

Supporting Information

Ultrafast N-Arylation of Sulfoximines Enabled by Micellar Catalysis in Water

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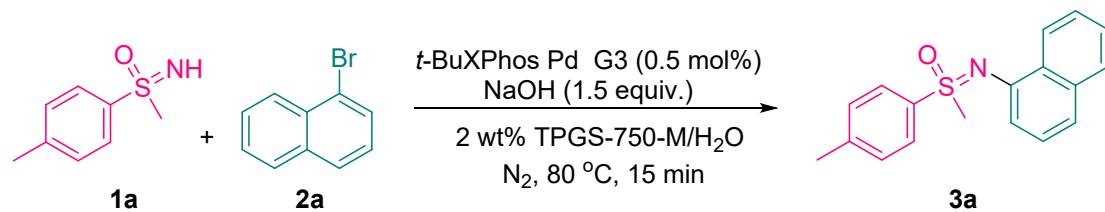
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1. General information

All commercially available reagents are used without further purification. All precatalysts were purchased from commercial sources. Compound **1a**, **1c**, **1d**, **1e**, **1f**, **1g**, **1h**, **1j**, **1k**, **1l** was prepared according to reported literature procedure.¹ TPGS-750-M was synthesized according to Lipshutz's work.² ¹H NMR and ¹³C NMR were recorded on a 400 MHz Bruker spectrometer (400 MHz for ¹H NMR and 100 MHz for ¹³C NMR). Chemical shifts (δ) of ¹H NMR and ¹³C NMR are reported in ppm relative to TMS and the residual solvent peak were converted to the TMS scale (CDCl₃: δ H = 7.26 ppm, δ C = 77.16 ppm, H₂O: δ H: 1.56; DMSO-d₆: δ H = 2.50 ppm, δ C = 39.52 ppm, H₂O: δ H: 3.33). The coupling constants (J) are in Hertz (Hz). The used abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), ddd (doublet of doublet of doublets), dt (doublet of triplets), td (triplet of doublets), tt (triplet of triplets), qd (quartet of doublets), m (multiplet). The high resolution mass spectra (HRMS) data were measured on a UHPLC Q-TOF HR-MS by means of the ESI technique. The low resolution mass spectra (LRMS) data were measured on the SHIMADZU GCMS-QP 2010 SE mass spectrometer (Kyoto, Japan) by means of EI technique. The melting points of these compounds were determined by an X-4A micro-melting point apparatus (Shanghai, China).

Table S1. Surfactant screening.^a



Entry	Variations from the standard condition	Yield[%] ^b
1	DDAB	25
2	TBAB	26
3	DODAB	28
4	Tween 80	44
5	PEG-750	36
6	1 wt% TPGS-750-M	80
7	3 wt% TPGS-750-M	82

8	2 mL 2 wt% TPGS-750-M/H ₂ O	87
9	0.5 mL 2 wt% TPGS-750-M/H ₂ O	75
10	Na'Obu, toluene, 4 h	65
11	DMF, 12 h	trace

[a] Reaction condition: **1a** (0.2 mmol), **2a** (0.2 mmol), *t*-BuXPhos-Pd-G3 (0.5 mol%), NaOH (1.5 equiv.), 2 wt% TPGS-750-M/H₂O (1 mL), N₂, 80 °C, 15 min. [b] Isolated yield.

2. Preparation of a stock solution

The catalyst solution was prepared by dissolving the corresponding precatalyst (2.5 mol%) in 200 μL THF. This stock solution was used freshly or can be stored up to a few weeks under argon in a freezer). For 0.5 mol% catalyst loading, 40 μL of this stock solution was used.

3. General procedure for C-N coupling

To an oven-dried 25 mL schlenk tube with a magnetic stir bar was added NH-sulfoximine **1** (0.2 mmol), NaOH (1.5 equiv.), and TPGS-750-M (2 wt%, 1 mL) aqueous solution. Then, aryl bromide **2** (1.0 equiv.) was added to the solution. The tube was sealed with rubber septum, evacuated, and backfilled with nitrogen three times. Subsequently, 40 μL *t*-BuXPhos-Pd-G3 (0.5 mol%, 4% THF) were added to the previous solution by syringe. Then the reaction was placed into an oil bath and stirred (1000-1500 rpm) at 80 °C for 15 min. The schlenk tube was removed from oil bath and allowed to cool to room temperature. Ethyl acetate (250 μL) was added to the schlenk tube and stirred briefly. Stirring was halted and after separation, the organic layer was removed via pipette. An additional extraction was performed with ethyl acetate (125 μL). The organic layers were combined, and dried with Na₂SO₄. Volatiles were removed under vacuum, and the crude residue was purified by silica gel column chromatography to give the product **3a-4k**.

4. Reaction Process monitoring the yield versus the reaction time

To three oven-dried 25 mL schlenk tubes with a magnetic stir bar were added imino(methyl)(*p*-tolyl)-λ⁶-sulfanone **1a** (0.2 mmol, 34 mg), NaOH (1.5 equiv.), and TPGS-750-M (2 wt%, 1 mL) aqueous solution. Then, 4-bromophenyl methyl sulfone

2i (0.2 mmol, 48 mg) was added to the solution. The three tubes were sealed with rubber septum, evacuated, and backfilled with nitrogen three times. Subsequently, 40 μ L *t*-BuXPhos-Pd-G3 (0.5 mol%, 4% THF) were added to the previous solution by syringe. Then the three reactions were placed into an oil bath and stirred (1000-1500 rpm) at 80 °C for 5 min, 10 min, 15 min, respectively. The three schlenk tubes were removed from oil bath and allowed to cool to room temperature. Ethyl acetate (250 μ L) was added to the three schlenk tubes and stirred briefly. Stirring was halted and after separation, the organic layer was removed via pipette. An additional extraction was performed with ethyl acetate (125 μ L). The organic layes were combined, and dried with Na₂SO₄. Volatiles were removed under vacuum, and the crude residue was purified by silica gel column chromatography to give the product **3i**.

5. Synthesis of bisulffoximines

To an oven-dried 25 mL schlenk tube with a magnetic stir bar was added imino(methyl)(*p*-tolyl)-λ⁶-sulfanone **1a** (0.4 mmol, 68 mg), NaOH (1.5 equiv.), and TPGS-750-M (2 wt%, 2 mL) queous solution. Then, 4,4'-dibromobiphenyl **2q** (0.2 mmol, 63 mg) was added to the solution. The tube was sealed with rubber septum, evacuated, and backfilled with nitrogen three times. Subsequently, 80 μ L *t*-BuXPhos-Pd-G3 (0.5 mol%, 1.6 mg) was added to the previous solution by syringe. Then the reaction was placed into an oil bath and stirred (1000-1500 rpm) at 80 °C for 0.5 h. The schlenk tube was removed from oil bath and allowed to cool to room temperature. Ethyl acetate (250 μ L) was added to the schlenk tube and stirred briefly. Stirring was halted and after separation, the organic layer was removed via pipette. An additional extraction was performed with ethyl acetate (125 μ L). The organic layes were combined, and dried with Na₂SO₄. Volatiles were removed under vacuum, and the crude residue was purified by silica gel column chromatography to give the product **5a**.

6. Gram-Scale synthesis of **3e**

To an oven-dried 100 mL schlenk tube with a magnetic stir bar was added 1.016 g imino(methyl)(*p*-tolyl)-λ⁶-sulfanone **1a** (6.0 mmol, 1.0 equiv.), 360 mg NaOH (1.5 equiv.), and TPGS-750-M (30 mL, 2 wt%) queous solution. Then, 24.0 mg *t*-BuXPhos-

Pd-G3 and 3'-bromoacetophenone **2e** (1.0 equiv.) was added to the solution. The tube was sealed with rubber septum, evacuated, and backfilled with nitrogen three times. Then the reaction was placed into an oil bath and stirred (1000-1500 rpm) at 80 °C for 6 h. The schlenk tube was removed from oil bath and allowed to cool to room temperature. Ethyl acetate (1 mL) was added to the schlenk tube and stirred briefly. Stirring was halted and after separation, the organic layer was removed via pipette. An additional extraction was performed with ethyl acetate (0.5 mL). The organic layers were combined, and dried with Na₂SO₄. Volatiles were removed under vacuum, and the crude residue was purified by silica gel column chromatography to give the product **3e** (1.5 g).

E Factor calculations:

Note: Using the density of each liquid at 25 °C, toluene = 0.867 g/mL, water = 1.00 g/mL, dichloromethane = 1.325 g/mL, ethyl acetate = 0.897 g/mL. Additionally, the using solvents of silica gel column chromatography is NOT included as we are only considering solvents from the experimental procedure.

Previous work (Harmata³):

Solvents:

$$\begin{array}{l} 7 \text{ mL Toluene (6 g)} \\ 10 \text{ mL Dichloromethane (13.25 g)} \end{array} \quad \frac{19.25 \text{ g waste}}{0.179 \text{ g product}} = 108 \text{ E Factor}$$

This work:

Water NOT included as waste:

Solvents:

$$1.5 \text{ mL Ethyl acetate (1.35 g)} \quad \frac{1.35 \text{ g waste}}{1.5 \text{ g product}} = 0.9 \text{ E Factor}$$

Water included as waste:

Solvents:

30 mL H ₂ O (30 g)	<u>31.35 g waste</u>	= 20.9 E Factor
1.5 mL Ethyl acetate (1.35 g)	1.5 g product	

Water and base included as waste:

Solvents:

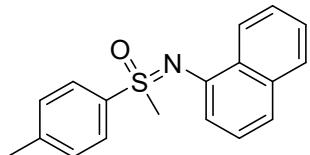
30 mL H ₂ O (30 g)		
1.5 mL Ethyl acetate (1.35 g)	<u>31.71 g waste</u>	
Base:		= 21.14 E Factor
360 mg NaOH	1.5 g product	

2 wt% TPGS-750-M/H₂O and base included as waste:

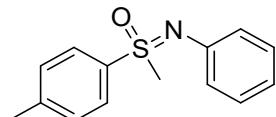
Solvents:

30 mL 2 wt% TPGS-750-M/H ₂ O (30.6 g)		
1.5 mL Ethyl acetate (1.35 g)	<u>32.31 g waste</u>	
Base:		= 21.54 E Factor
360 mg NaOH	1.5 g product	

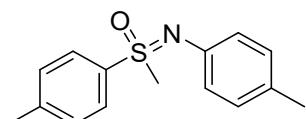
7. Characterization data of all products



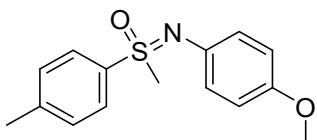
methyl(naphthalen-1-ylimino)(p-tolyl)- λ^6 -sulfanone (3a) Light yellow oil (51 mg, 87% yield), (hexane/EA = 3:1 as eluent). ¹H NMR (400 MHz, CDCl₃) δ 8.57 – 8.50 (m, 1H), 7.90 – 7.84 (m, 2H), 7.75 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.53 – 7.43 (m, 2H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.29 – 7.26 (m, 2H), 7.19 – 7.14 (m, 1H), 7.08 (dd, *J* = 7.4, 1.1 Hz, 1H), 3.33 (s, 3H), 2.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 144.3, 141.8, 136.3, 134.6, 130.3, 130.2, 128.6, 127.8, 126.1, 125.9, 125.1, 124.1, 121.5, 116.6, 46.2. HRMS (ESI) calcd for C₁₈H₁₈NOS ([M+H]⁺): 296.1104, Found: 296.1108.



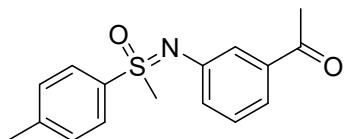
methyl(phenylimino)(*p*-tolyl)- λ^6 -sulfanone (3b)⁴ Light yellow oil (35 mg, 80% yield), (hexane/EA = 3:1 as eluent). ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.12 (t, *J* = 7.8 Hz, 2H), 7.03 – 6.98 (m, 2H), 6.86 (t, *J* = 7.3 Hz, 1H), 3.22 (s, 3H), 2.40 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 145.2, 144.2, 136.3, 130.3, 129.0, 128.7, 123.3, 121.6, 77.4, 77.1, 76.8, 46.3, 21.6. LRMS (EI): m/z calcd for C₁₄H₁₅NOS [M]⁺, 245.09; found, 244.90.



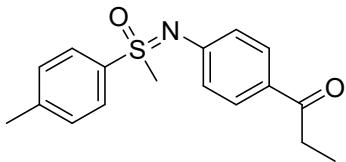
methyl(*p*-tolylimino)(*p*-tolyl)- λ^6 -sulfanone (3c)⁴ Light yellow oil (40 mg, 78% yield), (hexane/EA = 3:1 as eluent). ¹H NMR (400 MHz, CDCl₃) δ 7.87 – 7.81 (m, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 6.91 (d, *J* = 1.3 Hz, 4H), 3.20 (s, 3H), 2.40 (s, 3H), 2.20 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 144.1, 142.4, 136.5, 130.9, 130.2, 129.6, 128.8, 123.2, 77.4, 77.1, 76.8, 46.1, 21.6, 20.7. LRMS (EI): m/z calcd for C₁₅H₁₇NOS [M]⁺, 259.10; found, 259.10.



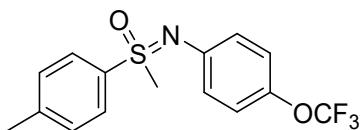
((4-methoxyphenyl)imino)(methyl)(*p*-tolyl)- λ^6 -sulfanone (3d) White solid (45 mg, 82% yield), (hexane/EA = 3:1 as eluent); mp 82–85 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.13 – 8.06 (m, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.17 (m, 2H), 6.97 – 6.90 (m, 2H), 3.95 (s, 3H), 3.45 (s, 3H), 2.66 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 154.7, 144.1, 138.1, 136.4, 130.2, 128.8, 124.4, 114.3, 55.4, 45.9, 21.6. HRMS (ESI) calcd for C₁₅H₁₈NO₂S ([M+H]⁺): 276.1053, Found: 276.1055.



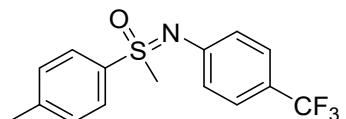
((3-acetylphenyl)imino)(methyl)(*p*-tolyl)- λ^6 -sulfanone (3e) Light yellow oil (49 mg, 95% yield), (hexane/EA = 3:1 as eluent). ¹H NMR (400 MHz, CDCl₃) δ 7.87 – 7.81 (m, 2H), 7.58 – 7.56 (m, 1H), 7.47 – 7.44 (m, 1H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.20 – 7.17 (m, 2H), 3.25 (s, 3H), 2.50 (s, 3H), 2.41 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 198.4, 145.8, 144.5, 138.1, 135.9, 130.4, 129.2, 128.7, 127.7, 123.4, 121.5, 46.4, 26.8, 21.6. HRMS (ESI) calcd for C₁₆H₁₈NO₂S ([M+H]⁺): 288.1053, Found: 288.1056.



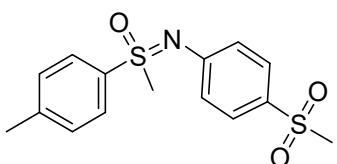
methyl((4-propionylphenyl)imino)(*p*-tolyl)- λ^6 -sulfanone (3f**)** Light yellow solid (49 mg, 82% yield), (hexane/EA = 3:1 as eluent); mp 90–92 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.85 – 7.79 (m, 2H), 7.76 – 7.72 (m, 2H), 7.35 – 7.29 (m, 2H), 7.03 – 6.97 (m, 2H), 3.26 (s, 3H), 2.87 (q, J = 7.3 Hz, 2H), 2.41 (s, 3H), 1.15 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 199.9, 150.6, 144.7, 135.7, 130.5, 130.3, 129.5, 128.6, 122.5, 46.7, 31.3, 21.6, 8.5. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{20}\text{NO}_2\text{S}$ ($[\text{M}+\text{H}]^+$): 302.1209, Found: 302.1212.



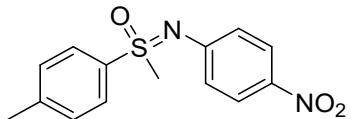
methyl(*p*-tolyl)((4-(trifluoromethoxy)phenyl)imino)- λ^6 -sulfanone (3g**)** Colorless oil (60 mg, 91% yield), (hexane/EA = 3:1 as eluent). ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.00 – 6.92 (m, 4H), 3.22 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.5, 144.1, 143.7 (q, J = 2.0 Hz), 136.0, 130.4, 128.7, 124.0, 121.8, 120.7 (q, J = 254.5 Hz), 46.4, 21.6. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{15}\text{F}_3\text{NO}_2\text{S}$ ($[\text{M}+\text{H}]^+$): 330.0770, Found: 330.0770.



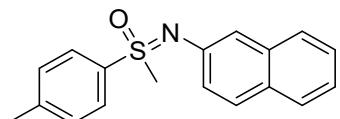
methyl(*p*-tolyl)((4-(trifluoromethyl)phenyl)imino)- λ^6 -sulfanone (3h**)**¹ White solid (53 mg, 85% yield), (hexane/EA = 3:1 as eluent); mp 39–44 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.85 – 7.79 (m, 2H), 7.33 (dd, J = 8.4, 4.4 Hz, 4H), 7.04 (d, J = 8.4 Hz, 2H), 3.25 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.0, 144.7, 135.7, 130.5, 128.6, 126.3 (2C, q, J = 3.8 Hz), 124.8 (q, J = 269.7 Hz), 123.2 (q, J = 32.2 Hz), 122.9, 46.6, 21.6. LRMS (EI): m/z calcd for $\text{C}_{15}\text{H}_{14}\text{F}_3\text{NOS}$ [$\text{M}]^+$, 313.07; found, 313.05.



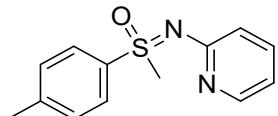
methyl((4-(methylsulfonyl)phenyl)imino)(*p*-tolyl)- λ^6 -sulfanone (3i**)** White solid (62 mg, 96% yield), (EA as eluent); mp 138–144 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.82 – 7.78 (m, 2H), 7.67 – 7.61 (m, 2H), 7.37 – 7.31 (m, 2H), 7.10 – 7.04 (m, 2H), 3.27 (s, 3H), 2.97 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 151.4, 145.1, 135.3, 132.2, 130.6, 128.7, 128.6, 123.0, 46.8, 44.8, 21.7. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{18}\text{NO}_3\text{S}_2$ ($[\text{M}+\text{H}]^+$): 324.0723, Found: 324.0724.



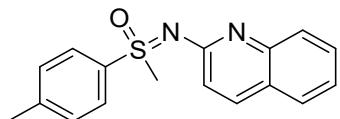
methyl((4-nitrophenyl)imino)(*p*-tolyl)- λ^6 -sulfanone (3j**)**⁵ Light yellow solid (46 mg, 81% yield), (hexane/EA = 3:1 as eluent); mp 112–114 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.01 – 7.96 (m, 2H), 7.84 – 7.78 (m, 2H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.02 – 6.96 (m, 2H), 3.29 (s, 3H), 2.43 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 152.9, 145.2, 141.7, 135.1, 130.7, 128.5, 125.2, 122.5, 46.8, 21.7. LRMS (EI): m/z calcd for C₁₄H₁₄N₂O₃S [M]⁺, 290.07, found, 290.10.



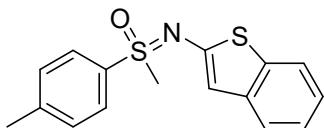
methyl(naphthalen-2-ylimino)(*p*-tolyl)- λ^6 -sulfanone (3k**)** Light brown solid (49 mg, 83% yield), (hexane/EA = 3:1 as eluent); mp 85–89 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.85 (m, 2H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 2.2 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.29 – 7.23 (m, 3H), 3.28 (s, 3H), 2.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 144.3, 143.2, 136.1, 134.5, 130.3, 129.5, 128.8, 128.7, 127.5, 126.9, 125.9, 124.9, 123.7, 118.6, 46.4, 21.6. HRMS (ESI) calcd for C₁₈H₁₈NOS ([M+H]⁺): 296.1104, Found: 296.1108.



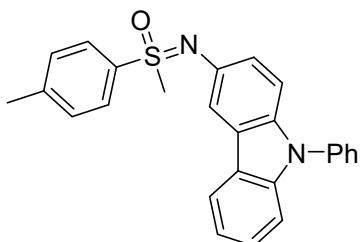
methyl(pyridin-2-ylimino)(*p*-tolyl)- λ^6 -sulfanone (3l**)** Light yellow oil (45 mg, 92% yield), (hexane/EA = 3:1 as eluent). ¹H NMR (400 MHz, CDCl₃) δ 8.09 (ddd, *J* = 5.0, 2.0, 0.9 Hz, 1H), 7.93 – 7.86 (m, 2H), 7.46 (ddd, *J* = 8.2, 7.2, 2.0 Hz, 1H), 7.36 – 7.30 (m, 2H), 6.85 (dt, *J* = 8.2, 1.0 Hz, 1H), 6.72 (ddd, *J* = 7.3, 5.0, 1.1 Hz, 1H), 3.35 (s, 3H), 2.42 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 159.1, 148.0, 144.0, 137.7, 137.2, 130.2, 128.0, 116.8, 116.2, 45.8, 21.6. HRMS (ESI) calcd for C₁₃H₁₅N₂OS ([M+H]⁺): 247.0900, Found: 247.0903.



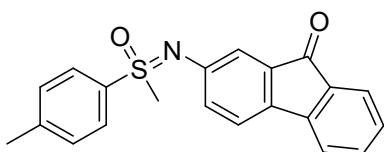
methyl(quinolin-2-ylimino)(*p*-tolyl)- λ^6 -sulfanone (3m**)** White solid (24 mg, 55% yield), (hexane/EA = 3:1 as eluent); mp 102–105 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.00 – 7.94 (m, 2H), 7.90 (dd, *J* = 8.8, 0.8 Hz, 1H), 7.69 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.62 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.50 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.30 – 7.26 (m, 1H), 7.04 (d, *J* = 8.7 Hz, 1H), 3.49 (s, 3H), 2.42 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 158.3, 147.5, 144.1, 137.6, 137.3, 130.1, 129.0, 127.9, 127.7, 127.2, 124.6, 123.6, 118.3, 45.5, 21.6. HRMS (ESI) calcd for C₁₇H₁₇N₂OS ([M+H]⁺): 297.1056, Found: 297.1056.



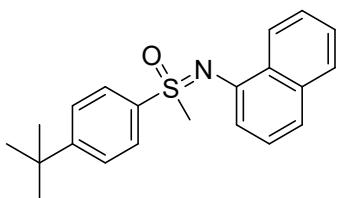
(benzo[*b*]thiophen-2-ylimino)(methyl)(*p*-tolyl)- λ^6 -sulfanone (3n) Colorless oil (49 mg, 82% yield), (hexane/EA = 4:1 as eluent). ^1H NMR (400 MHz, CDCl_3) δ 8.01 (d, J = 7.4 Hz, 1H), 7.86 (d, J = 8.3 Hz, 2H), 7.73 (d, J = 7.9 Hz, 1H), 7.39 (ddd, J = 8.1, 7.1, 1.2 Hz, 1H), 7.35 – 7.32 (m, 1H), 7.30 (d, J = 8.0 Hz, 2H), 6.58 (s, 1H), 3.32 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.5, 138.2, 137.3, 137.3, 135.9, 130.3, 128.7, 124.5, 123.6, 122.7, 121.8, 107.9, 45.4, 21.6. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{16}\text{NOS}_2$ ($[\text{M}+\text{H}]^+$): 302.0668, Found: 302.0671.



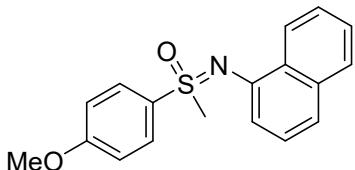
methyl((9-phenyl-9*H*-carbazol-3-yl)imino)(*p*-tolyl)- λ^6 -sulfanone (3o) Light yellow solid (67 mg, 80% yield), (hexane/EA = 1:1 as eluent); mp 142–146 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, J = 7.7 Hz, 2H), 7.94 – 7.90 (m, 2H), 7.39 (s, 1H), 7.36 (dt, J = 6.5, 1.3 Hz, 2H), 7.34 (d, J = 1.2 Hz, 1H), 7.31 (s, 1H), 7.30 – 7.28 (m, 1H), 7.27 (d, J = 2.2 Hz, 1H), 7.26 – 7.24 (m, 1H), 7.23 (t, J = 1.0 Hz, 1H), 7.22 – 7.18 (m, 2H), 7.18 (d, J = 2.1 Hz, 1H), 3.28 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.7, 144.5, 141.2, 136.3, 131.1, 130.5, 128.7, 127.9, 125.8, 124.2, 123.1, 120.2, 119.6, 109.9, 46.6, 21.7. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{23}\text{N}_2\text{OS}$ ($[\text{M}+\text{H}]^+$): 411.1526, Found: 411.1526.



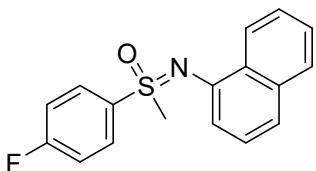
methyl((9-oxo-9*H*-fluoren-2-yl)imino)(*p*-tolyl)- λ^6 -sulfanone (3p) Orange solid (60 mg, 86% yield), (hexane/EA = 2:1 as eluent); mp 77–81 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.86 – 7.79 (m, 2H), 7.53 (d, J = 7.3 Hz, 1H), 7.37 (td, J = 7.4, 1.2 Hz, 1H), 7.32 (d, J = 7.4 Hz, 3H), 7.27 (d, J = 2.1 Hz, 1H), 7.23 (d, J = 7.9 Hz, 1H), 7.14 (td, J = 7.4, 1.2 Hz, 1H), 7.09 (dd, J = 8.0, 2.1 Hz, 1H), 3.25 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 194.2, 146.9, 145.1, 144.6, 137.5, 135.8, 135.4, 134.7, 134.4, 130.4, 128.7, 128.6, 127.8, 124.2, 121.0, 119.5, 119.5, 46.4, 21.6. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{18}\text{NO}_2\text{S}$ ($[\text{M}+\text{H}]^+$): 348.1053, Found: 348.1052.



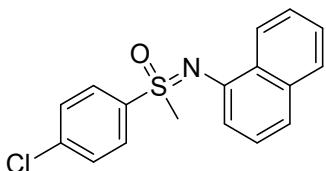
(4-(*tert*-butyl)phenyl)(methyl)(naphthalen-1-ylimino)-λ⁶-sulfanone (4a) Brown solid (63 mg, 93% yield), (hexane/EA = 2:1 as eluent); mp 107-112 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.58 – 8.54 (m, 1H), 7.94 – 7.90 (m, 2 H), 7.77 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.54 – 7.44 (m, 4H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 7.14 (dd, *J* = 7.4, 1.2 Hz, 1H), 3.32 (s, 3H), 1.31 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 157.2, 141.9, 136.4, 134.6, 130.2, 128.4, 127.8, 126.7, 126.2, 125.9, 125.0, 124.1, 121.4, 116.6, 46.1, 35.2, 31.1. HRMS (ESI) calcd for C₂₁H₂₄NOS ([M+H]⁺): 338.1573, Found: 338.1571.



(4-methoxyphenyl)(methyl)(naphthalen-1-ylimino)-λ⁶-sulfanone (4b)⁶ White solid (46 mg, 74% yield), (hexane/EA = 3:1 as eluent); mp 135-139 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.54 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.95 – 7.87 (m, 2H), 7.79 – 7.72 (m, 1H), 7.53 – 7.44 (m, 2H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.10 (dd, *J* = 7.5, 1.1 Hz, 1H), 6.96 – 6.90 (m, 2H), 3.81 (s, 3H), 3.32 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 163.5, 141.9, 134.6, 130.7, 130.5, 130.2, 127.8, 126.1, 125.9, 125.0, 124.1, 121.4, 116.6, 114.8, 55.7, 46.44. LRMS (EI): m/z calcd for C₁₈H₁₇NO₂S [M]⁺, 311.10; found, 311.05.

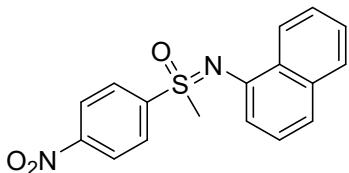


(4-fluorophenyl)(methyl)(naphthalen-1-ylimino)-λ⁶-sulfanone (4c) White solid (58 mg, 97% yield), (hexane/EA = 3:1 as eluent); mp 111-115 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.52 (dd, *J* = 8.4, 1.6 Hz, 1H), 8.03 – 7.97 (m, 2H), 7.77 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.49 (m, *J* = 14.6, 8.3, 6.8, 1.5 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.21 – 7.12 (m, 3H), 7.08 (dd, *J* = 7.5, 1.1 Hz, 1H), 3.35 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 165.7 (d, *J* = 254.4 Hz), 141.4, 135.2 (d, *J* = 3.0 Hz), 134.6, 131.4, 131.3, 130.1, 127.9, 126.1 (d, *J* = 3.6 Hz), 125.2, 123.9, 121.8, 117.0, 116.8, 116.6, 46.2. HRMS (ESI) calcd for C₁₇H₁₅FNOS ([M+H]⁺): 300.0853, Found: 300.0855.

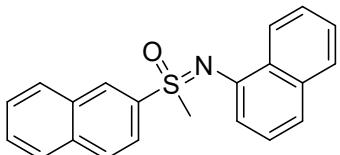


(4-chlorophenyl)(methyl)(naphthalen-1-ylimino)-λ⁶-sulfanone (4d) White solid (29 mg, 46% yield), (hexane/EA = 3:1 as eluent); mp 100-103 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.54 – 8.46 (m, 1H), 7.95 – 7.90 (m, 2H), 7.76 (dd, *J* = 7.4, 2.2 Hz, 1H), 7.54 – 7.43 (m, 4H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.06 (dd, *J* = 7.4, 1.1 Hz, 1H), 3.35 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 141.3, 140.1, 137.9, 134.6, 130.1,

130.0, 127.9, 126.1, 125.2, 123.9, 121.9, 116.6, 46.2. HRMS (ESI) calcd for C₁₇H₁₅ClNOS ([M+H]⁺): 316.0557, Found: 316.0554.



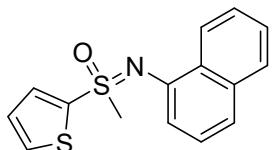
methyl(naphthalen-1-ylimino)(4-nitrophenyl)- λ^6 -sulfanone (4e) Light yellow solid (54 mg, 83% yield), (hexane/EA = 3:1 as eluent); mp 150–155 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.48 (dd, *J* = 8.4, 1.4 Hz, 1H), 8.33 – 8.27 (m, 2H), 8.21 – 8.14 (m, 2H), 7.77 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.55 – 7.46 (m, 2H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.19 – 7.13 (m, 1H), 7.05 (dd, *J* = 7.5, 1.1 Hz, 1H), 3.42 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 150.7, 145.6, 140.7, 134.6, 130.0, 128.0, 126.3, 126.0, 125.5, 124.8, 123.7, 122.5, 116.7, 77.4, 77.1, 76.8, 45.9. HRMS (ESI) calcd for C₁₇H₁₅N₂O₃S ([M+H]⁺): 327.0798, Found: 327.0798.



methyl(naphthalen-1-ylimino)(naphthalen-2-yl)- λ^6 -sulfanone (4f) Light yellow oil (64 mg, 96% yield), (hexane/EA = 3:1 as eluent). ¹H NMR (400 MHz, CDCl₃) δ 8.63 (dd, *J* = 12.4, 1.5 Hz, 2H), 7.94 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.91 – 7.89 (m, 2H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 7.4 Hz, 1H), 7.65 – 7.58 (m, 2H), 7.54 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.48 (ddd, *J* = 8.1, 6.8, 1.4 Hz, 1H), 7.37 (dt, *J* = 7.2, 3.6 Hz, 1H), 7.17 – 7.12 (m, 2H), 3.42 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 141.7, 136.41, 135.2, 134.6, 132.6, 130.7, 130.2, 129.9, 129.4, 129.1, 128.0, 127.9, 127.6, 126.1, 126.0, 125.1, 124.1, 123.0, 121.6, 116.6, 46.1. HRMS (ESI) calcd for C₂₁H₁₈NOS ([M+H]⁺): 332.1104, Found: 332.1104.

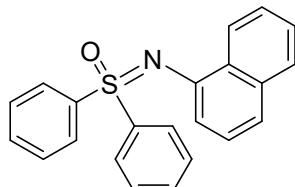


methyl(naphthalen-1-ylimino)(pyridin-4-yl)- λ^6 -sulfanone (4g) White solid (26 mg, 46% yield), (hexane/EA = 21:1 as eluent); mp 174–176 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.84 – 8.79 (m, 2H), 8.48 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.86 – 7.82 (m, 2H), 7.77 (dd, *J* = 7.5, 2.1 Hz, 1H), 7.54 – 7.46 (m, 2H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.20 – 7.15 (m, 1H), 7.06 (dd, *J* = 7.5, 1.1 Hz, 1H), 3.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 151.6, 140.8, 128.0, 126.2, 126.0, 125.4, 123.8, 122.4, 121.9, 116.8, 77.4, 77.1, 76.8, 45.5. HRMS (ESI) calcd for C₁₆H₁₅N₂OS ([M+H]⁺): 283.0900, Found: 283.0907.

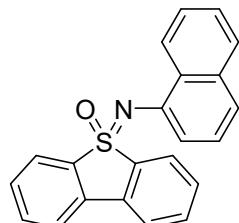


methyl(naphthalen-1-ylimino)(thiophen-2-yl)- λ^6 -sulfanone (4h) Light brown solid

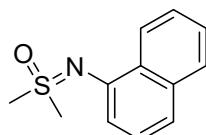
(50 mg, 87% yield), (hexane/EA = 2:1 as eluent); mp 123-126 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.47 (dd, J = 8.2, 1.6 Hz, 1H), 7.77 (dd, J = 8.0, 1.5 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.49 (qd, J = 7.1, 1.5 Hz, 2H), 7.46 – 7.41 (m, 1H), 7.26 – 7.21 (m, 2H), 7.03 (dd, J = 5.0, 3.8 Hz, 1H), 3.49 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 141.2, 140.8, 134.6, 134.2, 134.1, 130.2, 128.2, 127.8, 126.1, 126.0, 125.2, 124.1, 122.2, 117.0, 47.8. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{14}\text{NOS}_2$ ($[\text{M}+\text{H}]^+$): 288.0511, Found: 288.0512.



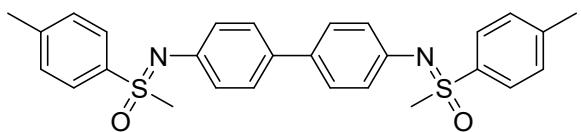
(naphthalen-1-ylimino)diphenyl- λ^6 -sulfanone (4i)⁷ White solid (62 mg, 90% yield), (hexane/EA = 3:1 as eluent); mp 169-174 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.74 (d, J = 7.8 Hz, 1H), 8.15 – 8.10 (m, 4H), 7.78 (dd, J = 8.1, 1.3 Hz, 1H), 7.57 (ddd, J = 8.3, 6.8, 1.4 Hz, 1H), 7.54 – 7.44 (m, 7H), 7.39 (dd, J = 7.1, 2.0 Hz, 1H), 7.21 – 7.14 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 141.2, 141.1, 134.72, 132.8, 130.5, 129.4, 128.5, 127.9, 126.2, 126.0, 125.2, 124.1, 121.6, 117.1. LRMS (EI): m/z calcd for $\text{C}_{22}\text{H}_{17}\text{NOS}$ $[\text{M}]^+$, 343.10; found, 343.05.



5-(naphthalen-1-ylimino)-5H-5 λ^4 -dibenz[b,d]thiophene 5-oxide (4j)⁸ Orange solid (53 mg, 78% yield), (hexane/EA = 3:1 as eluent); mp 175-179 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 7.7 Hz, 2H), 7.81 (d, J = 7.5 Hz, 2H), 7.76 (d, J = 8.1 Hz, 1H), 7.62 (td, J = 7.6, 1.1 Hz, 2H), 7.58 – 7.53 (m, 2H), 7.44 (td, J = 7.6, 1.0 Hz, 2H), 7.39 (ddd, J = 8.2, 6.9, 1.3 Hz, 2H), 7.29 (ddd, J = 8.2, 6.7, 1.3 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 140.4, 139.2, 134.7, 133.2, 132.0, 130.5, 130.3, 127.7, 126.1, 126.0, 125.2, 124.5, 123.0, 122.6, 121.7, 118.7. LRMS (EI): m/z calcd for $\text{C}_{22}\text{H}_{15}\text{NOS}$ $[\text{M}]^+$, 341.09; found, 341.05.



dimethyl(naphthalen-1-ylimino)- λ^6 -sulfanone (4k) White solid (20 mg, 47% yield), (hexane/EA = 3:1 as eluent); mp 114-117 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.32 – 8.26 (m, 1H), 7.82 – 7.76 (m, 1H), 7.51 (d, J = 8.1 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.35 (t, J = 7.7 Hz, 1H), 7.29 (dd, J = 7.4, 1.3 Hz, 1H), 3.23 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 141.6, 134.8, 130.3, 127.9, 126.2, 126.1, 125.2, 124.1, 122.3, 117.3, 42.2. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{13}\text{NOSNa}$ ($[\text{M}+\text{Na}]^+$): 242.0610, Found: 242.0611.



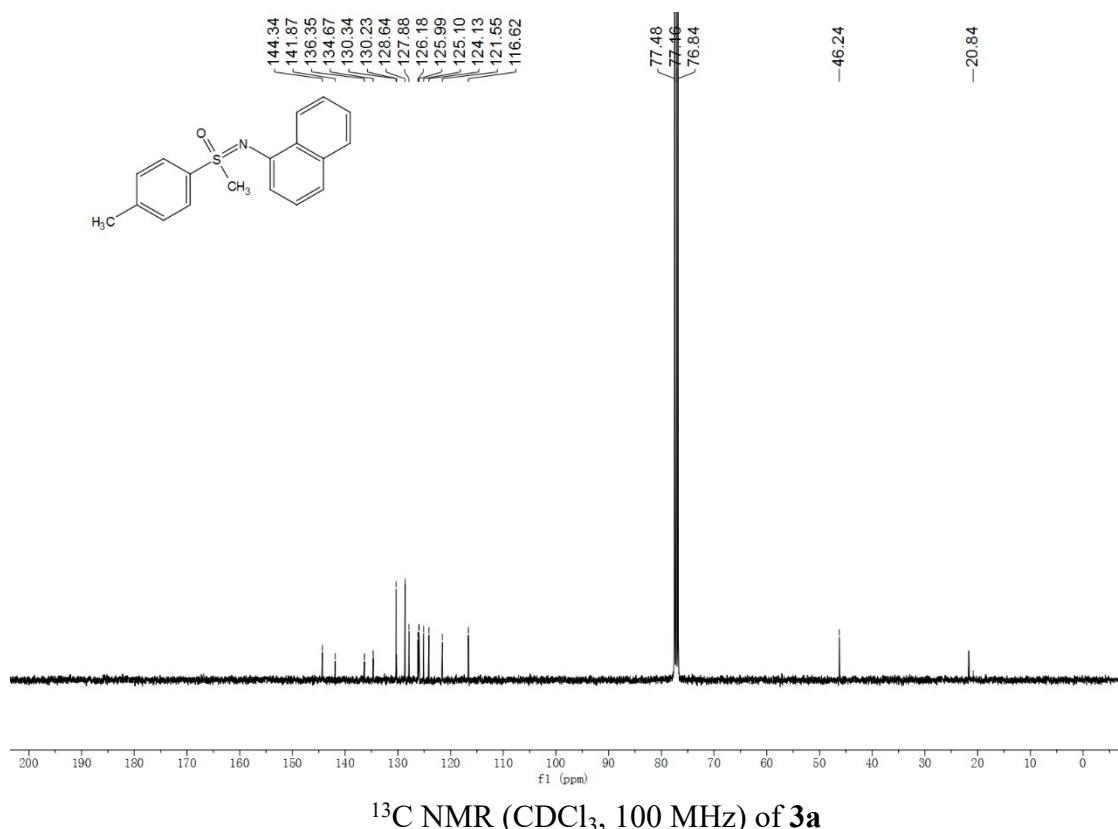
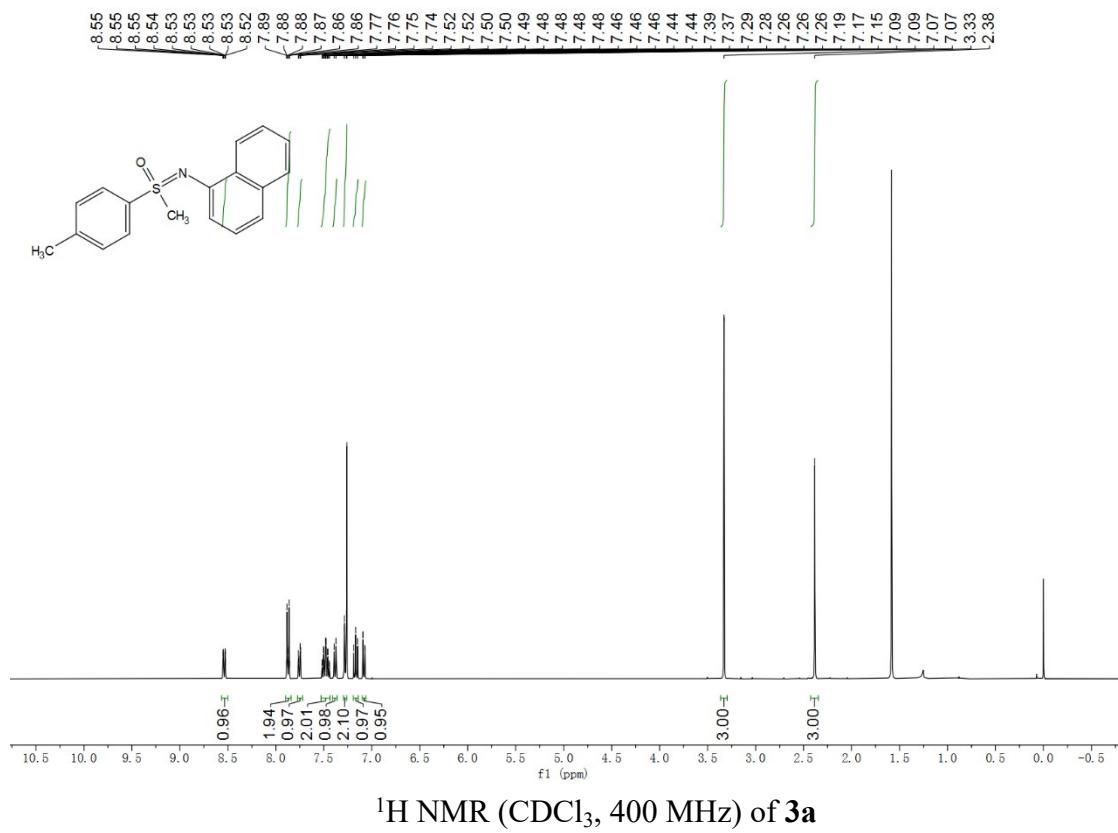
([1,1'-biphenyl]-4,4'-diylbis(azanylylidene)bis(methyl(*p*-tolyl)- λ^6 -sulfanone) (5a) Light yellow solid (67 mg, 69% yield), (EA as eluent); mp 83–87 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.87 – 7.80 (m, 4H), 7.29 (d, *J* = 8.1 Hz, 4H), 7.27 – 7.24 (m, 4H), 7.02 – 6.96 (m, 4H), 3.22 (s, 6H), 2.39 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 144.2, 144.0, 136.3, 134.1, 130.3, 128.8, 127.0, 123.5, 46.3, 21.6. HRMS (ESI) calcd for C₂₈H₂₉N₂O₂S₂ ([M+H]⁺): 489.1665, Found: 489.1663.

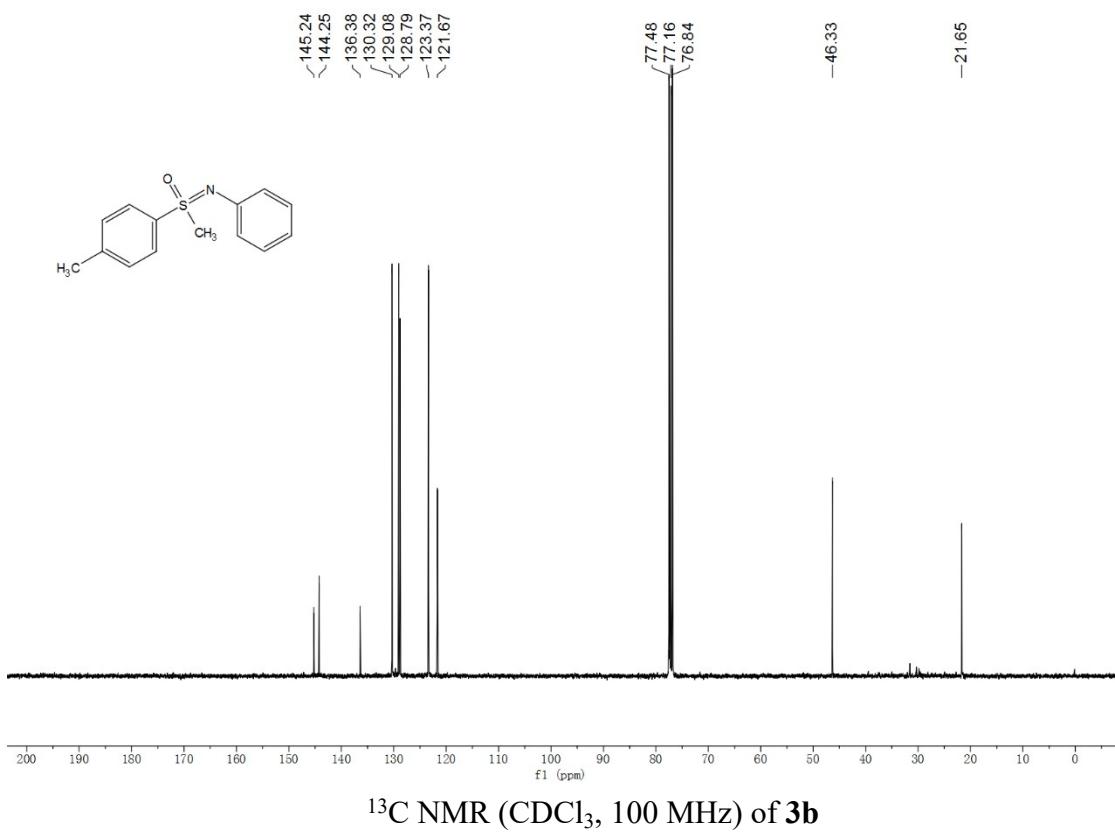
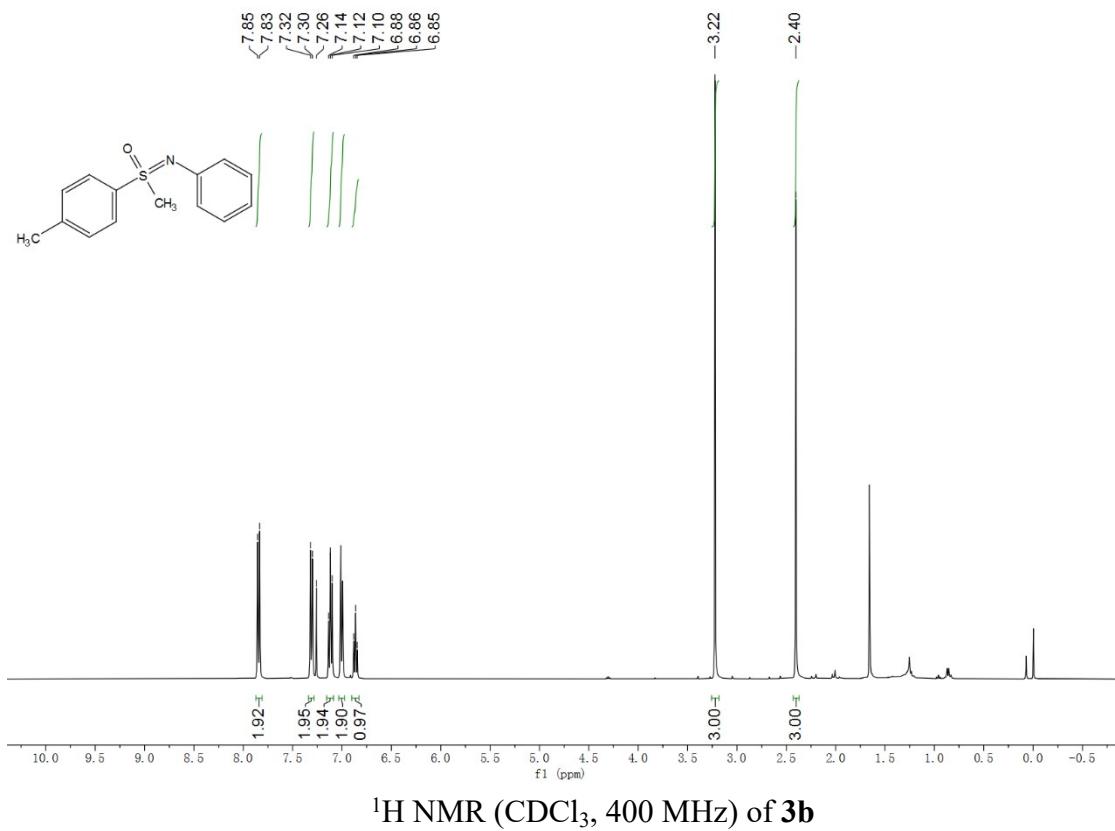
8. References

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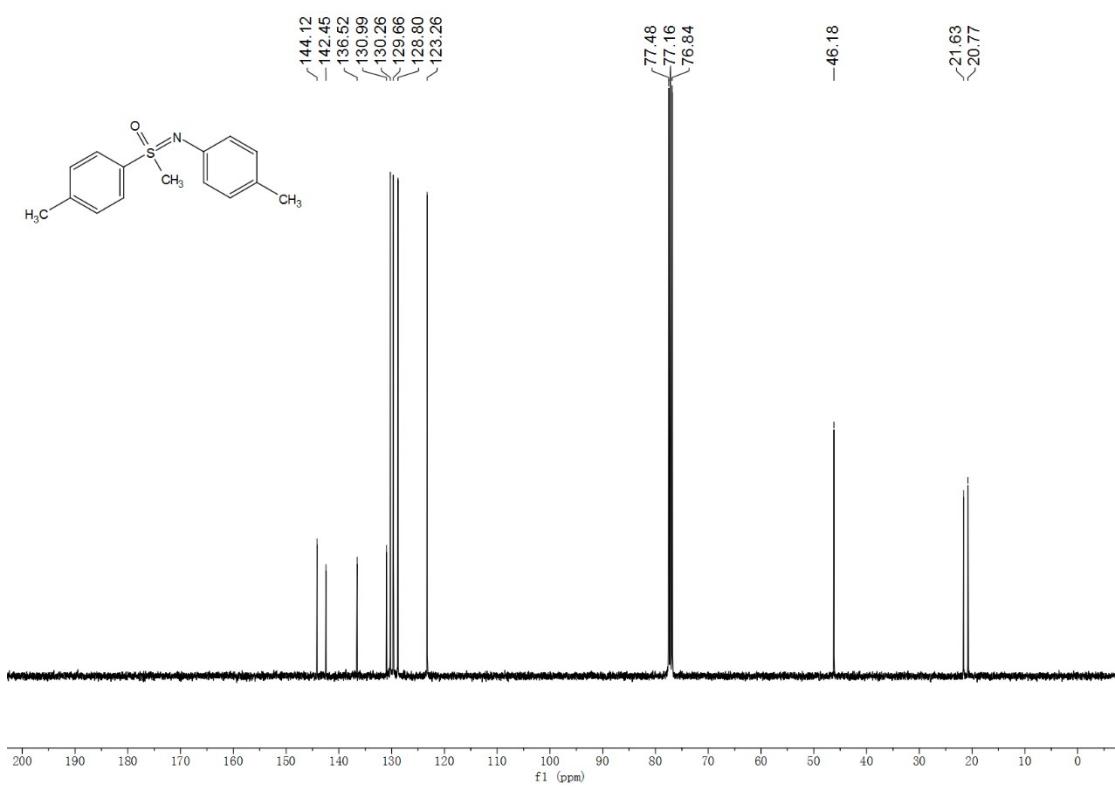
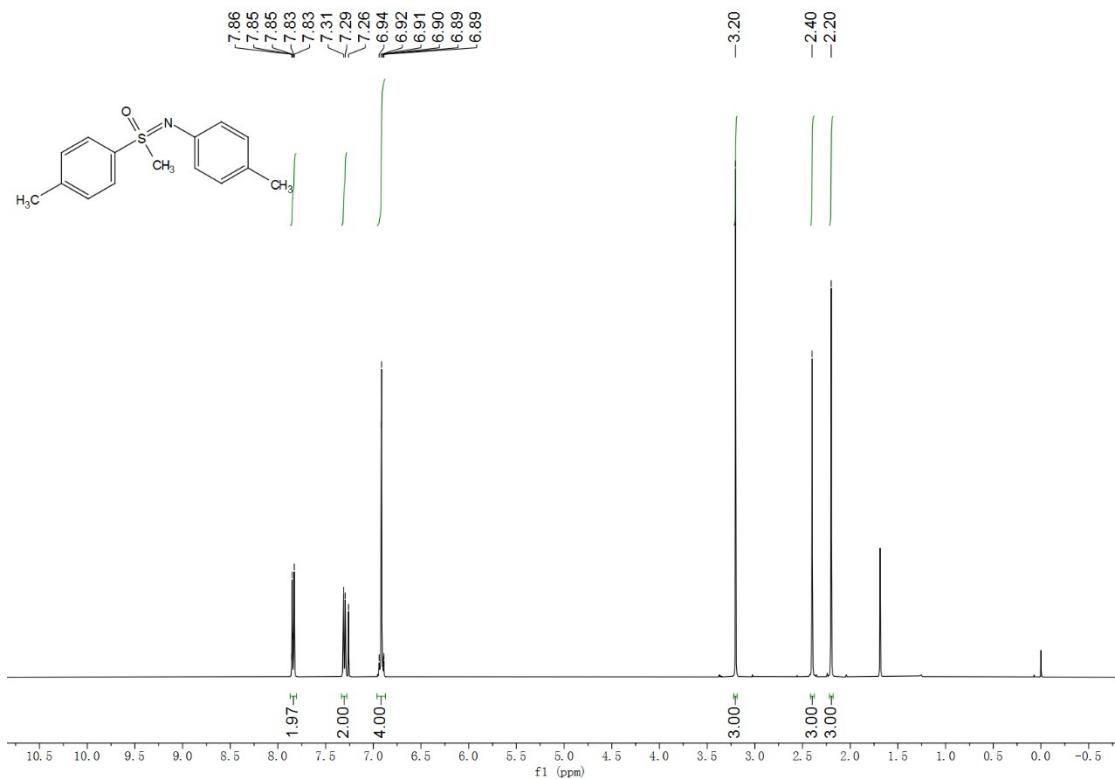
9. The NMR spectra of all products

methyl(naphthalen-1-ylimino)(*p*-tolyl)- λ^6 -sulfanone (3a)

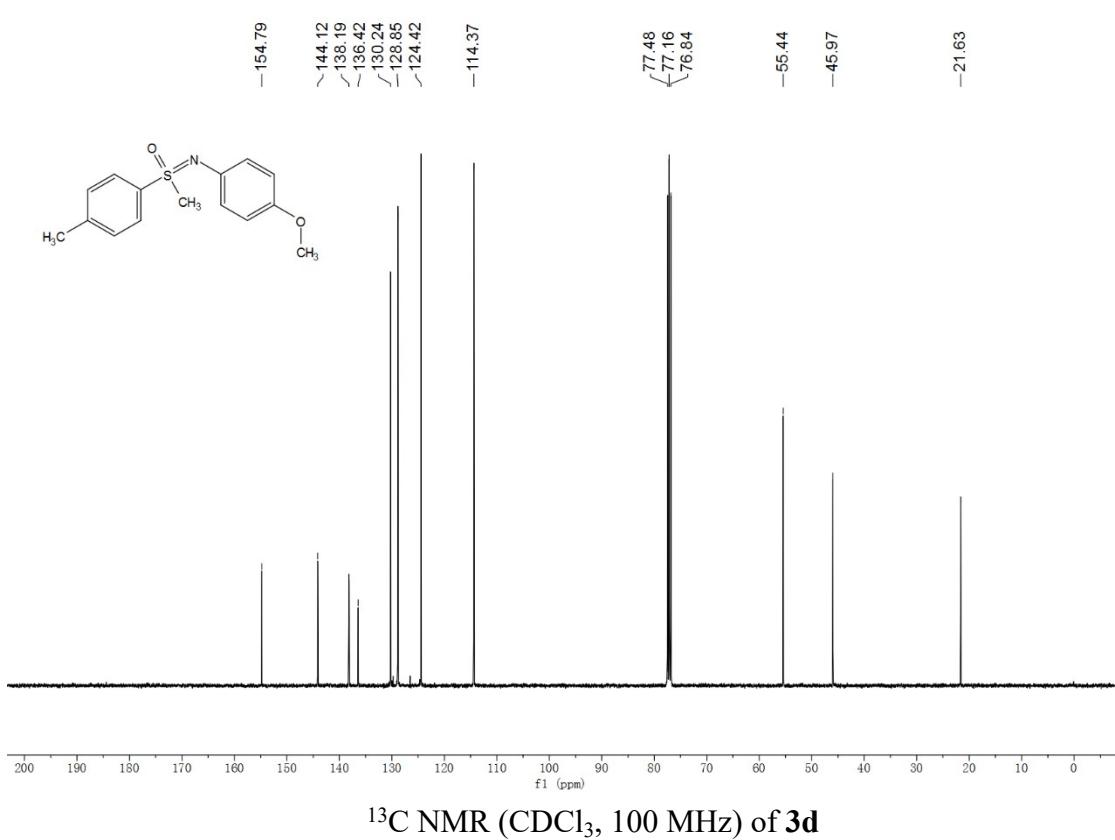
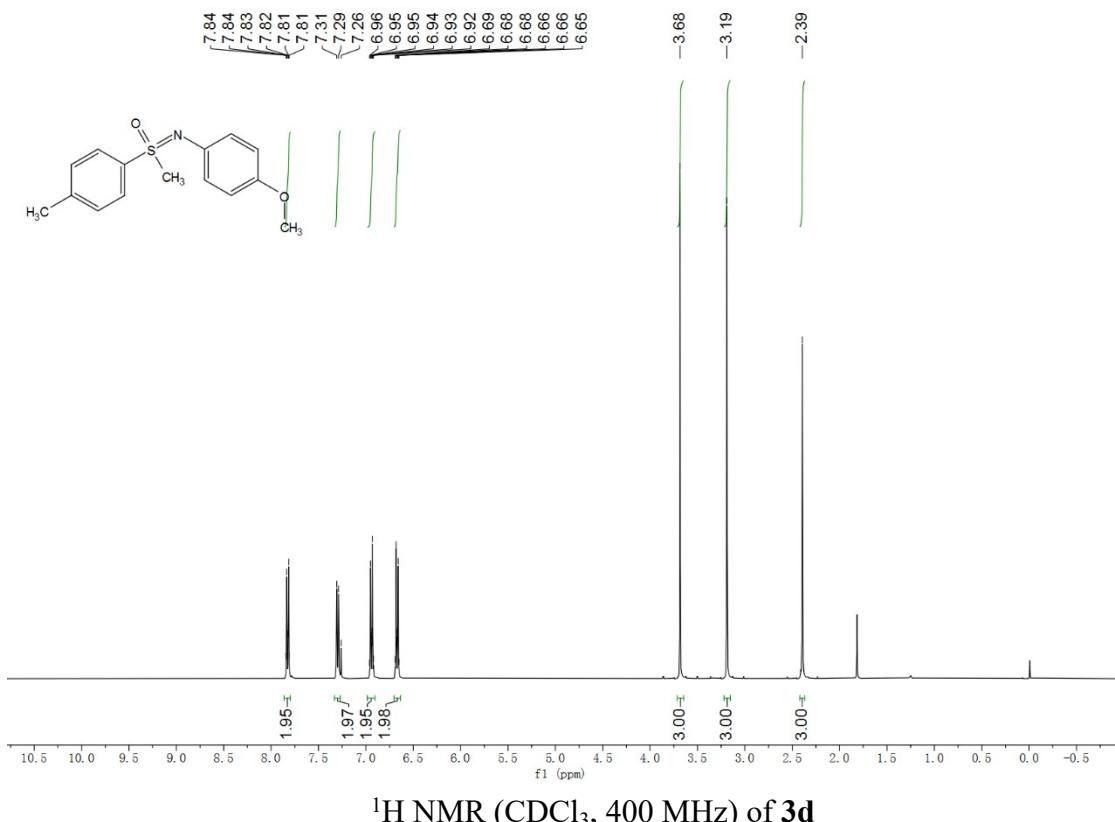




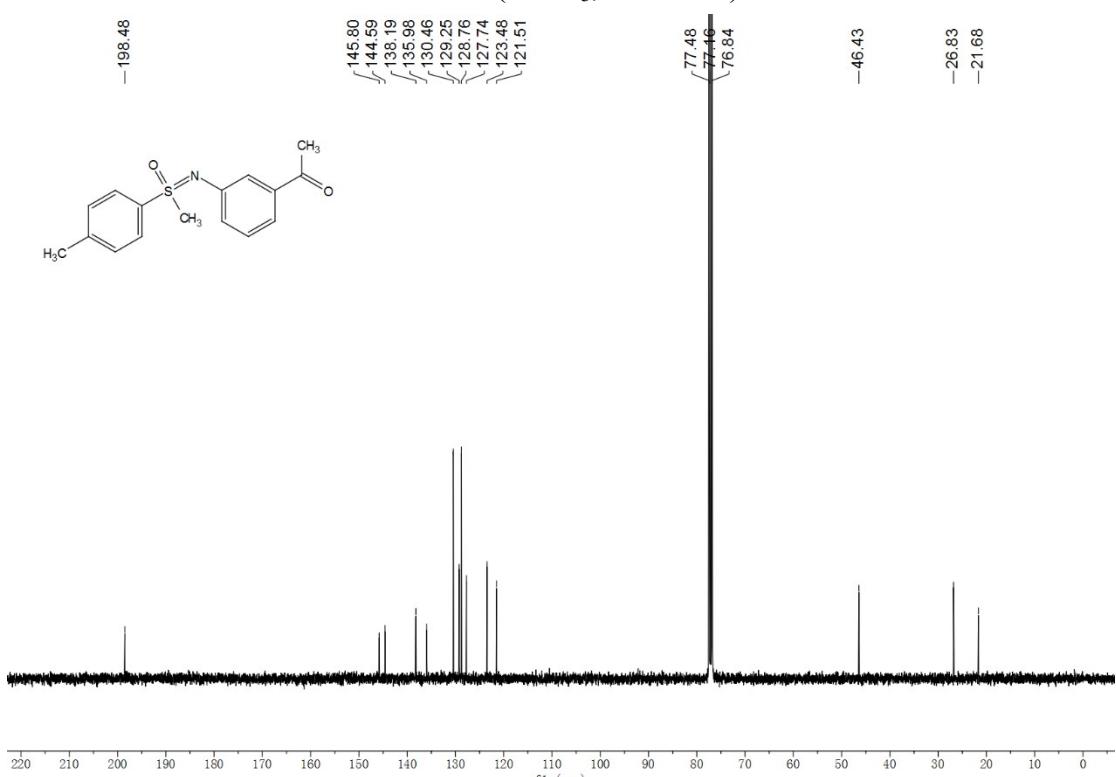
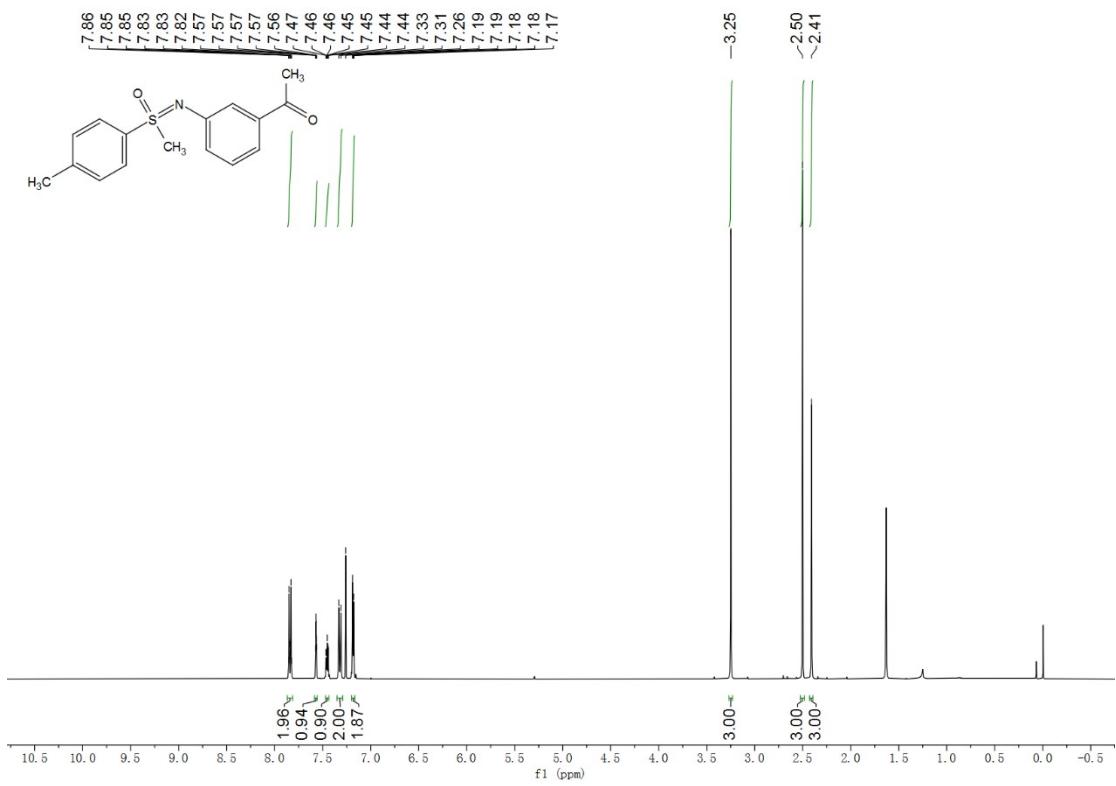
methyl(*p*-tolyl)(*p*-tolylimino)- λ^6 -sulfanone (3c)



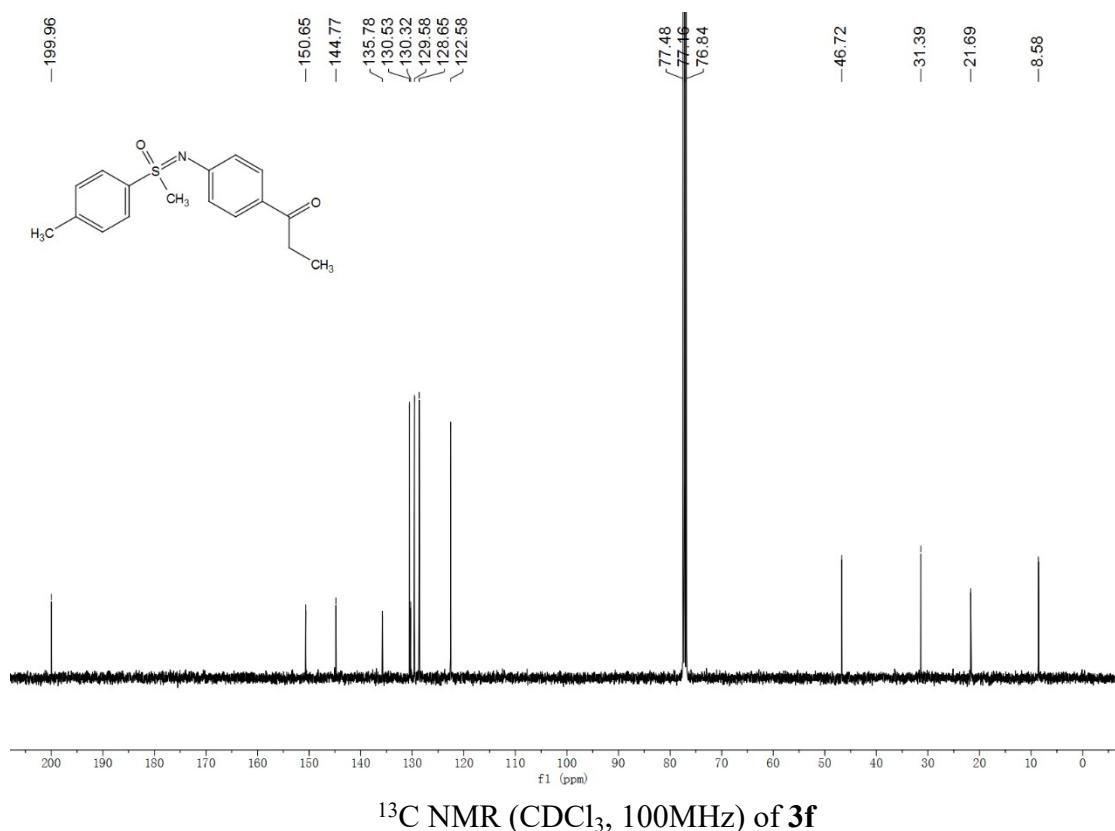
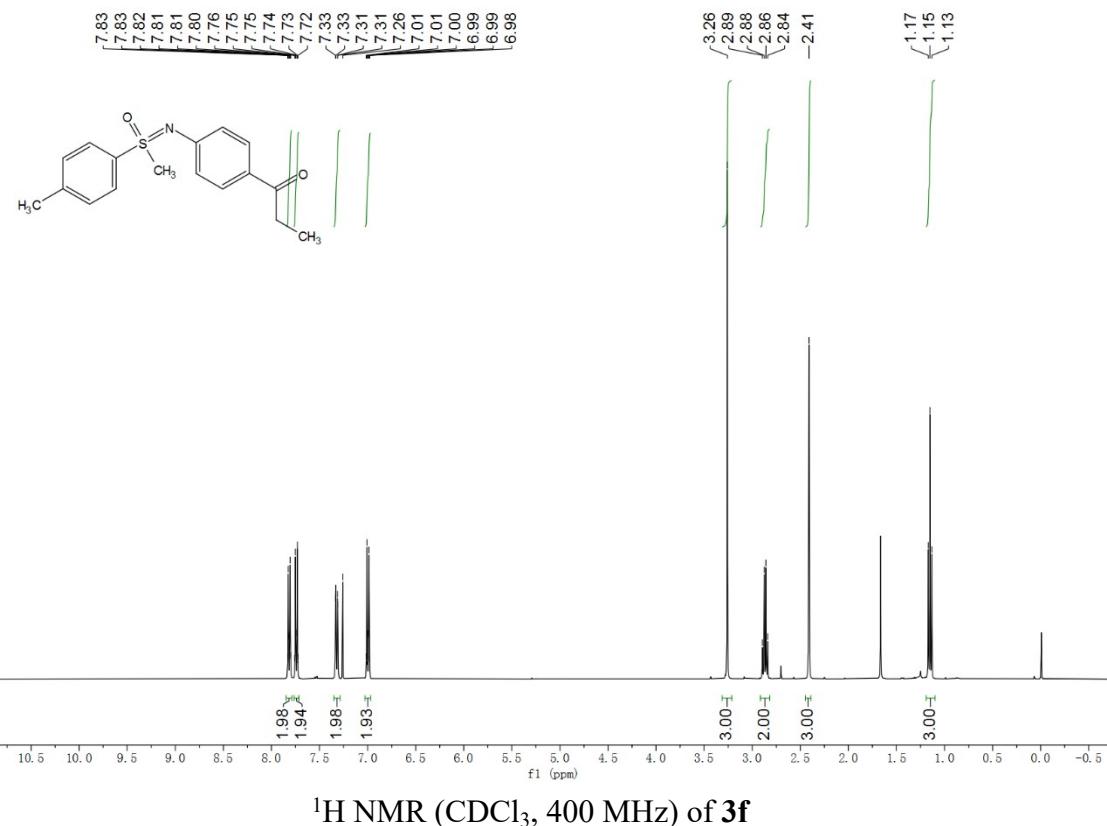
((4-methoxyphenyl)imino)(methyl)(*p*-tolyl)- λ^6 -sulfanone (3d)



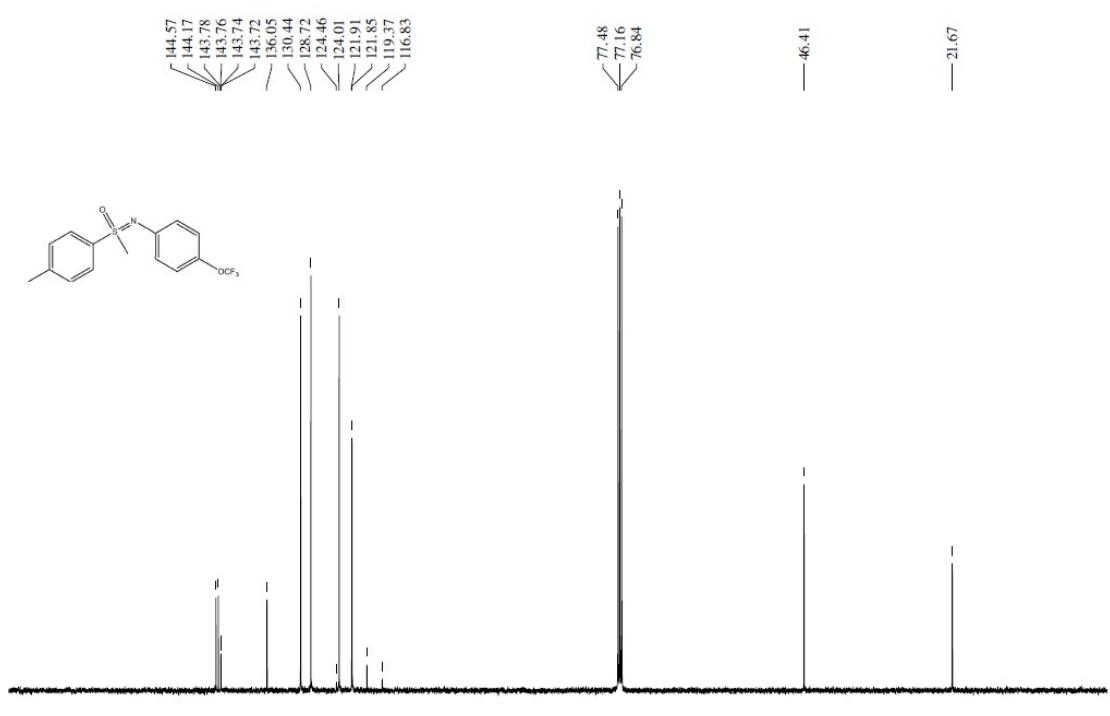
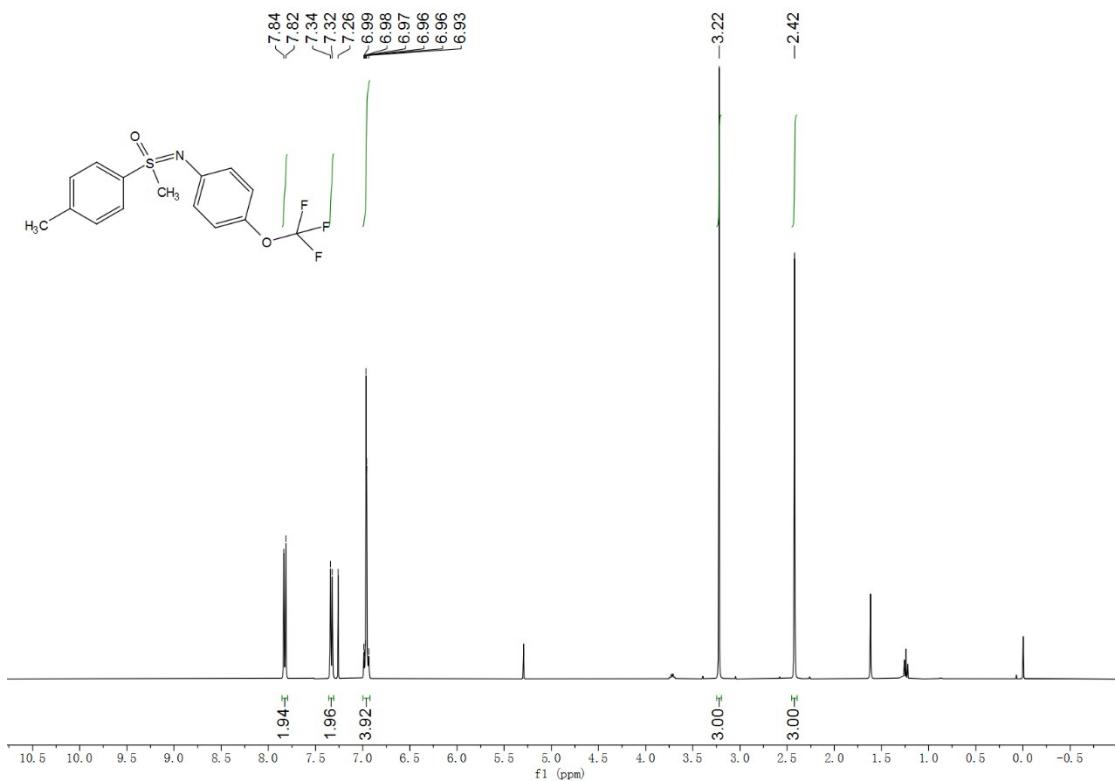
((3-acetylphenyl)imino)(methyl)(*p*-tolyl)- λ^6 -sulfanone (3e)



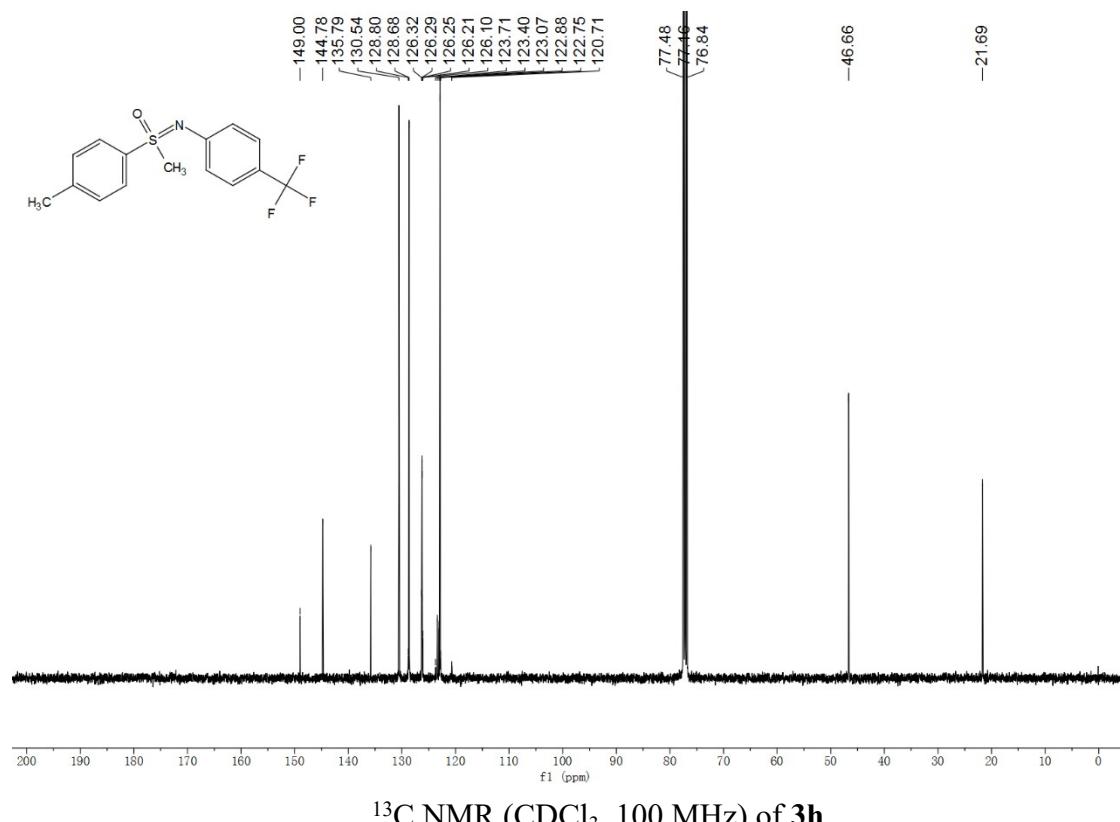
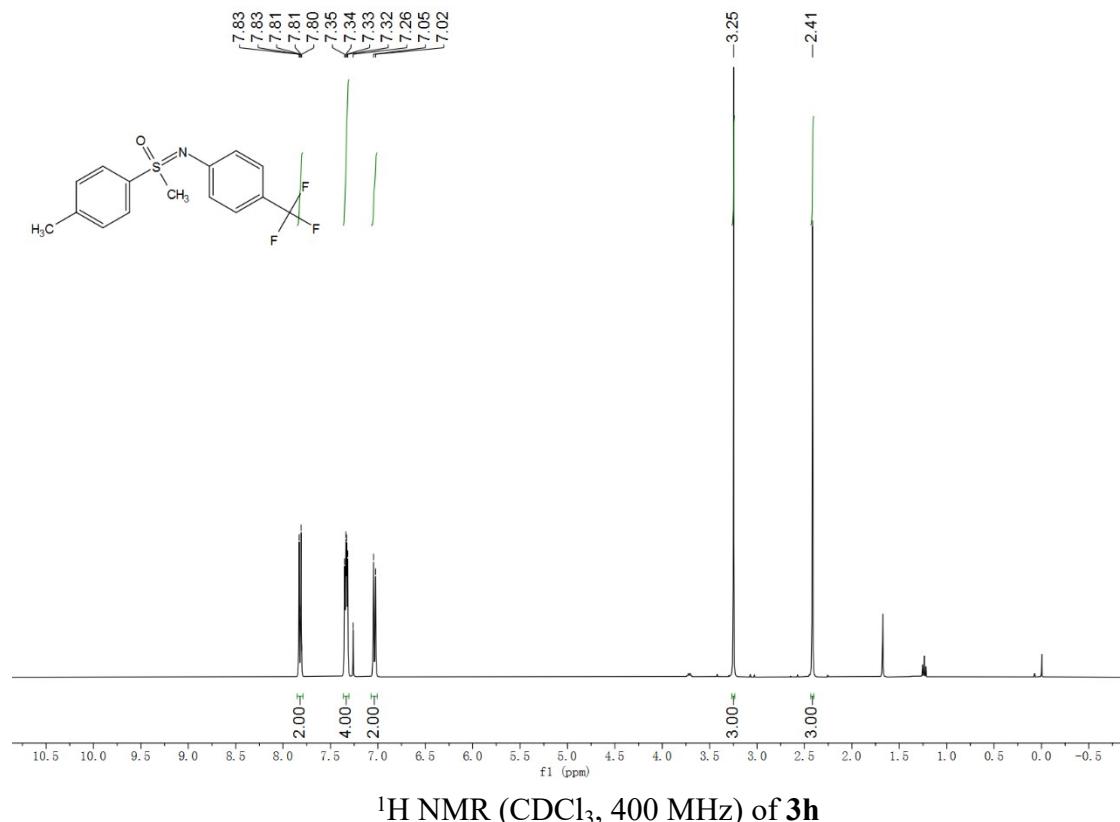
methyl((4-propionylphenyl)imino)(*p*-tolyl)- λ^6 -sulfanone (3f)



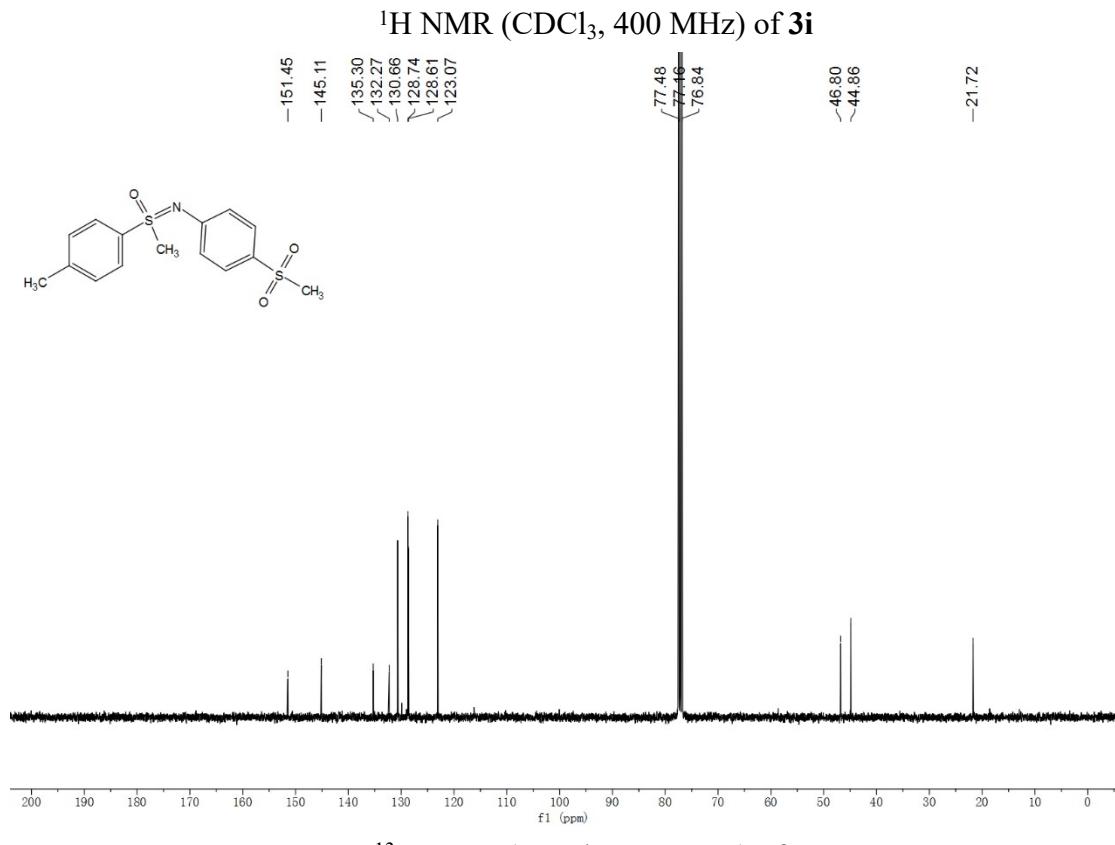
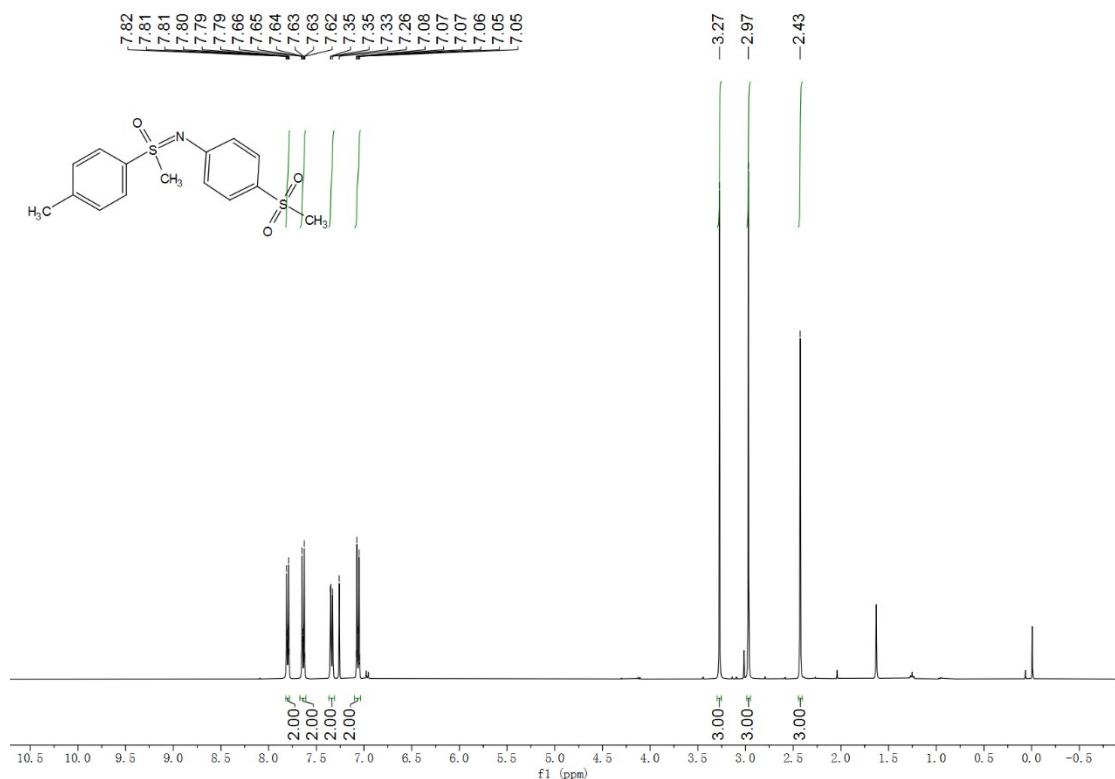
methyl(*p*-tolyl)((4-(trifluoromethoxy)phenyl)imino)- λ^6 -sulfanone (3g)



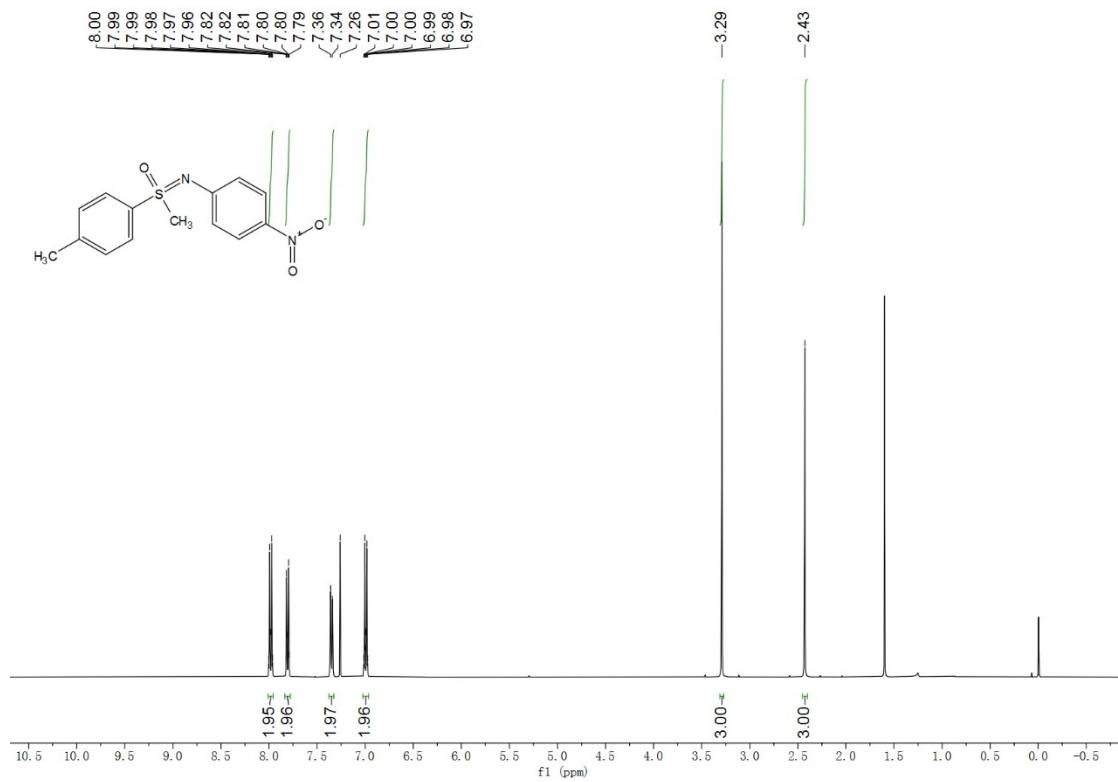
methyl(*p*-tolyl)((4-(trifluoromethyl)phenyl)imino)- λ^6 -sulfanone (3h**)**



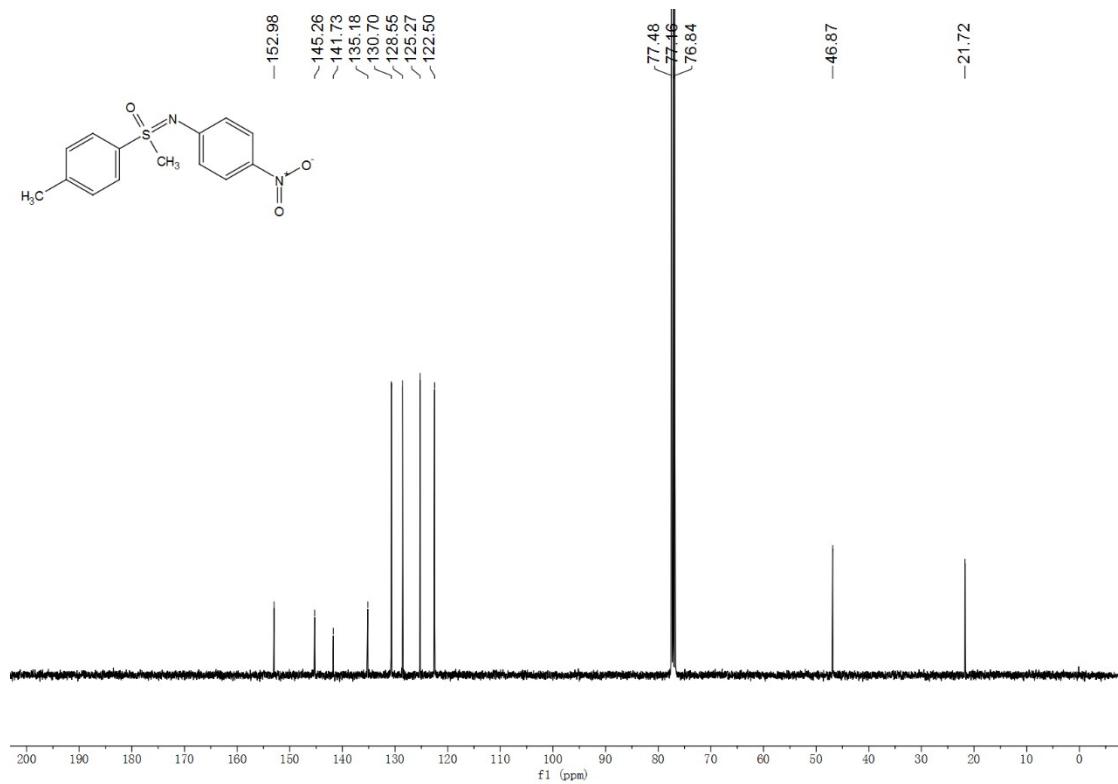
methyl((4-(methylsulfonyl)phenyl)imino)(*p*-tolyl)-λ⁶-sulfanone (3i**)**



methyl((4-nitrophenyl)imino)(*p*-tolyl)-λ⁶-sulfanone (3j)

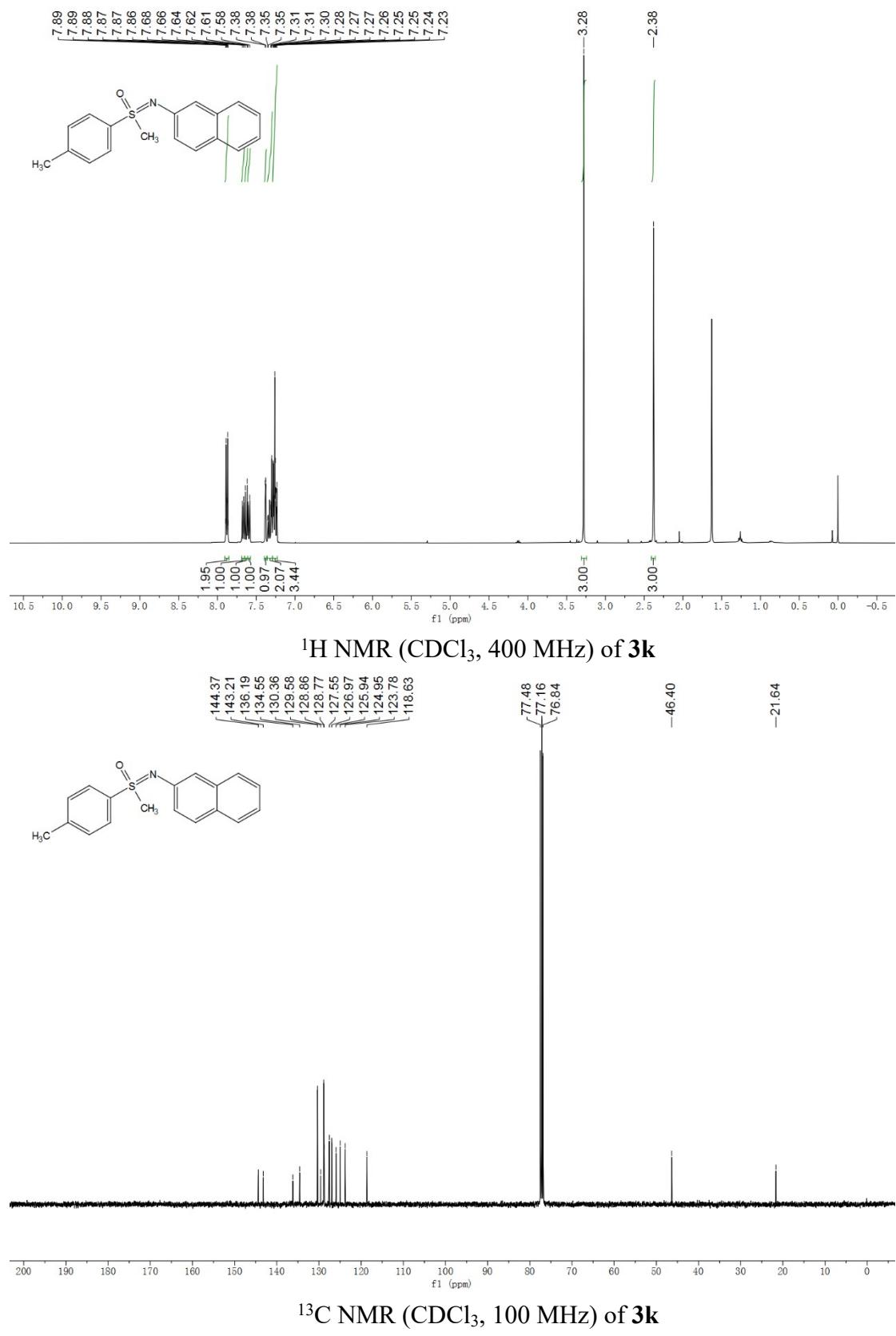


¹H NMR (CDCl_3 , 400 MHz) of **3j**

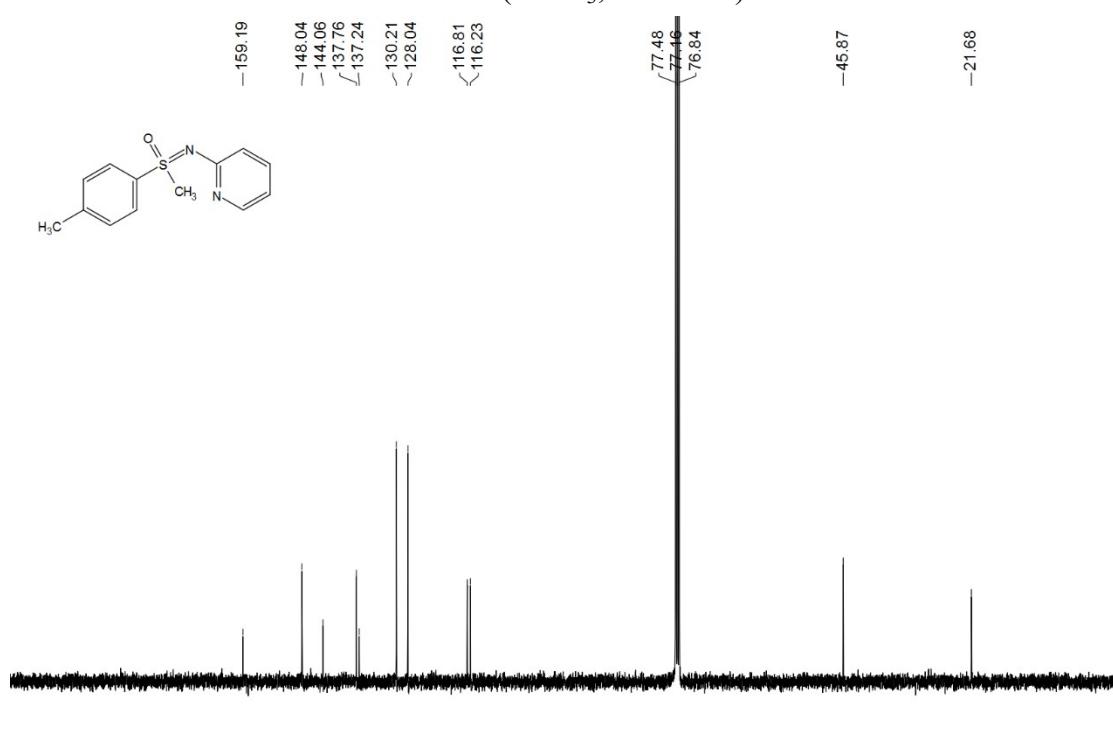
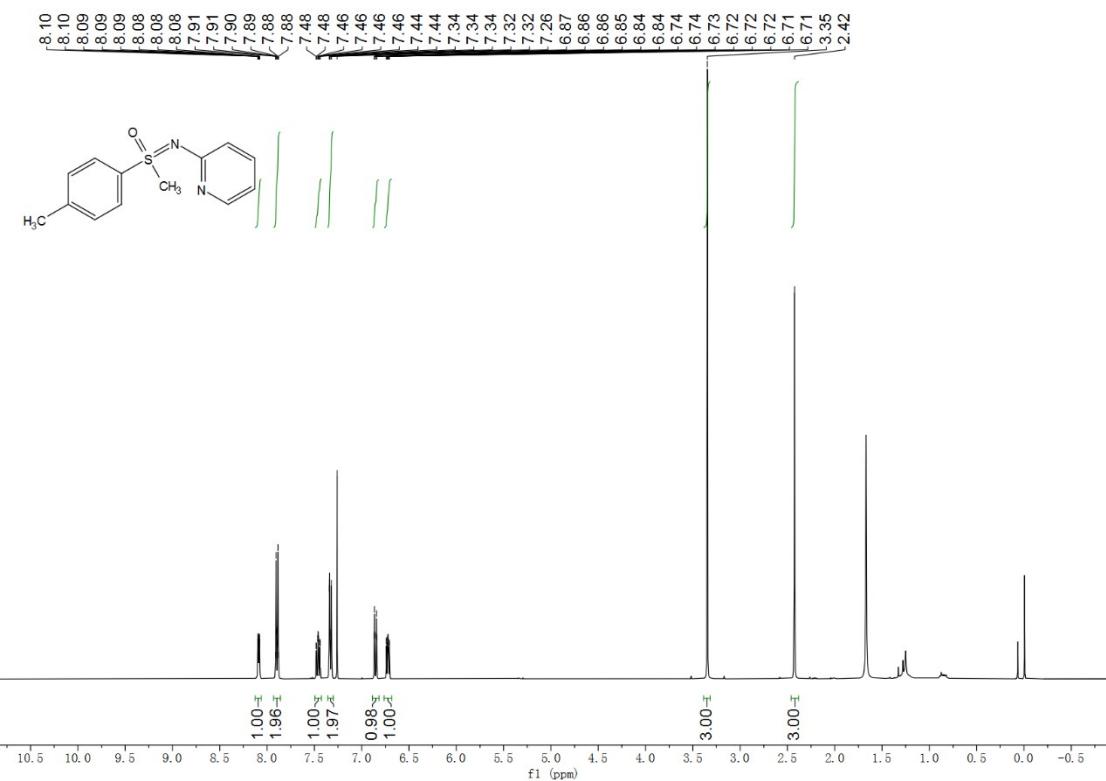


¹³C NMR (CDCl_3 , 100 MHz) of **3j**

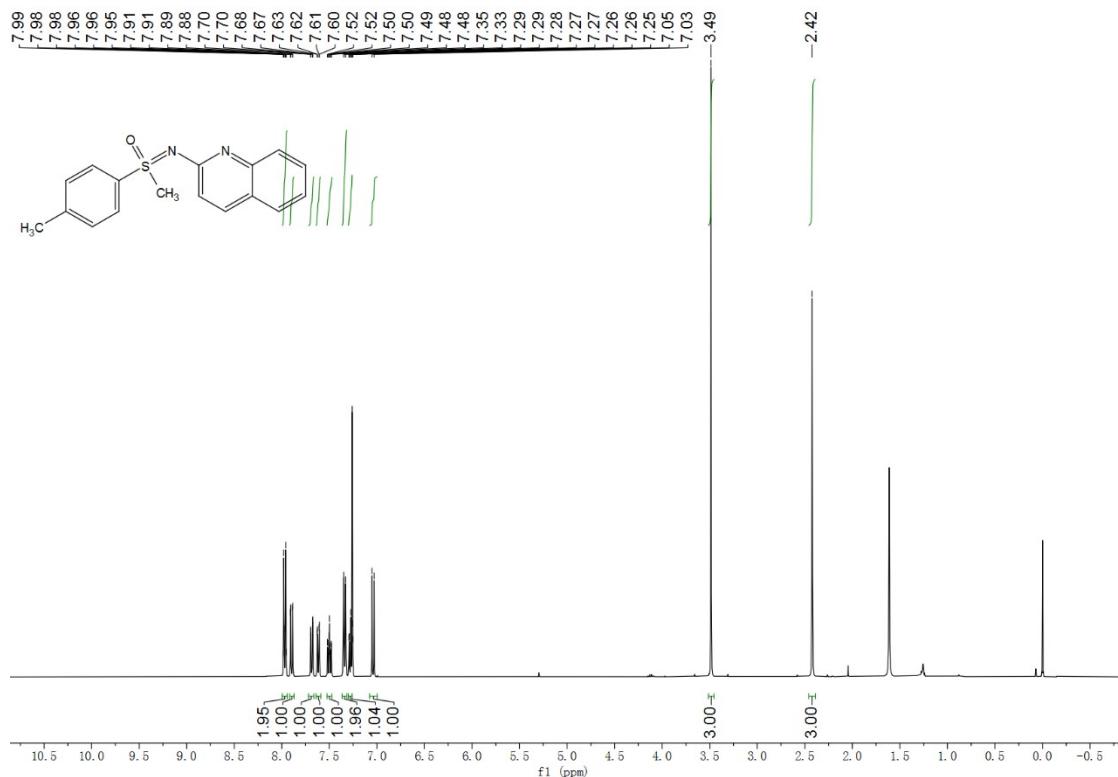
methyl(naphthalen-2-ylimino)(*p*-tolyl)-λ⁶-sulfanone (3k)



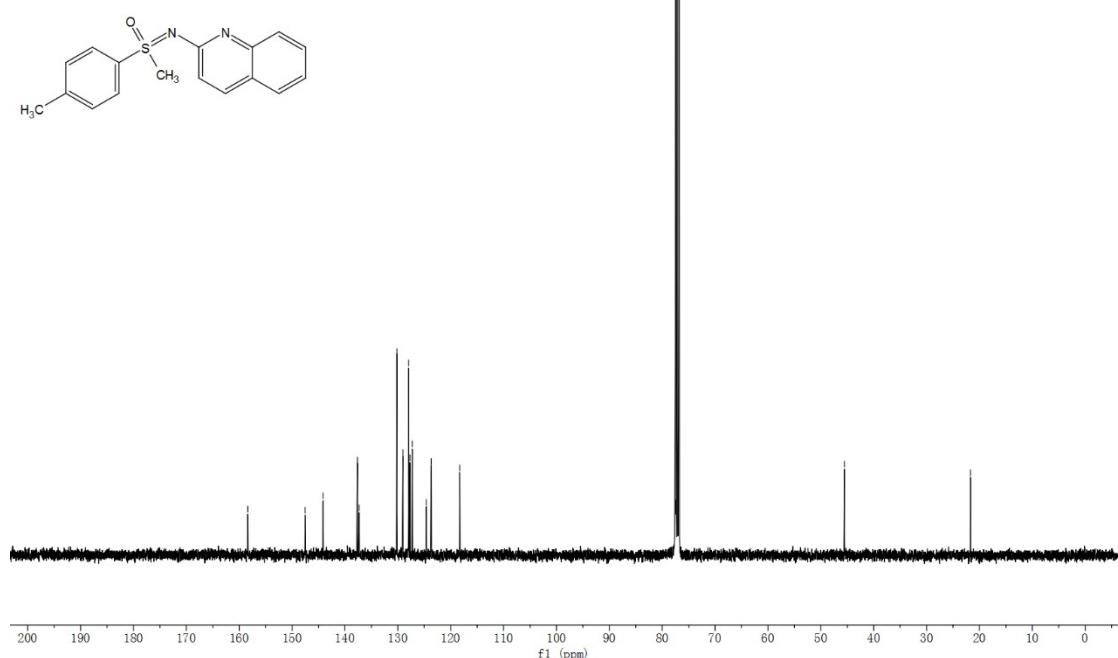
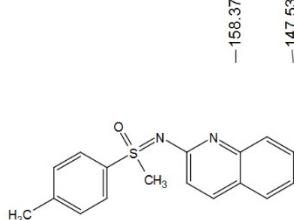
methyl(pyridin-2-ylimino)(*p*-tolyl)-λ⁶-sulfanone (3l**)**



methyl(quinolin-2-ylimino)(*p*-tolyl)-λ⁶-sulfanone (3m)

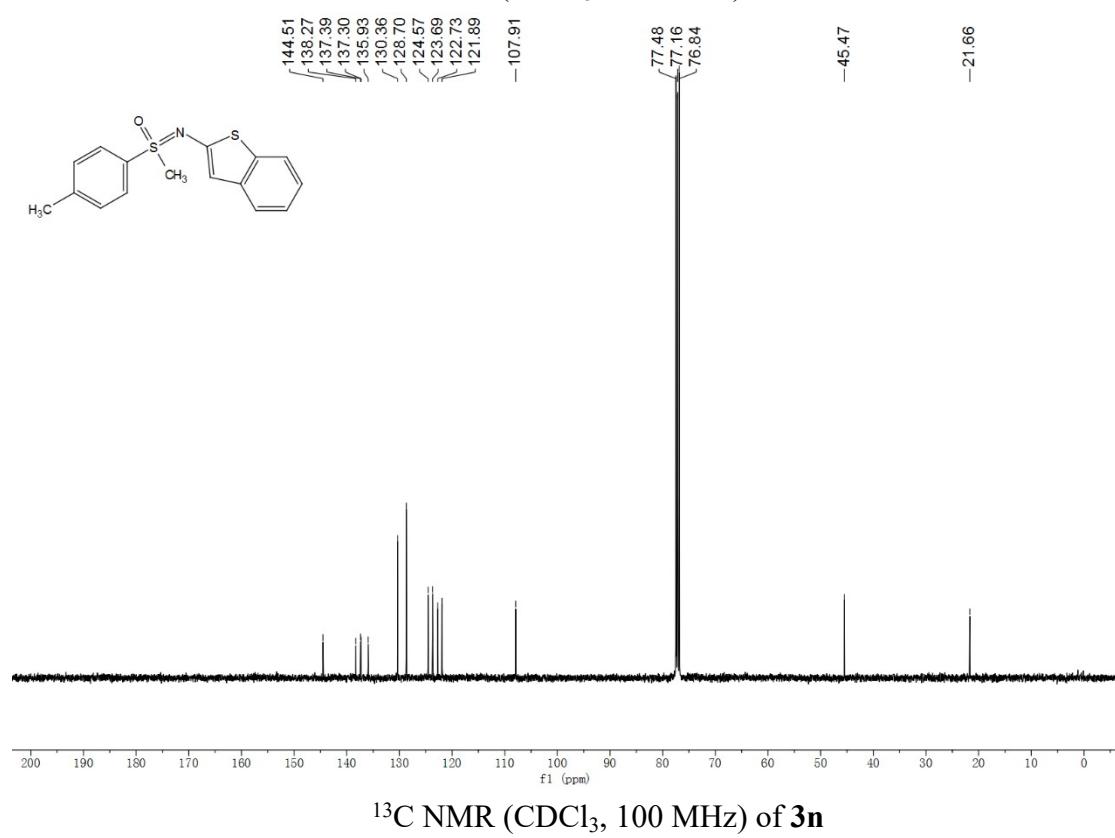
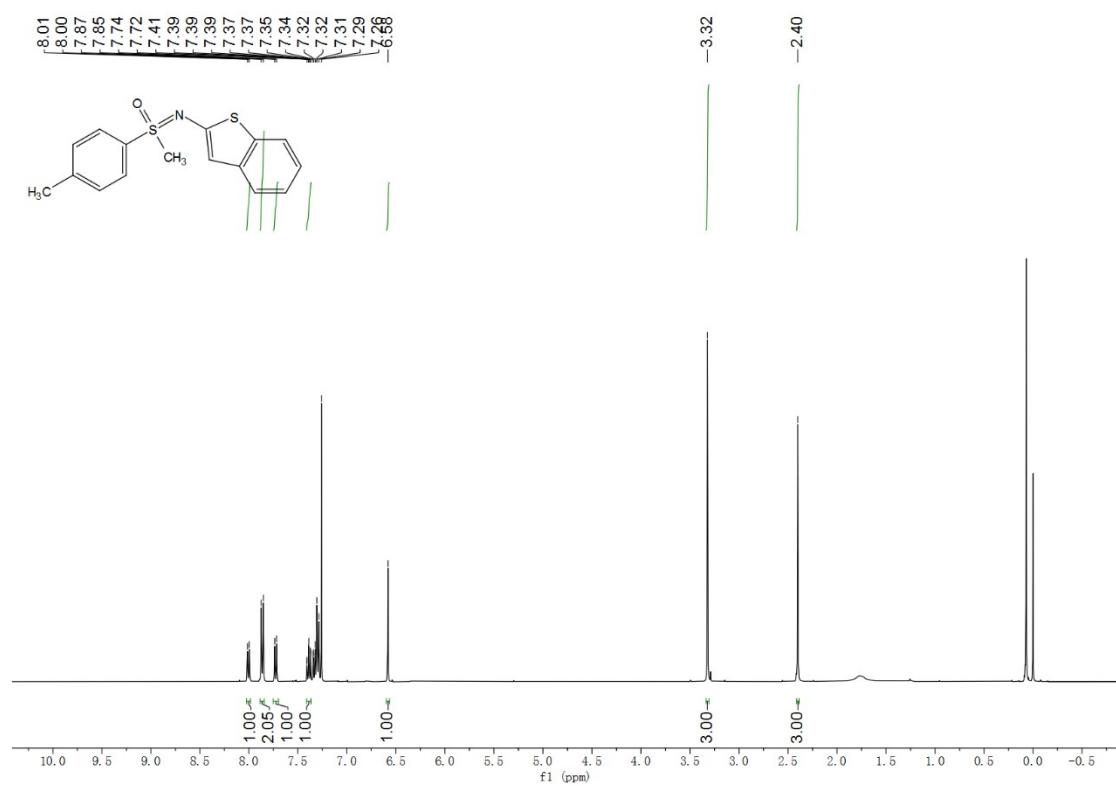


¹H NMR (CDCl₃, 400 MHz) of 3m

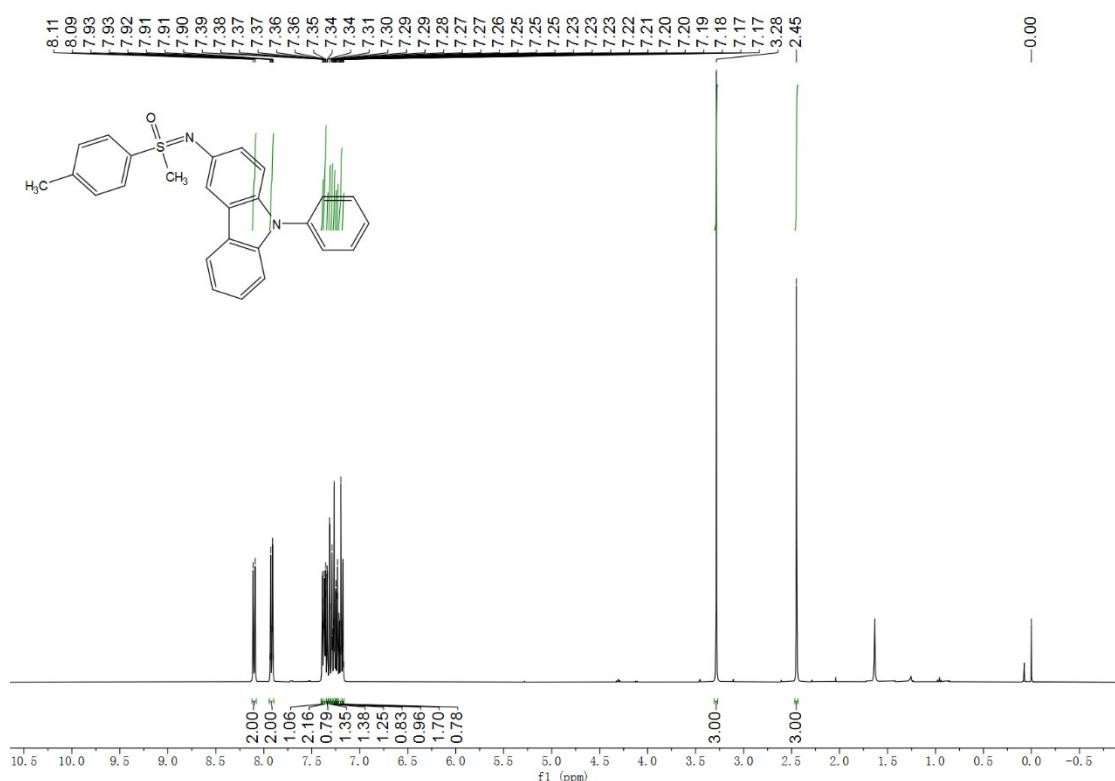


¹³C NMR (CDCl_3 , 100 MHz) of **3m**

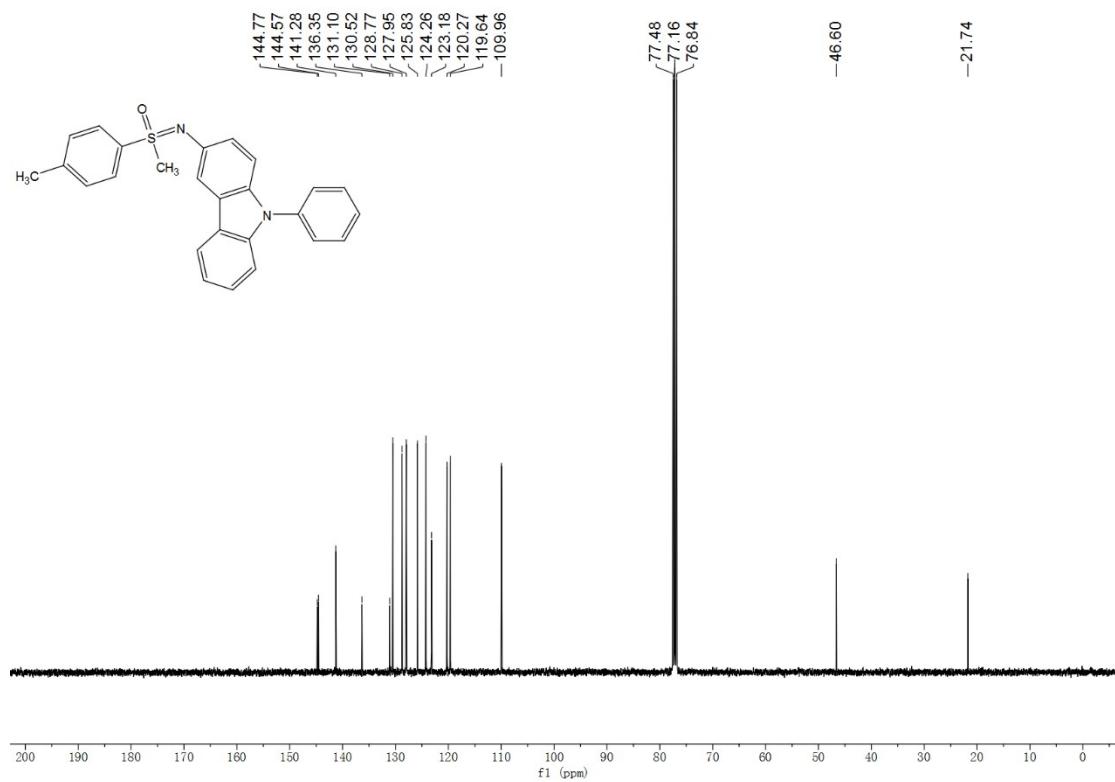
(benzo[*b*]thiophen-2-ylimino)(methyl)(*p*-tolyl)-λ⁶-sulfanone (3n)



methyl((9-phenyl-9*H*-carbazol-3-yl)imino)(*p*-tolyl)-λ⁶-sulfanone (3o)

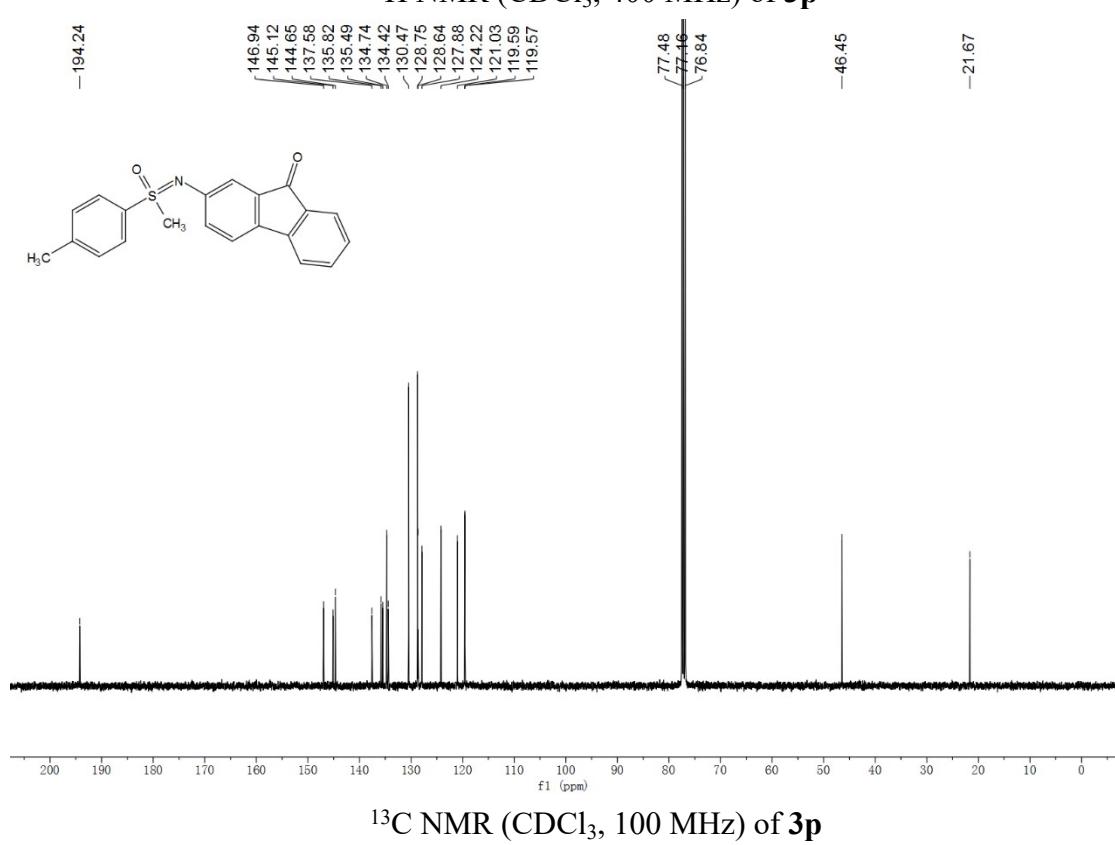
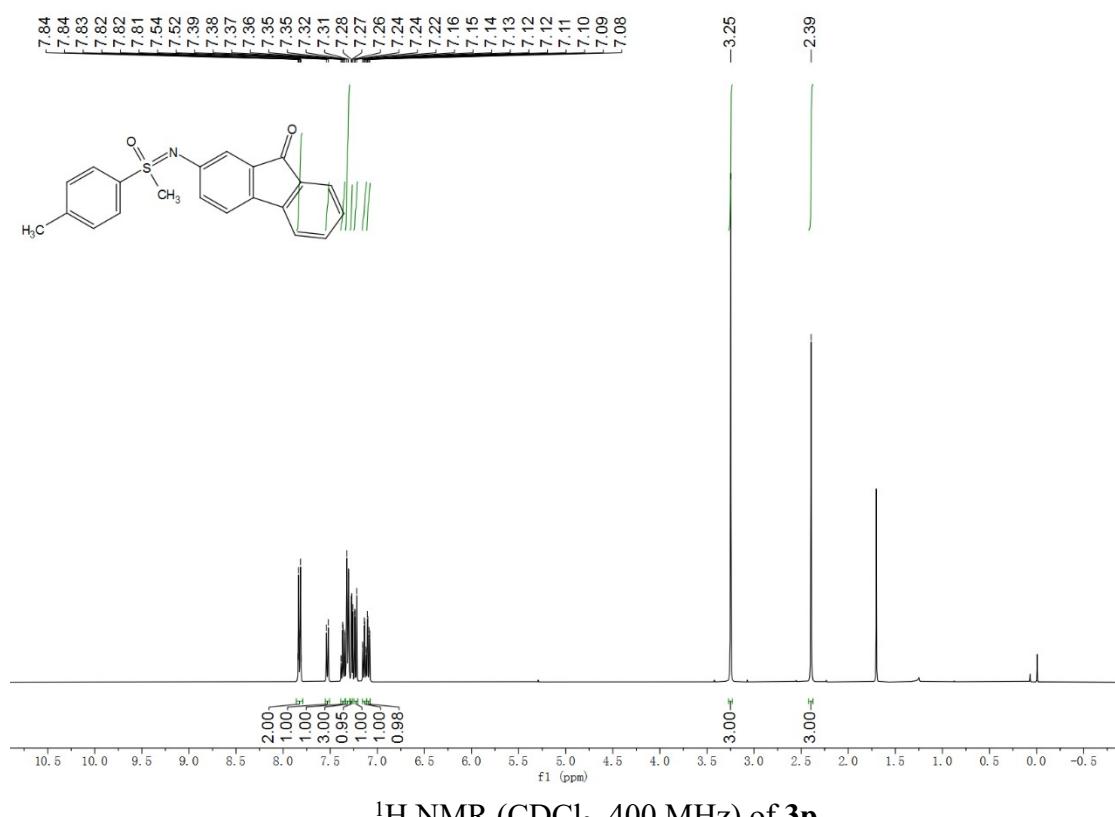


¹H NMR (CDCl_3 , 400 MHz) of **3o**

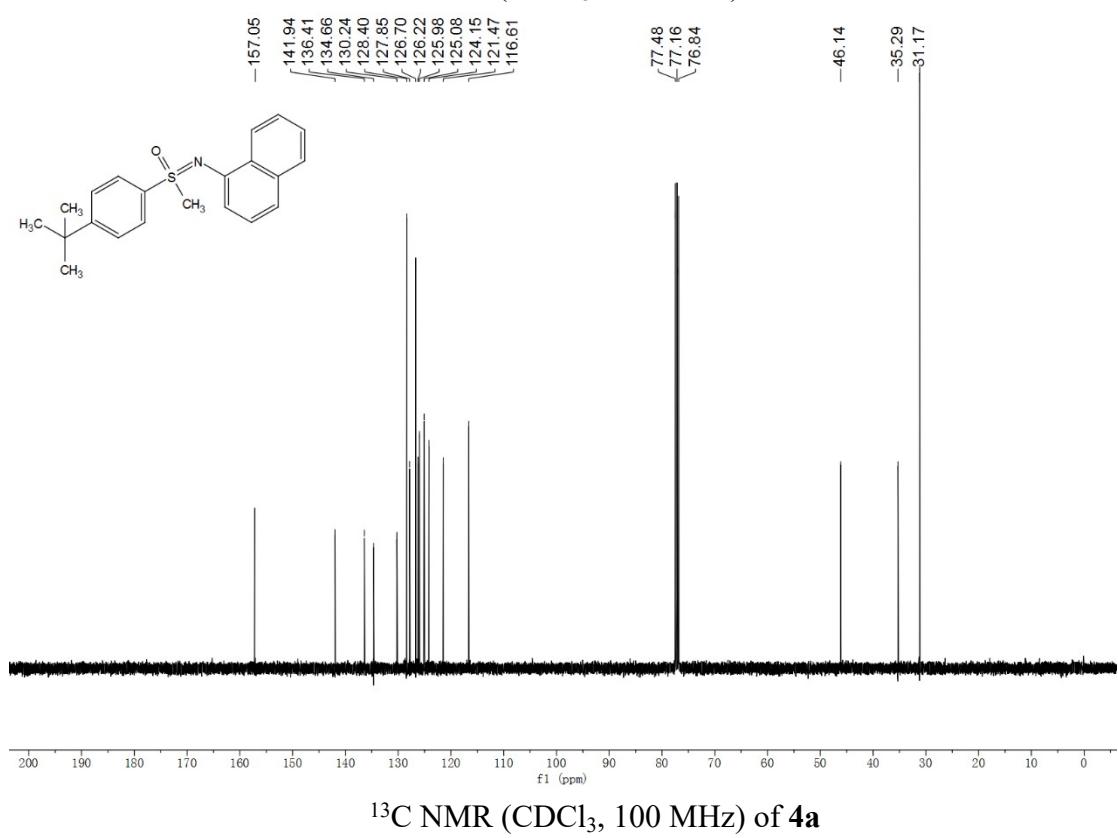
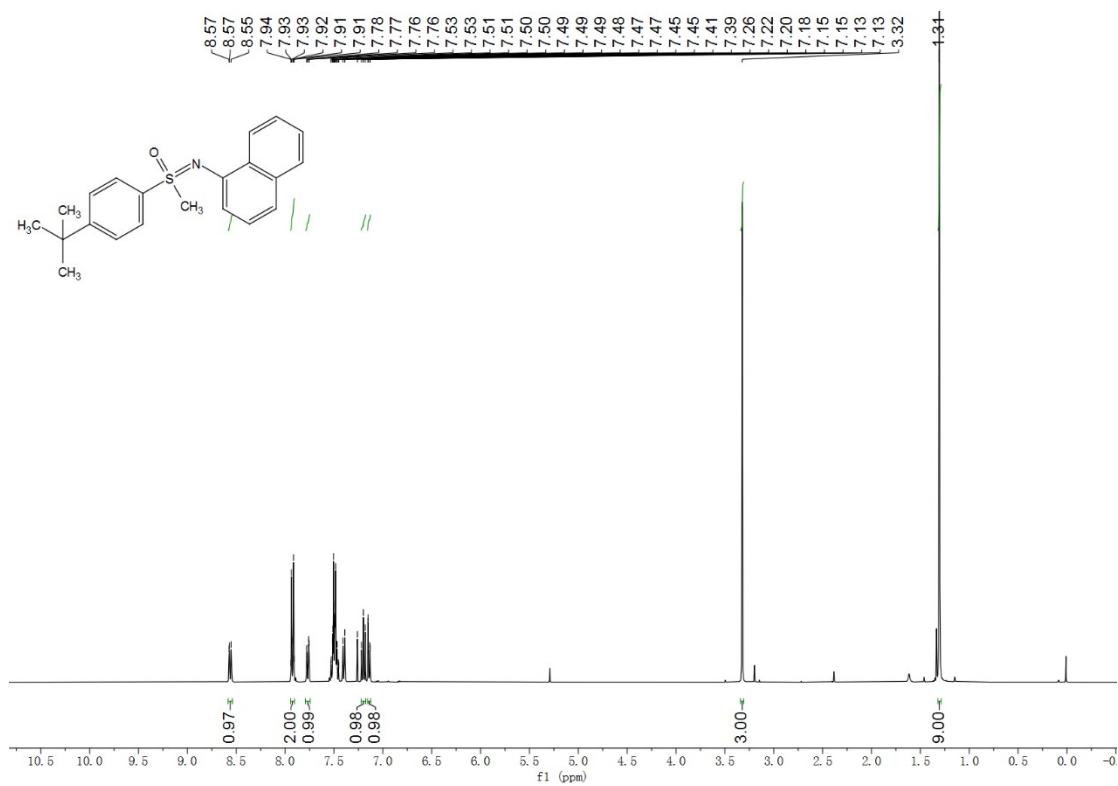


¹³C NMR (CDCl_3 , 100 MHz) of **3o**

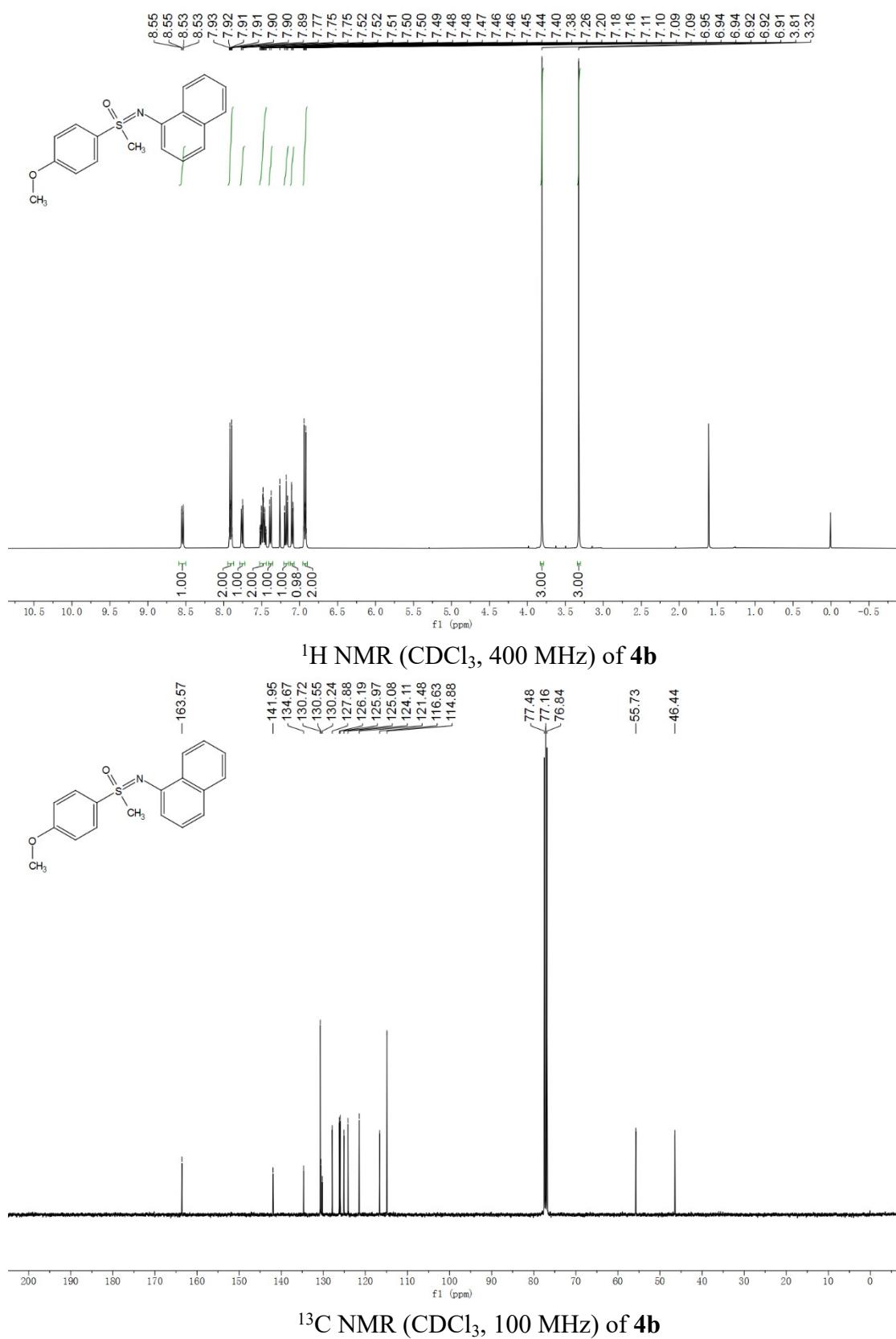
methyl((9-oxo-9H-fluoren-2-yl)imino)(*p*-tolyl)-λ⁶-sulfanone (3p)



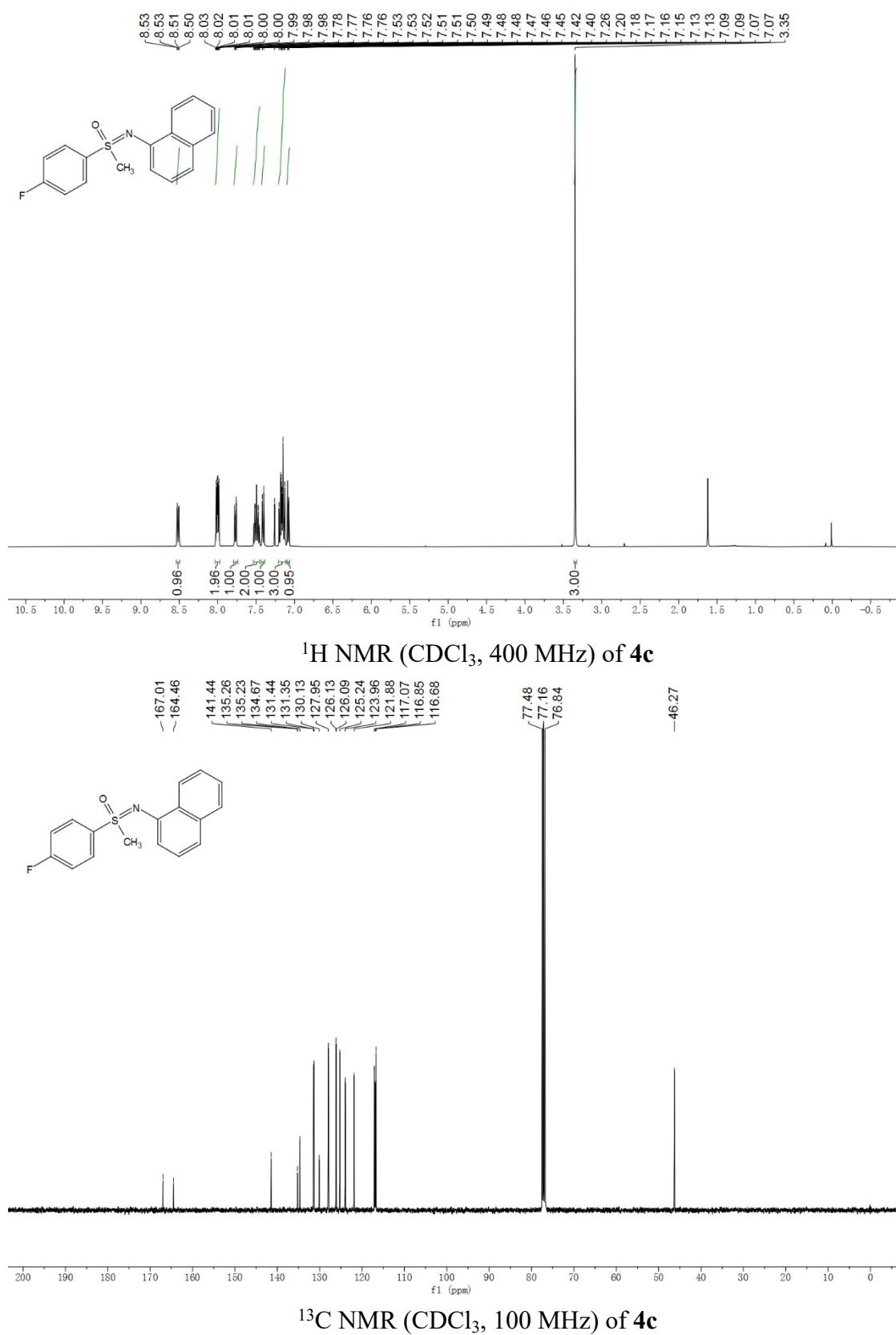
(4-(*tert*-butyl)phenyl)(methyl)(naphthalen-1-ylimino)-λ⁶-sulfanone (4a)



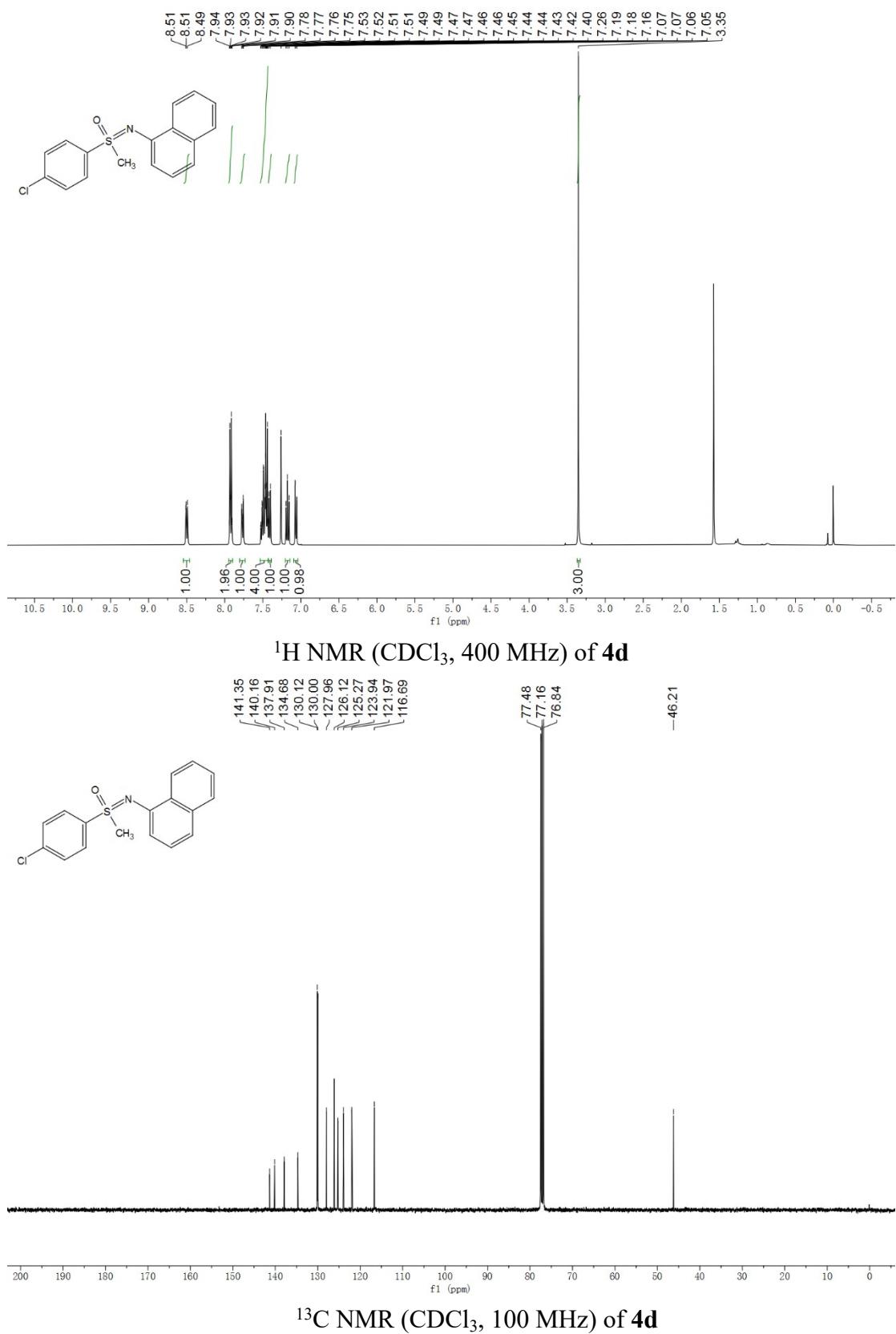
(4-methoxyphenyl)(methyl)(naphthalen-1-ylimino)- λ^6 -sulfanone (4b**)**



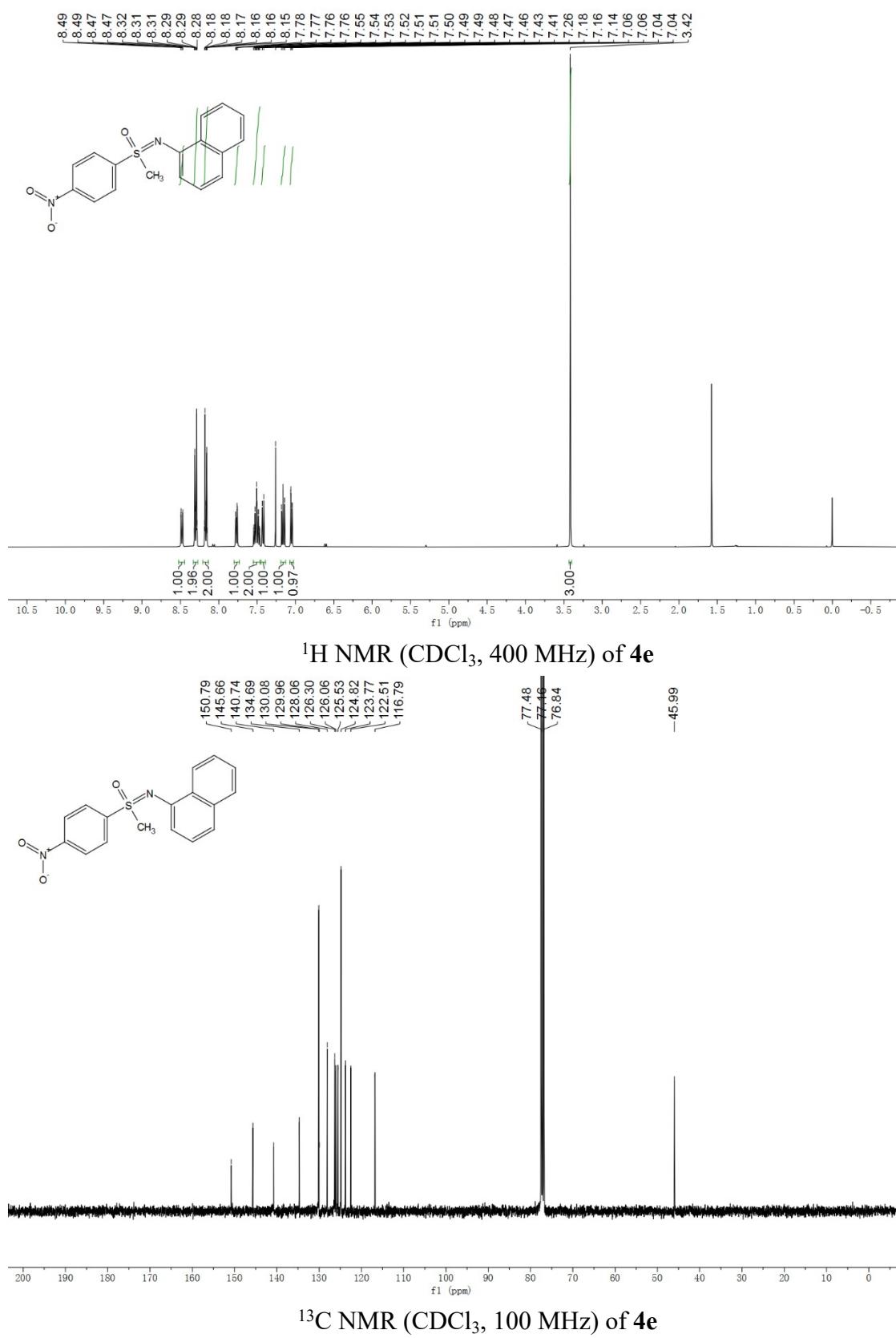
(4-fluorophenyl)(methyl)(naphthalen-1-ylimino)- λ^6 -sulfanone (4c)



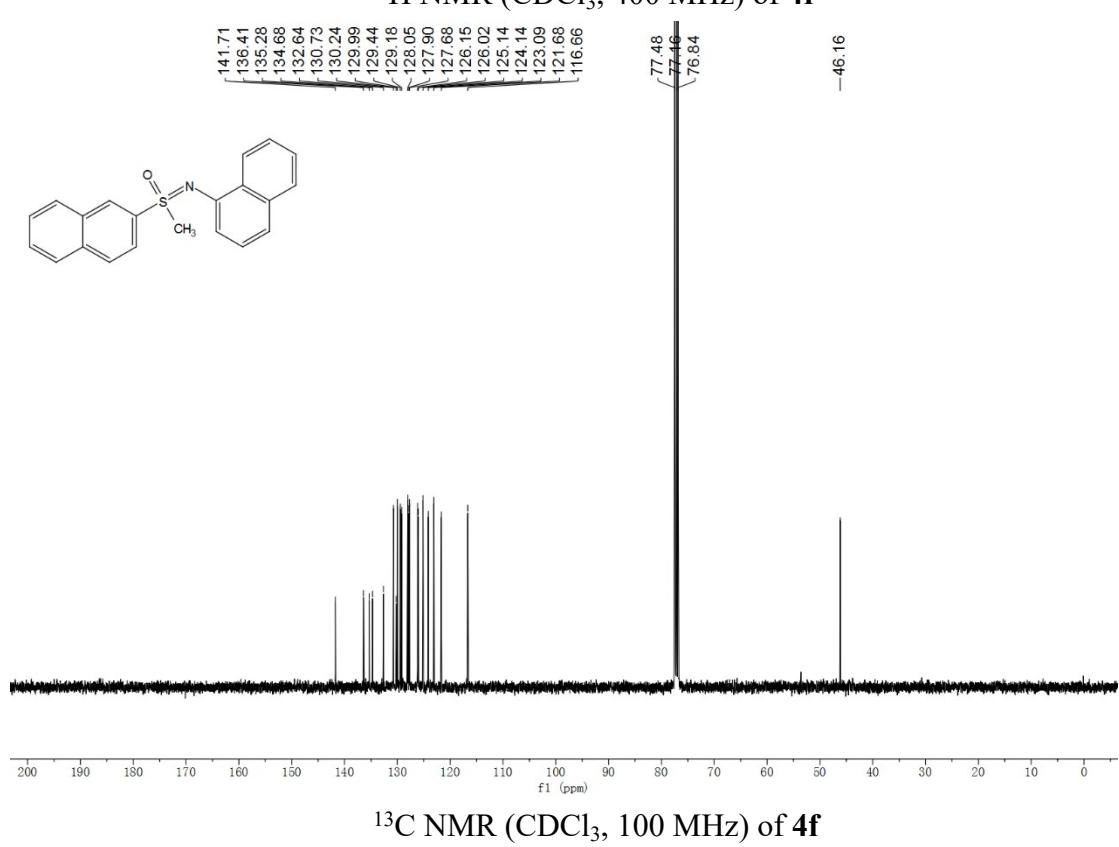
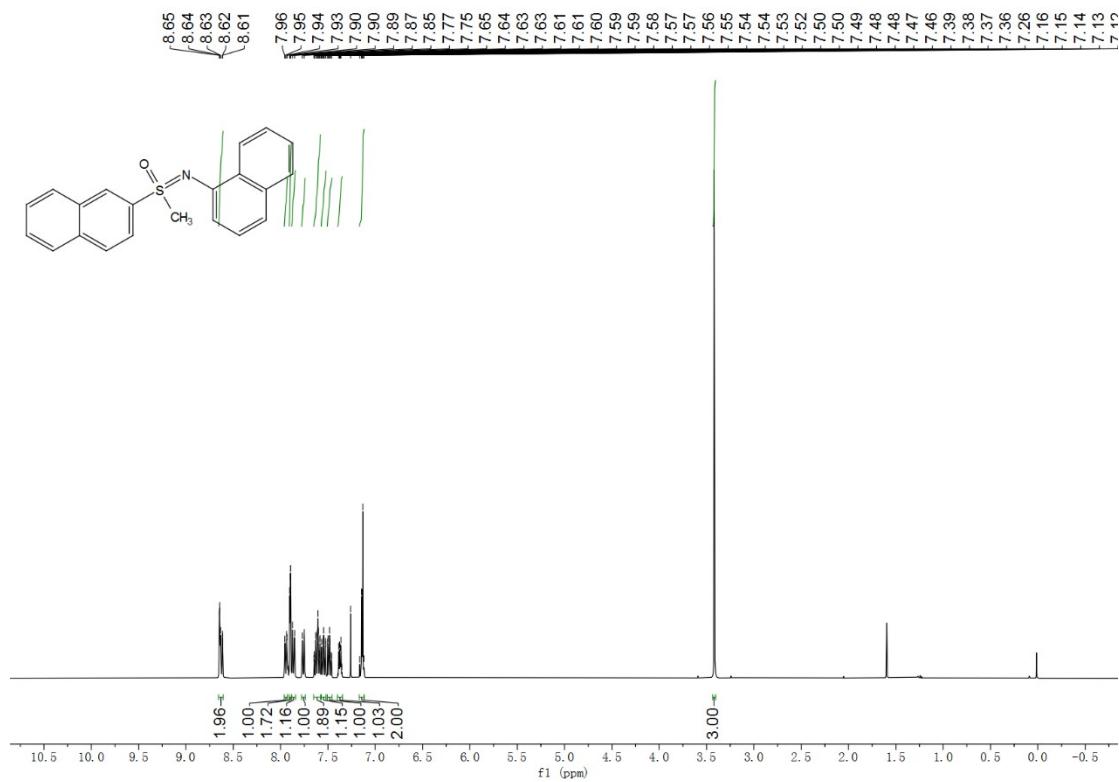
(4-chlorophenyl)(methyl)(naphthalen-1-ylimino)- λ^6 -sulfanone(4d)



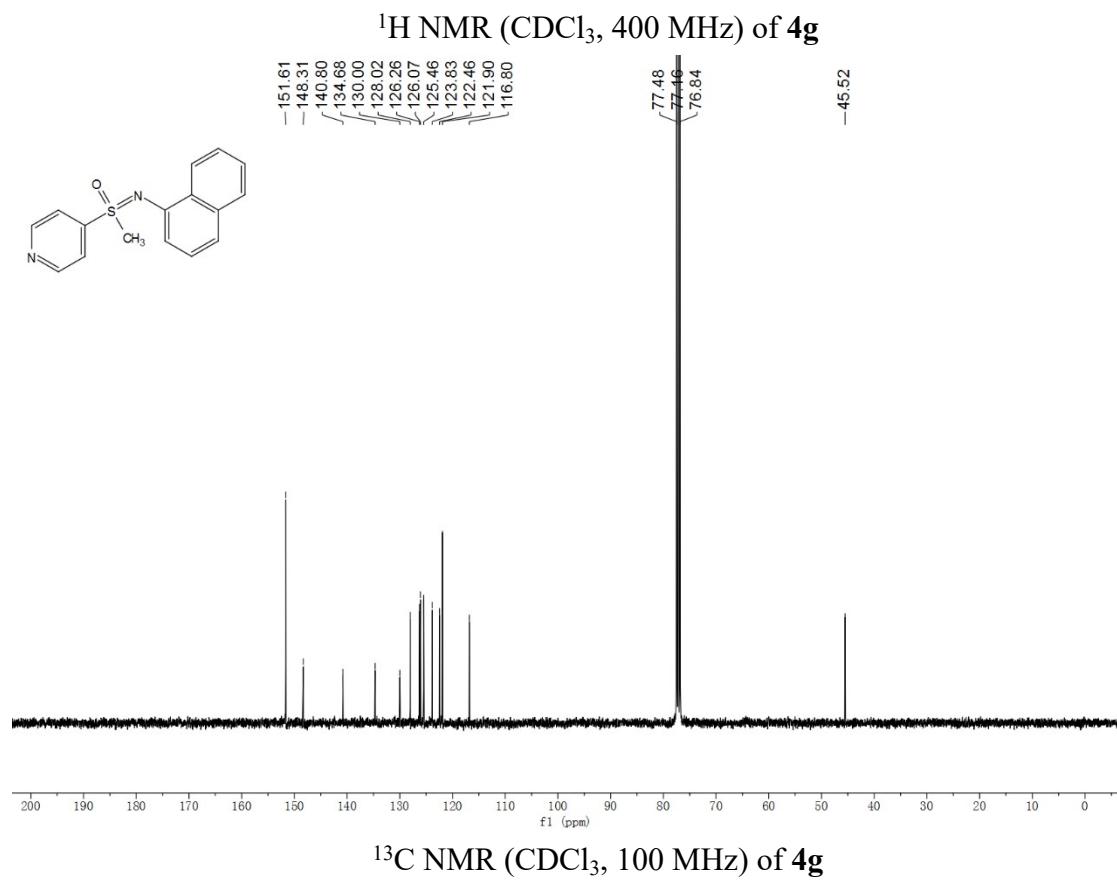
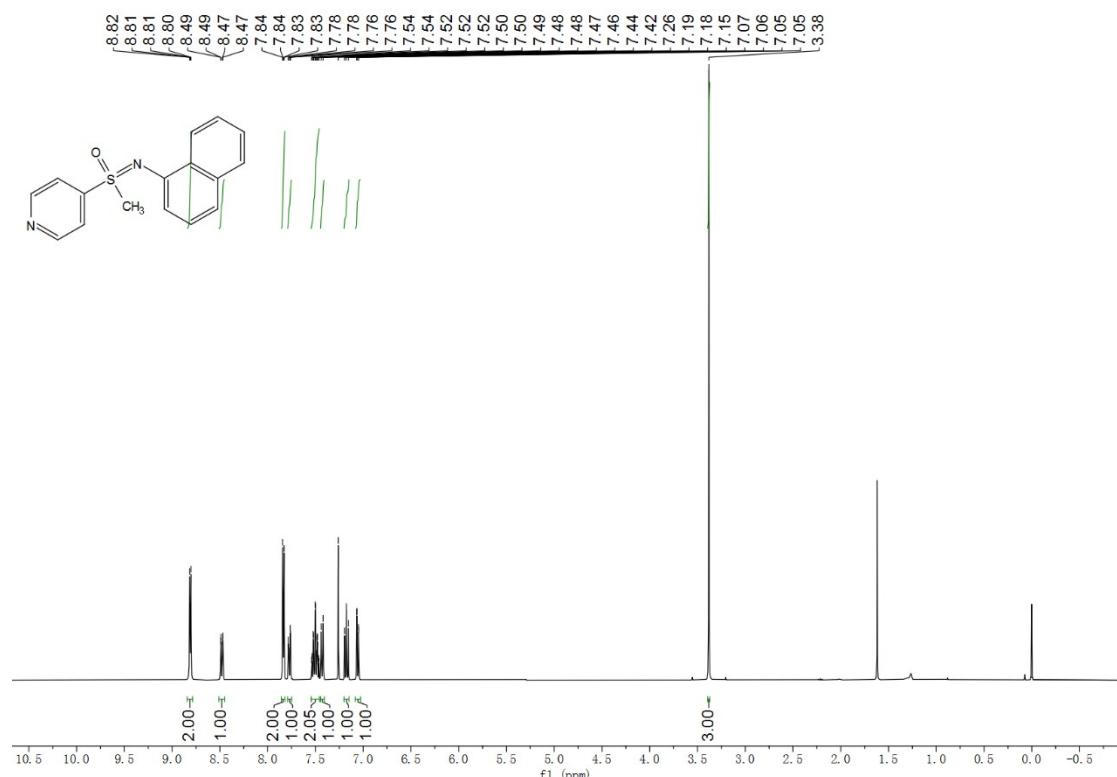
methyl(naphthalen-1-ylimino)(4-nitrophenyl)-λ⁶-sulfanone (4e)



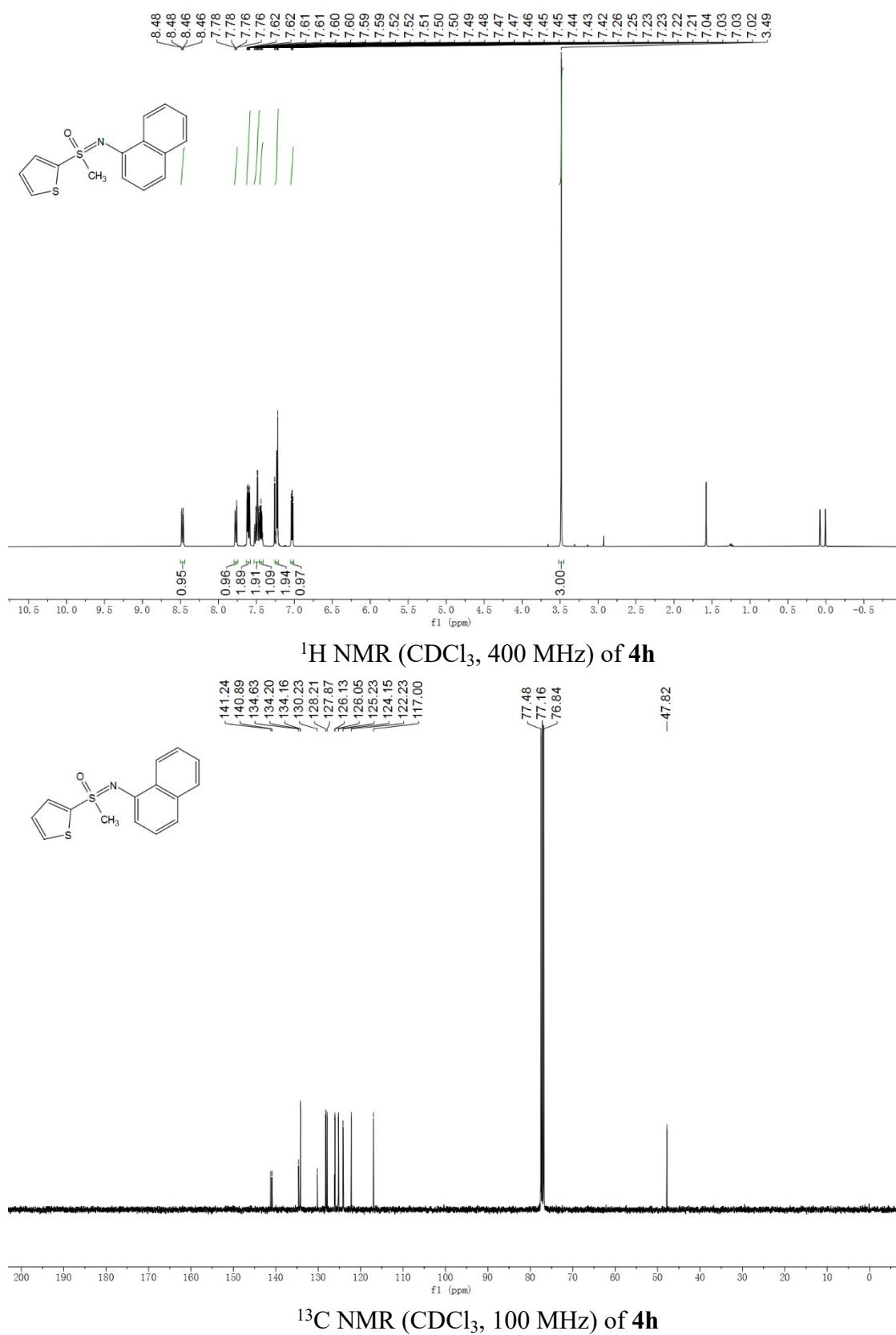
methyl(naphthalen-1-ylimino)(naphthalen-2-yl)-λ⁶-sulfanone (4f)



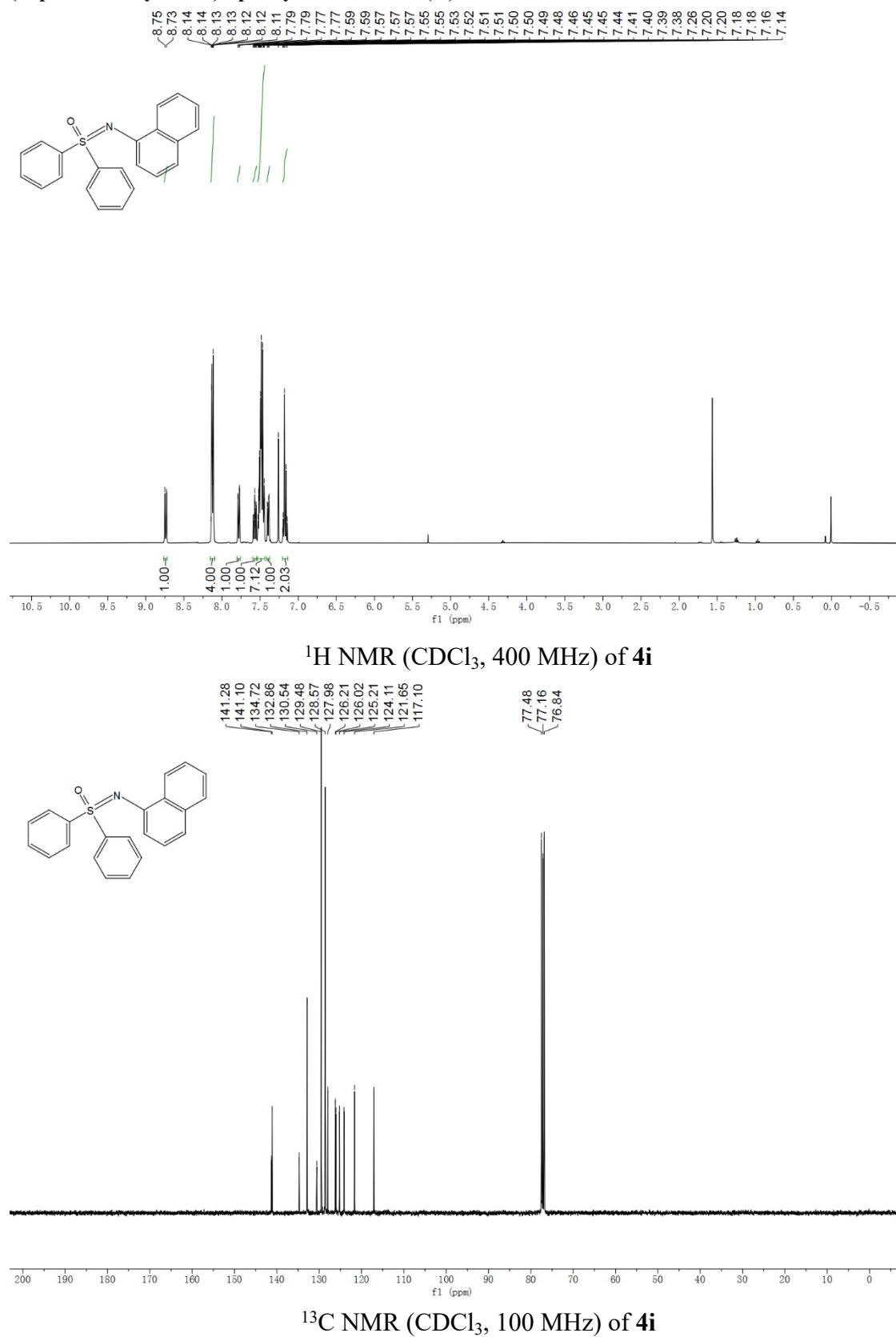
methyl(naphthalen-1-ylimino)(pyridin-4-yl)- λ^6 -sulfanone (4g)



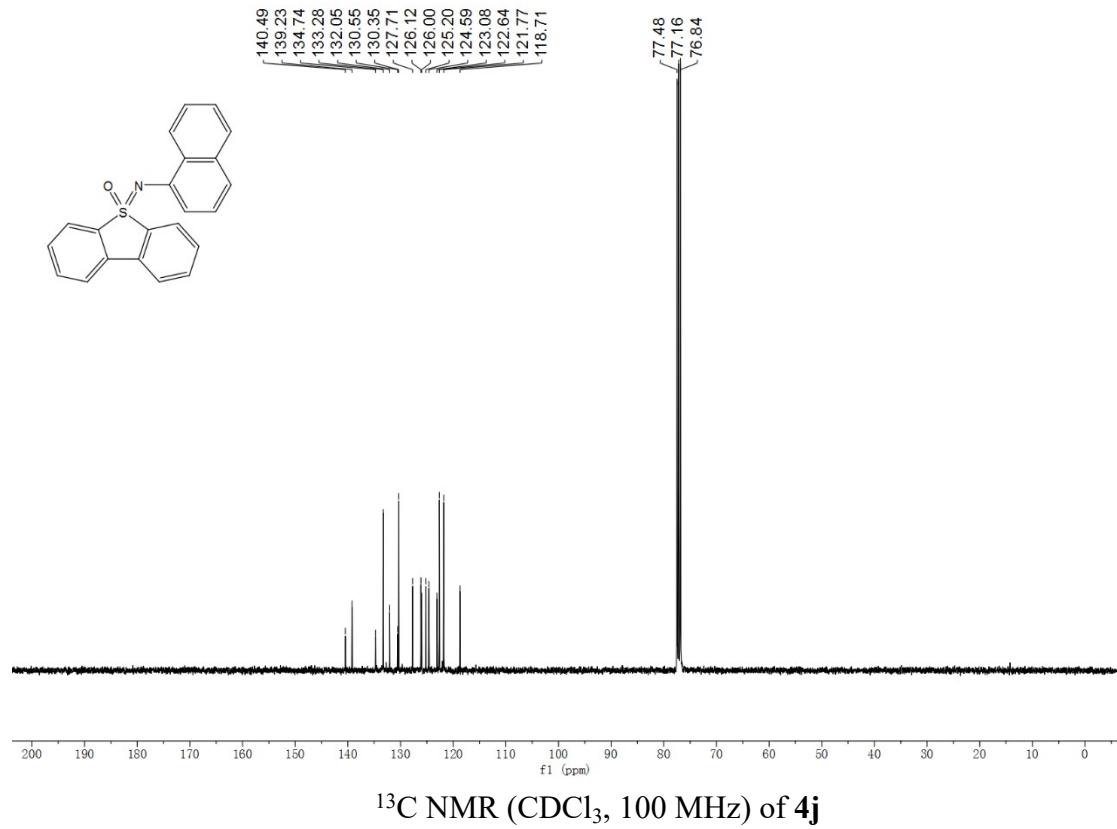
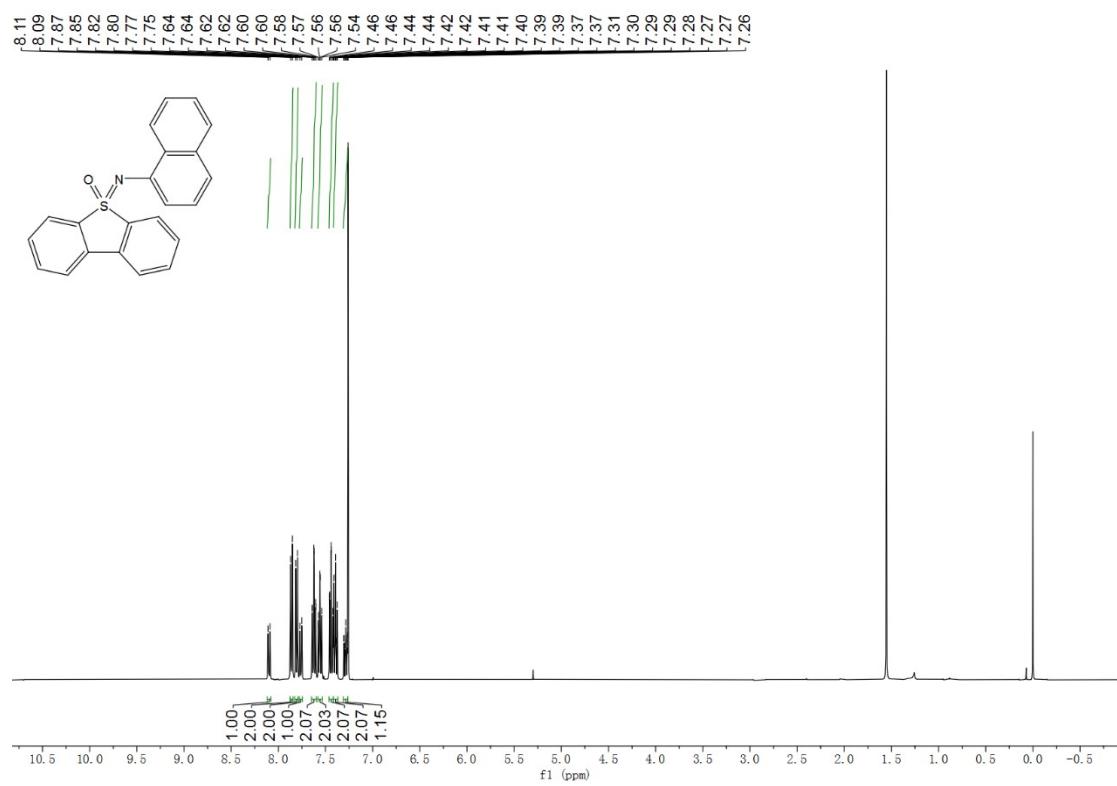
methyl(naphthalen-1-ylimino)(thiophen-2-yl)-λ⁶-sulfanone (4h)



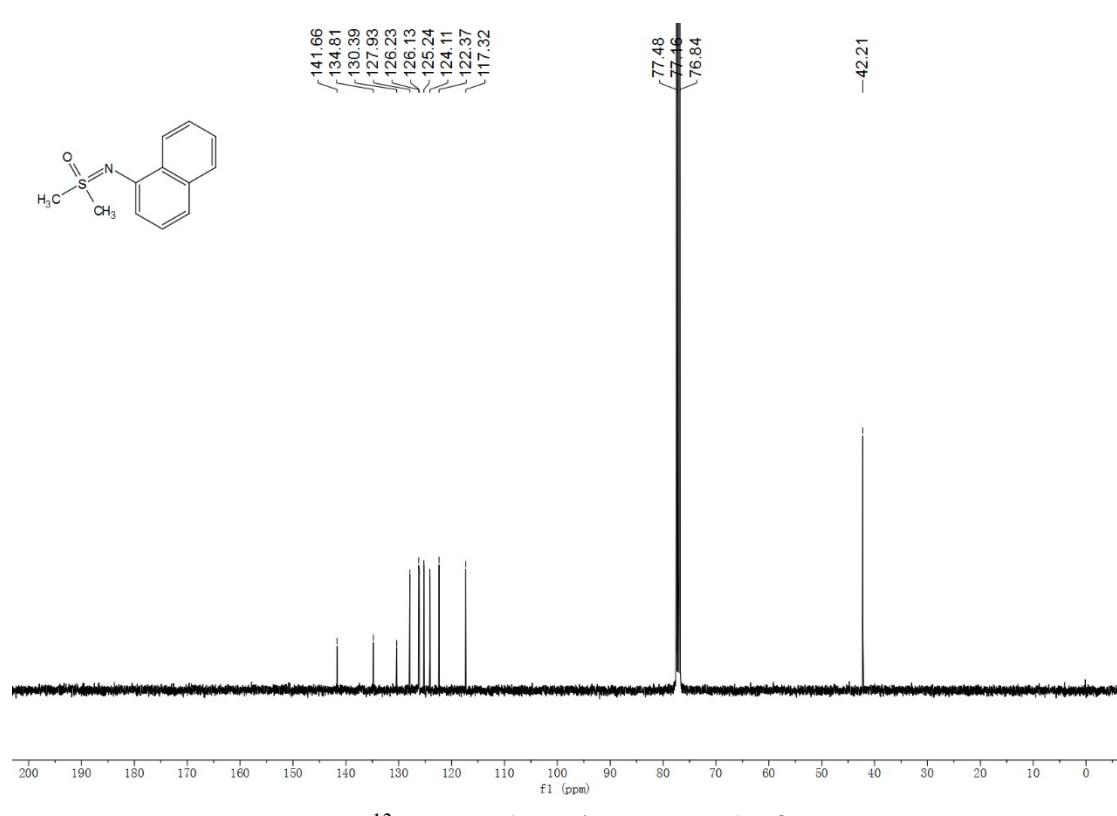
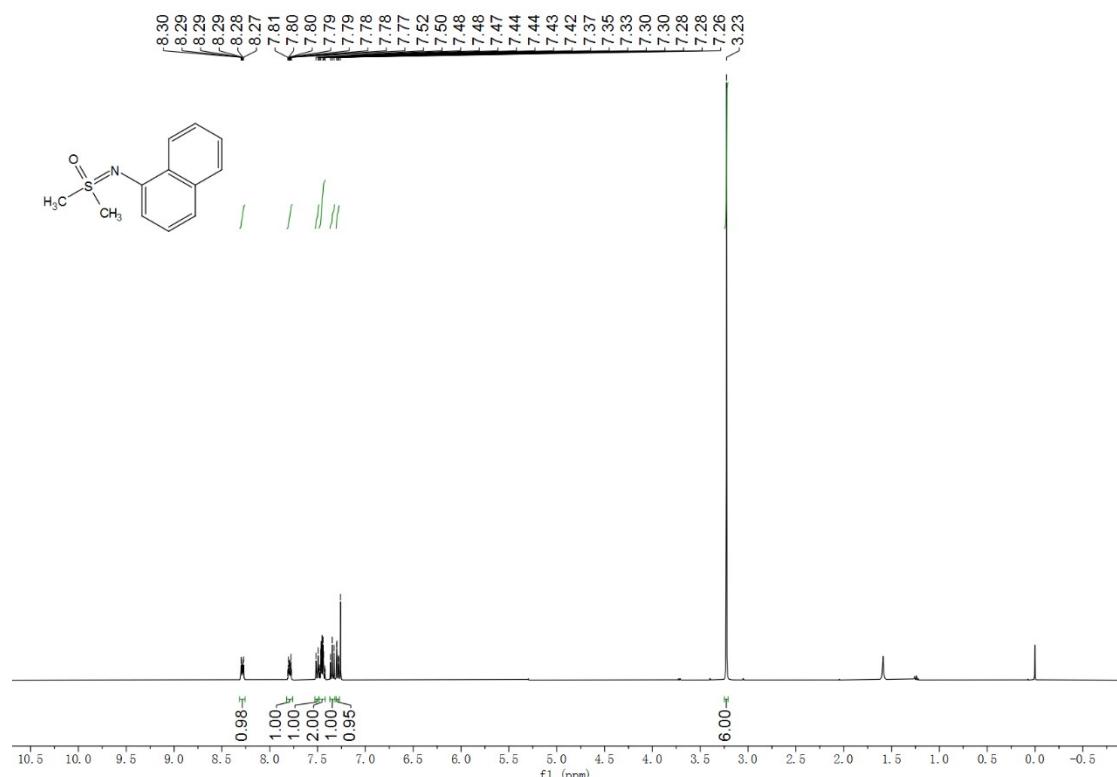
(naphthalen-1-ylimino)diphenyl- λ^6 -sulfanone (4i**)**



5-(naphthalen-1-ylimino)-5*H*-5λ⁴-dibenzo[*b,d*]thiophene 5-oxide (4j)



dimethyl(naphthalen-1-ylimino)- λ^6 -sulfanone (4k**)**



([1,1'-biphenyl]-4,4'-diylbis(azanylylidene))bis(methyl(*p*-tolyl)- λ^6 -sulfanone)(5a)

