Supporting Information

Palladium-Catalyzed Regio- and Stereoselective Phosphination of Cyclic Biarylsulfonium Salts to Access Atropoisomeric Phosphines

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1. General Information

All air-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or argon. Solvents were degassed prior to use when necessary. NMR spectra were recorded on Bruker AMX 500 spectrophotometer (500 MHz for ^{1}H, 126 MHz for ^{13}C, 202 MHz for ^{31}P and 471 Hz for ^{19}F). Chemical shifts are reported in δ (ppm) referenced to an internal $SiMe_4$ standard (δ = 0 ppm) for ^{1}H NMR, chloroform-*d* (δ = 77.0 ppm) for ^{13}C NMR. The following abbreviations were used; s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br: broad. Optical rotations were measured on an Anton Paar MCP 200 polarimeter. HRMS (ESI-TOF) were recorded on a time-of-fligh (TOF) LC/MS instrument. Flash column chromatography was performed with Silica gel 60 (Merck) or Al_2O_3 (activated 200) (Merck). X-ray diffraction studies were performed on a 'Bruker D8 Venture' diffractometer. Enantiomeric excesses (ee%) were determined by HPLC analysis on Shimadzu HPLC with Daicel or Chiralcel chiral columns. All chemicals and solvents were purchased from commercial companies (Macklin, Energy Chemical, Sigma-Aldrich) and used as received. Solvents were degassed before use if necessary.

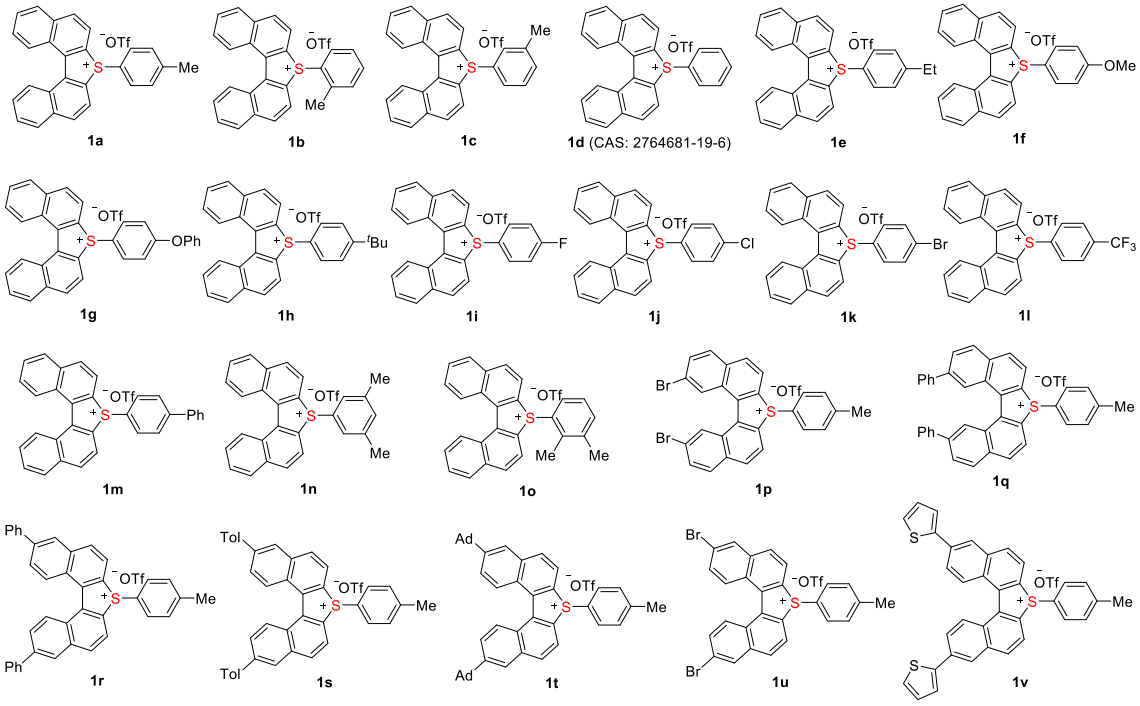
2. Experimental Details

2.1 Preparation of Substrates

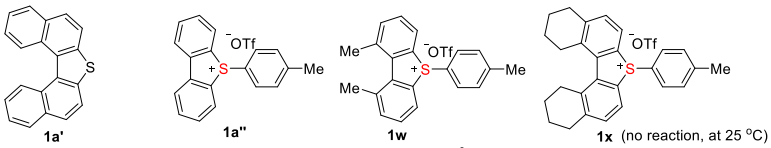
The cyclic biarylsulfonium salt substrates **1a-1c**, **1e-1x** are new compounds and they were prepared by the method shown below.[1,2] **1d** (CAS: 2764681-19-6)[3] is a known compound and was prepared by the same method as shown below. The good cyclic biarylsulfonium salt substrates and the limitation of the cyclic biarylsulfonium salt substrates which we tested are shown below (Scheme S1).

The secondary arylphosphine substrates **2a** (CAS: 829-85-6), **2d** (CAS: 71360-06-0) was purchased from commercial company and used as received. **2b** (CAS: 1017-60-3),[4] **2c** (CAS: 78871-06-4),[4] **2e** (CAS: 141868-58-8),[5] **2f** (CAS: 92025-78-0),[6] **2h** (CAS: 2764725-33-7)[7] are known compounds which were prepared according to the reported literature procedure. **2g** and **2i** are new compounds which were prepared according to the reported method.[5] The good secondary arylphosphine substrates and the limitation of the secondary phosphine substrates which we tested are shown below (Scheme S2).

Good cyclic biarylsulfonium salt substrates

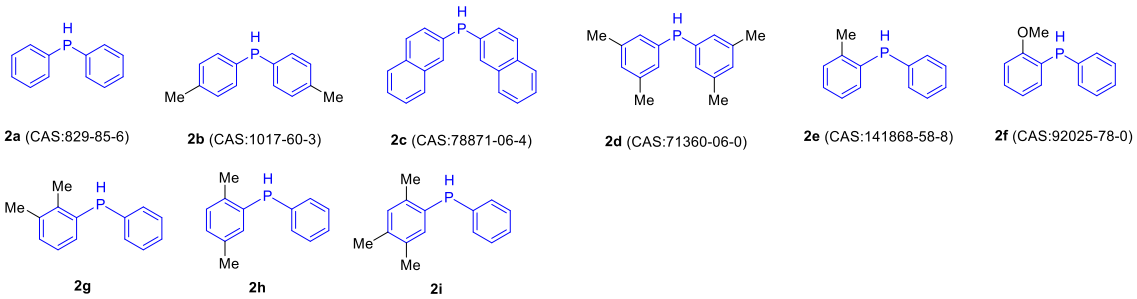


Limitation of cyclic biarylsulfonium salt substrates (Not appropriate substrates)

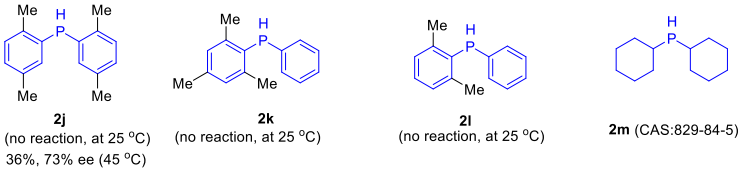


Scheme S1. Cyclic biarylsulfonium salt substrates

Good secondary arylphosphine substrates



Limitation of secondary arylphosphine substrates (Not appropriate substrates)

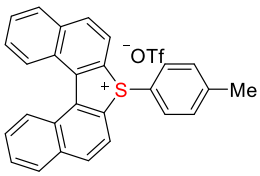


Scheme S2. Secondary arylphosphine substrates

2.1.1 General Procedure A (GPA) for the Synthesis of Substrates 1[1-3]

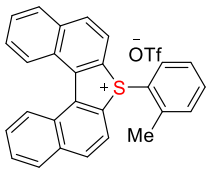
To a solution of binols **S1**[8] (10 mmol) in dry DMF (20 mL) was added NaH (60% oil dispersion, 0.88 g, 22 mmol) in portions at 0 °C. The resulting yellow mixture was added dimethylthiocarbamoyl chloride (2.8 g, 22 mmol), and the solution was heated to 85 °C and kept stirring for 2 h. After completion, the reaction mixture was cooled to room temperature and quenched with 1 N KOH (80 mL) at 0 °C. The precipitate was filtered, washed thoroughly with water, and dissolved in CH_2CI_2. The CH_2Cl_2 solution was dried over Na_2SO_4. After evaporation of the solvent, the crude solid was recrystallized from CH_2Cl_2/petroleum ether to afford the intermediate **S2** which was heated in an autoclave at 290 °C for 12 h. The reaction mixture was cooled to room temperature and then purified by column chromatography on silica gel (hexane/ethyl acetate = 95/5) to afford the intermediate **S3** which was directed used for next step.[1,2]

Under an inert atmosphere, an oven dried flask was charged with the above obtained **S3** (0.50 mmol, 1.0 equiv), diaryliodonium salt $Ar^1{}_2I^+OTf^-$ (0.50 mmol, 1.0 equiv), copper (II) acetate (9.1 mg, 0.050 mmol, 10 mol%). The mixture was then heated to 130 °C and kept vigorous stirring for 1 h. After completion, the mixture was cooled to room temperature and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (eluting with PE/EA 90/10, then DCM/MeOH 92/8) to afford the crude product. The crude product was the further purified by recrystallization (with ether), and the solid was collected by filtration and dried under vacuum to give the substrate **1.**[3]

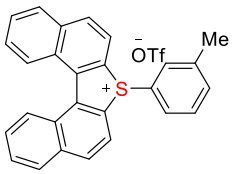


7-(*p*-Tolyl)-7*H*-dinaphtho[2,1-*b*:1',2'-*d*]thiophen-7-ium trifluoromethanesulfonate (1a). Following General Procedure A (GPA), **1a** was prepared as a brown solid (139.4 mg, 53% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.57 (d,

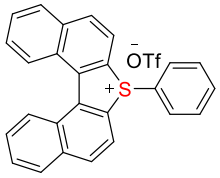
J = 8.5 Hz, 2H), 8.19 (d, *J* = 8.7 Hz, 2H), 8.16 (d, *J* = 8.7 Hz, 2H), 8.11 (d, *J* = 7.8 Hz, 2H), 7.80 (t, *J* = 7.7 Hz, 2H), 7.75 (t, *J* = 7.7 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 2.36 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.0, 137.8, 136.6, 133.2, 132.5, 131.1, 130.9, 129.5, 129.4 129.1, 127.6, 127.4, 121.9, 121.0 (q, *J* = 320.8 Hz), 120.8, 21.7. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.1. **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{27}H_{19}S^+$: 375.1202; Found: 375.1207.



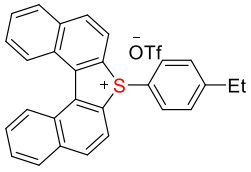
7-(*o*-Tolyl)-7*H*-dinaphtho[2,1-*b*:1',2'-*d*]thiophen-7-ium trifluoromethanesulfonate (1b). Following General Procedure A (GPA), **1b** was prepared as a brown solid (89.4 mg, 34% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.5 Hz, 2H), 8.22 (d, *J* = 8.5 Hz 2H), 8.13-8.10 (m, 4H), 7.81 (t, *J* = 7.6 Hz, 2H), 7.75 (t, *J* = 7.6 Hz, 2H), 7.52-7.51 (m, 2H), 7.12 (brs, 1H), 6.70 (brs, 1H), 3.00 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.9, 138.1, 136.6, 135.2, 133.8, 133.3, 130.5, 129.5, 129.4, 129.3, 129.2 127.6, 127.5, 121.9, 120.8 (q, *J* = 321.3 Hz), 20.3. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.2. **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{27}H_{19}S^+$: 375.1202; Found: 375.1202.



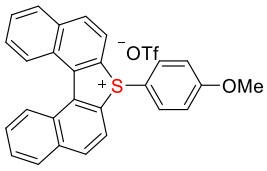
7-(*m*-Tolyl)-7*H*-dinaphtho[2,1-*b*:1',2'-*d*]thiophen-7-ium trifluoromethanesulfonate (1c). Following General Procedure A (GPA), **1c** was prepared as a brown solid (105.2 mg, 40% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.52 (d, *J* = 8.5 Hz, 2H), 8.13 (d, *J* = 8.7 Hz, 2H), 8.10 (d, *J* = 8.7 Hz, 2H), 8.05 (d, *J* = 8.0 Hz, 2H), 7.74 (t, *J* = 7.5 Hz, 2H), 7.69 (t, *J* = 7.5 Hz, 2H), 7.63 (s, 1H), 7.36 (t, *J* = 4.6 Hz, 1H), 7.27 (d, *J* = 4.6 Hz, 2H), 2.28 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.8, 137.9, 136.7, 136.3, 133.3, 131.6, 130.6, 129.5, 129.4, 129.1, 127.7, 127.4, 124.4, 122.0, 120.9 (q, *J* = 321.3 Hz), 21.3. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.2. **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{27}H_{19}S^+$: 375.1202; Found: 375.1205.



7-Phenyl-7*H*-dinaphtho[2,1-*b*:1',2'-*d*]thiophen-7-ium trifluoromethanesulfonate (1d) (CAS: 2764681-19-6).[3] Following General Procedure A (GPA), **1d** was prepared as a brown solid (161.3 mg, 63% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.5 Hz, 2H), 8.24-8.20 (m, 4H), 8.14 (d, *J* = 8.1 Hz, 2H), 7.84 (t, *J* = 7.4 Hz, 2H), 7.79-7.75 (m, 4H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.9, 136.6, 135.2, 133.3, 131.8, 131.0, 130.8, 129.5, 129.1, 127.7, 127.4, 125.0, 122.1, 121.3 (q, *J* = 321.3 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.1. **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{26}H_{17}S^+$: 361.1045; Found: 361.1048.

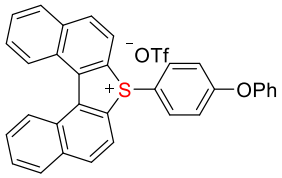


7-(4-Ethylphenyl)-7*H*-dinaphtho[2,1-*b*:1',2'-*d*]thiophen-7-ium trifluoromethanesulfonate (1e). Following General Procedure A (GPA), **1e** was prepared as a brown solid (183.6 mg, 68% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.5 Hz, 2H), 8.18 (d, *J* = 8.4 Hz, 2H), 8.13 (d, *J* = 8.4 Hz, 2H), 8.09 (d, *J* = 8.1 Hz, 2H), 7.79 (t, *J* = 7.6 Hz, 2H), 7.73 (t, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.63 (q, *J* = 7.6 Hz, 2H), 1.16 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.9, 137.7, 136.6, 133.1, 131.4, 131.2, 131.1, 129.5, 129.4, 129.1, 127.6, 127.4, 122.0, 121.0, 121.7 (q, *J* = 321.0 Hz), 28.9, 14.7. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.1. **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{28}H_{21}S^+$: 389.1358; Found: 389.1353.

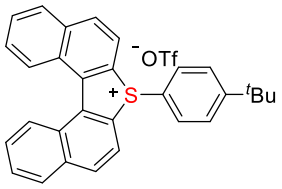


7-(4-Methoxyphenyl)-7*H*-dinaphtho[2,1-*b*:1',2'-*d*]thiophen-7-ium trifluoromethanesulfonate (1f). Following General Procedure A (GPA), **1f** was prepared as a brown solid (62.3 mg, 23% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.52 (d, *J* = 8.2 Hz, 2H), 8.14 (d, *J* = 8.2 Hz, 2H), 8.07 (d, *J* = 8.1 Hz, 2H), 8.06 (d, *J* = 8.1 Hz, 2H), 7.70-7.69 (m, 4H), 7.46 (d, *J* = 8.1 Hz, 2H), 6.88 (d, *J* = 8.1 Hz, 2H), 3.72 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.3, 137.5, 136.5, 133.3, 133.1, 131.5, 129.5, 129.4,

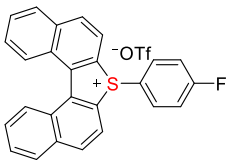
129.0, 127.6, 127.4, 121.6, 117.5, 112.4, 56.1. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.1. **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{27}H_{19}OS^+$: 391.1151; Found: 391.1156.



7-(4-Phenoxyphenyl)-7*H*-dinaphtho[2,1-*b*:1',2'-*d*]thiophen-7-ium trifluoromethanesulfonate (1g). Following General Procedure A (GPA), **1g** was prepared as a brown solid (166.1 mg, 55% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.6 Hz, 2H), 8.11 (d, *J* = 8.6 Hz, 2H), 8.07 (d, *J* = 8.6 Hz, 2H), 8.01 (d, *J* = 8.2 Hz, 2H), 7.70 (t, *J* = 7.6 Hz, 2H), 7.63 (t, *J* = 7.6 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.27 (t, *J* = 7.8 Hz, 2H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.2, 153.9, 137.6, 136.6, 133.5, 133.2, 131.5, 130.4, 129.5, 129.4, 129.1, 127.6, 127.4, 125.8, 122.0, 120.9 (d, *J* = 321.0 Hz), 120.7, 119.7, 115.0. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.0. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{32}H_{21}SOH^+$: 454.1386; Found: 454.1387.

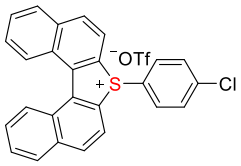


7-(4-(T*ert*-butyl)phenyl)-7*H*-dinaphtho[2,1-*b*:1',2'-*d*]thiophen-7-ium trifluoromethanesulfonate (1h). Following General Procedure A (GPA), **1h** was prepared as a brown solid (247.1 mg, 87% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.5 Hz, 2H), 8.11 (d, *J* = 8.5 Hz, 2H), 8.07 (d, *J* = 8.5 Hz, 2H), 8.02 (d, *J* = 8.1 Hz, 2H), 7.71 (t, *J* = 7.5 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 2H), 7.53(d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 1.16 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.7, 137.8, 136.6, 133.2, 131.2, 130.8, 129.5, 129.4, 129.1, 129.0, 127.6, 127.4, 122.1, 120.8 (q, *J* = 320.0 Hz), 120.7, 35.5, 30.8. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.1. **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{30}H_{25}S^+$: 417.1671; Found: 417.1672.

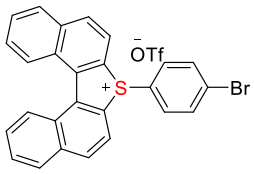


7-(4-Fluorophenyl)-7*H*-dinaphtho[2,1-*b*:1',2'-*d*]thiophen-7-ium trifluoromethanesulfonate (1i). Following General Procedure A (GPA), **1i** was prepared

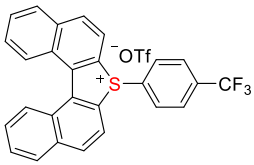
as a brown solid (185.5 mg, 70% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.5 Hz, 2H), 8.21 (brs, 4H), 8.12 (d, *J* = 8.1 Hz, 2H), 7.84-7.75 (m, 6H), 7.12 (t, *J* = 7.7 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.6 (d, *J* = 260.6 Hz), 137.8, 136.7, 134.1 (d, *J* = 10.0 Hz), 133.3, 30.9, 129.6, 129.5, 129.1, 127.7, 127.4, 122.0, 120.9 (q, *J* = 314.8 Hz), 120.0, 119.3 (d, *J* = 23.5 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.2, -99.5. **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{26}H_{16}SF^+$: 379.0951; Found: 379.0956.



7-(4-Chlorophenyl)-7*H*-dinaphtho[2,1-*b*:1',2'-*d*]thiophen-7-ium trifluoromethanesulfonate (1j). Following General Procedure A (GPA), **1j** was prepared as a brown solid (226.2 mg, 83% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.52 (d, *J* = 8.5 Hz, 2H), 8.14 (brs, 4H), 8.06 (d, *J* = 8.1 Hz, 2H), 7.76 (t, *J* = 7.6 Hz, 2H), 7.70 (t, *J* = 7.6 Hz, 2H), 7.64 (d, *J* = 8.7 Hz, 2H), 7.39 (d, *J* = 8.7 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.3, 138.0, 136.7, 133.4, 132.4, 132.0, 130.8, 129.6, 129.5, 129.2, 127.7, 127.5, 123.4, 122.2, 120.7 (q, *J* = 320.8 Hz,). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.2. **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{26}H_{16}SCl^+$: 395.0656; Found: 395.0652.

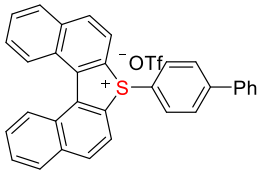


7-(4-Bromophenyl)-7*H*-dinaphtho[2,1-*b*:1',2'-*d*]thiophen-7-ium trifluoromethanesulfonate (1k). Following General Procedure A (GPA), **1k** was prepared as a brown solid (205.8 mg, 70% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.5 Hz, 2H), 8.23 (brs, 4H), 8.14 (d, *J* = 7.5 Hz, 2H), 7.84 (t, *J* = 7.5 Hz, 2H), 7.78 (t, *J* = 7.5Hz, 2H), 7.64 (brs, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.0, 136.7, 135.0, 133.4, 132.4, 130.8, 130.6, 129.6, 129.5, 129.2, 127.7, 127.5, 124.1, 122.2, 120.8 (q, *J* = 320.1 Hz,). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.2. **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{26}H_{16}SBr^+$: 439.0151; Found: 439.0147.

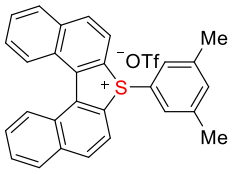


7-(4-(Trifluoromethyl)phenyl)-7*H*-dinaphtho[2,1-*b*:1',2'-*d*]thiophen-7-ium trifluoromethanesulfonate (1l). Following General Procedure A

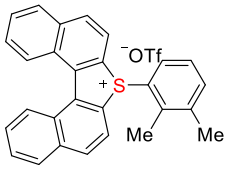
(GPA), **1l** was prepared as a brown solid (95.7 mg, 33% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.6 Hz, 2H), 8.19 (d, *J* = 8.6 Hz, 2H), 8.14 (d, *J* = 8.6 Hz, 2H), 8.04 (d, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.75 (t, *J* = 7.4 Hz, 2H), 7.70-7.64 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.3, 136.8, 136.4 (q, *J* = 34.0 Hz), 133.5, 131.4, 130.3, 130.0, 129.6, 129.5, 129.1, 128.5 (q, *J* = 3.8 Hz), 127.8, 127.4, 122.5 (q, *J* = 274.1 Hz), 122.2, 120.5 (q, *J* = 320.8 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ –63.6, -78.2. **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{27}H_{16}SF_3^+$: 429.0919; Found: 429.0914.



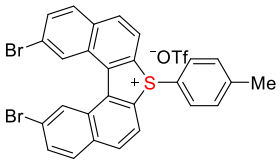
7-([1,1'-biphenyl]-4-yl)-7*H*-dinaphtho[2,1-*b*:1',2'-*d*]thiophen-7-ium trifluoromethanesulfonate (1m). Following General Procedure A (GPA), **1m** was prepared as a brown solid (61.7 mg, 21% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.5 Hz, 2H), 8.20 (brs, 4H), 8.12 (d, *J* = 8.1 Hz, 2H), 7.83-7.74 (m, 6H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 6.9 Hz, 2H), 7.43-7.37 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.2, 138.0, 137.9, 136.6, 133.3, 131.5, 130.9, 130.2, 129.6, 129.5, 129.2, 129.1, 127.7, 127.4, 127.3, 122.7, 122.0, 121.2 (q, *J* = 321.3 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.13. **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{32}H_{21}S^+$: 437.1358; Found: 437.1356.



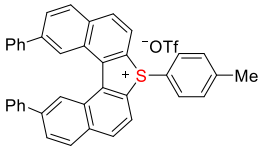
7-(3,5-Dimethylphenyl)-7*H*-dinaphtho[2,1-*b*:1',2'-*d*]thiophen-7-ium trifluoromethanesulfonate (1n). Following General Procedure A (GPA), **1n** was prepared as a brown solid (54.0 mg, 20% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.5 Hz, 2H), 8.14 (d, *J* = 8.5 Hz, 2H), 8.09 (d, *J* = 8.5 Hz, 2H), 8.05 (d, *J* = 7.8 Hz, 2H), 7.74 (t, *J* = 7.6 Hz, 2H), 7.68 (t, *J* = 7.6 Hz, 2H), 7.23 (s, 2H), 7.17 (s, 1H), 2.20 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.4, 137.7, 137.3, 136.6, 133.2, 130.6, 129.5, 129.4, 129.1, 128.1, 127.6, 127.4, 123.7, 121.9, 121.0 (q, *J* = 321.3 Hz), 21.2. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.13. **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{28}H_{21}S^+$: 389.1358; Found: 389.1357.



7-(2,3-Dimethylphenyl)-7*H*-dinaphtho[2,1-*b*:1',2'-*d*]thiophen-7-ium trifluoromethanesulfonate (1o). Following General Procedure A (GPA), **1o** was prepared as a brown solid (110.7 mg, 41% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.5 Hz, 2H), 8.12 (d, *J* = 8.7 Hz, 2H), 8.10 (d, *J* = 8.7 Hz, 2H), 7.80 (t, *J* = 7.5 Hz, 2H), 7.74 (t, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 7.3 Hz, 1H), 6.89-6.97 (m, 1H), 6.36 (brs, 1H), 3.06 (brs, 3H), 2.40 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.6, 141.8, 137.8, 136.5, 136.4, 133.4, 130.8, 129.6, 129.5, 129.2, 129.0, 127.7, 127.3, 121.8, 121.2 (q, *J* = 318.6 Hz), 20.8, 15.3. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.2. **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{28}H_{21}S^+$: 389.1358; Found: 389.1359.

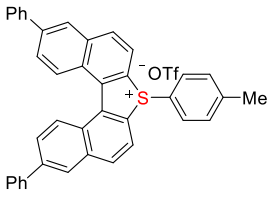


2,12-Dibromo-7-(*p*-tolyl)-7*H*-dinaphtho[2,1-*b*:1',2'-*d*]thiophen-7-ium trifluoromethanesulfonate (1p). Following General Procedure A (GPA), **1p** was prepared as a brown solid (242.5 mg, 71% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.57 (s, 2H), 8.11(s, 4H), 7.90 (d, *J* = 8.7 Hz, 2H), 7.75 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 2.28 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.3, 135.8, 134.8, 133.3, 132.8, 132.6, 132.3, 131.1, 131.0, 129.4, 129.3, 122.6, 122.5, 120.6 (q, *J* = 320.0 Hz), 120.2, 21.7. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.1. **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{27}H_{17}SBr_2^+$: 530.9412; Found: 530.9414.

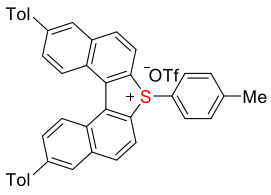


2,12-Diphenyl-7-(*p*-tolyl)-7*H*-dinaphtho[2,1-*b*:1',2'-*d*]thiophen-7-ium trifluoromethanesulfonate (1q). Following General Procedure A (GPA), **1q** was prepared as a brown solid (169.0 mg, 50% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (brs, 2H), 8.16 (d, *J* = 8.1 Hz, 2H), 8.06 (d, *J* = 8.5 Hz, 4H), 7.82 (d, *J* = 6.8 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.22-7.14 (m, 12H), 2.27 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.0, 140.5, 139.3, 137.6, 135.6, 133.0, 132.5, 131.0, 130.1, 129.4, 129.2, 129.1, 128.4,

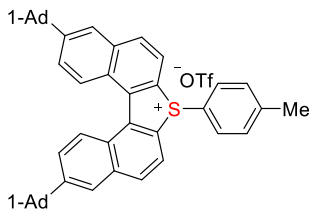
127.3, 125.3, 122.0, 121.2 (d, J = 321.3 Hz), 121.0, 21.7. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.0. **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{39}H_{27}S^+$: 527.1828; Found: 527.1823.



3,11-Diphenyl-7-(*p*-tolyl)-7*H*-dinaphtho[2,1-*b*:1',2'-*d*]thiophen-7-ium trifluoromethanesulfonate (1r). Following General Procedure A (GPA), **1r** was prepared as a brown solid (145.8 mg, 43% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.58 (d, J = 8.8 Hz, 2H), 8.21-8.13 (m, 6H), 7.97 (d, J = 8.8 Hz, 2H), 7.77 (d, J = 7.5 Hz, 4H), 7.59-7.53 (m, 6H), 7.50-7.45 (m, 2H), 7.30 (d, J = 8.4 Hz, 2H), 2.36 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.9, 141.8, 138.9, 137.5, 137.0, 133.3, 132.5, 130.9, 130.8, 129.3, 128.7, 128.0, 127.9, 127.4, 127.0, 126.7, 122.5, 121.1,121.0 (q, J = 323.1 Hz), 21.7. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.0. **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{39}H_{27}S^+$: 527.1828; Found: 527.1828.

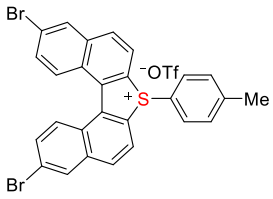


3,7,11-Tri-*p*-tolyl-7*H*-dinaphtho[2,1-*b*:1',2'-*d*]thiophen-7-ium trifluoromethanesulfonate (1s). Following General Procedure A (GPA), **1s** was prepared as a brown solid (91.8 mg, 26% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.59 (d, J = 8.9 Hz, 2H), 8.20-8.10 (m, 6H), 7.96 (d, J = 8.9 Hz, 2H), 7.67 (d, J = 8.0 Hz, 4H), 7.56 (t, J = 7.6 Hz, 2H), 7.34 (d, J = 7.9 Hz, 4H), 7.28 (d, J = 8.8 Hz, 2H), 2.45 (s, 6H), 2.35 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.9, 141.6, 138.7, 137.5, 137.0, 135.9, 133.2, 132.5, 130.9, 130.5, 130.0, 127.8, 127.2, 126.8, 126.2, 122.3, 121.1 (d, J = 321.9 Hz), 21.7, 21.2. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.08. **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{41}H_{31}S^+$: 555.2141; Found: 555.2144.

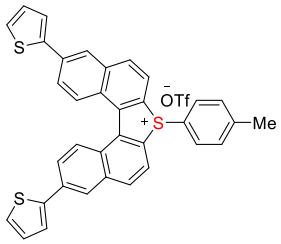


3,11-Di((3*r*,5*r*,7*r*)-adamantan-1-yl)-7-(*p*-tolyl)-7*H*-dinaphtho[2,1-*b*:1',2'-*d*]thiophen-7-ium trifluoromethanesulfonate (1t). Following

General Procedure A (GPA), **1t** was prepared as a brown solid (119.1 mg, 30% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 9.0 Hz, 2H), 8.07 (d, *J* = 8.6 Hz, 2H), 8.01 (d, *J* = 8.6 Hz, 2H), 7.94 (s, 2H), 7.85 (d, *J* = 9.0 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 2.35 (s, 3H), 2.20 (s, 6H), 2.07 (s, 12H), 1.89-1.80 (m, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.8, 146.7, 137.7, 133.1, 132.4, 130.9, 130.3, 127.5, 127.4, 125.9, 124.5, 122.0, 120.6 (d, *J* = 321.0 Hz), 42.9, 36.8, 36.7, 28.8, 21.7. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.1. **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{47}H_{47}S^+$: 643.3393; Found: 643.3388.

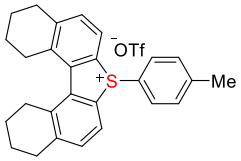


3,11-Dibromo-7-(*p*-tolyl)-7*H*-dinaphtho[2,1-*b*:1',2'-*d*]thiophen-7-ium trifluoromethanesulfonate (1u). Following General Procedure A (GPA), **1u** was prepared as a brown solid (47.8 mg, 14% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.68-8.65 (m, 2H), 8.16 (d, *J* = 2.1 Hz, 1H), 7.88 (d, *J* = 8.6 Hz, 2H), 7.84 (d, *J* = 8.6 Hz, 2H), 7.80 (d, *J* = 1.8 Hz, 1H), 7.82-7.78 (m, 2H), 7.53 (dd, *J* = 2.1, 9.1 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.7 Hz, 1H), 7.13 (d, *J* = 8.2 Hz, 2H), 2.31 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.6, 137.3, 132.6, 132.3, 131.6, 131.5, 131.1, 130.9, 128.3, 127.3, 124.0, 123.2, 120.5 (d, *J* = 308.8 Hz), 119.5, 21.7. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.0. **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{27}H_{17}SBr_2^+$: 530.9412; Found: 530.9417.



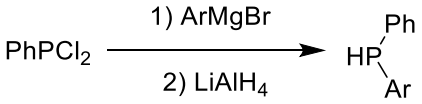
3,11-Di(thiophen-2-yl)-7-(*p*-tolyl)-7*H*-dinaphtho[2,1-*b*:1',2'-*d*]thiophen-7-ium trifluoromethanesulfonate (1v). Following General Procedure A (GPA), **1v** was prepared as a brown solid (324.3 mg, 47% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.9 Hz, 2H), 8.03-7.91 (m, 6H), 7.80 (d, *J* = 8.6 Hz, 2H), 7.66 (s, 2H), 7.49-7.41 (m, 6H), 7.21 (d, *J* = 7.9 Hz, 2H), 2.29 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.9, 140.0, 137.2, 137.0, 136.1, 133.1, 132.4, 130.8, 130.1, 127.7, 127.6, 127.2, 126.3, 126.0, 125.3, 122.8, 122.2, 121.1 (d, *J* = 321.3 Hz), 121.0, 21.7. **^{19}F NMR**

(471 MHz, $CDCl_3$) δ -78.0. **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{35}H_{23}S_3^+$: 539.0956; Found: 539.0958.

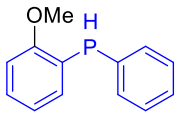


7-(*p*-Tolyl)-2,3,4,7,10,11,12,13-octahydro-1*H*-dinaphtho[2,1-*b*:1',2'-*d*]thiophen-7-ium trifluoromethanesulfonate (1x). Following General Procedure A (GPA), **1x** was prepared as a brown solid (189.7 mg, 71% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 3.00-2.95 (m, 8H), 2.38 (s, 3H), 1.96-1.91 (m, 4H), 1.73-1.68 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.4, 146.3, 139.9, 138.5, 132.3, 132.0, 130.2, 128.4, 125.7, 124.7, 120.9 (q, *J* = 321.3 Hz), 32.0, 28.9, 22.1, 21.6, 21.1. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.1. **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{27}H_{27}S^+$: 383.1828; Found: 383.1828.

2.1.2 General Procedure B (GPB) for the Synthesis of Substrates 2[5]

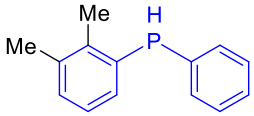


To a solution of $PhPCl_2$ (4.49 g, 25.1 mmol) in THF (50 mL) was added slowly ArMgBr (25.1 mmol in 50 mL of THF, prepared from ArBr (5.00 g, 25.1 mmol) and Mg (0.72 g, 30.1 mmol) in 50 mL of THF) at -80 °C under N_2, and the mixture was stirred at -80 °C for 2 h before it was warmed to room temperature and stirred for another 2 h. The mixture was cooled to 0 °C and $LiAlH_4$ (1.14 g, 30.1 mmol) was added slowly. The mixture was kept stirring at room temperature for 2 h. Degassed water (10 mL) was added dropwise at 0 °C and the mixture was extracted with ether (40 mL×3). The organic layer was combined and dried over $MgSO_4$. The solvent was removed by distillation, the product was prepared and purified by high vacuum microdistillation as a colorless liquid.

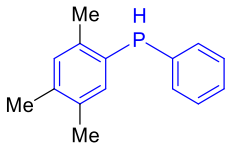


(2-Methoxyphenyl)(phenyl)phosphane (2f) (CAS: 92025-78-0)**.**[6] Following General Procedure B (GPB), **2f** was prepared as a colorless liquid (1.2 g, 23%

yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42-7.38 (m, 2H), 7.17-7.16 (m, 2H), 7.14-7.09 (m, 1H), 7.04-7.01 (m, 1H), 6.77-6.67 (m, 3H), 5.60 (brs, 1H), 3.63 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.4 (d, J = 10.1 Hz), 155.1, 133.7 (d, J = 7.6 Hz), 133.5 (d, J = 17.6 Hz), 129.4, 128.4, 127.6, 127.4 (d, J = 6.3 Hz), 120.0 (d, J = 2.5 Hz), 119.1, 114.5, 109.2 (d, J = 1.1 Hz), 54.5. **^{31}P NMR** (202 MHz, $CDCl_3$) δ -54.4 (s, 1P). **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{13}OPH^+$ 217.0777; Found 217.0778.



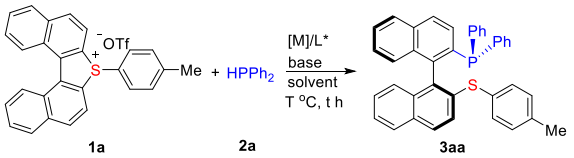
(2,3-Dimethylphenyl)(phenyl)phosphane (2g). Following General Procedure B (GPB), **2g** was prepared as a colorless liquid (2.8 g, 52% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41-7.38 (m, 2H), 7.23-7.19 (m, 4H), 7.08-7.07 (m, 1H), 7.00-6.97 (m, 1H), 5.35-4.94 (brs, 1H), 2.29 (s, 3H), 2.21 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.1 (d, J = 17.6 Hz), 137.2 (d, J = 3.8 Hz), 134.3 (d, J = 17.4 Hz), 134.2 (d, J = 20.6 Hz), 133.2 (d, J = 6.3 Hz), 130.9, 128.8, 128.7, 128.6, 126.0 (d, J = 2.5 Hz), 20.8, 18.4 (d, J = 18.9 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$) δ -45.2 (s, 1P). **HRMS** (ESI-TOF) m/z: $[M+K]^+$ Calcd for $C_{14}H_{15}PK^+$: 253.0543; Found: 253.0539.



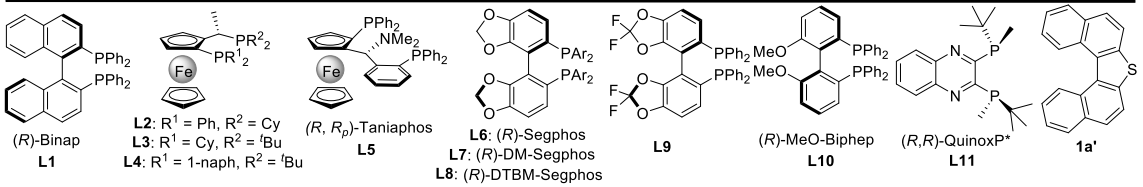
Phenyl(2,4,5-trimethylphenyl)phosphane (2i). Following General Procedure B (GPB), **2h** was prepared as a colorless liquid (4.5 g, 79% yield).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31-7.30 (m, 2H), 7.20-7.18 (m, 3H), 7.11 (d, J = 6.7 Hz, 1H), 6.89 (s, 1H), 4.71 (brs, 1H), 2.22 (s, 3H), 2.13 (s, 3H), 2.10 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.1 (d, J = 3.8 Hz), 137.8 (d, J = 5.4 Hz), 136.8 (d, J = 11.3 Hz), 136.7, 134.2, 133.8 (d, J = 17.6 Hz), 133.6 (d, J = 17.6 Hz), 131.7 (d, J = 3.8 Hz), 128.5 (d, J = 6.3 Hz), 128.2, 21.0 (d, J = 10.1 Hz), 19.5, 19.2. **^{31}P NMR** (202 MHz, $CDCl_3$) δ -49.8 (s, 1P). **HRMS** (ESI-TOF) m/z: $[M+K]^+$ Calcd for $C_{15}H_{17}PK^+$: 267.0699; Found: 267.0695.

2.2 Optimization of Conditions

Table S1. Optimization of conditions[a]



1a 2a 3aa



(*R*)-Binap **L1**

L2: R^1 = Ph, R^2 = Cy
L3: R^1 = Cy, R^2 = ^{t}Bu
L4: R^1 = 1-naph, R^2 = ^{t}Bu

(*R*, R_p)-Taniaphos **L5**

L6: (*R*)-Segphos
L7: (*R*)-DM-Segphos
L8: (*R*)-DTBM-Segphos

L9

(*R*)-MeO-Biphep **L10**

(*R*,*R*)-QuinoxP* **L11**

1a'

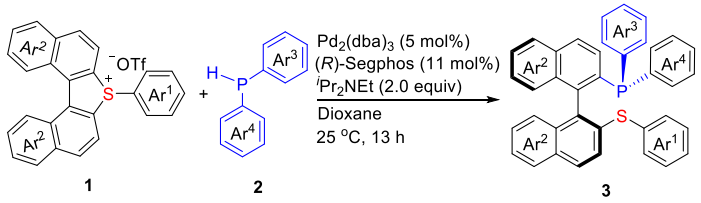
entry	1	L*	solvent	base	yield[b] (%)	*ee*[c] (%)
1	**1a**	**L1**	THF	Et_3N	96	62
2	**1a**	**L2**	THF	Et_3N	42	53
3	**1a**	**L3**	THF	Et_3N	58	5
4[d]	**1a**	**L4**	THF	Et_3N	53	0
5	**1a**	**L5**	THF	Et_3N	93	65
6	**1a**	**L6**	THF	Et_3N	58	79
7	**1a**	**L7**	THF	Et_3N	72	52
8	**1a**	**L8**	THF	Et_3N	87	0
9	**1a**	**L9**	THF	Et_3N	39	58
10	**1a**	**L10**	THF	Et_3N	80	63
11	**1a**	**L11**	THF	Et_3N	10	-64
12	**1a**	**L6**	THF	Barton'base	41	<5
13	**1a**	**L6**	THF	Cs_2CO_3	69	40
14	**1a**	**L6**	THF	K_3PO_4	82	77
15	**1a**	**L6**	dioxane	K_3PO_4	62	87
16	**1a**	**L6**	toluene	K_3PO_4	85	64
17	**1a**	**L6**	MTBE	K_3PO_4	91	60
18	**1a**	**L6**	DCE	K_3PO_4	81	70
19[e]	**1a**	**L6**	dioxane	K_2HPO_4	64	90
20[e]	**1a**	**L6**	dioxane	^{i}Pr$_2$NEt	74	90
21[e][f]	**1a**	**L6**	dioxane	^{i}Pr$_2$NEt	95	93
22[e]	**1a'**	**L6**	dioxane	^{i}Pr$_2$NEt	0	n.a.
23[g]	**1a**	**none**	THF	Et_3N	35	-
24[h]	**1a**	**none**	THF	Et_3N	42	-
25	**1a**	**none**	THF	Et_3N	46	-
26[h]	**1a**	**L3**	THF	Et_3N	37.5	5

[a] Reaction conditions: **1** (0.120 mmol), **2a** (0.120 mmol), base (1.5 equiv), and $Pd_2(dba)_3$ (2.5 mol%) in solvent (4.0 mL) at 25 °C for 13 h, unless otherwise noted. THF = tetrahydrofuran, MTBE = methyl *tert*-butyl ether. [b] The yields were obtained by ^{1}H NMR analysis of the crude reaction mixture with the aid of $Cl_2CHCHCl_2$ as an internal standard. [c] The ee was determined by HPLC on a chiral stationary phase column. [d] The reaction was performed at 60 °C (no reaction at 25 °C). [e] $Pd_2(dba)_3$ (5 mol%). [f] **1a** (0.132 mmol), base (2.0 equiv). [g] $Pd_2(dba)_3$ instead of [Pd(Allyl)Cl]$_2$ [h] $Pd_2(dba)_3$ instead of $Pd(OAc)_2$

A typical procedure for entry 21:

To a solution of $Pd_2(dba)_3$ (5.5 mg, 0.006 mmol, 5 mol%) in degassed dioxane (4 mL) in a Schlenk tube under nitrogen was added (*R*)-Segphos (8.1 mg, 0.0132 mmol, 11 mol%). The solution was stirred at room temperature (25 °C) for 30 min, and then sulfonium salt **1a** (69.4 mg, 0.132 mmol, 1.10 equiv), $^{i}Pr_2NEt$ (31.0 mg, 0.240 mmol, 2.00 equiv) and $HPPh_2$ **2a** (22.3 mg, 0.120 mmol, 1.00 equiv) were added. The mixture was stirred at 25 °C for 13 h. After completion, the reaction mixture was passed through a short column of silica-gel with EtOAc as eluent. The solvent was removed on a rotary evaporator and the residue was subjected to silica gel chromatography (EtOAc/petroleum ether = 1/10) to give **3aa** as a white solid (63.9 mg, 95% yield, 93% ee).

2.3 Synthesis of the Atropoisomeric Phosphine Products

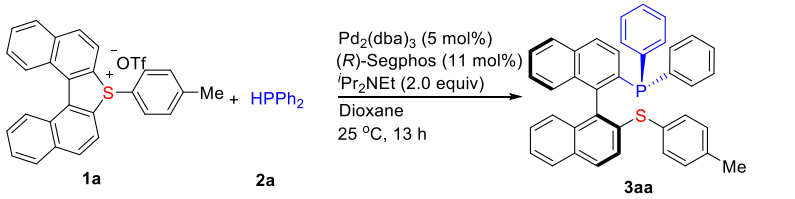


General Procedure C (GPC):

To a solution of $Pd_2(dba)_3$ (5.5 mg, 0.006 mmol, 5 mol%) in degassed dioxane (4 mL) in a Schlenk tube under nitrogen was added (*R*)-Segphos (8.1 mg, 0.0132 mmol, 11 mol%). The solution was stirred at room temperature for 30 min, and then sulfonium salt **1** (0.132 mmol, 1.10 equiv), $^{i}Pr_2NEt$ (31.0 mg, 0.240 mmol, 2.00 equiv) and diarylphosphine **2** (0.120 mmol, 1.00 equiv) were added. The mixture was stirred at 25 °C for 13 h. After completion, the reaction mixture was passed through a short column of silica-gel with EtOAc as eluent. The solvent was removed on a rotary evaporator and the residue was subjected to silica gel chromatography (EtOAc/petroleum ether = 1/10) to give **3** as a white solid.

3. Scale-Up Synthesis of Enantiomerically Pure 3aa and 3ae

(1) Scaled-up synthesis of enantiomerically pure 3aa (2 mmol scale)



1a **2a** **3aa**

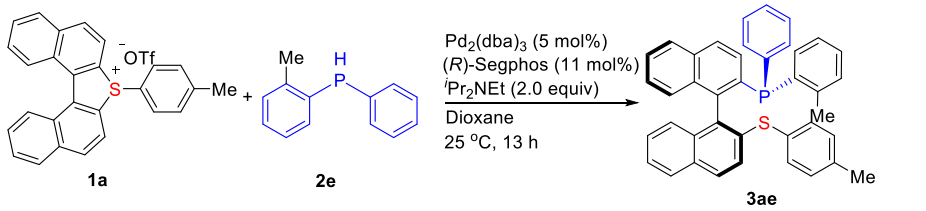
1.159 g, 2.20 mmol 0.372 g, 2.00 mmol 92% yield, 90% ee (1.11 g)

Recrystallization: 82% yield, >99% ee (0.910 g)

To a solution of $Pd_2(dba)_3$ (91.9 mg, 0.100 mmol, 5 mol%) in degassed dioxane (70 mL) in a Schlenk tube under nitrogen was added (*R*)-Segphos (135.3 mg, 0.220 mmol, 11 mol%). The solution was stirred at room temperature (25 °C) for 30 min, and then sulfonium **1a** (1.159 g, 2.20 mmol, 1.10 equiv), $^iPr_2NEt$ (0.157 g, 4.00 mmol, 2.00 equiv), $HPPh_2$ **2a** (372.0 mg, 2.00 mmol, 1.00 equiv) were added. The mixture was stirred at 25 °C for 13 h. After completion, the reaction mixture was passed through a short column of silica-gel with EtOAc as eluent. The solvent was removed on a rotary evaporator and the residue was subjected to silica gel chromatography (EtOAc/petroleum ether = 1/10) to give **3aa** as a white solid (1.11 g, 92% yield, 90% ee).

The above obtained **3aa** was recrystallized from $CHCl_3$/acetone (via evaporation) to afford enantiomerically pure **3aa** (0.91 g, 82% yield, >99% ee) as colorless crystals.

(2) **Scaled-up synthesis of enantiomerically pure 3ae (2 mmol scale)**



1a **2e** **3ae**

1.159 g, 2.20 mmol 0.400 g, 2.00 mmol 62% yield, 98% ee (0.715 g)

Recrystallization: 88% yield, >99% ee (0.629 g)

To a solution of $Pd_2(dba)_3$ (91.9 mg, 0.100 mmol, 5 mol%) in degassed dioxane (70 mL) in a Schlenk tube under nitrogen was added (*R*)-Segphos (135.3 mg, 0.220 mmol, 11 mol%). The solution was stirred at room temperature (25 °C) for 30 min, and then sulfonium **1a** (1.159 g, 2.20 mmol, 1.10 equiv), $^iPr_2NEt$ (0.157 g, 4.00 mmol, 2.00 equiv), **2e** (0.400 g, 2.00 mmol, 1.00 equiv) were added. The mixture was stirred at 25 °C for 13 h. After completion, the reaction mixture was passed through a short column of silica-gel with EtOAc as eluent. The solvent was removed on a rotary evaporator and the residue

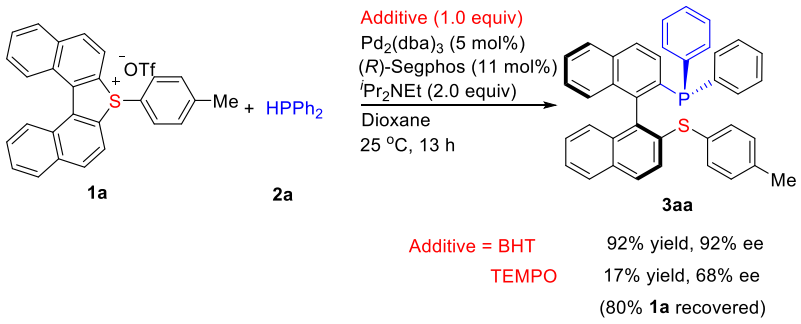
was subjected to silica gel chromatography (EtOAc/petroleum ether = 1/10) to give **3ae** as a white solid (0.715 g, 68% yield, 98% ee).

The above obtained **3ae** was recrystallized from $CHCl_3$/acetone (via evaporation) to afford enantiomerically pure **3ae** (0.629 g, 88% yield, >99% ee) as colorless crystals.

4. Mechanistic Considerations

4.1 Radical Trapping Experiments

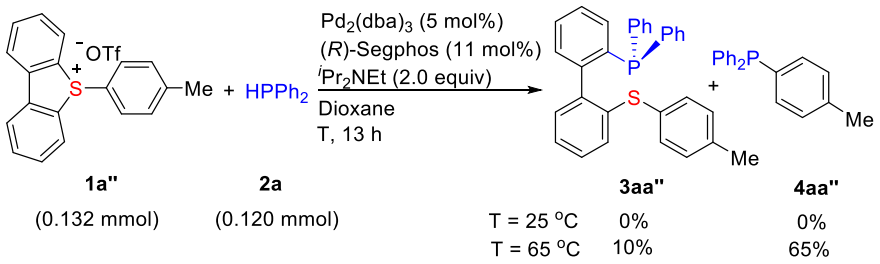
Radical trapping experiments using BHT (2,6-di-tert-butyl-4-methylphenol)/TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) as a radical scavenger have been conducted as shown below and the results excluded the radical pathway.



To a solution of $Pd_2(dba)_3$ (5.5 mg, 0.006 mmol, 5 mol%) in degassed dioxane (4 mL) in a Schlenk tube under nitrogen was added (*R*)-Segphos (8.1 mg, 0.0132 mmol, 11 mol%). The solution was stirred at room temperature (25 °C) for 30 min, and then sulfonium **1a** (69.4 mg, 0.132 mmol, 1.10 equiv), ^{i}Pr$_2$NEt (31.0 mg, 0.240 mmol, 2.00 equiv), $HPPh_2$ **2a** (22.3 mg, 0.120 mmol, 1.00 equiv), BHT (2,6-di-tert-butyl-4-methylphenol, 26.4 mg, 0.120 mmol, 1.00 equiv) were added. The mixture was stirred at 25 °C for 13 h. After completion, the reaction mixture was passed through a short column of silica-gel with EtOAc as eluent. The solvent was removed on a rotary evaporator and the residue was subjected to silica gel chromatography (EtOAc/petroleum ether = 1/10) to give **3aa** as a white solid (61.9 mg, 92% yield, 92% ee).

When TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) (18.7 mg, 0.120 mmol, 1.00 equiv)] was used instead of BHT as a radical scavenger under otherwise identical conditions, the yield and enantioselectivity of **3aa** were low (17% yield, 68% ee), **1a** (80%) being recovered.

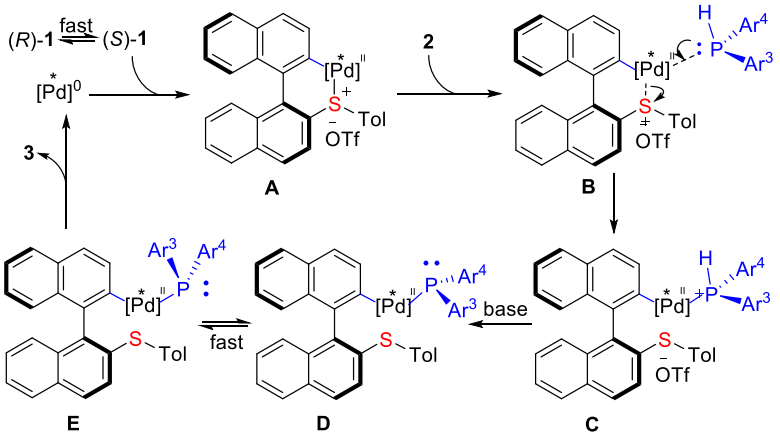
4.2 The reaction of 1a'' with 2a



To a solution of $Pd_2(dba)_3$ (5.5 mg, 0.006 mmol, 5 mol%) in degassed dioxane (4 mL) in a Schlenk tube under nitrogen was added (*R*)-Segphos (8.1 mg, 0.0132 mmol, 11 mol%). The solution was stirred at room temperature (25 °C) for 30 min, and then sulfonium salt **1a'** (51.2 mg, 0.132 mmol, 1.10 equiv), $^{i}Pr_2NEt$ (31.0 mg, 0.240 mmol, 2.00 equiv) and $HPPh_2$ **2a** (22.3 mg, 0.120 mmol, 1.00 equiv) were added. The mixture was stirred at 25 °C for 13 h. No reaction was observed.

When the reaction was carried out at 65 °C instead of 25 °C under otherwise identical conditions, **4aa'** (21.6 mg, 65% yield) and **3aa'** (5.5 mg, 10% yield) were isolated (EtOAc/petroleum ether = 1/10).

4.3 Proposed Catalytic Cycle



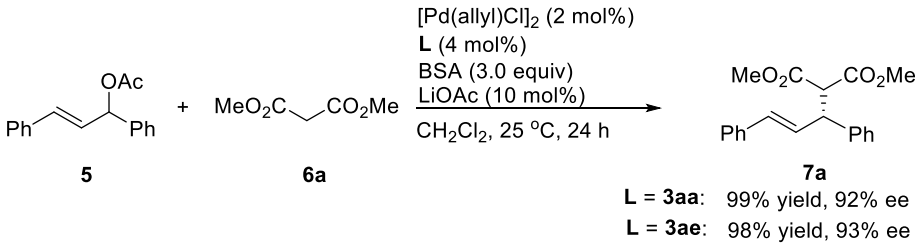
Scheme S3. Proposed catalytic cycle

A plausible catalytic cycle was proposed as depicted in Scheme S3. (R_a)-**1** and (S_a)-**1** are in rapid equilibrium[3,9] with each other via the rotation of the C_{aryl}-C_{aryl} single bond.

The (*R*)-Segphos-ligated $Pd^{(0)}$ complex undergoes oxidative addition preferentially to (S)-**1** cleaving an endo C-S bond to form biaryl $[Pd]^{II}$ species **A**. The following coordination of **2** (**B**) leads to the formation of complex **C** followed by the abstraction of a proton to give the $[Pd]^{II}$-phosphido species[10,11] **D** and **E** which undergo a rapid equilibrium (when $Ar^3 \neq Ar^4$). Subsequent reductive elimination of the more thermodynamic stable **D** furnishes the chiral phosphine product **3** and regenerates the $[Pd]^0$ species, closing a catalytic cycle. The key point is that the equilibrium between **D** and **E** must be much faster than the reductive elimination in this dynamic kinetic resolution process in order to achieve high enantio-control of P-stereogenic centre. Notably, the exist of P,S-ligands which have high affinity to metals does not interrupt the catalytic cycle, presumably due to the stronger chelating ability of Segphos coordinated with palladium.

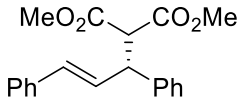
5. Application of 3aa/3ae as a Chiral Ligand

(1) Pd-catalyzed asymmetric allylic alkylation reaction[12]



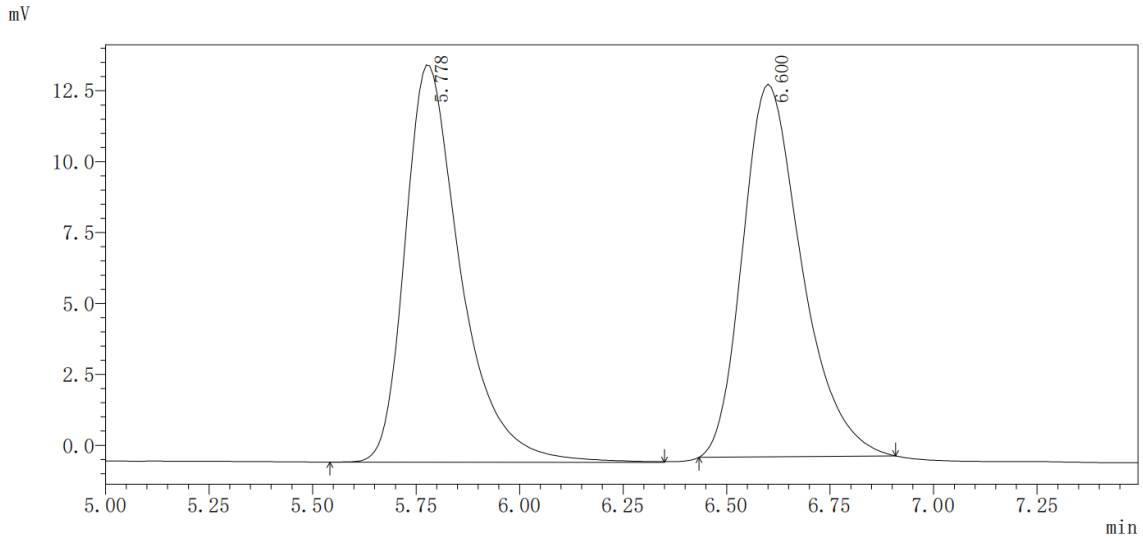
$[PdCl(C_3H_5)]_2$ (1.4 mg, 2 mol%), LiOAc (1.3 mg, 10 mol%), **3aa** (4.5 mg, 4 mol%) and CH_2Cl_2 (1 mL) were placed in a Schlenk tube under argon. The resulting mixture was stirred at room temperature (25 °C) for 30 min. Racemic 1,3-diphenyl-2-propenyl acetate **5** (50.4 mg, 0.200 mmol) in CH_2Cl_2 (1 mL), dimethyl malonate **6a** (79.8 mg, 0.600 mmol) in CH_2Cl_2 (1 mL) and N,O-bis(trimethylsilyl)-acetamide (BSA) (122.0 mg, 0.600 mmol) in CH_2Cl_2 (1 mL) were added subsequently, and the reaction mixture was stirred at room temperature (25 °C) for 24 h. After completion, the reaction mixture was quenched with saturated NH_4Cl aqueous solution (10.0 mL) and extracted with Et_2O (3 x 10 mL). The combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (hexanes/EtOAc = 20/1) to afford product **7a** (64.2 mg, 99% yield, 92% ee) as a colorless oil.

When **3ae** (4.7 mg, 4 mol%) was used instead of **3aa** under otherwise identical conditions, product **7a** was obtained (63.6 mg, 98% yield, 93% ee) as a colorless oil.



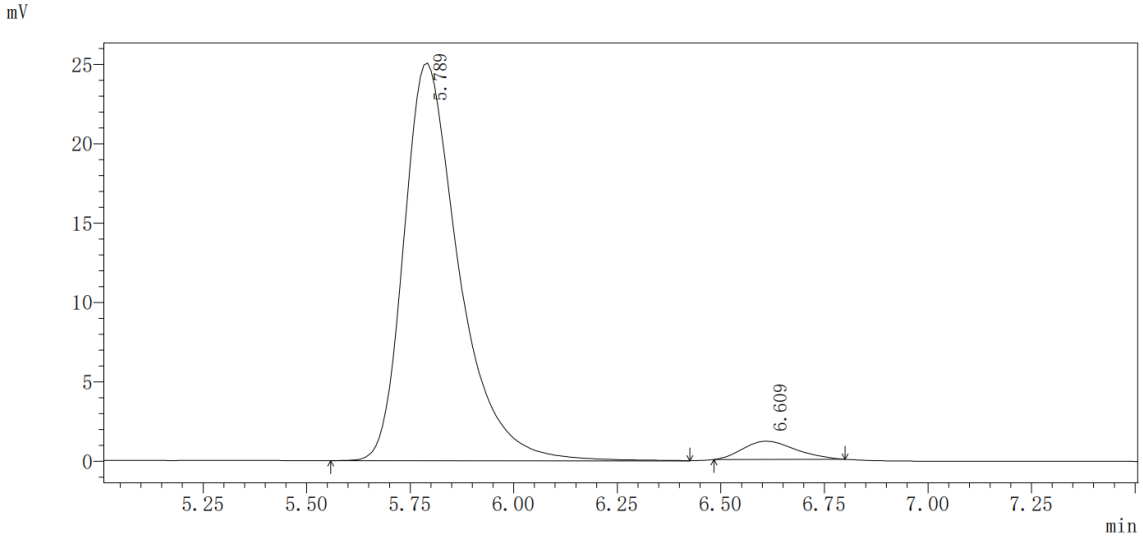
Dimethyl (*R*,*E*)-2-(1,3-diphenylallyl)malonate (7a). **7a** was prepared according to above method (64.2 mg, 99% yield, 93% ee) and purified by flash column chromatography (hexanes/EtOAc = 20/1) as a colorless oil. **[α]$_D^{23}$** +17.2 (*c* 0.61, $CHCl_3$) for 93% *ee.* **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25-7.10 (m, 10H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.26 (dd, *J* = 15.7, 8.6 Hz, 1H), 4.19 (dd, *J* = 10.7, 8.8 Hz, 1H), 3.88 (d, *J* = 10.9 Hz, 1H), 3.62 (s, 3H), 3.43 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.2, 167.8, 140.2, 136.8, 131.9, 129.1, 128.7, 128.5, 127.9, 127.6, 127.2, 126.4, 57.7, 52.7, 52.6, 52.5, 49.2, 41.1. The ^{1}H NMR matched the literature reported data.[6] The ee was determined on a Chiralcel IA column with 15% i-PrOH/hexane, flow = 1.0 mL/min, λ = 254 nm, λ = 254 nm, t (major) = 5.8 min, t (minor) = 6.7 min.

HPLC charts (with 3aa as the ligand):



Detector A channel 254 nm

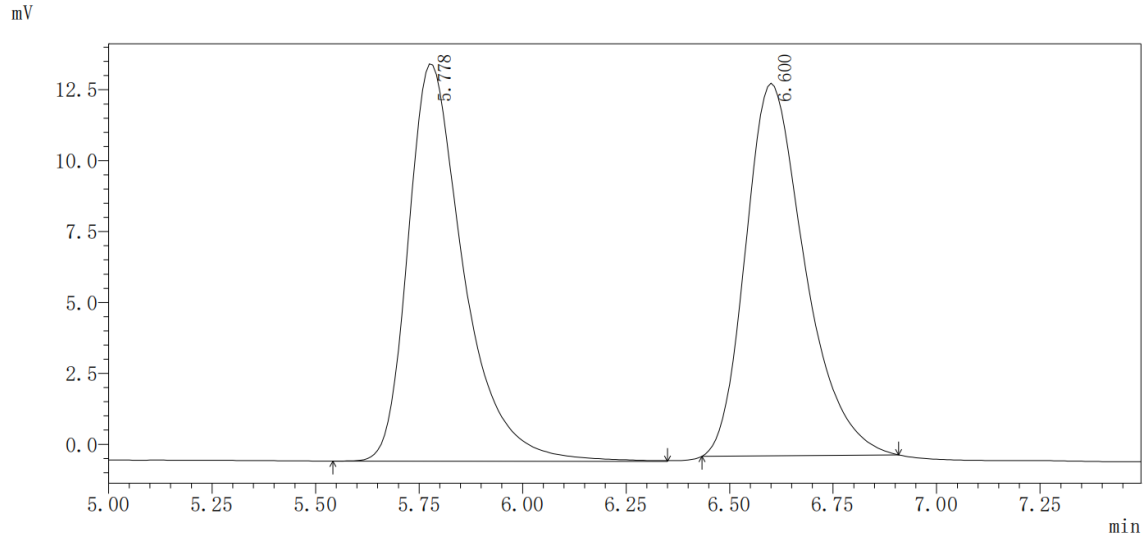
Peak	Ret. Time	Area	Height	Conc.
1	5.778	130985	14008	50.033
2	6.600	130811	13136	49.967
Total		261796	27145	



Detector A channel 254 nm

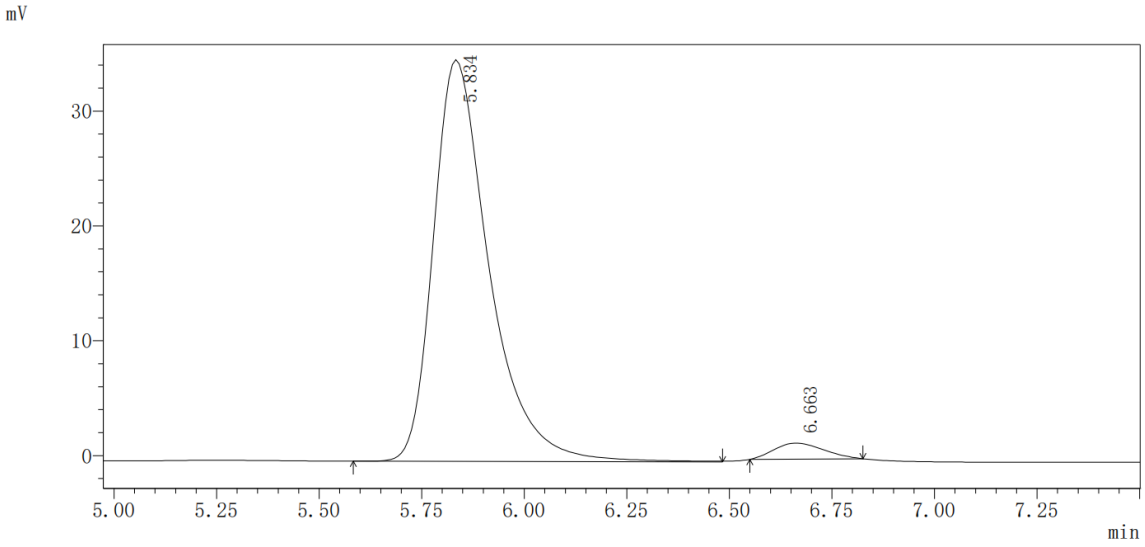
Peak	Ret. Time	Area	Height	Conc.
1	5.789	232267	25061	95.810
2	6.609	10158	1150	4.190
Total		242424	26211	

HPLC charts (with 3ae as the ligand):



Detector A channel 254 nm

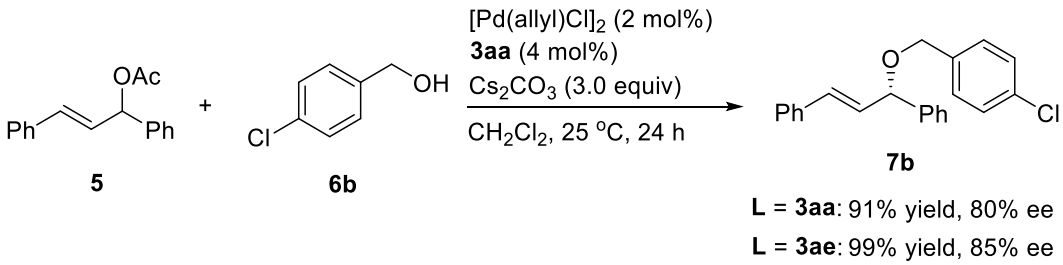
Peak	Ret. Time	Area	Height	Conc.
1	5.778	130985	14008	50.033
2	6.600	130811	13136	49.967
Total		261796	27145	



Detector A channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	5.834	327704	34961	96.414
2	6.663	12190	1420	3.586
Total		339894	36380	

(2) Pd-catalyzed asymmetric allylic etherification reaction[13]

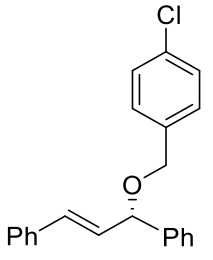


L = **3aa**: 91% yield, 80% ee

L = **3ae**: 99% yield, 85% ee

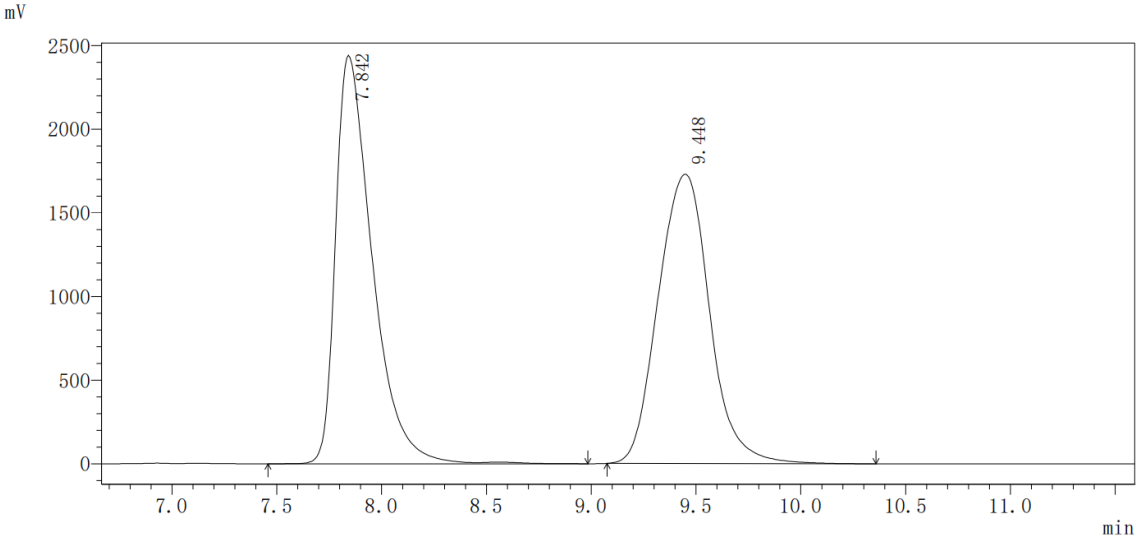
$[PdCl(C_3H_5)]_2$ (1.4 mg, 2 mol%), **3aa** (4.5 mg, 4 mol%) and CH_2Cl_2 (1 mL) were placed in a Schlenk tube under argon. The resulting mixture was stirred at room temperature (25 °C) for 30 min. Racemic 1,3-diphenyl-2-propenyl acetate **5** (50.4 mg, 0.200 mmol) was added and the mixture was stirred for another 10 min. (4-Chlorophenyl) methanol **6b** (85.8 mg, 0.600 mmol) and Cs_2CO_3 (195.0 mg, 0.600 mmol) were added. After stirring at room temperature for 24 h, the solvent was evaporated in vacuo and the residue was purified by flash column chromatography on silica gel to give product **7b** as a colorless oil (60.8 mg, 91% yield, 80% ee).

When **3ae** (4.7 mg, 4 mol%) was used instead of **3aa** under otherwise identical conditions, product **7b** was obtained (66.3 mg, 99% yield, 85% ee) as a colorless oil.



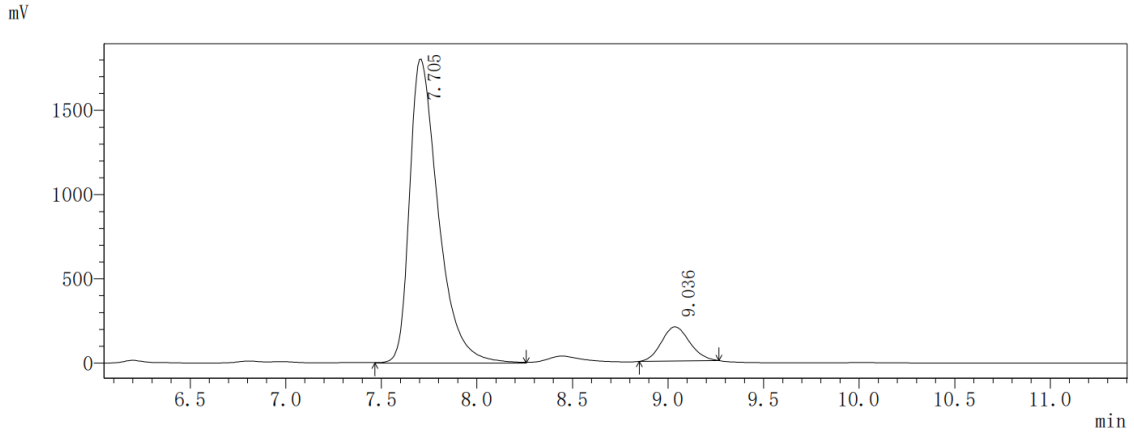
(S,E)-(3-((4-chlorobenzyl)oxy)prop-1-ene-1,3-diyl)dibenzene (7b). **7b** was prepared according to above method and purified by flash column chromatography (hexanes/EtOAc = 10/1) as a colorless oil (66.3 mg, 99% yield, 85% ee). $[\alpha]_D^{23}$ +20.0 (*c* 0.5, $CHCl_3$) for 85% *ee*. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32-7.08 (m, 14H), 6.52 (d, *J* = 15.9 Hz, 1H), 6.22 (dd, *J* = 15.9, 7.1 Hz, 1H), 4.88 (d, *J* = 7.1 Hz, 1H), 4.24 (dd, *J* = 12.2, 18.6 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.9, 135.9, 135.4, 132.2, 130.7, 129.0, 128.0, 127.6, 127.5, 127.4, 126.8, 125.9, 125.6, 80.8, 68.3. The ee was determined on a Chiralcel IB column with 0.1% i-PrOH/hexane, flow = 0.8 mL/min, λ = 254 nm, t (major) = 8.3 min, t (minor) = 9.6 min.

HPLC charts (with 3aa as the ligand):



Detector A channel 254 nm

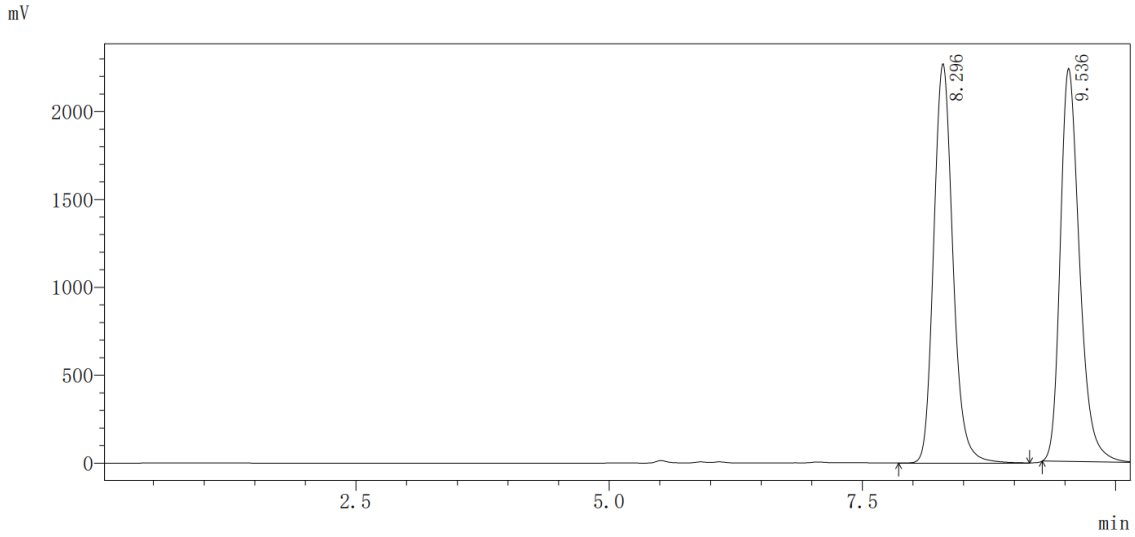
Peak	Ret. Time	Area	Height	Conc.
1	7.842	29789108	2442504	50.267
2	9.448	29472236	1729292	49.733
Total		59261343	4171796	



Detector A channel 254 nm

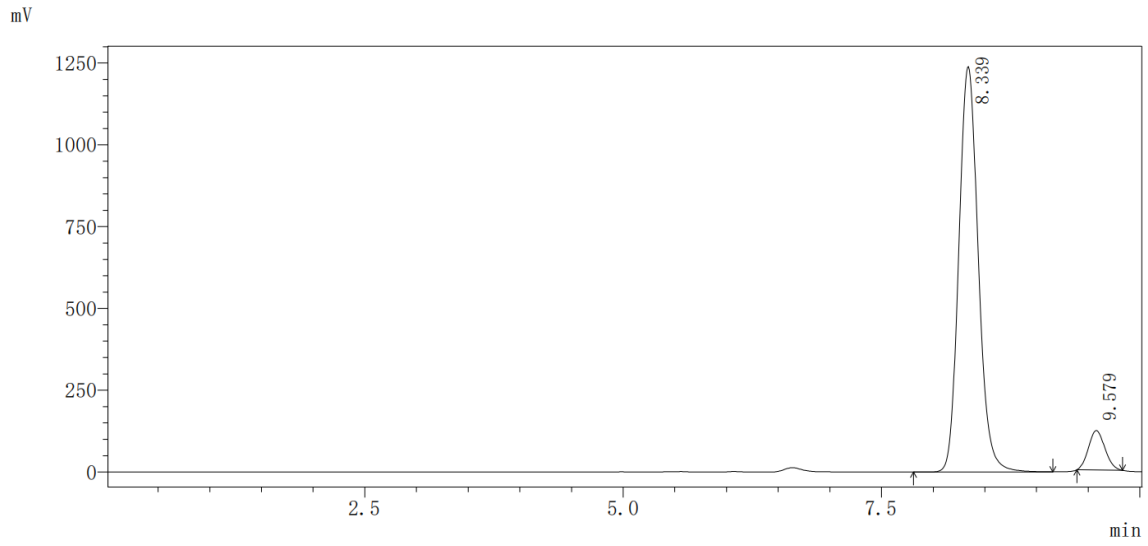
Peak	Ret. Time	Area	Height	Conc.
1	7.705	18909207	1804991	90.397
2	9.036	2008701	199244	9.603
Total		20917908	2004235	

HPLC charts (with 3ae as the ligand):



Detector A channel 254 nm

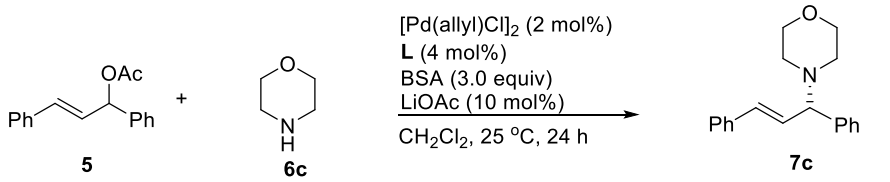
Peak	Ret. Time	Area	Height	Conc.
1	8.296	29998950	2271585	50.326
2	9.536	29610120	2237289	49.674
Total		59609070	4508874	



Detector A channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	8.339	16263381	1239419	92.401
2	9.579	1337577	120581	7.599
Total		17600958	1360000	

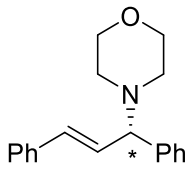
(3) Pd-catalyzed asymmetric allylic amination reaction[14,15]



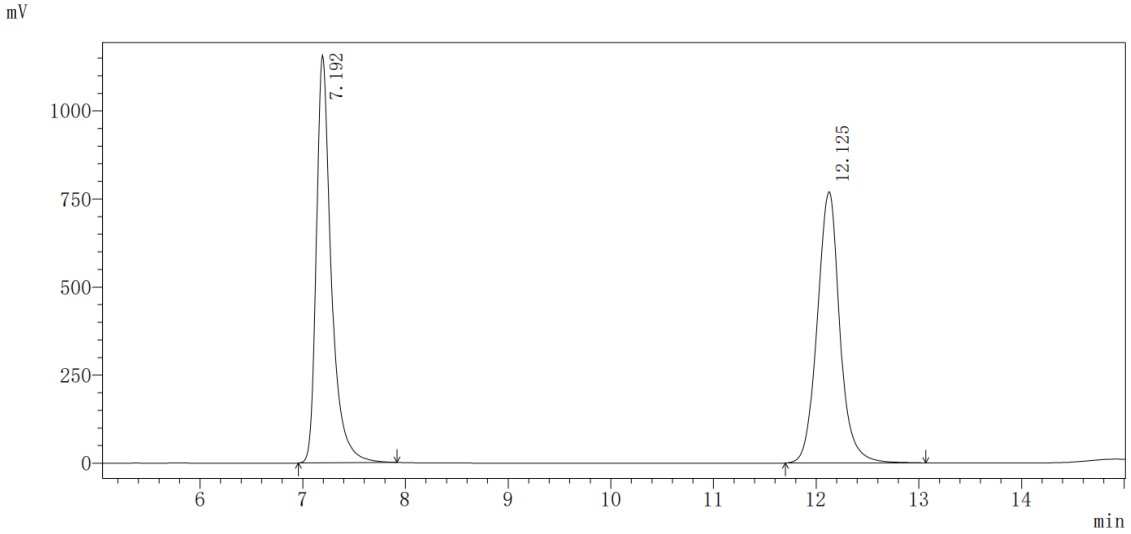
73% yield, 75% ee

$[PdCl(C_3H_5)]_2$ (1.4 mg, 2 mol%), LiOAc (1.3 mg, 10 mol%), **3aa** (4.5 mg, 4 mol%) and CH_2Cl_2 (1 mL) were placed in a Schlenk tube under argon. The resulting mixture was stirred at room temperature (25 ˚C) for 30 min. Racemic 1,3-diphenyl-2-propenyl acetate **5** (50.4 mg, 0.200 mmol) in CH_2Cl_2 (0.4 mL), morpholine **6c** (52.3 mg, 0.600 mmol) in CH_2Cl_2 (1mL), and N,O-bis(trimethylsilyl)-acetamide (BSA) (122.0 mg, 0.600 mmol) in CH_2Cl_2 (1 mL) were added subsequently. The reaction mixture was stirred at room temperature (25 ˚C) for 24 h. After completion, the reaction mixture was quenched with saturated NH_4Cl aqueous solution (10.0 mL) and extracted with Et_2O (3 x 10 mL). The combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, filtered, and

concentrated. The residue was purified by flash chromatography on silica gel (hexanes/EtOAc = 10/1) to afford product **7c** (40.8 mg, 73% yield, 75% ee) as a colorless oil.

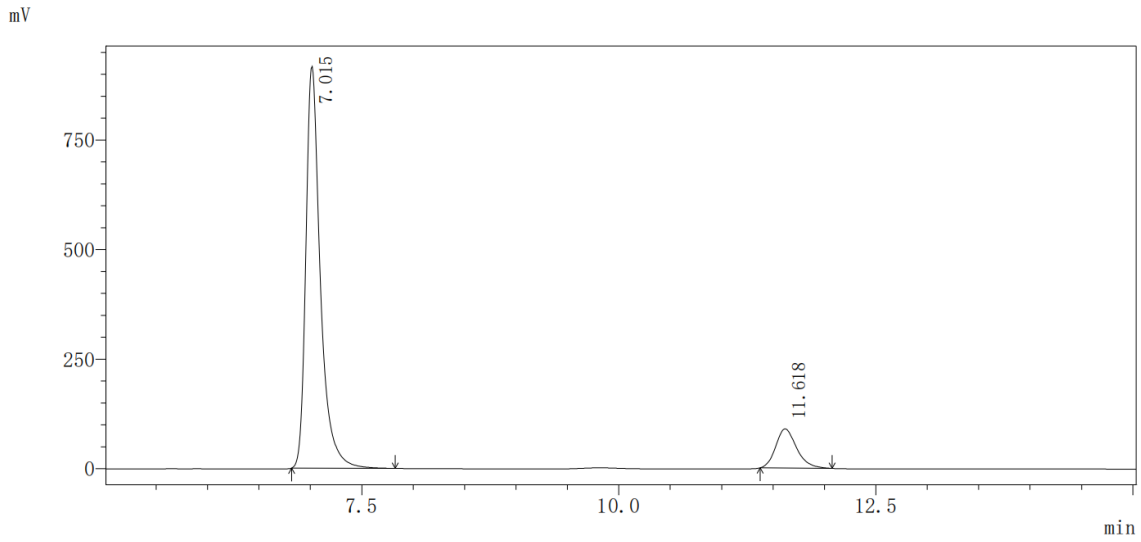


(*S,E*)-4-(1,3-diphenylallyl)morpholine (7c). 7c was prepared according to above method and purified by flash column chromatography (hexanes/EtOAc = 10/1) as a colorless oil (40.8 mg, 73% yield, 75% ee). **[α]$_D^{23}$**+13.7 (*c* 0.73, $CHCl_3$) for 75% *ee*. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33-7.11 (m, 10H), 6.49 (d, *J* = 15.8 Hz, 1H), 6.20 (dd, *J* = 15.8, 8.9 Hz, 1H), 3.71 (d, *J* = 8.9 Hz, 1H), 3.63 (t, *J* = 4.6 Hz, 4H), 2.42-2.52 (m, 2H), 2.34-2.29 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.6, 136.8, 131.6, 131.4, 128.7, 128.6, 128.1, 127.6, 127.4, 126.4, 74.9, 67.2, 52.4. The ^{1}H NMR matched the literature reported data.[8] The ee was determined on a Chiralcel IB column with 1% i-PrOH/hexane, flow = 1.0 mL/min, λ = 254 nm, t (major) = 7.02 min, t (minor) = 11.62 min.



Detector A channel 254 nm

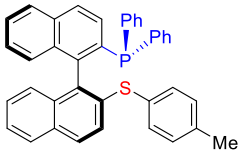
Peak	Ret. Time	Area	Height	Conc.
1	7.192	11663217	1156499	49.871
2	12.125	11723581	769899	50.129
Total		23386797	1926398	



Detector A channel 254 nm

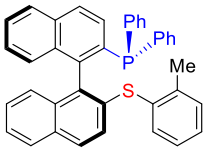
Peak	Ret. Time	Area	Height	Conc.
1	7.015	8911796	916980	87.574
2	11.618	1264537	89360	12.426
Total		10176334	1006340	

6. Characterization of the Products

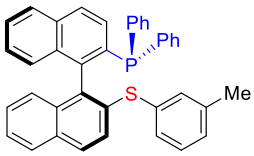


(*S*)-Diphenyl(2'-(*p*-tolylthio)-[1,1'-binaphthalen]-2-yl) phosphane (3aa). Following General Procedure C (GPC), **3aa** was prepared and purified by flash column chromatography (EtOAc/petroleum ether = 1/10) as a white solid (63.9 mg, 95% yield, 93% ee). **$[\alpha]_D^{23}$** -134.0 (*c* 1.0, $CHCl_3$) for 93% ee. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96-7.94 (m, 2H), 7.82 (d, *J* = 8.5 Hz, 2H), 7.55-7.52 (m, 2H), 7.38-7.28 (m, 9H), 7.24-7.21 (m, 3H), 7.19-7.12 (m, 4H), 7.07 (d, *J* = 7.8 Hz, 2H), 7.00-6.97 (m, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 2.35 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.0, 143.7, 138.1 (d, *J* = 12.6 Hz), 137.8, 137.2 (d, *J* = 13.6 Hz), 136.7 (d, *J* = 2.9 Hz), 135.9 (d, *J* = 10.8 Hz), 134.9 (d, *J* = 8.6 Hz), 134.1 (d, *J* = 21.0 Hz), 133.8, 133.7 (d, *J* = 2.6 Hz), 133.6, 133.1 (d, *J* = 18.2 Hz), 132.7 (d, *J* = 7.7 Hz), 131.4, 130.8, 130.7 (d, *J* = 2.0 Hz), 129.9, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 126.8 (d, *J* = 29.2 Hz), 126.5 (d, *J* = 2.5 Hz), 126.3, 126.2, 126.1, 125.2, 21.2. **^{31}P NMR** (202 MHz, $CDCl_3$) δ -14.5 (s, 1P). The enantiomeric excess was determined by Daicel Chiralpak IA, n-hexane/isopropanol =

99.5/0.5, 0.5 mL/min, λ = 254 nm, t (major) = 10.4 min, t (minor) = 11.0 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{39}H_{29}PSH^+$: 561.1800; Found: 561.1803.

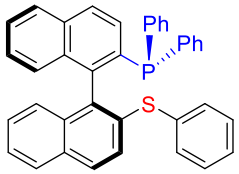


(*S*)-Diphenyl(2'-(*o*-tolylthio)-[1,1'-binaphthalen]-2-yl)phosphane (3ba). Following General Procedure C (GPC), **3ba** was prepared and purified by flash column chromatography (EtOAc/petroleum ether = 1/10) as a white solid (57.8 mg, 86% yield, 96% ee). **$[\alpha]_D^{23}$** -84.4 (*c* 0.64, $CHCl_3$) for 96% ee. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85-7.82 (m, 2H), 7.69 (t, *J* = 8.9 Hz, 2H), 7.44-7.39 (m, 2H), 7.28-7.24 (m, 3H), 7.22-7.17 (m, 6H), 7.12-7.10 (m, 3H), 7.10-7.03 (m, 2H), 7.02-6.98 (m, 3H), 6.95 (d, *J* = 8.8 Hz, 1H), 6.87-6.83 (m, 1H), 6.65 (d, *J* = 8.5 Hz, 1H), 2.10 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.7 (d, *J* = 34.9 Hz), 141.8, 138.3 (d, *J* = 12.8 Hz), 137.2 (d, *J* = 13.8 Hz), 136.4 (d, *J* = 11.3 Hz), 136.1 (d, *J* = 2.9 Hz), 135.3, 134.3 (d, *J* = 8.6 Hz), 134.1, 134.0, 133.9, 133.8 (d, *J* = 2.8 Hz), 133.1 , 133.0, 132.6, 132.5 (d, *J* = 7.6 Hz), 131.2, 130.8 (d, *J* = 2.3 Hz), 130.5, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.0, 126.7, 126.6, 126.5, 126.2, 126.0, 125.0, 124.9, 20.8. **^{31}P NMR** (202 MHz, $CDCl_3$) δ -14.4 (s, 1P). The enantiomeric excess was determined by Daicel Chiralpak IB, n-hexane/isopropanol = 99.9/0.1, 0.5 mL/min, λ = 254 nm, t (major) = 11.0 min, t (minor) = 12.3 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{39}H_{29}PSH^+$: 561.1800; Found: 561.1795.

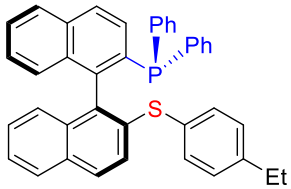


(*S*)-Diphenyl(2'-(*m*-tolylthio)-[1,1'-binaphthalen]-2-yl)phosphane (3ca). Following General Procedure C (GPC), **3ca** was prepared and purified by flash column chromatography (EtOAc/petroleum ether = 1/10) as a white solid (65.4 mg, 97% yield, 85% ee). **$[\alpha]_D^{23}$** -161.5 (*c* 0.52, $CHCl_3$) for 85% ee. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83-7.81 (m, 2H), 7.72 (d, *J* = 8.6 Hz, 2H), 7.42-7.38 (m, 2H), 7.24-7.17 (m, 6H), 7.15-7.10 (m, 4H), 7.07-6.98 (m, 6H), 6.95-6.88 (m, 3H), 6.72 (d, *J* = 8.1 Hz, 1H), 2.11 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.9 (d, *J* = 34.9 Hz), 138.8, 137.9 (d, *J* = 12.4 Hz), 137.4 (d, *J* = 13.7 Hz), 136.2 (d, *J* = 2.4 Hz), 135.8 (d, *J* = 6.9 Hz), 135.5 (d, *J* = 26.1 Hz), 134.4, 134.0, 133.9, 133.8, 133.7, 133.6, 133.5, 133.1, 133.0, 132.8 (d, *J* =

7.7 Hz), 131.6, 130.8, 130.7, 130.1, 128.8, 128.7, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.0, 126.8, 126.7, 126.5 (d, J = 2.6 Hz), 126.3, 126.2, 125.3, 21.2. **^{31}P NMR** (202 MHz, $CDCl_3$) δ -14.7 (s, 1P). The enantiomeric excess was determined by Daicel Chiralpak IA, n-hexane/isopropanol = 98.6/1.4, 0.5 mL/min, λ = 230 nm, t (major) = 16.4 min, t (minor) = 17.3 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{39}H_{29}PSH^+$: 561.1800; Found: 561.1798.

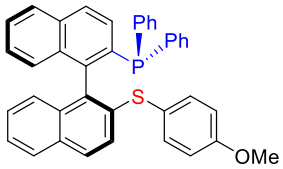


(*S*)-Diphenyl(2'-(phenylthio)-[1,1'-binaphthalen]-2-yl)phosphane (3da). Following General Procedure C (GPC), **3da** was prepared and purified by flash column chromatography (EtOAc/petroleum ether = 1/10) as a white solid (57.2 mg, 87% yield, 92% ee). **$[\alpha]_D^{23}$** -151.8 (*c* 0.54, $CHCl_3$) for 92% ee. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84-7.82 (m, 2H), 7.73-7.71 (m, 2H), 7.43-7.39 (m, 2H), 7.23-7.17 (m, 7H), 7.16-7.10 (m, 8H), 7.07-7.00 (m, 4H), 6.88 (t, J = 7.7 Hz, 1H), 6.70 (d, J = 8.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.8 (d, J = 34.7 Hz), 138.0 (d, J = 12.7 Hz), 137.2 (d, J = 13.6 Hz), 135.9 (d, J = 2.9 Hz), 135.8 (d, J = 2.0 Hz), 135.8, 134.9, 134.1, 133.9, 133.8, 33.7 (d, J = 2.9 Hz), 133.1, 133.0, 132.9, 132.8, 132.7 (d, J = 7.7 Hz), 131.6, 130.7 (d, J = 2.2 Hz), 129.0, 128.7, 128.4, 128.2 (d, J = 12.8 Hz), 128.1, 127.8 (d, J = 1.8 Hz), 127.4, 127.0, 126.9, 126.7, 126.5 (d, J = 2.6 Hz), 126.3, 126.2, 125.4. **^{31}P NMR** (202 MHz, $CDCl_3$) δ -14.6 (s, 1P). The enantiomeric excess was determined by Daicel Chiralpak IA, n-hexane/isopropanol = 98.6/1.4, 0.5 mL/min, λ = 230 nm, t (major) = 17.2 min, t (minor) = 18.0 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{38}H_{27}PSH^+$: 547.1644; Found: 547.1640.

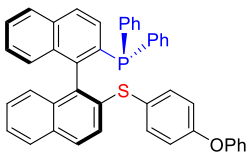


(*S*)-(2'-((4-Ethylphenyl)thio)-[1,1'-binaphthalen]-2-yl)diphenylphosphane (3ea). Following General Procedure C (GPC), **3ea** was prepared and purified by flash column chromatography (EtOAc/petroleum ether = 1/10) as a white solid (58.7 mg, 85% yield, 92% ee). **$[\alpha]_D^{23}$** -155.0 (*c* 1.0, $CHCl_3$) for 92% ee. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81-7.78 (m, 2H), 7.68-7.66 (m, 2H), 7.40-7.36 (m, 2H), 7.24-7.12

(m, 10H), 7.09-7.07 (m, 2H), 7.04-6.98 (m, 4H), 6.94 (d, J = 8.5 Hz, 2H), 6.85-6.82 (m, 1H), 6.67 (d, J = 8.4 Hz, 1H), 2.49 (q, J = 7.6 Hz, 2H), 1.10 (t, J = 7.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.1, 143.9 (d, J = 34.6 Hz), 138.2 (d, J = 12.8 Hz), 137.2 (d, J = 13.7 Hz), 136.7 (d, J = 2.9 Hz), 135.9 (d, J = 10.8 Hz), 135.1 (d, J = 8.6 Hz), 134.2, 134.0, 133.8, 133.6, 133.2, 133.0, 132.7 (d, J = 7.6 Hz), 131.5, 131.2, 130.8, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.0, 126.7, 126.5 (d, J =2.6 Hz), 126.4, 126.3, 125.3, 28.6, 15.4. **^{31}P NMR** (202 MHz, $CDCl_3$) δ -14.5 (s, 1P). The enantiomeric excess was determined by Daicel Chiralpak IA, n-hexane/isopropanol = 98.6/1.4, 0.5 mL/min, λ = 230 nm, t (major) = 9.5 min, t (minor) = 10.0 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{40}H_{31}PSH^+$: 575.1957; Found: 575.1956.

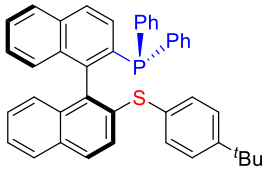


(*S*)-(2'-((4-Methoxyphenyl)thio)-[1,1'-binaphthalen]-2-yl)diphenylphosphane (3fa). Following General Procedure C (GPC), **3fa** was prepared and purified by flash column chromatography (EtOAc/petroleum ether = 1/5) as a white solid (35.5 mg, 51% yield, 94% ee). **$[\alpha]_D^{23}$** -84.4 (*c* 0.64, $CHCl_3$) for 94% ee. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84-7.82 (m, 2H), 7.70-7.67 (m, 2H), 7.43-7.39 (m, 2H), 7.27-6.98 (m, 16H), 6.86 (t, J = 7.7 Hz, 1H), 6.71-6.68 (m, 2H), 6.67 (d, J = 8.5 Hz, 1H), 3.70 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.8, 143.8 (d, J = 35.3 Hz), 138.1 (d, J = 12.9 Hz), 137.5 (d, J = 3.0 Hz), 137.2 (d, J = 13.6 Hz), 136.0, 135.9 (d, J = 10.8 Hz), 134.1, 134.0, 133.9, 133.8, 133.6 (d, J = 2.7 Hz), 133.2, 133.0, 132.7 (d, J = 7.7 Hz), 131.3, 130.7 (d, J = 2.2 Hz), 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 126.9, 126.7, 126.5 (d, J = 2.6 Hz), 126.2, 126.0, 125.5, 125.0, 124.5, 114.8, 55.3. **^{31}P NMR** (202 MHz, $CDCl_3$) δ -14.4 (s, 1P). The enantiomeric excess was determined by Daicel Chiralpak IA, n-hexane/isopropanol = 98.6/1.4, 0.5 mL/min, λ = 230 nm, t (major) = 22.2 min, t (minor) = 25.0 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{39}H_{29}POSH^+$: 577.1749; Found: 577.1747.

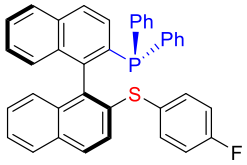


(*S*)-(2'-((4-Phenoxyphenyl)thio)-[1,1'-binaphthalen]-2-yl)diphenylphosphane (3ga). Following General Procedure C (GPC), **3ga** was prepared

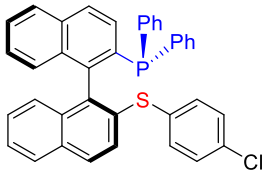
and purified by flash column chromatography (EtOAc/petroleum ether = 1/10) as a white solid (74.2 mg, 97% yield, 93% ee). **[α]$_D^{23}$** -120.0 (*c* 1.0, $CHCl_3$) for 93% ee. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83-7.80 (m, 2H), 7.73-7.69 (m, 2H), 7.41-7.38 (m, 2H), 7.27-7.14 (m, 12H), 7.13-7.08 (m, 2H), 7.05-6.98 (m, 5H), 6.92-6.85 (m, 3H), 6.75-6.72 (m, 2H), 6.68 (d, *J* = 8.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.5, 156.6, 143.8 (d, *J* = 34.6 Hz), 138.0 (d, *J* = 12.7 Hz), 137.2 (d, *J* = 13.6 Hz), 136.5 (d, *J* = 3.0 Hz), 135.9 (d, *J* = 10.8 Hz), 135.3, 135.1 (d, *J* = 8.6 Hz), 134.1, 133.9, 133.8, 133.7 (d, *J* = 2.6 Hz), 133.2, 133.0, 132.8 (d, *J* = 7.7 Hz), 131.5, 130.8, 129.9, 128.7, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.0, 126.8, 126.5 (d, *J* = 2.6 Hz), 126.3, 126.2, 125.3, 123.8, 119.4, 119.1. **^{31}P NMR** (202 MHz, $CDCl_3$) δ -14.5 (s, 1P). The enantiomeric excess was determined by Daicel Chiralpak IA, n-hexane/isopropanol = 99.9/0.1, 0.5 mL/min, λ = 254 nm, t (minor) = 9.1 min, t (major) = 11.2 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{44}H_{31}POSH^+$: 639.1906; Found: 639.1906.



(*S*)-(2'-((4-(*Tert*-butyl)phenyl)thio)-[1,1'-binaphthalen]-2-yl)diphenylphosphane (3ha). Following General Procedure C (GPC), **3ha** was prepared and purified by flash column chromatography (EtOAc/petroleum ether = 1/10) as a white solid (55.1 mg, 76% yield, 94% ee). **[α]$_D^{23}$** -107.0 (*c* 1.0, $CHCl_3$) for 94% ee. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81-7.79 (m, 2H), 7.70-7.67(m, 2H), 7.40-7.37 (m, 2H), 7.23-6.99 (m, 14H), 7.05-6.98 (m, 4H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 6.1 Hz, 1H), 1.19 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.8, 143.9 (d, *J* = 34.7 Hz), 138.1 (d, *J* = 12.8 Hz), 137.2 (d, *J* = 13.7 Hz), 136.4 (d, *J* = 3.2 Hz), 153.9 (d, *J* = 10.8 Hz), 135.4 (d, *J* = 8.6 Hz), 134.2, 134.0, 133.8, 133.7 (d, *J* = 2.7 Hz), 133.2, 133.0, 132.9, 132.8 (d, *J* = 7.6 Hz), 131.5, 131.1, 130.7, 130.6, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.8, 126.9, 126.7, 126.5, 126.4, 126.3, 126.2, 126.1, 125.3, 34.6, 31.3. **^{31}P NMR** (202 MHz, $CDCl_3$) δ -14.5 (s, 1P). The enantiomeric excess was determined by Daicel Chiralpak IB, n-hexane/isopropanol = 99.9/0.1, 0.5 mL/min, λ = 254 nm, t (minor) = 11.5 min, t (major) = 12.5 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{42}H_{35}PSH^+$: 603.2270; Found: 603.2273.

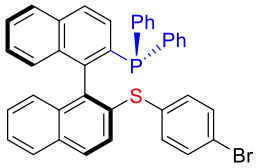


(*S*)-(2'-((4-Fluorophenyl)thio)-[1,1'-binaphthalen]-2-yl)diphenylphosphane (3ia). Following General Procedure C (GPC), **3ia** was prepared and purified by flash column chromatography (EtOAc/petroleum ether = 1/10) as a white solid (61.8 mg, 91% yield, 90% ee). **[α]$_D^{23}$** -148.5 (*c* 1.0, $CHCl_3$) for 90% ee. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82-7.80 (m, 2H), 7.71-7.69 (m, 2H), 7.40-7.37 (m, 2H), 7.22-7.08 (m, 12H), 7.05-6.97 (m, 4H), 6.90-6.86 (m, 1H), 6.80-6.75 (m, 2H), 6.70 (d, *J* = 2.1 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.5 (d, *J* = 248.4 Hz), 143.7 (d, *J* = 34.5 Hz), 137.9 (d, *J* = 12.6 Hz), 137.2 (d, *J* = 13.4 Hz), 136.0 (d, *J* = 2.5 Hz), 135.8 (d, *J* = 10.7 Hz), 135.6 (d, *J* = 8.6 Hz), 135.3, 135.2, 134.1, 133.9, 133.8, 133.7 (d, *J* = 2.7 Hz), 133.2, 133.0, 132.8 (d, *J* = 7.7 Hz), 131.6, 130.7, 129.8 (d, *J* = 3.3 Hz), 128.9, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.0, 126.8, 126.5, 126.4, 126.3, 125.5, 116.3, 116.1. **^{31}P NMR** (202 MHz, $CDCl_3$) δ -14.6 (s, 1P). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -133.7. The enantiomeric excess was determined by Daicel Chiralpak IB, n-hexane/isopropanol = 99.9/0.1, 0.5 mL/min, λ = 254 nm, t (minor) = 13.6 min, t (major) = 14.4 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{38}H_{26}PFSH^+$: 565.1550; Found: 565.1551.

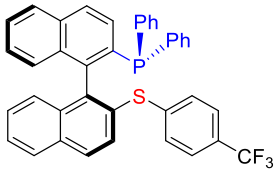


(*S*)-(2'-((4-Chlorophenyl)thio)-[1,1'-binaphthalen]-2-yl)diphenylphosphane (3ja). Following General Procedure C (GPC), **3ja** was prepared and purified by flash column chromatography (EtOAc/petroleum ether = 1/10) as a white solid (67.7 mg, 97% yield, 81% ee). **[α]$_D^{23}$** -102.1 (*c* 1.0, $CHCl_3$) for 81% ee. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83-7.81 (m, 2H), 7.75-7.72 (m, 2H), 7.42-7.37 (m, 2H), 7.26-7.10 (m, 10H), 7.07-6.98 (m, 8H), 6.93-6.90 (m, 1H), 6.73 (d, *J* = 8.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.7 (d, *J* = 34.4 Hz), 137.7 (d, *J* = 12.3 Hz), 137.2 (d, *J* = 13.4 Hz), 136.7 (d, *J* = 8.6 Hz), 135.6 (d, *J* = 10.8 Hz), 135.0 (d, *J* = 3.0 Hz), 134.0, 133.9, 133.8, 133.7 (d, *J* = 2.7 Hz), 133.6, 133.5, 133.3, 133.1, 133.0, 132.8 (d, *J* = 7.6 Hz), 131.8, 130.7, 129.1, 128.9, 128.5, 128.3, 128.2, 128.1, 127.9, 127.8, 127.1, 127.0, 126.8, 126.5, 126.4 (d, *J* = 2.6 Hz), 125.7. **^{31}P NMR** (202 MHz, $CDCl_3$) δ -14.8 (s, 1P). The enantiomeric excess was determined by Daicel Chiralpak IA, n-hexane/isopropanol = 98.6/1.4, 0.5

mL/min, λ = 230 nm, t (major) = 21.8 min, t (minor) = 23.9 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{38}H_{26}PClSH^+$: 581.1254; Found: 581.1251.

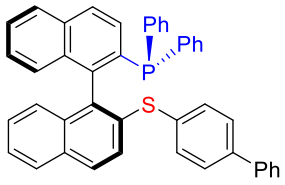


(*S*)-(2'-((4-Bromophenyl)thio)-[1,1'-binaphthalen]-2-yl)diphenylphosphane (3ka). Following General Procedure C (GPC), **3ka** was prepared and purified by flash column chromatography (EtOAc/petroleum ether = 1/10) as a white solid (70.5 mg, 94% yield, 80% ee). **$[\alpha]_D^{23}$** -136.0 (*c* 1.0, $CHCl_3$) for 80% ee. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83-7.81 (m, 2H), 7.75 (t, *J* = 7.8 Hz, 2H), 7.43-7.37 (m, 2H), 7.27-7.19 (m, 4H), 7.17-7.10 (m, 8H), 7.07-7.04 (m, 2H), 7.01-6.96 (m, 4H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 8.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.7 (d, *J* = 34.5 Hz), 137.6 (d, *J* = 12.2 Hz), 137.2 (d, *J* = 13.4 Hz), 136.8 (d, *J* = 8.6 Hz), 135.6 (d, *J* = 10.7 Hz), 134.7 (d, *J* = 3.0 Hz), 134.6, 134.0, 133.9, 133.7 (d, *J* = 2.7 Hz), 133.6, 133.5, 133.1, 132.9, 132.8 (d, *J* = 7.6 Hz), 132.0, 131.9, 130.7 (d, *J* = 2.0 Hz), 129.0, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9 (d, *J* = 4.2 Hz), 127.3, 127.0, 126.8, 126.5 (d, *J* = 34.5 Hz), 126.4 (d, *J* = 2.5 Hz), 125.8, 121.3. **^{31}P NMR** (202 MHz, $CDCl_3$) δ -14.8. (s, 1P). The enantiomeric excess was determined by Daicel Chiralpak IA, n-hexane/isopropanol = 98.6/1.4, 0.5 mL/min, λ = 230 nm, t (major) = 22.0 min, t (minor) = 23.9 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{38}H_{26}PBrSH^+$: 625.0749; Found: 625.0749.

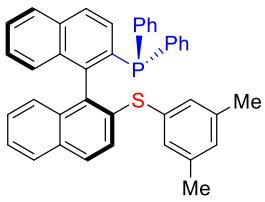


(*S*)-Diphenyl(2'-((4-(trifluoromethyl)phenyl)thio)-[1,1'-binaphthalen]-2-yl)phosphane (3la). Following General Procedure C (GPC), **3la** was prepared and purified by flash column chromatography (EtOAc/petroleum ether = 1/10) as a white solid (54.7 mg, 74% yield, 48% ee). **$[\alpha]_D^{23}$** +134.0 (*c* 1.0, $CHCl_3$) for 48% ee. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81-7.75 (m, 4H), 7.39-7.35 (m, 3H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.18-7.15 (m, 3H), 7.12-6.85 (m, 14H), 6.81 (d, *J* = 8.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.8 (d, *J* = 34.6 Hz), 141.6 (d, *J* = 0.9 Hz), 139.1 (d, *J* = 8.7 Hz), 137.4 (d, *J* = 2.7 Hz), 137.3 (d, *J* = 0.7 Hz), 135.4 (d, *J* = 10.8 Hz), 134.0, 133.9 (d, *J* = 2.6 Hz), 133.8, 133.6, 133.0, 132.9 (d, *J* = 7.9 Hz), 132.8, 132.7 (d, *J* = 2.9 Hz), 132.4, 130.7, 129.9,

129.3, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.1, 126.8, 126.6, 126.4 (d, J = 2.6 Hz), 126.3, 125.5, 125.4 (d, J = 11.2 Hz), 125.3, 124.1 (q, J = 272.3 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$) δ -15.1 (s, 1P). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.5. The enantiomeric excess was determined by Daicel Chiralpak IA, n-hexane/isopropanol = 98.6/1.4, 0.5 mL/min, λ = 230 nm, t (major) = 18.7 min, t (minor) = 20.0 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{39}H_{26}PF_3SH^+$: 615.1518; Found: 615.1518.

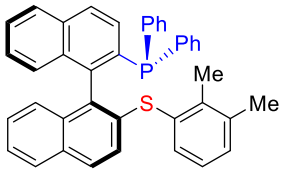


(*S*)-(2'-([1,1'-Biphenyl]-4-ylthio)-[1,1'-binaphthalen]-2-yl)diphenylphosphane (3ma). Following General Procedure C (GPC), **3ma** was prepared and purified by flash column chromatography (EtOAc/petroleum ether = 1/10) as a white solid (71.1 mg, 95% yield, 89% ee). **$[\alpha]_D^{23}$** -144.6 (*c* 1.0, $CHCl_3$) for 89% ee. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84-7.81 (m, 2H), 7.76-7.72 (m, 2H), 7.46-7.44 (m, 2H), 7.42-7.39 (m, 2H), 7.35-7.29 (m, 5H), 7.26-7.19 (m, 6H), 7.18-7.10 (m, 6H), 7.07-7.00 (m, 4H), 6.92-6.89 (m, 1H), 6.73 (d, J = 8.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.9 (d, J = 34.5 Hz), 140.3 (2C), 137.9 (d, J = 12.4 Hz), 137.2 (d, J = 13.6 Hz), 136.2 (d, J = 8.5 Hz), 135.7 (d, J = 11.4 Hz), 135.6 (d, J = 2.9 Hz), 134.2, 134.1, 134.0, 133.8, 133.7 (d, J = 1.2 Hz), 133.1, 133.0, 132.9, 132.8, 132.7, 131.7, 130.7, 128.8, 128.7, 128.4, 128.2, 128.1, 127.9, 127.6, 127.5, 127.2, 127.0, 126.7, 126.5 (d, J = 2.6 Hz), 126.4, 126.3, 125.5. **^{31}P NMR** (202 MHz, $CDCl_3$) δ -14.7 (s, 1P). The enantiomeric excess was determined by Daicel Chiralpak IA, n-hexane/isopropanol = 98.6/1.4, 0.5 mL/min, λ = 230 nm, t (major) = 12.8 min, t (minor) = 14.3 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{44}H_{31}PSH^+$: 623.1957; Found: 623.1955.

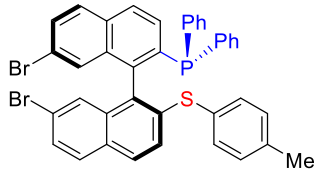


(*S*)-(2'-((3,5-Dimethylphenyl)thio)-[1,1'-binaphthalen]-2-yl)diphenylphosphane (3na). Following General Procedure C (GPC), **3na** was prepared and purified by flash column chromatography (EtOAc/petroleum ether = 1/10) as a white solid (67.0 mg, 97% yield, 89% ee). **$[\alpha]_D^{23}$** -247.8 (*c* 0.57, $CHCl_3$) for 89% ee.**^{1}H NMR**

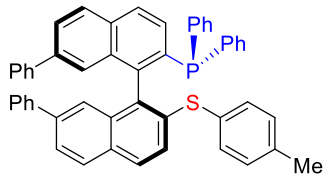
(500 MHz, $CDCl_3$) δ 7.82-7.80 (m, 2H), 7.72-7.70 (m, 2H), 7.42-7.38 (m, 2H), 7.24-7.21 (m, 3H), 7.20-7.13 (m, 6H), 7.12-7.10 (m, 1H), 7.07-7.00 (m, 4H), 6.93-6.89 (m, 1H), 6.77 (s, 2H), 6.74-6.72 (m, 2H), 2.07 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.0 (d, *J* = 34.8 Hz), 138.6, 137.9 (d, *J* = 12.5 Hz), 137.5 (d, *J* = 13.9 Hz), 136.4 (d, *J* = 2.8 Hz), 135.6 (d, *J* = 10.4 Hz), 135.4 (d, *J* = 8.4 Hz), 134.0, 133.9, 133.8. 133.7 (d, *J* = 2.7 Hz), 133.2, 133.0, 132.8 (d, *J* = 7.7 Hz), 131.5, 131.0, 130.8, 129.5, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.0, 126.7, 126.6, 126.5 (d, *J* = 2.6 Hz), 126.3, 126.2, 125.3, 125.2, 21.1. **^{31}P NMR** (202 MHz, $CDCl_3$) δ -14.7 (s, 1P). The enantiomeric excess was determined by Daicel Chiralpak IA, n-hexane/isopropanol = 98.6/1.4, 0.5 mL/min, λ = 254 nm, t (major) = 18.2 min, t (minor) = 19.1 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{40}H_{31}PSH^+$: 575.1957; Found: 575.1960.



(*S*)-(2'-((2,3-Dimethylphenyl)thio)-[1,1'-binaphthalen]-2-yl)diphenylphosphane (3oa). Following General Procedure C (GPC), **3oa** was prepared and purified by flash column chromatography (EtOAc/petroleum ether = 1/10) as a white solid (63.1 mg, 91% yield, 84% ee). **$[\alpha]_D^{23}$** -54.0 (*c* 0.5, $CHCl_3$) for 84% ee. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85-7.81 (m, 2H), 7.68 (t, *J* = 19.1 Hz, 2H), 7.44-7.39 (m, 2H), 7.29-7.26 (m, 2H), 7.21-7.16 (m, 7H), 7.13-7.10 (m, 1H), 7.06-6.99 (m, 5H), 6.93-6.88 (m, 2H), 6.86-6.82 (m, 1H), 6.64 (d, *J* = 2.1 Hz, 1H), 2.18 (s, 3H), 2.07 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.7 (d, *J* = 35.2 Hz), 140.5, 138.4 (d, *J* = 13.0 Hz), 137.7, 137.4 (d, *J* = 13.8 Hz), 136.7 (d, *J* = 2.7 Hz), 136.5 (d, *J* = 10.9 Hz), 134.1, 134.0, 133.8, 133.7 (d, *J* = 2.6 Hz), 133.5, 133.1, 133.0, 132.4 (d, *J* = 7.7 Hz), 131.1, 130.8 (d, *J* = 2.2 Hz), 130.3, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 126.9, 126.6, 126.2, 126.1, 125.9, 124.9, 124.8, 21.0, 17.2. **^{31}P NMR** (202 MHz, $CDCl_3$) δ -14.41 (s, 1P). The enantiomeric excess was determined by Daicel Chiralpak IA, n-hexane/isopropanol = 99.9/0.1, 0.5 mL/min, λ = 254 nm, t (minor) = 8.7 min, t (major) = 9.0 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{40}H_{31}PSH^+$: 575.1957; Found: 575.1961.

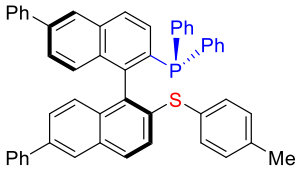


(*S*)-(7,7'-Dibromo-2'-(*p*-tolylthio)-[1,1'-binaphthalen]-2-yl)diphenylphosphane (3pa). Following General Procedure C (GPC), **3pa** was prepared and purified by flash column chromatography (EtOAc/petroleum ether = 1/10) as a white solid (69.6 mg, 81% yield, 87% ee). **[α]$_D^{23}$** -120.0 (*c* 1.0, $CHCl_3$) for 87% ee. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.5 Hz, 1H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.48 (dd, *J* = 2.1, 8.6 Hz, 1H), 7.39 (dd, *J* = 2.7, 8.5 Hz, 1H), 7.26-7.24 (m, 2H), 7.20-7.09 (m, 11H), 7.01-6.97 (m, 4H), 6.71 (d, *J* = 1.6 Hz, 1H), 2.23 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.7 (d, *J* = 34.4 Hz), 138.7 (d, *J* = 2.9 Hz), 138.4, 138.1 (d, *J* = 12.5 Hz), 137.6 (d, *J* = 12.6 Hz), 136.0 (d, *J* = 12.9 Hz), 134.6 (d, *J* = 2.9 Hz), 134.2, 134.1, 134.0, 133.9, 133.6 (d, *J* = 7.4 Hz), 133.1, 133.0 (d, *J* = 8.2 Hz), 132.9, 132.3, 131.0 (d, *J* = 1.8 Hz), 130.5, 130.1, 130.0, 129.9, 129.8, 129.6, 129.0, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1 (d, *J* = 2.7 Hz), 128.0, 127.9, 126.6, 121.2, 121.1, 21.2. **^{31}P NMR** (202 MHz, $CDCl_3$) δ -13.8 (s, 1P). The enantiomeric excess was determined by Daicel Chiralpak IA, n-hexane/isopropanol = 98.6/1.4, 0.5 mL/min, λ = 230 nm, t (minor) = 10.7 min, t (major) = 11.7 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{39}H_{27}PBr_2SH^+$: 717.0011; Found: 717.0015.

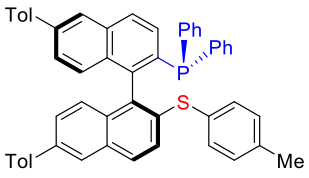


(*S*)-(7,7'-Diphenyl-2'-(*p*-tolylthio)-[1,1'-binaphthalen]-2-yl)diphenylphosphane (3qa). Following General Procedure C (GPC), **3qa** was prepared and purified by flash column chromatography (EtOAc/petroleum ether = 1/10) as a white solid (55.3 mg, 65% yield, 75% ee). **[α]$_D^{23}$** -113.4 (*c* 1.0, $CHCl_3$) for 75% ee. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.65 (dd, *J* = 1.7, 8.5 Hz, 1H), 7.48-7.45 (m, 2H), 7.37 (s, 1H), 7.30 (d, *J* = 7.5 Hz, 2H), 7.23-7.07 (m, 16H), 7.02-6.91 (m, 8H), 2.20 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.2 (d, *J* = 35.0 Hz), 141.2, 141.0, 139.4, 139.1, 138.7 (d, *J* = 12.9 Hz), 137.8, 137.1 (d, *J* = 13.9 Hz), 137.0 (d, *J* = 2.8 Hz), 136.5 (d, *J* = 10.7 Hz), 135.5 (d, *J* = 8.8 Hz), 134.2, 134.1, 134.0, 133.5, 133.1, 133.0 (d, *J* = 7.7 Hz), 132.9, 132.8,

131.0, 130.9 (d, J = 2.2 Hz), 130.7, 129.9, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.7, 127.5, 127.4, 127.2, 127.0, 126.9, 126.5, 125.1, 124.5 (d, J = 2.6 Hz), 124.3, 21.2. **^{31}P NMR** (202 MHz, $CDCl_3$) δ -14.8 (s, 1P). The enantiomeric excess was determined by Daicel Chiralpak IA, n-hexane/isopropanol = 98.6/1.4, 0.5 mL/min, λ = 254 nm, t (minor) = 12.5 min, t (major) = 13.7 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{51}H_{37}PSH^+$: 713.2426; Found: 713.2425.

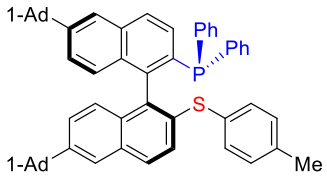


(*S*)-(6,6'-Diphenyl-2'-(*p*-tolylthio)-[1,1'-binaphthalen]-2-yl)diphenylphosphane (3ra). Following General Procedure C (GPC), **3ra** was prepared and purified by flash column chromatography (EtOAc/petroleum ether = 1/10) as a white solid (82.2 mg, 96% yield, 91% ee). **$[\alpha]_D^{23}$** -59.0 (*c* 1.0, $CHCl_3$) for 91% ee. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (d, J = 1.5 Hz, 1H), 7.88-7.85(m, 2H), 7.73 (d, J = 8.8 Hz, 1H), 7.57 (d, J = 7.4 Hz, 2H), 7.50 (d, J = 7.4 Hz, 2H), 7.46 (dd, J = 1.9, 8.9 Hz, 1H), 7.42 (dd, J = 2.8, 8.5 Hz, 1H), 7.34-7.21 (m, 10H), 7.19-7.08 (m, 7H), 7.02-7.01 (m, 4H), 6.92 (d, J = 8.0 Hz, 2H), 6.73 (d, J = 8.8 Hz, 1H), 2.18 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.5 (d, J = 34.5 Hz), 140.9, 141.0, 139.7, 138.0 (d, J = 12.9 Hz), 137.9, 137.8, 137.1 (d, J = 13.4 Hz), 136.9 (d, J = 2.8 Hz), 136.2 (d, J = 11.0 Hz), 134.8 (d, J = 8.5 Hz), 134.4, 134.2, 134.1, 133.7, 133.2, 133.1, 132.9 (d, J = 2.6 Hz), 132.0 (d, J = 7.6 Hz), 131.8, 131.2, 130.8, 130.0, 129.0, 128.9, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 127.9, 127.6, 127.5, 127.3, 127.1 (d, J = 2.4 Hz), 126.8, 126.7, 126.5, 126.1, 125.9, 125.8, 21.3. **^{31}P NMR** (202 MHz, $CDCl_3$) δ -14.3 (s, 1P). The enantiomeric excess was determined by Daicel Chiralpak IA, n-hexane/isopropanol = 98.6/1.4, 0.5 mL/min, λ = 254 nm, t (minor) = 17.2 min, t (major) = 18.7 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{51}H_{37}PSH^+$: 713.2426; Found: 713.2422.



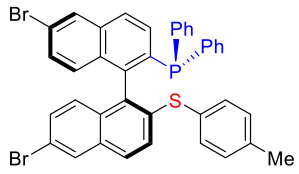
(*S*)-(6,6'-Di-*p*-tolyl-2'-(*p*-tolylthio)-[1,1'-binaphthalen]-2-yl)diphenylphosphane (3sa). Following General Procedure C (GPC), **3sa** was prepared and purified by flash column chromatography (EtOAc/petroleum ether = 1/10) as a white

solid (81.0 mg, 91% yield, 94% ee). **$[\alpha]_D^{23}$** -27 (*c* 1.0, $CHCl_3$) for 94% ee. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 1.7 Hz, 1H), 7.88-7.86 (m, 2H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.50-7.41 (m, 6H), 7.27-7.23 (m, 4H), 7.19-7.02 (m, 12H), 7.04-7.02 (m, 3H), 6.94 (d, *J* = 7.9 Hz, 2H), 6.73(d, *J* = 8.8 Hz, 1H), 2.30 (s, 6H), 2.21 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.5 (d, *J* = 34.6 Hz), 139.5, 138.1, 138.0 (d, *J* = 12.8 Hz), 137.9, 137.8, 137.7, 137.4, 137.1 (d, *J* = 13.4 Hz), 137.0, 136.6 (d, *J* = 2.8 Hz), 135.9 (d, *J* = 10.8 Hz), 134.9 (d, *J* = 8.5 Hz), 134.3, 134.1, 133.6, 133.2, 133.0, 132.8 (d, *J* = 2.6 Hz), 131.8 (d, *J* = 7.4 Hz), 131.7, 131.1 (d, *J* = 2.1 Hz), 130.9, 129.9, 129.7, 129.6, 129.5, 128.8, 128.7, 128.4, 128.3, 128.2, 128.1, 127.9, 127.3, 127.2, 127.1, 127.0 (d, *J* = 2.6 Hz), 126.8, 126.7, 126.4, 125.8, 125.7, 125.4, 121.3, 21.2, 21.1, 21.0. **^{31}P NMR** (202 MHz, $CDCl_3$) δ -14.3 (s, 1P). The enantiomeric excess was determined by Daicel Chiralpak IA, n-hexane/isopropanol = 98.6/1.4, 0.5 mL/min, λ = 254 nm, t (minor) = 18.9 min, t (major) = 21.9 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{53}H_{41}PSH^+$: 741.2739; Found: 741.2741.

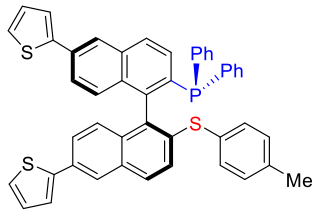


((*S*)-6,6'-Di((3S,5S,7S)-adamantan-1-yl)-2'-(*p*-tolylthio)-[1,1'-binaphthalen]-2-yl)diphenylphosphane (3ta). Following General Procedure C (GPC), **3ta** was prepared and purified by flash column chromatography (EtOAc/petroleum ether = 1/10) as a white solid (85.6 mg, 86% yield, 97% ee). **$[\alpha]_D^{23}$** +75.0 (*c* 1.0, $CHCl_3$) for 97% ee. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89-7.84 (m, 2H), 7.69 (d, *J* = 1.8 Hz, 1H), 7.66-7.62 (m, 2H), 7.40-7.36 (m, 2H), 7.34 (d, *J* = 1.7 Hz, 1H), 7.23-7.15 (m, 7H), 7.06-7.02 (m, 2H), 6.99-6.97 (m, 2H), 6.94-6.92 (m, 2H), 6.87-6.83 (m, 2H), 6.74 (d, *J* = 8.7 Hz, 1H), 2.24 (s, 3H), 2.05-2.03 (s, 6H), 1.90-1.87 (m, 12H), 1.75-1.66 (m, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.0, 148.3, 139.9 (d, *J* = 7.7 Hz), 137.9, 136.0, 134.6 (d, *J* = 2.3 Hz), 133.8, 132.9 (d, *J* = 11.3 Hz), 132.4, 132.3, 132.0, 131.9, 131.6 (d, *J* = 4.7 Hz), 131.3, 130.8 (d, *J* = 11.8 Hz), 130.6, 130.5, 130.4, 130.3, 129.8, 129.7, 129.3, 128.4, 128.3, 127.5, 127.4, 126.9, 126.8, 126.6, 125.9, 125.5, 125.2, 124.7, 123.1, 122.6, 43.3, 42.9, 36.8, 36.7, 36.4, 36.1, 28.9, 28.8, 21.2. **^{31}P NMR** (202 MHz, $CDCl_3$) δ -14.5 (s, 1P). The enantiomeric excess was determined by Daicel Chiralpak IA, n-hexane/isopropanol = 95.0/5.0, 1.0 mL/min, λ = 254 nm, t (major) = 6.7 min, t (minor) =

14.8 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{59}H_{57}PSH^+$: 829.3991; Found: 829.3993.

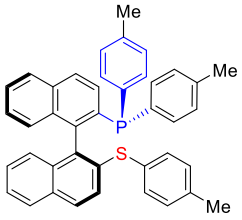


(*S*)-(6,6'-Dibromo-2'-(*p*-tolylthio)-[1,1'-binaphthalen]-2-yl)diphenylphosphane (3ua). Following General Procedure C (GPC), **3ua** was prepared and purified by flash column chromatography (EtOAc/petroleum ether = 1/10) as a white solid (58.5 mg, 68% yield, 81% ee). **$[\alpha]_D^{23}$** +41.0 (*c* 1.0, $CHCl_3$) for 81% ee. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 1.9 Hz, 1H), 7.84 (d, *J* = 1.9 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.41 (dd, *J* = 2.1, 8.5 Hz, 1H), 7.28 (dd, *J* = 2.0, 9.0 Hz, 1H), 7.23-7.10 (m, 9H), 7.07 (t, *J* = 7.5 Hz, 2H), 6.99-6.93 (m, 5H), 6.84 (dd, *J* = 2.0, 9.0 Hz, 1H), 6.38 (d, *J* = 9.0 Hz, 1H), 2.25 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.9 (d, *J* = 34.3 Hz), 138.7 (d, *J* = 22.7 Hz), 138.4, 138.0, 134.9, 134.3, 134.2, 134.1, 134.0, 133.9, 133.8 (d, *J* = 3.4 Hz), 133.5, 133.1, 133.0, 132.7, 132.6 (d, *J* = 35.1 Hz), 130.6, 130.3, 130.2 (d, *J* = 10.8 Hz), 130.1, 129.8 (d, *J* = 13.6 Hz), 129.5, 128.68 (d, *J* = 14.4 Hz), 128.4, 128.3, 128.2, 128.1, 128.0 (d, *J* = 3.1 Hz), 127.7 (d, *J* = 19.2 Hz), 127.5, 127.1, 126.5, 126.4 (d, *J* = 2.9 Hz), 122.0, 121.5, 121.3, 119.3, 118.8, 21.2. **^{31}P NMR** (202 MHz, $CDCl_3$) δ -14.1 (s, 1P). The enantiomeric excess was determined by Daicel Chiralpak IA, n-hexane/isopropanol = 99.9/0.1, 0.5 mL/min, λ = 254 nm, t (minor) = 11.1 min, t (major) = 11.7 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{39}H_{27}PBr_2SH^+$: 717.0011; Found: 717.0010.

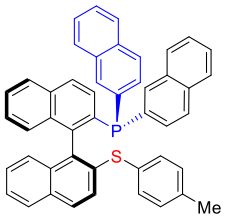


(S)-(6,6'-Di(thiophen-2-yl)-2'-(p-tolylthio)-[1,1'-binaphthalen]-2-yl)diphenylphosphane (3va). Following General Procedure C (GPC), **3va** was prepared and purified by flash column chromatography (EtOAc/petroleum ether = 1/10) as a white solid (45.9 mg, 53% yield, 89% ee). **$[\alpha]_D^{23}$** -71.4 (*c* 0.64, $CHCl_3$) for 89% ee. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 1.7 Hz, 1H), 7.90 (d, *J* = 1.7 Hz, 1H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.48 (dd, *J* = 1.8, 8.8 Hz, 1H), 7.45 (dd, *J* = 1.3, 2.9 Hz, 1H), 7.43-7.40 (m, 2H), 7.37-7.34 (m, 2H), 7.33-7.30 (m, 2H), 7.26-7.20

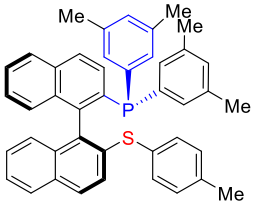
(m, 4H), 7.18-7.17 (m, 2H), 7.14-7.10 (m, 4H), 7.08-7.02 (m, 5H), 6.95 (d, J = 8.0 Hz, 2H), 6.69 (d, J = 8.8 Hz, 1H), 2.23 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.4, 142.2, 142.0, 137.9, 136.7 (d, J = 2.9 Hz), 135.9 (d, J = 10.8 Hz), 134.8, 134.3, 134.2, 134.1, 133.7, 133.2, 133.0, 132.8 (d, J = 2.5 Hz), 132.6 (d, J = 2.4 Hz), 132.5, 131.7, 131.2 (d, J = 2.2 Hz), 130.7, 130.5, 130.0, 139.0, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.0 (d, J = 2.7 Hz), 126.8, 126.6, 126.5, 126.4, 126.3, 126.2, 125.9, 125.4, 125.3, 125.0, 124.8, 121.0, 120.5, 21.2. **^{31}P NMR** (202 MHz, $CDCl_3$) δ -14.4 (s, 1P). The enantiomeric excess was determined by Daicel Chiralpak IA, n-hexane/isopropanol = 98.6/1.4, 0.5 mL/min, λ = 254 nm, t (major) = 14.0 min, t (minor) = 16.7 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{47}H_{33}PS_3H^+$: 725.1555; Found: 725.1552.



(S)-Di-*p*-tolyl(2'-(*p*-tolylthio)-[1,1'-binaphthalen]-2-yl)phosphane (3ab). Following General Procedure C (GPC), **3ab** was prepared and purified by flash column chromatography (EtOAc/petroleum ether = 1/10) as a white solid (65.8 mg, 93% yield, 91% ee). **$[\alpha]_D^{23}$** -92.0 (*c* 1.0, $CHCl_3$) for 91% ee. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (d, J = 8.4 Hz, 2H), 7.70-7.68 (m, 2H), 7.42-7.38 (m, 2H), 7.16-7.18 (m, 2H), 7.15-7.10 (m, 4H), 7.07 (d, J = 8.0 Hz, 2H), 6.96-6.86 (m, 9H), 6.69 (d, J = 8.5 Hz, 1H), 2.21 (s, 3H), 2.20 (s, 3H), 2.18 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.5 (d, J = 34.2 Hz), 138.2, 137.6, 137.5, 136.7 (d, J = 2.9 Hz), 126.4 (d, J = 11.3 Hz), 135.2 (d, J = 8.5 Hz), 134.5 (d, J = 11.2 Hz), 134.1, 133.9, 133.8 (d, J = 17.3 Hz), 133.7, 133.4, 133.2, 133.1, 132.7 (d, J = 7.5 Hz), 131.5, 131.0, 130.6 (d, J = 1.9 Hz), 129.8, 129.1, 129.0, 128.9, 128.8, 128.7, 128.5, 128.3, 128.1, 127.8, 126.8, 126.6, 126.4 (d, J = 2.5 Hz), 126.3, 126.2, 126.1, 125.1, 21.3, 21.2, 21.1. **^{31}P NMR** (202 MHz, $CDCl_3$) δ -16.0 (s, 1P). The enantiomeric excess was determined by Daicel Chiralpak IB, n-hexane/isopropanol = 99.9/0.1, 0.5 mL/min, λ = 254 nm, t (minor) = 11.3 min, t (major) = 12.6 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{41}H_{33}PSH^+$: 589.2113; Found: 589.2109.

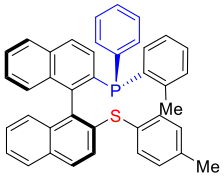


(*S*)-Di(naphthalen-2-yl) (2'-(p-tolylthio)-[1,1'-binaphthalen]-2-yl) phosphane (3ac). Following General Procedure C (GPC), **3ac** was prepared and purified by flash column chromatography (EtOAc/petroleum ether = 1/10) as a white solid (65.9 mg, 83% yield, 96% ee). **[α]$_D^{23}$** -159.1 (*c* 0.45, $CHCl_3$) for 96% ee.**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84-7.81 (m, 2H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.70-7.63 (m, 5H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.53-7.49 (m, 2H), 7.44-7.41 (m, 3H), 7.38-7.19 (m, 9H), 7.10-7.07 (m, 1H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.83 (d, *J* = 8.0 Hz, 2H), 6.67 (d, *J* = 3.8 Hz, 2H), 2.15 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.0 (d, *J* = 34.3 Hz), 137.6, 136.5 (d, *J* = 3.1 Hz), 135.2, 135.0, 134.4, 134.3, 133.8, 133.7 (d, *J* = 2.5 Hz), 133.3, 133.2 (d, *J* = 2.1 Hz), 133.1 (2C), 133.0, 132.9, 132.8 (d, *J* = 7.6 Hz), 131.5, 130.8, 130.6 (d, *J* = 2.2 Hz), 130.3, 130.1, 129.9, 129.8, 129.7, 128.7, 128.5, 128.2, 128.1, 128.0, 127.7 (3C), 127.6 (2C), 127.5, 127.0, 126.7, 126.5 (3C), 126.1 (3C), 126.0 (2C), 125.2, 21.1. **^{31}P NMR** (202 MHz, $CDCl_3$) δ -13.1 (s, 1P). The enantiomeric excess was determined by Daicel Chiralpak IB, n-hexane/isopropanol = 99.9/0.1, 0.5 mL/min, λ = 254 nm, t (minor) = 10.6 min, t (major) = 15.6 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{47}H_{33}PSH^+$: 661.2113; Found: 661.2115.

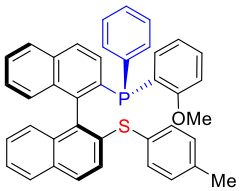


(*S*)-Bis(3,5-dimethylphenyl)(2'-(*p*-tolylthio)-[1,1'-binaphthalen]-2-yl)phosphane (3ad). Following General Procedure C (GPC), **3ad** was prepared and purified by flash column chromatography (EtOAc/petroleum ether = 1/10) as a white solid (68.8 mg, 93% yield, 81% ee). **[α]$_D^{23}$** -160.0 (*c* 1.0, $CHCl_3$) for 81% ee. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.5 Hz, 2H), 7.68 (dd, *J* = 3.2, 8.4 Hz, 2H) 7.46 (dd, *J* = 2.8, 8.6 Hz, 1H), 7.39-7.36 (m, 1H), 7.21-7.16 (m, 4H), 7.11 (d, *J* = 8.1 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 7.7 Hz, 3H), 6.72 (d, *J* = 21.6 Hz, 2H), 6.67 (d, *J* = 8.5 Hz, 1H), 6.61 (d, *J* = 8.1 Hz, 2H), 2.20 (s, 3H), 2.06 (s, 6H), 2.02 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.5 (d, *J* = 34.2 Hz), 137.8 (d, *J* = 12.0 Hz), 137.6, 137.5, 137.4, 137.3, 137.2,

136.8, 136.7, 136.6, 136.4 (d, J = 3.3 Hz), 135.6 (d, J = 8.4 Hz), 133.8 (d, J = 2.5 Hz), 133.7, 133.2, 133.1, 132.8 (d, J = 7.5 Hz), 132.1, 131.9, 131.6, 131.3, 130.9, 130.8 (d, J = 1.8 Hz), 130.7, 130.3, 129.8, 129.6, 128.6, 128.4, 128.2, 127.7, 126.8, 126.7, 126.6, 126.5, 126.4, 126.0, 125.2, 21.4, 21.3, 21.2. **^{31}P NMR** (202 MHz, $CDCl_3$) δ -13.7 (s, 1P). The enantiomeric excess was determined by Daicel Chiralpak IA, n-hexane/isopropanol = 98.6/1.4, 0.5 mL/min, λ = 230 nm, t (major) = 15.5 min, t (minor) = 19.4 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{43}H_{37}PSH^+$: 617.2426; Found: 617.2424.

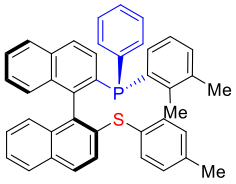


(S)-Phenyl(*o*-tolyl)((*S*)-2'-(*p*-tolylthio)-[1,1'-binaphthalen]-2-yl)phosphane (3ae). Following General Procedure C (GPC), **3ae** was prepared and purified by flash column chromatography (EtOAc/petroleum ether = 1/10) as a white solid (45.7 mg, 66% yield, 97% ee, 13:1 dr). **[α]$_D^{23}$** -78.0 (*c* 1.0, $CHCl_3$) for 97% ee. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83-7.81 (m, 2H), 7.66 (d, J = 8.6 Hz, 2H), 7.40 (t, J = 7.4 Hz, 1H), 7.32 (dd, J = 2.8, 8.5 Hz, 1H), 7.21-7.10 (m, 12H), 6.96 (d, J = 8.1 Hz, 2H), 6.94-6.92 (m, 2H), 6.80-6.73 (m, 2H), 6.61 (d, J = 8.5 Hz, 1H), 2.23 (s, 3H), 1.75 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.4 (d, J = 21.9 Hz), 143.1 (d, J = 16.3 Hz), 137.8, 137.5 (d, J = 12.8 Hz), 136.8 (d, J = 2.8 Hz), 136.0 (d, J = 11.6 Hz), 135.3 (d, J = 14.2 Hz), 134.6 (d, J = 8.1 Hz), 134.4, 133.7, 133.6, 133.5, 133.4 (d, J = 2.6 Hz), 132.8 (d, J = 7.2 Hz), 131.5, 131.0, 130.5 (d, J = 1.3 Hz), 139.9, 129.7 (d, J = 5.0 Hz), 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.6, 126.7, 126.6, 126.3 (d, J = 2.7 Hz), 126.2, 125.9, 125.7, 125.1, 21.3 (d, J = 23.4 Hz), 21.2. **^{31}P NMR** (202 MHz, $CDCl_3$) δ -24.1 (s, 1P). The enantiomeric excess was determined by Daicel Chiralpak IA, n-hexane/isopropanol = 98.6/1.4, 0.5 mL/min, λ = 280 nm, t (major) = 9.3 min, t (minor) = 11.0 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{40}H_{31}PSH^+$: 575.1957; Found: 575.1958.



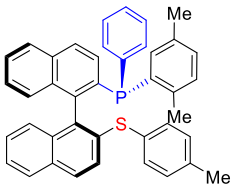
(*R*)-(2-Methoxyphenyl)(phenyl)((*S*)-2'-(p-tolylthio)-[1,1'-binaphthalen]-2-yl)phosphane (3af). Following General Procedure C (GPC), **3af** was prepared and purified by flash column chromatography (EtOAc/petroleum ether = 1/10)

as a white solid (45.4 mg, 64% yield, 50% ee, 6:1 dr). **[α]$_D^{23}$** -68.0 (*c* 0.64, $CHCl_3$) for 50% ee. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.41-7.38 (m, 1H), 7.35-7.32 (m, 1H), 7.27-7.11 (m, 10H), 7.05-6.98 (m, 3H), 6.91-6.87 (m, 3H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.66-6.61 (m, 2H), 3.41 (s, 3H), 2.21 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.1 (d, *J* = 15.3 Hz), 143.2 (d, *J* = 35.0 Hz), 137.6, 137.1 (d, *J* = 2.9 Hz), 136.7 (d, *J* = 12.7 Hz), 135.4 (d, *J* = 11.0 Hz), 134.6 (d, *J* = 33.2 Hz), 134.3 (d, *J* = 3.5 Hz), 134.2, 134.1, 133.7, 133.6, 132.8 (d, *J* = 7.8 Hz), 131.5, 130.8 (d, *J* = 2.1 Hz), 130.7, 129.9, 129.8, 129.0, 128.4, 128.2, 128.1, 128.0, 127.8, 126.7, 126.6, 126.5, 126.4, 126.3 (d, *J* = 2.5 Hz), 126.0, 125.2, 120.7, 110.1, 55.2, 21.2. **^{31}P NMR** (202 MHz, $CDCl_3$) δ -25.3 (s, 1P). The enantiomeric excess was determined by Daicel Chiralpak IA, n-hexane/isopropanol = 98.6/1.4, 0.5 mL/min, λ = 280 nm, t (major) = 11.8 min, t (minor) = 13.8 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{40}H_{31}POSH^+$: 591.1906; Found: 591.1903.

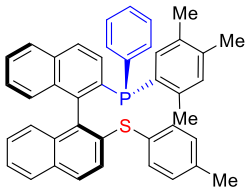


(*S*)-(2,3-Dimethylphenyl)(phenyl)((*S*)-2'-(p-tolylthio)-[1,1'-binaphthalen]-2-yl)phosphane (3ag). Following General Procedure C (GPC), **3ag** was prepared and purified by flash column chromatography (EtOAc/petroleum ether = 1/10) as a white solid (43.2 mg, 61% yield, 92% ee, 10:1 dr). **[α]$_D^{23}$** -120.6 (*c* 1.0, $CHCl_3$) for 92% ee. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.66-7.63 (m, 2H), 7.38-7.35 (m, 1H), 7.33 (dd, *J* = 2.8, 8.5 Hz, 1H), 7.23-7.10 (m, 12H), 6.96 (d, *J* = 8.1 Hz, 2H), 6.86-6.83 (m, 2H), 6.70-6.66 (m, 1H), 6.51 (d, *J* = 8.4 Hz, 1H), 2.22 (s, 3H), 1.92 (s, 3H), 1.62 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.0 (d, *J* = 33.9 Hz), 142.1 (d, *J* = 27.8 Hz), 138.0 (d, *J* = 12.9 Hz), 137.8, 136.9 (d, *J* = 12.1 Hz), 136.8 (d, *J* = 2.8 Hz), 136.4 (d, *J* = 4.8 Hz), 135.1 (d, *J* = 11.7 Hz), 134.7 (d, *J* = 8.1 Hz), 133.7, 133.6, 133.5 (d, *J* = 2.6 Hz), 133.4, 132.7, 131.6, 131.1, 130.4, 130.1, 129.9, 129.8, 128.4, 128.3, 128.2, 128.1, 127.9, 127.4, 126.7, 126.6, 126.5, 126.4, 126.3 (d, *J* = 2.6 Hz), 126.1, 125.8, 125.4, 125.0, 21.2, 20.5 (d, *J* = 2.9 Hz), 17.6 (d, *J* = 29.4 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$) δ -23.9 (s, 1P). The enantiomeric excess was determined by Daicel Chiralpak IA, n-hexane/isopropanol = 98.6/1.4, 0.5 mL/min, λ = 280 nm, t (major) = 8.6 min, t (minor) =

9.8 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{41}H_{33}PSH^+$: 589.2113; Found: 589.2117.



(*S*)-(2,5-Dimethylphenyl)(phenyl)((*S*)-2'-(p-tolylthio)-[1,1'-binaphthalen]-2-yl)phosphane (3ah). Following General Procedure C (GPC), **3ah** was prepared and purified by flash column chromatography (EtOAc/petroleum ether = 1/10) as a white solid (50.1 mg, 71% yield, 91% ee, 16:1 dr). $[\alpha]_D^{23}$ -37.0 (*c* 1.0, $CHCl_3$) for 91% ee. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83-7.80 (m, 2H), 7.64 (d, *J* = 8.6 Hz, 2H), 7.41-7.37 (m, 1H), 7.31 (dd, *J* = 2.8, 8.5 Hz, 1H), 7.21-7.11 (m, 11H), 6.95 (d, *J* = 7.9 Hz, 1H), 6.80-6.74 (m, 2H), 6.69-6.62 (m, 2H), 6.61 (d, *J* = 8.4 Hz, 1H), 2.22 (s, 3H), 2.05 (s, 3H), 1.70 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.2 (d, *J* = 33.7 Hz), 140.0 (d, *J* = 28.0 Hz), 137.8, 137.5 (d, *J* = 12.9 Hz), 126.8 (d, *J* = 2.8 Hz), 126.2 (d, *J* = 11.9 Hz), 134.9, 134.8, 134.7 (d, *J* = 7.8 Hz), 133.8, 133.7, 133.6, 133.4 (d, *J* = 2.6 Hz), 133.2 (d, *J* = 1.6 Hz), 133.1 (d, *J* = 1.0 Hz), 132.8 (d, *J* = 7.2 Hz), 131.5, 131.1, 130.6, 129.9, 129.8 (d, *J* = 5.9 Hz), 129.6 (d, *J* = 4.2 Hz), 129.2, 128.5, 128.4, 128.3, 128.2, 128.1 (d, *J* = 8.0 Hz), 128.0, 127.6, 126.7, 126.6, 126.5, 126.3, 125.8, 125.1, 21.2, 21.1, 20.8 (d, *J* = 23.0 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$) δ -23.2 (s, 1P). The enantiomeric excess was determined by Daicel Chiralpak IA, n-hexane/isopropanol = 98.6/1.4, 0.5 mL/min, λ = 230 nm, t (major) = 16.3 min, t (minor) = 20.0 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{41}H_{33}PSH^+$: 589.2113; Found: 589.2116.



(*S*)-Phenyl((*S*)-2'-(p-tolylthio)-[1,1'-binaphthalen]-2-yl)(2,4,5-trimethylphenyl)phosphane (3ai). Following General Procedure C (GPC), **3ai** was prepared and purified by flash column chromatography (EtOAc/petroleum ether = 1/10) as a white solid (47.0 mg, 65% yield, 89% ee, 10:1 dr). $[\alpha]_D^{23}$ -92.0 (*c* 1.0, $CHCl_3$) for 89% ee. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82-7.79 (m, 2H), 7.64-7.63 (m, 2H), 7.40-7.34 (m, 2H), 7.23-7.11 (m, 10H), 7.00-6.98 (m, 1H), 6.95(d, *J* = 7.9 Hz, 2H), 6.75-6.73 (m, 1H), 6.63(d, *J* = 4.4 Hz, 1H), 6.58(d, *J* = 8.6 Hz, 1H), 6.53(d, *J* = 5.0 Hz, 1H), 2.22 (s,

3H), 2.03 (s, 3H), 1.96 (s, 3H), 1.67 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.0 (d, *J* = 33.5 Hz), 140.6 (d, *J* = 28.2 Hz), 137.8 (d, *J* = 12.6 Hz), 137.7, 136.9, 135.7, 134.7, 134.5, 133.7, 133.6, 133.5, 133.4 (d, *J* = 1.2 Hz), 133.3 (d, *J* = 2.5 Hz), 132.8 (d, *J* = 7.2 Hz), 132.7, 131.6 (d, *J* = 12.4 Hz), 131.5, 131.2, 131.1, 130.5, 129.9, 129.7, 128.4, 128.3, 128.2, 128.1, 127.9, 127.6, 126.6, 126.5, 126.4, 136.3, 126.2, 125.7, 125.0, 21.2, 20.7 (d, *J* = 22.7 Hz), 19.4, 19.3. **^{31}P NMR** (202 MHz, $CDCl_3$) δ -24.1 (s, 1P). The enantiomeric excess was determined by Daicel Chiralpak IA, n-hexane/isopropanol = 98.6/1.4, 0.5 mL/min, λ = 254 nm, t (major) = 8.2 min, t (minor) = 9.7 min. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{42}H_{35}PSH^+$: 603.2270; Found: 603.2274.

7. References

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8. X-Ray Crystallographic Data of 1a, 3aa, 3ae

(1) Crystal data and structure refinement for compound 1a

Colorless crystals of product **1a** (CCDC-2303113) suitable for X-ray crystallographic analysis were obtained by recrystallization from $CHCl_3$/acetone (via evaporation). The ORTEP drawing of compound **1a** is shown in Figure S1.

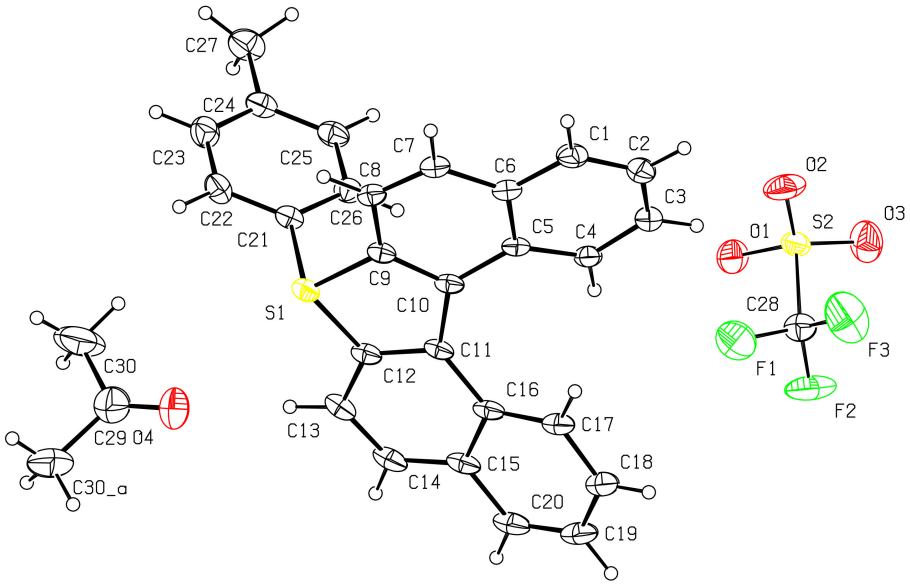


Figure S1. ORTEP illustration of compound 1an with thermal ellipsoids drawn at 50% probability level.

Table S2. Crystal data and structure refinement for compound 1a

Identification code	230914_HYH_S1
Empirical formula	$C_{59}H_{44}F_6O_7S_4$
Formula weight	1107.18
Temperature/K	170.00
Crystal system	orthorhombic
Space group	Pbcn
a/Å	23.6038(16)
b/Å	12.3774(9)
c/Å	17.1095(11)

α /°	90
β /°	90
γ /°	90
Volume/Å^3	4998.6(6)
Z	4
ρ_{calc}g/cm^3	1.471
μ /mm^{-1}	1.587
F(000)	2288.0
Crystal size/mm^3	0.15 × 0.09 × 0.04
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	6.516 to 114.454
Index ranges	-29 ⩽ h ⩽ 29, -15 ⩽ k ⩽ 15, -16 ⩽ l ⩽ 21
Reflections collected	71816
Independent reflections	5159 [R_{int} = 0.1416, R_{sigma} = 0.0759]
Data/restraints/parameters	5159/241/419
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0667, wR_2 = 0.1613
Final R indexes [all data]	R_1 = 0.1018, wR_2 = 0.1835
Largest diff. peak/hole / e Å^{-3}	0.70/-0.44

(2) Crystal data and structure refinement for compound 3aa

Colorless crystals of product **3aa** (CCDC-2303114) suitable for X-ray crystallographic analysis were obtained by recrystallization from $CHCl_3$/acetone (via evaporation). The ORTEP drawing of compound **3aa** is shown in Figure S2.

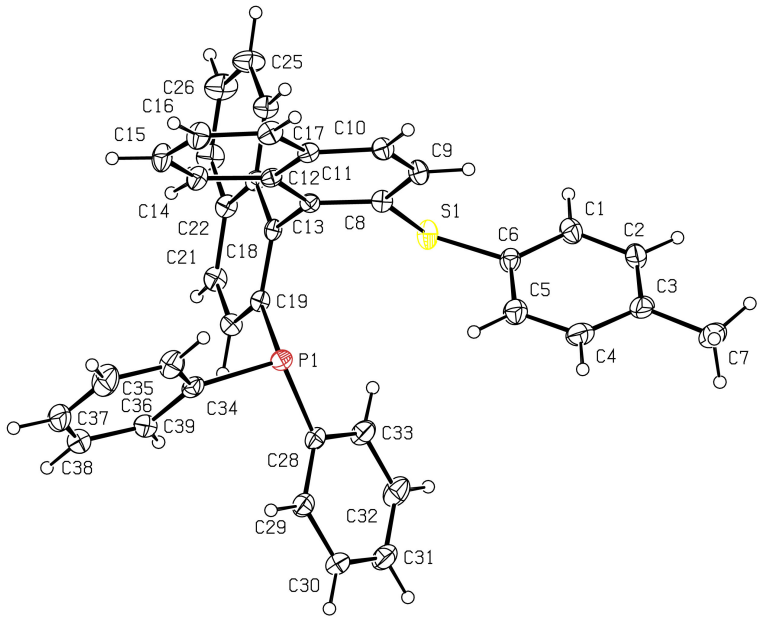


Figure S2. ORTEP illustration of compound 3aa with thermal ellipsoids drawn at 50% probability level.

Table S3. Crystal data and structure refinement for compound 3aa

Identification code	mo_230915_HYH_P1_0m
Empirical formula	$C_{39}H_{29}PS$
Formula weight	560.65
Temperature/K	170.00
Crystal system	triclinic
Space group	P1
a/Å	11.0390(6)
b/Å	15.1879(8)
c/Å	16.0708(7)
α/°	112.211(2)
β/°	104.135(2)

γ /°	103.663(2)
Volume/Å^3	2251.2(2)
Z	3
ρ_{calc}g/cm^3	1.241
μ /mm^{-1}	0.188
F(000)	882.0
Crystal size/mm^3	0.18 × 0.16 × 0.07
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.088 to 55.106
Index ranges	-14 ≤ h ≤ 14, -19 ≤ k ≤ 19, -20 ≤ l ≤ 20
Reflections collected	109565
Independent reflections	20597 [R_{int} = 0.0626, R_{sigma} = 0.0453]
Data/restraints/parameters	20597/3/1111
Goodness-of-fit on F^2	1.080
Final R indexes [I>=2σ (I)]	R_1 = 0.0470, wR_2 = 0.1012
Final R indexes [all data]	R_1 = 0.0591, wR_2 = 0.1094
Largest diff. peak/hole / e Å^{-3}	0.56/-0.24
Flack parameter	0.010(18)

(3) Crystal data and structure refinement for compound 3ae

Colourless crystals of product **3ae** (CCDC-2306477) suitable for X-ray crystallographic analysis were obtained by recrystallization from $CHCl_3$/acetone (via evaporation). The ORTEP drawing of compound **3ae** is shown in Figure S3.

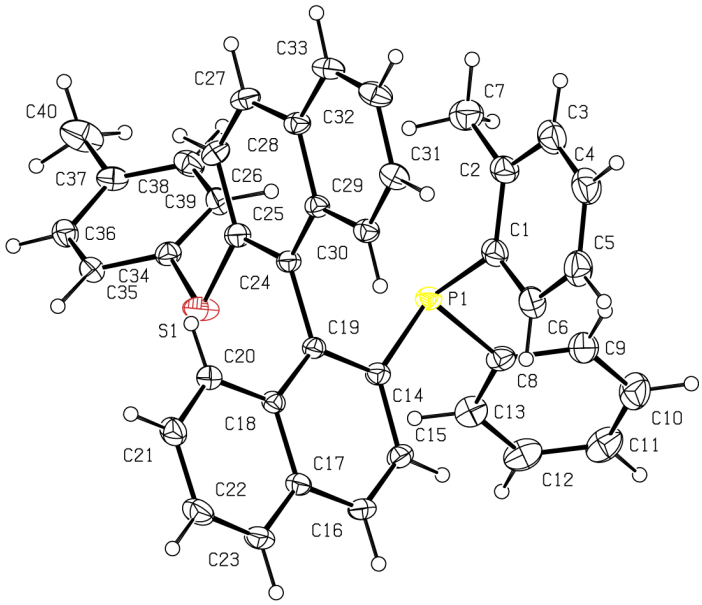


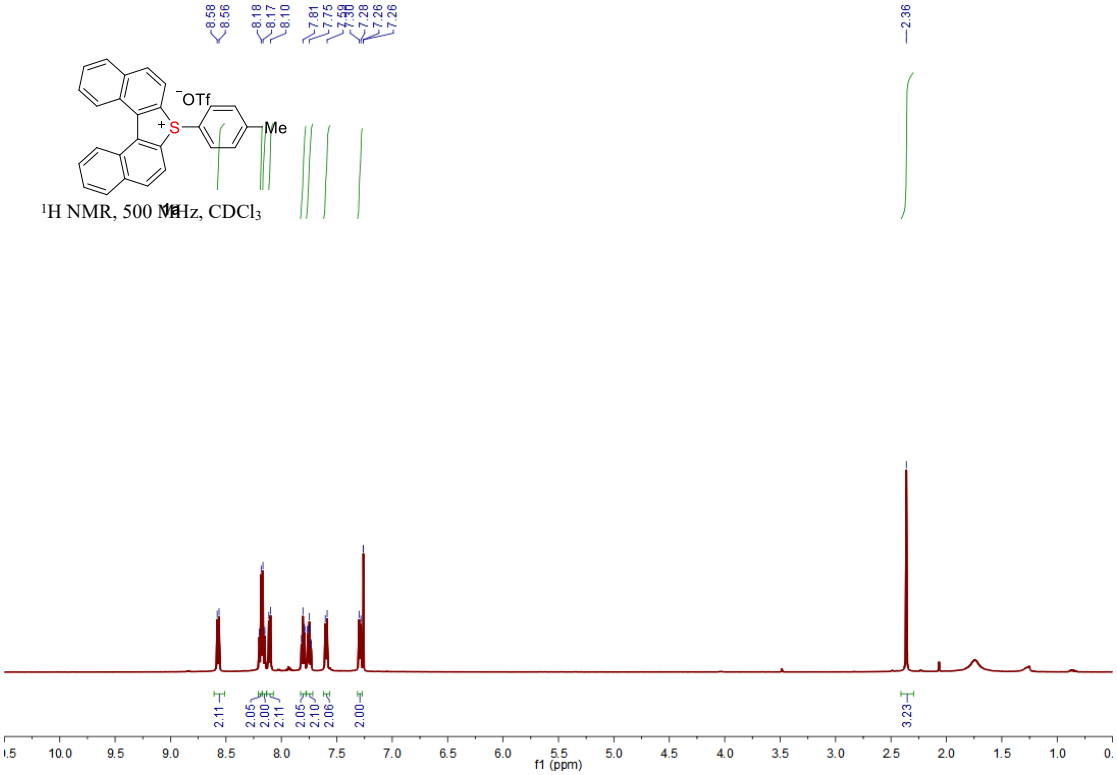
Figure S3. ORTEP illustration of compound 3ae with thermal ellipsoids drawn at 50% probability level.

Table S4. Crystal data and structure refinement for compound 3ae

Table 1 Crystal data and structure refinement for mo_231106_SJH_HP1_0m.	
Identification code	mo_231106_SJH_HP1_0m
Empirical formula	$C_{40}H_{31}PS$
Formula weight	574.68
Temperature/K	170.00
Crystal system	monoclinic
Space group	$P2_1$
a/Å	8.1621(3)
b/Å	11.2980(4)
c/Å	16.5498(6)

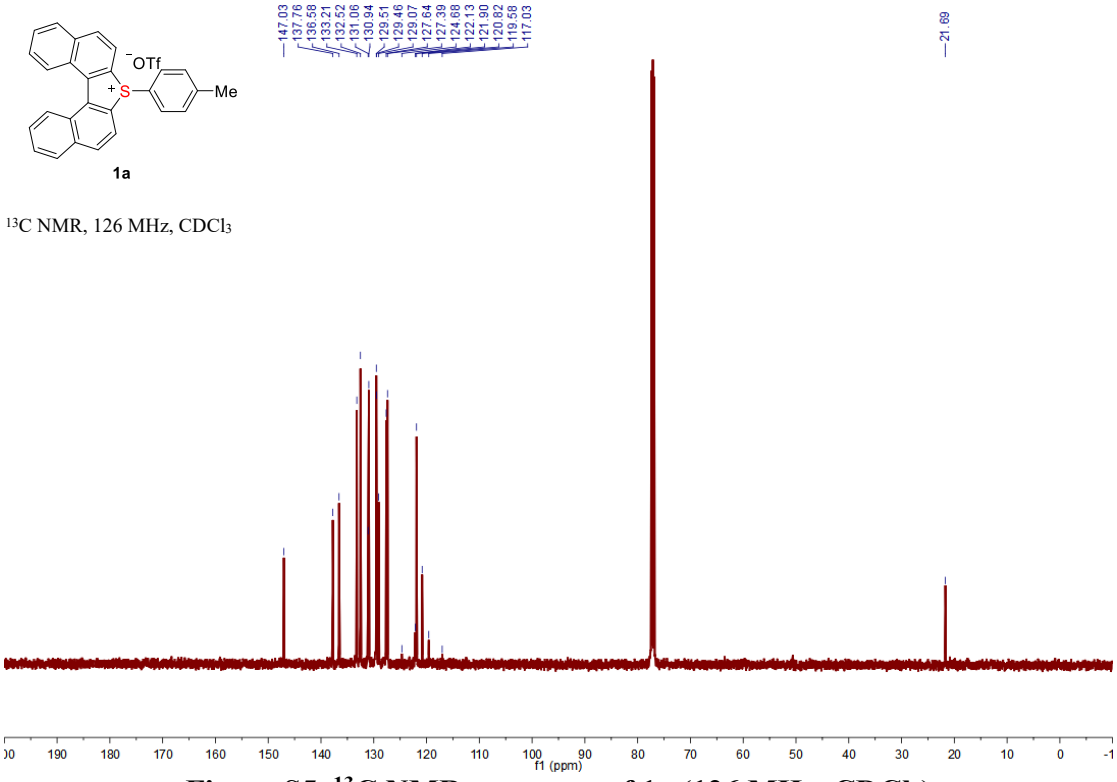
α /°	90
β /°	94.610(2)
γ /°	90
Volume/Å^3	1521.21(10)
Z	2
ρ_{calc}g/cm^3	1.255
μ /mm^{-1}	0.187
F(000)	604.0
Crystal size/mm^3	0.42 × 0.19 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.37 to 55.08
Index ranges	-10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -21 ≤ l ≤ 21
Reflections collected	48812
Independent reflections	7005 [R_{int} = 0.0388, R_{sigma} = 0.0260]
Data/restraints/parameters	7005/1/381
Goodness-of-fit on F^2	1.074
Final R indexes [I>=2σ (I)]	R_1 = 0.0371, wR_2 = 0.0925
Final R indexes [all data]	R_1 = 0.0401, wR_2 = 0.0951
Largest diff. peak/hole / e Å^{-3}	0.34/-0.19
Flack parameter	0.001(17)

9. NMR Spectra and Chiral HPLC Charts



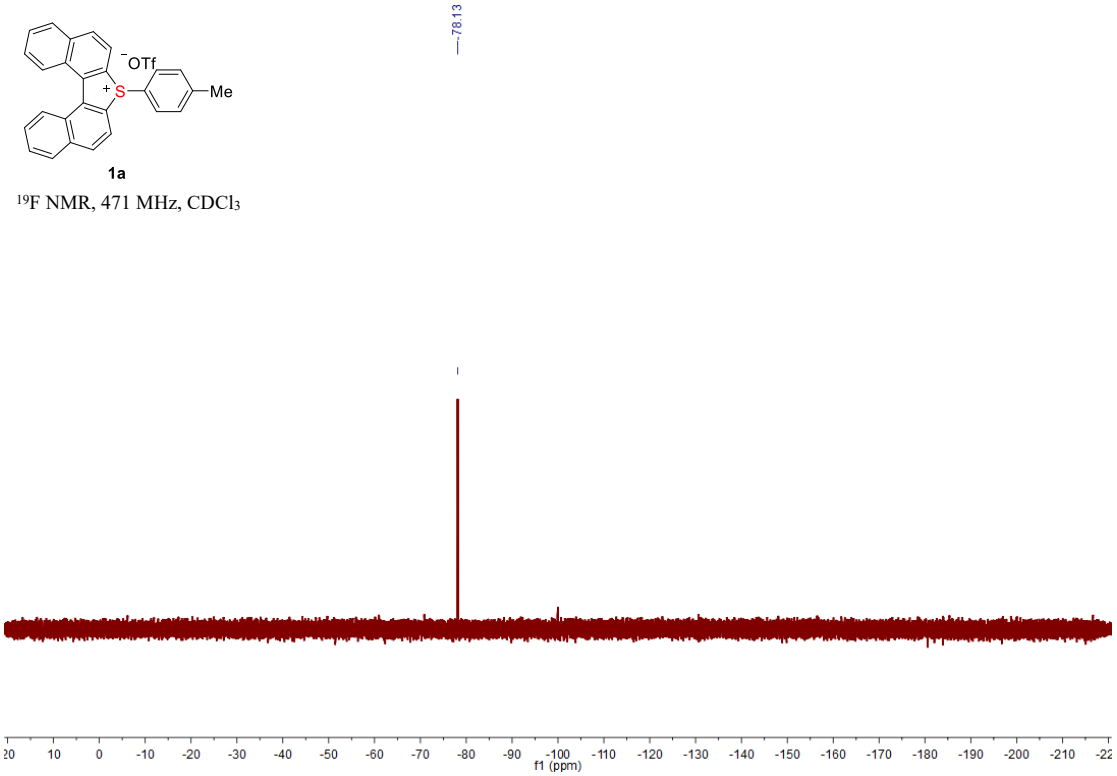
^{1}H NMR, 500 MHz, $CDCl_3$

Figure S4. ^{1}H NMR spectrum of 1a (500 MHz, $CDCl_3$)



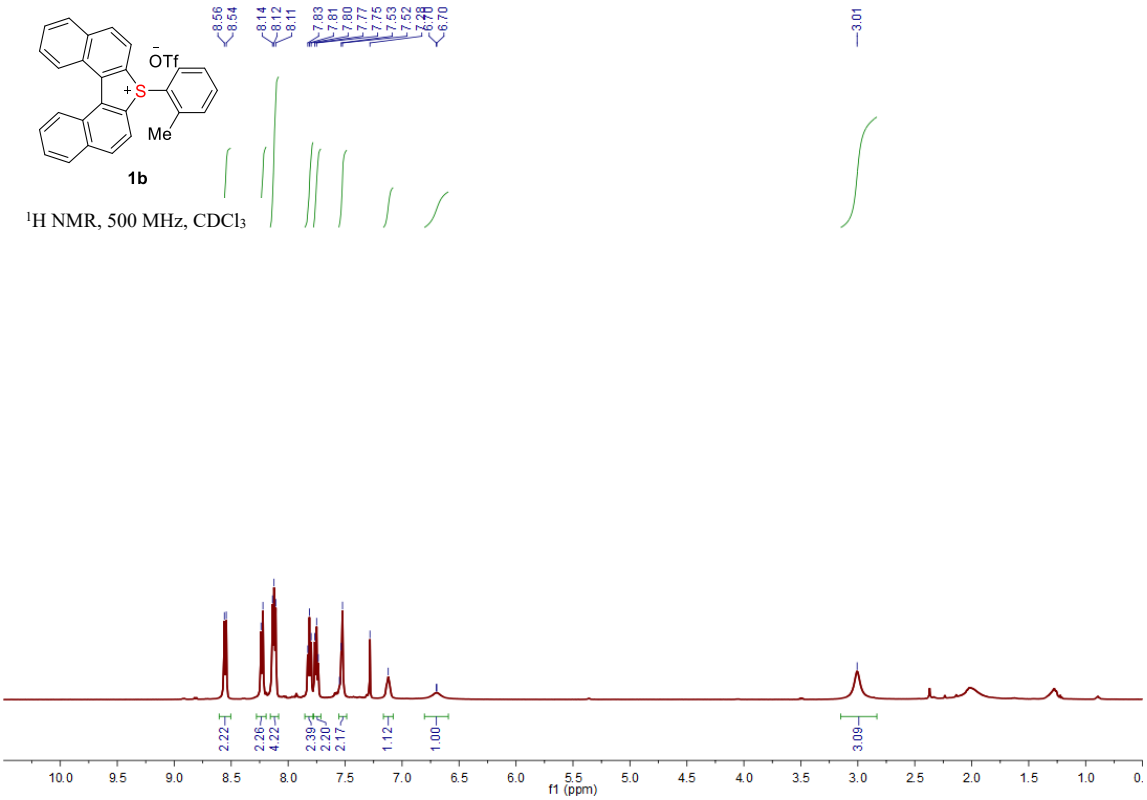
^{13}C NMR, 126 MHz, $CDCl_3$

Figure S5. ^{13}C NMR spectrum of 1a (126 MHz, $CDCl_3$)



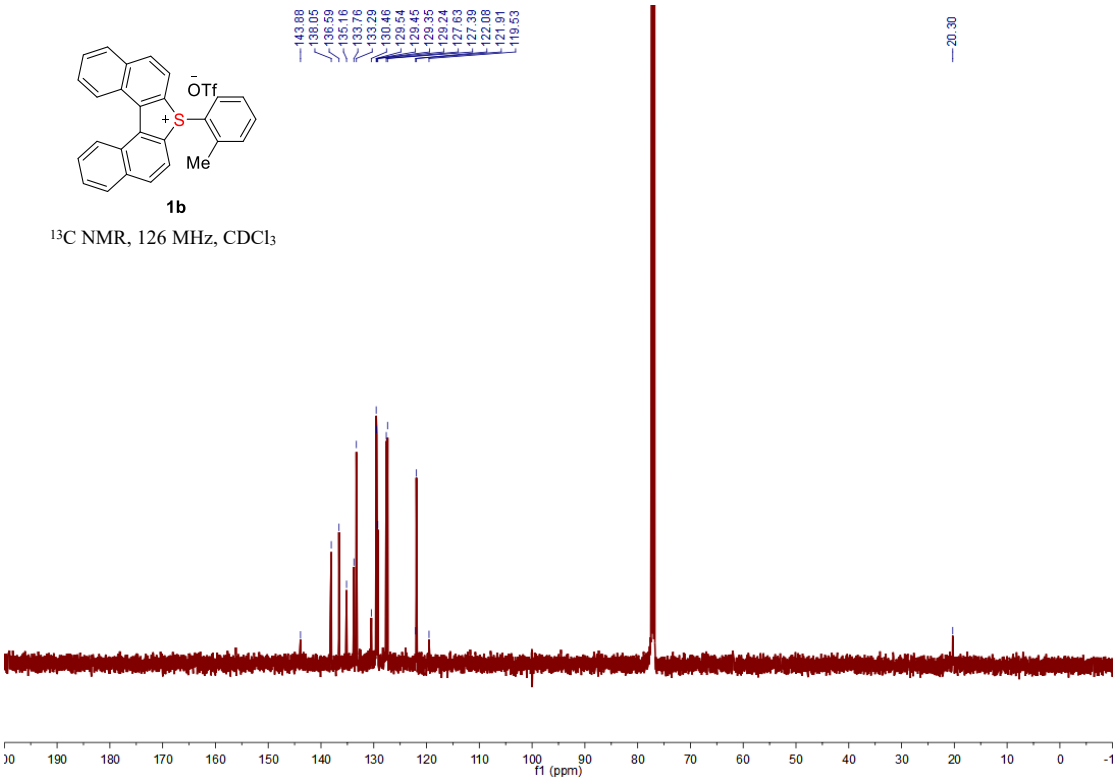
^{19}F NMR, 471 MHz, $CDCl_3$

Figure S6. ^{19}F NMR spectrum of 1a (471 MHz, $CDCl_3$)



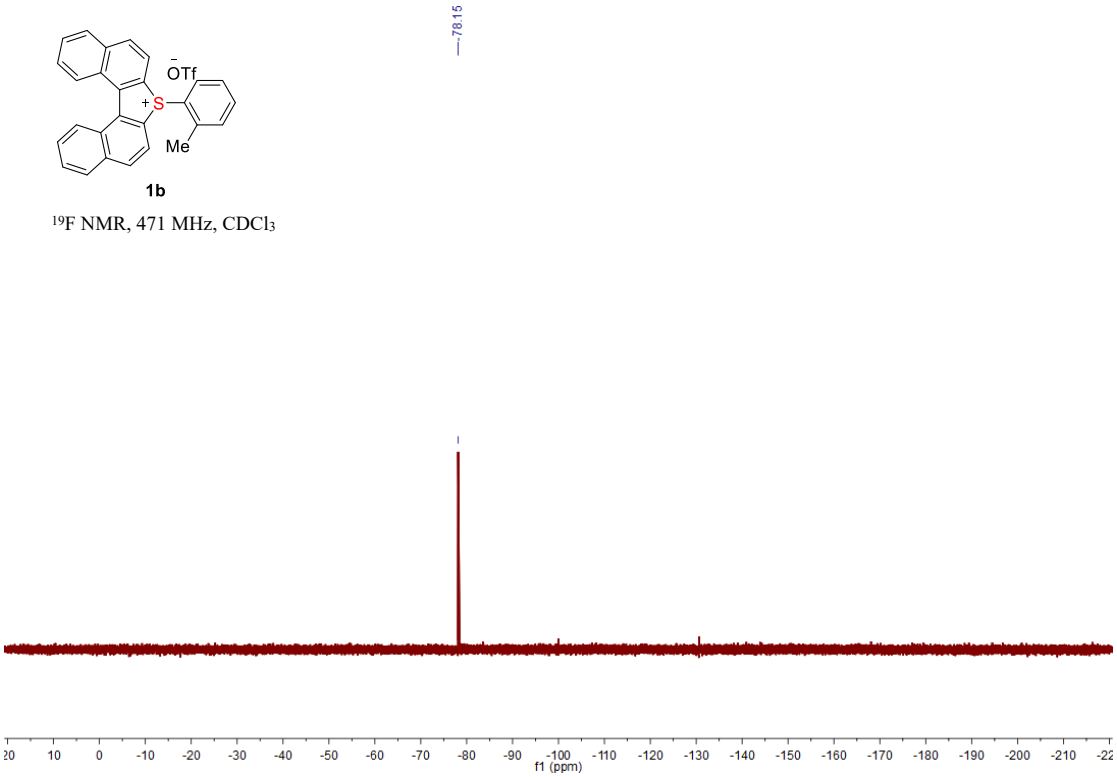
^{1}H NMR, 500 MHz, $CDCl_3$

Figure S7. ^{1}H NMR spectrum of 1b (500 MHz, $CDCl_3$)



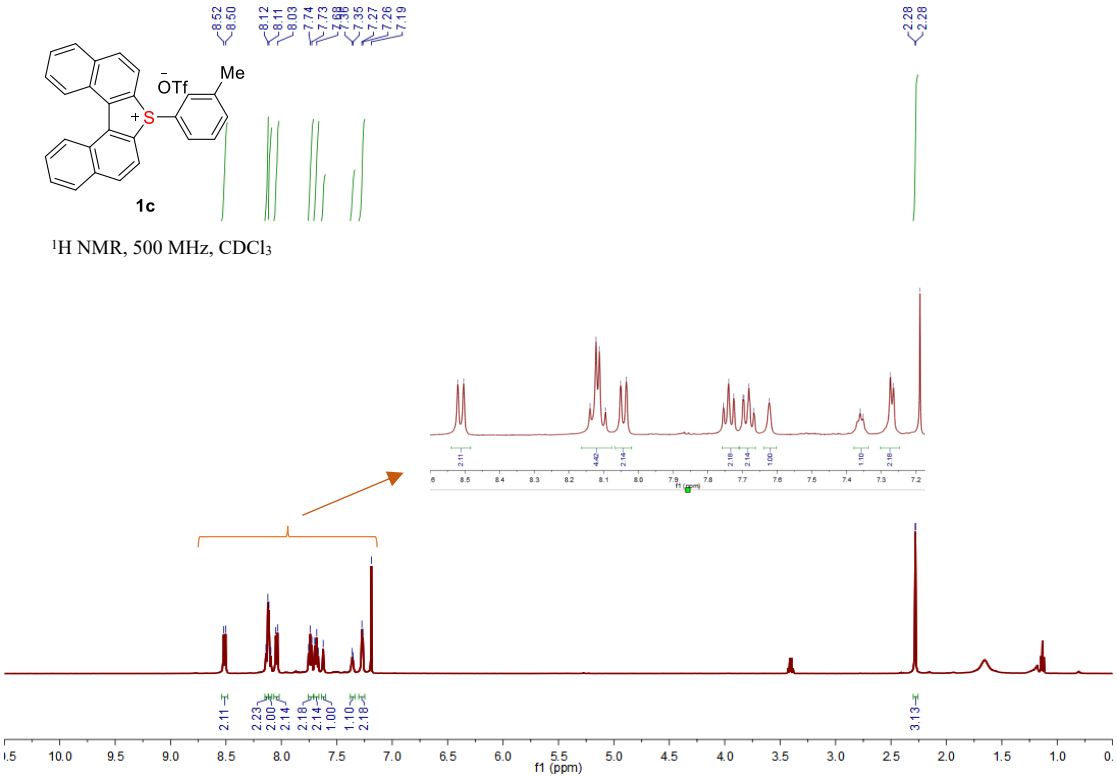
^{13}C NMR, 126 MHz, $CDCl_3$

Figure S8. ^{13}C NMR spectrum of 1b (126 MHz, $CDCl_3$)



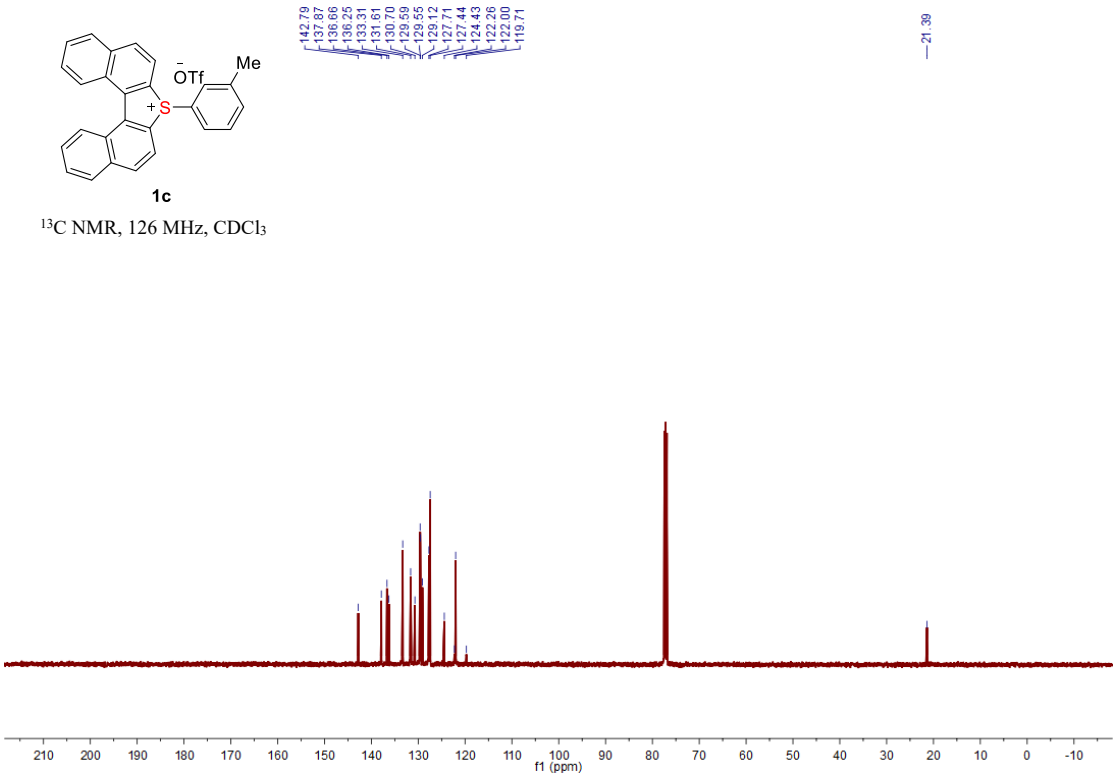
^{19}F NMR, 471 MHz, $CDCl_3$

Figure S9. ^{19}F NMR spectrum of 1b (471 MHz, $CDCl_3$)



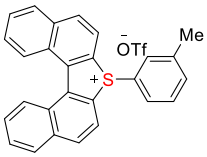
^{1}H NMR, 500 MHz, $CDCl_3$

Figure S10. ^{1}H NMR spectrum of 1c (500 MHz, $CDCl_3$)



^{13}C NMR, 126 MHz, $CDCl_3$

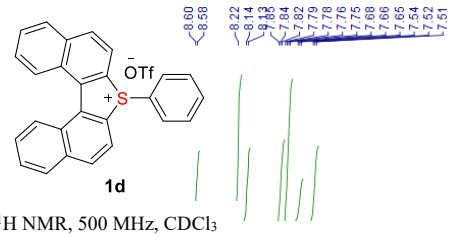
Figure S11. ^{13}C NMR spectrum of 1c (126 MHz, $CDCl_3$)



1c

^{19}F NMR, 471 MHz, $CDCl_3$

Figure S12. ^{19}F NMR spectrum of 1c (471 MHz, $CDCl_3$)



1d

^{1}H NMR, 500 MHz, $CDCl_3$

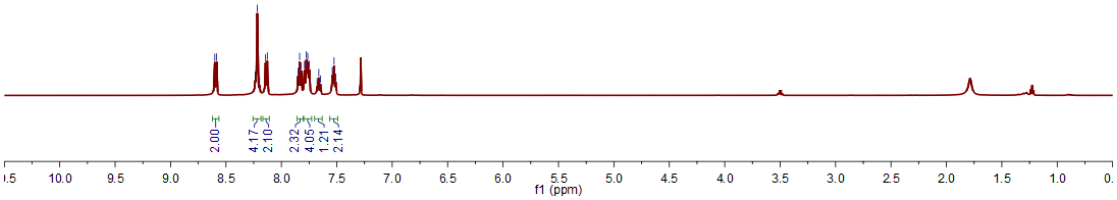
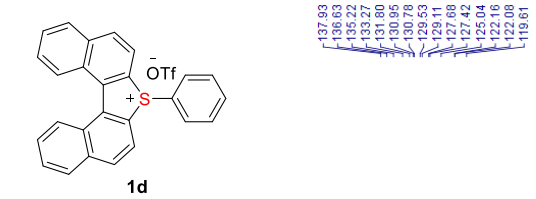


Figure S13. ^{1}H NMR spectrum of 1d (500 MHz, $CDCl_3$)



^{13}C NMR, 126 MHz, $CDCl_3$

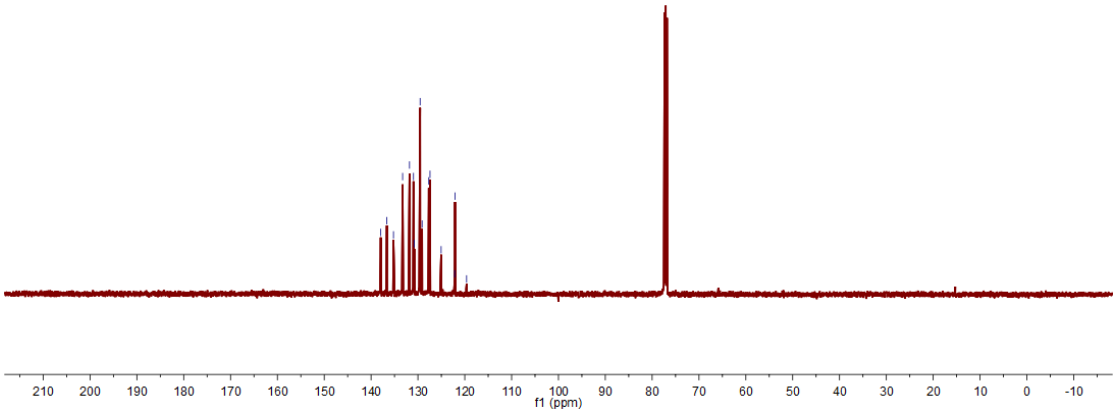
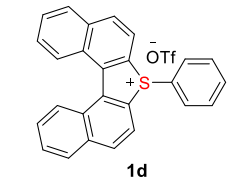


Figure S14. ^{13}C NMR spectrum of 1d (126 MHz, $CDCl_3$)



^{19}F NMR, 471 MHz, $CDCl_3$

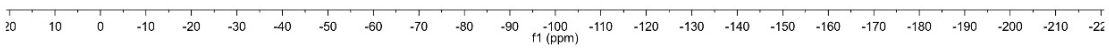
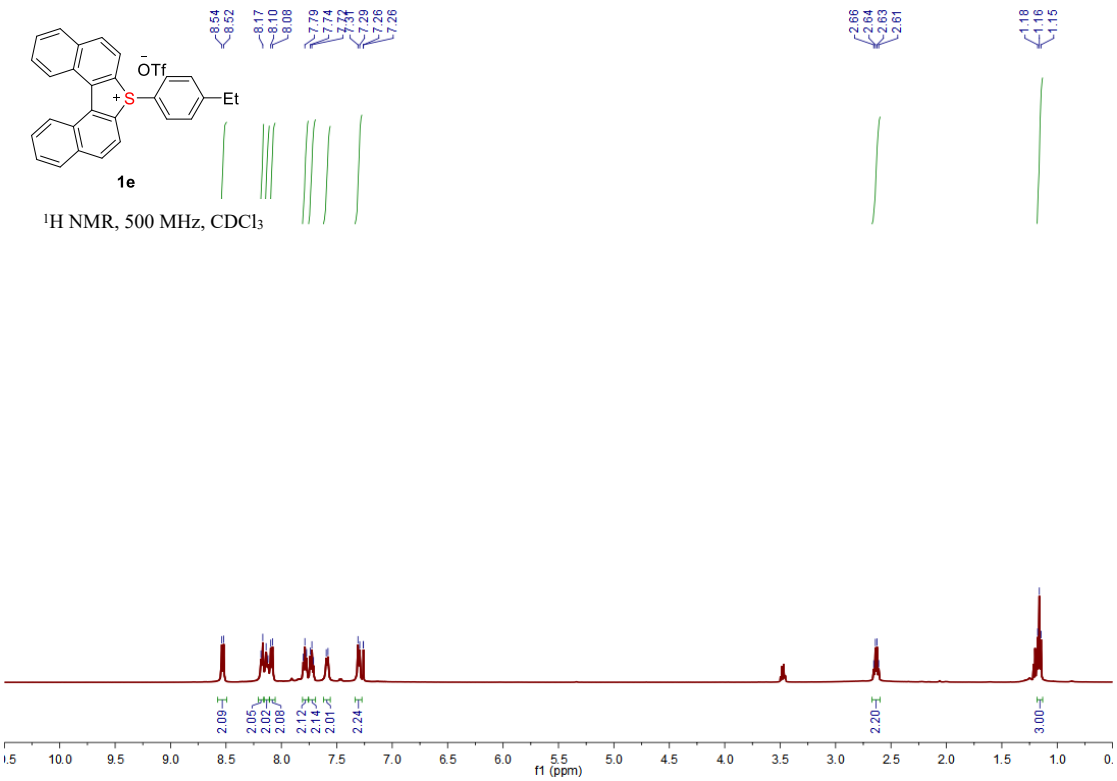
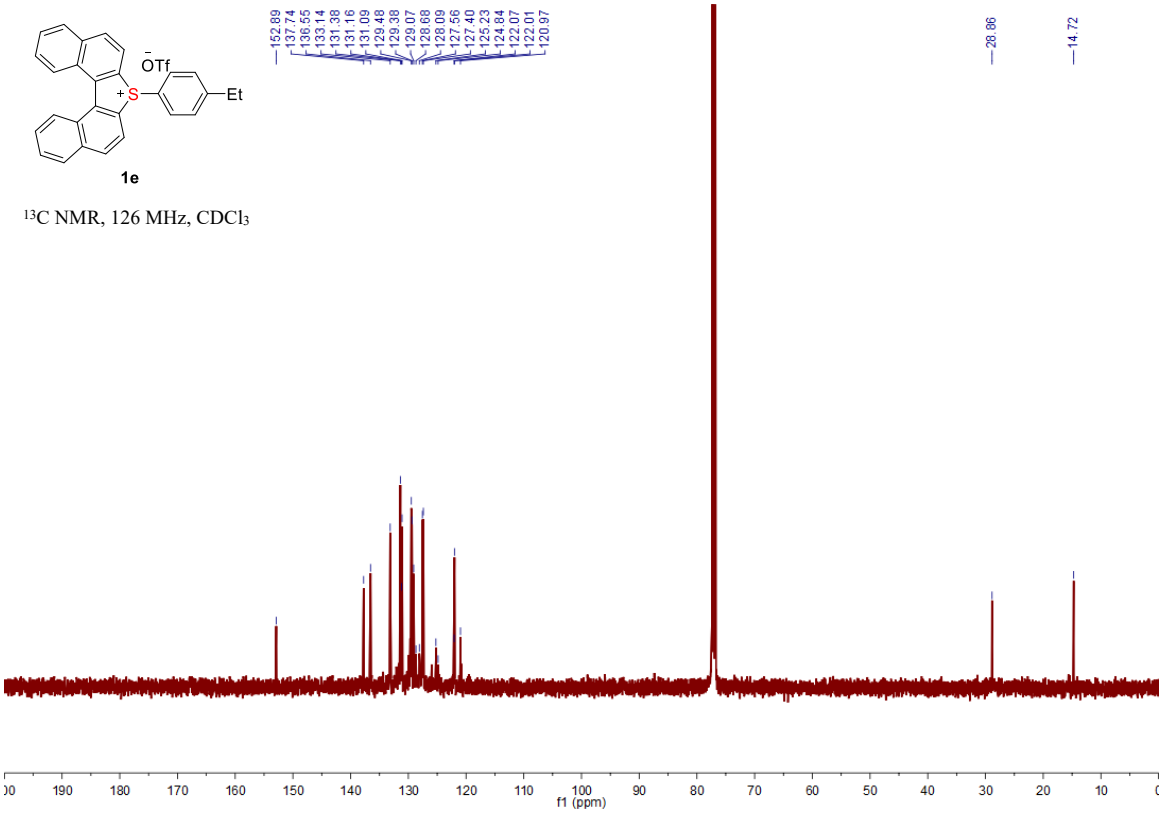


Figure S15. ^{19}F NMR spectrum of 1d (471 MHz, $CDCl_3$)



^{1}H NMR, 500 MHz, $CDCl_3$

Figure S16. ^{1}H NMR spectrum of 1e (500 MHz, $CDCl_3$)



^{13}C NMR, 126 MHz, $CDCl_3$

Figure S17. ^{13}C NMR spectrum of 1e (126 MHz, $CDCl_3$)

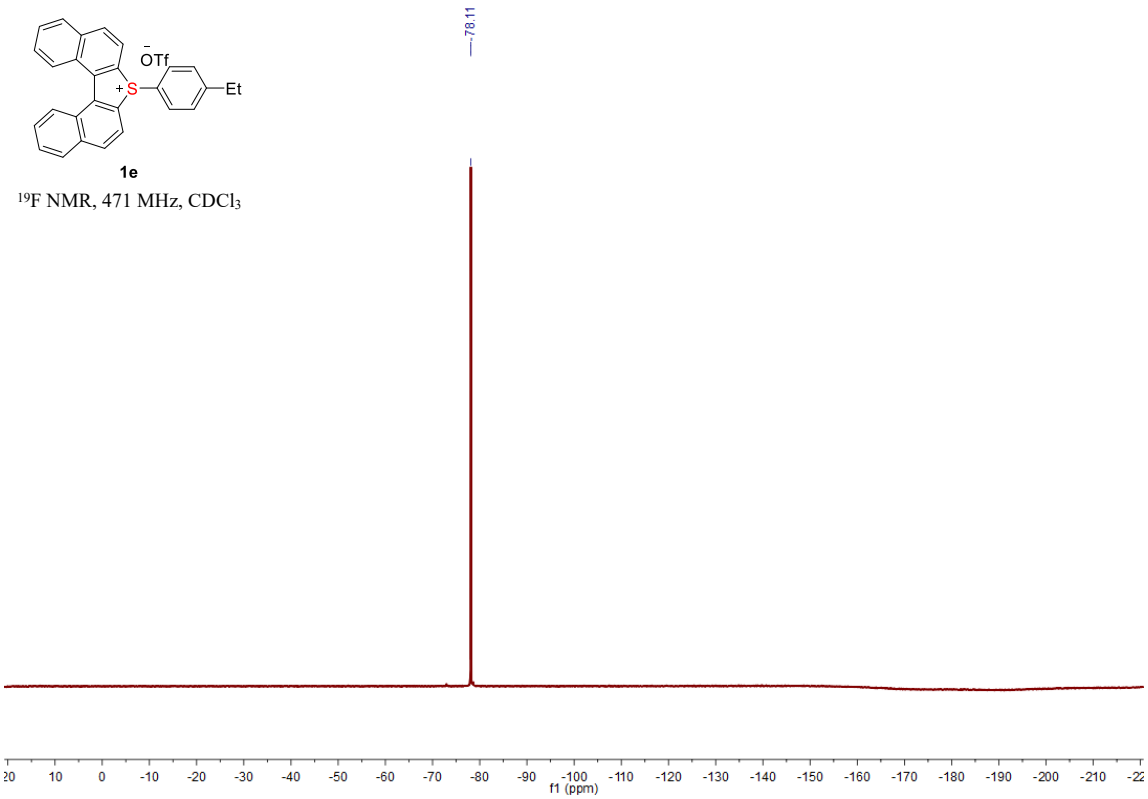


Figure S18. ^{19}F NMR spectrum of 1e (471 MHz, $CDCl_3$)

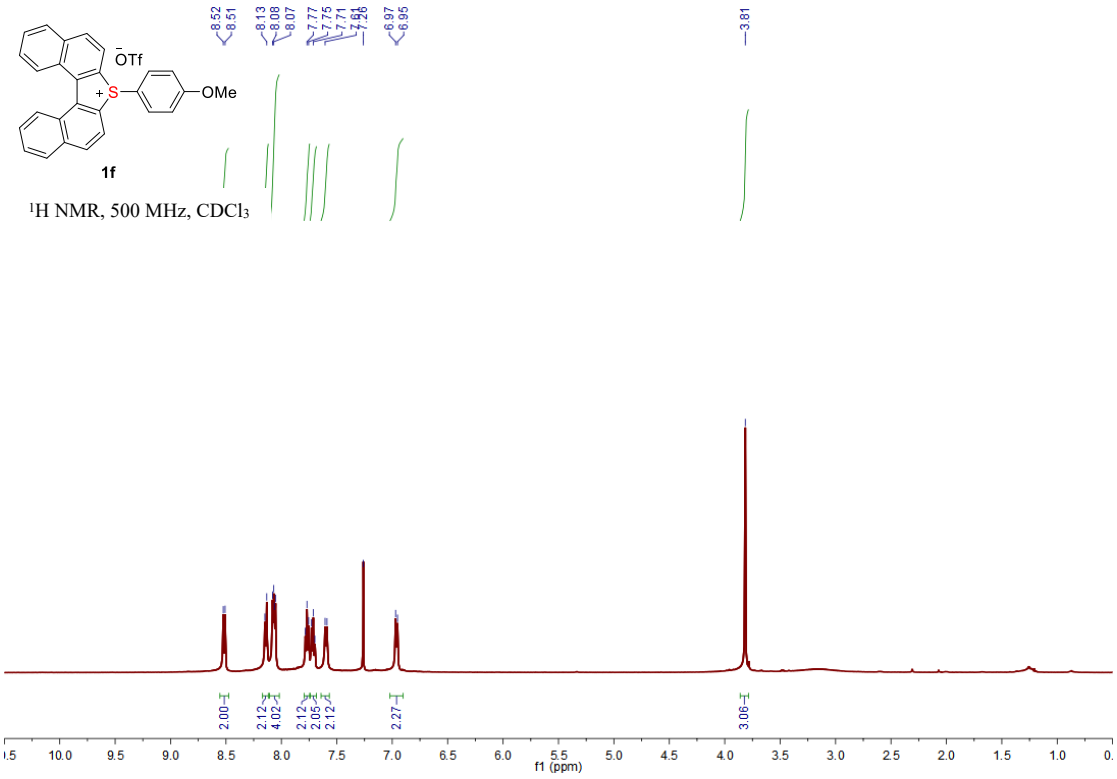
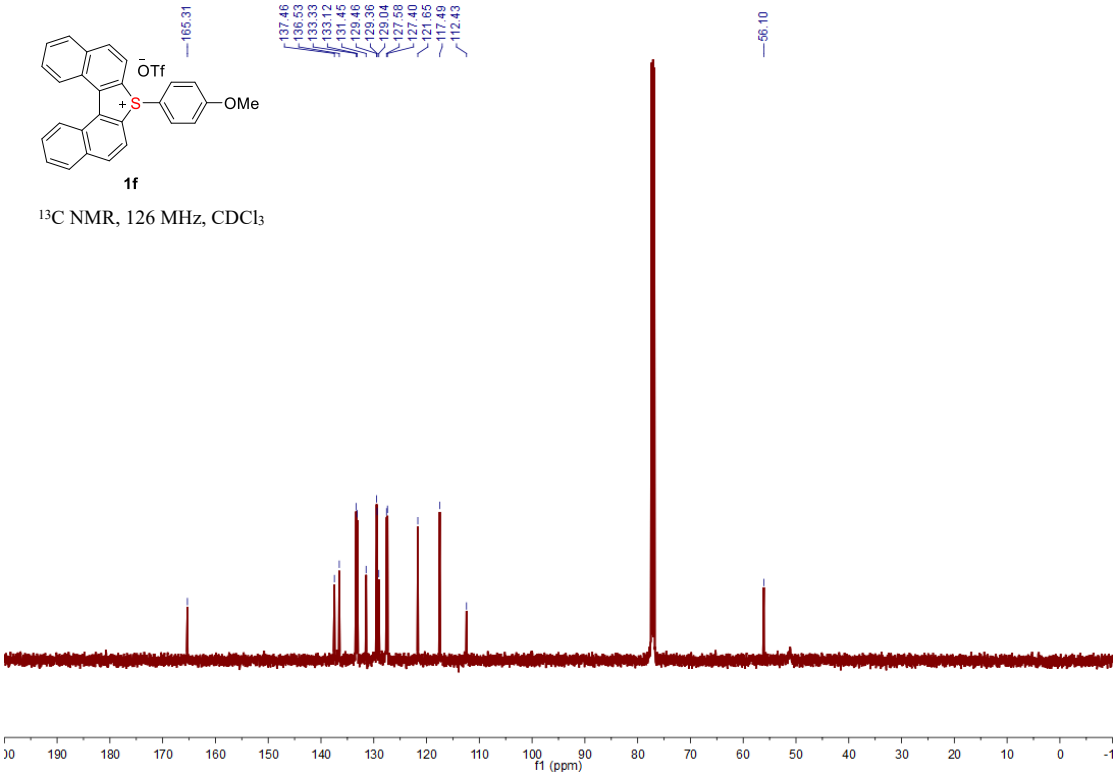
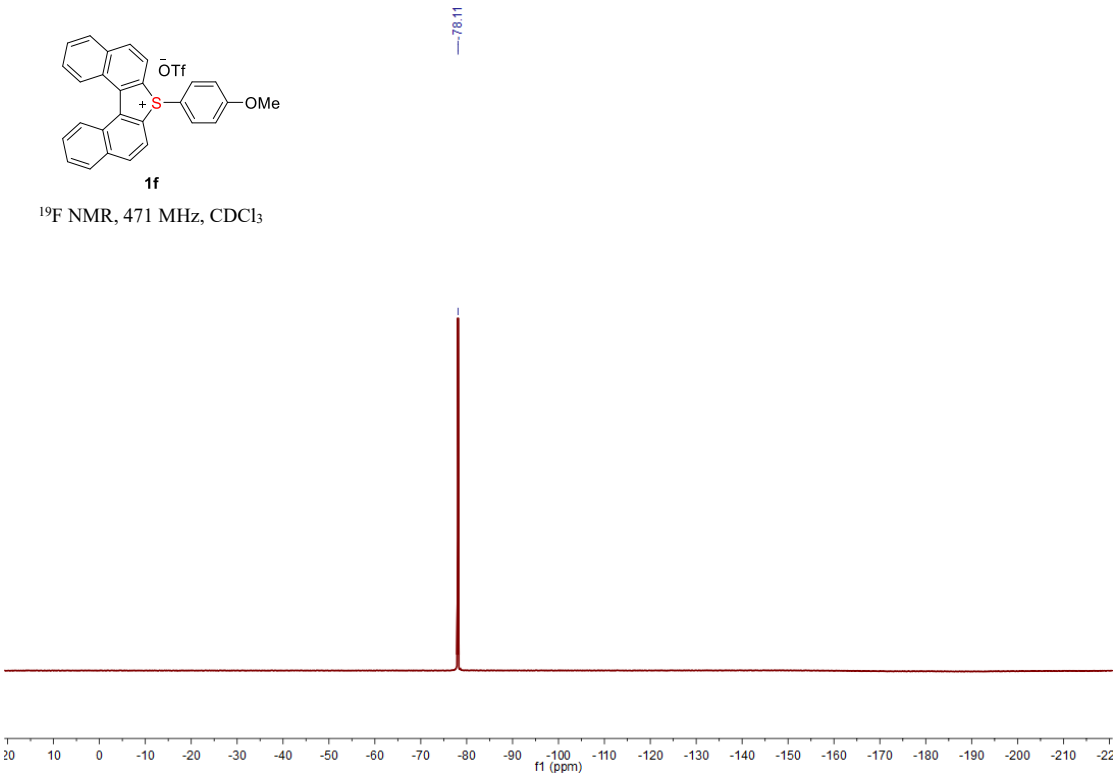


Figure S19. ^{1}H NMR spectrum of 1f (500 MHz, $CDCl_3$)



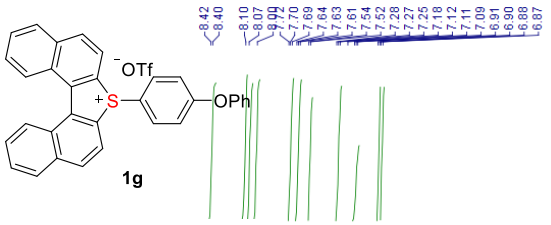
^{13}C NMR, 126 MHz, $CDCl_3$

Figure S20. ^{13}C NMR spectrum of 1f (126 MHz, $CDCl_3$)



^{19}F NMR, 471 MHz, $CDCl_3$

Figure S21. ^{19}F NMR spectrum of 1f (471 MHz, $CDCl_3$)



^{1}H NMR, 500 MHz, $CDCl_3$

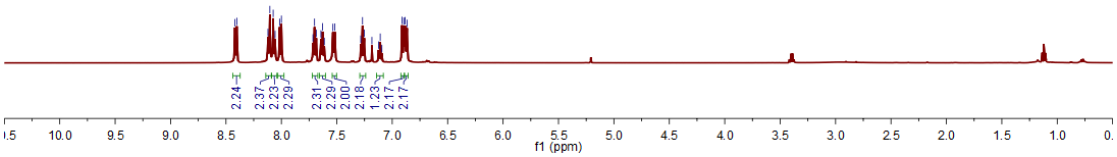
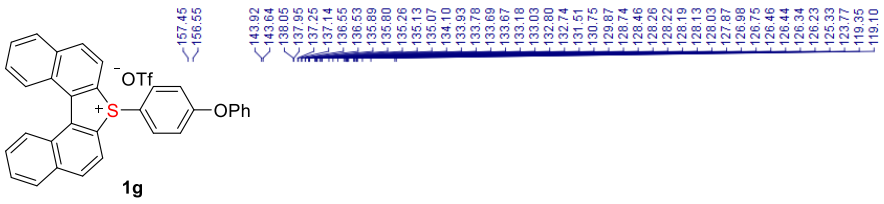


Figure S22. ^{1}H NMR spectrum of 1g (500 MHz, $CDCl_3$)



^{13}C NMR, 126 MHz, $CDCl_3$

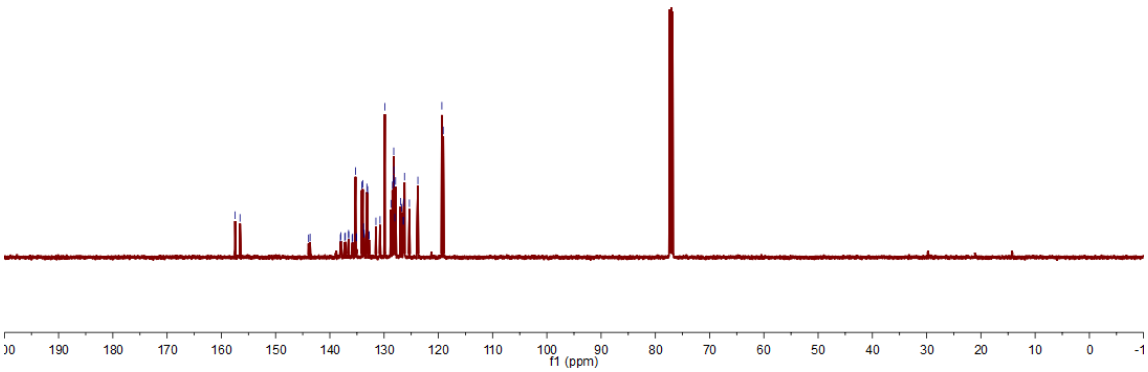
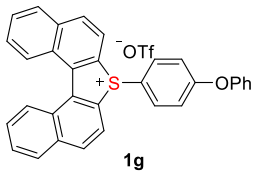


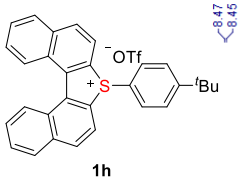
Figure S23. ^{13}C NMR spectrum of 1g (126 MHz, $CDCl_3$)



1g

^{19}F NMR, 471 MHz, $CDCl_3$

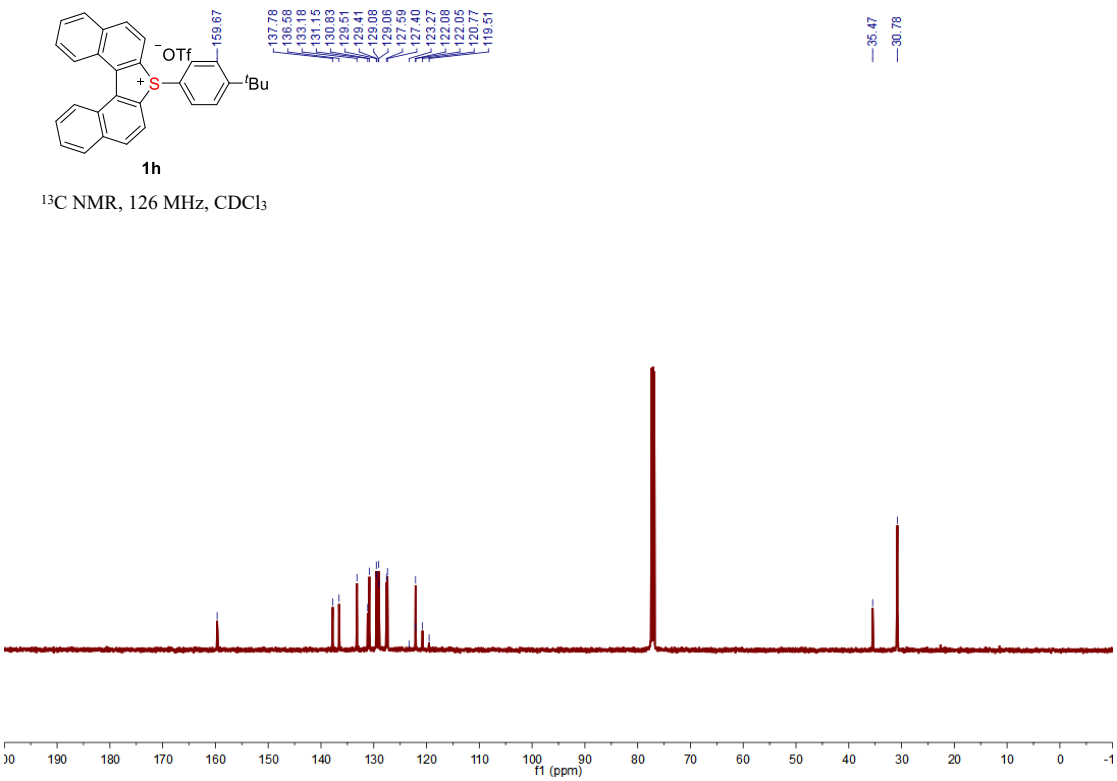
Figure S24. ^{19}F NMR spectrum of 1g (471 MHz, $CDCl_3$)



1h

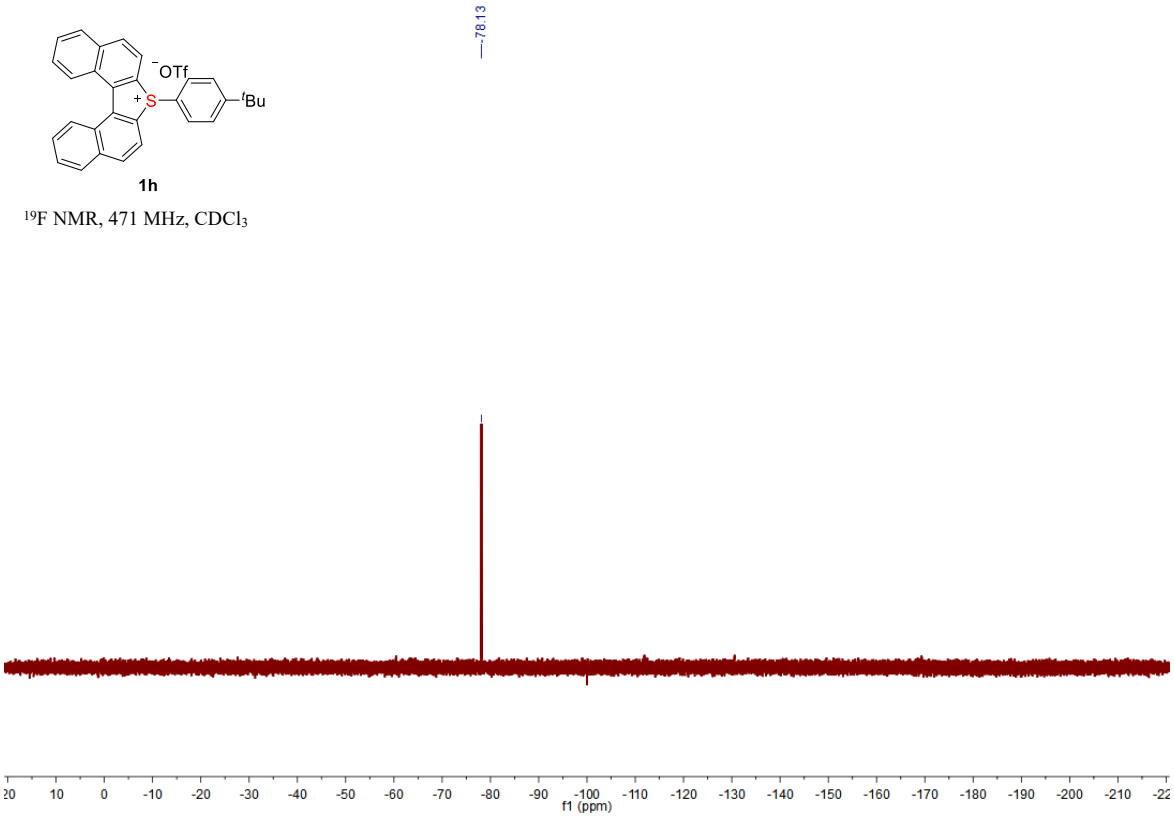
^{1}H NMR, 500 MHz, $CDCl_3$

Figure S25. ^{1}H NMR spectrum of 1h (500 MHz, $CDCl_3$)



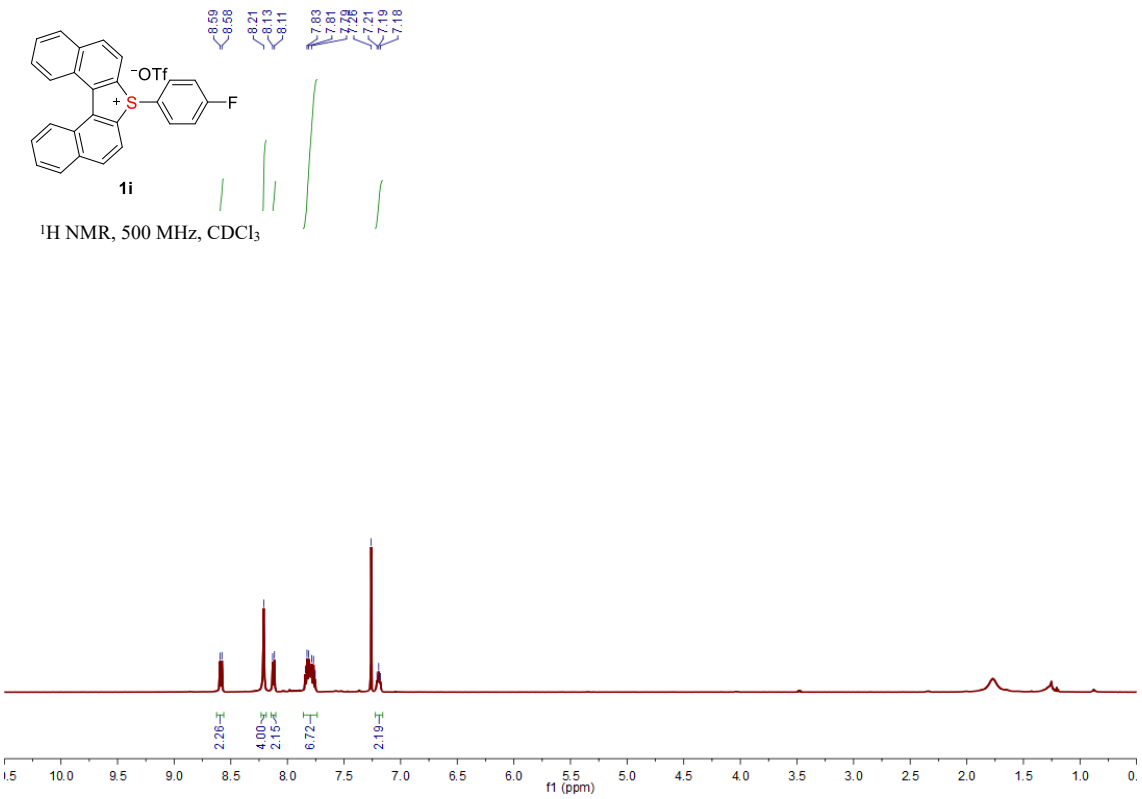
^{13}C NMR, 126 MHz, $CDCl_3$

Figure S26. ^{13}C NMR spectrum of 1h (126 MHz, $CDCl_3$)



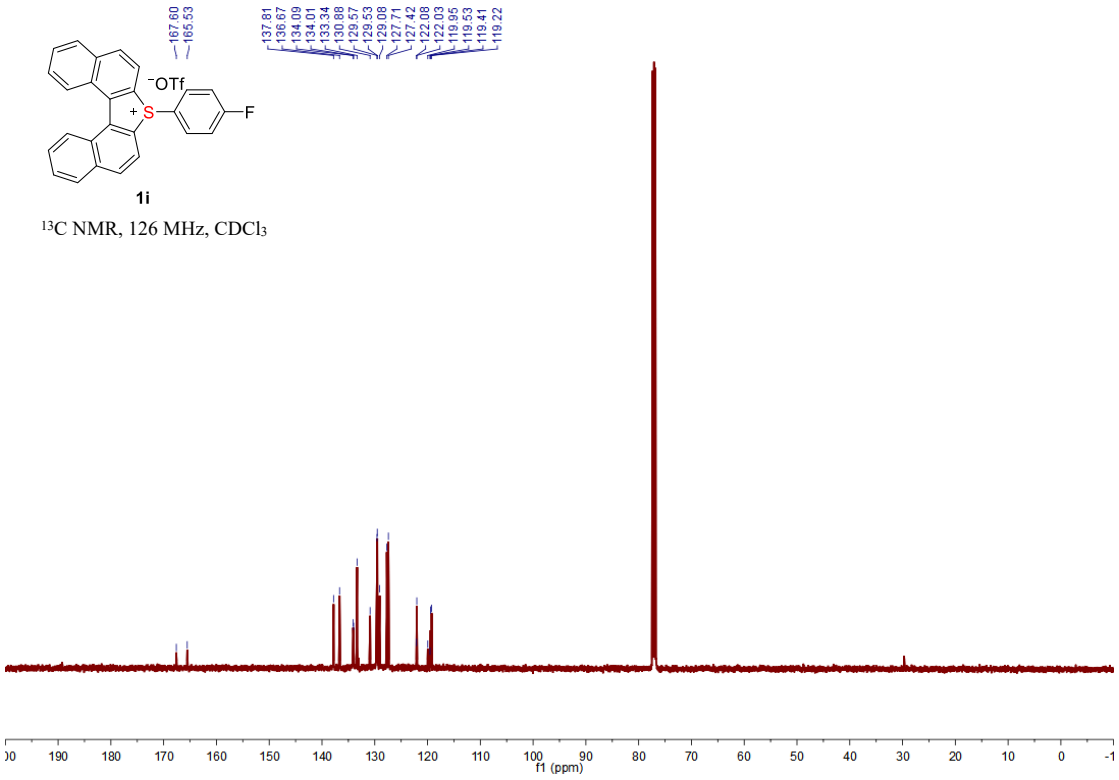
^{19}F NMR, 471 MHz, $CDCl_3$

Figure S27. ^{19}F NMR spectrum of 1h (471 MHz, $CDCl_3$)



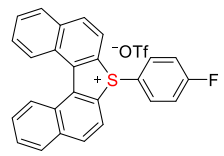
^{1}H NMR, 500 MHz, $CDCl_3$

Figure S28. ^{1}H NMR spectrum of 1i (500 MHz, $CDCl_3$)



^{13}C NMR, 126 MHz, $CDCl_3$

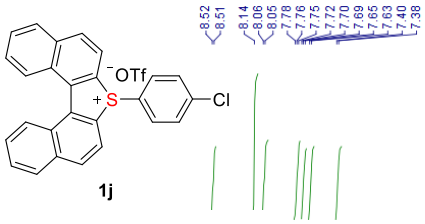
Figure S29. ^{13}C NMR spectrum of 1i (126 MHz, $CDCl_3$)



1i

^{19}F NMR, 471 MHz, $CDCl_3$

Figure S30. ^{19}F NMR spectrum of 1i (471 MHz, $CDCl_3$)



1j

^{1}H NMR, 500 MHz, $CDCl_3$

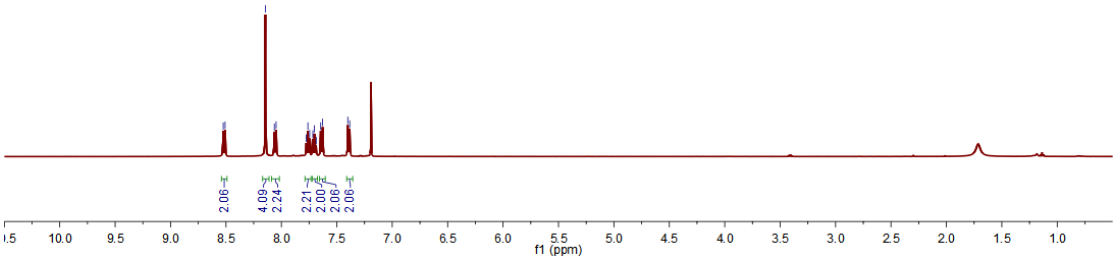
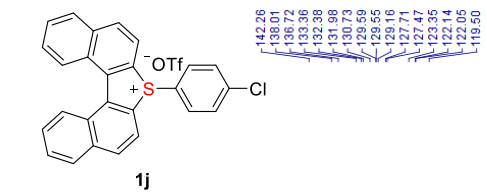


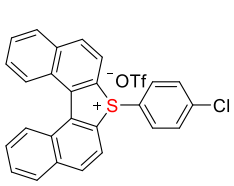
Figure S31. ^{1}H NMR spectrum of 1j (500 MHz, $CDCl_3$)



1j

^{13}C NMR, 126 MHz, $CDCl_3$

Figure S32. ^{13}C NMR spectrum of 1j (126 MHz, $CDCl_3$)



1j

^{19}F NMR, 471 MHz, $CDCl_3$

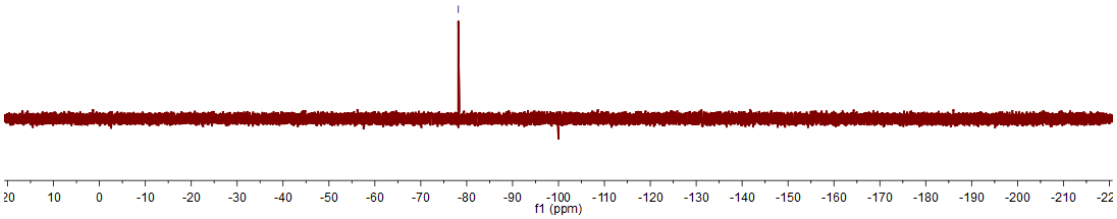
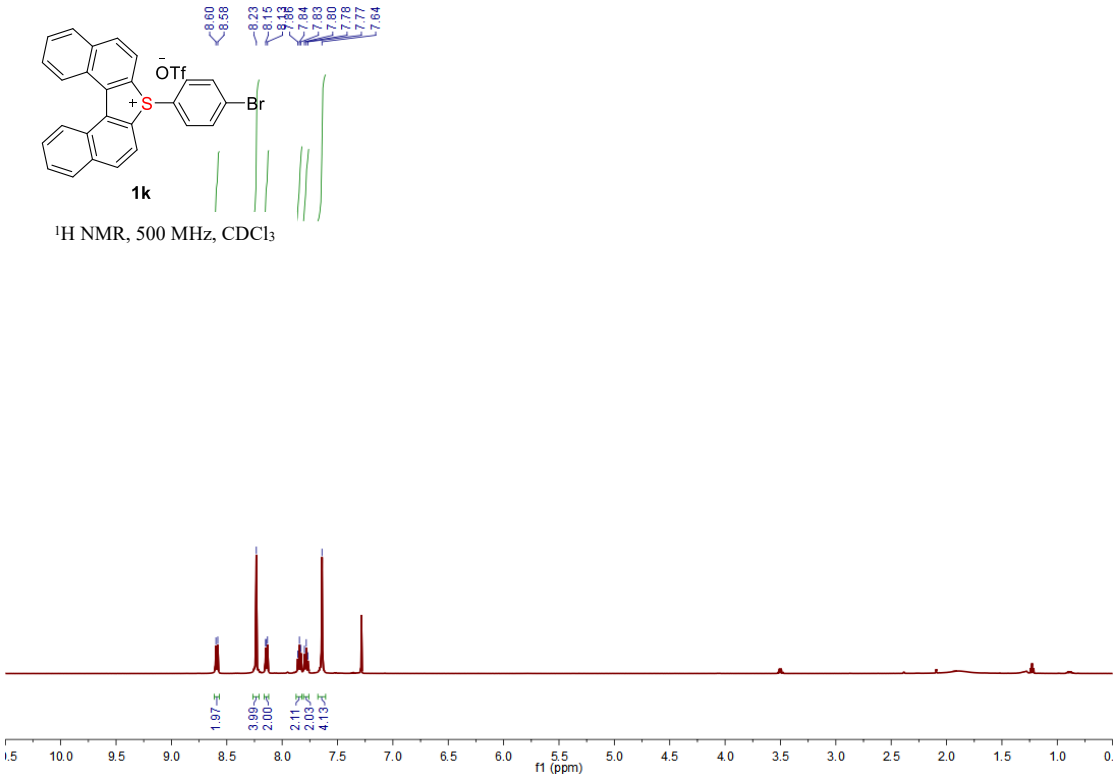
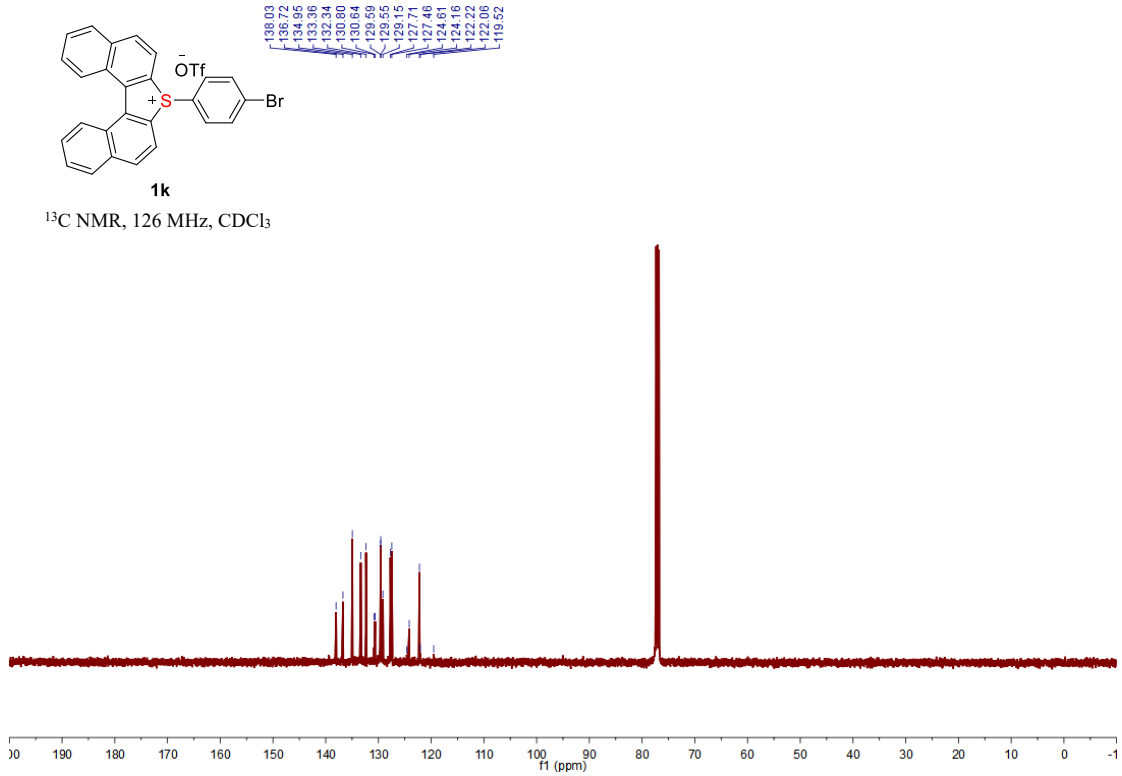


Figure S33. ^{19}F NMR spectrum of 1j (471 MHz, $CDCl_3$)



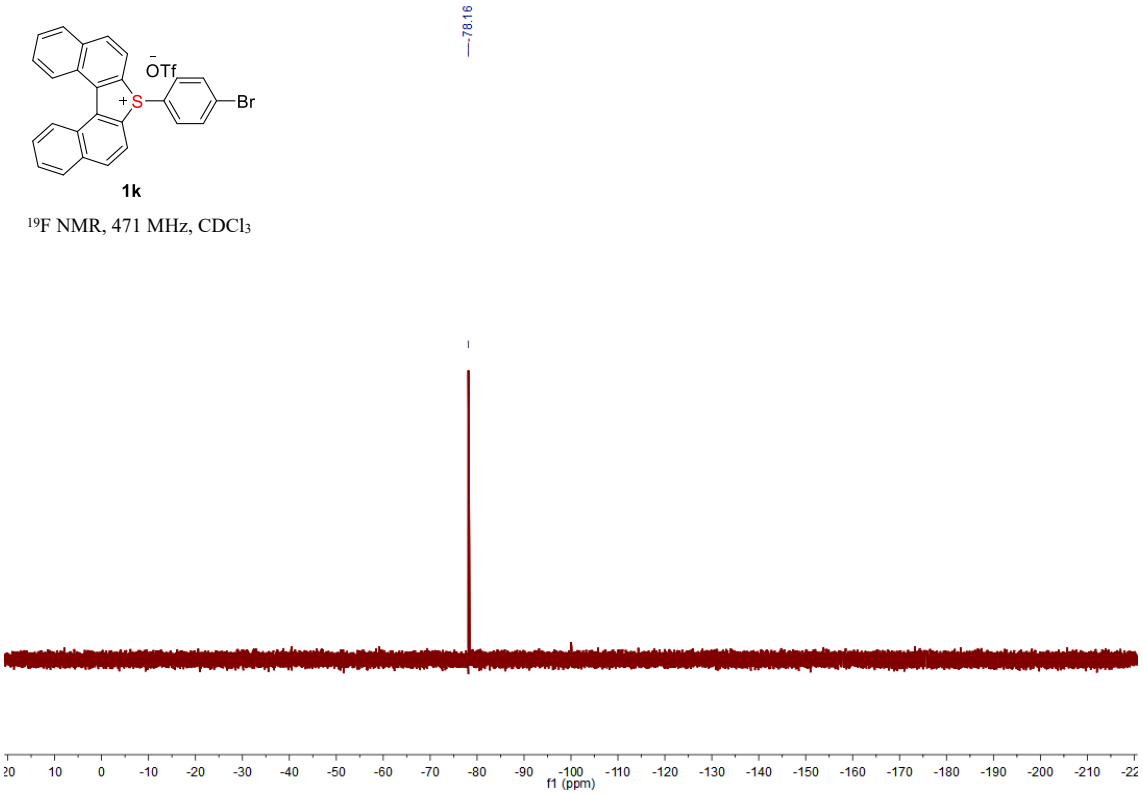
^{1}H NMR, 500 MHz, $CDCl_3$

Figure S34. ^{1}H NMR spectrum of 1k (500 MHz, $CDCl_3$)



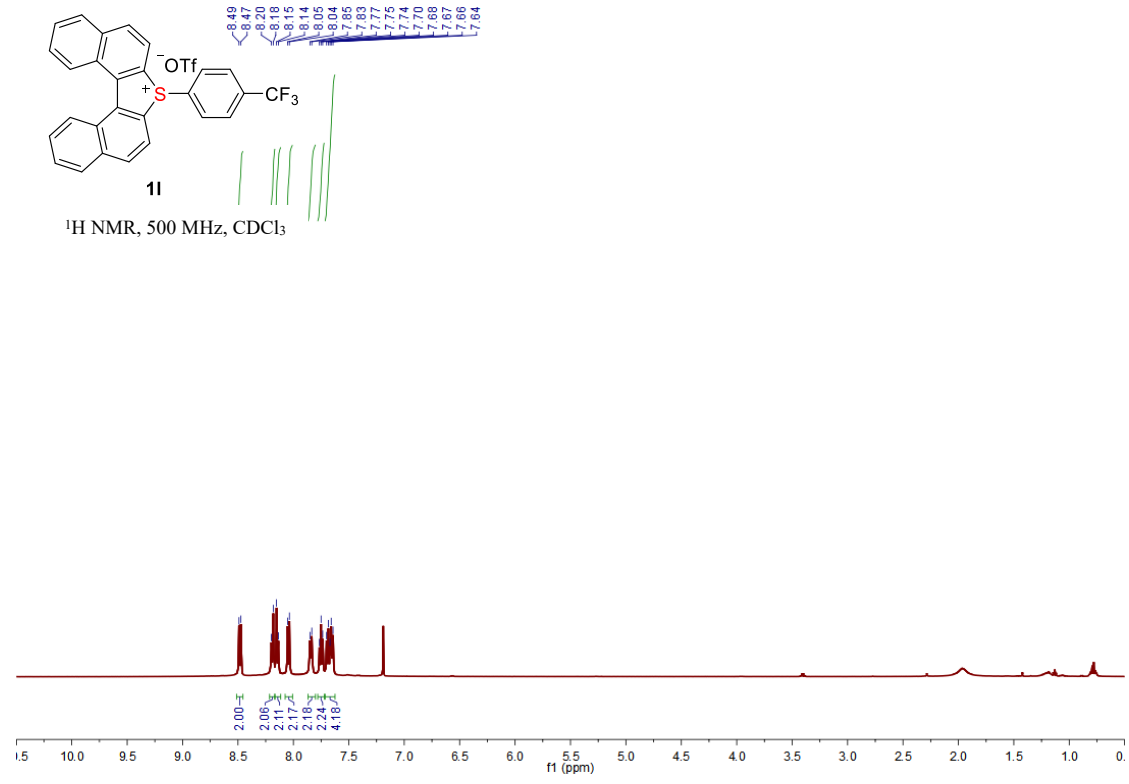
^{13}C NMR, 126 MHz, $CDCl_3$

Figure S35. ^{13}C NMR spectrum of 1k (126 MHz, $CDCl_3$)



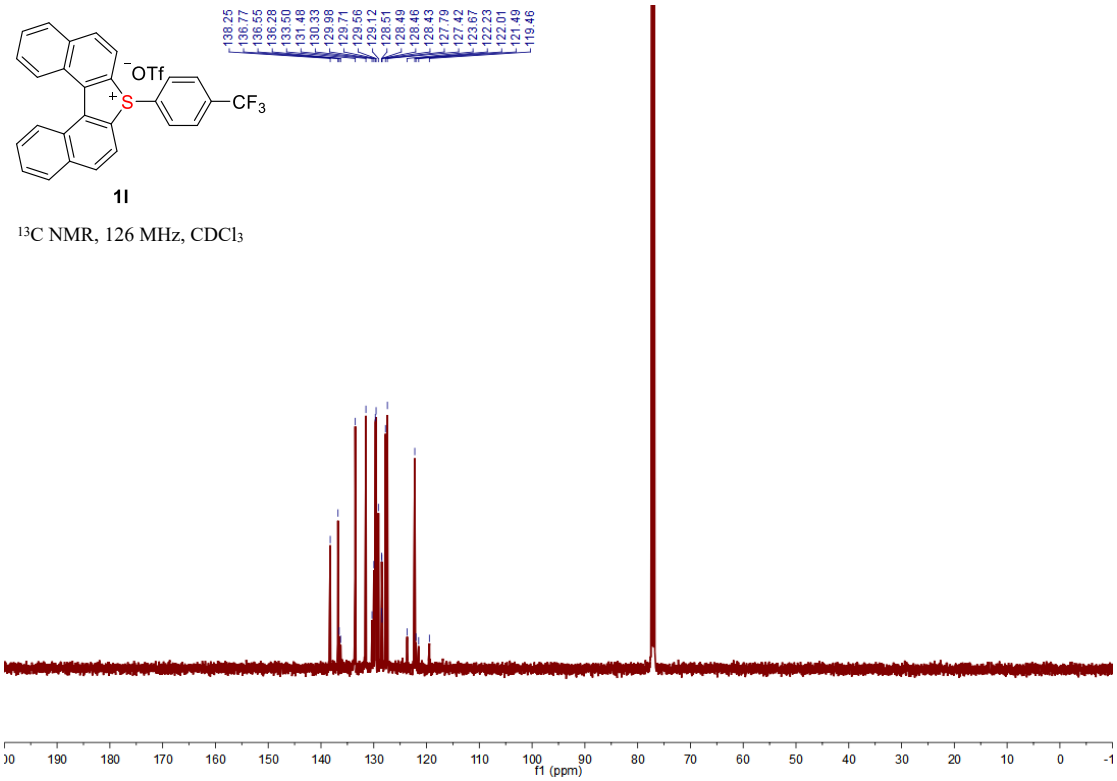
^{19}F NMR, 471 MHz, $CDCl_3$

Figure S36. ^{19}F NMR spectrum of 1k (471 MHz, $CDCl_3$)



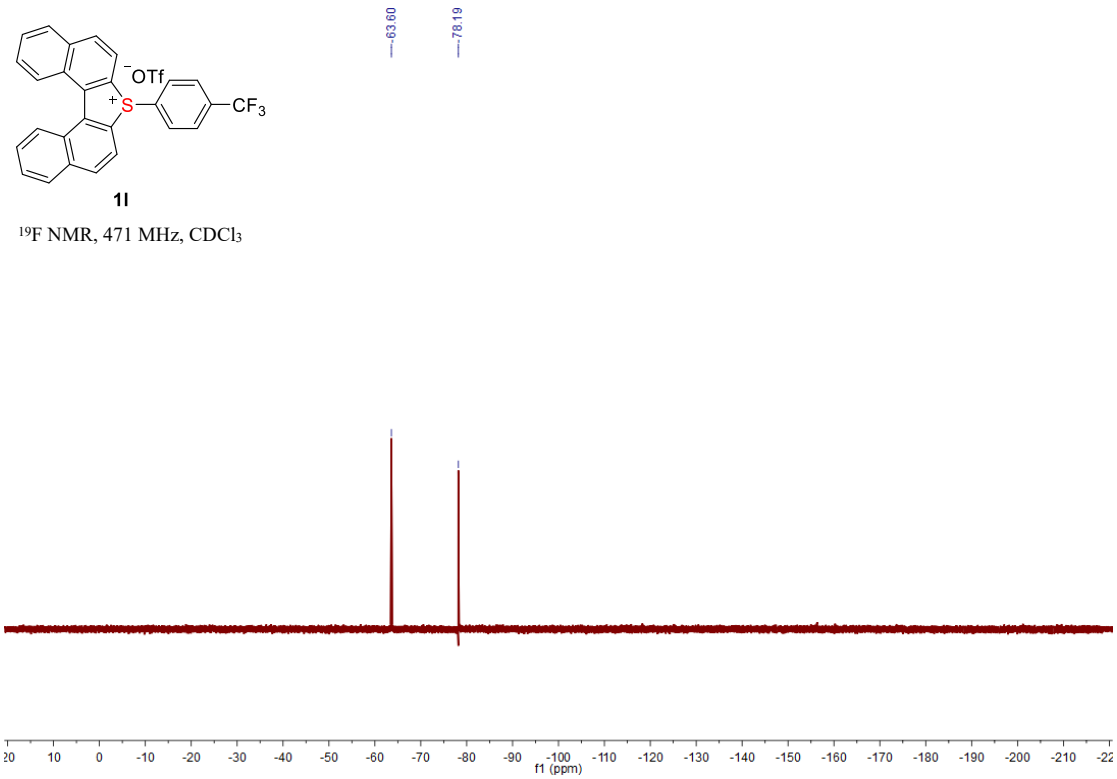
^{1}H NMR, 500 MHz, $CDCl_3$

Figure S37. ^{1}H NMR spectrum of 1l (500 MHz, $CDCl_3$)



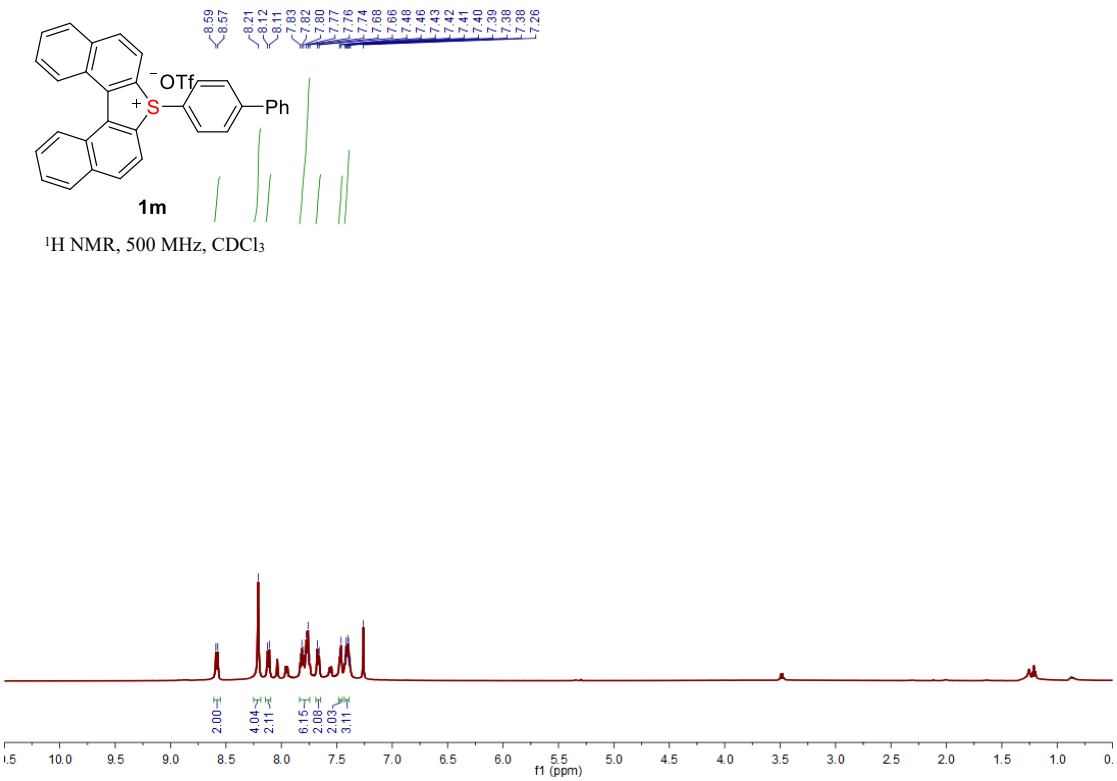
^{13}C NMR, 126 MHz, $CDCl_3$

Figure S38. ^{13}C NMR spectrum of 1l (126 MHz, $CDCl_3$)



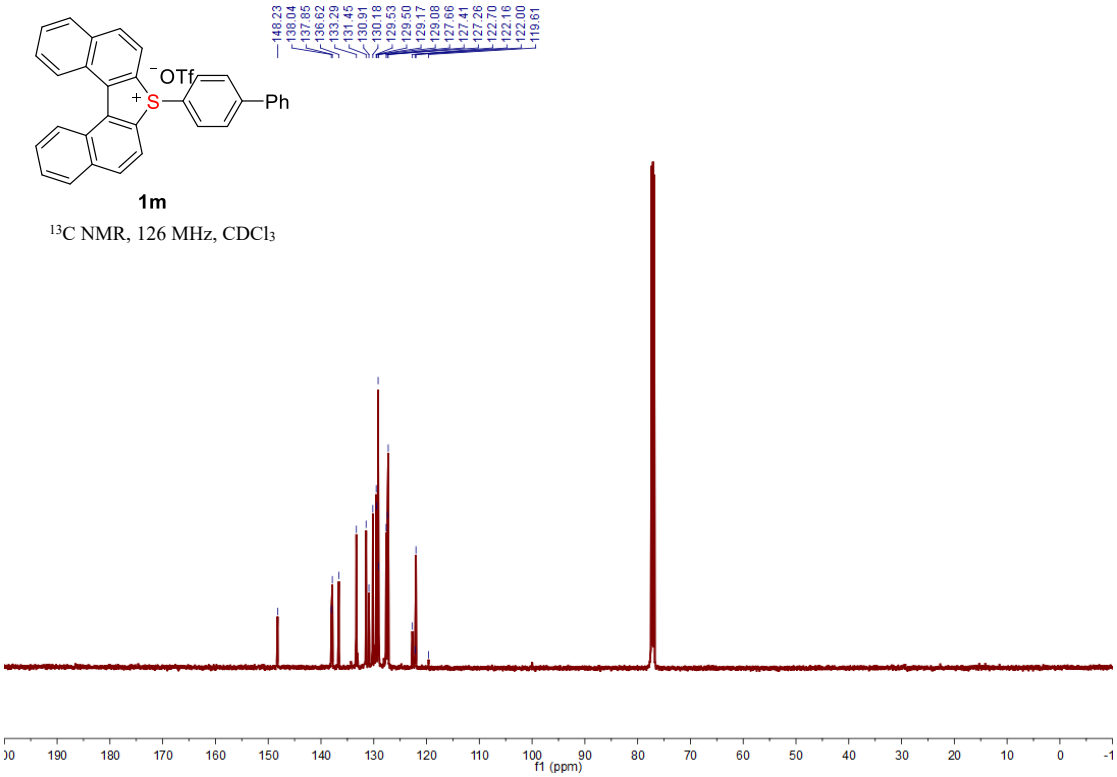
^{19}F NMR, 471 MHz, $CDCl_3$

Figure S39. ^{19}F NMR spectrum of 1l (471 MHz, $CDCl_3$)



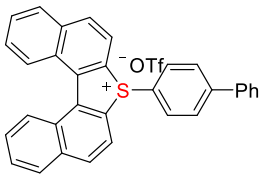
^{1}H NMR, 500 MHz, $CDCl_3$

Figure S40. ^{1}H NMR spectrum of 1m (500 MHz, $CDCl_3$)



^{13}C NMR, 126 MHz, $CDCl_3$

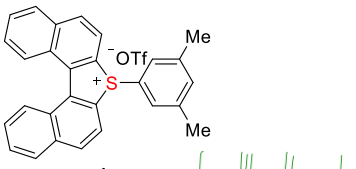
Figure S41. ^{13}C NMR spectrum of 1m (126 MHz, $CDCl_3$)



1m

^{19}F NMR, 471 MHz, $CDCl_3$

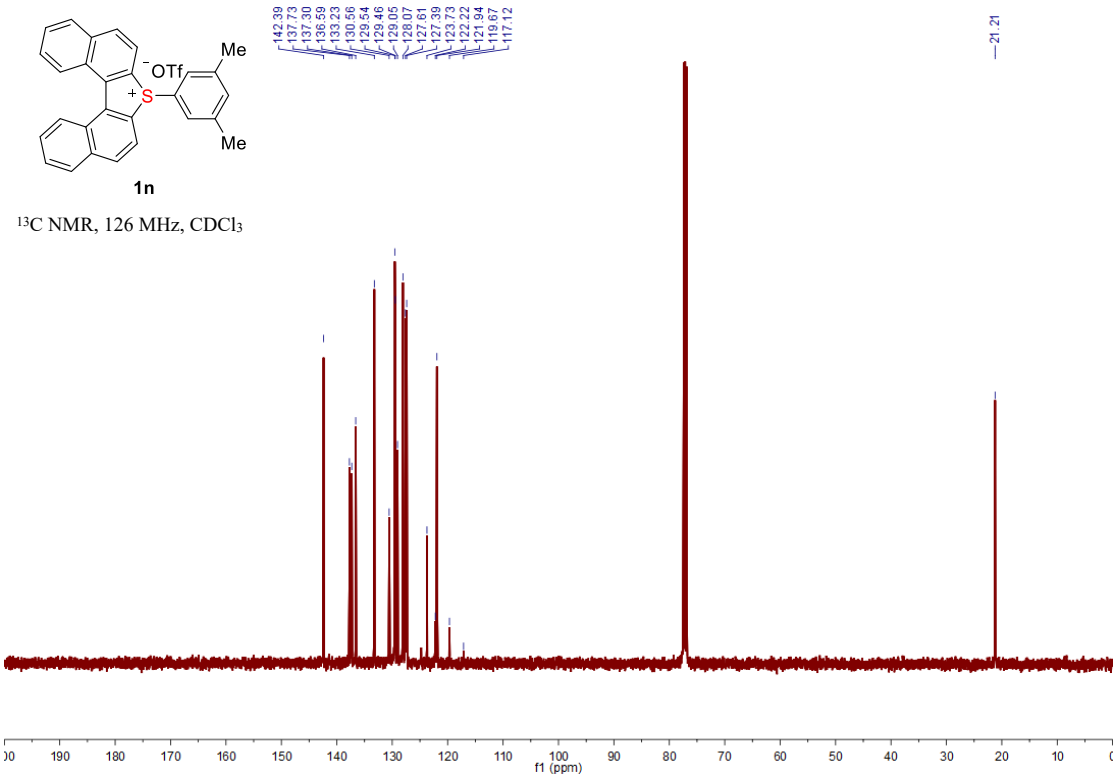
Figure S42. ^{19}F NMR spectrum of 1m (471 MHz, $CDCl_3$)



1n

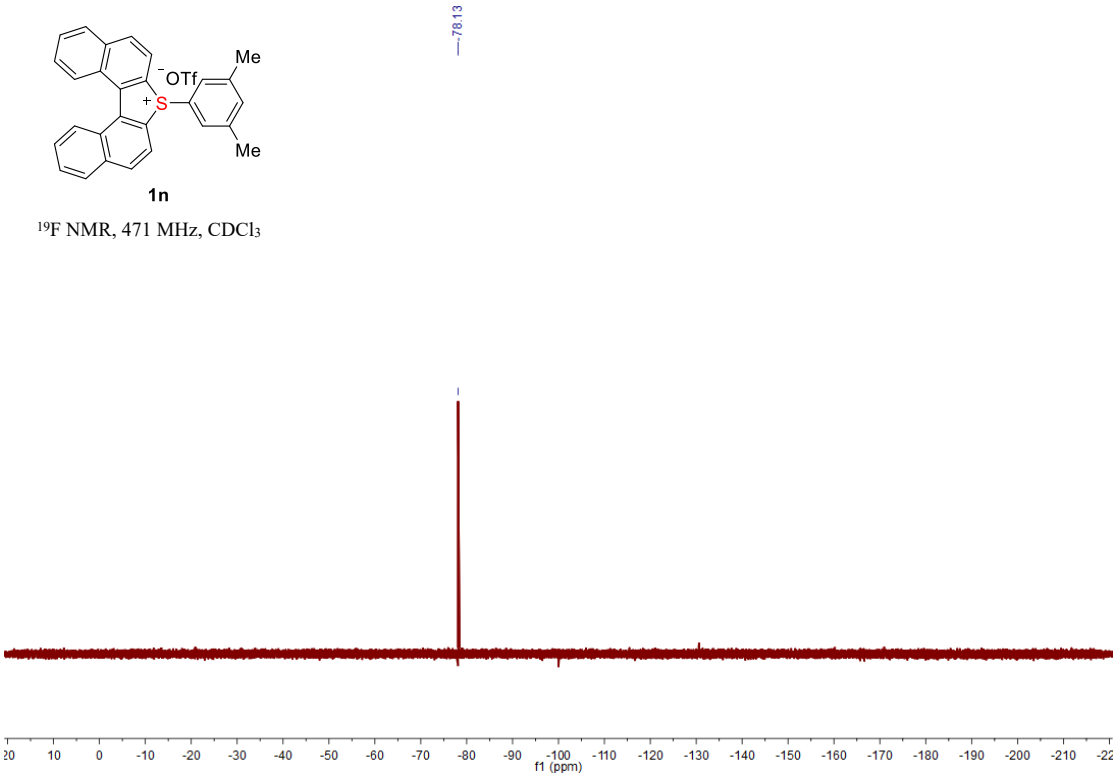
^{1}H NMR, 500 MHz, $CDCl_3$

Figure S43. ^{1}H NMR spectrum of 1n (500 MHz, $CDCl_3$)



^{13}C NMR, 126 MHz, $CDCl_3$

Figure S44. ^{13}C NMR spectrum of 1n (126 MHz, $CDCl_3$)



^{19}F NMR, 471 MHz, $CDCl_3$

Figure S45. ^{19}F NMR spectrum of 1n (471 MHz, $CDCl_3$)

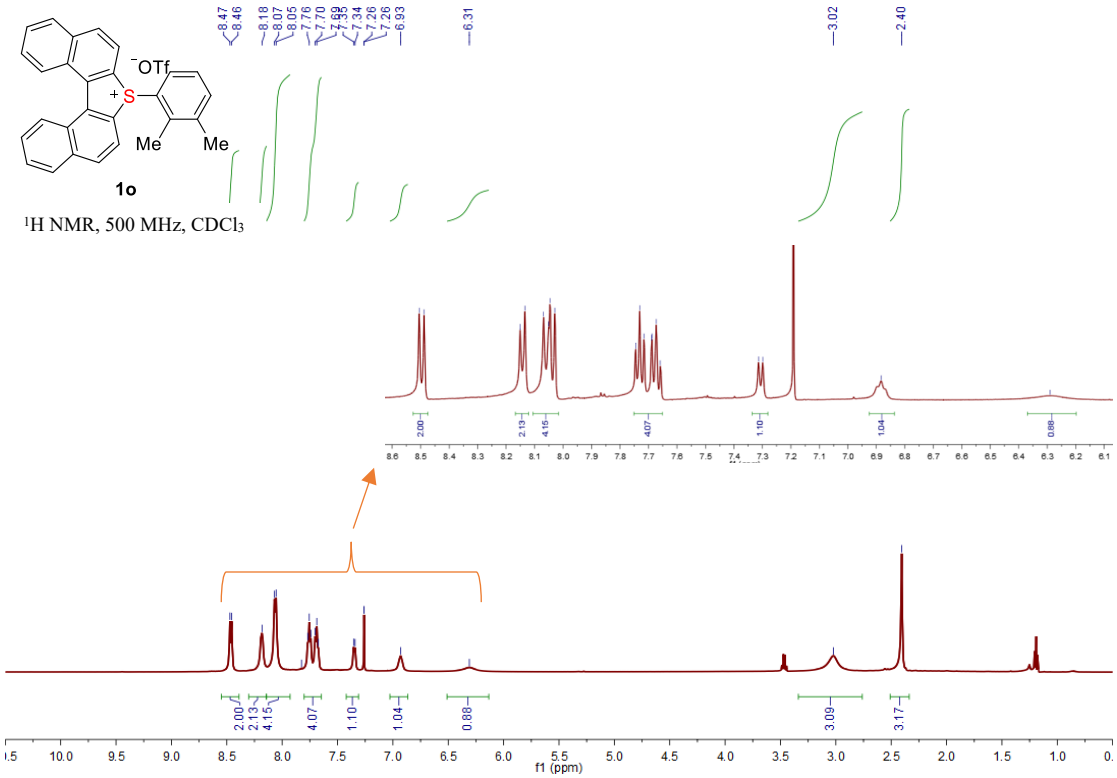


Figure S46. ^{1}H NMR spectrum of 1o (500 MHz, $CDCl_3$)

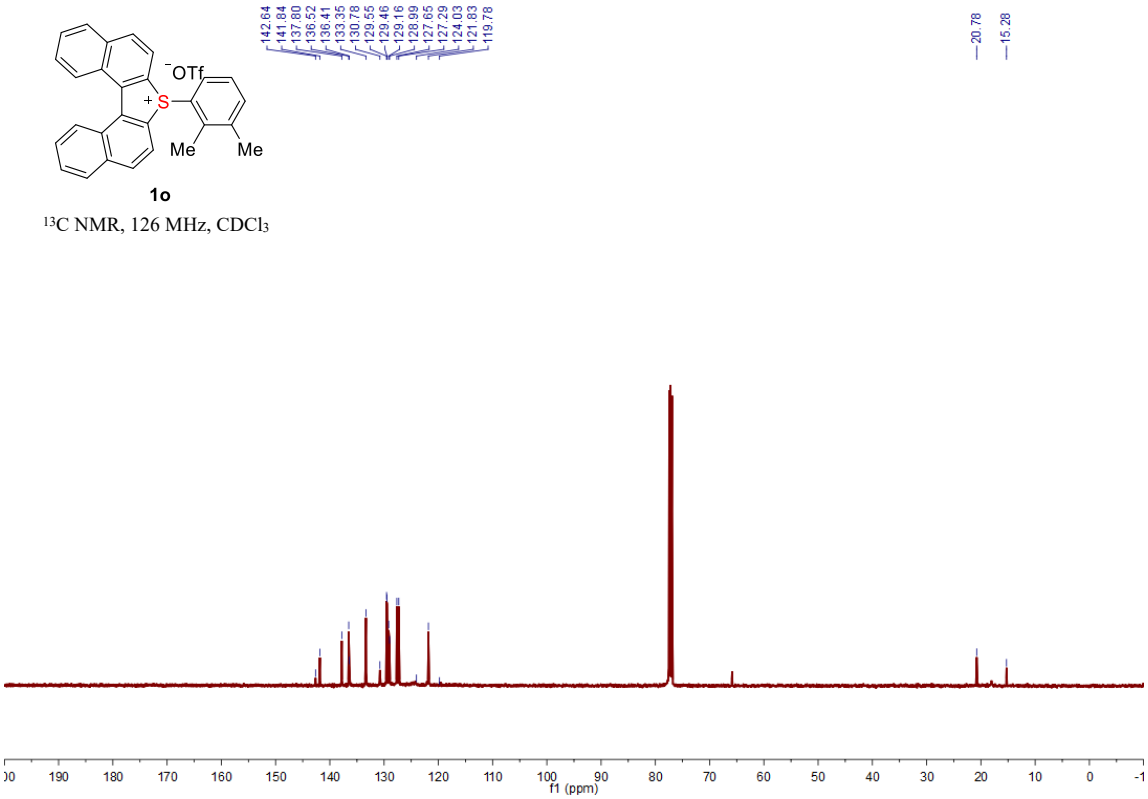
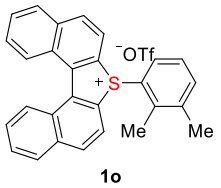


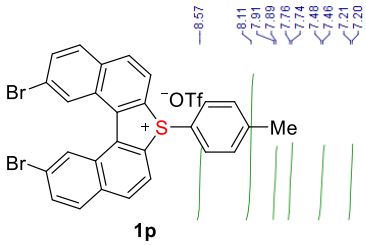
Figure S47. ^{13}C NMR spectrum of 1o (126 MHz, $CDCl_3$)



1o

^{19}F NMR, 471 MHz, $CDCl_3$

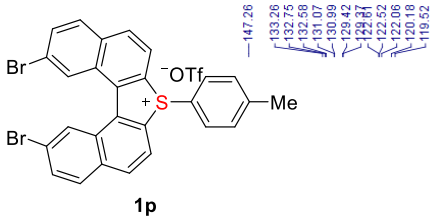
Figure S48. ^{19}F NMR spectrum of 1o (471 MHz, $CDCl_3$)



1p

^{1}H NMR, 500 MHz, $CDCl_3$

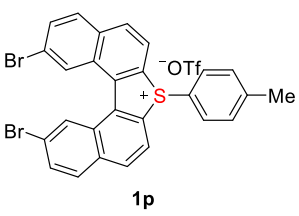
Figure S49. ^{1}H NMR spectrum of 1p (500 MHz, $CDCl_3$)



1p

^{13}C NMR, 126 MHz, $CDCl_3$

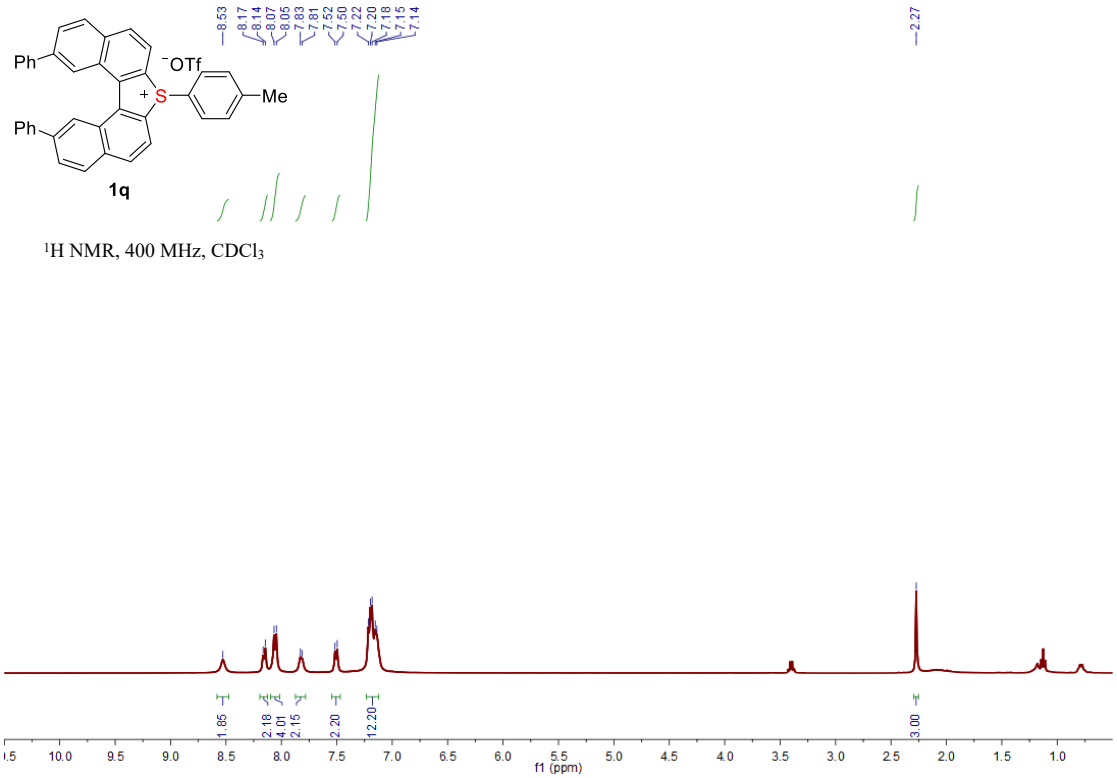
Figure S50. ^{13}C NMR spectrum of 1p (126 MHz, $CDCl_3$)



1p

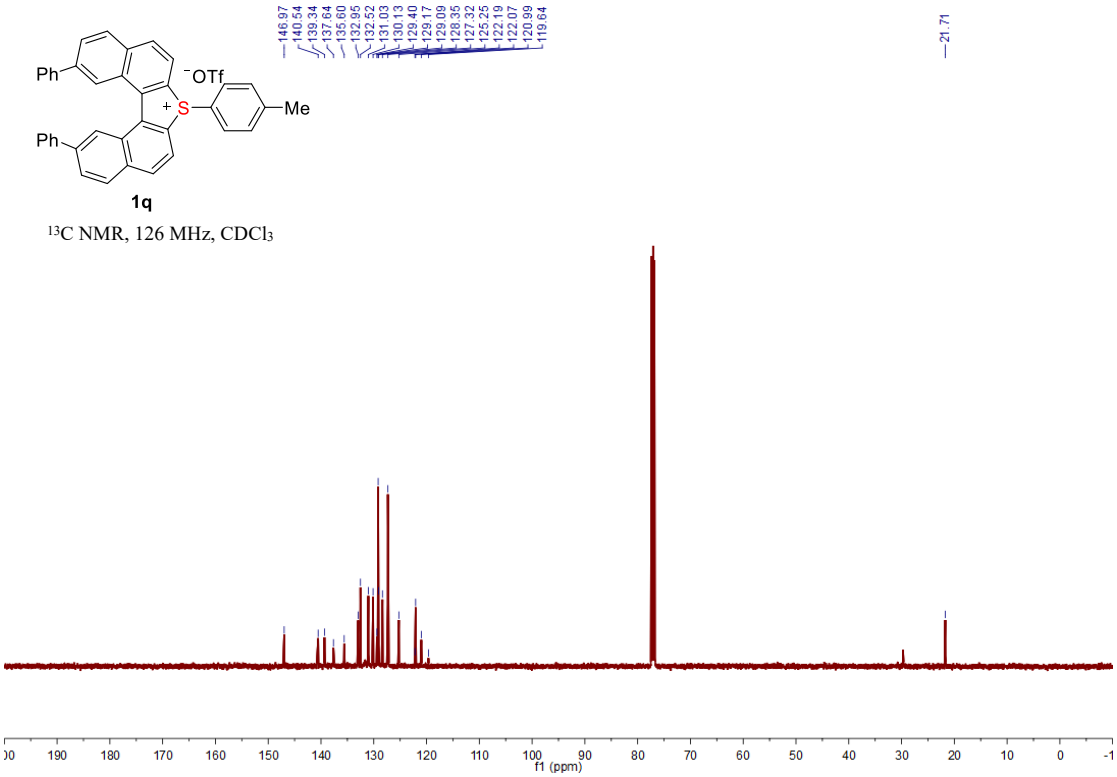
^{19}F NMR, 471 MHz, $CDCl_3$

Figure S51. ^{19}F NMR spectrum of 1p (471 MHz, $CDCl_3$)



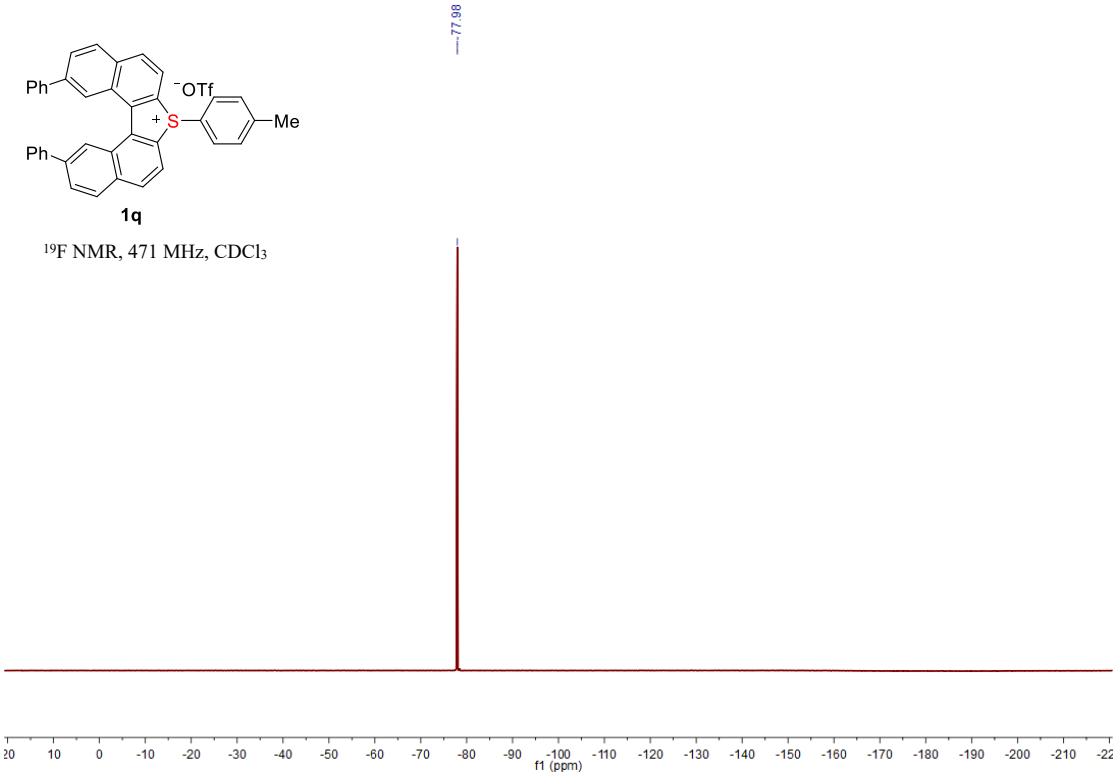
^{1}H NMR, 400 MHz, $CDCl_3$

Figure S52. ^{1}H NMR spectrum of 1q (400 MHz, $CDCl_3$)



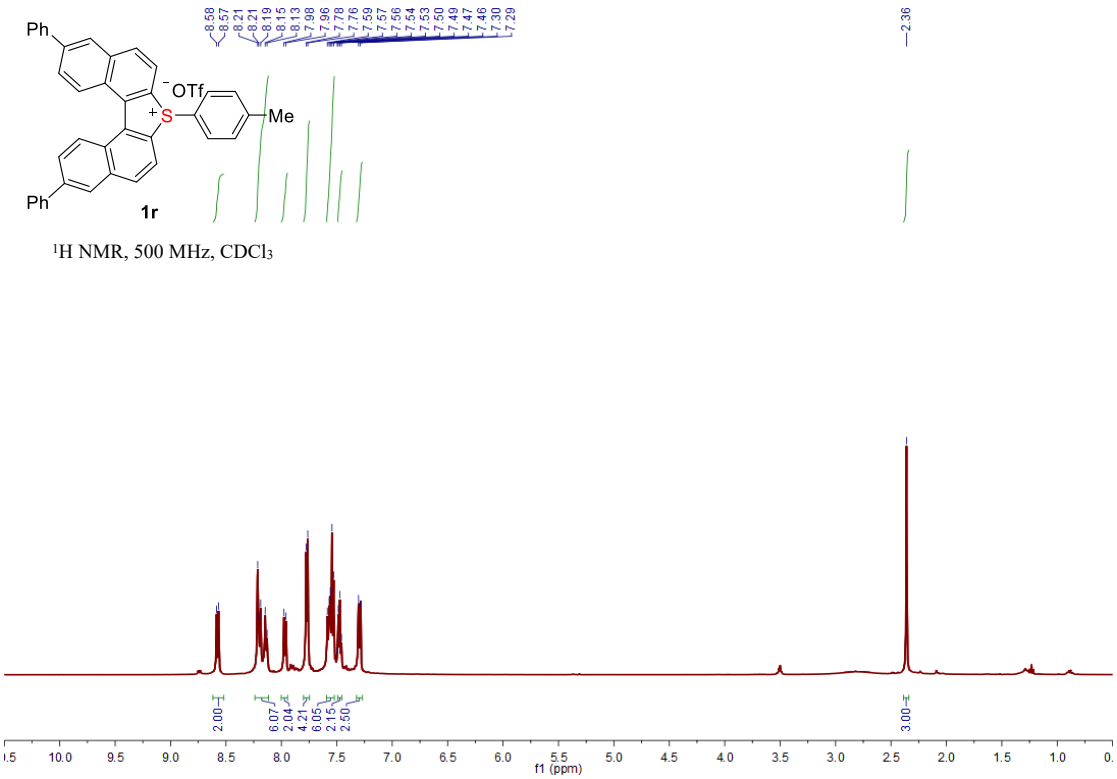
^{13}C NMR, 126 MHz, $CDCl_3$

Figure S53. ^{13}C NMR spectrum of 1q (126 MHz, $CDCl_3$)



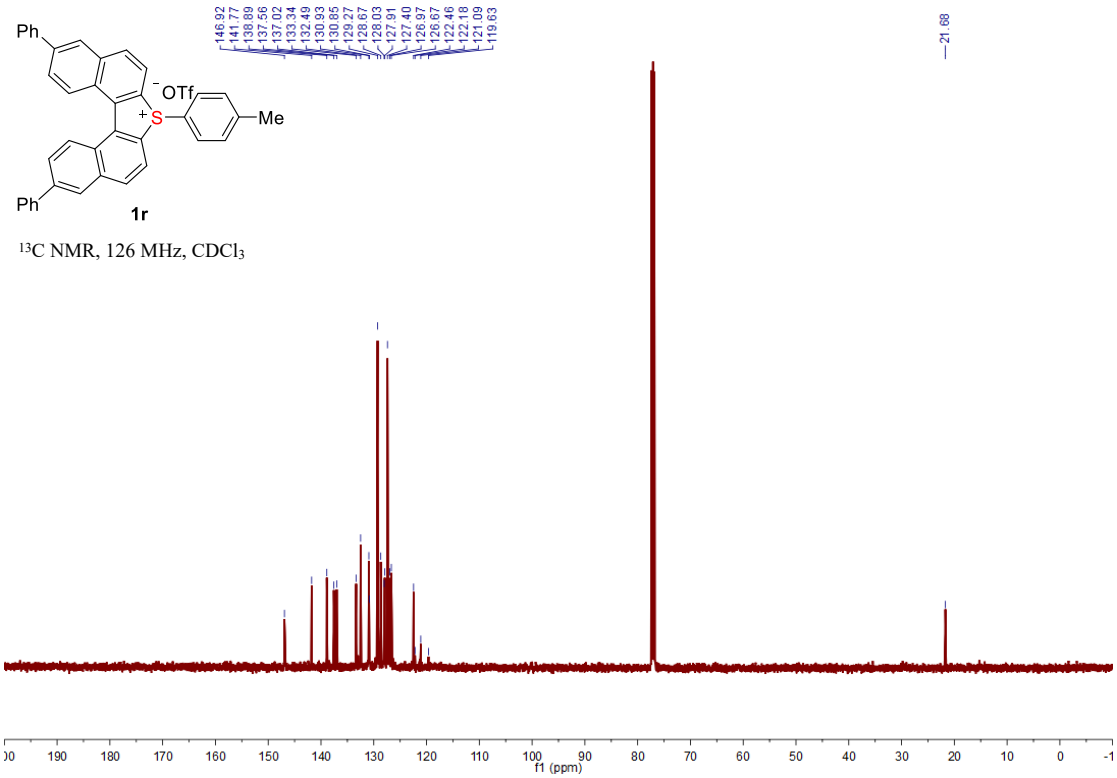
^{19}F NMR, 471 MHz, $CDCl_3$

Figure S54. ^{19}F NMR spectrum of 1q (471 MHz, $CDCl_3$)



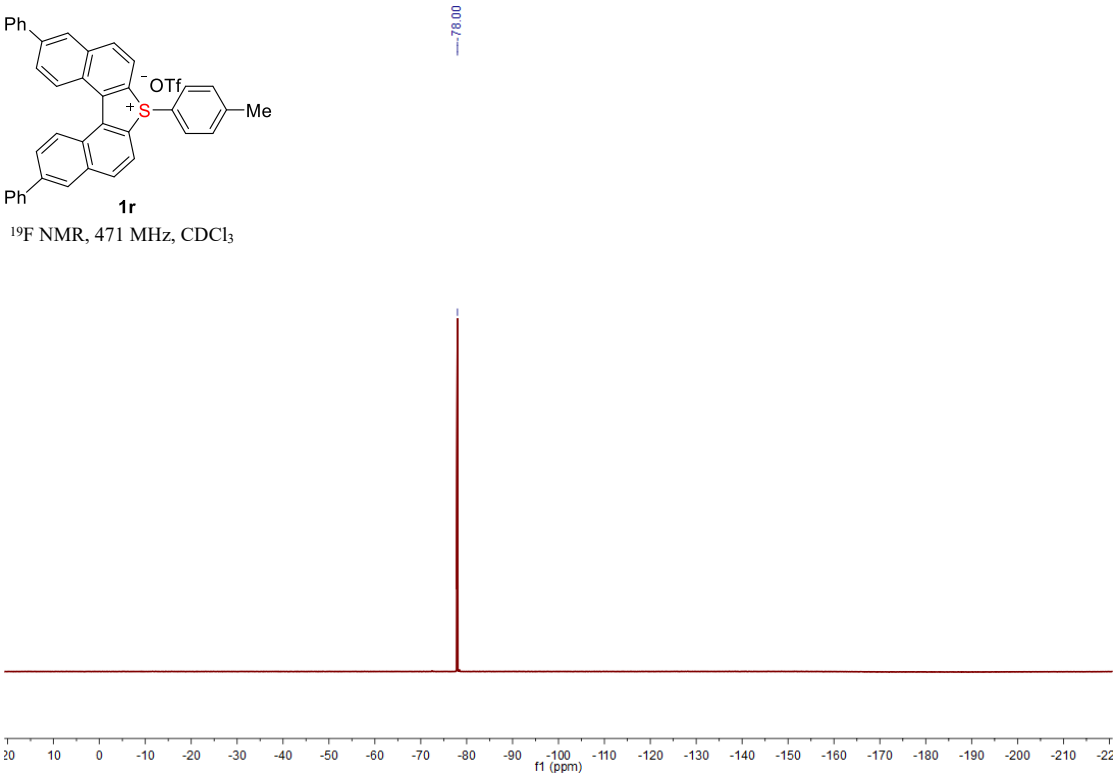
^{1}H NMR, 500 MHz, $CDCl_3$

Figure S55. ^{1}H NMR spectrum of 1r (500 MHz, $CDCl_3$)



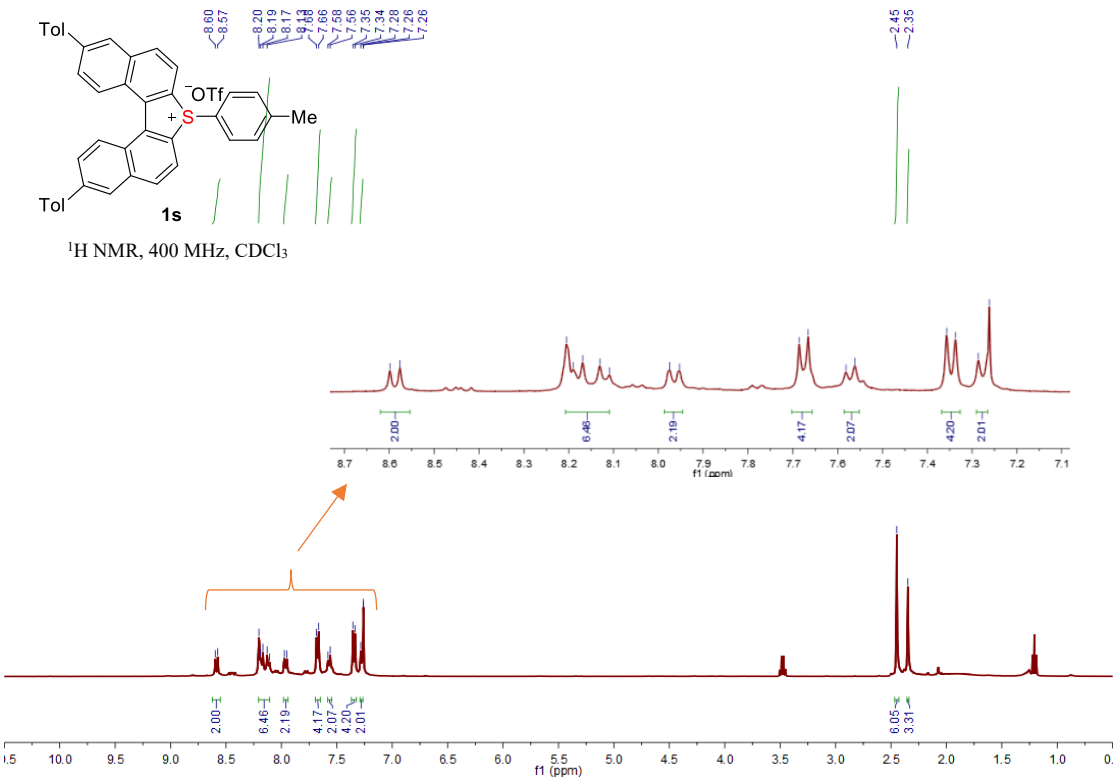
^{13}C NMR, 126 MHz, $CDCl_3$

Figure S56. ^{13}C NMR spectrum of 1r (126 MHz, $CDCl_3$)



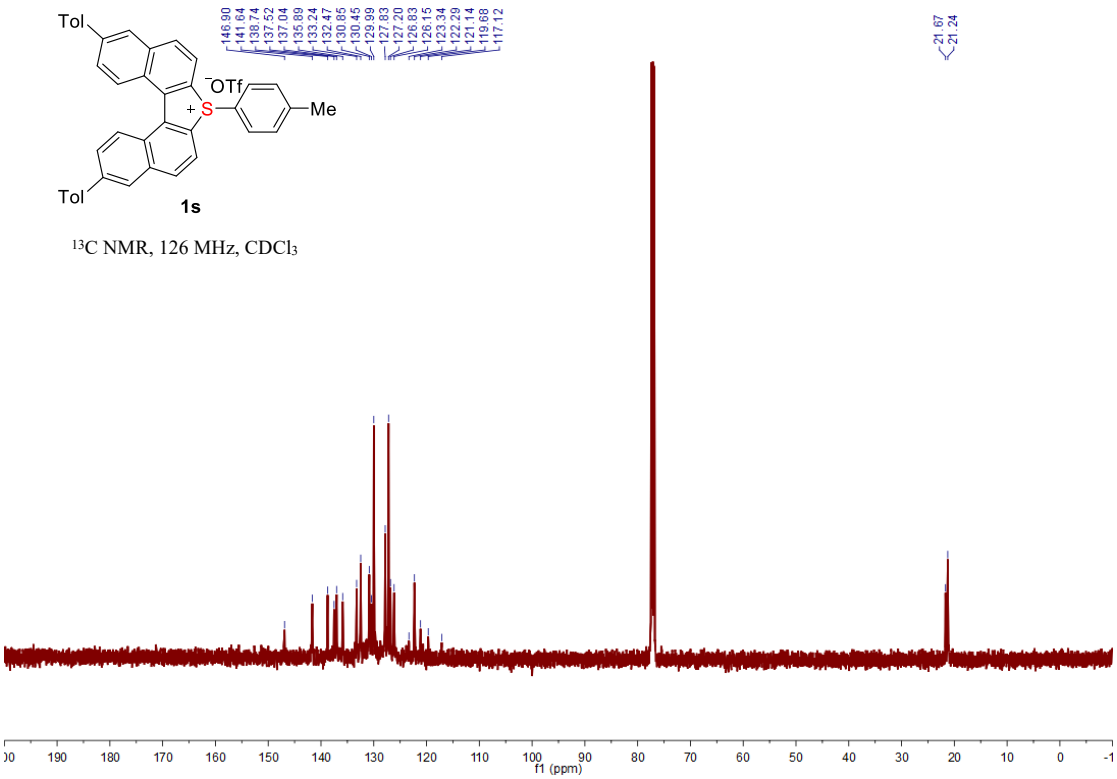
^{19}F NMR, 471 MHz, $CDCl_3$

Figure S57. ^{19}F NMR spectrum of 1r (471 MHz, $CDCl_3$)



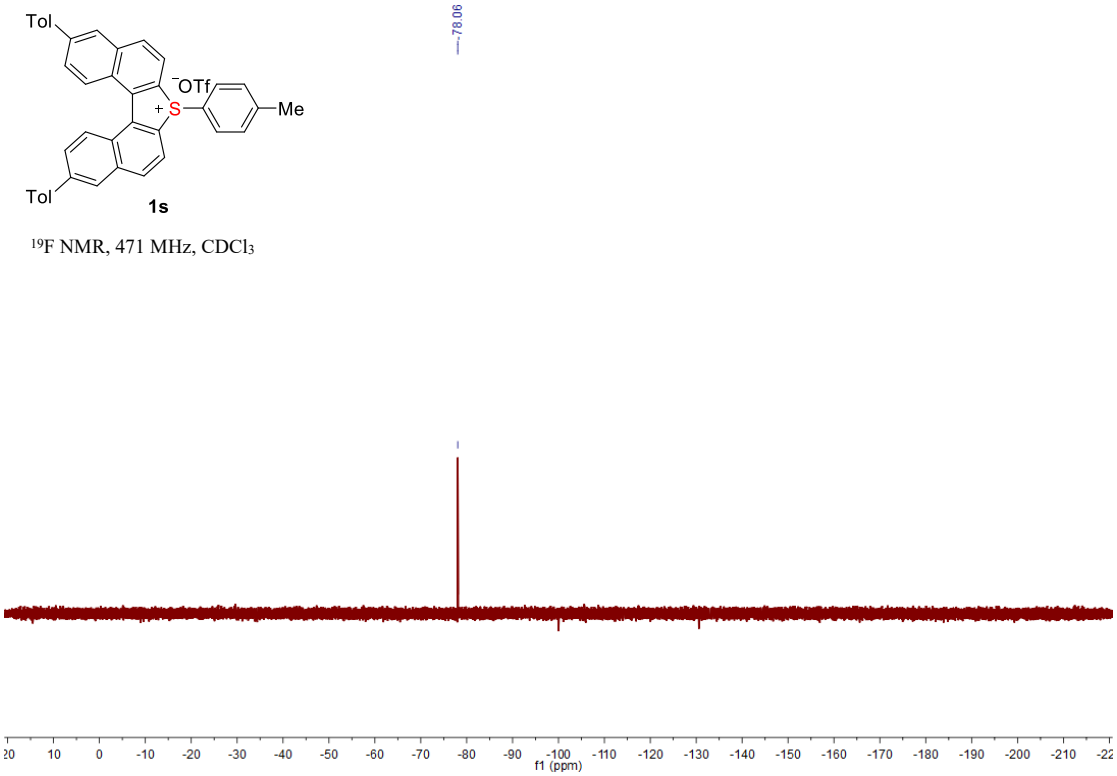
^{1}H NMR, 400 MHz, $CDCl_3$

Figure S58. ^{1}H NMR spectrum of 1s (400 MHz, $CDCl_3$)



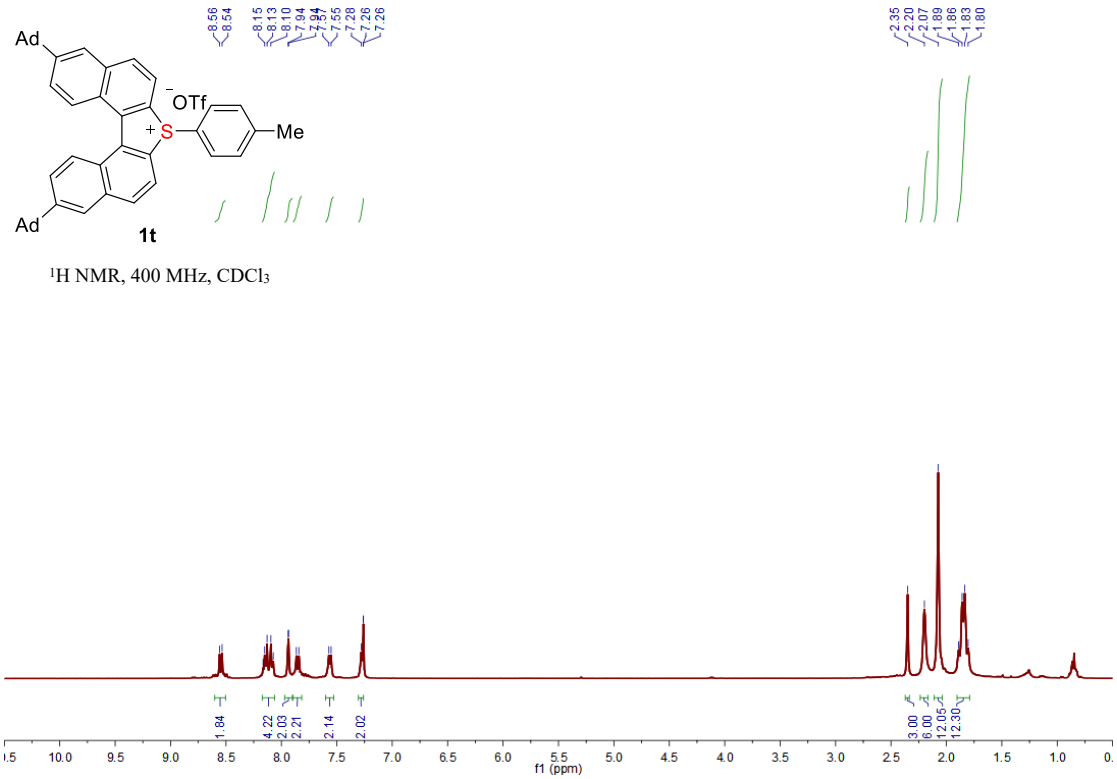
^{13}C NMR, 126 MHz, $CDCl_3$

Figure S59. ^{13}C NMR spectrum of 1s (126 MHz, $CDCl_3$)



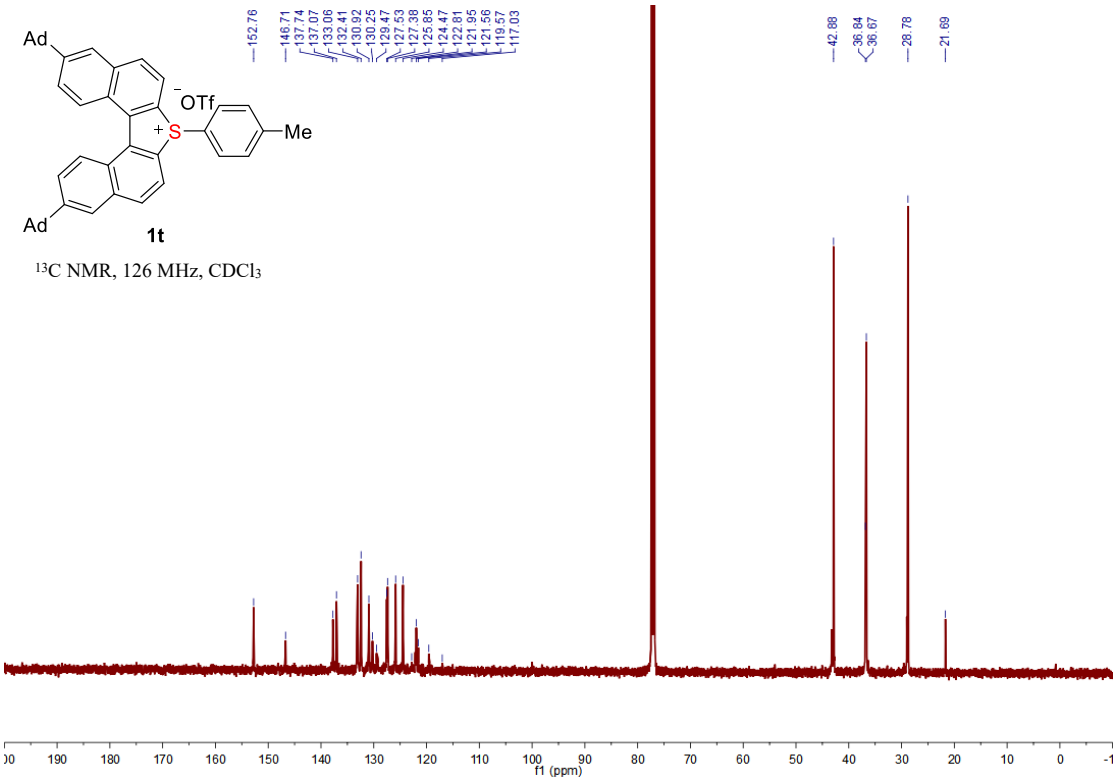
^{19}F NMR, 471 MHz, $CDCl_3$

Figure S60. ^{19}F NMR spectrum of 1s (471 MHz, $CDCl_3$)



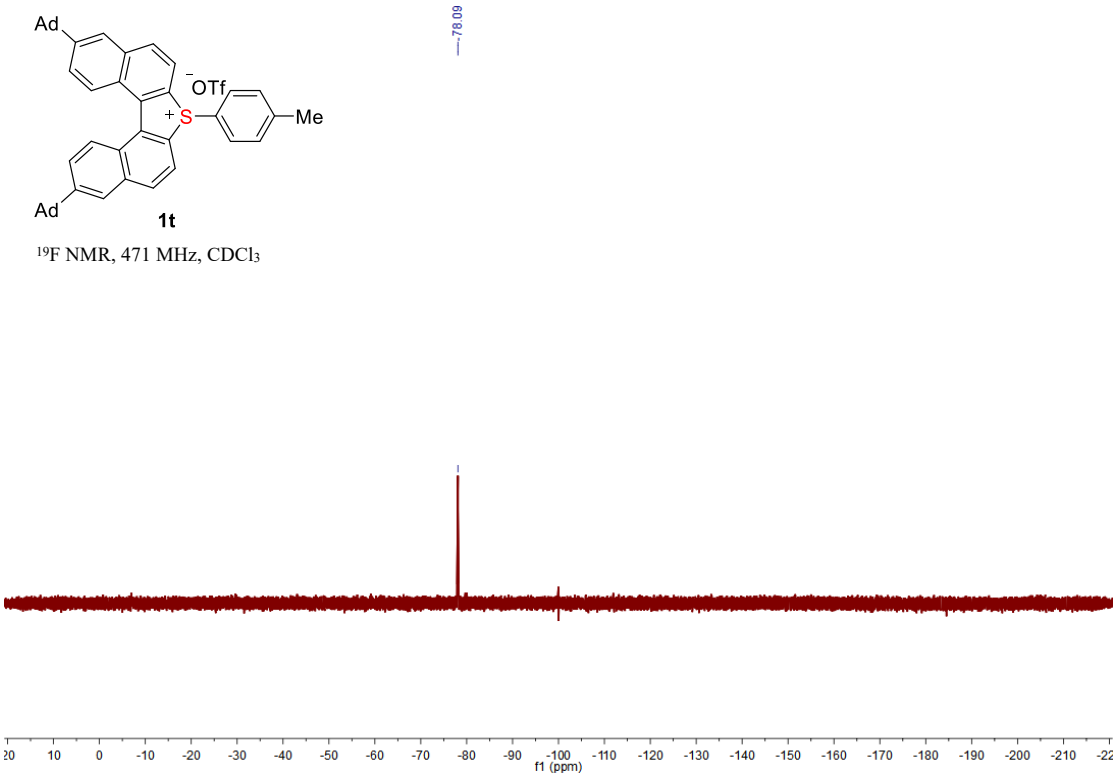
^{1}H NMR, 400 MHz, $CDCl_3$

Figure S61. ^{1}H NMR spectrum of 1t (400 MHz, $CDCl_3$)



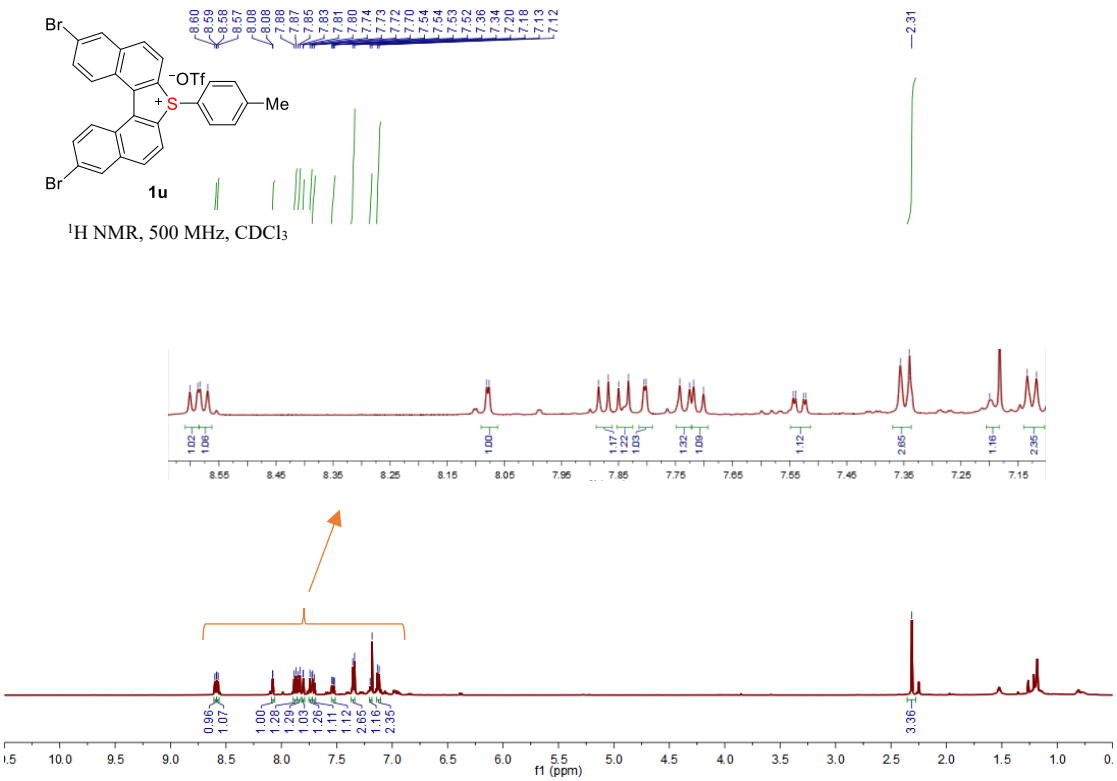
^{13}C NMR, 126 MHz, $CDCl_3$

Figure S62. ^{13}C NMR spectrum of 1t (126 MHz, $CDCl_3$)



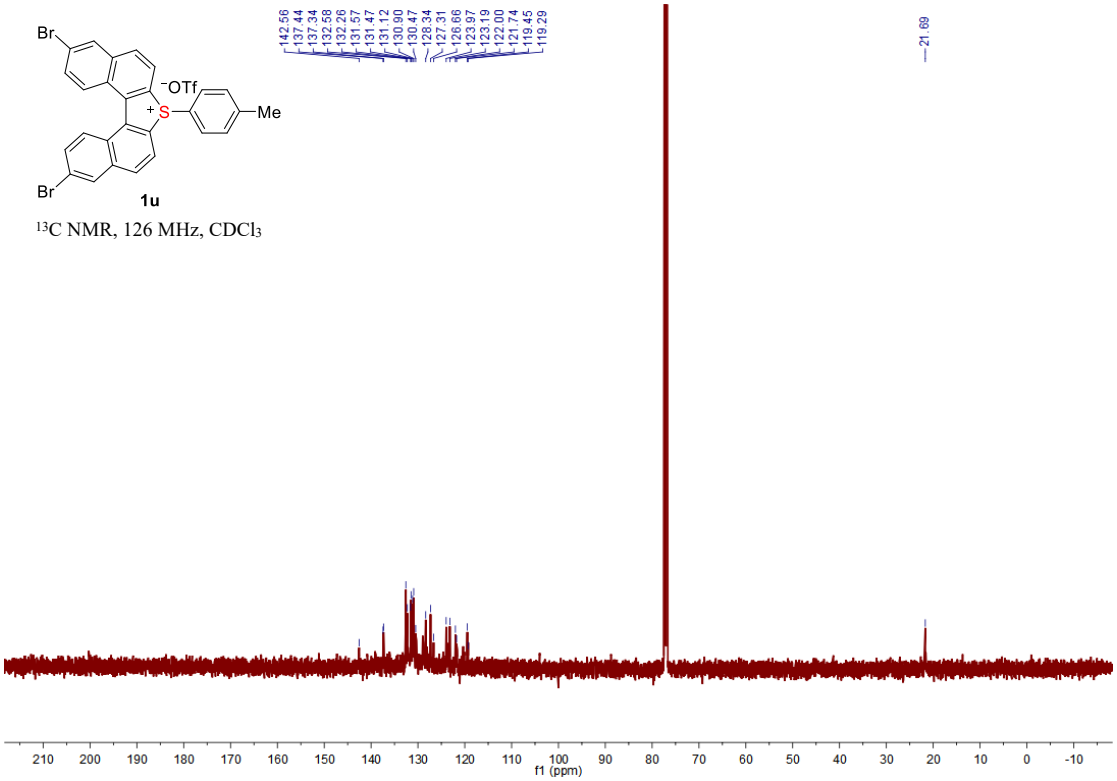
^{19}F NMR, 471 MHz, $CDCl_3$

Figure S63. ^{19}F NMR spectrum of 1t (471 MHz, $CDCl_3$)



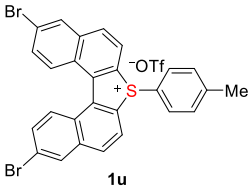
^{1}H NMR, 500 MHz, $CDCl_3$

Figure S64. ^{1}H NMR spectrum of 1u (500 MHz, $CDCl_3$)



^{13}C NMR, 126 MHz, $CDCl_3$

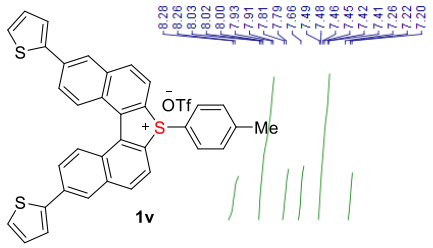
Figure S65. ^{13}C NMR spectrum of 1u (126 MHz, $CDCl_3$)



1u

^{19}F NMR, 471 MHz, $CDCl_3$

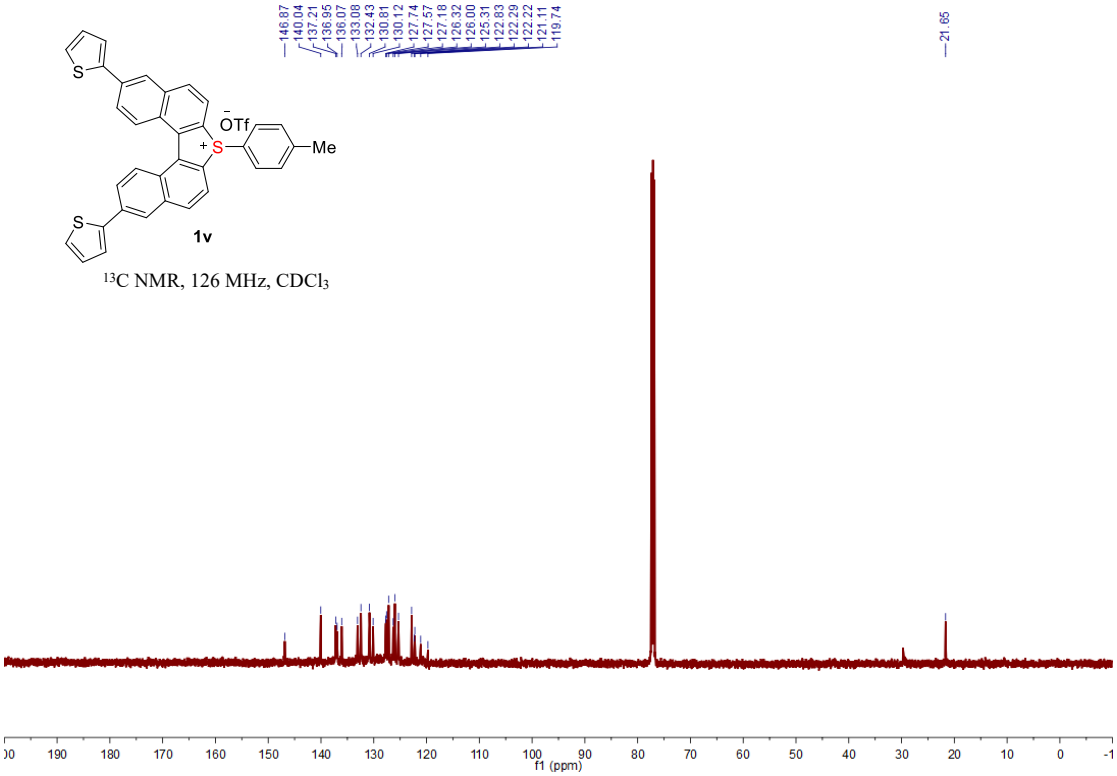
Figure S66. ^{19}F NMR spectrum of 1u (471 MHz, $CDCl_3$)



1v

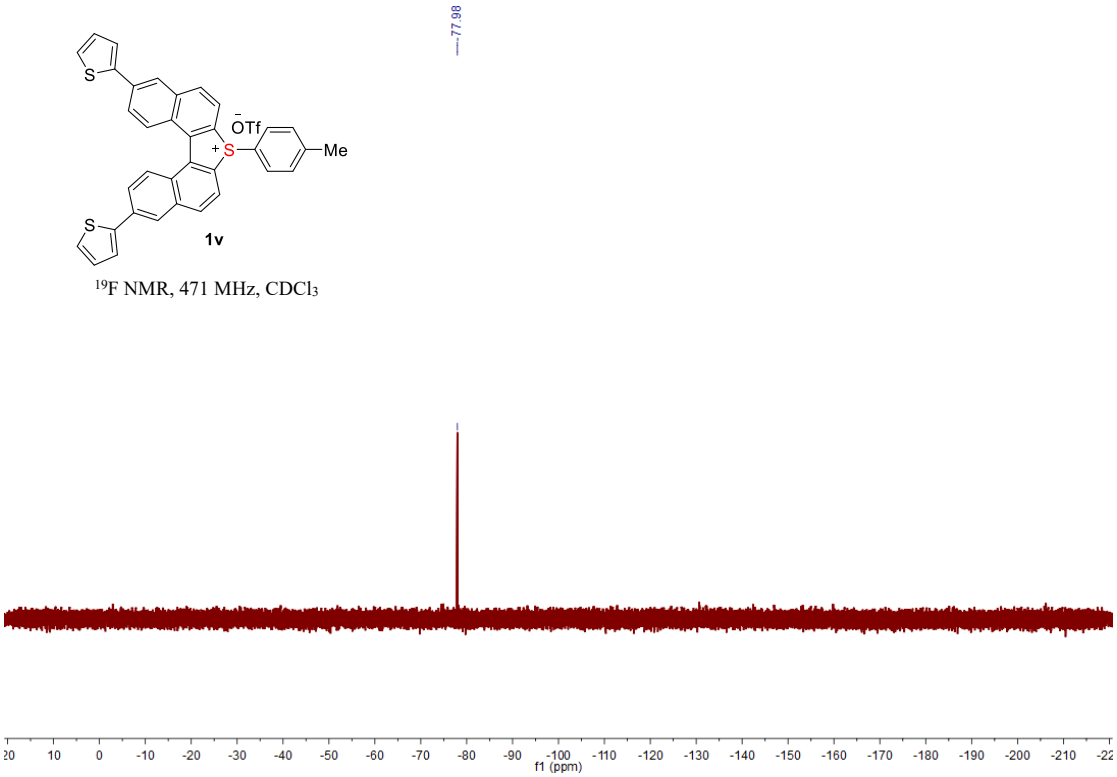
^{1}H NMR, 500 MHz, $CDCl_3$

Figure S67. ^{1}H NMR spectrum of 1v (500 MHz, $CDCl_3$)



^{13}C NMR, 126 MHz, $CDCl_3$

Figure S68. ^{13}C NMR spectrum of 1v (126 MHz, $CDCl_3$)



^{19}F NMR, 471 MHz, $CDCl_3$

Figure S69. ^{19}F NMR spectrum of 1v (471 MHz, $CDCl_3$)

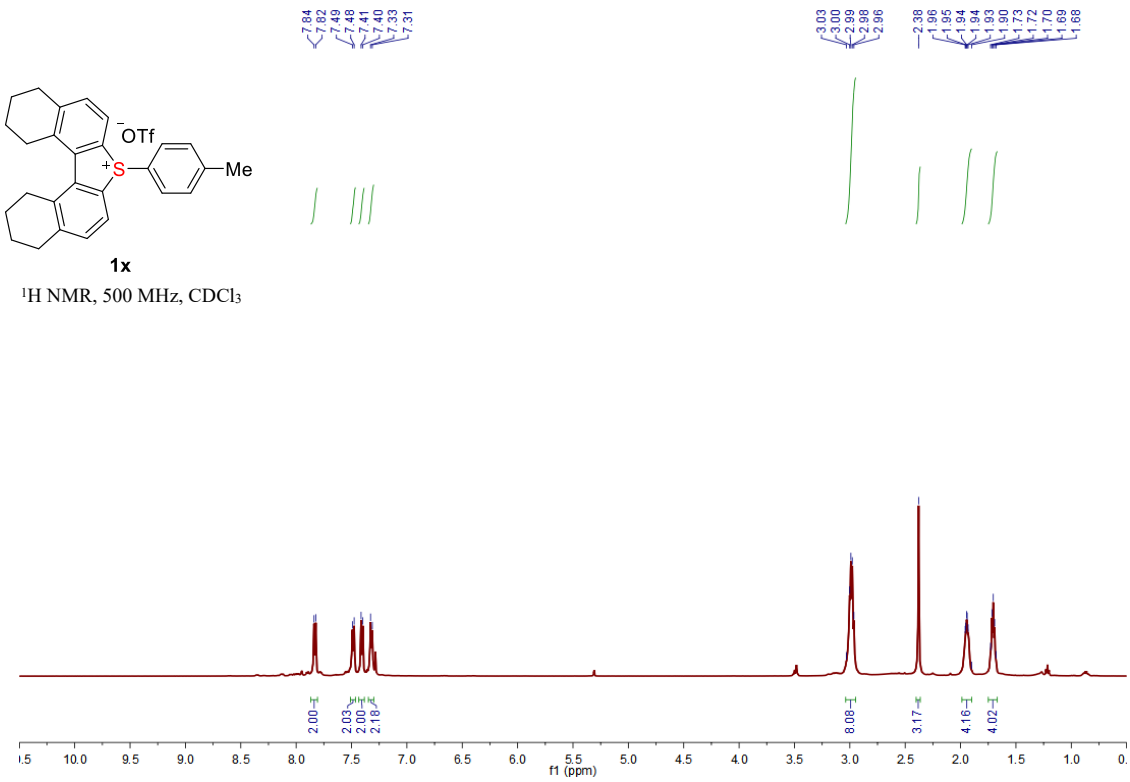


Figure S70. ^{1}H NMR spectrum of 1x (500 MHz, $CDCl_3$

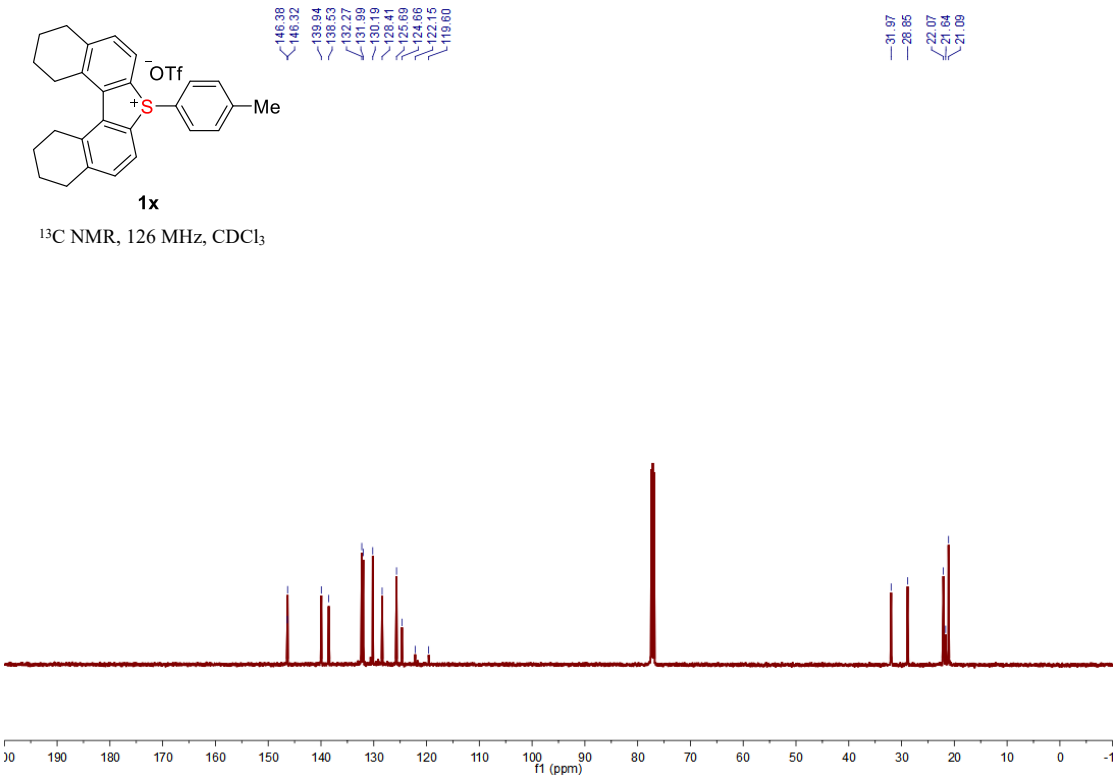
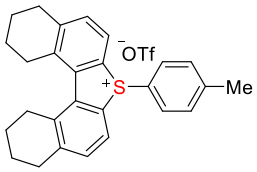


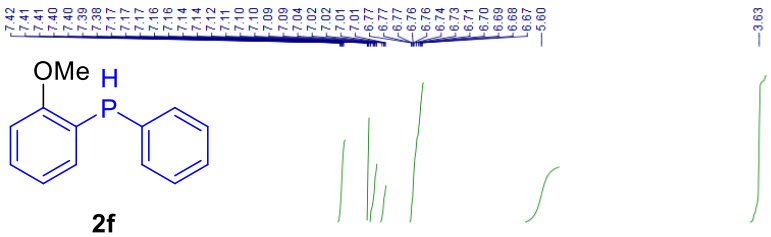
Figure S71. ^{13}C NMR spectrum of 1x (126 MHz, $CDCl_3$)



1x

^{19}F NMR, 471 MHz, $CDCl_3$

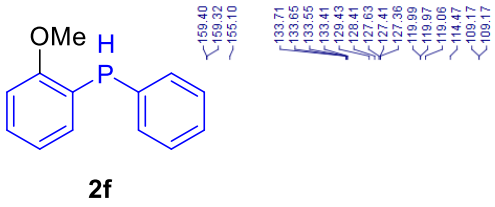
Figure S72. ^{19}F NMR spectrum of 1x (471 MHz, $CDCl_3$)



2f

^{1}H NMR, 500 MHz, $CDCl_3$

Figure S73. ^{1}H NMR spectrum of 2f (500 MHz, $CDCl_3$)



2f

^{13}C NMR, 126 MHz, $CDCl_3$

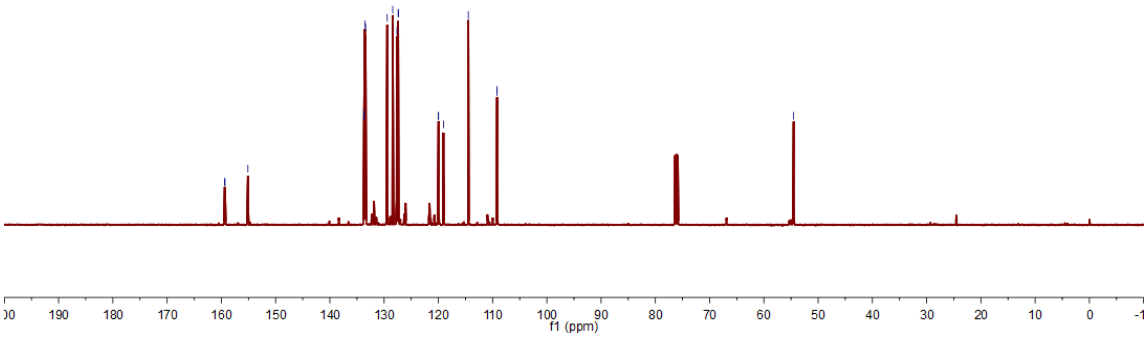
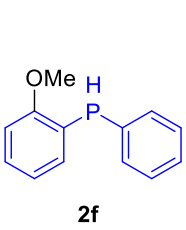


Figure S74. ^{13}C NMR spectrum of 2f (126 MHz, $CDCl_3$)



2f

^{31}P NMR, 220 MHz, $CDCl_3$

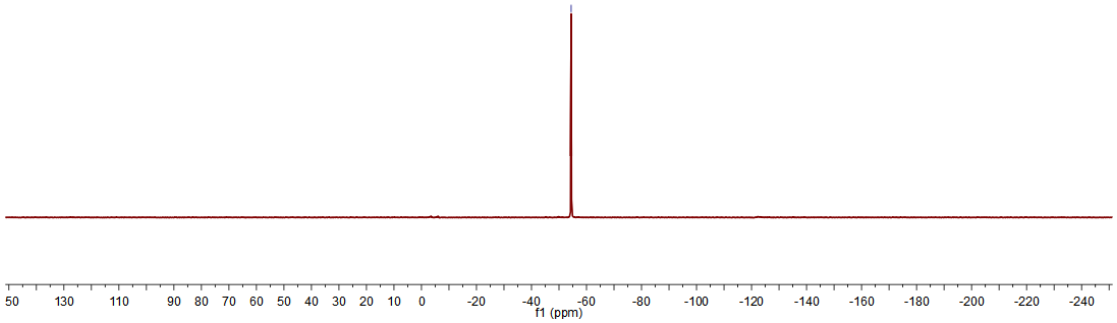
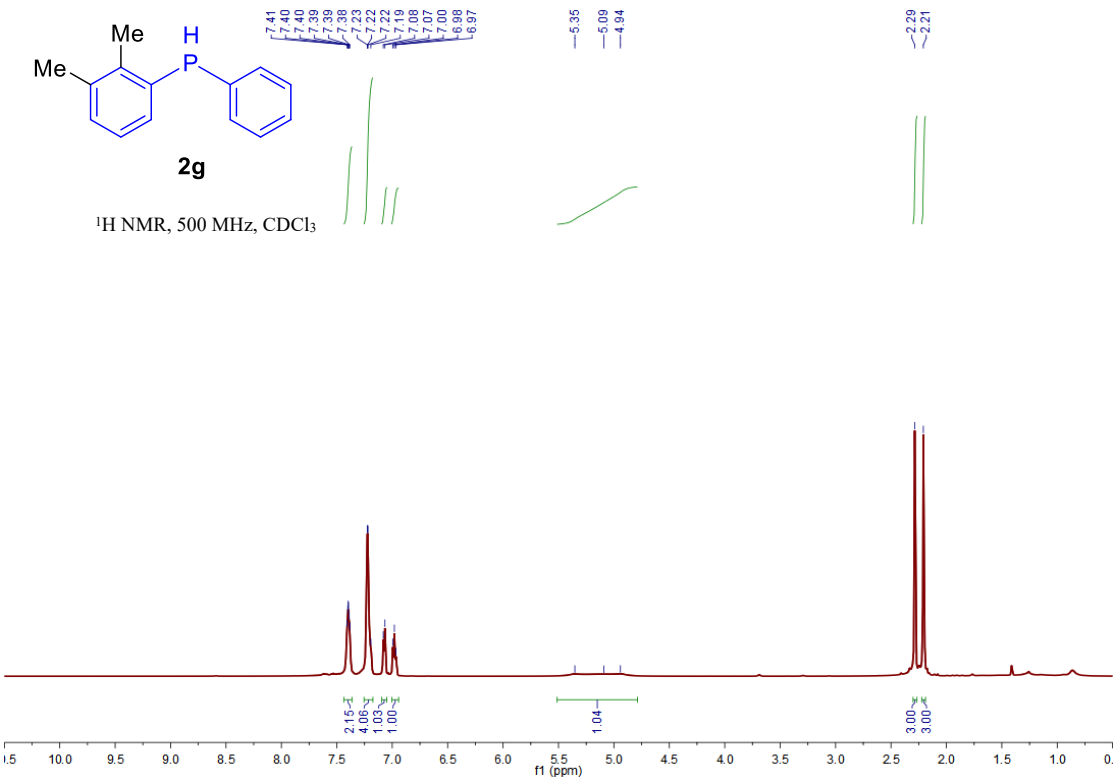
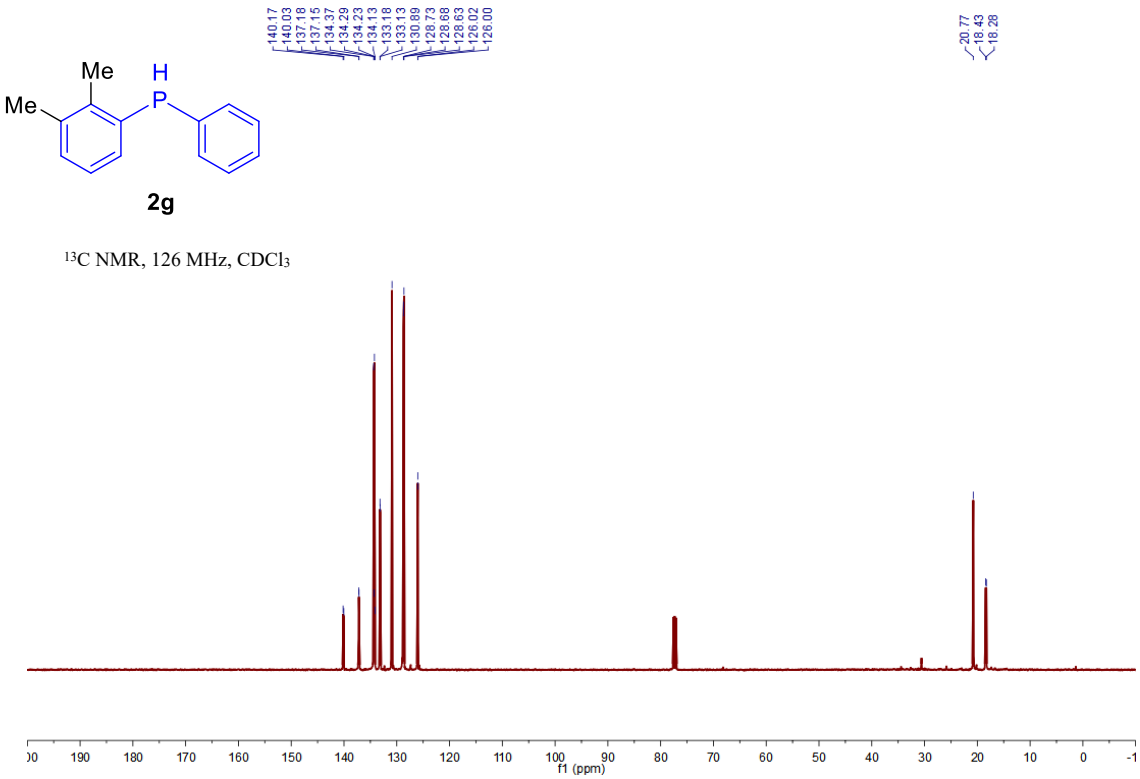


Figure S75. ^{31}P NMR spectrum of 2f (220 MHz, $CDCl_3$)



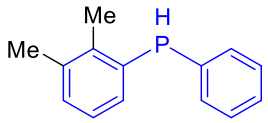
^{1}H NMR, 500 MHz, $CDCl_3$

Figure S76. ^{1}H NMR spectrum of 2g (500 MHz, $CDCl_3$)



^{13}C NMR, 126 MHz, $CDCl_3$

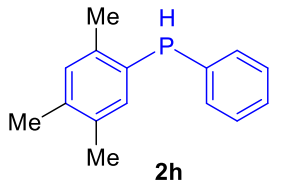
Figure S77. ^{13}C NMR spectrum of 2g (126 MHz, $CDCl_3$)



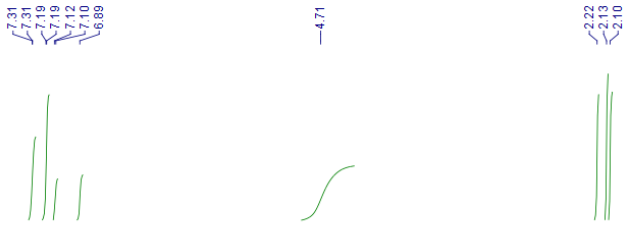
2g

^{31}P NMR, 220 MHz, $CDCl_3$

Figure S78. ^{31}P NMR spectrum of 2g (202 MHz, $CDCl_3$)



2h



^{1}H NMR, 500 MHz, $CDCl_3$

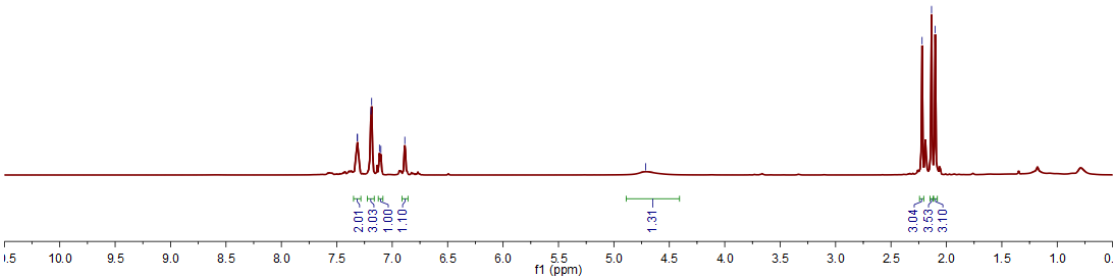
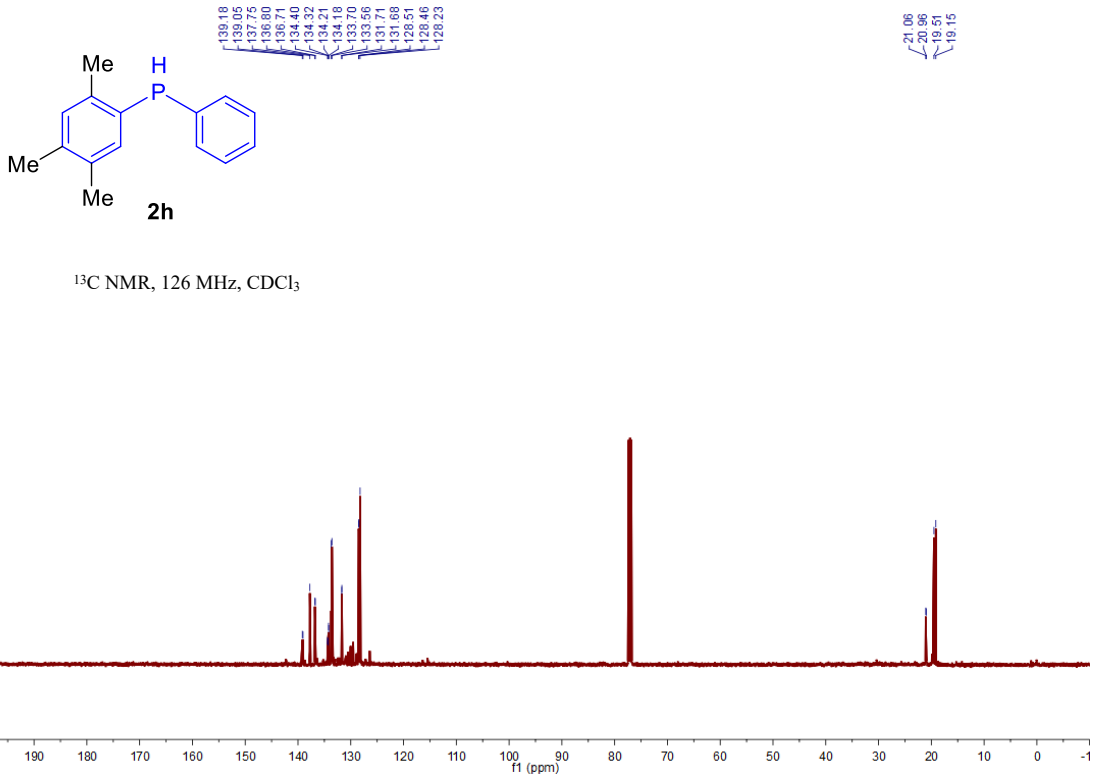
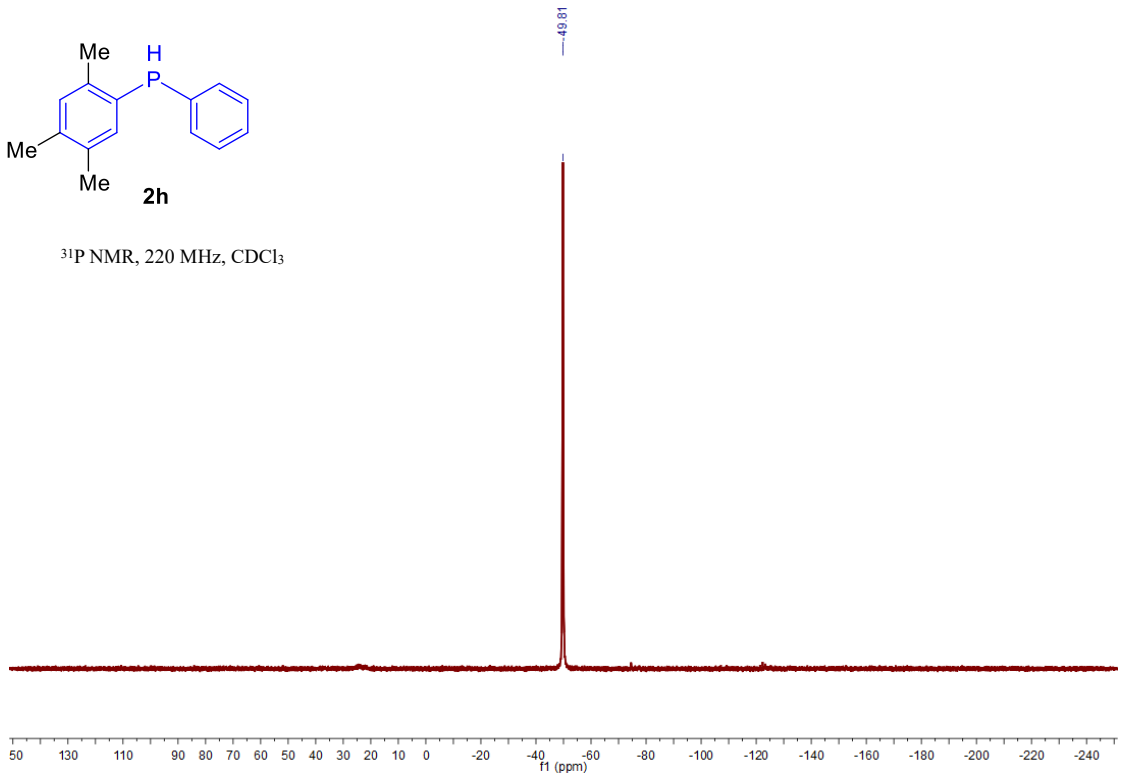


Figure S79. ^{1}H NMR spectrum of 2h (500 MHz, $CDCl_3$)



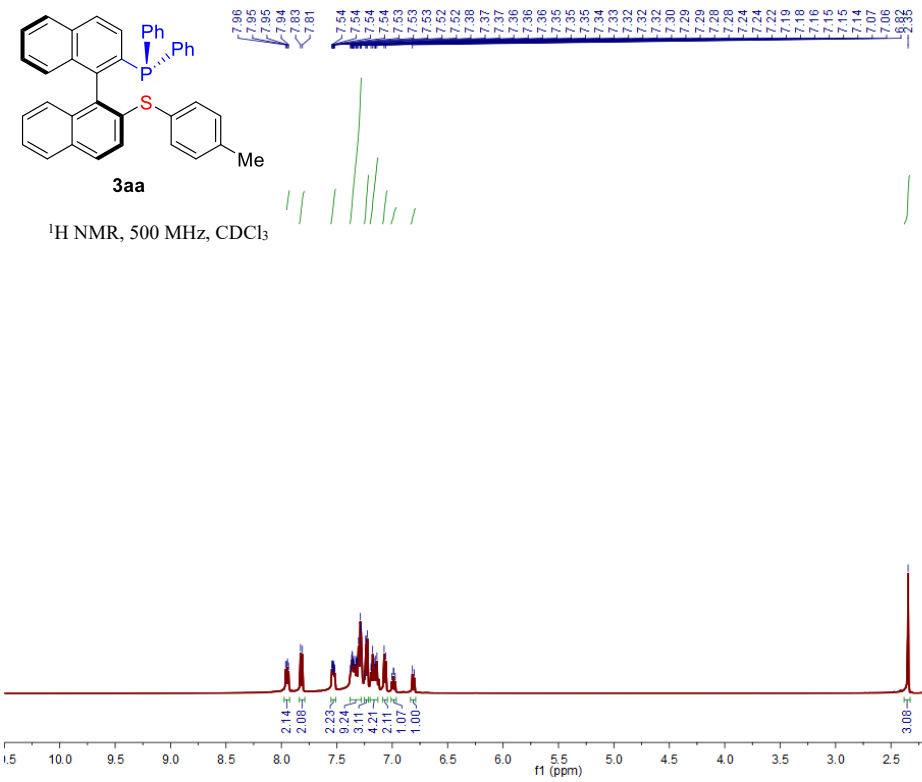
^{13}C NMR, 126 MHz, $CDCl_3$

Figure S80. ^{13}C NMR spectrum of 2h (126 MHz, $CDCl_3$)



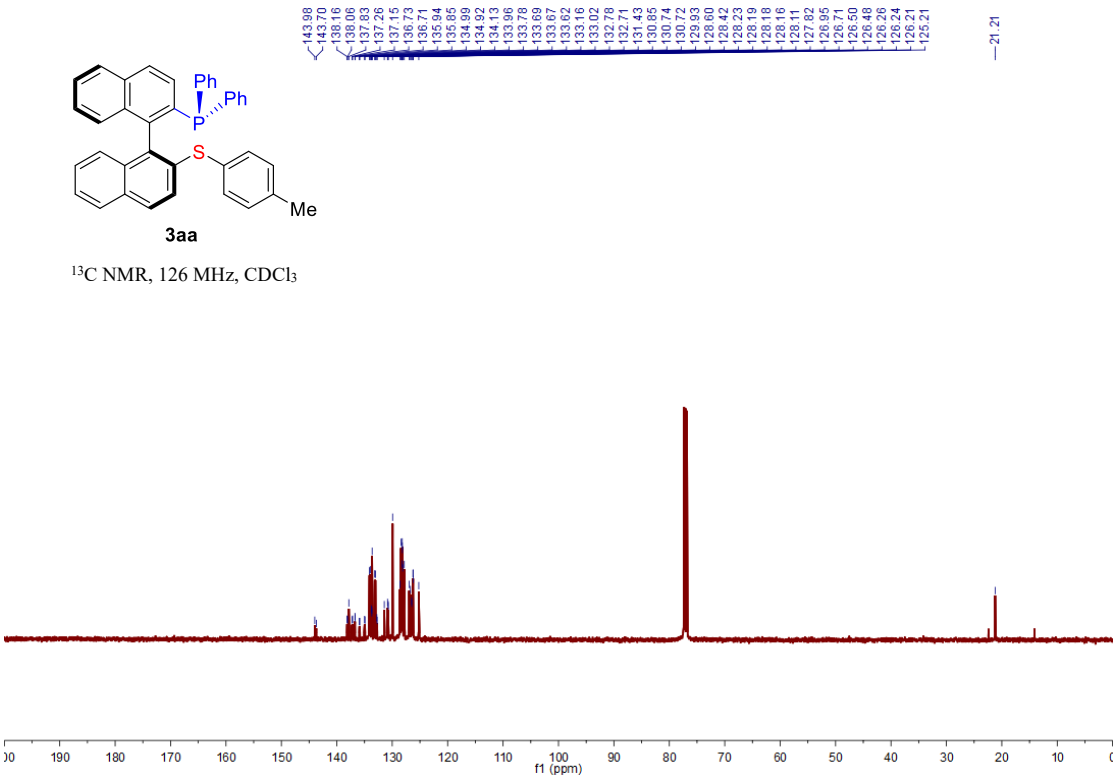
^{31}P NMR, 220 MHz, $CDCl_3$

Figure S81. ^{31}P NMR spectrum of 2h (202 MHz, $CDCl_3$)



^{1}H NMR, 500 MHz, $CDCl_3$

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



^{13}C NMR, 126 MHz, $CDCl_3$

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

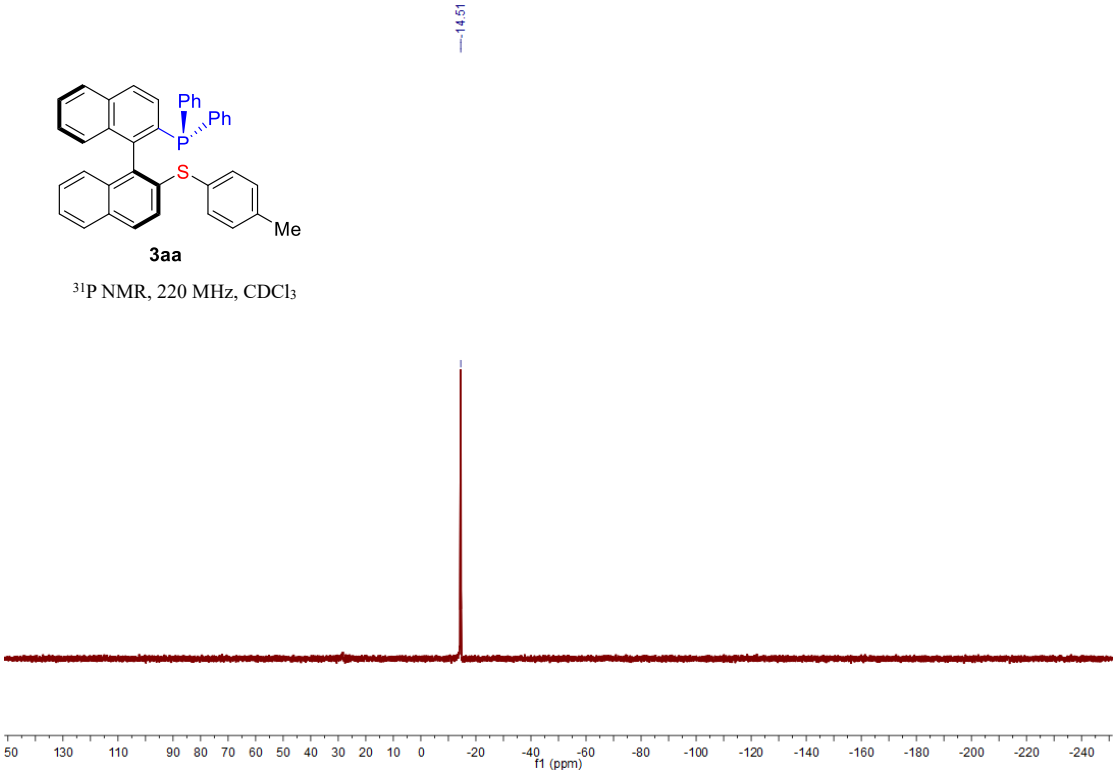


Figure S84. ^{31}P NMR spectrum of 3aa (202 MHz, $CDCl_3$)

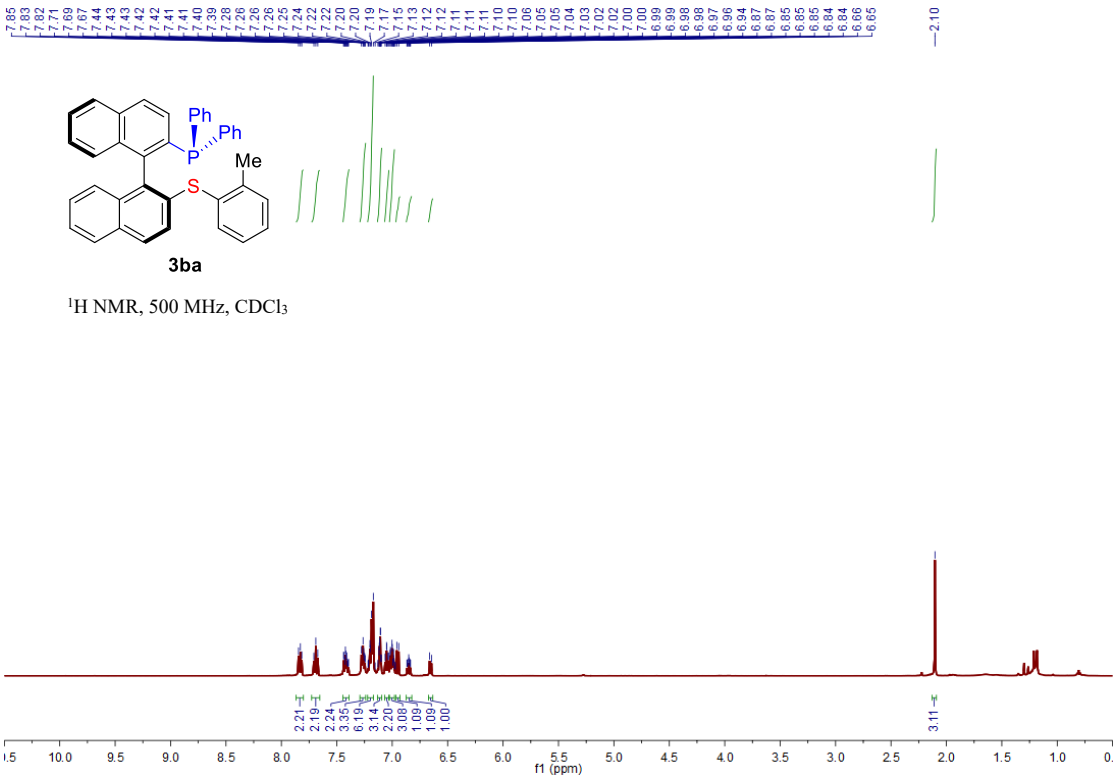


Figure S85. ^{1}H NMR spectrum of 3ba (500 MHz, $CDCl_3$)

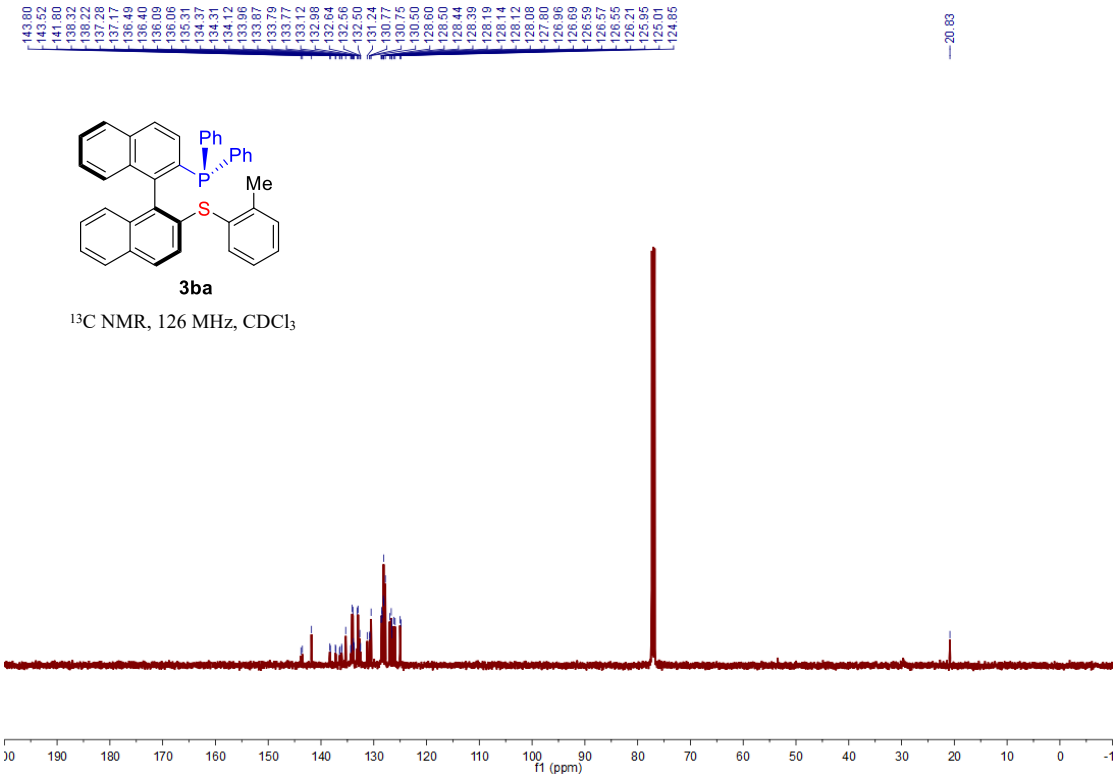


Figure S86. ^{13}C NMR spectrum of 3ba (126 MHz, $CDCl_3$)

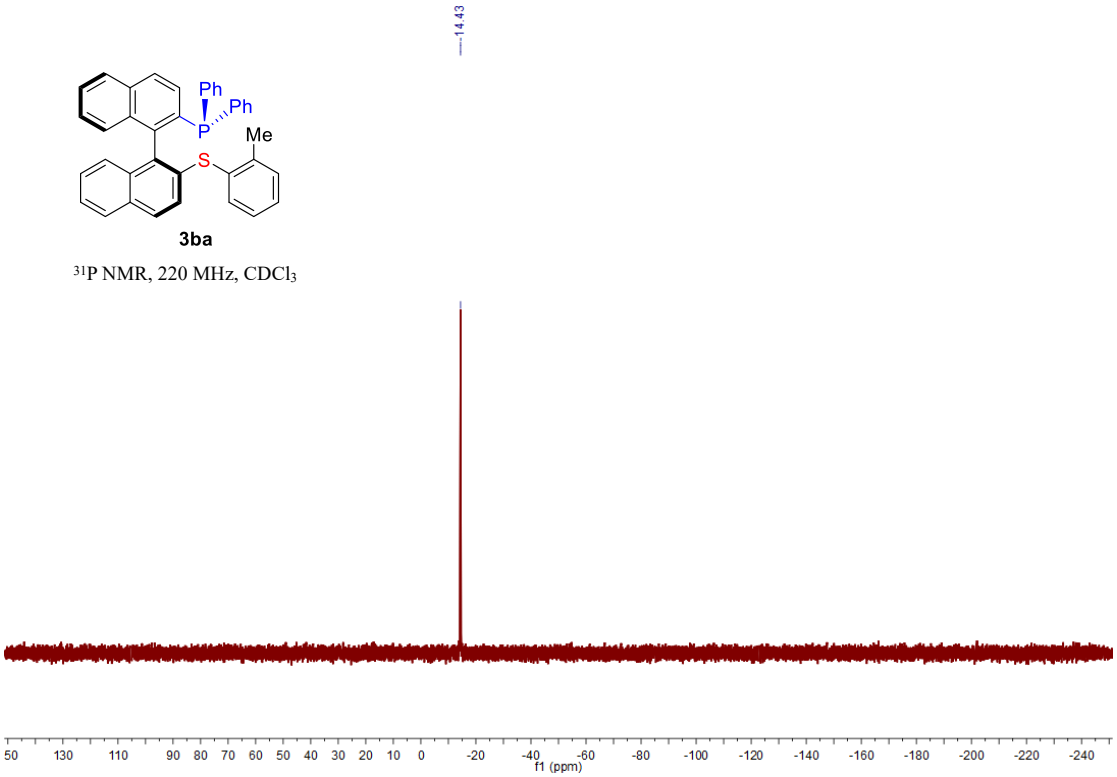


Figure S87. ^{31}P NMR spectrum of 3ba (202 MHz, $CDCl_3$)

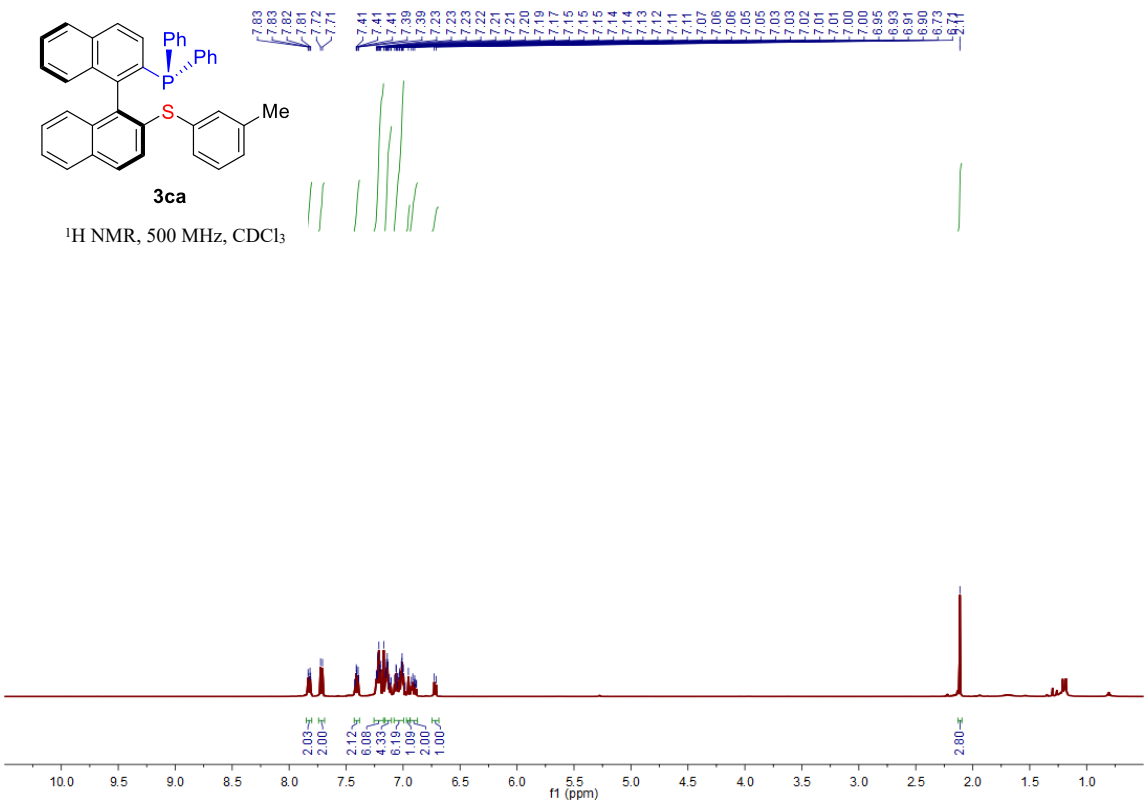


Figure S88. ^{1}H NMR spectrum of 3ca (500 MHz, $CDCl_3$)

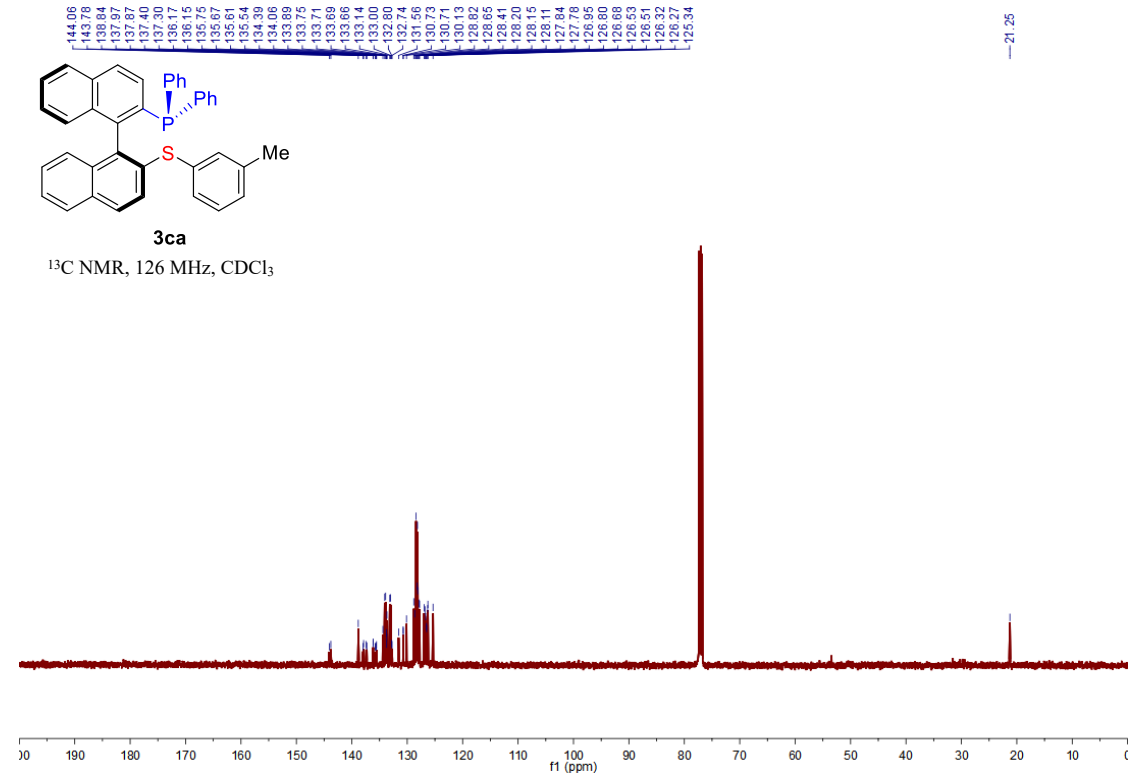
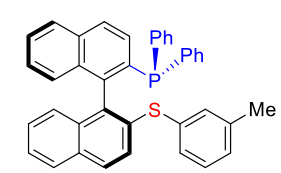


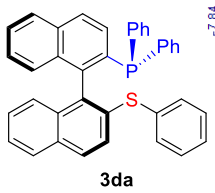
Figure S89. ^{13}C NMR spectrum of 3ca (126 MHz, $CDCl_3$)



3ca

^{31}P NMR, 220 MHz, $CDCl_3$

Figure S90. ^{31}P NMR spectrum of 3ca (202 MHz, $CDCl_3$)



3da

^{1}H NMR, 500 MHz, $CDCl_3$

Figure S91. ^{1}H NMR spectrum of 3da (500 MHz, $CDCl_3$)

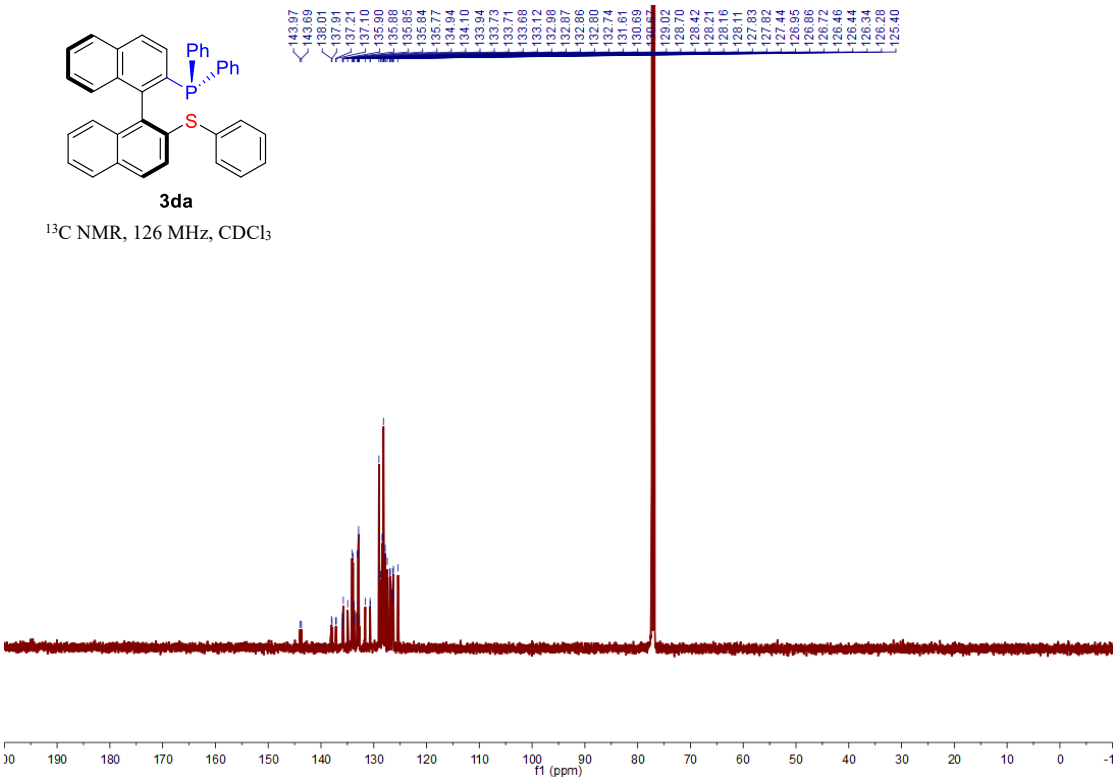


Figure S92. ^{13}C NMR spectrum of 3da (126 MHz, $CDCl_3$)

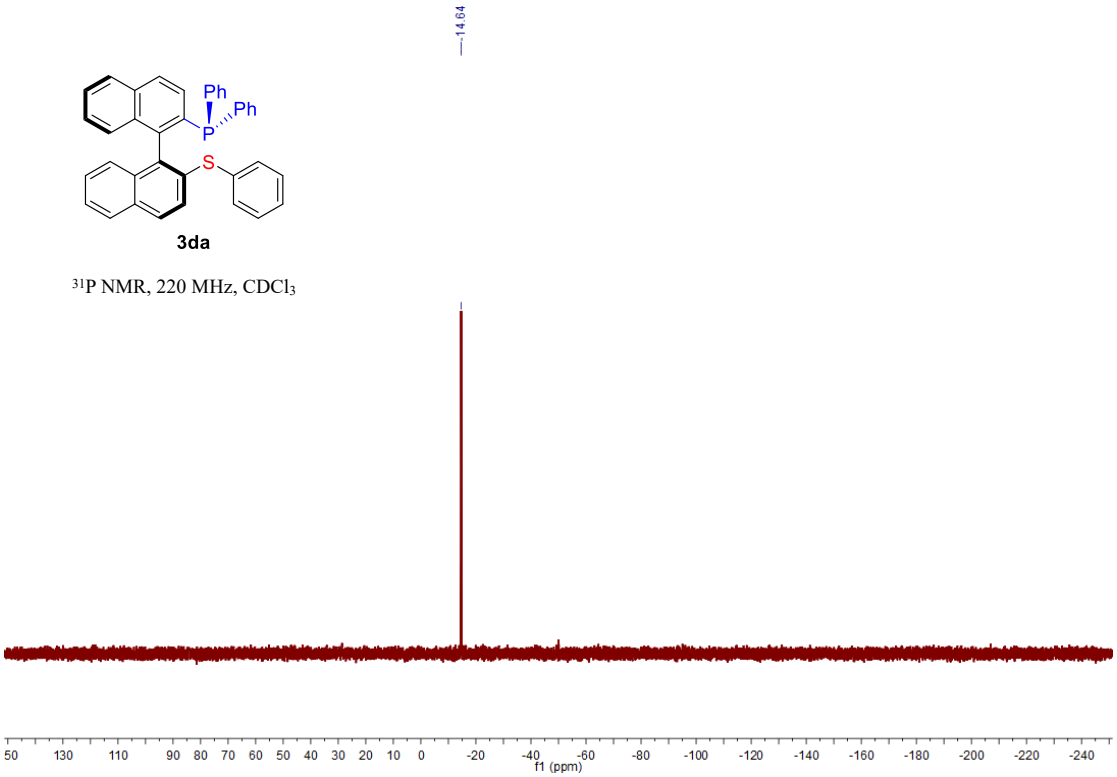


Figure S93. ^{31}P NMR spectrum of 3da (202 MHz, $CDCl_3$)

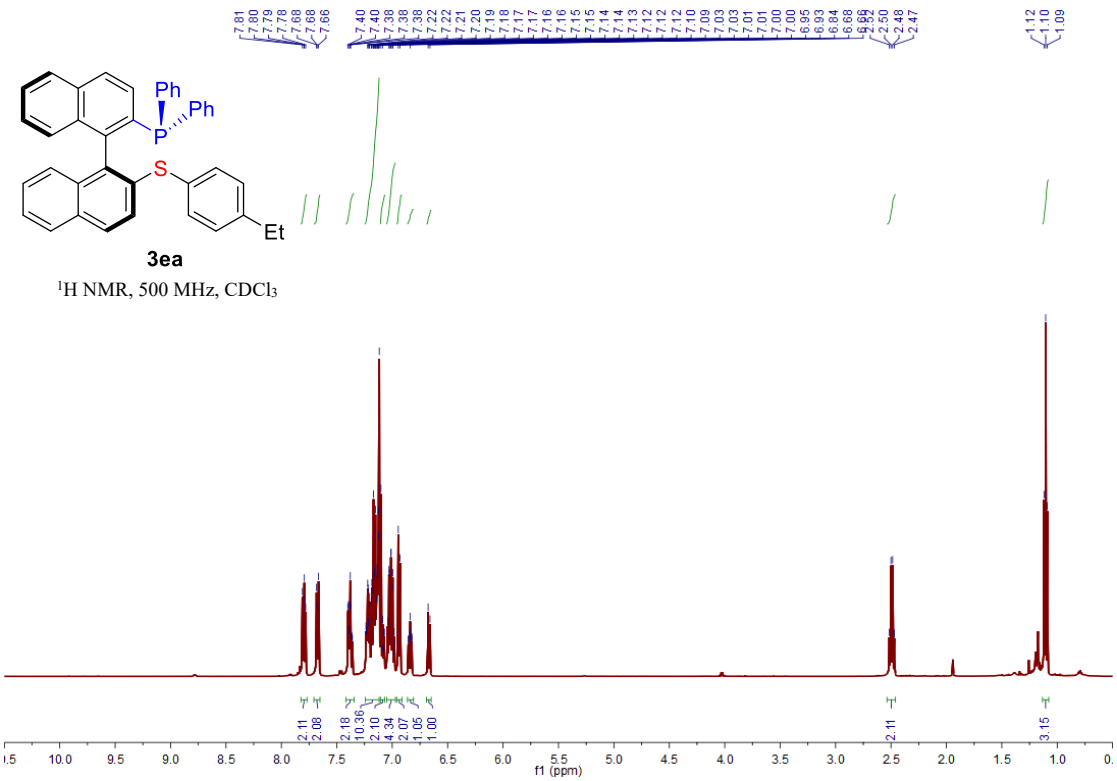


Figure S94. ^{1}H NMR spectrum of 3ea (500 MHz, $CDCl_3$)

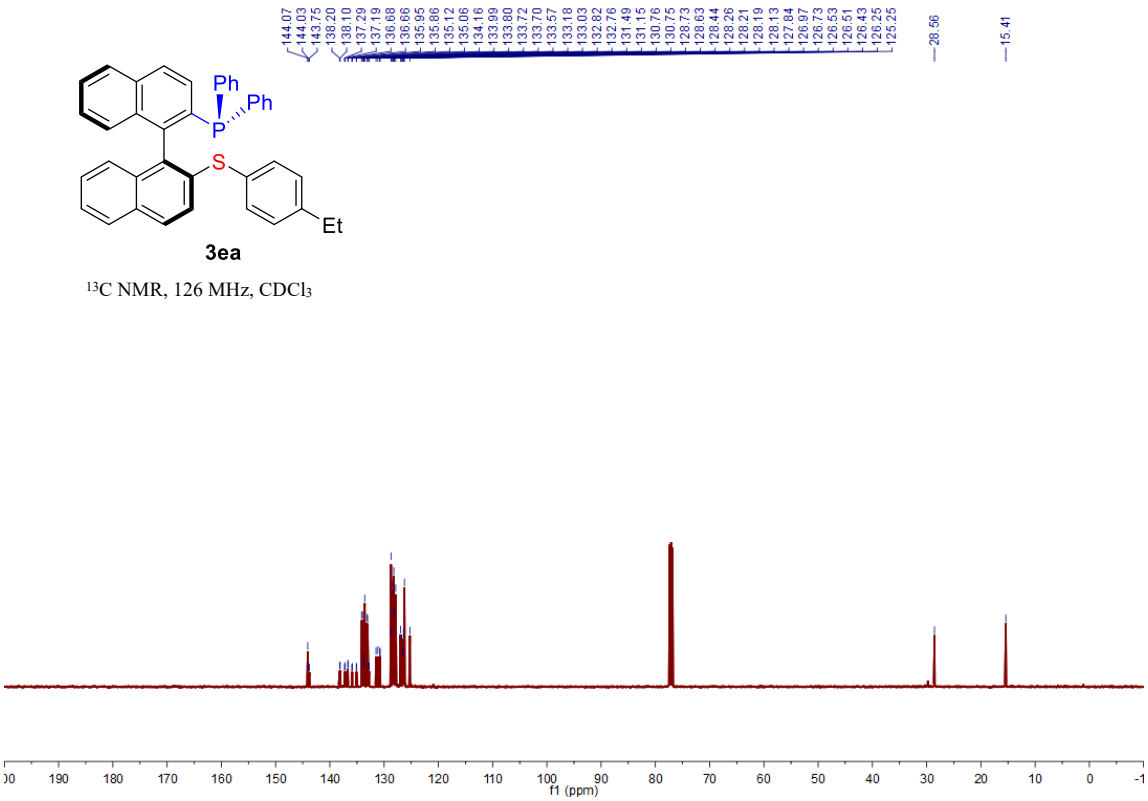
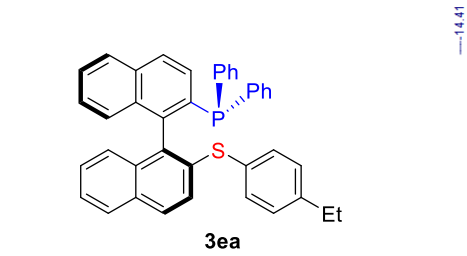


Figure S95. ^{13}C NMR spectrum of 3ea (126 MHz, $CDCl_3$)



^{31}P NMR, 220 MHz, $CDCl_3$

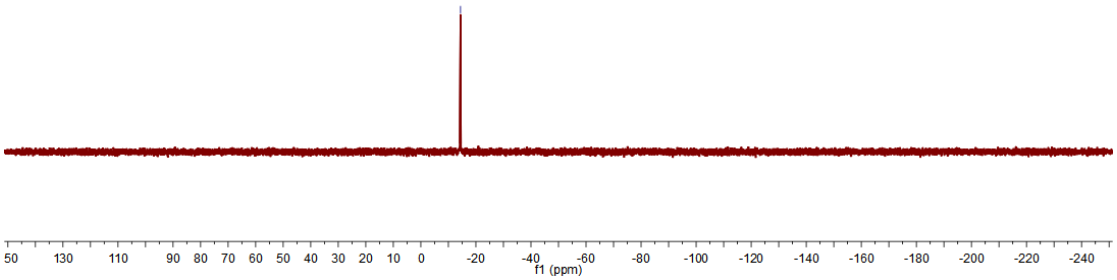
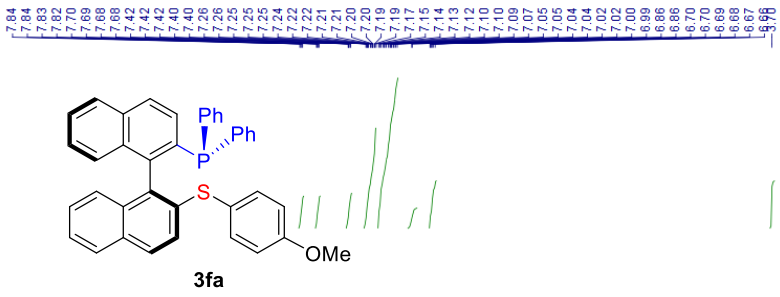


Figure S96. ^{31}P NMR spectrum of 3ea (202 MHz, $CDCl_3$)



^{1}H NMR, 500 MHz, $CDCl_3$

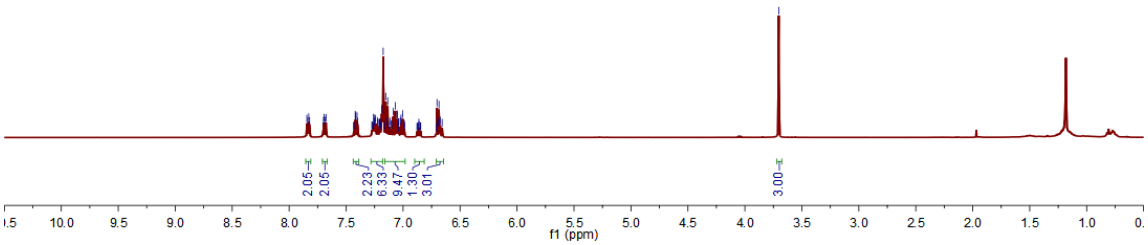
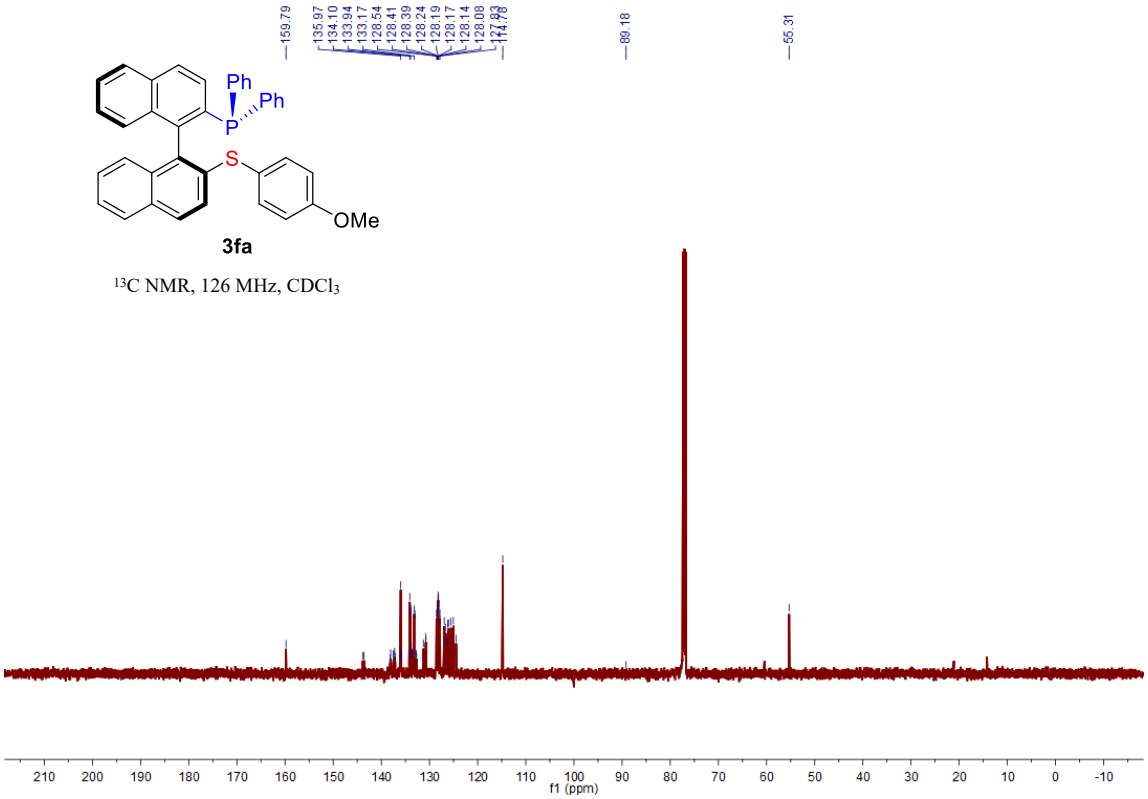
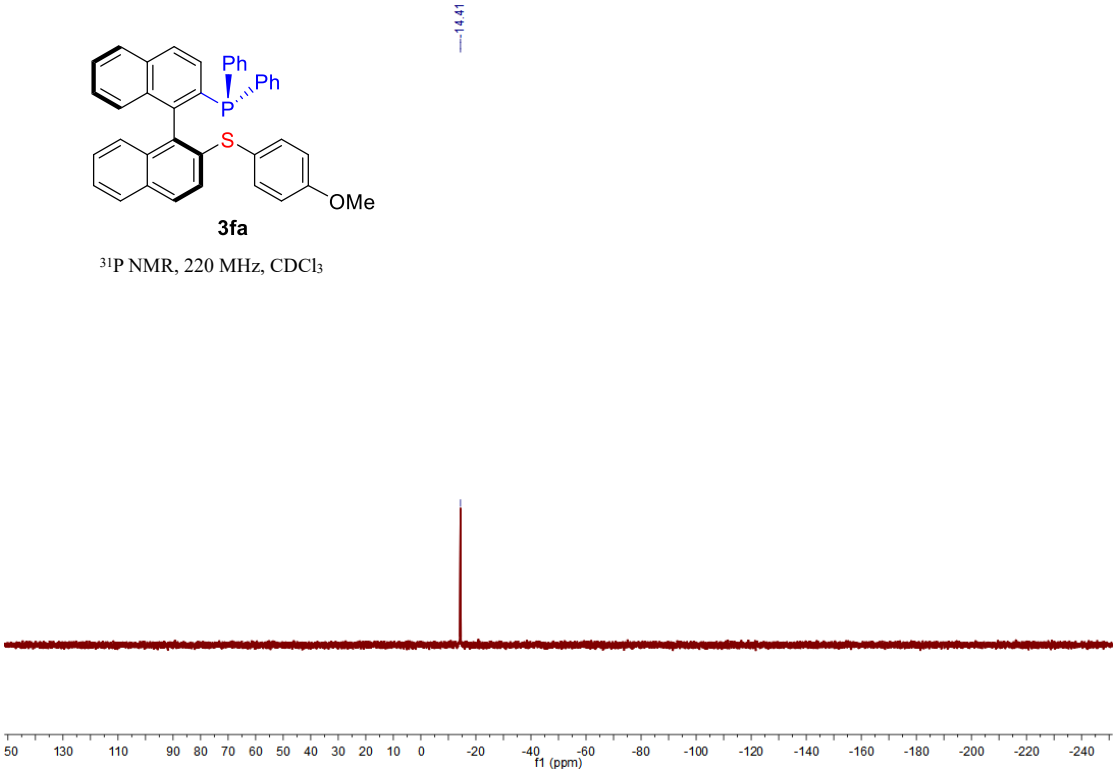


Figure S97. ^{1}H NMR spectrum of 3fa (500 MHz, $CDCl_3$)



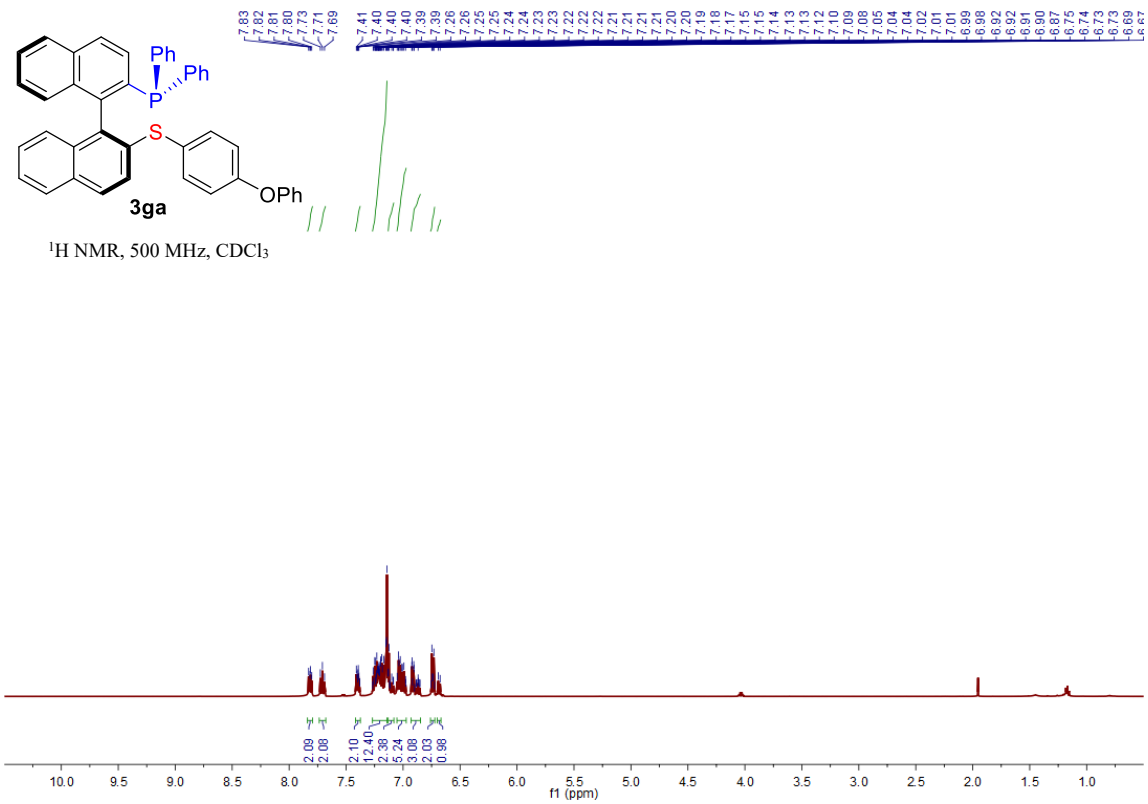
^{13}C NMR, 126 MHz, $CDCl_3$

Figure S98. ^{13}C NMR spectrum of 3fa (126 MHz, $CDCl_3$)



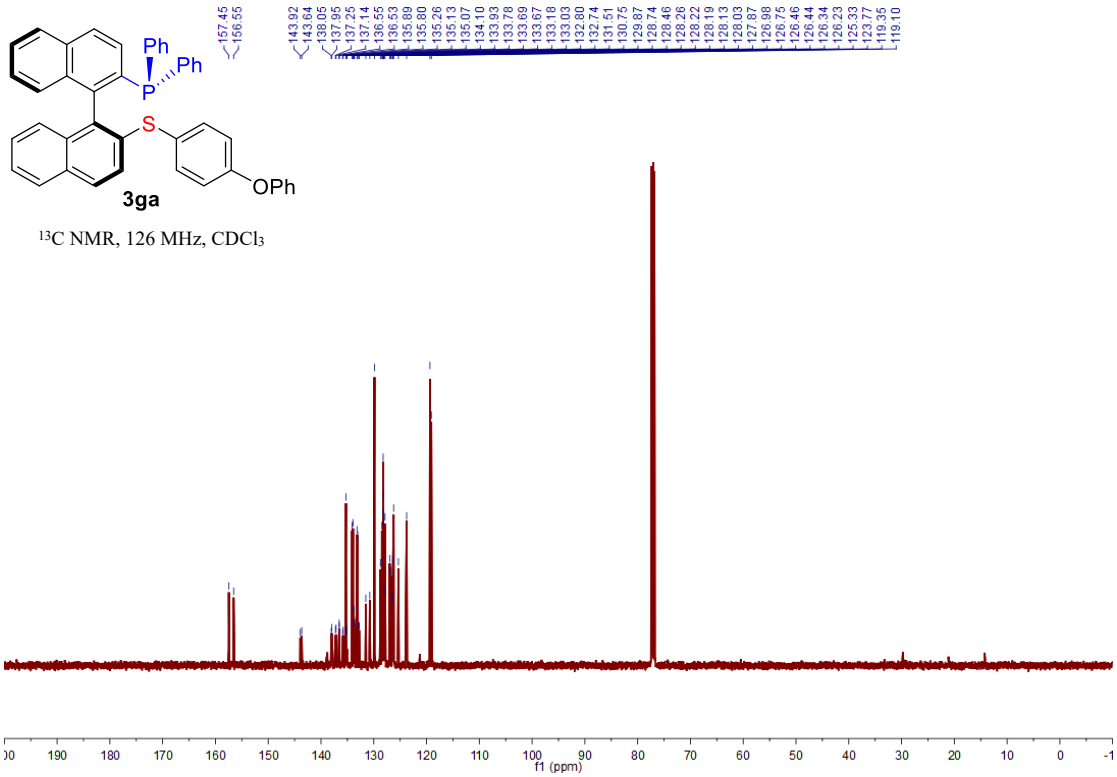
^{31}P NMR, 220 MHz, $CDCl_3$

Figure S99. ^{31}P NMR spectrum of 3fa (202 MHz, $CDCl_3$)



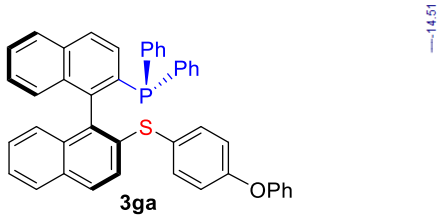
^{1}H NMR, 500 MHz, $CDCl_3$

Figure S100. ^{1}H NMR spectrum of 3ga (500 MHz, $CDCl_3$)



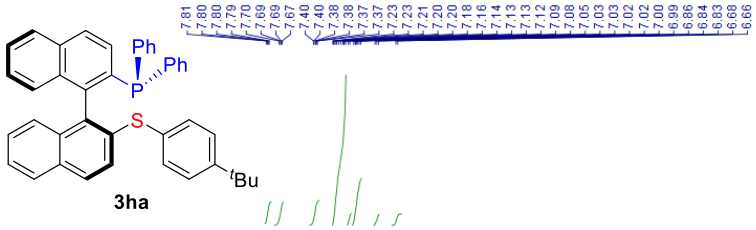
^{13}C NMR, 126 MHz, $CDCl_3$

Figure S101. ^{13}C NMR spectrum of 3ga (126 MHz, $CDCl_3$)



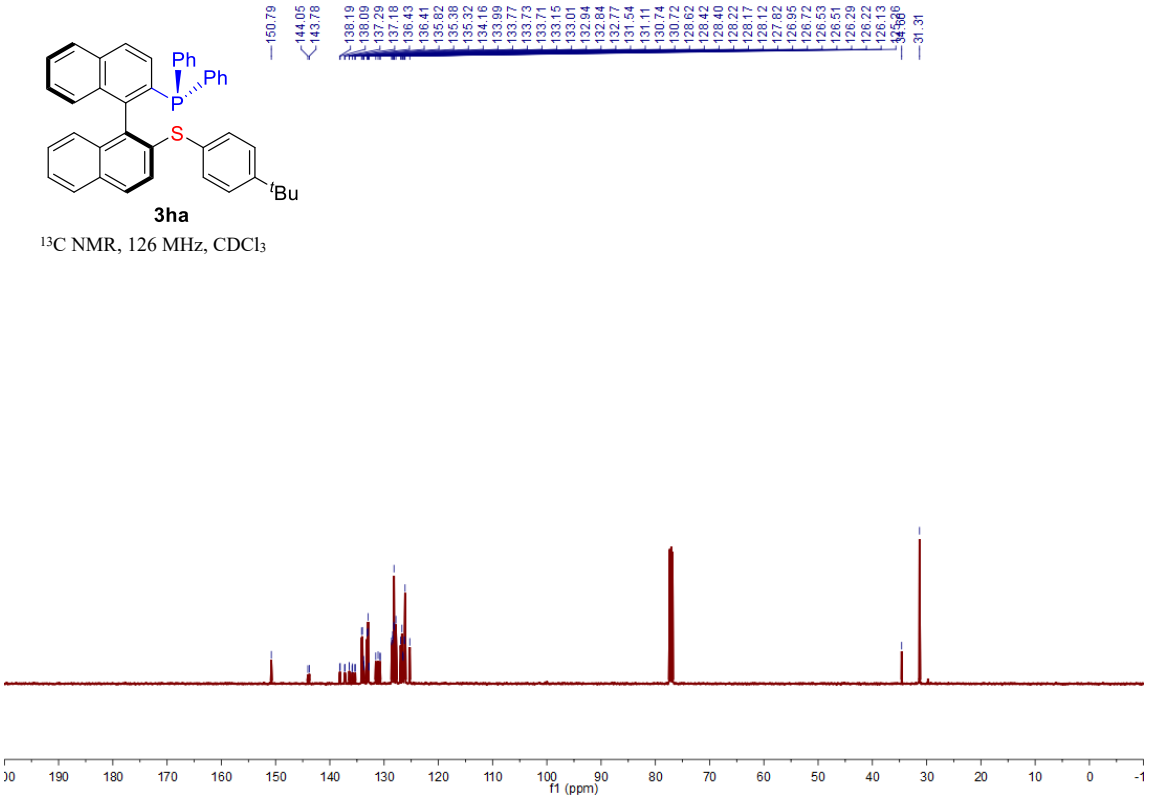
^{31}P NMR, 220 MHz, $CDCl_3$

Figure S102. ^{31}P NMR spectrum of 3ga (202 MHz, $CDCl_3$)



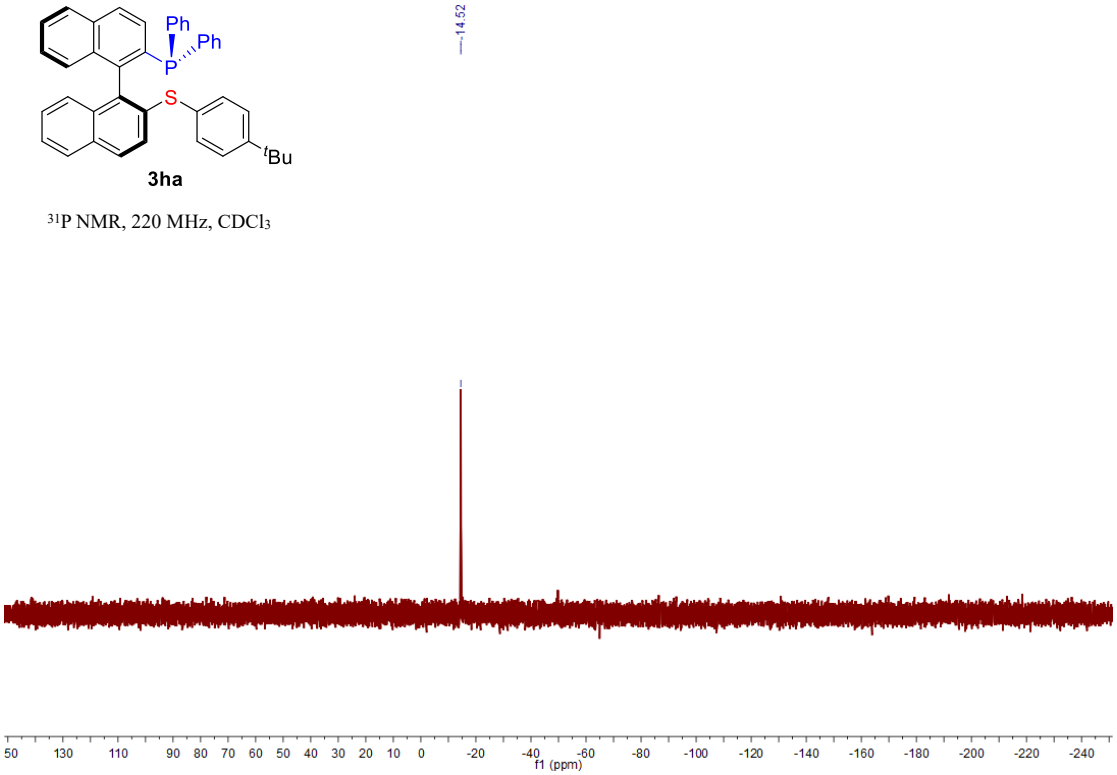
^{1}H NMR, 500 MHz, $CDCl_3$

Figure S103. ^{1}H NMR spectrum of 3ha (500 MHz, $CDCl_3$)



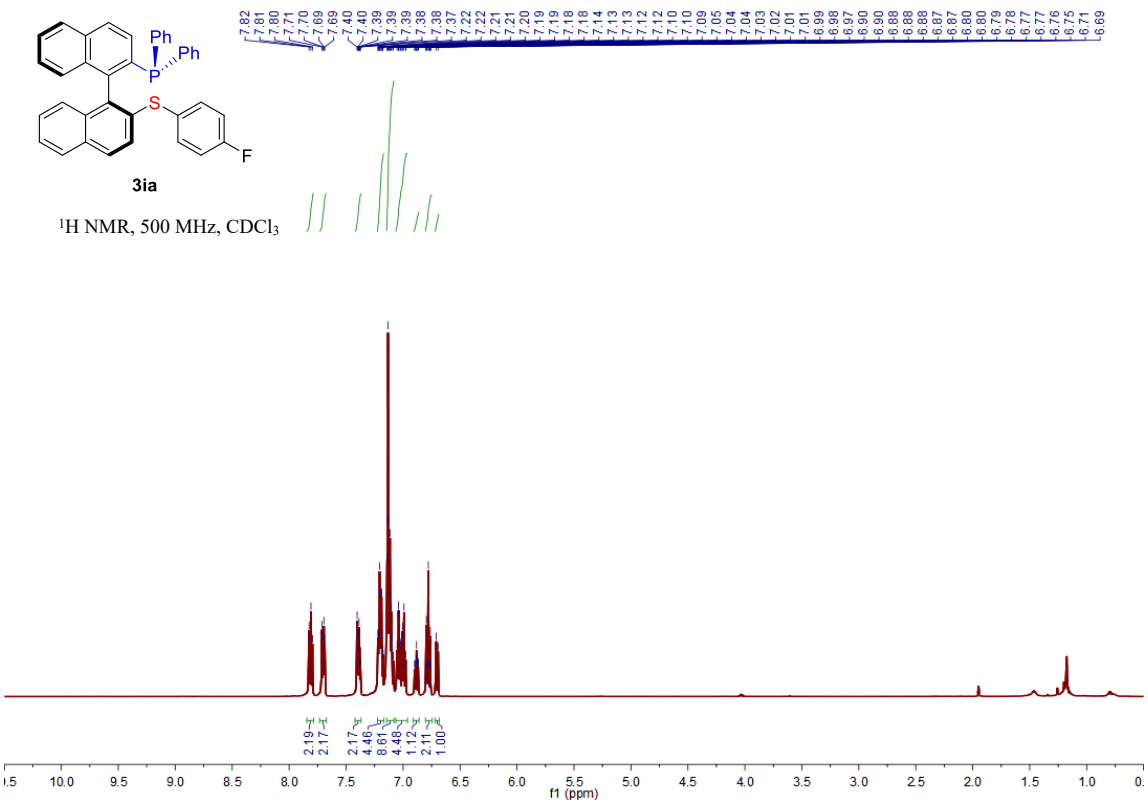
^{13}C NMR, 126 MHz, $CDCl_3$

Figure S104. ^{13}C NMR spectrum of 3ha (126 MHz, $CDCl_3$)



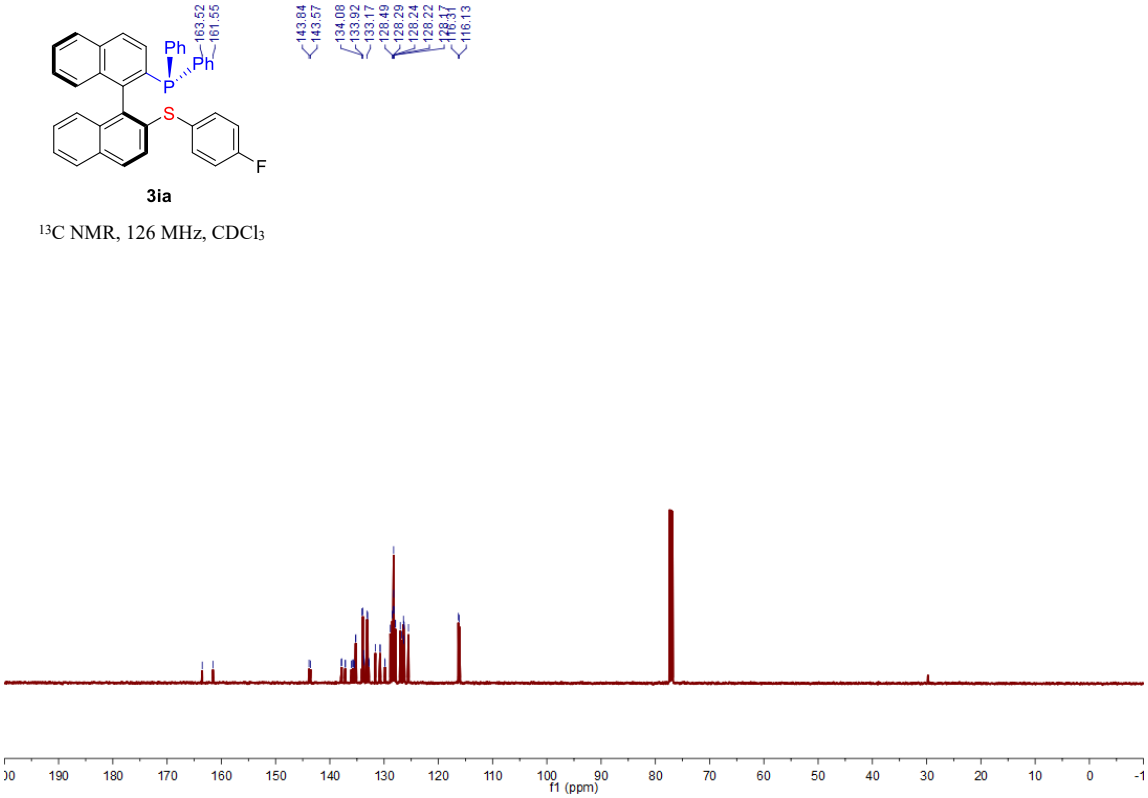
^{31}P NMR, 220 MHz, $CDCl_3$

Figure S105. ^{31}P NMR spectrum of 3ha (202 MHz, $CDCl_3$)



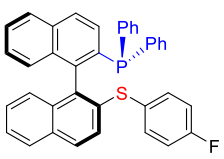
^{1}H NMR, 500 MHz, $CDCl_3$

Figure S106. ^{1}H NMR spectrum of 3ia (500 MHz, $CDCl_3$)



^{13}C NMR, 126 MHz, $CDCl_3$

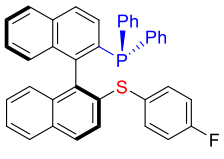
Figure S107. ^{13}C NMR spectrum of 3ia (126 MHz, $CDCl_3$)



3ia

^{31}P NMR, 220 MHz, $CDCl_3$

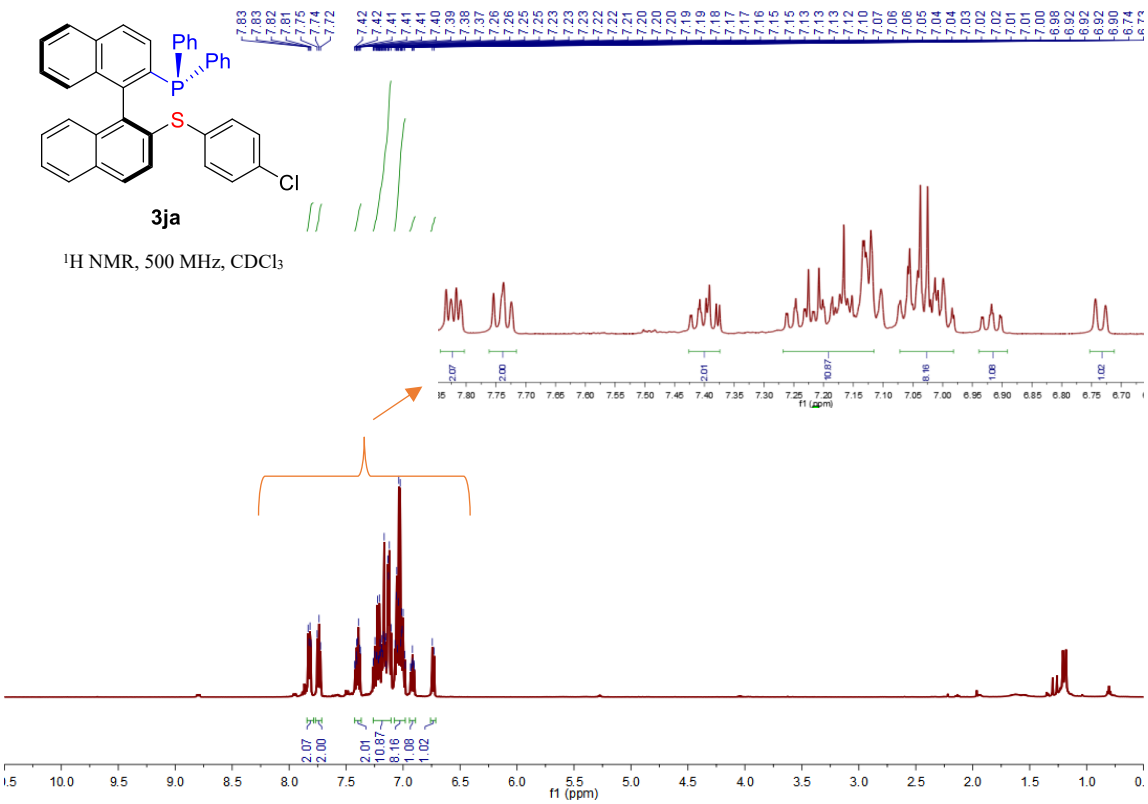
Figure S108. ^{31}P NMR spectrum of 3ia (202 MHz, $CDCl_3$)



3ia

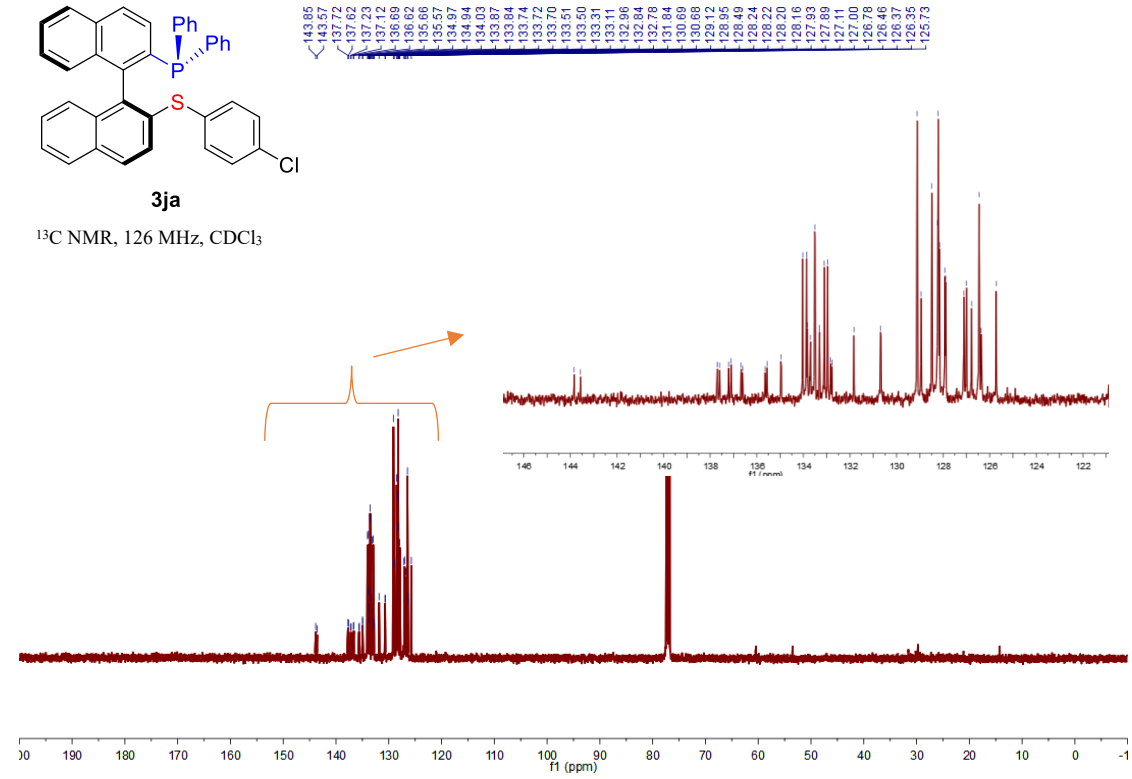
^{19}F NMR, 471 MHz, $CDCl_3$

Figure S109. ^{19}F NMR spectrum of 3ia (471 MHz, $CDCl_3$)



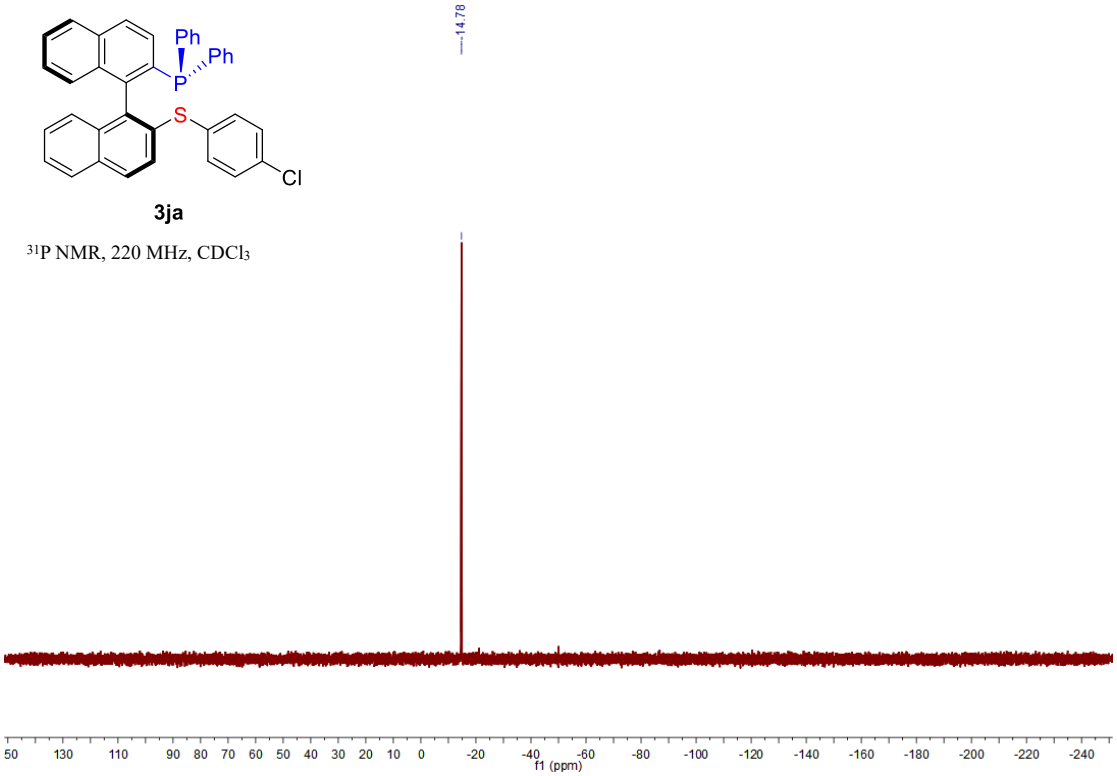
^{1}H NMR, 500 MHz, $CDCl_3$

Figure S110. ^{1}H NMR spectrum of 3ja (500 MHz, $CDCl_3$)



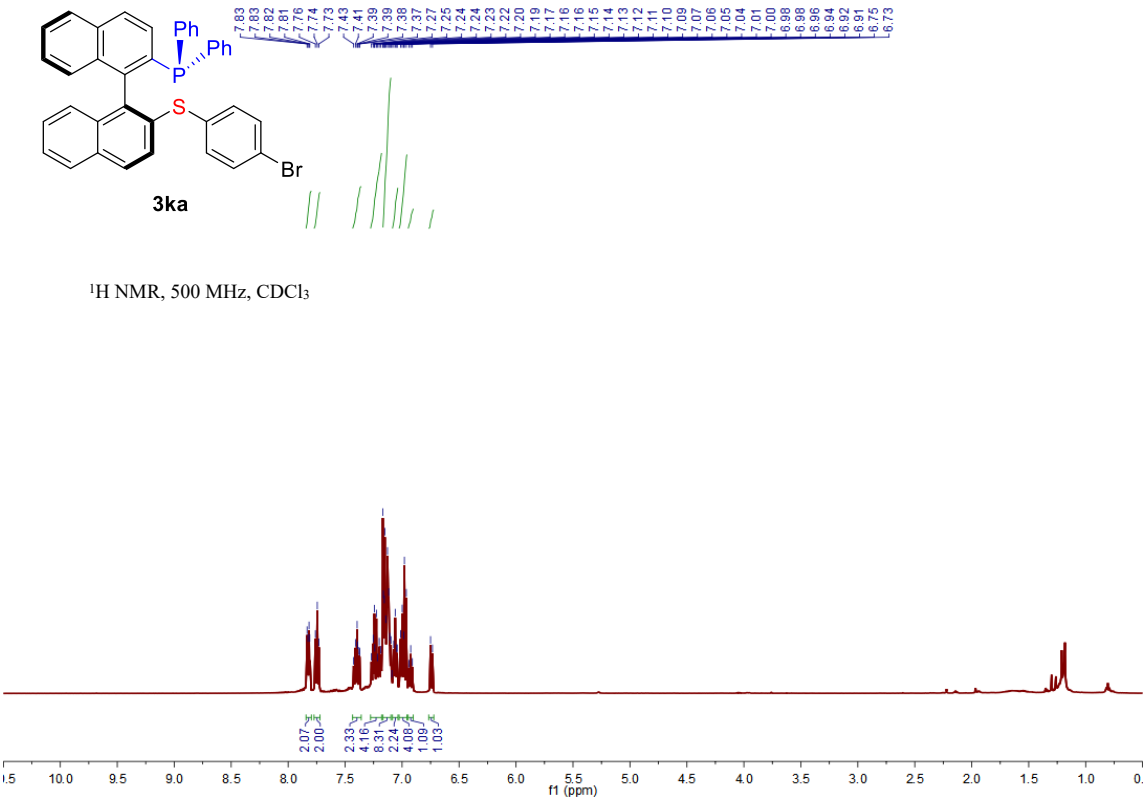
^{13}C NMR, 126 MHz, $CDCl_3$

Figure S111. ^{13}C NMR spectrum of 3ja (126 MHz, $CDCl_3$)



^{31}P NMR, 220 MHz, $CDCl_3$

Figure S112. ^{31}P NMR spectrum of 3ja (202 MHz, $CDCl_3$)



^{1}H NMR, 500 MHz, $CDCl_3$

Figure S113. ^{1}H NMR spectrum of 3ka (500 MHz, $CDCl_3$)

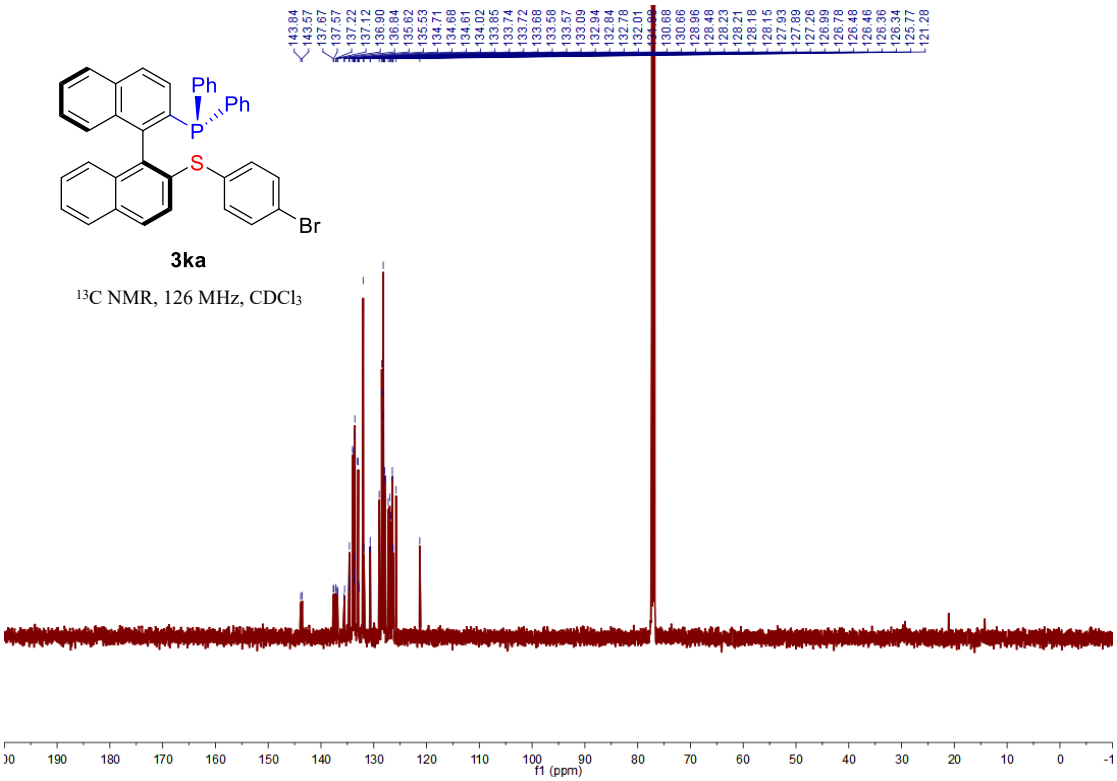


Figure S114. ^{13}C NMR spectrum of 3ka (126 MHz, $CDCl_3$)

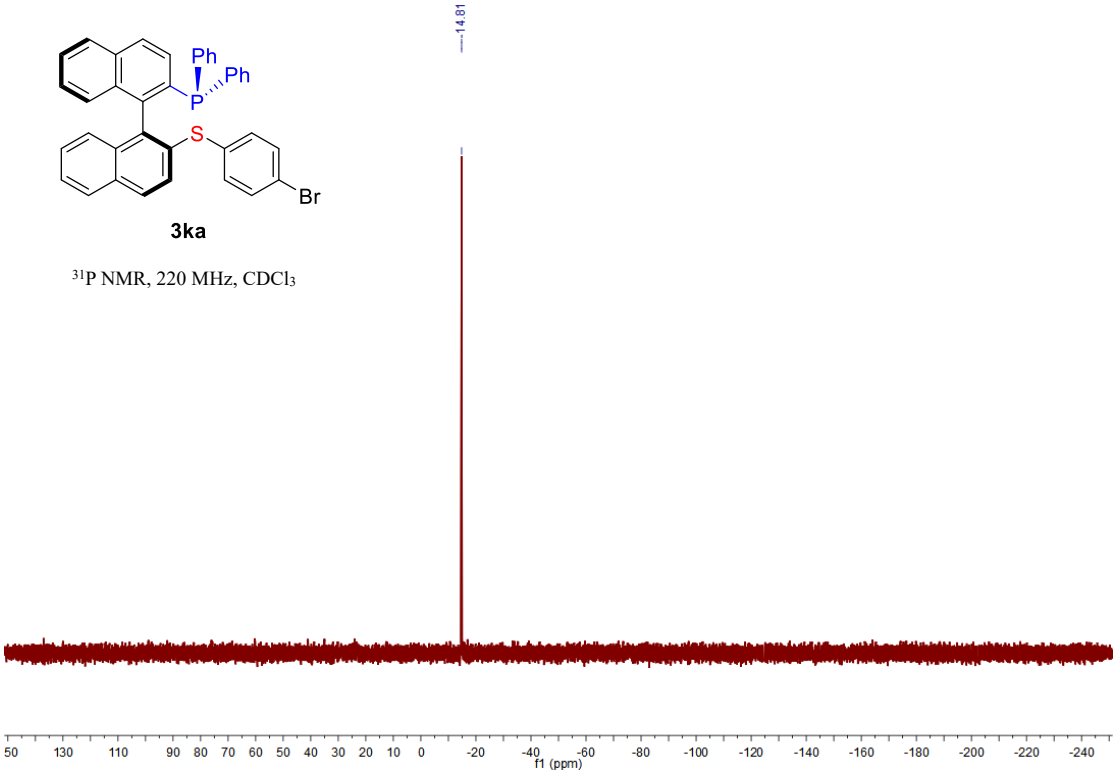
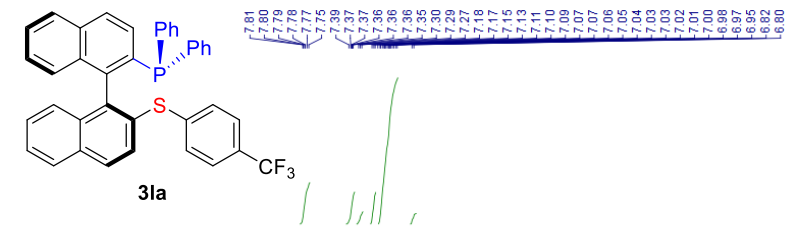


Figure S115. ^{31}P NMR spectrum of 3ka (202 MHz, $CDCl_3$)



^{1}H NMR, 500 MHz, $CDCl_3$

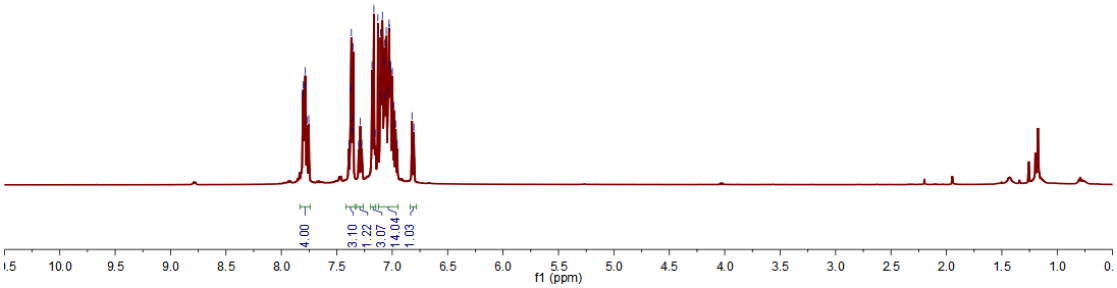
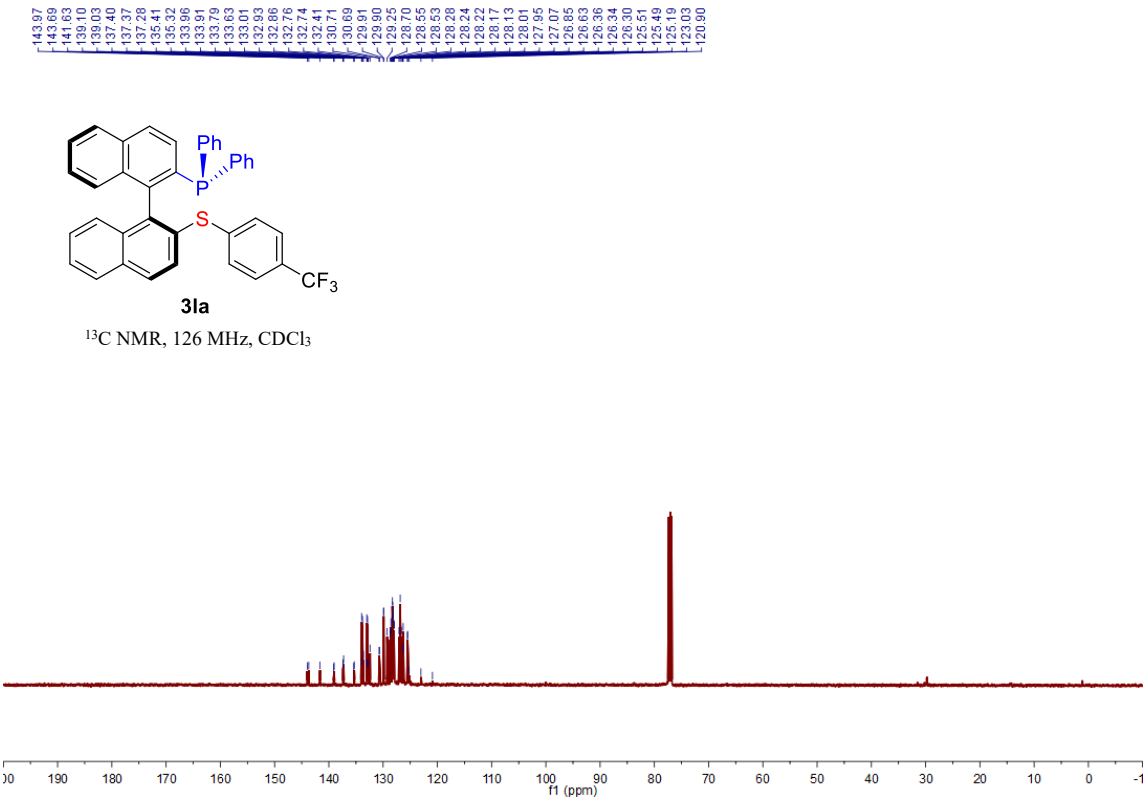


Figure S116. ^{1}H NMR spectrum of 3la (500 MHz, $CDCl_3$)



^{13}C NMR, 126 MHz, $CDCl_3$

Figure S117. ^{13}C NMR spectrum of 3la (126 MHz, $CDCl_3$)

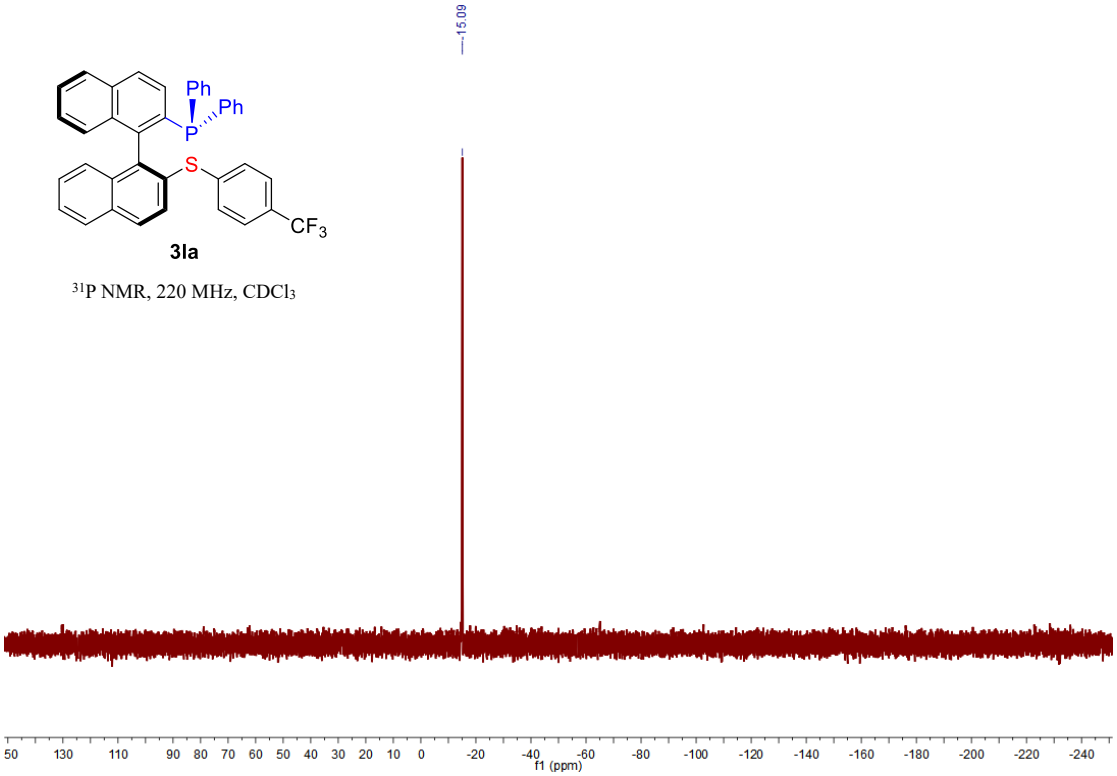


Figure S118. ^{31}P NMR spectrum of 3la (202 MHz, $CDCl_3$)

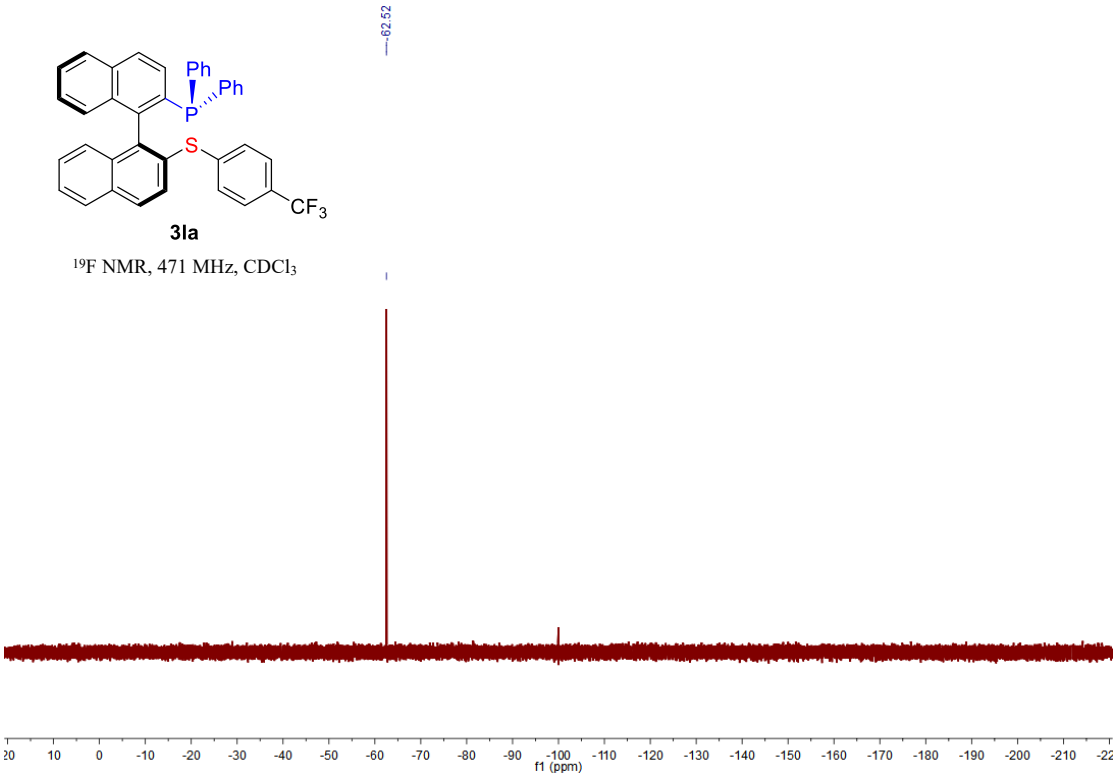
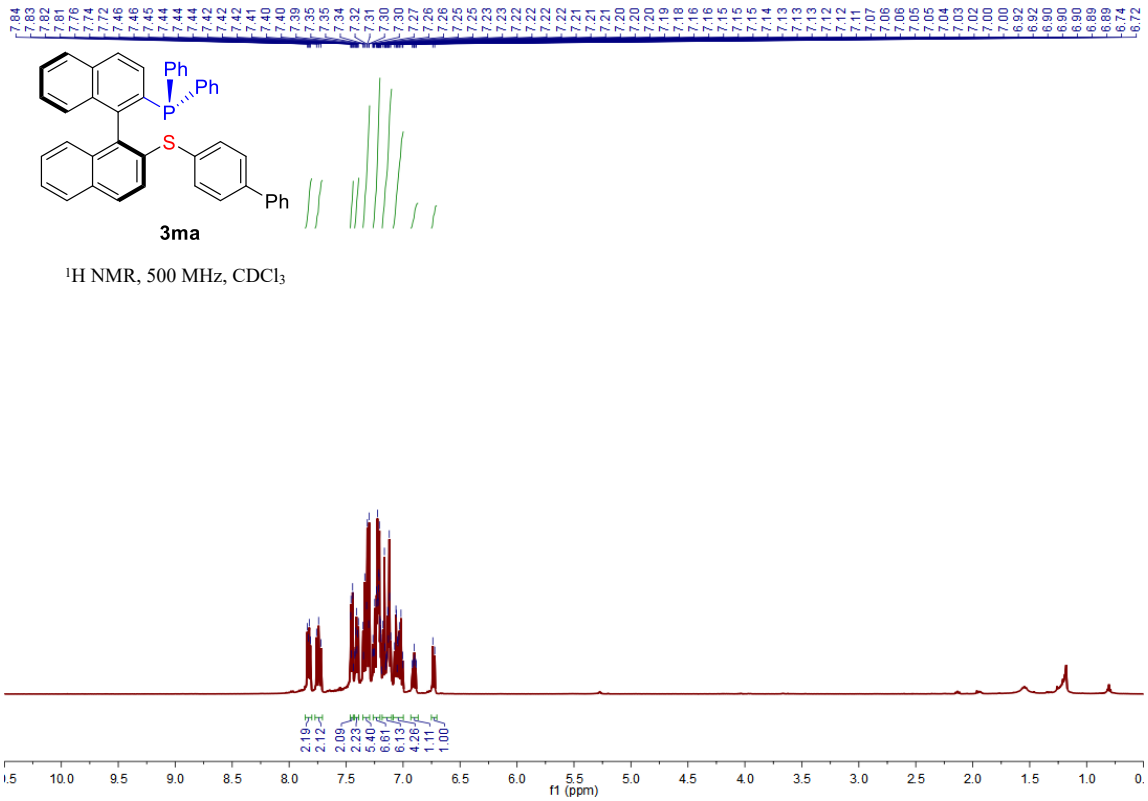
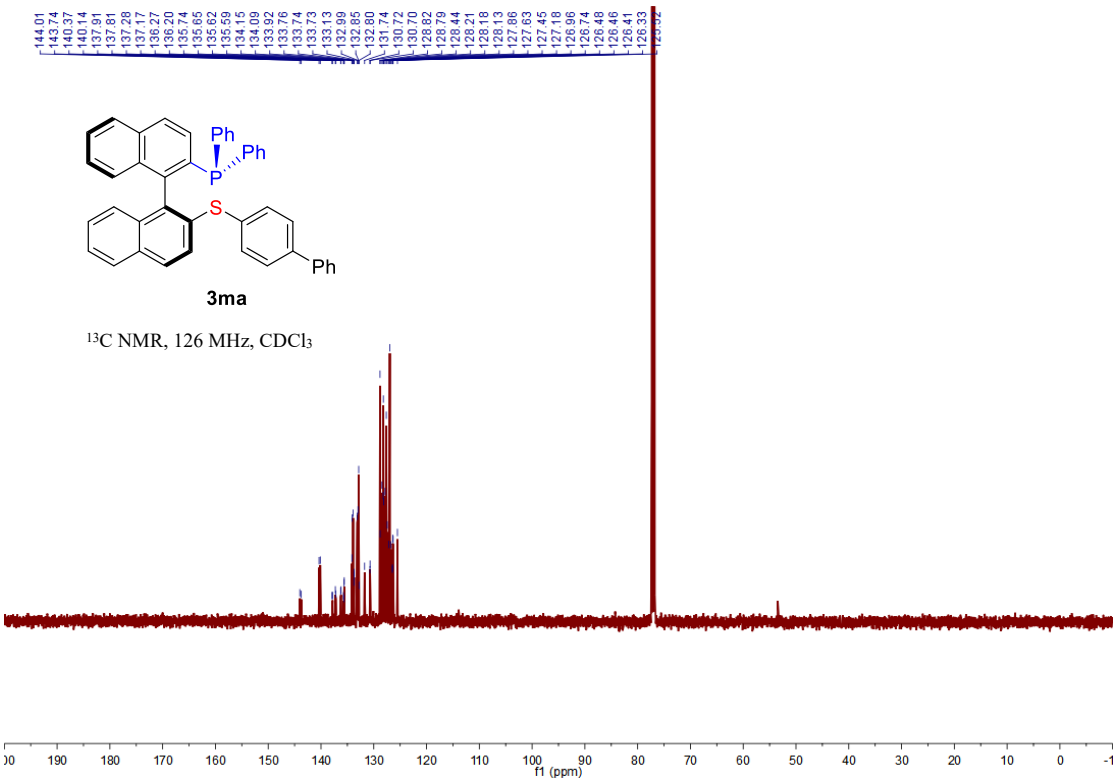


Figure S119. ^{19}F NMR spectrum of 3la (471 MHz, $CDCl_3$)



^{1}H NMR, 500 MHz, $CDCl_3$

Figure S120. ^{1}H NMR spectrum of 3ma (500 MHz, $CDCl_3$)



^{13}C NMR, 126 MHz, $CDCl_3$

Figure S121. ^{13}C NMR spectrum of 3ma (126 MHz, $CDCl_3$)

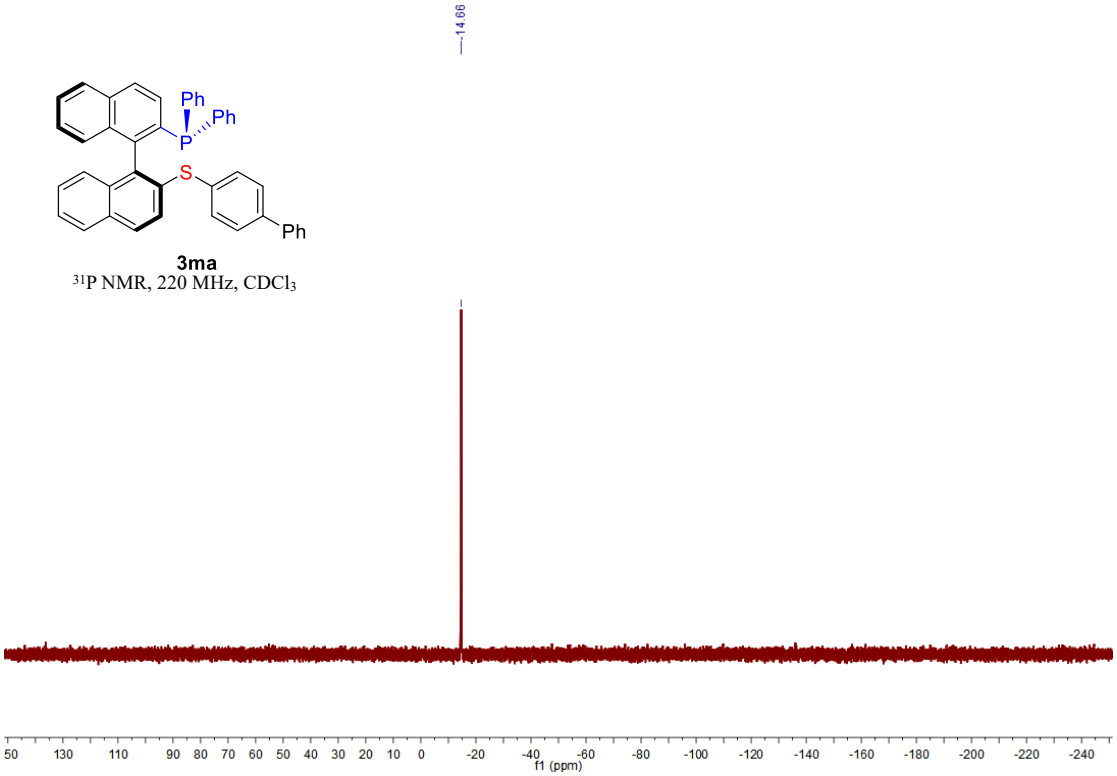


Figure S122. ^{31}P NMR spectrum of 3ma (202 MHz, $CDCl_3$)

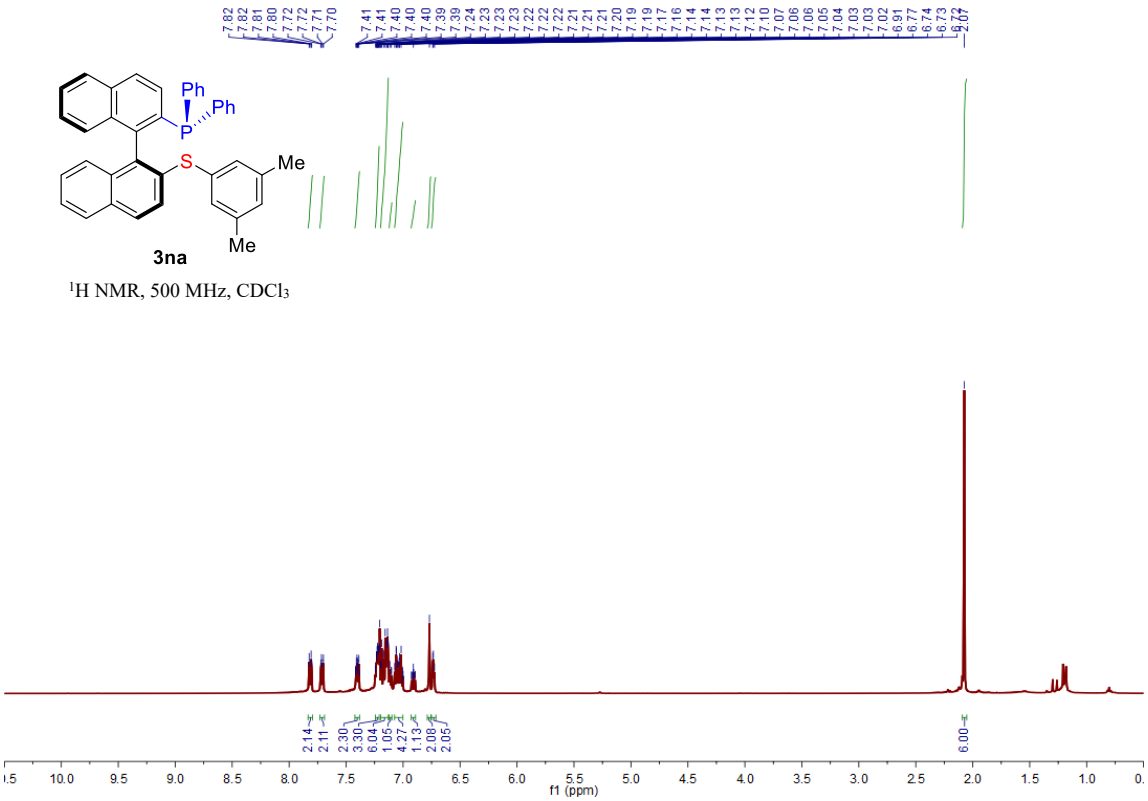


Figure S123. ^{1}H NMR spectrum of 3na (500 MHz, $CDCl_3$)

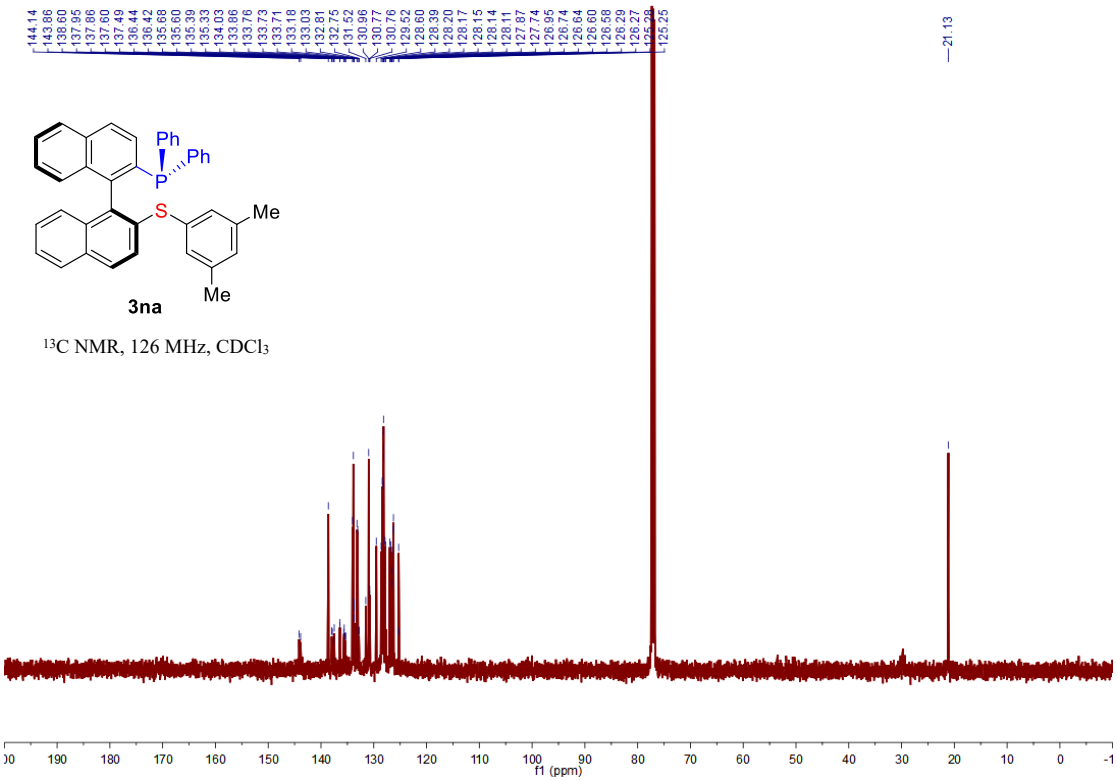


Figure S124. ^{13}C NMR spectrum of 3na (126 MHz, $CDCl_3$)

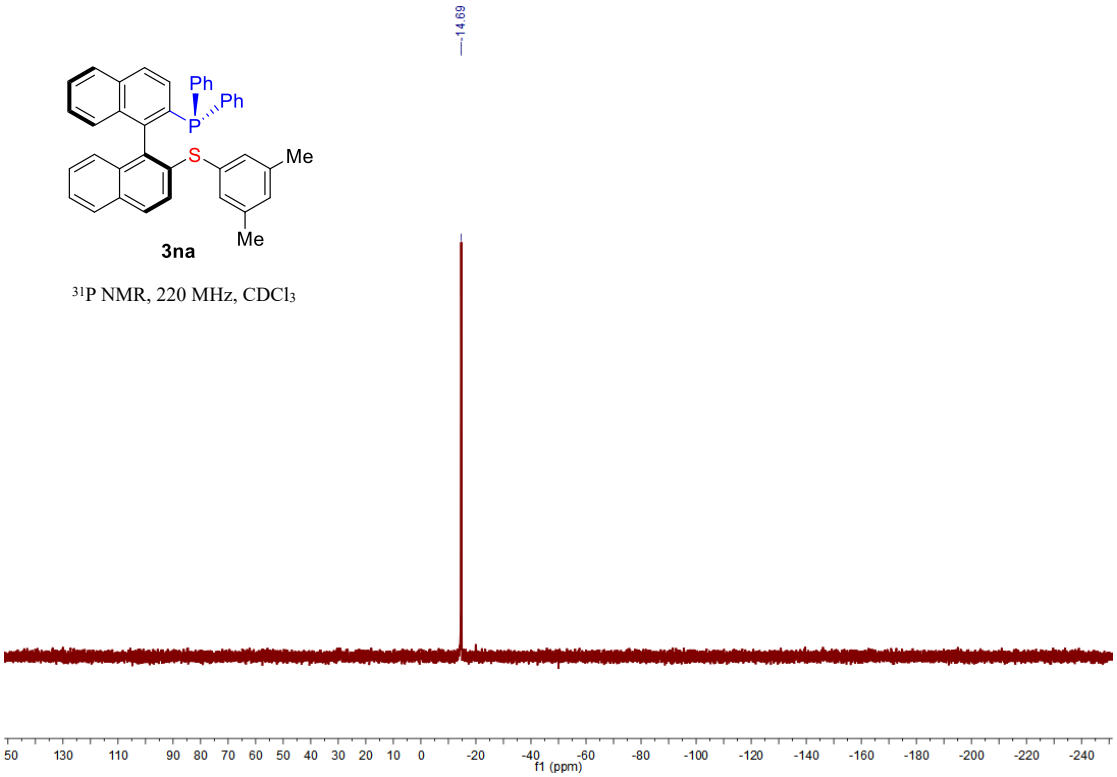


Figure S125. ^{31}P NMR spectrum of 3na (202 MHz, $CDCl_3$)

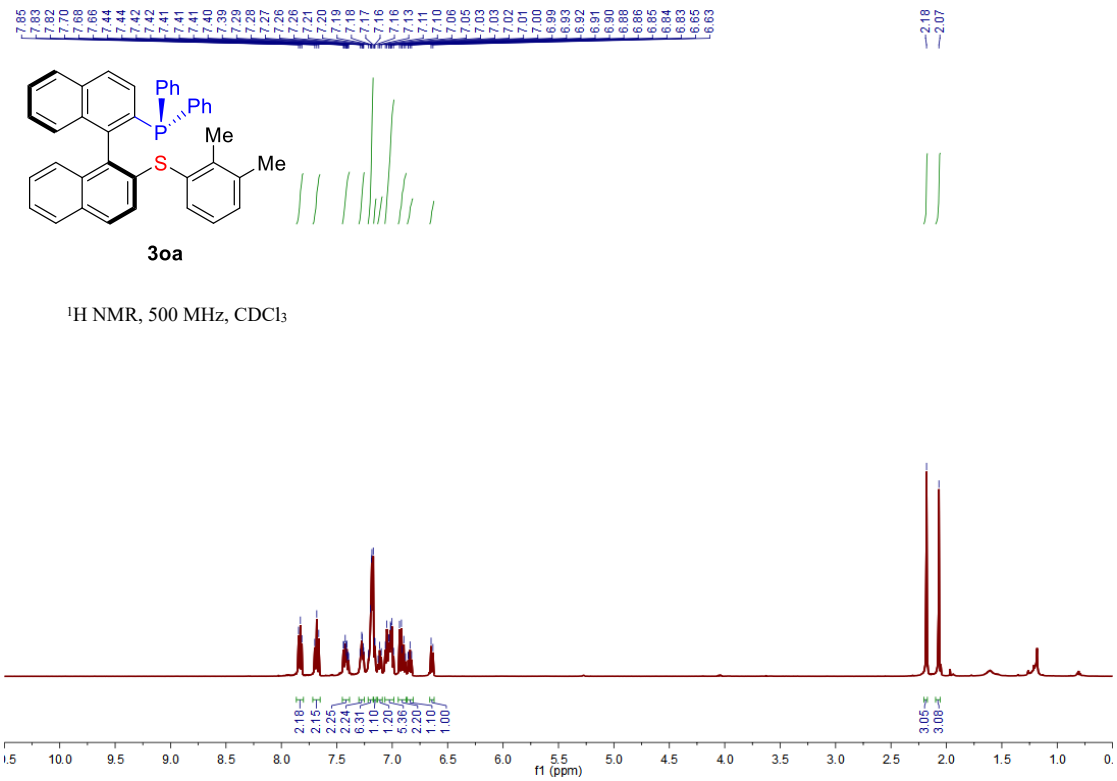


Figure S126. ^{1}H NMR spectrum of 3oa (500 MHz, $CDCl_3$)

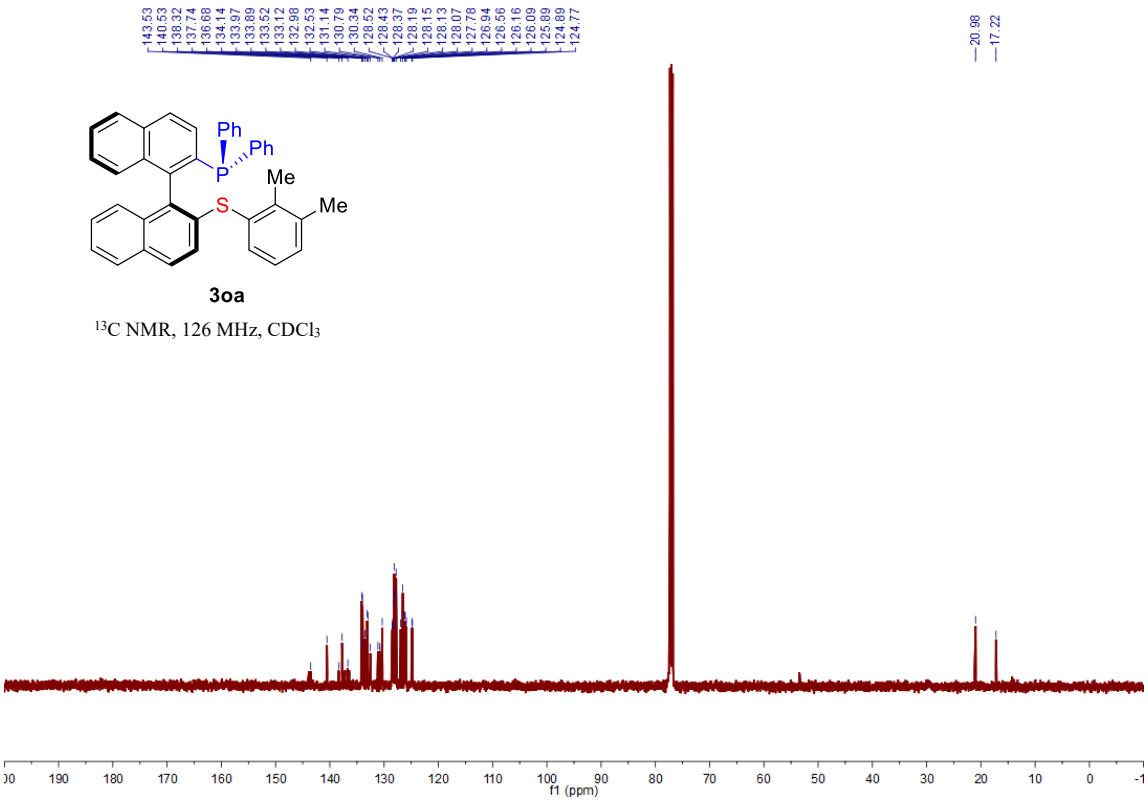


Figure S127. ^{13}C NMR spectrum of 3oa (126 MHz, $CDCl_3$)

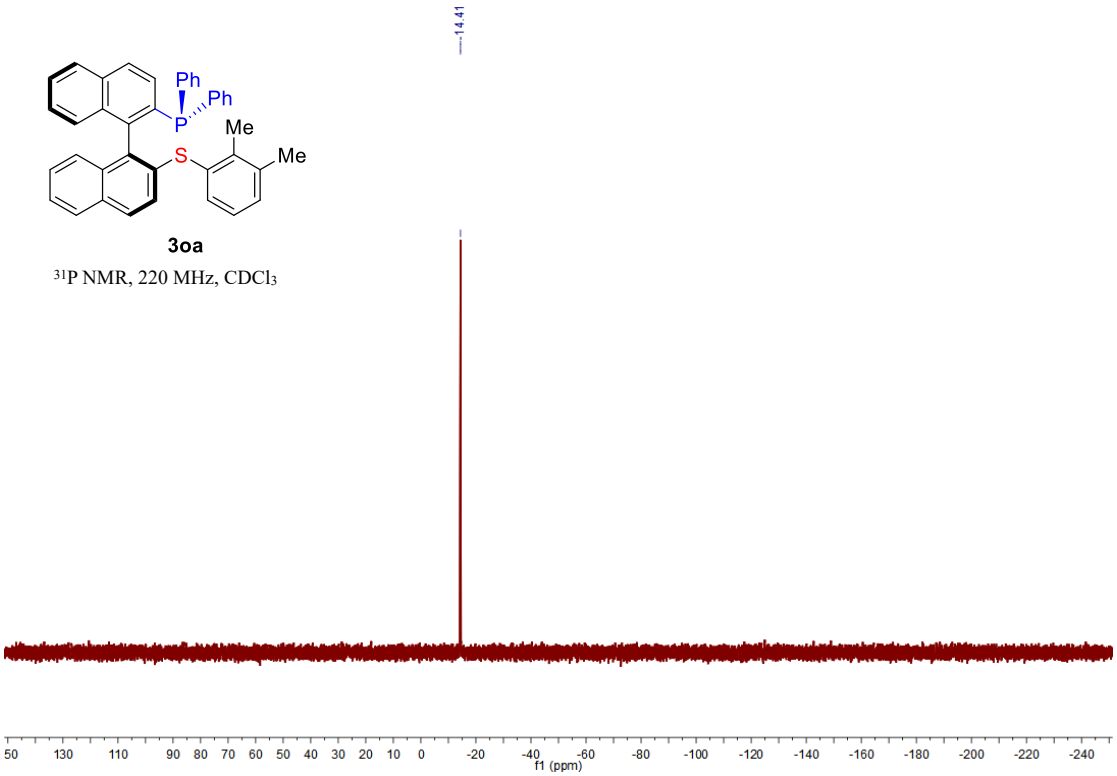


Figure S128. ^{31}P NMR spectrum of 3oa (202 MHz, $CDCl_3$)

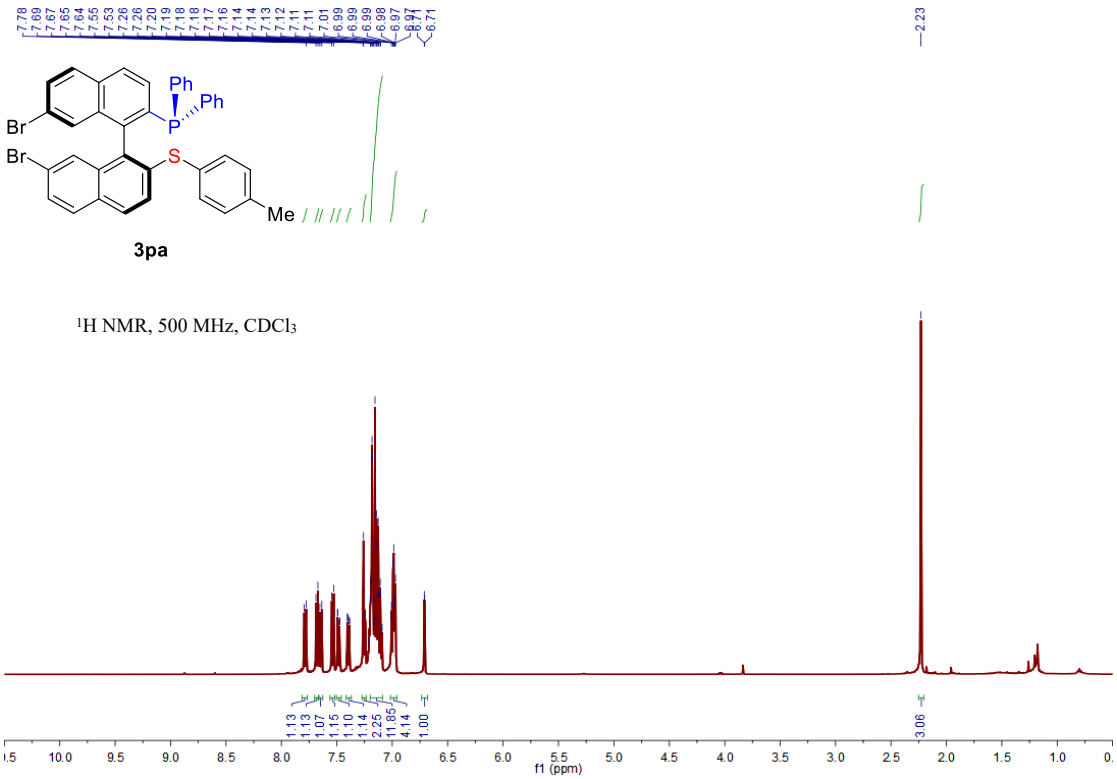


Figure S129. ^{1}H NMR spectrum of 3pa (500 MHz, $CDCl_3$)

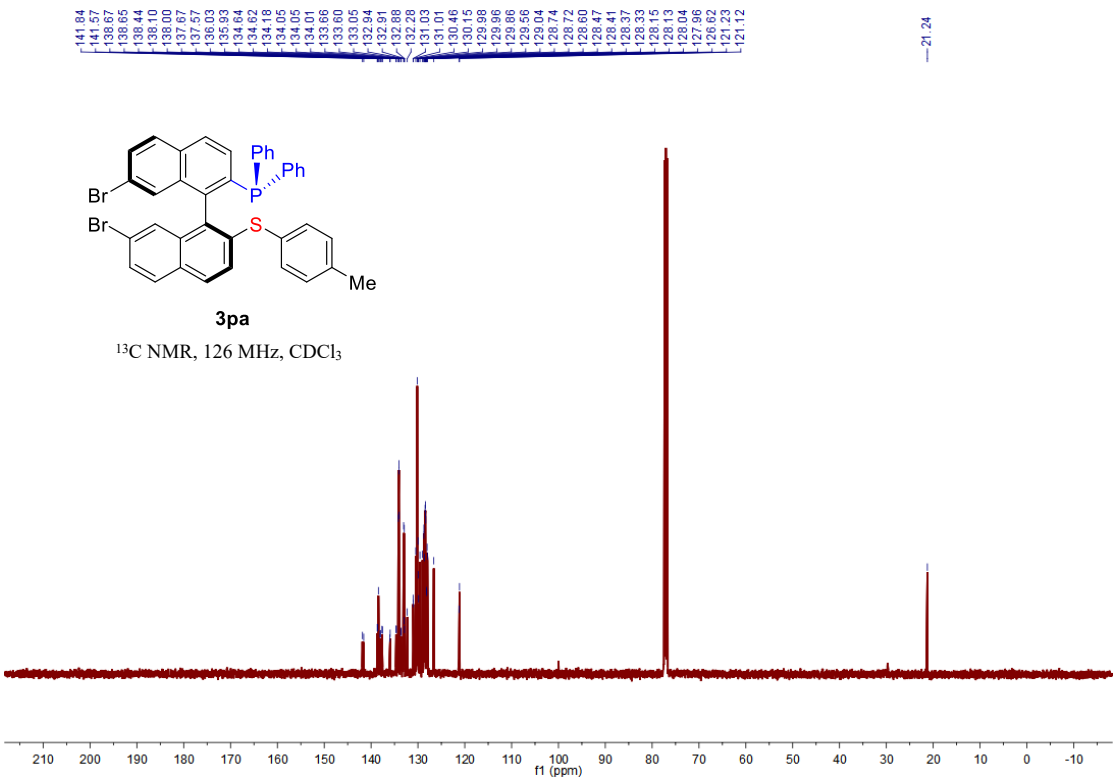


Figure S130. ^{13}C NMR spectrum of 3pa (126 MHz, $CDCl_3$)

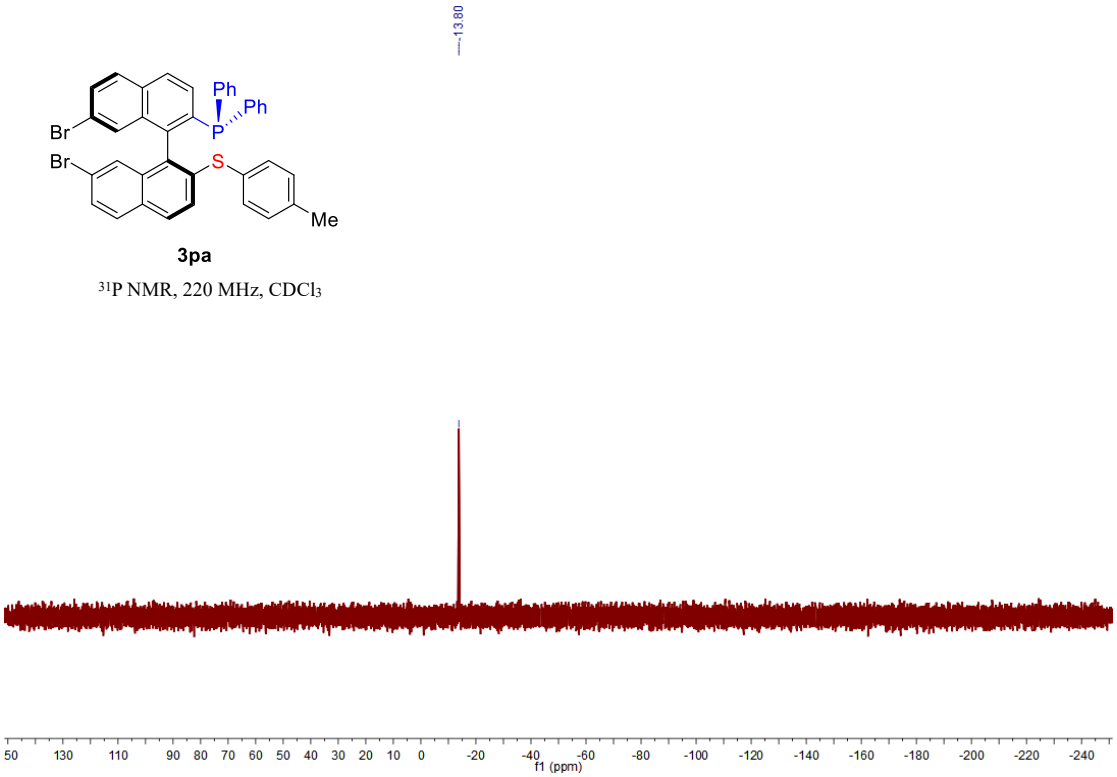


Figure S131. ^{31}P NMR spectrum of 3pa (202 MHz, $CDCl_3$)

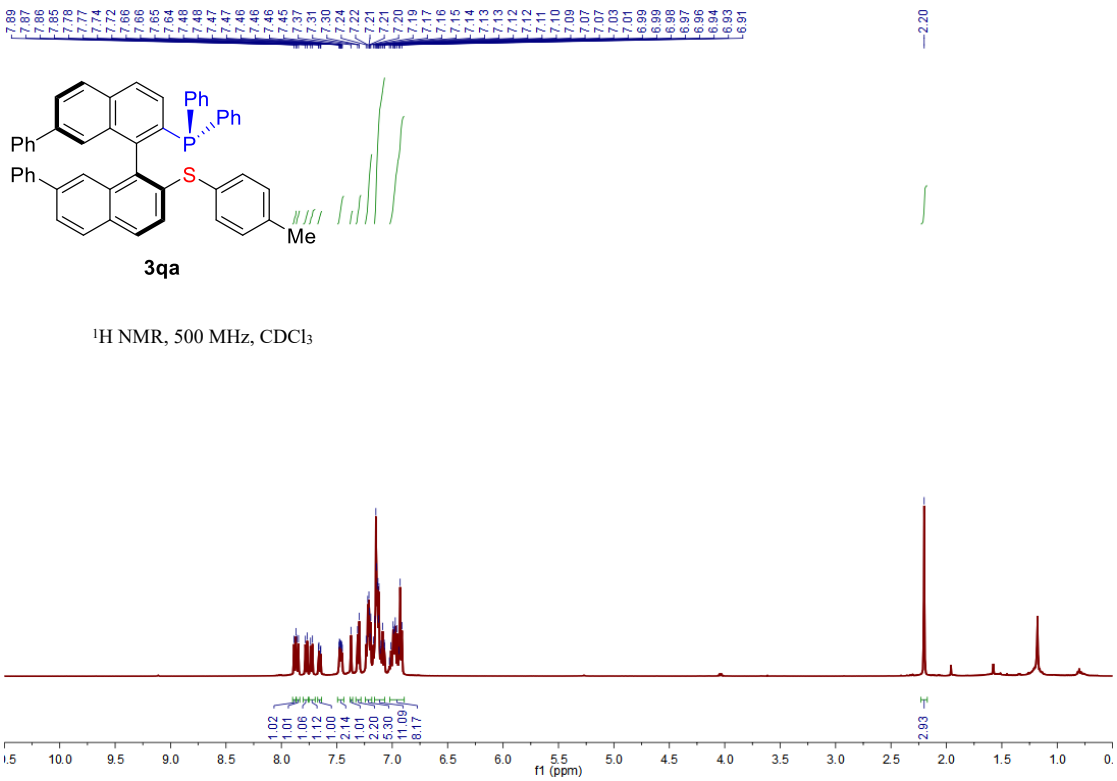


Figure S132. ^{1}H NMR spectrum of 3qa (500 MHz, $CDCl_3$)

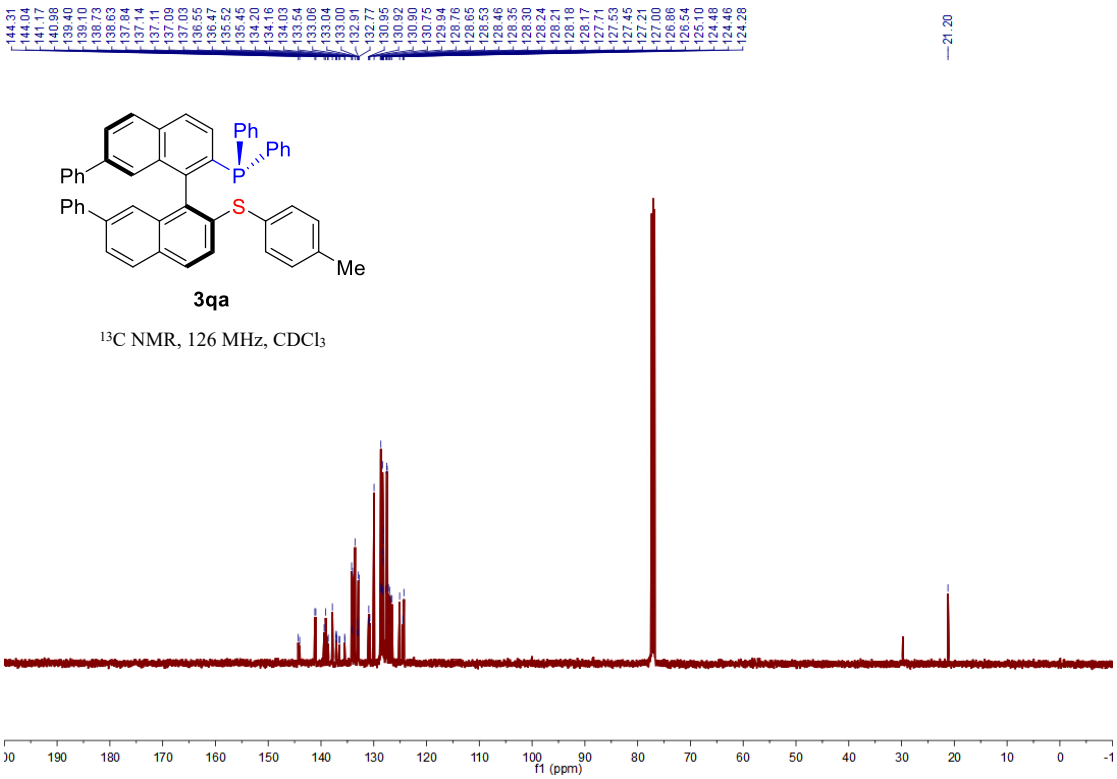
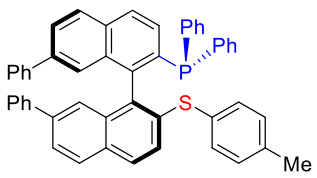


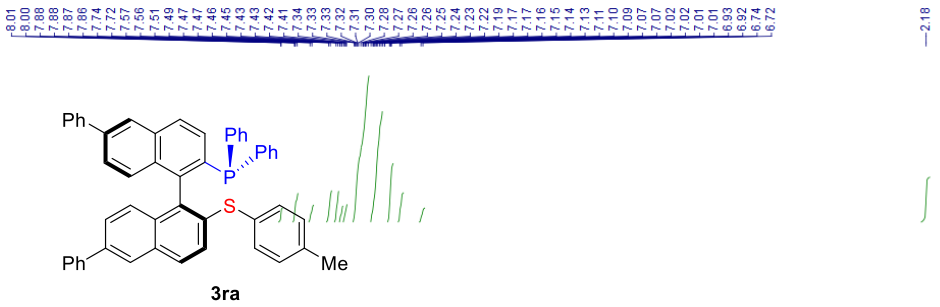
Figure S133. ^{13}C NMR spectrum of 3qa (126 MHz, $CDCl_3$)



3qa

^{31}P NMR, 220 MHz, $CDCl_3$

Figure S134. ^{31}P NMR spectrum of 3qa (202 MHz, $CDCl_3$)



3ra

^{1}H NMR, 500 MHz, $CDCl_3$

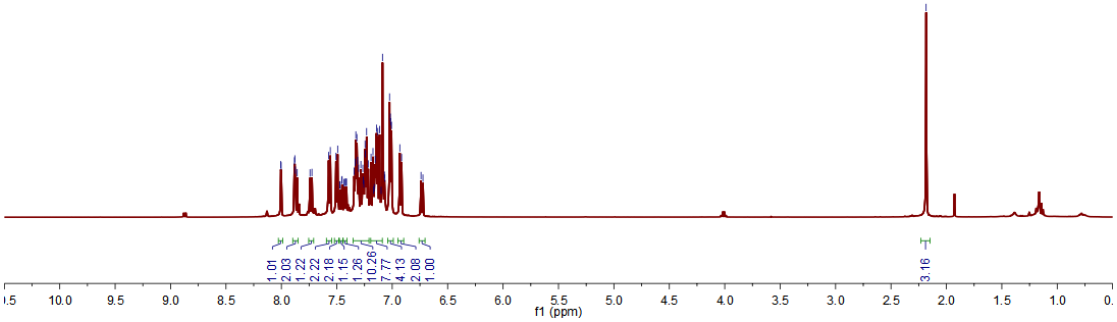
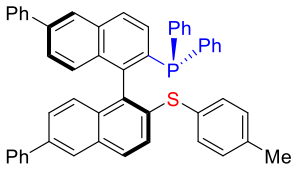


Figure S135. ^{1}H NMR spectrum of 3ra (500 MHz, $CDCl_3$)



3ra

^{13}C NMR, 126 MHz, $CDCl_3$

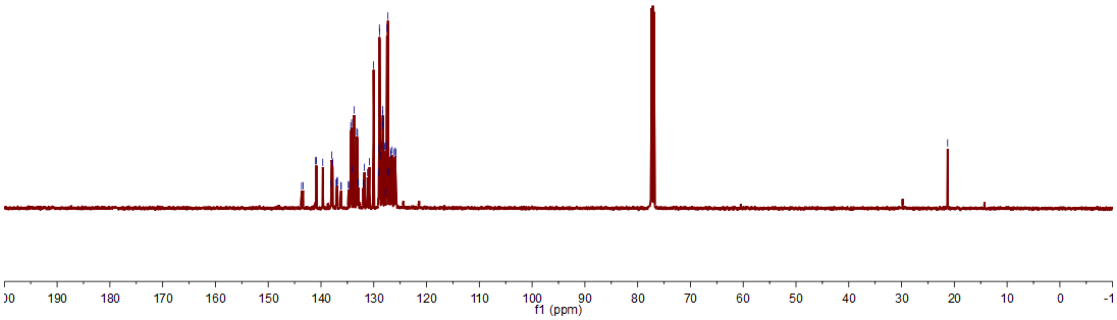
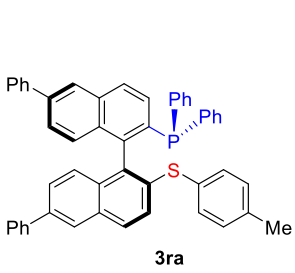


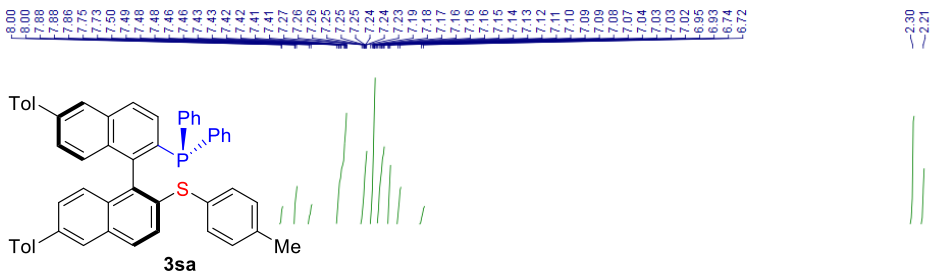
Figure S136. ^{13}C NMR spectrum of 3ra (126 MHz, $CDCl_3$)



3ra

^{31}P NMR, 220 MHz, $CDCl_3$

Figure S137. ^{31}P NMR spectrum of 3ra (202 MHz, $CDCl_3$)



^{1}H NMR, 500 MHz, $CDCl_3$

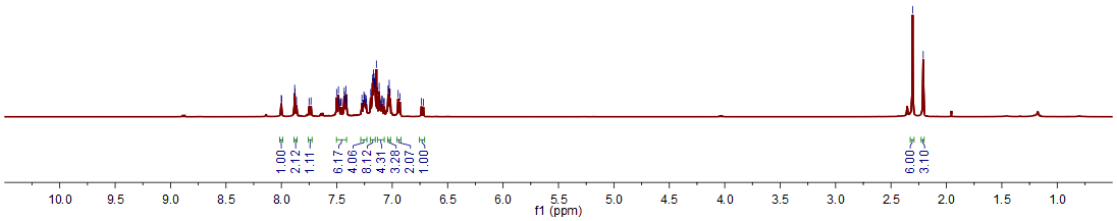
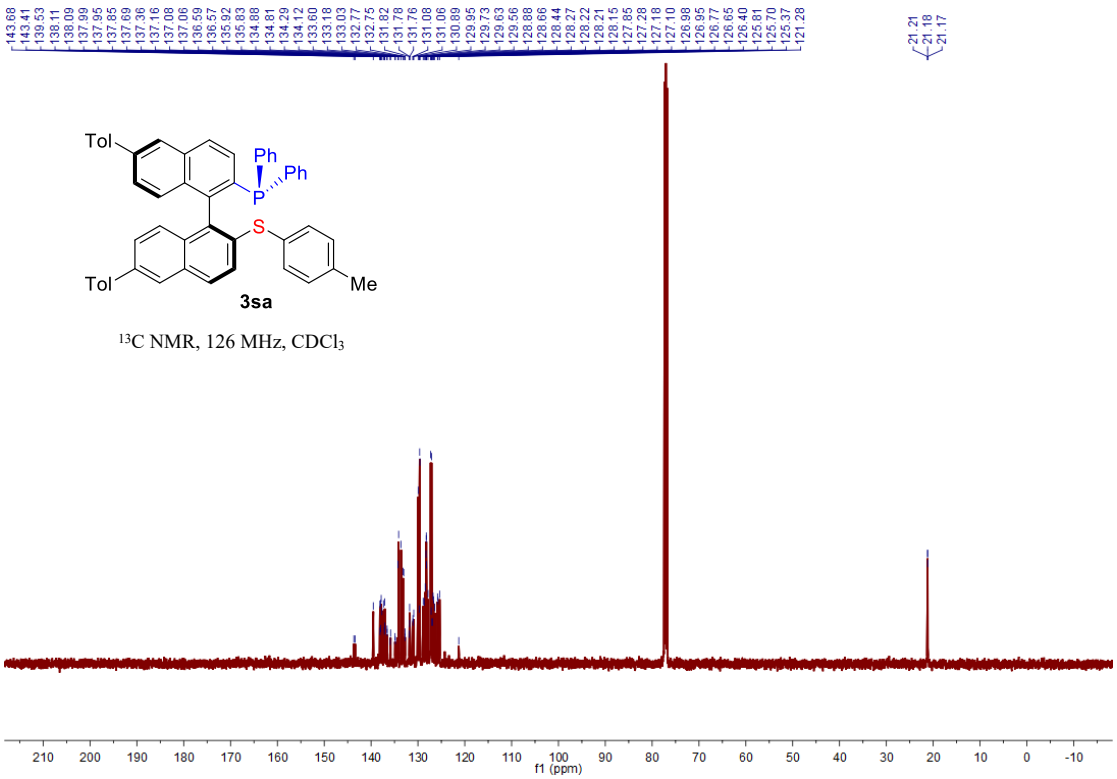


Figure S138. ^{1}H NMR spectrum of 3sa (500 MHz, $CDCl_3$)



^{13}C NMR, 126 MHz, $CDCl_3$

Figure S139. ^{13}C NMR spectrum of 3sa (126 MHz, $CDCl_3$)

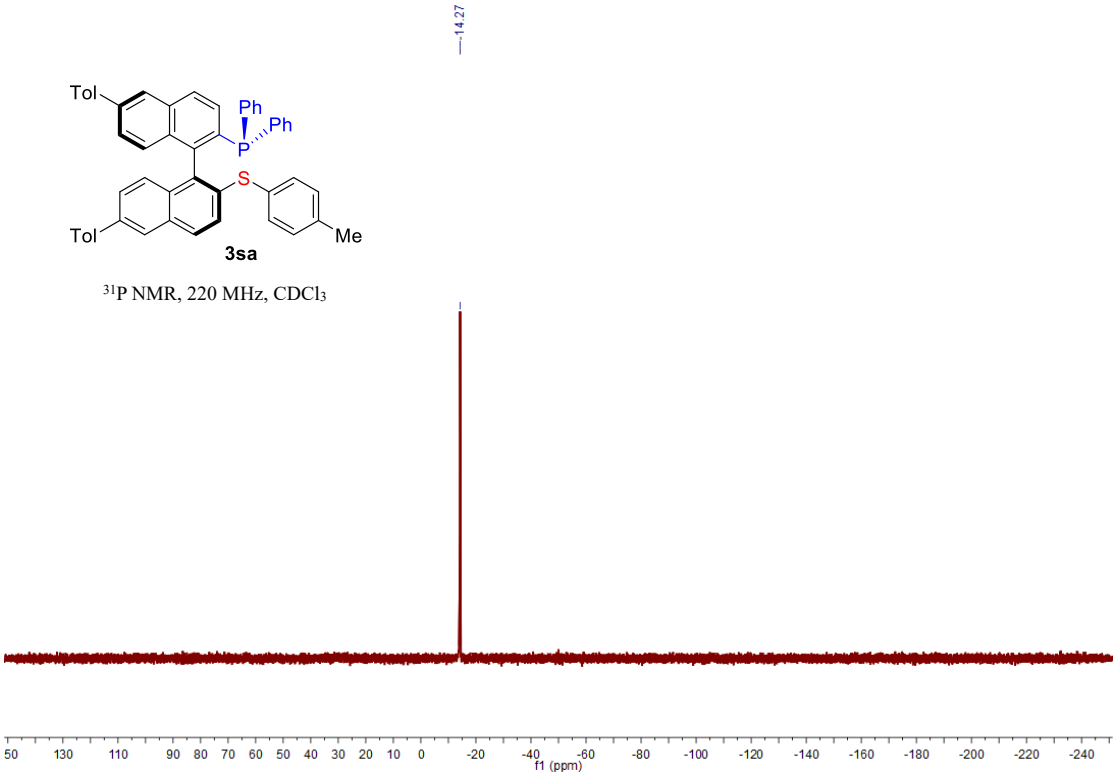


Figure S140. ^{31}P NMR spectrum of 3sa (202 MHz, $CDCl_3$)

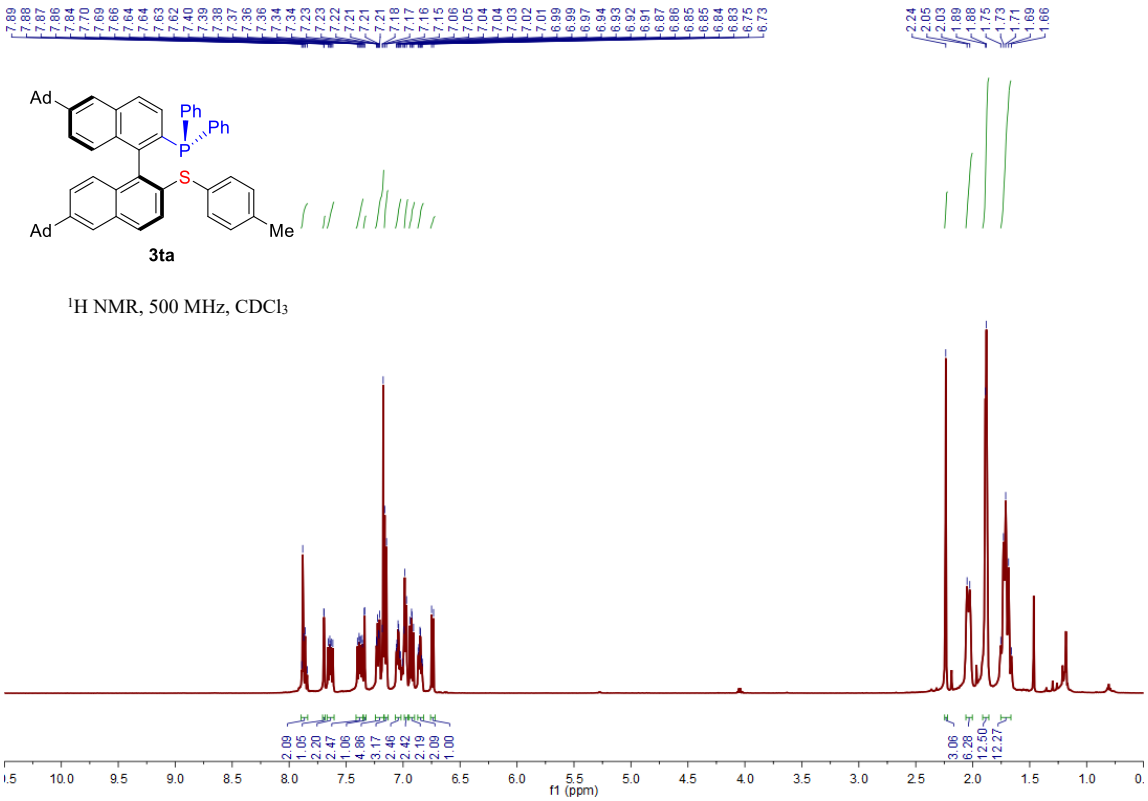


Figure S141. ^{1}H NMR spectrum of 3ta (500 MHz, $CDCl_3$)

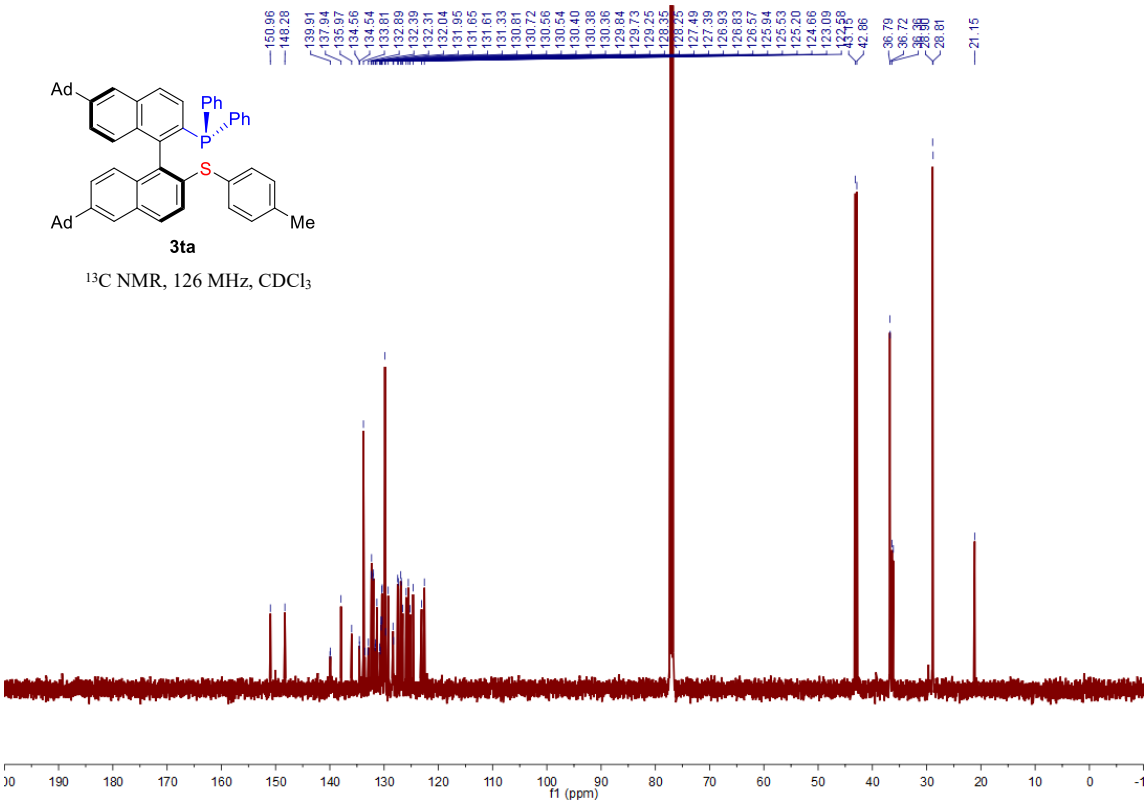


Figure S142. ^{13}C NMR spectrum of 3ta (126 MHz, $CDCl_3$)

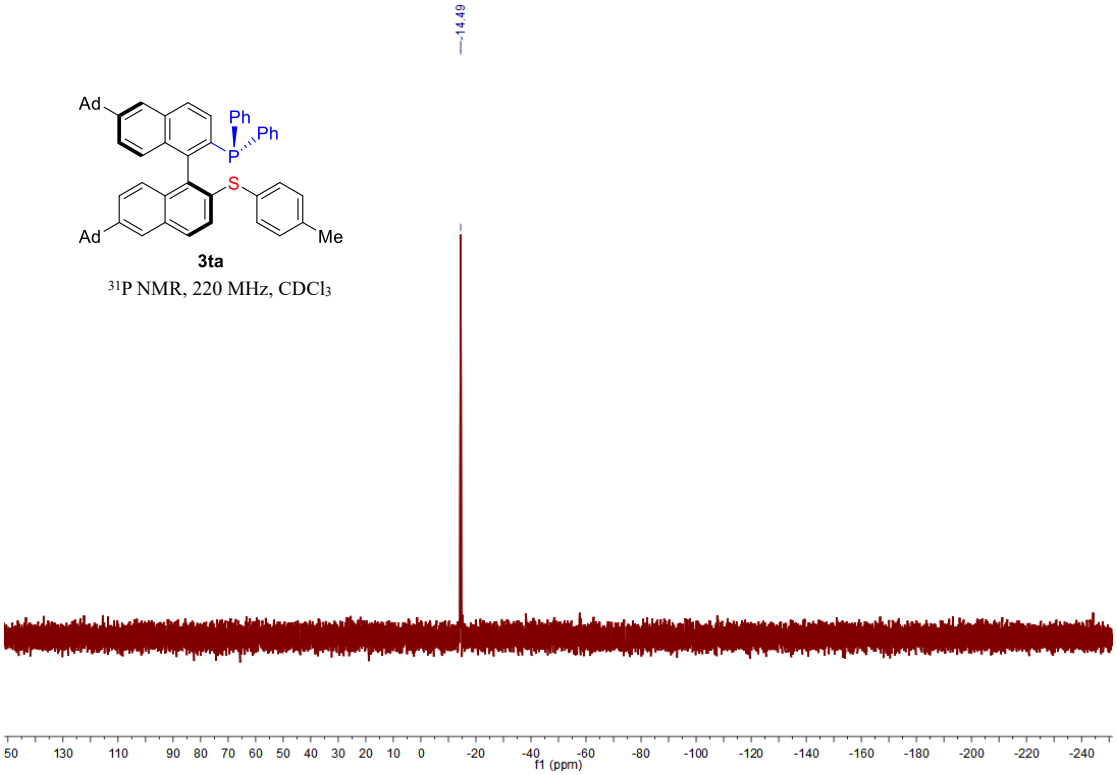
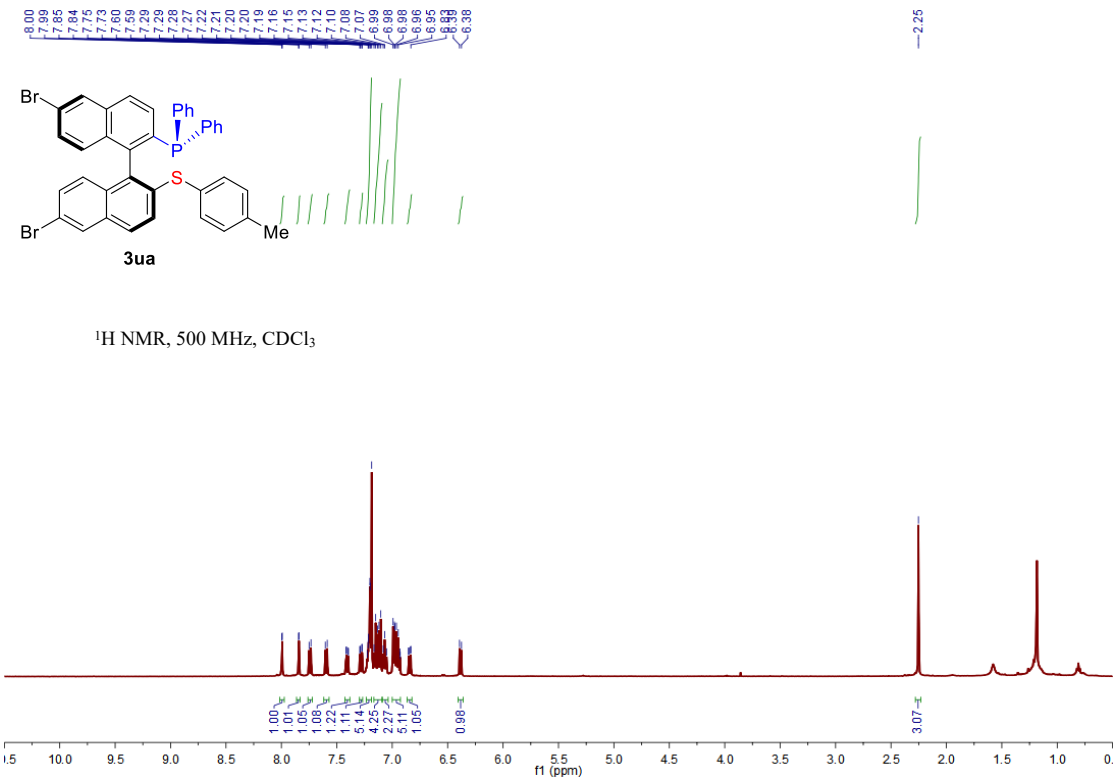
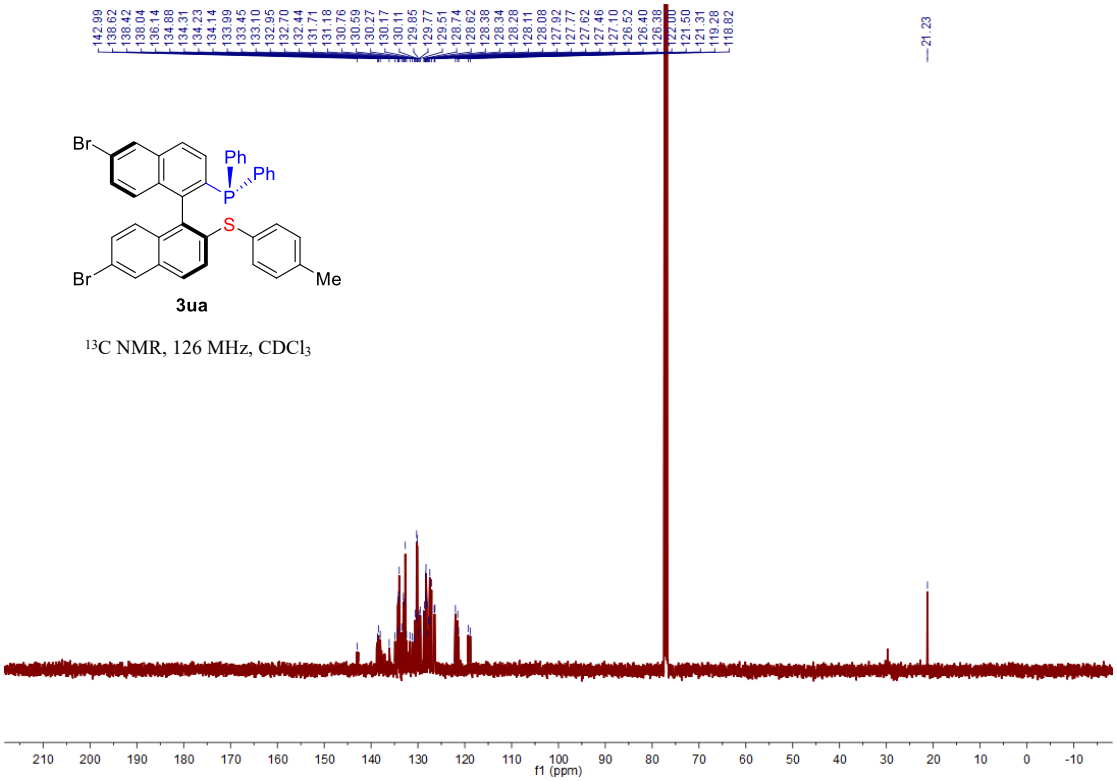


Figure S143. ^{31}P NMR spectrum of 3ta (202 MHz, $CDCl_3$)



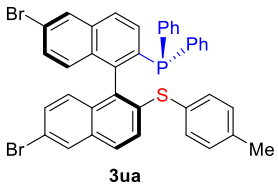
^{1}H NMR, 500 MHz, $CDCl_3$

Figure S144. ^{1}H NMR spectrum of 3ua (500 MHz, $CDCl_3$)



^{13}C NMR, 126 MHz, $CDCl_3$

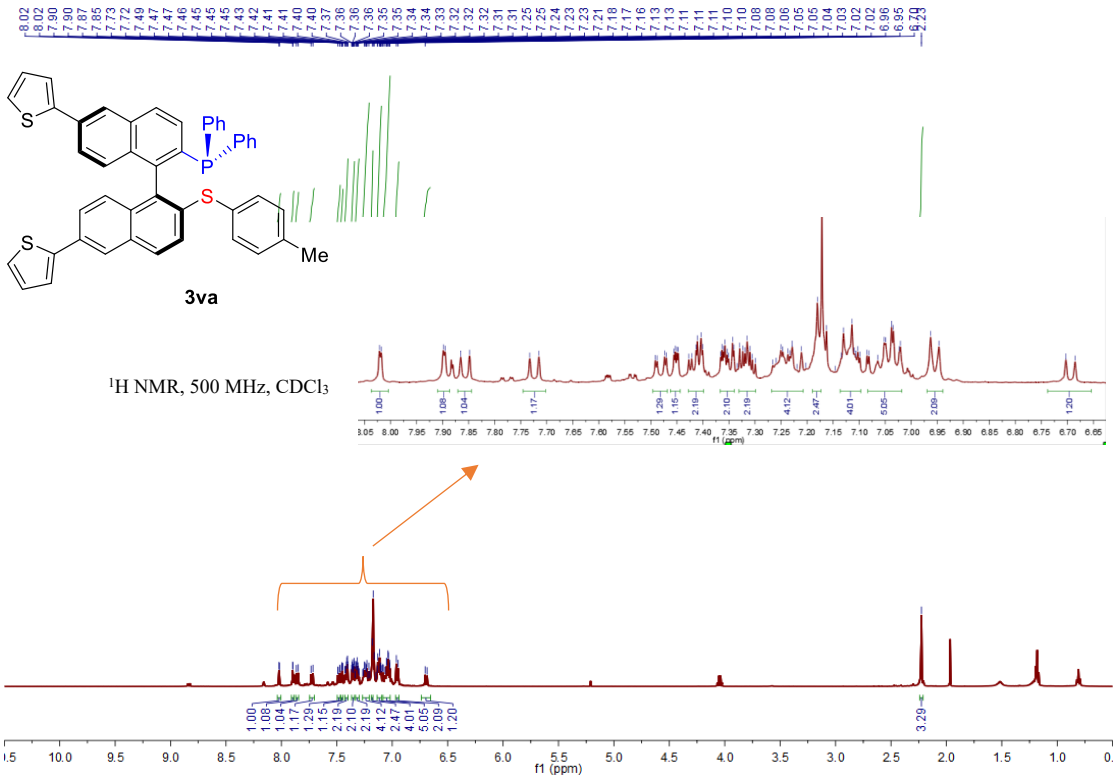
Figure S145. ^{13}C NMR spectrum of 3ua (126 MHz, $CDCl_3$)



3ua

^{31}P NMR, 220 MHz, $CDCl_3$

Figure S146. ^{31}P NMR spectrum of 3ua (202 MHz, $CDCl_3$)



3va

^{1}H NMR, 500 MHz, $CDCl_3$

Figure S147. ^{1}H NMR spectrum of 3va (500 MHz, $CDCl_3$)

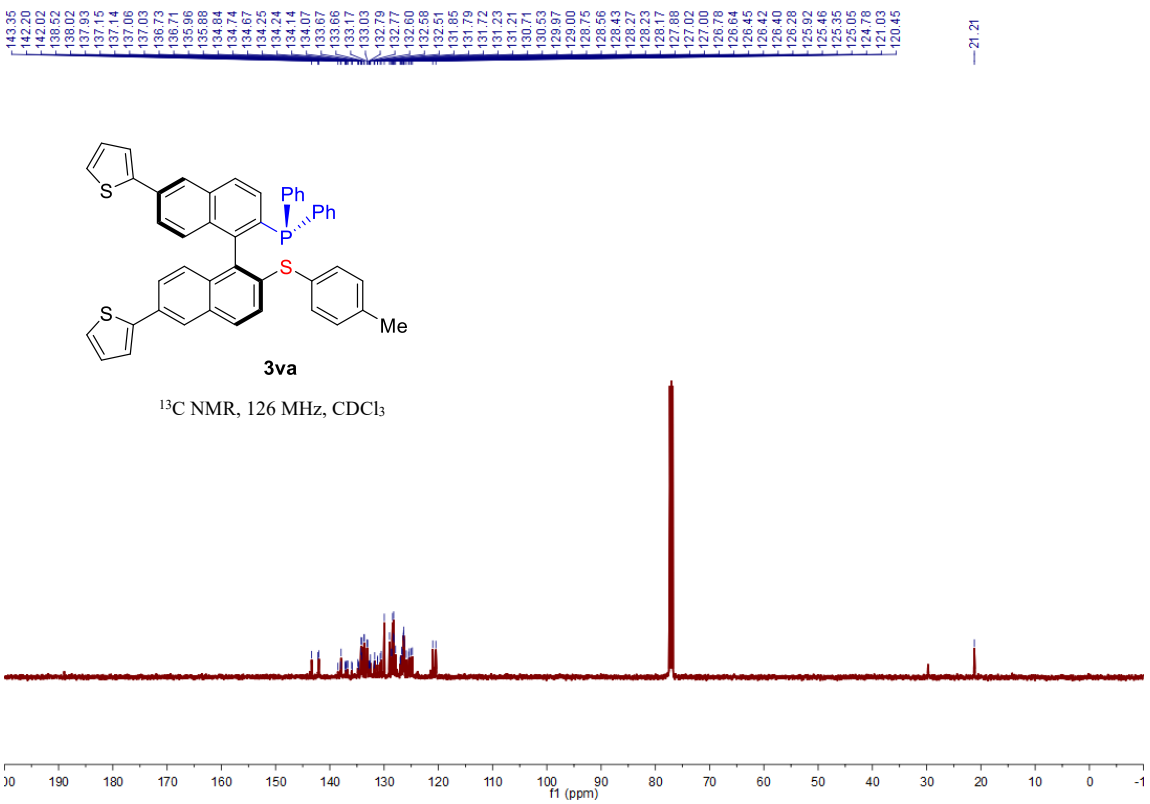


Figure S148. ^{13}C NMR spectrum of 3va (126 MHz, $CDCl_3$)

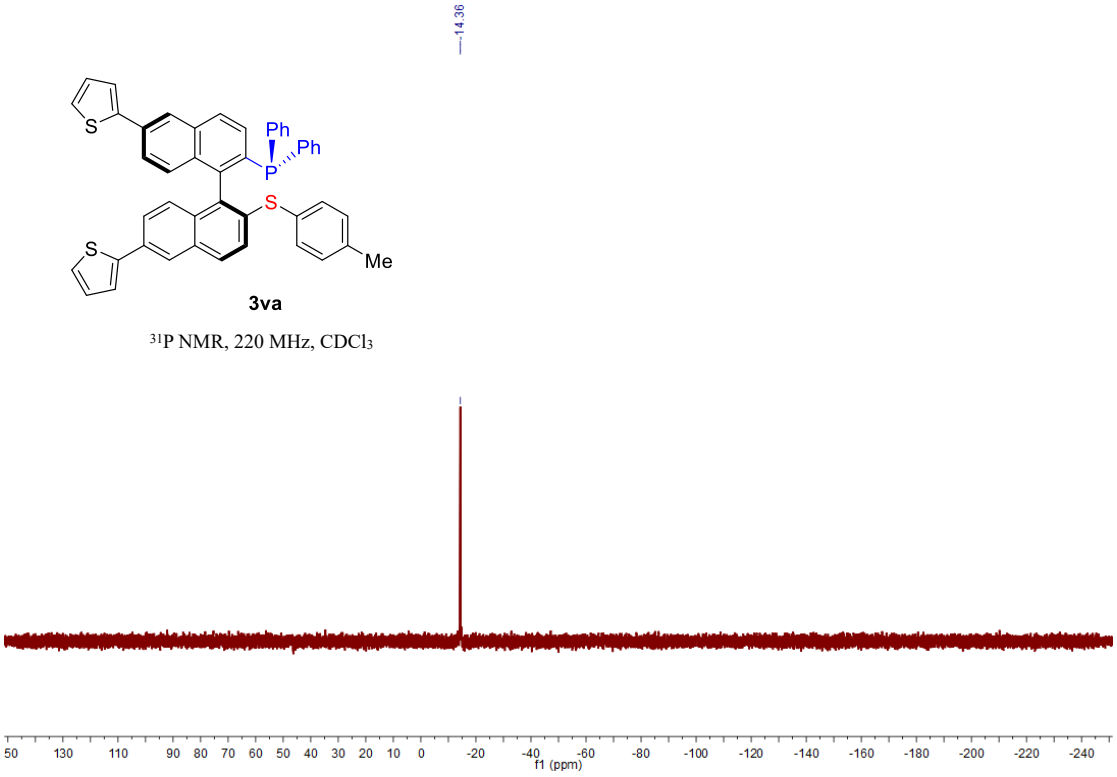


Figure S149. ^{31}P NMR spectrum of 3va (202 MHz, $CDCl_3$)

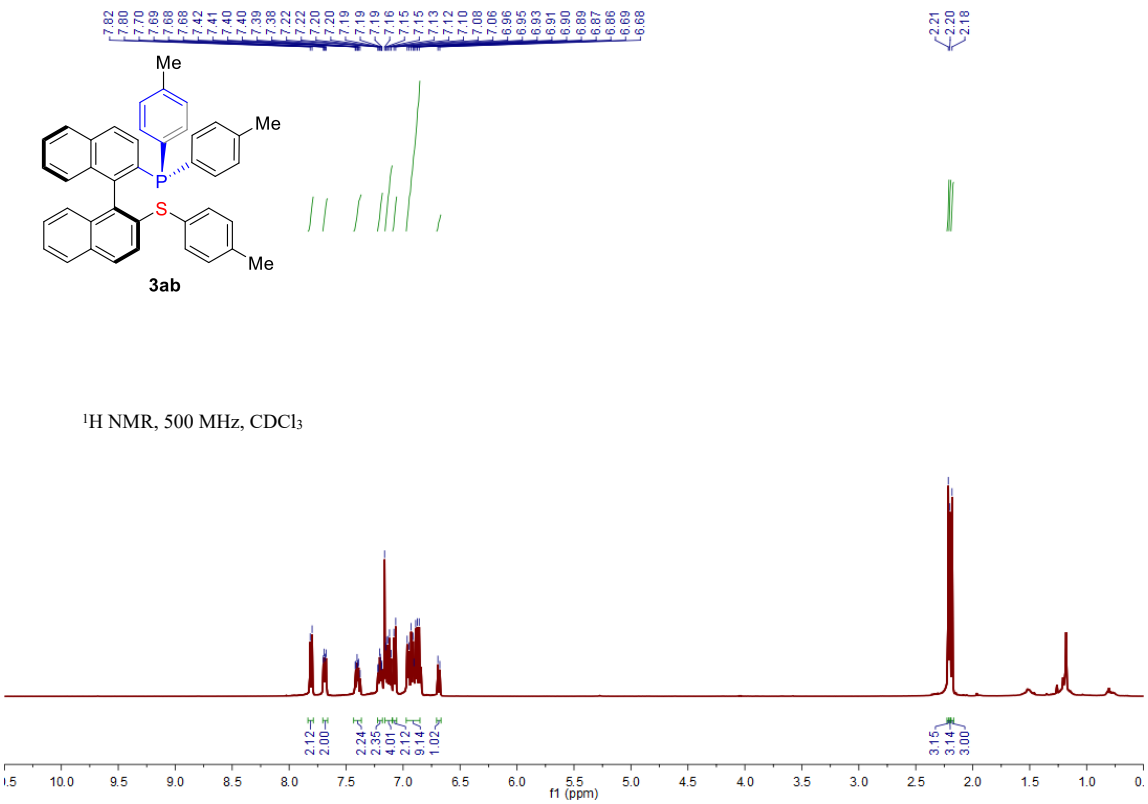


Figure S150. ^{1}H NMR spectrum of 3ab (500 MHz, CDCl$_3$)

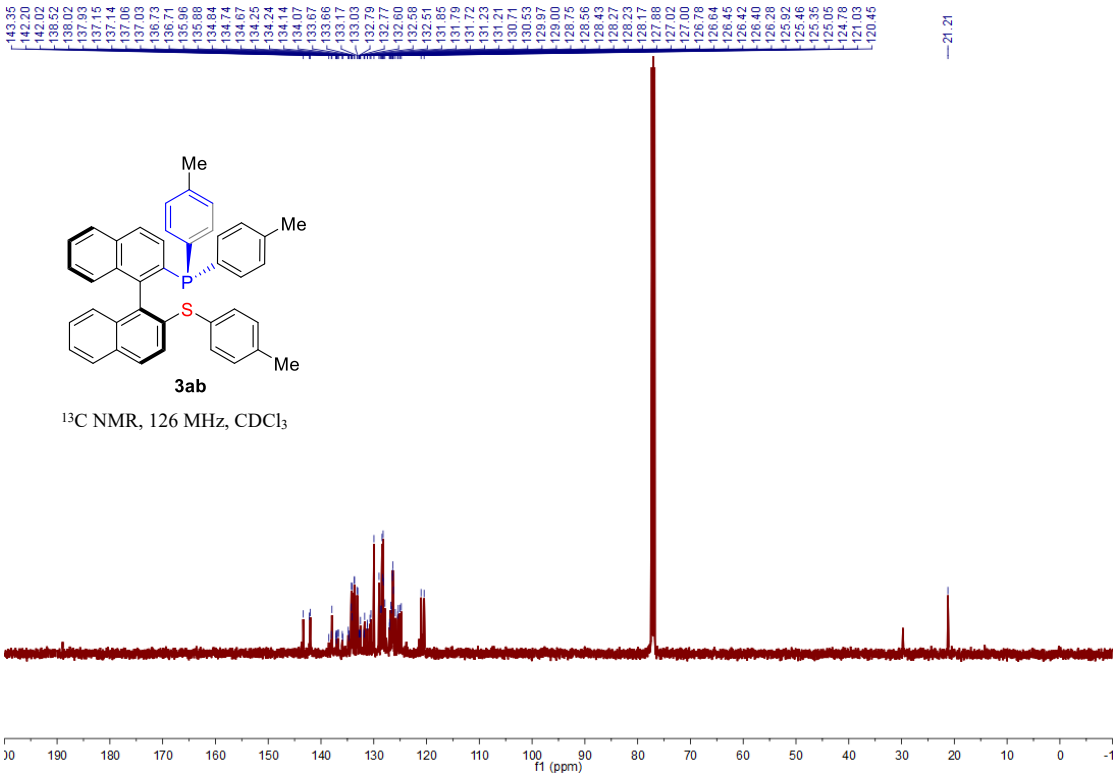


Figure S151. ^{13}C NMR spectrum of 3ab (126 MHz, CDCl$_3$)

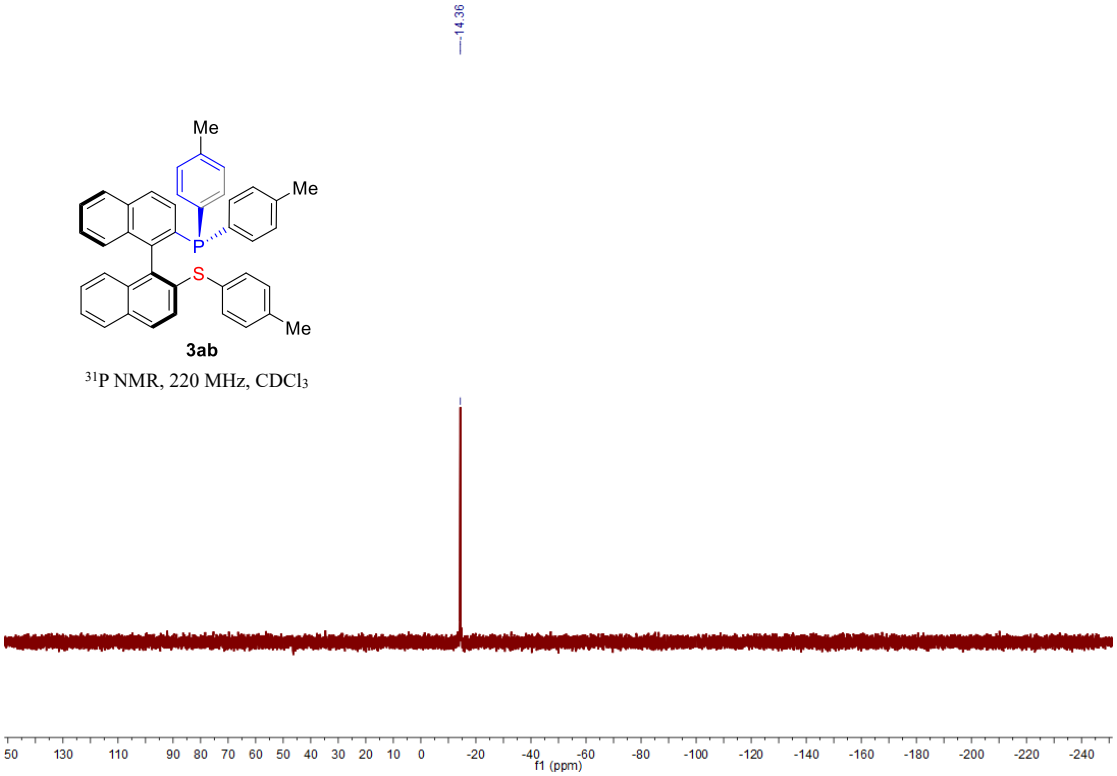


Figure S152. ^{31}P NMR spectrum of 3ab (202 MHz, $CDCl_3$)

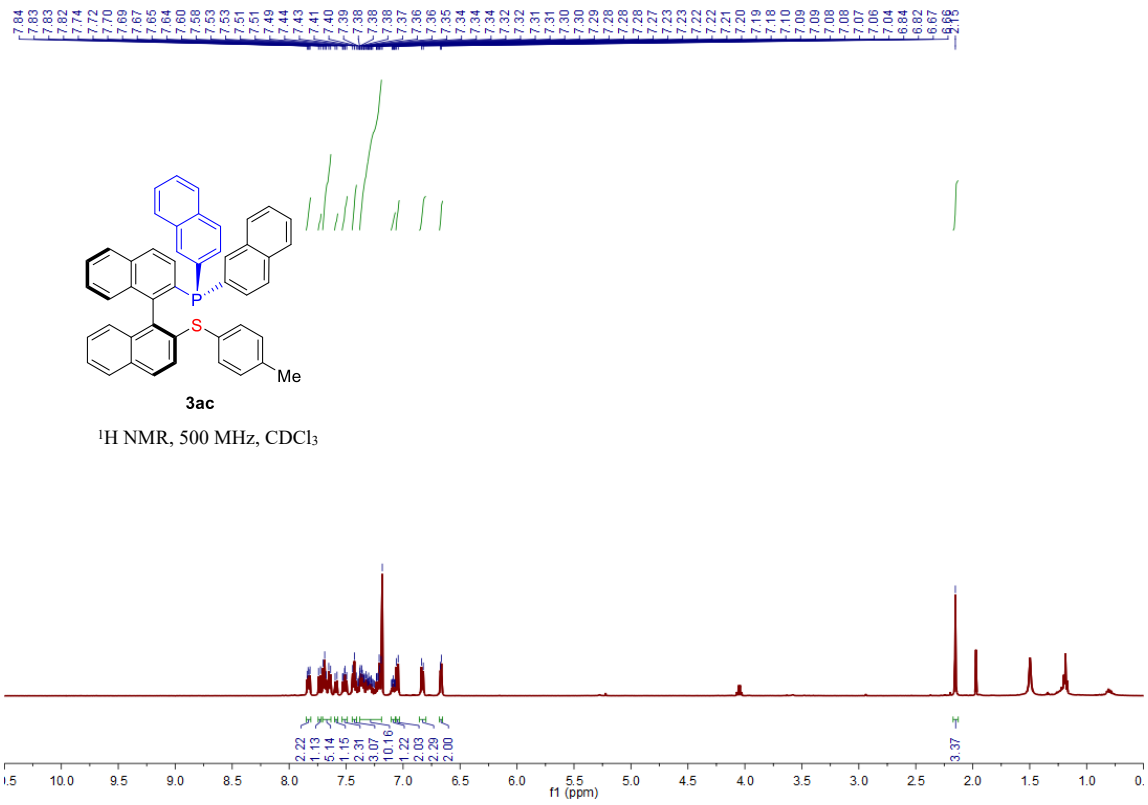


Figure S153. ^{1}H NMR spectrum of 3ac (500 MHz, $CDCl_3$)

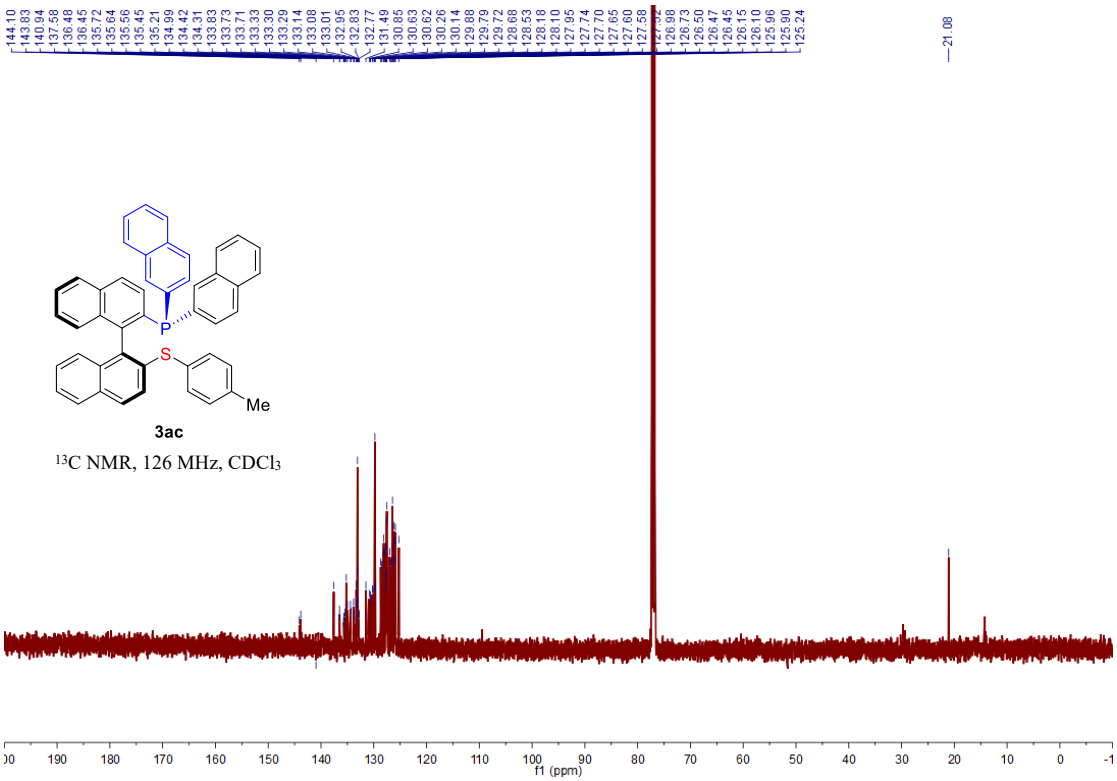


Figure S154. ^{13}C NMR spectrum of 3ac (126 MHz, $CDCl_3$)

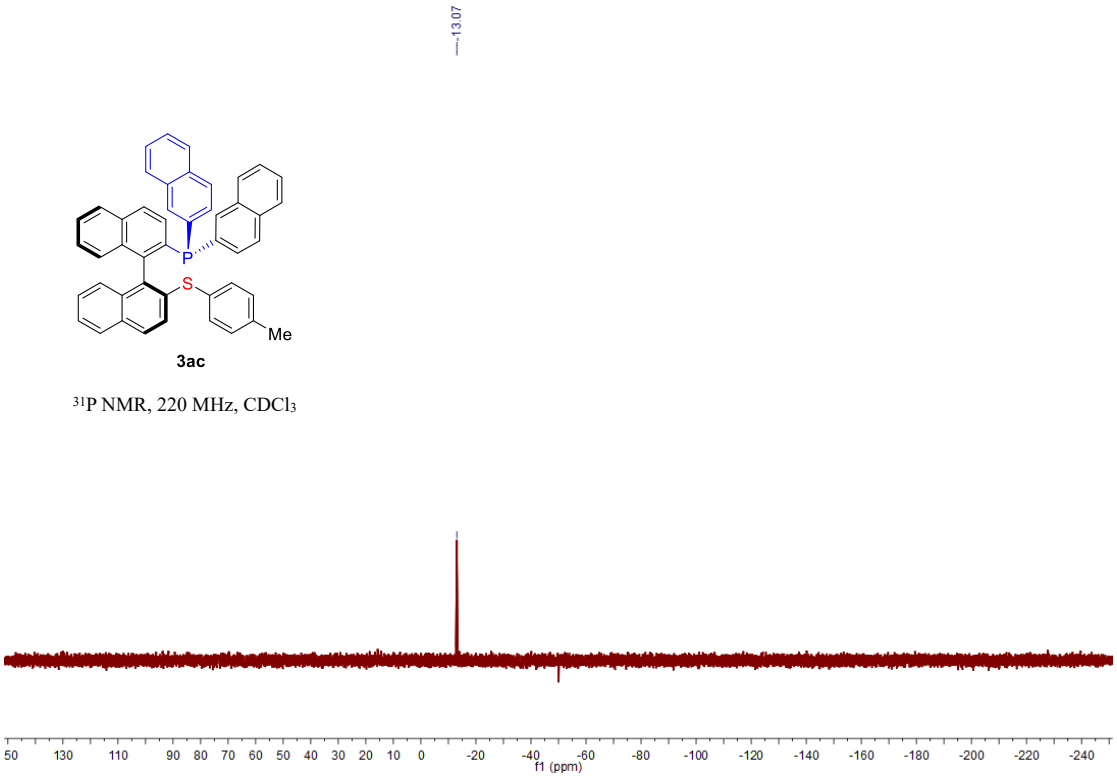


Figure S155. ^{31}P NMR spectrum of 3ac (202 MHz, $CDCl_3$)

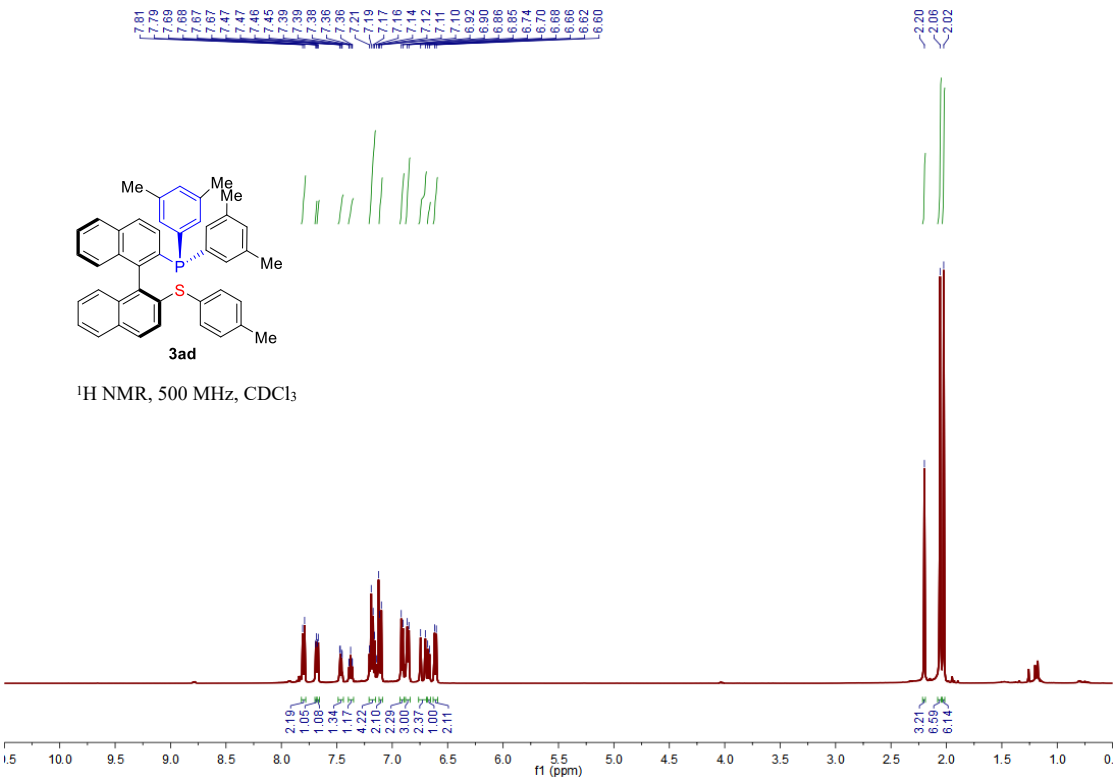


Figure S156. ^{1}H NMR spectrum of 3ad (500 MHz, $CDCl_3$)

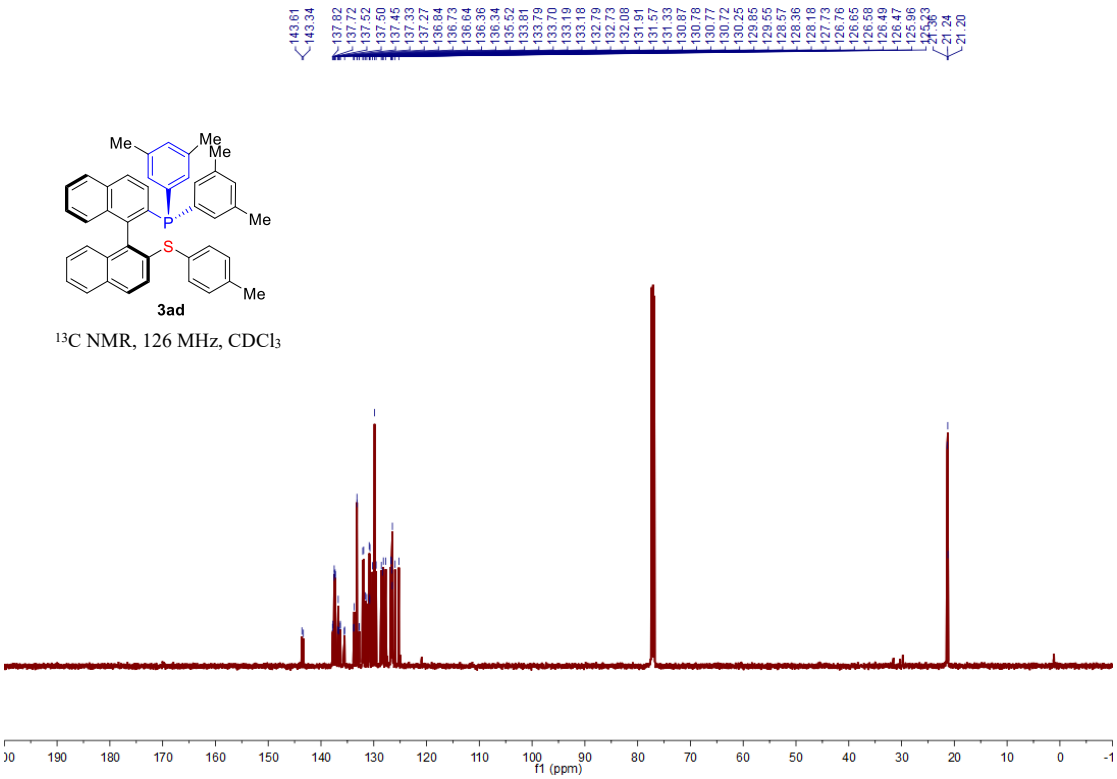
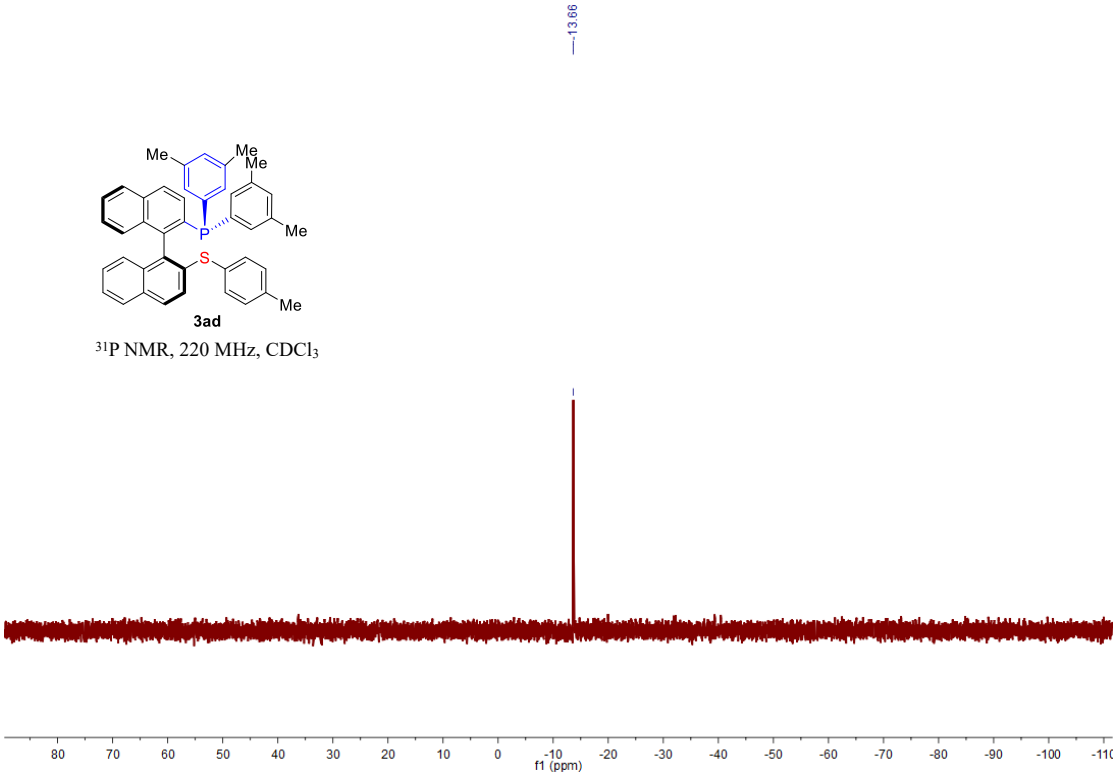
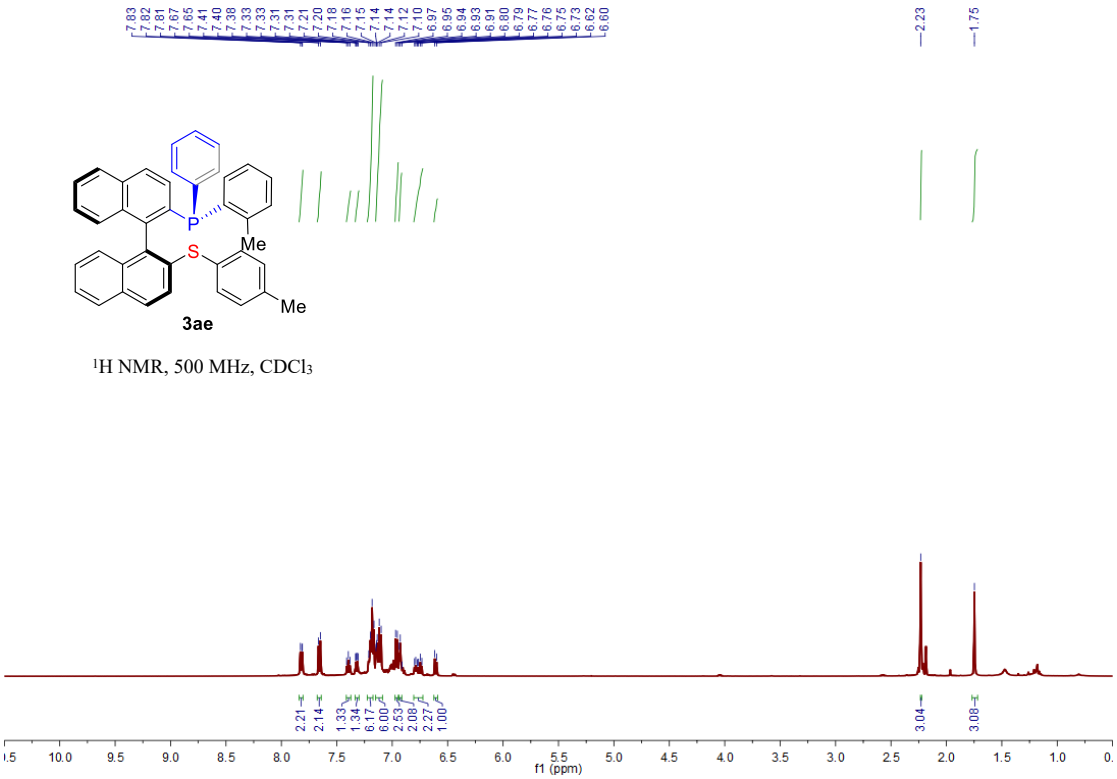


Figure S157. ^{13}C NMR spectrum of 3ad (126 MHz, $CDCl_3$)



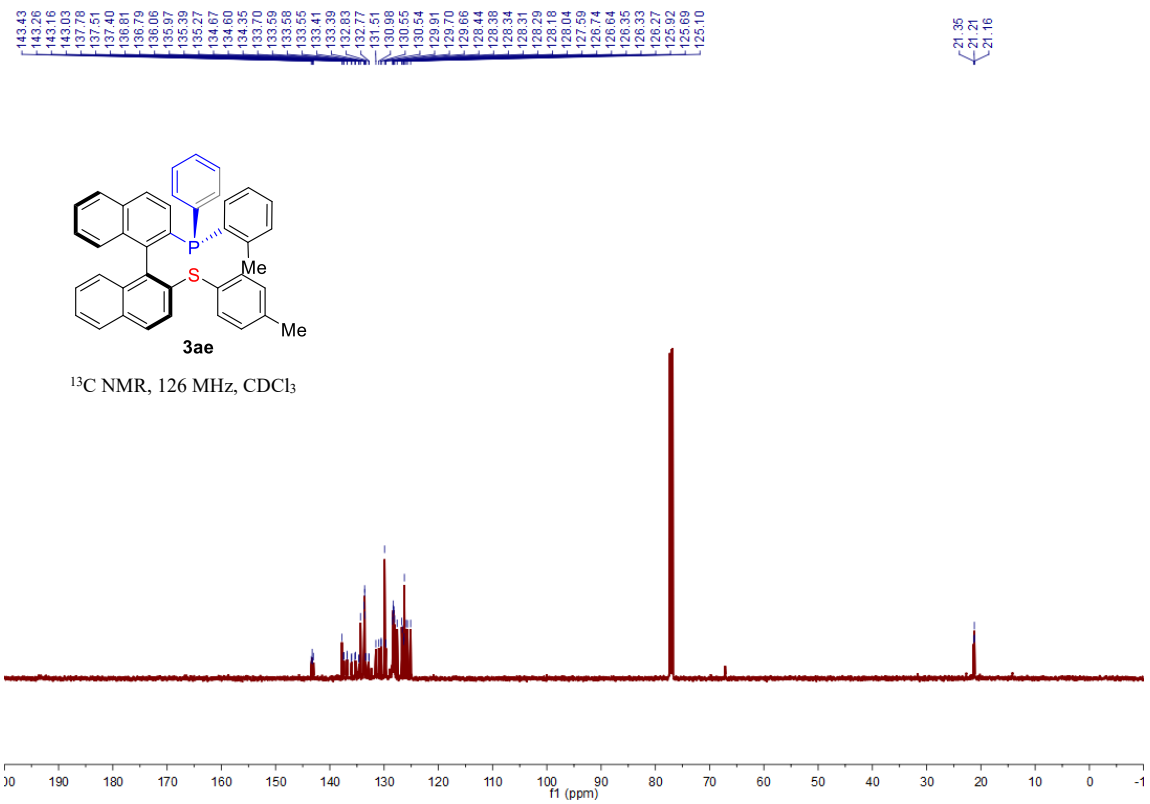
^{31}P NMR, 220 MHz, $CDCl_3$

Figure S158. ^{31}P NMR spectrum of 3ad (202 MHz, $CDCl_3$)



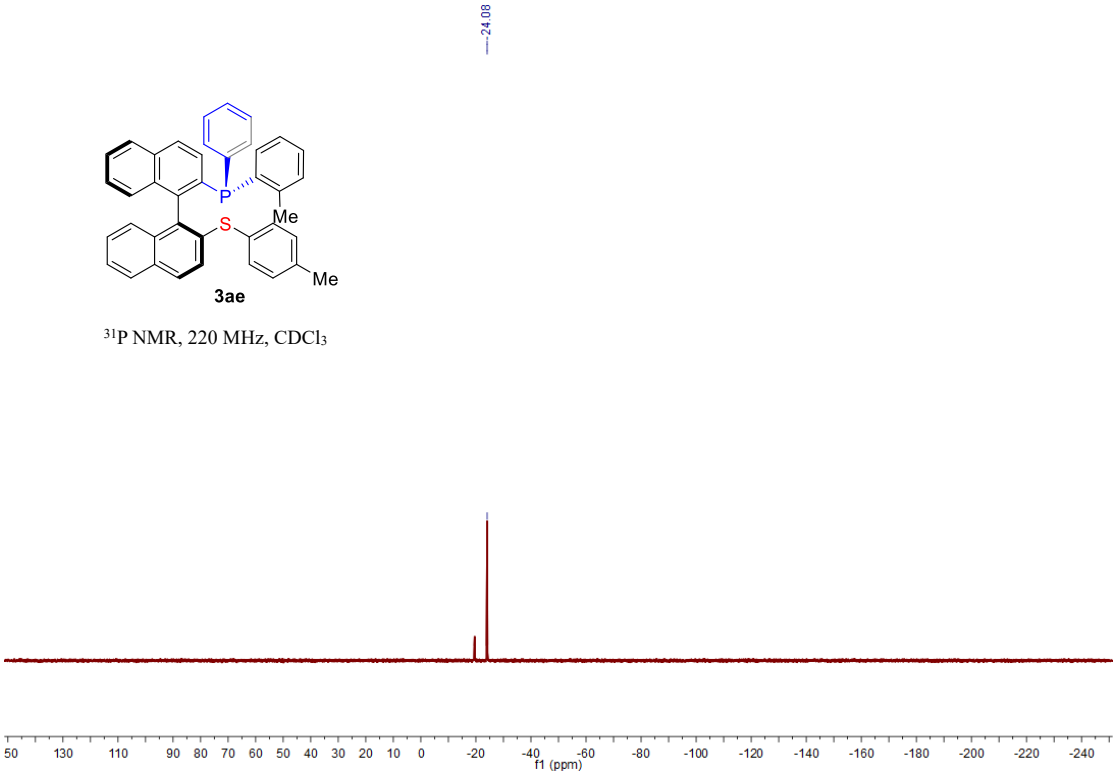
^{1}H NMR, 500 MHz, $CDCl_3$

Figure S159. ^{1}H NMR spectrum of 3ae (500 MHz, $CDCl_3$)



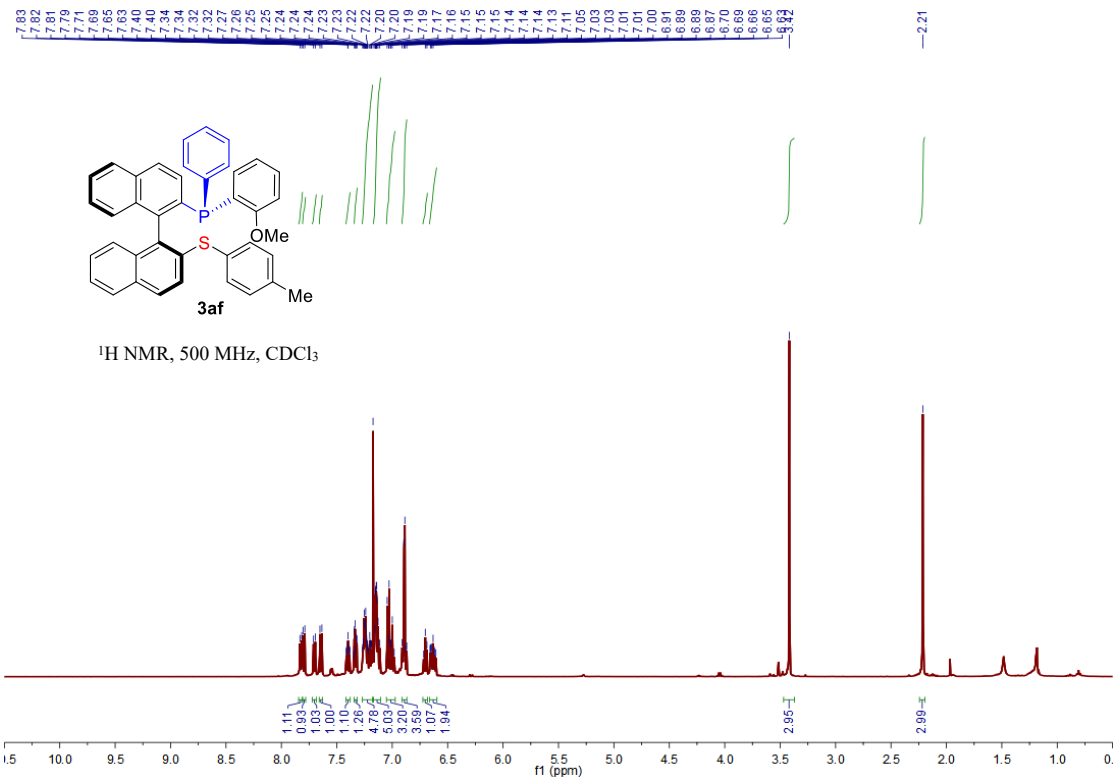
^{13}C NMR, 126 MHz, $CDCl_3$

Figure S160. ^{13}C NMR spectrum of 3ae (126 MHz, $CDCl_3$)



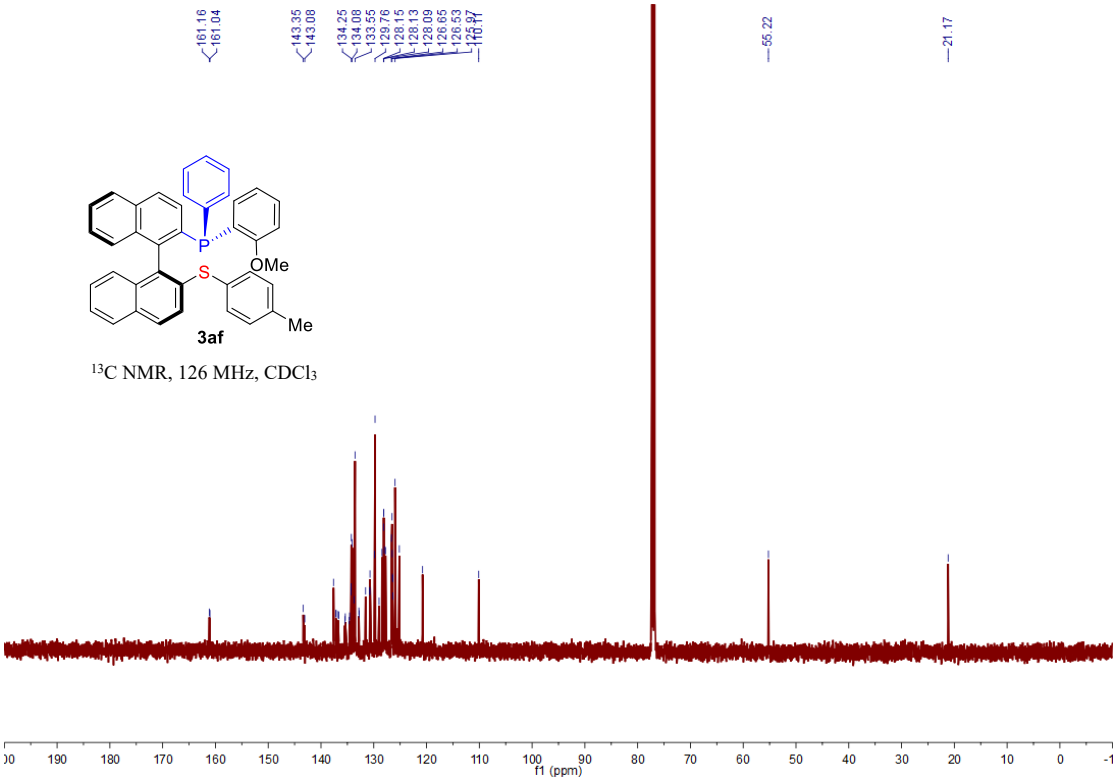
^{31}P NMR, 220 MHz, $CDCl_3$

Figure S161. ^{31}P NMR spectrum of 3ae (202 MHz, $CDCl_3$)



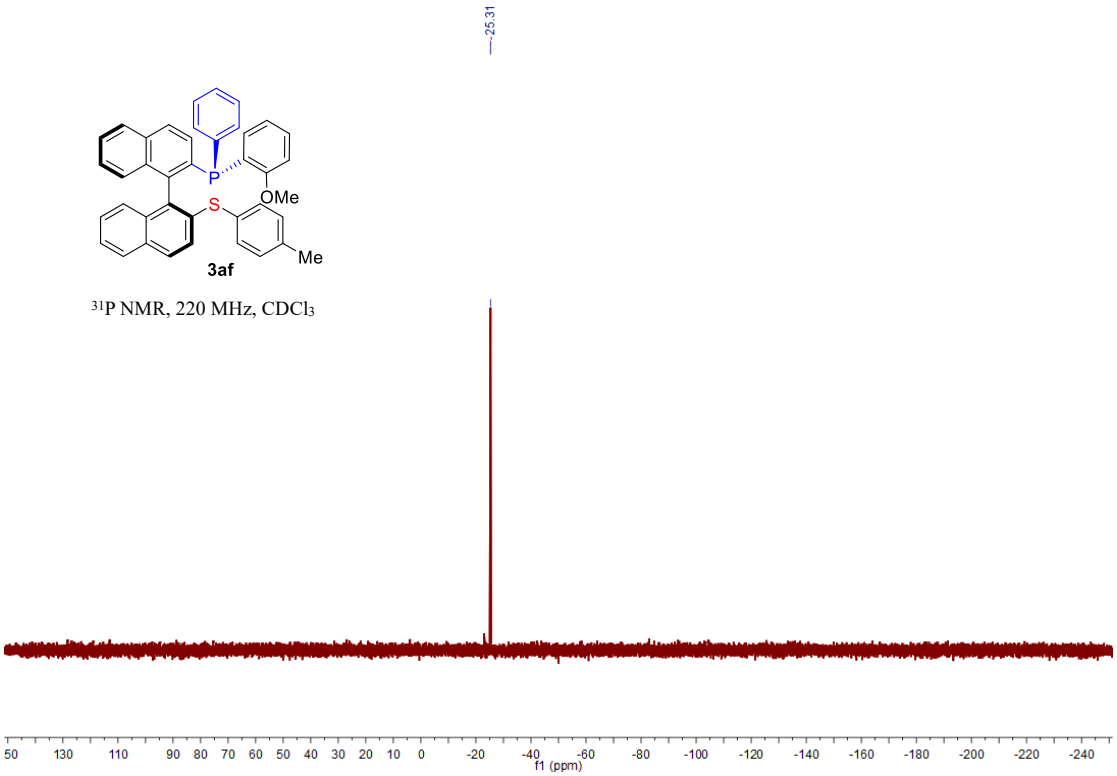
^{1}H NMR, 500 MHz, $CDCl_3$

Figure S162. ^{1}H NMR spectrum of 3af (500 MHz, $CDCl_3$)



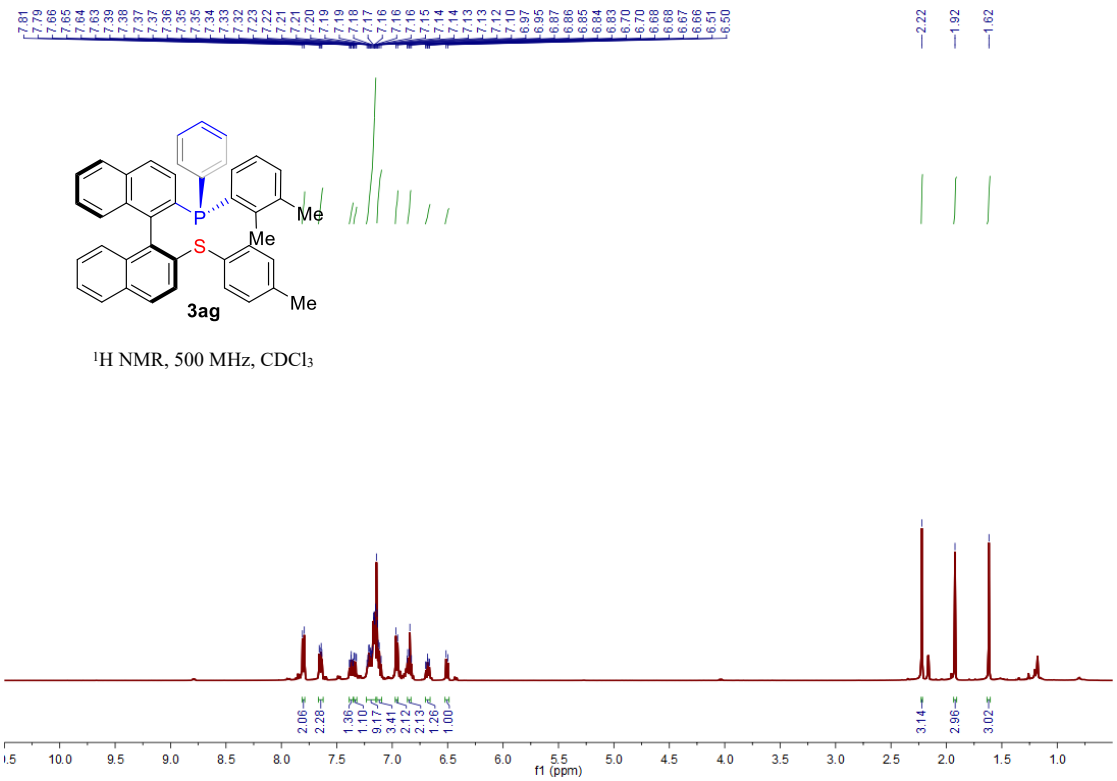
^{13}C NMR, 126 MHz, $CDCl_3$

Figure S163. ^{13}C NMR spectrum of 3af (126 MHz, $CDCl_3$)



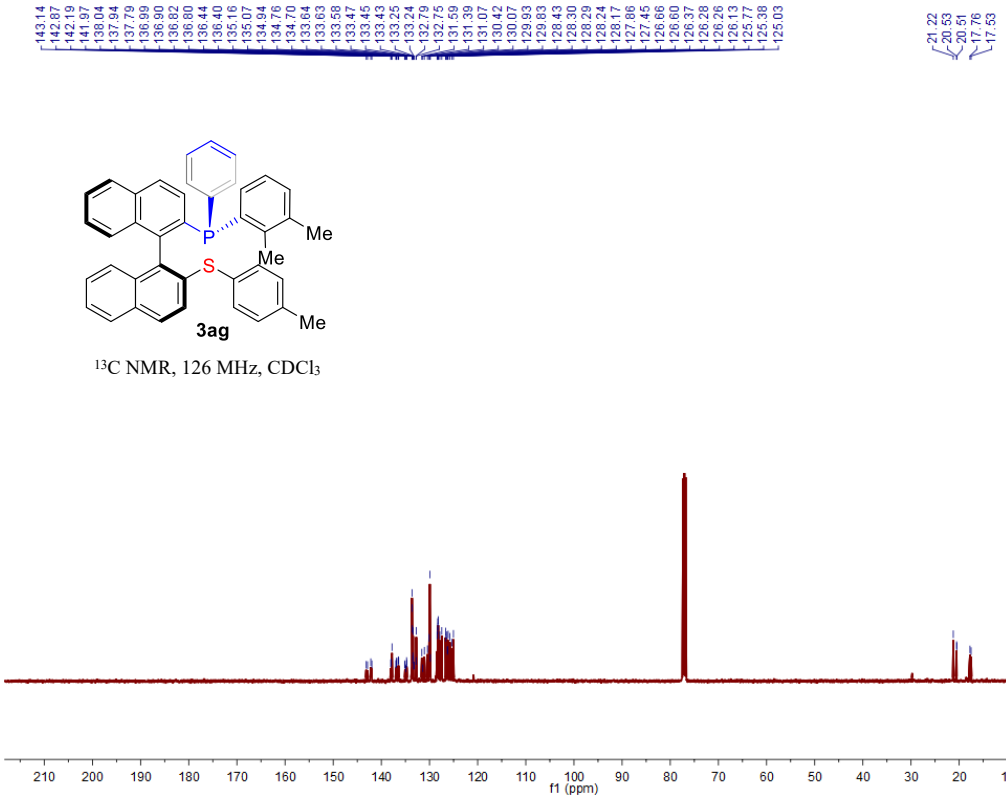
^{31}P NMR, 220 MHz, $CDCl_3$

Figure S164. ^{31}P NMR spectrum of 3af (202 MHz, $CDCl_3$)



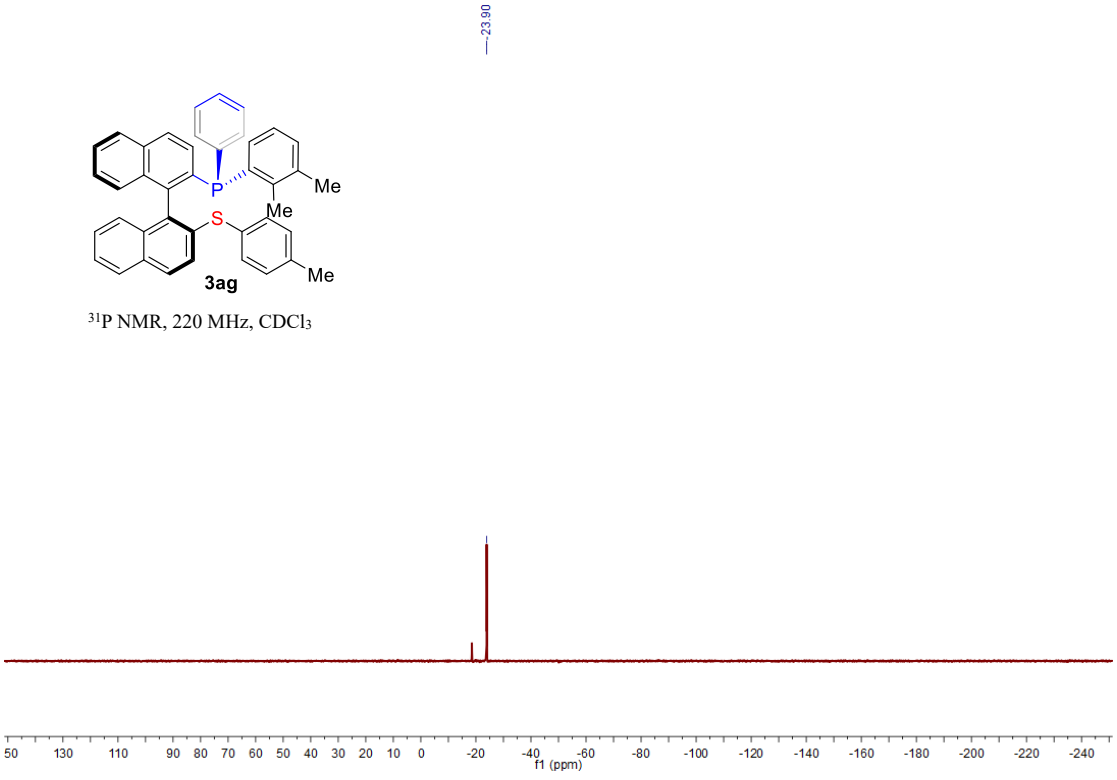
^{1}H NMR, 500 MHz, $CDCl_3$

Figure S165. ^{1}H NMR spectrum of 3ag (500 MHz, $CDCl_3$)



^{13}C NMR, 126 MHz, $CDCl_3$

Figure S166. ^{13}C NMR spectrum of 3ag (126 MHz, $CDCl_3$)



^{31}P NMR, 220 MHz, $CDCl_3$

Figure S167. ^{31}P NMR spectrum of 3ag (202 MHz, $CDCl_3$)

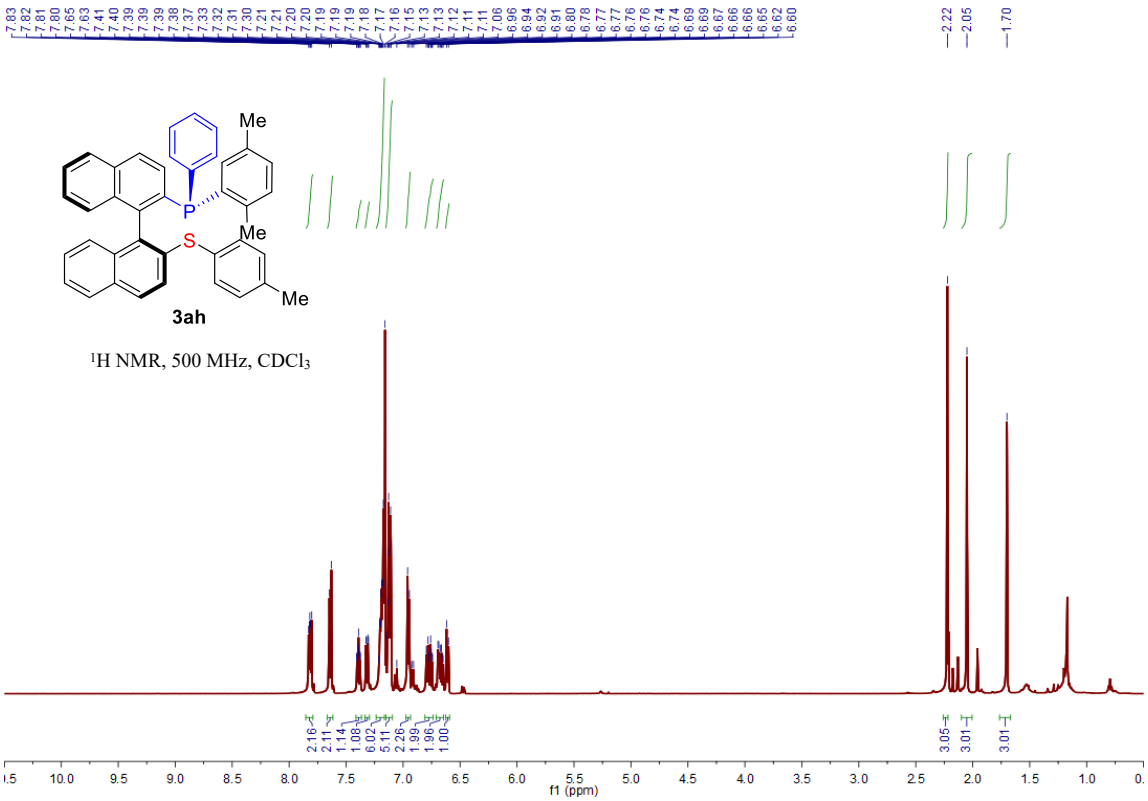


Figure S168. ^{1}H NMR spectrum of 3ah (500 MHz, $CDCl_3$)

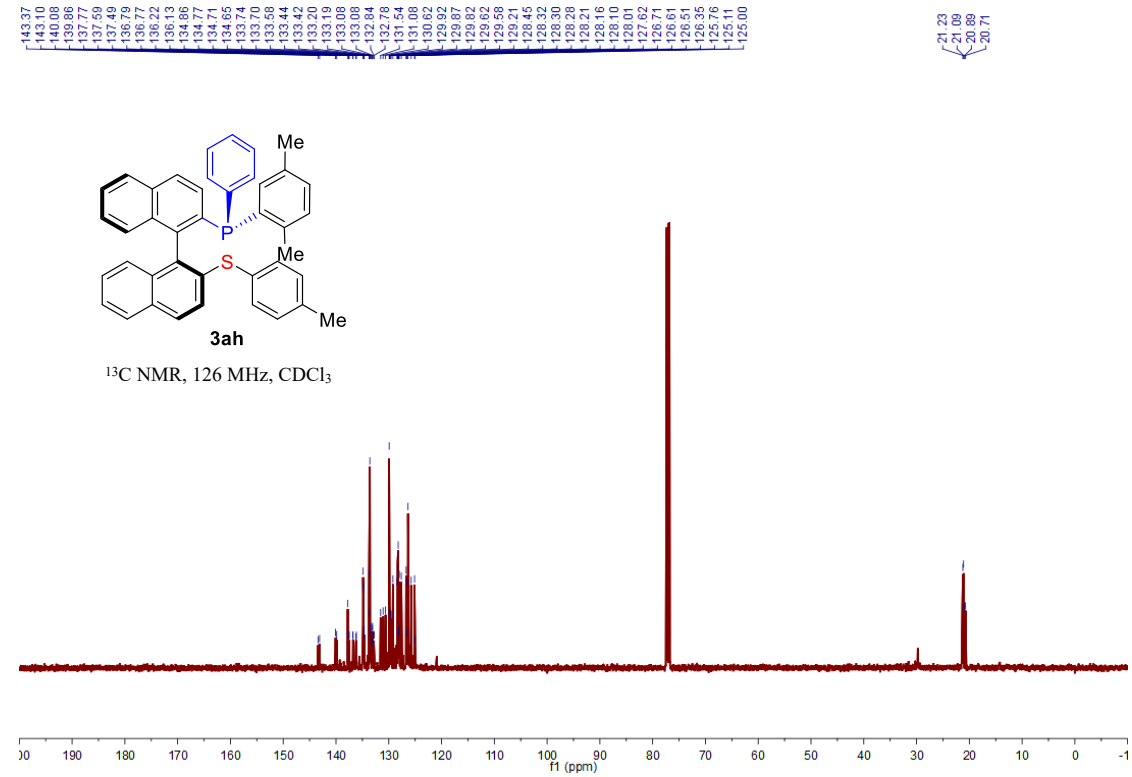


Figure S169. ^{13}C NMR spectrum of 3ah (126 MHz, $CDCl_3$)

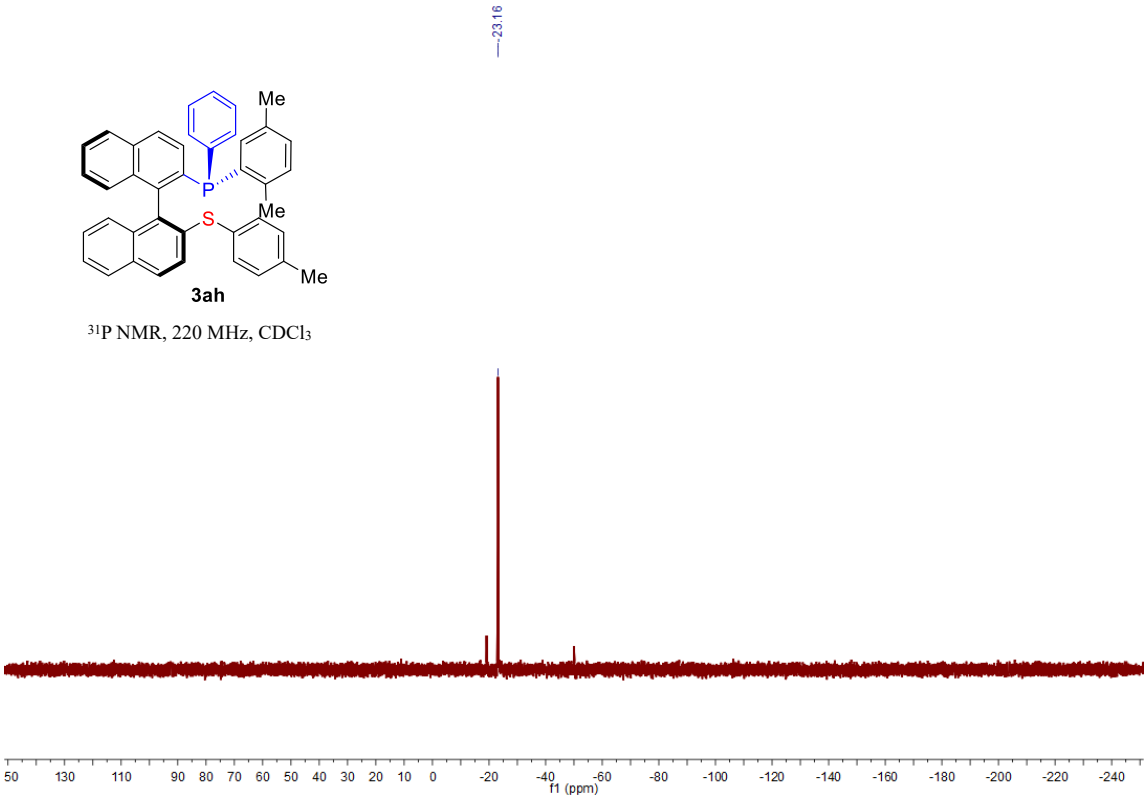


Figure S170. ^{31}P NMR spectrum of 3ah (202 MHz, $CDCl_3$)

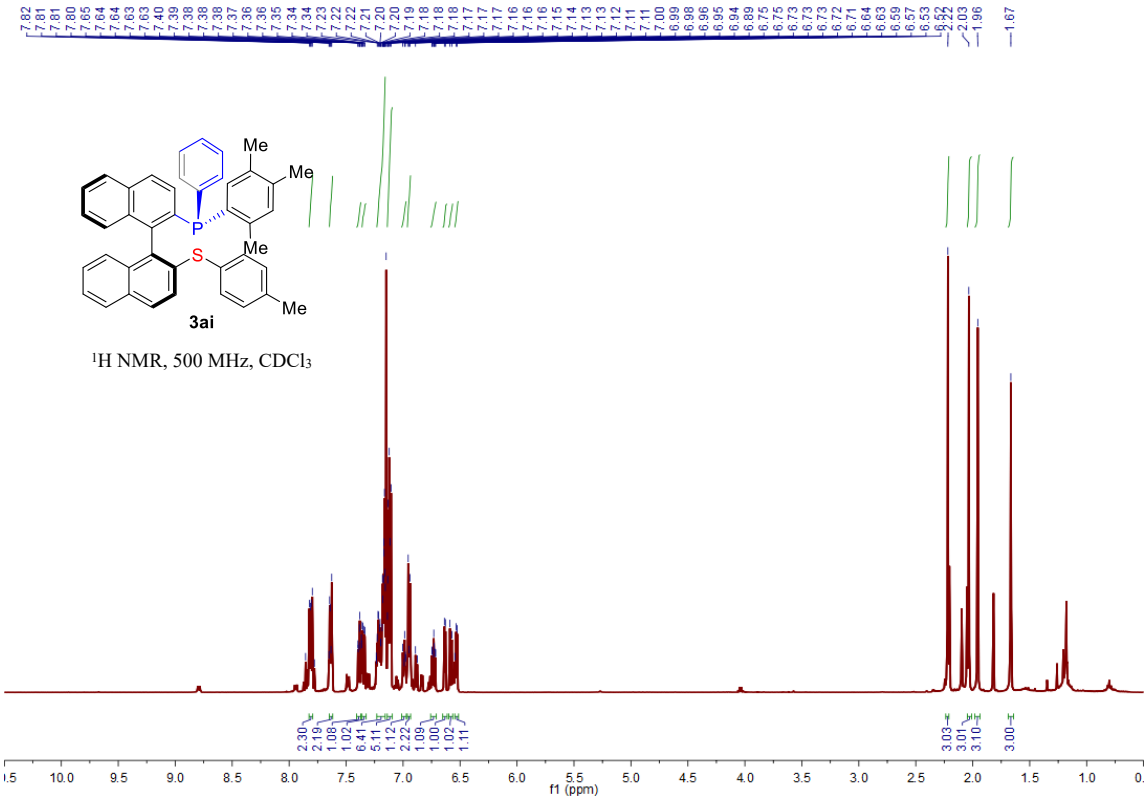
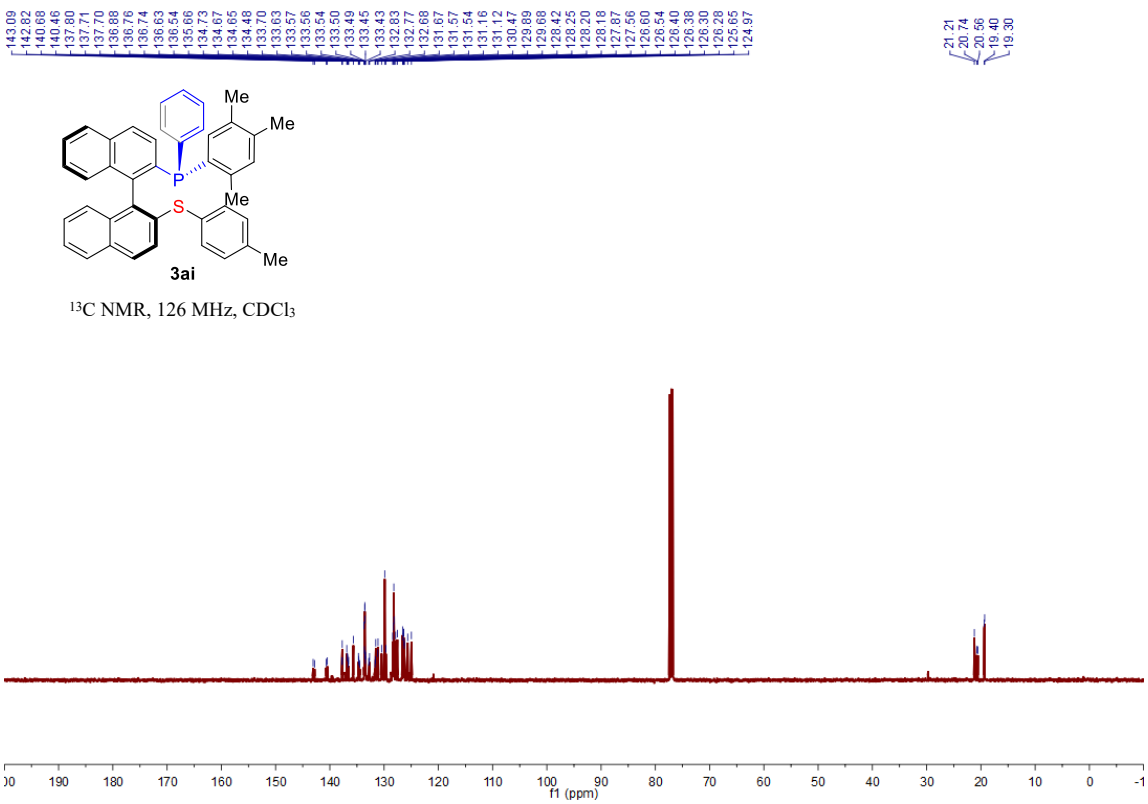
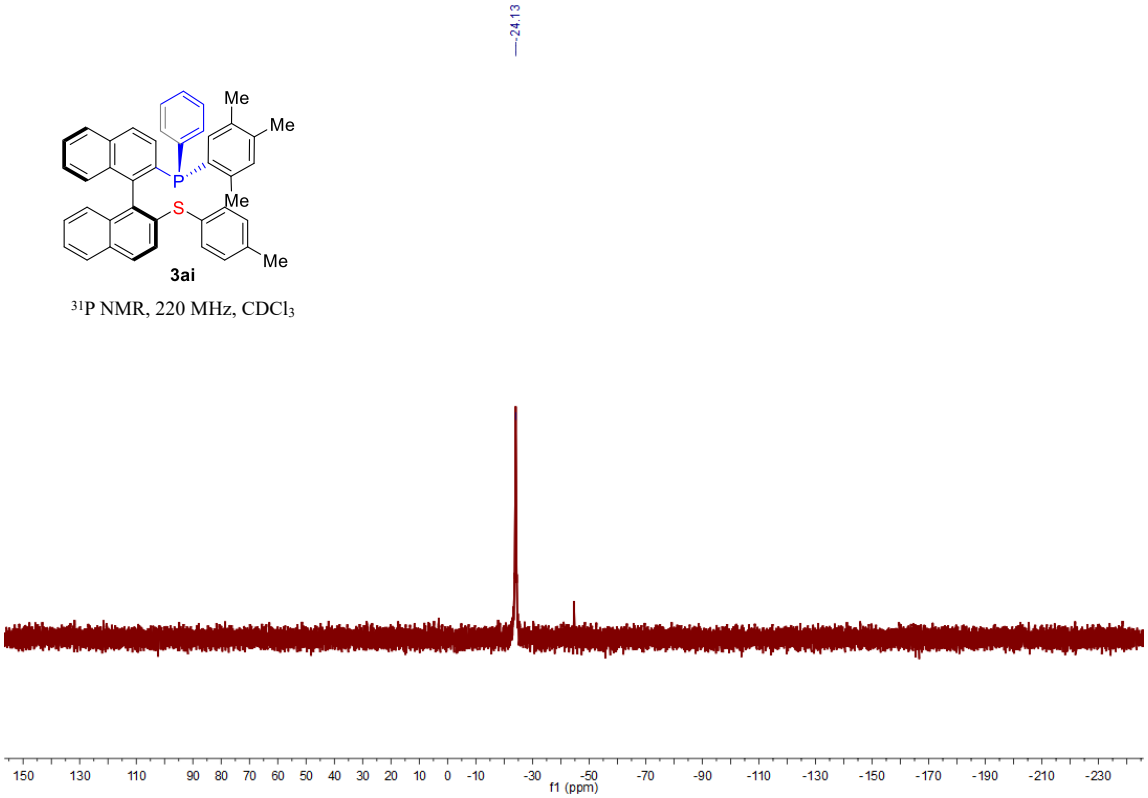


Figure S171. ^{1}H NMR spectrum of 3ai (500 MHz, $CDCl_3$)



^{13}C NMR, 126 MHz, $CDCl_3$

Figure S172. ^{13}C NMR spectrum of 3ai (126 MHz, $CDCl_3$)



^{31}P NMR, 220 MHz, $CDCl_3$

Figure S173. ^{31}P NMR spectrum of 3ai (202 MHz, $CDCl_3$)

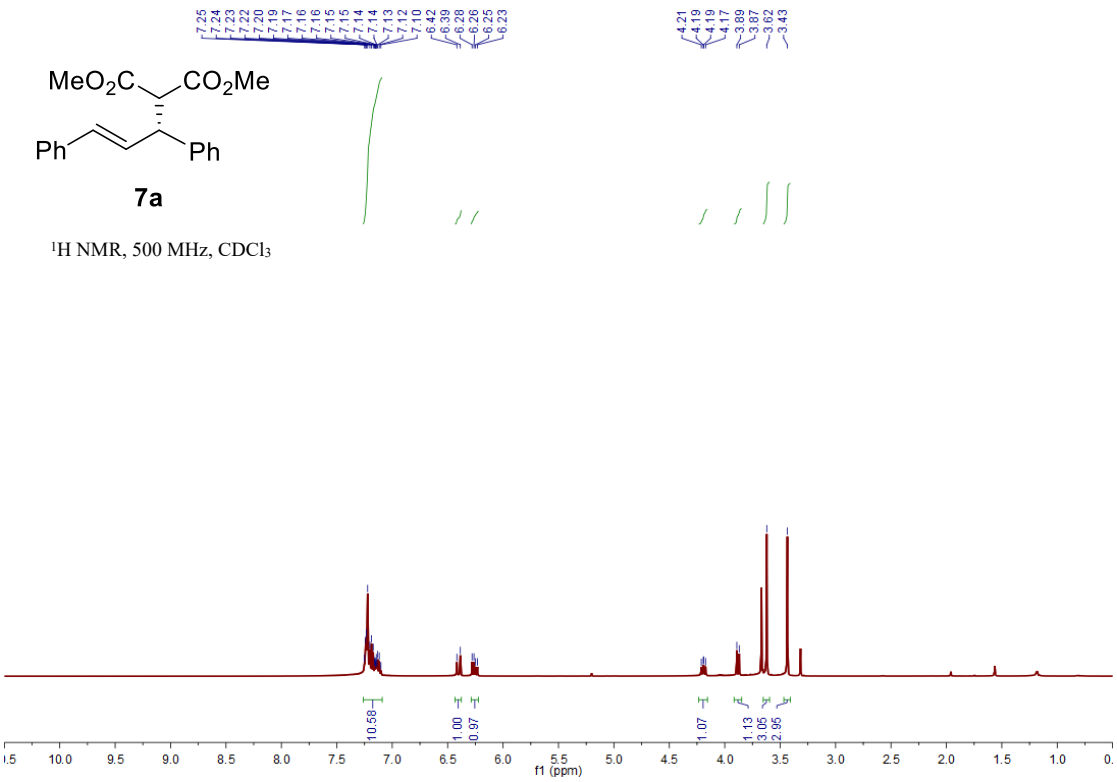


Figure S174. ^{1}H NMR spectrum of 7a (500 MHz, $CDCl_3$)

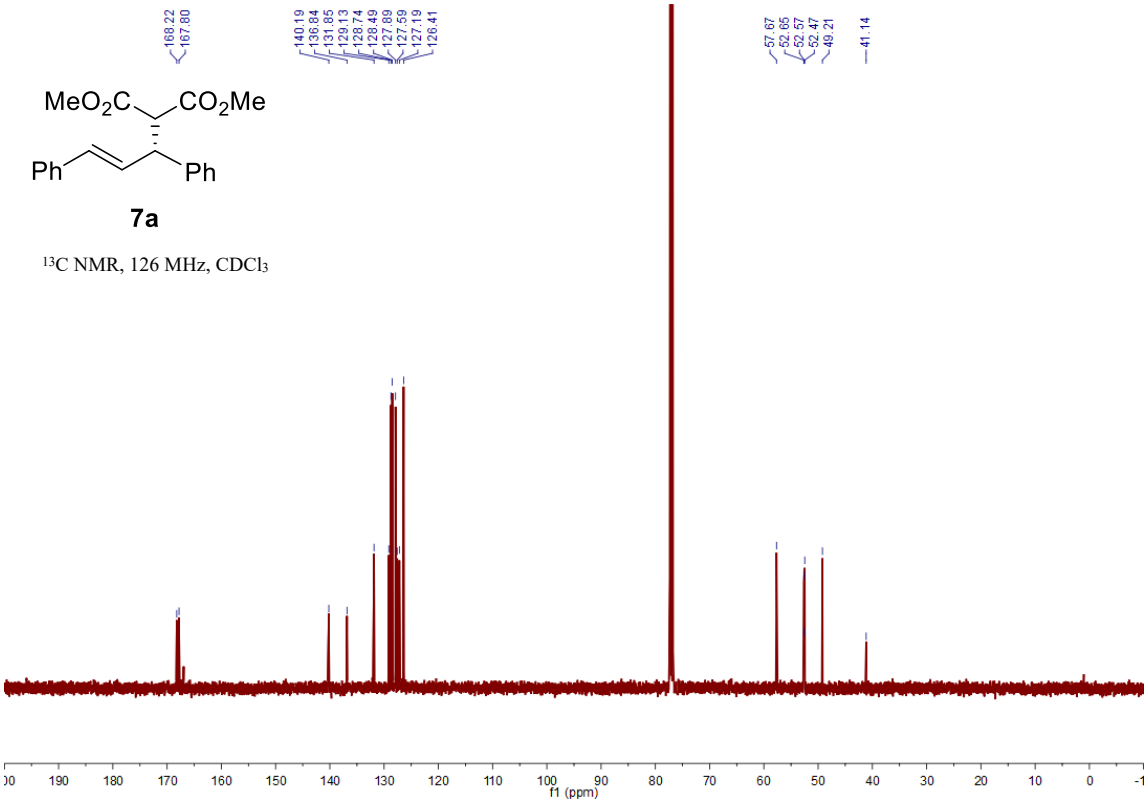


Figure S175. ^{13}C NMR spectrum of 7a (126 MHz, $CDCl_3$)

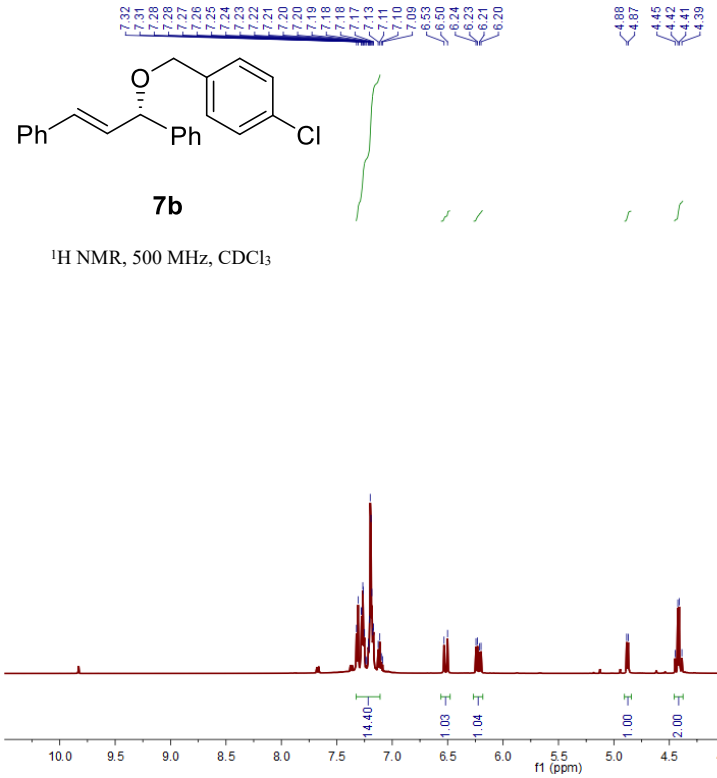


Figure S176. ^{1}H NMR spectrum of 7b (500 MHz, $CDCl_3$)

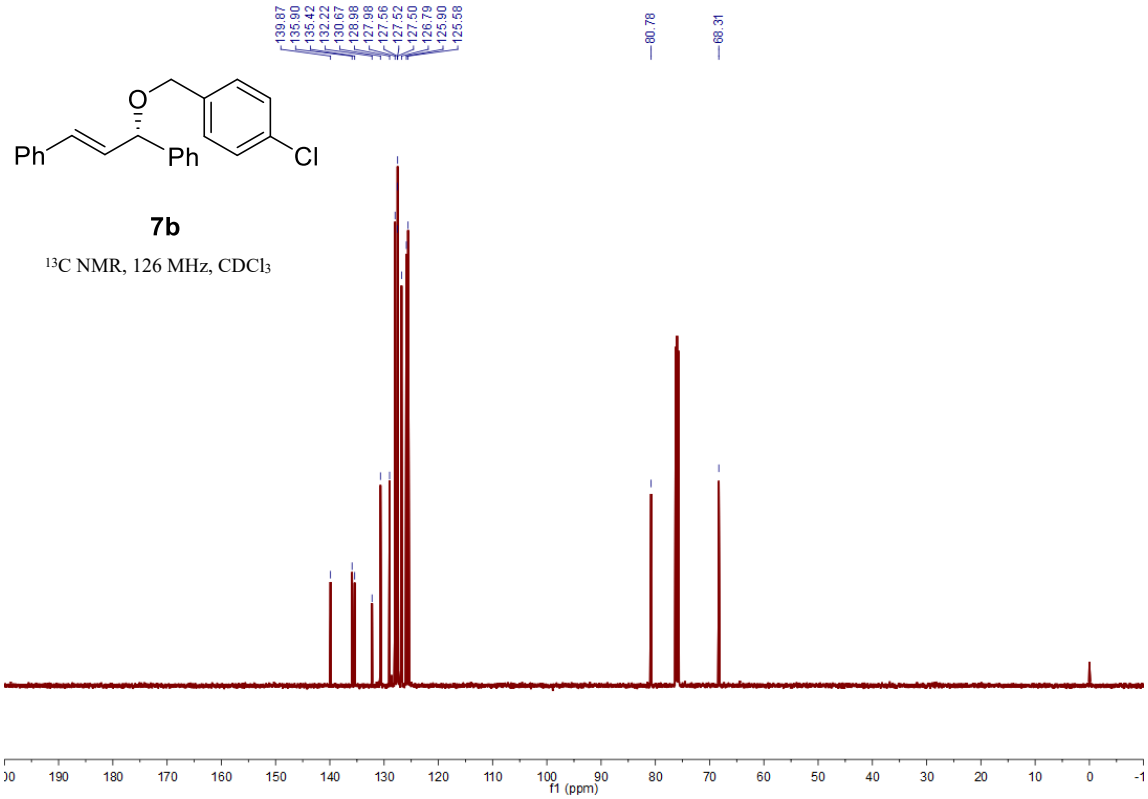
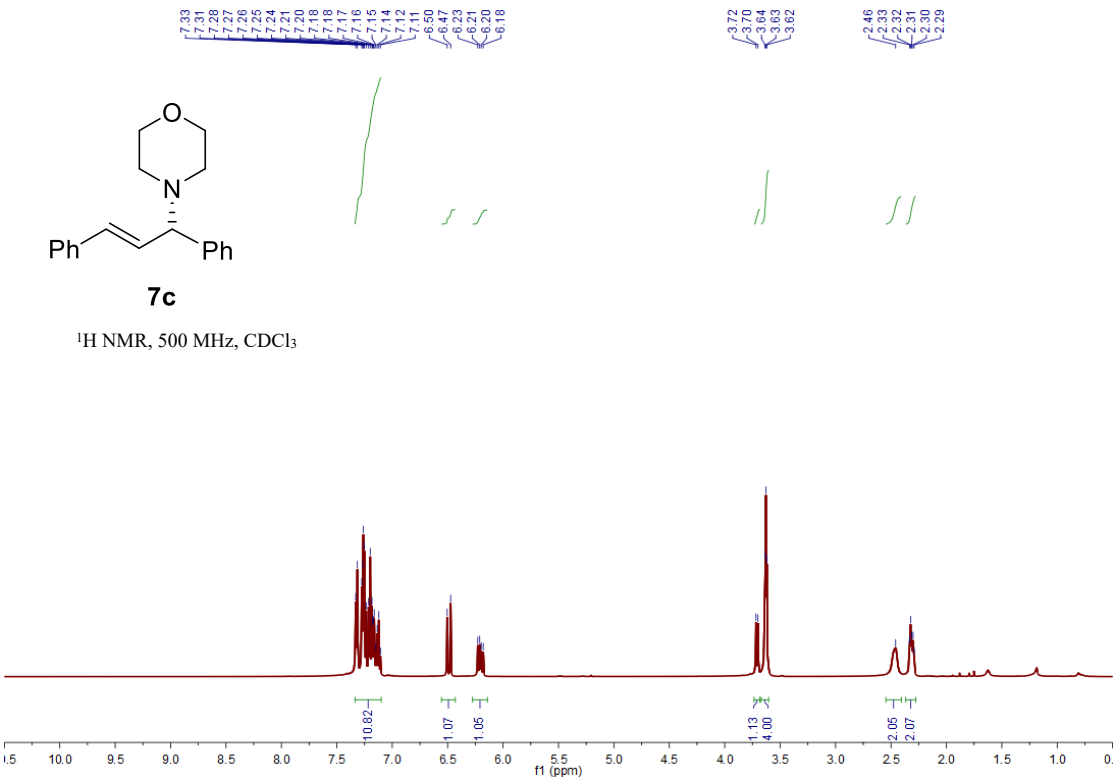


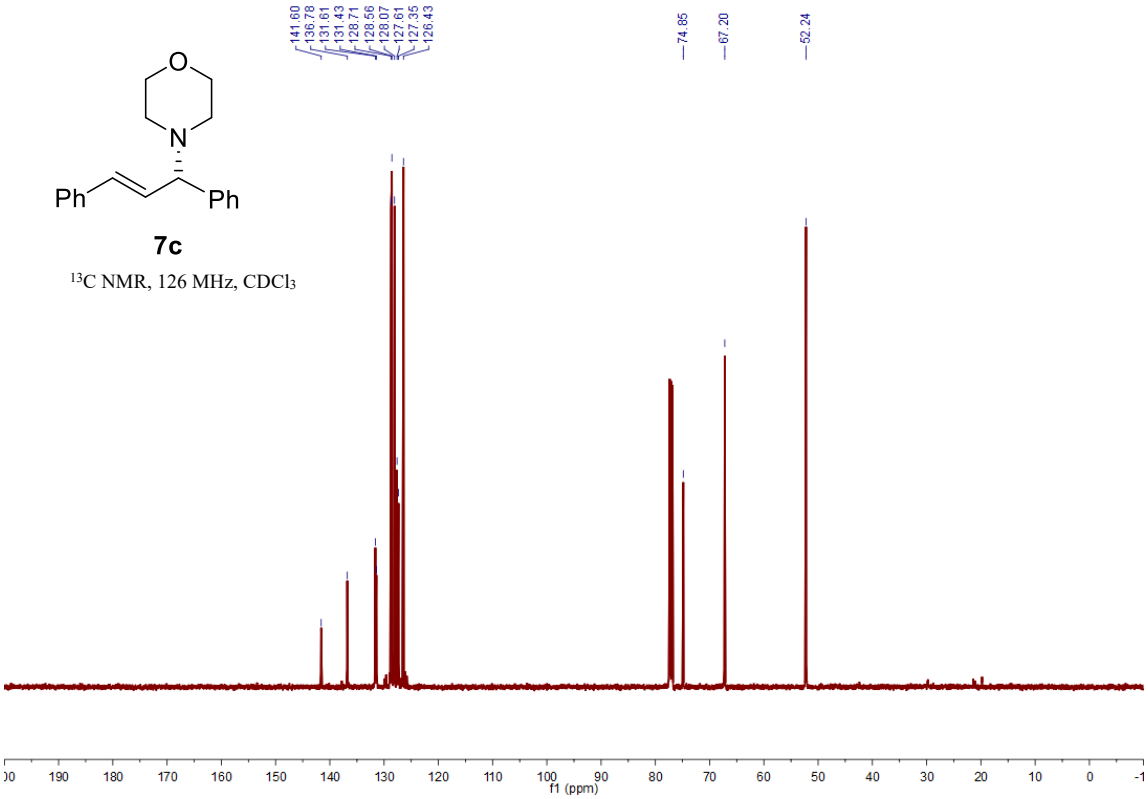
Figure S177. ^{13}C NMR spectrum of 7b (126 MHz, $CDCl_3$)



7c

^{1}H NMR, 500 MHz, $CDCl_3$

Figure S178. ^{1}H NMR spectrum of 7c (500 MHz, $CDCl_3$)

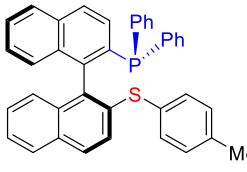


7c

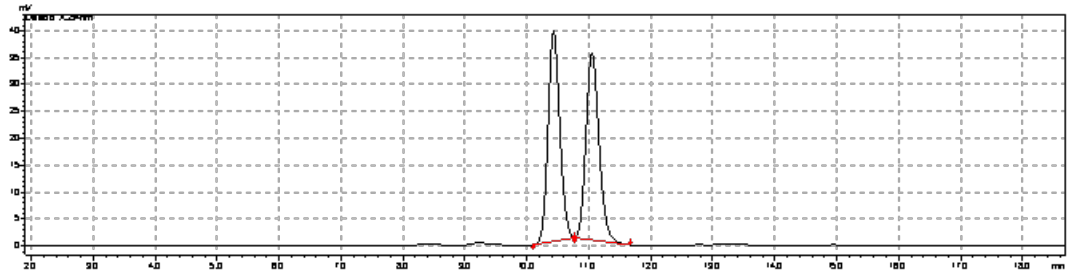
^{13}C NMR, 126 MHz, $CDCl_3$

Figure S178. ^{13}C NMR spectrum of 7c (126 MHz, $CDCl_3$)

HPLC Charts

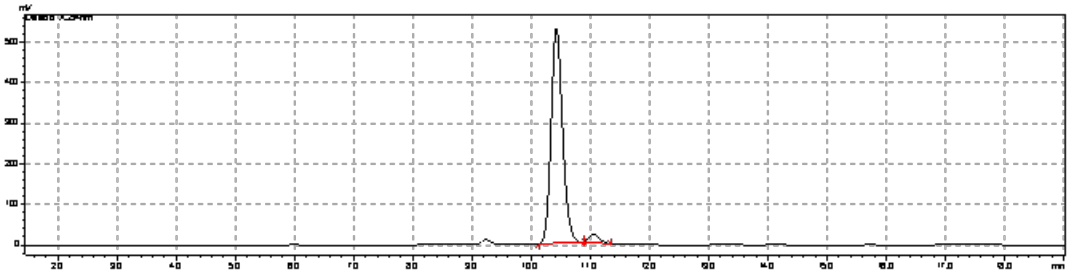


3aa



Detector A channel 254 nm

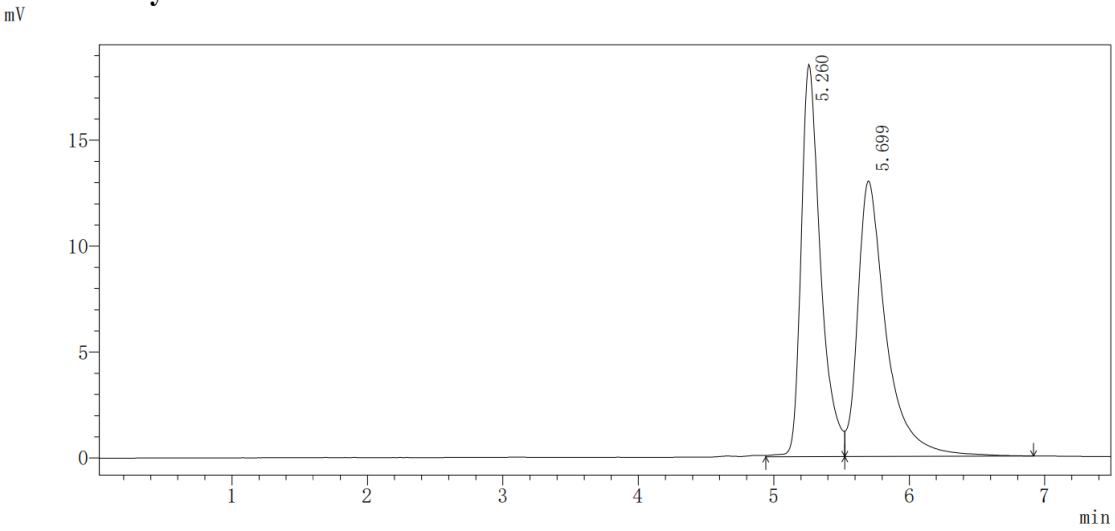
Peak	Ret. Time	Area	Height	Conc.
1	10.426	515491	38951	50.243
2	11.046	510509	34763	49.757
Total		1026000	73714	100.000



Detector A channel 254 nm

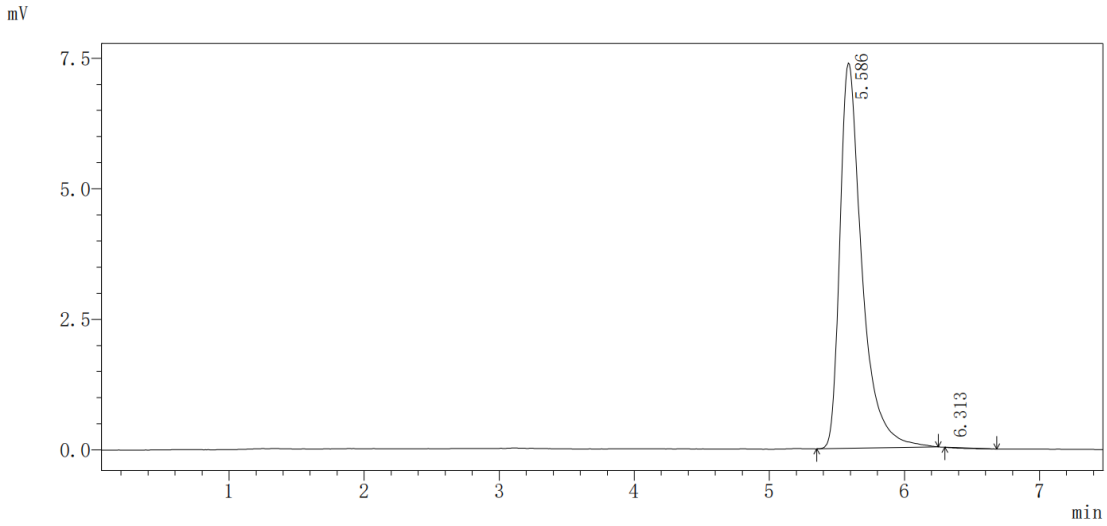
Peak	Ret. Time	Area	Height	Conc.
1	10.420	7085790	528525	96.572
2	11.048	251555	20128	3.428
Total		7337345	548653	100.000

After Recrystallization:



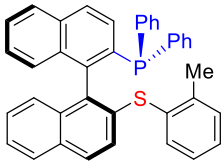
channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	5.260	185738	18514	49.569
2	5.699	188964	13014	50.431
Total		374702	31527	

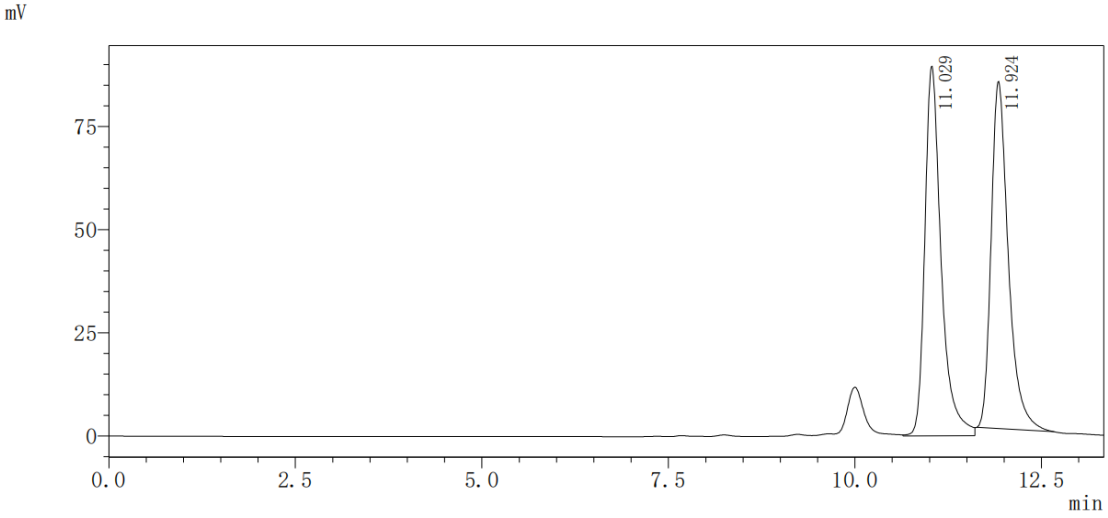


channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	5.586	83682	7376	99.771
2	6.271	192	24	0.229
Total		83874	7400	

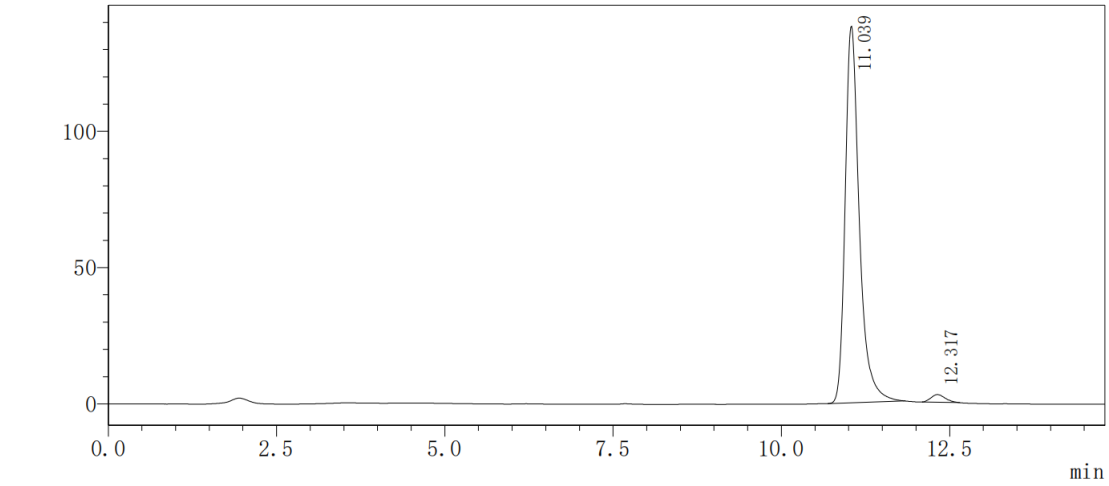


3ba



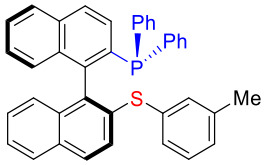
Detector A channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	11.029	1366805	89528	50.364
2	11.924	1347036	84083	49.636
Total		2713841	173610	

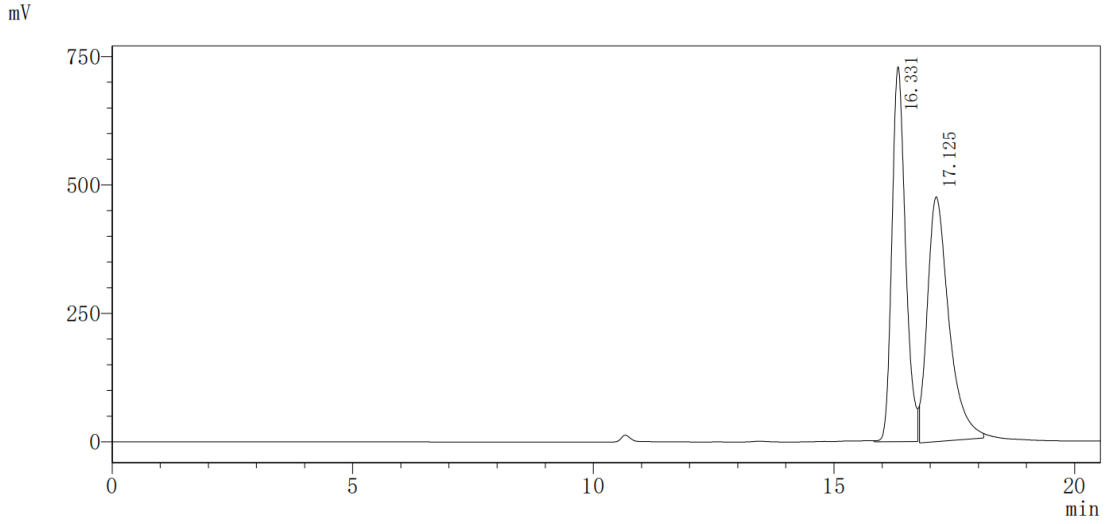


Detector A channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	11.039	2011711	138131	97.971
2	12.317	41671	2834	2.029
Total		2053382	140965	

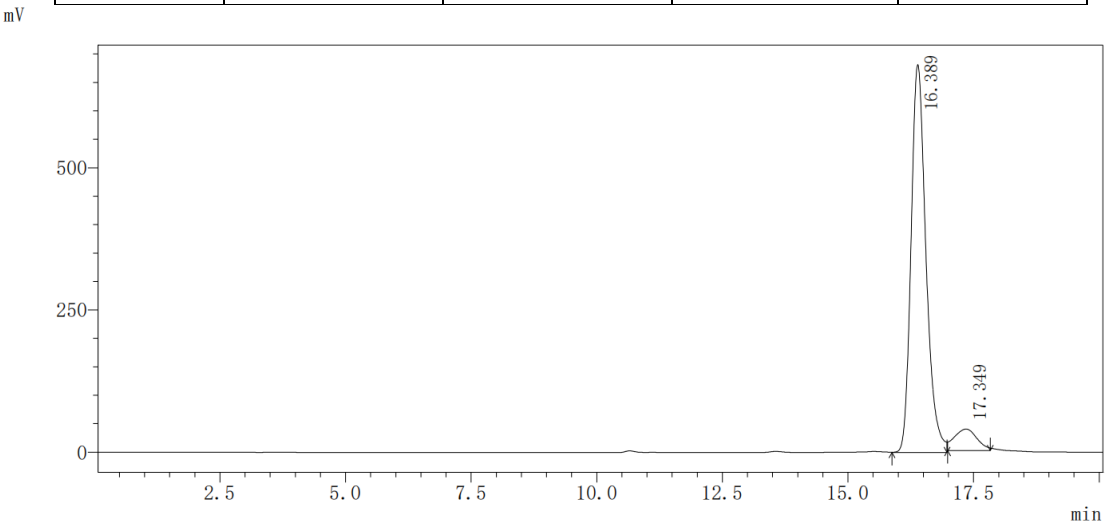


3ca



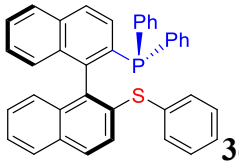
Detector A channel 230 nm

Peak	Ret. Time	Area	Height	Conc.
1	16.331	14342519	729557	49.162
2	17.125	14831466	476772	50.838
Total		29173985	1206329	

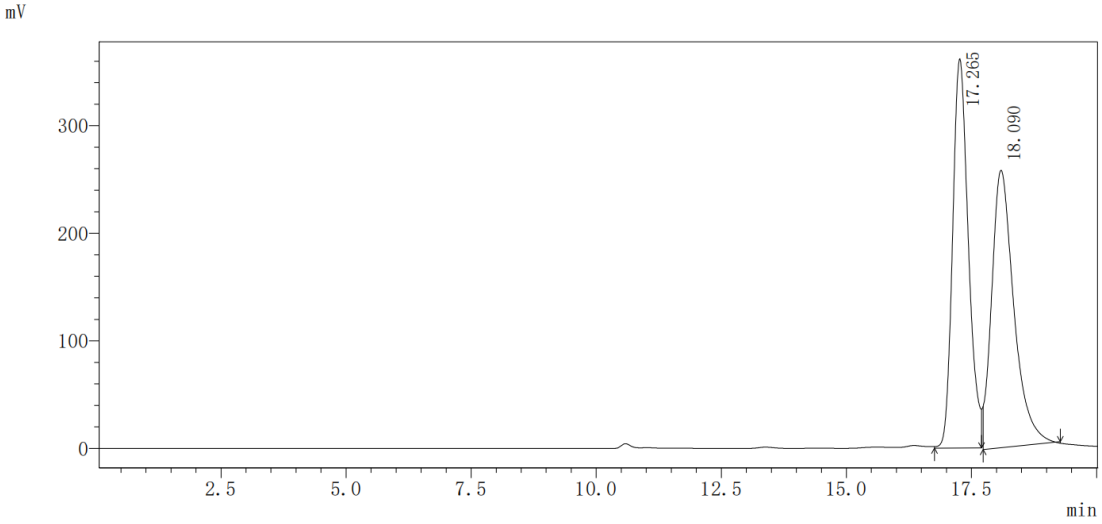


Detector A channel 230 nm

Peak	Ret. Time	Area	Height	Conc.
1	16.389	14076368	682075	92.249
2	17.349	1182727	37754	7.751
Total		15259095	719830	

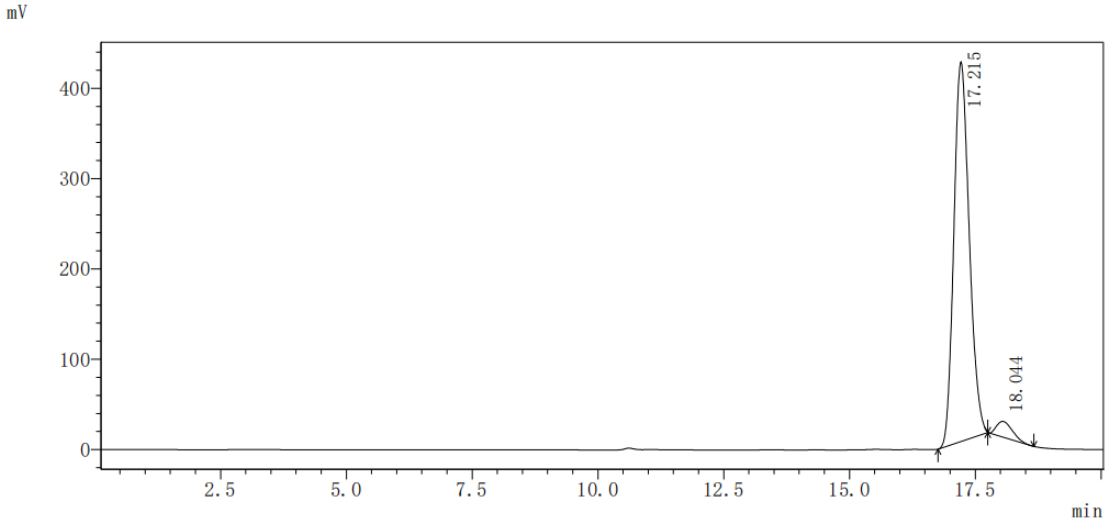


3da



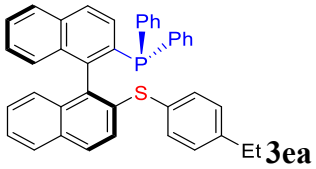
Detector A channel 230 nm

Peak	Ret. Time	Area	Height	Conc.
1	17.265	7907065	361841	49.923
2	18.090	7931431	257962	50.077
Total		15838496	619803	

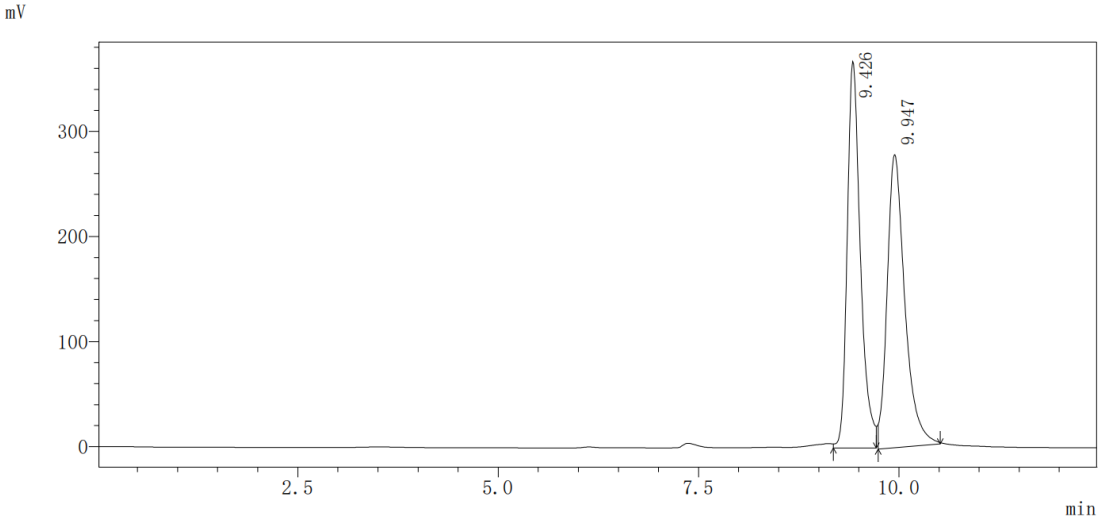


Detector A channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	17.215	8945100	420426	95.971
2	18.044	375524	17237	4.029
Total		9320624	437663	

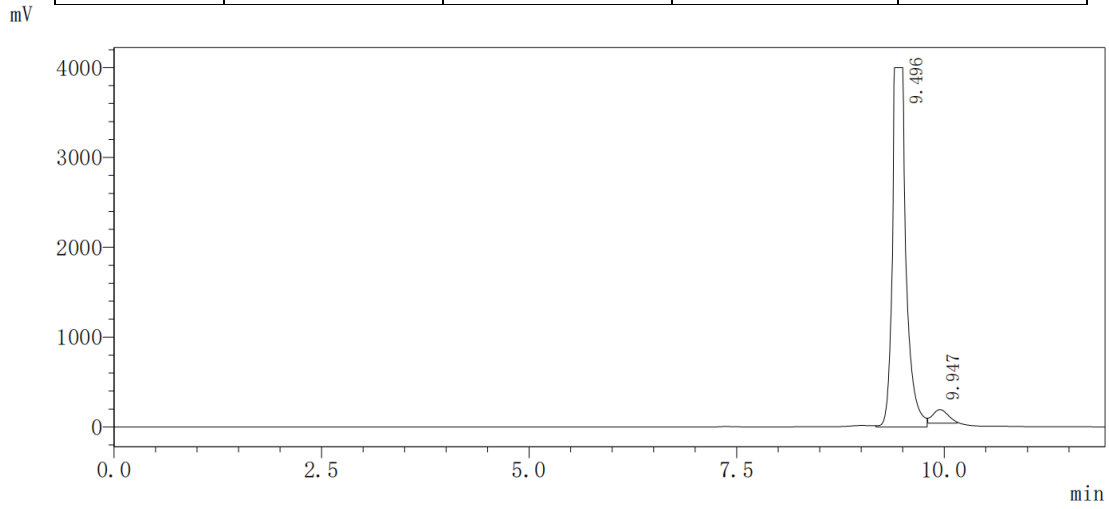


3ea



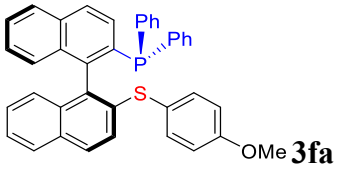
Detector A channel 230 nm

Peak	Ret. Time	Area	Height	Conc.
1	9.426	4205311	367695	49.565
2	9.947	4279044	278777	50.435
Total		8484355	646472	

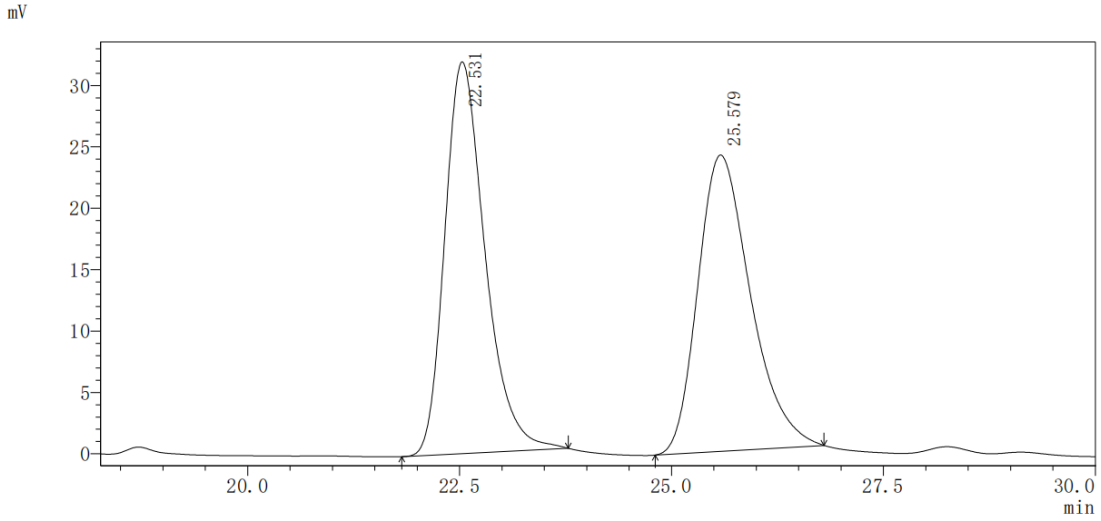


Detector A channel 230 nm

Peak	Ret. Time	Area	Height	Conc.
1	9.496	46577763	3999403	95.962
2	9.947	1959851	151525	4.038
Total		48537614	4150928	

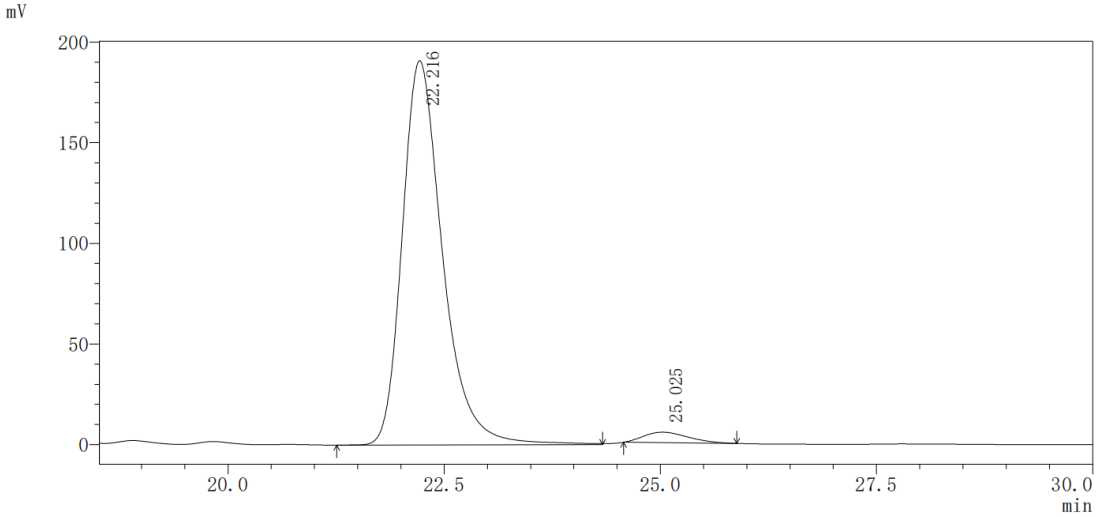


3fa



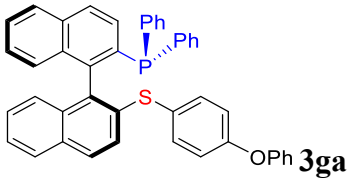
Detector A channel 230 nm

Peak	Ret. Time	Area	Height	Conc.
1	22.531	1057075	31917	50.350
2	25.579	1042363	24126	49.650
Total		2099438	56042	



Detector A channel 230 nm

Peak	Ret. Time	Area	Height	Conc.
1	22.216	6208063	190972	97.074
2	25.025	187139	5205	2.926
Total		6395202	196177	



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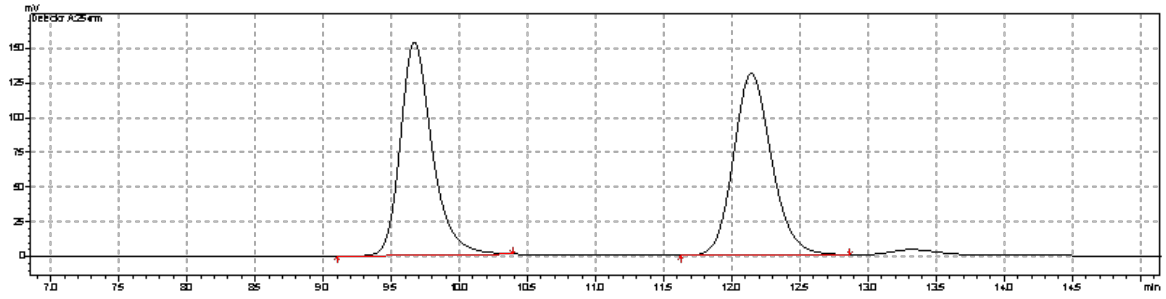
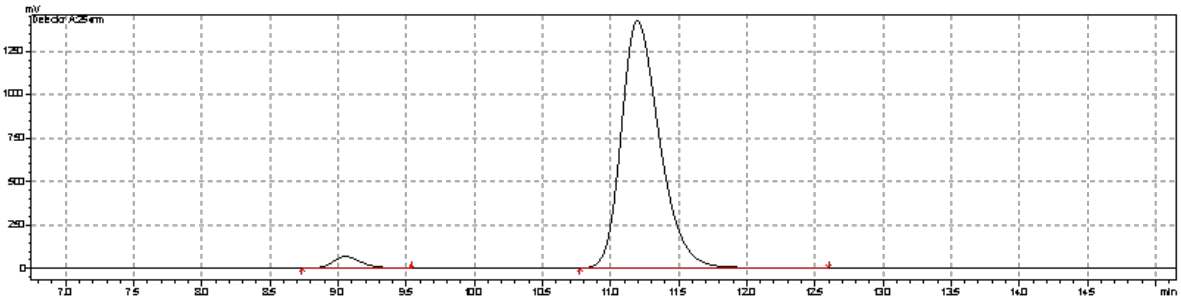


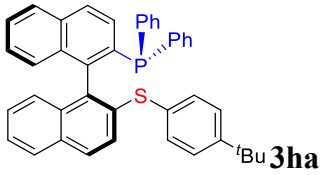
Detector A channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	9.664	2493696	153561	49.445
2	12.138	2549694	130844	50.555
Total		5043390	284405	

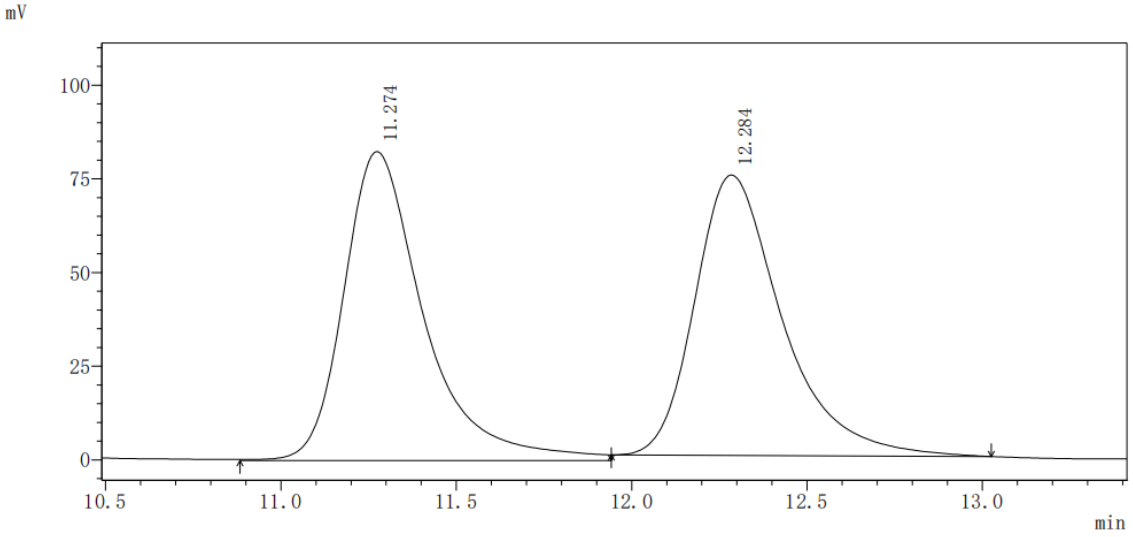


Detector A channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	9.050	1027705	68490	3.573
2	11.193	27737484	1422924	96.427
Total		28765189	1491415	

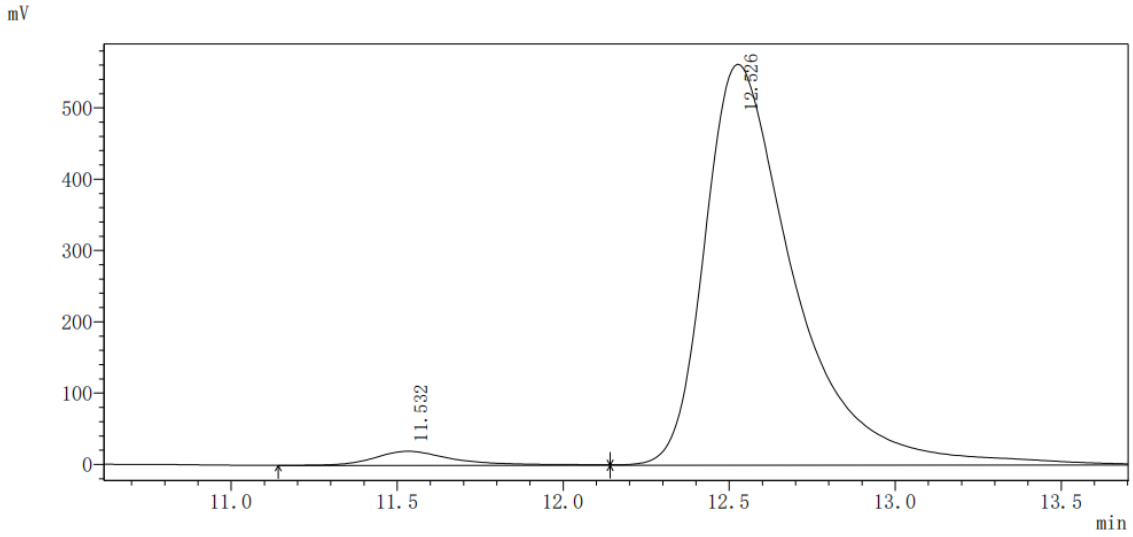


3ha



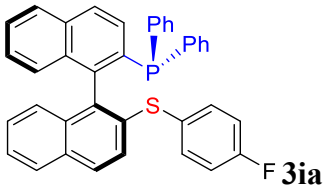
Detector A channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	11.274	1314358	82520	50.384
2	12.284	1294302	74877	49.616
Total		2608659	157397	

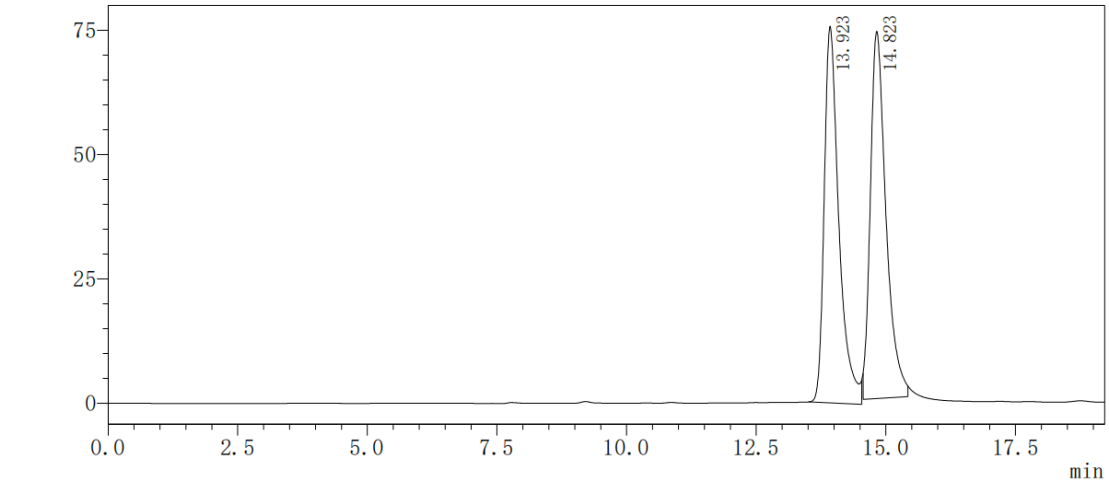


Detector A channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	11.532	345067	19950	3.143
2	12.526	10634208	562637	96.857
Total		10979274	582588	

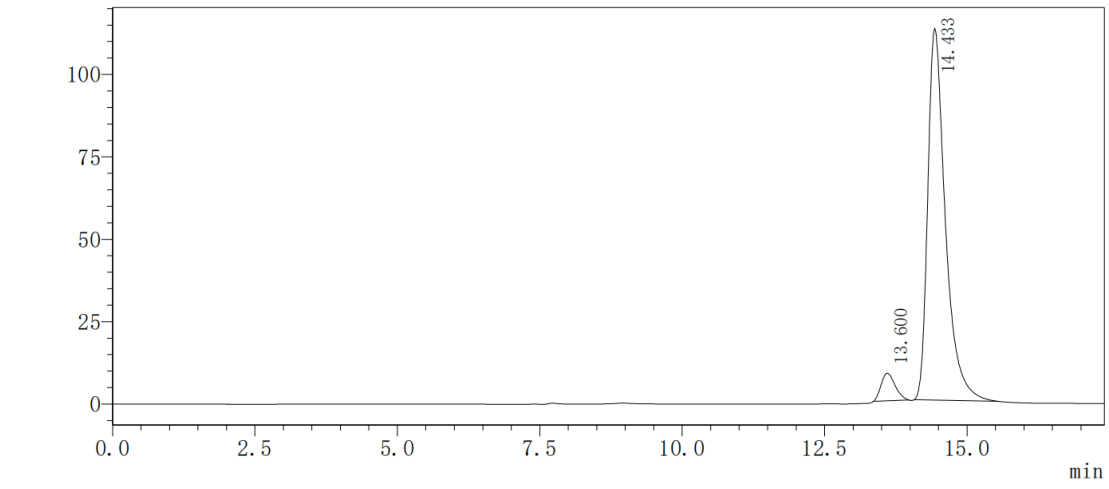


3ia



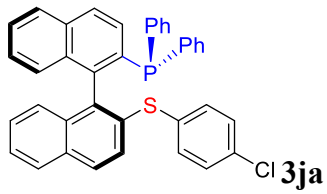
Detector A channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	13.923	1469358	75533	46.993
2	14.823	1657433	74524	53.007
Total		3126791	150057	

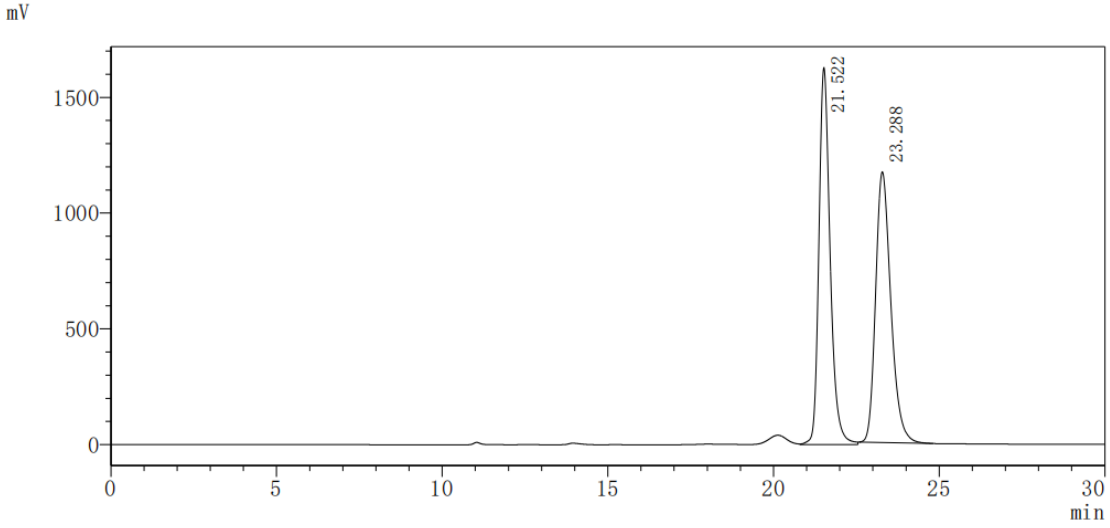


Detector A channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	13.600	132050	8064	5.133
2	14.433	2440535	112942	94.867
Total		2572585	121006	

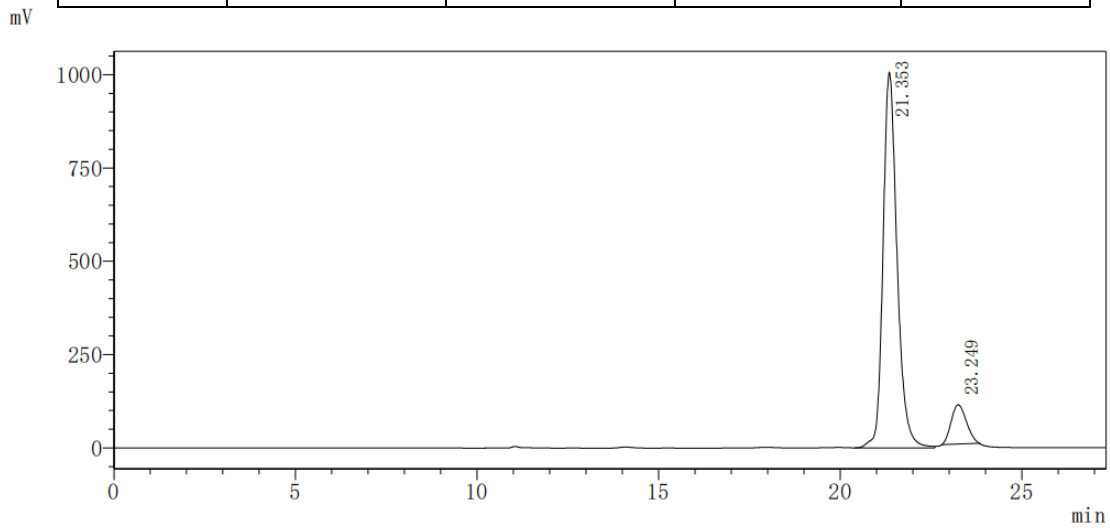


3ja



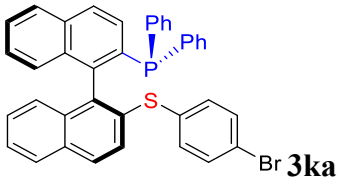
Detector A channel 230 nm

Peak	Ret. Time	Area	Height	Conc.
1	21.522	38483085	1628009	50.739
2	23.288	37361593	1168771	49.261
Total		75844678	2796780	

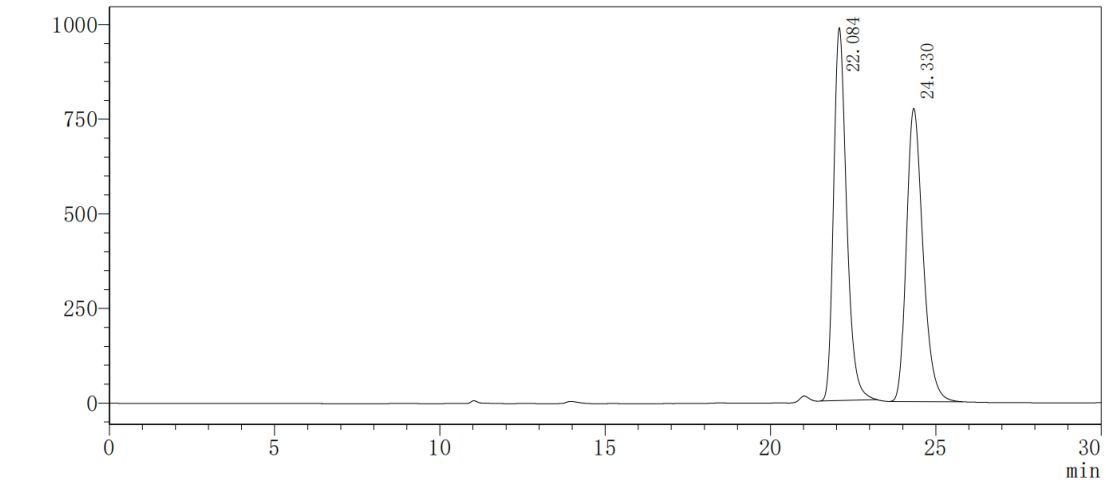


Detector A channel 230 nm

Peak	Ret. Time	Area	Height	Conc.
1	21.820	2093391	63840	90.780
2	23.944	212611	6711	9.220
Total		2306001	70551	

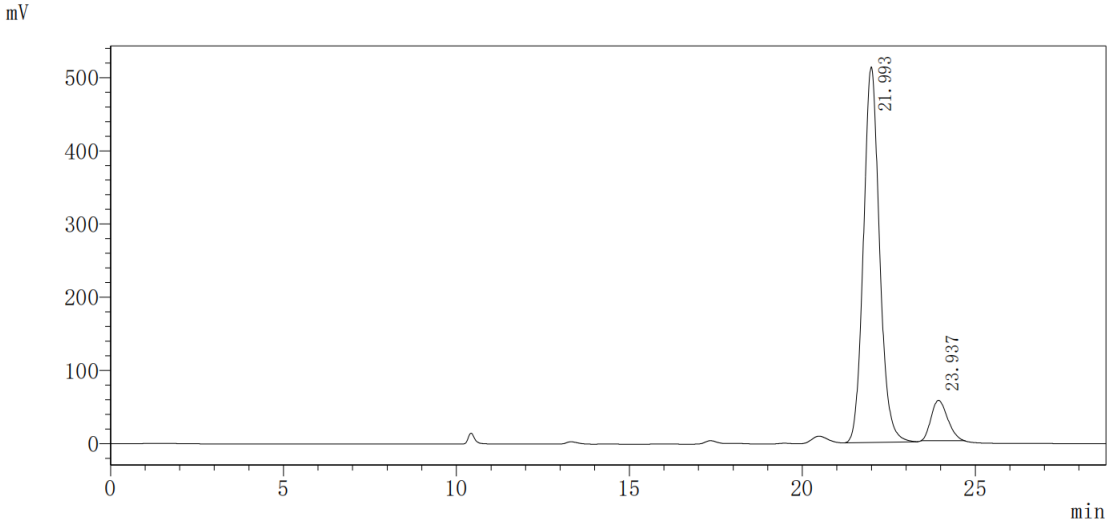


3ka



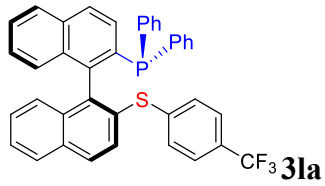
Detector A channel 230 nm

Peak	Ret. Time	Area	Height	Conc.
1	22.084	28079549	992408	50.293
2	24.330	27737294	779191	49.680
Total		55832224	1772027	



Detector A channel 230 nm

Peak	Ret. Time	Area	Height	Conc.
1	21.993	16580572	512733	90.040
2	23.937	1834118	55265	9.960
Total		18414690	567998	



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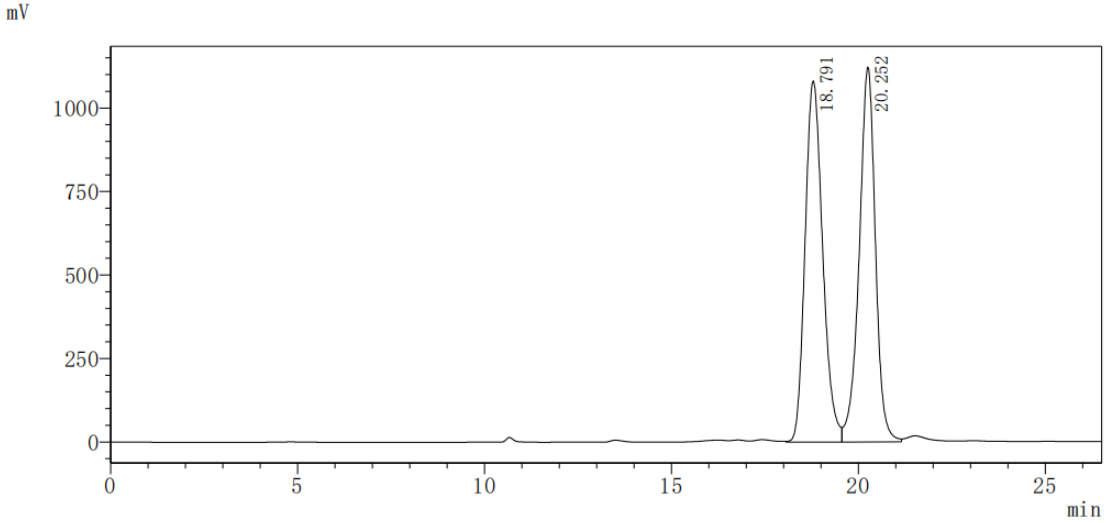
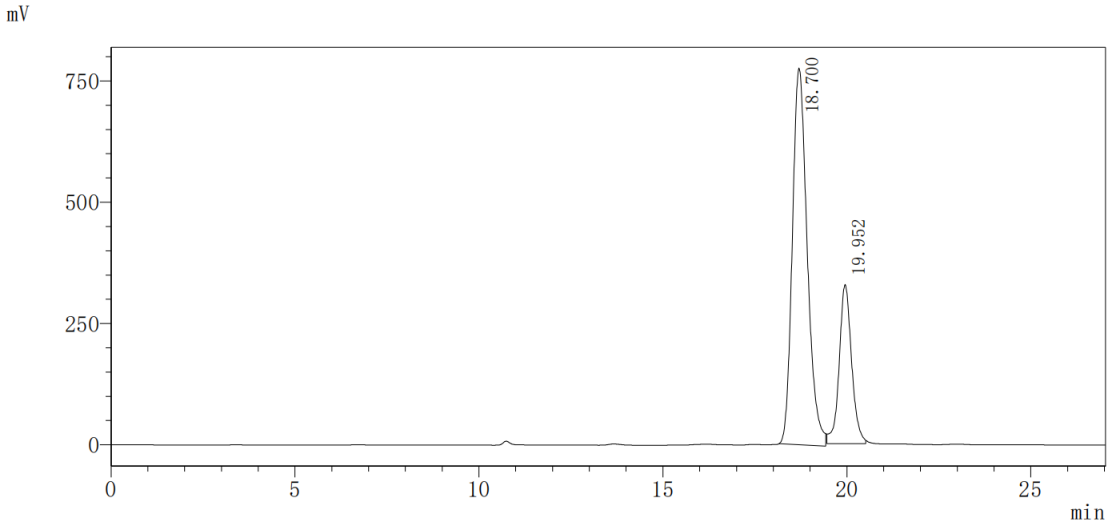


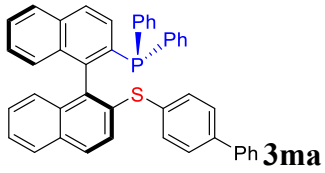
Detector A channel 230 nm

Peak	Ret. Time	Area	Height	Conc.
1	18.791	35361704	1081141	51.089
2	20.252	33853805	1121921	48.911
Total		69215509	2203063	

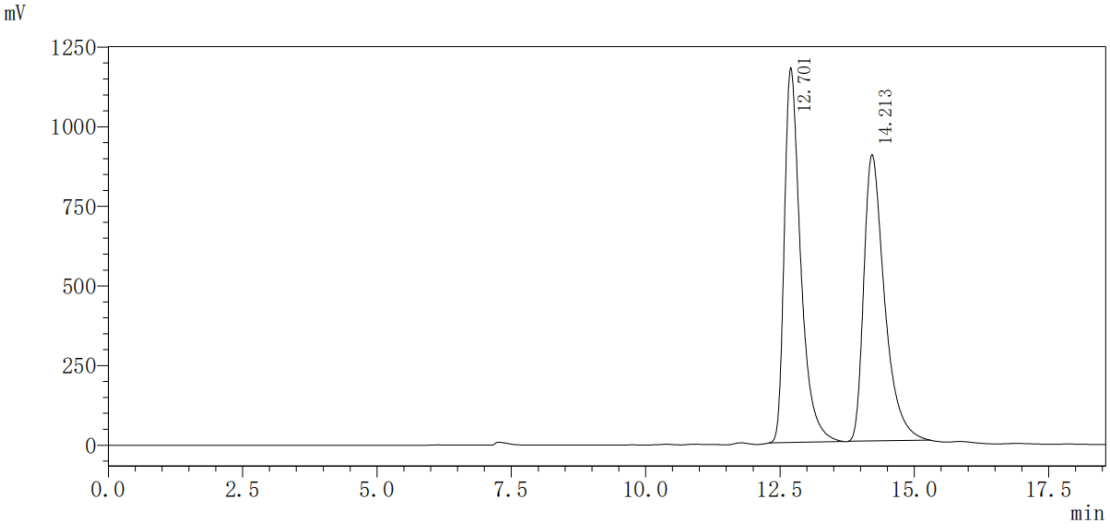


Detector A channel 230 nm

Peak	Ret. Time	Area	Height	Conc.
1	18.700	21920315	776657	73.694
2	19.952	7824858	330649	26.306
Total		29745172	1107307	

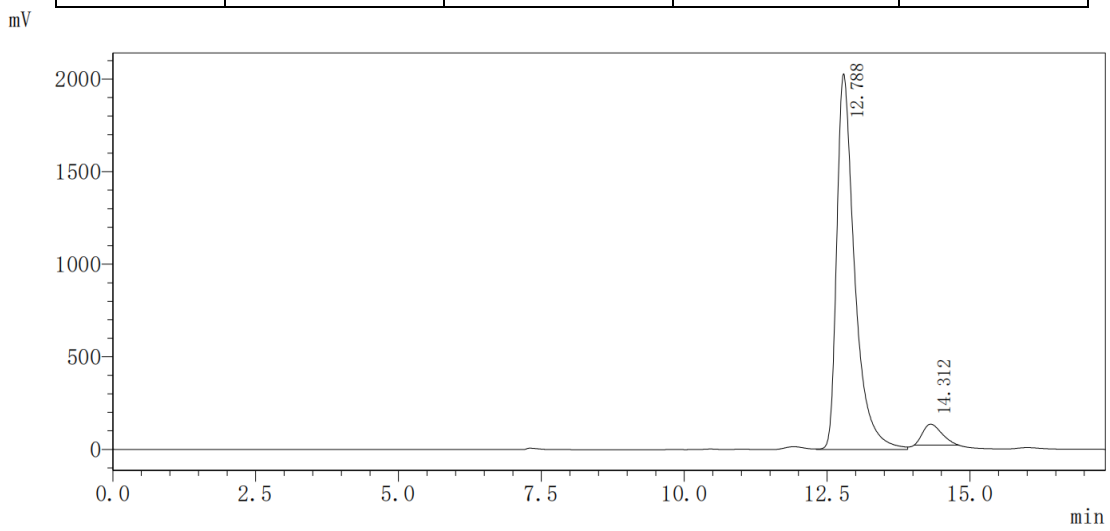


3ma



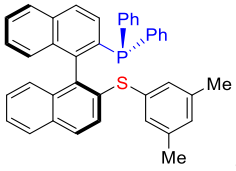
Detector A channel 230 nm

Peak	Ret. Time	Area	Height	Conc.
1	12.701	24807405	1176326	50.618
2	14.213	24201275	899144	49.382
Total		49008680	2075470	

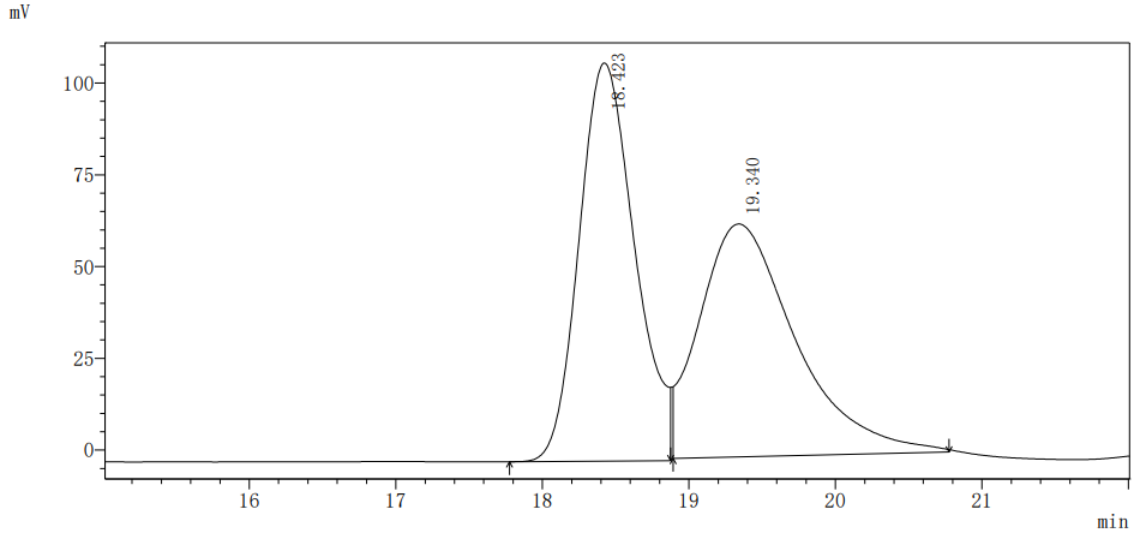


Detector A channel 230 nm

Peak	Ret. Time	Area	Height	Conc.
1	12.788	44222438	2028831	94.439
2	14.312	2603904	112887	5.561
Total		46826342	2141717	

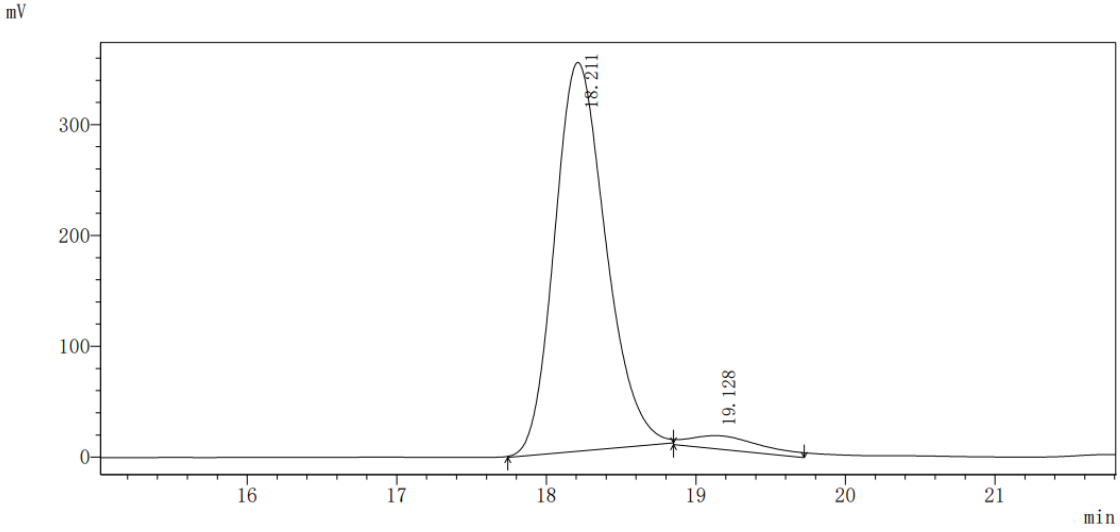


3na



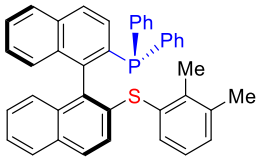
Detector A channel 230 nm

Peak	Ret. Time	Area	Height	Conc.
1	18.423	2867401	108487	49.705
2	19.340	2901420	63469	50.295
Total		5768821	171956	

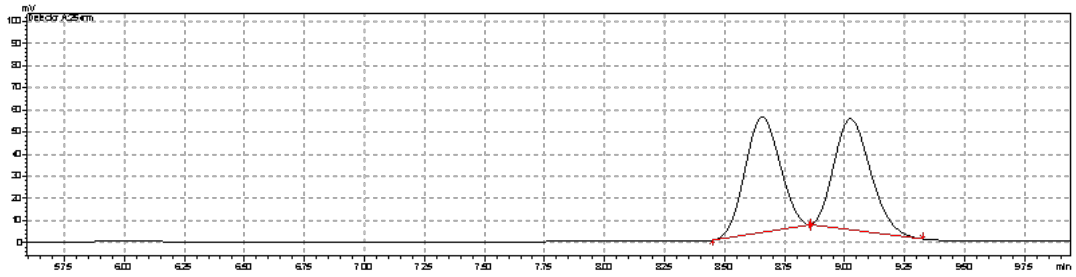


Detector A channel 230 nm

Peak	Ret. Time	Area	Height	Conc.
1	18.211	8823734	356128	94.593
2	19.128	504374	17109	5.407
Total		9328108	373237	

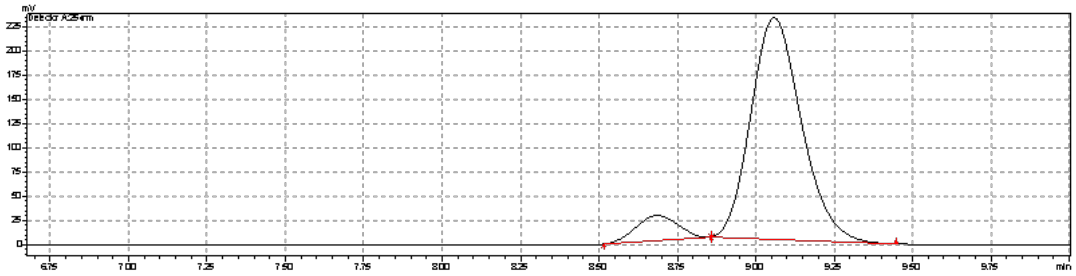


3oa



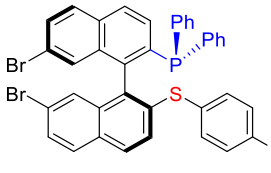
Detector A channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	8.652	526852	52115	49.960
2	9.019	527698	50045	50.040
Total		1054549	102160	

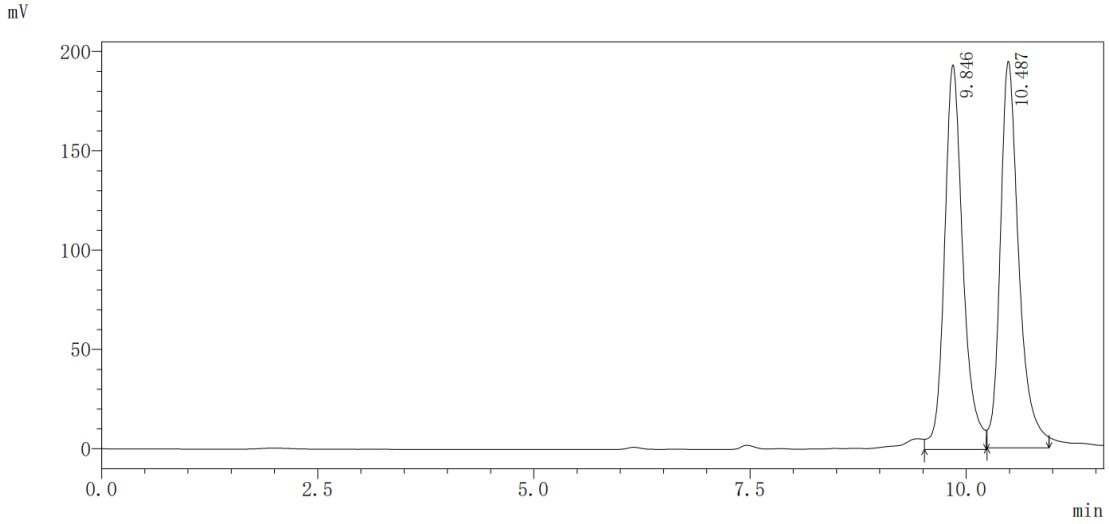


Detector A channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	8.648	61465	6520	8.192
2	9.029	688828	58566	91.808
Total		750293	65085	

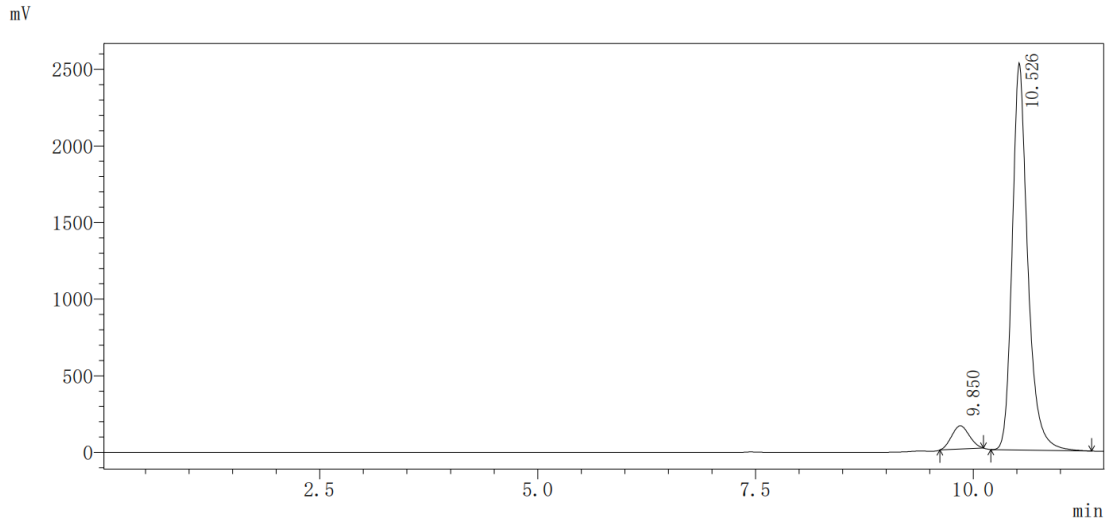


3pa



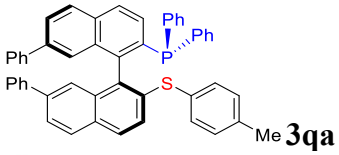
Detector A channel 230 nm

Peak	Ret. Time	Area	Height	Conc.
1	9.846	2882126	193541	49.799
2	10.487	2905338	194566	50.201
Total		5787464	388107	

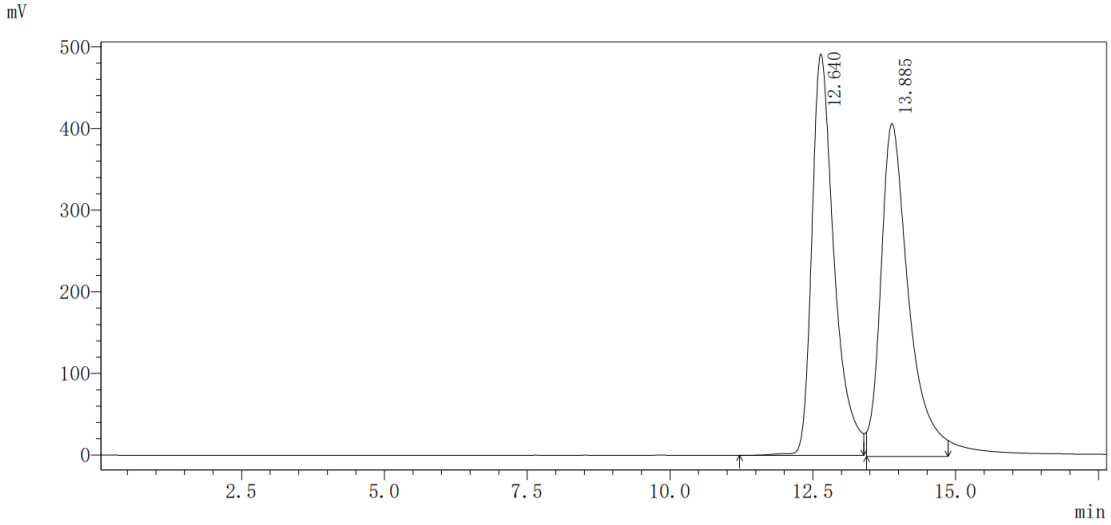


Detector A channel 230 nm

Peak	Ret. Time	Area	Height	Conc.
1	9.850	2148147	152642	6.413
2	10.526	31350153	2525115	93.587
Total		33498299	2677757	

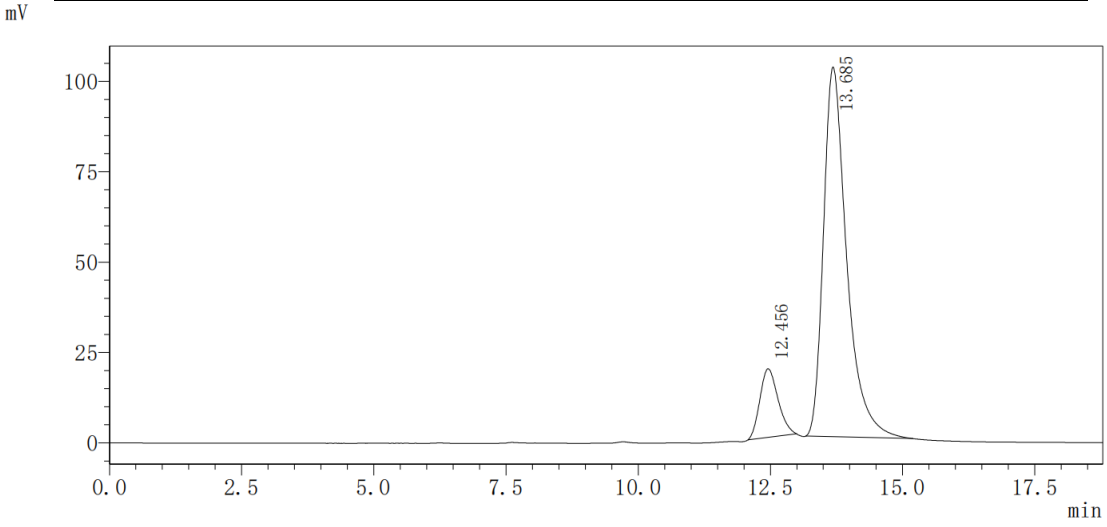


3qa



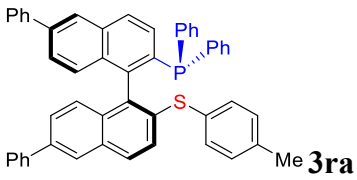
Detector A channel 230 nm

Peak	Ret. Time	Area	Height	Conc.
1	12.640	13384161	491437	49.267
2	13.885	13782649	407551	50.733
Total		27166810	898988	

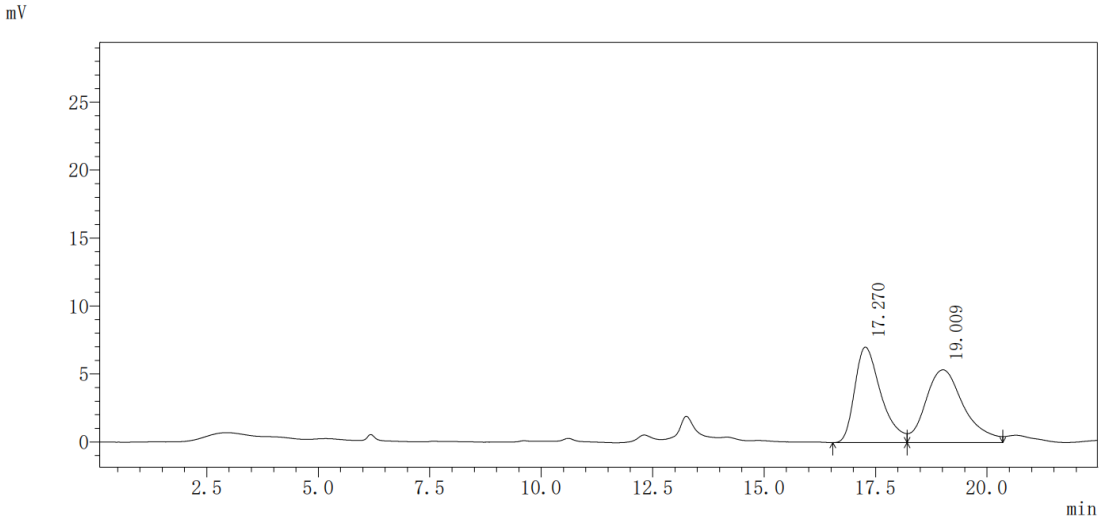


Detector A channel 230 nm

Peak	Ret. Time	Area	Height	Conc.
1	12.456	452906	18980	12.638
2	13.685	3130802	102248	87.362
Total		3583708	121228	

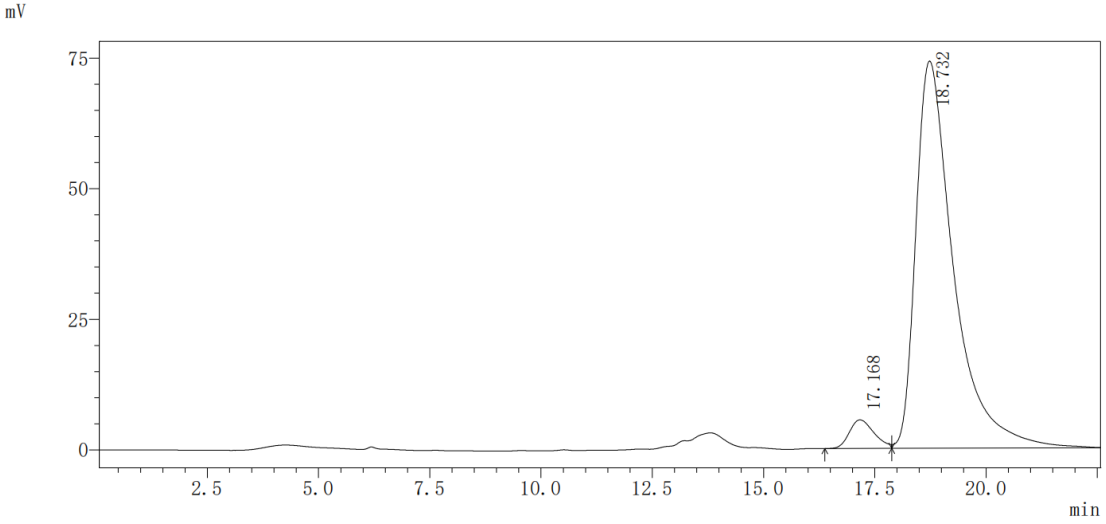


3ra



Detector A channel 254 nm

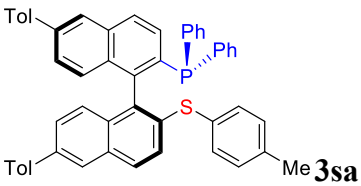
Peak	Ret. Time	Area	Height	Conc.
1	17.270	289144	7041	49.573
2	19.009	294130	5268	50.427
Total		583274	12308	



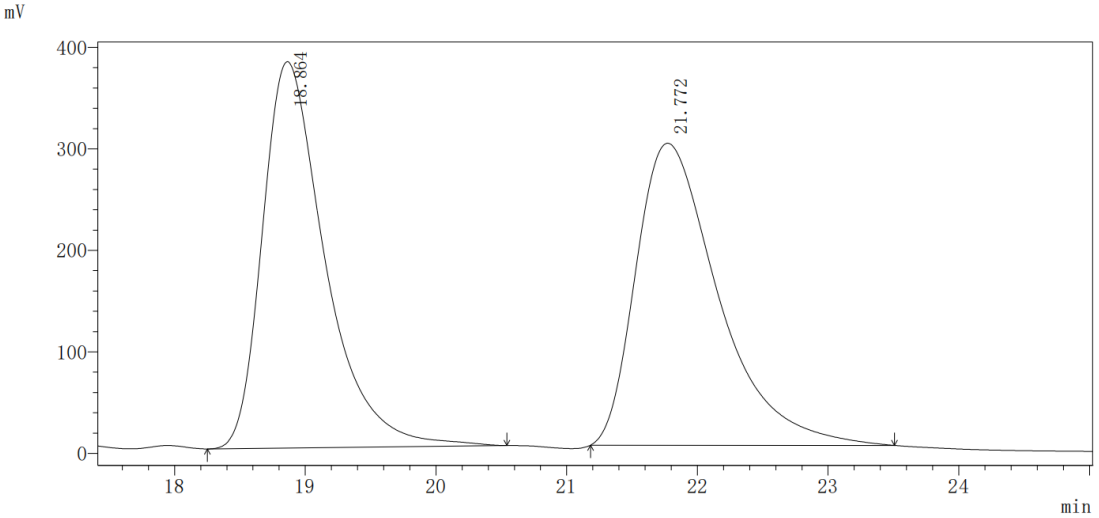
A

channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	17.168	212565	5489	4.630
2	18.732	4378801	74107	95.370
Total		4591366	79596	

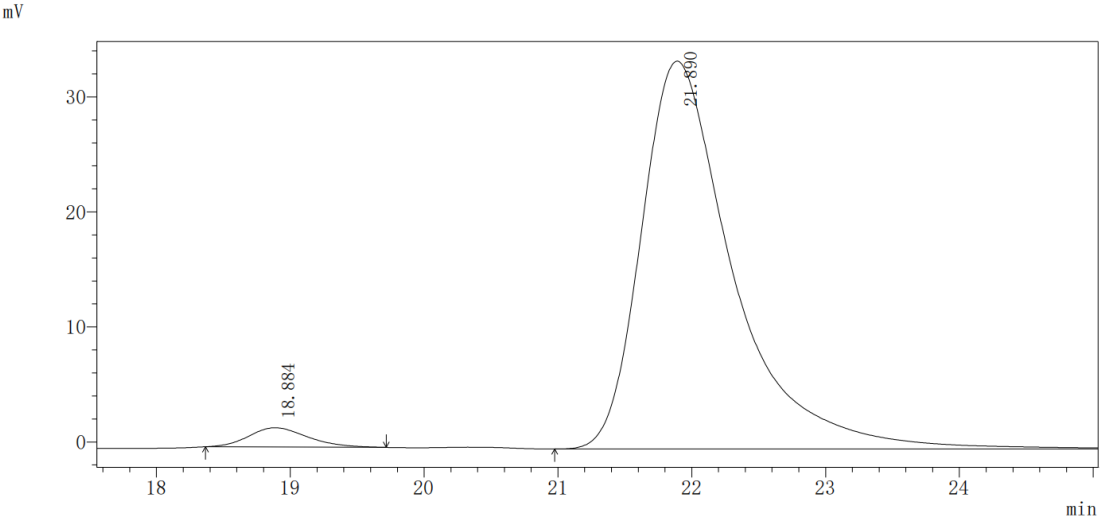


3sa



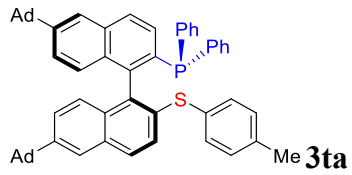
A channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	18.864	12682222	380682	50.015
2	21.772	12674691	294658	49.985
Total		25356913	675340	

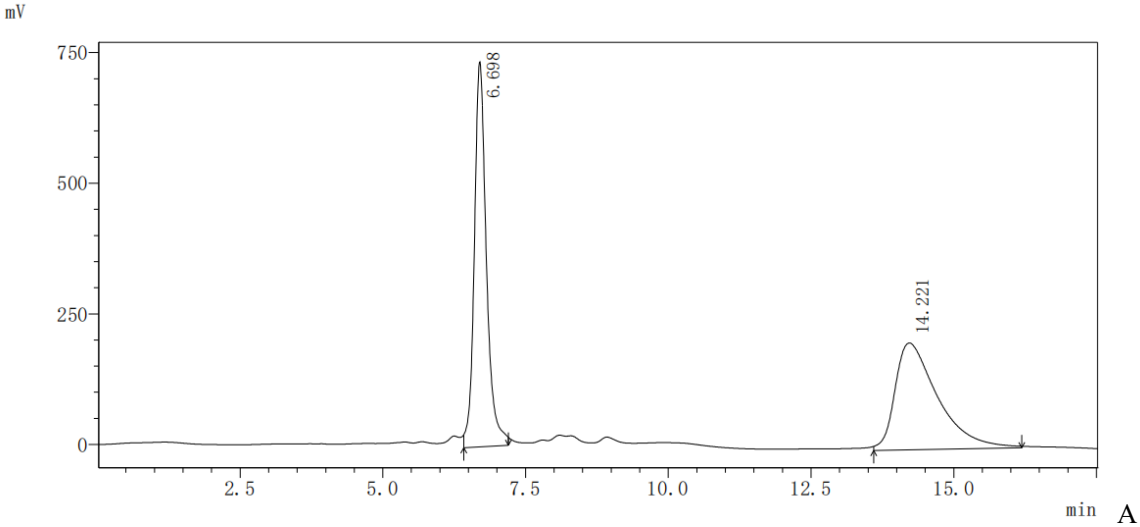


A channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	18.884	51219	1673	3.081
2	21.890	1611103	33723	96.919
Total		1662322	35397	

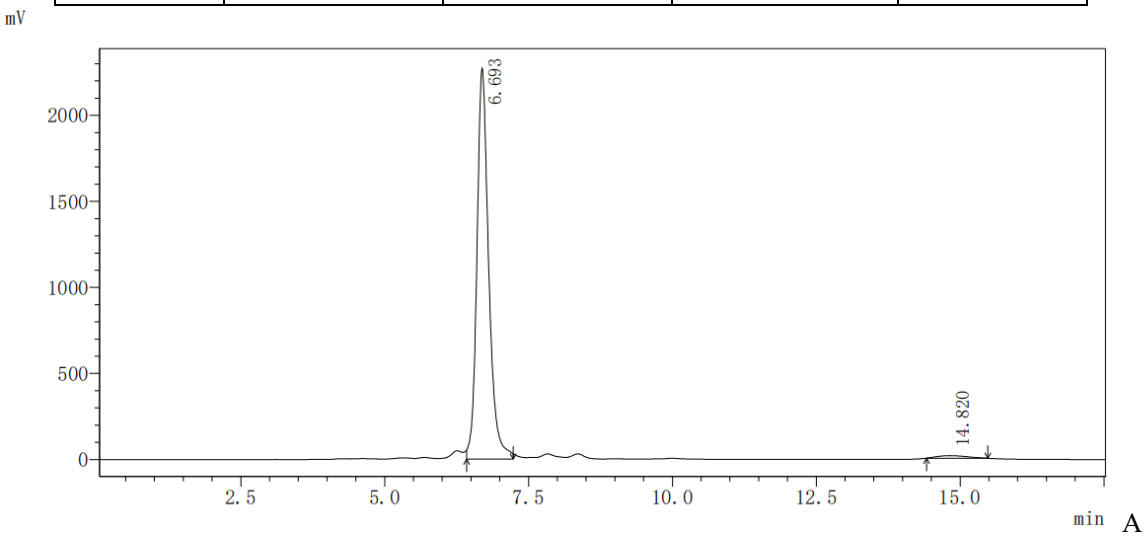


3ta



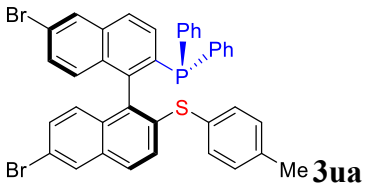
channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	6.698	10812421	736933	50.325
2	14.221	10672856	204493	49.675
Total		21485277	941426	

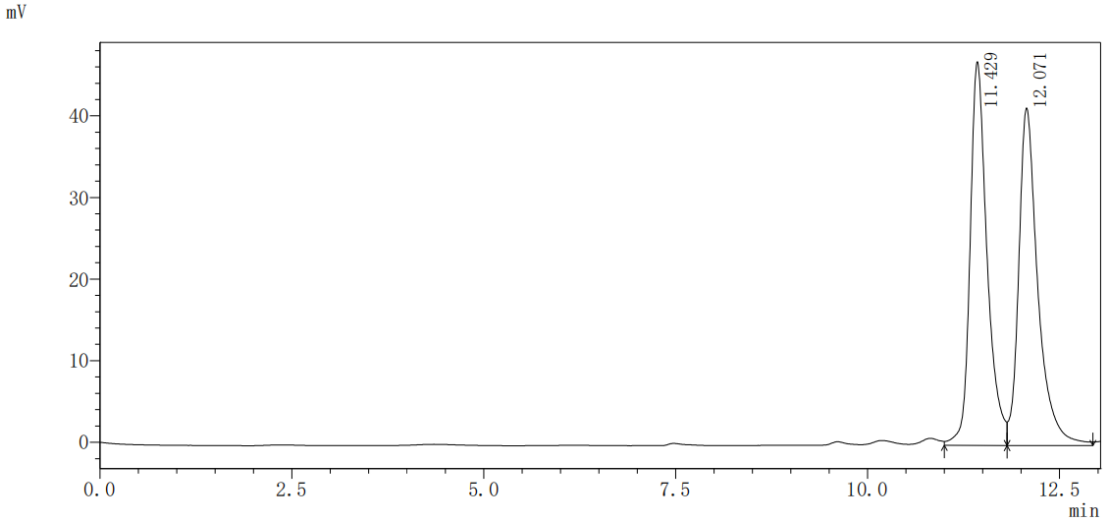


channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	6.693	32227823	2270379	98.341
2	14.820	543519	14943	1.659
Total		32771342	2285323	

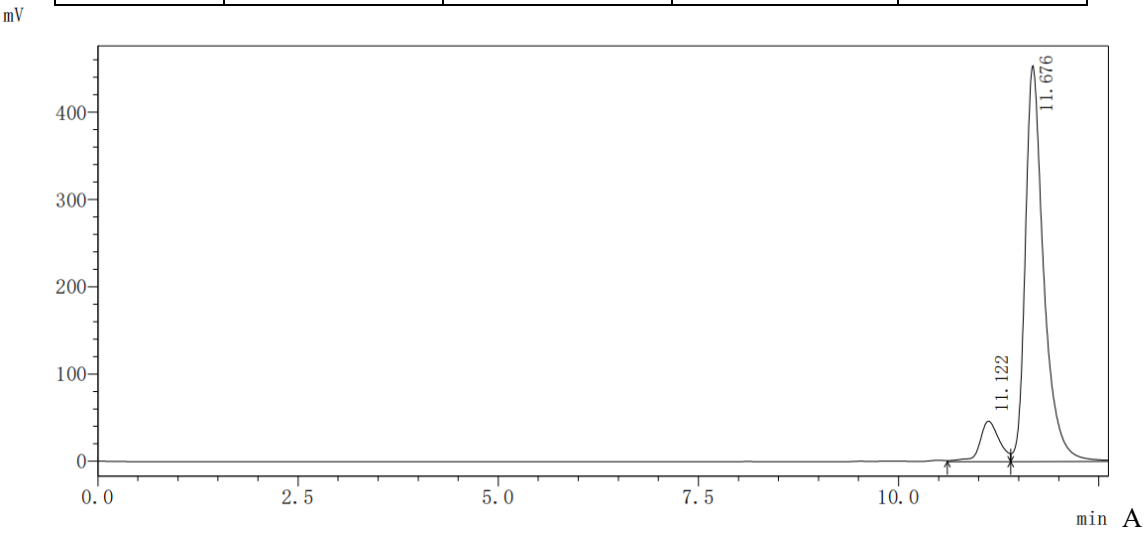


3ua



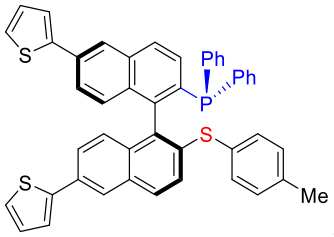
A channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	11.429	727190	46993	50.245
2	12.071	720101	41355	49.755
Total		1447292	88348	

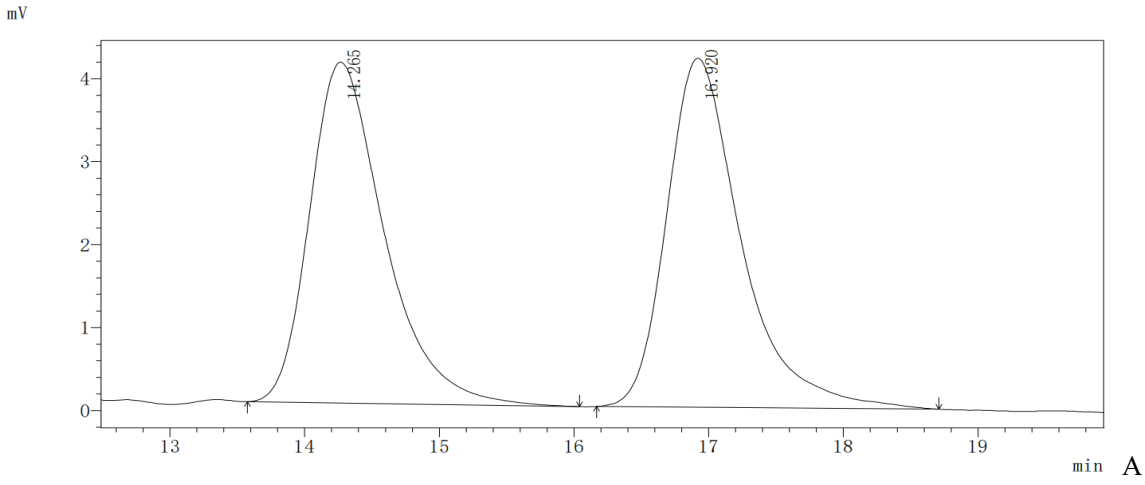


channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	11.122	783729	46371	9.746
2	11.676	7257643	453235	90.254
Total		8041372	499607	

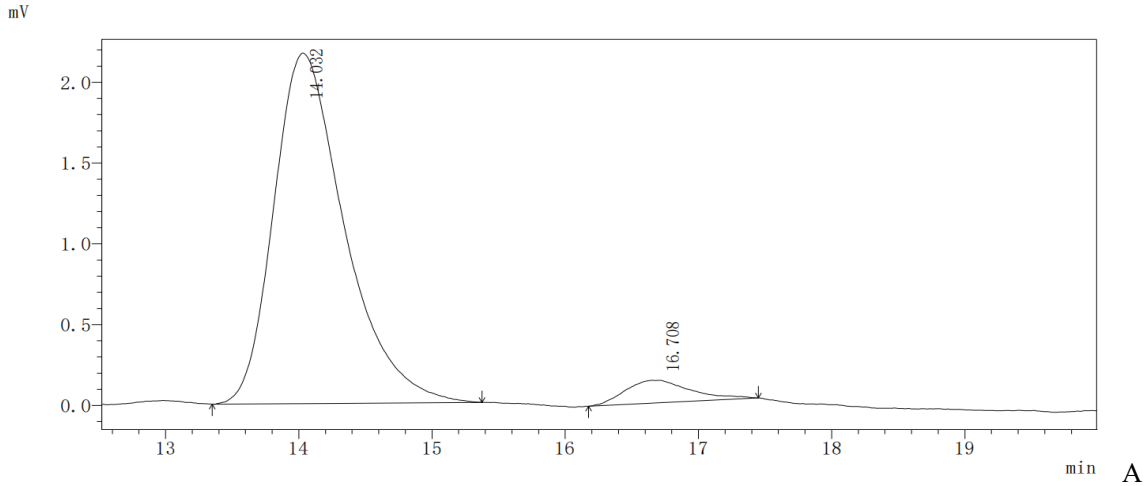


3va



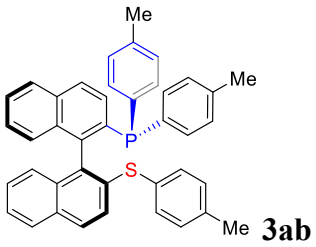
channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	14.265	158720	4110	49.543
2	16.920	161650	4206	50.457
Total		320370	8316	

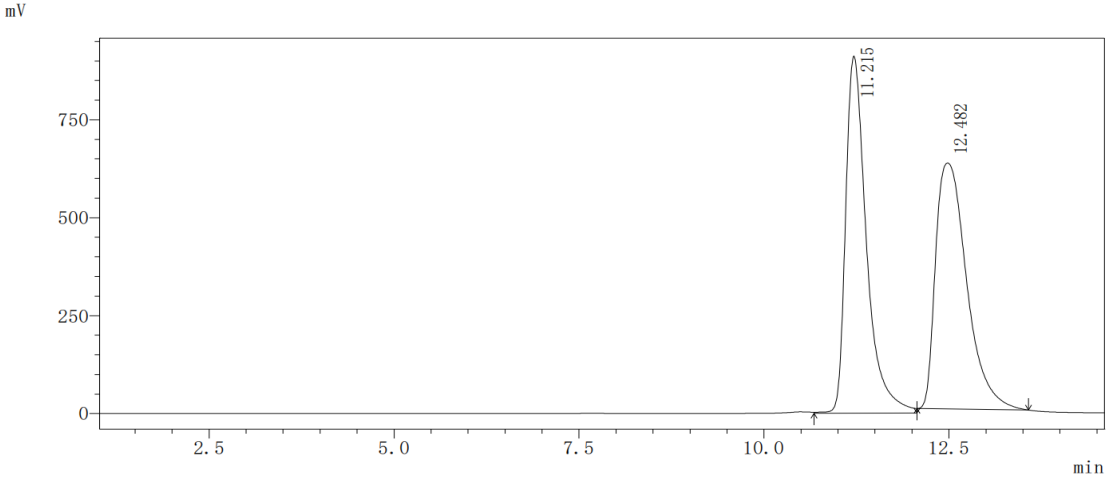


channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	14.032	80235	2170	94.403
2	16.708	4757	139	5.597
Total		84992	2308	

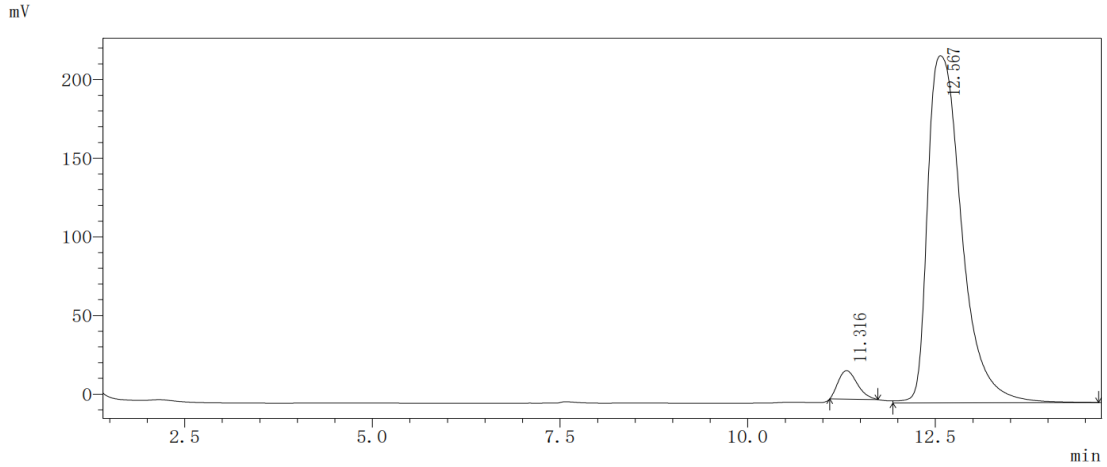


3ab



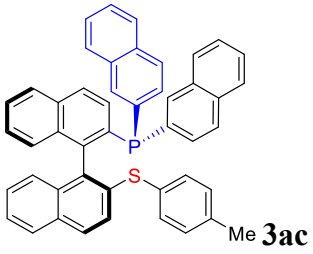
channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	11.215	17870355	911391	49.294
2	12.482	18381924	627899	50.706
Total		36252278	1539289	

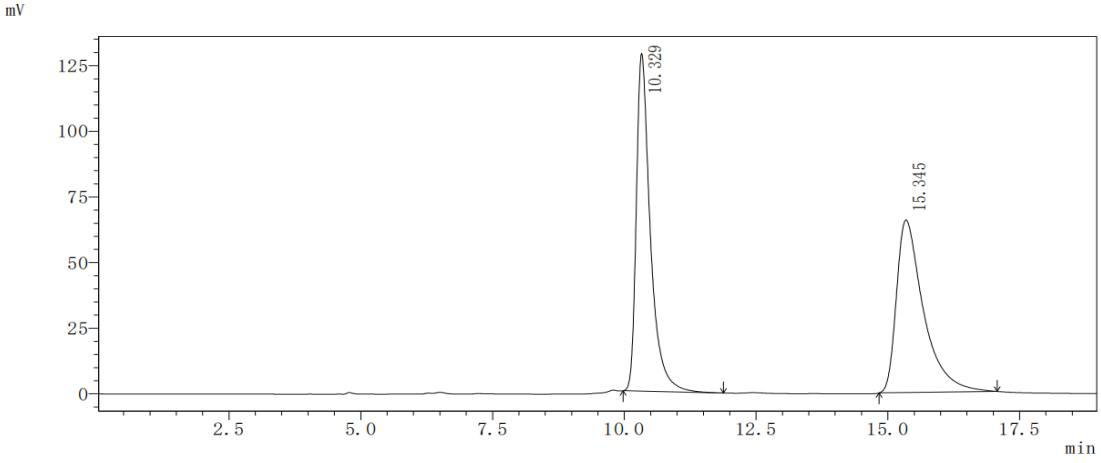


channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	11.316	318894	18051	4.374
2	12.567	6970982	220774	95.626
Total		7289876	238826	

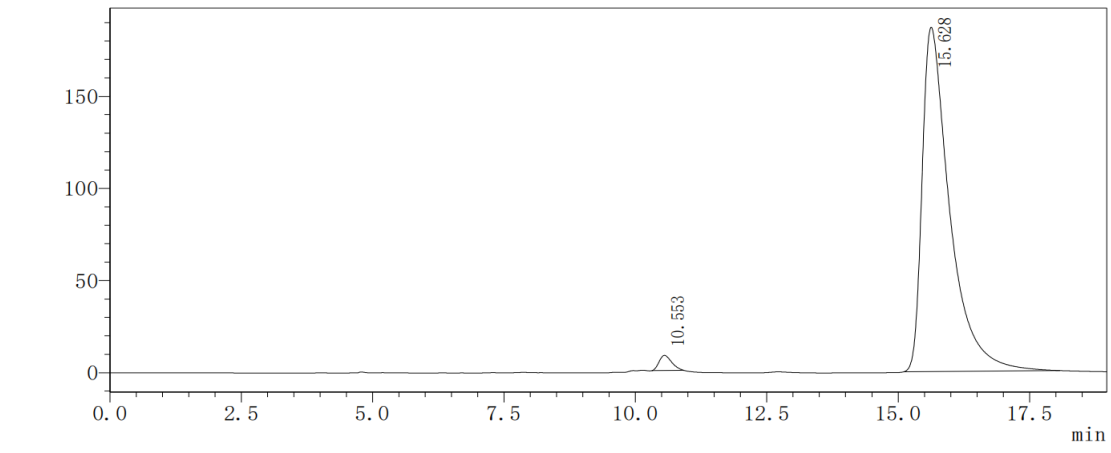


3ac



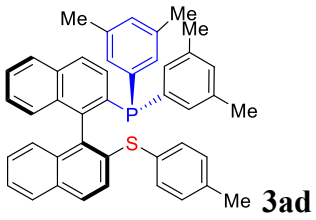
channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	10.329	2346624	128159	50.052
2	15.345	2341720	65648	49.948
Total		4688343	193806	

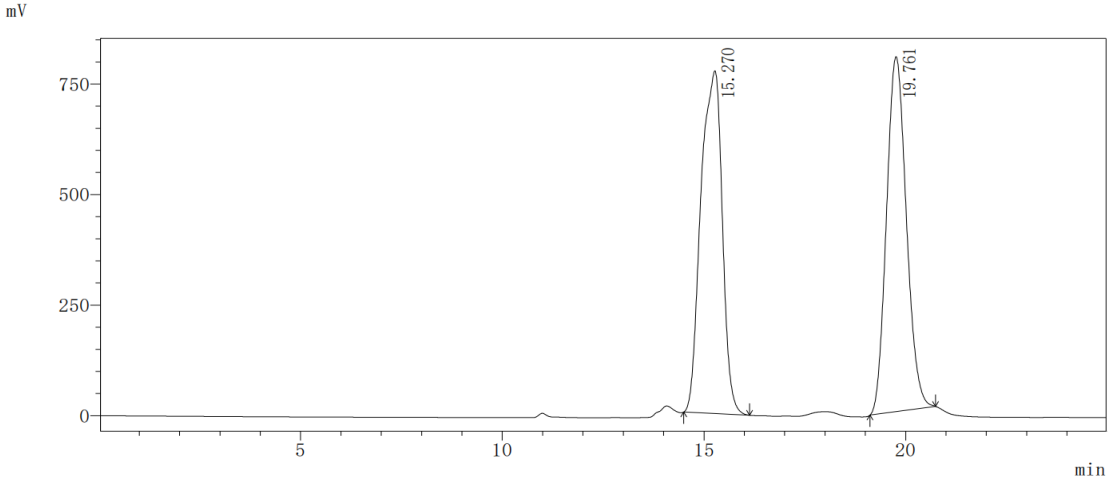


channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	10.553	135889	8193	1.950
2	15.628	6834009	186820	98.050
Total		6969898	195013	

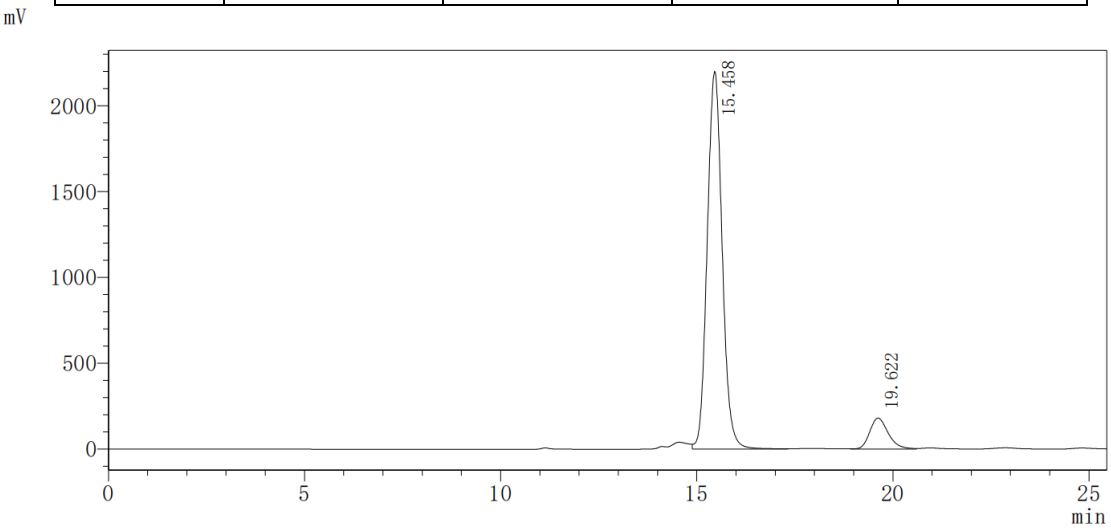


3ad



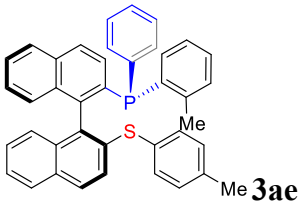
channel 230 nm

Peak	Ret. Time	Area	Height	Conc.
1	15.270	28460037	774810	50.890
2	19.761	27464875	802525	49.110
Total		55924912	1577335	

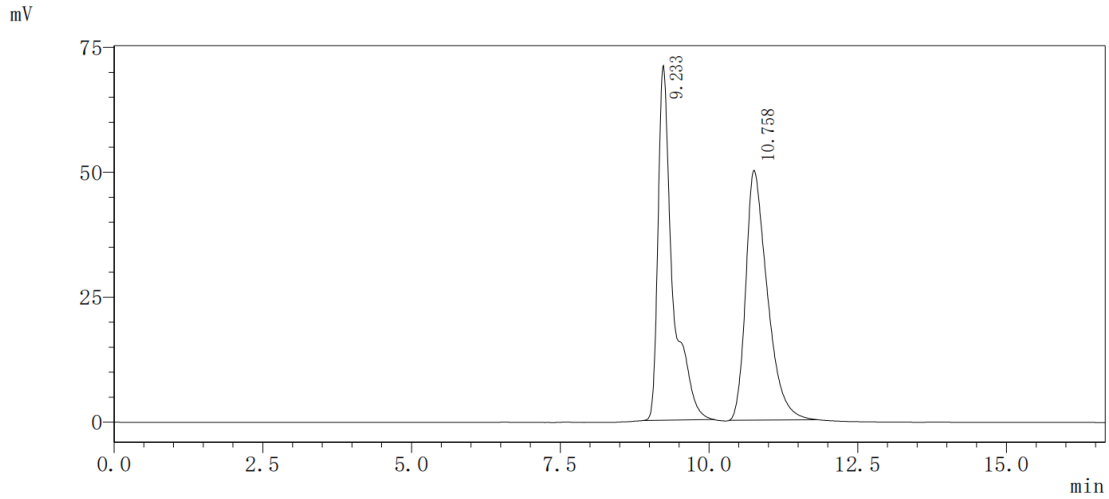


channel 230 nm

Peak	Ret. Time	Area	Height	Conc.
1	15.458	58360888	2200430	90.716
2	19.622	5972676	180840	9.284
Total		64333564	2381270	

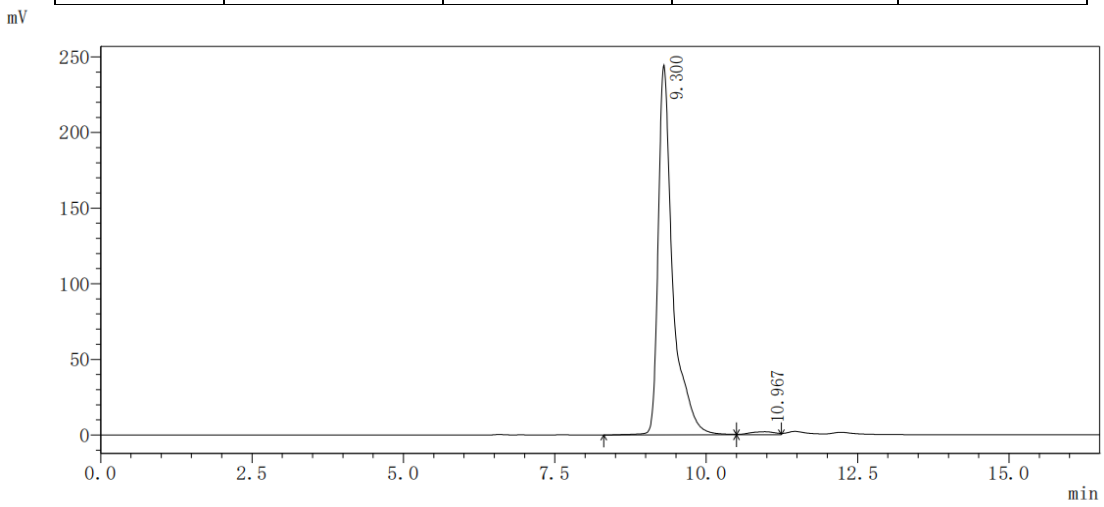


3ae



channel 280 nm

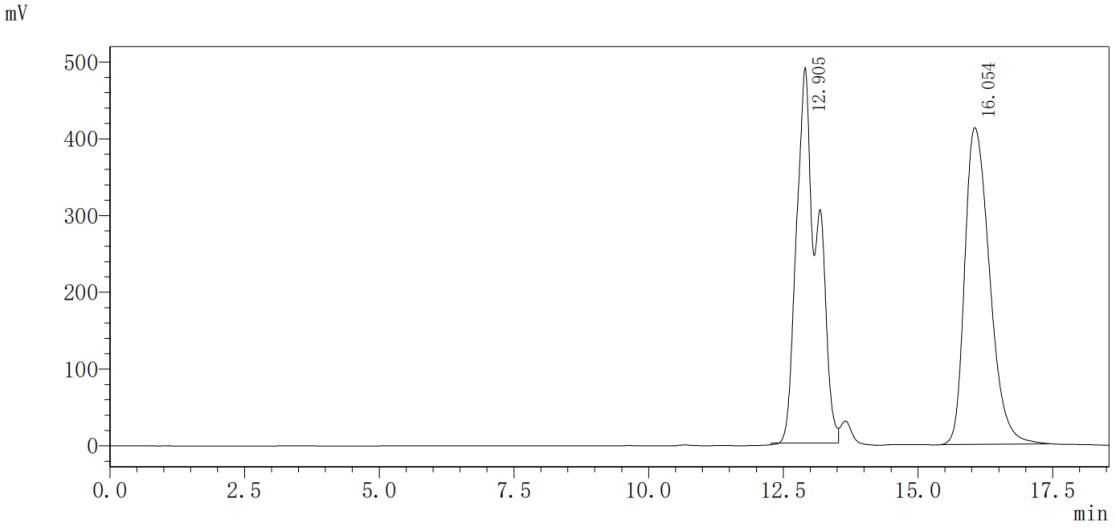
Peak	Ret. Time	Area	Height	Conc.
1	9.233	1206934	70941	48.884
2	10.758	1262034	49993	51.116
Total		2468968	120933	



channel 280 nm

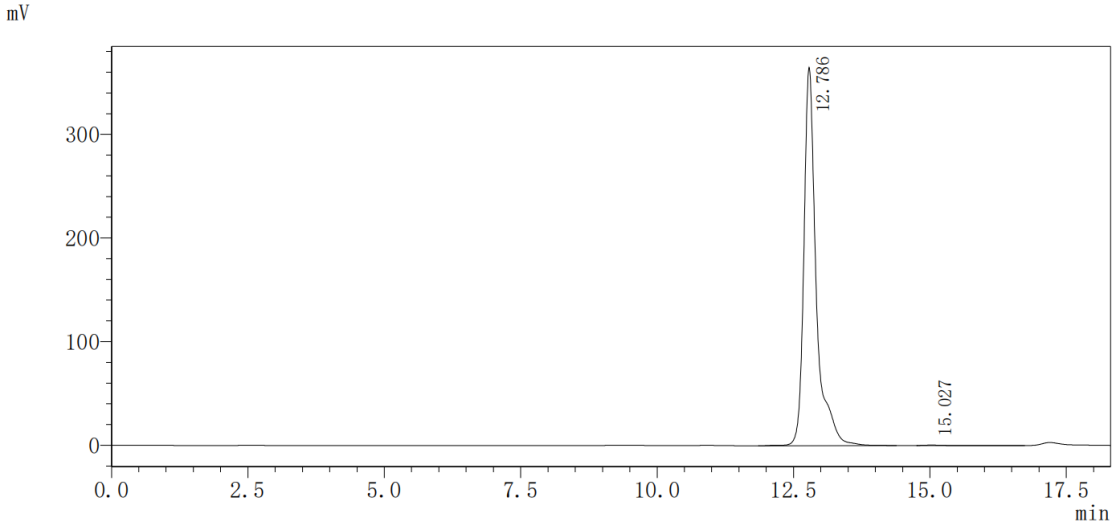
Peak	Ret. Time	Area	Height	Conc.
1	9.300	4086665	244530	98.565
2	10.967	59495	2034	1.435
Total		4146160	246564	

After recrystallization



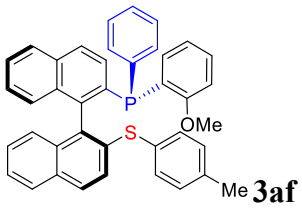
channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	12.905	13336701	488730	50.064
2	16.054	13302745	412692	49.936
Total		26639446	901422	

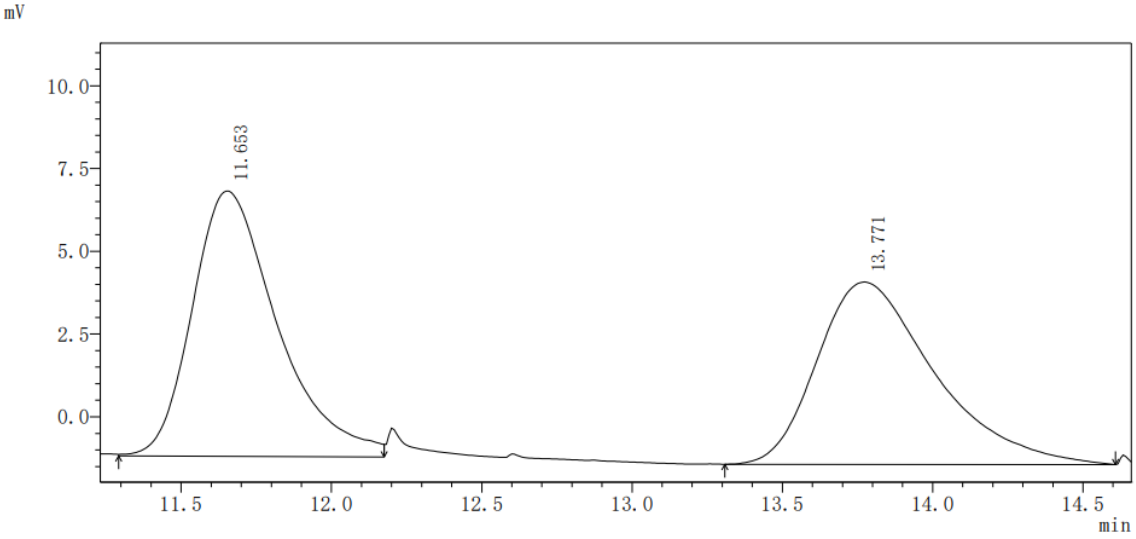


channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	12.786	5763209	364836	99.903
2	15.027	5575	402	0.097
Total		5768784	365237	

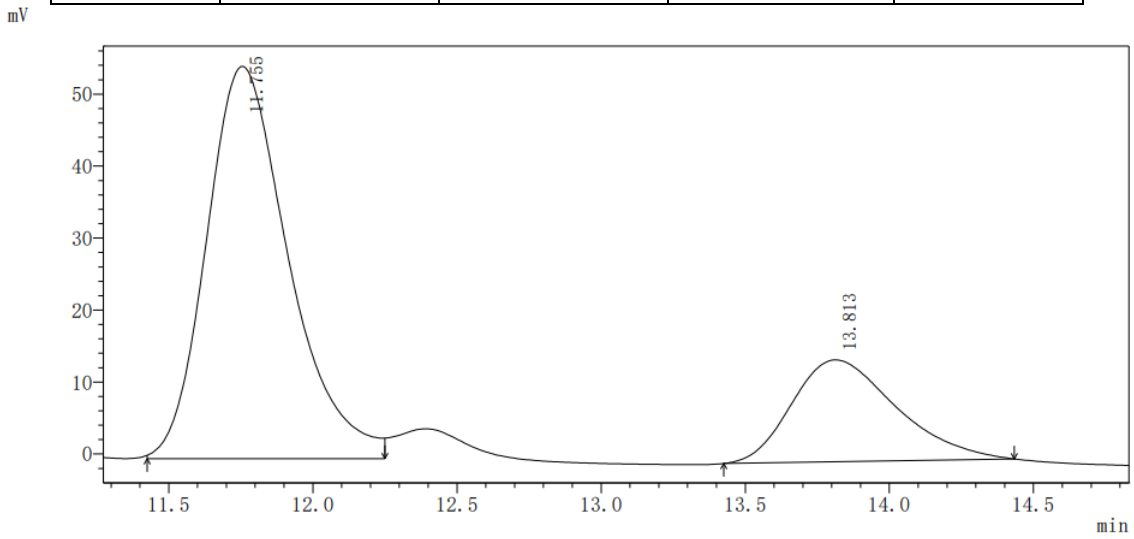


3af



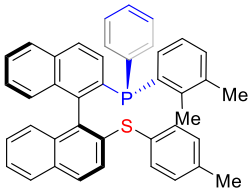
channel 280 nm

Peak	Ret. Time	Area	Height	Conc.
1	11.653	157805	8015	51.358
2	13.771	149461	5509	48.642
Total		307266	13524	

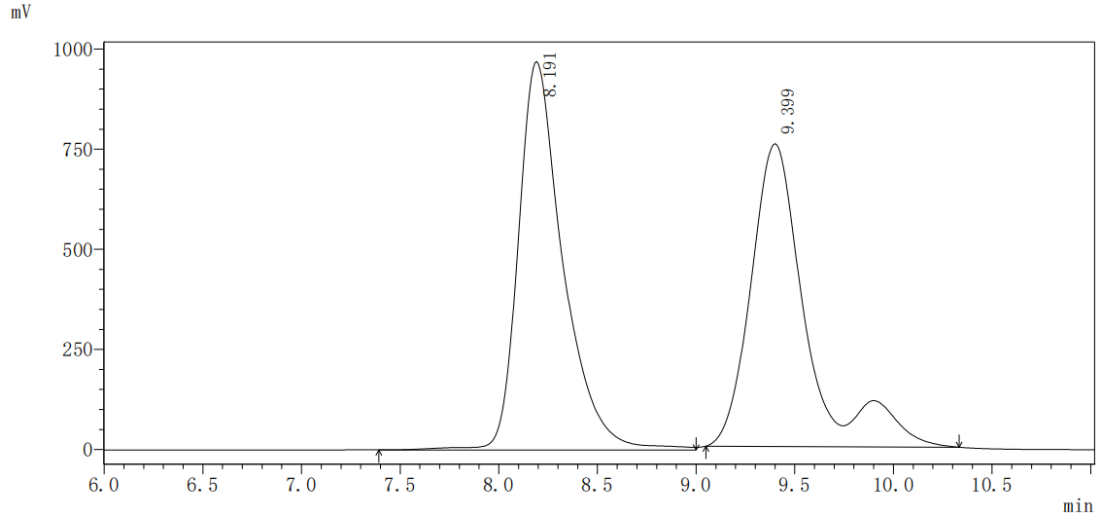


channel 280 nm

Peak	Ret. Time	Area	Height	Conc.
1	11.755	1078708	54492	75.204
2	13.813	355677	14143	24.796
Total		1434385	68635	



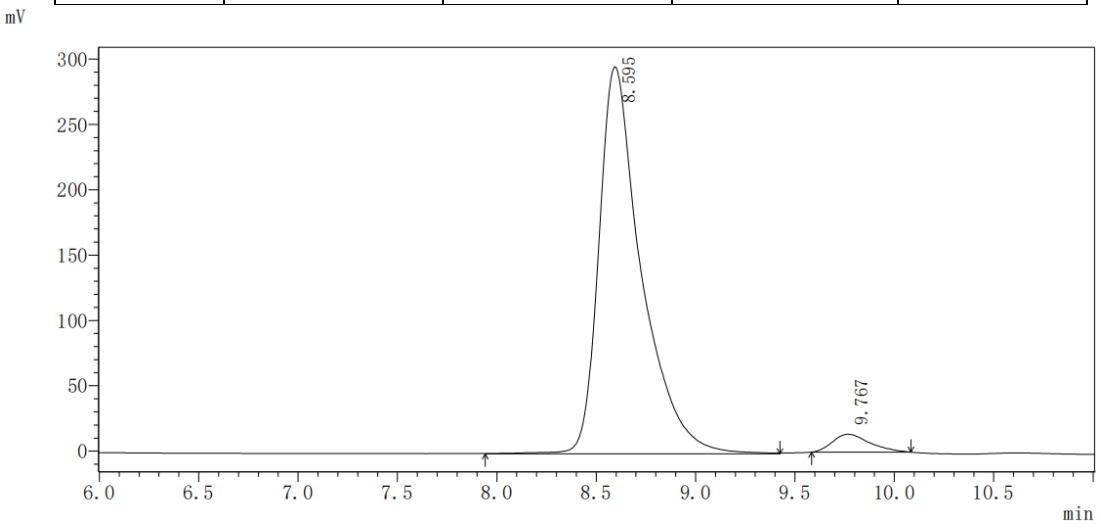
3ag



(mixed with diastereomers)

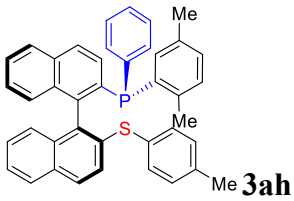
channel 280 nm

Peak	Ret. Time	Area	Height	Conc.
1	8.191	15343105	970125	50.863
2	9.399	14822576	756019	49.137
Total		30165680	1726145	

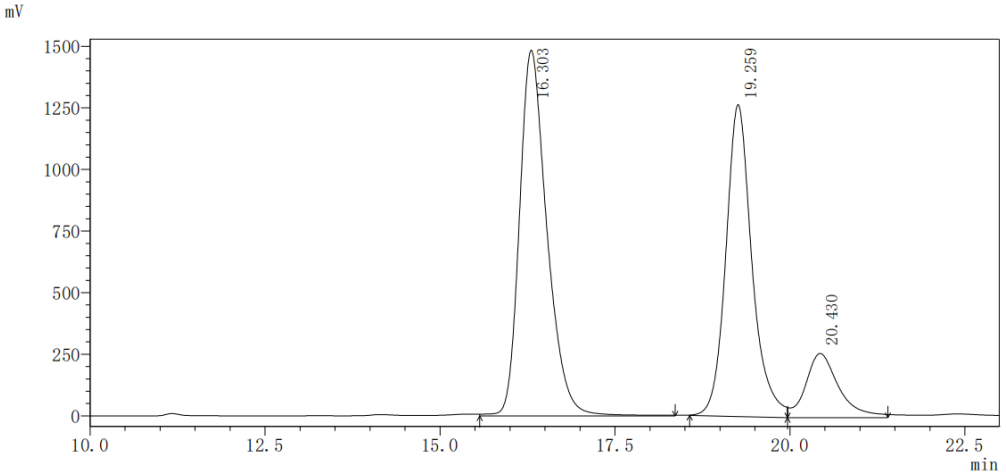


channel 280 nm

Peak	Ret. Time	Area	Height	Conc.
1	8.595	4411947	296094	96.119
2	9.767	178132	13671	3.881
Total		4590079	309765	



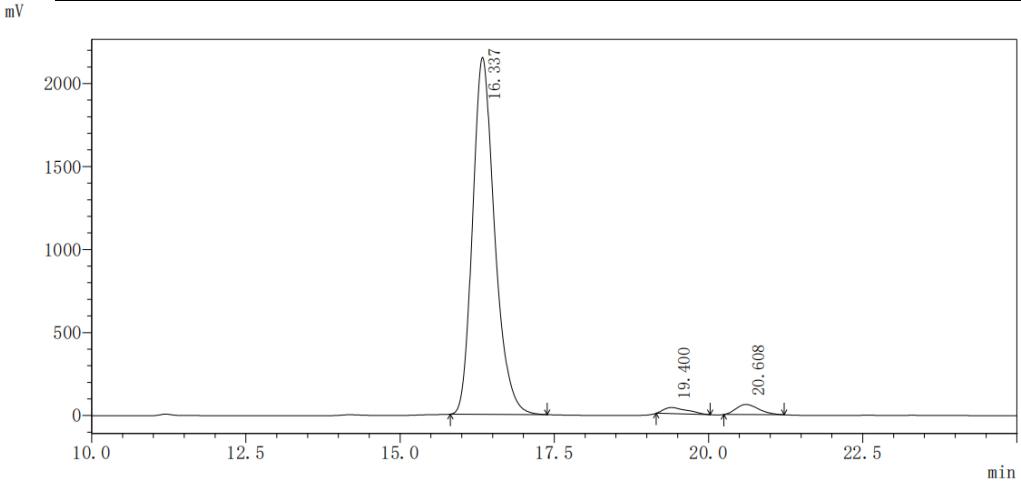
3ah



(mixed with diastereomers)

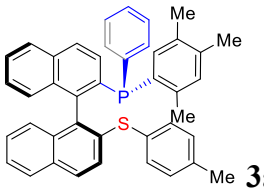
channel 230 nm

Peak	Ret. Time	Area	Height	Conc.
1	16.303	40550639	1483927	49.440
2	19.259	32848704	1266227	40.050
3	20.430	8620300	260844	10.510
Total		82019644	3010999	

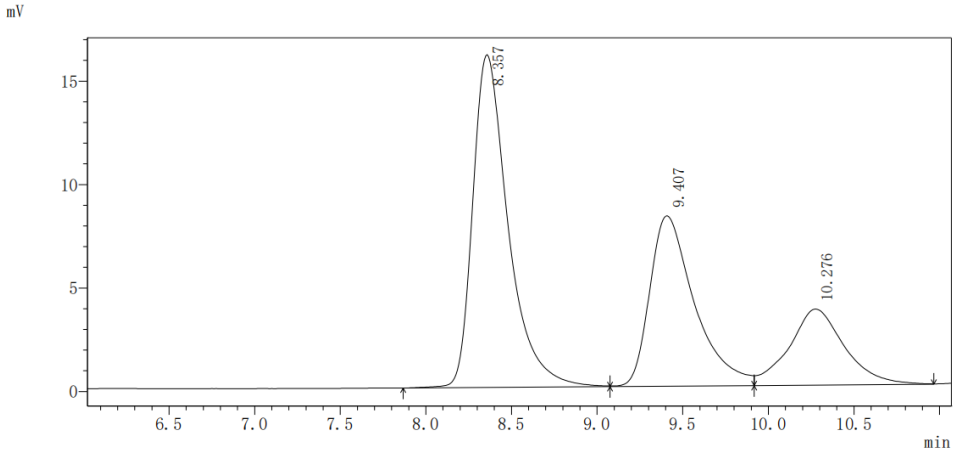


channel 230 nm

Peak	Ret. Time	Area	Height	Conc.
1	16.337	53459749	2149621	95.443
2	19.400	996853	37245	1.780
3	20.608	1555660	60929	2.777
Total		56012261	2247795	



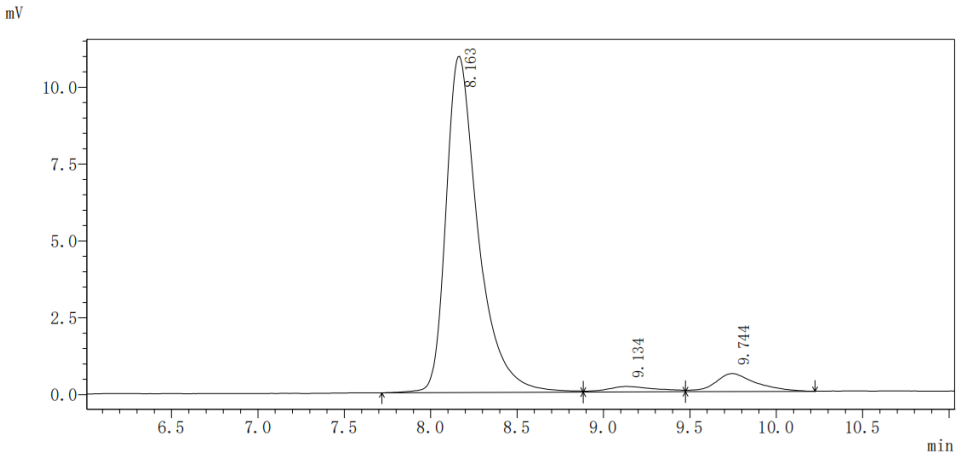
3ai



(mixed with diastereomers)

channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	8.357	231668	16078	49.908
2	9.407	149720	8235	32.254
3	10.276	82803	3679	17.838
Total		464191	27992	



channel 254 nm

Peak	Ret. Time	Area	Height	Conc.
1	8.163	141650	10930	93.626
2	9.134	3534	178	2.336
3	9.744	6109	486	4.038
Total		151293	11594	