Supporting Information

Evolution of a privileged P-alkene ligand: Added planar chirality beats BINOL axial chirality in catalytic asymmetric C–C bond formation

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1. Syntheses of compounds

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 and 1,4-dioxane from Na, C_6D_6 from Na/K alloy, CH_2Cl_2 and 1,2-difluorobenzene (DFB) 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 the glovebox. Compounds **4**,[1] and $[Rh(COE)_2Cl]_2$,[2] epin pinacol boronic ester **12b**,[3] and 1,3-diphenylallyl acetate[4] were synthesized according to known procedures. Indole was recrystallized from dry hexane/Et_2O, sublimed, and kept in a glovebox. 6-Fluoroindole was dissolved in Et_2O, slurried in CaH_2, filtered and dried in high vacuum. 4-Methyl indole (abcr) was purified by Kugelrohr distillation and slurried over CaH_2, filtered and dried in high vacuum. Arylboronic acids (purchased from Sigma Aldrich and abcr), $AgBF_4$ (abcr) and NaBArF (abcr) were used as received. Sealed bottles of BH_3•THF (Sigma Aldrich, 0.77 mol/L and TCI, 0.88 mol/L, determined by titration with PPh_3), (*R*)-BINOL (abcr) and $[Pd(allyl)Cl]_2$ (abcr) were opened in the glovebox and used as received. Elemental analyses (EA) were performed on a Euro EA 3000 analyzer, and air-sensitive samples were handled and prepared in a glovebox. NMR spectra were recorded on Jeol EX 270, ECP 400, and ECX 400 instruments operating at 269.71, 399.78, and 400.18 MHz for ^1H, at 67.82, 100.52, and 100.62 MHz for ^{13}C, and at 161.83 and 162.00 MHz for ^{31}P, respectively. Chemical shifts are given in ppm and are reported relative to residual solvent peaks as secondary standards. Jeol's Delta NMR Processing and Control Software/Mestrelab Research S.L. NMR Processing software was used to process and visualize the NMR data. HPLC was performed on a Shimadzu LC10 series instrument.

5-(*R*)-(dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)-10-phenyl-5H-dibenzo[*b*,*f*]azepine ((enriched (p*S*,*R*)-5 + enriched (p*R*,*R*)-5). Inside a glovebox, (*R*)-BINOL (8.755 g, 30.58 mmol) was dissolved in CH_2Cl_2 (450 mL) and transferred to an addition funnel with pressure equalizer, which was connected to a 1000 mL flask containing a yellowish solution of **4** (11.32 g, 30.58 mmol) and NEt_3 (15.47 g, 152.9 mmol) in 400 mL of CH_2Cl_2. The (*R*)-BINOL solution was added dropwise over 5-10 min and the resulting mixture was stirred overnight. Then, the volatiles were removed under reduced pressure and Et_2O (225 mL) added. The resulting slurry was stirred for 1 h, filtered (GF/B glass fiber filter), and the mother liquor evaporated to dryness. The resulting solid was slurried and washed with pentane (100 mL)

for 18 h. Separation by filtration and HV drying yielded an off-white powder (6.46 g, 36%). This product consists of mainly (p*S*,*R*)-**5** with *dr* = 2.5:1. The solid that remained from the first extraction with Et_2O (containing all of the $HNEt_3Cl$ enriched (p*R*,*R*)-5) was re-extracted with toluene (1 x 170 mL, then 2 x 50 mL) and filtered over GF/B. The combined mother liquor was evacuated to dryness, slurried in heptane (110 mL) for 16h, filtered through GF/B and dried in HV until no heptane was detected in the NMR to yield an off-white powder (6.12 g, 34%). This product consists of mainly (p*R*,*R*)-**5** with *dr* = 2:1.[5]

Purification of (p*R*,*R*)-5. The enriched diastereomer (p*R*,*R*)-**5** (*vide supra*, 6.12 g, 10.49 mmol) was dissolved in toluene (31 mL) and the pale yellowish solution was layered carefully with pentane (109 mL) in a 500 mL flask. The flask was left undisturbed at -35° C for 3 d. After this time, the solvent mixture was decanted off and the remaining white solid was dried under high vacuum to yield (p*R*,*R*)-**5** in a 4:1 *dr* ratio. Repeating the procedure twice more leads to a diastereomerically pure product (4.08 g, 23% with respect to **4**). $[\alpha]_D^{25}$ -269° (*c* = 0.7, THF). EA calc. for $C_{40}H_{26}NO_2P\bullet(CH_2Cl_2)_{0.1}$: C 81.34, H 4.46, N 2.37. Found: C 81.18, H 4.77, N 2.29. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ: 140.9. ^1H NMR (400 MHz, C_6D_6, δ): 7.62 (d, *J* = 8.0 Hz, 1H), 7.54 – 7.25 (m, 10H), 7.21 – 7.01 (m, 7H), 6.94 (dd, *J* = 8.0 Hz, 3.6 Hz, 1H), 6.89 – 6.80 (m, 2H), 6.78 – 6.62 (m, 5H). $^{13}C\{1H\}$ NMR (101 MHz, C_6D_6, δ): 150.4, 150.3, 149.5, 144.7, 144.6, 144.2, 144.1, 144.0, 143.3, 138.3, 136.4, 133.5, 133.4, 132.0, 131.0, 130.9, 130.7, 129.8, 129.8, 129.7, 129.6, 129.5, 128.8, 128.7, 128.6, 128.4, 128.0, 127.9, 127.6, 127.4, 126.7, 126.6, 126.5, 126.4, 125.1, 125.0, 124.7, 124.6, 123.1, 123.0, 122.5, 122.4. The spectra indicate the presence of CH_2Cl_2, which was used to transfer the product for yield determination.

p*S*-5-(*R*)-(dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yl)-10-phenyl-5H dibenzo[*b*,*f*]azepine borane complex ((p*S*,*R*)-6). Enriched (p*S*,*R*)-**5** (*vide supra*, 6.462 g, 11.07 mmol) was dissolved in C_6H_6 (35 ml) in a 250mL round bottom flask followed by addition of $BH_3\bullet$THF solution in THF (38 mL, 17 mmol) via syringe.[6] The resulting yellow solution was stirred for 1.5 h at room temperature. The volatiles were removed under reduced pressure and the remaining white glassy solid slurried in pentane (30 mL) for 2 h before filtration. Additional washing with pentane (3 x 20 mL) and drying in HV yielded a finely divided white powder (4.14 g, 63 %) with *dr* = 2.2:1 (by ^1H NMR). Depending on the quality of the employed commercial $BH_3\bullet$THF solution, additional purification may be necessary by flash filtration through silica (hexane/EtOAc 95:5) and subsequent *n*-pentane washing (100 mL) to remove unidentified contaminants that affect crystallization. The enriched (p*S*,*R*)-**6** (4.14 g) was then transferred to a 250 mL Schlenk tube and dissolved in DFB (85 mL). The pale-yellow solution was carefully layered with *n*-heptane (298 mL) and cooled to -40 °C for 2 h. After this time, the tube was let to warm up to RT and

kept at 26 °C in a thermostated bath for the solvents to slowly diffuse over the course of 12 d (Picture P1). This afforded large sized crystals. The mother liquor was decanted off and the crystals washed with heptane (6.00 mL) and dried under HV to yield a white microcrystalline powder (940 mg, 44 %) with *dr* > 99:1. EA calcd. for $C_{40}H_{29}BNO_2P$: C 80.41, H 4.89, N 2.34. Found: C 80.70, H 4.88, N 2.34. 8.00. ^{31}P NMR (162 MHz, C_6D_6, coupled, δ): 124.4. ^{1}H NMR (400 MHz, $CDCl_3$, δ) 8.00 (d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.59 – 7.52 (m, 4H), 7.44 – 7.36 (m, 6H), 7.27 – 7.07 (m, 11), 7.00 (d, *J* = 7.1 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 1H), 6.76 – 6.71 (qt, 1H), 0.39 (bm, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, δ) 148.4 (d, *J* = 14.1 Hz), 147.5 (d, *J* = 6 Hz), 144.1, 143.0, 142.2 (d, *J* = 9.5 Hz), 141.1, 138.0 (d, *J* = 3.5 Hz), 136.1 (d, *J* = 2.5 Hz), 132.5 (d, *J* = 1.5 Hz), 132.2, 131.9,131.0, 130.9, 130.3, 129.9, 129.6, 129.4, 129.2 (2C), 128.9 (2C), 128.8, 128.7, 128.5 (2C), 128.1, 128.0 (2C), 127.4, 127.3, 127.2, 127.1, 126.5, 126.3, 125.6, 125.4, 122.0 (d, *J* = 2.5 Hz), 121.8 (d, *J* = 3.0 Hz), 121.0 (d, *J* = 2.5 Hz), 120.5 (d, *J* = 2.0 Hz).

Picture S1. Photograph of a 250 ml Schlenk tube containing diastereomerically pure crystals of (p*S*,*R*)-**6** in a DFB/heptane solvent mixture. The tube is inside a thermostatisized water-filled beaker.

Deprotection of (p*S*,*R*)-6 to p*S*-5-(*R*)-(dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yl)-10-phenyl-5H dibenzo[*b*,*f*]azepine ((p*S*,*R*)-5). (p*S*,*R*)-**6** (940 mg, 1.57 mmol) was dissolved in benzene (15 mL) in a 40 mL vial. To this clear solution, NEt_3 (1.168 g, 11.3 mmol) was added neat, under vigorous stirring. The resulting solution was heated to 50 °C for 24 h. After this time, the volatiles were removed under reduced pressure and the remaining off-white solid was thoroughly washed with pentane and filtered through GF/B (3 x 10 mL). Finally, the residue was dried under high vacuum to yield a white powder (660 mg, 72%, 4% overall from *rac*-**4**) with *dr* > 99:1. $[\alpha]_D^{25}$ = -312° (*c* = 1, THF). EA calcd. for $C_{40}H_{26}NO_2P\bullet(CH_2Cl_2)_{0.1}$: C 81.34, H 4.46, N 2.37. Found: C 81.18, H 4.77, N 2.29. ^{31}P NMR (162 MHz, C_6D_6, coupled, δ): 140.4. ^{1}H NMR (400 MHz, C_6D_6, δ): 7.58 (d, *J* = 8.0 H, 1H), 7.51 (m, 2H), 7.47 – 7.36 (m, 7H), 7.20 – 7.04 (m, 11H), 6.97 – 6.95 (d, *J* = 7.7 Hz, 1H), 6.91 – 6.78 (m, 4H), 6.70 – 6.66 (t, *J* = 7.5 Hz, 1H), 6.59 – 6.55 (t, *J* = 7.2 Hz, 1H). ^{13}C{1H} NMR (101 MHz, C_6D_6, δ): 150.1 (d, *J* = 15.0 Hz), 149.3, 144.9 (d, *J* = 15 Hz), 144.2, 143.8, 143.8, 138.4 (d, *J* = 2.3 Hz), 136.2, 133.2, 132.7, 131.7, 130.7, 130.6, 130.4, 129.7, 129.3, 129.3, 129.2, 129.1, 128.9, 128.7, 128.4 (2C), 128.3 (2C), 127.9, 127.6, 127.2, 127.1, 126.3 (d, *J* = 3.5 Hz), 126.2, 126.0, 124.8, 124.5, 122.3 (d, *J* = 2.3 Hz), 122.2, 122.0.

[((p*R*,*R*)-5)$_2$ClRh]$_2$ ((p*R*,*R*)-8). A solution of ligand (p*R*,*R*)-**5** (319 mg, 0.547 mmol) in 4 mL of C_6H_6 was slowly added dropwise to a slurry of $[Rh(COE)_2Cl]_2$ (98.2 mg, 0.137 mmol) in 4 mL of C_6H_6. After a few seconds, an orange precipitate was formed, and the reaction mixture was stirred for 16 h. After this time, *n*-hexane (4 mL) was added and the mixture was filtered through GF/B. The product was washed with hexane (3 x 2.5 mL) and dried in HV to afford 253 mg (71%) of an orange powder. Single crystals were obtained by vapor diffusion of pentane into a saturated solution of (p*R*,*R*)-**8** in CH_2Cl_2. EA calcd. for $C_{160}H_{104}Cl_2N_4O_8P_4Rh_2.(CH_2Cl_2)_{0.46}\bullet(C_6H_6)_{0.15}$: C 72.59, H 4.41, N 2.18. Found: C 72.59, H 4.41, N 2.18. ^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2) δ: 143.4 (d, $J_{P,Rh}$ = 305 Hz). ^{1}H NMR (600 MHz, CD_2Cl_2) δ: 8.61 – 8.58 (m, 4H), 7.96 (d, *J* = 6.0 Hz, 2H), 7.86 (d, *J* = 12.0 Hz, 2H), 7.60 (d, *J* = 6.0 Hz, 2H), 7.55 (t, *J* = 12.0 Hz, 2H), 7.47 – 7.44 (m, 4H), 7.39 – 7.34 (m, 4H) 7.30 – 7.26 (m, 4H), 7.21 – 7.18 (m, 6H), 7.07 (d, *J* = 6.0 Hz, 4H), 6.97 – 6.91 (m, 6H), 6.71 (dd, *J* = 6.0 Hz, 3 Hz, 2H), 6.58 – 6.54 (m, 4H), 6.33 (t, *J* = 12.0 Hz, 2H), 6.26 (t, *J* = 12.0 Hz, 2H), 5.50 (d, *J* = 6.0 Hz, 2H). ^{13}C{1H} NMR (151 MHz, CD_2Cl_2, δ): 150.3, 149.8, 146.3, 142.3, 140.3, 135.8, 135.1, 133.2, 132.5, 132.3. 131.5, 130.9, 130.7, 130.2, 130.1, 129.6, 129.2, 129.0, 128.9, 128.7, 128.6, 128.5, 128.4, 128.2, 128.1, 127.6, 127.3, 126.0, 125.7, 125.3, 125.0, 124.9, 124.7, 123.2, 122.5, 121.1.

[((p*R*,*R*)-5)$_2$Rh][BF$_4$] (*cis*-(p*R*,*R*)-9). In a dark glovebox, complex **5** (123 mg, 0.0471 mmol) and $AgBF_4$ (18 mg, 0.095 mmol) were mixed in a vial and toluene (4 mL) was added. The resulting orange mixture was stirred for 3 h, during which lots of white precipitate formed. The solvent was removed in HV,

extracted with CH_2Cl_2 (5 mL) and centrifuged (5000 rpm for 5 min). The supernatant was decanted into a vial, evacuated to dryness, washed with *n*-pentane (3 x 3 mL), filtered (GF/B), and dried in HV to yield 122 mg (95 %). EA calcd. for $C_{80}H_{52}BF_4N_2O_4P_2Rh•(CH_2Cl_2)_{0.1}$: C, 70.46; H, 3.85; N, 2.05. Found: C, 70.38; H, 3.80; N, 1.99. $^{31}P\{^1H\}$ NMR (243 MHz, CD_2Cl_2) δ: 163.9 (d, $J_{P,\,Rh}$ = 289.9 Hz). ^1H NMR (400 MHz, CD_2Cl_2) δ: 8.12 – 7.85 (br.m, C_{Ph}–*H*, 4H), 7.89 (d, $^3J_{H,H}$ = 6.9 Hz, 2H), 7.81 – 7.77 (m, C_{Ph}–*H*, 2H), 7.77 – 7.73 (m, 4H), 7.69 – 7.50 (br.m, C_{Ph}–*H*, 4H), 7.53 (td, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1.3 Hz, 2H), 7.48 (d, $^3J_{H,H}$ = 8.9 Hz, 2H), 7.39 – 7.34 (m, 2H), 7.37 – 7.33 (m, 4H), 7.23 – 7.19(m, 4H), 7.17 – 7.13 (m, 4H), 7.16 – 7.12 (m, 2H), 7.07 (ddd, $^3J_{H,H}$ = 8.3 Hz, $^3J_{H,H}$ = 6.8 Hz, $^4J_{H,H}$ = 1.3 Hz, 2H), 6.83 (d, $^3J_{H,H}$ = 8.6 Hz, 4H), 6.69 (ddd, $^3J_{H,H}$ = 8.3 Hz, $^3J_{H,H}$ = 6.9 Hz, $^4J_{H,H}$ = 1.2 Hz, 2H), 6.43 (dd, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.6 Hz, 2H), 6.29 (d, $^3J_{H,H}$ = 8.6 Hz, 2H), 5.62 (s, $C_{olef.}$–*H*, 2H), 5.59 (d, $^3J_{H,H}$ = 8.9 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, δ) 147.5, 146.5, 141.1, 140.4, 140.2, 138.6, 136.7, 132.9, 131.9, 131.8, 131.7, 131.6, 131.5, 130.9, 130.8, 130.1, 129.7, 129.4, 128.8, 128.7, 128.3, 128.1, 127.3, 126.6, 126.5, 126.2, 126.1, 126.0, 125.5, 122.3, 120.2, 120.1, 199.7, 102.0.

[((p*R*,*R*)-2)$_2$Pd][BArF] ((p*R*,*R*)-10). Inside a glovebox, a 3 mL solution of (p*R*,*R*)-**2** (302 mg, 0.518 mmol) in CH_2Cl_2 was added dropwise to a well stirred 2 mL solution of $[PdCl(allyl)]_2$ (47 mg, 0.13 mmol) in CH_2Cl_2. The resulting pale yellowish solution was stirred for 30 min. After this time, NaBArF (230 mg, 0.259 mmol) was added, forming a white precipitate. The resulting orange slurry was stirred for 2.5 h. After this time, the mixture was centrifuged for 10 min at 6000 rpm. The supernatant was carefully decanted and evacuated to dryness to yield an orange solid (532 mg, 94%). EA calcd. for $C_{115}H_{69}BF_{24}N_2O_4P_2Pd$: C, 63.42%; H, 3.19%; N, 1.29%. Found: C, 63.06%; H, 3.09%; N, 1.36%. $^{31}P\{^1H\}$ NMR (242 MHz, CD_2Cl_2) δ: 134.2, 134.3. ^1H NMR (600 MHz, CD_2Cl_2) δ: 7.98 (dd, *J* = 15.7, 8.5 Hz, 2H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.80 (dd, *J* = 13.6, 8.5 Hz, 2H), 7.67 (d, *J* = 8.7 Hz, 1H), 7.64–7.60 (m, 9H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.50 (dd, *J* = 13.5, 8.1 Hz, 3H), 7.45 (s, 6H), 7.44–7.35 (m, 4H), 7.32 (d, *J* = 8.7 Hz, 1H), 7.31–7.14 (m, 15H), 7.12–7.05 (m, 4H), 7.03 (d, *J* = 8.7 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 6.90–6.83 (m, 3H), 6.80–6.74 (m, 1H), 6.70–6.66 (m, 2H), 6.66–6.59 (m, 2H), 6.56 (d, *J* = 7.9 Hz, 1H), 6.42 (t, *J* = 7.6 Hz, 1H), 6.39–6.32 (m, 2H), 6.31–6.22 (m, 2H), 6.15–6.07 (m, 1H), 5.79 (t, *J* = 7.5 Hz, 1H), 5.48 (d, *J* = 8.1 Hz, 1H), 5.38 (d, *J* = 7.5 Hz, 1H), 5.24–5.14 (m, 1H), 4.89–4.74 (m, 1H), 4.72–4.64 (m, 1H), 3.13 (td, *J* = 12.9, 4.3 Hz, 1H), 2.67 (td, *J* = 12.7, 4.1 Hz, 1H). ^{13}C NMR (151 MHz, CD_2Cl_2, δ) 162.3, 161.9, 161.6, 161.3, 147.3, 147.2, 146.0, 141.6, 141.2, 140.9, 140.8, 140.0, 135.9, 135.4, 134.8, 132.7, 132.7, 132.3, 132.1, 132.1, 131.2, 131.1, 131.0, 130.9, 130.7, 130.6, 130.3, 130.1, 129.2, 129.1, 129.0 (2C), 128.9, 128.8, 128.7, 128.6, 128.6, 128.5, 128.4, 128.3, 128.3, 128.2, 128.0, 127.9, 127.6, 127.6, 127.5, 127.4, 127.4, 127.3, 127.3, 127.2, 127.1, 127.1, 126.9, 126.8,

126.7, 126.6, 126.4, 126.1, 126.0, 125.5, 124.4, 123.7, 121.9, 120.3, 119.8, 119.7, 119.0, 117.5, 117.5, 117.5.

[((p*S*,*R*)-5)$_2$ClRh]$_2$ ((p*S*,*R*)-8). In a glovebox, a 3 mL solution of (p*S*,*R*)-**5** (125.4 mg; 0.214 mmol; 4 eq) in C_6H_6 was added to a 2 mL solution of $[Rh(COE)_2Cl]_2$ (38.7 mg; 0.054 mmol; 1 eq) in C_6H_6. After 18 h of stirring at room temperature, the remaining solution was evaporated to dryness. The resultant orange solid was slurried in pentane (4.00 mL) for 15 min and filtered through GF/B (3 x 4 mL). After drying in HV, the product was obtained as a fine, orange powder (125 mg, 88 %). From the pentane mother liquor, X-ray quality crystals were formed after 3 d. EA found: C 73.25 H 3.95 N 1.97; calcd. for $C_{160}H_{104}Cl_2N_4O_8P_4Rh_2$: C 73.60 H 4.01 N 2.15. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ: 146.4 (d, $^1J_{P,Rh}$ = 309.95 Hz, 4P) . ^1H NMR (400 MHz, C_6H_6) δ: 10.12 (bs, 1H), 9.02 (bd, *J* = 6.6 Hz, 1H), 8.10 (bd, *J* = 6.0 Hz, 1H) , 7.74 (bs, 1H), 7.63 (d, *J* = 8.6 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 2H) , 7.40 (bd, *J* = 8.9 Hz, 2H) , 7.25 (bd, *J* = 6.1 Hz, 2H), 7.0–7.1 (m, 5H), 6.69‑6.65 (m, 7H), 6.67 (bt, *J* = 7.4 Hz, 1H), 6.52 (bs, 1H), 6.37 (d, *J* = 7.4 Hz, 1H), 5.58 (bs, 1H). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6) δ: 149.6, 149.3, 143.8, 143.7, 142.8, 141.4, 137.3, 135.0, 134.9, 133.0, 132.5, 132.2, 131.8, 131.5, 131.2, 130.6, 130.3, 129.6, 129.0, 128.8, 128.7, 128.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.1, 127.9, 127.6, 125.6, 125.5, 125.1, 124.8, 124.6, 124.0, 123.1, 122.4.

[*cis*-((p*S*,*R*)-5)$_2$Rh][BF$_4$] (*cis*-(p*S*,*R*)-9). In a dark glovebox, complex (p*S,R*)-**8** (101 mg, 0.039 mmol) was mixed with $AgBF_4$ (15 mg, 0.077 mmol) in a tin foil wrapped vial. Toluene (4.00 mL) was added and the orange mixture was stirred for 3 h at room temperature. After this time, the solvent was removed in HV and the resulting pale-orange solid was extracted with CH_2Cl_2 (5.00 mL) and centrifuged (5000 rpm, 5 min). The orange supernatant was decanted and evaporated to dryness. The resulting orange solid was washed with *n*-pentane and separated by filtration (3 x 3 mL). HV drying yielded a bright orange powder (104 mg, >99%). EA found: C 62.94, H 3.55, N 1.75; calculated for $C_{80}H_{52}BF_4N_2O_4P_2Rh\bullet(CH_2Cl_2)_{2.5}$: C 63.14, H 3.66, N 1.79. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): 142.5 (dd, $^1J_{P\text{-}Rh}$ = 269.3 Hz, $^2J_{P\text{-}P}$ = 40.4 Hz 1P), 139.6 (dd, $^1J_{P\text{-}Rh}$ = 269.3 Hz, $^2J_{P\text{-}P}$ = 40.4 Hz 1P). ^1H NMR (600 MHz, CD_2Cl_2): 9.29 (bs, 1H), 8.43–8.22 (dt, 6H), 7.98–7.85 (m, 7H), 7.73–7.54 (m, 16H), 7.46–7.08 (m, 24H), 6.99–6.84 (m, 8H), 6.71 (s, 1H), 6.58–6.45 (m, 6H), 6.20 (s, 2H), 5.67–5.64 (m, 1H), 4.89–4.86 (m, 1H), 4.45 (m, 1H). $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2) δ: 145.7, 144.2, 140.0, 139.9, 139.7, 138.7, 138.6, 137.0, 136.2, 132.9, 132.0, 131.9, 131.6, 131.5, 131.4, 131.3, 131.3, 131.2, 131.1, 131.0, 130.9, 130.3, 130.2, 130.0, 129.8, 129.7, 129.6, 129.5, 129.4.

[((p*R*,*R*)-5)$_2$Pd][BArF] ((p*R*,*R*)-10). Inside a glovebox, a 3 mL solution of (p*R*,*R*)-**2** (302 mg, 0.518 mmol) in CH_2Cl_2 was added dropwise to a well stirred 2 mL solution of $[PdCl(allyl)]_2$ (47 mg, 0.13 mmol)

in CH_2Cl_2. The resulting pale yellowish solution was stirred for 30 min. After this time, NaBArF (230 mg, 0.259 mmol) was added, forming a white precipitate. The resulting orange slurry was stirred for 2.5 h. After this time, the mixture was centrifuged for 10 min at 6000 rpm. The supernatant was carefully decanted and evacuated to dryness to yield an orange solid (532 mg, 94%). EA calcd. for $C_{115}H_{69}BF_{24}N_2O_4P_2Pd$: C, 63.42%; H, 3.19%; N, 1.29%. Found: C, 63.06%; H, 3.09%; N, 1.36%. ^{31}P NMR (242 MHz, CD_2Cl_2) δ: 134.3 (dd, *J* = 110.5, 17.3 Hz, 1P). ^{1}H NMR (600 MHz, CD_2Cl_2) δ: 7.98 (dd, *J* = 15.7, 8.5 Hz, 2H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.80 (dd, *J* = 13.6, 8.5 Hz, 2H), 7.67 (d, *J* = 8.7 Hz, 1H), 7.64–7.60 (m, 9H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.50 (dd, *J* = 13.5, 8.1 Hz, 3H), 7.45 (s, 6H), 7.44–7.35 (m, 4H), 7.32 (d, *J* = 8.7 Hz, 1H), 7.31–7.14 (m, 15H), 7.12–7.05 (m, 4H), 7.03 (d, *J* = 8.7 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 6.90–6.83 (m, 3H), 6.80–6.74 (m, 1H), 6.70–6.66 (m, 2H), 6.66–6.59 (m, 2H), 6.56 (d, *J* = 7.9 Hz, 1H), 6.42 (t, *J* = 7.6 Hz, 1H), 6.39–6.32 (m, 2H), 6.31–6.22 (m, 2H), 6.15–6.07 (m, 1H), 5.79 (t, *J* = 7.5 Hz, 1H), 5.48 (d, *J* = 8.1 Hz, 1H), 5.38 (d, *J* = 7.5 Hz, 1H), 5.24–5.14 (m, 1H), 4.89–4.74 (m, 1H), 4.72–4.64 (m, 1H), 3.13 (td, *J* = 12.9, 4.3 Hz, 1H), 2.67 (td, *J* = 12.7, 4.1 Hz, 1H). ^{13}C NMR (151 MHz, CD_2Cl_2, δ) 162.3, 161.9, 161.6, 161.3, 147.3, 147.2, 146.0, 141.6, 141.2, 140.9, 140.8, 140.0, 135.9, 135.4, 134.8, 132.7, 132.7, 132.3, 132.1, 132.1, 131.2, 131.1, 131.0, 130.9, 130.7, 130.6, 130.3, 130.1, 129.2, 129.1, 129.0 (2C), 128.9, 128.8, 128.7, 128.6, 128.6, 128.5, 128.4, 128.3, 128.3, 128.2, 128.0, 127.9, 127.6, 127.6, 127.5, 127.4, 127.4, 127.3, 127.3, 127.2, 127.1, 127.1, 126.9, 126.8, 126.7, 126.6, 126.4, 126.1, 126.0, 125.5, 124.4, 123.7, 121.9, 120.3, 119.8, 119.7, 119.0, 117.5, 117.5, 117.5.

[((p*S*,*R*)-2)$_2$Pd][BArF] ((p*S*,*R*)-10). Inside a glovebox, a 3 mL solution of (p*S*,*R*)-**5** (233 mg, 0.399 mmol) in CH_2Cl_2 was added dropwise to a well stirred 2 mL solution of $[PdCl(allyl)]_2$ (39 mg, 0.11 mmol) in CH_2Cl_2. The resulting pale yellowish solution was stirred for 30 min. After this time, NaBArF (180 mg, 0.203 mmol) was added. After 2.5h, the mixture turned violet and a white precipitate formed, which was separated by centrifugation (10 min, 6000 rpm) by carefully decanting the supernatant. Evacuation to dryness yielded a violet solid (271 mg, 98%). EA found: C 58.09 H 2.98 N 0.92; calcd. for $C_{115}H_{69}BF_{24}N_2O_4P_2Pd(CH_2Cl_2)_3$: C, 58.26%; H, 3.11%; N, 1.15%. $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, δ): 137.6 (s). ^{1}H NMR (400 MHz, CD_2Cl_2) δ: 8.41 (dd, *J* = 8.6, 6.4 Hz, 2H), 8.11–8.24 (m, 6H), 8.08 (dd, *J* = 5.08, 3.02 Hz, 2H), 8.01 (s, 4H), 7.95 (dd, *J* = 4.95, 3.85 Hz, 2H), 7.19-7.80 (m, 50H), 7.16 (d, *J* = 7.97 Hz, 1H), 6.98 (d, *J* = 6.98 Hz, 1H), 6.91–6.85 (m, 4H), 6.77 (d, *J* = 3.30 Hz, 2H), 6.67–6.64 (m, 4H), 6.29–6.25 (m, 2H), 5.93–5.88 (m, 2H), 5.78 (dd, *J* = 8.0, 3.4 Hz, 2H), 5.53 (t, *J* = 7.6 Hz, 1H), 5.43 (t, *J* = 7.6 Hz, 1H), 4.90 (m, 1H), 4.35 (bm, 1H), 4.22 (bm, 1H), 2.76–2.72 (bm, 1H), 2.49–2.44 (bm, 1H), 1.92–1.89 (m, 1H). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, CD_2Cl_2) δ: 162.6, 161.6, 161.1, 145.0, 144.8, 142.3,

137.1, 134.9, 134.4, 133.1, 133.0, 132.2, 131.9, 131.5, 131.2, 130.6, 130.0, 129.9, 129.2, 128.8, 128.7, 128.5, 128.5, 128.3, 128.0, 127.5, 127.4, 127.3, 127.1, 127.0, 126.4, 126.0, 125.7, 125.3, 124.8, 123.3, 122.9, 122.7, 122.3, 122,2, 121.2, 120.6, 119.6, 119.3, 117.6, 54.0, 54.0, 53.8, 53.7, 53.5, 53.2, 52.9.

NMR scale synthesis of [((*S*)-1)$_2$Pd][BArF] ((*S*)-11). In an NMR tube, an intensely yellow solution of [PdCl(allyl)]$_2$ (7.6 mg, 0.021 mmol) in CD_2Cl_2 was combined with a pale-yellow solution of (*S*)-**1** (21.3 mg, 0.0415 mmol) in CD_2Cl_2. Upon mixing, the intensely yellow color disappeared instantly and NMR was measured. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, δ): 142.84 (s), 142.77 (s). ^1H NMR (400 MHz, CD_2Cl_2, δ): 8.41 (d, *J* = 8.8 Hz, 1H) , 8.33 (d, *J* = 8.9 Hz, 1H) , 8.06 (d, *J* = 8.9 Hz, 1H) , 8.01 (d, *J* = 8.9 Hz, 1H), 7.93 (m, 2H), 7.81 (m, 2H), 7.61–7.58 (m, 4H), 7.42–7.36 (m, 5H), 7.29 – 7.13 (m, 24H), 7.10–7.01 (m, 8H), 6.91 (m, 2H), 6.69 (m, 2H), 5.19 (m, 1H), 4.42–4.29 (m, 3H), 3.70 (d, *J* = 6.5 Hz, 1H), 3.61 (d, *J* = 5.9 Hz, 1H) , 3.30 (m, 1H), 2.92 (d, *J* = 14.8 Hz, 1H), 2.49 (d, *J* = 12.1 Hz, 1H), 1.68 (d, *J* = 12.1 Hz, 1H). These signals coincide with the *supine/supra* isomers with complex formula (*S*)-[(**1**)Pd(allyl)Cl]. After 3 h, (*S*)-**1** (21.4 mg, 0.0415 mmol) and NaBArF (36.7 mg, 0.0415 mmol) were added. Upon addition the pale-yellow solution turned more intense and a white precipitate was formed after 15 min, which was removed by centrifugation (6000 rpm, 4 min). The NMR of intense yellow supernatant was measured and showed formation of the cationic complex along with 5% of free ligand. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, δ): 140.31 (s, free (*S*)-**1**), 135.5 (d, J_{PP} = 104 Hz), 134.9 (d, J_{PP} = 104 Hz). ^1H NMR (400 MHz, CD_2Cl_2, δ): 8.12 – 8.08 (m, 2H), 8.01 – 7.90 (m, 6H), 7.83 – 7.81 (d, 2H), 7.77 – 7.73 (m, 13H), 7.76 – 7.58 (m, 8H), 7.54 – 7.41 (m, 7H), 7.38 – 7.20 (m, 9H), 7.02 – 7.00 (d, 2H), 6.96 – 6.90 (m, 3H), 6.77 (t, 1H), 6.66 (m, 1H), 6.60 – 6.46 (m, 7H), 6.39 (t, 1H), 6.16 – 6.13 (d, 1H), 6.08 – 5.99 (m, 2H), 5.93 – 5.91 (d, 1H), 5.56 – 5.5 (d, 1H), 5.24 – 5.22 (d, 1H), 5.11 – 4.99 (m, 2H), 4.93 (bt, 1H), 3.08 – 2.99 (m, 2H), 2.03 (s, 3H)

Preparative scale synthesis of [((*S*)-1)$_2$Pd][BArF] ((*S*)-11). [PdCl(allyl)]$_2$ (36.5 mg, 0.100 mmol) was placed in a vial with a stir bar and dissolved in CH_2Cl_2 (2 mL). A solution of (*S*)-**1** (102.7 mg, 0.200 mmol) in CH_2Cl_2 (2 mL) was added dropwise. The resulting yellow solution was stirred at room temperature for 2 h. After this time, the solvent was removed in HV and the remaining yellow solid was washed with *n*-pentane, filtered (3 x 3 mL) and dried in HV. The product was obtained as off-white solid (133 mg, 94%). This product shows the same NMR signal pattern as the previous synthesis. To prepare the cationic complex, 67 mg (0.097 mmol) were dissolved in CH_2Cl_2 (2 mL) and a solution ligand (*S*)-**1** (50 mg, 0.097 mmol) in 2 mL of CH_2Cl_2 was added dropwise. After 3 min, NaBArF (86 mg, 0.097 mmol) was added and the turbid yellow solution was stirred for 2 h at room temperature, centrifuged (6000 rpm, 7 min) and the supernatant decanted and evaporated to dryness. The product was obtained as pale-orange solid (176 mg, 86 %). This product shows the same NMR signal pattern as the previous synthesis.

2. X-ray crystallography

CCDC-2295527 for (p*S,R*)-**5**, CCDC-2295528 for (p*R,R*)-**5**, CCDC-2295529 for (p*S,R*)-**8**, and CCDC-2295530 for (p*R,R*)-**8** 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 on a microscope slide and a single specimen was selected and subsequently transferred to the cold nitrogen gas stream of the diffractometer. Intensity data for (p*S,R*)-**5** and (p*S,R*)-**8** were collected using MoK_α radiation (λ = 0.71073 Å) on a Bruker Kappa PHOTON2 $I\mu S$ Duo diffractometer equipped with QUAZAR focusing Montel optics. Intensity data for (p*R,R*)-**5** were collected using MoK_α radiation (λ = 0.71073 Å) on a Bruker Kappa APEX2 $I\mu S$ Duo diffractometer equipped with QUAZAR focusing Montel optics. Intensity data for (p*R,R*)-**8** were collected using CuK_α radiation (λ = 1.54184 Å) on an Agilent SuperNova diffractometer equipped with an Atlas S2 detector. All intensity data sets were collected at a temperature of 100 K. For (p*S,R*)-**5**, (p*R,R*)-**5**, and (p*S,R*)-**8** data were corrected for Lorentz and polarization effects, semi-empirical absorption corrections were performed on the basis of multiple scans using *SADABS*.[7] The structures were solved by direct methods (SHELX XT 2014/5)[8] and refined by full-matrix least-squares procedures on F^2 using SHELXL 2018/3.[9] The data set of (p*S,R*)-**8** was refined in blocked matrix mode using three roughly equally sized refinement blocks. All non-hydrogen atoms were refined with anisotropic displacement parameters. For (p*S,R*)-**5** and (p*R,R*)-**5** the positions of the B1 bound hydrogen atoms were taken from a difference Fourier synthesis and their positional parameters were refined. All other hydrogen atoms were placed in positions of optimized geometry, their isotropic displacement parameters were tied to those of the corresponding carrier atoms by a factor of either 1.2 or 1.5. The asymmetric unit in the crystal structure of (p*S,R*)-**8** contained two independent molecules of the Rh complex and a total of 15 molecules of benzene and 0.5 molecules of *n*-pentane. Similarity and, in part, pseudo-isotropic restraints were applied in the refinement of the anisotropic displacement parameters of the atoms of the solvent molecules. Additional fixed distance restraints were applied in the refinement of the *n*-pentane molecule. Olex2[10] was used to prepare material for publication. The measured data for (p*R,R*)-**8** were processed with the CrysAlisPro software package.[11] Using Olex2,[9] the structures were solved with the ShelXT[12] structure solution program using Intrinsic Phasing and refined with the ShelXL 2016/6[8] refinement package using Least Squares Minimization. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in

ideal positions and refined as riding atoms with relative isotropic displacement parameters. The asymmetric unit in the crystal structure of (p*R,R*)-**8** contained one molecule of the Rh complex, 4 molecules of benzene and 1 molecule of *n*-hexane. Two of the benzene molecules are disordered over two positions. In order to obtain a satisfying disorder model, these moieties (as well as a third benzene) were refined as rigid hexagons. Additionally, rigid bond restraints (RIGU),[1314] similarity restraints (SIMU) and in some cases even pseudo-isotropic restraints (ISOR) were applied to the disordered solvent molecules.

Crystallographic data, data collection, and structure refinement details are given in Table S1.

Table S1. Crystallographic data and refinement details for (p*S,R*)-**5**, (p*R,R*)-**5**, (p*S,R*)-**8**, (p*R,R*)-**8**

Compound CCDC-no.	(p*S,R*)-**5** 2295527	(p*R,R*)-**5** 2295528	(p*S,R*)-**8** 2295529	(p*R,R*)-**8** 2295530
Empirical formula	$C_{40}H_{29}BNO_2P$	$C_{40}H_{29}BNO_2P$	$C_{206.25}H_{152}Cl_2N_4O_8P_4Rh_2$	$C_{190}H_{142}Cl_2N_4O_8P_4Rh_2$
Molecular weight	583.63	583.63	3214.91	3009.67
Crystal shape, color	block, colorless	needle, colorless	block, yellow	needle, orange
Crystal size [mm]	0.22 × 0.17 × 0.15	0.28 × 0.07 × 0.07	0.34 × 0.23 × 0.17	0.262 × 0.143 × 0.047
Temperature [K]	100	100	100	100
Crystal system	monoclinic	trigonal	triclinic	monoclinic
Space group	$P2_1$	$R3$	$P1$	$P2_1$
a [Å]	7.8461 (10)	28.285(3)	17.4039(12)	12.44859(10)
b [Å]	15.3010 (19)	28.285(3)	19.9901(14)	37.3327(2)
c [Å]	13.0363 (15)	10.097(2)	25.7764(17)	16.40694(15)
α [°]	90	90	67.834(2)	90
β [°]	98.601(4)	90	80.669(3)	102.2954(8)
γ [°]	90	120	76.916(3)	90
V [Å^3]	1547.4 (3)	6996(2)	8060(1)	7450.06(10)
Z	2	9	2	2
ρ [g cm^{-3}] (calc.)	1.282	1.276	1.325	1.342
μ [mm^{-1}]	0.13	0.126	0.342	3.031
F (000)	624	2808	3331	3116.0
T_{min}; T_{max}	0.673; 0.746	0.476; 0.746	0.698; 0.746	0.624; 0.867
2θ interval [°]	$5.7 \leq 2\theta \leq 61.0$	$4.3 \leq 2\theta \leq 53.1$	$3.7 \leq 2\theta \leq 59.2$	$7.268 \leq 2\theta \leq 144.8$
Collected refl.	119304	67265	472238	83261
Independent refl.; R_{int}	9440, 0.045	6374, 0.117	90374, 0.085	28917, 0.0493
Obs. refl. $F_o \geq 4\sigma(F_o)$	9154	5839	74503	27880
No. ref. param.	415	407	4072	1943
wR_2 (all data)	0.0812	0.1310	0.1170	0.1315
R_1 ($F_o \geq 4\sigma(F_o)$)	0.0307	0.0594	0.0510	0.0500
GooF on F^2	1.054	1.212	1.041	1.020
$\Delta\rho_{max/min}$ [e Å^{-3}]	0.284; –0.228	0.25; –0.41	1.093; –0.894	0.88; 0.88
Absolute struct. param.[14]	–0.013(14)	0.04(5)	–0.009(5)	–0.021(3)

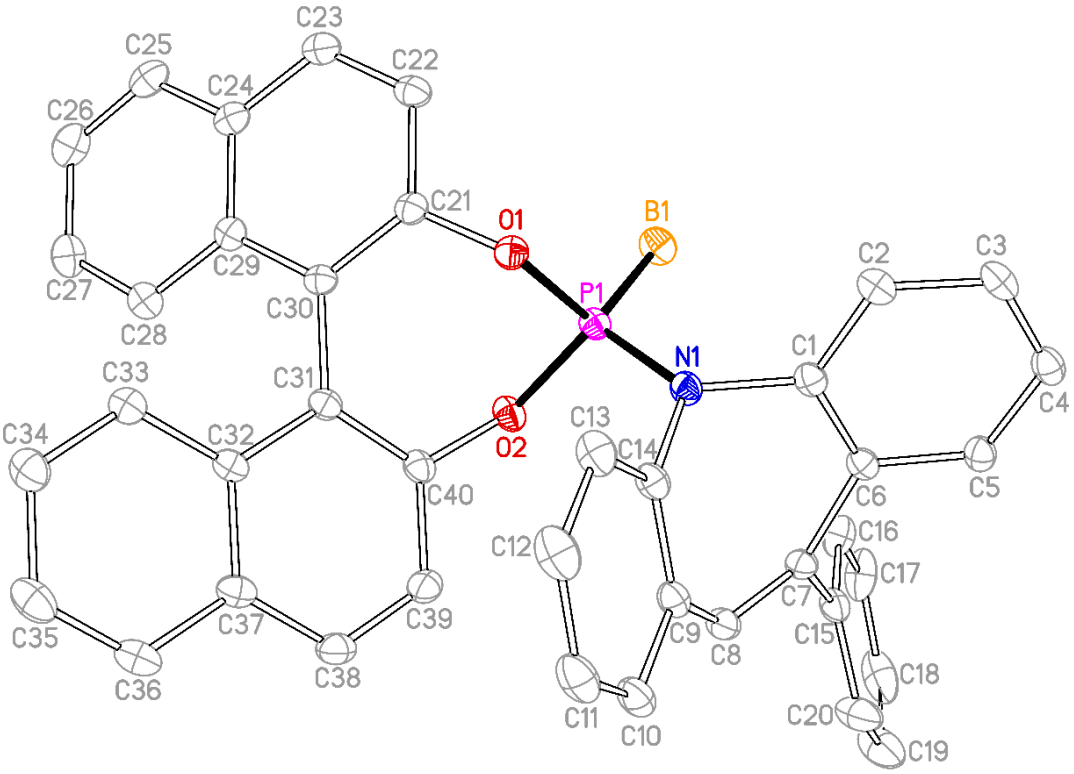

Figure S1. Thermal ellipsoid representation of the molecular structure of (p*S,R*)-**5** with the applied numbering scheme (50 % probability ellipsoids, H atoms omitted for clarity).

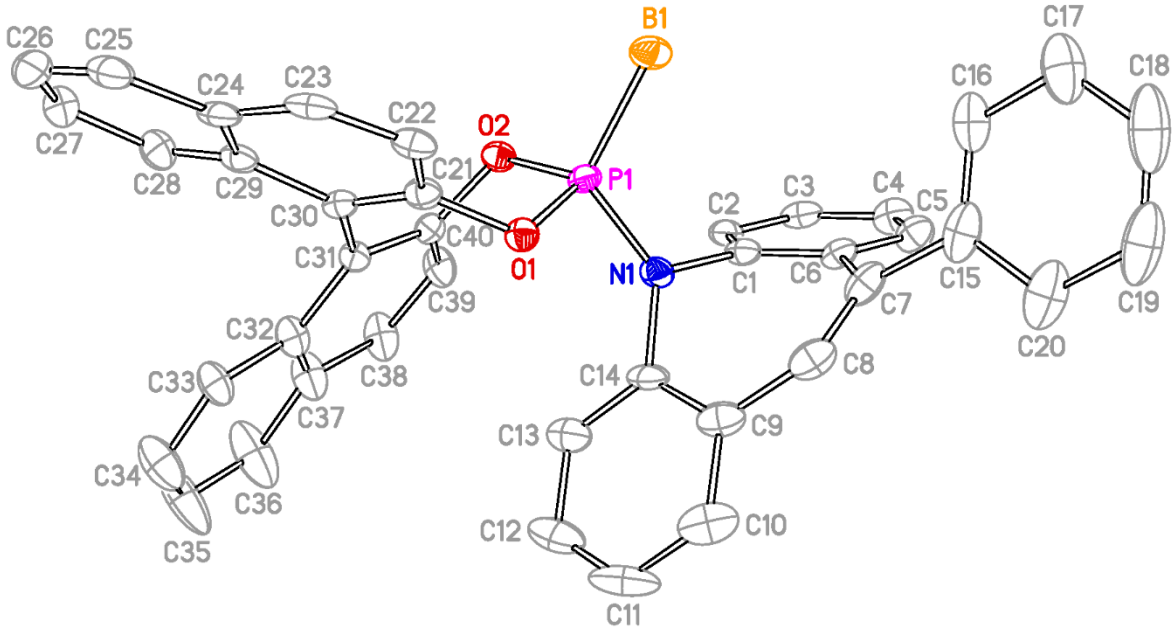

Figure S2. Thermal ellipsoid representation of the molecular structure of (p*R,R*)-**5** with the applied numbering scheme (50 % probability ellipsoids, H atoms omitted for clarity).

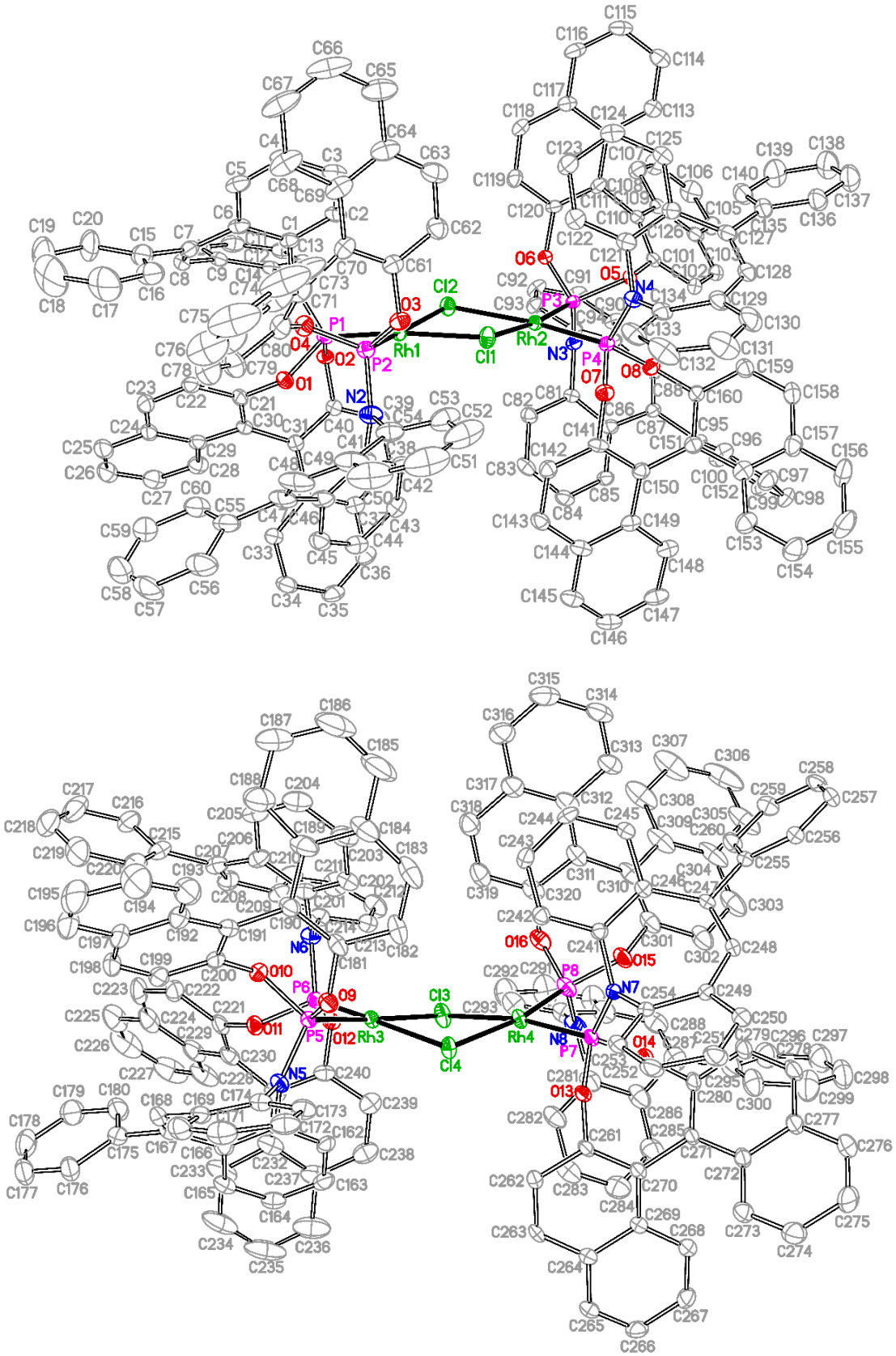

Figure S3. Thermal ellipsoid representation of the molecular structure of the two independent molecules of (p*S,R*)-**8** in crystals of (p*S,R*)-**8**·$(C_6H_6)_{7.5}$·$(n\text{-}C_5H_{12})_{0.25}$ with the applied numbering scheme (50 % probability ellipsoids, H atoms and solvent molecules omitted for clarity).

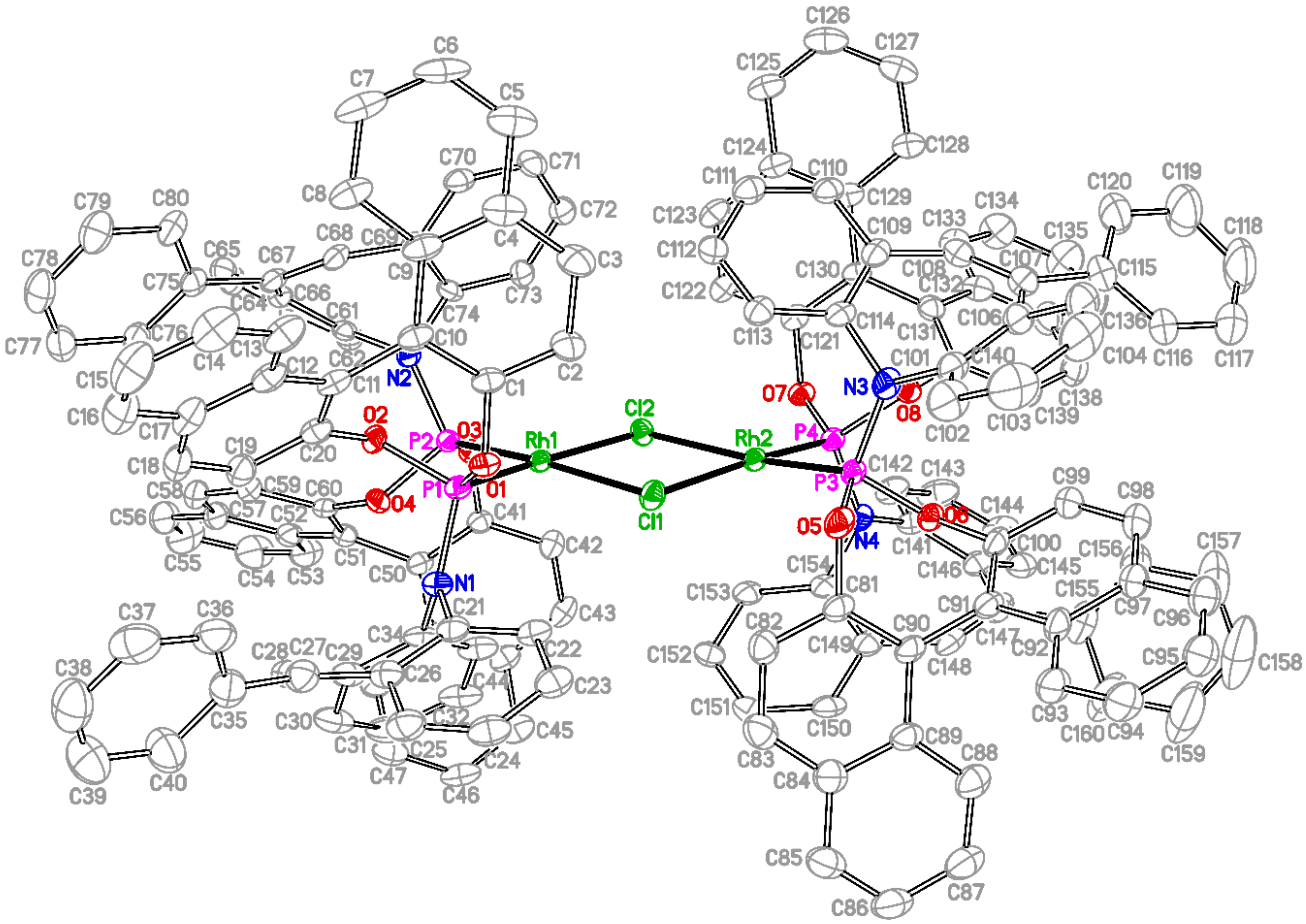

Figure S4. Thermal ellipsoid representation of the molecular structure of (p*R,R*)-**8** in crystals of (p*S,R*)-**8**·$(C_6H_6)_4$·*n*-C_6H_{14} with the applied numbering scheme (50 % probability ellipsoids, H atoms and solvent molecules omitted for clarity).

3. NMR spectra

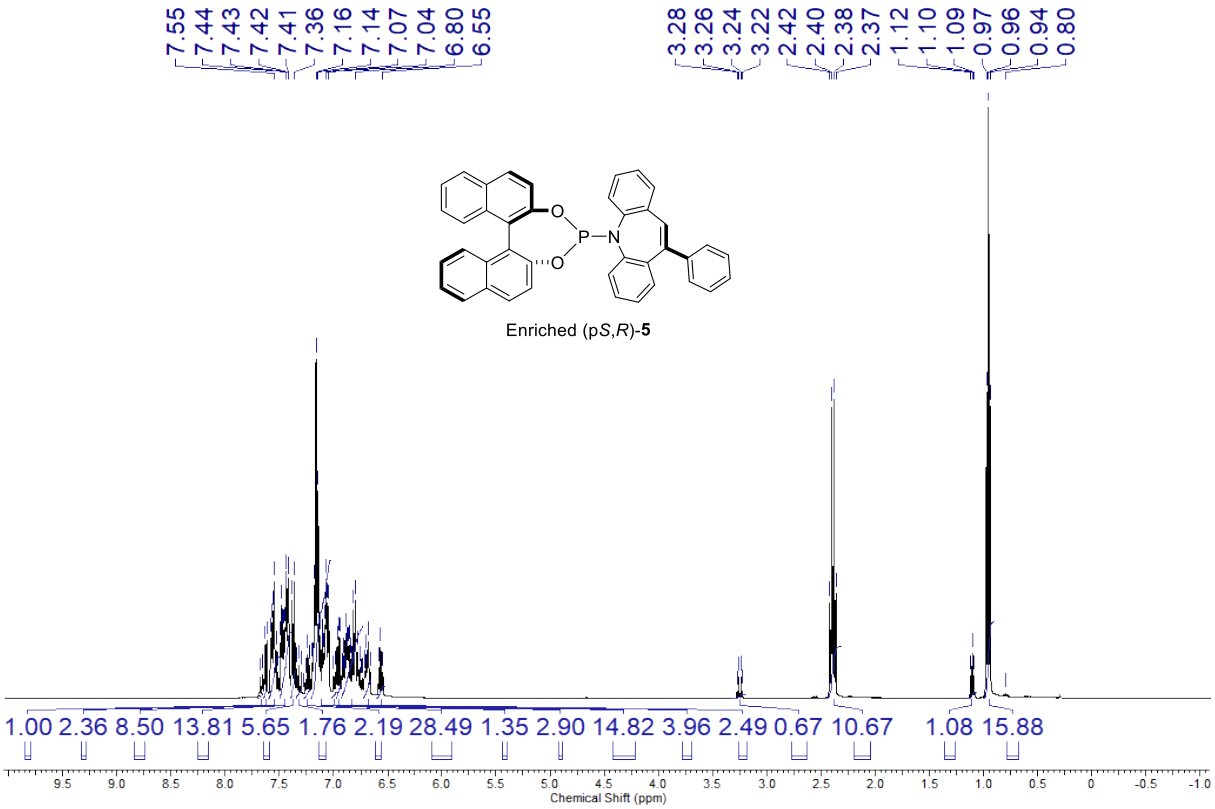

Figure S5. ^{1}H NMR of the enriched diastereomeric mixture of **5** in C_6D_6

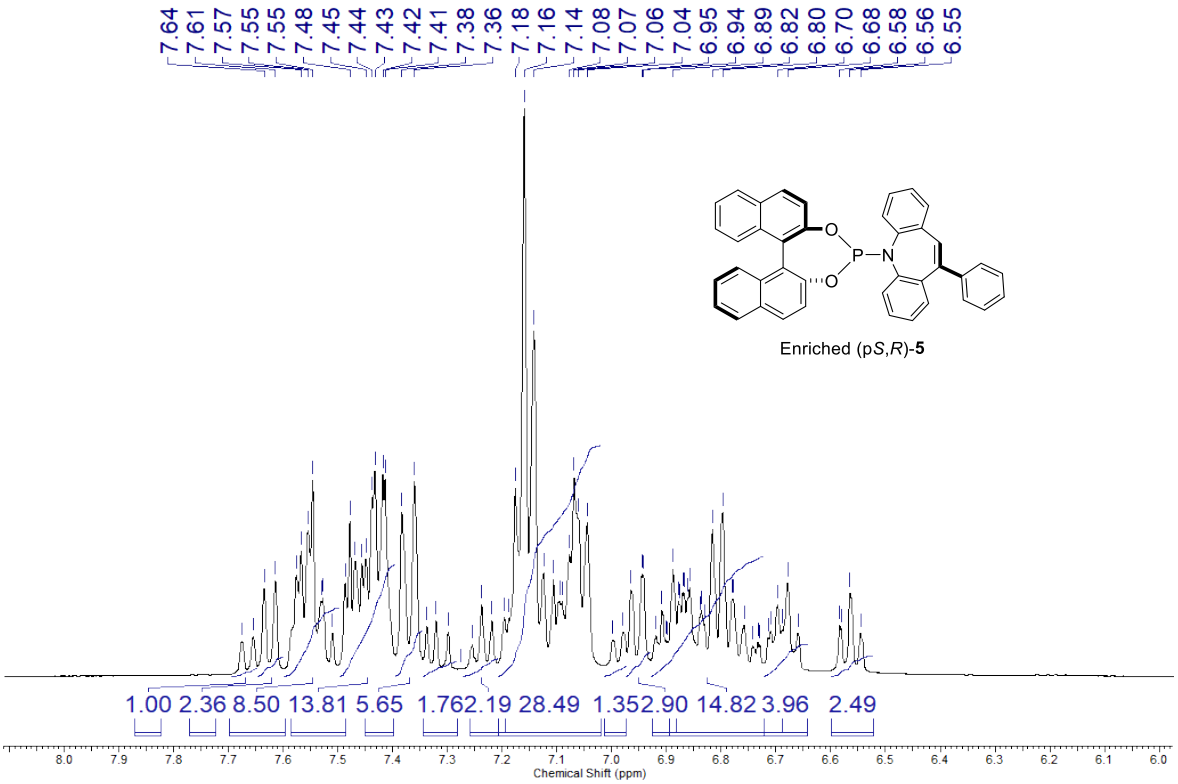

Figure S6. ^{1}H NMR of the aromatic region of the enriched diastereomeric mixture of **5** in C_6D_6

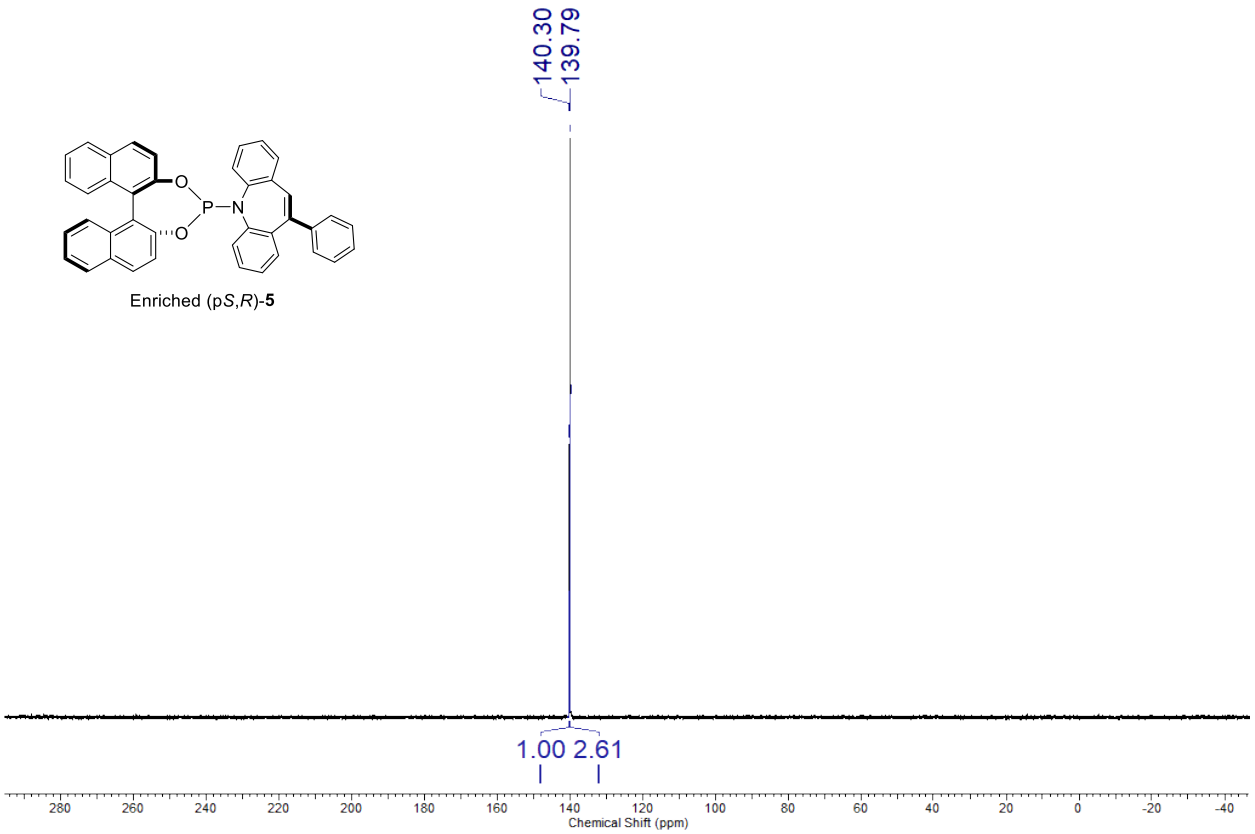

Figure S7. $^{31}P\{^{1}H\}$ NMR of the enriched diastereomeric mixture of compound **5** in C_6D_6

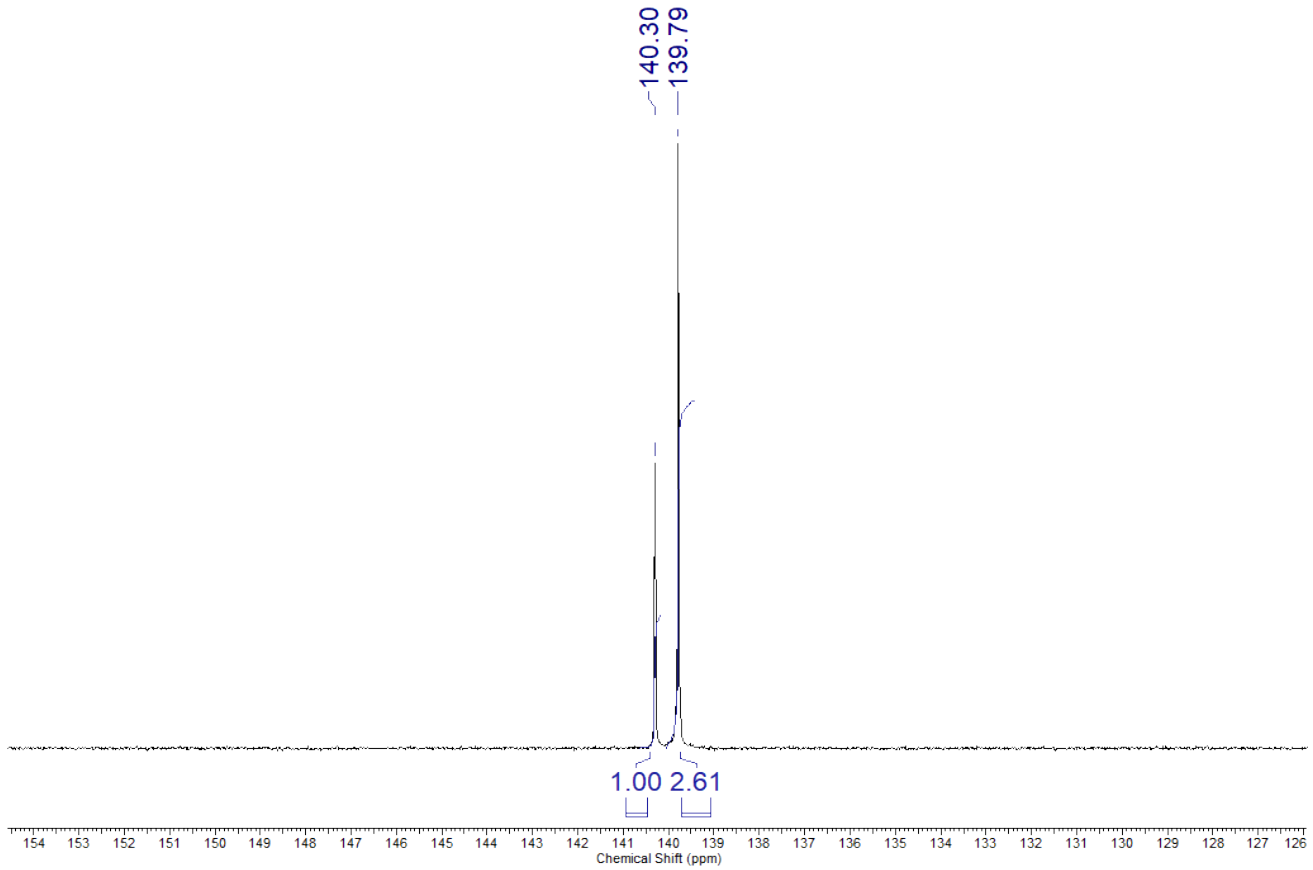

Figure S8. Zoom-in on Figure S7

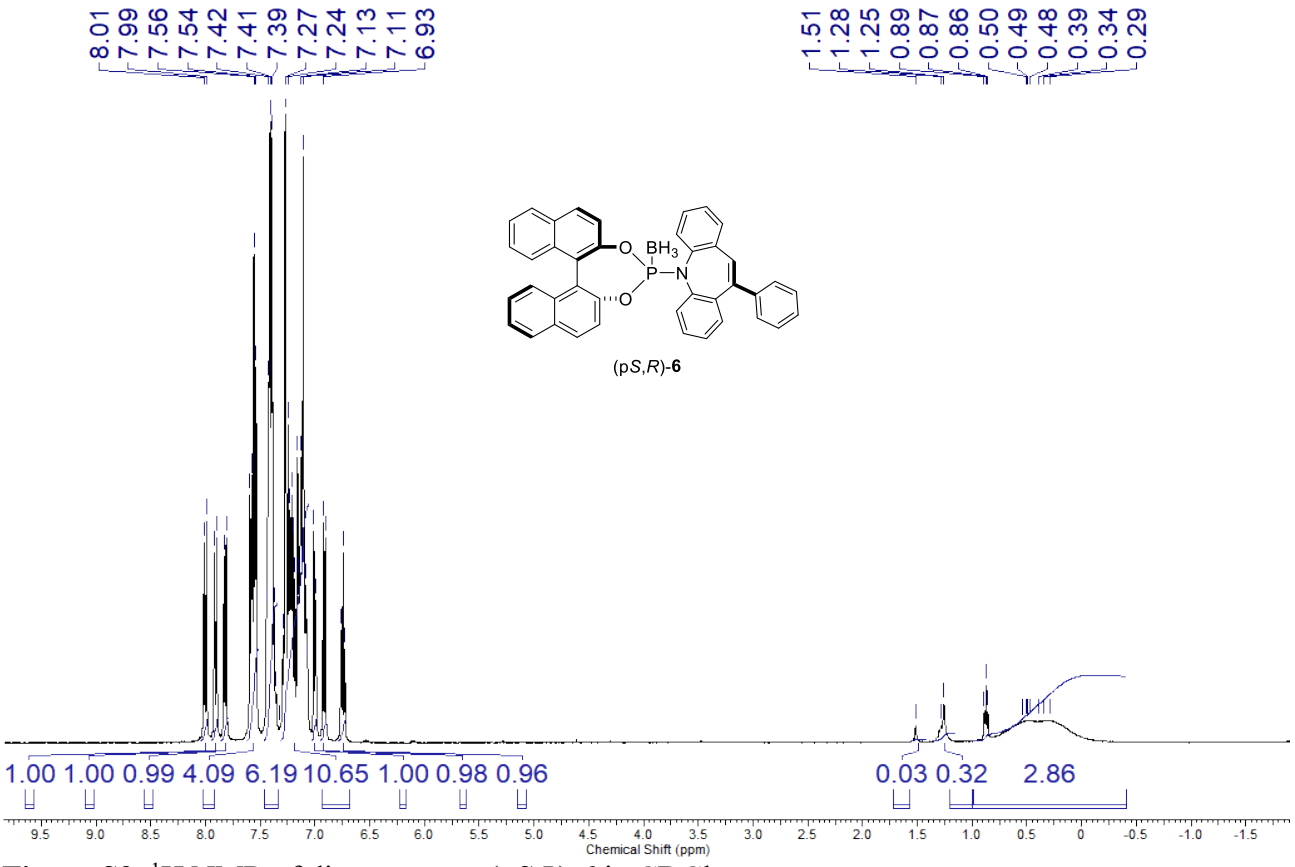

Figure S9. ^{1}H NMR of diastereopure (p*S*,*R*)-**6** in $CDCl_3$

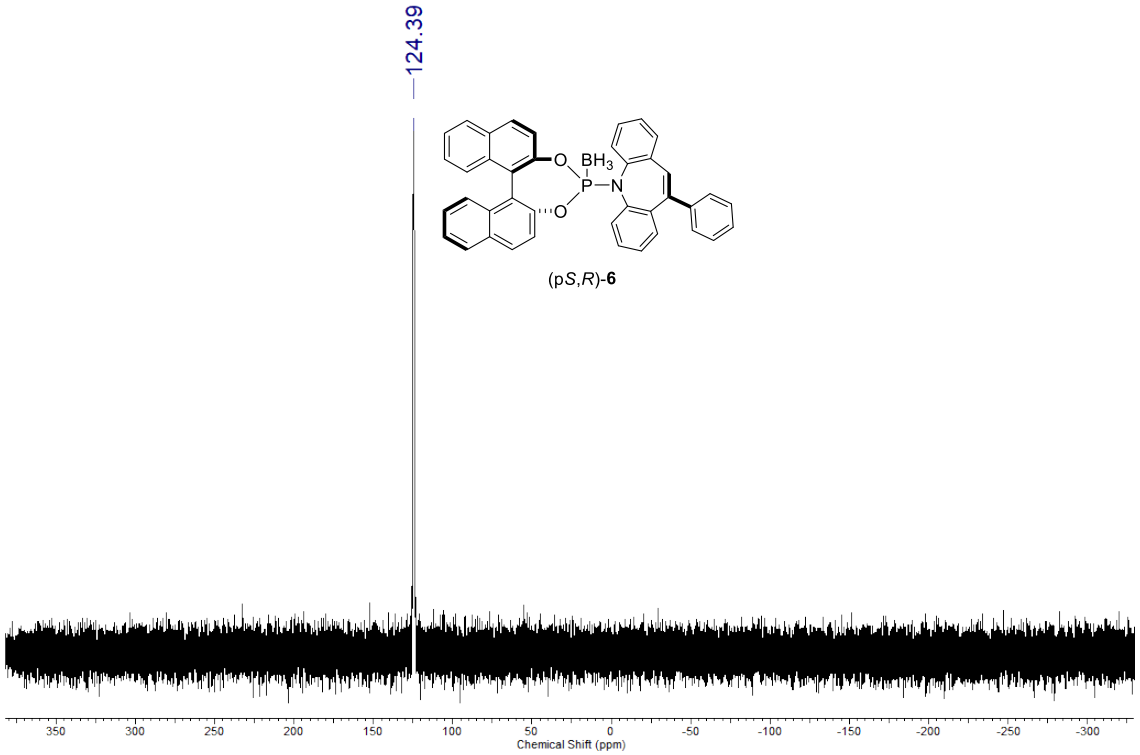

Figure S10. ^{31}P{^{1}H} NMR of diastereopure (p*S*,*R*)-**6** in $CDCl_3$

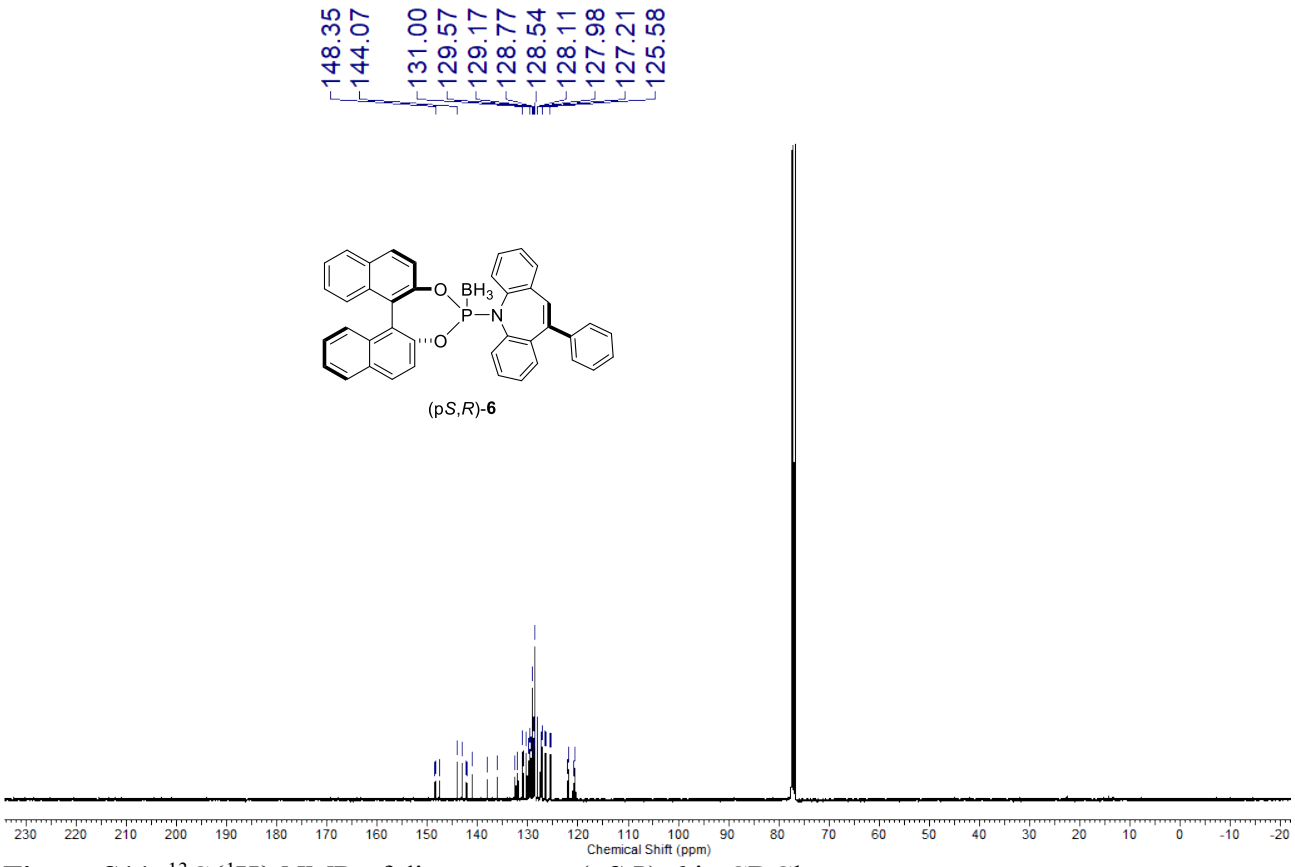

Figure S11. $^{13}C\{^{1}H\}$ NMR of diastereopure (p*S*,*R*)-**6** in $CDCl_3$

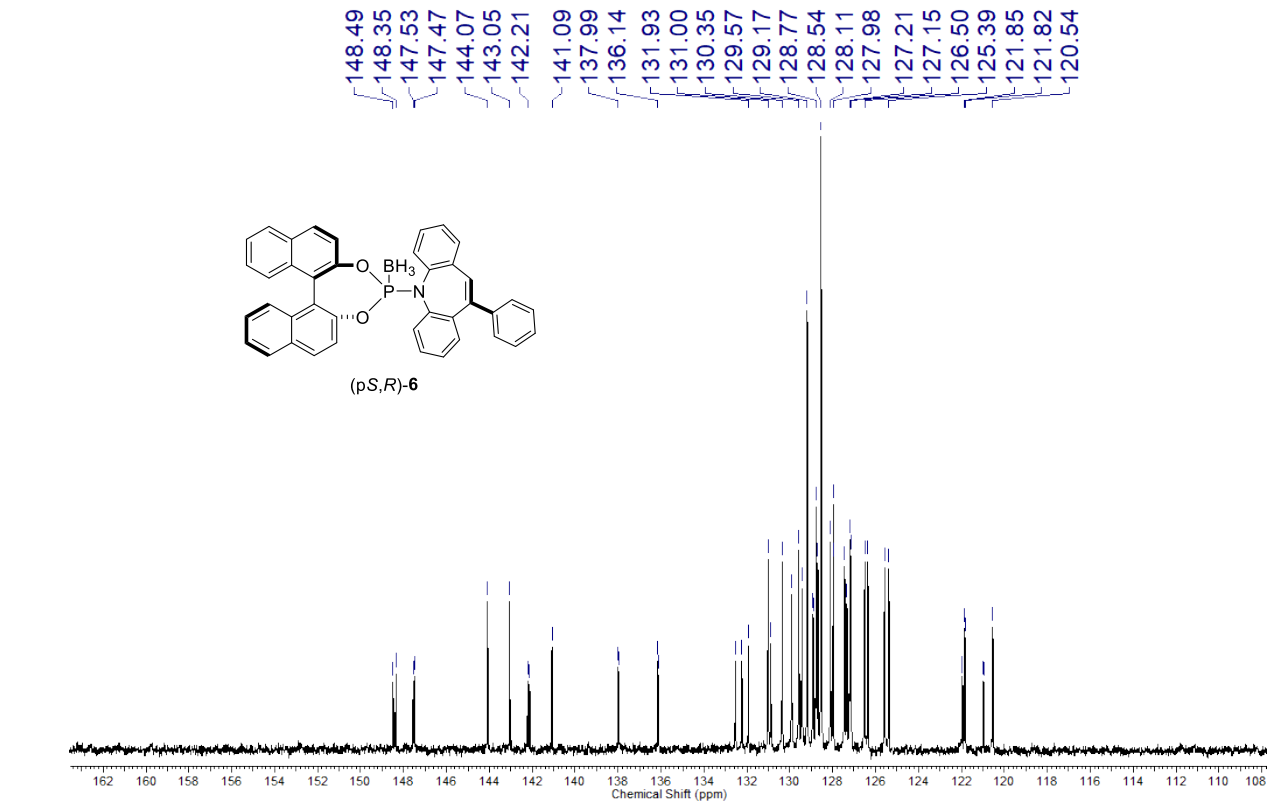

Figure S12. Zoom-in on Figure S11

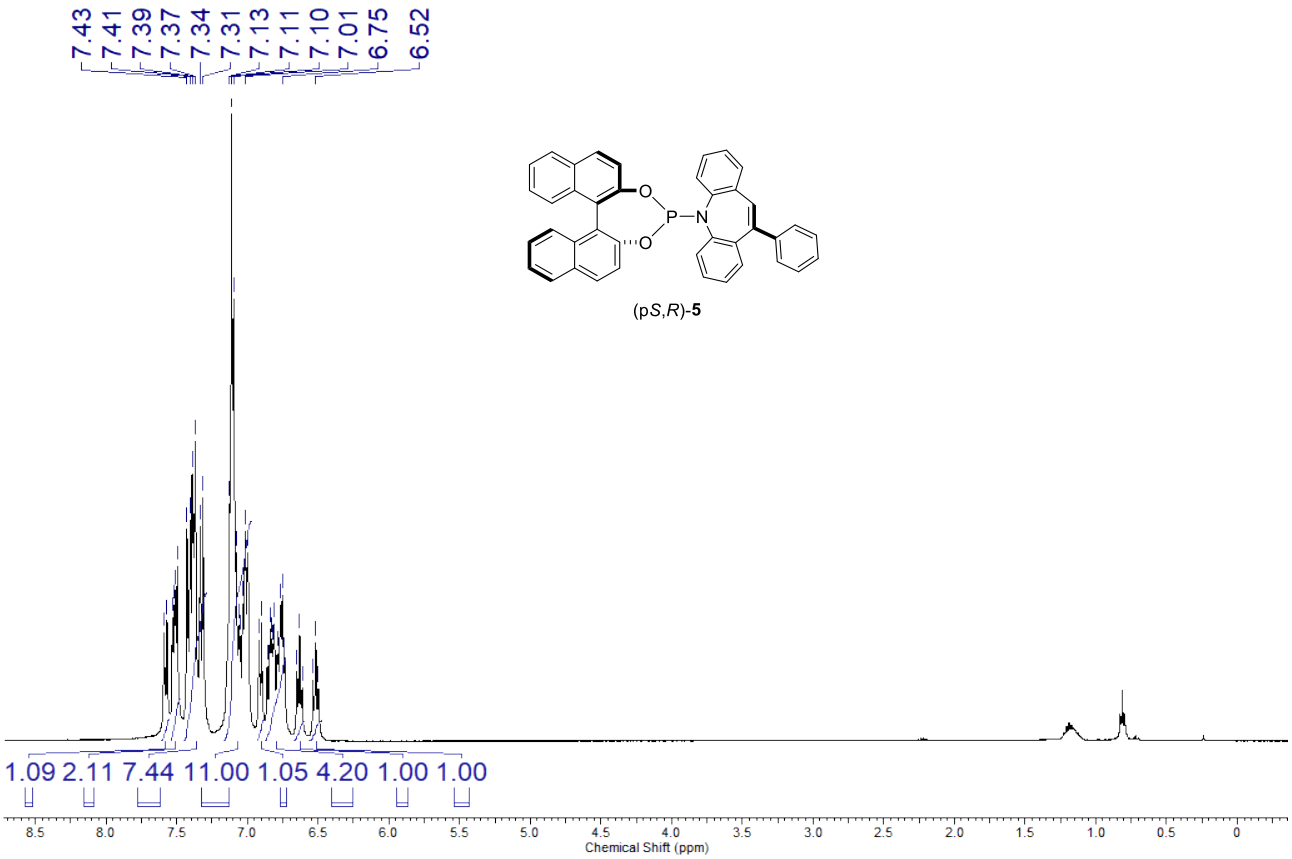

Figure S13. ^{1}H NMR of diastereopure (p*S*,*R*)-**5** in C_6D_6

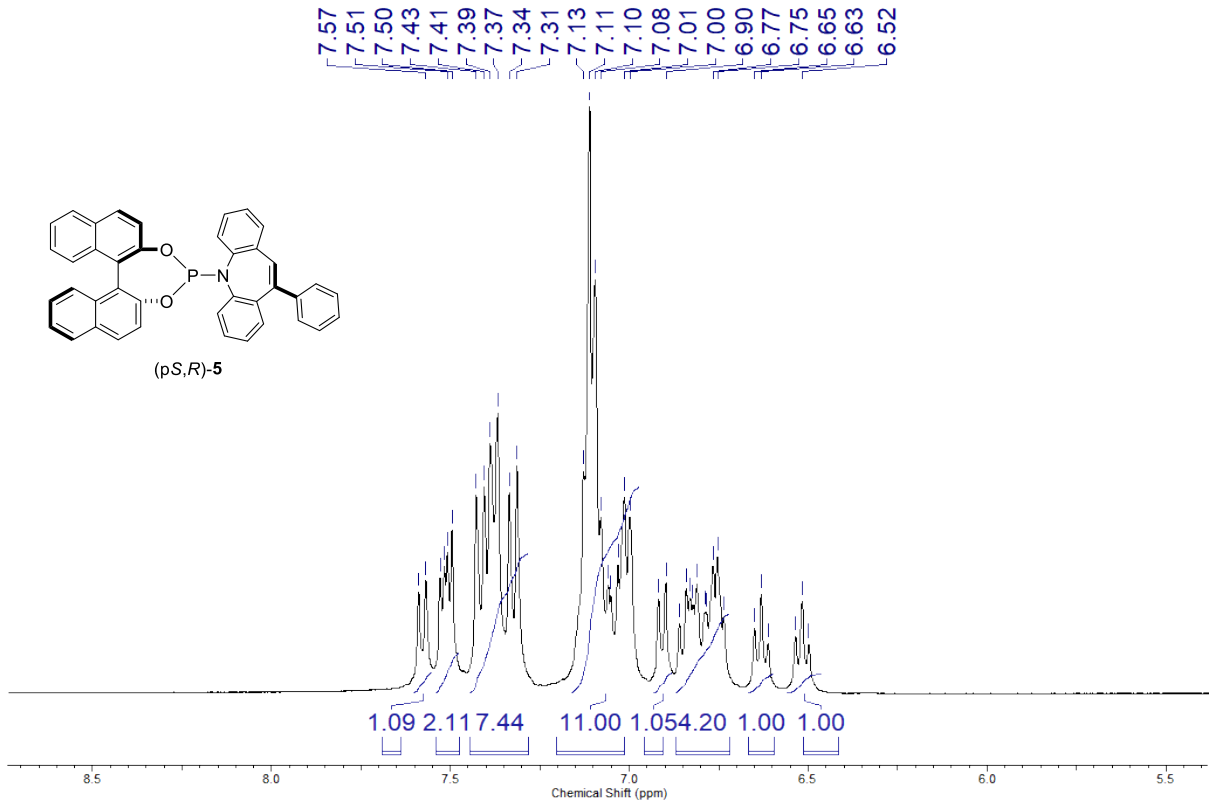

Figure S14. Zoom-in on Figure S13

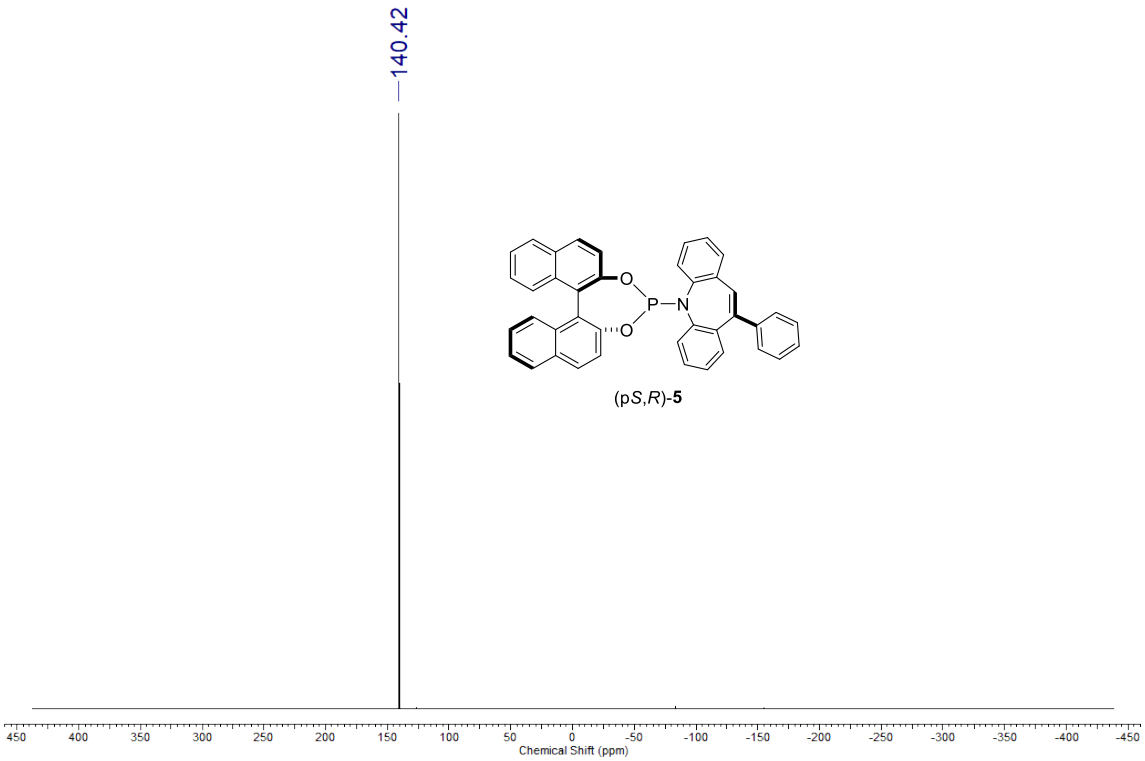

Figure S15. $^{31}P\{^{1}H\}$ NMR of diastereopure (p*S*,*R*)-**5** in C_6D_6

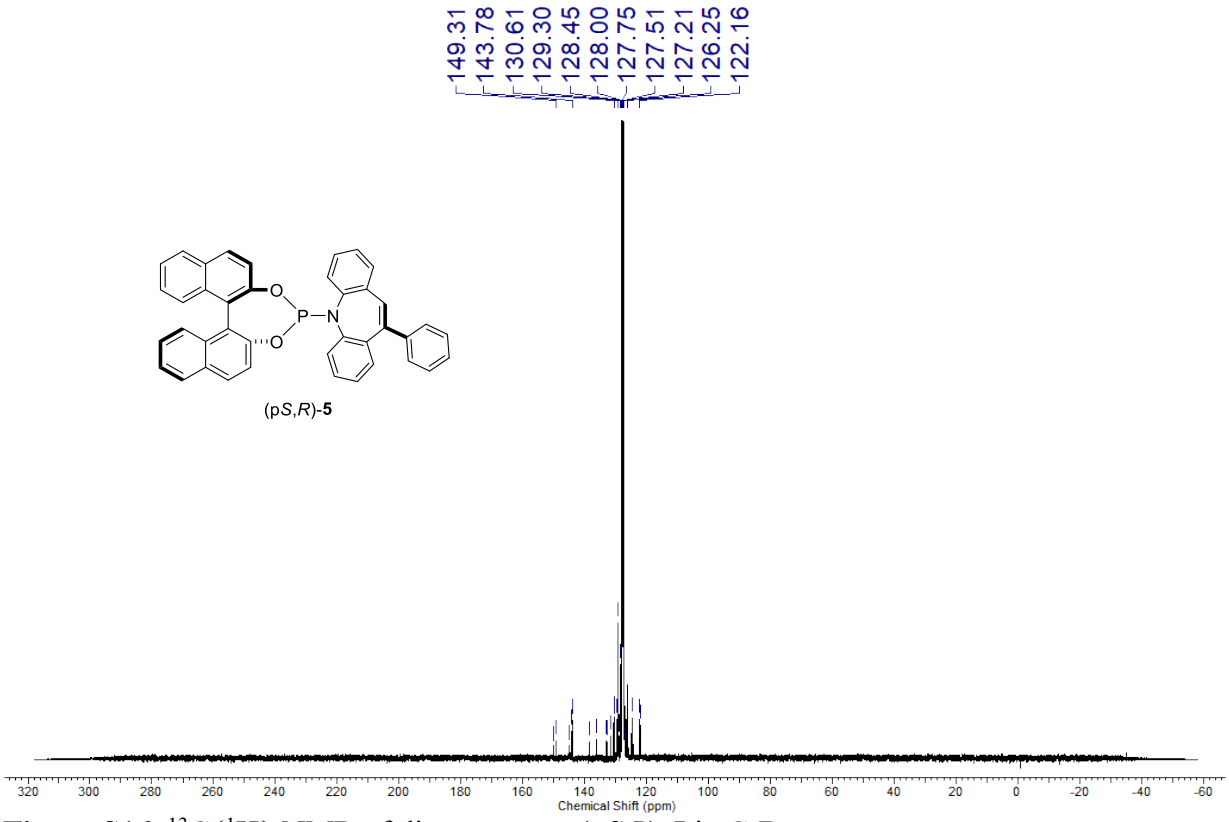

Figure S16. $^{13}C\{^{1}H\}$ NMR of diastereopure (p*S*,*R*)-**5** in C_6D_6

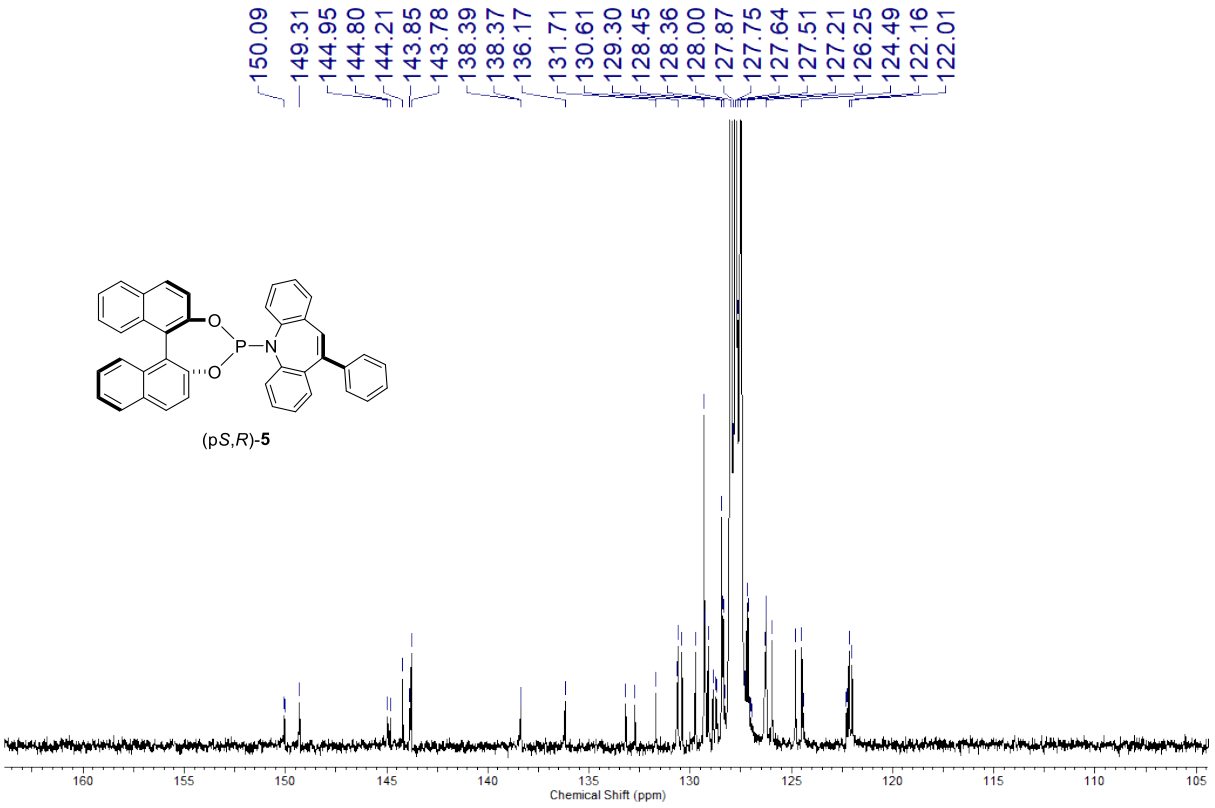

Figure S17. Zoom-in on Figure S16

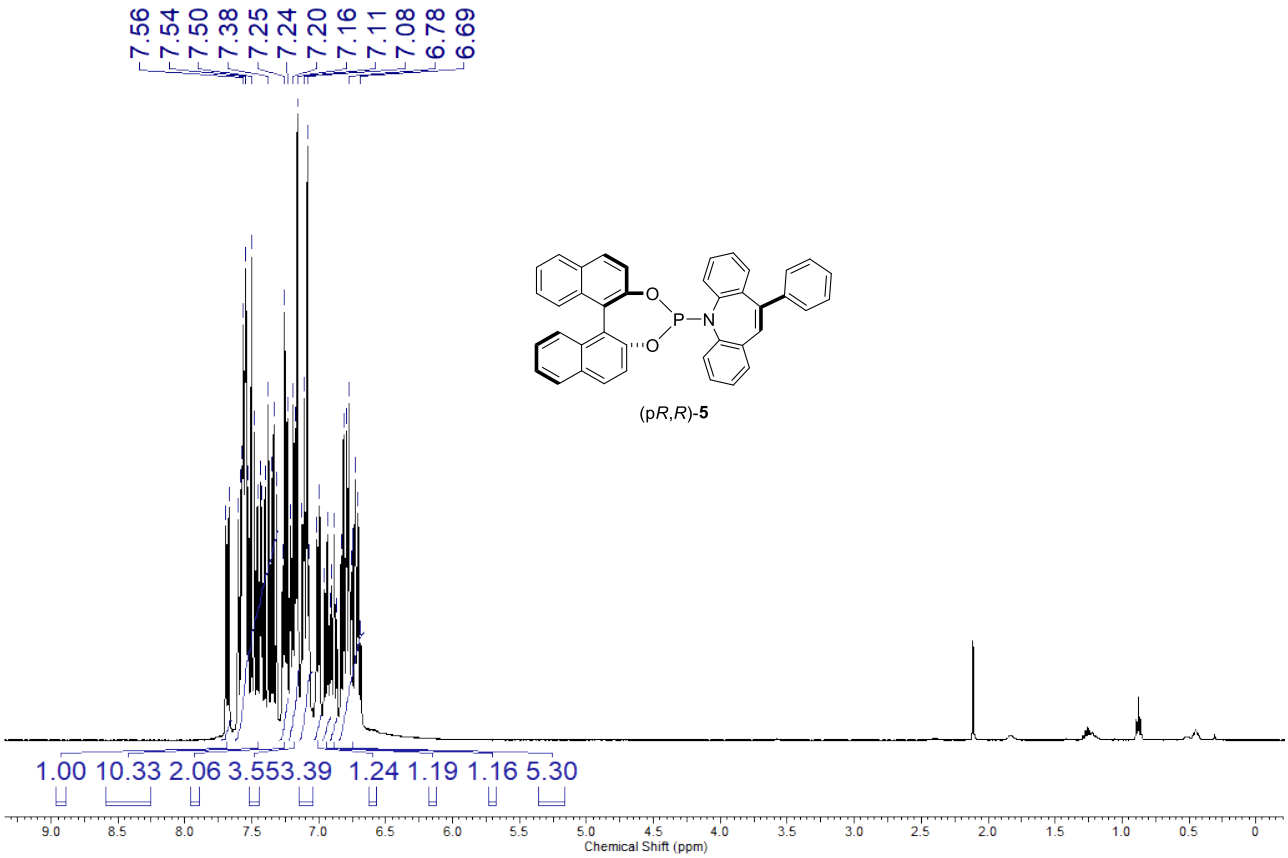

Figure S18. ^{1}H NMR of diastereopure (p*R*,*R*)-**5** in C_6D_6

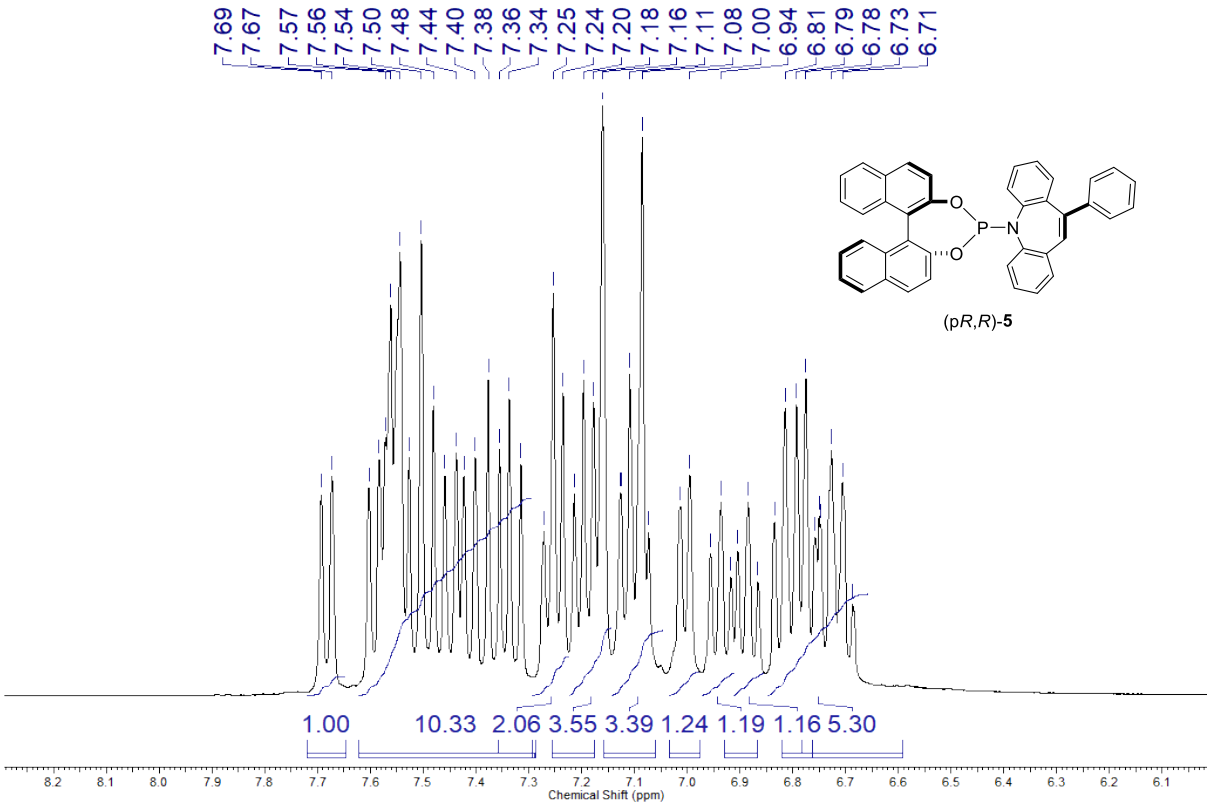

Figure S19. Zoom-in on Figure S18

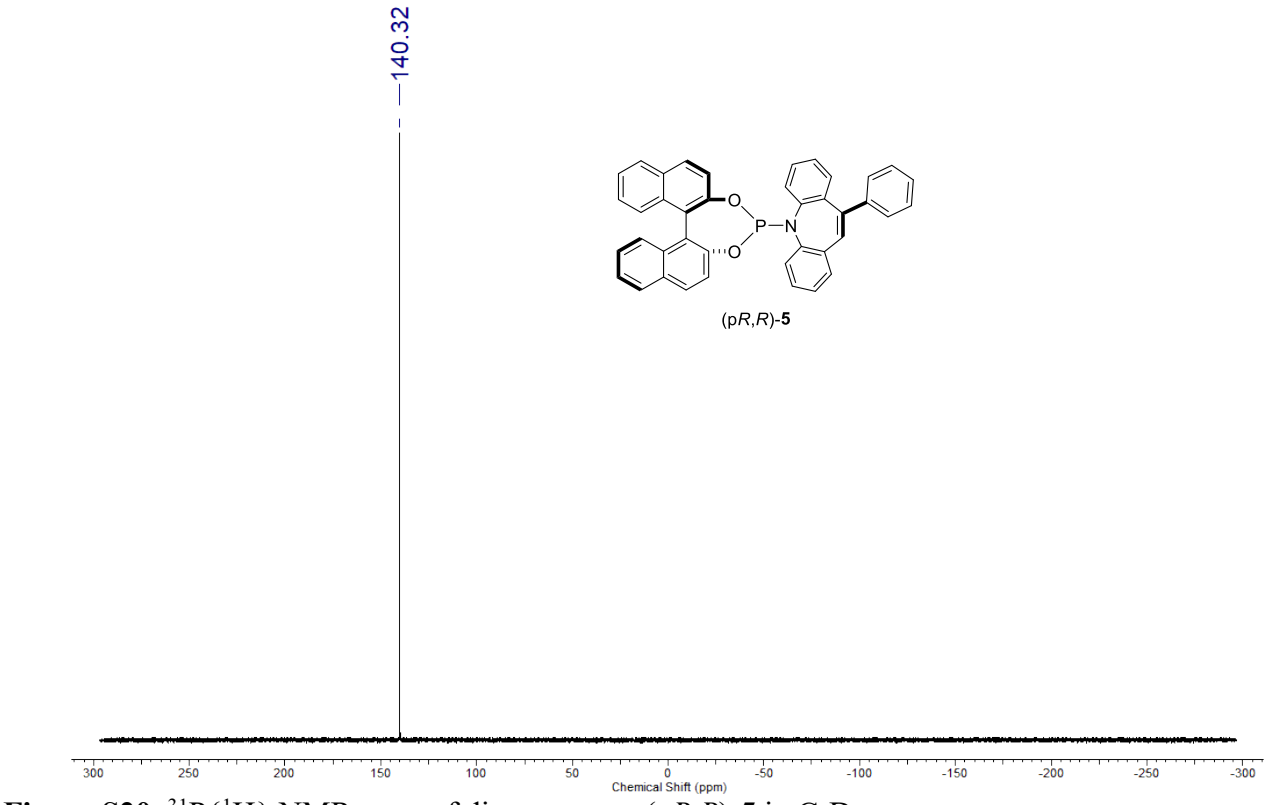

Figure S20. $^{31}P\{^{1}H\}$ NMR trace of diastereopure (p*R*,*R*)-**5** in C_6D_6

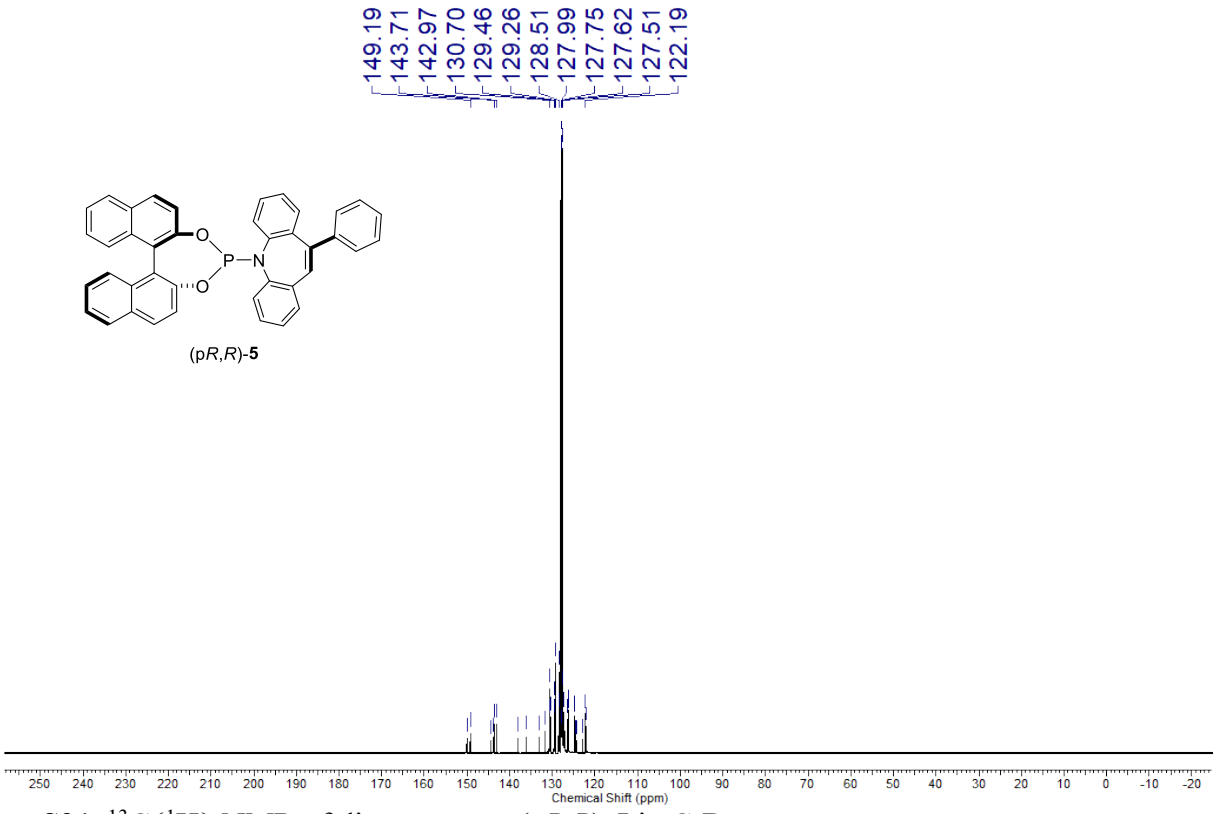

Figure S21. $^{13}C\{^{1}H\}$ NMR of diastereopure (p*R*,*R*)-**5** in C_6D_6

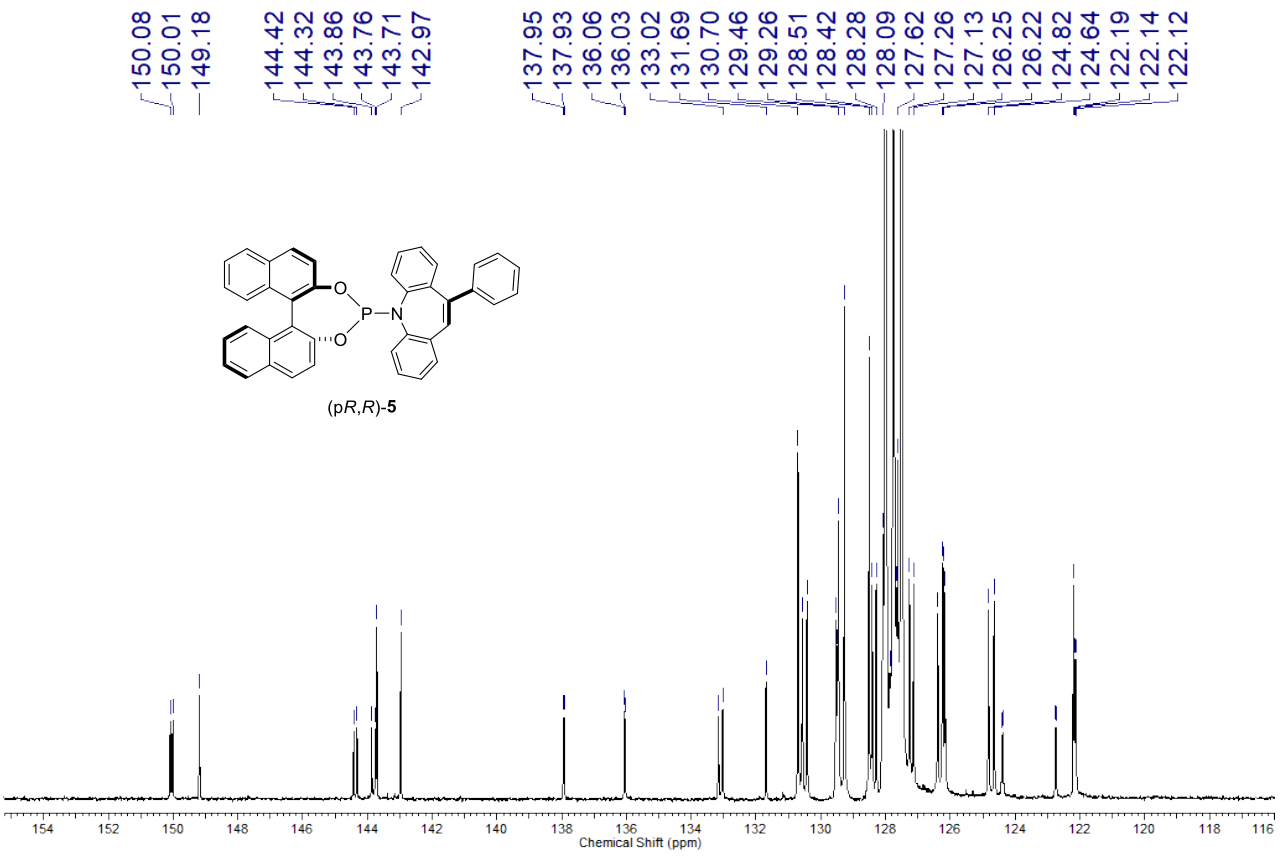

Figure S22. Zoom-in on Figure S21

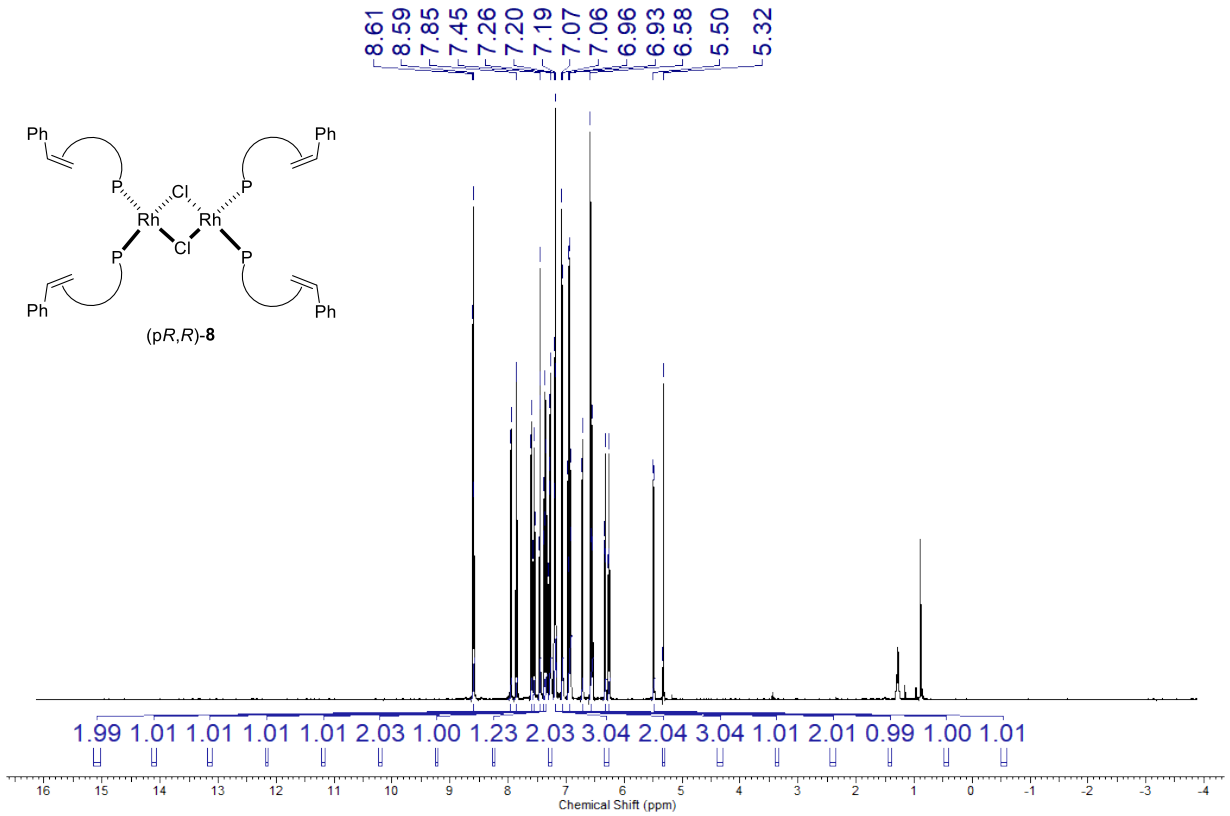

Figure S23. ^{1}H NMR of complex (p*R*,*R*)-**8** in CD_2Cl_2

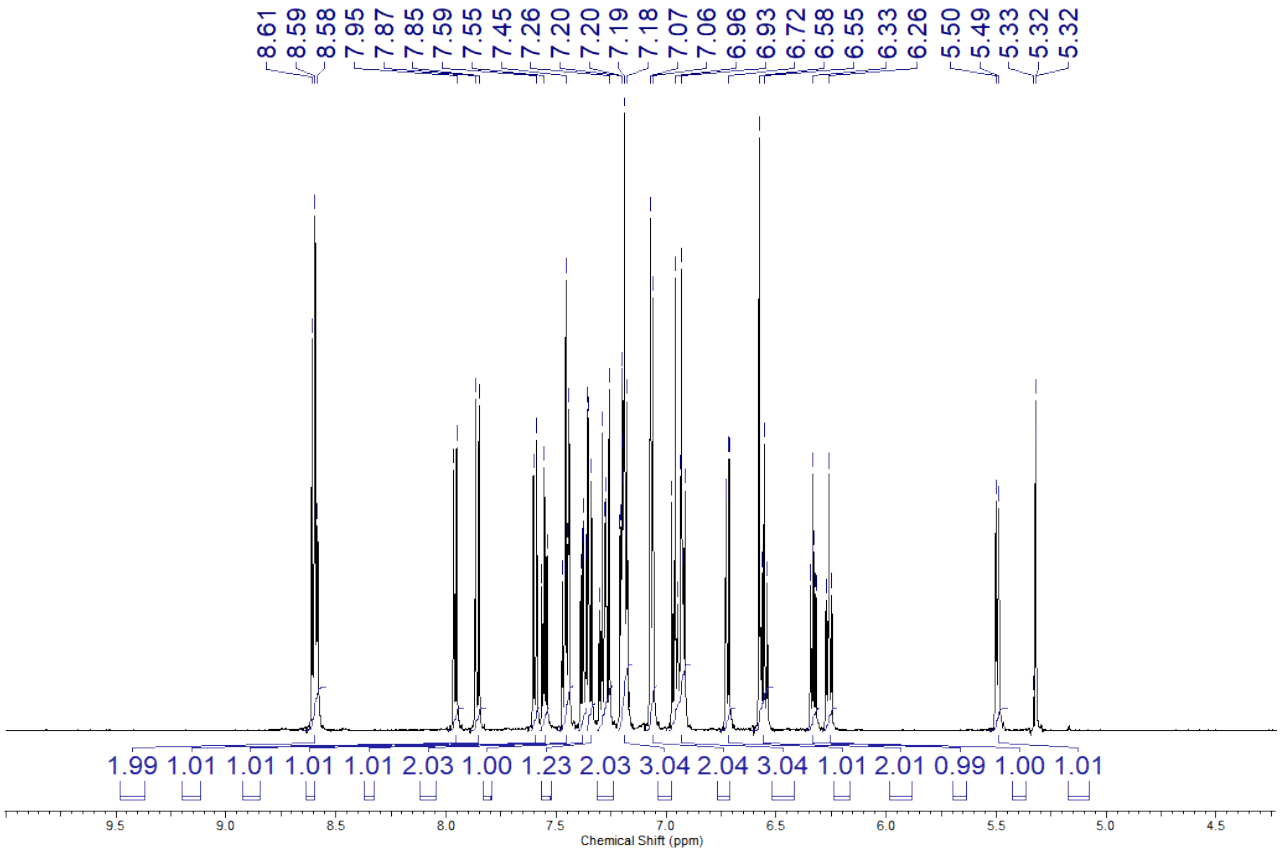

Figure S24. Zoom-in on Figure S23

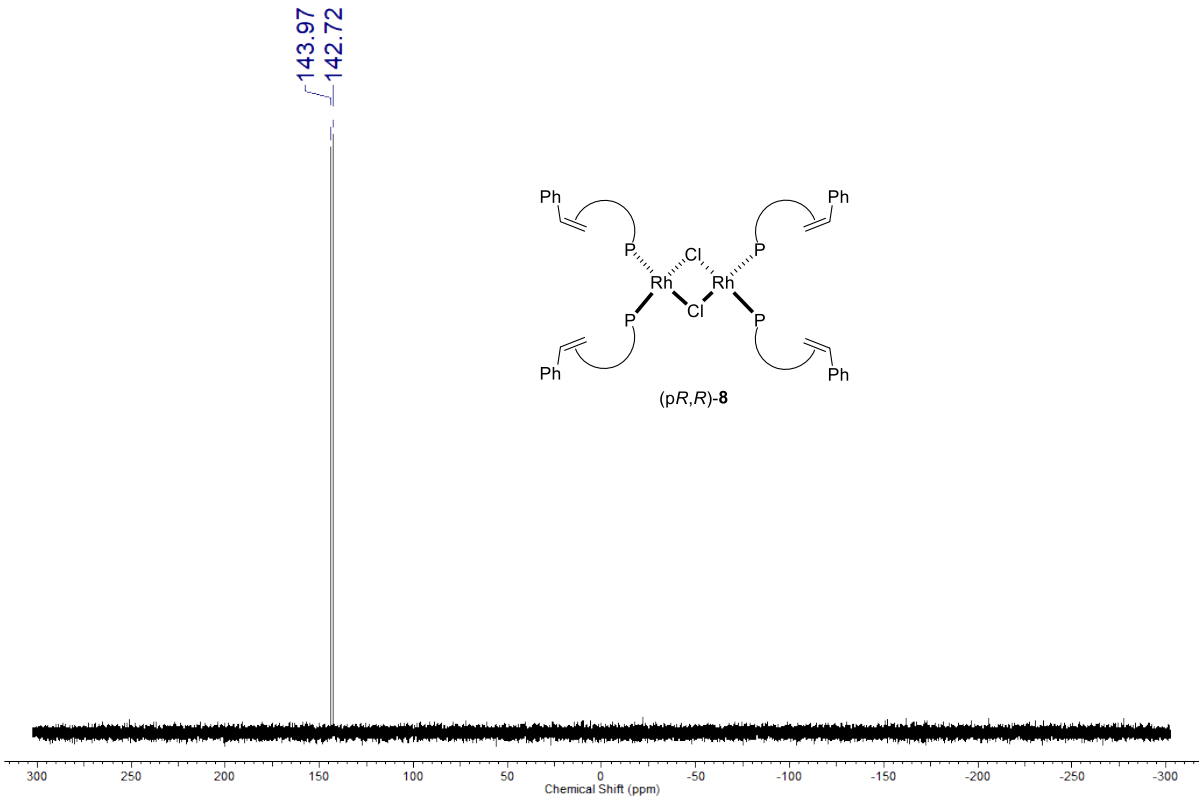

Figure S25. $^{31}P\{^{1}H\}$ NMR trace of complex (p*R*,*R*)-**8** in CD_2Cl_2

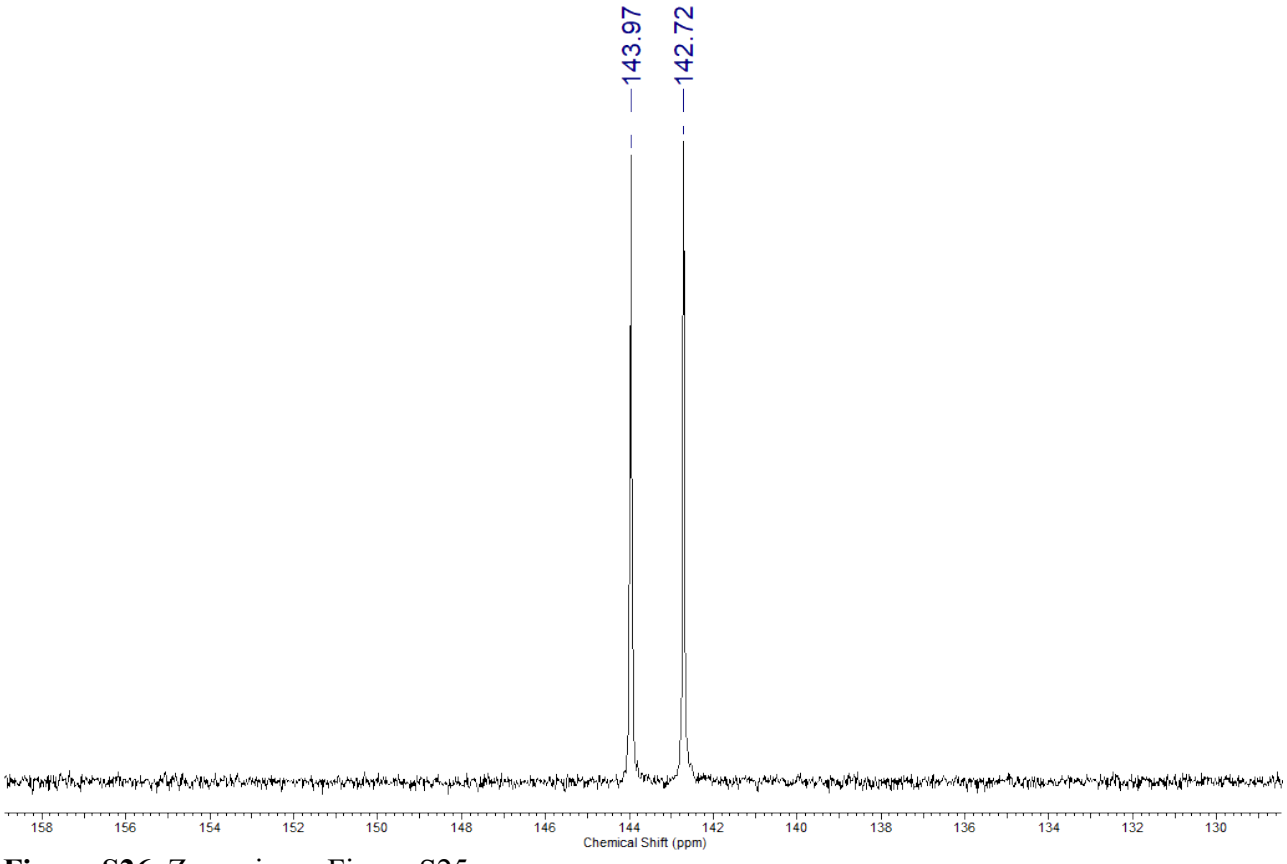

Figure S26. Zoom-in on Figure S25

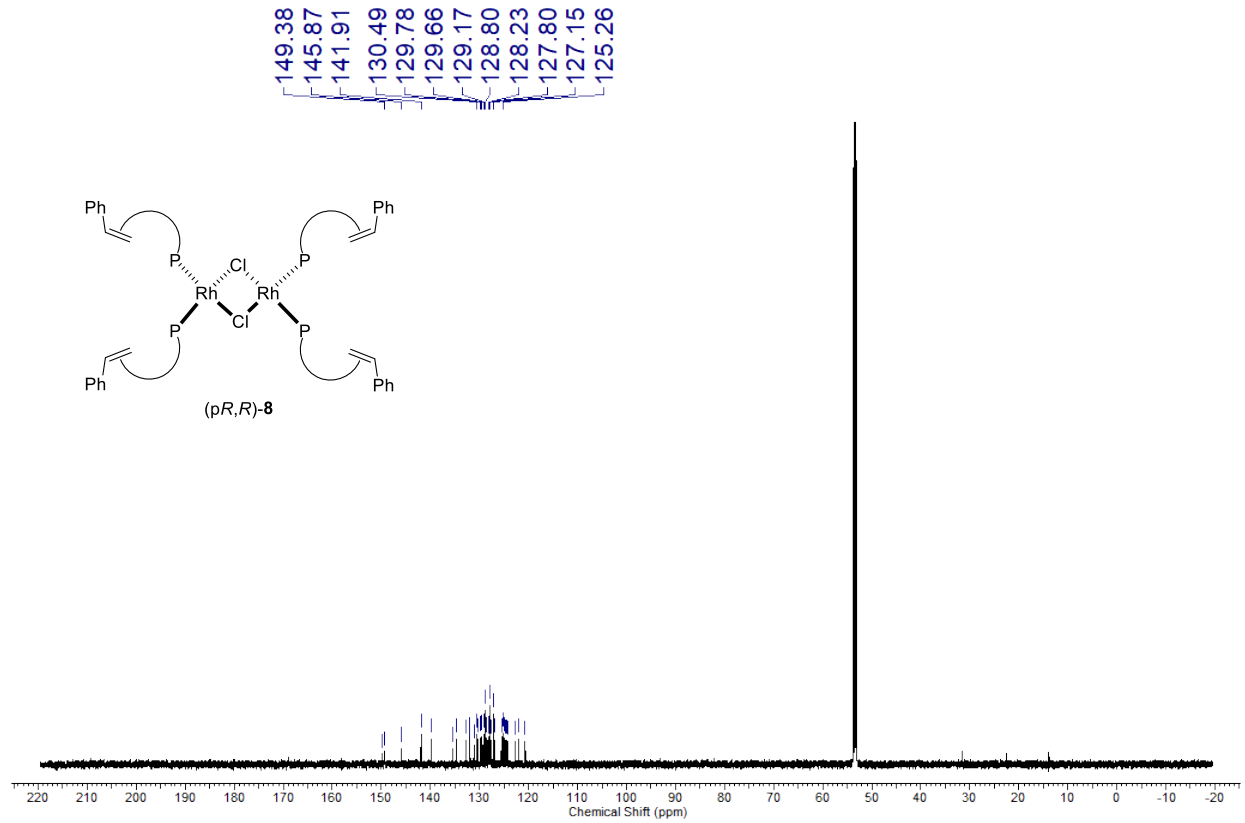

Figure S27. $^{13}C\{^{1}H\}$ NMR of complex (p*R*,*R*)-**8** in CD_2Cl_2

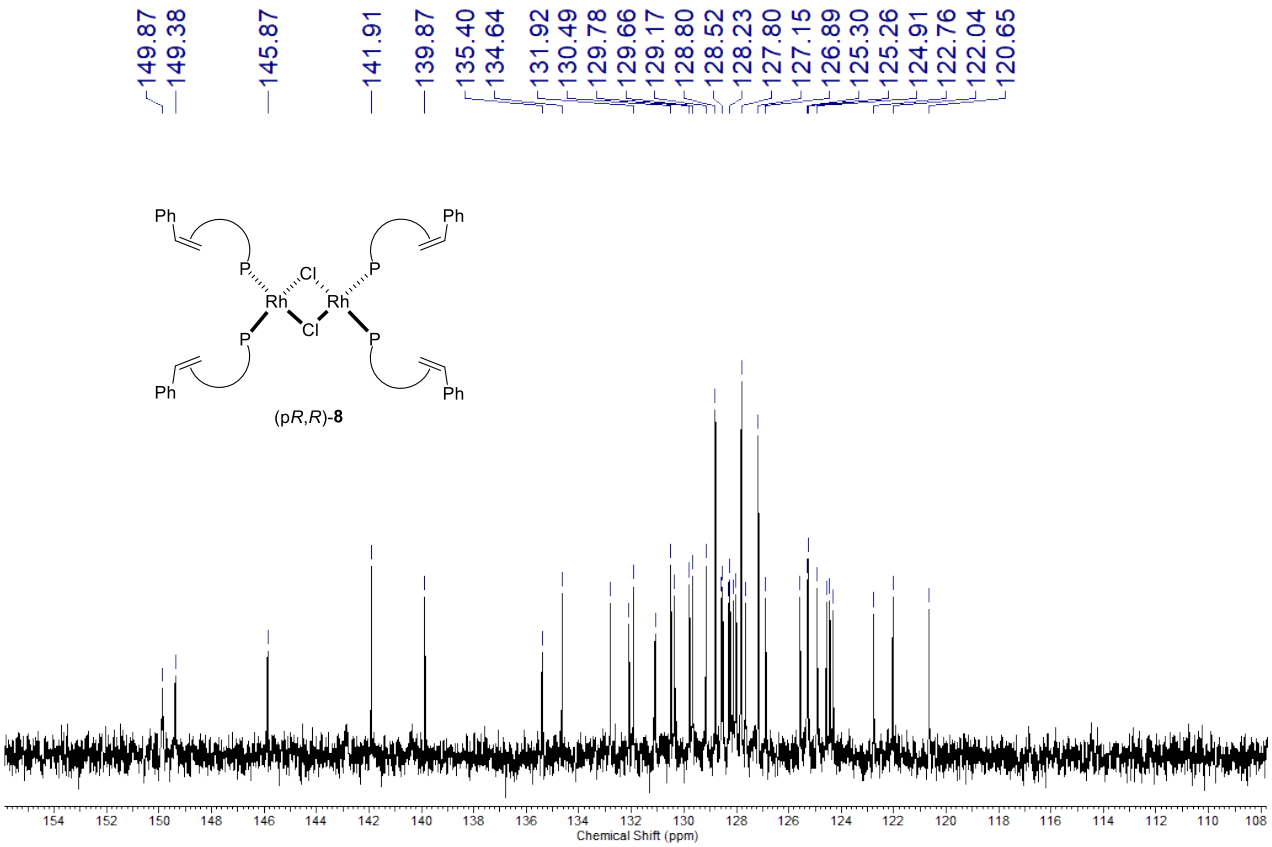

Figure S28. Zoom-in on Figure S27

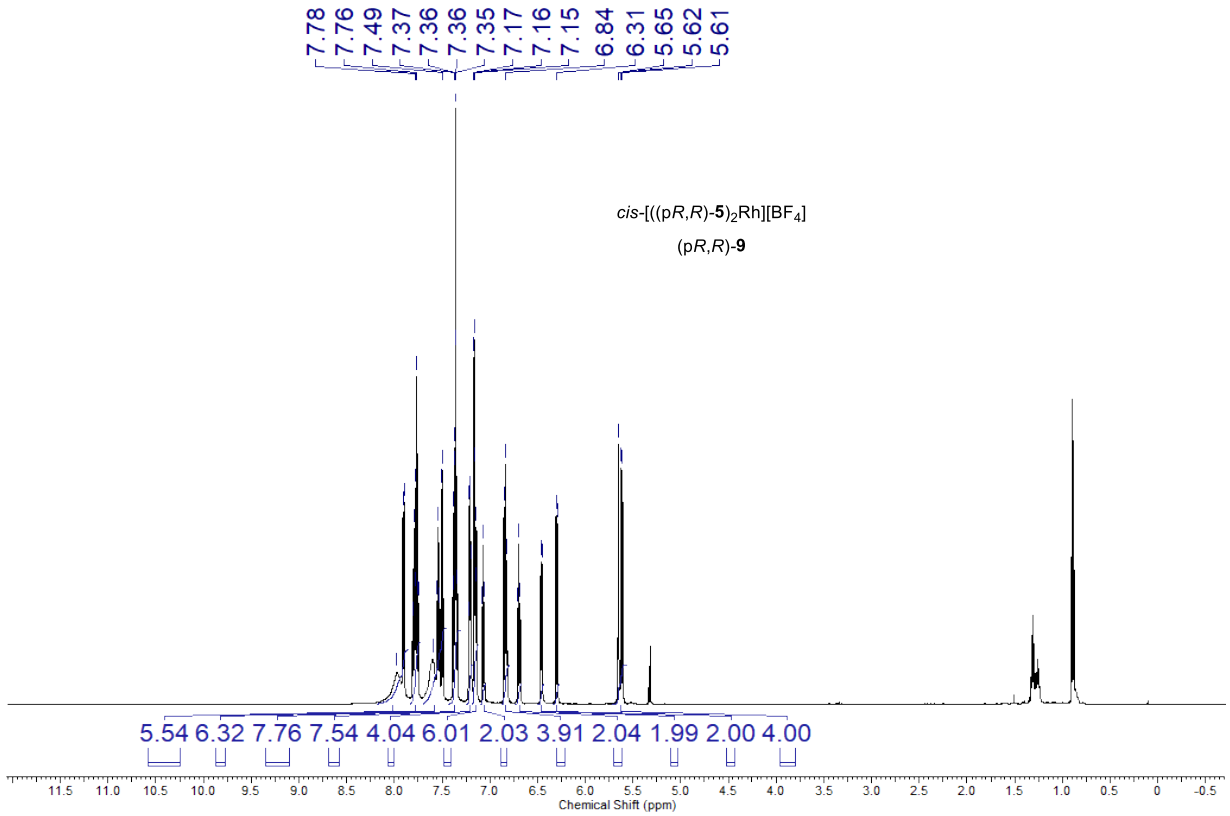

Figure S29. ^{1}H NMR trace of complex (p*R*,*R*)-**9** in CD_2Cl_2

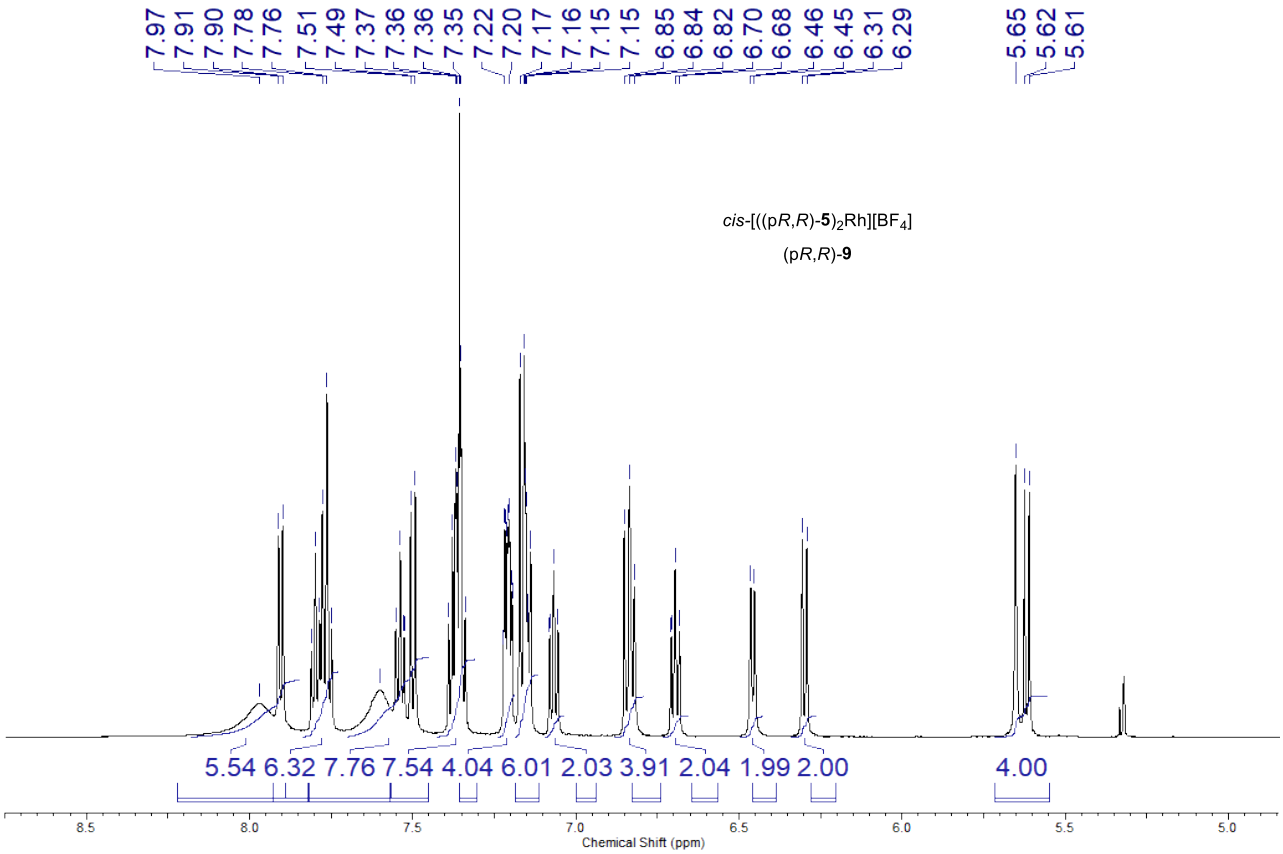

Figure S30. Zoom-in on Figure S29

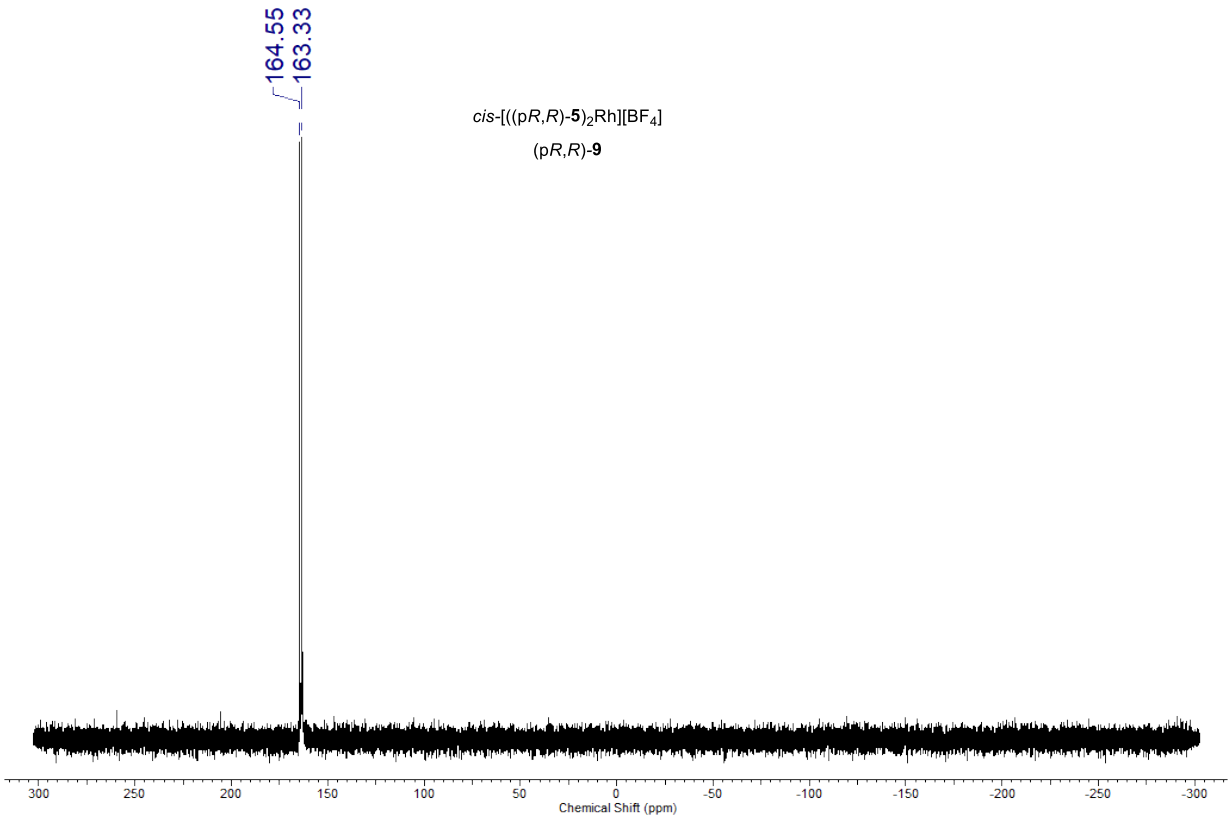

Figure S31. $^{31}P\{^{1}H\}$ NMR of complex (p*R*,*R*)-**9** in CD_2Cl_2

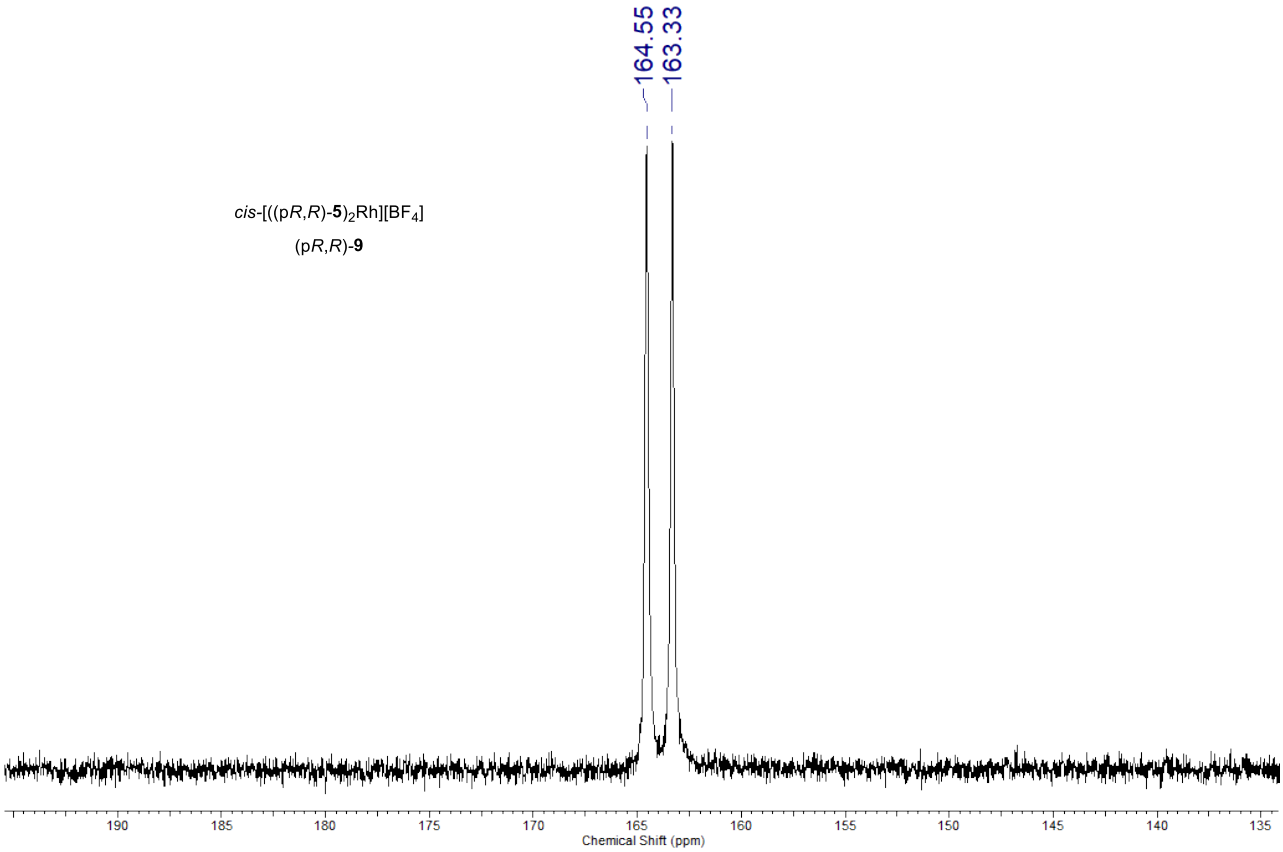

Figure S32. Zoom-in on Figure S31

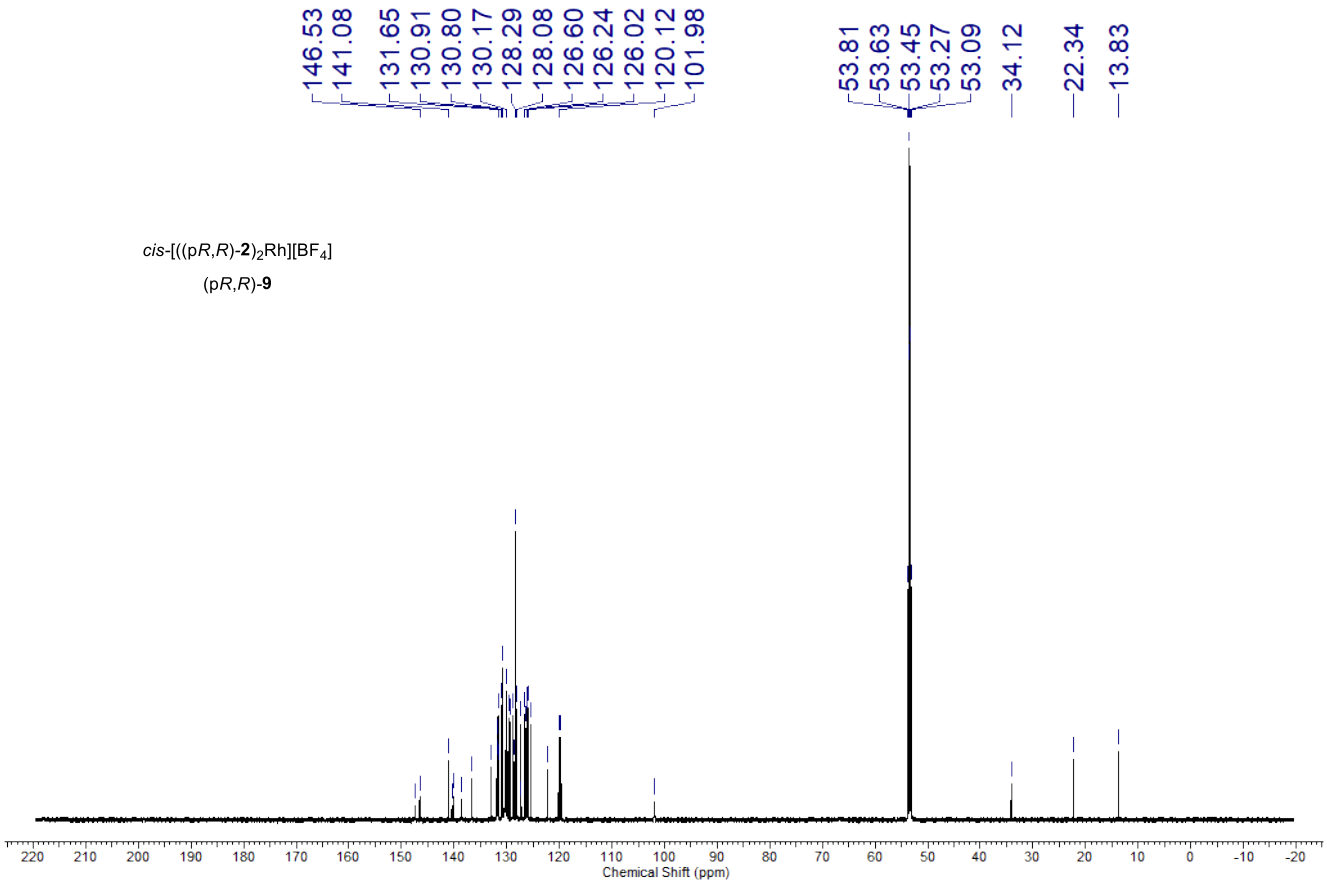

Figure S33. $^{13}C\{^{1}H\}$ NMR of complex (p*R*,*R*)-**9** in CD_2Cl_2

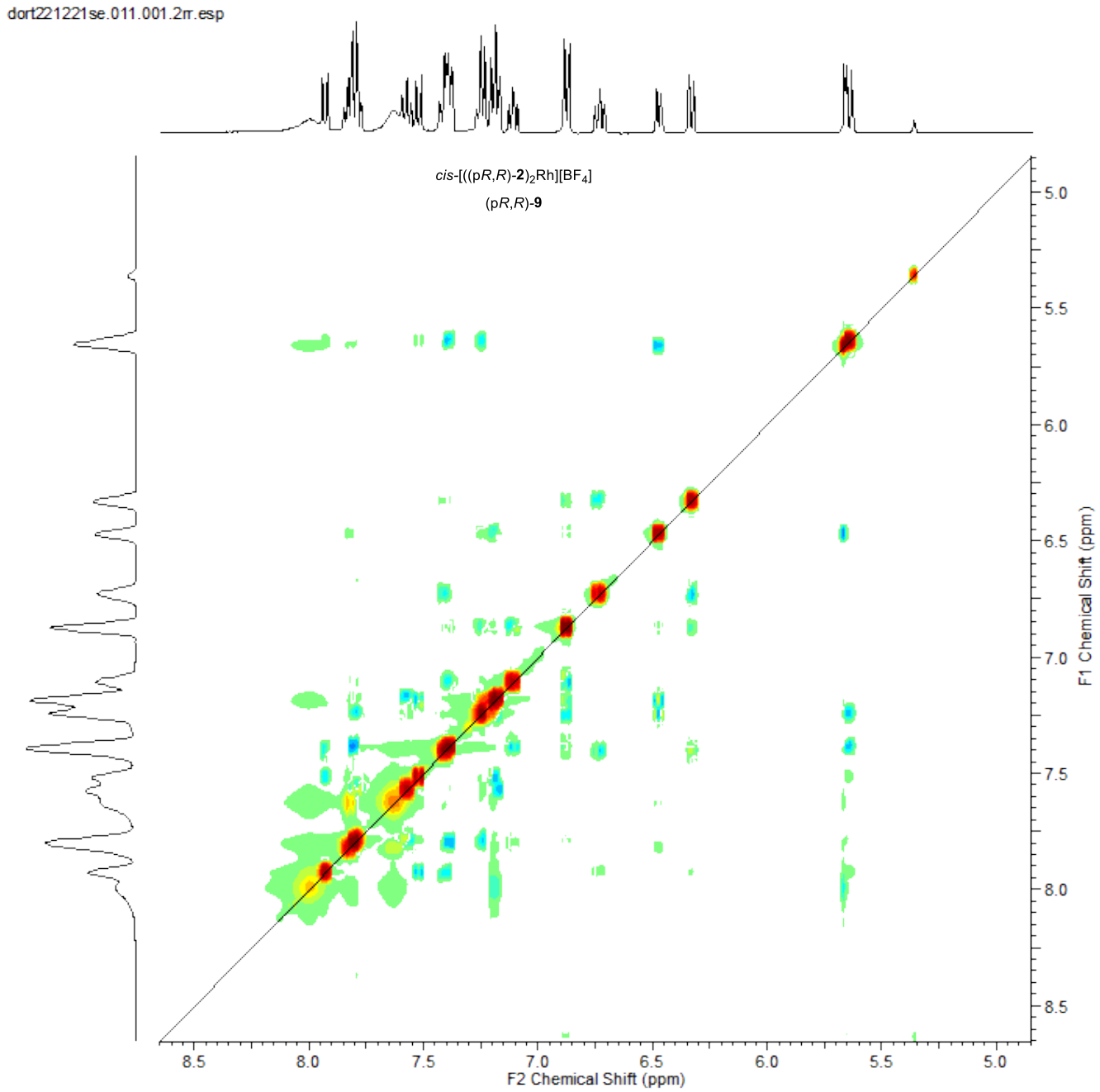

Figure S34. 2D-NOESY of complex (p*R*,*R*)-**9** in CD_2Cl_2

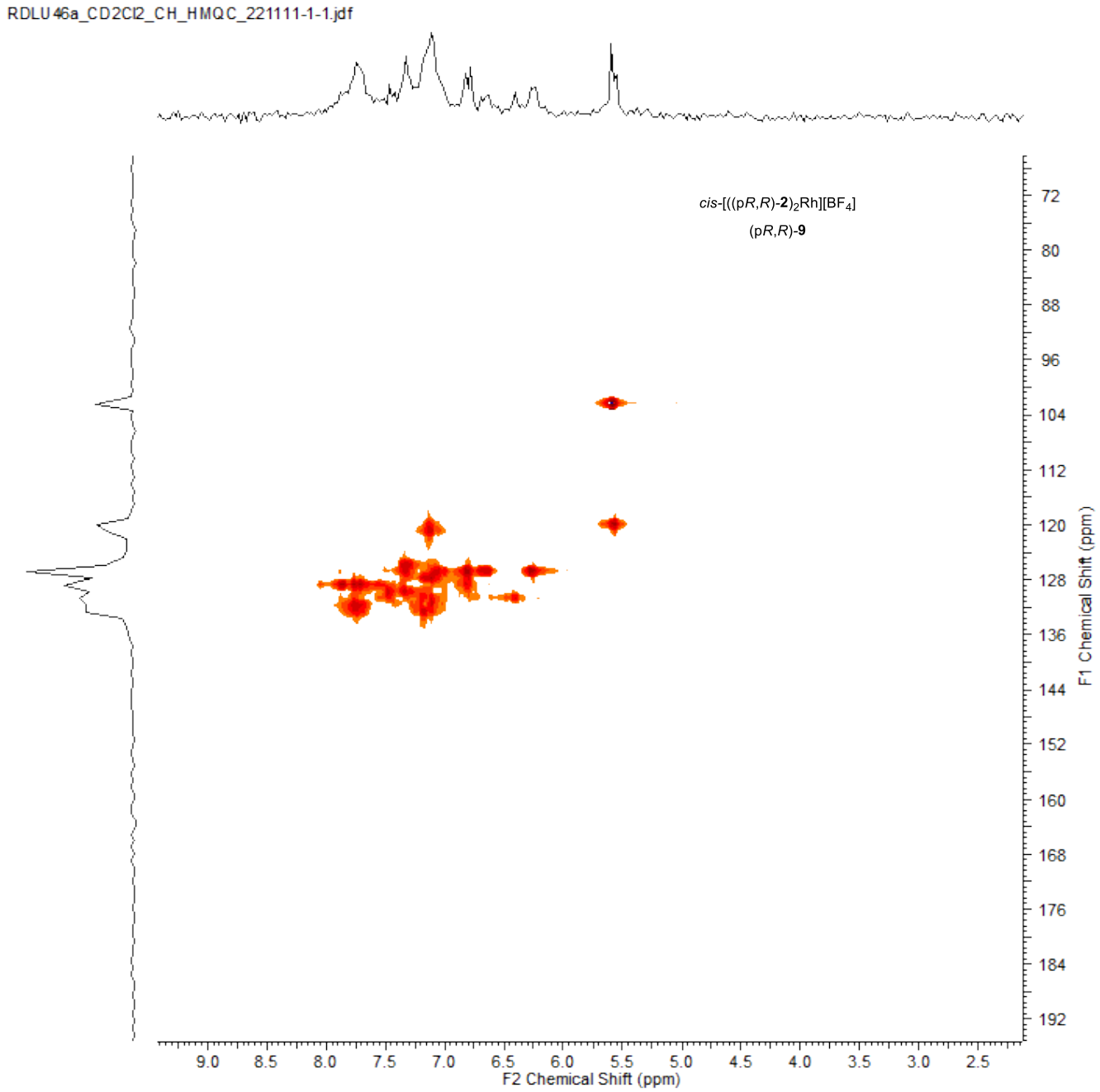

Figure S35. 2D-HMQC of complex (p*R*,*R*)-**9** in CD_2Cl_2

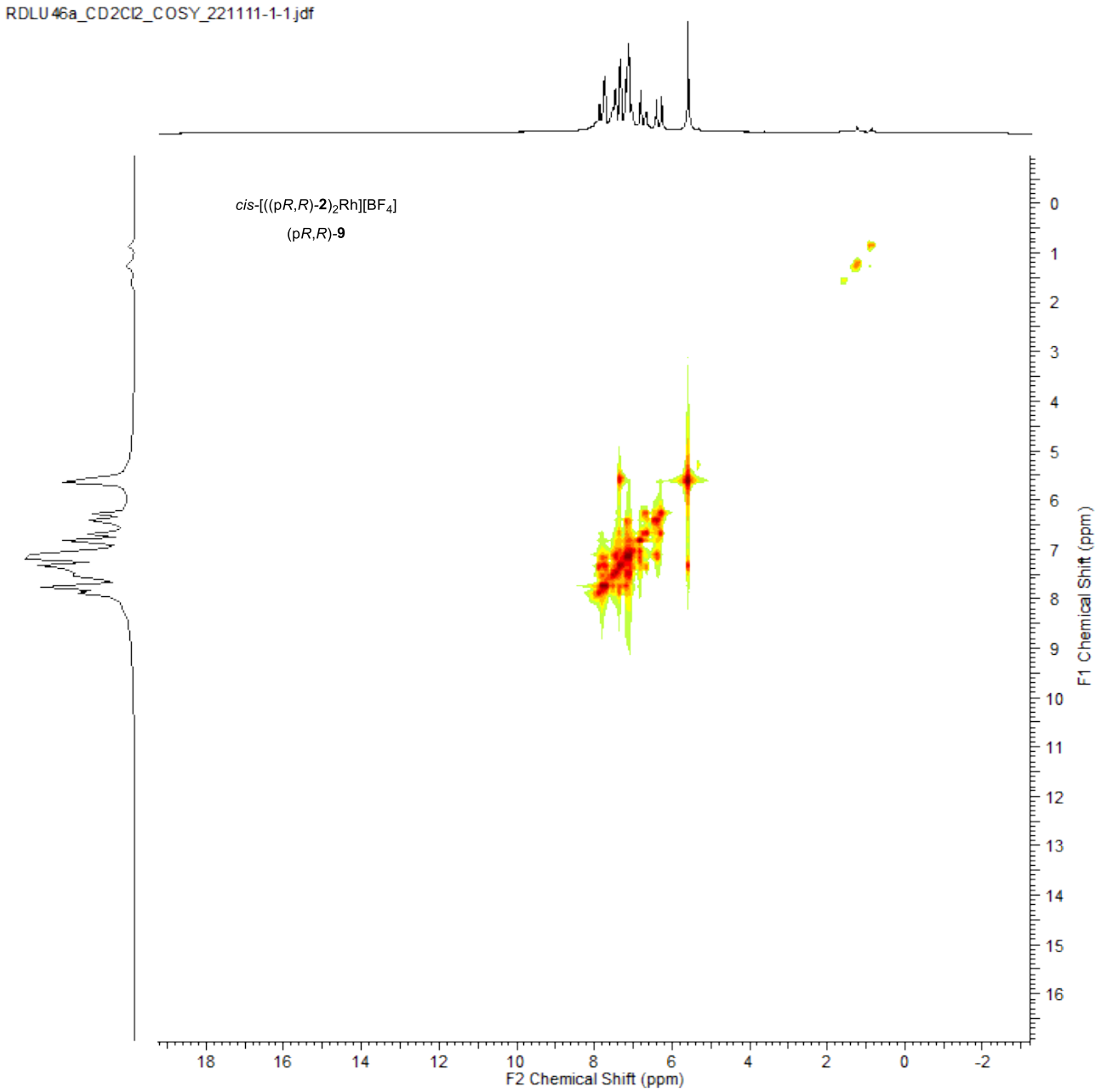

Figure S36. 2D-COSY of complex (p*R*,*R*)-**9** in CD_2Cl_2

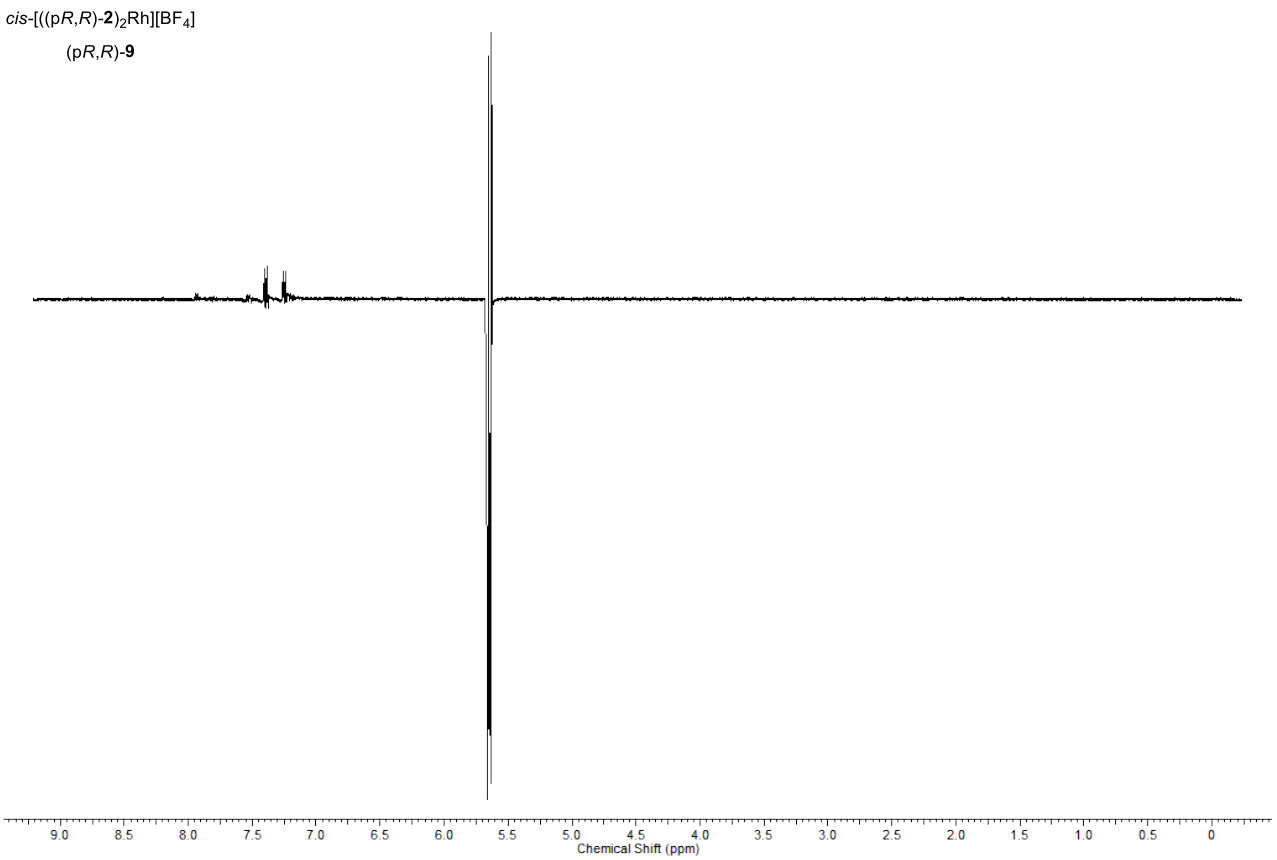

Figure S37. 1D-NOESY of complex (p*R*,*R*)-**9** in CD_2Cl_2

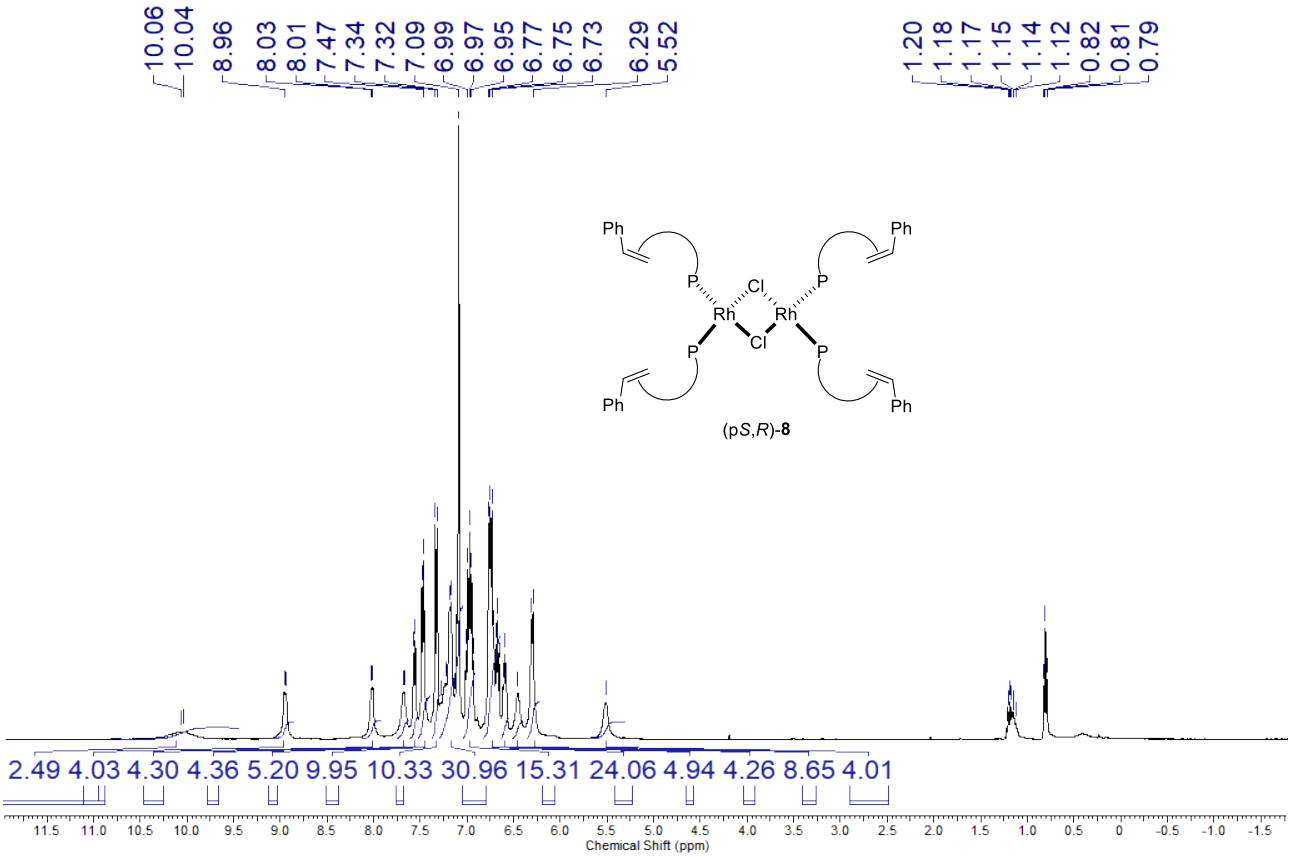

Figure S38. ^{1}H NMR of complex (p*S*,*R*)-**8** in C_6D_6

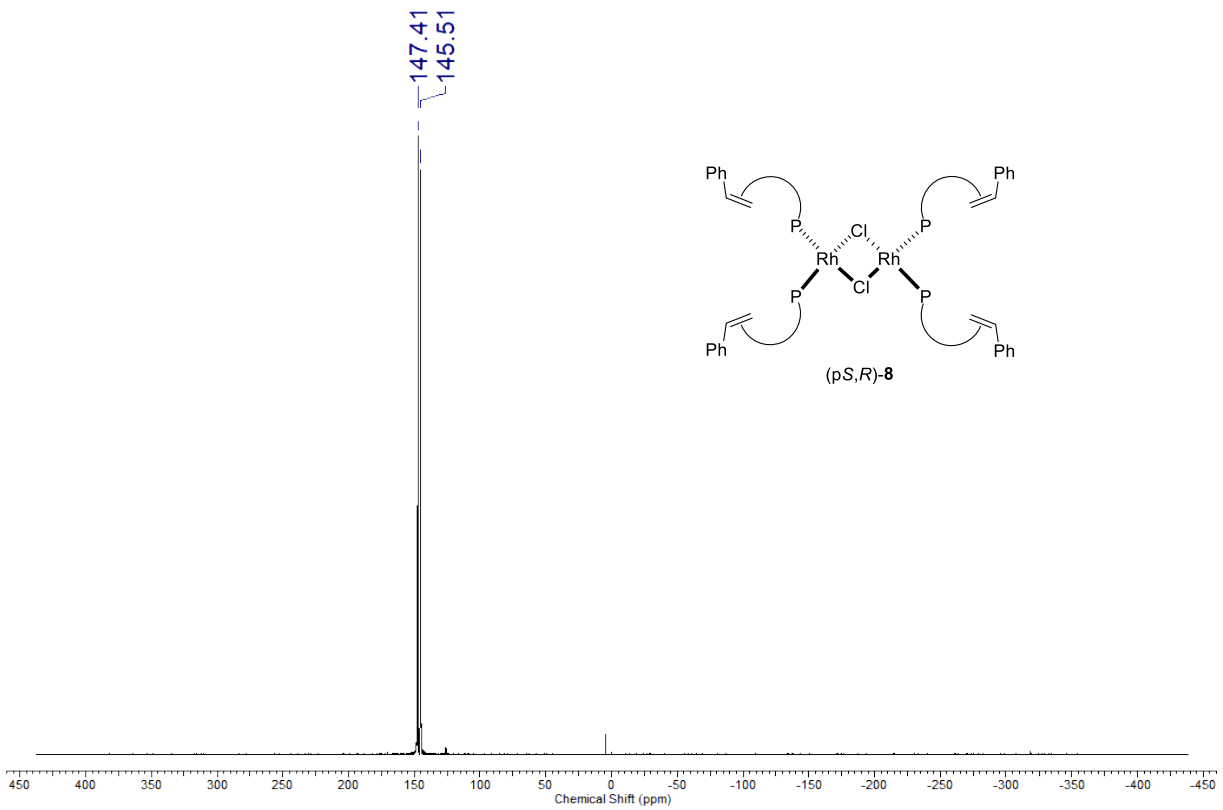

Figure S39. $^{31}P\{^{1}H\}$ NMR of complex (p*S*,*R*)-**8** in C_6D_6

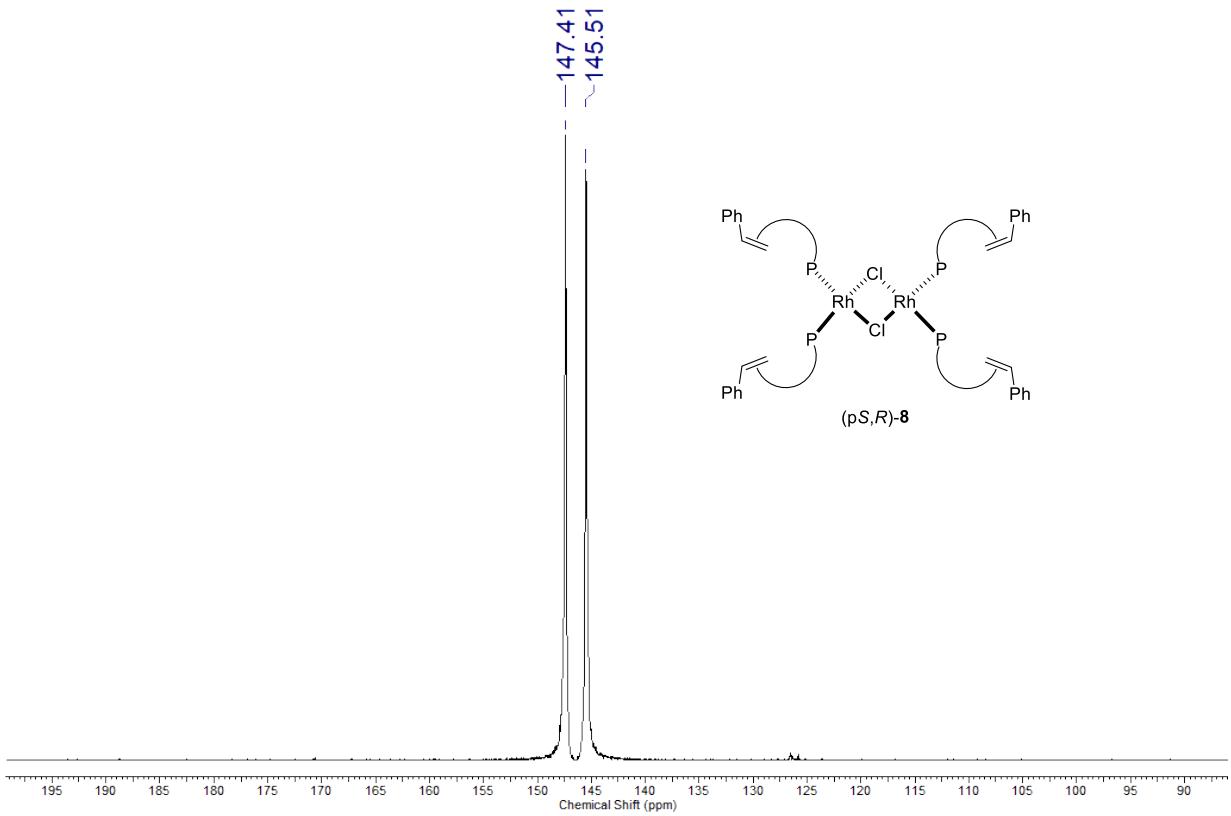

Figure S40. Zoom-in on Figure S39

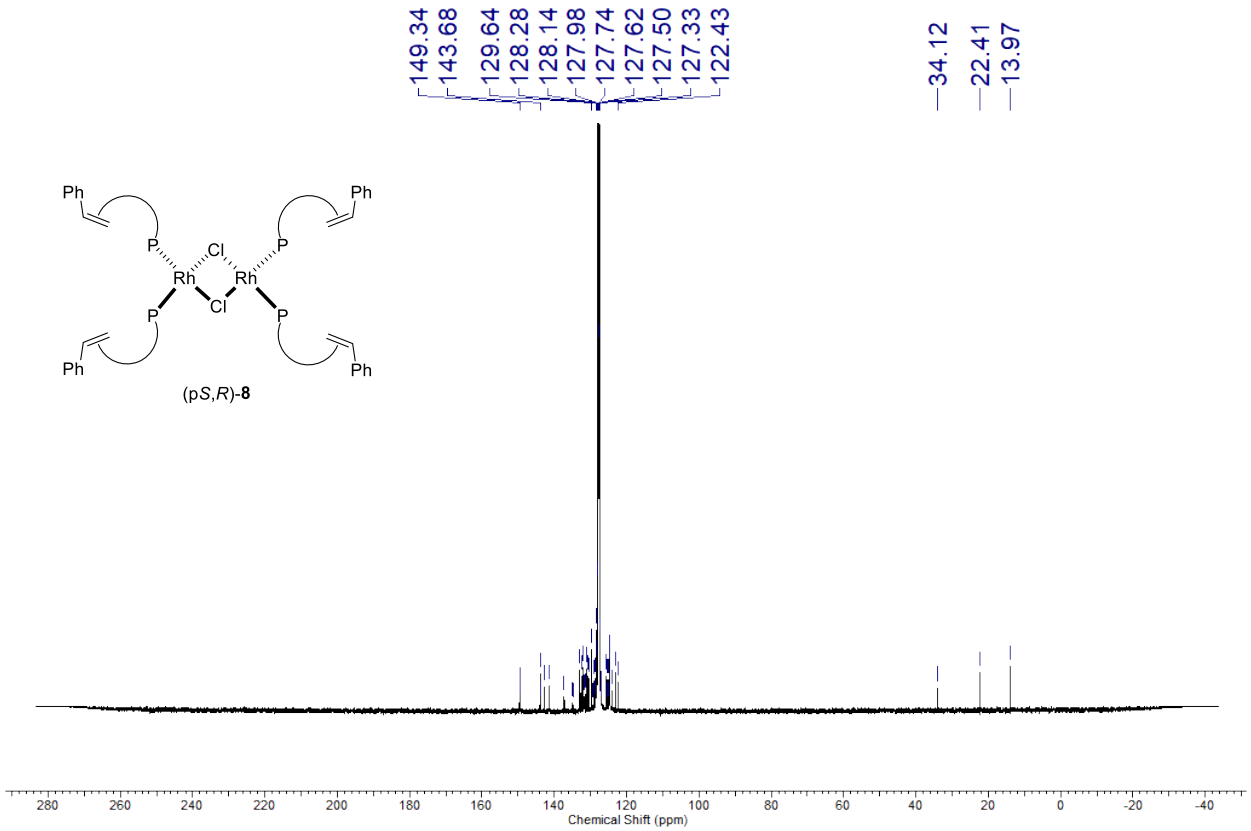

Figure S41. $^{13}C\{^{1}H\}$ NMR of complex (p*S*,*R*)-**8** in C_6D_6

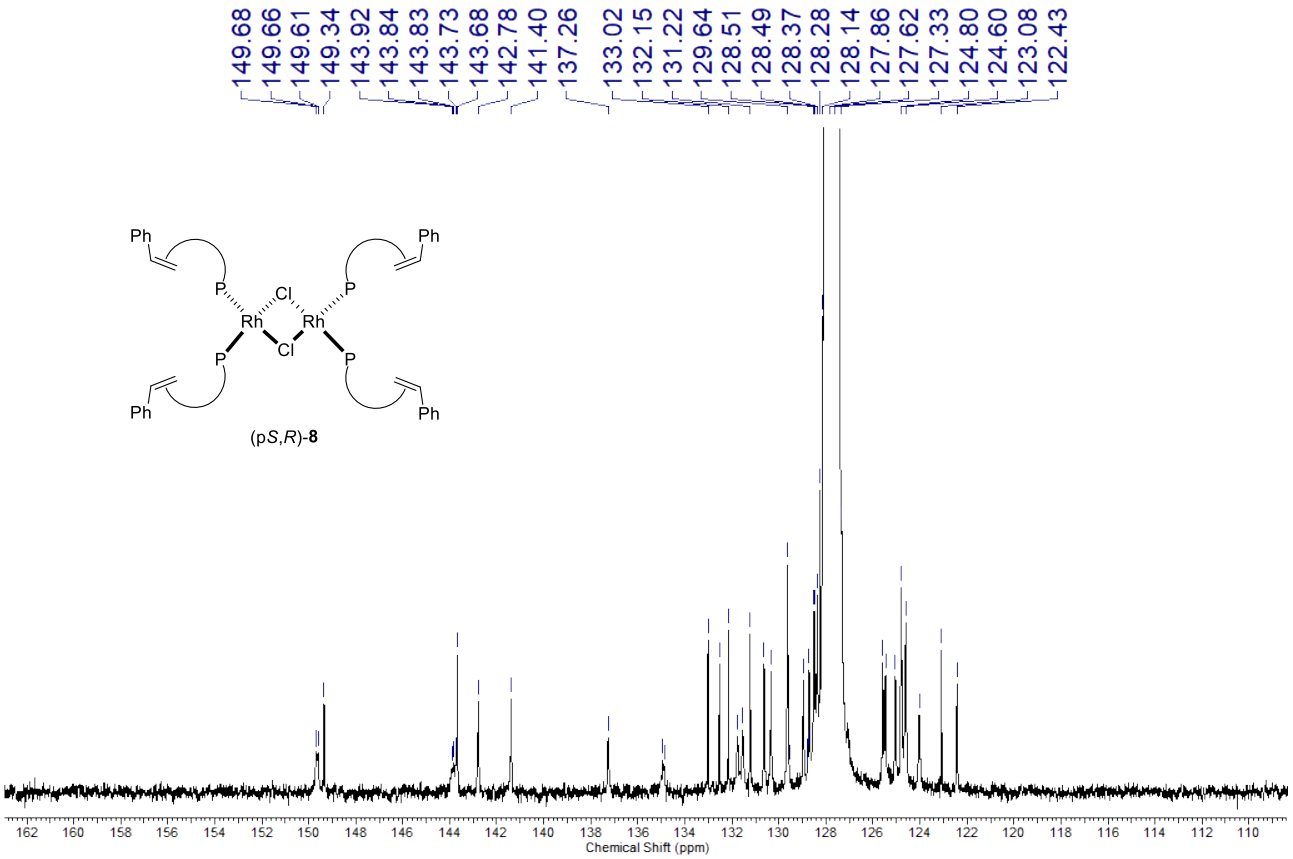

Figure S42. Zoom-in on Figure S41

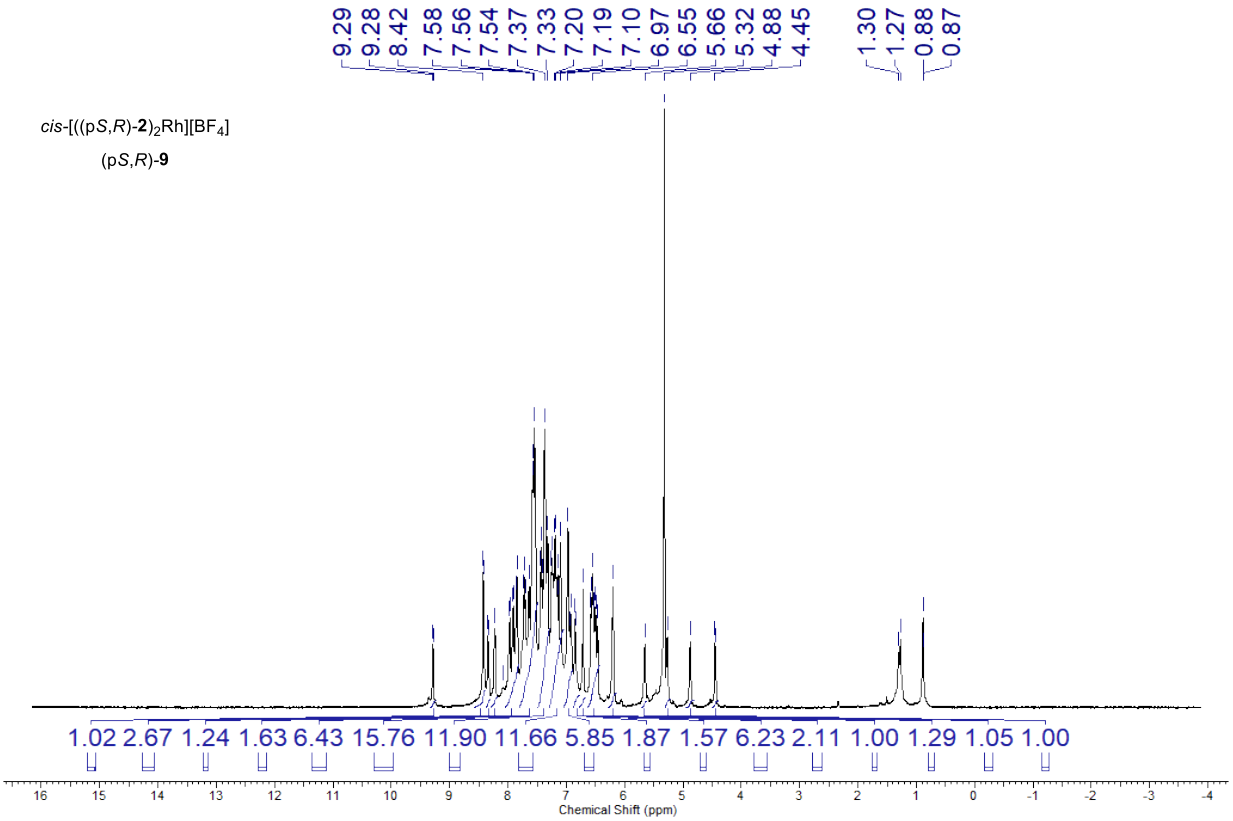

Figure S43. ^{1}H NMR of complex (p*S*,*R*)-**9** in CD_2Cl_2

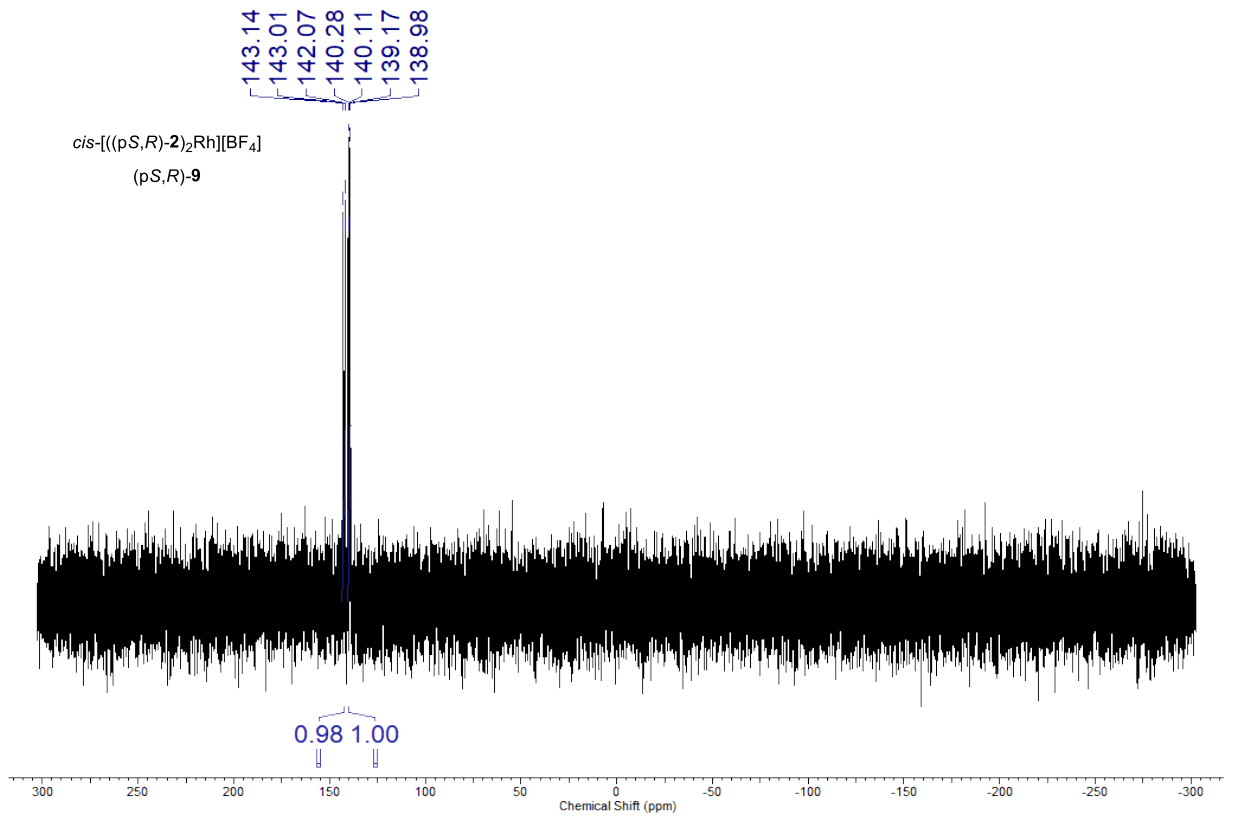

Figure S44. $^{31}P\{^{1}H\}$ NMR of complex (p*S*,*R*)-**9** in CD_2Cl_2

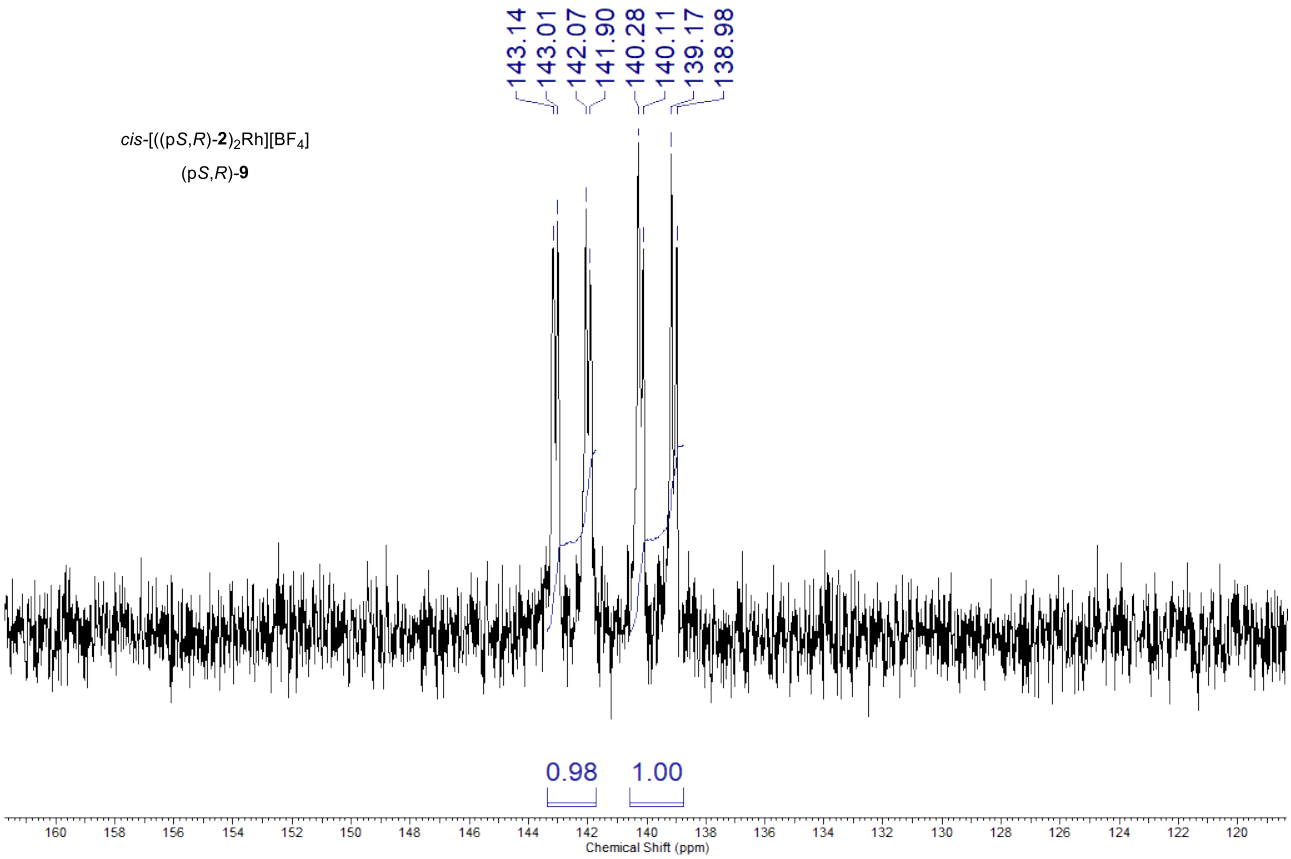

Figure S45. Zoom-in on Figure S44

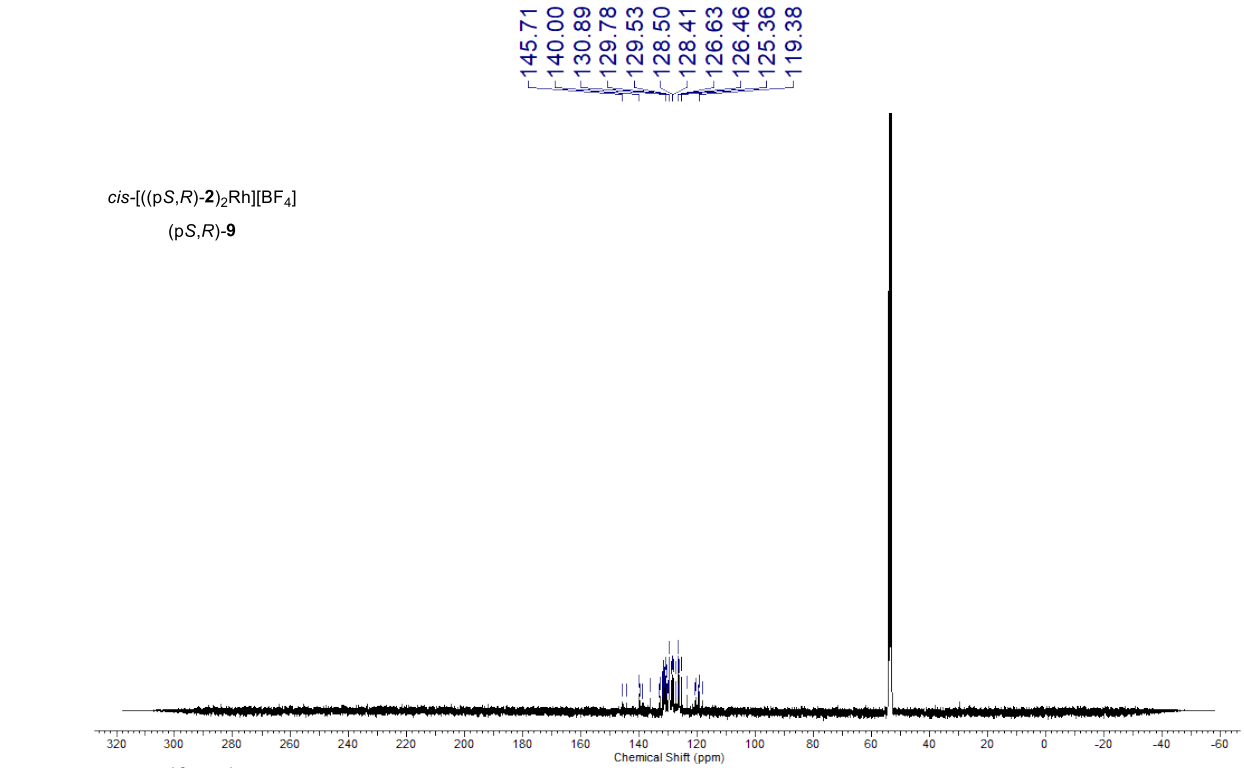

Figure S46. $^{13}C\{^{1}H\}$ NMR of complex (p*S*,*R*)-**9** in CD_2Cl_2

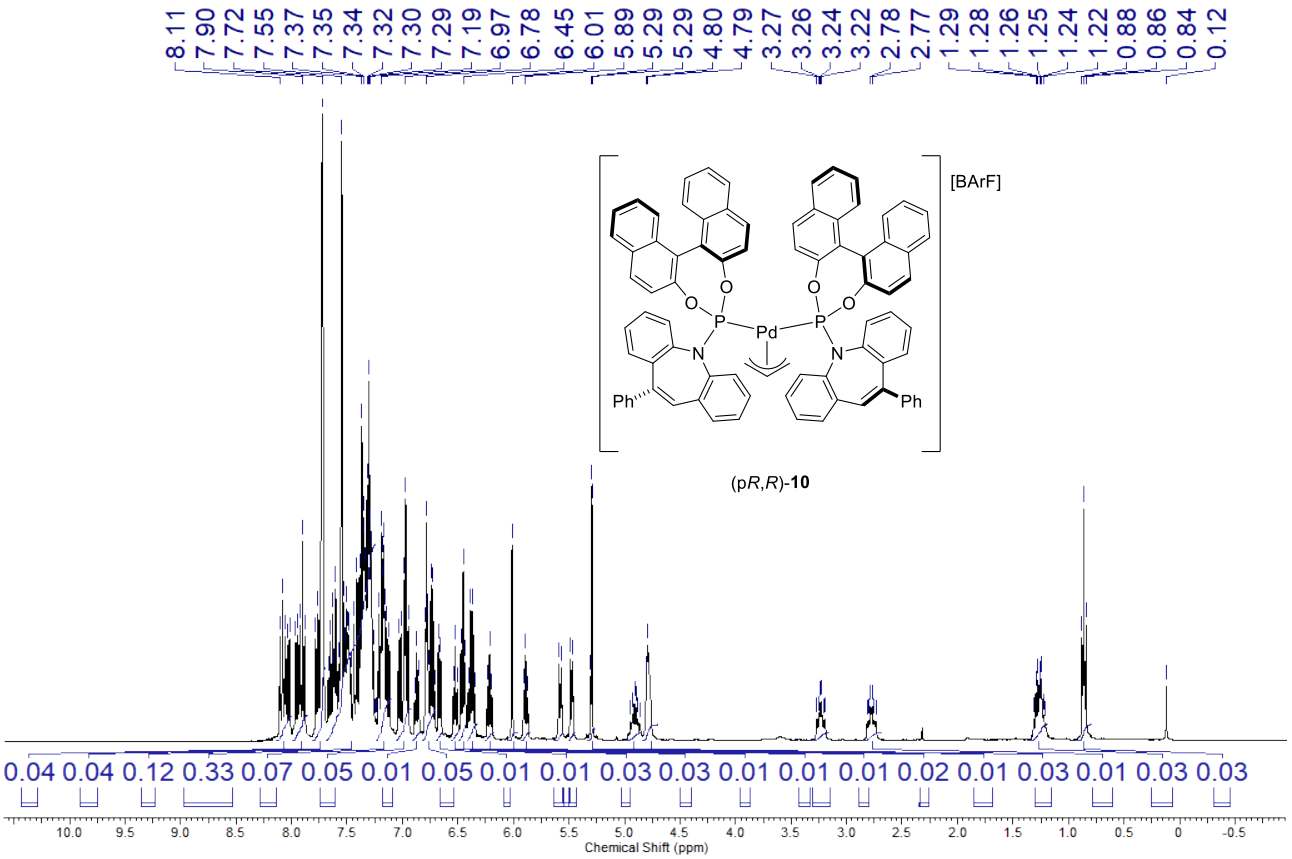

Figure S47. ^{1}H NMR of complex (p*R*,*R*)-**10** in CD_2Cl_2

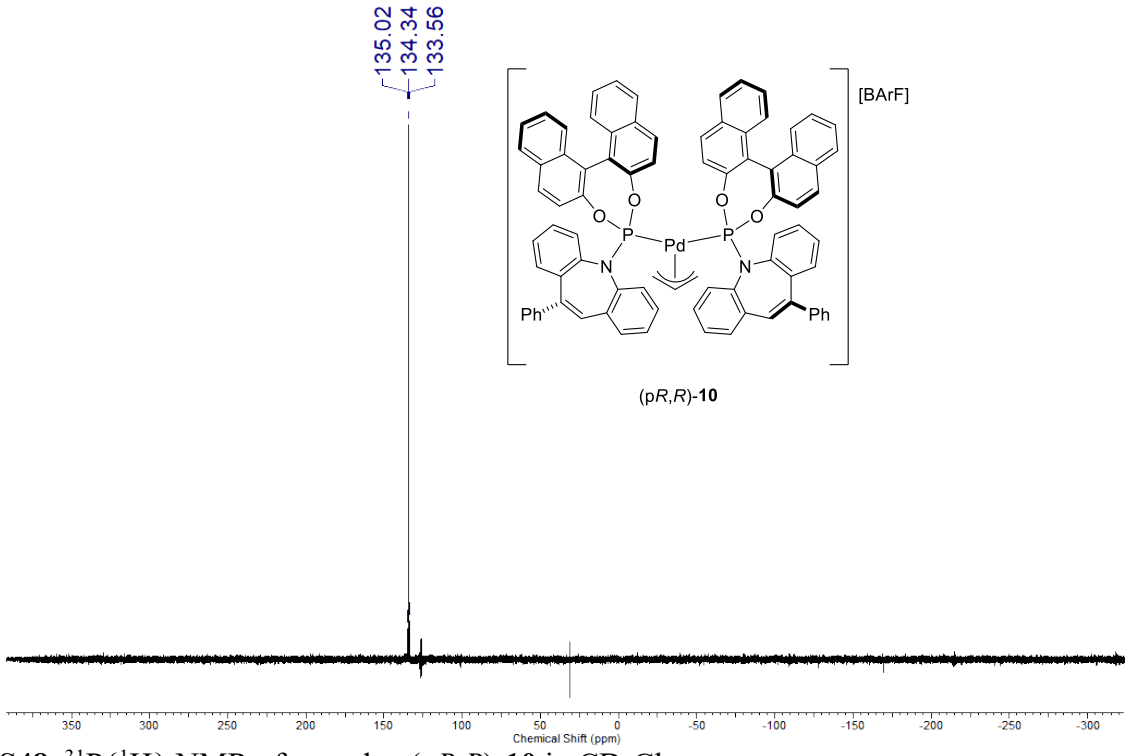

Figure S48. ^{31}P{^{1}H} NMR of complex (p*R*,*R*)-**10** in CD_2Cl_2

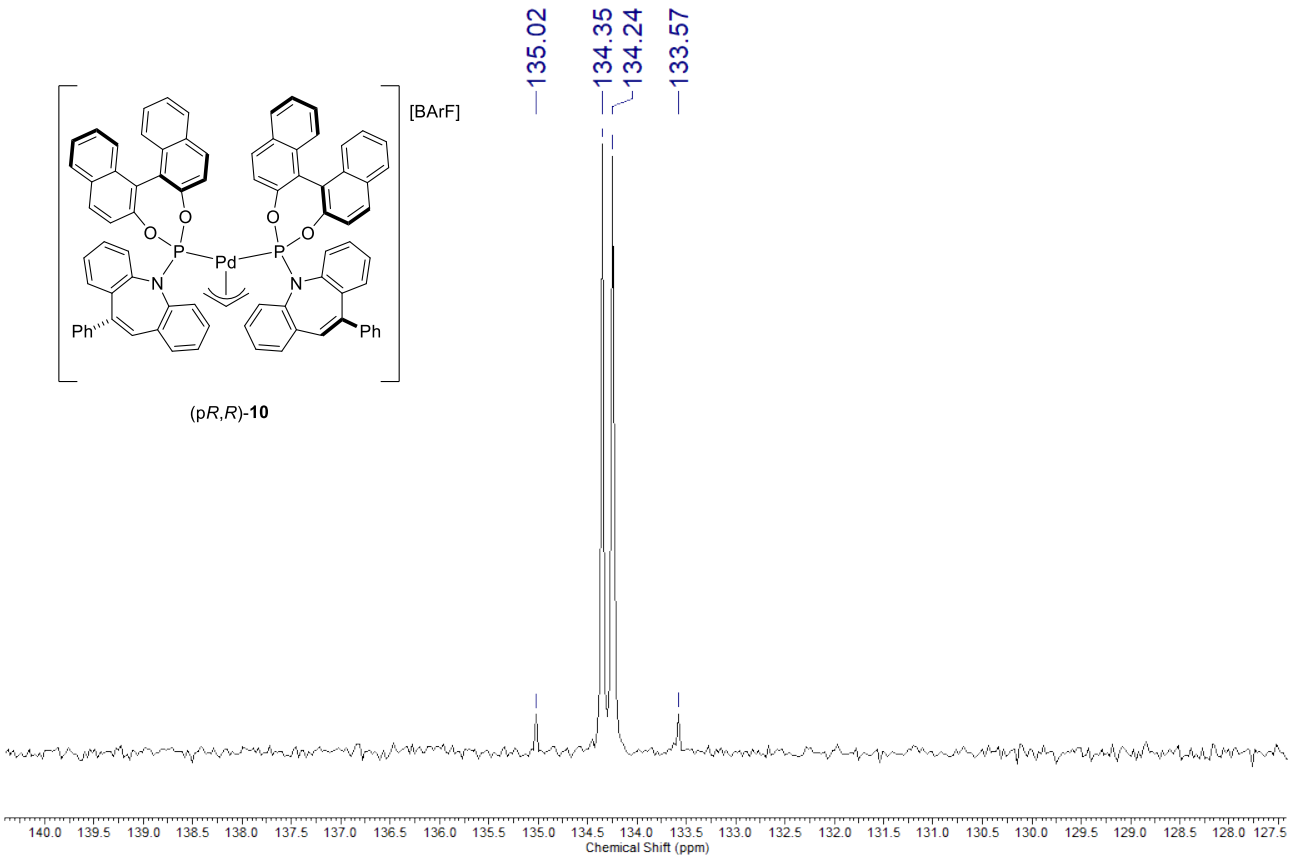

Figure S49. Zoom-in on Figure S48

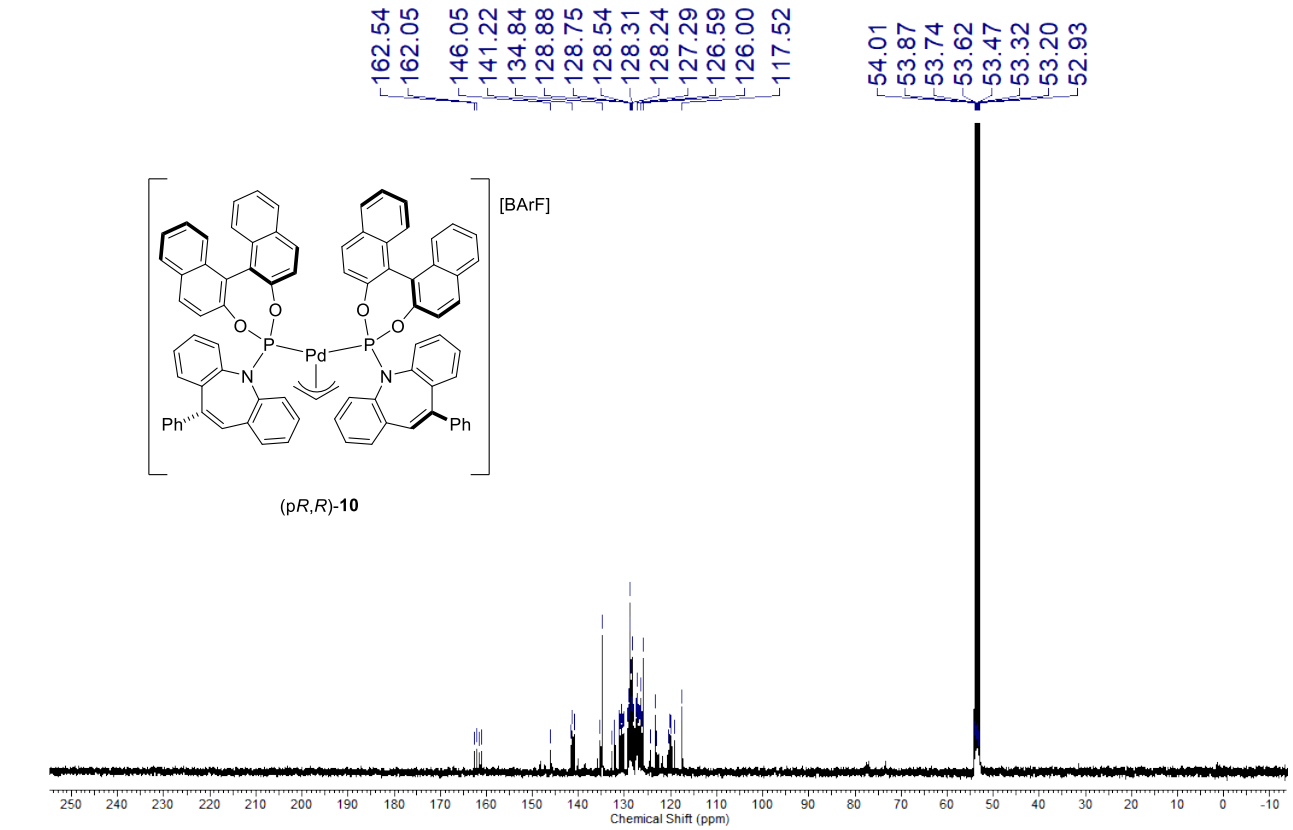

Figure S50. $^{13}C\{^{1}H\}$ NMR of complex (p*R*,*R*)-**10** in CD_2Cl_2

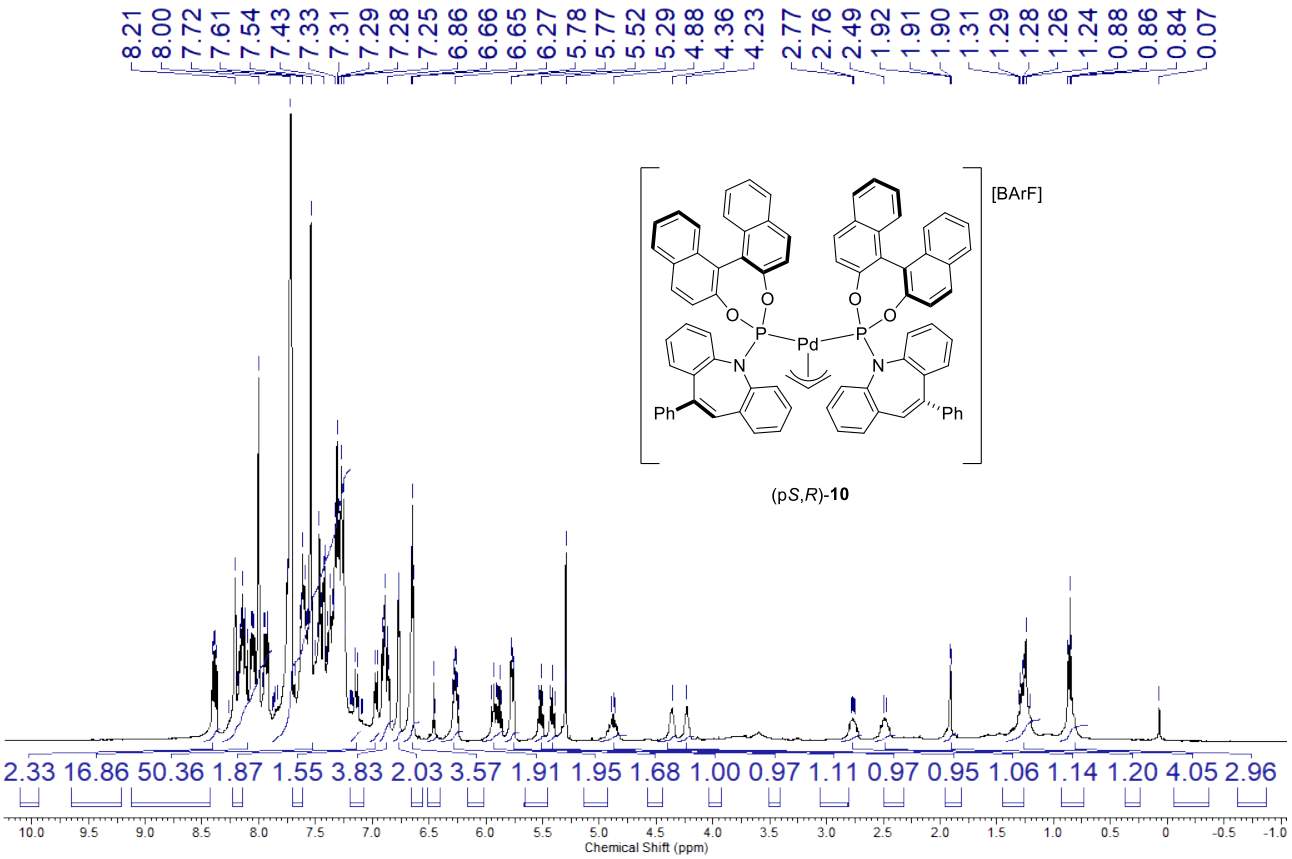

Figure S51. ^{1}H NMR of complex (p*S*,*R*)-**10** in CD_2Cl_2

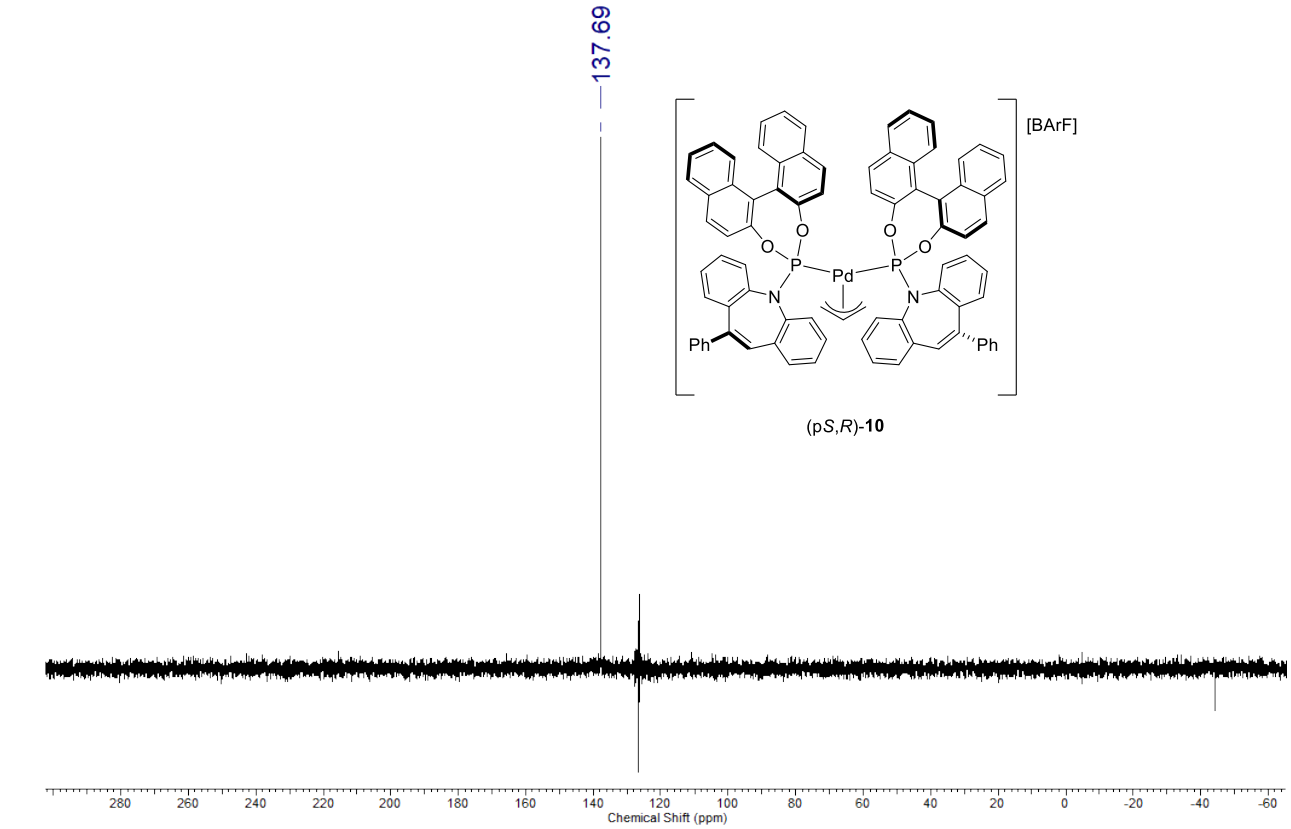

Figure S52. ^{31}P{^{1}H} NMR of complex (p*S*,*R*)-**10** in CD_2Cl_2

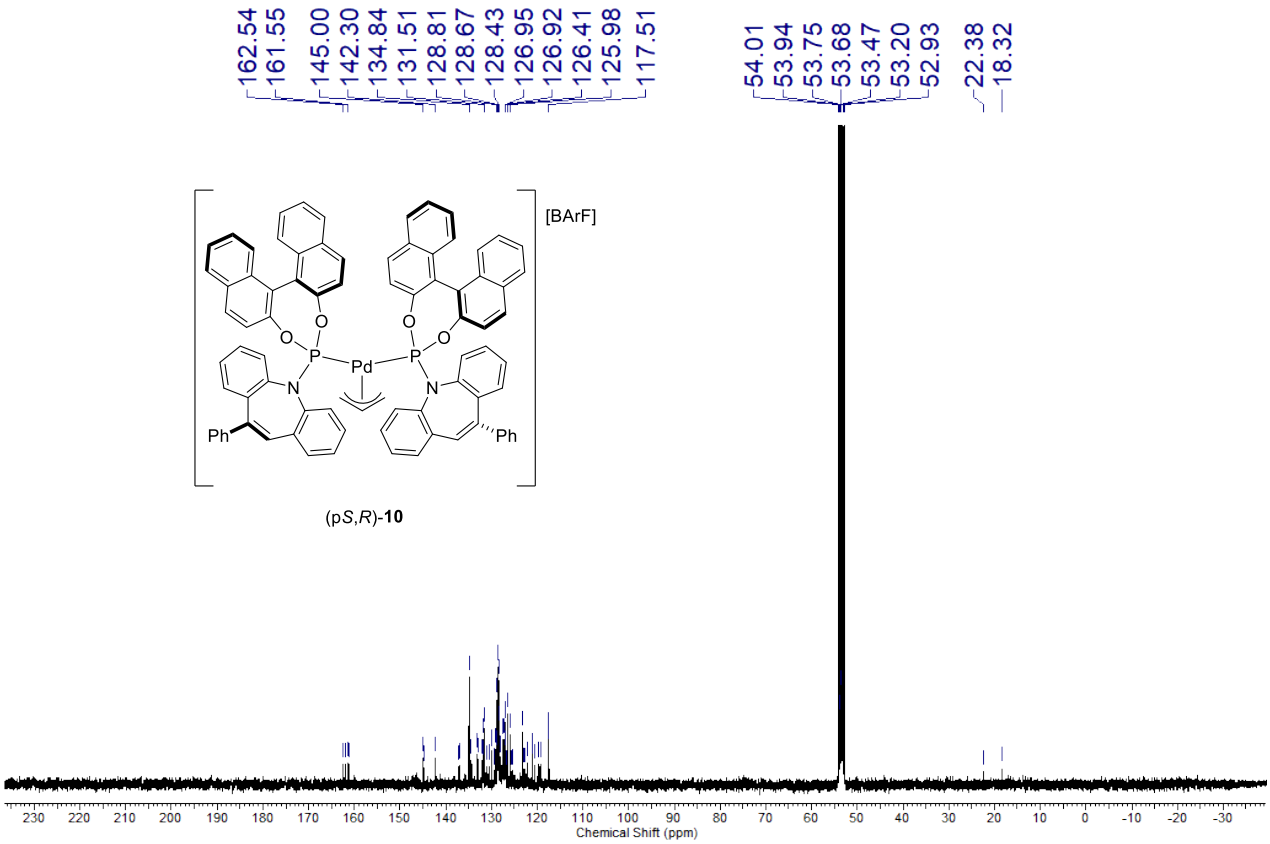

Figure S53. $^{13}C\{^{1}H\}$ NMR of complex (p*S*,*R*)-**10** in CD_2Cl_2

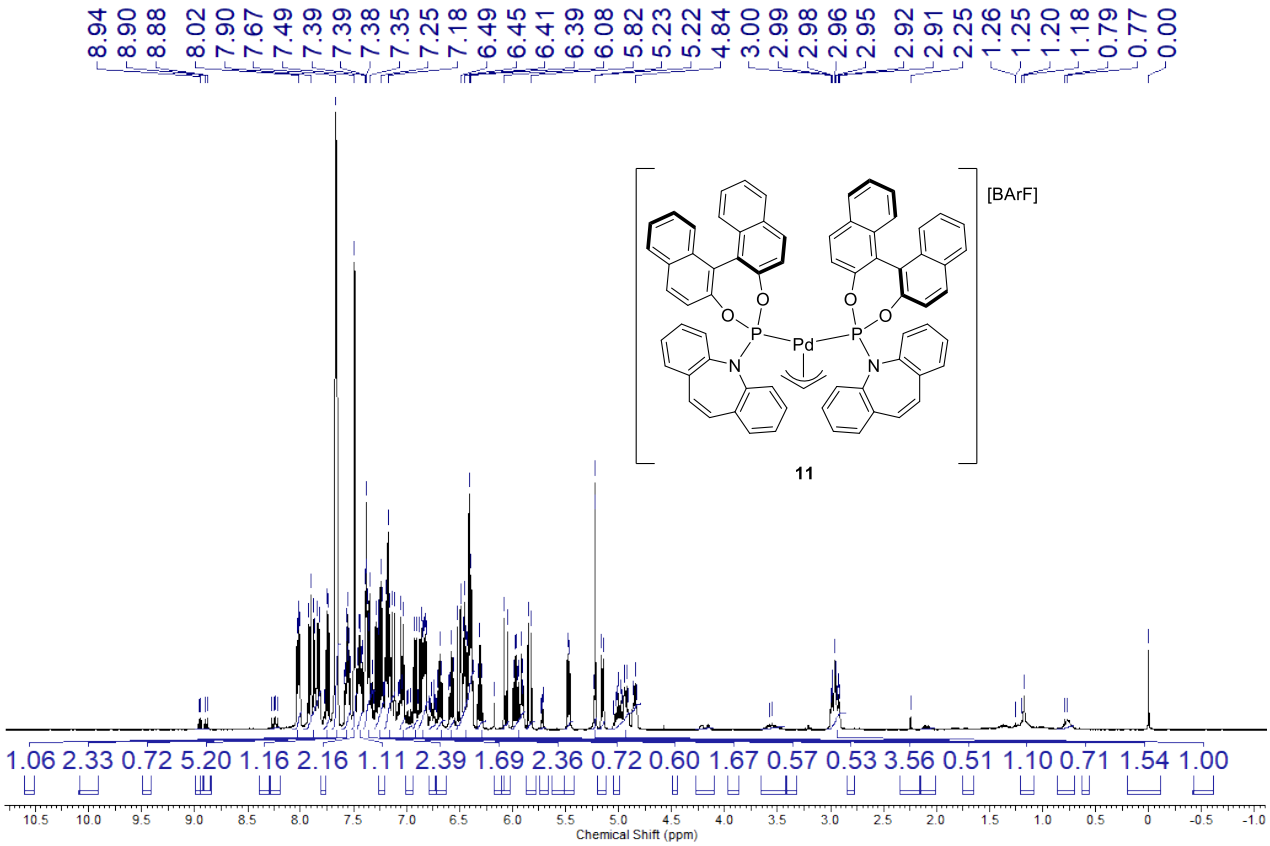

Figure S54. ^{1}H NMR of complex (*S*)-**11** in CD_2Cl_2

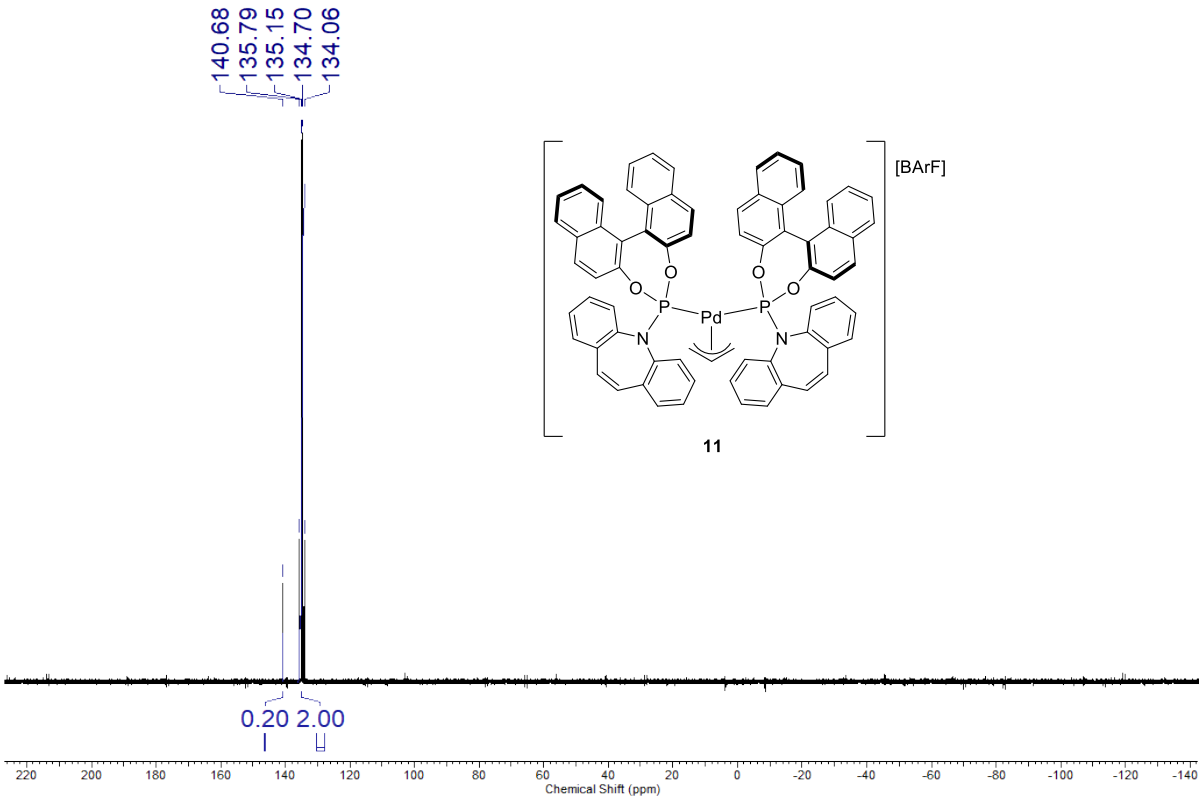

Figure S55. $^{31}P\{^{1}H\}$ NMR of complex (*S*)-**11** in CD_2Cl_2

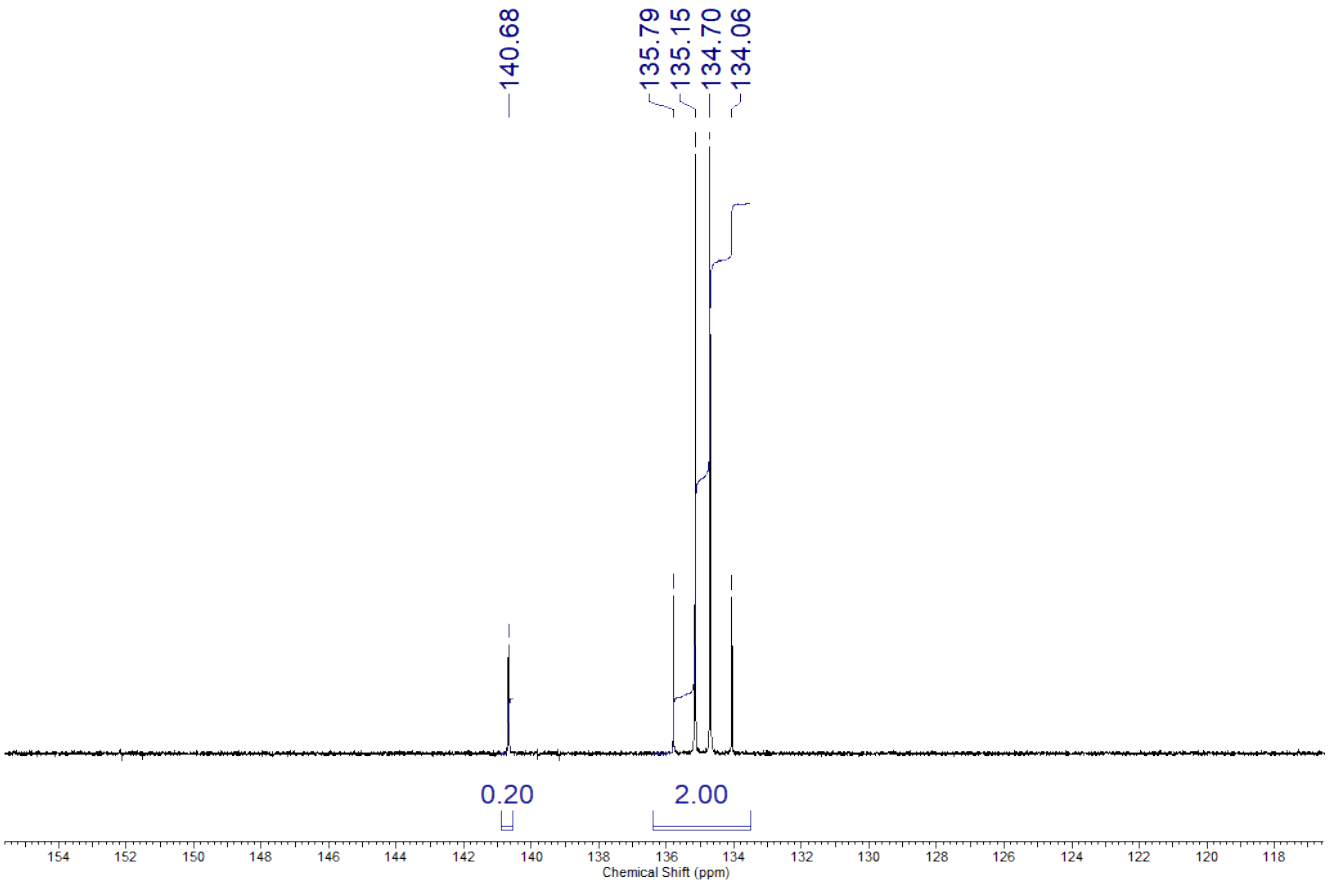

Figure S56. Zoom-in on Figure S55

4. Catalytic reactions and HPLC traces

Rh catalyzed addition of $PhB(OH)_2$ to cyclohexenone

Method A. Inside a glovebox, the Rh catalyst (0.0096 mmol, 0.02 equiv) was combined with boronic nucleophile (0.75 mmol, 1.5 equiv.) in a 20 mL vial. Dioxane (1.0 mL), enone (0.50 mmol, 1 equiv) and degassed aqueous KOH solution (1.0 M, 0.25 mL, 0.5 equiv) were added. The reaction mixture was stirred at 50 °C for 48 h. The vial was taken out of the glovebox. The reaction mixture was diluted in Et_2O (10 mL) and washed with water (3 x 10 mL). The aqueous phase was extracted with Et_2O (10 mL). The combined organic phases were dried over $MgSO_4$ and all volatiles were removed under reduced pressure. The product was purified by flash column chromatography. Enantiomeric excess was determined from the purified product by chiral stationary HPLC.[15]

Method B. In the glovebox, a vial was loaded with Rh catalyst (0.0083 mmol, 0.02 equiv), boronic nucleophile (0.830 mmol, 2 equiv) and solid K_3PO_4 (0.207 mmol, 0.5 equiv). Enone (0.415 mmol, 1 equiv) was dissolved in toluene (2 mL) and added to the reaction mixture. Finally, H_2O (0.2 mL) was added *via* syringe. The reaction mixture was stirred for 24 h at 40 °C, then taken out of the glove box, diluted with Et_2O (15 mL), washed with H_2O (3 x 20 mL), and the aqueous phase extracted with Et_2O (20 mL). The combined organic phases were dried over $MgSO_4$, filtered, the volatiles removed under reduced pressure, and the product purified by flash column chromatography. Enantiomeric excess was determined by chiral stationary HPLC.

3-(4-Methylphenyl)cyclohexanone 14aa: The product was purified with flash column chromatography (Hexane/EtOAc 12:1) and obtained as a yellowish oil Chiral stationary HPLC: Chiracel AD-H, hexane/isopropanol 95:5, $t_{(S)}$ = 9.0 min, $t_{(R)}$ = 9.5 min. ^{1}H NMR ($CDCl_3$, 600 MHz, δ): 7.41 – 7.31 (m, 2H), 7.15 – 7.11 (m, 7H), 6.97 – 6.94 (m, 1H), 6.85 – 6.70 (m, 2H), 3.00 – 2.96 (m, 1H), 2.59 – 2.44 (m, 4H), 2.33 (s, 3H), 2.16 – 2.05 (m, 3H), 1.84 – 1.76 (m, 3H).

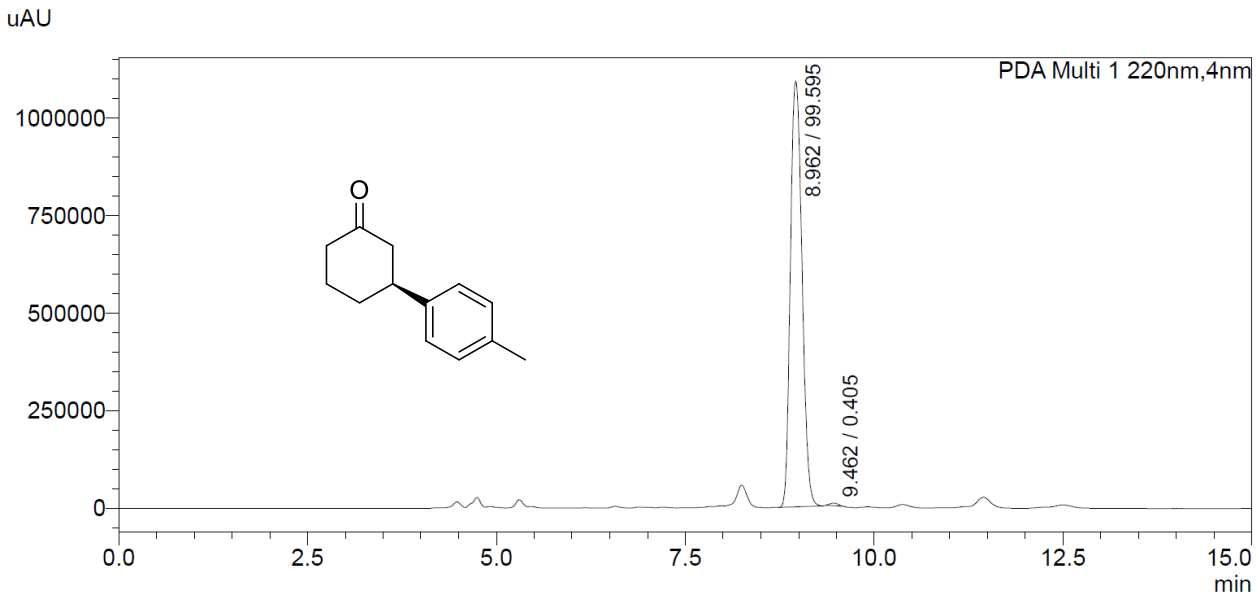

Figure S56. HPLC trace entry 1, Table 1: Chiracel AD-H; Hexane/Isopropanol 95:5; flow = 0.5 mL/min

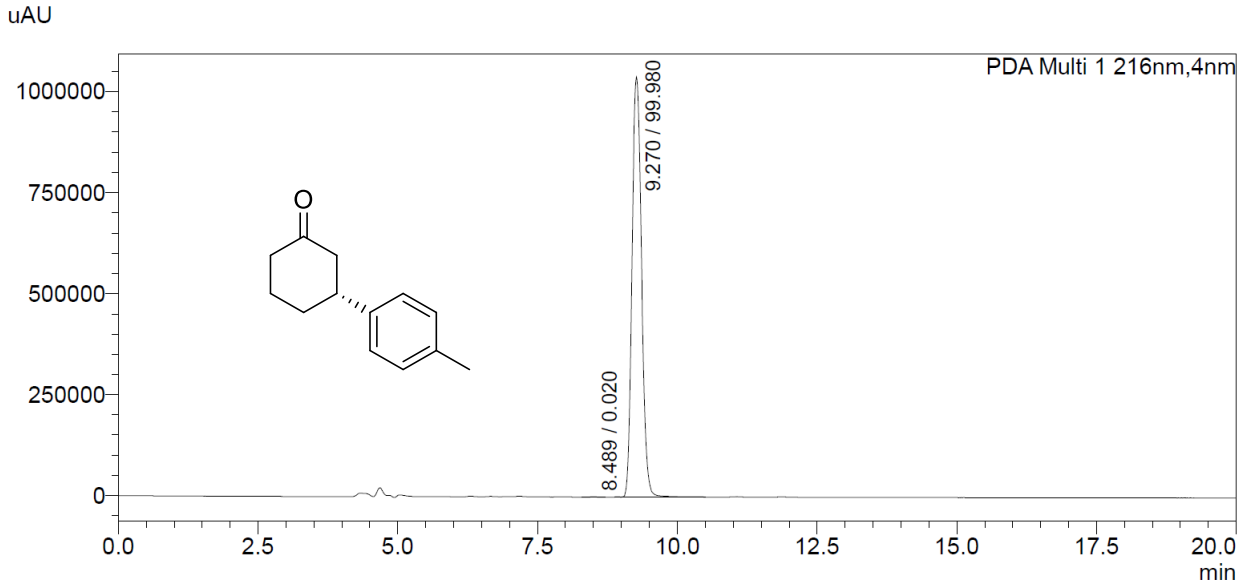

Figure S57. HPLC trace entry 2, Table 1: Chiracel AD-H; Hexane/Isopropanol 95:5; flow = 0.5 mL/min

3-Phenylcyclohexanone 14ab: The product was purified by flash column chromatography (Hexane/EtOAc 9:1) and obtained as a colorless oil. Chiral stationary HPLC (Chiracel AD-H; Hexane/Isopropanol 98:2; flow = 0.5 mL/min; $t_{(S)}$ = 16.71 min; $t_{(R)}$ = 19.50 min, Chiracel OD-H

Hexane/Isopropanol 98:2; flow = 0.5 mL/min; $t_{(S)}$ = 24.39 min; $t_{(R)}$ = 26.37 min). ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 7.61–7.42 (m, 1H), 7.38–7.31 (m, 2H), 7.24–7.17 (m, 3H), 3.51–3.45 (q, 0.3H), 3.19–3.12 (tt, 0.2H), 3.05–2.97 (tt, 1H), 2.63–2.58 (m, 1H), 2.55–2.53 (m, 1H), 2.50–2.44 (m, 1H), 2.42–2.34 (m, 1H), 2.16–2.05 (m, 2H), 1.93–1.87 (m, 1H), 1.85–1.79 (m, 2H).

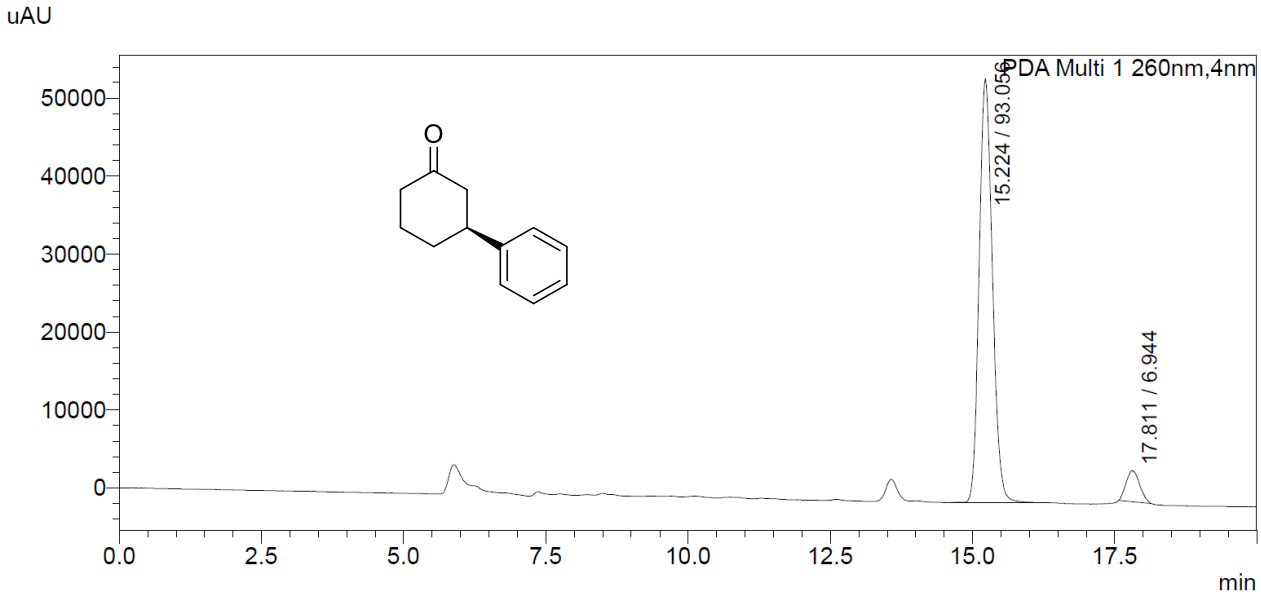

Figure S58. HPLC trace entry 3, Table 1: Chiracel AD-H; Hexane/Isopropanol 98:2; flow = 0.5 mL/min

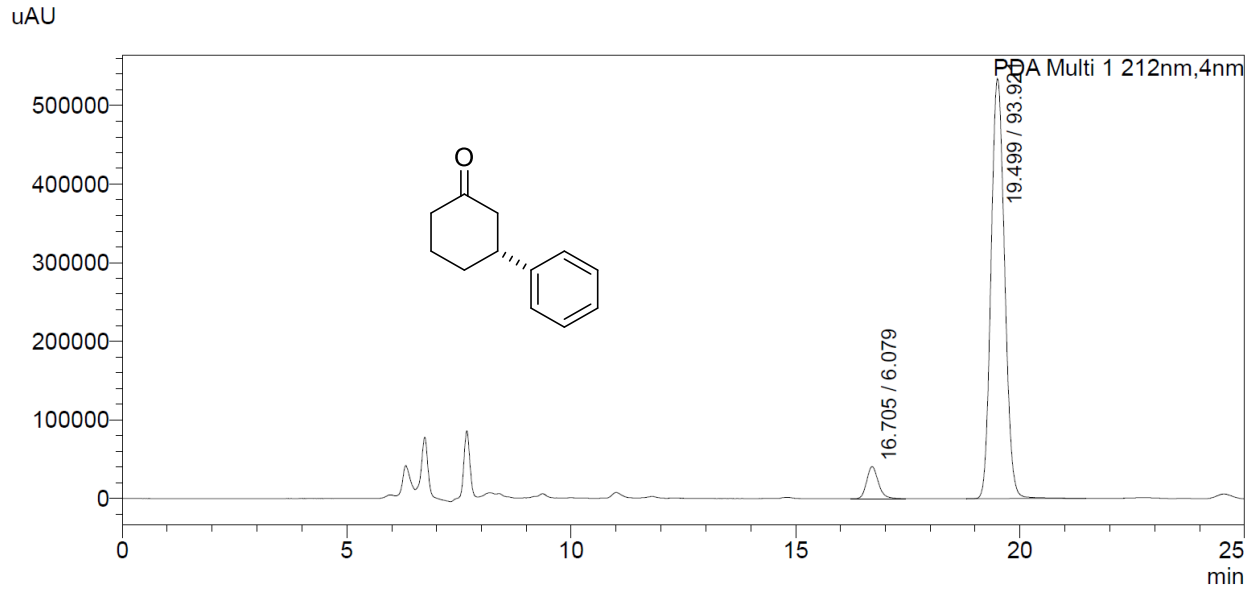

Figure S59. HPLC trace entry 4, Table 1: Chiracel OD-H; Hexane/Isopropanol 98:2; flow = 0.5 mL/min

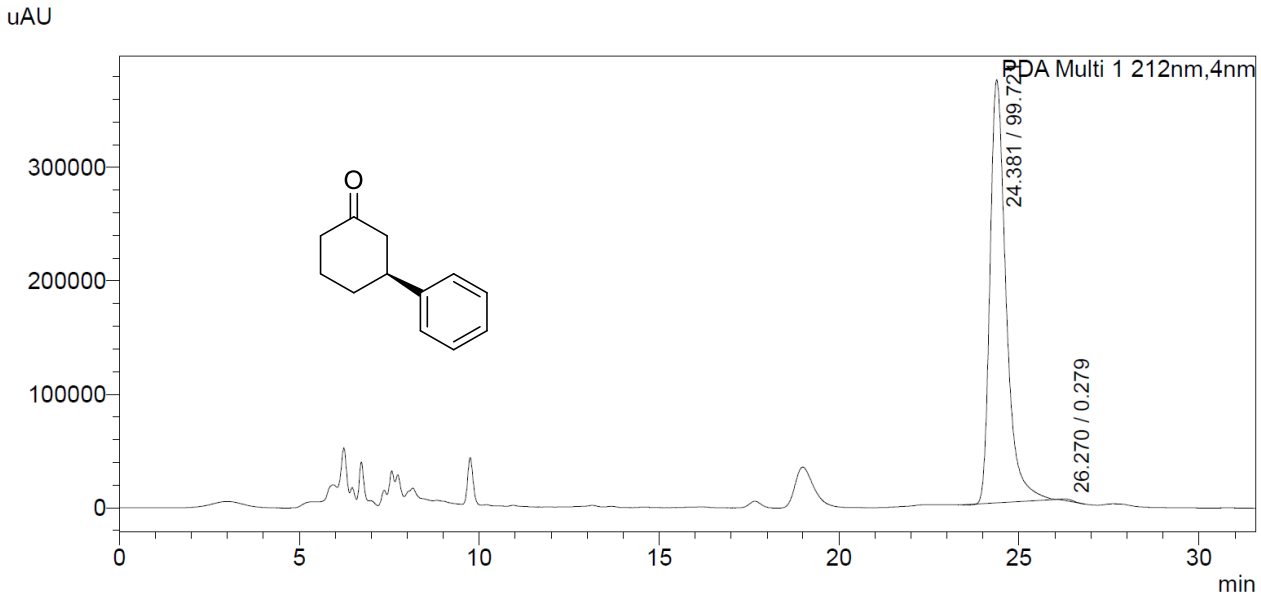

Figure S60. HPLC trace entry 5, Table 1: Chiracel OD-H; Hexane/Isopropanol 98:2; flow = 0.5 mL/min

4-Phenyl-2-octanone 14bb: The product was purified by flash column chromatography (hexane/EtOAc 9:1) and obtained as a yellowish oil. Chiral stationary HPLC: Chiracel OD-H, hexane/*i*-PrOH 98:2, $t_{(S)}$ = 13.013 min, $t_{(R)}$ = 13.437 min. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 7.30–7.28 (m, 1H), 7.20–7.16 (m, 3H), 3.12–3.06 (m, 1H), 2.72–2.70 (d, 2H), 2.01 (s, 3H), 1.67–1.53 (m, 3H), 1.39–1.32 (m, 3H), 0.81 (t, 3H).

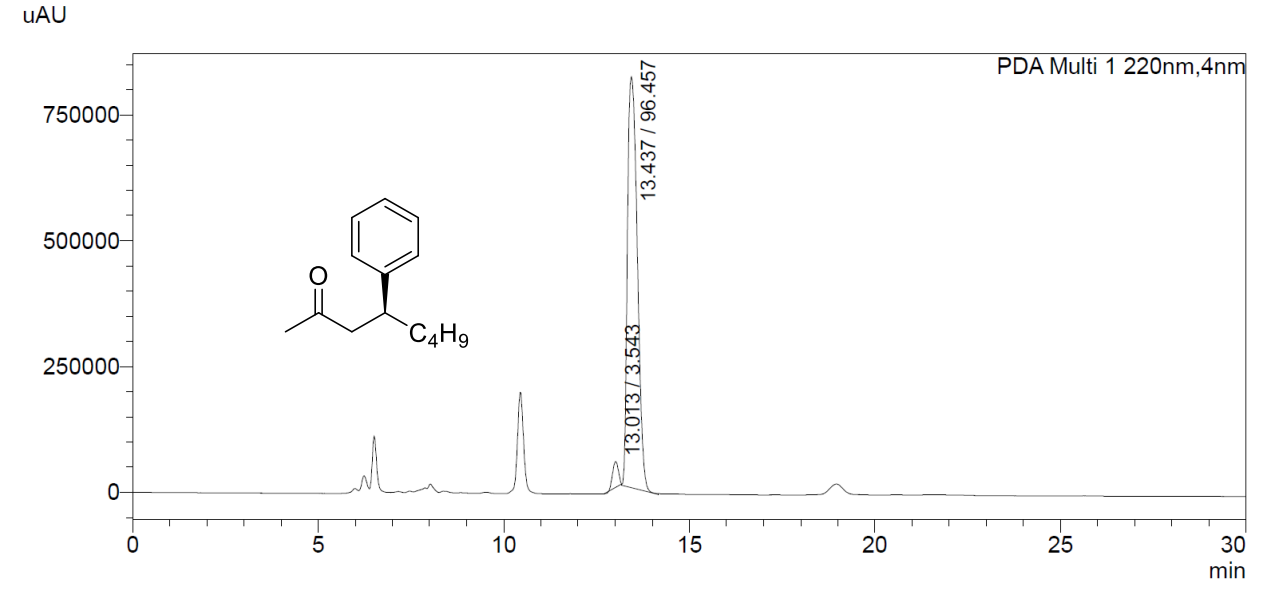

Figure S61. HPLC trace entry 6, Table 1: Chiracel OD-H; Hexane/Isopropanol 98:2; flow = 0.5 mL/min

Pd catalyzed allylic alkylation

Inside a glovebox, a solution of cationic Pd complex (24 mg, 0.01 mmol) in 0.5 mL CH_2Cl_2 was added to a stirring slurry of 1,3-diphenylallyl acetate **16** (190 mg, 0.75 mmol), indole **15** (88 mg, 0.75 mmol) and $CsCO_3$ (488 mg, 1.50 mmol) in 3 mL 1,2-difluorobenzene. The resulting brownish slurry was stirred for 72 h at 40 °C and then evacuated to dryness and purified by flash column chromatography.

[1,3-Diphenyl-2-propen-1-yl]-1*H*-indole 17a: The product was purified by flash column chromatography (Hexane/EtOAc 95:5) and obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.80 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.03 (m, 12H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.74 – 6.57 (m, 1H), 6.40 (s, 1H), 6.36 (s, 1H), 5.05 (d, *J* = 7.4 Hz, 1H).

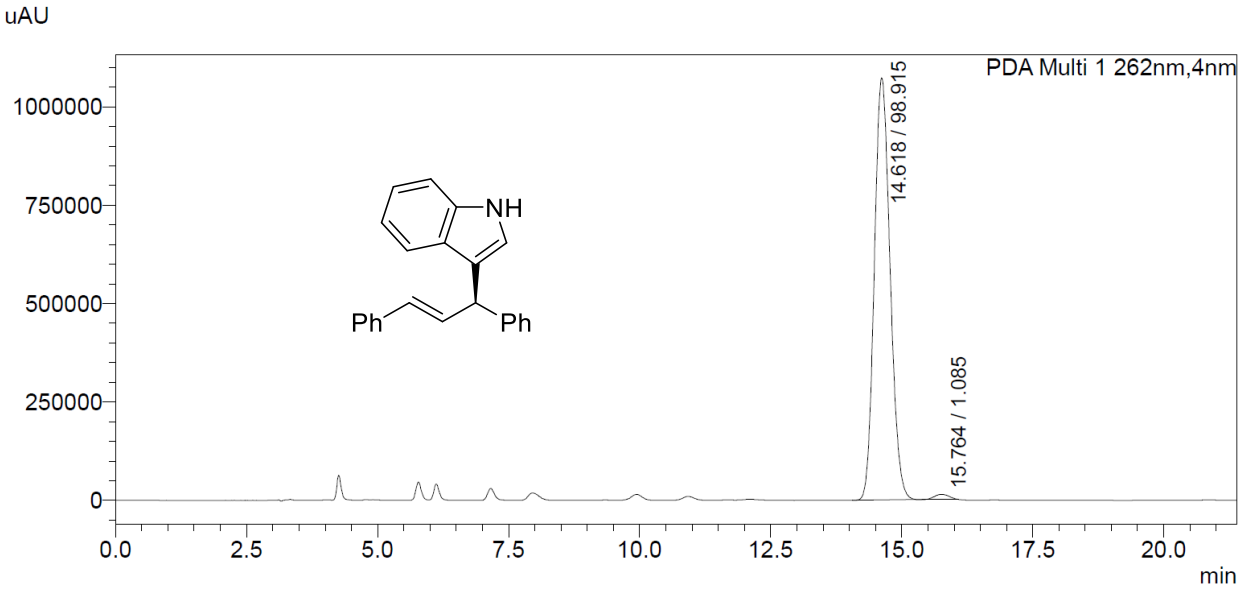

Figure S62. HPLC trace of entry 1, Table 2: Chiracel AD-H, 90:10 Hex/*i*PrOH, flow: 1.0 mL/min

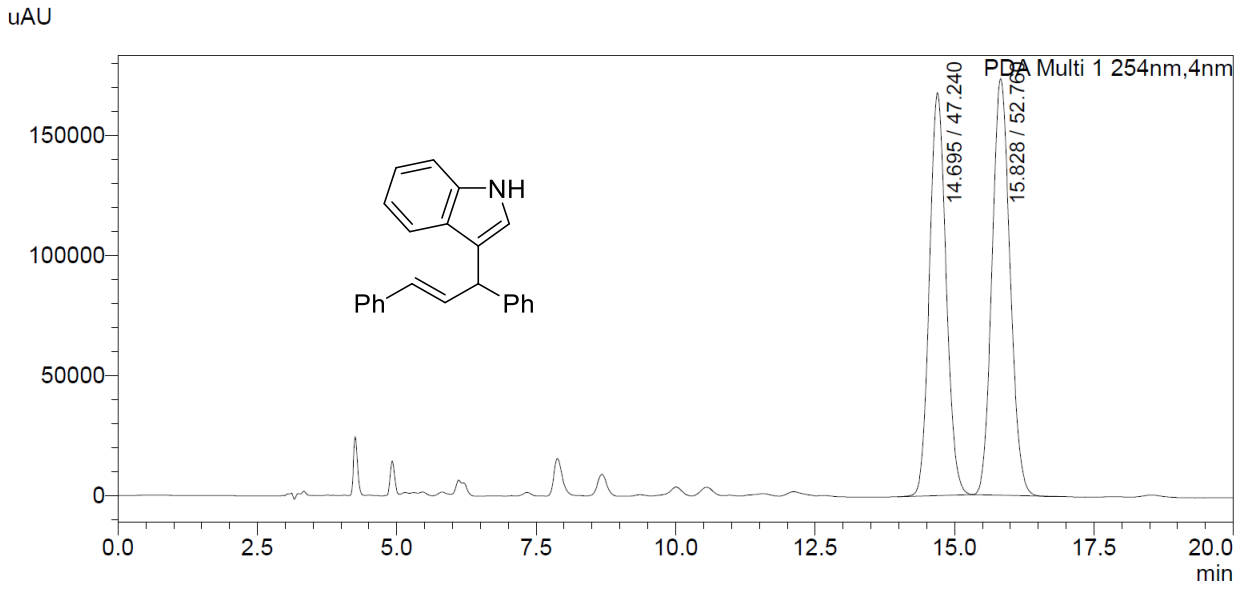

Figure S63. HPLC trace of entry 2, Table 2: Chiracel AD-H, 90:10 Hex/*i*PrOH, flow: 1.0 mL/min

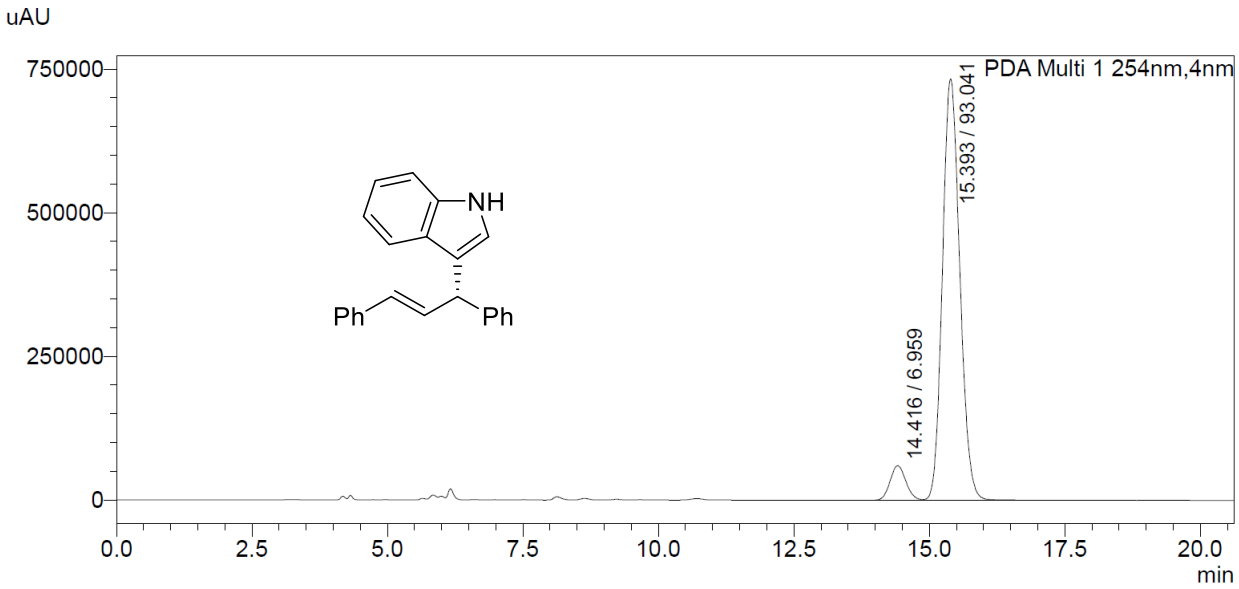

Figure S64. HPLC trace of entry 3, Table 2: Chiracel AD-H, 90:10 Hex/*i*PrOH, flow: 1.0 mL/min

[1,3-Diphenyl-2-propen-1-yl]-6-fluoro-1*H*-indole 17b: The product was purified by flash column chromatography (Hexane/EtOAc 98:2) and obtained as a yellow oil. Chiral stationary HPLC: Chiracel AD-H; Hexane/Isopropanol 97:3; t1 = 40.56 min, t2 = 43.14 min. ^{1}H NMR ($CDCl_3$; 400 MHz; Fig. A61, A62): 7.90 (bs, 1H), 7.43 – 7.24 (m, 12H), 7.04 – 7.01 (dd, 1H), 6.87 – 6.82 (m, 2H), 6.78 – 6.72 (dd, 1H), 6.51 – 6.47 (d, 1H), 5.13 – 5.12 (d, 1H).

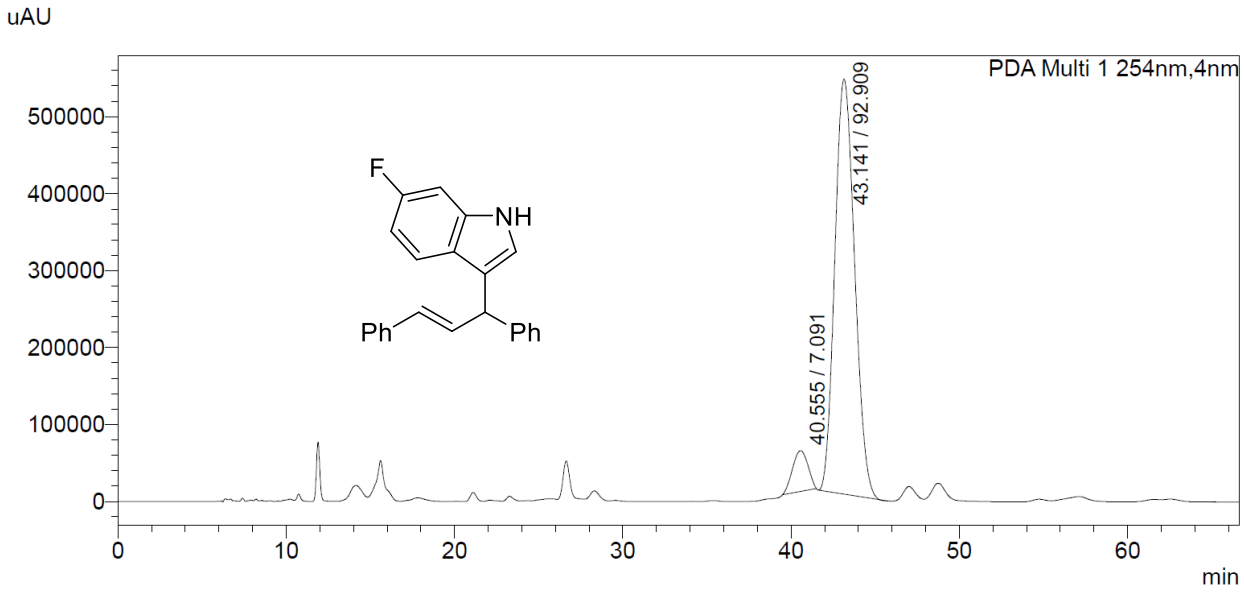

Figure S65. HPLC trace entry 4, Table 2: Chiracel AD-H, 97:3 Hex/*i*PrOH, flow: 0.5 mL/min

[1,3-Diphenyl-2-propen-1-yl]-4-methyl-1*H*-indole 17c: The product was purified by flash column chromatography (Hexane/EtOAc 15:1) and obtained as white solid. Chiral stationary HPLC: Chiracel OD-H; Hexane/Isopropanol 99:1; t1 = 42.99 min, t2 = 63.53 min. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 8.01 (bs, 1H), 7.36 – 7.18 (m, 12H), 7.06 (t, 1H), 6.86 – 6.76 (m, 2H), 6.72 – 6.72 (d, 1H), 6.25 – 6.22 (d, 1H), 5.46 – 5.44 (d, 1H), 2.52 (s, 3H).

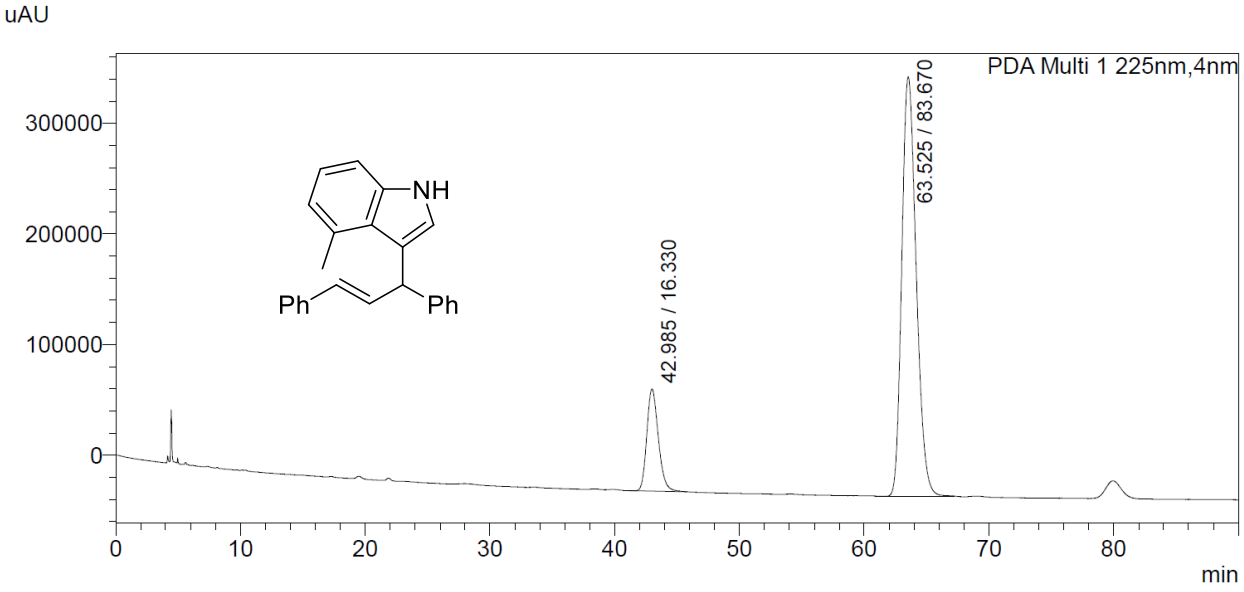

Figure S66. HPLC trace entry 5, Table 2: Chiracel OD-H, 99:1 Hex/*i*PrOH, flow: 0.7 mL/min

5. References

[1] Herrera, A.; Grasruck, A.; Heinemann, F. W.; Scheurer, A.; Chelouan, A.; Frierss, S.; Seidel, F.; Dorta, R. *Organometallics* **2017**, *36*, 714-720.

[2] Van Der Ent, A.; Onderdelinden, A. L.; Schunn, R. A. *Inorg. Synth.* **2007**, 92-95.

[3] N. Oka, T.; Yamada, H.; Sajiki, S.; Akai, T.; Ikawa, T. *Org. Lett*. **2022**, *24*, 3510–3514.

[4] Imrich, M.R., Maichle-Mössmer, C. and Ziegler, T. *Eur. J. Org. Chem.* **2019**, 3955-3963

[5] The use of toluene as extracting solvent affords a 1:1 diastereomeric mixture.

[6] We have observed that the quality of the BH_3•THF has an important influence on the reproducibilty of the crystallizations reported herein. BH_3•THF from various commercial sources has more often than not proven to be of shaky quality. Preliminary titration is therefore strongly advised.

[7] Bruker AXS, I., *SADABS 2014/5, Bruker AXS Area Detector Scaling and Absorption Correction* **2014**.

[8] Sheldrick, G. M., A Short History of SHELX. *Acta. Crystallogr. A* **2008,** *64* (Pt 1), 112-122.

[9] Sheldrick, G. M., Crystal Structure Refinement with SHELXL. *Acta. Crystallogr. C Struct. Chem.* **2015,** *71* (Pt 1), 3-8.

[10] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A.; Puschmann, H., OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009,** *42* (2), 339-341.

[11] Rigaku Oxford Diffraction, **2019**, CrysAlisPro Software system, version 1.171.40.53 , Rigaku Corporation, Oxford, UK.

[12] Sheldrick, G. M., SHELXT – Integrated space-group and crystal-structure determination. *Acta. Crystallogr. A* **2015,** *71*, 3-8.

[13] Thorn, A.; Dittrich B. and Sheldrick, G. M. Enhanced rigid-bond restraints. *Acta Cryst. A*, 2012, 68, 448–451.

[14] Parsons, S.; Flack, H. D.; Wagner, T. *Acta Crystallogr. Section B*, **2013**, *69*, 249–259.

[15] Okamoto, K.; Hayashi, T.; Rawal, V. H. *Org. Lett.* **2008**, *10*, 4387–4389.