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Supplementary Material

Recyclable self-assembled composite catalyst consisted of Fe_3O_4-rose bengal-layered double hydroxide for highly efficient visible light photocatalysis in water

Yuxing Huang‡, Zhuo Xin‡, Wenlong Yao, Qi Hu, Zhuohua Li, Liuqing Xiao, Bo Yang and Junmin Zhang*

College of Chemistry and Environmental Engineering, Shenzhen University,
Shenzhen, 518060, P. R. China
E-mail: zhangjm@szu.edu.cn

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I. General Information

All commercially available materials were purchased from Alfa Aesar or Aladdin without further purification, except for the alkenes (4-tert-butylcatechol (TBC) radical inhibitor was removed via passing through basic alumina column). All solvents used in the reactions were without distilled from appropriate drying agents. Proton and carbon NMR spectra were recorded on a Varian 400 spectrometer using $CDCl_3$ as a solvent. Chemical shifts are reported in ppm (δ) relative to internal tetramethylsilane (TMS, δ 0.0 ppm), or with the solvent reference relative to TMS employed as an internal standard ($CDCl_3$, δ 7.26 ppm). The following abbreviations were used to identify the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad and all combinations thereof can be explained by their integral parts. SEM images were measured and analyzed on a scanning electron microscope (Zeiss supra55). Powder X-ray Diffraction (XRD) patterns were recorded on a Bruker D8 diffractometer. Solid UV-vis spectra were recorded on SHIMADZU UV-2600. Zeta potential were measured with Zetasizer Nano-ZS. Green light-emitting diode (LED, 12 W), white compact fluorescent lamp (CFL, 15 W), and white light-emitting diode (LED, 15 W) were used as the visible-light source in reported photocatalytic reactions.

II. Preparation of Fe_3O_4-RB/LDH composite photocatalyst

II-1. Preparation of MgAl-LDH and Fe_3O_4 nanoparticles

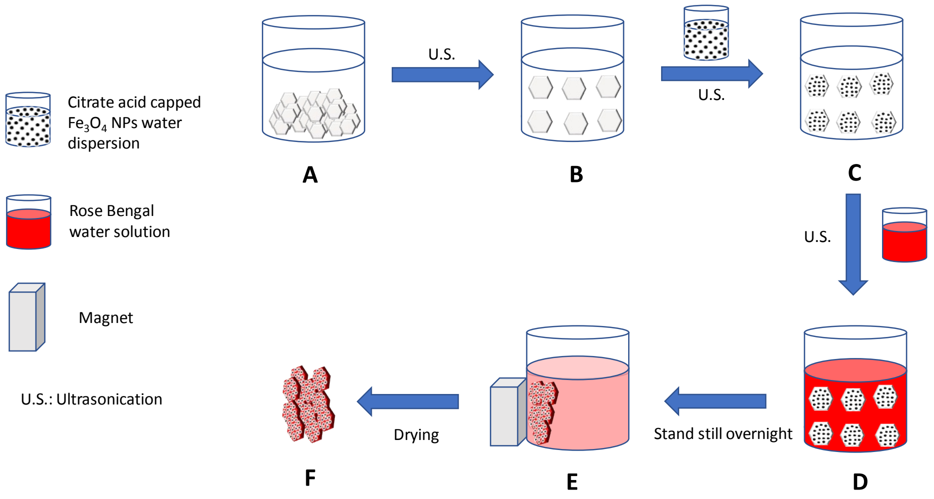
II-1.1 Synthesis of MgAl-LDH[S1]

The magnesium aluminum carbonate layered double hydroxide (designated as MgAl-LDH) was synthesized by a conventional precipitation method. A solution of 14.9760 g NaOH and 33.0690 g Na_2CO_3 in 300 mL deionized water was added dropwise to a solution of 40.0014 g of $Mg(NO_3)_2{\cdot}6H_2O$ and 29.2614 g of $Al(NO_3)_3{\cdot}9H_2O$ in 300 mL deionized water. A pH probe was inserted to the mixture to monitor the pH change. The pH was increased from 3 to 9.7 when the addition was finished. The resulting white precipitate was aged for 24 hours at 90 °C, then filtered through a Buchner funnel. The precipitate was washed with copious water and dried at 70 °C in an oven.

II-1.1 Synthesis of Fe_3O_4 nanoparticles ^{S2}

Fe$_3$O$_4$ nanoparticles capped with citrate groups were prepared according to the literature. Briefly, 2.3597 g $FeCl_3 \cdot 6H_2O$ and 0.8688g $FeCl_2 \cdot 4H_2O$ were dissolved in 40 mL of deionized water. The solution mixture was purged with Ar and heated to 80 °C under vigorous stirring. Then 5 mL of aqueous ammonia solution (28-30 wt%) was added quickly via syringe. After 30 min, the precipitates were collected by a magnet and then washed with deionic water. Later, the precipitates were redispersed into 80 mL of deionized water at 80 °C. The solution was added 5 mL 0.1g/mL citric acid solution and then kept under Ar with vigorous stirring for 2 h. The final product was collected by a magnet.

Ⅱ-2. Preparation of Fe_3O_4-RB/LDH composite photocatalyst



Scheme S1. A schematic procedure of preparation of Fe_3O_4-RB/LDH via self-assembly in water by ultrasonication. A: MgAl-LDH water suspension, B: Well dispersed MgAl-LDH in water after ultrasonication, C: citrate acid capped Fe_3O_4 adsorpted on MgAl-LDH, D: Mixture of Rose Bengal and Fe_3O_4/LDH solution, E: Collection of Fe_3O_4-RB/LDH by a magnet, F: Fe_3O_4-RB/LDH.

MgAl-LDH water suspension (160 mg in 40 mL of demi-water) was subjected to ultrasonication for 1 h. The resulted dispersion was then added with citrate acid capped Fe_3O_4 NPs dispersion in different mass ratio (MgAl-LDH: Fe_3O_4 = 1:0.1, 1:0.2, 1:0.3, 1:0.4, and 1:0.5). The mixture was ultrasonicated for 0.5 h. After that, a water solution of Rose Bengal (80 mg/mL) was added to the mixture and the three components were further ultrasonicated for 1 h. The suspension was stood still overnight and the three components' self-assembly was collected by a magnet. The supernatant was examined by UV-Vis spectroscopy to determine the loading of RB in Fe_3O_4-RB/LDH and the self-assembly collected was dried in the oven to afford Fe_3O_4-RB/LDH.

II-3. Characterization of Fe_3O_4-RB/LDH composite photocatalyst

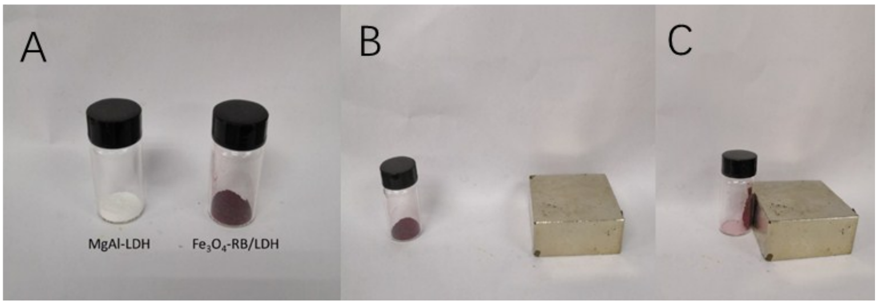


Figure S1. (A) MgAl-LDH and Fe_3O_4-RB/LDH solid; (B, C) Magnetism of Fe_3O_4-RB/LDH.

The red color of Fe_3O_4-RB/LDH indicates the existence of Rose Bengal on MgAl-LDH support (Figure S1 A). Fe_3O_4-RB/LDH can be attracted to an extra magnetic field, suggesting the existence of Fe_3O_4 on MgAl-LDH support (Figure S1 B, C).

Rose Bengal disodium salt was subjected to powder XRD diffractometer, but no analyzable pattern was observed (Figure S2).

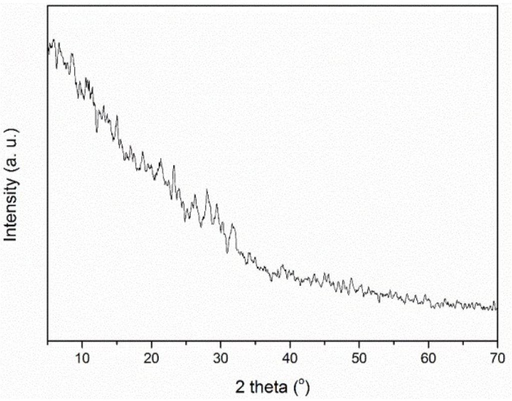


Figure S2. XRD spectrum of Rose Bengal disodium salt

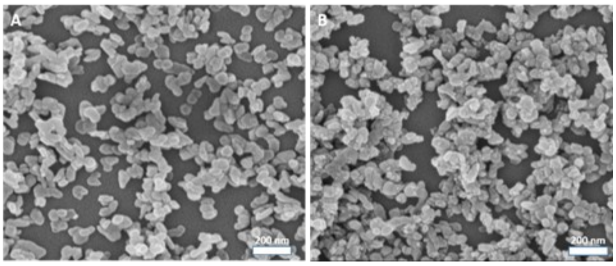


Figure S3. SEM image of (A) MgAl-LDH; (B) Fe_3O_4-RB/LDH composite.

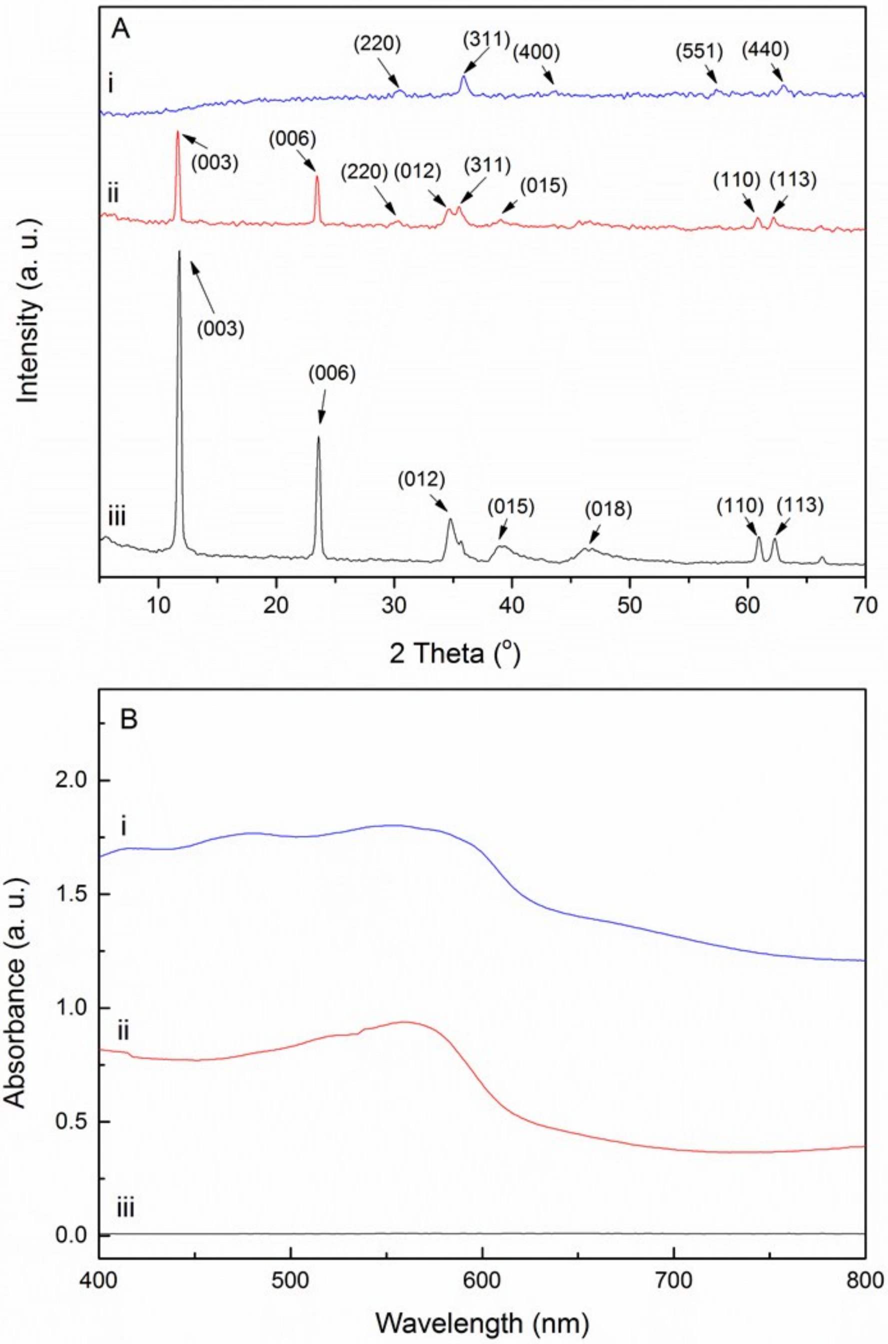


Figure S4. (A) XRD spectra of samples, i: Fe_3O_4 NPs, ii: Fe_3O_4-RB/LDH composite, iii: MgAl-LDH; (B) Solid state UV-Vis spectra of samples, i: Rose Bengal, ii: Fe_3O_4-RB/LDH composite, iii: MgAl-LDH.

Energy-dispersive X-ray spectroscopy (EDS) was employed for quantitative analysis. The results shown in Figure S5 suggests that the elements C, O, Cl, I, Mg, Al, and Fe are homogeneously spread on the surface of Fe_3O_4-RB/LDH.

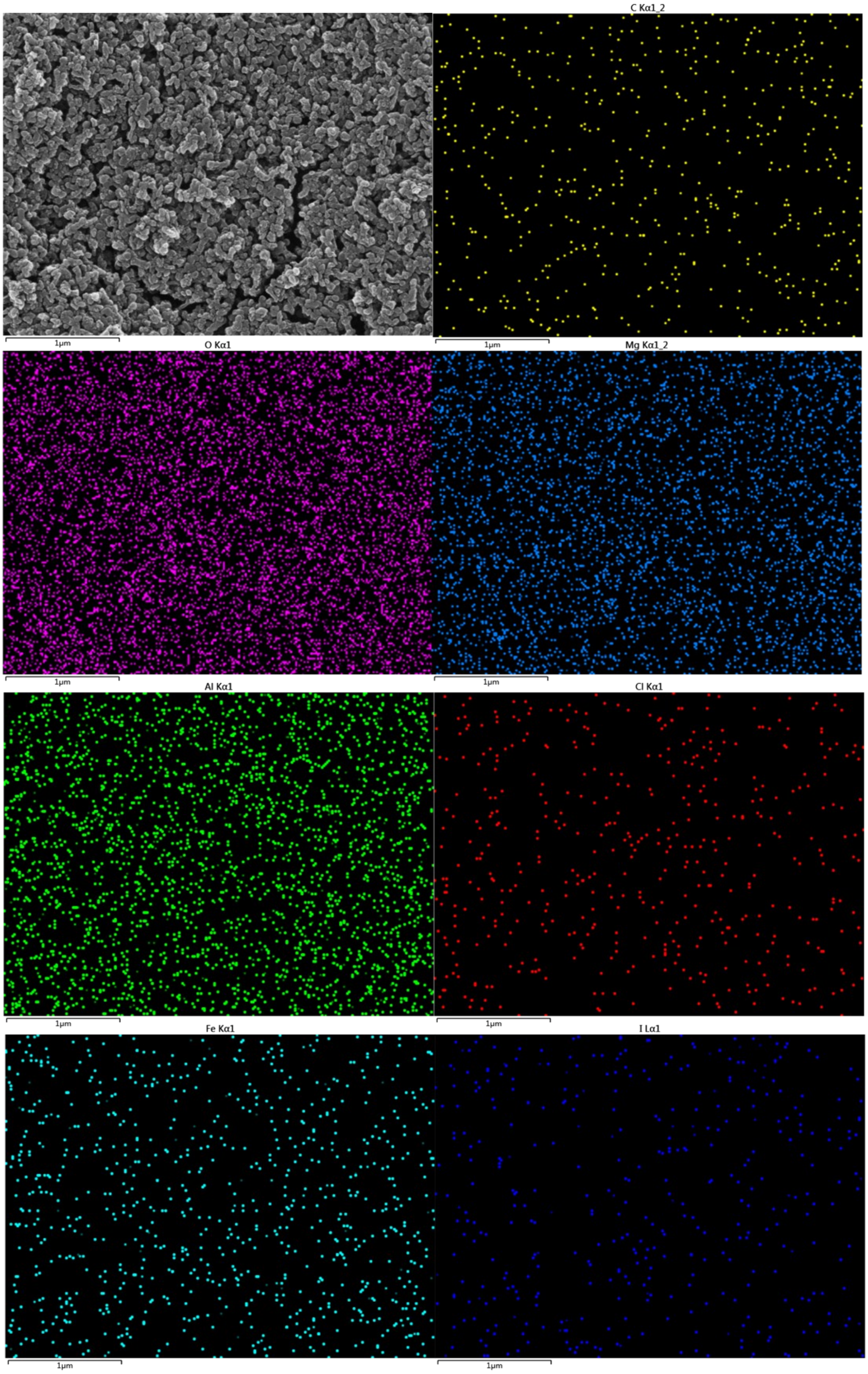


Figure S5. SEM of Fe_3O_4-RB/LDH and quantitative EDS mapping of C, O, Cl, I, Mg, Al, and Fe.

Ⅱ-4. Quantification of RB loading in Fe_3O_4-RB/LDH

A calibration curve was built by measuring series of Rose Bengal water solutions with different concentration. Then the supernatants from the reparation of Fe_3O_4-RB/LDH composite with different ratio of Fe_3O_4 were examined by UV-Vis spectroscopy. By determining the amount of Rose Bengal in the supernatant, we can estimate the loading of Rose Bengal in Fe_3O_4-RB/LDH, and the results are summarized in Table S1.

Table S1. Rose Bengal loading in Fe_3O_4-RB/LDH

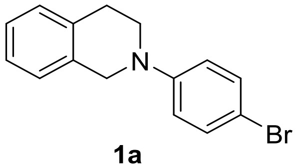
Mass Ratio (Fe_3O_4/MgAl-LDH)	**Rose Bengal Loading (μmol/g)**
0.1	149.8
0.2	140.0
0.3	117.6
0.4	44.4
0.5	31.0

As shown in Table 1, the amount of Rose Bengal loaded on MgAl-LDH was decreased when increasing the amount of Fe_3O_4 NPs in the self-assembly mixture. This is reasonable, as the zeta potential of the surface of MgAl-LDH is decreased when negatively charged Fe_3O_4 NPs was adsorbed. Therefore, increasing amount of Fe_3O_4 NPs in the system will further reduce the zeta potential and thus decrease the adsorption of negatively charged Rose Bengal.

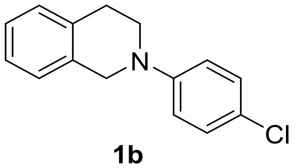
To maximize the catalytic activity one would prefer higher loading of Rose Bengal in Fe_3O_4-RB/LDH composite photocatalyst. On the other hand, the amount of Fe_3O_4 decides the magnetism of Fe_3O_4-RB/LDH. In a compromise of catalytic activity and magnetism, we chose mass ratio of 0.2 for preparation of Fe_3O_4-RB/LDH in our study.

Ⅲ. Synthesis of the substrates and general procedures for Fe_3O_4-RB/LDH photocatalysis

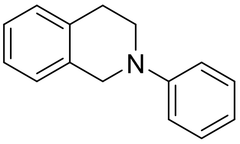
Ⅲ-1. Synthesis of the substrates



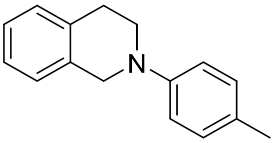
1a



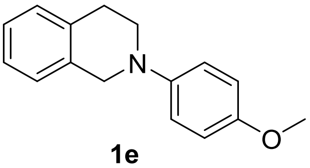
1b



1c



1d



1e

The substrates **1a-e** were synthesized according to literature procedures.[S4] A typical procedure is described as following for the synthesis of **1c**:

Copper (I) iodide (1.0 mmol, 200 mg) and potassium phosphate (20.0 mmol, 4.25 g) were added to a Schlenk tube. The tube was then evacuated and back filled with nitrogen for three times. After that, 2-propanol (10.0 mL), ethylene glycol (20.0 mmol, 1.1 mL), 1,2,3,4-tetrahydroisoquinoline (15 mmol, 2.0 mL), and 4-iodotoluene (10.0 mmol, 1.2 mL) were added successively via syringe at room temperature. The reaction mixture was heated at 85 °C and kept for 24 h and then allowed to cool to room temperature. Diethyl ether (20 mL) and water (20 mL) were added into the reaction mixture, and the aqueous layer was extracted by diethyl ether (2 × 20 mL). The combined organic phases were washed with brine and dried over magnesium sulfate. The solvent was removed via rotary evaporation, and the remaining residue was purified via column chromatography on silica gel (hexane/ethyl acetate=20:1) to give the desired product.

III-2. Fe_3O_4-RB/LDH catalyzed CDC reaction of N-phenyl-tetrahydroisoquinoline derivatives and nitroalkanes

Figure S6. Homemade visible light photoreactor

To a 10 mL test tube equipped with a magnetic stirring bar was charged with N-phenyl-tetrahydroisoquinoline **1c** (0.1 mmol), nitromethane (1.0 mmol), 2 mol% Fe_3O_4-RB/LDH and 5 mL H_2O. A needle was employed to connect the reaction system with atmosphere. The reaction mixture was stirred at room temperature with the irradiation of a 12 W green LEDs for 24 h. A magnet was used to separate the Fe_3O_4-RB/LDH from the reaction system. The recovered Fe_3O_4-RB/LDH was washed with ethanol for three times to extract the possible adsorbed product. The EtOH solution was combined with reaction solution and transferred to a 50 mL round bottom flask for evaporation to dry the solvent. The remaining residue was purified by Biotage medium pressure liquid chromatography (MPLC) to give the desired product, using a silica column.

III-3. Fe_3O_4-RB/LDH catalyzed sulfoxidation reactions

Figure S7. Homemade visible light photoreactor using a CFL bulb as the light source

To a 10 mL test tube equipped with a magnetic stir bar was charged with thioethers (0.5 mmol), Fe_3O_4-RB/LDH (2 mol %), and 5 mL H_2O. A needle was employed to connect the reaction system with atmosphere. The solution was stirred at room temperature with the irradiation of a 15 W CFL. After completion of the reaction, a magnet was used to separate the Fe_3O_4-RB/LDH from the reaction system. The recovered Fe_3O_4-RB/LDH was washed with ethanol for three times to extract the possible adsorbed product. The EtOH solution was combined with reaction solution and transferred to a 50 mL round bottom flask for evaporation to dry the solvent. The remaining residue was purified by Biotage medium pressure liquid chromatography (MPLC) to give the desired product, using a basic alumina column.

III-4. Fe_3O_4-RB/LDH catalyzed radical addition reactions of alkenes and thiols

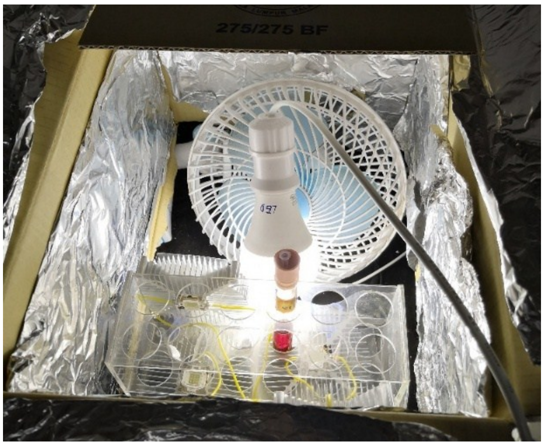


Figure S8. Homemade visible light photoreactor using a LED bulb as the light source

To a 10 mL test tube equipped with a magnetic stirring bar was charged with alkenes (0.2 mmol), thiols (0.3 mmol), 5 mol% Fe_3O_4-RB/LDH, and 5 mL H_2O. A needle was employed to connect the reaction system with atmosphere. The solution was stirred at room temperature with the irradiation of a 15 W white LED bulb for 2 h. A magnet was used to separate the Fe_3O_4-RB/LDH from the reaction system after the completion of the reaction. The recovered Fe_3O_4-RB/LDH was washed with ethanol for three times to extract the possible adsorbed product. The EtOH solution was combined with reaction solution and transferred to a 50 mL round bottom flask for evaporation to dry the solvent. The remaining residue was purified by Biotage medium pressure liquid chromatography (MPLC) to give the desired product, using a silica column.

Ⅳ. Recycling experiments

The reaction mixture of N-phenyl-tetrahydroisoquinoline (0.1 mmol), nitromethane (1.0 mmol), 4 mol % Fe_3O_4-RB/LDH and 5 mL H_2O was irradiated with a 12 W green LEDs for 24 h. After completion of the reaction, a magnet was used to separate the Fe_3O_4-RB/LDH from the reaction system. The recovered Fe_3O_4-RB/LDH was washed with ethanol for three times to extract the possible adsorbed product. The EtOH solution was combined with reaction solution and transferred to a 50 mL round bottom flask for evaporation to dry the solvent. The remaining residue was mixed with internal standard and the mixture was subjected for ^{1}H NMR quantification. The washed Fe_3O_4-RB/LDH was then dried in an oven and used for the next round of photocatalysis. The catalyst can be reused for 6 times without significant loss of the catalytic activity. The reduction of catalytic activity can be attributed to the leaching of Rose Bengal during the reaction since it is immobilized on MgAl-LDH through non-covalent interaction.

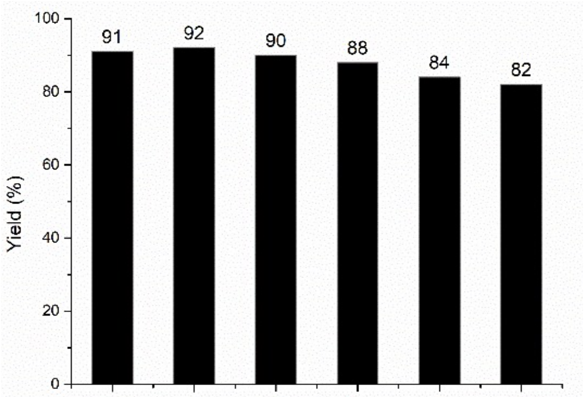


Figure S9. Recycling experiments of Fe_3O_4-RB/LDH for the CDC reaction of N-phenyl tetrahydroisoquinoline and nitromethane.

V. Proposed mechanisms for anti-Markovnikov thiol radical addition of alkenes

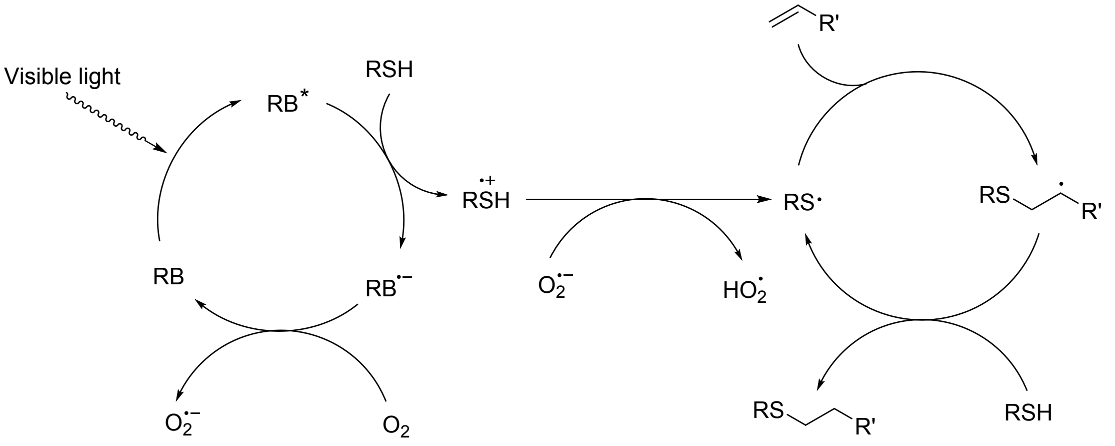
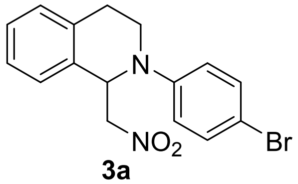


Figure S10. Proposed mechanism of Fe_3O_4-RB/LDH catalyzed thiol radical addition of alkenes

In the proposed mechanism, the Rose Bengal anchored on MgAl-LDH (RB) was converted into the excited sate (RB*). RB* is able to abstract an electron from thiol to form a thiol radical cation via single electron transfer (SET), and change into RB radical anion. RB radical anion can go back to the ground state RB by converting dioxygen into dioxygen radical anion, which further reacts with thiol radical cation to produce thiyl radical. The thiyl radical can go radical addition with alkene to form the final anti-Markovnikov addition product.

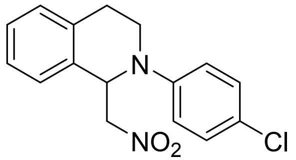
Ⅵ. ^{1}H and ^{13}C NMR data of products[S3]



3a

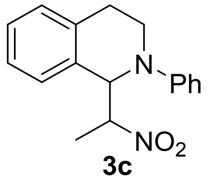
2-(4-bromophenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (3a): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.13 (m, 6H), 6.86 – 6.84 (d, J = 8.2 Hz, 2H), 5.51 – 5.47 (t, J = 7.2 Hz, 1H), 4.86 – 4.81 (dd, J = 12.0, 8.1 Hz, 1H), 4.59 – 4.54 (dd, J = 12.0, 6.4 Hz, 1H), 3.63 – 3.59 (m, 2H), 3.10

– 3.03 (m, 1H), 2.82 – 2.75 (dt, J = 16.4, 4.8 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 147.33, 134.89, 132.27, 132.05, 129.13, 128.12, 126.81, 126.66, 116.59, 111.34, 78.43, 57.93, 41.88, 26.00.



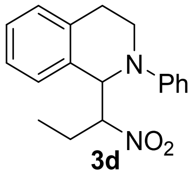
3b

2-(4-chlorophenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (3b): Yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.27 – 7.12 (m, 6H), 6.89 – 6.87 (d, J = 9.0 Hz, 2H), 5.49 – 5.46 (t, J = 7.1 Hz, 1H), 4.85 – 4.80 (dd, J = 8.2, 12.0 Hz, 1H), 4.58 – 4.53 (dd, J = 6.3, 12.0 Hz, 1H), 3.62 – 3.58 (m, 2H), 3.09 – 3.01 (m, 1H), 2.80 – 2.73 (dt, J = 16.4, 4.7 Hz, 1H).. ^{13}C NMR (100 MHz, CDCl$_3$) δ 146.95, 134.92, 132.29, 129.14, 128.09, 126.81, 126.65, 124.16, 116.31, 78.47, 58.04, 41.98, 25.96.



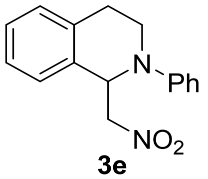
3c

1-(1-nitroethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3c): Yellow oil. Isolated diastereomeric ratio = 1.63 :1; ^{1}H NMR (400 MHz, CDCl$_3$) δ7.34 – 7.13 (m, 6 H), 7.06 – 7.02 (m, 2 H), 6.88 – 6.84 (m, 1 H), 5.31 – 5.26 (m, 1 H), 5.12 – 5.05 (m, 0.69 H, major isomers), 4.97 – 4.89 (m, 0.36 H, minor isomer), 3.91 – 3.84 (m, 0.71 H), 3.66 – 3.55 (m, 1.45 H), 3.13 – 3.05 (m, 1H), 2.98 – 2.88 (m, 1 H), 1.75 – 1.73 (d, J = 6.8 Hz, 1.12 H, minor isomer), 1.59 –1.57 (d, J = 6.6 Hz, 2.12 H, major isomer); ^{13}C NMR (100 MHz, CDCl$_3$, minor isomer marked *) δ 149.02*, 148.74, 135.48, 134.65*, 133.68*, 131.88, 129.30*, 129.18 (major and minor isomers), 128.98*, 128.59*, 128.22, 128.07, 127.12*, 126.46*, 126.00, 119.19, 118.64*, 115.27, 114.34*, 88.82*, 85.30, 62.60, 61.01*, 43.41*, 42.52, 26.61*, 26.24, 17.29*, 16.26



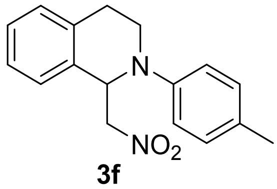
3d

1-(1-nitropropyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3d): Yellow oil. Isolated diastereomeric ratio = 1.37 :1;^{1}H NMR (400 MHz, CDCl$_3$) δ 7.33 – 7.16 (m, 6 H), 7.03 – 6.96 (m, 2 H), 6.87-6.80 (m, 1 H), 5.29 – 5.26 (d, J = 9.3 Hz, 0.59 H, major isomer), 5.18 – 5.15 (d, J = 9.5 Hz, 0.43 H, minor isomer), 4.93 – 4.87 (m, 0.43 H, minor isomer), 4.74 – 4.68 (m, 0.59 H, major isomer), 3.92 – 3.85 (m, 0.44 H, minor isomer), 3.73 – 3.52 (m, 2H), 3.15-3.06 (m, 1H), 2.97-2.87 (m, 1H), 2.30 – 2.08 (m, 1.67 H), 1.91 – 1.81 (m, 0.45 H), 0.99-0.95 (m, 3H). ^{13}C NMR (100 MHz, CDCl$_3$, minor isomer marked *) δ 148.96*, 148.87, 135.45*, 134.58, 133.80, 132.44*, 129.31, 129.22, 129.07 (major and minor isomers), 128.58*, 128.49, 128.12, 128.07*, 127.11, 126.52, 125.79 (major and minor isomers), 119.28*, 118.45, 115.71*, 114.00, 96.05, 92.94*, 62.07*, 60.59, 43.42, 42.19*, 26.72, 25.60*, 24.89, 24.51*, 10.57.



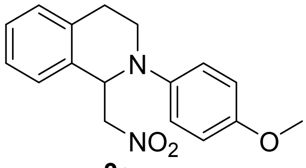
3e

1-(nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3e): Yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.19 – 7.02 (m, 6H), 6.89 – 6.87 (d, *J* = 8.0 Hz, 2H), 6.76 – 6.73 (t, *J* = 7.3 Hz, 1H), 5.46 – 5.43 (t, *J* = 7.2 Hz, 1H), 4.79 – 4.74 (dd, *J* = 11.8, 7.8 Hz, 1H), 4.48 – 4.43 (dd, *J* = 11.8, 6.6 Hz, 1H), 3.59 – 3.47 (m, 2H), 3.02 – 2.94 (m, 1H), 2.72 – 2.65 (dt, *J* = 16.3, 5.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 148.30, 135.16, 132.79, 129.39, 129.07, 128.00, 126.88, 126.58, 119.30, 114.97, 78.65, 58.07, 41.93, 26.32.



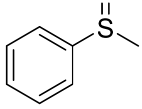
3f

1-(nitromethyl)-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (3f): Yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.25 – 7.05 (m, 6H), 6.89 – 6.86 (d, *J* = 8.6 Hz, 2H), 5.50 – 5.46 (t, *J* = 7.3 Hz, 1H), 4.85 – 4.80 (dd, *J* = 11.8, 8.1 Hz, 1H), 4.55 – 4.51 (dd, *J* = 11.8, 6.3 Hz, 1H), 3.65 – 3.52 (m, 2H), 3.08 – 3.00(m, 1H), 2.76 – 2.69 (dt, *J* = 16.4, 4.4 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 146.22, 135.19, 132.77, 129.81, 129.12, 128.91, 127.83, 126.81, 126.45, 115.72, 78.64, 58.22, 42.10, 26.02, 20.20.



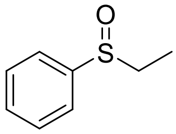
3g

2-(4-methoxyphenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (3g): Yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.24 – 7.12 (m, 4H), 6.92 – 6.89 (d, *J* = 9.1 Hz, 2H), 6.81 – 6.79 (d, *J* = 9.1 Hz, 2H), 5.39 – 5.36 (m, 1H), 4.84 – 4.79 (dd, *J* = 11.9, 8.6 Hz, 1H), 4.57 – 4.53 (dd, *J* = 11.9, 5.8 Hz, 1H), 3.74 (s, 3H), 3.57 – 3.53 (m, 2H), 3.04 – 2.96 (m, 1H), 2.71 – 2.65 (dt, *J* = 16.6, 4.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 153.86, 142.94, 135.32, 132.76, 129.34, 127.78, 126.80, 126.50, 118.74, 114.58, 78.84, 58.79, 55.47, 43.02, 25.67.



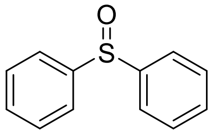
5a

methylsulfinylbenzene (5a): White solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.58-7.39 (m, 2H), 7.47-7.39 (m, 3H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 145.37, 130.73, 129.05, 123.17, 43.64.



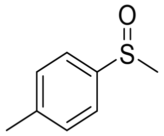
5b

ethylsulfinylbenzene (5b): White solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.45-7.42 (dd, *J* = 7.9 Hz, 1.84 Hz, 2H), 7.36-7.28 (m, 3H), 2.77-2.69 (m, 1H), 2.62-2.54 (m, 1H), 1.02-0.99 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 142.75, 130.38, 128.60, 123.60, 49.66, 5.37.



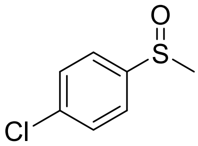
5c

sulfinyldibenzene (5c): White solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.58-7.56 (m, 2H), 7.35-7.31 (m, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 145.16, 130.67, 128.93, 124.31.



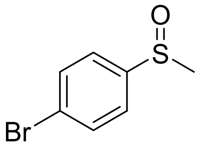
5d

1-methyl-4-(methylsulfinyl)benzene (5d): Yellow gummy solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.50-7.48 (d, *J* = 8.0 Hz, 2H), 7.29-7.27 (d, *J* = 7.9 Hz, 2H), 2.65 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 142.22, 141.22, 129.76, 123.27, 43.70, 21.10.



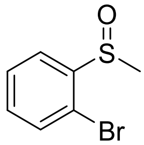
5e

1-chloro-4-(methylsulfinyl)benzene (5e): Colorless solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.54-7.52 (d, *J* = 8.5 Hz, 2H), 7.46-7.44 (d, *J* = 8.5 Hz, 2H), 2.66 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 144.10, 137.00, 129.42, 124.77, 43.88.



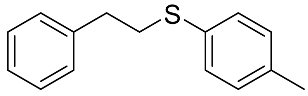
5f

1-bromo-4-(methylsulfinyl)benzene (5f): White solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.59-7.57 (d, *J* = 8.5 Hz, 2H), 7.46-7.43 (d, *J* = 8.5 Hz, 2H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 144.66, 132.34, 125.22, 124.94, 43.74.



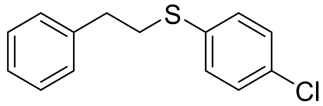
5g

1-bromo-2-(methylsulfinyl)benzene (5g): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.92 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.57-7.54 (m, 2H), 7.39-7.35 (m, 1H), 2.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.89, 132.47, 131.87, 128.29, 125.19, 117.96, 41.47.



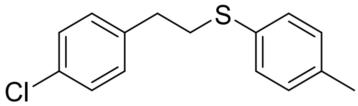
8a

phenethyl(*p*-tolyl)sulfane (8a): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.10 (m, 9H), 3.14-3.10 (t, *J* = 7.5 Hz, 2H), 2.92-2.88 (t, *J* = 8.4 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.24, 136.11, 132.39, 130.03, 129.62, 128.40, 128.37, 126.28, 35.74, 35.67, 20.90.



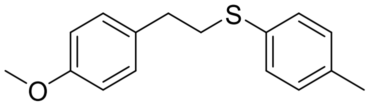
8b

phenethyl(*p*-chlorophenyl)sulfane (8b): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.15 (m, 9H), 3.13-3.09 (t, *J* = 7.4 Hz, 2H), 2.90-2.87 (t, *J* = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.77, 134.82, 131.79, 130.40, 128.88, 128.39, 128.34, 126.39, 35.37, 35.21.



8c

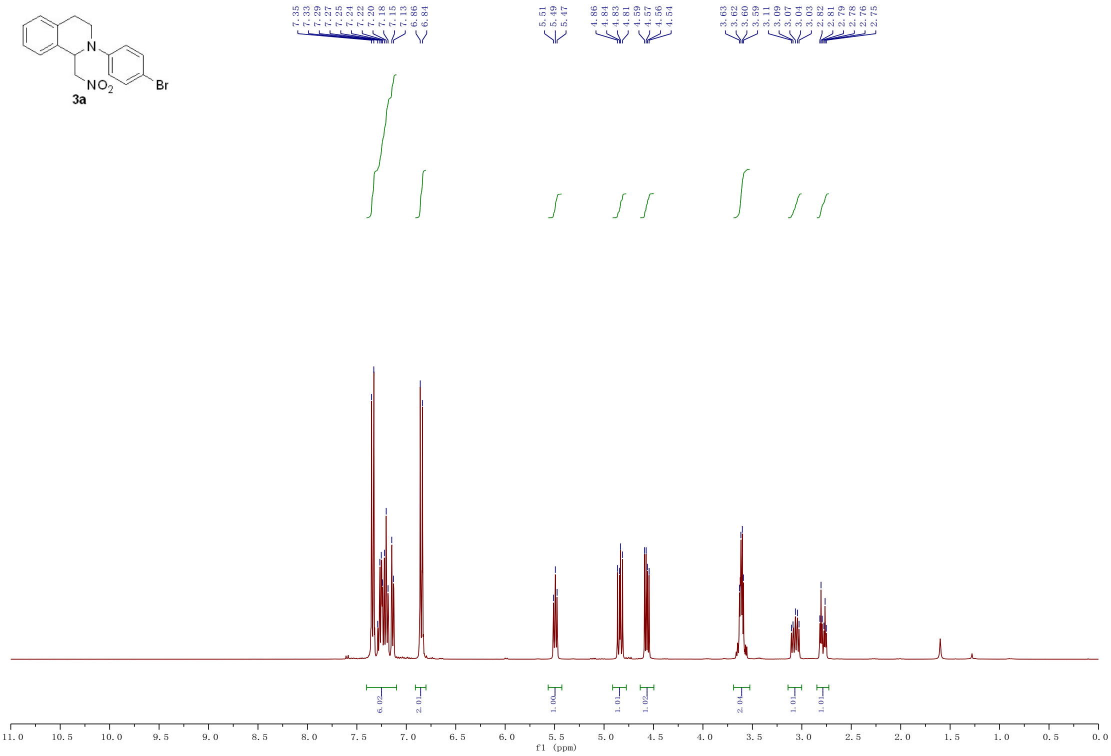
(4-chlorophenethyl)(*p*-tolyl)sulfane (8c): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 4H), 7.10 – 7.06 (m, 4H), 3.08 – 3.04 (t, *J* = 7.4 Hz, 2H), 2.85-2.81 (t, *J* = 8.2 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.51, 136.19, 132.01, 131.96, 130.11, 129.73, 129.60, 128.38, 35.56, 34.83, 20.86.

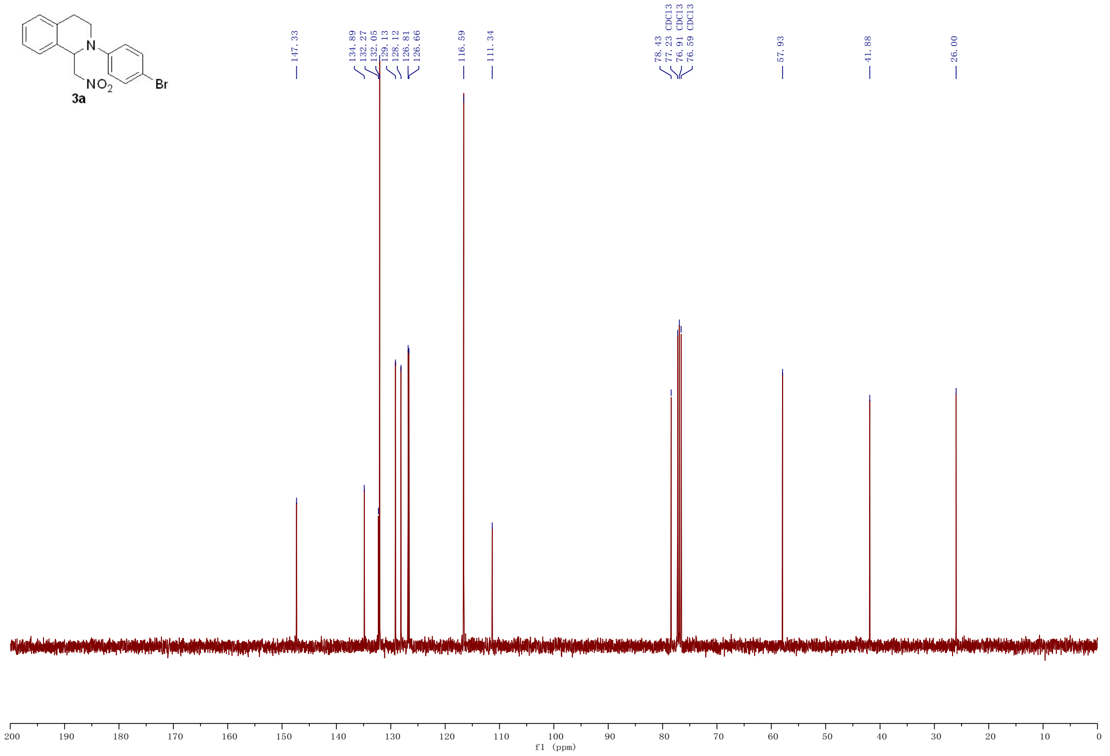


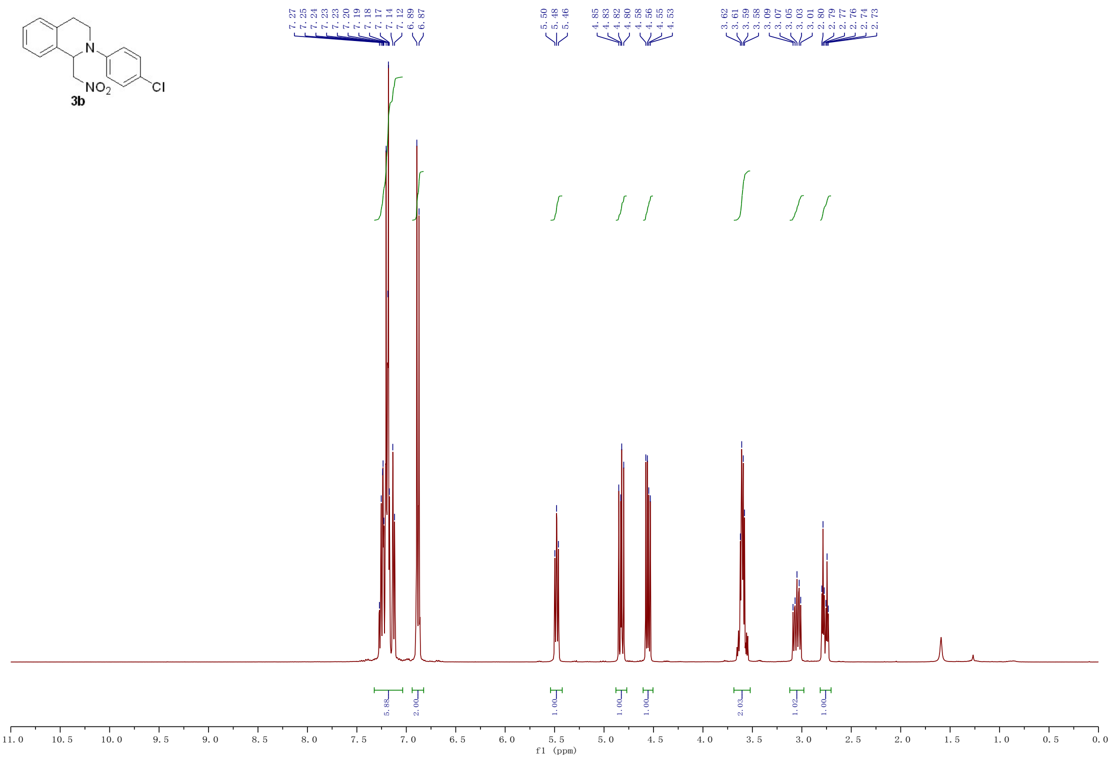
8d

(4-methoxyphenethyl)(*p*-tolyl)sulfane (8d): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.25 (d, *J* = 8.1 Hz, 2H), 7.10-7.07 (m, 4H), 6.82-6.80 (d, *J* = 8.5 Hz, 2H), 3.75 (s, 3H), 3.09-3.05 (t, *J* = 7.3 Hz, 2H), 2.85-2.81 (t, *J* = 8.3 Hz, 2H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.01, 135.88, 132.46, 132.23, 129.84, 129.52, 129.28, 113.71, 55.02, 35.87, 34.67, 20.82.

Ⅶ. ^{1}H NMR and ^{13}C NMR spectra



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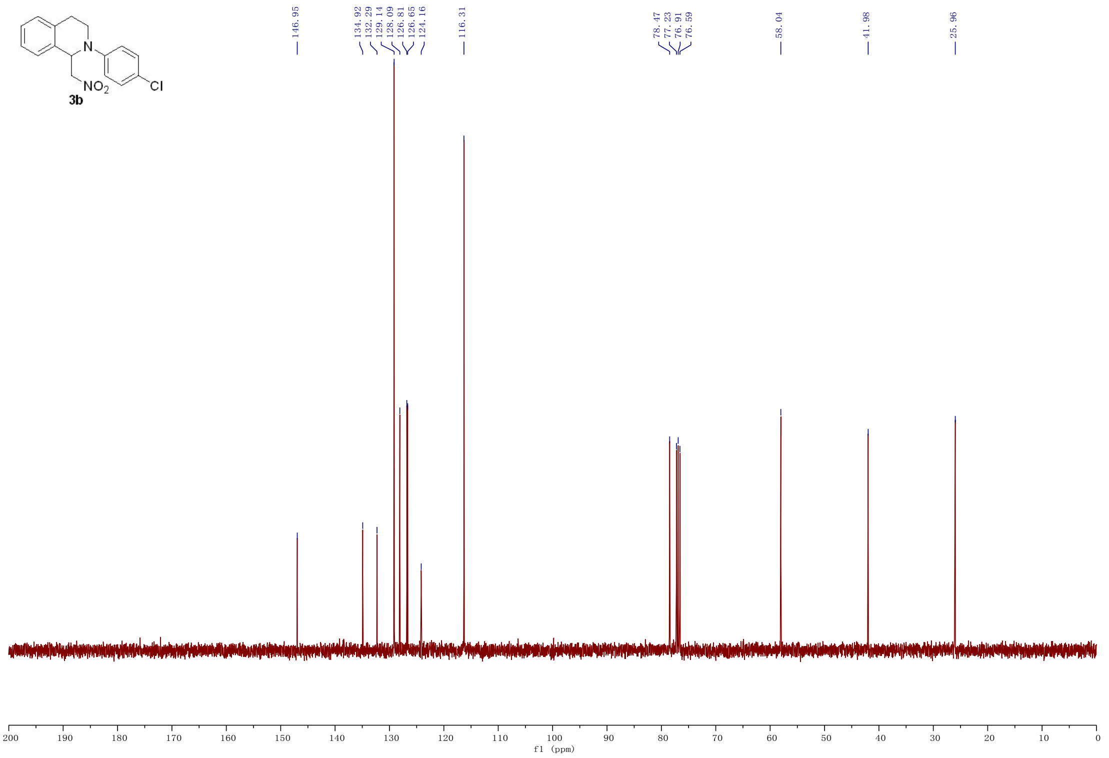
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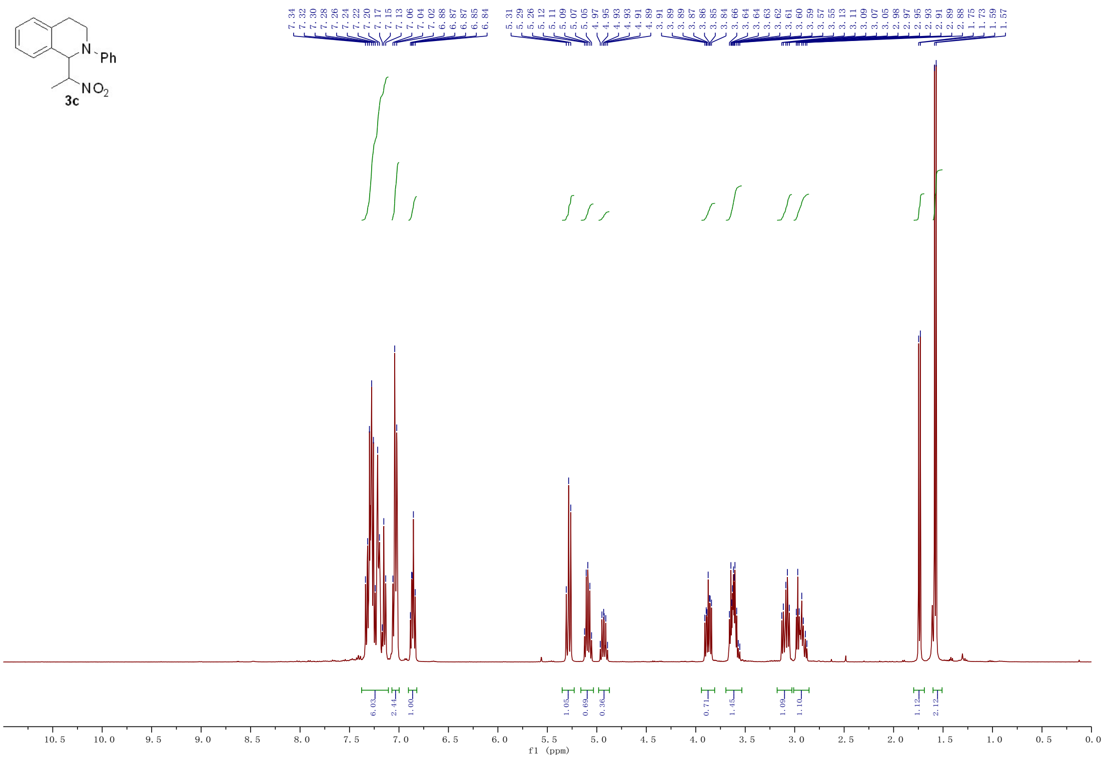
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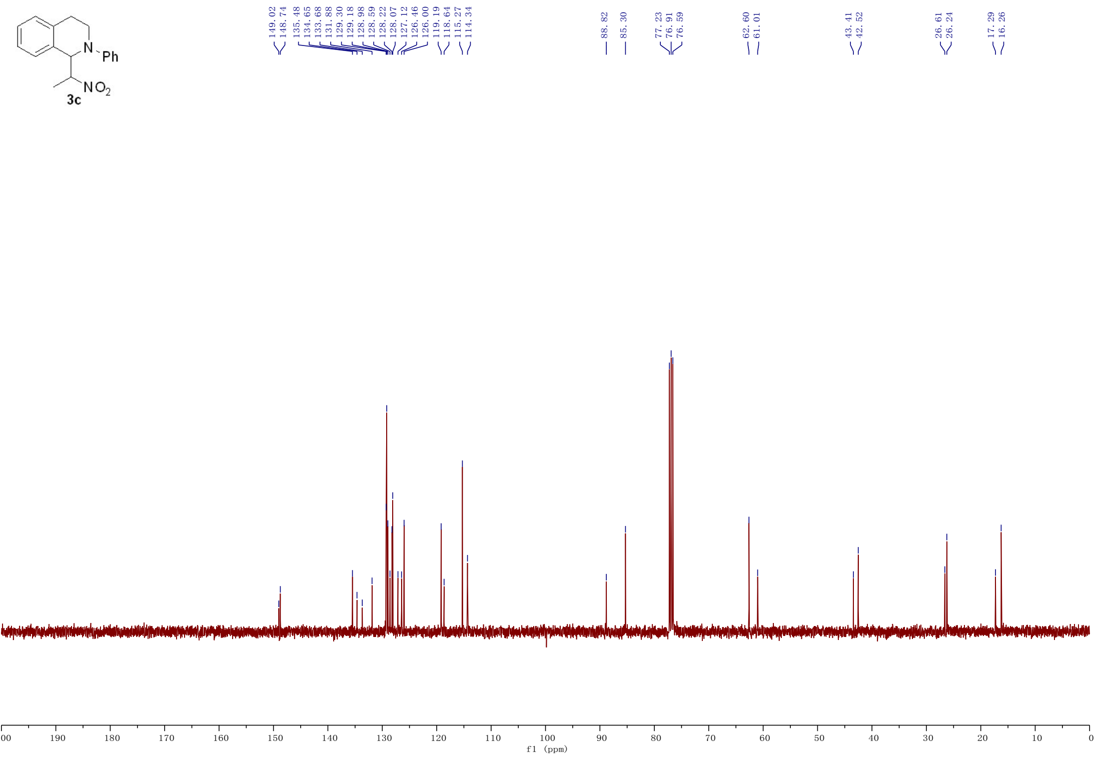
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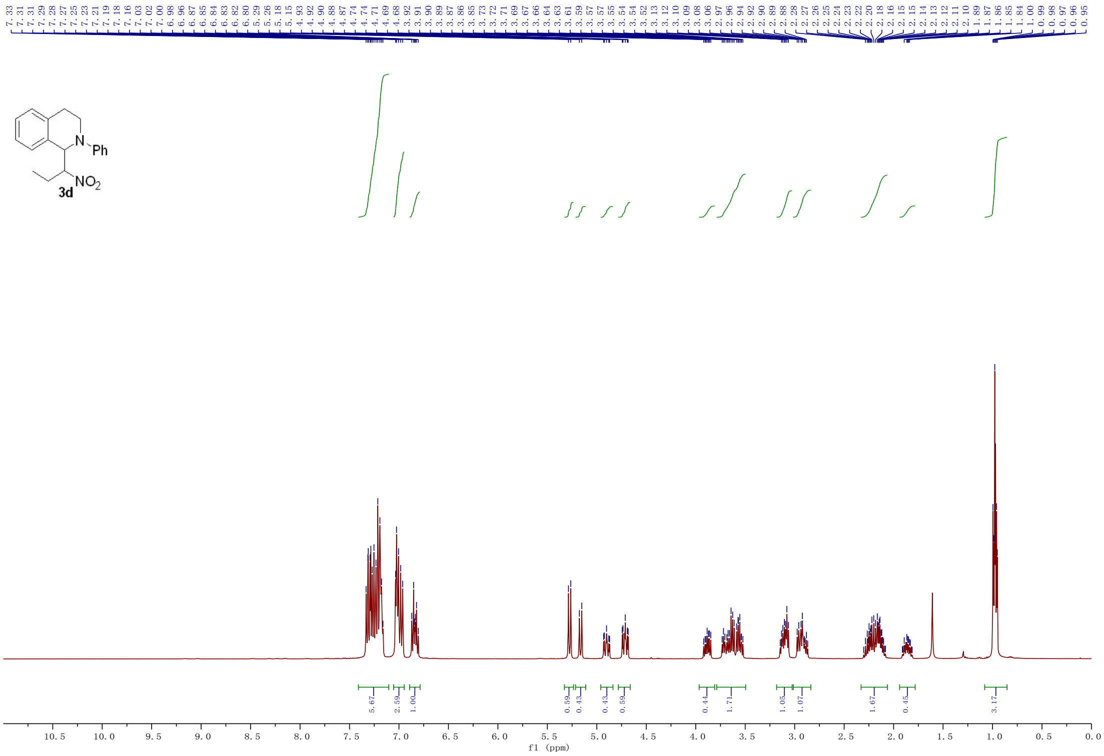
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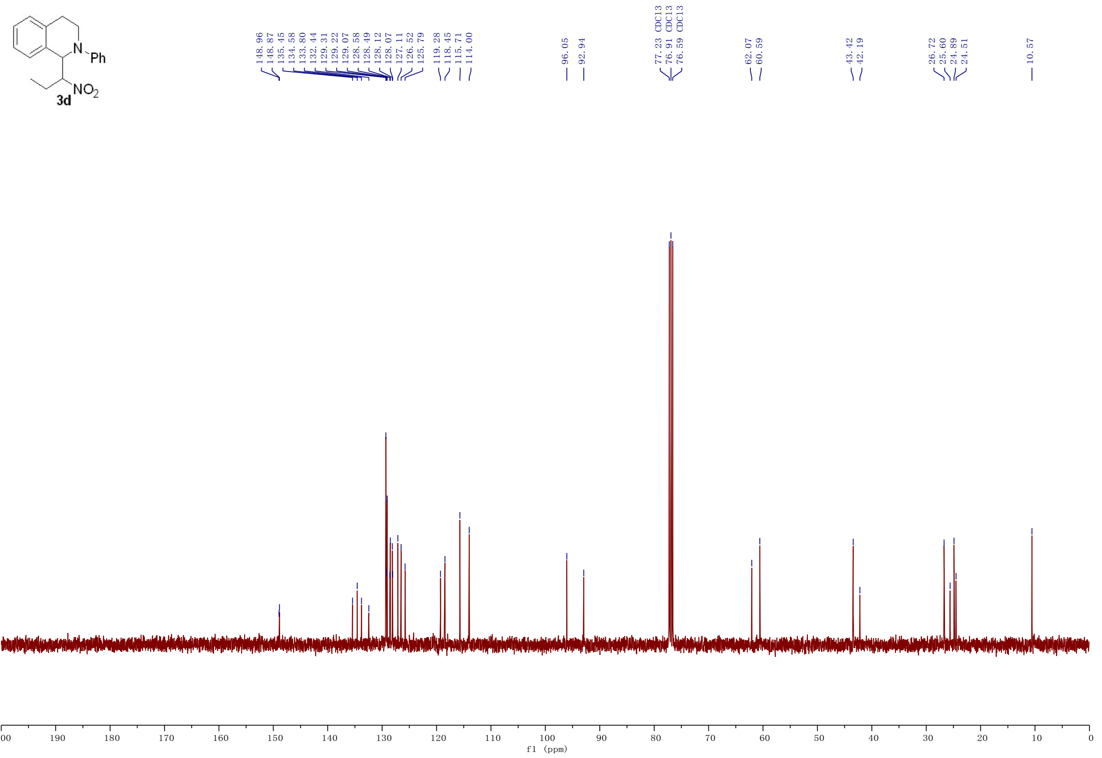
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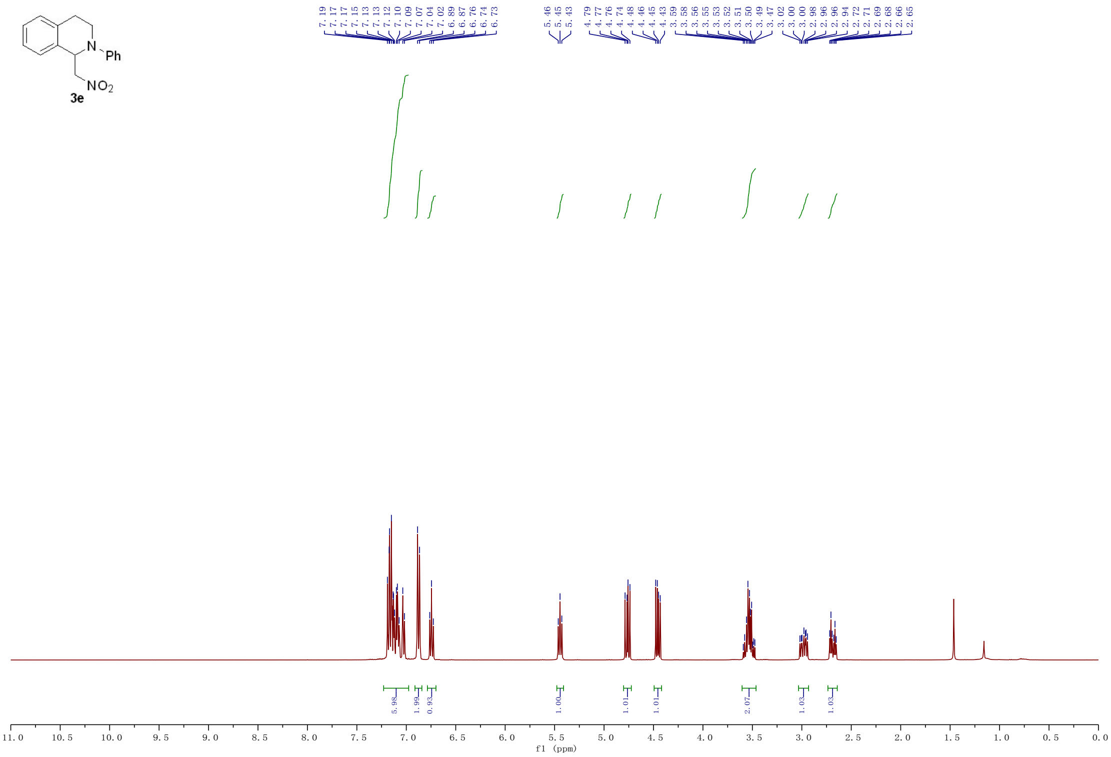
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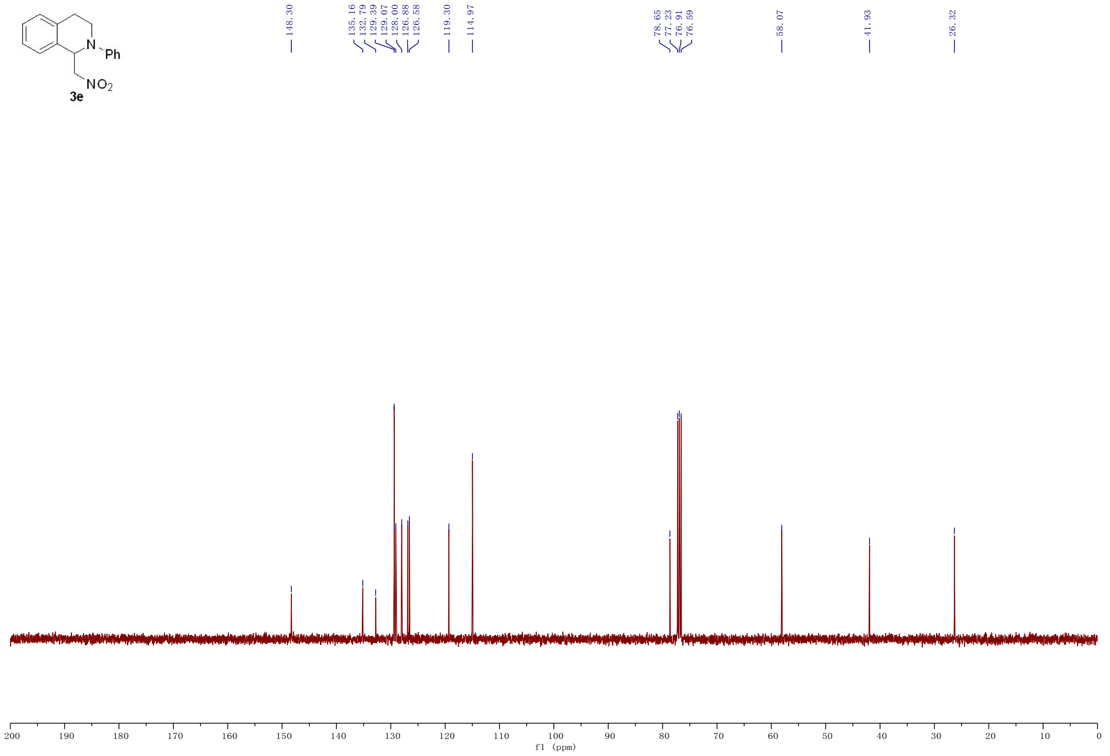
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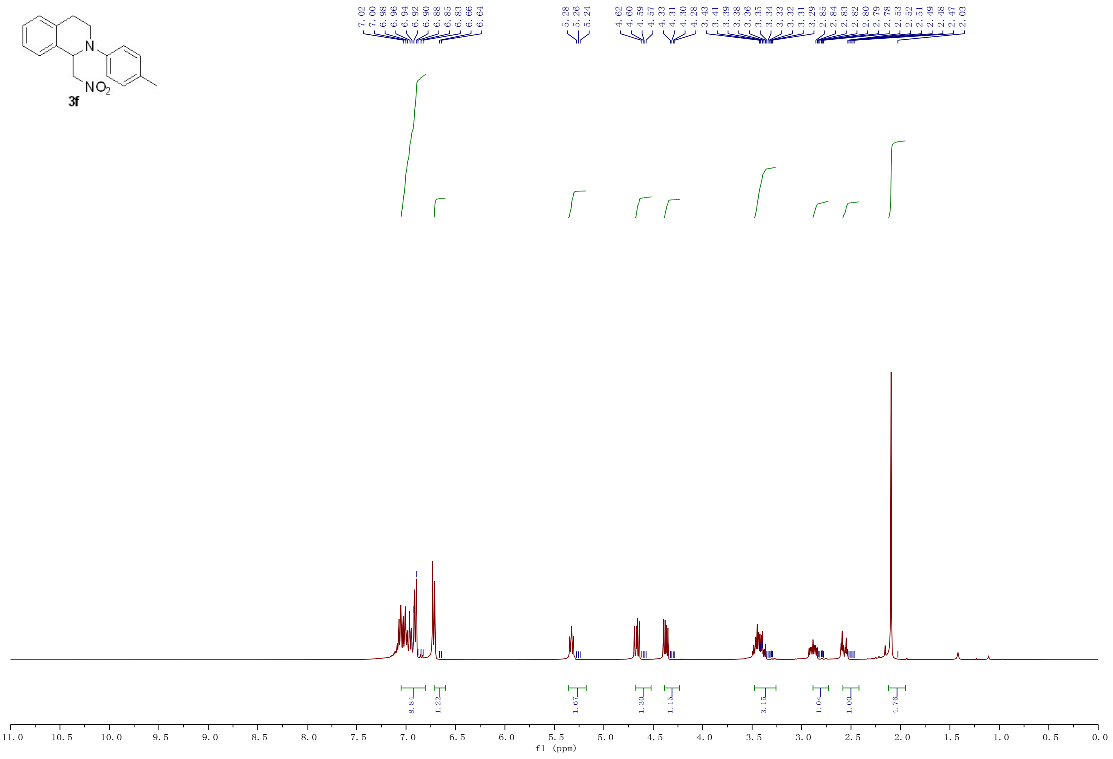
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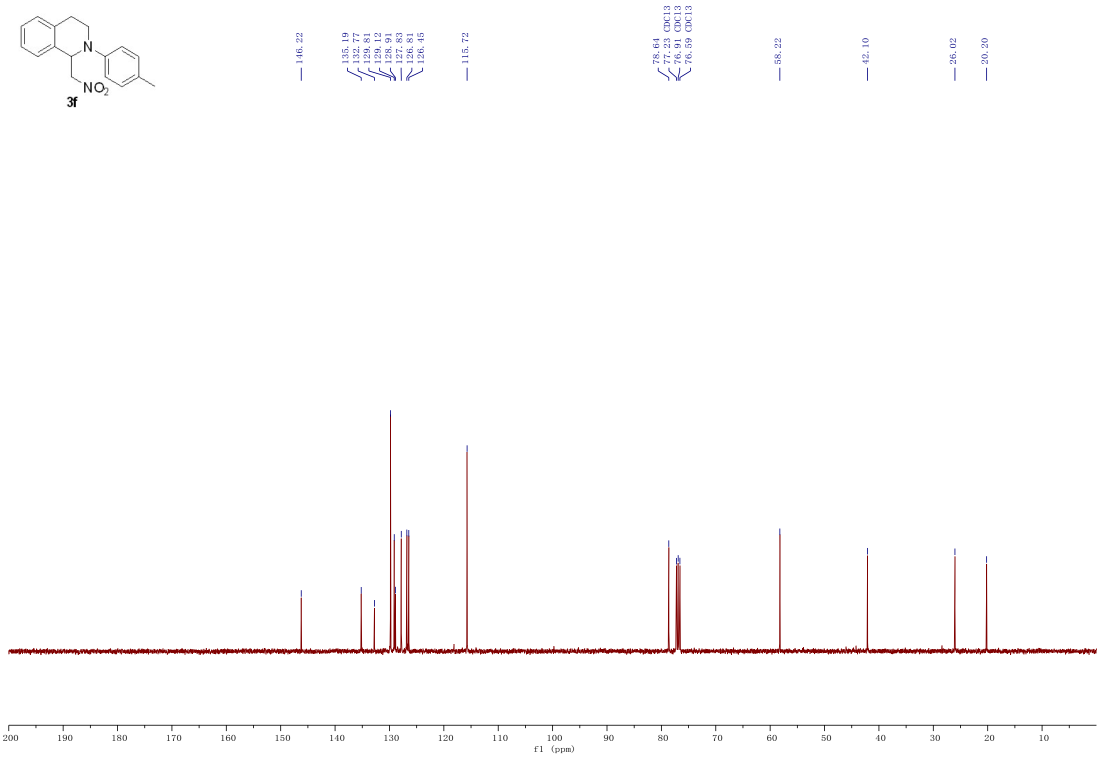
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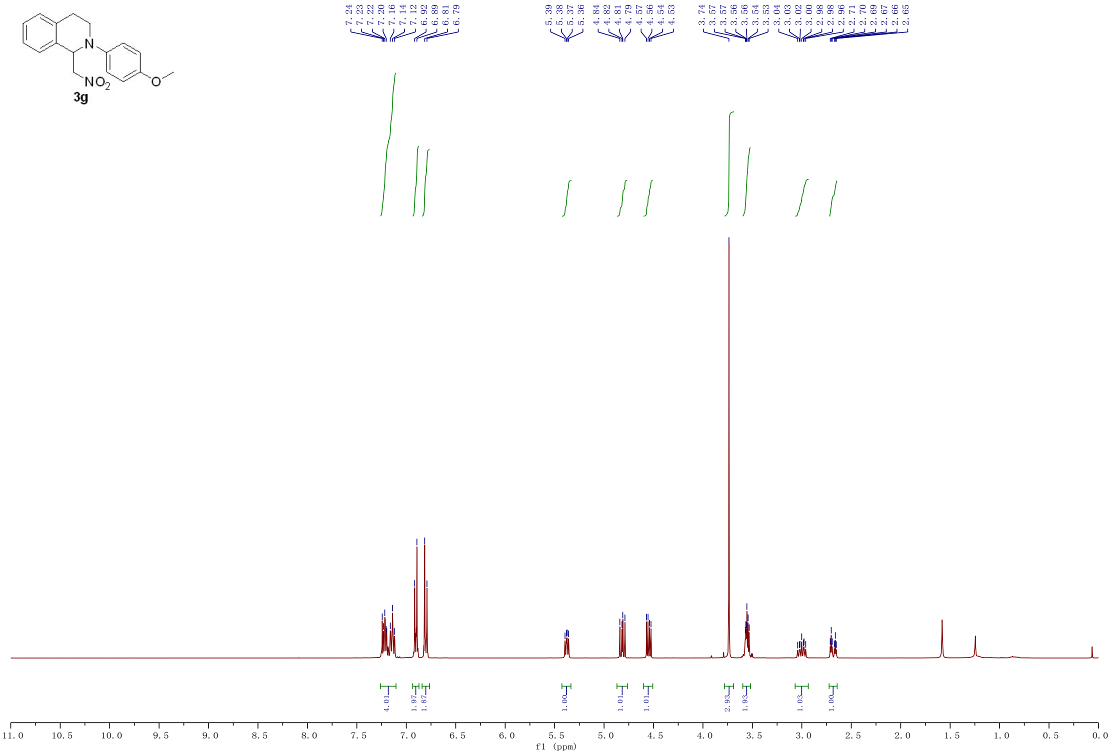
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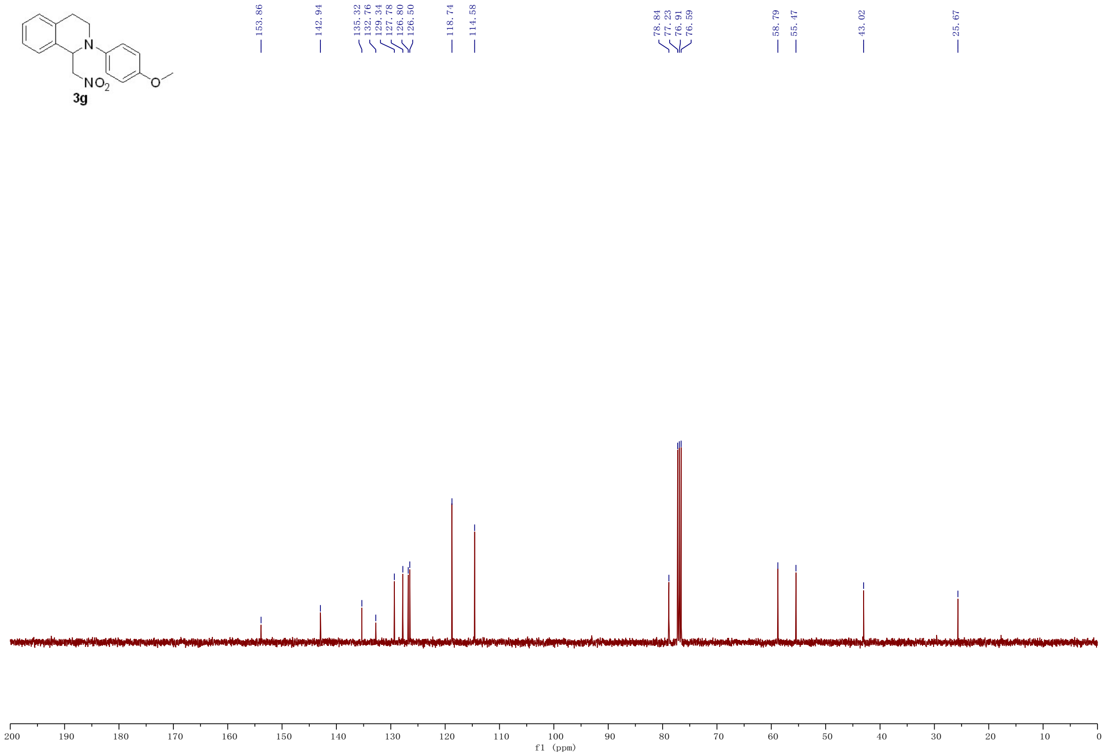
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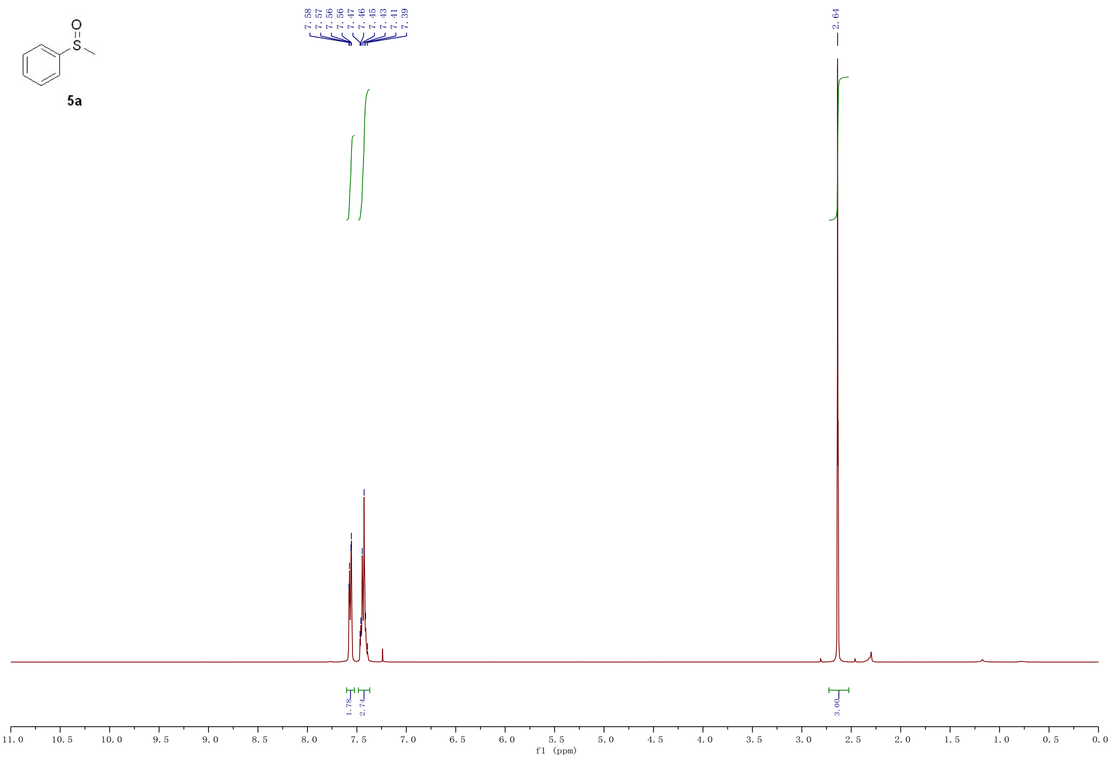
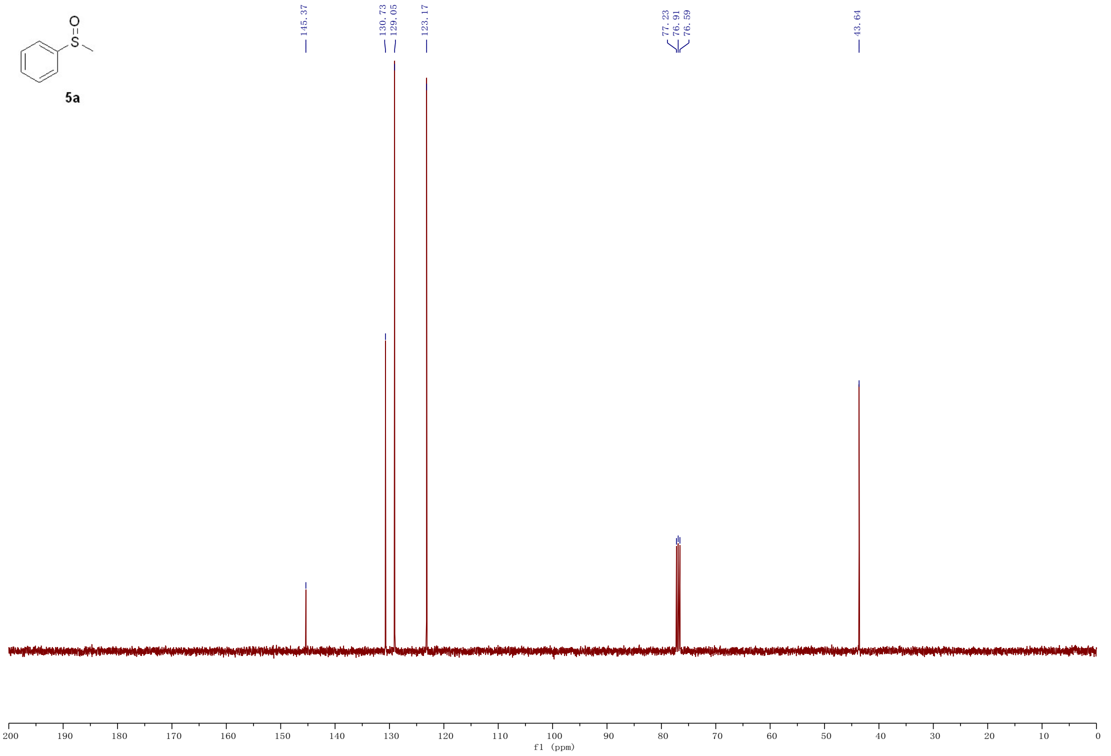
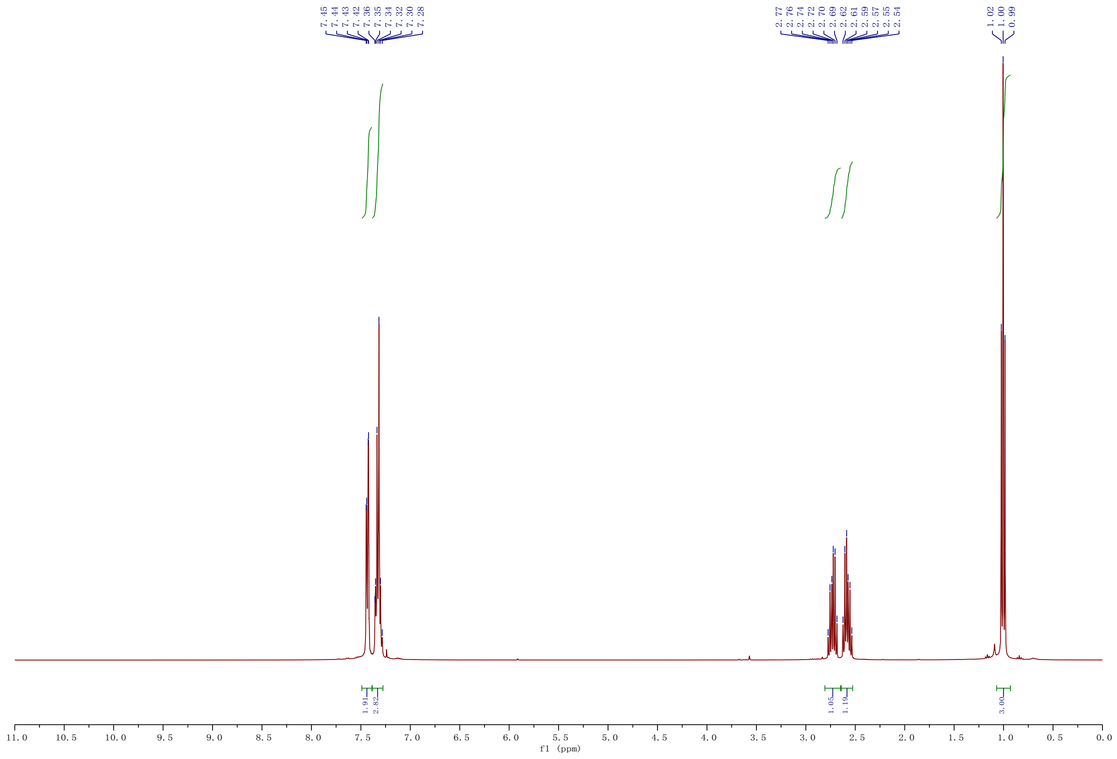
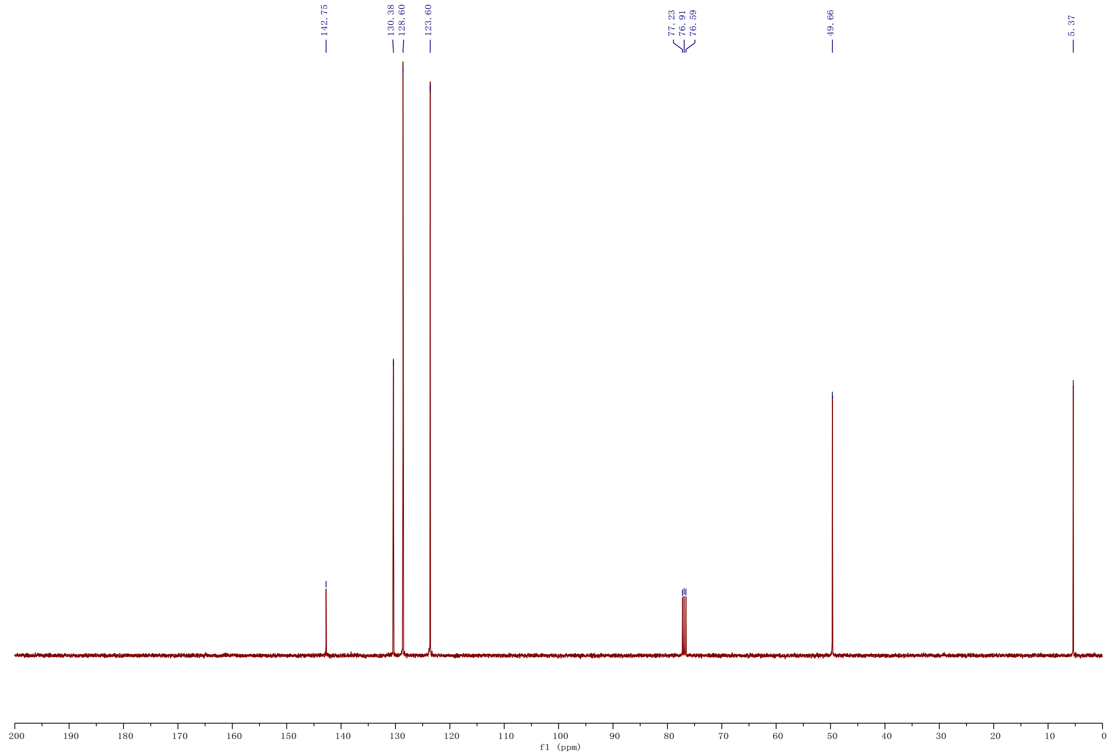
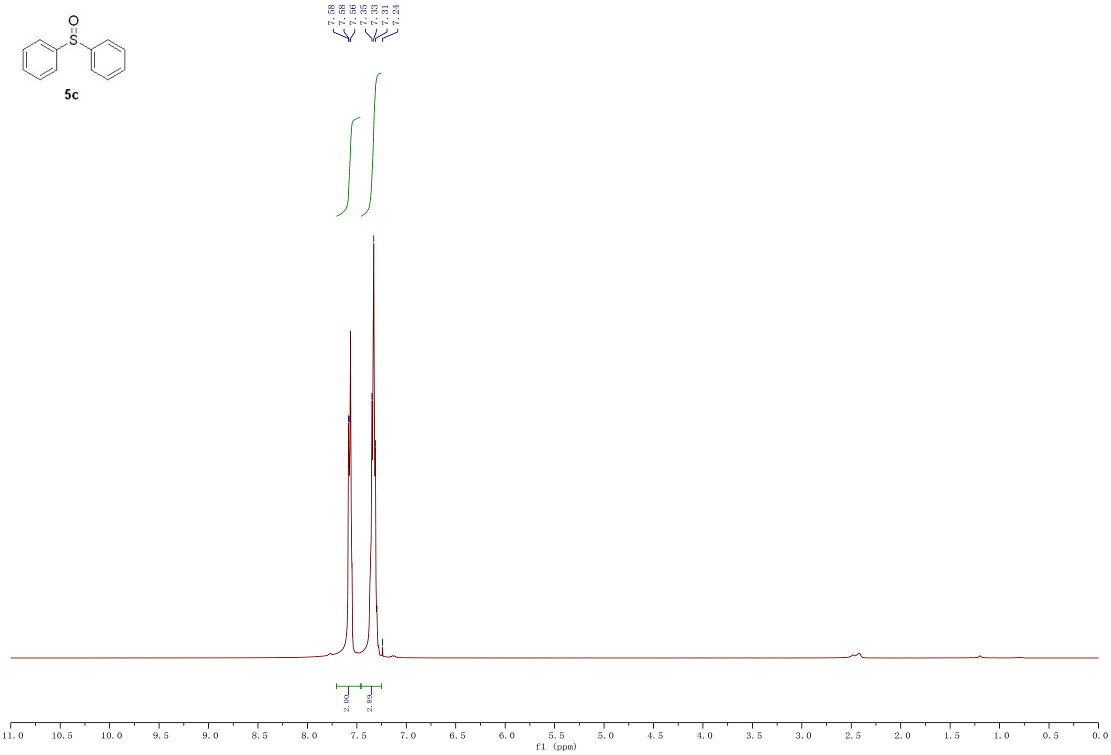
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

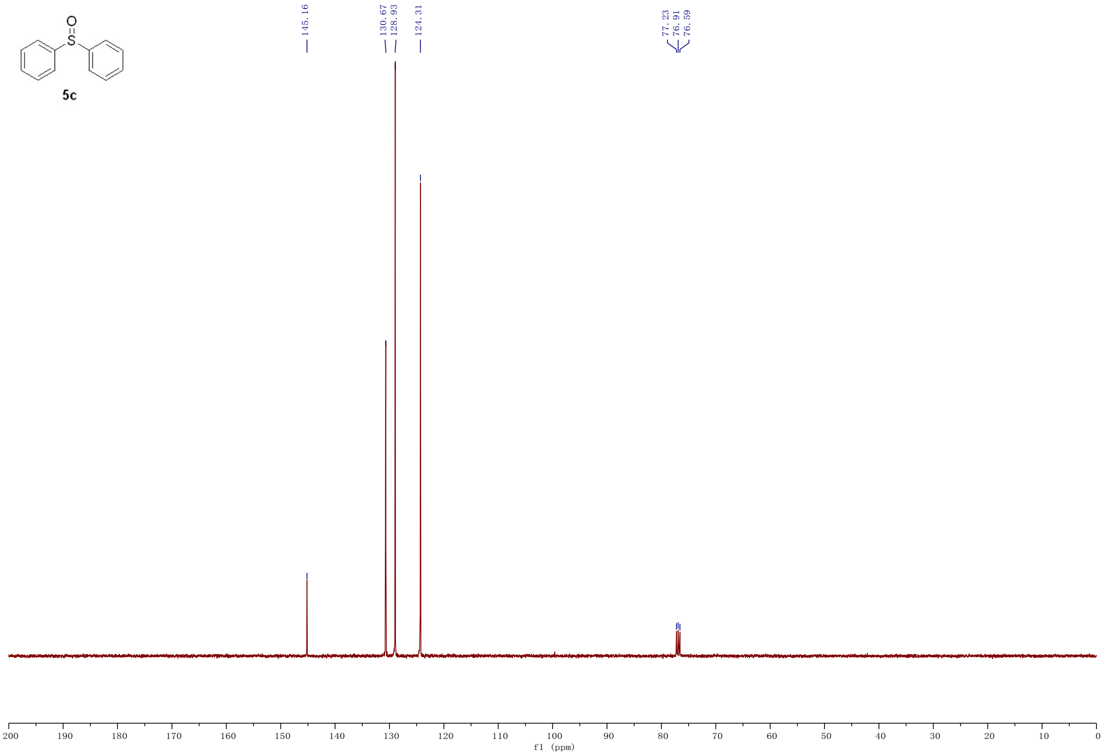

5a
7.58
7.57
7.56
7.56
7.47
7.46
7.45
7.43
7.41
7.39
2.64
1.78
2.74
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

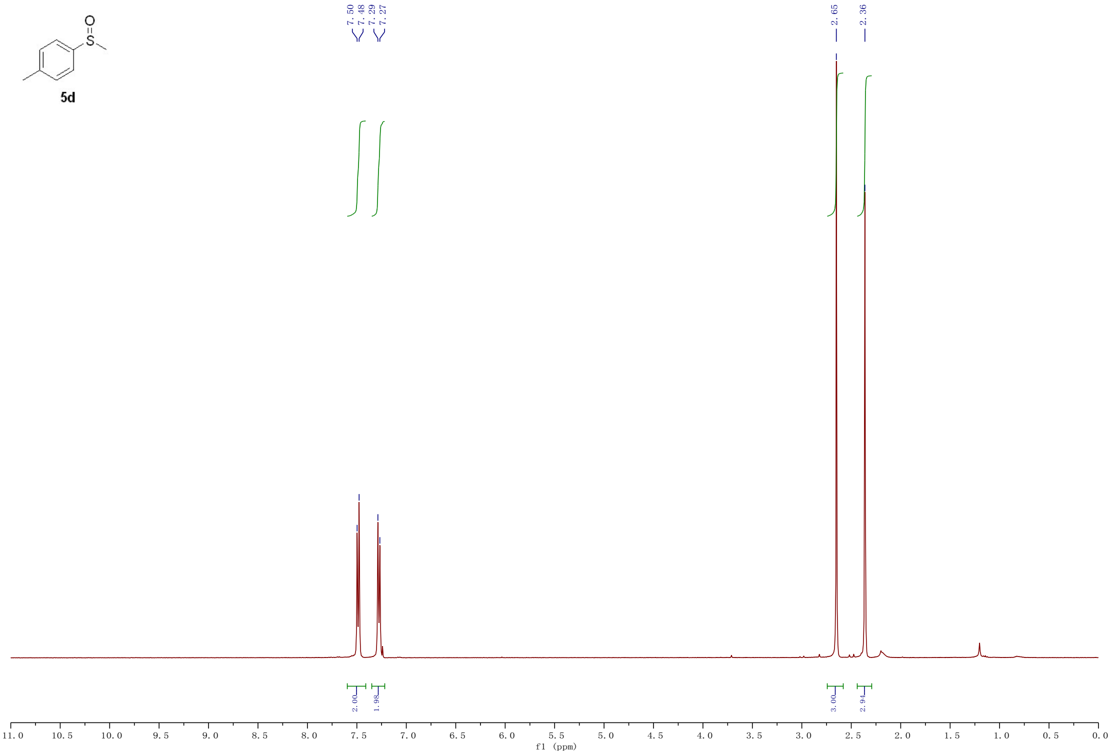

5a
145.37
130.73
129.05
123.17
77.23
76.91
76.59
43.64
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

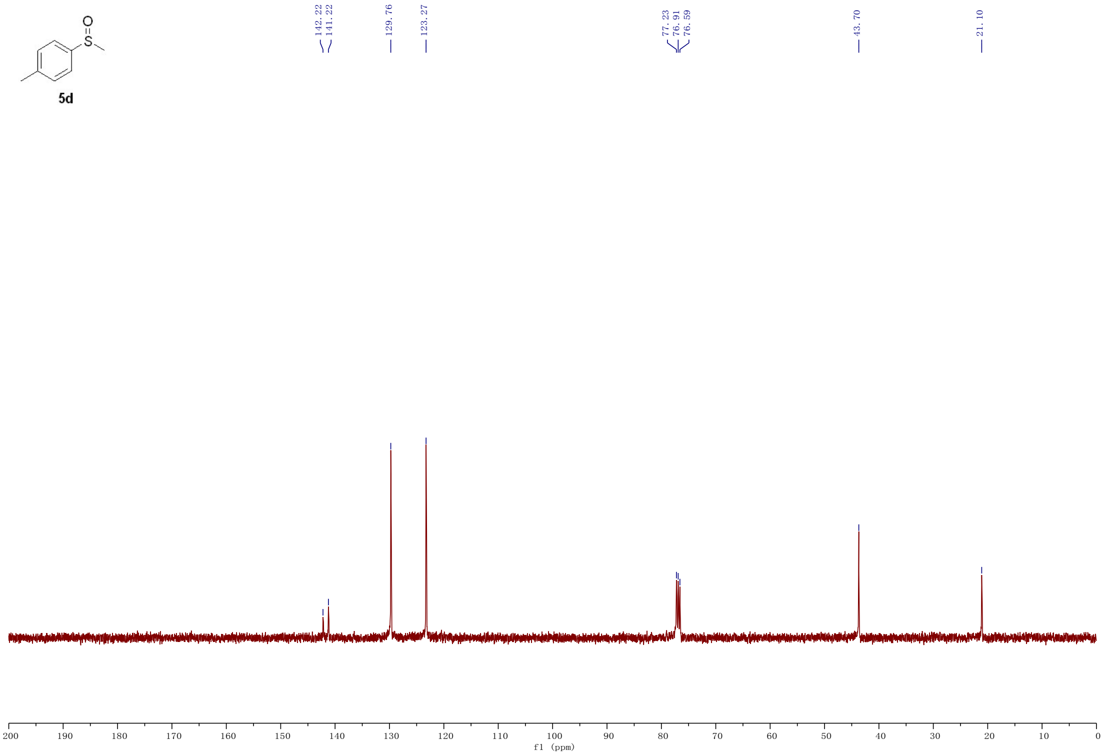

7.45
7.44
7.43
7.42
7.36
7.35
7.34
7.32
7.30
7.28
2.77
2.76
2.74
2.72
2.70
2.69
2.62
2.61
2.59
2.57
2.55
2.54
1.02
1.00
0.99
1.91
2.82
1.05
1.19
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

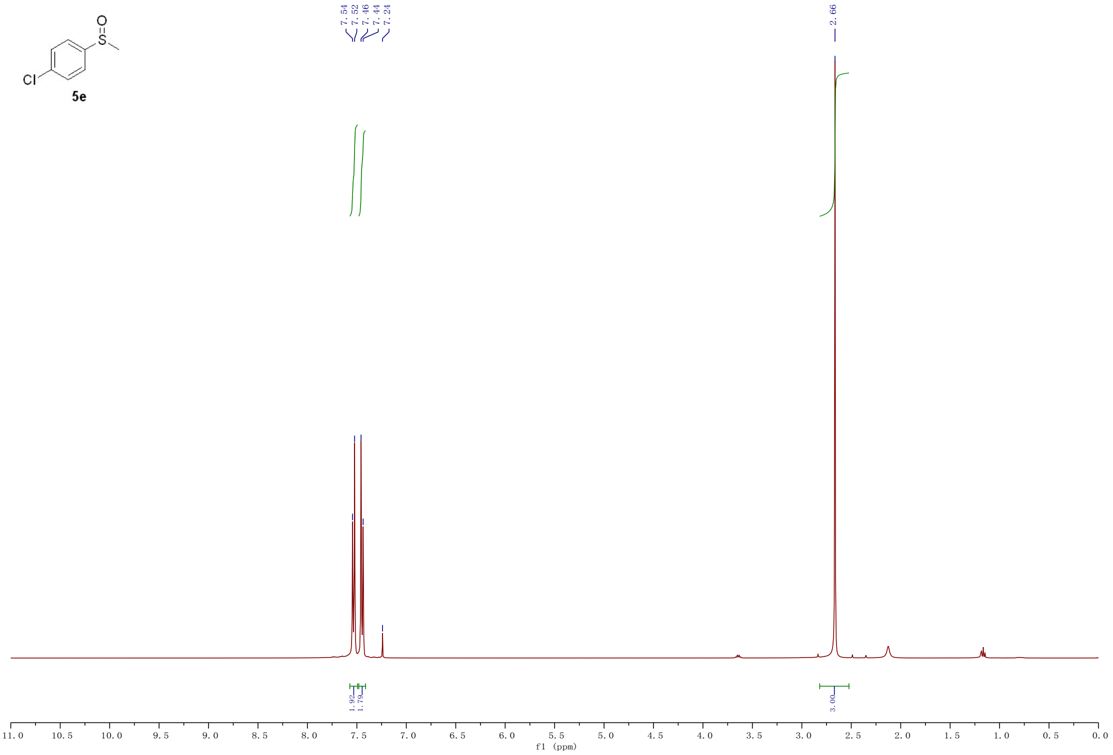

142.75
130.38
128.60
123.60
77.23
76.91
76.59
49.66
5.37
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

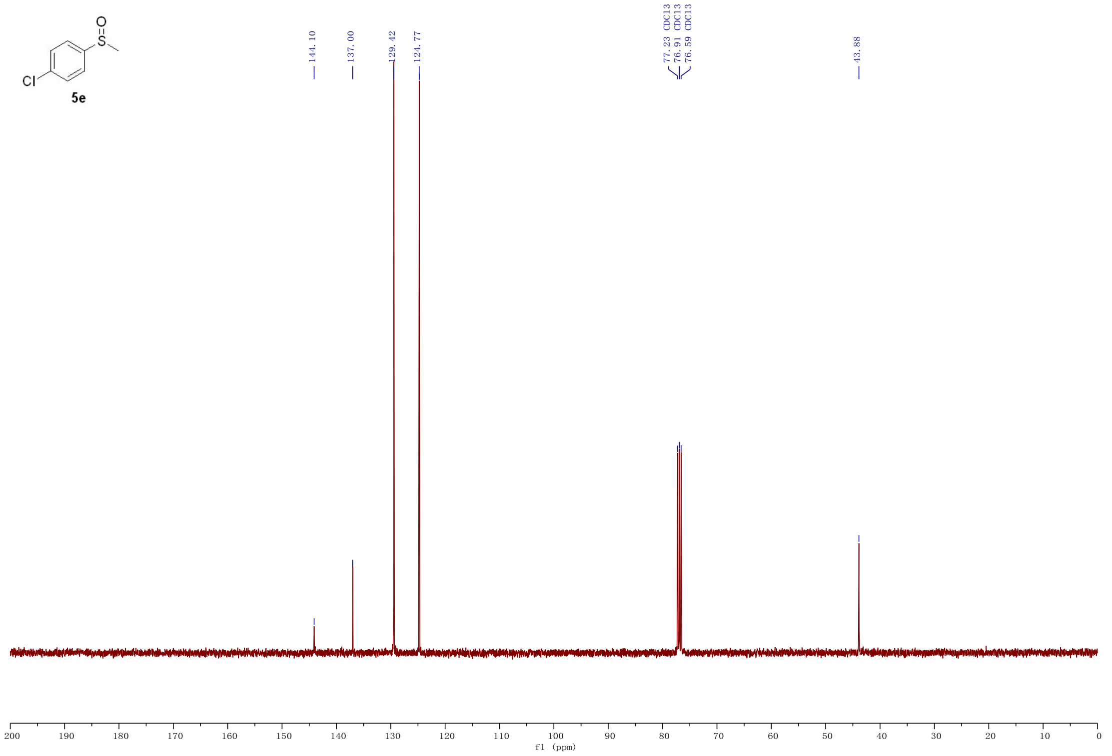

5c
7.58
7.58
7.56
7.35
7.33
7.31
7.24
2.00
2.89
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

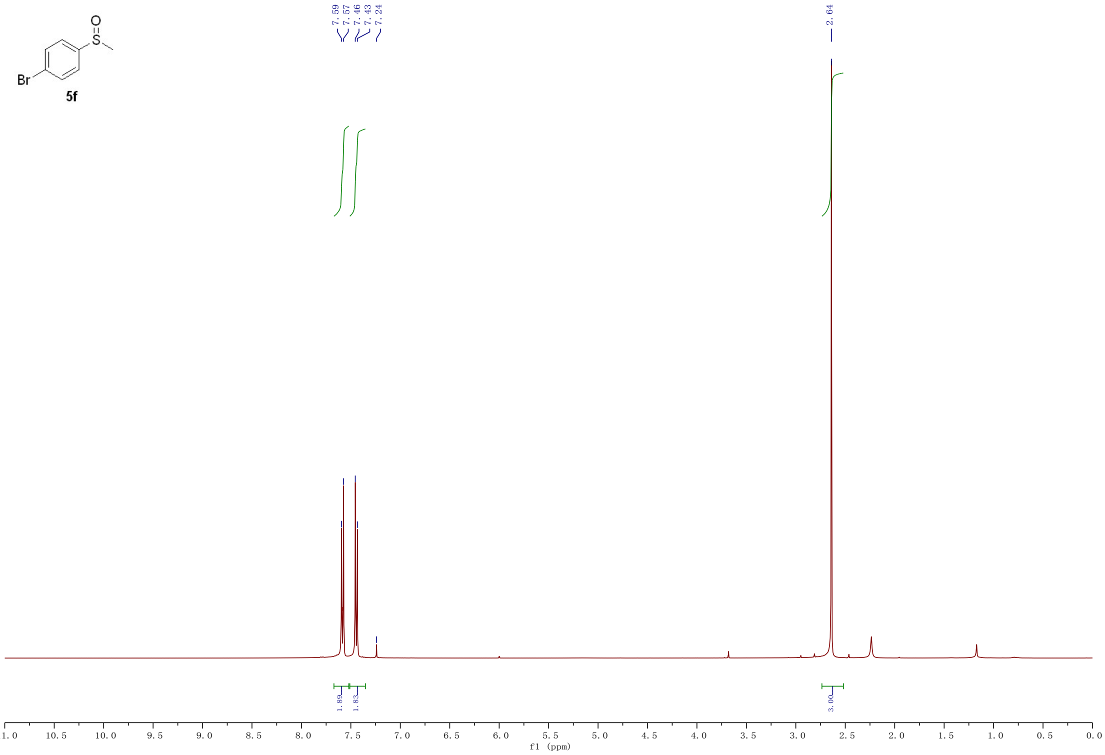

5c
145.16
130.67
128.93
124.31
77.23
76.91
76.59
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

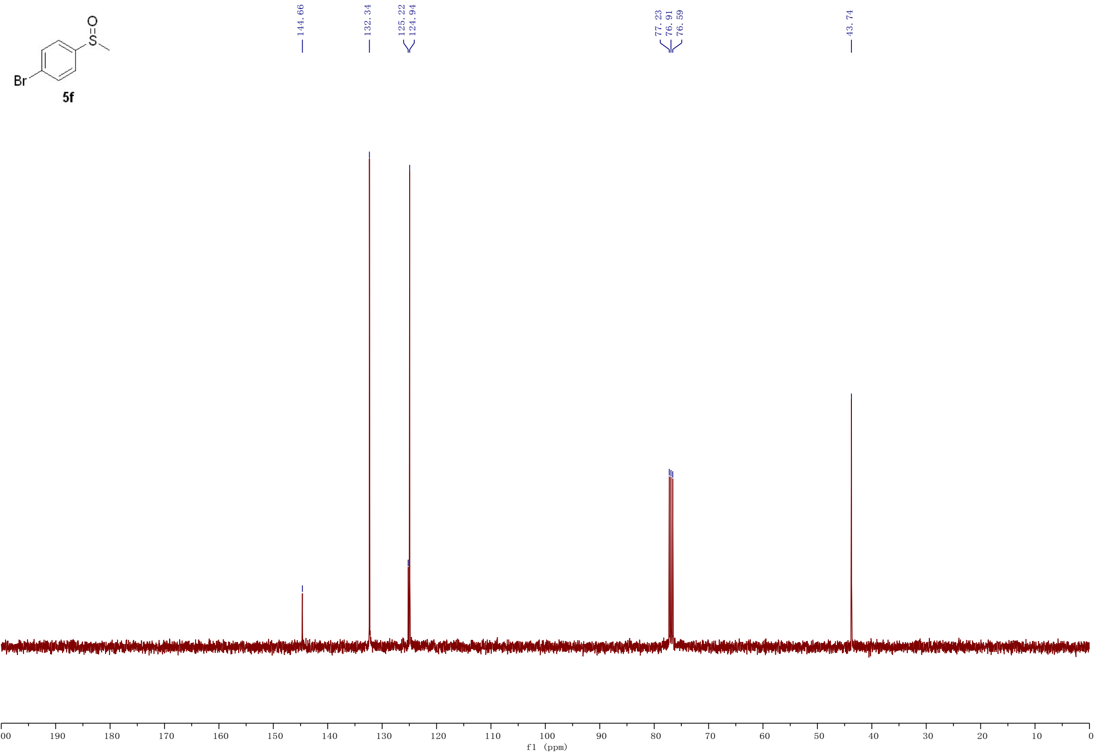

5d
7.50
7.48
7.29
7.27
2.65
2.36
2.00
1.98
3.00
2.94
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

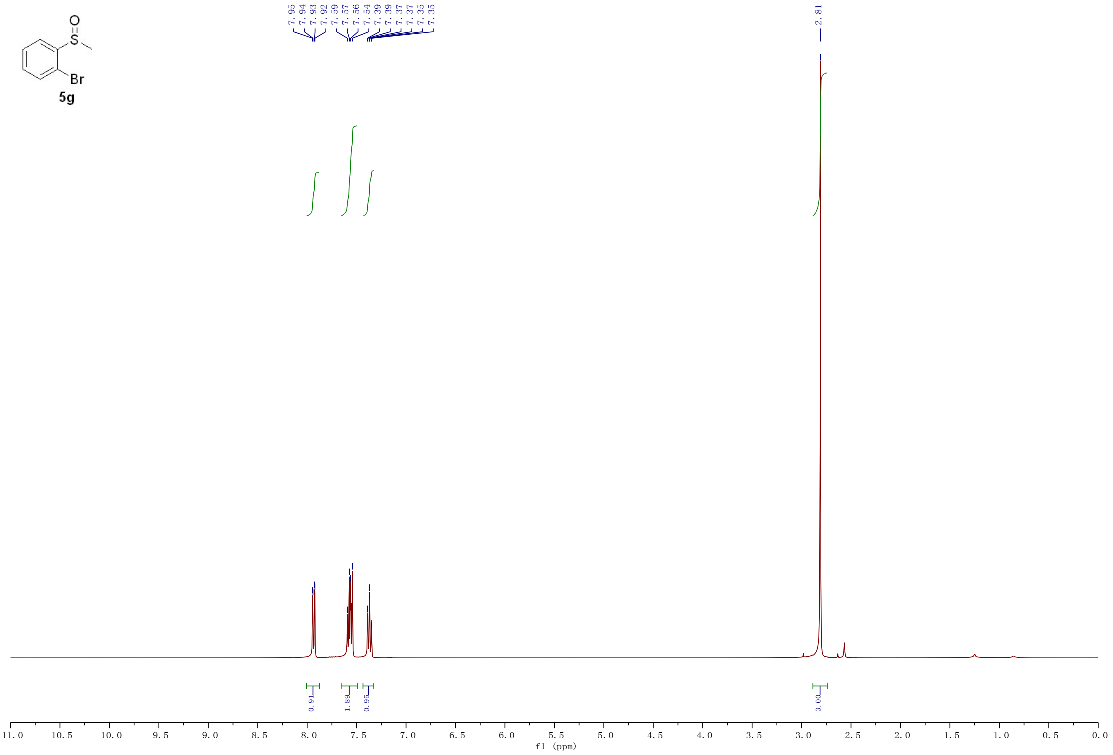

5d
142.22
141.22
129.76
123.27
77.23
76.91
76.59
43.70
21.10
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

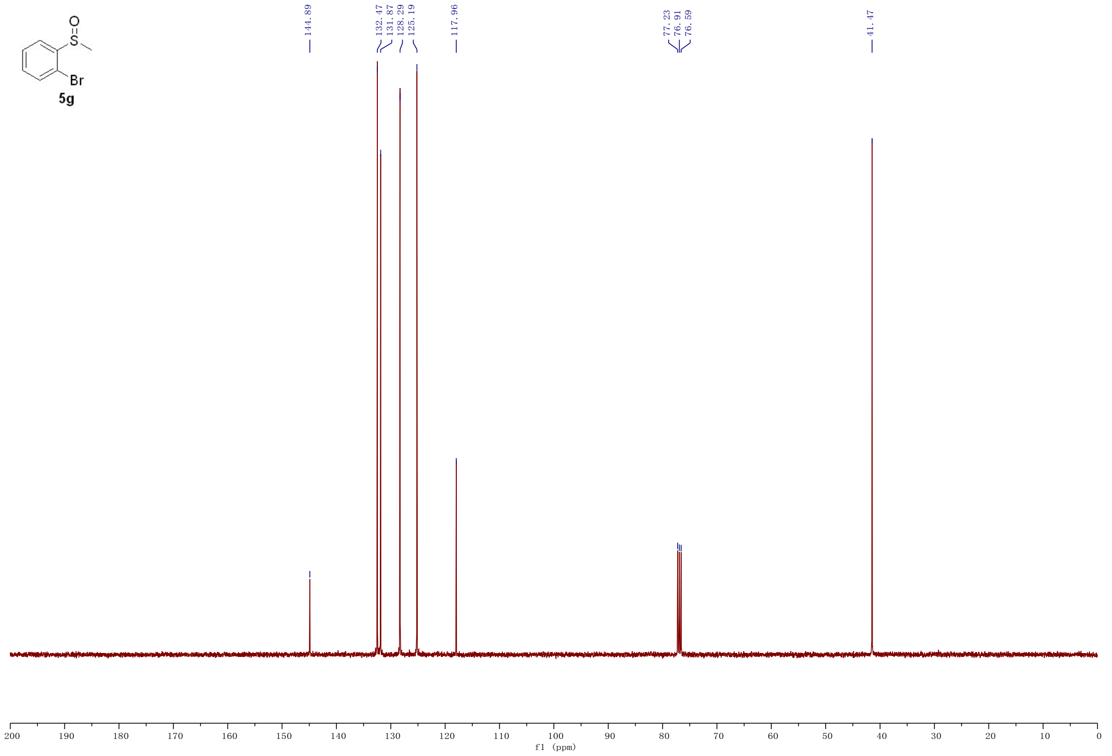

O
S
Cl
5e
7.54
7.52
7.46
7.44
7.24
2.66
1.92
1.79
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

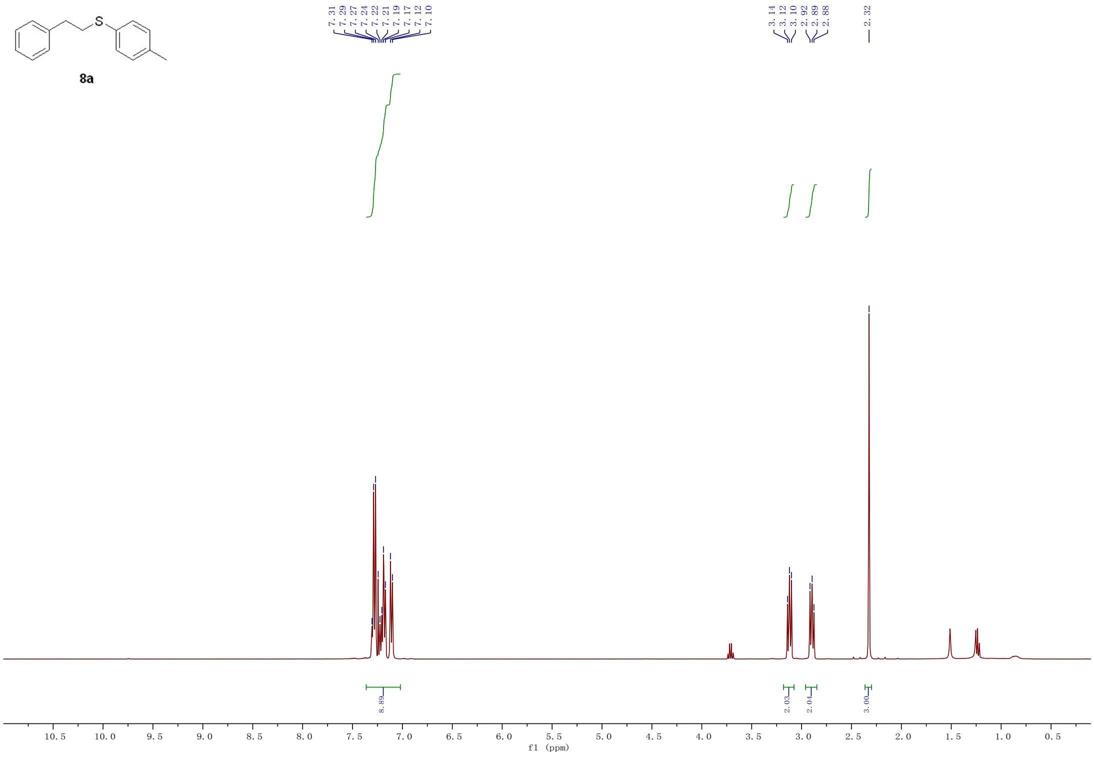

O
S
Cl
5e
144.10
137.00
129.42
124.77
77.23 CDCl3
76.91 CDCl3
76.59 CDCl3
43.88
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

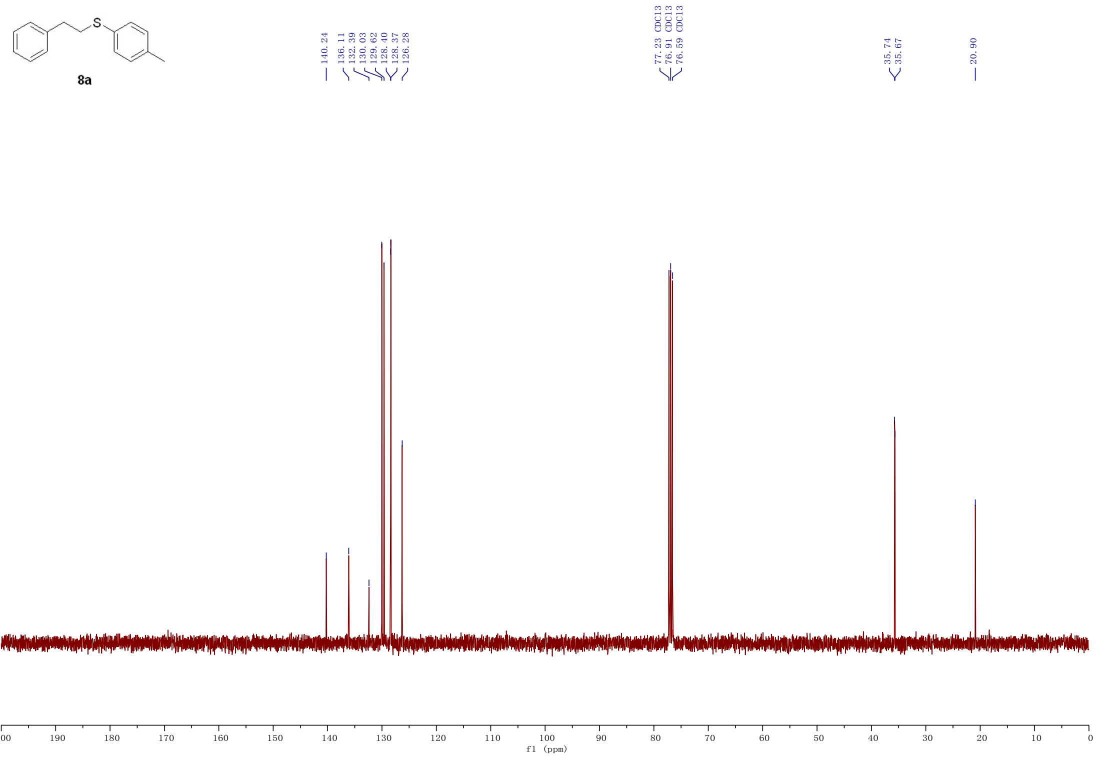

O
S
Br
5f
7.59
7.57
7.46
7.43
7.24
2.64
1.89
1.83
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

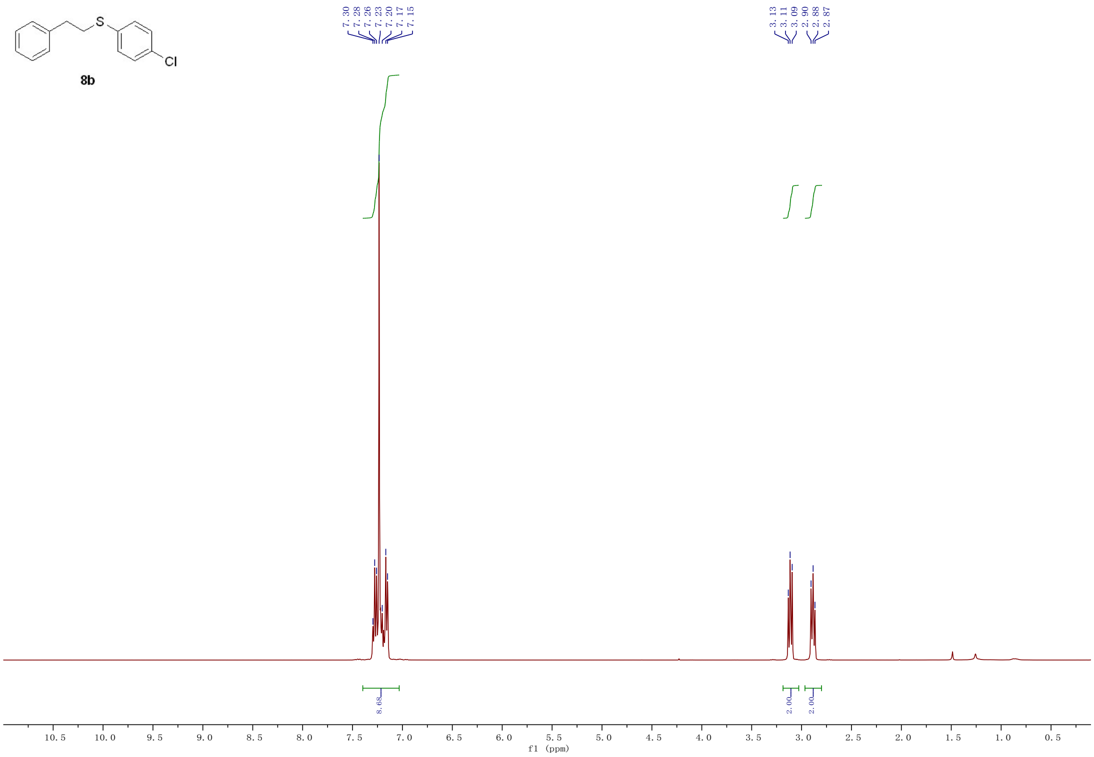

O
S
Br
5f
144.66
132.34
125.22
124.94
77.23
76.91
76.59
43.74
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
S
Br
5g
7.95
7.94
7.93
7.92
7.59
7.57
7.56
7.54
7.39
7.39
7.37
7.37
7.35
7.35
2.81
0.91
1.89
0.95
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

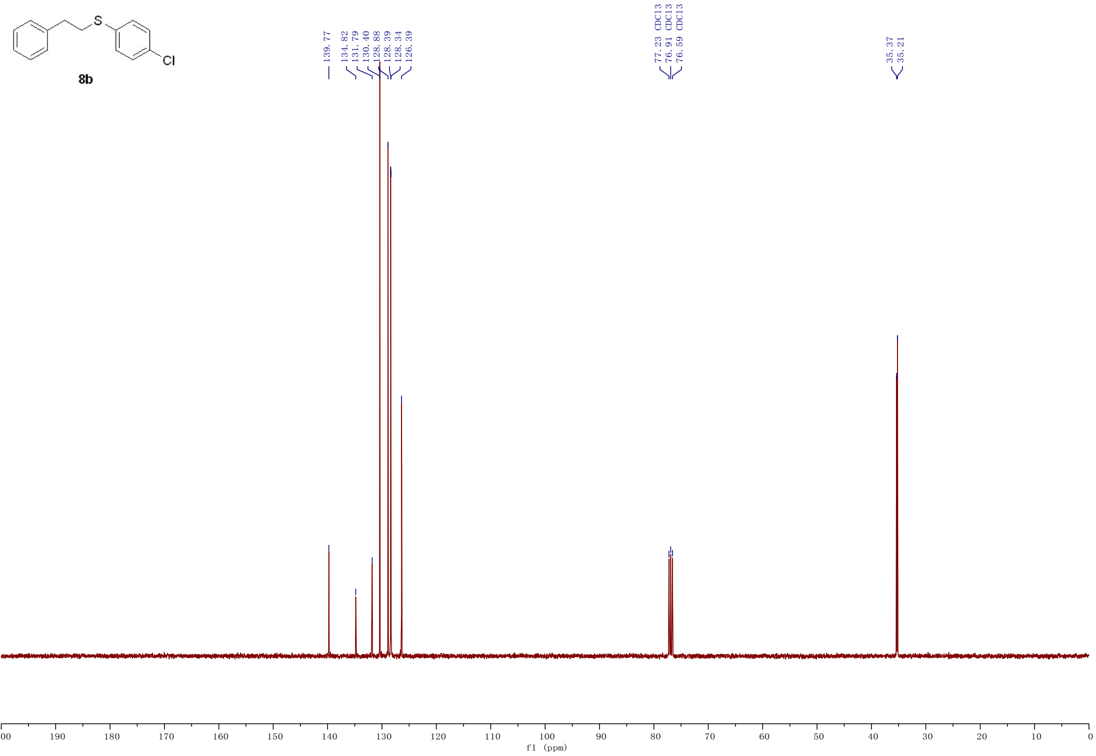

O
S
Br
5g
144.89
132.47
131.87
128.29
125.19
117.96
77.23
76.91
76.59
41.47
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8a
7.31
7.29
7.27
7.24
7.22
7.21
7.19
7.17
7.12
7.10
3.14
3.12
3.10
2.92
2.89
2.88
2.32
8.89
2.03
2.04
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

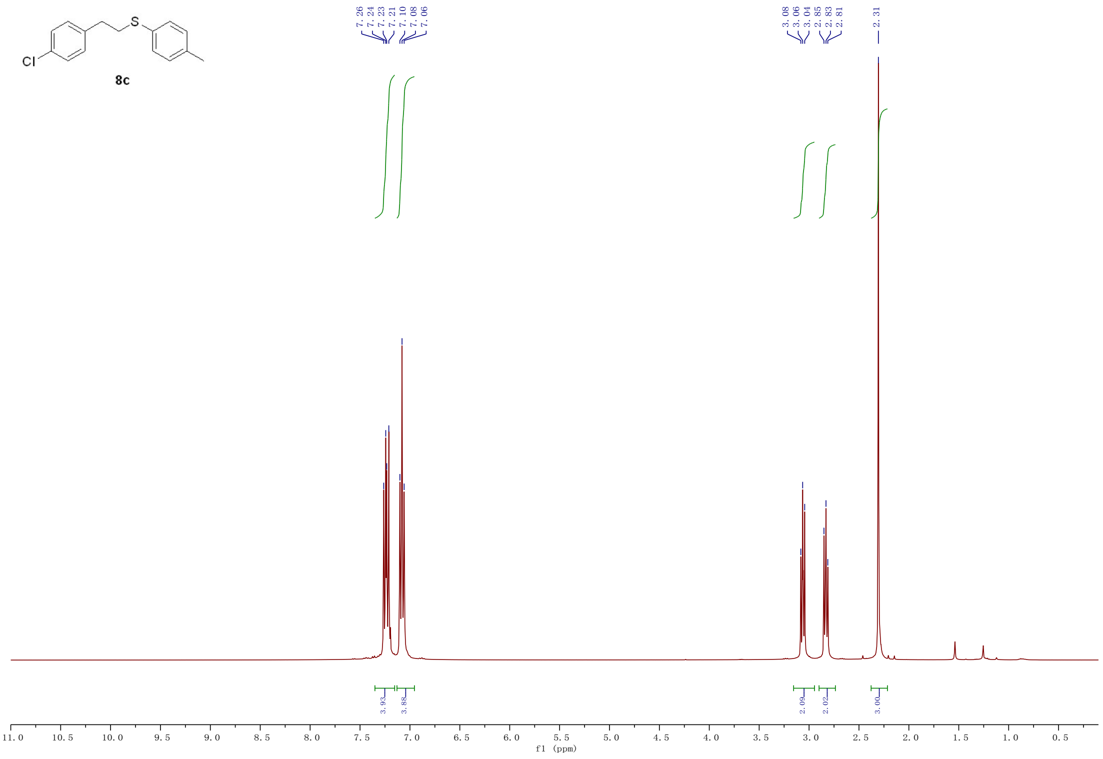

8a
140.24
136.11
132.39
130.03
129.62
128.40
128.37
126.28
77.23 CDCl3
76.91 CDCl3
76.59 CDCl3
35.74
35.67
20.90
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

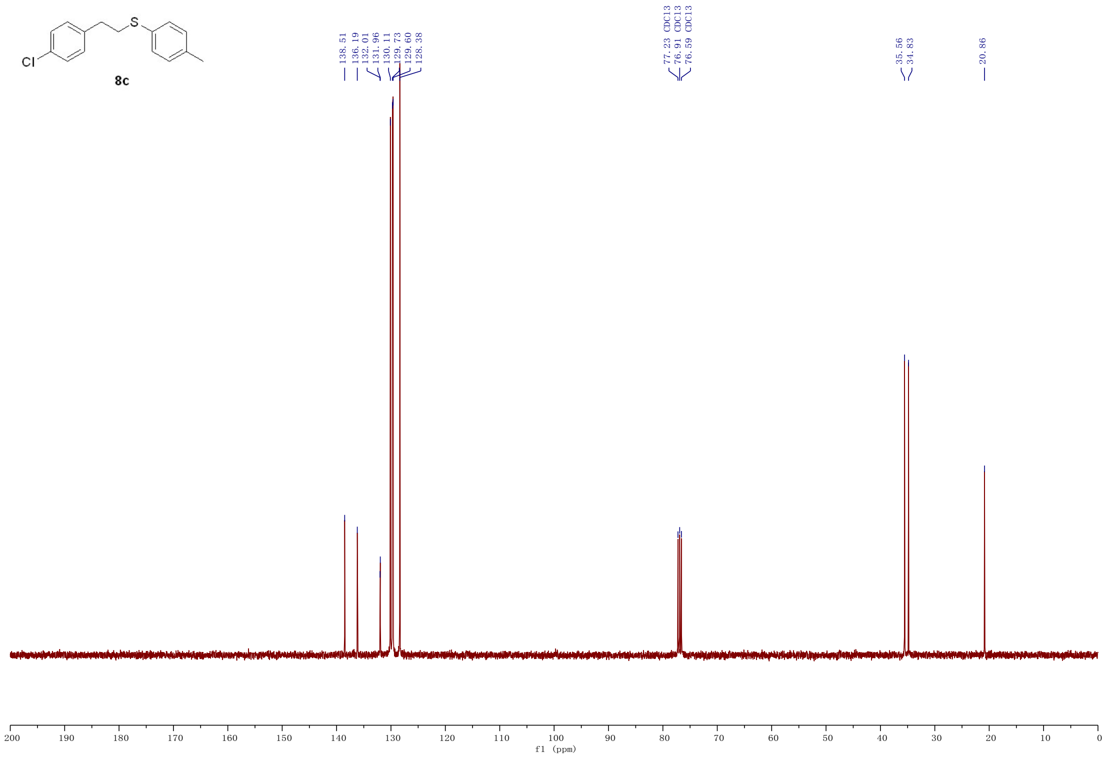


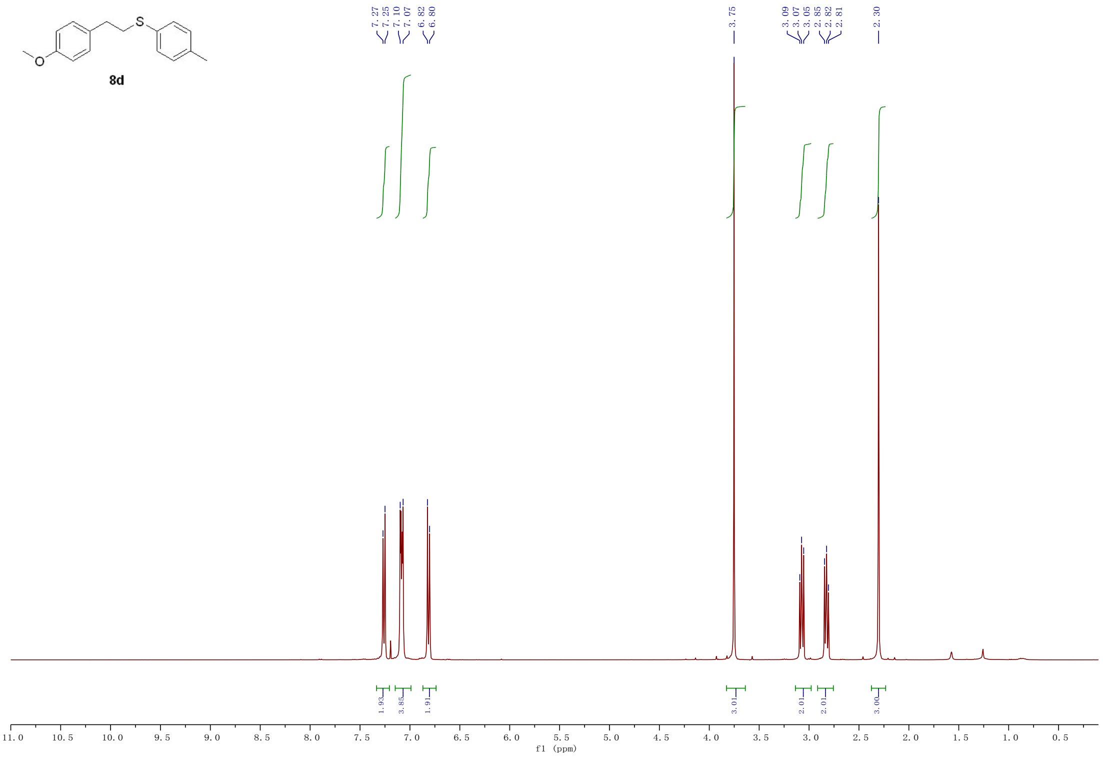
S
Cl
8b
7.30
7.28
7.26
7.23
7.20
7.17
7.15
3.13
3.11
3.09
2.90
2.88
2.87
8.68
2.00
2.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

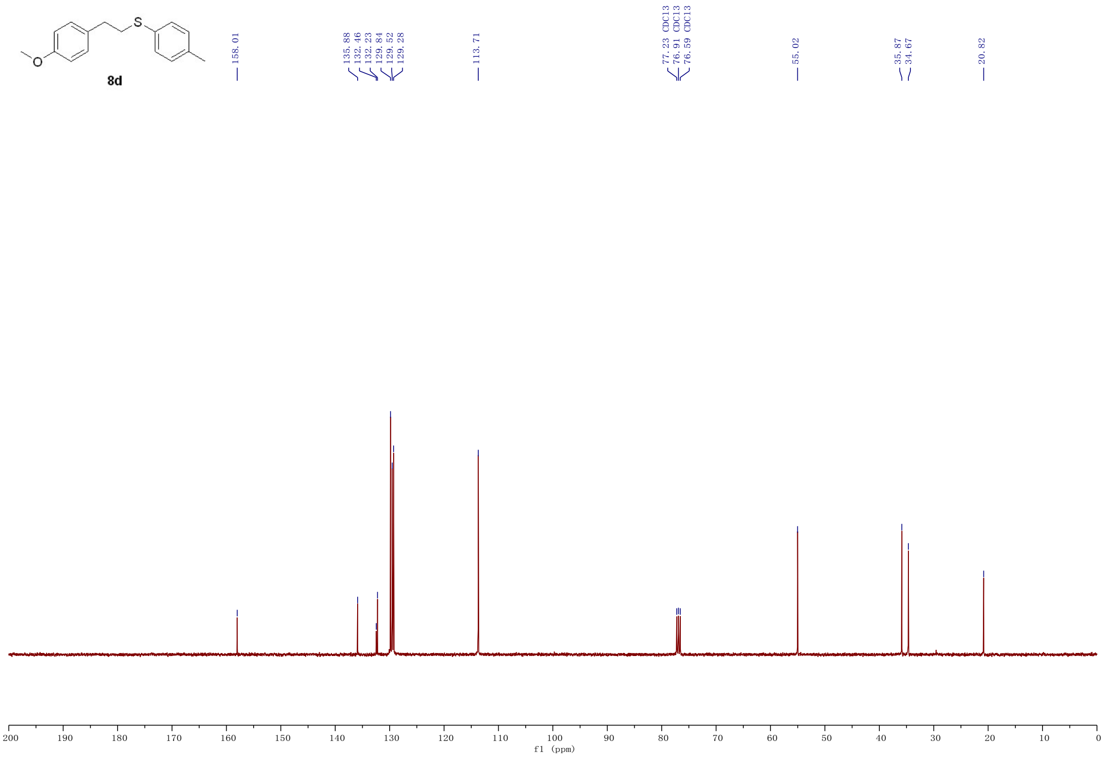


S
Cl
8b
139.77
134.82
131.79
130.40
128.88
128.39
128.34
126.39
77.23 CDCl3
76.91 CDCl3
76.59 CDCl3
35.37
35.21
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Cl
S
8c
7.26
7.24
7.23
7.21
7.10
7.08
7.06
3.08
3.06
3.04
2.85
2.83
2.81
2.31
3.93
3.88
2.09
2.02
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


Cl
S
8c
138.51
136.19
132.01
131.96
130.11
129.73
129.60
128.38
77.23 CDCl3
76.91 CDCl3
76.59 CDCl3
35.56
34.83
20.86
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8d
7.27
7.25
7.10
7.07
6.82
6.80
3.75
3.09
3.07
3.05
2.85
2.82
2.81
2.30
1.93
3.85
1.91
3.01
2.01
2.01
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


8d
158.01
135.88
132.46
132.23
129.84
129.52
129.28
113.71
77.23 CDCl3
76.91 CDCl3
76.59 CDCl3
55.02
35.87
34.67
20.82
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

VIII. **References (cited in SI)**

S1. U. Sharma, B. Tyagi and R. V. Jasra, *Ind. Eng. Chem. Res.*, 2008, **47**, 9588–9595.

S2. Y. Sahoo, A. Goodarzi, M. T. Swihart, T. Y. Ohulchanskyy, N. Kaur, E. P. Furlani, and P. N. Prasad, *J. Phys. Chem. B*, 2005, **109**, 3879–3885.

S3. All of the substrates and products are known compounds, see: a) Y. H. Pan, C. W. Kee, L. Chen, C. H. Tan, *Green Chem.,* 2011, **13**, 2682-2685; b) A. Tanoue, W. J. Yoo, S. Kobayashi, *Org. Lett.,* 2014, **16**, 2346-2349; c) X. Gu, X. Li, Y. Chai, Q. Yang, P. Li, and Y. Yao, *Green Chem.,* 2013, **15**, 357-361; d) Y. Lin, G. Lu, G. Wang, and W. Yi, *J. Org. Chem.,* 2017*,* **82***,* 382–389; e) B. C. Ranu and T. Mandal, *Synlett*, 2007, **6**, 925–928; f) C. H. Rosa, M. L. B. Peixoto, G. R. Rosa, B. Godoi, F. Z. Galetto, M. G. Montes D'Oca and M. Godoi, *Tetrahedron Lett.,* 2017, **58**, 3777-3781.