

# Tethered Counterion-Directed Catalysis: Merging the Chiral Ion-pairing and Bifunctional Ligand Strategies in Enantioselective Gold(I) Catalysis

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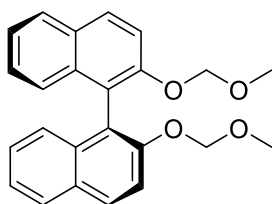
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## 1. General methods.

Unless otherwise noted, all of the reactions were performed under N<sub>2</sub> atmosphere, the solvents were distilled under N<sub>2</sub>, and the separations were carried out under flash-chromatographic conditions on silica gel (Redi Sep prepacked column, 230-400 mesh) with use of a CombiFlash Companion. Reagent-grade chemicals were obtained from diverse commercial suppliers (Sigma-Aldrich, Acros Organics, TCI and Alfa-Aesar) and were used as received. *n*-BuLi was used as commercially available solutions and titrated before use. <sup>1</sup>H NMR (300 and 500 MHz), <sup>31</sup>P (120 MHz and 200 MHz) and <sup>13</sup>C (75 and 125 MHz) NMR spectra were recorded on Bruker Advance spectrometers. The chemical shifts ( $\delta$ ) are reported in part per million (ppm) and coupling values (*J*) are given in hertz (Hz). Multiplicities are abbreviated as follows: s (singlet), d (doublet), t (triplet), q (quadruplet), bs (broad singlet) dd (doublet of doublet), dt (doublet of triplet), m (multiplet). Infrared spectra (IR) were recorded on a Perkin-Elmer FT-IR system using diamond window Dura SamplIR II and the data are reported in reciprocal centimeters (cm<sup>-1</sup>). Optical rotations were measured on a Anton Paar MCP 300 polarimeter at 589 nm.  $[\alpha]_D$  is expressed in deg.cm<sup>3</sup>.g<sup>-1</sup>.dm<sup>-1</sup> and *c* is expressed in g/100 cm<sup>3</sup>. Melting points were recorded in open capillary tubes on a Büchi B-540 apparatus and are uncorrected. High resolution mass spectra (HRMS) were recorded using a Micromass LCT Premier XE instrument (Waters) and were determined by electrospray ionization (ESI) with a TOF analyzer.

## 2. Synthesis and Characterization of the gold(I) complexes (S)-5, (S)-6, (S)-7 and (S)-11a

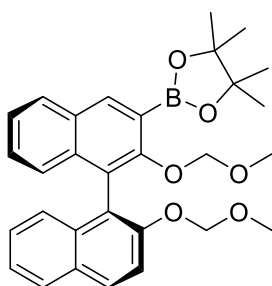
### Synthesis of (S)-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene



(S)-BINOL (14.3 g, 50.0 mmol, 1.0 equiv.) was dissolved in 80 mL of anhydrous THF and added dropwise to a suspension of NaH (60 % wt in mineral oil, 6.0 g, 150 mmol, 3 equiv.) in 80 ml of anhydrous THF at 0 °C. The reaction mixture was stirred for 1 h at room temperature and then MOM-Cl (11.4 mL, 150 mmol, 3 equiv.) was added dropwise at 0 °C. The reaction mixture was stirred for another 3 hours at room temperature. When the reaction was completed, it was quenched with saturated aqueous NaHCO<sub>3</sub> and extracted twice with CH<sub>2</sub>Cl<sub>2</sub>. Combined organic layers were then dried over MgSO<sub>4</sub> and evaporated. The crude product was used directly for further synthesis without purification (18.5 g, 49.4 mmol, 99 %).

**IR (neat)**  $\nu_{\max}$  = 3057, 2956, 2901, 2826, 1621, 1592, 1506, 1237, 1147, 1031, 1011, 920, 809, 749  $\text{cm}^{-1}$ .  **$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz)**  $\delta$  (ppm) = 7.92 (d,  $J$  = 9.0 Hz, 2H), 7.84 (d,  $J$  = 8.3 Hz, 2H), 7.55 (d,  $J$  = 9.0 Hz, 2H), 7.33-7.28 (m, 2H), 7.22-7.14 (m, 4H), 5.05 (d,  $J$  = 6.8 Hz, 2H), 4.94 (d,  $J$  = 6.8 Hz, 2H), 3.11 (s, 6H).  **$^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 75 MHz)**  $\delta$  (ppm) = 152.8, 134.2, 130.0, 129.5, 128.0, 126.5, 125.7, 124.2, 121.4, 117.4, 95.3, 56.0.

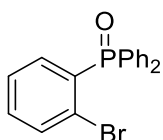
### Synthesis of (*S*)-2-(2,2'-bis(methoxymethoxy)-[1,1'-binaphthalen]-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(*S*)-1]



To a solution of (*S*)-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene (7.84 g, 21 mmol, 1.0 equiv.) in 140 mL of anhydrous THF, *n*-BuLi (19.6 mL, 29.4 mmol, 1.4 equiv.) was added dropwise at  $-78\text{ }^\circ\text{C}$ . The reaction mixture was stirred at  $-78\text{ }^\circ\text{C}$  for 4 hours, then isopropoxy-pinacolborate (5.6 mL, 27.3 mmol, 1.3 equiv.) was added to the flask and the resulting solution was allowed to warm to room temperature. It was stirred overnight at room temperature and then quenched with water and extracted with DCM. Combined organic layers were dried over  $\text{MgSO}_4$  and evaporated. The crude product was purified by flash column chromatography on silica gel (pure heptane to heptane:DCM = 2:1) yielding the product as a white solid (7.03 g, 14.1 mmol, 67 %).<sup>1</sup>

**IR (neat)**  $\nu_{\max}$  = 3411, 3054, 2956, 2825, 1909, 1622, 1592, 1436, 1241, 1146, 1014, 988, 923, 696  $\text{cm}^{-1}$ .  **$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz)**  $\delta$  = 8.49 (s, 1H), 7.92 (d,  $J$  = 8.9 Hz, 2H), 7.82 (d,  $J$  = 8.1 Hz, 1H), 7.55 (d,  $J$  = 9.0 Hz, 1H), 7.39-7.29 (m, 2H), 7.27-7.17 (m, 4H), 5.15 (d,  $J$  = 6.8 Hz, 1H), 4.93 (d,  $J$  = 7.0 Hz, 1H), 4.89 (d,  $J$  = 5.8 Hz, 1H), 4.84 (d,  $J$  = 5.8 Hz, 1H), 3.11 (s, 3H), 2.40 (s, 3H), 1.39 (s, 12H).  **$^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 75 MHz)**  $\delta$  (ppm) = 156.9, 153.1, 139.4, 135.9, 134.5, 130.5, 129.8, 129.5, 128.7, 127.7, 127.5, 126.5, 126.3, 126.1, 125.5, 124.8, 124.1, 121.8, 116.9, 100.2, 100.1, 95.2, 84.0, 56.0, 55.9, 25.0. **HRMS (ESI):**  $m/z$ : calcd for  $\text{C}_{30}\text{H}_{33}\text{BNaO}_6^+$  523.2262 [ $\text{M}+\text{Na}$ ]<sup>+</sup>, found, 523.2313.  **$[\alpha]_{\text{D}}$**  =  $-68$  (c 1.16,  $\text{CHCl}_3$ ).

### Synthesis of (2-bromophenyl)diphenylphosphine oxide<sup>2</sup>



Diphenylphosphine oxide (4.81 g, 23.8 mmol, 1.0 equiv.) was dissolved in PhMe (60 mL), and then  $\text{Pd}_2(\text{dba})_3$  (0.38 g, 0.4 mmol, 1.75 mol %), 1,3-bis(diphenylphosphino)propane (0.34 g, 0.8 mmol, 3.5 mol %), then bromiodobenzene (3.36 mL, 26.2 mmol, 1.1 equiv.), and  $i\text{Pr}_2\text{NEt}$  (4.9 mL, 29.7 mmol, 1.25

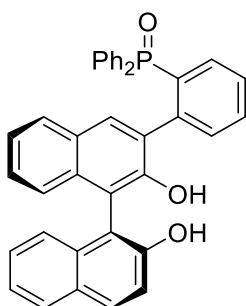
<sup>1</sup> L.-X. Gao; Ma, L.; Jin, R.-Z.; Lü, G.-H.; Bian, Z.; Ding, M.-X. *Synthesis* **2007**, 2461-2470.

<sup>2</sup> H.-L. Wang; Hu, R.-B.; Zhang, H.; Zhou, A.-X.; Yang, S.-D. *Org. Lett.* **2013**, 15, 5302-5305.

equiv.) were added and the mixture stirred at 90 °C for 4 days. After cooling to room temperature, water was added and the solution was extracted with DCM. Organic layers were dried over MgSO<sub>4</sub>, filtered and evaporated under vacuum. The crude product was purified by flash column chromatography (Hept: EA = 4:1 to EA), giving product as a pale yellow solid (6.0 g, 16.8 mmol, 64 %).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ = 7.75-7.65 (m, 5H), 7.58-7.53 (m, 2H), 7.60-7.45 (m, 4H), 7.41-7.30 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ = 136.1 (d, J<sub>C-P</sub> = 10.4 Hz), 135.0 (d, J<sub>C-P</sub> = 7.7 Hz), 133.6 (d, J<sub>C-P</sub> = 2.2 Hz), 133.2 (d, J<sub>C-P</sub> = 104.3 Hz), 132.3 (d, J<sub>C-P</sub> = 9.9 Hz), 132.1 (d, J<sub>C-P</sub> = 2.7 Hz), 131.9 (d, J<sub>C-P</sub> = 107.6 Hz), 128.7 (d, J<sub>C-P</sub> = 12.6 Hz), 127.1 (d, J<sub>C-P</sub> = 11.5 Hz), 127.1 (d, J<sub>C-P</sub> = 4.9 Hz). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 200 MHz) δ = 30.6.

### Synthesis of (S)-2-(2,2'-dihydroxy-[1,1'-binaphthalen]-3-yl)phenyl diphenylphosphine oxide [(S)-2]<sup>3</sup>



(2-bromophenyl)diphenylphosphine oxide (4.44 g, 12.5 mmol, 1.5 equiv.) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.48 g, 0.42 mmol, 5 mol %) were added to a flask, followed by anhydrous, degassed THF (100 mL) and H<sub>2</sub>O (50 mL). The mixture was stirred at room temperature for 10 min. To this solution were added (S)-2-(2,2'-bis(methoxymethoxy)-[1,1'-binaphthalen]-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.78 g, 8.3 mol, 1.0 equiv.) [(S)-1] and K<sub>2</sub>CO<sub>3</sub> (3.45 g, 24.9 mmol, 3 equiv.), and the solution was stirred at 100 °C for 24 h. After cooling to room temperature, water was added and the reaction mixture was extracted twice with methyl *tert*-butyl ether. The combined organic layers were dried over MgSO<sub>4</sub>, filtered and concentrated under vacuum.

The crude product was dissolved in a mixture of THF/MeOH 1:1 (80 mL), then *p*-TsOH·H<sub>2</sub>O was added to this solution and reaction mixture was stirred at 60 °C for 3 hours. After that, it was cooled down to room temperature and solvents were evaporated under reduced pressure. Water was added and the reaction mixture was extracted twice with DCM. The combined organic layers were dried over MgSO<sub>4</sub>, filtered and concentrated under vacuum. The crude product was purified by flash column chromatography (eluent: 100 % heptane to heptane/ethyl acetate, 30/70) giving the product as a white solid (3.43 g, 6.1 mmol, 74 %).

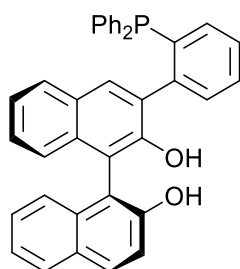
IR (neat) ν<sub>max</sub> = 3058, 1619, 1467, 1438, 1142, 750 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ = 8.11 (br s, 1H), 7.83 (d, J = 8.8 Hz, 1H), 7.77 (d, J = 8.2 Hz, 1H), 7.67 (dd, J<sub>1</sub> = 11.6 Hz, J<sub>2</sub> = 7.6 Hz, 2H), 7.61 (t, J = 7.6 Hz, 1H), 7.58-7.54 (m, 1H), 7.46 (t, J = 6.9 Hz, 1H), 7.42-7.30 (m, 4H), 7.29-7.06 (m, 12H), 6.97 (s, 1H), 6.93 (d, J = 7.9 Hz, 1H), 5.74 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ = 154.0, 151.4, 143.6 (d, J<sub>C-P</sub> = 7.3 Hz), 134.5, 133.9, 133.5 (d, J<sub>C-P</sub> = 13.7 Hz), 133.0, 132.6 (d, J<sub>C-P</sub> = 1.8 Hz), 132.5 (d, J<sub>C-P</sub> = 9.2 Hz), 132.4 (d, J<sub>C-P</sub> = 158.5 Hz), 132.2 (d, J<sub>C-P</sub> = 2.7 Hz), 132.0 (d, J<sub>C-P</sub> = 10.1 Hz), 131.9, 131.9, 131.4, 131.3, 131.3, 131.2 (d, J<sub>C-P</sub> = 106.3 Hz), 130.5, 130.1, 130.1, 129.0 (d, J<sub>C-P</sub> = 50.4 Hz), 128.7 (d, J<sub>C-P</sub> = 11.9 Hz), 128.4 (d, J<sub>C-P</sub> = 12.8 Hz), 128.3 (d, J<sub>C-P</sub> = 6.4 Hz), 127.4 (d, J<sub>C-P</sub> = 12.8 Hz), 126.7, 126.8, 125.4, 123.7, 123.3, 120.2, 115.4, 113.1. <sup>31</sup>P NMR (CDCl<sub>3</sub>,

<sup>3</sup> H. Sasai; Matsui, K.; Takizawa, S. *Synlett* **2006**, 5, 761-765.



**200 MHz**)  $\delta = 30.5$ . **HRMS (ESI)**:  $m/z$ : calcd for  $C_{38}H_{28}O_3P^+$  563.1771  $[M+H]^+$ , found, 563.1770.  $[\alpha]_D = +71$  (c 0.76,  $CHCl_3$ ), *lit* +86 (c 0.6,  $CHCl_3$ ).

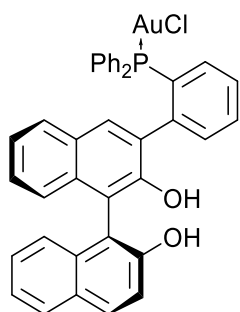
## 2.Synthesis of (S)-3-(2-(diphenylphosphaneyl)phenyl)-[1,1'-binaphthalene]-2,2'-diol [(S)-3]<sup>3</sup>



(S)-3-(2-(2,2'-dihydroxy-[1,1'-binaphthalen]-3-yl)phenyl)diphenylphosphine oxide [(S)-2] (3.43 g, 6.1 mmol, 1.0 equiv.) was dissolved in toluene (100 mL) at 0 °C, and then  $Et_3N$  (8.5 mL, 61 mmol, 10 equiv.) and  $Cl_3SiH$  (12.5 mL, 122.1 mmol, 20 equiv.) were added to the solution dropwise at 0 °C. The reaction was then stirred at 90 °C for 24 h. After cooling to room temperature, the reaction solution was quenched with 2 M NaOH and then THF was evaporated under reduced pressure. 2 M NaOH was added to dissolve the precipitated solid and then extracted twice with DCM, dried over  $MgSO_4$  and evaporated. The crude product was purified by flash column chromatography (eluent: heptane to DCM) giving the product as a white solid (2.61 g, 4.7 mmol, 78 %).

**IR (neat)**  $\nu_{max} = 3510, 3053, 1619, 1596, 1434, 1138, 734\text{ cm}^{-1}$ .  **$^1H$  NMR ( $CDCl_3$ , 500 MHz)**  $\delta = 7.94$  (d,  $J = 8.8$  Hz, 1H), 7.87 (d,  $J = 7.9$  Hz, 1H), 7.64-7.57 (m, 1H), 7.55-7.42 (m, 3H), 7.40-7.15 (m, 17H), 7.11-7.03 (m, 2H), 5.71 (bs, 1H), 5.15 (bs, 1H).  **$^{13}C$  NMR ( $CDCl_3$ , 125 MHz)**  $\delta = 153.2, 150.1, 143.2$  (d,  $J_{C-P} = 30.2$  Hz), 138.2 (d,  $J_{C-P} = 30.2$  Hz), 136.9 (d,  $J_{C-P} = 8.2$  Hz), 136.7 (d,  $J_{C-P} = 9.2$  Hz), 134.1, 134.0, 133.8 (d,  $J_{C-P} = 19.2$  Hz), 132.3, 131.2, 130.5, 130.3 (d,  $J_{C-P} = 3.7$  Hz), 129.6, 129.5, 128.8, 128.6, 128.5, 128.5, 128.5, 127.6, 127.5, 127.2, 125.1, 124.9, 124.2, 123.9, 118.1 (d,  $J_{C-P} = 82.5$  Hz), 112.1, 112.0.  **$^{31}P$  NMR ( $CDCl_3$ , 120 MHz)**  $\delta = -10.6, -12.3$ . **HRMS (ESI)**:  $m/z$ : calcd for  $C_{38}H_{28}O_2P^+$  547.1821  $[M+H]^+$ , found, 547.1801.  $[\alpha]_D = -80$  (c 0.94,  $CHCl_3$ ), *lit* -73 (c 0.6,  $CHCl_3$ ).

## Synthesis of (S)-3-(2-(2,2'-dihydroxy-[1,1'-binaphthalen]-3-yl)phenyl)diphenylphosphine gold(I) chloride [(S)-4]

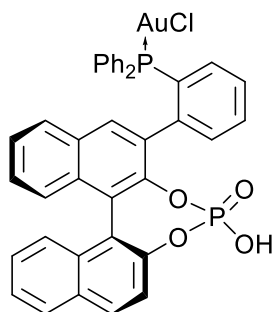


(S)-3-(2-(diphenylphosphaneyl)phenyl)-[1,1'-binaphthalene]-2,2'-diol [(S)-3] (2.63 g, 4.8 mmol, 1.0 equiv.) and  $Me_2S \cdot AuCl$  (1.41 g, 4.8 mmol, 1.0 equiv.) were dissolved in dry DCM (130 mL), and then the reaction solution was stirred at room temperature for 1 h. The solvent was evaporated and the crude product was purified by flash column chromatography (Heptane-DCM), yielding the product as a white

solid (3.4 g, 4.4 mmol, 89 %).

**IR (neat)**  $\nu_{\max}$  = 3515, 3405, 3057, 2926, 1619, 1597, 1437, 1131, 748  $\text{cm}^{-1}$ .  **$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)**  $\delta$  = 7.87 (d,  $J$  = 8.8 Hz, 1H), 7.79 (d,  $J$  = 7.9 Hz, 1H), 7.63-7.61 (m, 1H), 7.58-7.49 (m, 4H), 7.50-7.47 (m, 1H), 7.46-7.40 (m, 4H), 7.39-7.34 (m, 3H), 7.34-7.23 (m, 5H), 7.23-7.16 (m, 4H), 7.00 (d,  $J$  = 8.2 Hz, 1H), 6.53 (br s, 1H), 4.90 (br s, 1H).  **$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)**  $\delta$  = 154.3, 150.2, 144.0 (d,  $J_{\text{C-P}}$  = 15.6 Hz), 134.8 (d,  $J_{\text{C-P}}$  = 5.5 Hz), 134.5 (d,  $J_{\text{C-P}}$  = 13.7 Hz), 134.3 (d,  $J_{\text{C-P}}$  = 13.7 Hz), 134.2, 133.7 (d,  $J_{\text{C-P}}$  = 8.2 Hz), 133.5, 133.1, 132.1 (d,  $J_{\text{C-P}}$  = 1.8 Hz), 131.7 (d,  $J_{\text{C-P}}$  = 1.8 Hz), 131.6, 131.5 (d,  $J_{\text{C-P}}$  = 1.8 Hz), 130.9 (d,  $J_{\text{C-P}}$  = 62.3 Hz), 129.9, 129.6 (d,  $J_{\text{C-P}}$  = 12.8 Hz), 129.4, 129.2 (d,  $J_{\text{C-P}}$  = 11.9 Hz), 129.0, 128.7, 128.6, 128.6, 128.2, 128.1, 127.8, 127.4, 124.9, 124.8, 124.1, 123.8, 119.4, 113.6, 110.4.  **$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 200 MHz)**  $\delta$  = 24.2. **HRMS (ESI):**  $m/z$ : calculated for  $\text{C}_{40}\text{H}_{30}\text{AuNO}_2\text{P}^+$ : 784.1680 [ $\text{M}+\text{MeCN}-\text{Cl}$ ] $^+$ , found, 784.1688;  $m/z$ : calcd for  $\text{C}_{38}\text{H}_{26}\text{AuClO}_2\text{P}^-$ : 777.1030 [ $\text{M}-\text{H}$ ] $^-$ , found, 777.1016.  $[\alpha]_{\text{D}} = -149$  ( $c$  1.07,  $\text{CHCl}_3$ ).

### Synthesis of (S)-(2-(2,2'-diyl hydrogen phosphate-[1,1'-binaphthalen]-3-yl)phenyl) diphenylphosphine gold(I) chloride [(S)-5]



(S)-(2-(2,2'-dihydroxy-[1,1'-binaphthalen]-3-yl)phenyl)diphenylphosphine gold(I) chloride [(S)-4] (3.4 g, 4.3 mmol, 1.0 equiv.) was added to 10 mL pyridine, then  $\text{POCl}_3$  (0.48 mL, 5.11 mmol, 1.2 equiv.) was added to the solution dropwise under 0 °C. The resulting solution was stirred at room temperature for 24 h. After completion, it was quenched with water and the solvent were removed under vacuum. 2M HCl and THF were added, and the reaction mixture was stirred overnight at 50 °C. After cooling to room temperature, the reaction solution was extracted with DCM and  $\text{H}_2\text{O}$ . Crude product was purified by flash column chromatography (eluent: heptane to DCM) giving the product as a brown solid (3.15 g, 3.7 mmol, 88 %).

**m.p.:** 256.2-261.5 °C. **IR (neat)**  $\nu_{\max}$  = 3515, 3405, 3056, 2925, 1619, 1436, 1214, 1131, 748  $\text{cm}^{-1}$ . **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{40}\text{H}_{29}\text{AuNO}_4\text{P}_2^+$  846.1232 [ $\text{M}+\text{MeCN}-\text{Cl}$ ] $^+$ , found, 846.1245;  $m/z$  calcd for  $\text{C}_{38}\text{H}_{25}\text{AuClO}_4\text{P}_2^-$  839.0588 [ $\text{M}-\text{H}$ ] $^-$ , found, 839.0587.  $[\alpha]_{\text{D}} = +15$  ( $c$  1.03,  $\text{CHCl}_3$ ).

#### -NMR data in DMSO-d6:

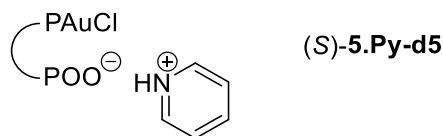
**$^1\text{H}$  NMR (DMSO-d6, 343K, 500 MHz)**  $\delta$  = 8.13-8.07 (m, 2H), 8.06 (d,  $J$  = 6.6 Hz, 1H), 8.03 (d,  $J$  = 8.2 Hz, 1H), 7.86 (d,  $J$  = 8.2 Hz, 1H), 7.72 (t,  $J$  = 7.6 Hz, 2H), 7.62 (d,  $J$  = 6.3 Hz, 1H), 7.60-7.48 (m, 7H), 7.43 (d,  $J$  = 8.8 Hz, 1H), 7.40 (d,  $J$  = 9.1 Hz, 1H), 7.37-7.28 (m, 4H), 7.18-7.10 (m, 2H), 7.00 (br s, 2H), 6.24 (br s, 1H).

**$^{13}\text{C}$  NMR (DMSO-d6, 343K, 125 MHz)**  $\delta$  = 146.9 (d,  $J_{\text{C-P}}$  = 9.2 Hz), 144.9 (d,  $J_{\text{C-P}}$  = 10.1 Hz), 141.5 (d,  $J_{\text{C-P}}$  = 13.7 Hz), 133.8 (d,  $J_{\text{C-P}}$  = 7.3 Hz), 133.6 (d,  $J_{\text{C-P}}$  = 13.7 Hz), 133.3 (d,  $J_{\text{C-P}}$  = 13.7 Hz), 132.9 (d,  $J_{\text{C-P}}$  = 6.4 Hz), 131.8, 131.5, 131.3 (d,  $J_{\text{C-P}}$  = 5.5 Hz), 131.2, 131.0 (d,  $J_{\text{C-P}}$  = 116.4 Hz), 130.7, 130.3, 129.8, 129.5, 129.4, 129.1 (d,  $J_{\text{C-P}}$  = 11.0 Hz), 128.4, 128.4 (d,  $J_{\text{C-P}}$  = 12.8 Hz), 128.0 (d,  $J_{\text{C-P}}$  = 9.2 Hz), 127.6, 127.6, 127.4 (d,  $J_{\text{C-P}}$  = 12.8 Hz), 126.9 (d,  $J_{\text{C-P}}$  = 15.6 Hz), 126.4, 125.9, 125.6, 125.2, 124.9, 121.7, 121.0, 120.7, 120.3.

<sup>31</sup>P NMR (DMSO-d<sub>6</sub>, 343 K, 200 MHz) δ = 26.4, 1.2 (major isomer) and 25.8, 2.5 (minor isomer).

<sup>31</sup>P NMR (DMSO-d<sub>6</sub>, 383 K, 200 MHz) δ = 26.8, 1.1.

-NMR data in deuterated pyridine:



<sup>1</sup>H NMR (Pyridine-d<sub>5</sub>, 500 MHz) δ = 11.86 (bs, 1H), 9.26 (t, *J* = 6.3 Hz, 1H), 7.97 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.84 (t, *J* = 7.7 Hz, 1H), 7.82-7.75 (m, 3H), 7.72 (d, *J* = 8.7 Hz, 1H), 7.63 (dd, *J*<sub>1</sub> = 13.2 Hz, *J*<sub>2</sub> = 7.7 Hz, 2H), 7.53 (t, *J* = 6.9 Hz, 1H), 7.49-7.33 (m, 9H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.15 (dd, *J*<sub>1</sub> = 12.1 Hz, *J*<sub>2</sub> = 7.9 Hz, 1H), 6.99 (t, *J* = 6.8 Hz, 2H), 6.92 (t, *J* = 6.9 Hz, 1H).

<sup>13</sup>C NMR (Pyridine-d<sub>5</sub>, 125 MHz) δ = 148.6 (d, *J*<sub>C-P</sub> = 10.1 Hz), 144.1 (d, *J*<sub>C-P</sub> = 13.7 Hz), 136.9 (d, *J*<sub>C-P</sub> = 7.3 Hz), 135.6 (d, *J*<sub>C-P</sub> = 14.7 Hz), 134.7, 134.7 (d, *J*<sub>C-P</sub> = 13.7 Hz), 134.1, 133.9, 133.7 (d, *J*<sub>C-P</sub> = 4.6 Hz), 133.5, 132.8, 132.4, 132.1, 131.7, 131.6 (d, *J*<sub>C-P</sub> = 62.3 Hz), 131.3, 130.7, 130.3 (d, *J*<sub>C-P</sub> = 11.9 Hz), 130.3, 129.9, 129.8, 129.7 (d, *J*<sub>C-P</sub> = 11.0 Hz), 129.4, 129.0 (d, *J*<sub>C-P</sub> = 10.1 Hz), 128.8, 128.7, 128.3, 127.8, 127.6, 127.3, 126.2, 126.0, 123.1.

<sup>31</sup>P NMR (Pyridine-d<sub>5</sub>, 200 MHz) δ = 29.2, 6.7.

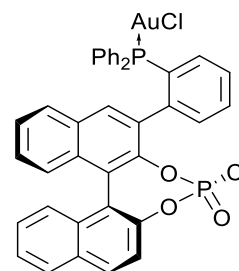
-NMR data in CDCl<sub>3</sub>:

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ = 8.30 (s, 1H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.77-7.72 (m, 1H), 7.58-7.48 (m, 5H), 7.46-7.39 (m, 3H), 7.35-7.19 (m, 8H), 6.97 (dd, *J*<sub>1</sub> = 11.9 Hz, *J*<sub>2</sub> = 7.9 Hz, 1H), 6.73-6.66 (m, 2H), 6.66-6.60 (m, 1H), 6.53 (bs, 1H).

<sup>31</sup>P NMR (CDCl<sub>3</sub>, 200 MHz) δ = 27.7, 2.9 (major isomer), 26.2, 4.6 (minor isomer).

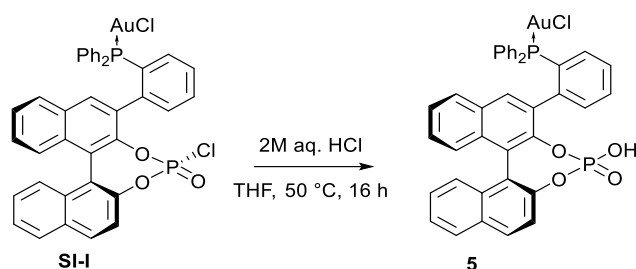
Isolation of the intermediate phosphoroyl chloride **SI-1**

In some reaction batch for the synthesis of **5**, one of the intermediate phosphoroyl chloride diastereoisomer was showed to be poorly reactive towards hydrolysis and could be isolated and characterized.



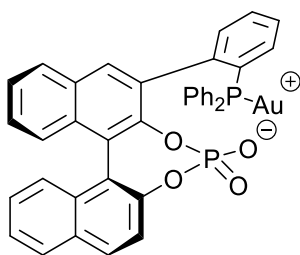
Data for (S)-(2-(2,2'-diylchlorogenphosphate-[1,1'-binaphthalen]-3-yl)phenyl) diphenylphosphine gold(I) chloride [SI-1]: m.p.: 193.4-194.2 °C. IR (neat)  $\nu_{\text{max}}$  = 3056, 2961, 2925, 2854, 1591, 1437, 1413, 1310, 1242, 1208, 1101, 1082, 970, 954, 904, 821, 876, 750, 693. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ = 8.37 (s, 1H), 8.09 (d, *J* = 8.2 Hz, 1H), 8.03 (d, *J* = 8.8 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.85 (t, *J* = 6.3 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.62-7.55 (m, 2H), 7.52-7.45 (m, 5H), 7.45-7.40 (m, 3H), 7.40-7.31 (m, 4H), 7.25 (d, *J* = 9.1 Hz, 1H), 7.07 (dd, *J*<sub>1</sub> = 12.0 Hz, *J*<sub>2</sub> = 8.2 Hz, 1H), 6.74-6.69 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ = 146.1 (d, *J*<sub>C-P</sub> = 11.9 Hz), 143.9 (d, *J*<sub>C-P</sub> = 11.9 Hz), 141.1 (d, *J*<sub>C-P</sub> = 12.8 Hz), 134.9 (d, *J*<sub>C-P</sub> = 14.7 Hz), 134.6 (d, *J*<sub>C-P</sub> = 14.7 Hz), 134.1 (d, *J*<sub>C-P</sub> = 7.3 Hz), 133.8, 133.2 (d, *J*<sub>C-P</sub> = 6.4 Hz), 132.6, 132.2, 131.9, 131.9, 131.9, 131.7, 131.7, 131.5, 130.9 (d, *J*<sub>C-P</sub> = 1.8 Hz), 129.8, 129.6, 129.4 (d, *J*<sub>C-P</sub> = 11.9 Hz), 129.0, 128.9 (d, *J*<sub>C-P</sub> = 8.2 Hz), 128.9, 128.8, 128.6, 128.4, 128.0, 127.5, 127.0 (d, *J*<sub>C-P</sub> = 68.7 Hz), 126.8, 122.1, 121.8, 121.8, 119.6 (d, *J*<sub>C-P</sub> = 2.7 Hz). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 200 MHz) δ = 26.8, 9.2. HRMS (ESI): *m/z* calcd for C<sub>40</sub>H<sub>28</sub>AuClINO<sub>3</sub>P<sub>2</sub><sup>+</sup> 864.0893 [M+MeCN-Cl]<sup>+</sup>, found, 864.0898.

This compound **SI-1** could be submitted to hydrolysis according to the following procedure.



To a solution of **SI-1** (436 mg, 0.51 mmol) in THF (30 mL) was added 2 M HCl (30 mL). The resulting mixture was then stirred overnight at 50 °C. After cooling to room temperature, the THF was removed under vacuum and the resulting solution was extracted with DCM. Organic layers were dried over MgSO<sub>4</sub>, filtered and evaporated under vacuum. The crude product was purified by flash column chromatography, giving product (**S**)-**5** as a brown solid (350.0 mg, 0.42 mmol, 82 %).

### Synthesis of (**S**)-**6**



To a suspension of Ag<sub>2</sub>CO<sub>3</sub> (82.8 mg, 0.3 mmol) in toluene (2 mL) and H<sub>2</sub>O (2 mL), (**S**)-**5** (84.1 mg, 0.1 mmol) was added. The mixture was stirred overnight at room temperature. Then the suspension was filtered on celite. The filter was rinsed with DCM and evaporated under vacuum. The product was obtained as an amorphous gray solid (56.1 mg, 0.07 mmol, 69 %). This Au(I) complex is also very cleanly generated by performing the reaction in pure CDCl<sub>3</sub> within 1 h.

**IR (neat) v<sub>max</sub>** = 3656, 3410, 3054, 2923, 2852, 1621, 1592, 1509, 1480, 1436, 1417, 1330, 1263, 1227, 1101, 1080, 1052, 997, 967, 950, 869, 850, 816, 749, 712, 694.

**HRMS (ESI):** *m/z* calcd for C<sub>40</sub>H<sub>29</sub>AuNO<sub>4</sub>P<sub>2</sub><sup>+</sup> 846.1232 [M+H+MeCN]<sup>+</sup>, found, 846.1232;

**HRMS (ESI):** *m/z* calcd for C<sub>39</sub>H<sub>26</sub>AuO<sub>6</sub>P<sub>2</sub><sup>-</sup> 849.0876 [M+HCOO]<sup>-</sup>, found, 849.0867.

[α]<sub>D</sub> = +39 (c 1.12, CHCl<sub>3</sub>).

### -NMR data in Pyridine-d<sub>5</sub>

**<sup>1</sup>H NMR (Pyridine, 500 MHz)** δ = 8.12-7.98 (m, 3H), 7.92 (d, *J* = 8.9 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.82-7.74 (m, 3H), 7.70 (td, *J*<sub>1</sub> = 7.6 Hz, *J*<sub>2</sub> = 1.8 Hz, 2H), 7.57 (d, *J* = 9.2 Hz, 1H), 7.50-7.44 (m, 3H), 7.44-7.32 (m, 7H), 7.30-7.27 (m, 1H), 7.20-7.08 (m, 4H).

**<sup>13</sup>C NMR (Pyridine, 125 MHz)** δ = 152.0 (d, *J*<sub>C-P</sub> = 9.2 Hz), 149.4 (d, *J*<sub>C-P</sub> = 8.2 Hz), 144.8 (d, *J*<sub>C-P</sub> = 14.7 Hz), 136.4, 135.8 (d, *J*<sub>C-P</sub> = 13.7 Hz), 135.6, 135.4 (d, *J*<sub>C-P</sub> = 5.5 Hz), 134.7 (d, *J*<sub>C-P</sub> = 12.8 Hz), 134.2 (d, *J*<sub>C-P</sub> = 8.2 Hz), 133.8, 133.2, 133.1, 133.1 (d, *J*<sub>C-P</sub> = 128.3 Hz), 132.1, 131.8 (d, *J*<sub>C-P</sub> = 45.8 Hz), 130.9, 130.5 (d, *J*<sub>C-P</sub> = 11.9 Hz), 130.4 (d, *J*<sub>C-P</sub> = 79.7 Hz), 129.9, 129.9, 129.6, 129.3, 129.0, 128.7 (d, *J*<sub>C-P</sub> = 9.2 Hz), 127.9, 127.4, 127.1,

126.7, 125.9, 125.0, 124.9 (d,  $J_{C-P}$  = 127.4 Hz), 123.8, 123.5, 122.8.

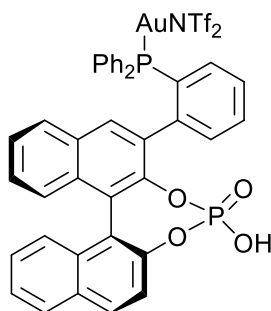
$^{31}\text{P}$  NMR (Pyridine, 200 MHz)  $\delta$  = 22.9, 8.6.

**-NMR data in  $\text{CDCl}_3$**

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  = 7.80 (d,  $J$  = 8.2 Hz, 1H), 7.76 (d,  $J$  = 8.9 Hz, 1H), 7.65 (brs, 2H), 7.52-7.23 (m, 16H), 7.20-7.10 (m, 2H), 7.00-6.85 (m, 3H).

$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  = 21.8, 8.3.

- **Synthesis of (S)-[2-(2,2'-diyl hydrogen phosphate-[1,1'-binaphthalen]-3-yl)phenyl] diphenylphosphine gold(I) bis(trifluoromethanesulfonyl)imide (S)-7a**



To a suspension of  $\text{AgNTf}_2$  (16.8 mg, 0.030 mmol) in toluene (1 mL), (**S**)-**6** (16.8 mg, 0.020 mmol) was added. The mixture was stirred overnight at room temperature. Then the suspension was filtered on celite. The filter was rinsed with DCM and evaporated under vacuum. The product was obtained as an amorphous gray solid (17.8 mg, 0.016 mmol, 82 %).

**IR (neat)**  $\nu_{\text{max}}$  = 3061, 1592, 1438, 1401, 1353, 1209, 1198, 1131, 1082, 1060, 1028, 958, 900, 830, 751.  $[\alpha]_{\text{D}}$  = +170 ( $c$  1.16,  $\text{CHCl}_3$ ). **HRMS (ESI)**:  $m/z$  calcd for  $\text{C}_{40}\text{H}_{29}\text{AuNO}_4\text{P}_2^+$  846.1232 [ $\text{M-NTf}_2+\text{H+MeCN}$ ] $^+$ , found, 846.1224.

**-NMR data in  $\text{CDCl}_3$**

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  = 8.32 (s, 1H), 8.17 (d,  $J$  = 8.2 Hz, 1H), 7.95 (d,  $J$  = 8.2 Hz, 1H), 7.92 (d,  $J$  = 8.8 Hz, 1H), 7.65-7.59 (m, 2H), 7.59-7.52 (m, 3H), 7.52-7.37 (m, 6H), 7.37-7.28 (m, 3H), 7.27-7.18 (m, 3H), 6.96 (dd,  $J_1$  = 12.3 Hz,  $J_2$  = 7.9 Hz, 1H), 6.60-6.52 (m, 1H), 6.50-6.38 (m, 2H), 5.69 (bs, 1H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  = 146.2 (d,  $J_{C-P}$  = 5.5 Hz), 143.7 (d,  $J_{C-P}$  = 4.6 Hz), 142.0 (d,  $J_{C-P}$  = 12.8 Hz), 135.3 (d,  $J_{C-P}$  = 14.7 Hz), 134.4 (d,  $J_{C-P}$  = 13.7 Hz), 133.3 (d,  $J_{C-P}$  = 7.3 Hz), 133.1 (d,  $J_{C-P}$  = 8.2 Hz), 132.6 (d,  $J_{C-P}$  = 108.1 Hz), 132.5 (d,  $J_{C-P}$  = 1.8 Hz), 132.5, 131.6, 131.5 (d,  $J_{C-P}$  = 46.7 Hz), 131.5 (d,  $J_{C-P}$  = 1.8 Hz), 131.4, 130.7 (d,  $J_{C-P}$  = 6.4 Hz), 129.8 (d,  $J_{C-P}$  = 12.8 Hz), 129.3, 129.0, 128.9, 128.9, 128.6, 128.0, 127.8 (d,  $J_{C-P}$  = 20.2 Hz), 127.8, 127.4, 127.3 (d,  $J_{C-P}$  = 20.2 Hz), 127.0, 126.7, 126.4, 124.4 (d,  $J_{C-P}$  = 67.8 Hz), 123.4, 121.6 (d,  $J_{C-P}$  = 103.6 Hz), 120.8, 119.5, 118.3.

$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  = 22.9, 2.9.

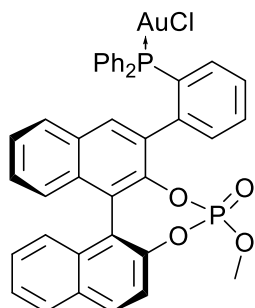
**-NMR data in deuterated pyridine**

$^1\text{H}$  NMR (Pyridine- $\text{d}_5$ , 500 MHz)  $\delta$  = 11.45 (br s, 1H), 8.05-7.97 (m, 3H), 7.93-7.80 (m, 3H), 7.75 (td,  $J_1$

= 7.6 Hz,  $J_2 = 1.8$  Hz, 1H), 7.69-7.28 (m, 15H), 7.25 (d,  $J = 7.5$  Hz, 1H), 7.19 (d,  $J = 7.6$  Hz, 1H), 7.11 (d,  $J = 8.5$  Hz, 1H).

$^{31}\text{P}$  NMR (Pyridine- $d_5$ , 200 MHz)  $\delta = 22.8, 7.6$  (major isomer), 27.9, 7.1 (minor isomer).

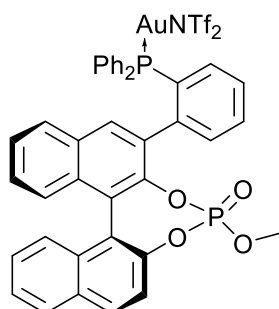
### Synthesis of SI-2



(*S*)-(2-(2,2'-diylchlorogenphosphate-[1,1'-binaphthalen]-3-yl)phenyl) diphenylphosphine gold(I) chloride [**SI-1**] (122 mg, 0.14 mmol, 1.0 equiv.) was added to methanol (5 mL), the result solution was then stirred overnight at 35 °C. The methanol was removed and the crude product was purified by flash column chromatography, giving product as a white solid (69.0 mg, 0.08 mmol, 57 %).

**IR (neat)**  $\nu_{\text{max}} = 3056, 2958, 2923, 2856, 1620, 1592, 1437, 1300, 1218, 1187, 1101, 1051, 993, 974, 955, 892, 829, 750, 694$ .  **$^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz)**  $\delta = 8.27$  (s, 1H), 8.01-7.95 (m, 3H), 7.93 (d,  $J = 8.2$  Hz, 1H), 7.71 (t,  $J = 7.6$  Hz, 1H), 7.56-7.47 (m, 5H), 7.47-7.39 (m, 4H), 7.39-7.31 (m, 4H), 7.30-7.24 (m, 1H), 7.20 (d,  $J = 8.5$  Hz, 1H), 7.05 (dd,  $J_1 = 11.6$  Hz,  $J_2 = 7.9$  Hz, 1H), 6.82-6.72 (m, 3H), 3.66 (d,  $J = 11.7$  Hz, 3H).  **$^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 125 MHz)**  $\delta = 147.0$  (d,  $J_{\text{C-P}} = 11.0$  Hz), 143.6 (d,  $J_{\text{C-P}} = 8.2$  Hz), 141.6 (d,  $J_{\text{C-P}} = 12.8$  Hz), 134.8 (d,  $J_{\text{C-P}} = 8.2$  Hz), 134.6 (d,  $J_{\text{C-P}} = 9.2$  Hz), 134.4 (d,  $J_{\text{C-P}} = 8.2$  Hz), 133.4, 133.2 (d,  $J_{\text{C-P}} = 7.3$  Hz), 132.5 (d,  $J_{\text{C-P}} = 43.1$  Hz), 131.9 (d,  $J_{\text{C-P}} = 1.8$  Hz), 131.7 (d,  $J_{\text{C-P}} = 1.8$  Hz), 131.6 (d,  $J_{\text{C-P}} = 2.7$  Hz), 131.3, 131.1, 131.1, 131.0, 130.5 (d,  $J_{\text{C-P}} = 143.0$  Hz), 129.5, 129.4, 129.3, 128.8, 128.7, 128.6, 128.6, 128.2, 127.8 (d,  $J_{\text{C-P}} = 135.6$  Hz), 127.7, 127.6, 127.2, 126.8, 126.4 (d,  $J_{\text{C-P}} = 64.2$  Hz), 122.2, 121.3, 119.7 (d,  $J_{\text{C-P}} = 2.7$  Hz), 55.8 (d,  $J_{\text{C-P}} = 5.5$  Hz).  **$^{31}\text{P}$  NMR (CDCl<sub>3</sub>, 200 MHz)**  $\delta = 27.2, 1.2$ . **HRMS (ESI):**  $m/z$  calcd for C<sub>41</sub>H<sub>31</sub>AuNO<sub>4</sub>P<sub>2</sub><sup>+</sup> 860.1388 [M+MeCN-Cl]<sup>+</sup>, found, 860.1390;  $m/z$  calcd for C<sub>38</sub>H<sub>25</sub>AuClO<sub>4</sub>P<sub>2</sub><sup>-</sup> 839.0588 [M-CH<sub>3</sub>]<sup>-</sup>, found, 839.0576.

### Synthesis of (S)-11a



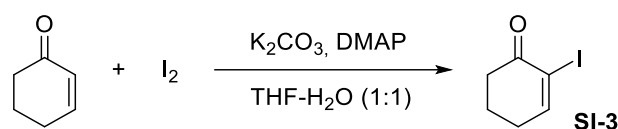
**SI-2** (16.7 mg, 0.02 mmol, 1.0 equiv.) and AgNTf<sub>2</sub> (7.5 mg, 0.02 mmol, 1.0 equiv.) were added to 1 mL CDCl<sub>3</sub>, the resulting solution was then stirred at room temperature for 2 h. The reaction solution was filtered and evaporated, giving product **11** as a white solid (18.8 mg, 0.02 mmol, 79 %).

**IR (neat)**  $\nu_{\text{max}} = 3059, 2961, 2927, 2856, 1537, 1438, 1400, 1354, 1300, 1261, 1210, 1193, 1131, 1102,$

1055, 975, 957, 895, 830, 751, 693.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  = 8.35 (s, 1H), 8.15 (d,  $J$  = 8.2 Hz, 1H), 7.96 (d,  $J$  = 8.8 Hz, 1H), 7.95 (d,  $J$  = 7.6 Hz, 1H), 7.85 (t,  $J$  = 6.3 Hz, 1H), 7.74 (t,  $J$  = 7.6 Hz, 1H), 7.59 (t,  $J$  = 7.6 Hz, 1H), 7.55 (t,  $J$  = 7.6 Hz, 1H), 7.55 (s, 1H), 7.51-7.42 (m, 5H), 7.38 (t,  $J$  = 7.6 Hz, 1H), 7.36 (t,  $J$  = 7.6 Hz, 1H), 7.29 (d,  $J$  = 8.8 Hz, 2H), 7.27-7.21 (m, 3H), 6.98 (dd,  $J_1$  = 12.6 Hz,  $J_2$  = 7.9 Hz, 1H), 6.58 (t,  $J$  = 6.9 Hz, 1H), 6.48 (t,  $J$  = 6.6 Hz, 2H), 3.71 (d,  $J$  = 11.7 Hz, 3H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  = 146.9 (d,  $J_{\text{C-P}}$  = 11.0 Hz), 143.2 (d,  $J_{\text{C-P}}$  = 8.2 Hz), 141.9 (d,  $J_{\text{C-P}}$  = 12.8 Hz), 135.2 (d,  $J_{\text{C-P}}$  = 15.6 Hz), 134.4 (d,  $J_{\text{C-P}}$  = 13.7 Hz), 134.2 (d,  $J_{\text{C-P}}$  = 7.3 Hz), 132.9 (d,  $J_{\text{C-P}}$  = 9.2 Hz), 132.8, 132.6 (d,  $J_{\text{C-P}}$  = 106.3 Hz), 132.4 (d,  $J_{\text{C-P}}$  = 2.7 Hz), 131.9 (d,  $J_{\text{C-P}}$  = 2.7 Hz), 131.8 (d,  $J_{\text{C-P}}$  = 1.8 Hz), 131.6, 131.3, 131.3, 130.6 (q,  $J_{\text{C-P}}$  = 2.7 Hz), 129.7 (d,  $J_{\text{C-P}}$  = 11.9 Hz), 129.1, 128.9 (d,  $J_{\text{C-P}}$  = 10.1 Hz), 128.8 (d,  $J_{\text{C-P}}$  = 12.8 Hz), 128.4, 128.1, 128.0, 127.7 (d,  $J_{\text{C-P}}$  = 54.1 Hz), 127.3, 127.3, 126.9, 126.9, 126.2, 124.8 (d,  $J_{\text{C-P}}$  = 67.8 Hz), 122.2, 121.0, 120.8, 119.6 (d,  $J_{\text{C-P}}$  = 2.7 Hz), 118.3, 55.5 (d,  $J_{\text{C-P}}$  = 4.6 Hz).  $^{31}\text{P NMR}$  ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  = 23.0, 2.3. HRMS (ESI):  $m/z$  calcd for  $\text{C}_{41}\text{H}_{31}\text{AuNO}_4\text{P}_2^+$  860.1388  $[\text{M}+\text{MeCN}-\text{NTf}_2]^+$ , found, 860.1387.  $[\alpha]_{\text{D}}$  = +28 ( $c$  1.83,  $\text{CHCl}_3$ ).

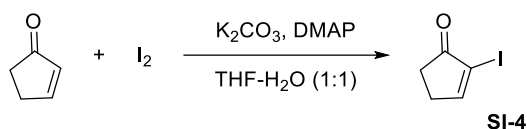
### 3. Synthesis of enones 8 and indole 9

#### Synthesis of 2-iodocyclohex-2-en-1-one (SI-3) <sup>4</sup>



To a stirred solution of cyclohex-2-en-1-one (4.05 mL, 42 mmol, 1.0 equiv.) in a 1:1 mixture of THF-H<sub>2</sub>O (200 mL) was added K<sub>2</sub>CO<sub>3</sub> (6.9 g, 50 mmol, 1.2 equiv.), I<sub>2</sub> (15.9 g, 63 mmol, 1.5 equiv.) and 4-dimethylaminopyridine (DMAP) (1.02 g, 8.3 mmol, 0.2 equiv.) successively. Then the reaction was stirred at room temperature for 2 h. Upon completion, the reaction solution mixture was diluted with ethyl acetate and washed with saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and aqueous 0.1 M HCl successively. The mixture was subsequently extracted with ethyl acetate and dried over MgSO<sub>4</sub>. Crude product was purified by flash column chromatography (heptane to 20 % EtOAc-Heptane), giving product SI-3 as a white solid (7.17 g, 32 mmol, 77 %).

#### Synthesis of 2-iodocyclopent-2-en-1-one<sup>4, 5</sup> (SI-4)



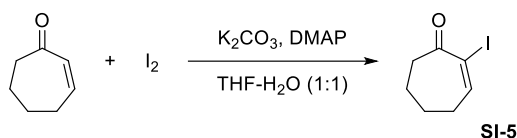
Compound SI-4 was prepared by following the general procedure for the synthesis of SI-3. To a stirred solution of cyclopent-2-en-1-one (0.42 mL, 5 mmol, 1.0 equiv.) in a 1:1 mixture of THF-H<sub>2</sub>O (30 mL) was

<sup>4</sup> (a) T. Yao; Zhang, X.; Larock, R. C. *J. Am. Chem. Soc.* **2004**, *126*, 11164-11165; (b) M. Krafft; Cran, J. *Synlett* **2005**, 1263-1266; (c) L.-E. Harim; Moises, R.-O.; F., O. H. *Eur. J. Org. Chem.* **2016**, 51-54.

<sup>5</sup> H. Sundén; Schäfer, A.; Scheepstra, M.; Leysen, S.; Malo, M.; Ma, J.-N.; Burstein, E. S.; Ottmann, C.; Brunsveldt, L.; Olsson, R. *J. Med. Chem.* **2016**, *59*, 1232-1238.

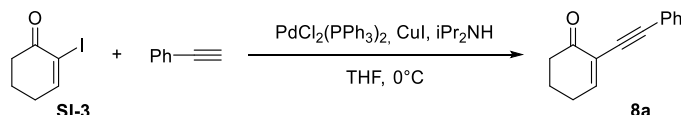
added  $K_2CO_3$  (0.83 g, 6 mmol, 1.2 equiv.),  $I_2$  (1.9 g, 7.5 mmol, 1.5 equiv.) and 4-dimethylaminopyridine (DMAP) (0.13 g, 1 mmol, 0.2 equiv.) successively. Then the reaction was stirred at room temperature for 2 h. Upon completion, the reaction solution mixture was diluted with ethyl acetate and washed with saturated aqueous  $Na_2S_2O_3$  and aqueous 0.1 M HCl successively. The mixture was subsequently extracted with ethyl acetate and dried over  $MgSO_4$ . Crude product was purified by flash column chromatography (heptane to 20 % EtOAc-Heptane), giving product **SI-4** as a pale yellow solid (0.57 g, 2.7 mmol, 55 %).

#### Synthesis of 2-iodocyclohept-2-en-1-one<sup>4,5</sup> (**SI-5**)



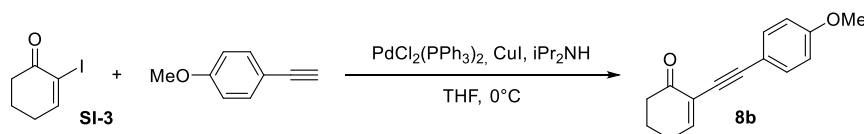
Compound **SI-5** was prepared by following the general procedure for the synthesis of **SI-3**. To a stirred solution of cyclohept-2-en-1-one (0.34 mL, 3.0 mmol, 1.0 equiv.) in a 1:1 mixture of THF- $H_2O$  (14 mL) was added  $K_2CO_3$  (0.50 g, 3.6 mmol, 1.2 equiv.),  $I_2$  (1.14 g, 4.5 mmol, 1.5 equiv.) and 4-dimethylaminopyridine (DMAP) (0.08 g, 0.6 mmol, 0.2 equiv.) successively. Then the reaction was stirred at room temperature for 2 h. Upon completion, the reaction solution mixture was diluted with ethyl acetate and washed with saturated aqueous  $Na_2S_2O_3$  and aqueous 0.1 M HCl successively. The mixture was subsequently extracted with ethyl acetate and dried over  $MgSO_4$ . Crude product was purified by flash column chromatography (heptane to 20 % EtOAc-Heptane), giving product **SI-5** as a pale yellow oil (0.37 g, 1.6 mmol, 52 %).

#### Synthesis of 2-(phenylethynyl)cyclohex-2-en-1-one<sup>4</sup> (**8a**)



A solution of 2-iodo-cyclohexenone (430.0 mg, 1.94 mmol, 1.0 equiv.) in THF (5.1 mL) was treated with  $PdCl_2(PPh_3)_2$  (69.0 mg, 0.1 mmol, 5 mol %) and  $CuI$  (37.0 mg, 0.19 mmol, 10 mol %) and cooled down to 0 °C under an Ar atmosphere and in the dark. After 10 min of stirring, phenylacetylene (0.44 mL, 409.2 mg, 4.01 mmol) and diisopropyl amine (0.82 mL, 59.0 mg, 5.85 mmol) were added, and the resulting yellow to dark brown solution was stirred at 0 °C. The reaction mixture was partitioned between  $CH_2Cl_2$  and 0.5 N aqueous HCl solution. The aqueous layer was extracted three times with  $CH_2Cl_2$  and the combined organic phases were washed with brine, dried over  $MgSO_4$ , filtered and concentrated under vacuum. The crude product was purified by flash column chromatography to yield alkyne **8a** as a yellow solid (334 mg, 1.75 mmol, 88 %).

#### Synthesis of 2-(phenylethynyl)cyclohex-2-en-1-one<sup>6</sup> (**8b**)

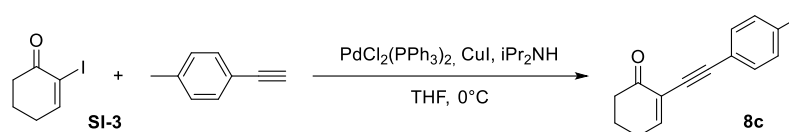


<sup>6</sup> Rauniyar, V.; Wang, Z. J.; Burks, H. E.; Toste, F. D., *J. Am. Chem. Soc.* **2011**, *133*, 8486-8489.



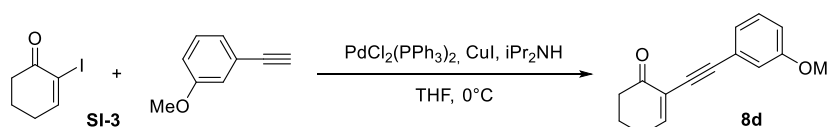
Compound **8b** was prepared by following the general procedure for the synthesis of **8a**. A solution of 2-iodo-cyclohexenone (444.0 mg, 2 mmol, 1.0 equiv.) in THF (5 mL) was treated with PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (70.2 mg, 0.1 mmol, 5 mol %) and CuI (38.1 mg, 0.2 mmol, 10 mol %) and cooled down to 0 °C under an Ar atmosphere. After 10 min of stirring, 1-ethynyl-4-methoxybenzene (528.6 mg, 4 mmol, 2 equiv.) and diisopropyl amine (0.87 mL, 627.4 mg, 6.2 mmol) were added, and the resulting solution was stirred at 0 °C. The reaction mixture was partitioned between CH<sub>2</sub>Cl<sub>2</sub> and 0.5 N aqueous HCl solution. The aqueous layer was extracted three times with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic phases were washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated under vacuum. The crude product was purified by flash column chromatography to yield alkyne **8b** as a brown solid (148.7 mg, 0.66 mmol, 33 %).

#### Synthesis of 2-(phenylethynyl)cyclohex-2-en-1-one<sup>5</sup> (**8c**)



Compound **8c** was prepared by following the general procedure for the synthesis of **8a**. A solution of 2-iodo-cyclohexenone (444.0 mg, 2 mmol, 1.0 equiv.) in THF (5 mL) was treated with PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (70.2 mg, 0.1 mmol, 5 mol %) and CuI (38.1 mg, 0.2 mmol, 10 mol %) and cooled down to 0 °C under an Ar atmosphere. After 10 min of stirring, 1-ethynyl-4-methylbenzene (464.6 mg, 4 mmol, 2 equiv.) and diisopropyl amine (0.87 mL, 627.4 mg, 6.2 mmol) were added, and the resulting solution was stirred at 0 °C. The reaction mixture was partitioned between CH<sub>2</sub>Cl<sub>2</sub> and 0.5 N aqueous HCl solution. The aqueous layer was extracted three times with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic phases were washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated under vacuum. The crude product was purified by flash column chromatography to yield alkyne **8c** as a gray solid (313.9 mg, 1.49 mmol, 75 %).

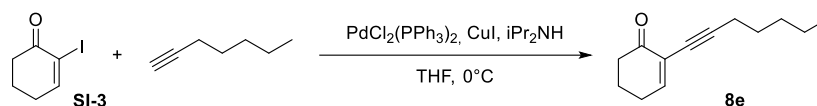
#### Synthesis of 2-(phenylethynyl)cyclohex-2-en-1-one (**8d**)<sup>7</sup>



Compound **8d** was prepared by following the general procedure for the synthesis of **8a**. A solution of 2-iodo-cyclohexenone (444.0 mg, 2 mmol, 1.0 equiv.) in THF (5 mL) was treated with PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (70.2 mg, 0.1 mmol, 5 mol %) and CuI (38.1 mg, 0.2 mmol, 10 mol %) and cooled down to 0 °C under an Ar atmosphere. After 10 min of stirring, 1-ethynyl-4-methoxybenzene (528.6 mg, 4 mmol, 2 equiv.) and diisopropyl amine (0.87 mL, 627.4 mg, 6.2 mmol) were added, and the resulting solution was stirred at 0 °C. The reaction mixture was partitioned between CH<sub>2</sub>Cl<sub>2</sub> and 0.5 N aqueous HCl solution. The aqueous layer was extracted three times with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic phases were washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated under vacuum. The crude product was purified by flash column chromatography to yield alkyne **8d** as a brown solid (366.6 mg, 1.62 mmol, 53 %).

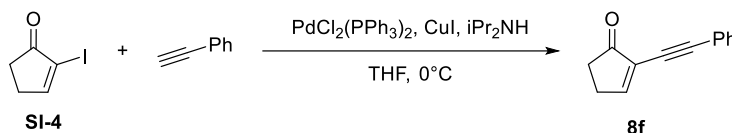
<sup>7</sup> Cho, C.-H.; Larock, R. C. *ACS Comb. Sci.* **2011**, *13*, 272-279.

### Synthesis of 2-(Heptane-1-yn-1-yl)cyclohex-2-en-1-one (**8e**)<sup>8</sup>



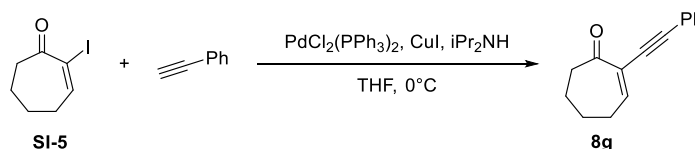
Compound **8e** was prepared by following the general procedure for the synthesis of **8a**. A solution of 2-iodo-cyclohexenone (444 mg, 2 mmol, 1.0 equiv.) in THF (6 mL) was treated with  $\text{PdCl}_2(\text{PPh}_3)_2$  (70.2 mg, 0.1 mmol, 5 mol %) and  $\text{CuI}$  (38.1 mg, 0.2 mmol, 10 mol %) and cooled down to  $0^\circ\text{C}$  under Ar atmosphere and in the dark. After 10 min of stirring, Hept-1-yne (0.53 mL, 4.0 mmol, 2 equiv.) and diisopropyl amine (0.83 mL, 6.3 mmol, 3.1 equiv.) were added, and the resulting yellow to dark brown solution was stirred from  $0^\circ\text{C}$ . The reaction mixture was partitioned between  $\text{CH}_2\text{Cl}_2$  and 1.0 N aqueous HCl solution. The aqueous layer was extracted three times with  $\text{CH}_2\text{Cl}_2$  and the combined organic phases were washed with brine, dried over  $\text{MgSO}_4$ , filtered and concentrated under vacuum. The crude product was purified by flash column chromatography to yield product **8e** as a white solid (231.9 mg, 1.2 mmol, 59 %).

### Synthesis of 2-(phenylethynyl)cyclopent-2-en-1-one (**8f**)<sup>9</sup>



Compound **8f** was prepared by following the general procedure for the synthesis of **8a**. A solution of 2-iodocyclopent-2-en-1-one (186 mg, 0.89 mmol, 1.0 equiv.) in THF (3 mL) was treated with  $\text{PdCl}_2(\text{PPh}_3)_2$  (31.4 mg, 0.04 mmol, 5 mol %) and  $\text{CuI}$  (17.1 mg, 0.09 mmol, 10 mol %) and cooled down to  $0^\circ\text{C}$  under Ar atmosphere and in the dark. After 10 min of stirring, phenylacetylene (0.2 mL, 1.79 mmol, 2 equiv.) and diisopropyl amine (0.39 mL, 2.77 mmol, 3.1 equiv.) were added, and the resulting yellow to dark brown solution was stirred from  $0^\circ\text{C}$ . The reaction mixture was partitioned between  $\text{CH}_2\text{Cl}_2$  and 1.0 N aqueous HCl solution. The aqueous layer was extracted three times with  $\text{CH}_2\text{Cl}_2$  and the combined organic phases were washed with brine, dried over  $\text{MgSO}_4$ , filtered and concentrated under vacuum. The crude product was purified by flash column chromatography to yield product **8f** as a pale yellow solid (156.7 mg, 0.86 mmol, 97 %).

### Synthesis of 2-(phenylethynyl)cyclohept-2-en-1-one (**8g**)<sup>9</sup>



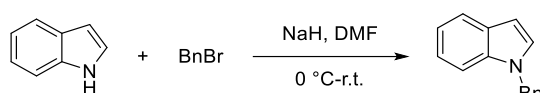
Compound **8g** was prepared by following the general procedure for the synthesis of **8a**. A solution of 2-iodocyclohept-2-en-1-one (219.3 mg, 0.93 mmol, 1.0 equiv.) in THF (3 mL) was treated with  $\text{PdCl}_2(\text{PPh}_3)_2$

<sup>8</sup> (a) Salacz, L.; Girard, N.; Suffert, J.; Blond, G. *Molecules* **2019**, *24*, 595. (b) Salacz, L.; Girard, N.; Blond, G.; Suffert, J. *Org. Lett.* **2018**, *20*, 3915-3918.

<sup>9</sup> T. Yao; Zhang, X.; Larock, R. C. *J. Org. Chem.* **2005**, *70*, 7679-7685.

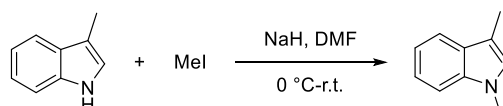
(312.6 mg, 0.05 mmol, 5 mol %) and CuI (17.7 mg, 0.09 mmol, 10 mol %) and cooled down to 0 °C under Ar atmosphere and in the dark. After 10 min of stirring, phenylacetylene (0.21 mL, 1.86 mmol, 2 equiv.) and diisopropyl amine (0.41 mL, 2.88 mmol, 3.1 equiv.) were added, and the resulting yellow to dark brown solution was stirred from 0 °C. The reaction mixture was partitioned between CH<sub>2</sub>Cl<sub>2</sub> and 1.0 N aqueous HCl solution. The aqueous layer was extracted three times with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic phases were washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated under vacuum. The crude product was purified by flash column chromatography to yield product **8g** as a pale yellow oil (188.0 mg, 0.89 mmol, 96 %).

#### Synthesis of 1-benzyl-1H-indole<sup>10</sup> (**9g**)



To a stirring solution of indole (352.5 mg, 3 mmol, 1 equiv.) in dry DMF (3 mL), NaH (144.0 mg, 3.6 mmol, 1.2 equiv.) was added portionwise under N<sub>2</sub> at 0 °C. The reaction mixture was then warmed to room temperature and stirred for 30 min. After cooling to 0 °C, BnBr (564.5 mg, 3.3 mmol, 1.1 equiv.) (1.2 mL) was added dropwise to the reaction mixture. The resulting mixture was stirred at room temperature overnight. The reaction was quenched with water and extracted three times with ethyl acetate, the combined organic phases were dried over MgSO<sub>4</sub>, filtered and concentrated under vacuum. The crude product was purified by flash column chromatography to yield product **9g** as pale yellow oil (553.4 mg, 2.67 mmol, 89 %).

#### Synthesis of 1,3-dimethyl-1H-indole<sup>11</sup> (**9i**)



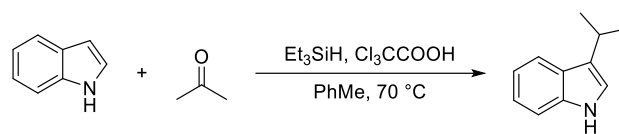
To a stirring solution of 60 % NaH (240 mg, 6 mmol, 2 equiv.) in dry DMF (2.4 mL), 3-methylindole (393.5 mg, 3 mmol, 1 equiv.) in DMF (2.4) was added dropwise at 0 °C. The mixture was allowed to warm to room temperature and stirred for 30 min. After cooling to 0 °C, a solution of MeI (0.38 mL, 6 mmol, 2 equiv.) in DMF (1.2 mL) was added dropwise. The resulting mixture was stirred at room temperature overnight. The reaction was quenched with water and extracted three times with ethyl acetate, the combined organic phases were dried over MgSO<sub>4</sub>, filtered and concentrated under vacuum. The crude product was purified by flash column chromatography to yield product **9i** as a clear oil (426.9 mg, 2.94 mmol, 98 %).

<sup>10</sup> K. Nemoto; Tanaka, S.; Konno, M.; Onozawa, S.; Chiba, M.; Tanaka, Y.; Sasaki, Y.; Okubo, R.; Hattori, T. *Tetrahedron* **2016**, *72*, 734-745.

<sup>11</sup> C. Shao; Shi, G.; Zhang, Y.; Pan, S.; Guan, X. *Org. Lett.* **2015**, *17*, 2652-2655.

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### Synthesis of 3-isopropyl-1H-indole<sup>12</sup> (**9k**)



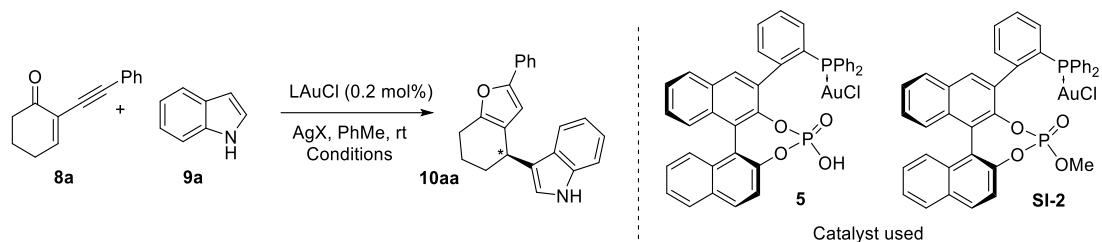
In a oven dried flask, triethylsilane (5.78 mL, 36.0 mmol, 2.4 equiv.) and trichloroacetic acid (2.26 g, 22.5 mmol, 1.5 equiv.) were dissolved in toluene (7.50 mL) and the resulting solution was heated to 70 °C. A solution of indole (1.76 g, 15.0 mmol, 1 equiv.) and acetone (1.23 mL, 16.5 mmol, 1.1 equiv.) in toluene (7.50 mL) were then added over 1 h. After an additional 20 min at 70 °C the solution was quenched with 10% aqueous solution of sodium carbonate, the organic layer was separated, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and purified by column chromatography to afford indole **9k** (1.61 g, 10.1 mmol, 67%) as a colorless solid.

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<sup>12</sup> Y. Zhang; Stephens, D.; Hernandez, G.; Mendoza, R.; Larionov, O. V. *Chem. Eur. J.* **2012**, *18*, 16612-16615.

## 4. Investigation with respect to the protocol for the activation of the catalysts

### 5 and SI-2 and the silver salts used



**Protocol A:** *In situ* activation of the active catalyst with the silver salt in the presence of all components of the reaction.

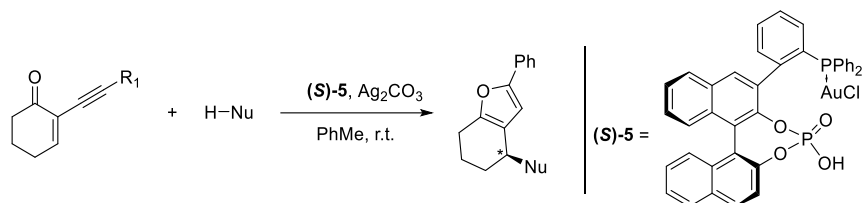
**Protocol B:** Activation of the active catalyst with the silver salt in  $\text{CDCl}_3$ , filtration of the solution and use of the solution.

**Protocol C:** Formation of the active catalyst in  $\text{CDCl}_3$ , filtration of the solution, evaporation and use of the resulting solid as the catalyst.

Experiments highlighted in grey are those reported within the manuscript.

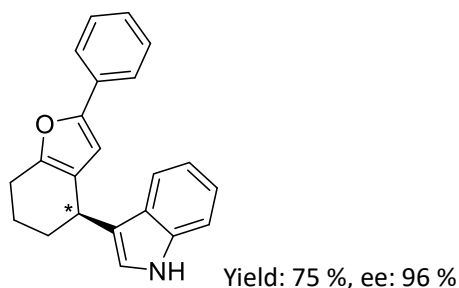
| entry | $\text{LAuCl}$ | $\text{AgX}$ (mol%)            | Actual catalyst | Yield (%) | ee (%) | protocol |
|-------|----------------|--------------------------------|-----------------|-----------|--------|----------|
| 1     | (S)- <b>5</b>  | $\text{Ag}_2\text{CO}_3$ (0.1) | <b>6</b>        | 75        | 96     | A        |
| 2     | (S)- <b>5</b>  | $\text{Ag}_2\text{CO}_3$ (0.1) | <b>6</b>        | 61        | 79     | B        |
| 3     | (S)- <b>5</b>  | $\text{Ag}_2\text{CO}_3$ (0.1) | <b>6</b>        | 65        | 26     | C        |
| 4     | (S)- <b>5</b>  | $\text{AgNTf}_2$ (0.2)         | <b>7a</b>       | 71        | 7      | A        |
| 5     | (S)- <b>5</b>  | $\text{AgNTf}_2$ (0.2)         | <b>7a</b>       | 85        | 29     | B        |
| 6     | (S)- <b>5</b>  | $\text{AgNTf}_2$ (0.2)         | <b>7a</b>       | 80        | 60     | C        |
| 7     | (S)- <b>5</b>  | $\text{AgSbF}_6$ (0.2)         | <b>7b</b>       | 85        | 47     | A        |
| 8     | (S)- <b>5</b>  | $\text{AgSbF}_6$ (0.2)         | <b>7b</b>       | 76        | 62     | B        |
| 9     | (S)- <b>5</b>  | $\text{AgSbF}_6$ (0.2)         | <b>7b</b>       | 93        | 67     | C        |
| 10    | <b>SI-2</b>    | $\text{AgNTf}_2$ (0.2)         | <b>11a</b>      | 85        | 15     | B        |
| 11    | <b>SI-2</b>    | $\text{AgSbF}_6$ (0.2)         | <b>11b</b>      | 90        | 12     | B        |

## 5. Scope of the reaction



To a flask was added 2-(1-alkynyl)-2-alken-1-one (0.55 mmol, 1.1 equiv.), Nucleophile (NuH, 0.5 mmol, 1.0 equiv.), **(S)-5** (0.001 mmol, 0.2 mol %), Ag<sub>2</sub>CO<sub>3</sub> (0.0005 mmol, 0.1 mol %) and toluene (2.5 mL). The resulting mixture was then stirred overnight at room temperature. The solvent was then removed under vacuum and the residue was purified by flash column chromatography.

### **(R)-3-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indole (10aa)**



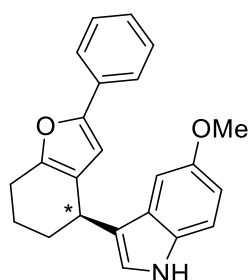
Compound **10aa** was prepared according to the general procedure from **8a** (107.9 mg, 0.55 mmol, 1.1 equiv.), **9a** (58.8 mg, 0.5 mmol, 1.0 equiv.), **(S)-5** (0.8 mg, 0.001 mmol, 0.2 mol %) and Ag<sub>2</sub>CO<sub>3</sub> (0.1 mg, 0.0005 mmol, 0.1 mol %) in toluene (2.5 mL), yielding product **10aa** (116.5 mg, 0.37 mmol, 75 %) as a white solid for which the spectroscopical data correspond to those reported in the literature.<sup>13</sup> [ $\alpha$ ]<sub>D</sub> = +38 (c 0.89, CHCl<sub>3</sub>). ee = 96 %, determined on a Chiralpak IA column (heptane:IPA = 95:5, 1 mL/min), retention times: T<sub>R</sub> (minor): 19.7 min, T<sub>R</sub> (major): 25.6 min.

**10aa** was alternatively obtained from the same protocol in the absence of Ag<sub>2</sub>CO<sub>3</sub> in 80% yield and 92% ee.

**m.p.**: 158.8-160.3 °C. **<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)**  $\delta$  = 7.89 (s, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.33-7.30 (m, 2H), 7.22-7.16 (m, 2H), 7.11 (t, *J* = 7.3 Hz, 1H), 6.86 (d, *J* = 1.8 Hz, 1H), 6.44 (s, 1H), 4.25 (br, 1H), 2.76-2.75 (m, 2H), 2.18-2.13 (m, 1H), 1.98-1.93 (m, 2H), 1.88-1.84 (m, 1H). **HRMS (ESI)**: *m/z*: calcd for C<sub>22</sub>H<sub>20</sub>NO<sup>+</sup> 314.1539 [M+H]<sup>+</sup>, found, 314.1543.

<sup>13</sup> (a) G. Force; Ki, Y. L. T.; Isaac, K.; Retailleau, P.; Marinetti, A.; Betzer, J.-F. *Adv. Synth. Catal.* **2018**, *360*, 3356-3366; (b) V. Rauniyar; Wang, Z. J.; Burks, H. E.; Toste, F. D. *J. Am. Chem. Soc.* **2011**, *133*, 8486-8489.

**(R)-5-methoxy-3-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indole (10ab)**



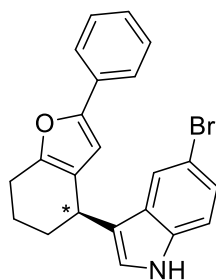
Yield: 81 %, ee: 97 %.

Compound **10ab** was prepared according to the general procedure from **8a** (107.9 mg, 0.55 mmol, 1.1 equiv.), **9c** (73.6 mg, 0.5 mmol, 1.0 equiv.), **(S)-5** (0.8 mg, 0.001 mmol, 0.2 mol %) and  $\text{Ag}_2\text{CO}_3$  (0.1 mg, 0.0005 mmol, 0.1 mol %) in toluene (2.5 mL), yielding product **10ab** (138.2 mg, 0.40 mmol, 81 %) as a white solid for which the spectroscopical data correspond to those reported in the literature.<sup>13</sup>  $[\alpha]_{\text{D}} = -7$  (c 0.98,  $\text{CHCl}_3$ ). ee = 97%, determined on a Chiralpak IA column (heptane:IPA = 95:5, 1 mL/min), retention times:  $T_{\text{R}}$  (minor): 29.2 min,  $T_{\text{R}}$  (major): 41.4 min.

**10ab** was alternatively obtained from the same protocol in the absence of  $\text{Ag}_2\text{CO}_3$  in 73% yield and 94% ee.

$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  = 7.79 (s, 1H), 7.58 (d,  $J$  = 7.6 Hz, 2H), 7.31 (t,  $J$  = 7.6 Hz, 2H), 7.23 (d,  $J$  = 8.2 Hz, 1H), 7.17 (t,  $J$  = 7.3 Hz, 1H), 7.06 (s, 1H), 6.86 (d,  $J$  = 8.5 Hz, 1H), 6.81 (s, 1H), 6.44 (s, 1H), 4.20 (t,  $J$  = 5.2 Hz, 1H), 3.84 (s, 3H), 2.80-2.71 (m, 2H), 2.16-2.11 (m, 1H), 1.98-1.90 (m, 2H), 1.87-1.82 (m, 1H). **HRMS (ESI)**:  $m/z$ : calculated for  $\text{C}_{23}\text{H}_{22}\text{NO}_2^+$ : 344.1645  $[\text{M}+\text{H}]^+$ , found, 344.1646.

**(R)-5-bromo-3-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indole (10ac)**



Yield: 77 %, ee: 97 %.

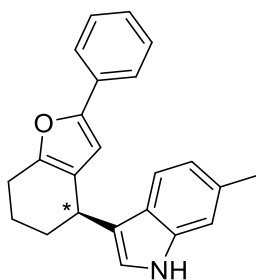
Compound **10ac** was prepared according to the general procedure from **8a** (107.9 mg, 0.55 mmol, 1.1 equiv.), **9d** (98.0 mg, 0.5 mmol, 1.0 equiv.), **(S)-5** (0.8 mg, 0.001 mmol, 0.2 mol %) and  $\text{Ag}_2\text{CO}_3$  (0.1 mg, 0.0005 mmol, 0.1 mol %) in toluene (2.5 mL), yielding product **10ac** (150.9 mg, 0.39 mmol, 77 %) as a white solid for which the spectroscopical data correspond to those reported in the literature.<sup>13</sup>  $[\alpha]_{\text{D}} = -10$  (c 1.02,  $\text{CHCl}_3$ ). ee = 97%, determined on a Chiralpak IA column (heptane:IPA = 95:5, 1 mL/min), retention times:  $T_{\text{R}}$  (minor): 19.4 min,  $T_{\text{R}}$  (major): 26.7 min.

**10ac** was alternatively obtained from the same protocol in the absence of  $\text{Ag}_2\text{CO}_3$  in 30% yield and 75% ee.

$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  = 7.93 (s, 1H), 7.74 (d,  $J$  = 1.3 Hz, 1H), 7.60-7.57 (m, 2H), 7.34-7.16 (m,

5H), 6.83 (d,  $J = 2.3$  Hz, 1H), 6.40 (s, 1H), 4.17 (t,  $J = 5.5$  Hz, 1H), 2.76-2.73 (m, 2H), 2.19-2.07 (m, 1H), 1.96-1.79 (m, 3H). **HRMS (ESI)**:  $m/z$ : calculated for  $C_{22}H_{19}BrNO^+$ : 392.0645  $[M+H]^+$ , found, 392.0638.

**(R)-6-methyl-3-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indole (10ad)**

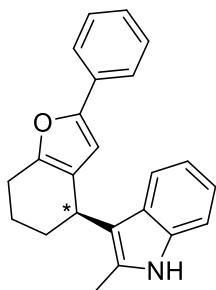


Yield: 44 %, ee: 96 %

Compound **10ad** was prepared according to the general procedure from **8a** (21.6 mg, 0.11 mmol, 1.1 equiv.), **9e** (13.1 mg, 0.1 mmol, 1.0 equiv.), **(S)-5** (0.2 mg, 0.0002 mmol, 0.2 mol %) and  $Ag_2CO_3$  (0.1 mg, 0.0001 mmol, 0.1 mol %) in toluene (2.5 mL), yielding product **10ad** (14.4 mg, 0.04 mmol, 44 %) as a white solid for which the spectroscopical data correspond to those reported in the literature.<sup>13</sup>

$[\alpha]_D^{25} = +28$  (c 1.21,  $CHCl_3$ ). ee = 96%, determined on a Chiralpak IA column (heptane:IPA = 95:5, 1 mL/min), retention times:  $T_R$  (minor): 19.5 min,  $T_R$  (major): 22.4 min.  **$^1H$  NMR ( $CDCl_3$ , 500 MHz)**  $\delta$  = 7.71 (s, 1H), 7.57 (d,  $J = 7.9$  Hz, 2H), 7.48 (d,  $J = 7.9$  Hz, 1H), 7.30 (t,  $J = 7.6$  Hz, 2H), 7.18-7.12 (m, 2H), 6.93 (d,  $J = 7.9$  Hz, 1H), 6.75 (s, 1H), 6.42 (s, 1H), 4.20 (br, 1H), 2.76-2.73 (m, 2H), 2.45 (s, 3H), 2.15-2.10 (m, 1H), 1.98-1.90 (m, 2H), 1.86-1.83 (m, 1H). **HRMS (ESI)**:  $m/z$ : calculated for  $C_{23}H_{22}NO^+$ : 328.1696  $[M+H]^+$ , found, 328.1696.

**(R)-2-methyl-3-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indole (10ae)**



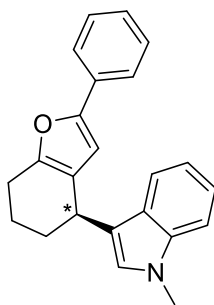
Yield: 49 %, ee: 82 %.

Compound **10ae** was prepared according to the general procedure from **8a** (107.9 mg, 0.55 mmol, 1.1 equiv.), **9f** (65.6 mg, 0.5 mmol, 1.0 equiv.), **(S)-5** (0.8 mg, 0.001 mmol, 0.2 mol %) and  $Ag_2CO_3$  (0.1 mg, 0.0005 mmol, 0.1 mol %) in toluene (2.5 mL), yielding product **10ae** (80.0 mg, 0.24 mmol, 49 %) as a white solid for which the spectroscopical data correspond to those reported in the literature.<sup>13</sup>

$[\alpha]_D^{25} = +26$  (c 1.20,  $CHCl_3$ ). ee = 82 %, determined on a Chiralpak AD-H column (heptane:IPA = 90:10, 1 mL/min), retention times:  $T_R$  (minor): 4.3 min,  $T_R$  (major): 5.3 min.  **$^1H$  NMR ( $CDCl_3$ , 500 MHz)**  $\delta$  = 7.69 (s, 1H), 7.54 (d,  $J = 7.9$  Hz, 2H), 7.30-7.24 (m, 4H), 7.15 (t,  $J = 7.3$  Hz, 1H), 7.06 (t,  $J = 7.3$  Hz, 1H), 6.94 (t,  $J = 7.6$  Hz, 1H), 6.28 (s, 1H), 4.14 (br, 1H), 2.82 (br, 2H), 2.31 (s, 3H), 2.11-2.04 (m, 2H), 1.96-1.88 (m, 2H). **HRMS (ESI)**:  $m/z$ : calculated for  $C_{23}H_{22}NO^+$ : 328.1696  $[M+H]^+$ , found, 328.1691.



**(R)-1-methyl-3-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indole (10af)**

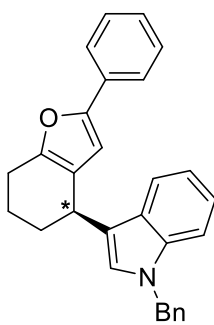


Yield: 92 %, ee: 94 %.

Compound **10af** was prepared according to the general procedure from **8a** (107.9 mg, 0.55 mmol, 1.1 equiv.), **9b** (65.6 mg, 0.5 mmol, 1.0 equiv.), **(S)-5** (0.8 mg, 0.001 mmol, 0.2 mol %) and  $\text{Ag}_2\text{CO}_3$  (0.1 mg, 0.0005 mmol, 0.1 mol %) in toluene (2.5 mL), yielding product **10af** (150.2 mg, 0.46 mmol, 92 %) as a white solid for which the spectroscopical data correspond to those reported in the literature.<sup>13, 4a</sup>

$[\alpha]_D = -5$  (c 0.78,  $\text{CHCl}_3$ ). ee: 94 %, determined on a Chiralpak IC column (heptane:IPA = 95:05, 1 mL/min), retention times:  $T_R$  (minor): 4.7 min,  $T_R$  (major): 5.1 min.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta = 7.60$  (t,  $J = 7.6$  Hz, 3H), 7.33-7.29 (m, 3H), 7.24-7.21 (m, 1H), 7.18 (t,  $J = 7.3$  Hz, 1H), 7.10 (t,  $J = 7.3$  Hz, 1H), 6.72 (s, 1H), 6.44 (s, 1H), 4.24 (t,  $J = 5.5$  Hz, 1H), 3.71 (s, 3H), 2.76-2.75 (m, 2H), 2.16-2.12 (m, 1H), 1.97-1.91 (m, 2H), 1.87-1.84 (m, 1H). **HRMS (ESI)**:  $m/z$ : calcd for  $\text{C}_{23}\text{H}_{22}\text{NO}^+$  328.1696  $[\text{M}+\text{H}]^+$ , found, 328.1696.

**(R)-1-benzyl-3-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indole (10ag)**

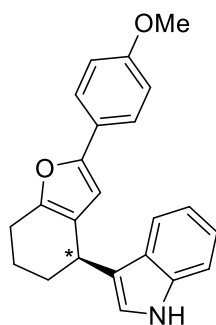


Yield: 83 %, ee: 92 %.

Compound **10ag** was prepared according to the general procedure from **8a** (21.6 mg, 0.11 mmol, 1.1 equiv.), **9g** (20.7 mg, 0.1 mmol, 1.0 equiv.), **(S)-5** (0.2 mg, 0.0002 mmol, 0.2 mol %) and  $\text{Ag}_2\text{CO}_3$  (0.1 mg, 0.0001 mmol, 0.1 mol %) in toluene (0.5 mL), yielding product **10ag** (33.3 mg, 0.08 mmol, 83 %) as a pale yellow solid

$[\alpha]_D = +34$  (c 1.00,  $\text{CHCl}_3$ ). ee: 92 %, determined on a Chiralpak IA column (heptane:IPA = 95:05, 1 mL/min), retention times:  $T_R$  (major): 6.5 min,  $T_R$  (minor): 11.3 min.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta = 7.54$  (d,  $J = 7.6$  Hz, 1H), 7.49 (d,  $J = 7.9$  Hz, 2H), 7.23-7.13 (m, 6H), 7.08 (t,  $J = 7.6$  Hz, 2H), 7.02-7.97 (m, 3H), 6.73 (s, 1H), 6.35 (s, 1H), 5.14 (dd,  $J_1 = 21.3$  Hz,  $J_2 = 16.2$  Hz, 2H), 4.17 (t,  $J = 6.1$  Hz, 1H), 2.68-2.64 (m, 2H), 2.10-2.05 (m, 1H), 1.90-1.84 (m, 2H), 1.80-1.73 (m, 1H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz)  $\delta = 151.9, 151.4, 138.0, 137.2, 131.6, 128.9, 128.7, 127.7, 127.6, 126.9, 126.8, 126.6, 123.5, 122.4, 121.9, 119.6, 119.6, 119.2, 110.0, 106.3, 50.2, 31.6, 31.1, 23.6, 21.4$ . **HRMS (ESI)**:  $m/z$ : calcd for  $\text{C}_{29}\text{H}_{24}\text{NO}^+$  402.1852  $[\text{M}+\text{H}-\text{H}_2]^+$ , found, 402.1858.

**(R)-3-(2-(4-methoxyphenyl)-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indole (10ba)**

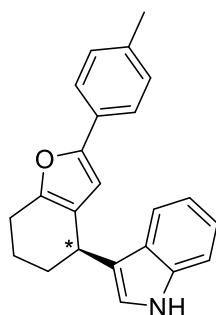


Yield: 87 %, ee: 91 %.

Compound **10ba** was prepared according to the general procedure from **8b** (24.9 mg, 0.11 mmol, 1.1 equiv.), **9a** (11.7 mg, 0.1 mmol, 1.0 equiv.), (**S**)-**5** (0.2 mg, 0.0002 mmol, 0.2 mol %) and  $\text{Ag}_2\text{CO}_3$  (0.1 mg, 0.0001 mmol, 0.1 mol %) in toluene (0.5 mL), yielding product **10ba** (29.8 mg, 0.09 mmol, 87 %) as a pale yellow solid for which the spectroscopical data correspond to those reported in the literature.<sup>13</sup>

$[\alpha]_D^{25} = +11$  (c 1.90,  $\text{CHCl}_3$ ). ee = 91 %, determined on a Chiralpak IC column (heptane:IPA = 95:5, 1 mL/min), retention times:  $T_R$  (minor): 9.5 min,  $T_R$  (major): 10.5 min.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta = 7.89$  (s, 1H), 7.62 (d,  $J = 7.9$  Hz, 1H), 7.51 (d,  $J = 8.5$  Hz, 2H), 7.34 (d,  $J = 7.9$  Hz, 1H), 7.19 (t,  $J = 7.6$  Hz, 1H), 7.10 (t,  $J = 7.6$  Hz, 1H), 6.86-6.84 (m, 3H), 6.29 (s, 1H), 4.24-4.22 (m, 1H), 3.79 (s, 3H), 2.75-2.72 (m, 2H), 2.61-2.11 (m, 1H), 1.98-1.91 (m, 2H), 1.86-1.81 (m, 1H). **HRMS (ESI)**:  $m/z$ : calculated for  $\text{C}_{23}\text{H}_{22}\text{NO}_2^+$ : 344.1645  $[\text{M}+\text{H}]^+$ , found, 344.1645.

**(R)-3-(2-(p-tolyl)-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indole (10ca)**

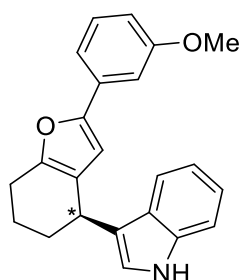


Yield: 95 %, ee: 95 %.

Compound **10ca** was prepared according to the general procedure from **8c** (23.1 mg, 0.11 mmol, 1.1 equiv.), **9a** (11.7 mg, 0.1 mmol, 1.0 equiv.), (**S**)-**5** (0.2 mg, 0.0002 mmol, 0.2 mol %) and  $\text{Ag}_2\text{CO}_3$  (0.1 mg, 0.0001 mmol, 0.1 mol %) in toluene (0.5 mL), yielding product **10ca** (31.0 mg, 0.09 mmol, 95 %) as a pale yellow solid for which the spectroscopical data correspond to those reported in the literature.<sup>13</sup>

$[\alpha]_D^{25} = +68$  (c 1.01,  $\text{CHCl}_3$ ). ee = 95 %, determined on a Chiralpak IC column (heptane:IPA = 95:5, 1 mL/min), retention times:  $T_R$  (minor): 6.3 min,  $T_R$  (major): 7.2 min.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta = 7.71$  (s, 1H), 7.52 (d,  $J = 7.9$  Hz, 1H), 7.38 (d,  $J = 7.9$  Hz, 2H), 7.21 (d,  $J = 8.2$  Hz, 1H), 7.09 (t,  $J = 7.6$  Hz, 1H), 7.03-7.00 (m, 3H), 6.70-6.69 (m, 1H), 6.27 (s, 1H), 4.13 (t,  $J = 5.5$  Hz, 1H), 2.66-2.63 (m, 2H), 2.22 (s, 3H), 2.06-2.01 (m, 1H), 1.86-1.81 (m, 2H), 1.76-1.71 (m, 1H). **HRMS (ESI)**:  $m/z$ : calculated for  $\text{C}_{23}\text{H}_{20}\text{NO}^+$ : 326.1539  $[\text{M}+\text{H}-\text{H}_2]^+$ , found, 326.1537.

**(R)-3-(2-(3-methoxyphenyl)-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indole (10da)**

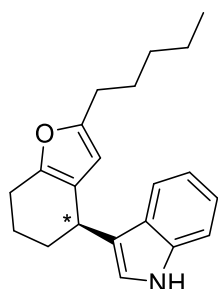


Yield : 77 %, ee : 84 %.

Compound **10da** was prepared according to the general procedure from **8d** (24.9 mg, 0.11 mmol, 1.1 equiv.), **9a** (11.7 mg, 0.1 mmol, 1.0 equiv.), **(S)-5** (0.2 mg, 0.0002 mmol, 0.2 mol %) and  $\text{Ag}_2\text{CO}_3$  (0.1 mg, 0.0001 mmol, 0.1 mol %) in toluene (0.5 mL), yielding product **10da** (26.4 mg, 0.08 mmol, 77 %) as a pale yellow solid.

$[\alpha]_D^{25} = +15$  (c 1.29,  $\text{CHCl}_3$ ). ee = 84 %, determined on a Chiralpak IA column (heptane:IPA = 90:10, 1 mL/min), retention times:  $T_R$  (minor): 12.1 min,  $T_R$  (major): 23.7 min.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta = 7.92$  (s, 1H), 7.61 (d,  $J = 7.9$  Hz, 1H), 7.36 (d,  $J = 8.2$  Hz, 1H), 7.24-7.09 (m, 5H), 6.86 (d,  $J = 1.8$  Hz, 1H), 6.74 (dd,  $J_1 = 7.9$  Hz,  $J_2 = 1.8$  Hz, 1H), 6.43 (s, 1H), 4.25 (t,  $J = 5.5$  Hz, 1H), 3.82 (s, 3H), 2.78-2.74 (m, 2H), 2.18-2.13 (m, 1H), 1.98-1.92 (m, 2H), 1.88-1.82 (m, 1H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz)  $\delta = 136.8, 132.9, 129.8, 126.9, 122.4, 122.3, 122.2, 120.5, 119.5, 119.4, 116.1, 112.9, 111.4, 108.6, 106.6, 160.1, 151.7, 151.5, 55.5, 31.4, 31.1, 23.6, 21.4$ . HRMS (ESI):  $m/z$ : calculated for  $\text{C}_{23}\text{H}_{22}\text{NO}_2^+$ : 344.1645  $[\text{M}+\text{H}]^+$ , found, 344.1641.

**(R)-3-(2-pentyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indole (10ea)**

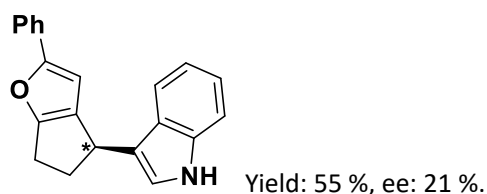


Yield: 46 %, ee: 87 %.

Compound **10ea** was prepared according to the general procedure from **8e** (20.9 mg, 0.11 mmol, 1.1 equiv.), **9a** (11.7 mg, 0.1 mmol, 1.0 equiv.), **(S)-5** (0.8 mg, 0.001 mmol, 1 mol %) and  $\text{Ag}_2\text{CO}_3$  (0.1 mg, 0.0005 mmol, 0.5 mol %) in toluene (0.5 mL), yielding product **10ea** (14 mg, 0.05 mmol, 46 %) as a white solid.

$[\alpha]_D^{25} = +2$  (c 0.14,  $\text{CHCl}_3$ ). ee = 87 %, determined on a Chiralpak IA column (heptane:IPA = 95:5, 1 mL/min), retention times:  $T_R$  (minor): 8.7 min,  $T_R$  (major): 10.5 min.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta = 7.88$  (bs, 1H), 7.59 (d,  $J = 7.9$  Hz, 1H), 7.34 (d,  $J = 7.9$  Hz, 1H), 7.18 (t,  $J = 7.6$  Hz, 1H), 7.09 (t,  $J = 7.6$  Hz, 1H), 6.83 (s, 1H), 5.74 (s, 1H), 4.17 (t,  $J = 5.5$  Hz, 1H), 2.67-2.60 (m, 2H), 2.54 (t,  $J = 7.6$  Hz, 2H), 2.14-2.09 (m, 1H), 1.94-1.86 (m, 2H), 1.82-1.76 (m, 1H), 1.62-1.57 (m, 2H), 1.32-1.28 (m, 4H), 0.88 (t,  $J = 6.7$  Hz, 3H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz)  $\delta = 154.4, 149.2, 136.8, 127.0, 122.2, 122.1, 120.8, 120.4, 119.5, 119.3, 111.3, 105.6, 31.7, 31.5, 31.1, 28.4, 28.2, 23.5, 22.6, 21.5, 14.2$ . HRMS (ESI):  $m/z$ : calculated for  $\text{C}_{21}\text{H}_{24}\text{NO}^+$ : 306.1852  $[\text{M}+\text{H}-\text{H}_2]^+$ , found, 306.1857.

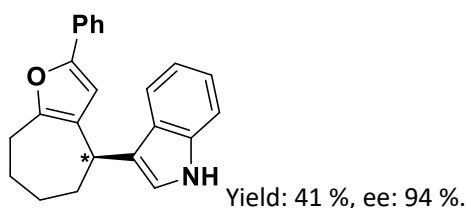
**(R)-3-(2-phenyl-5,6-dihydro-4H-cyclopenta[b]furan-4-yl)-1H-indole (10fa)**



Compound **10fa** was prepared according to the general procedure from **8f** (20.1 mg, 0.11 mmol, 1.1 equiv.), **9a** (11.7 mg, 0.1 mmol, 1.0 equiv.), (**S**)-**5** (1.7 mg, 0.002 mmol, 2 mol %) and  $\text{Ag}_2\text{CO}_3$  (0.3 mg, 0.001 mmol, 1 mol %) in toluene (0.5 mL), yielding product **10fa** (16.4 mg, 0.06 mmol, 55 %) as a white solid.

$[\alpha]_{\text{D}} = -18$  (c 0.75,  $\text{CHCl}_3$ ). ee = 21 %, determined on a Chiralpak IA column (heptane:IPA = 95:05, 1 mL/min), retention times:  $T_{\text{R}}$  (major): 26.1 min,  $T_{\text{R}}$  (minor): 29.9 min.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta = 7.88$  (bs, 1H), 7.61 (d,  $J = 7.3$  Hz, 2H), 7.58 (d,  $J = 7.9$  Hz, 1H), 7.36-7.32 (m, 3H), 7.19 (t,  $J = 7.6$  Hz, 2H), 7.09 (t,  $J = 7.6$  Hz, 1H), 6.93 (d,  $J = 1.9$  Hz, 1H), 6.57 (s, 1H), 4.47 (t,  $J = 6.6$  Hz, 1H), 3.07-3.00 (m, 1H), 2.96-2.83 (m, 2H), 2.52-2.46 (m, 1H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz)  $\delta = 159.6, 158.0, 137.0, 132.1, 130.3, 128.8, 126.9, 126.9, 123.3, 122.3, 120.9, 120.7, 119.5$  (2C), 111.4, 103.8, 37.7, 34.2, 25.0. HRMS (ESI):  $m/z$ : calculated for  $\text{C}_{21}\text{H}_{16}\text{NO}^+$ : 298.1226  $[\text{M}+\text{H}-\text{H}_2]^+$ , found, 298.1227.

**(R)-3-(2-phenyl-5,6,7,8-tetrahydro-4H-cyclohepta[b]furan-4-yl)-1H-indole (10ga)**

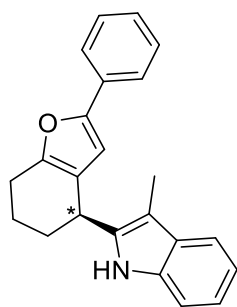


Compound **10ga** was prepared according to the general procedure from **8g** (23.1 mg, 0.11 mmol, 1.1 equiv.), **9a** (11.7 mg, 0.1 mmol, 1.0 equiv.), (**S**)-**5** (0.17 mg, 0.0002 mmol, 0.2 mol %) and  $\text{Ag}_2\text{CO}_3$  (0.1 mg, 0.0001 mmol, 0.1 mol %) in toluene (0.5 mL), yielding product **10ga** (13.5 mg, 0.04 mmol, 41 %) as a white solid.  $[\alpha]_{\text{D}} = +107$  (c 0.59,  $\text{CHCl}_3$ ). ee = 94 %, determined on a Chiralpak IA column (heptane:IPA = 95:05, 1 mL/min), retention times:  $T_{\text{R}}$  (minor): 14.8 min,  $T_{\text{R}}$  (major): 16.8 min.

**10ga** was alternatively obtained from the same protocol in the absence of  $\text{Ag}_2\text{CO}_3$  in 55% yield and 95% ee.

$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta = 7.92$  (bs, 1H), 7.61 (d,  $J = 7.9$  Hz, 1H), 7.51 (d,  $J = 7.3$  Hz, 2H), 7.36 (d,  $J = 8.2$  Hz, 1H), 7.28 (t,  $J = 7.9$  Hz, 2H), 7.19 (t,  $J = 7.6$  Hz, 1H), 7.14 (t,  $J = 7.6$  Hz, 1H), 7.10 (t,  $J = 7.6$  Hz, 1H), 6.81 (d,  $J = 1.9$  Hz, 1H), 6.25 (s, 1H), 4.27 (dd,  $J_1 = 7.6$  Hz,  $J_2 = 3.2$  Hz, 1H), 2.95 (t,  $J = 5.7$  Hz, 2H), 2.33-2.28 (m, 1H), 2.09-2.04 (m, 1H), 1.83-1.76 (m, 3H), 1.74-1.69 (m, 1H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz)  $\delta = 153.0, 150.0, 136.9, 131.4, 128.7, 126.8, 126.6, 126.2, 123.4, 122.6, 122.1, 120.0, 119.8, 119.4, 111.4, 109.1, 35.5, 34.6, 29.3, 27.6, 26.9$ . HRMS (ESI):  $m/z$ : calculated for  $\text{C}_{23}\text{H}_{22}\text{NO}^+$ : 328.1696  $[\text{M}+\text{H}]^+$ , found, 328.1696.

**(S)-3-methyl-2-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indole (14ah)**

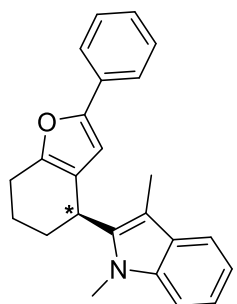


Yield : 83 %, ee : 93 %.

Compound **14ah** was prepared according to the general procedure from **8a** (21.6 mg, 0.11 mmol, 1.1 equiv.), **9g** (13.1 mg, 0.1 mmol, 1.0 equiv.), **(S)-5** (0.2 mg, 0.0002 mmol, 0.2 mol %) and  $\text{Ag}_2\text{CO}_3$  (0.1 mg, 0.0001 mmol, 0.1 mol %) in toluene (0.5 mL), yielding product **14ah** (27.1 mg, 0.08 mmol, 83 %) as a pale yellow solid.

$[\alpha]_D^{25} = +83$  (*c* 1.29,  $\text{CHCl}_3$ ). ee = 93 %, determined on a Chiralpak IA column (heptane:IPA = 95:5, 1 mL/min), retention times:  $T_R$  (minor): 7.1 min,  $T_R$  (major): 10.3 min.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  = 7.63 (s, 1H), 7.58 (d,  $J$  = 7.6 Hz, 2H), 7.54-7.52 (m, 1H), 7.33 (t,  $J$  = 7.6 Hz, 2H), 7.22-7.19 (m, 2H), 7.12-7.07 (m, 2H), 6.35 (s, 1H), 4.25 (dd,  $J_1$  = 7.3 Hz,  $J_2$  = 5.8 Hz, 1H), 2.78 (t,  $J$  = 6.1 Hz, 2H), 2.33 (s, 3H), 2.17-2.11 (m, 1H), 2.05-1.98 (m, 1H), 1.93-1.85 (m, 1H), 1.83-1.76 (m, 1H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  = 152.6, 152.2, 137.2, 135.1, 131.2, 129.7, 129.0, 128.9, 128.7, 127.2, 123.5, 121.3, 120.1, 119.2, 118.3, 110.7, 107.0, 105.7, 31.8, 31.4, 23.4, 22.0, 8.7. **HRMS (ESI)**: *m/z*: calculated for  $\text{C}_{23}\text{H}_{20}\text{NO}^+$ : 326.1539  $[\text{M}+\text{H}-\text{H}_2]^+$ , found, 326.1541.

**(S)-1,3-dimethyl-2-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indole (14ai)**

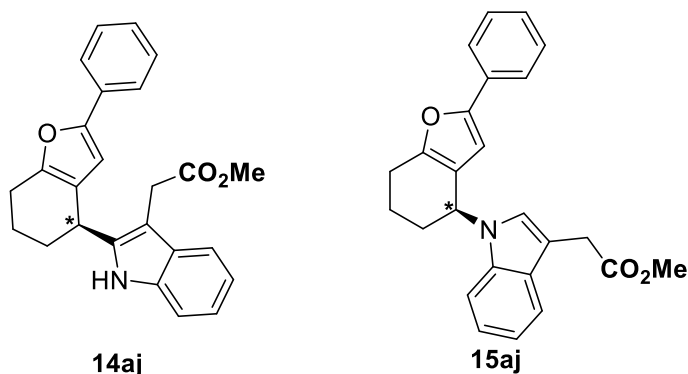


Yield: 65 %, ee: 97 %.

Compound **14ai** was prepared according to the general procedure from **8a** (21.6 mg, 0.11 mmol, 1.1 equiv.), **9i** (14.5 mg, 0.1 mmol, 1.0 equiv.), **(S)-5** (0.2 mg, 0.0002 mmol, 0.2 mol %) and  $\text{Ag}_2\text{CO}_3$  (0.1 mg, 0.0001 mmol, 0.1 mol %) in toluene (0.5 mL), yielding product **14ai** (20.5 mg, 0.07 mmol, 65 %) as a white solid.

$[\alpha]_D^{25} = +28$  (*c* 0.94,  $\text{CHCl}_3$ ). ee = 97 %, determined on a Chiralpak IC column (heptane:IPA = 95:5, 1 mL/min), retention times:  $T_R$  (major): 4.4 min,  $T_R$  (minor): 4.9 min.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  = 7.58 (d,  $J$  = 7.6 Hz, 2H), 7.55 (d,  $J$  = 7.9 Hz, 1H), 7.33 (t,  $J$  = 7.6 Hz, 2H), 7.26 (d,  $J$  = 8.2 Hz, 1H), 7.20 (td,  $J_1$  = 7.3 Hz,  $J_2$  = 3.1 Hz, 2H), 7.13 (t,  $J$  = 7.3 Hz, 1H), 6.32 (s, 1H), 4.37-4.35 (m, 1H), 3.58 (s, 3H), 2.84-2.81 (m, 2H), 2.23 (s, 3H), 2.20-2.11 (m, 2H), 2.00-1.87 (m, 2H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  = 152.5, 150.8, 137.4, 137.2, 131.3, 128.8, 128.7, 127.0, 123.5, 121.2, 118.9, 118.4, 108.8, 107.8, 105.6, 105.3, 32.0, 30.5, 23.4, 23.2, 9.2. **HRMS (ESI)**: *m/z*: calculated for  $\text{C}_{24}\text{H}_{24}\text{NO}^+$ : 342.1852  $[\text{M}+\text{H}]^+$ , found, 342.1853.

methyl (S)-2-(2-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indol-3-yl)acetate (**14aj**) and methyl (S)-2-(1-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indol-3-yl)acetate (**15aj**)



Compound **14aj** and **15aj** were prepared according to the general procedure from **8a** (23.1 mg, 0.11 mmol, 1.1 equiv.), **9j** (18.9 mg, 0.1 mmol, 1.0 equiv.), (**S**)-**5** (0.2 mg, 0.0002 mmol, 0.2 mol %) and Ag<sub>2</sub>CO<sub>3</sub> (0.1 mg, 0.0001 mmol, 0.1 mol %) in toluene (0.5 mL), yielding product **14aj** (20 mg, 0.05 mmol, 52 %) as a white solid and **15aj** (16.7 mg, 0.05 mmol, 46 %) as a white solid.

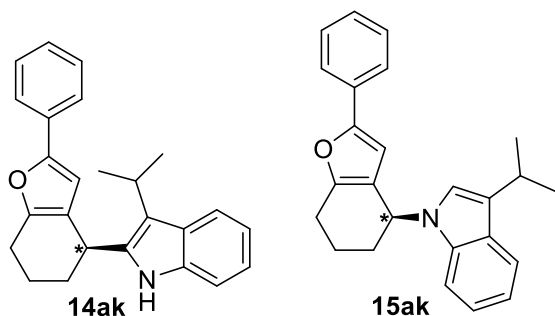
#### Data for **14aj**

[ $\alpha$ ]<sub>D</sub> = +59 (c 1.08, CHCl<sub>3</sub>). ee = 91 %, determined on a Chiralpak IC column (heptane:IPA = 98:2, 1 mL/min), retention times: T<sub>R</sub> (minor): 31.8 min, T<sub>R</sub> (major): 35.8 min. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  = 7.73 (bs, 1H), 7.54-7.50 (m, 3H), 7.26 (t, *J* = 7.9 Hz, 2H), 7.17-7.12 (m, 2H), 7.07-7.03 (m, 2H), 6.26 (s, 1H), 4.22 (dd, *J*<sub>1</sub> = 7.3 Hz, *J*<sub>2</sub> = 6.0 Hz, 1H), 3.73 (dd, *J*<sub>1</sub> = 22.8 Hz, *J*<sub>2</sub> = 15.4 Hz, 2H), 3.61 (s, 3H), 2.72 (t, *J* = 6.0 Hz, 2H), 2.16-2.11 (m, 1H), 1.99-1.96 (m, 1H), 1.88-1.80 (m, 1H), 1.78-1.71 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  = 172.6, 152.7, 152.3, 139.2, 135.1, 131.1, 128.9, 128.7, 128.7, 127.3, 123.5, 121.8, 119.9, 118.6, 110.9, 105.6, 104.5, 52.2, 31.9, 31.7, 30.4, 23.4, 22.1. HRMS (ESI): *m/z*: calculated for C<sub>25</sub>H<sub>24</sub>NO<sub>3</sub><sup>+</sup>: 386.1751 [M+H]<sup>+</sup>, found, 386.1751.

#### Data for **15aj**

[ $\alpha$ ]<sub>D</sub> = -4 (c 0.94, CHCl<sub>3</sub>). ee = 95 %, determined on a Chiralpak IC column (heptane:IPA = 98:2, 1 mL/min), retention times: T<sub>R</sub> (major): 23.1 min, T<sub>R</sub> (minor): 25.9 min. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  = 7.63 (d, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.34 (t, *J* = 7.9 Hz, 2H), 7.23-7.20 (m, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.99 (s, 1H), 6.40 (s, 1H), 5.53 (d, *J* = 5.4 Hz, 1H), 3.72 (dd, *J*<sub>1</sub> = 18.6 Hz, *J*<sub>2</sub> = 16.1 Hz, 2H), 3.66 (s, 3H), 2.85 (dt, *J*<sub>1</sub> = 16.7 Hz, *J*<sub>2</sub> = 6.3 Hz, 1H), 2.74 (dt, *J*<sub>1</sub> = 16.7 Hz, *J*<sub>2</sub> = 6.3 Hz, 1H), 2.19-2.13 (m, 1H), 2.09-2.03 (m, 1H), 1.98-1.85 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  = 172.5, 153.2, 153.0, 135.9, 130.8, 128.7, 128.4, 127.2, 125.4, 123.5, 121.6, 119.4, 119.3, 118.5, 109.7, 106.8, 104.8, 77.3, 77.0, 76.8, 51.9, 50.0, 31.3, 30.6, 23.1, 20.3. HRMS (ESI): *m/z*: calculated for C<sub>25</sub>H<sub>24</sub>NO<sub>3</sub><sup>+</sup>: 386.1751 [M+H]<sup>+</sup>, found, 386.1747.

**(S)-3-isopropyl-2-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indole (14ak) and (S)-3-isopropyl-1-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indole (15ak)**



Compound **14ak** and **15ak** were prepared according to the general procedure from **8a** (23.1 mg, 0.11 mmol, 1.1 equiv.), **9k** (15.9 mg, 0.1 mmol, 1.0 equiv.), (**S**)-**5** (0.2 mg, 0.0002 mmol, 0.2 mol %) and Ag<sub>2</sub>CO<sub>3</sub> (0.1 mg, 0.0001 mmol, 0.1 mol %) in toluene (0.5 mL), yielding product **14ak** (7.4 mg, 0.06 mmol, 21 %) as a pale yellow solid and **15ak** (20.7 mg, 0.02 mmol, 59 %) as a pale yellow solid.

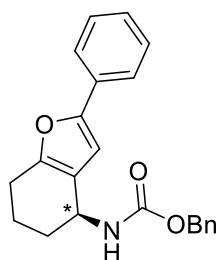
**Data for 14ak**

**[α]<sub>D</sub>** = -14 (c 1.00, CHCl<sub>3</sub>). ee = 49 %, determined on a Chiralpak IA column (heptane:IPA = 95:5, 1 mL/min), retention times: T<sub>R</sub> (minor): 5.2 min, T<sub>R</sub> (major): 6.9 min. **<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)** δ = 7.66 (d, *J* = 7.0 Hz, 1H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.26 (t, *J* = 7.7 Hz, 2H), 7.18-7.11 (m, 2H), 7.05-7.6.96 (m, 2H), 6.27 (s, 1H), 4.22 (dd, *J*<sub>1</sub> = 7.5 Hz, *J*<sub>2</sub> = 5.6 Hz, 1H), 3.22 (m, *J* = 7.1 Hz, 1H), 2.73-2.70 (m, 2H), 2.12-2.02 (m, 1H), 2.02-1.92 (m, 1H), 1.89-1.79 (m, 1H), 1.76-1.65 (m, 1H), 1.43 (t, *J* = 7.3 Hz, 6H). **<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)** δ = 152.6, 152.3, 135.9, 135.6, 131.1, 128.9, 127.4, 127.2, 123.5, 121.0, 120.3, 120.2, 118.9, 118.1, 111.0, 105.7, 32.3, 31.9, 26.1, 23.7, 23.6, 23.5, 22.1. **HRMS (ESI):** *m/z*: calculated for C<sub>25</sub>H<sub>26</sub>NO<sup>+</sup>: 356.2009 [M+H]<sup>+</sup>, found, 356.2009.

**Data for 15ak**

**[α]<sub>D</sub>** = +16 (c 0.50, CHCl<sub>3</sub>). ee = 92 %, determined on a Chiralpak IA column (heptane:IPA = 95:5, 1 mL/min), retention times: T<sub>R</sub> (minor): 4.2 min, T<sub>R</sub> (major): 4.6 min. **<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)** δ = 7.71 (d, *J* = 7.9 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.28-7.22 (m, 2H), 7.15 (d, *J* = 7.6 Hz, 1H), 6.81 (s, 1H), 6.45 (s, 1H), 5.56 (t, *J* = 5.5, 1H), 3.21 (m, *J* = 6.7 Hz, 1H), 2.93-2.88 (m, 1H), 2.82-2.77 (m, 1H), 2.23-2.17 (m, 1H), 2.12-2.06 (m, 1H), 2.03-1.92 (m, 2H), 1.35 (dd, *J*<sub>1</sub> = 6.7 Hz, *J*<sub>2</sub> = 4.6 Hz, 6H). **<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)** δ = 153.2, 153.0, 136.5, 131.1, 128.9, 128.0, 127.3, 123.7, 122.6, 121.7, 121.4, 119.9, 119.2, 118.8, 109.8, 105.1, 50.1, 30.9, 25.8, 23.7, 23.6, 23.3, 20.7. **HRMS (ESI):** *m/z*: calculated for C<sub>25</sub>H<sub>26</sub>NO<sup>+</sup>: 356.2009 [M+H]<sup>+</sup>, found, 356.2010.

**benzyl (S)-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)carbamate (16a)**

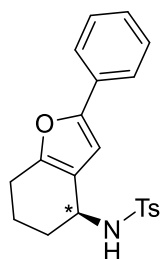


Yield: 88 %, ee: 94 %.

Compound **16a** was prepared according to a modified general procedure from **8a** (107.9 mg, 0.55 mmol, 1.1 equiv.), benzyl carbamate (75.6 mg, 0.5 mmol, 1.0 equiv.), (**S**)-**5** (8.4 mg, 0.01 mmol, 2 mol %) and  $\text{Ag}_2\text{CO}_3$  (1.4 mg, 0.005 mmol, 1 mol %) in toluene (2.5 mL), yielding product **16a** (151.7 mg, 0.44 mmol, 88 %) as a white solid for which the spectroscopical data correspond to those reported in the literature.<sup>13</sup>

$[\alpha]_D = -3$  (c 1.15,  $\text{CHCl}_3$ ). ee = 94%, determined on a Chiralpak IB column (heptane:IPA = 97:3, 1 mL/min), retention times:  $T_R$  (minor): 17.7 min,  $T_R$  (major): 22.5 min.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  = 7.56 (d,  $J$  = 7.6 Hz, 2H), 7.33-7.29 (m, 7H), 7.18 (t,  $J$  = 7.3 Hz, 1H), 6.53 (s, 1H), 5.11 (s, 2H), 5.03 (d,  $J$  = 7.9 Hz, 1H), 4.75-4.74 (m, 1H), 2.63-2.54 (m, 2H), 2.00-1.96 (m, 1H), 1.88-1.80 (m, 2H), 1.69-1.66 (m, 1H). **HRMS (ESI)**:  $m/z$ : calculated for  $\text{C}_{22}\text{H}_{22}\text{NO}_3^+$ : 348.1594  $[\text{M}+\text{H}]^+$ , found, 348.1597.

**(S)-4-methyl-N-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)benzenesulfonamide (16b)**



Yield: 80 %, ee: 88 %.

Compound **16b** was prepared according to the general procedure from **8a** (107.9 mg, 0.55 mmol, 1.1 equiv.), tosylamide (85.6 mg, 0.5 mmol, 1.0 equiv.), (**S**)-**5** (0.8 mg, 0.001 mmol, 0.2 mol %) and  $\text{Ag}_2\text{CO}_3$  (0.1 mg, 0.0005 mmol, 0.1 mol %) in toluene (2.5 mL), yielding product **16b** (146.4 mg, 0.40 mmol, 80 %) as a white solid for which the spectroscopical data correspond to those reported in the literature.<sup>13</sup>

When the reaction was performed with 0.2 mol% of catalyst (**S**)-**5**, the obtained ee was 94% but with a decrease of the yield to 17%.

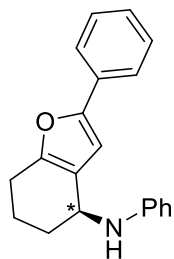
**16b** was alternatively obtained from the same protocol in the absence of  $\text{Ag}_2\text{CO}_3$  in 41% yield and 88% ee.

$[\alpha]_D = -99$  (c 1.14,  $\text{CHCl}_3$ ). ee = 87%, determined on a Chiralpak IC column (heptane:IPA = 90:10, 1 mL/min), retention times:  $T_R$  (major): 35.7 min,  $T_R$  (minor): 41.7 min.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  = 7.84 (d,  $J$  = 8.2 Hz, 2H), 7.46 (d,  $J$  = 7.3 Hz, 2H), 7.37 (d,  $J$  = 8.2 Hz, 2H), 7.33 (t,  $J$  = 7.6 Hz, 2H), 7.21 (t,  $J$  = 7.3 Hz, 1H), 5.86-5.85 (m, 1H), 4.59 (d,  $J$  = 8.2 Hz, 1H), 4.38-4.36 (m, 1H), 2.66-2.61 (m, 1H), 2.58-2.52 (1H), 2.48 (s, 3H),



1.90-1.73 (m, 4H). HRMS (ESI):  $m/z$ : calculated for  $C_{21}H_{20}NO_3S$ : 366.1169 [M-H]<sup>-</sup>, found, 366.1172.

**(S)-N,2-diphenyl-4,5,6,7-tetrahydrobenzofuran-4-amine (16c)**

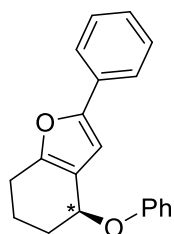


Yield: 89 %, ee: 65 %.

Compound **16c** was prepared according to the general procedure from **8a** (21.6 mg, 0.11 mmol, 1.1 equiv.), aniline (0.009 mL, 0.1 mmol, 1.0 equiv.), (**S**)-**5** (8.4 mg, 0.01 mmol, 2 mol %) and  $Ag_2CO_3$  (1.4 mg, 0.005 mmol, 1 mol %) in toluene (1 mL), yielding product **16c** (25.6 mg, 0.09 mmol, 89 %) as a white solid for which the spectroscopical data correspond to those reported in the literature.<sup>13</sup>

$[\alpha]_D^{25} = +4$  (c 0.95,  $CHCl_3$ ). ee = 65%, determined on a Chiralpak IB column (heptane:IPA = 98:02, 1 mL/min), retention times:  $T_R$  (major): 10.5 min,  $T_R$  (minor): 14.0 min.  $^1H$  NMR ( $CDCl_3$ , 500 MHz)  $\delta$  = 7.59 (t,  $J$  = 7.3 Hz, 2H), 7.33 (t,  $J$  = 7.6 Hz, 2H), 7.24-7.19 (m, 3H), 6.74-6.68 (m, 3H), 6.58 (s, 1H), 4.56 (br, 1H), 3.79 (bs, 1H), 2.75-2.62 (m, 2H), 2.02-1.95 (m, 2H), 1.88-1.80 (m, 2H). HRMS (ESI):  $m/z$ : calculated for  $C_{20}H_{18}NO^+$ : 288.1383 [M-H<sub>2</sub>+H]<sup>+</sup>, found, 288.1393.

**(S)-4-phenoxy-2-phenyl-4,5,6,7-tetrahydrobenzofuran (16d)**

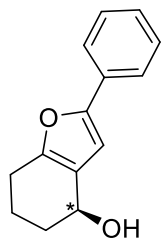


Yield: 93 %, ee: 90 %

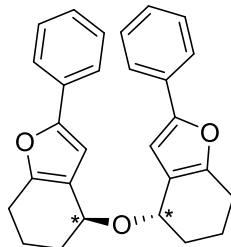
Compound **16d** was prepared according to the general procedure from **8a** (107.9 mg, 0.55 mmol, 1.1 equiv.), phenol (47.1 mg, 0.5 mmol, 1.0 equiv.), (**S**)-**5** (0.8 mg, 0.001 mmol, 0.2 mol %) and  $Ag_2CO_3$  (0.1 mg, 0.0005 mmol, 0.1 mol %) in toluene (2.5 mL), yielding product **16d** (133.9 mg, 0.46 mmol, 93 %) as a white solid for which the spectroscopical data correspond to those reported in the literature.<sup>13</sup>

$[\alpha]_D^{25} = -21$  (c 0.99,  $CHCl_3$ ). ee = 90%, determined on a Chiralpak IB column (heptane:IPA = 98:02, 1 mL/min), retention times:  $T_R$  (major): 6.1 min,  $T_R$  (minor): 9.2 min.  $^1H$  NMR ( $CDCl_3$ , 500 MHz)  $\delta$  = 7.60 (d,  $J$  = 7.3 Hz, 2H), 7.35-7.30 (m, 4H), 7.21 (t,  $J$  = 7.3 Hz, 1H), 7.03 (d,  $J$  = 7.9 Hz, 2H), 6.98 (t,  $J$  = 7.3 Hz, 1H), 6.58 (s, 1H), 5.36 (t,  $J$  = 4.3 Hz, 1H), 2.80 (dt,  $J_1$  = 16.8,  $J_2$  = 5.2 Hz, 1H), 2.69-2.63 (m, 1H), 2.16-2.08 (m, 2H), 2.00-1.93 (m, 1H), 1.92-1.85 (m, 1H). HRMS (ESI):  $m/z$ : calculated for  $C_{20}H_{17}O_2^+$ : 289.1223 [M-H<sub>2</sub>+H]<sup>+</sup>, found, 289.1224.

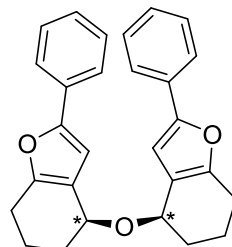
**(S)-2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-ol (16e),  
(4S,4'S)-4,4'-oxybis(2-phenyl-4,5,6,7-tetrahydrobenzofuran) (16eb) and  
(S)-2-phenyl-4-(((R)-2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)oxy)-4,5,6,7-tetrahydrobenzofuran  
(16ec)**



**16ea**  
Yield: 32 %  
ee: 79 %



**16eb**  
Yield: 50 %



**16ec**  
Yield: 18 %

Compound **16e** was prepared according to the general procedure from **8a** (98.1 mg, 0.5 mmol, 1.0 equiv.), water (0.03 mL, 1.5 mmol, 3.0 equiv.), **(S)-5** (0.8 mg, 0.001 mmol, 0.2 mol %) and  $\text{Ag}_2\text{CO}_3$  (0.1 mg, 0.0005 mmol, 0.1 mol %) in toluene (2.5 mL), yielding products **16ea** (34.3 mg, 0.16 mmol, 32 %), **16eb** (50.9 mg, 0.25 mmol, 50 %) and **16ec** (18.1 mg, 0.09 mmol, 18 %) as white solids.

**Data for 16ea:**<sup>13</sup>

$[\alpha]_D = +12$  (c 1.44,  $\text{CHCl}_3$ ). ee = 97%, determined on a Chiralpak IB column (heptane:IPA = 98:2, 1 mL/min), retention times:  $T_R$  (major): 28.3 min,  $T_R$  (minor): 34.5 min.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  = 7.62 (d,  $J$  = 7.3 Hz, 2H), 7.35 (t,  $J$  = 7.6 Hz, 2H), 7.22 (t,  $J$  = 7.6 Hz, 1H), 6.66 (s, 1H), 4.77-4.75 (m, 1H), 2.75-2.69 (m, 1H), 2.64-2.58 (m, 1H), 2.08-2.00 (m, 1H), 1.98-1.92 (m, 1H), 1.89-1.78 (m, 2H), 1.62 (s, 1H). **HRMS (ESI):**  $m/z$ : calculated for  $\text{C}_{14}\text{H}_{13}\text{O}_2^+$ : 213.0910  $[\text{M}-\text{H}_2+\text{H}]^+$ , found, 213.0912.

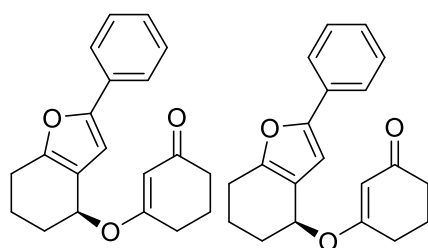
**Data for 16eb:**

$[\alpha]_D = +75$  (c 0.95,  $\text{CHCl}_3$ ).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  = 7.61 (d,  $J$  = 7.9 Hz, 4H), 7.34 (t,  $J$  = 7.9 Hz, 4H), 7.20 (t,  $J$  = 7.3 Hz, 2H), 6.61 (s, 2H), 4.62 (t,  $J$  = 3.8 Hz, 2H), 2.74 (dt,  $J_1$  = 16.4 Hz,  $J_2$  = 5.0 Hz, 2H), 2.64-2.58 (m, 2H), 2.16-2.11 (m, 2H), 2.03-1.99 (m, 2H), 1.92-1.87 (m, 4H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  = 153.0, 131.4, 128.9, 128.8, 127.1, 123.7, 120.9, 105.3, 69.2, 29.8, 23.5, 19.2. **HRMS (ESI):**  $m/z$ : calculated for  $\text{C}_{28}\text{H}_{27}\text{O}_3^+$ : 411.1955  $[\text{M}+\text{H}]^+$ , found, 411.1956.

**Data for 16ec:**

$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  = 7.62 (d,  $J$  = 7.9 Hz, 4H), 7.34 (t,  $J$  = 7.6 Hz, 4H), 7.20 (t,  $J$  = 7.3 Hz, 2H), 6.61 (s, 2H), 4.70 (t,  $J$  = 4.1 Hz, 2H), 2.75 (dt,  $J_1$  = 16.4 Hz,  $J_2$  = 5.3 Hz, 2H), 2.66-2.60 (m, 2H), 2.16-2.10 (m, 2H), 1.96-1.93 (m, 4H), 1.88-1.84 (m, 2H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  = 152.9, 131.4, 128.8, 127.1, 123.8, 123.7, 121.1, 105.3, 69.3, 30.2, 23.5, 19.5. **HRMS (ESI):**  $m/z$ : calculated for  $\text{C}_{28}\text{H}_{27}\text{O}_3^+$ : 411.1955  $[\text{M}+\text{H}]^+$ , found, 411.1953.

**(S)-3-((2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)oxy)cyclohex-2-en-1-one (16f)**



Na

\*

Yield: 77 %, ee: 89 %.

Compound **16f** was prepared according to the general procedure from **8a** (21.6 mg, 0.11 mmol, 1.1 equiv.), **9b** (11.2 mg, 0.1 mmol, 1.0 equiv.), **(S)-5** (0.2 mg, 0.0002 mmol, 0.2 mol %) and  $\text{Ag}_2\text{CO}_3$  (0.1 mg, 0.0001 mmol, 0.1 mol %) in toluene (0.5 mL), yielding product **16f** (23.6 mg, 0.77 mmol, 77 %) as a white solid for which the spectroscopical data correspond to those reported in the literature.<sup>13</sup>

$[\alpha]_D = -150$  (c 0.92,  $\text{CHCl}_3$ ). ee: 89 %, determined on a Chiralpak IA column (heptane:IPA = 98:02, 1 mL/min), retention times:  $T_R$  (major): 22.8 min,  $T_R$  (minor): 27.1 min.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz)  $\delta = 7.54$  (d,  $J = 7.3$  Hz, 2H), 7.28 (t,  $J = 7.5$  Hz, 2H), 7.16 (t,  $J = 7.7$  Hz, 1H), 6.53 (s, 1H), 5.54 (s, 1H), 5.19 (t,  $J = 3.6$  Hz, 1H), 2.72 (dt,  $J_1 = 16.8$  Hz,  $J_2 = 4.7$  Hz, 1H), 2.63-2.53 (m, 1H), 2.37-2.29 (m, 4H), 2.05-1.79 (m, 6H). **HRMS (ESI)**:  $m/z$ : calcd for  $\text{C}_{40}\text{H}_{40}\text{NaO}_6^+$  639.2723 [ $2\text{M}+\text{Na}$ ] $^+$ , found, 639.2717.

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## 6. X-ray Crystallography

X-ray diffraction data were measured for **10aa** and **(S)-5** using a RIGAKU diffractometer constituted by a MM007 HF rotating-anode generator, delivering copper radiation through Osmic CMF confocal optics, and a Rapid II curved Image Plate detector. *Fs\_process*<sup>14</sup> software under the *CrystalClear 2.0*<sup>15</sup> suite was used to integrate and scale the data, applying multi-scan *REQAB*<sup>6</sup> for the absorption correction. Regarding **SI-1**, the data collection was carried out with a RIGAKU XtaLabPro diffractometer equipped with a Mo microfocus sealed tube generator coupled to a double-bounce confocal Max-Flux® multilayer optic and a HPAD PILATUS3R 200K detector. *CrysAlisPro 1.171.39.46*<sup>16</sup> was employed for the data processing, with SCALE3 ABSPACK scaling algorithm implemented for the empirical absorption correction using spherical harmonics. The structures were solved either by dual-space direct methods (*SHELXD* program),<sup>17</sup> (regarding the two first ones) or by intrinsic phasing methods (*SHELXT* program),<sup>18</sup> and all were refined by full-matrix least-squares methods on  $F^2$  using *SHELXL*.<sup>19</sup> All non-hydrogen atoms of the molecules of interest improved by anisotropic refinement. Most of the H atoms were identified in difference maps. Methyl H atoms of the solvent isopropanol molecule present in the **(S)-5** structure were idealized and included as rigid groups allowed to rotate but not tip, and refined with  $U_{iso}$  set to  $1.5U_{eq}(C)$  of the parent carbon atom. All other H atoms bound to carbon atoms were positioned geometrically and refined with  $U_{iso}$  set to  $1.2U_{eq}(C)$  of the parent carbon atom. The position of the hydrogen atom in the NH group in **10aa** was refined freely with  $U_{iso}$  set to  $1.2U_{eq}(N)$ . The NH group is pointing perpendicularly toward the six-membered moiety of the indole at  $x+0.5$ ,  $0.5-y$ ,  $1-z$  at a 2.60 Å distance. The two hydroxy H atoms in **(S)-5** were allowed to change the torsion angle (instruction AFIX 147) and their displacement parameters were related with  $U_{iso}$  set to  $1.5U_{eq}(O)$ . A BUMP instruction was nevertheless applied to prevent steric clashes between them, the hydroxyl group of the solvent molecule bridging two phosphate moieties at  $x$ ,  $y$ ,  $z$  and  $x-0.5$ ,  $1.5-y$ ,  $1-z$  respectively, via O-H...O H-bonds generating the chain motifs  $C_2^2(6)$ .<sup>20</sup> The anisotropic displacement parameters of atoms in a phenyl group were restrained using the RIGU<sup>21</sup> instruction. Crystal data, data collection and structure refinement details are summarized in **Table S1**. The three structures have in common to belong to the same space group  $P 2_1 2_1 2_1$  and only the third one has more than one molecule in the asymmetric unit (*ie* 2). The absolute structures for **(S)-5** and **SI-1** were straightforwardly confirmed by dispersion effects, mainly provided by the Au  $M$  (at the Cu source excitation) and  $L$  (with the Mo source) far-absorption edges ( $> 5e^-$ ): both compounds synthesized from pure  $\alpha S$  binol conserved that axial chirality. Moreover the tetracoordinate phosphorus stereogenic centre in **SI-1** is ( $R_p$ ). Absence of strong anomalous scatterers in **10aa** could have hampered its absolute structure determination on  $C1(R)$  but highly redundant data quality coupled with intense microfocused copper

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<sup>14</sup> Rigaku - Higashi T. FS Process, Rigaku Corporation, **1998**, Tokyo, Japan.

<sup>15</sup> Rigaku. CrystalClear-SM Expert 2.0 r4 Rigaku Corporation, **2009**, Tokyo, Japan.

<sup>16</sup> Rigaku OD CrysAlis PRO. Rigaku Oxford Diffraction, Yarnton, Oxfordshire, **2015**, England.

<sup>17</sup> Sheldrick, G. M. *Acta Crystallogr.*, **2008**, A64, 112-122

<sup>18</sup> Drick, G. M. *Acta Crystallogr.*, **2015**, C71, 3-8.

<sup>19</sup> Drick, G. M. *Acta Crystallogr.*, **2015**, A71, 3-8.

<sup>20</sup> Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N. L. *Angew. Chem. Int. Ed. Engl.* **1995**, 34, 1555-1573.

<sup>21</sup> Thorn, A., Dittrich, B. & Sheldrick, G. M. *Acta Crystallogr.*, **2012**, A68, 448-451.

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radiation led to significant Flack<sup>22</sup> parameter estimate in favour of that assignment. This was corroborated later on by Bayesian-type analysis<sup>23</sup> upon 100 % Bijvoet pairs of reflections, as implemented within the PLATON program<sup>24</sup> (see **Table S1**).

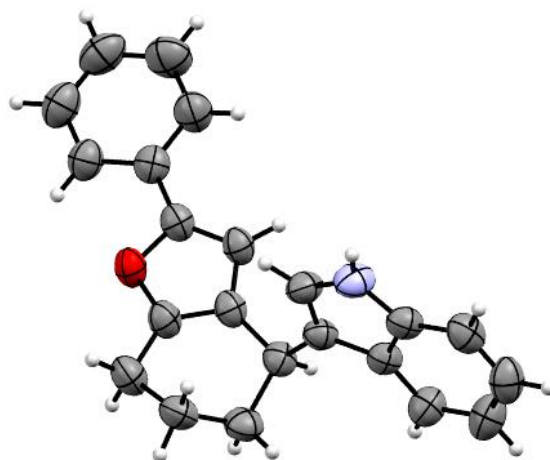


Figure S1. X-ray Molecular Structure of **10aa**

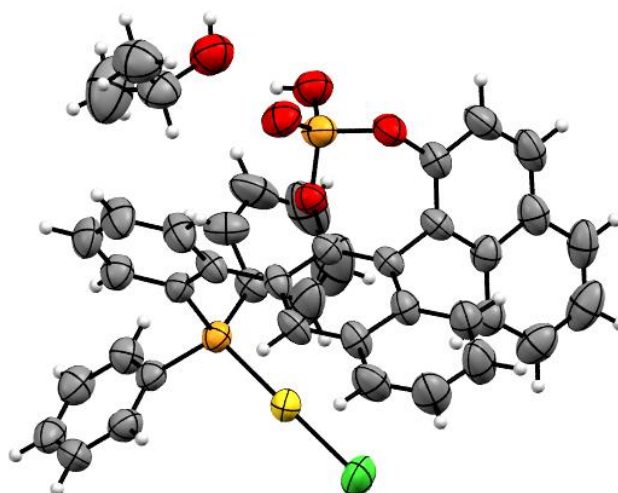


Figure S2. X-ray Molecular Structure of **(S)-5**

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<sup>22</sup> Flack, H.D. *Acta Crystallogr.*, **1983**, A39, 876-881.

<sup>23</sup> Hooft, R.W.W., Straver, L.H., Spek, A.L. *J. Appl. Cryst.*, **2008**, 41, 96-103.

<sup>24</sup> Spek, A. L. *Acta Crystallogr.*, **2009**, D65, 148-155.

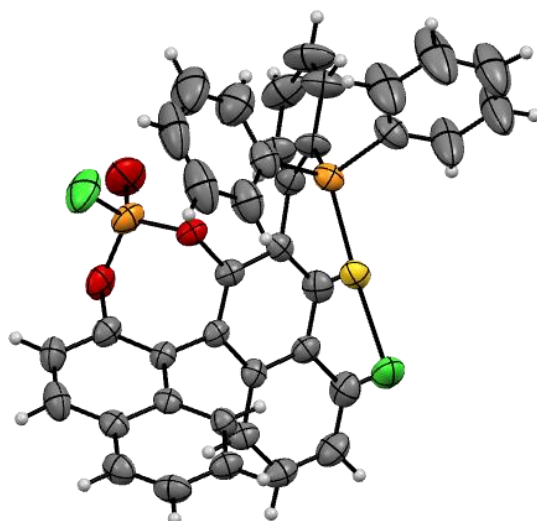


Figure S3. X-ray Molecular Structure of SI-1

**Table S1** Crystal data, data collection and structure refinement details for the 3 compounds.

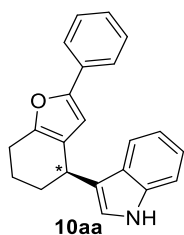
| Compound                                   | 10aa  | (S)-5  | SI-1  |
|--|---|--|---|
| Empirical formula                          | C <sub>22</sub> H <sub>19</sub> NO                              | C <sub>38</sub> H <sub>26</sub> AuClO <sub>4</sub> P <sub>2</sub> ,<br>C <sub>3</sub> H <sub>8</sub> O | C <sub>38</sub> H <sub>25</sub> AuCl <sub>2</sub> O <sub>3</sub> P <sub>2</sub> |
| Formula weight                             | 313.38  | 901.04   | 859.39  |
| Temperature (K)                            | 293(2)  | 293(2)   | 293(2)  |
| Wavelength (Å)                             | 1.54187   | 1.54187  | 0.71073   |
| Crystal system,<br>space group             | Orthorhombic,<br>P 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> | Orthorhombic,<br>P 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>  | Orthorhombic,<br>P 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>                 |
| Unit cell dimensions                       |   |  |   |
| a (Å)                                      | 6.6896(3)   | 10.8015(2)   | 11.26267(18)  |
| b (Å)                                      | 8.6995(3)   | 17.6790(3)   | 19.0781(4)  |
| c (Å)                                      | 28.863(2)   | 19.6851(14)  | 31.7278(6)  |
| α (°)                                      | 90  | 90   | 90  |
| β (°)                                      | 90  | 90   | 90  |
| γ (°)                                      | 90  | 90   | 90  |
| Volume (Å <sup>3</sup> )                   | 1679.72(15)   | 3759.1(3)  | 6817.4(2)   |
| Z,   | 4,  | 4,   | 8,  |
| Calculated density (mg/m <sup>3</sup> )    | 1.239   | 1.592  | 1.675   |
| Absorption coefficient (mm <sup>-1</sup> ) | 0.588   | 9.165  | 4.603   |
| F(000)                                     | 664   | 1784   | 3360  |
| Crystal size (mm)                          | 0.42 × 0.34 × 0.29  | 0.35 × 0.26 × 0.22   | 0.30 × 0.18 × 0.10  |
| θ range for data collection (°)            | 3.062 to 68.230   | 4.492 to 68.235  | 3.618 to 29.083   |
| Limiting indices                           | -7 ≤ h ≤ 7,<br>-10 ≤ k ≤ 7,<br>-34 ≤ l ≤ 34                     | -12 ≤ h ≤ 12,<br>-21 ≤ k ≤ 18,<br>-20 ≤ l ≤ 23   | -11 ≤ h ≤ 15,<br>-21 ≤ k ≤ 25,<br>-35 ≤ l ≤ 42                                  |
| Reflections collected / unique             | 21364 / 3065  | 32647 / 6835   | 78149 / 15931   |

|  |     |                                    |                  |                  |
|--|-----|------------------------------------|------------------|------------------|
| [R(int)]   |     | 0.0303                             | 0.0462           | 0.0614           |
| Completeness to $\theta_{\text{full}}$ (%)                 |     | 99.7                               | 99.0             | 99.5             |
| Absorption correction                                      |     | Semi-empirical from equivalents    |                  |                  |
| Max. and Min. transmission                                 |     | 1.000 and 0.815                    | 1.000 and 0.605  | 1.000 and 0.264  |
| Refinement method  |     | Full-matrix least-squares on $F^2$ |                  |                  |
| Data / restraints / parameters                             |     | 3063 / 0 / 221                     | 6802 / 39 / 456  | 15910 / 0 / 829  |
| Goodness-of-fit on $F^2$                                   |     | 1.074                              | 1.079            | 1.045            |
| Final R indices  | R1  | 0.0297                             | 0.0361           | 0.0437           |
| [ $I > 2\sigma(I)$ ]                                       | wR2 | 0.0746                             | 0.0837           | 0.0874           |
| R indices  | R1  | 0.0326                             | 0.0386           | 0.0661           |
| (all data)   | wR2 | 0.0788                             | 0.0867           | 0.0927           |
| Absolute structure parameters <sup>16</sup>                |     |                                    |                  |                  |
| Flack $x$ <sup>14</sup>                                    |     | 0.03(6)                            | -0.023(3)        | -0.005(3)        |
| Parsons $z$ <sup>25</sup>                                  |     | 0.00(7)                            | -0.023(4)        | -0.004(3)        |
| Hooft $y$ <sup>15</sup>                                    |     | 0.02(5)                            | -0.027(4)        | -0.011(4)        |
| P2 (true)  |     | 100%                               | 100%             | 100%             |
| P3 (true)  |     | 100%                               | 100%             | 100%             |
| Extinction coefficient                                     |     | 0.0017(6)                          | -                | -                |
| Largest diff. peak and hole ( $\text{e.}\text{\AA}^{-3}$ ) |     | 0.104 and<br>-0.123                | 1.607 and -0.460 | 1.700 and -1.761 |

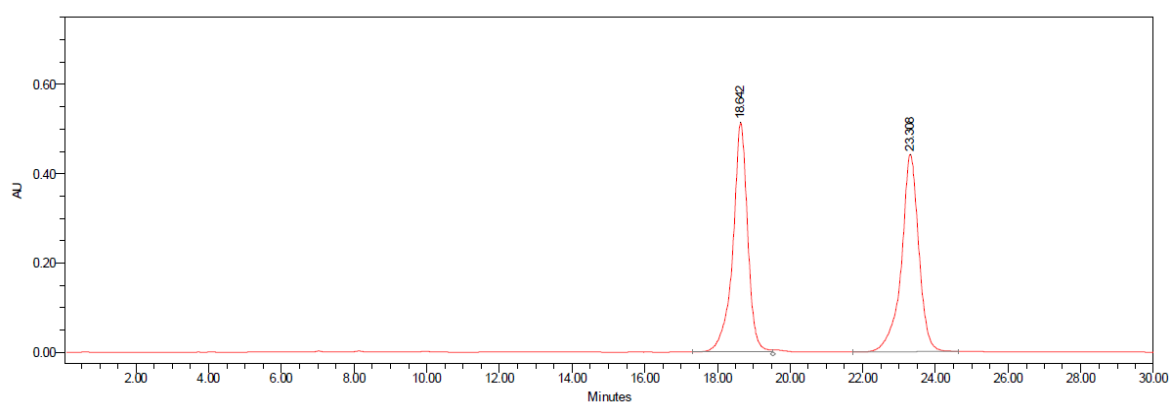
CCDC 1884441-1884443 (compounds **10aa**, **(S)-5**, and **SI-1** respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)

<sup>25</sup> Parsons, Flack and Wagner, *Acta Crystallogr.*, **2013**, B69 249-259.

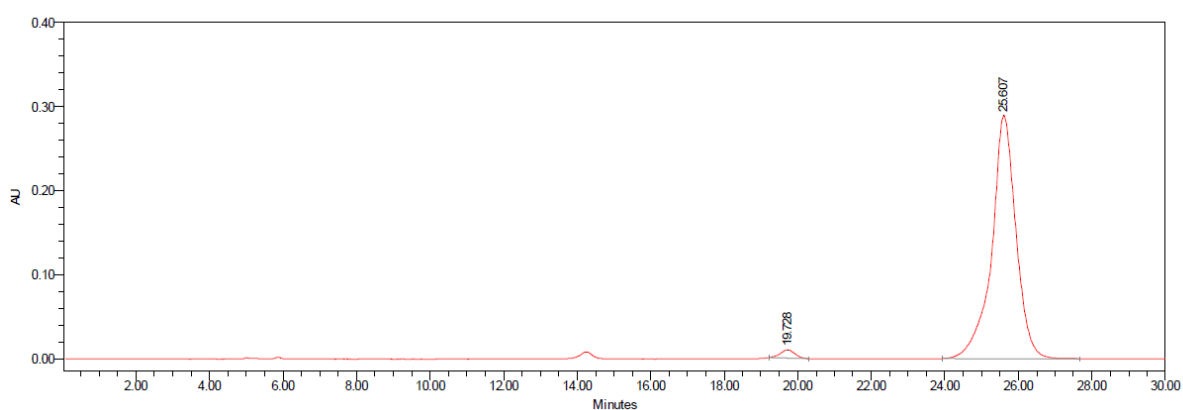
## 7. HPLC traces



**HPLC Analysis for 10aa:** HPLC Chiralpak IA column [heptane:IPA = 95:05, 1 mL/min,  $\lambda = 277$  nm, retention times:  $T_R$  (minor): 19.7 min,  $T_R$  (major): 25.6 min].

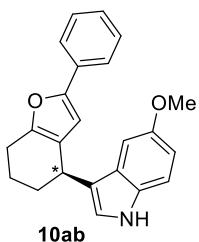


|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 18.642 | 14502314 | 49.78  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 23.308 | 14628255 | 50.22  |

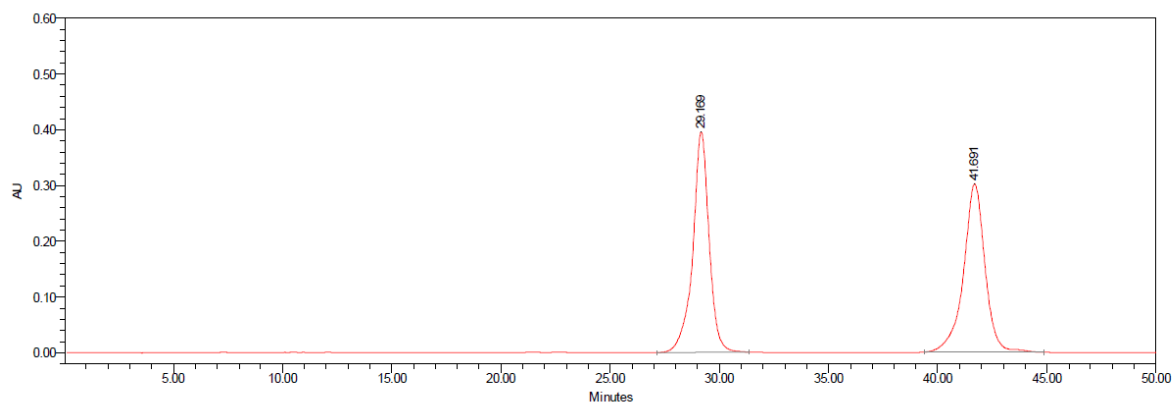


|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 19.728 | 261081   | 1.93   |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 25.607 | 13248494 | 98.07  |

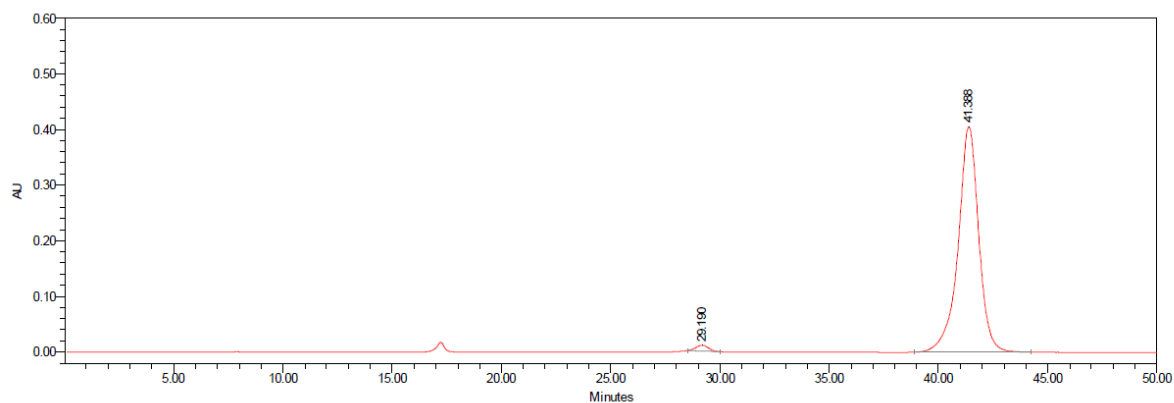




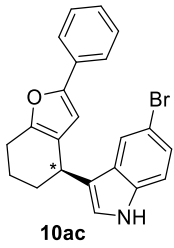
**HPLC Analysis for 10ab:** HPLC Chiralpak IA column [heptane:IPA = 95:05, 1 mL/min,  $\lambda = 277$  nm, retention times:  $T_R$  (minor): 29.2 min,  $T_R$  (major): 41.4 min].



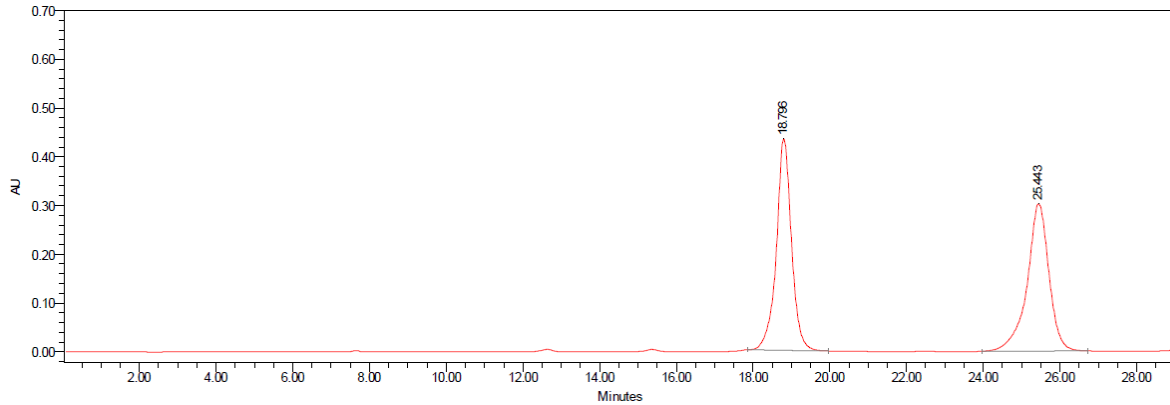
|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 29.169 | 20533331 | 49.83  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 41.691 | 20670930 | 50.17  |



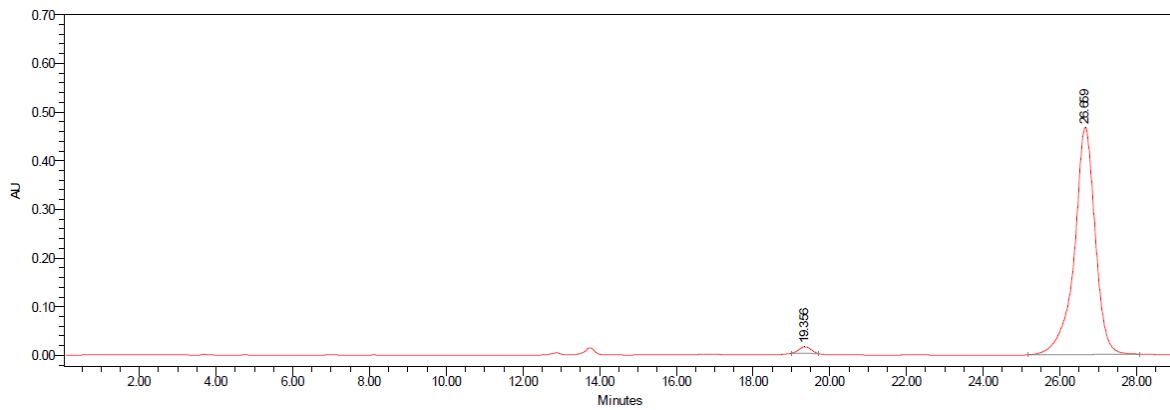
|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 29.190 | 407299   | 1.51   |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 41.388 | 26563035 | 98.49  |



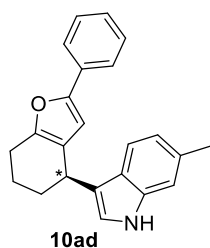
**HPLC Analysis for 10ac:** HPLC Chiralpak IA column [heptane:IPA = 95:05, 1 mL/min,  $\lambda = 277$  nm, retention times:  $T_R$  (minor): 19.4 min,  $T_R$  (major): 26.7 min].



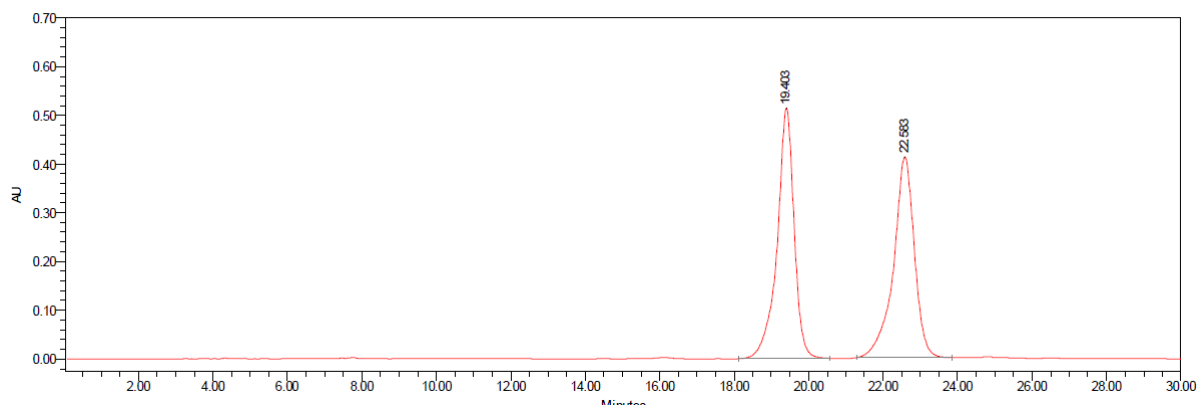
|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 18.796 | 11907602 | 49.92  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 25.443 | 11944609 | 50.08  |



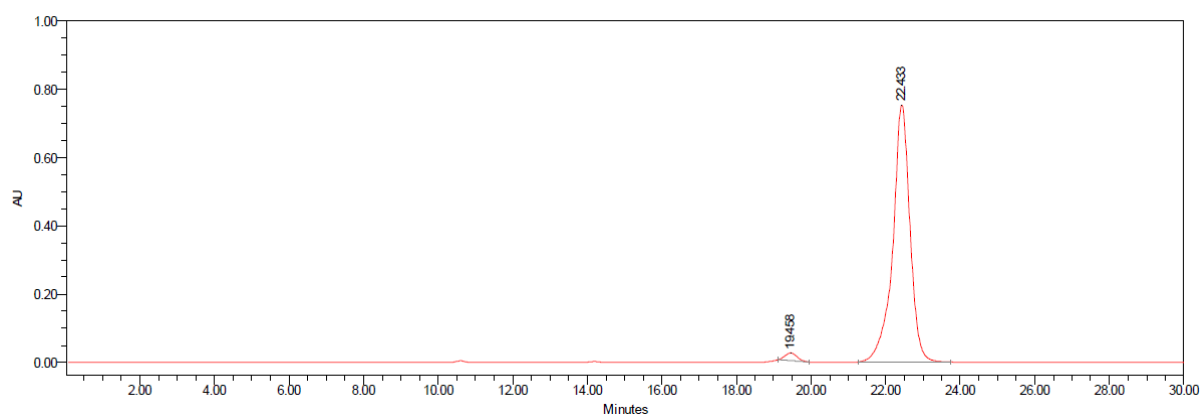
|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 19.356 | 280233   | 1.56   |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 26.659 | 17640550 | 98.44  |



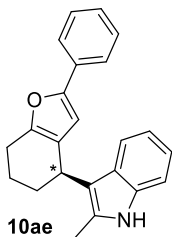
**HPLC Analysis for 10ad:** HPLC Chiralpak IA column [heptane:IPA = 95:05, 1 mL/min,  $\lambda$  = 277 nm, retention times:  $T_R$  (minor): 19.5 min,  $T_R$  (major): 22.4 min].



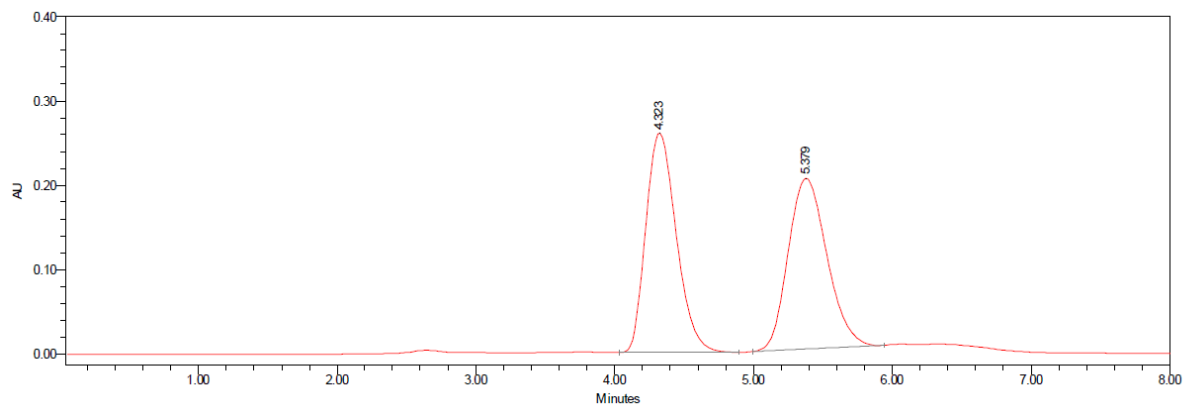
|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 19.403 | 16316844 | 50.42  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 22.583 | 16047118 | 49.58  |



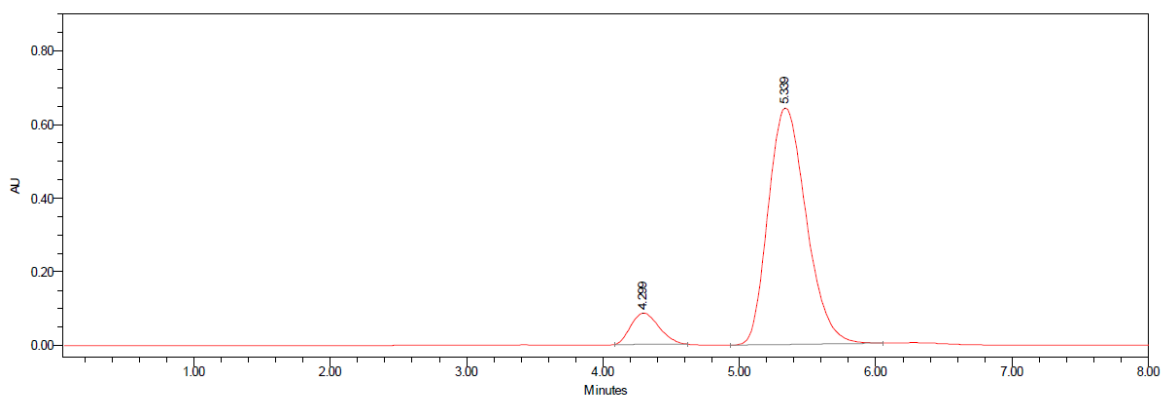
|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 19.458 | 497201   | 2.02   |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 22.433 | 24129004 | 97.98  |



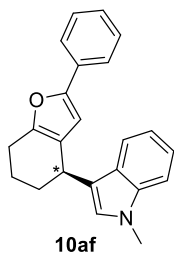
**HPLC Analysis for 10ae:** HPLC Chiralpak AD-H column [heptane:IPA = 90:10, 1 mL/min,  $\lambda = 277$  nm, retention times:  $T_R$  (minor): 4.3 min,  $T_R$  (major): 5.3 min].



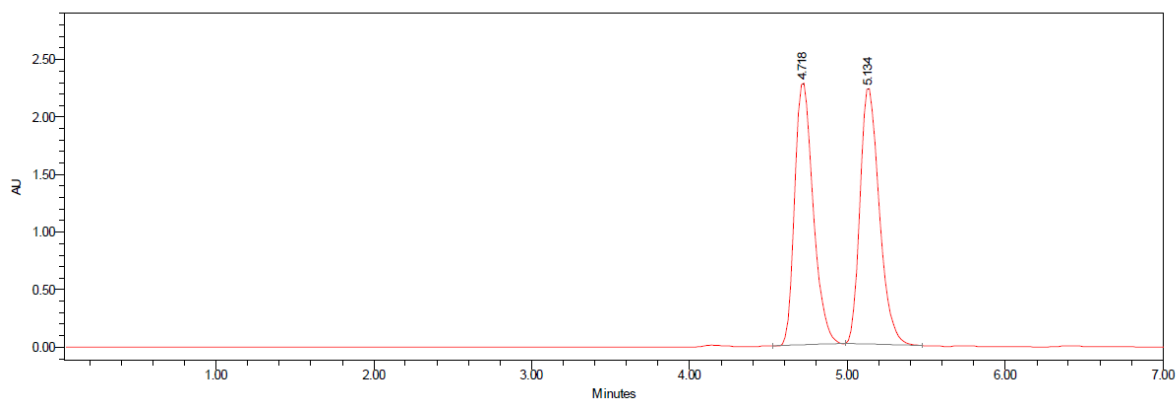
|   | Channel Description             | RT    | Area    | % Area |
|---|---------------------------------|-------|---------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 4.323 | 3967340 | 50.30  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 5.379 | 3920104 | 49.70  |



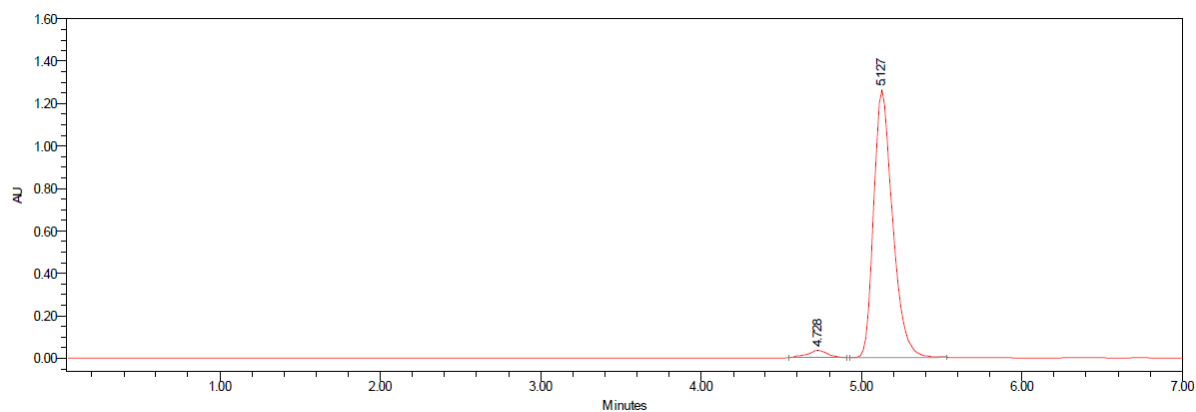
|   | Channel Description             | RT    | Area     | % Area |
|---|---------------------------------|-------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 4.299 | 1217284  | 8.92   |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 5.339 | 12435400 | 91.08  |



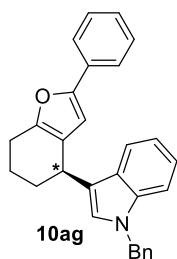
**HPLC Analysis for 10af:** HPLC Chiralpak IC column [heptane:IPA = 95:05, 1 mL/min,  $\lambda = 277$  nm, retention times:  $T_R$  (minor): 4.7 min,  $T_R$  (major): 5.1 min].



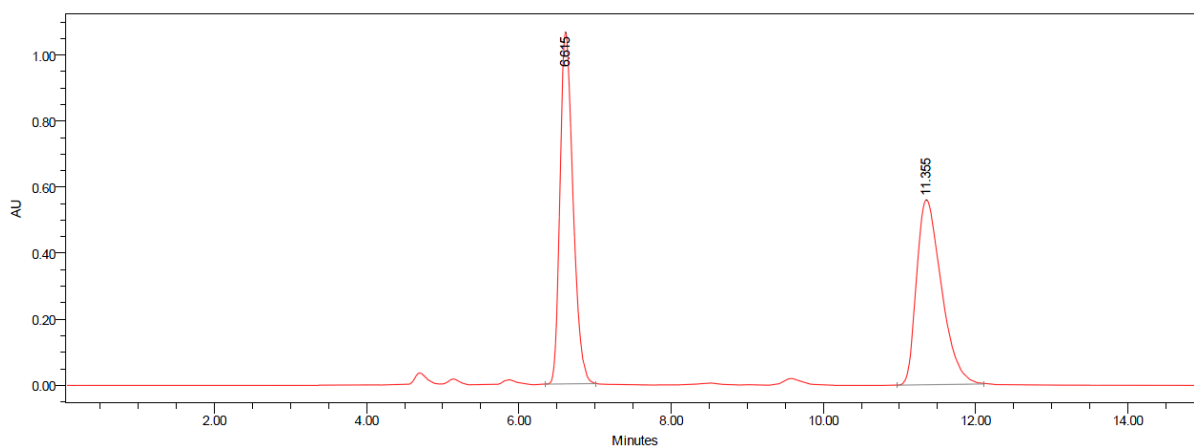
|   | Channel Description             | RT    | Area     | % Area |
|---|---------------------------------|-------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 4.718 | 18557092 | 49.53  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 5.134 | 18910286 | 50.47  |



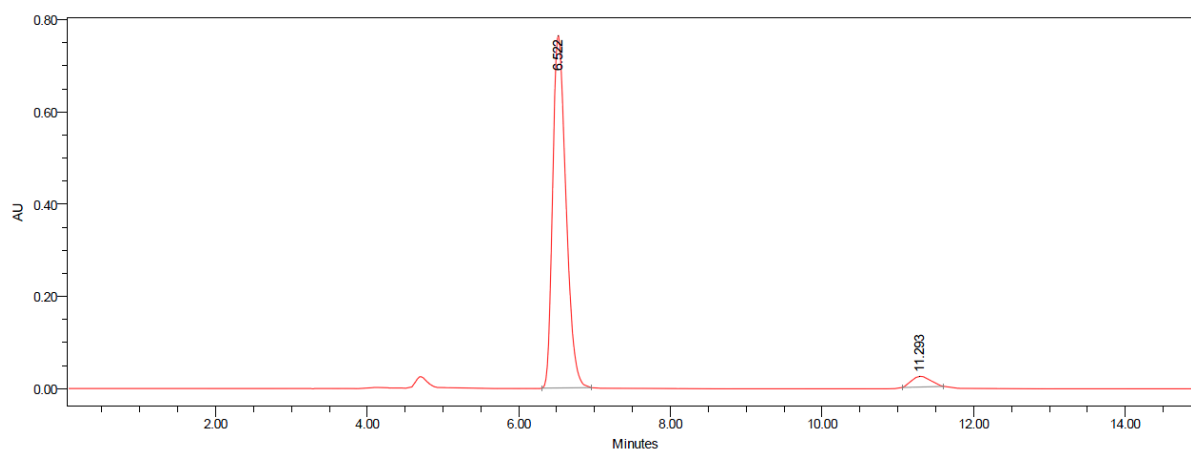
|   | Channel Description             | RT    | Area     | % Area |
|---|---------------------------------|-------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 4.728 | 305767   | 2.89   |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 5.127 | 10285879 | 97.11  |



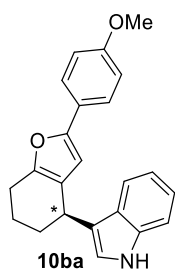
**HPLC Analysis for 10ag:** HPLC Chiralpak IA column [heptane:IPA = 95:05, 1 mL/min,  $\lambda = 277$  nm, retention times:  $T_R$  (minor): 6.5 min,  $T_R$  (major): 11.3 min].



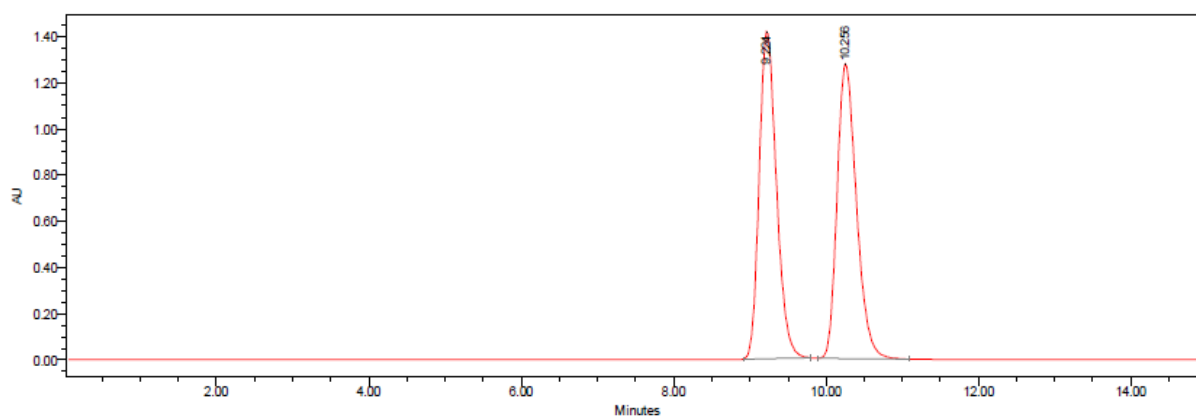
|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 6.615  | 12628104 | 50.00  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 11.355 | 12630238 | 50.00  |



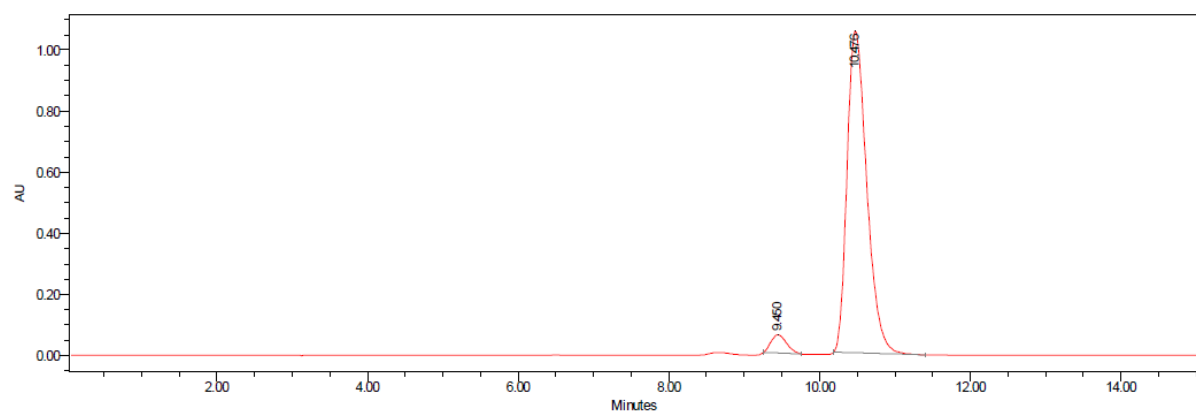
|   | Channel Description             | RT     | Area    | % Area |
|---|---------------------------------|--------|---------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 6.522  | 9323364 | 95.85  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 11.293 | 403790  | 4.15   |



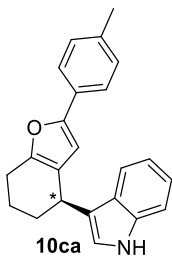
**HPLC Analysis for 10ba:** HPLC Chiralpak IC column [heptane:IPA = 95:05, 1 mL/min,  $\lambda = 277$  nm, retention times:  $T_R$  (minor): 9.5 min,  $T_R$  (major): 10.5 min].



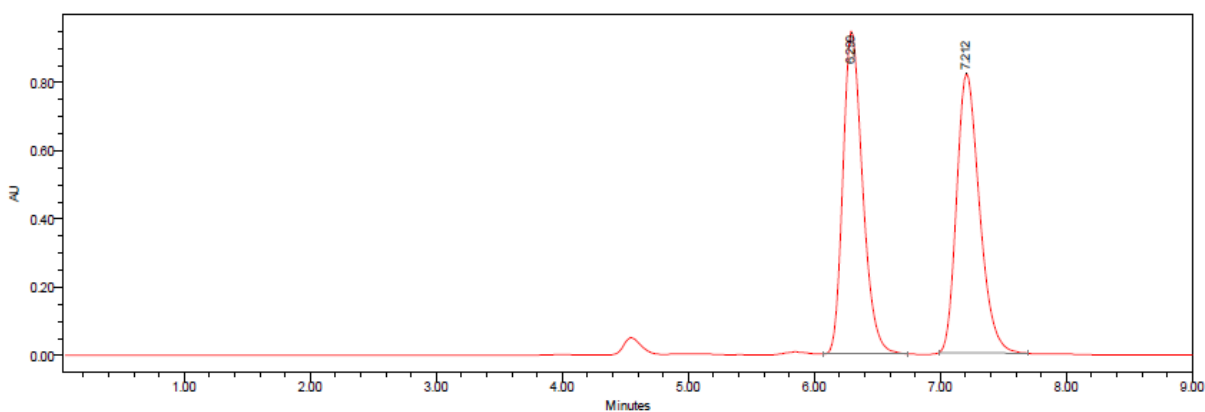
|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 9.224  | 22196993 | 49.76  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 10.256 | 22410909 | 50.24  |



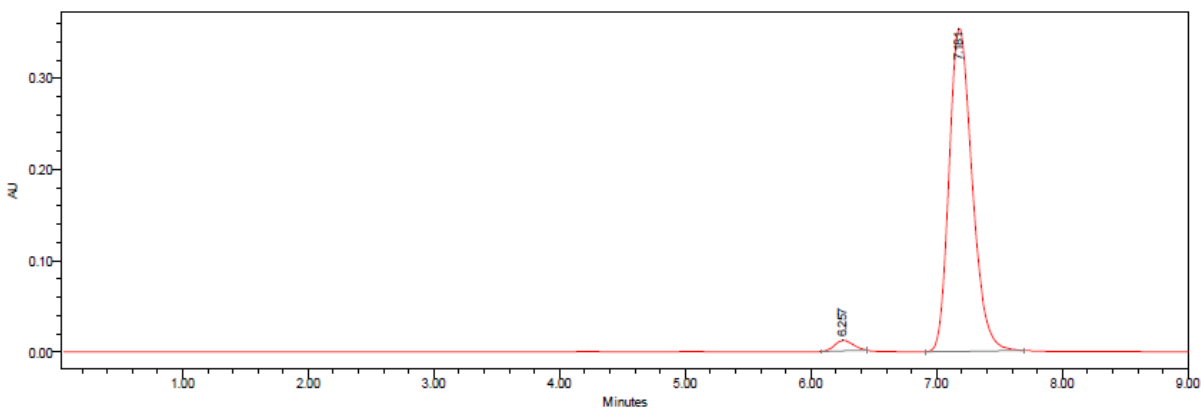
|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 9.450  | 859446   | 4.31   |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 10.476 | 19073662 | 95.69  |



**HPLC Analysis for 10ca:** HPLC Chiralpak IC column [heptane:IPA = 95:05, 1 mL/min,  $\lambda$  = 277 nm, retention times:  $T_R$  (minor): 6.3 min,  $T_R$  (major): 7.2 min].

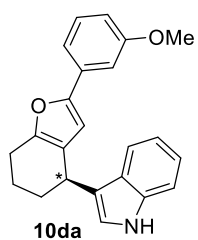


|   | Channel Description             | RT    | Area     | % Area |
|---|---------------------------------|-------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 6.299 | 10263174 | 49.94  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 7.212 | 10289115 | 50.06  |

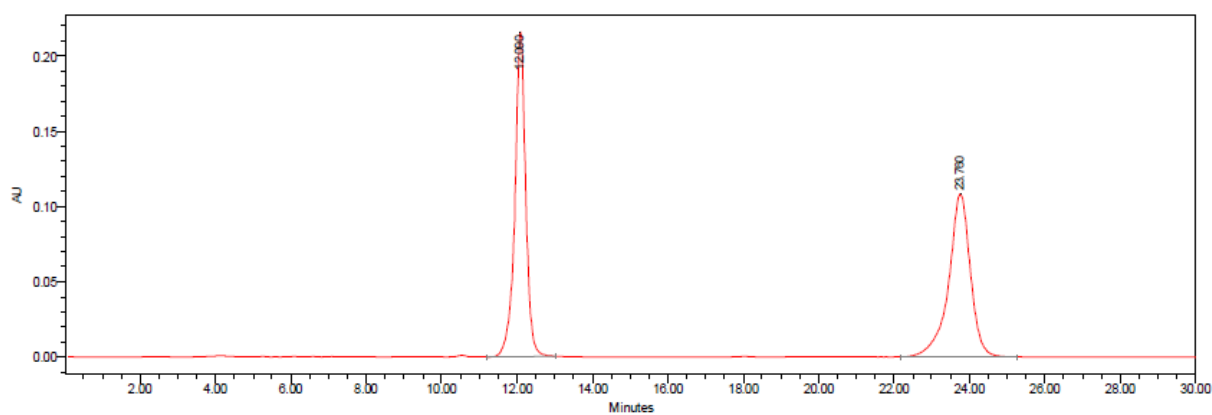


|   | Channel Description             | RT    | Area    | % Area |
|---|---------------------------------|-------|---------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 6.257 | 115884  | 2.54   |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 7.181 | 4446473 | 97.46  |

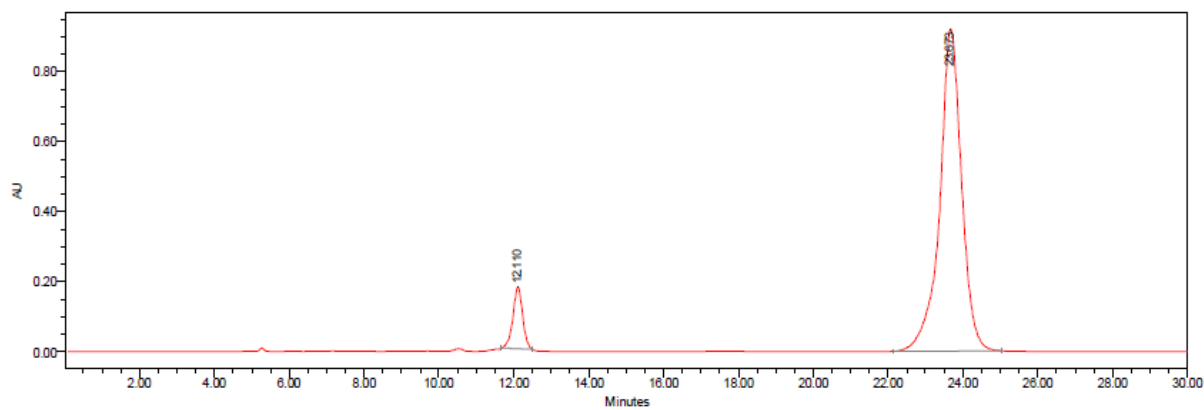




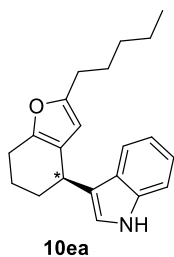
**HPLC Analysis for 10da:** HPLC Chiralpak IA column [heptane:IPA = 90:10, 1 mL/min,  $\lambda$  = 277 nm, retention times:  $T_R$  (minor): 12.1 min,  $T_R$  (major): 23.7 min].



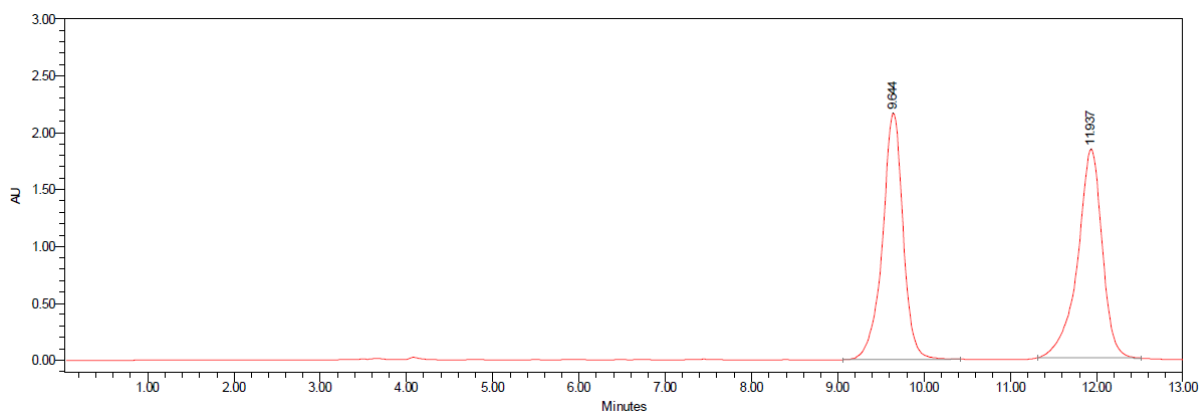
|   | Channel Description             | RT     | Area    | % Area |
|---|---------------------------------|--------|---------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 12.090 | 4312360 | 49.84  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 23.760 | 4339656 | 50.16  |



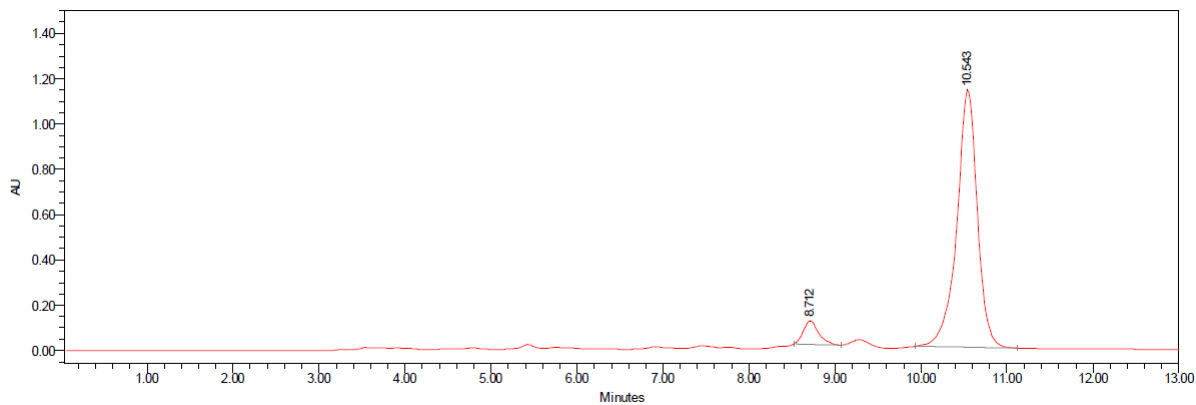
|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 12.110 | 3174489  | 7.83   |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 23.673 | 37371650 | 92.17  |



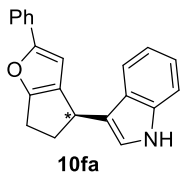
**HPLC Analysis for 10ea:** HPLC Chiralpak IA column [heptane:IPA = 95:05, 1 mL/min,  $\lambda = 277$  nm, retention times:  $T_R$  (minor): 8.7 min,  $T_R$  (major): 10.5 min].



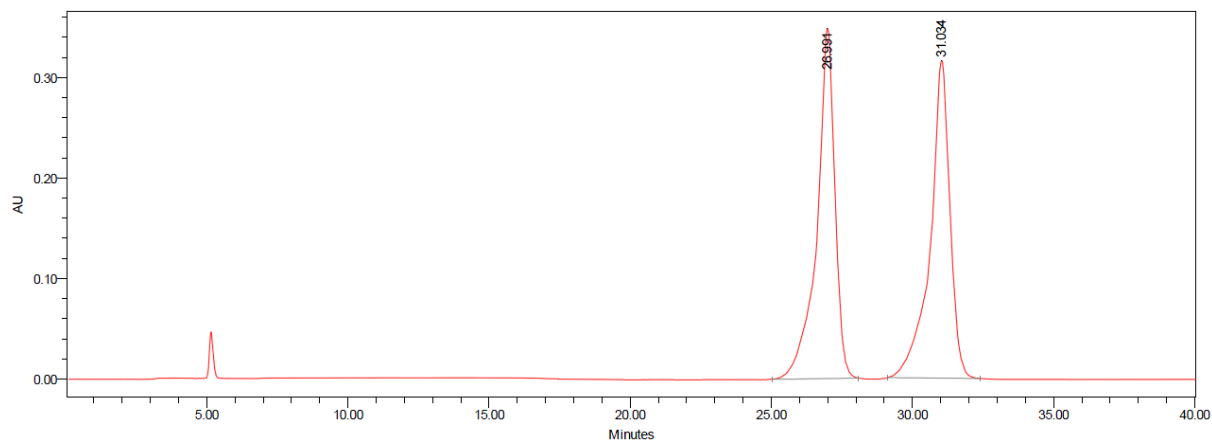
|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 9.644  | 35915017 | 49.72  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 11.937 | 36319260 | 50.28  |



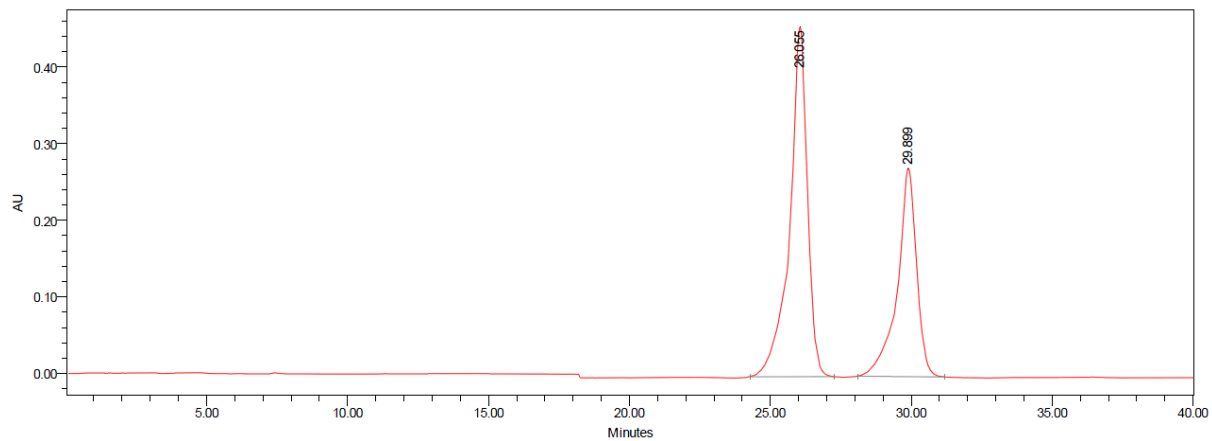
|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 8.712  | 1275487  | 6.34   |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 10.543 | 18829441 | 93.66  |



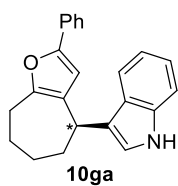
**HPLC Analysis for 10fa:** HPLC Chiralpak IA column [heptane:IPA = 95:05, 1 mL/min,  $\lambda$  = 277 nm, retention times:  $T_R$  (major): 26.1 min,  $T_R$  (minor): 29.9 min].



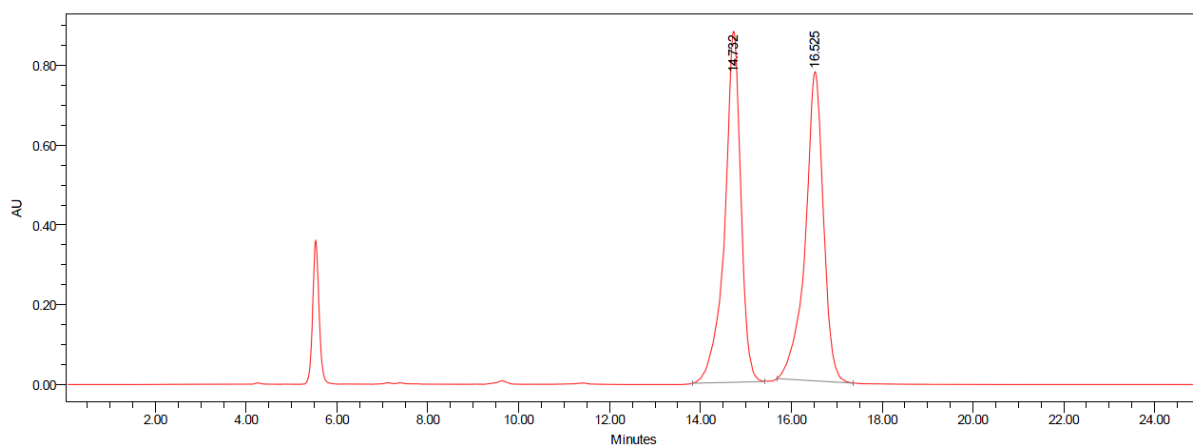
|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 26.991 | 15348618 | 50.11  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 31.034 | 15283917 | 49.89  |



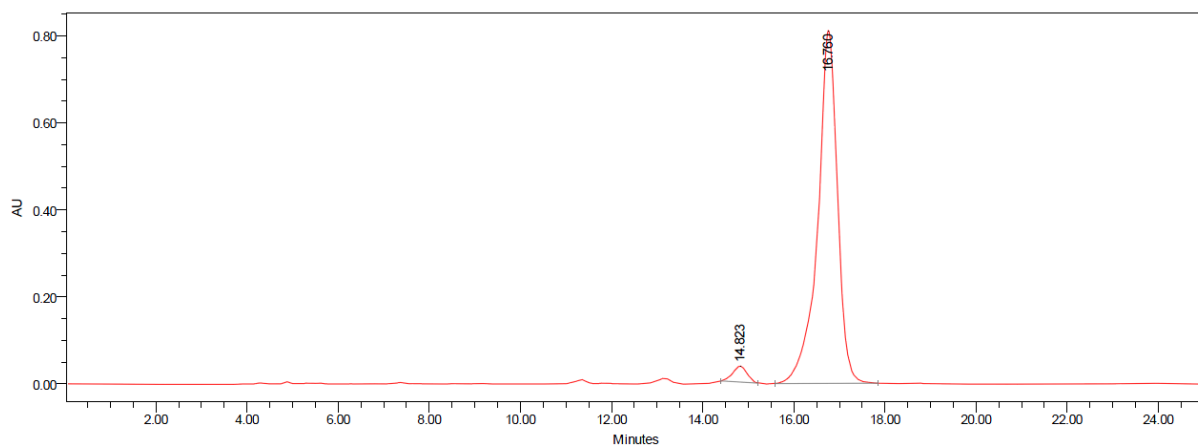
|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 26.055 | 19740973 | 60.60  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 29.899 | 12836253 | 39.40  |



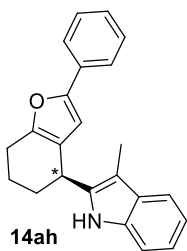
**HPLC Analysis for 10ga:** HPLC Chiralpak IA column [heptane:IPA = 95:05, 1 mL/min,  $\lambda = 277$  nm, retention times:  $T_R$  (minor): 14.8 min,  $T_R$  (major): 16.8 min].



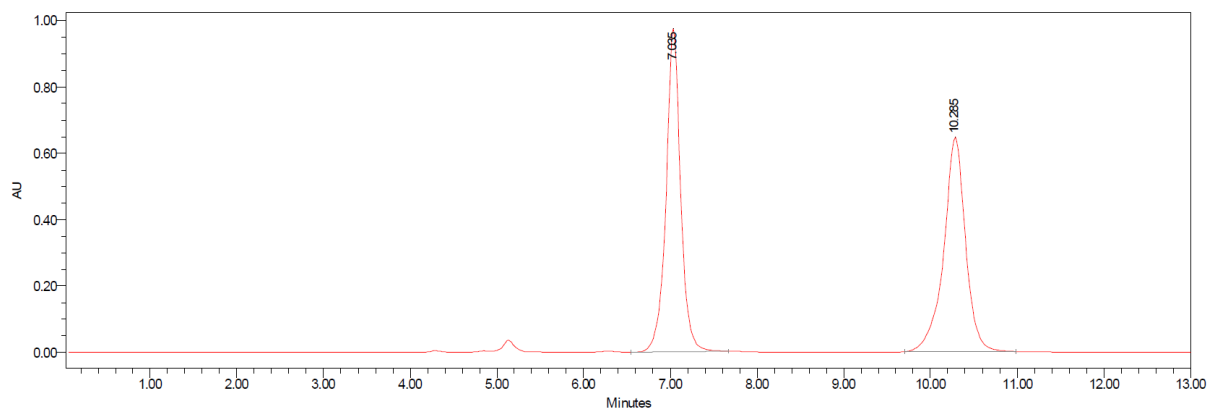
|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 14.732 | 21581390 | 50.25  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 16.525 | 21364017 | 49.75  |



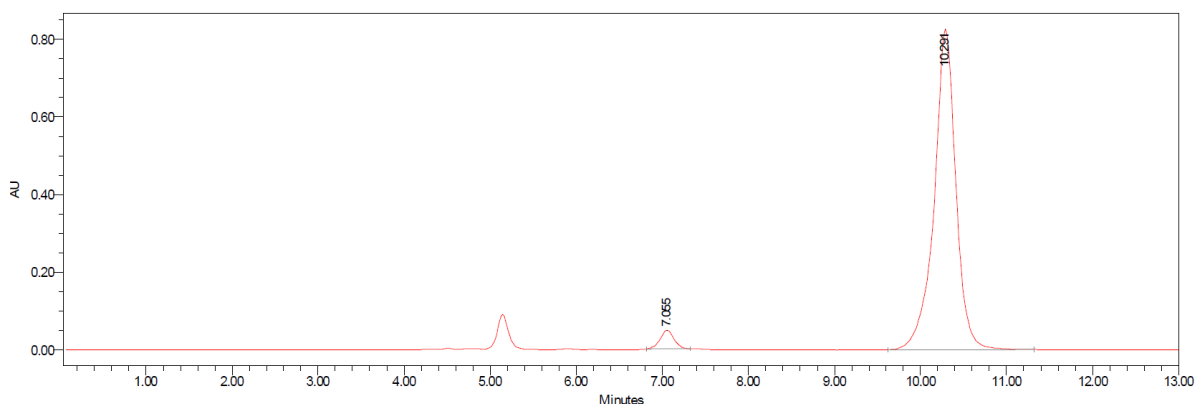
|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 14.823 | 794521   | 3.18   |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 16.760 | 24213709 | 96.82  |



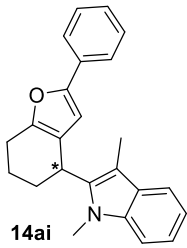
**HPLC Analysis for 14ah:** HPLC Chiralpak IA column [heptane:IPA = 95:05, 1 mL/min,  $\lambda = 277$  nm, retention times:  $T_R$  (minor): 7.1 min,  $T_R$  (major): 10.3 min].



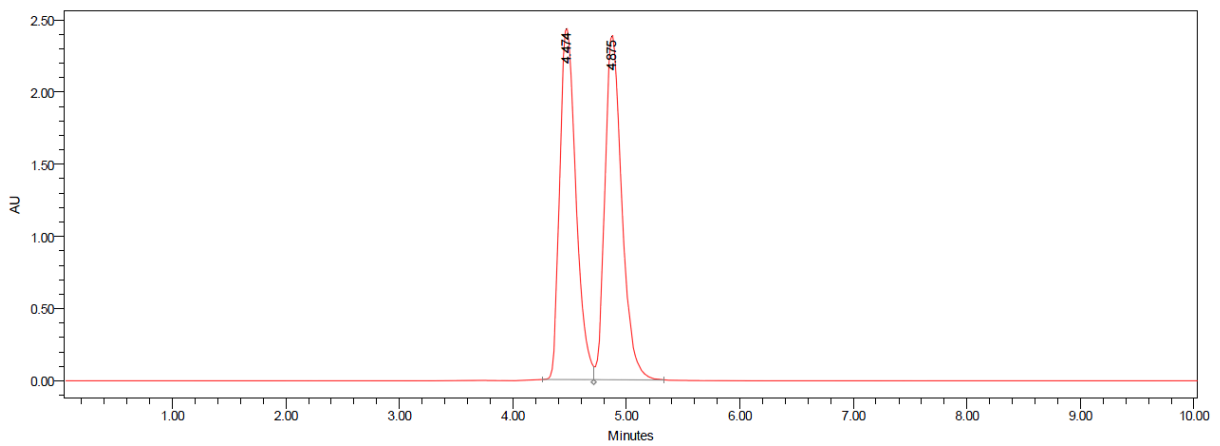
|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 7.035  | 11343652 | 50.11  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 10.285 | 11294023 | 49.89  |



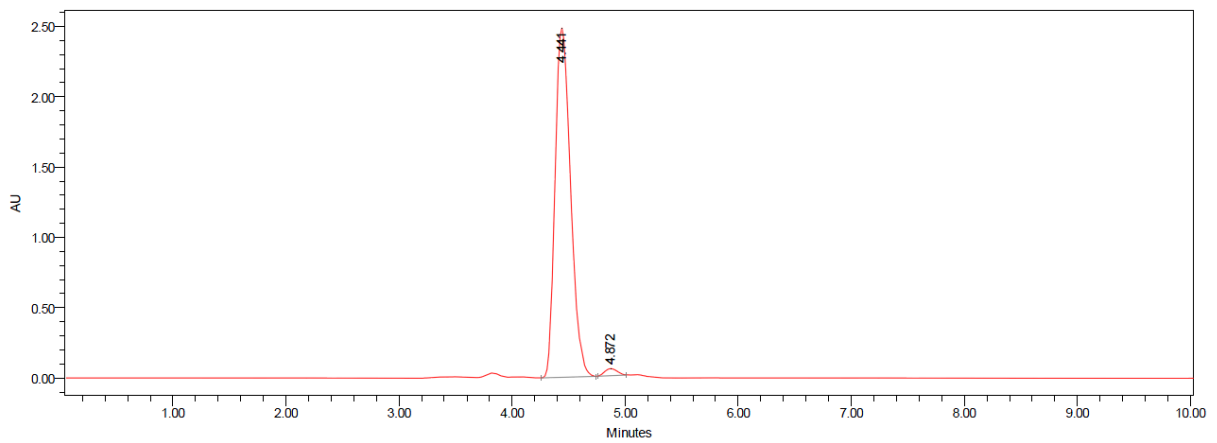
|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 7.055  | 535381   | 3.56   |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 10.291 | 14502158 | 96.44  |



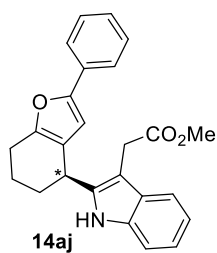
**HPLC Analysis for 14ai:** HPLC Chiralpak IC column [heptane:IPA = 95:05, 1 mL/min,  $\lambda$  = 277 nm, retention times:  $T_R$  (major): 4.4 min,  $T_R$  (minor): 4.9 min].



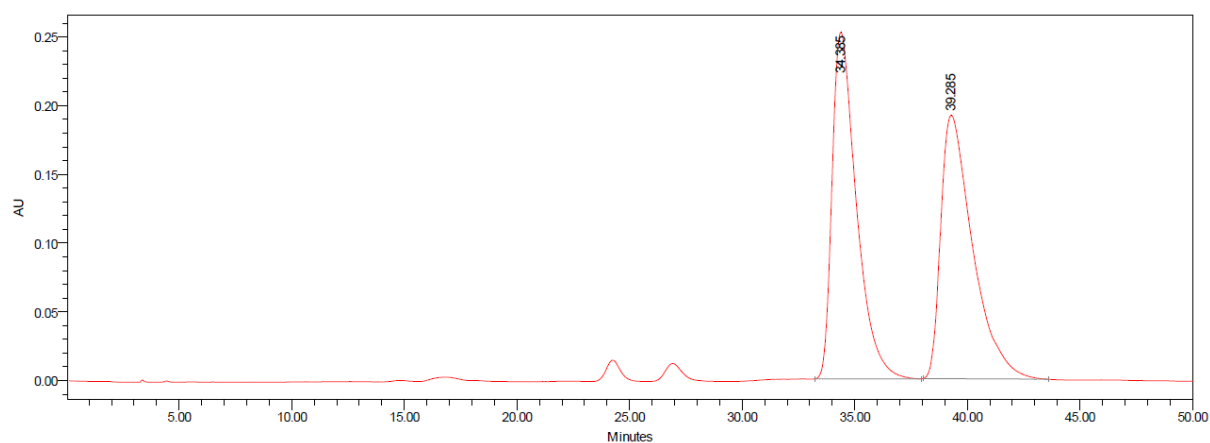
|   | Channel Description             | RT    | Area     | % Area |
|---|---------------------------------|-------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 4.474 | 24143180 | 49.41  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 4.875 | 24717306 | 50.59  |



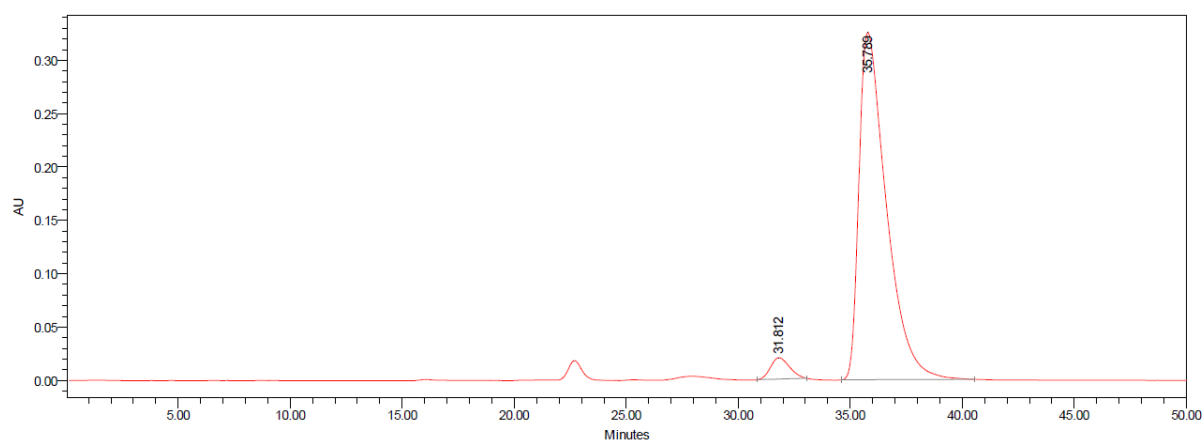
|   | Channel Description             | RT    | Area     | % Area |
|---|---------------------------------|-------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 4.441 | 23702749 | 98.39  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 4.872 | 387660   | 1.61   |



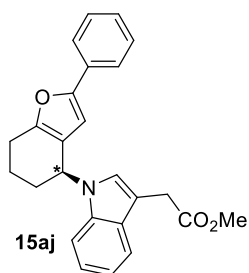
**HPLC Analysis for 14aj:** HPLC Chiralpak IC column [heptane:IPA = 98:02, 1 mL/min,  $\lambda$  = 277 nm, retention times:  $T_R$  (minor): 31.8 min,  $T_R$  (major): 35.8 min].



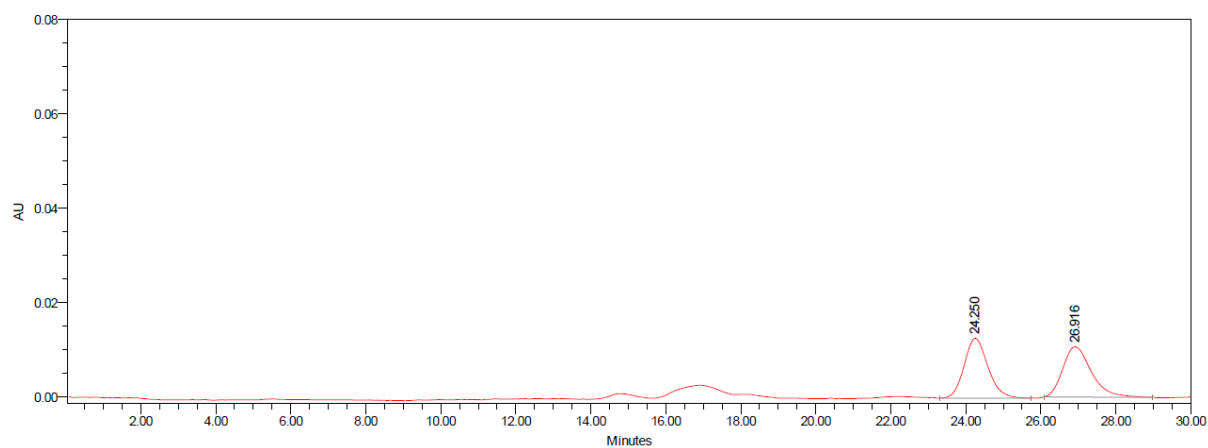
|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 34.385 | 18922963 | 50.07  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 39.285 | 18871860 | 49.93  |



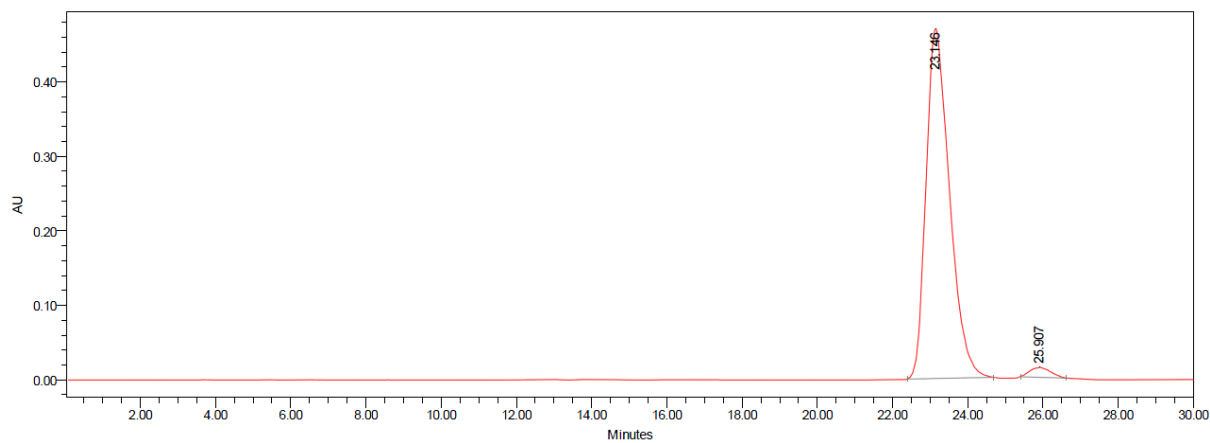
|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 31.812 | 1166654  | 4.05   |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 35.789 | 27660033 | 95.95  |



**HPLC Analysis for 15aj:** HPLC Chiralpak IC column [heptane:IPA = 98:02, 1 mL/min,  $\lambda$  = 277 nm, retention times:  $T_R$  (major): 23.1 min,  $T_R$  (minor): 25.9 min].

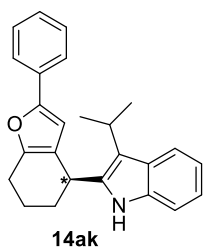


|   | Channel Description             | RT     | Area   | % Area |
|---|---------------------------------|--------|--------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 24.250 | 556623 | 49.69  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 26.916 | 563529 | 50.31  |

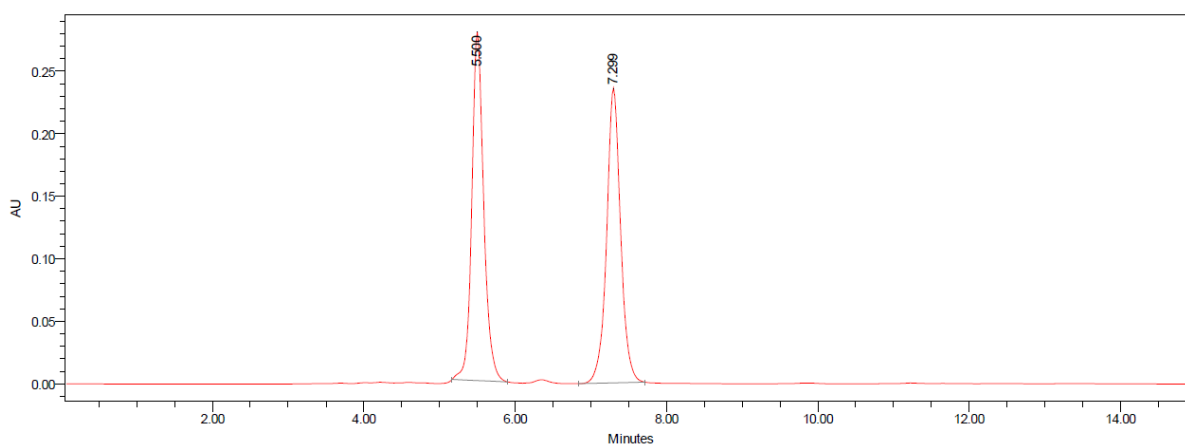


|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 23.146 | 20303913 | 97.56  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 25.907 | 508204   | 2.44   |

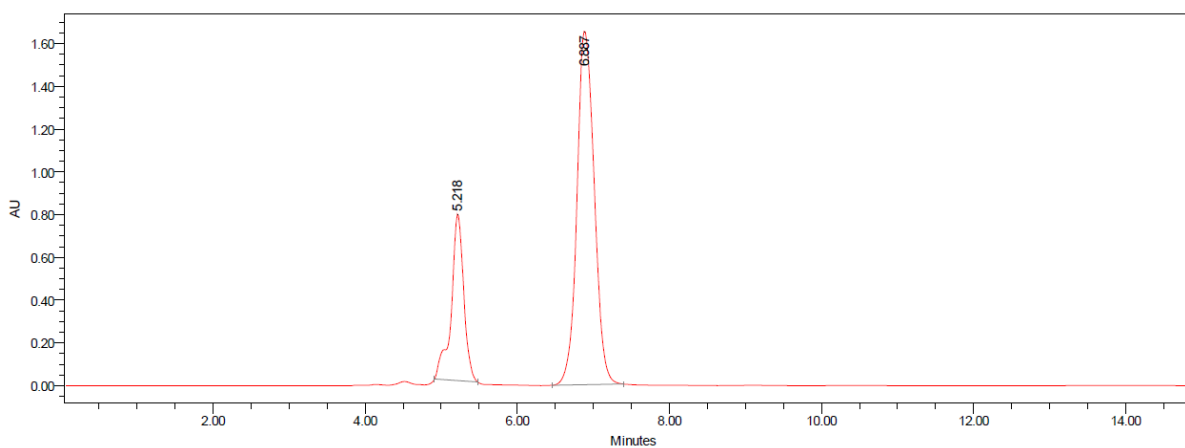




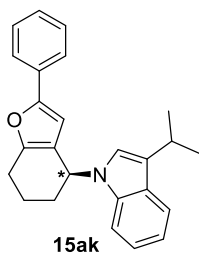
**HPLC Analysis for 14ak:** HPLC Chiralpak IA column [heptane:IPA = 95:05, 1 mL/min,  $\lambda = 277$  nm, retention times:  $T_R$  (minor): 5.2 min,  $T_R$  (major): 6.9 min].



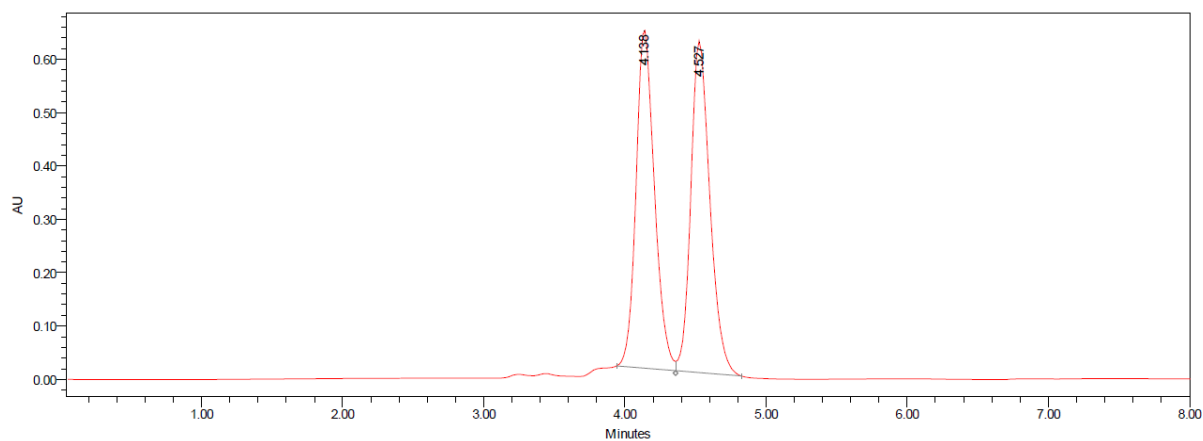
|   | Channel Description             | RT    | Area    | % Area |
|---|---------------------------------|-------|---------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 5.500 | 3042828 | 50.23  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 7.299 | 3015266 | 49.77  |



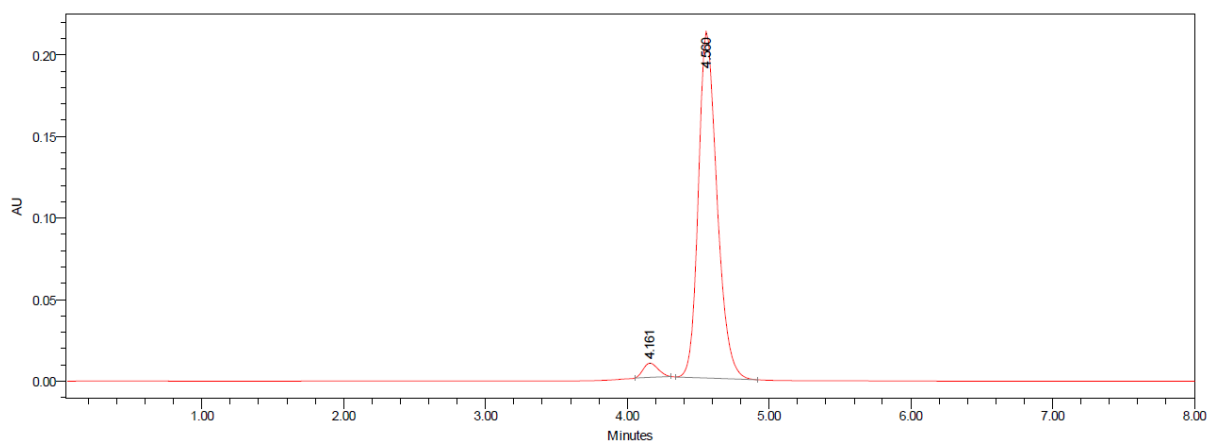
|   | Channel Description             | RT    | Area     | % Area |
|---|---------------------------------|-------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 5.218 | 8917970  | 25.43  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 6.887 | 26156996 | 74.57  |



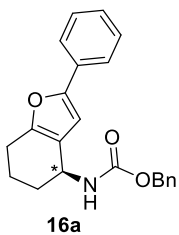
**HPLC Analysis for 15ak:** HPLC Chiralpak IA column [heptane:IPA = 95:05, 1 mL/min,  $\lambda = 277$  nm, retention times:  $T_R$  (minor): 4.2 min,  $T_R$  (major): 4.6 min].



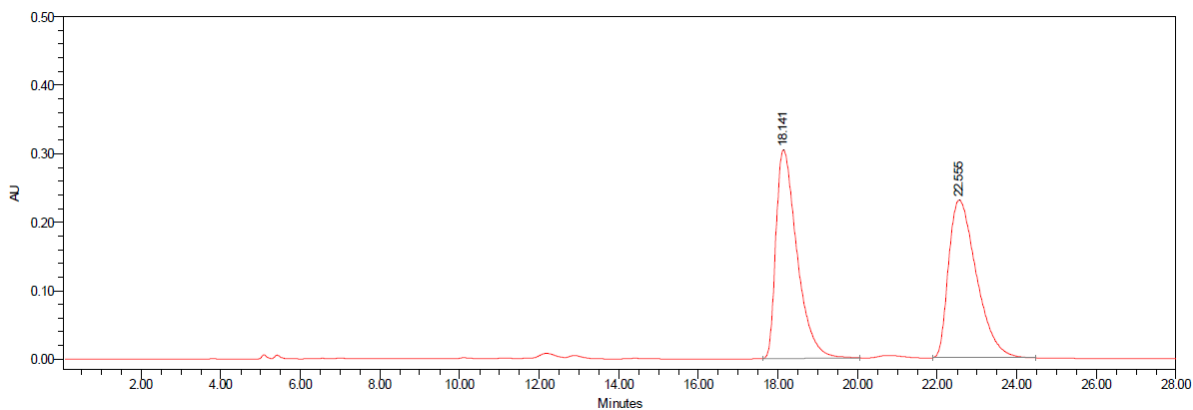
|   | Channel Description             | RT    | Area    | % Area |
|---|---------------------------------|-------|---------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 4.138 | 5764973 | 49.61  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 4.527 | 5856614 | 50.39  |



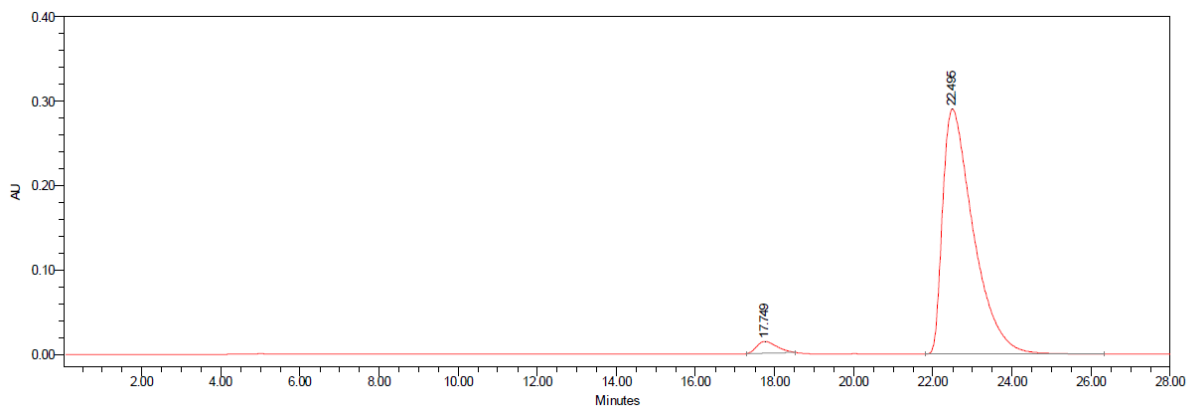
|   | Channel Description             | RT    | Area    | % Area |
|---|---------------------------------|-------|---------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 4.161 | 62349   | 3.10   |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 4.560 | 1946577 | 96.90  |



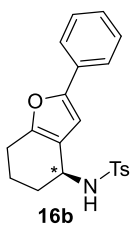
**HPLC Analysis for 16a:** HPLC Chiralpak IB column [heptane:IPA = 97:03, 1 mL/min,  $\lambda$  = 277 nm, retention times:  $T_R$  (minor): 17.7 min,  $T_R$  (major): 22.5 min].



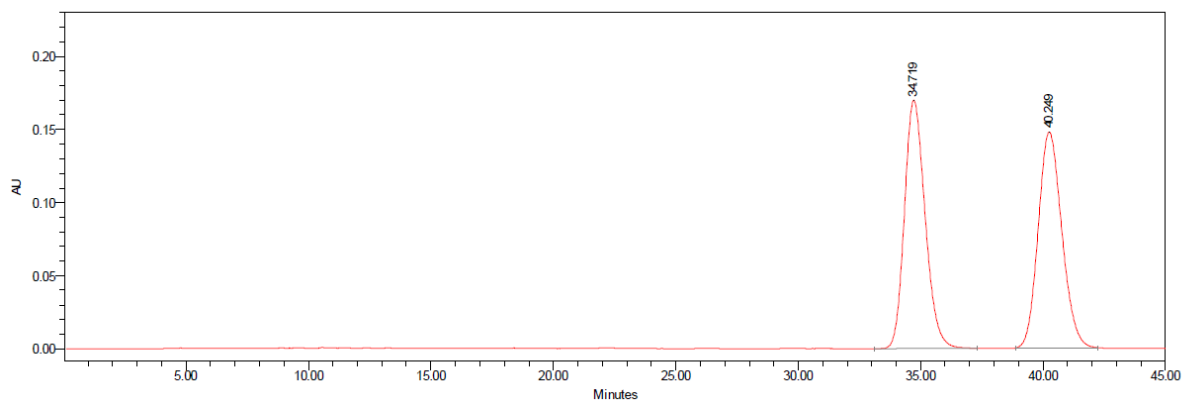
|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 18.141 | 11199041 | 49.99  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 22.555 | 11201882 | 50.01  |



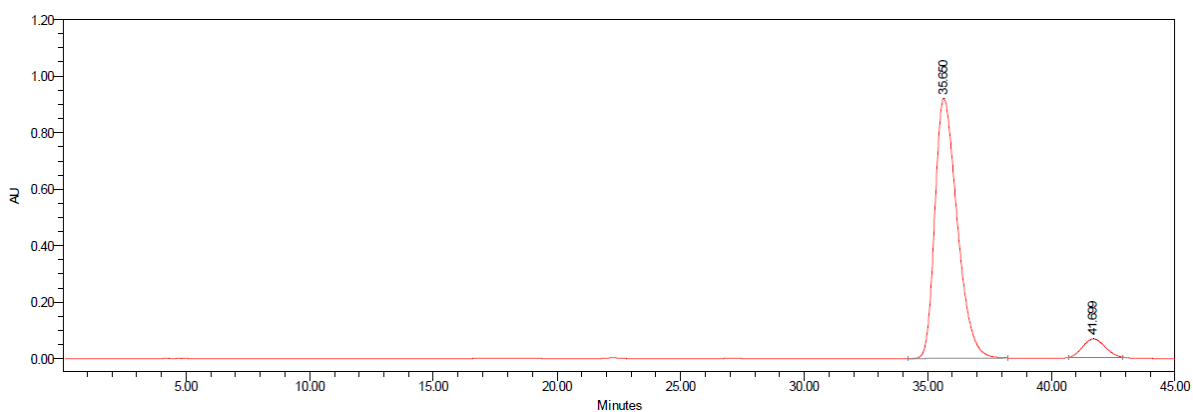
|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 17.749 | 486446   | 3.02   |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 22.495 | 15613303 | 96.98  |



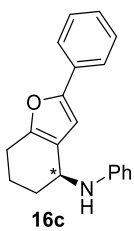
**HPLC Analysis for 16b:** HPLC Chiralpak IC column [heptane:IPA = 90:10, 1 mL/min,  $\lambda = 277$  nm, retention times:  $T_R$  (major): 35.7 min,  $T_R$  (minor): 41.7 min].



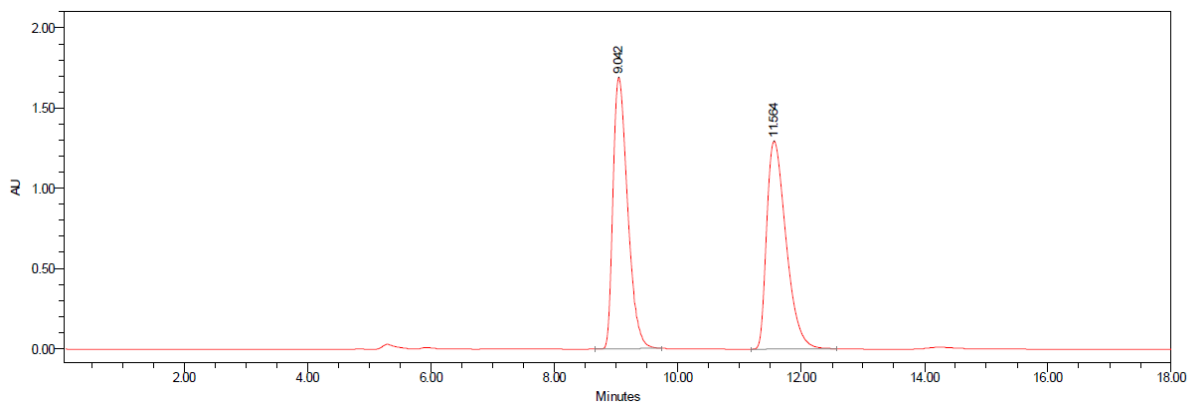
|   | Channel Description             | RT     | Area    | % Area |
|---|---------------------------------|--------|---------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 34.719 | 9948385 | 50.17  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 40.249 | 9882336 | 49.83  |



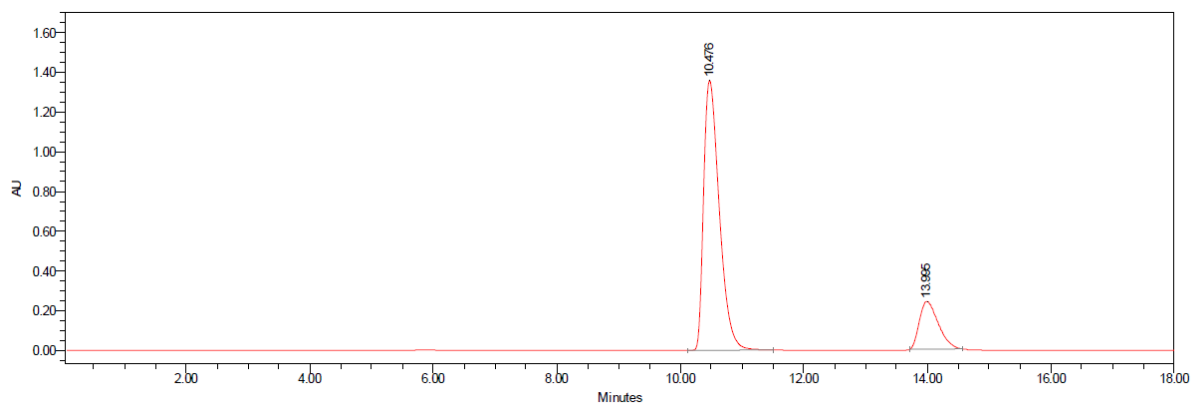
|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 35.650 | 57606806 | 93.50  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 41.699 | 4006807  | 6.50   |



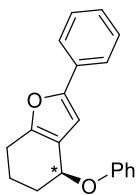
**HPLC Analysis for 16c:** HPLC Chiralpak IB column [heptane:IPA = 98:02, 1 mL/min,  $\lambda$  = 277 nm, retention times:  $T_R$  (major): 10.5 min,  $T_R$  (minor): 14.0 min].



|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 9.042  | 27706662 | 49.68  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 11.564 | 28064942 | 50.32  |

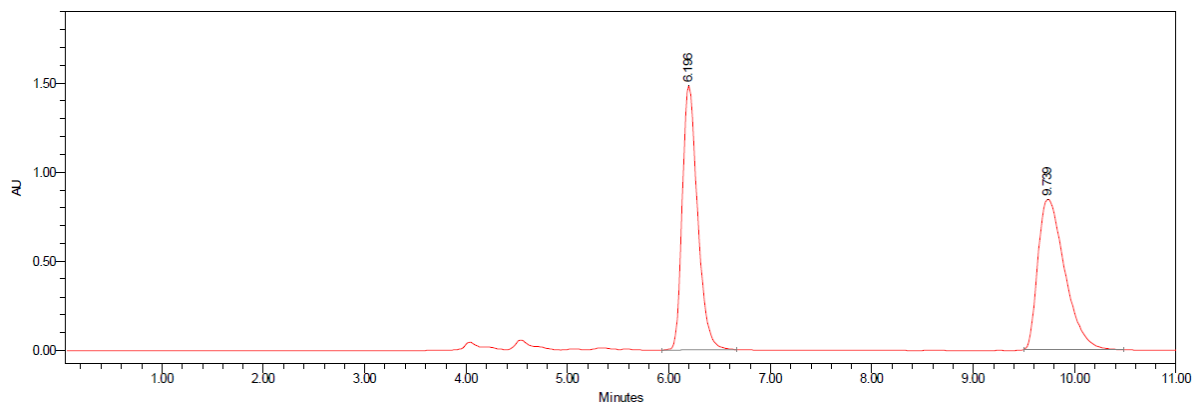


|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 10.476 | 23784879 | 82.29  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 13.995 | 5120127  | 17.71  |

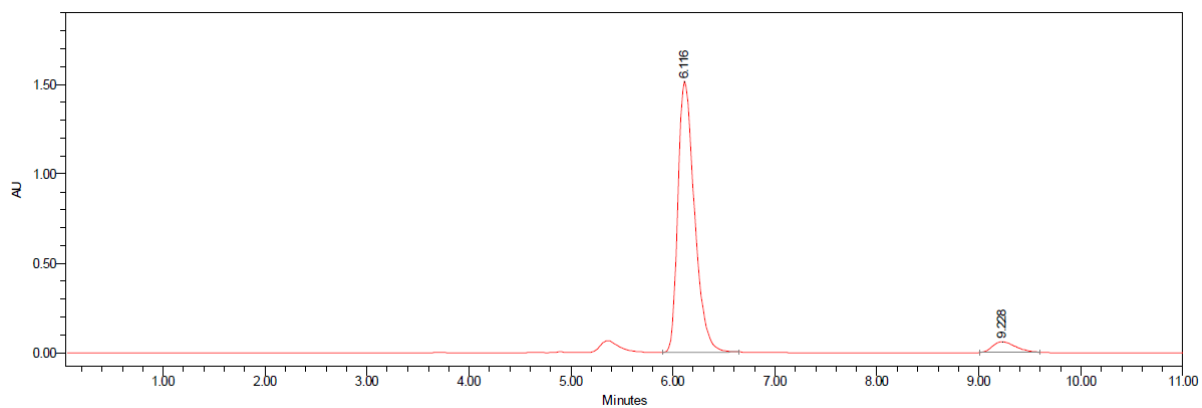


**16d**

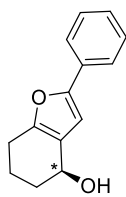
**HPLC Analysis for 16d:** HPLC Chiralpak IB column [heptane:IPA = 98:02, 1 mL/min,  $\lambda = 277$  nm, retention times:  $T_R$  (major): 6.1 min,  $T_R$  (minor): 9.2 min].



|   | Channel Description             | RT    | Area     | % Area |
|---|---------------------------------|-------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 6.196 | 15525085 | 50.00  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 9.739 | 15527509 | 50.00  |

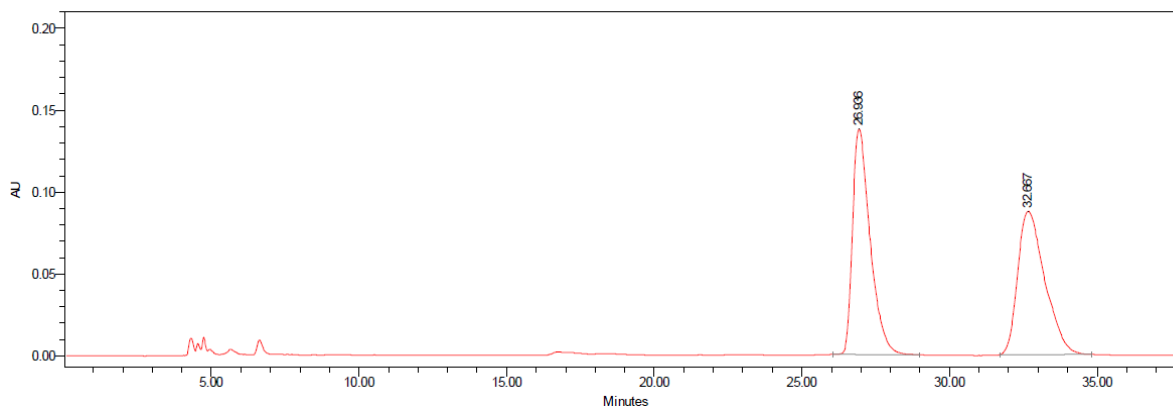


|   | Channel Description             | RT    | Area     | % Area |
|---|---------------------------------|-------|----------|--------|
| 1 | PDA 210.0 to 400.0 nm at 1.2 nm | 6.116 | 17023277 | 94.90  |
| 2 | PDA 210.0 to 400.0 nm at 1.2 nm | 9.228 | 914783   | 5.10   |

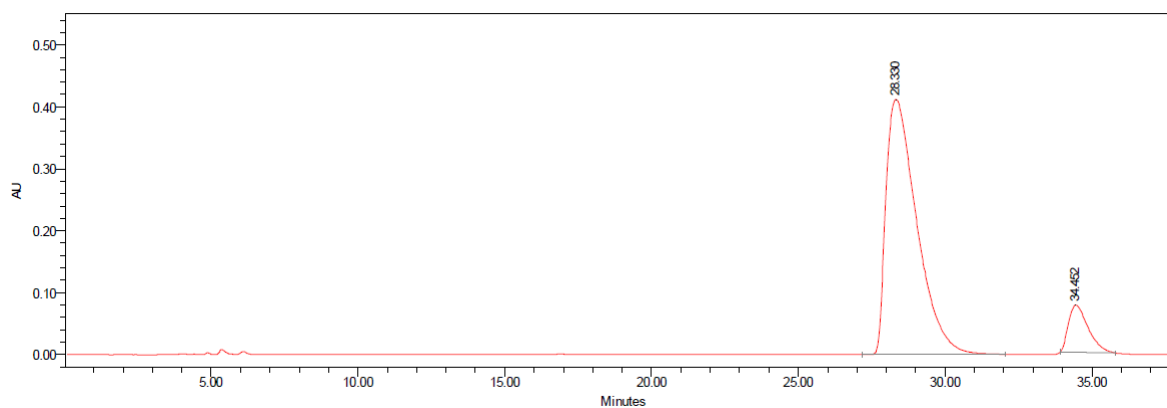


**16e**

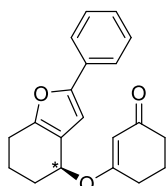
**HPLC Analysis for 16e:** HPLC Chiralpak IB column [heptane:IPA = 98:02, 1 mL/min,  $\lambda$  = 277 nm, retention times:  $T_R$  (major): 28.3 min,  $T_R$  (minor): 34.5 min].



|   | Channel Description             | RT     | Area    | % Area |
|---|---------------------------------|--------|---------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 26.936 | 5708912 | 50.56  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 32.667 | 5583065 | 49.44  |

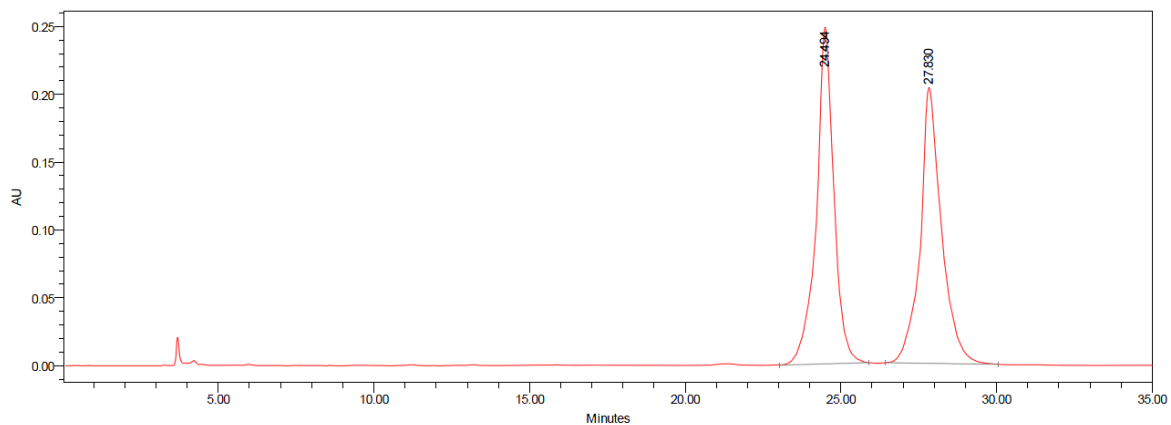


|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 28.330 | 29948802 | 89.41  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 34.452 | 3547065  | 10.59  |

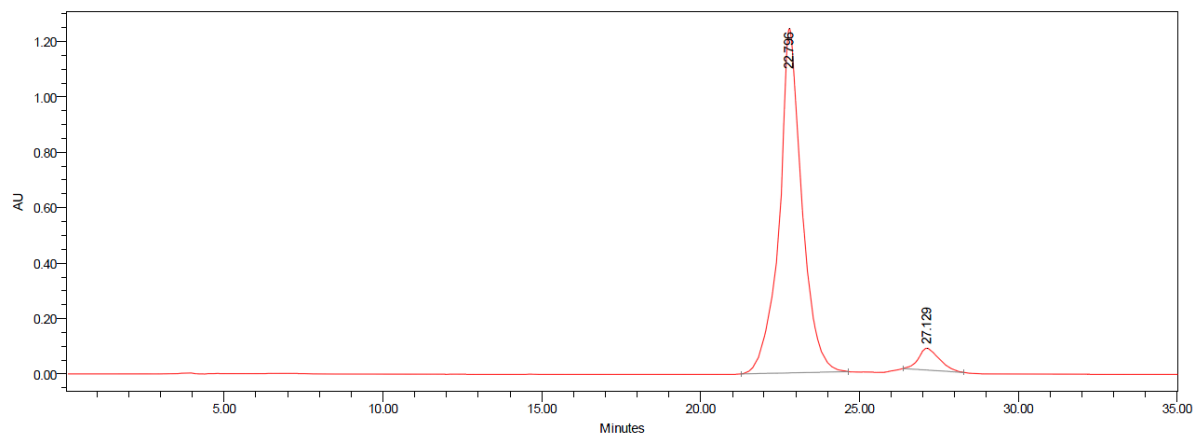


**16f**

**HPLC Analysis for 16f:** HPLC Chiralpak IA column [heptane:IPA = 95:05, 1 mL/min,  $\lambda$  = 277 nm, retention times:  $T_R$  (minor): 22.8 min,  $T_R$  (major): 27.1 min].



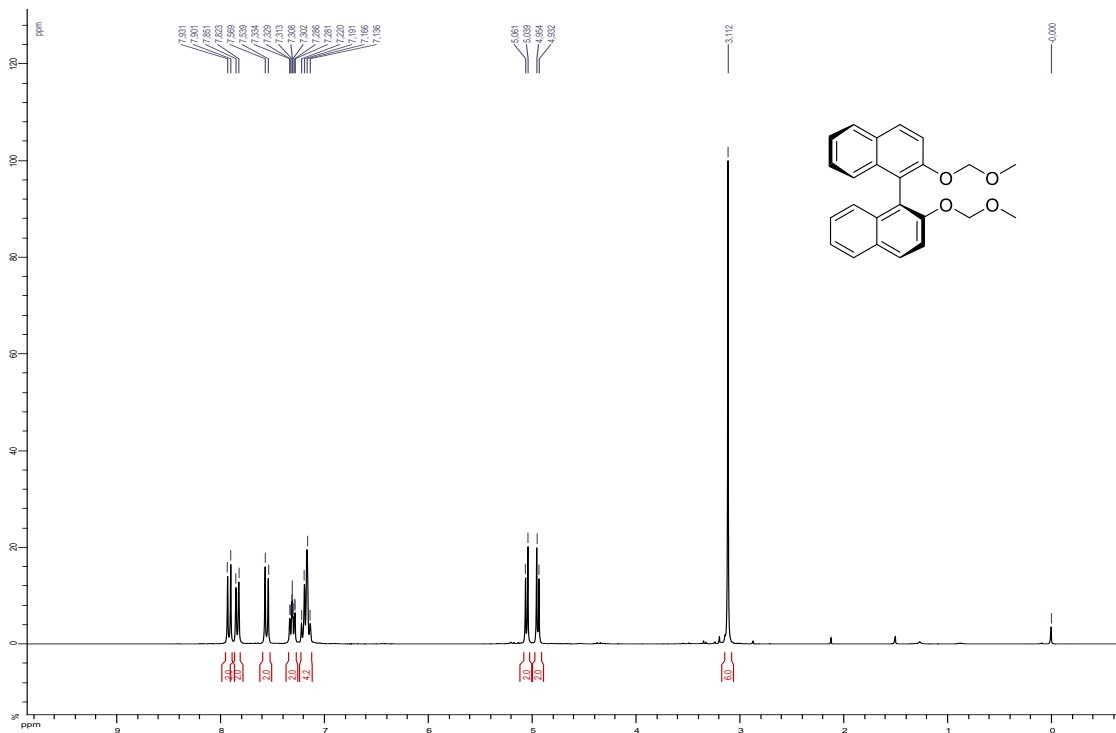
|   | Channel Description             | RT     | Area    | % Area |
|---|---------------------------------|--------|---------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 24.494 | 9643182 | 50.20  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 27.830 | 9565098 | 49.80  |



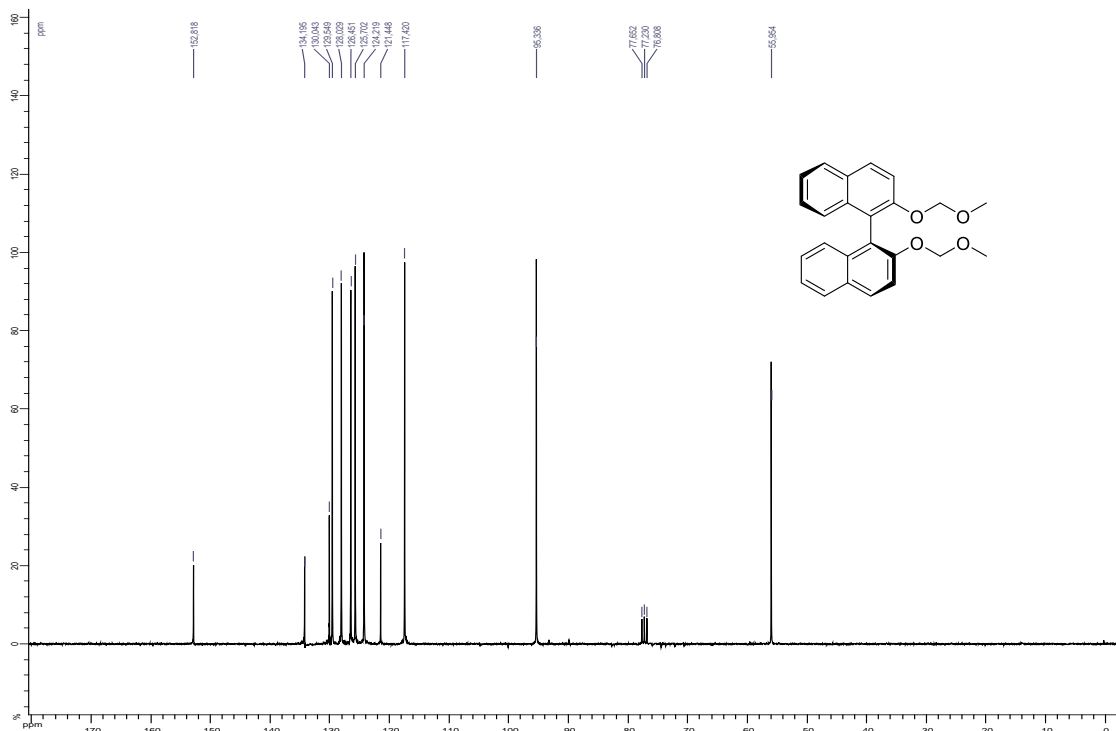
|   | Channel Description             | RT     | Area     | % Area |
|---|---------------------------------|--------|----------|--------|
| 1 | PDA 200.0 to 400.0 nm at 2.4 nm | 22.796 | 61326122 | 94.50  |
| 2 | PDA 200.0 to 400.0 nm at 2.4 nm | 27.129 | 3572509  | 5.50   |



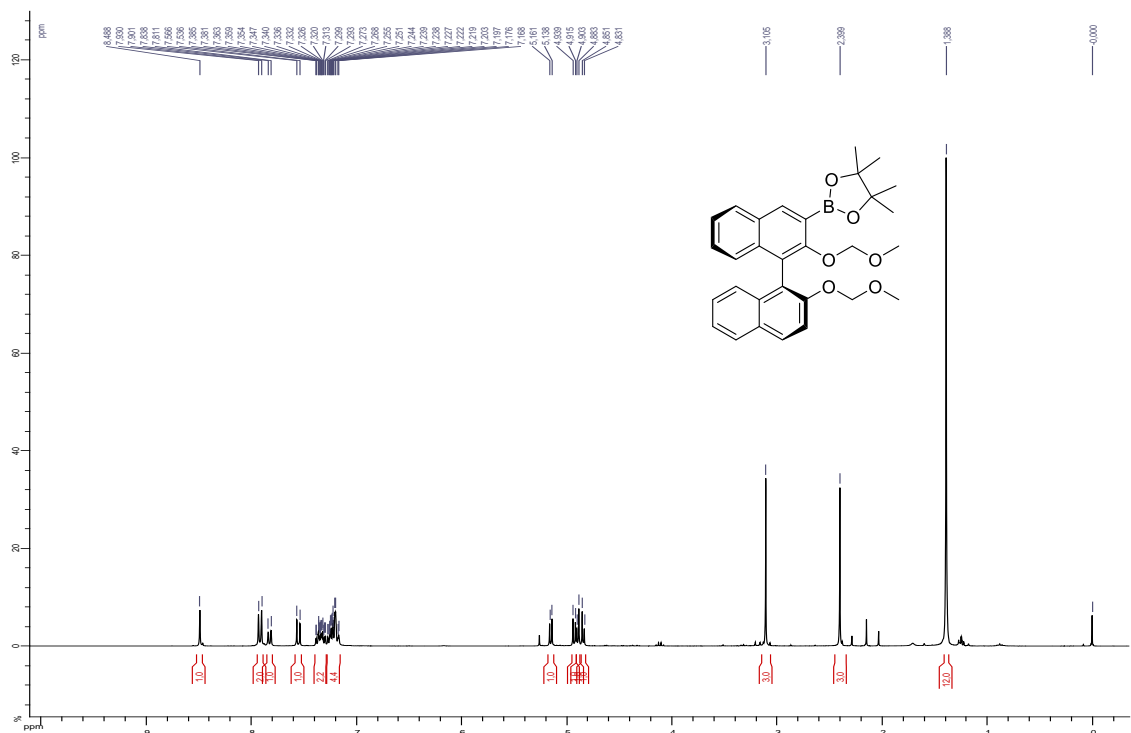
## 8. Copies of NMR Spectra



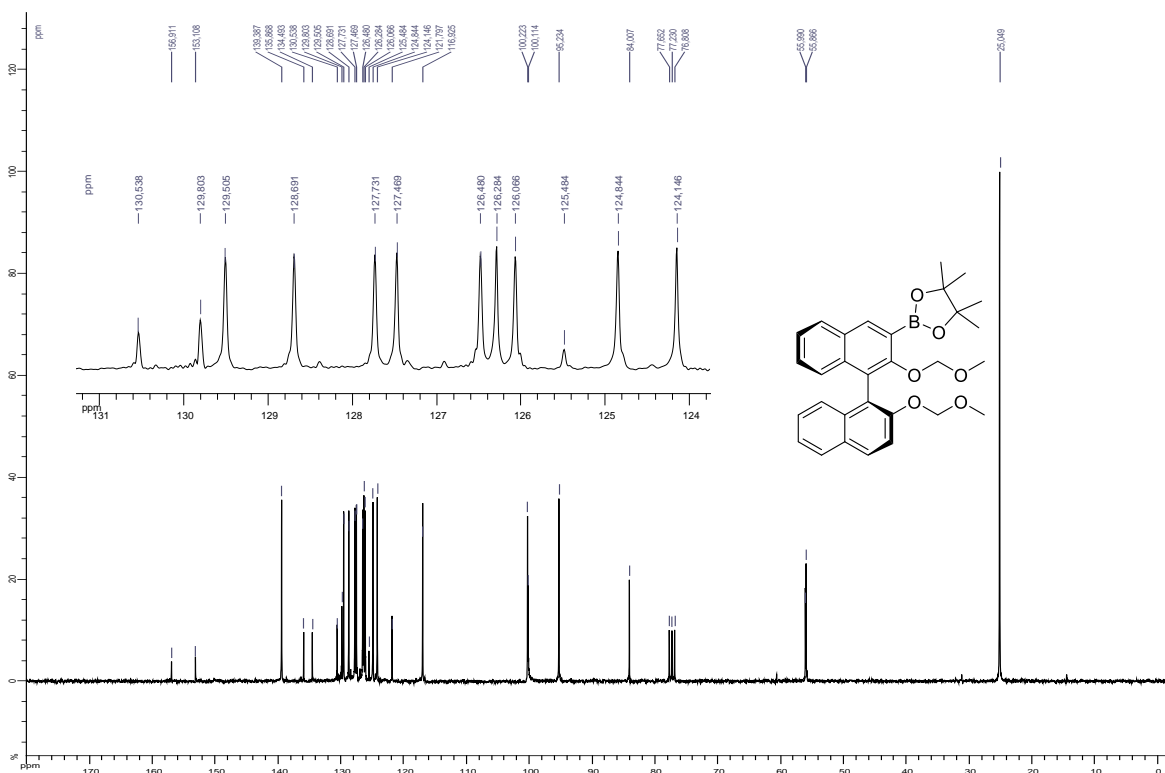
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) spectrum of (S)-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene



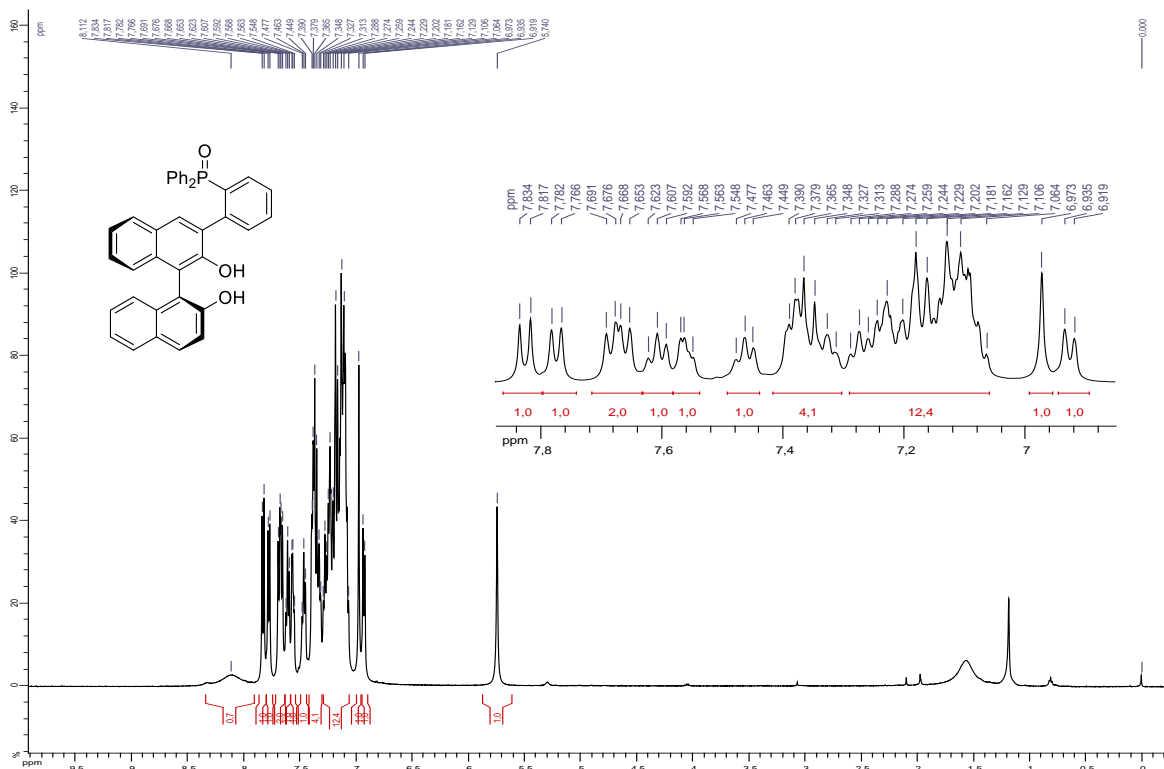
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) spectrum of (S)-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene



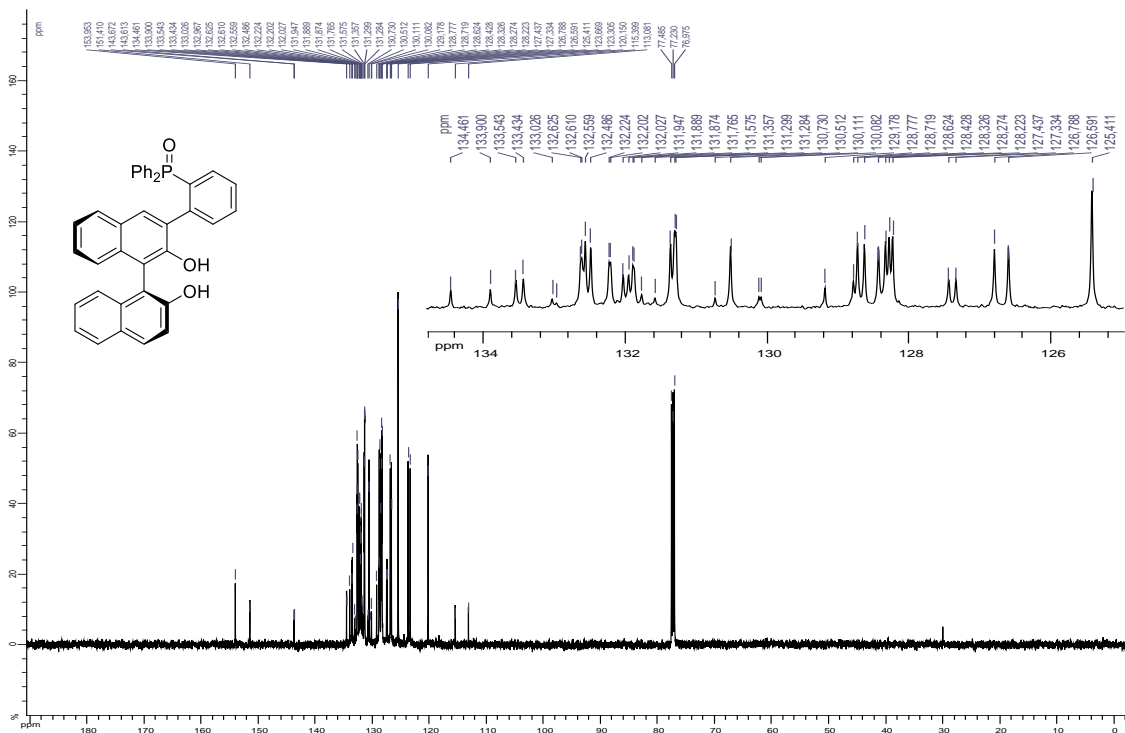
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) spectrum of (*S*)-2-(2,2'-bis(methoxymethoxy)-[1,1'-binaphthalen]-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(*S*)-1]



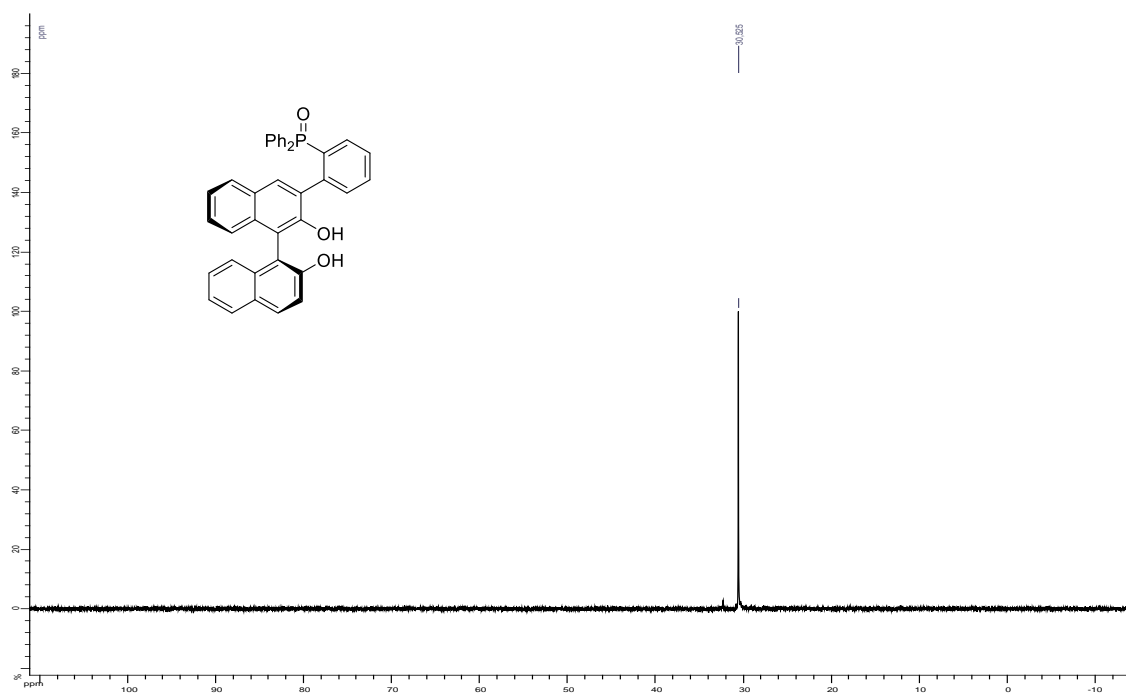
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) spectrum of (*S*)-2-(2,2'-bis(methoxymethoxy)-[1,1'-binaphthalen]-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(*S*)-1]



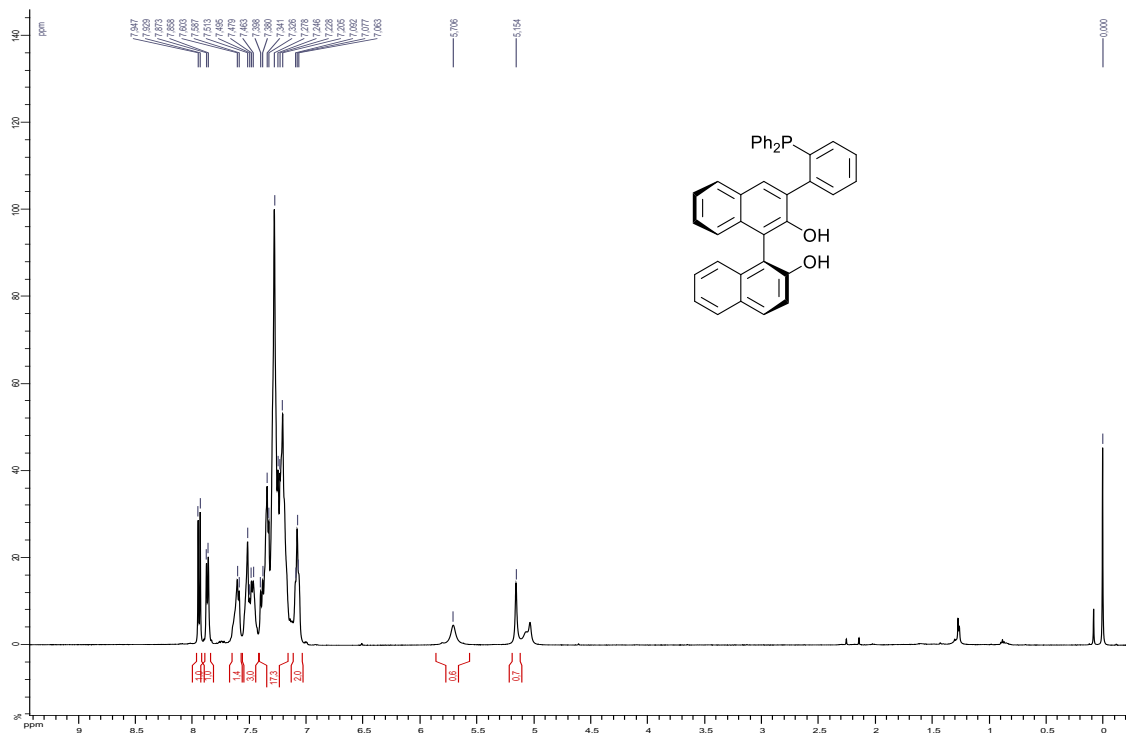
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (S)-2-(2,2'-dihydroxy-[1,1'-binaphthalen]-3-yl)phenyl)diphenylphosphine oxide ((S)-2)



<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) spectrum of (S)-2-(2,2'-dihydroxy-[1,1'-binaphthalen]-3-yl)phenyl)diphenylphosphine oxide ((S)-2)

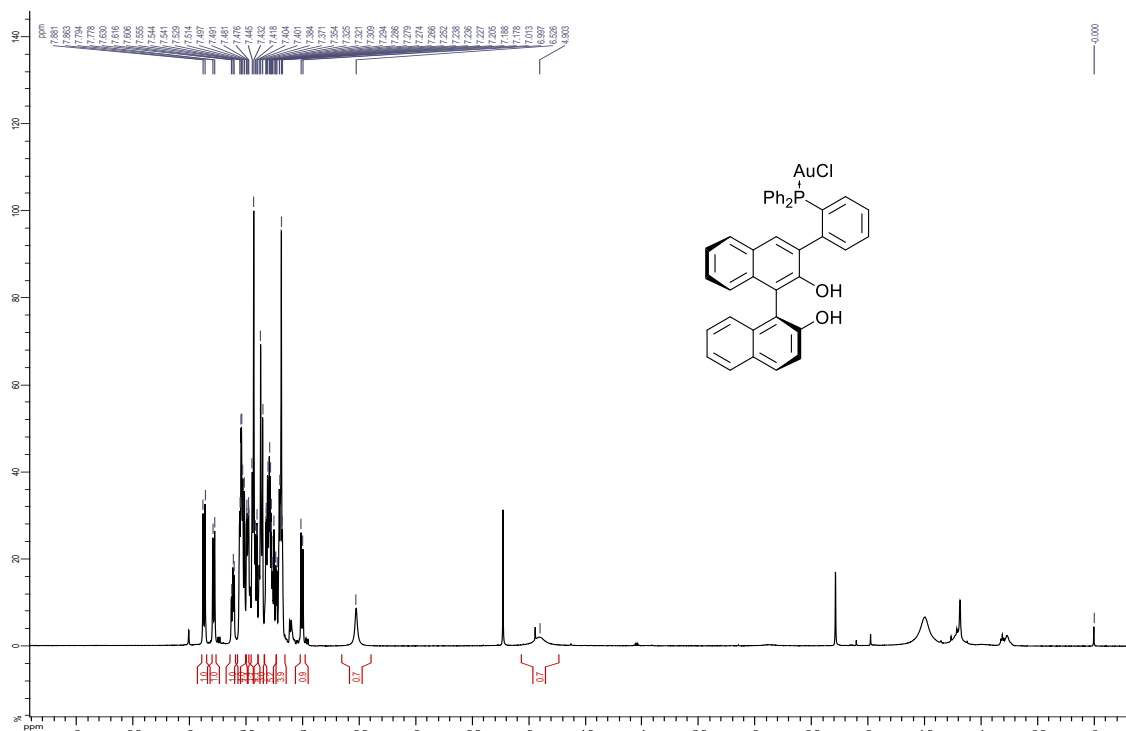


$^{31}\text{P}$  NMR (CDCl<sub>3</sub>, 200 MHz) spectrum of (S)-2-(2,2'-dihydroxy-[1,1'-binaphthalen]-3-yl)phenyl)diphenylphosphine oxide [(S)-2]

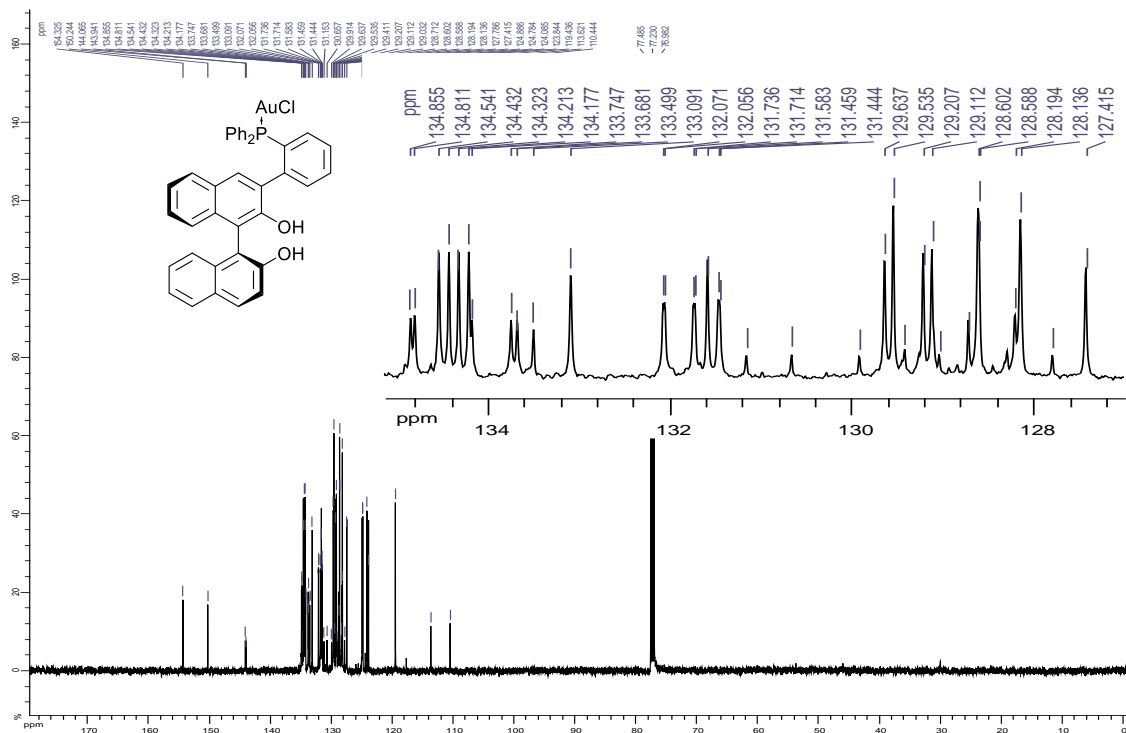


$^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (S)-3-(2-(diphenylphosphanyl)phenyl)-[1,1'-binaphthalene]-2,2'-diol [(S)-3]

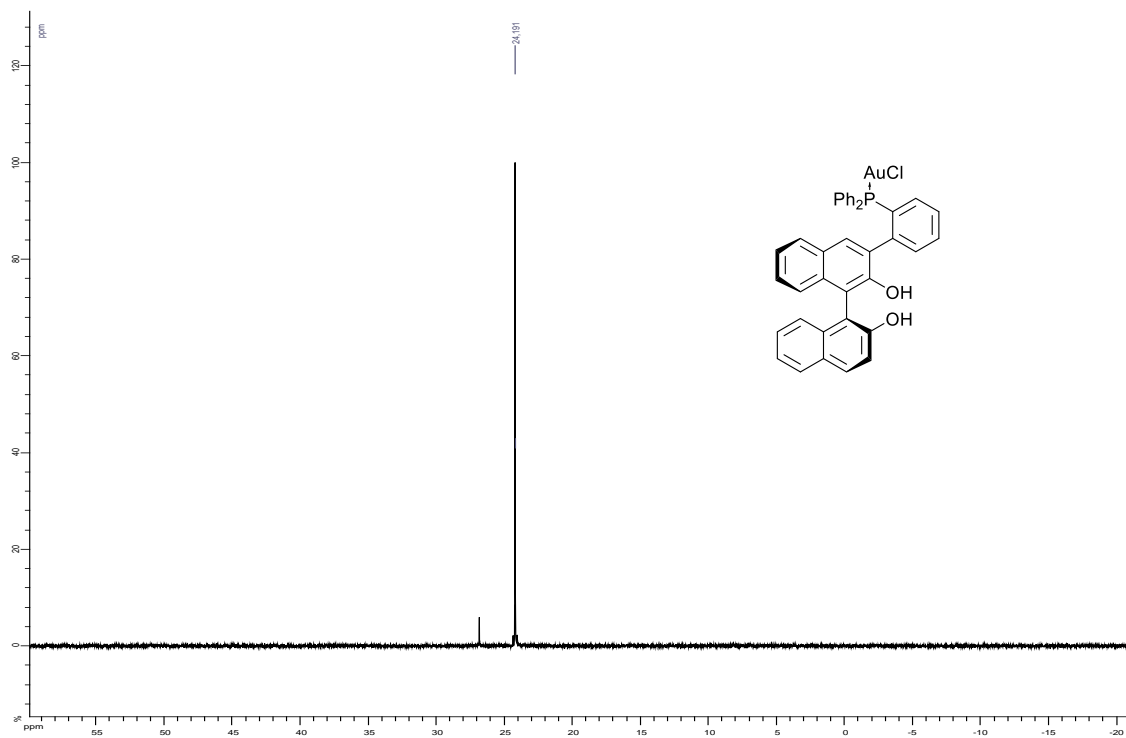




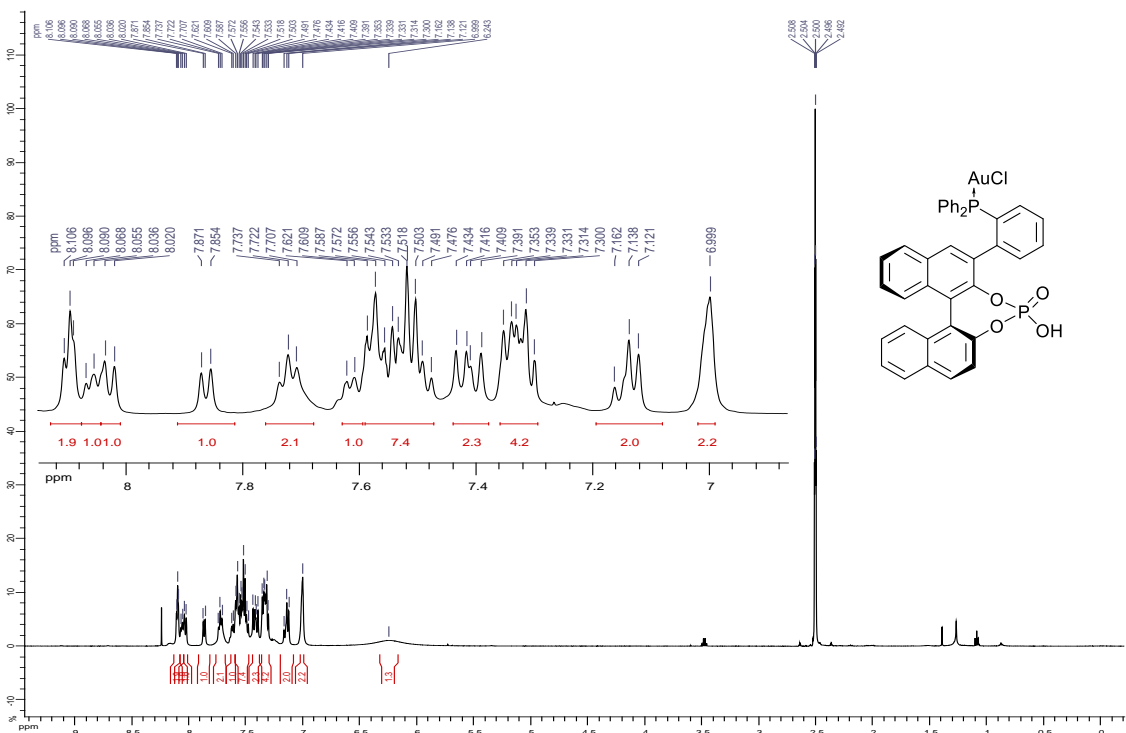
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of *(S)*-[2-(2,2'-dihydroxy-[1,1'-binaphthalen]-3-yl)phenyl]diphenylphosphine gold(I) chloride **[(S)-4]**



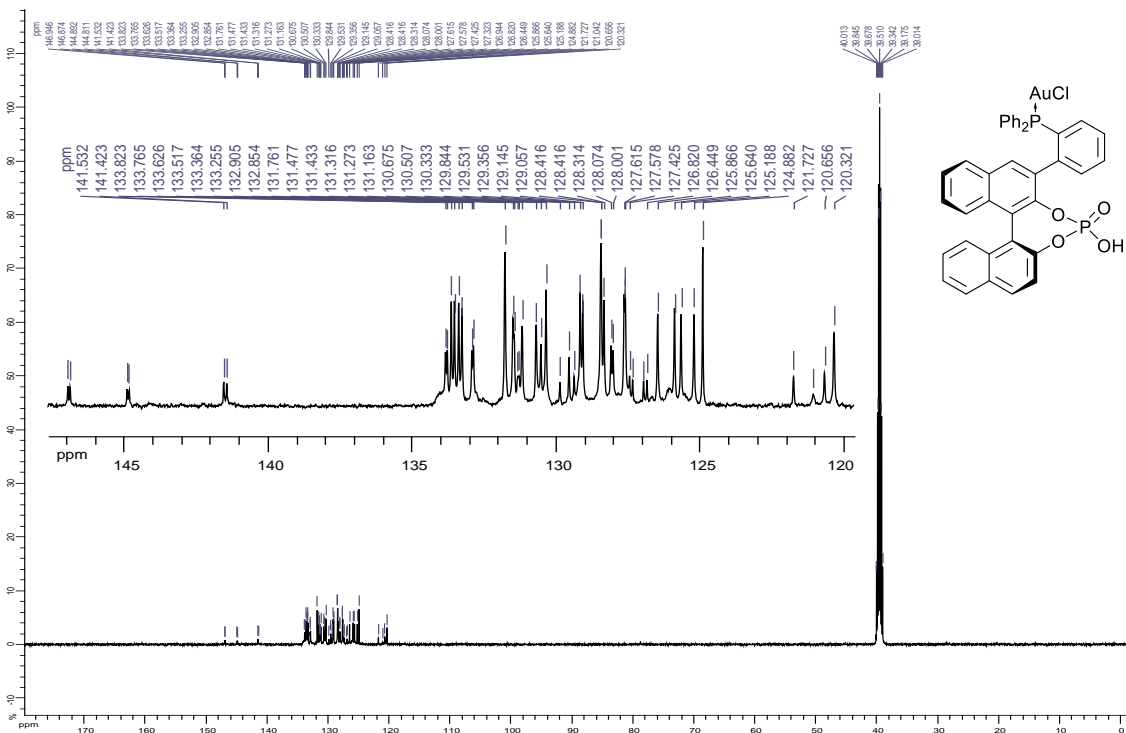
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) spectrum of *(S)*-[2-(2,2'-dihydroxy-[1,1'-binaphthalen]-3-yl)phenyl]diphenylphosphine gold(I) chloride **[(S)-4]**



$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 200 MHz) spectrum of (*S*)-2-(2,2'-dihydroxy-[1,1'-binaphthalen]-3-yl)phenyl)diphenylphosphine gold(I) chloride [(*S*)-4]

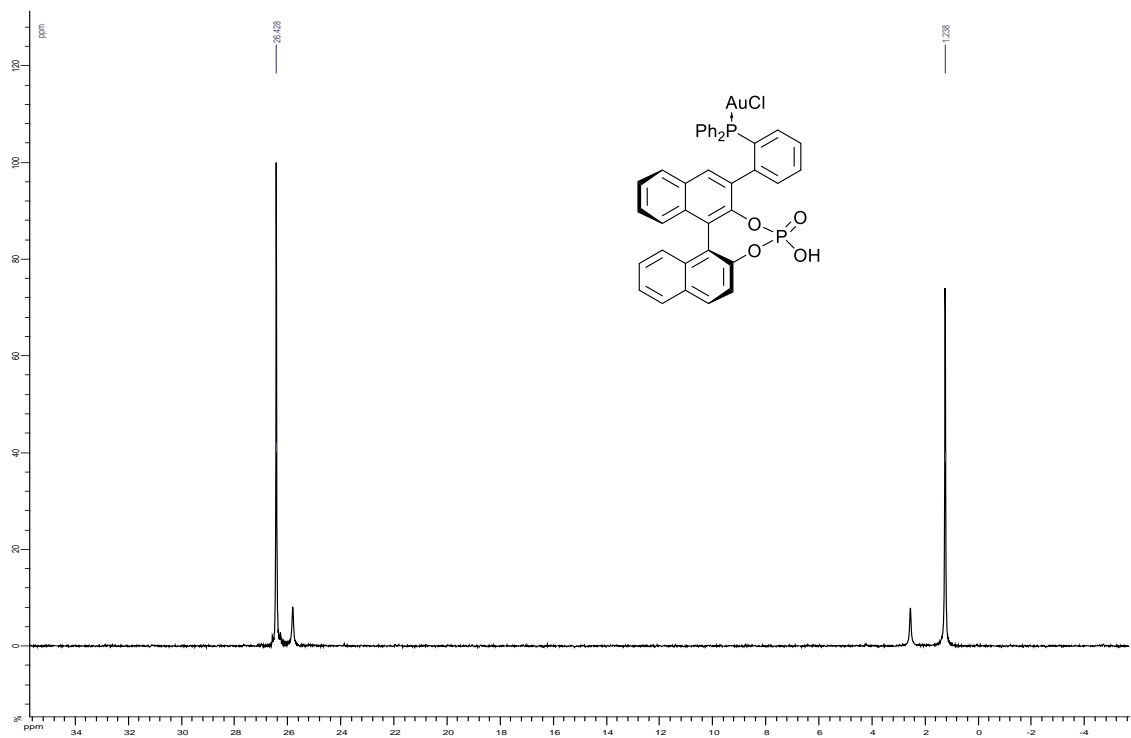


**<sup>1</sup>H NMR (DMSO, 343K, 500 MHz) spectrum of (S)-(2-(2,2'-diyl hydrogen phosphate-[1,1'-binaphthalen]-3-yl)phenyl)diphenylphosphine gold(I) chloride [(S)-5]**

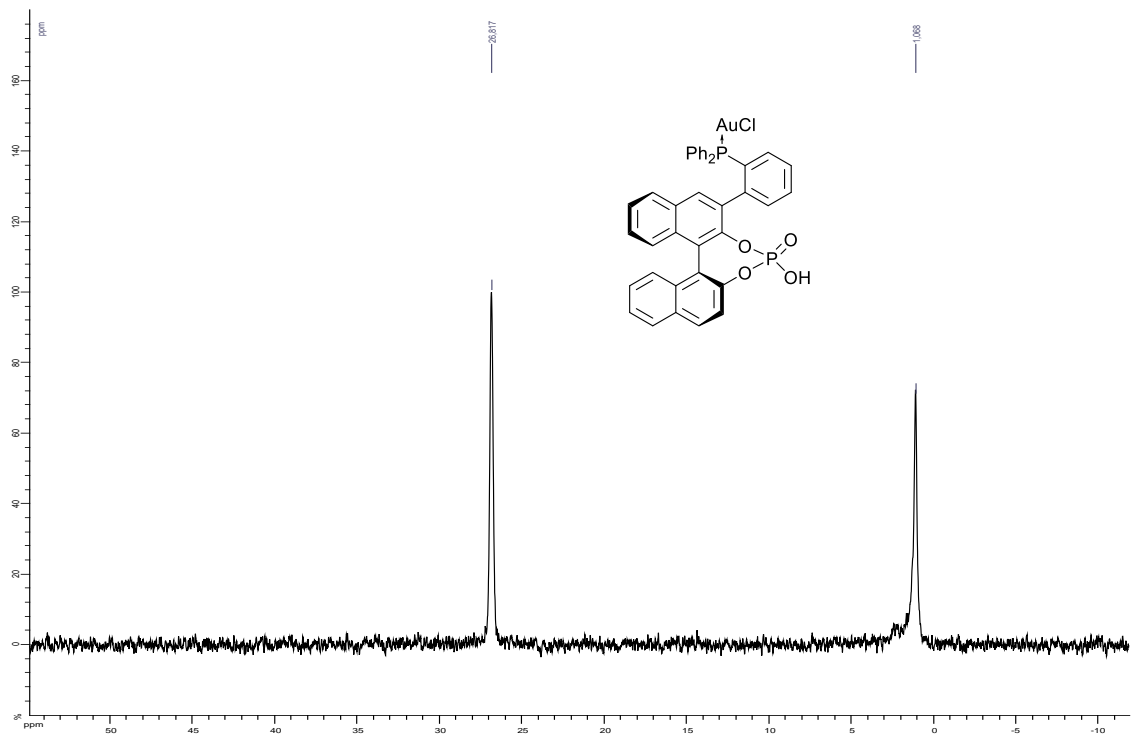


**<sup>13</sup>C NMR (DMSO, 343K, 125 MHz) spectrum of (S)-(2-(2,2'-diyl hydrogen phosphate-[1,1'-binaphthalen]-3-yl)phenyl)diphenylphosphine gold(I) chloride [(S)-5]**



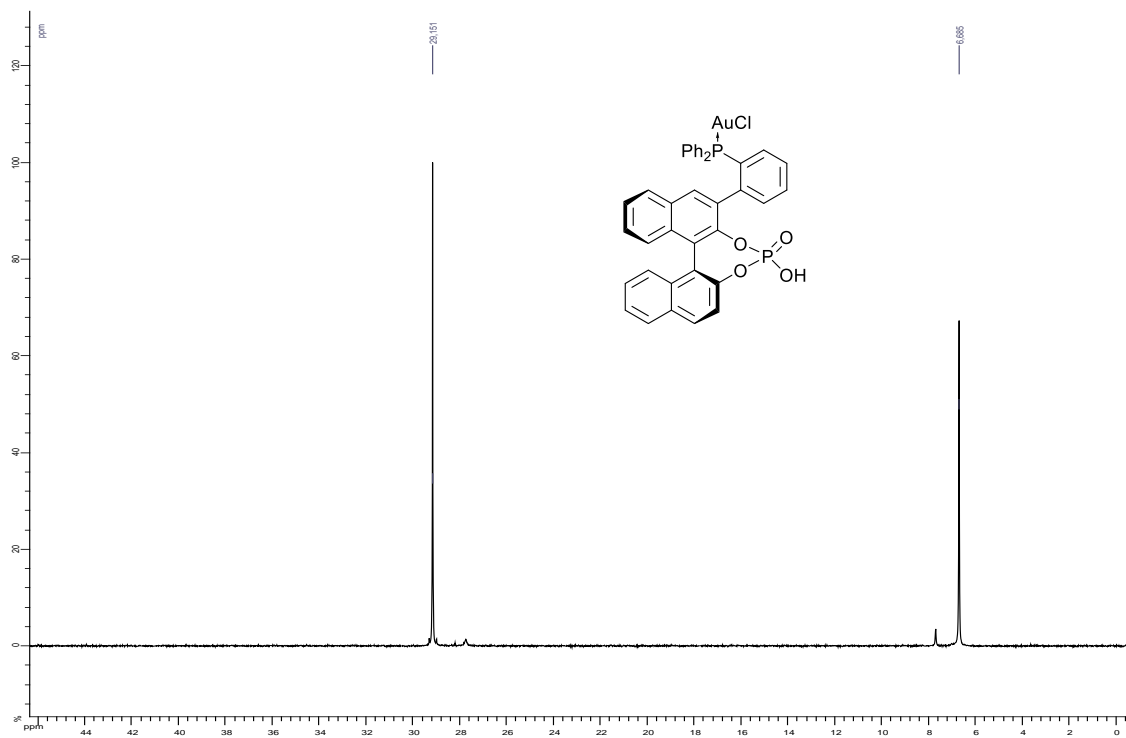


$^{31}\text{P}$  NMR (DMSO, 343K, 200 MHz) spectrum of  $(S)$ -(2-(2,2'-diyl hydrogen phosphate-[1,1'-binaphthalen]-3-yl)phenyl) diphenylphosphine gold(I) chloride [(*S*)-5]

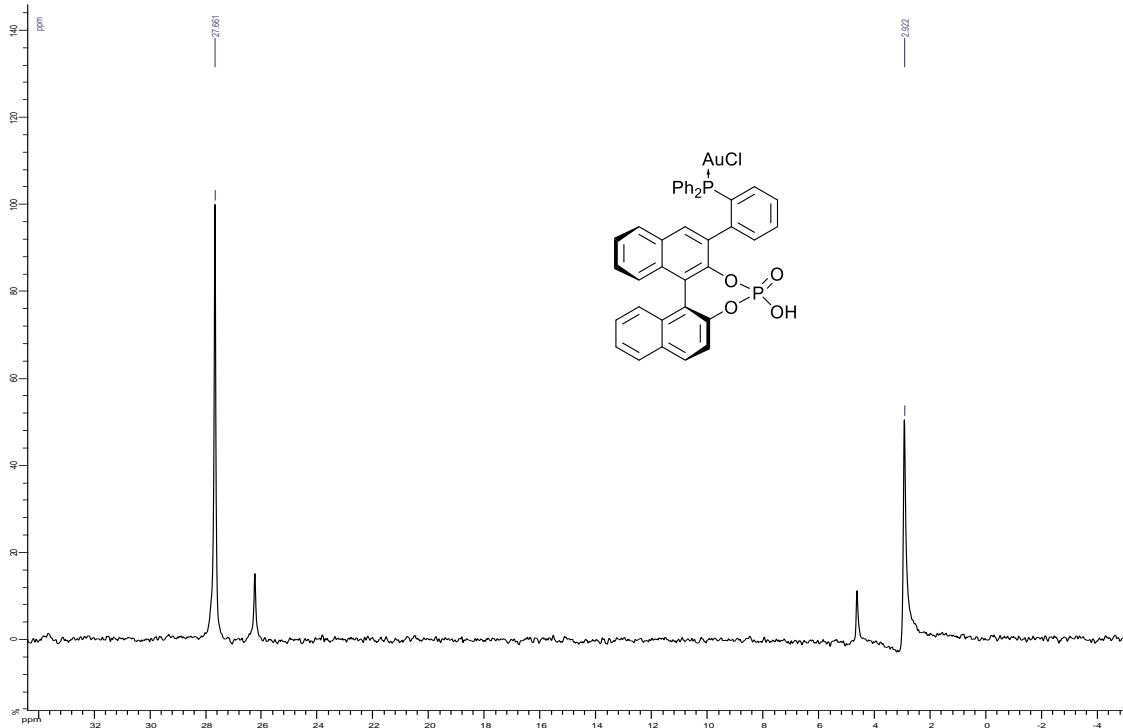
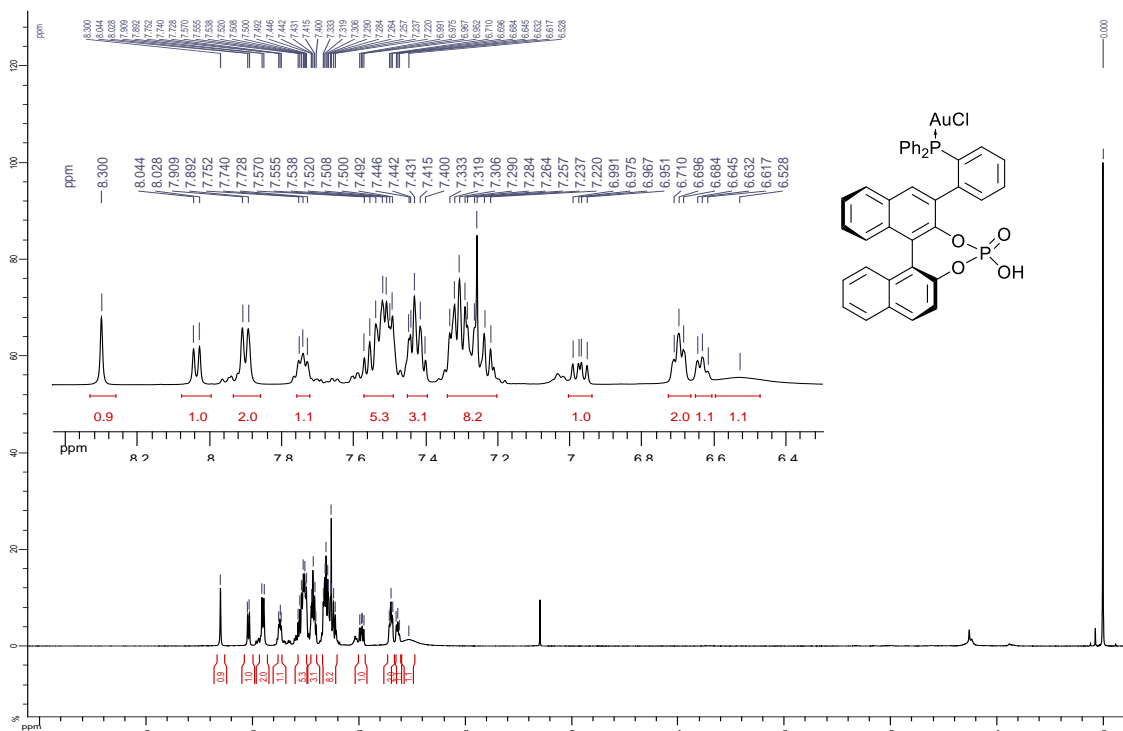


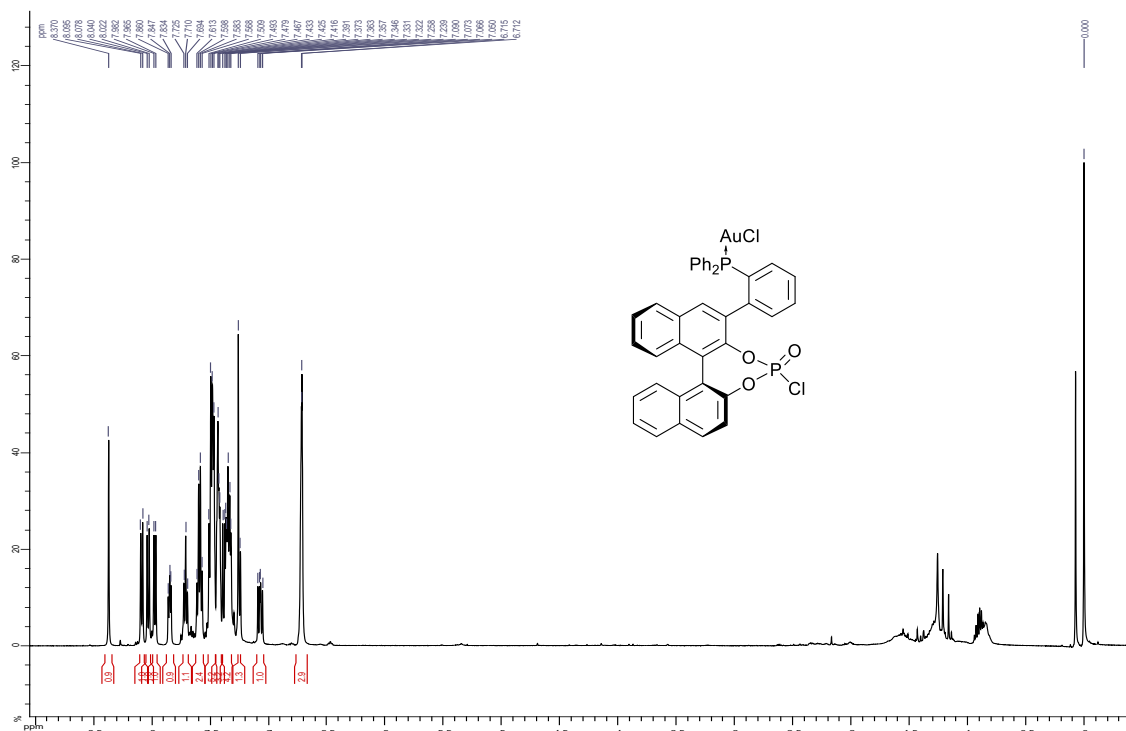
$^{31}\text{P}$  NMR (DMSO, 383K, 200 MHz) spectrum of  $(S)$ -(2-(2,2'-diyl hydrogen phosphate-[1,1'-binaphthalen]-3-yl)phenyl) diphenylphosphine gold(I) chloride [(*S*)-5]



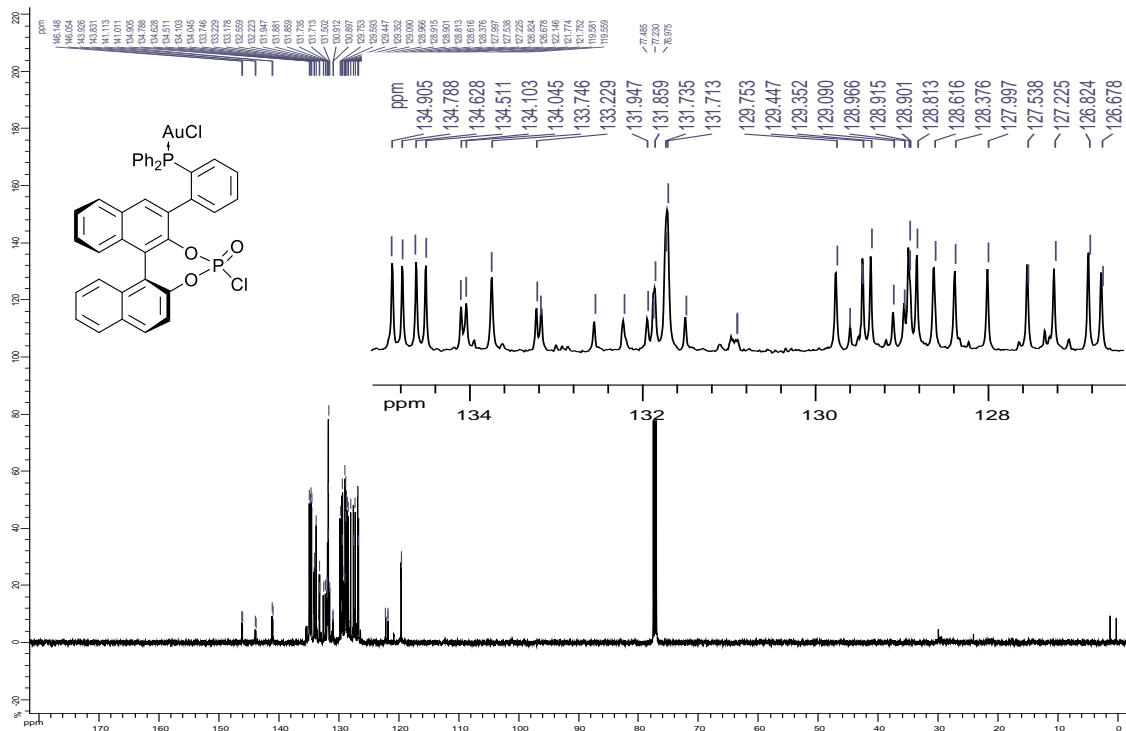


$^{31}\text{P}$  NMR (Pyridine, 200 MHz) spectrum of  $(S)$ -(2-(2,2'-diyl hydrogen phosphate-[1,1'-binaphthalen]-3-yl)phenyl)diphenylphosphine gold(I) chloride [( $S$ )-5]

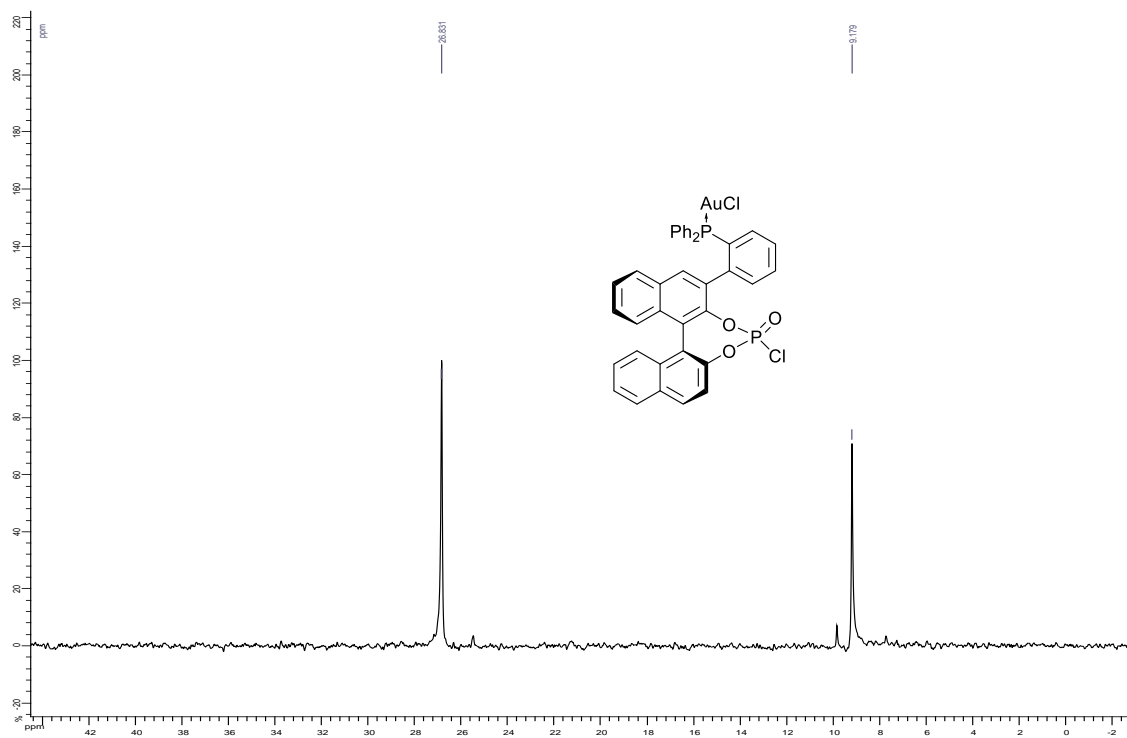




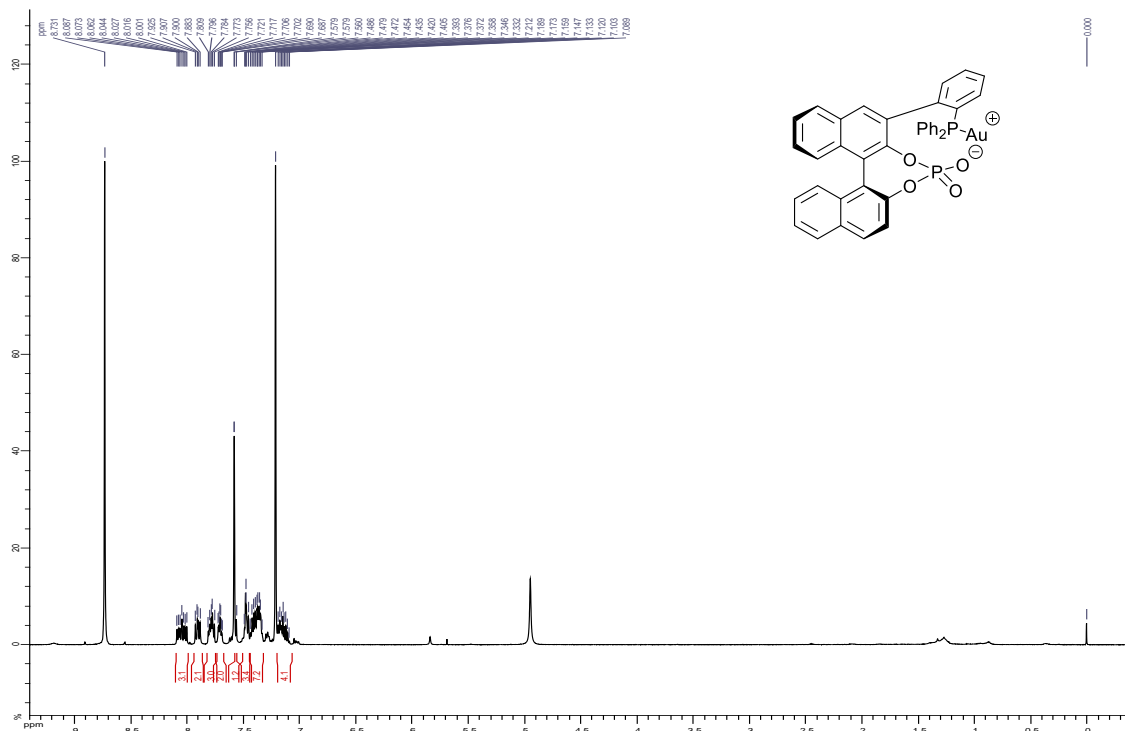
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (S)-(2-(2',2'-diylchlorogenphosphate-[1,1'-binaphthalen]-3-yl)phenyl)diphenylphosphine gold(I) chloride [SI-1]



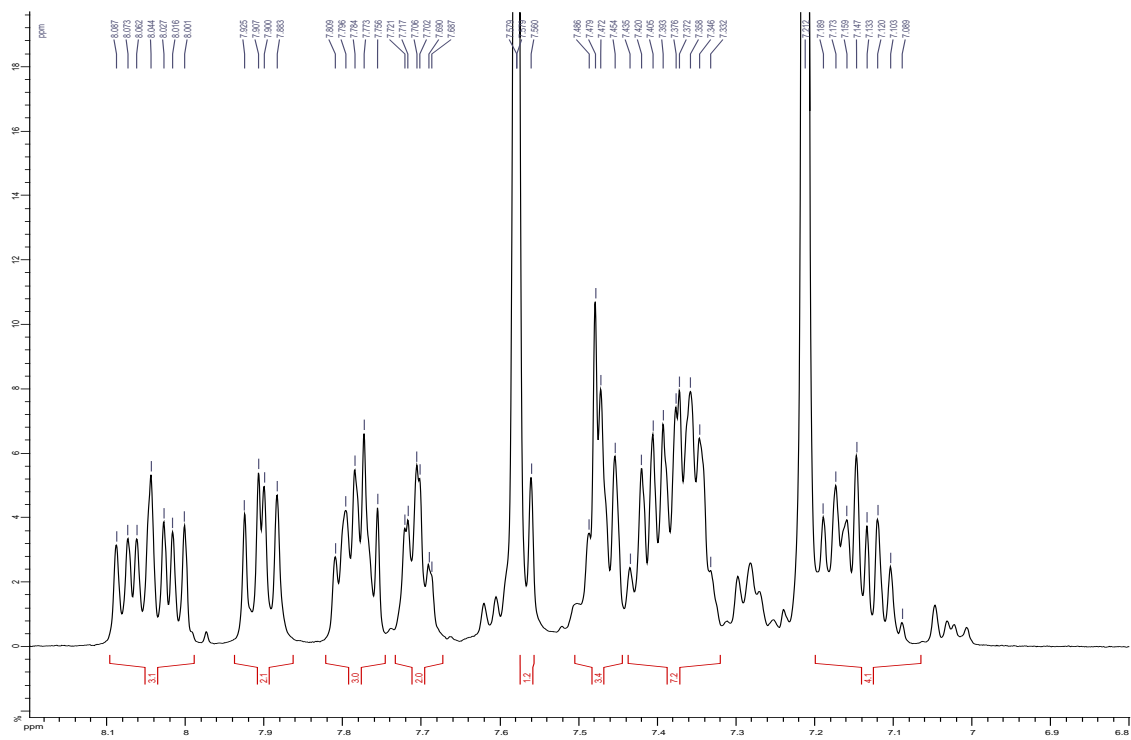
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (S)-(2-(2',2'-diylchlorogenphosphate-[1,1'-binaphthalen]-3-yl)phenyl)diphenylphosphine gold(I) chloride [SI-1]



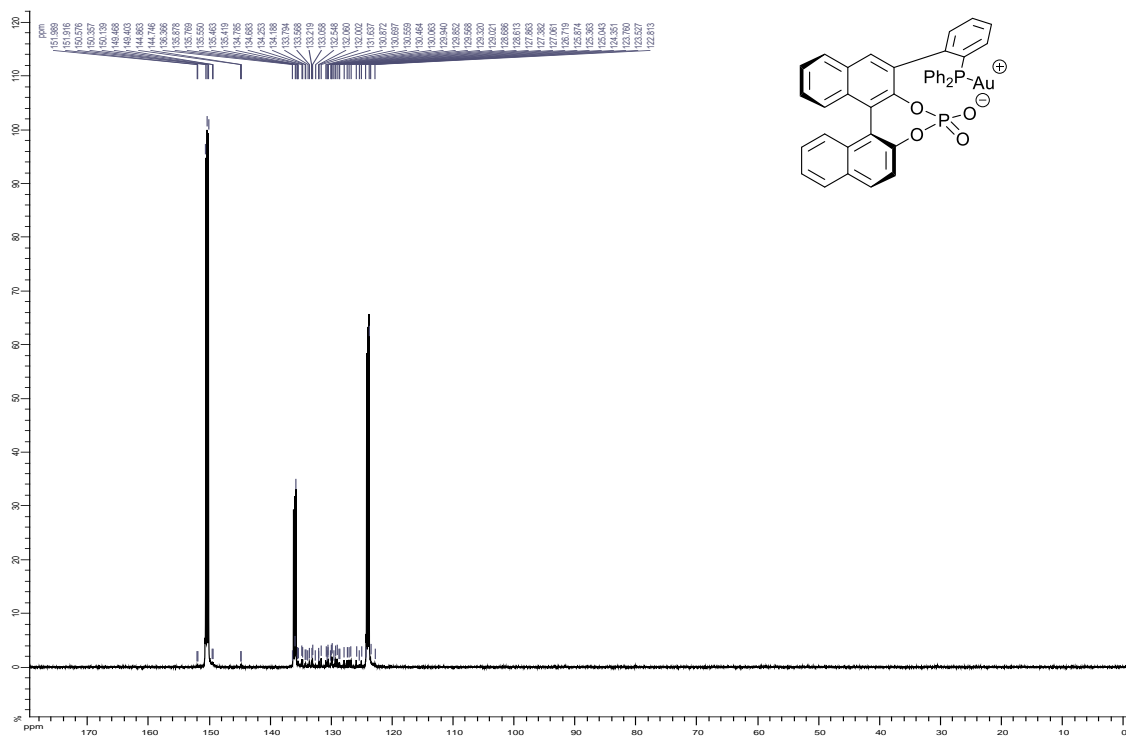
$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 200 MHz) spectrum of (*S*)-(2-(2,2'-diylchlorogenphosphate-[1,1'-binaphthalen]-3-yl)phenyl)diphenylphosphine gold(I) chloride [(*S*)-**5b**]



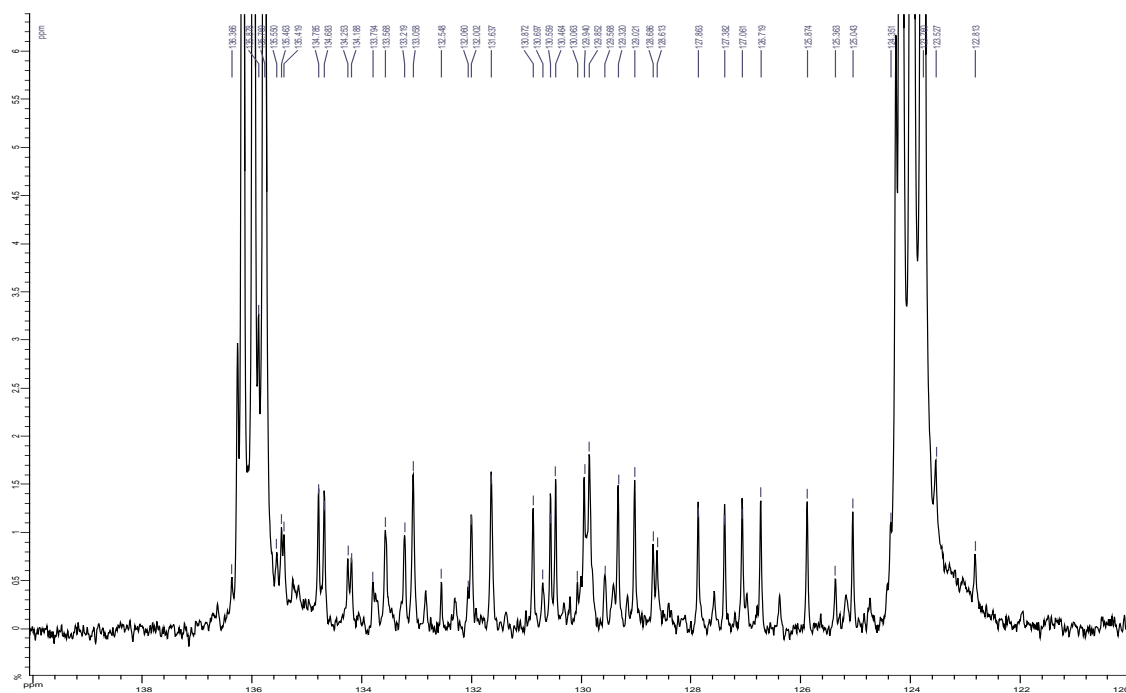
<sup>1</sup>H NMR (Pyridine, 500 MHz) spectrum of (S)-6



<sup>1</sup>H NMR (Pyridine, 500 MHz) spectrum of (S)-6 (zoom 6.8-8.2 ppm)

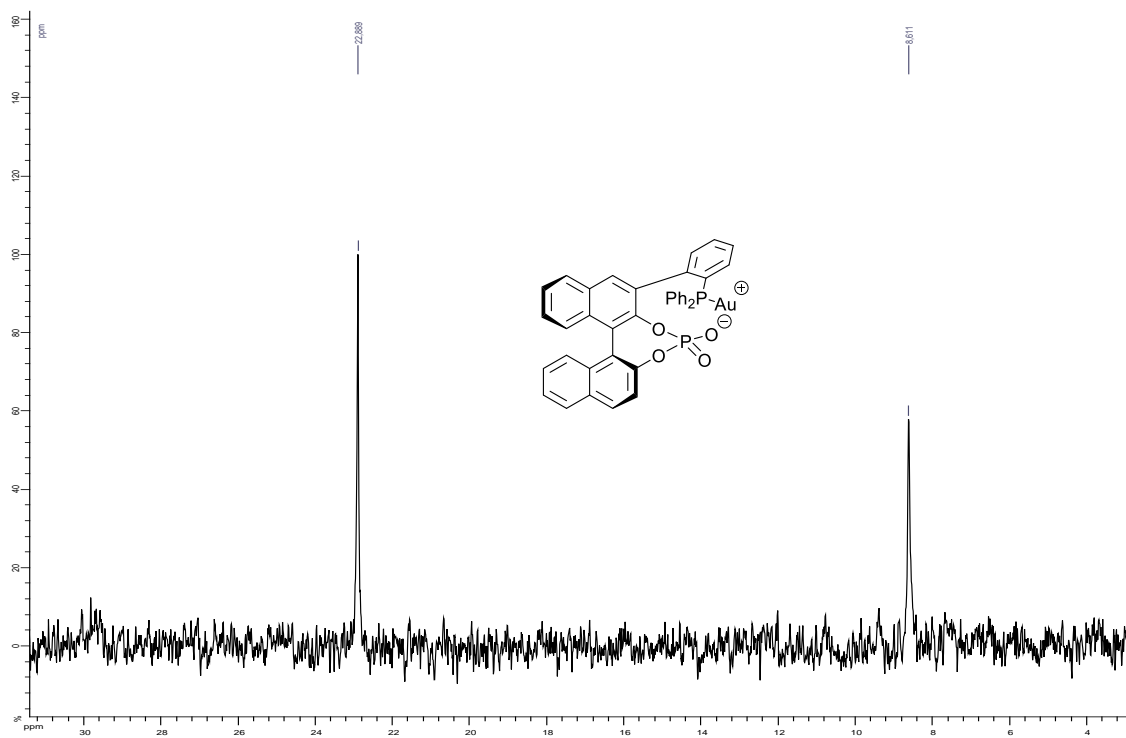


<sup>13</sup>C NMR (Pyridine, 125 MHz) spectrum of (S)-6

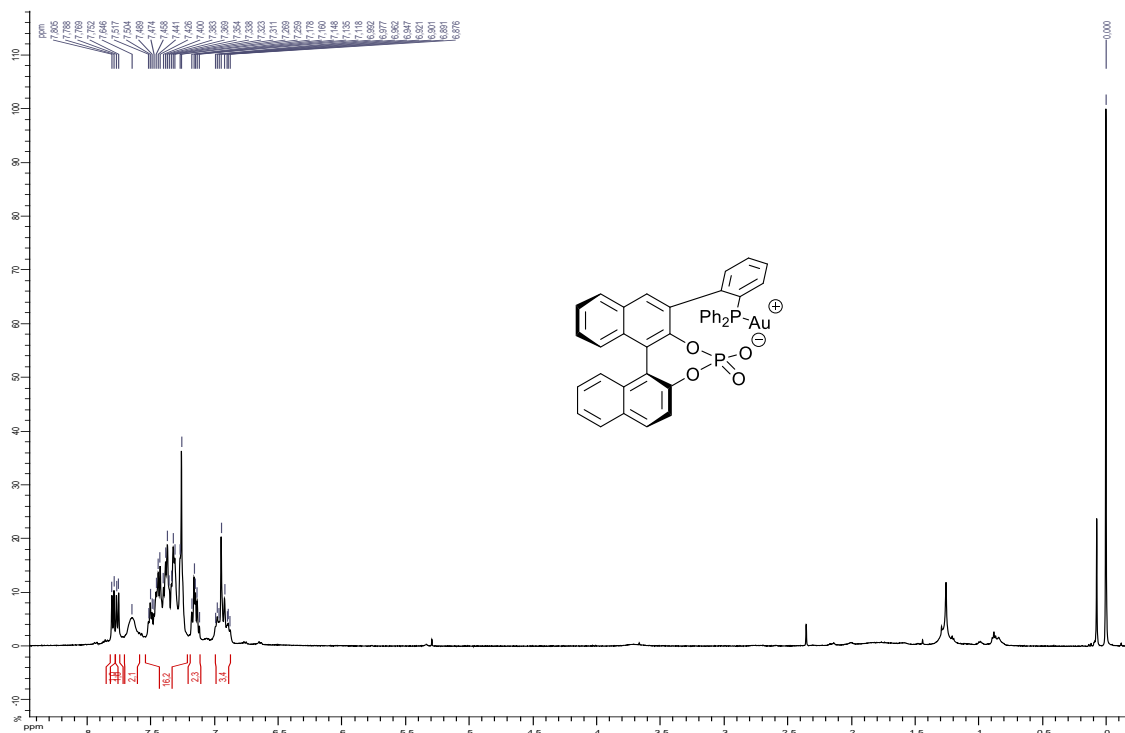


<sup>13</sup>C NMR (Pyridine, 125 MHz) spectrum of (S)-6 (zoom 120-140 ppm)

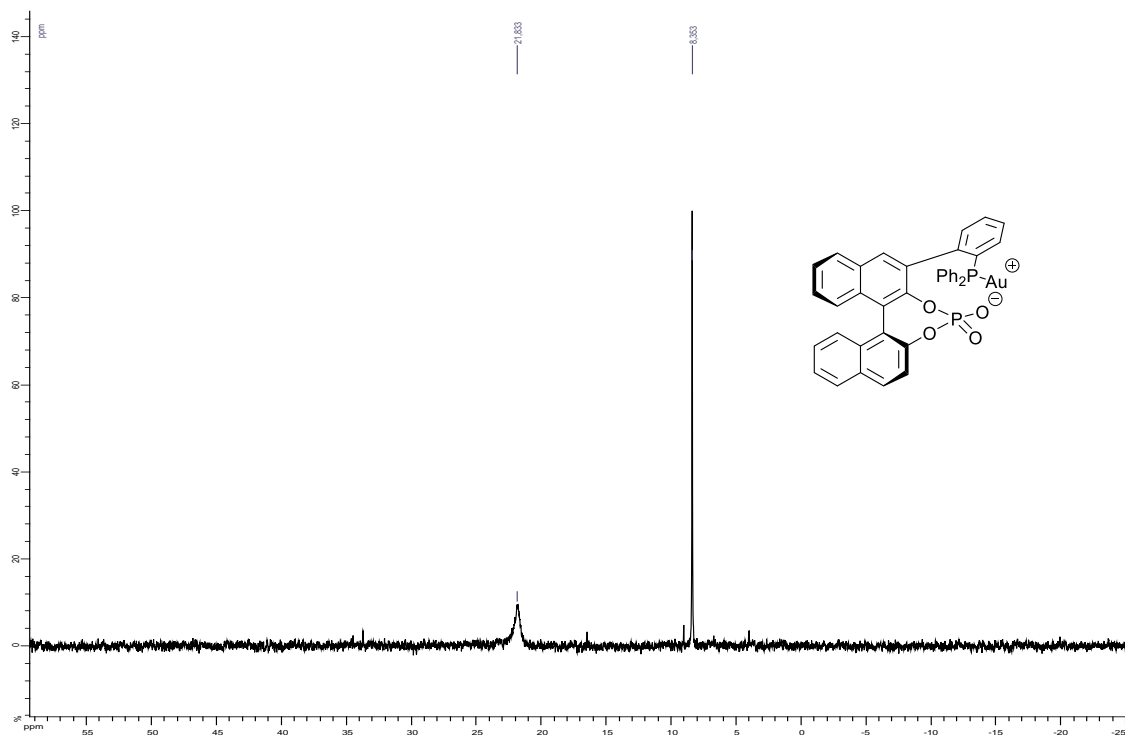




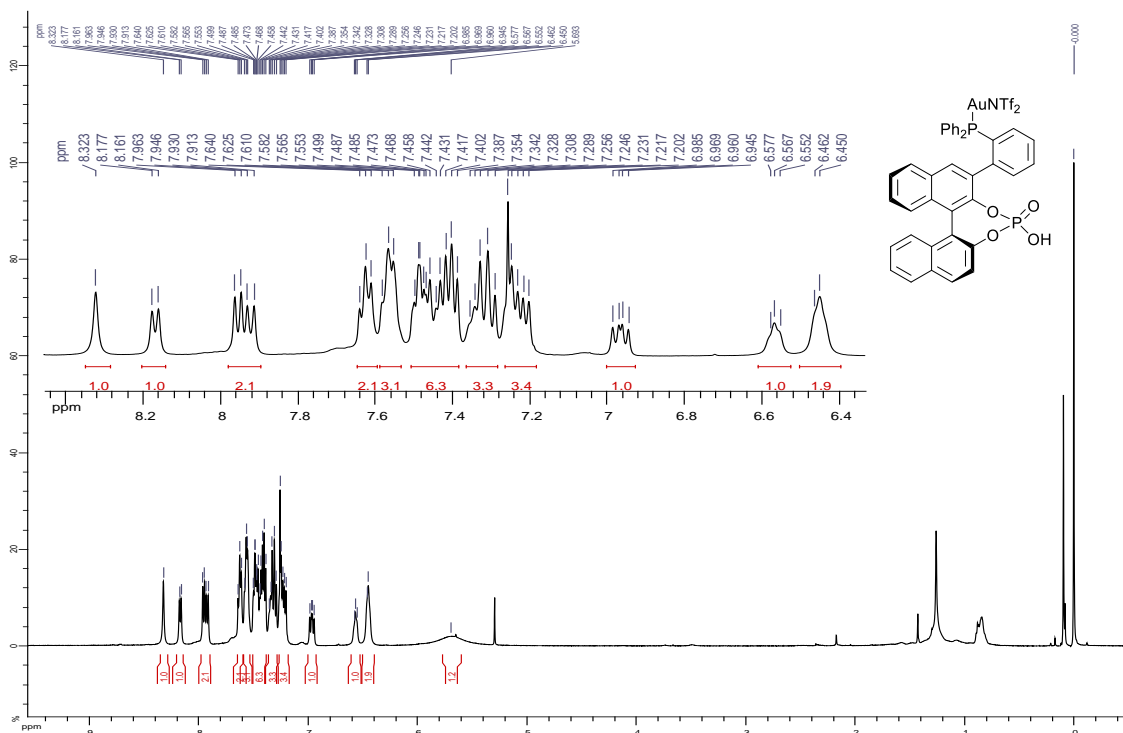
$^{31}\text{P}$  NMR (Pyridine, 200 MHz) spectrum of (S)-6



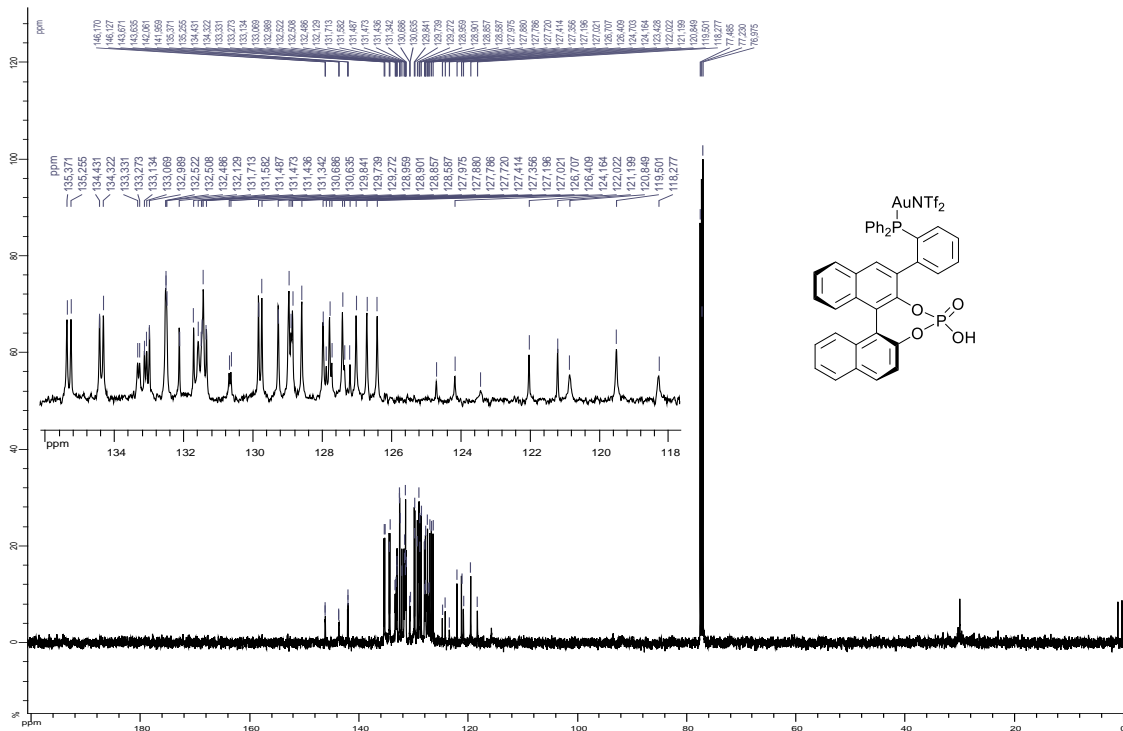
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) spectrum of (S)-6



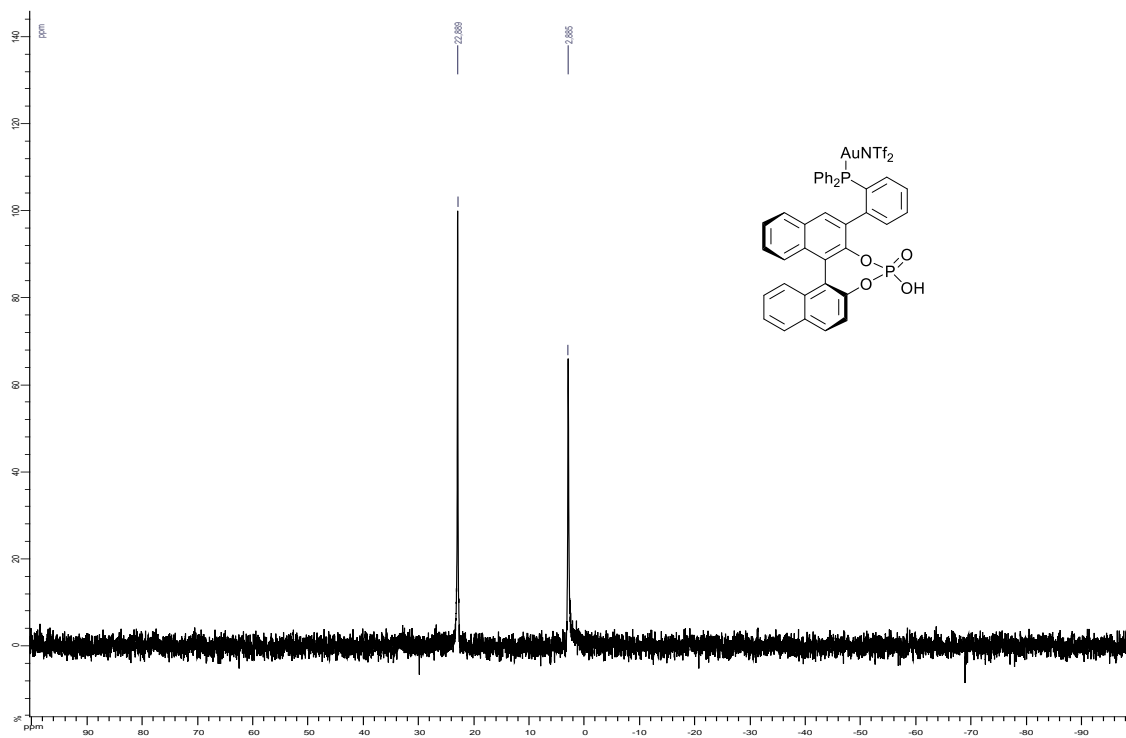
$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 200 MHz) spectrum of (S)-6



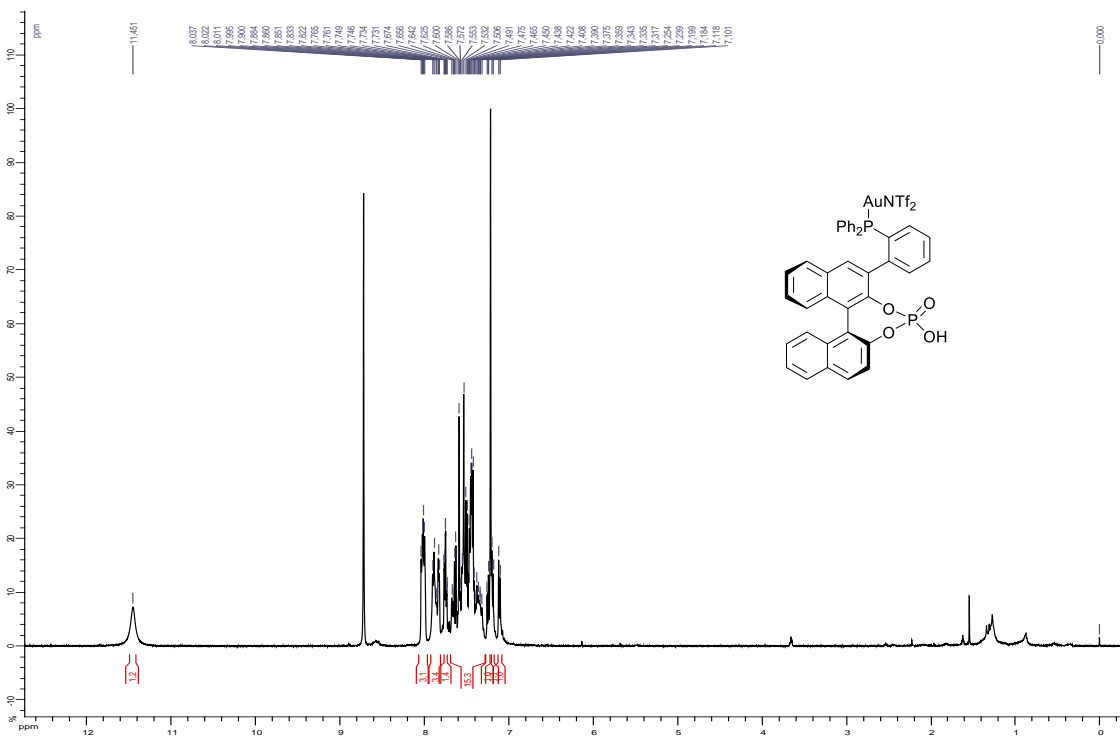
**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (S)-(2-(2,2'-diyl hydrogen phosphate-[1,1'-binaphthalen]-3-yl)phenyl)diphenylphosphine gold(I) bis(trifluoromethanesulfonyl)imide [(S)-7a]**



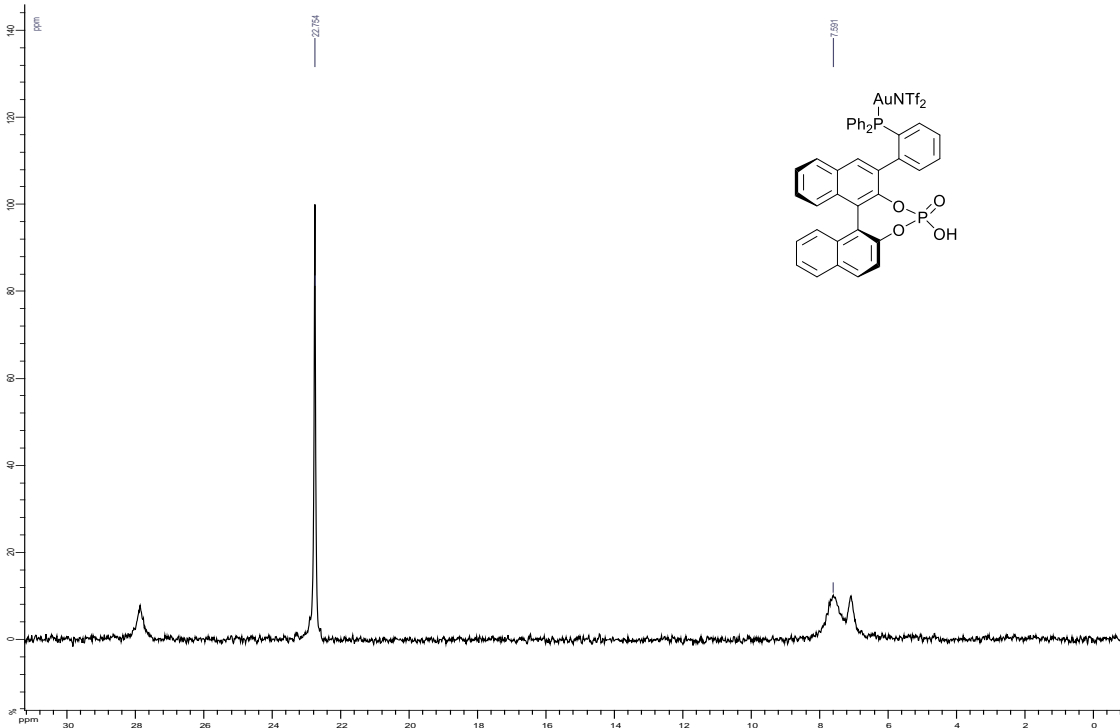
**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) spectrum of (S)-(2-(2,2'-diyl hydrogen phosphate-[1,1'-binaphthalen]-3-yl)phenyl)diphenylphosphine gold(I) bis(trifluoromethanesulfonyl)imide [(S)-7a]**



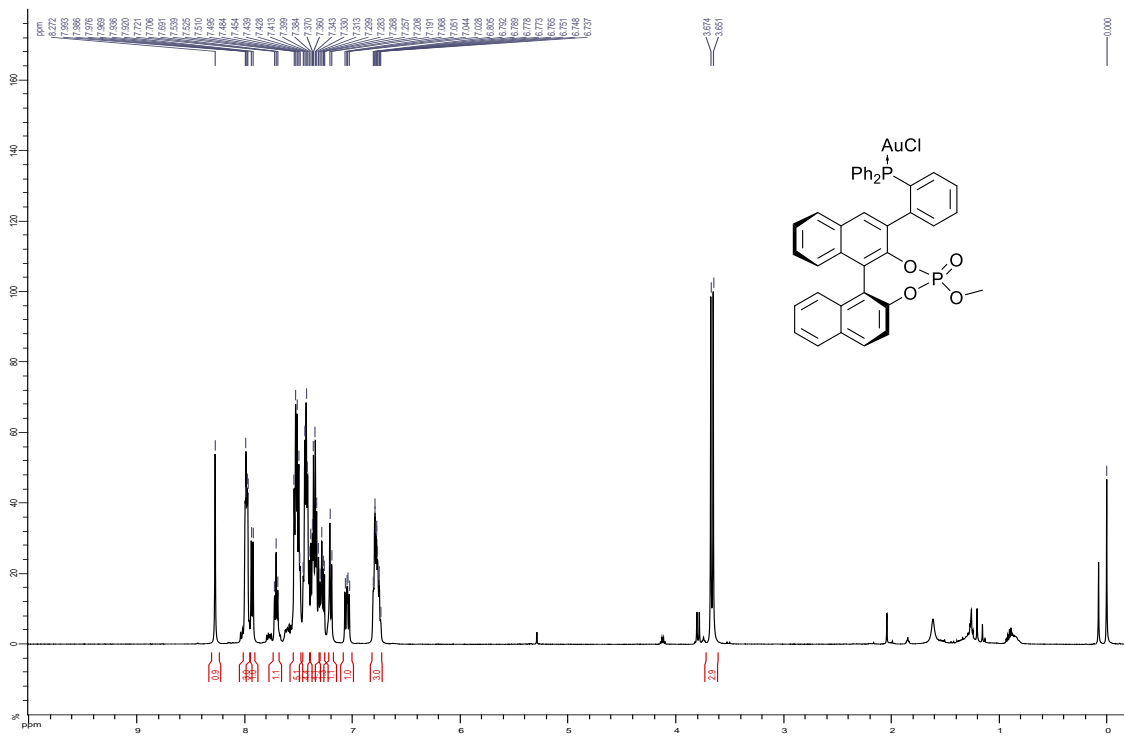
$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 200 MHz) spectrum of (*S*)-(2-(2,2'-diyl hydrogen phosphate-[1,1'-binaphthalen]-3-yl)phenyl) diphenylphosphine gold(I) bis(trifluoromethanesulfonyl)imide [(*S*)-7a]



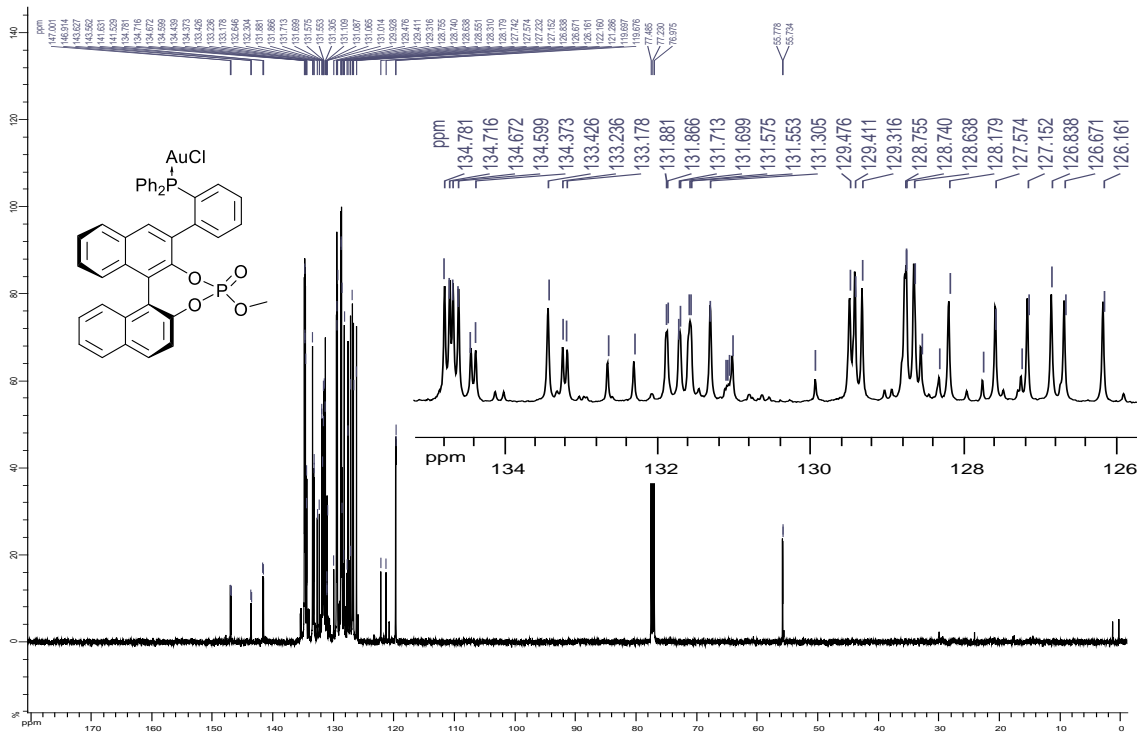
$^1\text{H}$  NMR (Pyridine, 500 MHz) spectrum of (S)-2-(2,2'-diyl hydrogen phosphate-[1,1'-binaphthalen]-3-yl)phenyl diphenylphosphine gold(I) bis(trifluoromethanesulfonyl)imide [(S)-7a]



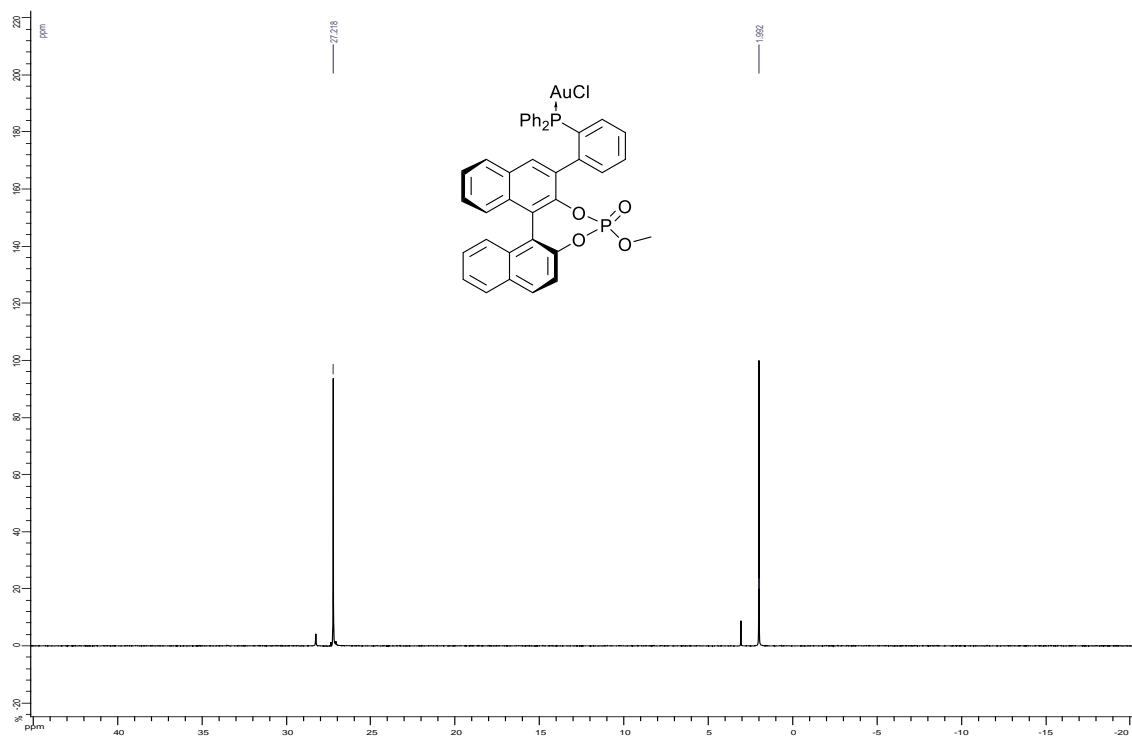
$^{31}\text{P}$  NMR (Pyridine, 200 MHz) spectrum of (S)-2-(2,2'-diyl hydrogen phosphate-[1,1'-binaphthalen]-3-yl)phenyl diphenylphosphine gold(I) bis(trifluoromethanesulfonyl)imide [(S)-7a]



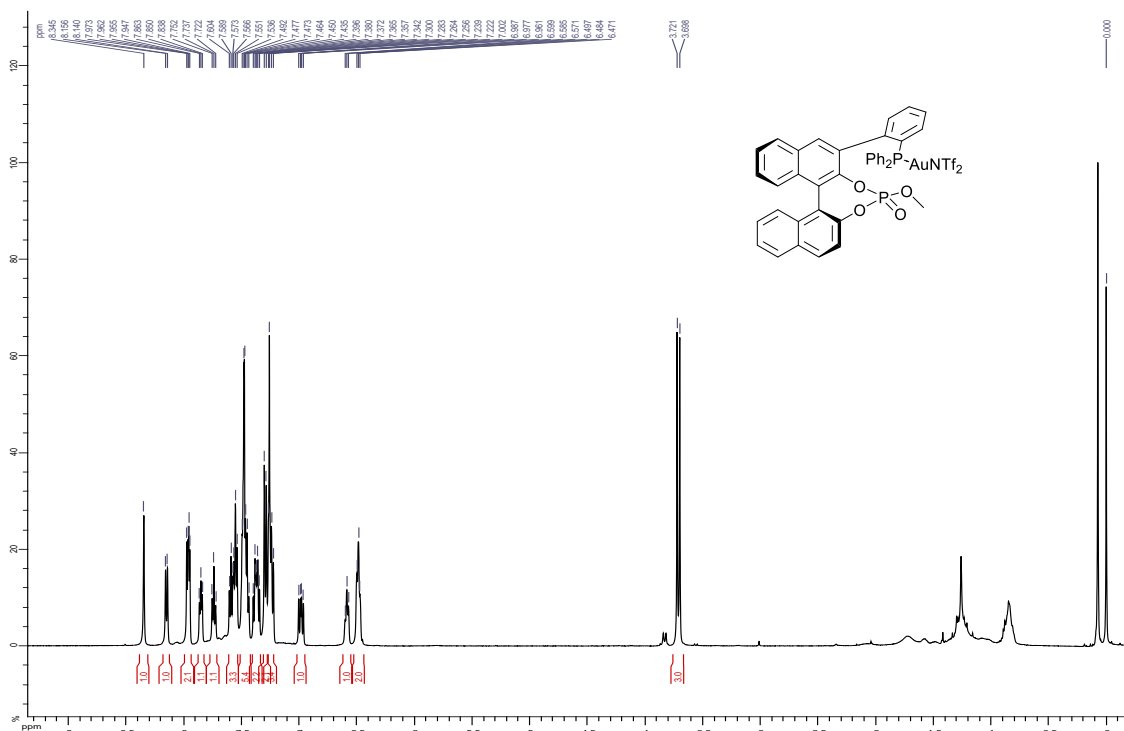
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) spectrum of SI-2



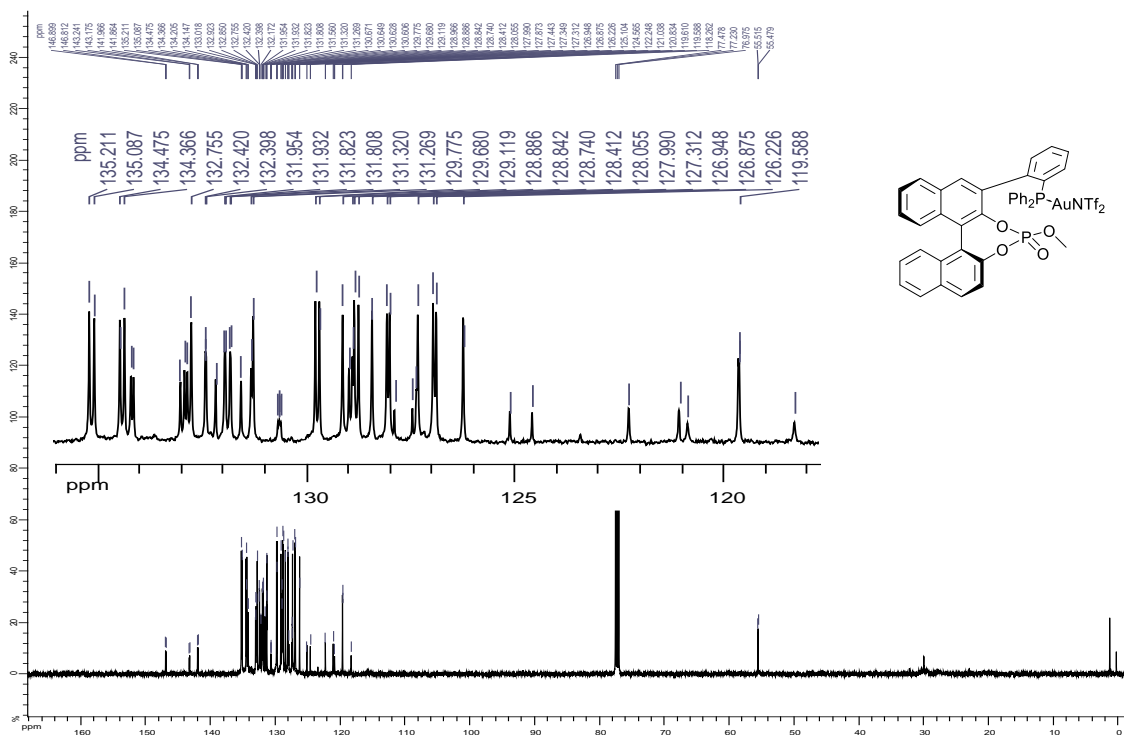
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz) spectrum of SI-2



$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 200 MHz) spectrum of SI-2

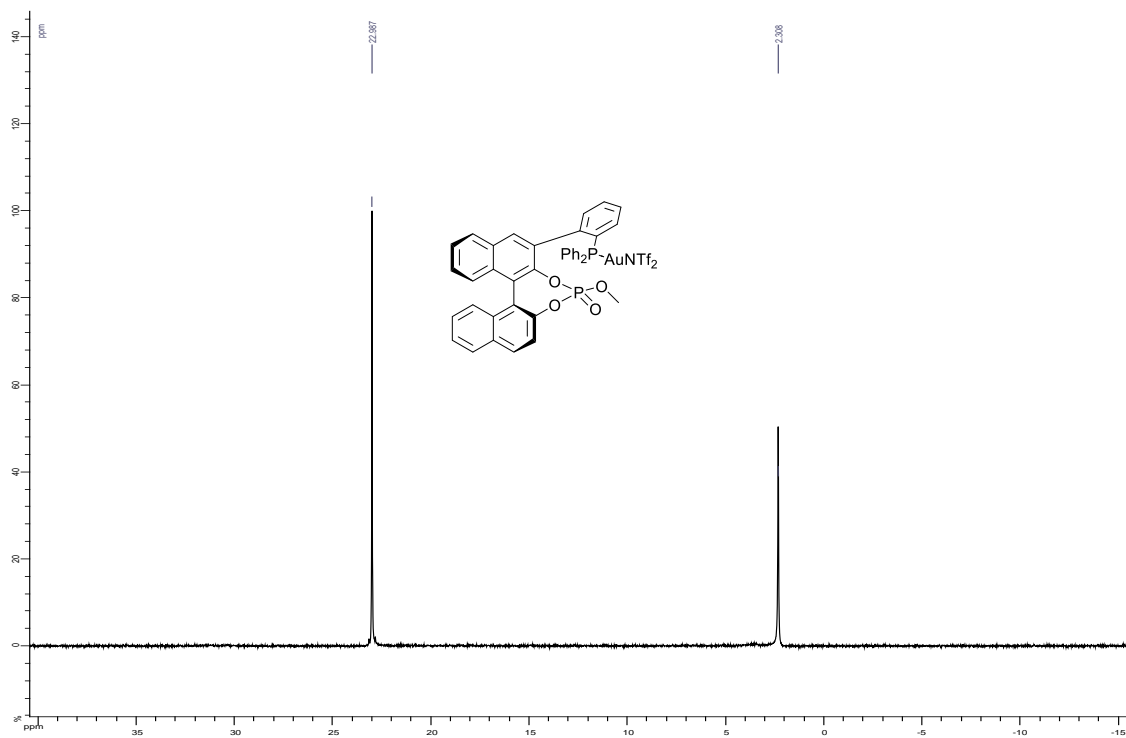


$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) spectrum of (S)-11a

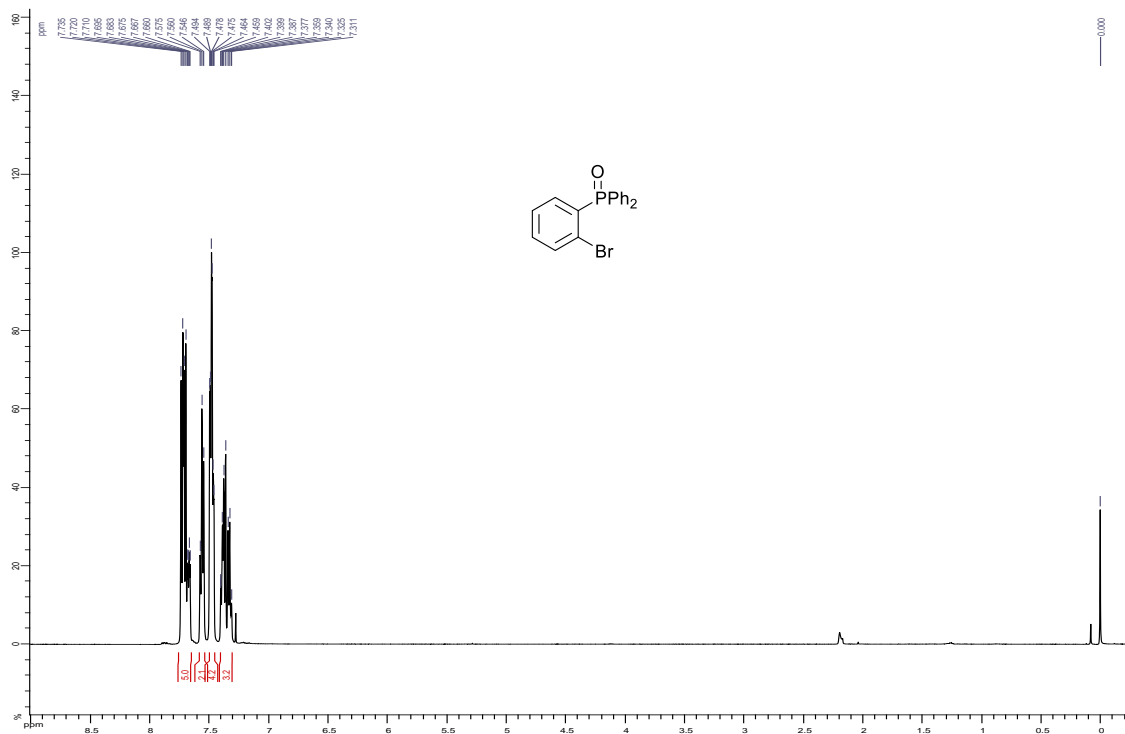


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz) spectrum of (S)-11a

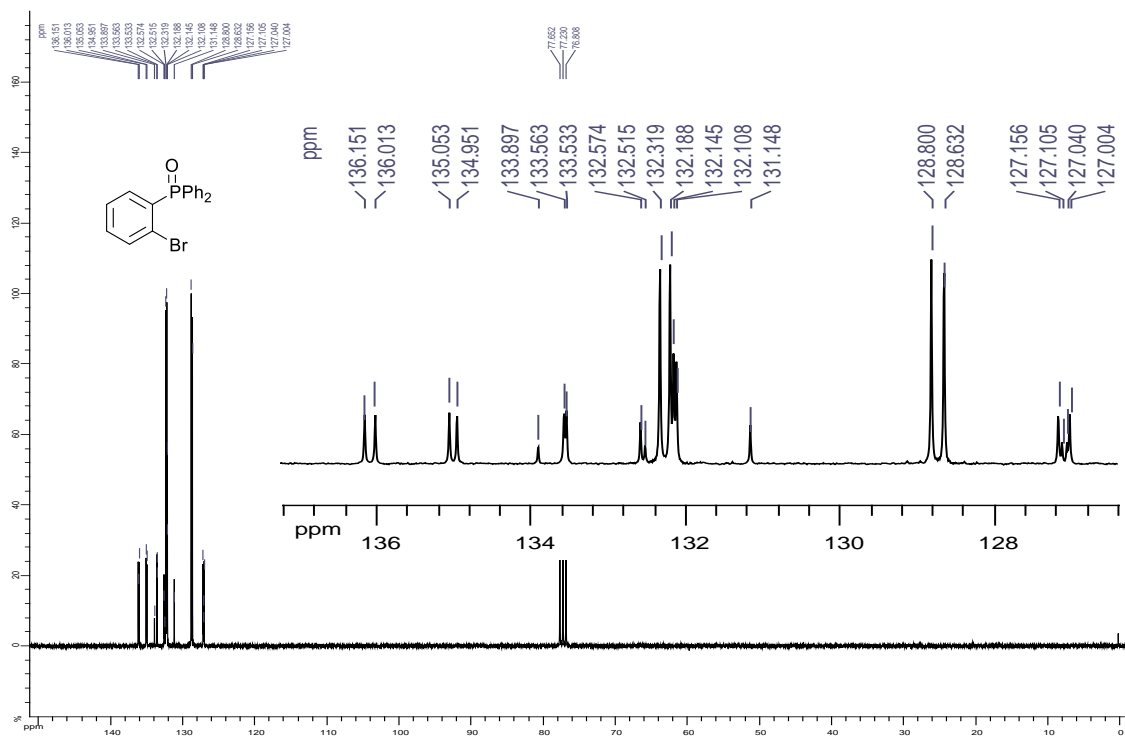




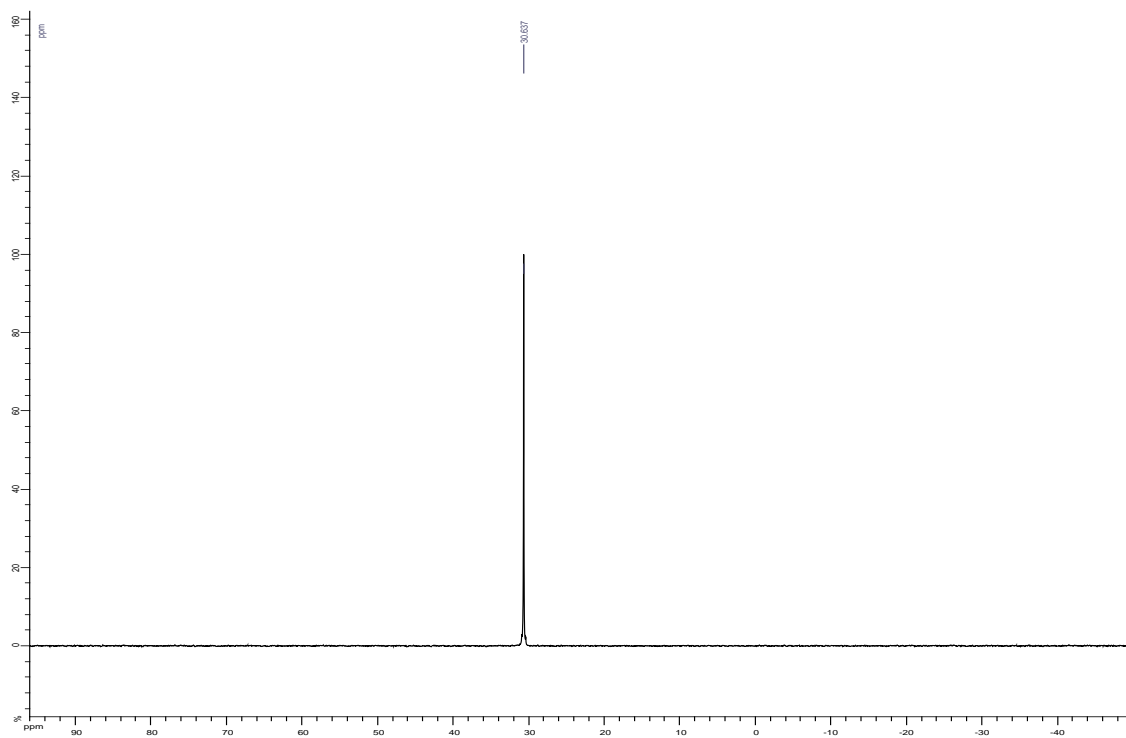
$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 200 MHz) spectrum of (S)-11a



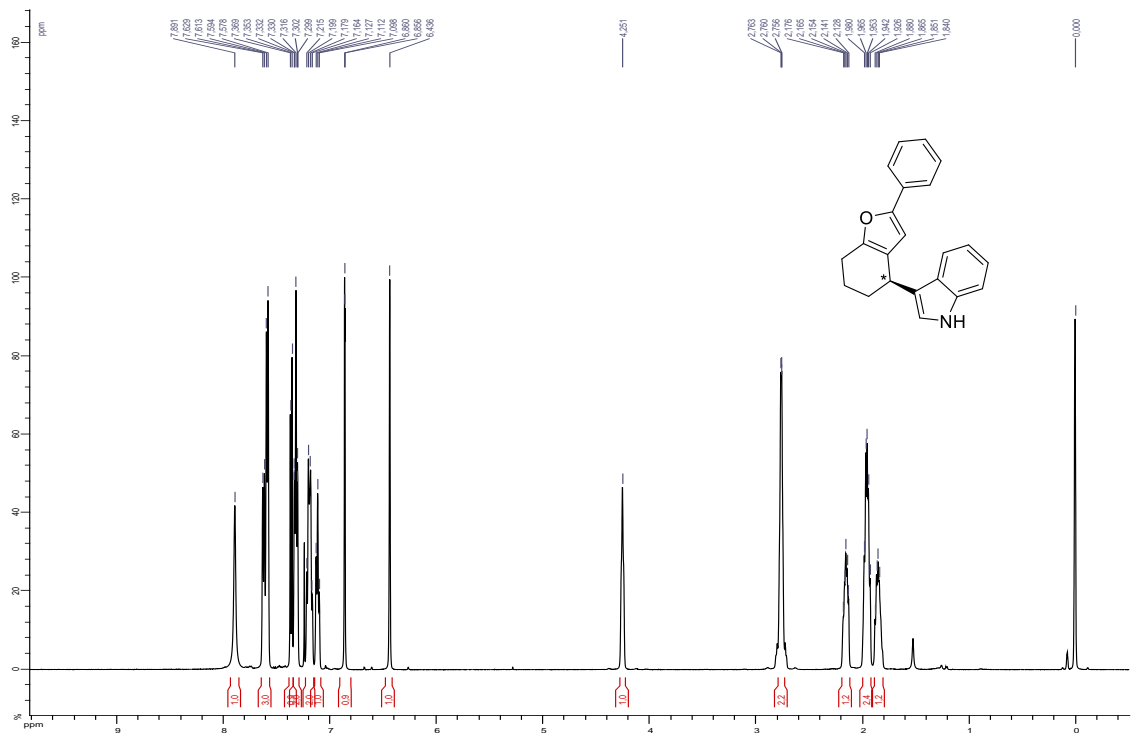
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (2-bromophenyl)diphenylphosphine oxide



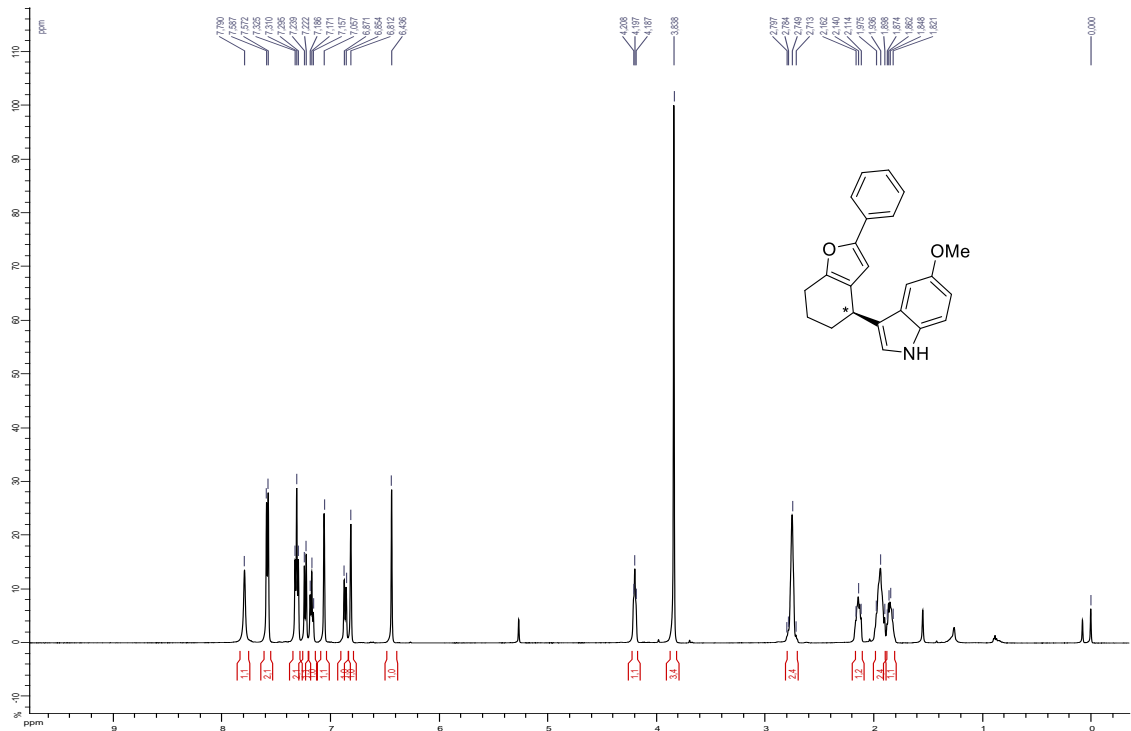
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) spectrum of (2-bromophenyl)diphenylphosphine oxide



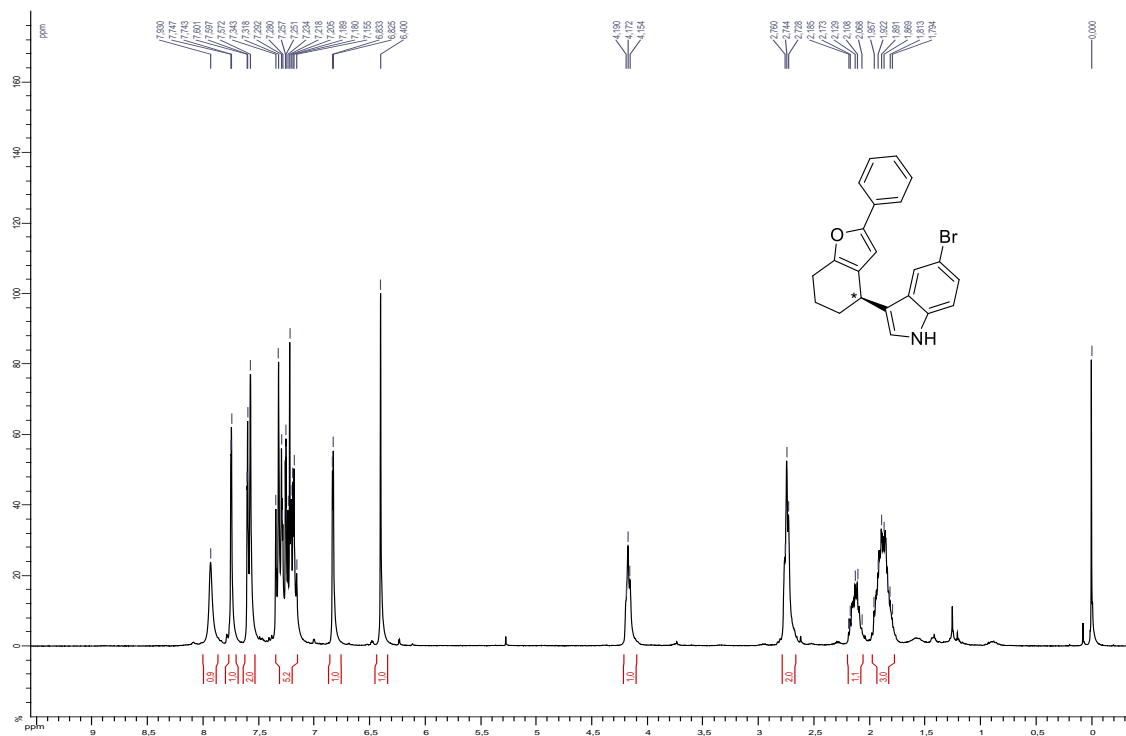
$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 200 MHz) spectrum of (2-bromophenyl)diphenylphosphine oxide



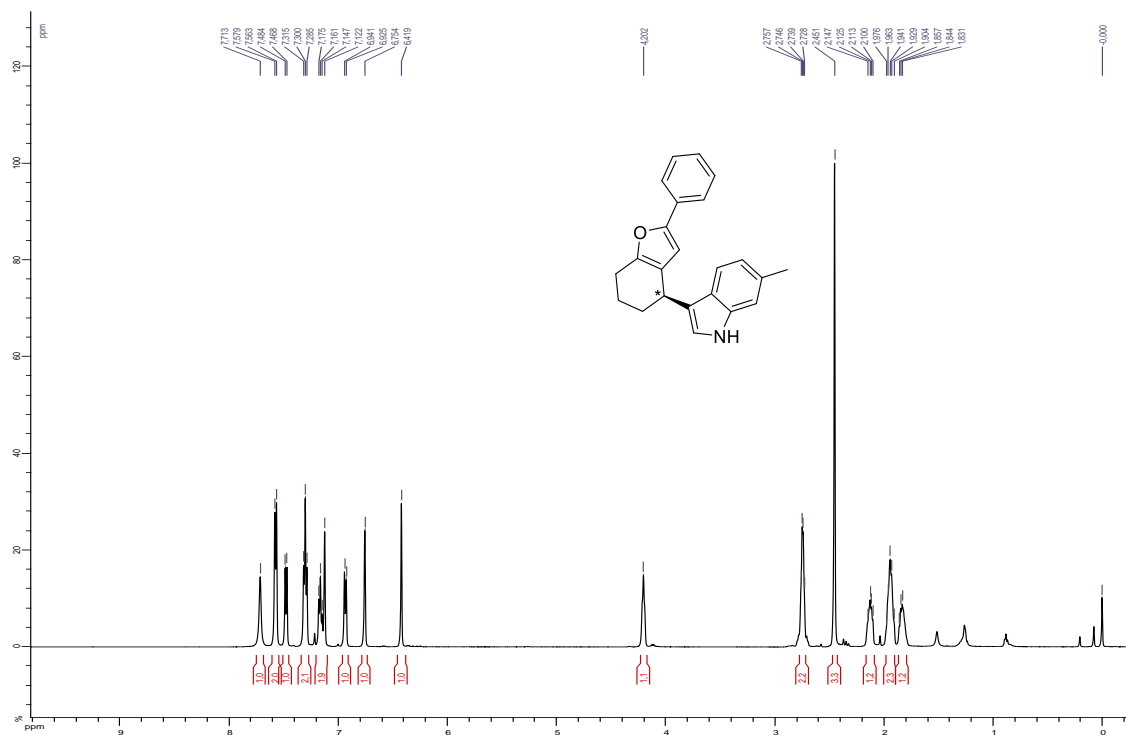
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (R)-3-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indole (10aa)



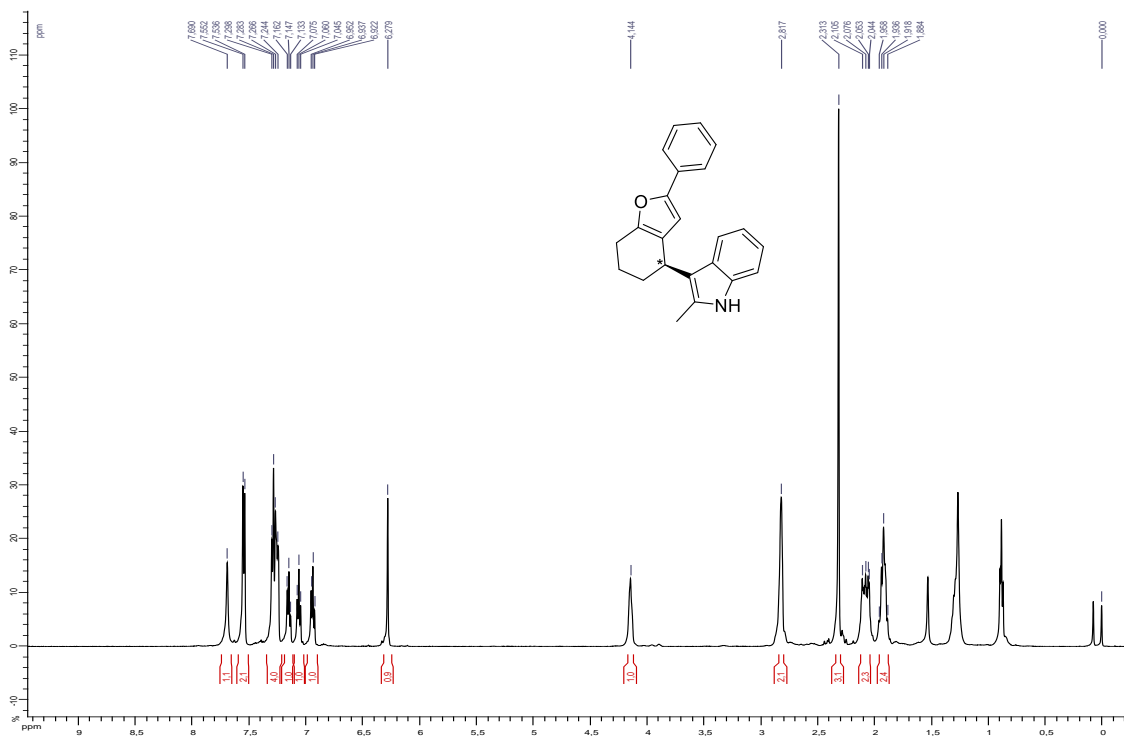
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (R)-5-methoxy-3-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indole (10ab)



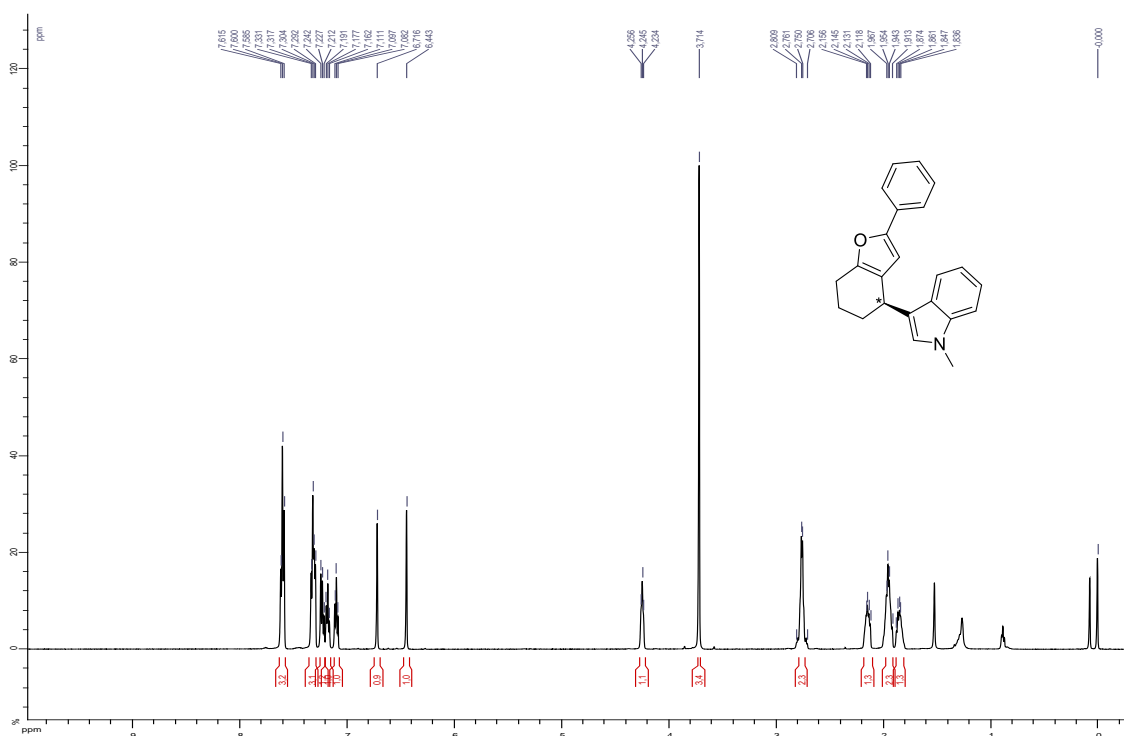
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) spectrum of (R)-5-bromo-3-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indole (**10ac**)



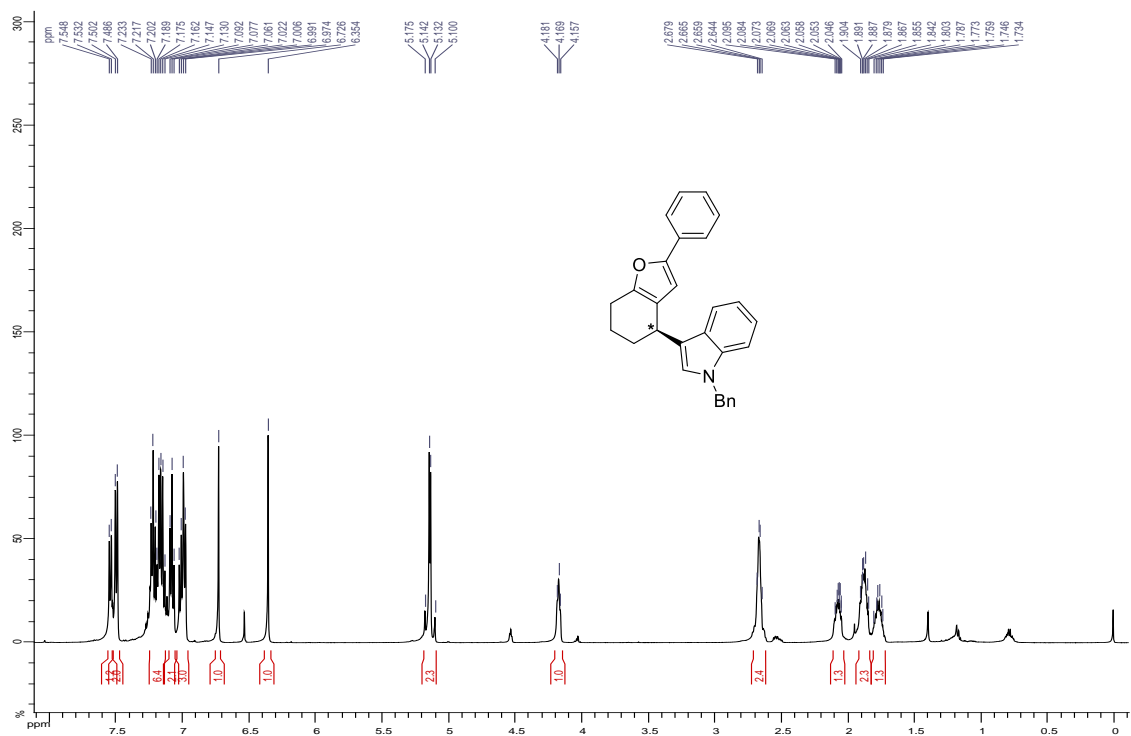
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (R)-6-methyl-3-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indole (**10ad**)



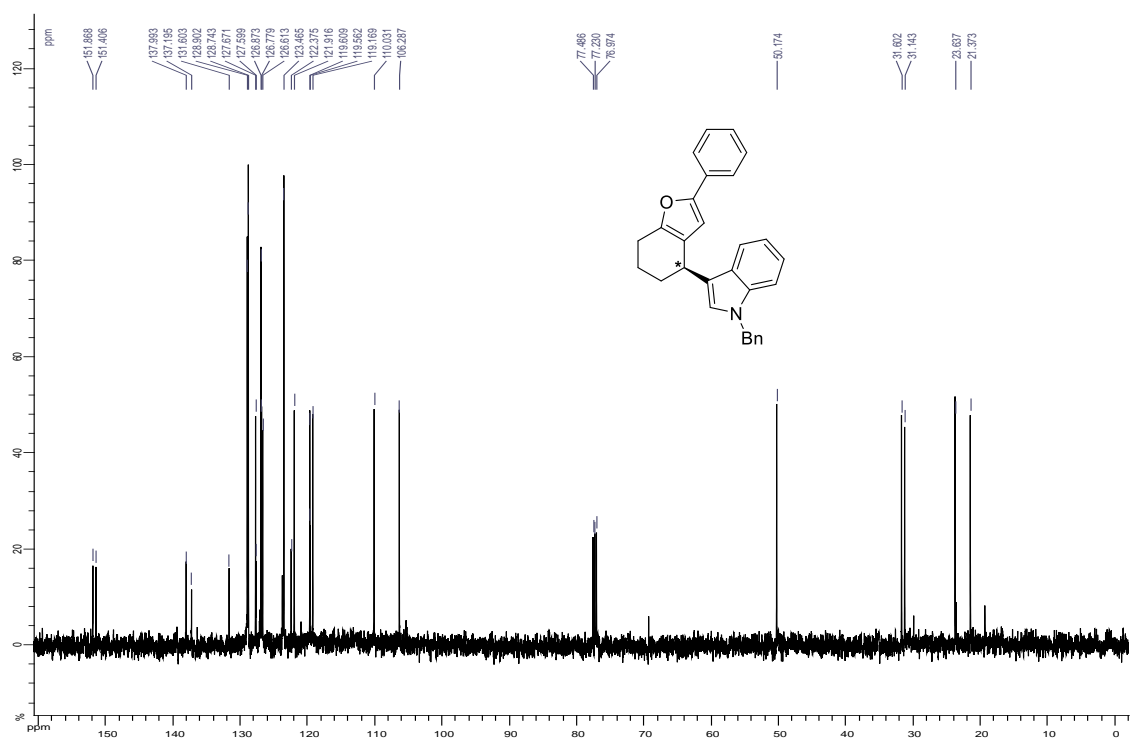
**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (R)-2-methyl-3-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indole (10ae)**



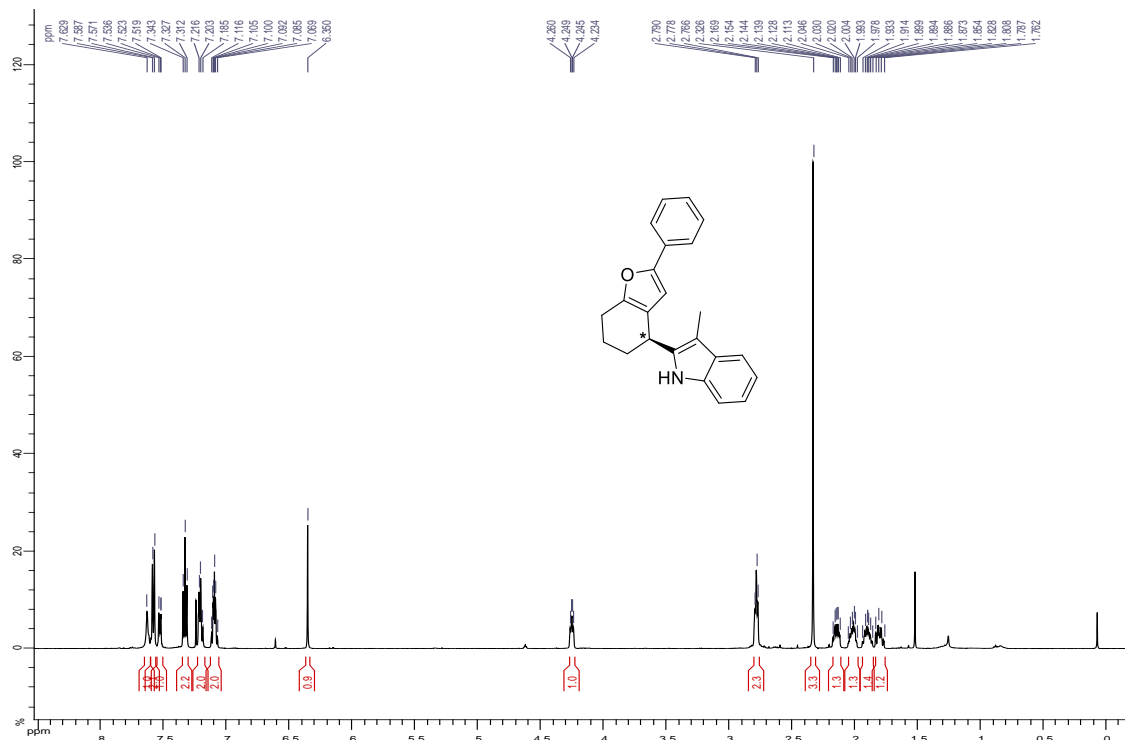
**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (R)-1-methyl-3-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-indole (10af)**



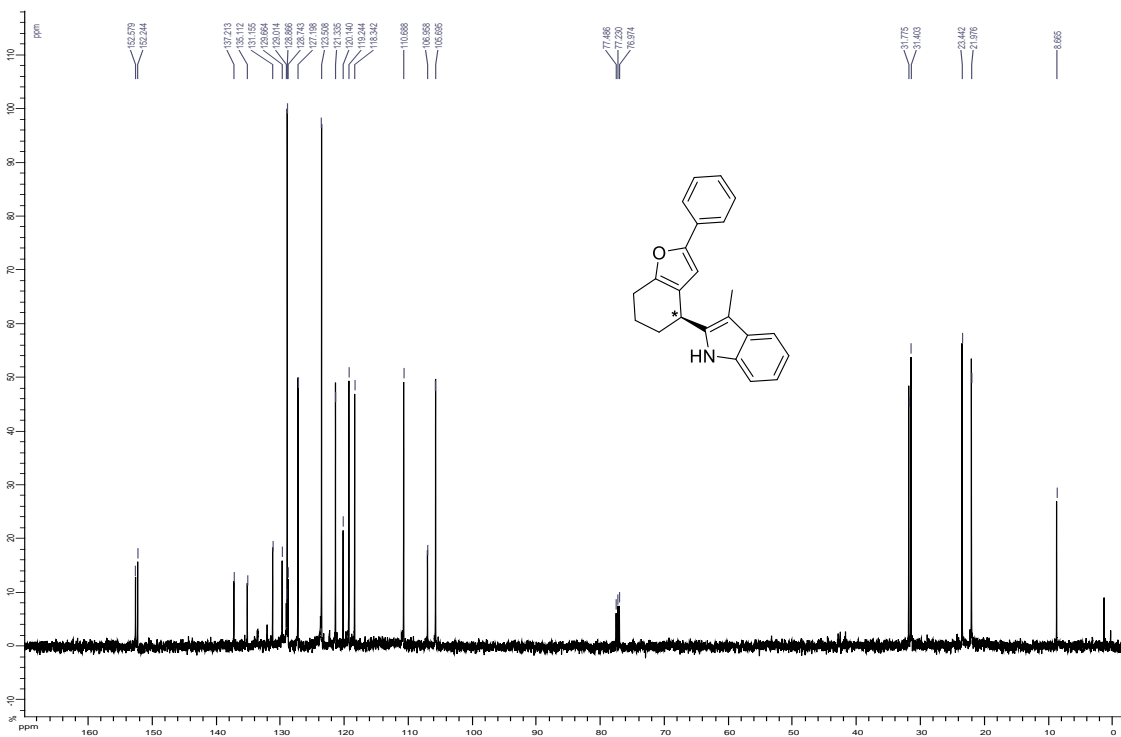
**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (R)-1-benzyl-3-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-indole (10ag)**



**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) spectrum of (R)-1-benzyl-3-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indole (10ag)**

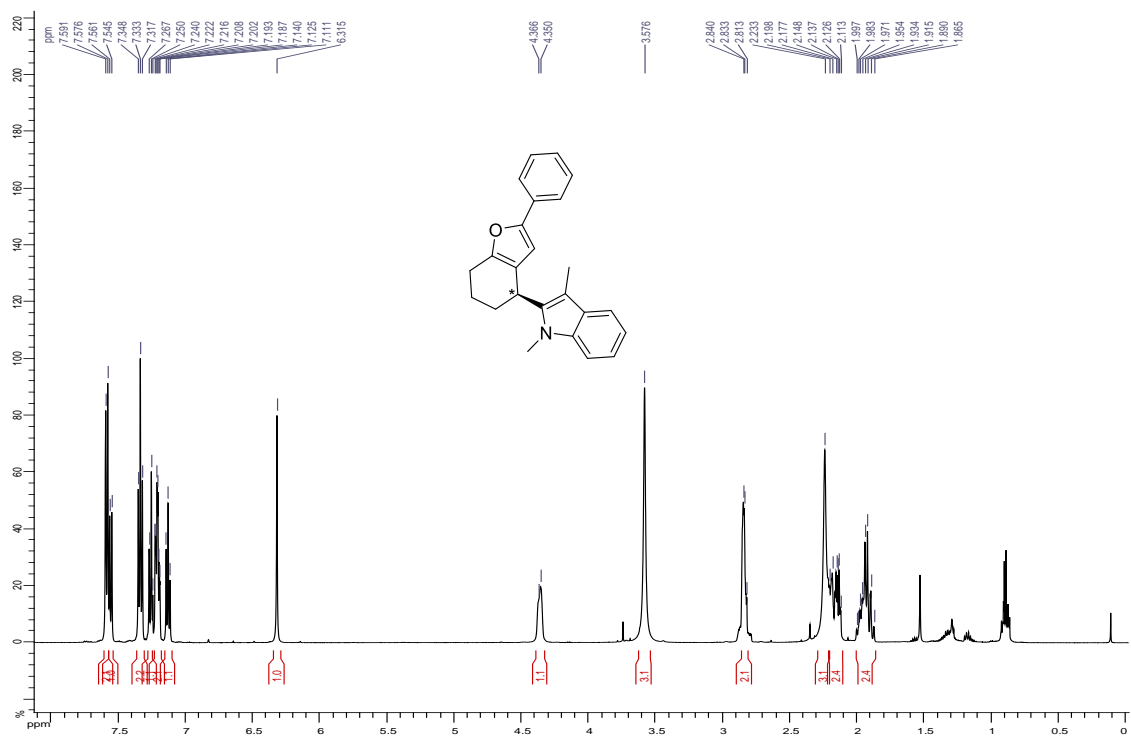


<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (S)-3-methyl-2-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-indole (14ah)

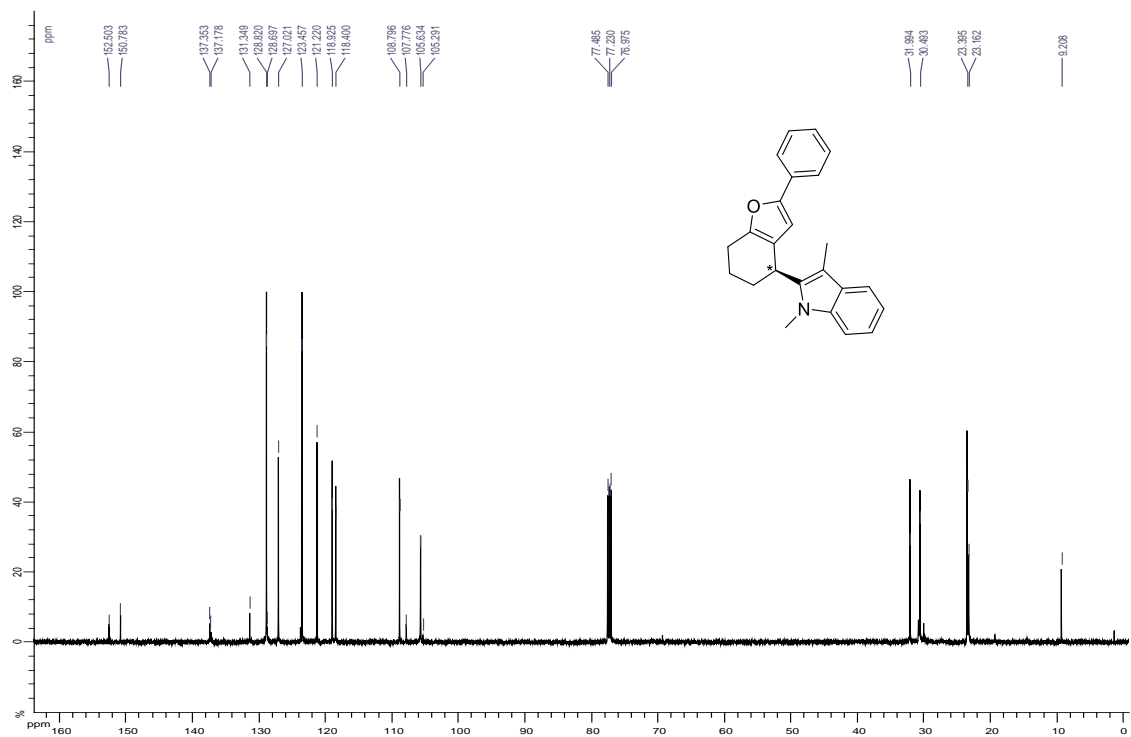


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) spectrum of (S)-3-methyl-2-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indole (14ah)

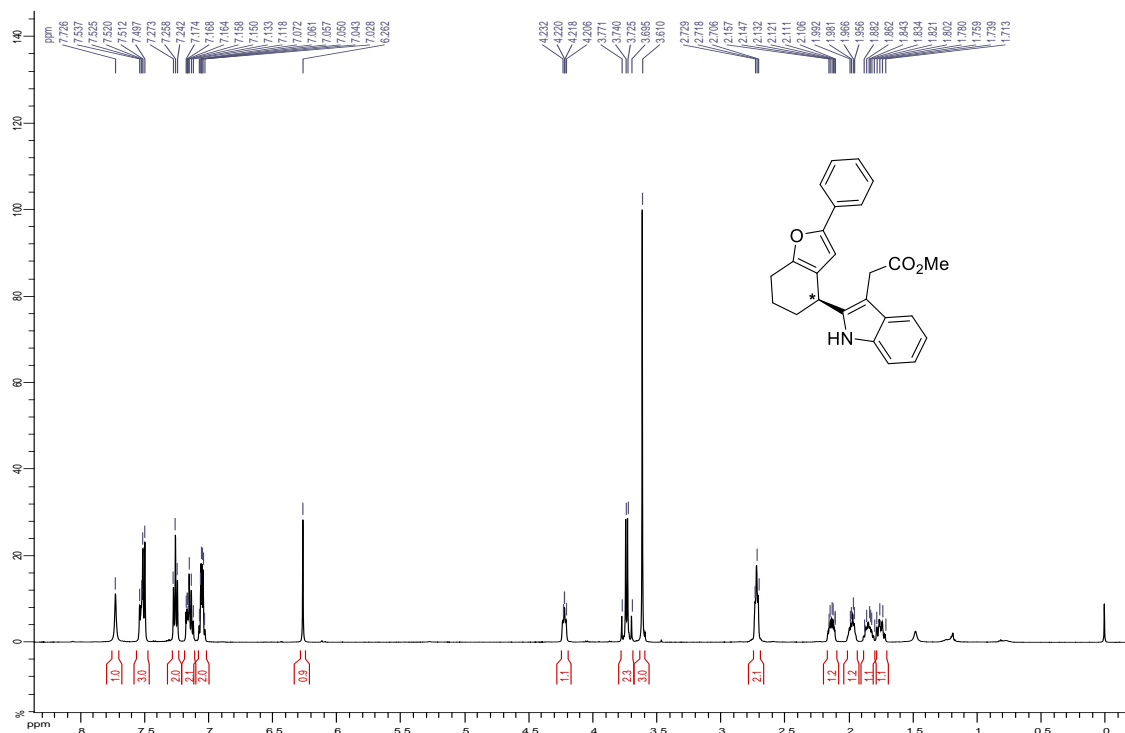




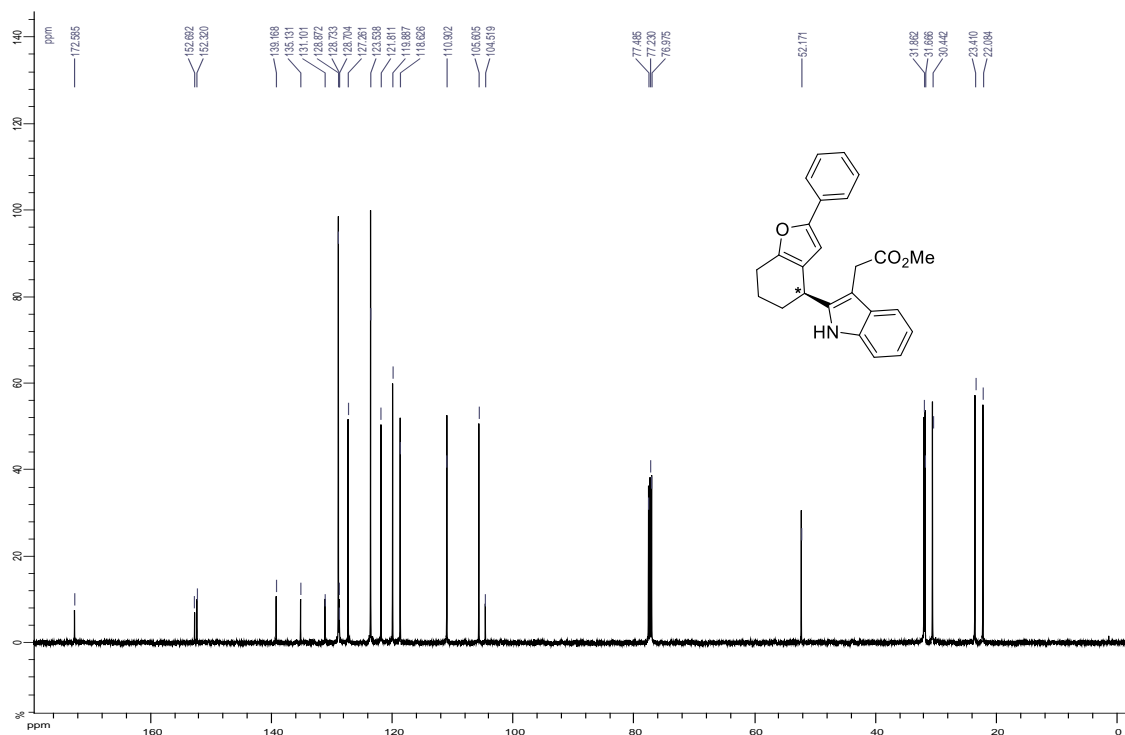
**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (S)-1,3-dimethyl-2-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-indole (14ai)**



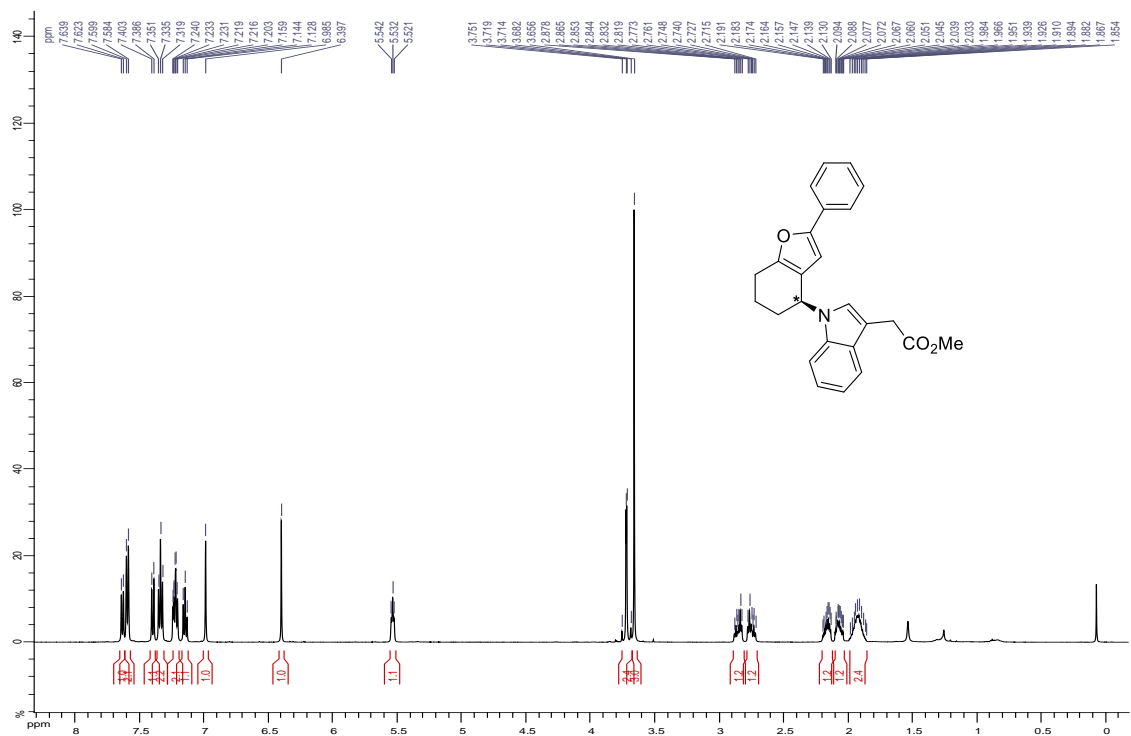
**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) spectrum of (S)-1,3-dimethyl-2-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-indole (14ai)**



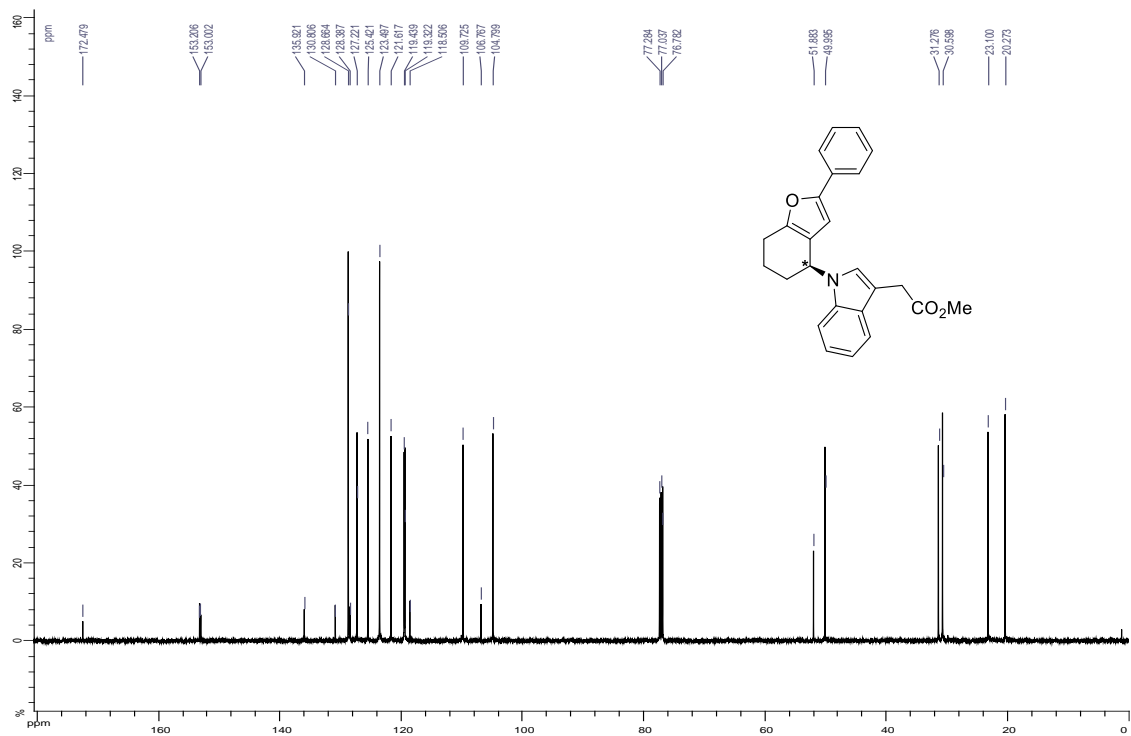
**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of methyl (S)-2-(2-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indol-3-yl)acetate (14aj)**



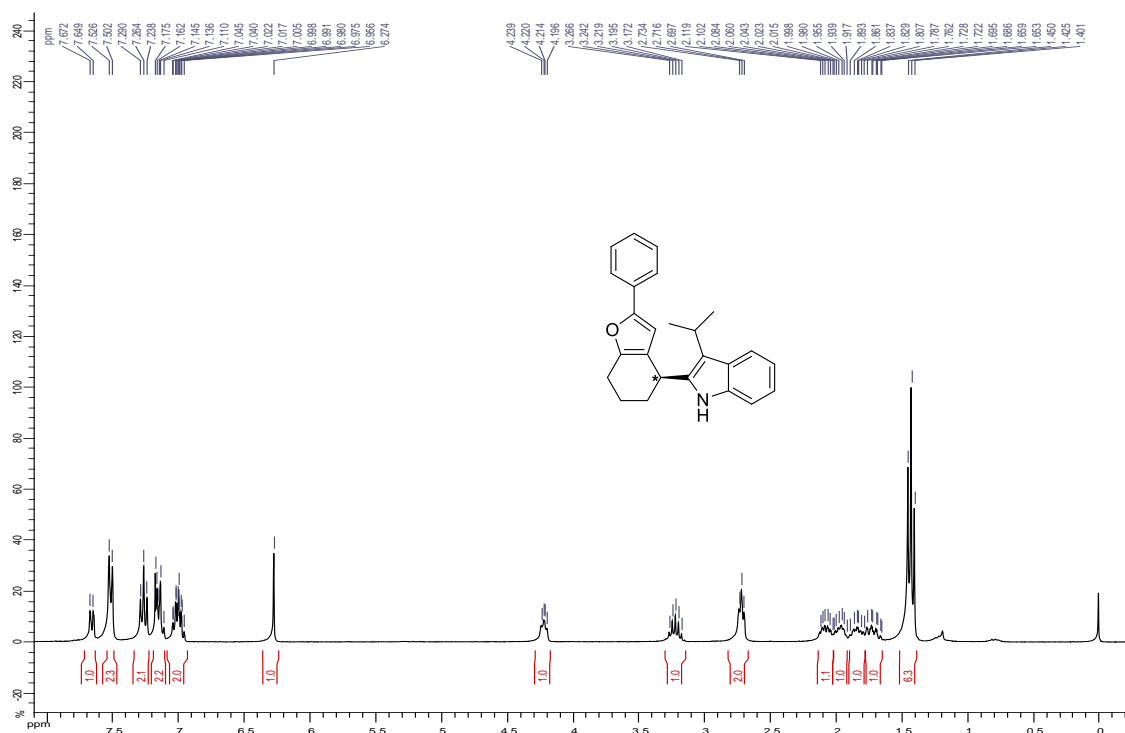
**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) spectrum of methyl (S)-2-(2-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indol-3-yl)acetate (14aj)**



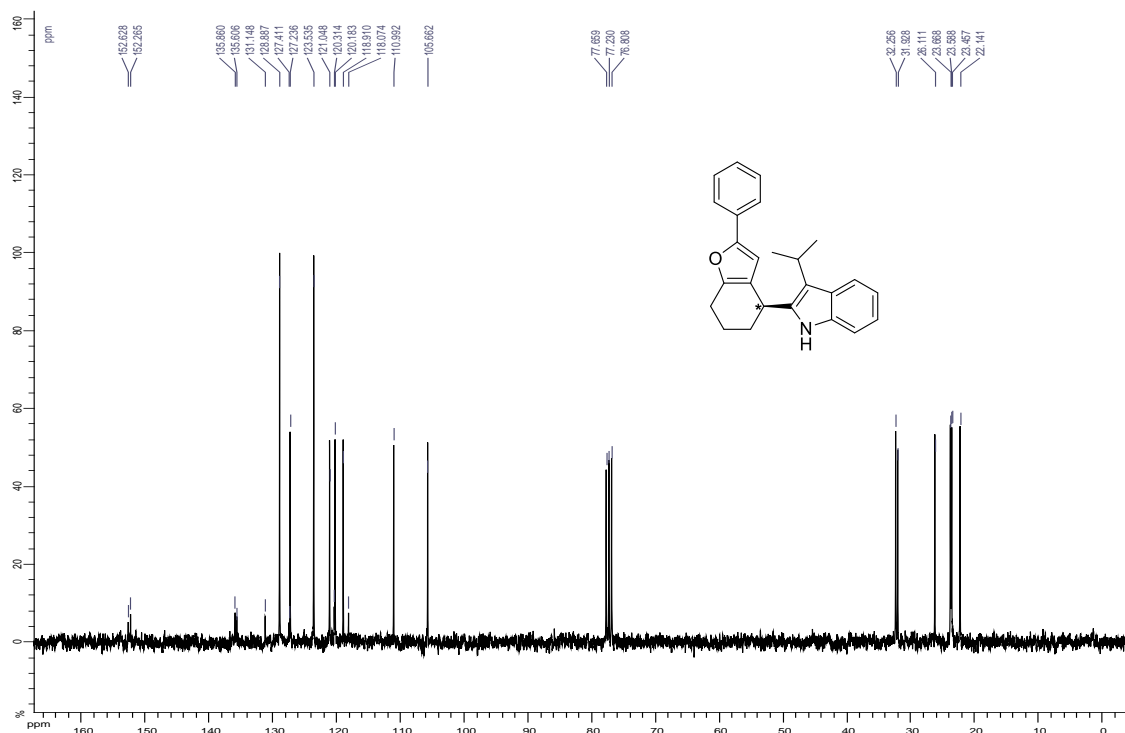
**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of methyl (S)-2-(1-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-indol-3-yl)acetate (15aj)**



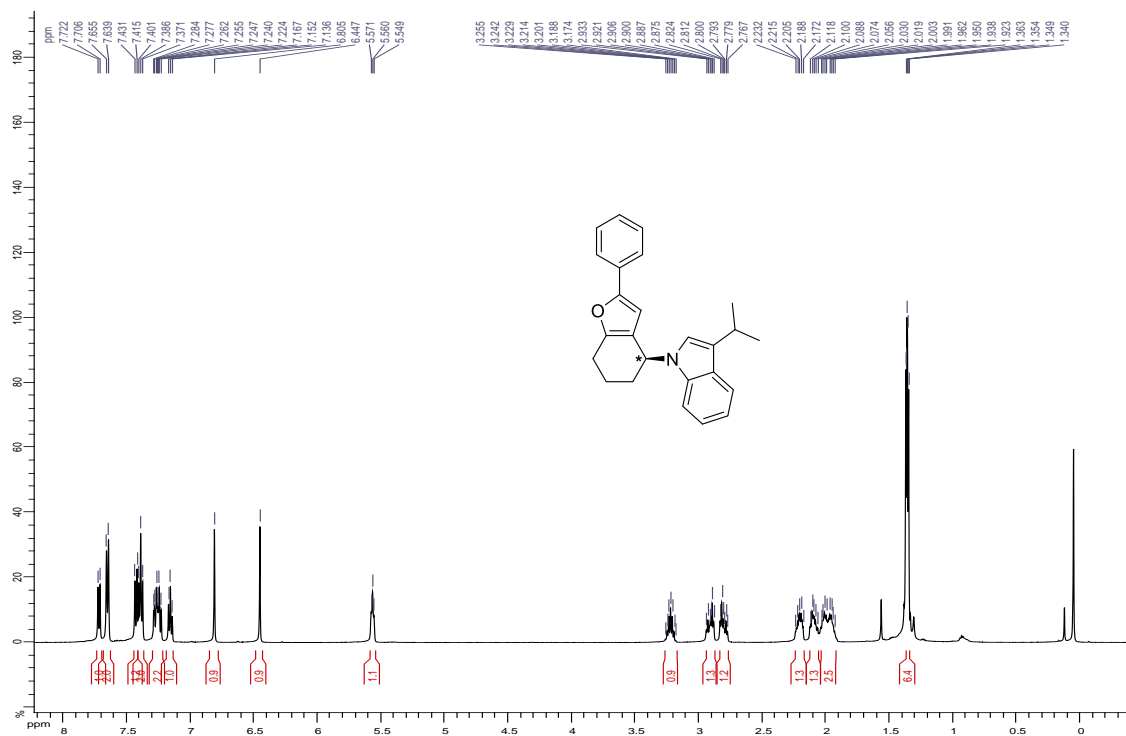
**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) spectrum of methyl (S)-2-(1-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-indol-3-yl)acetate (15aj)**



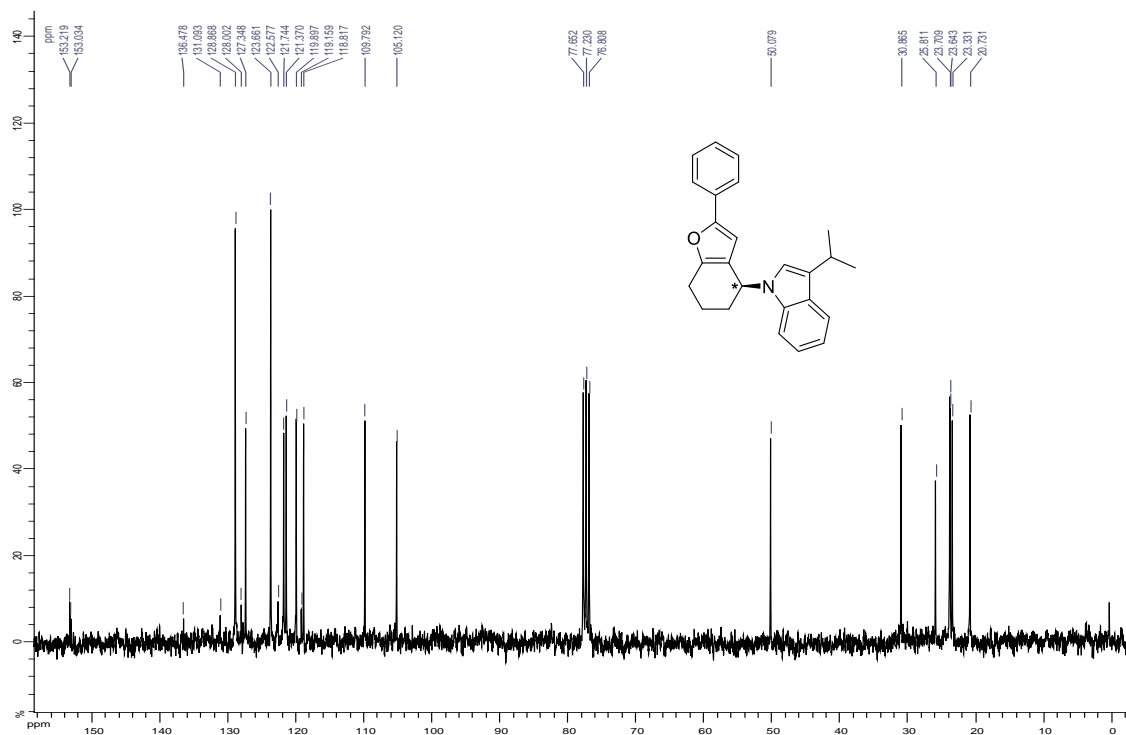
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of **(S)-3-isopropyl-2-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indole (14ak)**



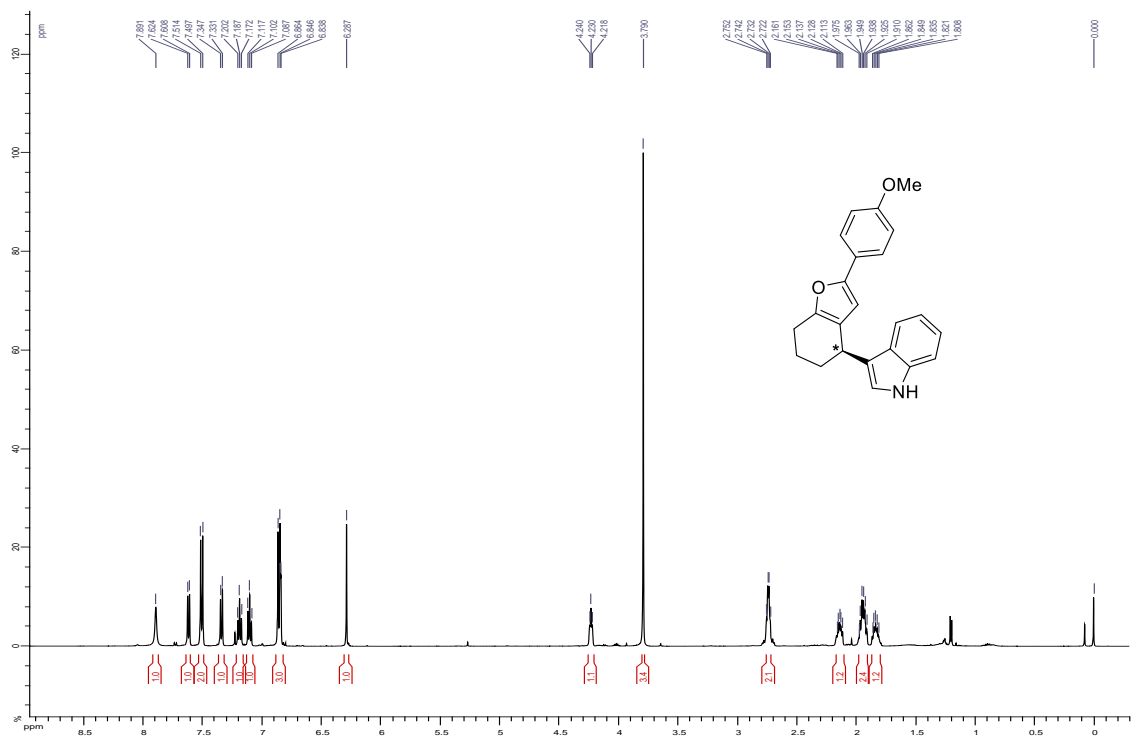
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) spectrum of **(S)-3-isopropyl-2-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indole (14ak)**



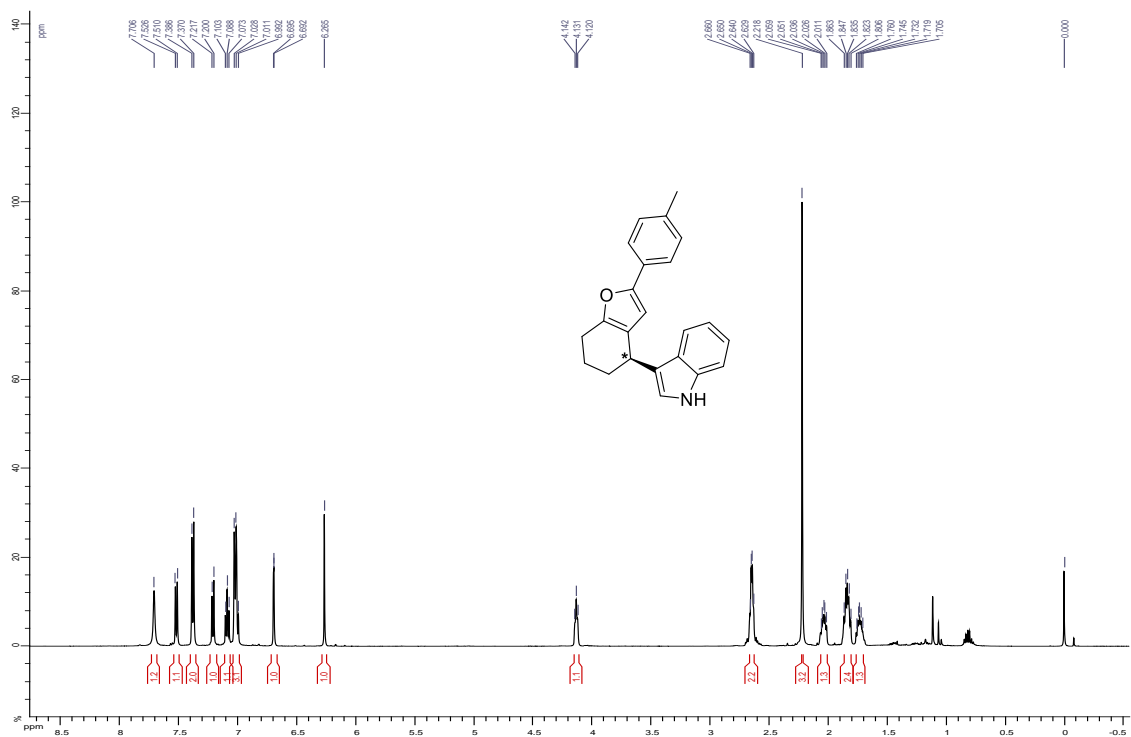
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (S)-3-isopropyl-1-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-indole (15ak)



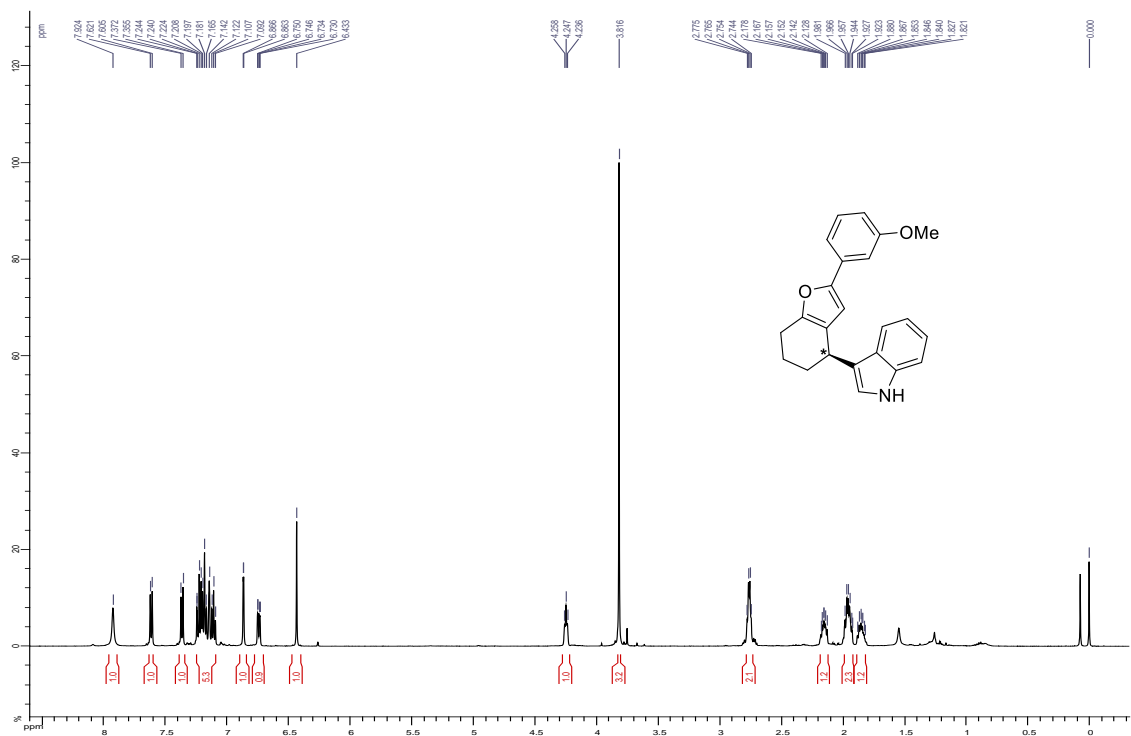
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) spectrum of (S)-3-isopropyl-1-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-indole (15ak)



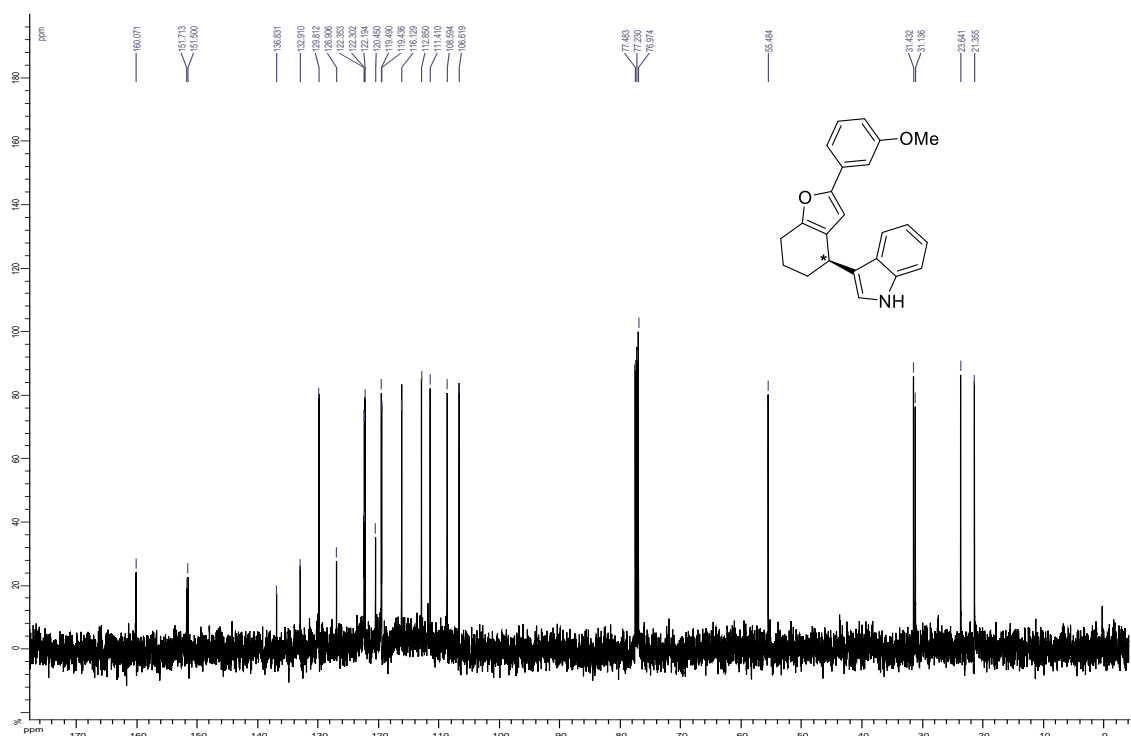
**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (R)-3-(2-(4-methoxyphenyl)-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indole (10ba)**



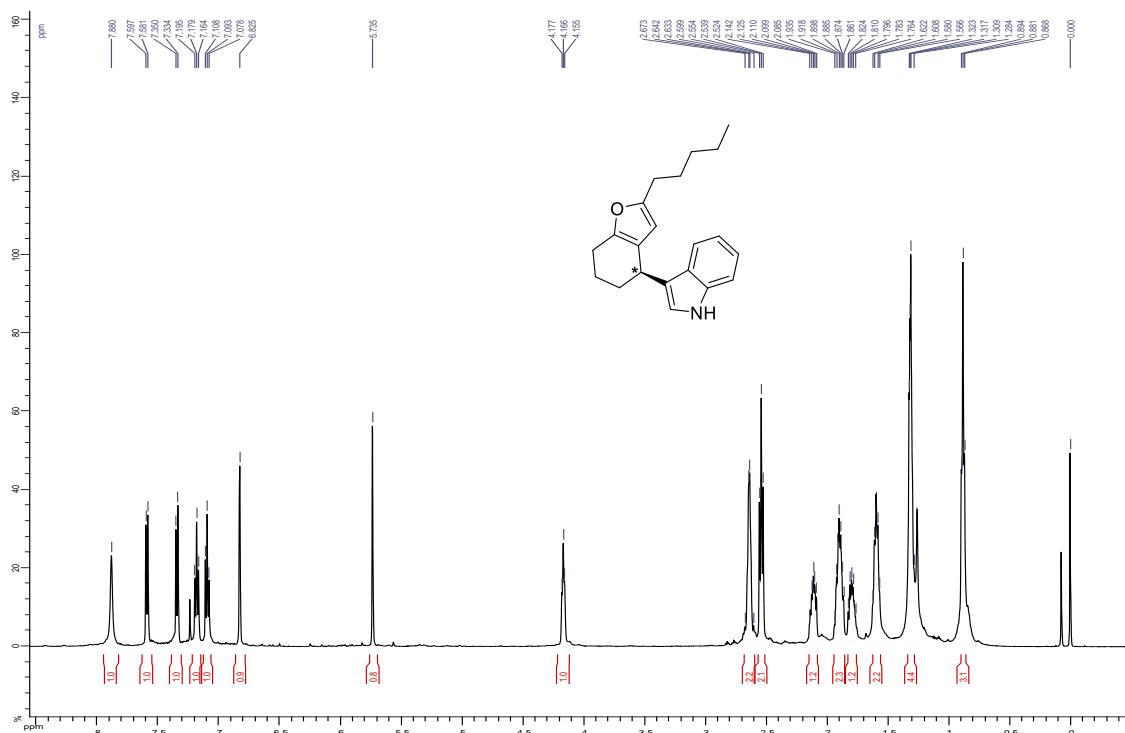
**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (R)-3-(2-(p-tolyl)-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indole (10ca)**



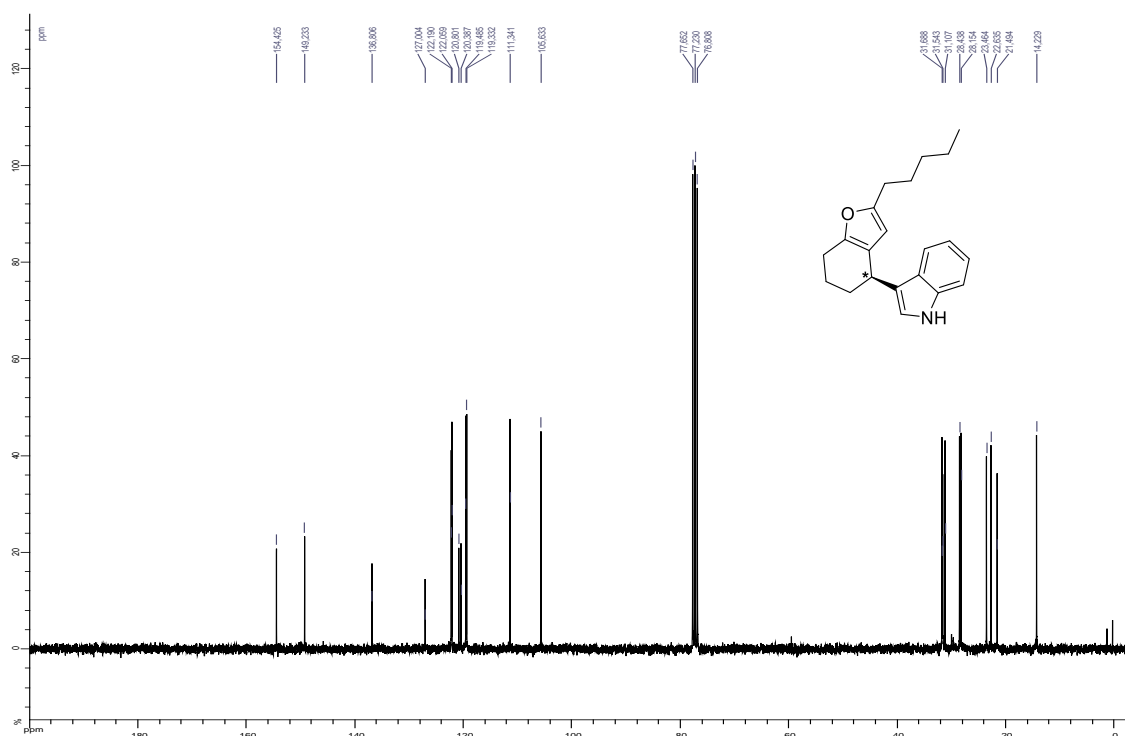
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (*R*)-3-(2-(3-methoxyphenyl)-4,5,6,7-tetrahydrobenzofuran-4-yl)-1*H*-indole (**10da**)



<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) spectrum of (*R*)-3-(2-(3-methoxyphenyl)-4,5,6,7-tetrahydrobenzofuran-4-yl)-1*H*-indole (**10da**)

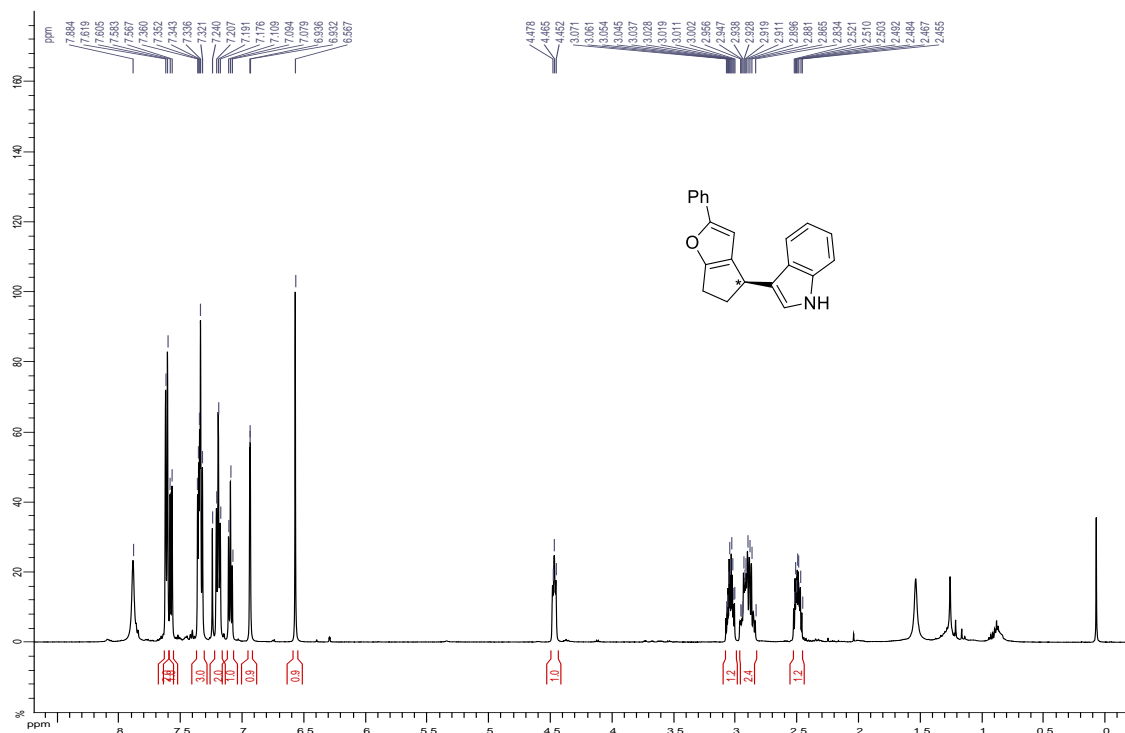


<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (R)-3-(2-pentyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indole (10ea)

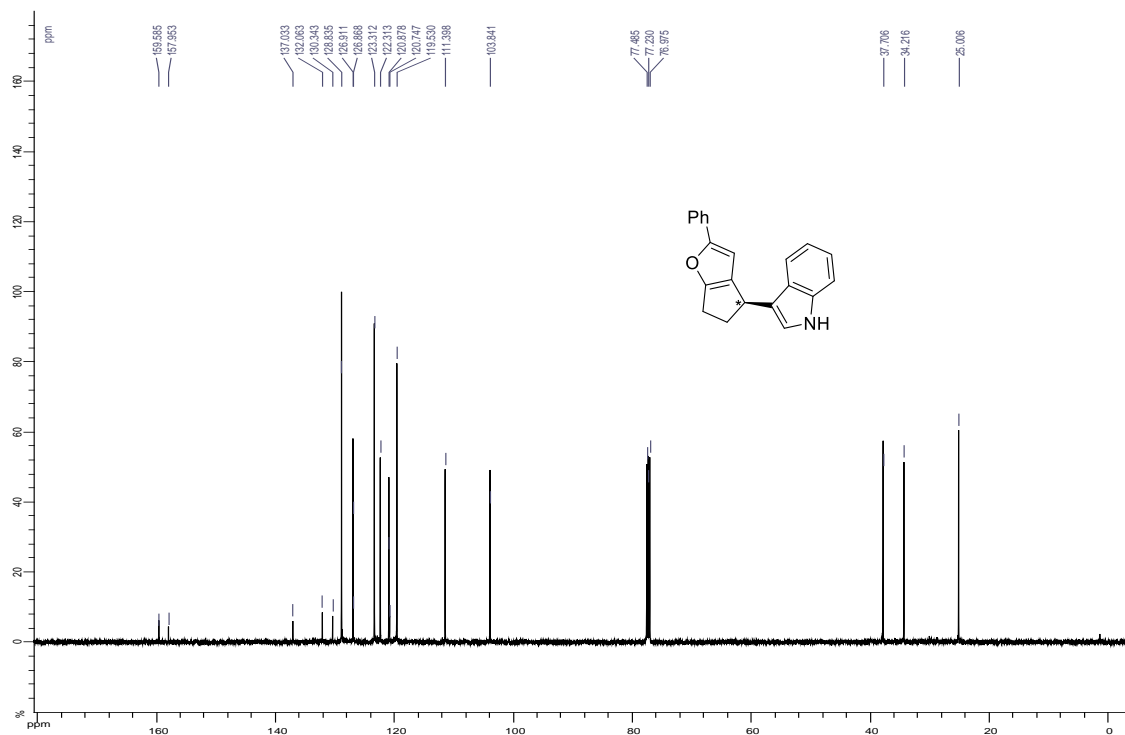


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) spectrum of (R)-3-(2-pentyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-1H-indole (10ea)

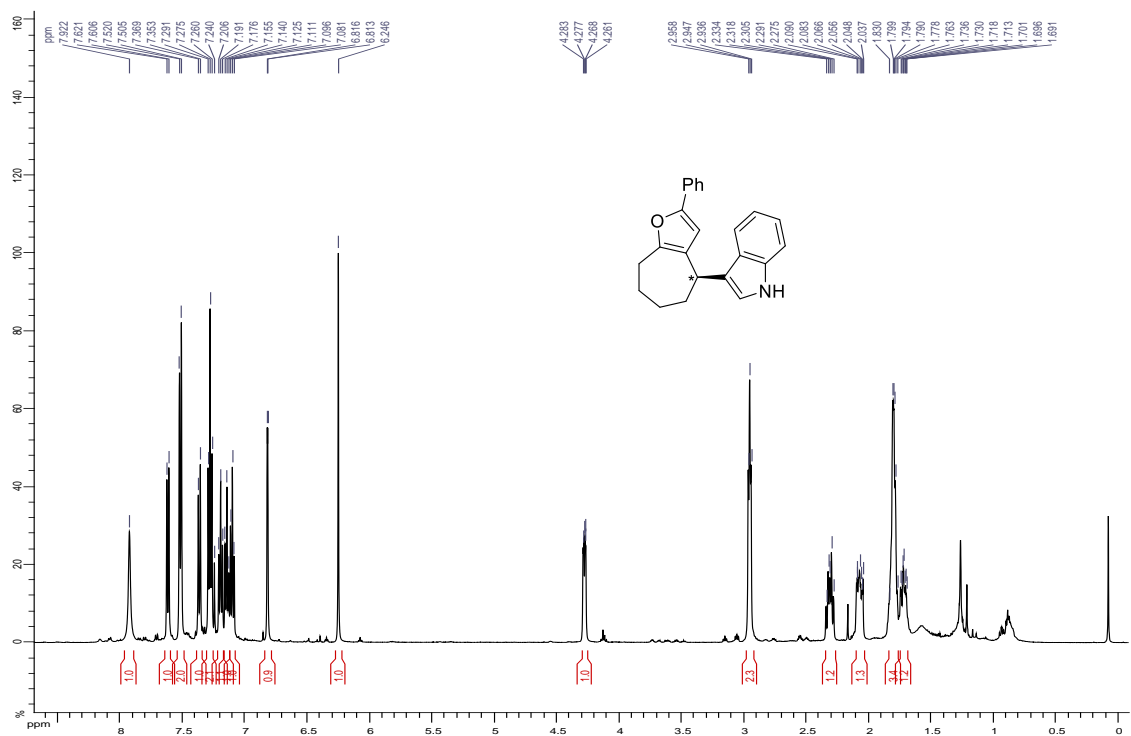




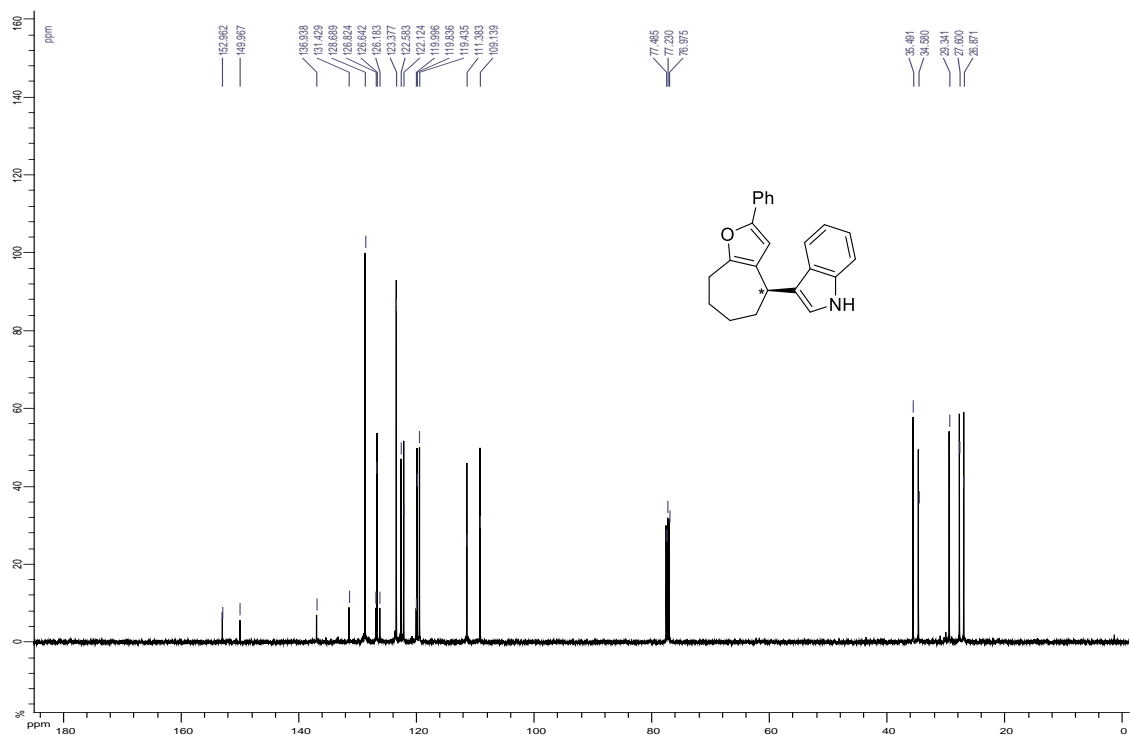
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (R)-3-(2-phenyl-5,6-dihydro-4H-cyclopenta[b]furan-4-yl)-1H-indole (10fa)



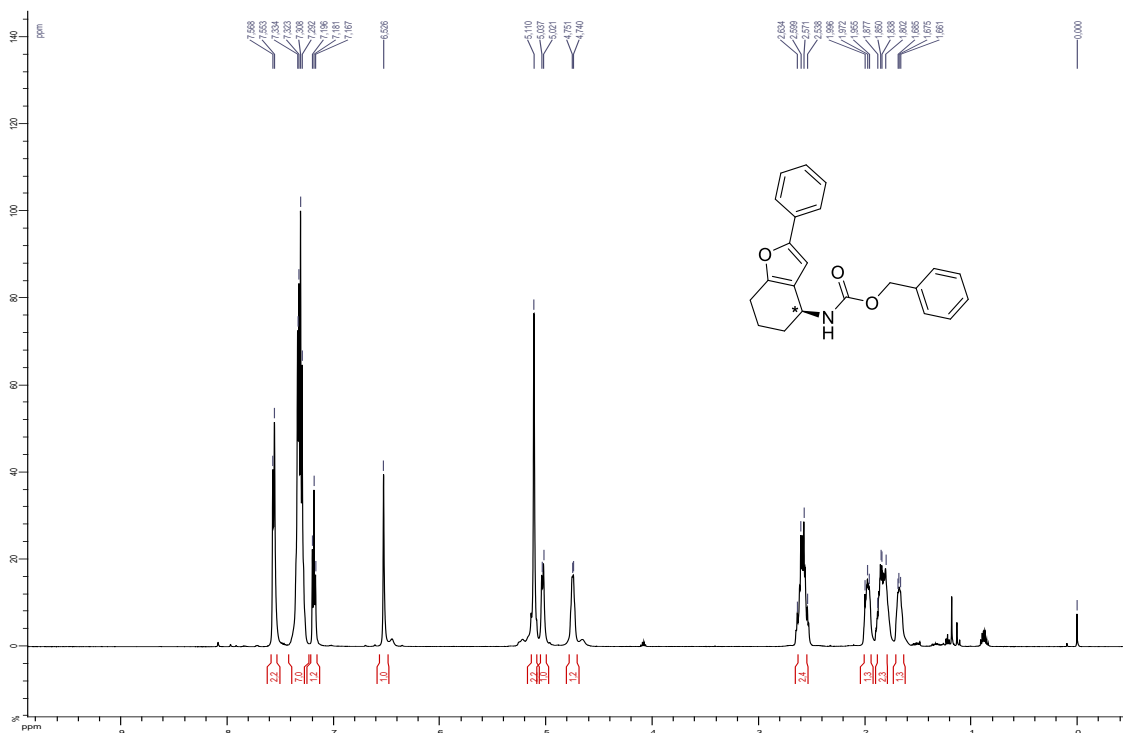
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) spectrum of (R)-3-(2-phenyl-5,6-dihydro-4H-cyclopenta[b]furan-4-yl)-1H-indole (10fa)



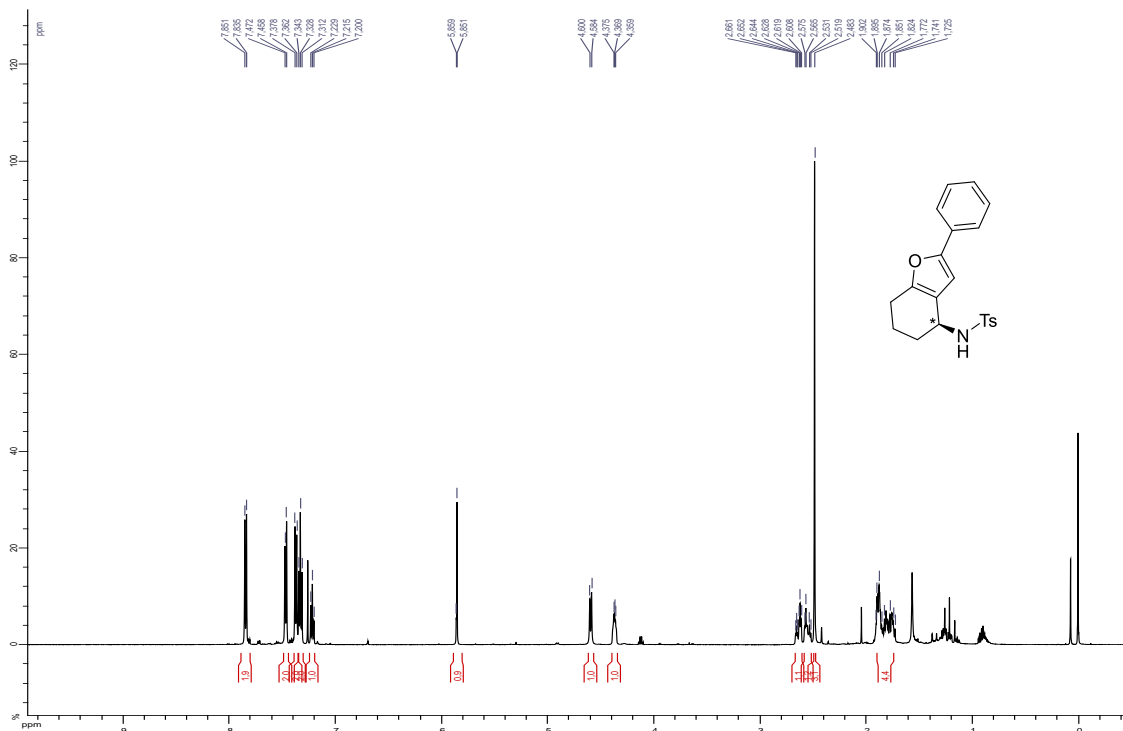
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of **(R)-3-(2-phenyl-5,6,7,8-tetrahydro-4H-cyclohepta[b]furan-4-yl)-1H-indole (10ga)**



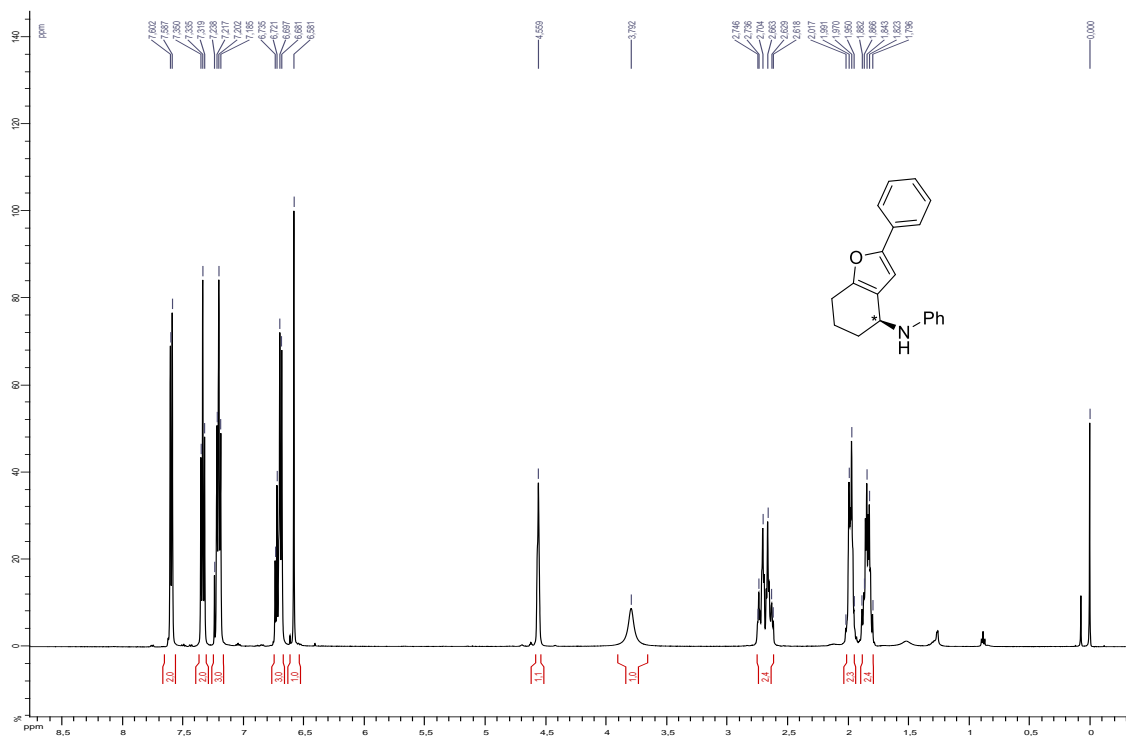
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) spectrum of **(R)-3-(2-phenyl-5,6,7,8-tetrahydro-4H-cyclohepta[b]furan-4-yl)-1H-indole (10ga)**



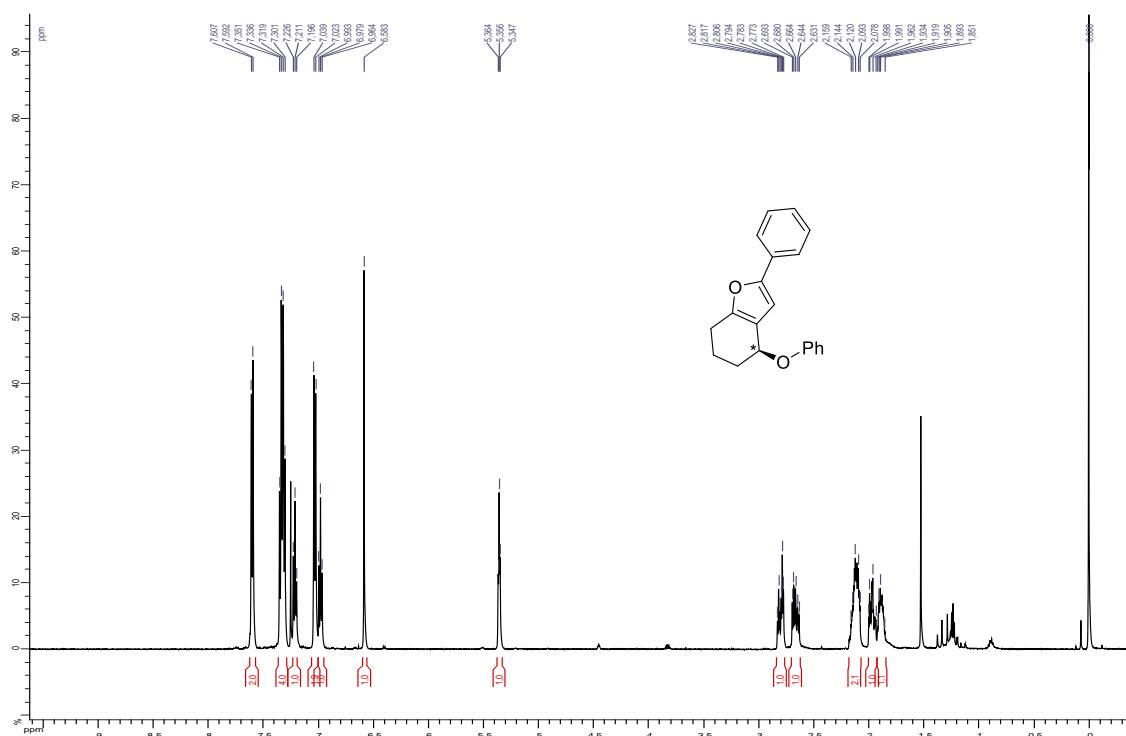
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of benzyl (S)-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)carbamate (16a)



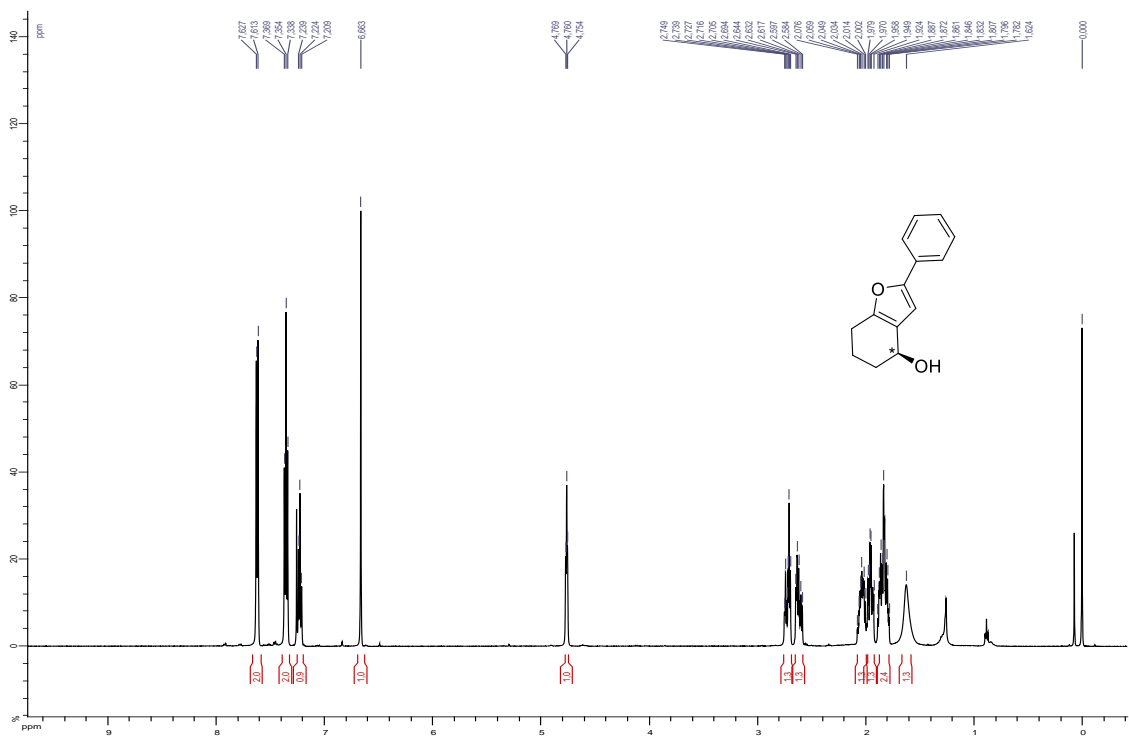
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (S)-4-methyl-N-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)benzenesulfonamide (16b)



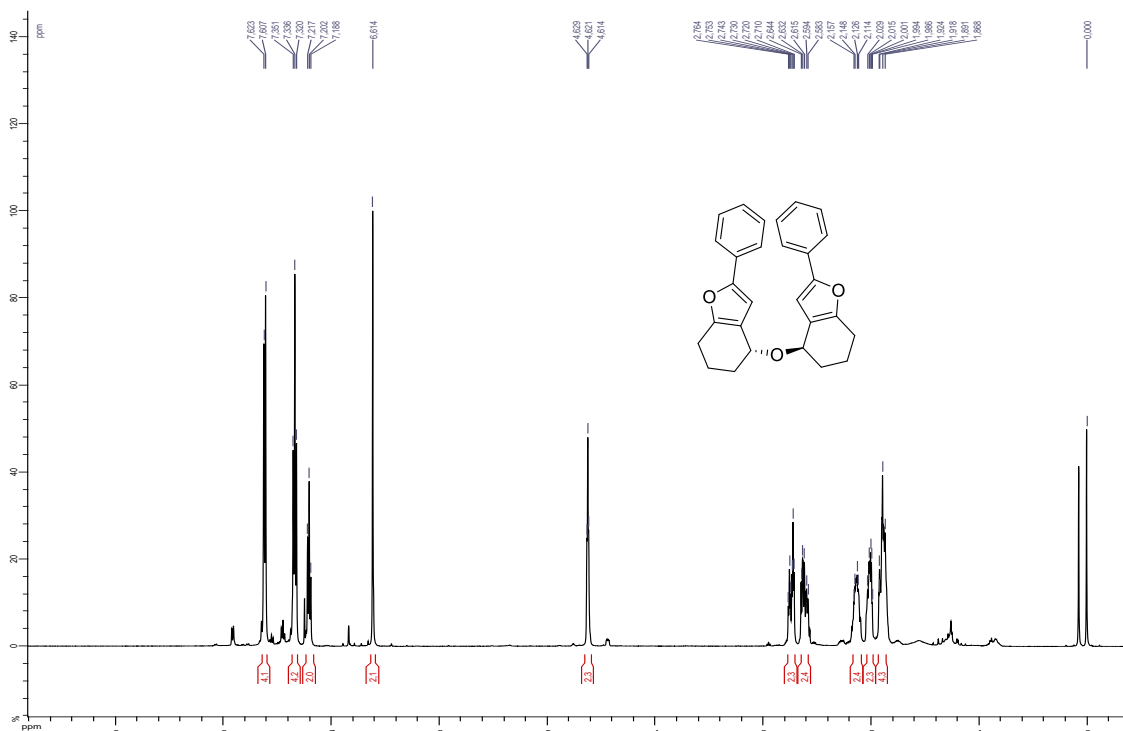
**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (S)-N,2-diphenyl-4,5,6,7-tetrahydrobenzofuran-4-amine (16c)**



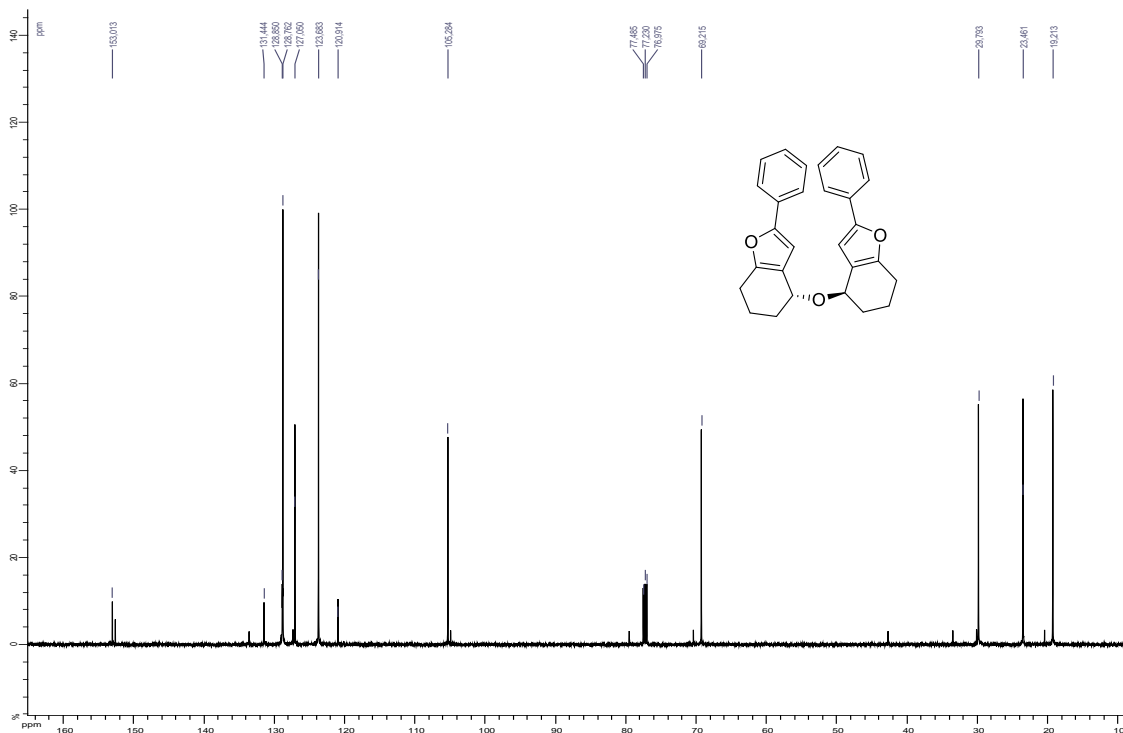
**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (S)-4-phenoxy-2-phenyl-4,5,6,7-tetrahydrobenzofuran (16d)**



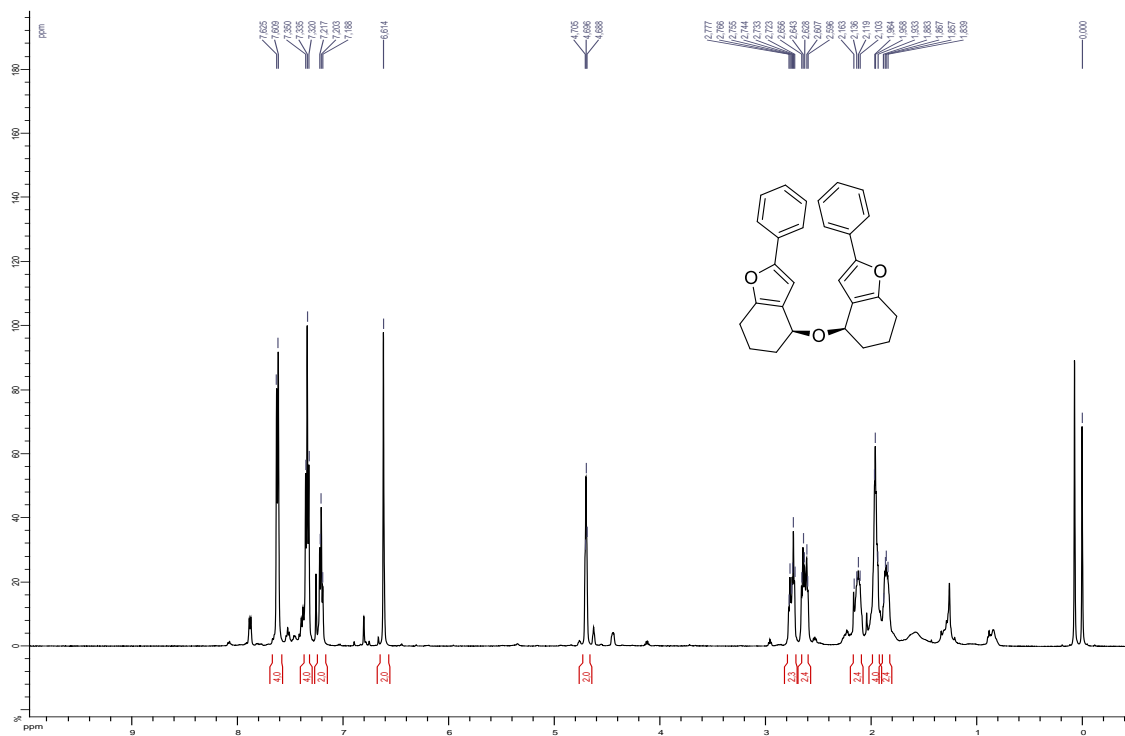
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) spectrum of (S)-2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-ol (16e)



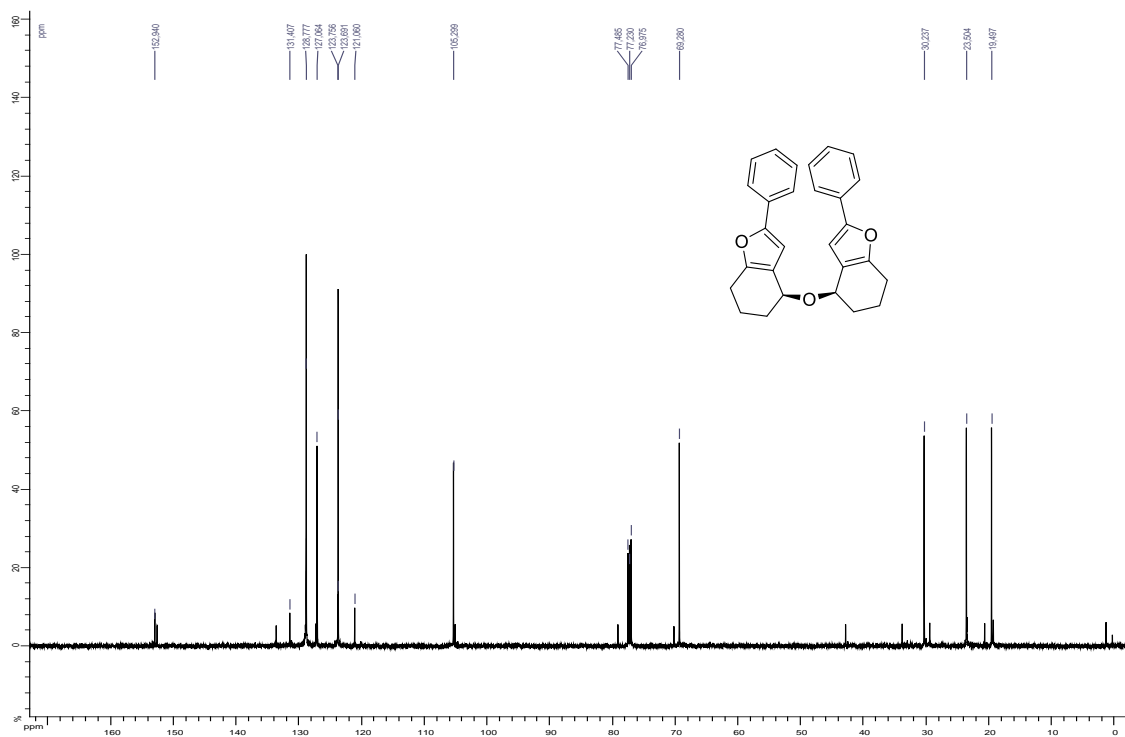
**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of  
(S)-2-phenyl-4-(((R)-2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)oxy)-4,5,6,7-tetrahydrobenzofuran (**16eb**)**



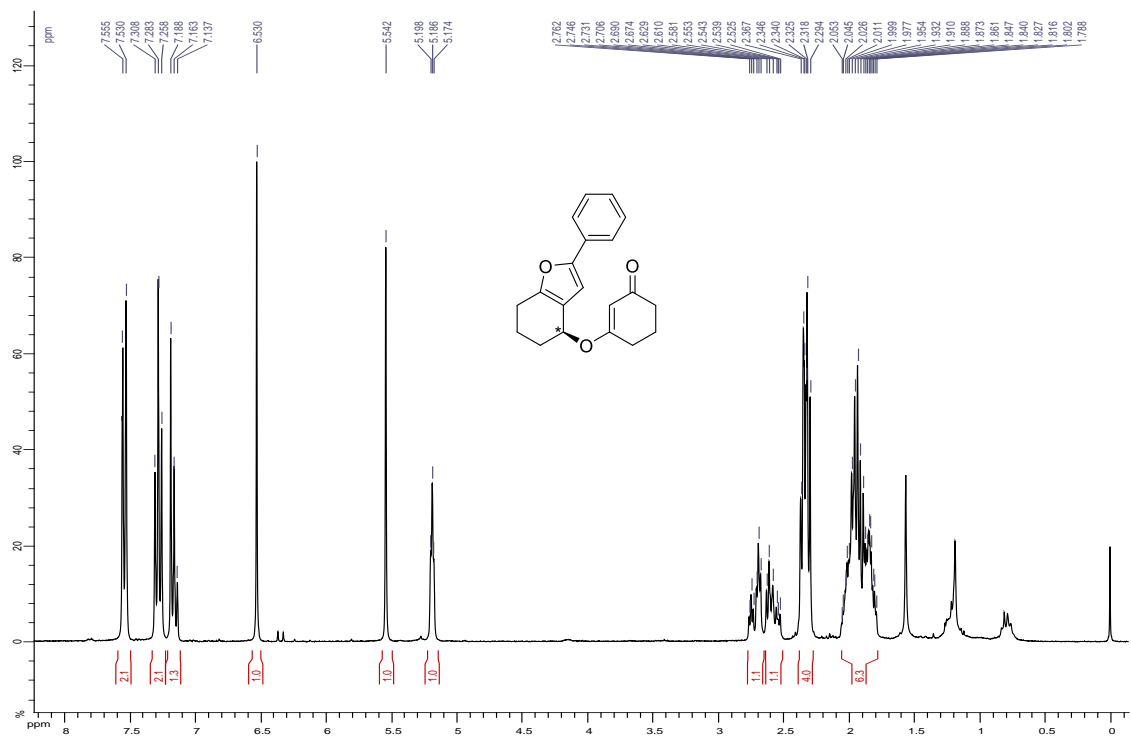
**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) spectrum of  
(S)-2-phenyl-4-(((R)-2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)oxy)-4,5,6,7-tetrahydrobenzofuran (**16eb**)**



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (4*R*,4'*R*)-4,4'-oxybis(2-phenyl-4,5,6,7-tetrahydrobenzofuran) (**16ec**)



<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) spectrum of (4*R*,4'*R*)-4,4'-oxybis(2-phenyl-4,5,6,7-tetrahydrobenzofuran) (**16ec**)



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) spectrum of (R)-2-(2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)cyclohexane-1,3-dione (16f)