Supporting Information

A crystalline chiral phosphide for the synthesis of the first P-stereogenic P(III) fluoride: A stable ligand for the Rh-catalyzed asymmetric arylation of isatins

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General Remarks

All reactions were carried out under anaerobic and anhydrous conditions, using standard Schlenk and glovebox techniques unless otherwise stated. All starting materials, reagents and solvents, were purchased from commercial sources and used without further purification, except if noted otherwise. All technical solvents were purified by distillation on a rotary evaporator before using. Et_2O, THF, benzene, *n*-hexane and *n*-pentane were distilled from purple Na/benzophenone solutions, toluene from Na, C_6D_6 from Na/K alloy, CH_2Cl_2 from CaH_2, and NEt_3 from K. $CDCl_3$ and CD_2Cl_2 were degassed with three freeze-pump-thaw cycles and then kept over activated molecular sieves (4 Å) in a glovebox. Sealed bottles of DME (TCI, >99%), BH_3•THF (Sigma-Aldrich, 1.0 M in THF), PCl_3 (Aldrich, 99%), and *p*-TolMgBr (TCI, 1M in THF) were opened in a glovebox and used as received. Isatins (BLD, 98%) were opened in a glovebox and recrystallized from acetone/*n*-pentane mixture before use. $LiAlH_4$ (abcr, 97 %) was purified by extraction with dry Et_2O before use, DABCO (Aldrich, ReagentPlus®, ≥99%) was dried over molecular sieves (4 Å) in Et_2O solution, filtered and dried in high vacuum, ICH_3 (abcr, 99%) and (–)-sparteine (Aldrich, 99%) were distilled from CaH_2, and *N*-Fluorobenzenesulfonimide (abcr, 97%) was recrystallized from dry Et_2O. *rac*-**3**,[1] $[Rh(COE)_2Cl]_2$,[2] *t*-BuMgCl,[3] and protected isatins[4] were synthesized according to published procedures. Elemental analyses (EAs) were performed on a Euro EA 3000 analyzer, and air-sensitive samples were handled and prepared in a glovebox. NMR spectra were recorded on a Bruker BioSpin 600 MHz or a JEOL 400 MHz spectroscope. HPLC was performed on a Shimadzu LC10 series instrument with a diode array UV-VIS detector.

Syntheses of compounds

***N*-(*tert*-butylphosphanyl)-10-phenyl-5H-dibenzo[*b*,*f*]azepine (*rac*-5).** A solution of $LiAlH_4$ (4.86 g, 128 mmol) in 200 mL of Et_2O was added to a cold slurry of *rac*-**3** (50.0 g, 128 mmol) in Et_2O (400 mL) over 30 min at -35 °C. The lime green mixture was warmed to RT and stirred for 3 h. The solvent was removed in HV and the residue extracted in benzene (400 mL), centrifuged (10 min, 6000 rpm), and the supernatant separated *via* decantation. The residue was re-extracted with benzene (2 x 200 mL) and centrifuged. The combined supernatants were evacuated to dryness to afford 40.5 g (89%) of a greenish solid. Anal. EA found: C, 80.98, H, 6.79, N 3.84.; calcd. for $C_{24}H_{24}NP$: C, 80.65, H 6.77, N 3.92. ^{31}P NMR (242 MHz, C_6D_6, no H-decoupling): δ 60.9 (dm, $^1J_{PH}$ = 206 Hz, $^3J_{HP}$ = 14.6 Hz). ^1H NMR (600 MHz, C_6D_6): δ 7.50 (m, 2H); 7.45 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 1H); 7.20 – 7.25 (m, 2H); 7.14 – 7.19 (m, 2H); 7.12 (td, *J* = 7.7 Hz, *J* = 1.5 Hz, 1H); 7.04 – 7.09 (m, 2H); 7.01 (d, *J* = 7.3 Hz, 1H); 6.97 (dd, *J* = 7.9 Hz, *J* = 1.3 Hz, 1H); 6.91 (m, 1H); 6.75 (m, 1H); 5.92 (d, $^1J_{HP}$ = 206 Hz, 1H); 1.03 (d, $^3J_{H,P}$ = 13.5 Hz, 9H). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6): δ 153.0 (d, $J_{C,P}$ = 7.7 Hz), 151.7 (d, $J_{C,P}$ = 24.2

Hz), 143.7, 143.6, 137.4, 135.2 (d, $J_{C,P}$ = 3.3 Hz), 130.8, 130.3, 129.8, 129.1, 129.0, 128.9, 128.4, 128.2, 127.9, 127.3, 127.2, 125.7, 124.6, 124.5, 32.8 (d, $J_{C,P}$ = 14.3 Hz, P*C*$(CH_3)_3$), 27.5 (d, $J_{C,P}$ = 15.4 Hz, PC(CH$_3)_3$).

***N*-(Boranato-*tert*-butylphosphinyl)-10-phenyldibenzo[*b,f*]azepine (*rac*-6).** A solution of BH_3•THF[5] (0.8 M, 172.5 mL, 138 mmol) was added dropwise at room temperature to a solution of *rac*-**5** (43.0 g, 120 mmol) in 215 mL of benzene over 10 min. The resulting colorless solution was stirred for 2 h. After this time, the solvent was removed in HV and the residue was washed with pentane and filtered through GF/B (2 x 200 mL) to give 42.0 g (94%) of a white solid. EA found: C, 76.68; H, 7.52; N, 3.51; calcd. for $C_{24}H_{27}BNP(THF)_{0.12}$: C, 76.76; H, 7.64; N, 3.47. ^{31}P NMR (242 MHz, C_6D_6, H-coupled) δ 87.4 (dm, $^1J_{P,H}$ = 380 Hz). ^{1}H NMR (600 MHz, C_6D_6) δ 8.18 (d, J = 7.9 Hz, 1H); 7.7 (d, J = 7.2 Hz, 2H); 7.61 (d, J = 7.9 Hz, 1H); 7.48 (t, J = 7.2 Hz, 2H); 7.40 – 7.45 (m, 2H); 7.34 (t, J = 8.0 Hz, 1H); 7.24 – 7.32 (m, 3H); 7.01 (t, J = 7.5 Hz, 1H); 6.35 (dq, J = 380 Hz, J = 6.3 Hz, 1H); 1.21 (d, $J_{H,P}$ = 15.0 Hz, 9H). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6) δ 149.8, 144.9 (d, $J_{C,P}$ = 5.5 Hz), 144.4, 143.7, 137.8, 136.5 (d, $J_{C,P}$ = 2.2 Hz), 131.2, 130.9, 130.6, 130.0, 129.8 (2C), 129.6, 129.1 (2C), 128.9, 128.7, 127.9 (d, $J_{C,P}$ = 2.2 Hz), 126.9, 126.6, 124.6, 33.5 (d, $J_{C,P}$ = 30.8 Hz, P*C*$(CH_3)_3$), 26.5 (d, $J_{C,P}$ = 3.3 Hz, PC(CH$_3)_3$).

[Lithium (–)-Sparteine] [*N*-(Boranato-*tert*-butylphosphide)-10-phenyldibenzo[*b,f*]azepine] ((p*R*,*S*$_P$)-7). Finely ground *rac*-**6** (23.39 g, 63.00 mmol) and (–)-sparteine (22.16 g, 94.55 mmol) were mixed in Et_2O (100 mL) to form a white emulsion and cooled to –40 °C, to which *n*-BuLi (77.5 mL, 1.0 M in *n*-hexane) was added dropwise under vigorous stirring over 5 min to form a yellow solution. This solution was allowed to warm to room temperature, during which time a mustard yellow precipitate formed and the supernatant solution turned orange. The mixture was stirred for 1 h at RT and then filtered through a glass fiber filter (Whatman GF/B). The solid was washed thoroughly with Et_2O (4 x 30 mL) and dried in HV to yield 13.71 g (36%) of a mustard yellow powder.[6] EA found: C, 76.67; H, 8.80; N, 6.90; calcd. for $C_{39}H_{52}BLiN_3P$: C, 76.59; H, 8.57; N, 6.87. ^{7}Li NMR (155 MHz, C_6D_6) δ 0.80 (s, 1Li). ^{11}B NMR (128 MHz, C_6D_6) δ -31.5 (m, 1B). ^{11}B NMR {^{1}H} (128 MHz, C_6D_6) δ -31.5 (d, J = 39.70 Hz 1B). ^{31}P NMR (242 MHz, C_6D_6) δ 96 (m, 1P). ^{1}H NMR (600 MHz, C_6D_6) δ 8.23 (d, J = 8.1 Hz, 1H); 7.93 (d, J = 7.9 Hz, 1H); 7.60 (d, J = 7.3 Hz, 2H); 7.32 (t, J = 7.2 Hz, 1H); 7.25 (m, 2H); 7.12 – 7.23 (m, 5H); 7.03 (m, 1H); 6.82 (d, J = 7.4 Hz, 1H); 3.30 (t, J = 12.2 Hz, 1H); 2.98 (d, J = 11.0 Hz, 1H); 2.83 (d, J = 11.2 Hz, 1H); 2.71 (d, J = 11.9 Hz, 1H); 2.51 (d, J = 13.4 Hz, 1H), 2.41 (d, J = 10.5 Hz, 1H); 2.0 (m, 2H); 1.79 (dd, J = 12.1 Hz, J = 2.8 Hz, 1H); 1.58 (m, 1H); 1.54 (d, J = 11.2 Hz, 9H) 0.81 – 1.5 (m, 16H); 0.76 (d, J = 11.9 Hz, 1H), 0.59 (d, J = 13.2 Hz, 1H). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6) δ 158.4 (d, $J_{C,P}$ = 17.6 Hz), 144.8, 144.6, 137.1, 136.7, 131.5, 130.6, 129.9, 129.8, 129.3, 129.2, 129.1, 128.9, 128.8, 128.7, 128.2, 128.1, 128.0, 126.9, 123.0, 122.7, 66.1, 60.5, 59.1, 57.1, 53.2, 45.4, 34.5, 34.4, 33.5 (d, $J_{C,P}$ = 22.0

Hz, P*C*(CH_3)$_3$), 30.2, 29.1 (d, $J_{C,P}$ = 14.0 Hz, PC(*C*H_3)$_3$), 27.7, 25.1, 24.5, 24.1, 23.7, 17.7. X-ray quality crystals were grown from vapor diffusion of Et_2O into a concentrated 1,2-difluorobenzene solution of (p*R*,*S*$_P$)-**7** at –35 °C. The (p*S*,*R*$_P$)-**7** antipode was synthesized by the same procedure, using 1.027 g (2.693 mmol) of *rac*-**6** and 0.956 g (4.039 mmol) of (+)-sparteine, obtaining 0.708 g (43%) of product. All NMR data are consistent with (p*R*,*S*$_P$)-**7**.

(p*R*,*R*$_P$)-*N*-(boronato-*tert*-Butyl(methyl)phosphinyl)-10-phenyl-dibenzo[*b,f*]-azepine ((p*R*,*R*$_P$)-8). CH_3I (0.28 mL, 4.5 mmol) was added to a well stirred slurry of phosphide (p*R*,*S*$_P$)-**7** (1400 mg, 2.289 mmol) in 20 mL of Et_2O at -40 °C. The resulting white mixture was stirred for 1h before evacuating to dryness and submitting to flash column chromatography (9:1 hexane-NEt_3). The resulting colorless crystalline solid was washed with cold pentane (5 mL) to yield 752 mg (85%) of a white solid. EA found: C 77.91, H 7.65, N, 3.61; calcd. for $C_{25}H_{26}NP$: C 77.93, H 7.69, N, 3.64. ^{31}P NMR (162 MHz, $CDCl_3$) δ 84 (m, 1P). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.8 Hz, 1H); 7.59 (m, 2H); 7.3 – 7.5 (m, 7H); 7.25 (m, 1H); 7.13 (s, 1H); 7.10 (t, *J* = 7.4 Hz, 1H); 6.98 (dd, *J* = 7.7 Hz, *J* = 1.2 Hz, 1H); 1.29 (d, *J* = 8.4 Hz, 3H), 1.19 (d, *J* = 14.2 Hz, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.9 (d, $J_{C,P}$ = 5.0 Hz), 144.2, 143.4, 142.9, 138.4 (d, $J_{C,P}$ = 1.5 Hz), 137.3 (d, $J_{C,P}$ = 1.0 Hz), 130.4, 129.6, 129.4 (2C), 129.3, 129.1 (2C), 128.9, 128.5 (2C), 128.0, 126.7, 126.3 (d, $J_{C,P}$ = 2.2 Hz), 33.1 (d, $J_{C,P}$ = 33.6 Hz, P*C*(CH_3)$_3$), 26.4 (d, $J_{C,P}$ = 3.0 Hz, PC(*C*H_3)$_3$), 10.0 (d, $J_{C,P}$ = 37.6 Hz, P*C*H_3). Chiral HPLC: 99 % *ee* (Daicel OD-H column, 99:1 hexane/*i*-PrOH; 0.4 mL/min, 15.6 min (major isomer), 23.2 min).

(p*R*,*R*$_P$)-*N*-(*tert*-Butyl(methyl)phosphinyl)-10-phenyl-dibenzo[*b,f*]-azepine ((p*R*,*R*$_P$)-3). (p*R*,*R*$_P$)-**8** (720 mg, 1.87 mmol) and DABCO (629 mg, 5.61 mmol) were dissolved in 12 mL of benzene and stirred at 50 °C for 15 h. Then, the solvent was removed in HV, the product extracted with pentane (2 x 9 mL, filtration over GF/B). The combined extracts were evaporated to dryness and the excess DABCO was sublimed off to afford 583 mg (84%) of an off-white powder. EA found: C 80.92, H 7.09, N 3.80; calcd. for $C_{25}H_{29}BNP$: C 80.84, H 7.06, N 3.77. %. ^{31}P NMR (162 MHz, $CDCl_3$) δ 69.6 (s, 1P). ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.40 – 7.46 (m, 2H); 7.10 – 7.38 (m, 8H); 7.01 – 7.08 (m, 1H); 6.99 (s, 1H); 6.96 (t, *J* = 6.87 Hz, 1H); 6.89 (dd, *J* = 7.9 Hz, *J* = 1.5 Hz, 1H); 1.29 (d, *J* = 7.2 Hz, 3H), 0.92 (d, *J* = 13.0 Hz, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.0, 148.9, 147.8, 142.4 (d, J_{CP} = 3.4 Hz), 137.5, 134.9 (d, J_{CP} = 2.6 Hz), 129.5 (d, J_{CP} = 3.4 Hz), 128.4, 128.03, 127.96, 127.9 (2C), 127.6, 127.3 (2C), 127.2, 127.1 (2C), 126.5, 124.1, 123.9, 31.7 (d, J_{CP} = 17.2 Hz, P*C*(CH_3)$_3$), 25.5 (d, J_{CP} = 16.4 Hz, PC(*C*H_3)$_3$), 11.4 (d, J_{CP} = 24.14 Hz, P*C*H_3). This product (100 mg, 0.269 mmol) was re-protected with BH_3•THF (1 M, 0.3 mL, 0.3 mmol) and after column chromatography, all analytical data corresponded to (p*R*,*R*$_P$)-**8** with no alteration of optical purity.

(p*R*,*R*P) *N*-(boranato-*tert*-Butylfluorophosphinyl)-10-phenyl-dibenzo[*b*,*f*]-azepine ((p*R*,*R*P)-9). A solution of (p*R*,*S*P)-**7** (2.028 g, 3.316 mmol) in toluene (30 mL) was added dropwise over 5 min to a solution of *N*-fluorobenzenesulfonimide (1.046 g, 3.317 mmol) in toluene (30 mL) at –35 °C. The reaction mixture was allowed to warm to room temperature forming a white mixture. After stirring for 20 h, the solvent was removed in HV. The product was extracted with Benzene and subjected to centrifugation for 10 min at 6000 rpm (3 x 50 mL). The combined supernatants were evaporated to dryness. The residue was slurried in pentane (50 mL) for 3 h, filtered over GF/B and further washed with pentane (2 x 30.0 mL; from the pentane washings (–)-sparteine was recovered quantitatively after evaporation and purification by Kugelrohr distillation. ^{1}H NMR (see Figure S39) and $[\alpha]_D$ correspond with literature data). The remaining solid was HV dried and 35 mL of CH_2Cl_2 were added, centrifuged for 10 min at 6000 rpm. The supernatant solution was separated from a white solid by decantation and layered with 80 mL of pentane. This afforded white crystals, which were separated by decantation and HV dried to yield a first crop of crystalline material (967 mg). A second crop of 116 mg crystallized from the mother liquor after cooling to –35 °C and was recovered by filtration for a total yield of 84%. EA found: N 3.82%, C 73.48%, H 6.45%; calcd. for $(C_{24}H_{26}BFNP)(CHCl_3)_{0.03}$: N 3.57%, C 73.47%, H 6.68%. $[\alpha]_D$ = +223° (c = 0.9, THF). ^{31}P{H} NMR (162 MHz, $CDCl_3$): δ 155.9 (dm, J_{PF} = 1051.3 Hz). ^{19}F NMR (377 MHz, $CDCl_3$): δ -109.39 (dq, J_{FP} = 1049.1 Hz, J_{FH} = 16.1 Hz). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 (d, J = 8.0 Hz, 1H), 7.51 – 7.48 (m, 3H), 7.45 – 7.42 (m, 2H), 7.42 – 7.37 (m, 4H), 7.32 – 7.28 (m, 2H), 7.20 (t, J = 8.2 Hz, 1H), 7.12 (dd, J = 7.9, 1.4 Hz, 1H), 1.09 (d, $^{3}J_{H,P}$ = 15.7 Hz, 9H), 0.45 – 0.26 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.43 (dd, J = 4.5, 3.3 Hz), 142.33, 142.23, 142.03 (dd, J = 7.7, 3.7 Hz), 136.33 (t, J = 3.5 Hz), 135.12 (t, J = 5.5 Hz), 131.05, 130.13, 129.65, 129.19, 128.93, 128.84, 128.67, 128.17, 127.87, 127.25 (d, J = 6.6 Hz), 35.13 (dd, J = 42.7, 14.6 Hz), 26.01 (d, J = 3.9 Hz). Optical purity was determined to be >99 % *ee via* chiral HPLC analysis. Column: OD-H, 99:1 hexane/*i*-PrOH, flow: 0.8 mL/min, 6.057 (major isomer).

***N*-(*tert*-butylfluorophosphinyl)-10-phenyl-dibenzo[*b*,*f*]-azepine ((p*R*,*R*P)-10).** NEt_3 (11.20 g, 110.7 mmol) was added via syringe to a solution of (p*R*,*R*P)-**8** (1080 mg, 2.774 mmol) in benzene (20 mL). The resulting colorless solution was stirred for 7 d at RT. After this time, the solvent was removed in vacuo and the residue slurried in cold pentane (10 mL) for 1 h, rapidly filtered (GF/B) while cold and further washed with cold pentane (5 mL). Drying in HV yielded 1020 mg (98%) of a white powder. EA found: N 4.32%, C 77.28%, H 6.01%; calcd. for $(C_{24}H_{23}FNP)(C_6H_6)_{0.08}$ $(NEt_3)_{0.09}$: N 3.91%, C 76.90%, H 6.40%. $[\alpha]_D$ = +166° (c = 1, toluene). ^{31}P{H} NMR (162 MHz, C_6D_6) δ 176.67 (d, J_{PF} = 970.7 Hz). ^{19}F NMR (376 MHz, C_6D_6) δ -132.25 (d, J_{FP} = 970.6 Hz). ^{1}H NMR (400 MHz, C_6D_6) δ 7.59 (d, J = 8.9 Hz, 1H), 7.50 (d, J = 7.9 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.19 – 7.13 (m, 1H), 7.12 – 7.08 (m,

2H), 7.05 – 6.99 (m, 2H), 6.97 – 6.92 (m, 3H), 6.89 – 6.83 (m, 1H), 6.73 – 6.67 (m, 1H), 0.89 (d, $^{3}J_{H,P}$ = 13.8 Hz, 9H). $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6) δ 149.00 (dd, J = 27.0, 2.6 Hz), 146.52 (d, J = 8.7 Hz), 143.60 (d, J = 0.4 Hz), 143.40, 136.63 (d, J = 3.2 Hz), 135.40 (dd, J = 5.5, 5.0 Hz), 130.77, 130.13 (d, J = 0.7 Hz), 130.01, 129.82 , 129.42, 129.40, 128.94 (t, J = 2.4 Hz), 128.82, 126.80 (dd, J = 14.5, 1.0 Hz), 126.32 (d, J = 0.7 Hz), 125.93 (d, J = 1.1 Hz), 35.71 (dd, J = 25.3, 12.1 Hz), 25.42 (dd, J = 19.5, 1.7 Hz. (p*R*,*R*$_P$)-**10** (100 mg, 0.266 mmol) was re-protected with BH_3•THF (1 M, 0.3 mL, 0.3 mmol) and after pentane washing, filtration and HV drying, all analytical data of the product corresponded to (p*R*,*R*$_P$)-**9** with no alteration of optical purity.

[((p*R*,*R*$_P$)-1)RhCl]$_2$ ((*R*$_N$,*S*$_P$)-11): A solution of (p*R*,*R*$_P$)-**3** (200.3 mg, 0.5392 mmol) in of C_6H_6 (1.5 mL) was added dropwise to a well stirred slurry of $[RhCl(COE)_2]_2$ (193.6 mg, 0.2698 mmol) in C_6H_6 (1 mL). The resulting deep red solution was stirred for 2 h and evaporated to a red solid, which was washed with pentane (3 x 2 mL, GF/B filtration), and dried for 4 h in HV to give 272 mg (99%) of a brick red powder. EA found: C 58.94, H 5.30, N 2.81; calcd. for $C_{50}H_{52}Cl_2N_2P_2Rh_2$: C 58.90, H 5.14, N 2.75. ^{31}P NMR (162 MHz, C_6D_6) δ 169 (d, $J_{P\text{-}Rh}$ = 203.75 Hz, 2P). ^{1}H NMR (400 MHz, C_6D_6) δ 8.76 (d, J = 7.7 Hz, 2H); 7.37 (m, 2H); 7.29 (d, J = 7.4 Hz, 2H); 7.04 – 7.15 (m, 10H); 6.91 – 7.01 (m, 4H); 6.75 – 6.86 (m, 4H); 6.63 (t, J = 7.6 Hz, 2H); 5.16 (s, 2H); 1.11 (d, J = 8.8 Hz, 6H); 0.95 (d, J = 14.0 Hz, 18H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 145.7, 144.7 (d, $J_{C,P}$ = 7.7 Hz), 144.6, 144.1, 142.5 (d, $J_{C,P}$ = 7.7 Hz), 134.7, 129.7, 129.3 (d, $J_{C,P}$ = 3.3 Hz), 128.6, 128.5, 128.0, 127.1, 126.6, 126.5, 126.2, 126.1, 68.5 (d, $J_{C,P}$ = 15.4 Hz, P*C*$(CH_3)_3$), 59.7 (d, $J_{C,P}$ = 15.4 Hz, P*C*H_3), 35.7 (d, $J_{C,P}$ = 26.4 Hz), 27.2 (d, $J_{C,P}$ = 2.2 Hz, PC(*C*$H_3)_3$), 11.6 (d, $J_{C,P}$ = 33.0 Hz).

[((p*R*,*R*$_P$)-9)RhCl]$_2$ (*anti*-(*R*,*S*)-12). A solution of (p*R*,*R*$_P$)-**10** (203.6 mg, 0.5423 mmol) in C_6H_6 (1.5 mL) was added dropwise to a well stirred slurry of $[Rh(COE)_2Cl]_2$ (194.6 mg, 0.2712 mmol) in C_6H_6 (0.5 mL). The resulting red solution was left undisturbed for 3 d at RT to produce diffraction-quality red single crystals, which were separated from the solution by decantation, washed with cold pentane (2 x 0.5 mL), and dried in HV to yield a microcrystalline orange powder (237 mg, 85%). EA found: N 3.06%, C 57.51%, H 4.49%; calcd. for $(C_{48}H_{46}Cl_2F_2N_2P_2Rh_2)(C_6H_6)_{0.4}$: N 2.65%, C 57.17%, H 4.61%. $^{31}P\{H\}$ NMR (162 MHz, toluene-d_8) δ 231.50 (dd, J_{PF} = 1065.9 Hz, J_{PRh} = 249.6 Hz). ^{1}H NMR (600 MHz, toluene-d_8) δ 8.45 (d, J = 7.8 Hz, 2H), 7.29 – 7.24 (m, 6H), 7.15 – 7.13 (m, 2H), 7.12 – 7.09 (m, 6H), 7.03 (td, J = 7.6, 1.4 Hz, 2H), 6.99 – 6.96 (m, 2H), 6.80 (td, J = 7.7, 1.4 Hz, 2H), 6.76 (td, J = 7.5, 1.2 Hz, 2H), 6.61 (t, J = 8.4 Hz, 2H), 5.70 (s, 2H), 1.11 (d, $^{3}J_{H,P}$ = 15.6 Hz, 18H). ^{19}F NMR (376 MHz, tol-d_8) δ -104.77 (dd, J = 1065.3, 16.4 Hz). $^{13}C\{^{1}H\}$ NMR (101 MHz, tol-d_8) δ 145.11 (d, J = 1.8 Hz), 144.91 (d, J = 7.1 Hz), 143.94, 142.21 (d, J = 7.6 Hz), 140.72 (d, J = 12.0 Hz), 134.77, 130.00, 129.80 (d, J =

3.7 Hz), 128.51, 128.30, 128.27, 128.22 (t, J = 1.2 Hz), 127.77, 127.51, 127.30 (d, J = 4.1 Hz), 127.10, 126.98, 72.76 (dd, J = 14.5, 1.0 Hz), 64.79 (dd, J = 13.7, 0.7 Hz), 25.98 (d, J = 4.7 Hz).

X-ray crystal structure determinations

CCDC-2390089 for (p*R*,*S*P)-**7**, **CCDC-2390090** for (p*R*,*R*P)-**9**, **CCDC-2390091** for (p*R*,*R*P)-**10**, **CCDC-2390092** for (p*R*,*S*P)-**11**, and **CCDC-2390093** for (p*R*,*R*P)-**12** contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: ++44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Suitable single crystals of the investigated compounds were embedded in protective perfluoropolyalkyether oil (viscosity 1800 cSt; ABCR GmbH) on a microscope slide and a single specimen was selected and subsequently transferred to the cold nitrogen gas stream of the diffractometer. Intensity data of (p*R*,*S*P)-**7**, (p*R*,*R*P)-**10**, (p*R*,*R*P)-**12**, and (p*R*,*S*P)-**11** was collected at 100 K on a Bruker Kappa *IμS* Duo diffractometer using MoK_α radiation (λ = 0.71073 Å) and QUAZAR focusing Montel optics, while intensity data for (p*R*,*R*P)-**9**, was collected at 100 K on a Bruker Smart diffractometer using MoK_α radiation (λ = 0.71073 Å, curved graphite monochromator). The measured data were processed with the APEX2[7] software package. Data were corrected for Lorentz and polarization effects, and a semi-empirical absorption correction based on multiple scans was applied. The structures were solved by direct methods (SHELXT)[8] and refined by full-matrix least-squares procedures on F^2 using SHELXL.[9] All non-hydrogen atoms were refined with anisotropic displacement parameters. If not otherwise noted all hydrogen atoms were placed in geometrically calculated positions and refined by using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2U_{eq} (CH or CH_2) or 1.5U_{eq} (CH_3) of its parent C-atom. Material for publication was prepared using Olex2.[109] The asymmetric unit of the crystal structure of (p*R*,*S*P)-**7** contained two symmetrically independent molecules of the Li complex and two molecules of diethyl ether. In the crystal structure of (p*R*,*R*P)-**9** the positions of the B1 bound hydrogen atoms were derived from a difference Fourier synthesis and their positional parameters were refined. In the crystal structure of (p*R*,*R*P)-**12** the complex molecule was located on a crystallographic twofold axis (Wyckoff position 2*b*) and, consequently, exhibits crystallographically imposed C_2 molecular symmetry. The compound crystallized with a total of 0.785(5) molecules of benzene and 0.215(5) molecules of *n*-pentane per formula unit. These solvent molecules shared a common site on a crystallographic twofold axis (Wyckoff position 2*a*).

Table S1. Crystallographic data, data collection, and refinement details for (p*R*,*S*P)-**7**, (p*R*,*R*P)-**9**, and (p*R*,*R*P)-**10**.

Compound	(p*R*,*S*P)-**7**	(p*R*,*R*P)-**9**	(p*R*,*R*P)-**10**
CCDC number	2390089	2390090	2390091
Identification code	RD2403	RD2102	RD2405
Empirical formula	$C_{43}H_{62}BLiN_3OP$	$C_{24}H_{26}BFNP$	$C_{24}H_{23}FNP$
Formula weight	685.67	389.24	375.40
Temperature/K	100(2)	100(2)	100(2)
Crystal system	trigonal	orthorhombic	orthorhombic
Space group	$P3_2$	$P2_12_12_1$	$P2_12_12_1$
a/Å	10.5231(4)	8.6965(4)	9.9288(4)
b/Å	10.5231(4)	14.1627(6)	12.0550(5)
c/Å	61.139(4)	16.9737(7)	16.3841(7)
α/°	90	90	90
β/°	90	90	90
γ/°	120	90	90
Volume/Å^3	5863.2(6)	2090.6(2)	1961.0(2)
Z	6	4	4
ρ_{calc}g/cm^3	1.165	1.237	1.272
μ/mm^{-1}	0.107	0.149	0.157
T_{min} / T_{max}	0.690 / 0.746	0.715 / 0.746	0.709 / 0.746
F(000)	2232	824	792
Crystal size/mm^3	0.36 × 0.18 × 0.16	0.18 × 0.12 × 0.11	0.28 × 0.25 × 0.23
Radiation	Mo$K\alpha$ (λ = 0.71073)	Mo$K\alpha$ (λ = 0.71073)	Mo$K\alpha$ (λ = 0.71073)
2Θ range for data collection/°	4.00 to 63.00	3.74 to 61.09	4.19 to 63.03
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -89 ≤ l ≤ 89	-12 ≤ h ≤ 12, -18 ≤ k ≤ 20, -22 ≤ l ≤ 22	-14 ≤ h ≤ 14, -17 ≤ k ≤ 17, -24 ≤ l ≤ 24
Reflections collected	164038	83783	72974
Independent reflections	26012 [R_{int} = 0.053]	6330 [R_{int} = 0.039]	6508 [R_{int} = 0.040]
Observed reflections [I>=2σ (I)]	24021	5585	6222
Data/restraints/parameters	26012/1/929	6330/0/265	6508/0/247
Goodness-of-fit on F^2	1.038	1.028	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0406, wR_2 = 0.0944	R_1 = 0.0328, wR_2 = 0.0719	R_1 = 0.0292, wR_2 = 0.0788
Final R indexes [all data]	R_1 = 0.0455, wR_2 = 0.0964	R_1 = 0.0441, wR_2 = 0.0760	R_1 = 0.0312, wR_2 = 0.0800
Largest diff. peak/hole / e Å^{-3}	0.540/-0.363	0.305/-0.198	0.359/-0.218
Absolute structure parameter[7]	0.039(14)	-0.013(16)	-0.040(16)

Table S2. Crystallographic data, data collection, and refinement details for (p*R*,*S*P)-**11**, and (p*R*,*R*P)-**12**.

Compound	(p*R*,*S*P)-**11**	(p*R*,*R*P)-**12**
CCDC number	2390092	2390093
Identification code	RD1717	RD2404
Empirical formula	$C_{50}H_{52}Cl_2N_2P_2Rh_2$	$C_{53.78}H_{53.28}Cl_2F_2N_2P_2Rh_2$
Formula weight	1019.59	1104.35
Temperature/K	100(2)	100(2)
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$C2$
a/Å	15.1140(9)	19.4283(12)
b/Å	15.1878(9)	9.8678(6)
c/Å	19.5291(11)	13.4258(9)
α/°	90	90
β/°	90	108.417(2)
γ/°	90	90
Volume/Å^3	4482.9(5)	2442.1(3)
Z	4	2
ρ_{calc}g/cm^3	1.511	1.502
μ/mm^{-1}	0.964	0.897
T_{min} / T_{max}	0.606 / 0.746	0.680 / 0.746
F(000)	2080	1124
Crystal size/mm^3	0.15 × 0.12 × 0.06	0.26 × 0.18 × 0.10
Radiation	Mo$K\alpha$ (λ = 0.71073)	Mo$K\alpha$ (λ = 0.71073)
2Θ range for data collection/°	3.40 to 59.17	6.05 to 65.18
Index ranges	$-20 \le h \le 20$, $-20 \le k \le 21$, $-26 \le l \le 26$	$-29 \le h \le 29$, $-14 \le k \le 14$, $-20 \le l \le 20$
Reflections collected	73987	115682
Independent reflections	12557 [R_{int} = 0.058]	8902 [R_{int} = 0.030]
Observed reflections [I>=2σ (I)]	11544	8746
Data/restraints/parameters	12557/0/531	8902/1/328
Goodness-of-fit on F^2	1.037	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0253, wR_2 = 0.0499	R_1 = 0.0128, wR_2 = 0.0322
Final R indexes [all data]	R_1 = 0.0318, wR_2 = 0.0523	R_1 = 0.0133, wR_2 = 0.0324
Largest diff. peak/hole / e Å^{-3}	0.454/-0.347	0.289/-0.228
Absolute structure parameter[7]	-0.023(10)	-0.010(4)

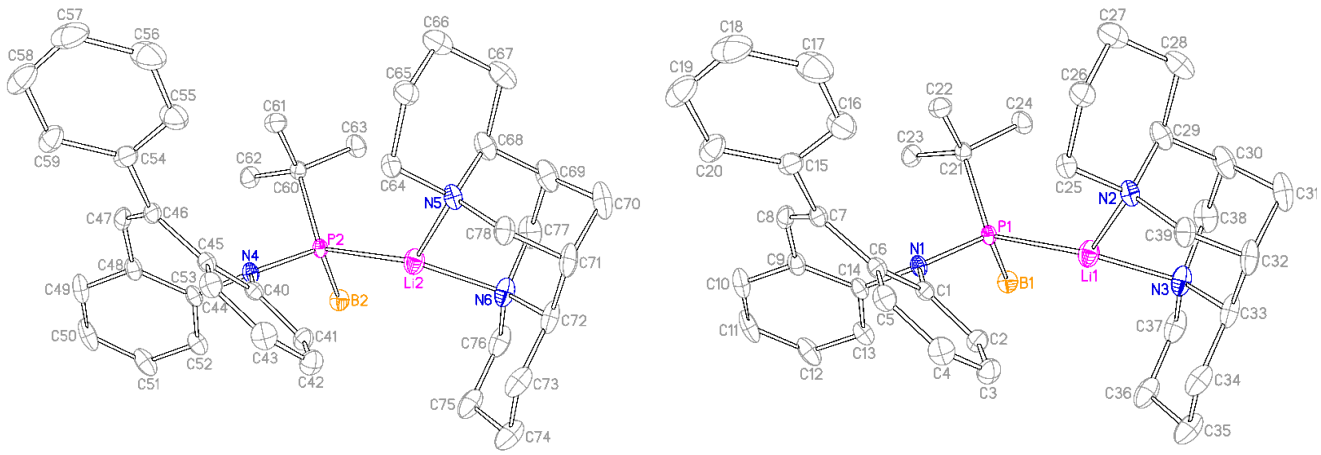


Figure S1. Molecular structures of the two independent molecules of (p*R*,*S*P)-**7** with the applied numbering scheme in crystals of (p*R*,*S*P)-**7** · $C_4H_{10}O$ (50% displacement ellipsoids, H atoms and solvent molecules omitted for clarity).

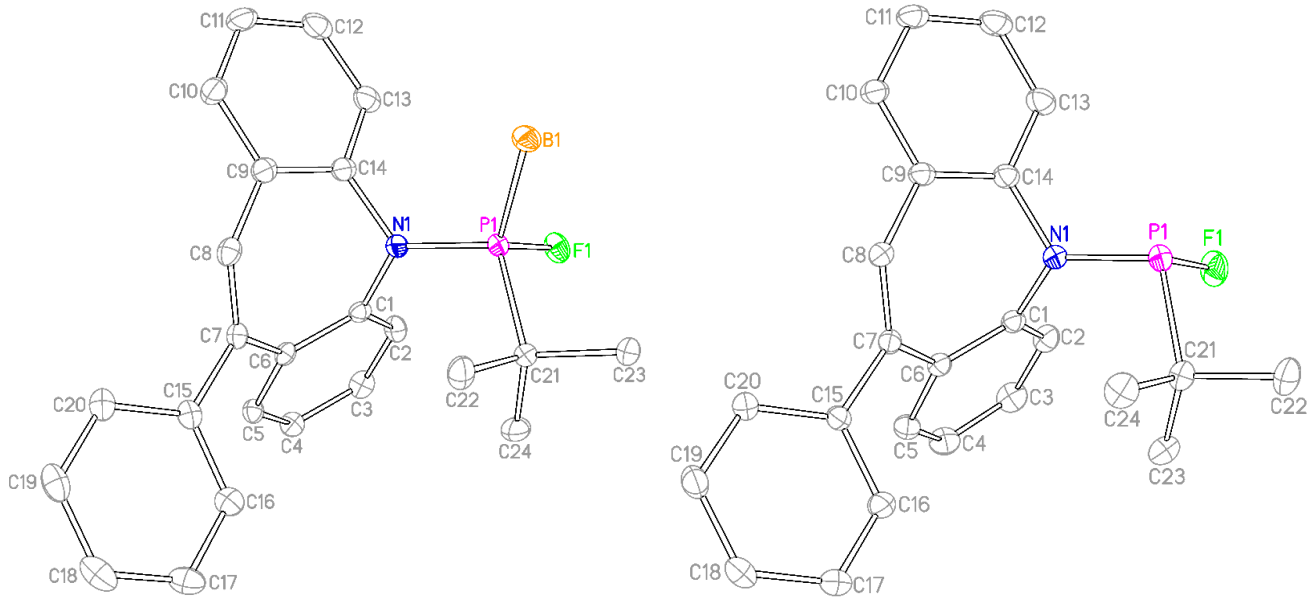


Figure S2. Molecular structures of (p*R*,*R*P)-**9** (left) and (p*R*,*R*P)-**10** (right) with their respective numbering schemes (50% displacement ellipsoids, H atoms omitted for clarity).

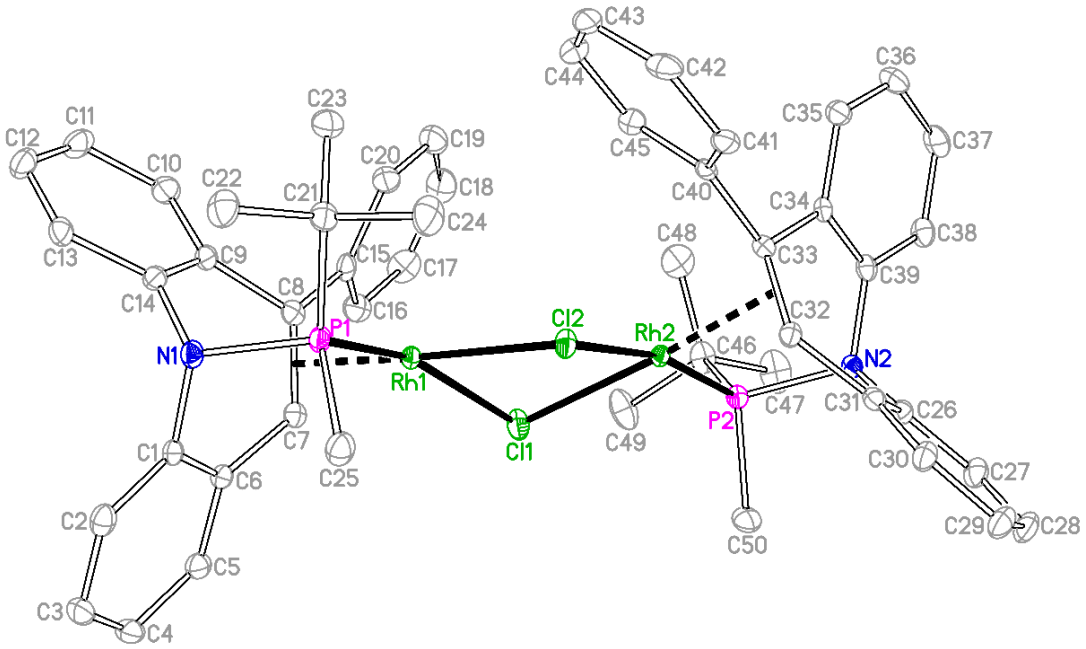


Figure S3. Molecular structure of (p*R*,*S*P)-**11** with the applied numbering scheme (50% displacement ellipsoids, H atoms omitted for clarity). Selected bond distances (Å) and angles (°): Rh1—Cl1 2.5444(8), Rh1—Cl2 2.3638(7), Rh1—P1 2.1622(9), Rh1—C7 2.108(3), Rh1—C8 2.134(3), Rh2—Cl1 2.3739(8), Rh2—Cl2 2.5146(8), Rh2—P2, P1–C25 1819(3), P2–C50 1818(3), 2.1697(8), Rh2—C32 2.107(3), Rh2—C33 2.132(3), N1—P1—Rh1 110.83(9), N2—P2—Rh2 111.10(9), C21—P1—Rh1 122.54(11), C46—P2—Rh2 121.43(11).

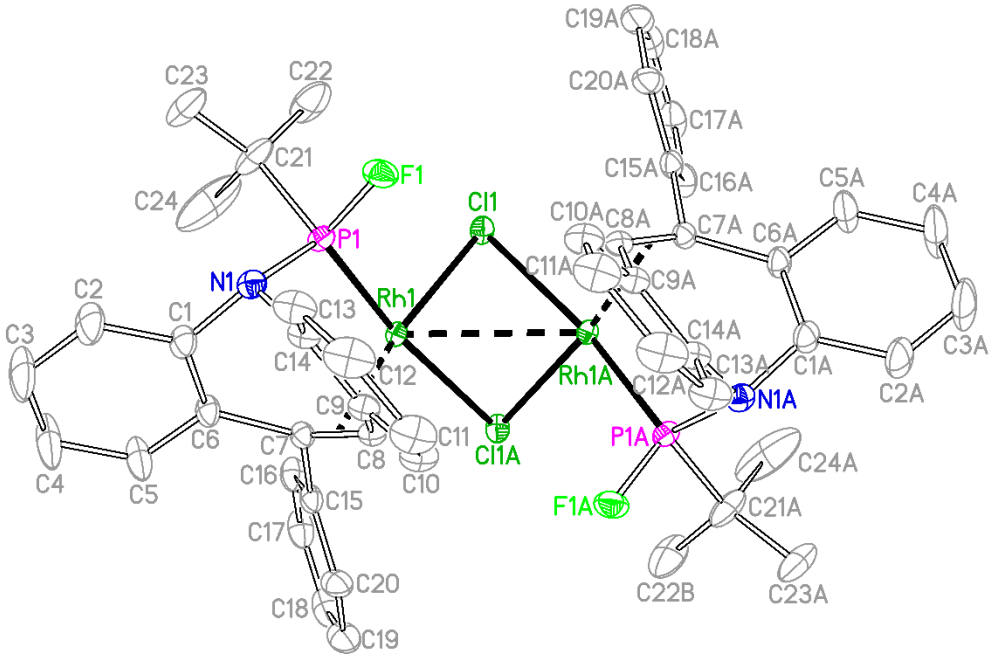


Figure S4. Molecular structure of (p*R*,*R*P)-**12** with the applied numbering scheme (50% displacement ellipsoids, H atoms and disordered solvent molecules omitted for clarity).

NMR Spectra

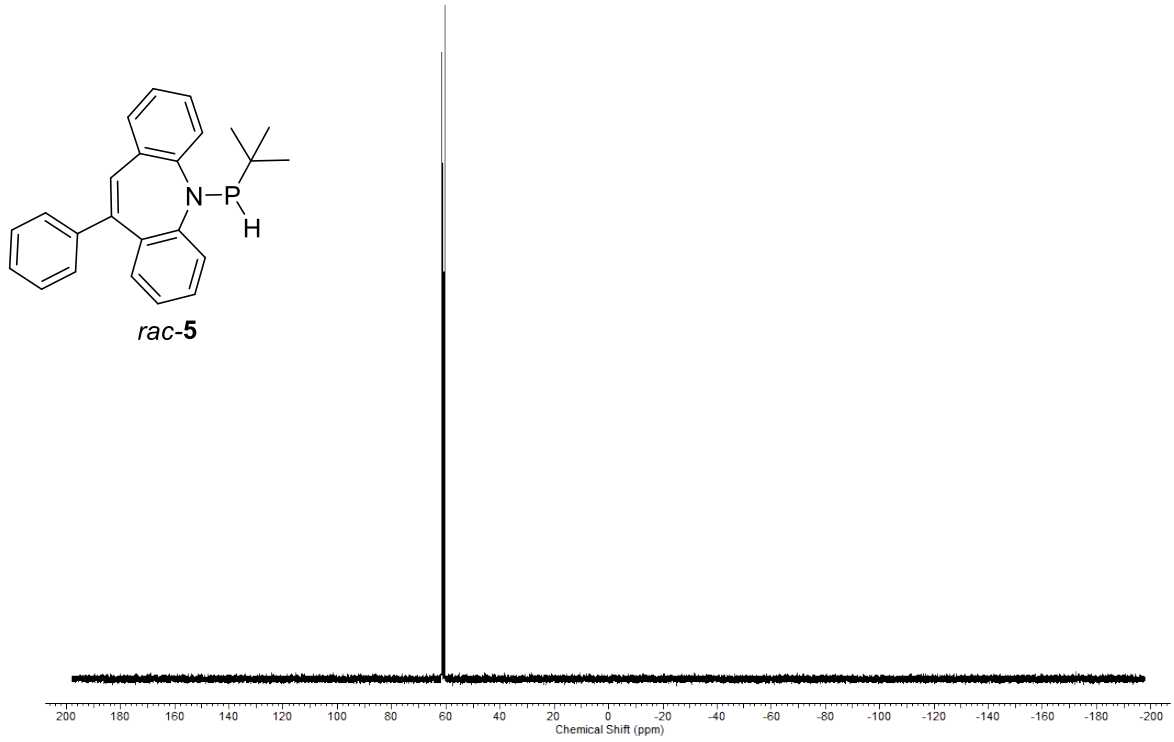


Figure S5. Non-decoupled ^{31}P NMR spectrum (242 MHz, C_6D_6) of *rac*-**5**

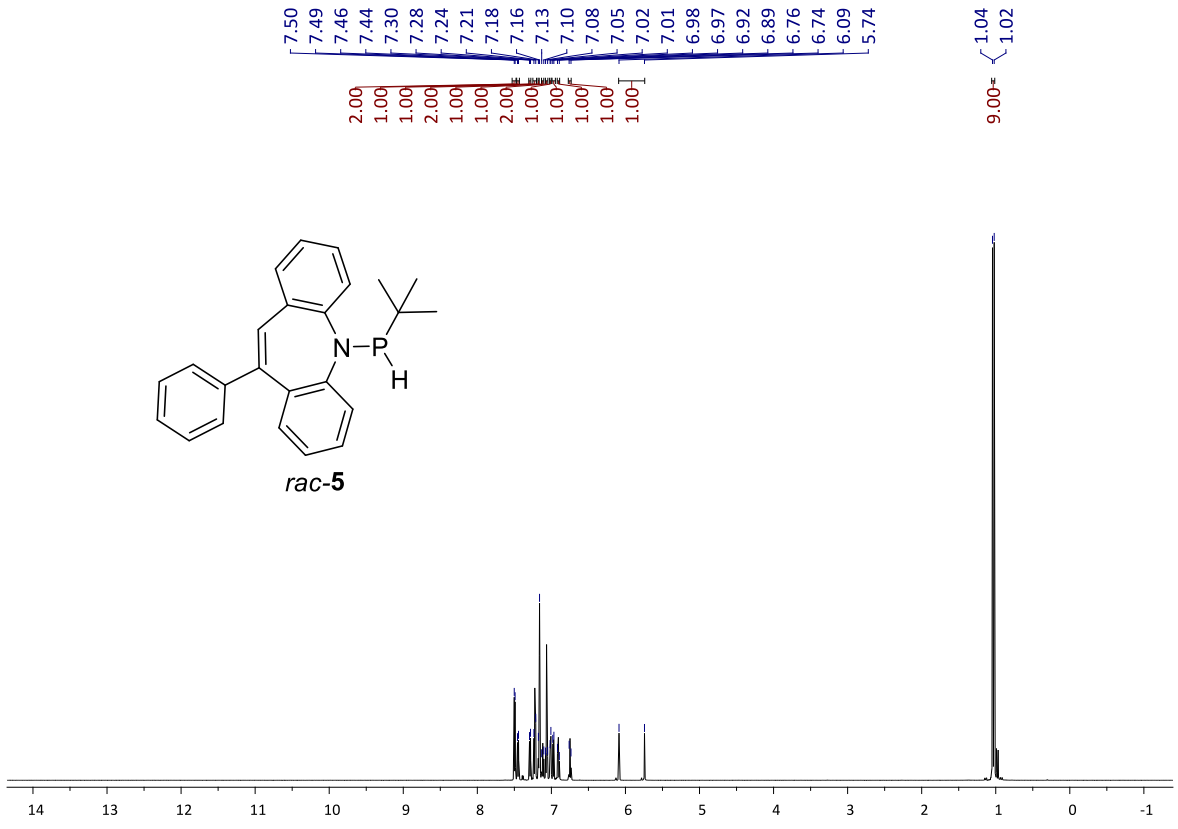


Figure S6. ^{1}H NMR spectrum (600 MHz, C_6D_6) of *rac*-**5**

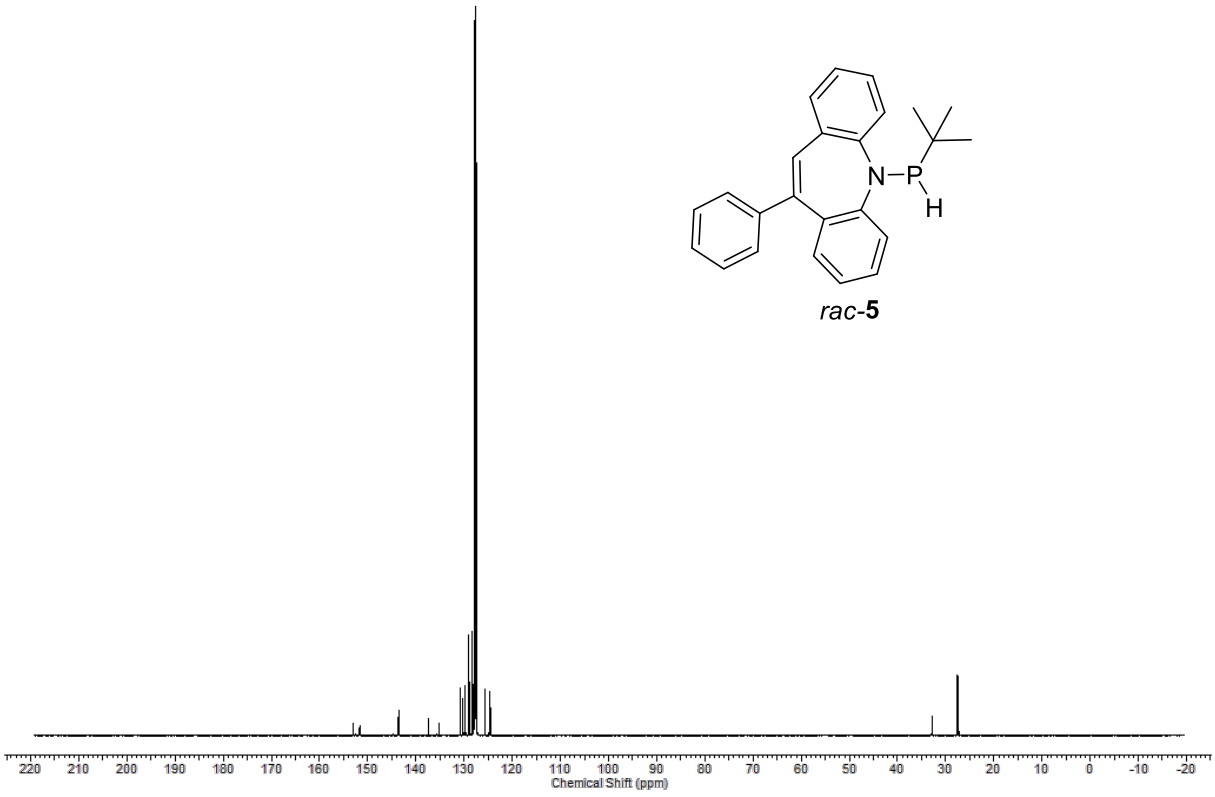


Figure S7. ^{13}C NMR spectrum (151 MHz, C_6D_6) of *rac*-**5**

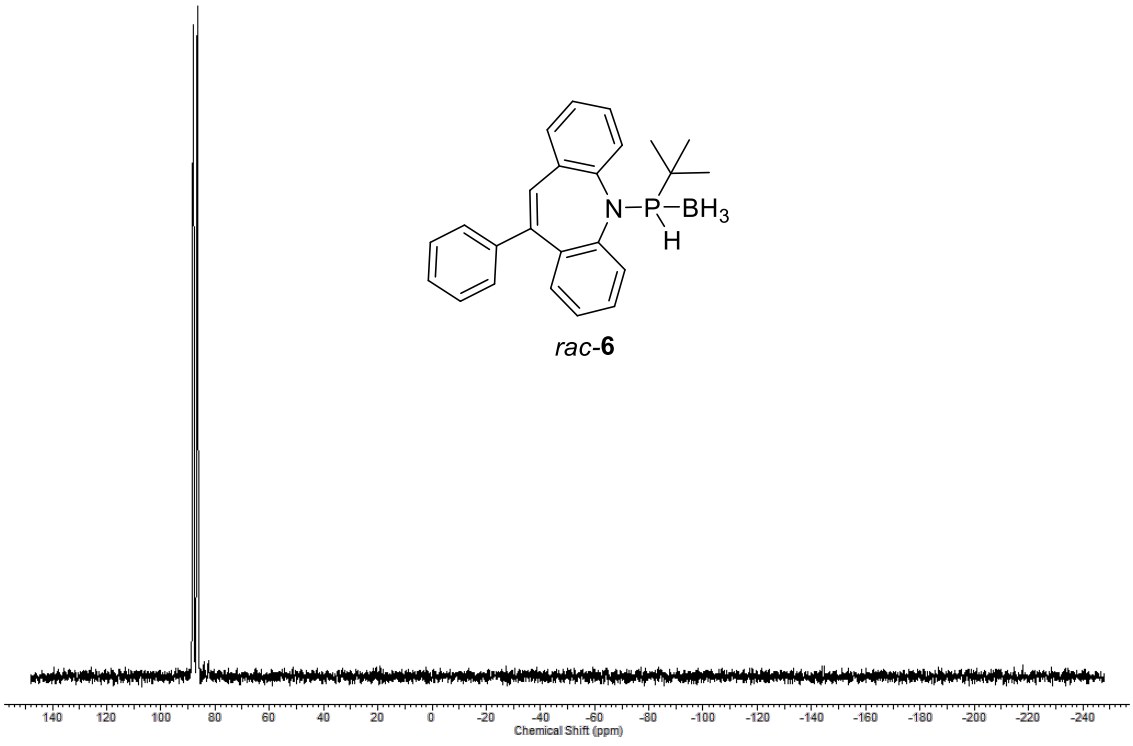


Figure S8. Non-decoupled ^{31}P NMR spectrum (242 MHz, C_6D_6) of *rac*-**6**

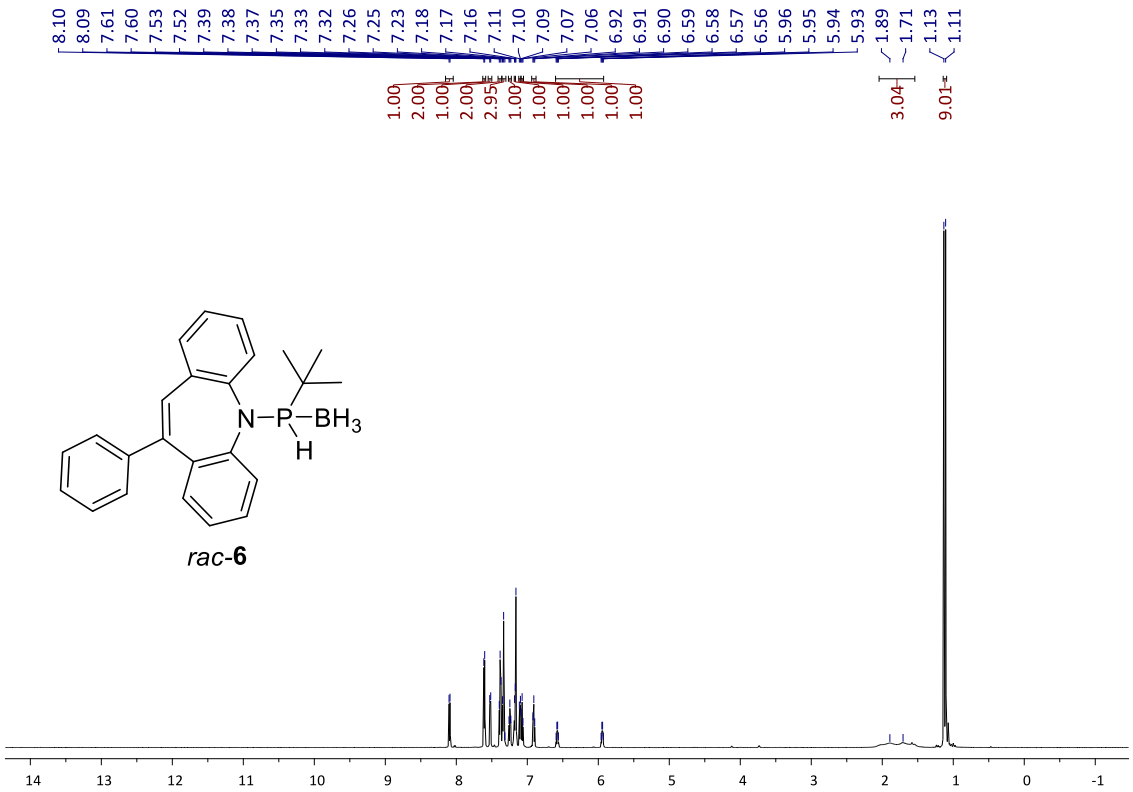


Figure S9. ^{1}H NMR spectrum (600 MHz, C_6D_6) of *rac*-**6**

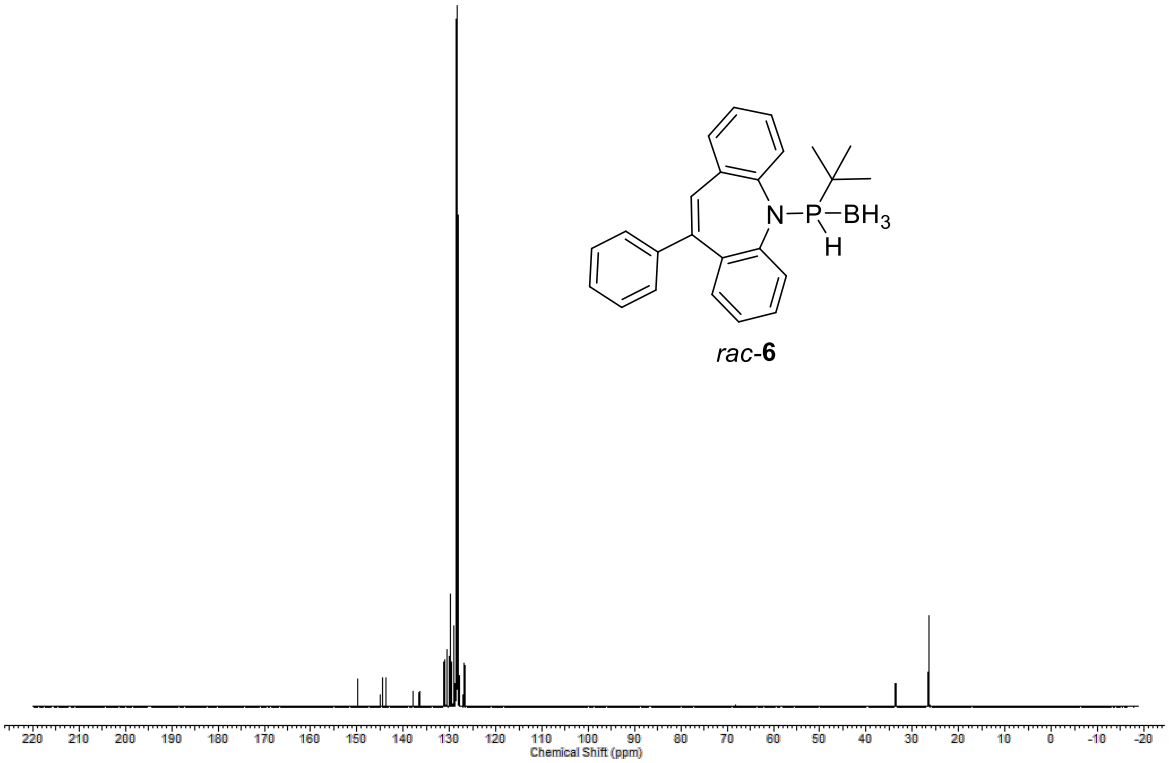


Figure S10. ^{13}C NMR spectrum (151 MHz, C_6D_6) of *rac*-**6**

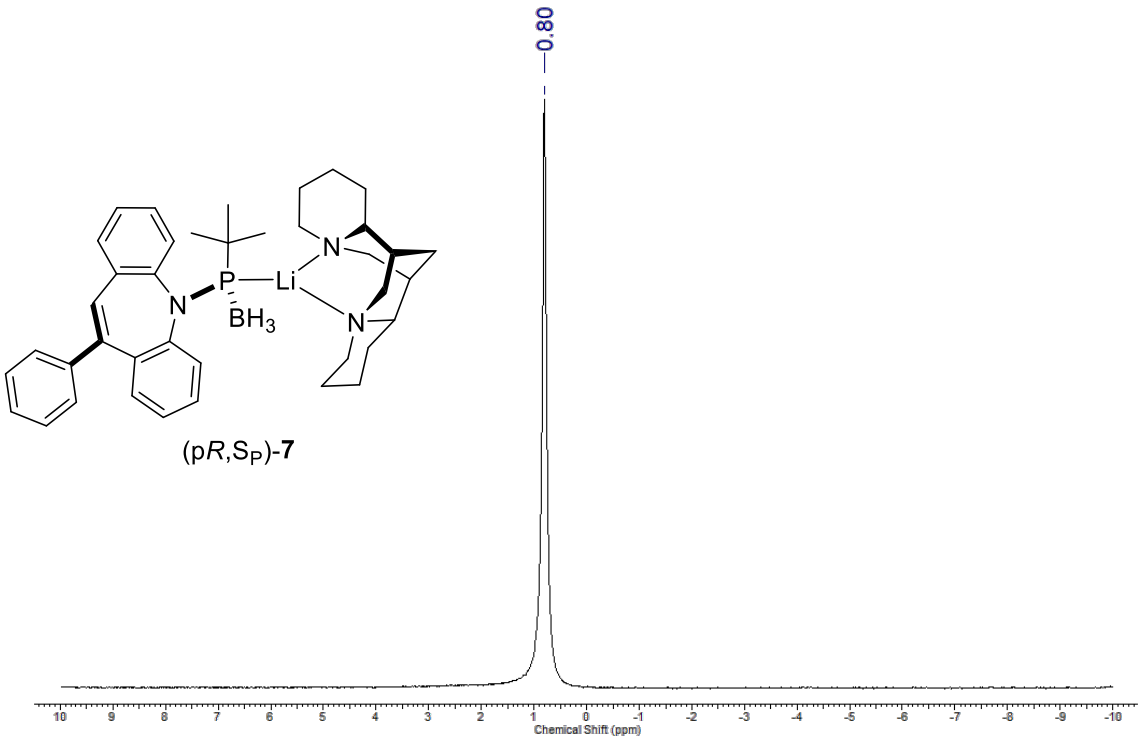


Figure S11. ^{7}Li NMR spectrum (155 MHz, C_6D_6) of (p*R*,*S*$_P$)-**7**

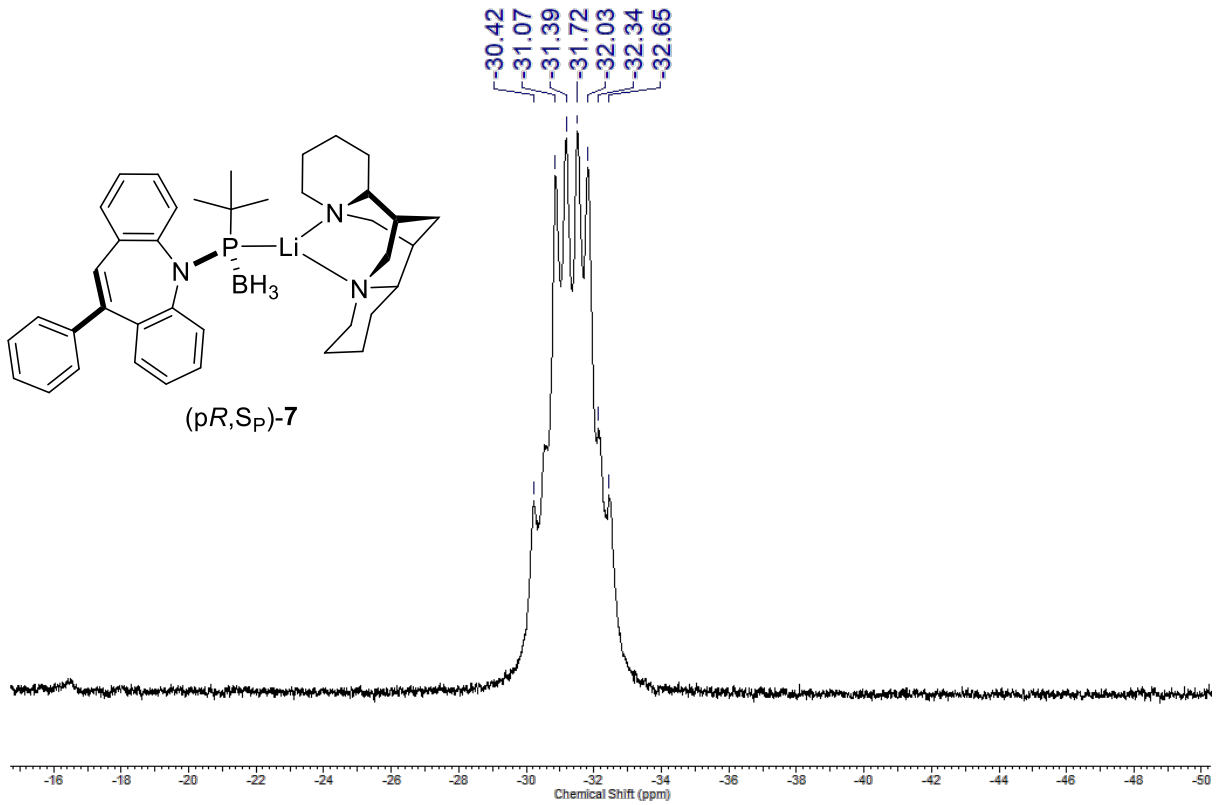


Figure S12. ^{11}B NMR spectrum (128 MHz, C_6D_6) of (p*R*,*S*$_P$)-**7**

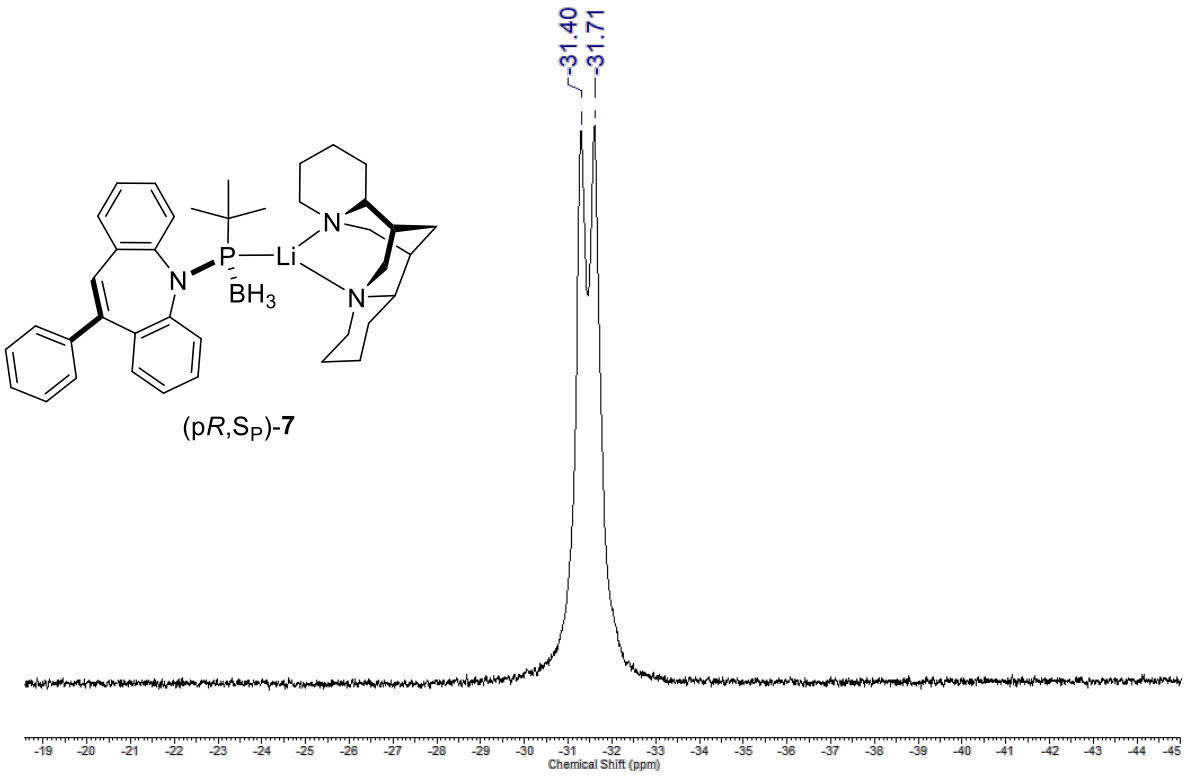


Figure S13. $^{11}B\{^{1}H\}$ NMR spectrum (128 MHz, C_6D_6) of (p*R*,*S*$_P$)-**7**

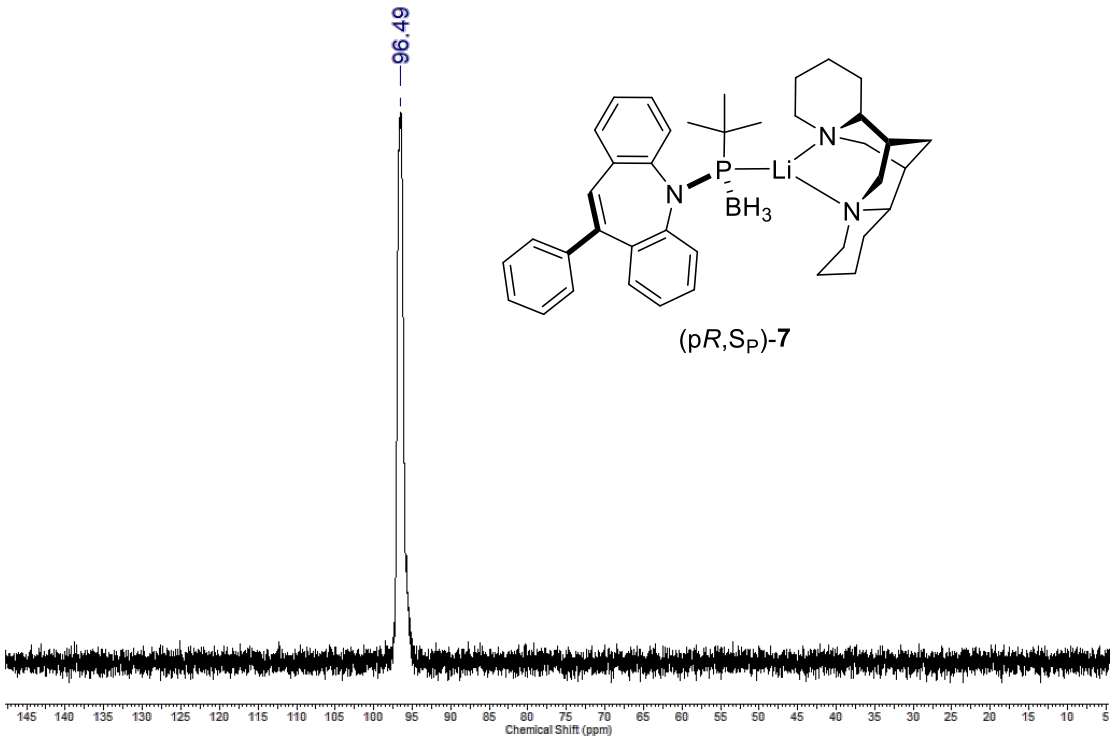


Figure S14. ^{31}P NMR spectrum (242 MHz, C_6D_6) of (p*R*,*S*$_P$)-**7**

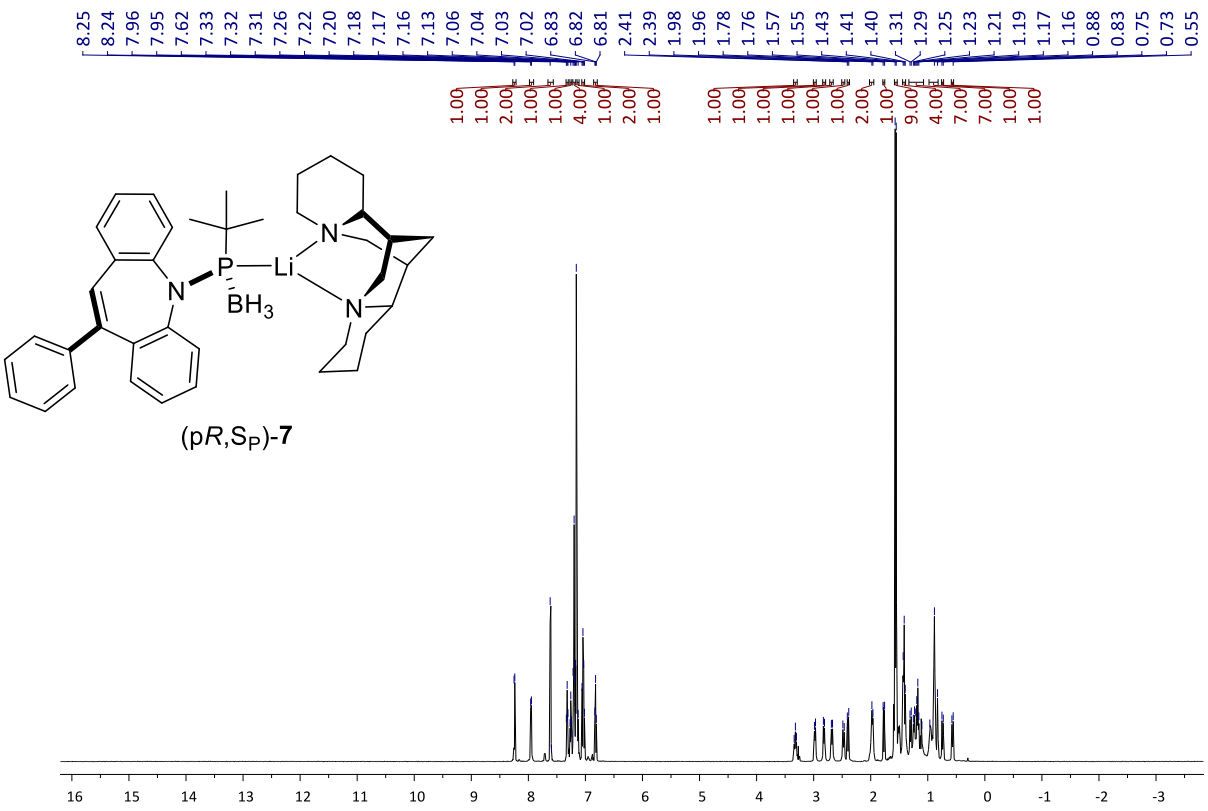


Figure S15. ^{1}H NMR spectrum (600 MHz, C_6D_6) of (p*R*,*S*$_P$)-**7**

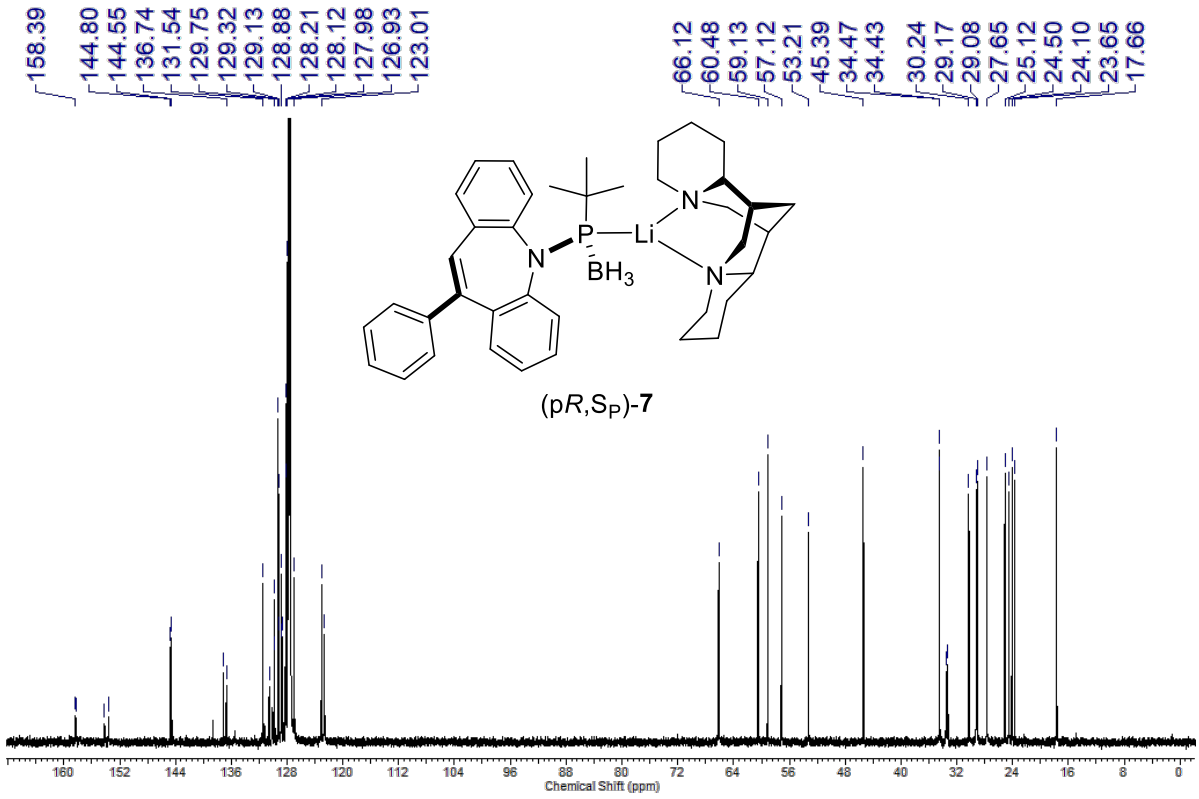


Figure S16. ^{13}C NMR spectrum (151 MHz, C_6D_6) of (p*R*,*S*$_P$)-**7**

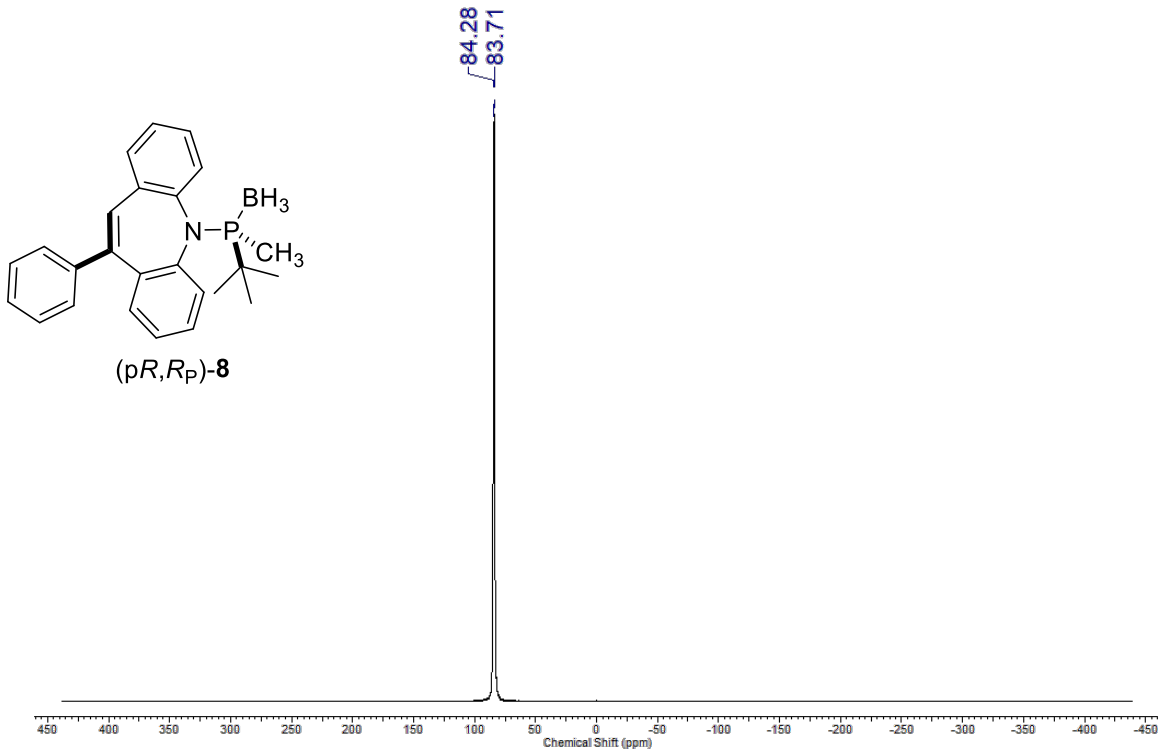


Figure S17. ^{31}P NMR spectrum (242 MHz, $CDCl_3$) of (p*R*,*R*$_P$)-**8**

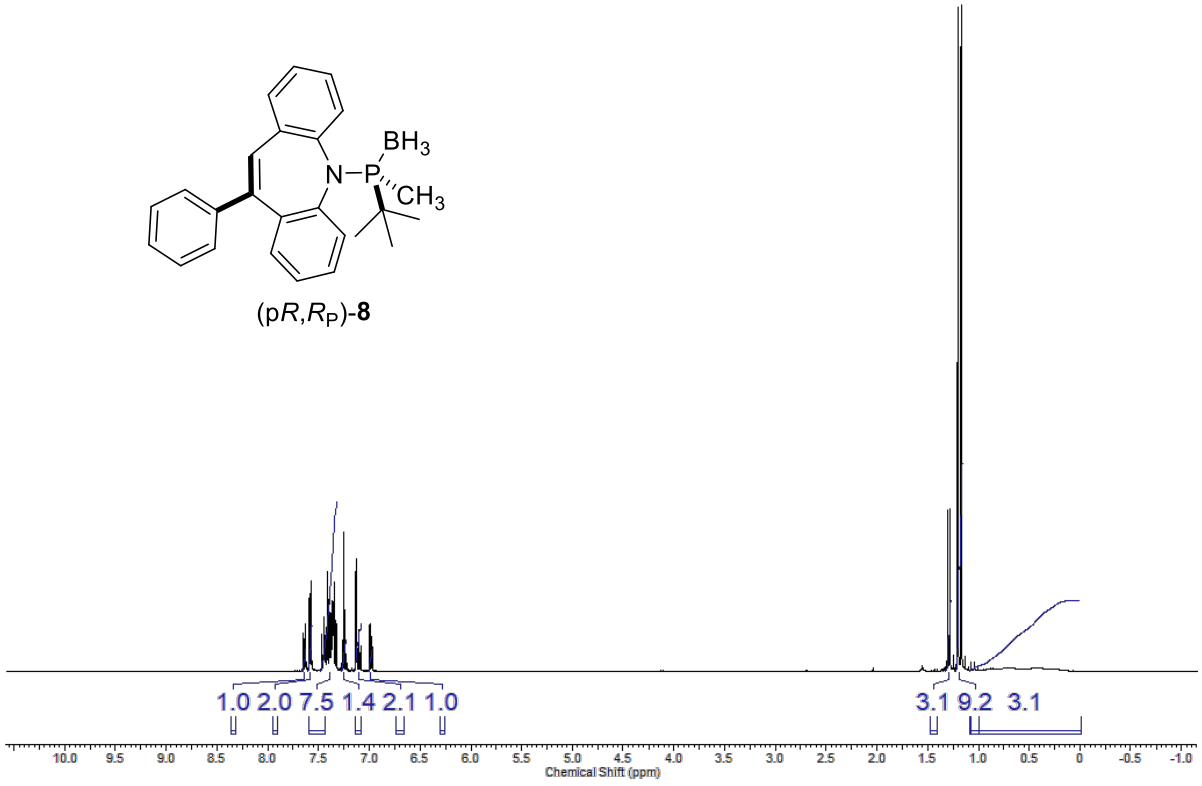


Figure S18. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of (p*R*,*R*$_P$)-**8**

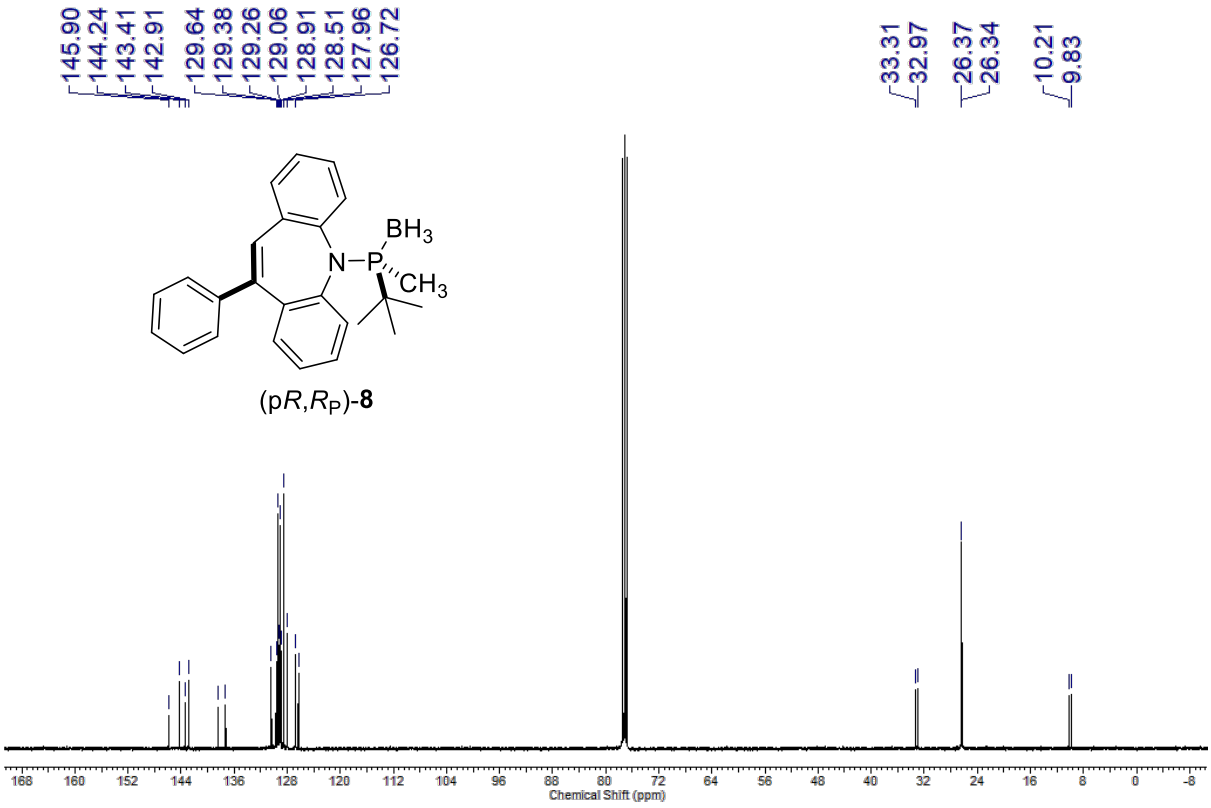


Figure S19. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of (p*R,R*P)-**8**

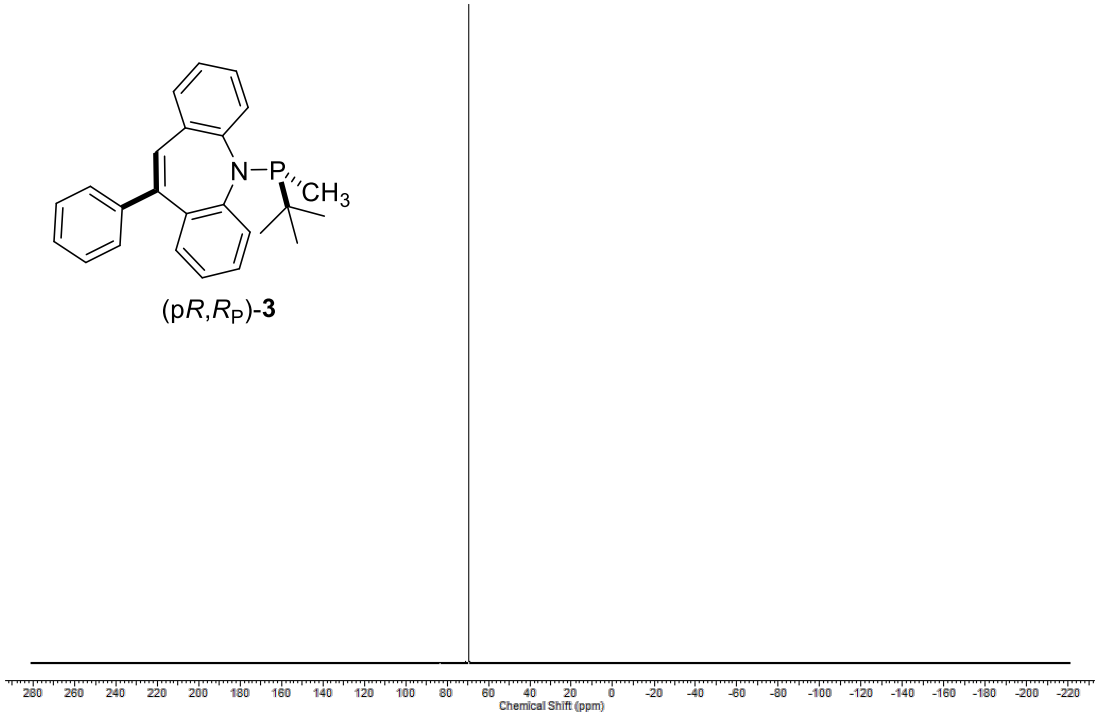


Figure S20. ^{31}P NMR spectrum (242 MHz, $CDCl_3$) of (p*R,R*P)-**3**

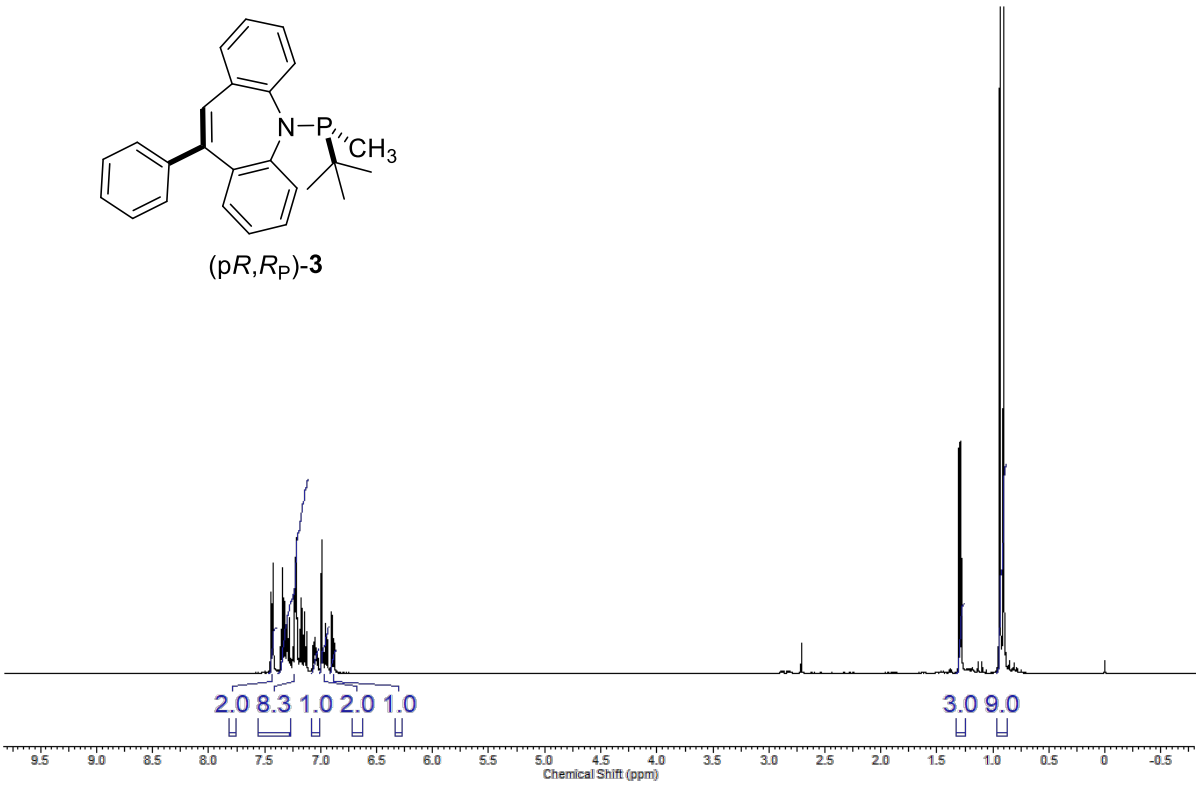


Figure S21. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of (p*R,R*$_P$)-**3**

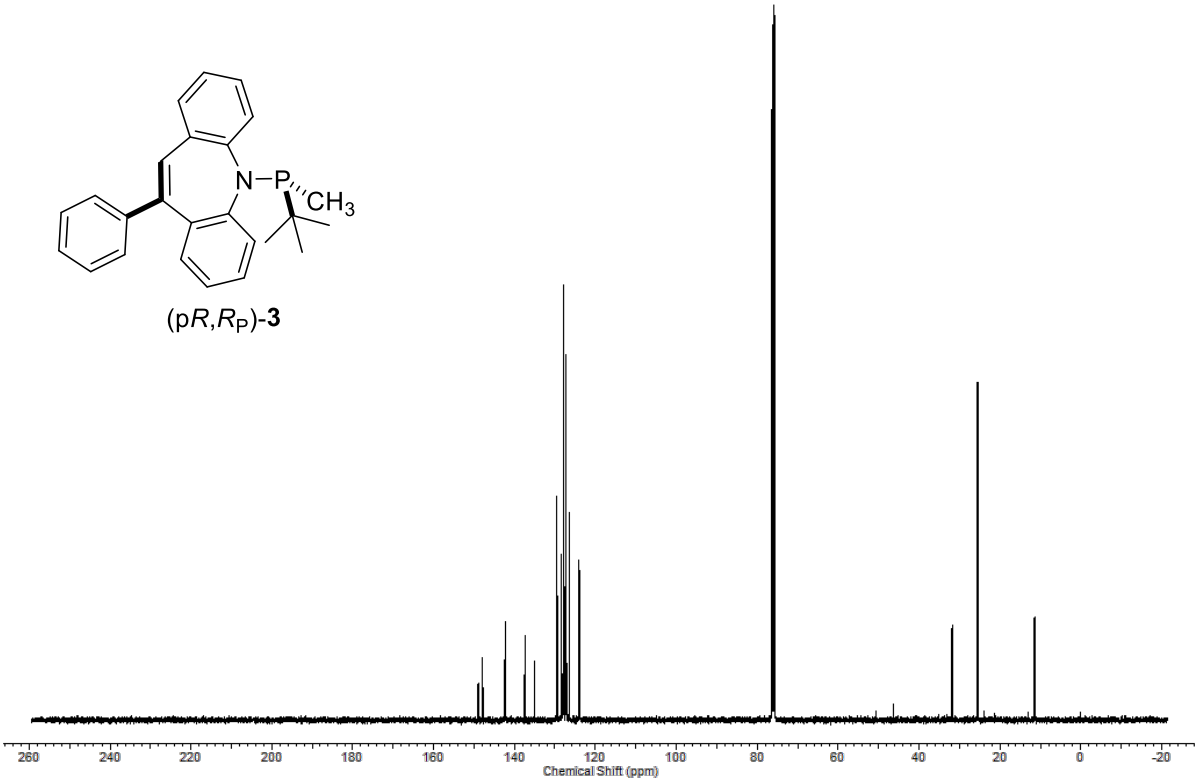


Figure S22. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of (p*R,R*$_P$)-**3**

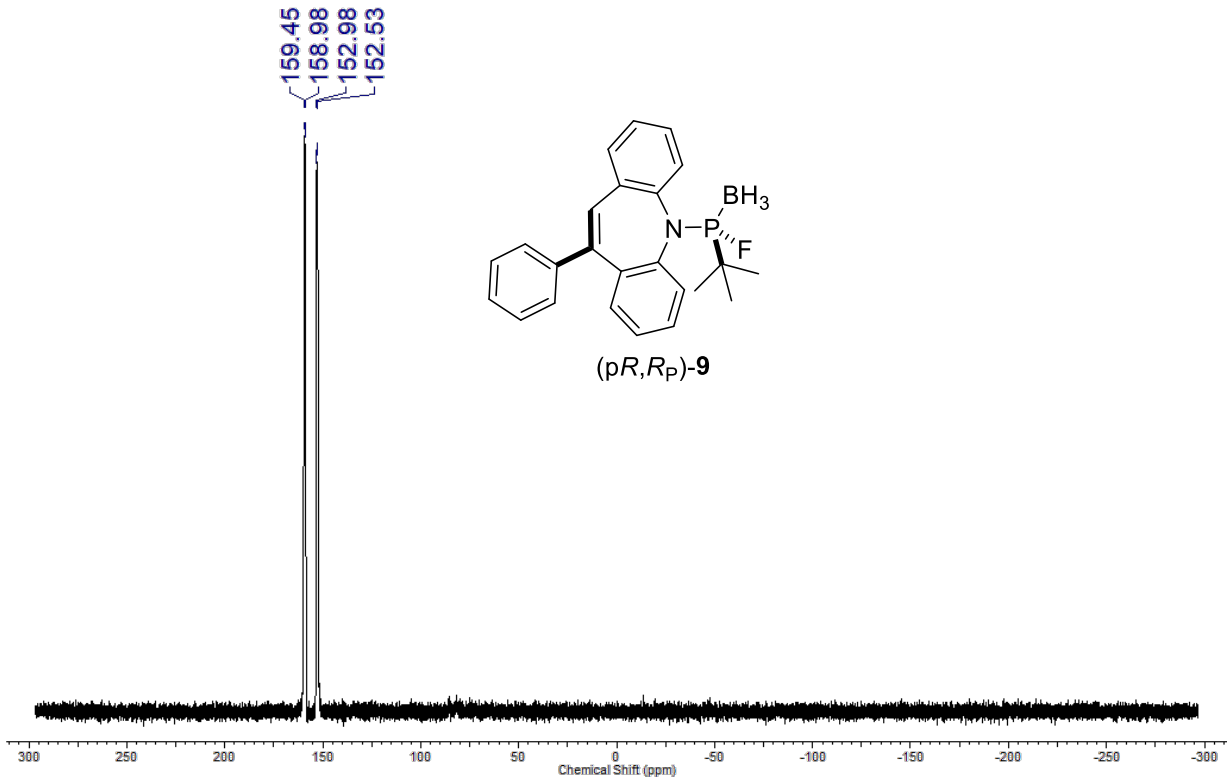


Figure S23. $^{31}P\{^{1}H\}$ NMR spectrum (161 MHz, $CDCl_3$) of (p*R*,*R*$_P$)-**9**

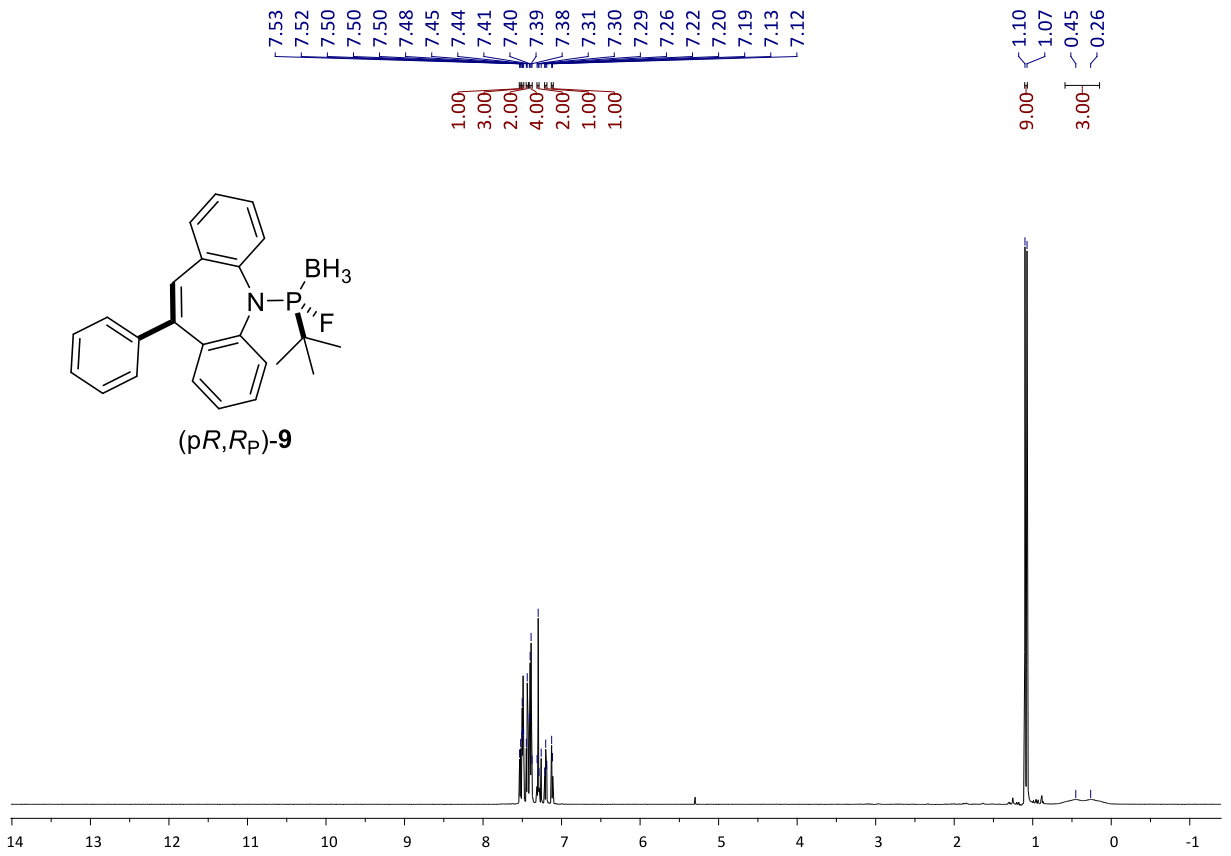


Figure S24. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of (p*R*,*R*$_P$)-**9**

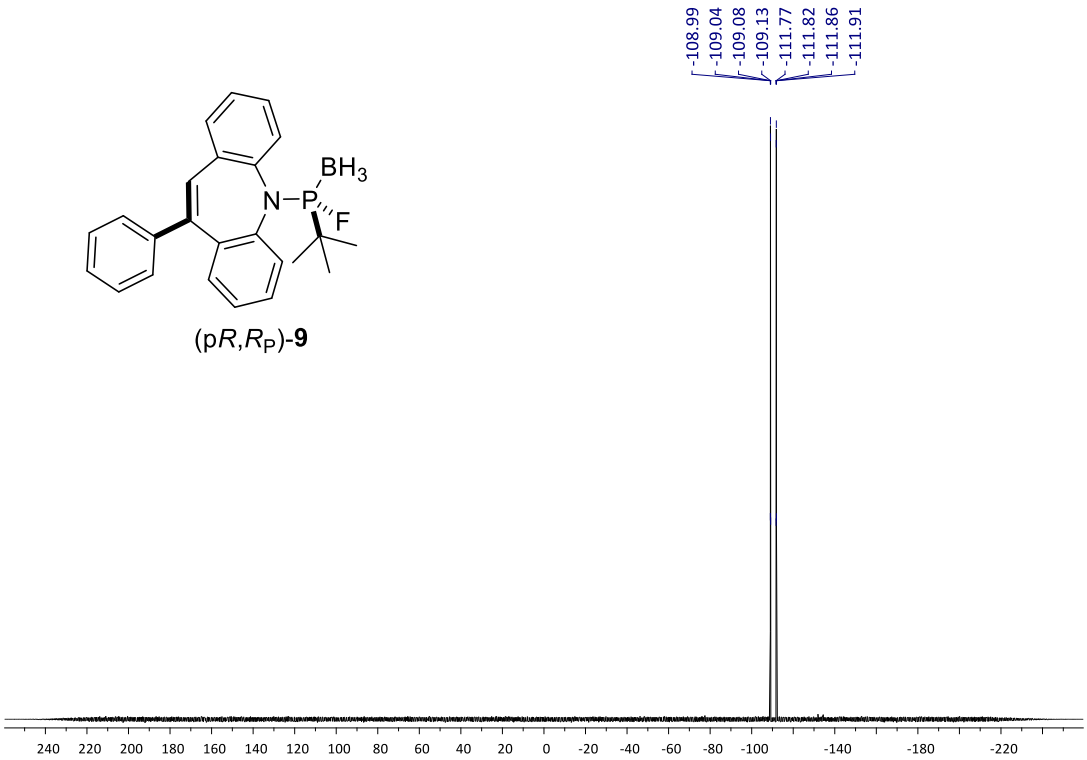


Figure S25. ^{19}F NMR spectrum (377 MHz, $CDCl_3$) of (p*R,R*$_P$)-**9**

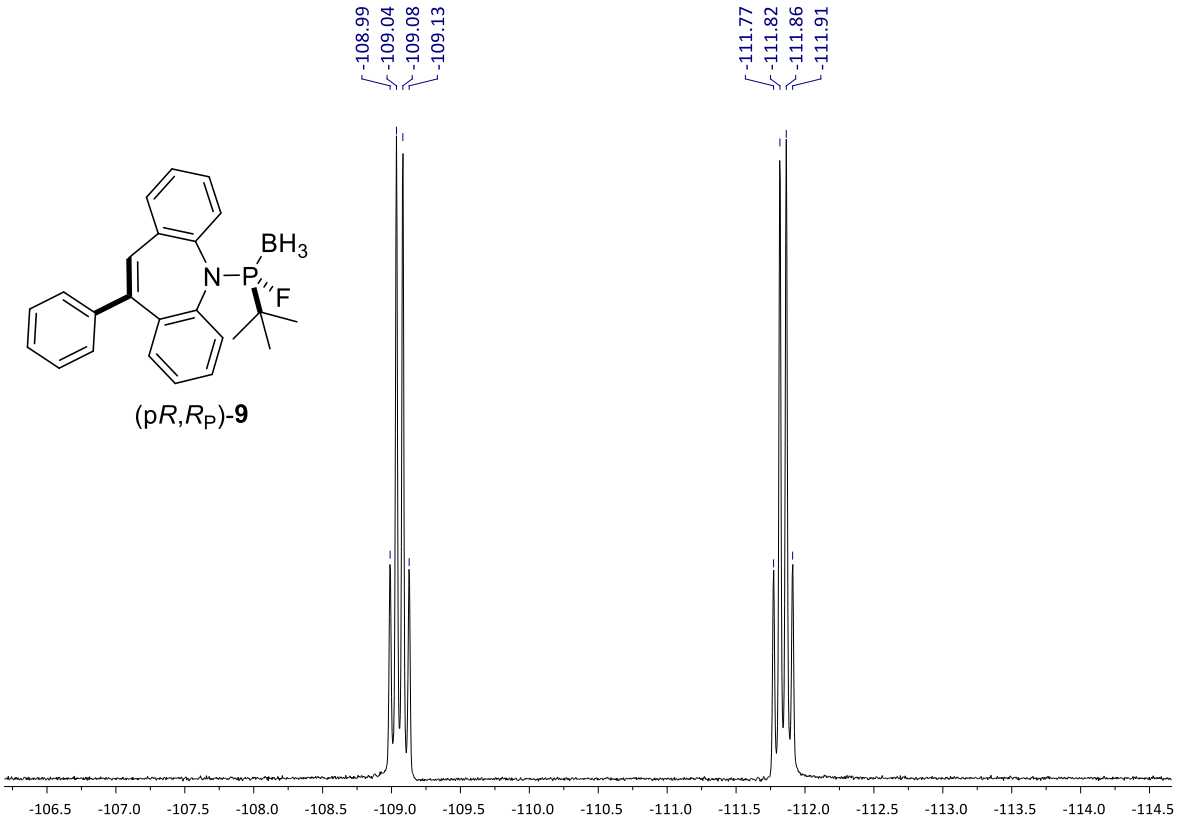


Figure S26. Zoom-in of the above ^{19}F NMR spectrum (377 MHz, $CDCl_3$) of (p*R,R*$_P$)-**9**

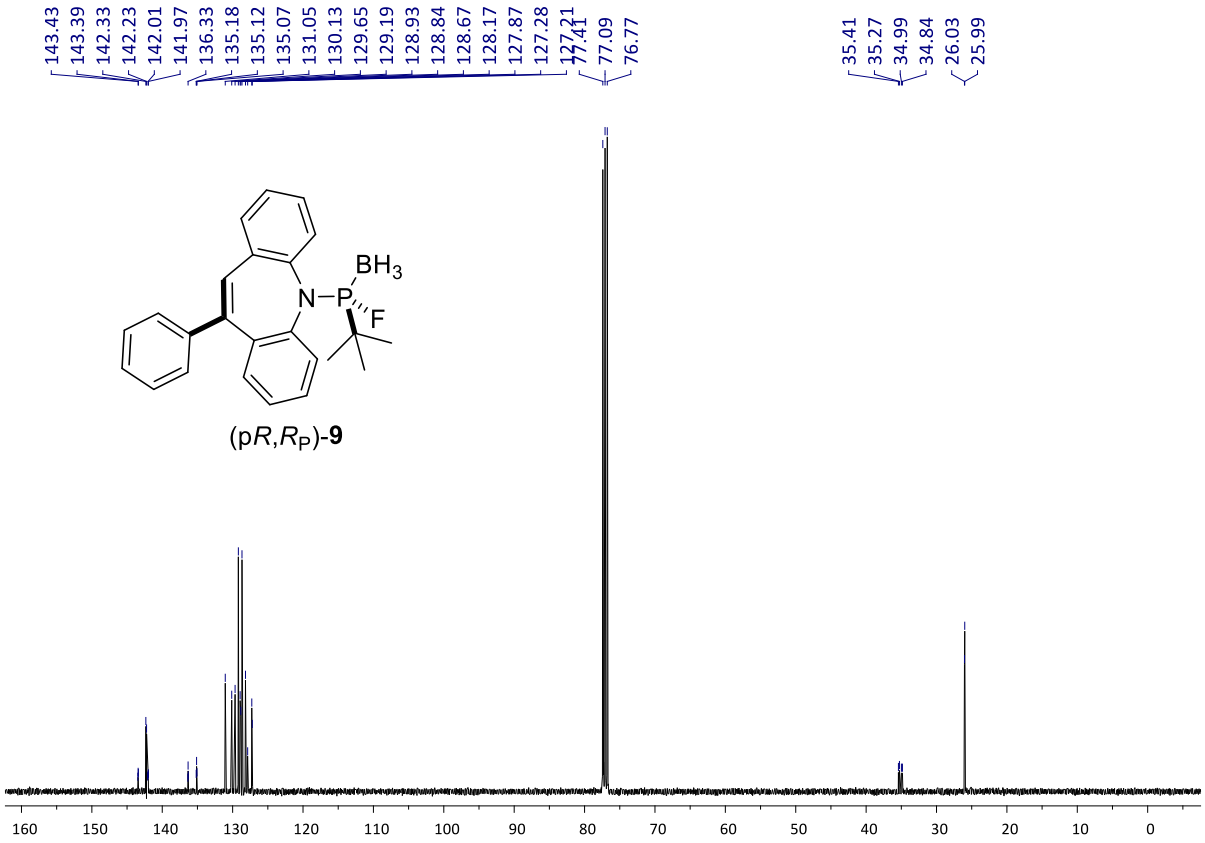


Figure S27. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of (p*R,R*P)-**9**

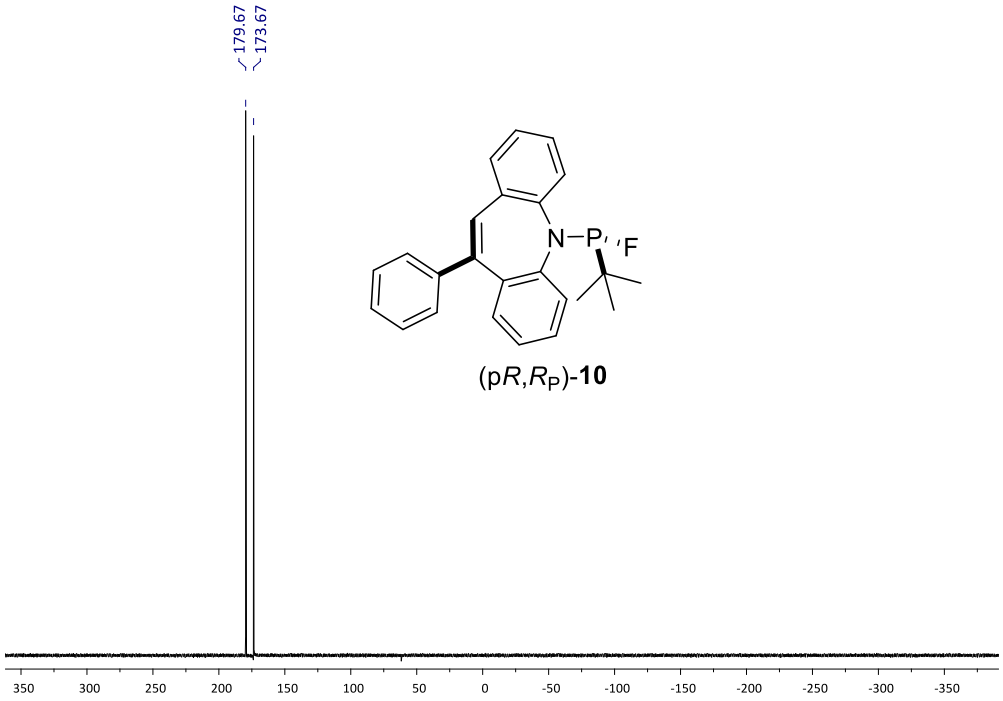


Figure S28. ^{31}P NMR spectrum (242 MHz, C_6D_6) of (p*R,R*P)-**10**

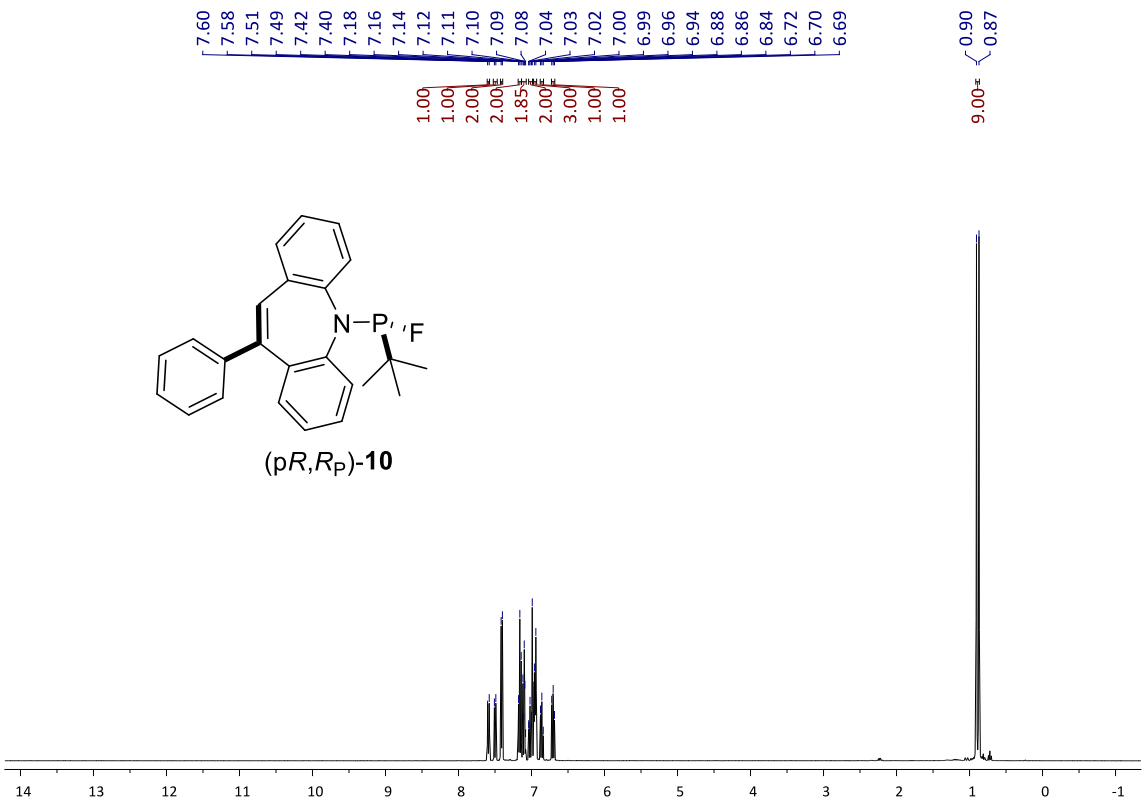


Figure S29. ^{1}H NMR spectrum (600 MHz, C_6D_6) of (p*R,R*$_P$)-**10**

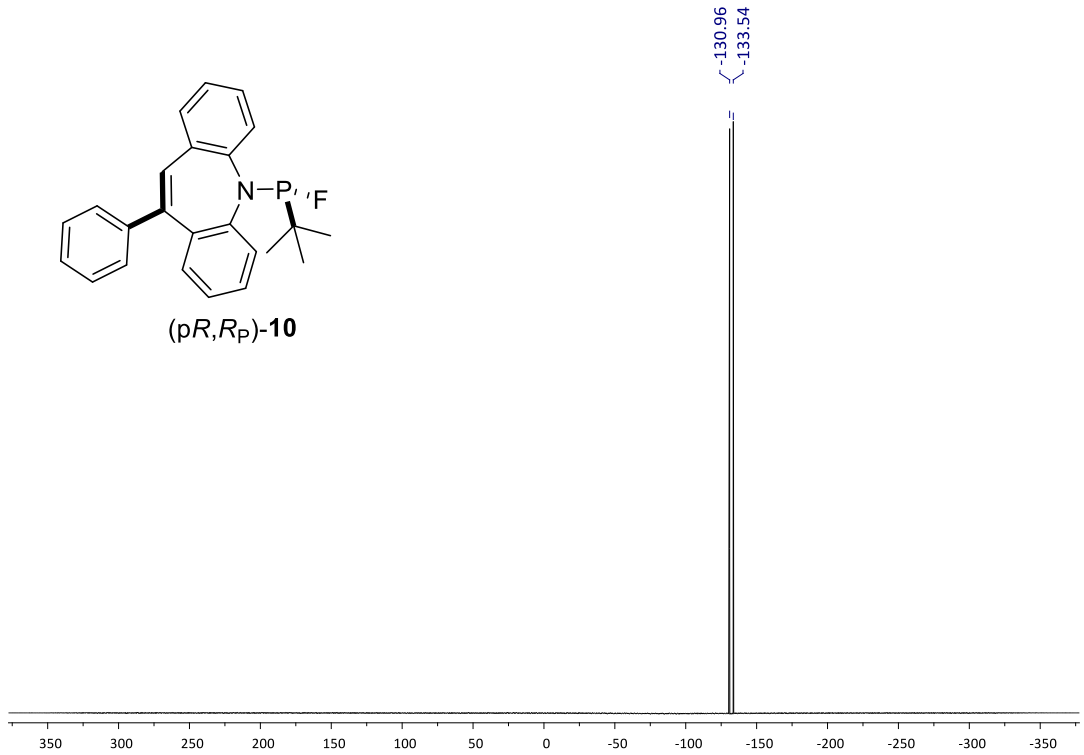


Figure S30. ^{19}F NMR spectrum (377 MHz, C_6D_6) of (p*R,R*$_P$)-**10**

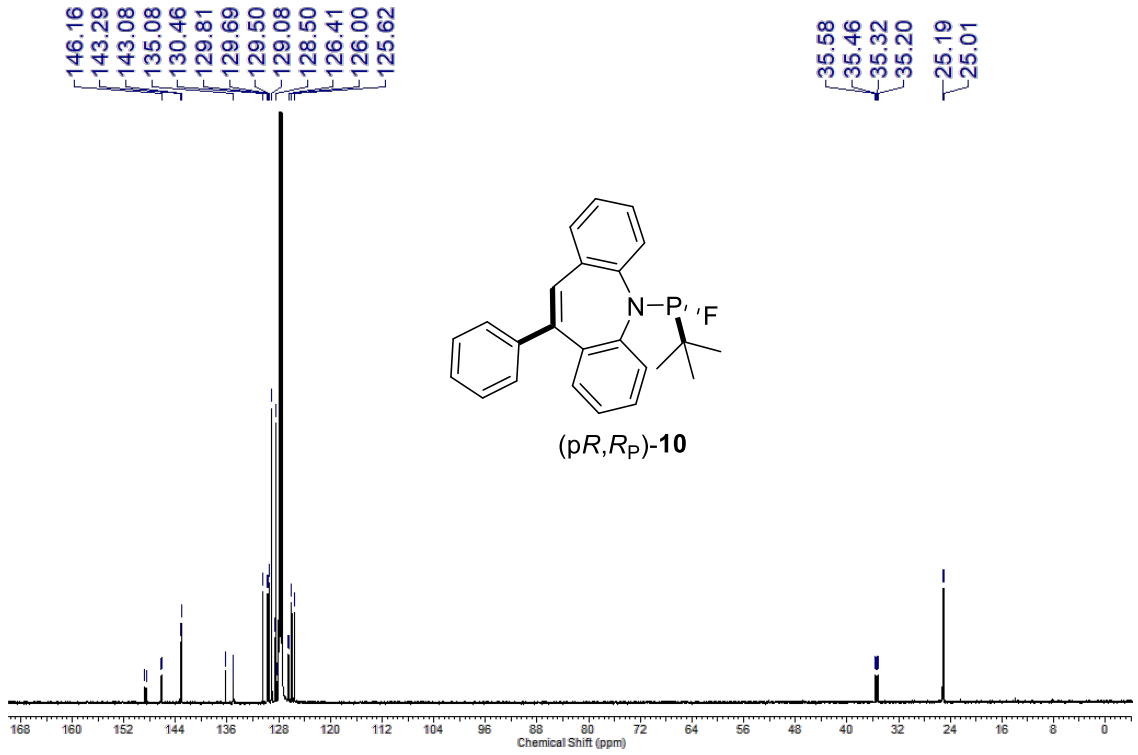


Figure S31. ^{13}C NMR spectrum (151 MHz, C_6D_6) of (p*R*,R_P)-**10**

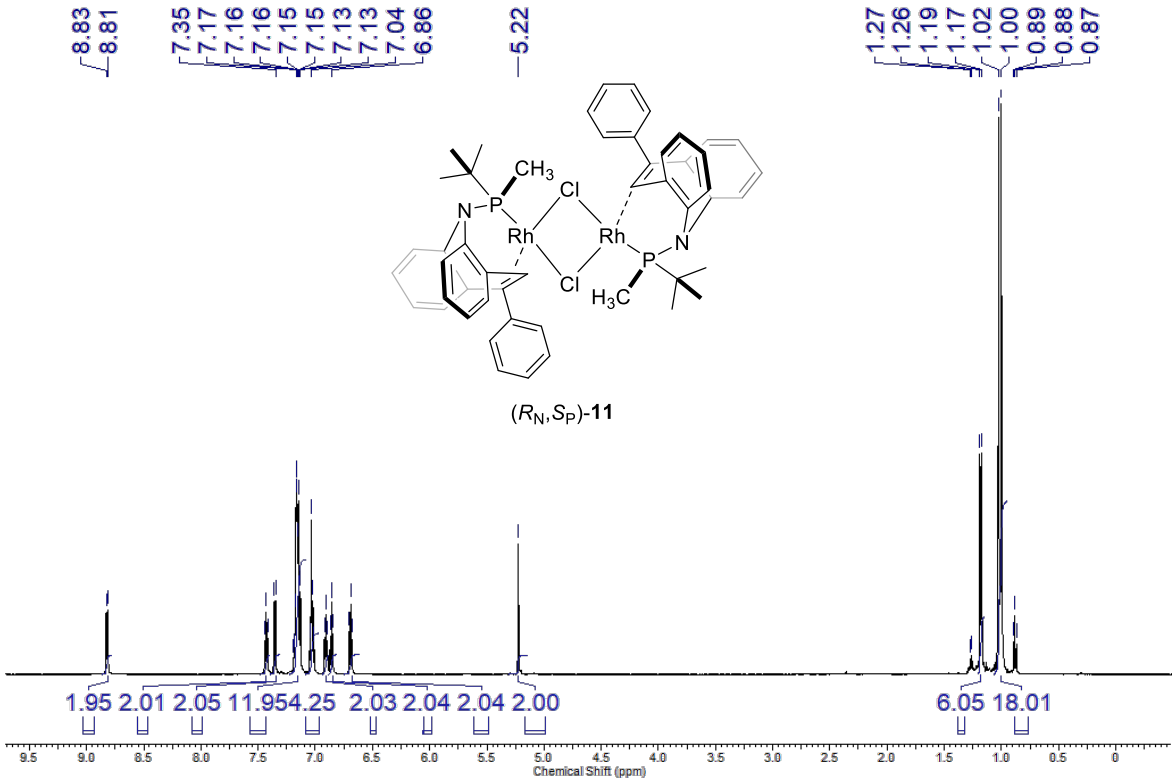
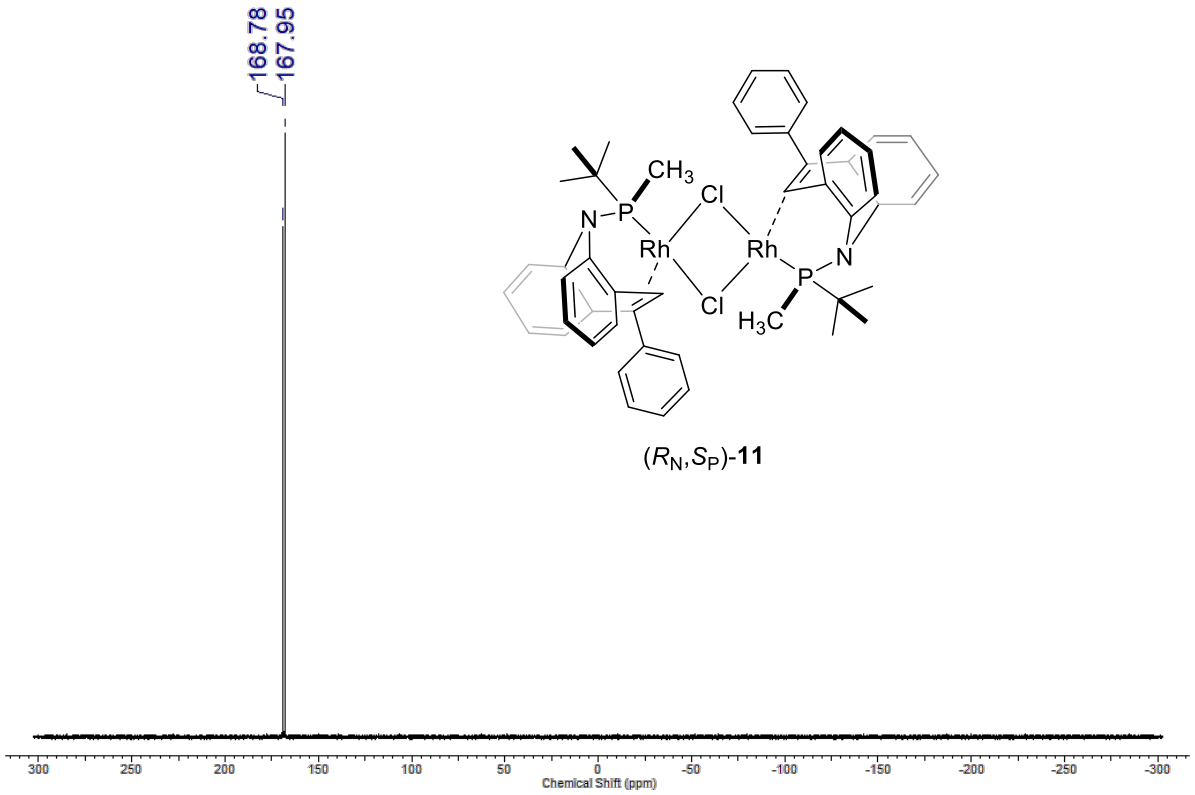
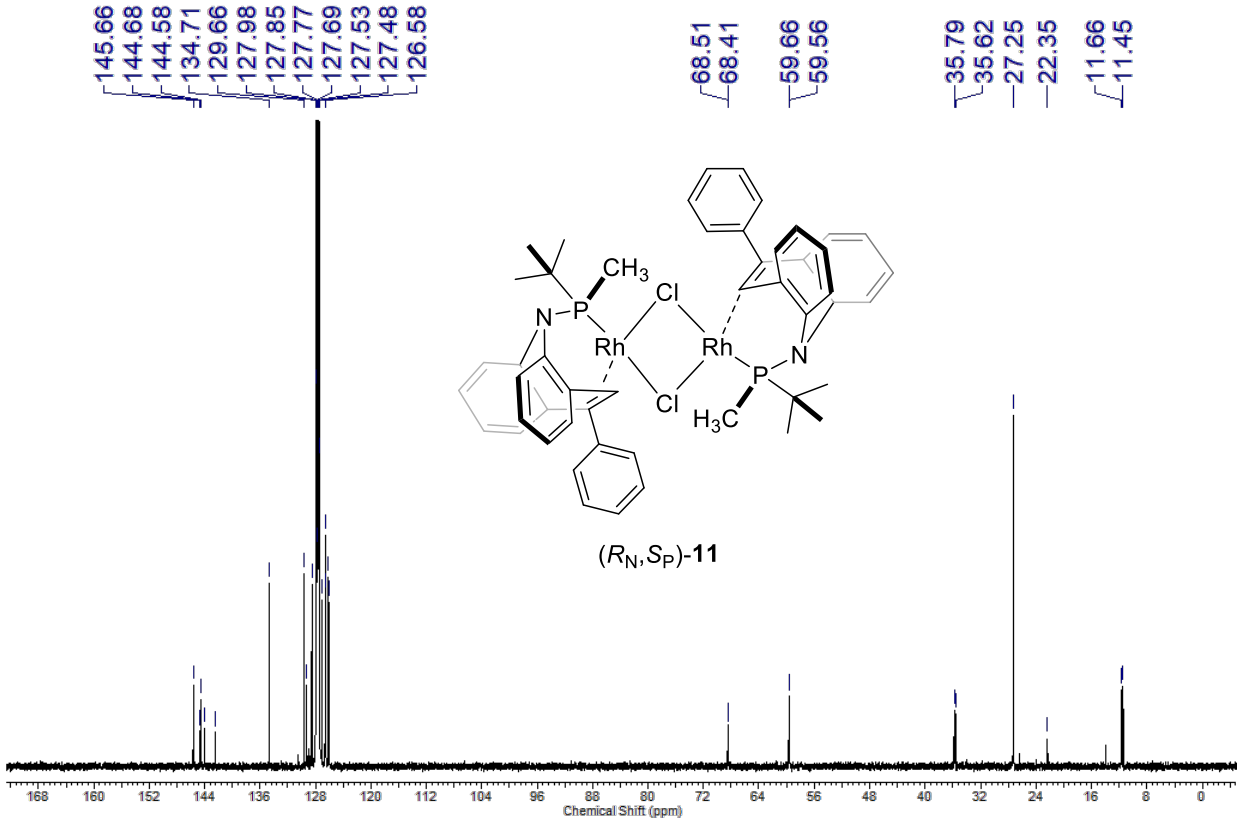


Figure S32. ^{1}H NMR spectrum (600 MHz, C_6D_6) of complex *anti*-(*R*,*S*)-**11**



(R_N,S_P)-**11**

Figure S33. ^{31}P NMR spectrum (242 MHz, C_6D_6) of complex *anti*-(*R,S*)-**11**



(R_N,S_P)-**11**

Figure S34. ^{13}C NMR spectrum (151 MHz, C_6D_6) of complex *anti*-(*R,S*)-**11**

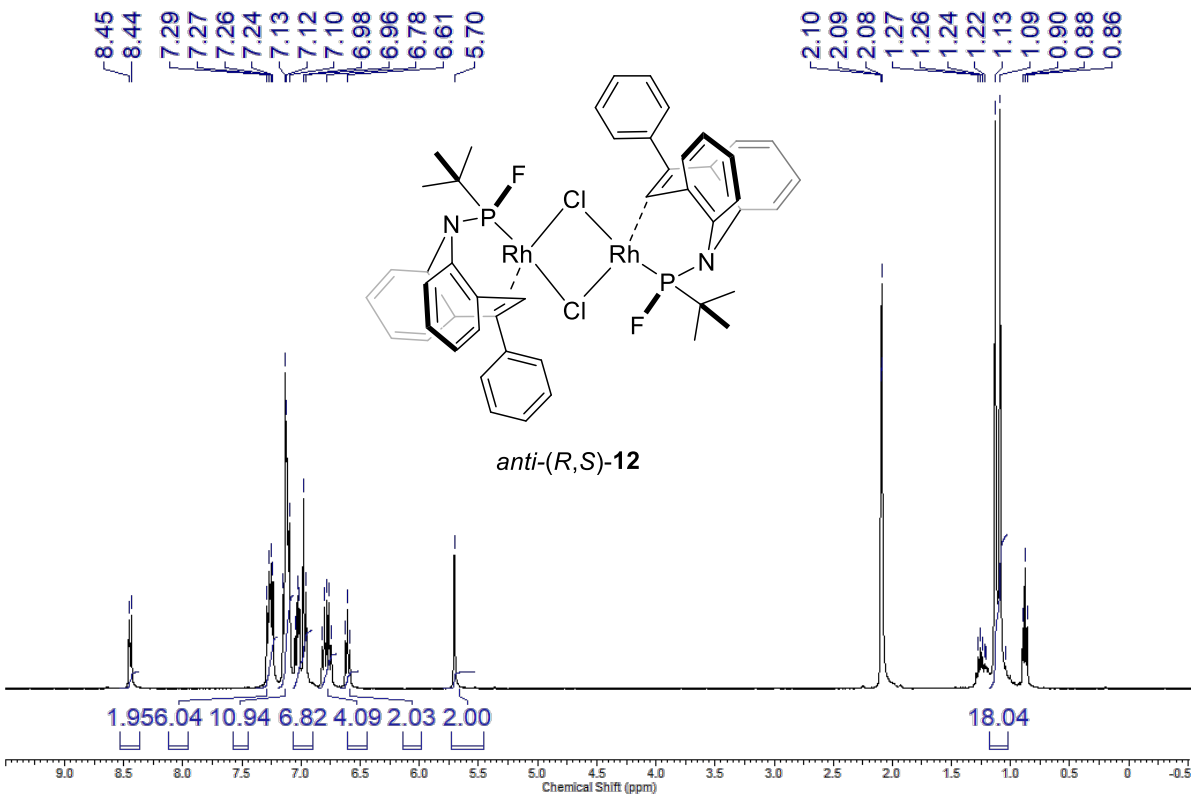


Figure S35. ^{1}H NMR spectrum (600 MHz, C_6D_6) of complex *anti*-(*R,S*)-**12**

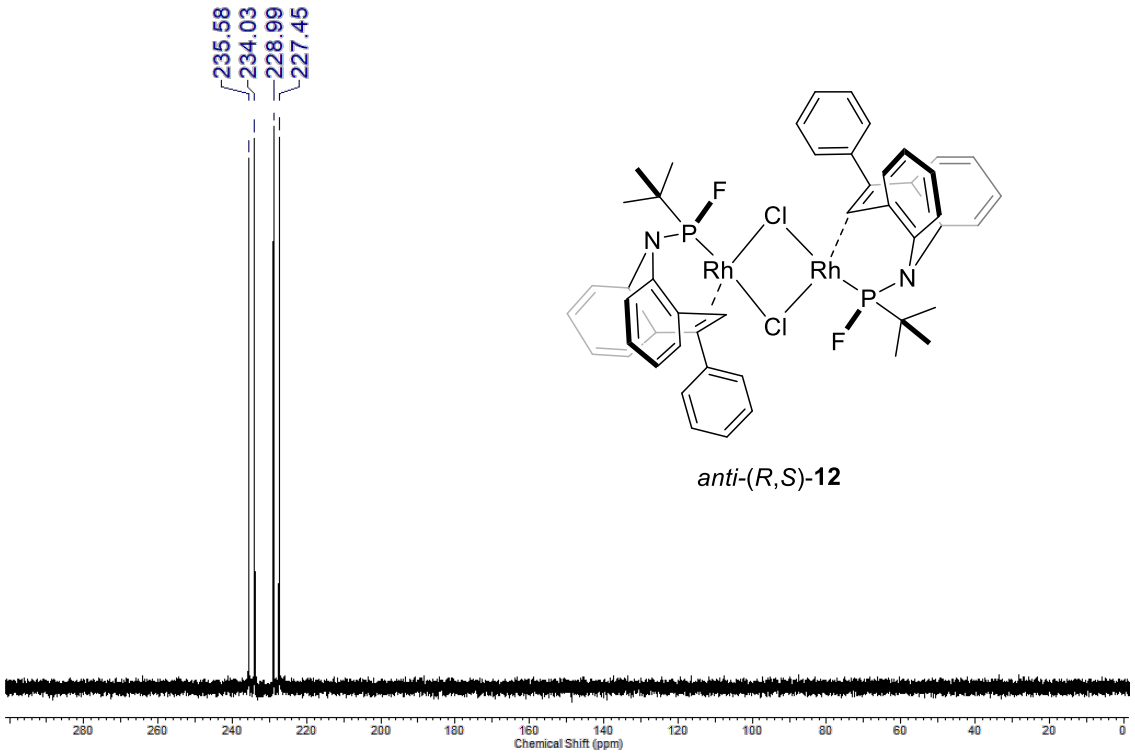


Figure S36. ^{31}P NMR spectrum (242 MHz, C_6D_6) of complex *anti*-(*R,S*)-**12**

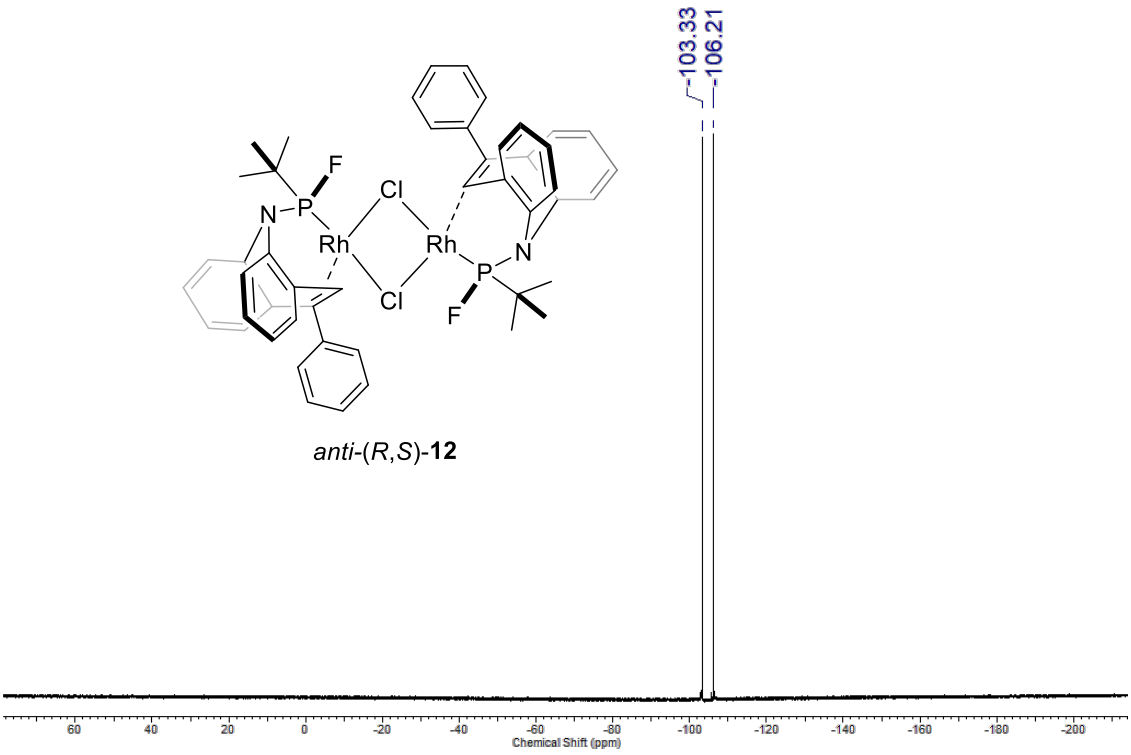


Figure S37. ^{19}F NMR spectrum (377 MHz, C_6D_6) of complex *anti*-(*R,S*)-**12**

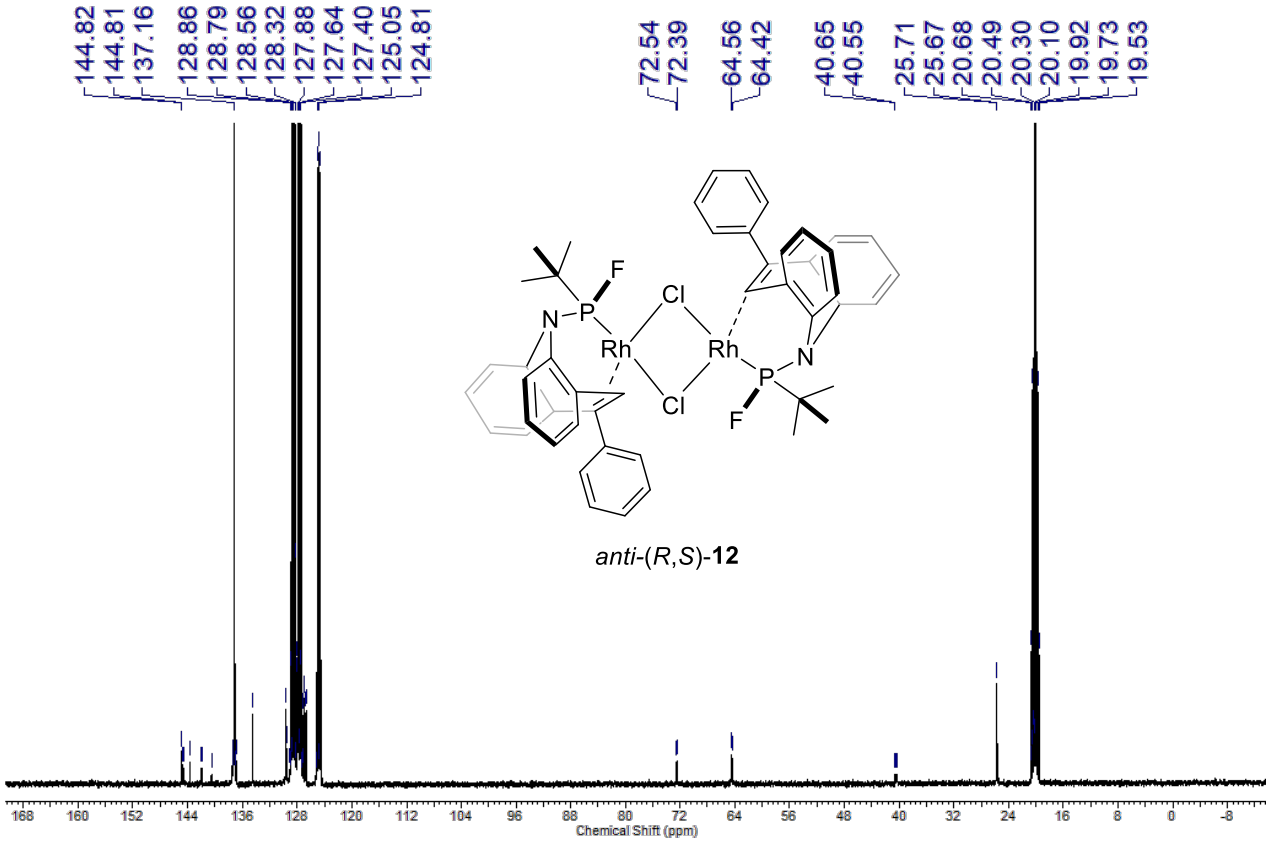


Figure S38. ^{13}C NMR spectrum (151 MHz, C_6D_6) of complex *anti*-(*R,S*)-**12**

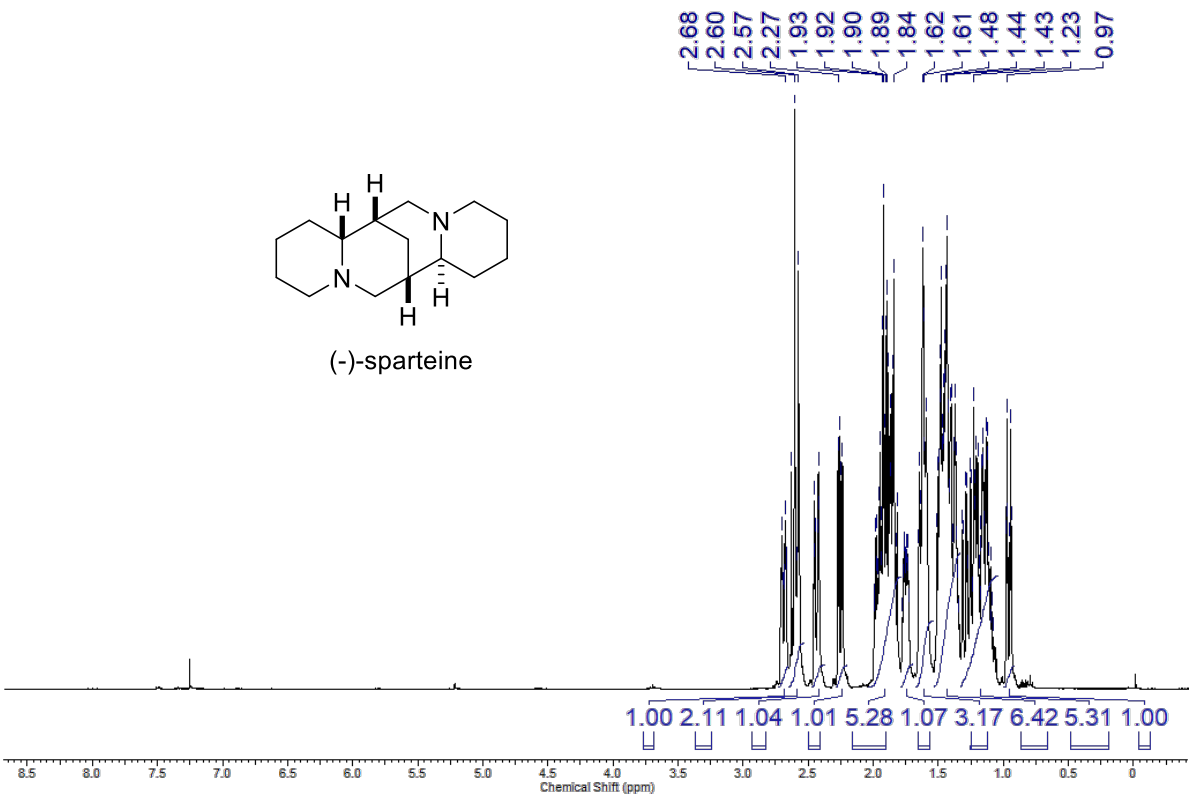


Figure S39. ^{1}H NMR spectrum (400 MHz, C_6D_6) of recovered (-)-Sparteine

HPLC traces of ligands

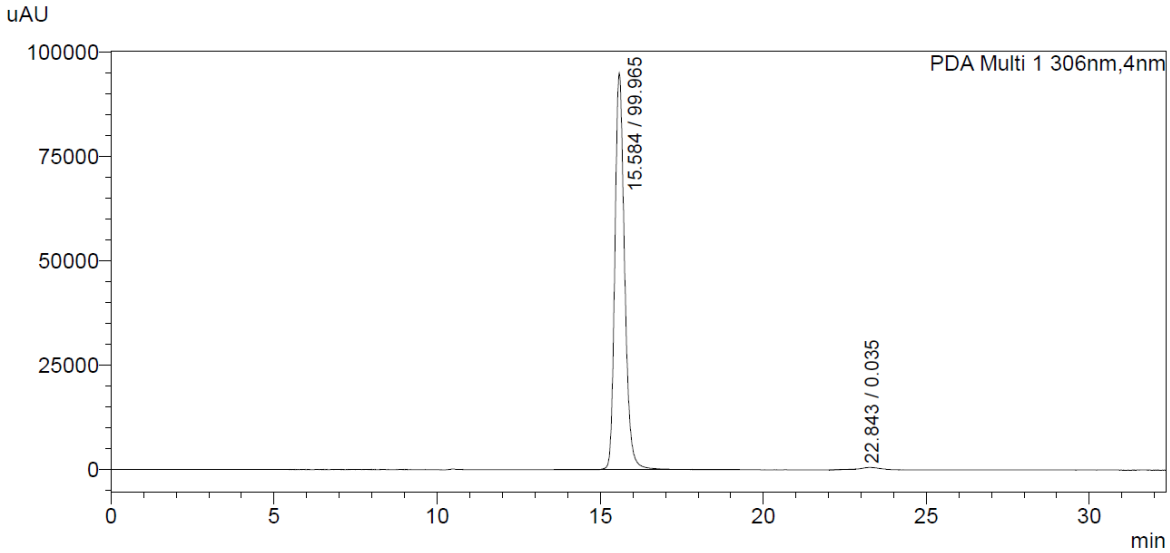


Figure S40. HPLC trace of (p*R,R*$_P$)-**8**. OD-H column, 99:1 hexane/*i*-PrOH, 0.4 mL/min

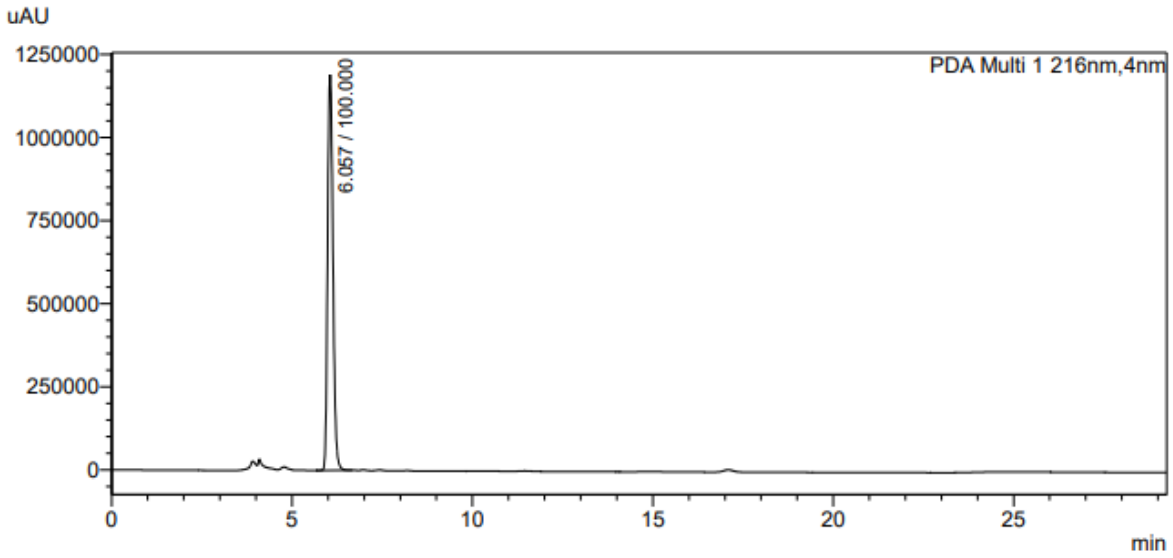
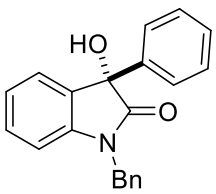


Figure S41. HPLC trace of (p*R,R*P)-**9**. OD-H column, 99:1 hexane/*i*-PrOH, 0.8 mL/min. The minor impurity at 17 minutes accounts for < 1% of surface area and its UV-VIS spectrum differs from that of the main peak.

General procedure for the catalytic arylation of isatins with sodium tetraarylborates

Inside a glovebox, complex **12**[11] (13 mg, 0.013 mmol), Isatin (75 mg, 0.51 mmol) and $NaBAr_4$ (1.02 mmol) were mixed with 1,4-dioxane (3 mL) in a 20 mL vial. Then the orange reaction mixture was stirred for 5 min before adding MeOH (0.25 mL, 6.2 mmol). The resulting red solution was stirred at 45°C for 18 h. After this time, the color faded into a light orange and the vial was taken out of the glovebox. The reaction mixture was quenched with H_2O (20 mL) followed by 5 mL of brine. Et_2O (20 mL) was added and the phases were separated. The aqueous layer was again extracted with Et_2O (3 × 10 mL). The combined organic phases were dried over Na_2SO_4, filtered and all volatiles removed under reduced pressure. The product was purified using a silica column chromatography (CH_2Cl_2/MeOH 95:5). Enantiomeric excess (*ee*) was determined from the purified product by chiral stationary HPLC.



(*S*)-1-benzyl-3-hydroxy-3-phenylindolin-2-one (16aa). Analytical data correspond to literature values:[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 4.75 (d, *J* = 15.65 Hz, 1 H), 4.97 (d, *J* = 15.65 Hz, 1 H), 6.71 (d, *J* = 7.82 Hz, 1 H), 6.94 - 6.99 (m, 1 H), 7.12 - 7.17 (m, 1 H), 7.24 (m, 9 H), 7.30 - 7.37 (m, 2 H). Optical purity was determined *via* chiral HPLC analysis. Column: OD-H, 80:20 hexane/*i*-PrOH, flow: 0.5 mL/min, 12.986 (major isomer), 14.105.

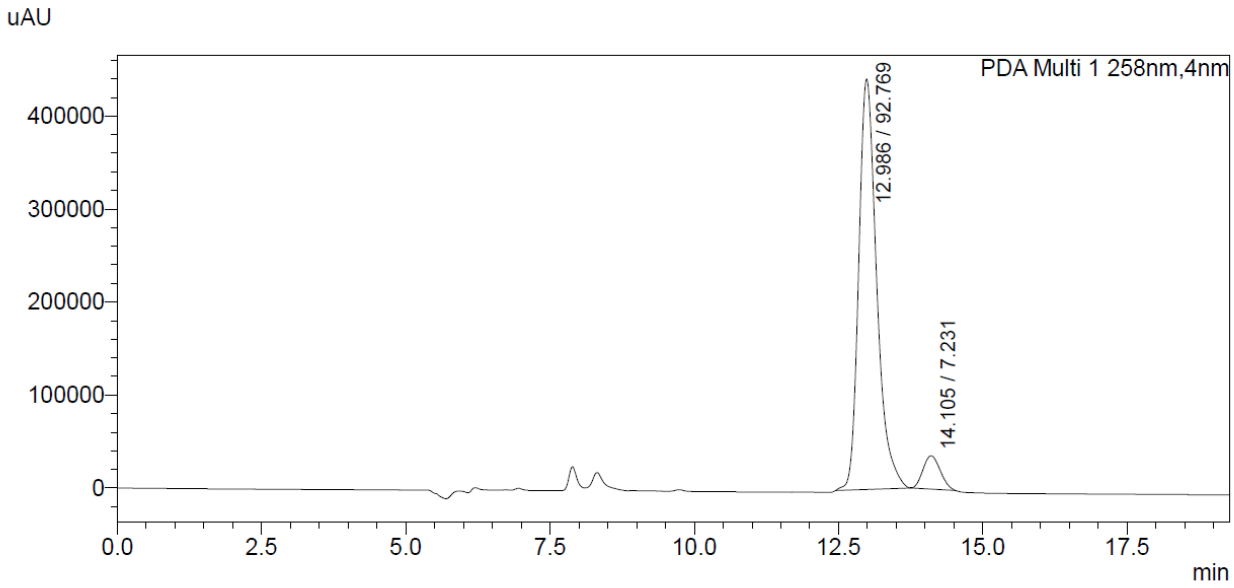
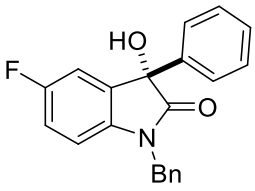


Figure S42. HPLC trace of **16aa**. OD-H, 80:20 hexane/*i*-PrOH, 0.5 mL/min



(*S*)-1-benzyl-5-fluoro-3-hydroxy-3-phenylindolin-2-one (16ba). Analytical data correspond to literature values:[13] ^{1}H NMR (400 MHz $CDCl_3$) δ ppm 4.77 (d, *J* = 15.65 Hz, 1 H), 4.97 (d, *J* = 15.65 Hz, 1 H), 6.63 (dd, *J* = 8.68, 4.03 Hz, 1 H), 6.85 (td, *J* = 8.80, 2.57 Hz, 1 H), 6.96 (dd, *J* = 7.58, 2.57 Hz, 1 H), 7.21 - 7.37 (m, 10 H). Optical purity was determined *via* chiral HPLC analysis. Column: AD-H, 90:10 hexane/*i*-PrOH, flow: 1.0 mL/min, 23.5 min, 26.5 min (major isomer).

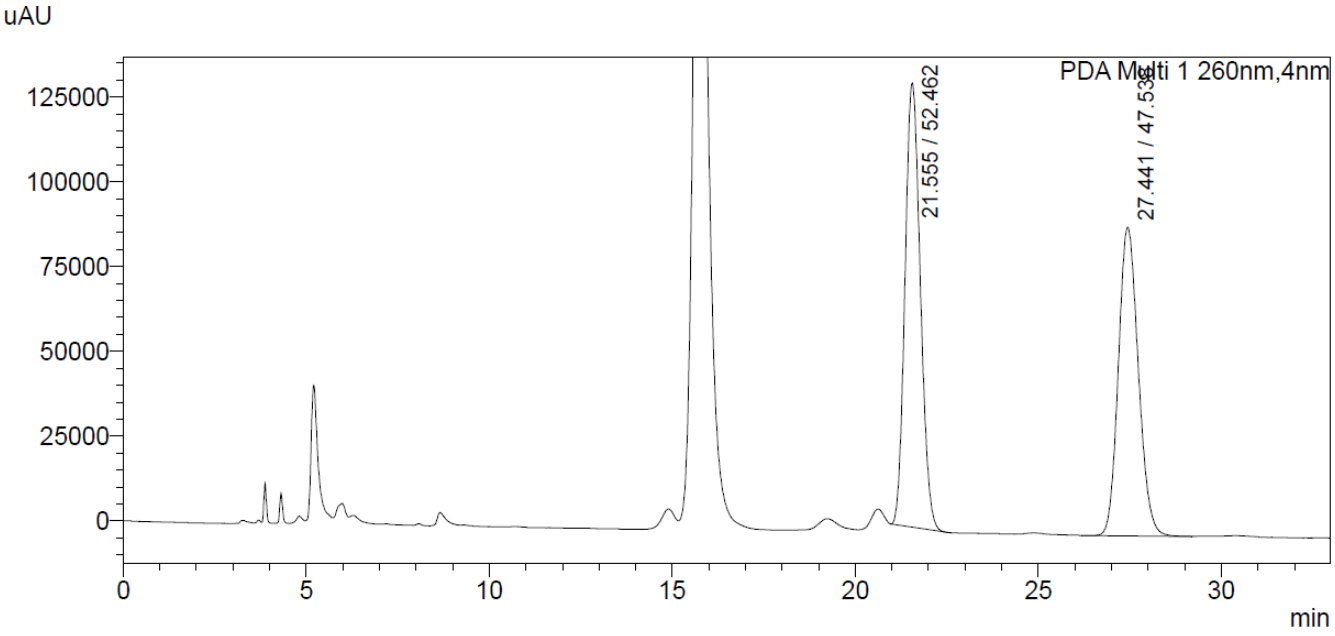


Figure S43. HPLC trace of **16ba**. AD-H, 90:10 hexane/*i*-PrOH, 1.0 mL/min. Reaction performed with [Rh(p*R*,*R*)-**2**)$_2$][BF_4] as catalyst.

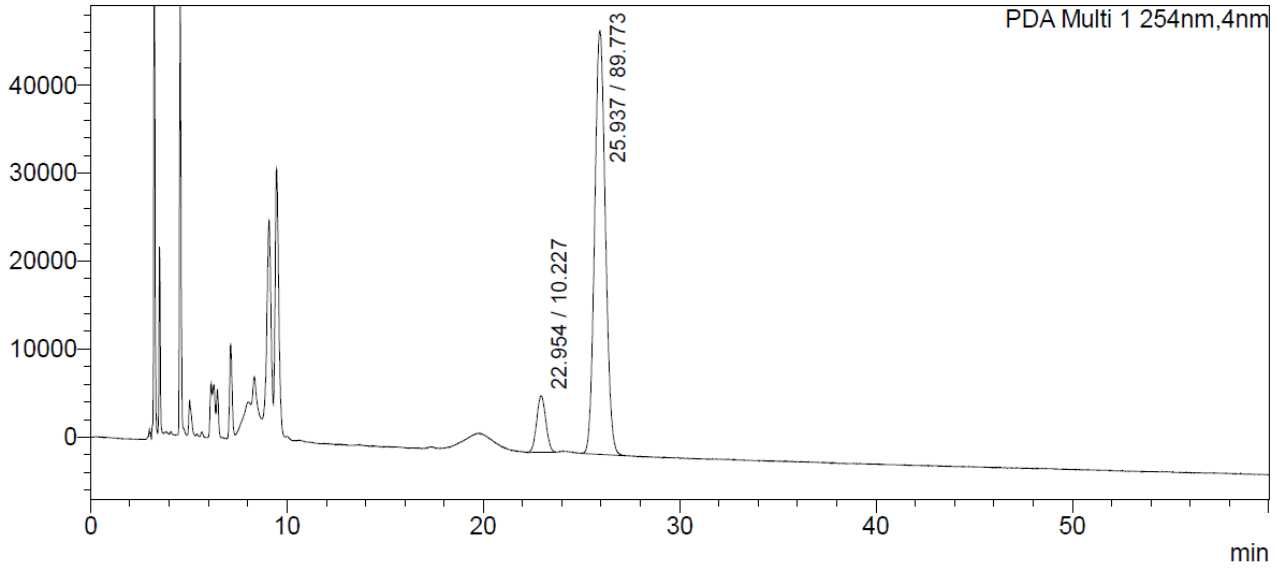


Figure S44. HPLC trace of **16ba**. AD-H, 90:10 hexane/*i*-PrOH, 1.0 mL/min. Reaction performed with (p*R*,*R*P)-**11** as catalyst.

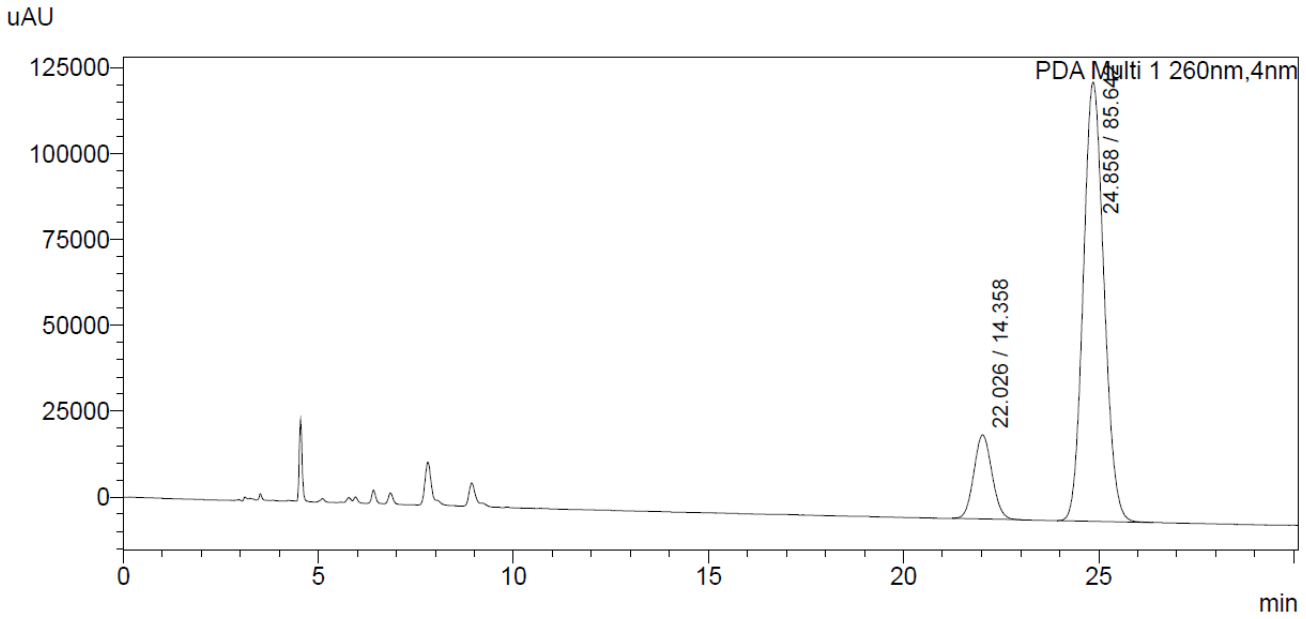
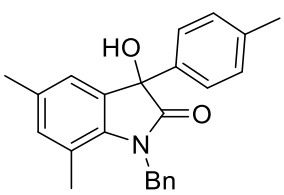


Figure S45. HPLC trace of **16ba**. AD-H, 90:10 hexane/*i*-PrOH, 1.0 mL/min. Reaction performed with (p*R*,*R*P)-**12** as catalyst.



1-benzyl-3-hydroxy-5,7-dimethyl-3-(p-tolyl)indolin-2-one (16cb).[14] ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.14 (s, 3 H), 2.17 (s, 3 H), 2.26 (s, 3 H), 5.10 (s, 2 H), 6.72 (s, 1 H), 6.90 (s, 1 H), 7.04 - 7.12 (m, 4 H), 7.13 - 7.28 (m, 5 H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 178.8, 138.2, 138.0, 137.7, 137.3, 134.1,

133.3, 132.5, 129.4, 128.9, 127.3, 125.7, 125.3, 123.7, 120.2, 45.2, 21.2, 20.7, 18.7. Chiral HPLC: Column: OD-H, 88:12 hexane/*i*-PrOH, flow: 0.5 mL/min, 17.1 min, 22.6 min (major isomer).

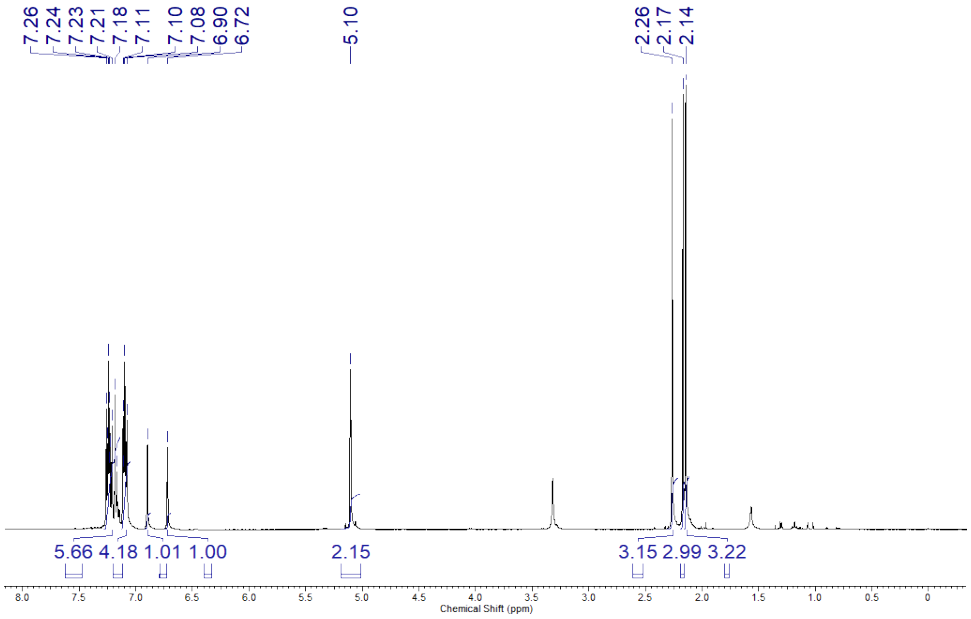


Figure S46. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **16cb**

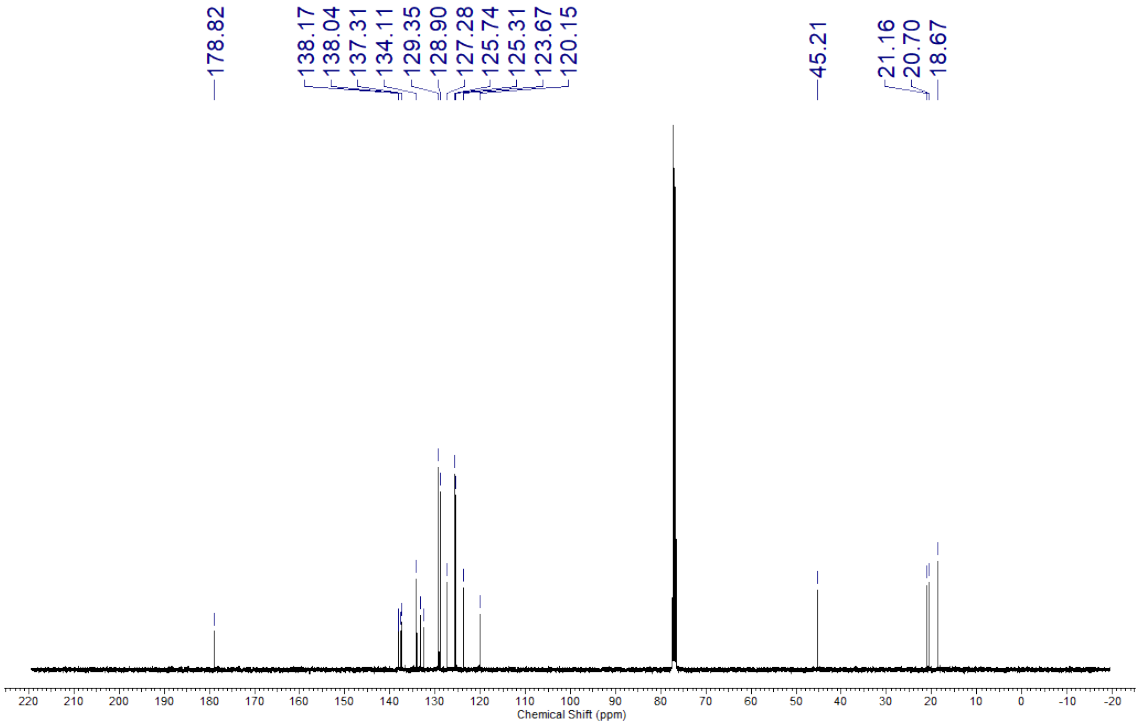


Figure S47. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **16cb**

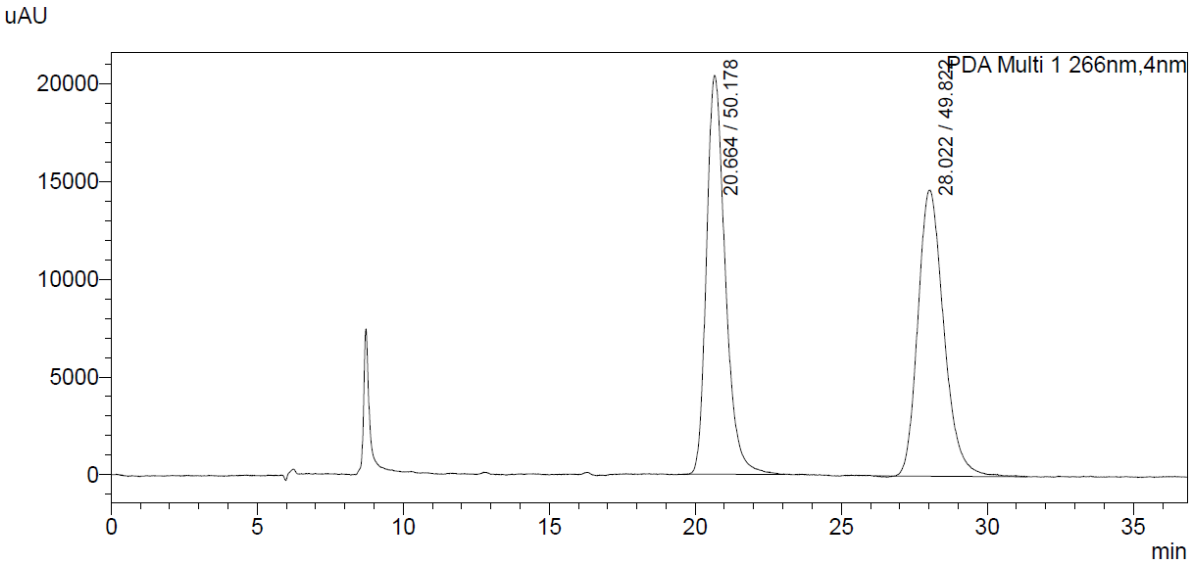


Figure S48. HPLC trace of *rac*-**16cb**. OD-H, 88:12 hexane/*i*-PrOH, 0.5 mL/min (T = 20 ºC)[15]

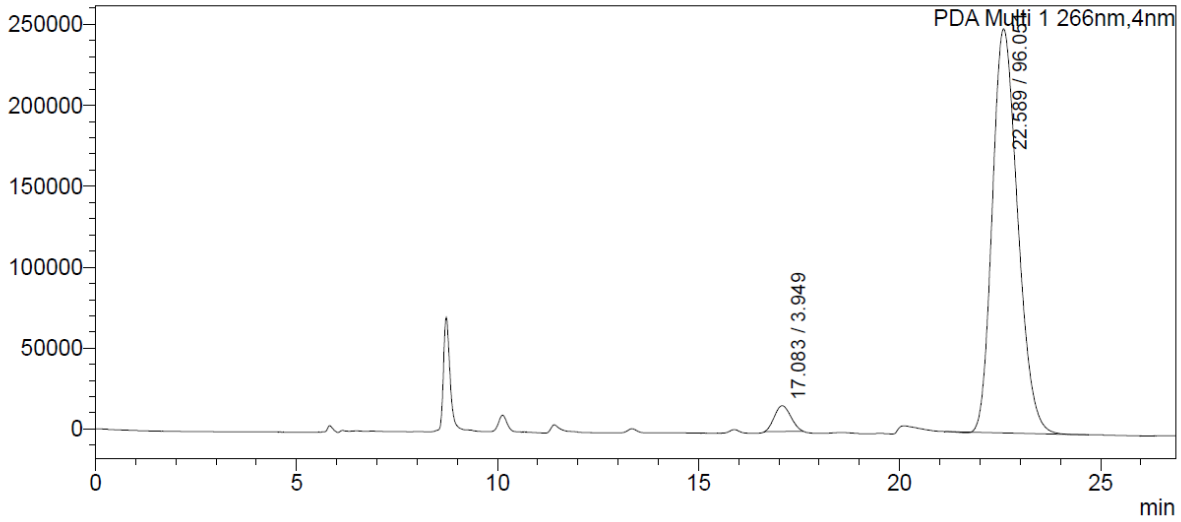
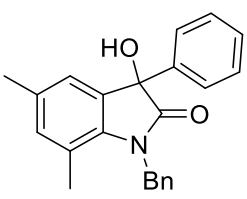


Figure S49. HPLC trace of **16cb**. OD-H, 88:12 hexane/*i*-PrOH, 0.5 mL/min (T = 25 ºC)[15]



1-benzyl-3-hydroxy-5,7-dimethyl-3-phenylindolin-2-one (16ca).[16] ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.15 (s, 3 H), 2.18 (s, 3 H), 5.12 (s, 2 H), 6.74 (s, 1 H), 6.90 (s, 1 H), 7.11 (d, J = 7.09 Hz, 2 H), 7.14 - 7.32 (m, 7 H), 7.33 - 7.40 (m, 2 H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 178.7, 140.7, 138.2, 137.3, 134.2, 133.4, 132.5, 128.9, 128.7, 128.2, 127.3, 125.7, 125.4, 123.7, 120.2, 45.2, 20.7, 18.7. Optical purity was determined *via* chiral HPLC analysis. Column: OD-H, 75:15 hexane/*i*-PrOH, flow: 0.5 mL/min, 16.0 min, 18.9 min (major isomer).

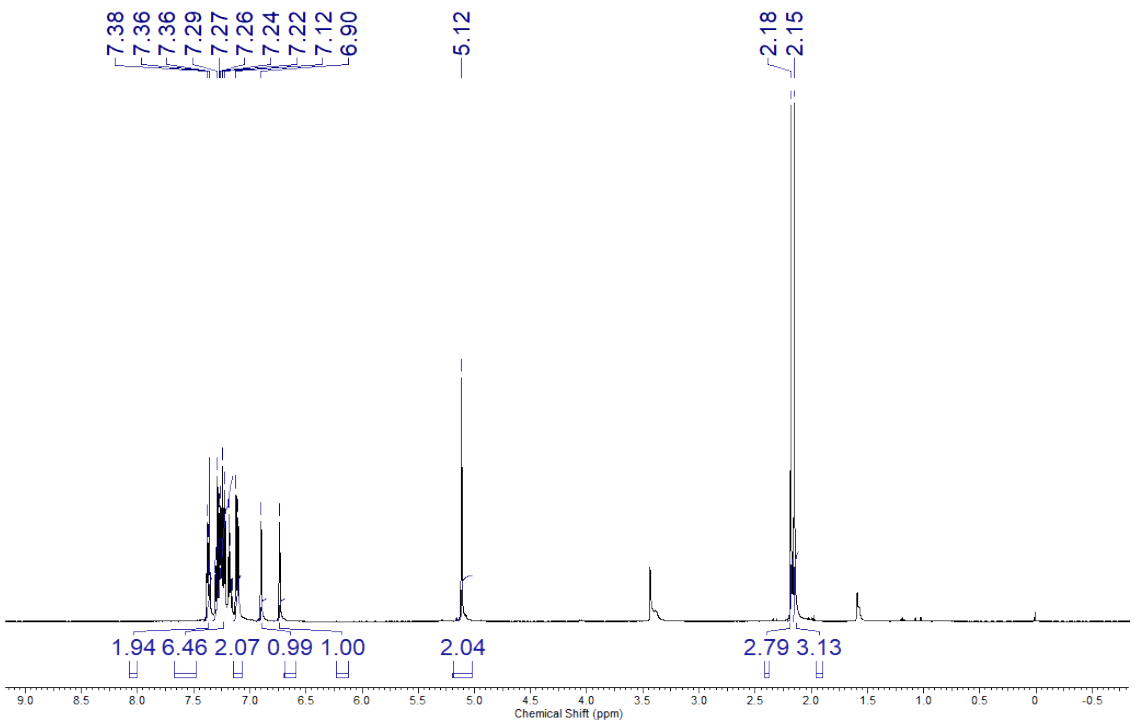


Figure S50. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) **of 16ca**

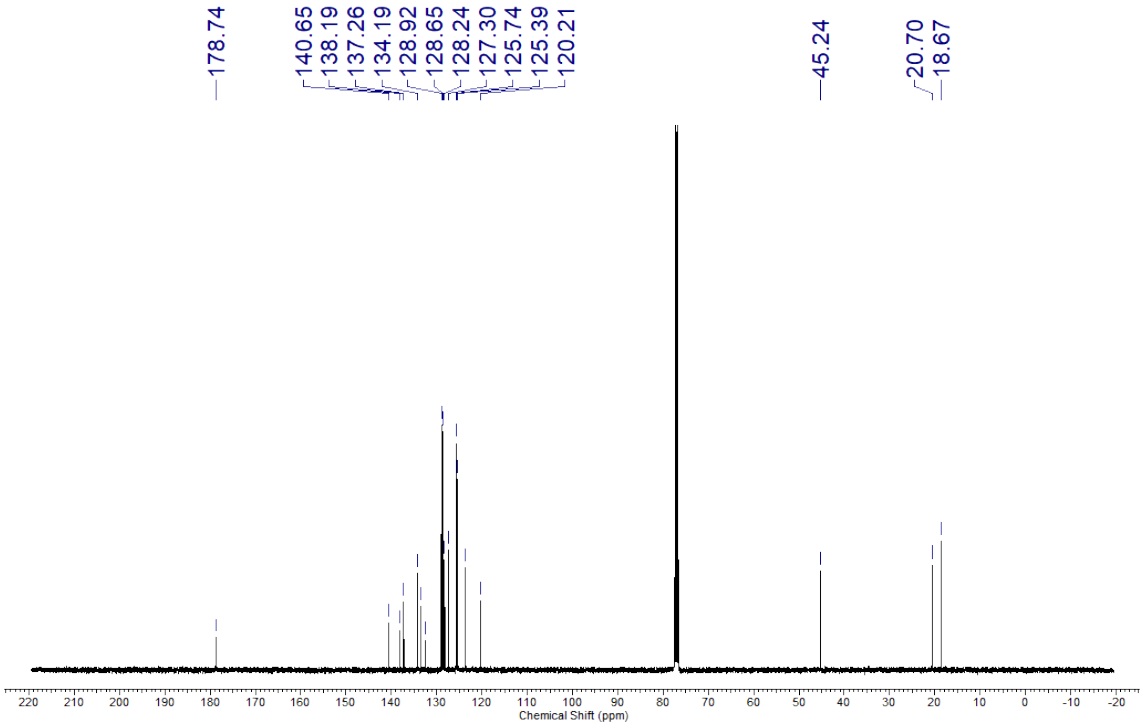


Figure S51. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **16ca**

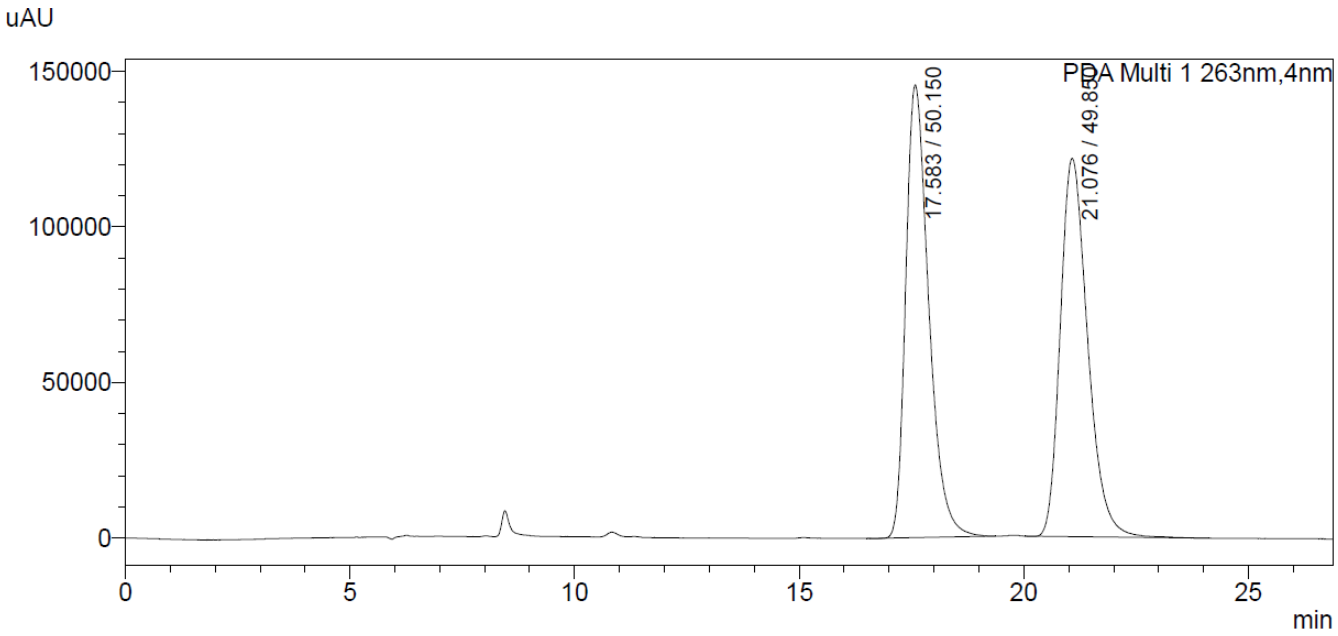


Figure S52. HPLC trace of *rac*-**16ca**. OD-H, 75:25 hexane/*i*-PrOH, 0.5 mL/min (T = 20 ºC)[15]

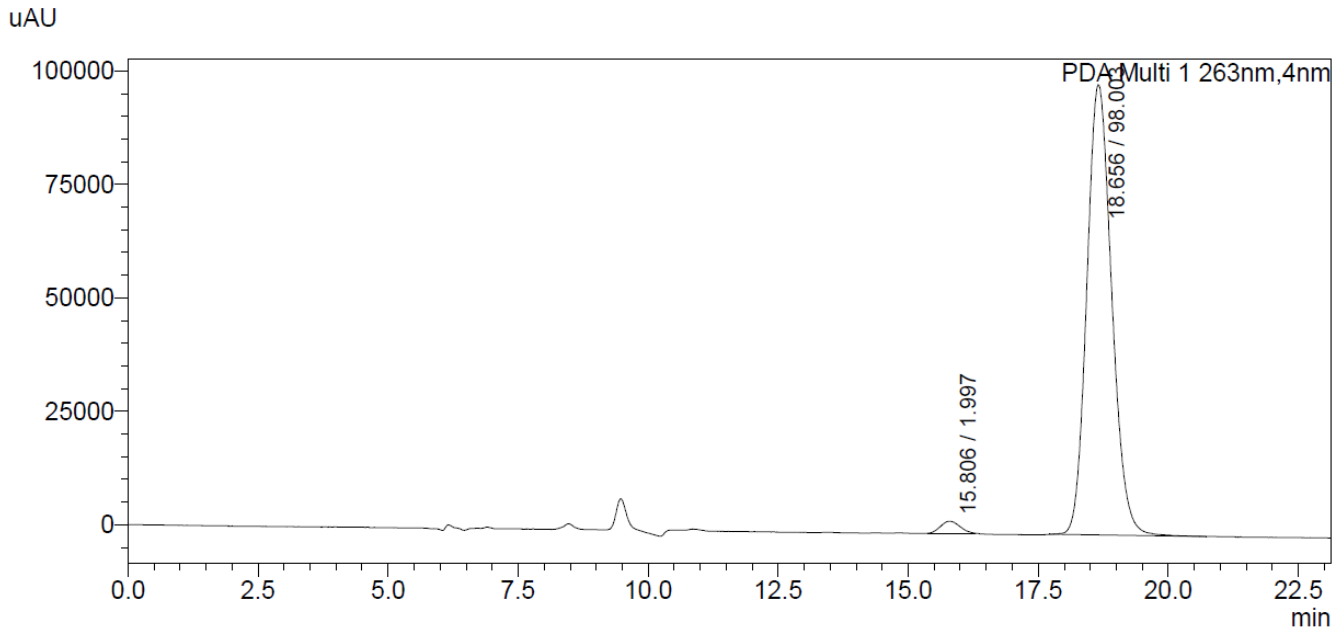
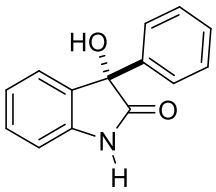


Figure S53. HPLC trace of **16ca**. OD-H, 75:25 hexane/*i*-PrOH, 0.5 mL/min (T = 25 ºC)[15]



(*S*)-3-hydroxy-3-phenylindolin-2-one (16da). Analytical data correspond to published values:[17] ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 6.61 (s, 1H), 6.89 (d, J = 7.58 Hz, 1H), 6.95 (t, J = 7.52 Hz, 1H), 7.09 (d, J = 7.34 Hz, 1H) 7.20 - 7.35 (m, 5 H), 10.39 (s, 1H). Optical purity was determined *via* chiral HPLC analysis. Column: OD-H, 95:5 hexane/*i*-PrOH, flow: 1.0 mL/min, 25.416 (major isomer), 27.508.

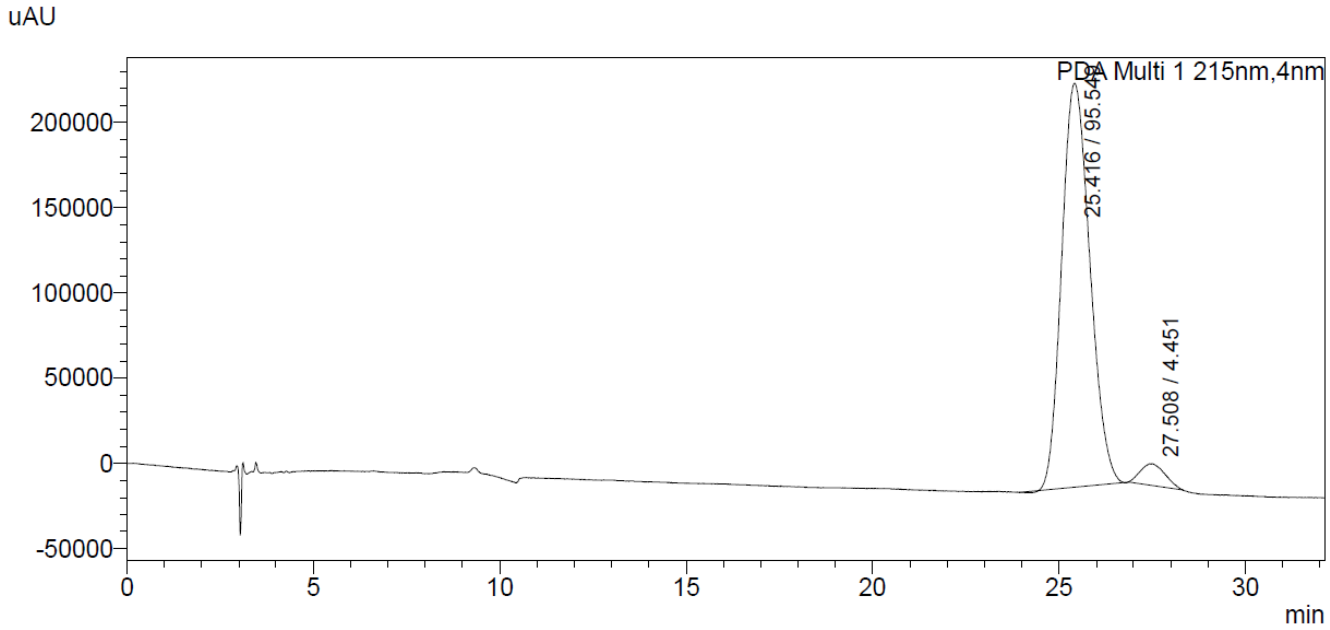
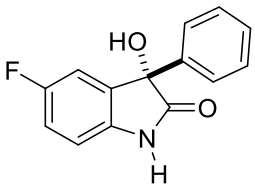


Figure S54. HPLC trace of **16da**. OD-H, 95:5 hexane/*i*-PrOH, 1.0 mL/min



(*S*)-5-fluoro-3-hydroxy-3-phenylindolin-2-one (16ea). Analytical data correspond to literature values:[18] ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 6.76 (s, 1H), 6.89 (dd, J = 8.44, 4.28 Hz, 1H) 6.95 (dd, J = 8.01, 2.63 Hz, 1H) 7.02 - 7.13 (m, 1H) 7.20 - 7.36 (m, 5H) 10.43 (s, 1H). Optical purity was determined *via* chiral HPLC analysis. Column: OD-H, 93:7 hexane/*i*-PrOH, flow: 0.5 mL/min, 46.145 min (major isomer), 55.036 min.

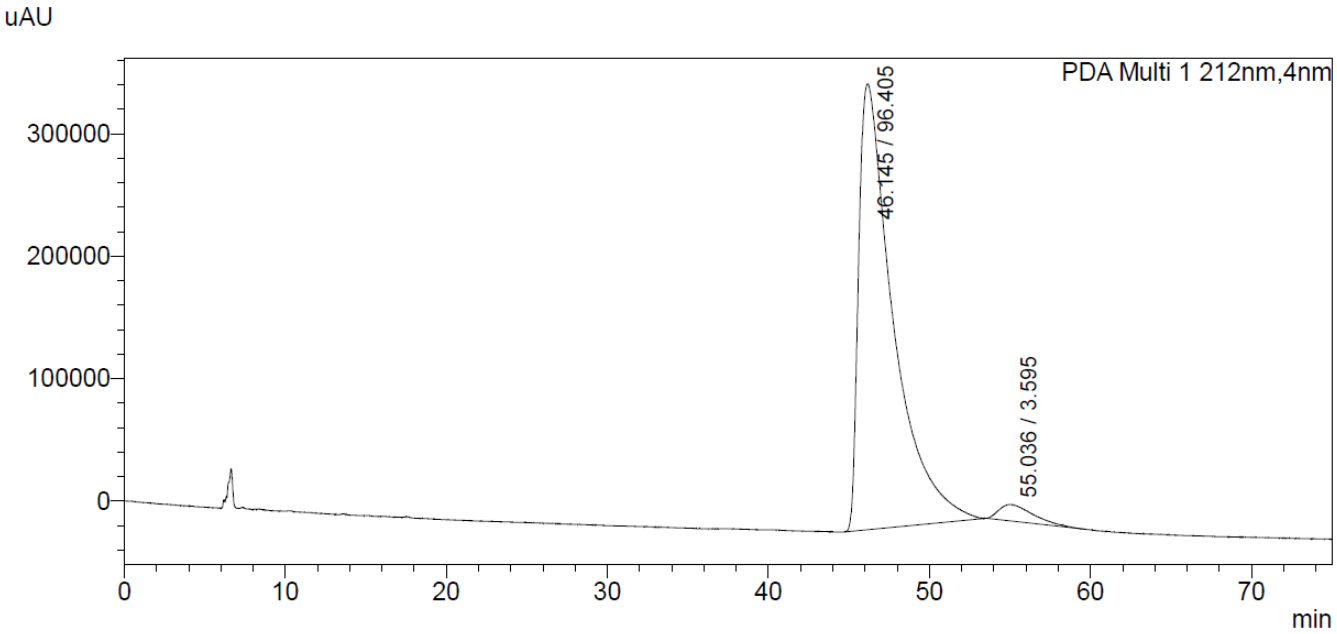
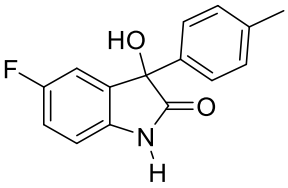


Figure S55. HPLC trace of **16ea**. OD-H, 93:7 hexane/*i*-PrOH, 0.5 mL/min



5-fluoro-3-hydroxy-3-(p-tolyl)indolin-2-one (16eb). ^{1}H NMR (600 MHz, DMSO-d_6) δ ppm 2.26 (s, 3H), 6.69 (s, 1H), 6.88 (dd, J = 8.44, 4.22 Hz, 1H), 6.94 (dd, J = 8.07, 2.38 Hz, 1H), 7.05 - 7.10 (m, 1H), 7.10 - 7.18 (m, 4H), 10.40 (s, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ ppm 21.11, 77.92, 111.20 (d, J = 7.70 Hz), 112.70 (d, J = 24.21 Hz), 115.93 (d, J = 23.11 Hz), 125.78, 129.18, 135.96 (d, J = 7.70 Hz), 137.31, 138.49, 158.75 (d, J = 237.69 Hz), 178.96. Optical purity was determined *via* chiral HPLC analysis. Column: OD-H, 96:4 hexane/*i*-PrOH, flow: 0.5 mL/min, 84.927 min (major isomer), 93.716 min.

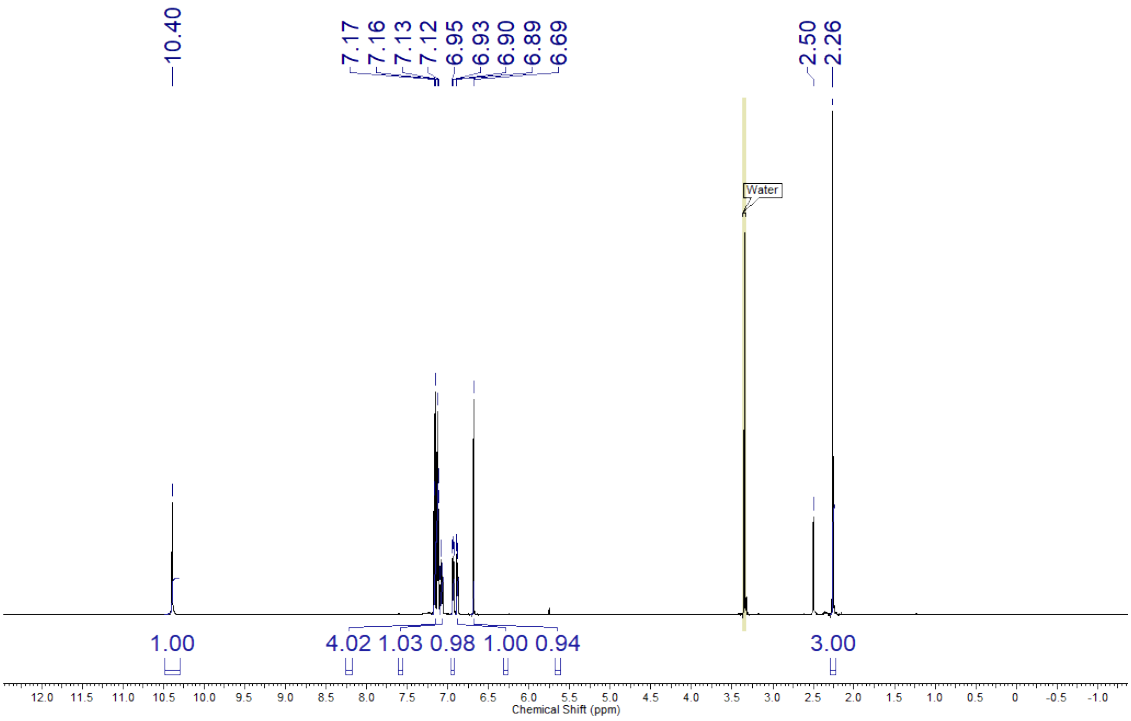


Figure S56. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **16eb**

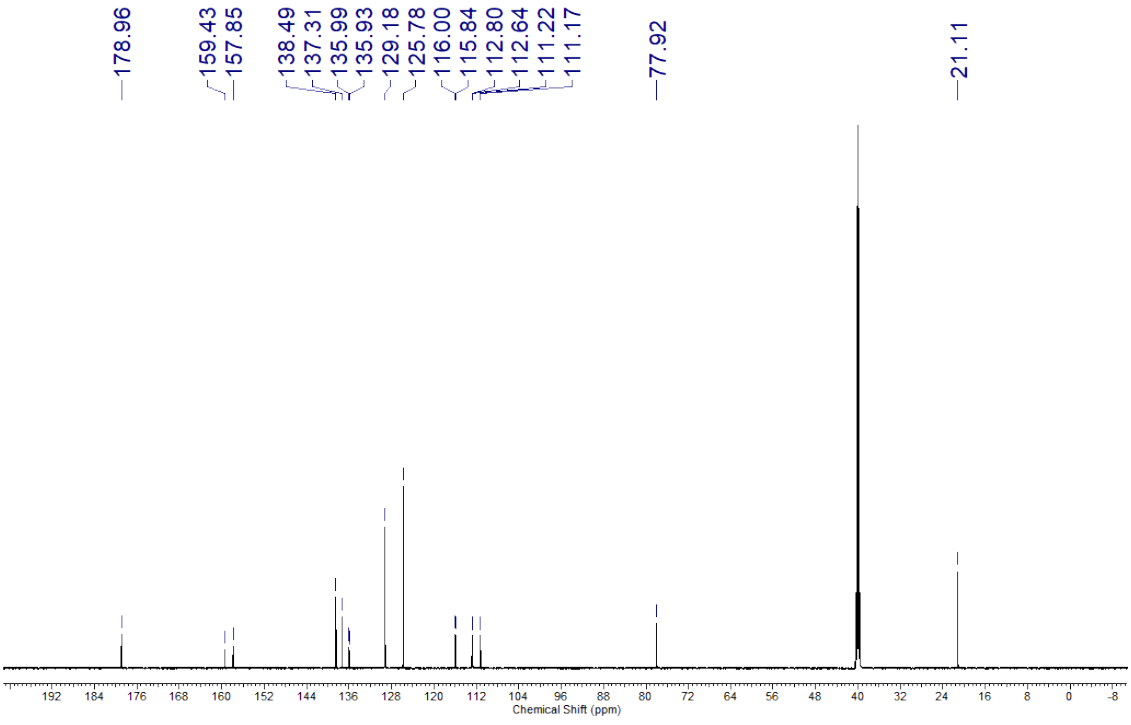


Figure S57. ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of **16eb**

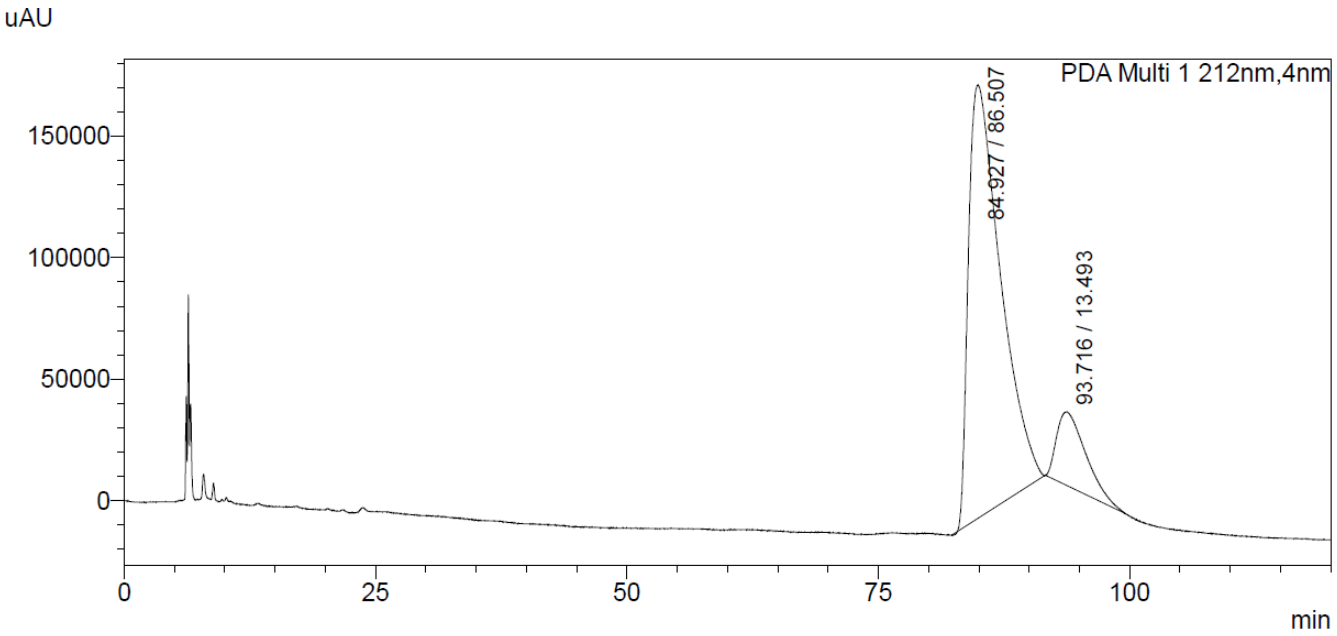
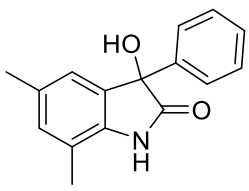


Figure S58. HPLC trace of **16eb**. OD-H, 96:4 hexane/*i*-PrOH, 0.5 mL/min



3-hydroxy-5,7-dimethyl-3-phenylindolin-2-one (16fa). Analytical data correspond to literature values:[19] ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 2.16 (s, 3H), 2.20 (s, 3H), 6.51 (s, 1H), 6.70 (s, 1H), 6.86 (s, 1H), 7.11 - 7.34 (m, 5H), 10.33 (s, 1H). Optical purity was determined *via* chiral HPLC analysis. Column: AD-H, 95:5 hexane/*i*-PrOH, flow: 1.0 mL/min, 16.0 min, 18.9 min (major isomer).

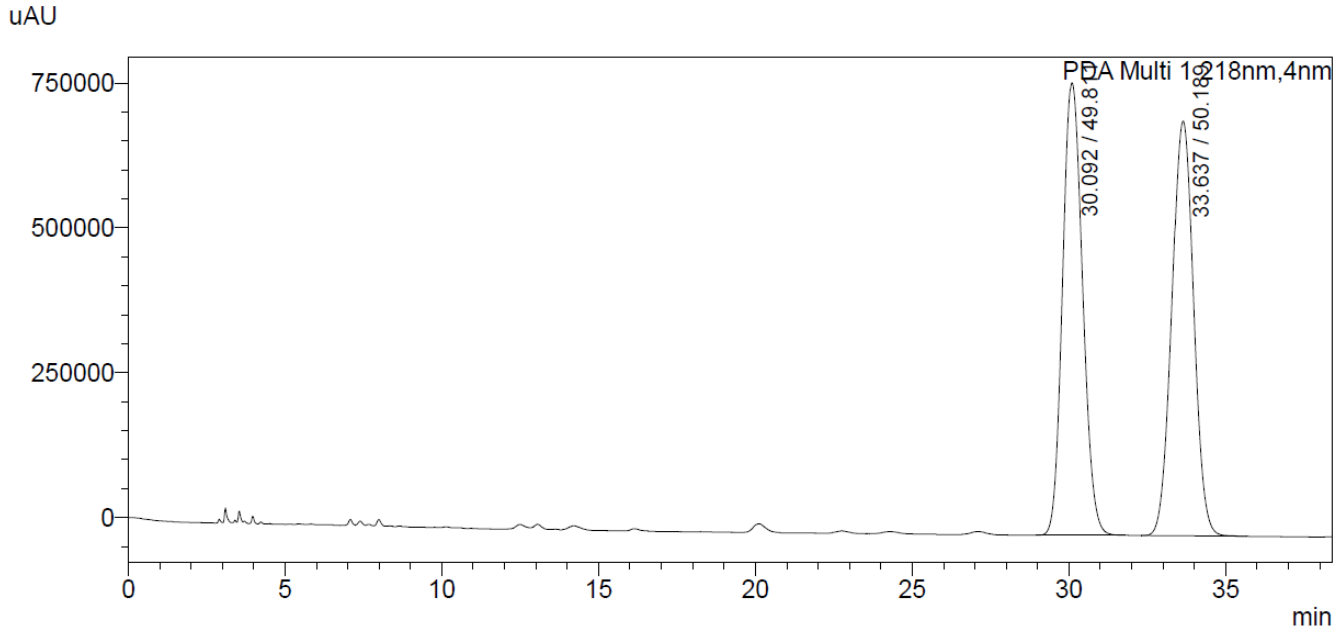


Figure S59. HPLC trace of *rac*-**16fa.** AD-H, 95:5 hexane/*i*-PrOH, 1.0 mL/min

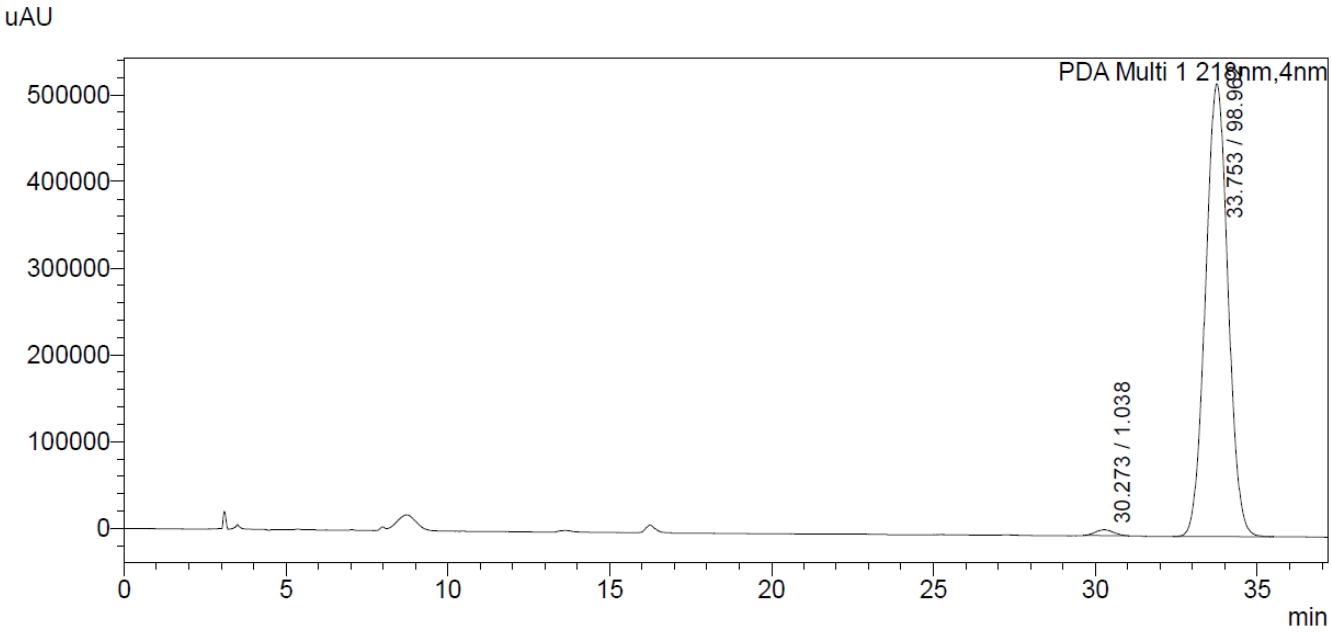
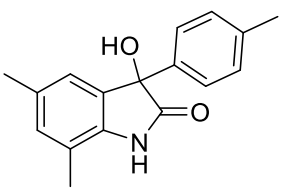


Figure S60. HPLC trace of **16fa**. Entry 10 in Table 1. AD-H, 95:5 hexane/*i*-PrOH, 1.0 mL/min



3-hydroxy-5,7-dimethyl-3-(p-tolyl)indolin-2-one (16fb).[20] ^{1}H NMR (600 MHz, DMSO-d_6) δ ppm 2.17 (s, 3H), 2.20 (s, 3H), 2.26 (s, 3H), 6.44 (s, 1H), 6.70 (s, 1H), 6.86 (s, 1H), 7.07 - 7.18 (m, 4H), 10.30 (s, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ ppm 16.76, 21.00, 21.11, 77.94, 119.24, 123.03, 125.79, 129.01, 131.14, 131.18, 134.17, 136.86, 138.38, 139.36, 179.56. Optical purity was determined *via* chiral HPLC analysis. Column: AD-H, 95:5 hexane/*i*-PrOH, flow: 1.0 mL/min, 31.826 min (major isomer), 36.928 min.

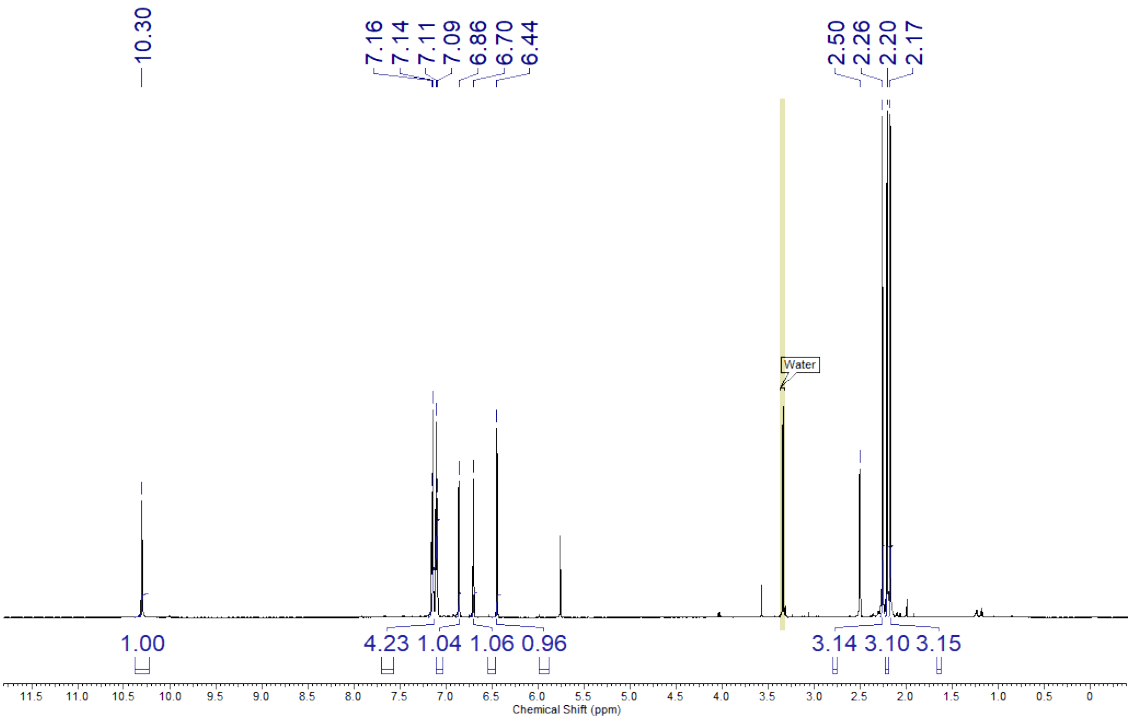


Figure S61. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **16fb**

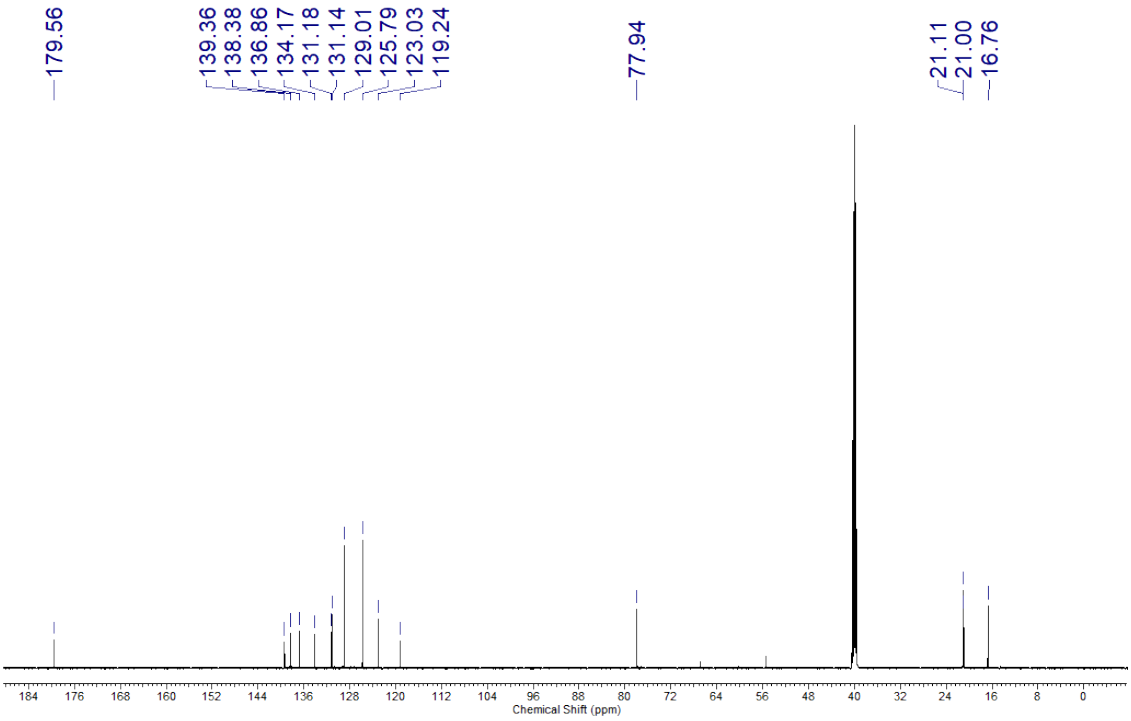


Figure S62. ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of **16fb**

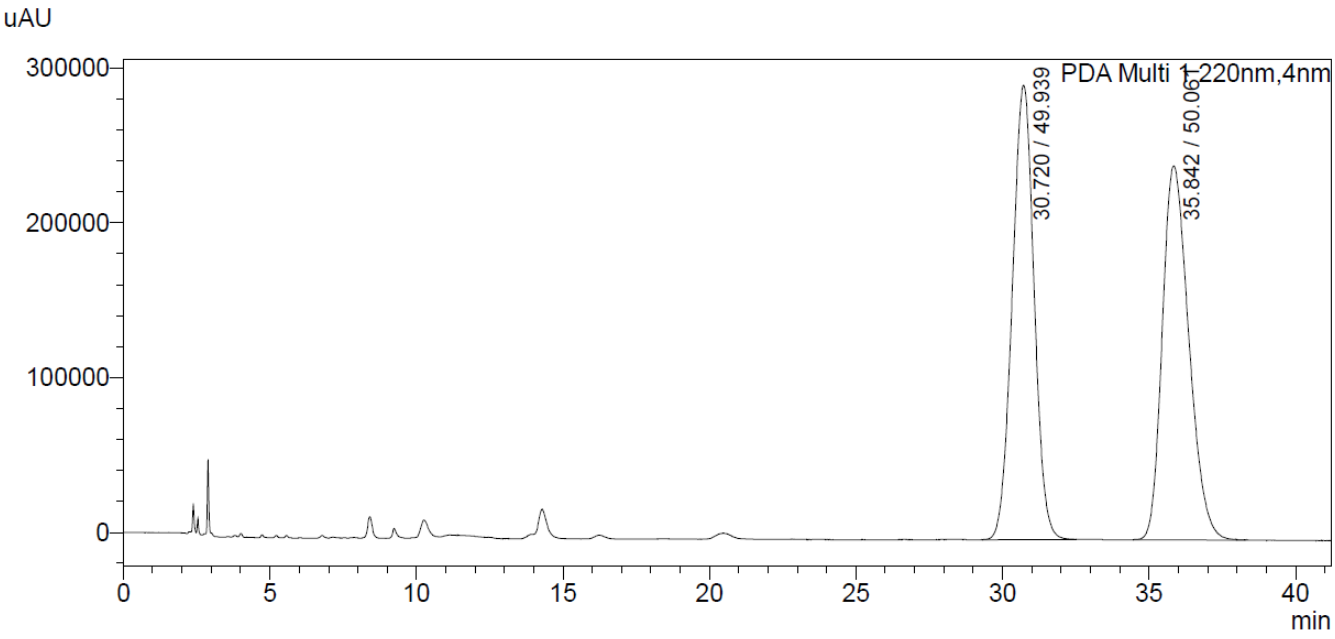


Figure S63. HPLC trace of *rac*-**16fb**. AD-H, 95:5 hexane/*i*-PrOH, 1.0 mL/min

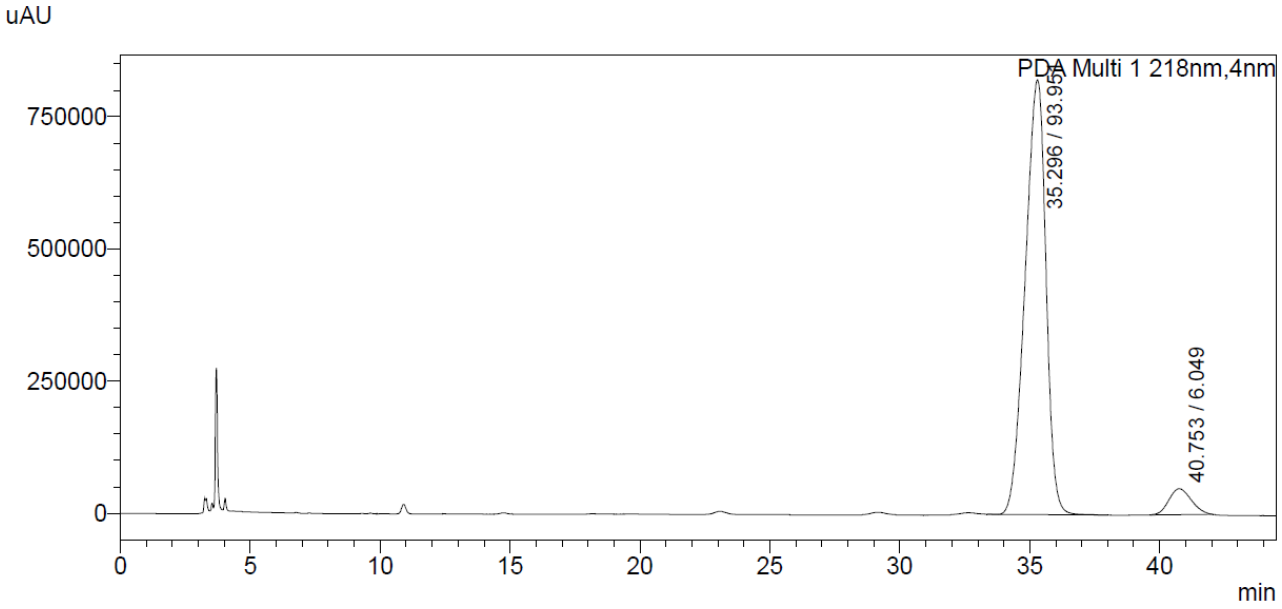


Figure S64. HPLC trace of **16fb**. AD-H, 95:5 hexane/*i*-PrOH, 1.0 mL/min

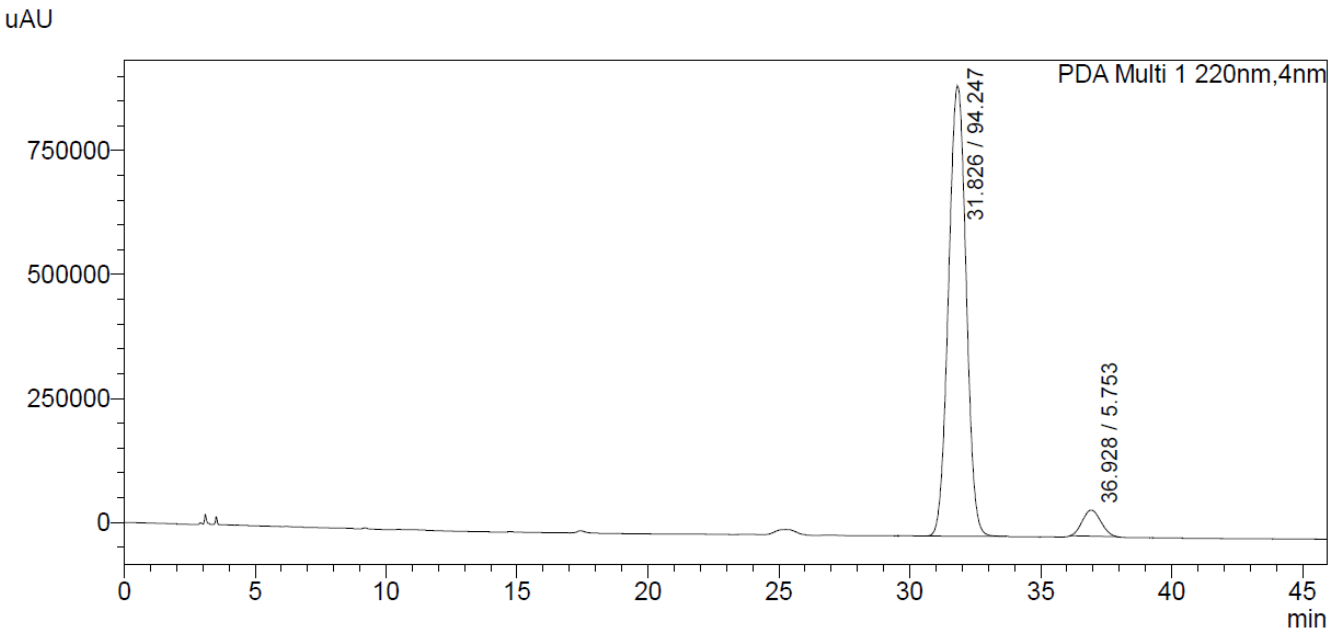
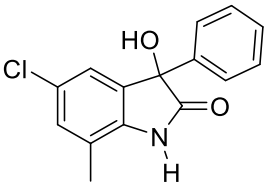


Figure S65. HPLC trace of **16fb**. AD-H, 95:5 hexane/*i*-PrOH, 1.0 mL/min. Reaction performed with 1 equiv. of **15b**



5-chloro-3-hydroxy-7-methyl-3-phenylindolin-2-one (16ga).[21] ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 2.25 (s, 3H), 6.74 (s, 1H), 6.92 (d, J = 1.71 Hz, 1H), 7.17 (d, J = 1.22 Hz, 1H), 7.23 - 7.36 (m, 5H) 10.61 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ ppm 16.64, 77.98, 122.00, 122.39, 125.79, 126.30, 128.10, 128.68, 130.41, 135.67, 139.91, 141.42, 179.02. Optical purity was determined *via* chiral HPLC analysis. Column: AD-H, 98:2 hexane/*i*-PrOH, flow: 1.0 mL/min, 100.212 min, 109.278 min (major isomer).

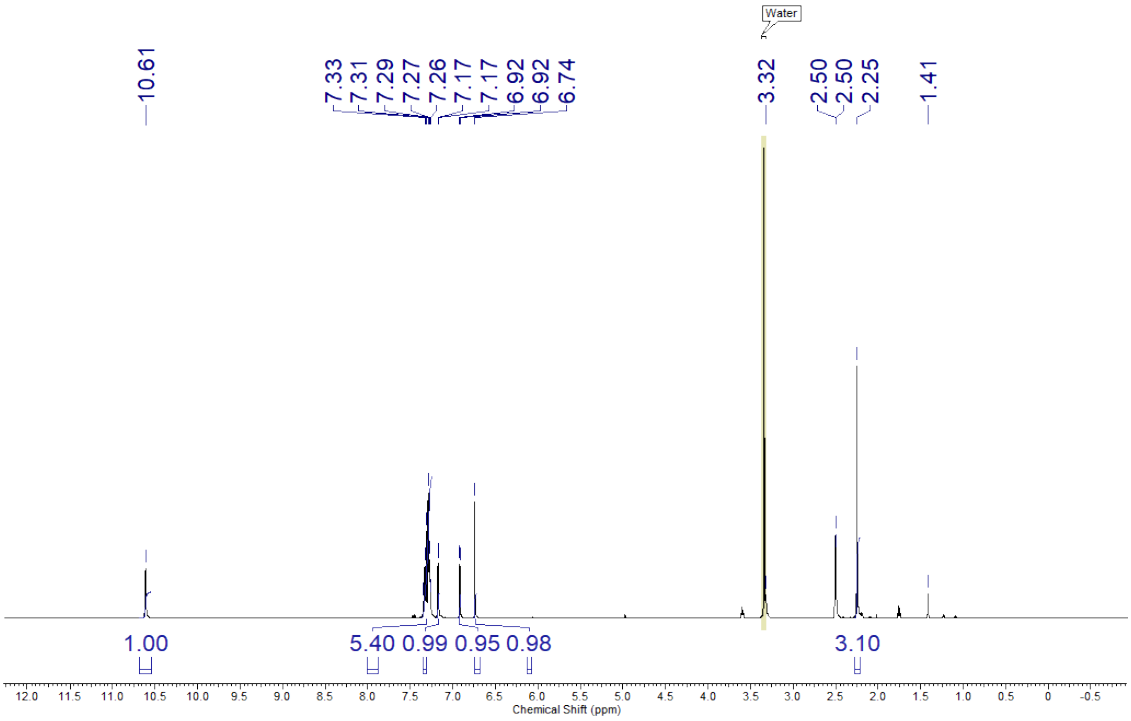


Figure S66. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **16ga**

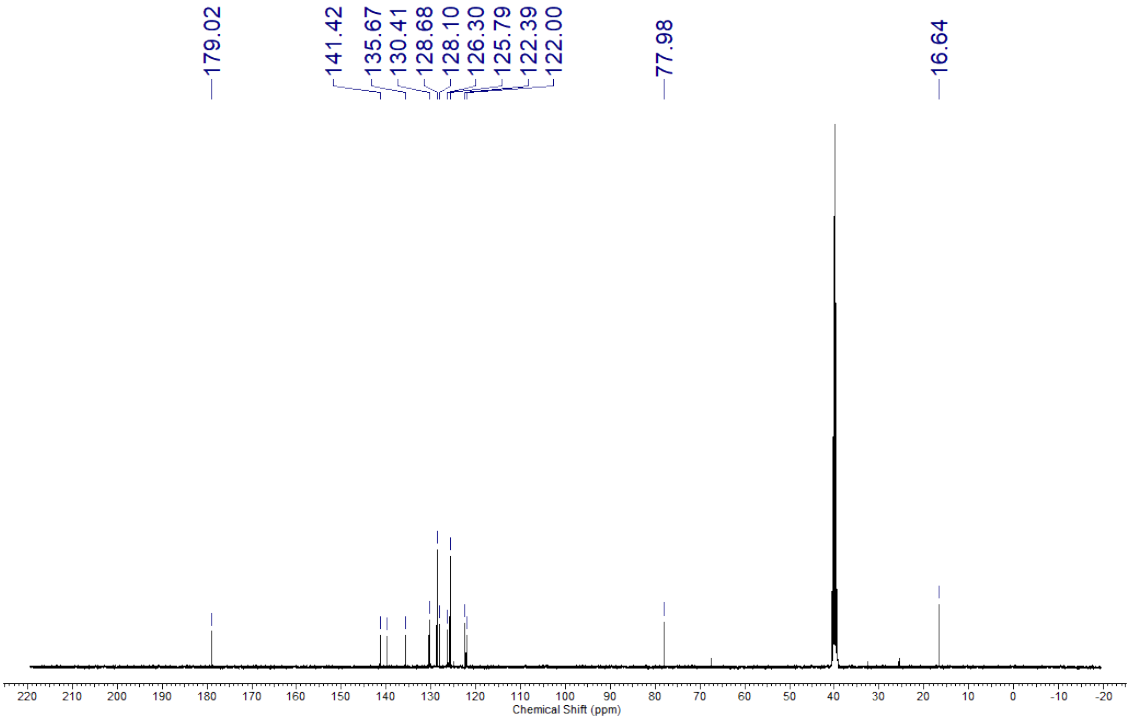


Figure S67. ^{13}C NMR spectrum (101 MHz, DMSO-d_6) of **16ga**

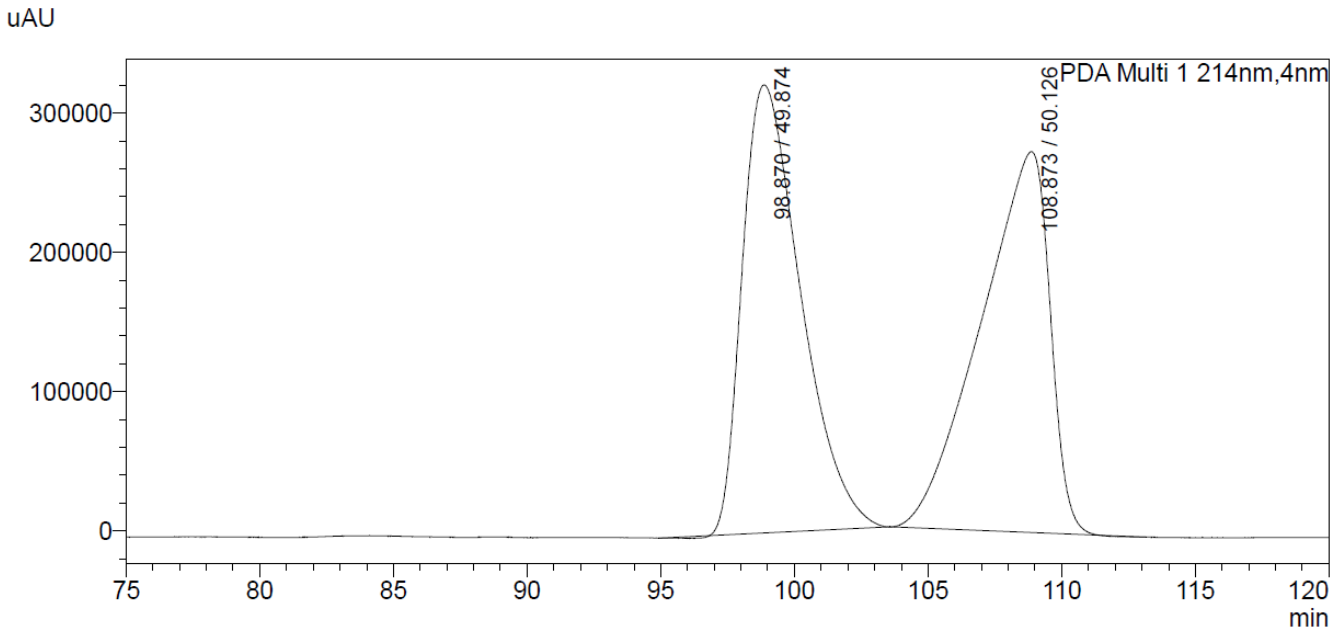


Figure S68. HPLC trace of *rac*-**16ga**. AD-H, 98:2 hexane/*i*-PrOH, 1.0 mL/min

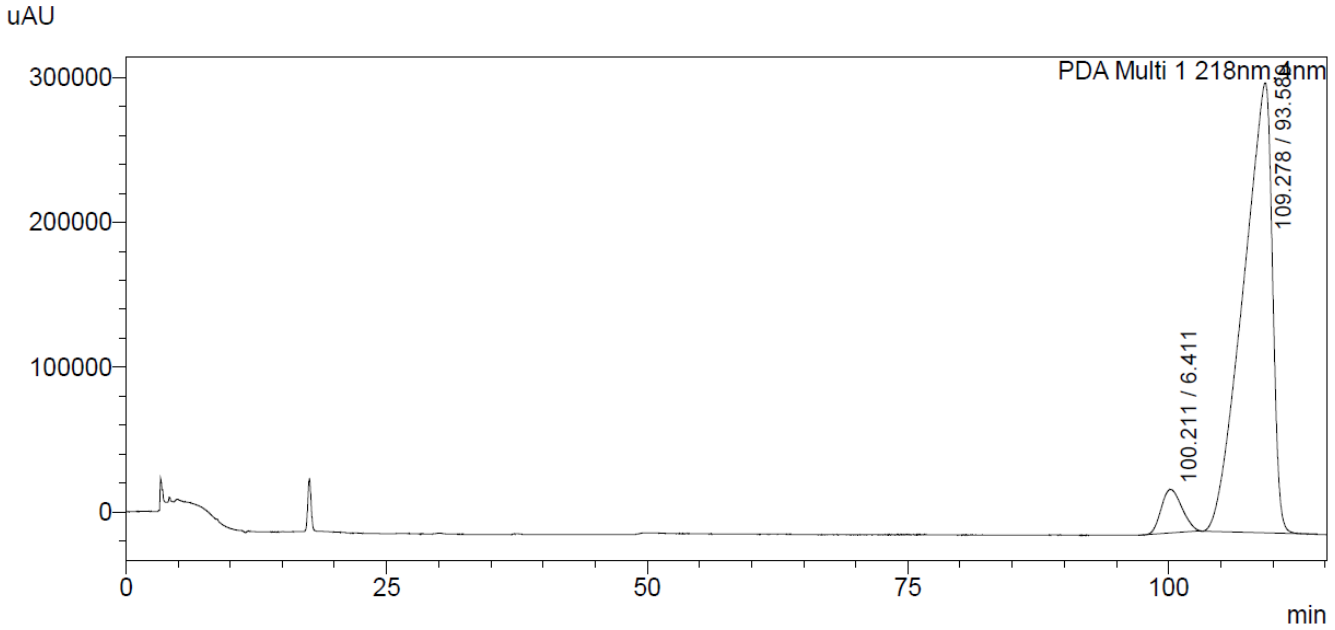
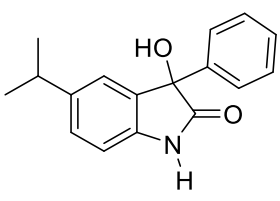


Figure S69. HPLC trace of **16ga**. AD-H, 98:2 hexane/*i*-PrOH, flow: 1.0 mL/min



3-hydroxy-5-isopropyl-3-phenylindolin-2-one (16ha). Analytical data correspond to literature values:[22] ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 1.12 (m, 6H), 2.72 - 2.86 (m, 1H), 6.56 (s, 1H), 6.81 (d, J = 7.95 Hz, 1H), 6.96 (s, 1H), 7.11 (dd, J = 8.01, 1.41 Hz, 1H), 7.20 - 7.34 (m, 5H), 10.28 (s, 1H). Optical purity was determined *via* chiral HPLC analysis. Column: AD-H, 95:5 hexane/*i*-PrOH, flow: 1.0 mL/min, 25.981 min (major isomer), 33.998 (minor isomer).

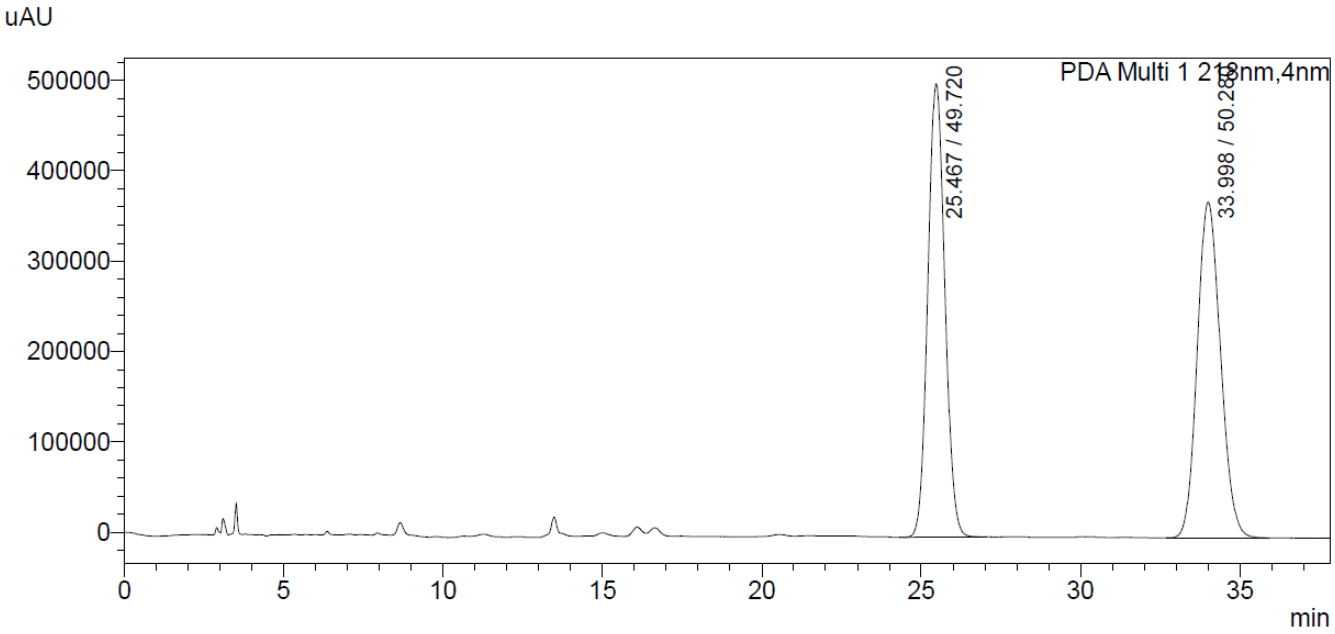


Figure S70. HPLC trace of *rac*-**16ha.** AD-H, 95:5 hexane/*i*-PrOH, 1.0 mL/min

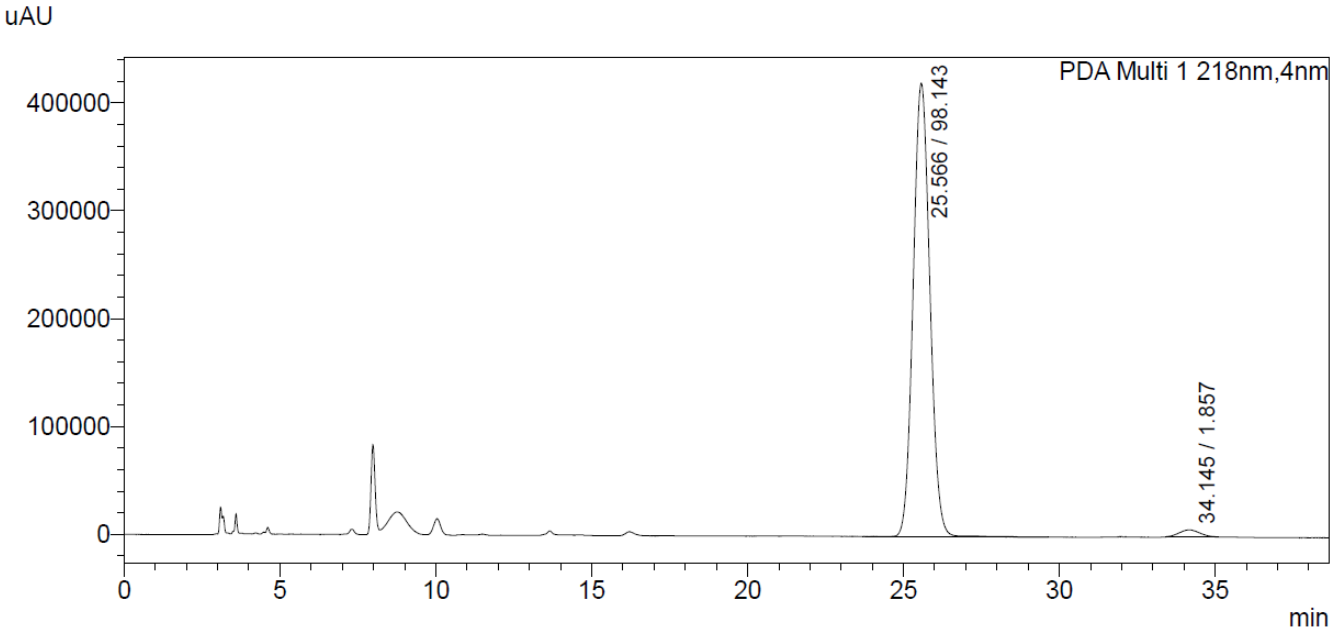


Figure S71. HPLC trace of **16ha**. Entry 14 in Table 1. AD-H, 95:5 hexane/*i*-PrOH, 1.0 mL/min

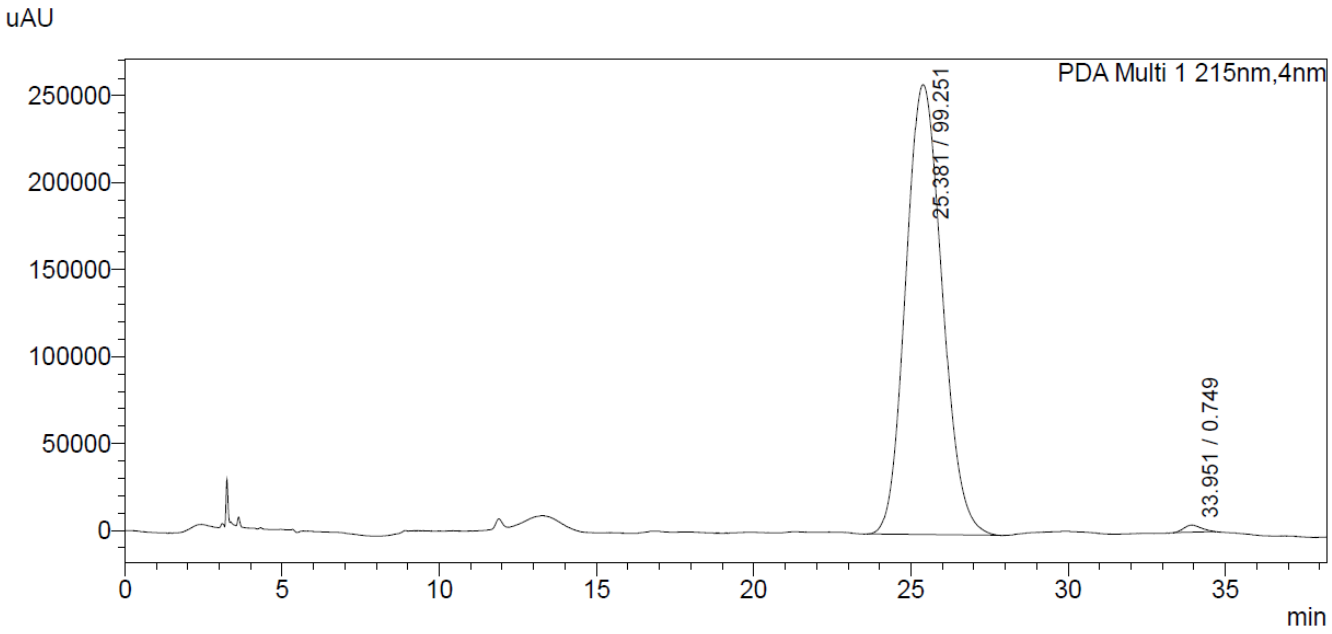
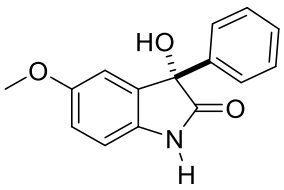


Figure S72. HPLC trace of **16ha**. AD-H, 95:5 hexane/*i*-PrOH, 1.0 mL/min



(*S*)-3-hydroxy-5-methoxy-3-phenylindolin-2-one (16ia). Analytical data correspond to literature values:[23] $[\alpha]_D = +41.3°$ (c = 0.48, MeOH). ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 3.65 (s, 3H), 6.62 (s, 1H), 6.69 (s, 1H) 6.81 - 6.83 (m, 2H), 7.21 - 7.34 (m, 5H), 10.22 (s, 1H). Optical purity was determined *via* chiral HPLC analysis. Column: AD-H, 80:20 hexane/*i*-PrOH, flow: 1.0 mL/min, 13.774, 15.125 (major isomer).

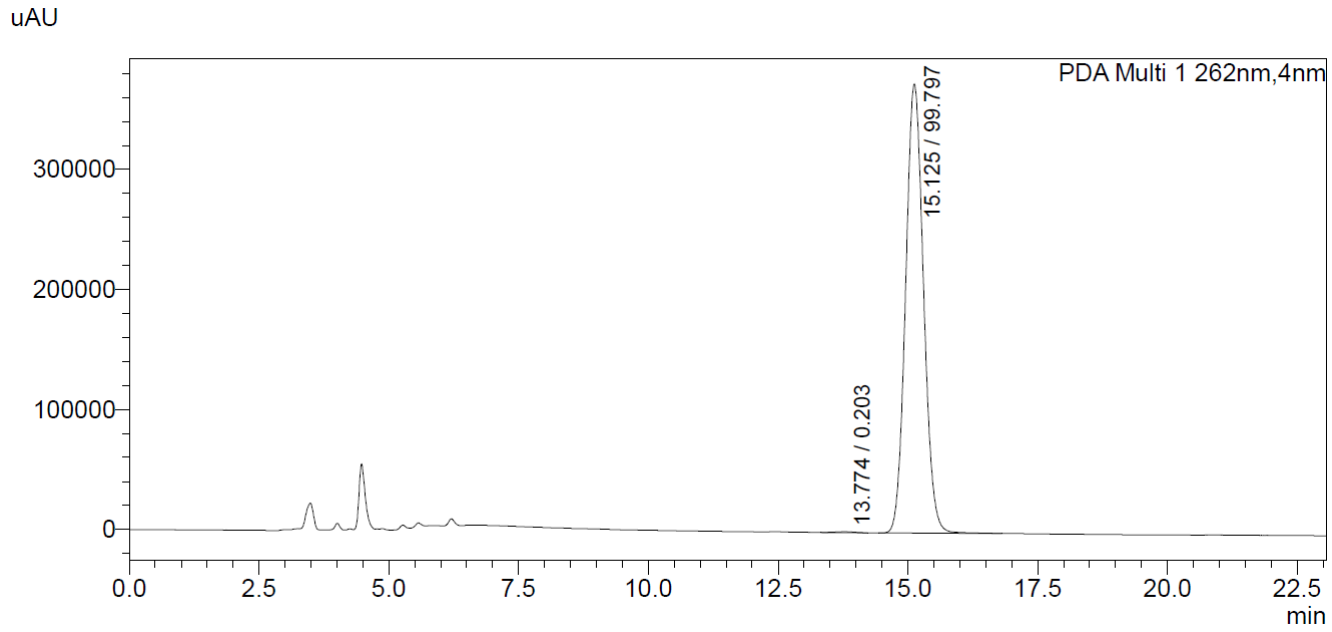


Figure S73. HPLC trace of **16ia**. AD-H, 80:20 hexane/*i*-PrOH, 1.0 mL/min

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[5] It is strongly recommended to check the molarity of commercial borane solutions *via* ^{31}P NMR by titration with PPh_3. In the course of this investigation we have repeatedly received products of inferior quality with significantly lower-than-declared molarities.

[6] At smaller scale yields tend to be higher (>40%). With increasing scale the final washing steps become more challenging, in which product is lost.

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[11] For reactions with cationic complex $[Rh((pR,R)\text{-}\mathbf{10})_2]^{[NTf]}$, the catalyst was prepared by adding 2 equiv of $AgNtf_2$ to a previously prepared solution of 2 equiv of ligand **10** and (pR,R_P)-**12** in CH_2Cl_2. The resulting deep red mixture was centrifuged at 6000 rpm and the supernatant was carefully transferred to a vial. After evacuation to dryness, the remaining mixture was used as catalyst following the standard procedure.

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[14] Racemate synthesis: inside a glovebox, *p*-TolylMgBr (0.6 mL, 1 M in THF) was added dropwise to a well stirred solution of **14c** (151 mg, 0.568 mmol) in 5 mL of THF at -35 °C. The reaction was allowed to warm up to room temperature and it was stirred for 18 h. After this time the reaction was quenched with 3 mL of saturated NH_4Cl solution and extracted with Et_2O (3 x 10 mL). The combined organic phase was dried with Na_2SO_4, filtered and evacuated to dryness. After purification *via* flash column chromatography, 178 mg (88 %) of a white powder were obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.14 (s, 3 H), 2.17 (s, 3 H), 2.26 (s, 3 H), 5.10 (s, 2 H), 6.72 (s, 1 H), 6.90 (s, 1 H), 7.04 - 7.12 (m, 4 H), 7.13 - 7.28 (m, 5 H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *δ* 178.8, 138.2, 138.0, 137.7, 137.3, 134.1, 133.3, 132.5, 129.4, 128.9, 127.3, 125.7, 125.3, 123.7, 120.2, 45.2, 21.2, 20.7, 18.7.

[15] Racemate traces of **16cb** and **16ca** were added in proof in the winter of 2025 (average laboratory T = 20 ºC), while the respective catalysis products were analyzed in the summer of 2025 (average laboratory T = 25 ºC).

[16] Racemate synthesis: inside a glovebox, a solution of $MgPh_2(Et_2O)_{0.8}$ (82.3 mg, 0.346 mmol) in 2 mL of THF was added dropwise to a well stirred solution of **14c** (152 mg, 0.572 mmol) in 2 mL of THF at -35 °C. The reaction was allowed to warm up to room temperature and it was stirred for 18 h. After this time the reaction was quenched with 3 mL of saturated NH_4Cl solution and extracted with Et_2O (3 x 10 mL). The combined organic phase was dried with Na_2SO_4, filtered and evacuated to dryness. After purification *via* flash column chromatography, 187 mg (95 %) of a white powder were obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.15 (s, 3 H), 2.18 (s, 3 H), 5.12 (s, 2 H), 6.74 (s, 1 H), 6.90 (s, 1 H), 7.11 (d, *J* = 7.09 Hz, 2 H), 7.14 - 7.32 (m, 7 H), 7.33 - 7.40 (m, 2 H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *δ* 178.7, 140.7, 138.2, 137.3, 134.2, 133.4, 132.5, 128.9, 128.7, 128.2, 127.3, 125.7, 125.4, 123.7, 120.2, 45.2, 20.7, 18.7.

[17] a) Toullec, P.; Jagt, R. B. C.; de Vries, J.; Feringa, B. L.; Minnaard, A. J. Rhodium-Catalyzed Addition of Arylboronic Acids to Isatins: An Entry to Diversity in 3-Aryl-3-Hydroxyoxindoles. *Org. Lett.* **2006**, *8*, 2715-2718. b) Yin, L.; Kanai, M.; Shibasaki, M. A Facile Pathway to Enantiomerically Enriched 3-Hydroxy-2- Oxindoles: Asymmetric Intramolecular Arylation of a-Keto Amides Catalyzed by a Palladium–DifluorPhos Complex. *Angew. Chem. Int. Ed.* **2011**, *50*, 7620 –7623.

[18] (a) For conditions of enantiomer separation, see: Shintani, R.; Takatsu, K.; Hayashi, T. Copper-catalyzed asymmetric addition of arylboronates to isatins: a catalytic cycle involving alkoxocopper

intermediates. *Chem. Commun.*, **2010**, *46*, 6822–6824. (b) Saleh, N.; Besnard, C.; Lacour, J. Concave P-Stereogenic Phosphorodiamidite Ligands for Enantioselective Rh(I) Catalysis. *Org. Lett.* **2024**, *26*, 2202−2206.

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[20] Racemate synthesis: Inside a glovebox, *p*-tolylMgBr (1.73 mL, 1 M in THF) was added dropwise to a stirred solution of **14f** (151 mg, 0.862 mmol) in 5 mL of THF at -35 °C. The reaction was allowed to reach room temperature and was stirred for 18 h. Then the reaction was quenched with 3 mL of saturated NH_4Cl(aq) and extracted with Et_2O (3 x 10 mL). The combined organic phases were dried over Na_2SO_4, filtered, and evacuated to dryness to afford 228 mg (99 %) of an off-white powder. ^{1}H NMR (600 MHz, DMSO-d_6) δ ppm 2.17 (s, 3H), 2.20 (s, 3H), 2.26 (s, 3H), 6.44 (s, 1H), 6.70 (s, 1H), 6.86 (s, 1H), 7.07 - 7.18 (m, 4H), 10.30 (s, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ ppm 16.76, 21.00, 21.11, 77.94, 119.24, 123.03, 125.79, 129.01, 131.14, 131.18, 134.17, 136.86, 138.38, 139.36, 179.56.

[21] Racemate synthesis: Inside a glovebox, a solution of $MgPh_2(Et_2O)_{0.8}$ (129.3, 0.5437 mmol) in 2 mL of THF was added dropwise to a well stirred solution of **14g** (104.7 mg, 0.5353 mmol) in 2 mL of THF at -35 °C. The reaction was allowed to reach room temperature and was stirred for 18 h. Then the reaction was quenched with 3 mL of saturated NH_4Cl(aq) and extracted with Et_2O (3 x 10 mL). The combined organic phases were dried over Na_2SO_4, filtered and evacuated to dryness to afford 100.2 mg (96 %) of an off-white powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 2.25 (s, 3H), 6.74 (s, 1H), 6.92 (d, J = 1.71 Hz, 1H), 7.17 (d, J = 1.22 Hz, 1H), 7.23 - 7.36 (m, 5H) 10.61 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ ppm 16.64, 77.98, 122.00, 122.39, 125.79, 126.30, 128.10, 128.68, 130.41, 135.67, 139.91, 141.42, 179.02.

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