Supplementary Information for:

Chiral Recognition in Contact Ion-pairs; Observation, Characterization and Analysis.

Jevgenij A. Raskatov, Amber L. Thompson, Andrew R. Cowley, Timothy D. W. Claridge and John. M. Brown

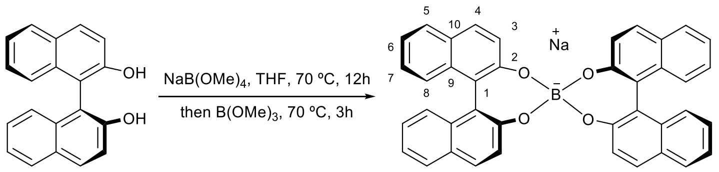
Chemistry Research Laboratory, University of Oxford, 12 Mansfield Rd., Oxford OX1 3TA.

A. Synthesis of substituted BINOL Borates

B. General Experimental Details

Solvents were dried by passage through an activated alumina column.[i] Preparative chromatography was performed on Merck 60Å, 230-400 mesh silica gel. NMR solvents were stored over 4Å molecular sieves and degassed before all experiments (3 freeze-pump-thaw cycles). NMR spectra were recorded on a Bruker DRX500, AVC500 or DPX250 spectrometer. Mass spectra were recorded on the Bruker MicroTOF spectrometer. Melting points were measured on a Reichert-Koffler block apparatus. IR spectra were recorded on a Bruker Tensor 27 FTIR (thin films) or on a Nicolet 6700 FTIR with Goldengate ATR accessory (neat solids). Chemical shifts (δ) are reported in parts per million (ppm) and referenced to the residual solvent peak (^{1}H and ^{13}C NMR) or *via* external reference (^{11}B NMR, ^{31}P NMR). All precious metals were generous loans from Johnson Matthey. The organometallic complexes $[Rh(cod)Cl]_2$, $[Rh(nbd)Cl]_2$, $[Ir(cod)Cl]_2$, $[Rh(cod)_2]BF_4$ and $[Rh(nbd)_2]BF_4$ were synthesised from $RhCl_3$ and $IrCl_3$, following established synthetic protocols. All neutral rhodium and iridium complexes were stable over several months, whereas the cationic BF_4-salts were found prone to slow decomposition upon formation of rhodium black, typically over weeks. BINOL used in preparation of all chiral borates was purchased in bulk quantities from Reuter Chemische Apparatebau (Freiburg). The enantiomeric ratios of both (*R*)- and (*S*)-BINOL were given as 99.9 : 0.1. DFT calculations were carried out using Gaussian03[ii] and dispersion corrected by the method of Grimme.[iii] We thank Dr. Robert Paton for help with this procedure.

Sodium *Bis*((*S*)-1,1'-binaphthalene-2,2'-dioxy)-borate[§]

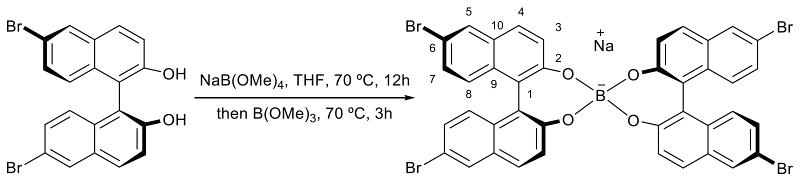


(*S*)-1,1'-binaphthalene-2,2'-diol (3.20 g, 11.2 mmol) and $NaB(OMe)_4$ (0.90 g, 5.7 mmol) were dissolved in 30 ml THF and heated to reflux for 10 h. The suspension was then allowed to cool down to 40 ºC and treated with $B(OMe)_3$ (0.75 g, 1.00 ml, 7.1 mmol). Upon cooling, a white precipitate spontaneously formed. The resulting suspension was stirred at 40 ºC for 1 h and then refluxed for 3 h. The suspension was subsequently allowed to cool down to 20 ºC and the title compound allowed to crystallise over 5 h. The thus obtained white precipitate was filtered off and washed with 20 ml THF, followed by 2 x 20 ml Et_2O and 20 ml pentane. Drying *in vacuo* yielded the title compound as a white crystalline solid (3.31 g, 5.5 mmol, 98 %).[1] m.p. > 300 ºC; $[\alpha]_D^{20}$ +279 (*c* 1.0, DMSO); IR (neat) 3059, 1618, 1591, 1506, 1464, 1429, 1367, 1333, 1265, 1246, 1070, 985, 949, 908 cm^{-1}; δ_H (500 MHz, DMSO-d$_6$): 7.13 (1H, d, $J_{8,7}$ = 8 Hz, H-8), 7.16 (1H, t, J = 8 Hz, H-7), 7.29 (1H, t, J = 7 Hz, H-6), 7.33 (1H, d, $J_{3,4}$ = 9 Hz, H-3), 7.93 (1H, d, $J_{5,6}$ = 9 Hz, H-5), 7.97 (1H, d, $J_{4,3}$ = 9 Hz, H-4); δ_C (126 MHz, DMSO-d$_6$): 121.8 (C-1), 122.3 (C-6), 124.5 (C-3), 124.8 (C-7), 125.8 (C-8), 128.0 (C-5), 128.1 (C-4), 128.9 (C-9), 132.8 (C-10), 156.1 (C-2); δ_B (160 MHz, DMSO-d$_6$): 9.2 ppm; *m/z* (ESI -) calc. for $[C_{40}H_{24}BO_4]^-$ 579.1773, found 579.1791.

Following the general borate preparation procedure from (*R*)-1,1'-binaphthalene-2,2'-diol (4.50 g, 15.7 mmol) the (*R*)-enantiomer of the product (4.41 g, 7.3 mmol, 93 %) was afforded. $[\alpha]_D^{20}$ -278 (*c* 1.0, DMSO); the spectroscopic characterisation of the title compound was identical to the (S)-enantiomer. The only literature example quotes an optical rotation of $[\alpha]_D^{20}$ +173.6 (*c* 1.04, DMSO) for the (*R*)-enantiomer without giving any further characterisation details.[25] This value conflicts the optical rotation the authors claimed for the same borate as the triethylammonium salt, stated as $[\alpha]_D^{20}$ -232.4 (*c* 1.01, DMSO). Given the fact that the anion is sensitive to water and the use of aqueous THF in their procedure, it is likely that the authors isolated a sodium salt of (*R*)-BINOL instead of the claimed product).

Following the general borate preparation procedure from (±)-1,1'-binaphthalene-2,2'-diol (1.00 g, 3.5 mmol) afforded the racemate of the title product (1.01 g, 1.75 mmol, 96 %); the spectroscopic characterisation of the title compound was identical to that for the enantiopure analogues.

Sodium *Bis*((*S*)-6,6'-dibromo-1,1'-binaphthalene-2,2'-dioxy)-borate;



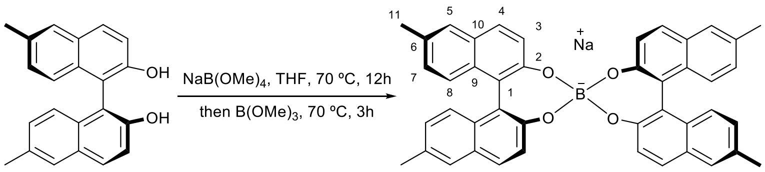
Following the general borate preparation procedure from (*S*)-6,6'-dibromo-1,1'-binaphthalene-2,2'-diol (1.252 g, 2.82 mmol) afforded the title compound (0.580 g, 0.63 mmol, 45 %). m.p. > 300 ºC; $[\alpha]_D^{20}$ +70 (*c* 0.2, DMSO); IR (neat) 3056, 1583, 1489, 1462, 1371, 1354, 1329, 1265, 1246, 1066, 984, 944, 872 cm^{-1}; δ_H (500 MHz, DMSO-d$_6$): 7.02 (1H, d, $J_{8,7}$ = 9 Hz, H-8), 7.29-7.38 (2H, m, H-3 and H-7), 8.00 (1H, d, $J_{4,3}$ = 9 Hz, 1H, 4-H), 8.22 (1H, d, $J_{5,7}$ = 2 Hz, 1H, 5-H); δ_C (126 MHz, DMSO-d$_6$): 115.5 (C-6), 121.5 (C-1), 125.6 (C-3), 127.8 (C-4 or C-8), 127.9 (C-4 or C-8), 128.1

[§] This procedure is later described as the general borate preparation procedure, utilised in other cases. When spontaneous crystallisation did not occur, the ion-pair was precipitated with Et$_2$O.

(C-7), 129.9 (C-5), 130.3 (C-9 or C-10), 131.3 (C-9 or C-10), 156.5 (C-2); δ_B (80 MHz, DMSO-d$_6$): 8.8 ppm; *m/z* (ESI -) calc. for $[C_{40}H_{20}BBr_4O_4]^-$ 890.8188, found 890.8194.

Following the general borate preparation procedure from (±)-6,6'-dibromo-1,1'-binaphthalene-2,2'-diol (221 mg, 0.50 mmol) afforded the racemate of the title product (80 mg, 0.087 mmol, 35 %); the spectroscopic characterisation was identical to the enantiopure analogue.

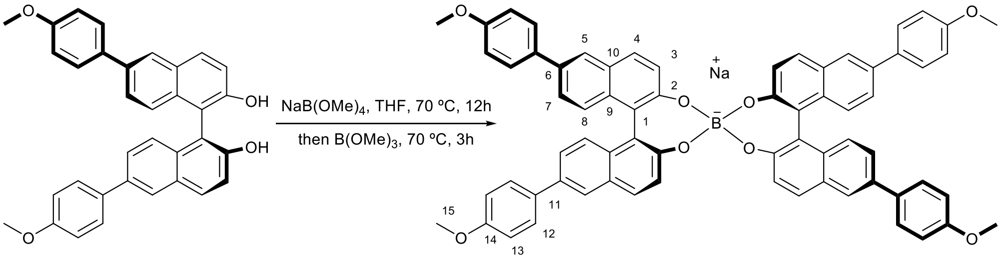
Sodium *Bis*((*S*)-6,6'-dimethyl-1,1'-binaphthalene-2,2'-dioxy)-borate;



Following the general borate preparation procedure from (*S*)-6,6'-dimethyl-1,1'-binaphthalene-2,2'-diol (1.121 g, 3.57 mmol) afforded the title compound (0.68 g, 1.0 mmol, 65 %). m.p. > 300 ºC; IR (neat) 2974, 1591, 1500, 1473, 1363, 1336, 1273, 1246, 1072, 1057, 1026, 1003, 982, 957, 914, 876, 818 cm^{-1}; $[\alpha]_D^{20}$ +197 (*c* 0.3, DMSO); δ_H (500 MHz, DMSO-d$_6$): 2.42 (3H, s, H-11), 6.98 (1H, d, $J_{7,8}$ = 9 Hz, H-7 or H-8), 7.04 (1H, d, $J_{7,8}$ = 9 Hz, H-7 or H-8), 7.26 (1H, d, $J_{3,4}$ = 9 Hz, H-3), 7.67 (1H, s, H-5), 7.83 (1H, d, $J_{4,3}$ = 9 Hz, H-4); δ_C (126 MHz, DMSO-d$_6$): 20.9, 121.9, 124.6, 125.9, 126.9, 127.4, 129.1, 131.0, 131.1, 155.5; δ_B (160 MHz, DMSO-d$_6$): 9.2 ppm; *m/z* (ESI -) calc. for $[C_{44}H_{32}BO_4]^-$ 635.2399, found 635.2415.

Following the general borate preparation procedure from (±)-6,6'-dimethyl-1,1'-binaphthalene-2,2'-diol (660 mg, 2.1 mmol) afforded the racemate of the title product (470 mg, 0.71 mmol, 68 %). Single crystals of X-Ray quality were obtained by allowing the refluxing concentrated THF solution of the title compound to cool down to 20 ºC over 5 h. The spectroscopic characterisation was identical to that of the enantiopure material.

Sodium *Bis*((*S*)-6,6'-*bis*(4-methoxyphenyl)-1,1'-binaphthalene-2,2'-dioxy)-borate;



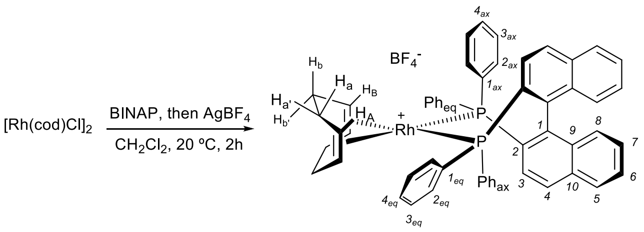
Following the general borate preparation procedure from (*S*)-6,6'-*bis*(4-methoxyphenyl)-1,1'-binaphthalene-2,2'-diol (360 mg, 0.73 mmol) afforded the title compound (244 mg, 65 %). m.p. > 300 ºC; IR (thin film) 3017, 1608, 1518, 1495, 1469, 1341, 1247, 1179, 1079, 1027, 819 cm^{-1}; $[\alpha]_D^{20}$ +171 (*c 0*.1, DMSO); δ_H (500 MHz, DMSO-d$_6$): 3.82 (3H, s, H-15), 7.06 (2H, d, $J_{13,12}$ = 9.0 Hz, H-13), 7.27 (1H, d, $J_{8,7}$ = 9.0 Hz, H-8), 7.38 (1H, d, $J_{3,4}$ = 9.0 Hz, H-3), 7.55 (1H, dd, $J_{7,8}$ = 9.0

Hz, $J_{7,5}$ = 1.5 Hz, H-7), 7.76 (2H, d, $J_{12,13}$ = 9.0 Hz, H-12), 8.07 (1H, d, $J_{4,3}$ = 9.0 Hz, H-4), 8.22 (1H, d, $J_{5,7}$ = 1.5 Hz, H-5); δ_C (126 MHz, DMSO-d_6): 56.0 (C-15), 115.3 (C-13), 122.6, 124.6 (C-7), 125.5 (C-5), 125.8 (C-3), 127.3 (C-8), 128.5 (C-12), 129.4 (C-4), 130.2, 132.6, 133.3, 134.4, 157.0 (C-2), 159.5 (C-14); δ_B (160 MHz, DMSO-d_6): 9.0 ppm; *m/z* (ESI -) calc. for $[C_{68}H_{48}BO_8]^-$ 1003.3448, found 1003.3465.

Following the general borate preparation procedure from (±)-(*S*)-6,6'-*bis*(4-methoxyphenyl)-1,1'-binaphthalene-2,2'-diol (150 mg, 0.30 mmol) afforded the racemate of the title product (90 mg, 58 %). The spectroscopic characterisation was identical to that of the enantiopure material.

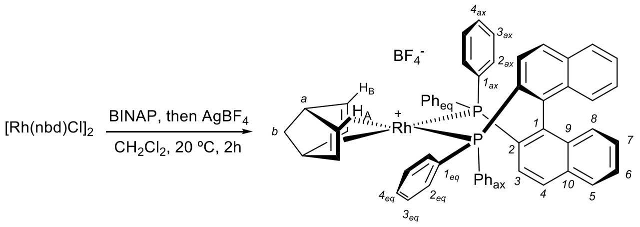
B1. Precursor complexes and NMR assigments:

((*S*)-2,2’-Bis(diphenylphosphino)-1,1’-binaphthyl)(1,5-cyclooctadiene)rhodium(I)tetrafluoroborate



$[Rh(cod)Cl]_2$ (10.3 mg, 0.02 mmol) was dissolved in 2 ml CH_2Cl_2 under argon and (*S*)- 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (25.2 mg, 0.04 mmol) added. After stirring for 5 min, $AgBF_4$ (15 mg, 0.08 mmol) was added as a solid. After stirring at 20 ºC for 2 h, the suspension was filtered over a Celite pad and washed with CH_2Cl_2. The yellow solution was concentrated to 1 ml and the complex precipitated with Et_2O. Subsequent washing with Et_2O and drying under high vacuum afforded the title compound (28.1 mg, 78 %). m.p. 202-205 ºC (decomp.); δ_H (500 MHz, $CDCl_3$): 2.19 (1H, m, $H_{b'}$), 2.40 (1H, m, H_b), 2.46 (1H, m, $H_{a'}$), 2.67 (1H, m, H_a), 4.66 (1H, m, H_B), 4.84 (1H, m, H_A), 6.51 (1H, d, $J_{8,7}$ = 8.6 Hz, H-8), 6.76 (2H, t, J = 7.6 Hz, H-3_{ax}), 6.84 (1H, t, $J_{4,3}$ = 7.6 Hz, H-4_{ax}), 7.03 (1H, t, J = 7.7 Hz, H-7), 7.39 (1H, t, J = 7.7 Hz, H-6), 7.44 (2H, m, H-2_{ax}), 7.58 (2H, m, H-2_{eq}), 7.60 (3H, m, H-3,4_{eq}), 7.66 (1H, d, $J_{5,6}$ = 8.2 Hz, H-5), 7.78 (1H, d, $J_{4,3}$ = 8.9 Hz, H-4), 7.93 (1H, m, H-3); δ_C (126 MHz, $CDCl_3$): 29.3 (C_b), 32.3 (C_a), 98.1 (m, C_A), 103.4 (m, C_B), 127.0 (BINAP $\underline{C}$H), 127.3 (t, $J_{C,P}$ = 4 Hz, BINAP $\underline{C}$H), 127.4 (BINAP $\underline{C}$H), 128.0 (BINAP $\underline{C}$H), 128.3 (t, $J_{C,P}$ = 6 Hz, BINAP $\underline{C}$H), 128.5 (BINAP $\underline{C}$H), *128.6*, *128.7*, *128.9*, *129.1*, 129.3 (t, $J_{C,P}$ = 5 Hz, BINAP $\underline{C}$H), 129.6 (t, $J_{C,P}$ = 4 Hz, BINAP $\underline{C}$H), 130.5 (BINAP $\underline{C}$H), 131.5 (BINAP $\underline{C}$H), 133.9 (t, $J_{C,P}$ = 3 Hz, BINAP $\underline{C}$H), 134.1 (BINAP $\underline{C}$H), 134.3 (t, $J_{C,P}$ = 4 Hz, BINAP $\underline{C}$H), 135.1 (t, $J_{C,P}$ = 7 Hz, BINAP $\underline{C}$H), 139.0 (t, $J_{C,P}$ = 7 Hz, BINAP $\underline{C}$H); δ_P (202 MHz, $CDCl_3$): 25.4 (d, $J_{P,Rh}$ = 145 Hz) ppm.

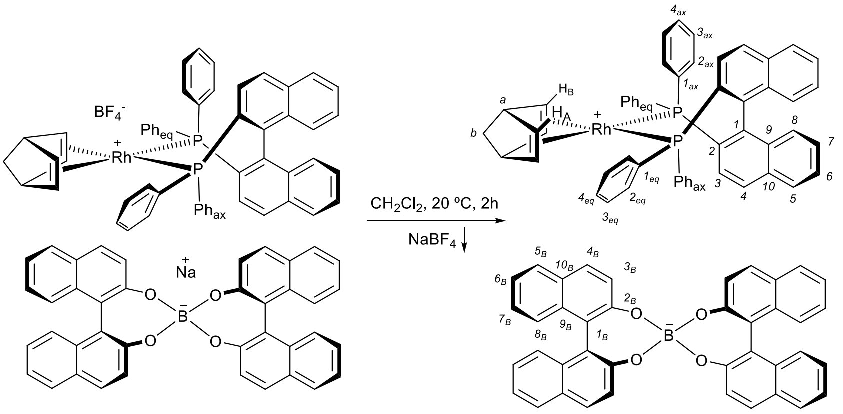
((±)-2,2’-Bis(diphenylphosphino)-1,1’-binaphthyl)(2,5-norbornadiene) rhodium (I) tetrafluoroborate.



$[Rh(nbd)Cl]_2$ (0.200 g, 0.43 mmol) were dissolved in 20 ml CH_2Cl_2 and the solution stirred at 20 ºC for 5 min. Then (±)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (0.543 g, 0.87 mmol) was added as a solid and stirring continued for further 1 h. The clear light orange solution was subsequently treated with $AgBF_4$ (0.180 mg, 0.92 mmol) as a solid. The resulting suspension was filtered over a Celite pad and the off-white residue washed with CH_2Cl_2 until the filtrate was colourless. The obtained light orange solution was concentrated to 5 ml and the complex precipitated by a slow addition of 50 ml Et_2O under vigorous stirring. Subsequent washing of the orange solid with Et_2O (2 x 20 ml) and drying under high vacuum afforded the title compound (0.76 g, 0.84 mmol, 98 %). m.p. 218-220 ºC (decomp.); δ_H (500 MHz, $CDCl_3$): 1.65 (1H, s, H_b), 4.19 (1H, s, H_a), 4.98 (2H, m, H_A and H_B), 6.53 (1H, d, $J_{8,7}$ =8.5 Hz, H-8), 6.77 (2H, t, J = 7.5 Hz, H-3_{ax}), 6.83 (1H, t, $J_{4ax,3ax}$ = 7.5 Hz, H-4_{ax}), 7.04 (1H, m, H-7), 7.38 (1H, t, J = 7.5 Hz, H-6), 7.48 (4H, m, H-2_{ax} and H-2_{eq}), 7.55 (1H, t, $J_{4eq,3eq}$ = 7 Hz, H-4_{eq}), 7.60 (2H, t, J = 7.5 Hz, H-3_{eq}), 7.65 (1H, d, $J_{5,6}$ =8 Hz, H-5), 7.75 (2H, m, H-3 and H-4); δ_C (126 MHz, $CDCl_3$, unassigned multiplet contributions italicised): 54.1 (C_a), 70.1 (C_b), 82.3 (q, J = 5 Hz, C_B), 90.1 (q, J = 5 Hz, C_A), 127.0 127.1 (m), *127.4*, *127.6*, 127.8 (C-4_{ax}), *128.0*, *128.4*, 128.5 (t, J = 6 Hz), 128.5, *128.7*, *129.1*, *129.2*, *129.3*, *129.4*, 129.5 (t, J = 4.5 Hz), 129.7 (t, J = 4.5 Hz), 130.5, 131.3 (C-4_{eq}), 133.7 (t, J = 5 Hz, C-2_{eq}), 133.9 (t, J = 4 Hz, C-9), 134.2 (C-10), 134.8 (t, J = 7 Hz, C-2_{ax}), 139.1 (t, J = 7 Hz, C-1); δ_B (160 MHz, $CDCl_3$): -1.3 ppm; δ_P (202 MHz, $CDCl_3$): 27.2 (d, $J_{P,Rh}$ = 156 Hz) ppm.

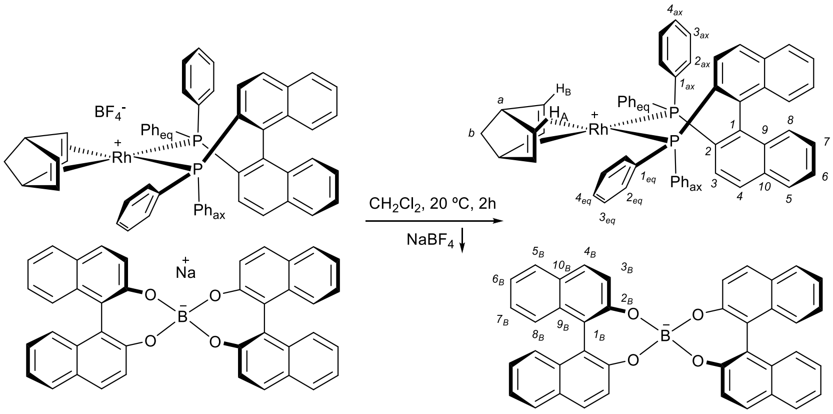
B 2 Ion Pairs of Organometallic Complexes with Chiral Borates

(*S*)-(2,2’-Bis(diphenylphosphino)-1,1’-binaphthyl)(2,5-norbornadiene)rhodium (I) bis-(*S*)-(2,2’)-binaphtholatoborate; [(*S*)-(5)](*S*,*S*)-B_H



[Rh(nbd)(*S*)-BINAP]BF_4 (19.1 mg, 0.021 mmol) was dissolved in 2 ml CH_2Cl_2 and Na(*S*,*S*)-$\mathbf{B}_\mathbf{H}$ (13.2 mg, 0.022 mmol) added. The suspension was stirred for 2 h and the quantitative ion exchange demonstrated *via* ^{11}B NMR by showing the complete disappearance of the BF_4^- resonance at δ_B = -1.3 ppm along with the new signal at 9.1 ppm. The $NaBF_4$ precipitate was removed by filtering the suspension over Celite. The residue was washed with CH_2Cl_2 until the filtrate became colourless. The solution was concentrated to 1 ml and the compound precipitated with 25 ml Et_2O, followed by 10 ml pentane. The resulting orange solid was dried in vacuo to afford the ion pair as a bright orange solid. This general procedure was used in preparation of all subsequently described chiral ion pairs, unless denoted otherwise. δ_H (500 MHz, $CDCl_3$): 1.03 (1H, m, H_b), 3.45 (1H, m, H_a), 4.40 (1H, m, H_B), 4.62 (1H, m, H_A), 6.38 (3H, m, H-8 and H-3_{ax}), 6.59 (1H, t, $J_{4ax,3ax}$ = 8 Hz, H-4_{ax}), 6.93 (1H, t, *J* = 7 Hz, H-7), 7.04 (3H, m, H-7_B and H-4_{eq}), 7.16 (2H, t, *J* = 7 Hz, H-3_{eq}), 7.18 (4H, m, H-2_{ax} and H-2_{eq}), 7.23 (2H, m, H-6_B), 7.29 (1H, t, *J* = 8 Hz, H-6), 7.34 (2H, d, $J_{8B,7B}$ = 9 Hz, H-8_B), 7.45 (2H, m, H-4 and H-5), 7.50 (1H, m, H-3), 7.60 (2H, d, $J_{3B,4B}$ = 8 Hz, H-3_B), 7.89 (2H, d, $J_{5B,6B}$ = 8 Hz, H-5_B), 7.91 (2H, d, $J_{4B,3B}$ = 8 Hz, H-4_B); δ_B (160 MHz, $CDCl_3$): 9.1 ppm; δ_P (202 MHz, $CDCl_3$): 27.2 (d, $J_{P,Rh}$ = 161 Hz) ppm.

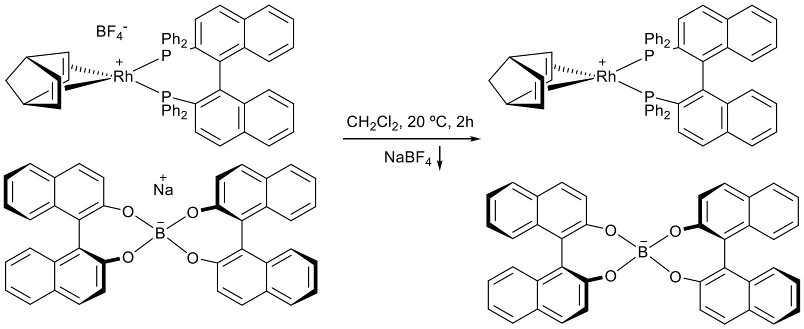
(*S*)-(2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl)(2,5-norbornadiene) rhodium (I) bis-(*R*)-(2,2')-binaphtholato-borate; [(*S*)-(5)](*R*,*R*)-$\mathbf{B}_\mathbf{H}$



The ion pair was prepared from the precursor salts according to the standard ion exchange procedure. Single crystals of X-Ray quality were obtained by slow diffusion of Et_2O into the CH_2Cl_2 solution of the title compound. δ_H (500 MHz, CD_2Cl_2): 1.46 (1H, m, H_b), 3.91 (1H, m, H_a) 4.69 (1H, m, H_B), 4.89 (1H, m, H_A), 6.50 (1H, d, $J_{8,7}$ = 9 Hz, H-8), 6.64 (2H, t, *J* = 7 Hz, H-3_{ax}), 6.75 (1H, t, $J_{4ax,3ax}$ = 7 Hz, H-4_{ax}), 7.02 (1H, m, H-7), 7.14 (2H, m, H-7_B), 7.28-7.40 (9H, m, H-6_B, H-8_B, H-3_{eq}, H-4_{eq}, H-4, H-6), 7.48 (3H, m, H-3 and phenyl H-2), 7.56 (2H, d, $J_{3B,4B}$ = 9 Hz, H-3_B), 7.59 (1H, d, $J_{5,6}$ = 8 Hz, H-5), 7.66 (2H, m, phenyl H-2), 7.92

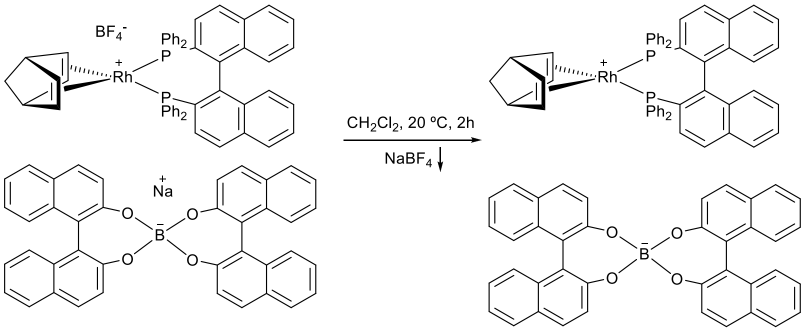
(2H, d, $J_{5B,6B}$ = 8 Hz, H-5$_B$), 7.96 (2H, d, $J_{4B,3B}$ = 9 Hz, H-4$_B$); δ_B (160 MHz, CD_2Cl_2): 9.2 ppm; δ_P (202 MHz, CD_2Cl_2): 26.9 (d, $J_{P,Rh}$ = 161 Hz) ppm.

(±)-(2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl)(2,5-norbornadiene) rhodium (I) bis-(*S*)-(2,2')-binaphtholato-borate; [(±)-(5)](*S*,*S*)-B$_H$



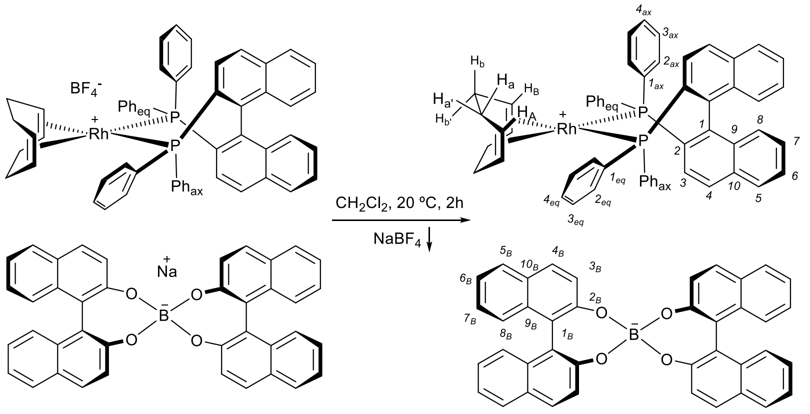
The ion pair was prepared from the precursor salts according to the standard ion exchange procedure. δ_B (80 MHz, $CDCl_3$): 9.1; δ_P (101 MHz, $CDCl_3$): 27.3 (d, $J_{P,Rh}$ = 161 Hz), 27.6 (d, $J_{P,Rh}$ = 161 Hz) ppm.

(±)-(2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl)(2,5-norbornadiene) rhodium (I) (±)-(2,2')-binaphtholatoborate; [(±)-(5)](±)-B$_H$



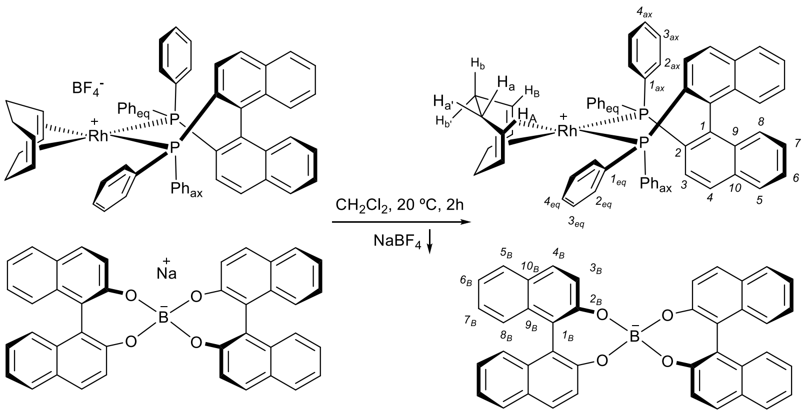
The ion pair was prepared from the precursor salts according to the standard ion-exchange procedure. Single crystals of X-Ray quality were obtained *via* either slow evaporation of a $CHCl_3$ solution of the title compound or slow diffusion of Et_2O into the CH_2Cl_2 solution of the ion pair. δ_B (80 MHz, $CDCl_3$): 9.1; δ_P (101 MHz, $CDCl_3$): 27.5 (d, $J_{P,Rh}$ = 161 Hz) ppm.

(*S*)-(2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl)(1,5-cyclooctadiene) rhodium (I) bis-(*S*)-(2,2')-binaphtholato-borate; [(*S*)-(6)](*S*,*S*)-B$_H$



The ion pair was prepared from the precursor salts according to the standard ion exchange procedure. Single crystals of X-Ray quality were obtained by slow diffusion of Et_2O into the CH_2Cl_2 solution of the title compound. δ_H (500 MHz, $CDCl_3$): 1.69 (1H, m, $H_{b'}$), 1.86 (1H, m, $H_{a'}$), 2.03 (1H, m, H_b), 2.17 (1H, m, H_a), 4.30 (1H, m, H_B), 4.53 (1H, m, H_A), 6.38 (1H, d, $J_{8,7}$ = 9 Hz, H-8), 6.49 (1H, t, J = 8 Hz, H-3_{ax}), 6.61 (1H, t, $J_{4ax,3ax}$ = 8 Hz, H-4_{ax}), 6.94 (1H, t, J = 8 Hz, H-7), 7.07 (2H, t, J = 8 Hz, H-7_B), 7.16 (1H, m, H-2_{ax}), 7.21-7.31 (6H, m, H-3_{eq}, H-4_{eq}, H-6, H-6_B), 7.33 (1H, m, H-2_{eq}), 7.38 (2H, d, $J_{8B,7B}$ = 9 Hz, H-8_B), 7.45 (1H, d, $J_{5,6}$ = 8 Hz, H-5), 7.47, (1H, d, $J_{4,3}$ = 9 Hz, H-4), 7.59 (2H, d, $J_{3B,4B}$ = 9 Hz, H-3_B), 7.66 (1H, m, H-3), 7.86 (2H, d, $J_{5B,6B}$ = 8 Hz, H-5_B), 7.87 (2H, d, $J_{4B,3B}$ = 9 Hz, H-4_B); δ_B (160 MHz, $CDCl_3$): 9.1; δ_P (202 MHz, $CDCl_3$): 25.4 (d, $J_{P,Rh}$ = 146 Hz) ppm.

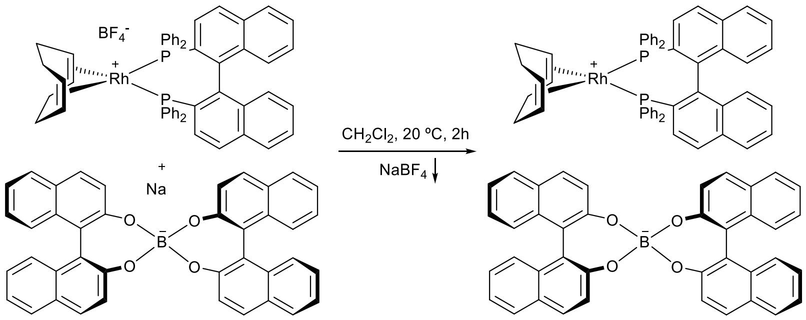
(*S*)-(2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl)(1,5-cyclooctadiene)rhodium (I) bis-(*R*)-(2,2')-binaphtholato-borate; [(*S*)-(6)](*R*,*R*)-B_H



The ion pair was prepared from the precursor salts according to the standard ion exchange procedure. δ_H (500 MHz, $CDCl_3$): 1.45 (1H, m, $H_{a'}$), 1.66 (1H, m, $H_{b'}$), 1.99 (1H, m, H_b), 2.35 (1H, m, H_a), 4.11 (1H, m, H_B), 4.29 (1H, m, H_A), 6.33 (3H, m, H-3_{ax} and H-4_{ax}), 6.46 (1H, d, J = 9 Hz, H-8), 6.89 (1H, t, J = 8 Hz, H-7), 7.02 (1H, m, H-2_{ax}), 7.04 (1H, d, $J_{5,6}$ = 8 Hz, H-5), 7.07 (2H, t, J = 8 Hz, H-7_B), 7.13 (3H, m, H-3_{eq} and H-4_{eq}), 7.17 (1H, t, J = 8 Hz, H-6), 7.22 (2H, d, $J_{8B,7B}$ = 9 Hz, H-8_B), 7.23 (2H, m, H-2_{eq}), 7.27 (2H, t, J = 8 Hz, H-6_B), 7.52 (1H, d, $J_{4,3}$ = 9 Hz, H-4), 7.73 (2H, d, $J_{3B,4B}$ = 9 Hz, H-3_B), 7.75 (1H, m, H-3), 7.92 (2H, d,

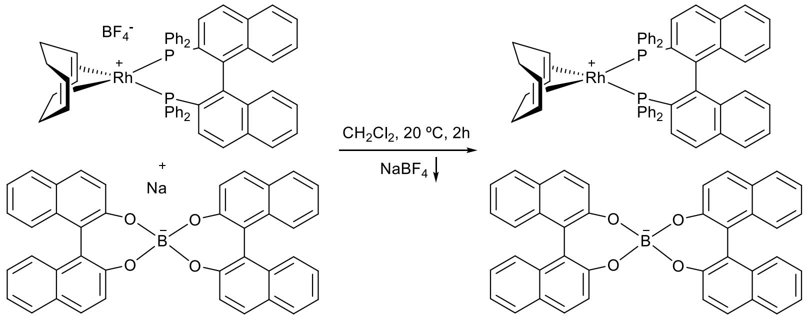
$J_{5B,6B}$ = 8 Hz, H-5$_B$), 7.97 (2H, d, $J_{4B,3B}$ = 8 Hz, H-4$_B$); δ_B (160 MHz, CDCl$_3$): 9.1; δ_P (202 MHz, CDCl$_3$): 26.2 (d, $J_{P,Rh}$ = 145 Hz) ppm.

(±)-(2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl)(1,5-cyclooctadiene) rhodium (I) bis-(*S*)-(2,2')-binaphtholato-borate; [(±)-(6)](*S*,*S*)-B$_H$



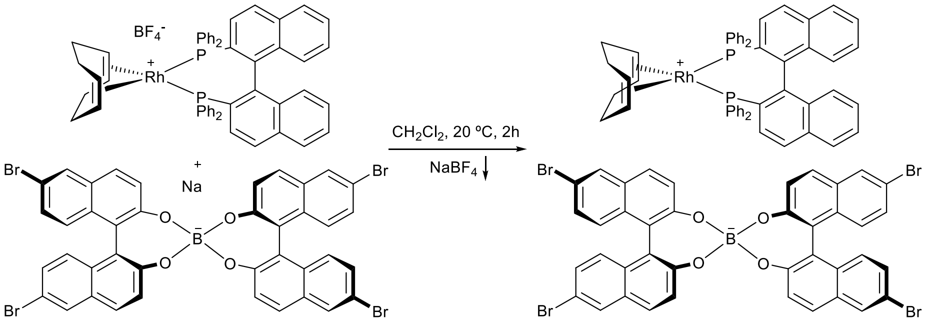
The ion pair was prepared from the precursor salts according to the standard ion exchange procedure. δ_B (80 MHz, CDCl$_3$): 9.1; δ_P (101 MHz, CDCl$_3$): 26.7 (d, $J_{P,Rh}$ = 145 Hz), 27.5 (d, $J_{P,Rh}$ = 145 Hz) ppm.

(±)-(2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl)(1,5-cyclooctadiene) rhodium (I) (±)-(2,2')-binaphtholato-borate; [(±)-(6)](±)-B$_H$



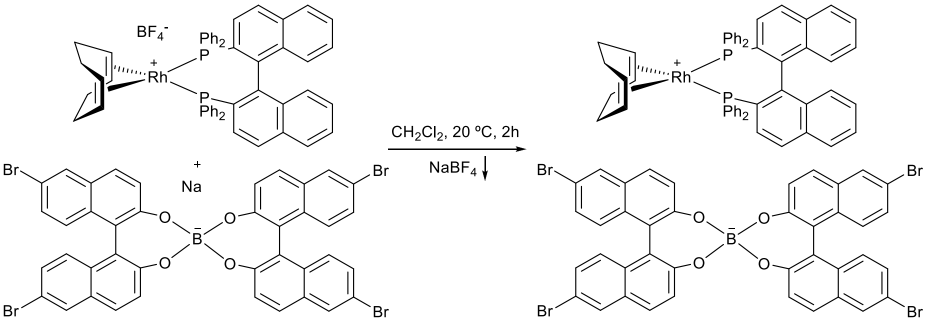
The ion pair was prepared from the precursor salts according to the standard ion exchange procedure. Single crystals of X-Ray quality were obtained by slow diffusion of Et$_2$O into the CH$_2$Cl$_2$ solution of the title compound. δ_B (80 MHz, CDCl$_3$): 9.1; δ_P (101 MHz, CDCl$_3$): 27.2 (d, $J_{P,Rh}$ = 145 Hz) ppm.

(±)-(2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl)(1,5-cyclooctadiene) rhodium (I) bis-(*S*)-binaphtholato-borate; [(±)-(7b)](*S*,*S*)-B$_{Br}$



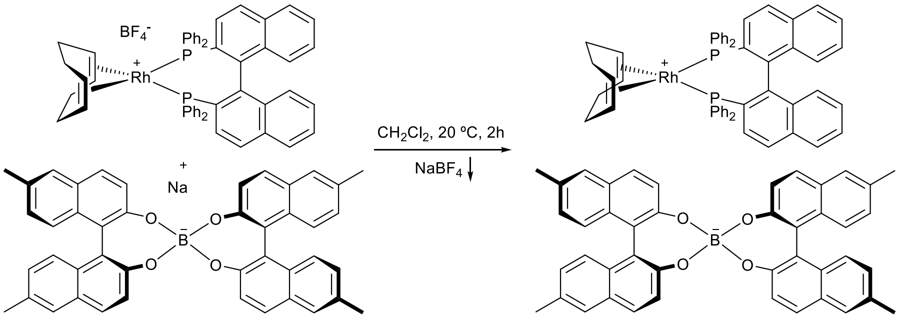
The ion pair was prepared from the precursor salts according to the standard ion exchange procedure. δ_B (80 MHz, CD_2Cl_2): 9.0; δ_P (101 MHz, $CDCl_3$): 26.5 (d, $J_{P,Rh}$ = 145 Hz), 27.3 (d, $J_{P,Rh}$ = 145 Hz) ppm.

(±)-(2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl)(1,5-cyclooctadiene) rhodium (I) (±)-binaphtholato-borate; [(±)-(7b)](±)-B$_{Br}$



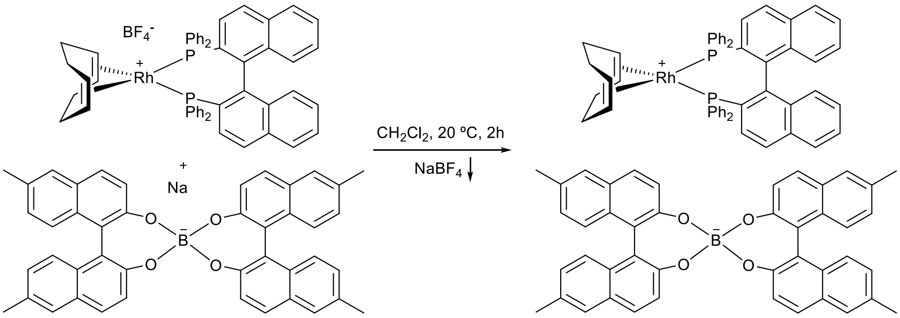
The ion pair was prepared from the precursor salts according to the standard ion exchange procedure. δ_B (80 MHz, CD_2Cl_2): 9.0; δ_P (101 MHz, $CDCl_3$): 27.1 (d, $J_{P,Rh}$ = 145 Hz) ppm.

(±)-(2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl)(1,5-cyclooctadiene) rhodium (I) bis-(*S*)-binaphtholato-borate; [(±)-(7a)](*S*,*S*)-B$_{Me}$



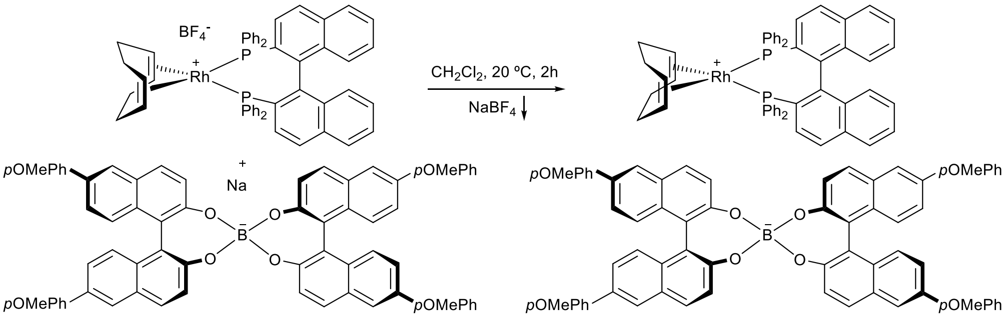
The ion pair was prepared from the precursor salts according to the standard ion exchange procedure. δ_B (80 MHz, CD_2Cl_2): 9.1; δ_P (101 MHz, $CDCl_3$): 26.8 (d, $J_{P,Rh}$ = 145 Hz), 27.6 (d, $J_{P,Rh}$ = 145 Hz) ppm.

(±)-(2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl)(1,5-cyclooctadiene) rhodium (I) (±)-binaphtholato-borate; [(±)-(7a)](±)-B$_{Me}$



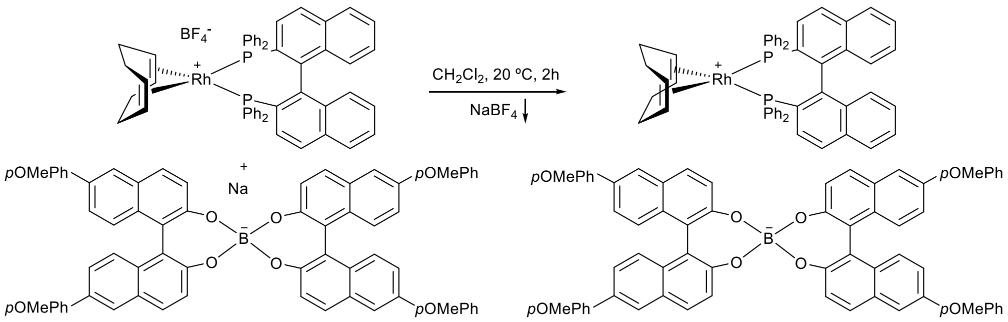
The ion pair was prepared from the precursor salts according to the standard ion exchange procedure. Single crystals of X-Ray quality were obtained by slow diffusion of Et_2O into the CH_2Cl_2 solution of the title compound. δ_B (80 MHz, CD_2Cl_2): 9.1; δ_P (101 MHz, $CDCl_3$): 27.4 (d, $J_{P,Rh}$ = 145 Hz) ppm.

(±)-(2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl)(1,5-cyclooctadiene) rhodium (I) bis-(*S*)-binaphtholato-borate; [(±)-(7c)](*S*,*S*)-B$_{\mathbf{pOMePh}}$



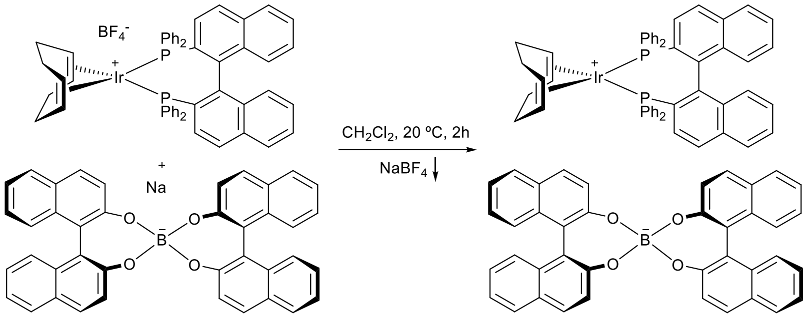
The ion pair was prepared from the precursor salts according to the standard ion exchange procedure. δ_B (80 MHz, CD_2Cl_2): 9.1; δ_P (101 MHz, $CDCl_3$): 26.7 (d, $J_{P,Rh}$ = 145 Hz), 27.7 (d, $J_{P,Rh}$ = 145 Hz) ppm.

(±)-(2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl)(1,5-cyclooctadiene) rhodium (I) (±)-binaphtholato-borate; [(±)-(7c)](±)-B$_{\mathbf{pOMePh}}$



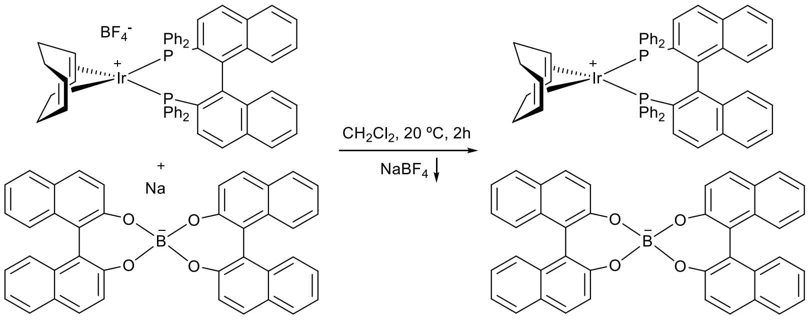
The ion pair was prepared from the precursor salts according to the standard ion exchange procedure. δ_B (80 MHz, CD_2Cl_2): 9.1; δ_P (101 MHz, $CDCl_3$): 27.3 (d, $J_{P,Rh}$ = 145 Hz) ppm.

(±)-(2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl)(1,5-cyclooctadiene) iridium (I) bis-(*S*)-binaphtholato-borate; [(±)-(8)](*S*,*S*)-B$_H$



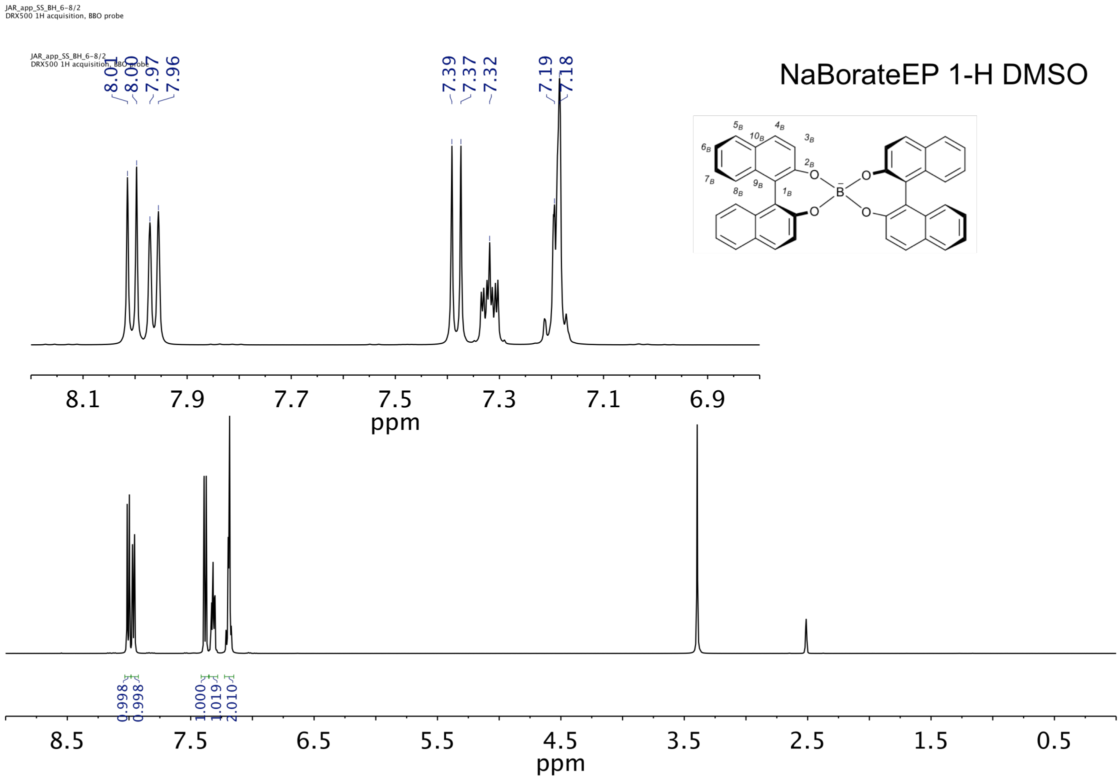
The ion pair was prepared from the precursor salts according to the standard ion exchange procedure. δ$_B$ (80 MHz, $CDCl_3$): 9.1; δ$_P$ (101 MHz, $CDCl_3$): 16.4, 17.6 ppm.

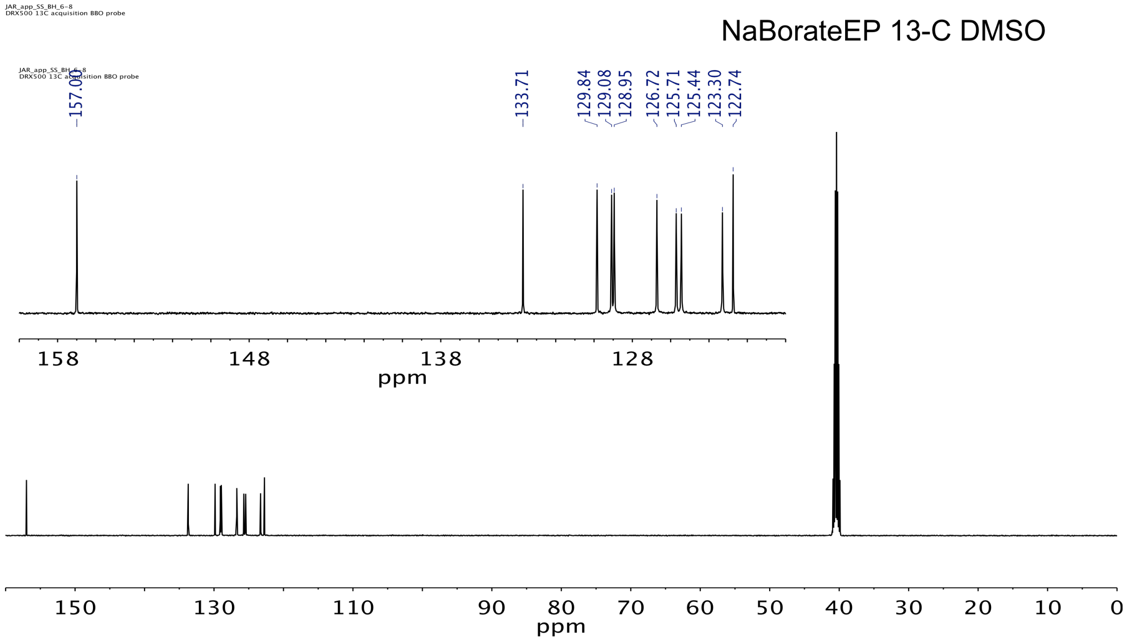
(±)-(2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl)(1,5-cyclooctadiene) iridium (I) (±)-binaphtholato-borate; [(±)-(8)](±)-B$_H$

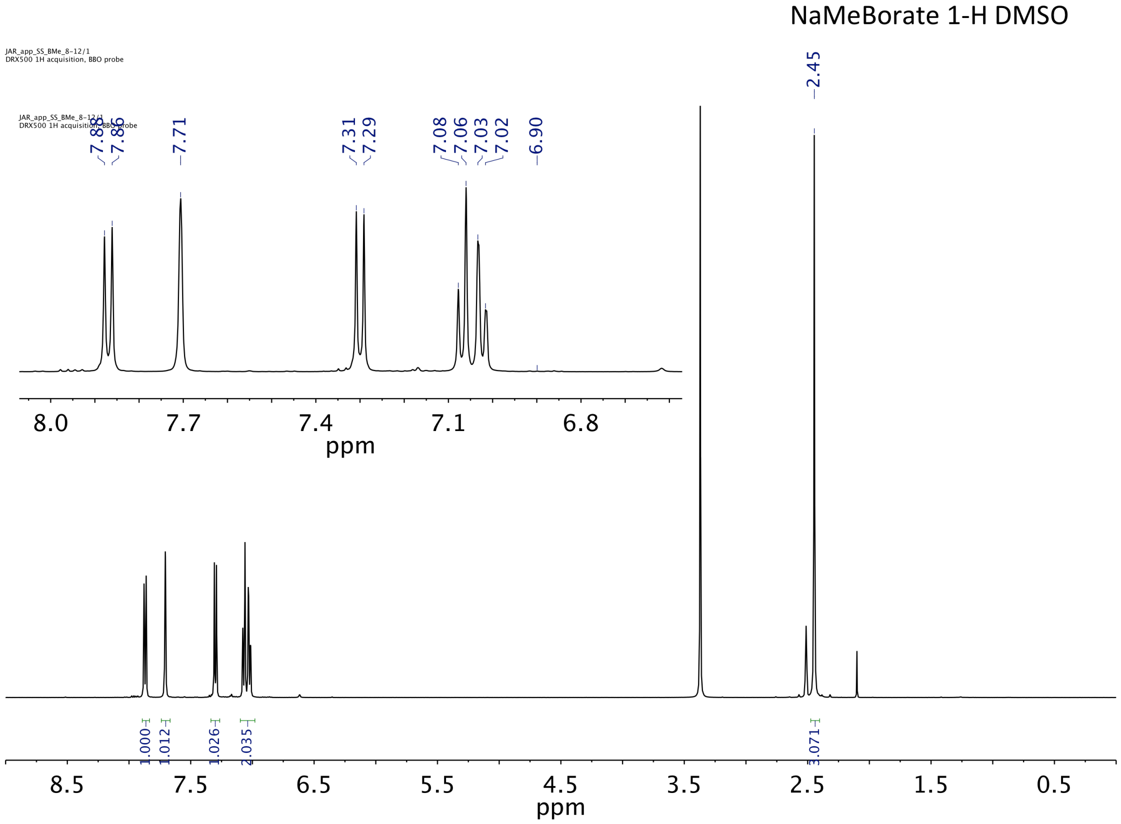


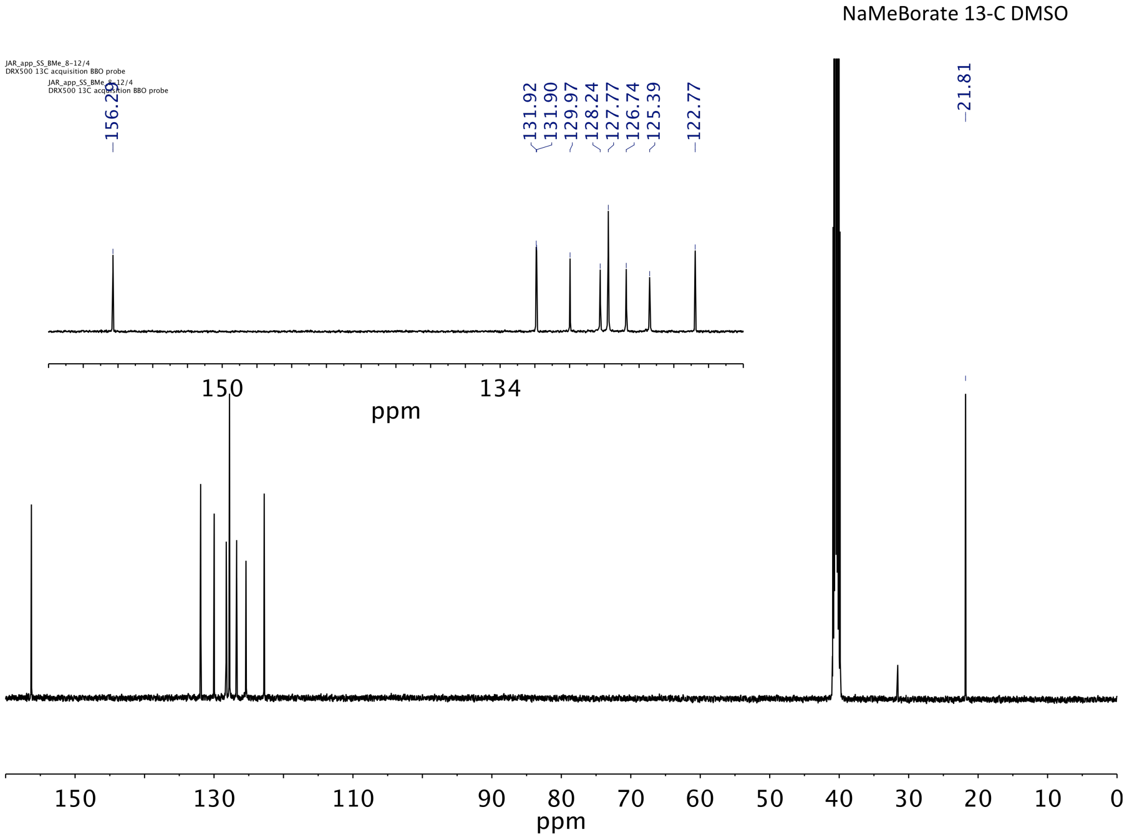
The ion pair was prepared from the precursor salts according to the standard ion exchange procedure. δ$_B$ (80 MHz, $CDCl_3$): 9.1; δ$_P$ (101 MHz, $CDCl_3$): 17.2 ppm.

C1. NMR Spectra of Na Borates

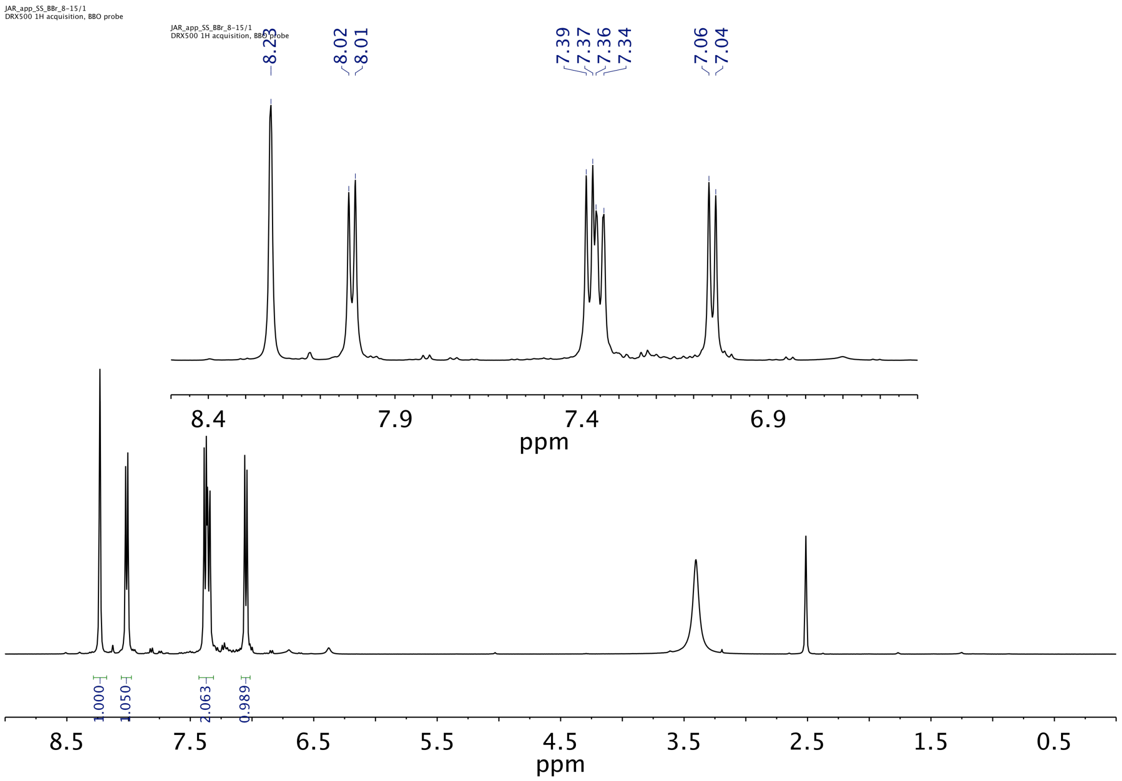




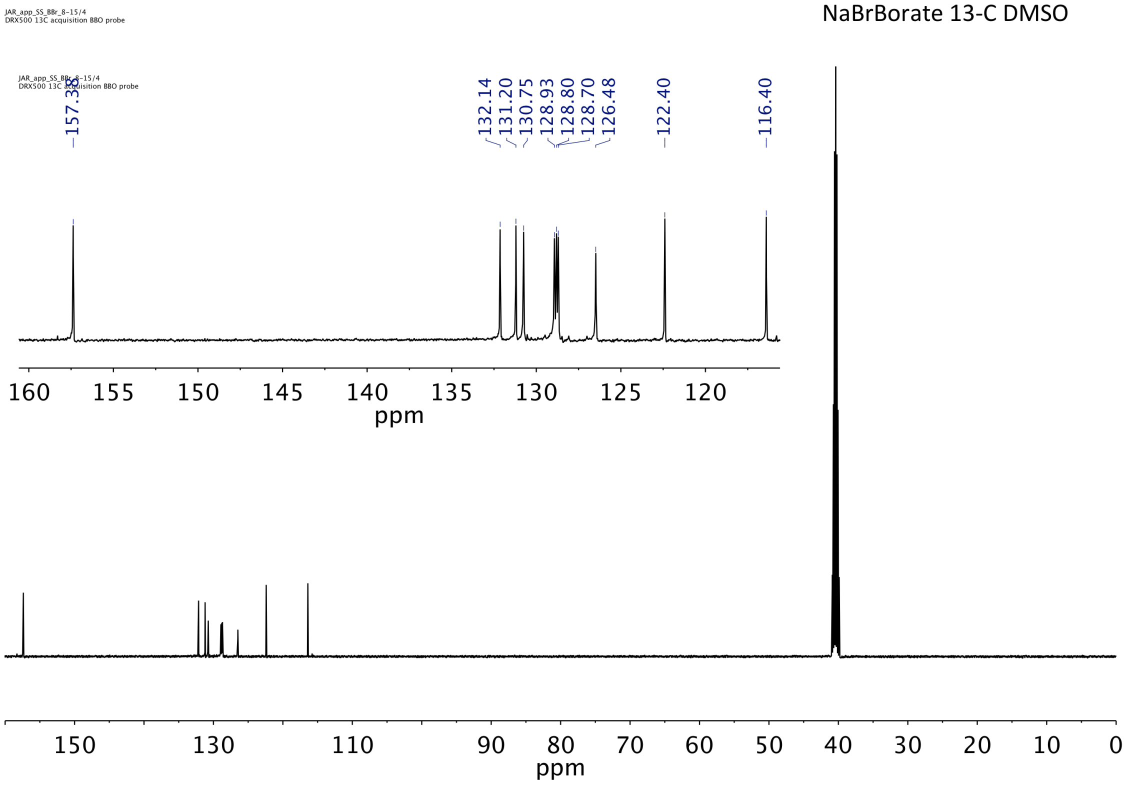

NaMeBorate 1-H DMSO

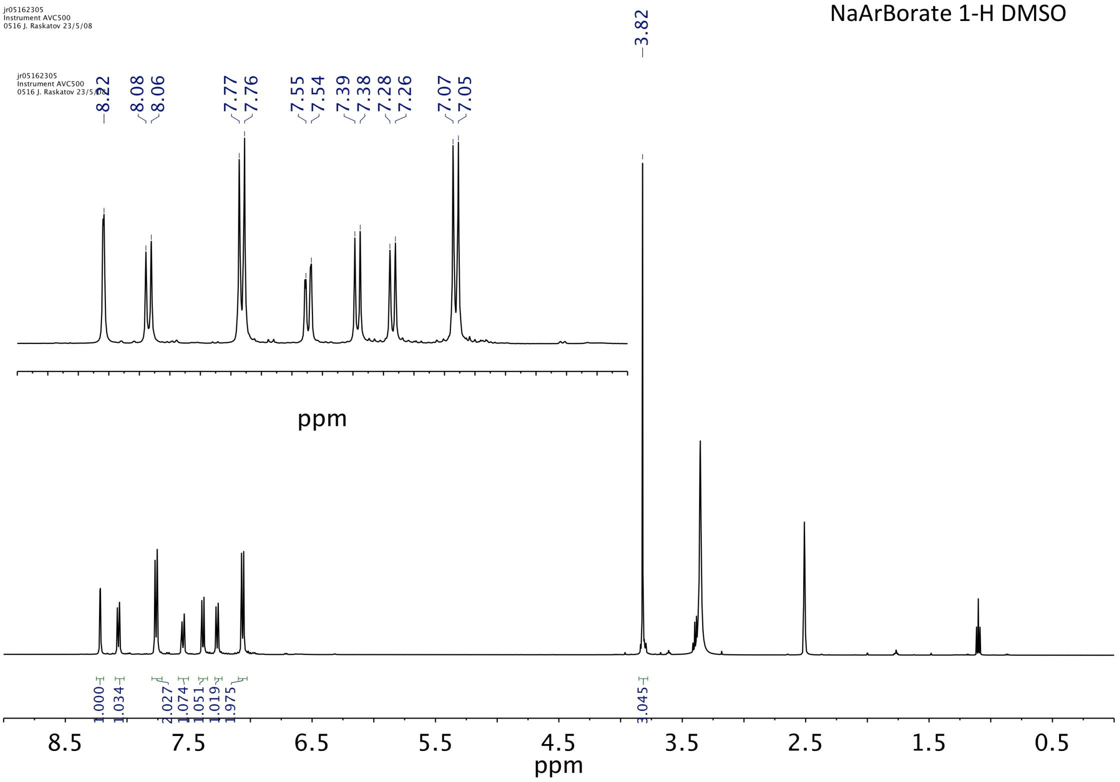

NaMeBorate 13-C DMSO

NaBrBorate 1-H DMSO

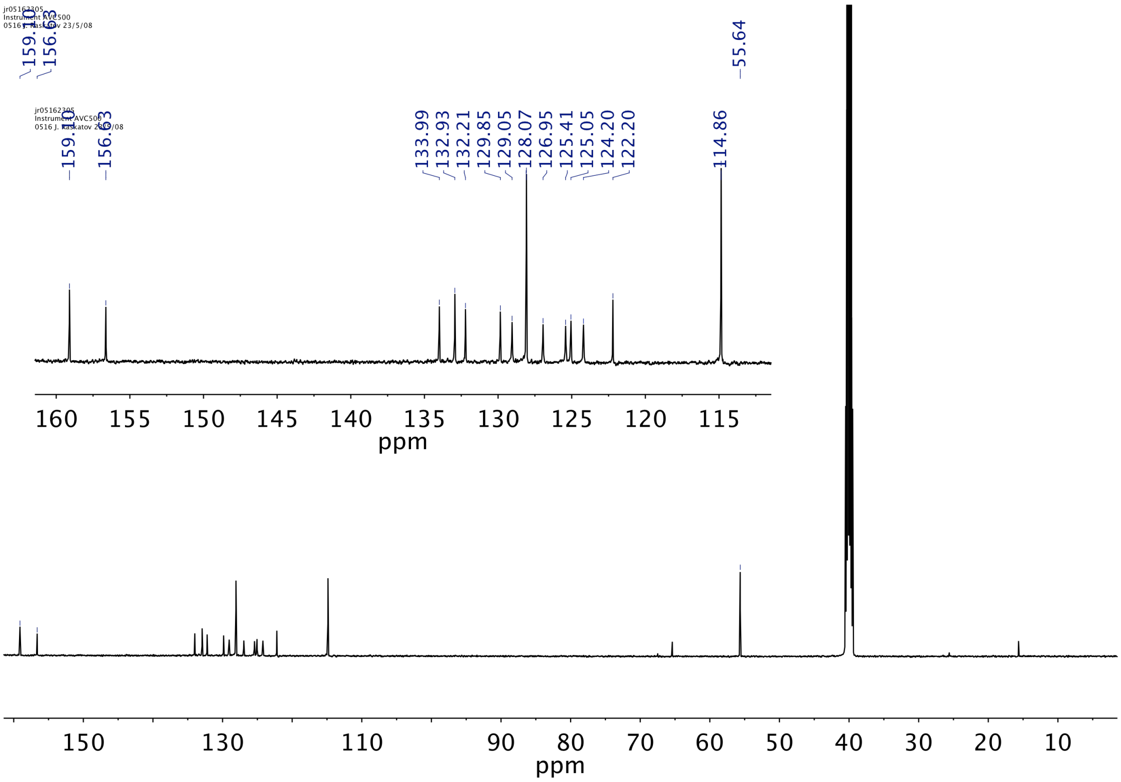


NaBrBorate 13-C DMSO





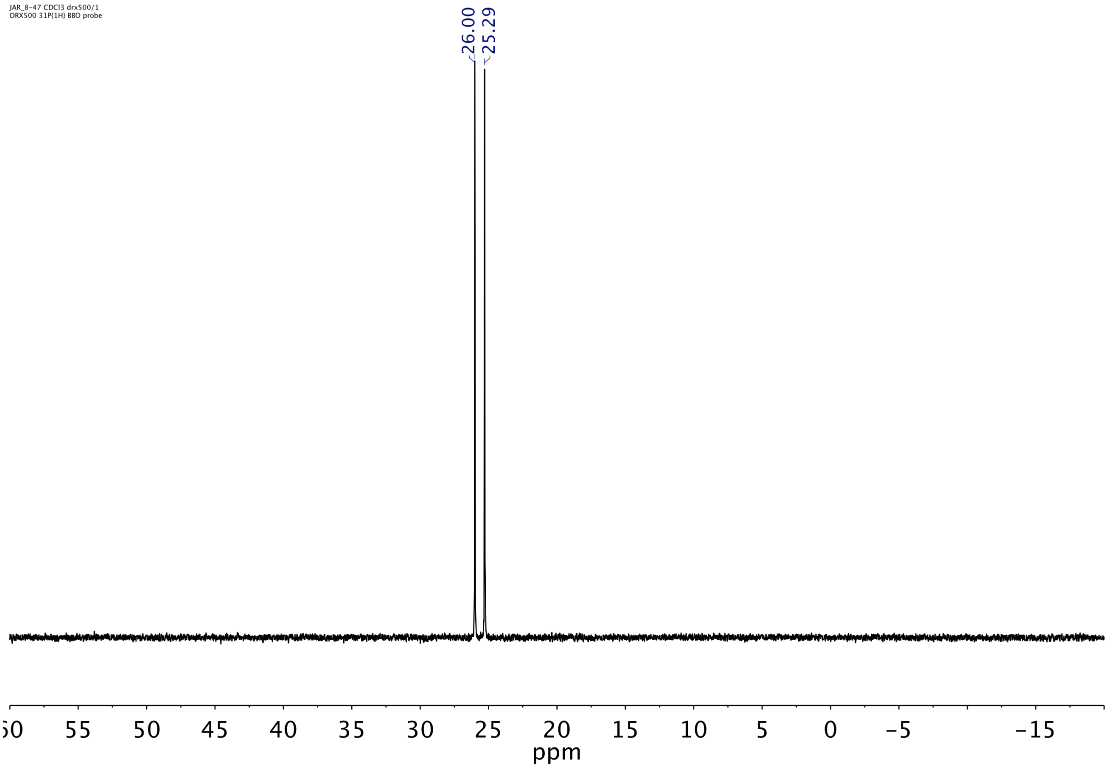
NaArBorate 1-H DMSO



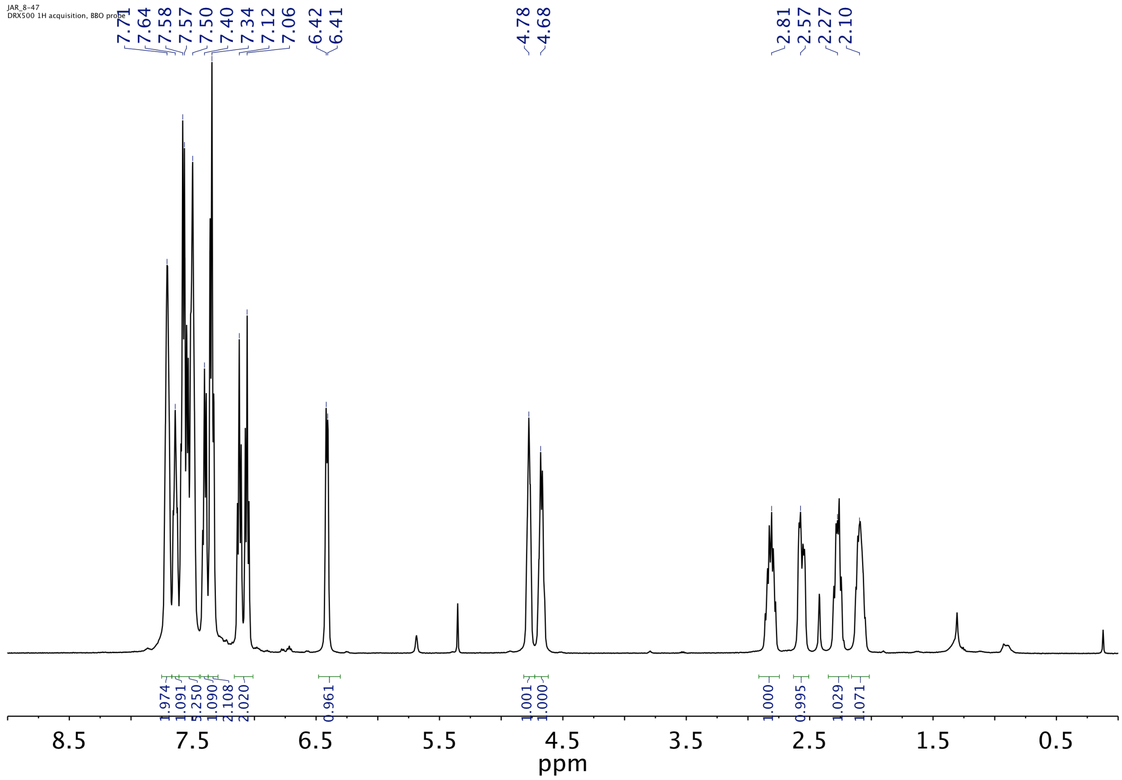
NaArBorate 13-C DMSO

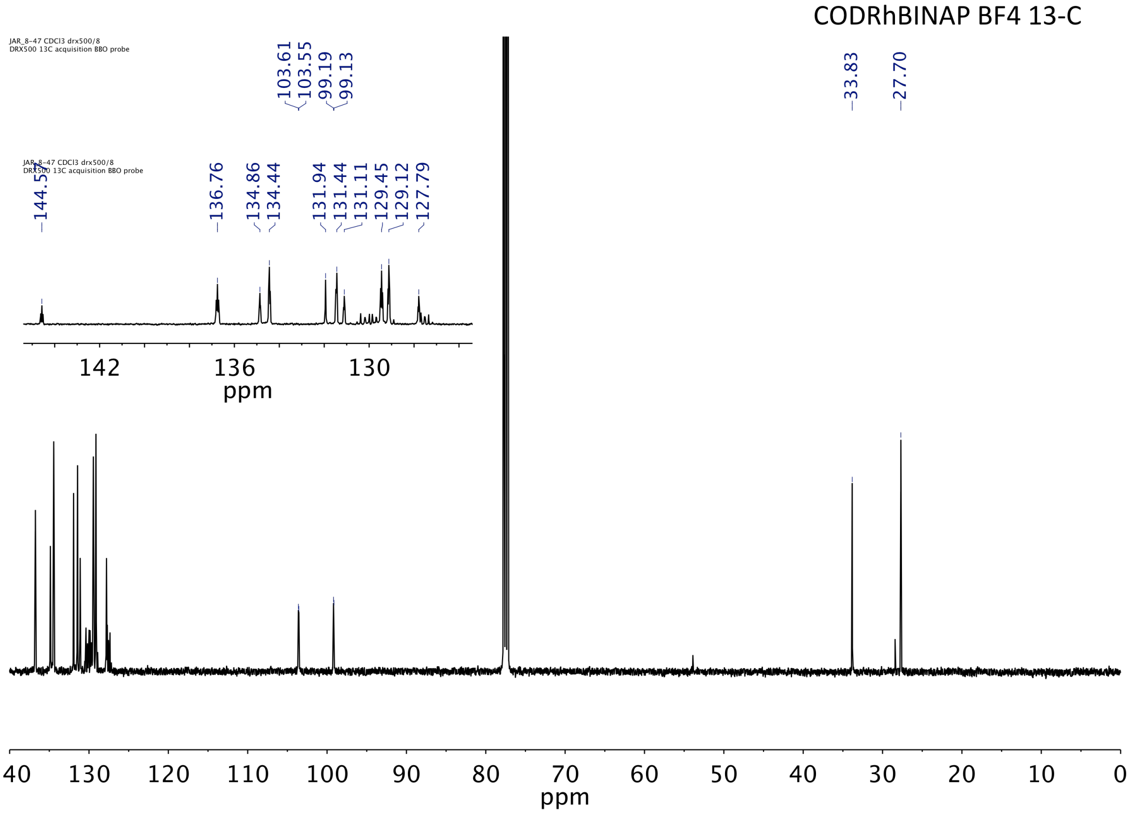
C2. BINAP cationic complexes as BF_4 salts, $CDCl_3$

CODRhBINAP BF4 31-P

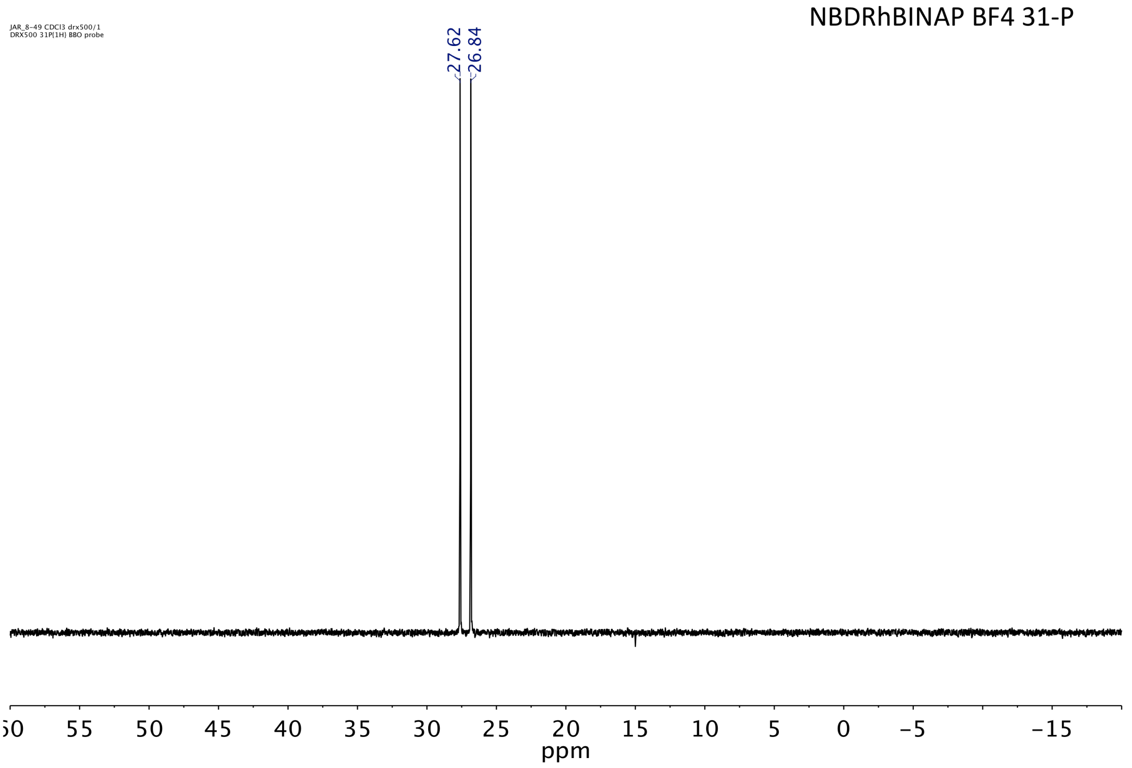


CODRhBINAP BF4 1-H



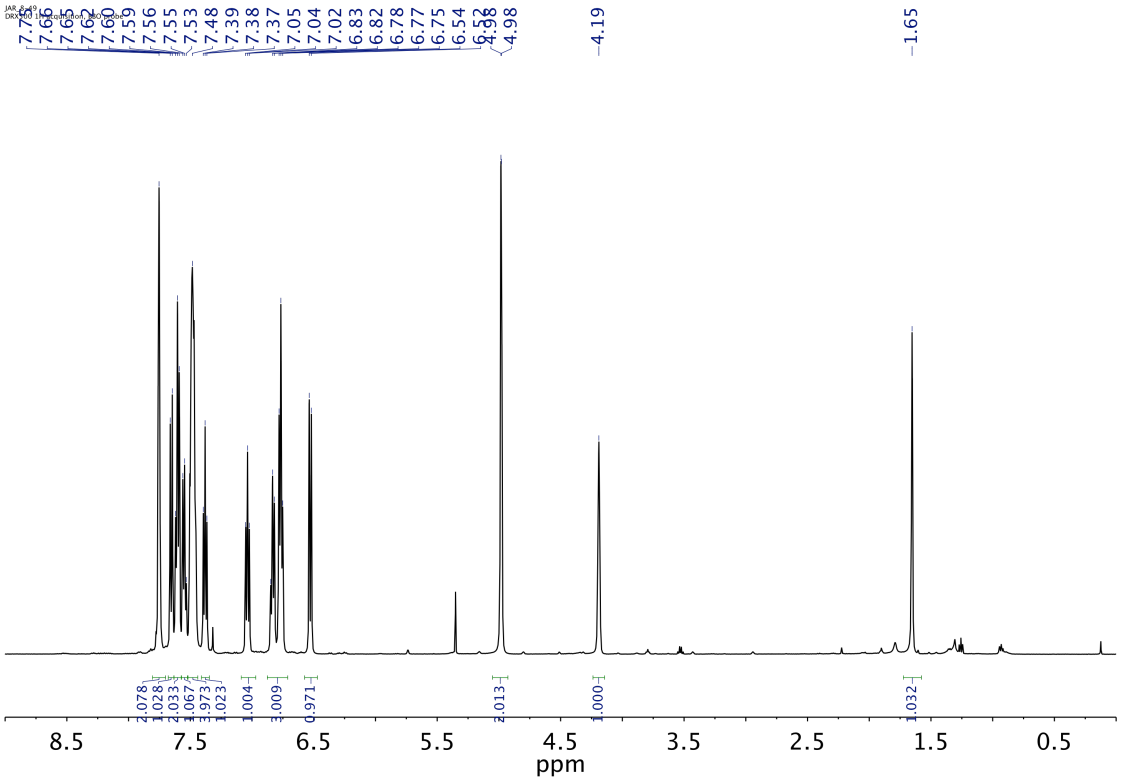


CODRhBINAP BF4 13-C

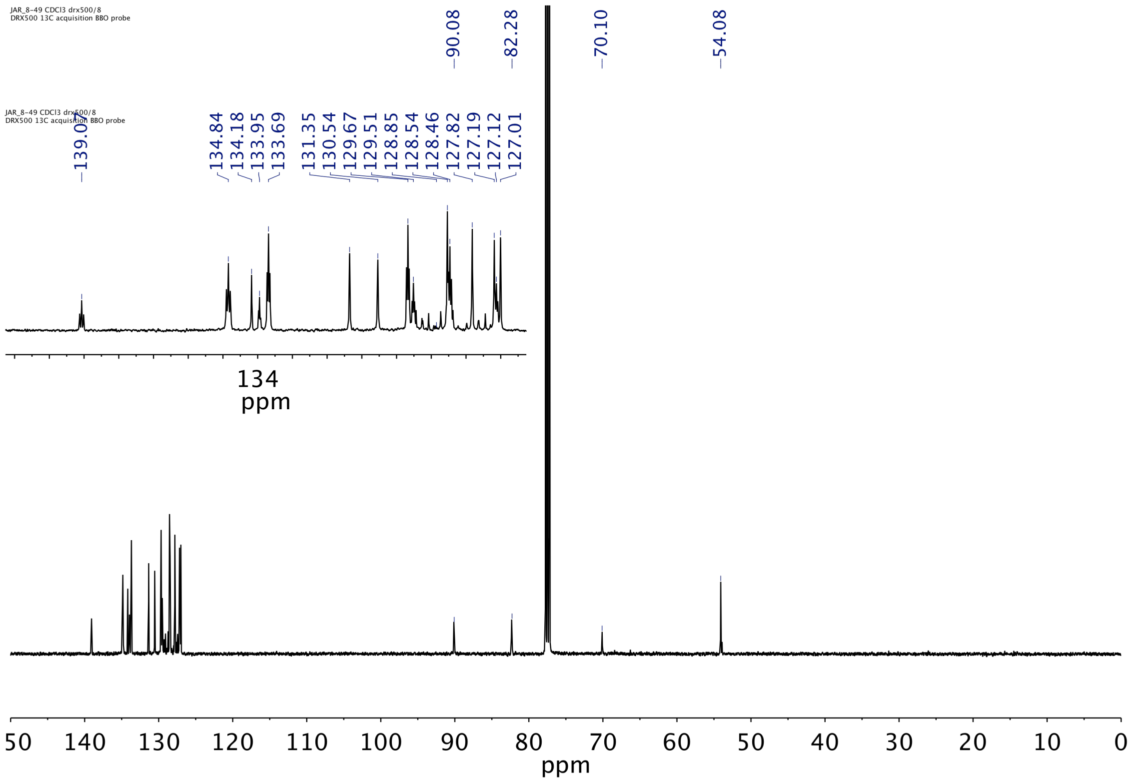


NBDRhBINAP BF4 31-P

NBDRhBINAP BF4 1H

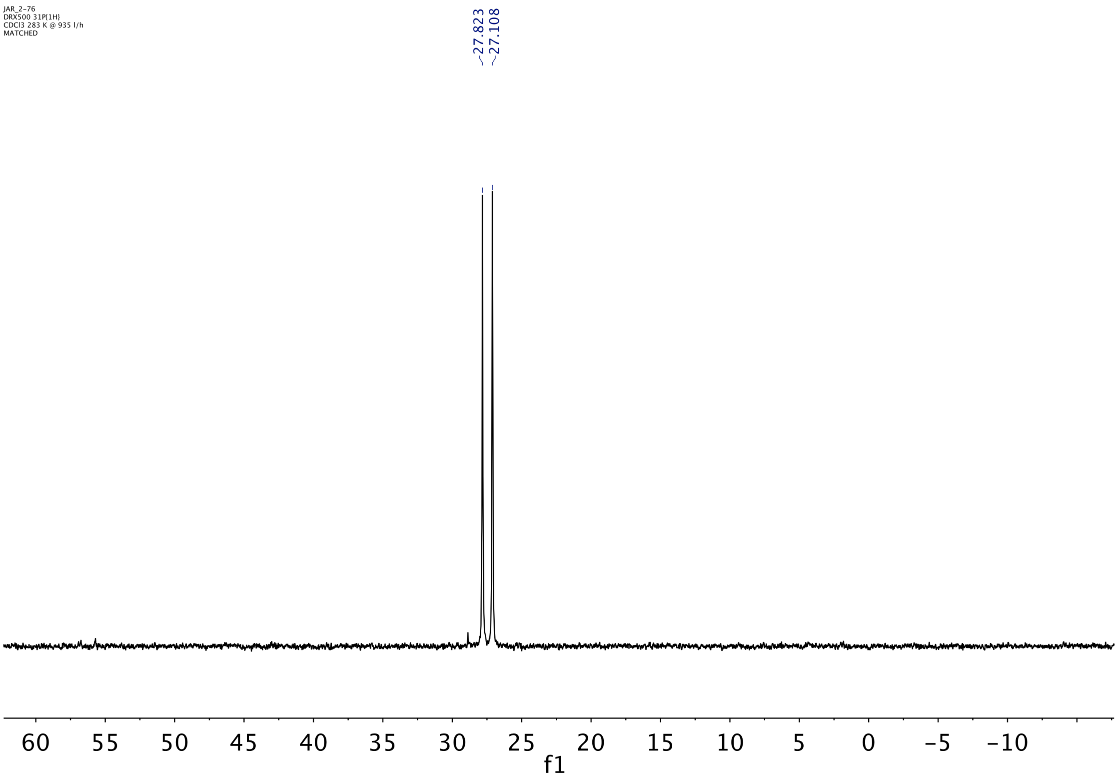


NBDRhBINAPBF4 13-C

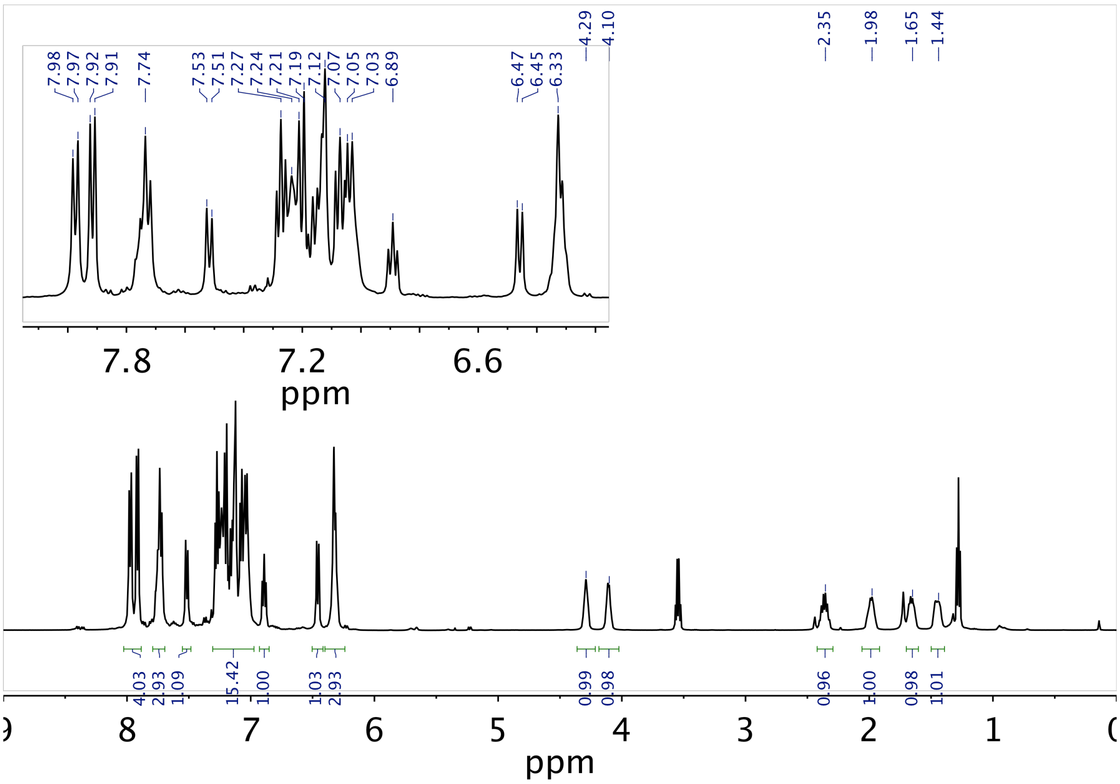


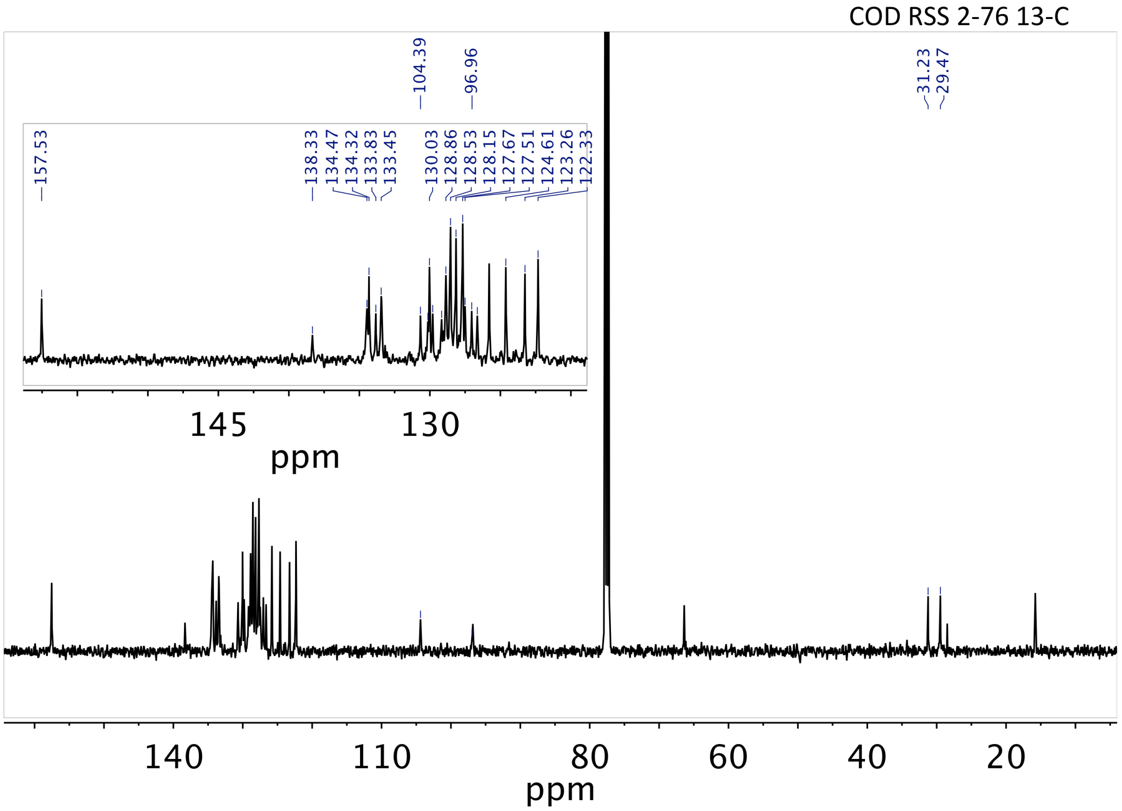
C3. Alkene BINAP Rh borate complexes

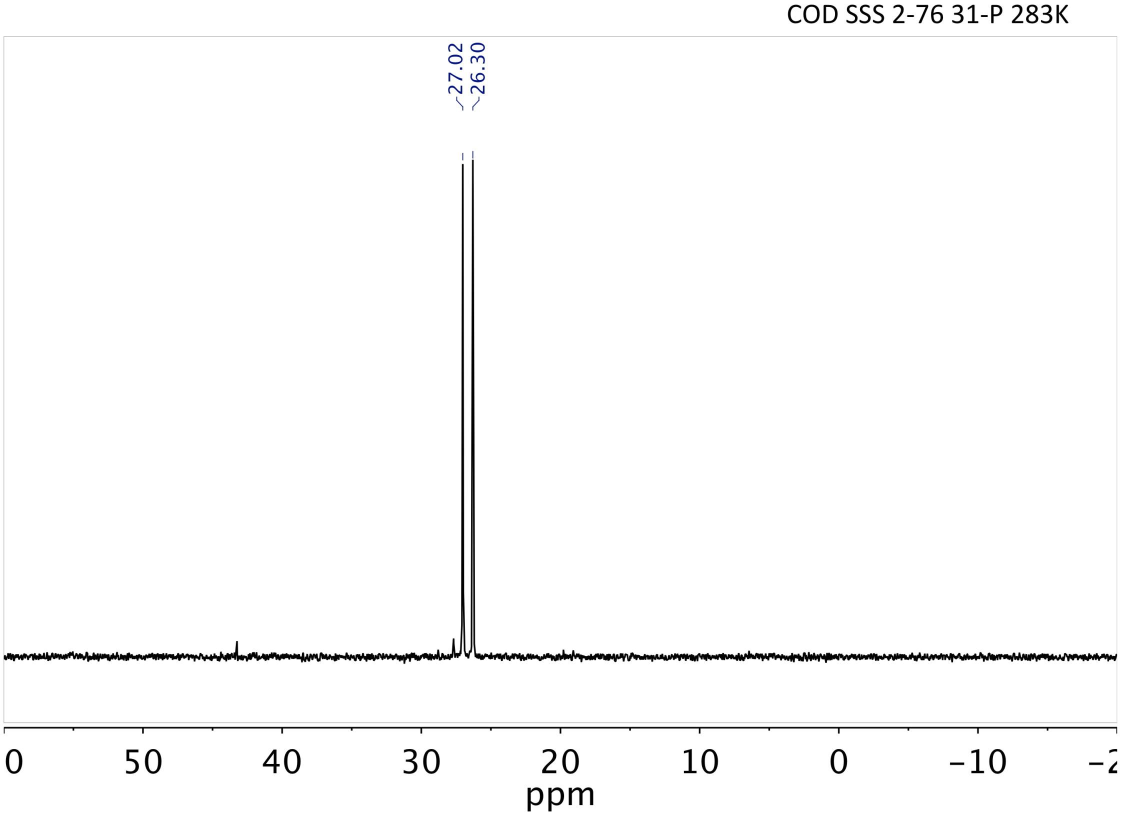
COD 6 RSS 31-P

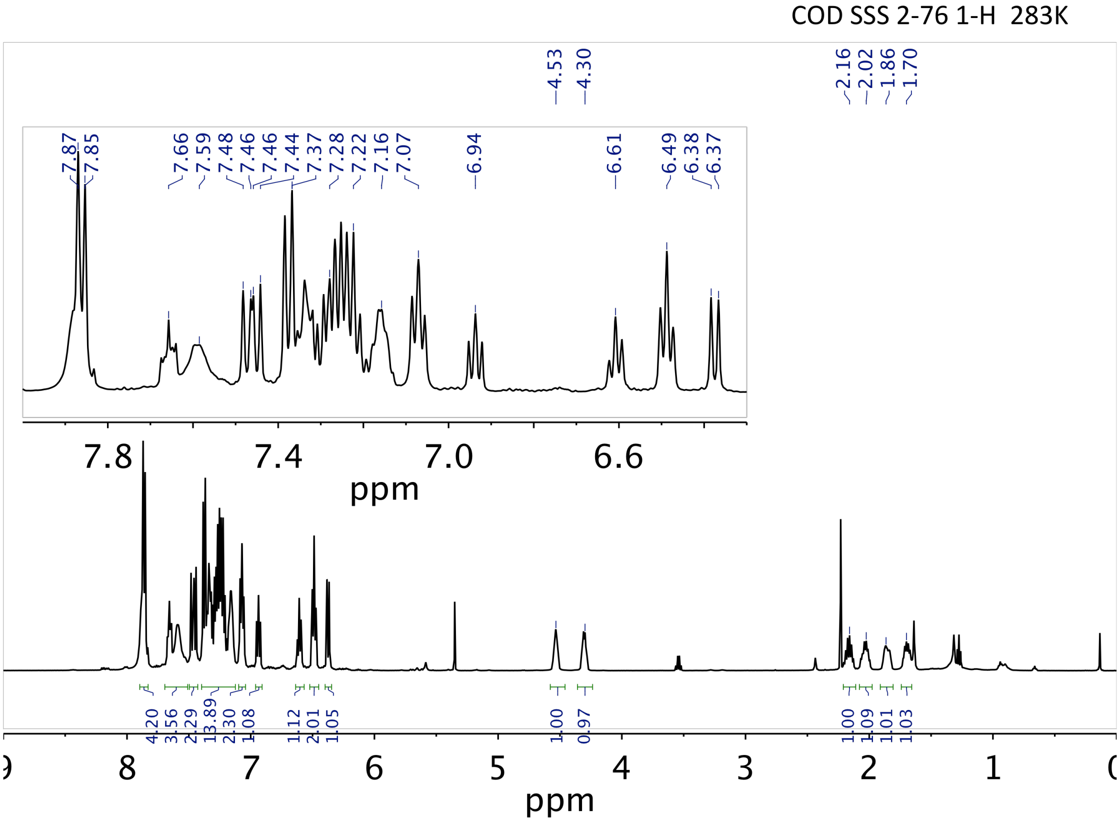


COD RSS 2-76 1H 283K

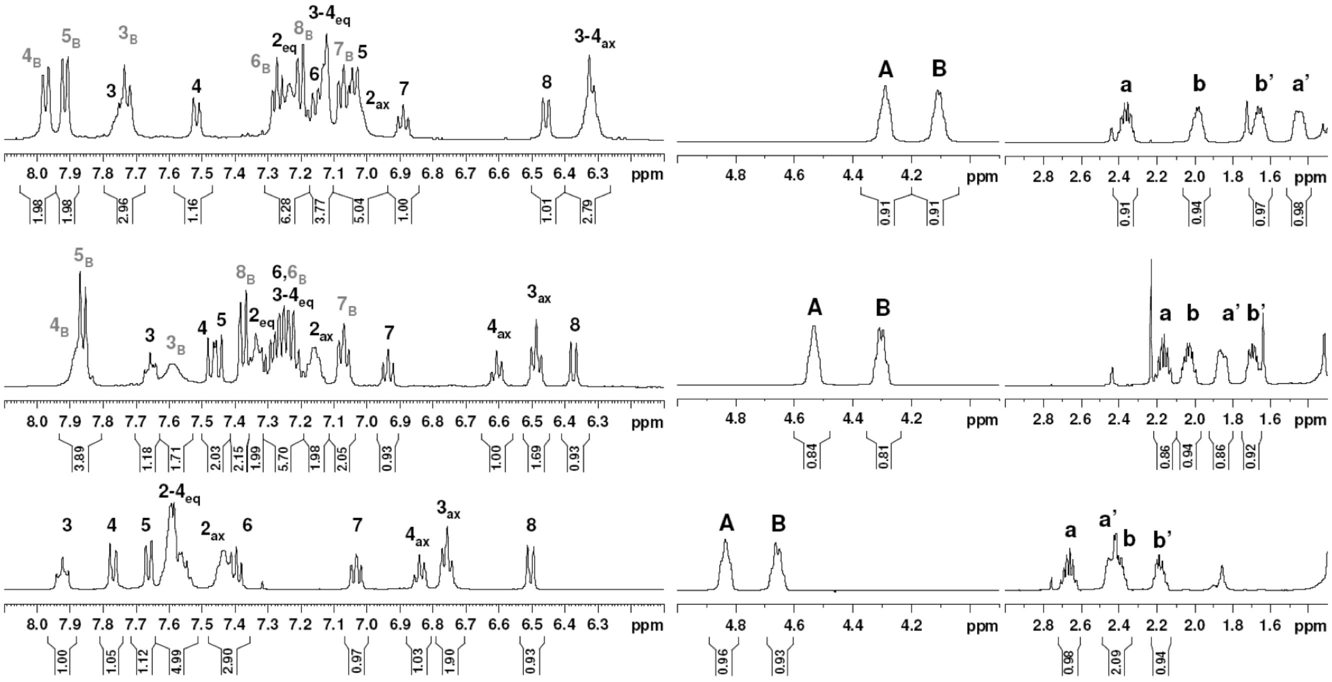



COD RSS 2-76 13-C
104.39
96.96
31.23
29.47
157.53
138.33
134.47
134.32
133.83
133.45
130.03
128.86
128.53
128.15
127.67
127.51
124.61
123.26
122.33
145
130
ppm
140
110
80
60
40
20
ppm


COD SSS 2-76 31-P 283K
27.02
26.30
0
50
40
30
20
10
0
−10
ppm

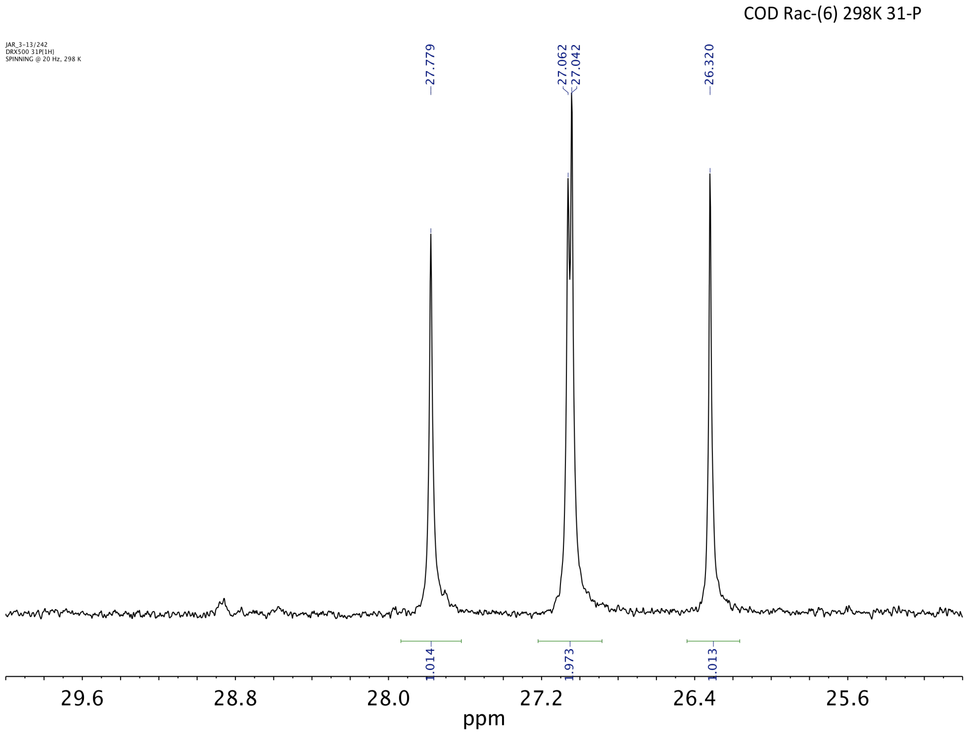


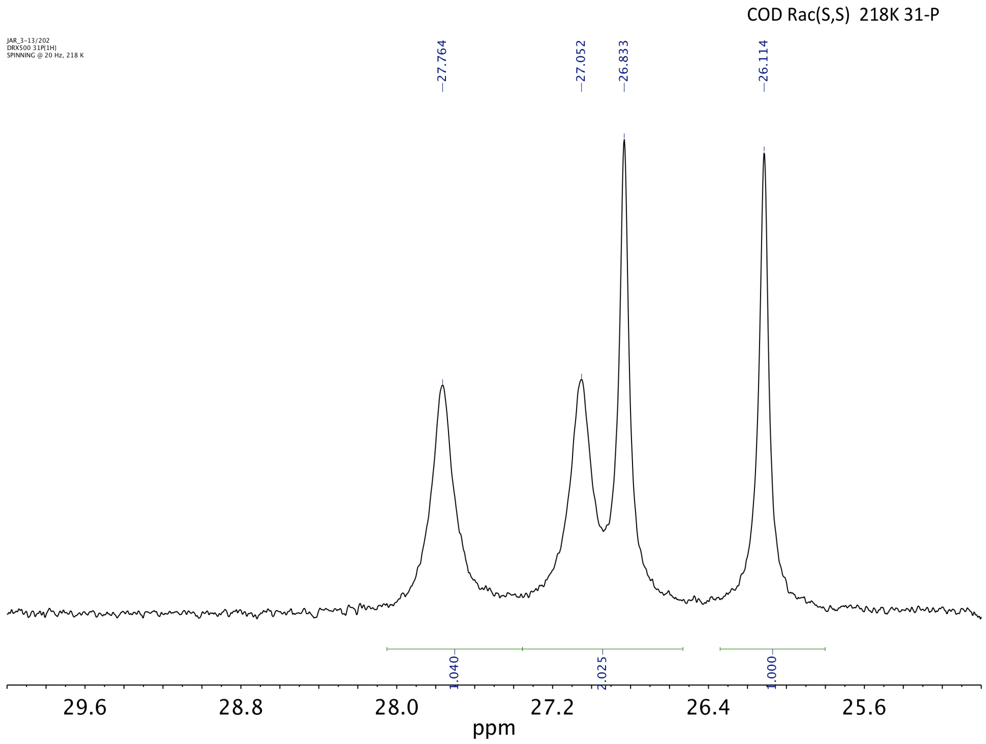
^{1}H Assignments for (COD)RhBINAP complexes, CDCl$_3$, 500 MHz. Top (R),(S,S)- **6**, middle (S),(S,S)- **6**, bottom (COD)RhBINAP.BF$_4$



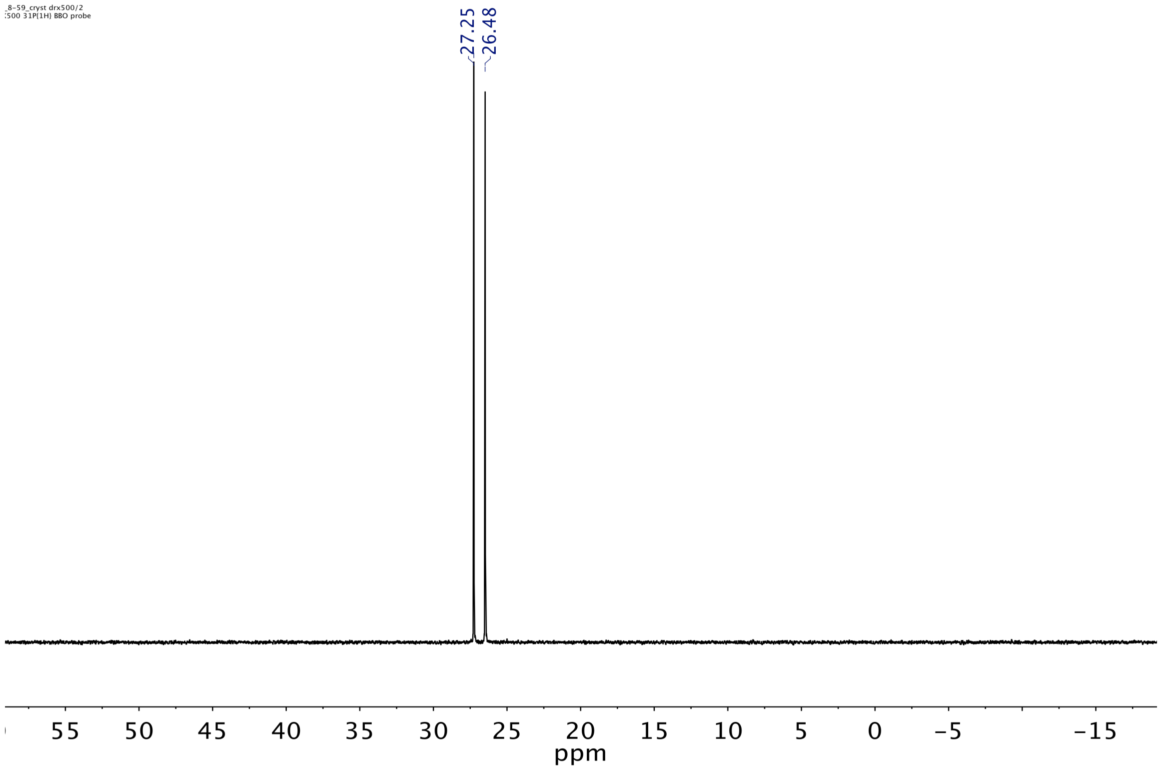
VT Comparison of *(R),(S,S)*-6 and *(S),(S,S)*-6 BINAPRh BINOLBorates (from racemic BINAP) by 31-P NMR:

***(R),(S,S)*-6** ***(S),(S,S)*-6**

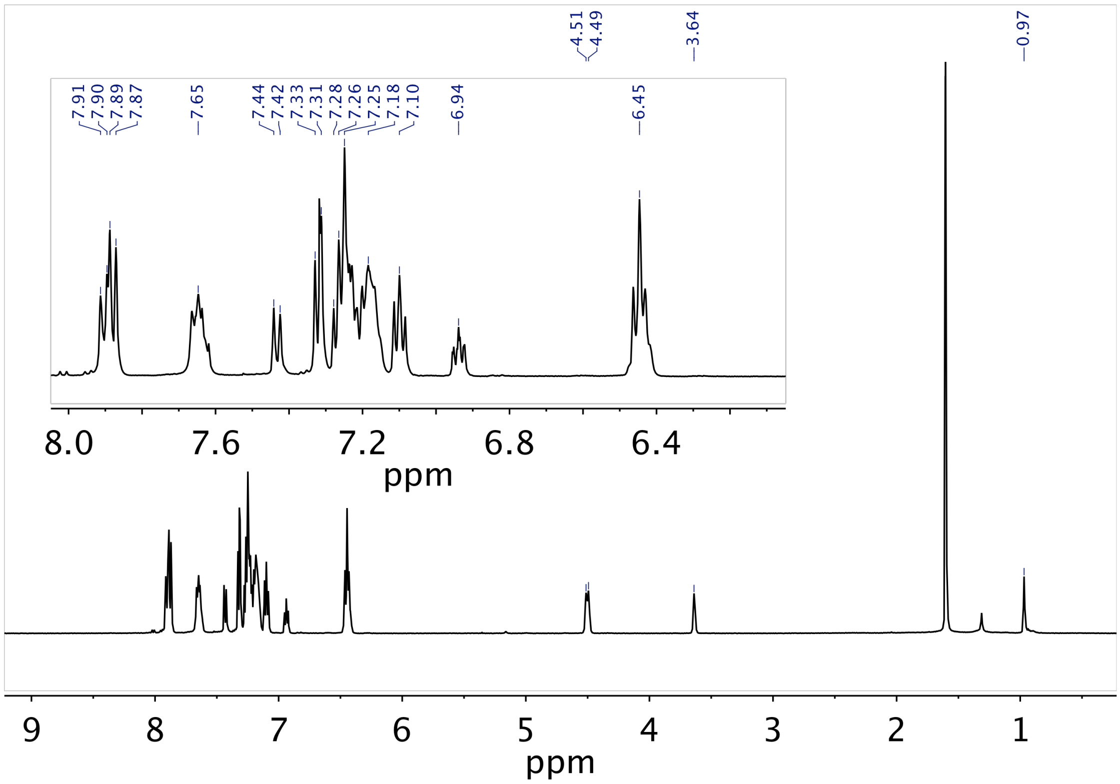


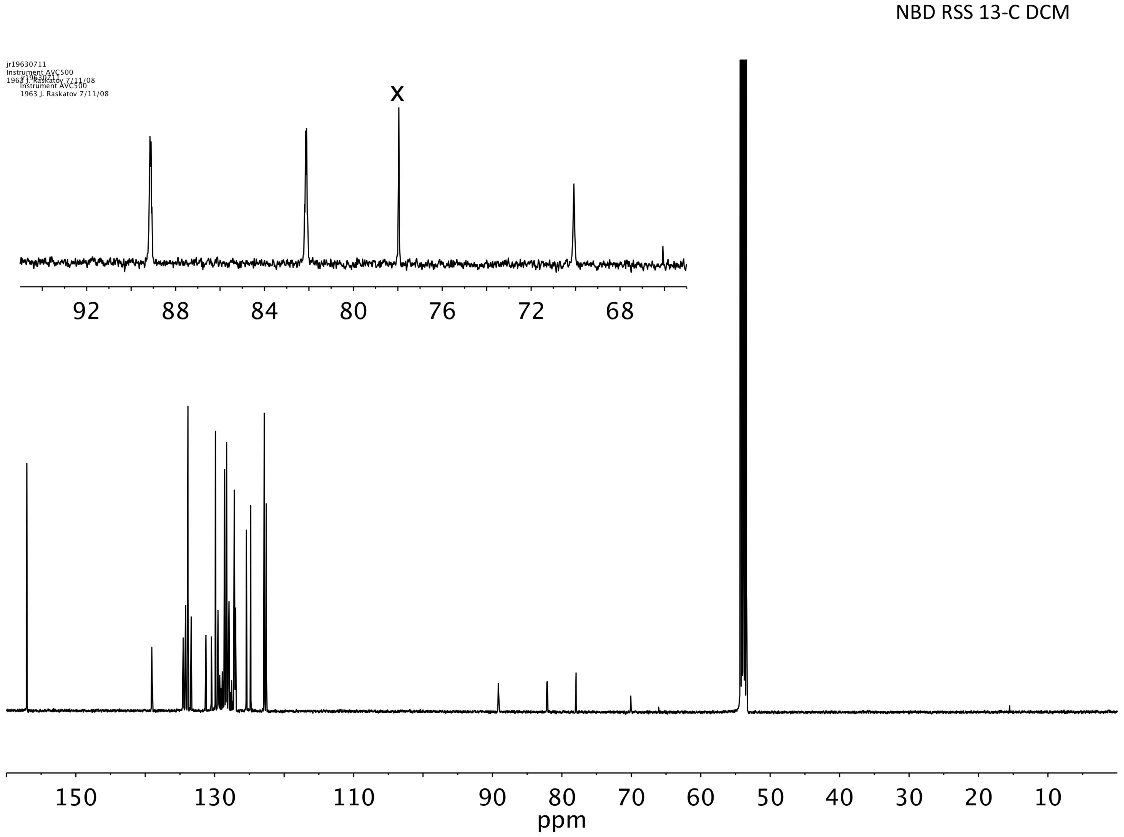


NBD RSS 31-P CHCl3

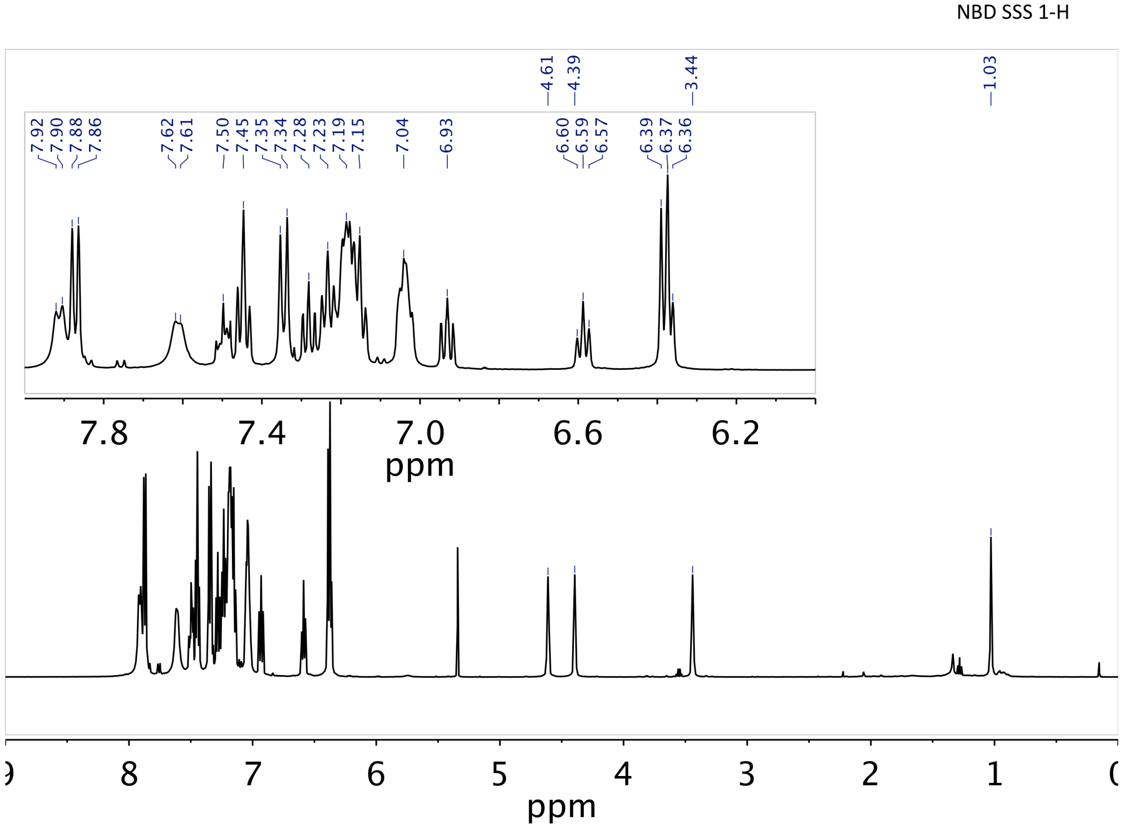


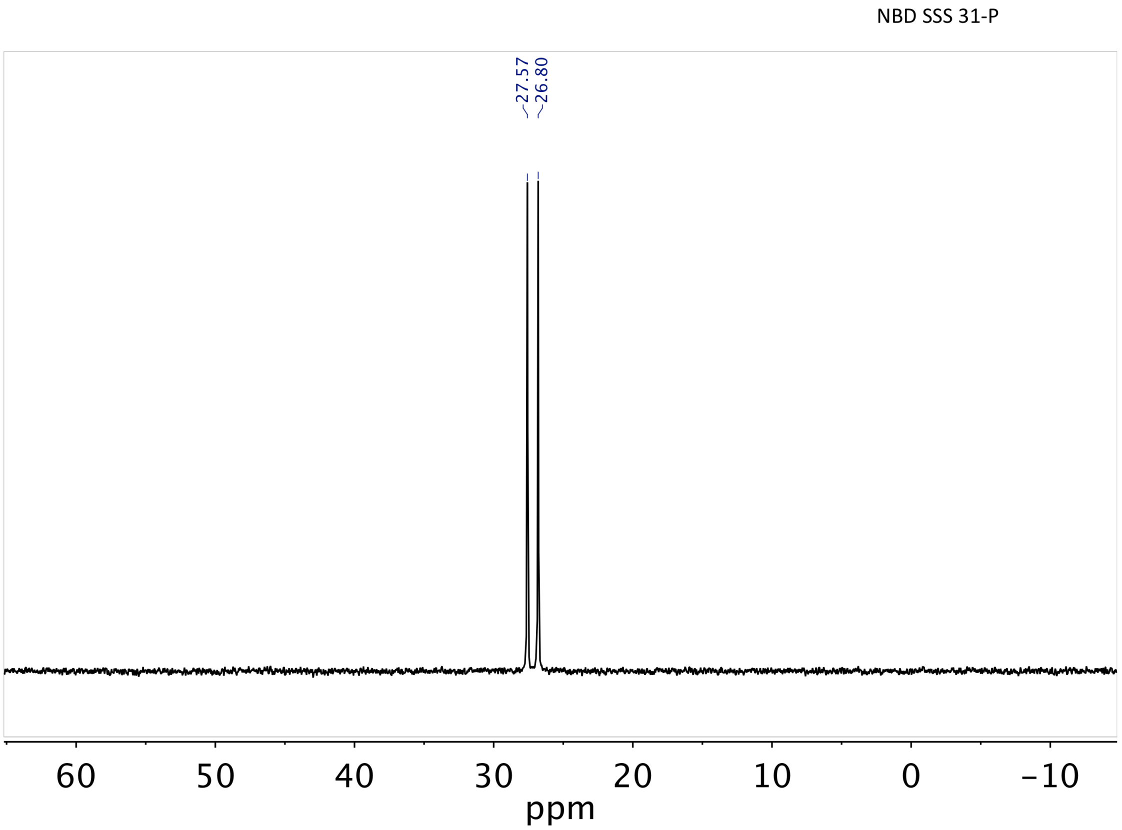
NBD RSS 1-H CHL



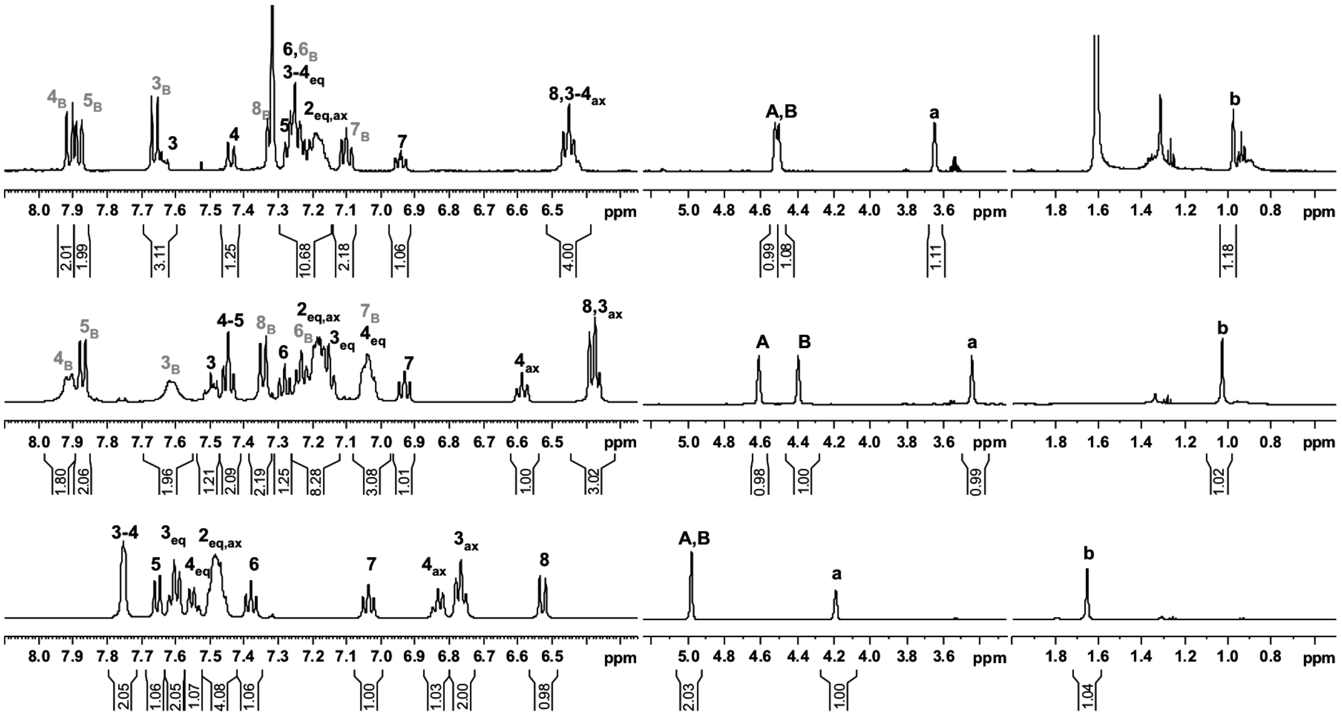


NB One $^{13}CH_2$ signal is obscured by the solvent; insufficient solubility in $CDCl_3$.





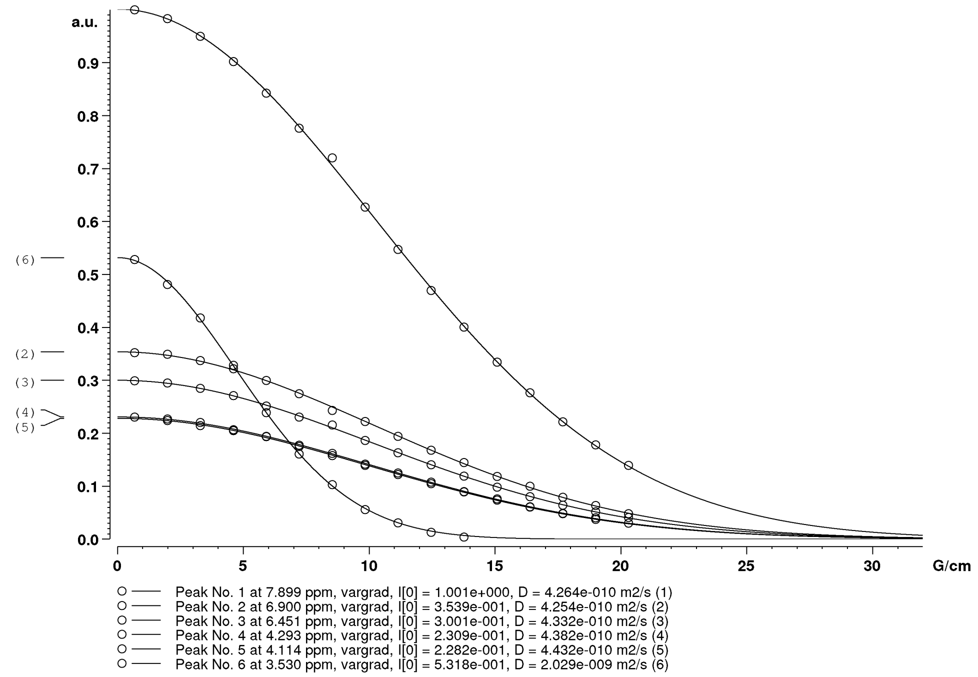
^{1}H Assignments for (NBD)RhBINAP complexes, CDCl$_3$, 500 MHz. Top (R),(S,S)- **5**, middle (S),(S,S)-**5**, bottom (NBD)RhBINAP.BF$_4$



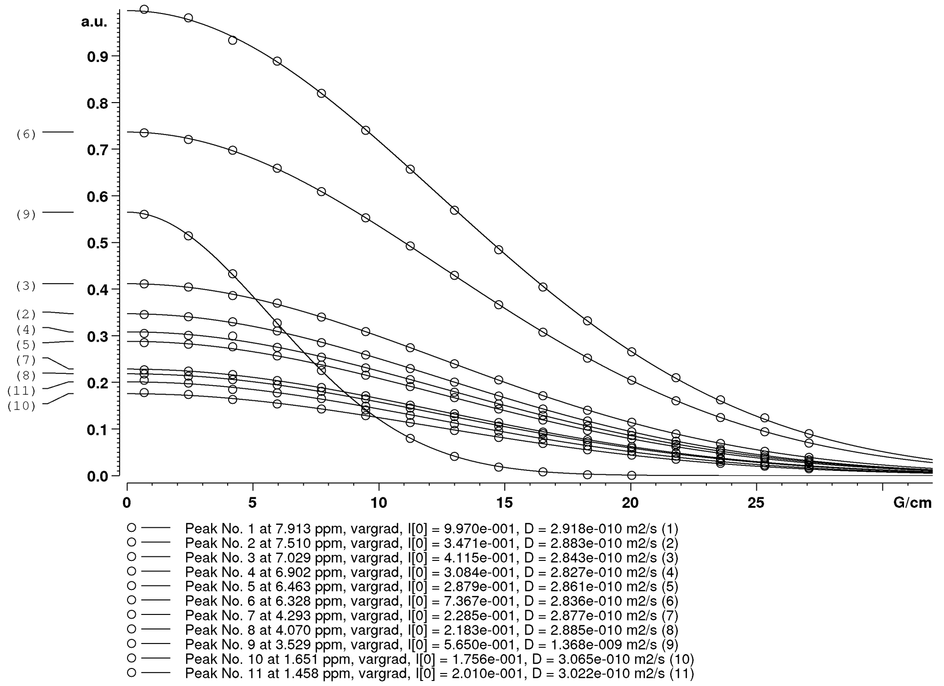
D. PGSE DOSY experiments

All diffusion experiments were performed on a Bruker DRX-500 spectrometer equipped with a tuneable multinuclear triple (TBI) resonance probe. 5 mm NMR tubes of quality appropriate for high field experiments were used in all experiments. All studies used degassed $CDCl_3$ as the NMR solvent, using 0.6 ml of the solvent for each sample. Because of the low solvent viscosity, convection complications were encountered. Different approaches to convection suppression were tested with a standard quinine sample. An efficient approach used the DSTE pulse sequence with the integrated convection suppression. Data acquisition needed to be performed with static samples, the sample spinning leading to offset values irrespective of the spinning rate. Convection suppression was also successfully achieved by spinning the NMR samples and acquiring data with the LED-BPP pulse sequence. The spinning rate had to be set to such a value that an integer number of sample rotations were completed during the diffusion time D, however. Mismatched spinning rates led to strongly offset values. Hence the DSTE pulse sequence was used, because it performed better at temperatures below 238 K. The data was analysed using the Bruker TOPSPIN software package; data for both 283 K and 258 K is shown in the following pages:

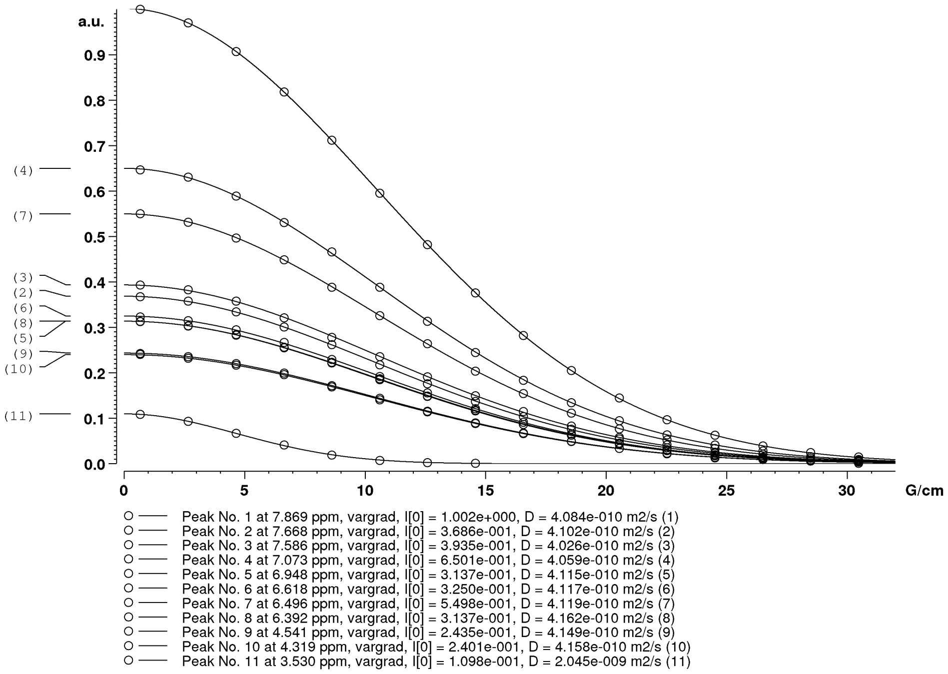
(R), (S,S)-**6**, 283 K, 0.02 M in $CDCl_3$ NB Et_2O, 3.53 ppm



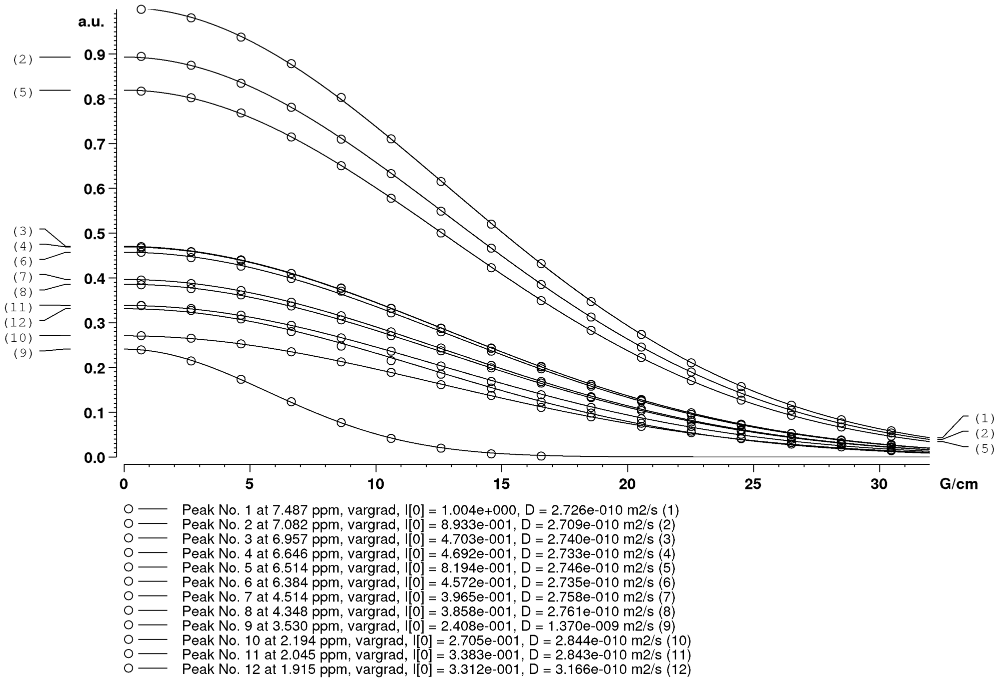
(R), (S,S)-**6**, 258 K, 0.02 M in $CDCl_3$



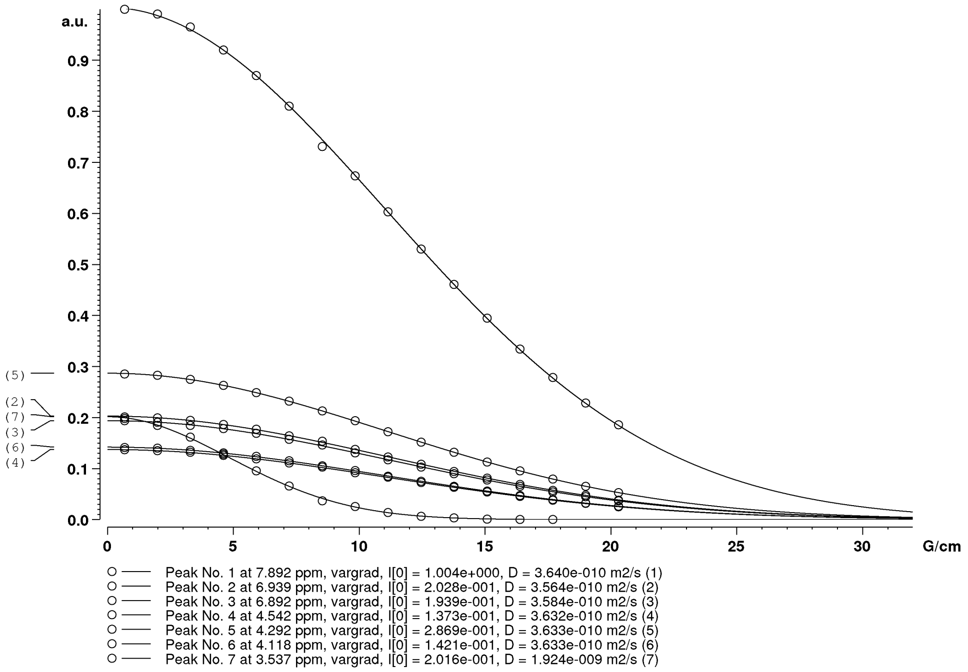
(S), (S,S)-**6**, 283 K, 0.02 M in $CDCl_3$



(S), (S,S)-**6**, 258 K, 0.02 M in $CDCl_3$

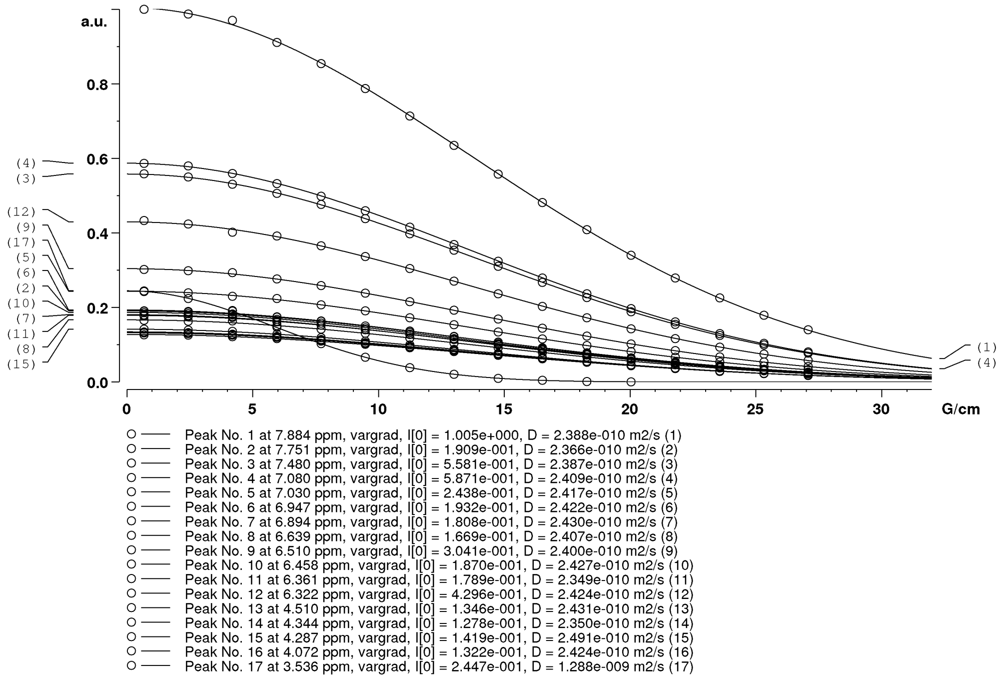


(rac), (S,S)-**6**, 283 K, 0.02 M in $CDCl_3$



○ —— Peak No. 1 at 7.892 ppm, vargrad, I[0] = 1.004e+000, D = 3.640e-010 m2/s (1)
○ —— Peak No. 2 at 6.939 ppm, vargrad, I[0] = 2.028e-001, D = 3.564e-010 m2/s (2)
○ —— Peak No. 3 at 6.892 ppm, vargrad, I[0] = 1.939e-001, D = 3.584e-010 m2/s (3)
○ —— Peak No. 4 at 4.542 ppm, vargrad, I[0] = 1.373e-001, D = 3.632e-010 m2/s (4)
○ —— Peak No. 5 at 4.292 ppm, vargrad, I[0] = 2.869e-001, D = 3.633e-010 m2/s (5)
○ —— Peak No. 6 at 4.118 ppm, vargrad, I[0] = 1.421e-001, D = 3.633e-010 m2/s (6)
○ —— Peak No. 7 at 3.537 ppm, vargrad, I[0] = 2.016e-001, D = 1.924e-009 m2/s (7)

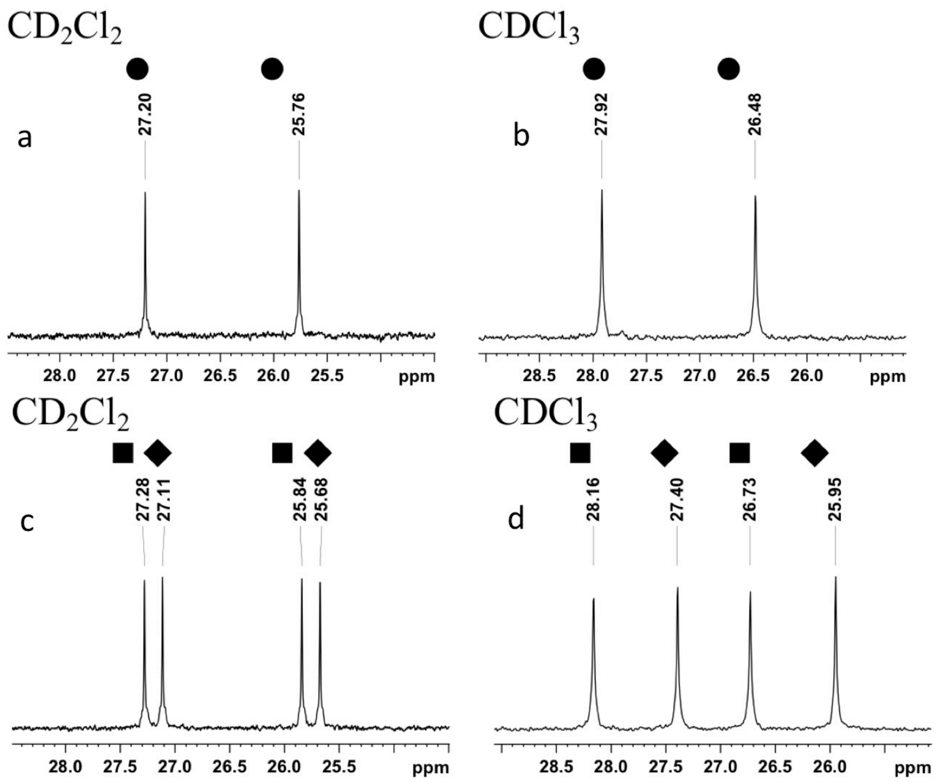
(rac), (S,S)-**6**, 258 K, 0.02 M in $CDCl_3$



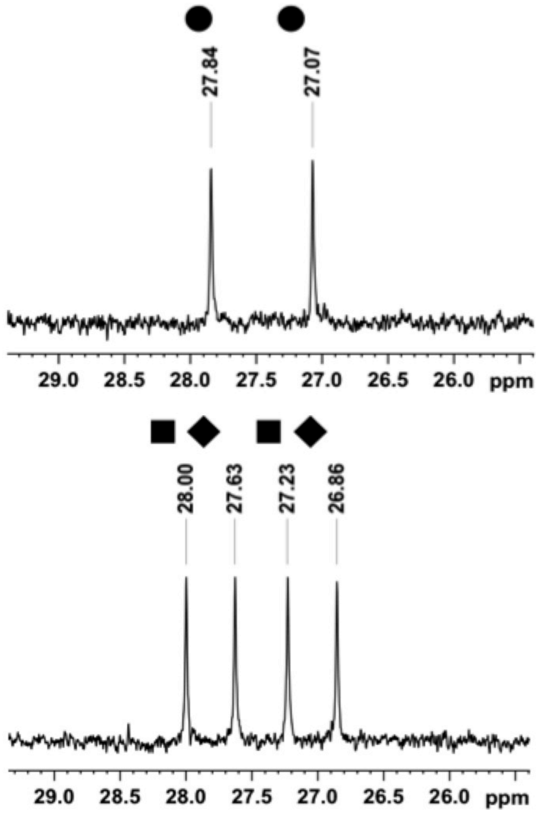
○ —— Peak No. 1 at 7.884 ppm, vargrad, I[0] = 1.005e+000, D = 2.388e-010 m2/s (1)
○ —— Peak No. 2 at 7.751 ppm, vargrad, I[0] = 1.909e-001, D = 2.366e-010 m2/s (2)
○ —— Peak No. 3 at 7.480 ppm, vargrad, I[0] = 5.581e-001, D = 2.387e-010 m2/s (3)
○ —— Peak No. 4 at 7.080 ppm, vargrad, I[0] = 5.871e-001, D = 2.409e-010 m2/s (4)
○ —— Peak No. 5 at 7.030 ppm, vargrad, I[0] = 2.438e-001, D = 2.417e-010 m2/s (5)
○ —— Peak No. 6 at 6.947 ppm, vargrad, I[0] = 1.932e-001, D = 2.422e-010 m2/s (6)
○ —— Peak No. 7 at 6.894 ppm, vargrad, I[0] = 1.808e-001, D = 2.430e-010 m2/s (7)
○ —— Peak No. 8 at 6.639 ppm, vargrad, I[0] = 1.669e-001, D = 2.407e-010 m2/s (8)
○ —— Peak No. 9 at 6.510 ppm, vargrad, I[0] = 3.041e-001, D = 2.400e-010 m2/s (9)
○ —— Peak No. 10 at 6.458 ppm, vargrad, I[0] = 1.870e-001, D = 2.427e-010 m2/s (10)
○ —— Peak No. 11 at 6.361 ppm, vargrad, I[0] = 1.789e-001, D = 2.349e-010 m2/s (11)
○ —— Peak No. 12 at 6.322 ppm, vargrad, I[0] = 4.296e-001, D = 2.424e-010 m2/s (12)
○ —— Peak No. 13 at 4.510 ppm, vargrad, I[0] = 1.346e-001, D = 2.431e-010 m2/s (13)
○ —— Peak No. 14 at 4.344 ppm, vargrad, I[0] = 1.278e-001, D = 2.350e-010 m2/s (14)
○ —— Peak No. 15 at 4.287 ppm, vargrad, I[0] = 1.419e-001, D = 2.491e-010 m2/s (15)
○ —— Peak No. 16 at 4.072 ppm, vargrad, I[0] = 1.322e-001, D = 2.424e-010 m2/s (16)
○ —— Peak No. 17 at 3.536 ppm, vargrad, I[0] = 2.447e-001, D = 1.288e-009 m2/s (17)

E. Experiments for Chiral Discrimination in Solution

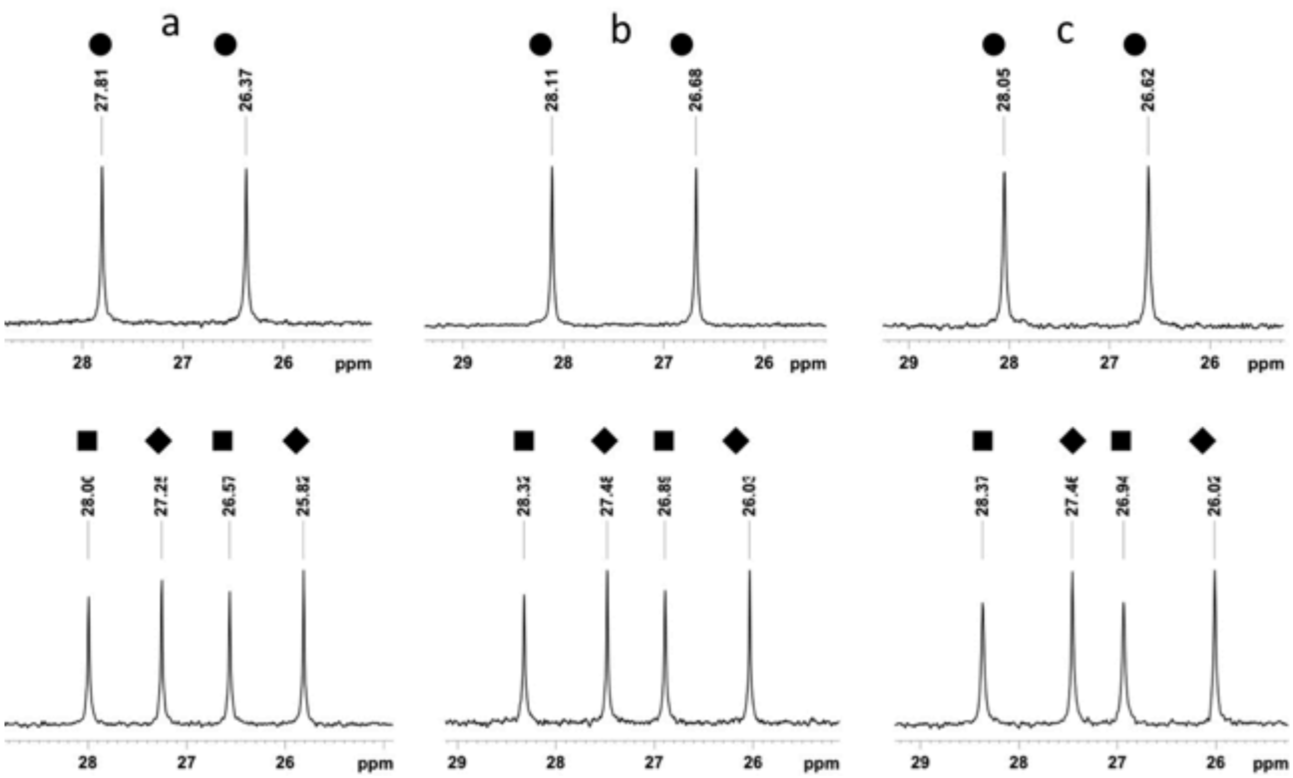
COD complex chiral shift comparison; ^{31}P NMR in $CDCl_3$ vs. CD_2Cl_2; a, b: (*rac*),(*rac*)-**6**, c,d *(rac),(S,S)*-**6**.



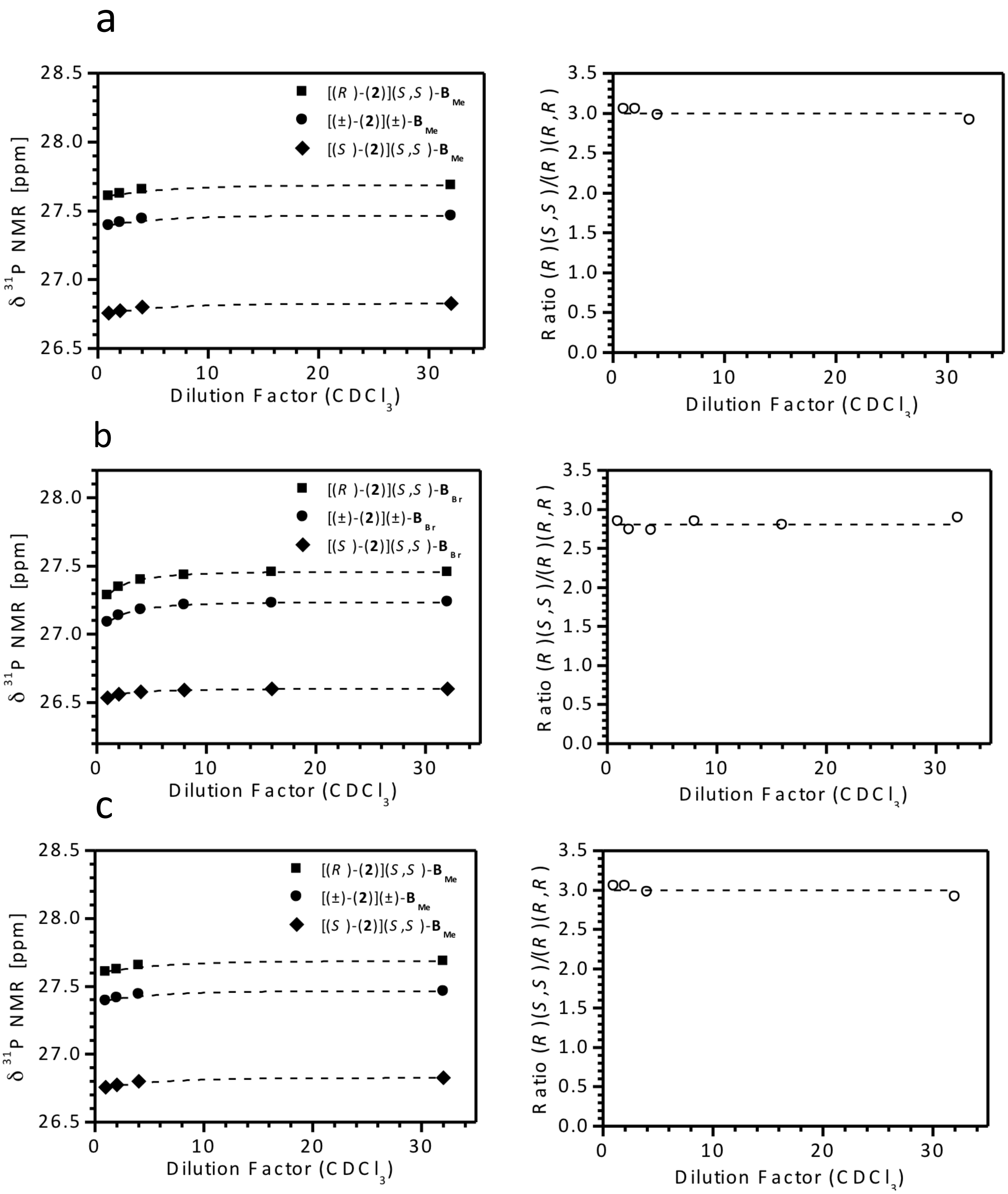
NBD complex chiral shift; ^{31}P NMR in $CDCl_3$ for: (*rac*),(*rac*)-5 (above) *(rac),(S,S)*-5 (below).



Chiral solvation of **[(±)-(7b)](*S*,*S*)-**B$_{\text{Br}}$ (a), **[(±)-(7a)](*S*,*S*)-**B$_{\text{Me}}$ (b) and **[(±)-(7c)](*S*,*S*)-**B$_{\text{pOMePh}}$ (c); homochiral ion pairs shown as ◆ heterochiral as ■ (^{31}P NMR, 101 MHz, 298 K).



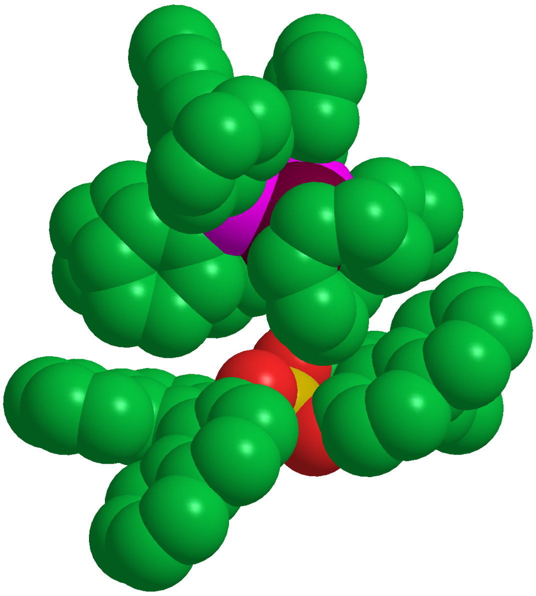
Dilution experiments **(7a)** (a), **(7b)** (b) and **(7c)** (c); ^{31}P NMR, 101 MHz; see text of MS.



F. DFT calculations on *(R),(S,S)*- and *(S),(S,S)*-6

(*R*)-(2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl)(1,5-cyclooctadiene) rhodium (I) bis-(*S*)-(2,2')-binaphtholatoborate; [(*R*)-(6)](*S*,*S*)-B_H

Zero-point correction= 1.341460 (Hartree/Particle)
Thermal correction to Energy= 1.421738
Thermal correction to Enthalpy= 1.422683
Thermal correction to Gibbs Free Energy= 1.222306
Sum of electronic and zero-point Energies= -4664.624997
Sum of electronic and thermal Energies= -4664.544718
Sum of electronic and thermal Enthalpies= -4664.543774
Sum of electronic and thermal Free Energies= -4664.744150
DFTD3 dispersion correction -0.033789 au
Corrected ZPE= -4464.658786 **E_{rel} = 0 Kcal.mol^{-1}**



***(R),(S,S)*-6**

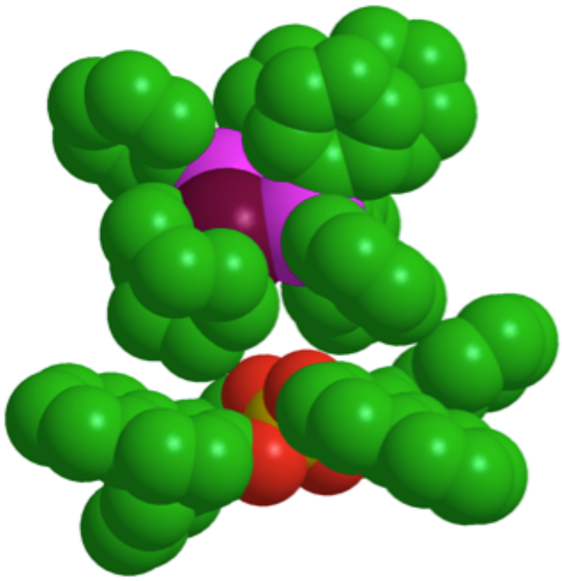
C	2.506400	5.518800	3.323500
C	3.102600	4.493900	2.541300
C	2.792500	4.395100	1.141100
C	1.840100	5.316500	0.615800
C	1.264600	6.288600	1.406100
C	1.607800	6.406200	2.774100
C	3.404400	3.367500	0.340800
C	4.159300	2.380200	0.985400
C	4.479700	2.505300	2.367300
C	3.988700	3.543500	3.117600
O	4.661500	1.320200	0.334700
B	3.784700	0.343700	-0.327900
O	4.663900	-0.321500	-1.298400
C	4.435300	-1.567500	-1.737500
C	4.387000	-2.674700	-0.881000
C	4.039700	-3.957200	-1.434100
C	3.910800	-4.115000	-2.856900
C	4.086700	-2.978900	-3.692500
C	4.314300	-1.741200	-3.146200
C	3.592300	-5.389500	-3.398900
C	3.369900	-6.478000	-2.585500
C	3.455200	-6.323000	-1.181500
C	3.780800	-5.103700	-0.625600
C	3.260000	3.301600	-1.140900
C	3.586300	4.409500	-2.001800
C	3.368300	4.300800	-3.418200
C	2.883500	3.076600	-3.950700
C	2.662600	1.999100	-3.129400
C	2.865000	2.097900	-1.726700
C	3.671500	5.401600	-4.264100
C	4.203000	6.565300	-3.757000
C	4.466300	6.662200	-2.370300
C	4.168500	5.618300	-1.521600
O	2.618700	0.996100	-0.974900

C	4.671200	-2.481000	0.568400
C	4.007800	-1.463500	1.256100
C	4.168000	-1.308300	2.659400
C	5.017100	-2.121400	3.366000
C	5.799500	-3.100200	2.698400
C	5.647600	-3.266400	1.280000
C	6.747800	-3.889500	3.402400
C	7.553900	-4.790300	2.744600
C	7.445500	-4.923500	1.340500
C	6.522100	-4.185700	0.631900
O	3.165400	-0.613400	0.616900
H	5.128700	1.746700	2.794300
H	4.250100	3.636700	4.169900
H	4.396000	5.707600	-0.466200
H	4.918500	7.566200	-1.970000
H	4.438700	7.396700	-4.416100
H	3.490300	5.297100	-5.332200
H	2.728800	2.993900	-5.024700
H	2.336000	1.042500	-3.525900
H	3.845700	-5.008500	0.452200
H	3.269500	-7.176000	-0.532900
H	3.127500	-7.447000	-3.014000
H	3.522300	-5.486300	-4.480900
H	4.017600	-3.102000	-4.771600
H	4.428200	-0.855900	-3.764600
H	6.467700	-4.291200	-0.445100
H	8.103700	-5.608700	0.812200
H	8.281500	-5.382400	3.293700
H	6.835600	-3.753100	4.478400
H	5.130800	-2.001000	4.441400
H	3.607400	-0.516100	3.146200
H	1.556800	5.237500	-0.427300
H	0.538100	6.970900	0.971400
H	1.159500	7.186000	3.384600
H	2.772500	5.584200	4.376900
C	-0.427700	-0.038400	-1.574100
C	-1.843300	-0.046500	-1.393200
C	-2.573700	-1.189800	-1.718000
C	-1.912900	-2.294600	-2.370800
C	-0.504000	-2.222000	-2.623900
C	0.218000	-1.089200	-2.173500
C	-2.593100	-3.484500	-2.759700
C	-1.925600	-4.514300	-3.386800
C	-0.538400	-4.426400	-3.646200
C	0.157500	-3.302700	-3.264200
C	-4.008200	-1.371900	-1.318900
C	-4.358600	-1.598800	0.017700
C	-5.704000	-1.941200	0.330700
C	-6.674700	-2.009600	-0.639200
C	-6.373200	-1.718900	-1.990800
C	-5.020300	-1.403800	-2.337500
C	-4.730500	-1.110000	-3.701100
C	-5.720300	-1.128200	-4.658200
C	-7.054900	-1.449200	-4.309400
C	-7.371000	-1.739300	-3.002500
P	-3.114800	-1.382300	1.405600
C	-4.037200	-1.952000	2.910300
C	-3.667500	-3.091400	3.638700
C	-4.343200	-3.435100	4.814300
C	-5.399100	-2.651600	5.276900
C	-5.774500	-1.509200	4.563500
C	-5.092300	-1.157500	3.400200
P	-2.520800	1.366100	-0.415400
C	-4.306600	1.666800	-0.776000
C	-5.212100	1.788800	0.286400
C	-6.537100	2.163200	0.049300
C	-6.966800	2.420700	-1.252600
C	-6.067500	2.309900	-2.317000
C	-4.743800	1.944800	-2.080500
C	-1.866100	-2.694400	1.089400
C	-2.261300	-4.007200	0.776200
C	-1.301600	-4.986000	0.524100
C	0.059100	-4.665800	0.565700
C	0.460000	-3.364600	0.868700
C	-0.498900	-2.384200	1.133000
C	-1.853700	2.937300	-1.150500
C	-2.363900	4.133900	-0.609600
C	-1.966700	5.372400	-1.107900
C	-1.050100	5.442700	-2.160200
C	-0.549600	4.266300	-2.714700
C	-0.951700	3.021600	-2.220500
Rh	-2.037100	0.766100	1.806200
H	-5.975900	-2.170600	1.352500
H	-7.692000	-2.285300	-0.371200
H	-3.102900	4.099000	0.186500
H	-2.376700	6.281100	-0.675700
H	-0.731800	6.407000	-2.546100
H	0.170200	4.303500	-3.526300
H	-0.552600	2.129700	-2.685100
H	-4.868000	1.601000	1.300900
H	-7.228900	2.258800	0.882100
H	-7.996300	2.714100	-1.439000
H	-6.396200	2.512200	-3.332300
H	-4.047500	1.882900	-2.911400
H	0.182500	0.774100	-1.198900
H	1.299300	-1.062400	-2.267200
H	-3.653500	-3.584000	-2.563700
H	-2.472300	-5.407400	-3.678100
H	-0.020300	-5.250500	-4.128100
H	1.228100	-3.229000	-3.430500
H	-3.711900	-0.867100	-3.982200
H	-5.475300	-0.897900	-5.691400
H	-7.824600	-1.465700	-5.076100
H	-8.391900	-1.986100	-2.721200
H	-3.316400	-4.260400	0.715900
H	-1.616600	-5.995600	0.274700
H	0.806800	-5.419500	0.336700
H	1.512100	-3.097700	0.875600
H	-0.183000	-1.366900	1.338000
H	-2.852300	-3.716800	3.292400
H	-4.038700	-4.321000	5.364800
H	-5.923900	-2.922800	6.188500
H	-6.591900	-0.887100	4.918000
H	-5.382900	-0.256900	2.865000

C	-1.067800	-0.028000	3.735400
C	0.361100	0.478400	3.863100
C	0.886600	1.191300	2.594700
C	-0.155800	1.982700	1.843700
C	-1.155500	2.779600	2.391900
C	-1.317700	3.073700	3.875000
C	-2.299900	2.106600	4.562500
C	-2.215400	0.684100	4.052500
H	0.098700	2.156200	0.799500
H	-1.620000	3.498800	1.725400
H	-1.685600	4.099100	3.992300
H	-0.339800	3.048800	4.364500
H	-2.152000	2.119000	5.654300
H	-3.325400	2.457100	4.392200
H	-3.118000	0.103000	4.218800
H	-1.173400	-1.108500	3.663500
H	0.434200	1.137600	4.734600
H	1.014100	-0.375400	4.074000
H	1.717000	1.862300	2.858300
H	1.320500	0.459600	1.906400

(*S*)-(2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl)(1,5-cyclooctadiene) rhodium (I) bis-(*S*)-(2,2')-binaphtholatoborate; [(*S*)-(6)](*S*,*S*)-B_H

Zero-point correction= 1.341214 (Hartree/Particle)
Thermal correction to Energy= 1.421597
Thermal correction to Enthalpy= 1.422542
Thermal correction to Gibbs Free Energy= 1.220910
Sum of electronic and zero-point Energies= -4664.624347
Sum of electronic and thermal Energies= -4664.543964
Sum of electronic and thermal Enthalpies= -4664.543020
Sum of electronic and thermal Free Energies= -4664.744651
Corrected ZPE= -4464.657733 **E_{rel} = 0.66 Kcal.mol^{-1}**



(S),(S,S)-**6**

B	-3.741300	0.571000	0.137400
C	-4.787800	-1.227700	-1.175800
C	-4.993200	-1.321000	-2.582300
C	-4.924500	-2.528000	-3.230600
C	-4.596800	-3.712800	-2.517200
C	-4.428300	-4.955300	-3.184800
C	-4.054400	-6.090500	-2.500800
C	-3.826700	-6.016300	-1.106100
C	-4.001400	-4.829700	-0.425600
C	-4.409800	-3.637500	-1.094100
C	-4.590200	-2.383700	-0.411000
C	-4.533700	-2.268600	1.072900
C	-5.357100	-3.066500	1.944500
C	-6.387300	-3.924900	1.462900
C	-7.161400	-4.673600	2.322600
C	-6.953700	-4.614400	3.720800
C	-5.986500	-3.775900	4.225900
C	-5.184800	-2.976200	3.367900
C	-4.233800	-2.060800	3.890700
C	-3.528300	-1.233800	3.052100
C	-3.690500	-1.313800	1.642500
C	-3.714300	2.565700	1.563900
C	-3.661400	2.639400	2.985700
C	-2.969100	3.641700	3.617500
C	-2.250400	4.608300	2.863800
C	-1.455600	5.598300	3.500200
C	-0.724200	6.507800	2.769800
C	-0.763600	6.453600	1.356900
C	-1.538700	5.514900	0.710200
C	-2.321100	4.564400	1.429100
C	-3.127400	3.565100	0.778600
C	-3.334000	3.529800	-0.697000
C	-3.834200	4.658000	-1.439900
C	-4.295600	5.852500	-0.815000
C	-4.768000	6.916000	-1.553300
C	-4.809600	6.853700	-2.966000
C	-4.400900	5.704900	-3.604500
C	-3.925700	4.584200	-2.871900
C	-3.568500	3.375100	-3.525300
C	-3.188900	2.276300	-2.797300
C	-3.090800	2.338300	-1.382100

H	-3.820700	-4.794100	0.642600
H	-5.210700	-0.398300	-3.111900
H	-5.094600	-2.589100	-4.303700
H	-4.593500	-4.988900	-4.260200
H	-3.926600	-7.033900	-3.025200
H	-3.511900	-6.904500	-0.563500
H	-1.429100	5.616800	4.588000
H	-6.574000	-3.972200	0.396500
H	-7.946300	-5.309800	1.921400
H	-7.566700	-5.213900	4.388700
H	-5.830200	-3.696900	5.300000
H	-4.102300	-1.997200	4.969000
H	-2.833700	-0.493200	3.436700
H	-4.196700	1.874500	3.540100
H	-2.946700	3.698500	4.704100
H	-0.117300	7.257300	3.270800
H	-0.178400	7.160900	0.774000
H	-1.566200	5.496400	-0.372900
H	-5.121700	7.808300	-1.042800
H	-5.179800	7.700400	-3.538200
H	-4.452500	5.628100	-4.688900
H	-3.636300	3.323100	-4.610000
H	-2.961000	1.328500	-3.275800
H	-4.288300	5.914000	0.266800
O	-2.973500	-0.457200	0.874600
O	-4.394000	1.540800	1.029300
O	-2.716800	1.210600	-0.726600
O	-4.853700	-0.004100	-0.632100
C	2.395700	0.763600	5.314600
C	1.040500	1.128800	5.490600
C	0.247200	1.356000	4.390100
C	0.775400	1.241500	3.076400
C	-0.053100	1.412900	1.940700
C	0.466200	1.323000	0.674900
C	1.858600	1.093900	0.463500
C	2.131100	-2.421700	1.705500
C	0.733000	-2.336500	1.644600
C	-0.044300	-2.651900	2.762100
C	0.570800	-3.055100	3.947100
C	1.964700	-3.130600	4.021900
C	4.089600	-3.585300	-0.126100
C	3.809300	-4.795100	0.525000
C	4.469100	-5.972400	0.157400
C	5.420800	-5.960100	-0.860400
C	5.704900	-4.762400	-1.523500
C	5.037700	-3.591500	-1.168500
C	4.123400	1.307200	-1.588900
C	4.945600	0.432300	-2.311300
C	6.236400	0.816600	-2.683600
C	6.714800	2.080000	-2.336300
C	7.553900	1.786900	2.176100
C	5.898100	2.961200	-1.621800
C	4.607200	2.582400	-1.258700
C	1.594500	2.218900	-2.297200
C	1.899200	2.212100	-3.672400
C	1.424800	3.212700	-4.517500
C	0.641000	4.247600	-4.002800
C	0.357800	4.281200	-2.639200
C	0.833100	3.280200	-1.786800
C	4.459400	-0.867200	0.920700
C	5.823200	-1.274200	0.930300
C	6.822400	-0.431200	1.351500
C	6.529900	0.886500	1.776300
C	2.742600	-2.809000	2.911400
C	7.248900	3.065700	2.580500
C	5.899700	3.495500	2.602000
C	4.885300	2.642300	2.228600
C	5.162400	1.310500	1.804900
C	4.123100	0.406700	1.392600
C	2.692000	0.830500	1.552000
C	2.156000	0.906800	2.889200
C	2.937600	0.651600	4.053000
H	3.972900	3.282800	-0.723700
H	2.542000	1.437300	-4.082000
H	1.672200	3.185000	-5.575300
H	0.260800	5.025600	-4.658500
H	-0.241300	5.086600	-2.227000
H	0.602700	3.347600	-0.730700
H	8.038500	3.747900	2.883100
H	6.088100	-2.274100	0.612900
H	7.855000	-0.772100	1.357400
H	8.585700	1.444700	2.152100
H	5.662700	4.507400	2.918700
H	3.857300	2.985400	2.254000
H	3.977700	0.367700	3.947300
H	3.017900	0.568800	6.184200
H	0.629900	1.221400	6.492400
H	-0.798000	1.632000	4.499400
H	-1.114400	1.594600	2.068500
H	-0.222900	1.407200	-0.157600
H	0.250200	-2.000400	0.732900
H	-1.125200	-2.566400	2.706100
H	-0.034500	-3.299600	4.815600
H	2.447000	-3.430800	4.948300
H	3.825800	-2.857600	2.983000
H	3.075800	-4.826800	1.322600
H	4.233800	-6.898800	0.674100
H	5.934200	-6.875200	-1.141700
H	6.440100	-4.741600	-2.323400
H	5.257700	-2.672900	-1.705900
H	4.562900	-0.546700	-2.590400
H	6.863000	0.130700	-3.247700
H	7.717600	2.381900	-2.626200
H	6.264900	3.947200	-1.351300
P	3.156400	-2.021300	0.229300
P	2.356900	0.854000	-1.295800
Rh	1.795400	-1.400400	-1.685600
C	-0.224500	-0.880100	-2.509900
C	0.629600	-1.021900	-3.599400
C	0.654400	-2.219400	-4.538100
C	1.699800	-3.272900	-4.124200
C	1.828300	-3.449200	-2.626300
C	0.799800	-3.477200	-1.695700
C	-0.684800	-3.357600	-2.001200

C	-1.205500	-1.901700	-1.991100
H	1.473700	-4.243500	-4.593700
H	-0.426100	0.130600	-2.157800
H	1.052100	-0.109400	-4.006000
H	2.783700	-3.861500	-2.314300
H	1.042600	-3.894400	-0.720600
H	-0.341400	-2.669000	-4.593300
H	0.885000	-1.868900	-5.550800
H	2.683000	-2.972800	-4.507800
H	-0.898600	-3.835800	-2.962200
H	-1.248400	-3.928500	-1.257400
H	-2.134600	-1.834400	-2.575700
H	-1.492700	-1.607500	-0.977200

References:

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[i] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.

[ii] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

[iii] S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104/154101-154104/154119.