Supporting Information

Torsional Strain Inversed Chemoselectivity in Pd-Catalyzed Atroposelective Carbonylation Reaction of Dibenzothiophenium

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Contents

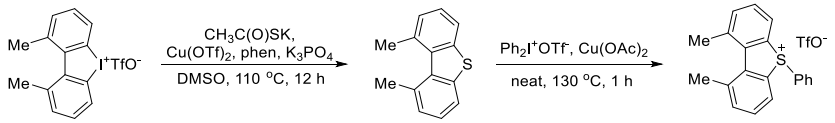
1. General Information

All reactions were carried out under a nitrogen atmosphere in oven dried glassware, unless the reaction procedure states otherwise. All NMR spectra were recorded on a Bruker AC-400 FT or AC-500 FT spectrometer using solvent residue as an internal reference (7.26 and 77.16 ppm for $CDCl_3$, 2.52 and 39.52 ppm for DMSO-d_6, 3.31 and 49.00 ppm for MeOH-d_4). Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad singlet. High resolution mass spectra (HRMS (ESI)) was recorded on a high-resolution mass spectrometer (Waters XEVO-G2 Q-TOF). All the amines from commercial sources were purified by recrystallization, distillation or flash column chromatography (except for $MeNH_2$ and Me_2NH are aqueous solution, which were used as received). All other reagents were used as received from commercial sources and used without further purification. Flash column chromatography was performed by using 200-300 mesh silica gel as the stationary phase.

2. Synthetic details

Procedures for preparation of the sulfoniums:

Typical Procedure:[1-4]



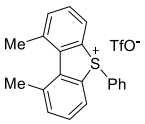
1a

All cyclic diarylsulfoniums, except **1f**, were synthesized using the following method: under an inert atmosphere, to an oven dried round bottom flask charged with the cyclic diaryliodonium salt (1.0 mmol, 1.0 equiv), potassium thioacetate (137.0 mg, 1.2 mmol, 2.0 equiv), copper(II) triflate (36.2 mg, 0.10 mmol, 10 mol%), 1,10-phenanthroline (21.6 mg, 0.12 mmol, 12 mol%) and potassium phosphate (424.2 mg, 2.0 mmol, 2.0 equiv) was added dry dimethyl sulfoxide (10 mL). The mixture was heated at 110 °C overnight with vigorous stirring. After completion of the reaction, it was cooled to room temperature and diluted with 20 mL of ethyl acetate. The mixture was then filtered through a celite pad. The filtrate was poured into 50 mL of water, the mixture was then extracted three times with ethyl acetate (30 mL×3), the combined organic layer was washed with brine, dried over Na_2SO_4, filtered and then concentrated. The residue was then flushed with PE through column of silica gel to afford the crude diarylthiophen intermediate, which was used in the next step without further purification.

Under an inert atmosphere, an oven dried round bottom flask was charged with the diarylthiophen (0.50 mmol, 1.0 equiv), the diaryliodonium salt (0.50 mmol, 1.0 equiv) and copper(II) acetate (9.1 mg, 0.050 mmol, 10 mol%). The mixture, which liquefied to a black oil upon heating, was heated to 130 °C with vigorous stirring for 1 h. After being cooled to room temperature, the reacting mixture was dissolved in a small amount of dichloromethane and directly purified by flash column chromatography (PE/EA 90/10, then DCM/MeOH 97/3) on silica gel to afford the crude product as a brown oil. The crude product was the further purified by vigorous stirring under ether for about 1

h, and the solid was collected by filtration and dried under vacuum.

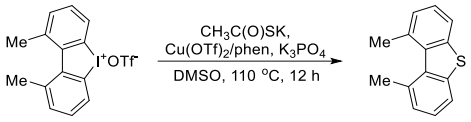
1,9-dimethyl-5-phenyl-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (1a)



1a

The reaction of 2,2'-dimethyl-[1,1'-biphenyl]iodonium trifluoromethanesulfonate salt (9.12 g, 20 mmol) afforded **1a** (5.33 g, 61% overall yield) as a light yellow powder. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.8 Hz, 2H), 7.68 (d, *J* = 7.7 Hz, 2H), 7.65 – 7.45 (m, 7H), 2.75 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -78.1. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.9, 138.2, 137.6, 135.0, 131.7, 131.3, 131.0, 130.4, 128.2, 126.6, 120.9 (q, *J* = 321.3 Hz), 24.9. **HRMS (ESI)** calcd for: $C_{20}H_{17}S^+$ [M-OTf^-]$^+$ 289.1045, found: 289.1053.

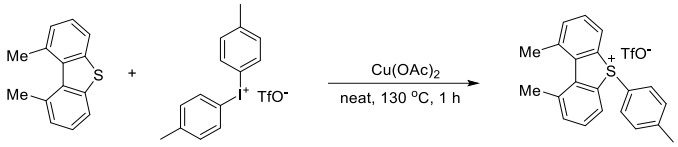
1,9-dimethyldibenzo[2,1-*b*:1',2'-*d*]thiophene (S1) [5]



S1

Compound **S1** can be isolated, pure **S1** was used in some small scale reactions. The reaction of 2,2'-dimethyl-[1,1'-biphenyl]iodonium trifluoromethanesulfonate salt (9.12 g, 20 mmol, 1.0 equiv) with potassium thioacetate (2.74 g, 24 mmol, 1.2 equiv) afforded **S1**, it was separated by flash column chromatography (PE) as a white solid (2.77 g, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.8 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 3H), 2.79 (s, 6H).

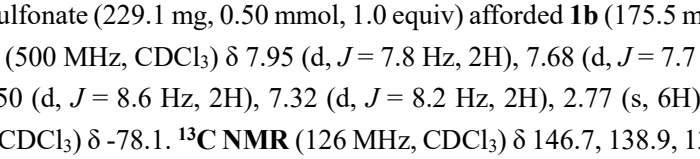
1,9-dimethyl-5-(*p*-tolyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (1b)



S1 **1b**

The reaction of **S1** (105.5 mg, 0.50 mmol, 1.0 equiv) and bis(4-methylphenyl)iodonium trifluoromethanesulfonate (229.1 mg, 0.50 mmol, 1.0 equiv) afforded **1b** (175.5 mg, 78%) as a white powder. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.8 Hz, 2H), 7.68 (d, *J* = 7.7 Hz, 2H), 7.57 (t, *J* = 7.7 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 2.77 (s, 6H), 2.38 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.1. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.7, 138.9, 138.1, 137.5, 132.4, 131.8, 131.0, 130.6, 126.6, 124.3, 121.0 (q, *J* = 321.2 Hz), 24.9, 21.8. **HRMS (ESI)** calcd for: $C_{21}H_{19}S^+$ [M-OTf^-]$^+$ 303.1202, found: 303.1205.

1,9-dimethyl-5-(*m*-tolyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (1c)

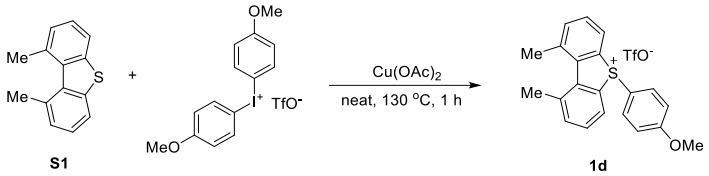


S1 **1c**

The reaction of **S1** (105.5 mg, 0.50 mmol, 1.0 equiv) and bis(3-methylphenyl)iodonium trifluoromethanesulfonate (229.1 mg, 0.50 mmol, 1.0 equiv) afforded **1c** (182.4 mg, 81%) as a light yellow powder. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.8 Hz, 2H), 7.67 (d, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 7.8 Hz, 3H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 1H),

2.75 (s, 6H), 2.35 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.1. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.5, 138.9, 138.2, 137.5, 135.9, 131.5, 131.3, 131.1, 131.0, 127.7, 126.9, 126.6, 120.9 (q, *J* = 321.3 Hz), 24.9, 21.4. **HRMS (ESI)** calcd for: $C_{21}H_{19}S^+$ [M-OTf$^-$]$^+$ 303.1202, found: 303.1206.

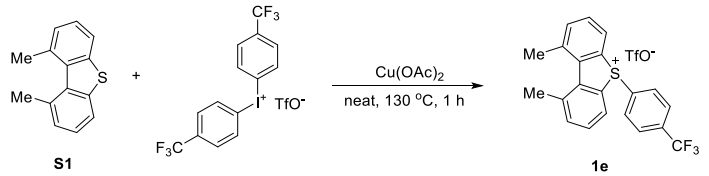
5-(4-methoxyphenyl)-1,9-dimethyl-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (1d)



S1 1d

The reaction of **S1** (105.5 mg, 0.50 mmol, 1.0 equiv) and bis(4-anisyl)iodonium triflate (735.4 mg, 1.5 mmol, 3 equiv) afforded **1d** (112.1 mg, 48%) as a brown powder. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.8 Hz, 2H), 7.65 (d, *J* = 7.7 Hz, 2H), 7.60 – 7.51 (m, 4H), 6.99 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 3H), 2.75 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -78.2. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.0, 138.6, 138.0, 137.4, 133.1, 132.3, 130.9, 126.5, 120.9 (q, *J* = 321.8 Hz), 117.3, 116.3, 56.2, 24.9. **HRMS (ESI)** calcd for: $C_{21}H_{19}OS^+$ [M-OTf$^-$]$^+$ 319.1151, found: 319.1159.

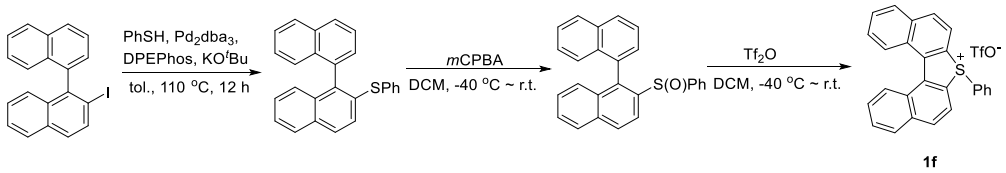
1,9-dimethyl-5-(4-(trifluoromethyl)phenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium (1e)



S1 1e

The reaction of **S1** (105.5 mg, 0.50 mmol, 1.0 equiv) and bis(4-(trifluoromethyl)phenyl)iodonium trifluoromethanesulfonate (283.1 mg, 0.50 mmol, 1.0 equiv) afforded **1e** (214.6 mg, 85%) as a light brown powder. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.8 Hz, 2H), 2.78 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.5, -78.3. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.1, 138.6, 137.9, 136.2 (q, *J* = 33.7 Hz), 133.1, 131.2, 131.1, 130.5, 128.4 (q, *J* = 3.7 Hz), 127.1, 122.7 (q, *J* = 274.6 Hz), 120.8 (q, *J* = 321.7 Hz), 24.9. **HRMS (ESI)** calcd for: $C_{21}H_{16}F_3S^+$ [M-OTf$^-$]$^+$ 357.0919, found: 357.0925.

Synthesizing of 7-phenyl-7*H*-dinaphtho[2,1-*b*:1',2'-*d*]thiophen-7-ium trifluoromethanesulfonate (1f) [6,7]**:**



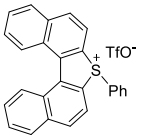
1f

Under an inert atmosphere an oven dried sealed tube charged with 2-iodo-1,1'-binaphthalene (760.5 mg, 2.0 mmol, 1.0 equiv), Pd_2dba_3 (36.6 mg, 0.040 mmol, 2.0 mol%), DPEPhos (43.1 mg, 0.080 mmol, 4.0 mol%), and potassium *tert*-butoxide (246.9 mg, 2.2 mmol, 1.0 equiv) was added dry toluene (5 mL), and the thiophenol (242.4 mg, 2.2 mmol, 1.0 equiv) was then added to the mixture. The mixture was then stirred at 110 °C for 12 h. After being cooled to room temperature, the mixture was filtered through a small pad of celite and silica gel. The solvent was removed under reduced pressure, and the crude product was used in the next step without further purification.

To a solution of above thioether in 5 mL of DCM was added 3-chloroperoxybenzoic acid

(*m*CPBA, 75%, 506.2 mg, 2.2 mmol, 1.0 equiv) in portions at -40 °C. The resulting mixture was slowly warmed to room temperature and stirred at the same temperature for 2 h. The mixture was filtered through a silica gel pad (washed with PE to remove the impurities and collected with PE/EA 3/1) and the solvent was removed under reduced pressure to afford the crude sulfoxide.

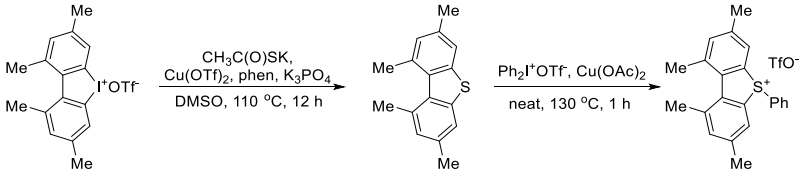
To a solution of the above sulfoxide in DCM (5 mL) was added trifluoromethanesulfonic anhydride (0.34 mL, 2.0 mmol, 1.0 equiv) dropwise at -40 °C. The mixture was stirred at the same temperature for 30 min, and then slowly warmed to room temperature within 12 h. The solvent was removed under reduced pressure and the residue was then purified by flash column chromatography (PE/EA 90/10, then DCM/MeOH 97/3) on silica gel to afford the crude product as a brown oil, the crude product was stirred vigorously under ether for about 1 h. Then the solid was collected by filtration and dried under vacuum as a brown powder (141.5 mg, 11% overall yield).



1f

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.5 Hz, 2H), 8.26 – 8.17 (m, 4H), 8.12 (d, *J* = 8.3 Hz, 2H), 7.90 – 7.70 (m, 6H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.9 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -78.1. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.1, 136.8, 135.3, 133.3, 131.9, 131.14, 131.08, 129.65, 129.69, 129.3, 127.7, 127.6, 125.2, 122.3, 121.0 (q, *J* = 321.1 Hz). **HRMS (ESI)** calcd for: $C_{26}H_{17}S^+$ [M-OTf$^-$]$^+$ 361.1045, found: 361.1049.

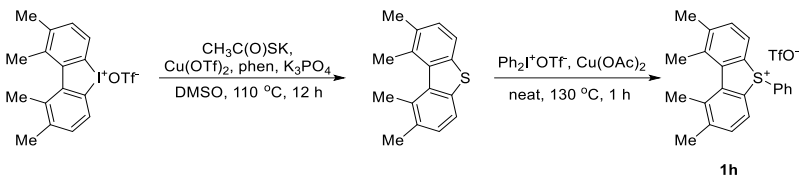
1,3,7,9-tetramethyl-5-phenyl-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (1g)



1g

The reaction of 2,2',4,4'-tetramethyl-[1,1'-biphenyl]-cyclic iodonium triflate (484.3 mg, 1.0 mmol) afforded **1g** (272.5 mg, 58% overall yield) as a brown powder. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (s, 2H), 7.67 – 7.61 (m, 3H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.43 (s, 2H), 2.71 (s, 6H), 2.41 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -78.2. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.7, 139.0, 136.6, 136.5, 134.8, 131.7, 131.5, 130.6, 128.7, 127.0, 121.0 (q, *J* = 321.8 Hz), 25.0, 21.1. **HRMS (ESI)** calcd for: $C_{22}H_{21}S^+$ [M-OTf$^-$]$^+$ 317.1358, found: 317.1360.

1,2,8,9-tetramethyl-5-phenyl-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (1h)

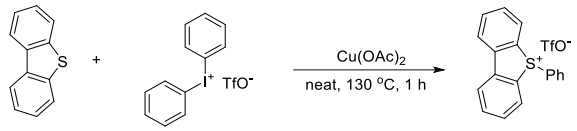


1h

The reaction of 2,2',3,3'-tetramethyl-[1,1'-biphenyl]-cyclic iodonium triflate (484.3 mg, 1.0 mmol) afforded **1h** (258.4 mg, 55% overall yield) as a brown powder. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.9 Hz, 2H), 7.59 (q, *J* = 7.6 Hz, 3H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 7.6 Hz, 2H), 2.51 (s, 6H), 2.47 (s, 6H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.1. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.8,

139.4, 136.5, 134.8, 132.5, 131.6, 130.3, 128.8, 128.6, 126.0, 120.9 (q, J = 321.3 Hz), 21.8, 20.8. **HRMS (ESI)** calcd for: $C_{22}H_{21}S^+$ [M-OTf$^-$]$^+$ 317.1358, found: 317.1362.

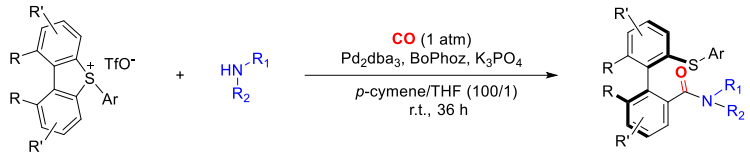
5-phenyl-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (1i)



1i

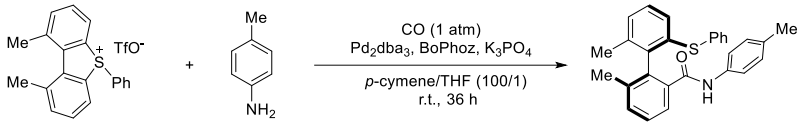
The reaction of dibenzo[*b*,*d*]thiophene (0.92 g, 5.0 mmol, 1.0 equiv) and diphenyliodonium triflate (2.2 g, 5.0 mmol, 1.0 equiv) afforded **1i** (1.9 g, 93%) as a white powder. **^{1}H NMR** (400 MHz, MeOH-d_4) δ 8.44 (d, J = 7.9 Hz, 2H), 8.19 (d, J = 8.1 Hz, 2H), 7.96 (t, J = 7.7 Hz, 2H), 7.74 (td, J_1 = 7.8 Hz, J_2 = 1.3 Hz, 3H), 7.67 – 7.57 (m, 4H). **^{19}F NMR** (376 MHz, MeOH-d_4) δ -79.9. **^{13}C NMR** (101 MHz, MeOH-d_4) δ 140.8, 136.0, 135.5, 133.8, 132.70, 132.68, 131.2, 129.1, 129.0, 125.6, 121.8 (q, J = 319.9 Hz). **HRMS (ESI)** calcd for: $C_{18}H_{13}S^+$ [M-OTf$^-$]$^+$ 261.0732, found: 261.0735

General Procedure of Pd-Catalyzed Carbonylation Reaction of Sulfoniums:



Under a N_2 atmosphere a dried Schlenk tube was charged with the cyclic sulfonium (0.20 mmol, 1.0 equiv), the amine (0.40 mmol, 2.0 equiv), Pd_2dba_3 (4.6 mg, 0.0050 mmol, 2.5 mol%), BoPhoz (9.4 mg, 0.015 mmol, 7.5 mol%) and potassium phosphate (42.4 mg, 0.20 mmol, 1.0 equiv). After the N_2 was replaced by CO via purging with a CO balloon, *p*-cymene/THF (2mL, 100/1) was added, and then the mixture was stirred at room temperature for 36 h. After complete consumption of the starting material, the mixture directly purified by flash column chromatography (PE, then PE/EA 10/1) on silica gel to afford the desired product.

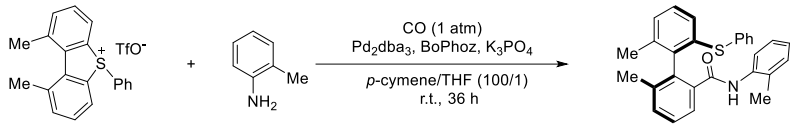
2',6-dimethyl-6'-(phenylthio)-*N*-(*p*-tolyl)-[1,1'-biphenyl]-2-carboxamide (3a)



1a **3a**

The reaction of **1a** (84.7 mg, 0.20 mmol, 1.0 equiv) and *p*-toluidine (42.9 mg, 0.40 mmol, 2.0 equiv) under standard condition afforded **3a** (84.6 mg, 99%, 89% ee) as a light yellow oil. HPLC conditions: Chiralpak IC, isopropanol/hexane = 10: 90, flow: 1.0 mL/min, λ = 254 nm, tr = 15.488 min (minor), 19.520 min (major). $[\alpha]_D^{20}$ = -17.15 (c 0.66, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (bs, 1H), 7.80 (dd, J_1 = 6.5 Hz, J_2 = 2.6 Hz, 1H), 7.49 – 7.46 (m, 2H), 7.45 – 7.41 (m, 2H), 7.39 – 7.31 (m, 3H), 7.15 – 7.08 (m, 4H), 7.05 (d, J = 8.3 Hz, 2H), 6.79 (dd, J_1 = 7.5 Hz, J_2 = 1.7 Hz, 1H), 2.29 (s, 3H), 2.12 (s, 3H), 2.00 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.9, 137.69, 137.67, 137.4, 136.5, 136.4, 135.5, 135.4, 134.7, 133.9, 132.5, 131.7, 129.7, 129.4, 128.9, 128.7, 128.6, 128.0, 126.9, 124.4, 120.4, 21.0, 20.2, 19.9. **HRMS (ESI)** calcd for: $C_{28}H_{26}NOS^+$ [M+H]$^+$ 424.1730, found: 424.1734.

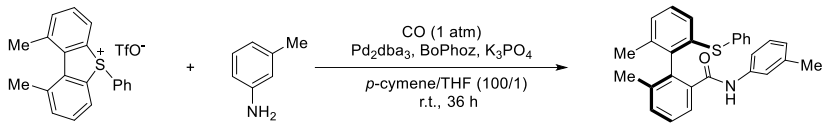
2',6-dimethyl-6'-(phenylthio)-*N*-(*o*-tolyl)-[1,1'-biphenyl]-2-carboxamide (3b)



1a **3b**

The reaction of **1a** (84.7 mg, 0.20 mmol, 1.0 equiv) and *o*-toluidine (42.9 mg, 0.40 mmol, 2.0 equiv) under standard condition afforded **3b** (83.2 mg, 98%, 91% ee) as a light yellow oil. HPLC conditions: Chiralpak IC, isopropanol/hexane = 30: 70, flow: 1.0 mL/min, λ = 210 nm, tr = 9.489 min (minor), 23.533 min (major). $[\alpha]_D^{20}$ = -14.74 (c 0.42, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.70 (dd, J_1 = 6.1 Hz, J_2 = 3.0 Hz, 1H), 7.66 (bs, 1H), 7.47 – 7.42 (m, 2H), 7.36 – 7.25 (m, 6H), 7.14 – 7.07 (m, 4H), 7.07 – 7.03 (m, 1H), 6.76 – 6.70 (m, 1H), 2.08 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.7, 137.8, 137.6, 137.5, 136.9, 136.6, 135.62, 135.57, 134.3, 132.3, 132.0, 131.1, 130.5, 129.7, 128.7, 128.6, 128.6, 128.0, 126.6, 126.4, 125.7, 124.6, 124.1, 20.3, 19.9, 17.8. **HRMS (ESI)** calcd for: $C_{28}H_{26}NOS^+$ $[M+H]^+$ 424.1730, found: 424.1729

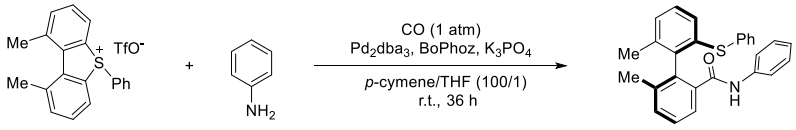
2',6-dimethyl-6'-(phenylthio)-*N*-(*m*-tolyl)-[1,1'-biphenyl]-2-carboxamide (3c)



1a **3c**

The reaction of **1a** (84.7 mg, 0.20 mmol, 1.0 equiv) and *m*-toluidine (42.9 mg, 0.40 mmol, 2.0 equiv) under standard condition afforded **3c** (84.8 mg, 99%, 86% ee) as a light yellow oil. HPLC conditions: Chiralpak AD-H, isopropanol/hexane = 10: 90, flow: 1.0 mL/min, λ = 254 nm, tr = 7.812 min (major), 8.736 min (minor). $[\alpha]_D^{20}$ = -7.08 (c 0.30, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (bs, 1H), 7.76 (dd, J_1 = 6.3 Hz, J_2 = 2.8 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.44 – 7.38 (m, 2H), 7.37 – 7.28 (m, 3H), 7.17 – 7.06 (m, 4H), 6.95 (dd, J_1 = 8.1 Hz, J_2 = 2.2 Hz, 1H), 6.87 (d, J = 7.5 Hz, 1H), 6.79 (dd, J_1 = 7.2 Hz, J_2 = 2.0 Hz, 1H), 2.27 (s, 3H), 2.09 (s, 3H), 1.99 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.1, 138.8, 137.9, 137.8, 137.6, 137.5, 136.6, 136.5, 135.5, 134.7, 132.6, 131.9, 129.7, 128.9, 128.7, 128.6, 128.1, 126.9, 125.1, 124.6, 121.0, 117.3, 21.6, 20.3, 19.9. **HRMS (ESI)** calcd for: $C_{28}H_{26}NOS^+$ $[M+H]^+$ 424.1730, found: 424.1754.

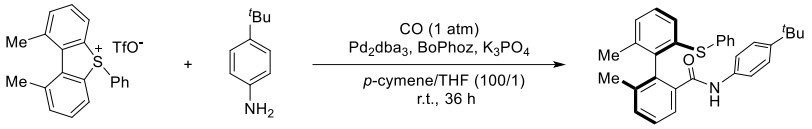
2',6-dimethyl-*N*-phenyl-6'-(phenylthio)-[1,1'-biphenyl]-2-carboxamide (3d)



1a **3d**

The reaction of **1a** (84.7 mg, 0.20 mmol, 1.0 equiv) and aniline (37.2 mg, 0.40 mmol, 2.0 equiv) under standard condition afforded **3d** (81.5 mg, >99%, 80% ee) as a light yellow oil. HPLC conditions: Chiralpak ID, isopropanol/hexane = 20: 80, flow: 1.0 mL/min, λ = 254 nm, tr = 9.165 min (major), 10.882 min (minor). $[\alpha]_D^{20}$ = -12.51 (c 0.30, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (bs, 1H), 7.79 (dd, J_1 = 6.4 Hz, J_2 = 2.7 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.42 – 7.38 (m, 2H), 7.36 – 7.29 (m, 3H), 7.26 – 7.20 (m, 4H), 7.15 – 7.08 (m, 2H), 7.05 (tt, J_1 = 6.6 Hz, J_2 = 2.2 Hz, 1H), 6.79 (dd, J_1 = 7.3 Hz, J_2 = 1.9 Hz, 1H), 2.10 (s, 3H), 1.99 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.0, 138.0, 137.8, 137.7, 137.5, 136.6, 136.3, 135.6, 134.7, 132.7, 131.9, 129.8, 129.0, 128.8, 128.6, 128.1, 127.0, 124.6, 124.3, 120.3, 20.3, 19.9. **HRMS (ESI)** calcd for: $C_{27}H_{24}NOS^+$ $[M+H]^+$ 410.1573, found: 410.1577.

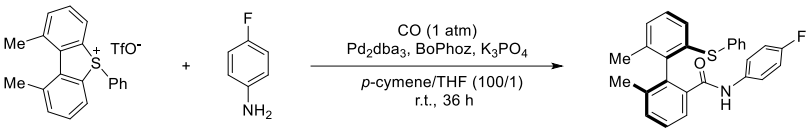
***N*-(4-(*tert*-butyl)phenyl)-2',6-dimethyl-6'-(phenylthio)-[1,1'-biphenyl]-2-carboxamide (3e)**



1a 3e

The reaction of **1a** (84.7 mg, 0.20 mmol, 1.0 equiv) and 4-*tert*-butylaniline (59.7 mg, 0.40 mmol, 2.0 equiv) under standard condition afforded **3e** (68.3 mg, 73%, 90% ee) as a brown oil. HPLC conditions: Chiralpak IC, isopropanol/hexane = 5: 95, flow: 1.0 mL/min, λ = 254 nm, tr = 15.386 min (minor), 18.759 min (major). $[\alpha]_D^{20}$ = -10.01 (c 0.38, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 – 7.76 (m, 2H), 7.44 (d, *J* = 6.2 Hz, 2H), 7.42 – 7.38 (m, 2H), 7.34 – 7.29 (m, 3H), 7.27 – 7.22 (m, 2H), 7.16 – 7.06 (m, 4H), 6.78 (dd, J_1 = 7.6 Hz, J_2 = 1.5 Hz, 1H), 2.09 (s, 3H), 1.98 (s, 3H), 1.27 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.0, 147.3, 137.8, 137.4, 136.6, 136.4, 135.5, 135.4, 134.8, 132.6, 131.9, 129.8, 128.9, 128.8, 128.6, 128.1, 127.1, 125.8, 124.5, 120.2, 34.5, 31.5, 20.3, 19.9. **HRMS (ESI)** calcd for: $C_{31}H_{32}NOS^+$ $[M+H]^+$ 466.2199, found: 466.2206.

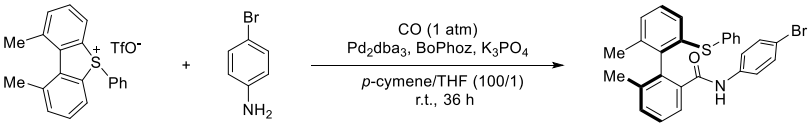
***N*-(4-fluorophenyl)-2',6-dimethyl-6'-(phenylthio)-[1,1'-biphenyl]-2-carboxamide (3f)**



1a 3f

The reaction of **1a** (84.7 mg, 0.20 mmol, 1.0 equiv) and 4-fluoroaniline (44.4 mg, 0.40 mmol, 2.0 equiv) under standard condition afforded **3f** (59.7 mg, 70%, 85% ee) as a light yellow oil. HPLC conditions: Chiralpak AD-H, isopropanol/hexane = 10: 90, flow: 1.0 mL/min, λ = 254 nm, tr = 8.814 min (major), 10.054 min (minor). $[\alpha]_D^{20}$ = -29.52 (c 0.16, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (bs, 1H), 7.76 (dd, J_1 = 6.3 Hz, J_2 = 2.7 Hz, 1H), 7.51 – 7.42 (m, 2H), 7.40 – 7.28 (m, 5H), 7.17 – 7.05 (m, 4H), 6.97 – 6.87 (m, 2H), 6.78 (dd, J_1 = 7.2 Hz, J_2 = 2.0 Hz, 1H), 2.10 (s, 3H), 1.98 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -118.0. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.1, 159.5 (d, *J* = 244.1 Hz), 137.9, 137.7, 137.5, 136.6, 136.2, 135.6, 134.6, 133.9 (d, *J* = 3.0 Hz), 132.7, 131.8, 129.8, 129.0 128.8, 128.7, 128.1, 126.9, 124.6, 122.2 (d, *J* = 7.9 Hz), 115.6 (d, *J* = 22.4 Hz), 20.2, 19.9. **HRMS (ESI)** calcd for: $C_{27}H_{23}FNOS^+$ $[M+H]^+$ 428.1479, found: 428.1474.

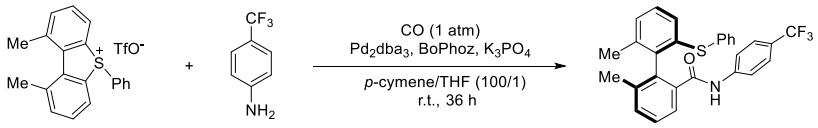
***N*-(4-bromophenyl)-2',6-dimethyl-6'-(phenylthio)-[1,1'-biphenyl]-2-carboxamide (3g)**



1a 3g

The reaction of **1a** (84.7 mg, 0.20 mmol, 1.0 equiv) and 4-bromoaniline (68.8 mg, 0.40 mmol, 2.0 equiv) under standard condition afforded **3g** (70.1 mg, 72%, 85% ee) as a brown oil. HPLC conditions: Chiralpak IC, isopropanol/hexane = 10: 90, flow: 1.0 mL/min, λ = 254 nm, tr = 8.544 min (major), 9.316 min (minor). $[\alpha]_D^{20}$ = -20.16 (c 0.09, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (bs, 1H), 7.77 (dd, J_1 = 7.1 Hz, J_2 = 2.0 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.39 – 7.30 (m, 7H), 7.14 – 7.03 (m, 4H), 6.79 (dd, J_1 = 7.3 Hz, J_2 = 1.8 Hz, 1H), 2.09 (s, 3H), 1.97 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.0, 137.8, 137.61, 137.56, 137.1, 136.5, 136.0, 135.6, 134.6, 132.9, 131.9, 131.7, 129.8, 129.1, 128.9, 128.7, 128.2, 127.0, 124.7, 121.8, 116.9, 20.2, 19.9. **HRMS (ESI)** calcd for: $C_{27}H_{23}{}^{79}BrNOS^+$ $[M+H]^+$ 488.0678, found: 488.0682.

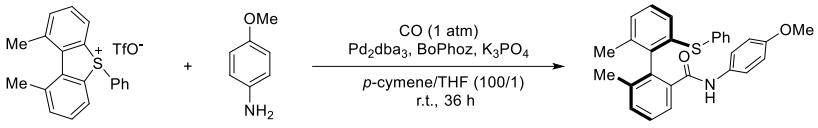
2',6-dimethyl-6'-(phenylthio)-*N*-(4-(trifluoromethyl)phenyl)-[1,1'-biphenyl]-2-carboxamide (3h)



1a **3h**

The reaction of **1a** (84.7 mg, 0.20 mmol, 1.0 equiv) and 4-(trifluoromethyl)aniline (64.4 mg, 0.40 mmol, 2.0 equiv) under standard condition afforded **3h** (93.0 mg, 97%, 82% ee) as a pale yellow solid. HPLC conditions: Chiralpak OD-H, isopropanol/hexane = 5: 95, flow: 1.0 mL/min, λ = 254 nm, tr = 6.873 min (minor), 7.641 min (major). $[\alpha]_D^{20}$ = -7.97 (c 0.29, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (bs, 1H), 7.80 (dd, J_1 = 7.2 Hz, J_2 = 1.8 Hz, 1H), 7.53 – 7.42 (m, 4H), 7.40 – 7.28 (m, 7H), 7.18 – 7.08 (m, 2H), 6.82 (dd, J_1 = 7.5 Hz, J_2 = 1.8 Hz, 1H), 2.10 (s, 3H), 1.98 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.1. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.1, 141.1, 137.8, 137.7, 137.6, 136.4, 135.7, 134.6, 133.1, 131.7, 129.8, 129.1, 129.0, 128.7, 128.2, 127.1, 126.2 (q, J = 3.8 Hz), 126.0 (q, J = 32.8 Hz), 124.8, 124.2 (q, J = 272.1 Hz), 119.7, 20.2, 19.9. **HRMS (ESI)** calcd for: $C_{28}H_{23}F_3NOS^+$ $[M+H]^+$ 478.1447, found: 478.1454.

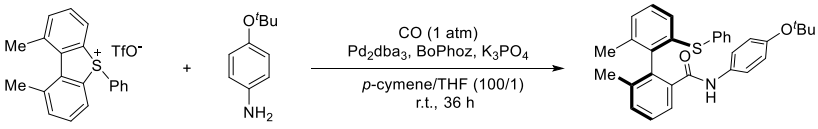
***N*-(4-methoxyphenyl)-2',6-dimethyl-6'-(phenylthio)-[1,1'-biphenyl]-2-carboxamide (3i)**



1a **3i**

The reaction of **1a** (84.7 mg, 0.20 mmol, 1.0 equiv) and 4-methoxyaniline (49.3 mg, 0.40 mmol, 2.0 equiv) under standard condition afforded **3i** (97.3 mg, >99%, 81% ee) as a brown oil. HPLC conditions: Chiralpak IA, isopropanol/hexane = 10: 90, flow: 1.0 mL/min, λ = 254 nm, tr = 12.988 min (major), 14.281 min (minor). $[\alpha]_D^{20}$ = -52.06 (c 0.16, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (bs, 1H), 7.79 – 7.76 (m, 1H), 7.49 – 7.43 (m, 2H), 7.42 – 7.39 (m, 2H), 7.38 – 7.30 (m, 3H), 7.16 – 7.07 (m, 4H), 6.82 – 6.74 (m, 3H), 3.76 (s, 3H), 2.11 (s, 3H), 2.00 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.9, 156.4, 137.71, 137.66, 137.3, 136.5, 136.4, 135.4, 134.7, 132.4, 131.7, 131.0, 129.7, 128.9, 128.7, 128.6, 128.0, 126.9, 124.4, 122.2, 114.0, 55.5, 20.2, 19.9. **HRMS (ESI)** calcd for: $C_{28}H_{25}NO_2SNa^+$ $[M+Na]^+$ 462.1498, found: 462.1503.

***N*-(4-(*tert*-butoxy)phenyl)-2',6-dimethyl-6'-(phenylthio)-[1,1'-biphenyl]-2-carboxamide (3j)**

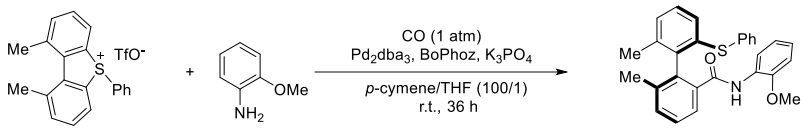


1a **3j**

The reaction of **1a** (84.7 mg, 0.20 mmol, 1.0 equiv) and 4-(*tert*-butoxy)aniline (66.1 mg, 0.40 mmol, 2.0 equiv) under standard condition afforded **3j** (87.1 mg, >99%, 80% ee) as a light yellow oil. HPLC conditions: Chiralpak IC, isopropanol/hexane = 10: 90, flow: 1.0 mL/min, λ = 254 nm, tr = 17.285 min (major), 19.100 min (minor). $[\alpha]_D^{20}$ = -21.40 (c 0.09, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (bs, 1H), 7.77 (dd, J_1 = 6.8 Hz, J_2 = 2.4 Hz, 1H), 7.50 – 7.41 (m, 2H), 7.41 – 7.35 (m, 2H), 7.35 – 7.27 (m, 3H), 7.15 – 7.03 (m, 4H), 6.86 (dt, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 2H), 6.80 (dd, J_1 = 7.1 Hz, J_2 = 2.1 Hz, 1H), 2.09 (s, 3H), 2.00 (s, 3H), 1.31 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.9, 151.8, 137.7, 137.5, 137.4, 136.7, 136.3, 135.6, 134.5, 133.5, 132.5, 132.0, 129.7, 128.8,

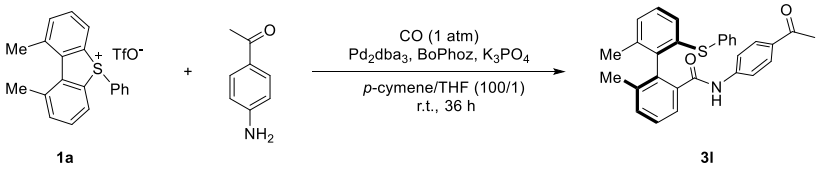
128.7, 128.5, 128.1, 126.8, 124.7, 124.6, 121.1, 78.6, 28.8, 20.3, 19.9. **HRMS (ESI)** calcd for: $C_{31}H_{32}NO_2S^+$ $[M+H]^+$ 482.2148, found: 482.2150.

***N*-(2-methoxyphenyl)-2',6-dimethyl-6'-(phenylthio)-[1,1'-biphenyl]-2-carboxamide (3k)**



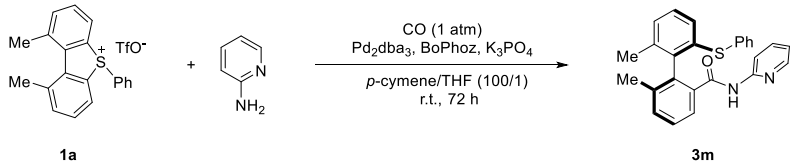
The reaction of **1a** (84.7 mg, 0.20 mmol, 1.0 equiv) and 4-methoxyaniline (49.3 mg, 0.40 mmol, 2.0 equiv) under standard condition afforded **3k** (75.6 mg, 72%, 93% ee) as a light yellow oil. HPLC conditions: Chiralpak AD-H, isopropanol/hexane = 10: 90, flow: 1.0 mL/min, λ = 254 nm, tr = 8.848 min (major), 10.406 min (minor). $[\alpha]_D^{20}$ = -27.38 (c 0.28, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.29 (dd, J_1 = 8.0 Hz, J_2 = 1.7 Hz, 1H), 8.15 (bs, 1H), 7.67 (dd, J_1 = 6.0 Hz, J_2 = 3.1 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.30 – 7.26 (m, 2H), 7.21 – 7.13 (m, 3H), 7.11 – 7.04 (m, 2H), 6.99 (td, J_1 = 7.8 Hz, J_2 = 1.7 Hz, 1H), 6.89 (td, J_1 = 7.8 Hz, J_2 = 1.4 Hz, 1H), 6.84 (dd, J_1 = 7.5 Hz, J_2 = 1.6 Hz, 1H), 6.75 (dd, J_1 = 8.1 Hz, J_2 = 1.3 Hz, 1H), 3.57 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.2, 148.3, 137.7, 137.6, 137.5, 137.0, 136.9, 136.4, 133.9, 133.4, 132.3, 129.2, 128.35, 128.29, 128.0, 127.91, 127.86, 126.2, 126.1, 123.8, 120.9, 120.4, 109.8, 55.3, 20.4, 19.9. **HRMS (ESI)** calcd for: $C_{28}H_{26}NO_2S^+$ $[M+H]^+$ 440.1679, found: 440.1680.

***N*-(4-acetylphenyl)-2',6-dimethyl-6'-(phenylthio)-[1,1'-biphenyl]-2-carboxamide (3l)**



The reaction of **1a** (84.7 mg, 0.20 mmol, 1.0 equiv) and 4-acetylaniline (54.1 mg, 0.40 mmol, 2.0 equiv) under standard condition afforded **3l** (37.0 mg, 41%, 88% ee) as a yellow solid. HPLC conditions: Chiralpak IC, isopropanol/hexane = 20: 80, flow: 1.0 mL/min, λ = 254 nm, tr = 22.873 min (major), 25.975 min (minor). $[\alpha]_D^{20}$ = -25.07 (c 0.14, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (bs, 1H), 7.84 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 7.3 Hz, 1H), 7.53 – 7.43 (m, 2H), 7.39 (d, J = 7.9 Hz, 2H), 7.35 – 7.30 (m, 5H), 7.19 – 7.05 (m, 2H), 6.81 (d, J = 7.4 Hz, 1H), 2.54 (s, 3H), 2.10 (s, 3H), 1.98 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.0, 167.1, 142.4, 137.8, 137.64, 137.60, 136.4, 135.72, 135.69, 134.6, 133.1, 132.9, 131.6, 129.8, 129.7, 129.1, 129.0, 128.7, 128.2, 127.1, 124.7, 119.2, 26.5, 20.2, 19.9. **HRMS (ESI)** calcd for: $C_{29}H_{26}NO_2S^+$ $[M+H]^+$ 452.1679, found: 452.1674.

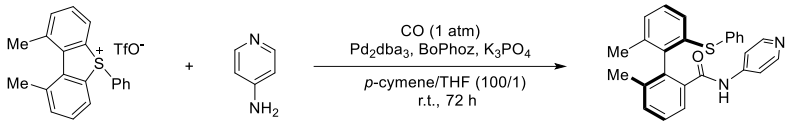
2',6-dimethyl-6'-(phenylthio)-*N*-(pyridin-2-yl)-[1,1'-biphenyl]-2-carboxamide (3m)



The reaction of **1a** (84.7 mg, 0.20 mmol, 1.0 equiv) and 2-aminopyridine (37.6 mg, 0.40 mmol, 2.0 equiv) under standard condition for 72 h afforded **3m** (75.0 mg, 91%, 84% ee) as a pale yellow solid. HPLC conditions: Chiralpak IA, isopropanol/hexane = 5: 95, flow: 1.0 mL/min, λ = 254 nm, tr =

8.333 min (major), 9.221 min (minor). $[\alpha]_D^{20}$ = -14.79 (c 0.14, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.78 (bs, 1H), 8.20 (dd, J_1 = 5.1 Hz, J_2 = 1.9 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.64 – 7.59 (m, 4H), 7.49 – 7.40 (m, 2H), 7.29 (dd, J_1 = 5.0 Hz, J_2 = 1.9 Hz, 3H), 7.07 – 7.00 (m, 2H), 6.96 (dd, J_1 = 7.3 Hz, J_2 = 4.9 Hz, 1H), 6.71 (dd, J_1 = 6.5 Hz, J_2 = 2.7 Hz, 1H), 2.08 (s, 3H), 2.01 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.9, 151.6, 147.9, 138.1, 137.8, 137.5, 137.4, 136.45, 136.43, 136.1, 134.72, 134.70, 132.6, 132.3, 129.5, 128.5, 128.44, 128.42, 127.6, 125.9, 124.8, 119.6, 114.0, 20.2, 19.8. **HRMS (ESI)** calcd for: $C_{26}H_{23}N_2OS^+$ $[M+H]^+$ 411.1526, found: 411.1531.

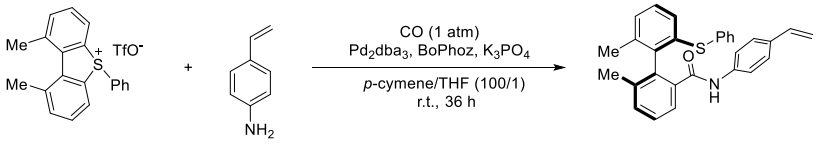
2',6-dimethyl-6'-(phenylthio)-*N*-(pyridin-4-yl)-[1,1'-biphenyl]-2-carboxamide (3n)



1a **3n**

The reaction of **1a** (84.7 mg, 0.20 mmol, 1.0 equiv) and 4-aminopyridine (37.6 mg, 0.40 mmol, 2.0 equiv) under standard condition for 72 h afforded **3n** (25.3 mg, 31%, 85% ee) as a light yellow oil. HPLC conditions: Chiralpak AD-H, isopropanol/hexane = 10: 90, flow: 1.0 mL/min, λ = 254 nm, tr = 9.082 min (minor), 10.902 min (major). $[\alpha]_D^{20}$ = -11.32 (c 0.23, $CHCl_3$). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.59 (s, 1H), 8.36 (d, J = 6.5 Hz, 2H), 7.59 – 7.41 (m, 5H), 7.26 – 7.17 (m, 5H), 7.16 – 7.09 (m, 2H), 6.83 (dd, J_1 = 5.7 Hz, J_2 = 3.5 Hz, 1H), 1.97 (s, 3H), 1.93 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 167.7, 150.2, 146.0, 138.9, 137.4, 136.8, 135.7, 135.0, 134.8, 132.2, 131.6, 129.4, 128.0, 127.9, 127.6, 127.5, 127.2, 125.4, 113.5, 20.2, 19.4. **HRMS (ESI)** calcd for: $C_{26}H_{23}N_2OS^+$ $[M+H]^+$ 411.1526, found: 411.1531.

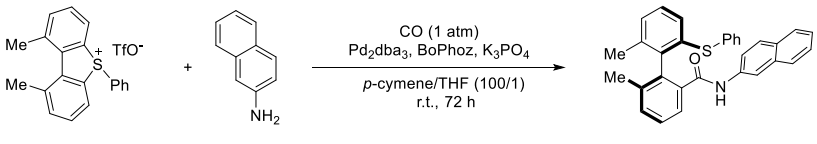
2',6-dimethyl-6'-(phenylthio)-*N*-(4-vinylphenyl)-[1,1'-biphenyl]-2-carboxamide (3o)



1a **3o**

The reaction of **1a** (84.7 mg, 0.20 mmol, 1.0 equiv) and 4-aminostyrene (37.6 mg, 0.40 mmol, 2.0 equiv) under standard condition afforded **3o** (45.8 mg, 53%, 87% ee) as a light yellow oil. HPLC conditions: Chiralpak IG, isopropanol/hexane = 5: 95, flow: 1.0 mL/min, λ = 254 nm, tr = 35.024 min (major), 41.869 min (minor). $[\alpha]_D^{20}$ = -22.52 (c 0.92, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85 (bs, 1H), 7.80 – 7.77 (m, 1H), 7.48 – 7.43 (m, 2H), 7.41 – 7.37 (m, 2H), 7.35 – 7.30 (m, 3H), 7.28 – 7.24 (m, 2H), 7.21 – 7.16 (m, 2H), 7.13 – 7.06 (m, 2H), 6.78 (dd, J_1 = 7.2 Hz, J_2 = 1.9 Hz, 1H), 6.63 (dd, J_1 = 17.6 Hz, J_2 = 10.9 Hz, 1H), 5.64 (dd, J_1 = 17.6 Hz, J_2 = 0.9 Hz, 1H), 5.16 (dd, J_1 = 10.8 Hz, J_2 = 0.9 Hz, 1H), 2.09 (s, 3H), 1.98 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.9, 137.8, 137.7, 137.6, 137.5, 136.5, 136.3, 135.6, 134.7, 133.7, 132.7, 131.8, 129.8, 129.1, 129.0, 128.8, 128.7, 128.5, 128.1, 127.1, 126.8, 124.6, 120.2, 113.0, 20.2, 19.9. **HRMS (ESI)** calcd for: $C_{29}H_{26}NOS^+$ $[M+H]^+$ 436.1730, found: 436.1734.

2',6-dimethyl-*N*-(naphthalen-2-yl)-6'-(phenylthio)-[1,1'-biphenyl]-2-carboxamide (3p)

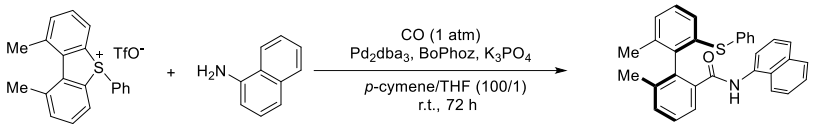


1a **3p**

The reaction of **1a** (84.7 mg, 0.20 mmol, 1.0 equiv) and 2-naphthylamine (57.3 mg, 0.40 mmol, 2.0

equiv) under standard condition for 72 h afforded **3p** (69.7 mg, 76%, 88% ee) as a brown oil. HPLC conditions: Chiralpak AD-H, isopropanol/hexane = 10: 90, flow: 1.0 mL/min, λ = 254 nm, temperature = 5 °C, tr = 18.775 min (major), 24.001 min (minor). $[\alpha]_D^{20}$ = -22.44 (c 1.47, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 – 7.97 (m, 2H), 7.83 (dd, J_1 = 5.8 Hz, J_2 = 3.3 Hz, 1H), 7.76 – 7.70 (m, 3H), 7.68 (d, J = 8.8 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.47 – 7.28 (m, 7H), 7.15 – 7.08 (m, 2H), 7.06 (dd, J_1 = 8.8 Hz, J_2 = 2.2 Hz, 1H), 6.81 (dd, J_1 = 6.5 Hz, J_2 = 2.6 Hz, 1H), 2.12 (s, 3H), 2.01 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.2, 137.8, 137.6, 137.5, 136.6, 136.3, 135.6, 135.4, 134.6, 133.9, 132.7, 131.8, 130.7, 129.8, 129.0, 128.8, 128.7, 128.6, 128.1, 127.8, 127.6, 127.0, 126.5, 125.0, 124.7, 120.2, 117.0, 20.3, 19.9. **HRMS (ESI)** calcd for: $C_{31}H_{26}NOS^+$ $[M+H]^+$ 460.1730, found: 460.1731.

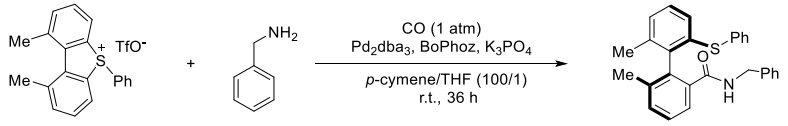
2',6-dimethyl-*N*-(naphthalen-1-yl)-6'-(phenylthio)-[1,1'-biphenyl]-2-carboxamide (3q)



1a **3q**

The reaction of **1a** (84.7 mg, 0.20 mmol, 1.0 equiv) and 1-naphthylamine (57.3 mg, 0.40 mmol, 2.0 equiv) under standard condition for 72 h afforded **3q** (30.2 mg, 33%, 90% ee) as a brown oil. HPLC conditions: Chiralpak IC, isopropanol/hexane = 20: 80, flow: 1.0 mL/min, λ = 254 nm, tr = 15.499 min (minor), 24.185 min (major). $[\alpha]_D^{20}$ = -25.89 (c 0.48, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.21 (bs, 1H), 7.86 – 7.78 (m, 2H), 7.66 (d, J = 8.2 Hz, 1H), 7.60 (d, J = 7.5 Hz, 1H), 7.49 (d, J = 4.4 Hz, 2H), 7.44 – 7.34 (m, 3H), 7.29– 7.24 (m, 4H), 7.18 (t, J = 7.5 Hz, 2H), 7.13 – 7.07 (m, 2H), 6.70 (dd, J_1 = 7.1 Hz, J_2 = 2.0 Hz, 1H), 2.13 (s, 3H), 2.06 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.4, 138.1, 138.0, 137.6, 137.1, 136.4, 135.4, 134.8, 134.1, 132.7, 132.5, 131.4, 129.7, 129.0, 128.72, 128.69, 128.5, 128.0, 126.8, 126.1, 126.0, 125.8, 124.2, 121.73, 121.71, 20.4, 20.0. **HRMS (ESI)** calcd for: $C_{31}H_{26}NOS^+$ $[M+H]^+$ 460.1730, found: 460.1741.

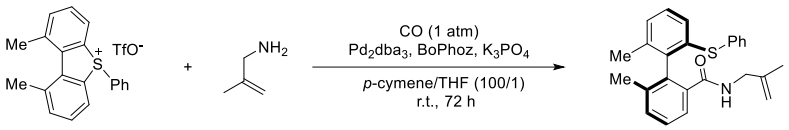
***N*-benzyl-2',6-dimethyl-6'-(phenylthio)-[1,1'-biphenyl]-2-carboxamide (3r)**



1a **3r**

The reaction of **1a** (84.7 mg, 0.20 mmol, 1.0 equiv) and benzylamine (42.9 mg, 0.40 mmol, 2.0 equiv) under standard condition afforded **3r** (50.7 mg, 60%, 82% ee) as a brown oil. HPLC conditions: Chiralpak IA, isopropanol/hexane = 10: 90, flow: 1.0 mL/min, λ = 254 nm, tr = 10.667 min (major), 13.181 min (minor). $[\alpha]_D^{20}$ = -19.57 (c 0.86, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (t, J = 4.6 Hz, 1H), 7.41 (d, J = 4.6 Hz, 2H), 7.30 (t, J = 7.4 Hz, 2H), 7.25 – 7.15 (m, 5H), 7.08 (d, J = 4.7 Hz, 2H), 6.96 (d, J = 7.4 Hz, 2H), 6.87 (d, J = 6.6 Hz, 2H), 6.55 – 6.46 (m, 2H), 4.51 (dd, J_1 = 14.6 Hz, J_2 = 6.5 Hz, 1H), 4.19 (dd, J_1 = 14.6 Hz, J_2 = 4.4 Hz, 1H), 2.04 (s, 3H), 1.98 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.3, 137.8, 137.7, 137.5, 137.3, 136.6, 136.3, 135.2, 134.8, 132.1, 131.3, 129.6, 128.8, 128.7, 128.5, 128.3, 128.1, 127.6, 127.4, 126.5, 123.9, 44.2, 20.2, 19.8. **HRMS (ESI)** calcd for: $C_{28}H_{26}NOS^+$ $[M+H]^+$ 424.1730, found: 424.1739.

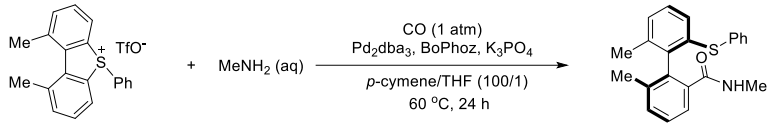
2',6-dimethyl-*N*-(2-methylallyl)-6'-(phenylthio)-[1,1'-biphenyl]-2-carboxamide (3s)



1a **3s**

The reaction of **1a** (84.7 mg, 0.20 mmol, 1.0 equiv) and 2-methylallylamine (28.4 mg, 0.40 mmol, 2.0 equiv) under standard condition for 72 h afforded **3s** (52.0 mg, 67%, 86% ee) as a white solid. HPLC conditions: Chiralpak AD-3, isopropanol/hexane = 3: 97, flow: 1.0 mL/min, λ = 210 nm, tr = 22.954 min (major), 32.893 min (minor). $[\alpha]_D^{20}$ = -5.90 (c 0.10, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 (dd, J_1 = 6.0 Hz, J_2 = 3.0 Hz, 1H), 7.44 – 7.38 (m, 4H), 7.38 – 7.32 (m, 3H), 7.10 – 7.05 (m, 2H), 6.71 (dd, J_1 = 6.3 Hz, J_2 = 2.9 Hz, 1H), 6.27 (t, J = 6.0 Hz, 1H), 4.81 – 4.66 (m, 1H), 4.62 – 4.47 (m, 1H), 3.77 (dd, J_1 = 15.4 Hz, J_2 = 6.3 Hz, 1H), 3.69 (dd, J_1 = 15.5 Hz, J_2 = 5.6 Hz, 1H), 2.04 (s, 3H), 1.97 (s, 3H), 1.50 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.3, 142.0, 137.7, 137.6, 137.3, 136.8, 136.7, 135.3, 134.6, 132.03, 132.00, 129.7, 128.9, 128.5, 128.4, 127.8, 126.4, 124.3, 111.5, 45.8, 20.2, 19.9. **HRMS (ESI)** calcd for: $C_{25}H_{26}NOS^+$ $[M+H]^+$ 388.1730, found: 388.1740.

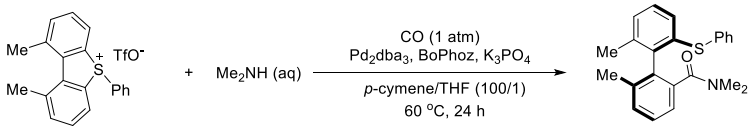
***N*,2',6-trimethyl-6'-(phenylthio)-[1,1'-biphenyl]-2-carboxamide (3t)**



1a **3t**

The reaction of **1a** (84.7 mg, 0.20 mmol, 1.0 equiv) and methylamine (40% aq w/w, 35.0 μL, 0.40 mmol, 2.0 equiv) under standard condition except at 60 °C for 24 h afforded **3t** (56.5 mg, 81%, 73% ee) as a white solid. HPLC conditions: Chiralpak ID, isopropanol/hexane = 10: 90, flow: 1.0 mL/min, λ = 254 nm, tr = 14.737 min (major), 16.292 min (minor). $[\alpha]_D^{20}$ = -1.38 (c 0.24, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (dd, J_1 = 6.2 Hz, J_2 = 2.7 Hz, 1H), 7.42 – 7.30 (m, 7H), 7.15 – 7.04 (m, 2H), 6.81 (dd, J_1 = 6.3 Hz, J_2 = 2.7 Hz, 1H), 6.04 (bs, 1H), 2.66 (d, J = 4.8 Hz, 3H), 2.03 (s, 3H), 1.97 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.1, 137.8, 137.5, 137.2, 136.8, 136.7, 135.8, 133.8, 132.9, 131.9, 129.6, 128.5, 128.4, 128.3, 128.1, 126.0, 125.2, 26.6, 20.3, 19.9. **HRMS (ESI)** calcd for: $C_{22}H_{22}NOS^+$ $[M+H]^+$ 348.1417, found: 348.1426.

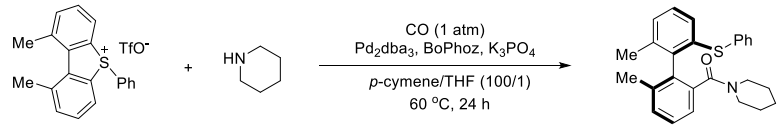
***N*,*N*,2',6-tetramethyl-6'-(phenylthio)-[1,1'-biphenyl]-2-carboxamide (3u)**



1a **3u**

The reaction of **1a** (84.7 mg, 0.20 mmol, 1.0 equiv) and dimethylamine (40% aq w/w, 49.5 μL, 0.40 mmol, 2.0 equiv) under standard condition except at 60 °C for 24 h afforded **3u** (52.1 mg, 72%, 75% ee) as a white solid. HPLC conditions: Chiralpak IA, isopropanol/hexane = 5: 95, flow: 1.0 mL/min, λ = 254 nm, tr = 10.417 min (major), 12.447 min (minor). $[\alpha]_D^{20}$ = -27.93 (c 0.17, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H), 7.27 – 7.22 (m, 2H), 7.23 – 7.18 (m, 3H), 7.18 – 7.09 (m, 3H), 7.01 (dd, J_1 = 7.0 Hz, J_1 = 2.2 Hz, 1H), 2.84 (s, 3H), 2.80 (s, 3H), 2.10 (s, 3H), 1.99 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.2, 139.4, 137.84, 137.75, 136.5, 135.5, 130.8, 130.6, 129.2, 128.5, 128.3, 128.1, 127.1, 126.8, 124.7, 39.6, 34.8, 20.6, 19.9. **HRMS (ESI)** calcd for: $C_{23}H_{24}NOS^+$ $[M+H]^+$ 362.1573, found: 362.1580.

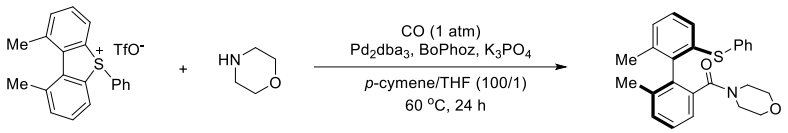
(2',6-dimethyl-6'-(phenylthio)-[1,1'-biphenyl]-2-yl)(piperidin-1-yl)methanone (3v)



1a **3v**

The reaction of **1a** (84.7 mg, 0.20 mmol, 1.0 equiv) and piperidine (34.1 mg, 0.40 mmol, 2.0 equiv) under standard condition except at 60 °C for 24 h afforded **3v** (47.6 mg, 59%, 50% ee) as a pale yellow solid. HPLC conditions: Chiralpak IA, isopropanol/hexane = 5: 95, flow: 1.0 mL/min, λ = 254 nm, tr = 9.670 min (major), 11.468 min (minor). $[\alpha]_D^{20}$ = +5.50 (c 0.66, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 – 7.21 (m, 7H), 7.18 (d, *J* = 7.1 Hz, 1H), 7.10 (d, *J* = 6.7 Hz, 2H), 6.92 (d, *J* = 7.2 Hz, 1H), 3.95 (d, *J* = 11.8 Hz, 1H), 3.60 (d, *J* = 13.5 Hz, 1H), 3.03 – 2.89 (m, 2H), 2.10 (s, 3H), 1.99 (s, 3H), 1.74 – 1.64 (m, 1H), 1.57 – 1.36 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.9, 139.3, 138.6, 137.9, 137.5, 135.9, 135.7, 135.0, 131.8, 130.6, 129.3, 128.2, 128.1, 127.24, 127.17, 126.8, 124.2, 48.8, 42.5, 26.5, 25.8, 24.7, 20.6, 19.9. **HRMS (ESI)** calcd for: $C_{26}H_{27}NOSNa^+$ $[M+Na]^+$ 424.1706, found: 424.1714.

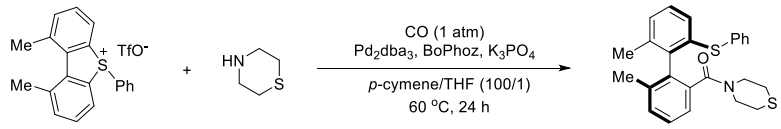
(2',6-dimethyl-6'-(phenylthio)-[1,1'-biphenyl]-2-yl)(morpholino)methanone (3w)



1a **3w**

The reaction of **1a** (84.7 mg, 0.20 mmol, 1.0 equiv) and morpholine (34.8 mg, 0.40 mmol, 2.0 equiv) under standard condition except at 60 °C for 24 h afforded **3w** (68.5 mg, 85%, 71% ee) as a pale yellow solid. HPLC conditions: Chiralpak IC, isopropanol/hexane = 20: 80, flow: 1.0 mL/min, λ = 254 nm, tr = 10.033 min (major), 11.937 min (minor). $[\alpha]_D^{20}$ = -18.67 (c 0.06, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 7H), 7.16 (dd, J_1 = 7.4 Hz, J_2 = 1.6 Hz, 1H), 7.11 (d, *J* = 5.0 Hz, 2H), 6.88 (bs, 1H), 3.74 – 3.45 (m, 7H), 3.35 (d, *J* = 13.6 Hz, 1H), 2.10 (s, 3H), 2.02 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.0, 139.1, 138.2, 137.8, 137.5, 135.3, 135.0, 134.6, 132.4, 131.1, 129.4, 128.3, 127.9, 127.8, 127.4, 126.0, 124.5, 67.1, 66.9, 48.1, 42.0, 20.5, 19.9. **HRMS (ESI)** calcd for: $C_{25}H_{25}NO_2SNa^+$ $[M+Na]^+$ 426.1498, found: 426.1497.

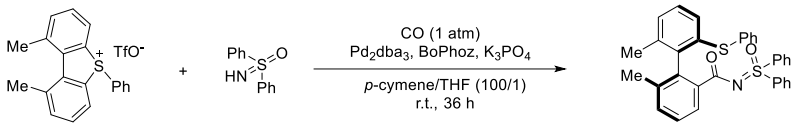
(2',6-dimethyl-6'-(phenylthio)-[1,1'-biphenyl]-2-yl)(thiomorpholino)methanone (3x)



1a **3x**

The reaction of **1a** (84.7 mg, 0.20 mmol, 1.0 equiv) and thiomorpholine (41.3 mg, 0.40 mmol, 2.0 equiv) under standard condition except at 60 °C for 24 h afforded **3x** (73.6 mg, 90%, 56% ee) as a brown solid. HPLC conditions: Chiralpak IA, isopropanol/hexane = 3: 97, flow: 1.0 mL/min, λ = 210 nm, tr = 15.986 min (major), 20.693 min (minor). $[\alpha]_D^{20}$ = -7.86 (c 0.33, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.22 (m, 7H), 7.16 (d, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 5.0 Hz, 2H), 6.95 – 6.83 (m, 1H), 4.24 (d, *J* = 11.5 Hz, 1H), 3.90 (d, *J* = 11.9 Hz, 1H), 3.33 (t, *J* = 11.1 Hz, 2H), 2.69 (t, *J* = 11.6 Hz, 2H), 2.46 (t, *J* = 12.9 Hz, 2H), 2.08 (s, 3H), 2.01 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.3, 139.3, 138.2, 138.0, 137.5, 135.3, 135.1, 135.0, 132.1, 131.0, 129.4, 128.3, 128.0, 127.6, 127.4, 126.5, 124.1, 50.1, 43.9, 28.1, 27.7, 20.5, 19.9. **HRMS (ESI)** calcd for: $C_{25}H_{26}NOS_2^+$ $[M+H]^+$ 420.1450, found: 420.1439.

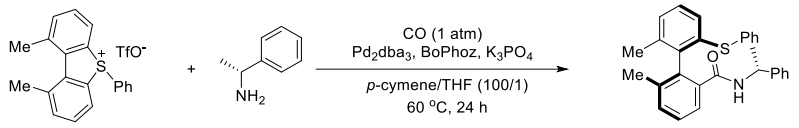
2',6-dimethyl-*N*-(oxodiphenyl-λ^6-sulfanylidene)-6'-(phenylthio)-[1,1'-biphenyl]-2-carboxamide (3y)



1a **3y**

The reaction of **1a** (84.7 mg, 0.20 mmol, 1.0 equiv) and *S*,*S*-diphenylsulphoximine (86.9 mg, 0.40 mmol, 2.0 equiv) under standard condition afforded **3y** (84.6 mg, 79%, 86% ee) as a brown oil. HPLC conditions: Chiralpak AD-H, isopropanol/hexane = 30: 70, flow: 1.0 mL/min, λ = 254 nm, tr = 8.509 min (major), 11.616 min (minor). $[\alpha]_D^{20}$ = -30.52 (c 0.23, $CHCl_3$). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.86 (d, J = 7.6 Hz, 1H), 7.76 (dt, J_1 = 8.3 Hz, J_2 = 1.2 Hz, 2H), 7.69 (dt, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 2H), 7.64 (t, J = 7.3 Hz, 2H), 7.55 (t, J = 7.6 Hz, 4H), 7.49 (d, J = 7.4 Hz, 1H), 7.40 (td, J_1 = 7.6 Hz, J_2 = 1.1 Hz, 1H), 7.35 – 7.30 (m, 3H), 7.30 – 7.25 (m, 2H), 7.17 (d, J = 4.3 Hz, 2H), 6.85 (t, J = 4.6 Hz, 1H), 1.92 (s, 3H), 1.88 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 174.9, 139.4, 139.23, 139.21, 137.2, 136.8, 136.5, 136.3, 136.0, 133.7, 133.6, 133.5, 132.74, 132.67, 129.75, 129.72, 129.54, 129.51, 128.0, 127.6, 127.5, 127.1, 127.0, 126.0, 124.1, 20.1, 19.5. **HRMS (ESI)** calcd for: $C_{33}H_{28}NO_2S_2^+$ $[M+H]^+$ 534.1556, found: 534.1563.

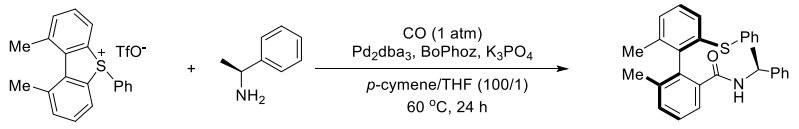
2',6-dimethyl-*N*-((*R*)-1-phenylethyl)-6'-(phenylthio)-[1,1'-biphenyl]-2-carboxamide (3z)



1a **3z**

The reaction of **1a** (84.7 mg, 0.20 mmol, 1.0 equiv) and *R*-1-phenylethylamine (42.9 mg, 0.40 mmol, 2.0 equiv) under standard condition except at 60 °C for 24 h afforded **3z** (45.3 mg, 52%, 1:7.5 dr) as a light yellow oil. $[\alpha]_D^{20}$ = -21.93 (c 1.29, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) for major compound: δ 7.79 – 7.62 (m, 1H), 7.44 – 7.37 (m, 2H), 7.37 – 7.25 (m, 4H), 7.21 – 7.11 (m, 4H), 7.06 (dt, J_1 = 16.0 Hz, J_2 = 7.5 Hz, 2H), 6.86 – 6.76 (m, 2H), 6.54 (dd, J_1 = 7.9 Hz, J_2 = 1.3 Hz, 1H), 6.43 (d, J = 7.7 Hz, 1H), 5.15 – 4.98 (m, 1H), 2.03 (s, 3H), 1.91 (s, 3H), 1.40 (d, J = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) for major compound: δ 168.3, 142.8, 138.2, 137.5, 137.2, 136.6, 136.2, 135.13, 135.05, 132.1, 131.2, 129.7, 129.0, 128.50, 128.47, 128.4, 127.6, 127.0, 126.9, 126.3, 123.7, 48.9, 21.4, 20.1, 19.8. **HRMS (ESI)** calcd for: $C_{29}H_{27}NOSNa^+$ $[M+Na]^+$ 460.1706, found: 460.1703.

2',6-dimethyl-*N*-((*S*)-1-phenylethyl)-6'-(phenylthio)-[1,1'-biphenyl]-2-carboxamide (3aa)

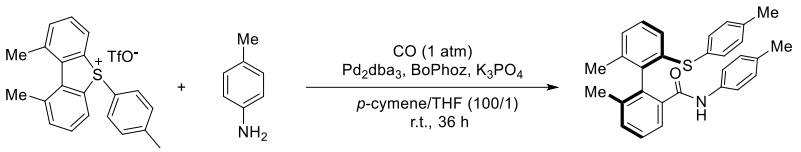


1a **3aa**

The reaction of **1a** (84.7 mg, 0.20 mmol, 1.0 equiv) and *S*-1-phenylethylamine (42.9 mg, 0.40 mmol, 2.0 equiv) under standard condition except at 60 °C for 24 h afforded **3aa** (54.2 mg, 62%, 1:9 dr) a light yellow oil. $[\alpha]_D^{20}$ = +18.23 (c 1.02, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) for major compound: δ 7.74 – 7.64 (m, 1H), 7.44 – 7.34 (m, 3H), 7.33 – 7.26 (m, 5H), 7.23 – 7.15 (m, 4H), 7.15 – 7.06 (m, 2H), 6.61 (dd, J_1 = 7.6 Hz, J_2 = 1.7 Hz, 1H), 6.40 (d, J = 8.1 Hz, 1H), 5.10 – 5.00 (m, 1H), 2.09 (s, 3H), 1.98 (s, 3H), 0.97 (d, J = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) for major compound: δ 168.0, 142.9, 138.5, 137.6, 137.1, 136.5, 136.2, 135.3, 135.2, 132.2, 130.9, 129.7, 129.2, 128.7, 128.53, 128.49, 127.5, 127.4, 126.9, 126.5, 123.2, 48.9, 20.7, 20.1, 19.9. **HRMS (ESI)** calcd for:

$C_{29}H_{27}NOSNa^+$ [M+Na]$^+$ 460.1706, found: 460.1711.

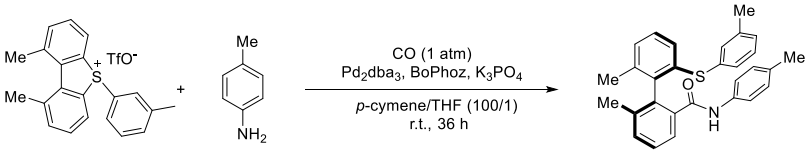
2',6-dimethyl-*N*-(*p*-tolyl)-6'-(*p*-tolylthio)-[1,1'-biphenyl]-2-carboxamide (3bb)



1b 3bb

The reaction of **1b** (90.5 mg, 0.20 mmol, 1.0 equiv) and *p*-toluidine (42.9 mg, 0.40 mmol, 2.0 equiv) under standard condition afforded **3bb** (86.8 mg, 99%, 87% ee) a light yellow oil. HPLC conditions: Chiralpak IC, isopropanol/hexane = 10: 90, flow: 1.0 mL/min, λ = 254 nm, tr = 15.608 min (minor), 20.567 min (major). $[\alpha]_D^{20}$ = -15.31 (c 0.93, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85 (bs, 1H), 7.78 (dd, J_1 = 6.4 Hz, J_2 = 2.7 Hz, 1H), 7.45 (d, J = 6.4 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 7.9 Hz, 2H), 7.10 – 7.06 (m, 3H), 7.04 (t, J = 8.4 Hz, 3H), 6.70 (dd, J_1 = 7.7 Hz, J_2 = 1.5 Hz, 1H), 2.36 (s, 3H), 2.27 (s, 3H), 2.10 (s, 3H), 1.96 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.0, 139.5, 138.4, 137.6, 137.4, 136.5, 136.1, 135.45, 135.42, 135.2, 133.9, 132.5, 130.6, 129.4, 128.7, 128.6, 127.8, 127.7, 127.1, 123.8, 120.54, 120.48, 21.4, 21.0, 20.2, 19.9. **HRMS (ESI)** calcd for: $C_{29}H_{28}NOS^+$ [M+H]$^+$ 438.1886, found: 438.1895.

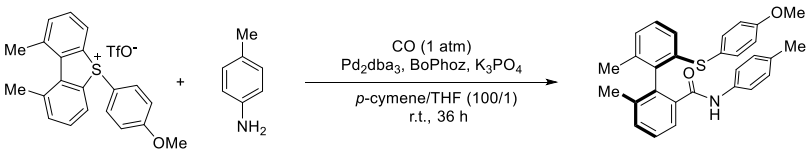
2',6-dimethyl-*N*-(*p*-tolyl)-6'-(*m*-tolylthio)-[1,1'-biphenyl]-2-carboxamide (3cc)



1c 3cc

The reaction of **1c** (90.5 mg, 0.20 mmol, 1.0 equiv) and *p*-toluidine (42.9 mg, 0.40 mmol, 2.0 equiv) under standard condition afforded **3cc** (89.4 mg, >99%, 80% ee) a light yellow oil. HPLC conditions: Chiralpak IA, isopropanol/hexane = 5: 95, flow: 1.0 mL/min, λ = 210 nm, tr = 13.083 min (minor), 15.066 min (major). $[\alpha]_D^{20}$ = -10.51 (c 0.32, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (bs, 1H), 7.77 (dd, J_1 = 5.7 Hz, J_2 = 3.4 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.23 – 7.14 (m, 4H), 7.14 – 7.06 (m, 4H), 7.03 (d, J = 8.2 Hz, 2H), 6.77 (dd, J_1 = 7.5 Hz, J_2 = 1.7 Hz, 1H), 2.28 (s, 3H), 2.24 (s, 3H), 2.10 (s, 3H), 1.98 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.0, 139.7, 137.9, 137.7, 137.4, 136.4, 135.5, 135.4, 134.0, 132.5, 131.9, 131.3, 129.9, 129.5, 129.4, 129.1, 128.7, 128.6, 128.5, 127.9, 127.0, 124.4, 120.5, 21.3, 21.0, 20.3, 19.9. **HRMS (ESI)** calcd for: $C_{29}H_{28}NOS^+$ [M+H]$^+$ 438.1886, found: 438.1897.

2'-((4-methoxyphenyl)thio)-6,6'-dimethyl-*N*-(*p*-tolyl)-[1,1'-biphenyl]-2-carboxamide (3dd)

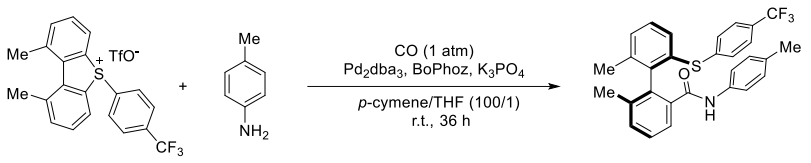


1d 3dd

The reaction of **1d** (93.7 mg, 0.20 mmol, 1.0 equiv) and *p*-toluidine (42.9 mg, 0.40 mmol, 2.0 equiv) under standard condition afforded **3dd** (46.9 mg, 52%, 68% ee) a yellow oil. HPLC conditions: Chiralpak AD-H, isopropanol/hexane = 10: 90, flow: 1.0 mL/min, λ = 254 nm, tr = 14.444 min (minor), 16.275 min (major). $[\alpha]_D^{20}$ = -14.32 (c 0.12, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89

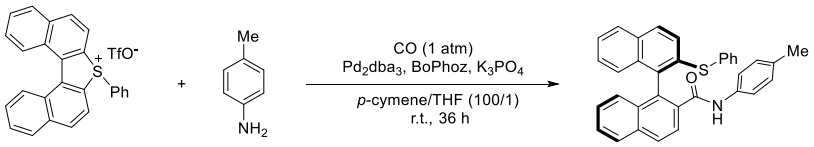
(bs, 1H), 7.79 (dd, J_1 = 6.1 Hz, J_2 = 3.0 Hz, 1H), 7.54 – 7.42 (m, 2H), 7.38 – 7.31 (m, 2H), 7.13 – 6.99 (m, 6H), 6.93 – 6.85 (m, 2H), 6.65 (d, J = 7.7 Hz, 1H), 3.82 (s, 3H), 2.27 (s, 3H), 2.11 (s, 3H), 1.95 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.0, 160.7, 139.0, 137.5, 137.4, 137.3, 136.5, 135.6, 135.4, 135.3, 134.0, 132.6, 129.5, 128.7, 128.6, 127.6, 127.2, 123.2, 121.4, 120.5, 115.5, 55.5, 21.0, 20.2, 19.9. **HRMS (ESI)** calcd for: $C_{29}H_{28}NO_2S^+$ $[M+H]^+$ 454.1835, found: 454.1847.

2',6-dimethyl-*N*-(*p*-tolyl)-6'-((4-(trifluoromethyl)phenyl)thio)-[1,1'-biphenyl]-2-carboxamide (3ee)



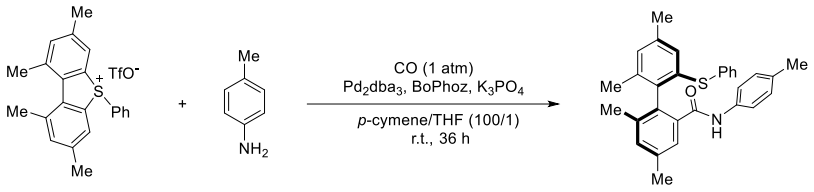
The reaction of **1e** (101.3 mg, 0.20 mmol, 1.0 equiv) and *p*-toluidine (42.9 mg, 0.40 mmol, 2.0 equiv) under standard condition afforded **3ee** (90.1 mg, 92%, 69% ee) a light yellow oil. HPLC conditions: Chiralpak AD-H, isopropanol/hexane = 10: 90, flow: 1.0 mL/min, λ = 254 nm, tr = 8.239 min (minor), 9.150 min (major). $[\alpha]_D^{20}$ = +10.50 (c 1.32, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68 (dd, J_1 = 5.9 Hz, J_2 = 3.2 Hz, 1H), 7.46 – 7.41 (m, 3H), 7.36 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 7.24 – 7.17 (m, 2H), 7.07 – 6.98 (m, 5H), 2.28 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.7. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.7, 139.6, 139.3, 138.6, 137.5, 136.3, 136.2, 135.3, 134.3, 134.1, 132.5, 131.6, 129.49, 129.48, 129.40 (q, J = 32.6 Hz), 129.0, 128.5, 127.9, 126.22, 126.15 (q, J = 3.7 Hz), 124.0 (q, J = 272.7 Hz), 120.0, 20.9, 20.5, 19.9. **HRMS (ESI)** calcd for: $C_{29}H_{25}F_3NOS^+$ $[M+H]^+$ 492.1603, found: 492.1613.

2'-(phenylthio)-*N*-(*p*-tolyl)-[1,1'-binaphthalene]-2-carboxamide (3ff)



The reaction of **1f** (102.1 mg, 0.20 mmol, 1.0 equiv) and *p*-toluidine (42.9 mg, 0.40 mmol, 2.0 equiv) under standard condition afforded **3ff** (104.4 mg, >99%, 89% ee) a white solid. HPLC conditions: Chiralpak IC, isopropanol/hexane = 30: 70, flow: 1.0 mL/min, λ = 210 nm, tr = 15.554 min (major), 20.563 min (minor). $[\alpha]_D^{20}$ = +57.61 (c 0.25, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 – 8.07 (m, 2H), 8.00 (d, J = 8.2 Hz, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.80 (d, J = 8.8 Hz, 1H), 7.57 (ddd, J_1 = 8.2 Hz, J_2 = 6.7 Hz, J_3 = 1.2 Hz, 1H), 7.45 (ddd, J_1 = 8.1, J_2 = 6.7, J_3 = 1.2 Hz, 1H), 7.38 – 7.30 (m, 4H), 7.28 – 7.21 (m, 5H), 7.17 (d, J = 8.4 Hz, 1H), 6.93 (d, J = 8.1 Hz, 2H), 6.85 – 6.77 (m, 2H), 2.22 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.4, 136.5, 135.2, 134.7, 134.4, 133.83, 133.82, 133.35, 133.32, 133.02, 132.96, 132.3, 131.9, 129.55, 129.50, 129.41, 129.39, 129.3, 128.5, 128.4, 128.0, 127.5, 127.3, 126.8, 126.3, 126.15, 126.07, 125.4, 119.9, 20.9. **HRMS (ESI)** calcd for: $C_{34}H_{26}NOSNa^+$ $[M+H]^+$ 496.1730, found: 496.1731.

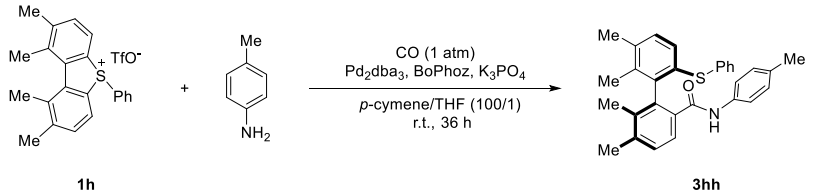
2',4,4',6-tetramethyl-6'-(phenylthio)-*N*-(*p*-tolyl)-[1,1'-biphenyl]-2-carboxamide (3gg)



1g **3gg**

The reaction of **1g** (93.3 mg, 0.20 mmol, 1.0 equiv) and *p*-toluidine (42.9 mg, 0.40 mmol, 2.0 equiv) under standard condition afforded **3gg** (96.0 mg, >99%, 86% ee) a light yellow oil. HPLC conditions: Chiralpak IG, isopropanol/hexane = 10: 90, flow: 1.0 mL/min, λ = 254 nm, tr = 14.662 min (major), 20.441 min (minor). $[\alpha]_D^{20}$ = -13.84 (c 2.63, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.78 (bs, 1H), 7.60 (s, 1H), 7.43 – 7.36 (m, 2H), 7.36 – 7.28 (m, 3H), 7.26 (s, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 2H), 6.89 (s, 1H), 6.59 (s, 1H), 2.42 (s, 3H), 2.27 (s, 3H), 2.17 (s, 3H), 2.04 (s, 3H), 1.93 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.1, 138.4, 138.2, 137.7, 137.44, 137.42, 136.3, 135.6, 134.5, 133.80, 133.76, 133.4, 132.7, 132.2, 129.7, 129.4, 129.1, 128.7, 127.6, 125.1, 120.3, 21.4, 21.3, 21.0, 20.2, 19.9. **HRMS (ESI)** calcd for: $C_{30}H_{30}NOS^+$ $[M+H]^+$ 452.2043, found: 452.2052.

2',3',5,6-tetramethyl-6'-(phenylthio)-*N*-(*p*-tolyl)-[1,1'-biphenyl]-2-carboxamide (3hh)



1h **3hh**

The reaction of **1h** (93.3 mg, 0.20 mmol, 1.0 equiv) and *p*-toluidine (42.9 mg, 0.40 mmol, 2.0 equiv) under standard condition afforded **3hh** (87.0 mg, 96%, 76% ee) a yellow solid. HPLC conditions: Chiralpak IA, isopropanol/hexane = 5: 95, flow: 1.0 mL/min, λ = 254 nm, tr = 17.230 min (minor), 19.324 min (major). $[\alpha]_D^{20}$ = +18.67 (c 0.07, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.9 Hz, 1H), 7.66 (bs, 1H), 7.35 – 7.29 (m, 3H), 7.29 – 7.22 (m, 3H), 7.08 – 6.98 (m, 5H), 6.79 (d, *J* = 8.0 Hz, 1H), 2.37 (s, 3H), 2.26 (s, 3H), 2.24 (s, 3H), 1.90 (s, 3H), 1.88 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.0, 139.9, 137.9, 136.5, 136.2, 135.8, 135.6, 135.5, 134.7, 134.2, 134.1, 133.7, 132.8, 130.2, 129.9, 129.5, 129.4, 128.5, 126.7, 125.3, 120.3, 21.1, 21.0, 20.4, 16.8, 16.1. **HRMS (ESI)** calcd for: $C_{30}H_{30}NOS^+$ $[M+H]^+$ 452.2043, found: 452.2043.

Method for crystal growth about 1a and 3gg

Compound **1a** (30 mg) was dissolved in about 1 mL of DCM, then about 2 mL of EA was added to the mixture, the solvent was slowly volatizing under open air to afford crystalline, which was suitable for single crystal X-ray analysis.

Compound **3hh** (40 mg) was dissolved in a about 1 mL of DCM, then about 3 mL of Et_3N was added to the mixture, the solvent was slowly volatizing under open air to afford crystalline, which was suitable for single crystal X-ray analysis.

DFT Calculations:

Computational Methods:

B2PLYPD3/def2-TZVP // B3LYP-D3BJ/6-311G(d,p)

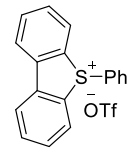
All of the DFT calculations were performed with Gaussian 16 software packages[8]. The optimization calculations were employed at B3LYP level of theory[9] at 298.15 K with the D3 version of Grimme's dispersion (with Becke-Johnson damping)[10]. The 6-311G(d,p) basis sets[11] were employed for the C, H, S atoms. Vibrational frequency analysis were calculated at the same level of theory to verify whether each optimized structure is an energy minimum and to evaluate its zero-point vibrational energy. All of the product structures were fully optimized without any symmetric restrictions. To obtain more accurate energies, single-point energy calculations were performed on all optimized structures applying the def2-TZVP basis set[12] at the B2PLYPD3 level of theory[13]. A standard state of 298.15 K and 1 atm was used. All discussed energies are Gibbs free energies in gas phase (ΔG_g).

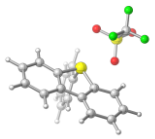
Table S1. Thermal correction of Gibbs free energy (TCG, hartree) and single-point energies (E, hartree) in 298.15 K and 1 atm for all species involved in this study.

Compd.	TCG	E	Compd.	TCG	E
1i	0.225717	-2051.219968	**7i**	0.244363	-2052.397802
H_2	-0.001444	-1.159449	**7i'**	0.142438	-860.471636
1i'	0.219326	-1091.106429	**Ph**	0.072747	-231.817104
HOTf	0.005336	-961.310496	**7a**	0.291119	-2130.871143
1a	0.278434	-2129.676067	**7a'**	0.166245	-899.708573
1a'	0.270240	-1169.578152	**Tol**	0.096100	-271.053733

Cartesian coordinates for all optimized geometries:

1i





0 1

C	4.37535000	-0.75024100	-2.29218800
C	3.95580300	-1.41749200	-1.14441800
C	2.72359200	-1.09230100	-0.57659200
C	1.94836400	-0.10218400	-1.19133600
C	2.34121800	0.56351300	-2.33905300
C	3.58010000	0.23240900	-2.88608000
H	5.33223600	-1.00028300	-2.73395600
H	4.57993400	-2.18229500	-0.69860200
H	1.71053100	1.31823400	-2.79188400
H	3.92223100	0.73720900	-3.78080600
C	2.08024600	-1.64693000	0.61613600
C	0.82544500	-1.07682500	0.88653000
C	2.55148700	-2.64115400	1.47256100
C	0.02898400	-1.45669100	1.95318200
C	1.77448200	-3.03029300	2.56060500
H	3.51182000	-3.10789200	1.29054700
C	0.52932600	-2.44692800	2.79891800
H	-0.93997700	-0.99804800	2.09404900
H	2.14014300	-3.80233900	3.22687800
H	-0.06552000	-2.76816700	3.64476200
S	0.36789600	0.14569900	-0.35588600
C	0.67829600	1.75240400	0.41903100
C	-0.16996900	2.78919000	0.05231000
C	1.74594600	1.92198200	1.29370600
C	0.07660700	4.05200600	0.58833600
H	-1.00628600	2.60085200	-0.61078900
C	1.96653600	3.18699500	1.82491300
H	2.38302800	1.08968800	1.56326500
C	1.13463700	4.24969200	1.47037200
H	-0.57564400	4.87485900	0.32335600
H	2.78577700	3.34178200	2.51641000
H	1.31097100	5.23284100	1.89017000
O	-1.93588800	0.35032700	0.87724700
S	-2.98993600	0.50666600	-0.17325000
O	-2.48527900	1.21157700	-1.36844600
O	-4.30592300	0.88622200	0.32536700
C	-3.18967900	-1.26007300	-0.76374900

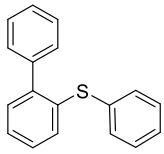
F	-2.00826300	-1.74477700	-1.21481500
F	-4.07498000	-1.34857500	-1.75786400
F	-3.59014900	-2.05351200	0.23938400

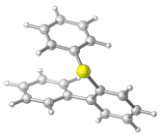
H_2

0 1

H	0.00000000	0.00000000	0.37226500
H	0.00000000	0.00000000	-0.37226500

1i'





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C	0.69923400	-1.42635800	1.17382800
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C	0.27613500	-1.92395200	-1.14444000
C	1.52842700	-2.52042900	-1.24336000
C	2.37426100	-2.56287600	-0.13648000
C	1.95579100	-2.01543600	1.07281200
H	0.38308900	-0.97574000	2.10677000
H	-0.37716800	-1.88031400	-2.00679000
H	1.84539600	-2.95182500	-2.18603800
H	3.35390900	-3.01951900	-0.21756300
H	2.61085600	-2.03599600	1.93581100
C	-1.48278700	-0.71925900	0.17504700
C	-1.82024900	0.44336500	-0.54594800
C	-2.44311000	-1.26991500	1.02891200
C	-3.09736200	0.99571300	-0.42776300
C	-3.71731000	-0.72099600	1.14061500
H	-2.18398700	-2.16021700	1.59015000
C	-4.04944600	0.40877200	0.40023500
H	-3.33118600	1.90041600	-0.97541400
H	-4.44618900	-1.17722600	1.80004000
H	-5.03747900	0.84675400	0.47984500
S	-0.65666200	1.26940200	-1.63602700
C	0.74061100	1.48272500	-0.53251100
C	2.00549700	1.07916200	-0.95642400
C	0.57283400	2.04712100	0.73343600
C	3.10060300	1.23523100	-0.11159000
H	2.12144300	0.61209900	-1.92565000
C	1.66803600	2.18304000	1.57862600

H	-0.41289100	2.35875800	1.05562900
C	2.93483200	1.77918800	1.15863200
H	4.07976800	0.90711800	-0.44004600
H	1.53342800	2.61235600	2.56492800
H	3.78643600	1.88622600	1.82015900

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O	-1.22897100	-1.35121800	-0.61851500
S	-0.86063400	-0.14809500	0.07763900
O	-1.25423500	0.16284200	1.43466800
O	-1.25162000	1.10230200	-0.88383200
C	1.00940300	0.00394100	-0.00303700
F	1.36174300	1.22438900	0.40352800
F	1.54327200	-0.90563000	0.80226700
F	1.42826600	-0.19086700	-1.24487900
H	-1.40718800	1.88343600	-0.33081800

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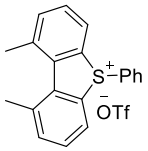

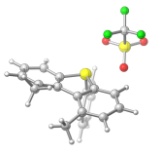

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C	-1.49621300	0.26780800	1.33129800
C	-1.56833800	0.74579500	2.62420000
C	-2.73388600	0.47807200	3.33782400
H	-4.55366600	-0.63985700	3.38548000
H	-0.74344000	1.29090300	3.06522500
H	-2.85082200	0.84969300	4.34809600
C	-2.15869600	-0.76384700	-0.71830900
C	-0.78849600	-0.53759200	-0.97619600
C	-2.96312000	-1.12104400	-1.81868800
C	-0.15242700	-0.81046300	-2.17027200
C	-2.32149000	-1.41024300	-3.03171800
C	-0.94783900	-1.30194000	-3.20356200
H	0.90877800	-0.62958400	-2.27189700
H	-2.93741600	-1.69769300	-3.87691100
H	-0.49760900	-1.54419600	-4.15809900
S	0.03299500	0.28959300	0.39197500
C	0.10379700	2.02018100	-0.13623500
C	1.20339400	2.75174400	0.29408700

C	-0.92678000	2.57673400	-0.88669900
C	1.26009900	4.10280300	-0.04443400
H	1.99361700	2.26785500	0.85633400
C	-0.84491500	3.92296600	-1.22113700
H	-1.76543200	1.97525500	-1.21197400
C	0.24581400	4.68418600	-0.79905900
H	2.11144000	4.69176400	0.27359700
H	-1.63089500	4.37638500	-1.81280900
H	0.30463600	5.73262800	-1.06607200
O	2.30099900	0.08410500	-0.93732500
S	3.37462900	-0.16827200	0.07270900
O	3.08469300	0.47763200	1.36882200
O	4.73715600	-0.06863100	-0.43615500
C	3.12993700	-1.99026900	0.43450500
F	1.87062300	-2.22162500	0.87610700
F	3.97696600	-2.42093400	1.37179900
F	3.30698800	-2.72363900	-0.67251300
C	-4.59168300	-1.94371500	1.08889200
H	-5.52226800	-1.54242000	0.68222100
H	-4.16414400	-2.62462100	0.35462600
H	-4.84987200	-2.52920800	1.97305500
C	-4.47152400	-1.06762600	-1.82124100
H	-4.93295100	-2.04071100	-1.64114200
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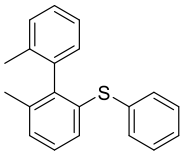

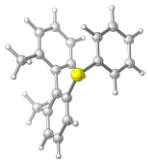

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C	0.56324800	1.12925300	-1.22275600
C	-0.33226500	1.07435300	-0.15246500
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C	0.89454200	2.84874100	0.91678000
C	1.79465600	2.88506200	-0.14381300
C	1.62559700	2.02447900	-1.22368600
H	0.43804400	0.43696700	-2.04627000
H	1.02057200	3.53053900	1.75130200
H	2.62151400	3.58596000	-0.12729800
H	2.32216100	2.03770500	-2.05315100
C	-1.44847600	0.08433700	-0.18603000
C	-1.38755100	-1.11308200	0.54984500

C	-2.58841200	0.35049100	-0.96685600
C	-2.44368200	-2.02570600	0.51316300
C	-3.63871500	-0.57091100	-0.98296200
C	-3.57246000	-1.74859300	-0.24814500
H	-2.36751300	-2.94719000	1.07651600
H	-4.51935600	-0.35564000	-1.57807800
H	-4.39391400	-2.45512200	-0.27504500
S	-0.01762300	-1.49882100	1.64543300
C	1.39420400	-1.40630900	0.54740300
C	2.49773500	-0.64835700	0.93520900
C	1.40885500	-2.09666300	-0.66589100
C	3.61359400	-0.57768000	0.10658000
H	2.46329900	-0.08773500	1.86047600
C	2.51843800	-2.00350100	-1.49846500
H	0.54849800	-2.68612100	-0.95768500
C	3.62483000	-1.24671400	-1.11391400
H	4.46438800	0.02308900	0.40595200
H	2.52346800	-2.53114800	-2.44550900
H	4.48918800	-1.17881500	-1.76400000
C	-2.69538000	1.63136800	-1.75778800
H	-2.48124700	2.50178500	-1.13287800
H	-1.97565400	1.65487000	-2.58026000
H	-3.69620200	1.74353200	-2.17775700
C	-1.14623000	1.94049300	2.08750400
H	-1.01638400	1.03651400	2.68880800
H	-0.99225400	2.80549500	2.73480700
H	-2.18270200	1.94928500	1.74096400

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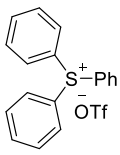

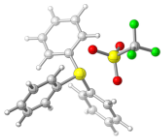

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S	0.71007700	-0.00007700	0.00028700
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C	2.66083200	-1.21383700	1.61290000
C	1.09275800	-3.52090000	1.84953600
H	-0.37280900	-2.45247900	0.64643600
C	3.11855000	-2.29756100	2.35526800
H	3.24442500	-0.30556100	1.54162700
C	2.33956100	-3.44914000	2.46633900
H	0.48019100	-4.40736000	1.95767300

H	4.07887300	-2.23853100	2.85289600
H	2.70162000	-4.28731200	3.04973800
C	1.41888800	1.51558700	0.64538500
C	0.60987000	2.18126100	1.56504800
C	2.65973100	2.00439100	0.24498200
C	1.09041000	3.36290200	2.12352500
H	-0.37424000	1.78577600	1.80012700
C	3.11659600	3.18974100	0.81176300
H	3.24373700	1.48849800	-0.50561600
C	2.33698900	3.86173500	1.75302000
H	0.47732500	3.89979600	2.83669900
H	4.07672900	3.59162800	0.51181700
H	2.69838600	4.78651800	2.18677200
C	1.41911300	-0.19881600	-1.63487100
C	0.60978500	0.26445100	-2.67111200
C	2.66041100	-0.78898300	-1.85805000
C	1.09039200	0.15786600	-3.97369300
H	-0.37452900	0.66518700	-2.44598800
C	3.11738700	-0.89015500	-3.16800400
H	3.24477200	-1.18069500	-1.03604200
C	2.33741500	-0.41142900	-4.22051500
H	0.47709000	0.50677800	-4.79519500
H	4.07789900	-1.35003400	-3.36615900
H	2.69891400	-0.49769700	-5.23828300
O	-2.08226100	0.89299300	-1.12418600
S	-2.44045200	-0.00020600	0.00003400
O	-2.08168000	0.52687200	1.33548900
O	-2.08163300	-1.42023500	-0.21139700
C	-4.31163000	-0.00060400	0.00035700
F	-4.78237200	1.23710100	0.20123500
F	-4.78220100	-0.44572500	-1.17195800
F	-4.78180400	-0.79352900	0.97200800

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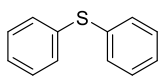

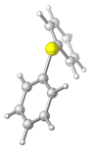

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S	-0.00063500	1.66997900	-0.00017600
C	1.38805100	0.54033400	0.07010600
C	1.40336000	-0.54137400	0.95543600
C	2.49540800	0.79102600	-0.74136200
C	2.51597000	-1.37212200	1.01214300

H	0.54449700	-0.73040000	1.58697900
C	3.61646700	-0.03280900	-0.66119900
H	2.47288100	1.62147300	-1.43649600
C	3.62816700	-1.11831000	0.20934600
H	2.52005100	-2.21375400	1.69524300
H	4.47407500	0.16821300	-1.29275000
H	4.49624000	-1.76453700	0.26266900
C	-1.38825100	0.53899200	-0.07012600
C	-2.49935500	0.79445100	0.73477200
C	-1.39938300	-0.54818200	-0.94876300
C	-3.61988000	-0.03004600	0.65461500
H	-2.48017300	1.62912400	1.42494600
C	-2.51164600	-1.37943900	-1.00536300
H	-0.53769800	-0.74108600	-1.57525800
C	-3.62752700	-1.12093400	-0.20924900
H	-4.48033000	0.17471600	1.28108300
H	-2.51243600	-2.22528400	-1.68325700
H	-4.49523400	-1.76765400	-0.26248100

Ph

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C	1.21107600	0.68938400	0.00000300
C	0.00839900	1.39361600	-0.00001800
C	-1.20262500	0.70401900	0.00001700
C	-1.21110900	-0.68948600	-0.00000200
C	-0.00845100	-1.39353100	-0.00001200
C	1.20271400	-0.70402400	0.00001200
H	2.15323900	1.22595100	0.00001800
H	-2.13829000	1.25184000	0.00003100
H	-2.15330600	-1.22584400	0.00000500
H	-0.01494400	-2.47774200	-0.00003400
H	2.13827800	-1.25186700	0.00002200
H	0.01500200	2.47779400	-0.00004200

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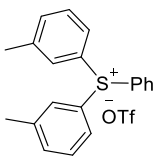

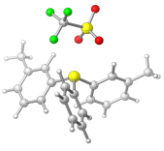

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S	-0.49969700	0.12488300	0.23270000
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C	-1.01541400	0.71203200	2.81147700

C	-2.99193600	0.06854900	1.54297500
C	-1.80655000	0.88929000	3.94190100
H	0.05685900	0.86050100	2.84773400
C	-3.76799100	0.24192500	2.68548500
H	-3.43733700	-0.26820400	0.61655700
C	-3.17893600	0.65690200	3.87842300
H	-3.78937600	0.78661900	4.76395100
C	-1.37324100	-0.98186800	-0.88335300
C	-1.04076900	-2.32517700	-0.76468500
C	-2.30391500	-0.51397000	-1.80719800
C	-1.67677800	-3.25961500	-1.58808800
H	-0.26796500	-2.62276200	-0.06332300
C	-2.93028700	-1.44841800	-2.62368900
H	-2.51458600	0.54247800	-1.90296800
C	-2.62178000	-2.80319300	-2.50990700
H	-3.65371600	-1.11739000	-3.35913100
H	-3.11252400	-3.51691400	-3.16230000
C	-0.57377100	1.72615700	-0.59397700
C	0.47775700	1.98154600	-1.46921600
C	-1.58749400	2.64906500	-0.35215500
C	0.51738500	3.20003700	-2.15259500
H	1.25272500	1.23376900	-1.60003800
C	-1.53773400	3.86180900	-1.03177500
H	-2.37926900	2.44012500	0.35366400
C	-0.50032800	4.12989300	-1.92186500
H	-2.30898300	4.60296700	-0.85935800
H	-0.47434600	5.08328700	-2.43792900
O	1.91465400	-0.66869300	-1.06071900
S	2.52302900	-1.42299200	0.06613100
O	1.51858800	-2.04000000	0.96274200
O	3.68473400	-2.23889900	-0.27084400
C	3.22039500	-0.04385700	1.13141100
F	4.10922400	0.69144200	0.45229800
F	2.23188800	0.80377300	1.53676000
F	3.81025400	-0.51840600	2.23092900
C	1.63872200	3.48230100	-3.11819400
H	1.45791100	2.98208800	-4.07475900
H	1.73741400	4.55165800	-3.31236800
H	2.58948500	3.10922400	-2.73295000
H	-1.34640400	1.19316500	4.87389800
H	-4.83269700	0.04711800	2.64283200
C	-1.31964900	-4.71870700	-1.47678100
H	-1.66682100	-5.13250800	-0.52540700
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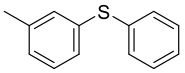

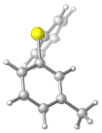

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S	0.40991800	-1.76358800	-0.54343000
C	-1.09785900	-0.88146400	-0.14484800
C	-2.07867500	-1.53060000	0.60183400
C	-1.32039900	0.41504100	-0.61849900
C	-3.28217400	-0.87679900	0.86336500
H	-1.89800300	-2.52960600	0.97859000
C	-2.50997000	1.08274000	-0.33832400
H	-0.55193000	0.90568500	-1.20395400
C	-3.49399800	0.41683900	0.40446300
H	-4.04997200	-1.37917400	1.44058000
H	-4.42995400	0.92030500	0.62215300
C	1.66288700	-0.56051800	-0.10545700
C	1.59126400	0.17281800	1.08239700
C	2.76039700	-0.40418300	-0.95365100
C	2.60636900	1.06530700	1.40595000
H	0.74100600	0.04714800	1.74071000
C	3.78487100	0.47543300	-0.61025400
H	2.80475600	-0.96258800	-1.88091500
C	3.70904100	1.21644100	0.56528100
H	2.54217200	1.63625000	2.32519900
H	4.63488400	0.59066400	-1.27286200
H	4.50115100	1.90841200	0.82552700
C	-2.73944400	2.49167900	-0.82507300
H	-3.69279900	2.57701000	-1.35362600
H	-2.76753300	3.19508000	0.01306500
H	-1.94632800	2.81181400	-1.50269600

Tol

0 1

C	0.91132300	0.00621500	-0.00001100
C	0.19800900	-1.19758000	-0.00000700
C	-1.19282700	-1.20548000	0.00000600
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C	-1.20328200	1.19983000	0.00000900
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C	2.41988200	0.00252000	-0.00000800
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H	2.81953600	1.01834600	-0.00018300
H	-1.72640700	-2.14942900	0.00000900

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4. Copies of NMR spectra

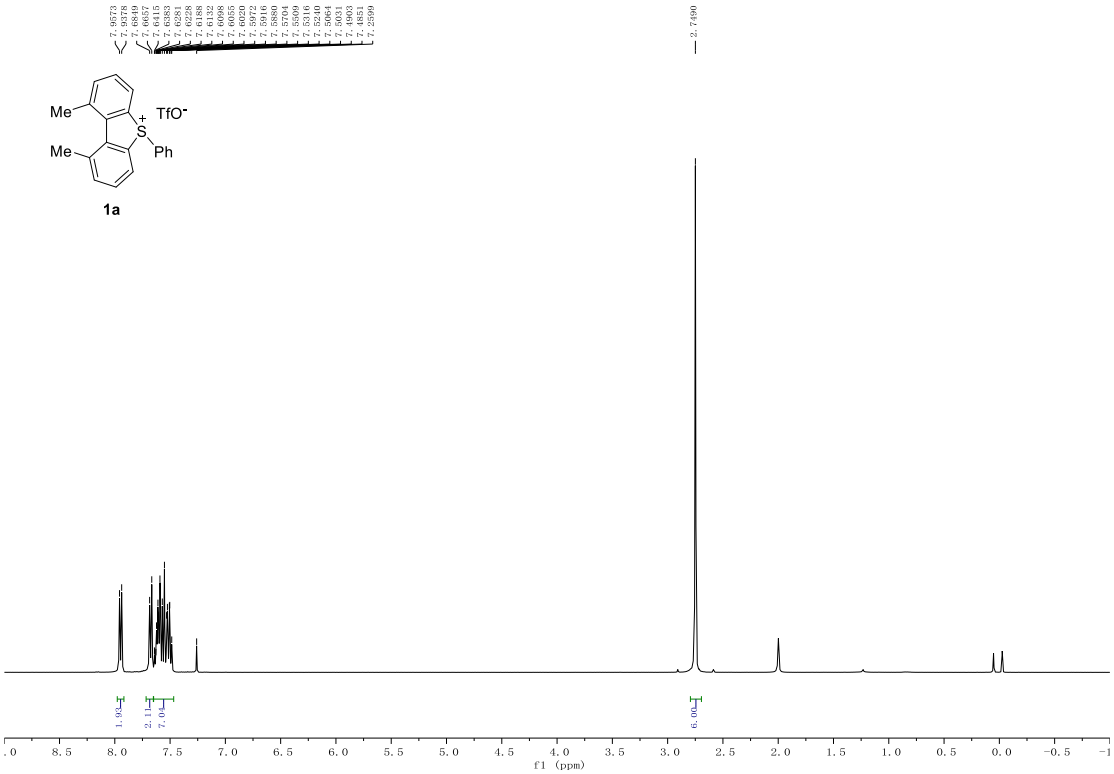


Figure **S1**. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of **1a**

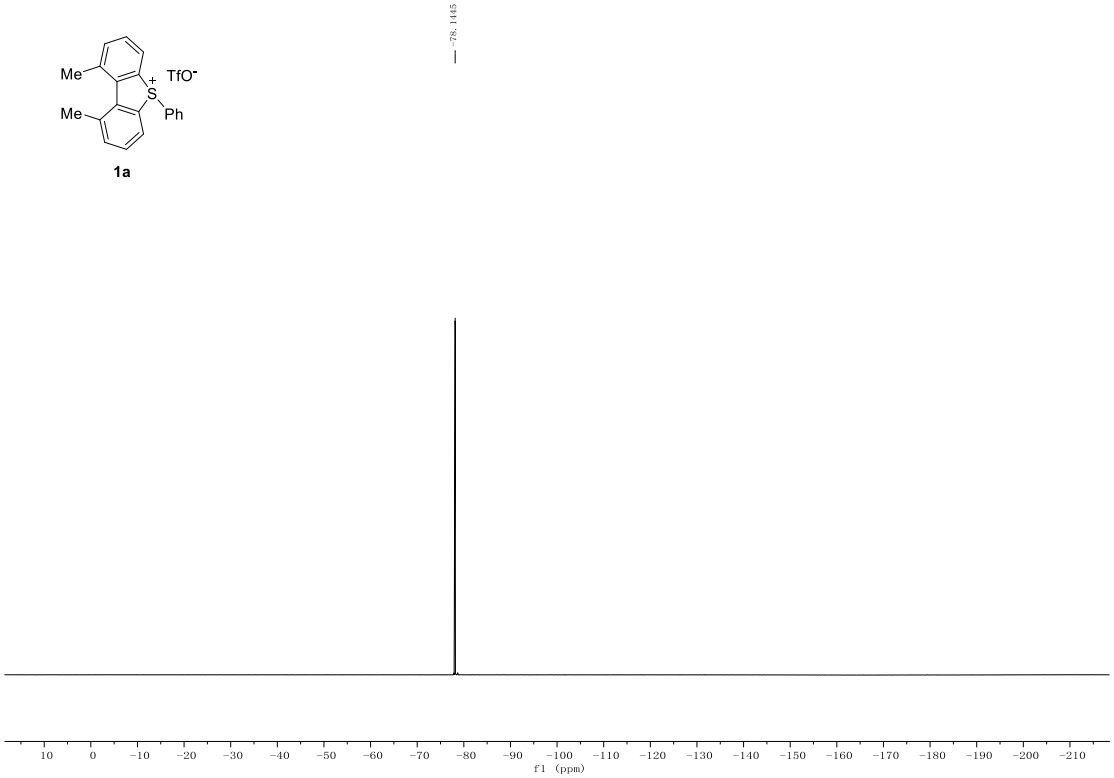


Figure **S2**. ^{19}F NMR spectra (376 MHz, $CDCl_3$) of **1a**

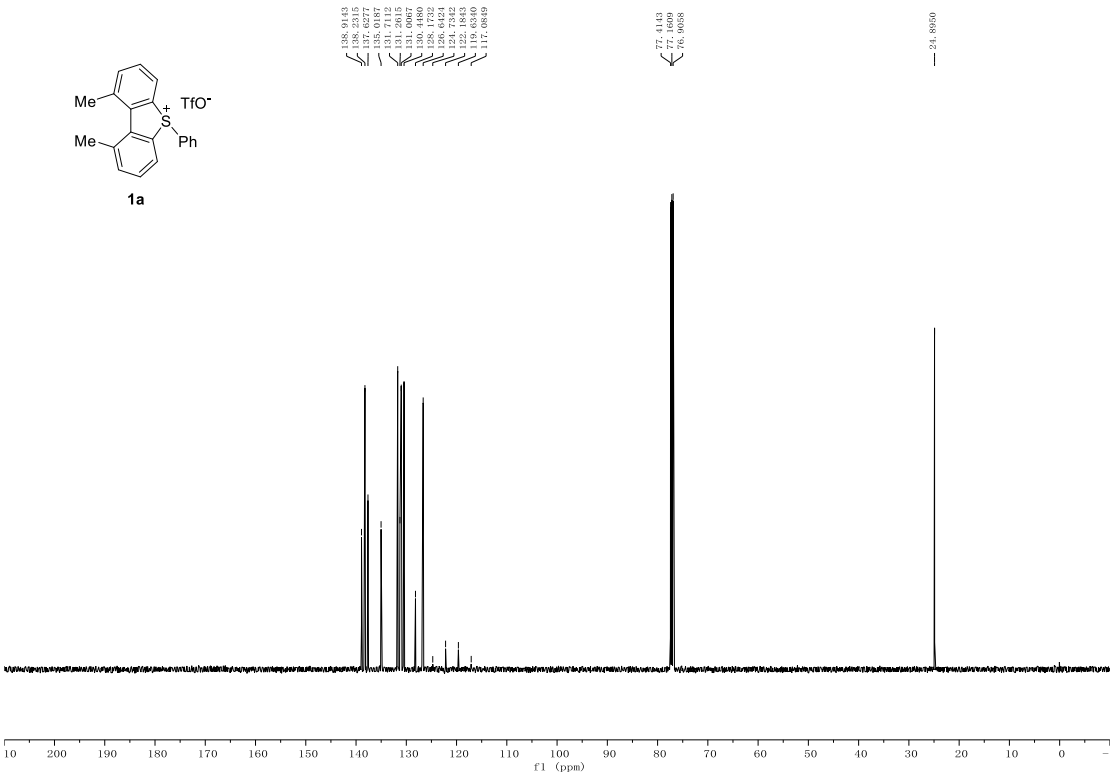


Figure **S3**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **1a**

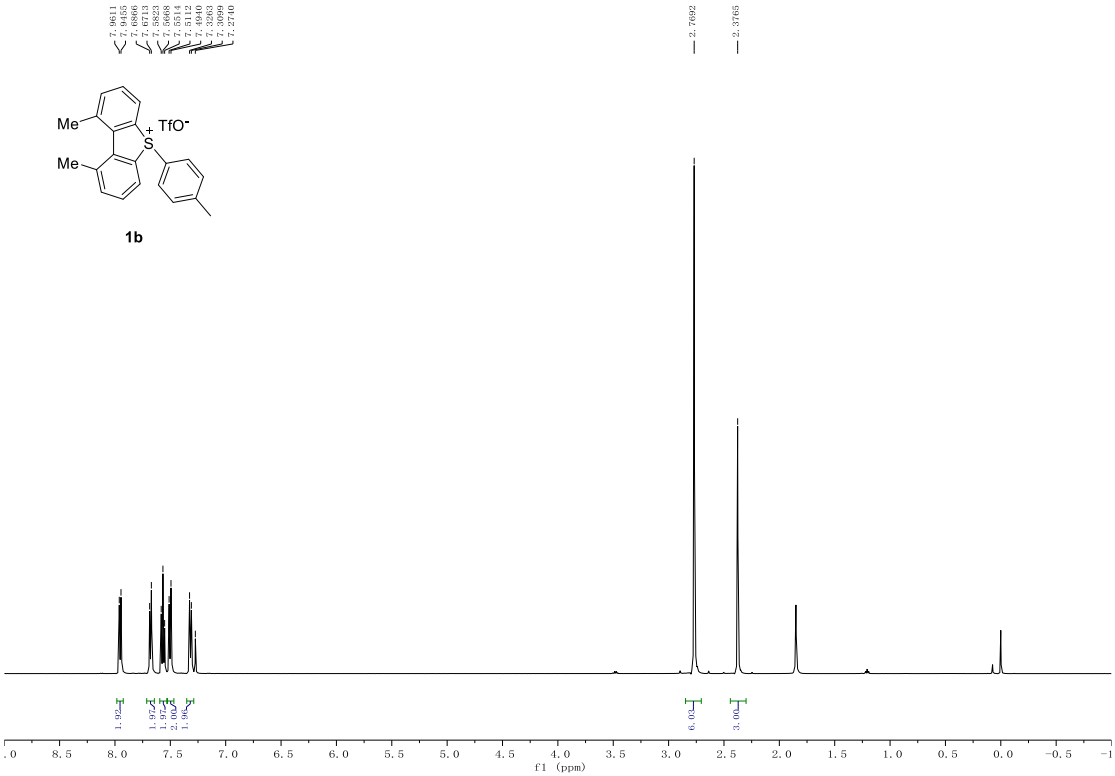


Figure **S4**. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **1b**

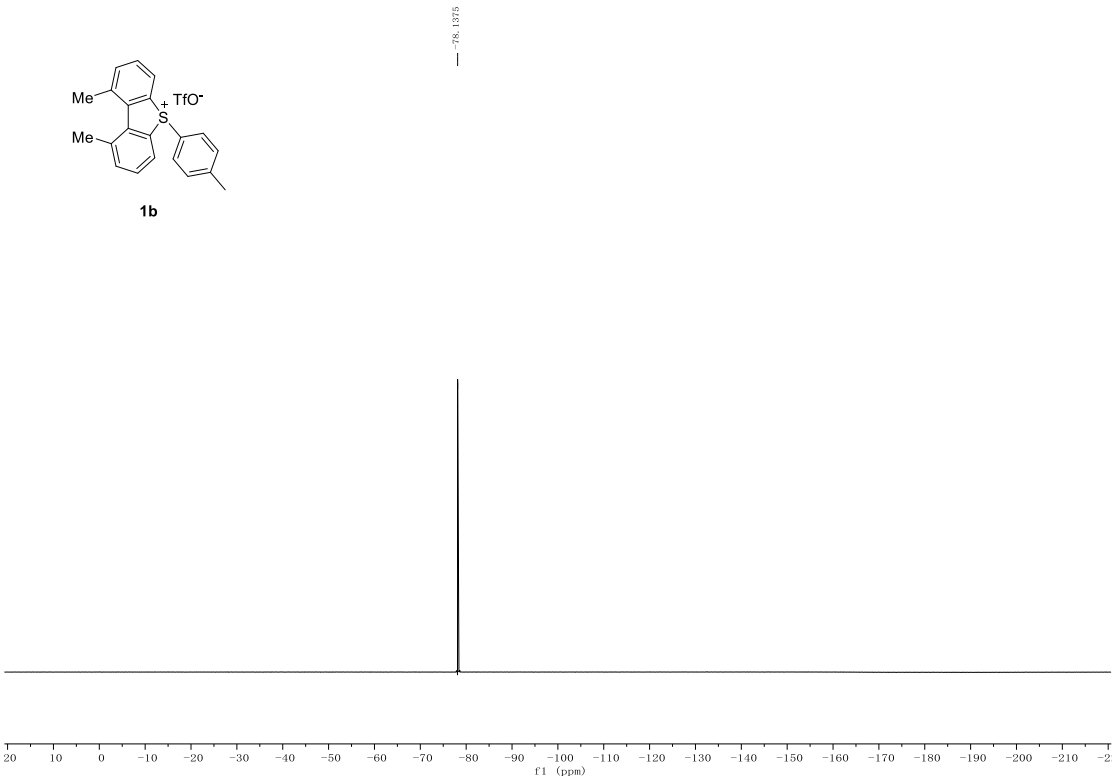


Figure **S5**. ^{19}F NMR spectra (471 MHz, $CDCl_3$) of **1b**

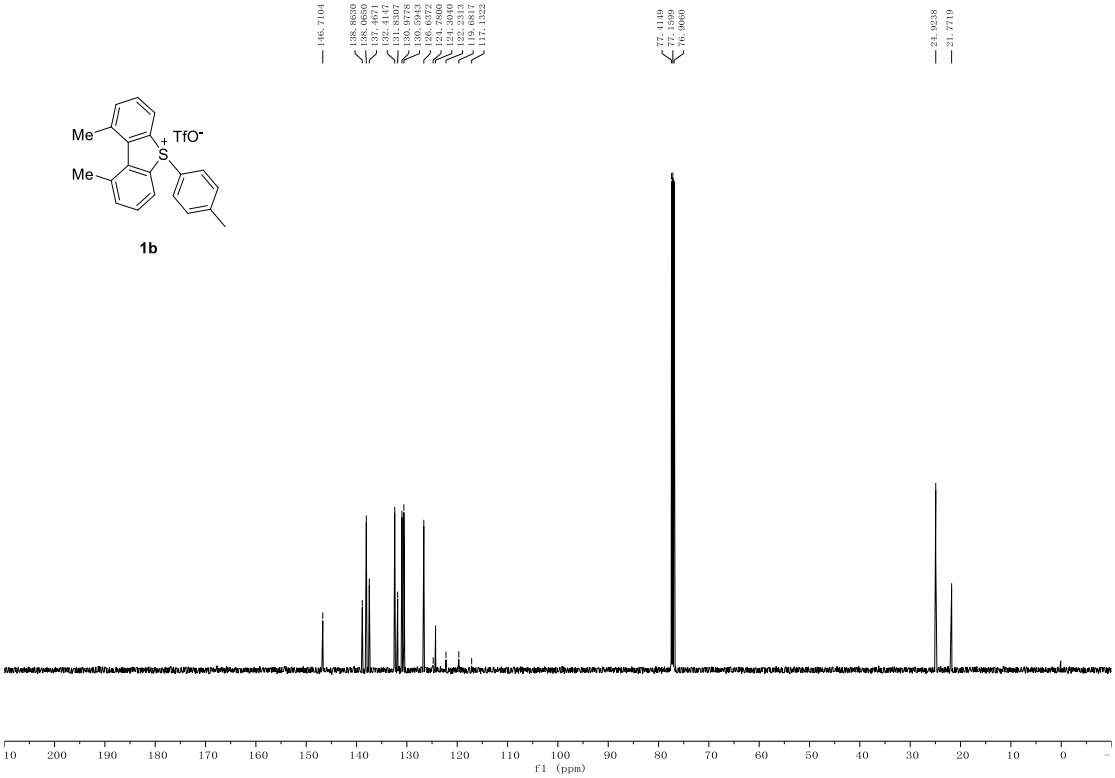


Figure **S6**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **1b**

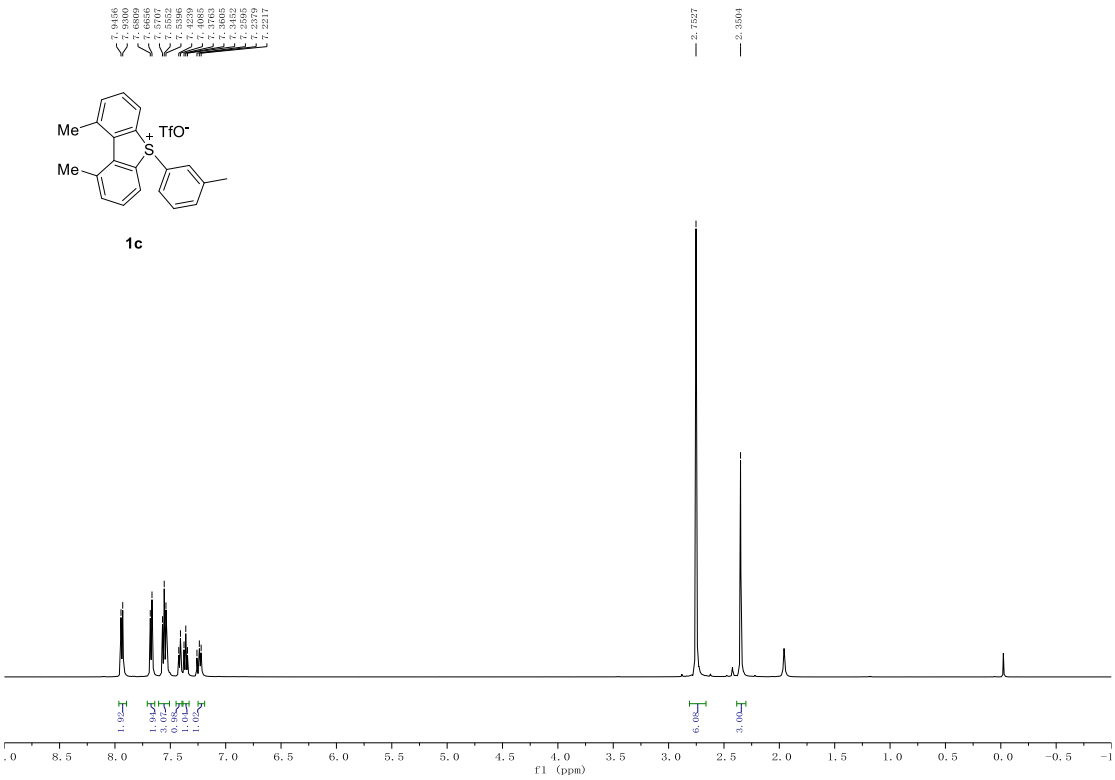


Figure **S7**. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **1c**

Figure **S8**. ^{19}F NMR spectra (471 MHz, $CDCl_3$) of **1c**

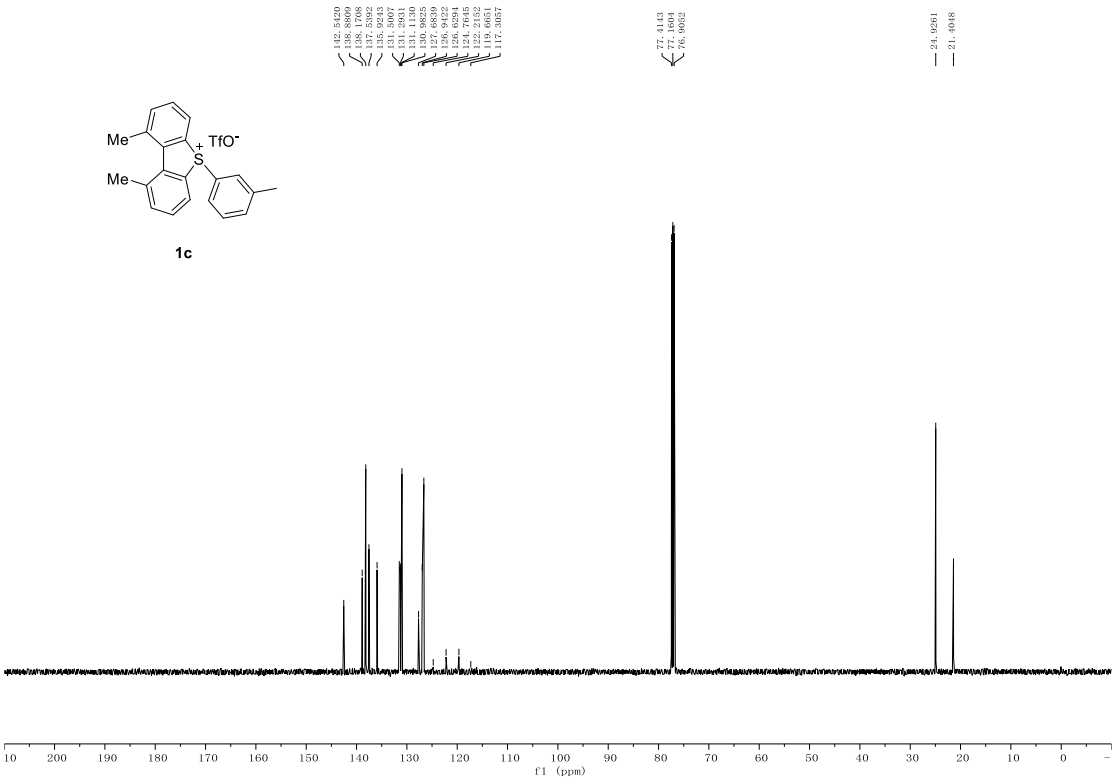


Figure **S9**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **1c**

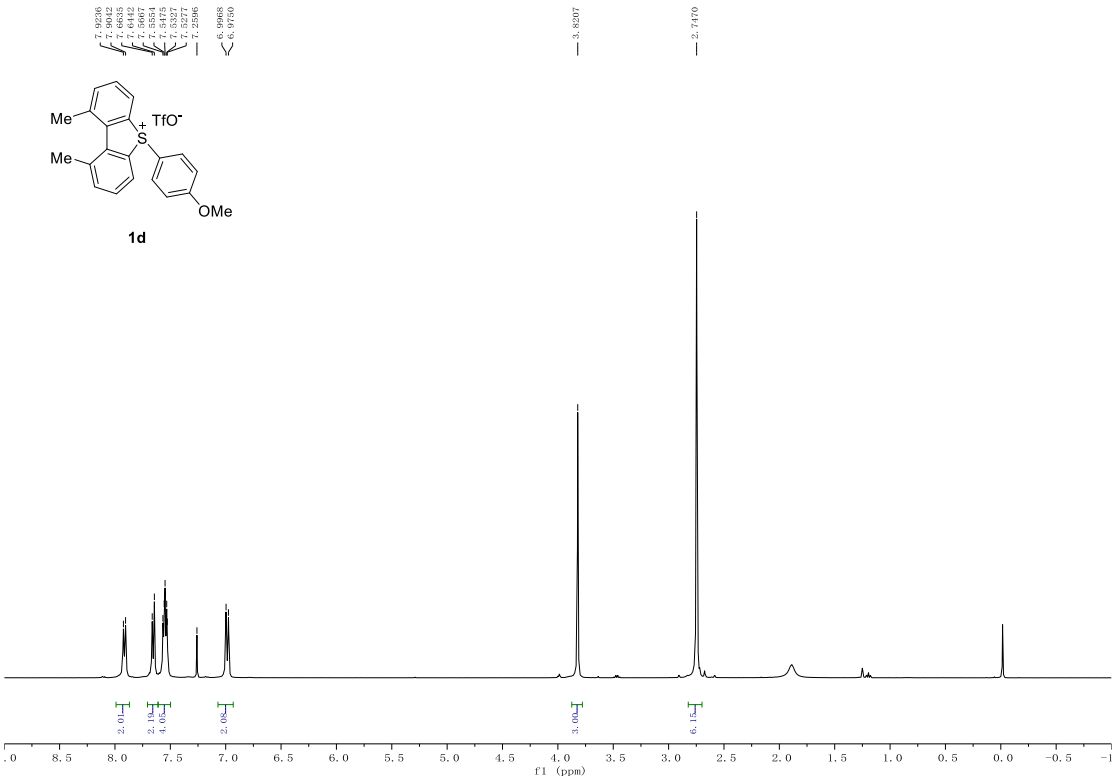


Figure **S10**. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of **1d**

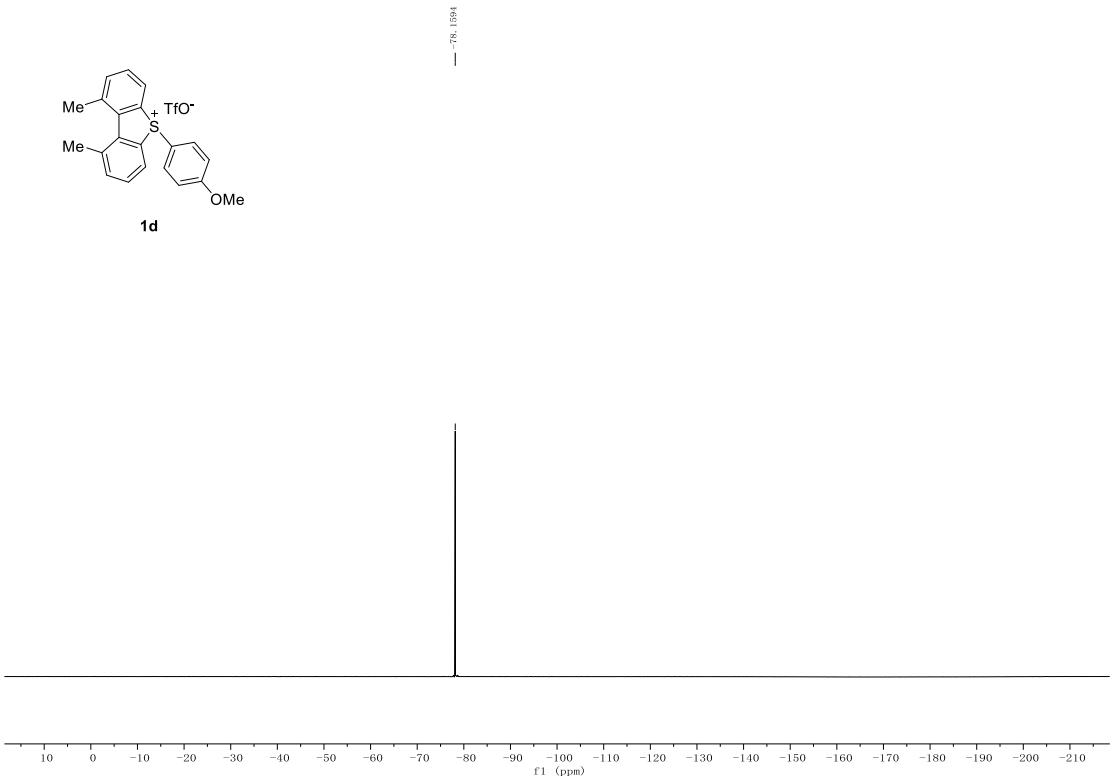


Figure **S11**. ^{19}F NMR spectra (376 MHz, $CDCl_3$) of **1d**

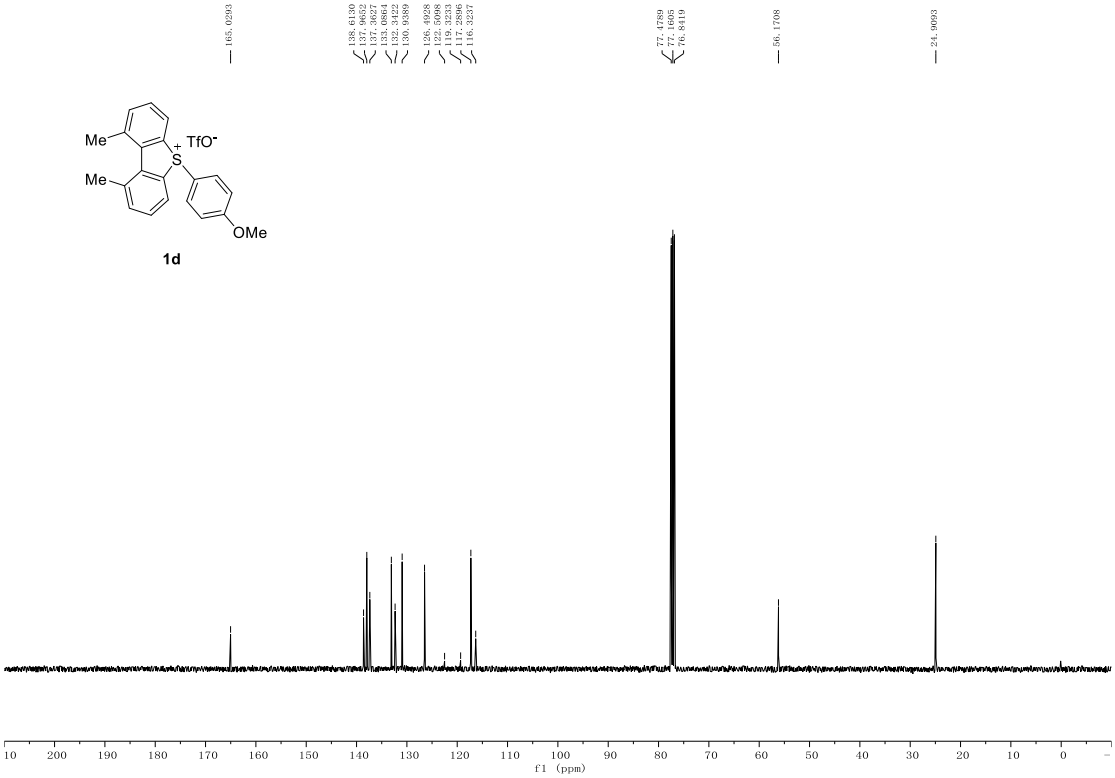


Figure **S12**. ^{13}C NMR spectra (101 MHz, $CDCl_3$) of **1d**

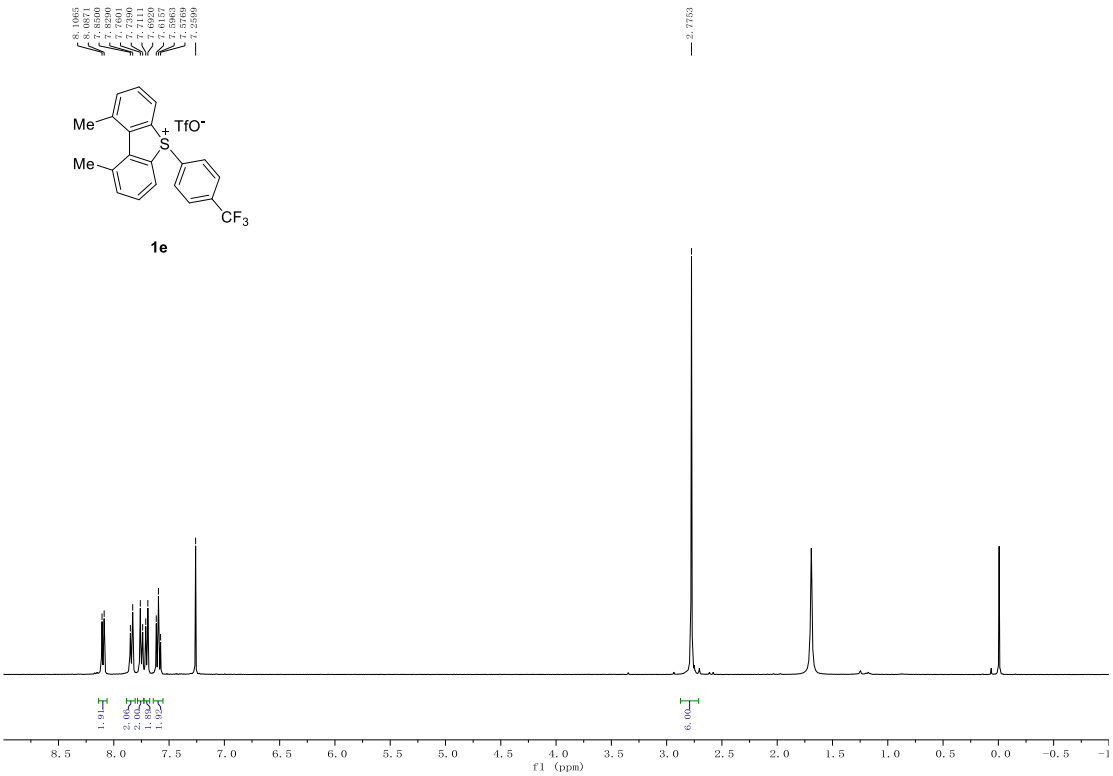


Figure **S13**. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of **1e**

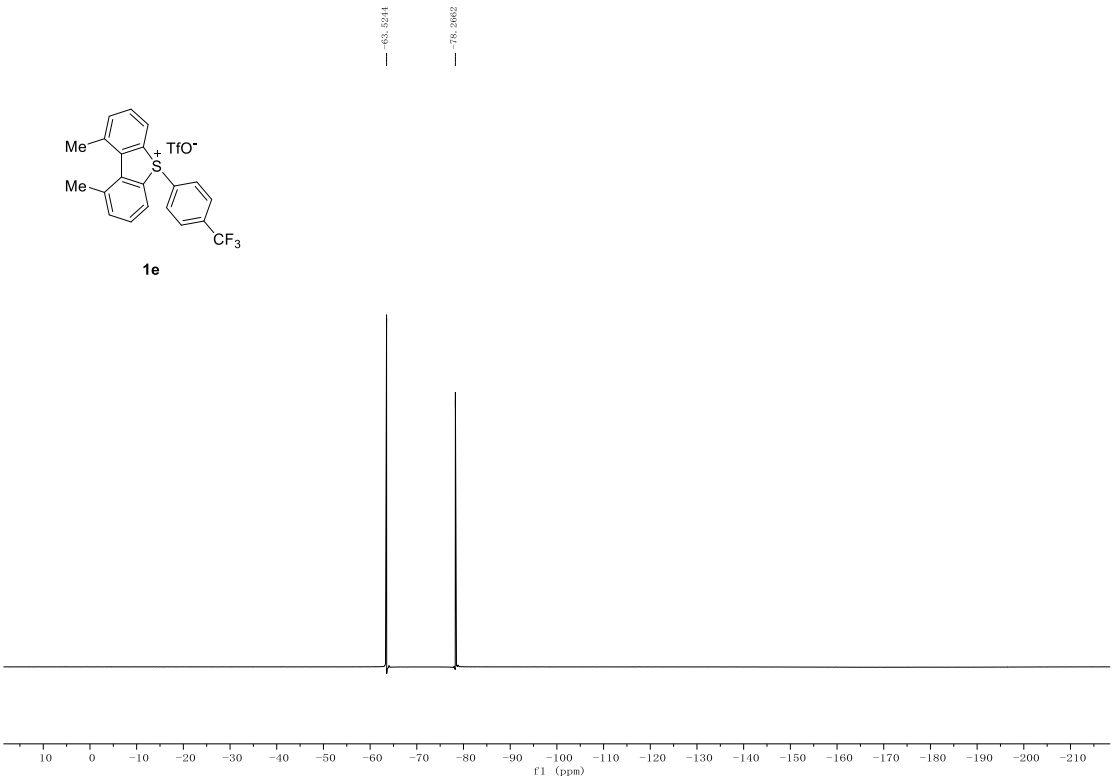


Figure **S14**. ^{19}F NMR spectra (376 MHz, $CDCl_3$) of **1e**

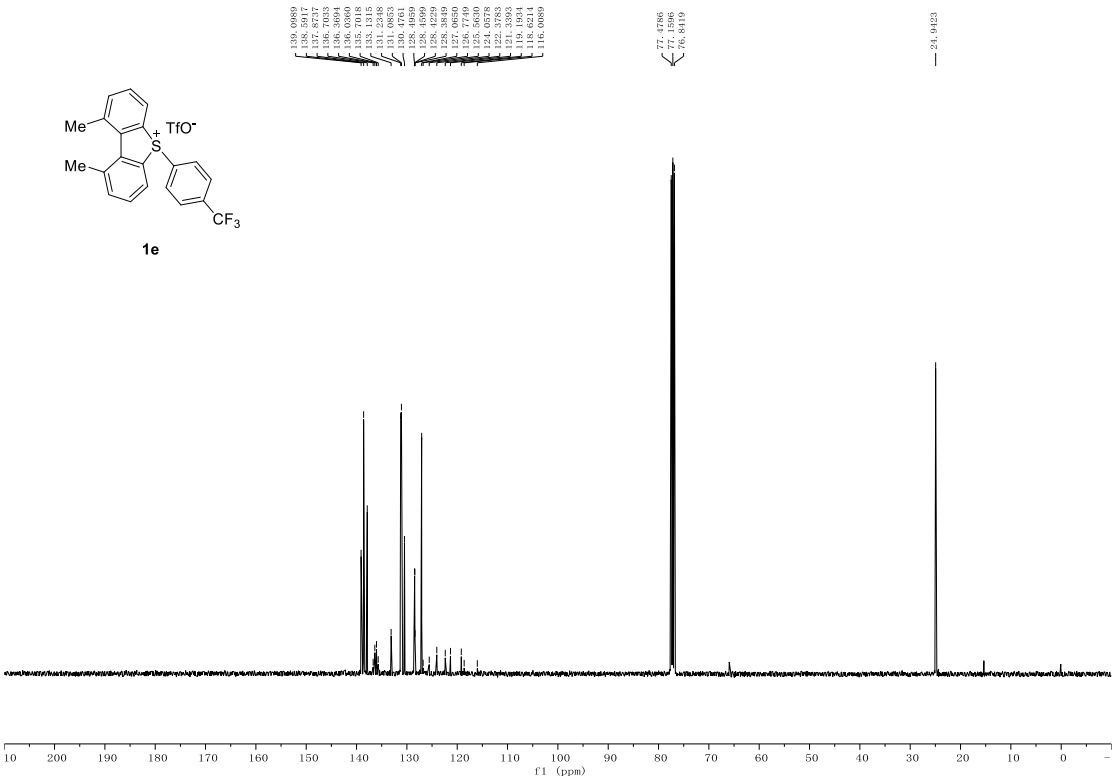


Figure **S15**. ^{13}C NMR spectra (101 MHz, $CDCl_3$) of **1e**

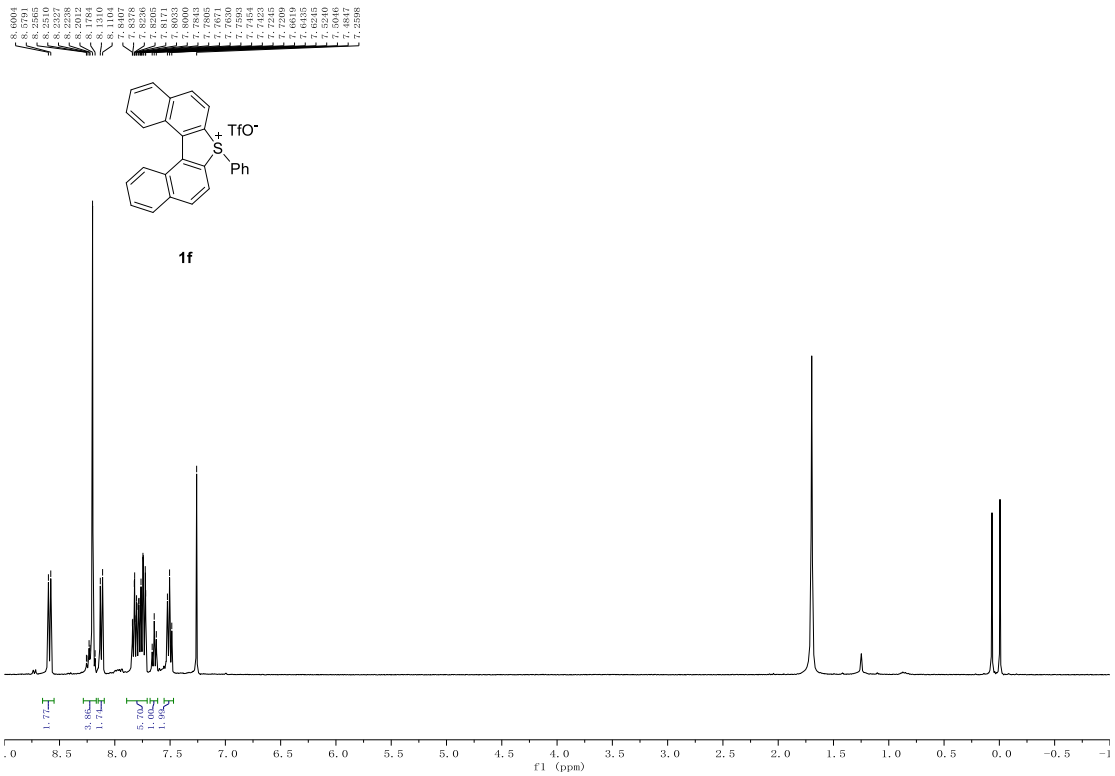


Figure **S16**. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of **1f**

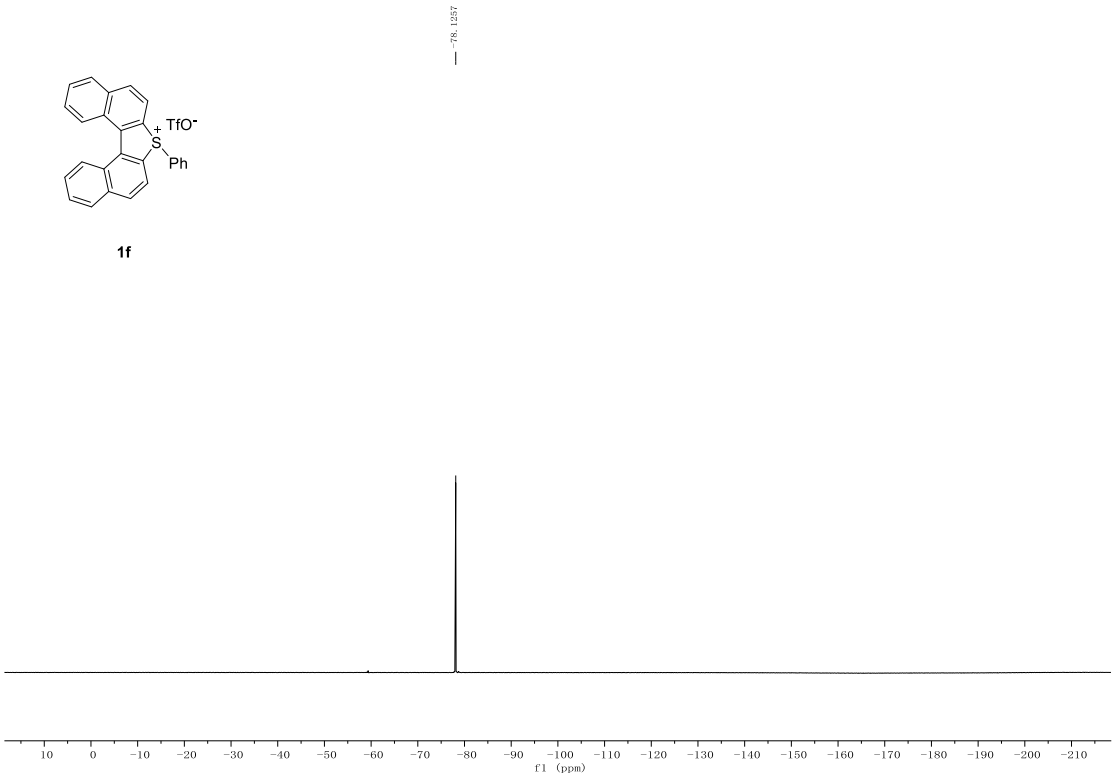


Figure **S17**. ^{19}F NMR spectra (376 MHz, $CDCl_3$) of **1f**

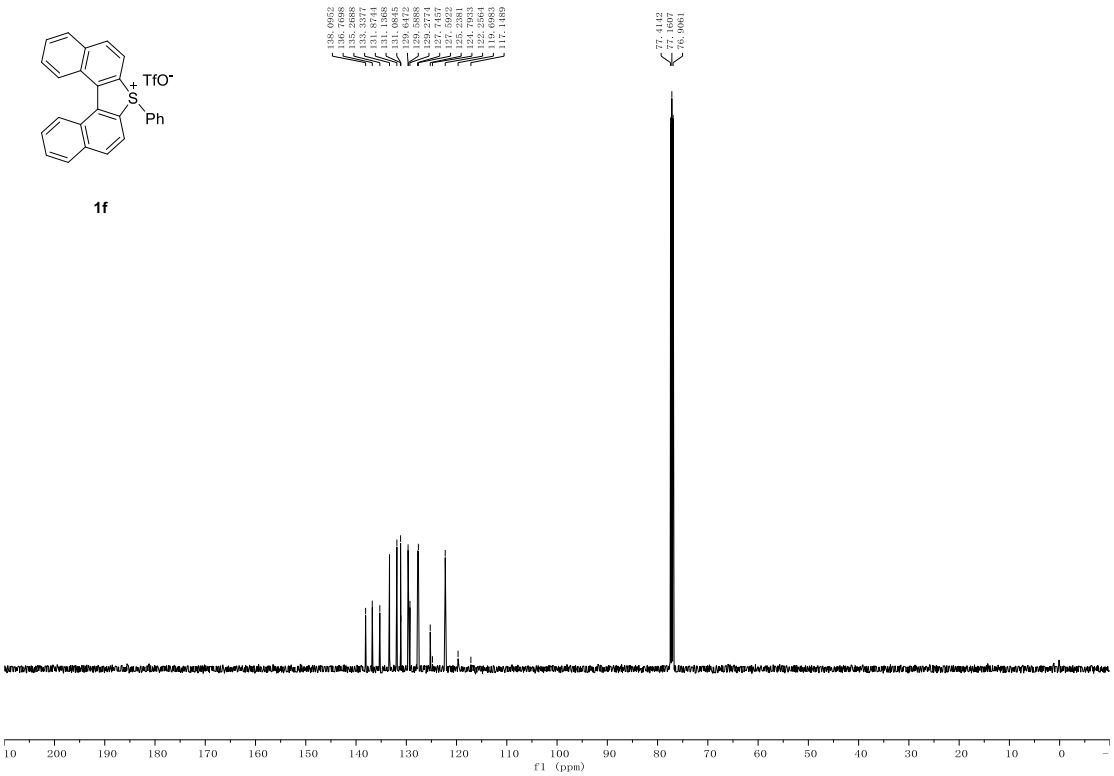


Figure **S18**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **1f**

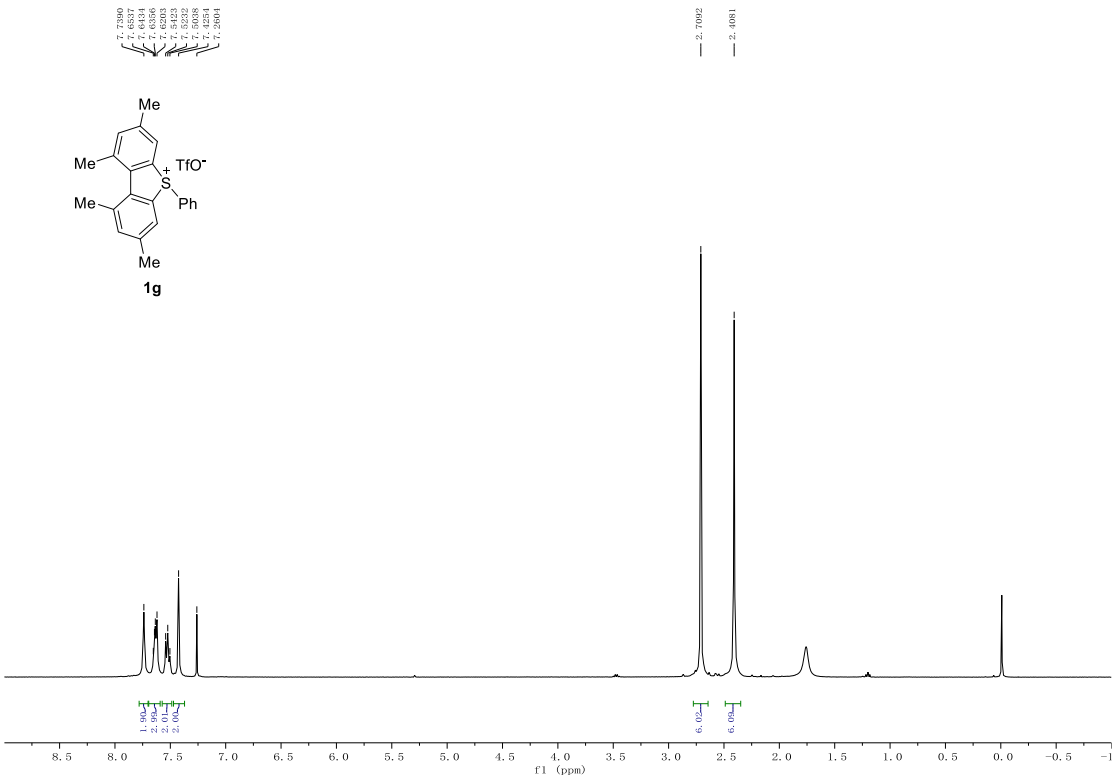


Figure **S19**. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of **1g**

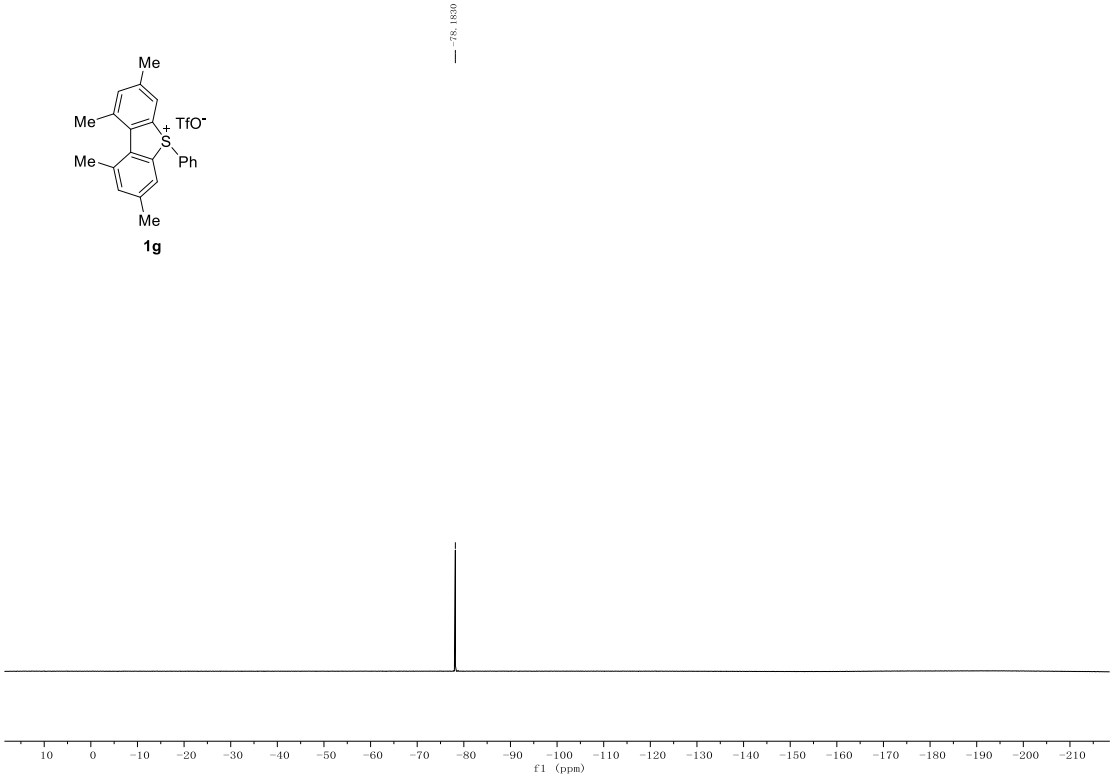


Figure **S20**. ^{19}F NMR spectra (376 MHz, $CDCl_3$) of **1g**

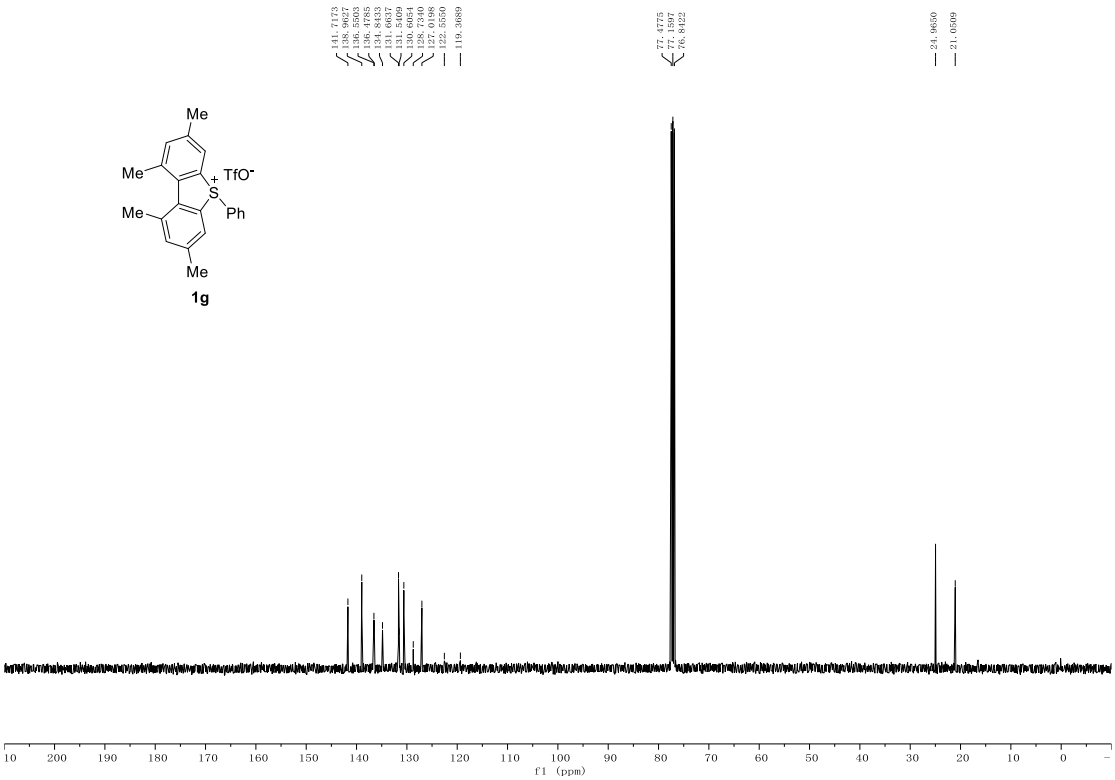


Figure **S21**. ^{13}C NMR spectra (101 MHz, $CDCl_3$) of **1g**

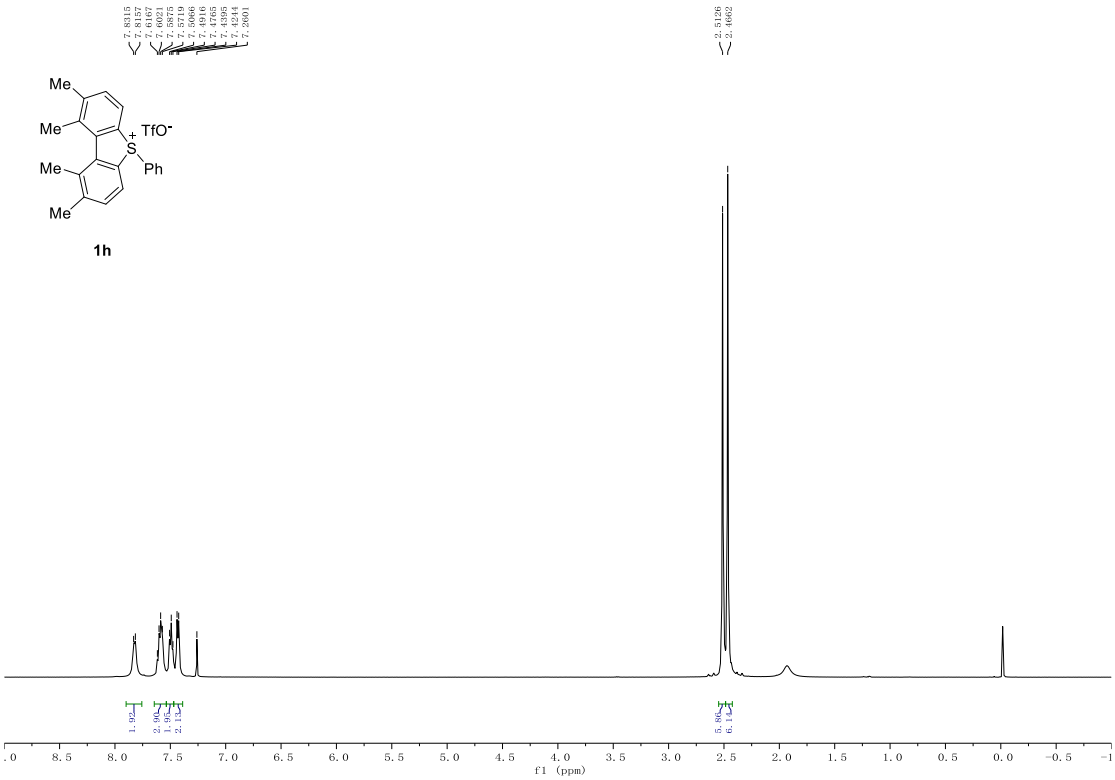


Figure **S22**. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **1h**

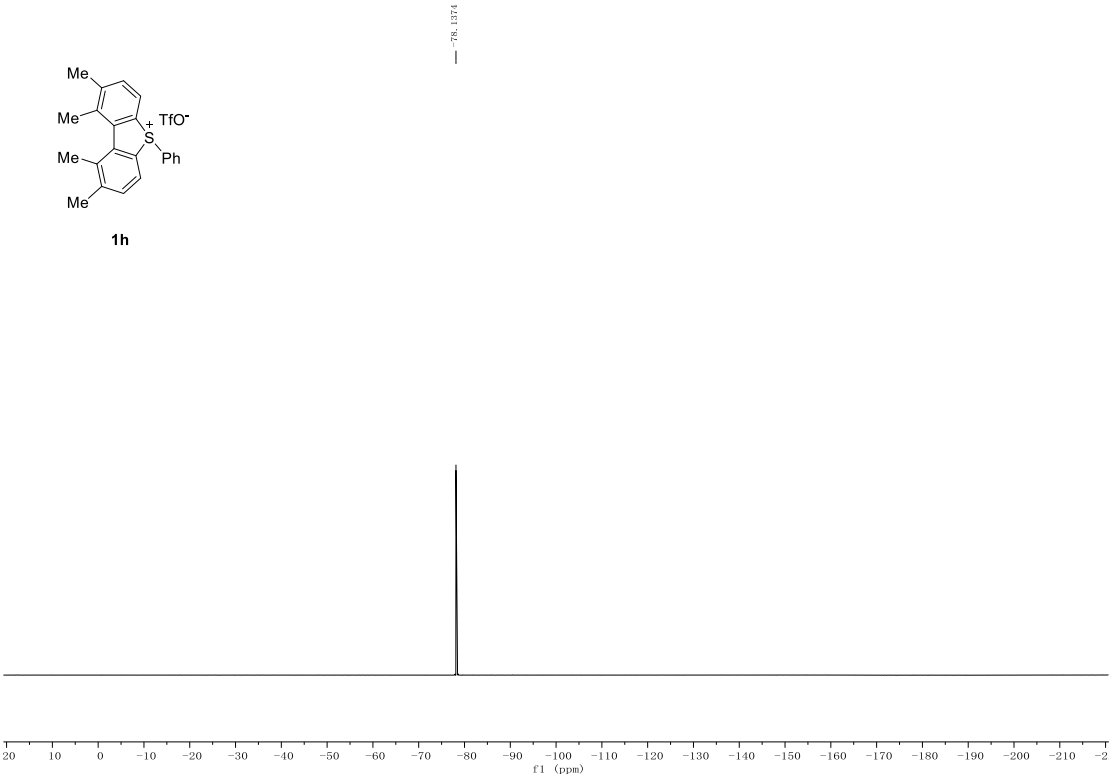


Figure **S23**. ^{19}F NMR spectra (471 MHz, $CDCl_3$) of **1h**

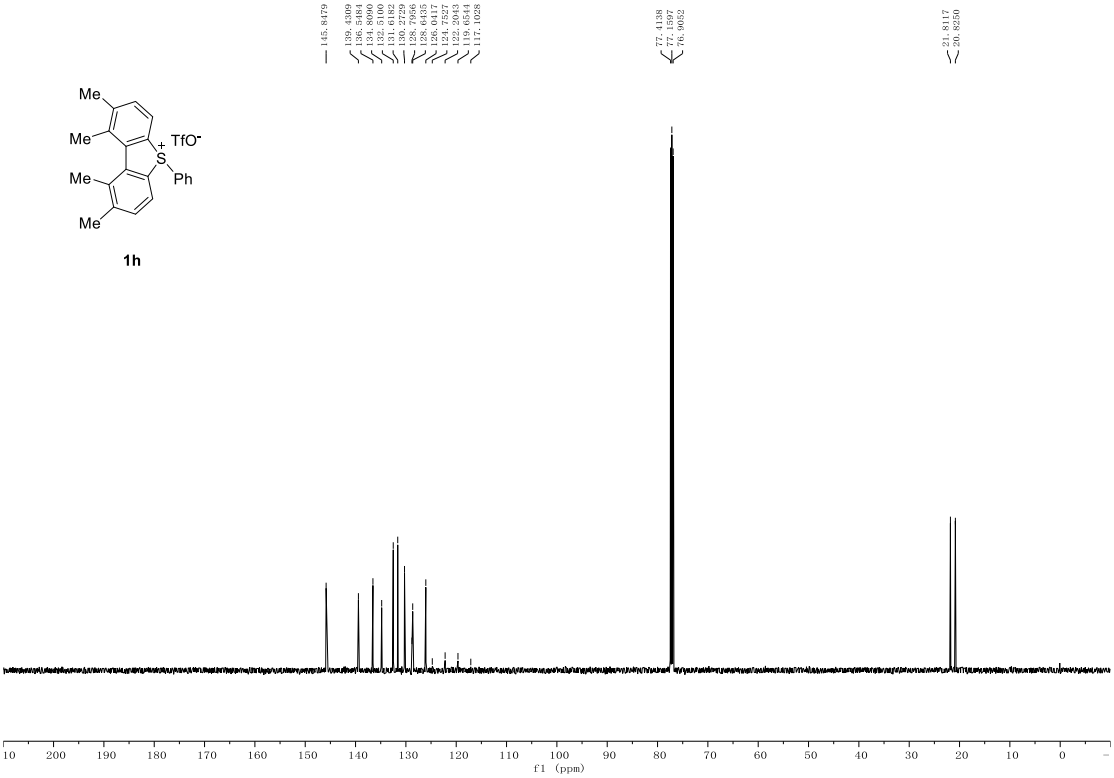


Figure **S24**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **1h**

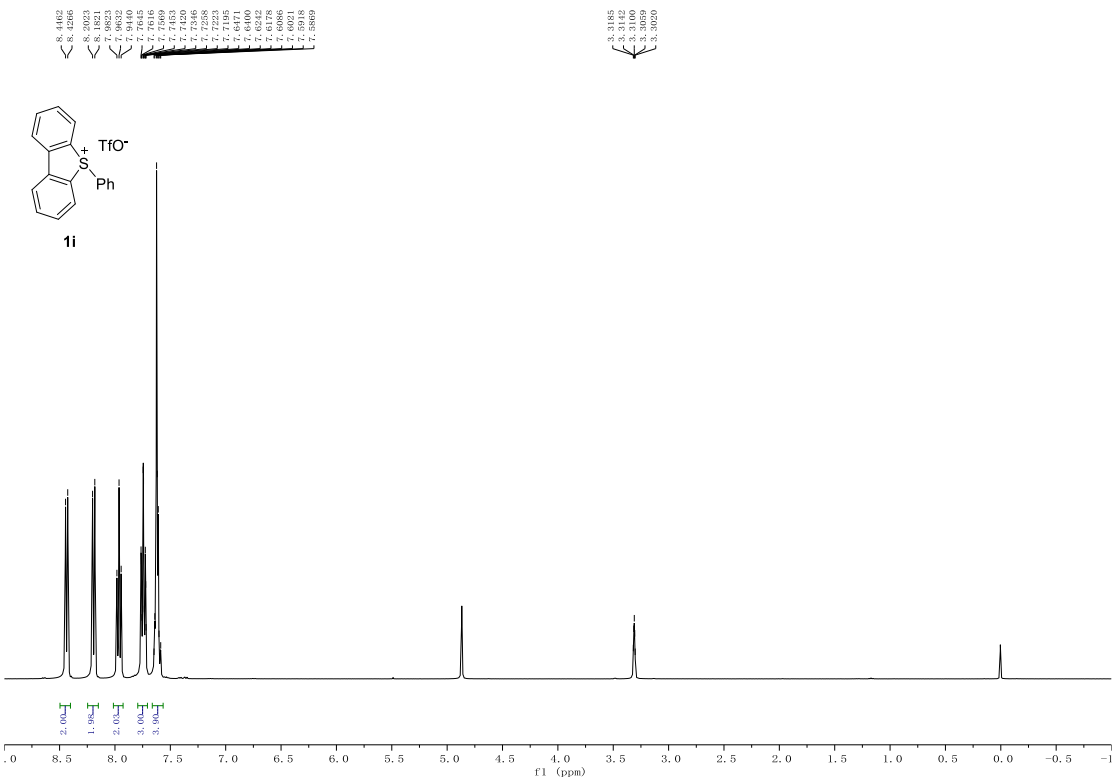


Figure **S25**. ^{1}H NMR spectra (400 MHz, MeOH-d_4) of **1i**

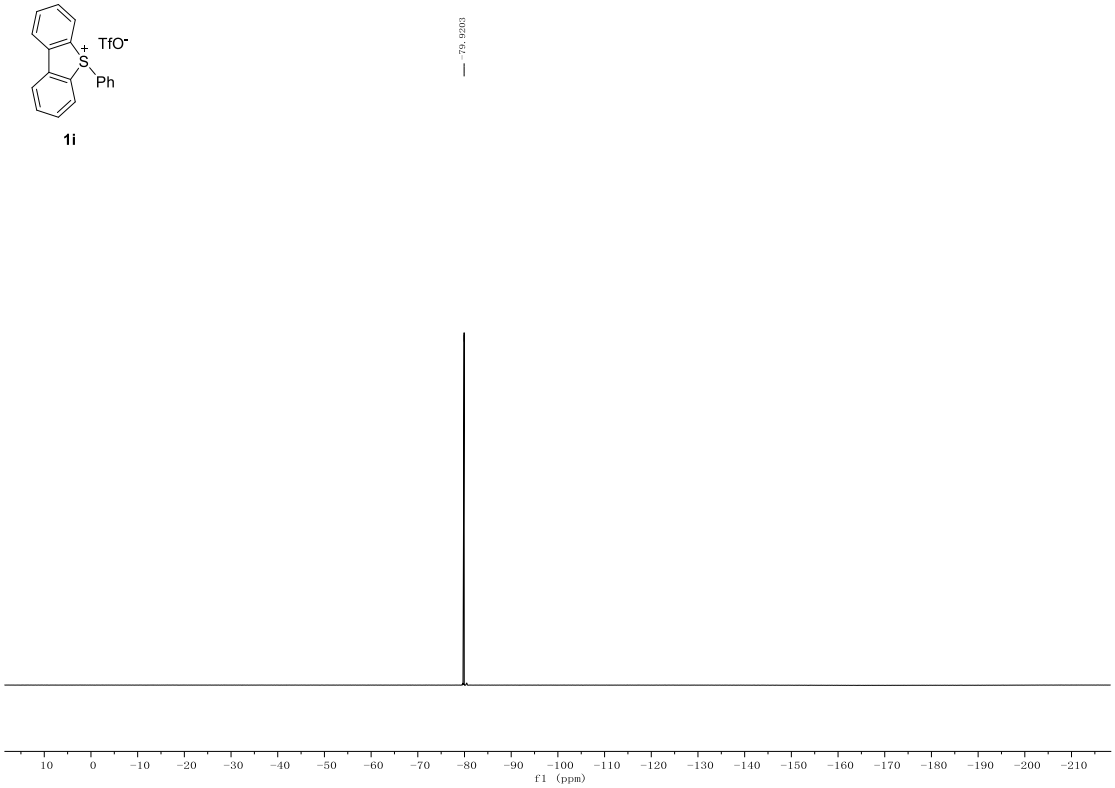


Figure **S26**. ^{19}F NMR spectra (376 MHz, MeOH-d_4) of **1i**

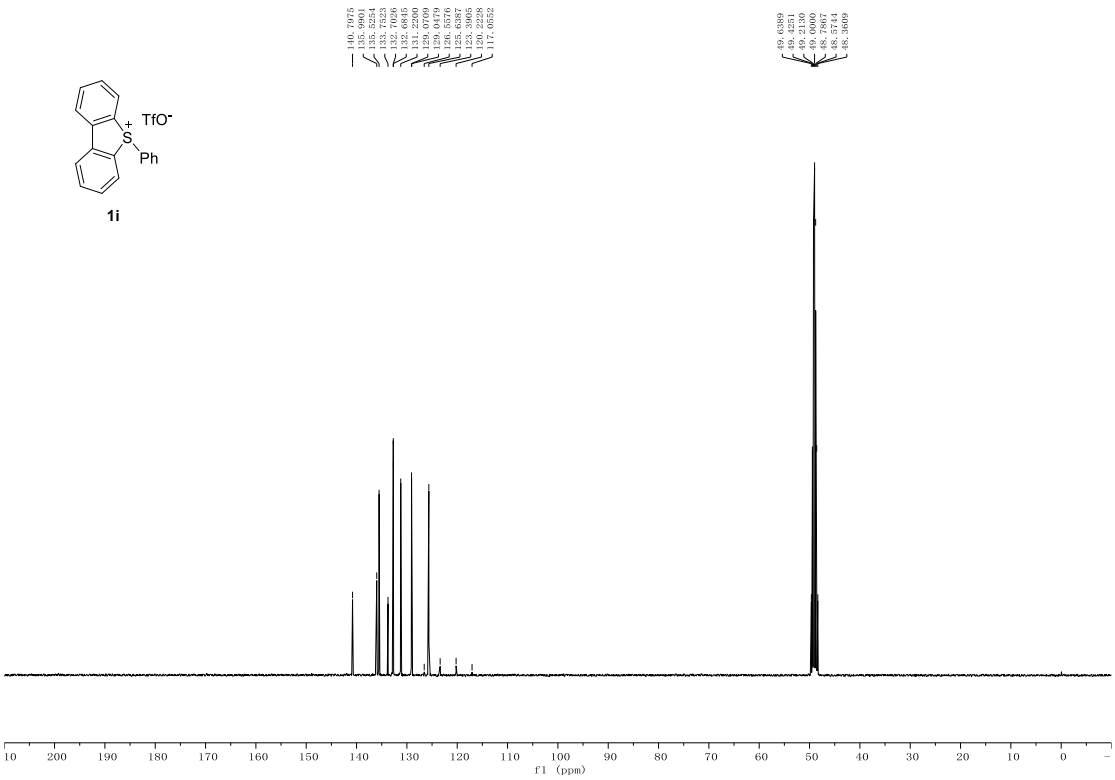


Figure **S27**. ^{13}C NMR spectra (101 MHz, MeOH-d_4) of **1i**

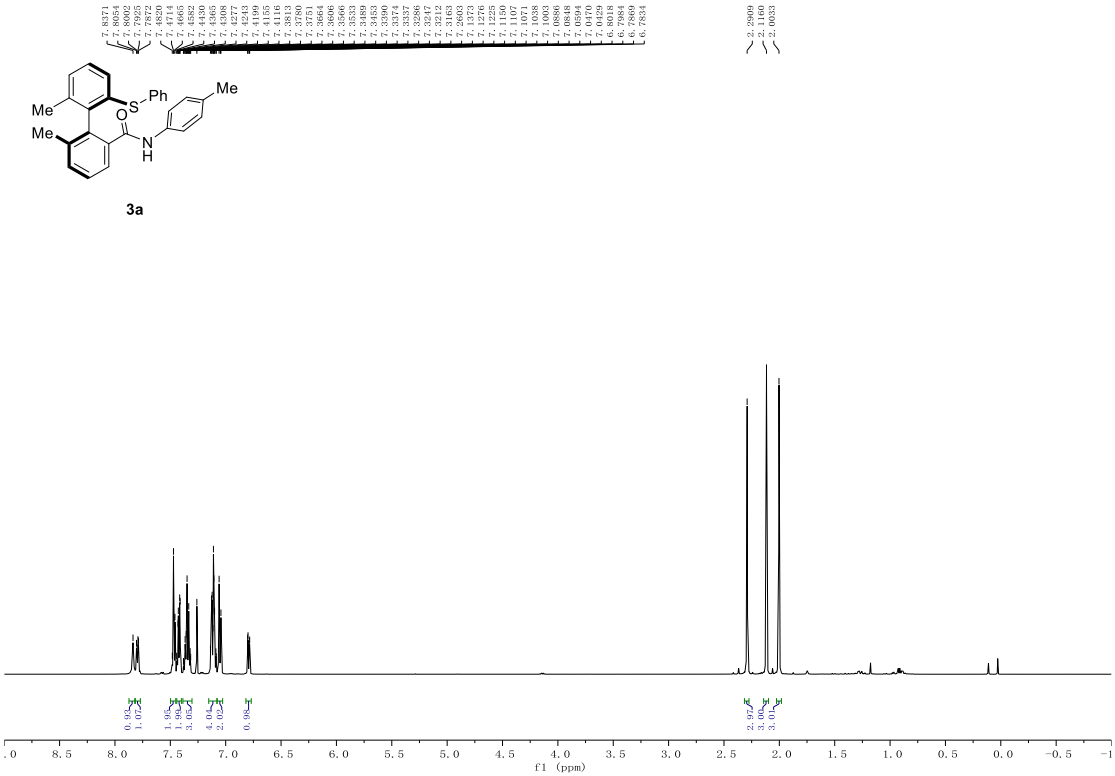


Figure **S28**. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3a**

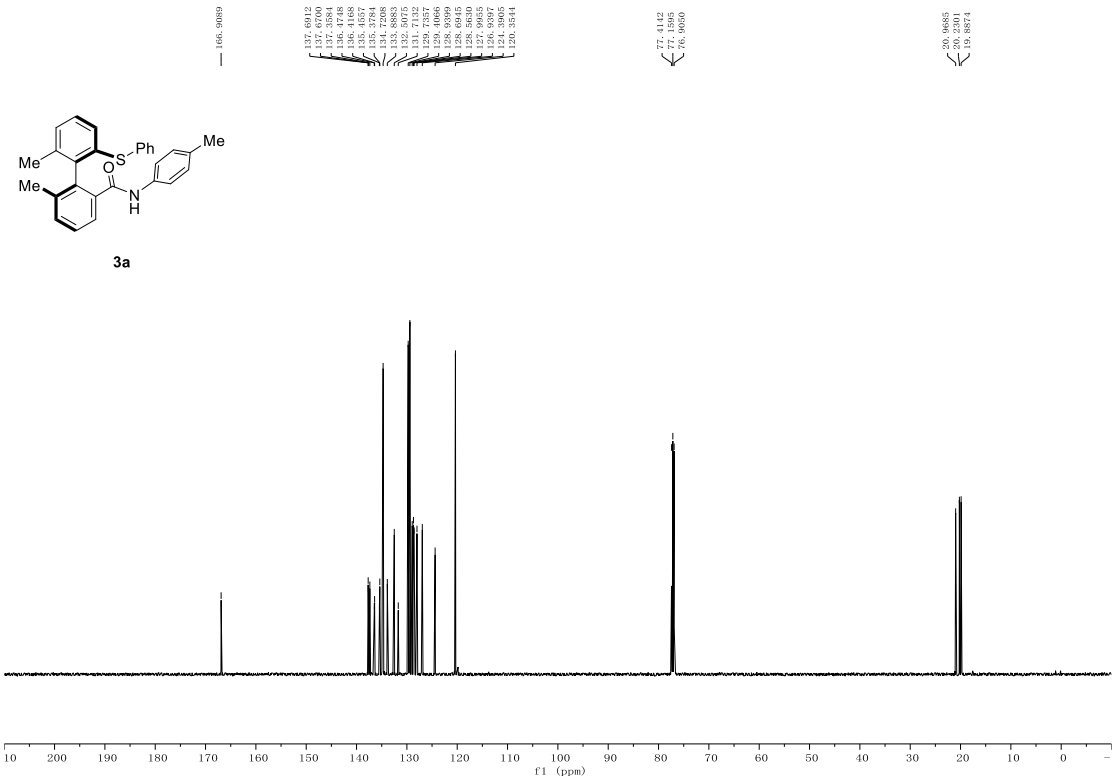


Figure **S29**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3a**

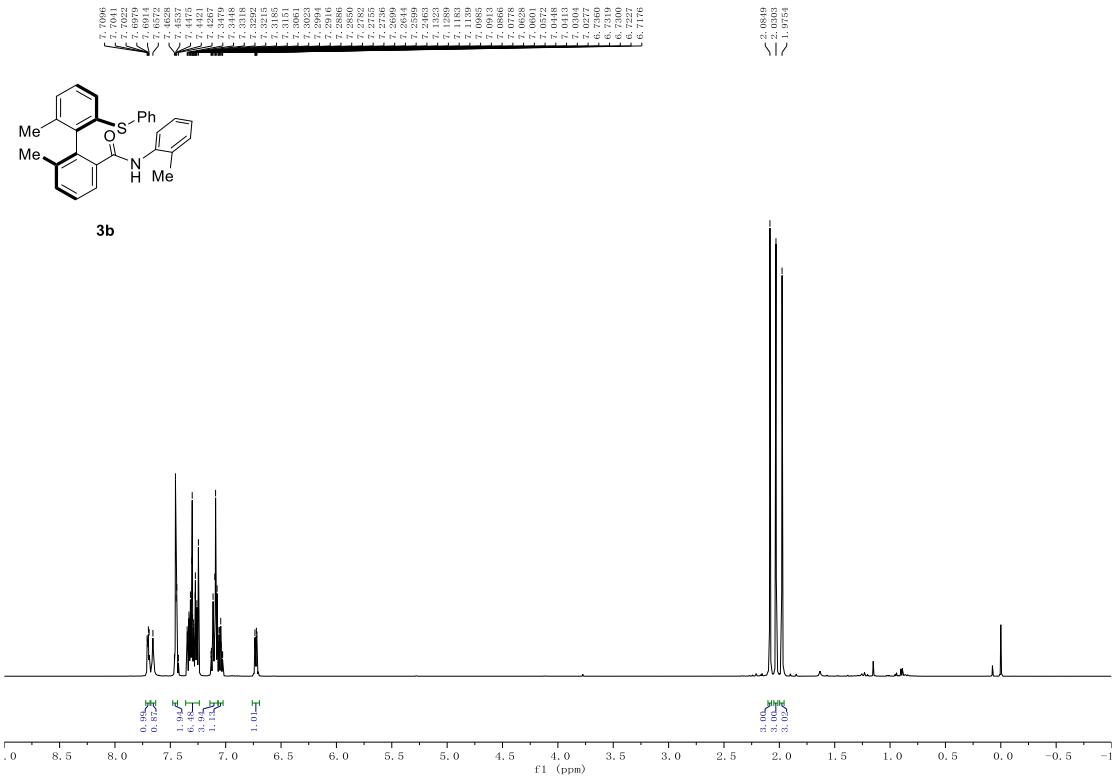


Figure **S30**. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3b**

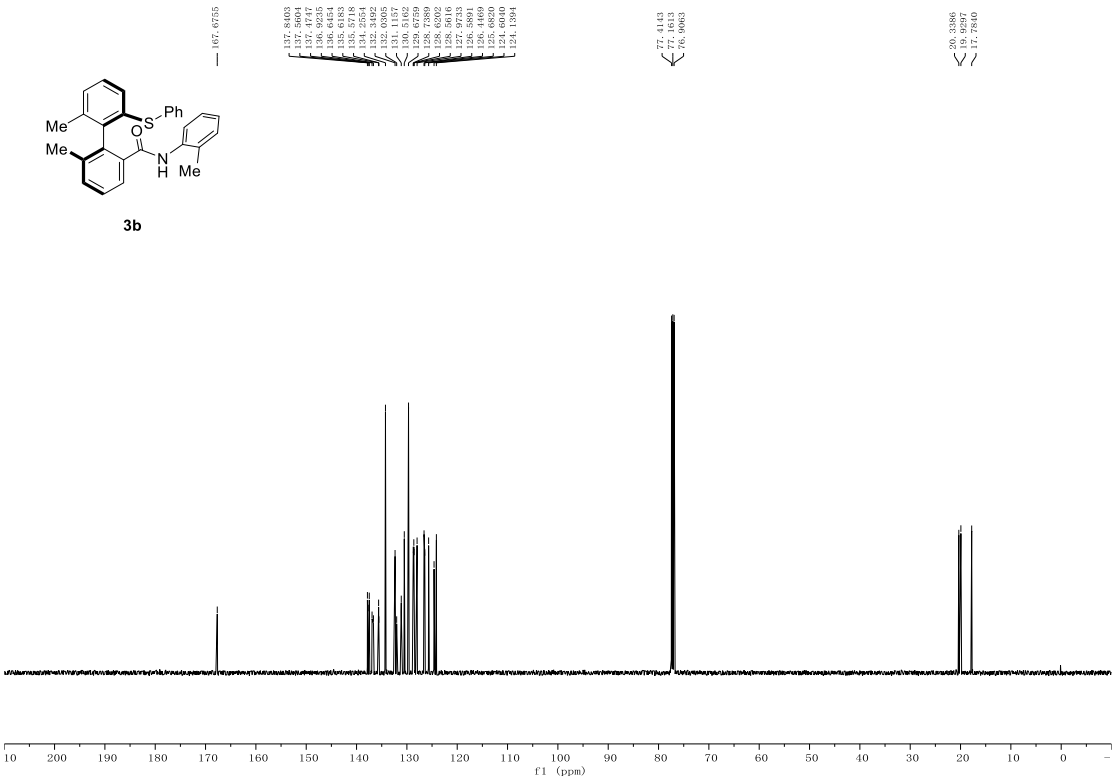


Figure **S31**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3b**

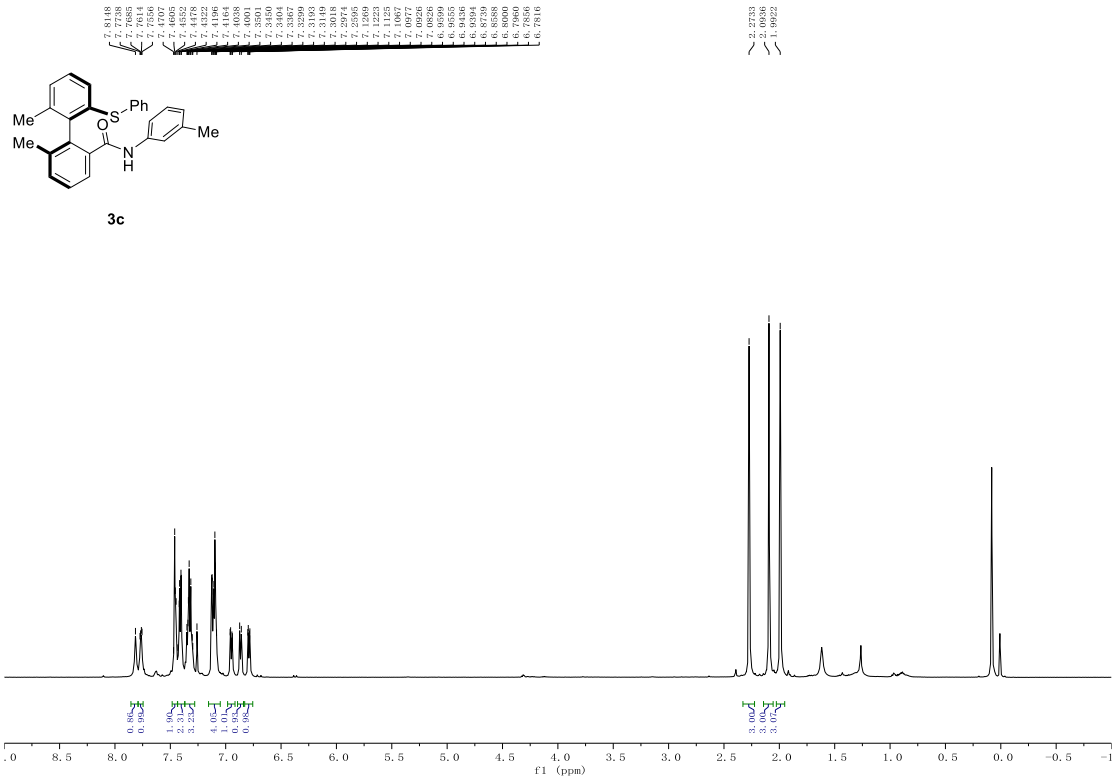


Figure **S32**. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3c**

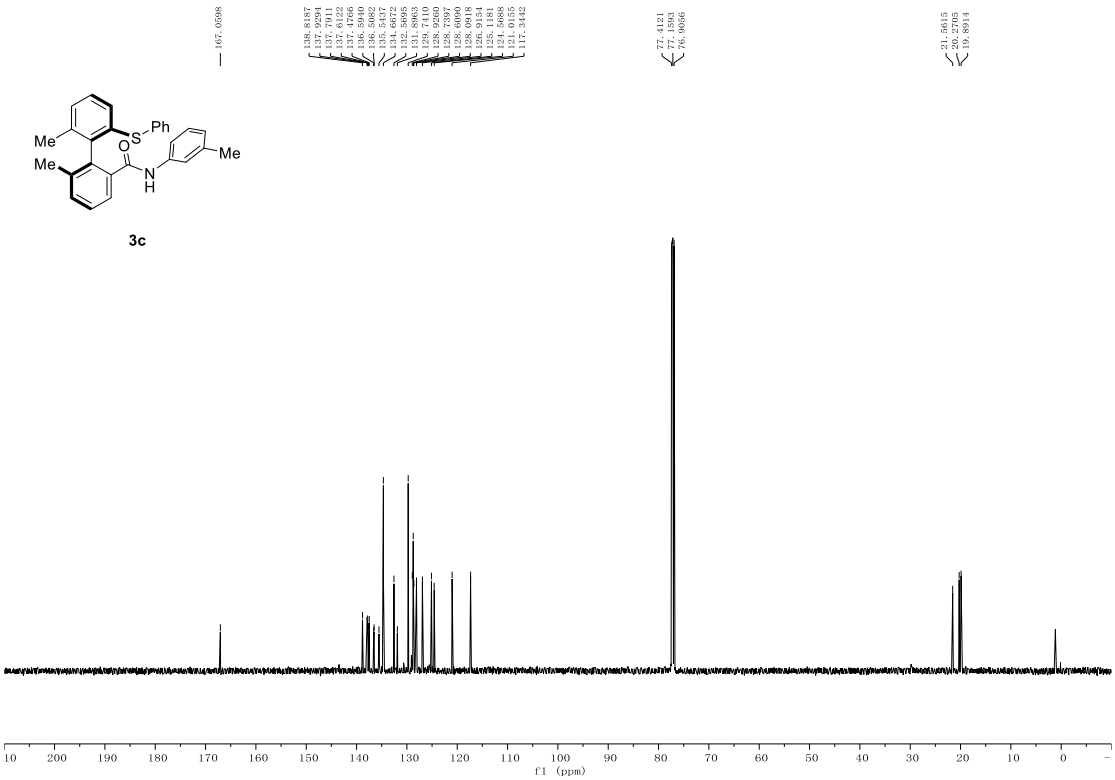


Figure **S33**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3c**

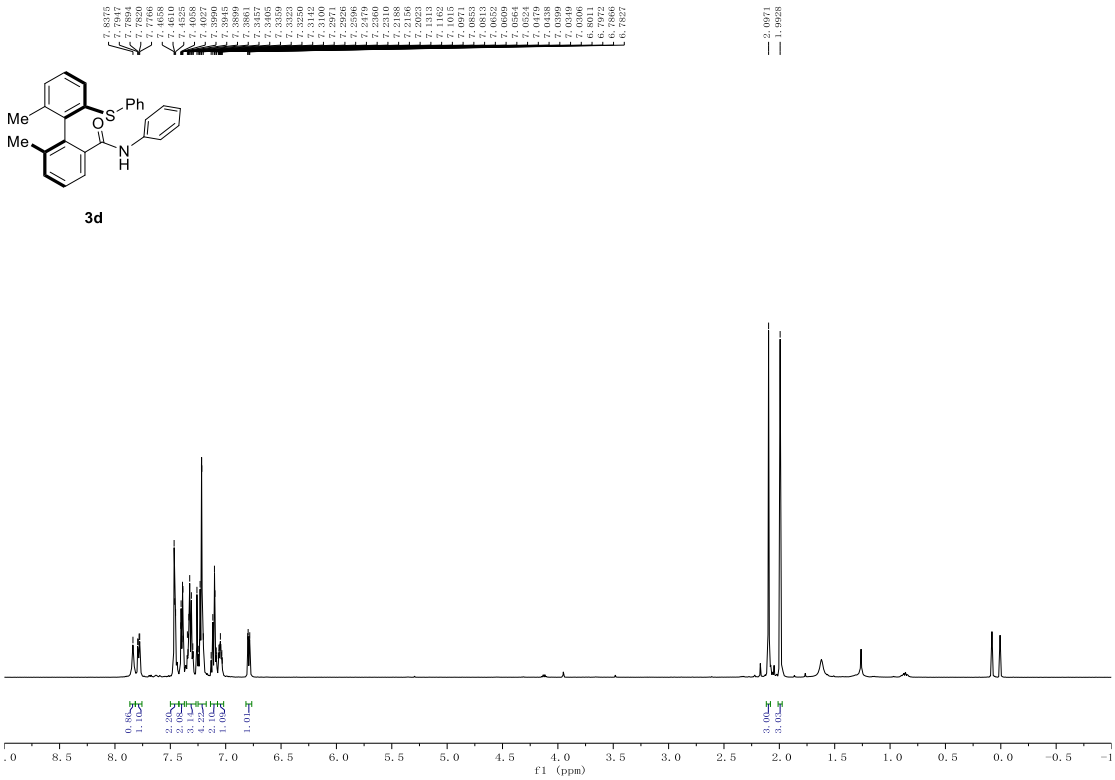


Figure **S34**. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3d**

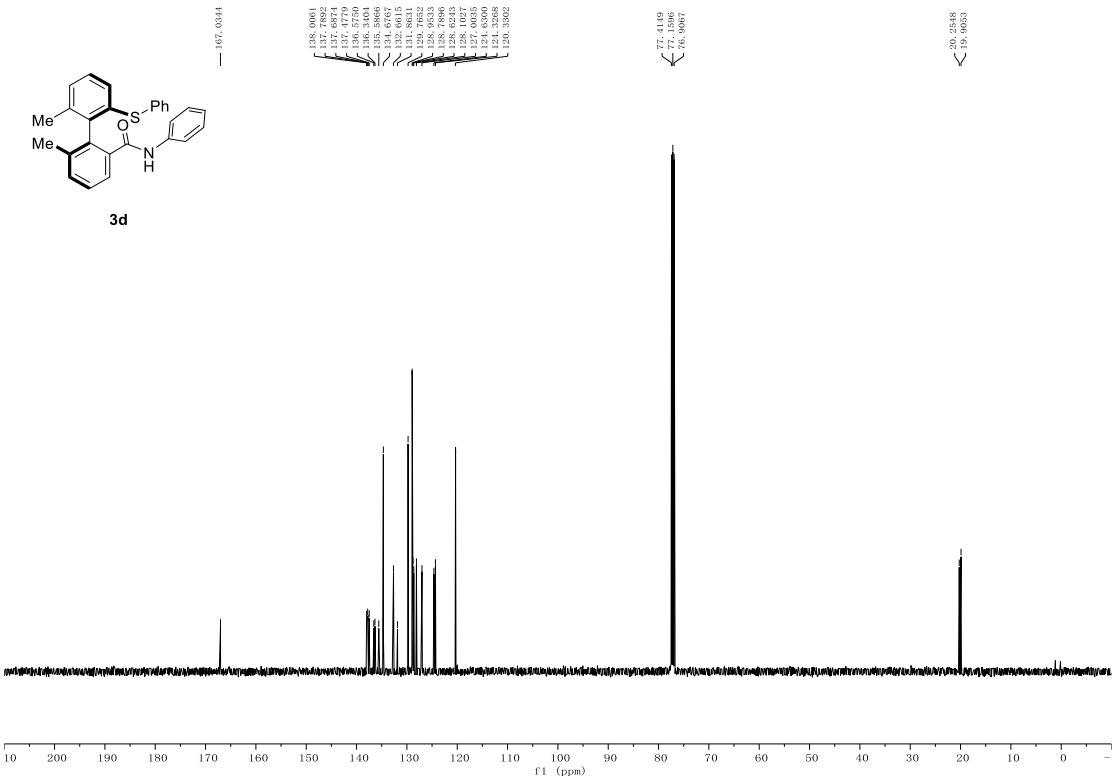


Figure **S35**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3d**

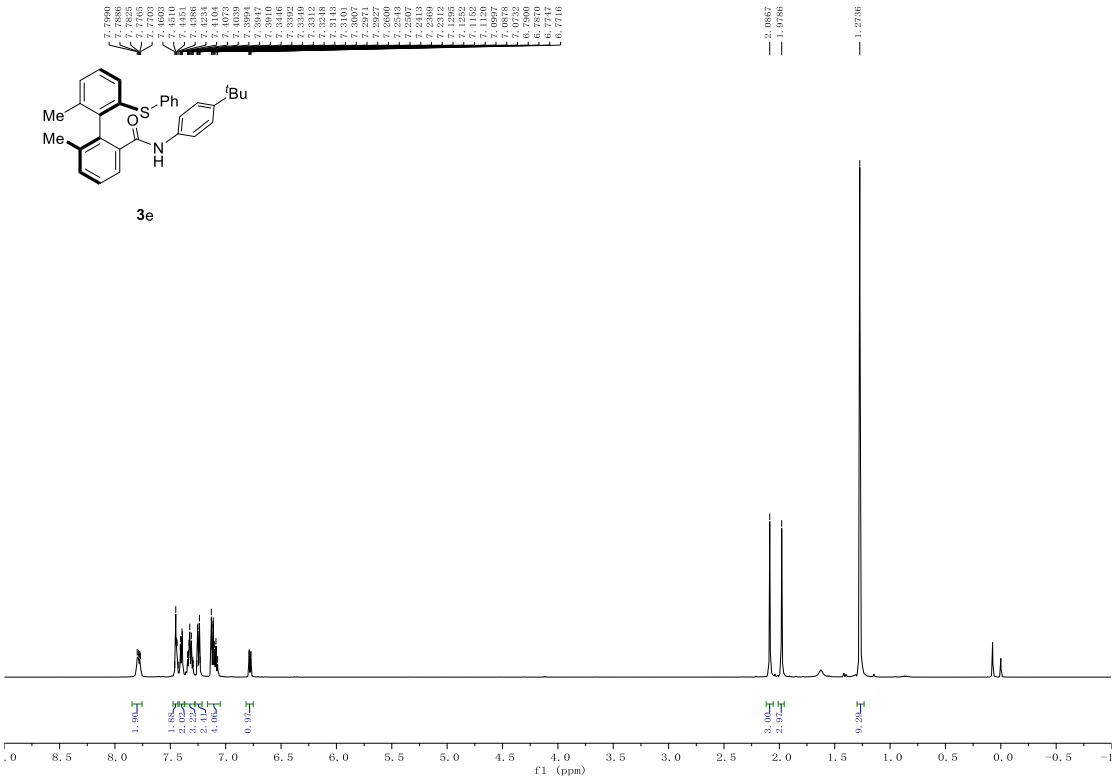


Figure **S36**. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3e**

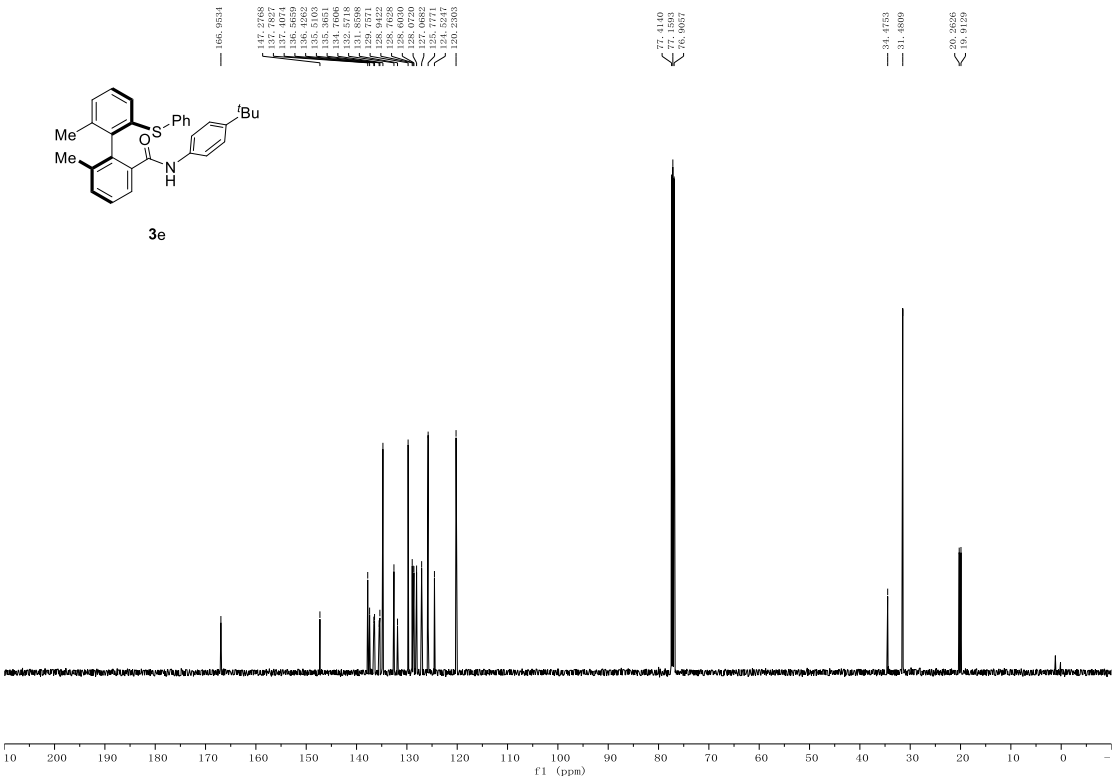


Figure **S37**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3e**

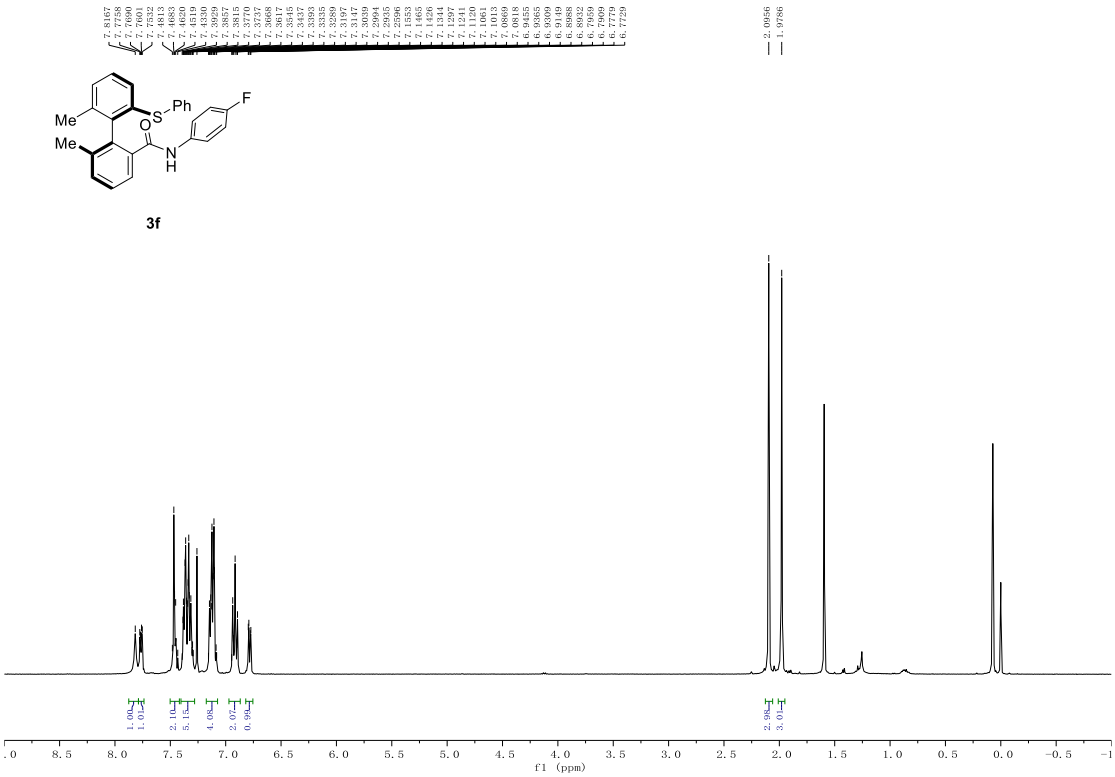


Figure **S38**. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3f**

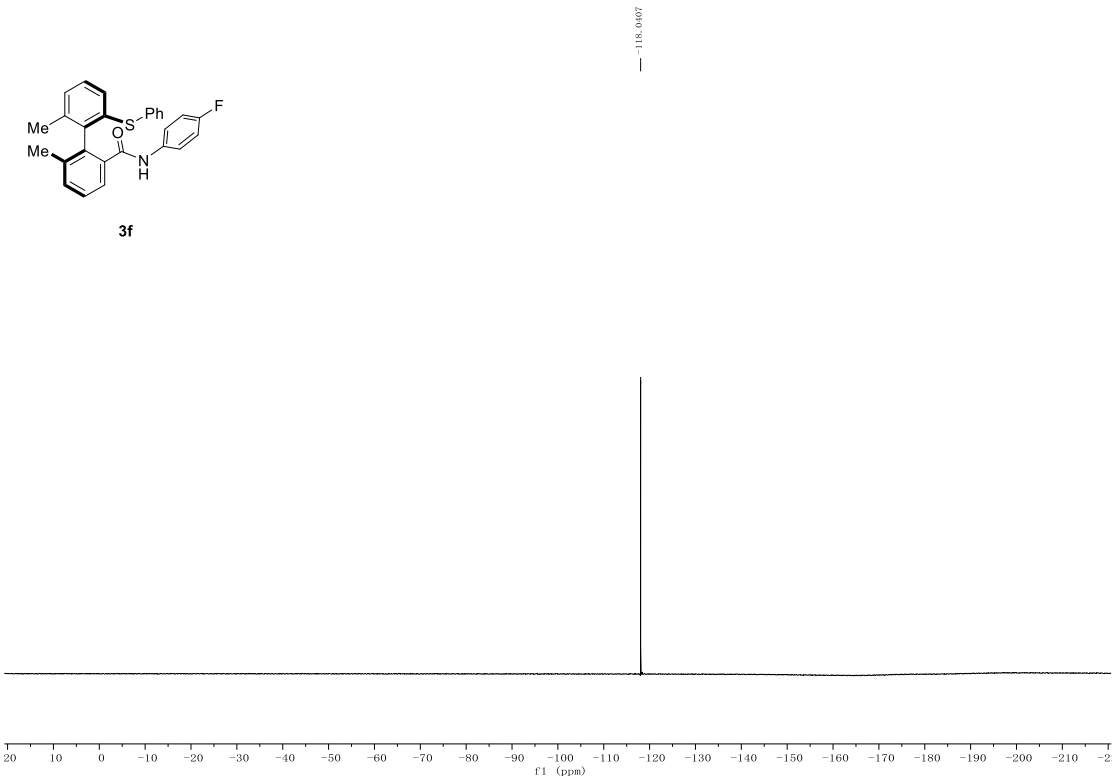


Figure **S39**. ^{19}F NMR spectra (471 MHz, $CDCl_3$) of **3f**

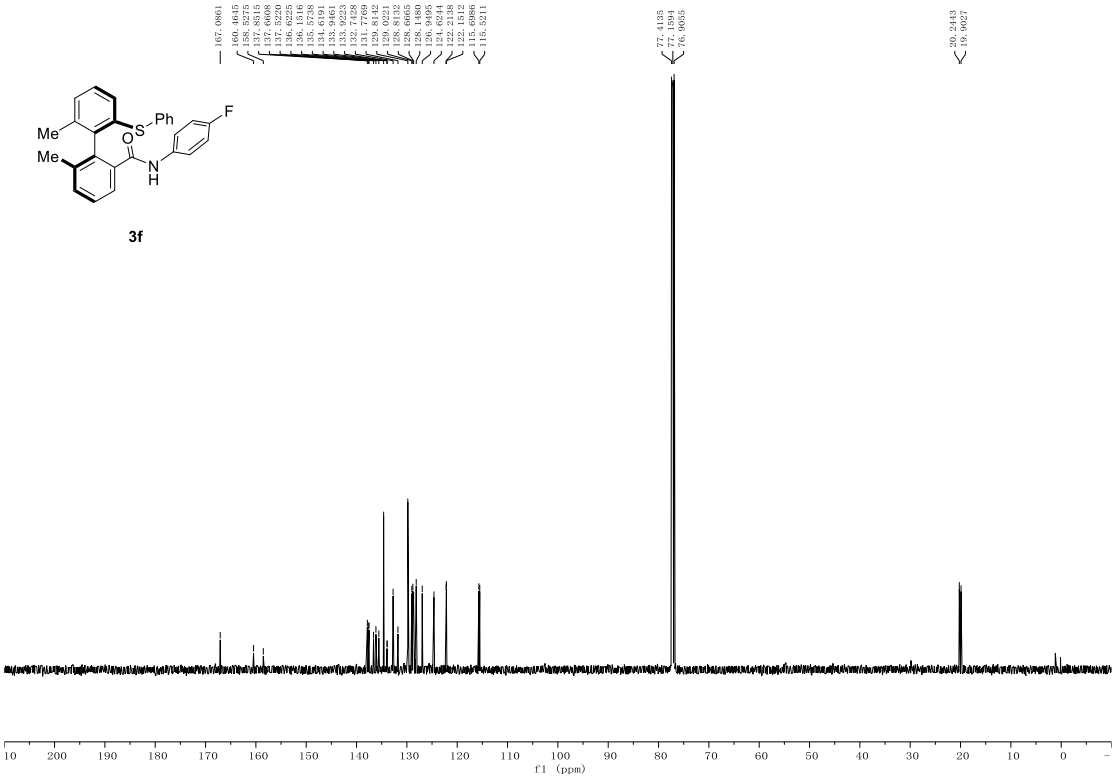


Figure **S40**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3f**

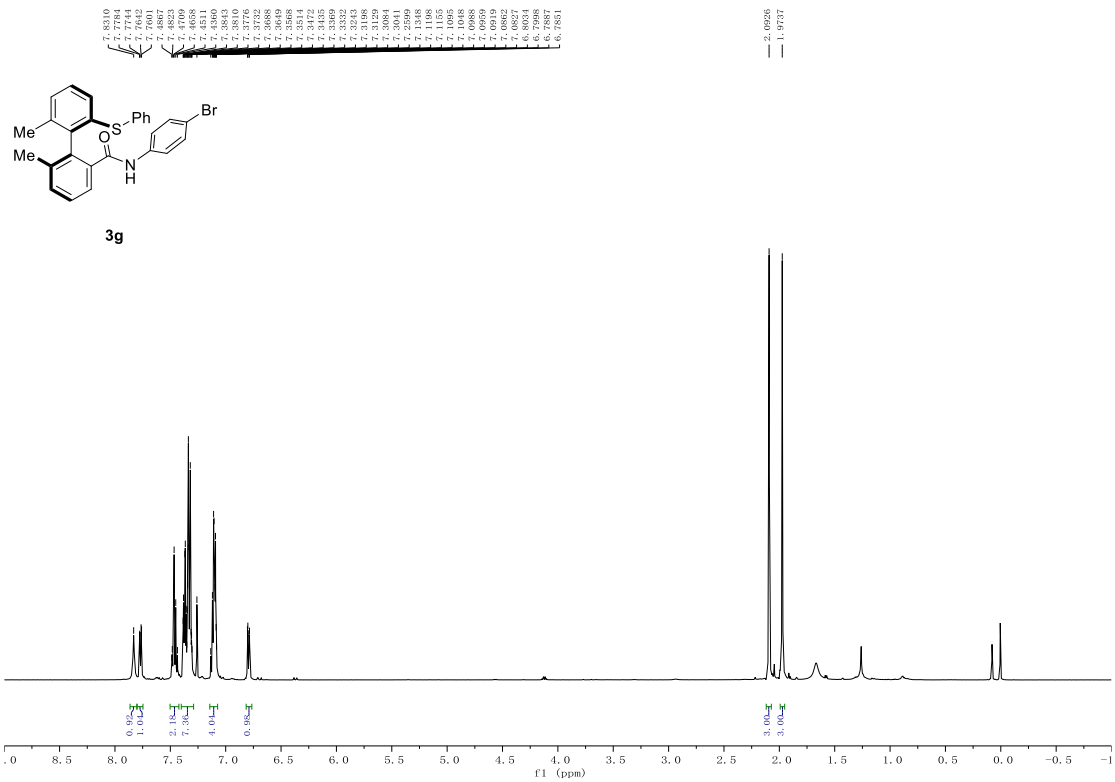


Figure **S41**. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3g**

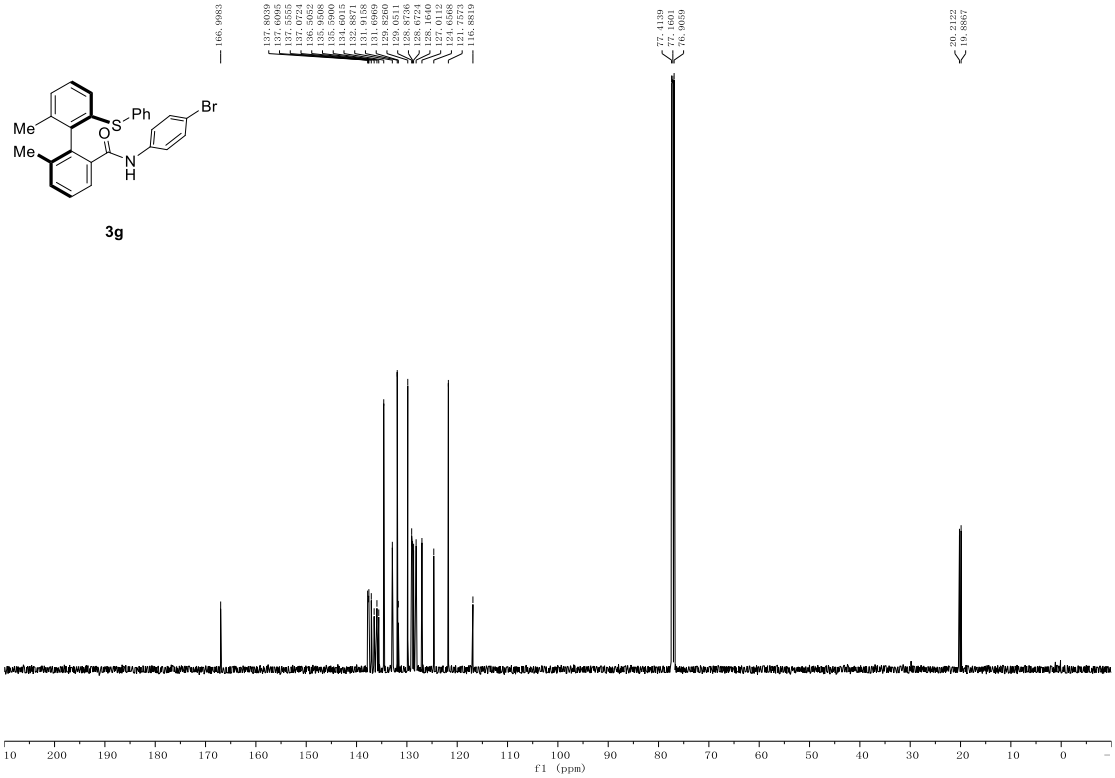


Figure **S42**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3g**

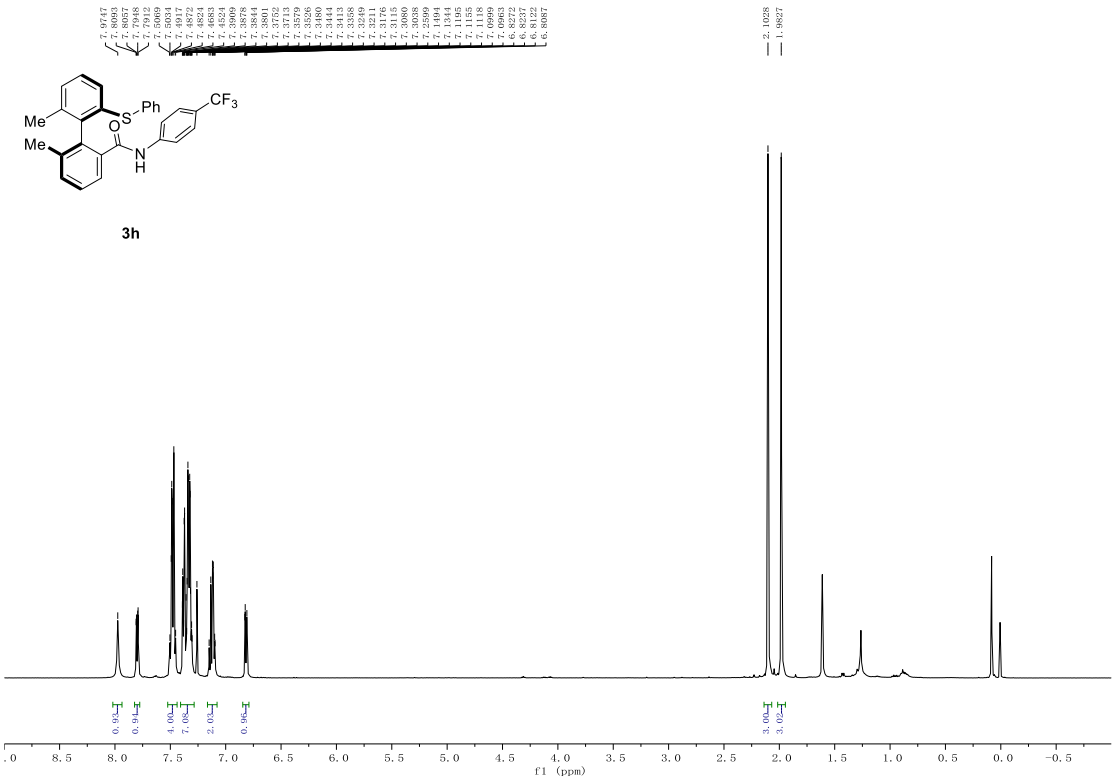


Figure **S43**. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3h**

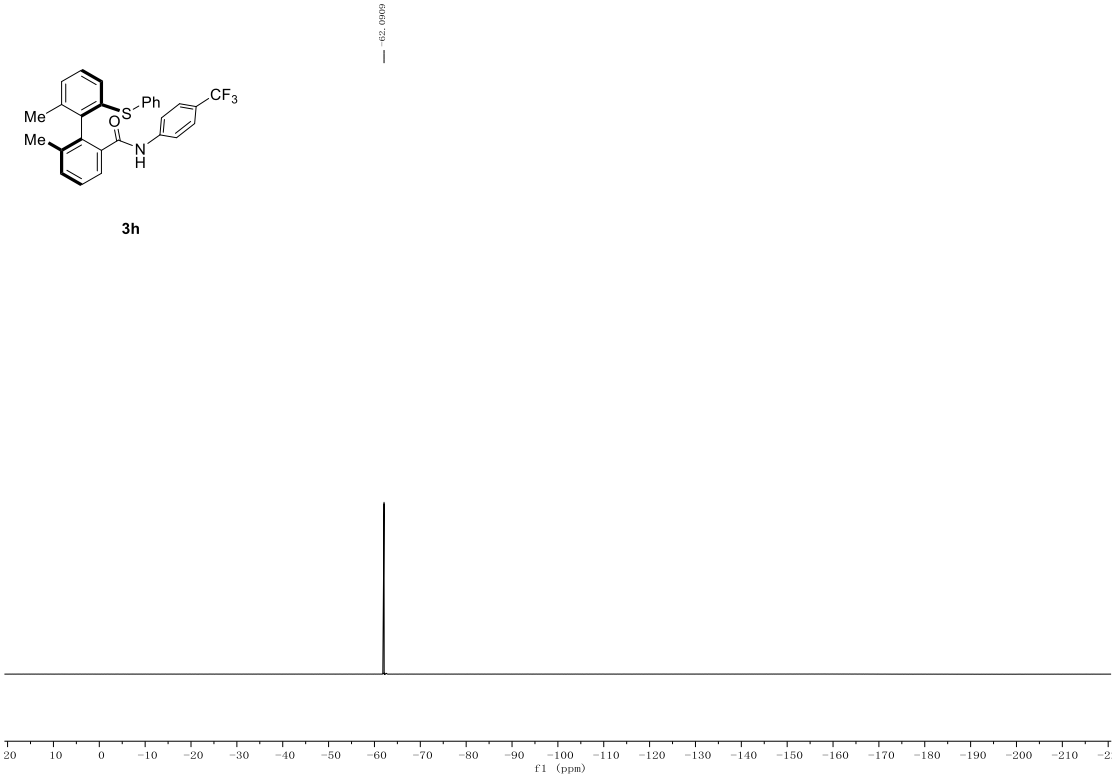


Figure **S44**. ^{19}F NMR spectra (471 MHz, $CDCl_3$) of **3h**

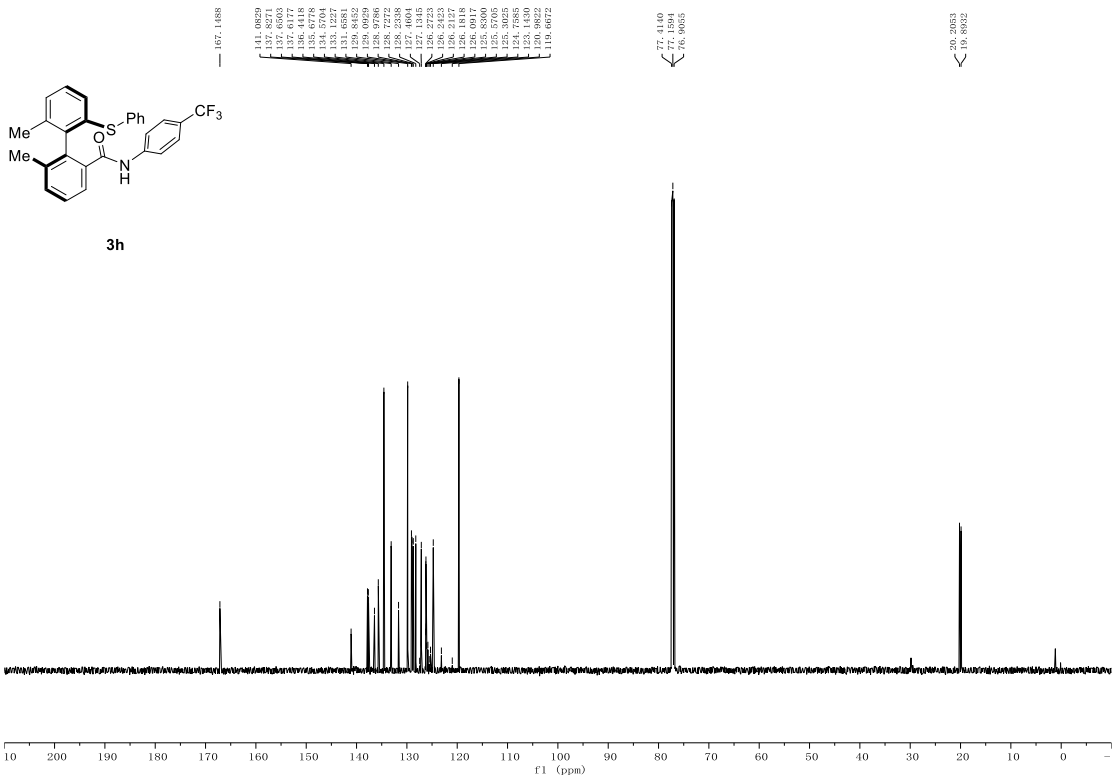


Figure **S45**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3h**

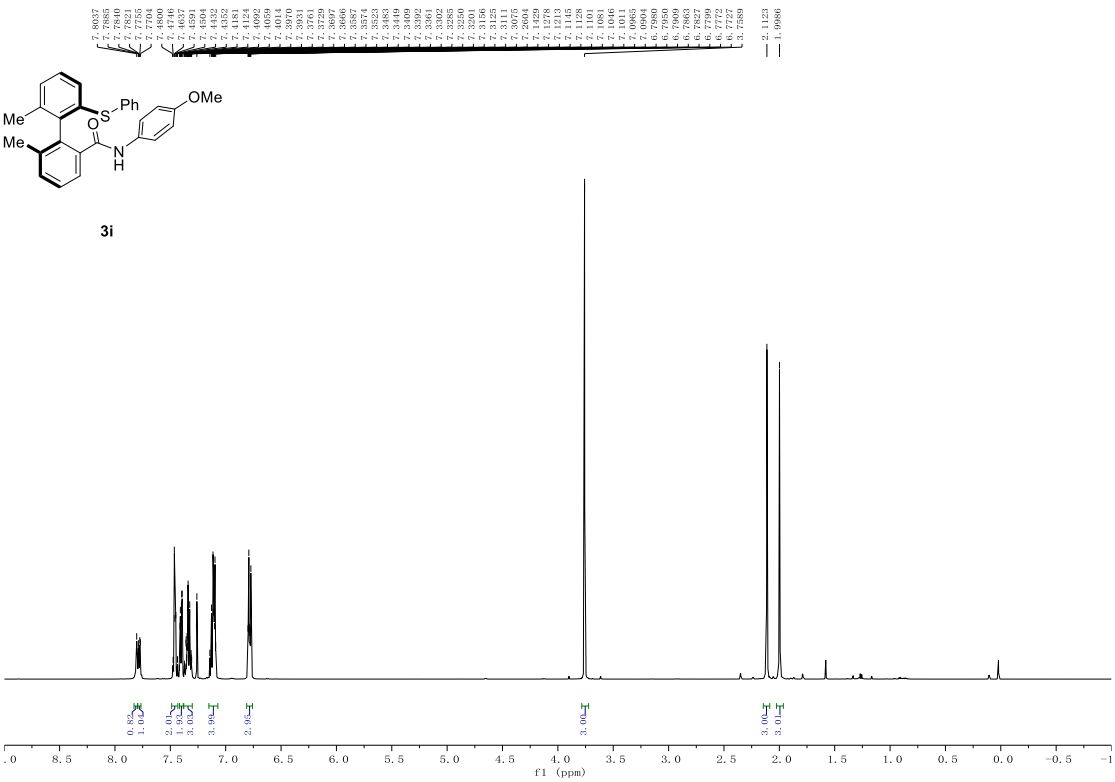


Figure **S46**. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3i**

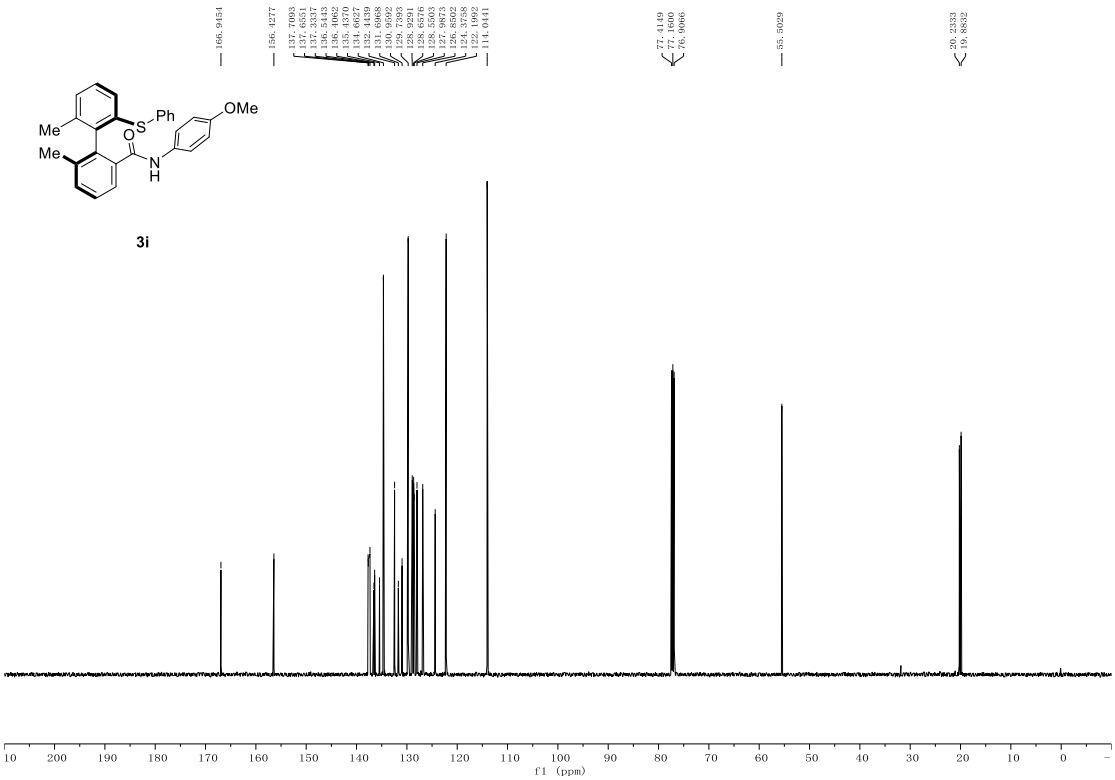


Figure **S47**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3i**

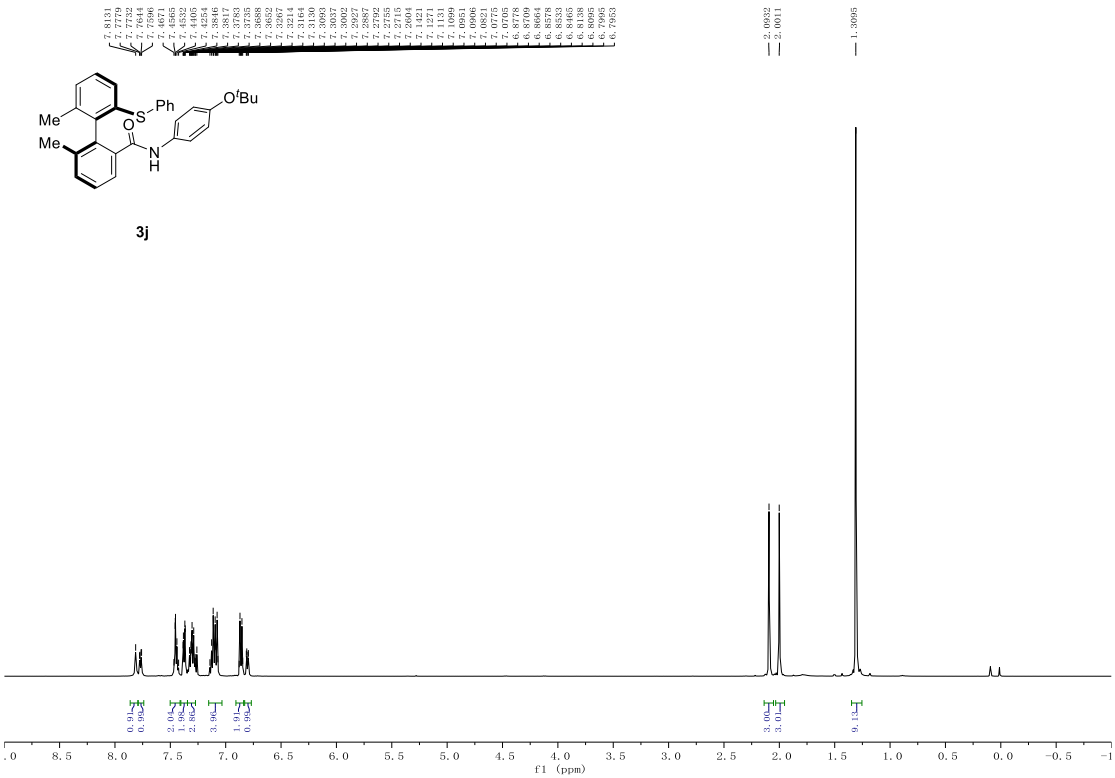


Figure **S48**. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3j**

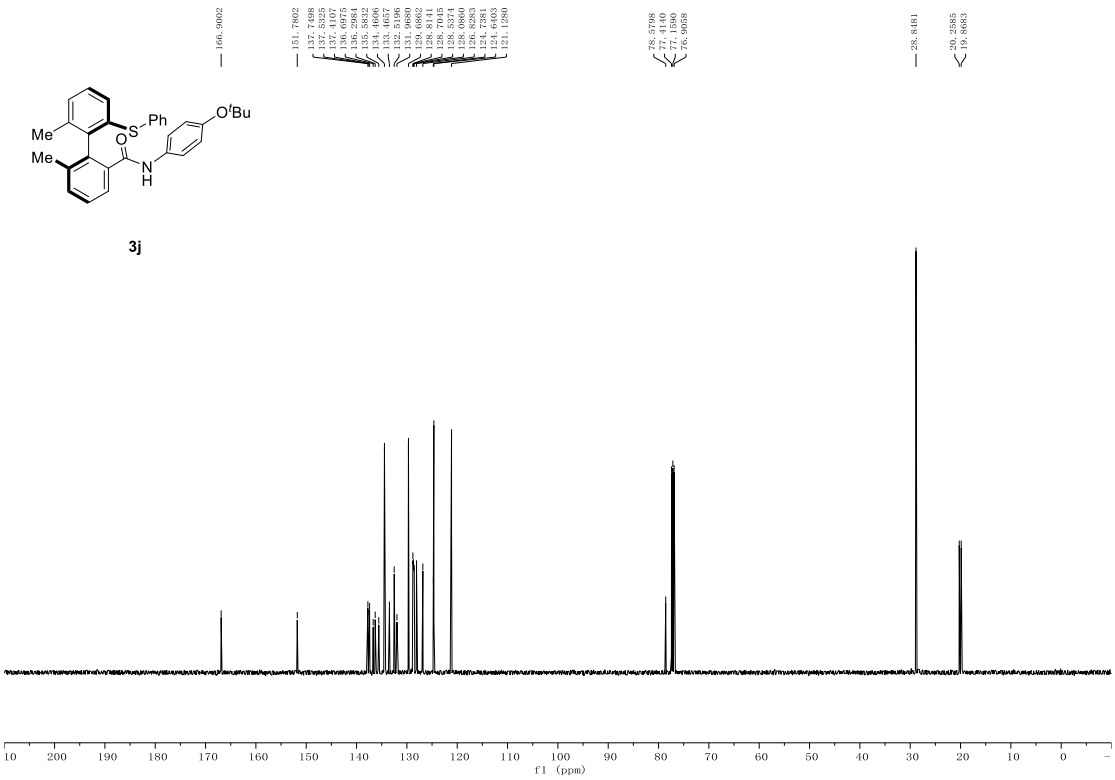


Figure **S49**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3j**

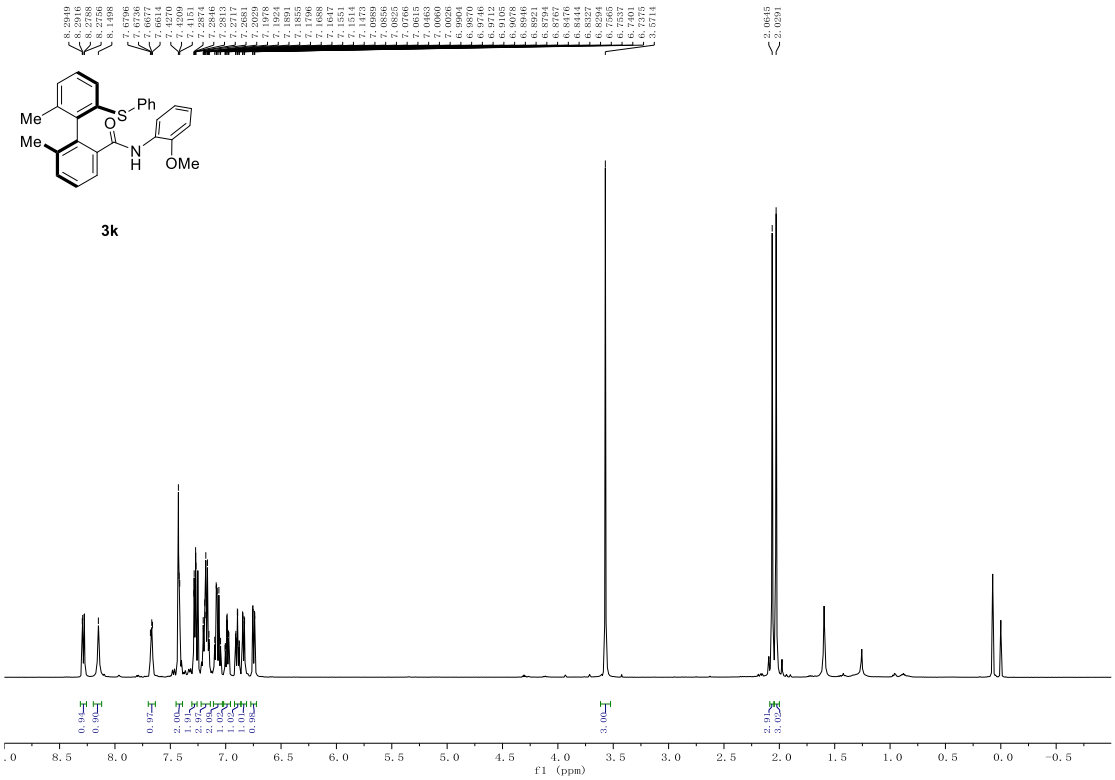


Figure **S50**. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3k**

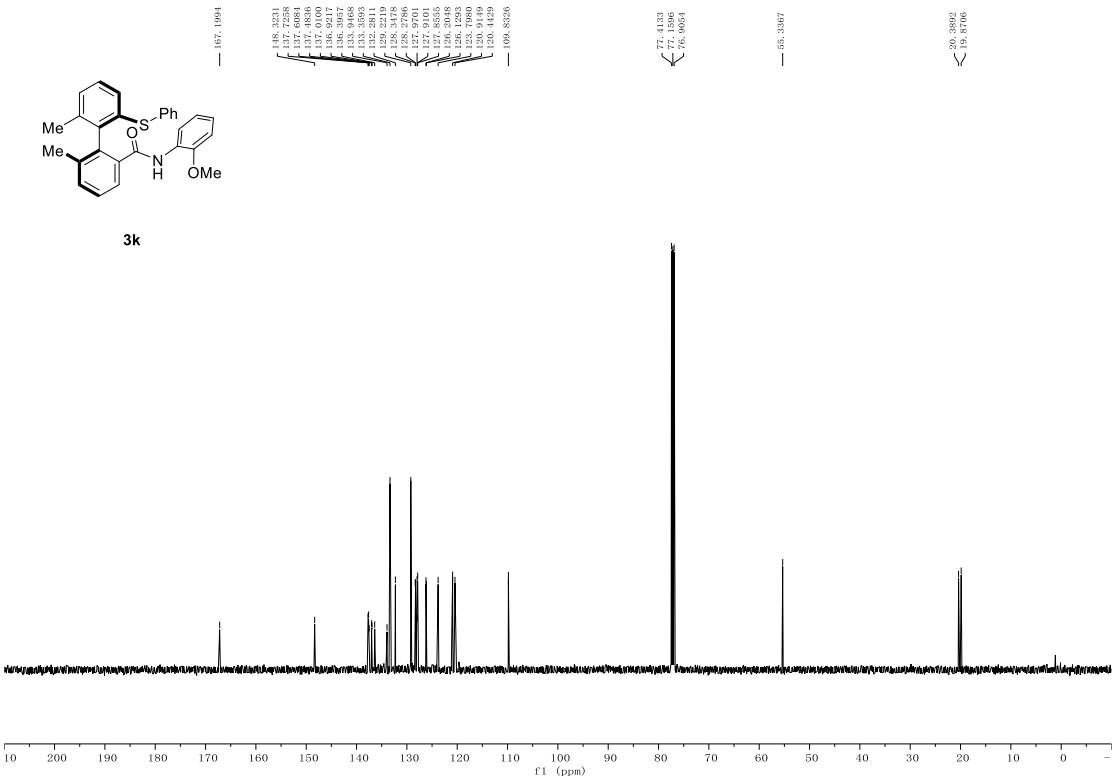


Figure **S51**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3k**

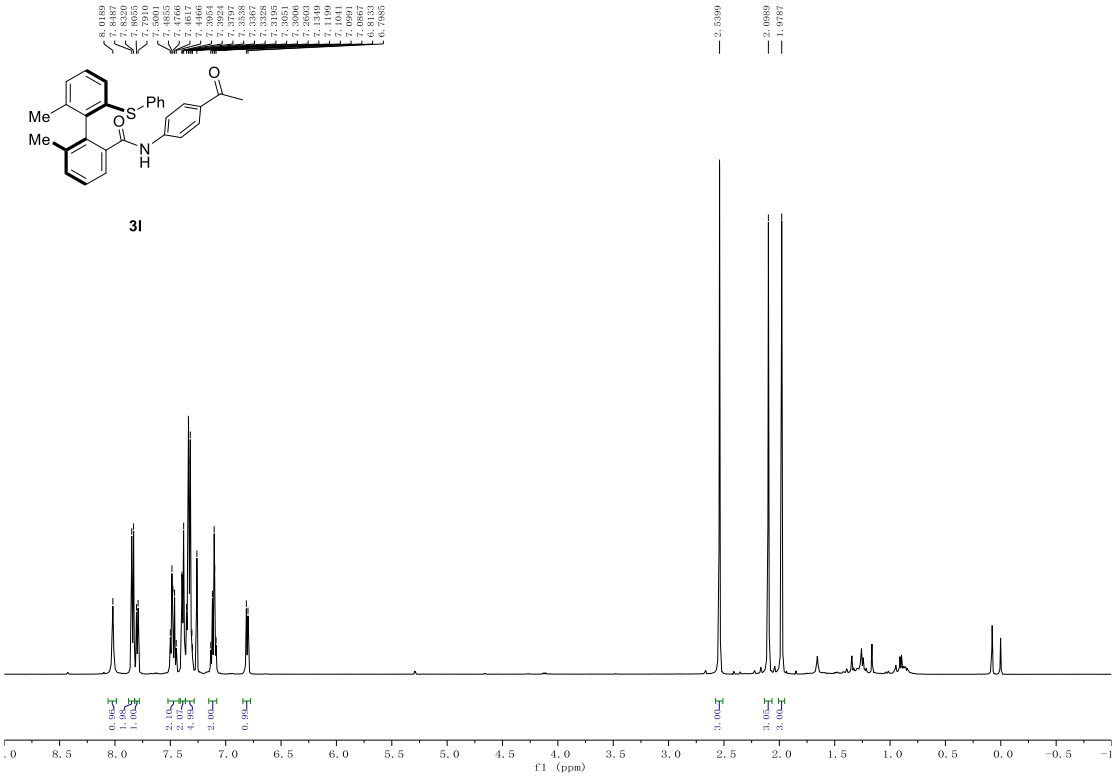


Figure **S52**. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3l**

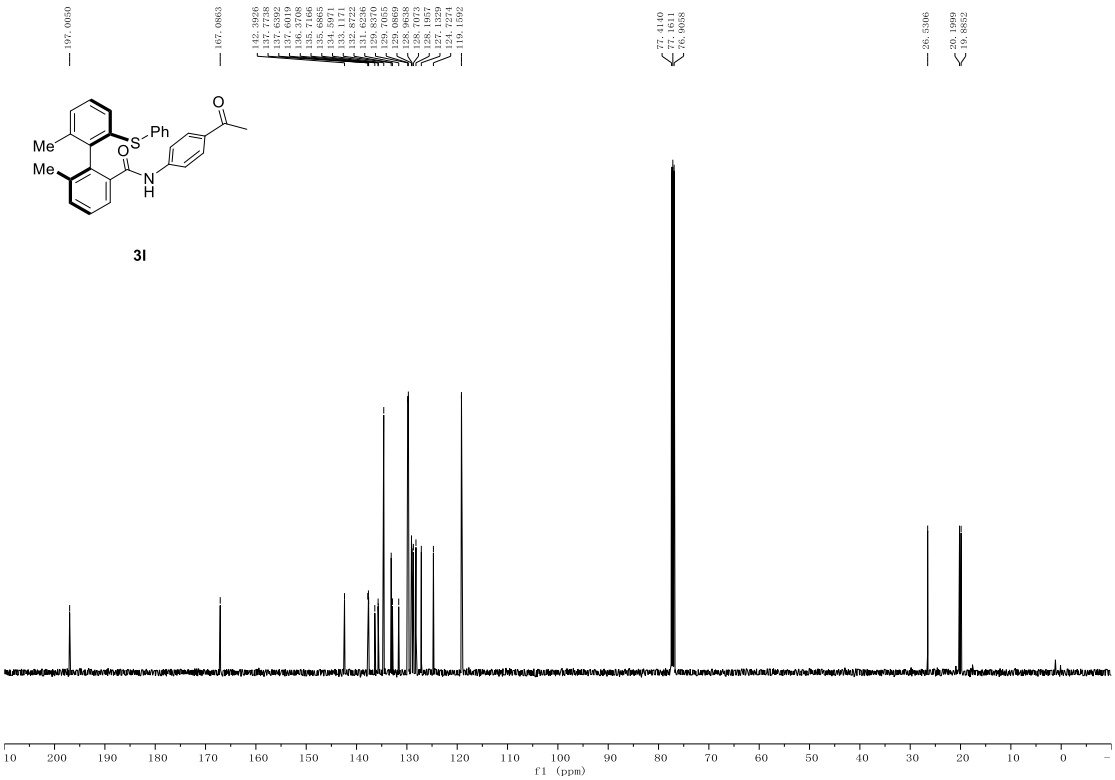


Figure **S53**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3l**

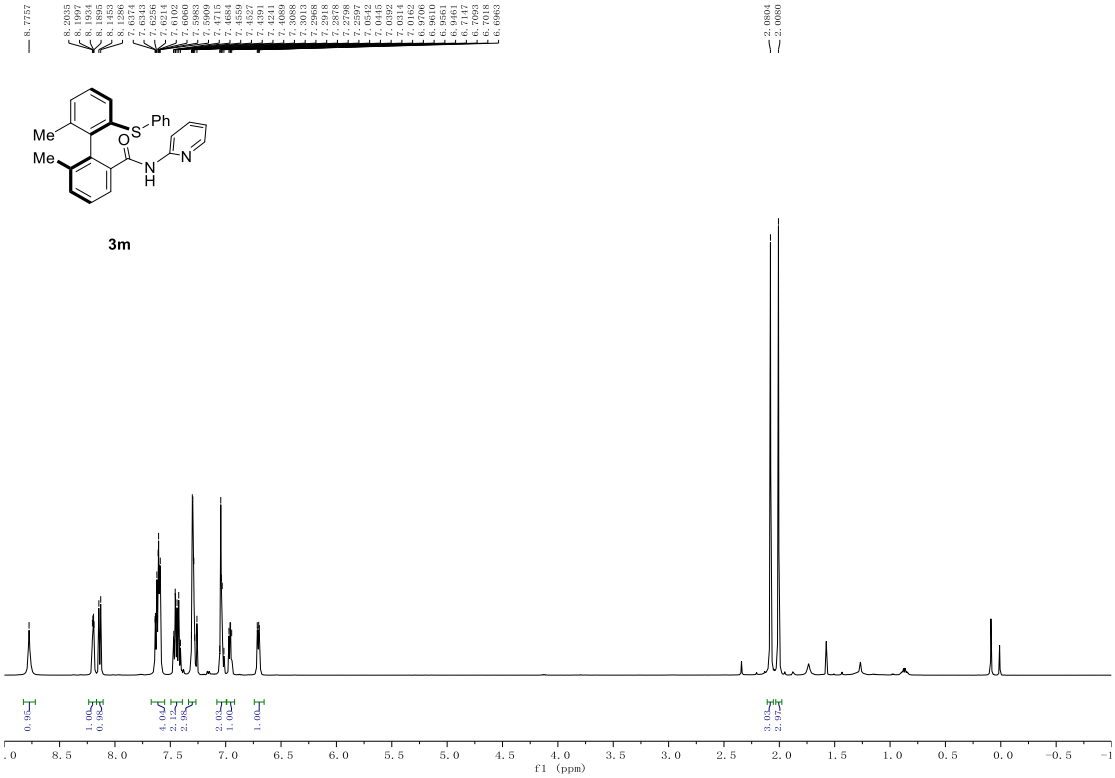


Figure **S54**. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3m**

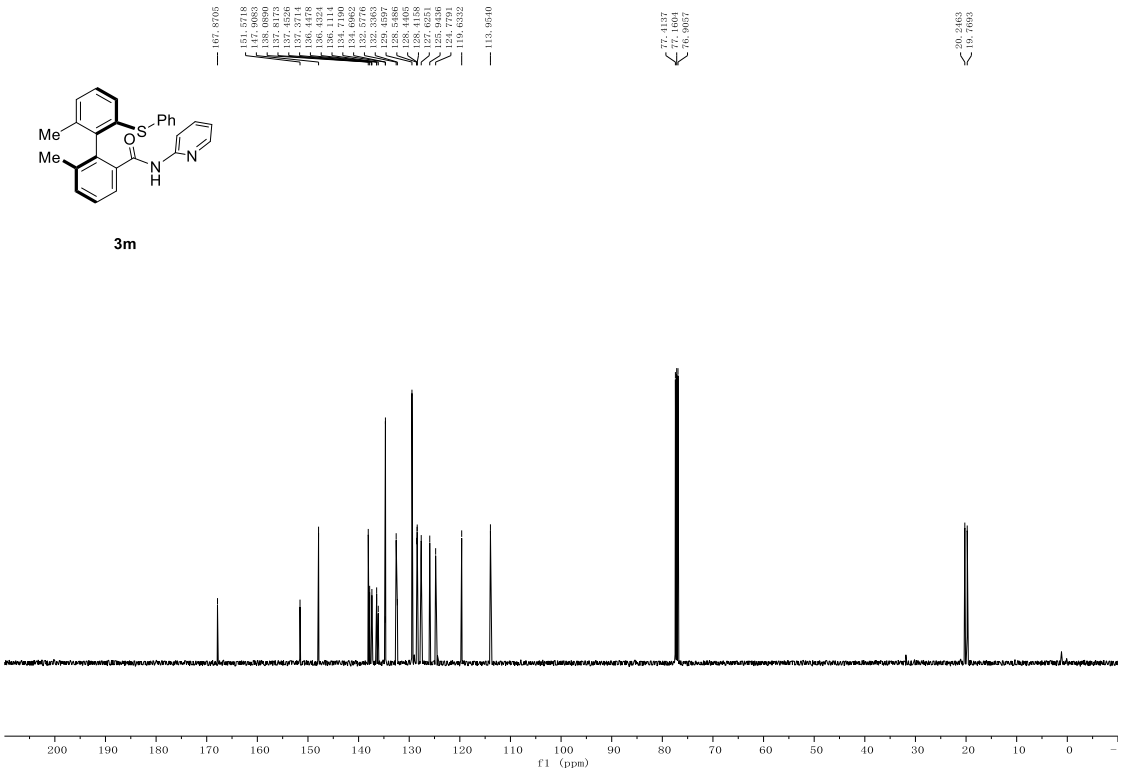


Figure **S55**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3m**

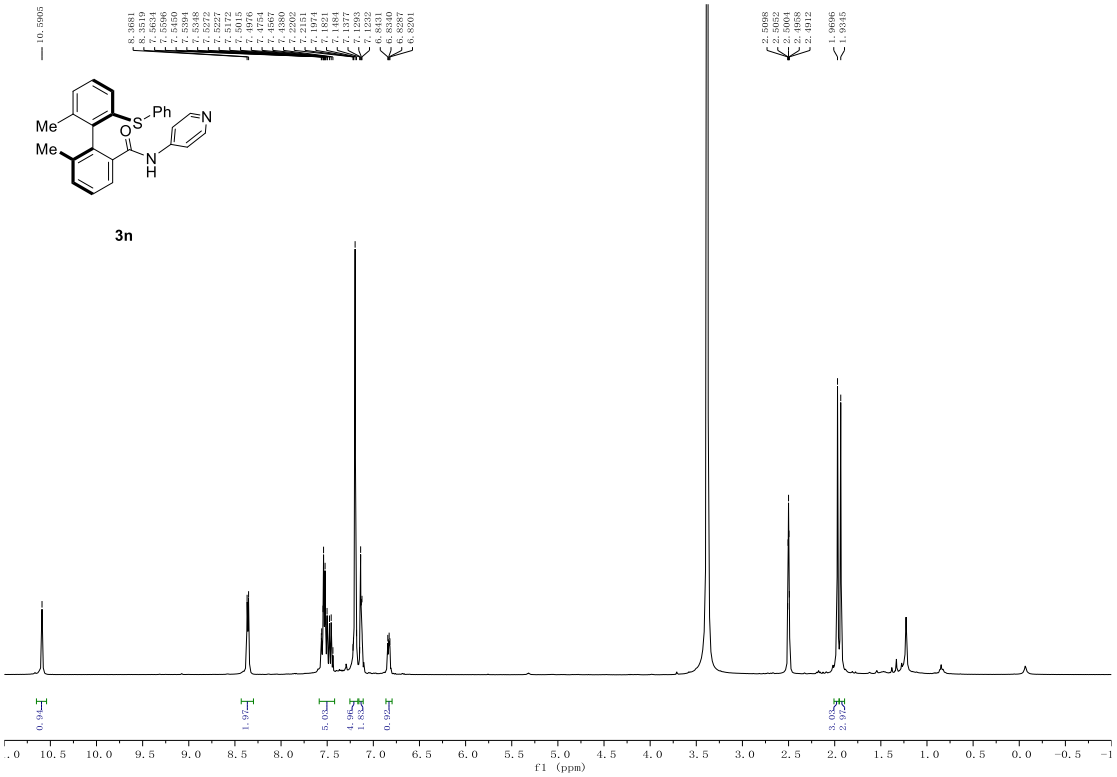


Figure **S56**. ^{1}H NMR spectra (400 MHz, DMSO-d_6) of **3n**

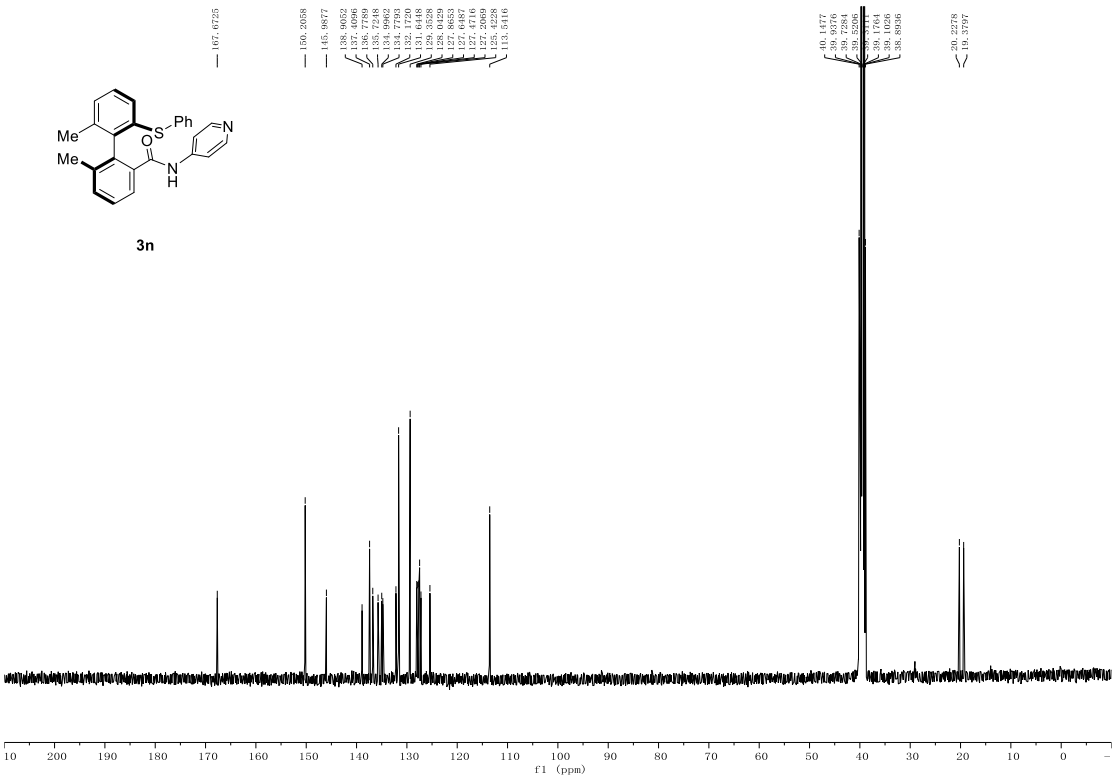


Figure **S57**. ^{13}C NMR spectra (101 MHz, DMSO-d_6) of **3n**

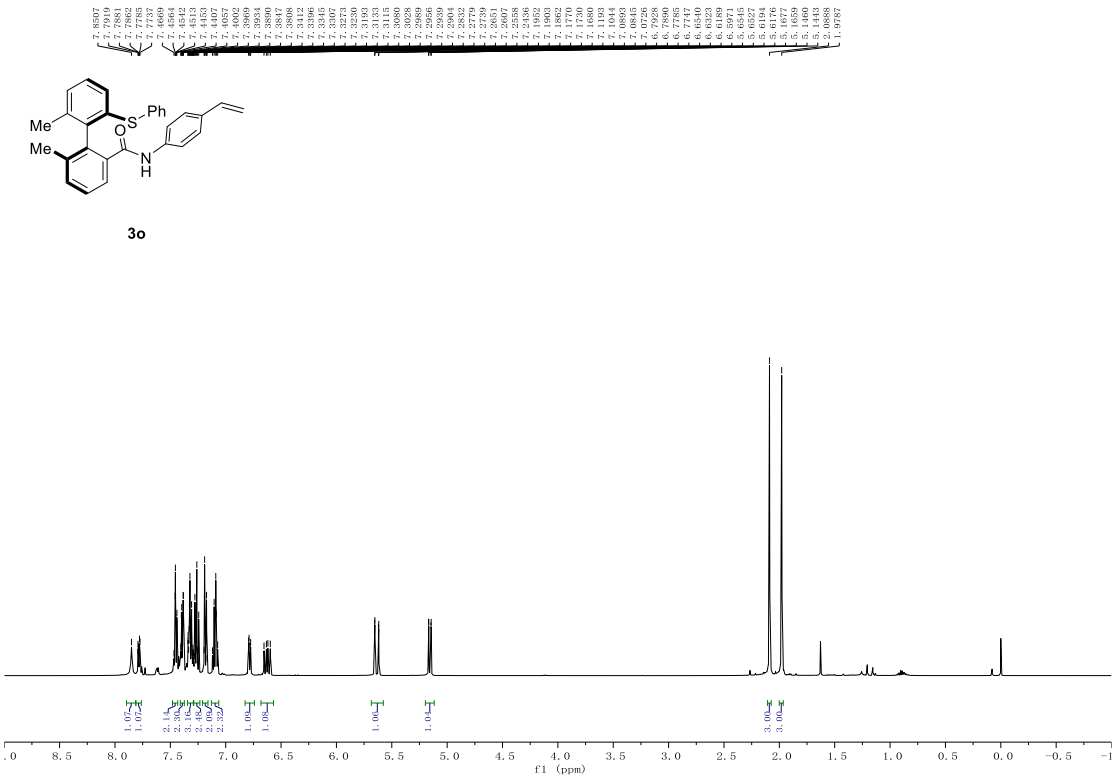


Figure **S58**. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3o**

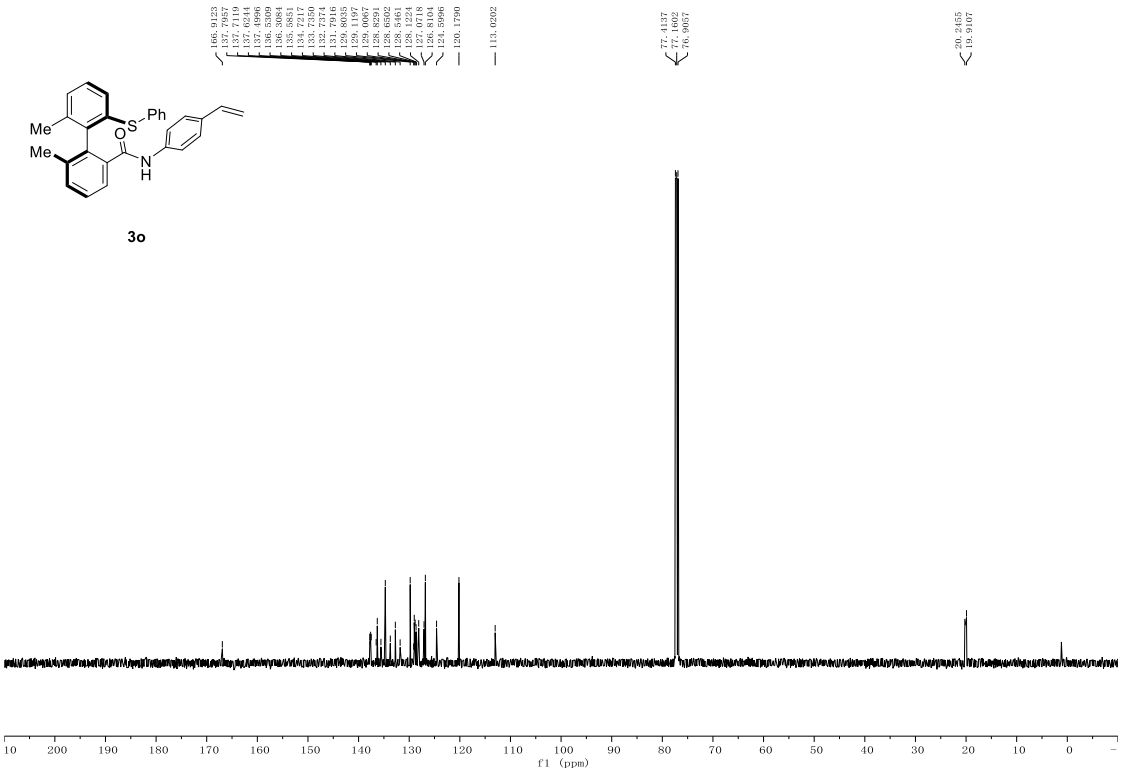


Figure **S59**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3o**

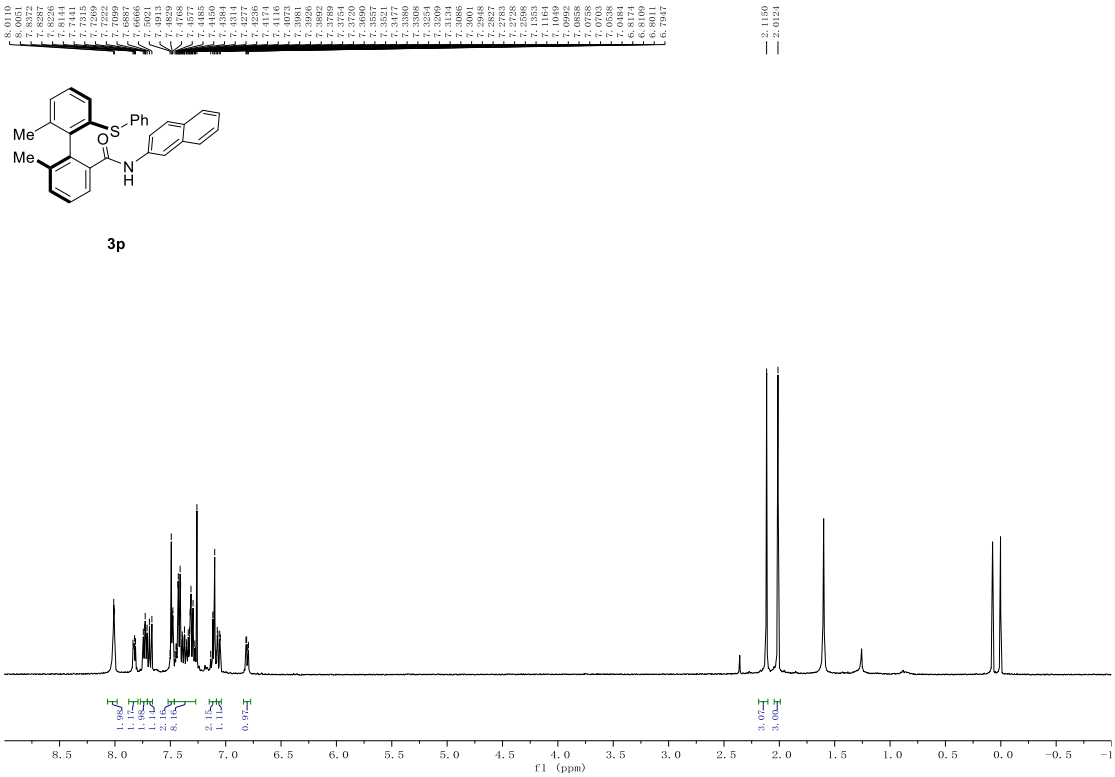


Figure **S60**. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3p**

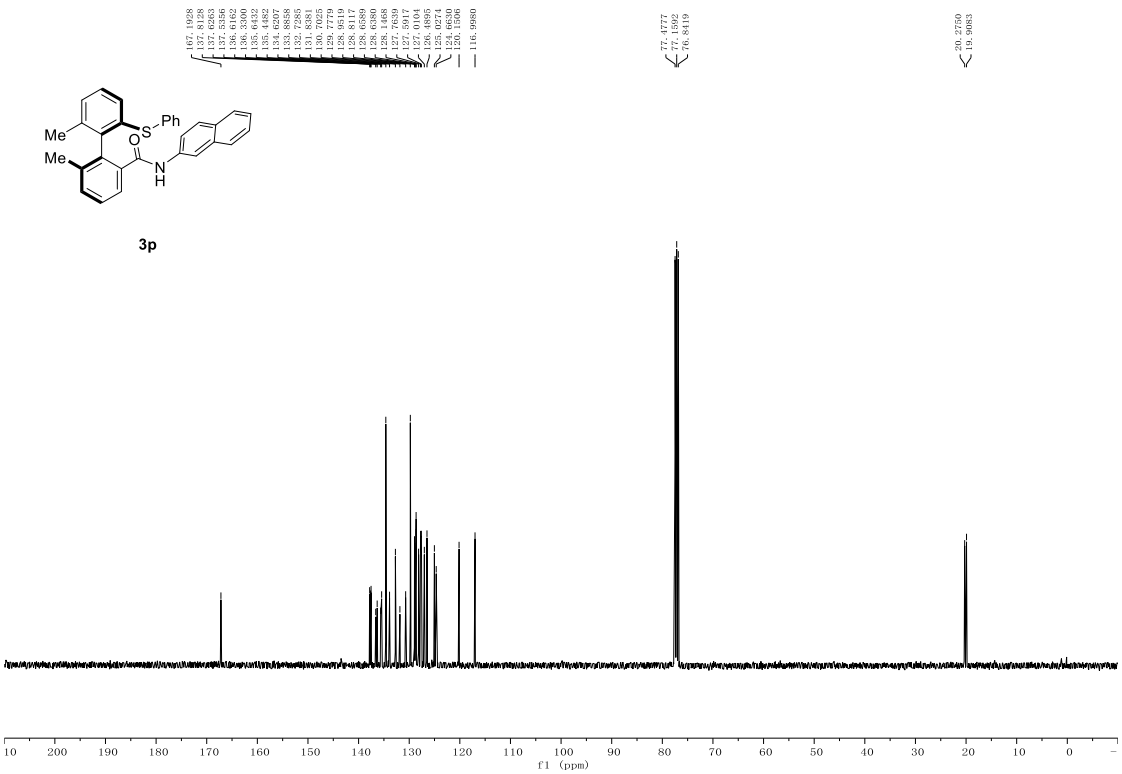


Figure **S61**. ^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3p**

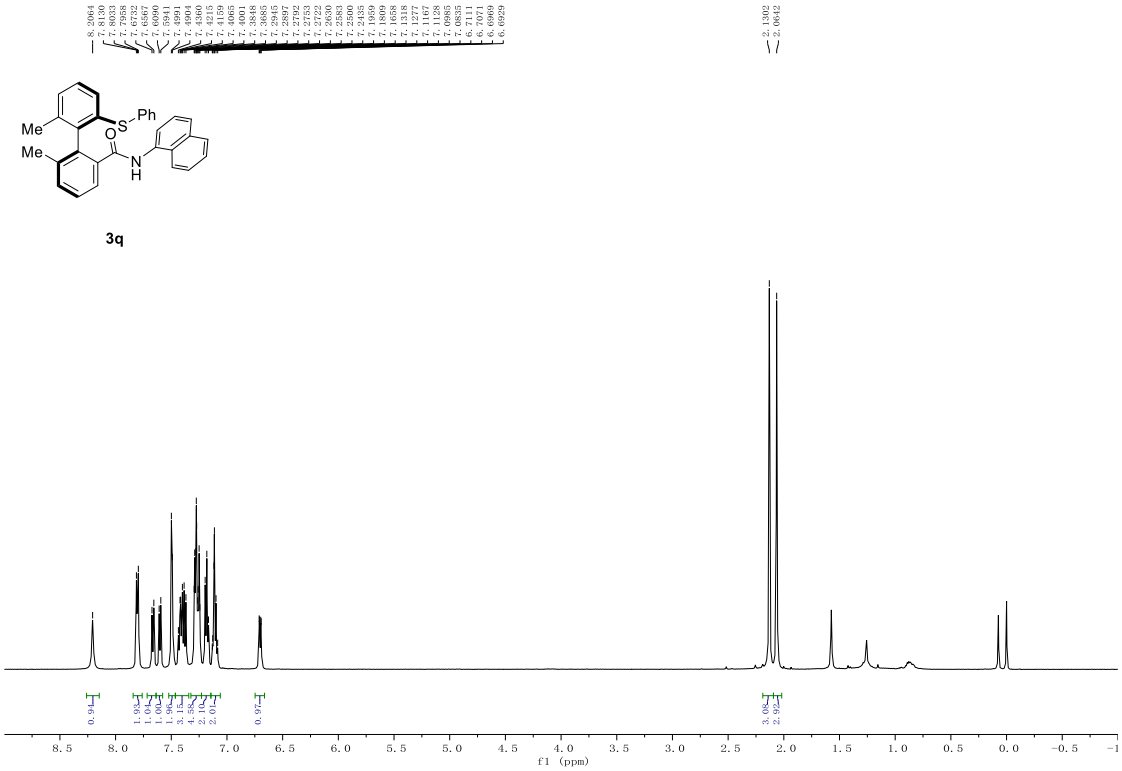


Figure **S62**. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3q**

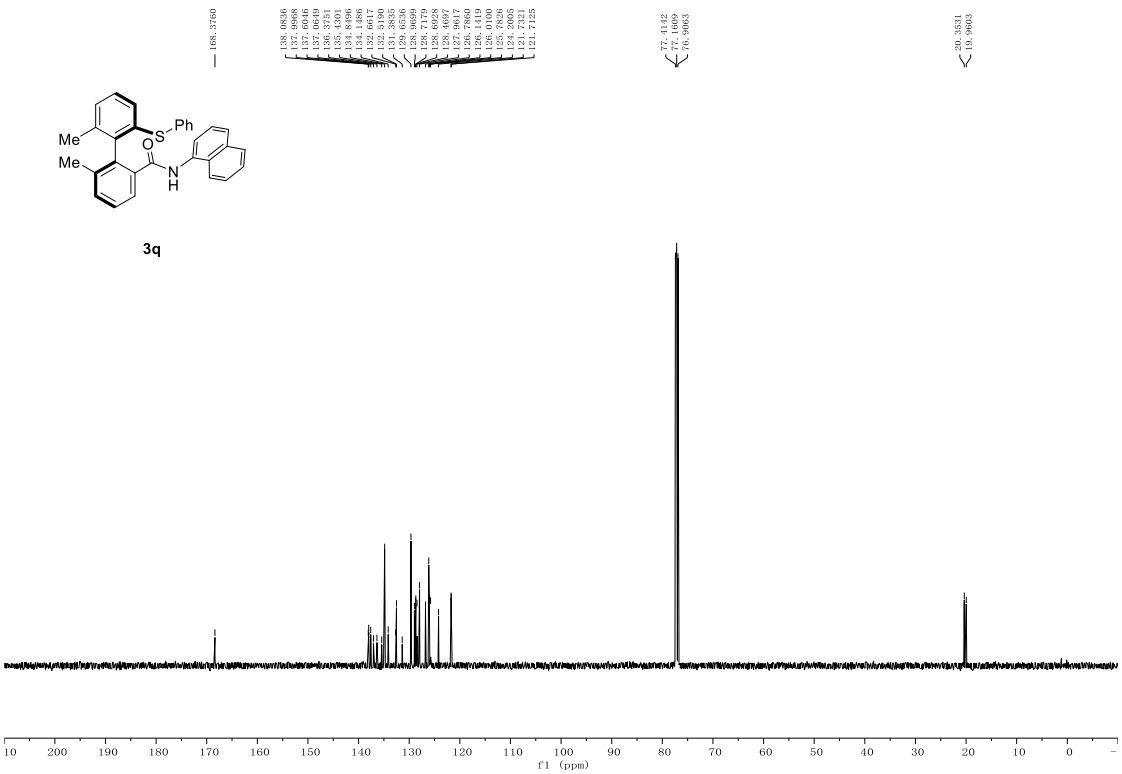


Figure **S63**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3q**

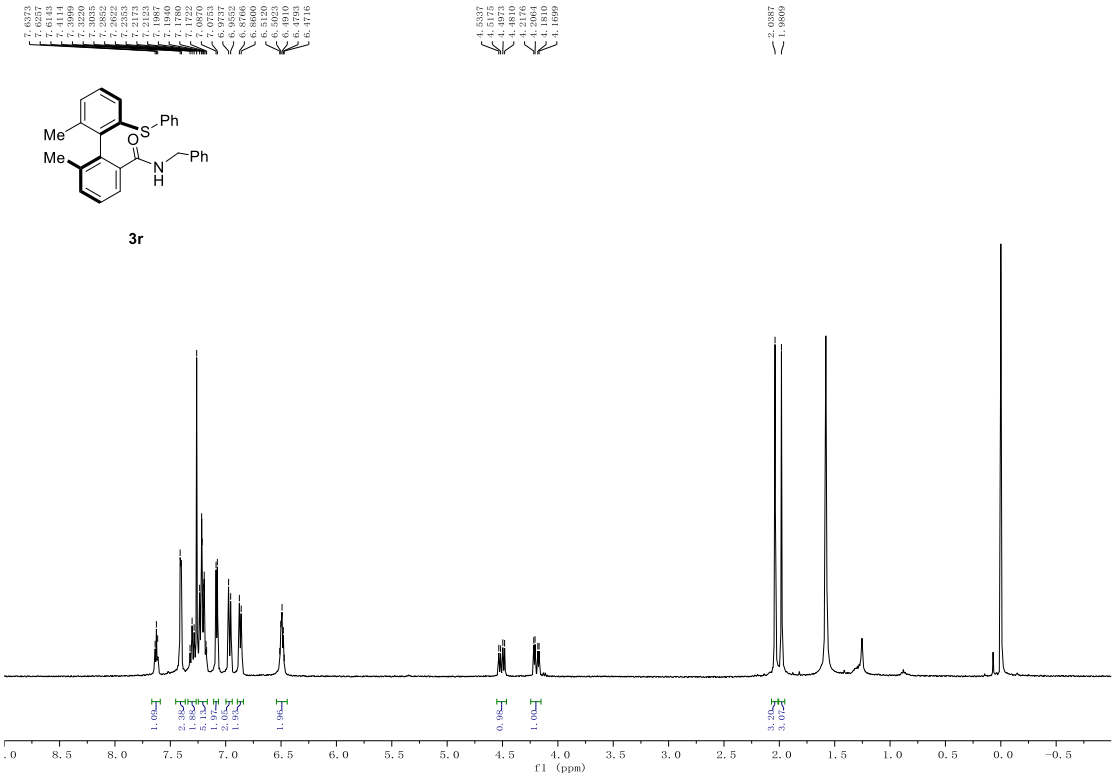


Figure **S64**. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3r**

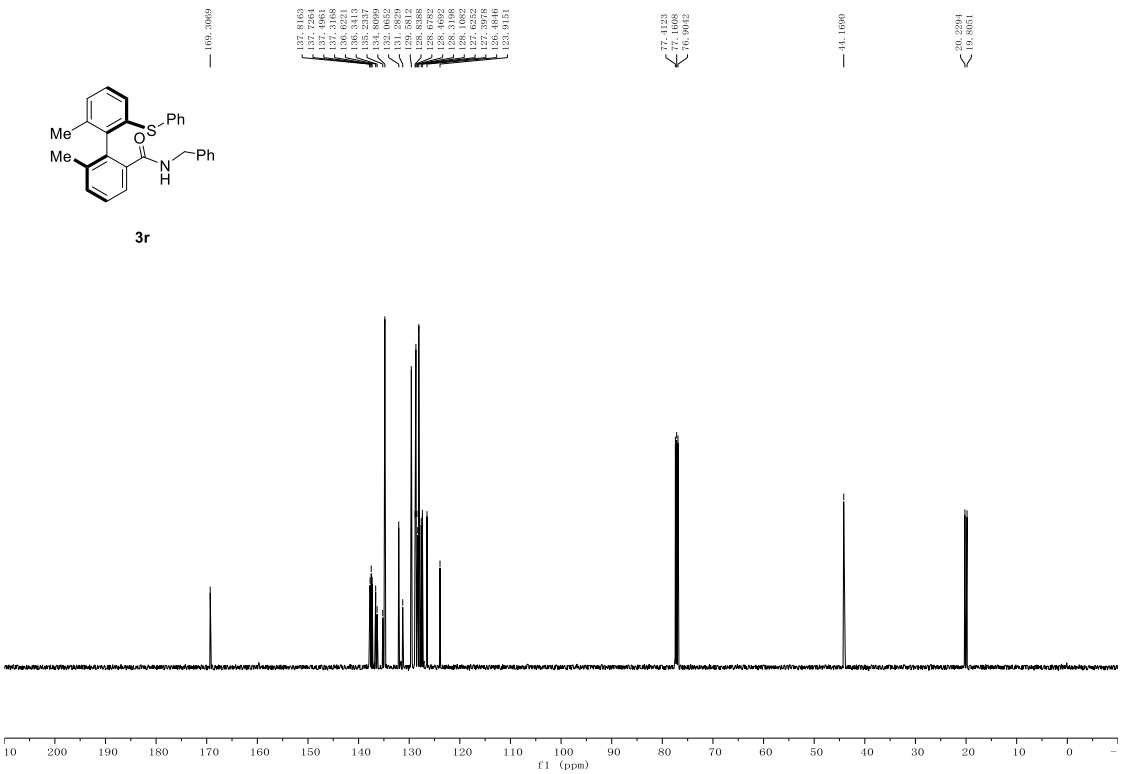


Figure **S65**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3r**

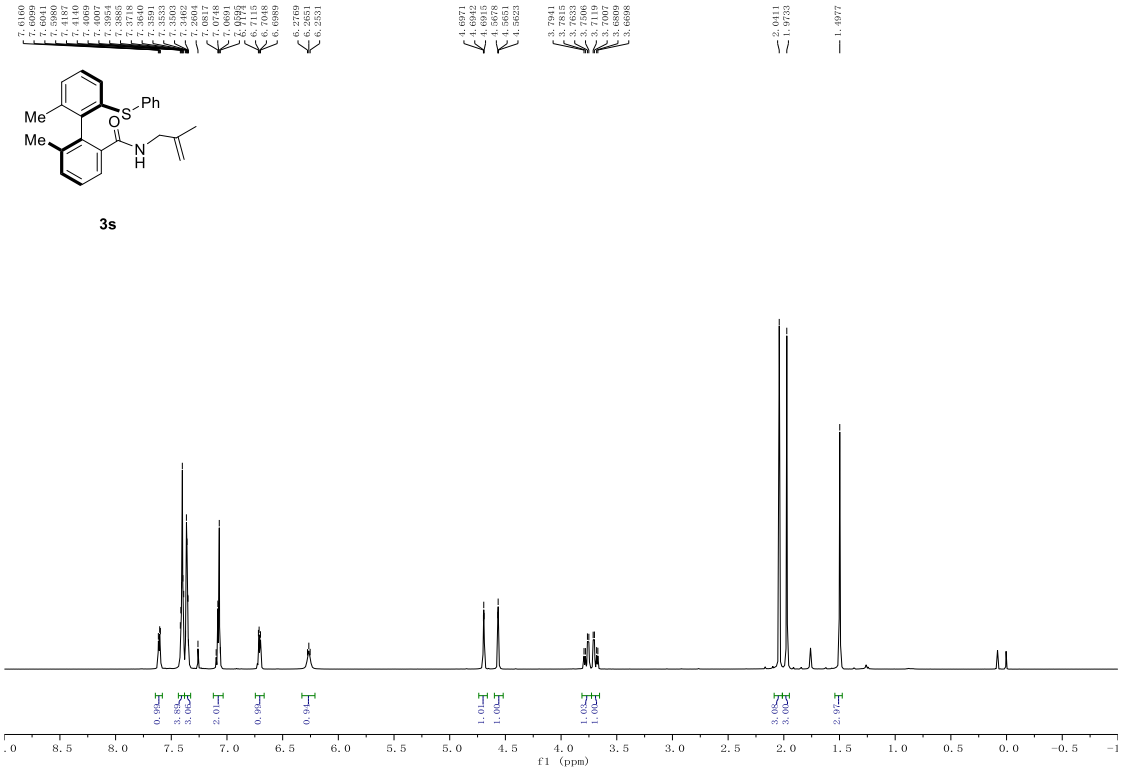


Figure **S66**. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3s**

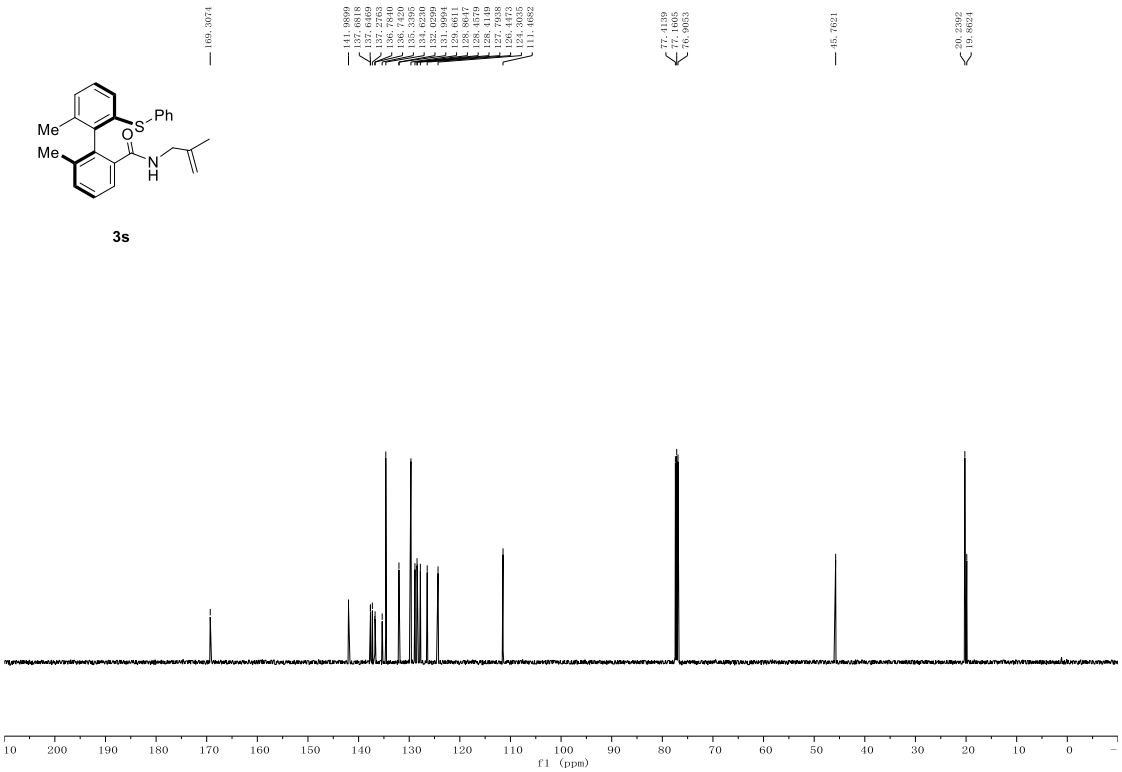


Figure **S67**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3s**

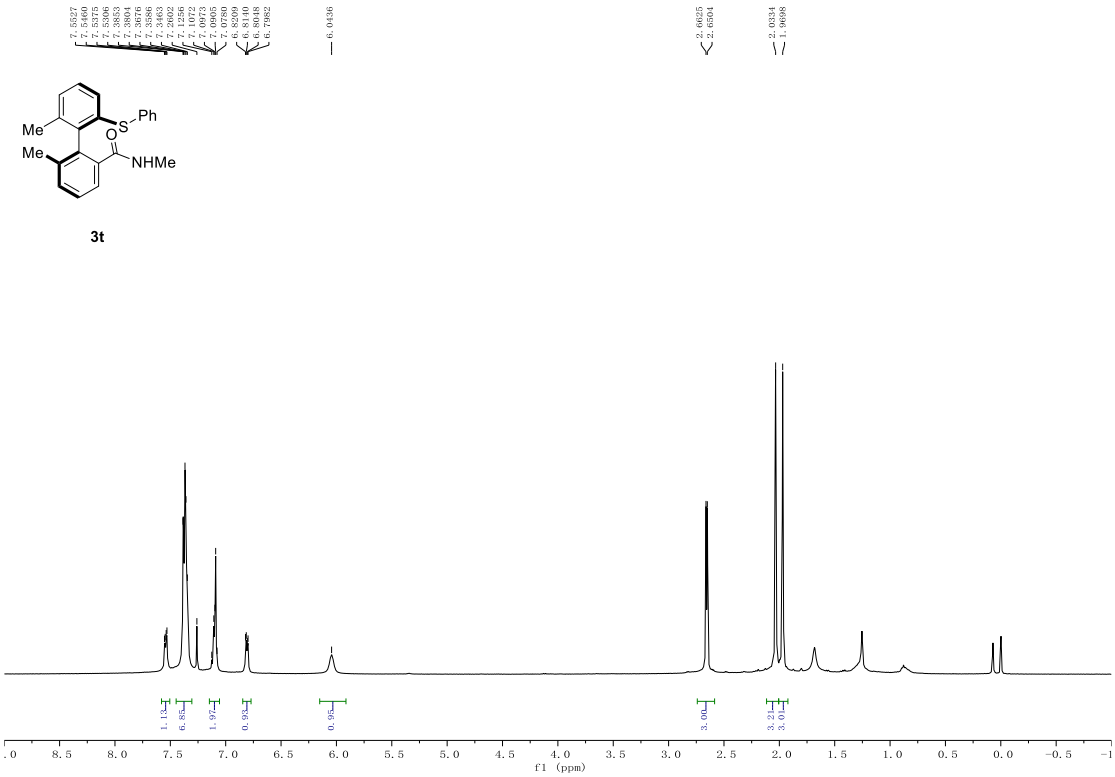


Figure **S68**. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3t**

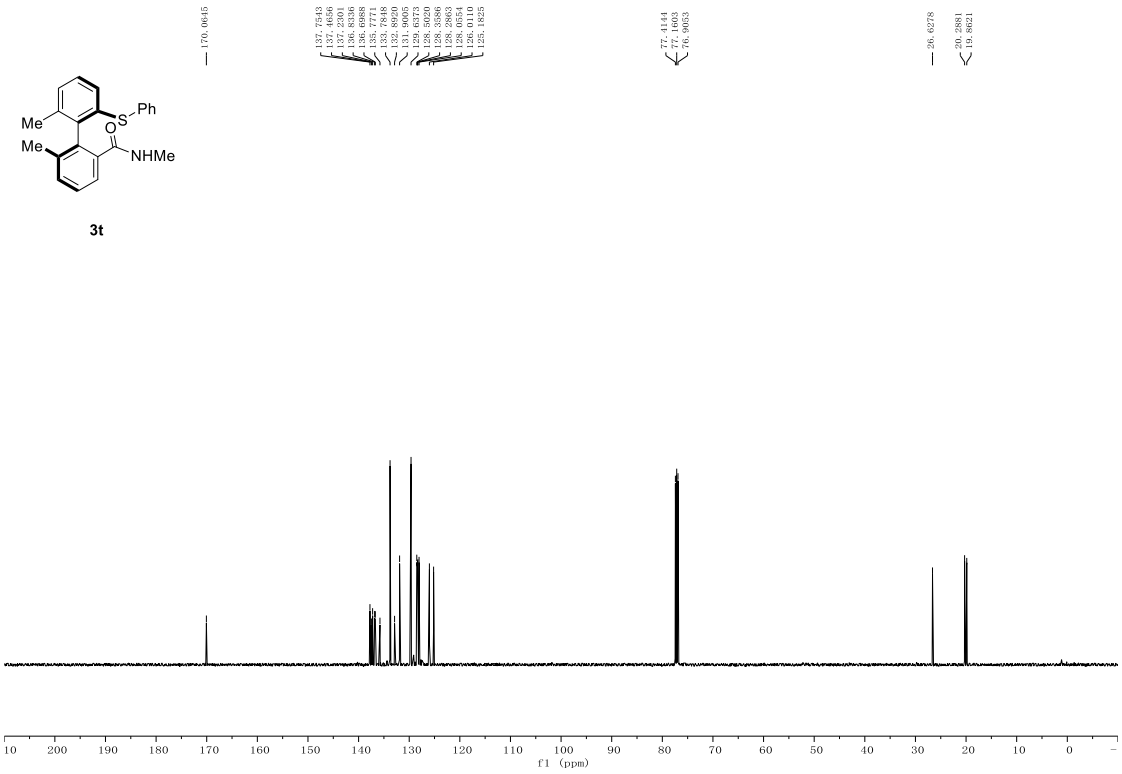


Figure **S69**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3t**

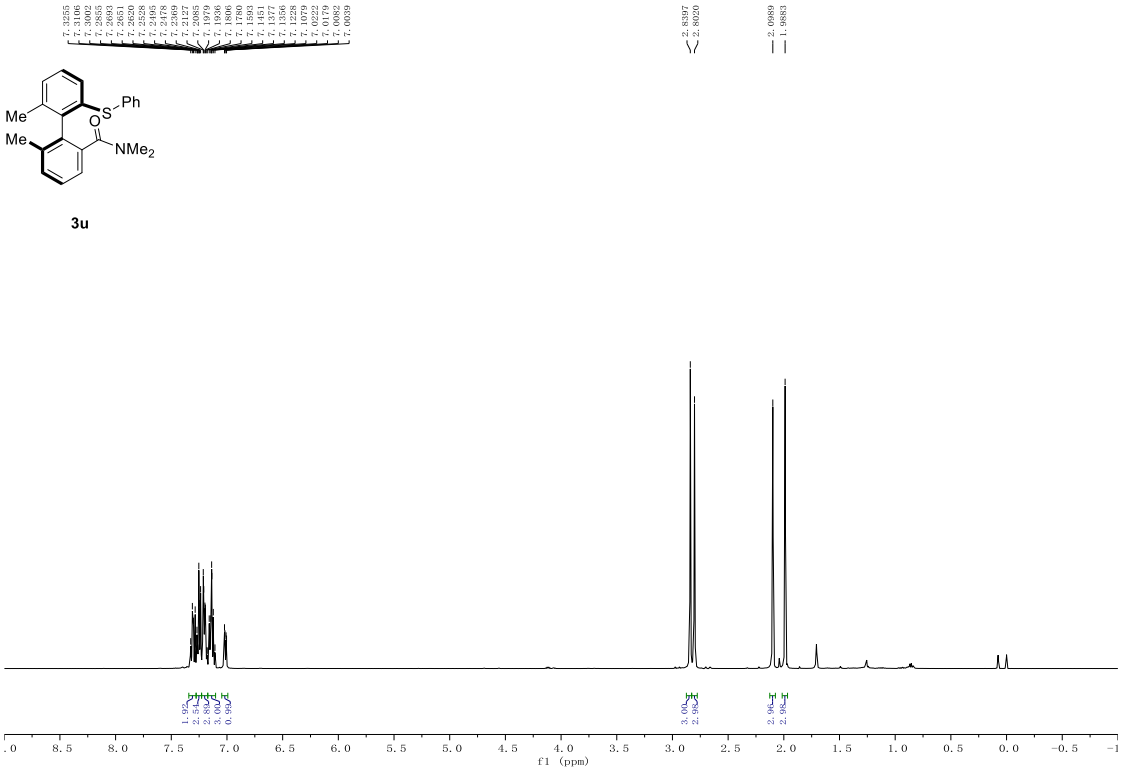


Figure **S70**. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3u**

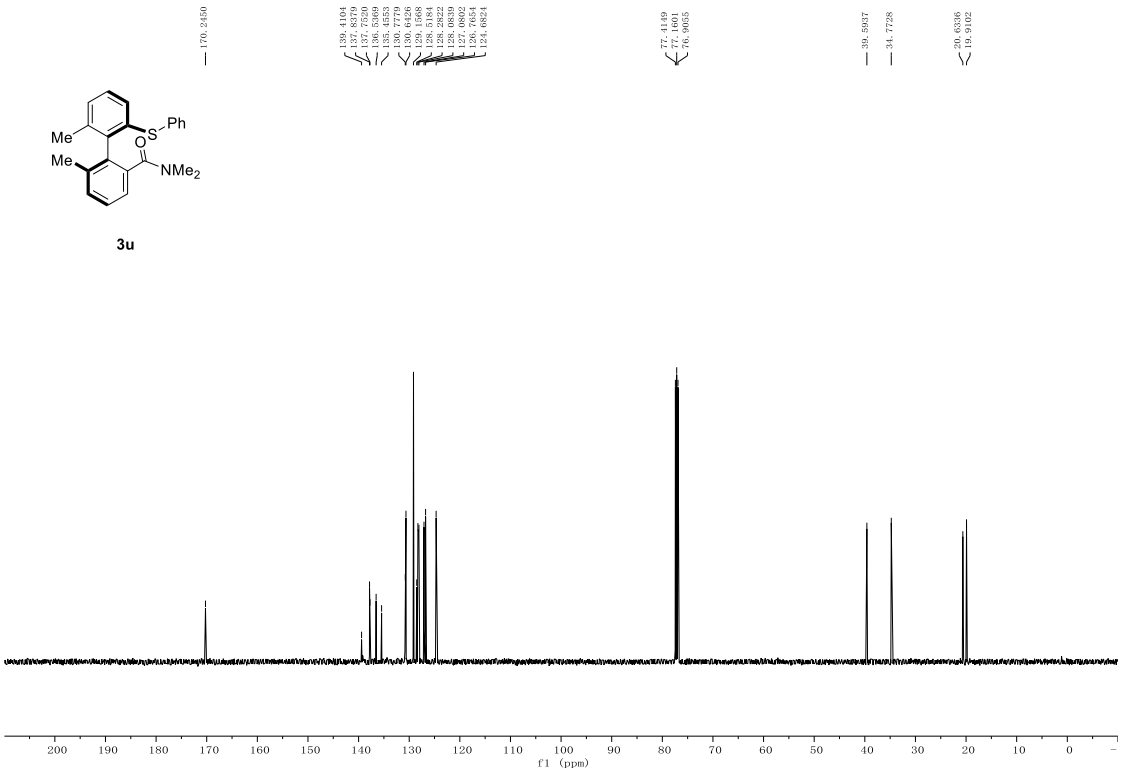


Figure **S71**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3u**

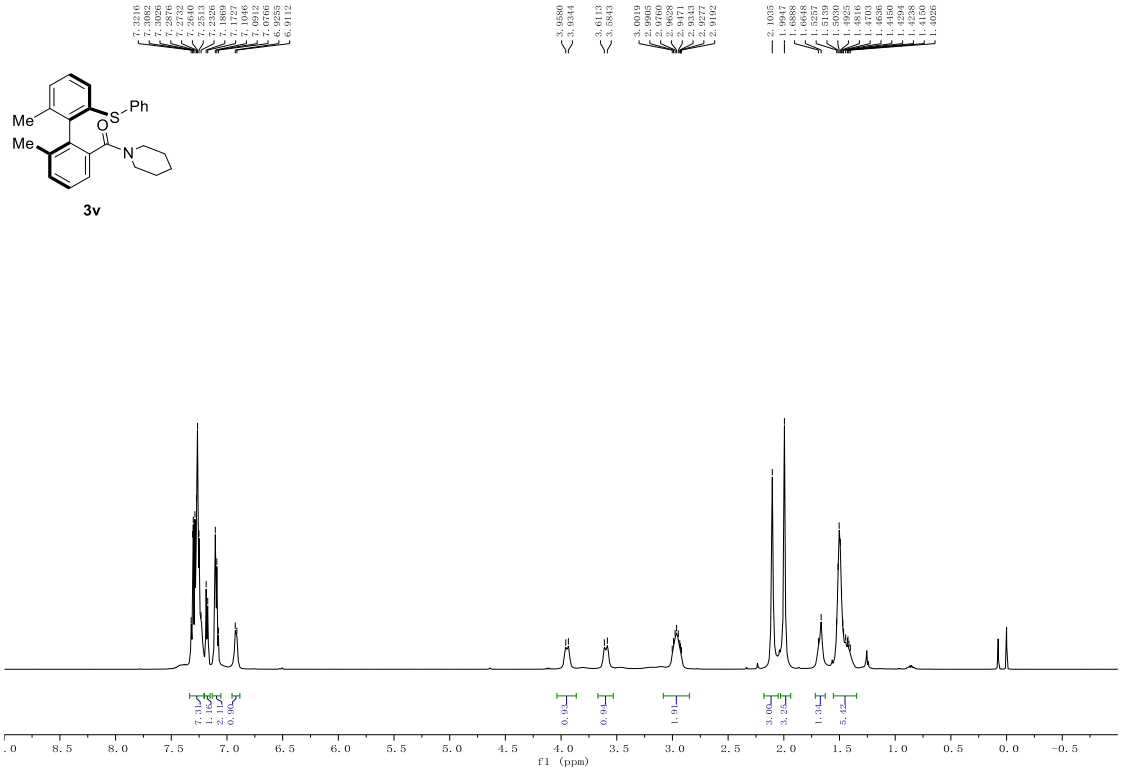


Figure **S72**. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3v**

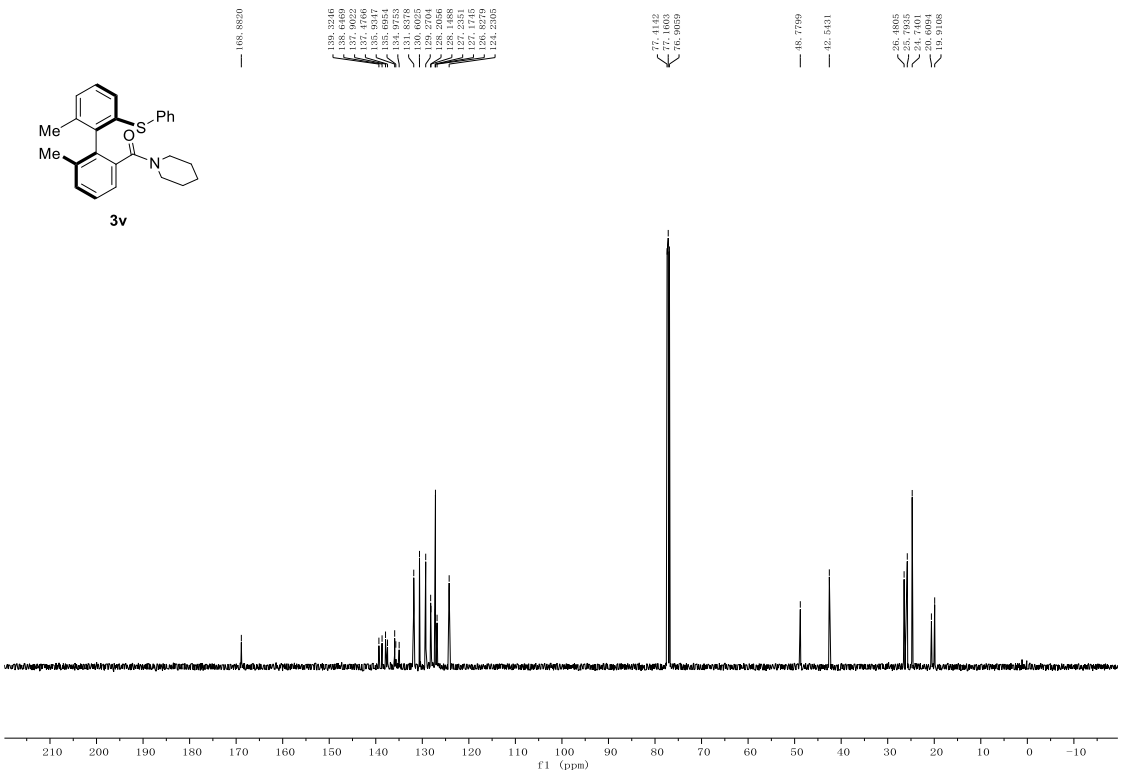


Figure **S73**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3v**

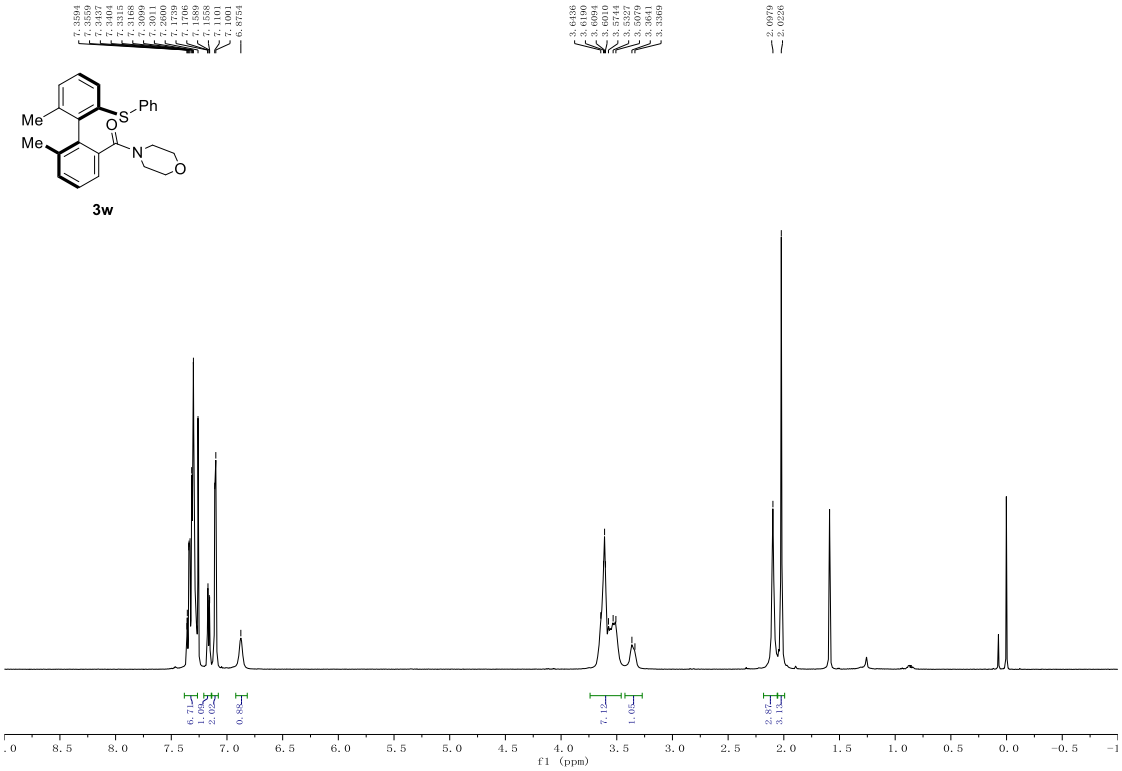


Figure **S74**. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3w**

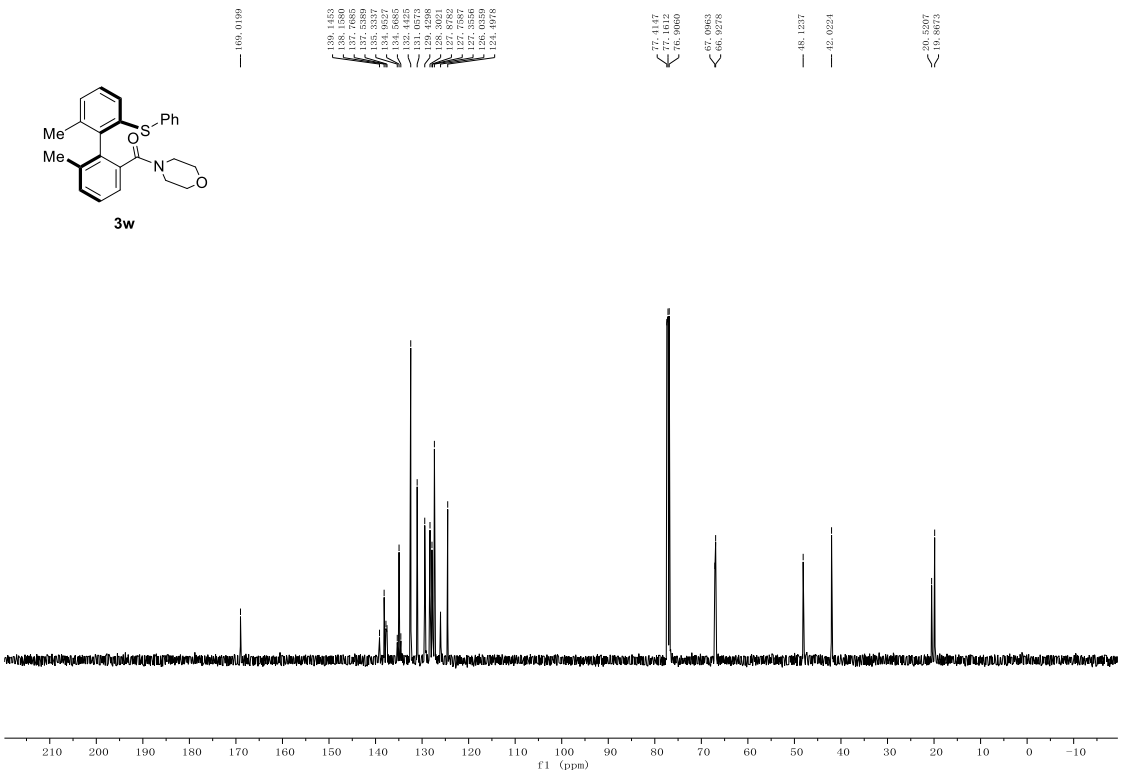


Figure **S75**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3w**

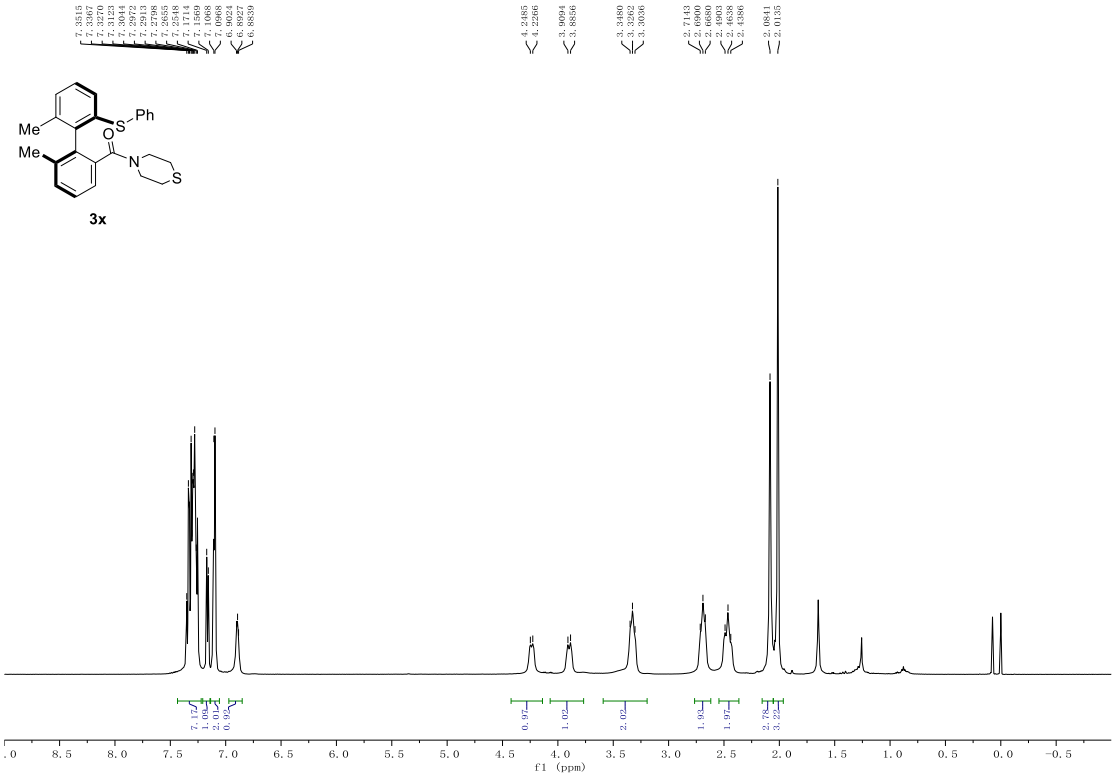


Figure **S76**. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3x**

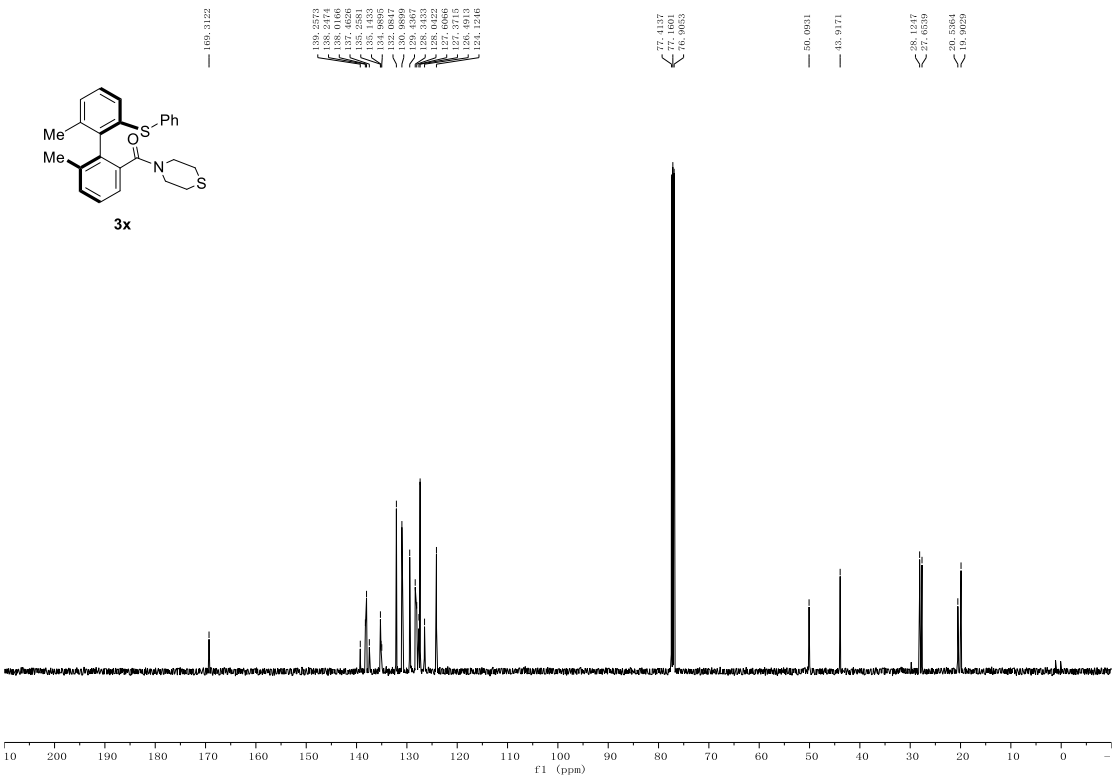


Figure **S77**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3x**

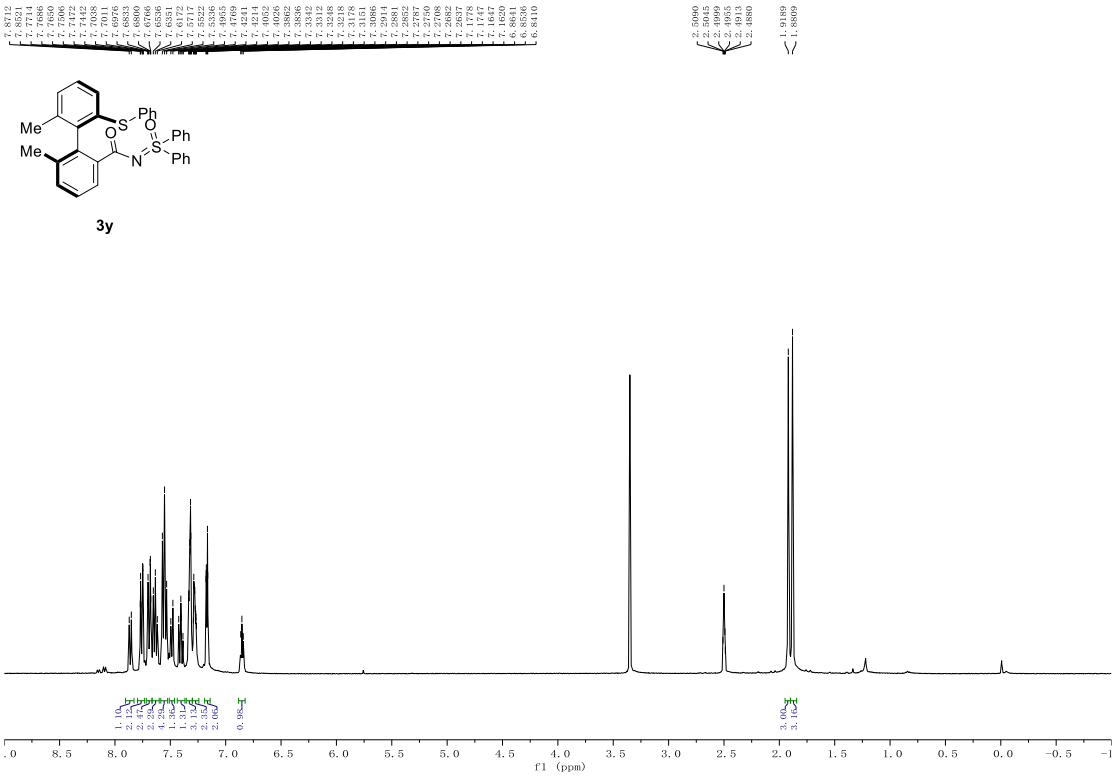


Figure **S78**. ^{1}H NMR spectra (400 MHz, DMSO-d_6) of **3y**

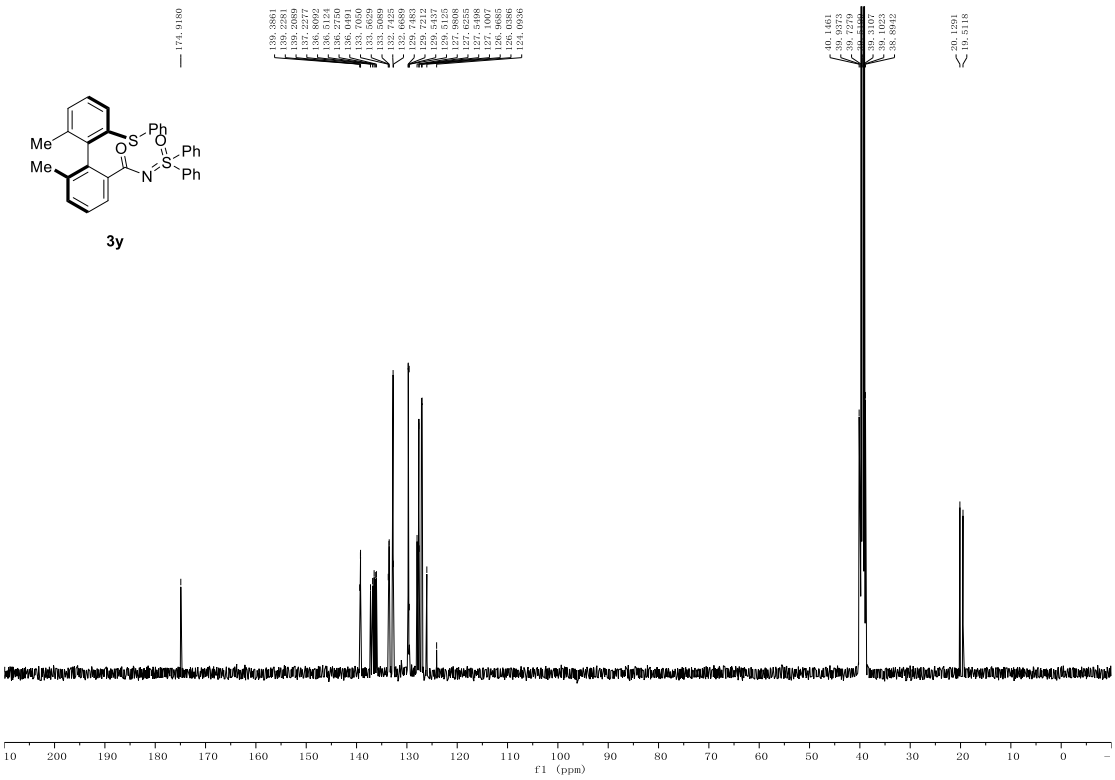


Figure **S79**. ^{13}C NMR spectra (101 MHz, DMSO-d_6) of **3y**

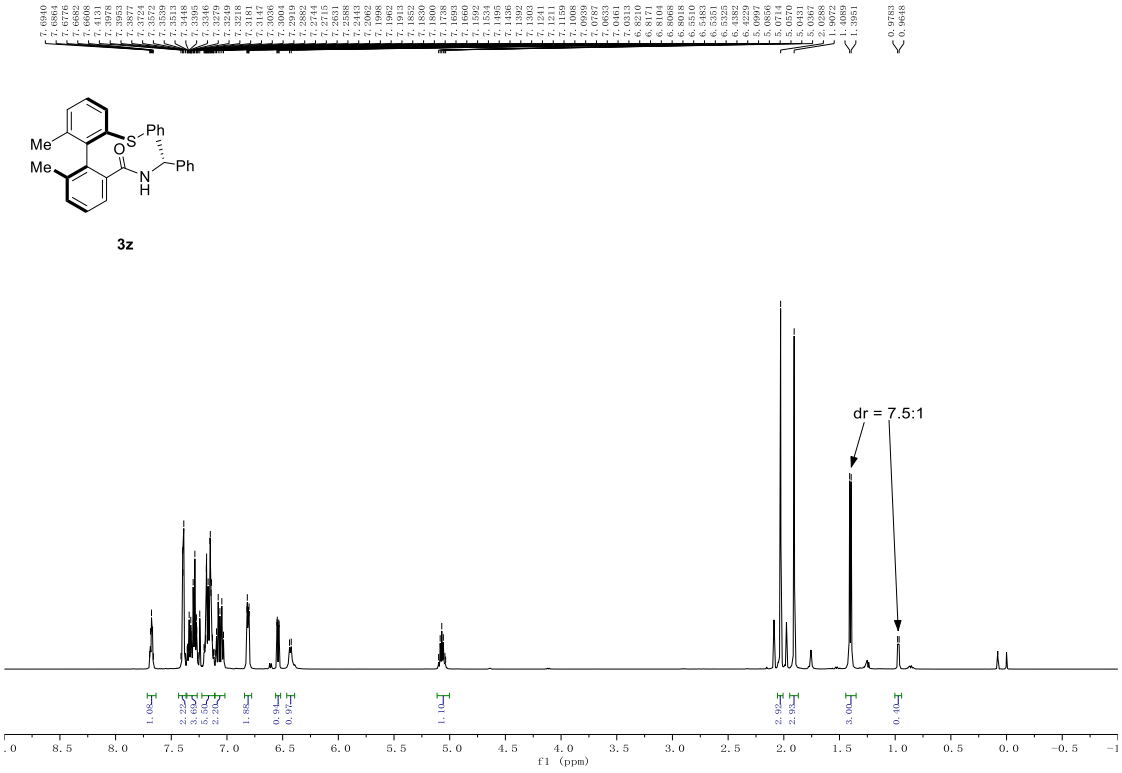


Figure **S80**. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3z**

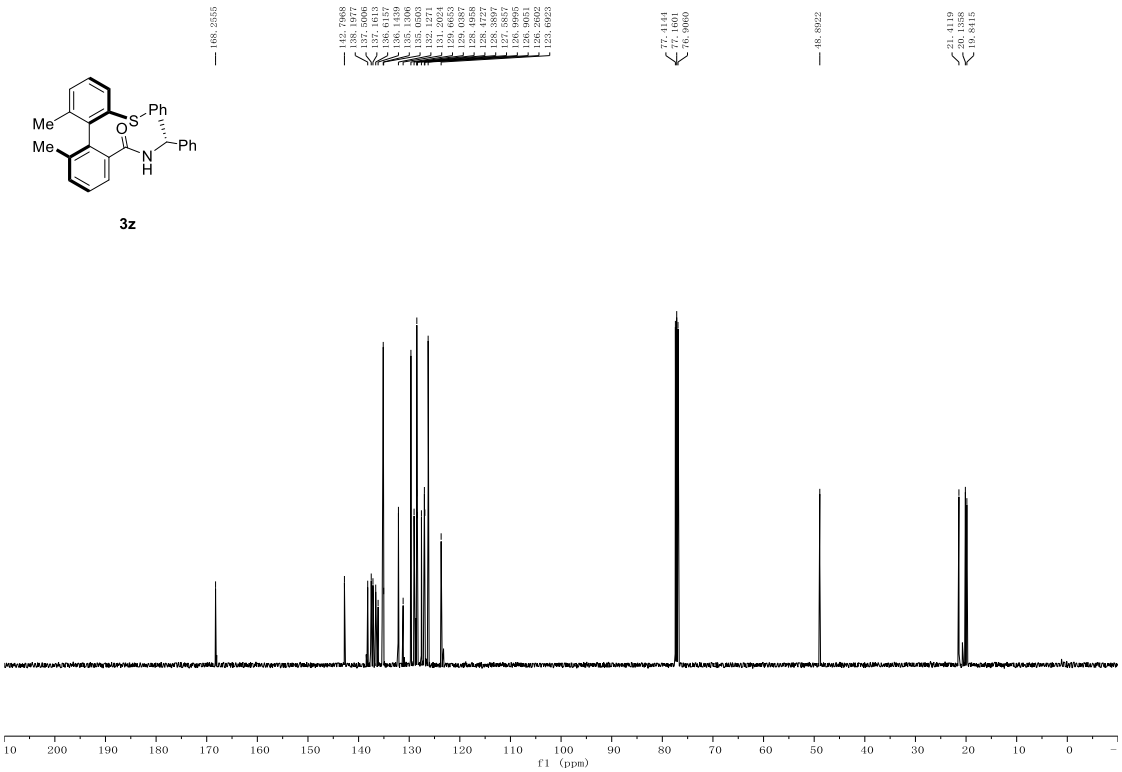


Figure **S81**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3z**

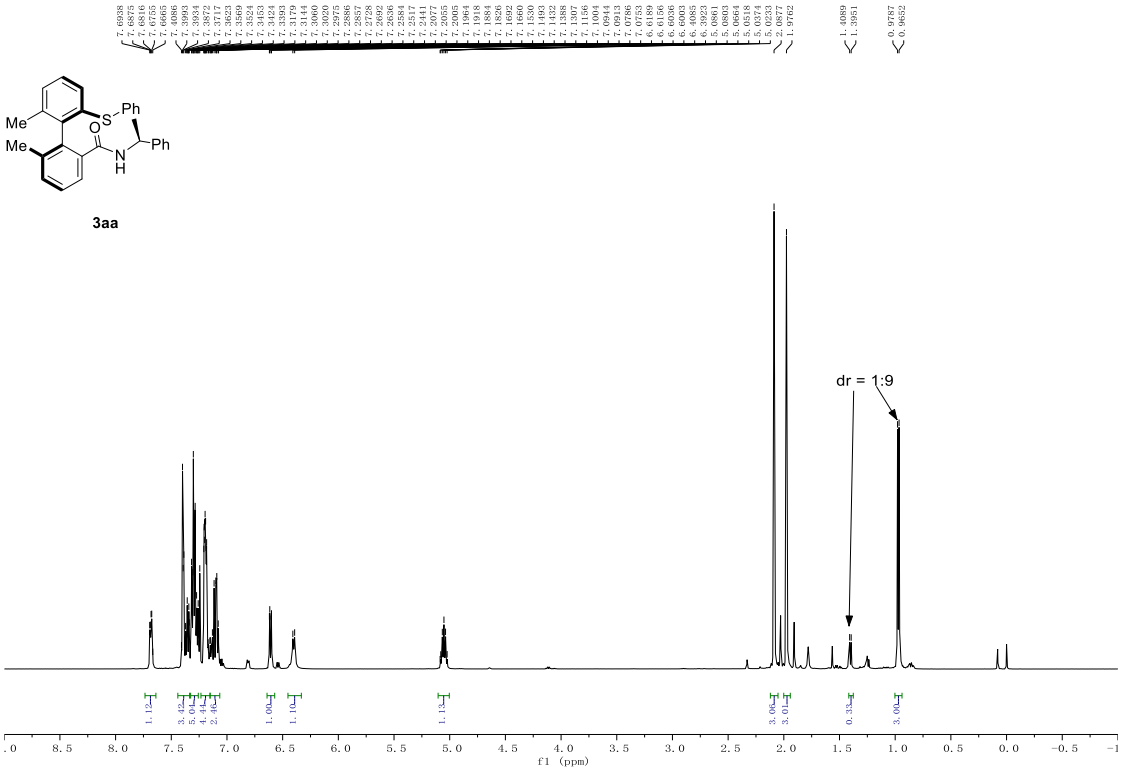


Figure **S82**. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3aa**

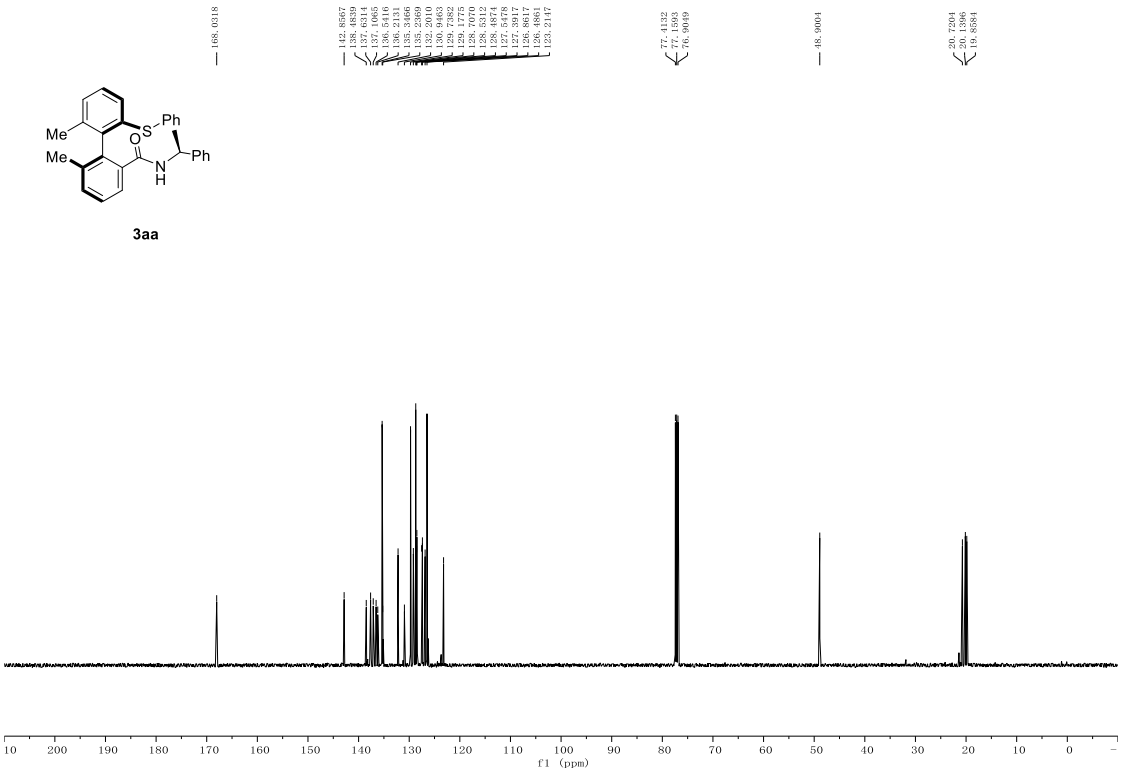


Figure **S83**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3aa**

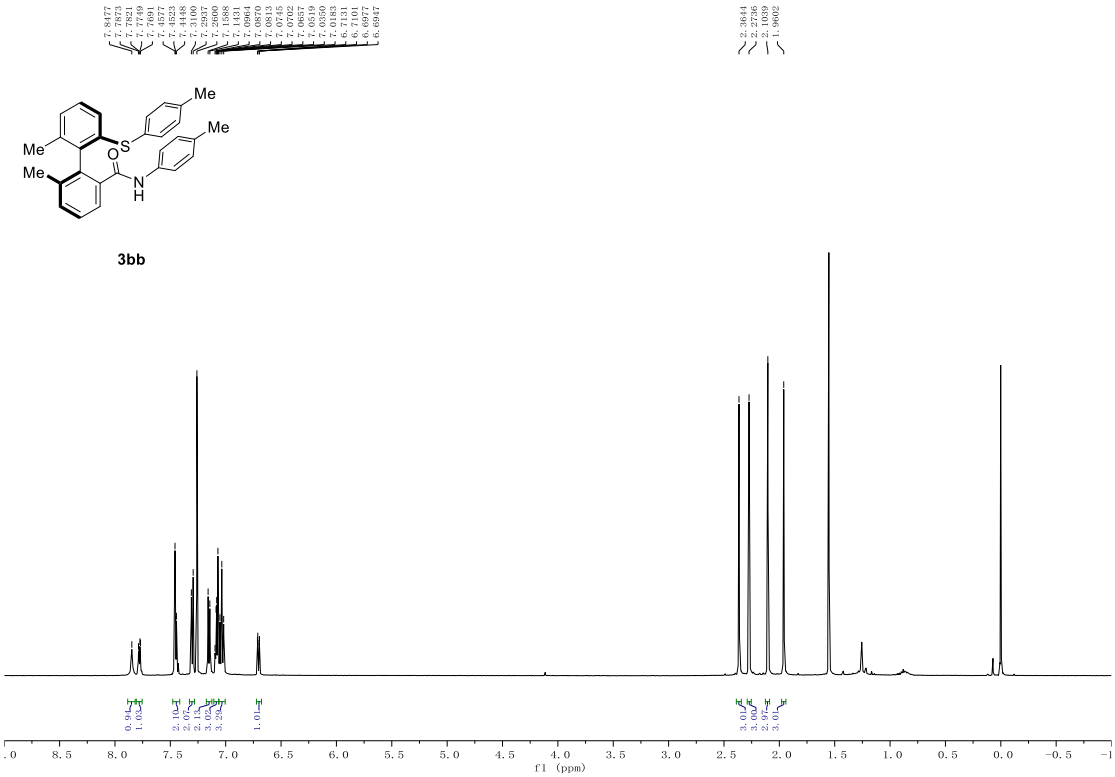


Figure **S84**. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3bb**

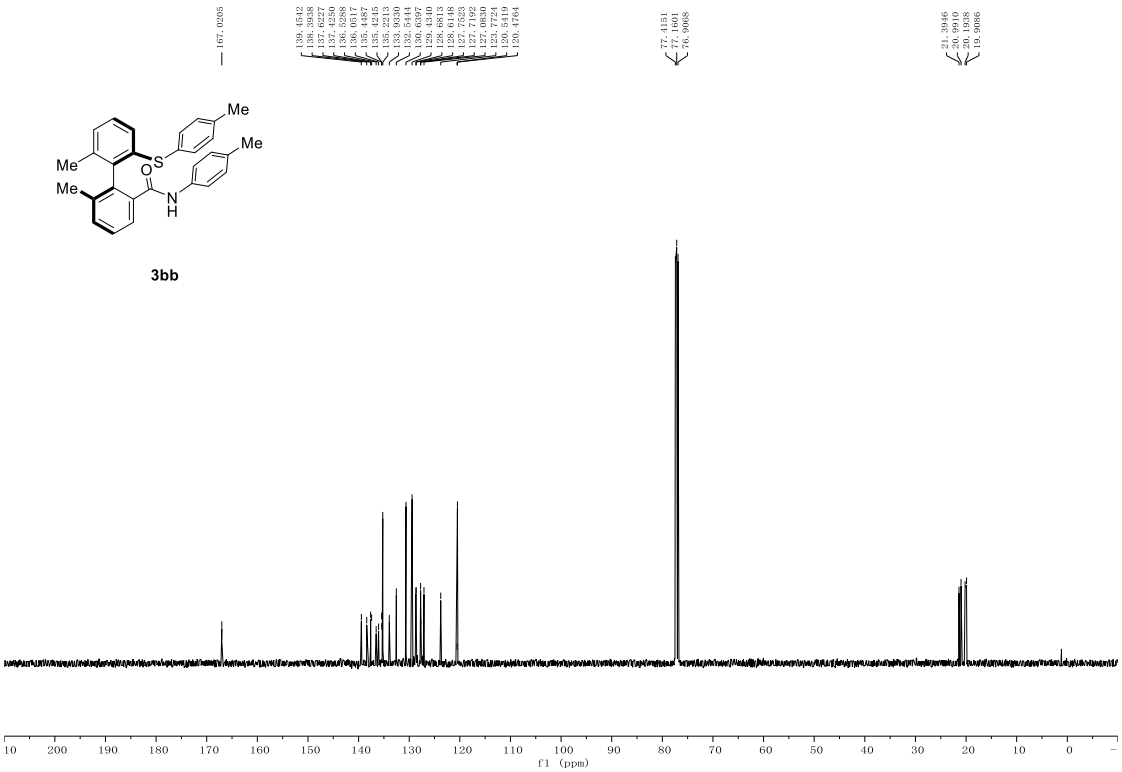


Figure **S85**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3bb**

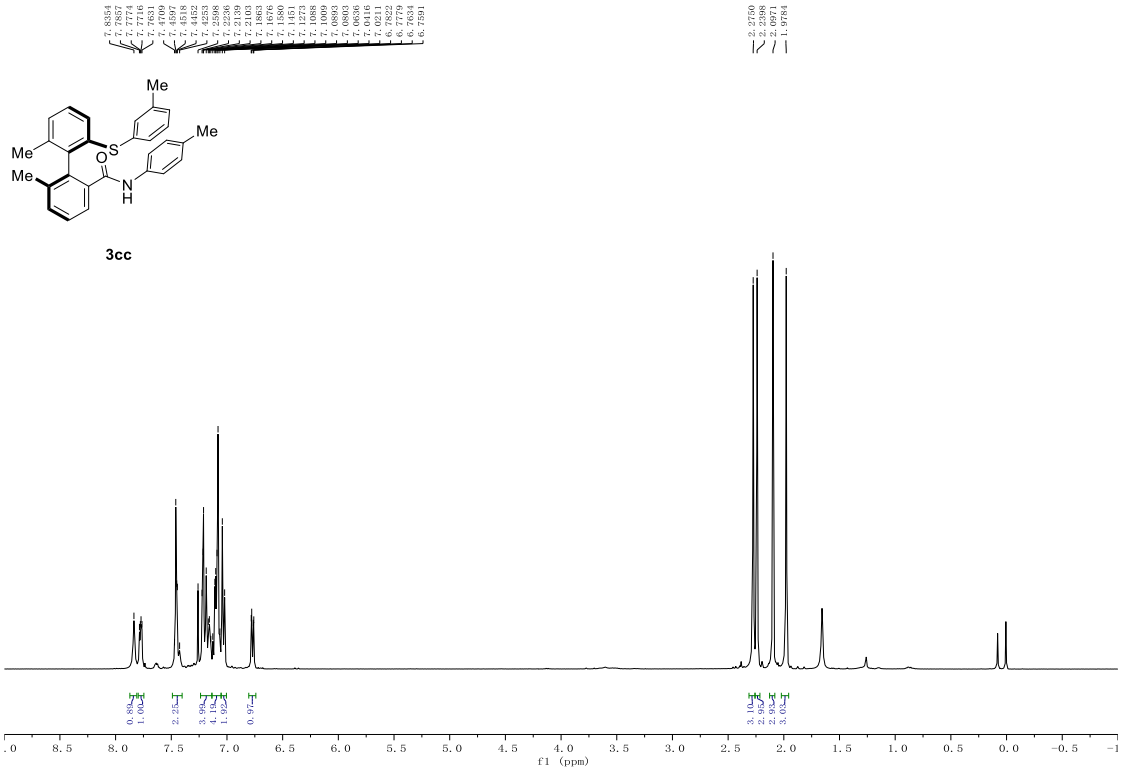


Figure **S86**. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3cc**

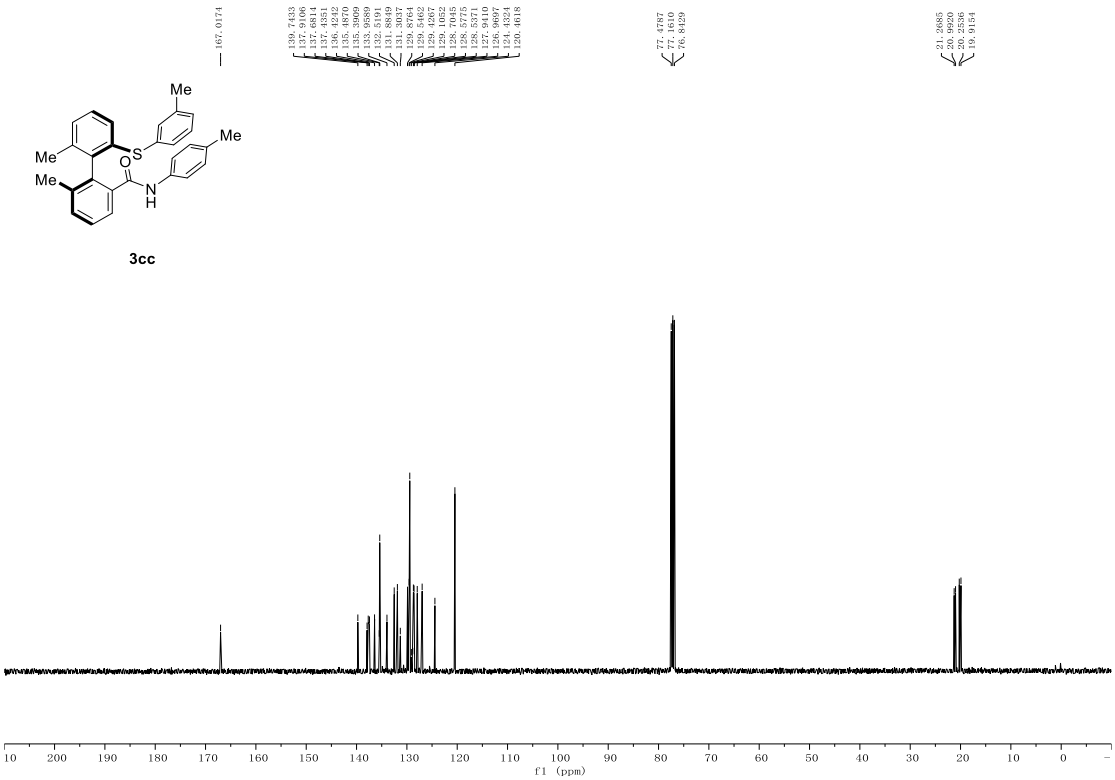


Figure **S87**. ^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3cc**

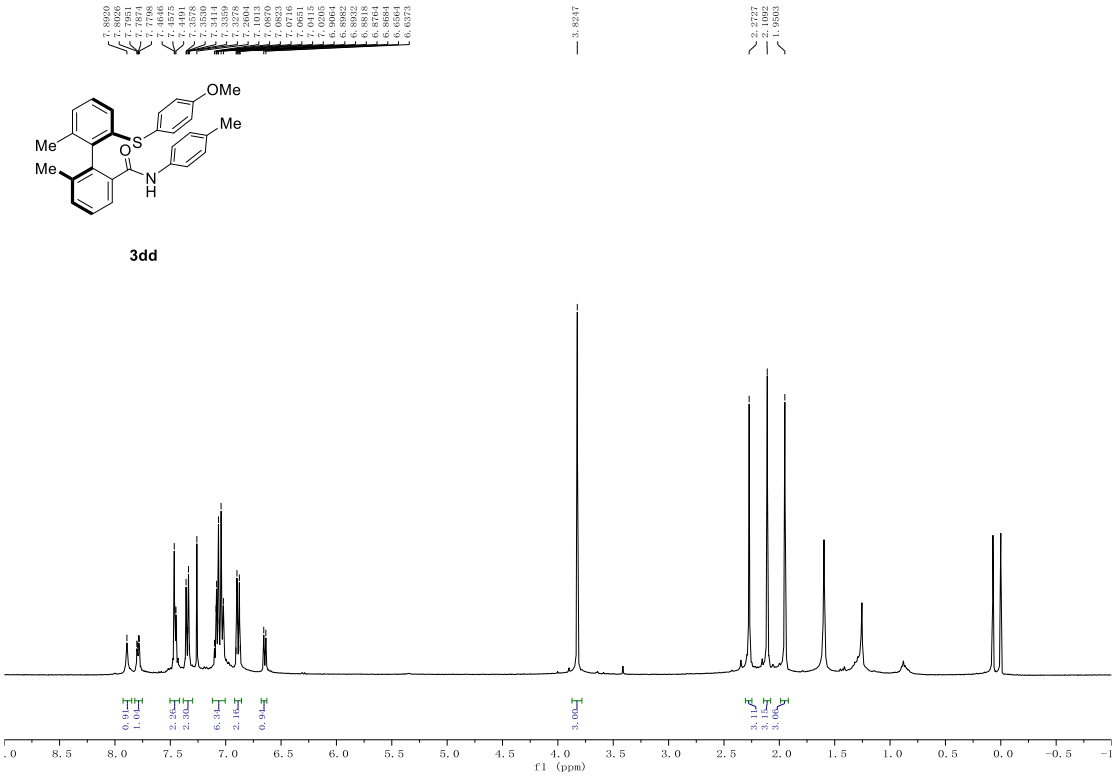


Figure **S88**. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3dd**

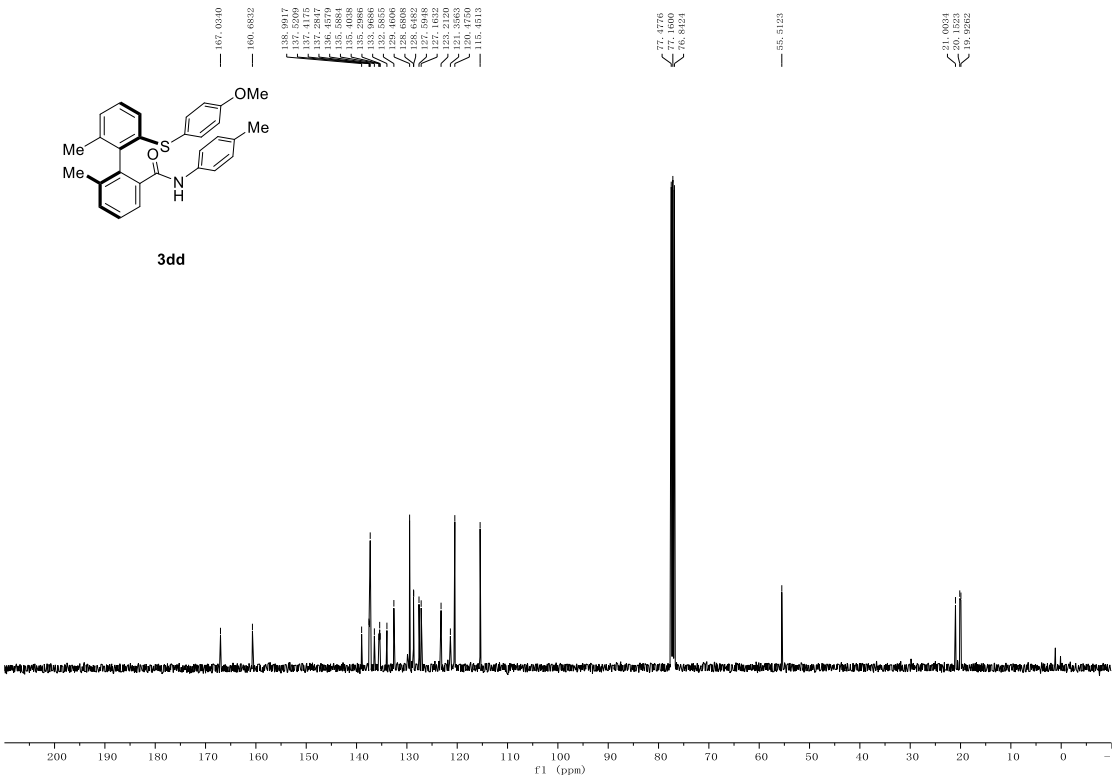


Figure **S89**. ^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3dd**

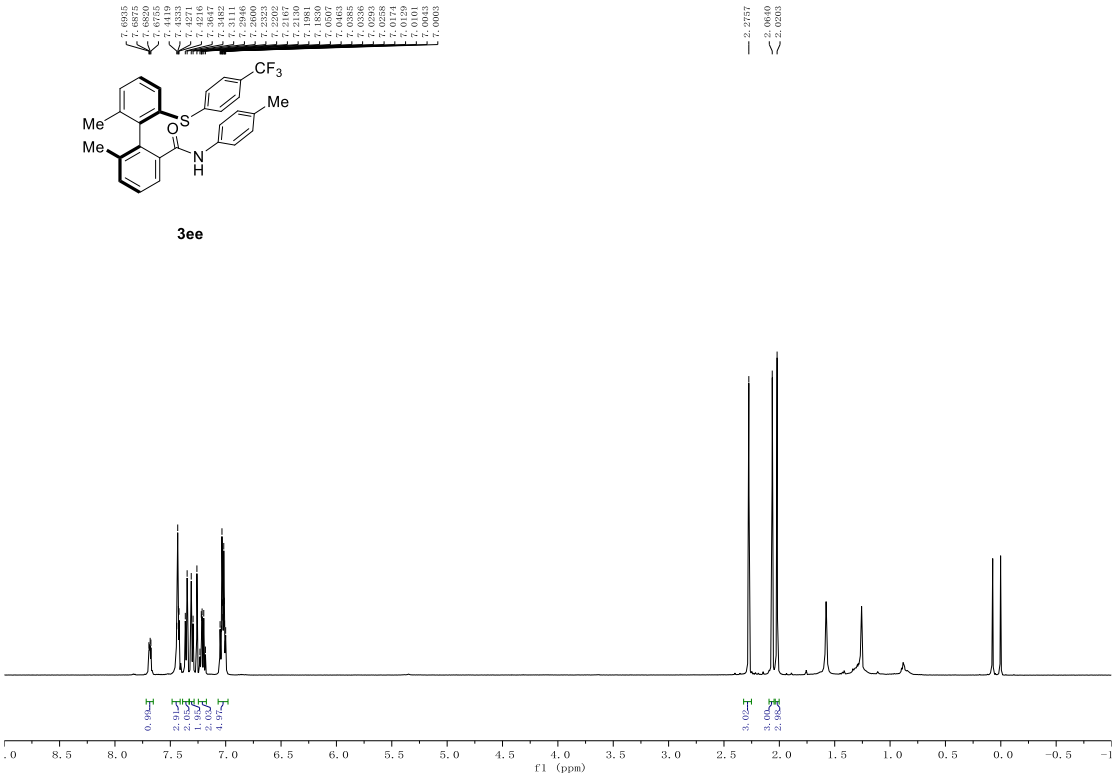


Figure **S90**. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3ee**

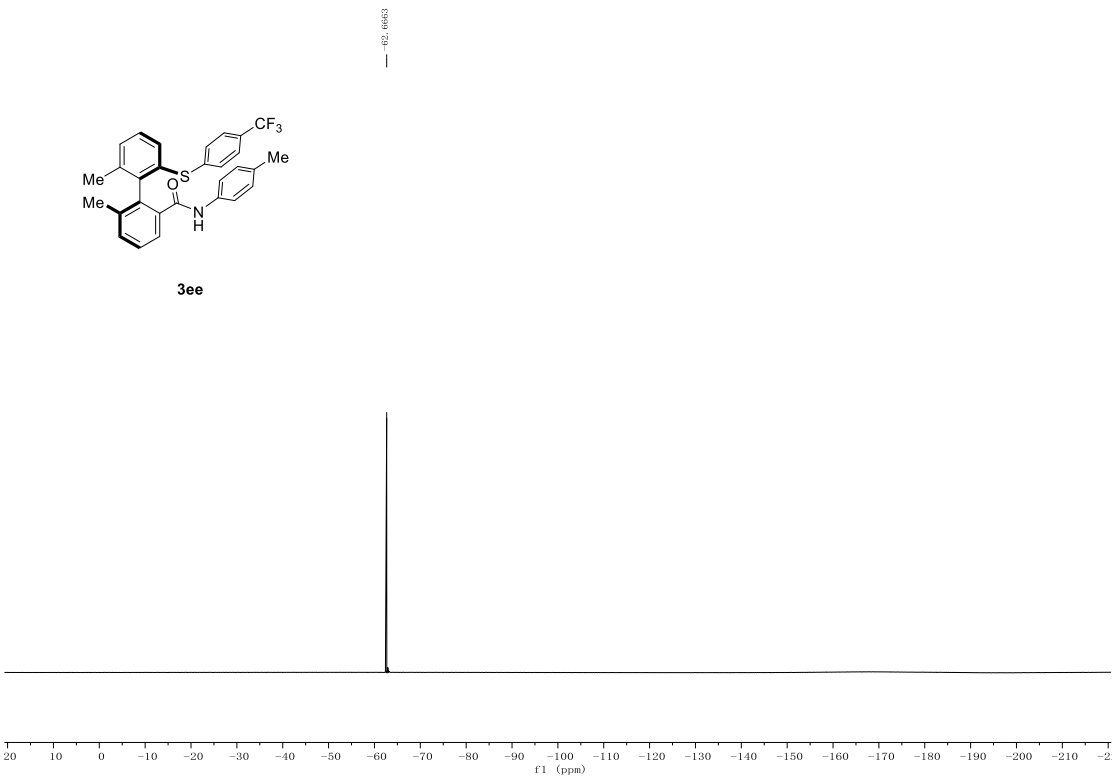


Figure **S91**. ^{19}F NMR spectra (471 MHz, $CDCl_3$) of **3ee**

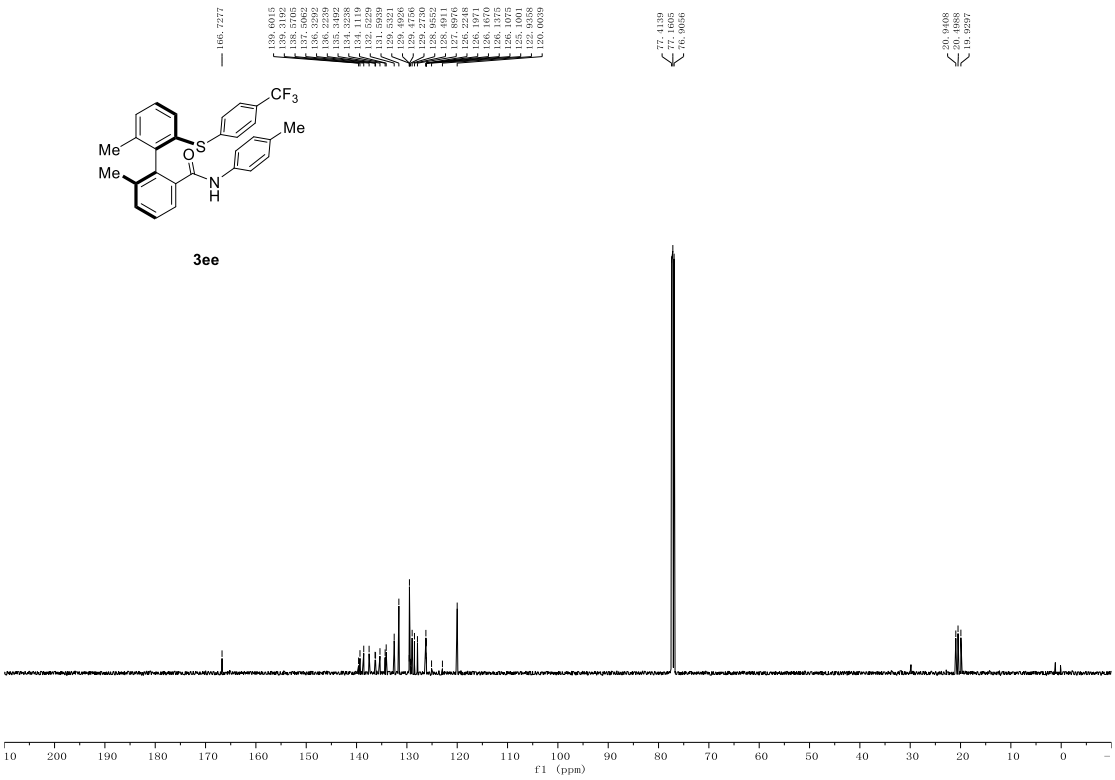


Figure **S92**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3ee**

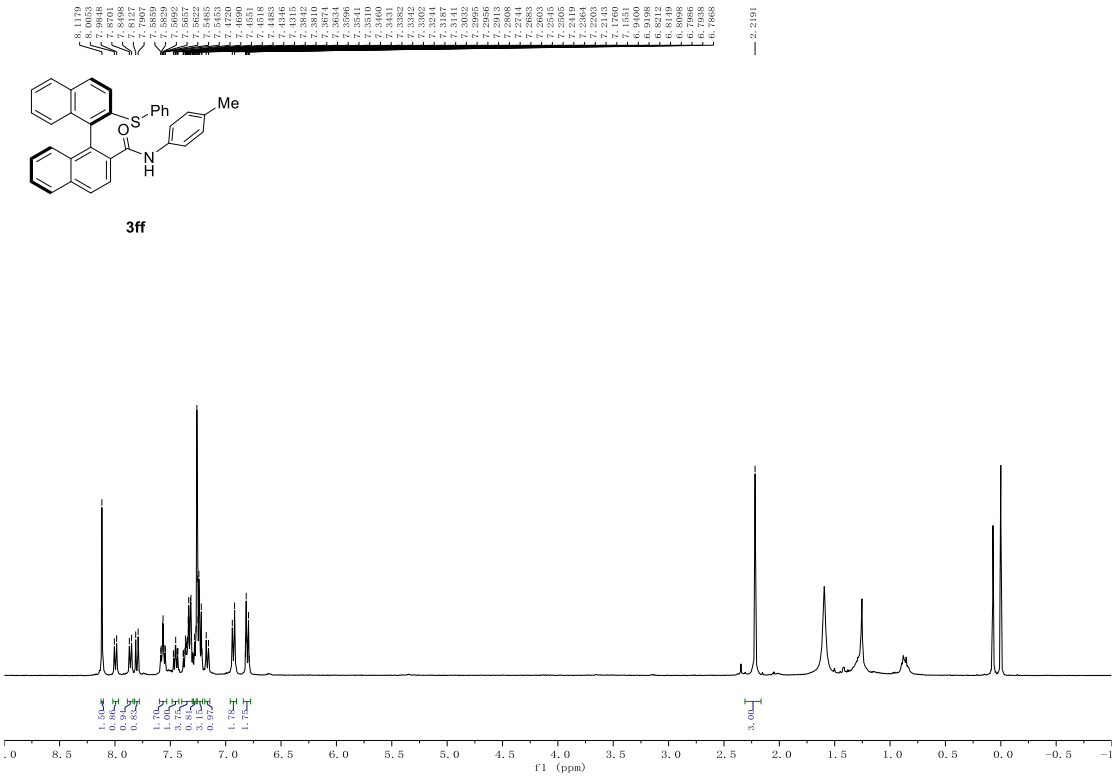


Figure **S93**. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3ff**

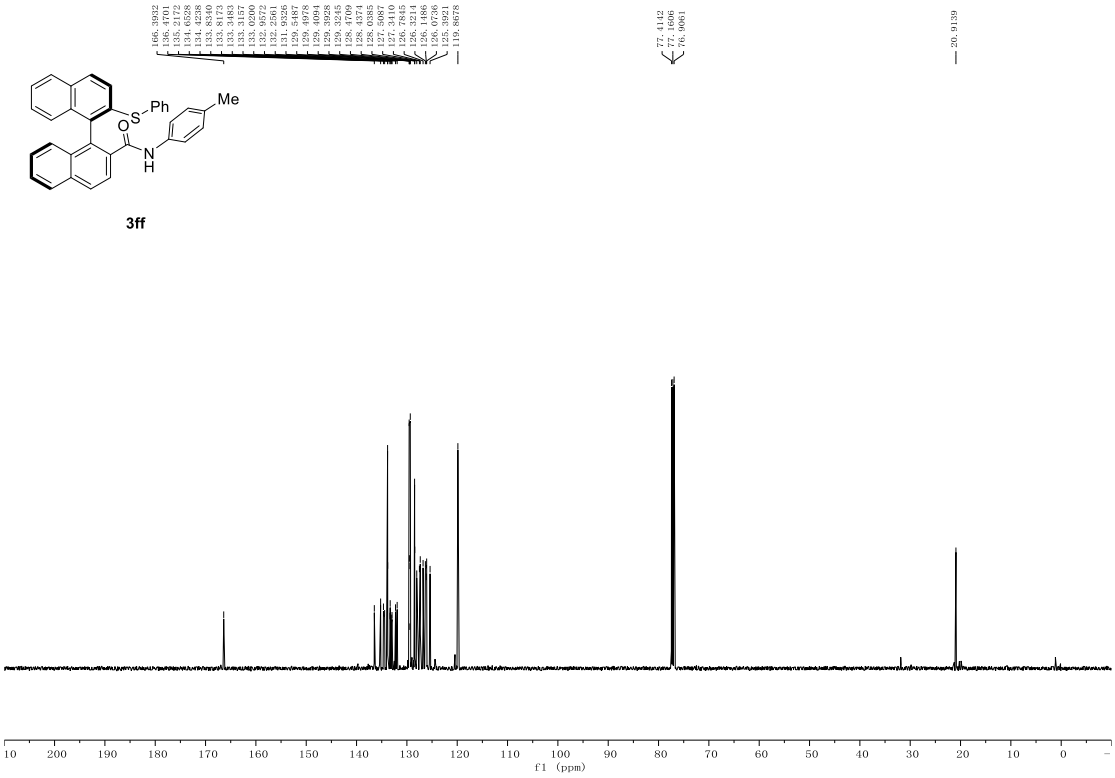


Figure **S94**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3ff**

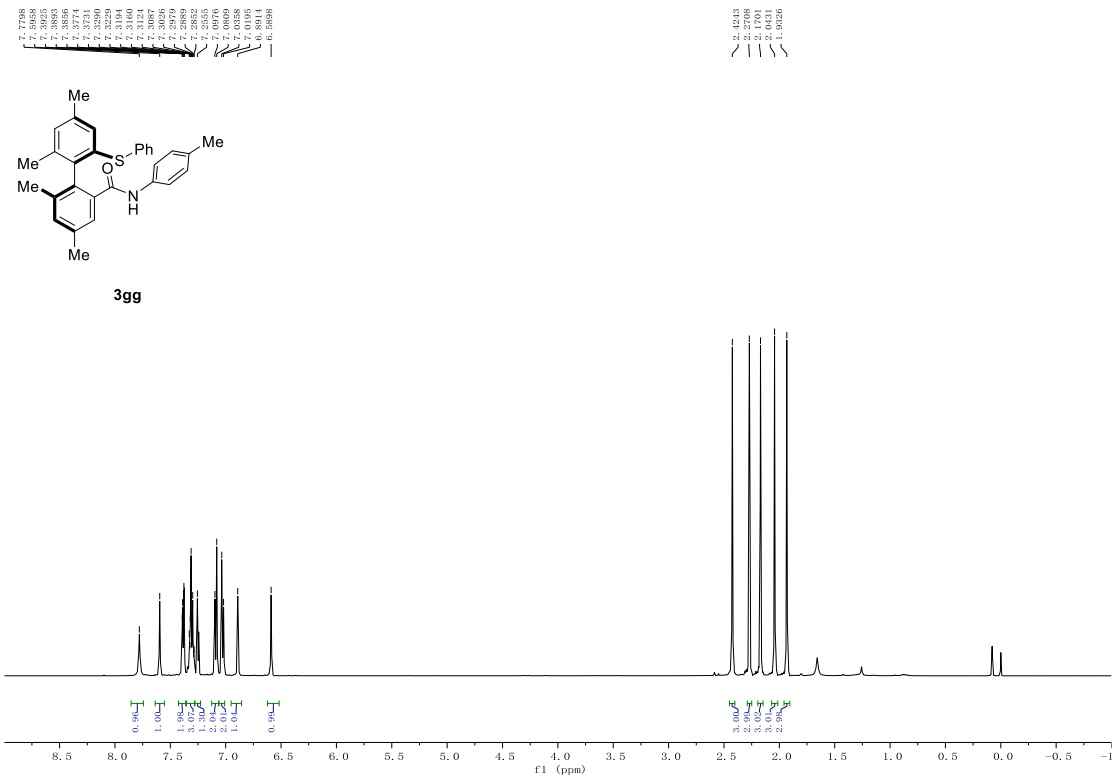


Figure **S95**. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3gg**

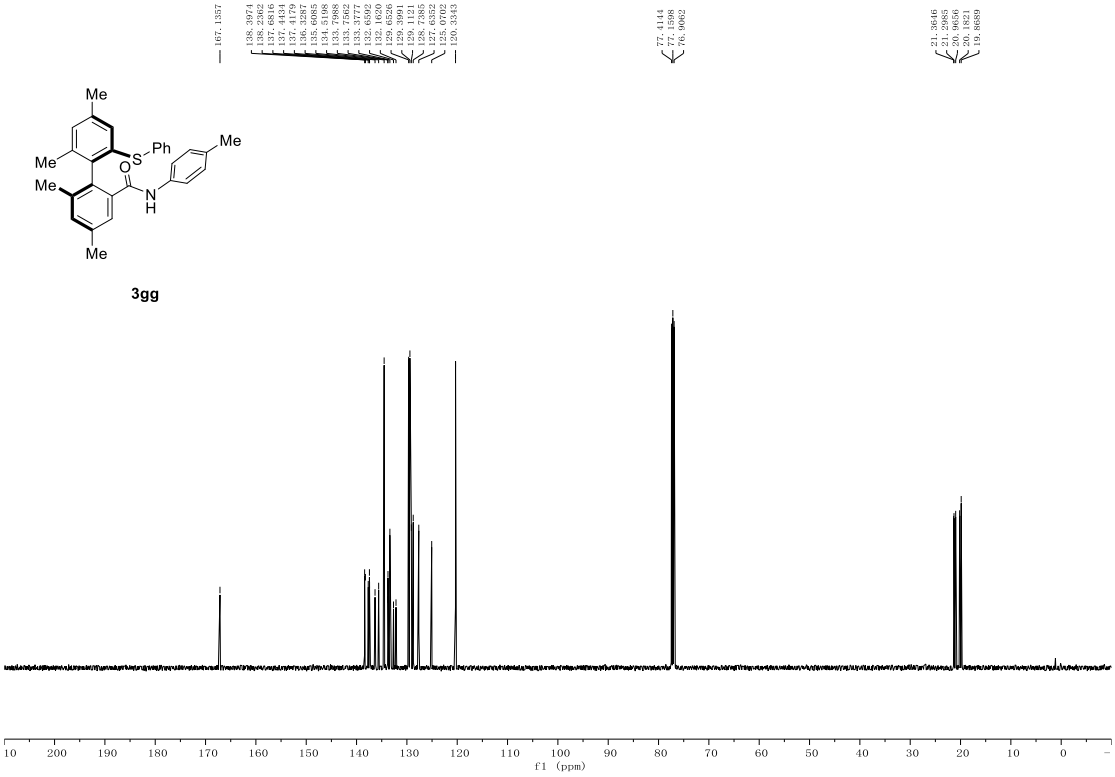


Figure **S96**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3gg**

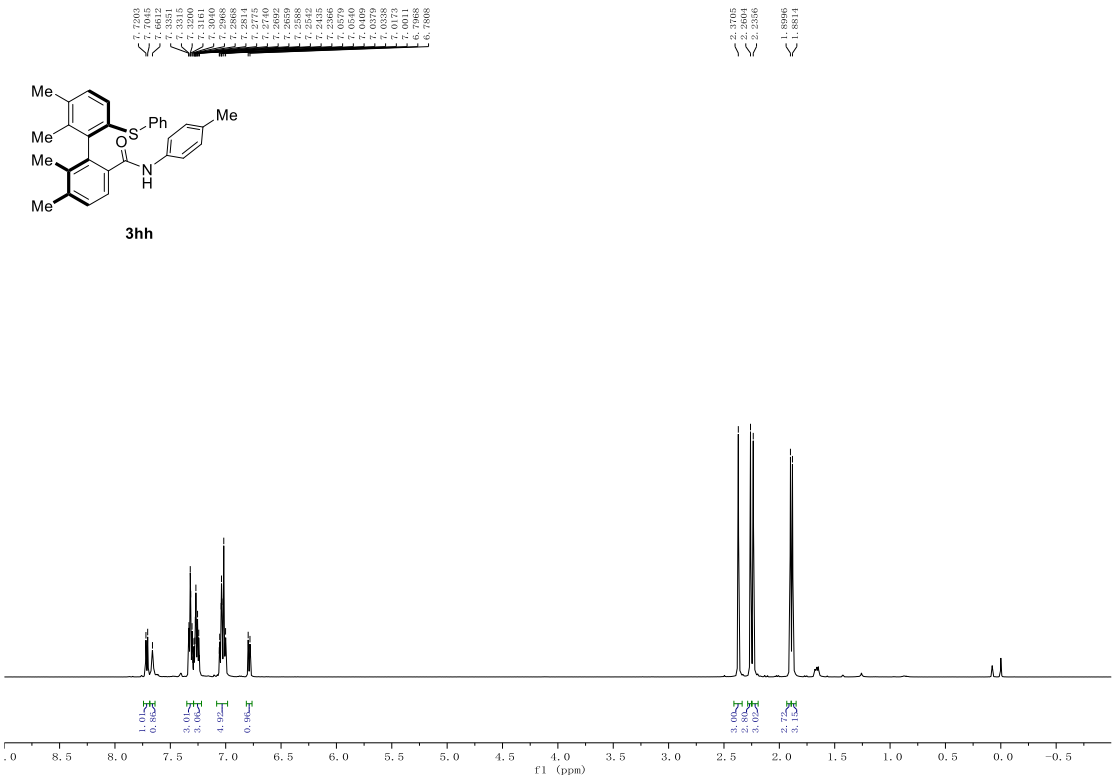


Figure **S97**. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3hh**

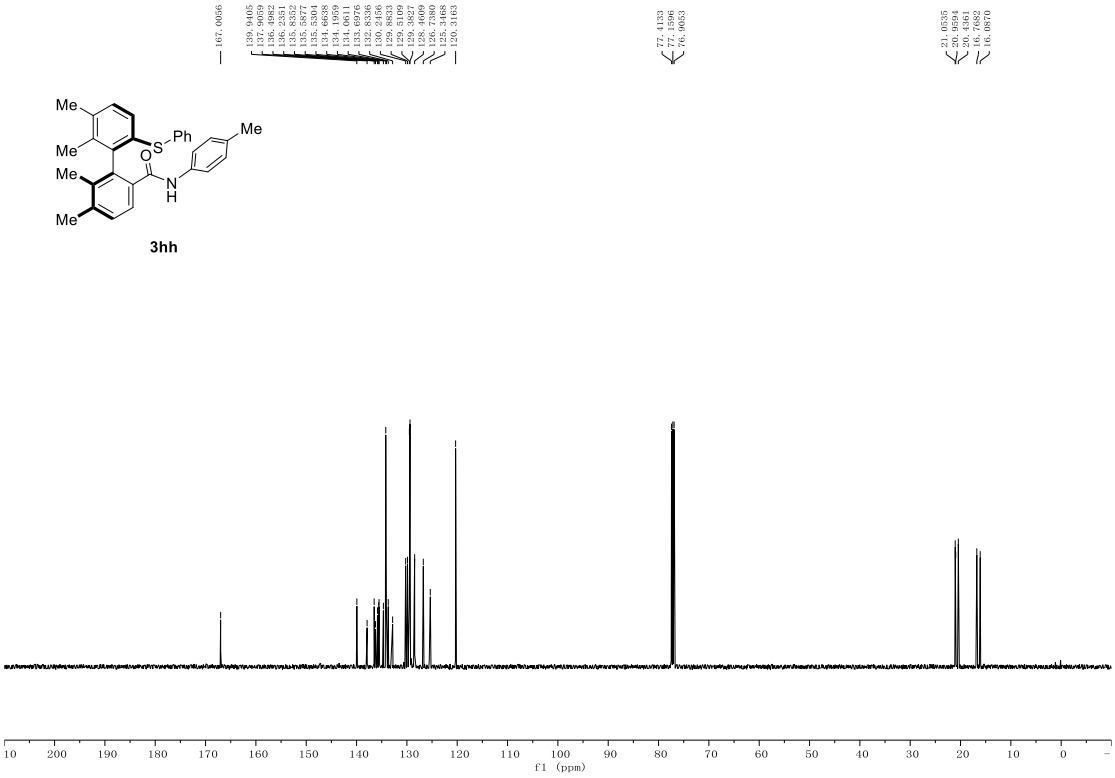
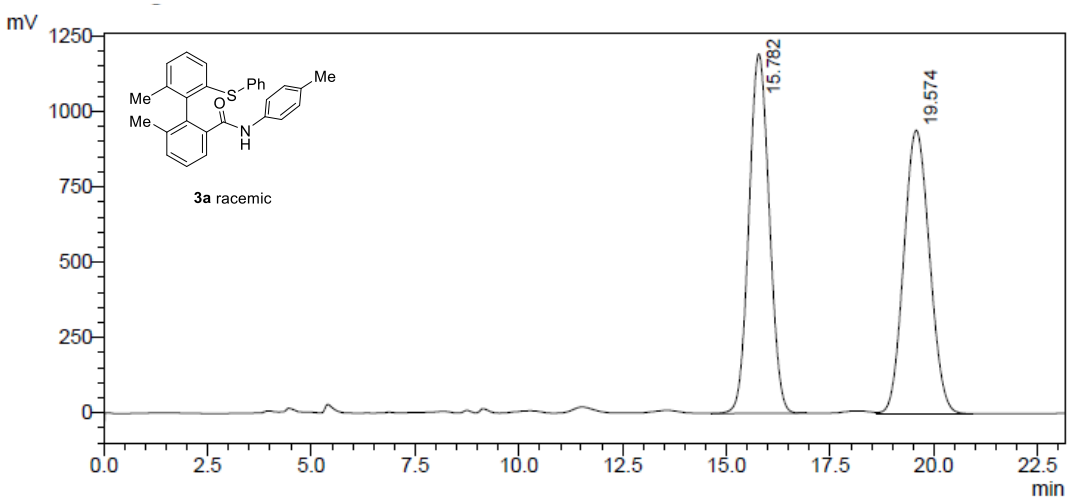


Figure **S98**. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3hh**

5. Copies of HPLC Traces

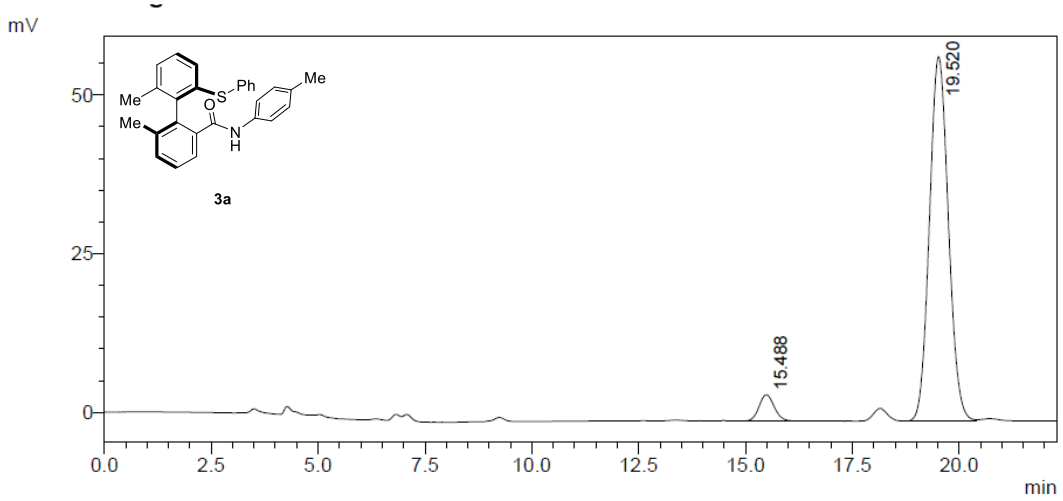


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.782	40651879	1193314	50.045		M	
2	19.574	40577992	941121	49.955		M	
Total		81229872	2134435				

Figure **S99**. HPLC data of racemic **3a**

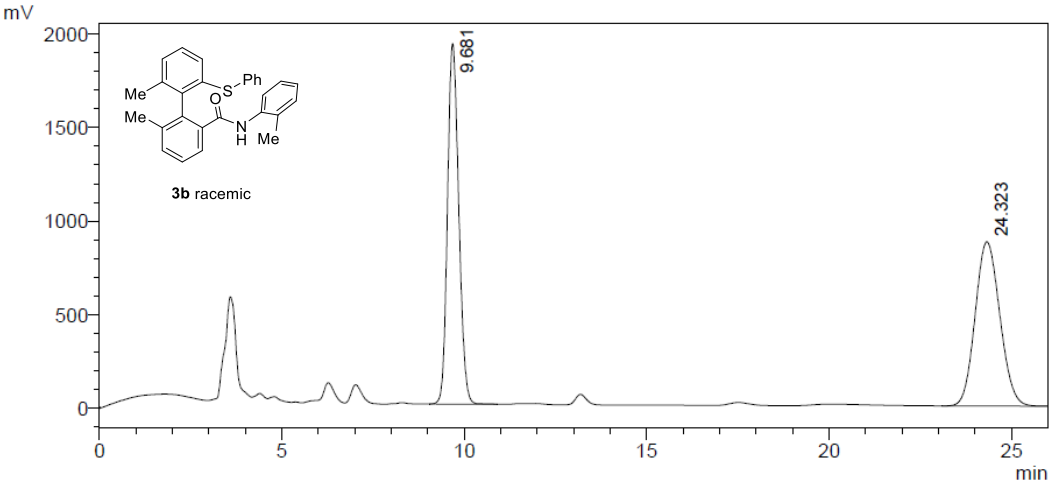


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.488	101747	4134	5.432			
2	19.520	1771299	57417	94.568			
Total		1873046	61551				

Figure **S100**. HPLC data of **3a**

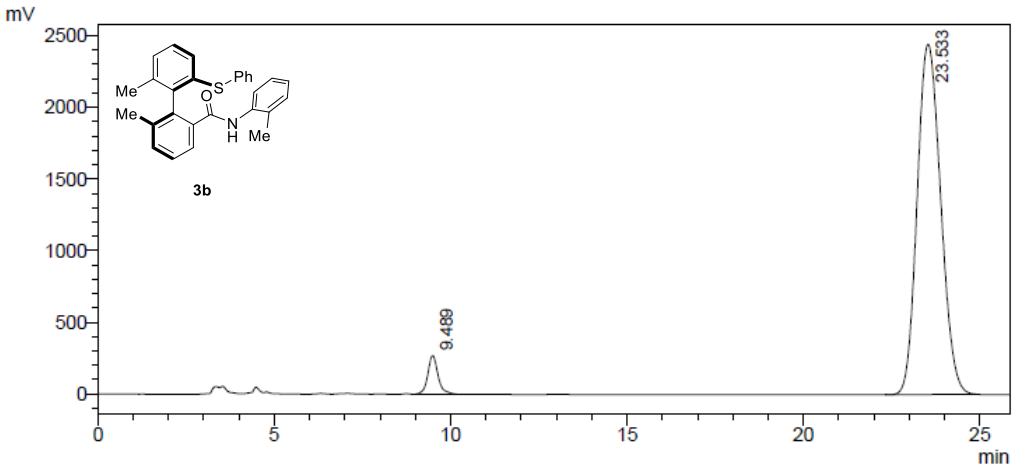


<Peak Table>

Detector A Channel 1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.681	41315791	1924825	50.054			
2	24.323	41226154	877081	49.946			
Total		82541944	2801906				

Figure **S101**. HPLC data of racemic **3b**

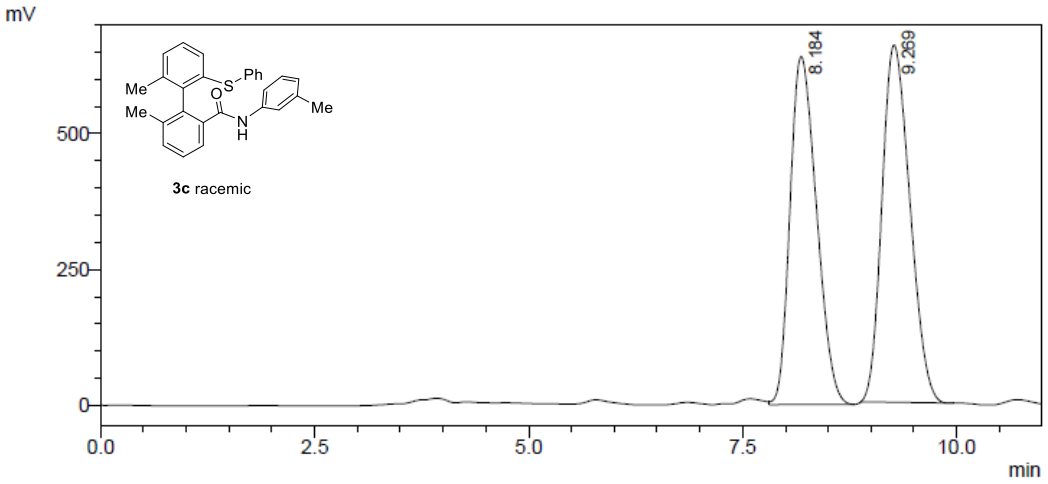


<Peak Table>

Detector A Channel 1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.489	5449628	269606	4.587			
2	23.533	113363309	2442572	95.413		M	
Total		118812937	2712178				

Figure **S102**. HPLC data of **3b**

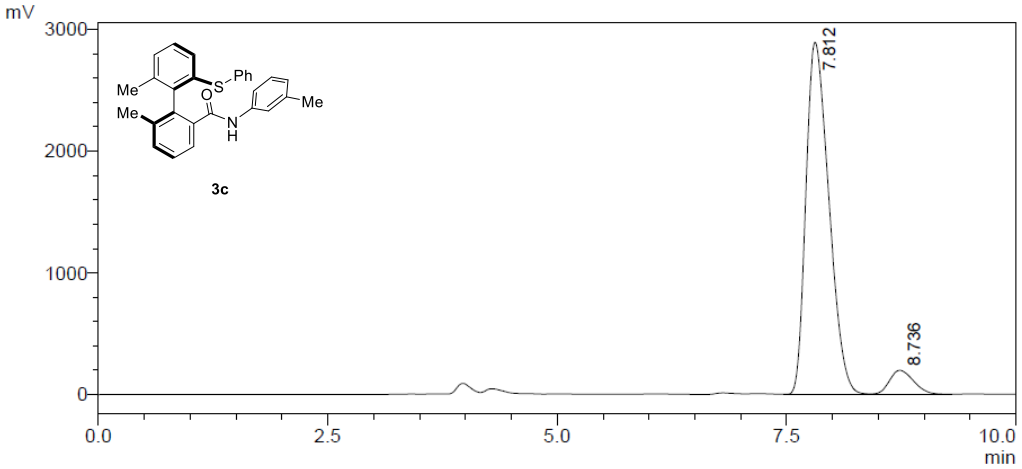


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.184	13785446	640814	48.037			
2	9.269	14911915	657244	51.963		M	
Total		28697361	1298058				

Figure **S103**. HPLC data of racemic **3c**

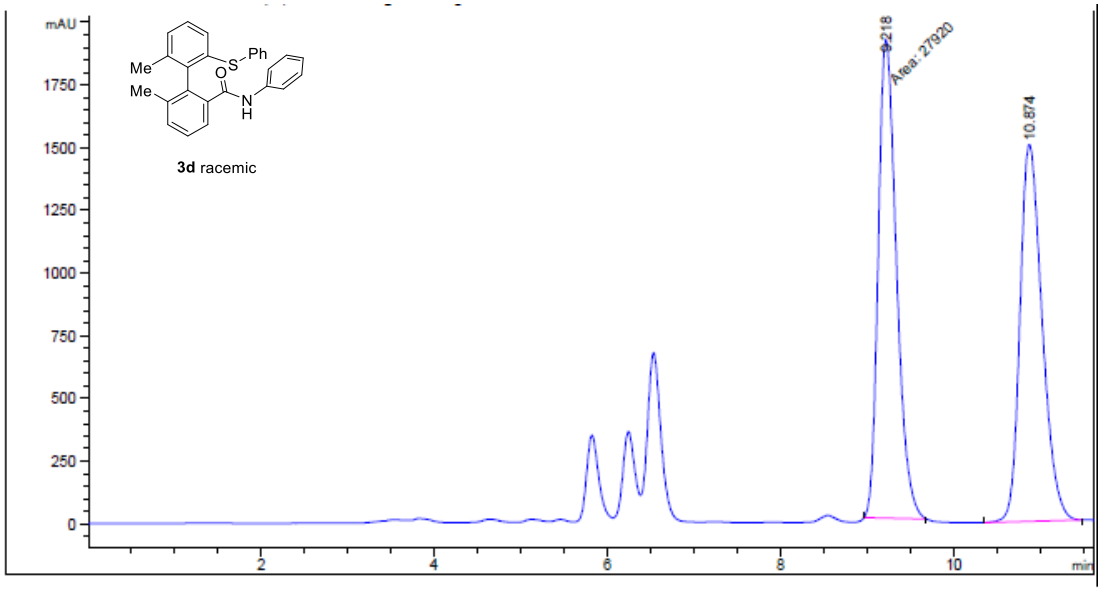


<Peak Table>

Detector A Channel 1 254nm

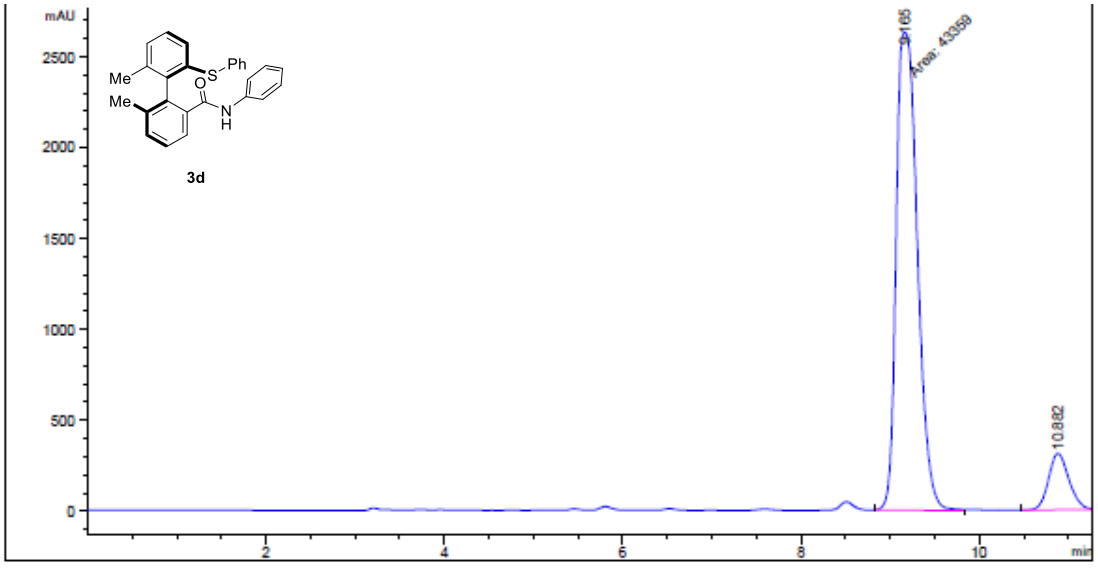
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.812	50591178	2893217	93.153			
2	8.736	3718596	199045	6.847		V	
Total		54309774	3092262				

Figure **S104**. HPLC data of **3c**



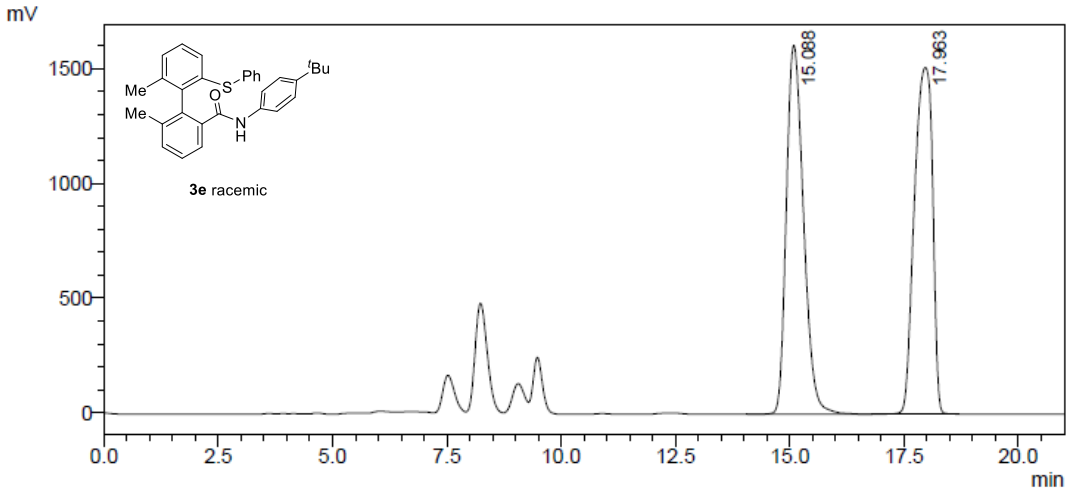
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.218	MM	0.2439	2.79200e4	1907.96667	51.1286
2	10.874	BB	0.2732	2.66874e4	1502.36133	48.8714

Figure **S105**. HPLC data of racemic **3d**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.165	MM	0.2747	4.33590e4	2630.26611	89.7722
2	10.882	BBA	0.2436	4939.92383	310.54840	10.2278
Totals :				4.82989e4	2940.81451	

Figure **S106**. HPLC data of **3d**

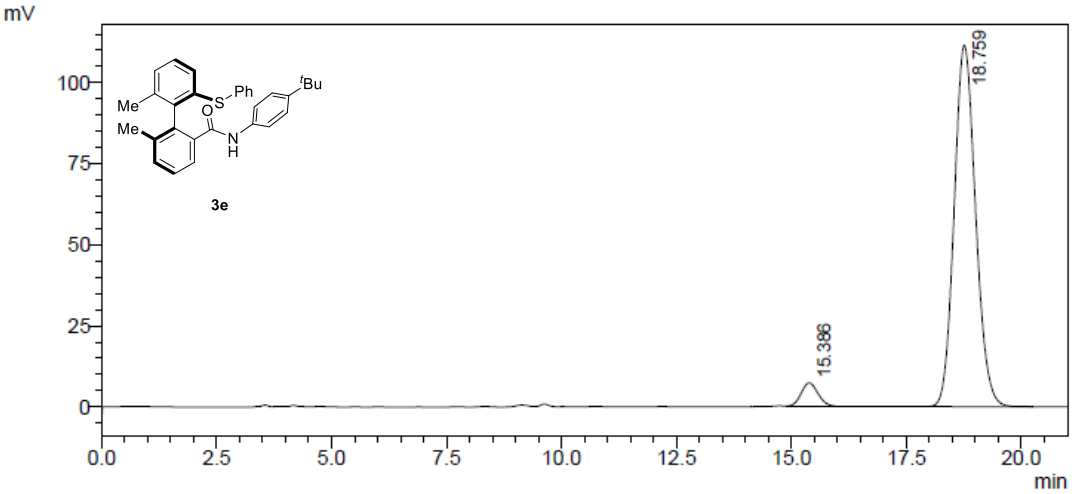


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.088	42086334	1606203	50.108			
2	17.963	41904672	1509682	49.892		M	
Total		83991005	3115885				

Figure **S107**. HPLC data of racemic **3e**

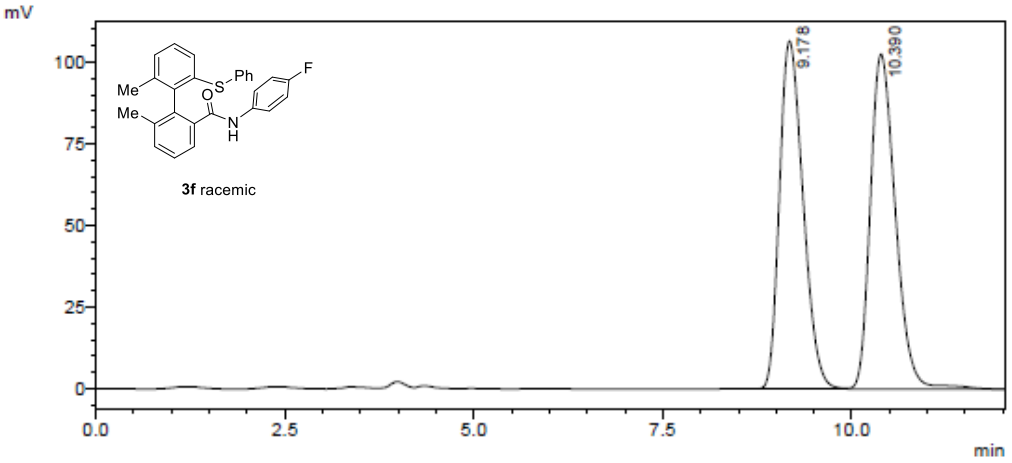


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.386	189398	7286	4.987			
2	18.759	3608597	111421	95.013		S	
Total		3797995	118708				

Figure **S108**. HPLC data of **3e**

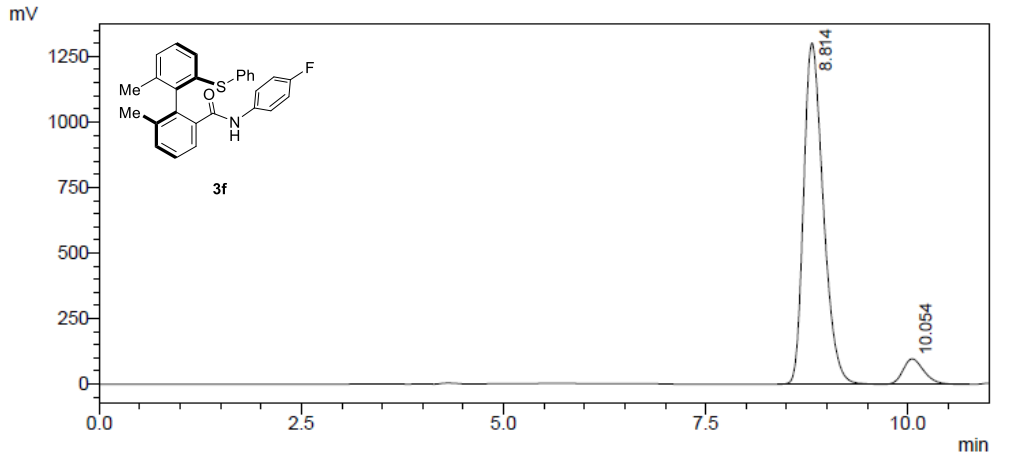


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.178	2320548	106595	49.429			
2	10.390	2374162	102614	50.571		V	
Total		4694709	209209				

Figure **S109**. HPLC data of racemic **3f**

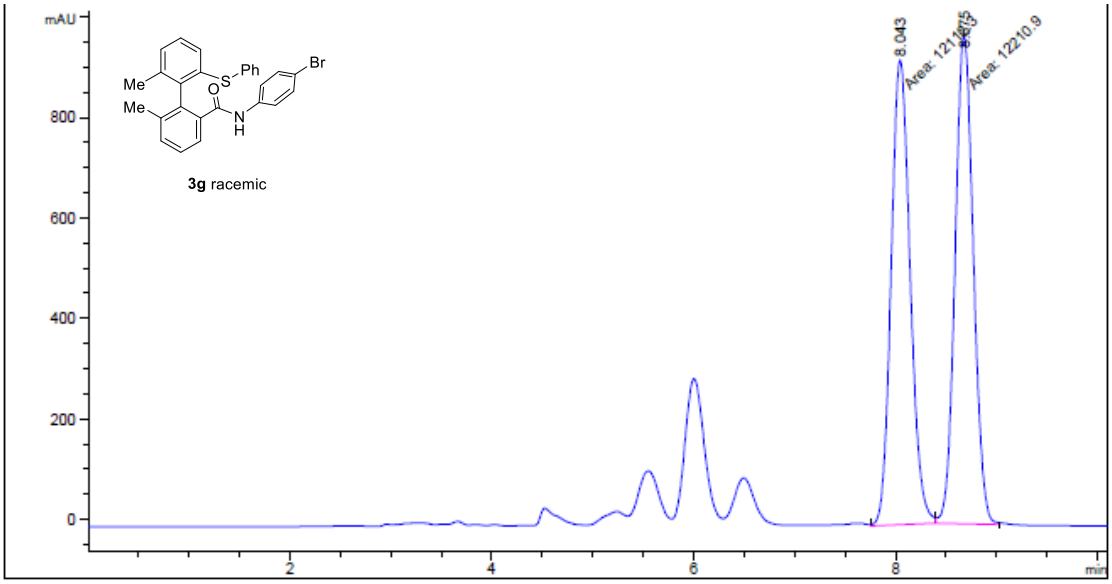


<Peak Table>

Detector A Channel 1 254nm

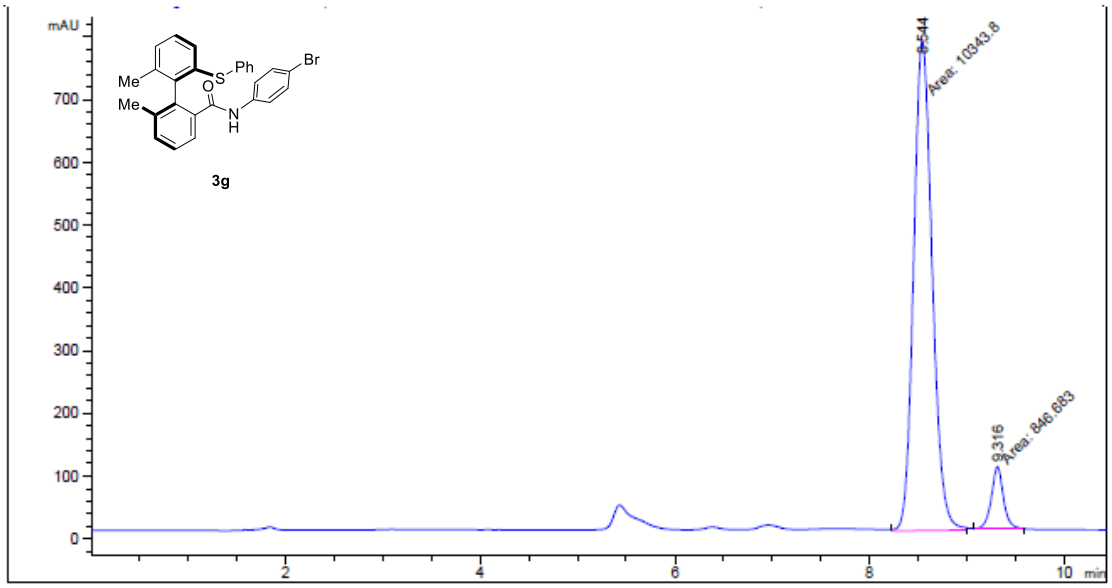
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.814	21980997	1301877	92.562			
2	10.054	1766382	97039	7.438		V	
Total		23747379	1398916				

Figure **S110**. HPLC data of **3f**



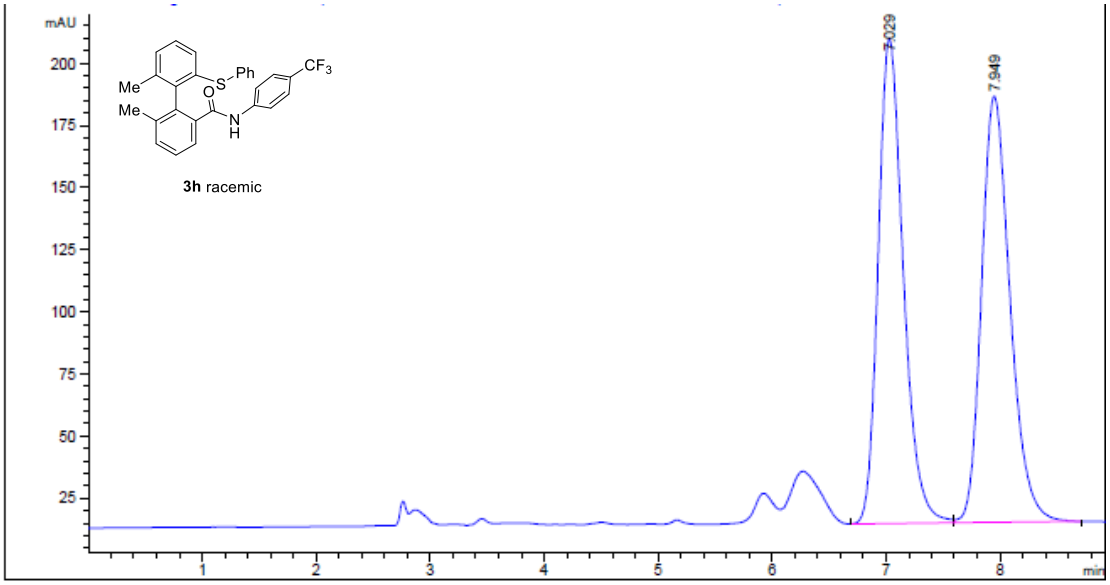
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.043	MM	0.2183	1.21123e4	924.67413	49.7972
2	8.675	MM	0.2091	1.22109e4	973.06921	50.2028
Totals :				2.43232e4	1897.74335	

Figure **S111**. HPLC data of racemic **3g**



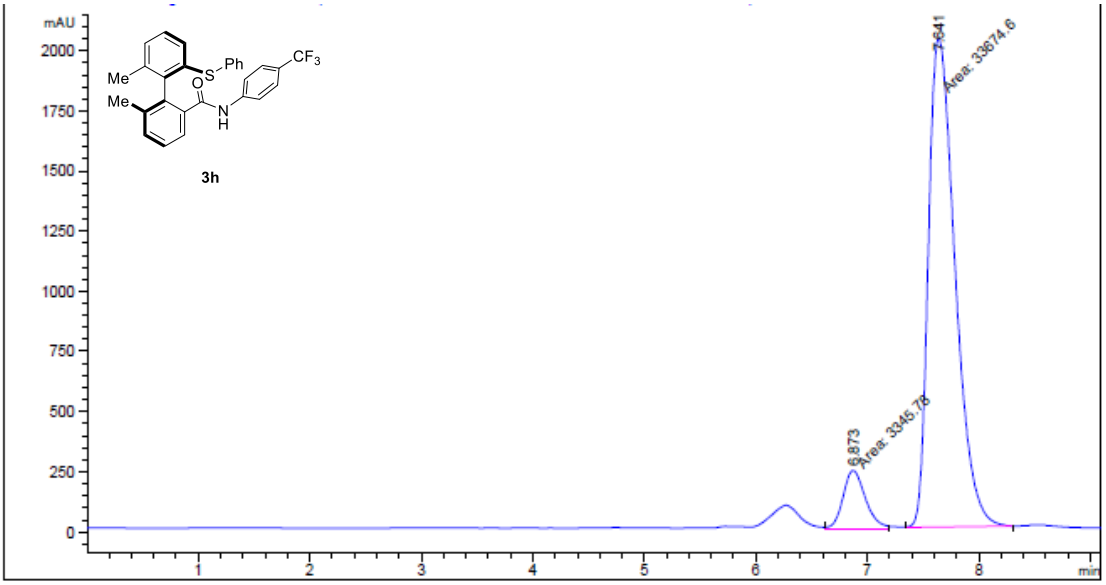
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.544	MM	0.2210	1.03438e4	780.08673	92.4339
2	9.316	MM	0.1423	846.68317	99.19771	7.5661
Totals :				1.11905e4	879.28444	

Figure **S112**. HPLC data of **3g**



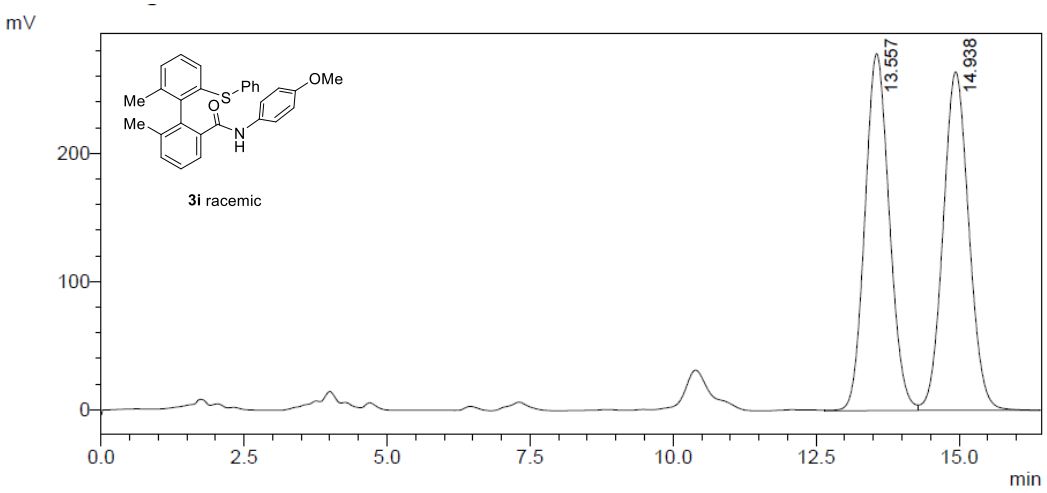
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.029	BV	0.2367	2988.20947	195.13609	50.0726
2	7.949	VB	0.2688	2979.54736	171.40535	49.9274
Totals :				5967.75684	366.54144	

Figure **S113**. HPLC data of racemic **3h**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.873	MM	0.2316	3345.78491	240.75006	9.0377
2	7.641	MM	0.2763	3.36746e4	2031.45410	90.9623
Totals :				3.70204e4	2272.20416	

Figure **S114**. HPLC data of racemic **3h**

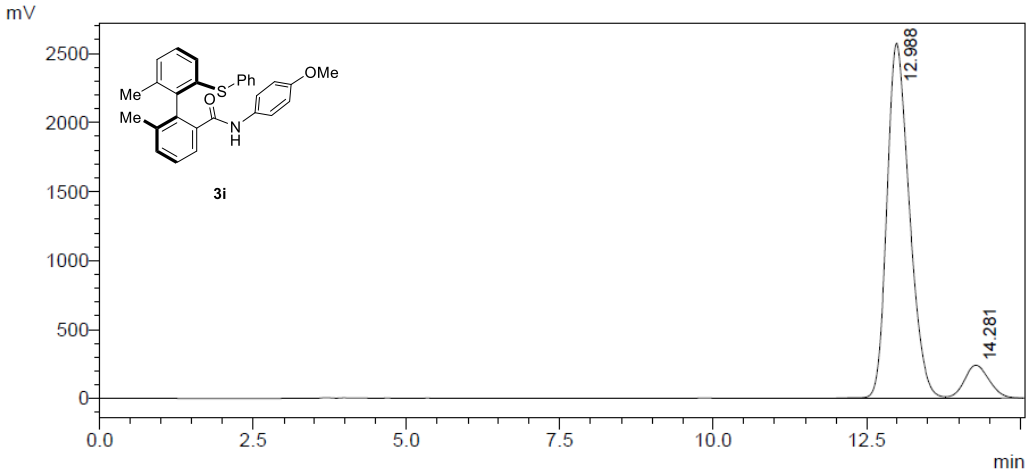


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.557	8262543	278155	49.984			
2	14.938	8267977	263817	50.016		V	
Total		16530520	541973				

Figure **S115**. HPLC data of racemic **3i**

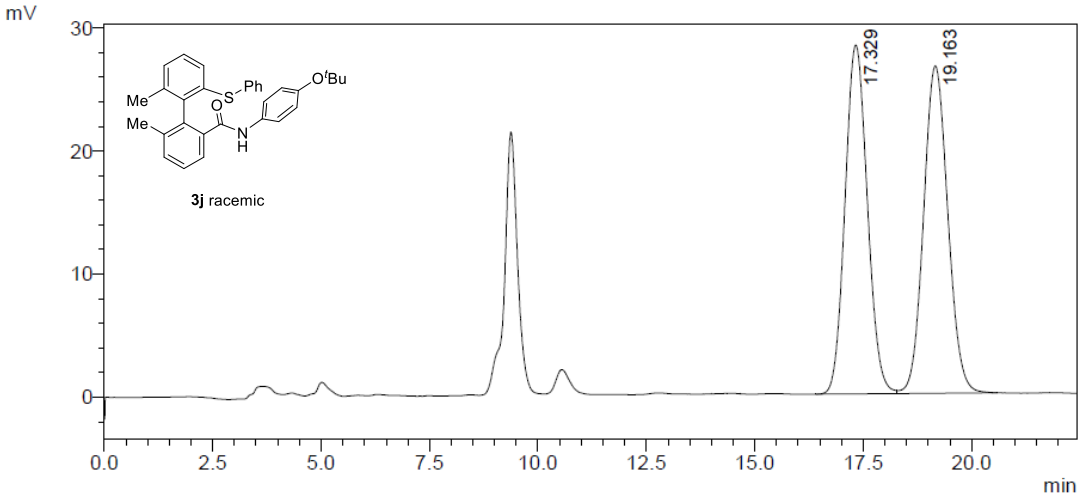


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.988	65641138	2574321	90.714			
2	14.281	6719358	239114	9.286		V	
Total		72360496	2813435				

Figure **S116**. HPLC data of **3i**

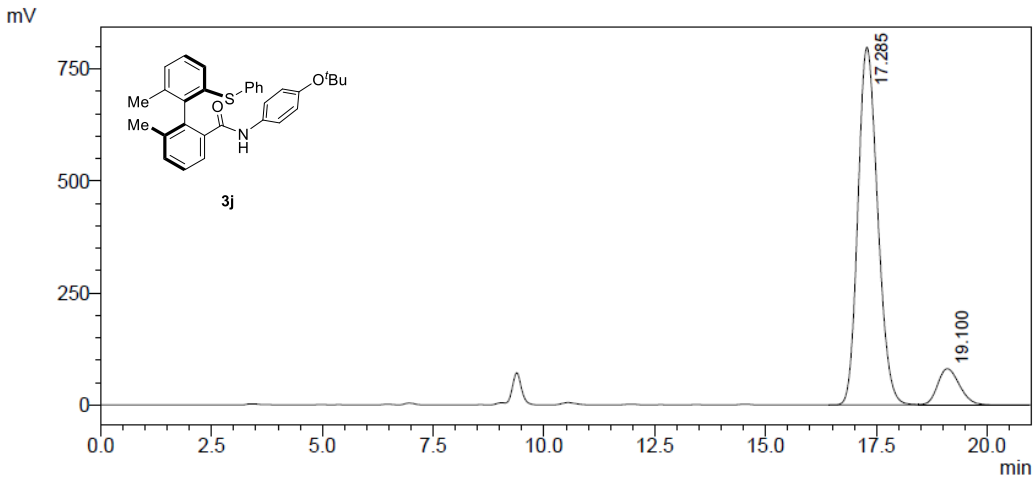


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.329	1014587	28331	49.513			
2	19.163	1034537	26596	50.487		SV	
Total		2049124	54926				

Figure **S117**. HPLC data of racemic **3j**

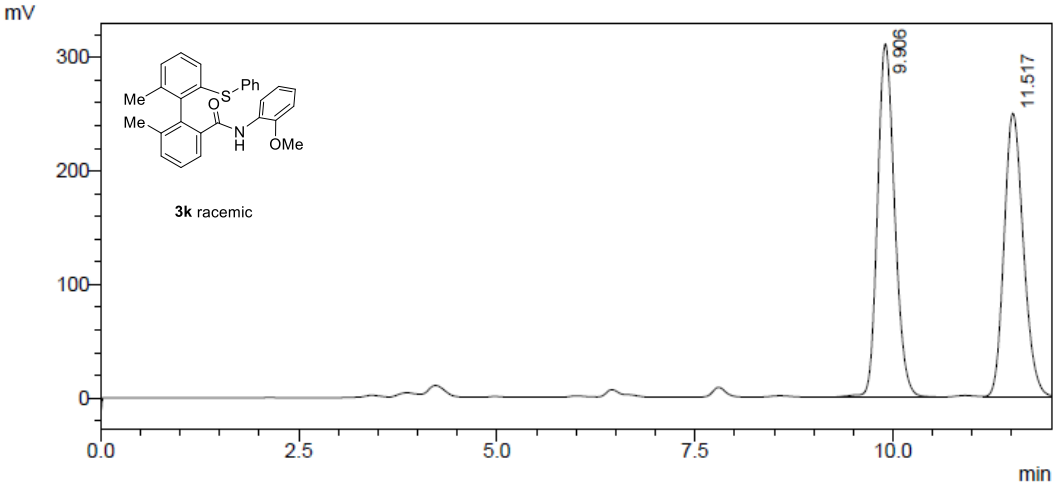


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.285	24767889	798698	89.903			
2	19.100	2781676	80846	10.097		SV	
Total		27549565	879544				

Figure **S118**. HPLC data of racemic **3j**

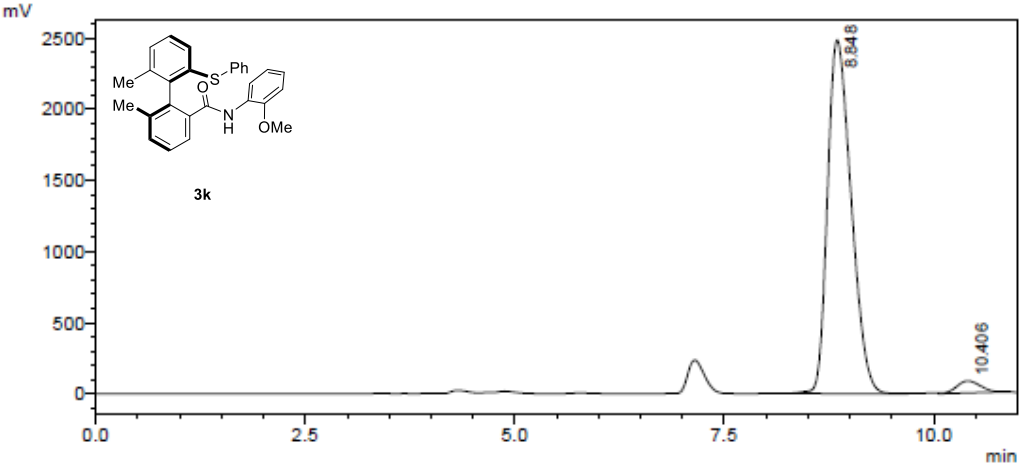


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.906	4697846	310941	52.451			
2	11.517	4258836	249891	47.549			
Total		8956682	560832				

Figure **S119**. HPLC data of racemic **3k**

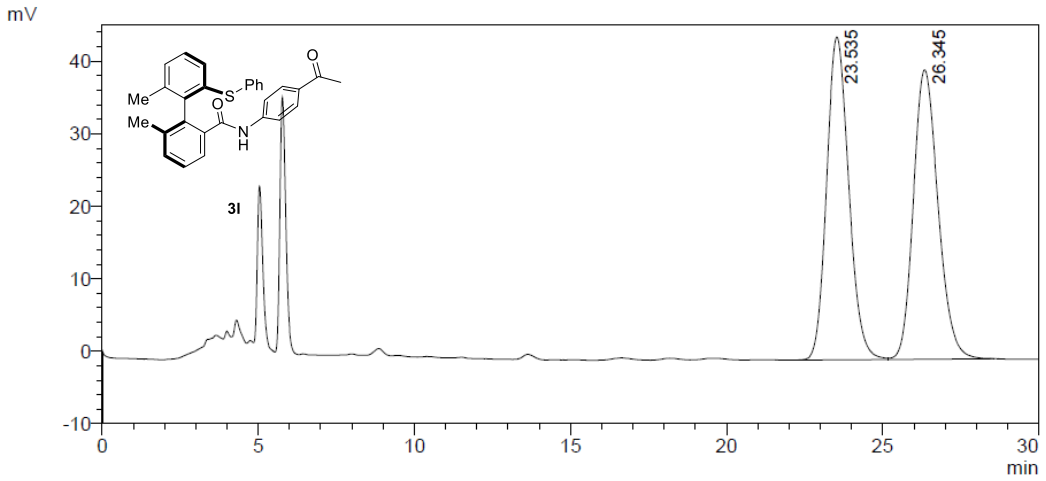


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.848	48915041	2484208	96.675		M	
2	10.406	1682155	84402	3.325		M	
Total		50597196	2568610				

Figure **S120**. HPLC data of **3k**

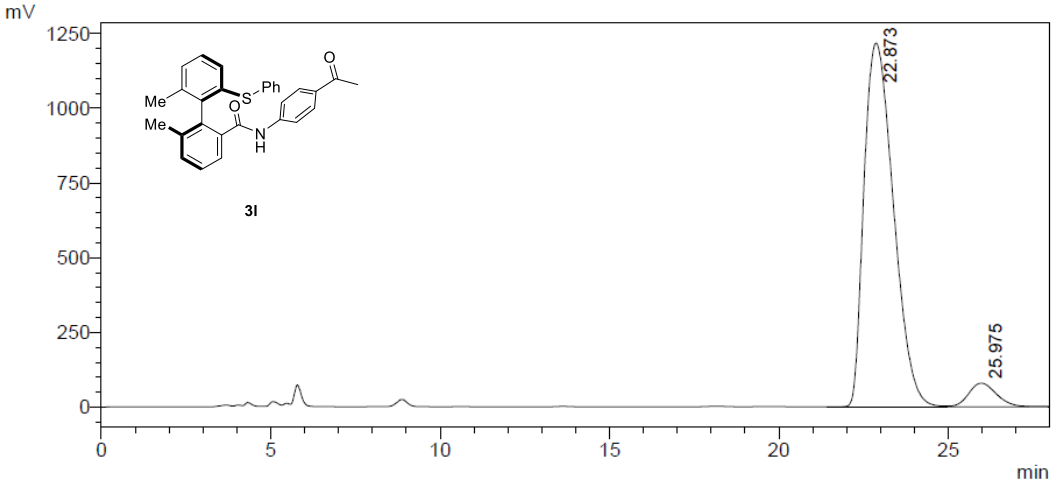


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	23.535	2197267	44503	49.997		V	
2	26.345	2197537	39912	50.003		SV	
Total		4394805	84414				

Figure **S121**. HPLC data of racemic **3l**

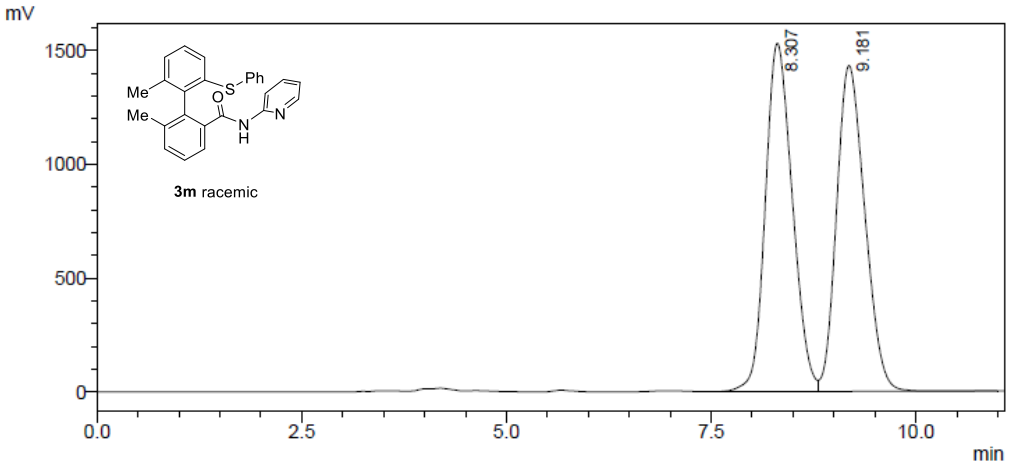


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	22.873	73621608	1216862	94.195		V	
2	25.975	4536751	79357	5.805		V	
Total		78158359	1296219				

Figure **S122**. HPLC data of **3l**

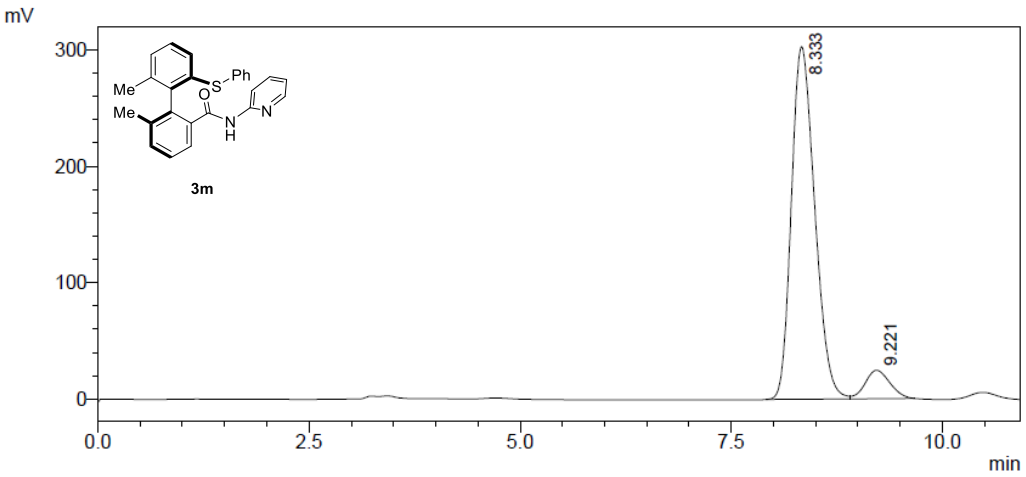


<Peak Table>

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.307	35144759	1530231	50.556			
2	9.181	34371988	1432019	49.444		V	
Total		69516747	2962250				

Figure **S123**. HPLC data of racemic **3m**

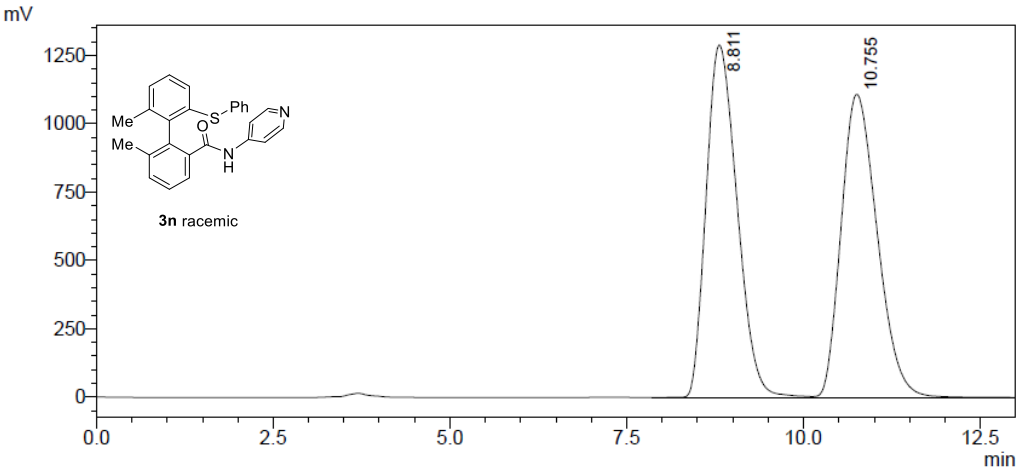


<Peak Table>

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.333	5819715	302523	92.112		M	
2	9.221	498338	24399	7.888		V M	
Total		6318053	326921				

Figure **S124**. HPLC data of **3m**

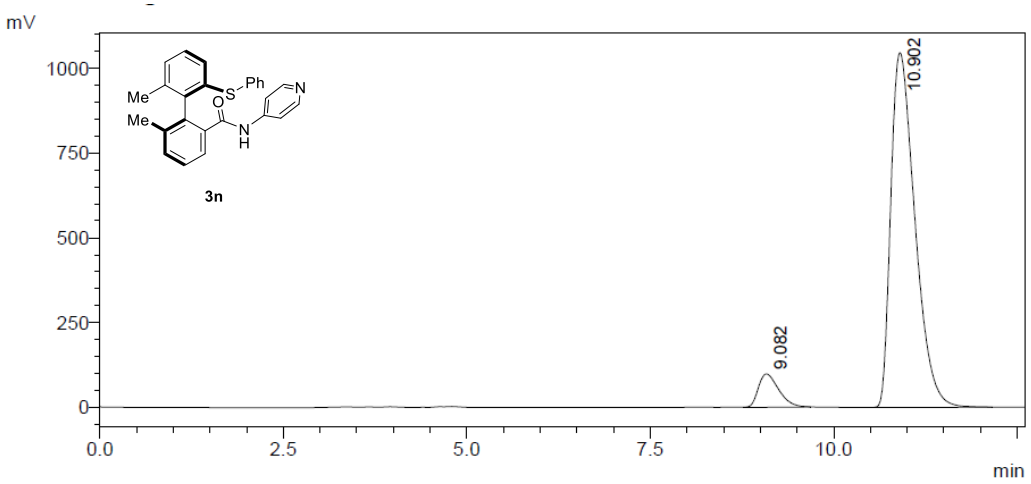


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.811	39403726	1289848	49.954			
2	10.755	39476383	1109811	50.046		V	
Total		78880109	2399658				

Figure **S125**. HPLC data of racemic **3n**

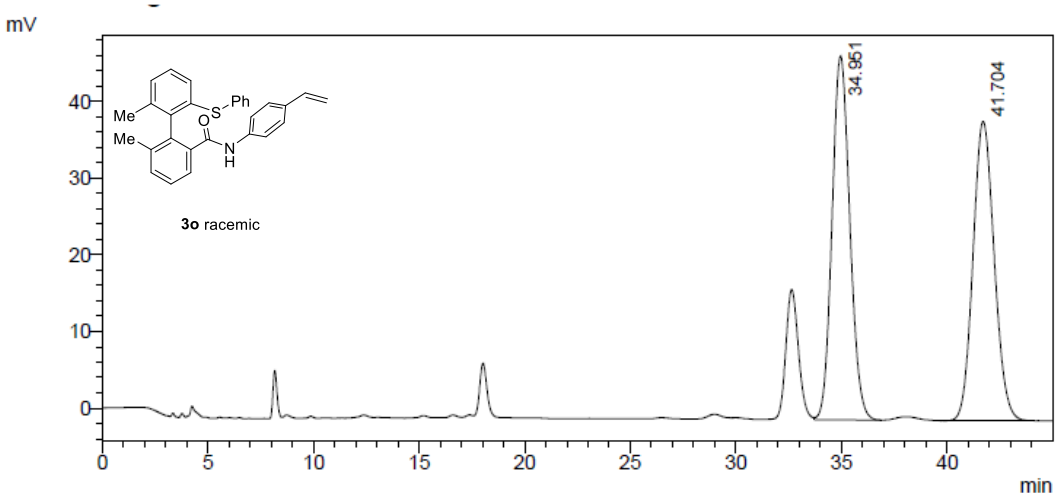


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.082	1902461	98445	7.364		M	
2	10.902	23933727	1046468	92.636		M	
Total		25836188	1144912				

Figure **S126**. HPLC data of **3n**

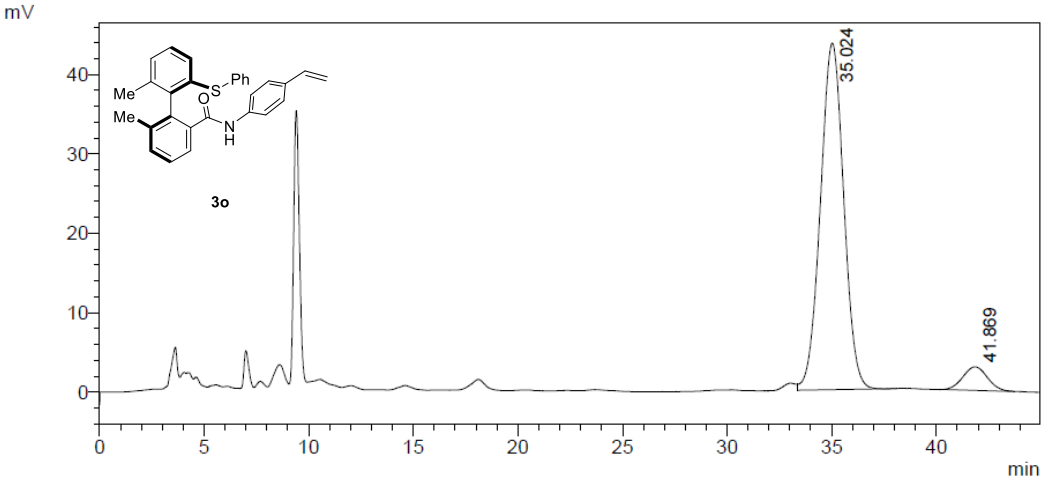


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	34.951	2780432	47477	50.524			
2	41.704	2722807	39017	49.476		V	
Total		5503239	86494				

Figure **S127**. HPLC data of racemic **3o**

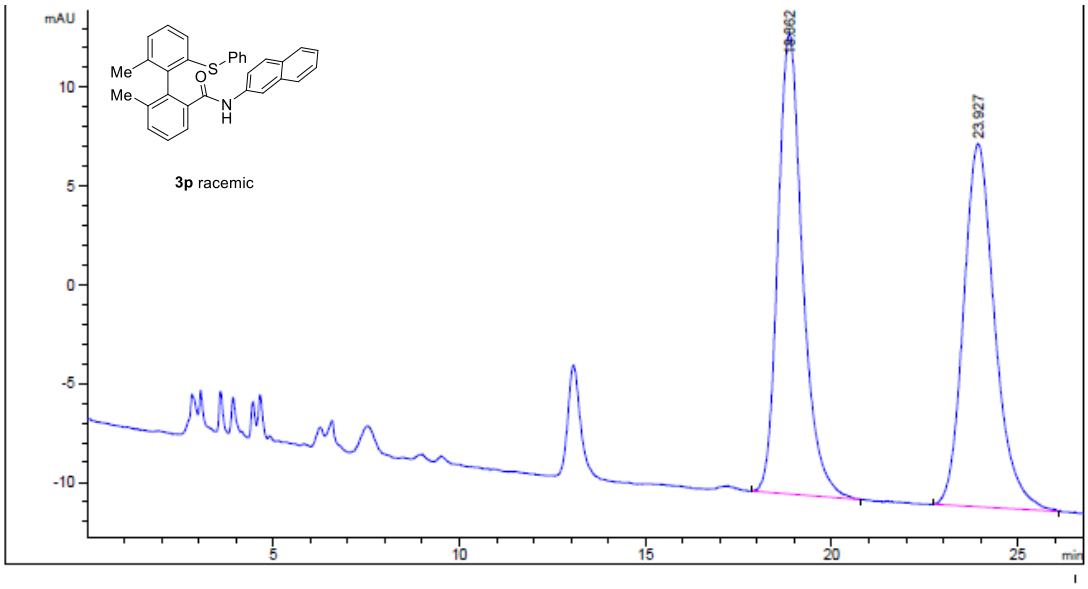


<Peak Table>

Detector A Channel 1 254nm

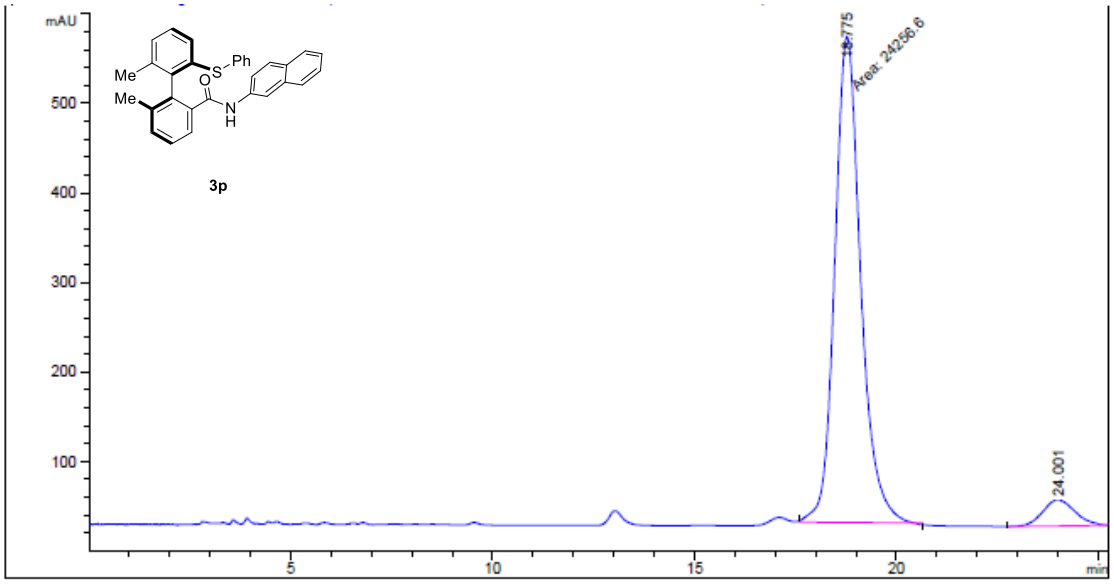
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	35.024	3382401	43680	93.314		S	
2	41.869	242332	2974	6.686			
Total		3624733	46654				

Figure **S128**. HPLC data of **3o**



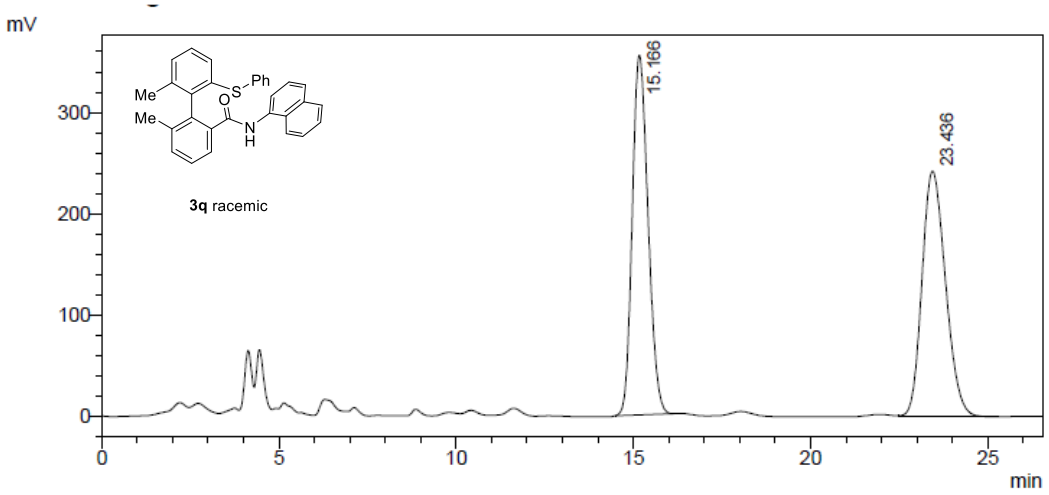
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.862	BB	0.6943	1071.35132	23.30531	49.9495
2	23.927	BB	0.8233	1073.51587	18.38181	50.0505

Figure **S129**. HPLC data of racemic **3p**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.775	MM	0.7452	2.42566e4	542.50702	93.8061
2	24.001	BBA	0.7521	1601.62585	29.10103	6.1939
Totals :				2.58582e4	571.60805	

Figure **S130**. HPLC data of **3p**

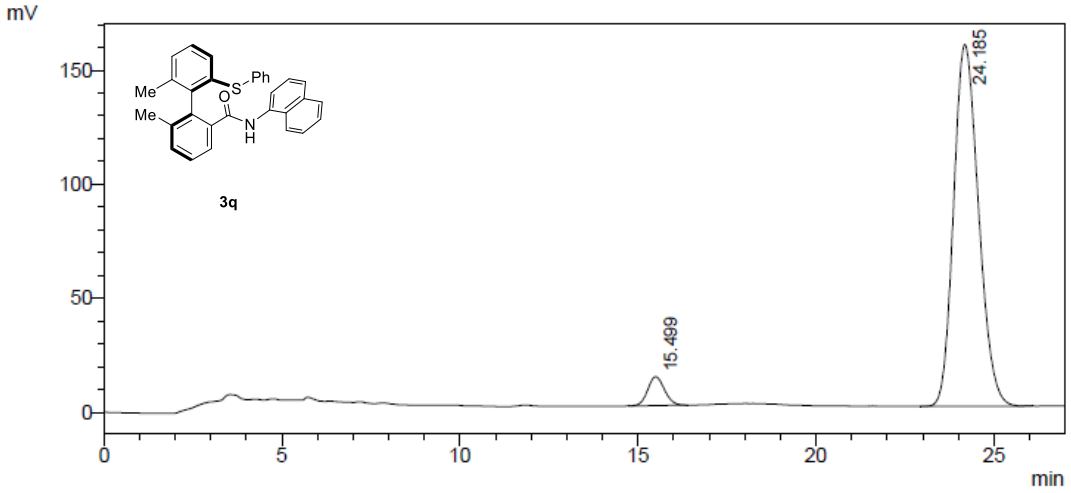


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.166	11035965	355278	49.622		M	
2	23.436	11204318	242485	50.378		S	
Total		22240283	597763				

Figure **S131**. HPLC data of racemic **3q**

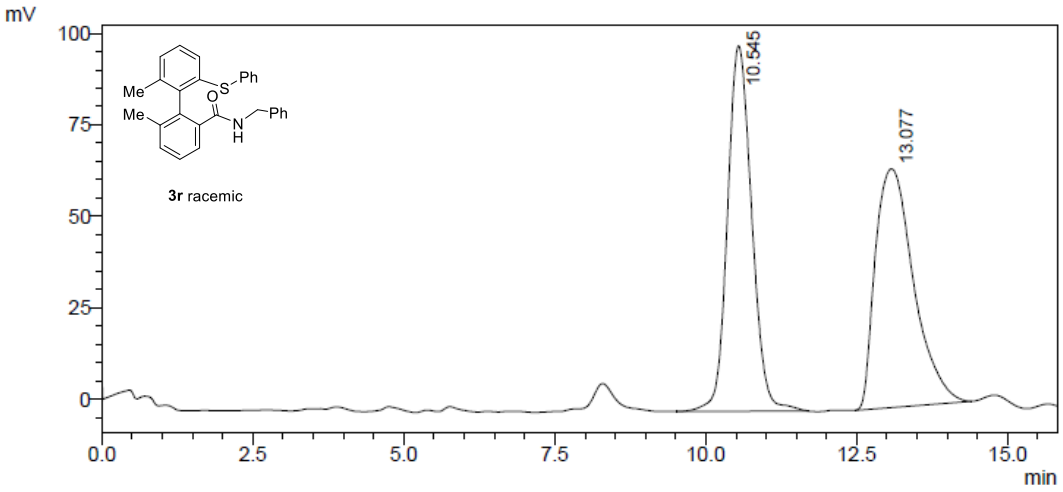


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.499	412537	12612	5.063		M	
2	24.185	7735136	158685	94.937		M	
Total		8147673	171297				

Figure **S132**. HPLC data of **3q**

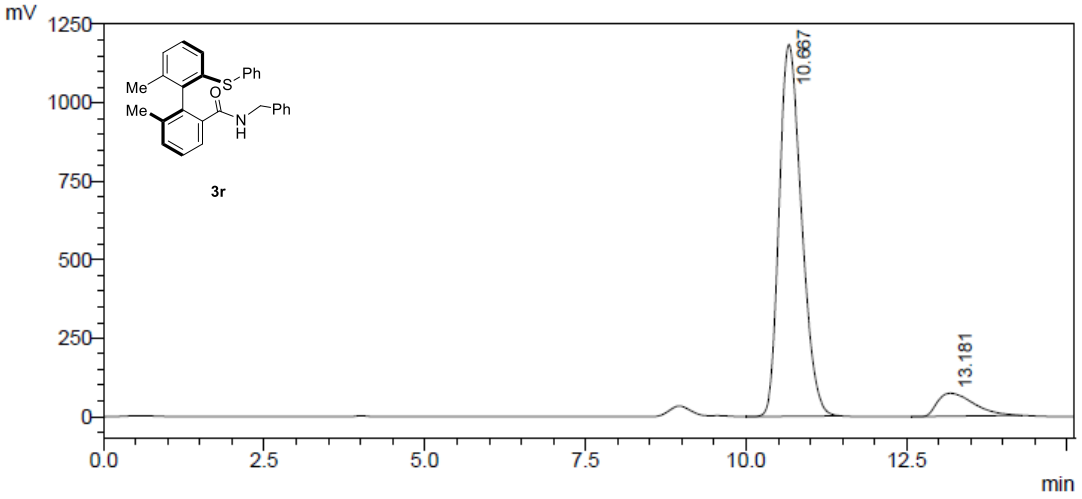


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.545	2799396	99819	49.269		M	
2	13.077	2882445	65205	50.731		M	
Total		5681841	165024				

Figure **S133**. HPLC data of racemic **3r**

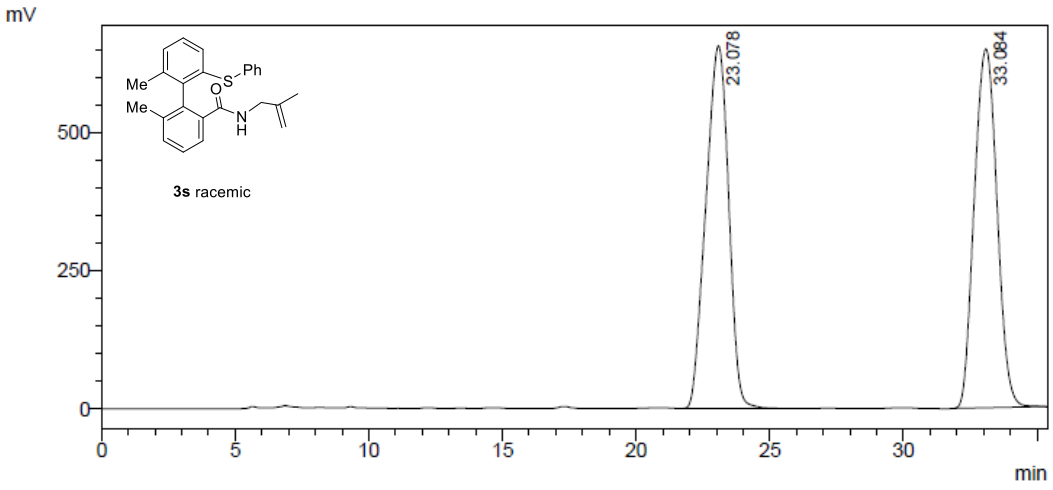


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.667	28711118	1184592	90.830		M	
2	13.181	2898553	73224	9.170		M	
Total		31609671	1257816				

Figure **S134**. HPLC data of **3r**

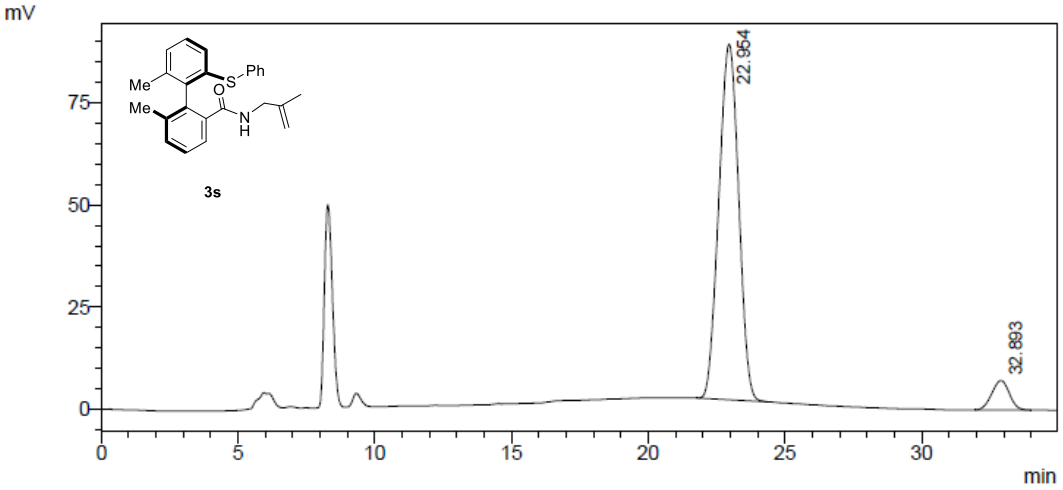


<Peak Table>

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	23.078	38993450	656726	50.361			
2	33.084	38433944	650050	49.639			
Total		77427394	1306776				

Figure **S135**. HPLC data of racemic **3s**

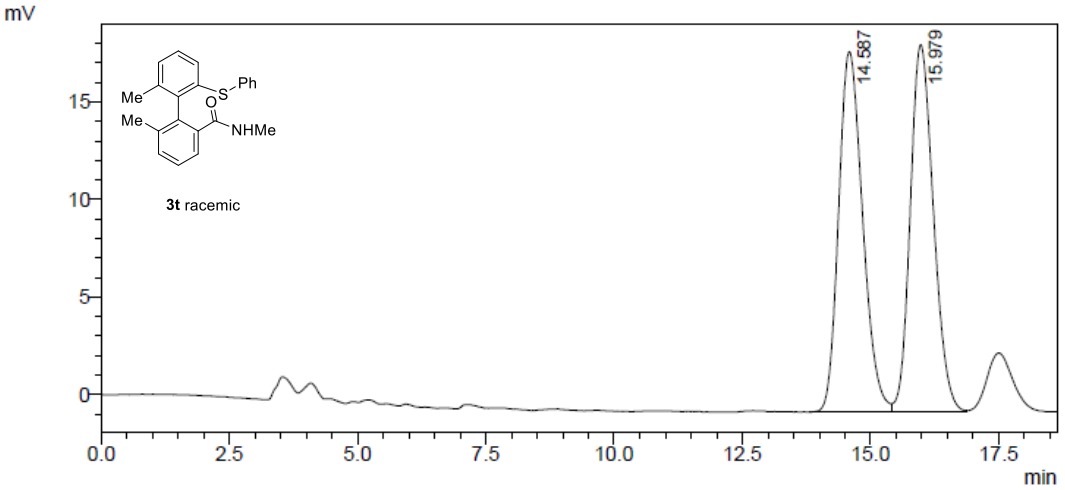


<Peak Table>

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	22.954	4388698	86979	93.195			
2	32.893	320450	7178	6.805		V	
Total		4709148	94157				

Figure **S136**. HPLC data of **3s**

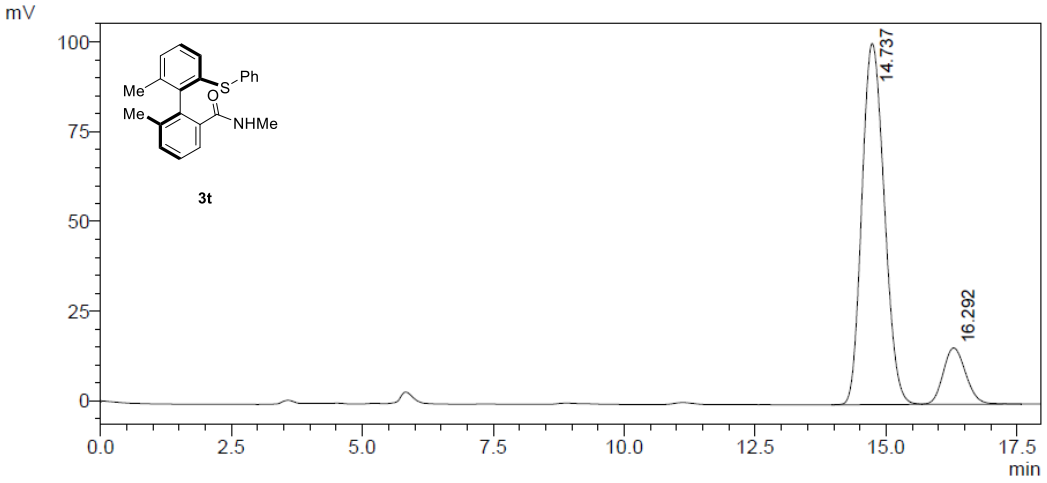


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.587	601278	18445	50.383			
2	15.979	592136	18791	49.617		V	
Total		1193414	37237				

Figure **S137**. HPLC data of racemic **3t**

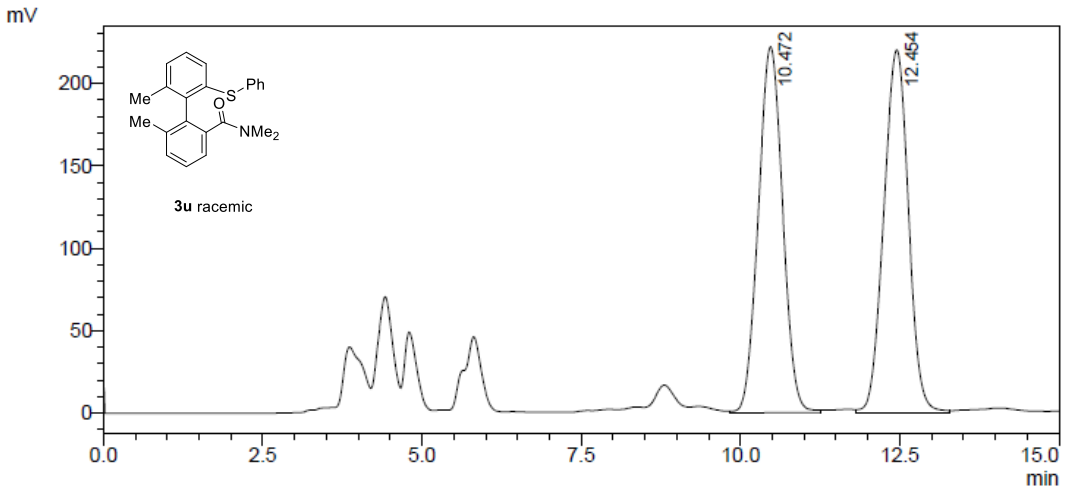


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.737	3000235	100563	86.396			
2	16.292	472400	15707	13.604		SV	
Total		3472635	116271				

Figure **S138**. HPLC data of **3t**

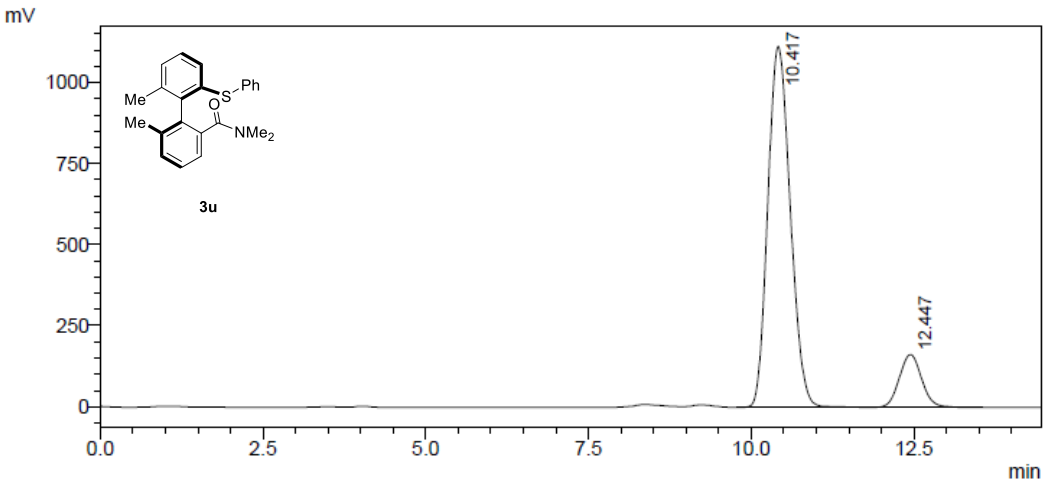


<Peak Table>

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.472	5894816	221971	49.863			
2	12.454	5927315	219931	50.137			
Total		11822131	441902				

Figure **S139**. HPLC data of racemic **3u**

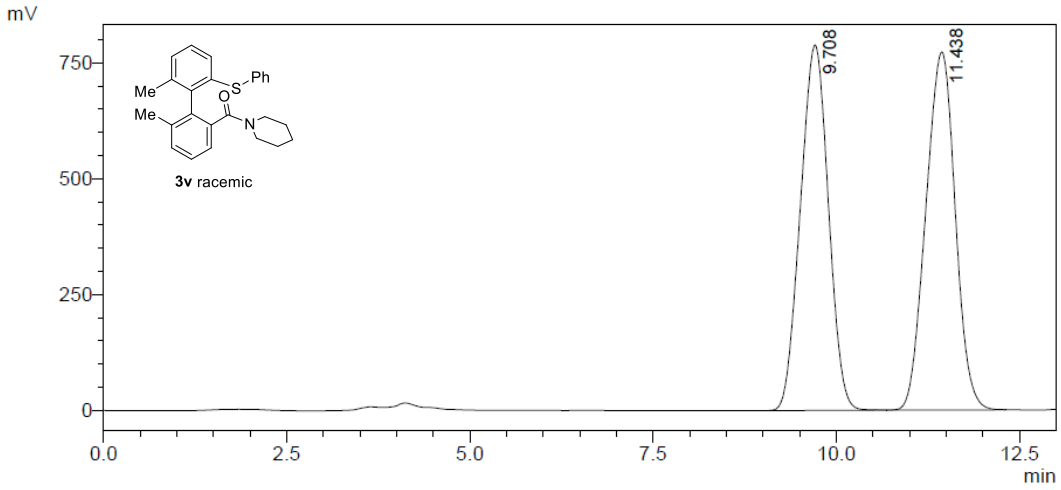


<Peak Table>

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.417	26765580	1112982	87.284			
2	12.447	3899431	162908	12.716		V	
Total		30665011	1275890				

Figure **S140**. HPLC data of **3u**

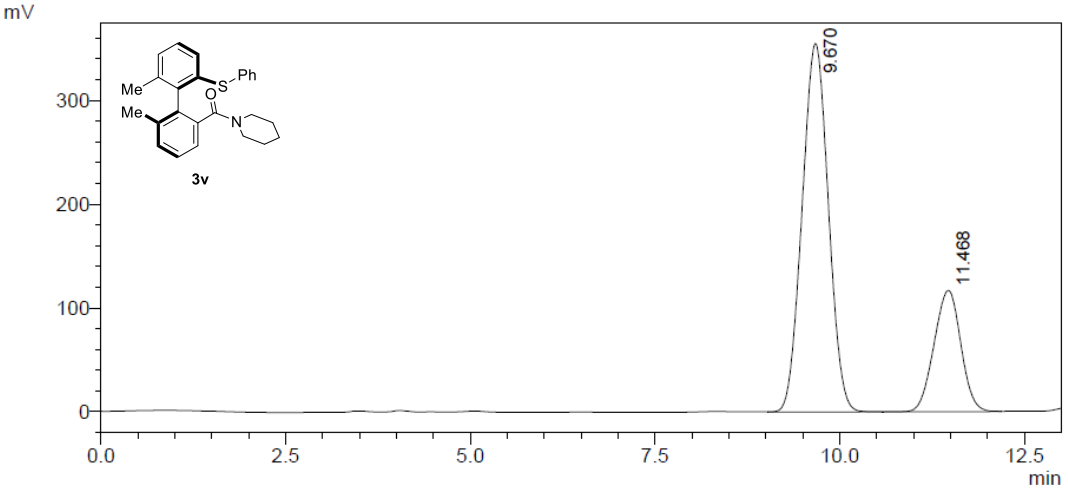


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.708	20974150	788229	49.297			
2	11.438	21572137	772123	50.703		V M	
Total		42546287	1560352				

Figure **S141**. HPLC data of racemic **3v**

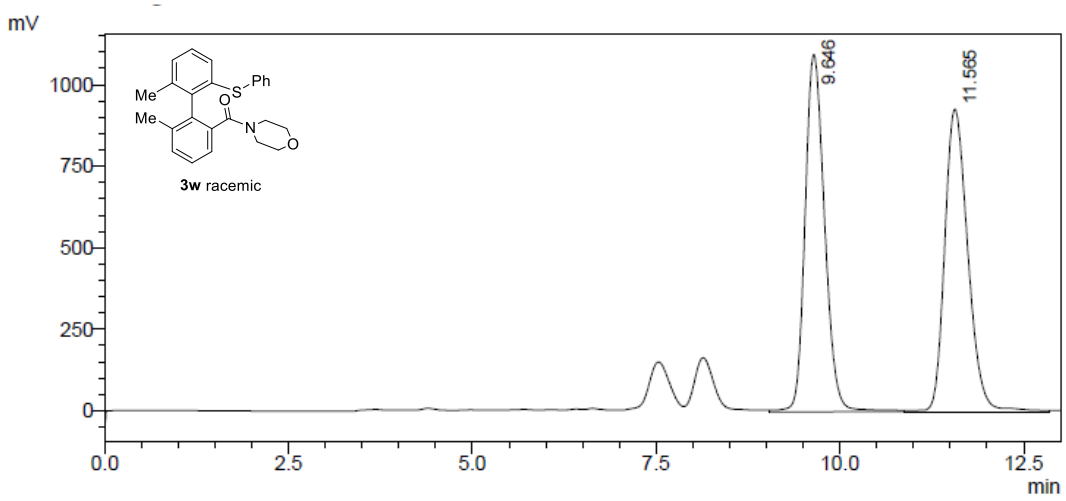


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.670	8792193	354967	74.863			
2	11.468	2952231	116833	25.137			
Total		11744424	471800				

Figure **S142**. HPLC data of **3v**

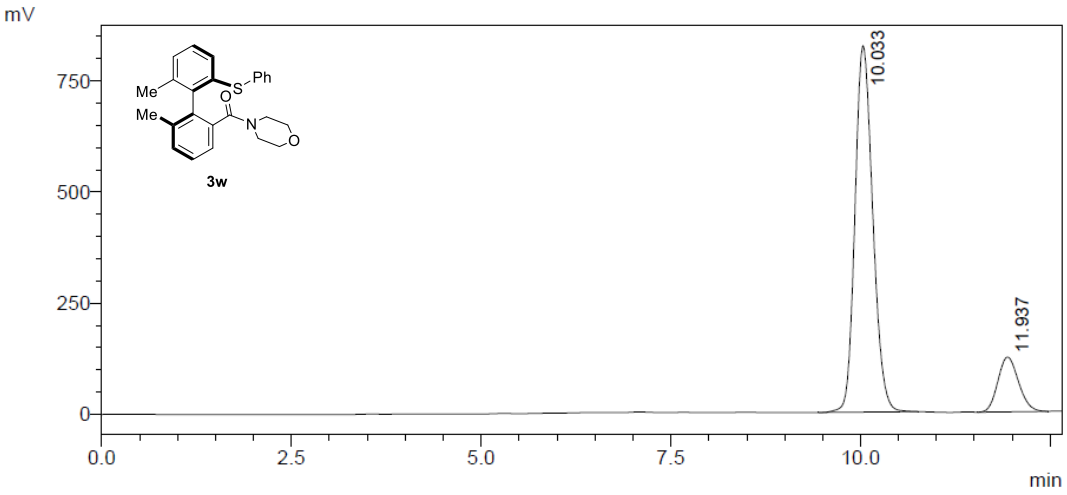


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.646	20372535	1095433	50.024			
2	11.565	20353028	927850	49.976		V	
Total		40725563	2023283				

Figure **S143**. HPLC data of racemic **3w**

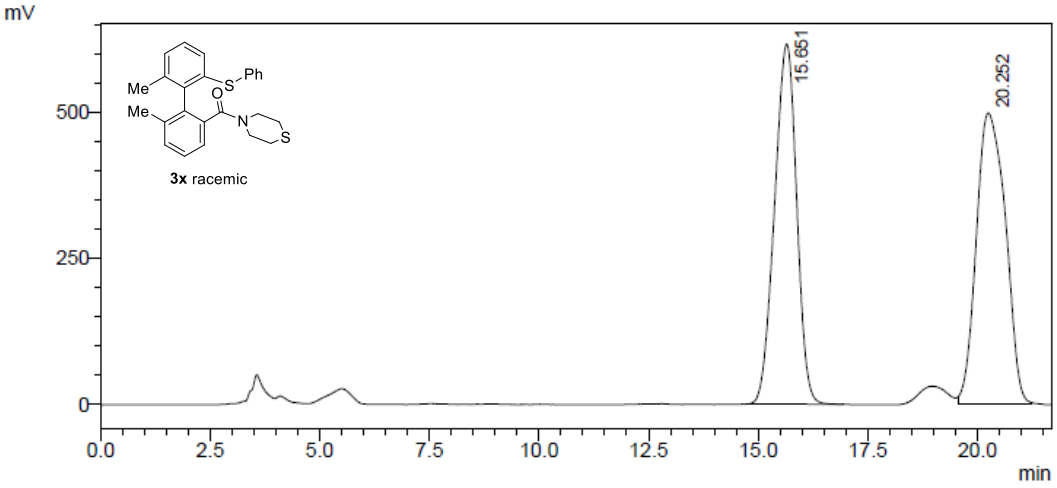


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.033	13476792	822997	85.286		M	
2	11.937	2325087	123020	14.714		M	
Total		15801879	946017				

Figure **S144**. HPLC data of **3w**

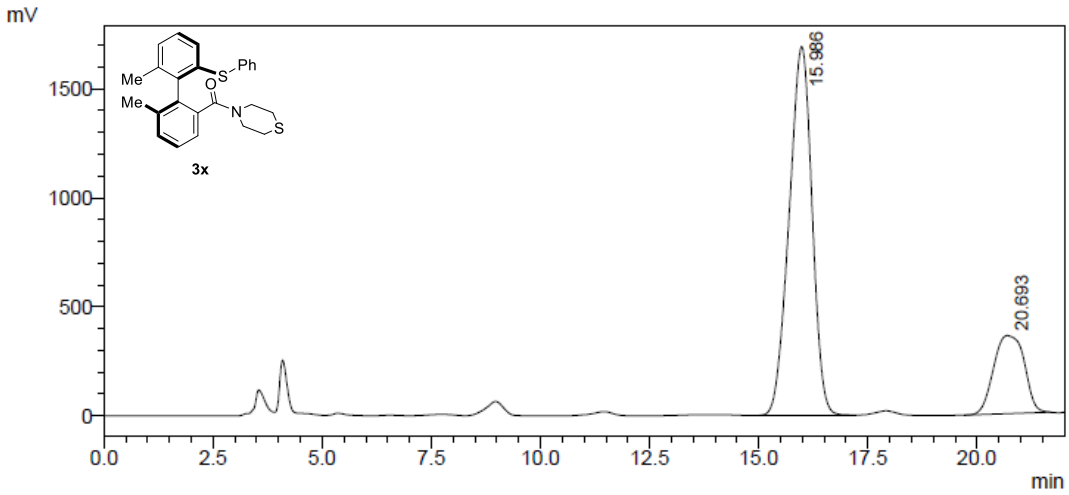


<Peak Table>

Detector A Channel 2 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.651	21651527	616068	48.472		M	
2	20.252	23016323	497853	51.528		M	
Total		44667850	1113920				

Figure **S145**. HPLC data of racemic **3x**

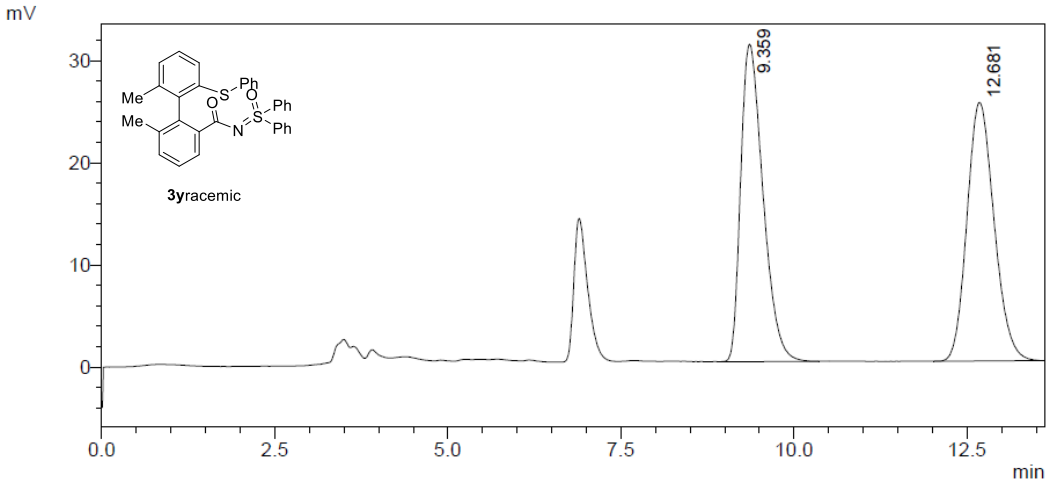


<Peak Table>

Detector A Channel 2 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.986	61948825	1691391	77.972			
2	20.693	17501512	357939	22.028		M	
Total		79450337	2049330				

Figure **S146**. HPLC data of **3x**

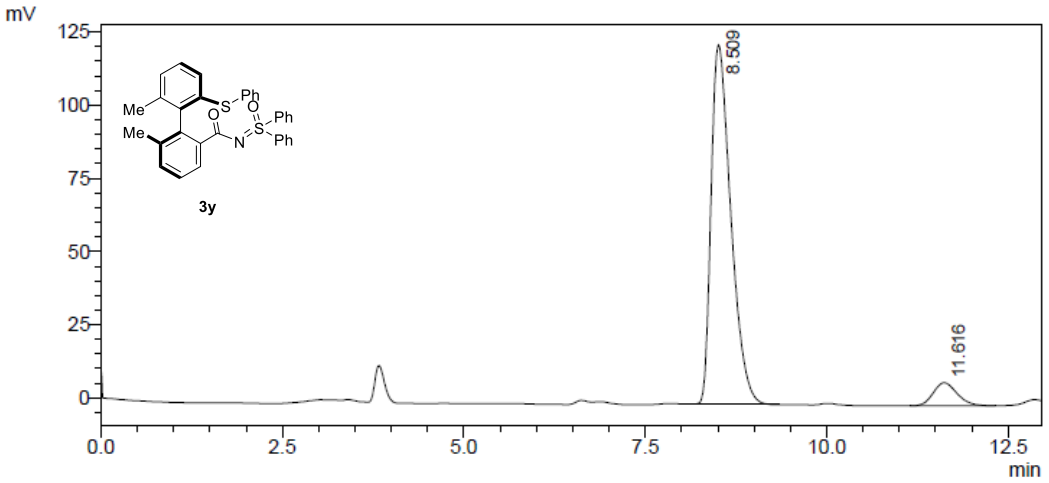


<Peak Table>

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.359	696090	31056	50.190			
2	12.681	690806	25321	49.810			
Total		1386896	56377				

Figure **S147**. HPLC data of racemic **3y**

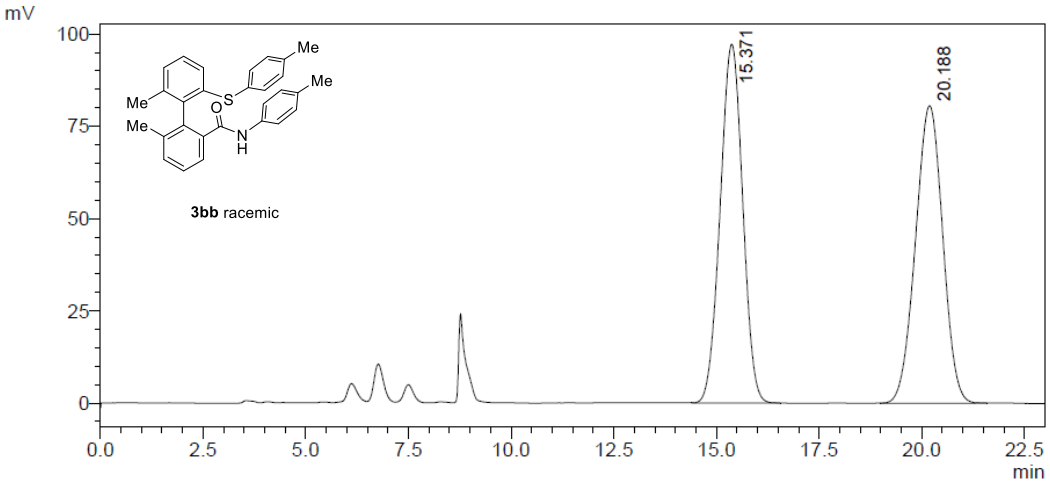


<Peak Table>

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.509	2329178	122844	92.926			
2	11.616	177305	7818	7.074			
Total		2506483	130661				

Figure **S148**. HPLC data of **3y**

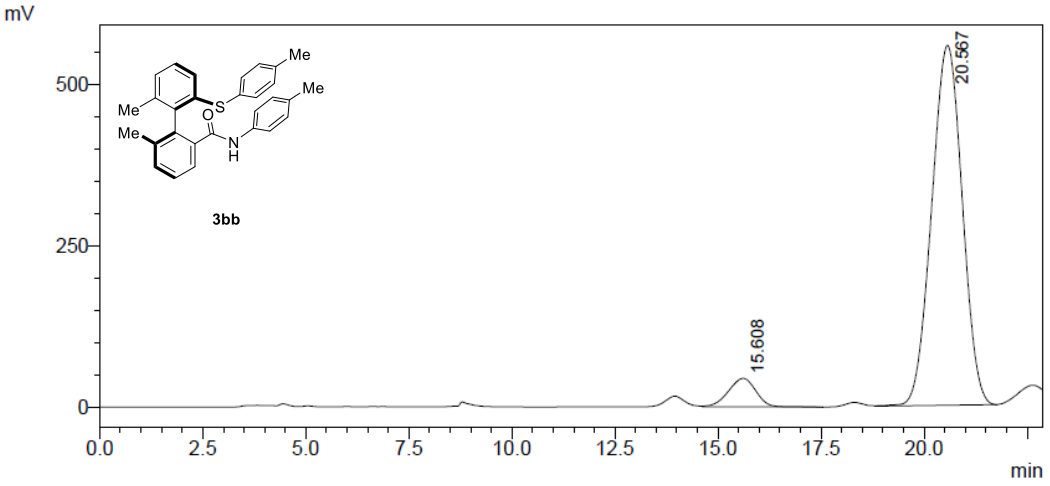


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.371	3707708	97189	49.847			
2	20.188	3730519	80616	50.153		V	
Total		7438228	177805				

Figure **S149**. HPLC data of racemic **3bb**

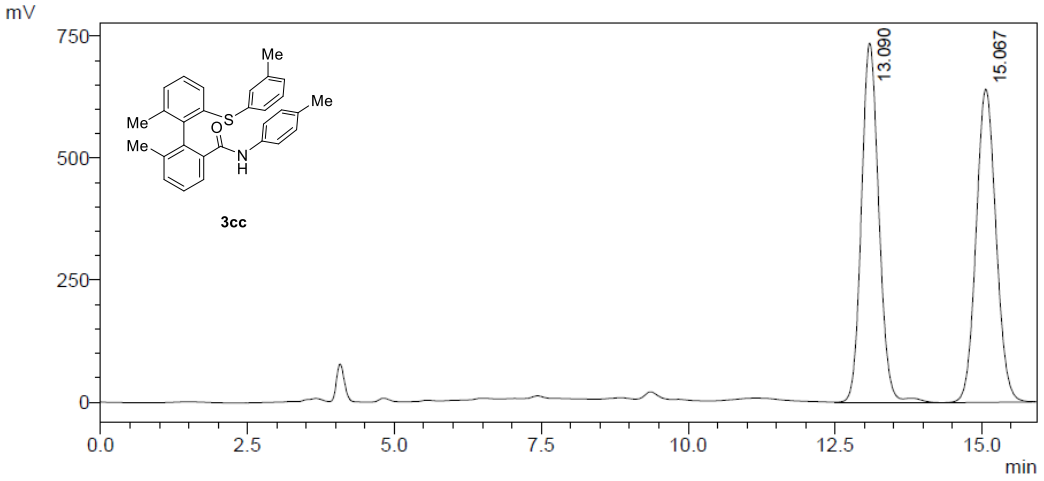


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.608	2038915	44011	6.615		S	
2	20.567	28781580	557644	93.385			
Total		30820495	601655				

Figure **S150**. HPLC data of **3bb**

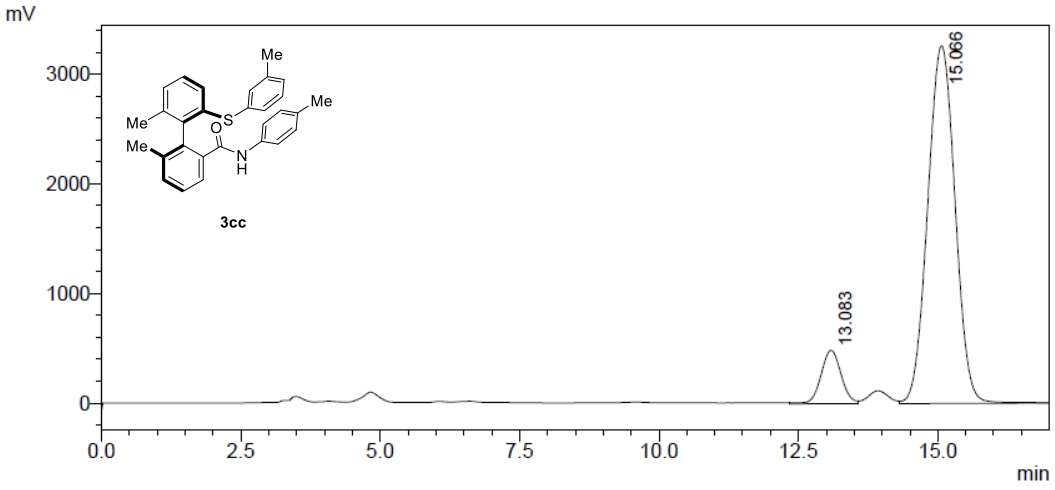


<Peak Table>

Detector A Channel 1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.090	15249867	736618	50.230			
2	15.067	15110049	641738	49.770			
Total		30359916	1378356				

Figure **S151**. HPLC data of racemic **3cc**

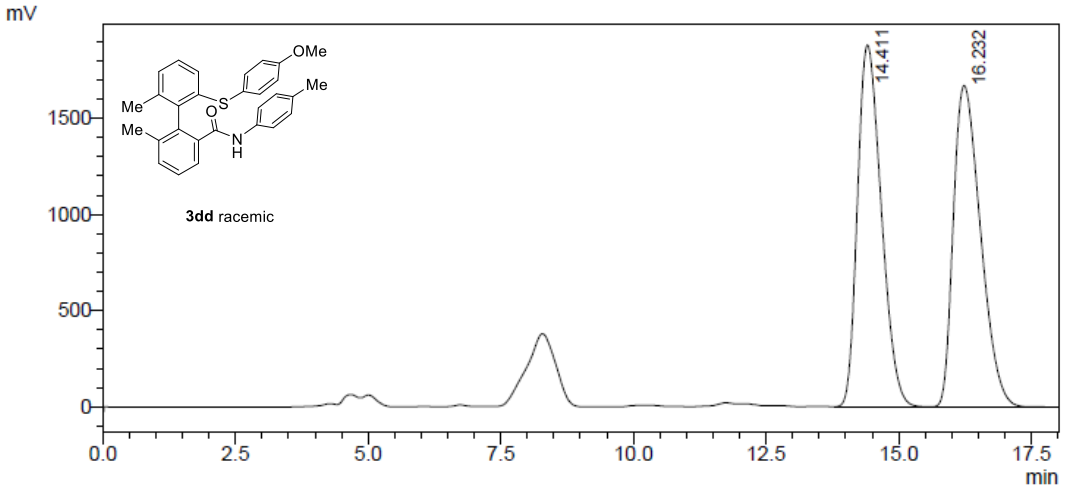


<Peak Table>

Detector A Channel 1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.083	12253437	488473	9.858			
2	15.066	112051650	3263436	90.142			
Total		124305087	3751910				

Figure **S152**. HPLC data of **3cc**

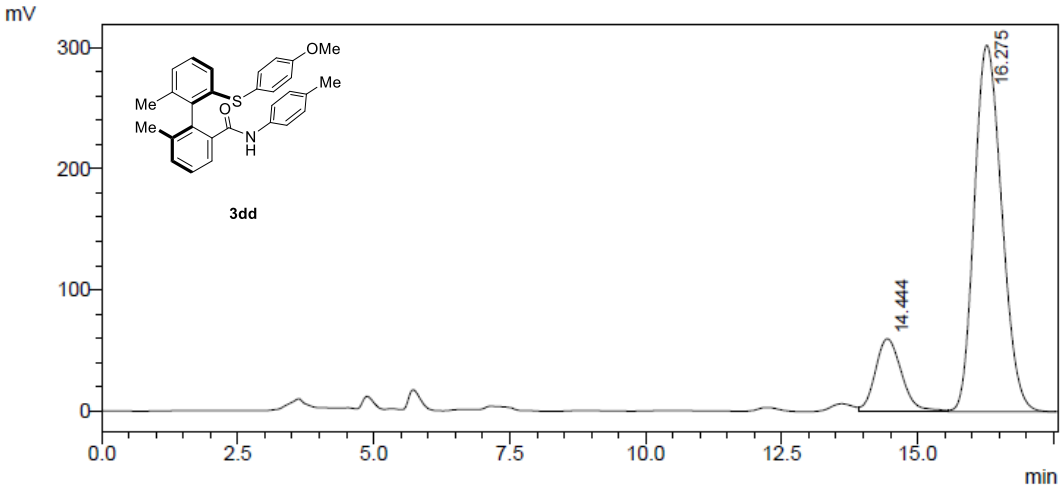


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.411	58954795	1882247	49.743			
2	16.232	59563400	1671292	50.257		V	
Total		118518195	3553539				

Figure **S153**. HPLC data of racemic **3dd**

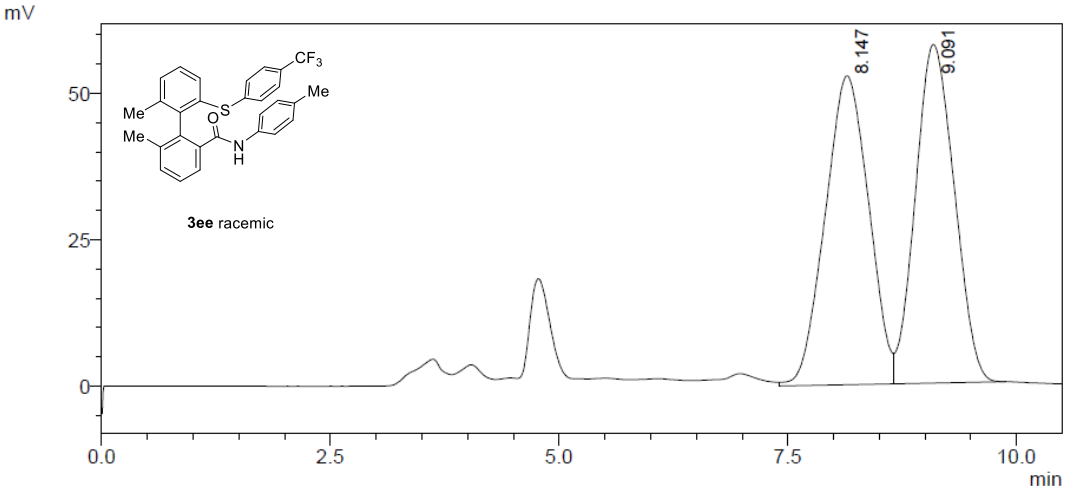


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.444	2029010	60123	16.034			
2	16.275	10625376	302392	83.966		V	
Total		12654387	362515				

Figure **S154**. HPLC data of **3dd**

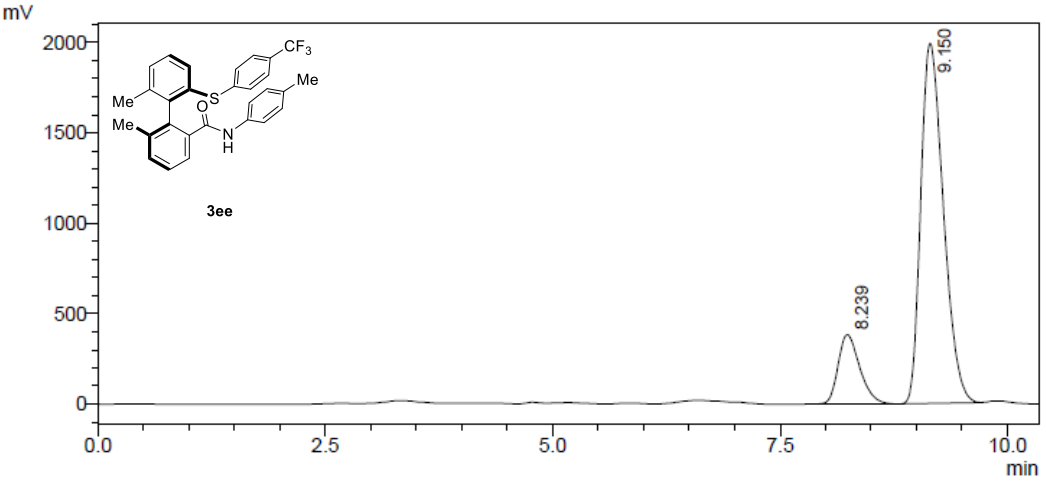


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.147	1748102	52746	50.549			
2	9.091	1710140	57827	49.451		V M	
Total		3458243	110572				

Figure **S155**. HPLC data of racemic **3ee**

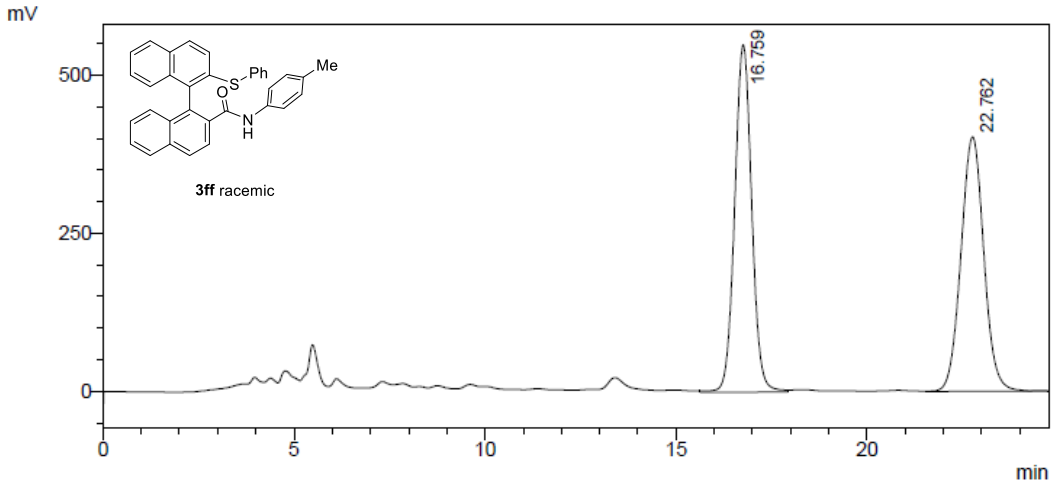


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.239	6340912	383032	15.541		M	
2	9.150	34460717	1989984	84.459		M	
Total		40801629	2373016				

Figure **S156**. HPLC data of **3ee**

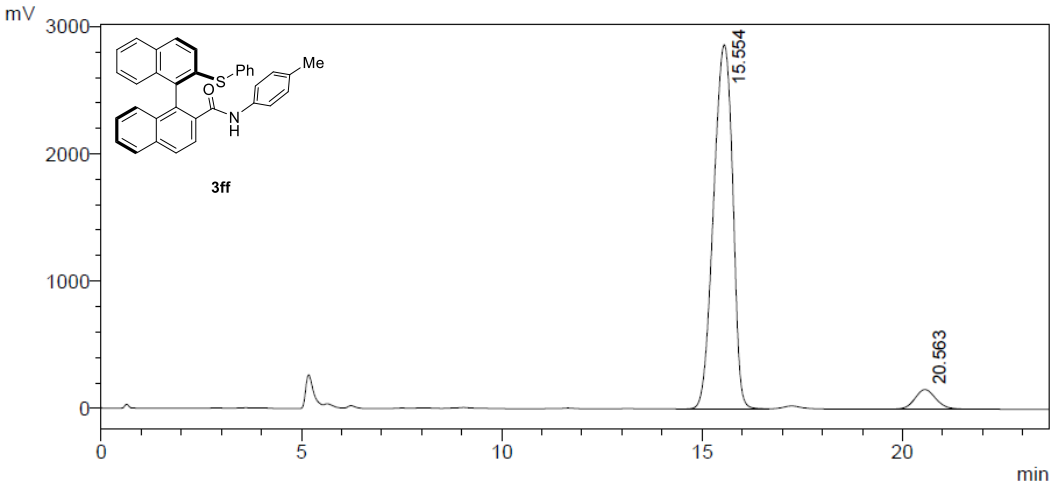


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.759	17074931	549212	50.461			
2	22.762	16762658	402371	49.539			
Total		33837589	951583				

Figure **S157**. HPLC data of racemic **3ff**

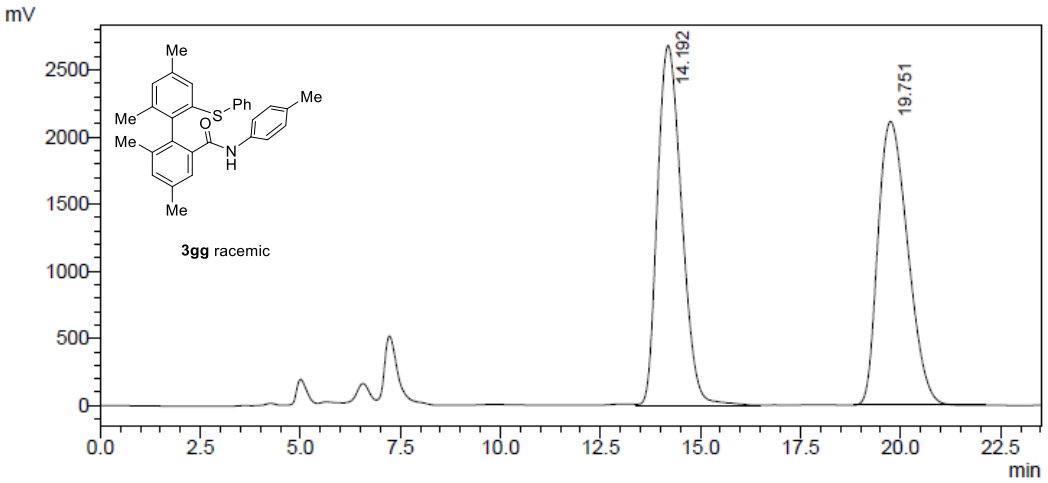


<Peak Table>

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.554	95229928	2862357	94.411			
2	20.563	5637316	154399	5.589		M	
Total		100867244	3016756				

Figure **S158**. HPLC data of **3ff**

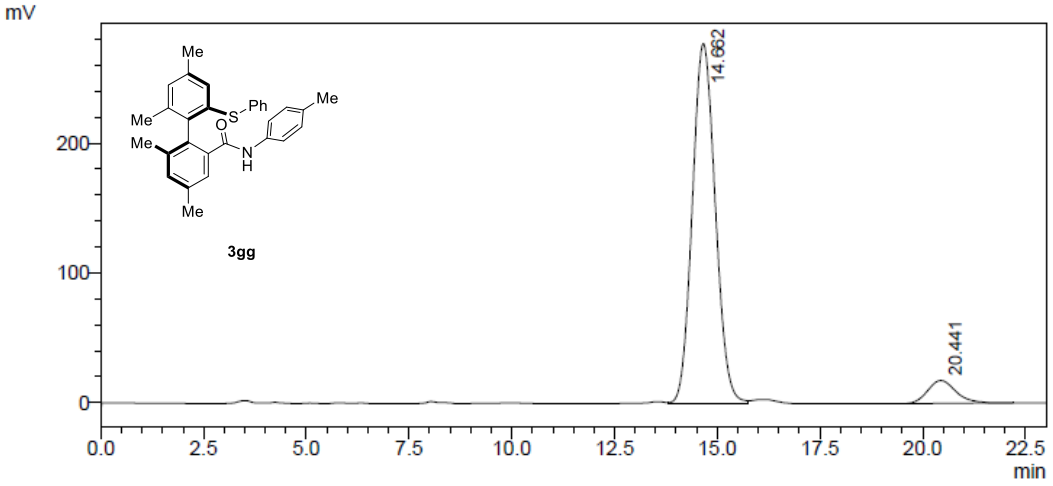


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.192	113270559	2683985	50.876		M	
2	19.751	109369659	2111990	49.124		M	
Total		222640217	4795974				

Figure **S159**. HPLC data of racemic **3gg**

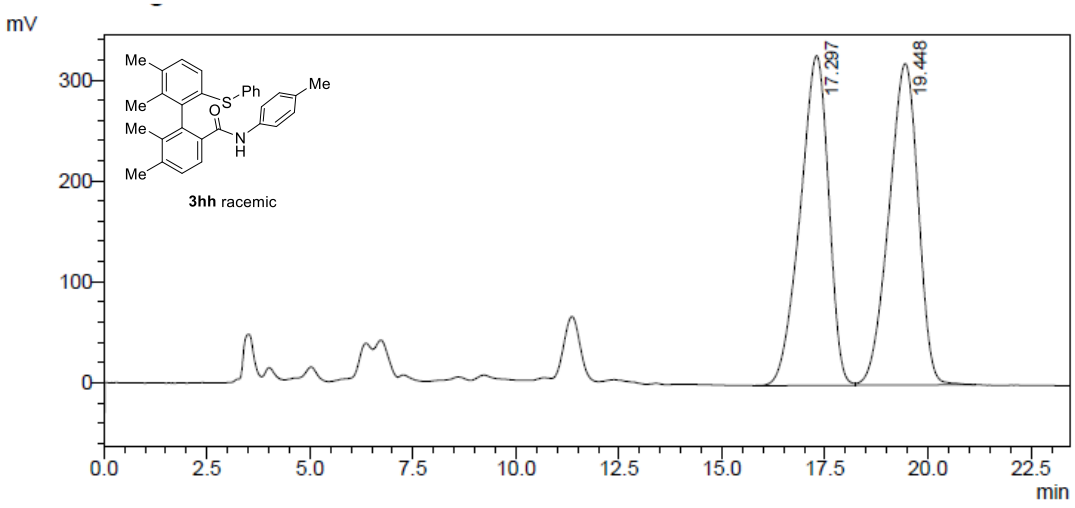


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.662	10792592	277247	92.806			
2	20.441	836566	17625	7.194		M	
Total		11629159	294873				

Figure **S160**. HPLC data of **3gg**

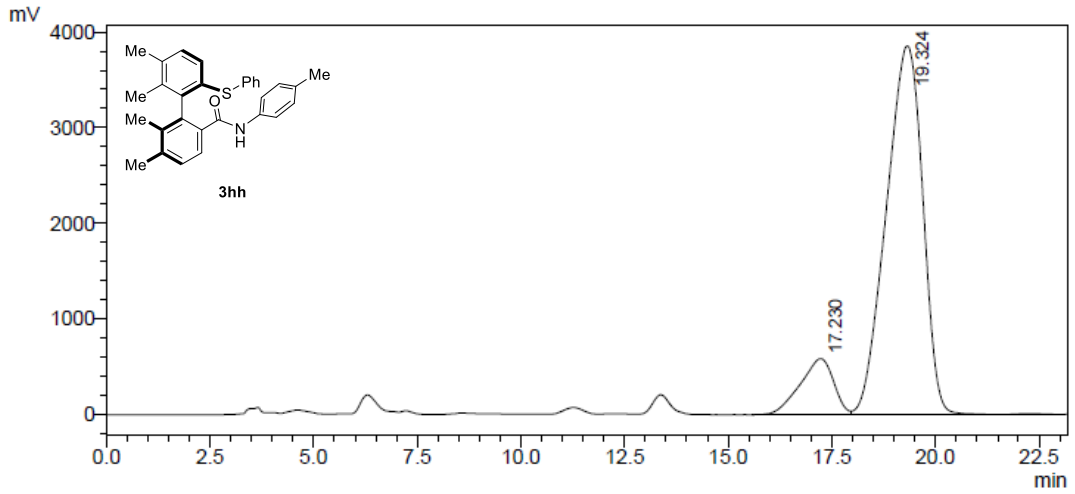


<Peak Table>

Detector A Channel 1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.297	15750641	327081	49.938			
2	19.448	15789456	319008	50.062		V M	
Total		31540096	646089				

Figure **S161**. HPLC data of racemic **3hh**



<Peak Table>

Detector A Channel 1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.230	32817819	583740	12.204			
2	19.324	236088158	3850452	87.796		SV	
Total		268905977	4434192				

Figure **S162**. HPLC data of **3hh**

6. Crystal data and structure refinement

Table S2 Crystal data and structure refinement for 1a.

Identification code	**1a**
Empirical formula	$C_{21}H_{17}F_3O_3S_2$
Formula weight	438.46
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.8793(2)
b/Å	13.4651(3)
c/Å	16.2393(3)
α/°	90
β/°	94.659(2)
γ/°	90
Volume/Å^3	1935.17(7)
Z	4
ρ_{calc}g/cm^3	1.505
μ/mm^{-1}	2.944
F(000)	904.0
Crystal size/mm^3	0.13 × 0.11 × 0.09
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.542 to 147.964
Index ranges	$-11 \leq h \leq 10$, $-16 \leq k \leq 12$, $-19 \leq l \leq 20$
Reflections collected	12756
Independent reflections	3845 [R_{int} = 0.0382, R_{sigma} = 0.0289]
Data/restraints/parameters	3845/2/284
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0456, wR_2 = 0.1181
Final R indexes [all data]	R_1 = 0.0470, wR_2 = 0.1194
Largest diff. peak/hole / e Å^{-3}	0.60/-0.41

Table S3 Crystal data and structure refinement for 3hh.

Identification code	**3hh**
Empirical formula	$C_{30}H_{29}NOS$
Formula weight	451.60
Temperature/K	219.99(10)
Crystal system	trigonal
Space group	$P3_121$
a/Å	10.0094(4)
b/Å	10.0094(4)
c/Å	42.946(2)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	3726.2(4)
Z	6
ρ_{calc}g/cm^3	1.207
μ/mm^{-1}	1.314
F(000)	1440.0
Crystal size/mm^3	0.14 × 0.13 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.174 to 147.91
Index ranges	$-11 \leq h \leq 12$, $-10 \leq k \leq 12$, $-52 \leq l \leq 53$
Reflections collected	19253
Independent reflections	4999 [R_{int} = 0.0421, R_{sigma} = 0.0312]
Data/restraints/parameters	4999/0/303
Goodness-of-fit on F^2	1.090
Final R indexes [I>=2σ (I)]	R_1 = 0.0436, wR_2 = 0.1060
Final R indexes [all data]	R_1 = 0.0471, wR_2 = 0.1089
Largest diff. peak/hole / e Å^{-3}	0.20/-0.24
Flack/Hooft parameter	0.002(10)/-0.005(10)

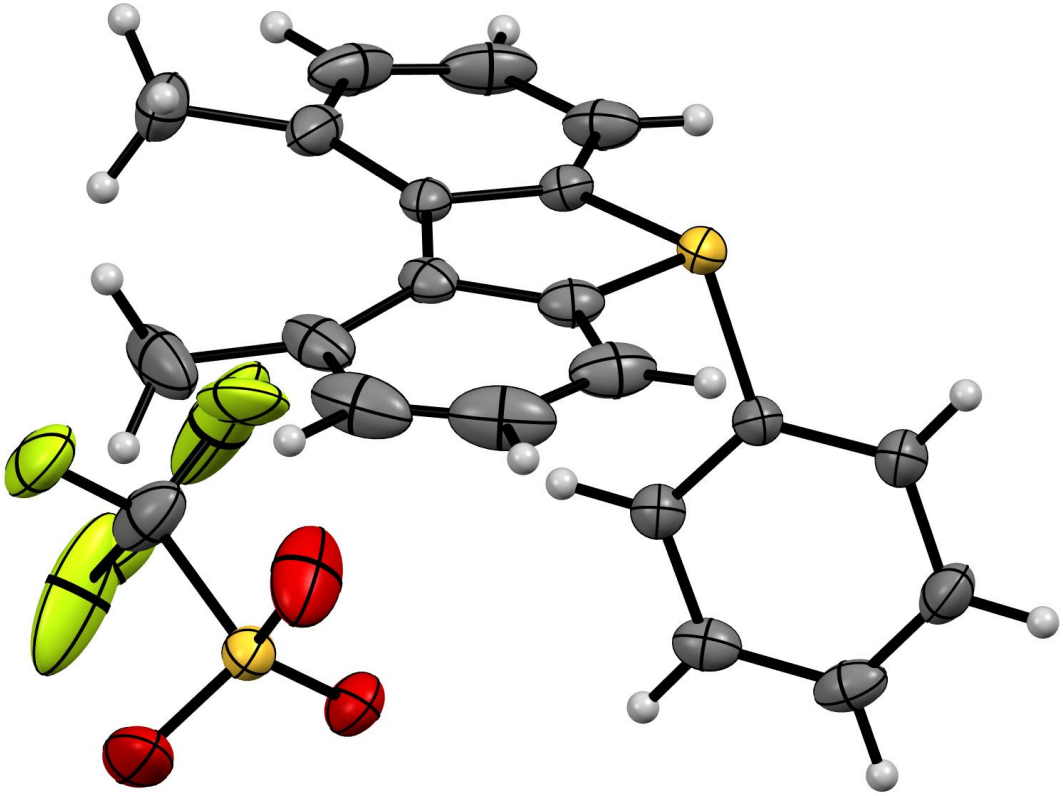


Figure **S163**. Thermal ellipsoid plot for the crystal structure for **1a**, probability levels (50%)

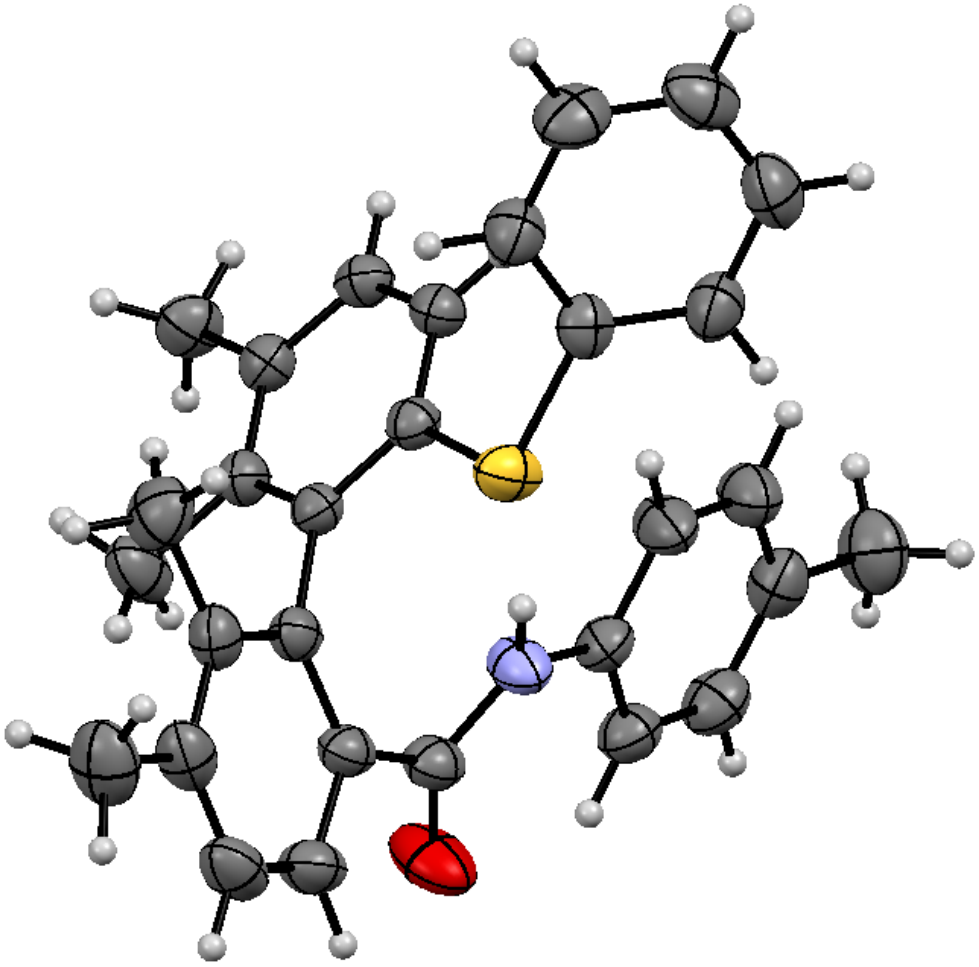


Figure **S164**. Thermal ellipsoid plot for the crystal structure for **3hh**, probability levels (50%)