.3, 4.6 Hz, 1.8H, major diastereoisomer), 4.75 (dd, *J* = 9.9, 5.3 Hz, 1H, minor diastereoisomer), 3.59 – 3.52 (m, 2.8H), 3.51 – 3.44 (m, 2.8H), 1.35 (s, 16.2H, major diastereoisomer), 1.33 (s, 9H, minor diastereoisomer). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.6, 155.4, 139.7, 139.0, 137.0, 136.9, 135.3, 129.9, 129.6, 127.8, 126.7, 126.6, 123.8, 123.7, 110.3, 110.2, 63.3, 60.4, 47.0, 46.4, 35.1, 35.0, 31.2, 31.1. HRMS (ESI) calculated for $C_{19}H_{22}NOS_2^+$ $[M+H]^+$: 344.1137; found: 344.1130.



2-(2-((4-(Tert-butyl)phenyl)sulfinyl)-1-phenylethyl)phenol (49)

Reaction with PhOH (28 mg). The desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 14.0 mg (37% yield, dr = 1.2:1) of **49** as white solid.

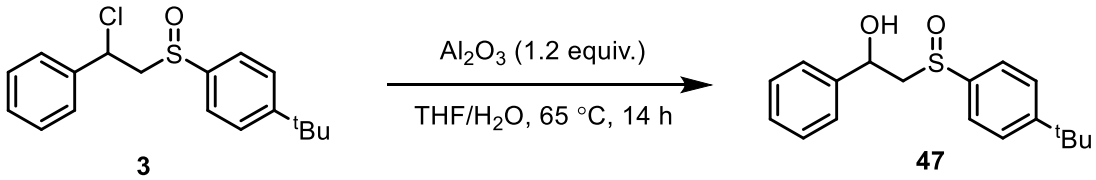
IR (neat, cm^{-1}): 3162(br), 3062(w), 2959(s), 2925(s), 2869(m), 1022(s), 829(m), 752(s), 698(m). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.54 (dd, *J* = 8.4, 1.4 Hz, 4.2H), 7.48 (t, *J* = 8.1 Hz, 4.4H), 7.41 – 7.34 (m, 4.8H), 7.30 – 7.25 (m, 1.2H), 7.25 – 7.21 (m, 2H), 7.20 – 7.12 (m, 4.2H), 7.03 (td, *J* = 7.8, 1.4 Hz, 2.2H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.92 (dd, *J* = 7.6, 1.2 Hz, 1.2H), 6.87 (d, *J* = 7.9 Hz, 2.2H), 6.72 (t, *J* = 7.5 Hz, 1.2H), 5.06 (dd, *J* = 10.0, 5.0 Hz, 1.2H, major diastereoisomer), 4.96 (t, *J* = 7.6 Hz, 1H, minor diastereoisomer), 3.67 (dd, *J* = 13.1, 5.0 Hz, 1.2H, major diastereoisomer), 3.57 (d, *J* = 7.7 Hz, 2H, minor diastereoisomer), 3.47 (dd, *J* = 13.1, 10.1 Hz, 1.2H, major diastereoisomer), 1.32 (s, 9H, minor diastereoisomer), 1.32 (s, 10.8H, major diastereoisomer). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.1, 154.9, 154.4, 154.0, 141.9, 140.8, 140.1, 139.1, 129.0, 128.8, 128.7, 128.5, 128.4, 128.06, 128.05, 128.0, 127.1, 126.7, 126.40, 126.37, 124.1, 124.0, 120.8, 120.0, 118.0, 116.7, 62.8, 62.0, 38.9, 37.8, 34.99, 34.97, 31.2. HRMS (ESI) calculated for $C_{24}H_{27}O_2S^+$ $[M+H]^+$: 379.1726; found: 379.1714.



4-(2-((4-(Tert-butyl)phenyl)sulfinyl)-1-phenylethyl)phenol (50)

Reaction with PhOH (28 mg). The desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 19.0 mg (50% yield, dr = 1.8:1) of **50** as white solid.

IR (neat, cm^{-1}): 3204(br), 3026(w), 2960(s), 2926(s), 2869(m), 1021(s), 832(m), 726(w), 699(m). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.56 – 7.49 (m, 11.4H), 7.32 (t, *J* = 7.5 Hz, 3.5H), 7.28 (d, *J* = 7.1 Hz, 3.7H), 7.24 (t, *J* = 6.4 Hz, 3.8H), 7.21 – 7.14 (m, 5H), 7.03 (d, *J* = 8.5 Hz, 3.5H), 6.81 (d, *J* = 8.5 Hz, 2H), 6.74 (d, *J* = 8.5 Hz, 3.5H), 4.54 (dd, *J* = 11.3, 4.7 Hz, 1H, minor diastereoisomer), 4.46 (dd, *J* = 10.3, 5.5 Hz, 1.8H, major diastereoisomer), 3.48 (ddd, *J* = 22.6, 12.9, 5.2 Hz, 2.8H), 3.37 (dd, *J* = 12.7, 10.6 Hz, 2.8H), 1.33 (s, 25.2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.4, 155.0, 154.97, 154.95, 142.8, 141.9, 140.5, 140.4, 134.0, 132.6, 129.4, 128.9, 128.8, 128.7, 128.1, 127.6, 127.1, 126.7, 126.4, 124.1, 124.0, 115.9, 115.7, 64.73, 64.65, 44.7, 44.6, 35.0, 31.2. HRMS (ESI) calculated for $C_{24}H_{27}O_2S^+$ $[M+H]^+$: 379.1726; found: 379.1716.



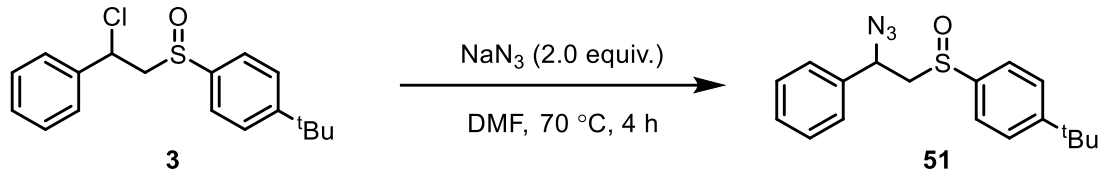
In an oven-dried Schleck tube (10 mL) equipped with a stirring bar, compound **3** (0.1 mmol, 32.1 mg), Al_2O_3 (1.2 equiv., 15.5 mg) were added. Under the protection of N_2, THF (1.5 mL) and H_2O (0.75 mL) were injected respectively into the tube via syringes. The reaction mixture was stirred at 60 ˚C for 14 h. After completition, the reaction mixture was concentrated in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product **47**.

2-((4-(Tert-butyl)phenyl)sulfinyl)-1-phenylethan-1-ol (47)

The desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 22.4 mg (74% yield, dr = 4.71) of **47** as white solid.

IR (neat, cm^{-1}): 3324(br), 3061(w), 2957(s), 2924(s), 2854(m), 1027(s), 824(m), 766(w), 709(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.62 – 7.50 (m, 22.7H), 7.39 (d, *J* = 7.3 Hz, 9H), 7.33 (dd, *J* = 14.4, 6.1 Hz, 13.5H), 7.30 – 7.24 (m, 6.1H), 5.40 (d, *J* = 9.8 Hz, 4.7H, major diastereoisomer), 5.27 (d, *J* = 9.3 Hz, 1H, minor diastereoisomer), 4.40 (s, 4H), 3.22 (dd, *J* = 13.1, 10.0 Hz, 6H), 2.94 (dd, *J* = 13.3, 2.4 Hz, 4.7H), 2.87 (d, *J* = 13.6 Hz, 0.7H), 1.34 (s, 9H, minor diastereoisomer), 1.33 (s, 42.3H, major

diastereoisomer). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.26, 142.01, 140.21, 128.62, 128.08, 126.52, 125.72, 123.73, 71.36, 64.04, 35.02, 31.17. HRMS (ESI) calculated for $C_{18}H_{23}O_2S^+$ $[M+H]^+$: 303.1413; found: 303.1403.

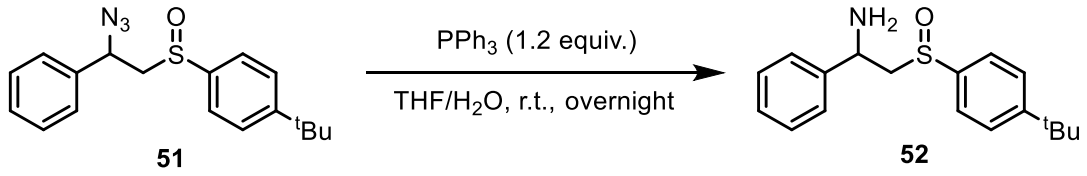


In an oven-dried Schleck tube (10 mL) equipped with a stirring bar, compound **3** (0.1 mmol, 32.1 mg), NaN_3 (2.0 equiv., 13.0 mg) were added. Under the protection of N_2, DMF (0.4 mL) were injected into the tube via syringes. The reaction mixture was stirred at 70 ˚C for 4 h. After completition, The reaction mixture was poured into a water. The aqueous layer was separated and extracted with dichloromethane (3×5 mL), and the combined organic layers were washed with brine and dried over sodium sulfate. the result reaction mixture was concentrated in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product **51**.

1-((2-Azido-2-phenylethyl)sulfinyl)-4-(tert-butyl)benzene (51)

The desired pure product was purified using silica gel chromatography (PE:EA = 7:1) to give 32.4 mg (99% yield, dr = 4:1) of **51** as yellow oil.

IR (neat, cm^{-1}): 3061(w), 2960(m), 2925(m), 2868(w), 2108(s), 1044(s), 832(m), 745(m), 703(s). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.60 – 7.51 (m, 22H), 7.45 – 7.32 (m, 23H), 5.15 (dd, *J* = 7.9, 6.6 Hz, 1H, minor diastereoisomer), 4.85 (t, *J* = 7.3 Hz, 4H, major diastereoisomer), 3.36 (dd, *J* = 13.1, 7.2 Hz, 4H, major diastereoisomer), 3.02 (dd, *J* = 13.1, 7.4 Hz, 4H, major diastereoisomer), 2.98 – 2.93 (m, 2H, minor diastereoisomer), 1.34 (s, 36H, major diastereoisomer), 1.32 (s, 9H, minor diastereoisomer). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.2, 155.0, 140.3, 139.8, 137.4, 137.1, 129.2, 129.14, 129.13, 129.0, 127.1, 126.8, 126.51, 126.47, 124.0, 123.7, 64.5, 63.0, 60.4, 60.0, 35.02, 34.97, 31.1. HRMS (ESI) calculated for $C_{18}H_{22}N_3OS^+$ $[M+H]^+$: 328.1478; found: 328.1468.

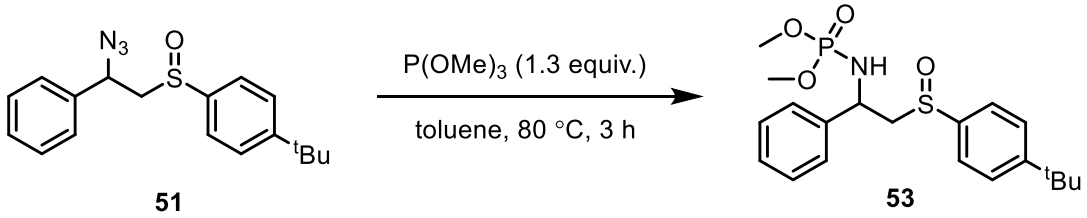


In an oven-dried Schleck tube (10 mL) equipped with a stirring bar, compound **51** (0.1 mmol, 32.7 mg), PPh_3 (1.2 equiv., 31.5 mg) were added. Under the protection of N_2, THF (1.0 mL) and water (0.25 mL) were injected respectively into the tube via syringes. The reaction mixture was stirred at room temperature for overnight. After completition, the reaction mixture was concentrated in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product **52**.

2-((4-(Tert-butyl)phenyl)sulfinyl)-1-phenylethan-1-amine (52)

The desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 40.4 mg (67% yield, dr = 1.5:1) of **52** as yellow oil.

IR (neat, cm^{-1}): 3365(br), 3292(br), 3059(w), 2961(s), 2926(m), 2868(m), 1035(s), 832(m), 766(m), 704(s). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.61 – 7.50 (m, 4H), 7.42 – 7.28 (m, 5H), 4.58 (dt, *J* = 9.8, 4.6 Hz, 1H), 3.21 (dd, *J* = 13.1, 8.5 Hz, 0.6H, major diastereoisomer), 3.05 – 2.86 (m, 1.4H), 1.33 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 154.9, 154.7, 143.7, 143.6, 140.9, 140.5, 128.8, 128.8, 127.9, 127.7, 126.42, 126.40, 126.38, 126.2, 123.83, 123.75, 66.9, 66.3, 53.1, 50.8, 34.99, 34.97, 31.2. HRMS (ESI) calculated for $C_{18}H_{24}NOS^+$ $[M+H]^+$: 302.1573; found: 302.1565.

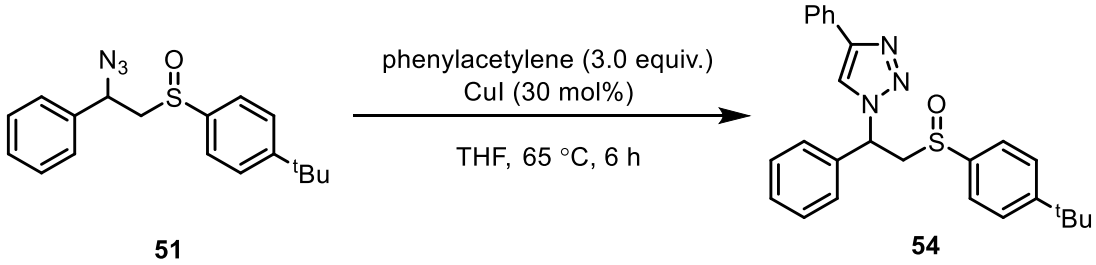


In an oven-dried Schleck tube (10 mL) equipped with a stirring bar, compound **51** (0.1 mmol, 32.7 mg) were added. Under the protection of N_2, $P(OMe)_3$ (1.3 equiv., 16 μL) and toluene (0.6 mL) were injected respectively into the tube via syringes. The reaction mixture was stirred at 80 ˚C for 3 h. After completition, the reaction mixture was concentrated in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product **53**.

Dimethyl (2-((4-(tert-butyl)phenyl)sulfinyl)-1-phenylethyl)phosphoramidate (53)

The desired pure product was purified using silica gel chromatography (PE:EA = 2:1) to give 40.1 mg (98% yield, dr = 1.5:1) of **53** as white solid.

IR (neat, cm^{-1}): 3200(br), 3061(w), 2955(m), 2924(m), 2852(w), 1236(m), 1033(s), 831(m), 767(w), 707(w). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.58 – 7.53 (m, 5H), 7.52 – 7.46 (m, 5H), 7.42 – 7.36 (m, 5H), 7.36 – 7.29 (m, 5H), 7.28 – 7.22 (m, 2.5H), 5.40 (dd, *J* = 12.0, 10.2 Hz, 1.5H, major diastereoisomer), 4.74 (td, *J* = 11.1, 10.4, 4.3 Hz, 2.5H), 4.71 – 4.63 (m, 1H, minor diastereoisomer), 3.83 (d, *J* = 11.2 Hz, 4.5H, major diastereoisomer), 3.65 (d, *J* = 11.2 Hz, 3H, minor diastereoisomer), 3.47 (d, *J* = 11.3 Hz, 3H, minor diastereoisomer), 3.37 (d, *J* = 11.3 Hz, 5.5H), 3.12 – 3.01 (m, 4H), 1.31 (s, 9H, minor diastereoisomer), 1.30 (s, 13.5H, major diastereoisomer). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.0, 154.6, 141.6, 141.4, 140.6, 140.4, 128.8, 128.7, 128.1, 127.8, 126.5, 126.4, 126.3, 123.9, 123.6, 66.2 (d, *J* = 7.5 Hz), 66.0 (d, *J* = 4.2 Hz), 53.3 (d, *J* = 5.4 Hz), 53.2 (d, *J* = 5.5 Hz), 53.0 (d, *J* = 5.2 Hz), 52.8 (d, *J* = 4.4 Hz), 51.8, 35.0, 34.9, 31.1. HRMS (ESI) calculated for $C_{20}H_{29}NO_4PS^+$ $[M+H]^+$: 410.1549; found: 410.1537.



51 **54**

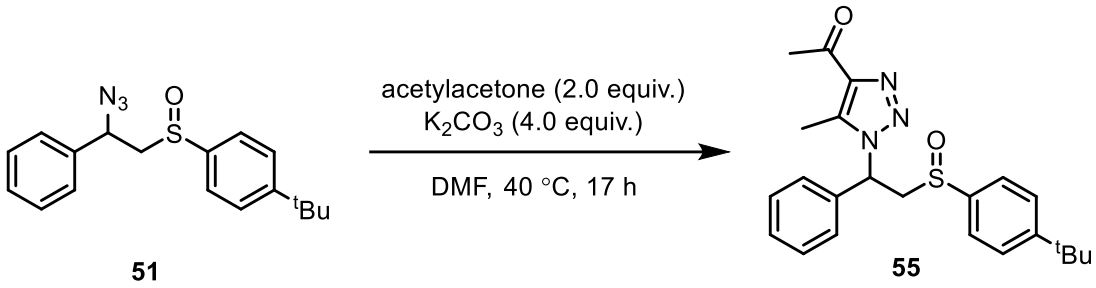
In an oven-dried Schleck tube (10 mL) equipped with a stirring bar, compound **51** (0.1 mmol, 32.7 mg), CuI (30 mol%, 6 mg) were added. Under the protection of N_2, phenylacetylene (3.0 equiv., 29 μL) and THF (1.0 mL) were injected respectively into the tube via syringes. The reaction mixture was stirred at 65 ˚C for 6 h. After completition, the reaction mixture was concentrated in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product **54**.

1-(2-((4-(Tert-butyl)phenyl)sulfinyl)-1-phenylethyl)-4-phenyl-1H-1,2,3-triazole (54)

The desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 40.0 mg (93% yield, >20:1 dr) of **54** as white solid.

IR (neat, cm^{-1}): 3086(w), 2957(m), 2924(m), 2869(w), 1041 (m), 826(m), 731(s), 694(s). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 7.3 Hz, 2H), 7.60 (s, 1H), 7.50 – 7.34 (m, 11H), 7.29 (t, *J* = 7.4 Hz, 1H), 6.10 (t, *J* = 6.9 Hz, 1H), 4.19 (dd, *J* = 13.6, 6.7 Hz, 1H), 3.78 (dd, *J* = 13.6, 7.2 Hz, 1H),

1.21 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.0, 147.6, 138.4, 137.4, 130.1, 129.3, 129.2, 128.7, 128.2, 127.1, 126.3, 125.6, 123.6, 119.9, 60.4, 57.9, 34.8, 31.0. HRMS (ESI) calculated for $C_{26}H_{28}N_3OS^+$ $[M+H]^+$: 430.1948; found: 430.1934.



51 **55**

In an oven-dried Schleck tube (10 mL) equipped with a stirring bar, compound **51** (0.1 mmol, 32.7 mg), K_2CO_3 (4.0 equiv., 55.0 mg) were added. Under the protection of N_2, acetylacetone (2.0 equiv., 20 μL) and DMF (1.0 mL) were injected respectively into the tube via syringes. The reaction mixture was stirred at 40 ˚C for 17 h. After completition, The reaction mixture was poured into a water. The aqueous layer was separated and extracted with dichloromethane (3×5 mL), and the combined organic layers were washed with brine and dried over sodium sulfate. the result reaction mixture was concentrated in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product **55**.

1-(1-(2-((4-(Tert-butyl)phenyl)sulfinyl)-1-phenylethyl)-5-methyl-1H-1,2,3-triazol-4-yl)ethan-1-one (55)

The desired pure product was purified using silica gel chromatography (PE:EA = 2:1) to give 37.7 mg (92% yield, dr = 1.8:1) of **55** as white solid.

IR (neat, cm^{-1}): 3062(w), 2961(m), 2926(m), 2869(w), 1683(s), 1045(s), 831(m), 731(m), 705(s). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.5 Hz, 3.6H), 7.52 (d, *J* = 8.5 Hz, 3.6H), 7.41 – 7.33 (m, 7H), 7.32 – 7.27 (m, 7H), 7.24 (t, *J* = 3.8 Hz, 4H), 5.96 (dd, *J* = 12.0, 2.9 Hz, 1.8H, major diastereoisomer), 5.91 (t, *J* = 6.5 Hz, 1H, minor diastereoisomer), 4.35 – 4.27 (m, 2.8H), 3.78 (dd, *J* = 14.0, 6.0 Hz, 1H, minor diastereoisomer), 3.30 (dd, *J* = 13.3, 3.0 Hz, 1.8H, major diastereoisomer), 2.72 (s, 5.4H, major diastereoisomer), 2.57 (s, 5.4H, major diastereoisomer), 2.56 (s, 3H, minor diastereoisomer), 2.37 (s, 3H, minor diastereoisomer), 1.31 (s, 16.2H, major diastereoisomer), 1.27 (s,

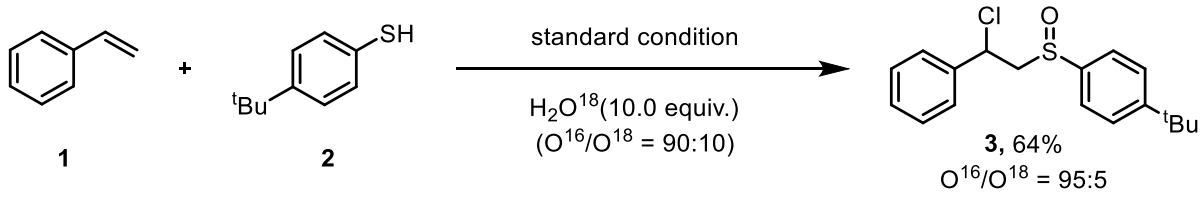
9H, minor diastereoisomer). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 194.2, 194.0, 155.2, 154.8, 144.0, 143.5, 139.8, 137.9, 137.8, 136.94, 136.91, 136.5, 129.44, 129.38, 129.1, 126.9, 126.60, 126.56, 126.2, 123.5, 123.4, 63.3, 59.5, 56.9, 54.3, 35.0, 34.9, 31.14, 31.08, 27.8, 27.6, 9.0, 8.9. HRMS (ESI) calculated for $C_{23}H_{28}N_3O_2S^+$ $[M+H]^+$: 410.1897; found: 410.1884.

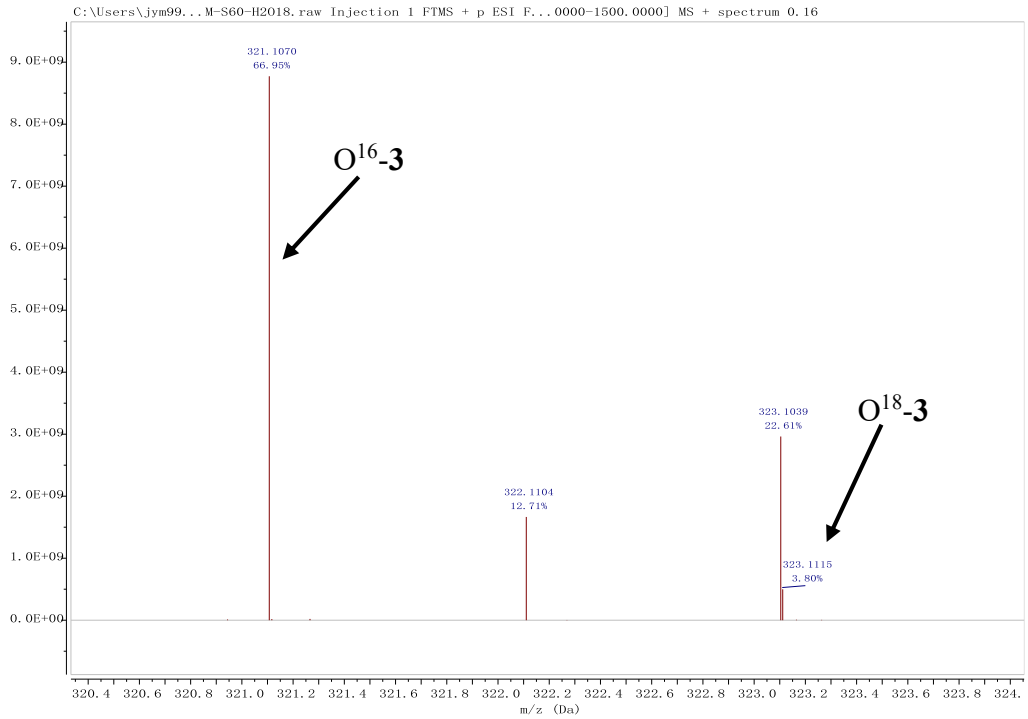
6 Mechanistic Experiments

6.1 O18 Labeling experiment

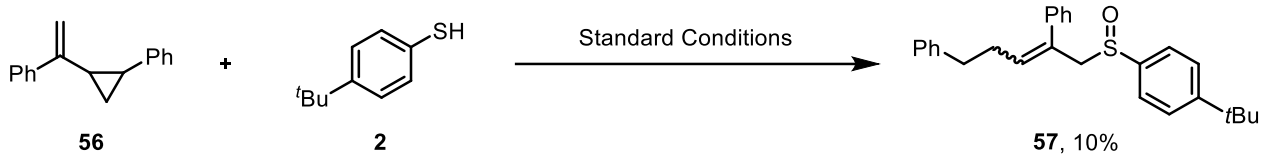
The procedure for O^{18} Labeling experiment: In an undivided three-necked glassware (25 mL) equipped with a stirring bar, *n*Bu_4NBF_4 (1.0 equiv.) was added. The glassware was equipped with carbon cloth (15 mm ×15 mm ×0.1 mm) as the anode and platinum plate (15 mm ×15 mm ×0.3 mm) as the cathode. Under the protection of N_2, 4-tert-butylbenzenethiol (0.3 mmol), styrene (1.7 equiv.), H_2O^{18} (10.0 equiv.), 1 M HCl in water (0.3 mL), water (0.2 mL), CH_3COOH (3.0 equiv.), and MeCN (10.0 mL) were injected respectively into the glassware via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 17 mA at 40 ˚C for 3 h. After completion, the resultant reaction mixture was concentrated in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product.

The ESI-MS spectra of **3** when 10.0 equiv. of H_2O^{18} was used:





6.2 Radical clock experiment



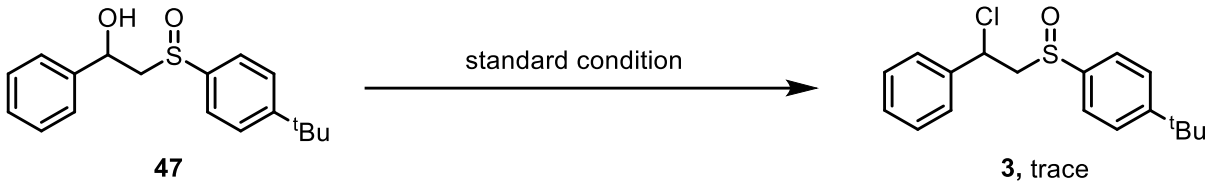
56 **2** **57**, 10%

In an undivided three-necked glassware (25 mL) equipped with a stirring bar, nBu$_4$NBF$_4$ (1.0 equiv.) were added. The glassware was equipped with carbon cloth (15 mm × 15 mm × 0.1 mm) as the anode and platinum plate (15 mm × 15 mm × 0.3 mm) as the cathode. Under the protection of N_2, 4-tert-butylbenzenethiol (**2,** 0.3 mmol), (1-(2-phenylcyclopropyl)-vinyl)benzene (**56,** 1.7 equiv.), 1 M HCl in water (0.3 mL), water (0.2 mL), CH_3COOH (3.0 equiv.), and MeCN (10.0 mL) were injected respectively into the glassware via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 17 mA at 40 ˚C for 3 h. After completion, the resultant reaction mixture was concentrated in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product **57** (12.5 mg, 10% yield, dr = 2:1).

(5-((4-(Tert-butyl)phenyl)sulfinyl)pent-3-ene-1,4-diyl)dibenzene (57):

IR (neat, cm^{-1}): 3057(w), 3026(w), 2960(s), 2863(m), 1677(w), 1048(s), 831(m), 746(m), 700(s). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 2.4 Hz, 3H), 7.47 – 7.44 (m, 4.5H), 7.42 – 7.39 (m, 4.5H), 7.30 – 7.21 (m, 24H), 7.14 – 7.11 (m, 3H), 7.07 – 7.04 (m, 3H), 5.97 (t, *J* = 7.4 Hz, 2H, major diastereoisomer), 5.65 (t, *J* = 7.3 Hz, 1H, minor diastereoisomer), 4.16 (d, *J* = 12.7 Hz, 2H, major diastereoisomer), 3.85 (dd, *J* = 12.6, 6.6 Hz, 3H), 3.67 (d, *J* = 12.6 Hz, 1H, minor diastereoisomer), 2.57 (dp, *J* = 13.8, 6.8, 6.1 Hz, 6H), 2.41 – 2.27 (m, 4H), 2.24 – 2.15 (m, 2H), 1.32 (s, 9H), 1.28 (s, 18H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.9, 154.7, 141.6, 141.3, 141.2, 141.1, 140.6, 140.1, 138.82, 138.81, 135.60, 135.58, 130.8, 129.8, 128.4, 128.40, 128.38, 128.37, 128.34, 128.28, 127.30, 127.28, 126.3, 126.03, 126.00, 125.9, 124.4, 124.3, 68.2, 59.7, 35.7, 35.4, 35.0, 34.9, 31.21, 31.16, 30.8, 29.7. HRMS (ESI) calculated for $C_{27}H_{31}OS^+$ $[M+H]^+$: 403.2090; found: 403.2077.

6.3 Substitution experiment of β-hydroxysulfoxide



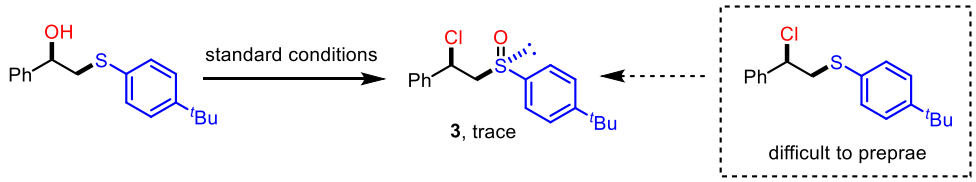
47 **3**, trace

In an undivided three-necked glassware (25 mL) equipped with a stirring bar, nBu$_4$NBF$_4$ (1.0 equiv.), compound **47** (0.3 mmol) were added. The glassware was equipped with carbon cloth (15 mm × 15 mm × 0.1 mm) as the anode and platinum plate (15 mm × 15 mm × 0.3 mm) as the cathode. Under the protection of N_2, 1 M HCl in water (0.3 mL), water (0.2 mL), CH_3COOH (3.0 equiv.), and MeCN (10.0 mL) were injected respectively into the glassware via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 17 mA at 40 ˚C for 1 h. After completion. The yield of desired product **3** was determined by ^{1}H NMR with dibromomethane as the internal standard.

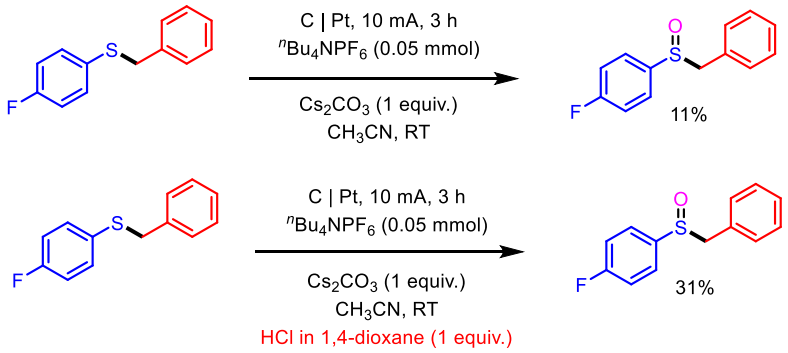
6.4 Probing the role of chloride

In the current transformation, Cl^- at least played two roles. It is not only a redox mediator in the oxidation of sulfide to sulfoxide but also the chloride source of the target β-chloro sulfoxide. Accordingly, our previous research[2] and other the related literature[3] do support the hypothesis that chlorine plays a key role in the oxidation of sulfides to sulfoxides.

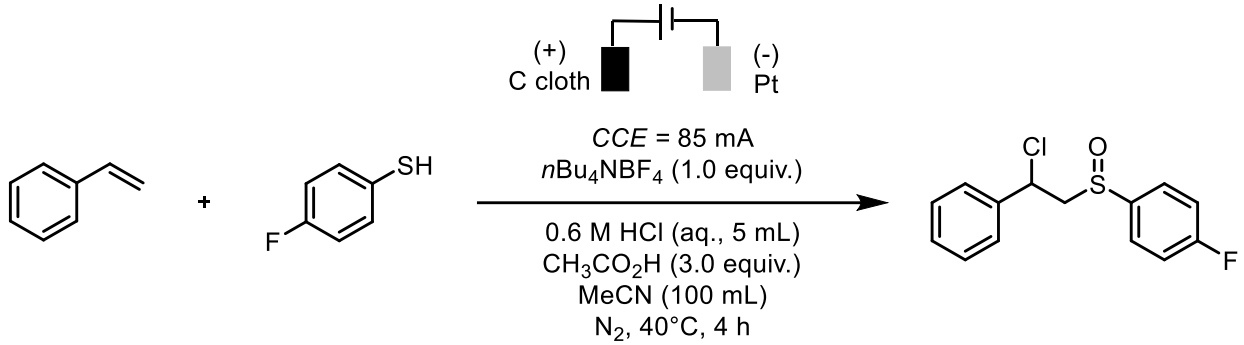
To further support our hypothesis, we attempted to provide some more direct evidence on the role of chloride in the oxidation of sulfide to sulfoxide. However, the electrolysis of β-hydroxyl sulfide only led to a trace amount of desired β-chloro sulfoxide. Efforts on the preparation of the analogous β-chloro sulfide was not successful, probably owing to the ease of intramolecular nucleophilic substitution to form the episulfonium ion intermediate (**F**).



Instead, we decided to take benzyl(4-fluorophenyl)sulfane, directly using our previous system[2b], as the model substrate to probe the essential role of chloride. Indeed, while the direct oxidation of sulfide was much less efficient, addition of extra chloride source (HCl in dioxane) indeed profoundly increased the yields of sulfoxide.



6.5 Sampling experiment



In an undivided three-necked round bottom flask (100 mL) equipped with a stirring bar. nBu$_4$NBF$_4$ (1.0 equiv.) were added. The flask was equipped with carbon cloth (30 mm × 30 mm × 0.1 mm) as the anode and platinum plate (30 mm × 30 mm × 0.3 mm) as the cathode. Under the protection of N_2, 4-fluorothiophenol (3 mmol, 0.32 mL), styrene (1.7 equiv., 0.60 mL), 1 M HCl in water (3.0 mL), water (2.0 mL), CH_3COOH (3.0 equiv., 0.52 mL), and MeCN (100 mL) were injected respectively into the glassware via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 85 mA at 40 °C. 0.5 mL of the reaction mixture was extracted every 15 minutes after the beginning of the reaction. The reaction mixture was added to 0.5 ml of 0.3 M trifluoromethoxylbenzene in MeCN, which was subsequently submitted for ^{19}F NMR analysis.

During the electrolysis, various intermediates, including diaryl disulfide (**Int$_1$**), various β-functionalized sulfides, such as β-hydrosulfides (**Int$_2$**), β-hydroxylsulfides (**Int$_3$**). β-chrolosulfides (**Int$_4$**), β-acetoxysulfides (**Int$_5$**), and β-hydroxylsulfoxide (**Int$_6$**) were all spectroscopically detected (**Figure S1**). The yield curves of various intermediates as the reaction time progresses were shown in **Figure S2**.

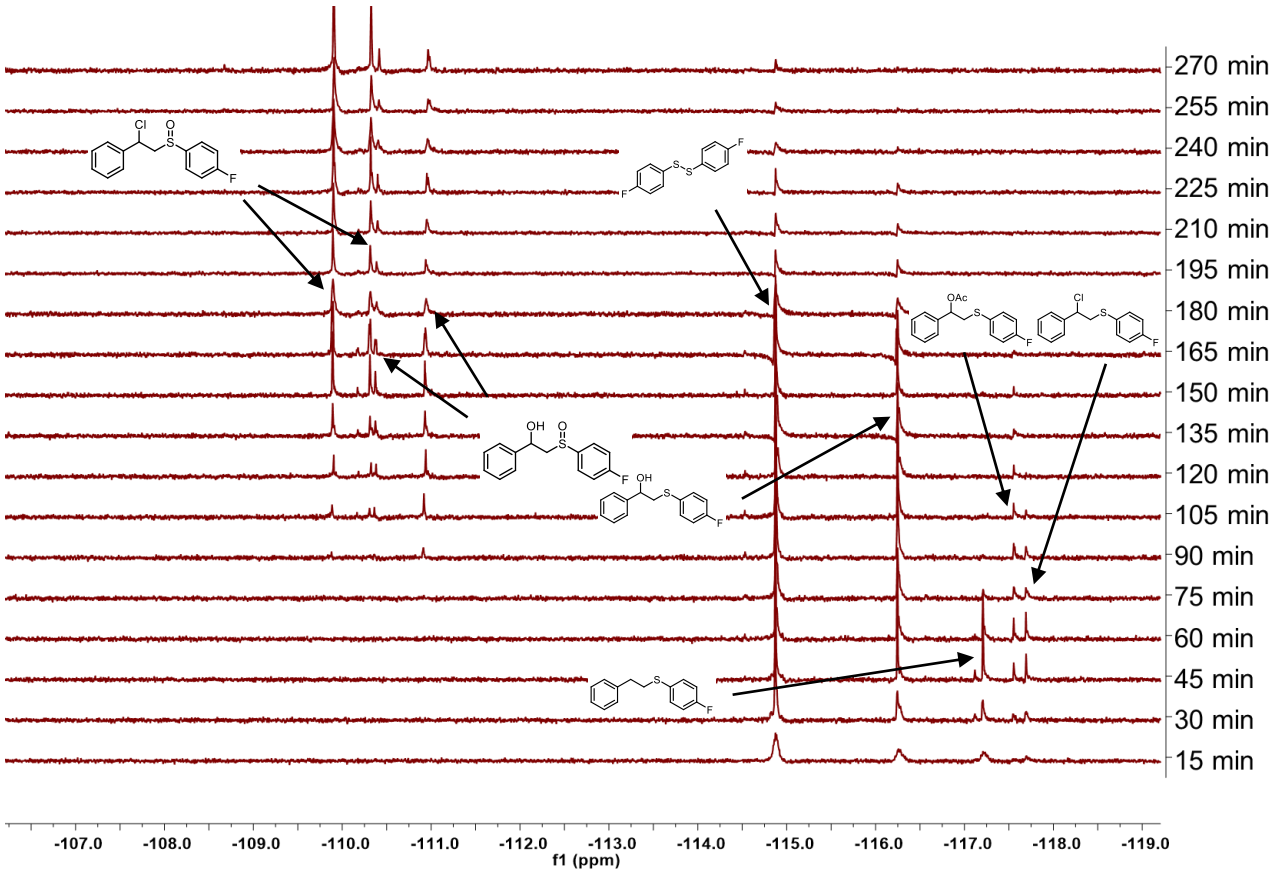


Figure S1. Sampling and tracking experiments

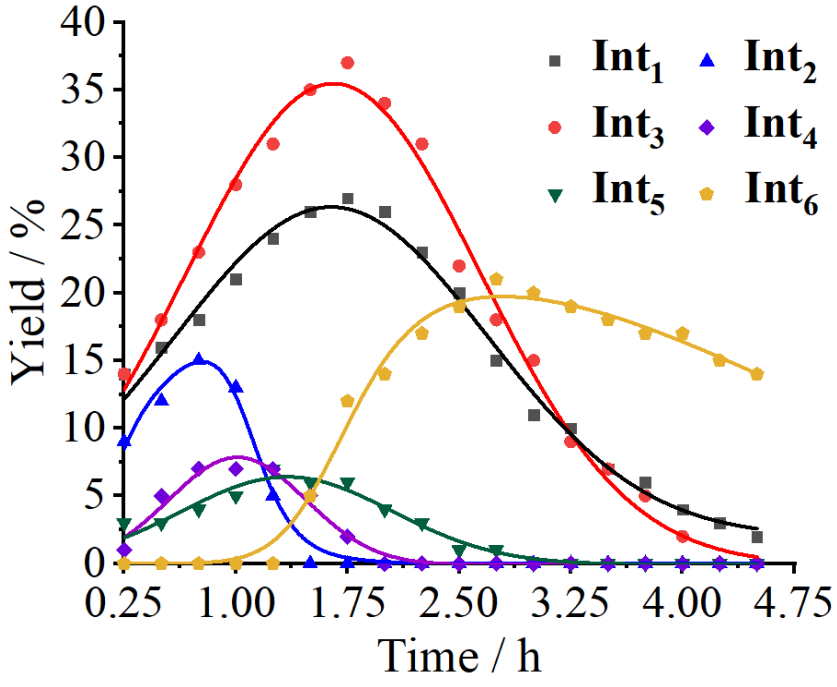


Figure S2. The yield curves of various intermediates

6.6 Cyclic voltammetry studies

General information: Cyclic voltammetry (CV) experiments were conducted in a 10 mL glass vial fitted with a glassy carbon working electrode (3 mm in diameter), a platinum wire auxiliary electrode, and submerged in a saturated calomel reference electrode. The current was reported in mA, while all potentials were reported in V.

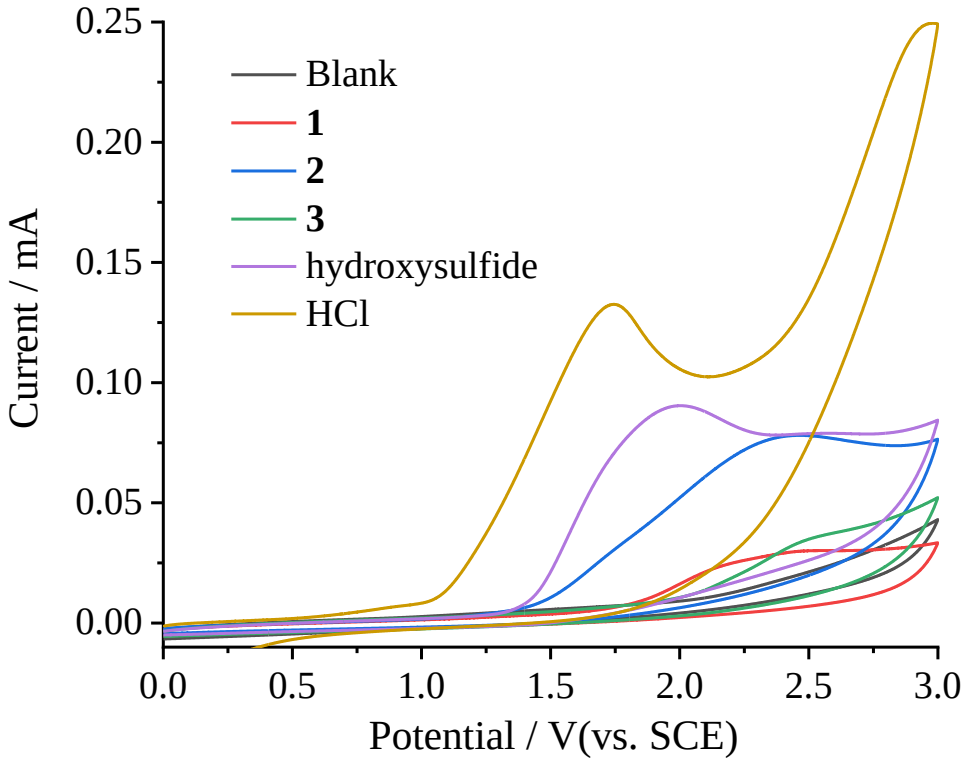
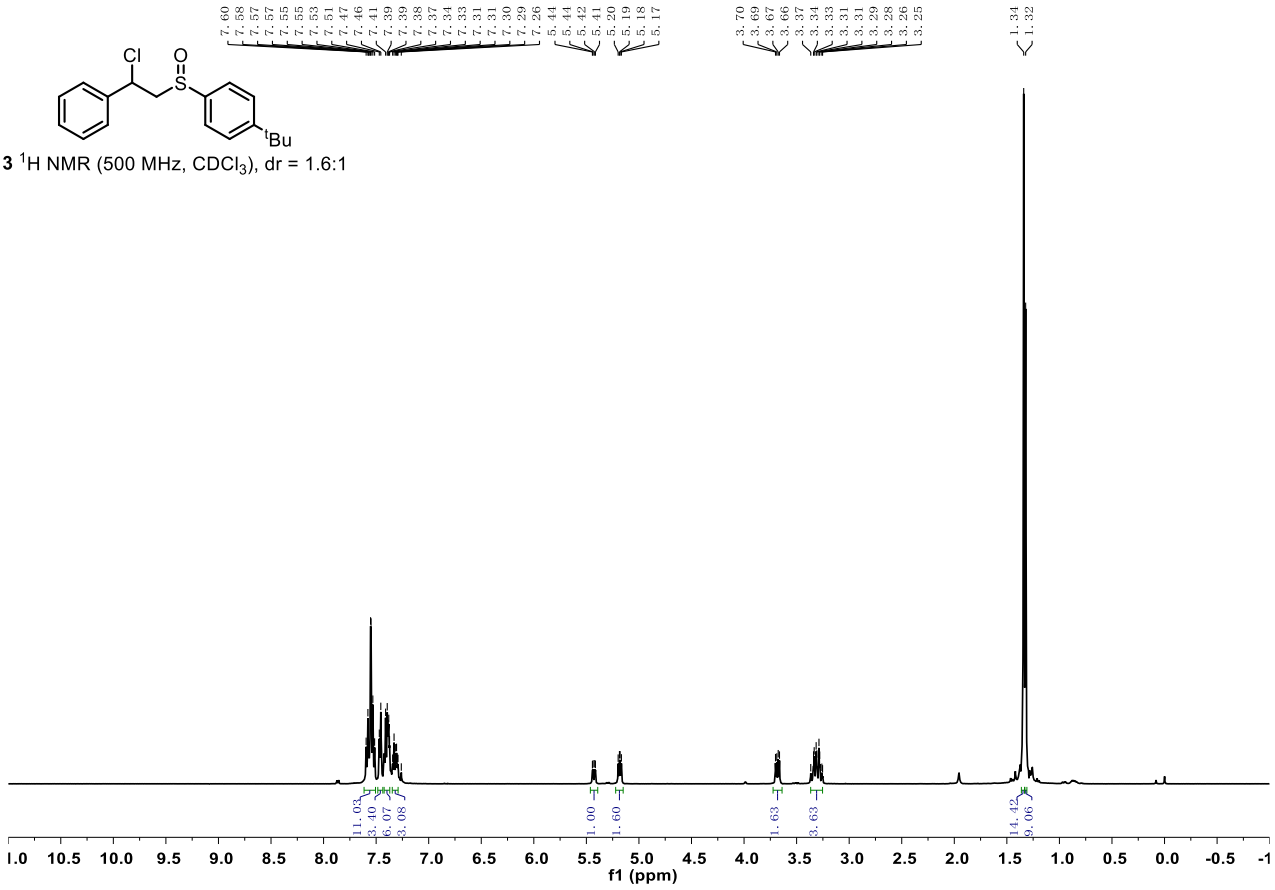


Figure S3: Cyclic voltammogram in MeCN (10 mL) with $^{n}Bu_4NBF_4$ (5 mM) as electrolyte; Conditions: $^{n}Bu_4NBF_4$ (5 mM in MeCN) with (black curve) none; (red curve) styrene (**1**, 30 mM); (blue curve) 4-tert-butylbenzenethiol (**2**, 10 mM); (green curve) compound **3** (10 mM); (purple curve) β-hydroxysulfide (6 mM); (brown curve) HCl (5 mM). Scan rate: 0.1 V/s.

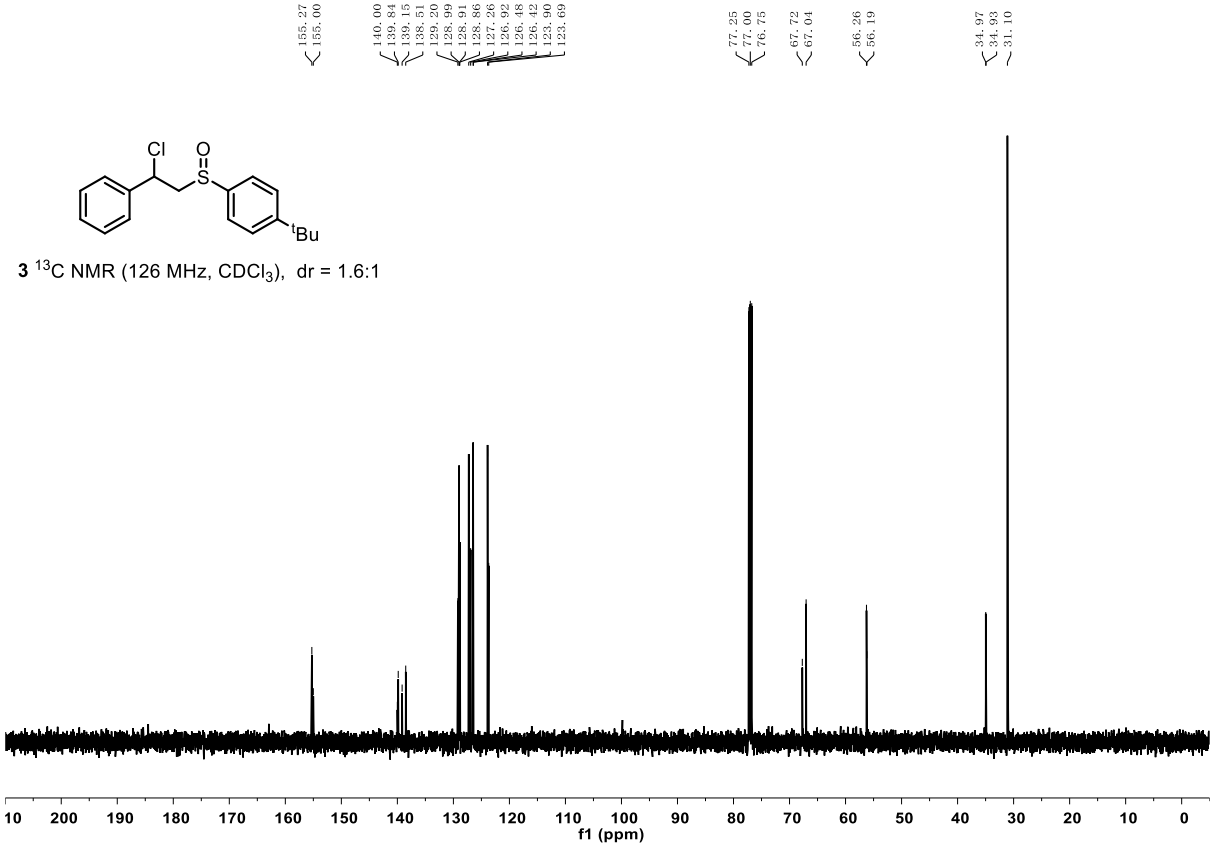
7 References

1. H. Ikeda, Y. Hoshi, H. Namai, F. Tanaka, J. L. Goodman and K. Mizuno, *Chem. Eur. J.*, 2007, **13**, 9207-9215.
2. (a) Y. Yu, Y. Jiang, S. Wu, Z. Shi, J. Wu, Y. Yuan and K. Ye, *Chin. Chem. Lett.*, 2022, **33**, 2009-2014; (b) Y. Yu, S.-F. Wu, X.-B. Zhu, Y. Yuan, Z. Li and K.-Y. Ye, *J. Org. Chem.*, 2022, **87**, 6942-6950.
3. (a) P. Kowalski, K. Mitka, K. Ossowska and Z. Kolarska, *Tetrahedron*, 2005, **61**, 1933-1953; (b) W. R. Leow, Y. Lum, A. Ozden, Y. Wang, D.-H. Nam, B. Chen, J. Wicks, T.-T. Zhuang, F. Li, D. Sinton and E. H. Sargent, *Science*, 2020, **368**, 1228-1233; (c) H. Wang, M. Yu, P. Zhang, H. Wan, H. Cong and A. Lei, *Sci. Bull.*, 2022, **67**, 79-84.

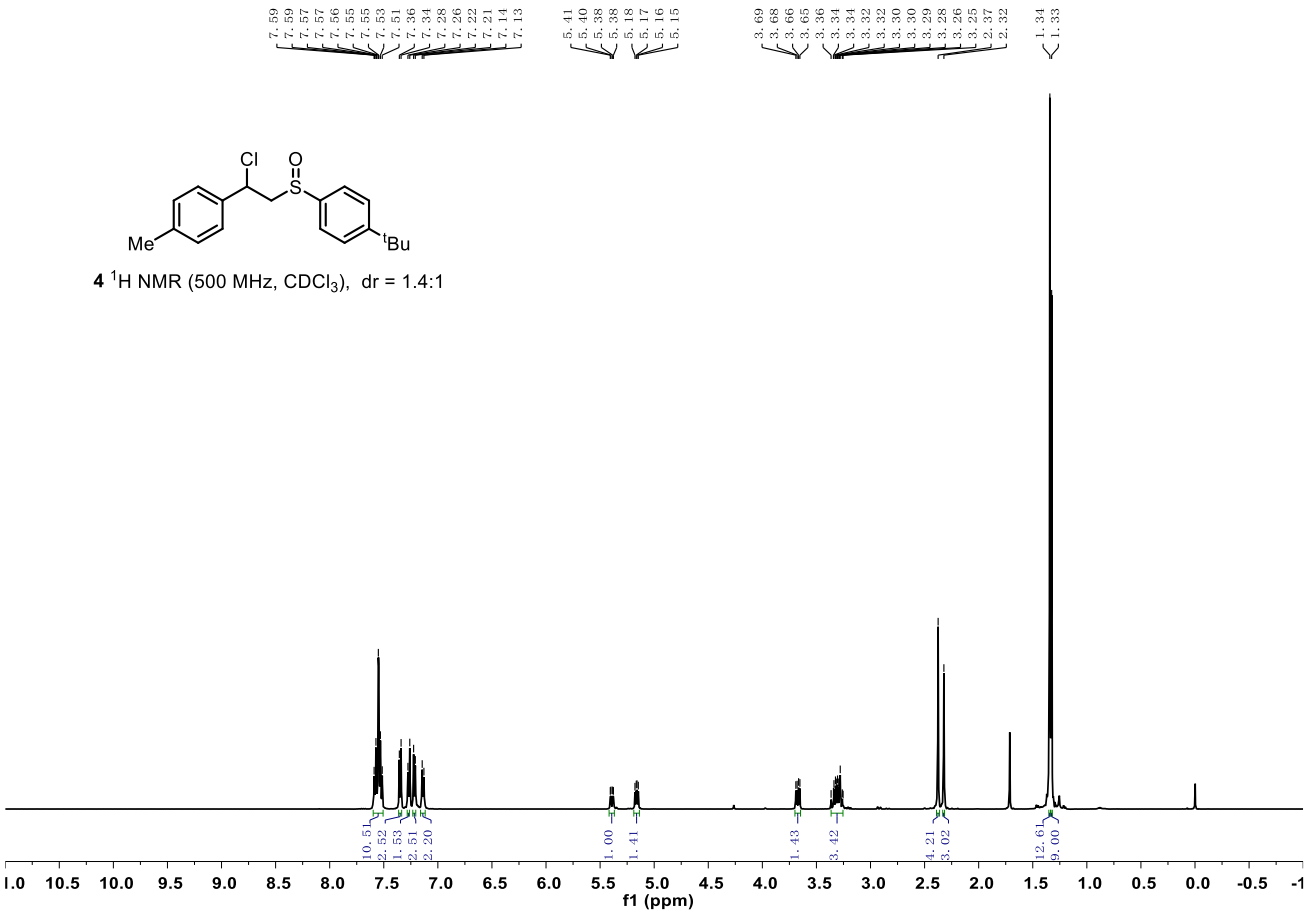
8 Spectral Data (^{1}H, ^{13}C, ^{19}F, ^{11}B) of Products



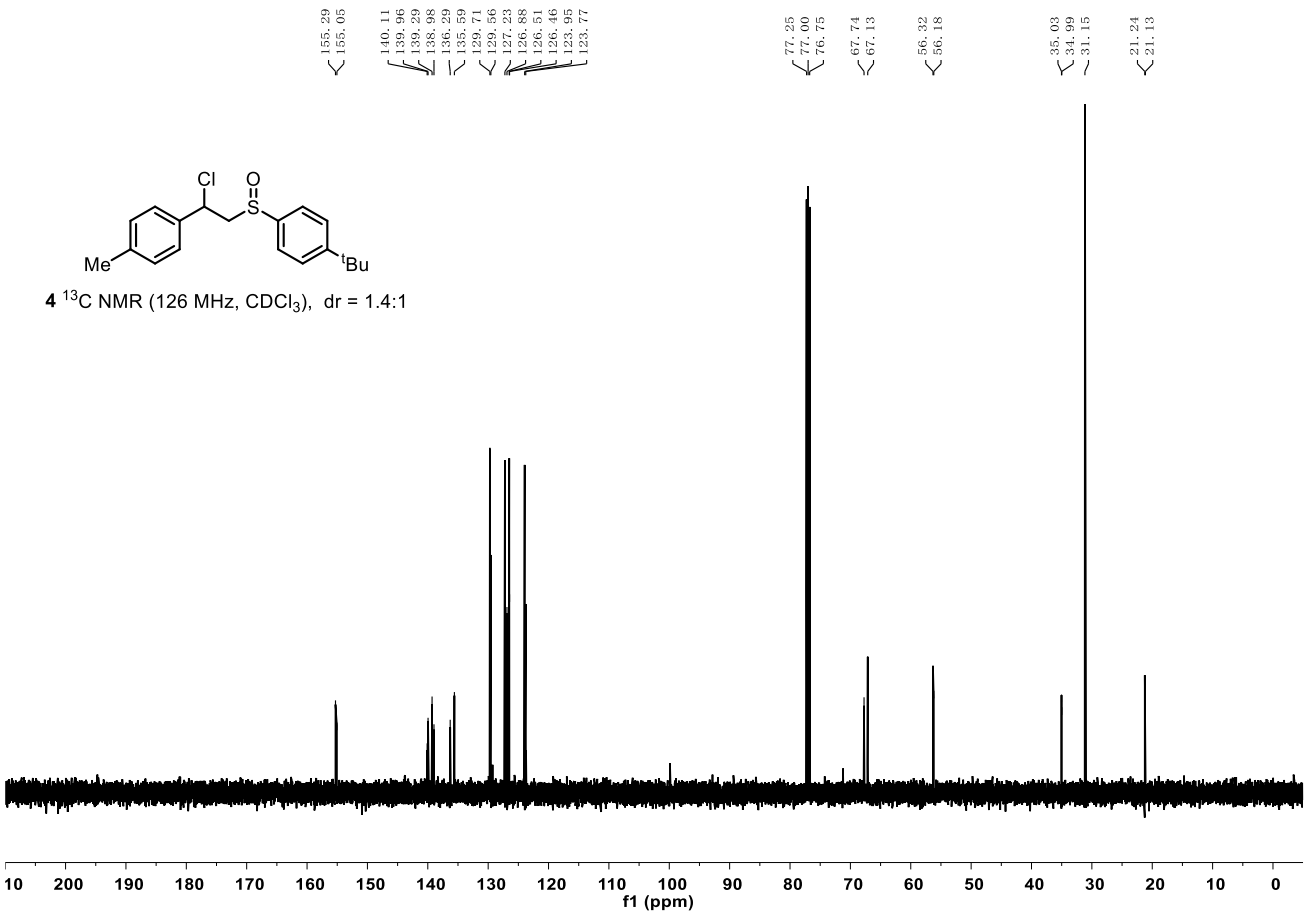
3 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.6:1



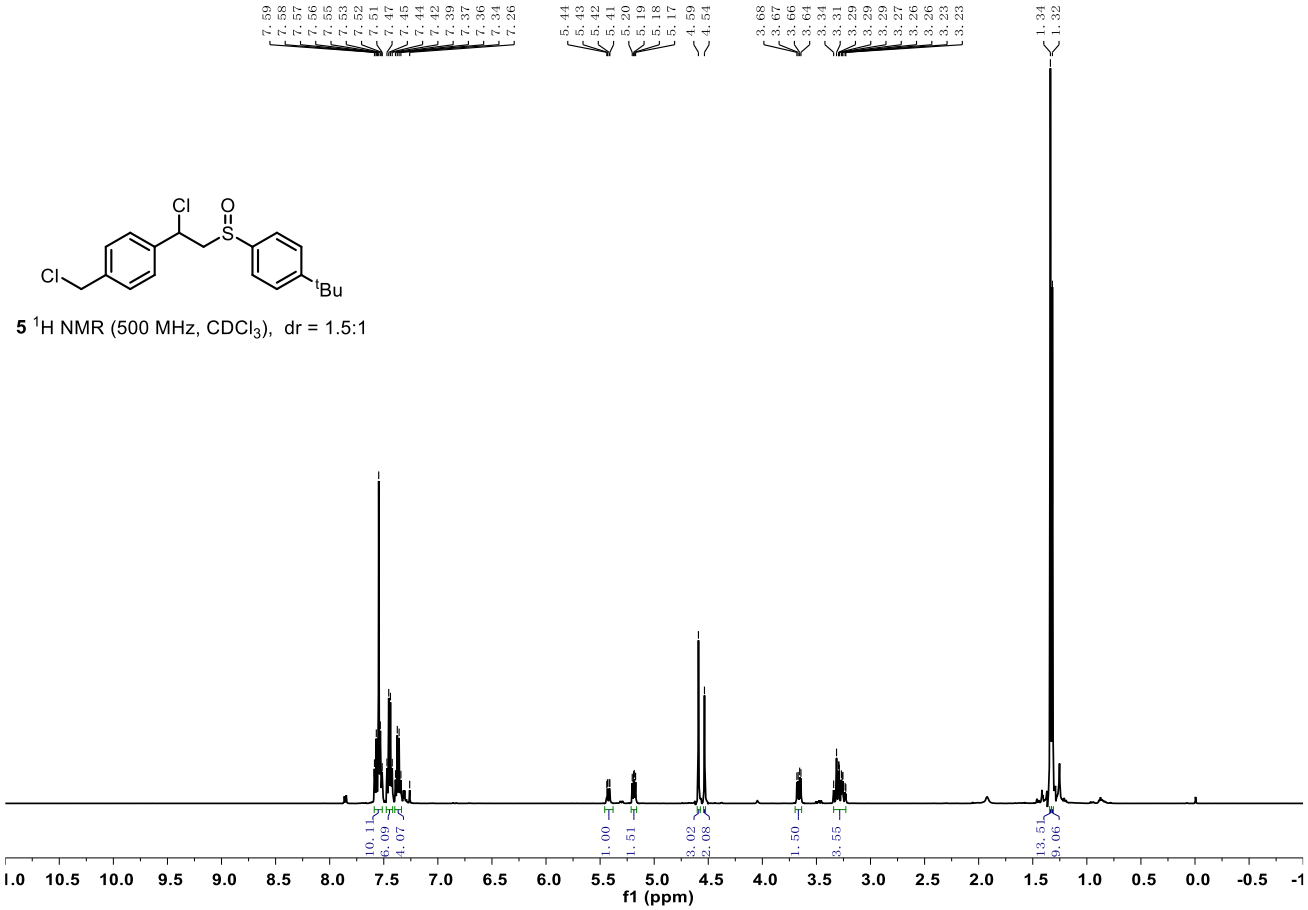
3 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 1.6:1



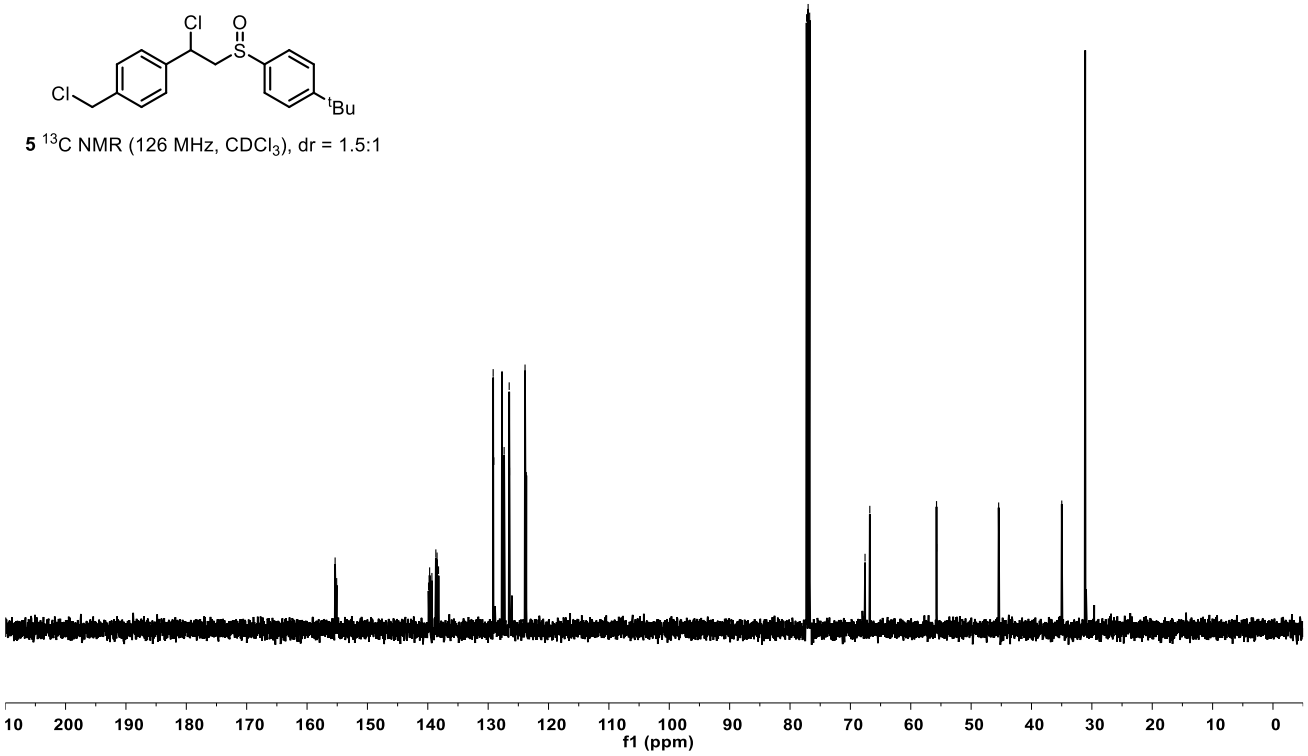
4 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.4:1



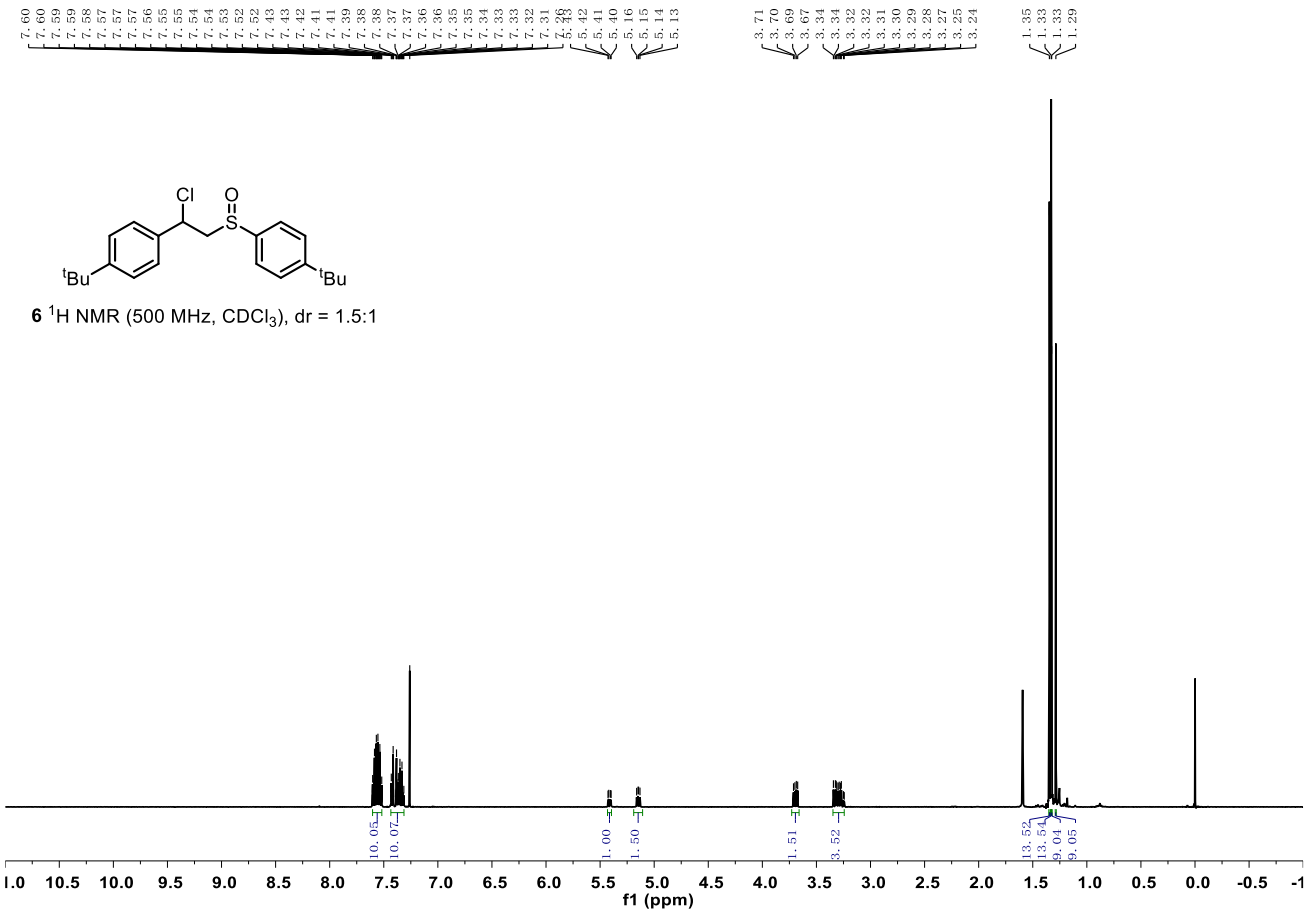
4 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 1.4:1



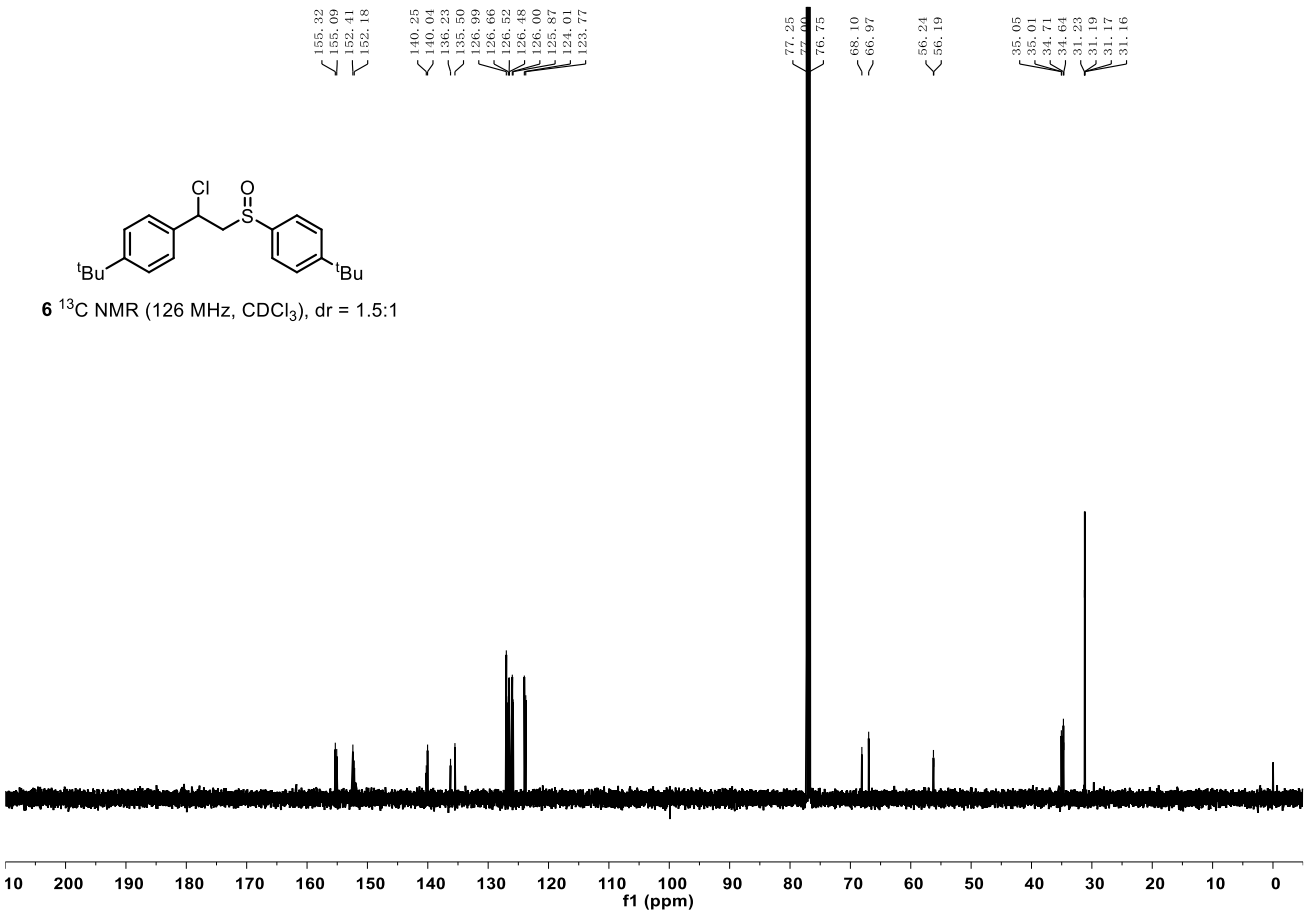
5 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.5:1



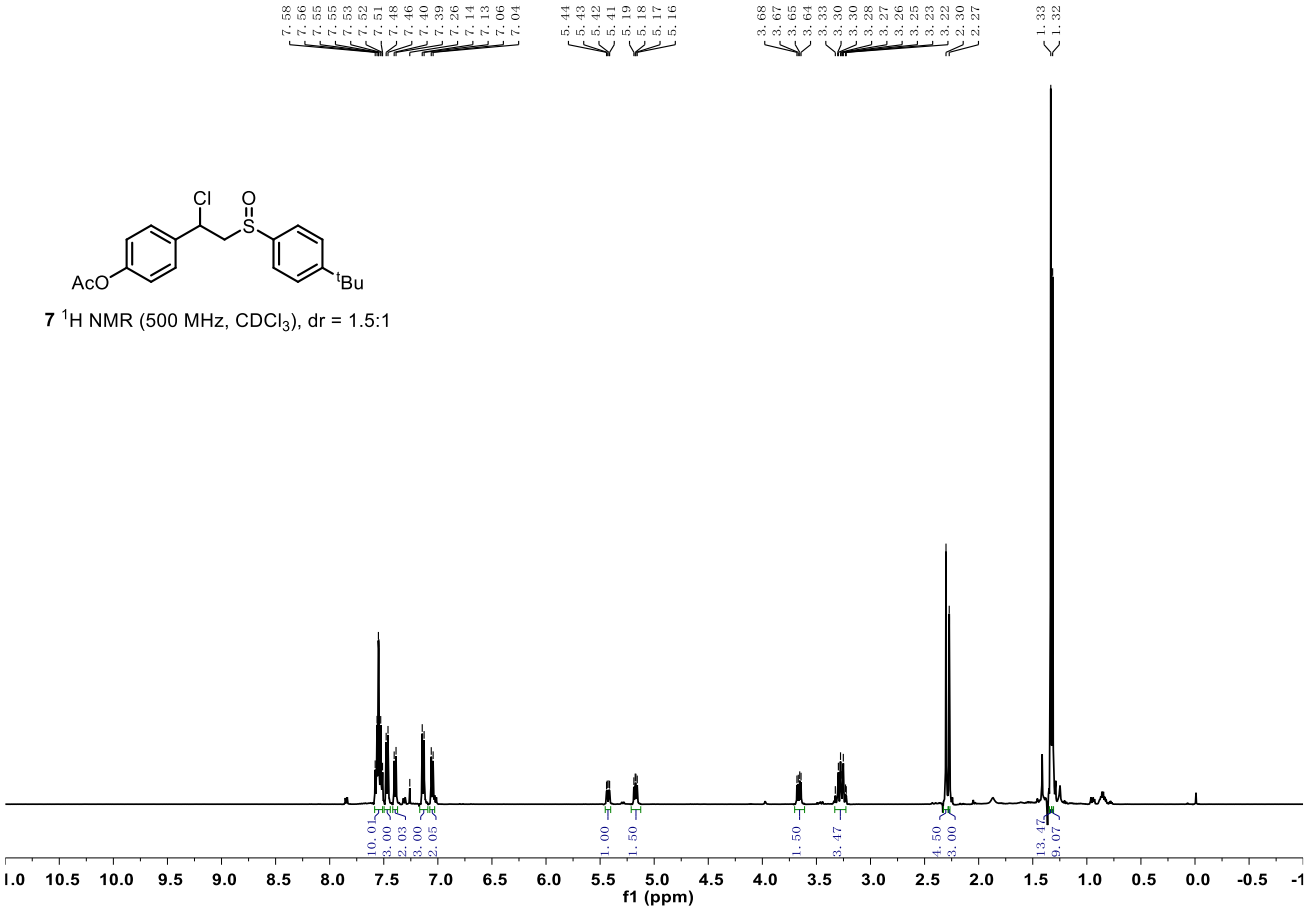
5 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 1.5:1



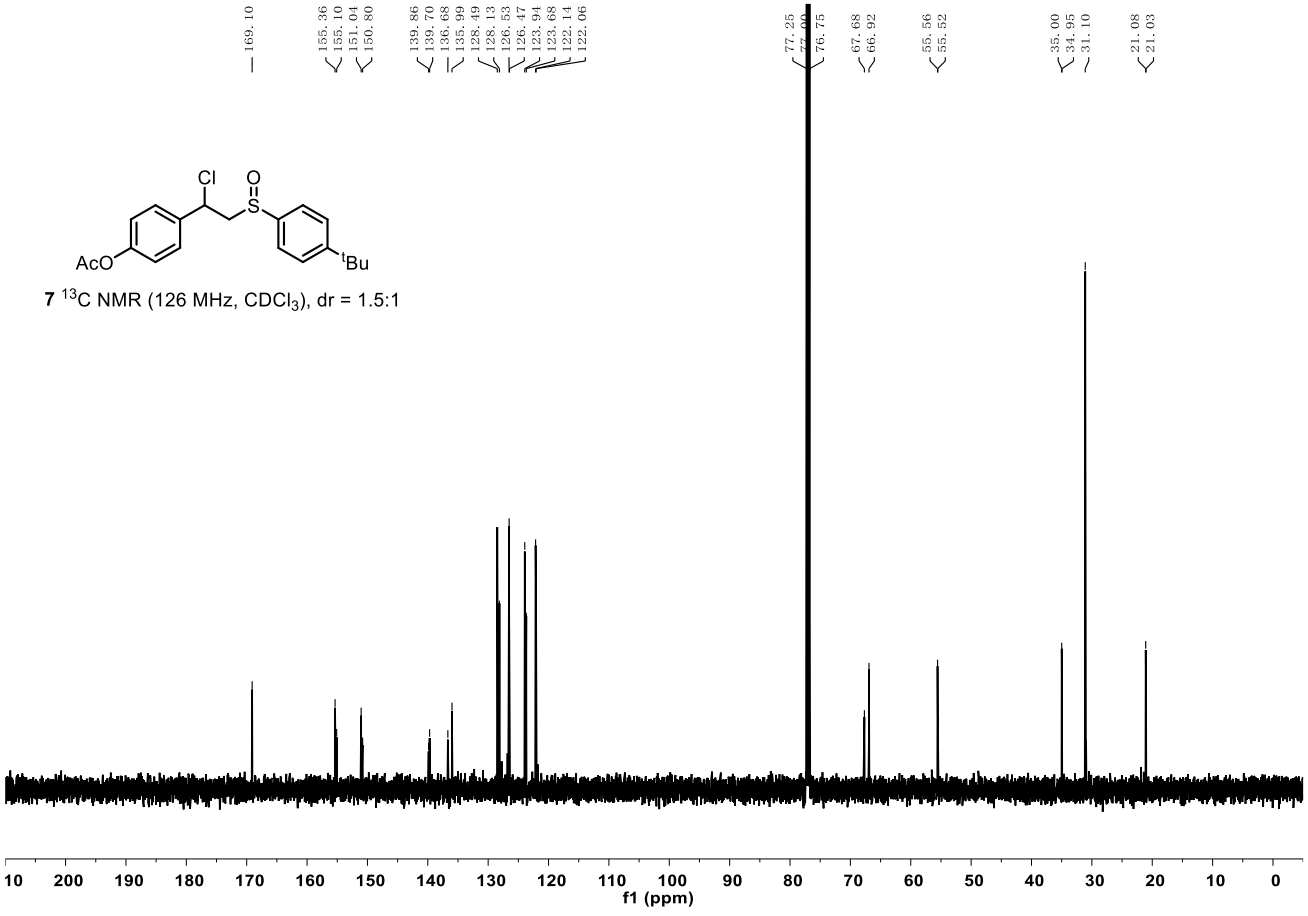
6 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.5:1



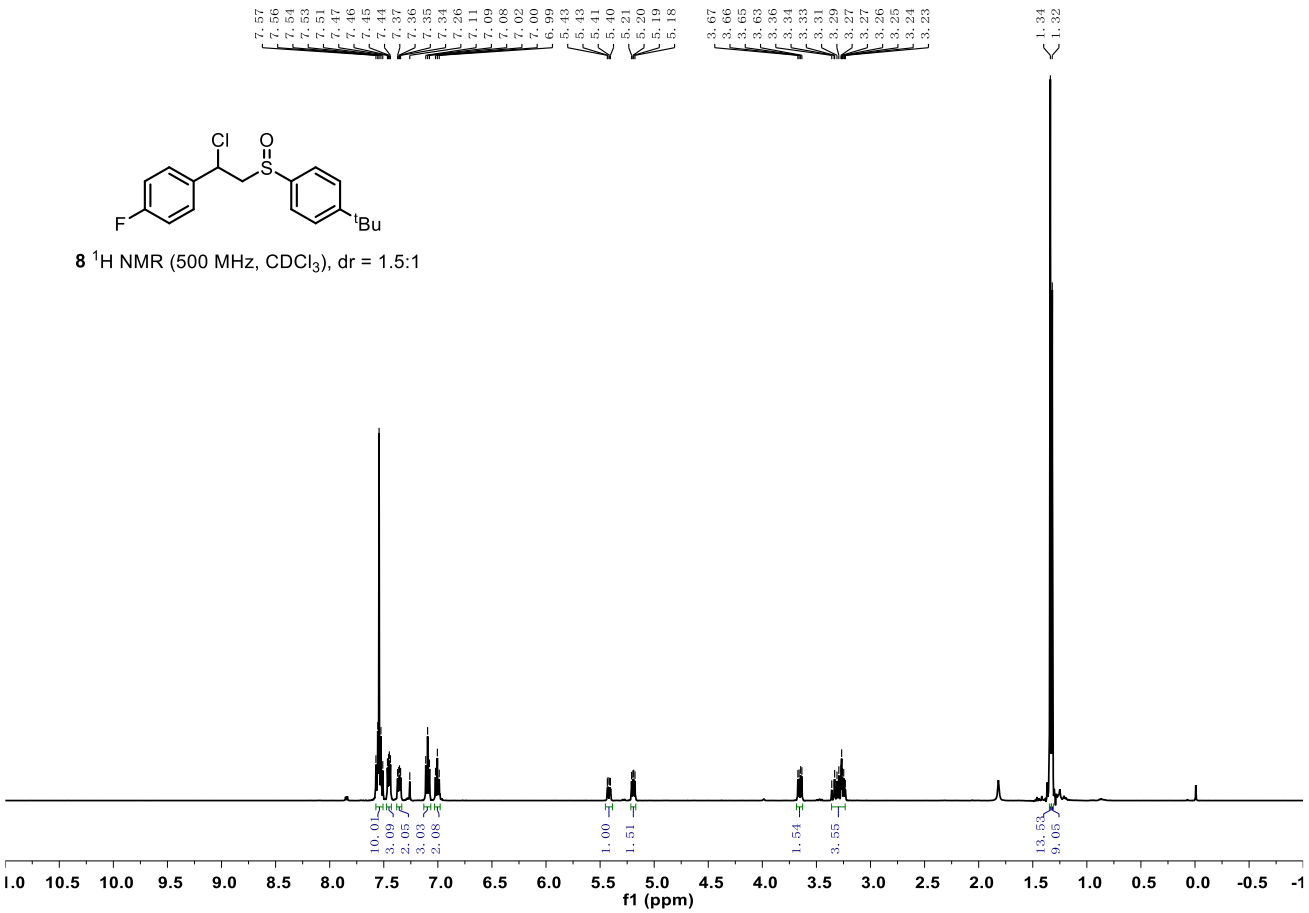
6 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 1.5:1



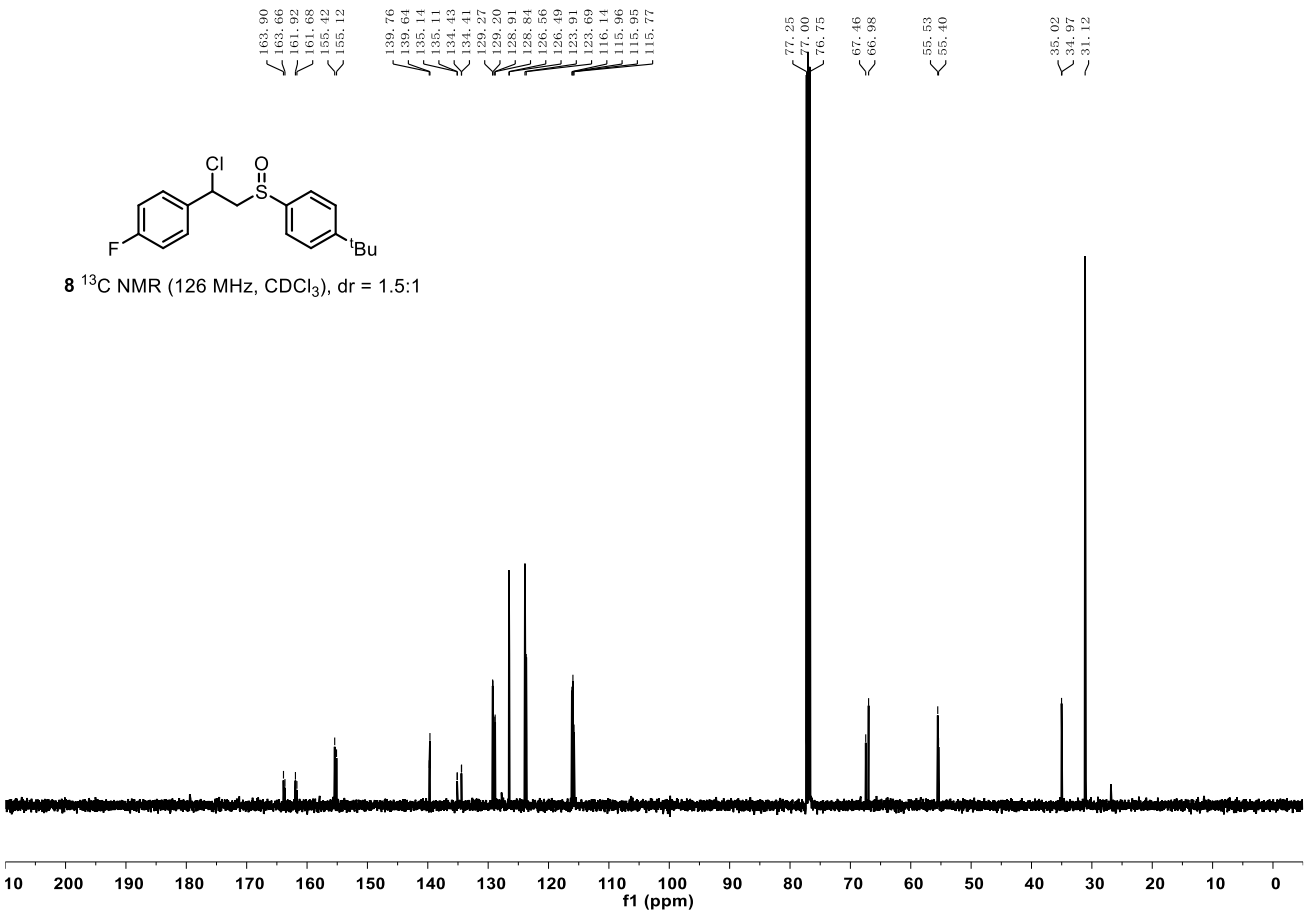
7 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.5:1



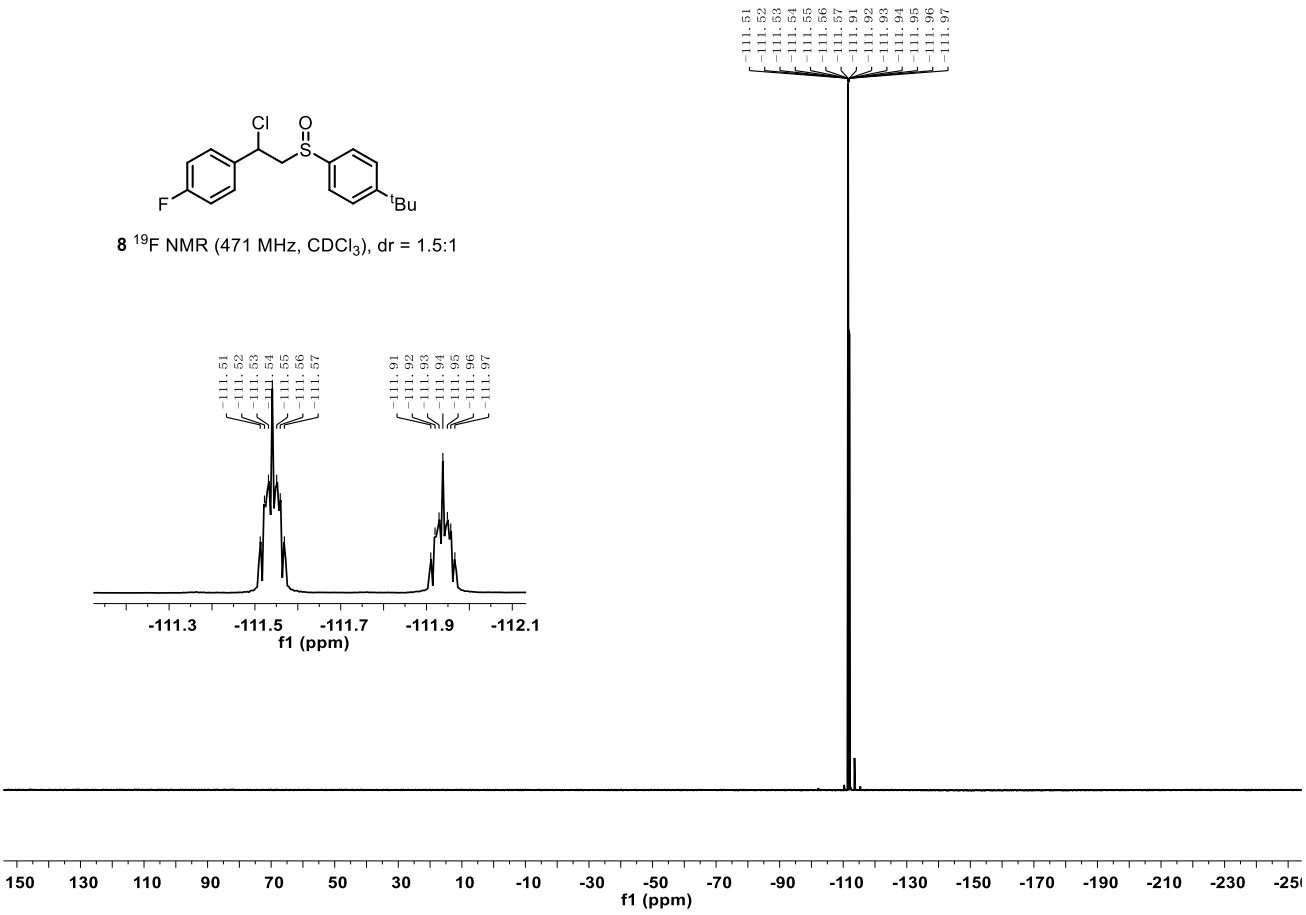
7 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 1.5:1



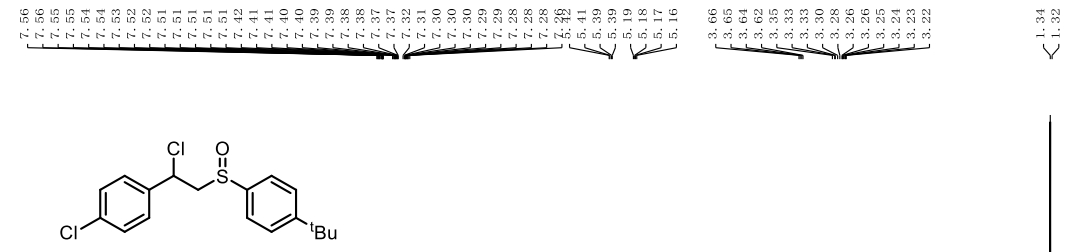
8 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.5:1



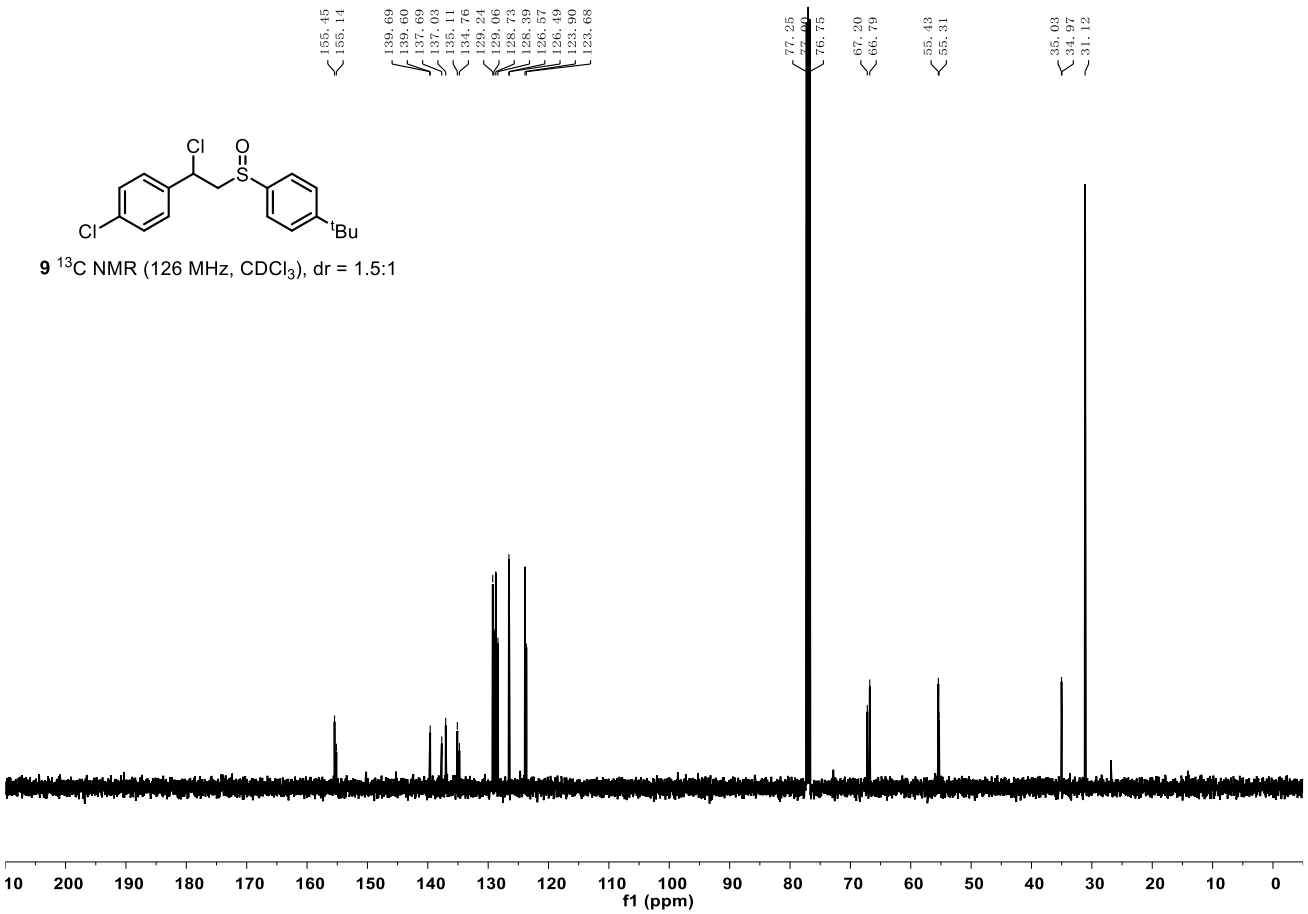
8 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 1.5:1



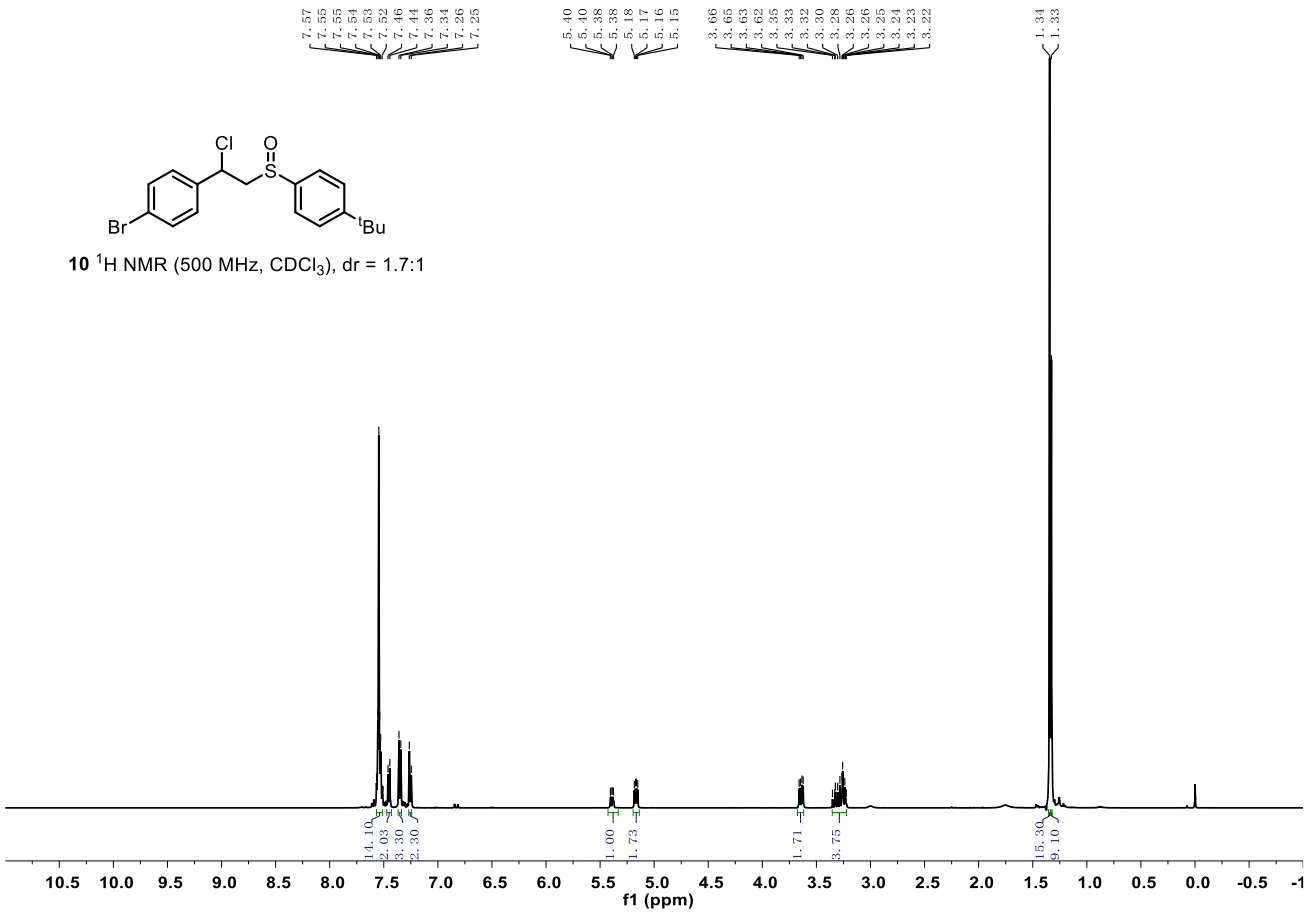
8 ^{19}F NMR (471 MHz, $CDCl_3$), dr = 1.5:1



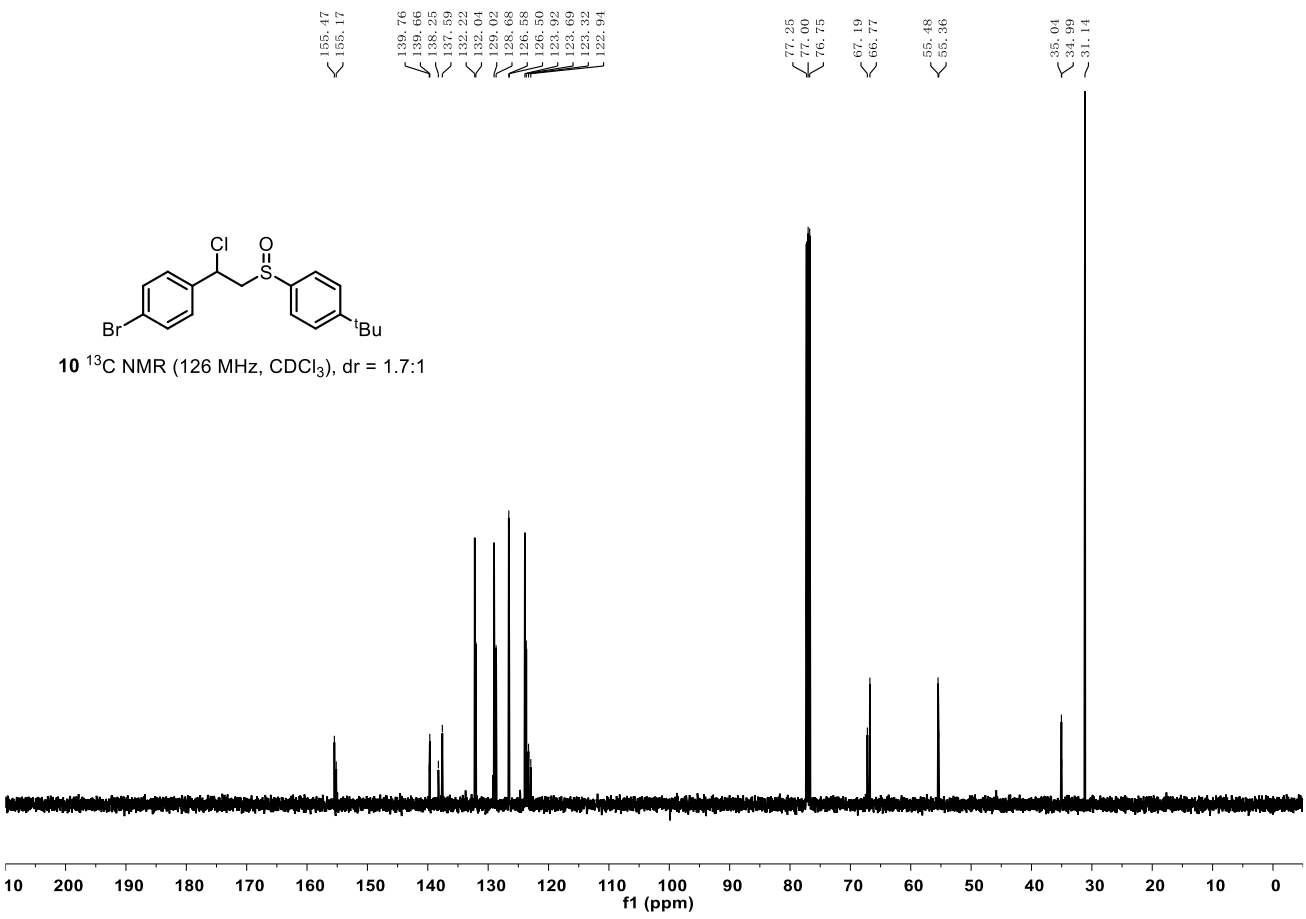
9 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.5:1



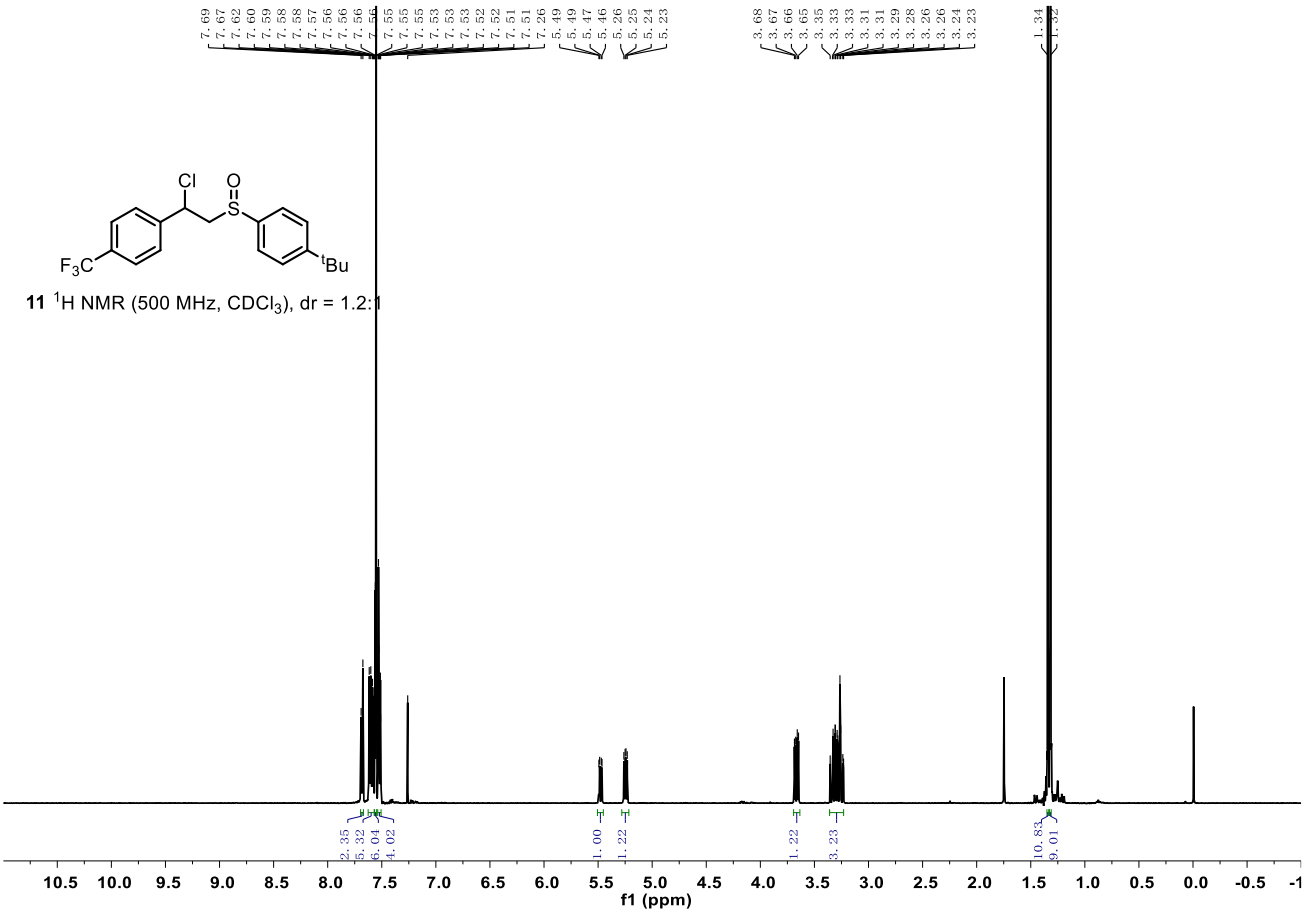
9 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 1.5:1



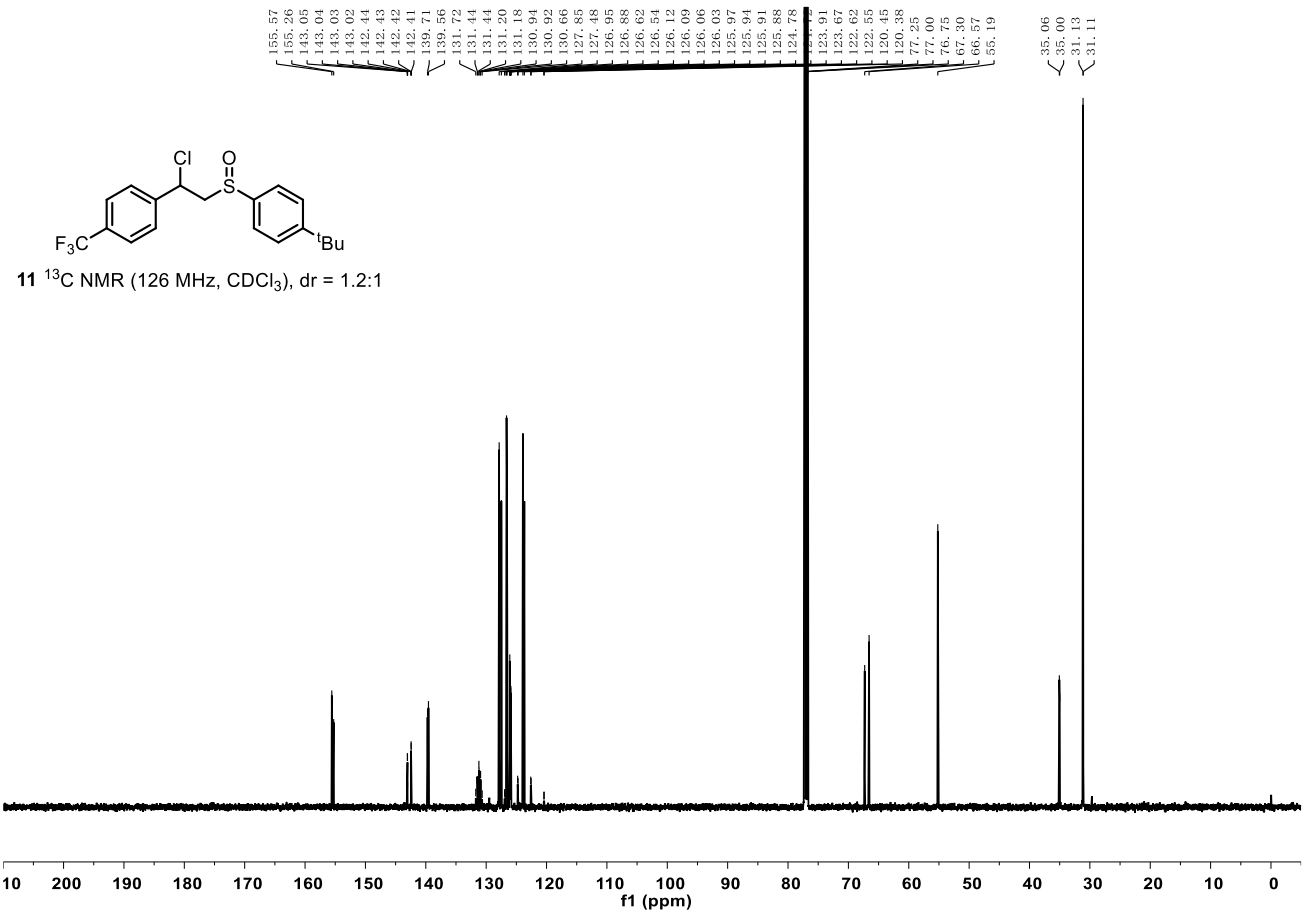
10 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.7:1



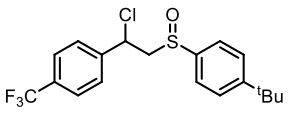
10 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 1.7:1



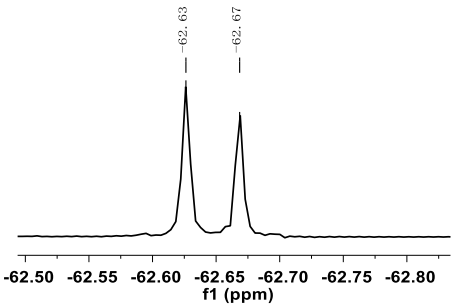
11 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.2:1

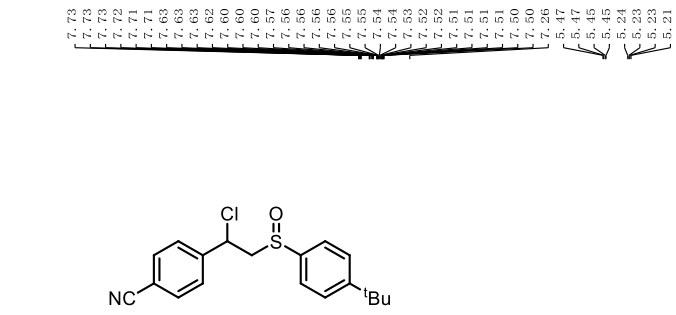


11 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 1.2:1

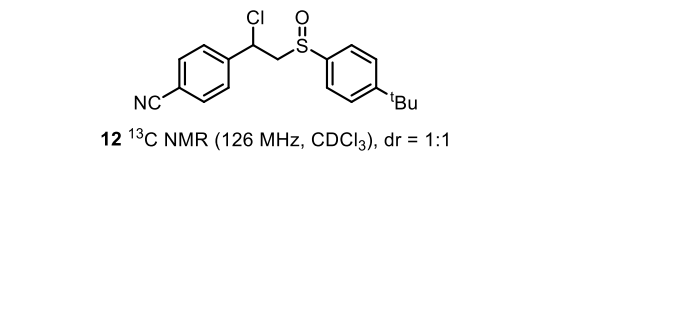


11 ^{19}F NMR (471 MHz, $CDCl_3$), dr = 1.2:1

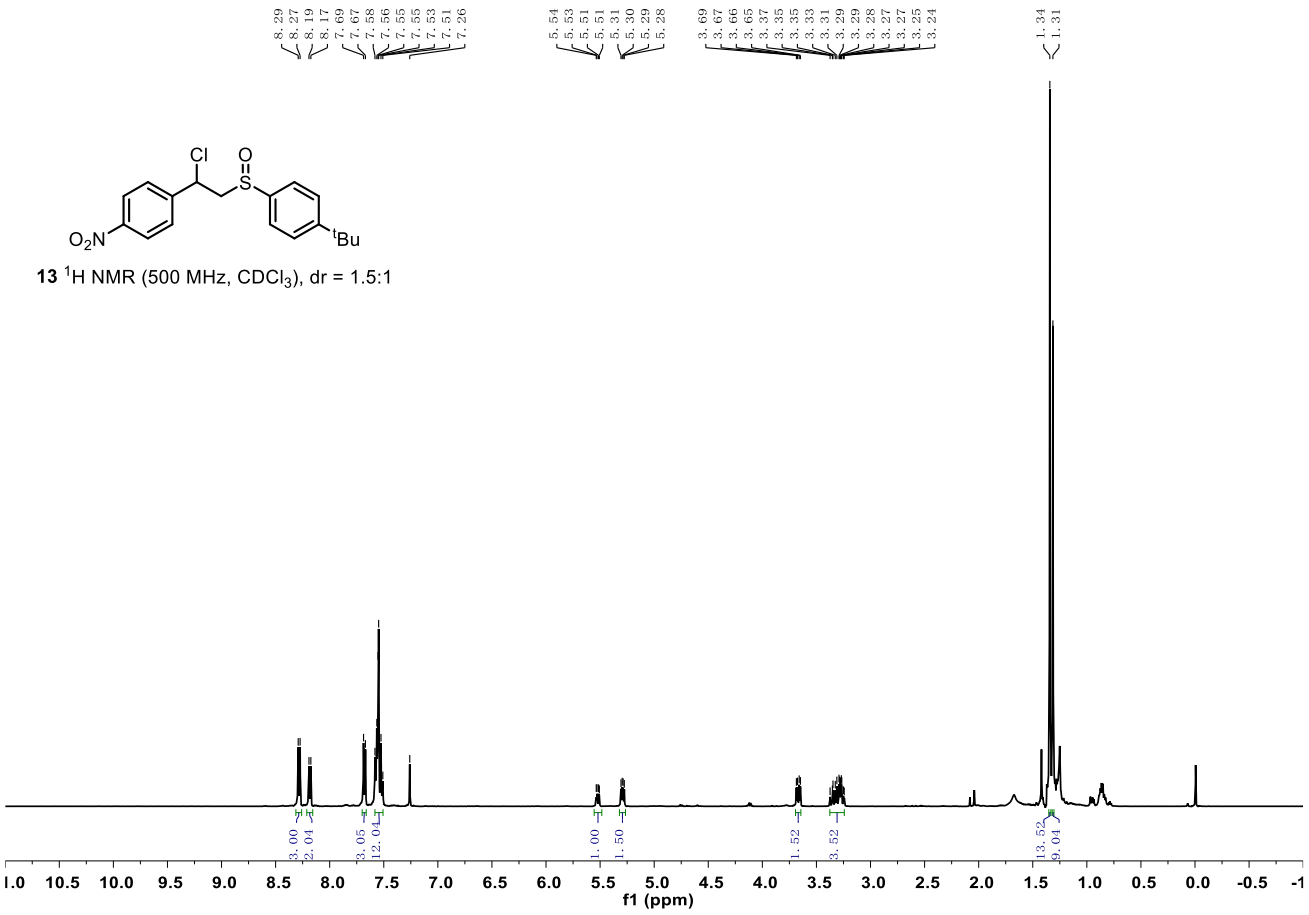




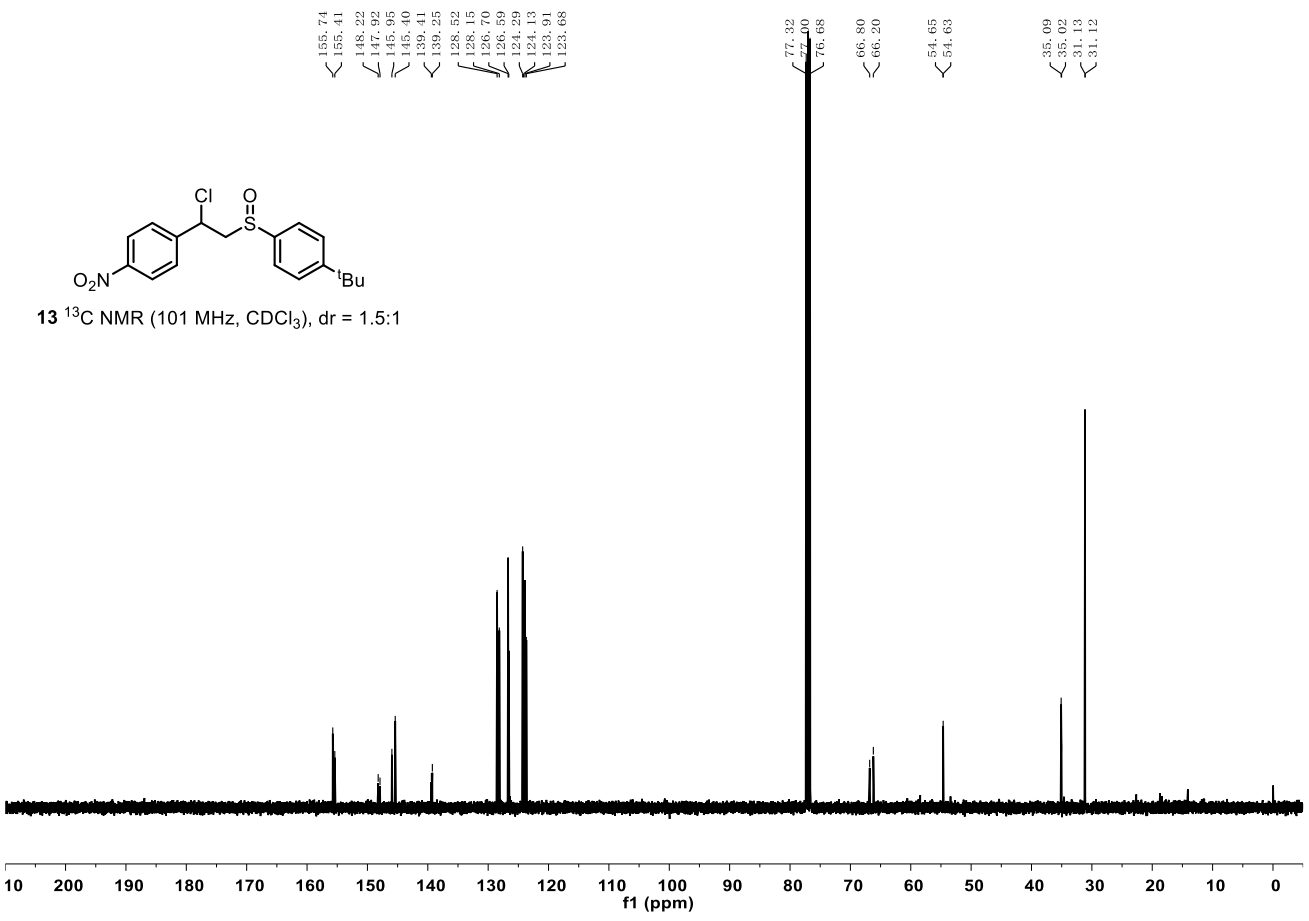
12 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1:1



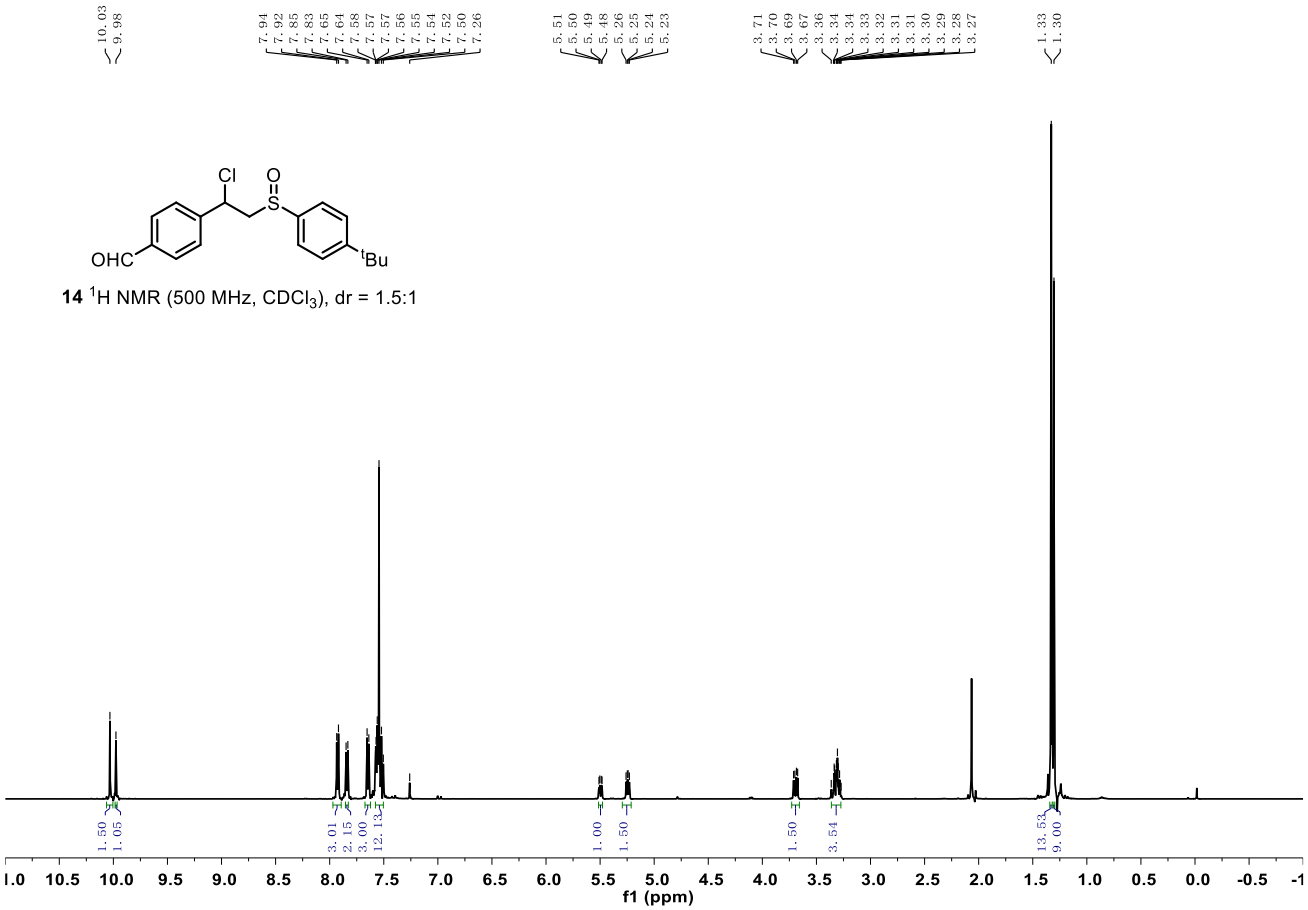
12 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 1:1



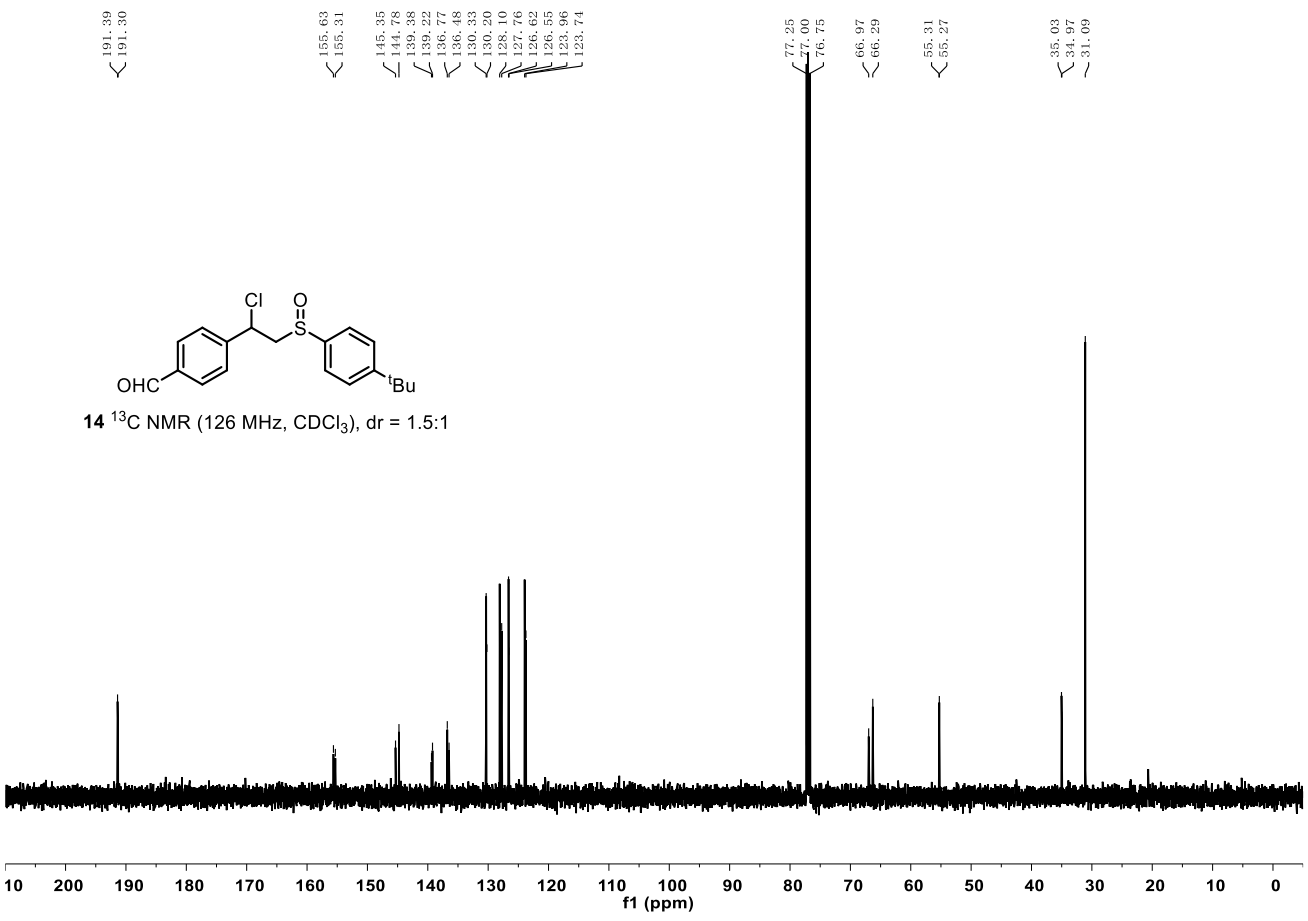
13 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.5:1



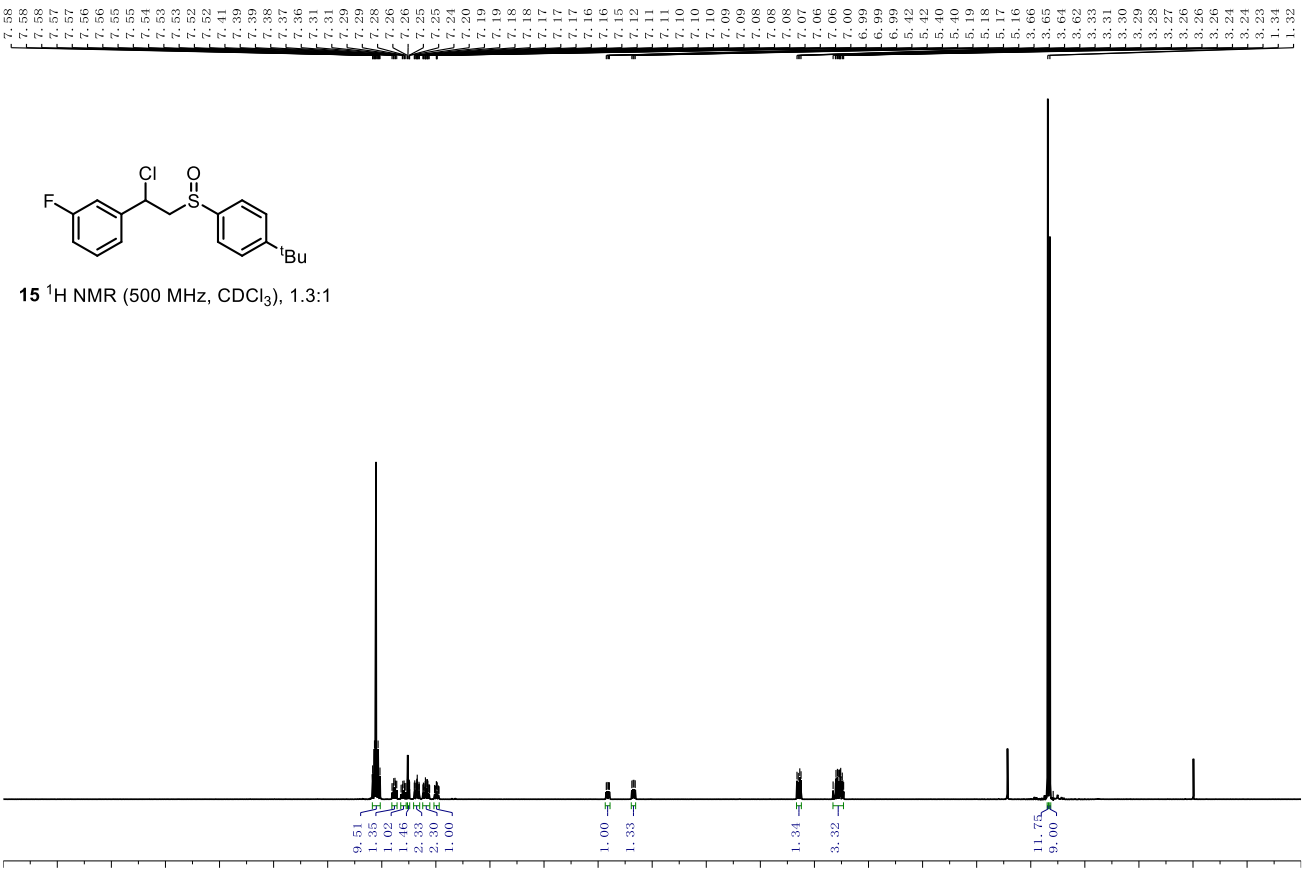
13 ^{13}C NMR (101 MHz, $CDCl_3$), dr = 1.5:1



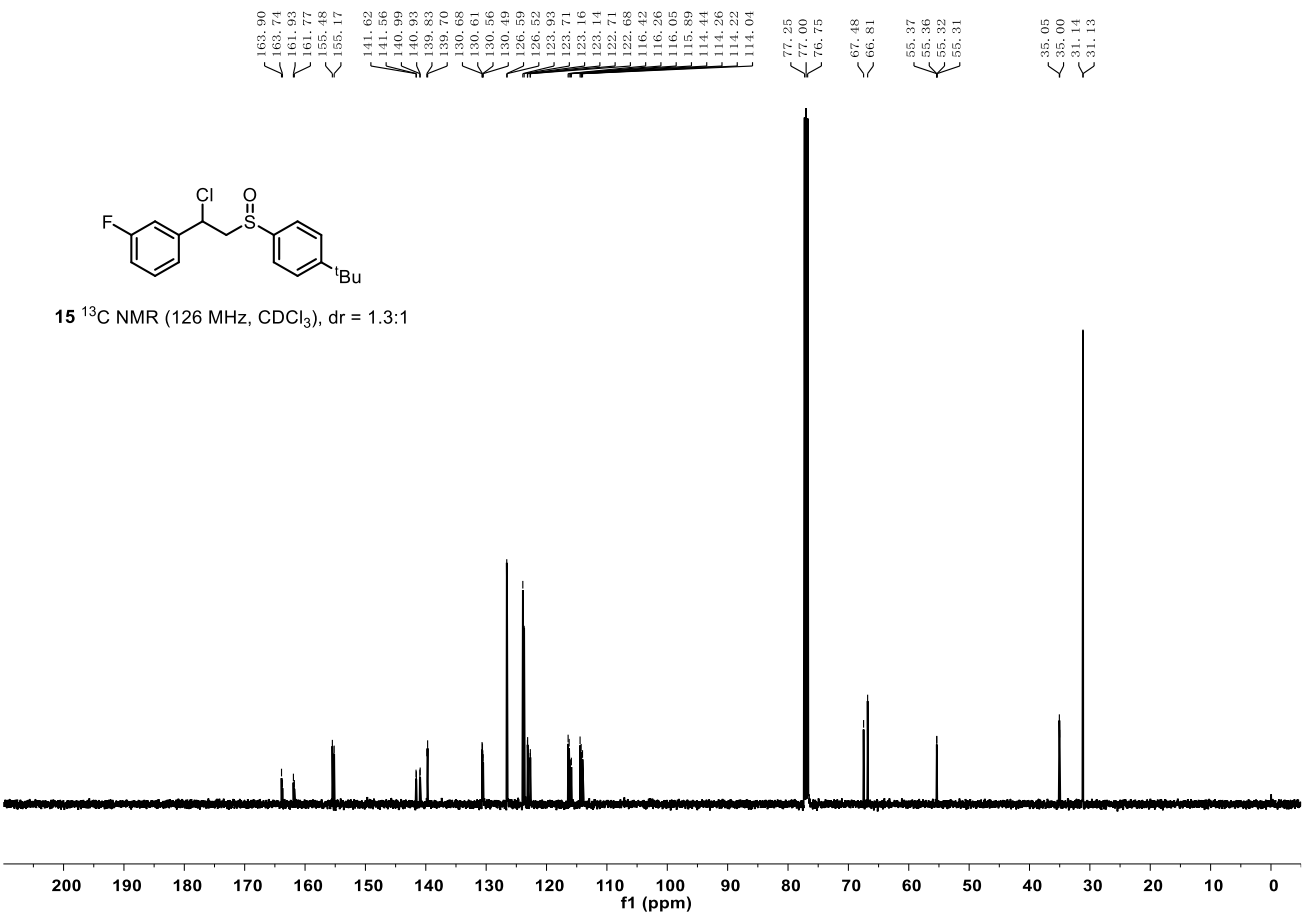
14 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.5:1



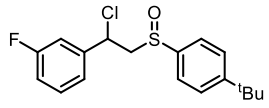
14 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 1.5:1



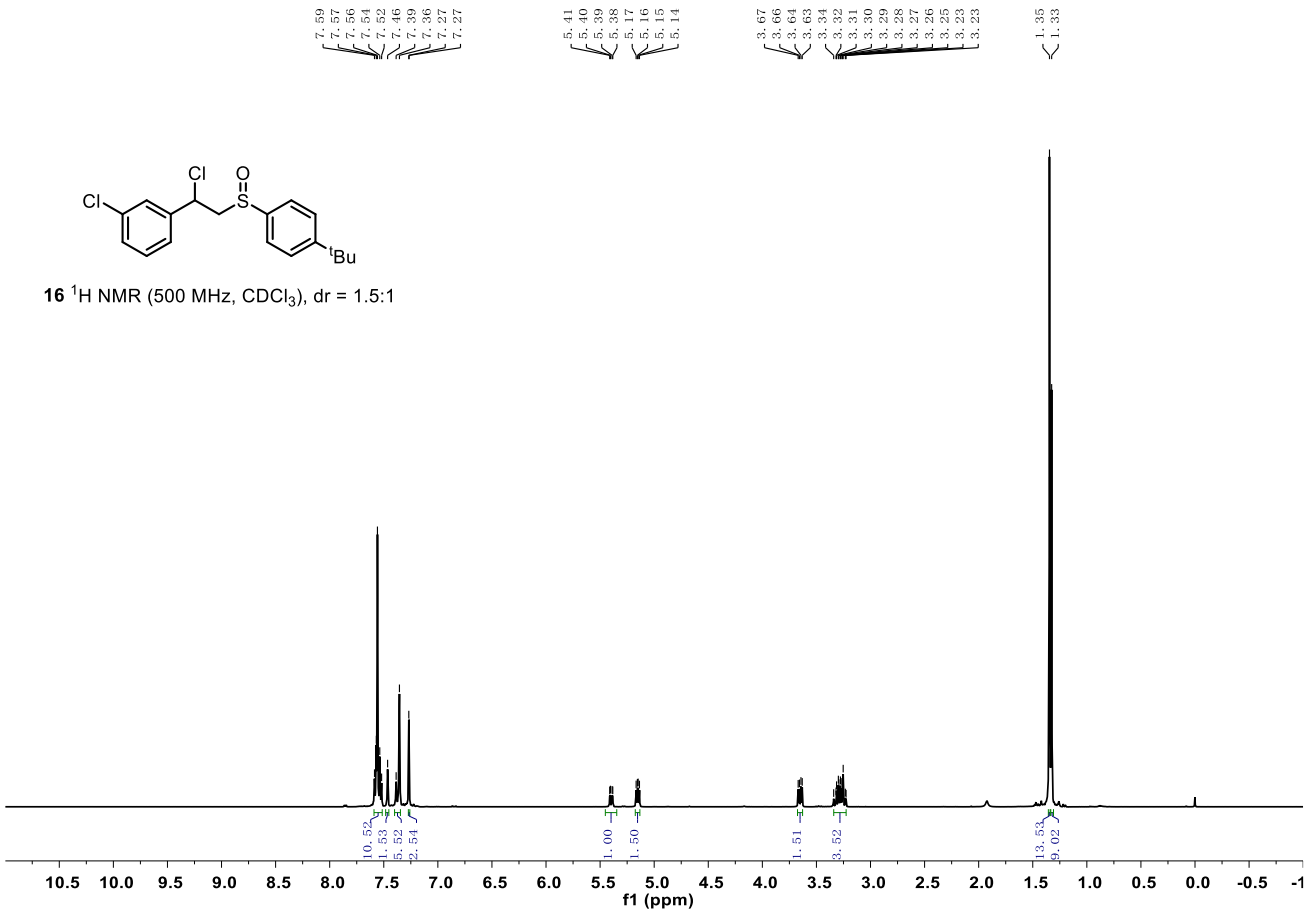
15 ^{1}H NMR (500 MHz, $CDCl_3$), 1.3:1



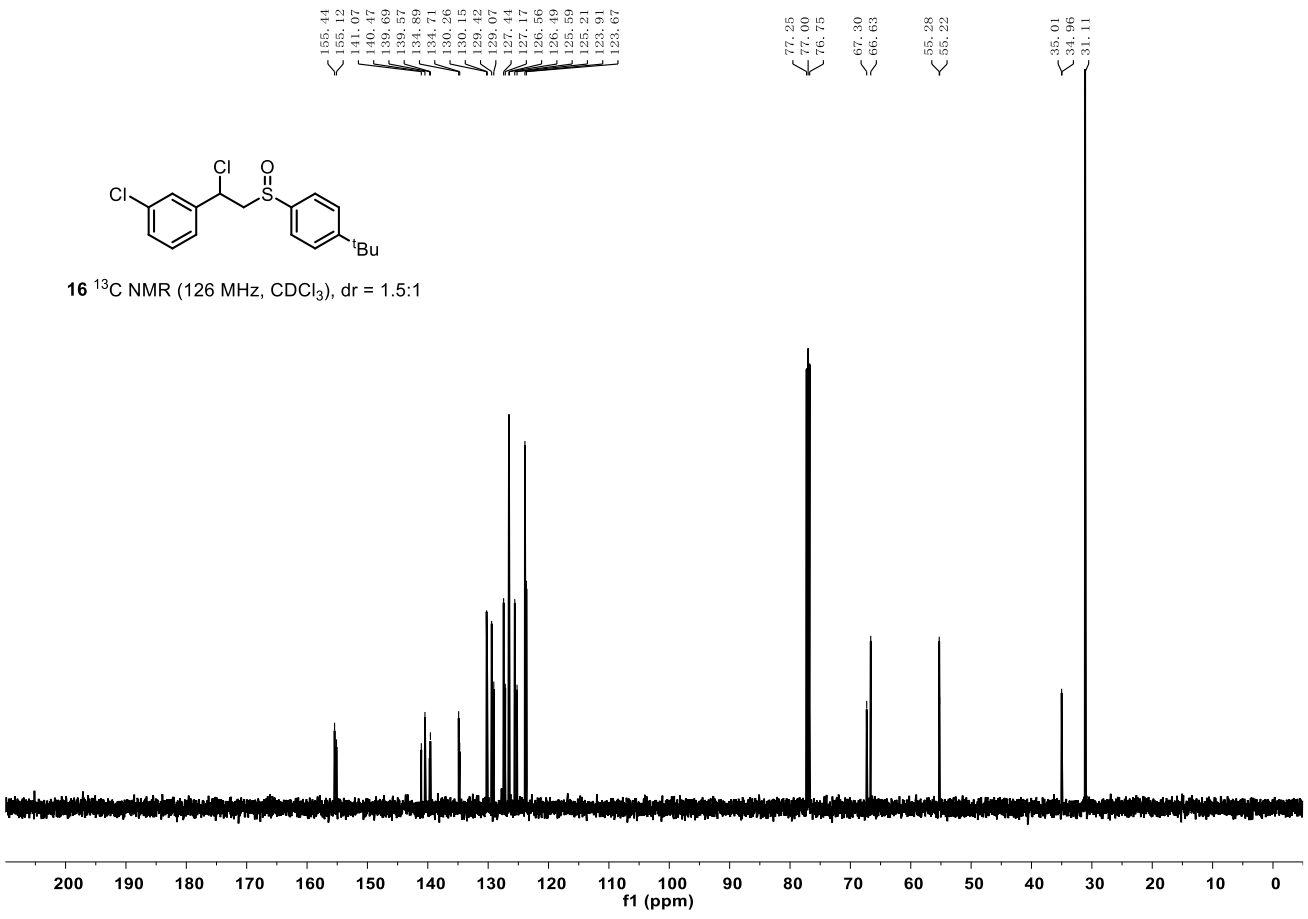
15 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 1.3:1



15 ^{19}F NMR (471 MHz, $CDCl_3$), dr = 1.3:1

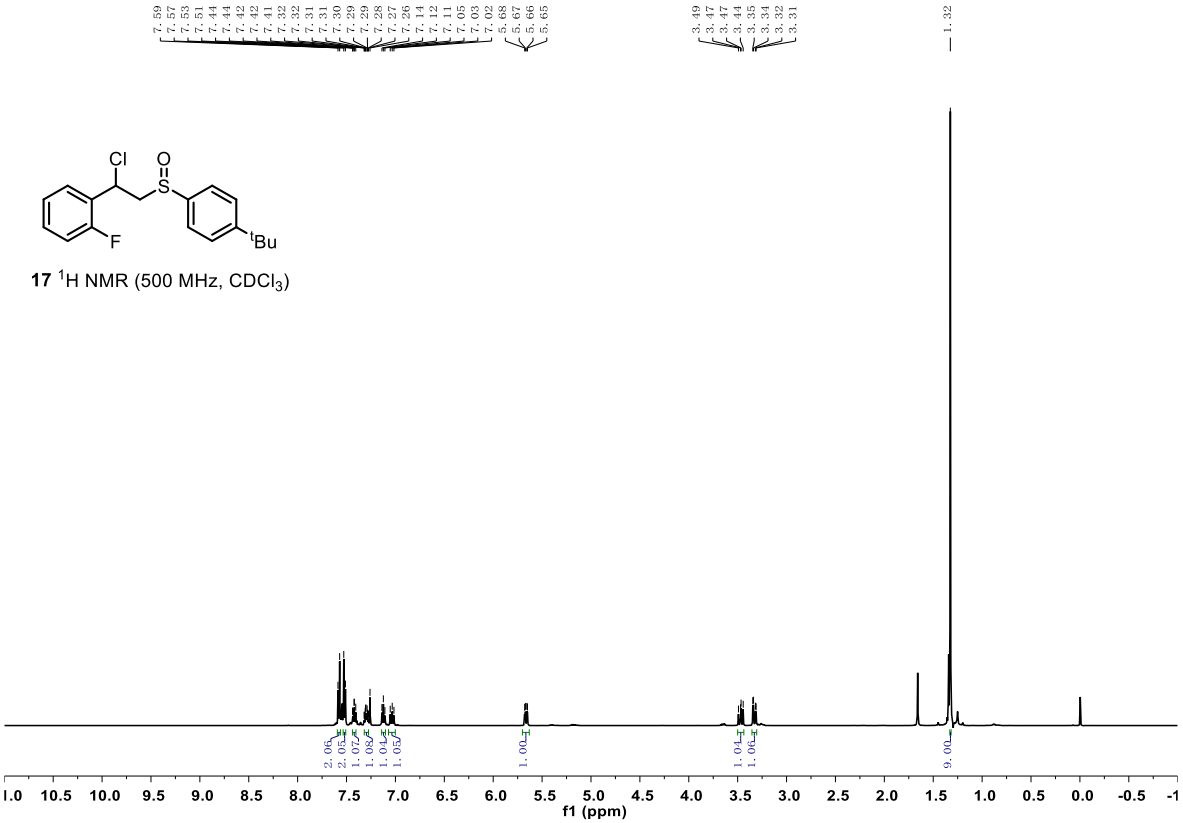


16 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.5:1

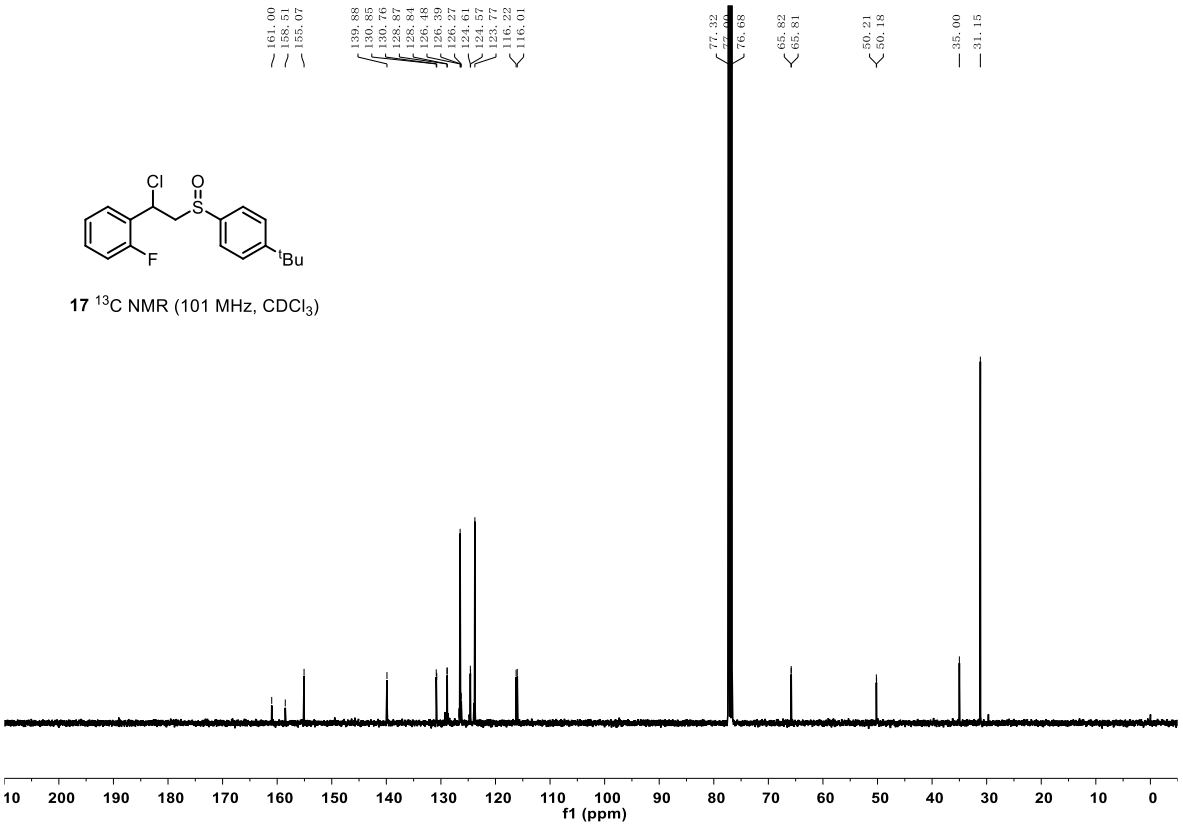


16 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 1.5:1

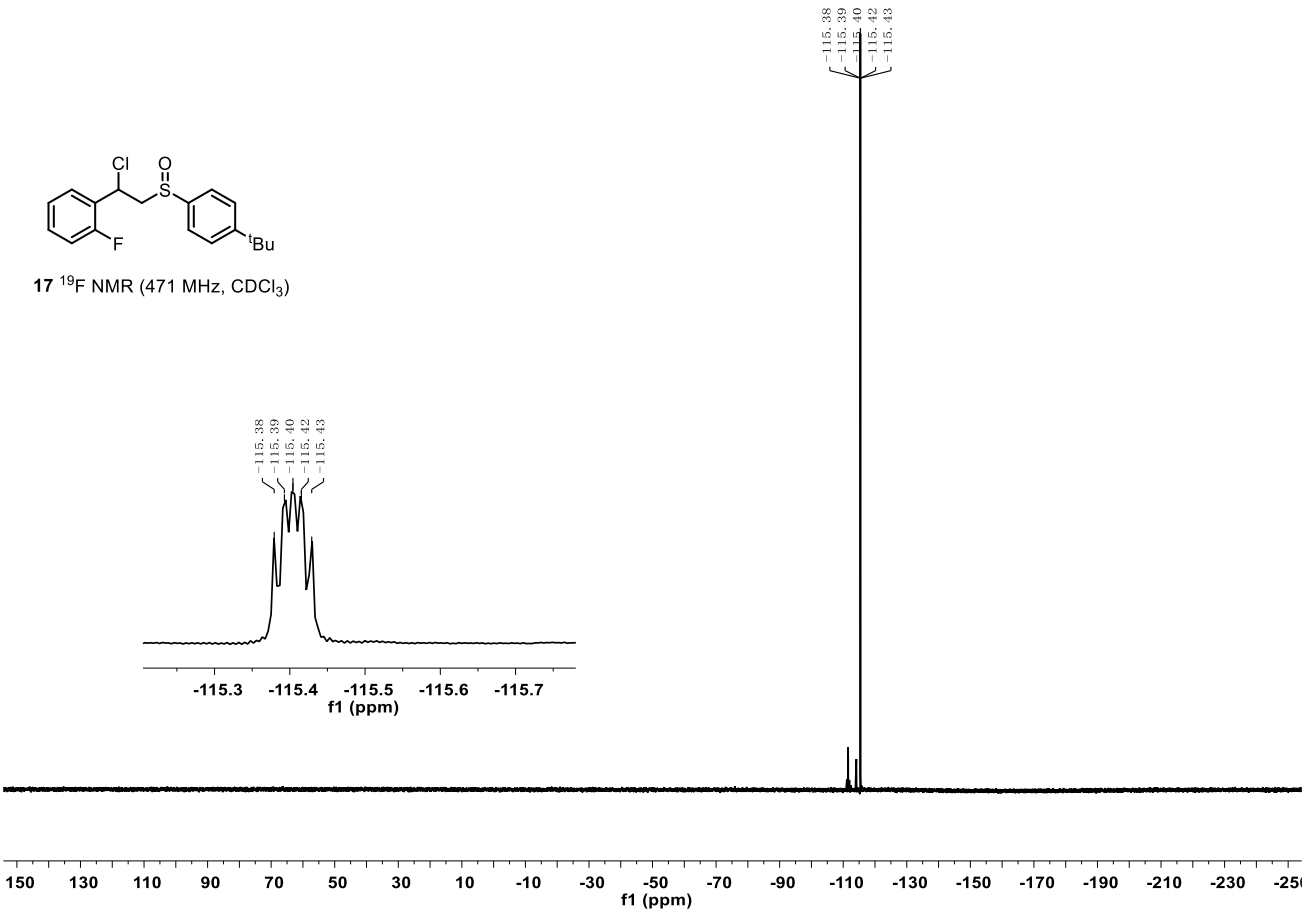
Diastereoisomer 1 (**17**)



17 ^{1}H NMR (500 MHz, $CDCl_3$)

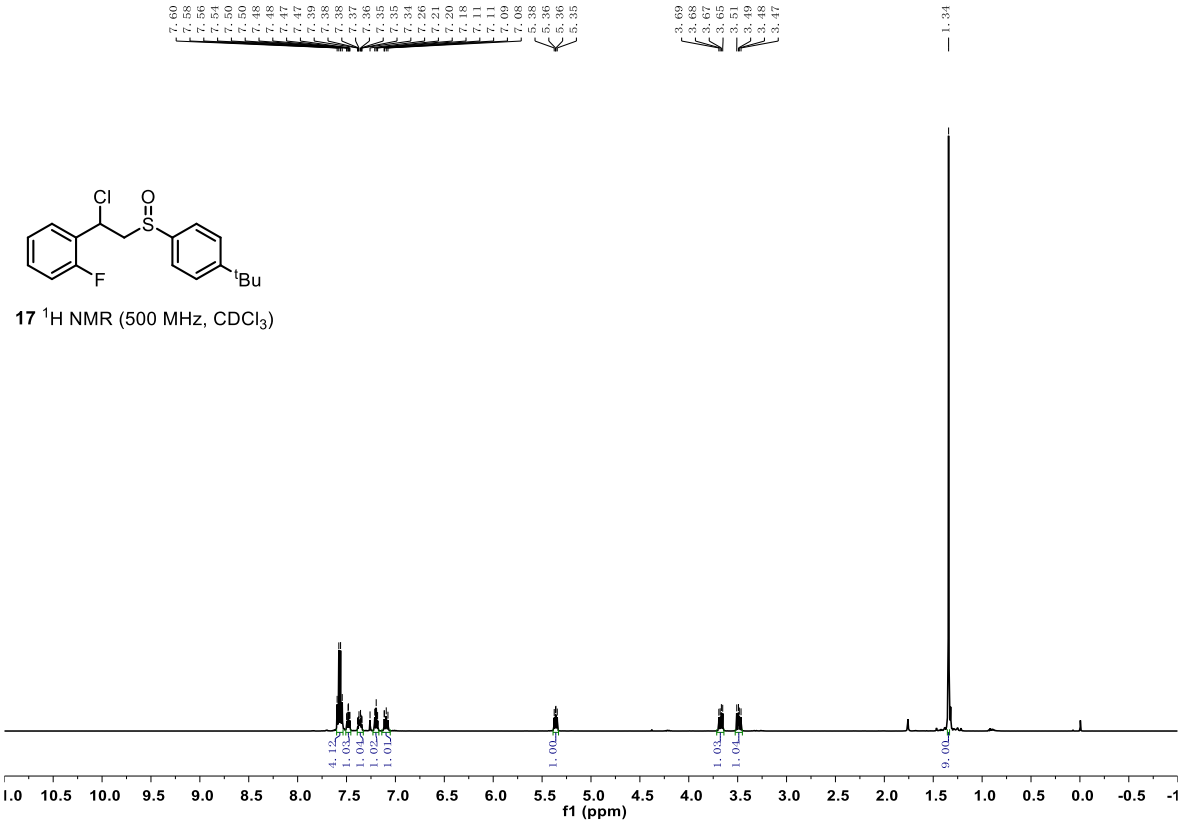


17 ^{13}C NMR (101 MHz, $CDCl_3$)

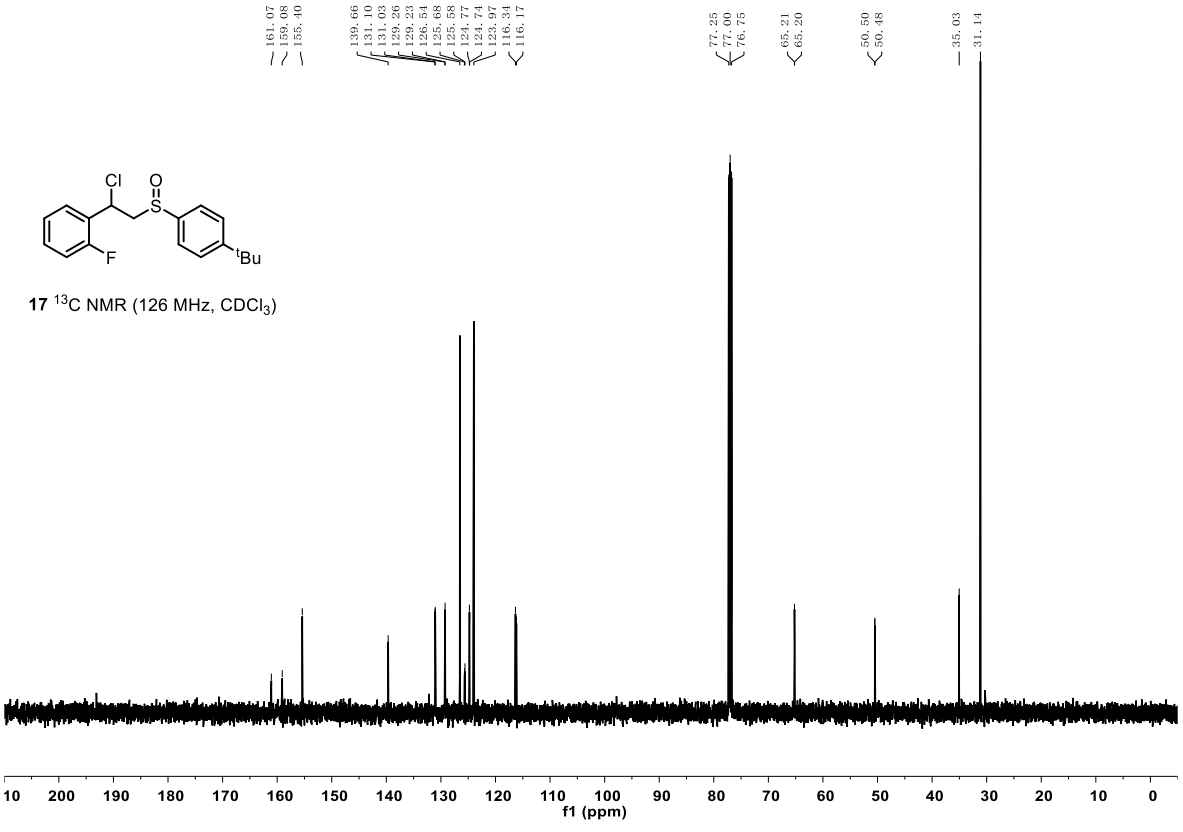


17 ^{19}F NMR (471 MHz, $CDCl_3$)

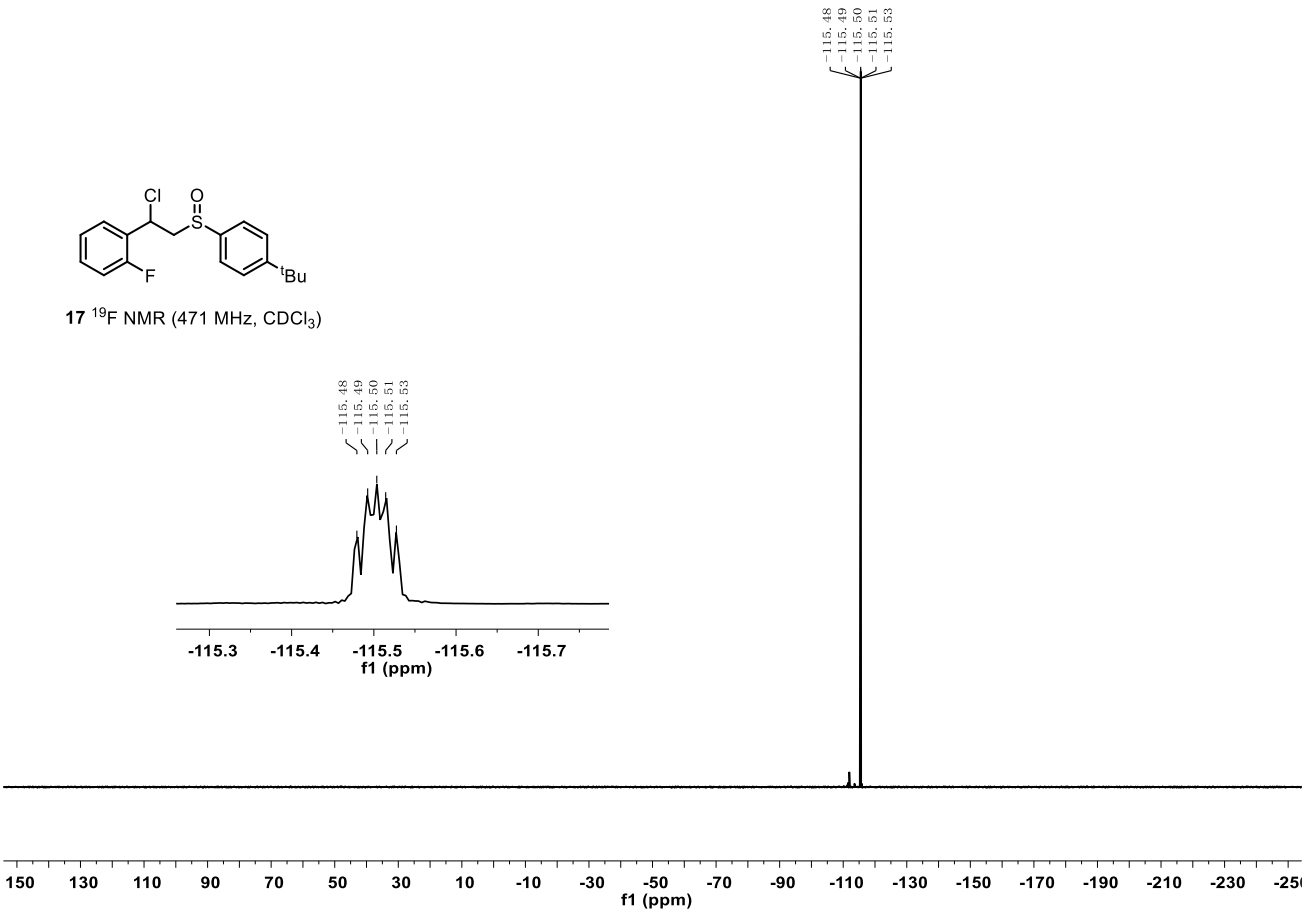
Diastereoisomer 2 (**17**)



17 ^{1}H NMR (500 MHz, $CDCl_3$)

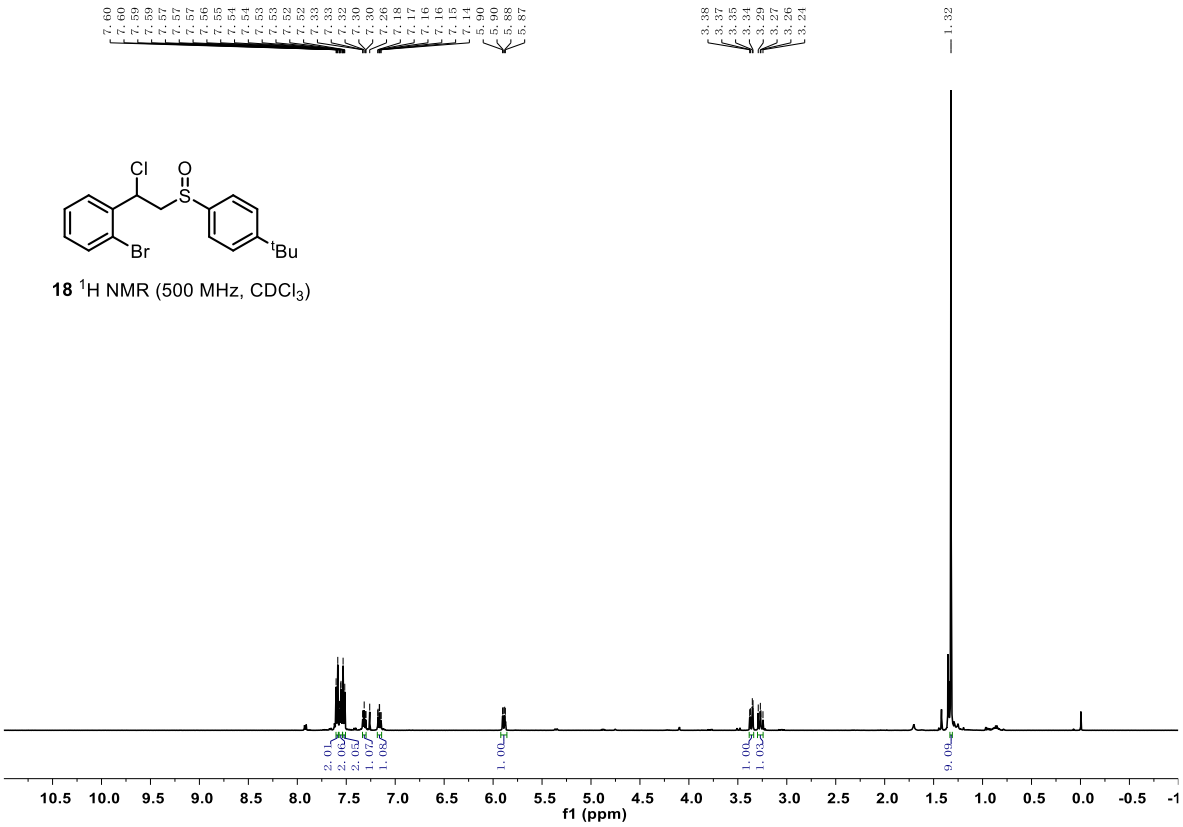


17 ^{13}C NMR (126 MHz, $CDCl_3$)

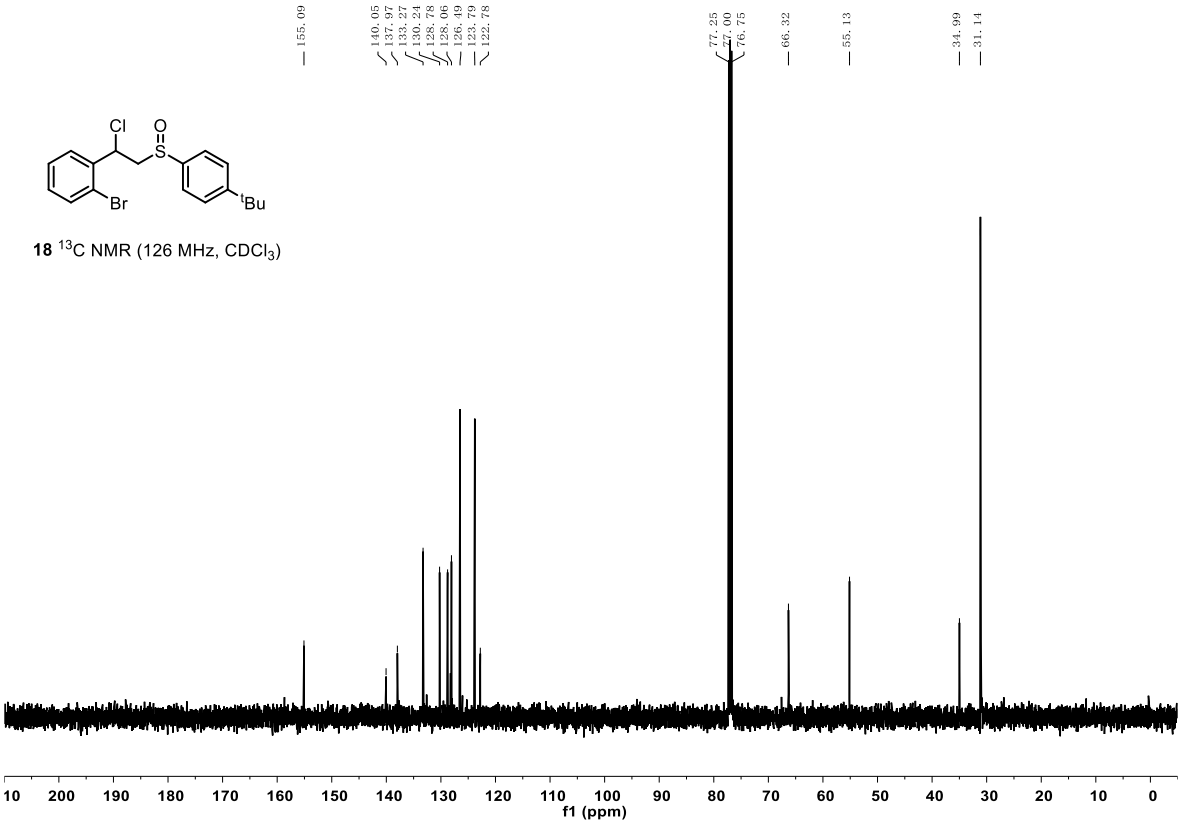


17 ^{19}F NMR (471 MHz, $CDCl_3$)

Diastereoisomer 1 (**18**)

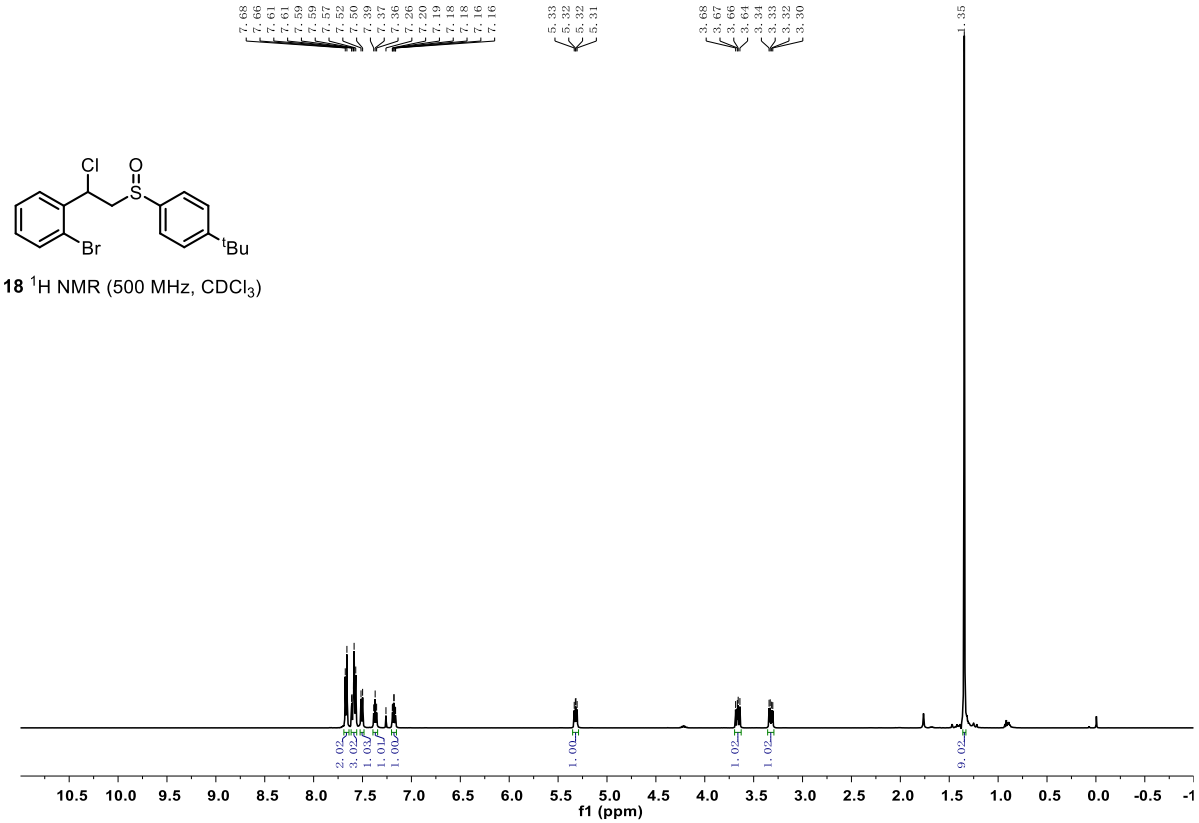


18 ^{1}H NMR (500 MHz, $CDCl_3$)

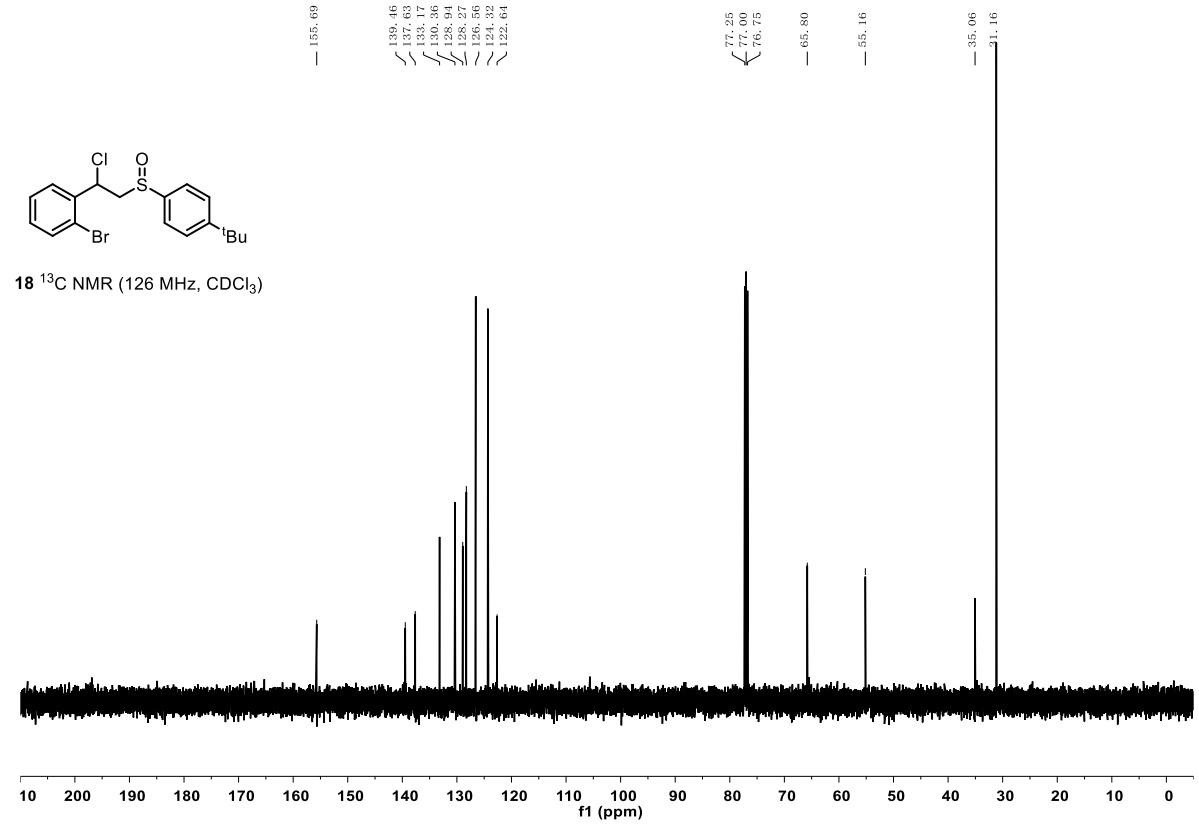


18 ^{13}C NMR (126 MHz, $CDCl_3$)

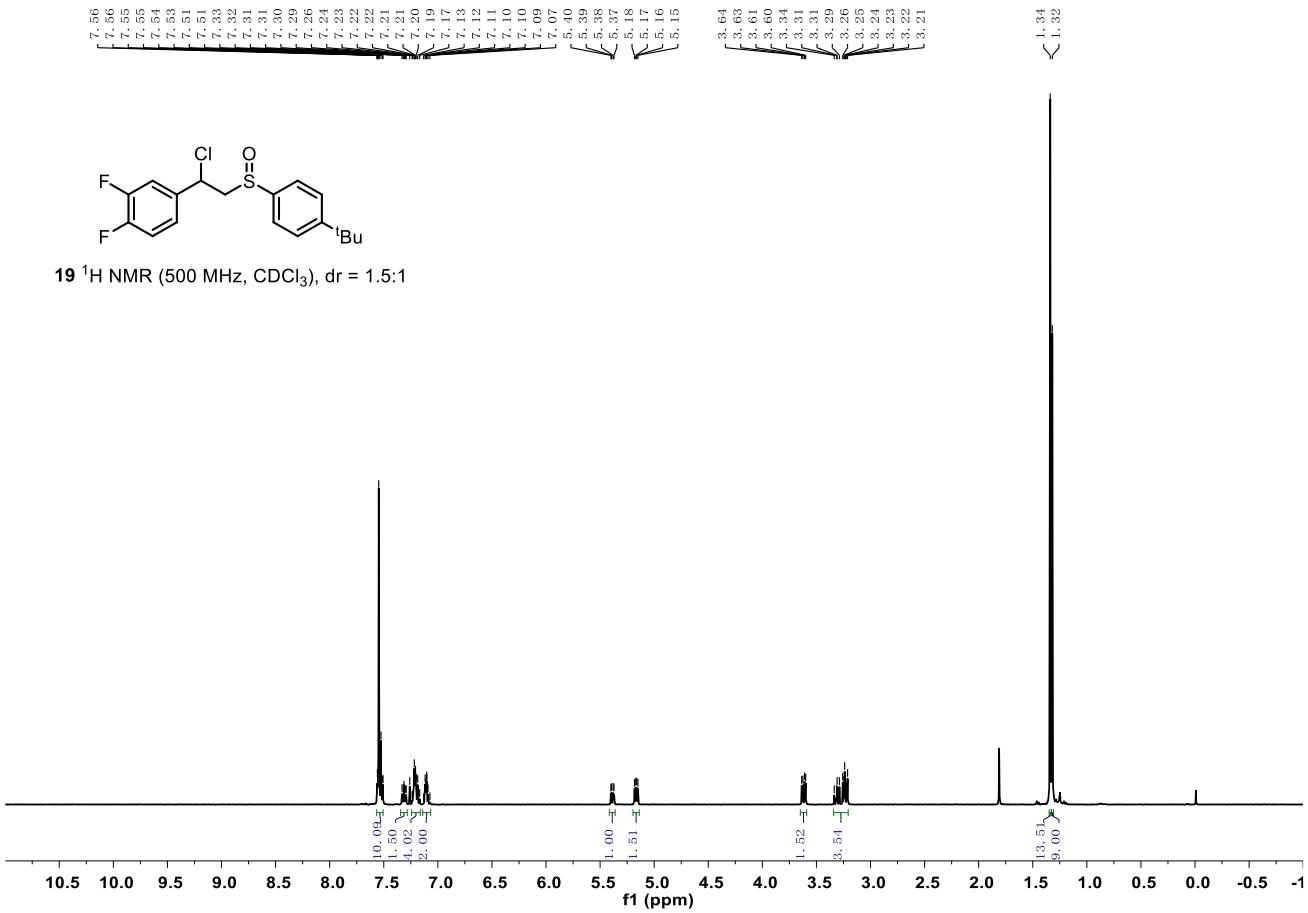
Diastereoisomer 2 (**18**)



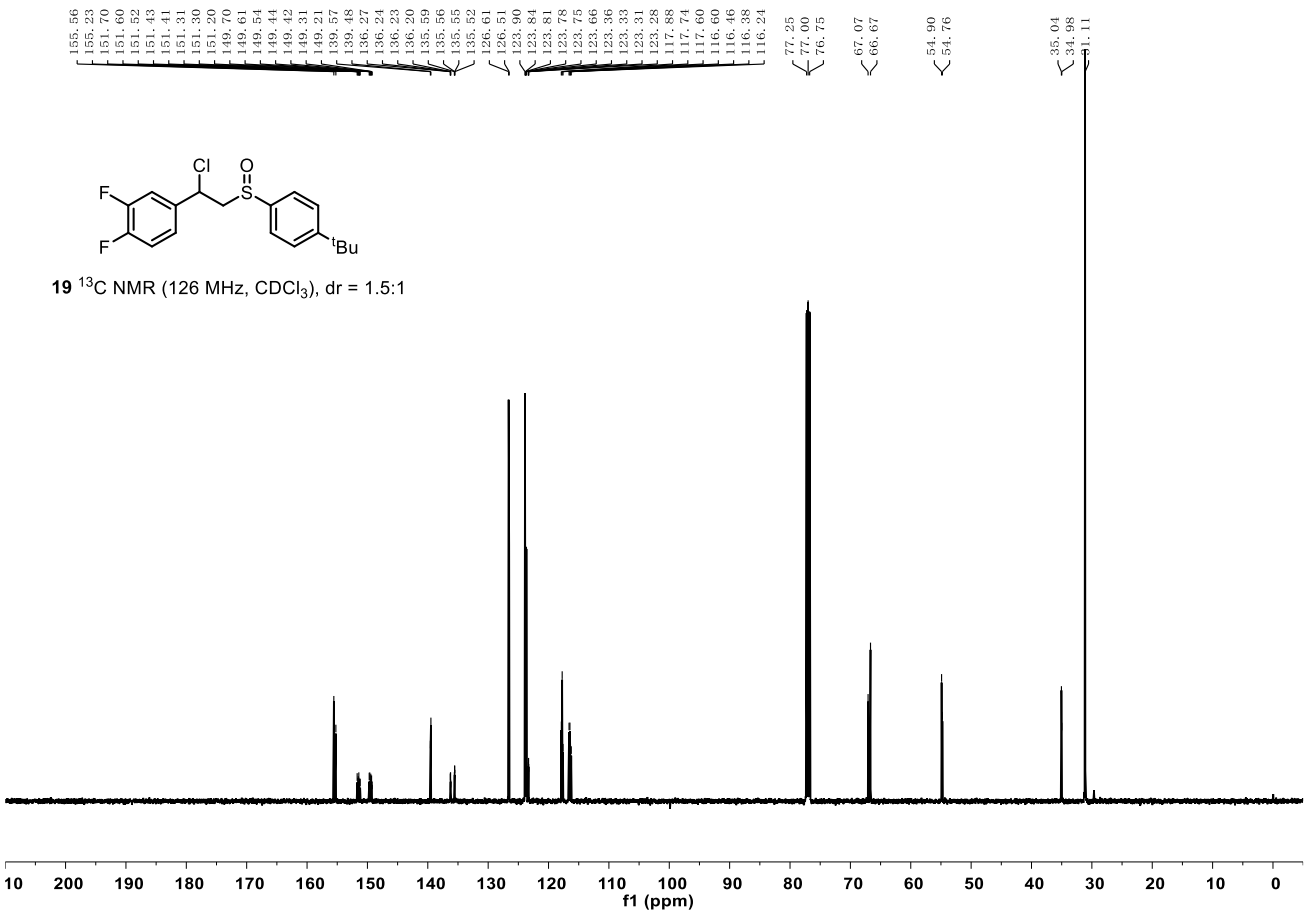
18 ^{1}H NMR (500 MHz, $CDCl_3$)



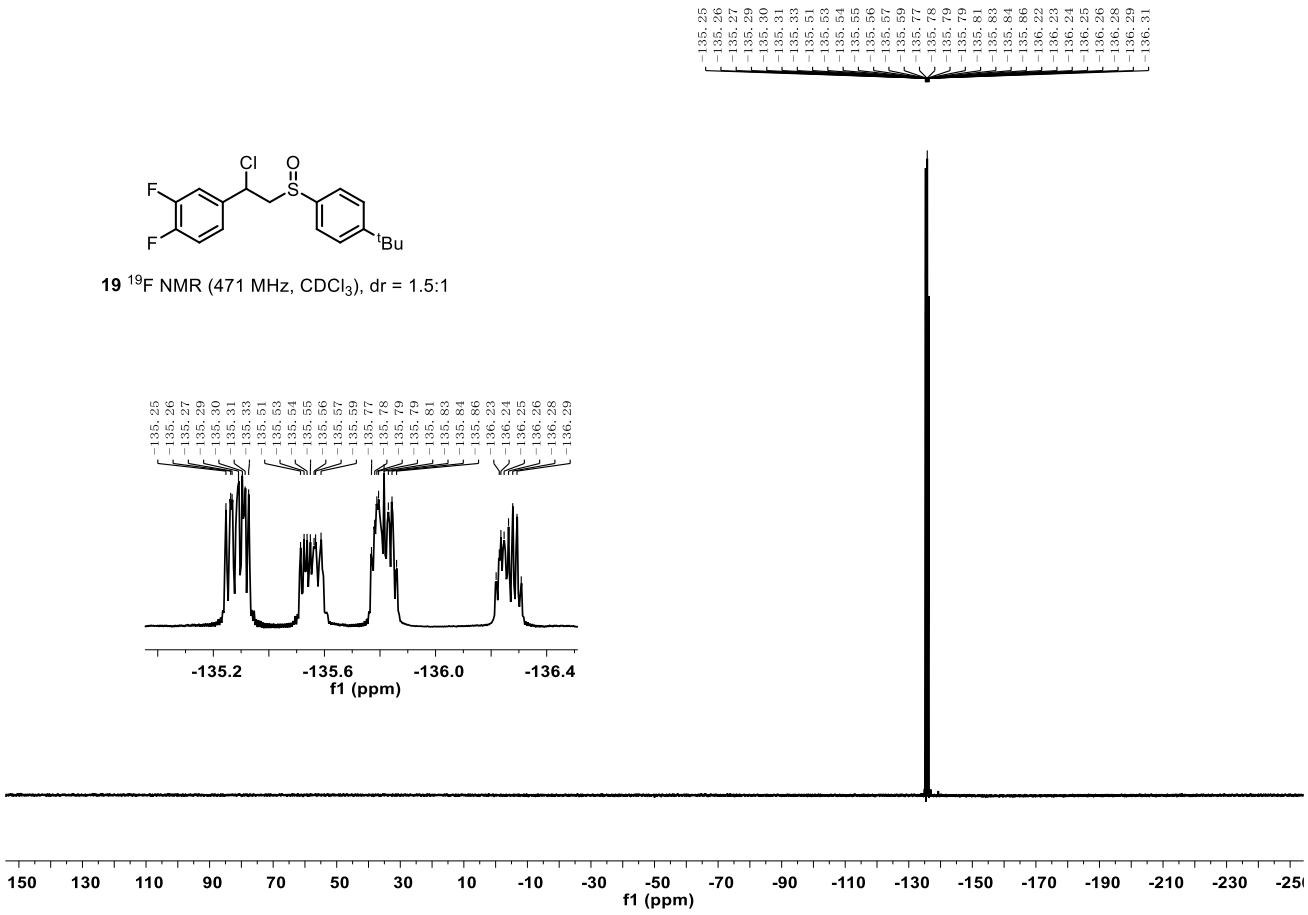
18 ^{13}C NMR (126 MHz, $CDCl_3$)



19 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.5:1

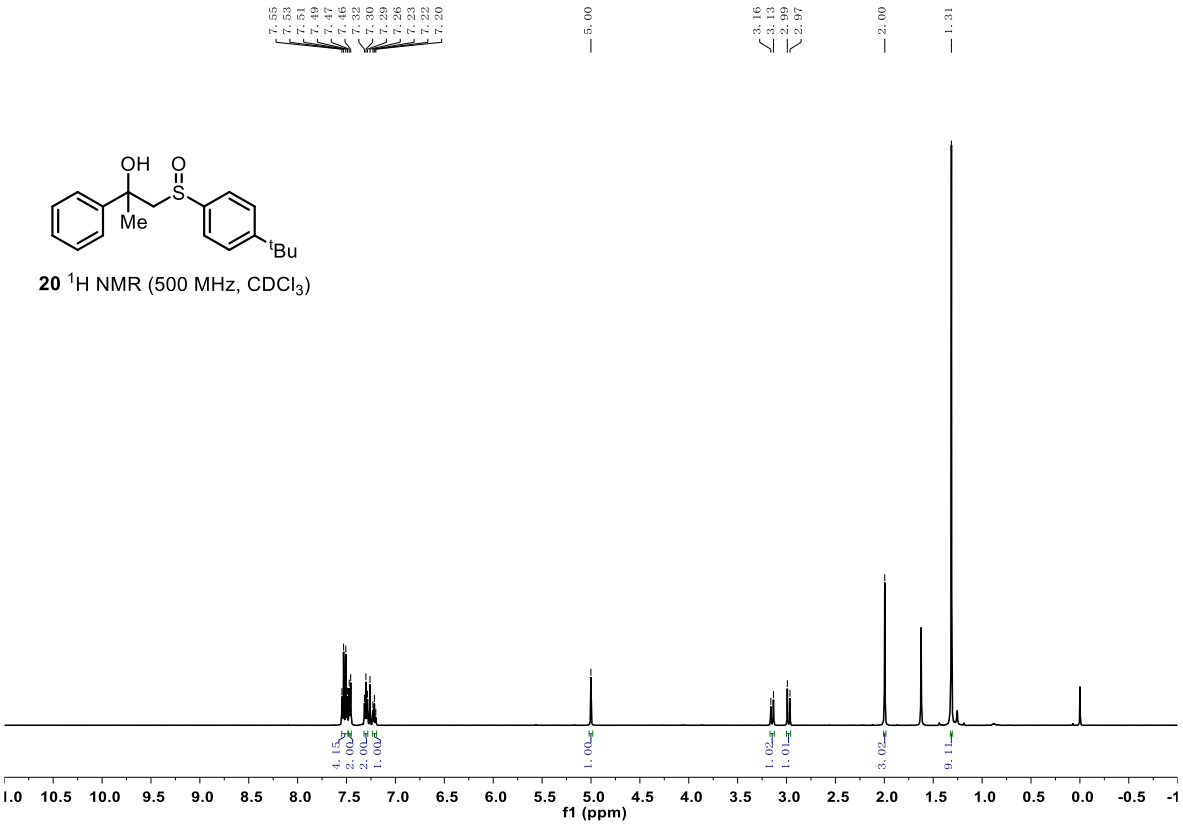


19 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 1.5:1

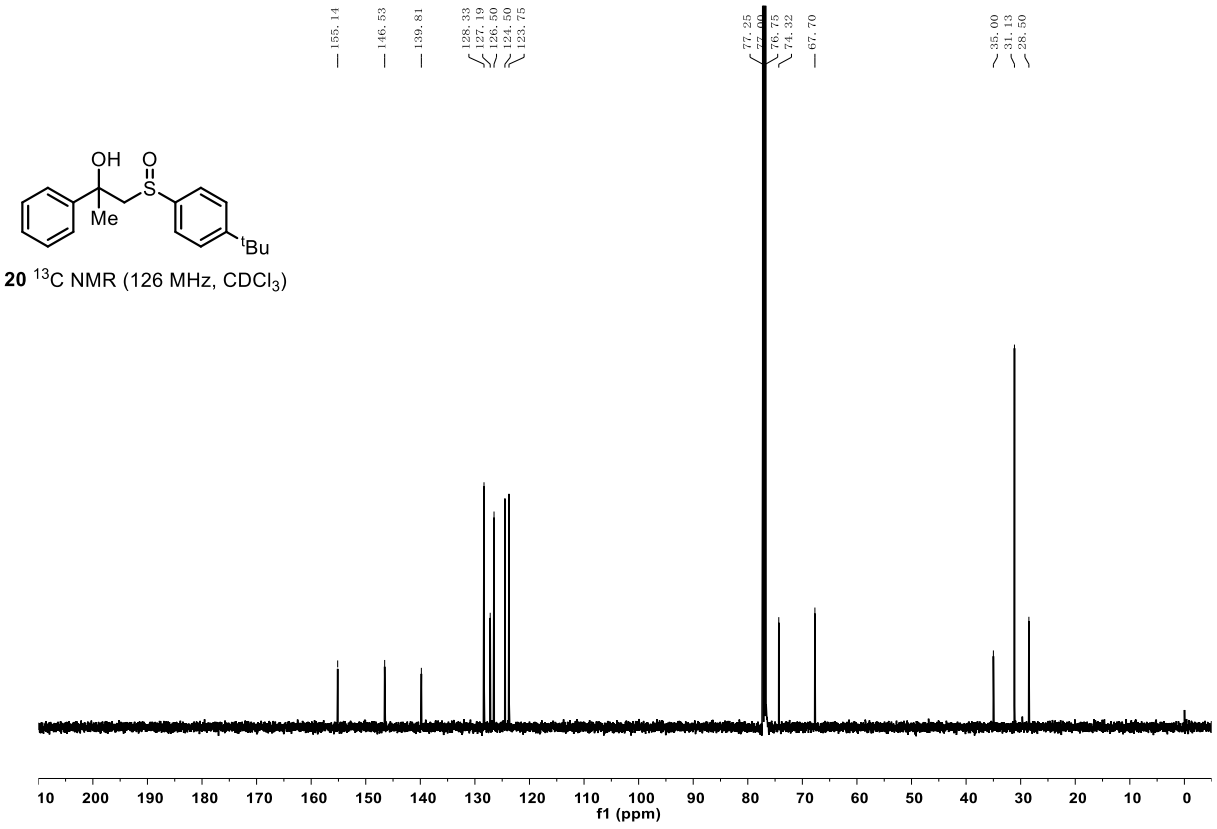


19 ^{19}F NMR (471 MHz, $CDCl_3$), dr = 1.5:1

Diastereoisomer 1 (**20**)

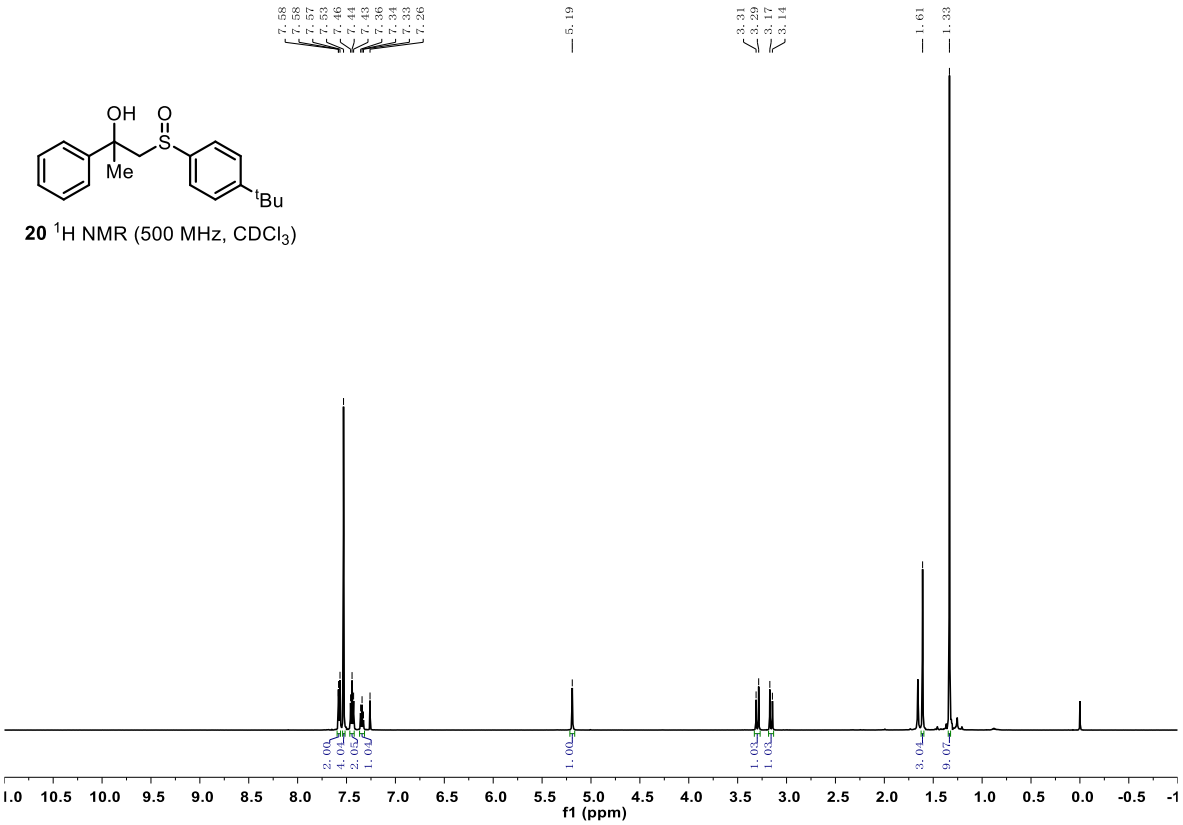


20 ^{1}H NMR (500 MHz, $CDCl_3$)

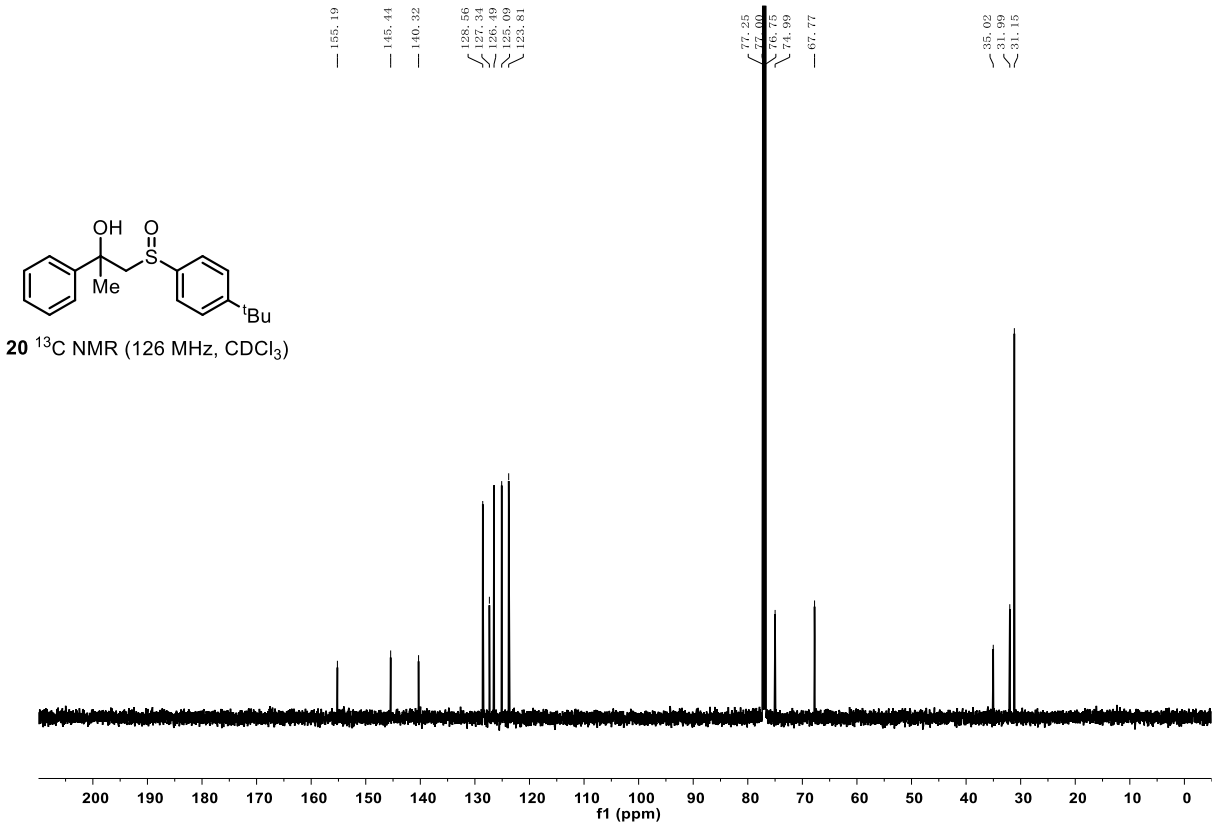


20 ^{13}C NMR (126 MHz, $CDCl_3$)

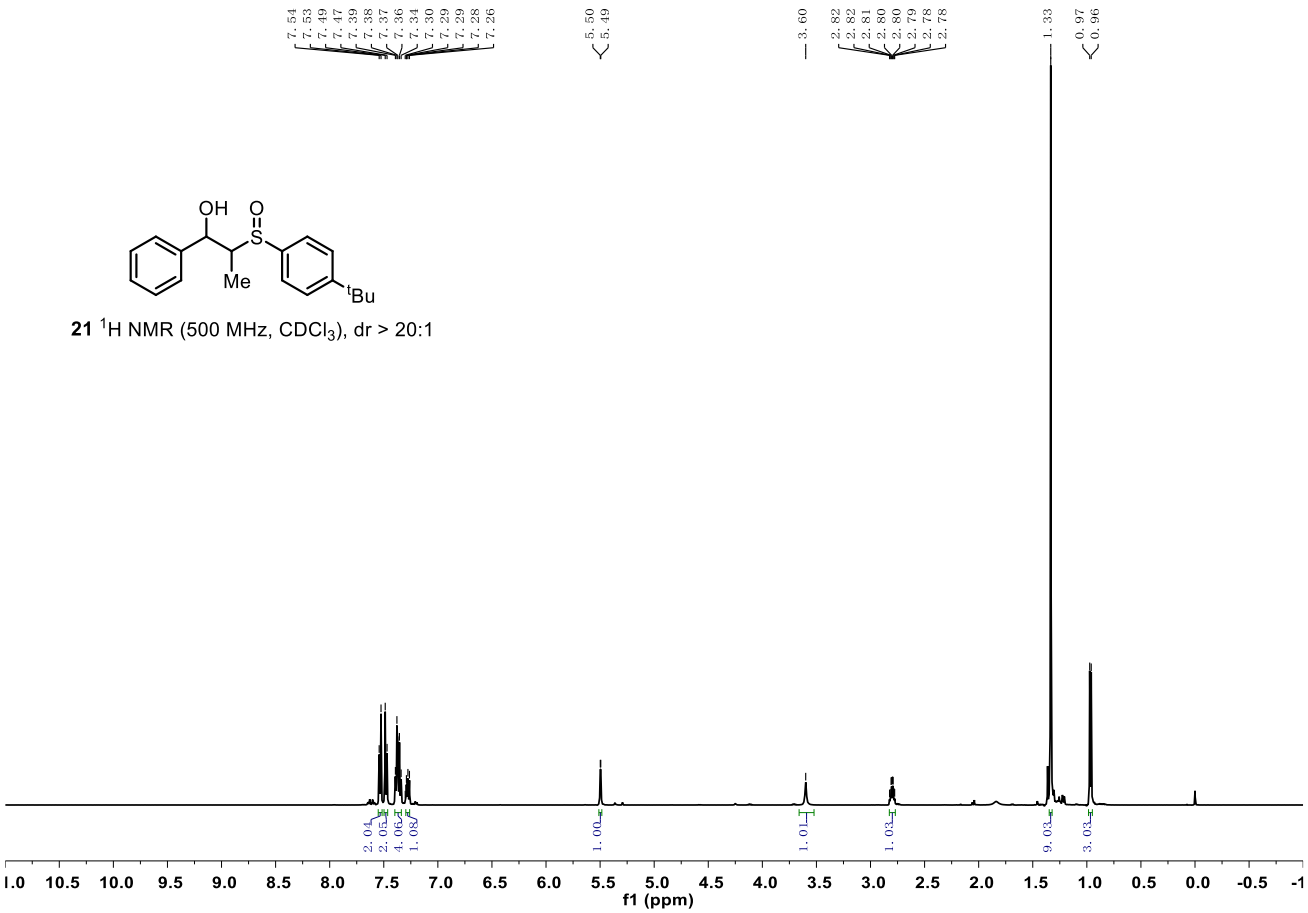
Diastereoisomer 2 (**20**)



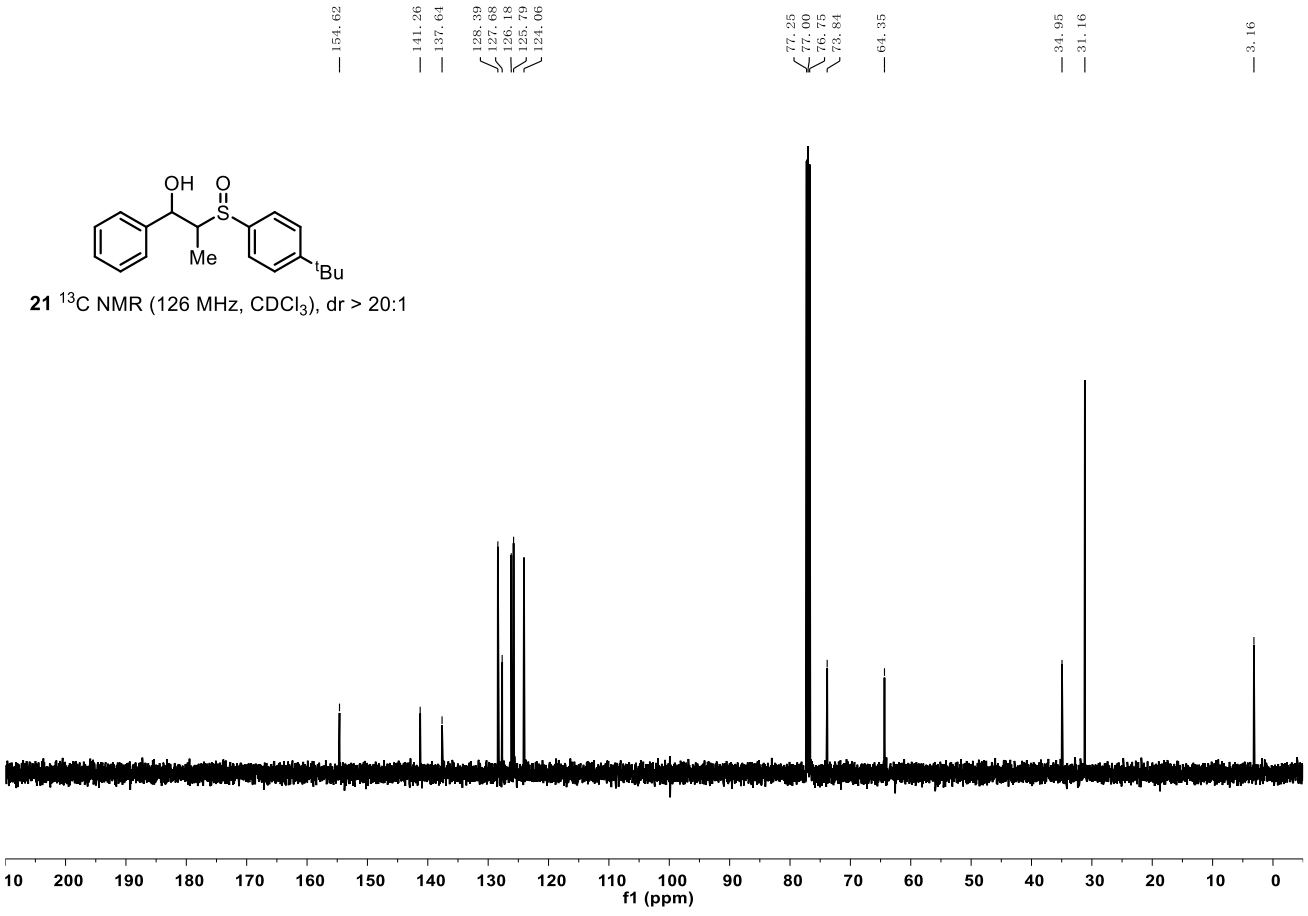
20 ^{1}H NMR (500 MHz, $CDCl_3$)



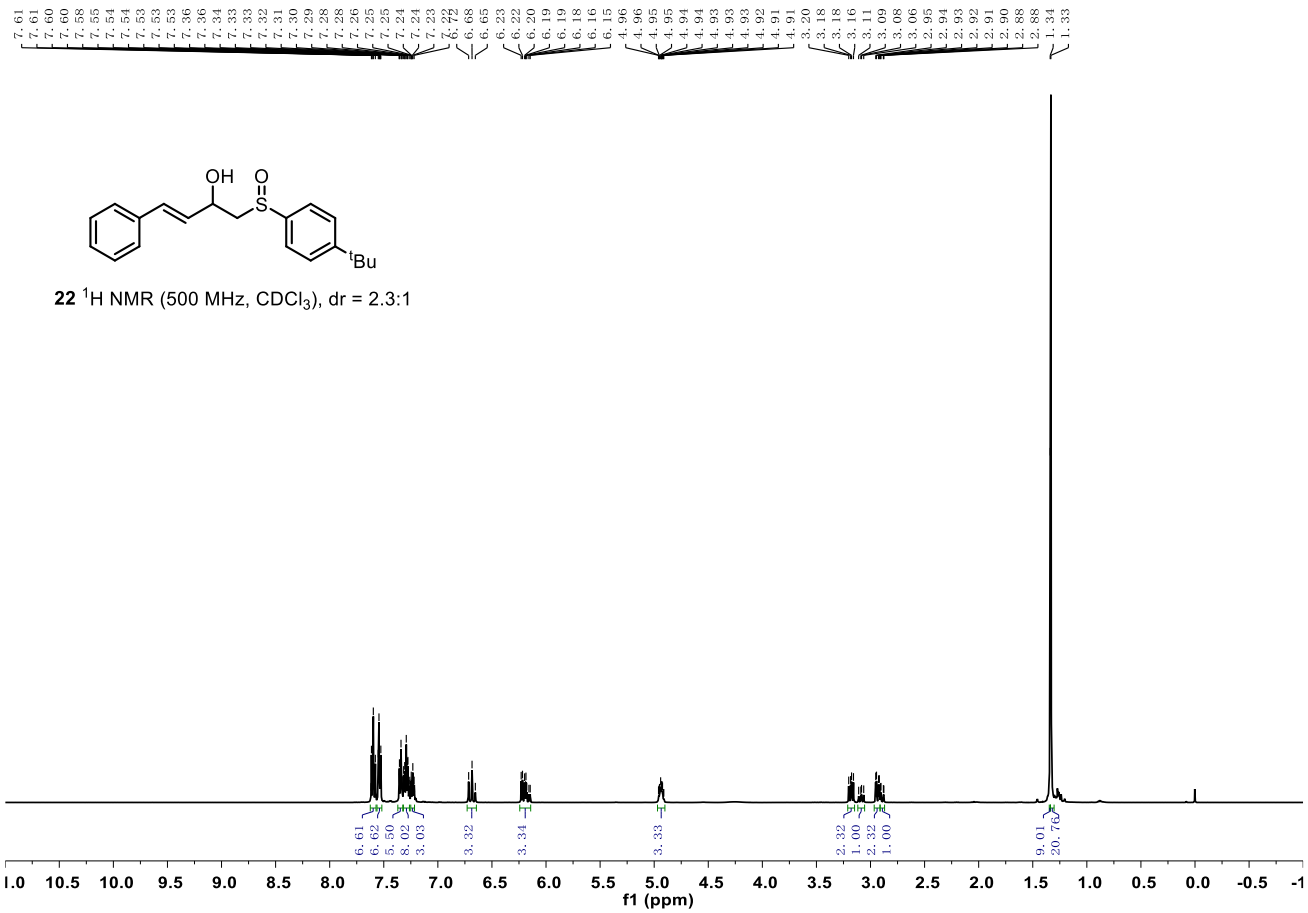
20 ^{13}C NMR (126 MHz, $CDCl_3$)



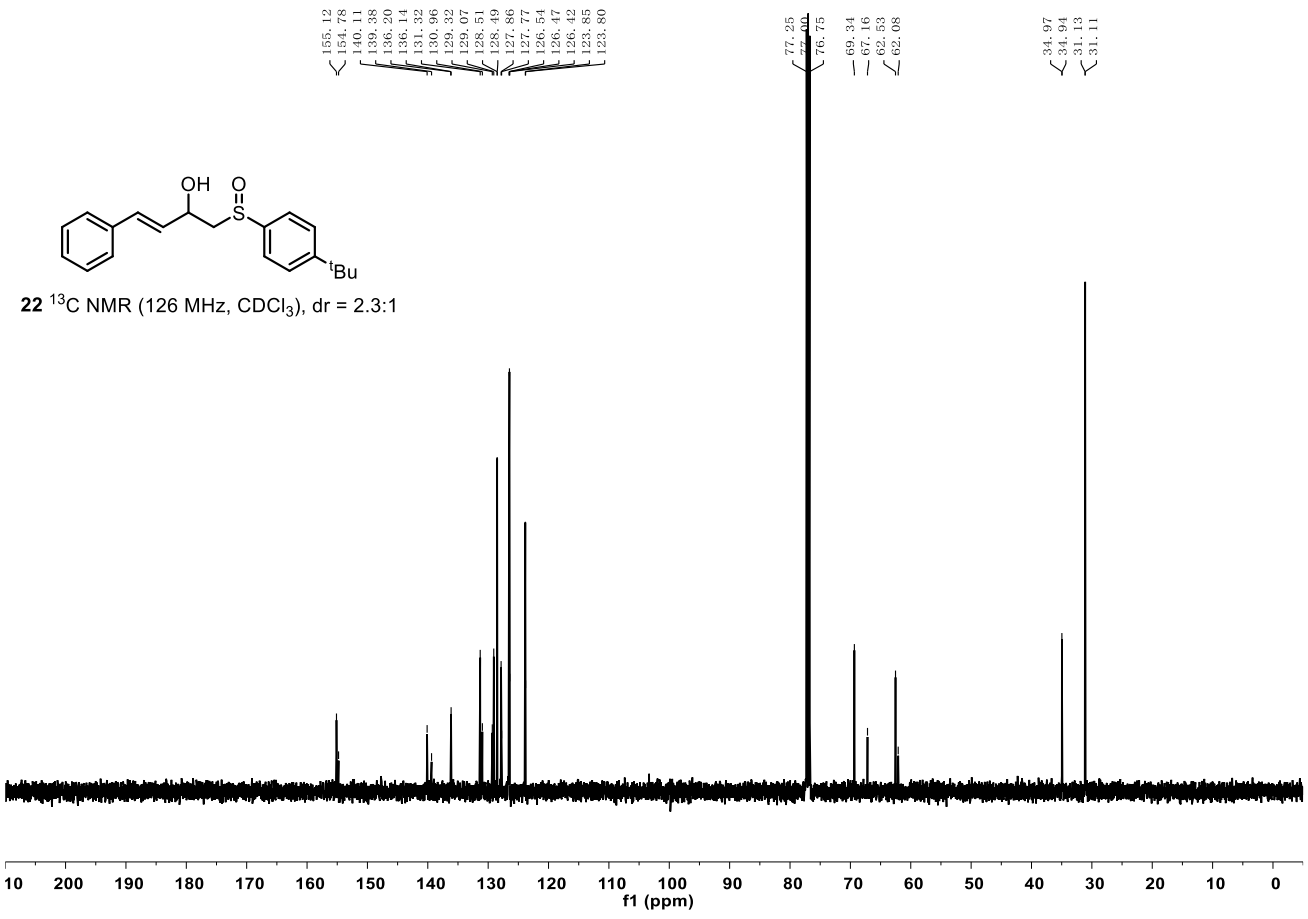
21 ^{1}H NMR (500 MHz, $CDCl_3$), dr > 20:1



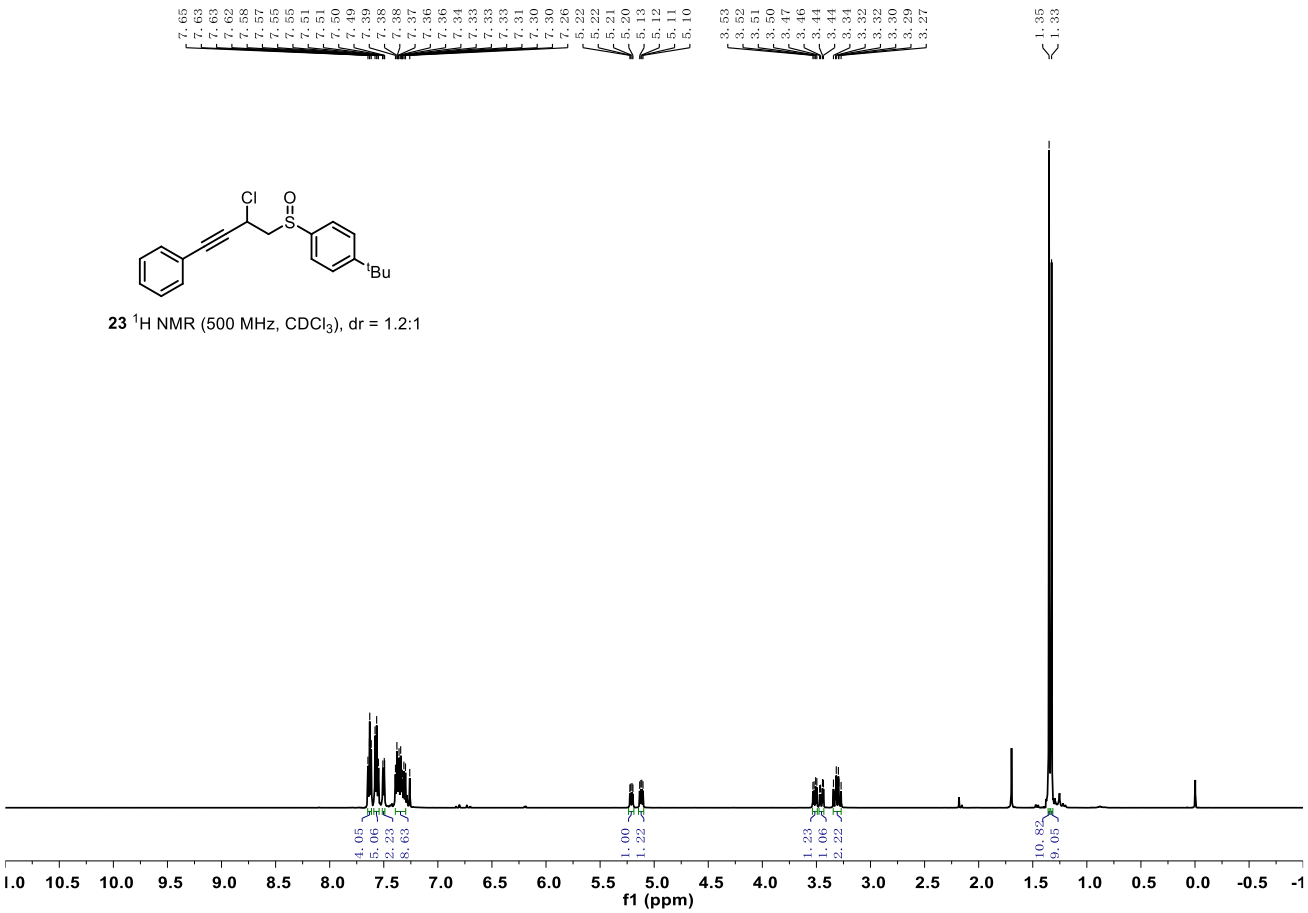
21 ^{13}C NMR (126 MHz, $CDCl_3$), dr > 20:1



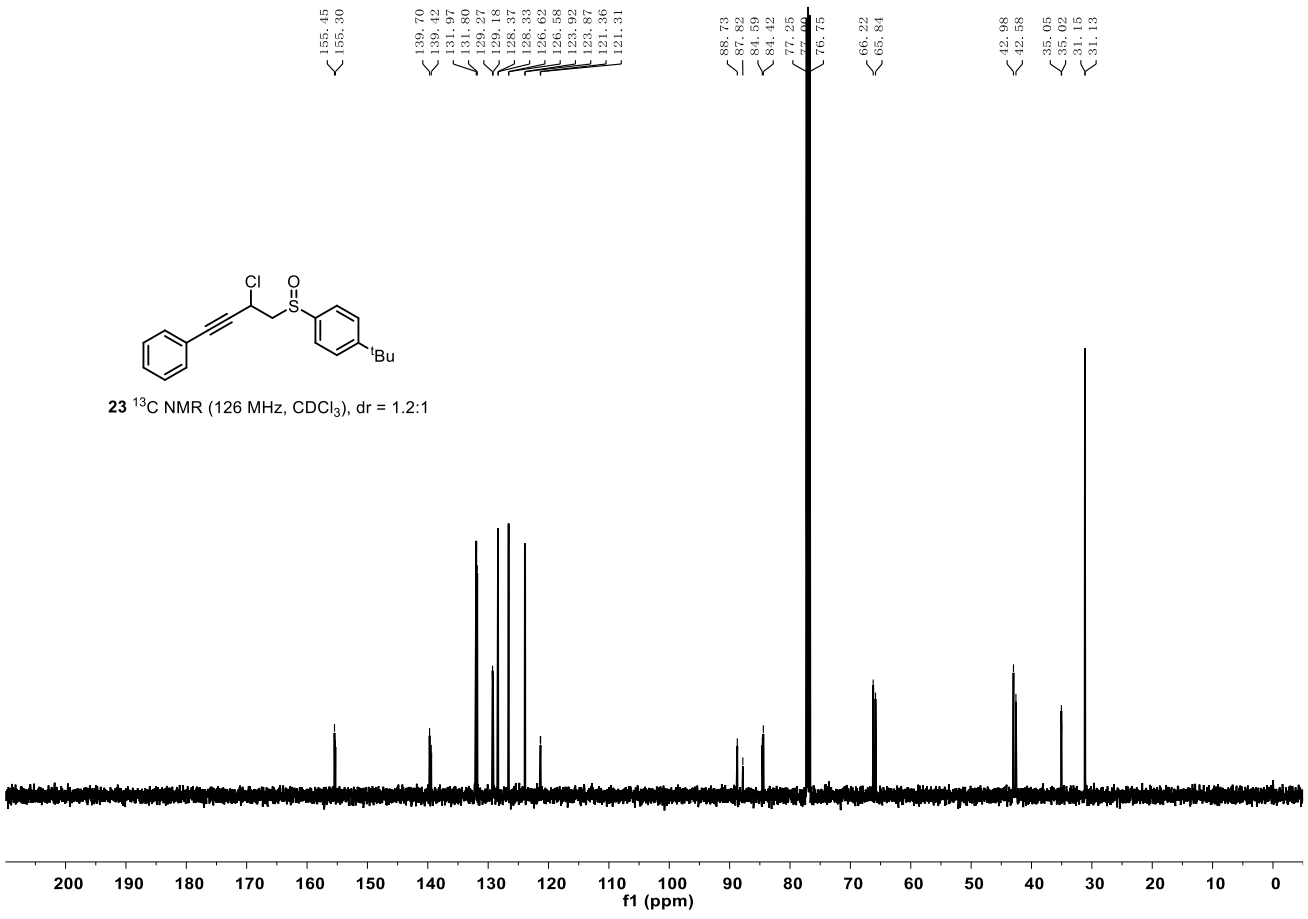
22 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 2.3:1



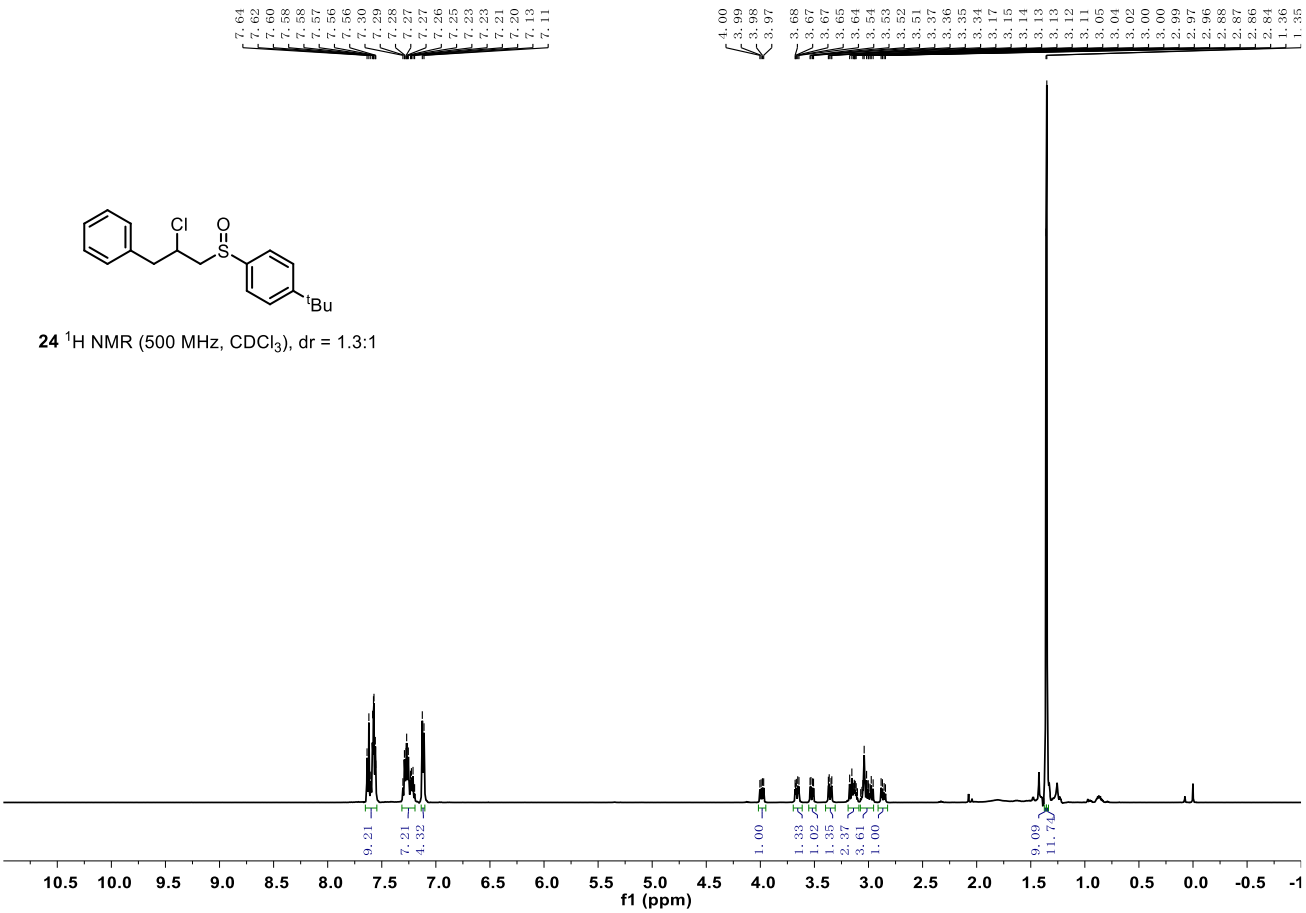
22 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 2.3:1



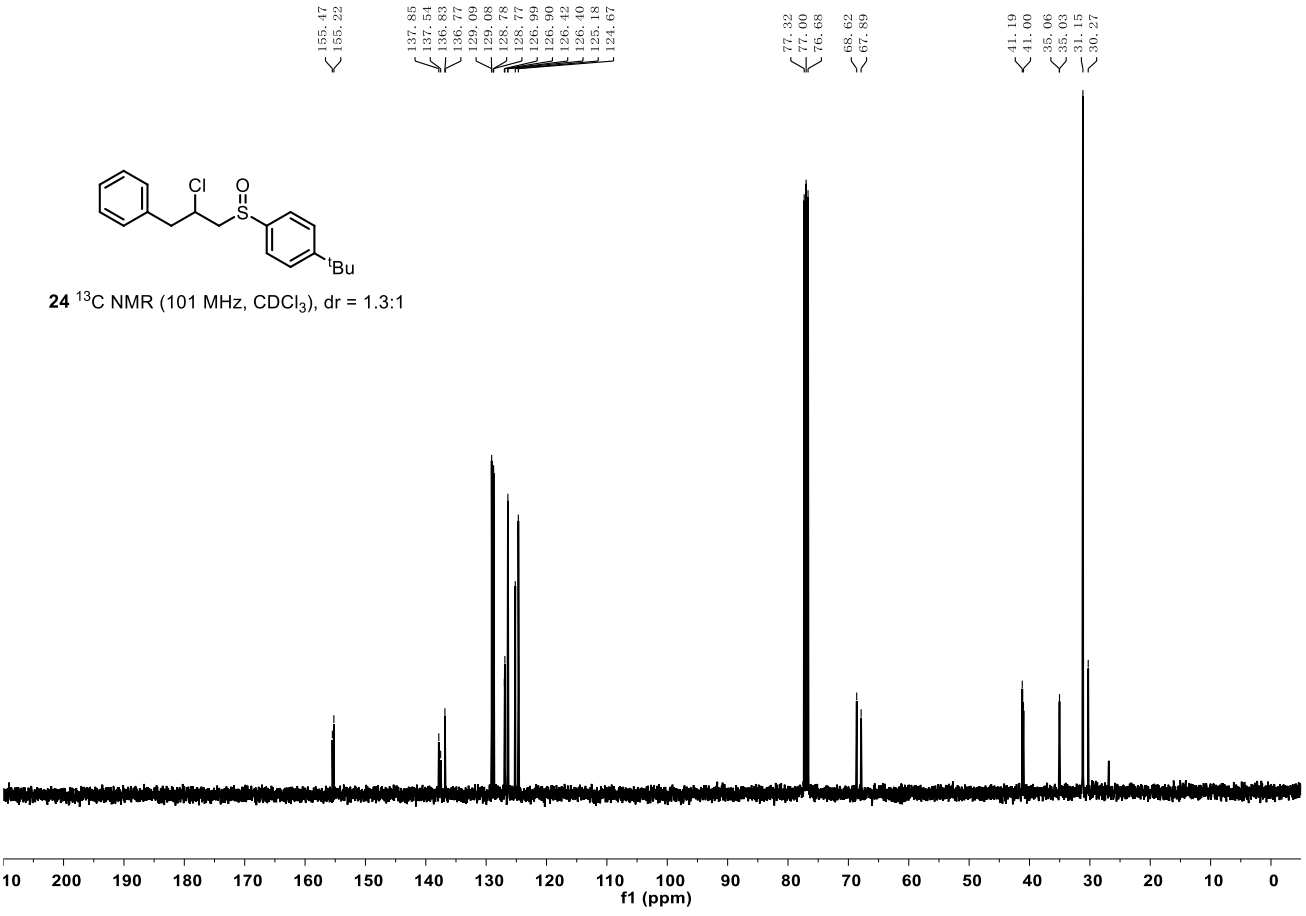
23 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.2:1



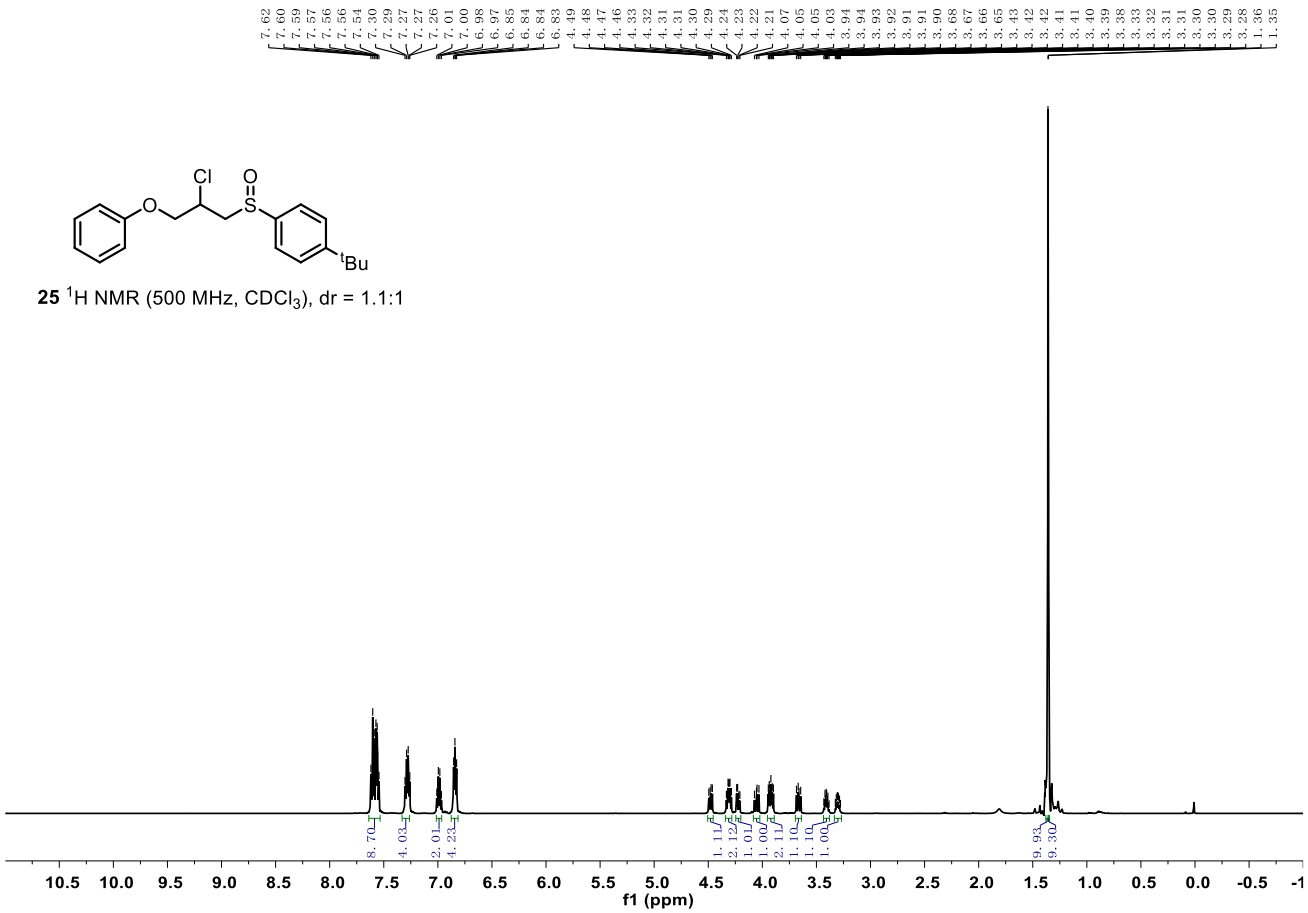
23 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 1.2:1



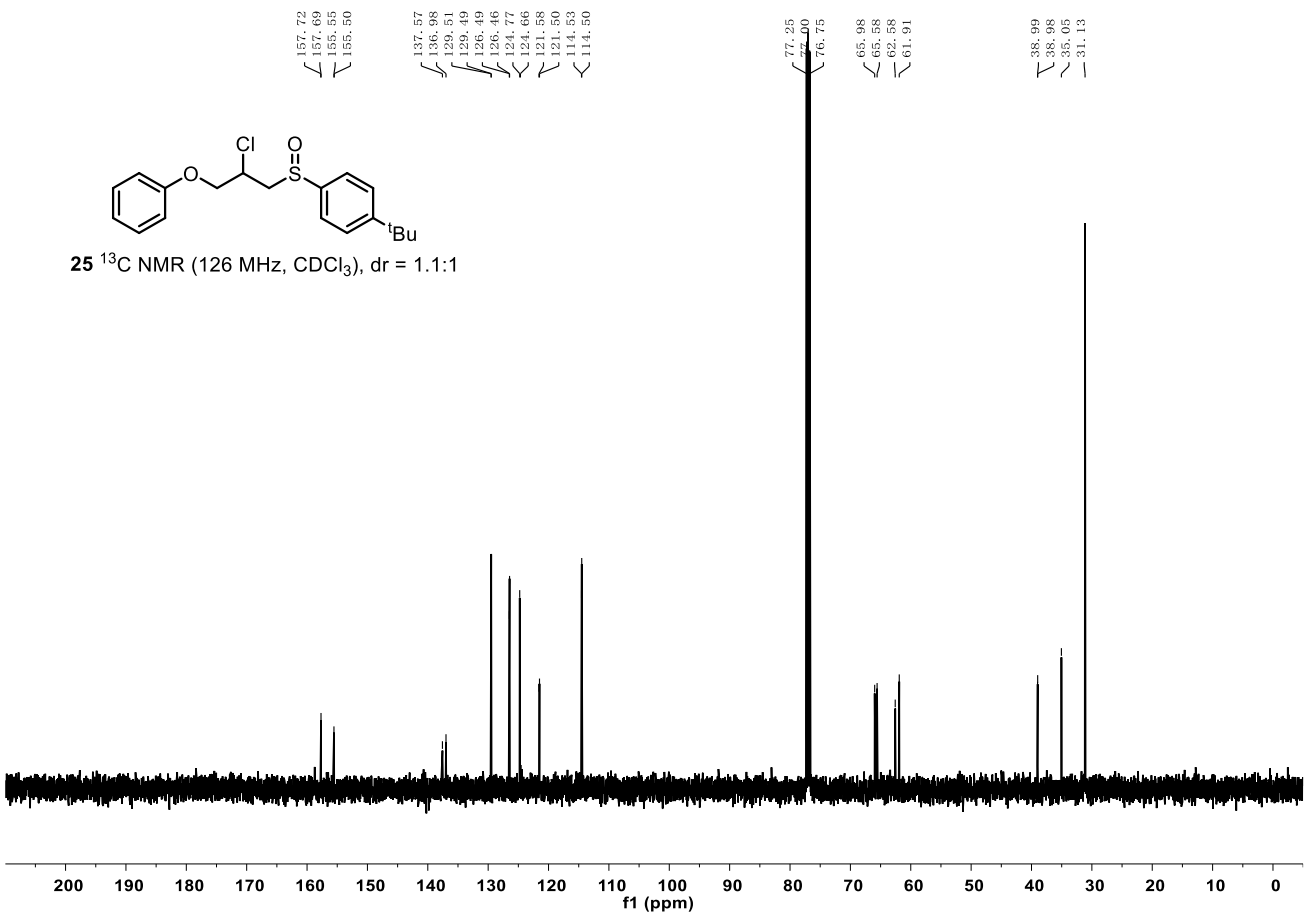
24 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.3:1



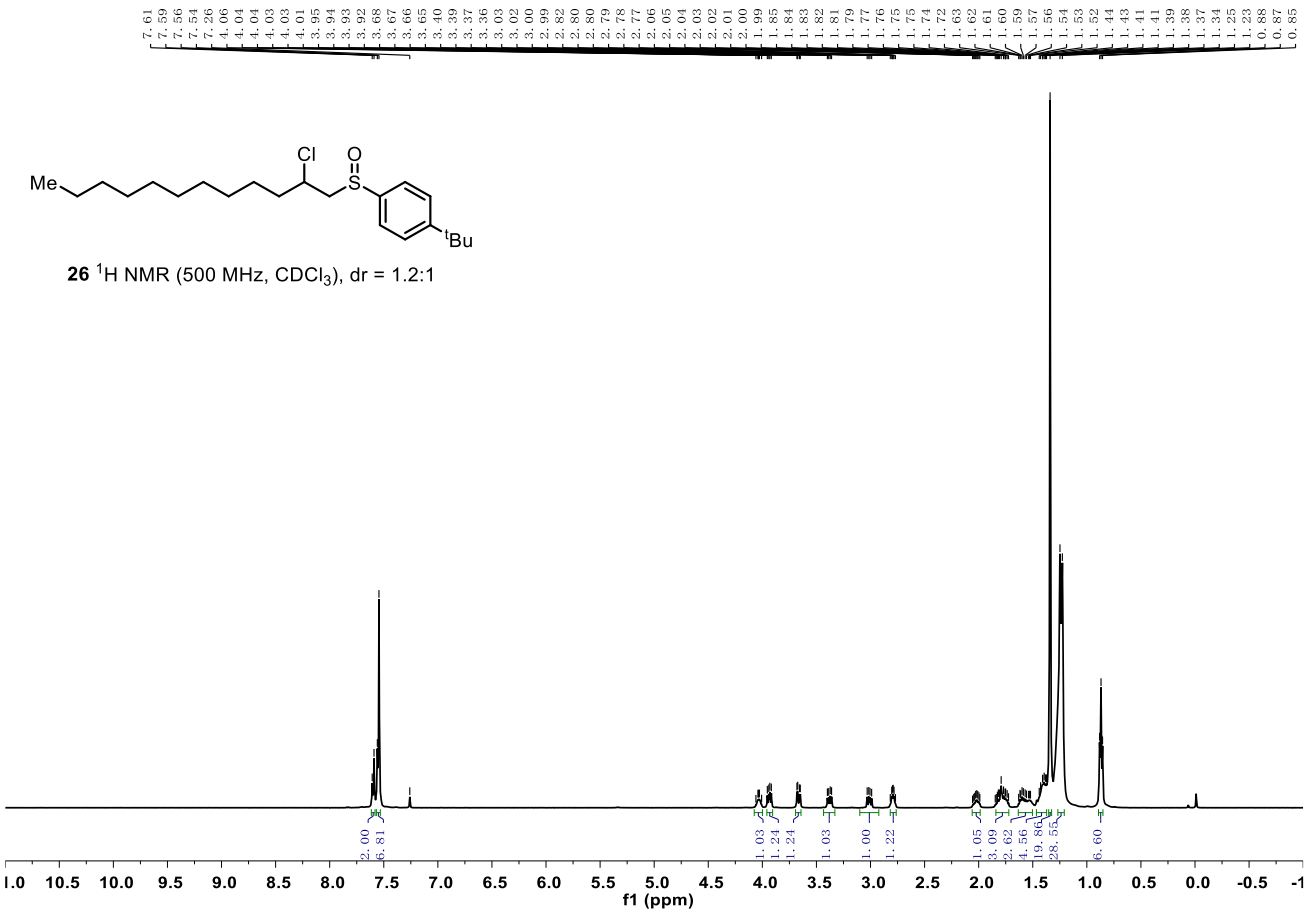
24 ^{13}C NMR (101 MHz, $CDCl_3$), dr = 1.3:1



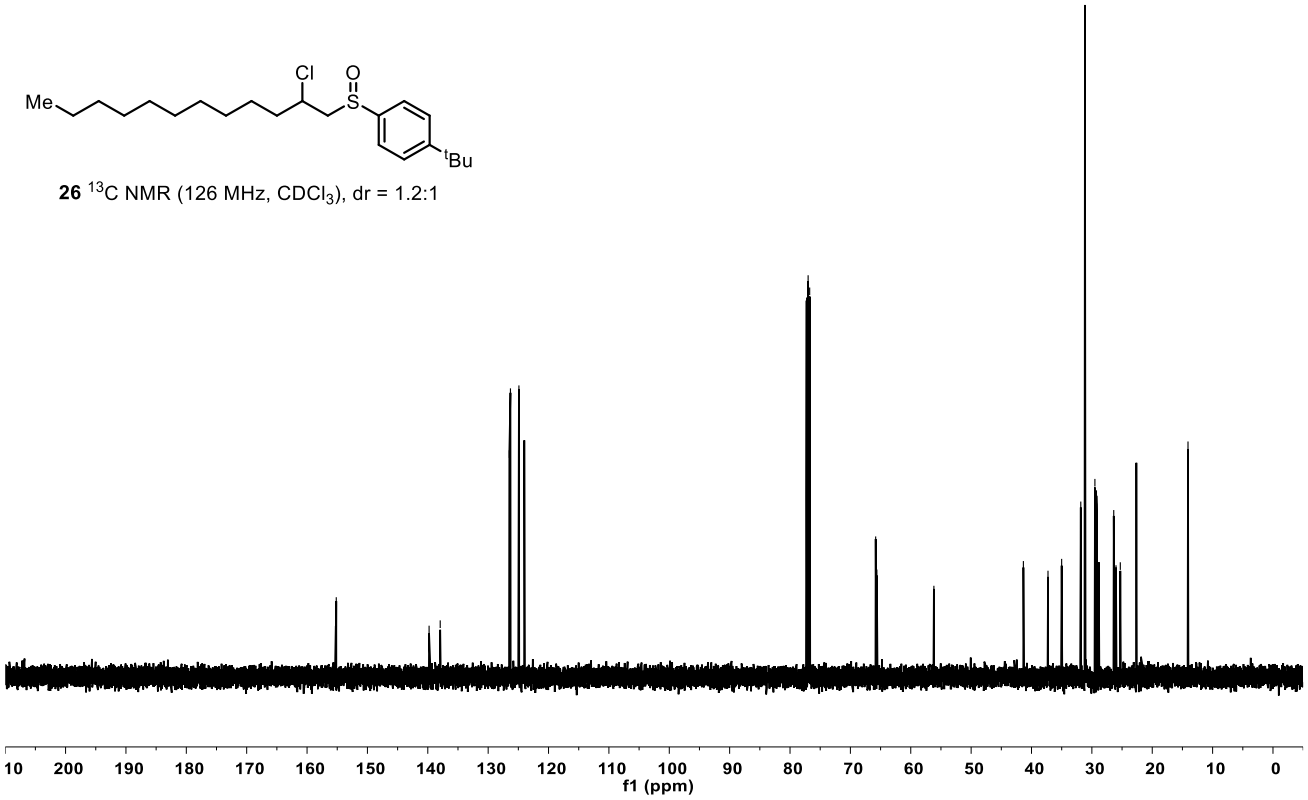
25 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.1:1



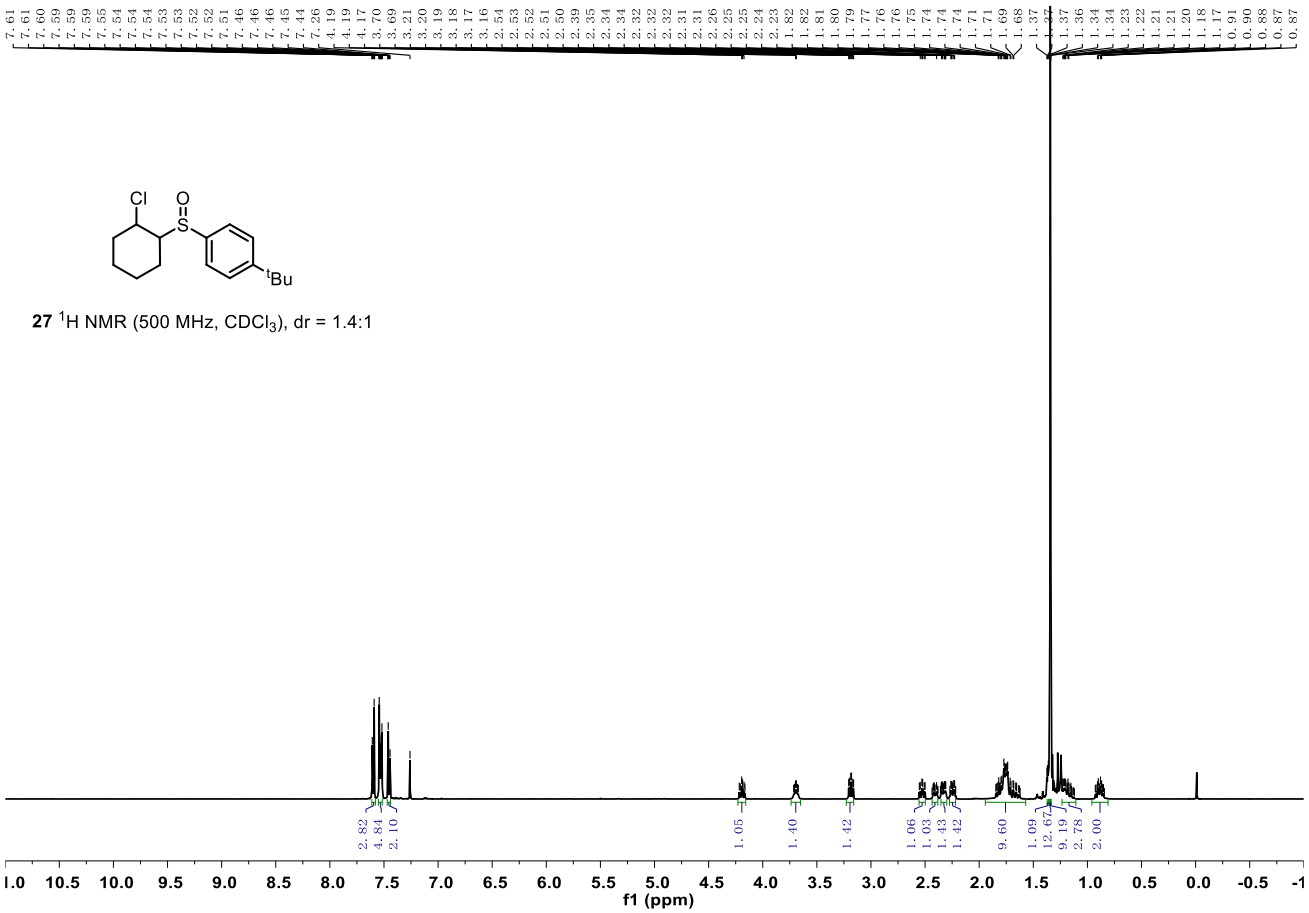
25 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 1.1:1



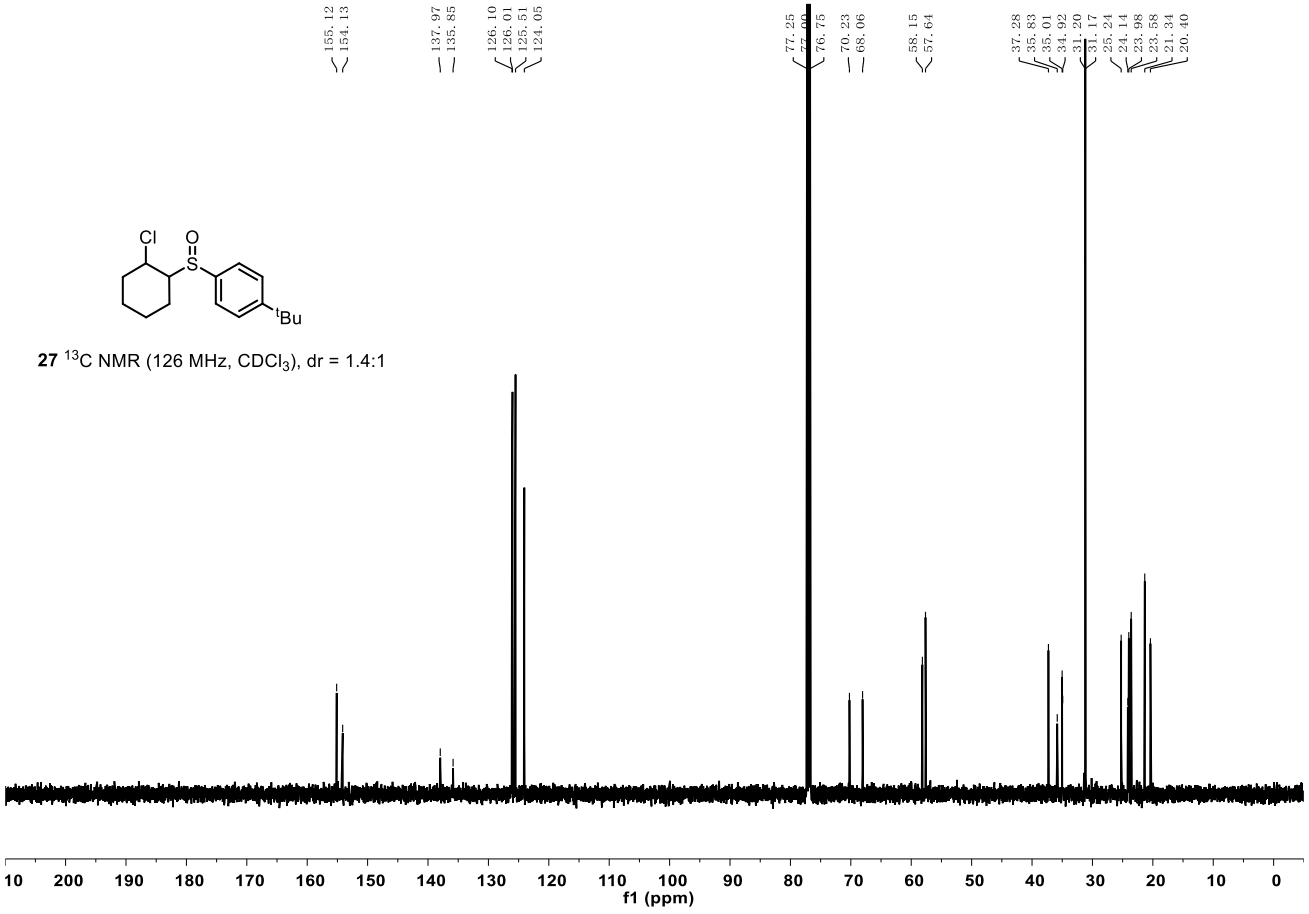
26 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.2:1



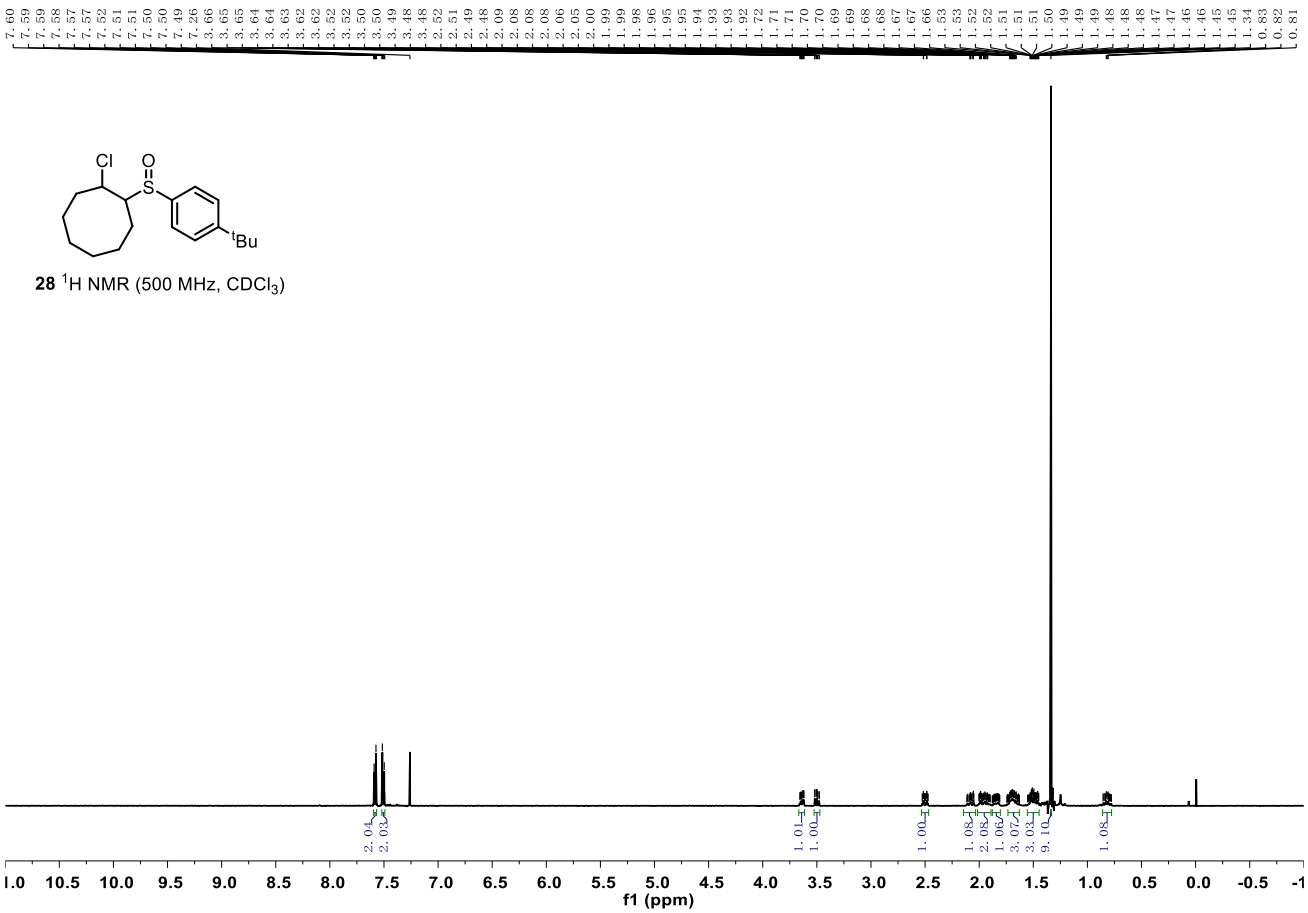
26 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 1.2:1



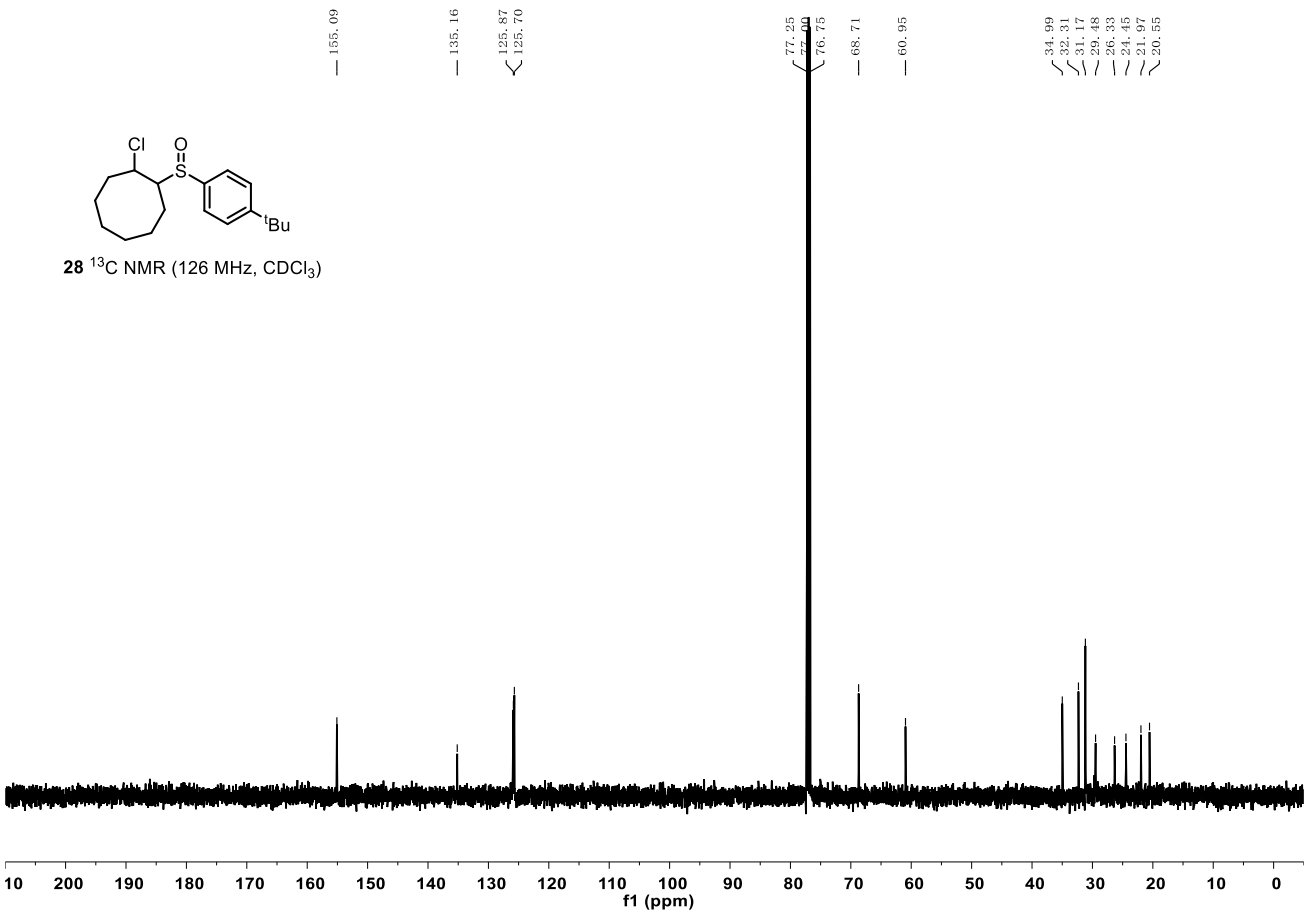
27 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.4:1



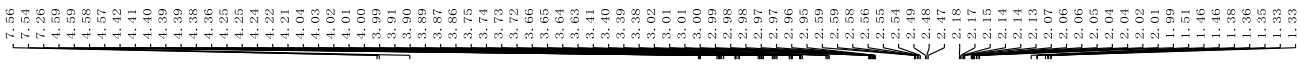
27 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 1.4:1

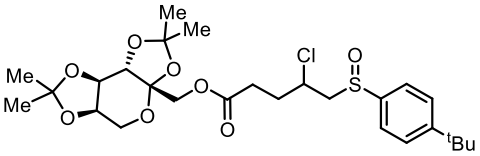


28 ^{1}H NMR (500 MHz, $CDCl_3$)

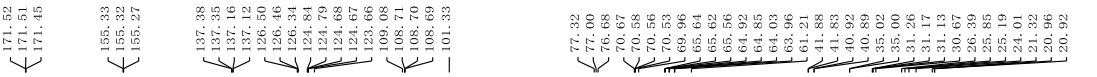


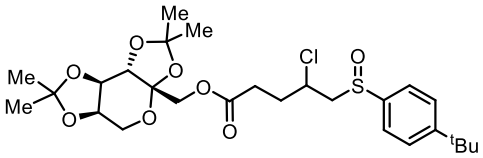
28 ^{13}C NMR (126 MHz, $CDCl_3$)



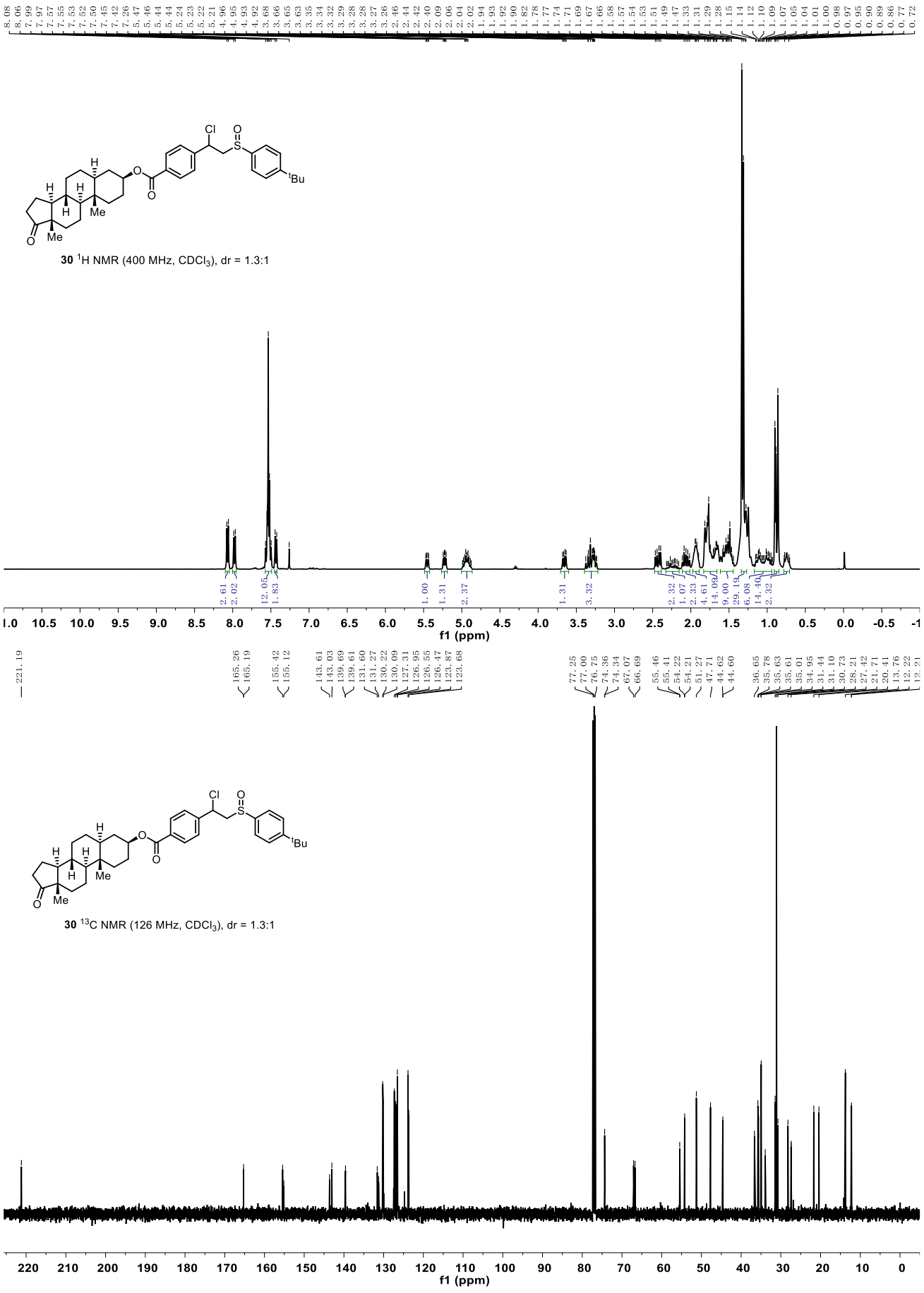


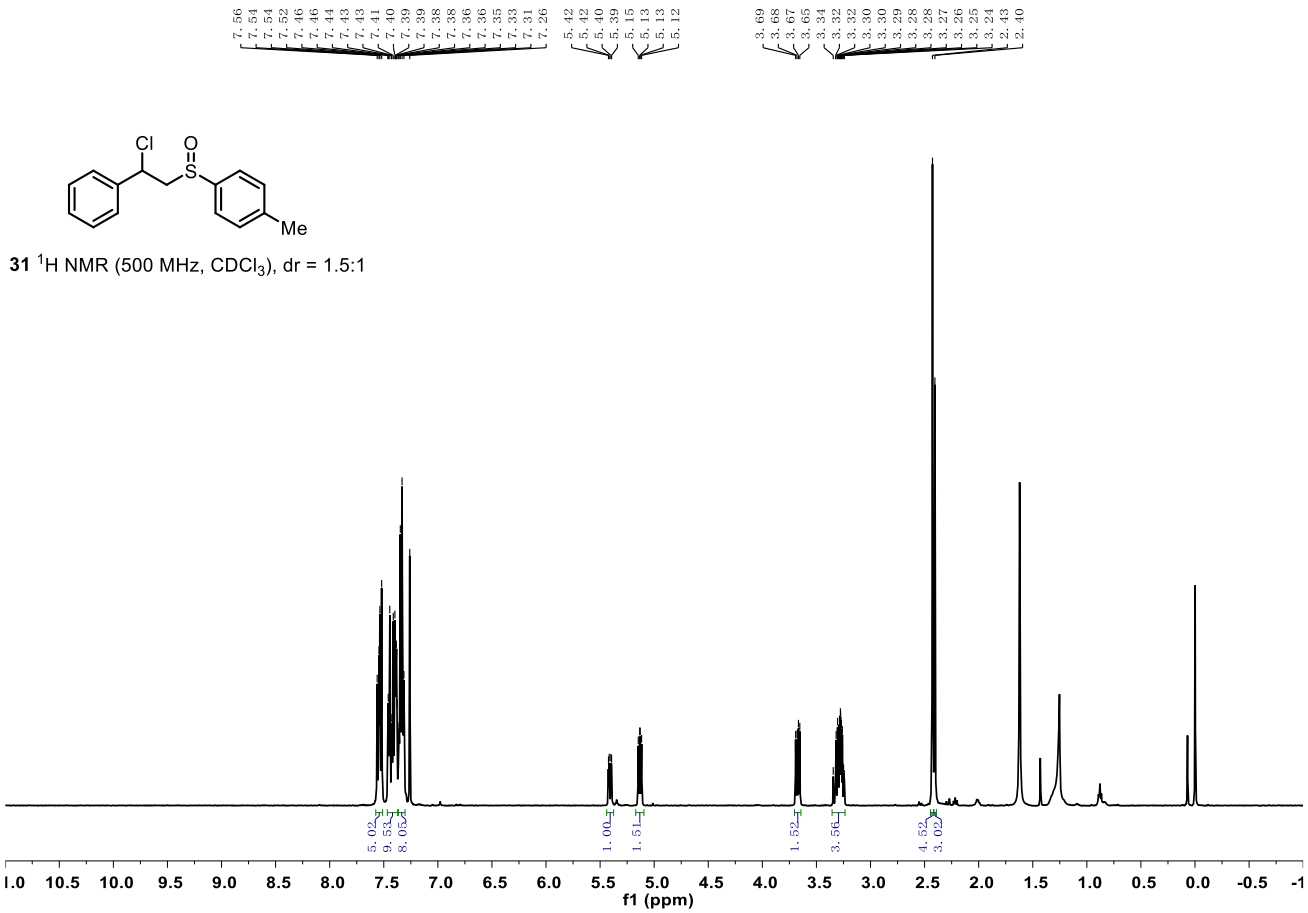
29 ^{1}H NMR (600 MHz, $CDCl_3$), dr = 1.4:1



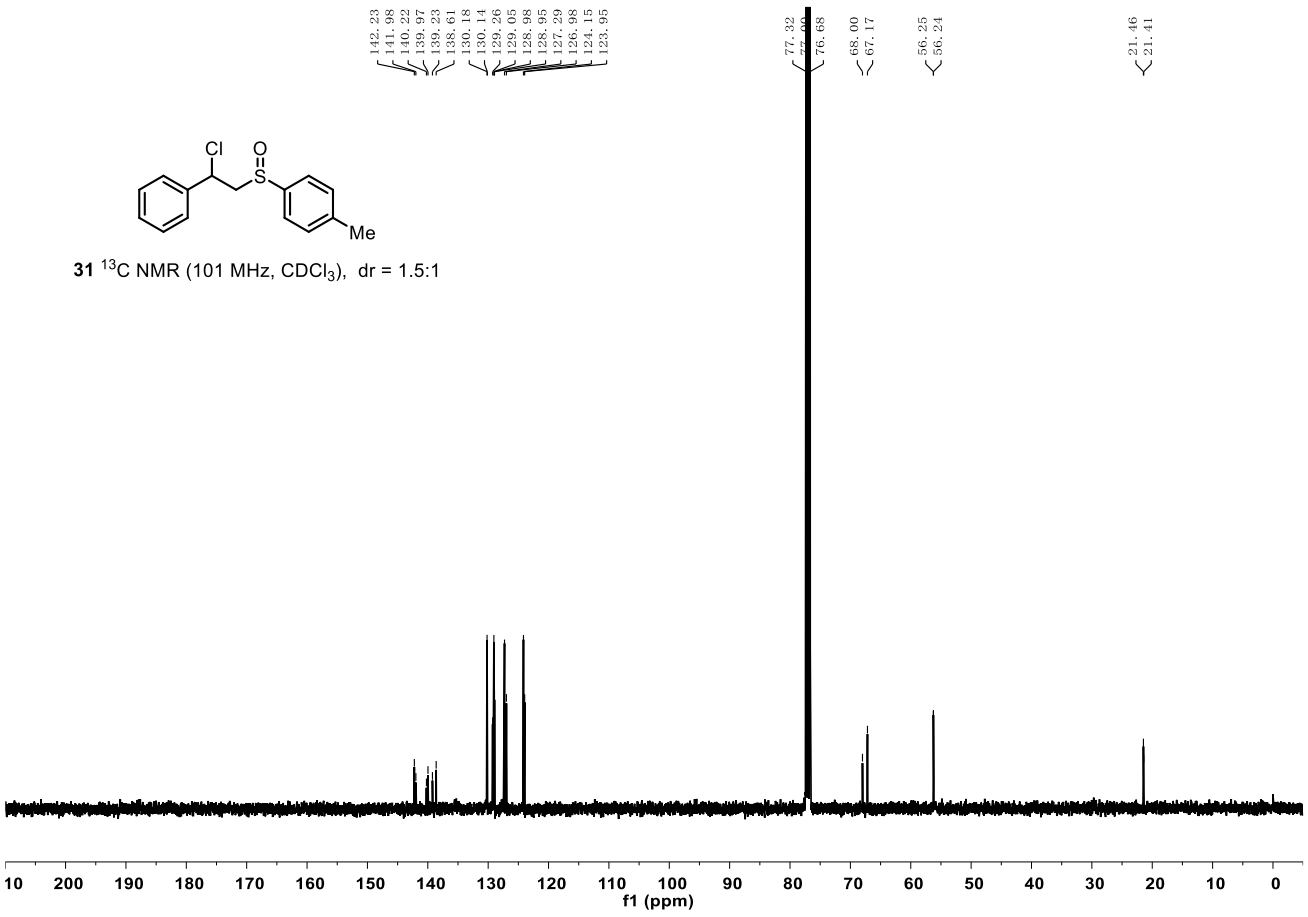


29 ^{13}C NMR (101 MHz, $CDCl_3$), dr = 1.4:1

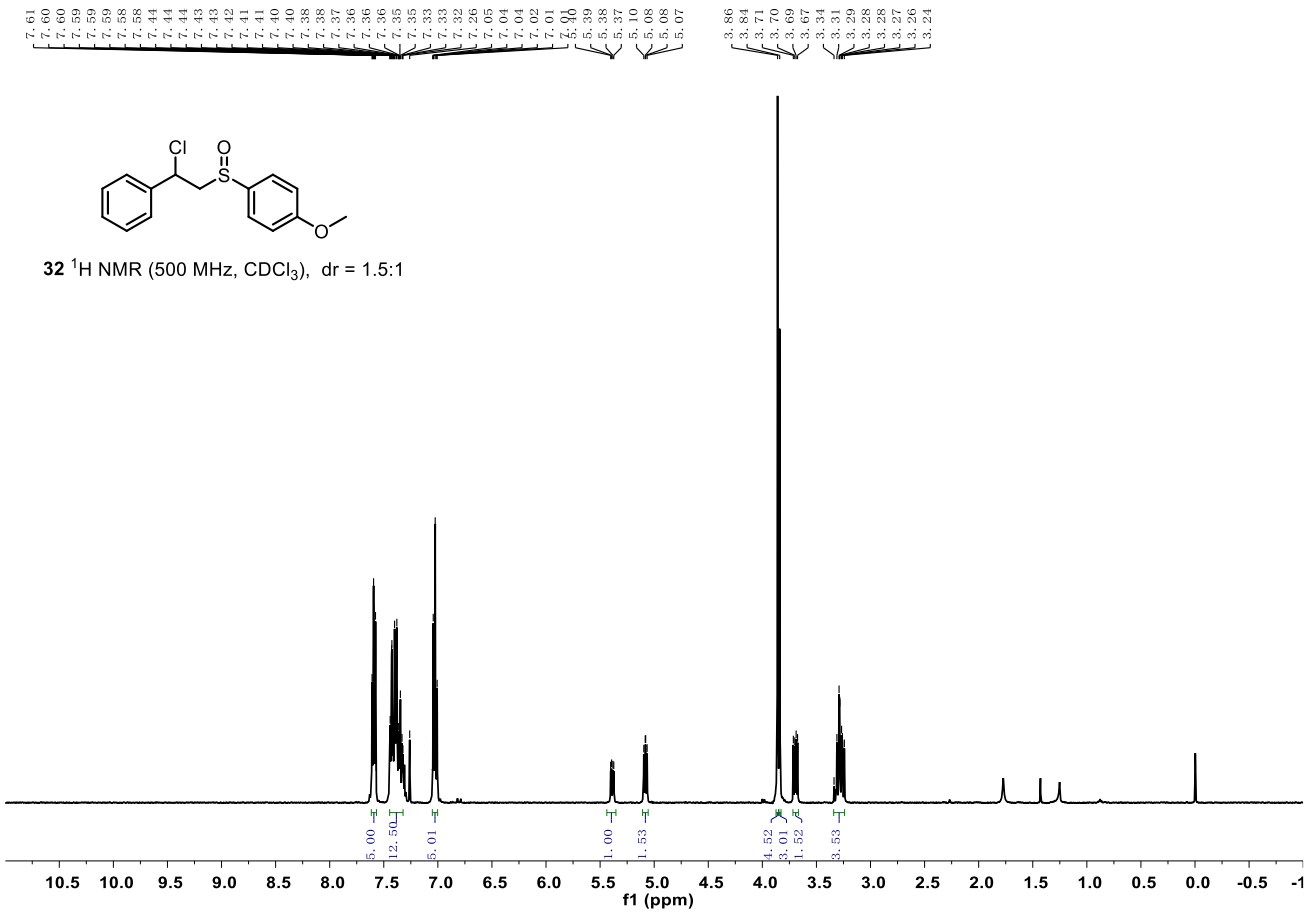

Cl
O
S
O
tBu
O
O
H
H
H
H
Me
Me
O
30 1H NMR (400 MHz, CDCl3), dr = 1.3:1
f1 (ppm)
30 13C NMR (126 MHz, CDCl3), dr = 1.3:1
f1 (ppm)

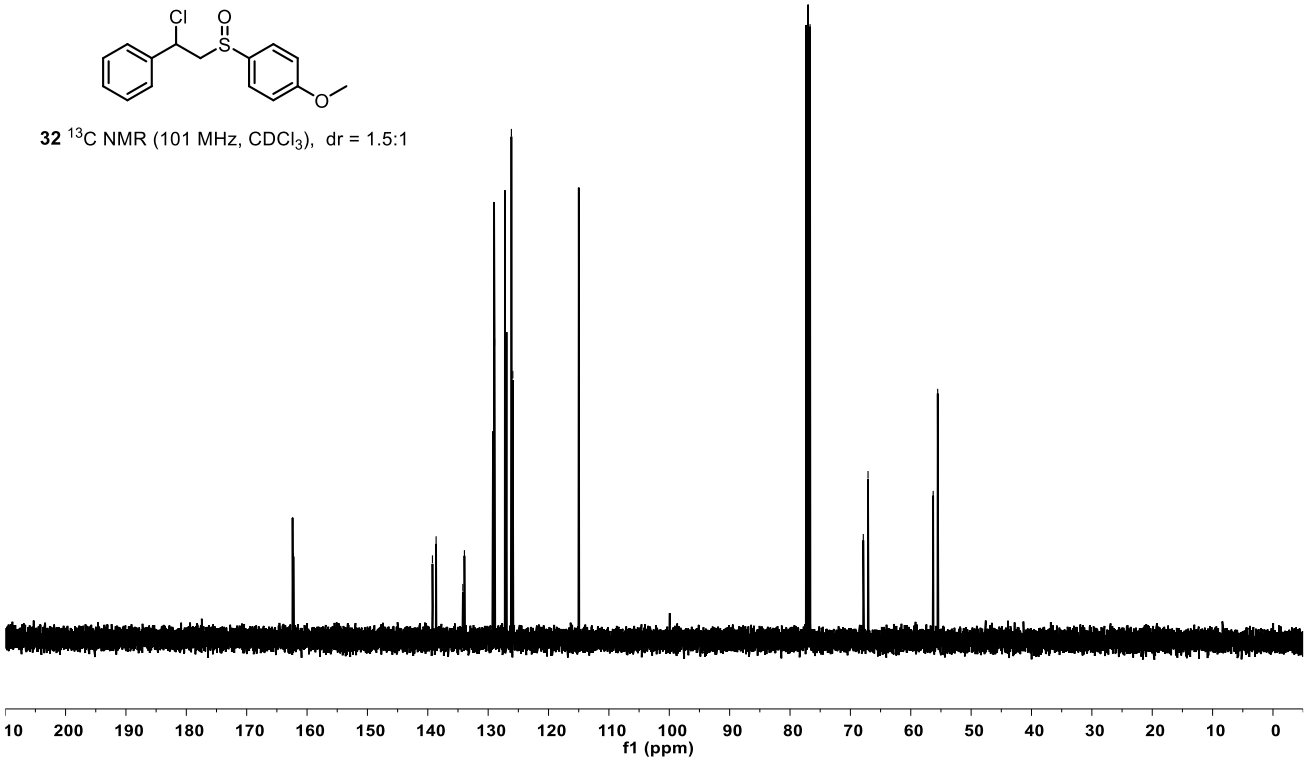


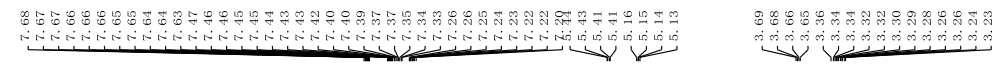
31 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.5:1

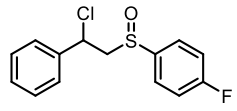


31 ^{13}C NMR (101 MHz, $CDCl_3$), dr = 1.5:1

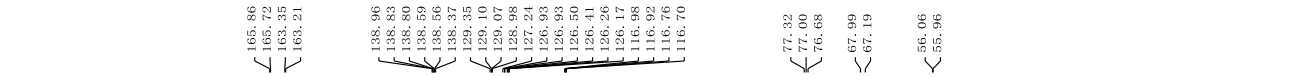

Cl
O
S
O
32 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.5:1
f1 (ppm)

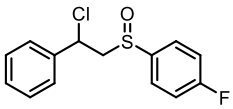

Cl
O
S
O
32 ^{13}C NMR (101 MHz, $CDCl_3$), dr = 1.5:1
f1 (ppm)



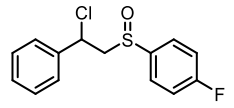


33 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.5:1

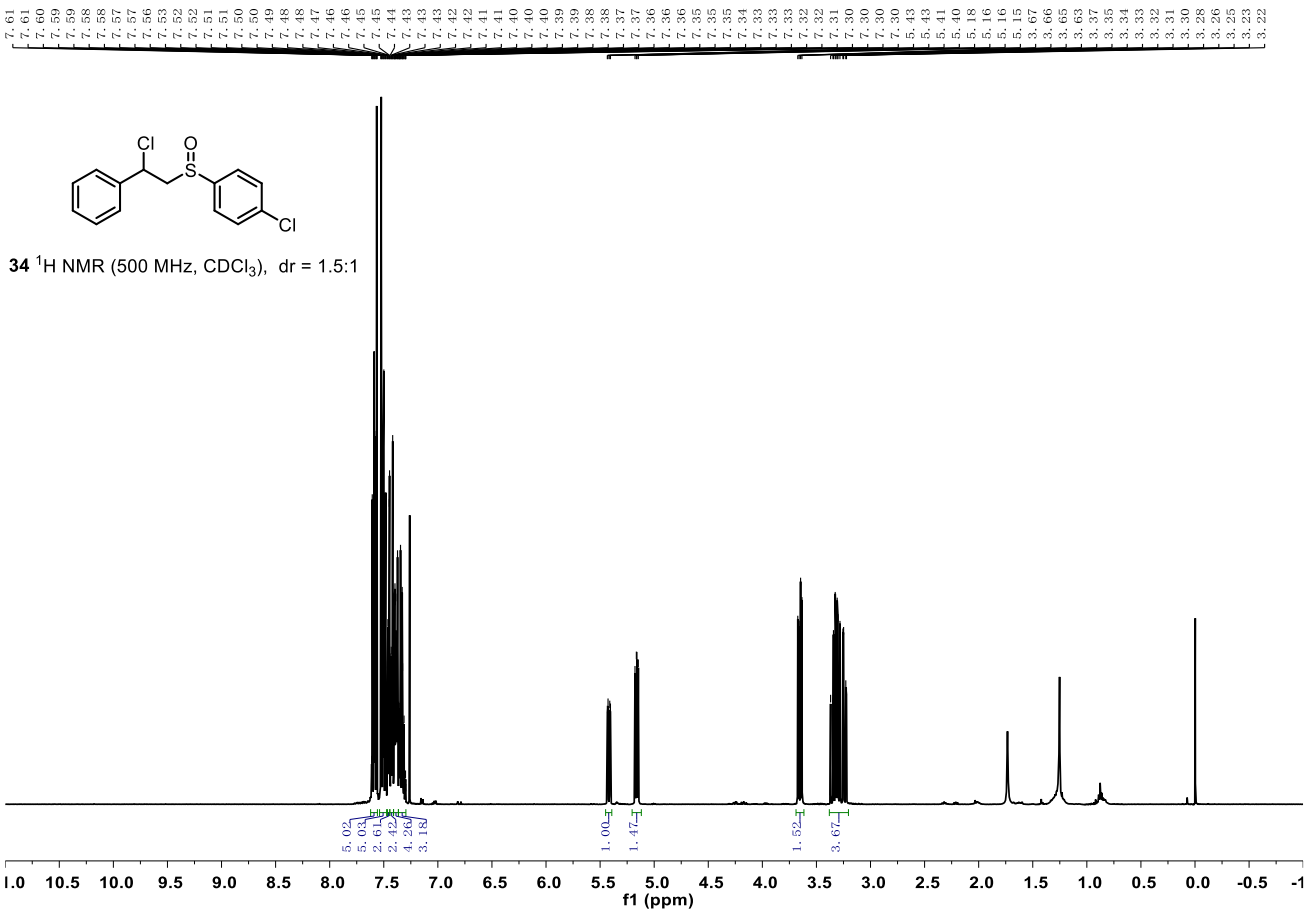


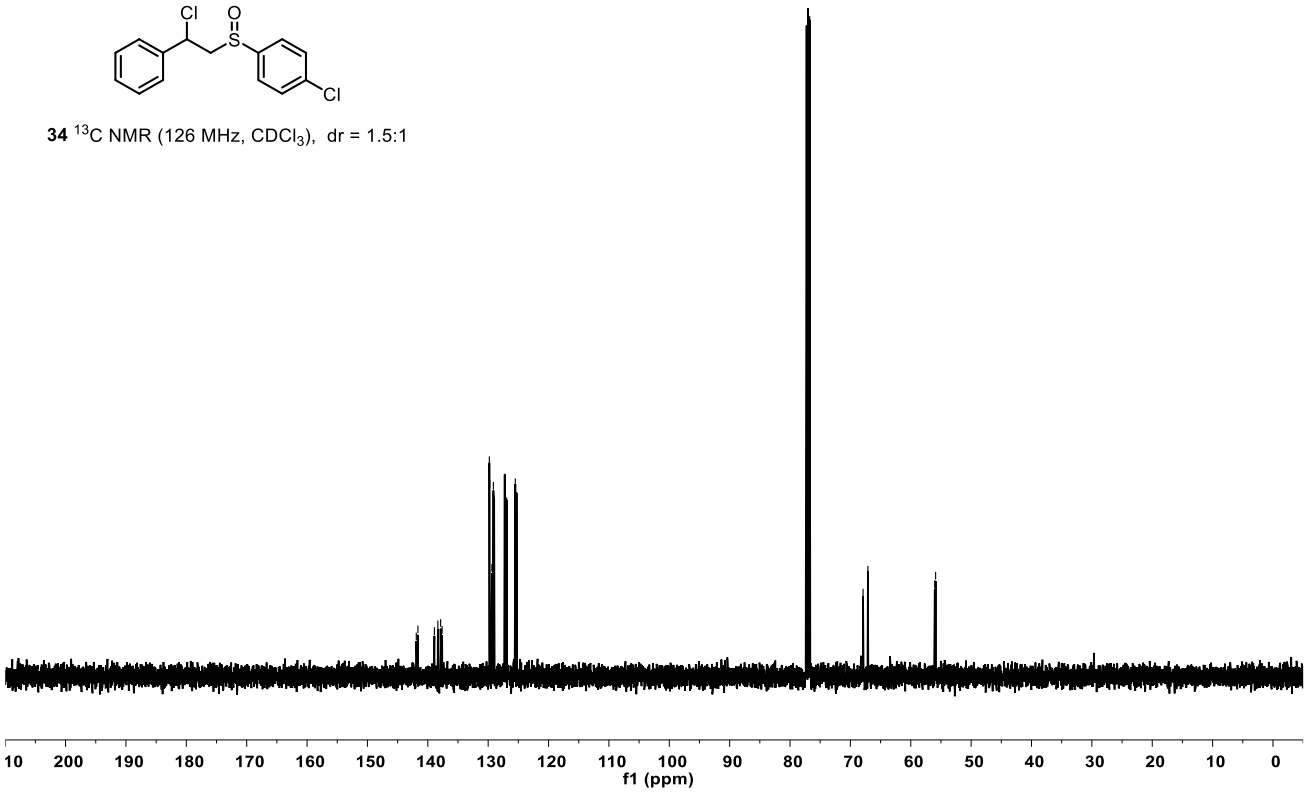


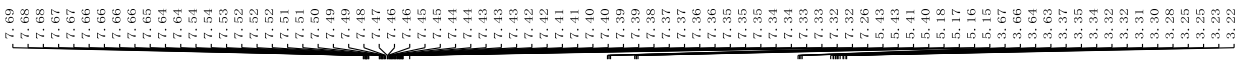
33 ^{13}C NMR (101 MHz, $CDCl_3$), dr = 1.5:1

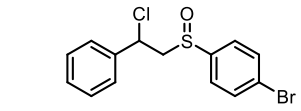


33 ^{19}F NMR (471 MHz, $CDCl_3$), dr = 1.5:1

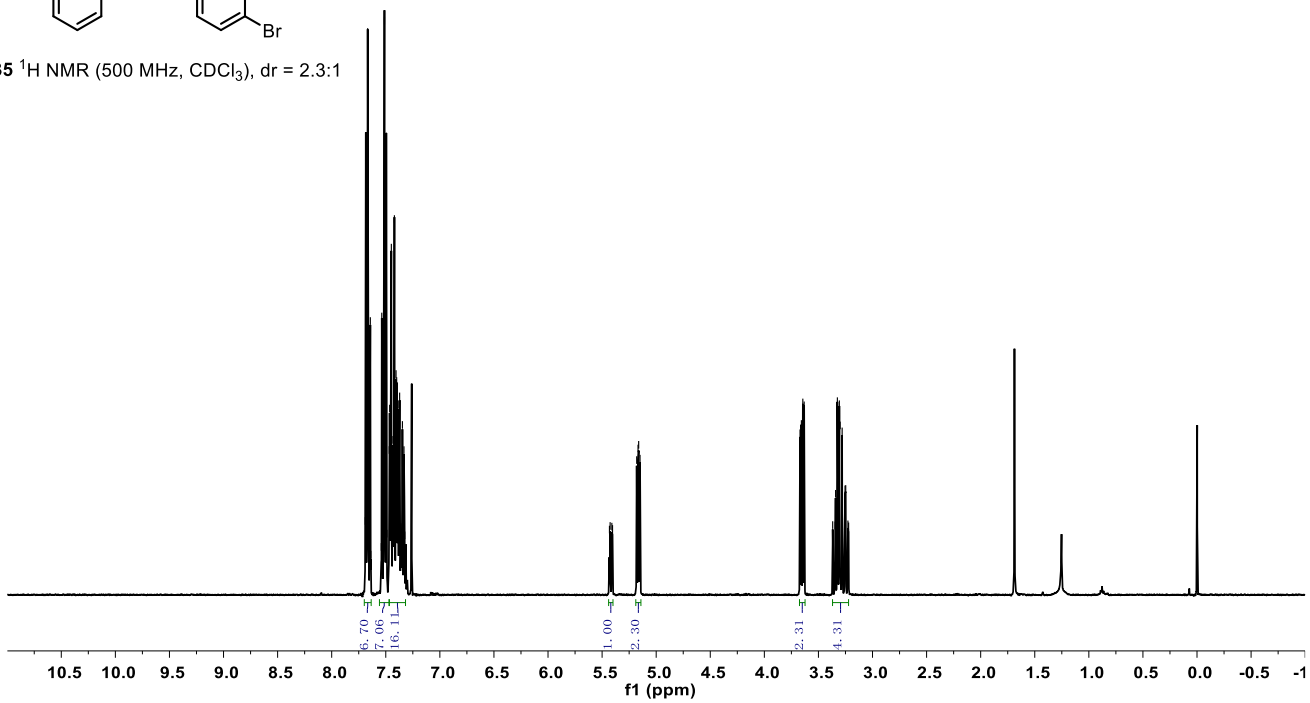

Cl
O
S
Cl
34 1H NMR (500 MHz, CDCl3), dr = 1.5:1
f1 (ppm)

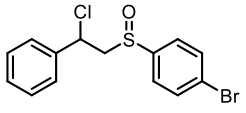

Cl
O
S
Cl
34 13C NMR (126 MHz, CDCl3), dr = 1.5:1
f1 (ppm)



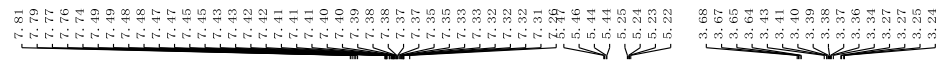


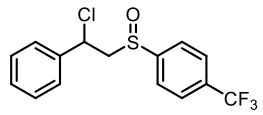
35 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 2.3:1



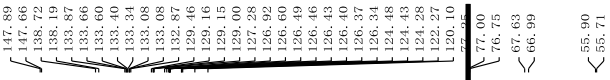


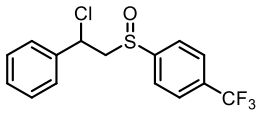
35 ^{13}C NMR (101 MHz, $CDCl_3$), dr = 2.3:1



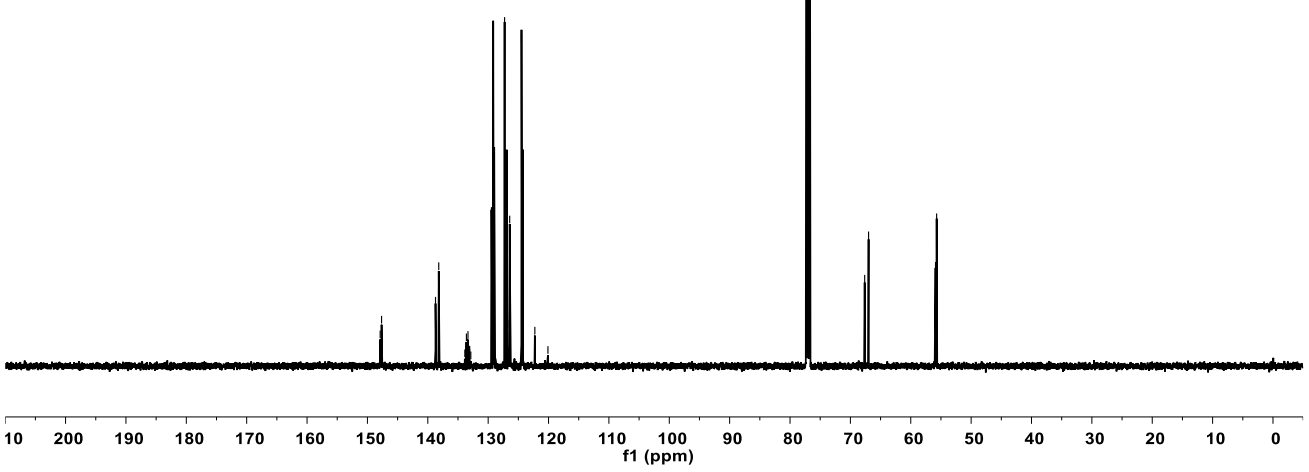


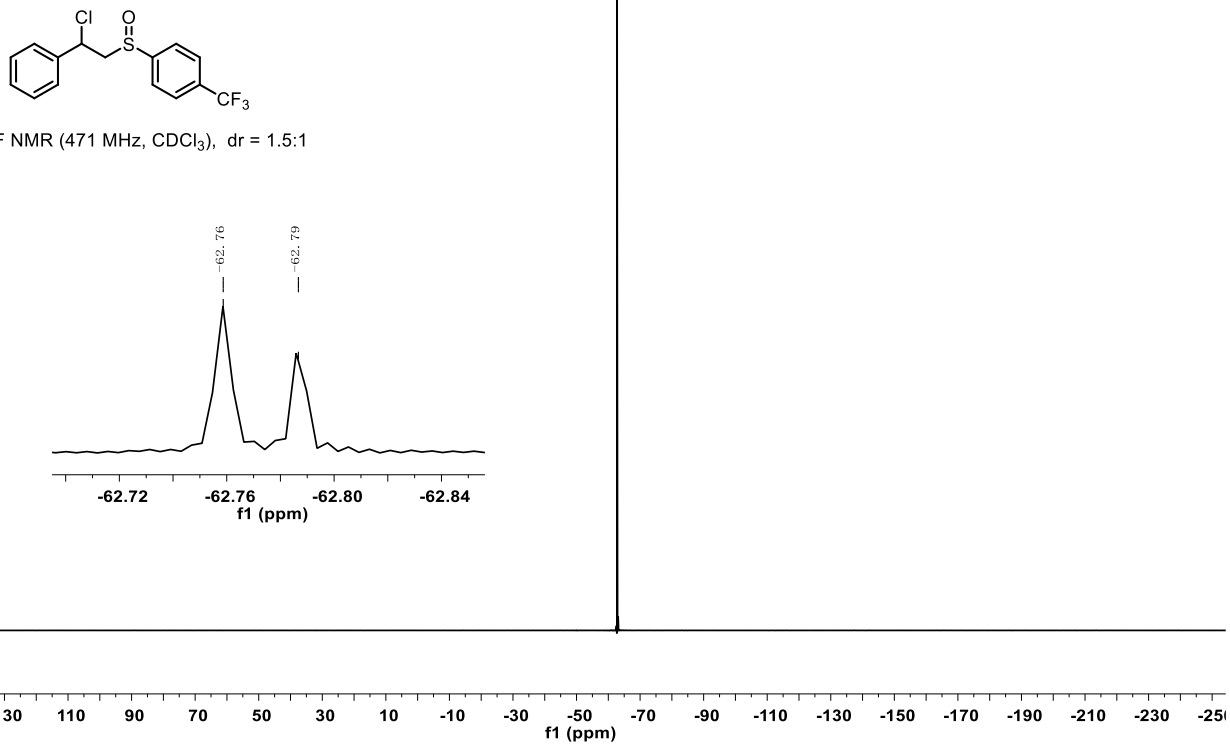
36 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.5:1



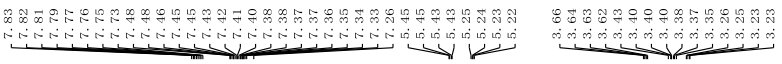


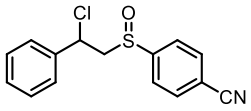
36 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 1.5:1



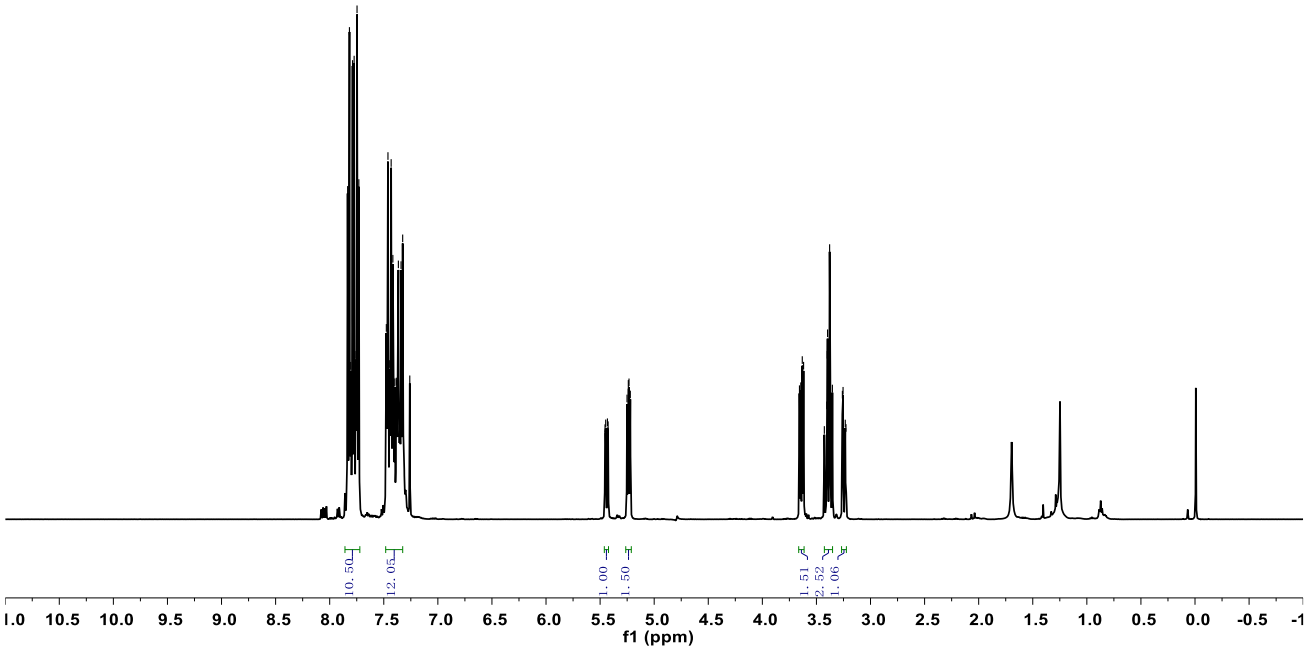


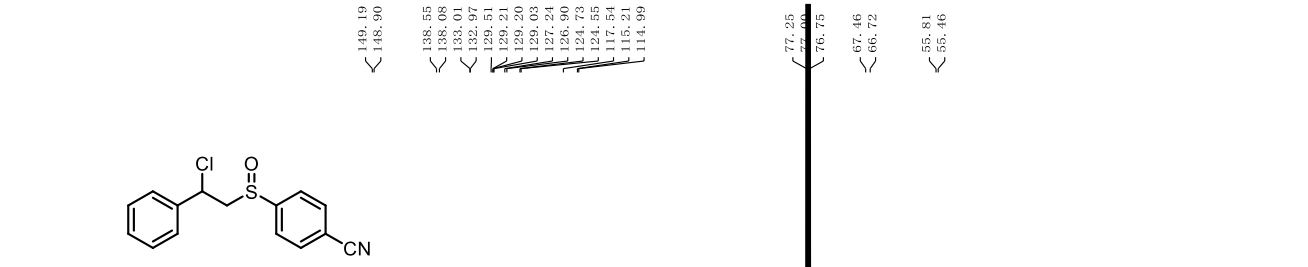
36 ^{19}F NMR (471 MHz, $CDCl_3$), dr = 1.5:1



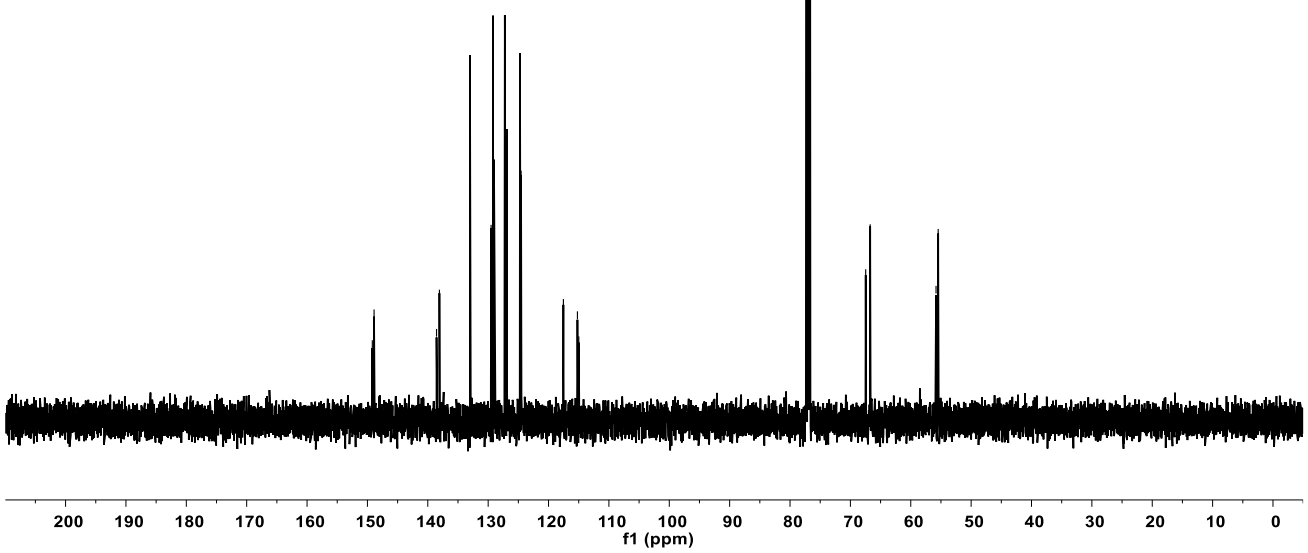


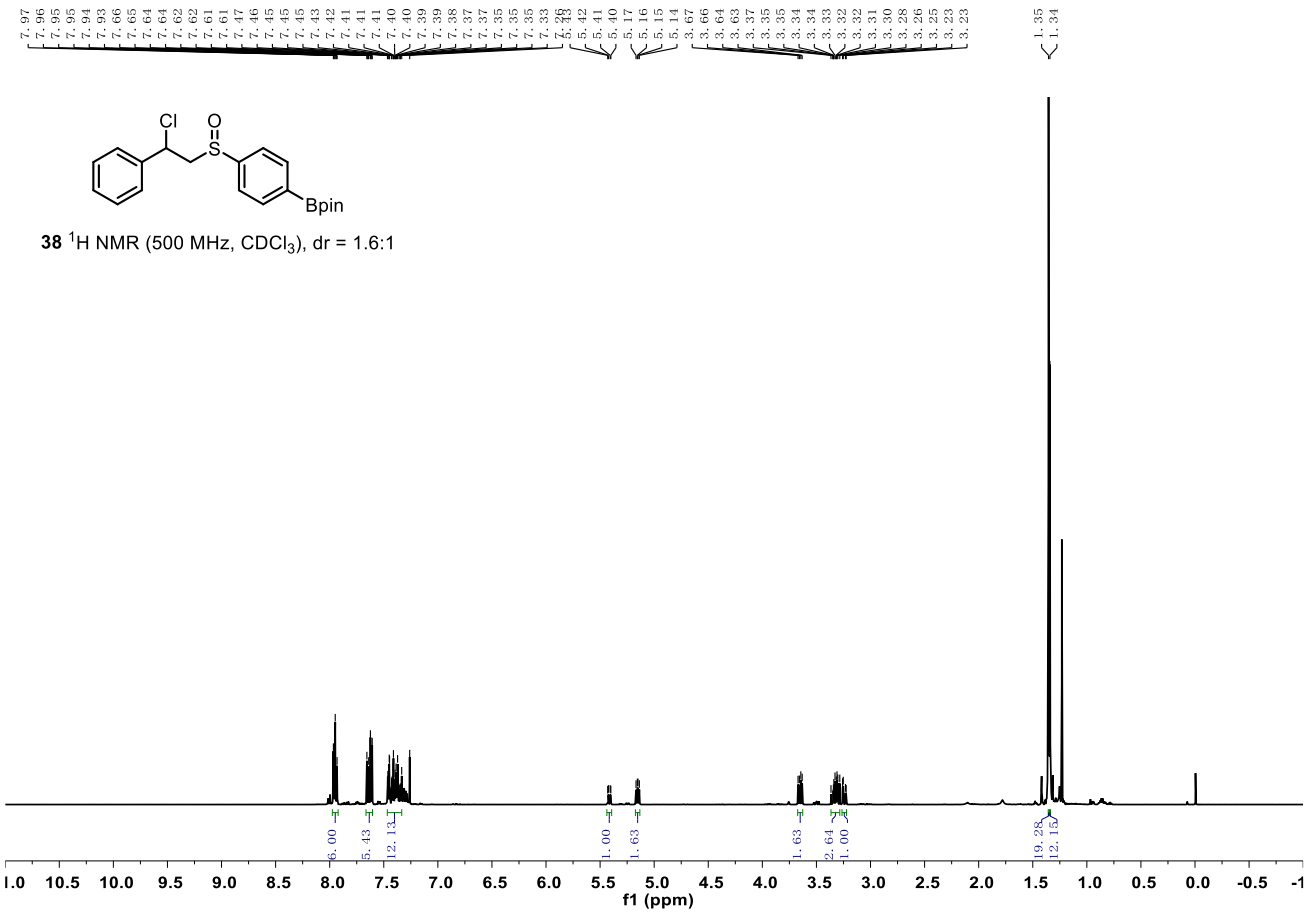
37 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.5:1



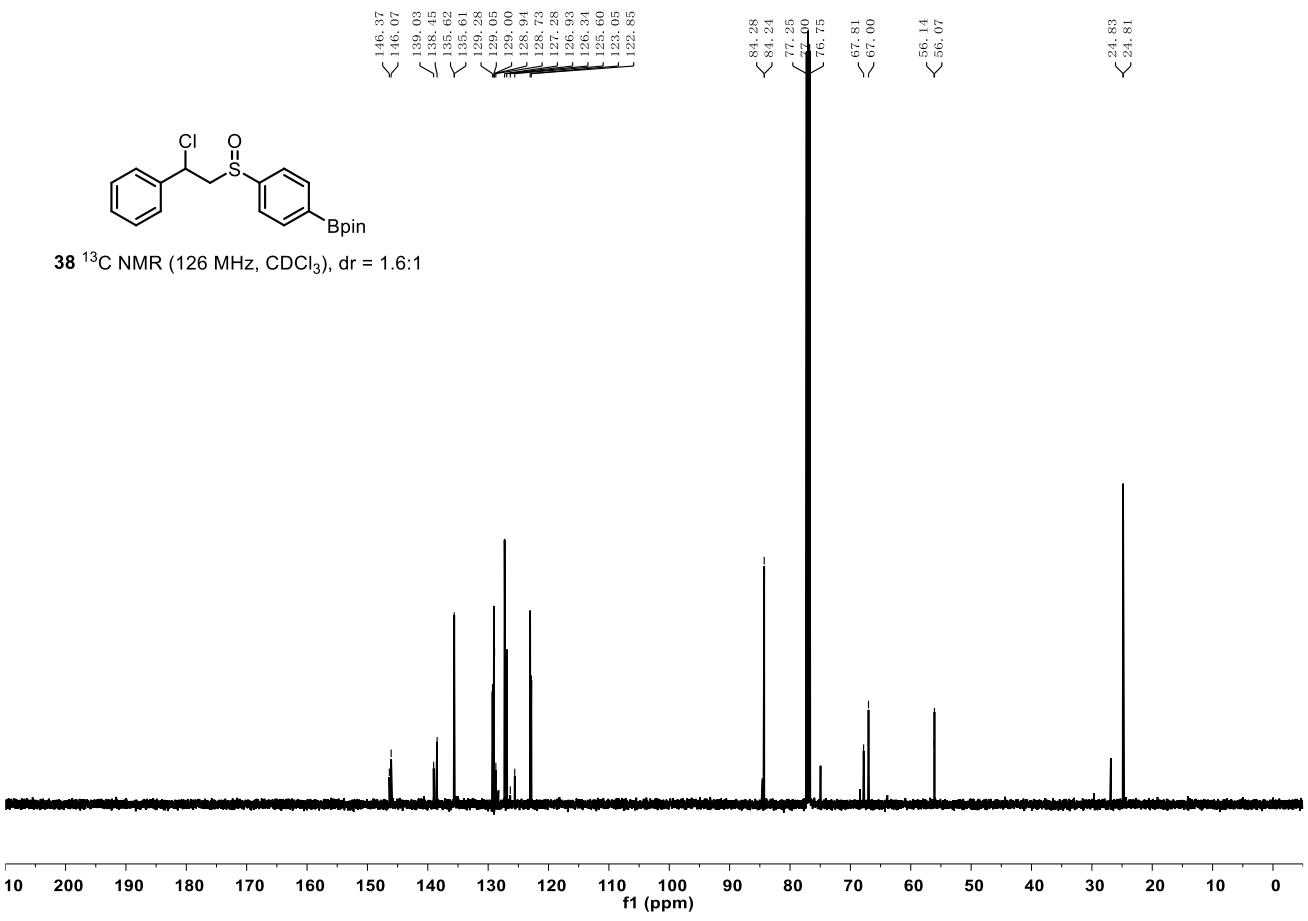


37 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 1.5:1

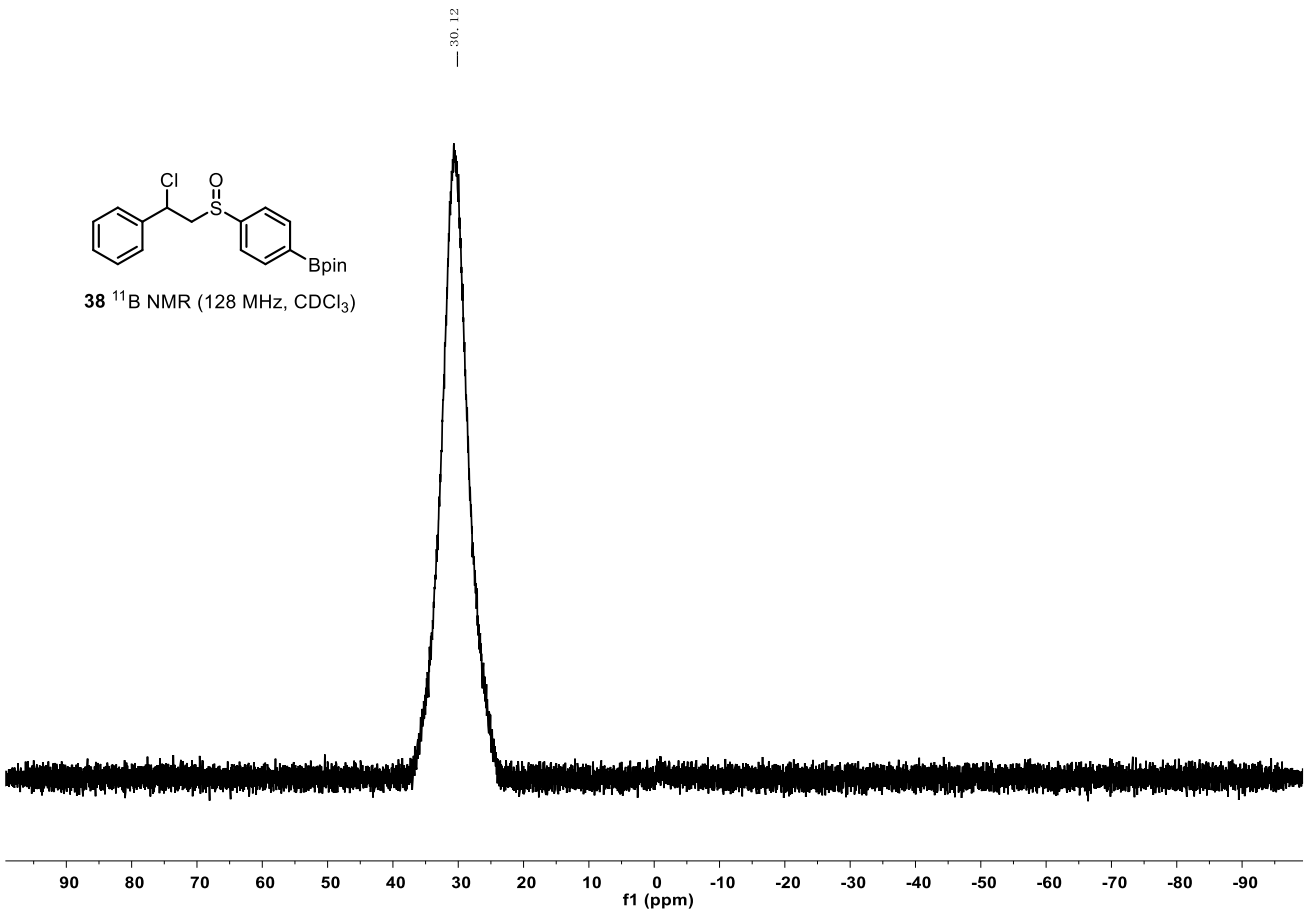




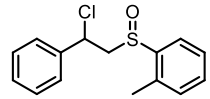
38 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.6:1



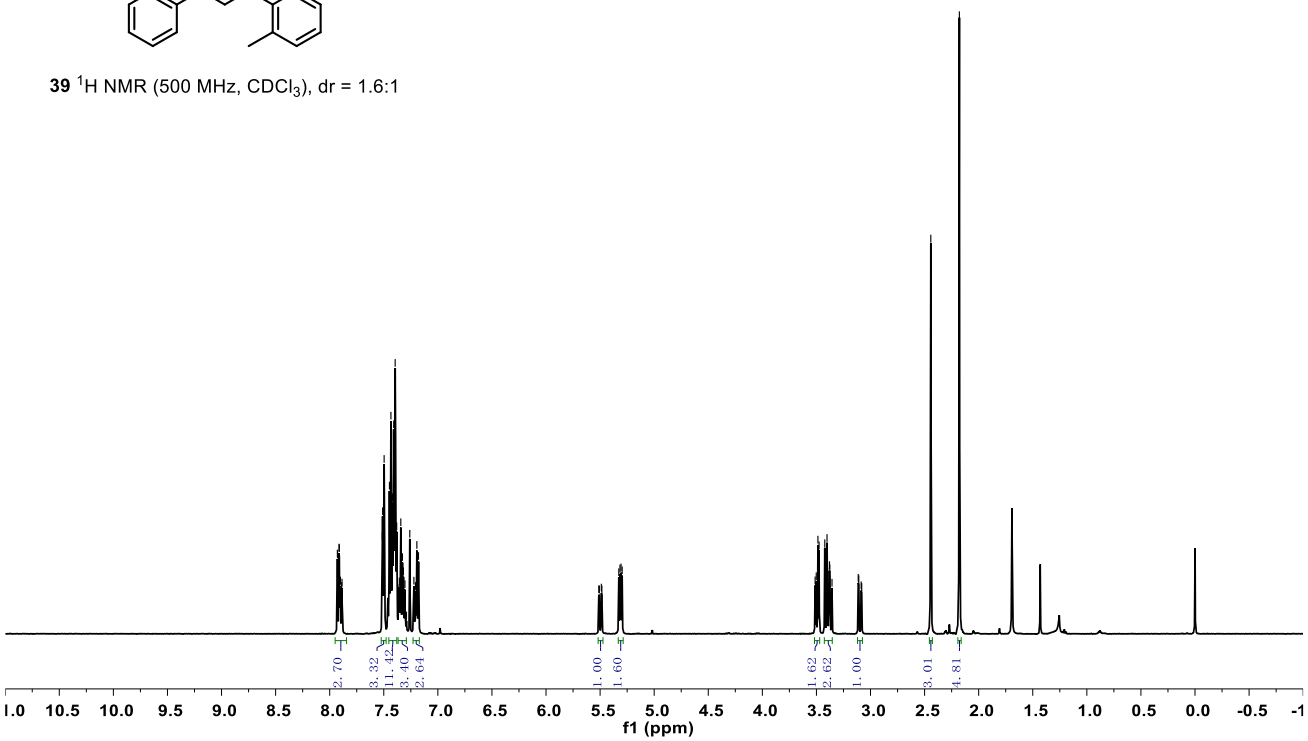
38 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 1.6:1

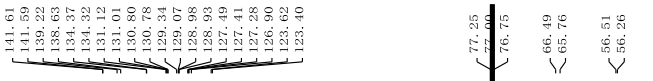


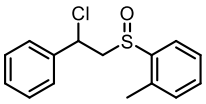
38 ^{11}B NMR (128 MHz, $CDCl_3$)



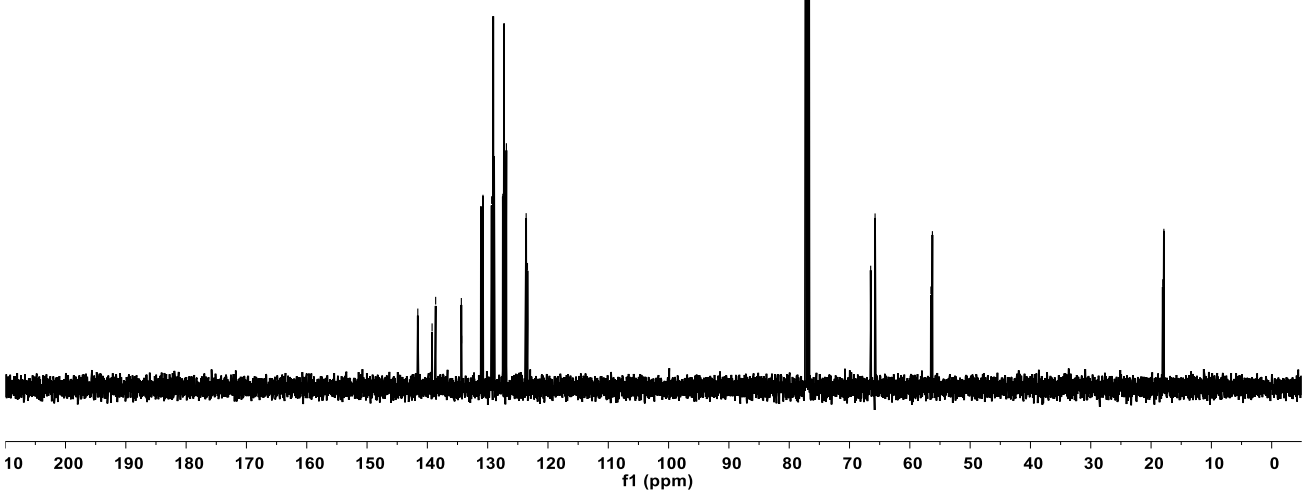
39 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.6:1

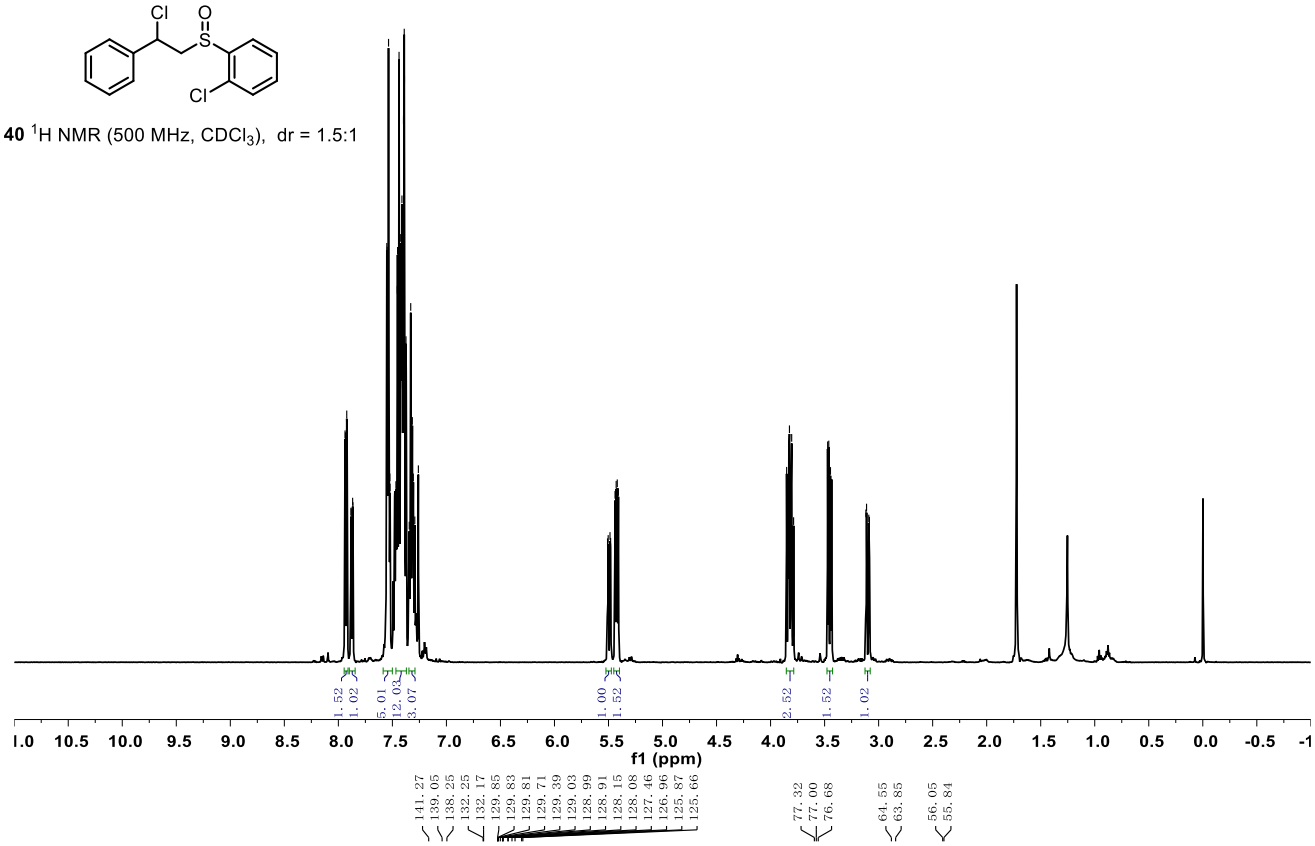


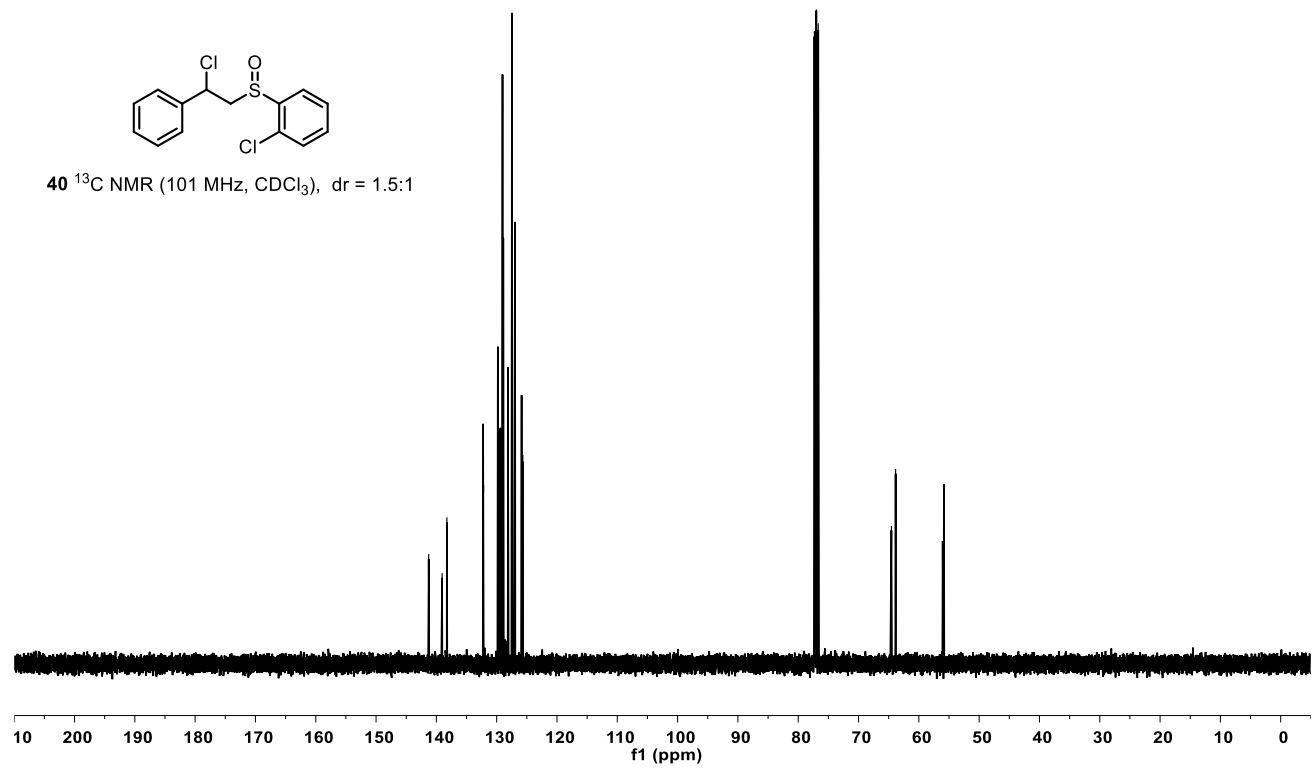


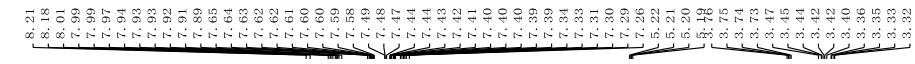


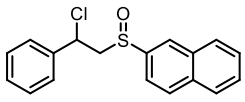
39 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 1.6:1



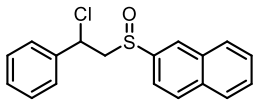

Cl
O
S
Cl
40 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.5:1
f1 (ppm)


Cl
O
S
Cl
40 ^{13}C NMR (101 MHz, $CDCl_3$), dr = 1.5:1
f1 (ppm)

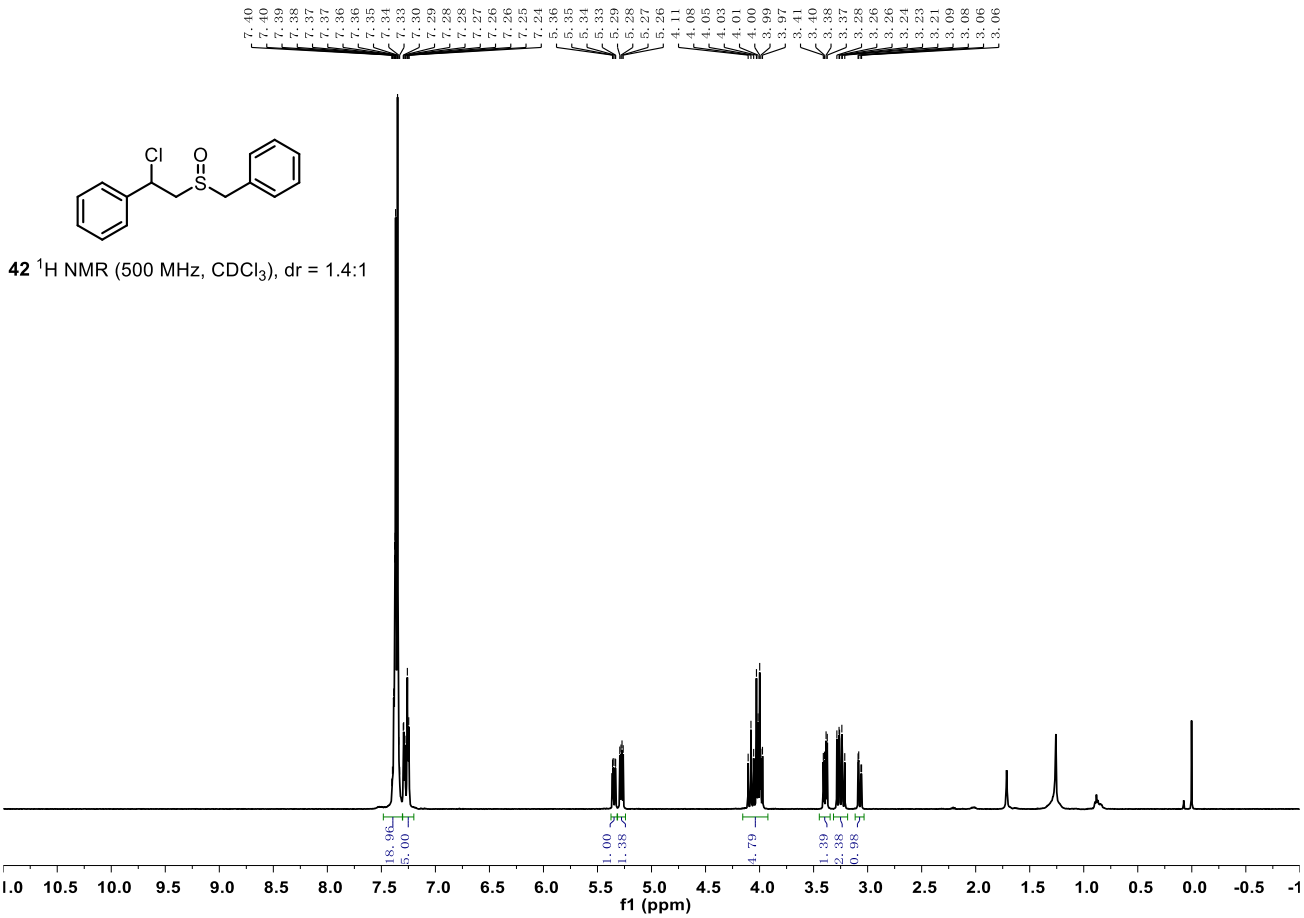




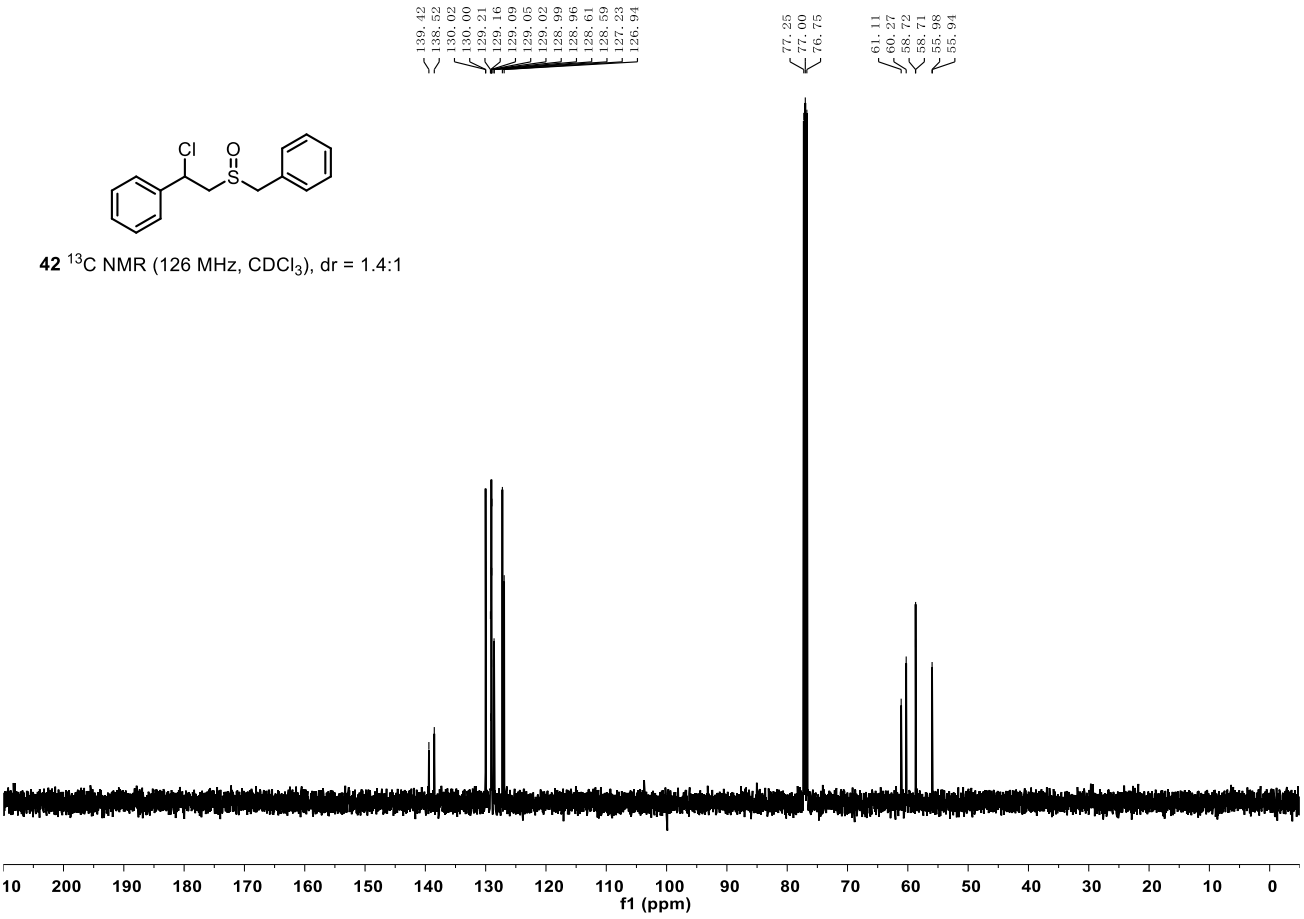
41 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.5:1



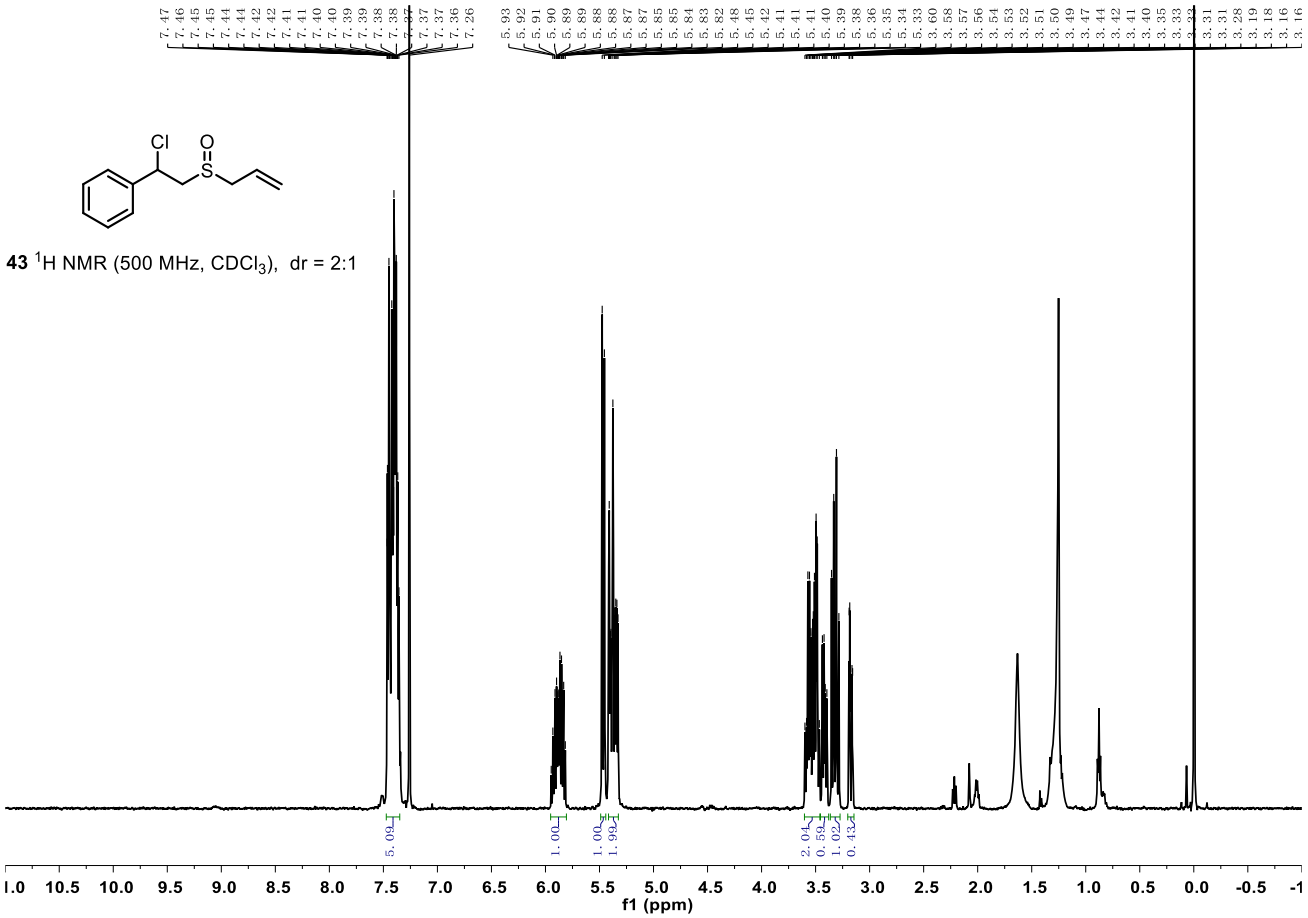
41 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 1.5:1



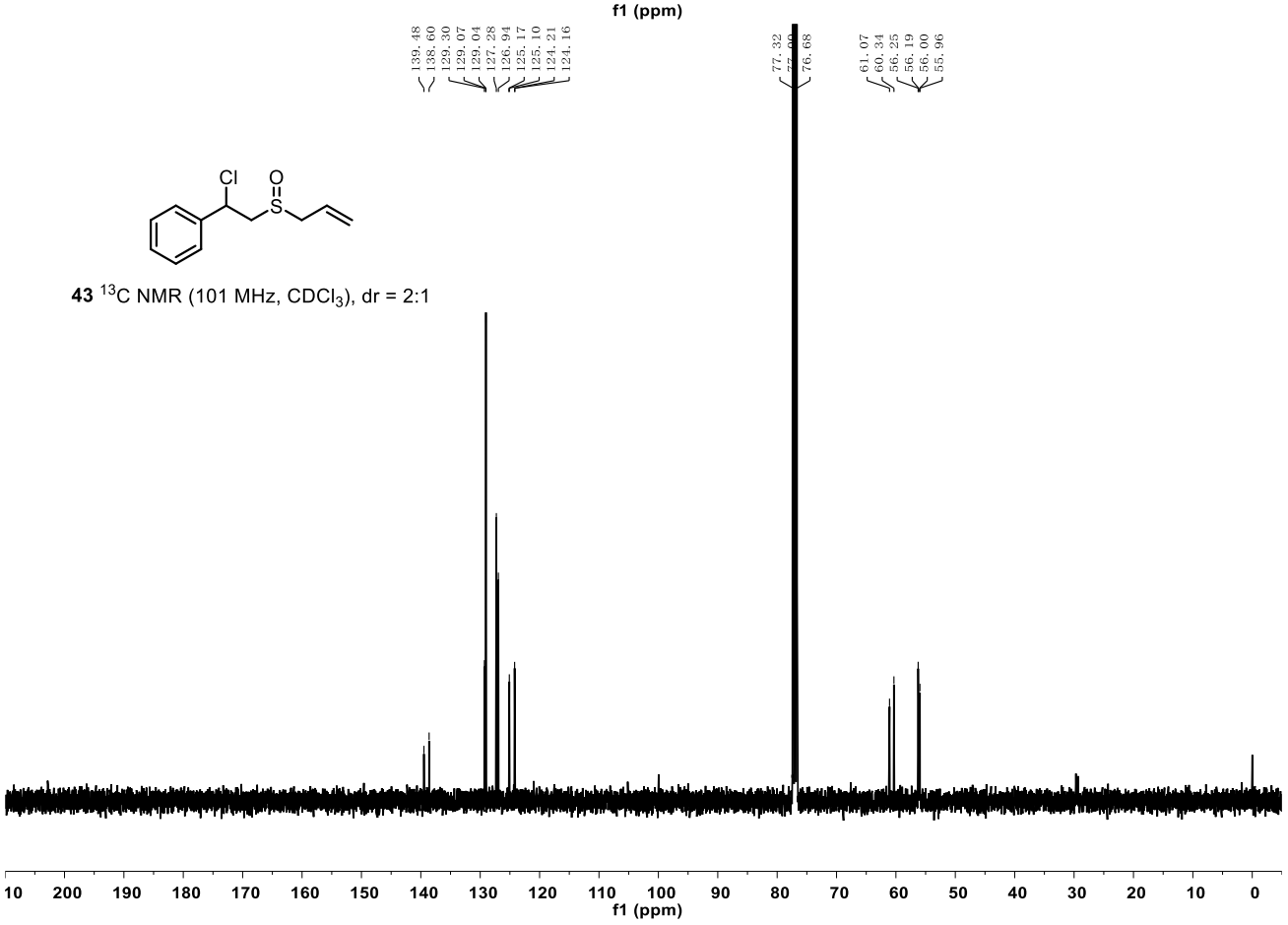
42 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.4:1



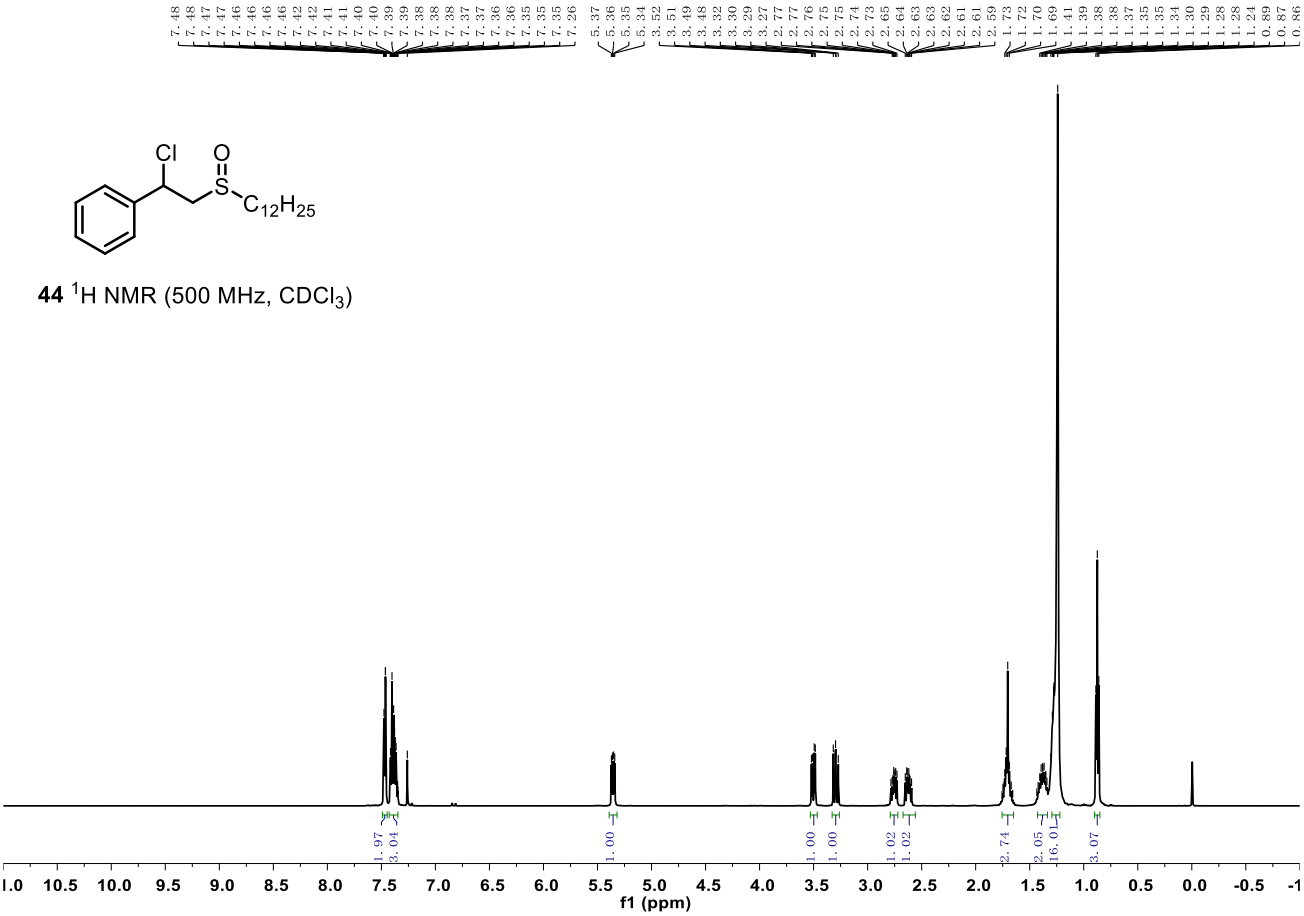
42 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 1.4:1



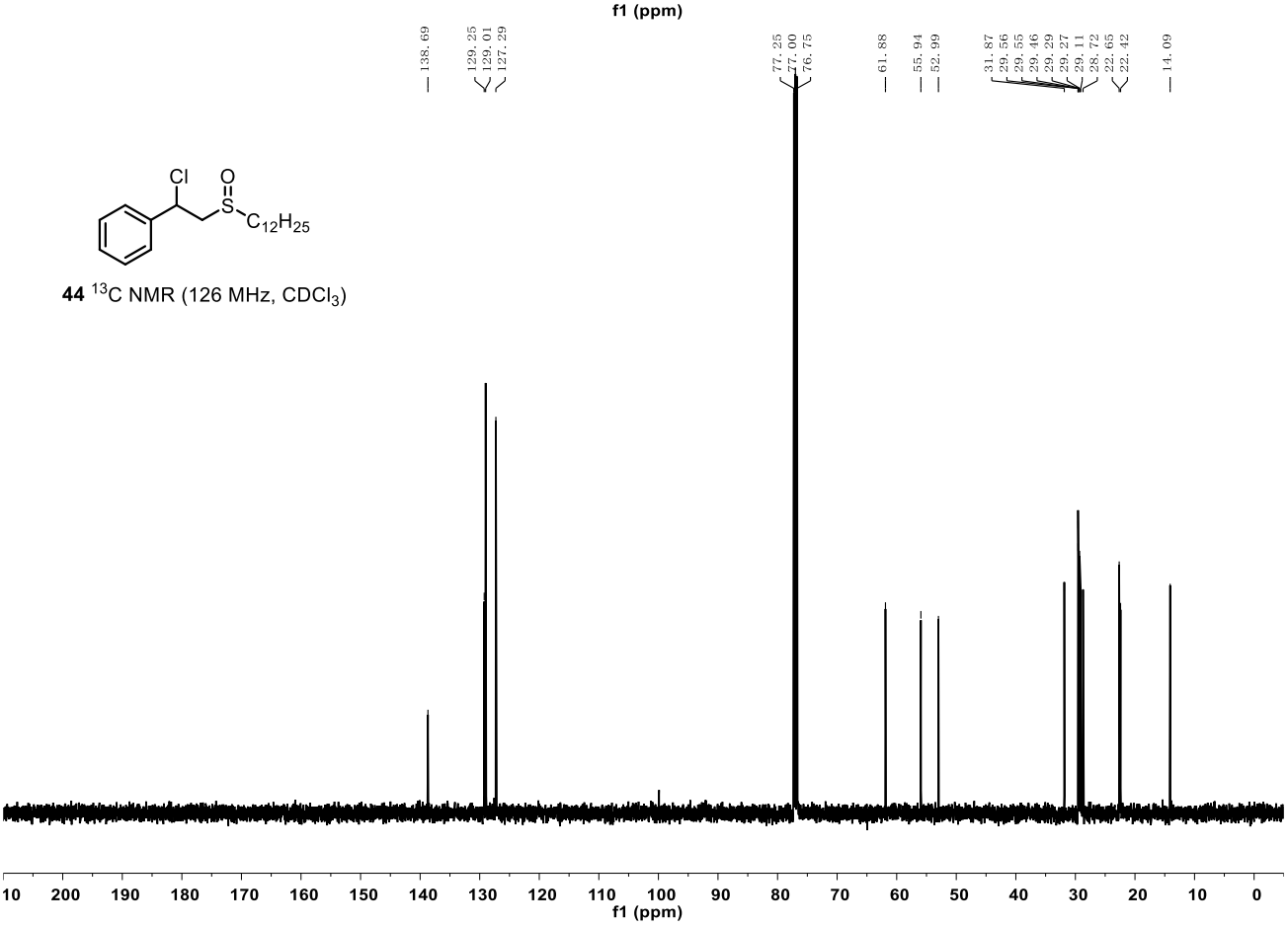
43 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 2:1



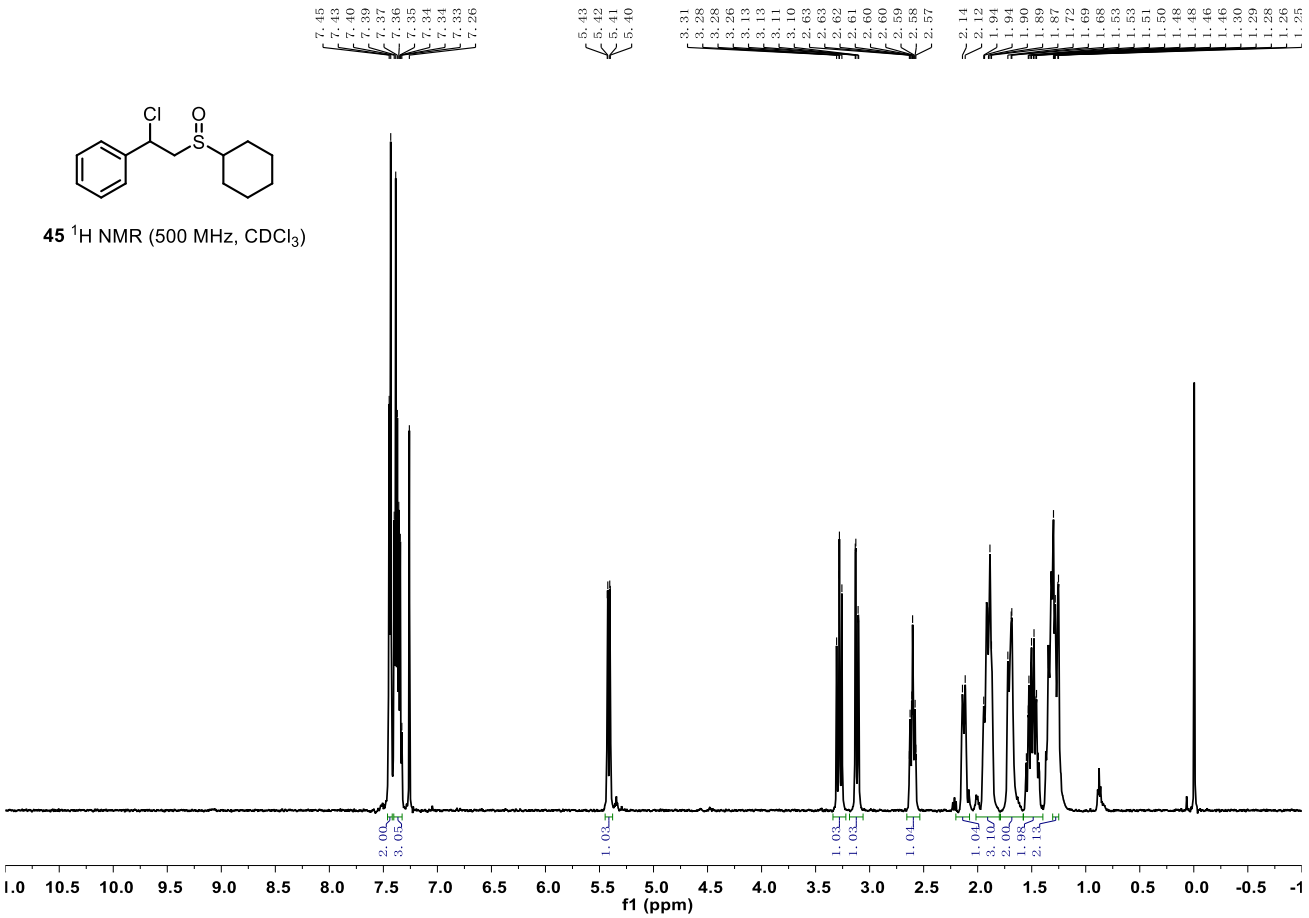
43 ^{13}C NMR (101 MHz, $CDCl_3$), dr = 2:1

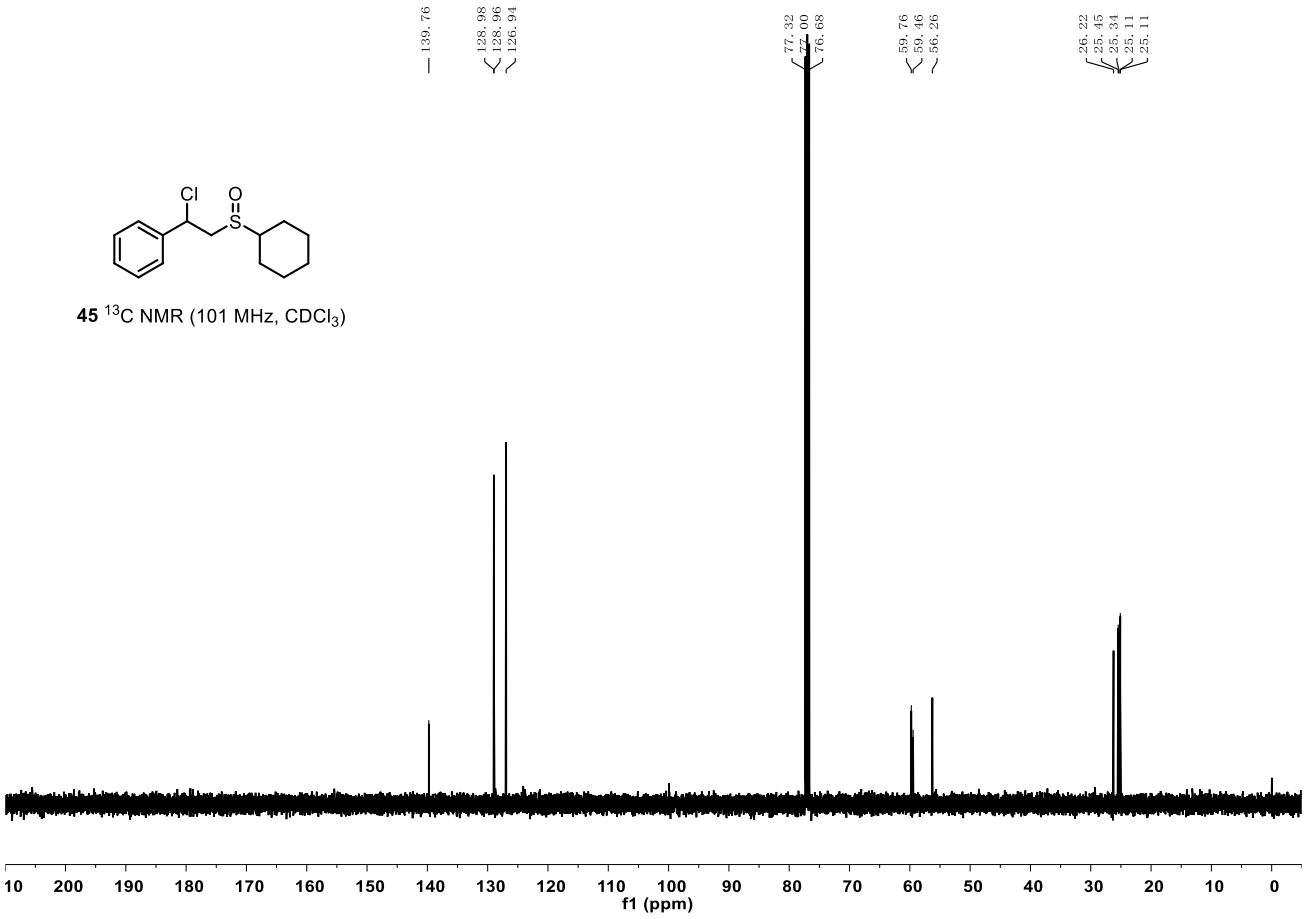


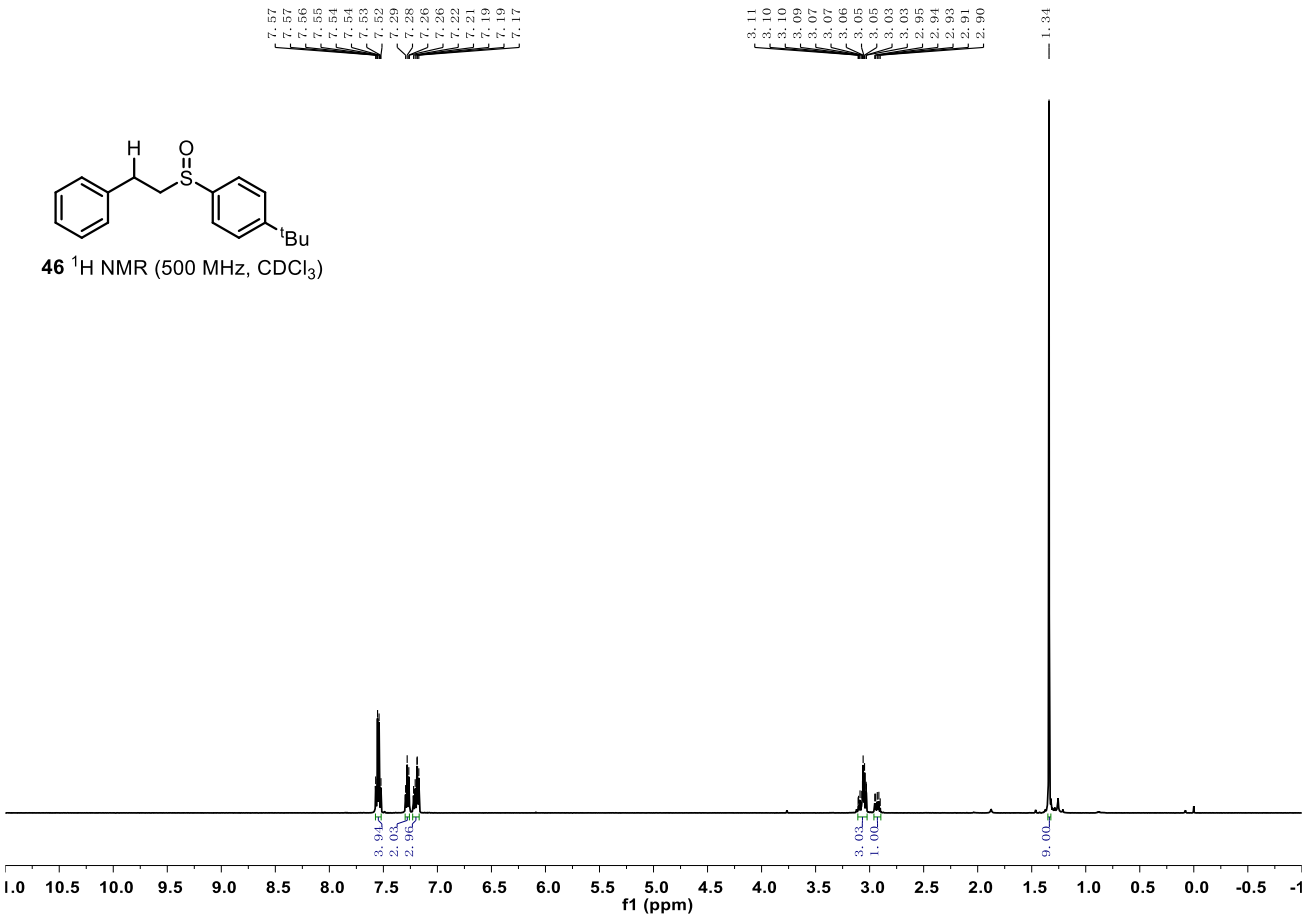
44 ^{1}H NMR (500 MHz, $CDCl_3$)



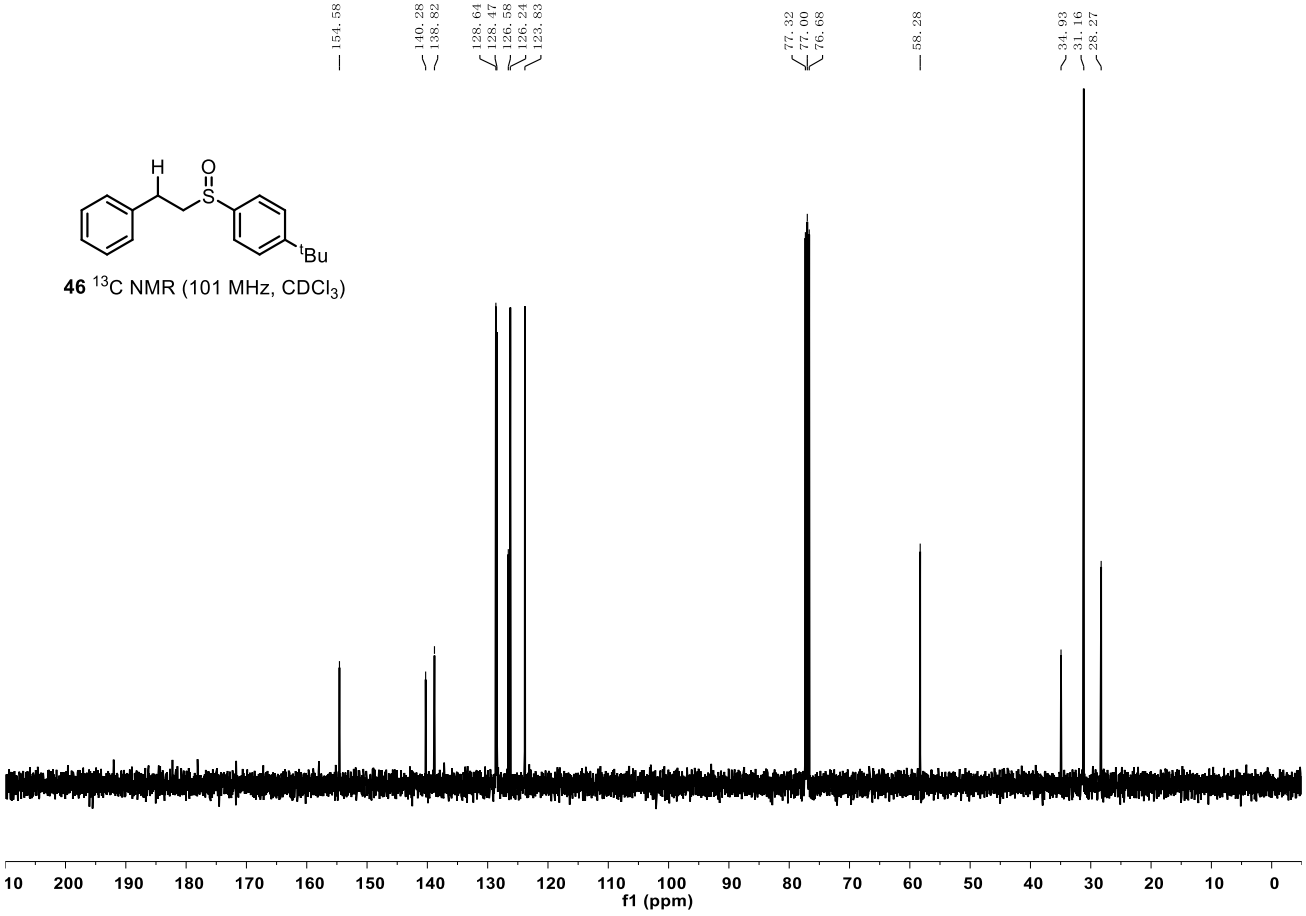
44 ^{13}C NMR (126 MHz, $CDCl_3$)


Cl
O
S
45 1H NMR (500 MHz, CDCl3)
f1 (ppm)

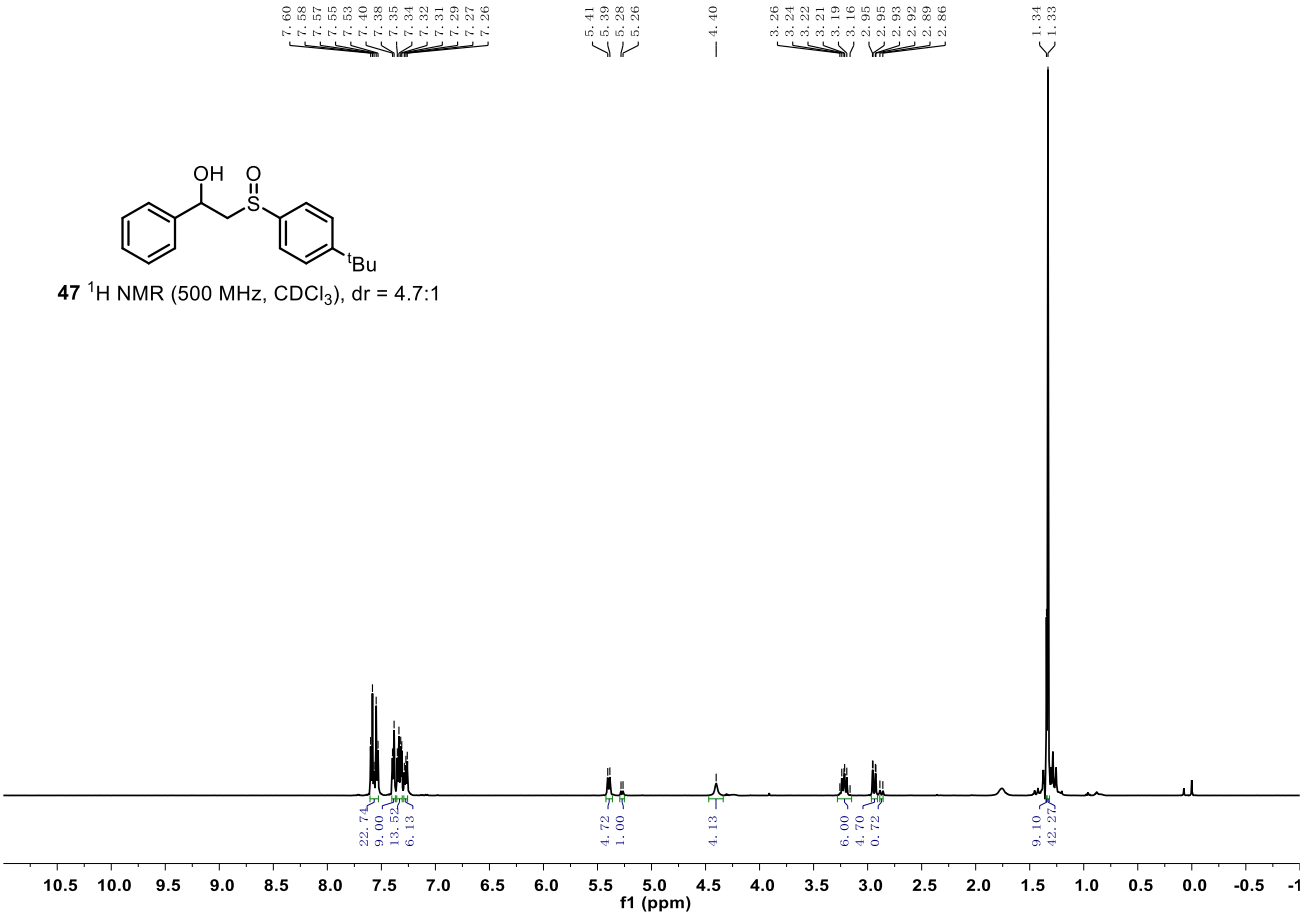

Cl
O
S
45 13C NMR (101 MHz, CDCl3)
f1 (ppm)



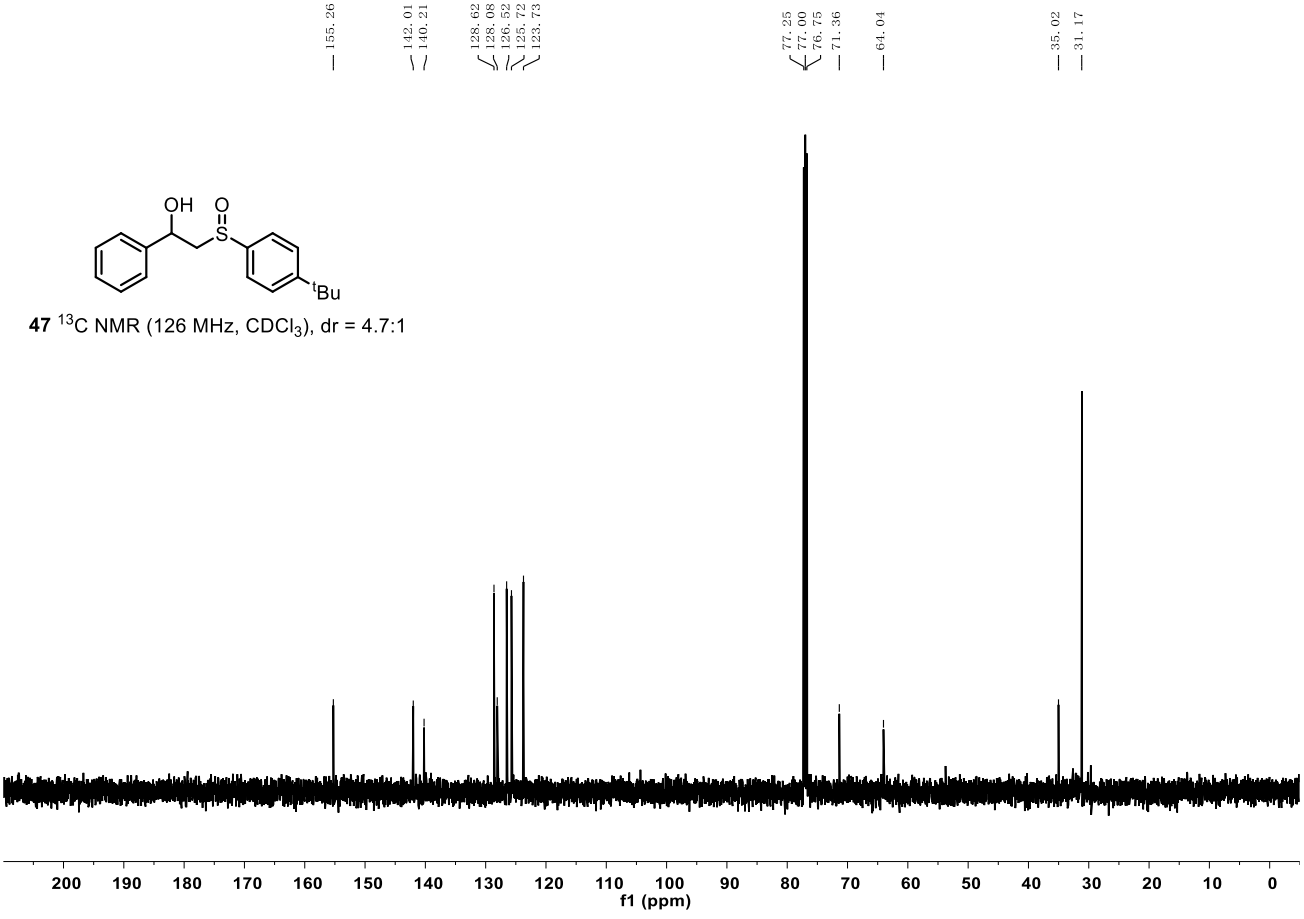
46 ^{1}H NMR (500 MHz, $CDCl_3$)



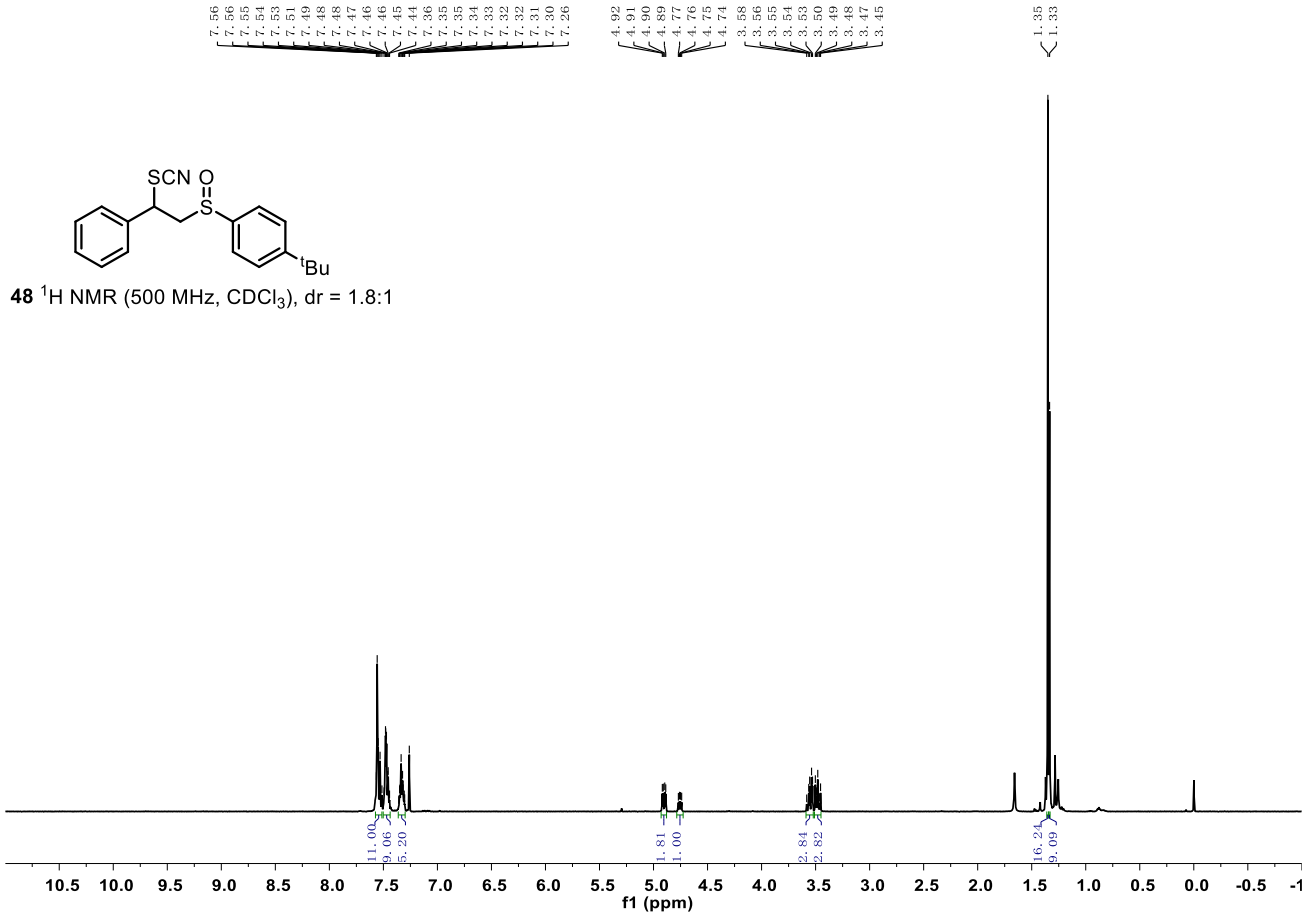
46 ^{13}C NMR (101 MHz, $CDCl_3$)



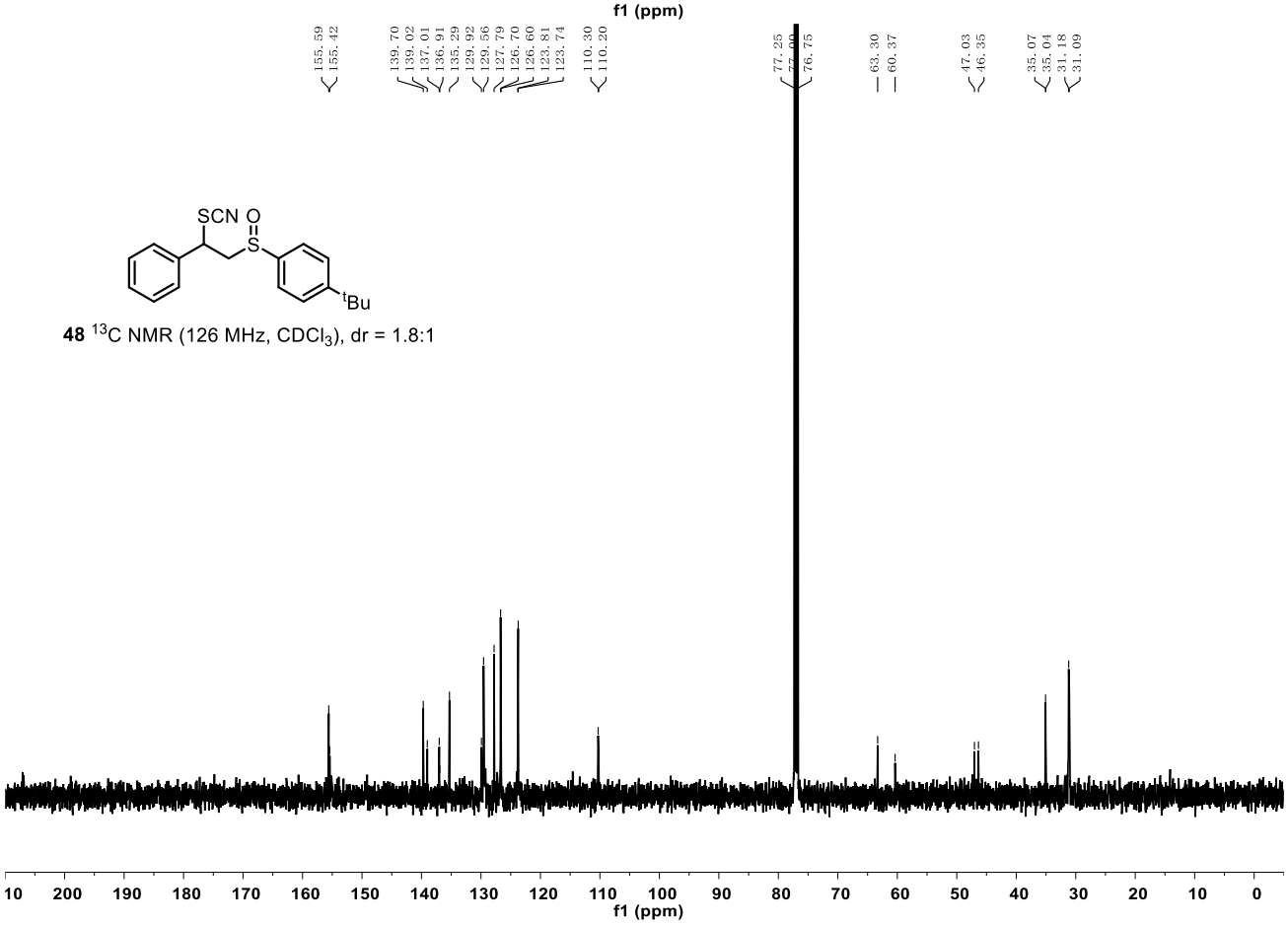
47 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 4.7:1



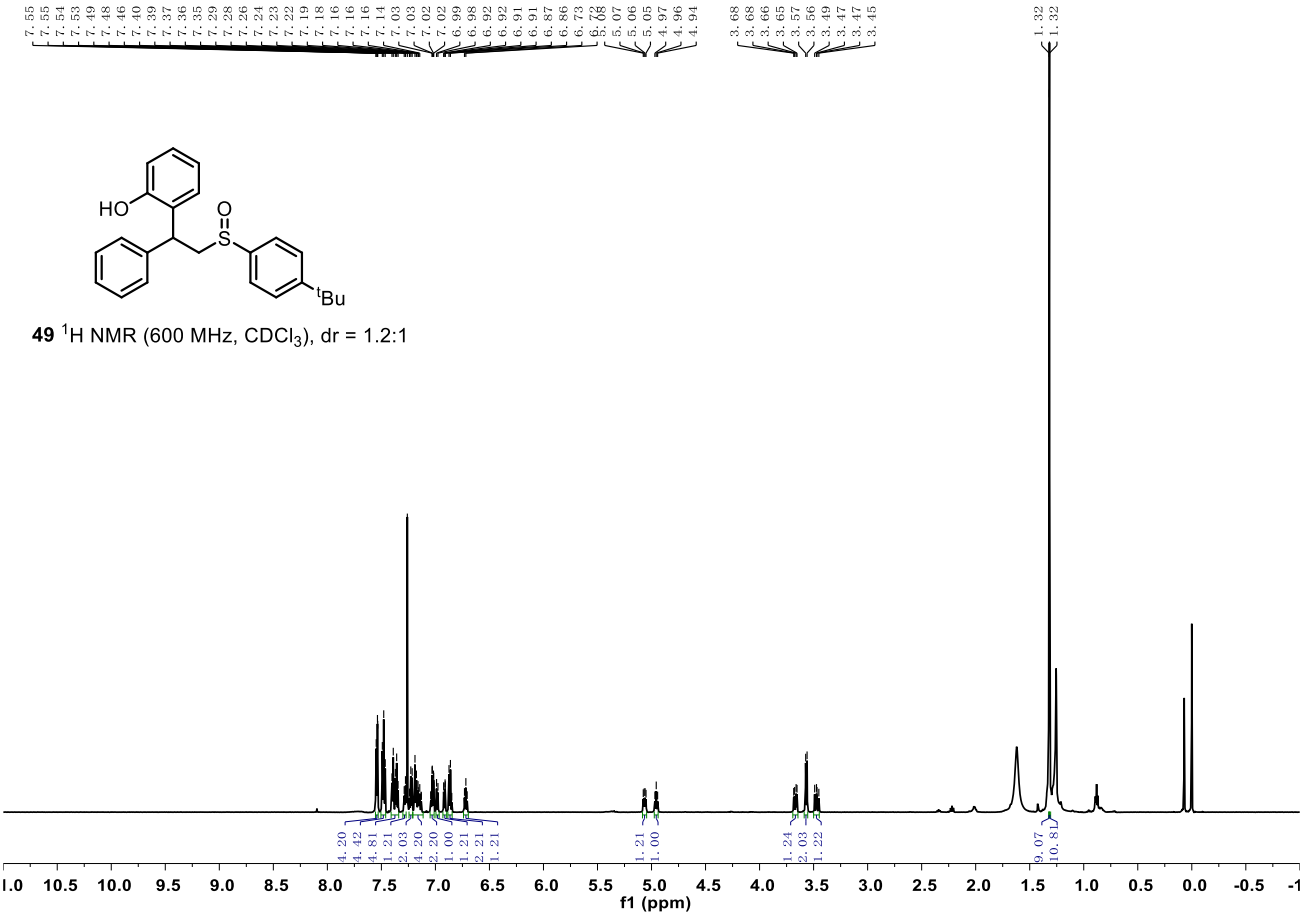
47 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 4.7:1



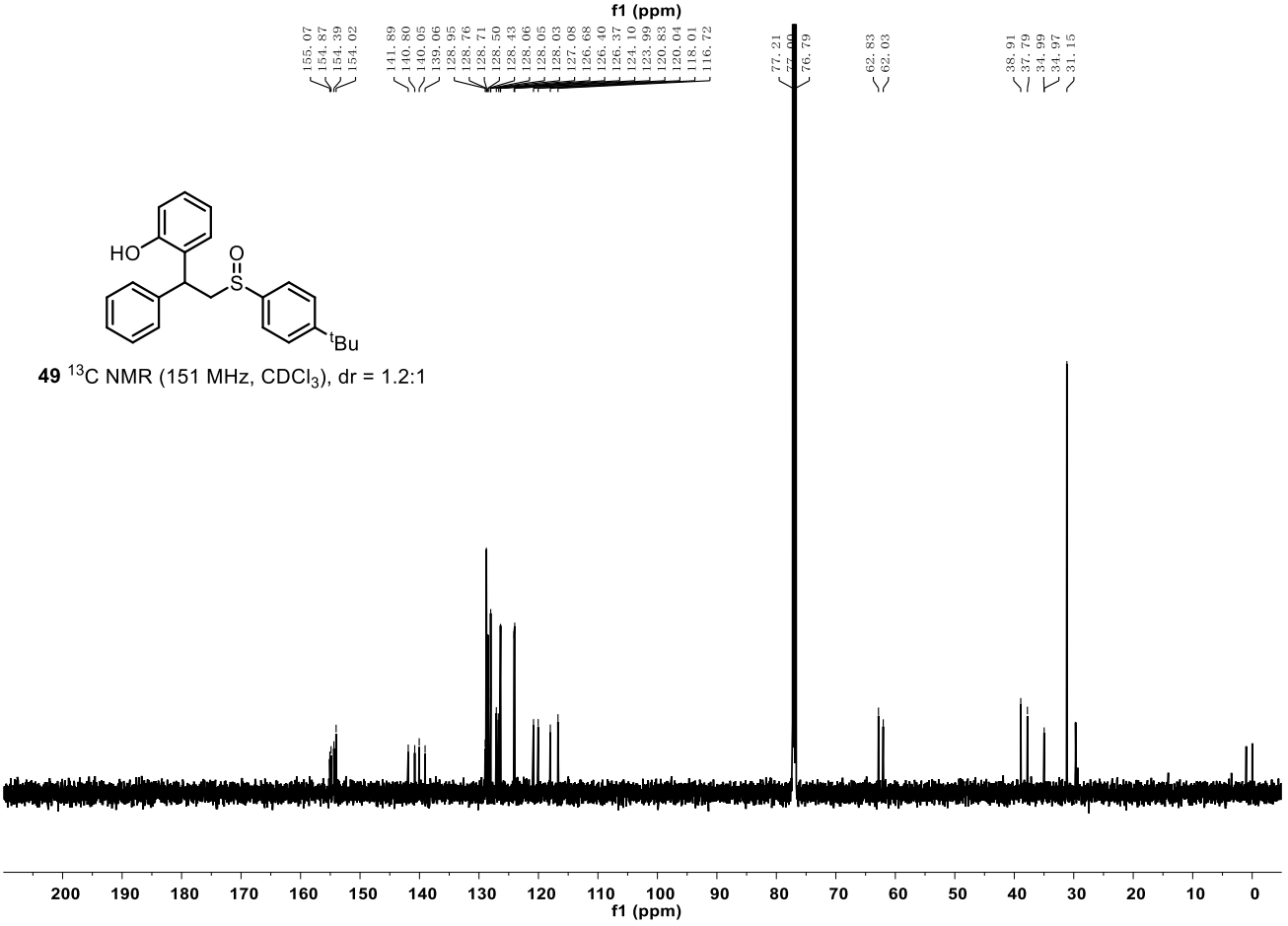
48 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.8:1



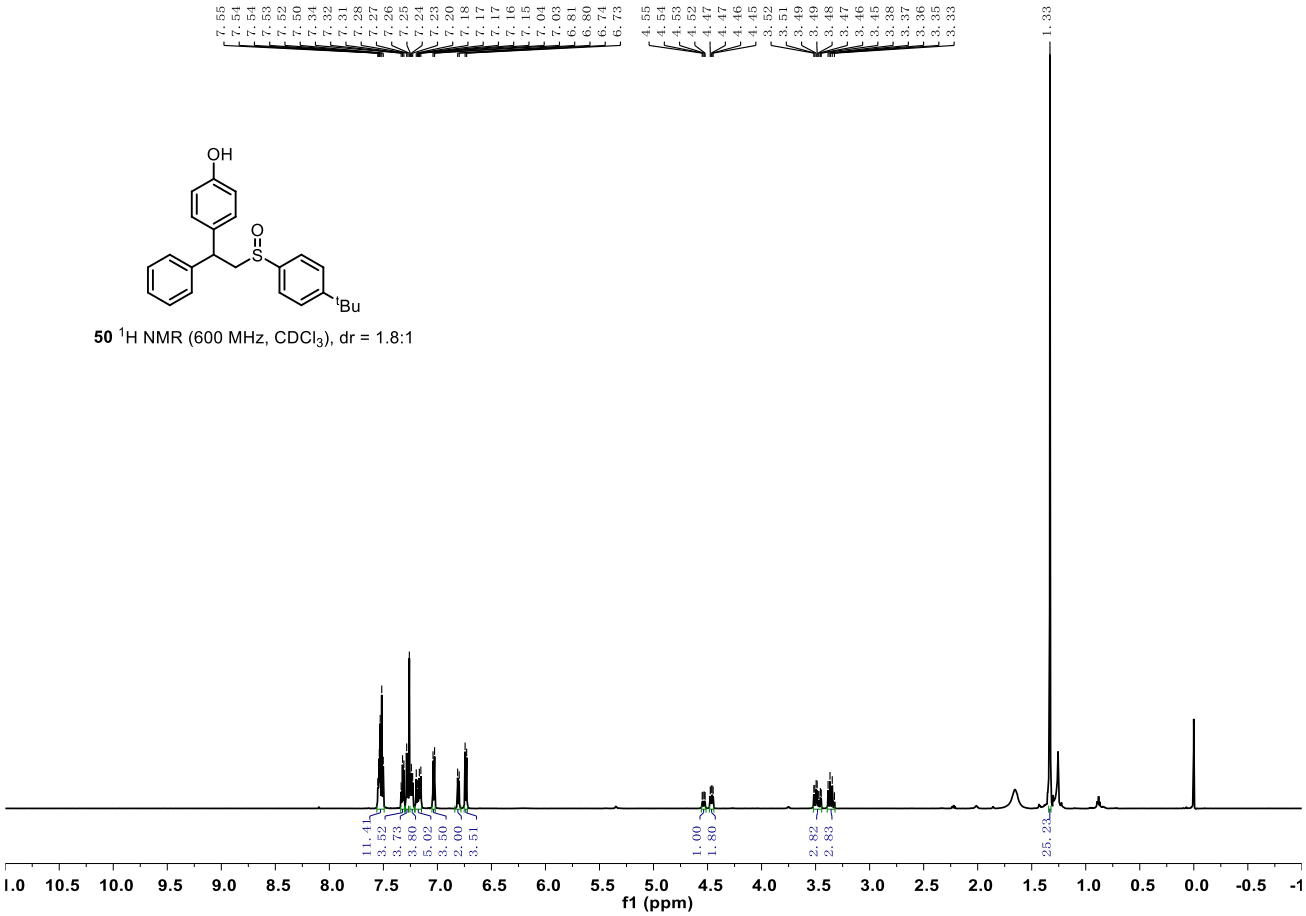
48 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 1.8:1



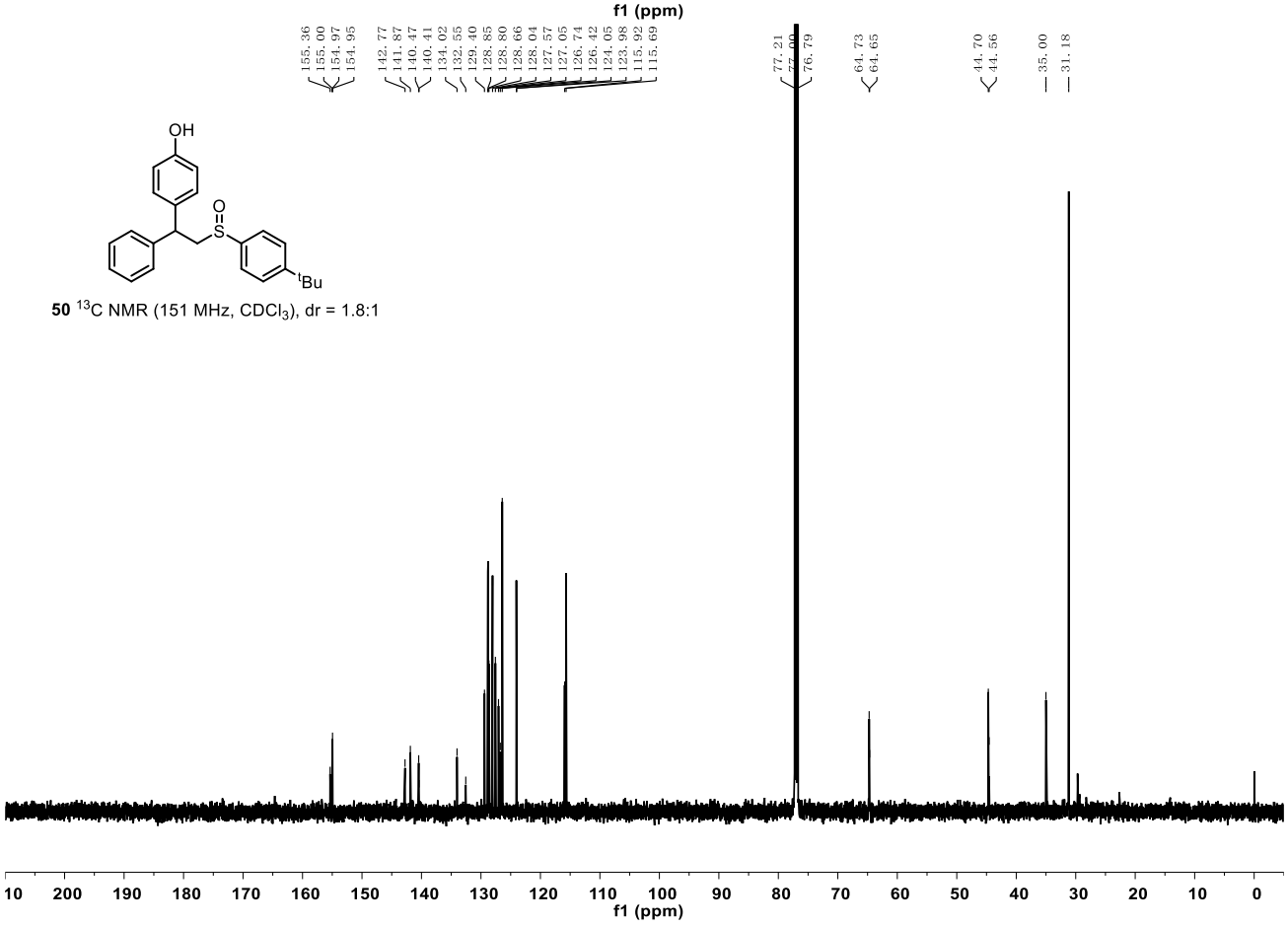
49 ^{1}H NMR (600 MHz, $CDCl_3$), dr = 1.2:1



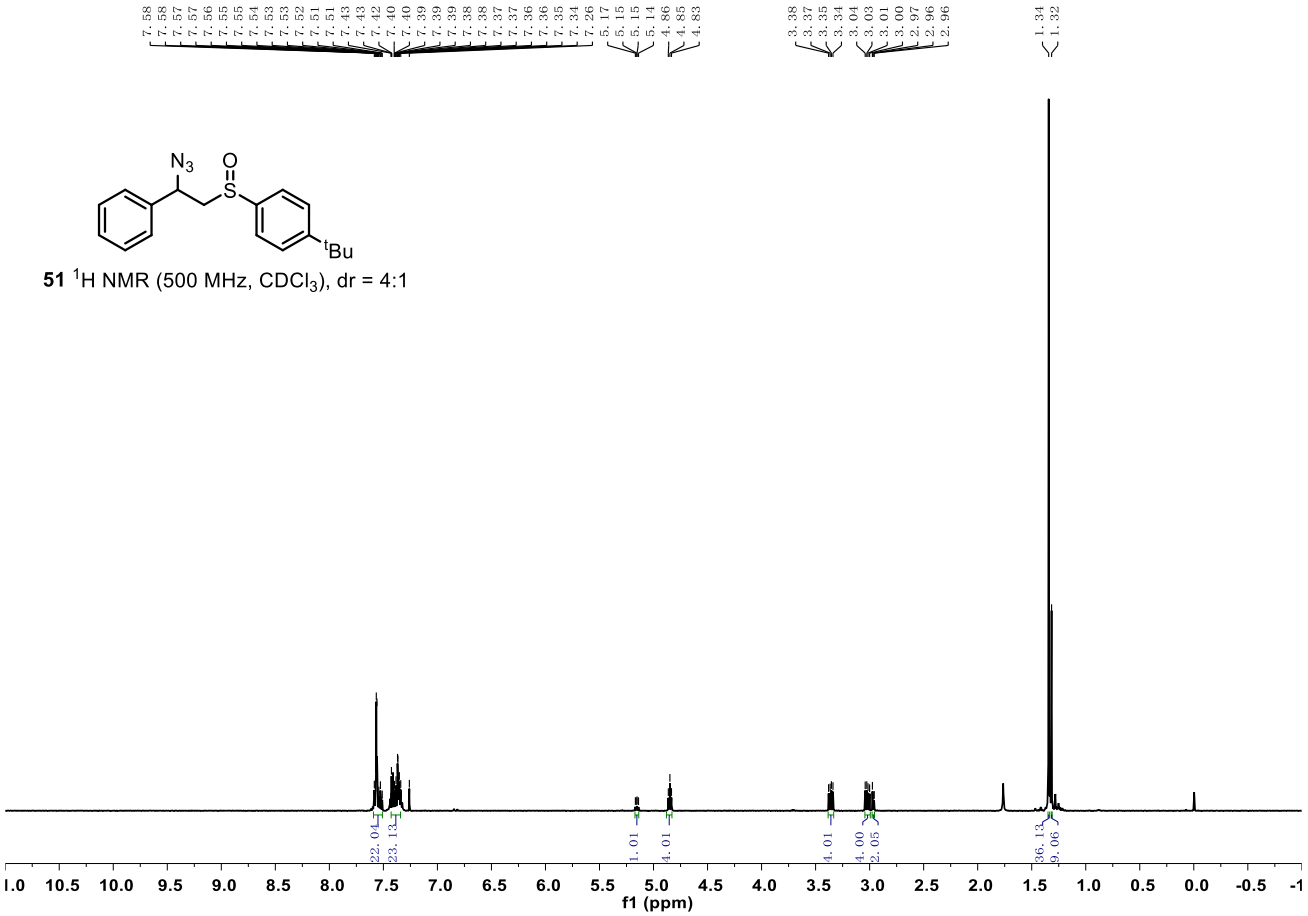
49 ^{13}C NMR (151 MHz, $CDCl_3$), dr = 1.2:1



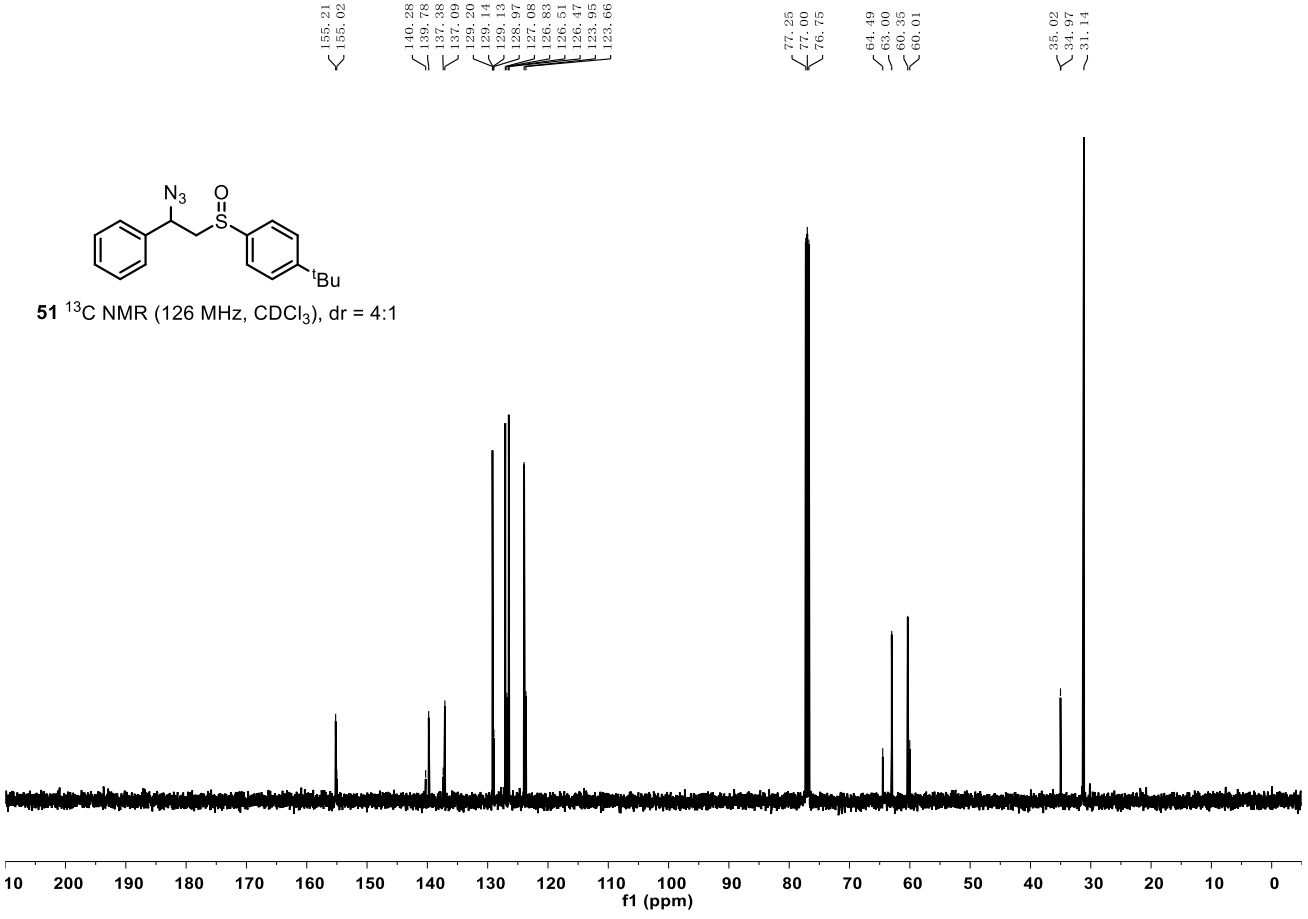
50 ^{1}H NMR (600 MHz, $CDCl_3$), dr = 1.8:1



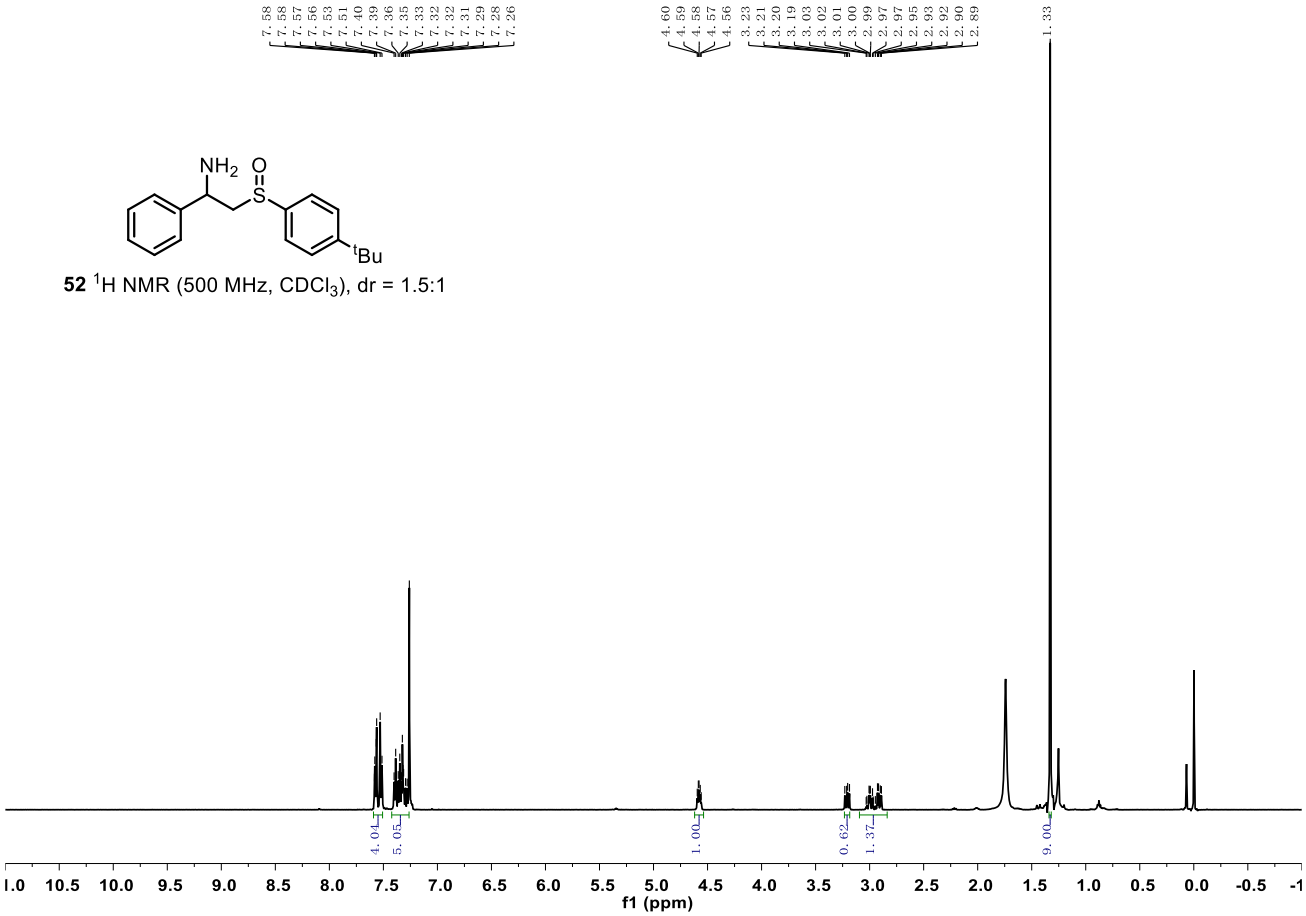
50 ^{13}C NMR (151 MHz, $CDCl_3$), dr = 1.8:1



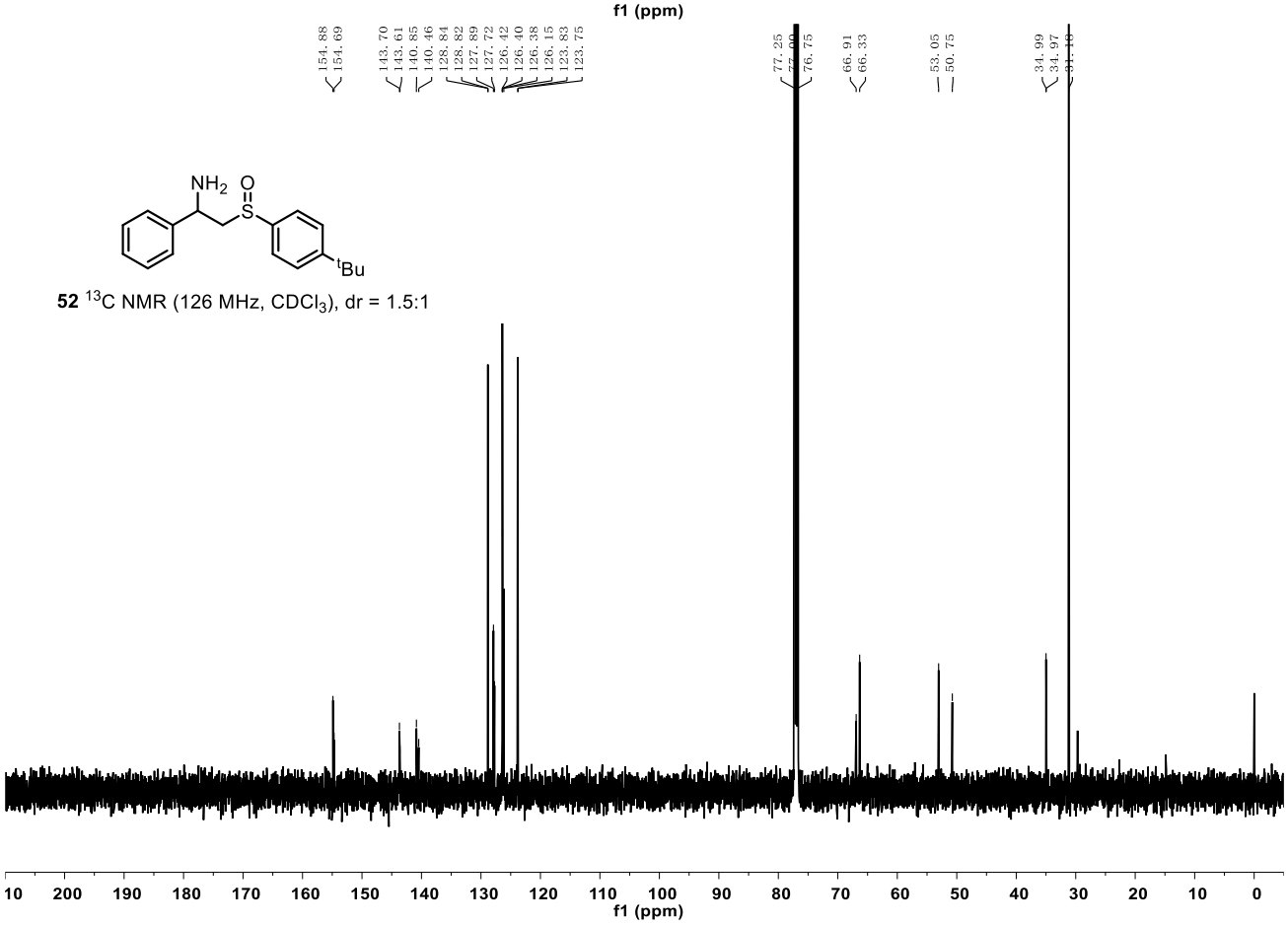
51 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 4:1



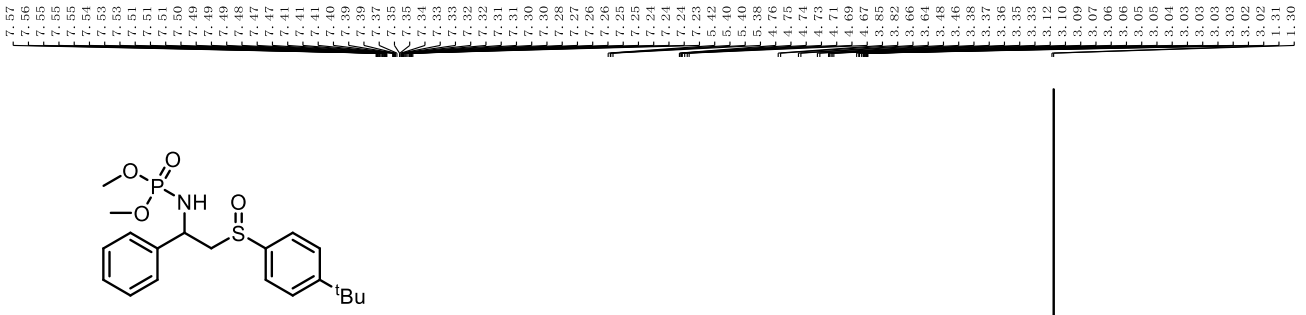
51 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 4:1



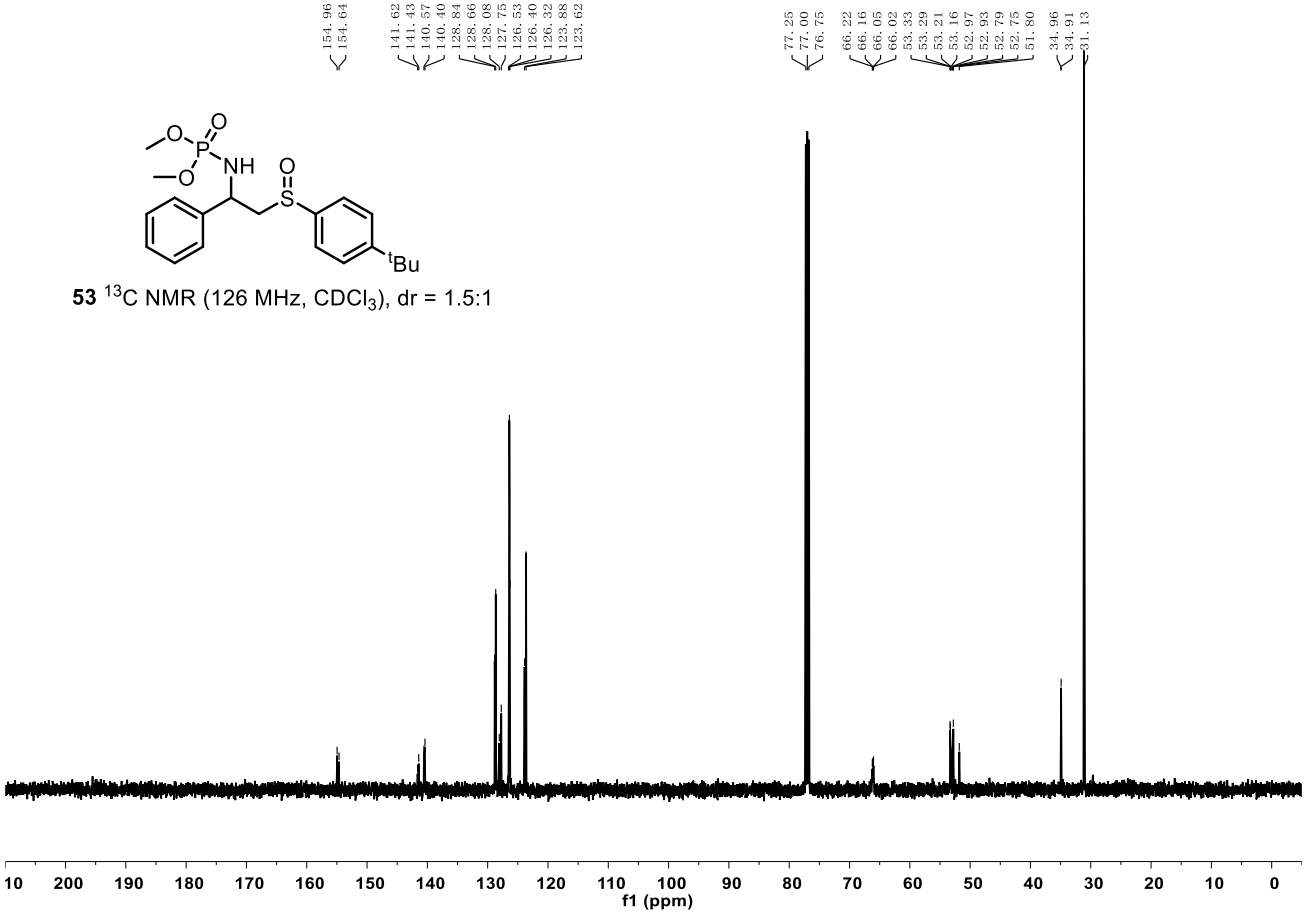
52 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.5:1



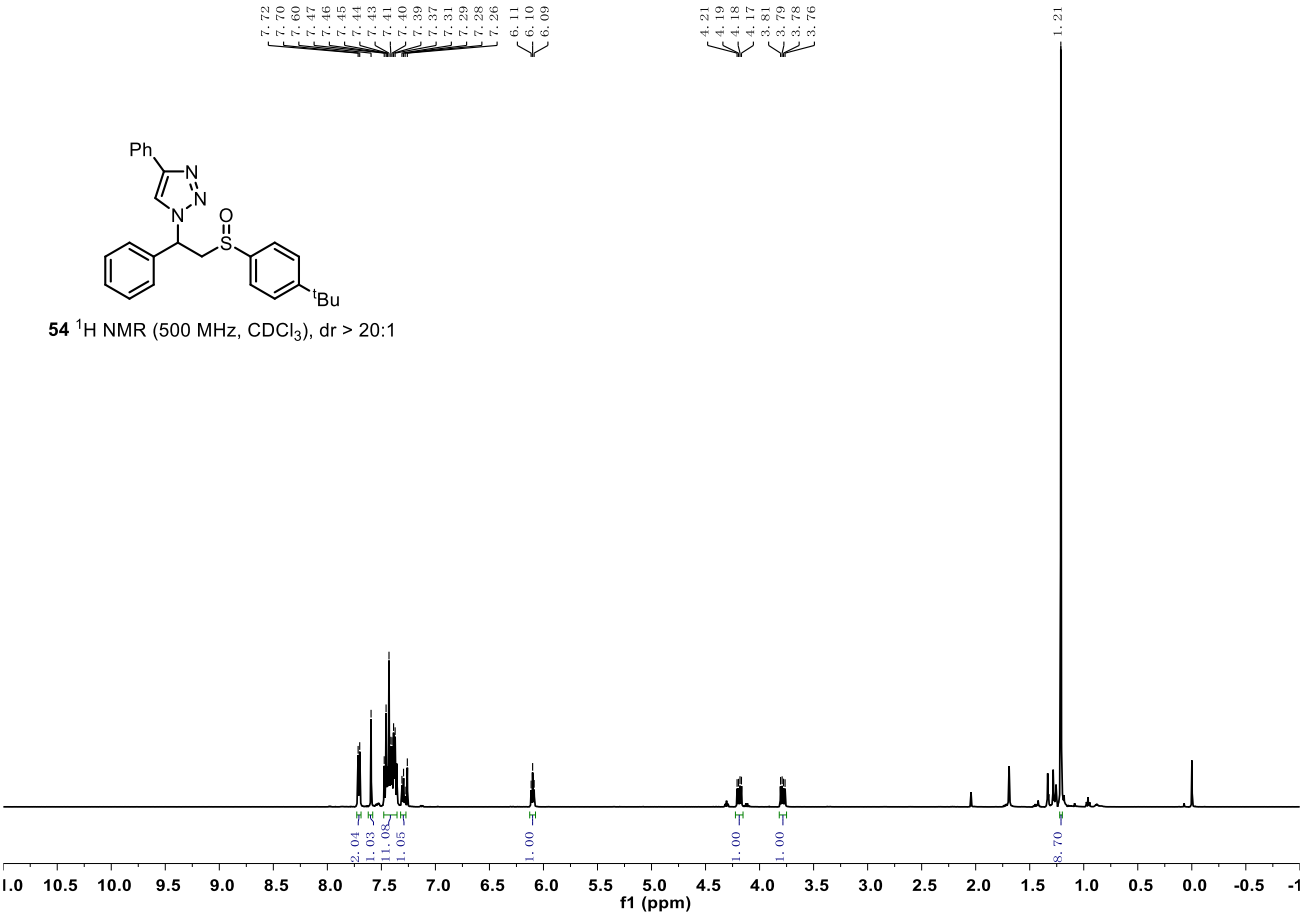
52 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 1.5:1



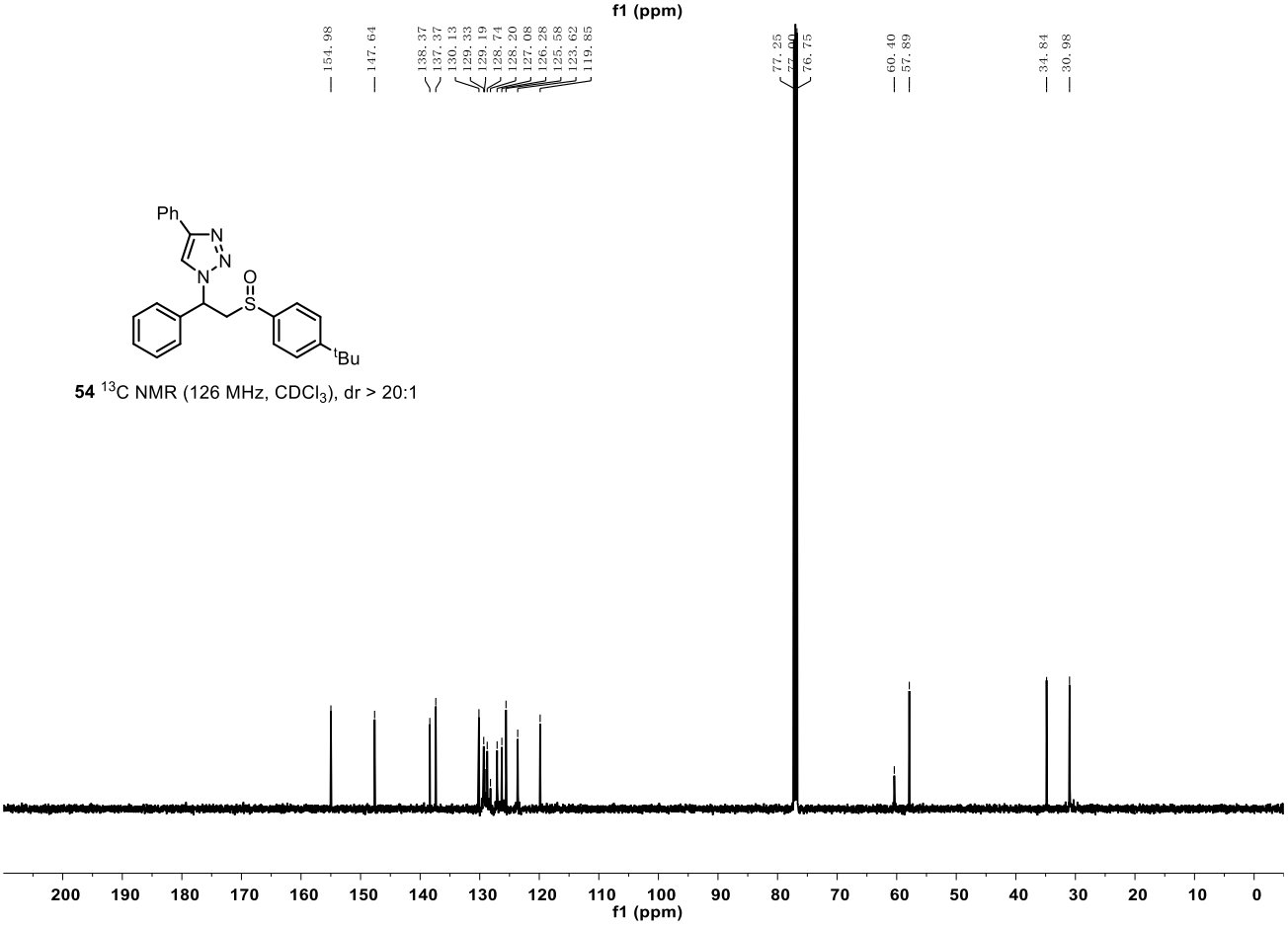
53 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.5:1



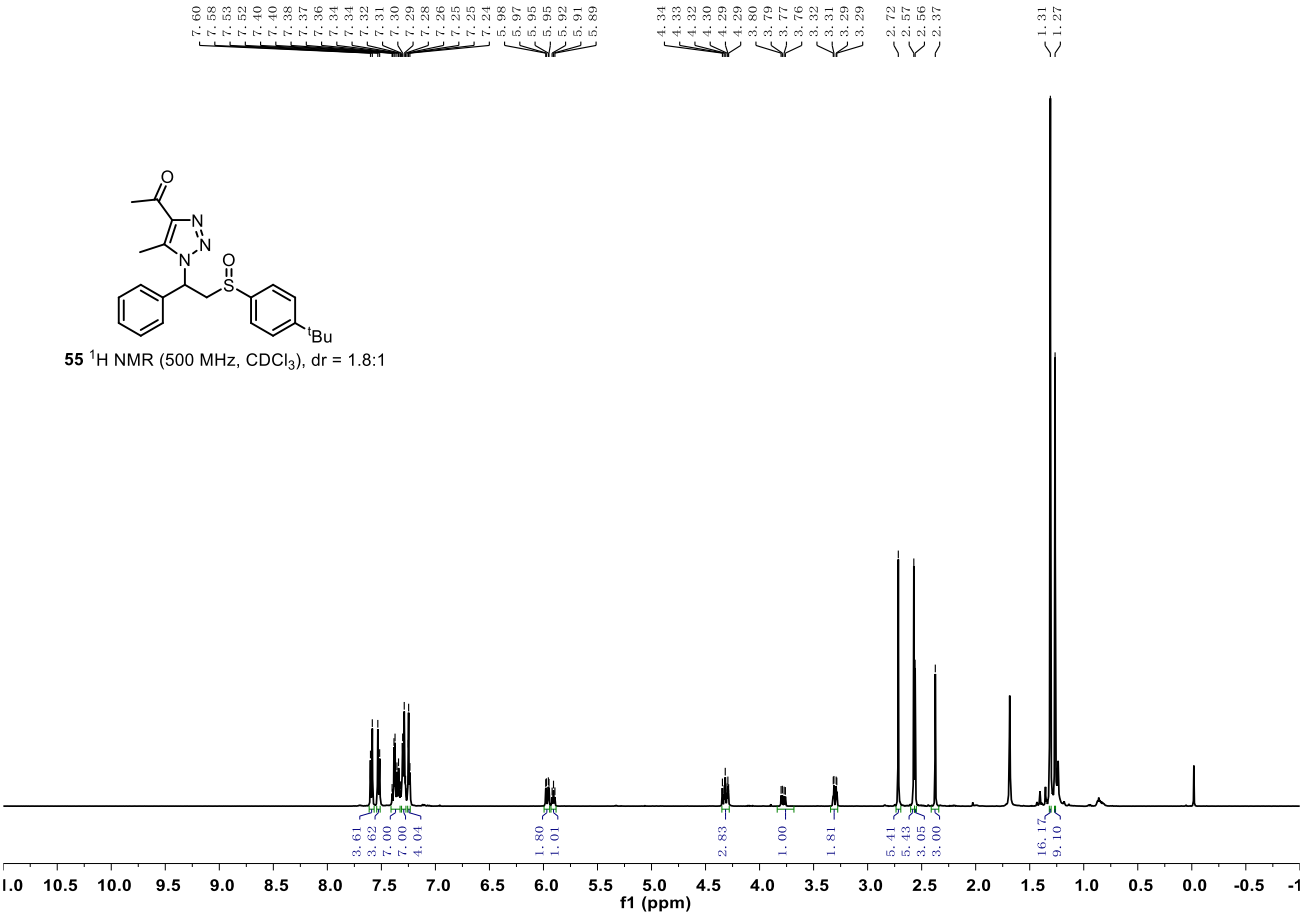
53 ^{13}C NMR (126 MHz, $CDCl_3$), dr = 1.5:1

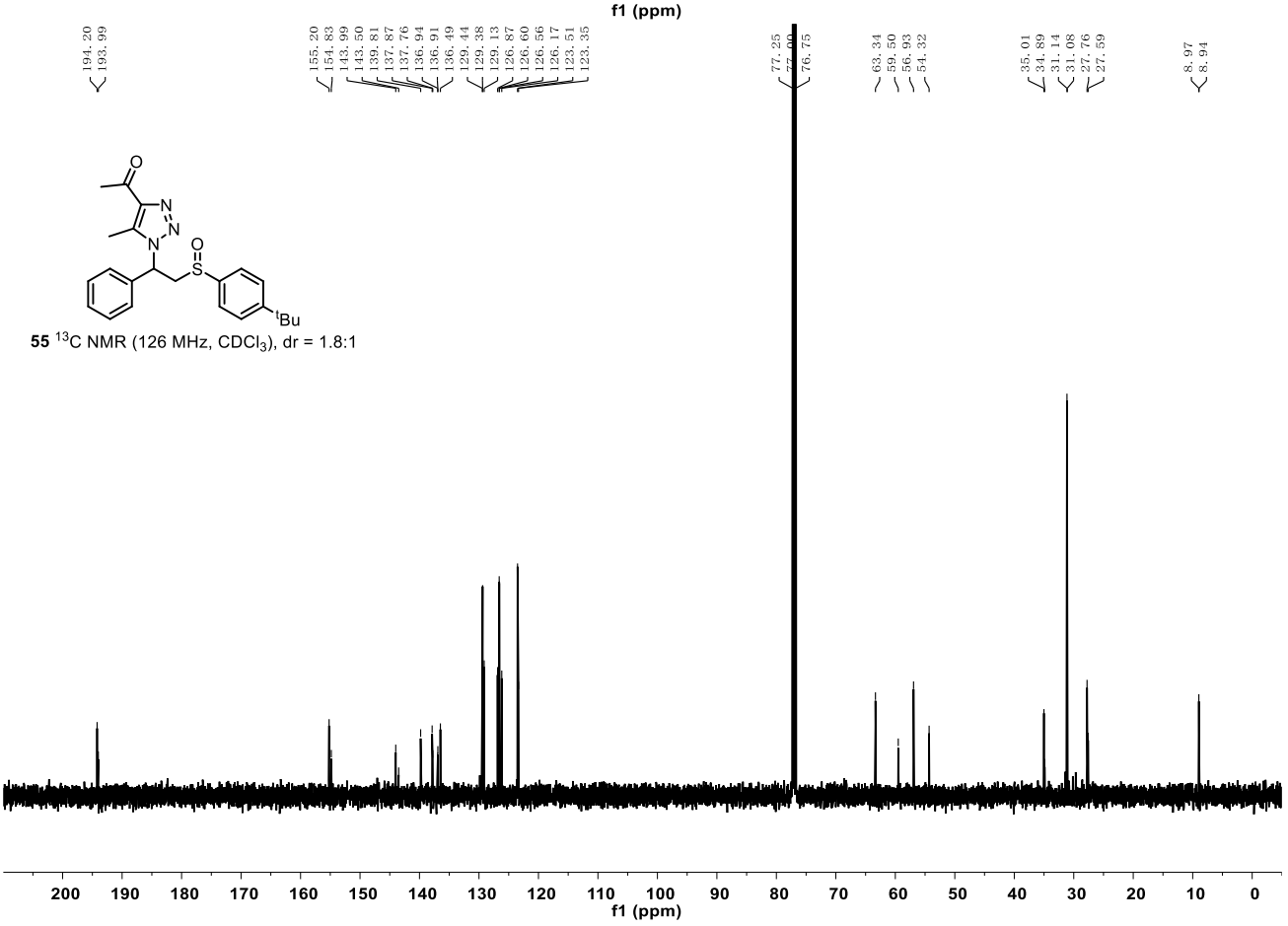


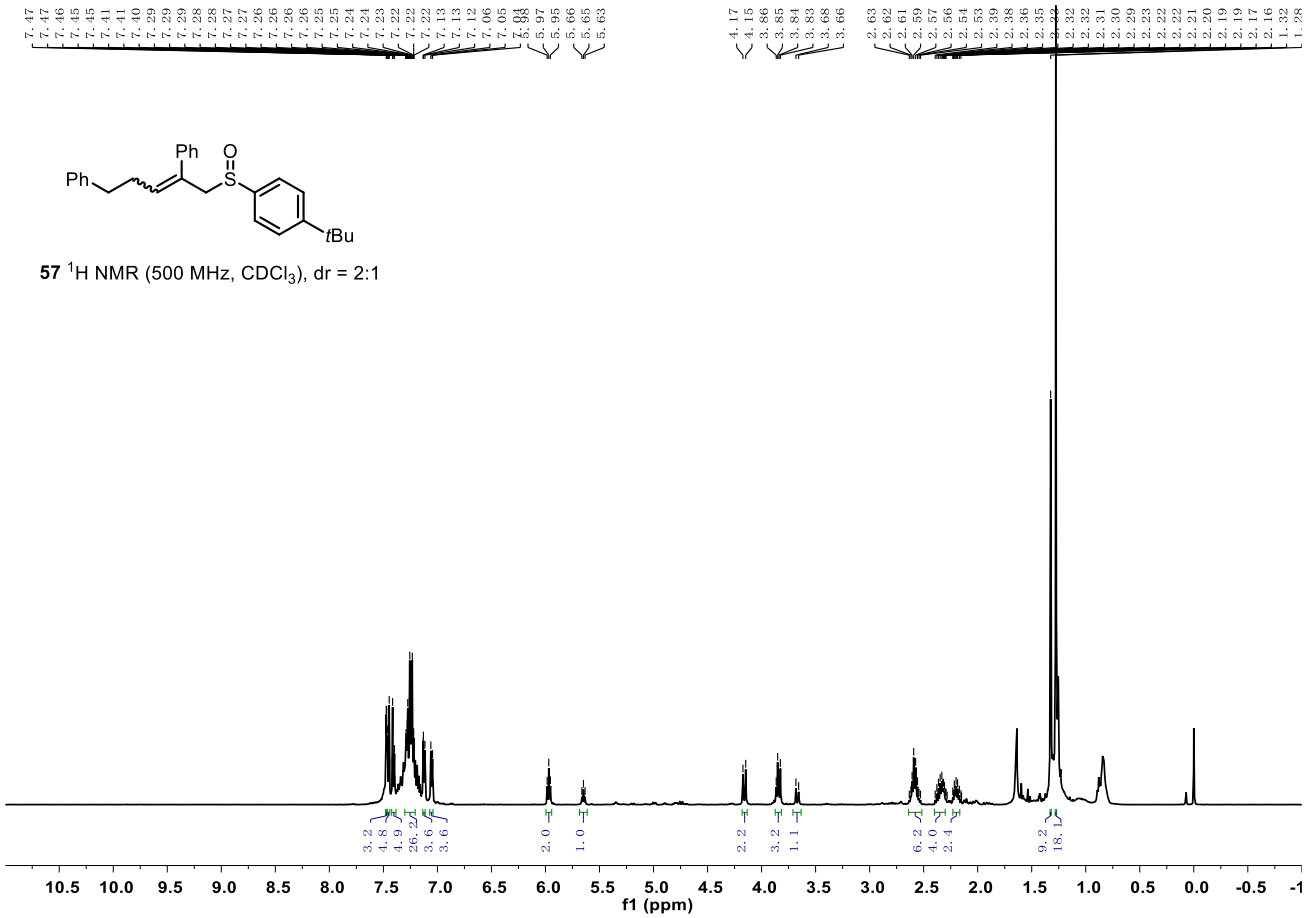
54 ^{1}H NMR (500 MHz, $CDCl_3$), dr > 20:1



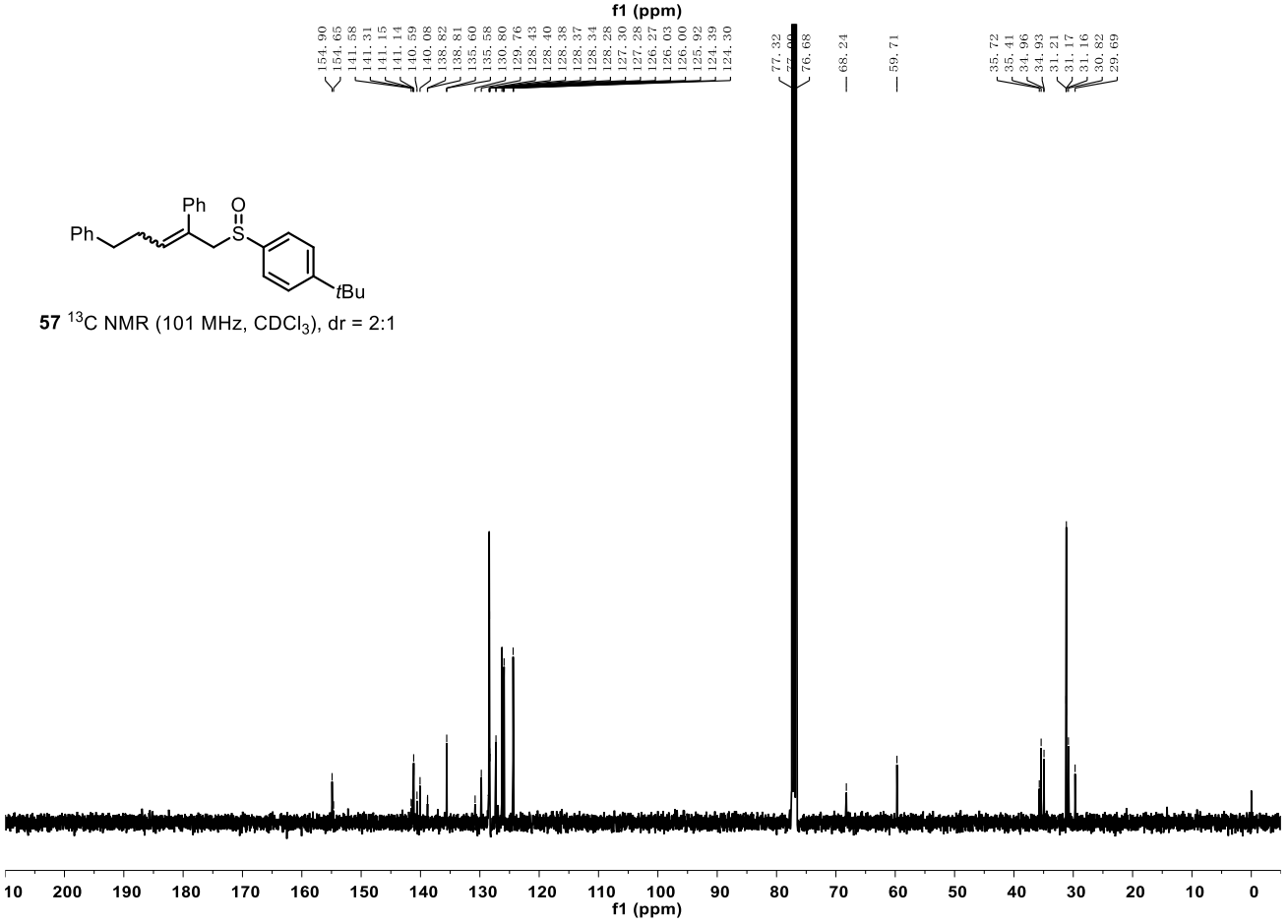
54 ^{13}C NMR (126 MHz, $CDCl_3$), dr > 20:1


7.60 7.58 7.53 7.52 7.40 7.40 7.38 7.37 7.36 7.34 7.34 7.32 7.31 7.30 7.29 7.28 7.26 7.25 7.25 7.24 5.98 5.97 5.95 5.95 5.92 5.91 5.89
4.34 4.33 4.32 4.30 4.29 4.29 3.80 3.79 3.77 3.76 3.32 3.31 3.29 3.29
2.72 2.57 2.56 2.37
1.31 1.27
O
N
N
N
O
S
tBu
55 1H NMR (500 MHz, CDCl3), dr = 1.8:1
3.61 3.62 7.00 7.00 4.04 1.80 1.01 2.83 1.00 1.81 5.41 5.43 3.05 3.00 16.17 9.10
f1 (ppm)

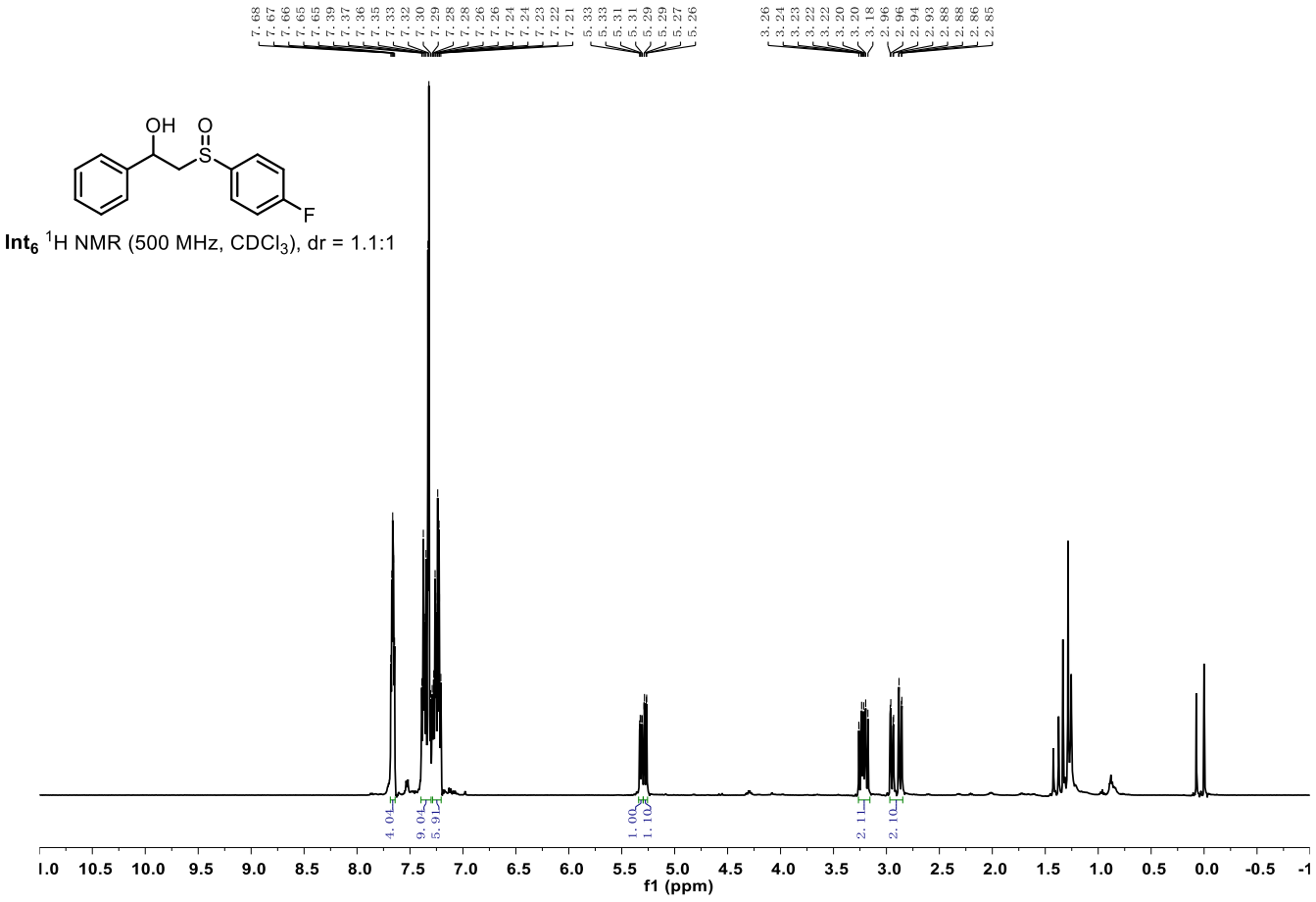

194.20 193.99
155.20 154.83 143.99 143.50 139.81 137.87 137.76 136.94 136.91 136.49 129.44 129.38 129.13 126.87 126.60 126.56 126.17 123.51 123.35
77.25 77.00 76.75
63.34 59.50 56.93 54.32
35.01 34.89 31.14 31.08 27.76 27.59
8.97 8.94
O
N
N
N
O
S
tBu
55 13C NMR (126 MHz, CDCl3), dr = 1.8:1
f1 (ppm)



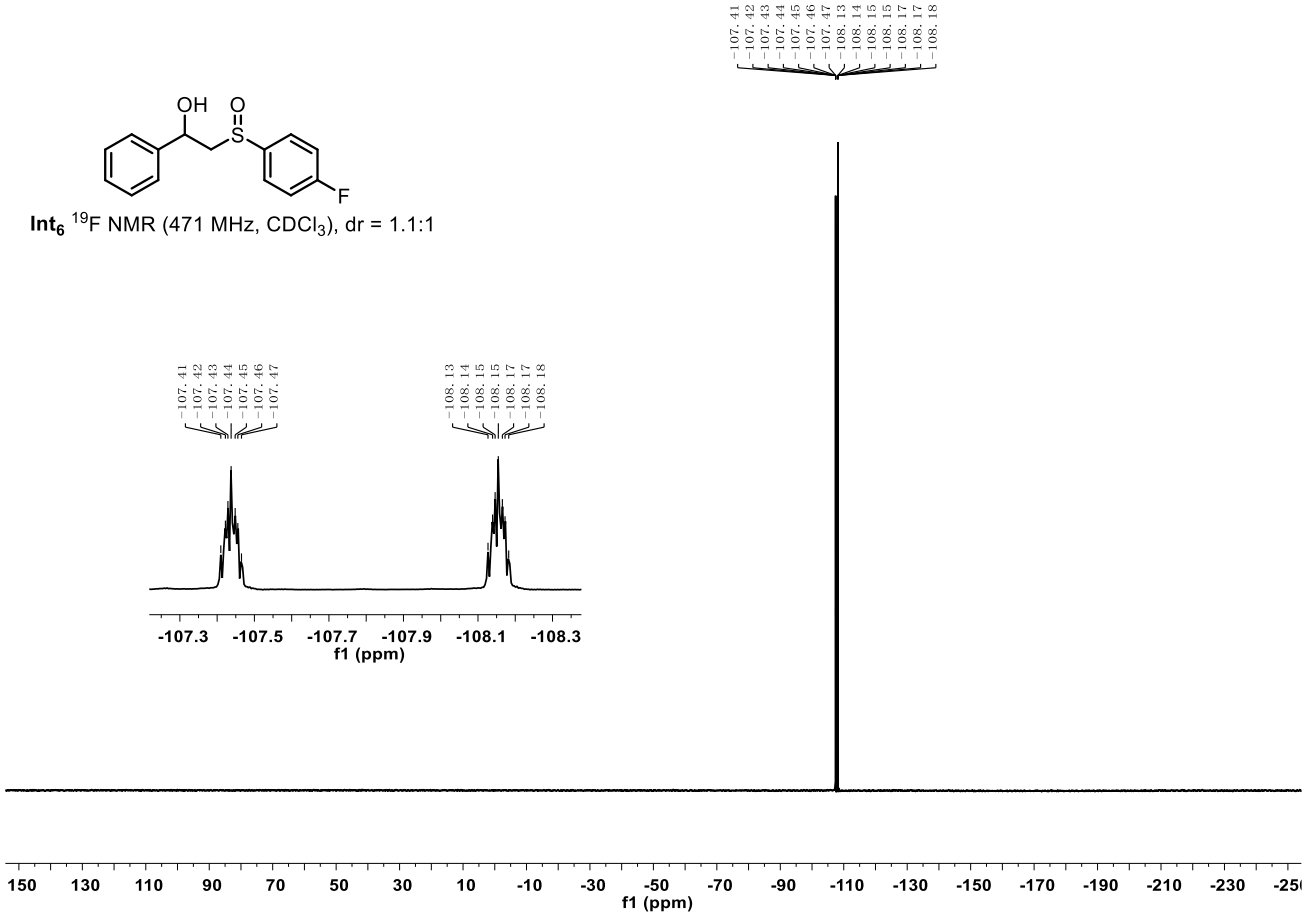
57 ^{1}H NMR (500 MHz, $CDCl_3$), dr = 2:1



57 ^{13}C NMR (101 MHz, $CDCl_3$), dr = 2:1



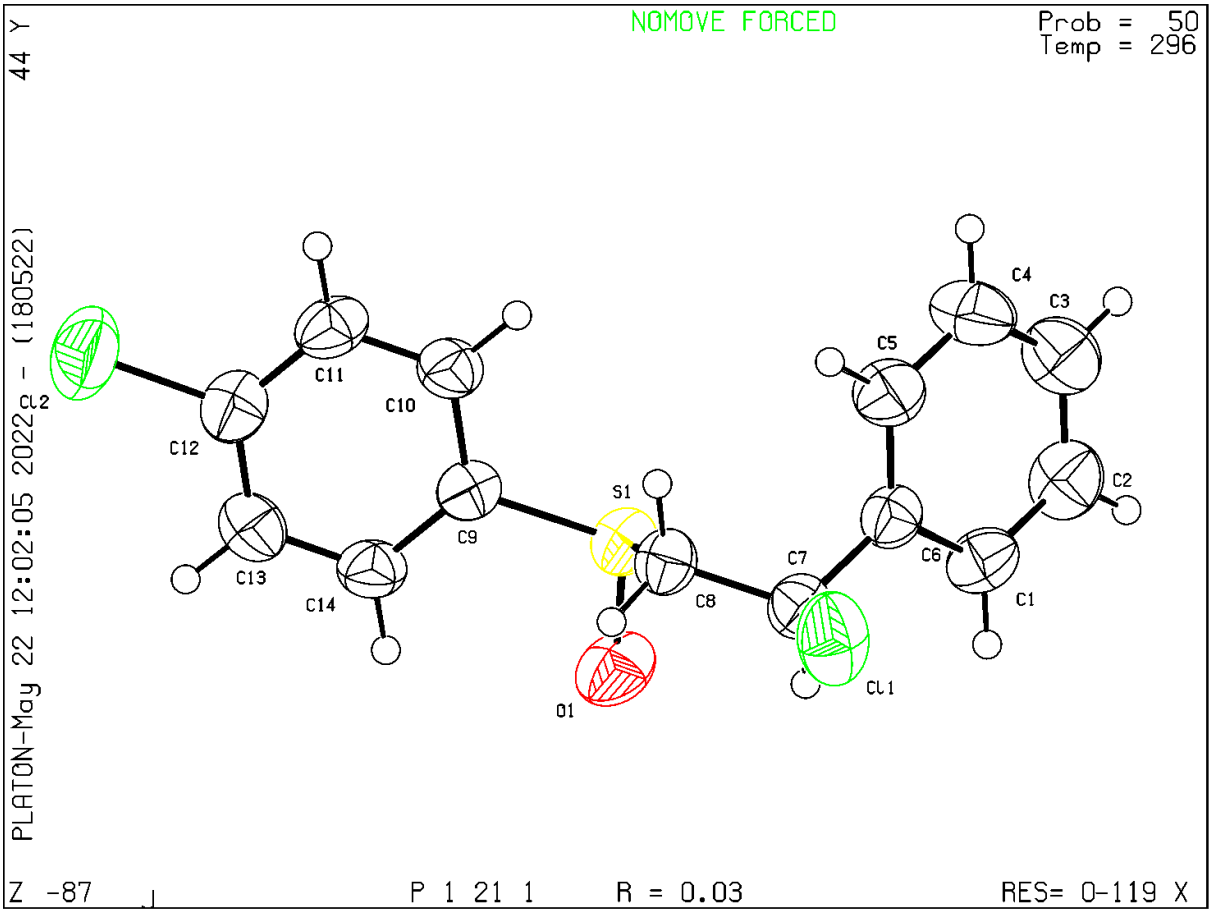
Int$_6$ ^{1}H NMR (500 MHz, $CDCl_3$), dr = 1.1:1



Int$_6$ ^{19}F NMR (471 MHz, $CDCl_3$), dr = 1.1:1

9 X-ray Crystallographic Data

The structure of **34** was determined by the X-ray diffraction. Recrystallized from DCM and hexane. Further information can be found in the CIF file (Deposition number: CCDC 2174243)



Bond precision: C-C = 0.0044 A Wavelength=0.71073

Cell: a=5.7105(4) b=13.5285(8) c=9.2312(6)
alpha=90 beta=94.574(2) gamma=90
Temperature: 296 K

	Calculated	Reported
Volume	710.88(8)	710.88(8)
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb
Moiety formula	C14 H12 Cl2 O S	C14 H12 Cl2 O S
Sum formula	C14 H12 Cl2 O S	C14 H12 Cl2 O S
Mr	299.20	299.20
Dx,g cm-3	1.398	1.398
Z	2	2
Mu (mm-1)	0.588	0.588
F000	308.0	308.0
F000'	308.93	
h,k,lmax	7,18,12	7,17,12
Nref	3521[1833]	3421
Tmin,Tmax	0.943,0.943	0.711,0.746
Tmin'	0.943	

Correction method= # Reported T Limits: Tmin=0.711 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 1.87/0.97 Theta(max)= 28.250

R(reflections)= 0.0329(2753) wR2(reflections)= 0.0746(3421)

S = 1.031 Npar= 163