Supplementary Information

Electrochemical N(sp^2)–H/C(sp^3)–H cross-coupling reaction between sulfoximines and alkylarenes

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I. General information

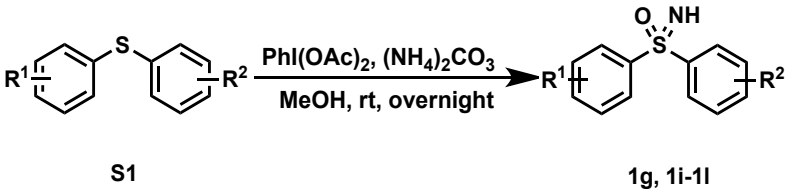
NMR spectra were recorded on Bruker-600 (600 MHz for ^{1}H; 150 MHz for ^{13}C). ^{1}H NMR spectra were referenced relative to internal $Si(Me)_4$ (TMS) at δ 0.00 ppm or $CDCl_3$ at δ 7.26 ppm. ^{13}C NMR spectra were recorded at ambient temperature on Bruker-600 (150 MHz) spectrometers and are referenced relative to $CDCl_3$ at δ 77.16 ppm. Data for ^{1}H, ^{13}C NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, quint = quintet, br = broad), integration, and coupling constant (Hz). High resolution mass spectra were recorded on P-SIMS-Gly of BrukerDaltonics Inc. using ESI-TOF (electrospray ionization-time of flight) and Aglient Technologies 7250 GCQTOF using EI-TOF. *n*-Bu_4NBF_4, HFIP, DCE were purchased from Energy Chemical. 1-Ethyl-4-methoxybenzene, 5,6-dimethyl-1*H*-benzo[*d*]imidazole were purchased from Bidepharm. Toxicity information: (1) DCE, harmful if swallowed, irritating to eyes, respiratory system and skin, may cause cancer; (2) HFIP, harmful by inhalation and if swallowed, causes burns.

II. Experimental procedures and data

1. Procedure for the synthesis of substrates **1** and **2**

Compounds **1a**[1], **1b**[1], **1c**[2], **1d**[2], **1e**[1], **1f**[3], **1h**[4], **1m**[1], **1n**[2], **1o**[5], **2g**[6], **2h**[7], **2o**[7], **2p**[8] were synthesized throught the known methods.

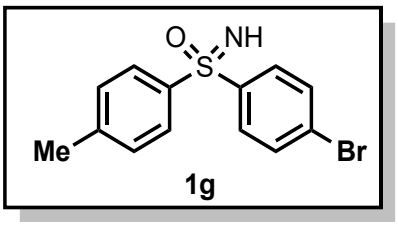
Procedure of synthesis of substrates **1g**, **1i-1l**



S1 **1g, 1i-1l**

The NH-sulfoximines **1g, 1i-1l** were prepared according to reported method[1]: Sulfide **S1** (10 mmol, 1.0 equiv.), $(NH_4)_2CO_3$ (15 mmol, 1.5 equiv), and MeOH (100 mL) were added into a round bottom flask equipped with a magnetic stir bar. Then the mixture was stired for five minutes, and followed by the addition of $PhI(OAc)_2$ (23 mmol, 2.3 equiv.). After being stired at room temperature overnight, the reaction mixture was evaporated under reduced pressure to romove the MeOH. The resulting crude product was further purified by flash column chromatography to give NH-sulfoximines **1g, 1i-1l**.

(4-Bromophenyl)(4-methylphenyl)(oxo)-λ^6-sulfanimine (**1g**)



1g

Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 2:1) to afford the product **1g** (2.04 g, 66% yield).

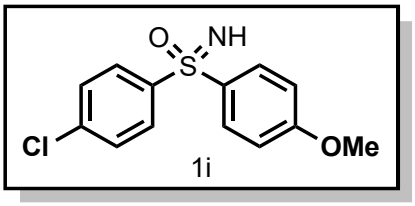
White solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90-7.87 (m, 4H), 7.60-7.57 (m, 2H), 7.28-7.27 (m, 2H), 3.05 (brs, 1H), 2.38 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 143.9, 143.0, 140.1, 132.4, 130.0, 129.5, 128.0, 127.7, 21.6.

HRMS (ESI) calcd. for $C_{13}H_{13}BrNOS^+$ ([M+H]$^+$): 309.9896, found: 309.9893.

(4-Chlorophenyl)(4-methoxyphenyl)(oxo)-λ^6-sulfanimine (**1i**)



1i

Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 1:1) to afford the product **1i** (2.61 g, 93% yield).

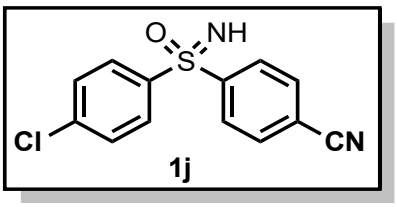
White solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95-7.92 (m, 4H), 7.43-7.40 (m, 2H), 6.95-6.93 (m, 2H), 3.83 (s, 3H), 3.04 (brs, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 163.3, 142.8, 139.0, 134.6, 130.2, 129.5, 129.3, 114.6, 55.8.

HRMS (ESI) calcd. for $C_{13}H_{13}ClNO_2S^+$ ([M+H]$^+$): 282.0350, found: 282.0350.

4-[Azanylidene(4-chlorophenyl)(oxo)-λ^6-sulfanyl]benzene-1-carbonitrile (**1j**)



Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 2:1) to afford the product **1j** (1.58 g, 57% yield).

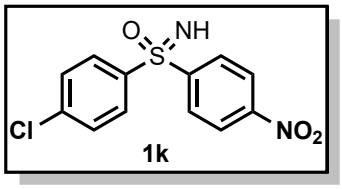
White solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13-8.11 (m, 2H), 7.96-7.94 (m, 2H), 7.78-7.76 (m, 2H), 7.48-7.45 (m, 2H), 3.23 (brs, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 147.6, 140.7, 140.3, 133.1, 129.9, 129.8, 128.6, 117.4, 116.6.

HRMS (ESI) calcd. for $C_{13}H_{10}ClN_2OS^+$ ($[M+H]^+$): 277.0197, found: 277.0194.

(4-Chlorophenyl)(4-nitrophenyl)(oxo)-λ^6-sulfanimine (**1k**)



1k

Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 2:1) to afford the product **1k** (1.65 g, 56% yield).

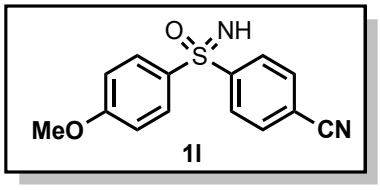
White solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31-8.30 (m, 2H), 8.20-8.19 (m, 2H), 8.00-7.97 (m, 2H), 7.49-7.48 (m, 2H), 3.26 (brs, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 150.3, 149.2, 140.7, 140.4, 129.9, 129.8, 129.3, 124.6.

HRMS (ESI) calcd. for $C_{12}H_{10}ClN_2O_3S^+$ ($[M+H]^+$): 297.0095, found: 297.0094.

4-[Azanylidene(4-methoxyphenyl)(oxo)-λ^6-sulfanyl]benzene-1-carbonitrile (**1l**)



1l

Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 1:1) to afford the product **1l** (1.97 g, 72% yield).

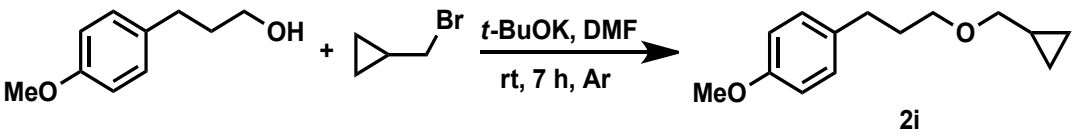
White solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12-8.10 (m, 2H), 7.95-7.93 (m, 2H), 7.75-7.73 (m, 2H), 6.97-6.95 (m, 2H), 3.83 (s, 3H), 3.12 (brs, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 163.7, 148.7, 133.4, 133.0, 130.5, 128.3, 117.5, 116.0, 114.8, 55.8.

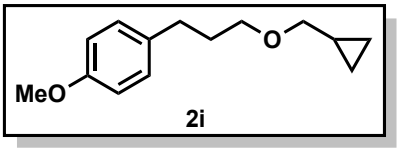
HRMS (ESI) calcd. for $C_{14}H_{13}N_2O_2S^+$ ($[M+H]^+$): 273.0692, found: 273.0693.

Procedure for the synthesis of substrate **2i**[9], **2q**[7]



t-BuOK (3.2 mmol, 1.28 equiv) was added into an oven-dried sealed tube and the vessel was evacuated and backfilled with Ar (3-times). 3-(4-methoxyphenyl)propan-1-ol (2.5 mmol, 1.0 equiv), (bromomethyl)cyclopropane (4.1 mmol, 1.64 equiv) and DMF (4 mL) were added via syringe. The tube was then sealed with a Teflon lined cap. After vigorous stiring for 7 h at room temperature, the reaction mixture was poured into saturated NH_4Cl solution and extracted with $CHCl_3$. The organic phase was seperated, washed with water, dried over anhydrous Na_2SO_4. Then, the solvent was evaperated under vacuum and the residue was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 20:1) to afford the **2i** as a colorless oil (121.0 mg, 22% yield).

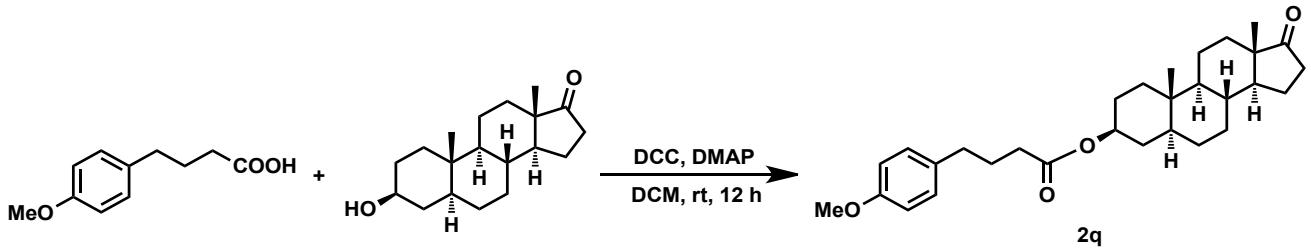
1-{3-[(Cyclopropylmethyl)oxy]propyl}-4-methoxybenzene (**2i**)



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 3.79 (s, 3H), 3.44 (t, *J* = 6.5 Hz, 2H), 3.25 (d, *J* = 6.9 Hz, 2H), 2.65 (t, *J* = 7.2 Hz, 2H), 1.91-1.86 (m, 2H), 1.11-1.04 (m, 1H), 0.55-0.52 (m, 2H), 0.22-0.20 (m, 2H).

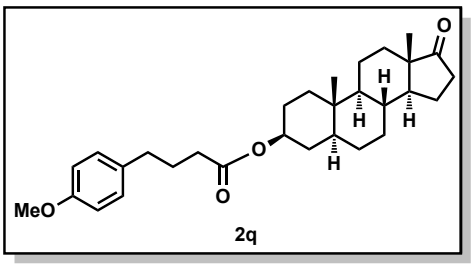
^{13}C NMR (150 MHz, $CDCl_3$) δ 157.8, 134.2, 129.5, 113.8, 75.7, 69.8, 55.3, 31.6, 31.5, 10.8, 3.1.

HRMS (ESI) calcd. for $C_{14}H_{20}NaO_2^+$ ([M+Na]$^+$): 243.1356, found: 243.1358.



4-(4-Methoxyphenyl)butanoic acid (3.0 mmol, 1.0 equiv), epiandrosterone (3.6 mmol, 1.2 equiv), DMAP (0.3 mmol, 0.1 equiv) and CH_2Cl_2 (10 mL) was combinded in a 50 mL round bottom flask. Then, DCC (4.5 mmol, 1.5 equiv) was added. After vigorous stiring for 12 h at room temperature, the reaction mixture was qunched by saturated solution of $NaHCO_3$. The mixture was extracted with CH_2Cl_2 (3 × 40 mL). The combined organic phase was evaporated to remove the solvent under vacuum and the residue was purified by silica gel flash chromatography with petroleum ether and ethylacetate (PE/EA = 5:1) to give the **2q** as a white solid (908.7 mg, 65% yield).

(3a*S*,3b*R*,5a*S*,7*S*,9a*S*,9b*S*,11a*S*)-9a,11a-Dimethyl-1-oxohexadecahydro-1*H*-cyclopenta[1,2-*i*]phenanthren-7-yl 4-(4-methoxyphenyl)butanoate (**2q**)



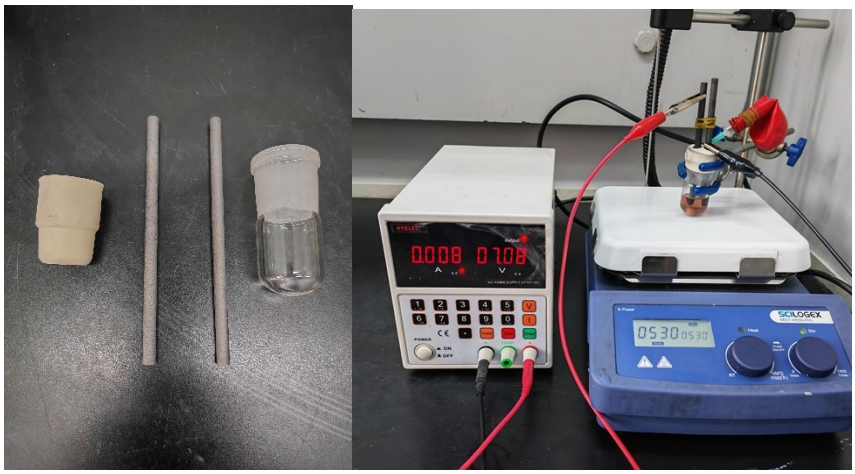
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.3 Hz, 2H), 6.82 (d, *J* = 8.3 Hz, 2H), 4.73-4.67 (m, 1H), 3.78 (s, 3H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.45-2.41 (m, 1H), 2.27 (t, *J* = 7.4 Hz, 2H), 2.09-2.03 (m, 1H), 1.95-1.87 (m, 3H), 1.82-1.78 (m, 3H), 1.75-1.73 (m, 1H), 1.66-1.63 (m, 2H), 1.55-1.45 (m, 3H), 1.39-1.17 (m, 7H), 1.06-0.94 (m, 2H), 0.85 (s, 3H), 0.84 (s, 3H), 0.75-0.69 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 221.4, 173.2, 158.0, 133.7, 129.5, 113.9, 73.5, 55.4, 54.4, 51.5, 47.9, 44.8, 36.8, 36.0, 35.8, 35.2, 34.4, 34.2, 34.1, 31.7, 30.9, 28.4, 27.6, 27.1, 21.9, 20.6, 14.0, 12.4.

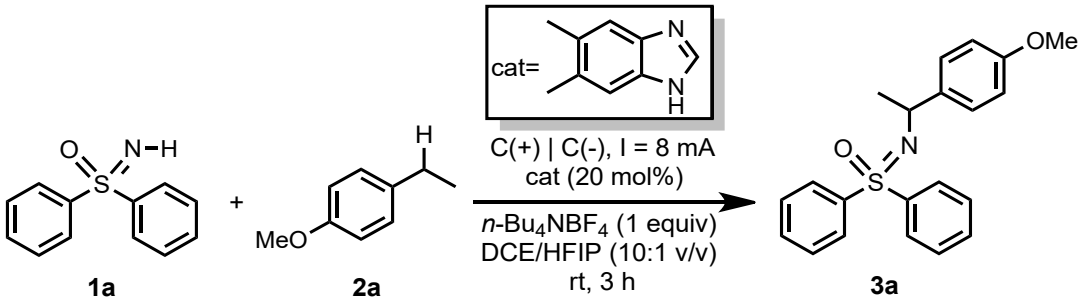
HRMS (ESI) calcd. for $C_{30}H_{42}NaO_4^+$ ([M+Na]$^+$): 489.2975, found: 489.2970.

2. Graphical guide for the set-up

As experimental setup, we used two carbon rod (Φ 6 mm) electrolytes, rubber stoppers, an undivided 10 mL columnar round-bottom flask, a DC adjustable power supply regulator (brand: HYELEC) (model: HY3005MT) and a magnetic stirrer.



3. General procedure for the electrochemical synthesis of products

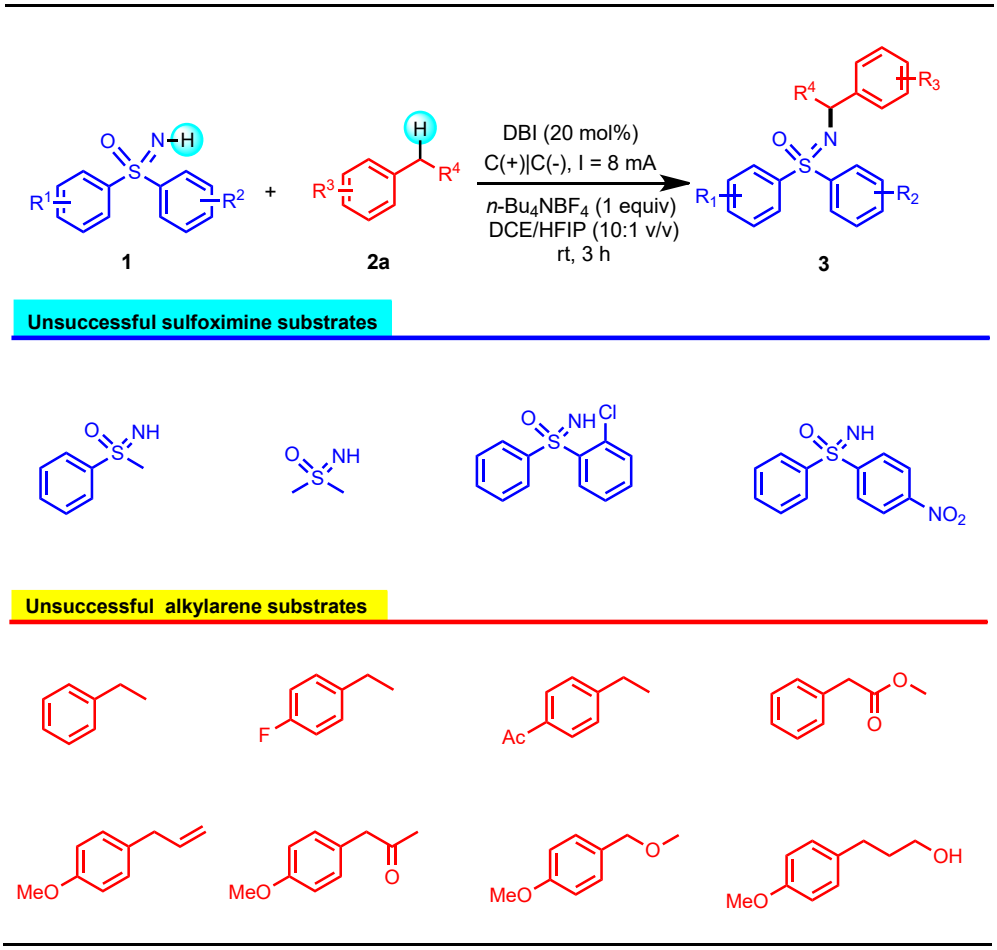


To an undivided cell (10 mL columnar round-bottom flask with a 24# mouth) equipped with a magnetic stir bar, sulfonimidoyldibenzene **1a** (0.3mmol, 1.0 equiv), 5,6-dimethyl-1*H*-benzo[*d*]imidazole (0.06 mmol, 20 mol%), *n*-Bu_4NBF_4 (0.3 mmol, 1 equiv) were added. Then, 1-ethyl-4-methoxybenzene **2a** (0.9 mmol, 3 equiv), DCE (5 mL), HFIP (0.5 mL) were added in sequence. The cell was then sealed with a rubber equipped with two carbon rods (Φ 6 mm). The reaction mixture was stirred and electrolyzed with constant current (8 mA) at room temperature. Three hours later, the solvent was evaporated under vacuum and the residue was purified by preparatory thin layer chromatography to yield product **3a** as a pale yellow oil (79.8 mg, 76 % yield).

4. Procedure for the electrochemical synthesis of **4q**

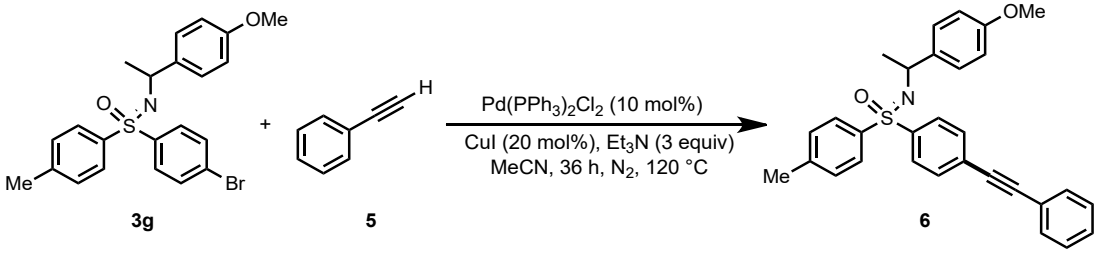
To an undivided cell (10 mL columnar round-bottom flask with a 24# mouth) equipped with a magnetic stir bar, sulfonimidoyldibenzene **1a** (0.3 mmol, 1.0 equiv), 5,6-dimethyl-1*H*-benzo[*d*]imidazole (0.09 mmol, 30 mol%), *n*-Bu_4NBF_4 (0.3 mmol, 1 equiv) were added. Then, **2q** (0.9 mmol, 3 equiv), DCE (5 mL), HFIP (0.5 mL) were added in sequence. The cell was then sealed with a rubber equipped with two carbon rods (Φ 6 mm). The reaction mixture was stirred and electrolyzed with constant current (8 mA) at room temperature. Six hours later, the solvent was evaporated under vacuum and the residue was purified by flash column chromatography to yield product **4q** as a pale yellow oil (143.1 mg, 70% yield). In addition, the excessive **2q** was recovered in 304.3 mg (0.65 mmol). (Note: the electrodes carbon rods can be used repeatedly in this electrochemical amination after simplify handling with sandpaper.)

5. The uncucessful examples



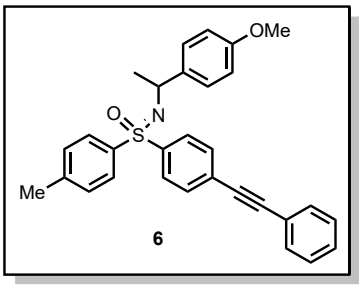
Scheme S1. The unsucessful examples

6. Products derivatization



The compound **6** were prepared according to reported method[10]: $Pd(PPh_3)_2Cl_2$ (0.02 mmol, 10 mol%), CuI (0.04 mmol, 20 mol%) were added to an oven-dried sealed tube and the vessel was evacuated and backfilled with N_2 (3-times). Then, **3g** (0.2 mmol, 1.0 equiv), **5** (0.6 mmol, 3.0 equiv), Et_3N (0.6 mmol, 3.0 equiv) and MeCN (4 mL) were added. The tube was then sealed with a Teflon lined cap. After vigorous stiring for 36 h at 120 °C, the mixture was cooled to room temperature and filtered through a plug of silica (eluted with EtOAc). The filtrate was concentrated under reduced pressure, and purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to give product **6** as a pale yellow oil (85.9 mg, 92% yield), dr~1:1.

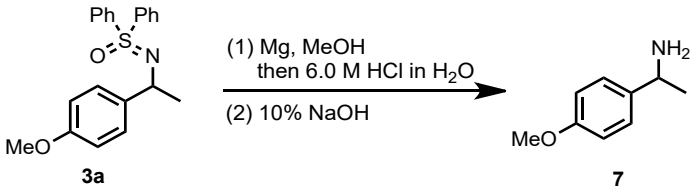
N-[1-(4-Methoxyphenyl)ethyl]-1-(4-methylphenyl)-1-oxo-1-[4-(phenylethynyl)phenyl]-λ^6-sulfanimine



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.54-7.49 (m, 6H), 7.36-7.31 (m, 10H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 6.87-6.84 (m, 4H), 4.36 (q, *J* = 6.4 Hz, 2H), 3.81 (s, 3H), 3.81 (s, 3H), 2.39 (s, 3H), 2.36 (s, 3H), 1.55-1.53 (m, 6H).

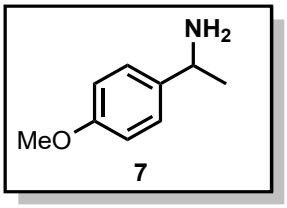
^{1}H NMR (600 MHz, $CDCl_3$) δ 158.3, 143.5, 143.4, 141.2, 140.7, 139.9, 139.9, 138.3, 137.6, 132.1, 132.1, 131.9, 131.9, 129.9, 129.9, 129.1, 129.0, 128.9, 128.6, 128.6, 128.4, 127.6, 127.5, 127.4, 122.6, 113.7, 92.6, 92.6, 88.2, 55.4, 53.8, 53.8, 28.3, 28.3, 21.6, 21.6.

HRMS (ESI) calcd. for $C_{30}H_{28}NO_2S^+$ ($[M+H]^+$): 466.1835, found: 466.1833.



The compound **7** were prepared according to reported method[11]: Under argon, **3a** (0.3 mmol, 1.0 equiv), Mg (3.0 mmol, 10.0 equiv) and anhydrous MeOH (4 mL) were mixed in a flamed flask equipped with a stir bar. The mixture was stirred at room temperature, When Mg was disappeared, the reaction mixture was cooled to 0 °C, and HCl (6.6 mmol, 22.0 equiv, 6.0 M in H_2O) was added at 0 °C. The reaction mixture was stirred at room temperature for 0.5 h. After completion (monitored by TLC), adjust the pH value to 10 with 10% aqueous NaOH solution, and the resulting mixture was extracted with CH_2Cl_2 three times. The combined organic phase was dried over anhydrous Na_2SO_4, concentrated under vacuum and purified by flash column chromatography (EtOAc/MeOH = 5:1) to afford the product **7** as a pale yellow oil (31.2 mg, 69% yield).

1-(4-Methoxyphenyl)ethanamine (**7**)

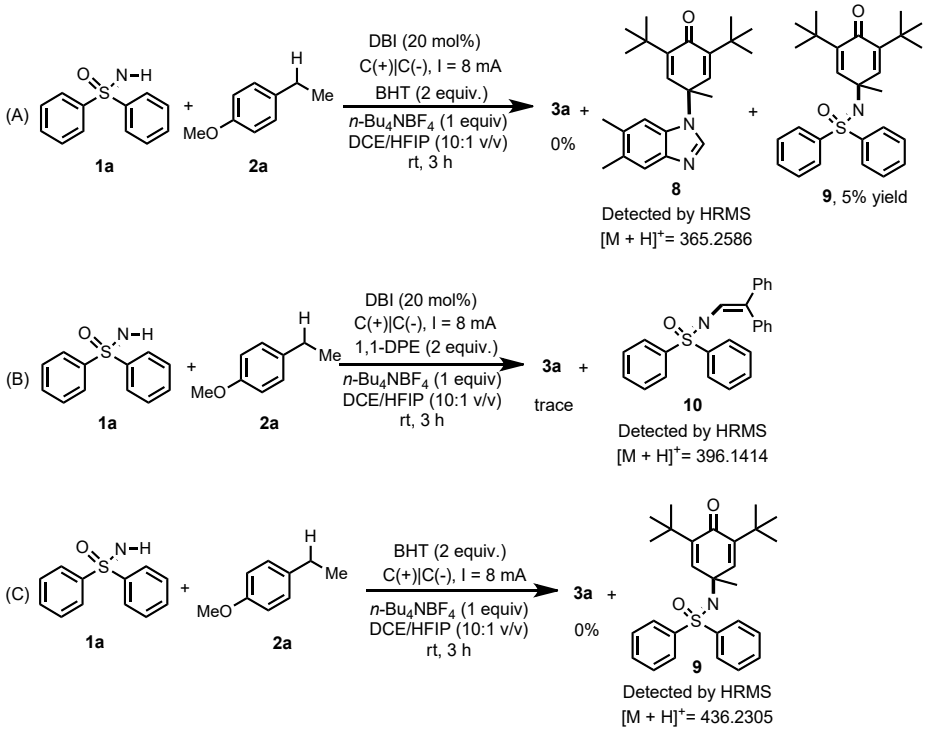


Known compound[12]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.3 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 4.09-4.08 (m, 1H), 3.80 (s, 3H), 1.90 (brs, 2H), 1.37 (d, *J* = 5.4 Hz, 3H).

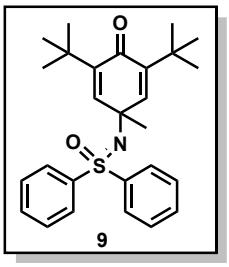
^{13}C NMR (150 MHz, $CDCl_3$) δ 158.6, 139.7, 126.9, 114.0, 55.4, 50.8, 25.7.

7. Mechanistic investigation



Scheme S2. Radical trapping experiments

(i) To an undivided cell (10 mL columnar round-bottom flask with a 24# mouth) equipped with a magnetic stir bar, sulfonimidoyldibenzene **1a** (0.3mmol, 1.0 equiv), 5,6-dimethyl-1*H*-benzo[*d*]imidazole (0.06 mmol, 20 mol%), *n*-Bu_4NBF_4 (0.3 mmol, 1 equiv), BHT (0.6 mmol, 2equiv) were added. Then, 1-ethyl-4-methoxybenzene **2a** (0.9 mmol, 3 equiv), DCE (5 mL), HFIP (0.5 mL) were added in sequence. The cell was then sealed with a rubber equipped with two carbon rods (Φ 6 mm). The reaction mixture was stirred and electrolyzed with constant current (8 mA) at room temperature for 3 hours (Scheme S2A). The reaction liquid was taken for HRMS identification analysis, and **8** and **9** were captured. Then, the reaction mixture was evaporated under reduced pressure to remove the solvent and the residue was purified by preparatory thin layer chromatography to give the BHT-adduct **9** in 5% yield (5.9 mg), which was confirmed by NMR and HRMS analysis (Figure S1-S2). No **3a** was formed.



Pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, J = 7.6 Hz, 4H), 7.46-7.43 (m, 2H), 7.40-7.38 (m, 4H), 6.74 (s, 2H), 1.51 (s, 3H), 1.05 (s, 18H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 186.2, 146.0, 143.4, 143.0, 132.3, 129.1, 128.2, 56.1, 34.4, 32.5, 29.3.

HRMS (ESI) calcd. for $C_{27}H_{34}NO_2S^+$ ($[M+H]^+$): 436.2305, found: 436.2305.

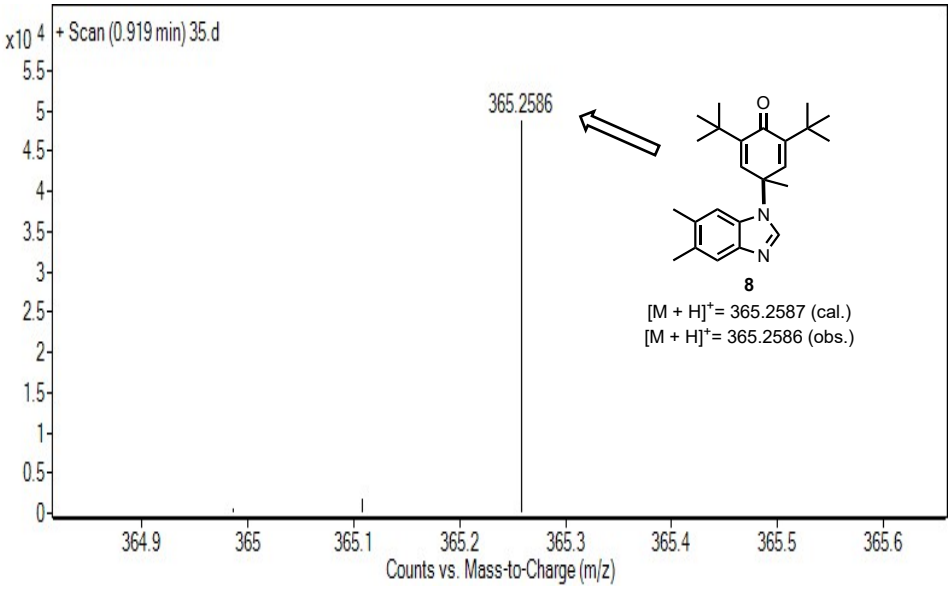


Figure S1. HRMS spectrum of **8**

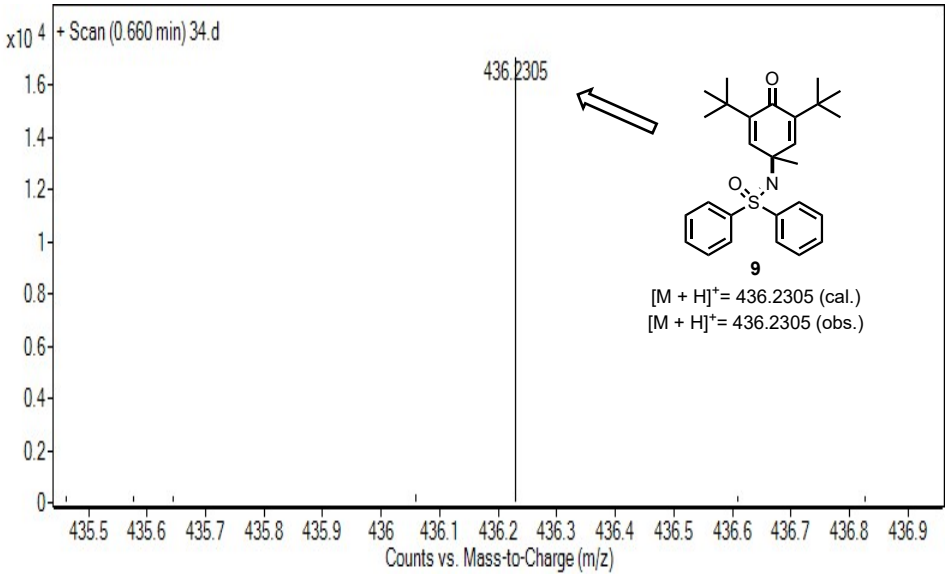


Figure S2. HRMS spectrum of BHT-adduct **9**

(ii) To an undivided cell (10 mL columnar round-bottom flask with a 24# mouth) equipped with a magnetic stir bar, sulfonimidoyldibenzene **1a** (0.3mmol, 1.0 equiv), 5,6-dimethyl-1*H*-benzo[*d*]imidazole (0.06 mmol, 20 mol%), *n*-Bu_4NBF_4 (0.3 mmol, 1 equiv), 1,1-DPE (0.6 mmol, 2 equiv) were added. Then,

1-ethyl-4-methoxybenzene **2a** (0.9 mmol, 3 equiv), DCE (5 mL), HFIP (0.5 mL) were added in sequence. The cell was then sealed with a rubber equipped with two carbon rods (Φ 6 mm). The reaction mixture was stirred and electrolyzed with constant current (8 mA) at room temperature for 3 hours (Scheme S2B). The reaction liquid was taken for HRMS identification analysis, and **10** were captured (Figure S3).

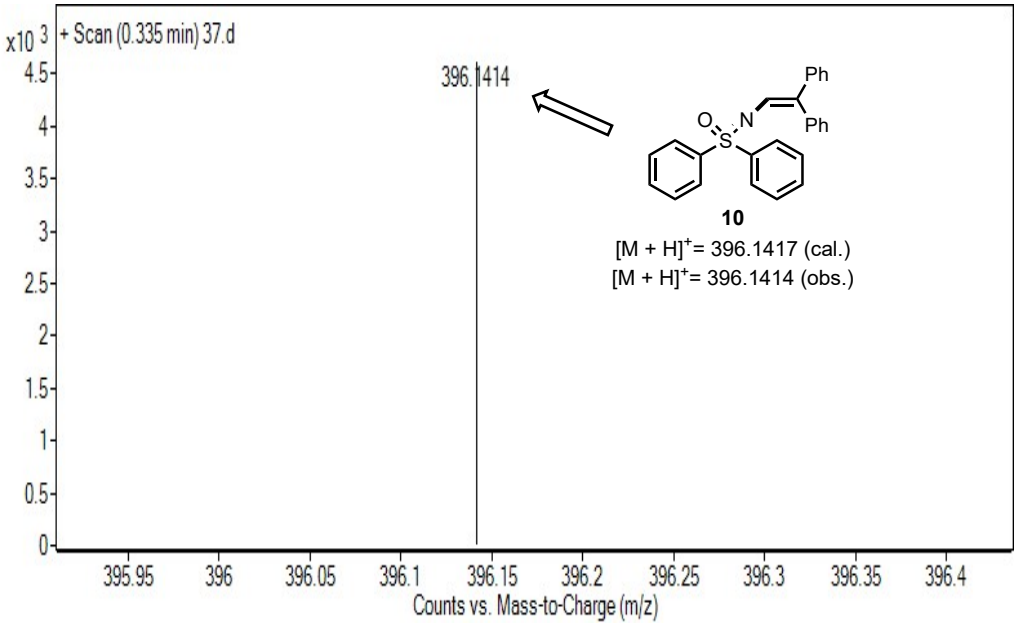


Figure S3. HRMS spectrum of **10**

(iii) To an undivided cell (10 mL columnar round-bottom flask with a 24# mouth) equipped with a magnetic stir bar, sulfonimidoyldibenzene **1a** (0.3mmol, 1.0 equiv), *n*-Bu_4NBF_4 (0.3 mmol, 1 equiv), BHT (0.6 mmol, 2equiv) were added. Then, 1-ethyl-4-methoxybenzene **2a** (0.9 mmol, 3 equiv), DCE (5 mL), HFIP (0.5 mL) were added in sequence. The cell was then sealed with a rubber equipped with two carbon rods (Φ 6 mm). The reaction mixture was stirred and electrolyzed with constant current (8 mA) at room temperature for 3 hours (Scheme S2C). The reaction liquid was taken for HRMS identification analysis, and BHT-addut **9** was captured (Figure S4). No **3a** was formed.

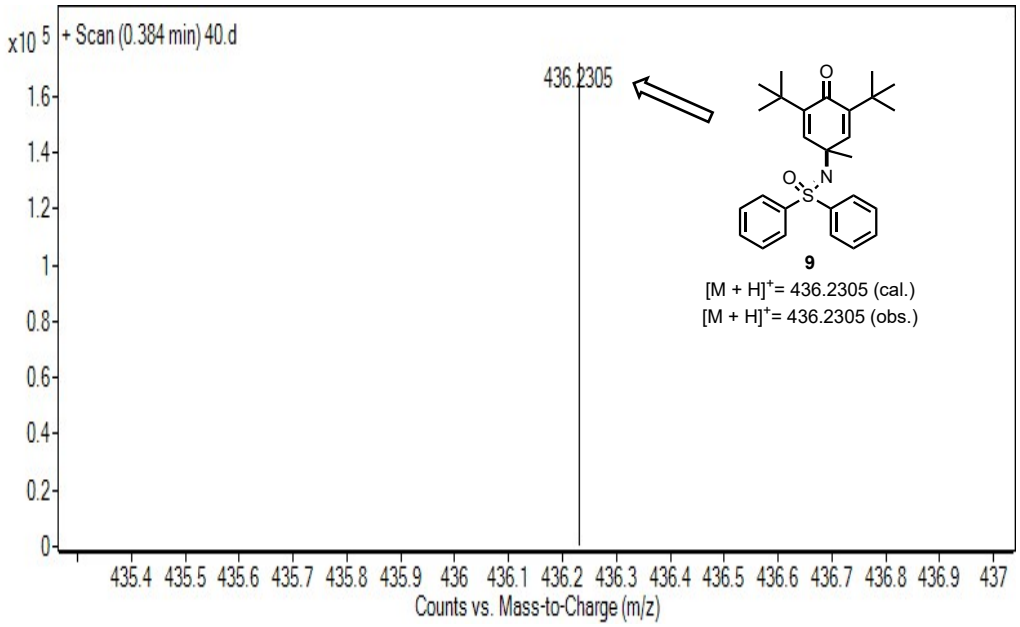
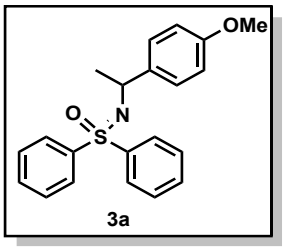


Figure S4. HRMS spectrum of **9**

8. Characterization data for the products

N-[1-(4-Methoxyphenyl)ethyl]-1-oxo-1,1-diphenyl-λ^6-sulfanimine (**3a**)



Prepared following general procedure and the reaction mixture was purified by preparatory thin layer chromatography with petroleum ether and ethylacetate (PE/EA = 5:1) to afford the product **3a** (79.8 mg, 76% yield).

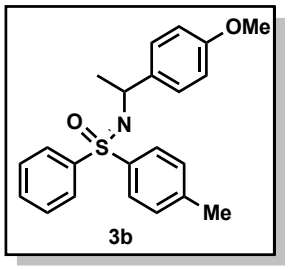
Pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05-8.03 (m, 2H), 7.84-7.82 (m, 2H), 7.52-7.44 (m, 4H), 7.39-7.37 (m, 2H), 7.34-7.32 (m, 2H), 6.86-6.84 (m, 2H), 4.36 (q, *J* = 6.6 Hz, 1H), 3.80 (s, 3H), 1.54 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.2, 141.6, 141.0, 140.0, 132.4, 132.3, 129.1, 129.0, 128.6, 127.3, 113.6, 55.4, 53.8, 28.3.

HRMS (ESI) calcd. for $C_{21}H_{22}NO_2S^+$ ($[M+H]^+$): 352.1366, found: 352.1370.

N-[1-(4-Methoxyphenyl)ethyl]-1-(4-methylphenyl)-1-oxo-1-phenyl-λ^6-sulfanimine (**3b**)



Prepared following general procedure and the reaction mixture was purified by preparatory thin layer chromatography with petroleumether and ethylacetate (PE/EA = 5:1) to afford the product **3b** (60.1 mg, 55% yield), dr~1:1.

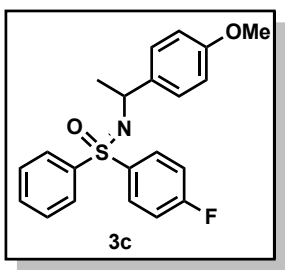
Pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.2 Hz, 2H), 7.91 (d, *J* = 8.2 Hz, 2H), 7.81 (d, *J* = 7.5 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.49-7.42 (m, 4H), 7.38-7.31 (m, 6H), 7.26-7.24 (m, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.86-6.83 (m, 4H), 4.37-7.33 (m, 2H), 3.80 (s, 3H), 3.79 (s, 3H), 2.37 (s, 3H), 2.34 (s, 3H), 1.53 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.2, 143.2, 143.1, 141.9, 141.3, 140.1, 140.0, 138.6, 137.8, 132.3, 132.2, 129.8, 129.8, 129.1, 129.1, 128.9, 128.6, 128.4, 127.3, 113.6, 55.4, 53.7, 53.7, 28.4, 28.3, 21.6, 21.5.

HRMS (ESI) calcd. for $C_{22}H_{24}NO_2S^+$ ($[M+H]^+$): 366.1522, found: 366.1521.

1-(4-Fluorophenyl)-*N*-[1-(4-methoxyphenyl)ethyl]-1-oxo-1-phenyl-λ^6-sulfanimine (**3c**)



Prepared following general procedure and the reaction mixture was purified by preparatory thin layer chromatography with petroleum ether and ethylacetate (PE/EA = 8:1) to afford the product **3c** (68.5 mg, 62% yield), dr~1:1.

Pale yellow oil.

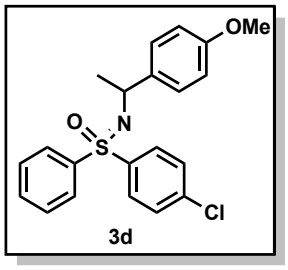
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06-8.02 (m, 4H), 7.83-7.80 (m, 4H), 7.53-7.45 (m, 4H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.32-7.31 (m, 4H), 7.13 (t, *J* = 8.6 Hz, 2H), 7.04 (t, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 4H), 4.38-4.34 (m, 2H), 3.80 (s, 6H), 1.55-1.53 (m, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 166.1, 166.0, 164.4, 164.3, 158.3, 141.5, 140.8, 139.8, 139.7, 137.6, 137.6, 137.0, 137.0, 132.6, 132.5, 131.8, 131.7, 131.3, 131.3, 129.3, 129.0, 128.4, 127.3, 116.4, 116.4, 116.3, 116.2, 113.7, 55.4, 53.9, 53.8, 28.3.

^{19}F NMR (565 MHz, $CDCl_3$) δ -106.29, -106.48.

HRMS (ESI) calcd. for $C_{21}H_{21}FNO_2S^+$ ($[M+H]^+$): 370.1272, found: 370.1268.

1-(4-Chlorophenyl)-*N*-[1-(4-methoxyphenyl)ethyl]-1-oxo-1-phenyl-λ^6-sulfanimine (**3d**)



Prepared following general procedure and the reaction mixture was purified by preparatory thin layer chromatography with petroleum ether and ethylacetate (PE/EA = 5:1) to afford the product **3d** (83.5 mg, 72% yield), dr~1:1.

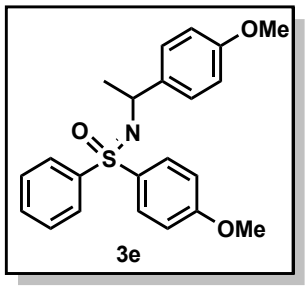
Pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03-8.01 (m, 2H), 7.97-7.95 (m, 2H), 7.82-7.80 (m, 2H), 7.74-7.71 (m, 2H), 7.53-7.46 (m, 4H), 7.44-7.38 (m, 4H), 7.34-7.29 (m, 6H), 6.86-6.83 (m, 4H), 4.38-4.34 (m, 2H), 3.80 (s, 3H), 3.80 (s, 3H), 1.54-1.52 (m, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.3, 158.3, 141.3, 140.6, 140.3, 139.7, 139.6, 139.1, 138.9, 132.7, 132.6, 130.5, 130.0, 129.4, 129.4, 129.3, 129.0, 128.5, 127.3, 113.7, 113.7, 55.4, 53.8, 53.7, 28.3, 28.2.

HRMS (ESI) calcd. for$C_{21}H_{21}ClNO_2S^+$ ([M+H]$^+$): 386.0976, found: 386.0978.

1-(4-Methoxyphenyl)-*N*-[1-(4-methoxyphenyl)ethyl]-1-oxo-1-phenyl-λ^6-sulfanimine (**3e**)



3e

Prepared following general procedure and the reaction mixture was purified by preparatory thin layer chromatography with petroleumether and ethylacetate (PE/EA = 5:1) to afford the product **3e** (78.7 mg, 69% yield), dr~1:1.

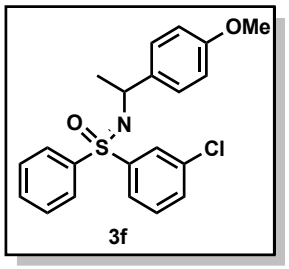
Pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03-8.01 (m, 2H), 7.98-7.95 (m, 2H), 7.81-7.79 (m, 2H), 7.76-7.74 (m, 2H), 7.49-7.41 (m, 4H), 7.38-7.31 (m, 6H), 6.95-6.92 (m, 2H), 6.87-6.83 (m, 6H), 4.38-4.32 (m, 2H), 3.81 (s, 3H), 3.80 (s, 3H), 3.79 (s, 3H), 3.79 (s, 3H), 1.54-1.53 (m, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) 162.9, 162.8, 158.2, 142.2, 141.5, 140.1, 140.0, 133.0, 132.2, 132.0, 131.1, 130.7, 129.0, 128.7, 128.2, 127.3, 127.3, 114.4, 114.4, 113.6, 113.6, 55.7, 55.6, 55.3, 53.7, 53.7, 28.4, 28.3.

HRMS (ESI) calcd. for $C_{22}H_{24}NO_3S^+$ ([M+H]$^+$): 382.1471, found: 382.1474.

1-(3-Chlorophenyl)-*N*-[1-(4-methoxyphenyl)ethyl]-1-oxo-1-phenyl-λ^6-sulfanimine (**3f**)



3f

Prepared following general procedure and the reaction mixture was purified by preparatory thin layer chromatography with petroleumether and ethylacetate (PE/EA = 5:1) to afford the product **3f** (59.0 mg, 51% yield), dr~1:1.

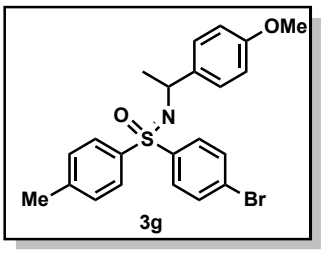
Pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04-8.01 (m, 3H), 7.90-7.88 (m, 1H), 7.84-7.82 (m, 2H), 7.77 (t, *J* = 1.8 Hz, 1H), 7.65-7.64 (m, 1H), 7.54-7.46 (m, 5H), 7.42-7.38 (m, 4H), 7.32-7.27 (m, 5H), 6.86-6.82 (m, 4H), 4.39-4.35 (m, 2H), 3.80 (s, 3H), 3.80 (s, 3H), 1.55 (d, *J* = 6.6 Hz, 3H), 1.53 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.3, 158.3, 143.6, 143.1, 141.0, 140.4, 139.6, 139.5, 135.3, 135.2, 132.8, 132.7, 132.6, 132.4, 130.4, 130.3, 129.3, 129.1, 129.1, 128.6, 127.3, 127.3, 127.0, 126.7, 113.7, 55.4, 53.8, 53.8, 28.2, 28.1.

HRMS (EI) calcd. for $C_{21}H_{21}ClNO_2S^+$ ($M+H^+$): 386.0976, found: 386.0975.

1-(4-Bromophenyl)-*N*-[1-(4-methoxyphenyl)ethyl]-1-(4-methylphenyl)-1-oxo-λ^6-sulfanimine (**3g**)



Prepared following general procedure and the reaction mixture was purified by preparatory thin layer chromatography with petroleum ether and ethylacetate (PE/EA = 5:1) to afford the product **3g** (75.9 mg, 57% yield), dr~1:1.

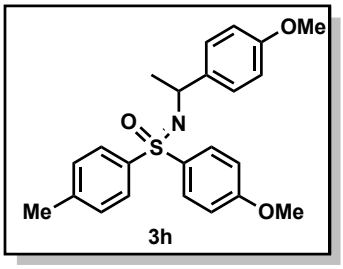
Pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90-7.86 (m, 4H), 7.69-7.68 (m, 2H), 7.65-7.62 (m, 2H), 7.59-7.56 (m, 2H), 7.49-7.47 (m, 2H), 7.33-7.26 (m, 6H), 7.19 (d, *J* = 8.1 Hz, 2H), 6.86-6.82 (m, 4H), 4.34 (q, *J* = 6.6 Hz, 2H), 3.80 (s, 3H), 3.80 (s, 3H), 2.38 (s, 3H), 2.35 (s, 3H), 1.53 (d, *J* = 6.7 Hz, 3H), 1.52 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.3, 158.3, 143.5, 143.5, 141.2, 140.6, 139.8, 139.7, 138.2, 137.4, 132.3, 132.3, 130.5, 130.0, 130.0, 129.9, 129.1, 128.5, 127.4, 127.3, 127.3, 113.7, 55.4, 53.8, 53.7, 28.3, 21.6, 21.6.

HRMS (ESI) calcd. for $C_{22}H_{23}BrNO_2S^+$ ([M+H]$^+$): 444.0627, found: 444.0627.

1-(4-Methoxyphenyl)-*N*-[1-(4-methoxyphenyl)ethyl]-1-(4-methylphenyl)-1-oxo-λ^6-sulfanimine (**3h**)



3h

Prepared following general procedure and the reaction mixture was purified by preparatory thin layer chromatography with petroleum ether and ethylacetate (PE/EA = 5:1) to afford the product **3h** (73.9 mg, 62% yield), dr~1:1.

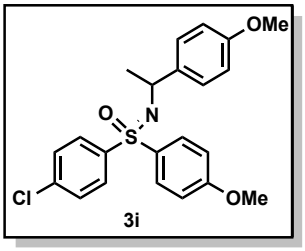
Pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.8 Hz, 2H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.7 Hz, 2H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.35-7.33 (m, 4H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.86-6.84 (m, 6H), 4.36-4.32 (m, 2H), 3.81 (s, 3H), 3.80 (s, 6H), 3.79 (s, 3H), 2.36 (s, 3H), 2.34 (s, 3H), 1.52 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 162.8, 162.7, 158.2, 142.9, 142.8, 140.2, 140.2, 139.2, 138.4, 133.4, 132.6, 131.0, 130.5, 129.8, 129.7, 128.8, 128.3, 127.3, 127.3, 114.3, 114.3, 113.6, 55.7, 55.6, 55.4, 53.7, 53.7, 28.4, 28.4, 21.5, 21.5.

HRMS (ESI) calcd. for $C_{23}H_{26}NO_3S^+$ ([M+H]$^+$): 396.1628, found: 396.1629.

1-(4-Chlorophenyl)-1-(4-methoxyphenyl)-*N*-[1-(4-methoxyphenyl)ethyl]-1-oxo-λ^6-sulfanimine (**3i**)



Prepared following general procedure and the reaction mixture was purified by preparatory thin layer chromatography with petroleum ether and ethylacetate (PE/EA = 5:1) to afford the product **3i** (83.8 mg, 67% yield), dr~1:1.

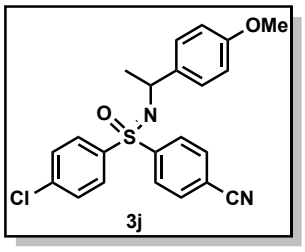
Pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95-7.92 (m, 4H), 7.73-7.69 (m, 4H), 7.42-7.40 (m, 2H), 7.33-7.29 (m, 6H), 6.95-6.93 (m, 2H), 6.87-6.83 (m, 6H), 4.36-4.31 (m, 2H), 3.82 (s, 3H), 3.81-3.79 (m, 9H), 1.53 (d, J = 6.8 Hz, 3H), 1.51 (d, J = 6.8 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 163.1, 163.0, 158.3, 140.9, 140.2, 139.9, 139.8, 138.7, 138.6, 132.6, 131.8, 131.1, 130.6, 130.2, 129.8, 129.3, 129.3, 127.3, 127.3, 114.5, 114.5, 113.7, 55.7, 55.7, 55.4, 53.7, 53.7, 28.3, 28.3.

HRMS (ESI) calcd. for $C_{22}H_{23}ClNO_3S^+$ ($[M+H]^+$): 416.1082, found: 416.1085.

4-[(4-Chlorophenyl){[1-(4-methoxyphenyl)ethyl]azanylidene}(oxo)-λ^6-sulfanyl]benzene-1-carbonitrile (**3j**)



Prepared following general procedure and the reaction mixture was purified by preparatory thin layer chromatography with petroleum ether and ethylacetate (PE/EA = 5:1) to afford the product **3j** (68.5 mg, 56% yield), dr~1:1.

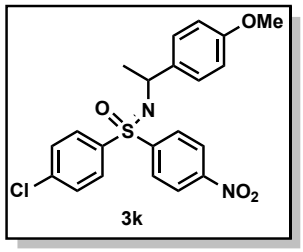
Pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11-8.10 (m, 2H), 7.96-7.94 (m, 2H), 7.85-7.84 (m, 2H), 7.76-7.75 (m, 2H), 7.72-7.70 (m, 2H), 7.64-7.63 (m, 2H), 7.47-7.45 (m, 2H), 7.38-7.36 (m, 2H), 7.28-7.25 (m, 2H), 7.24-7.22 (m, 2H), 6.85-6.79 (m, 4H), 4.38-4.33 (m, 2H), 3.80 (s, 3H), 3.79 (s, 3H), 1.54-1.51 (m, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.5, 146.0, 145.8, 140.0, 139.8, 139.0, 138.9, 138.9, 138.5, 133.0, 132.9, 130.7, 130.1, 129.7, 129.7, 129.5, 129.1, 127.3, 117.5, 116.3, 116.1, 113.8, 113.8, 55.4, 53.9, 53.8, 28.1, 28.0.

HRMS (ESI) calcd. for $C_{22}H_{20}ClN_2O_2S^+$ ($[M+H]^+$): 411.0929, found: 411.0930.

1-(4-Chlorophenyl)-*N*-[1-(4-methoxyphenyl)ethyl]-1-(4-nitrophenyl)-1-oxo-λ^6-sulfanimine (**3k**)



3k

Prepared following general procedure and the reaction mixture was purified by preparatory thin layer chromatography with petroleum ether and ethylacetate (PE/EA = 4:1) to afford the product **3k** (57.3 mg, 44% yield), dr~1:1.

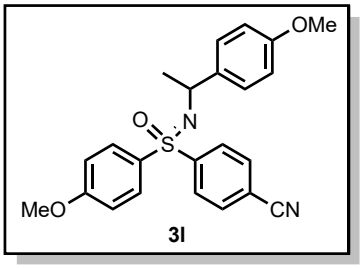
Pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31-8.28 (m, 2H), 8.18-8.16 (m, 4H), 7.98-7.96 (m, 2H), 7.92-7.89 (m, 2H), 7.75-7.72 (m, 2H), 7.48-7.46 (m, 2H), 7.39-7.37 (m, 2H), 7.29-7.27 (m, 2H), 7.24-7.22 (m, 2H), 6.85-6.83 (m, 2H), 6.81-6.79 (m, 2H), 4.40-4.36 (m, 2H), 3.80 (s, 3H), 3.78 (s, 3H), 1.54 (d, J = 6.6 Hz, 3H), 1.53 (d, J = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.6, 158.5, 150.2, 150.0, 147.5, 147.4, 140.1, 139.9, 138.9, 138.8, 138.8, 138.4, 130.7, 130.2, 130.1, 129.8, 129.8, 129.7, 127.3, 124.4, 124.3, 113.8, 113.8, 55.4, 55.4, 54.0, 53.9, 28.1, 28.0.

HRMS (ESI) calcd. for $C_{21}H_{19}ClN_2NaO_4S^+$ ($[M+Na]^+$): 453.0646, found: 453.0650.

4-[(4-Methoxyphenyl){[1-(4-methoxyphenyl)ethyl]azanylidene}(oxo)-λ^6-sulfanyl]benzene-1-carbonitrile (**3l**)



3l

Prepared following general procedure and the reaction mixture was purified by preparatory thin layer chromatography with petroleumether and ethylacetate (PE/EA = 2:1) to afford the product **3l** (63.5 mg, 52% yield), dr~1:1.

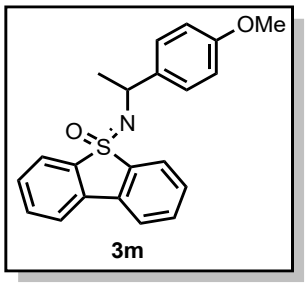
Pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10-8.09 (m, 2H), 7.96-7.93 (m, 2H), 7.84-7.83 (m, 2H), 7.74-7.72 (m, 4H), 7.61-7.60 (m, 2H), 7.32-7.29 (m, 2H), 7.25-7.23 (m, 2H), 6.97-6.95 (m, 2H), 6.90-6.84 (m, 4H), 6.82-6.79 (m, 2H), 4.38-4.31 (m, 2H), 3.83 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H), 3.79 (s, 3H), 1.53 (d, J = 6.6 Hz, 3H), 1.51 (d, J = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 163.5, 163.4, 158.4, 147.0, 146.7, 139.5, 139.3, 132.8, 132.7, 131.5, 131.4, 130.9, 130.8, 129.3, 128.9, 127.3, 127.3, 117.7, 115.8, 115.5, 114.8, 114.7, 113.7, 113.7, 55.8, 55.8, 55.4, 53.8, 53.7, 28.2.

HRMS (ESI) calcd. for $C_{23}H_{23}N_2O_3S^+$ ($[M+H]^+$): 407.1424, found: 407.1425.

5-{[1-(4-Methoxyphenyl)ethyl]azanylidene}-5λ^6-dibenzo[1,2-*b*:1',2'-*d*]thiophen-5-one (**3m**)



3m

Prepared following general procedure and the reaction mixture was purified by preparatory thin layer chromatography with petroleumether and ethylacetate (PE/EA = 2:1) to afford the product **3m** (66.5 mg, 63% yield).

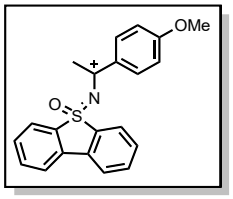
Pale yellow solid.

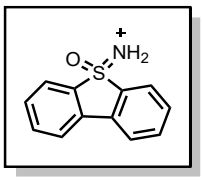
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72-7.68 (m, 3H), 7.56-7.47 (m, 2H), 7.43-7.39 (m, 1H), 7.29-7.27 (m, 1H), 7.20-7.16 (m, 3H), 6.76-6.73 (m, 2H), 4.72-4.69 (m, 1H), 3.76 (s, 3H), 1.53 (d, J = 6.7 Hz, 3H).

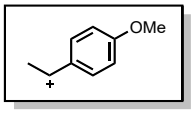
^{13}C NMR (150 MHz, $CDCl_3$) δ 158.6, 139.8, 139.4, 138.8, 133.2, 132.6, 132.4, 131.8, 130.1, 129.9, 127.6, 123.0, 122.8, 121.4, 113.8, 55.4, 53.8, 27.6.

HRMS (EI) calcd. for $C_{21}H_{20}NO_2S^+$ ($M+H^+$): 350.1209, found: 350.1211.

TOF-SIMS These peaks can be obtained and possible structures of the segments we speculated are listed bellow:







$C_{21}H_{18}NSO_2^+$ ([M-H]$^+$): 348.150 $C_{12}H_{10}NSO^+$: 216.080 $C_9H_{11}O^+$: 135.119

Instrument: **PHI nanoTOF II Time-of-Flight SIMS**	
Acquisition phase	
Ion species	**Bi_3^{++}**
Energy	**30 keV**
Ion current	**2 nA**
Raster size	**100 µm x 100 µm**
Mass range	**2 - 1,850 u**
Mode	**High mass resolution mode**

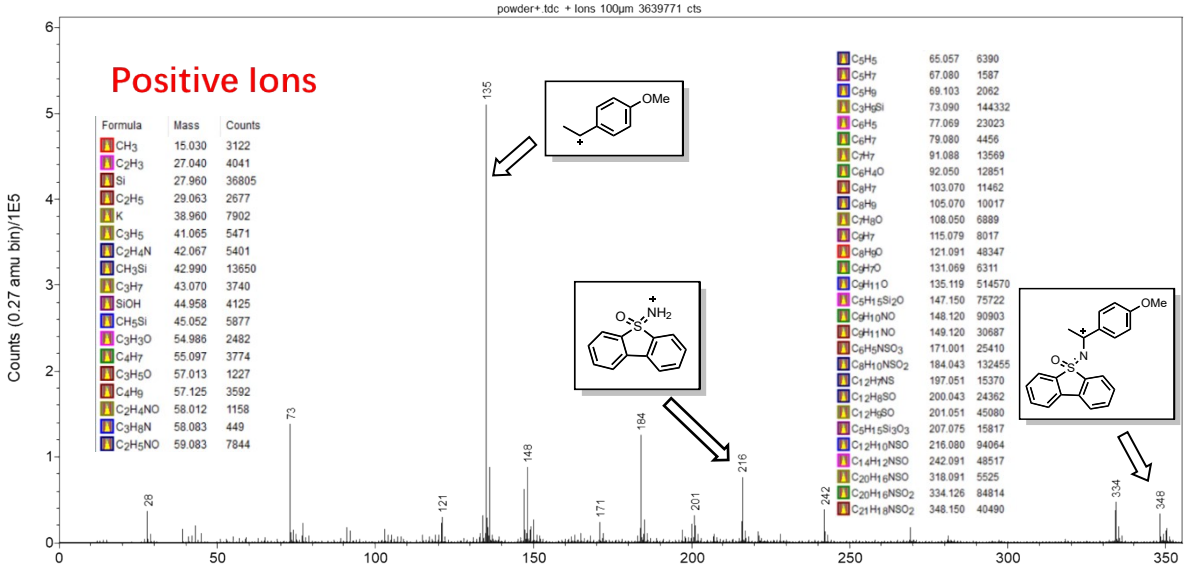
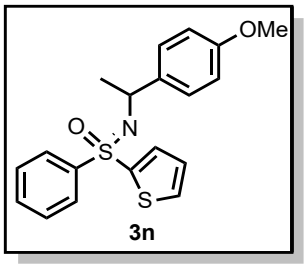


Figure S5. TOF-SIMS spectrum of **3m**

N-[1-(4-methoxyphenyl)ethyl]-1-oxo-1-phenyl-1-(thiophen-2-yl)-λ⁶-sulfanimine (**3n**)



Prepared following general procedure and the reaction mixture was purified by preparatory thin layer chromatography with petroleumether and ethylacetate (PE/EA = 5:1) to afford the product **3n** (81.2 mg, 76% yield), dr~1:1.

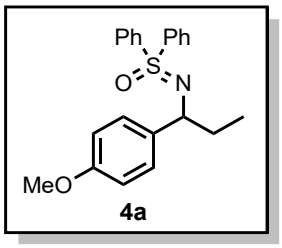
Pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12-8.10 (m, 2H), 7.95-7.94 (m, 2H), 7.59-7.58 (m, 2H), 7.53-7.47 (m, 5H), 7.43-7.41 (m, 2H), 7.38-7.33 (m, 4H), 7.31 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.04 (dd, *J* = 4.9, 3.9 Hz, 1H), 6.94 (dd, *J* = 4.9, 3.8 Hz, 1H), 6.89-6.83 (m, 4H), 4.57 (q, *J* = 6.6 Hz, 1H), 4.44 (q, *J* = 6.6 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 1.57 (d, *J* = 6.6 Hz, 3H), 1.55 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.2, 158.2, 143.7, 143.0, 142.2, 141.4, 139.8, 139.5, 133.7, 133.5, 133.3, 132.6, 132.5, 129.1, 128.5, 128.0, 128.0, 127.9, 127.3, 113.6, 113.6, 55.3, 55.3, 53.9, 53.9, 28.4, 28.0.

HRMS (ESI) calcd. for $C_{19}H_{20}NO_2S_2^+$ ([M+H]$^+$): 358.0930, found: 358.0931.

N-[1-(4-Methoxyphenyl)propyl]-1-oxo-1,1-diphenyl-λ^6-sulfanimine (**4a**)



4a

Prepared following general procedure and the reaction mixture was purified by preparatory thin layer chromatography with petroleum ether and ethylacetate (PE/EA = 4:1) to afford the product **4a** (79.7 mg, 73% yield).

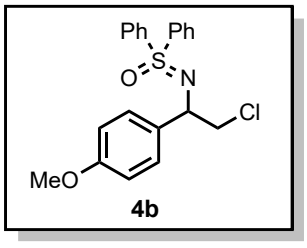
Pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02-8.00 (m, 2H), 7.77 (dd, *J* = 8.2, 0.9 Hz, 2H), 7.50-7.41 (m, 4H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.23-7.21 (m, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 4.03 (t, *J* = 6.7 Hz, 1H), 3.80 (s, 3H), 1.94-1.87 (m, 1H), 1.84-1.77 (m, 1H), 0.89 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.2, 141.5, 141.1, 138.6, 132.4, 132.3, 129.1, 129.1, 129.0, 128.6, 127.9, 113.5, 60.1, 55.3, 34.5, 11.1.

HRMS (ESI) calcd. for $C_{22}H_{24}NO_2S^+$ ([M+H]$^+$): 366.1522, found: 366.1525.

N-[2-Chloro-1-(4-methoxyphenyl)ethyl]-1-oxo-1,1-diphenyl-λ^6-sulfanimine (**4b**)



4b

Prepared following general procedure and the reaction mixture was purified by preparatory thin layer chromatography with petroleumether and ethylacetate (PE/EA = 2:1) to afford the product **4b** (74.3 mg, 64% yield).

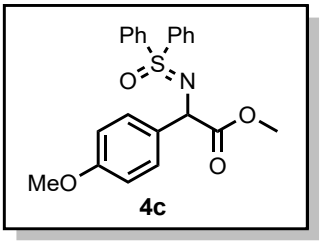
Pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.5 Hz, 2H), 7.89 (d, *J* = 7.6 Hz, 2H), 7.53-7.39 (m, 4H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 4.31 (t, *J* = 6.9 Hz, 1H), 3.87 (dd, *J* = 10.6, 7.0 Hz, 1H), 3.80 (s, 3H), 3.70 (dd, *J* = 10.7, 6.8 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.0, 140.8, 140.4, 134.9, 132.7, 129.2, 129.2, 129.0, 128.8, 128.4, 113.8, 59.9, 55.3, 51.6.

HRMS (EI) calcd. for $C_{21}H_{21}ClNO_2S^+$ ($M+H^+$): 386.0976, found: 386.0974.

Methyl 2-(4-methoxyphenyl)-2-[(oxodiphenyl-λ^6-sulfanylidene)amino]acetate (**4c)**



4c

Prepared following general procedure and the reaction mixture was purified by preparatory thin layer chromatography with petroleumether and ethylacetate (PE/EA = 5:1) to afford the product **4c** (64.4 mg, 54% yield).

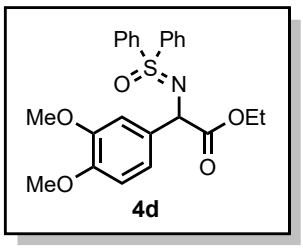
Pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.4 Hz, 2H), 7.91 (d, *J* = 7.6 Hz, 2H), 7.53-7.40 (m, 8H), 6.85 (d, *J* = 8.6 Hz, 2H), 4.89 (s, 1H), 3.78 (s, 3H), 3.64 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 173.3, 159.2, 140.6, 140.3, 132.8, 132.7, 132.2, 129.2, 129.2, 128.8, 128.7, 128.5, 113.9, 60.2, 55.3, 52.4.

HRMS (ESI) calcd. for $C_{22}H_{22}NO_4S^+$ ($[M+H]^+$): 396.1264, found: 396.1266.

Ethyl 2-(3,4-dimethoxyphenyl)-2-[(oxodiphenyl-λ^6-sulfanylidene)amino]acetate (**4d**)



4d

Prepared following general procedure and the reaction mixture was purified by preparatory thin layer chromatography with petroleumether and ethylacetate (PE/EA = 2:1) to afford the product **4d** (88.2 mg, 67% yield).

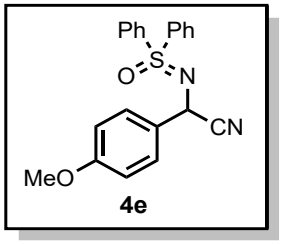
Pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.5 Hz, 2H), 7.93 (d, *J* = 7.6 Hz, 2H), 7.53-7.46 (m, 4H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.10 (d, *J* = 1.8 Hz, 1H), 7.00 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.79 (d, *J* = 8.3 Hz, 1H), 4.86 (s, 1H), 4.15-4.10 (m, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 172.7, 148.9, 148.6, 140.7, 140.5, 132.8, 132.7, 132.7, 129.3, 129.2, 128.9, 128.8, 119.7, 110.9, 110.7, 61.2, 60.7, 56.0, 56.0, 14.2.

HRMS (EI) calcd. for $C_{24}H_{26}NO_5S^+$ ($M+H^+$):440.1526, found: 440.1524.

2-(4-Methoxyphenyl)-2-[(oxodiphenyl-λ^6-sulfanylidene)amino]acetonitrile (**4e**)



4e

Prepared following general procedure and the reaction mixture was purified by preparatory thin layer chromatography with petroleumether and ethylacetate (PE/EA = 4:1) to afford the product **4e** (59.0 mg, 54% yield).

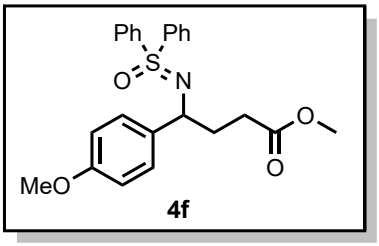
Pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, J = 7.9 Hz, 2H), 7.99 (d, *J* = 8.1 Hz, 2H), 7.60-7.53 (m, 4H), 7.49-7.46 (m, 4H), 6.89 (d, *J* = 8.4 Hz, 2H), 5.21 (s, 1H), 3.79 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.8, 139.8, 139.7, 133.4, 133.2, 129.6, 129.4, 129.3, 128.8, 128.4, 128.4, 120.1, 114.3, 55.4, 47.8.

HRMS (EI) calcd. for $C_{21}H_{19}N_2O_2S^+$ ($M+H^+$): 363.1162, found: 363.1158.

Methyl 4-(4-methoxyphenyl)-4-[(oxodiphenyl-λ^6-sulfanylidene)amino]butanoate (**4f**)



4f

Prepared following general procedure and the reaction mixture was purified by preparatory thin layer chromatography with petroleumether and ethylacetate (PE/EA = 3:2) to afford the product **4f** (72.1 mg, 57% yield).

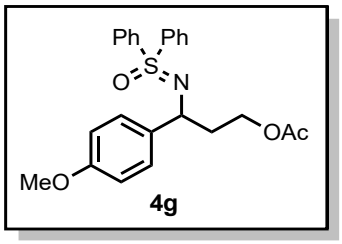
Pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.5 Hz, 2H), 7.75 (d, *J* = 7.7 Hz, 2H), 7.51-7.41 (m, 4H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 4.19 (t, *J* = 6.4 Hz, 1H), 3.79 (s, 3H), 3.59 (s, 3H), 2.51-2.41 (m, 2H), 2.17-2.07 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 174.5, 158.4, 141.3, 141.0, 137.8, 132.5, 132.3, 129.1, 129.0, 128.6, 127.8, 113.6, 57.4, 55.4, 51.5, 36.2, 31.0.

HRMS (EI) calcd. for $C_{24}H_{26}NO_4S^+$ ($M+H^+$): 424.1577, found: 424.1574.

3-(4-Methoxyphenyl)-3-[(oxodiphenyl-λ^6-sulfanylidene)amino]propyl acetate (**4g**)



4g

Prepared following general procedure and the reaction mixture was purified by preparatory thin layer chromatography with petroleumether and ethylacetate (PE/EA = 2:1) to afford the product **4g** (77.3 mg, 61% yield).

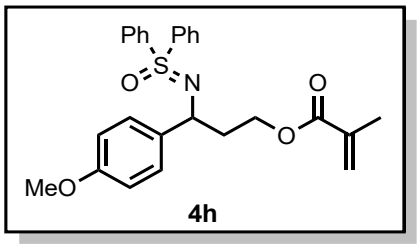
Pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.78 (d, *J* = 7.7 Hz, 2H), 7.49-7.42 (m, 4H), 7.35(t, *J* = 7.5 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 4.31-4.24 (m, 2H), 4.12-4.08 (m, 1H), 3.78 (s, 3H), 2.21-2.15 (m, 1H), 2.10-2.04 (m, 1H), 1.95 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 171.2, 158.4, 141.1, 140.9, 137.8, 132.4, 132.4, 129.1, 129.0, 128.9, 128.5, 127.7, 113.7, 62.3, 55.3, 55.1, 39.9, 21.1.

HRMS (EI) calcd. for $C_{24}H_{26}NO_4S^+$ ($M+H^+$): 424.1577, found: 424.1578.

3-(4-Methoxyphenyl)-3-[(oxodiphenyl-λ^6-sulfanylidene)amino]propyl 2-methylprop-2-enoate (**4h**)



4h

Prepared following general procedure and the reaction mixture was purified by preparatory thin layer chromatography with petroleumether and ethylacetate (PE/EA = 5:1) to afford the product **4h** (73.8 mg, 55% yield).

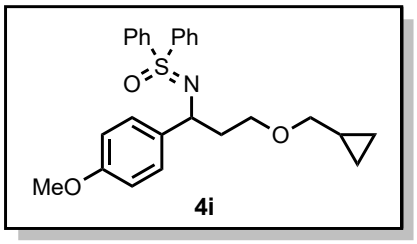
Pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.5 Hz, 2H), 7.80 (d, *J* = 7.6 Hz, 2H), 7.50-7.43 (m, 4H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 5.96 (s, 1H), 5.46 (s, 1H), 4.38-4.34 (m, 1H), 4.28-4.26 (m, 1H), 4.19-4.15 (m, 1H), 3.79 (s, 3H), 2.27-2.21 (m, 1H), 2.15-2.09 (m, 1H), 1.85 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 167.5, 158.5, 141.1, 140.9, 137.9, 136.6, 132.4, 132.4, 129.1, 129.0, 129.0, 128.6, 127.8, 125.2, 113.7,62.4, 55.4, 55.3, 40.1, 18.4.

HRMS (EI) calcd. for $C_{26}H_{28}NO_4S^+$ ($M+H^+$):450.1734, found: 450.1737.

N-{3-[(Cyclopropylmethyl)oxy]-1-(4-methoxyphenyl)propyl}-1-oxo-1,1-diphenyl-λ^6-sulfanimine (**4i**)



4i

Prepared following general procedure and the reaction mixture was purified by preparatory thin layer chromatography with petroleumether and ethylacetate (PE/EA = 3:2) to afford the product **4i** (69.3 mg, 53% yield).

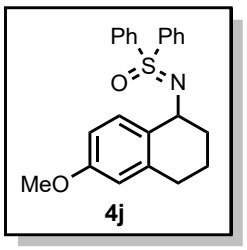
Pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.75 (d, *J* = 7.7 Hz, 2H), 7.50-7.41 (m, 4H), 7.35-7.32 (m, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 4.32-4.30 (m, 1H), 3.79 (s, 3H), 3.67-3.62 (m, 1H), 3.49-3.45 (m, 1H), 3.29-3.26 (m, 1H), 3.24-3.21 (m, 1H), 2.17-2.12 (m, 1H), 2.04-1.98 (m, 1H), 1.05- 0.98 (m, 1H), 0.49-0.47 (m, 2H), 0.19-0.15 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.2, 141.4, 141.1, 138.6, 132.4, 132.3, 129.1, 129.1, 129.0, 128.7, 127.8, 113.6, 75.5, 67.8, 55.4, 55.3, 41.2, 10.8, 3.2, 3.0.

HRMS (EI) calcd. for $C_{26}H_{30}NO_3S^+$ ($M+H^+$): 436.1941, found: 436.1942.

(6-methoxy-1,2,3,4-tetrahydro-1-naphthyl)(oxodiphenyl-λ^6-sulfanylidene)amine (**4j**)



4j

Prepared following general procedure and the reaction mixture was purified by preparatory thin layer chromatography with petroleumether and ethylacetate (PE/EA = 5:1) to afford the product **4j** (80.5 mg, 71% yield).

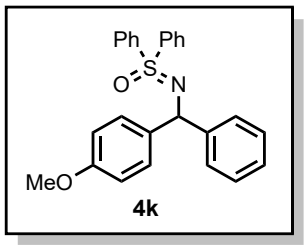
Pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 2H), 8.03-8.02 (m, 2H), 7.55-7.45 (m, 7H), 6.77 (d, *J* = 8.5 Hz, 1H), 6.58 (s, 1H), 4.31-4.29 (m, 1H), 3.77 (s, 3H), 2.86-2.81 (m, 1H), 2.71-2.66 (m, 1H), 2.09-2.02 (m, 2H), 1.99-1.93 (m, 1H), 1.72-1.65 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.1, 141.9, 141.0, 138.4, 132.9, 132.4, 132.4, 130.1, 129.2, 129.1, 128.8, 128.7, 113.2, 112.2, 55.3, 52.7, 34.2, 29.8, 20.6.

HRMS (ESI) calcd. for $C_{23}H_{23}NNaO_2S^+$ ($[M+Na]^+$): 400.1342, found: 400.1338.

N-[(4-Methoxyphenyl)phenylmethyl]-1-oxo-1,1-diphenyl-λ^6-sulfanimine (**4k**)



4k

Prepared following general procedure and the reaction mixture was purified by preparatory thin layer chromatography with petroleumether and ethylacetate (PE/EA = 5:1) to afford the product **4k** (91.6 mg, 74% yield).

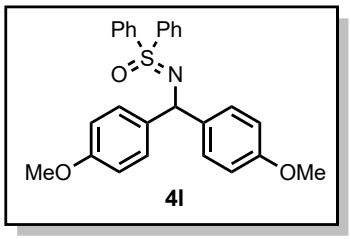
Pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (t, *J* = 7.1 Hz, 4H), 7.47-7.45 (m, 2H), 7.41-7.38 (m, 6H), 7.29-7.24 (m, 4H), 7.16 (t, *J* = 7.3 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 2H), 5.37 (s, 1H), 3.75 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.3, 146.2, 141.2, 141.1, 138.3, 132.4, 129.1, 129.1, 128.9, 128.6, 128.2, 127.5, 126.5, 113.6, 61.3, 55.3.

HRMS (EI) calcd. for $C_{26}H_{23}NNaO_2S^+$ ($M+Na^+$): 436.1342, found: 436.1345.

N-[bis(4-methoxyphenyl)methyl]-1-oxo-1,1-diphenyl-λ^6-sulfanimine (**4l**)



4l

Prepared following general procedure and the reaction mixture was purified by preparatory thin layer chromatography with petroleumether and ethylacetate (PE/EA = 2:1) to afford the product **4l** (69.1 mg, 52% yield).

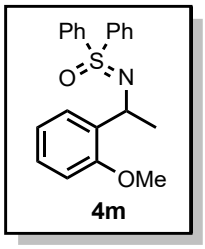
White solid.

Known compound[13]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.5 Hz, 4H), 7.54-7.40 (m, 6H), 7.29 (d, *J* = 8.6 Hz, 4H), 6.80 (d, *J* = 8.6 Hz, 4H), 5.35 (s, 1H), 3.77 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.2, 141.2, 138.6, 132.4, 129.1, 128.9, 128.5, 113.6, 60.7, 55.3.

N-[1-(2-Methoxyphenyl)ethyl]-1-oxo-1,1-diphenyl-λ^6-sulfanimine (**4m**)



4m

Prepared following general procedure and the reaction mixture was purified by preparatory thin layer chromatography with petroleumether and ethylacetate (PE/EA = 5:1) to afford the product **4m** (69.2 mg, 66% yield).

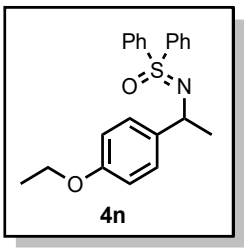
Pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) 8.06-8.05 (m, 2H), 7.91-7.89 (m, 1H), 7.81-7.80 (m, 2H), 7.50-7.41 (m, 4H), 7.36-7.34 (m, 2H), 7.20-7.17 (m, 1H), 7.04-7.02 (m, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 4.84 (q, *J* = 6.5 Hz, 1H), 3.62 (s, 3H), 1.50 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) 155.6, 141.9, 141.3, 136.2, 132.4, 132.2, 129.1, 129.0, 129.0, 128.6, 127.4, 127.3, 120.9, 110.2, 55.3, 47.6, 26.9.

HRMS (ESI) calcd. for $C_{21}H_{22}NO_2S^+$ ([M+H]$^+$): 352.1366, found: 352.1366.

N-[1-(4-Ethoxyphenyl)ethyl]-1-oxo-1,1-diphenyl-λ^6-sulfanimine (**4n**)



4n

Prepared following general procedure and the reaction mixture was purified by preparatory thin layer chromatography with petroleumether and ethylacetate (PE/EA = 5:1) to afford the product **4n** (74.7 mg, 68% yield).

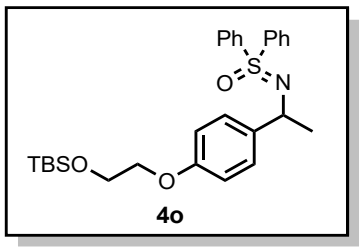
Pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.5 Hz, 2H), 7.83 (d, *J* = 7.8 Hz, 2H), 7.51-7.43 (m, 4H), 7.38(t, *J* = 7.7 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 4.36 (q, *J* = 6.5 Hz, 1H), 4.03 (q, *J* = 7.0 Hz, 2H), 1.54 (d, *J* = 6.6 Hz, 3H), 1.41 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 157.6, 141.6, 141.0, 139.8, 132.4, 132.3, 129.1, 129.0, 128.5, 127.3, 114.2, 63.5, 53.7, 28.3, 15.1.

HRMS (ESI) calcd. for $C_{22}H_{24}NO_2S^+$ ([M+H]$^+$): 366.1522, found: 366.1526.

1-oxo-1,1-Diphenyl-*N*-(1-{4-[(4,4,5,5-tetramethyl-3-oxa-4-silahex-1-yl)oxy]phenyl}ethyl)-λ^6-sulfanimine (**4o**)



Prepared following general procedure and the reaction mixture was purified by preparatory thin layer chromatography with petroleumether and ethylacetate (PE/EA = 10:1) to afford the product **4o** (94.0 mg, 63% yield).

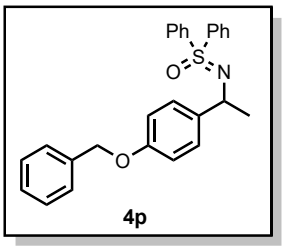
Pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05-8.03 (m, 2H), 7.83-7.82 (m, 2H), 7.51-7.44 (m, 4H), 7.39-7.36 (m, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 4.36 (q, *J* = 6.6 Hz, 1H), 4.03 (t, *J* = 5.3 Hz, 2H), 3.97 (t, *J* = 5.1 Hz, 2H), 1.54 (d, *J* = 6.6 Hz, 3H), 0.92 (s, 9H), 0.11 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 157.6, 141.6, 141.0, 140.0, 132.4, 132.3, 129.1, 129.1, 128.5, 127.3, 114.3, 69.4, 62.2, 53.8, 28.3, 26.1, 18.6, -5.0.

HRMS (EI) calcd. for $C_{28}H_{37}NNaO_3SSi^+$ (M+Na$^+$): 518.2156, found: 518.2155.

N-{1-[4-(Benzyloxy)phenyl]ethyl}-1-oxo-1,1-diphenyl-λ^6-sulfanimine (**4p**)



4p

Prepared following general procedure, and the reaction time was 6 hours. The reaction mixture was purified by preparatory thin layer chromatography with petroleumether and ethylacetate (PE/EA = 2:1) to afford the product **4p** (86.5 mg, 67% yield).

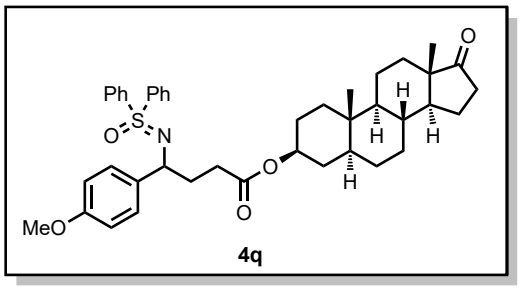
Pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.52-7.44 (m, 6H), 7.42-7.37 (m, 4H), 7.35-7.33 (m, 3H), 6.94 (d, *J* = 8.4 Hz, 2H), 5.07 (s, 2H), 4.38 (q, *J* = 6.5 Hz, 1H), 1.56 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 157.5, 141.5, 140.9, 140.2, 137.4, 132.5, 132.3, 129.1, 129.0, 128.7, 128.5, 128.0, 127.6, 127.4, 114.6, 70.1, 53.7, 28.2.

HRMS (EI) calcd. for $C_{27}H_{26}NO_2S^+$ ($M+H^+$): 428.1679, found: 428.1681.

(3a*S*,3b*R*,5a*S*,7*S*,9a*S*,9b*S*,11a*S*)-9a,11a-Dimethyl-1-oxohexadecahydro-1*H*-cyclopenta[1,2-*i*]phenanthren-7-yl 4-(4-methoxyphenyl)-4-[(oxodiphenyl-λ^6-sulfanylidene)amino]butanoate (**4q**)



4q

Prepared following general procedure with 30 mol% 5,6-dimethyl-1*H*-benzo[*d*]imidazole, and the reaction time was 6 hours. The reaction mixture was purified by flash column chromatography with petroleumether and ethylacetate (PE/EA =2:1) to afford the product **4q** (143.1 mg, 70% yield).

Pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.3 Hz, 2H), 7.74 (d, *J* = 7.4 Hz, 2H), 7.51-7.41 (m, 4H), 7.34-7.32 (m, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 4.64-4.61 (m, 1H), 4.21-4.14 (m, 1H), 3.79 (s, 3H), 2.45-2.39 (m, 3H), 2.15-2.03 (m, 3H), 1.94-1.90 (m, 1H), 1.79-1.63 (m, 6H), 1.54-1.42 (m, 3H), 1.34-1.21 (m, 7H), 1.01-0.93 (m, 2H), 0.85 (s, 3H), 0.82 (s, 3H), 0.71-0.68 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 221.4, 173.5, 158.4, 141.3, 141.0, 138.0, 132.5, 132.3, 129.2, 129.1, 129.0, 128.6, 127.9, 113.6, 73.3, 57.6, 55.4, 54.5, 51.5, 47.9, 44.8, 36.9, 36.5, 36.0, 35.8, 35.2, 34.1, 31.8, 31.7, 31.0, 28.4, 27.5, 21.9, 20.6, 14.0, 12.4.

HRMS (EI) calcd. For $C_{42}H_{52}NO_5S^+$ ($M+H^+$): 682.3561, found: 682.3560.

III. References:

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IV. NMR spectra of the products

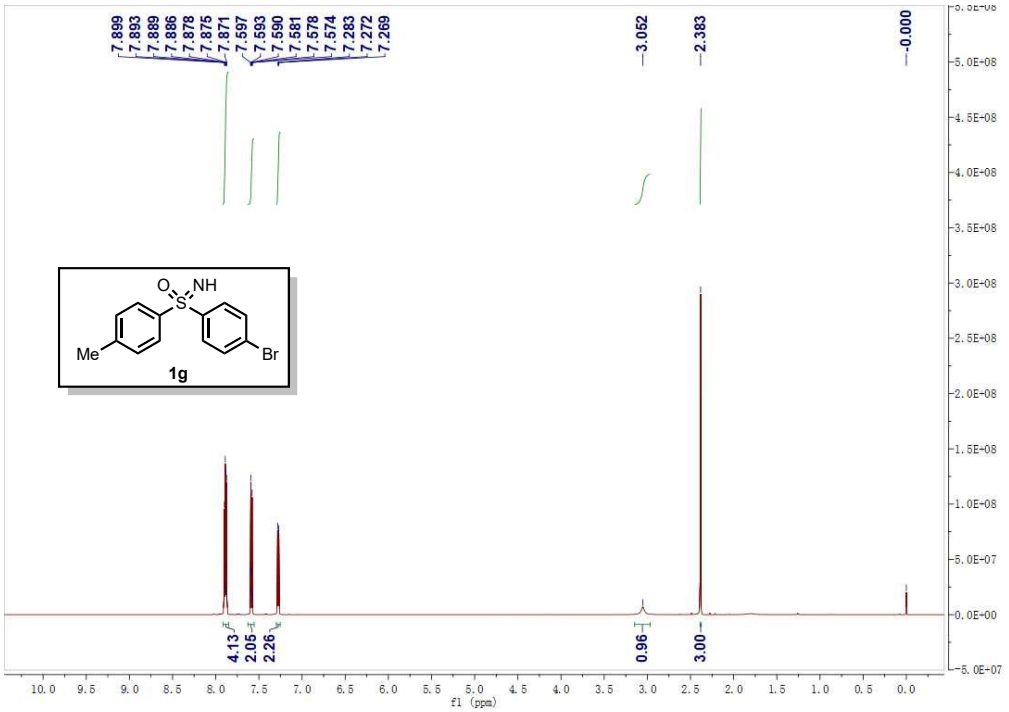

Figure S6. ^{1}H NMR of **1g**.

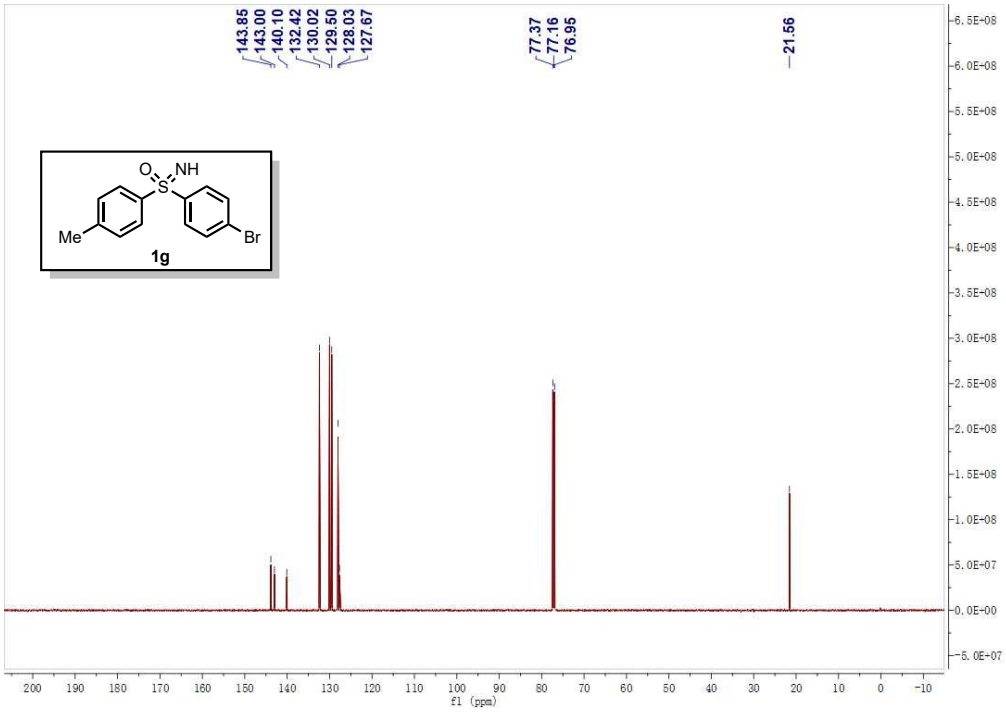

Figure S7. ^{13}C NMR of **1g**.

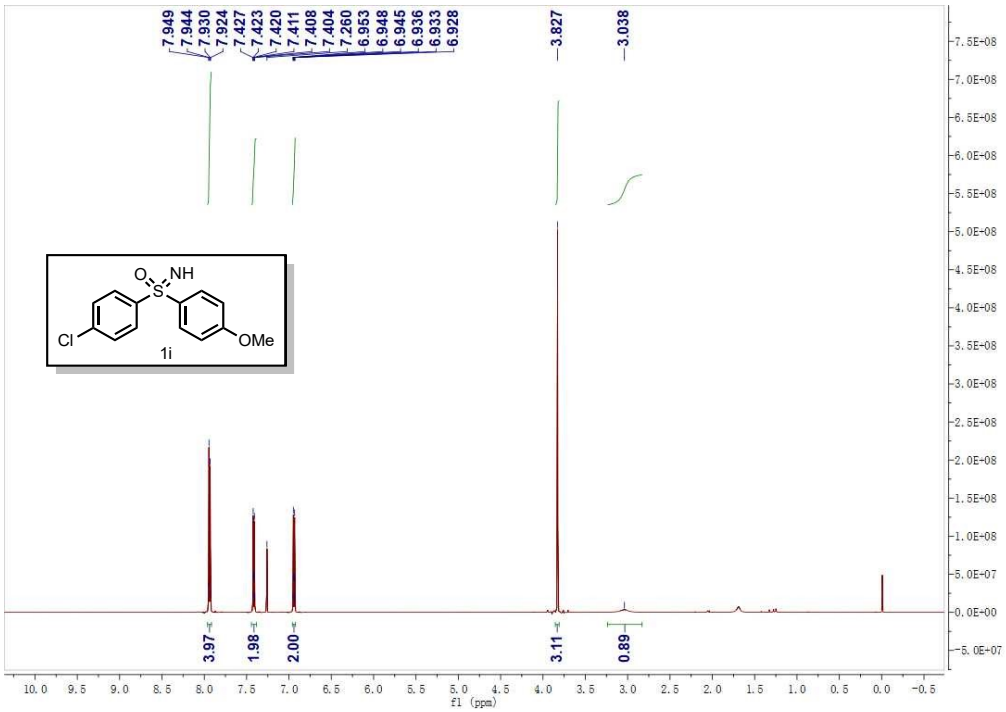

Figure S8. ^{1}H NMR of **1i**.

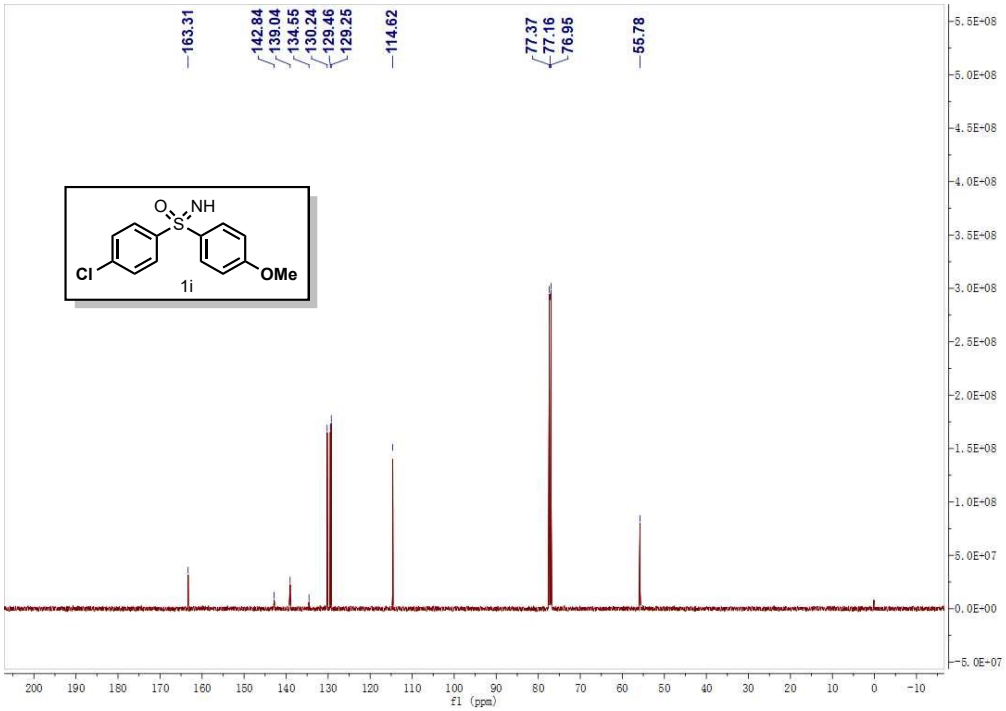

Figure S9. ^{13}C NMR of **1i**.

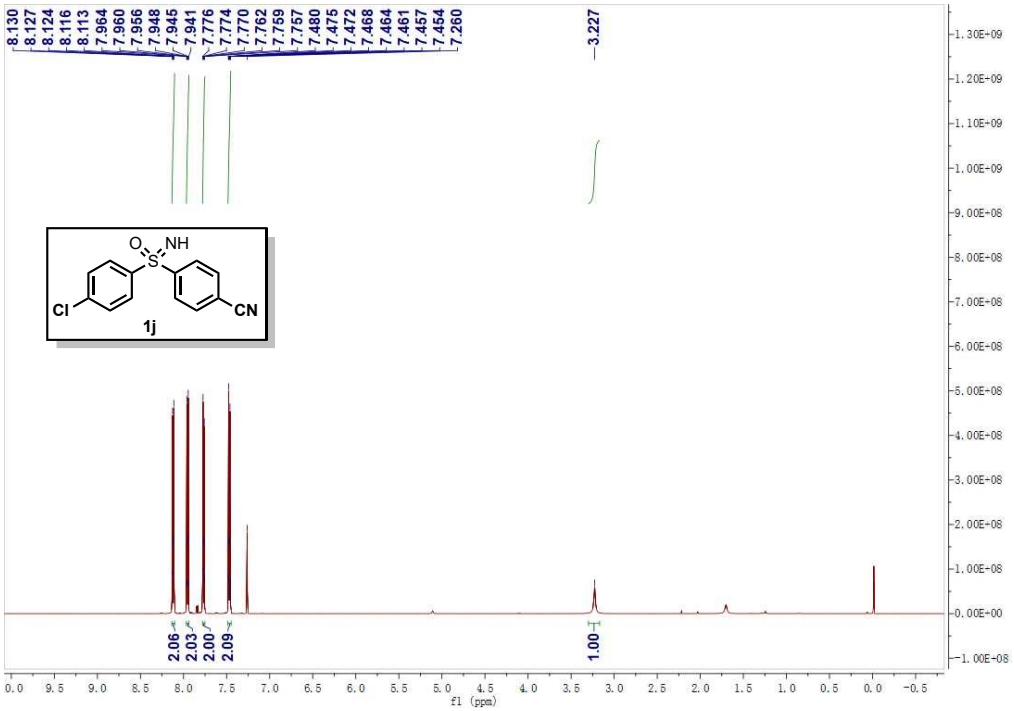

Figure S10. ^{1}H NMR of **1j**.

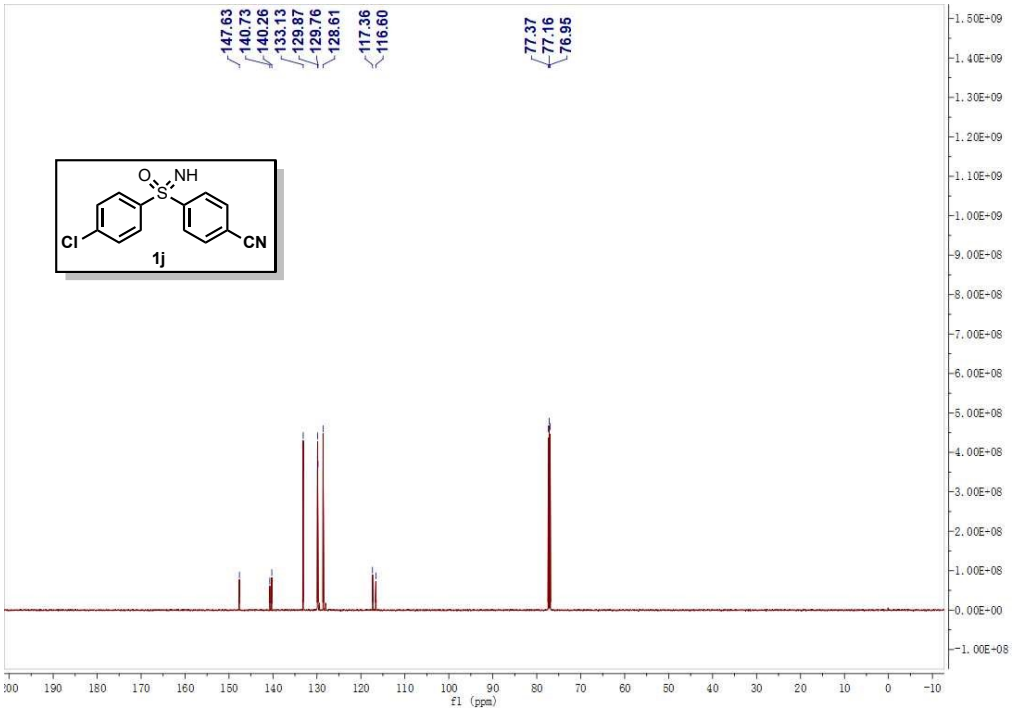

Figure S11. ^{13}C NMR of **1j**.

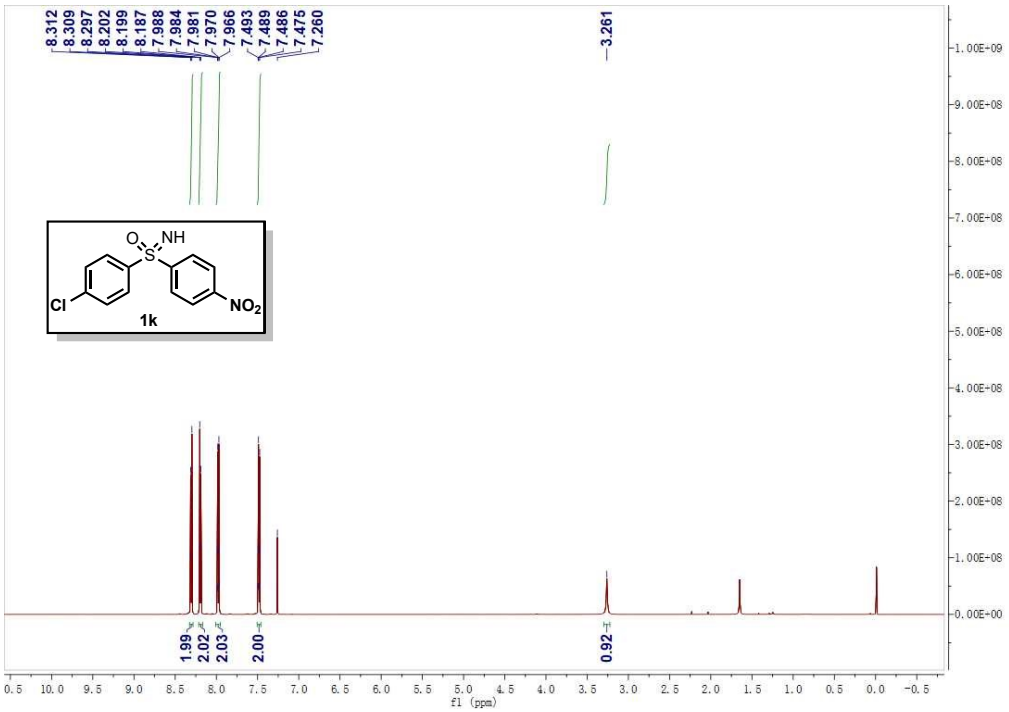

Figure S12. ^{1}H NMR of **1k**.

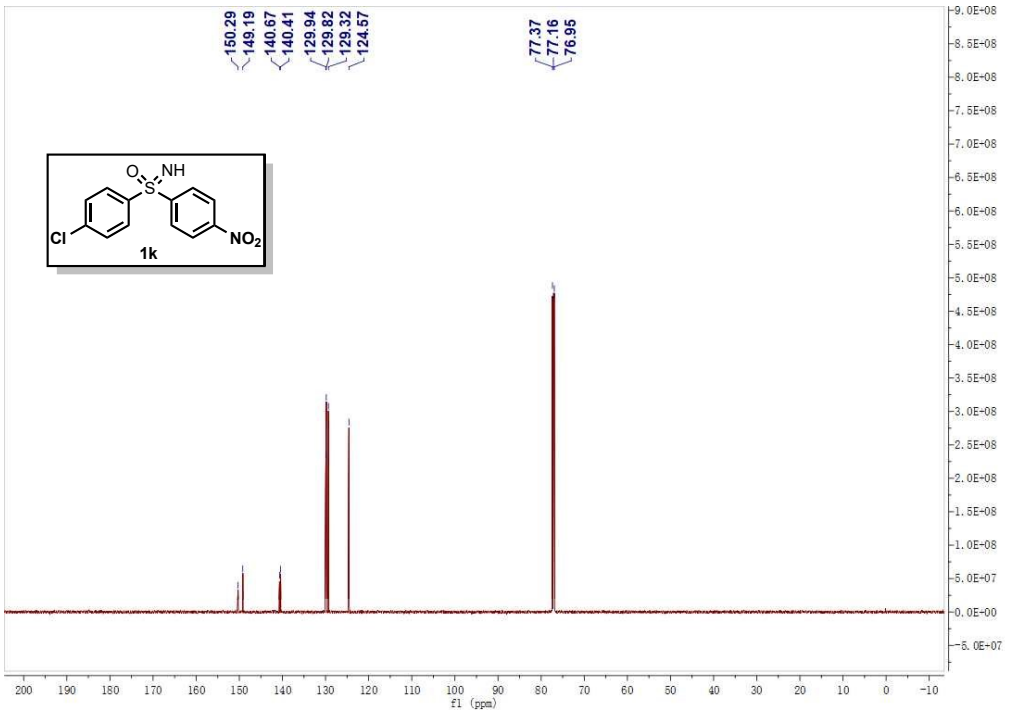

Figure S13. ^{13}C NMR of **1k**.

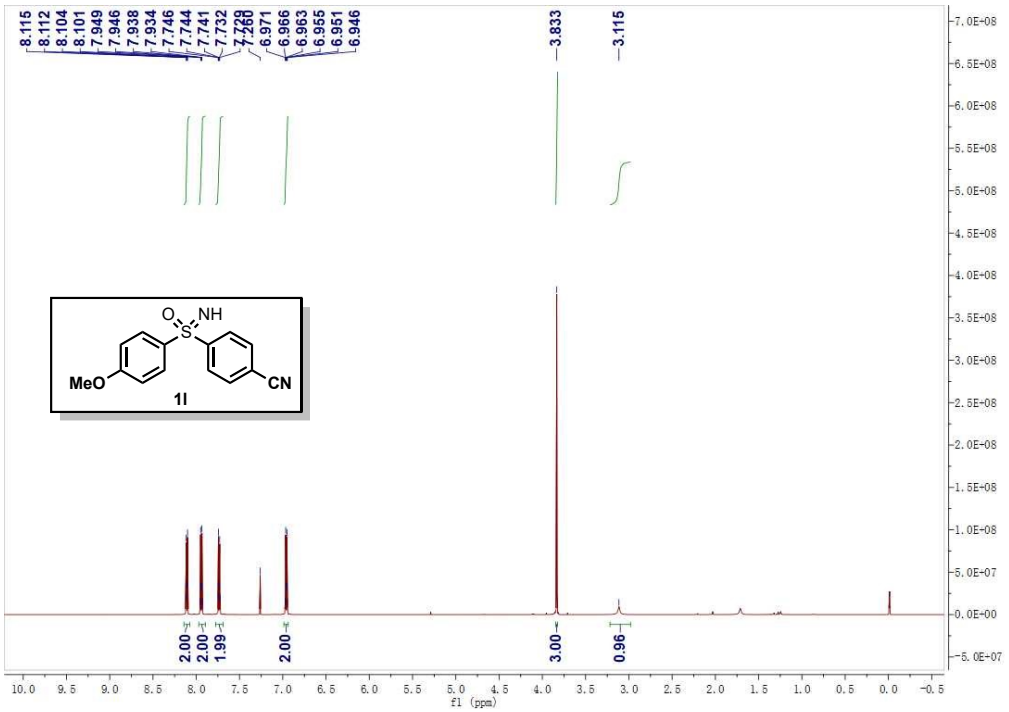

Figure S14. ^{1}H NMR of **1l**.

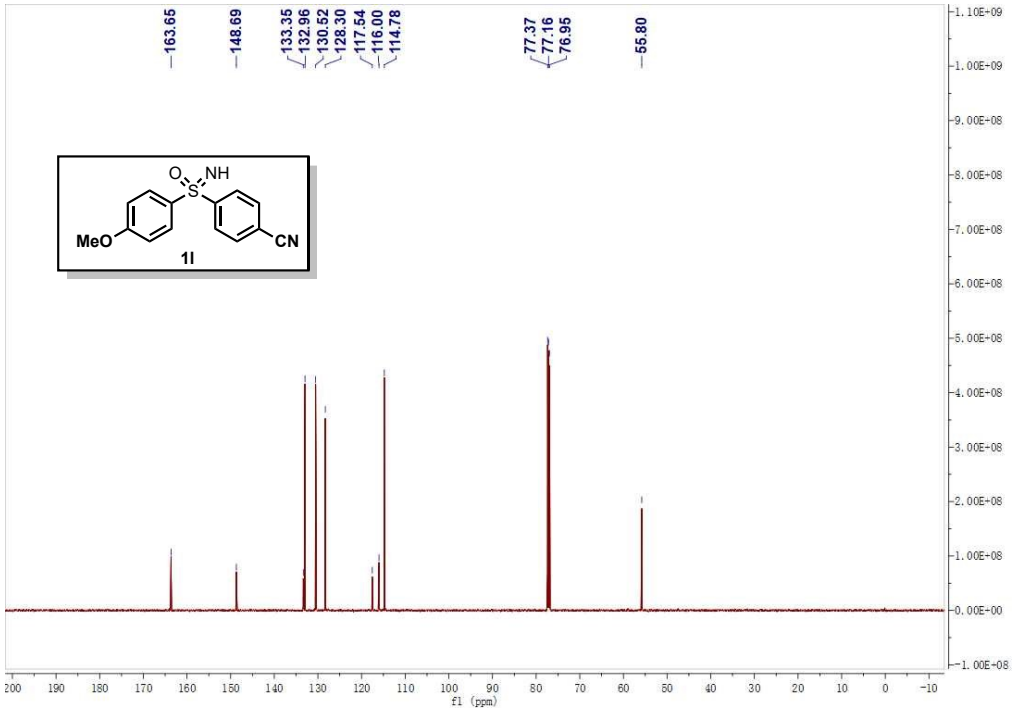

Figure S15. ^{13}C NMR of **1l**.

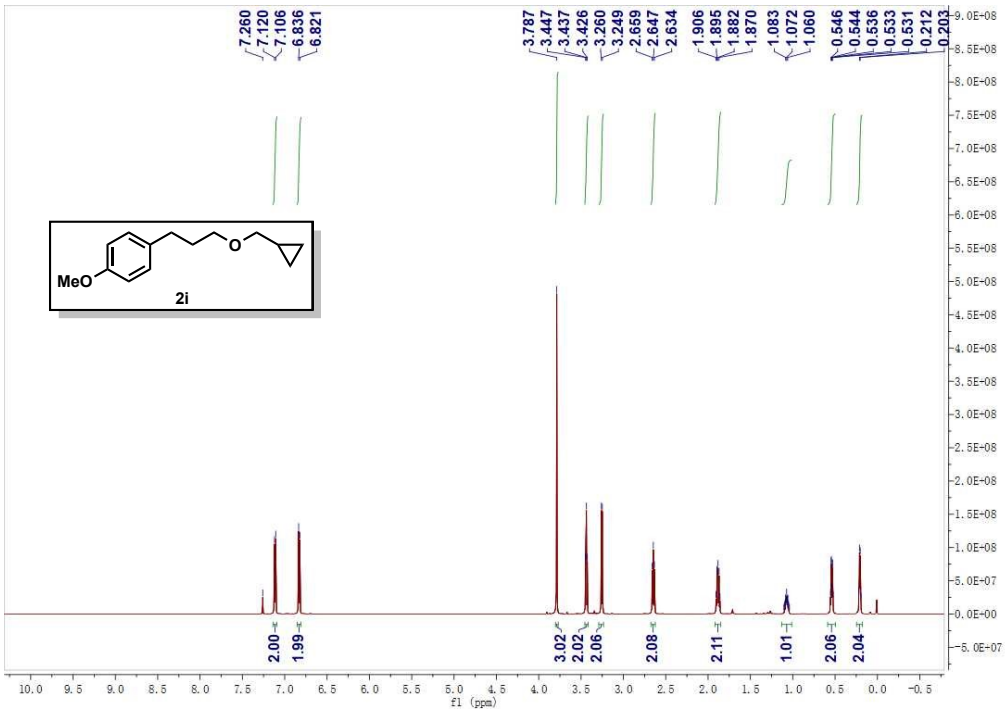

Figure S16. ^{1}H NMR of **2i**.

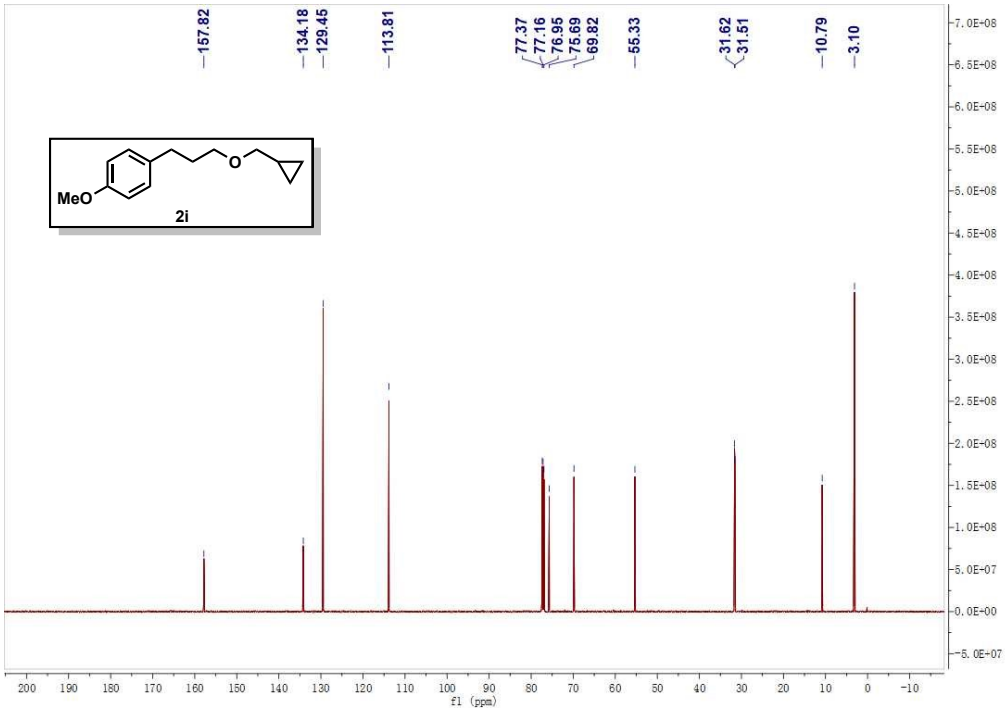

Figure S17. ^{13}C NMR of **2i**.

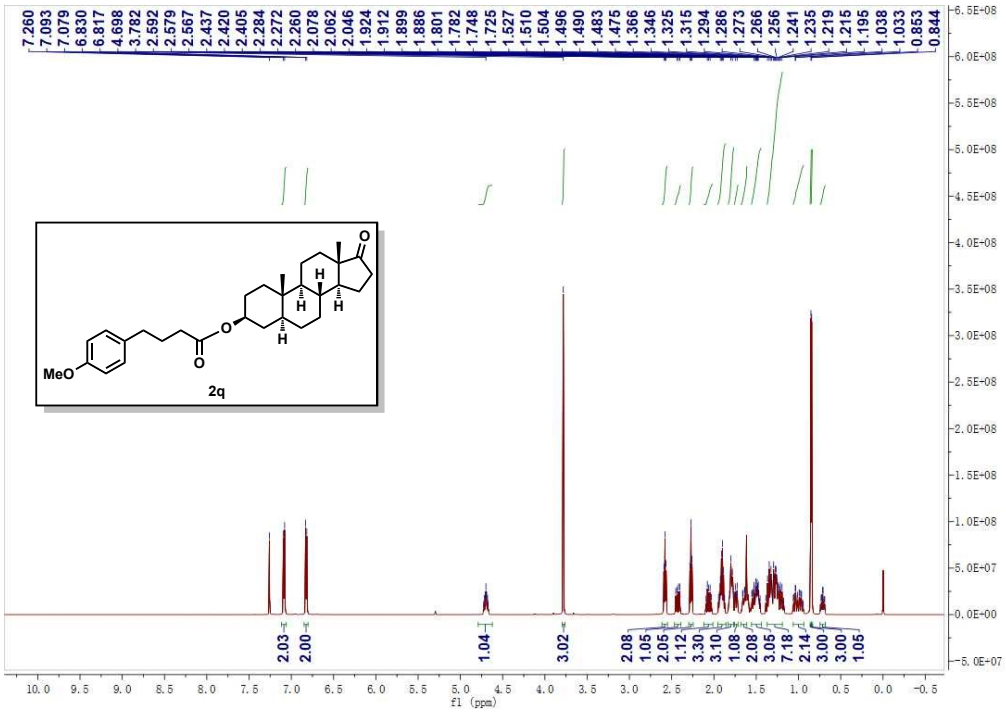

Figure S18. ^{1}H NMR of **2q**.

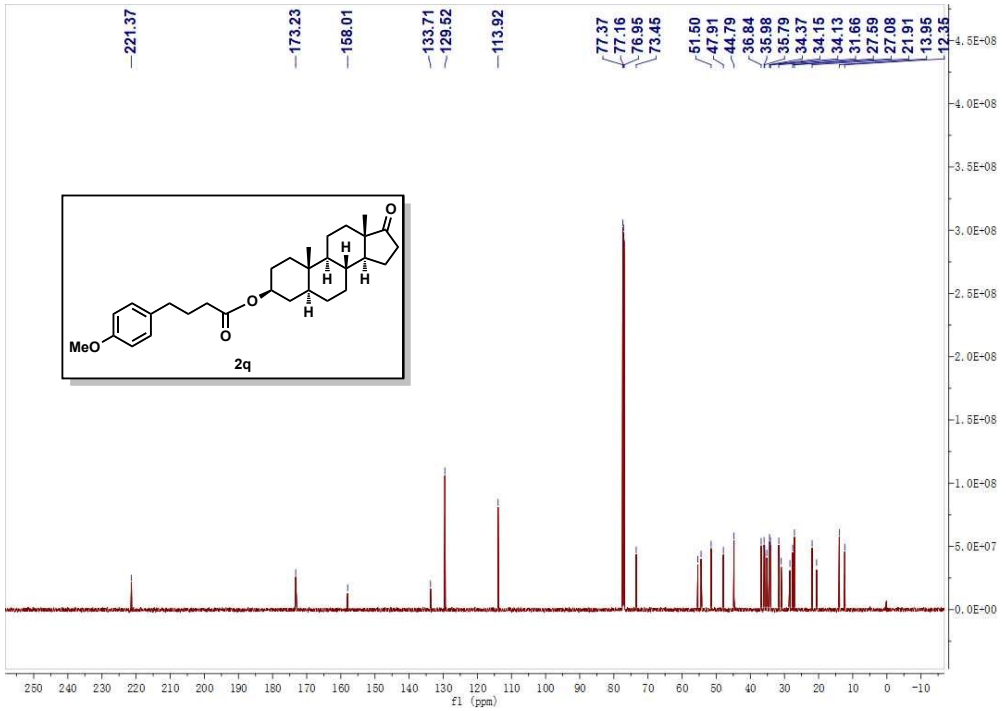

Figure S19. ^{13}C NMR of **2q** .

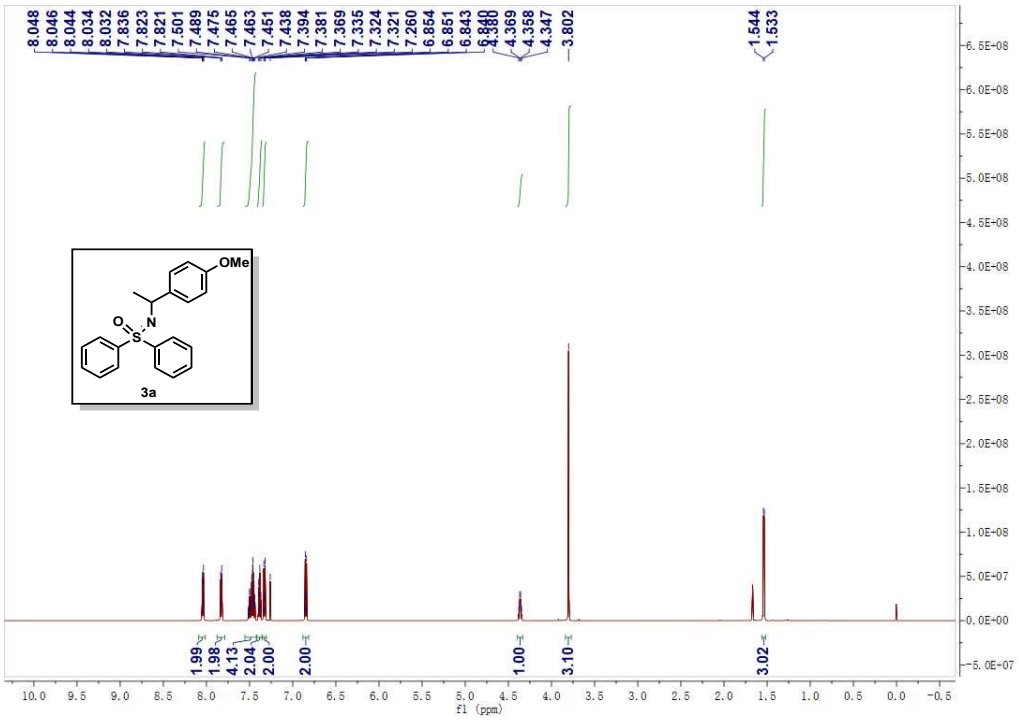

Figure S20. ^{1}H NMR of **3a**.

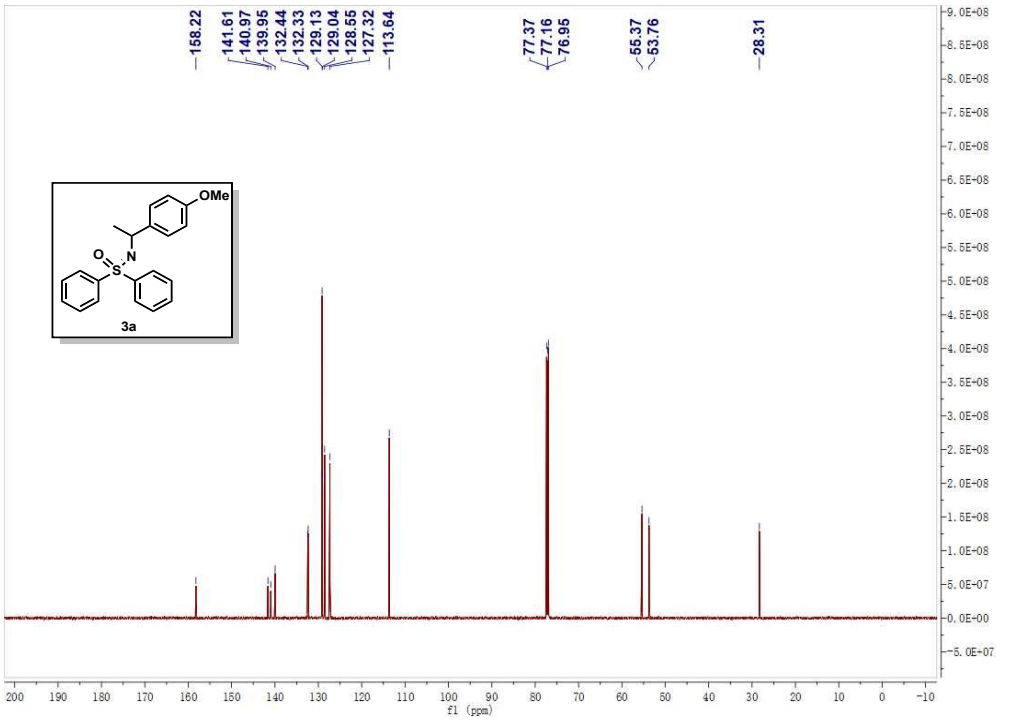

Figure S21. ^{13}C NMR of **3a**.

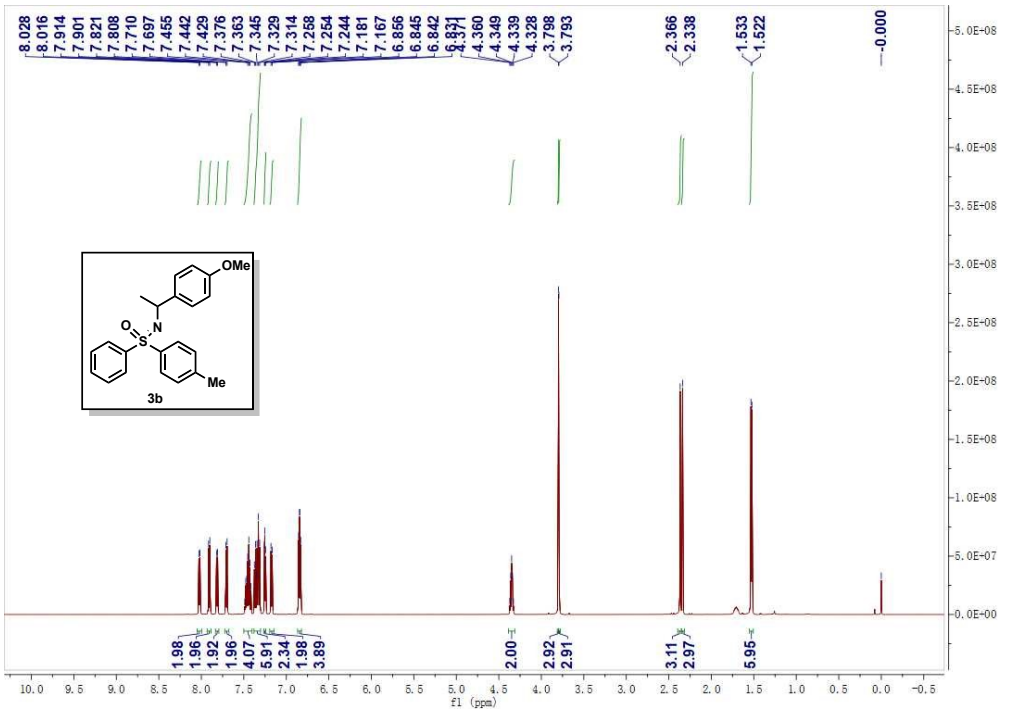

Figure S22. ^{1}H NMR of **3b**.

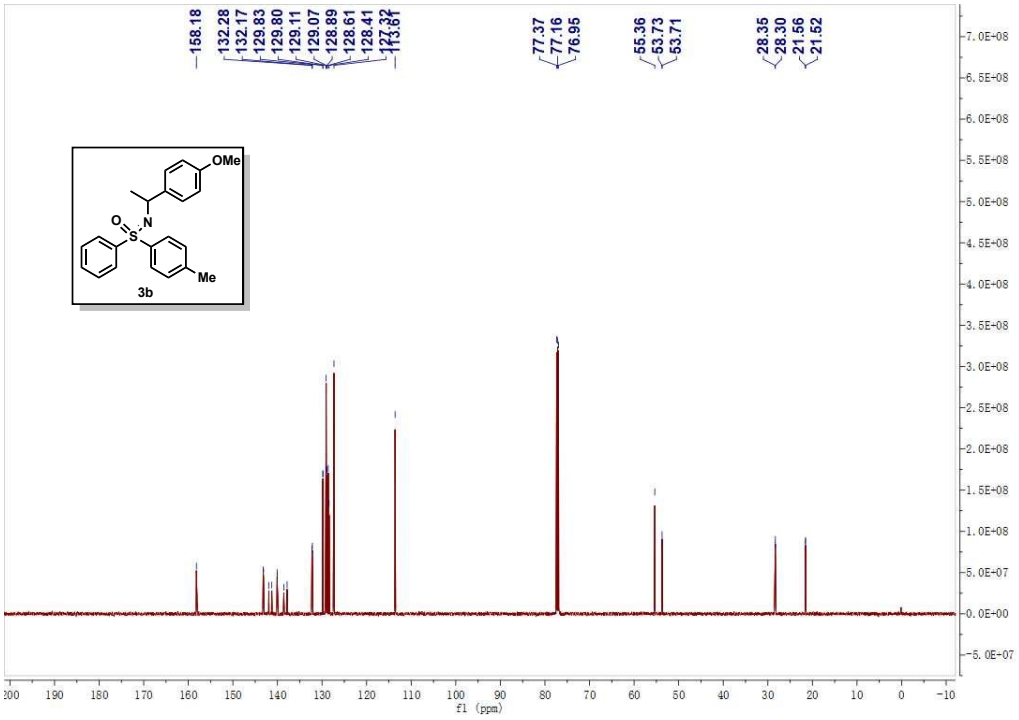

Figure S23. ^{13}C NMR of **3b**.

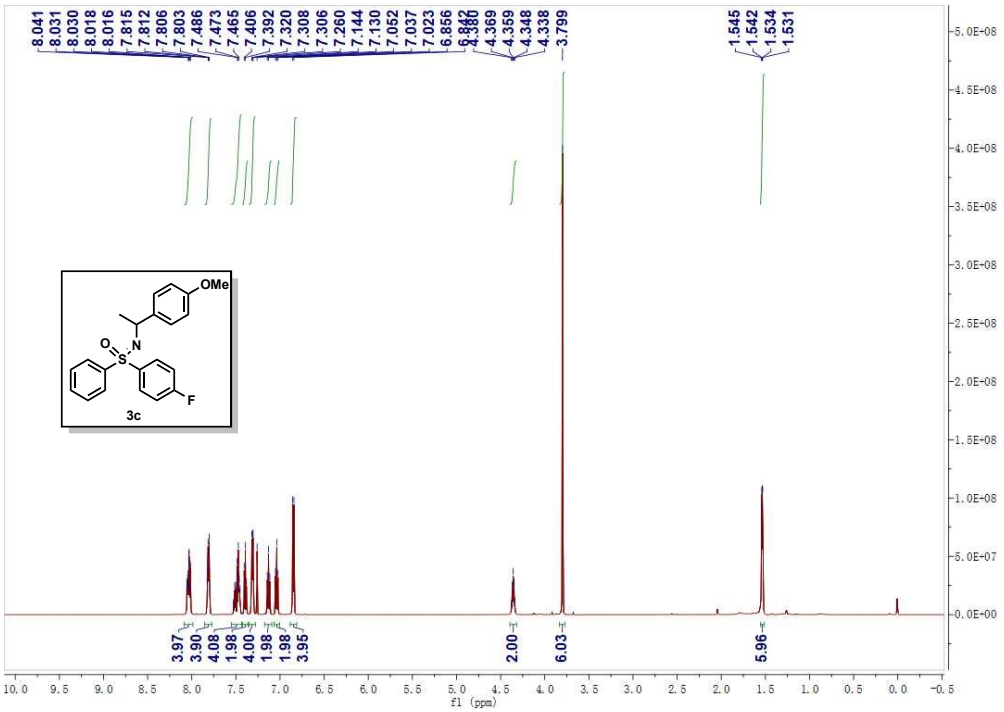

Figure S24. ^{1}H NMR of **3c**.

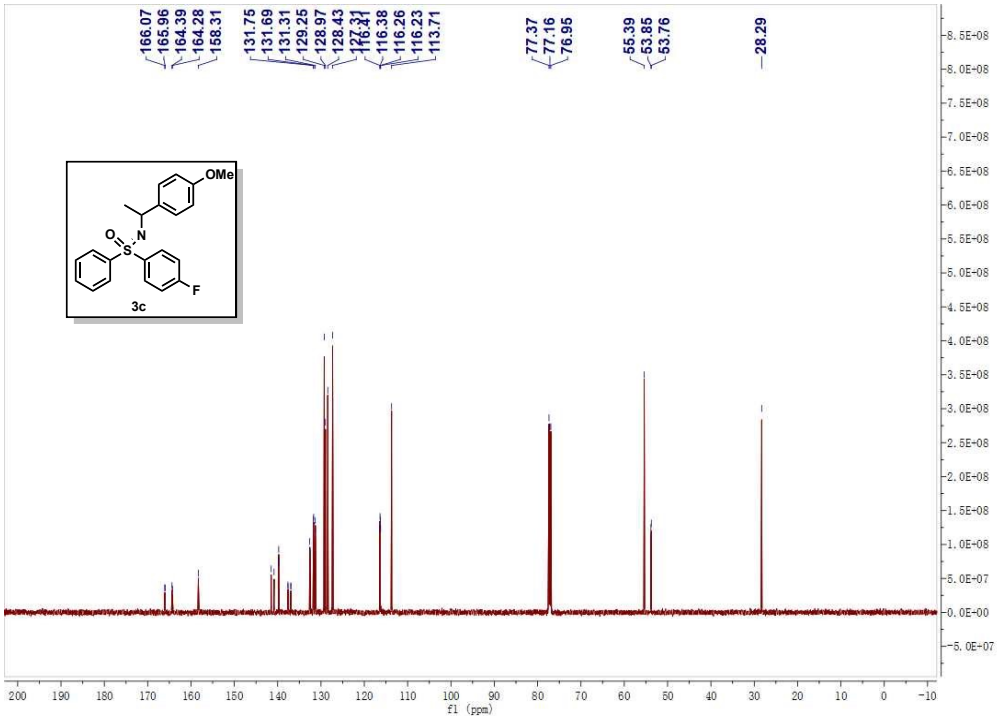

Figure S25. ^{13}C NMR of **3c**.

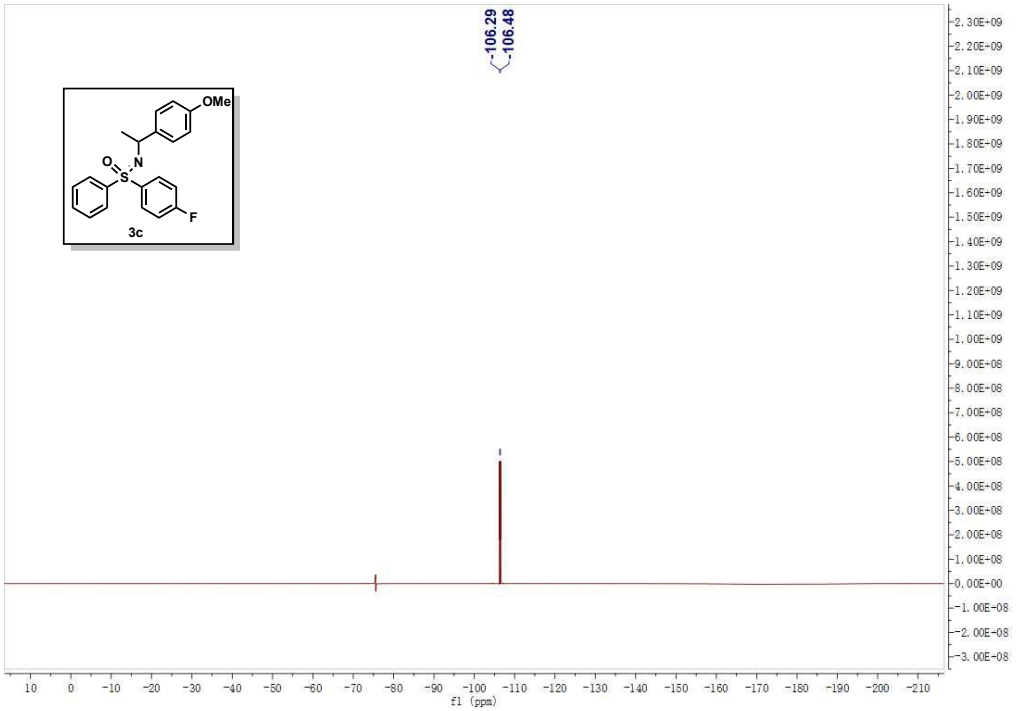

Figure S26. ^{19}F NMR of **3c**.

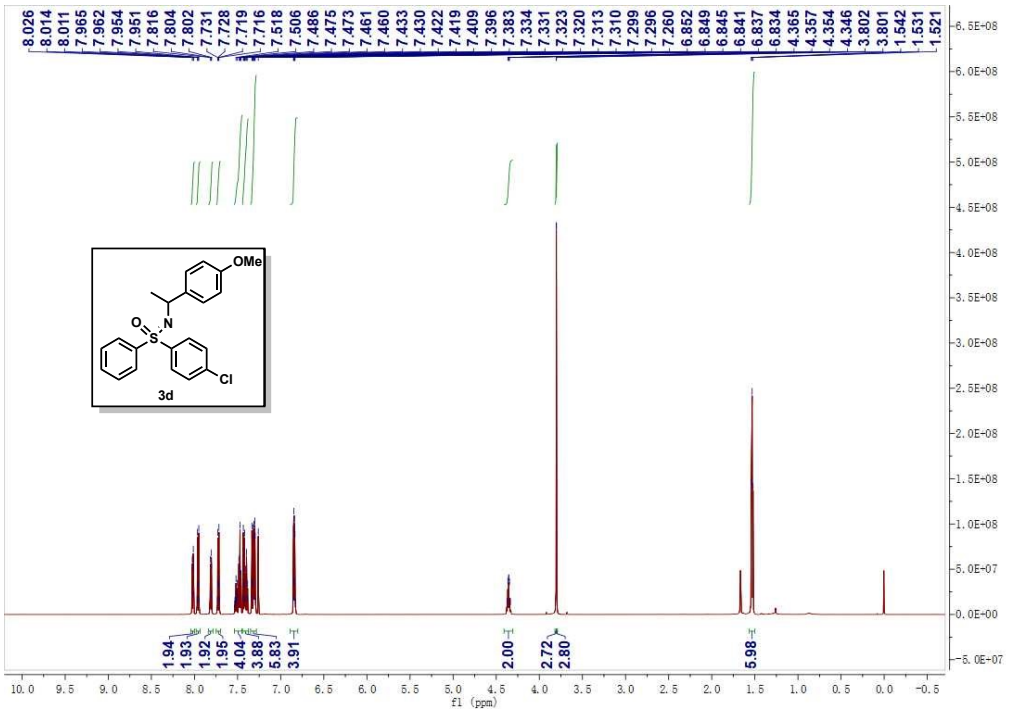

Figure S27. ^{1}H NMR of **3d**.

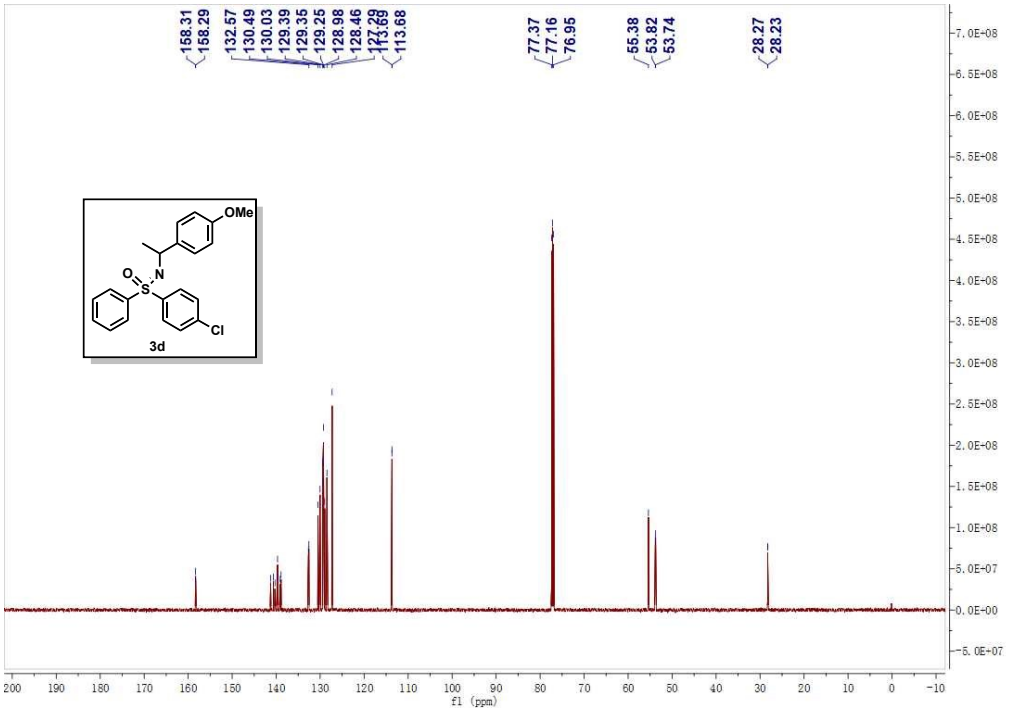

Figure S28. ^{13}C NMR of **3d**.

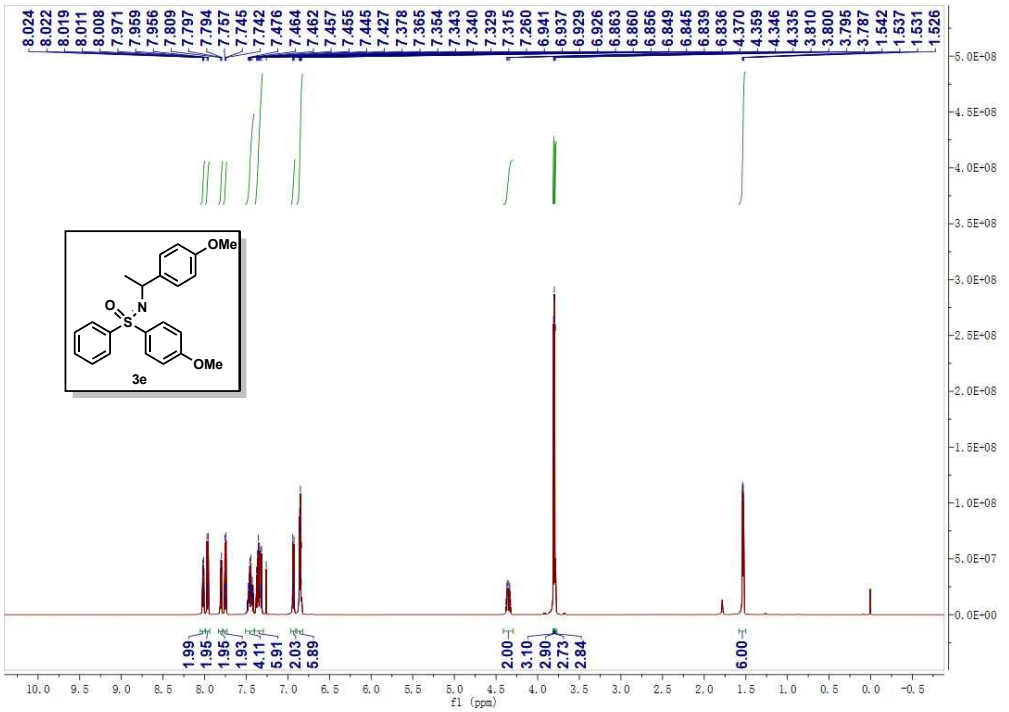

Figure S29. ^{1}H NMR of **3e**.

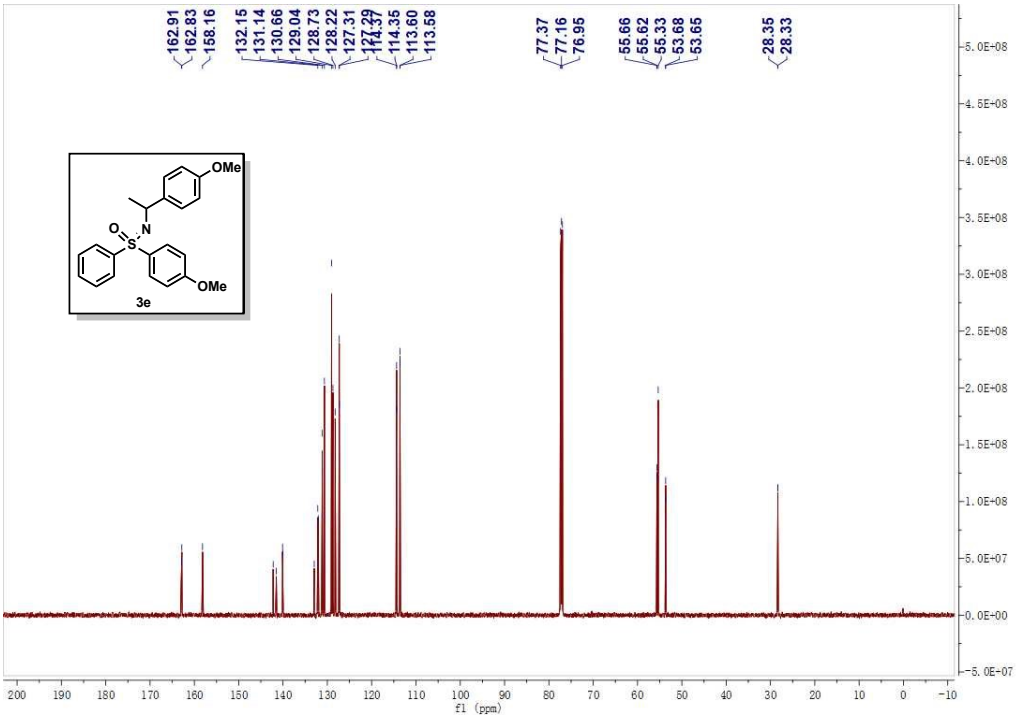

Figure S30. ^{13}C NMR of **3e**.

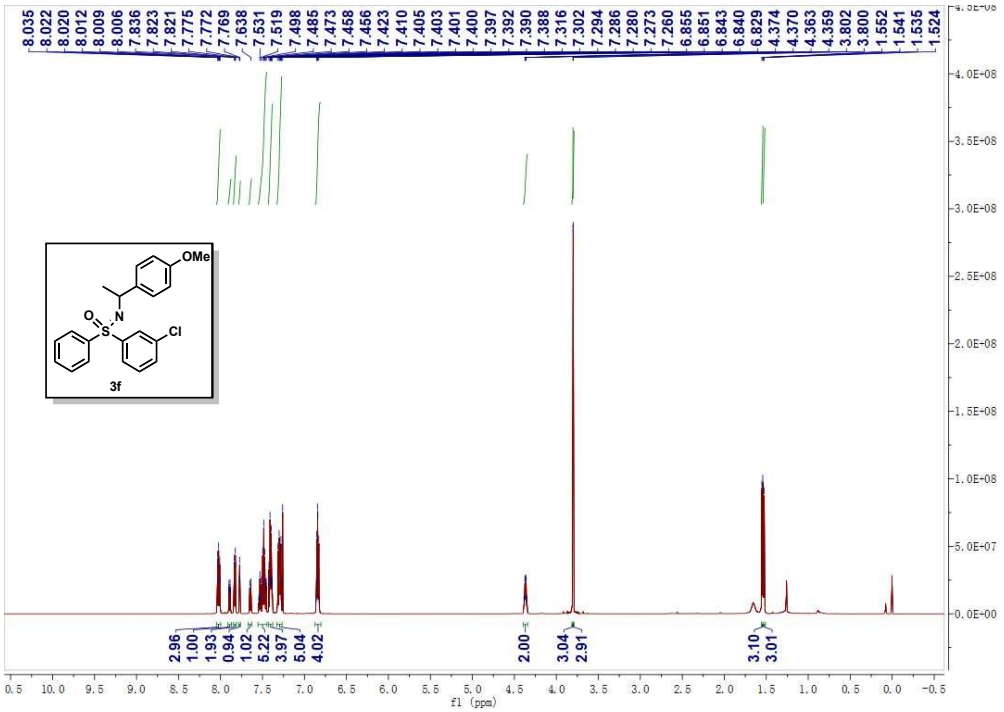

Figure S31. ^{1}H NMR of **3f**.

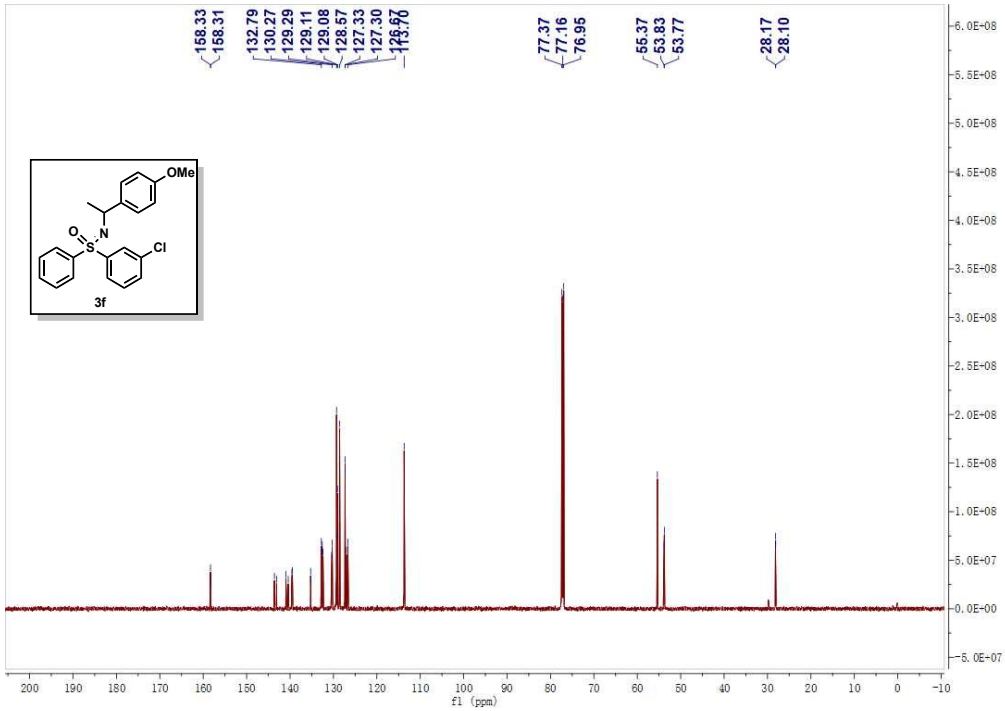

Figure S32. ^{13}C NMR of **3f**.

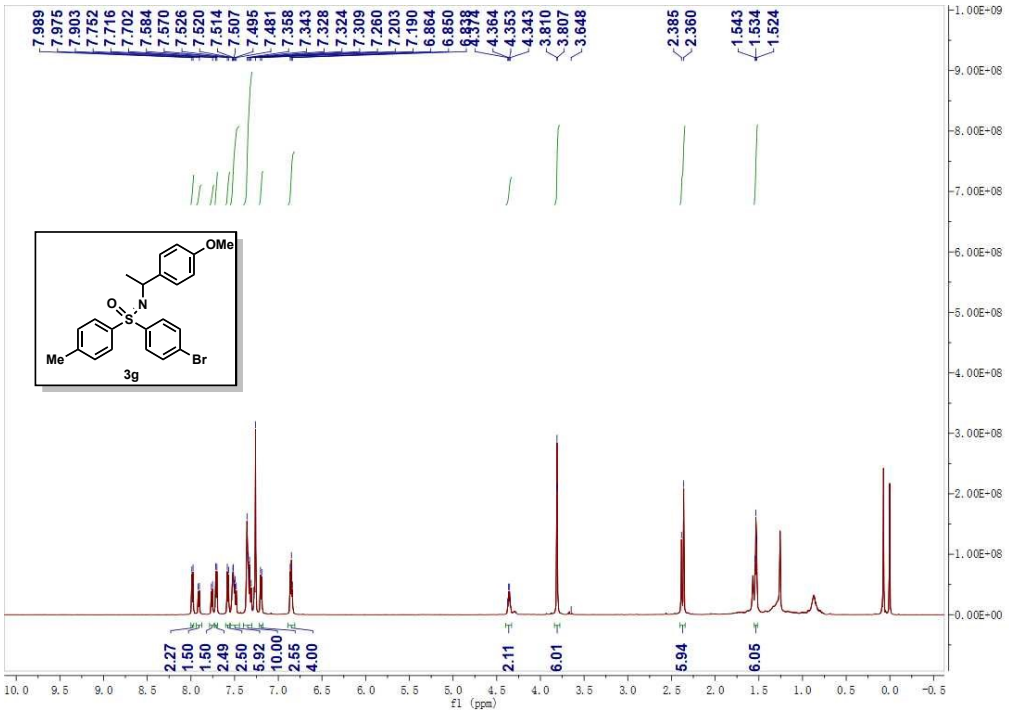

Figure S33. ^{1}H NMR of **3g**.

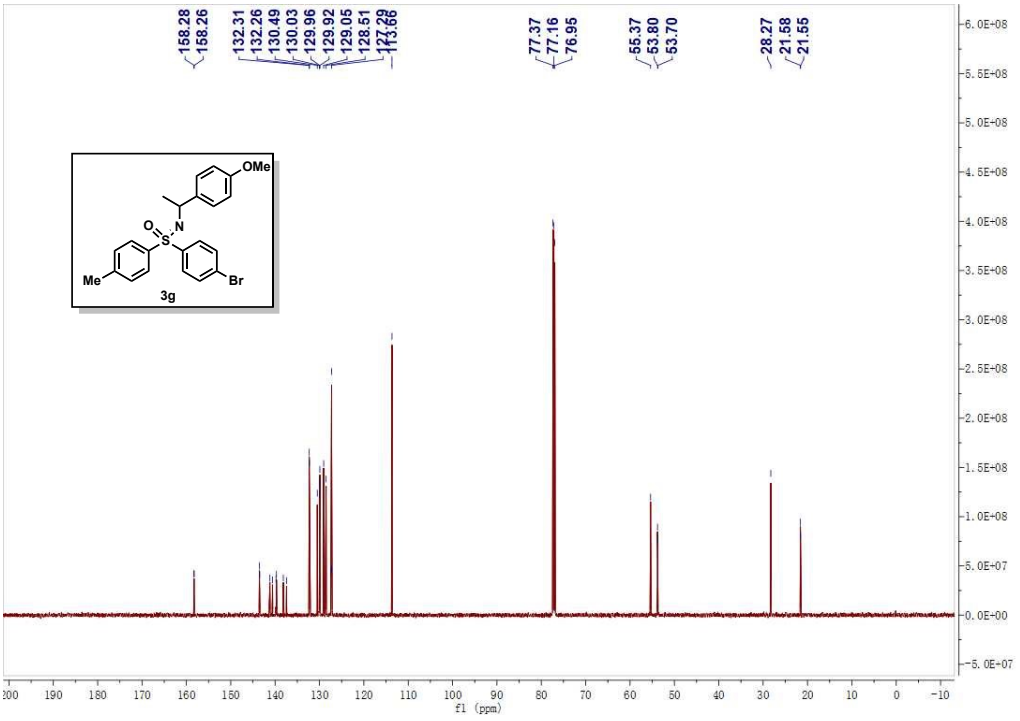

Figure S34. ^{13}C NMR of **3g**.

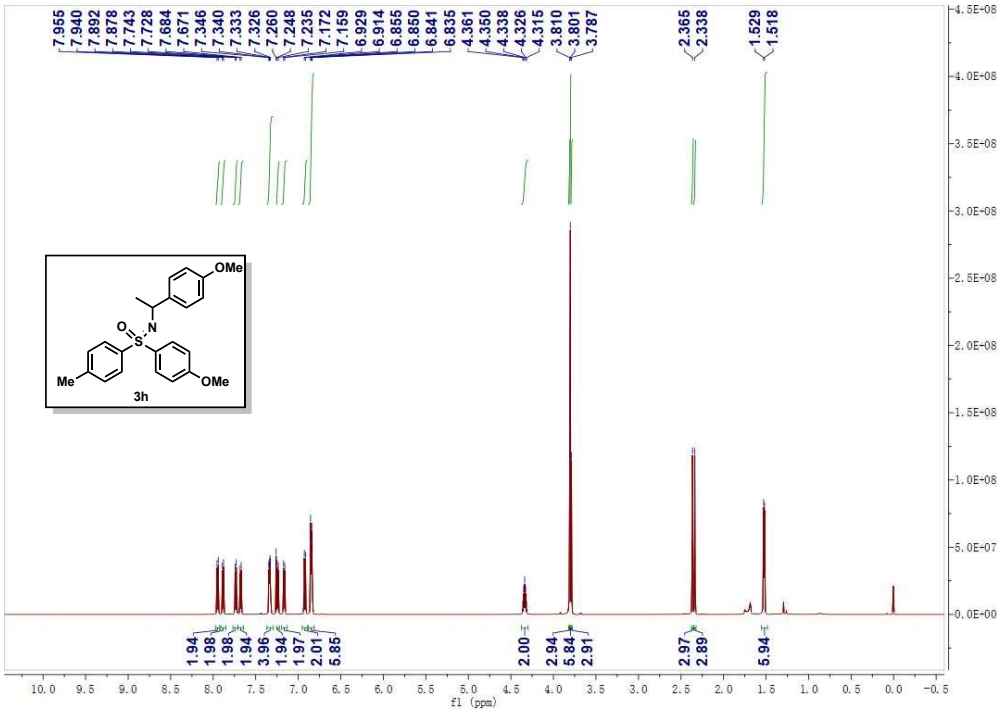

Figure S35. ^{1}H NMR of **3h**.

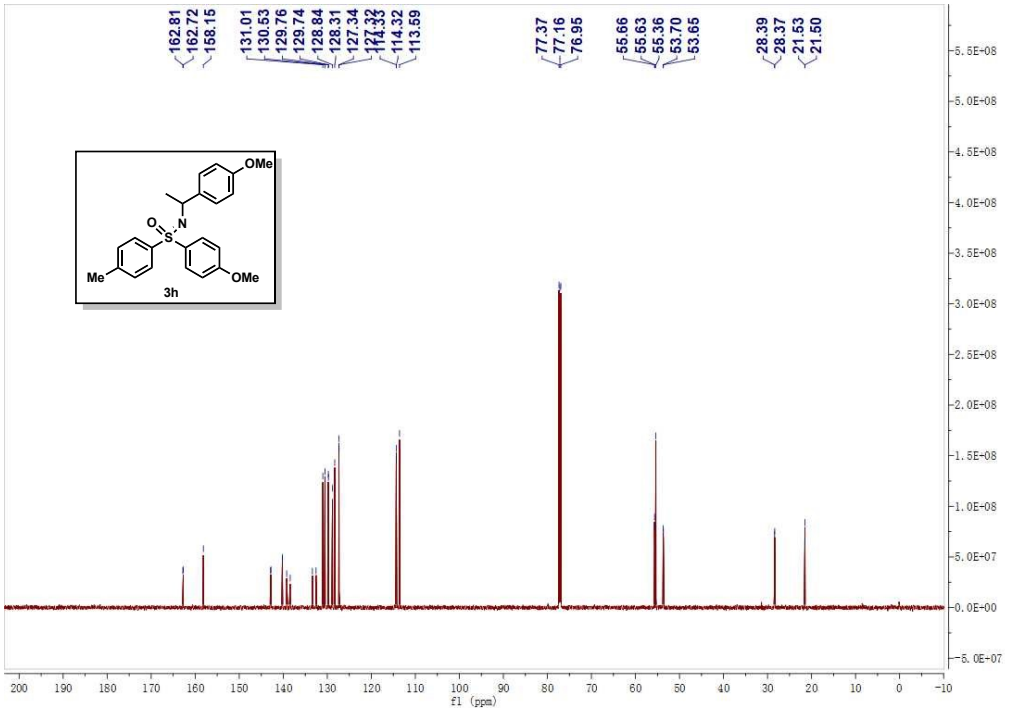

Figure S36. ^{13}C NMR of **3h**.

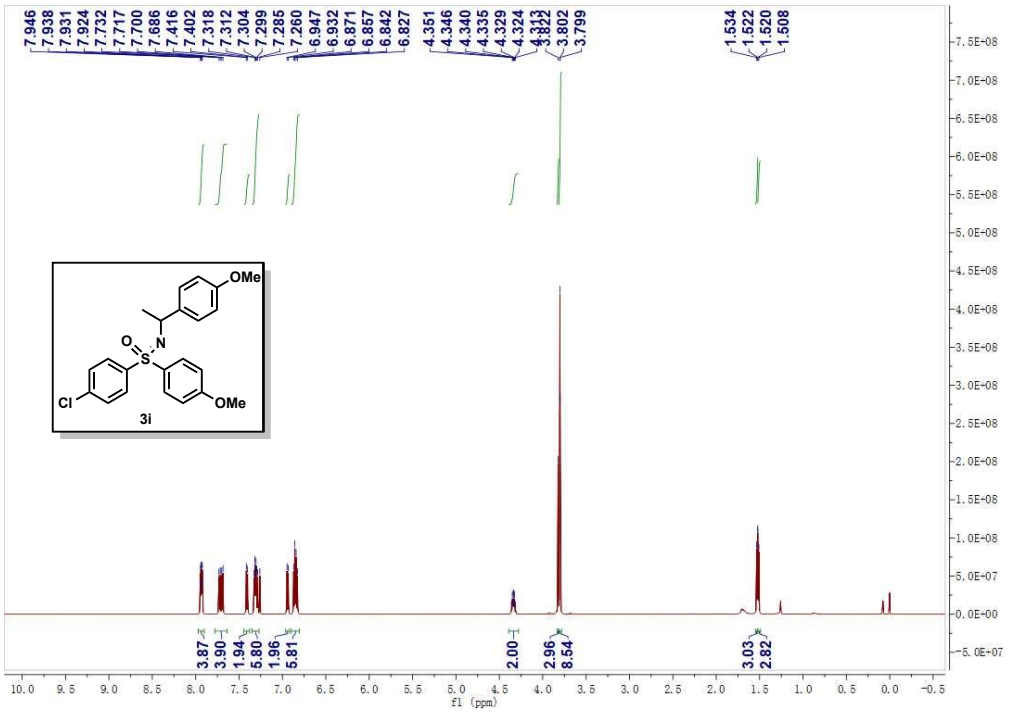

Figure S37. ^{1}H NMR of **3i**.

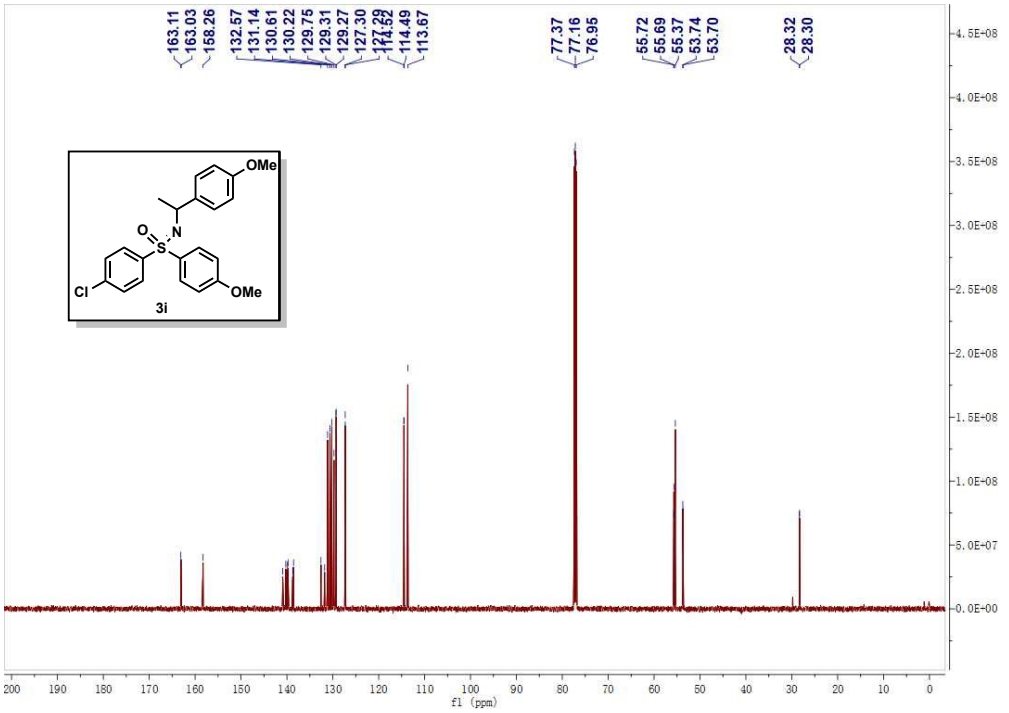

Figure S38. ^{13}C NMR of **3i**.

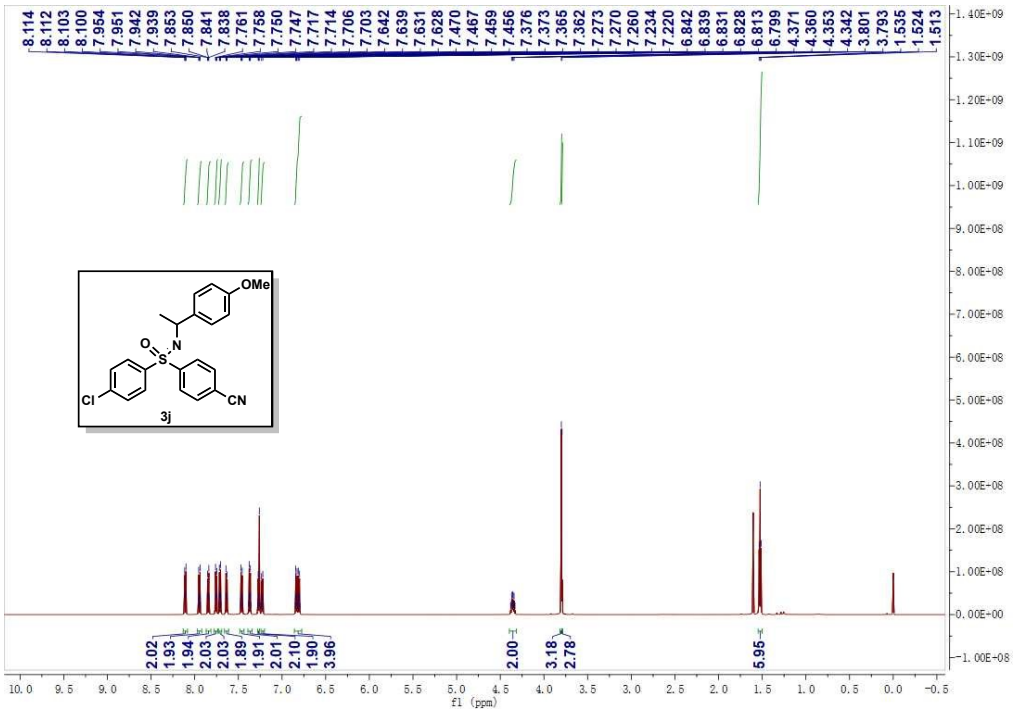

Figure S39. ^{1}H NMR of **3j**

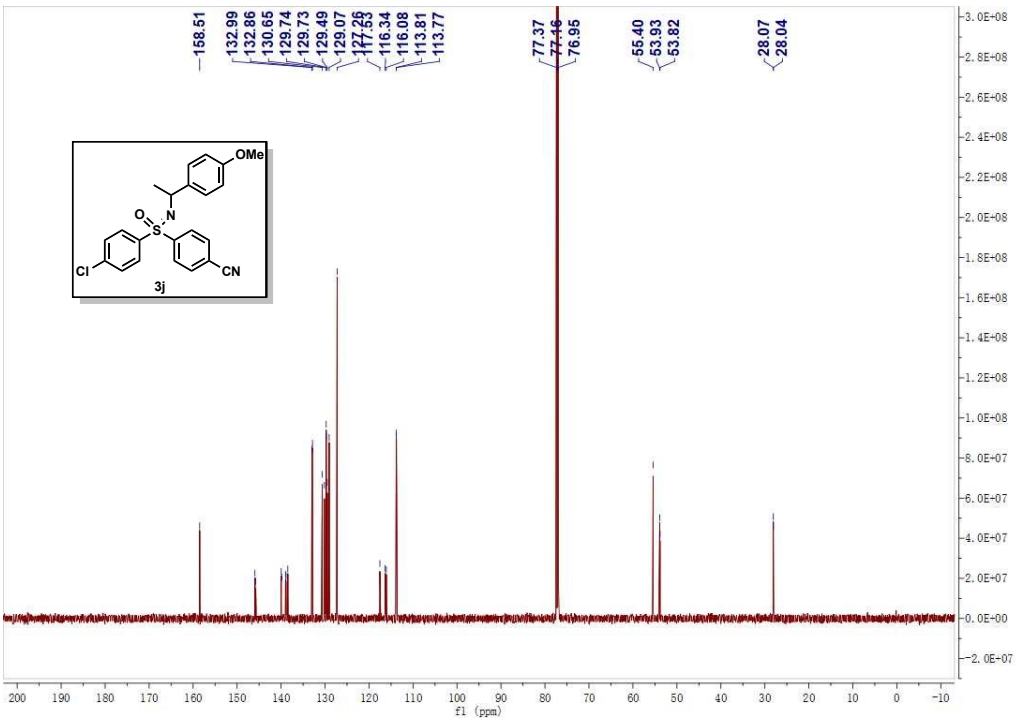

Figure S40. ^{13}C NMR of **3j**.

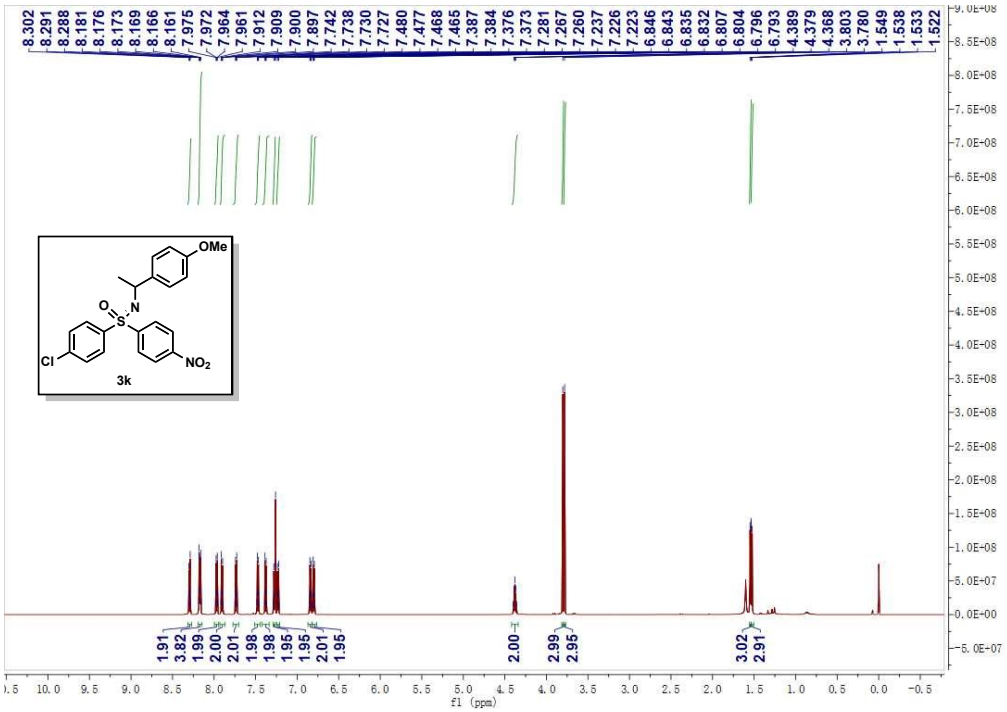

Figure S41. ^{1}H NMR of **3k**.

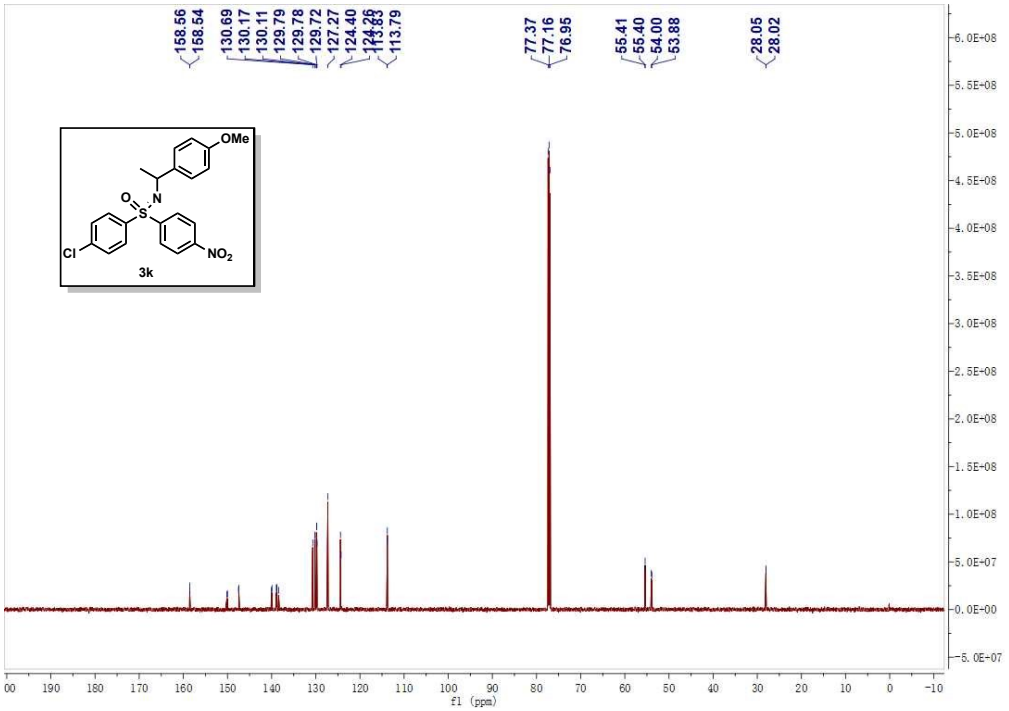

Figure S42. ^{13}C NMR of **3k**.

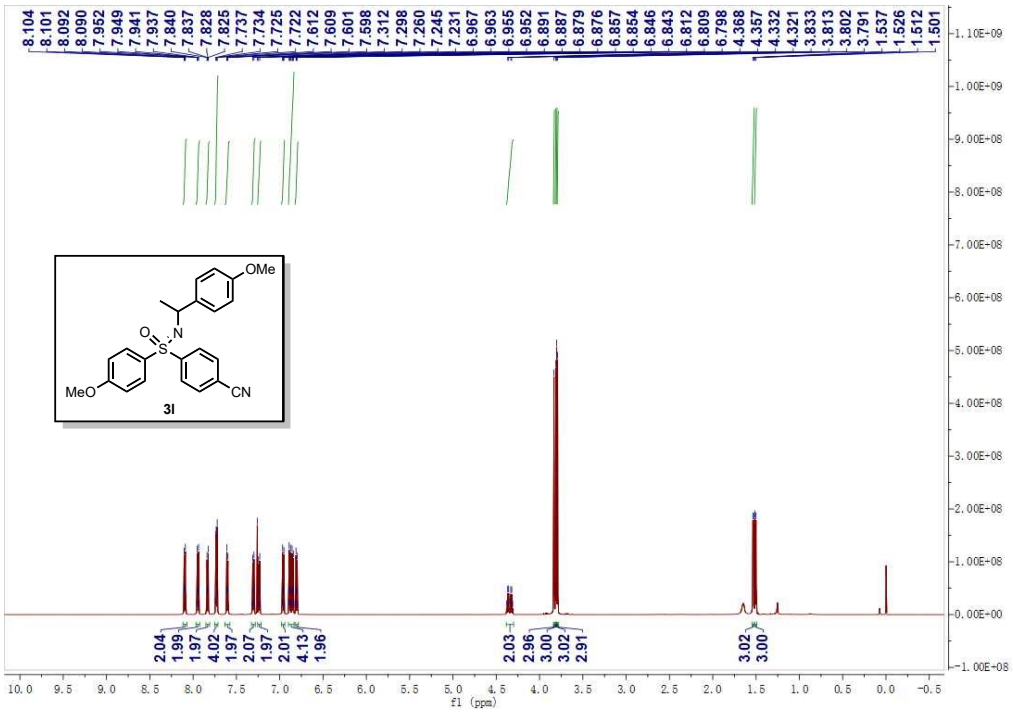

Figure S43. ^{1}H NMR of **3l**.

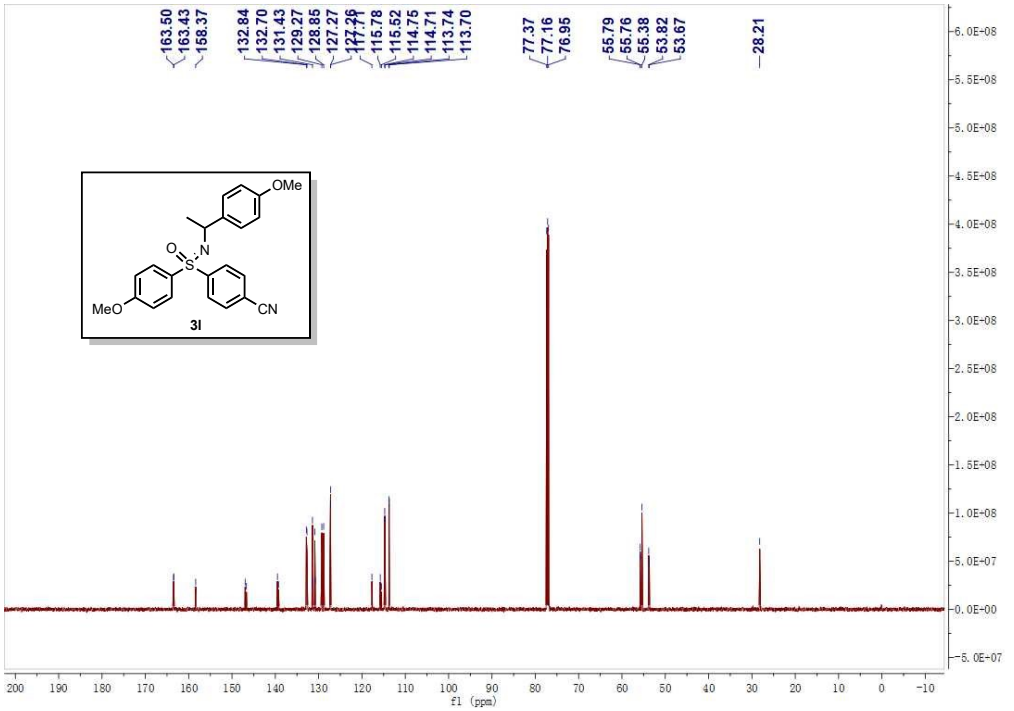

Figure S44. ^{13}C NMR of **3l**.

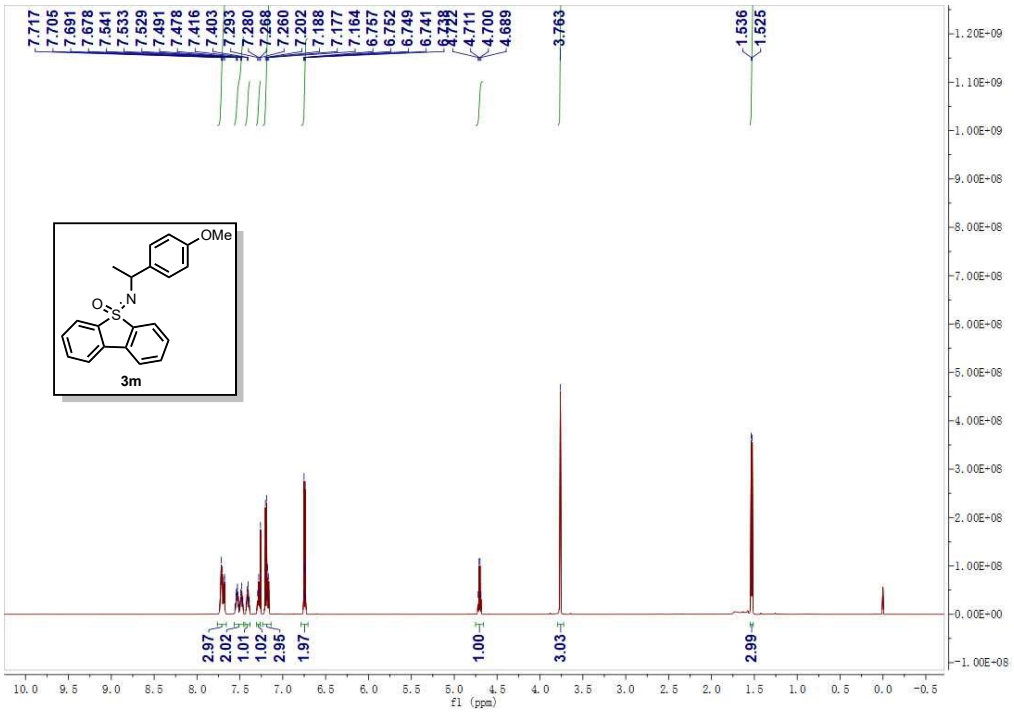

Figure S45. ^{1}H NMR of **3m**.

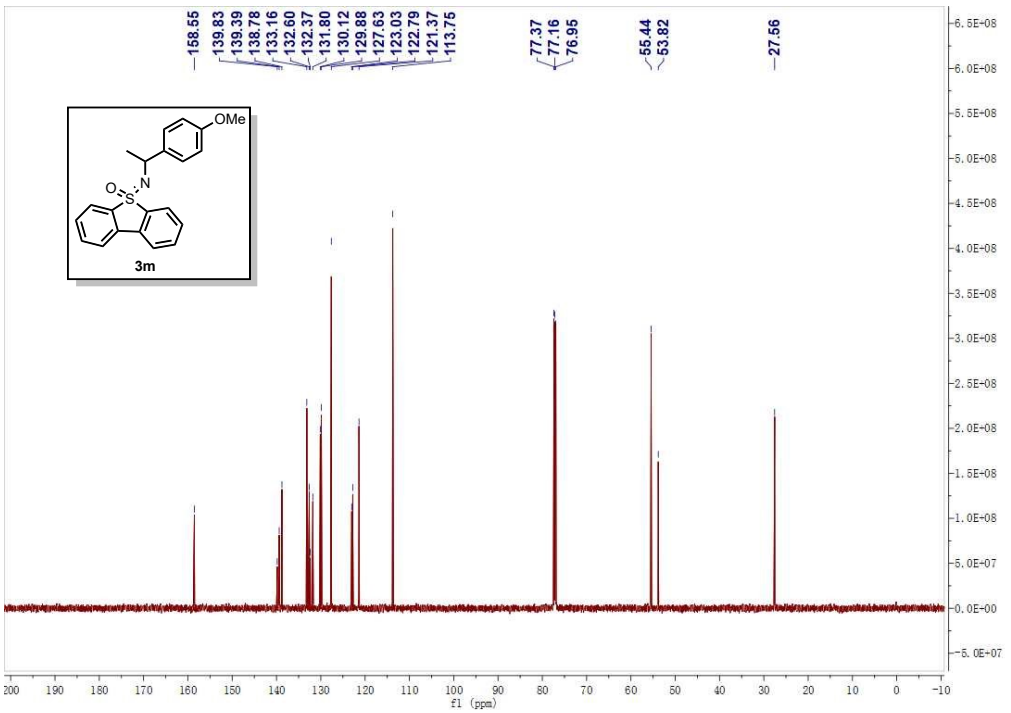

Figure S46. ^{13}C NMR of **3m**.

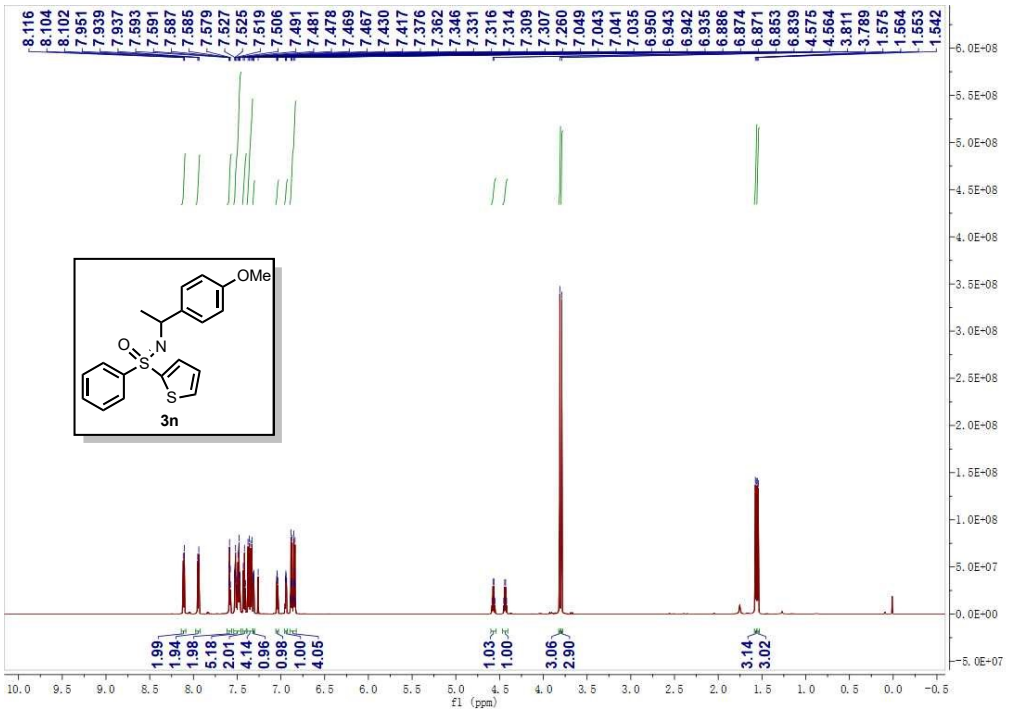

Figure S47. ^{1}H NMR of **3n**.

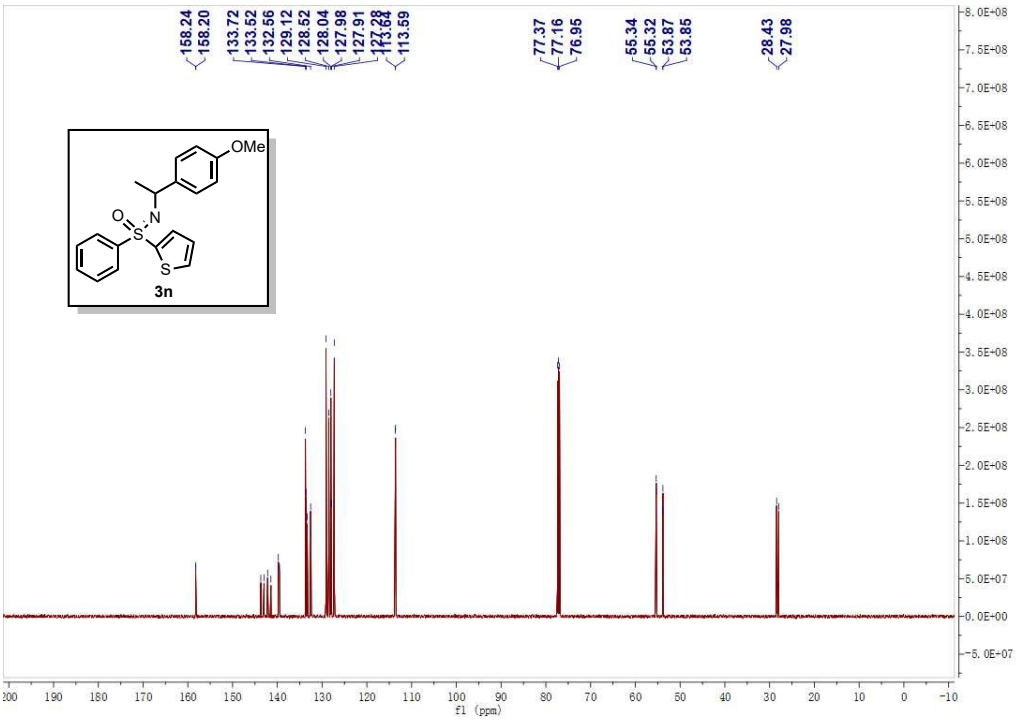

Figure S48. ^{13}C NMR of **3n**.

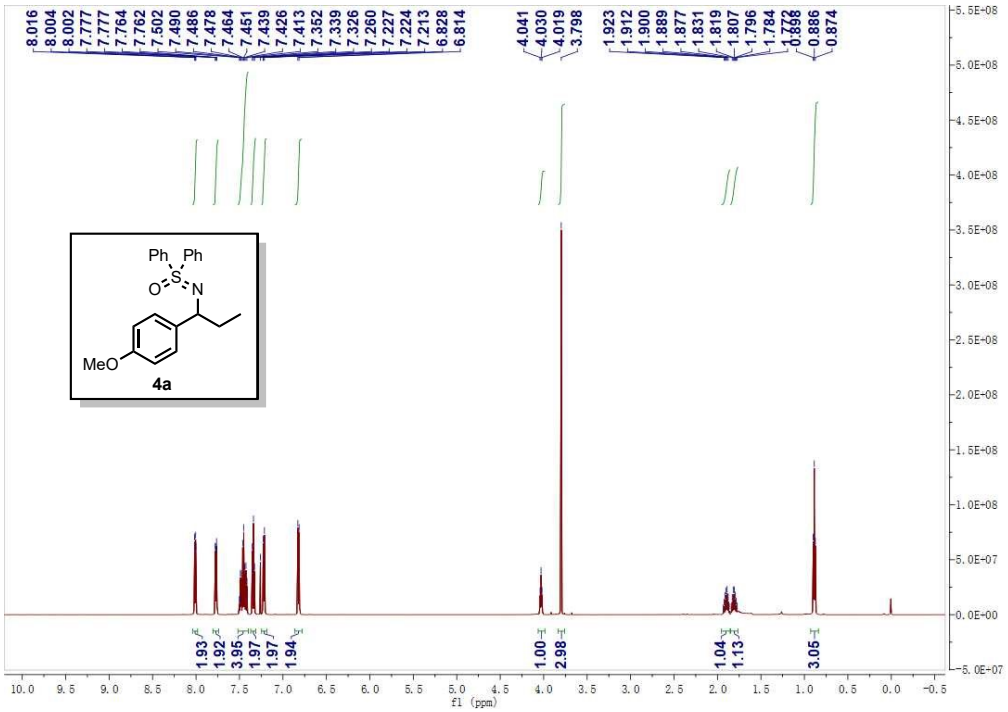

Figure S49. ^{1}H NMR of **4a**.

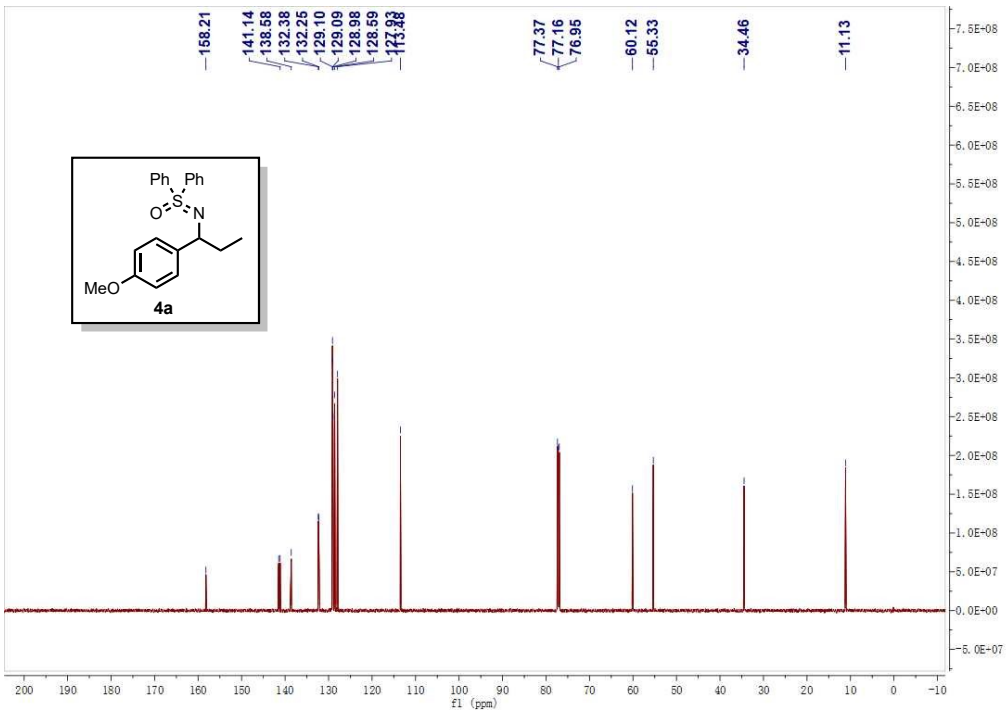

Figure S50. ^{13}C NMR of **4a**.

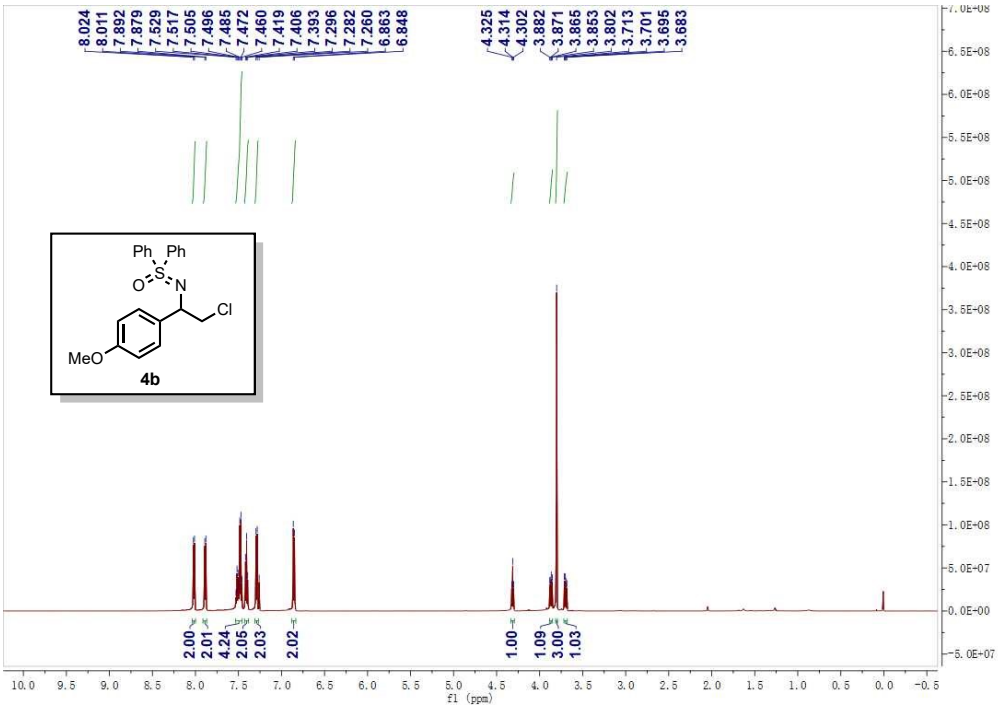

Figure S51. ^{1}H NMR of **4b**.

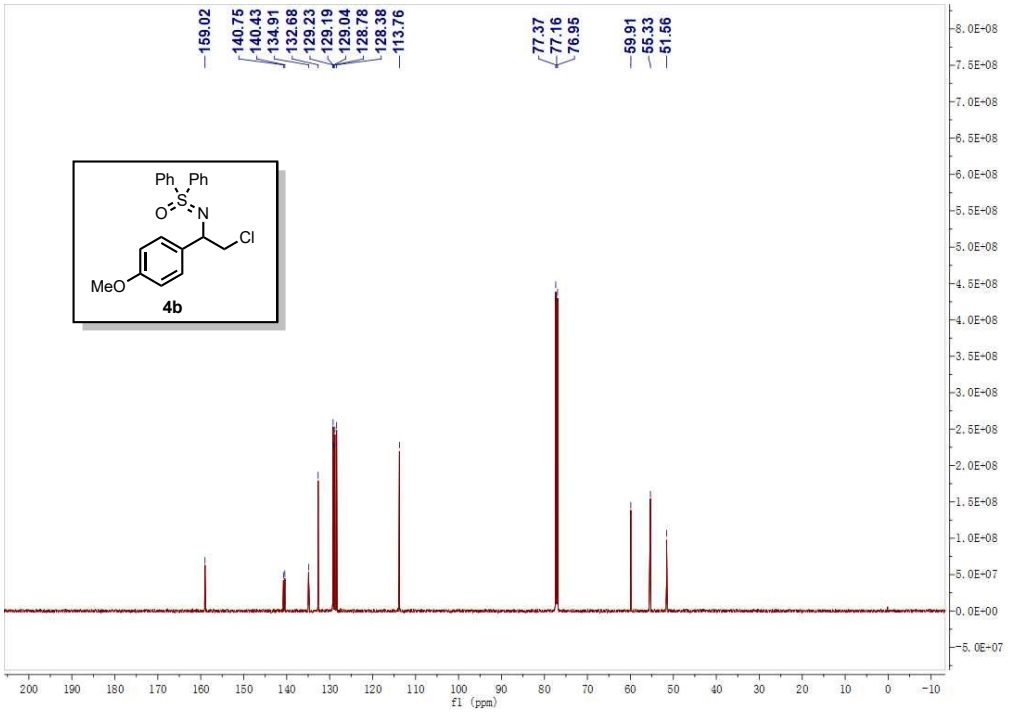

Figure S52. ^{13}C NMR of **4b**.

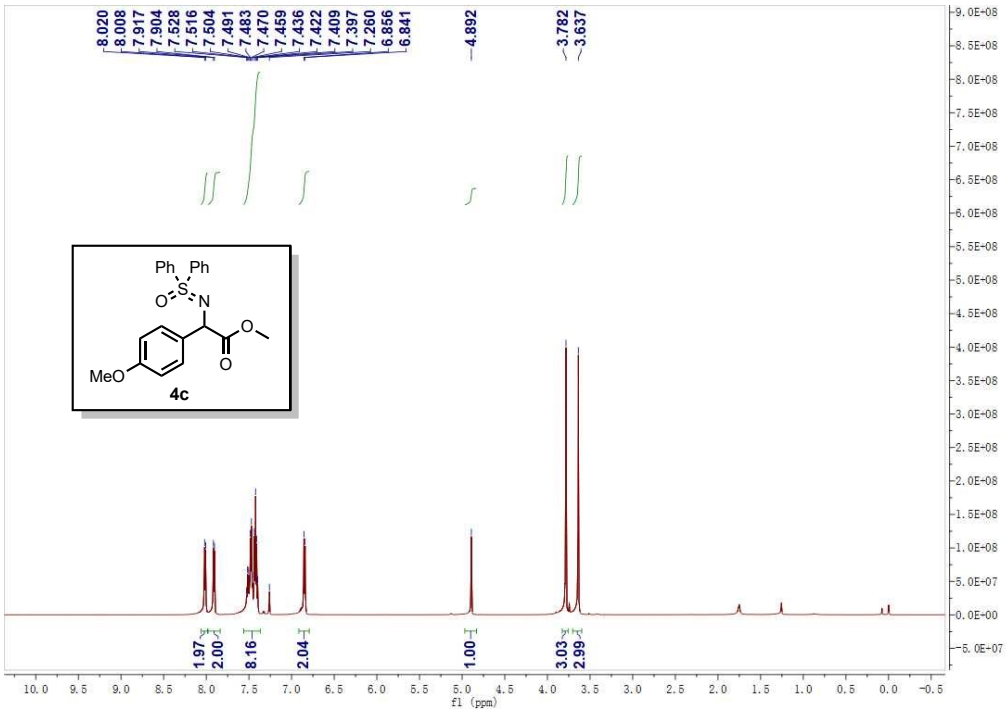

Figure S53. ^{1}H NMR of **4c**.

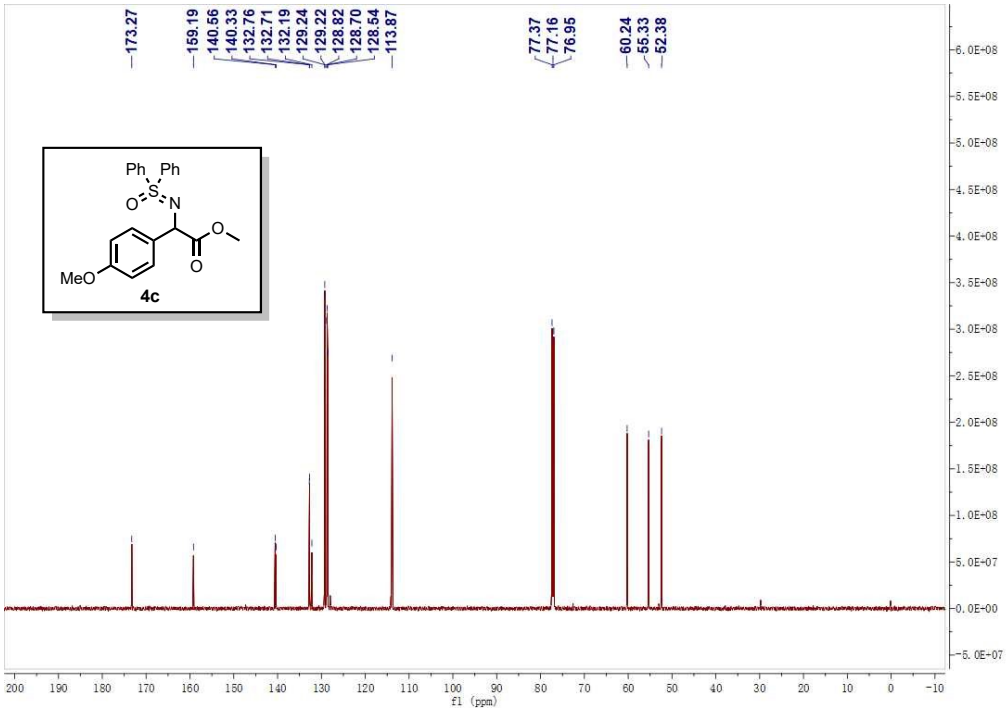

Figure S54. ^{13}C NMR of **4c**.

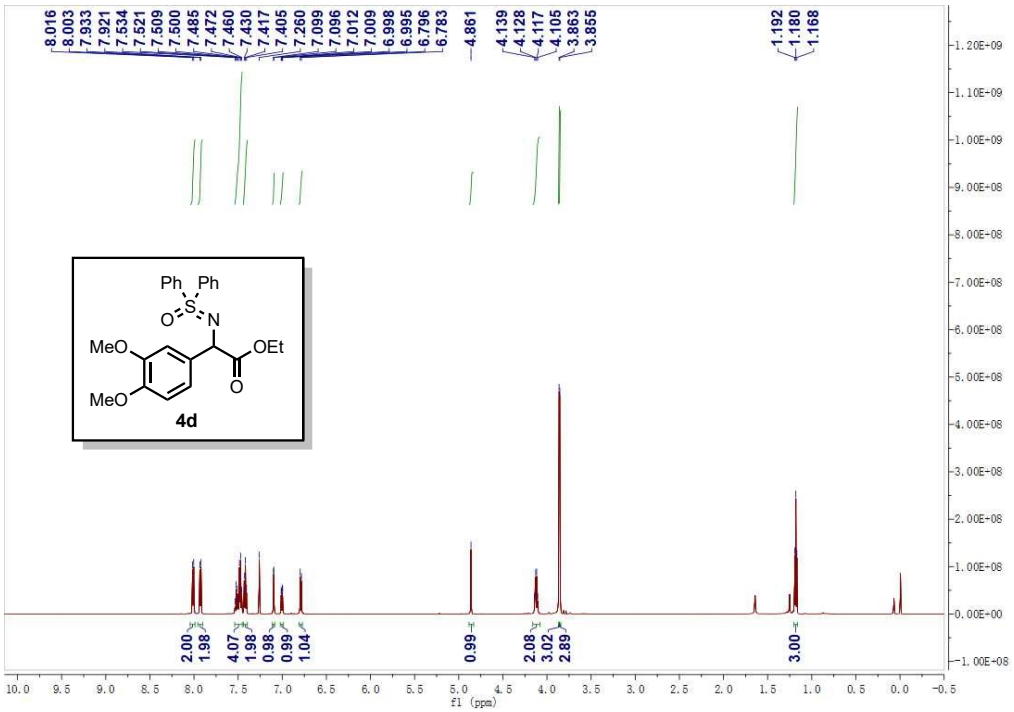

Figure S55. ^{1}H NMR of **4d**.

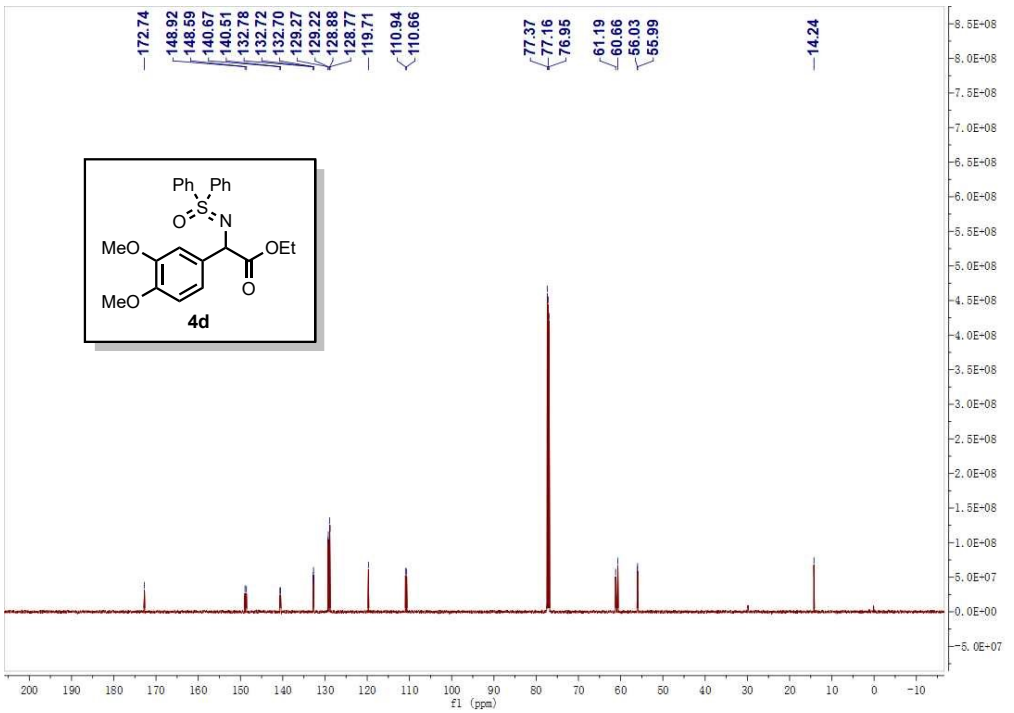

Figure S56. ^{13}C NMR of **4d**.

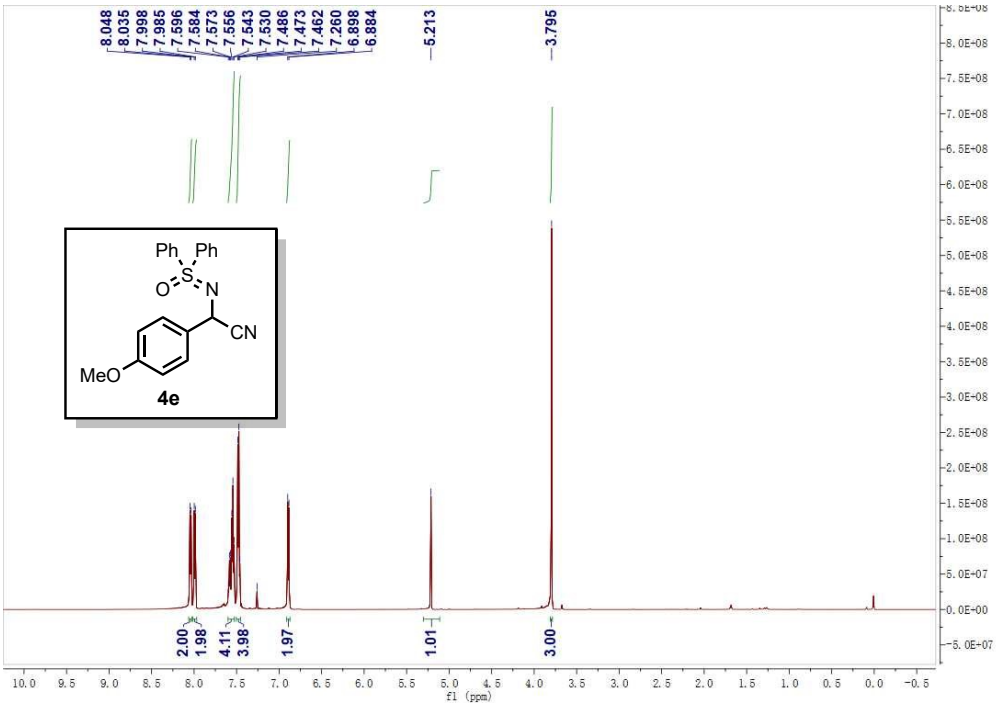

Figure S57. ^{1}H NMR of **4e**.

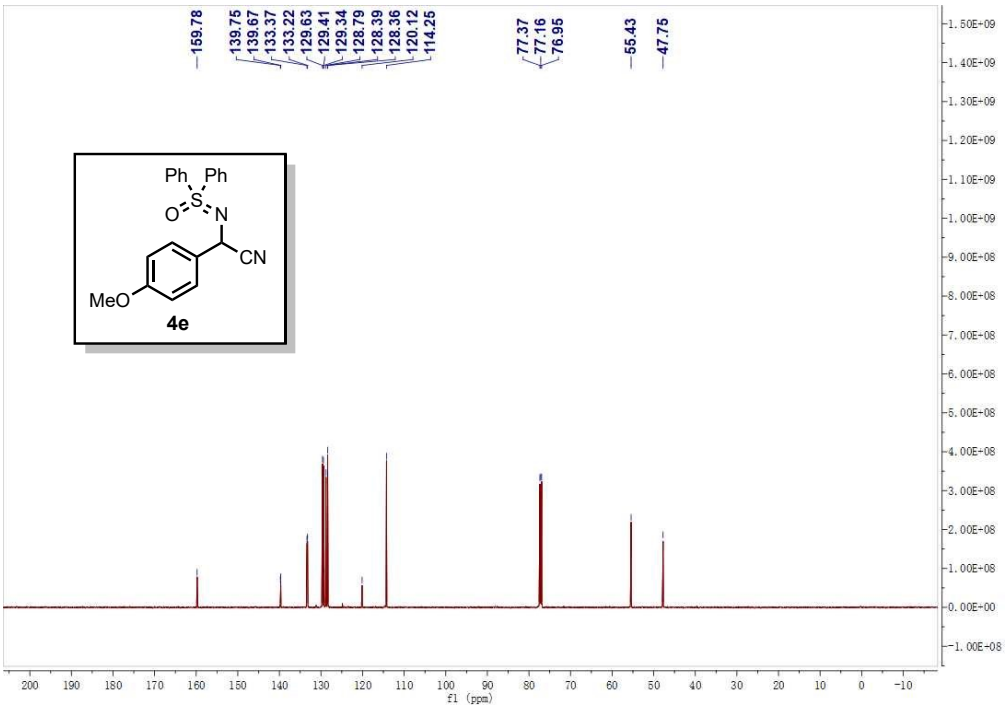

Figure S58. ^{13}C NMR of **4e**.

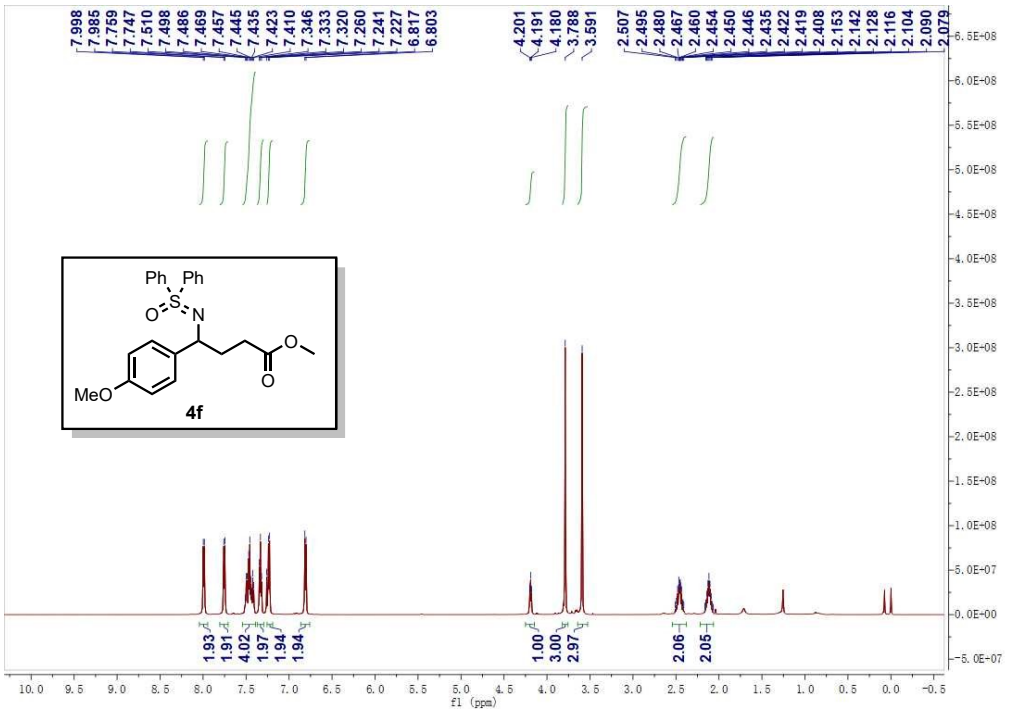

Figure S59. ^{1}H NMR of **4f**.

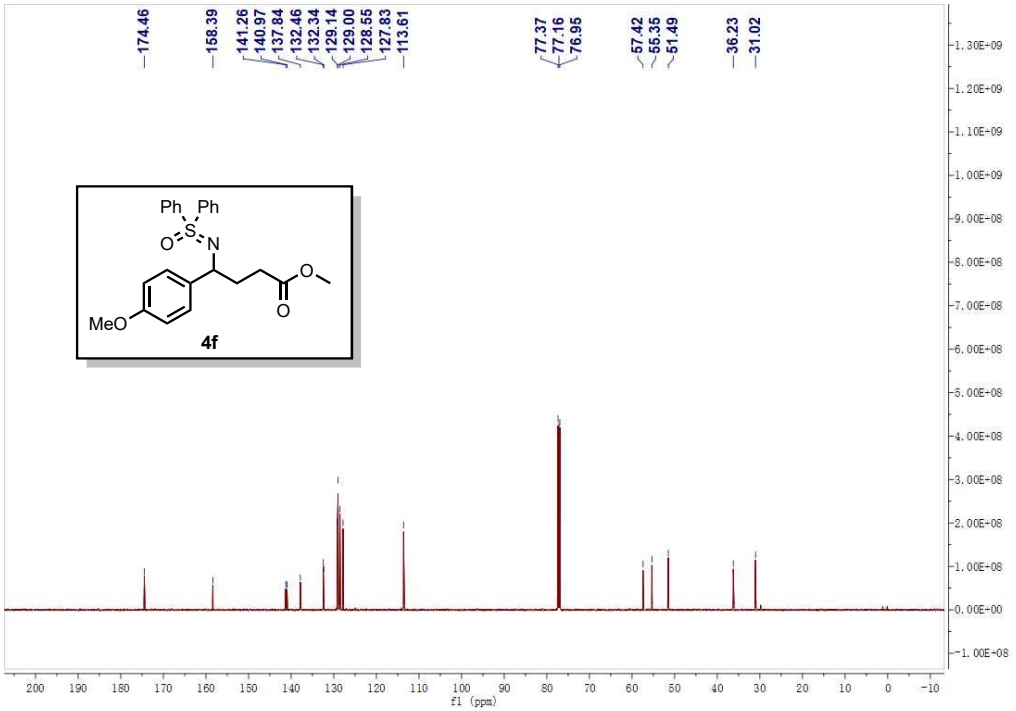

Figure S60. ^{13}C NMR of **4f**.

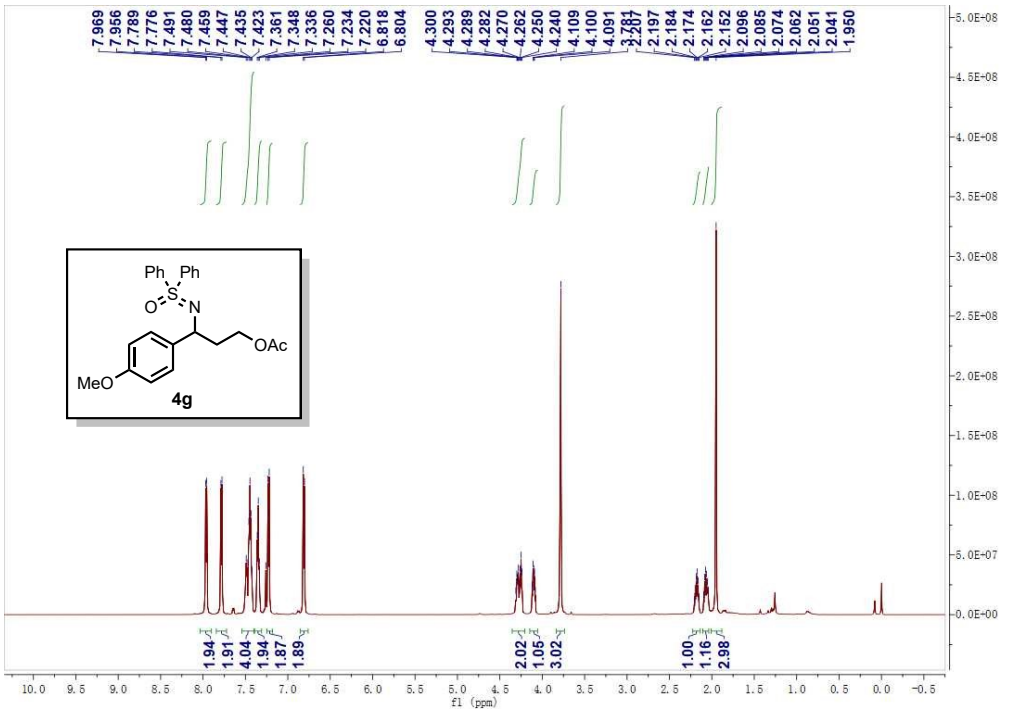

Figure S61. ^{1}H NMR of **4g**.

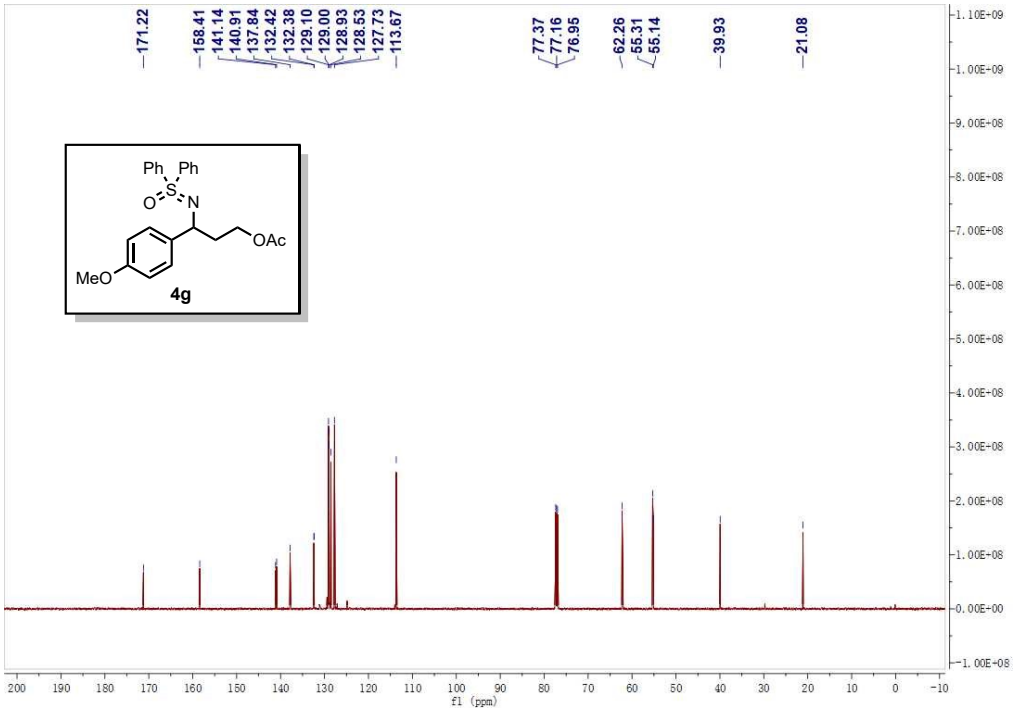

Figure S62. ^{13}C NMR of **4g**.

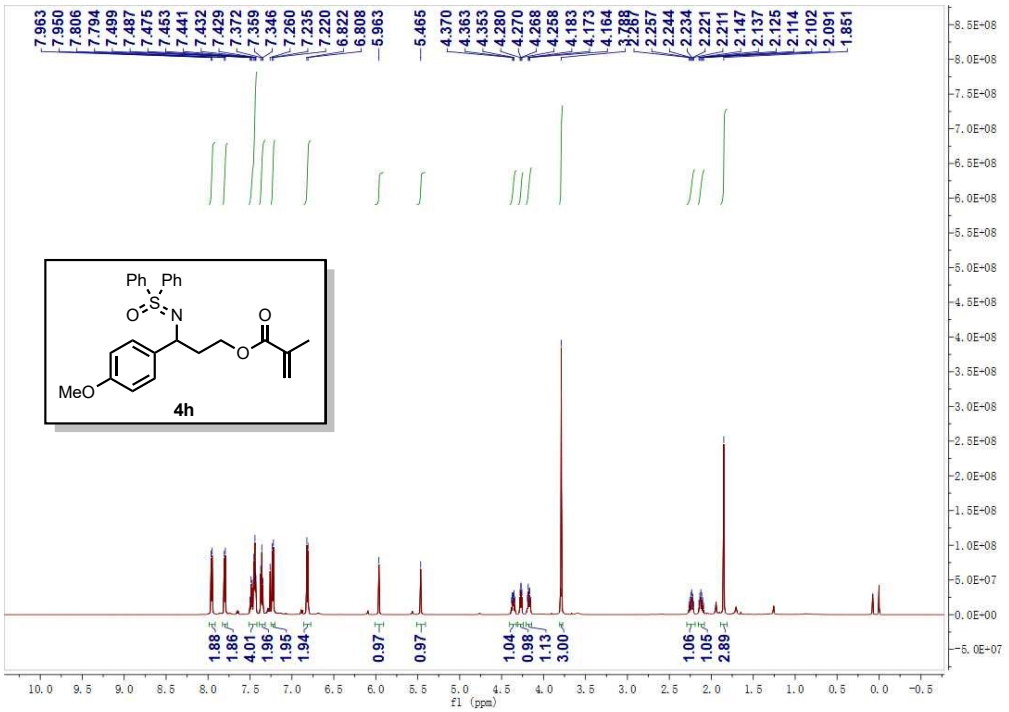

Figure S63. ^{1}H NMR of **4h**.

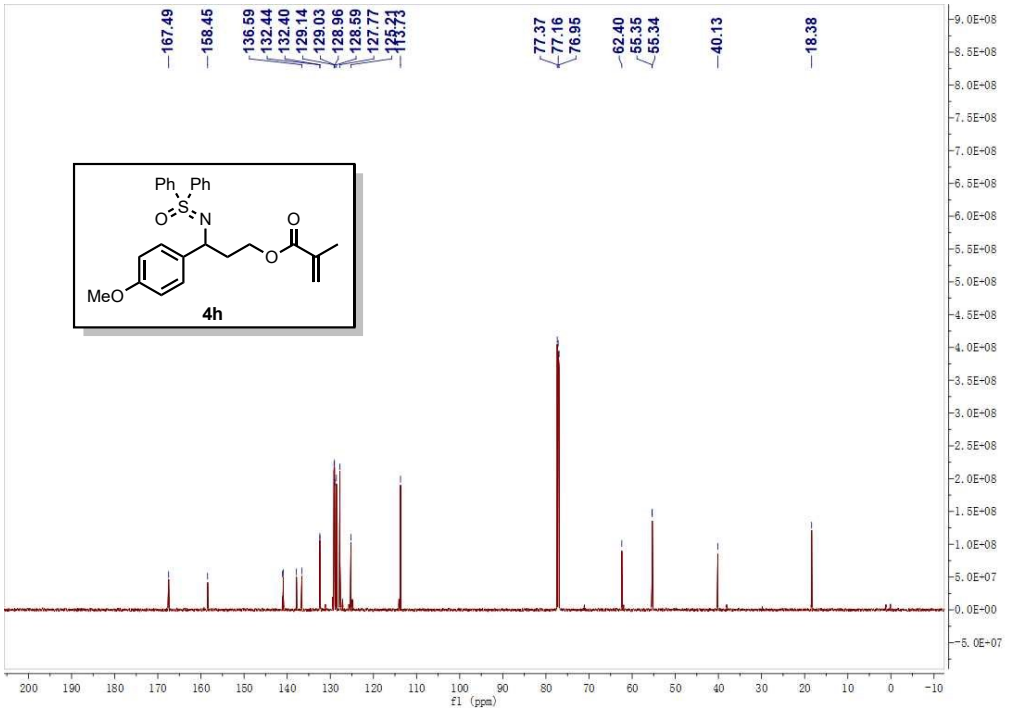

Figure S64. ^{13}C NMR of **4h**.

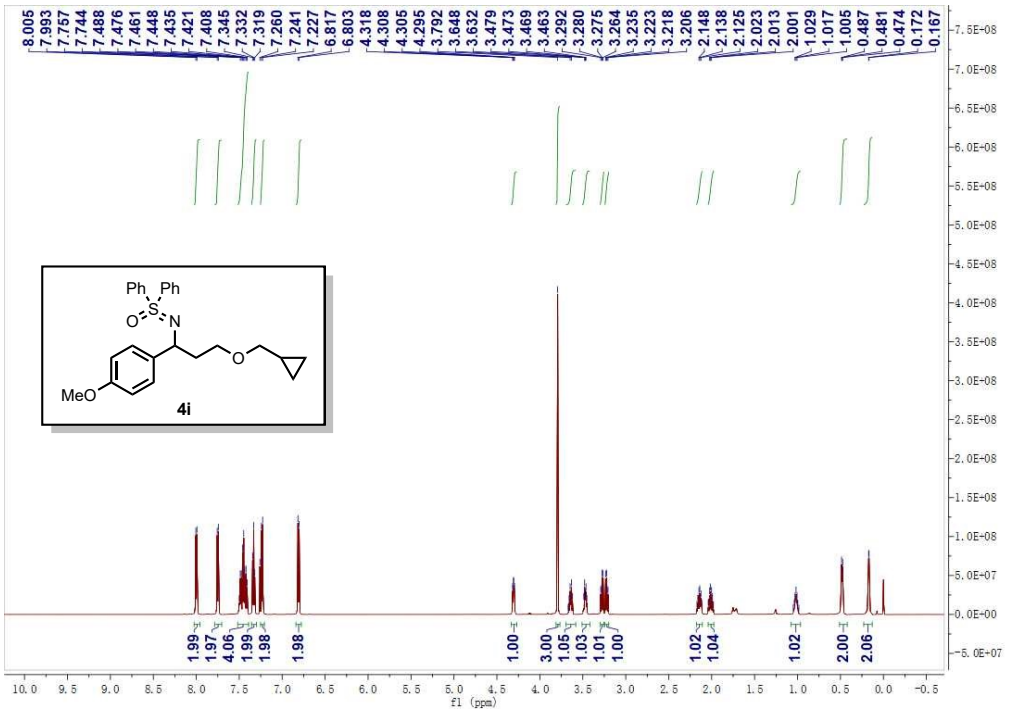

Figure S65. ^{1}H NMR of **4i**.

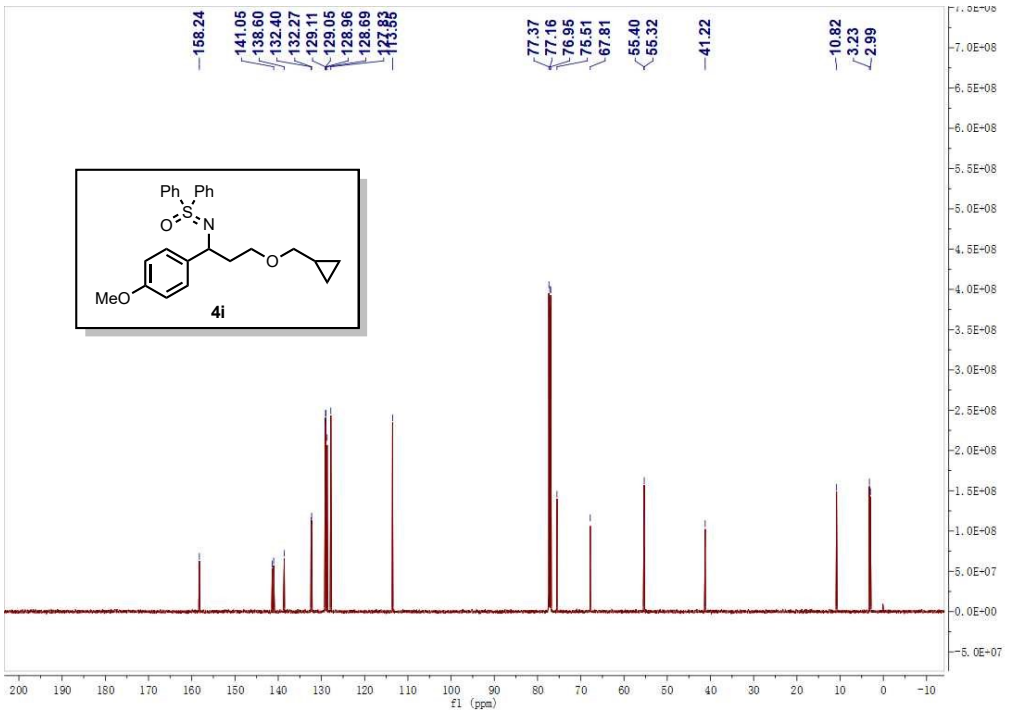

Figure S66. ^{13}C NMR of **4i**.

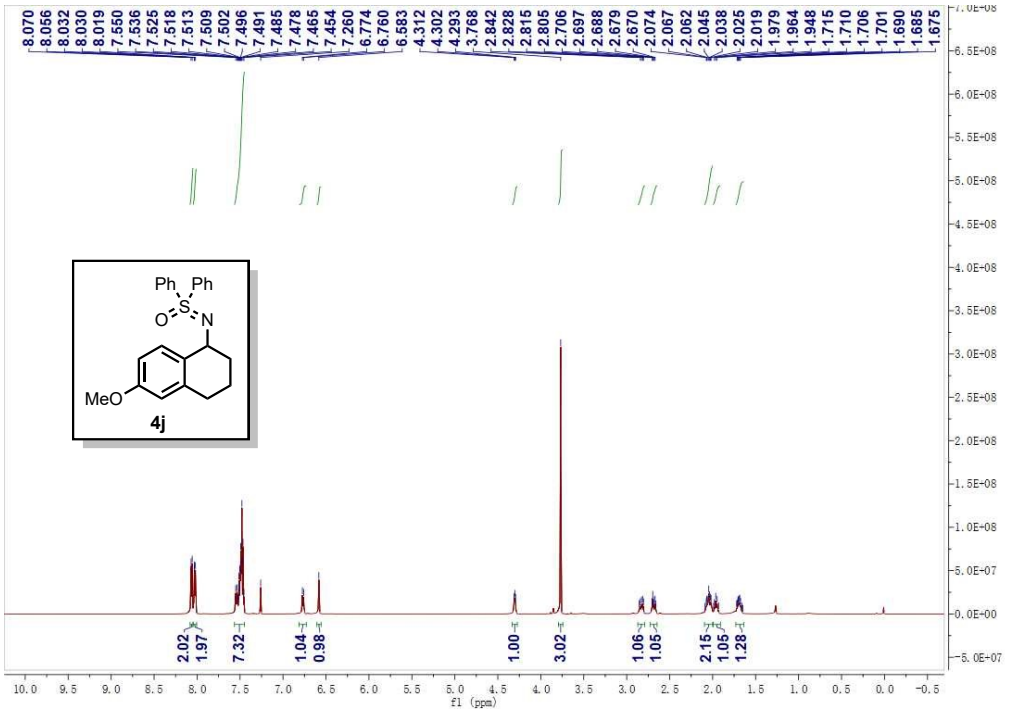

Figure S67. ^{1}H NMR of **4j**.

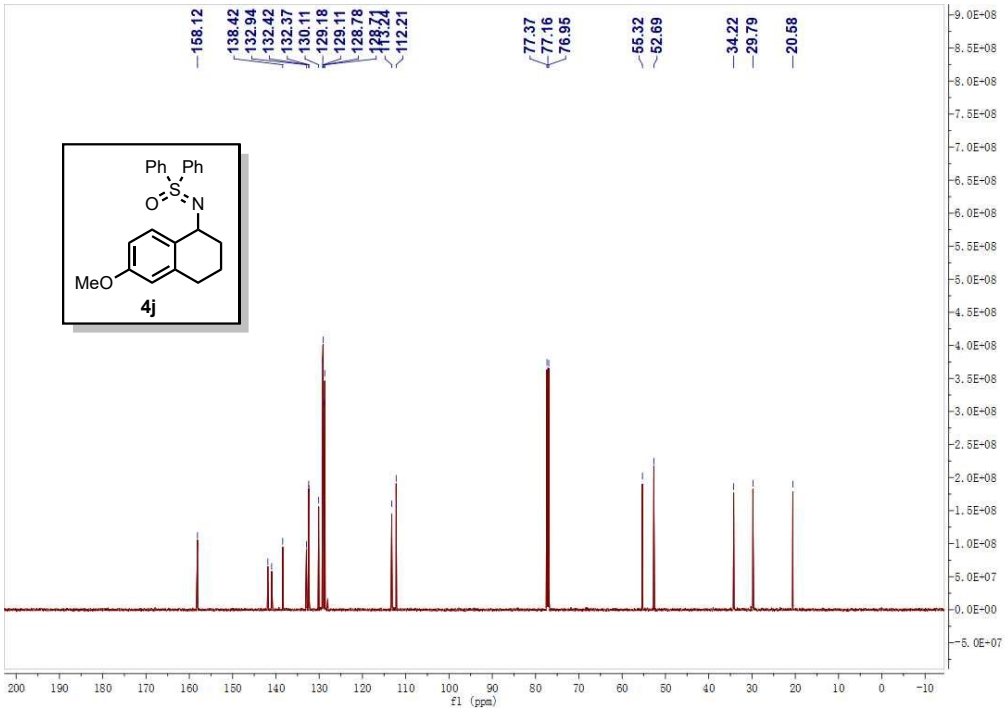

Figure S68. ^{13}C NMR of **4j**.

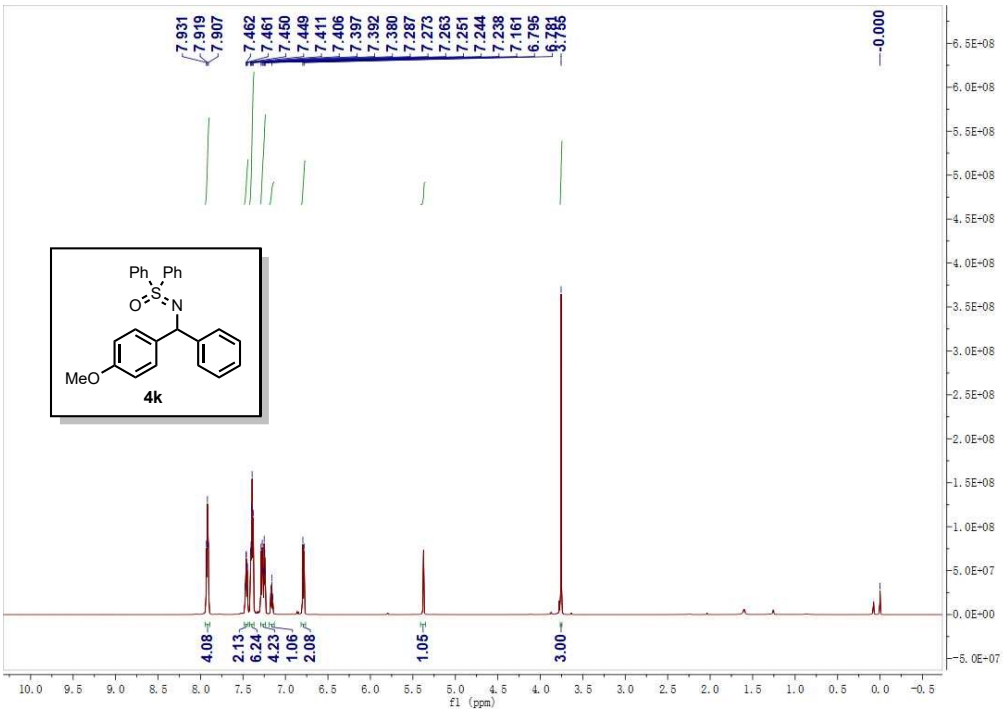

Figure S69. ^{1}H NMR of **4k**.

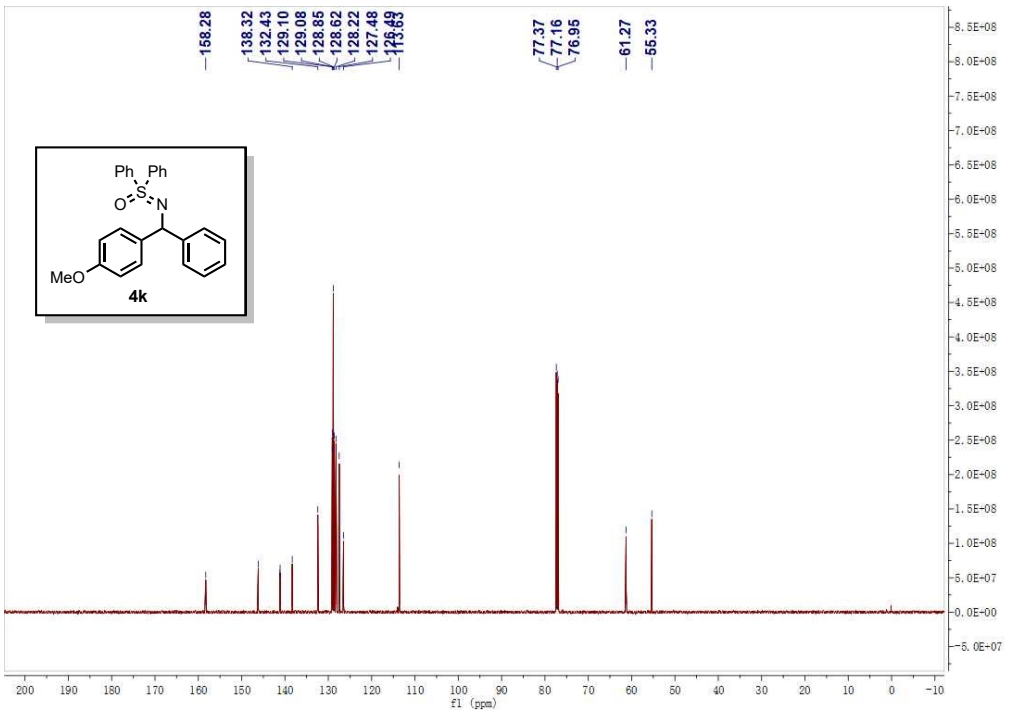

Figure S70. ^{13}C NMR of **4k**.

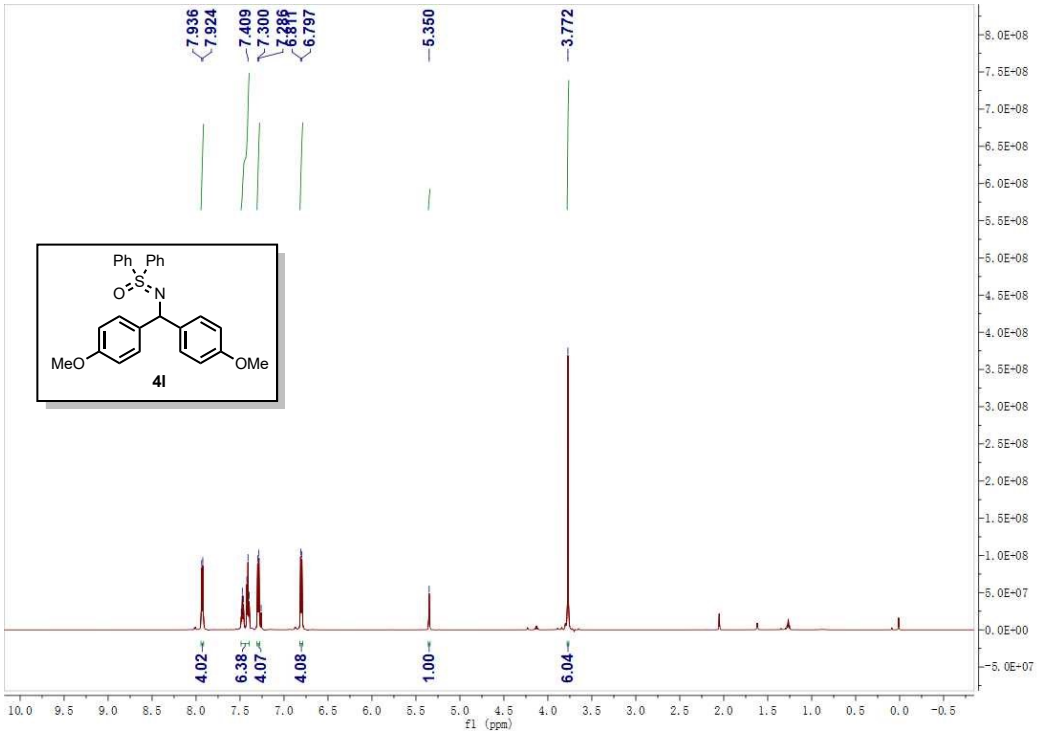

Figure S71. ^{1}H NMR of **4l**.

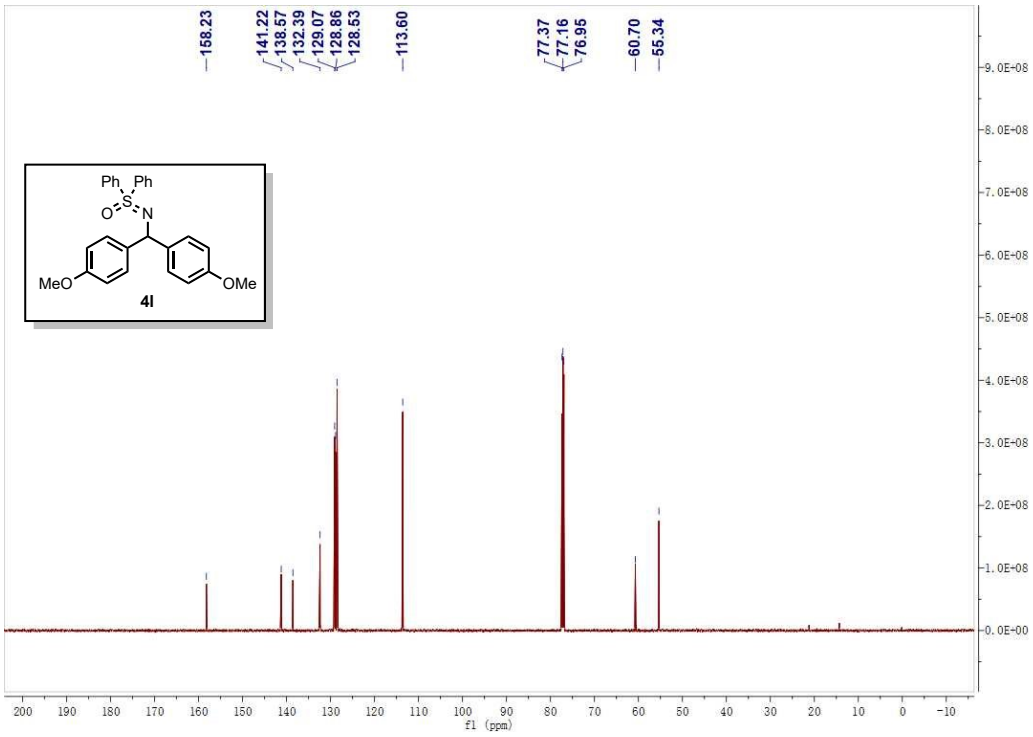

Figure S72. ^{13}C NMR of **4l**.

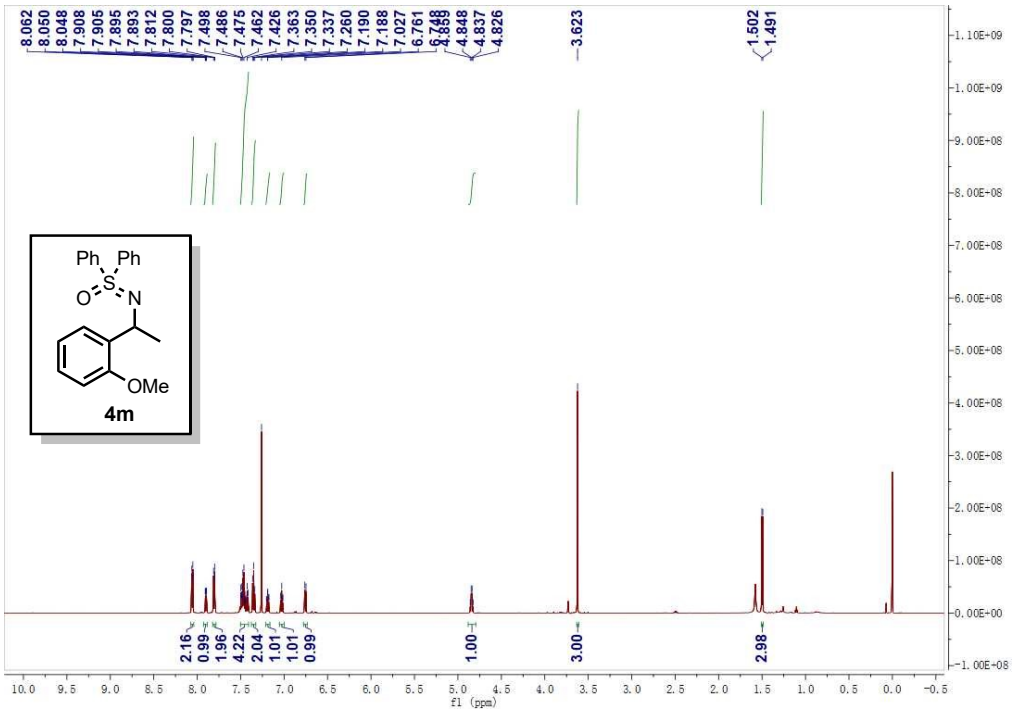

Figure S73. ^{1}H NMR of **4m**

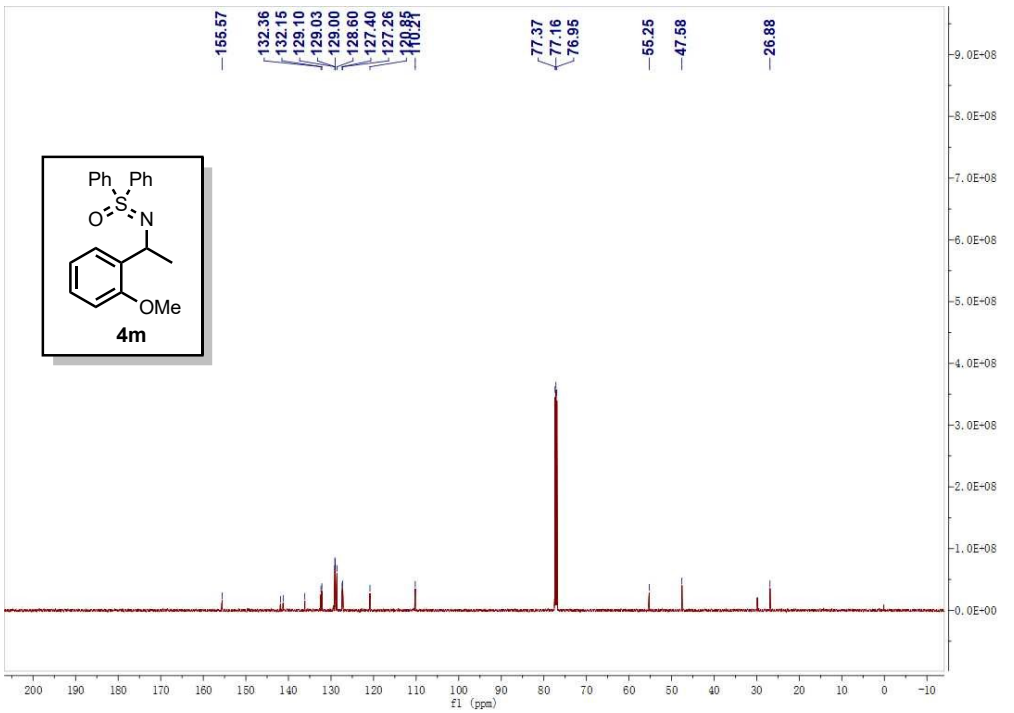

Figure S74. ^{13}C NMR of **4m**.

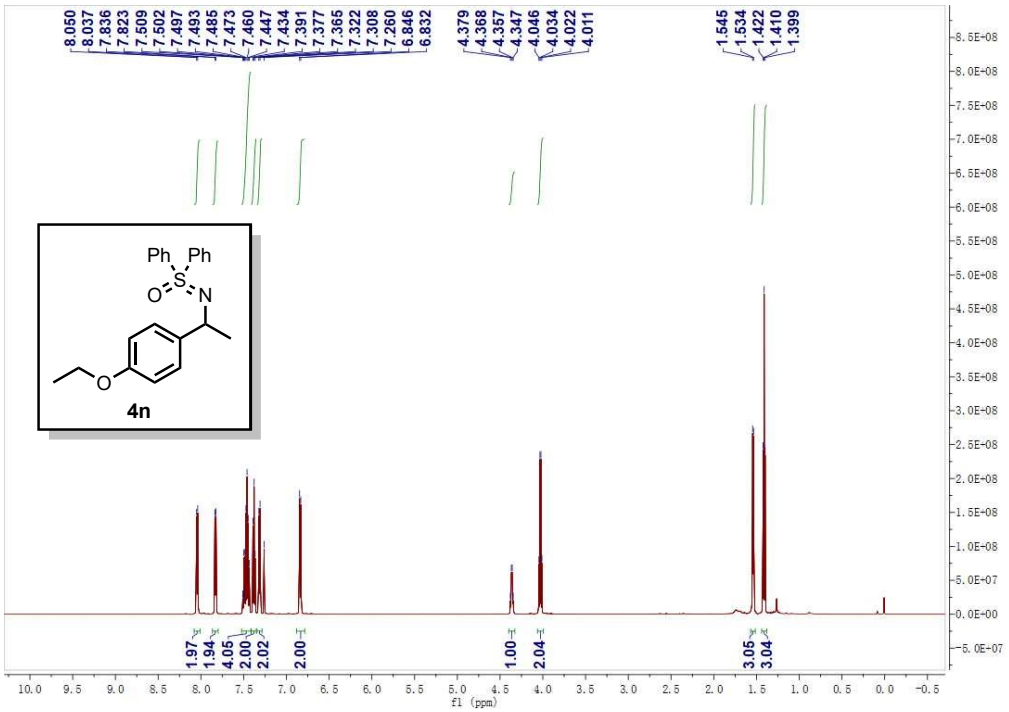

Figure S75. ^{1}H NMR of **4n**.

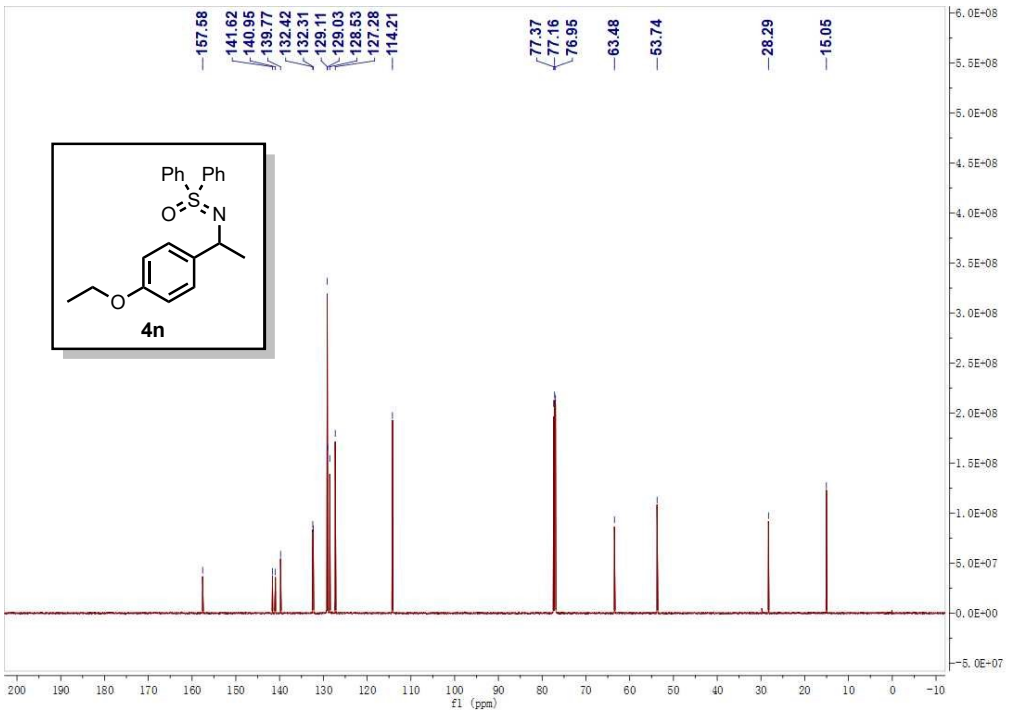

Figure S76. ^{13}C NMR of **4n**.

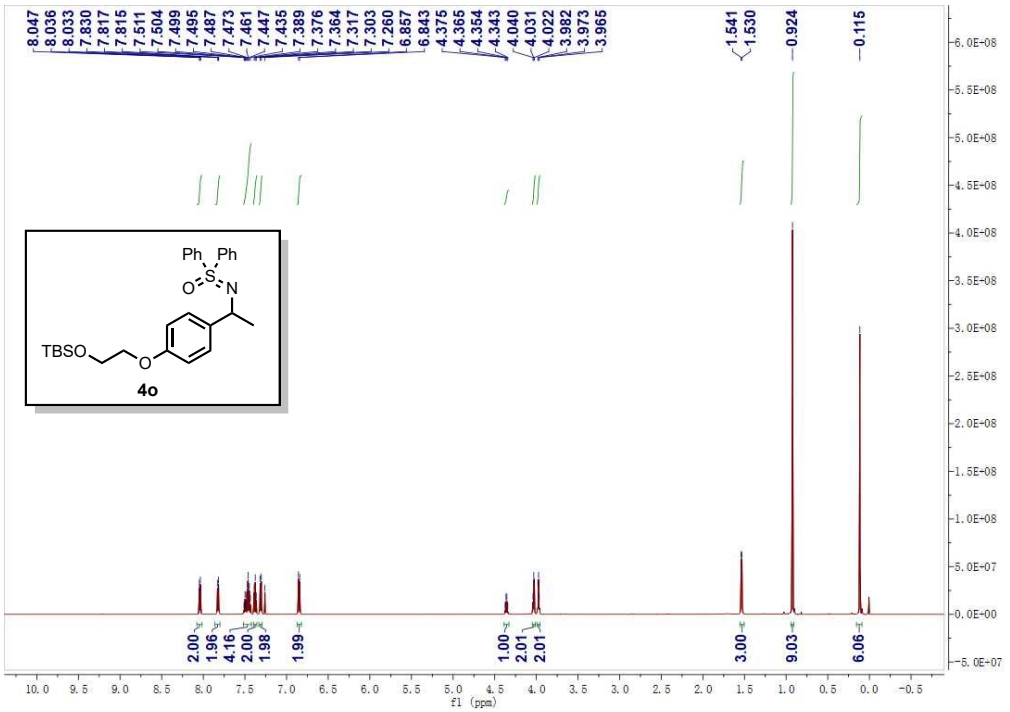

Figure S77. ^{1}H NMR of **4o**.

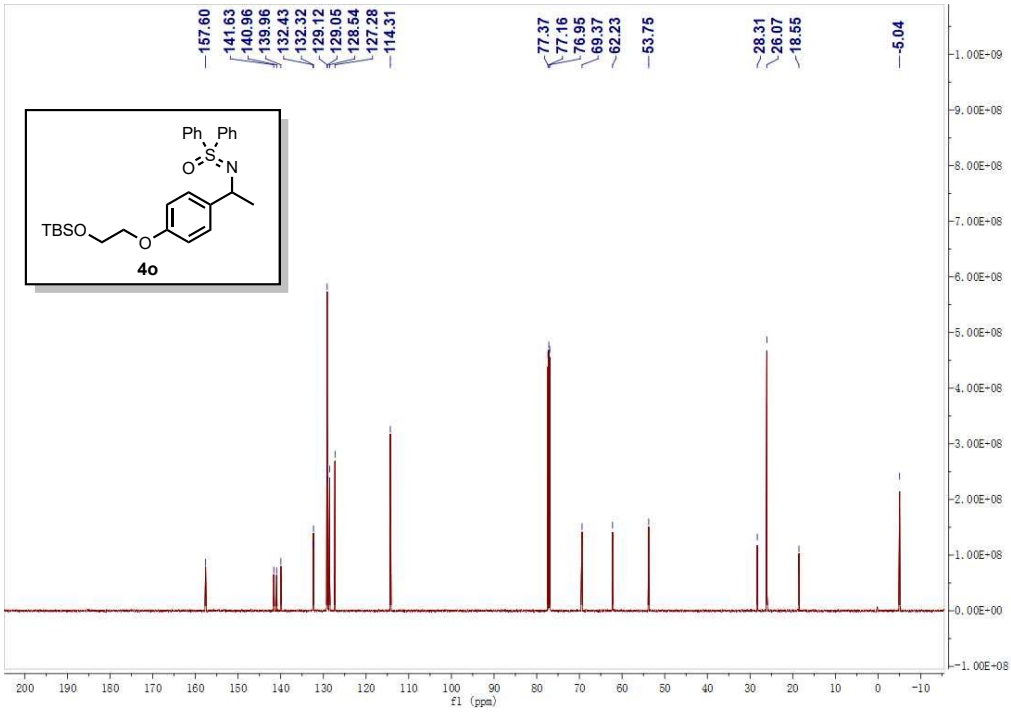

Figure S78. ^{13}C NMR of **4o**.

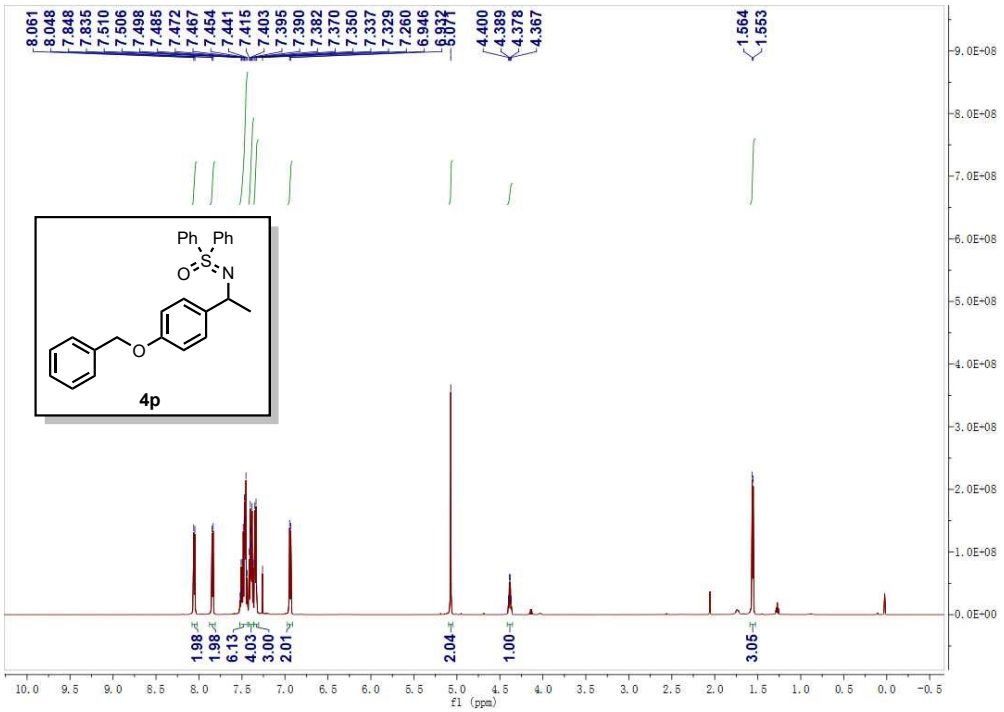

Figure S79. ^{1}H NMR of **4p**.

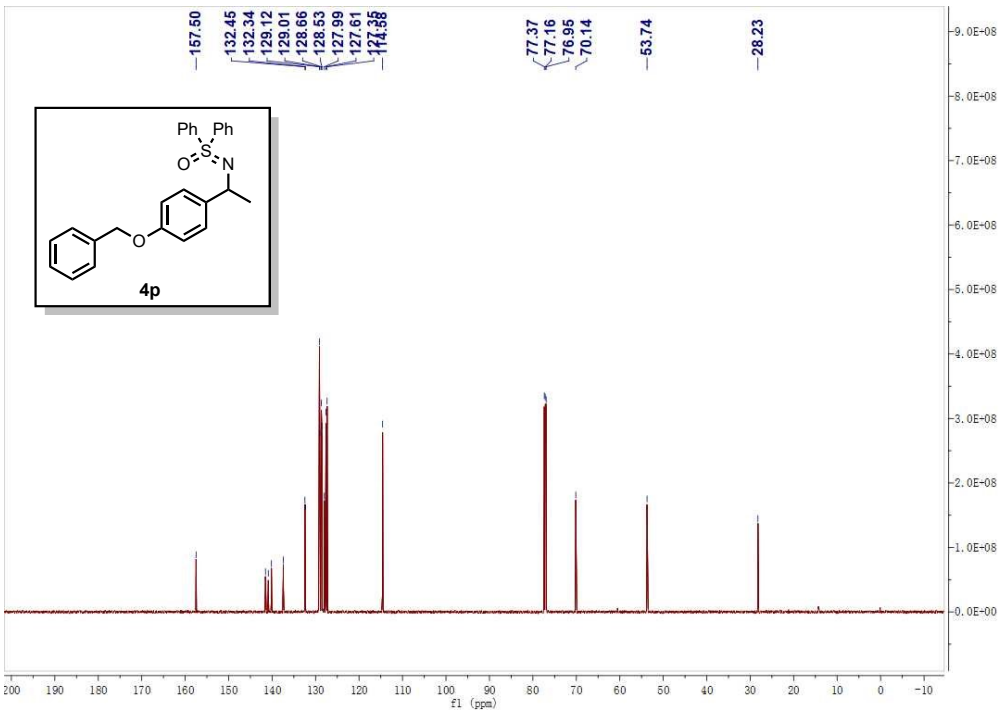

Figure S80. ^{13}C NMR of **4p**.

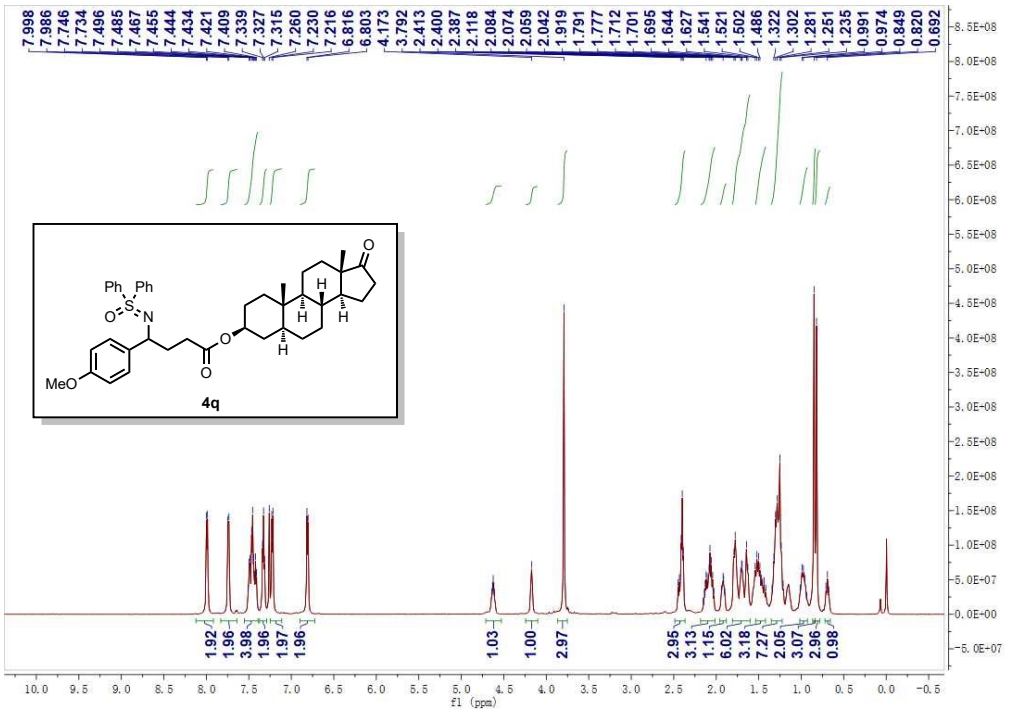

Figure S81. ^{1}H NMR of **4q**.

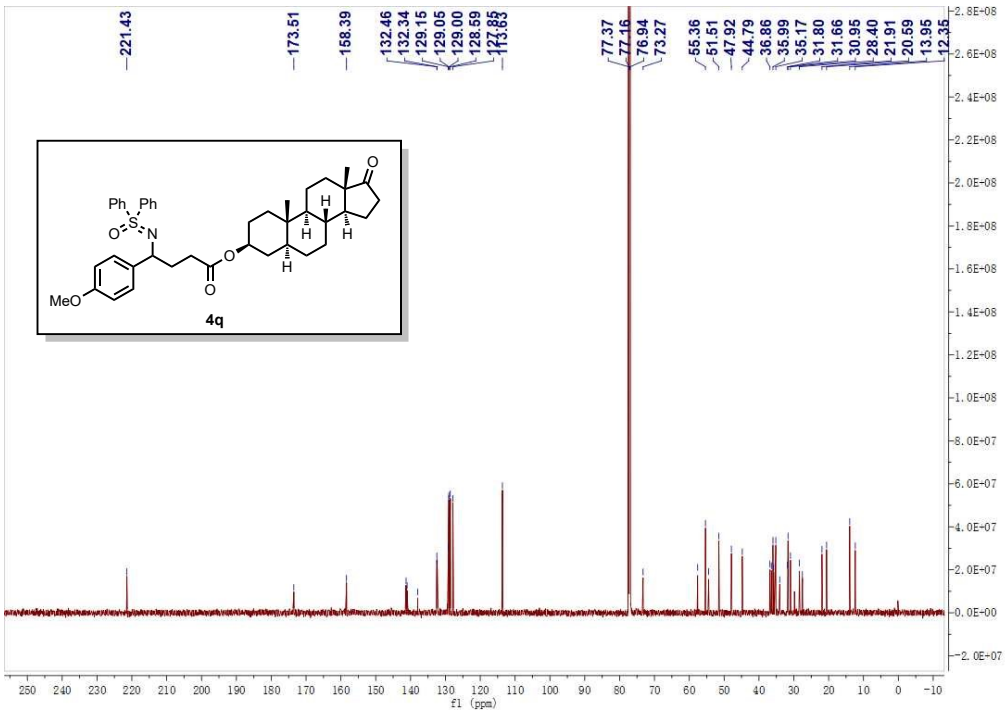

Figure S82. ^{13}C NMR of **4q**.

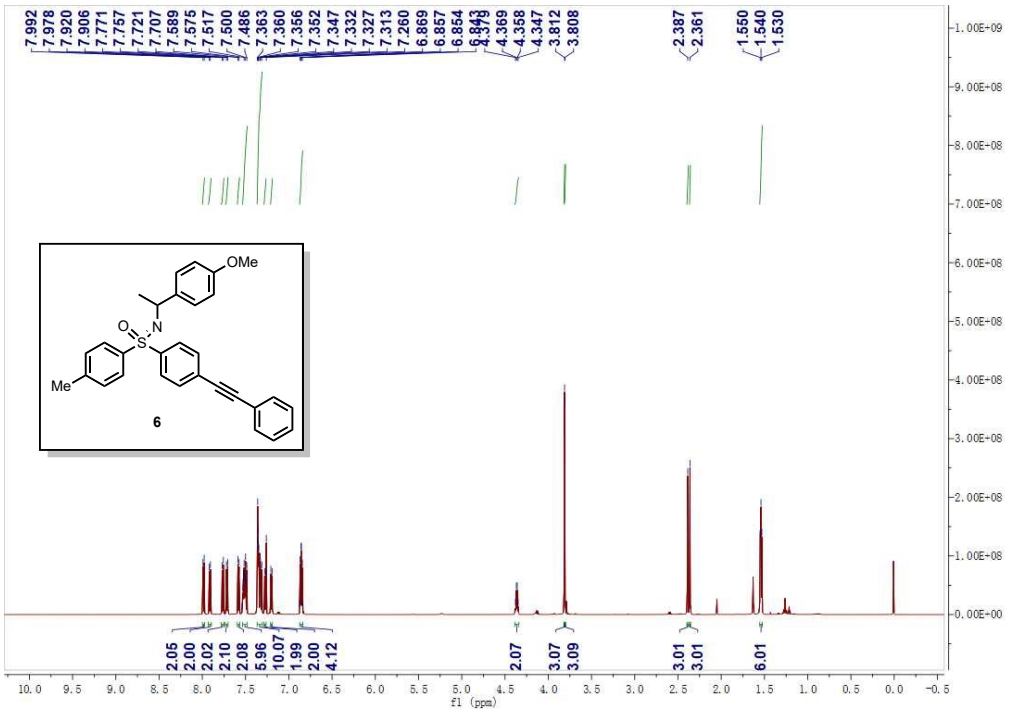

Figure S83. ^{1}H NMR of **6**.

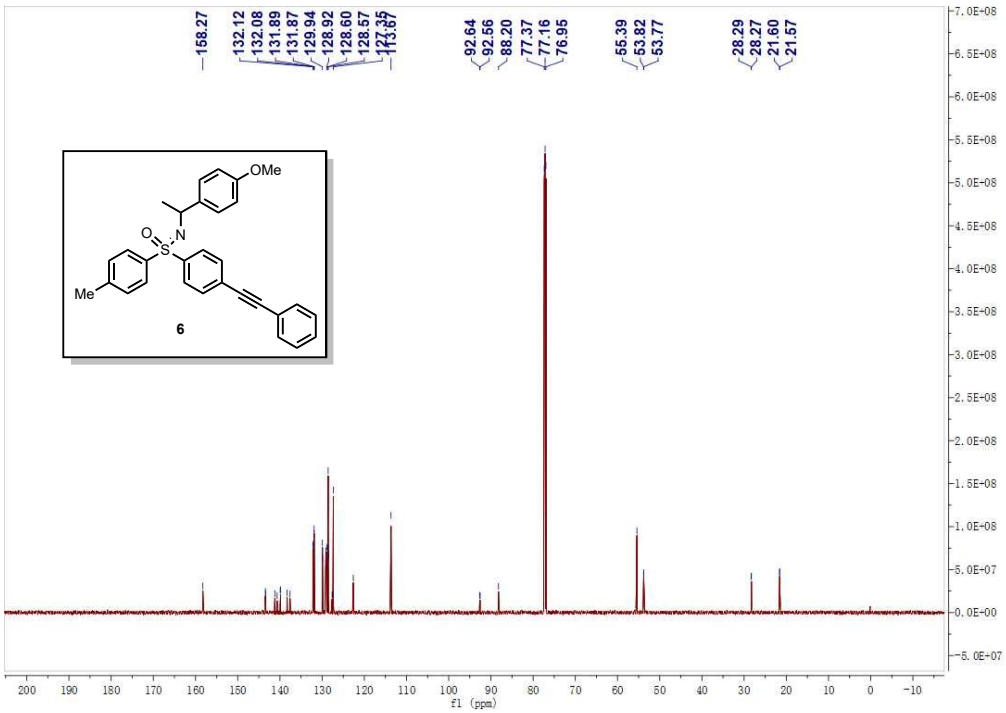

Figure S84. ^{13}C NMR of **6**.

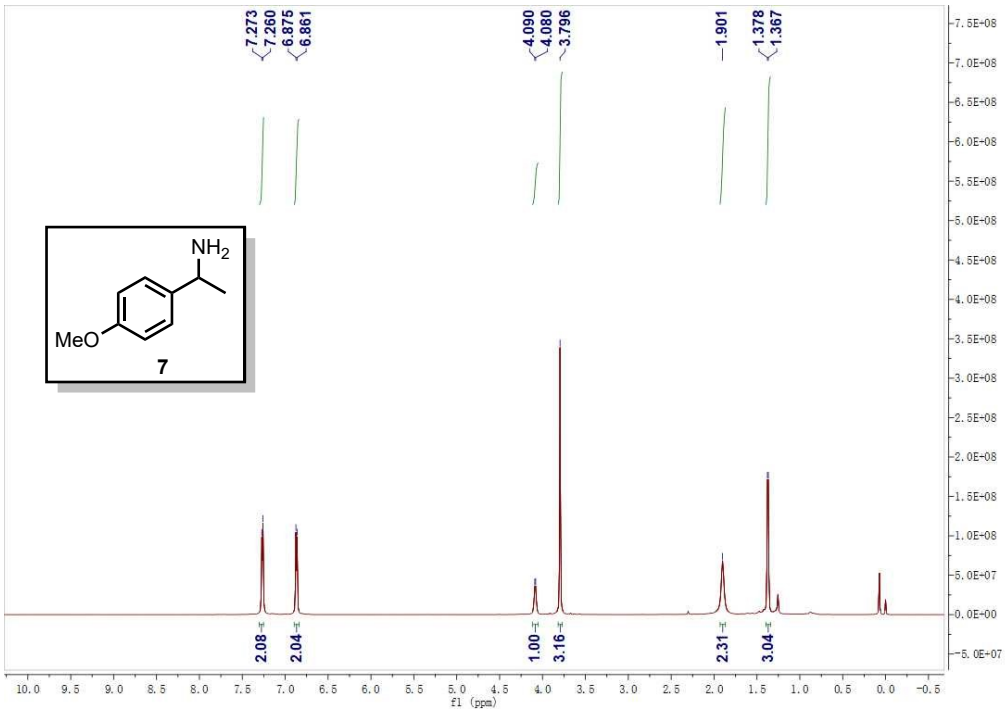

Figure S85. ^{1}H NMR of **7**.

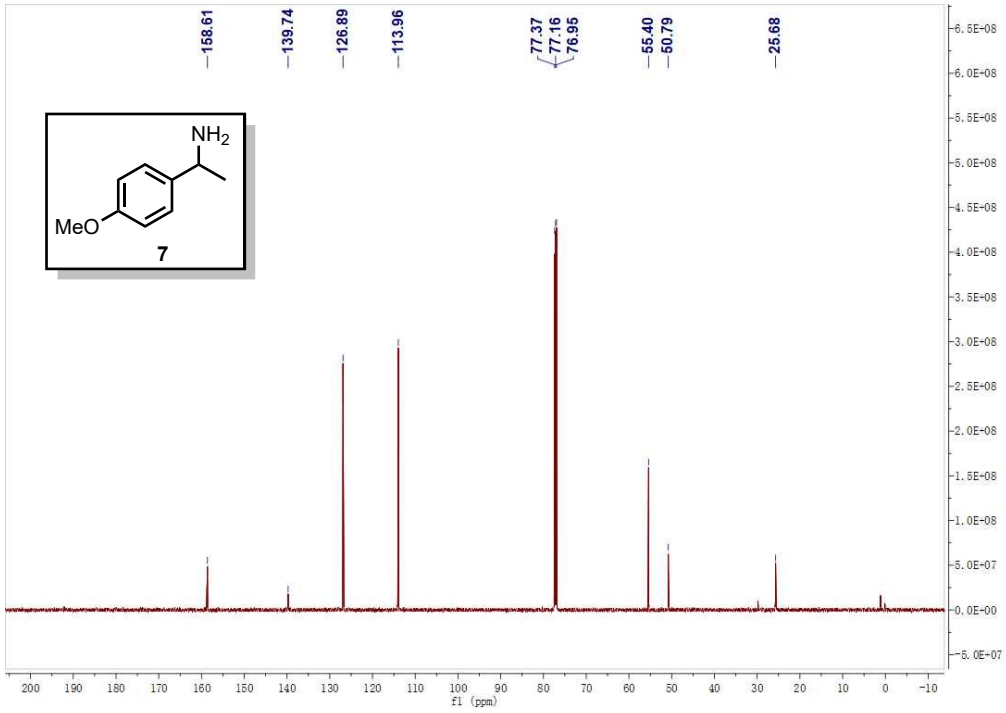

Figure S86. ^{13}C NMR of **7**.

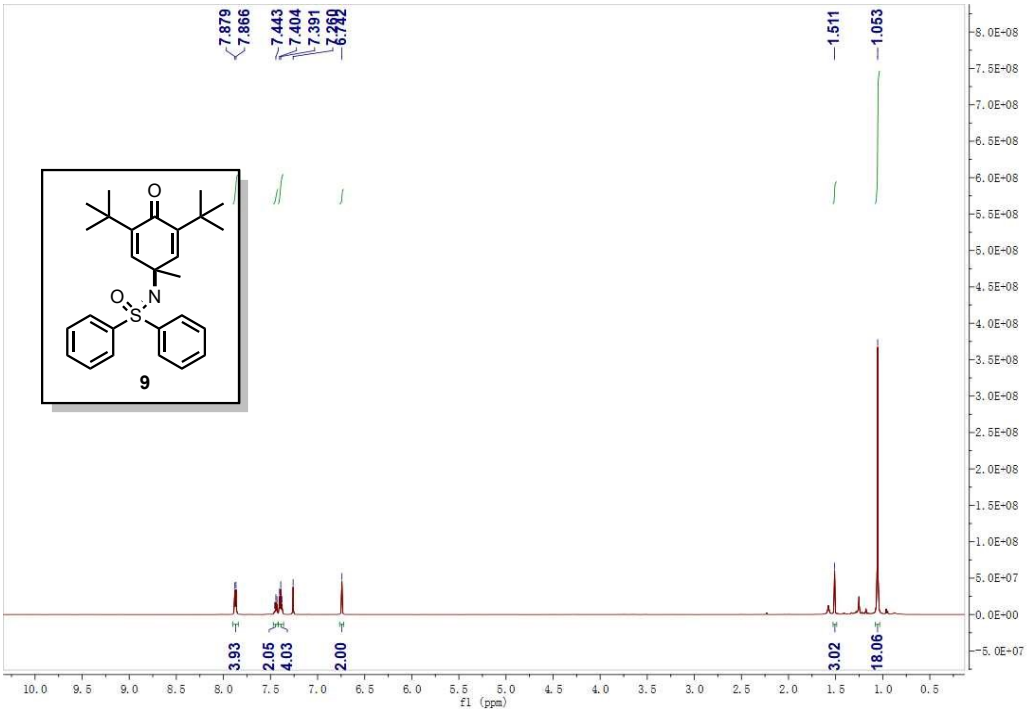

Figure S87. ^{1}H NMR of **9**.

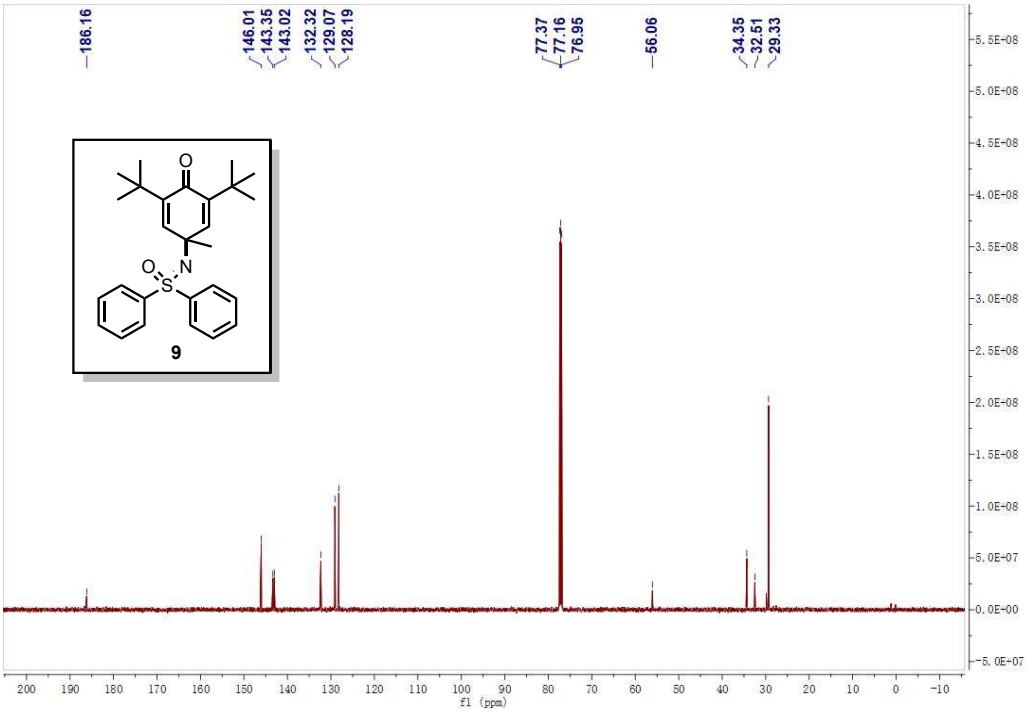

Figure S88. ^{1}H NMR of **9**.