Supplementary Information For

Asymmetric Synthesis of Metallacarboranes Using a Chiral Traceless Auxilliary

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1. General Information

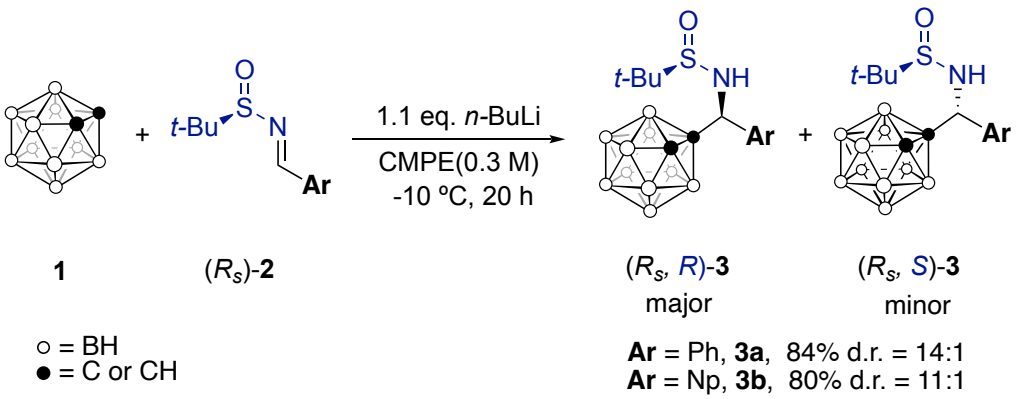
General. Unless otherwise noted, all reactions were carried out in a flame-dried, septum-sealed flask under an atmosphere of nitrogen. Analytical thin-layer chromatography was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck). Visualization was accomplished by exposure to a UV lamp, and/or treatment with chromogenic agents: a solution of $KMnO_4$, or a solution of phosphomolybdic acid (PMA), or palladium chloride in acid solution, followed by brief heating with a heating gun. Most of the products were compatible with standard silica gel chromatography. Column chromatography was performed on silica gel 60 N (spherical and neutral, 200–300 mesh) using standard methods.

Structural analysis. NMR spectra were measured on a Bruker Avance-400 spectrometer and chemical shifts (δ) are reported in parts per million (ppm). ^{1}H NMR spectra were recorded at 400 MHz, ^{13}C NMR spectra were recorded at 100 MHz, and referenced internally to the corresponding solvent resonances, ^{11}B NMR were measured at 128 MHz with $BF_3{\cdot}OEt_2$ as the external standard and ^{19}F NMR were measured at 360 MHz with $CFCl_3$ as the external standard. Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). High resolution mass spectra (HRMS) were obtained on a Bruker Apex IV FTMS spectrometer or an Agilent 6224 LC/MS TOF spectrometer. Infrared spectra were collected on a Thermo-Fisher Nicolet 6700 FT-IR spectrometer using ATR (Attenuated Total Reflectance) method, absorption maxima (ν_{max}) are reported in wavenumbers (cm^{-1}).

Materials. Commercial reagents were purchased from J&K, Energy, Sigma-Aldrich, Alfa Aesar, Acros Organics, Strem Chemicals or TCI and used as received unless otherwise stated. THF was purified by distillation over sodium/benzophenone and stored under N_2; Et_2O, MTBE, CPME, CH_2Cl_2, benzene were purchased from Acros Organics and used directly without further purification. Substrates **2a** and **2b** were prepared according to the literature procedure.[1]

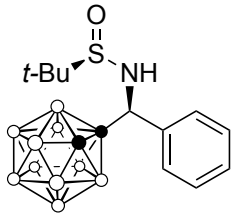
2. General procedure for optimization of 1,2-addition and its substrate scope

Scheme S1. Optimization of 1,2-addtions of *C*-lithiated-carborane to *N-tert*-sulfinyl imine **2a**[a]



To a solution of 0.2 mmol *o*-carborane in CPME, at –10 °C,*n*-butyllithium (2.5 M solution in pentane, 0.22 mmol, 1.1 equiv.) was added slowly and dropwise. The resulting pale-yellow solution was maintained at –10 °C for 5 minutes, then the reaction mixture was stirred for 10 minutes at room temperature. The solution was cooled to -10 °C again before (*R,E*)-*N*-benzylidene-2-methylpropane-2-sulfinamide **2** (0.3 M, 0.2 mmol, 1.0 equiv.) was added dropwise, and then the mixture was stirred at -10 °C for 20 h unless otherwise noted. The reaction was then quenched with saturated NH_4Cl aqueous solution (2.0 mL) and allowed to warm to room temperature. The aqueous layer was extracted with EA for three times. All the organic layers were combined, dried over $MgSO_4$, filtered and concentrated to give a slightly yellow oil. Conversion, yield, and diastereomer ratio (*Rs, R*)-**3**: (*Rs, S*)-**3** were determined based on ^1H NMR analysis with sulfinamide **2** as the limiting reagent.

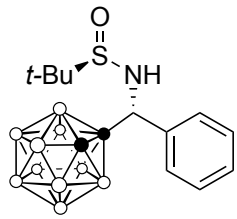
(-)-(*R*)-*N*-((*S*)-*o*-carboran-1-yl(phenyl)methyl)-2-methylpropane-2-sulfinamide (*Rs, R*)-3a



(R_s, *R*)-**3a**
Chemical Formula: $C_{13}H_{27}B_{10}NOS$
Exact Mass: 355.27
Molecular Weight: 353.53

The product (*Rs, R*)-**3a** was white solid after purification by silica gel flash chromatography (EtOAc/PE = 1:10 v/v);^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 2.0 Hz, 1H, Ar*H*), 7.39 (d, *J* = 2.0 Hz, 2H, Ar*H*), 7.22-7.24 (m, 2H, Ar*H*), 5.01 (d, *J* = 8.8 Hz, 1H, C*H*), 4.04 (d, *J* = 8.4 Hz, 1H, N*H*), 3.45 (s, $C_{cage}H$), 1.22 (s, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.67, 129.74, 129.38, 127.40, 78.70, 62.09, 60.26, 57.68, 22.65; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ -2.7 (1B), -3.9 (1B), -8.9 (2B), -11.1 (1B), -11.7 (1B), -13.3 (4B); ^{11}B NMR (128 MHz, $CDCl_3$): δ -2.7 (d, *J* = 154 Hz, 1B), -3.9 (d, *J* = 155 Hz, 1B), -8.9 (d, *J* = 151 Hz,2B), -11.1, -11.7 (in total 2B, br., partially overlapped and not resolved), -13.4 (d, *J* = 169 Hz, 4B); IR (ν cm^{-1}): 2961, 2575 (BH), 1474, 1455, 1391, 1188, 1064, 912, 880, 846, 766, 739, 706; HRMS (ESI): Calculated for $C_{13}H_{27}B_{10}NOS$: 378.2636 $[M+Na]^+$, Found: 378.2660; Anal. Calcd for $C_{13}H_{27}B_{10}NOS$: C, 44.17; H, 7.70; N, 3.96, S, 9.07. Found: C, 43.76; H, 7.87; N, 3.91; S, 8.88; $[\alpha]_D^{20}$ = -80.7 (c =0.01, CH_2Cl_2).

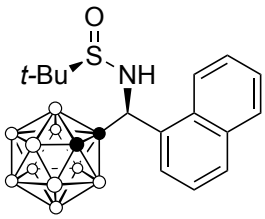
(-)-(*R*)-*N*-((*S*)-*o*-carboran-1-yl(phenyl)methyl)-2-methylpropane-2-sulfinamide (*Rs, S*)-3a



(R_s, *S*)-**3a**
Chemical Formula: $C_{13}H_{27}B_{10}NOS$
Exact Mass: 355.27
Molecular Weight: 353.53

The product (*Rs, S*)-**3a** was white solid after purification by silica gel flash chromatography (EtOAc/PE = 1:10 v/v); ^1H NMR (400 MHz, $CDSCl_3$) δ 7.42 (m, 3H, Ar*H*), 7.27-7.25 (m, 2H, Ar*H*), 5.05 (d, *J* = 4.4 Hz, C*H*), 4.10 (d, *J* = 4.4 Hz, N*H*), 3.54 (s, $C_{cage}H$), 1.22 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.8, 130.0, 129.2, 128.5, 78.1, 62.4, 61.1, 56.9, 22.6; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -2.9 (1B), -3.8 (1B), -8.5 (1B), -9.0 (1B), -10.6 (1B), -13.0 (5B); ^{11}B NMR (128 MHz, $CDCl_3$): δ -2.9 (d, *J* =142 Hz, 1B), -3.8 (d, *J* =127 Hz, 1B), -8.5 (d, *J* = 147 Hz, 1B), -9.0 (d, *J* = 154 Hz, 1B), -10.6, -13.0 (in total 6B, br., partially overlapped and not resolved); IR (ν cm^{-1}): 2925, 2576 (BH), 1456, 1262, 1055, 1029, 880, 792, 737, 704, 672; HRMS (ESI): Calculated for $C_{13}H_{27}B_{10}NOS$: 378.2636 $[M+Na]^+$, Found: 378.2657; Anal. Calcd for $C_{13}H_{27}B_{10}NOS$: C, 44.17; H, 7.70; N, 3.96, S, 9.07. Found: C, 44.22; H, 7.96; N, 3.91; S, 8.43; $[\alpha]_D^{20}$ = -0.34 (c =0.01, CH_2Cl_2),

(-)-(*R*)-*N*-((*S*)-*o*-carboran-1-yl(naphthalen-1-yl)methyl)-2-methylpropane-2-sulfinamide (*Rs, S*)-3b

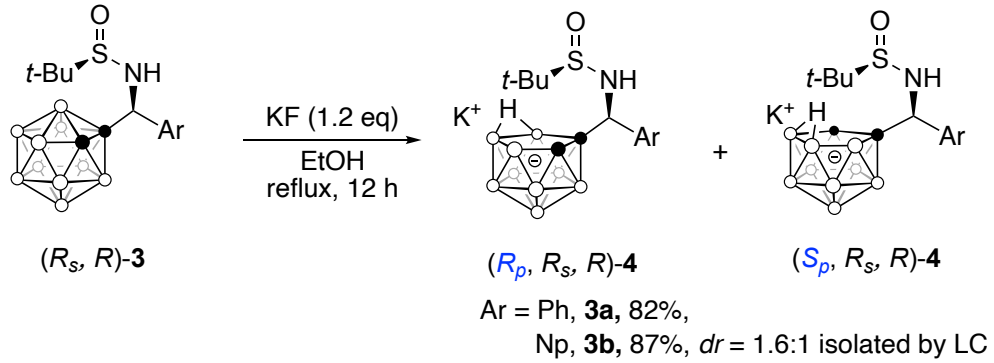


(R_s, R)-**3b**

Chemical Formula: $C_{17}H_{29}B_{10}NOS$
Exact Mass: 405.29
Molecular Weight: 403.59

The product **3b** was obtained as white solid after purification by silica gel flash chromatography (EtOAc/PE= 1:5 v/v);^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, J = 3.6 Hz, 1H, Ar*H*), 7.70 (d, J = 8.4 Hz, 1H, Ar*H*), 7.30 (d, J = 2.8 Hz, 2H, Ar*H*), 5.63 (d, J = 8.4 Hz, C*H*), 5.03 (d, J = 8.0 Hz, N*H*), 3.90 (s, $C_{cage}H$), 1.28 (s, C(CH_3)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$): δ 134.94, 133.80, 130.36, 130.20, 129.29, 127.51, 126.52, 124.98, 124.87, 122.06, 79.29, 59.95, 57.48, 54.99, 22.53; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ -2.5 (1B), -3.9 (1B), -9.3 (2B), -10.7(1B), -13.2 (5B); ^{11}B NMR (128 MHz, $CDCl_3$): δ -2.5 (d, J = 151 Hz, 1B), -3.9 (d, J = 179 Hz, 1B), -9.3 (d, J = 151 Hz, 2B), -10.7, -13.2 (in total 6B, br., partially overlapped, not well resolved); IR (ν cm^{-1}): 2955, 2924, 2854, 2583 (BH), 1457, 1090, 1062, 798, 775, 725; HRMS (ESI): Calculated for $C_{17}H_{29}B_{10}NOS$: 428.2793 $[M+Na]^+$, Found: 428.2818; $[\alpha]_D^{20}$ = -41.7 (c =0.01, CH_2Cl_2).

3. Selective deboration of compound (*Rs, R*)-3

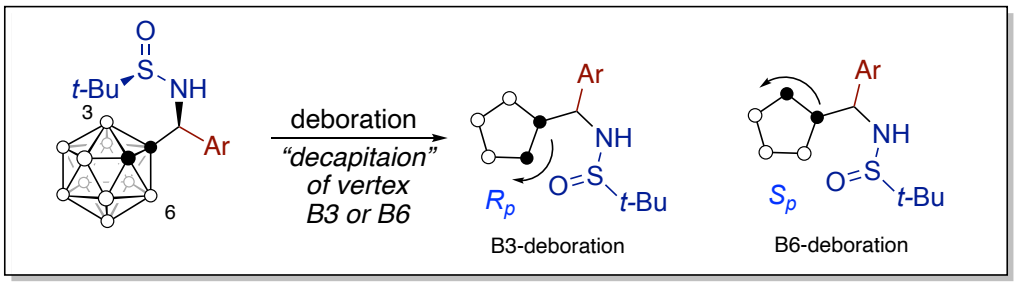


(R_s, R)-**3**

(R_p, R_s, R)-**4**

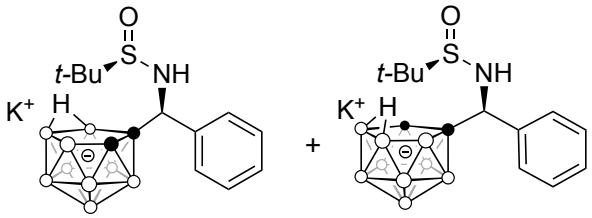
(S_p, R_s, R)-**4**

Ar = Ph, **3a,** 82%,
Np, **3b,** 87%, *dr* = 1.6:1 isolated by LC



In a 25 mL Schlenk tube, substrate **3** (1.0 mmol) and potassium fluoride (1.2 mmol) were added.[3-5] Under nitrogen, 50 mL of ethanol was added as a solvent. After stirring at 70 °C for 12 h, TLC indicated that the reaction was completed. The reaction tube was removed from oil bath to cool down to room temperature. The solvent was evaporated to give amorphous residue, which was washed with acetone to remove impurities, afforded a mixture of *nido*-carborane potassium salts **4**, which were directly used for the following complex preparation. Further elaborated purification of **4b** by preparative LC with reverse phase column (Megres, C18, 10*250, 5μm column), eluent solvent, MeCN:H_2O = 60:40, 1 mL/min,) afforded the corresponding product in pure form for characterization. The diastereomeric ratio was determined as 1.6:1.

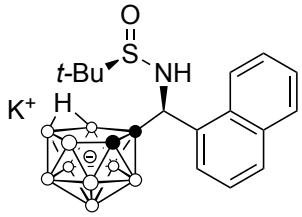
nido-Carborane potassium salts 4a



(R_p, R_s, R)-**4a** (S_p, R_s, R)-**4a**

The general procedure was followed using **3a** (1.0 mmol, 1.0 equiv) as substrate. The diastereomeric mixture of **4a** was obtained as white foam after purification by silica gel flash chromatography (EtOAc/PE = 1:3 v/v);^{1}H NMR (400 MHz, CD_3OD) δ 7.41 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.34 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.21 (m, 2H, Ar*H*), 4.13-4.22 (m, 1H), 1.30 (d, C(C*H*$_3$)$_3$), -2.80 (br., B$_{bridge}$*H*); ^{13}C NMR (100 MHz, CD_3OD): δ 150.6, 149.4, 134.3, 134.0, 133.8, 133.7, 133.4, 133.1, 73.6, 72.1, 66.8, 63.1, 62.9, 28.6, 28.3, 26.1, 19.7; ^{11}B{^{1}H} NMR (128 MHz, CD_3OD): δ -10.4 (1B), -11.8 (3B), -13.0 (1B), -15.7 (1B), -17.2 (3B), -19.1 (1B), -21.0 (3B), -22.4 (1B), -33.0 (2B), -36.6 (2B); ^{11}B NMR (128 MHz, CD_3OD): ^{11}B NMR (128 MHz, CD_3OD): δ -10.4 (d, *J* = 133 Hz, 1B), -11.8 (d, *J* = 174 Hz, 3B), -13.0 (d, *J* = 169 Hz, 1B), -15.7 (d, *J* = 190 Hz, 1B), -17.2 (d, *J* = 157 Hz, 3B), -19.1 -21.0 (in total 4B, br. partially overlapped, not resolved), -22.4 (d, *J* = 182 Hz, 1B), -33.0 (d, *J* = 100 Hz, 2B), -36.6 (d, *J* = 138 Hz, 2B); IR (ν cm^{-1}): 2961, 2520 (BH), 1472, 1386, 1293, 1178, 1127, 1026, 890, 737, 701; HRMS (ESI): Calculated for $C_{13}H_{27}B_9KNOS$: 384.2361 $[M+H]^+$, Found: 384.2307.

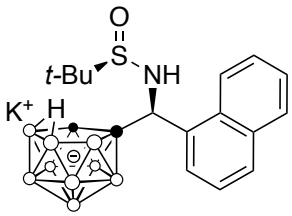
nido-Carborane potassium salts (*R*$_p$, *Rs*, *R*)-4b and (*S*$_p$, *Rs*, *R*)-4b



(R_p, R_s, R)-**4b**

Chemical Formula: $C_{17}H_{29}B_9KNOS$
Exact Mass: 433.24
Molecular Weight: 431.87

The product (*R*$_p$, *Rs*, *R*)-**4b** was obtained as white foam after purification by silica gel flash chromatography (EtOAc/PE = 1:3 v/v), followed by preparative LC (C18 reverse phase);^{1}H NMR (600 MHz, CD_3OD) *δ*8.18 (d, *J* = 6.0 Hz, 1H, Ar*H*), 7.85 (dd, *J* = 6.0 Hz, 1H, Ar*H*), 7.77 (t, *J* = 6.0 Hz, 2H, Ar*H*), 7.52-7.45 (m, 3H, Ar*H*), 5.26 (s, 1H), 4.62 (s, 2H), 1.25 (s, C(C*H*$_3$)$_3$), -2.70 (d, *J* = 6.0 Hz, 1H); ^{13}C NMR (150 MHz, CD_3OD): *δ* 140.0, 134.7, 132.3, 129.3, 128.4, 127.0, 126.4, 126.0, 125.9, 57.4, 23.1; ^{11}B{^{1}H} NMR (128 MHz, CD_3OD): *δ* -10.7 (1B), -11.4 (1B), -16.4 (2B), -17.8 (1B), -19.0 (1B), -21.4 (1B), -32.9 (1B), -36.8 (1B); ^{11}B NMR (128 MHz, CD_3OD): *δ* -10.7 (d, *J* = 104 Hz, 1B), -11.4 (d, *J* = 154 Hz, 1B), -16.4 (d, *J* = 123 Hz, 2B), -17.8 (d, *J* = 165 Hz, 1B), -19.0 (d, *J* = 149 Hz, 1B), -21.4 (d, *J* = 149 Hz, 1B), -32.9 (d, *J* = 129 Hz, 1B), -36.8 (d, *J* = 140 Hz, 1B); IR (ν cm^{-1}): 2925, 2521 (BH), 1466, 1366, 1262, 1027, 781, 735, 703; HRMS (ESI): Calculated for $C_{17}H_{29}B_9KNOS$: 456.2337 $[M+Na]^+$, Found: 456.2390.



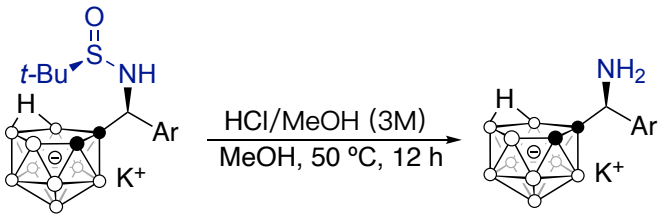
(S_p, R_s, R)-**4b**

Chemical Formula: $C_{17}H_{29}B_9KNOS$
Exact Mass: 433.24
Molecular Weight: 431.87

The product **(***S_p, Rs, R*)**-4b** was obtained as white foam after purification by silica gel flash chromatography (EtOAc/PE = 1:3 v/v);^{1}H NMR (600 MHz, CD_3OD) δ 8.17 (s, 1H, Ar*H*), 7.87 (dd, *J* = 6.0 Hz, 12.0 Hz, 2H, Ar*H*), 7.79 (d, *J* = 6.0 Hz, 2H, Ar*H*), 7.54-7.47 (m, 3H, Ar*H*), 5.29 (s, 1H), 4.62 (s, 1H), 1.28 (s, C(CH_3)$_3$), -2.80 (d, *J* = 6.6 Hz, 1H); ^{13}C NMR (150 MHz, CD_3OD): δ 140.5, 135.0, 132.5, 129.5, 128.5, 126.6, 126.1, 126.1, 57.7, 22.9; ^{11}B{^{1}H} NMR (128 MHz, CD_3OD): δ -10.1 (1B), -11.9 (1B), -13.0 (2B), -20.9 (2B), -22.1 (1B), -33.1 (1B), -36.4 (1B); ^{11}B NMR (128 MHz, CD_3OD): δ -10.1 (d, *J* = 115 Hz, 1B), -11.9 (d, *J* = 124 Hz, 1B), -13.0 (d, *J* = 140 Hz, 2B), -20.9 (d, *J* = 145 Hz, 2B), -22.1 (1B, br. partially overlapped, not resolved), -33.0 (d, *J* = 163 Hz, 1B), -36.5 (d, *J* = 141 Hz, 1B); HRMS (ESI): Calculated for $C_{17}H_{29}B_9KNOS$: 456.2337 $[M+Na]^+$, Found: 456.2367.

4. Removal of *tert*-butylsulfinyl group

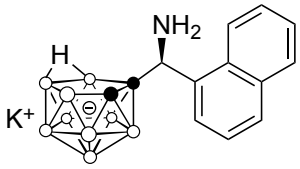
Scheme S2. Removal of *N*-*tert*-sulfinyl group leading to chiral amine (R_p, R)-**4b'**



(R_p, R_s, R)-**4b** (R_p, R)-**4b'**

In a 10 mL reaction flask, substrate **4b** (1.0 mmol) was added, then the reaction flask was purged with nitrogen three times, 2.6 mL of methanol was added and then hydrochloric acid (1.2 mmol, 3.0 M methanol solution) was added under protection of nitrogen and stirred at room temperature for 10 h, after the reaction was complete as monitored by TLC, 20% aqueous solution of sodium bicarbonate was added to adjust the pH of the solution to 7-8. The mixture was extracted three times with ether, and the organic phases were combined and dried over anhydrous sodium sulfate. The solvent was removed in vacuo and the residue was purified by silica gel flash chromatography to obtain the corresponding product (R_p, R)-**4b'**.[2]

***nido*-Carborane potassium salts** (R_p, R)-**4b'**

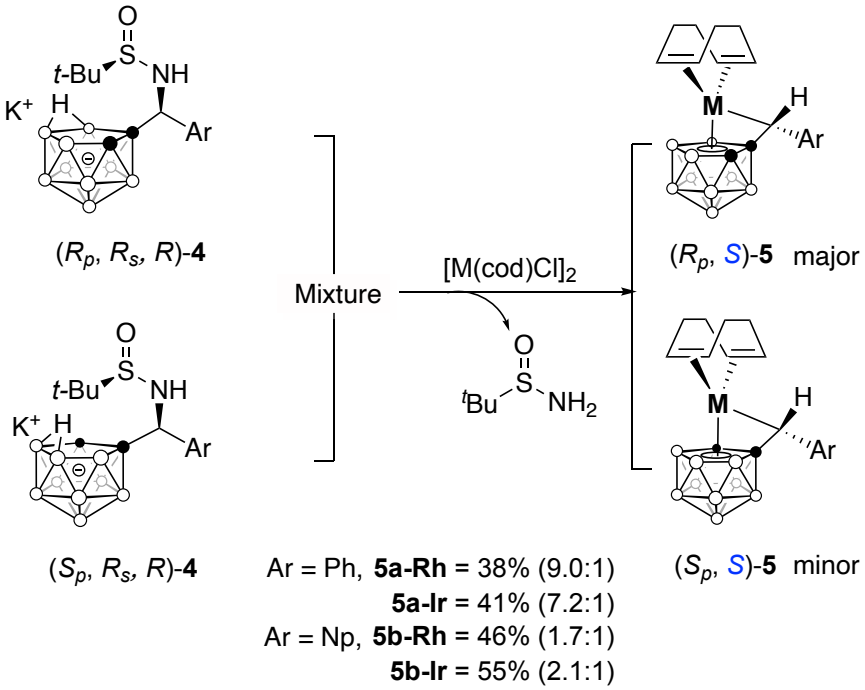


(R_p, R)-**4b'**

Chemical Formula: $C_{13}H_{21}B_9KN$
Exact Mass: 329.2149
Molecular Weight: 327.7063

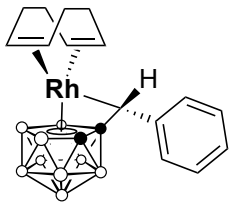
The product (R_p, R)-**4b'** was obtained as a white foam after purification by silica gel chromatography (EtOAc/PE= 3:1 v/v); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.16 (s, 2H, N*H*), 8.05 (d, J = 8.3 Hz, 1H, Ar*H*), 7.89 (dd, J = 15.9, 7.9 Hz, 2H, Ar*H*), 7.64 (d, J = 7.2 Hz, 1H, Ar*H*), 7.52 (p, J = 7.9, 7.0 Hz, 4H, Ar*H*), 5.03 (s, 1H, C*H*), 2.27 (s, 1H, $C_{cage}H$). ^{13}C NMR (101 MHz, DMSO-d_6) δ 134.8, 133.6, 131.0, 129.0, 128.9, 126.7, 126.2, 125.4, 125.1, 124.3, 60.7, 55.5, 45.3; ^{11}B{^{1}H} NMR (128 MHz, Methanol-d_4) δ -11.82 (2B), -16.87 (2B), -19.00 (1B), -21.28 (1B), -22.50 (1B), -33.64 (1B), -37.81 (1B). ^{11}B NMR (128 MHz, Methanol-d_4) δ -11.82 (d, *J* = 136.8 Hz, 2B), -16.88 (d, *J* = 142.3 Hz, 2B), -19.07 (d, *J* = 144.1 Hz, 1B), -22.47 (t, *J* = 151.9 Hz, 2B), -33.67 (d, *J* = 132.9 Hz, 1B), -37.81 (d, *J* = 141.9 Hz, 1B). HRMS (ESI): Calculated for C13H21B9NK: 352.2041 [M+Na]+, Found: 352.2035. [α]D25 = +176 (c = 0.01, EtOH).

5. Synthesis of chiral metallacarboranes 5



In a 25 mL flask, a mixture of **4** (1.0 mmol) were added, followed by the addition of $[MCl(COD)]_2$ (0.2 mmol), then the reaction flask was purged with nitrogen three times. Under nitrogen, 26 mL of benzene was added as a solvent. After stirring at room temperature for 3 h, the reaction was completed, as monitored by TLC. The solvent was removed in vacuo and the residue was purified by preparative TLC (EtOAc/PE = 1:10 v/v), easily giving pure diastereomers **(***R_p, S***)-5** and **(***S_p, S***)-5**, respectively.

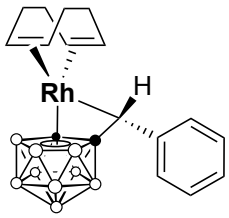
Rhodium complex (*Rp, S*)-5a-Rh



(R_p, S)-**5a-Rh**
Chemical Formula: $C_{17}H_{28}B_9Rh$
Exact Mass: 434.21
Molecular Weight: 432.61

The general procedure was followed using the mixture of **4a** as substrate. The product **(***R_p, S***)-5a-Rh**was obtained as darkred solid after purification by silica gel flash chromatography (EtOAc/PE = 1:10 v/v);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.30-7.37 (m, 3H, Ar*H*), 5.58 (s, C*H*), 5.49 (d, $COD_{olefinic}$ *H*), 5.34-5.46 (m, $COD_{olefinic}$ *H*), 4.63 (t, *J* = 8.0 Hz, $COD_{olefinic}$ *H*), 3.18-3.24(m, $COD_{olefinic}$ *H*), 3.03-3.11 (m, 2H), 2.65-2.87 (m, 6H), 2.37-2.44 (m, 2H), 2.01-2.08 (m, 2H), 1.88-1.96 (m, 2H), 1.78 (s, C_{cage}*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.2, 129.2, 129.1, 129.0, 101.0, 98.8, 95.5, 92.0, 91.0, 82.3, 58.3, 36.0, 30.6, 29.9, 27.7; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ 10.5 (2B), 1.3 (1B), 0.8 (1B), -3.3 (1B), -4.6 (1B), -17.7 (2B), -22.7 (1B); ^{11}B NMR (128 MHz, $CDCl_3$): δ 10.5 (d, *J* = 148 Hz, 2B), 1.3 (br. partially overlapped, not well unresolved, 1B), 0.8 (d, *J* = 187 Hz, 1B), -3.3 (d, *J* = 201 Hz, 1B), -4.6 (d, *J* = 154 Hz, 1B), -17.7 (d, *J* = 154 Hz, 2B), -22.7 (d, *J* = 179 Hz, 1B); IR (ν cm^{-1}): 2956, 2916, 2881, 2603 (BH), 2560 (BH), 2545 (BH), 1463, 1091, 999, 826, 752, 741, 724, 690; HRMS (ESI): Calculated for $C_{17}H_{28}B_9Rh$: 441.2338 $[M+Li]^+$, Found: 441.2225; Anal. Calcd for $C_{17}H_{28}B_9Rh$: C, 47.20; H, 6.52; Found: C, 47.27; H, 6.81.

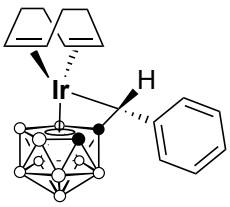
Rhodium complex (*Sp, S*)-**5a-Rh**



(*Sp, S*)-**5a-Rh**
Chemical Formula: $C_{17}H_{28}B_9Rh$
Exact Mass: 434.21
Molecular Weight: 432.61

The general procedure was followed using the mixture of **4a** as substrate. The product (*Sp, S*)-**5a-Rh**was obtained as darkred solid after purification by silica gel flash chromatography (EtOAc/PE = 1:10 v/v);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.41 (m, 2H, Ar*H*), 7.34-7.35 (m, 3H, Ar*H*), 5.87 (s, C*H*), 5.65 (dd, *J* = 4.0Hz, 8.0 Hz, $COD_{olefinic}$ *H*), 5.04-5.08 (m, $COD_{olefinic}$ *H*), 4.65-4.68 (m, $COD_{olefinic}$ *H*), 2.57-2.93 (m, 8H), 1.98-2.04 (m, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 138.4, 130.4, 129.7, 128.2, 104.6, 101.7, 93.0, 89.9, 82.3, 66.1, 34.1, 33.4, 33.3, 30.5, 27.1; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ 13.2 (1B), 11.5 (1B), -0.9 (1B), -2.5 (1B), -3.7 (1B), -6.7 (1B), -11.8 (1B), -14.4 (1B), -24.5 (1B); ^{11}B NMR (128 MHz, $CDCl_3$): δ 13.2 (d, *J* = 169 Hz, 1B), 11.5 (d, *J* = 141 Hz, 1B), -0.9 (d, *J* = 179 Hz, 1B), -2.5 (d, *J* = 186 Hz, 1B), -3.7 (d, *J* = 147 Hz, 1B), -6.7 (d, *J* = 146 Hz, 1B), -11.8 (d, *J* = 159 Hz, 1B), -14.4 (d, *J* = 166 Hz, 1B), -24.5 (d, *J* = 175 Hz, 1B); IR (ν cm^{-1}): 2919, 2849, 2565 (BH), 2534 (BH), 1260, 1230, 1119, 1013, 983, 751, 736; HRMS (ESI): Calculated for $C_{17}H_{28}B_9Rh$: 441.2238 $[M+Li]^+$, Found:435.2234.

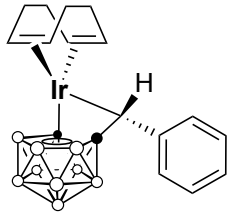
Iridium complex (*Rp, S***)-5a-Ir**



(*Rp, S*)-**5a-Ir**
Chemical Formula: $C_{17}H_{28}B_9Ir$
Exact Mass: 524.27
Molecular Weight: 521.92

The general procedure was followed using the mixture of **4a** as substrate. The product **(***Rp, S***)-5a-Ir**was obtained as yellow solid after purification by silica gel flash chromatography (EtOAc/PE = 1:10 v/v);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.51 (m , 2H, Ar*H*), 7.30-7.32 (m, 3H, Ar*H*), 5.60 (s, C*H*), 4.97-5.01 (m, $COD_{olefinic}$ *H*), 4.68-4.74 (m, $COD_{olefinic}$ *H*), 4.31-4.35 (m, $COD_{olefinic}$ *H*), 3.18-3.24 (m, $COD_{olefinic}$ *H*), 2.68-2.96 (m, 7H), 2.34-2.41 (m, 2H), 2.17 (br, 1H), 1.86-1.96 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.9, 128.9, 128.7, 103.9, 86.9, 82.5(4), 82.4(9), 77.3, 76.4, 62.1, 61.5, 53.4, 33.0, 30.7, 27.9; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ 12.9 (1B), 11.5 (1B), -2.4 (2B), -4.2 (1B), -6.3 (1B), -10.4 (1B), -14.5 (1B), -25.3 (1B); ^{11}B NMR (128 MHz, $CDCl_3$): δ 13.0 (d, *J* = 165 Hz, 1B), 11.7 (d, *J* = 174 Hz, 1B), -2.3 (d, *J* = 156 Hz, 2B), -5.2 (d, *J* = 122 Hz, 1B), -6.3 (d, *J* = 143 Hz, 1B), -10.3 (d, *J* = 160 Hz, 1B), -14.5 (d, *J* = 168 Hz, 1B), -25.3 (d, *J* = 178Hz, 1B); IR (ν cm^{-1}): 2920, 2549 (BH), 1262, 1094, 1056, 1027, 799, 738, 691; HRMS (ESI): Calculated for $C_{17}H_{28}B_9Ir$: 531.2812 $[M+Li]^+$, Found: 531.2797.

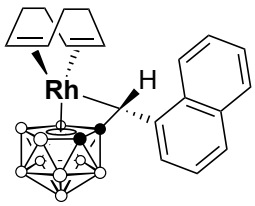
Iridium complex (*Sp, S*)-**5a-Ir**



(S_p, *S*)-**5a-Ir**
Chemical Formula: $C_{17}H_{28}B_9Ir$
Exact Mass: 524.27
Molecular Weight: 521.92

The general procedure was followed using the mixture of **4a** as substrate. The product (S_p, *S*)-**5a-Ir**was obtained as yellow solid after purification by silica gel flash chromatography (EtOAc/PE = 1:10 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.40 (m, 5H, Ar*H*), 5.69 (s, 1H, C*H*), 5.27-5.30 (m, $COD_{olefinic}H$), 4.16-4.18 (m, $COD_{olefinic}H$), 2.61-2.91 (m, 10H), 1.93-2.08 (m, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 138.4, 130.1, 129.3, 128.6, 92.1, 86.0, 83.4, 77.8, 70.2, 65.2, 35.7, 34.9, 34.3, 30.5, 28.5; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ 18.6 (1B), 14.2 (1B), -0.04 (1B), -4.1 (2B), -4.7 (2B), -8.1 (1B), -27.3 (1B); ^{11}B NMR (128 MHz, $CDCl_3$): δ 18.6 (d, *J* = 144 Hz, 1B), 14.2 (d, *J* = 146 Hz, 1B), -0.04 (d, *J* = 159 Hz, 1B), -4.1 (d, *J* = 136 Hz, 2B), -4.7 (d, *J* = 136 Hz, 2B), -8.0 (d, *J* = 166 Hz, 1B), -27.3 (d, *J* = 162 Hz, 1B); IR (ν cm^{-1}): 2950, 2919, 2848, 2541 (BH), 1463, 1263, 1111, 1000, 848, 840, 813, 754, 735. 692; HRMS (ESI): Calculated for $C_{17}H_{28}B_9Ir$: 531.2812 $[M+Li]^+$, Found: 531.2812; Anal. Calcd for $C_{17}H_{28}B_9Ir$: C, 39.12; H, 5.41; Found: C, 39.32; H, 5.53.

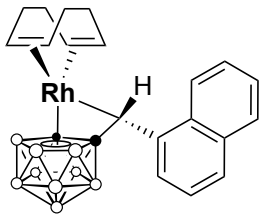
Rhodium complex (R_p, *S*)-**5b-Rh**



(R_p, *S*)-**5b-Rh**
Chemical Formula: $C_{21}H_{30}B_9Rh$
Exact Mass: 484.22
Molecular Weight: 482.67

The product (R_p, *S*)-**5b-Rh** was obtained as dark red crystals after purification by preparative TLC (EtOAc/PE = 1:10 v/v);^{1}H NMR (400 MHz, $CDCl_3$) *δ*8.25 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.97-7.90 (m, 3H, Ar*H*), 7.68 (t, *J* = 8.0 Hz, 1H, Ar*H*), 7.59 (t, *J* = 8.0 Hz, 1H, Ar*H*), 7.40 (t, *J* = 8.0 Hz, 1H, Ar*H*), 6.14 (s, C*H*), 5.55 (d, *J* = 8.0 Hz, 1H, $COD_{olefinic}H$), 5.42 (t, *J* = 8.0 Hz, 1H, $COD_{olefinic}H$), 5.11 (t, *J* = 8.0 Hz, 1H, $COD_{olefinic}H$), 3.39 (t, *J* = 8.0 Hz, 1H, $COD_{olefinic}H$), 3.18-3.10 (m , 1H), 2.99-2.89 (m, 1H), 2.68-2.64 (m, 2H), 1.85 (s, $C_{cage}H$); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 133.9, 132.9, 131.1, 130.1, 129.8, 126.9, 126.4, 125.9, 124.7, 121.3, 102.7, 95.6, 92.5, 91.3, 79.3, 34.3, 31.3, 30.9, 28.6; ^{11}B NMR (128 MHz, $CDCl_3$): *δ* 11.0 (2B), 1.6 (1B), -0.4 (1B), -3.3 (1B), -5.0 (1B), -17.2 (2B), -22.6 (1B); ^{11}B NMR (128 MHz, $CDCl_3$): δ 11.0 (d, *J* = 152 Hz, 2B), 1.28 (br. partially overlapped, not well resolved, 1B), -0.3 (d, *J* = 174 Hz, 1B), -3.3 (d, *J* = 138 Hz, 1B), -5.0 (d, *J* = 155 Hz, 1B), -17.3 (d, *J* = 128 Hz, 2B), -22.9 (d, *J* = 189 Hz, 1B); IR (ν cm^{-1}): 2923, 2851, 2546 (BH), 1455, 1262, 1068, 1005, 796, 774, 738; HRMS (ESI): Calculated for $C_{21}H_{30}B_9Rh$: 485.2313 $[M+H]^+$, Found: 485.2290. Anal. Calcd for $C_{21}H_{30}B_9Rh$: C, 52.26; H, 6.27; Found: C, 51.76; H, 6.47.

Rhodium complex (*Sp, S*)-**5b-Rh**

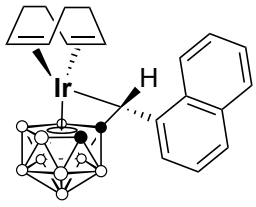


(*Sp, S*)-**5b-Rh**

Chemical Formula: $C_{21}H_{30}B_9Rh$
Exact Mass: 484.22
Molecular Weight: 482.67

The product (*Sp, S*)-**5b-Rh** was obtained as dark red crystals after purification by preparative TLC (EtOAc/PE = 1:10 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.97-7.90 (m, 3H, Ar*H*), 7.68 (t, *J* = 8.0 Hz, 1H, Ar*H*), 7.59 (t, *J* = 8.0 Hz, 1H, Ar*H*), 7.40 (t, *J* = 8.0 Hz, 1H, Ar*H*), 6.14 (s, C*H*), 5.55 (d, *J* = 8.0 Hz, $COD_{olefinic}H$), 5.42 (t, *J* = 8.0 Hz, $COD_{olefinic}H$), 5.11 (t, *J* = 8.0 Hz, $COD_{olefinic}H$), 3.39 (t, *J* = 8.0 Hz, $COD_{olefinic}H$), 3.18-3.12 (m, 1H), 2.99-2.89(m, 1H), 2.64-2.68(m, 1H), 2.26-2.31 (m, 1H), 1.99-2.18 (m, 4H), 1.85 (s, 1H); δ 134.1, 132.9, 129.9, 129.7, 127.0, 126.8, 125.8, 122.0, 120.3, 103.2, 103.1, 99.7,99.6, 92.2, 92.1, 88.5, 88.4, 78.7, 78.6, 36.7, 30.3, 29.0, 28.9; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ 12.1 (2B), -0.03 (1B), -2.0 (1B), -3.5 (1B), -6.1 (1B), -13.0 (1B), -14.9 (1B), -23.4 (1B); ^{11}B NMR (128 MHz, $CDCl_3$): δ 12.8 (br., not resolved, 2B), -0.2 (br. partially overlapped, not resolved, 1B), -2.0 (br., not resolved, 1B), -3.5 (d, *J* = 152 Hz, 1B), -6.1 (d, *J* = 146 Hz, 1B), -13.1 (d, *J* = 189 Hz, 1B), -14.9 (d, *J* = 164 Hz, not well resolved, 1B), -23.4 (br., not well resolved, 1B); IR (ν cm^{-1}): 2926,2853, 2541 (BH), 1455, 1263, 1085, 799, 738, 703; HRMS (ESI): Calculated for 507.2132 $[M+Li]^+$, Found: 507.2157.

Iridium complex (*Rp, S***)-5b-Ir**

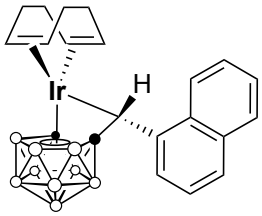


(*Rp, S*)-**5b-Ir**

Chemical Formula: $C_{21}H_{30}B_9Ir$
Exact Mass: 574.28
Molecular Weight: 571.98

The product **(***Rp, S***)-5b-Ir** was obtained as orange crystals after purification by preparative TLC (EtOAc/PE = 1:10 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.96 (d, *J* = 4.0 Hz, 1H, Ar*H*), 7.86 (d, *J* = 12.0 Hz, 1H, Ar*H*), 7.71-7.67 (m, 1H, Ar*H*), 7.63-7.58 (m, 2H, Ar*H*), 7.36 (t, *J* = 8.0 Hz, 1H, Ar*H*), 6.27 (s, C*H*), 5.19-5.14 (m, $COD_{olefinic}H$), 4.91-4.86 (m, $COD_{olefinic}H$), 4.68 (t, *J* = 8.0 Hz, $COD_{olefinic}H$), 3.43 (dd, *J* = 8.0 Hz, 16.0 Hz, $COD_{olefinic}H$), 2.99-2.61 (m , 5H), 2.31-2.02 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.8, 133.1, 130.9, 129.6, 129.4, 126.7, 126.3, 125.6, 124.1, 121.8, 90.2, 83.2, 82.3, 58.1, 36.3, 32.0, 31.8, 30.2; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ 14.3 (2B), -1.4 (1B), -2.6 (1B), -3.6 (1B), -5.7 (1B), -7.6 (1B), -11.8 (1B), -24.6 (1B); ^{11}B NMR (128 MHz, $CDCl_3$): δ 14.3 (d, *J* = 152 Hz, 1B), -1.4 (br., partially overlapped, not resolved, 1B), -2.6 (d, *J* = 140 Hz, 3B), -3.6 (br., partially overlapped, not resolved, 1B), -5.7 (d, *J* = 160 Hz, 1B), -7.6 (d, *J* = 165 Hz, 1B), -11.8 (d, *J* = 163 Hz, 1B), -24.6 (d, *J* = 176 Hz, 1B); IR (ν cm^{-1}): 2953, 2921, 2851, 2538 (BH), 1462, 1261, 1101, 1029, 1015, 837, 774, 727. HRMS (ESI): Calculated for $C_{21}H_{30}B_9Ir$: 613.2446 $[M+K]^+$, Found: 613.2456. Anal. Calcd for $C_{21}H_{30}B_9Ir$: C, 44.10; H, 5.29; Found: C, 43.82; H, 5.27.

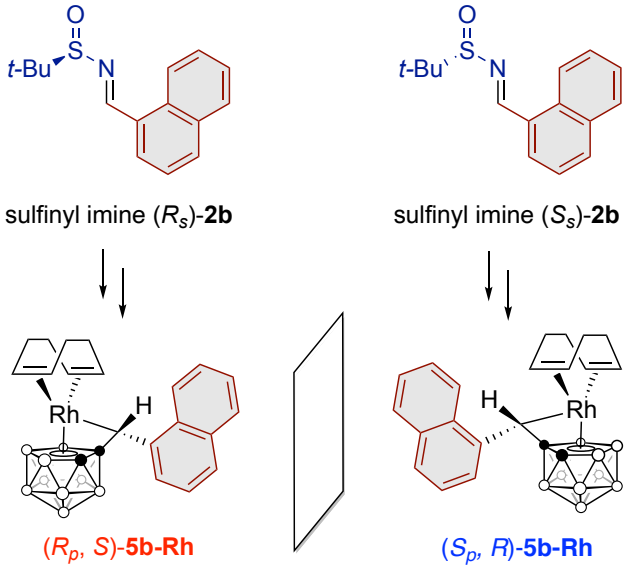
Iridium complex (S_p, S)-**5b-Ir**

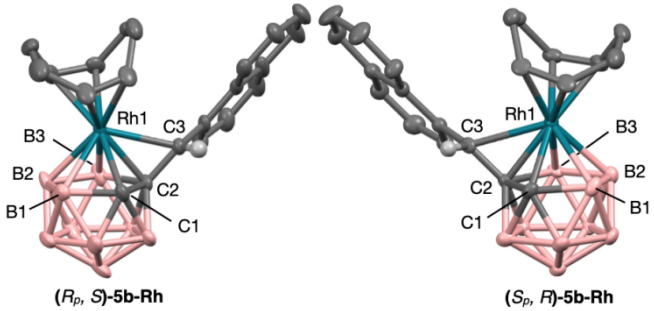


(S_p, S)-**5b-Ir**
Chemical Formula: $C_{21}H_{30}B_9Ir$
Exact Mass: 574.28
Molecular Weight: 571.98

The product (S_p, S)-**5b-Ir** was obtained as orange crystals after purification by preparative TLC (EtOAc/PE = 1:10 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 8.0 Hz , 1H, ArH), 7.97 (d, J = 8.0 Hz, 1H, ArH), 7.87 (t, J = 4.0 Hz, 1H, ArH), 7.72-7.68 (m, 1H, ArH), 7.61 (t, J = 8.0 Hz, 1H, ArH), 7.40 (t, J = 4.0 Hz, 2H, ArH), 6.36 (s, CH), 5.31 (dd, J = 8.0, 12.0 Hz, $COD_{olefinic}H$), 4.45-4.36 (m, 2H, $COD_{olefinic}H$), 3.48 (dd, J = 8.0, 16.0 Hz, 2H), 3.04-2.93 (m, 4H), 2.59-2.05 (m, 9H), 1.28-1.10 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.0, 133.1, 132.8, 129.6, 129.2, 126.9, 126.6, 125.5, 121.7, 121.3, 89.6, 84.6, 83.0, 76.0, 59.3, 38.4, 31.3, 31.1, 30.0; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ 16.7 (1B), 14.3 (1B), -2.3 (1B), -3.5 (3B), -5.2 (1B), -9.5 (1B), -27.0 (1B); ^{11}B NMR (128 MHz, $CDCl_3$): δ 16.7 (d, J = 159 Hz, 1B), 14.4 (d, J = 142 Hz, 1B), -2.3 (d, J = 168 Hz, 1B), -3.5 (d, J = 142 Hz, 3B), -5.2 (d, J = 125 Hz, 1B), -9.4 (d, J = 163 Hz, 1B), -27.1 (d, 170 Hz, 1B); IR (ν cm^{-1}): 2958, 2922, 2852, 2541 (BH), 2513 (BH),1463, 1260, 1092, 1016, 800; HRMS (ESI): Calculated for $C_{21}H_{30}B_9Ir$: 613.2446 $[M+K]^+$, Found: 613.2484.

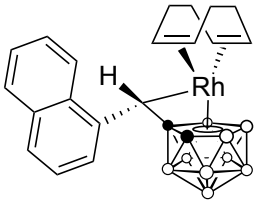
Scheme S2. Formation, crystal structures of the enantiomers 5b-Rh and selected bond length of (S_p, R)-**5b-Rh.** Hydrogen atom on C3 was demonstrated to clarify the absolute configuration of **5b-Rh**; other hydrogen atoms were omitted for clarity; thermal ellipsoids are shown in 50% probability: Selected bond lengths [Å] of (S_p, R)-**5b-Rh**: C1–C2 1.696(9), C2–C3 1.417(9), Rh–C1 2.160(7), Rh–C2 2.131(5), Rh–C3 2.407(6), B1–C1 1.72(1), B3–C2 1.816(9).





Synthesis of (S_p, R)-**5b-Rh**, the enantiomer of (R_p, S)-**5b-Rh**

Starting from the (*Ss*) Ellman's sulfonamides, via same synthetic procedures as that for (R_p, S)-**5b-Rh** mentioned above.



(S_p, R)-**5b-Rh**

Chemical Formula: $C_{21}H_{30}B_9Rh$
Exact Mass: 484.22
Molecular Weight: 482.67

The product (S_p, R)-**5b-Rh** was obtained as dark red crystals after purification by preparative TLC (EtOAc/PE = 1:10 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 8.0 Hz, 1H, Ar*H*), 7.97-7.90 (m, 3H, Ar*H*), 7.68 (t, J = 8.0 Hz, 1H, Ar*H*), 7.59 (t, J = 8.0 Hz, 1H, Ar*H*), 7.40 (t, J = 8.0 Hz, 1H, Ar*H*), 6.15 (s, C*H*), 5.55 (d, J = 8.0 Hz, $COD_{olefinic}H$), 5.42 (t, J = 8.0 Hz, $COD_{olefinic}H$), 5.10 (t, J = 8.0 Hz, $COD_{olefinic}H$), 3.39 (t, J = 8.0 Hz, $COD_{olefinic}H$), 3.16-3.12 (m, 1H, $COD_{olefinic}H$), 2.95-2.89 (m, 1H), 2.67-2.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.9, 132.9, 131.1, 130.0, 129.8, 126.9, 126.4, 125.9, 124.7, 121.3, 102.7, 95.5, 92.5, 91.3, 79.3, 34.3, 31.3, 30.9, 28.6; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ 11.0 (2B), 1.6 (1B), -0.4 (1B), -3.3 (1B), -5.0 (1B), -17.1 (2B), -22.6 (1B); ^{11}B NMR (128 MHz, $CDCl_3$): δ 11.0 (d, J = 145 Hz, 2B), 1.32 (d, J = 220 Hz, not well resolved, 1B), -0.4 (d, J = 159 Hz, 1B), -3.3 (d, J = 142 Hz, 1B), -5.0 (d, J = 162 Hz, 1B), -17.1 (d, J = 152 Hz, 2B), -22.7 (d, J = 184 Hz, 1B); IR (ν cm^{-1}): 2922, 2852, 2541 (BH), 1455, 1260, 1068, 1015, 796, 725; HRMS (ESI):Calculated for $C_{21}H_{30}B_9Rh$: 485.2313 [M+H]$^+$, Found: 485.2309.

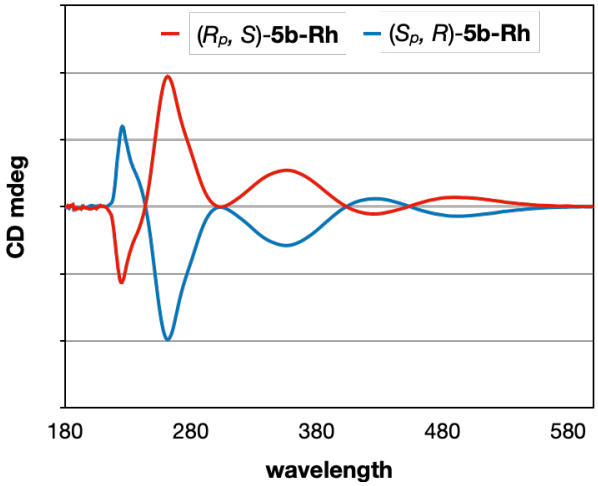


Figure S1. Circular dichroism spectra of the enantiomers (R_p, S)-**5b-Rh and** (S_p, R)-**5b-Rh**

6. Crystal data

The intensity data were collected on a Bruker APEXIJ DVO diffractometer (Mo-K α radiation, λ = 0.71073 Å, graphite monochromator) at 296 K. Data were corrected for Lorentz polarization and absorption effects (semi-empirical method). The structures were solved by direct methods (ShelXS)[6] and refined by least-squares methods based on F^2 (ShelXL)[6], both softwares were embedded in the interface of Olex2 system[7]. Part of the hydrogen atoms were located in the difference Fourier maps and other hydrogen atoms were put to the geometric positions, and all the hydrogen atoms were refined isotropically. All non-hydrogen atoms were refined anisotropically.

The following crystal structures are drawn with thermal ellipsoids at 50% probability level. Color scheme: B: pink; C: grey; N: light blue; O: red; S: yellow; Rh: dark green; Ir: dark blue).

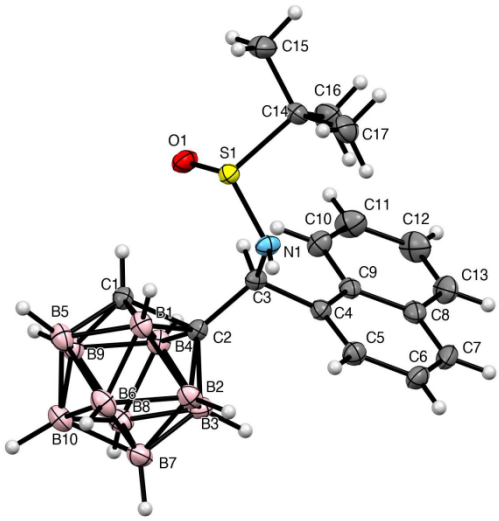


Table S2 Crystal data and structure refinement for (R_S, R)-**3b.**

Identification code	(R_S, R)-**3b (CCDC 2019604)**
Empirical formula	$C_{17}H_{29}B_{10}NOS$
Formula weight	403.57
Temperature/K	296.15
Crystal system	tetragonal
Space group	$P4_3$
a/Å	11.5419(6)
b/Å	11.5419(6)
c/Å	16.7630(17)
α/°	90
β/°	90
γ/°	90

Volume/Å^3	2233.1(3)
Z	4
ρ_{calc}g/cm^3	1.200
μ/mm^{-1}	0.155
F(000)	848.0
Crystal size/mm^3	0.3 × 0.22 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.528 to 51.126
Index ranges	-13 ≤ h ≤ 13, -12 ≤ k ≤ 13, -20 ≤ l ≤ 20
Reflections collected	18593
Independent reflections	4144 [R_{int} = 0.0176, R_{sigma} = 0.0170]
Data/restraints/parameters	4144/1/297
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0267, wR_2 = 0.0693
Final R indexes [all data]	R_1 = 0.0283, wR_2 = 0.0706
Largest diff. peak/hole / e Å^{-3}	0.21/-0.14
Flack parameter	0.054(16)

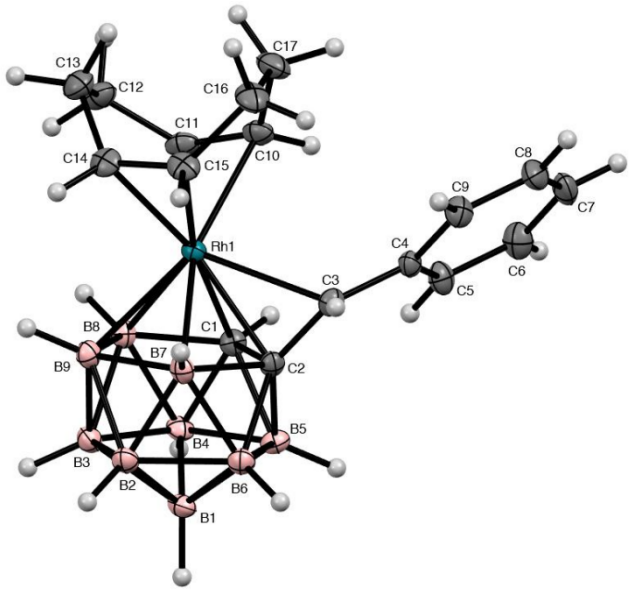


Table S3 Crystal data and structure refinement for (S_p,S)-5a-Rh.

Identification code	(S_p,S)-**5a-Rh (CCDC 1833991)**
Empirical formula	$C_{18}H_{29}B_9Cl_3Rh$

Formula weight	551.96
Temperature/K	150(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.6404(4)
b/Å	12.1876(4)
c/Å	17.9434(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2326.92(14)
Z	4
ρ_{calc}g/cm^3	1.576
μ/mm^{-1}	1.084
F(000)	1112.0
Crystal size/mm^3	0.18 × 0.14 × 0.10
Radiation	MoKα (λ = 0 71073)
2Θ range for data collection/°	4.04 to 53.11
Index ranges	-13 ≤ h ≤ 10, -15 ≤ k ≤ 15, -18 ≤ l ≤ 22
Reflections collected	17315
Independent reflections	4827 [R_{int} = 0.0203, R_{sigma} = 0.0220]
Data/restraints/parameters	4827/0/284
Goodness-of-fit on F^2	1 027
Final R indexes [I>=2σ (I)]	R_1 = 0.0189, wR_2 = 0.0500
Final R indexes [all data]	R_1 = 0.0199, wR_2 = 0.0506
Largest diffpeak/hole / e Å^{-3}	0.39/-0.26
Flack parameter	-0.004(9)

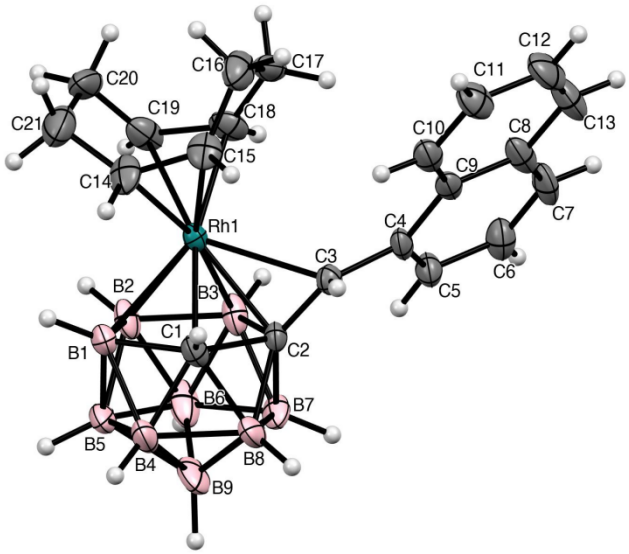


Table S3 Crystal data and structure refinement for (R_p,*S*)-5b-Rh.

Identification code	(R_p,*S*)-**5b-Rh (CCDC 2019607)**
Empirical formula	$C_{21}H_{30}B_9Rh$
Formula weight	482.65
Temperature/K	296.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.828(8)
b/Å	14.330(11)
c/Å	14.723(11)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2284(3)
Z	4
ρ_{calc}g/cm^3	1.403
μ/mm^{-1}	0.755
F(000)	984.0
Crystal size/mm^3	0.19 × 0.17 × 0.17
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.966 to 50.018

Index ranges	$-12 \le h \le 12$, $-17 \le k \le 17$, $-17 \le l \le 17$
Reflections collected	21405
Independent reflections	4030 [R_{int} = 0.1241, R_{sigma} = 0.0699]
Data/restraints/parameters	4030/0/284
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0341, wR_2 = 0.0658
Final R indexes [all data]	R_1 = 0.0401, wR_2 = 0.0682
Largest diff. peak/hole / e $Å^{-3}$	0.52/-0.46
Flack parameter	-0.01(3)

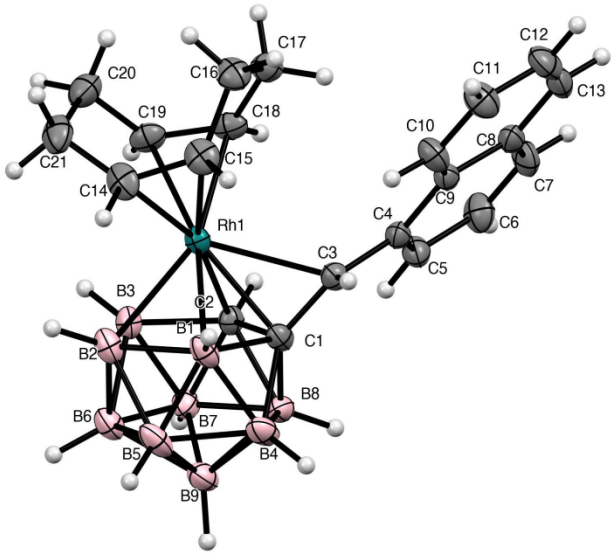


Table S4 Crystal data and structure refinement for (S_p,S)-5b-Rh.

Identification code	(S_p,R)-**5b-Rh (CCDC 2019608)**
Empirical formula	$C_{21}H_{30}B_9Rh$
Formula weight	482.65
Temperature/K	296.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	12.713(3)
b/Å	13.248(3)
c/Å	13.479(3)
α/°	90
β/°	90

γ/°	90
Volume/Å^3	2270.3(9)
Z	4
ρ_{calc}g/cm^3	1.412
μ/mm^{-1}	0.759
F(000)	984.0
Crystal size/mm^3	0.22 × 0.18 × 0.17
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.31 to 53.046
Index ranges	-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -16 ≤ l ≤ 16
Reflections collected	24339
Independent reflections	4691 [R_{int} = 0.0211, R_{sigma} = 0.0160]
Data/restraints/parameters	4691/0/280
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0180, wR_2 = 0.0461
Final R indexes [all data]	R_1 = 0.0188, wR_2 = 0.0465
Largest diff. peak/hole / e Å^{-3}	0.41/-0.32
Flack parameter	-0.011(8)

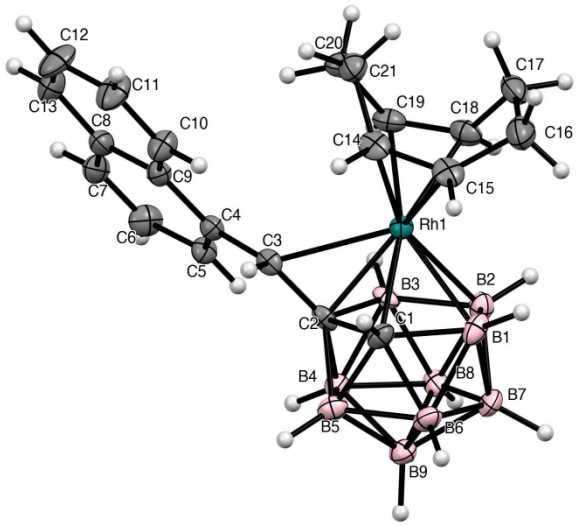


Table S5 Crystal data and structure refinement for (S_p,*R*)**-5b-Rh.**

Identification code	(S_p,*R*)**-5b-Rh (CCDC 2019609)**
Empirical formula	$C_{21}H_{30}B_9Rh$

Formula weight	482.65
Temperature/K	296.15
Crystal system	triclinic
Space group	P1
a/Å	12.807(3)
b/Å	13.250(4)
c/Å	13.613(4)
α/°	93.578(3)
β/°	94.625(3)
γ/°	92.707(3)
Volume/Å^3	2294.8(11)
Z	4
ρ_{calc}g/cm^3	1.397
μ/mm^{-1}	0.751
F(000)	984.0
Crystal size/mm^3	0.2 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.008 to 53.254
Index ranges	-16 ≤ h ≤ 16, -16 ≤ k ≤ 16, -17 ≤ l ≤ 17
Reflections collected	24728
Independent reflections	18492 [R_{int} = 0.0179, R_{sigma} = 0.0438]
Data/restraints/parameters	18492/3/1129
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0331, wR_2 = 0.0759
Final R indexes [all data]	R_1 = 0.0355, wR_2 = 0.0770
Largest diff. peak/hole / e Å^{-3}	1.19/-0.64
Flack parameter	0.013(10)

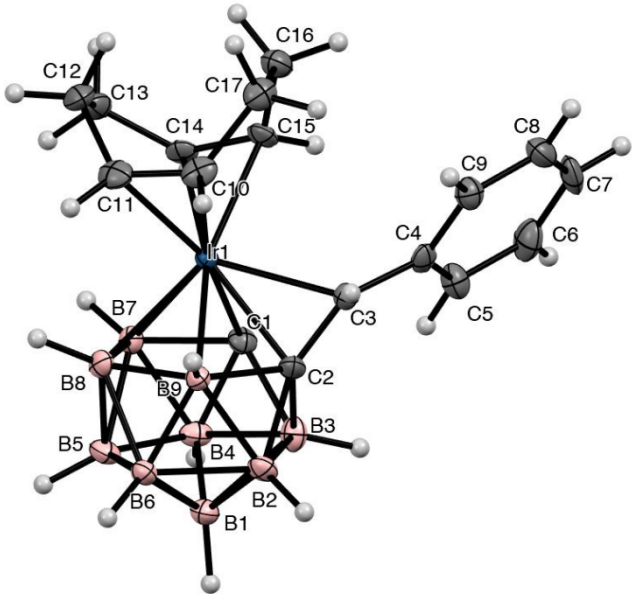


Table S6 Crystal data and structure refinement for (S_p,S)-5a-Ir.

Identification code	**(S_p,S)-5a-Ir (CCDC 1828008)**
Empirical formula	$C_{17}H_{27}B_9Ir$
Formula weight	520.87
Temperature/K	150.15
Crystal system	orthorhombic
Space group	Fdd2
a/Å	18.887(3)
b/Å	43.501(6)
c/Å	9.4381(13)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	7754.4(19)
Z	16
ρ_{calc}g/cm^3	1.785
μ/mm^{-1}	6.886
F(000)	4016.0
Crystal size/mm^3	0.2 × 0.5 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.746 to 50.866
Index ranges	-19 ⩽ h ⩽ 22, -52 ⩽ k ⩽ 52, -11 ⩽ l ⩽ 9
Reflections collected	8793
Independent reflections	3365 [R_{int} = 0.0190, R_{sigma} = 0.0309]
Data/restraints/parameters	3365/7/244
Goodness-of-fit on F^2	1.131

Final R indexes [I>=2σ (I)]	R_1 = 0.0174, wR_2 = 0.0440
Final R indexes [all data]	R_1 = 0.0179, wR_2 = 0.0442
Largest diffpeak/hole / e Å^{-3}	1.31/-0.95
Flack parameter	0.015(5)

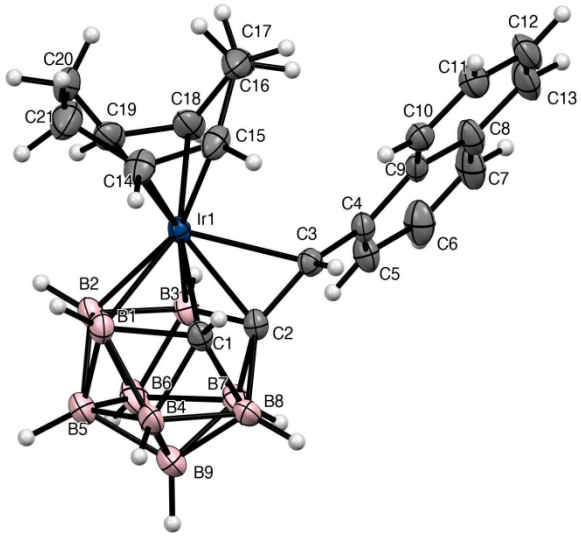


Table S7 Crystal data and structure refinement for (R_p,S)-5b-Ir.

Identification code	(R_p,S)**-5b-Ir (CCDC 2019610)**
Empirical formula	$C_{21}H_{30}B_9Ir$
Formula weight	571.94
Temperature/K	296.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	11.003(9)
b/Å	14.656(12)
c/Å	14.853(12)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2395(3)
Z	4
ρ_{calc}g/cm^3	1.586
μ/mm^{-1}	5.581

F(000)	1112.0
Crystal size/mm^3	0.21 × 0.17 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.904 to 52.29
Index ranges	-13 ≤ h ≤ 13, -18 ≤ k ≤ 18, -18 ≤ l ≤ 18
Reflections collected	23413
Independent reflections	4691 [R_{int} = 0.0313, R_{sigma} = 0.0271]
Data/restraints/parameters	4691/0/280
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0177, wR_2 = 0.0429
Final R indexes [all data]	R_1 = 0.0187, wR_2 = 0.0432
Largest diff. peak/hole / e Å^{-3}	0.87/-0.33
Flack parameter	0.000(4)

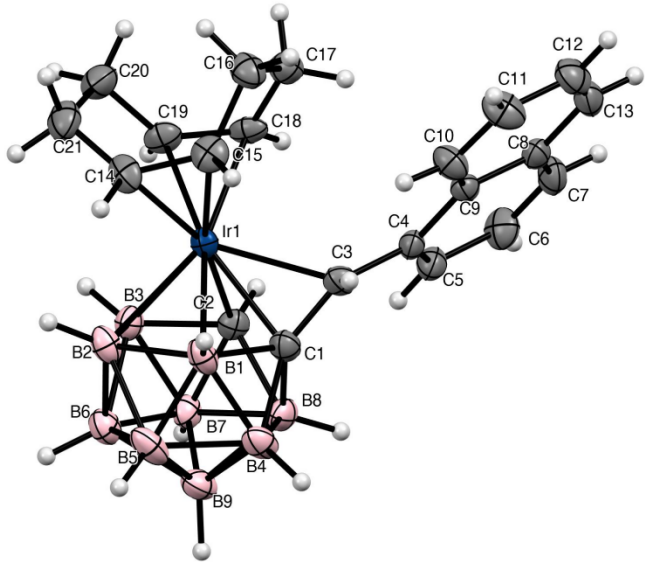


Table S8 Crystal data and structure refinement for (S_p, S)**-5b-Ir.**

Identification code	(S_p, S)-**5b-Ir (CCDC 2019611)**
Empirical formula	$C_{21}H_{30}B_9Ir$
Formula weight	571.94
Temperature/K	296.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$

a/Å	12.802(8)
b/Å	13.158(8)
c/Å	13.586(9)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2289(3)
Z	4
ρ_{calc}g/cm^3	1.660
μ/mm^{-1}	5.841
F(000)	1112.0
Crystal size/mm^3	0.2 × 0.18 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.31 to 52.93
Index ranges	-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -17 ≤ l ≤ 17
Reflections collected	22536
Independent reflections	4680 [R_{int} = 0.0326, R_{sigma} = 0.0300]
Data/restraints/parameters	4680/0/280
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0177, wR_2 = 0.0395
Final R indexes [all data]	R_1 = 0.0191, wR_2 = 0.0399
Largest diff. peak/hole / e Å^{-3}	0.79/-0.39
Flack parameter	-0.003(5)

7. References

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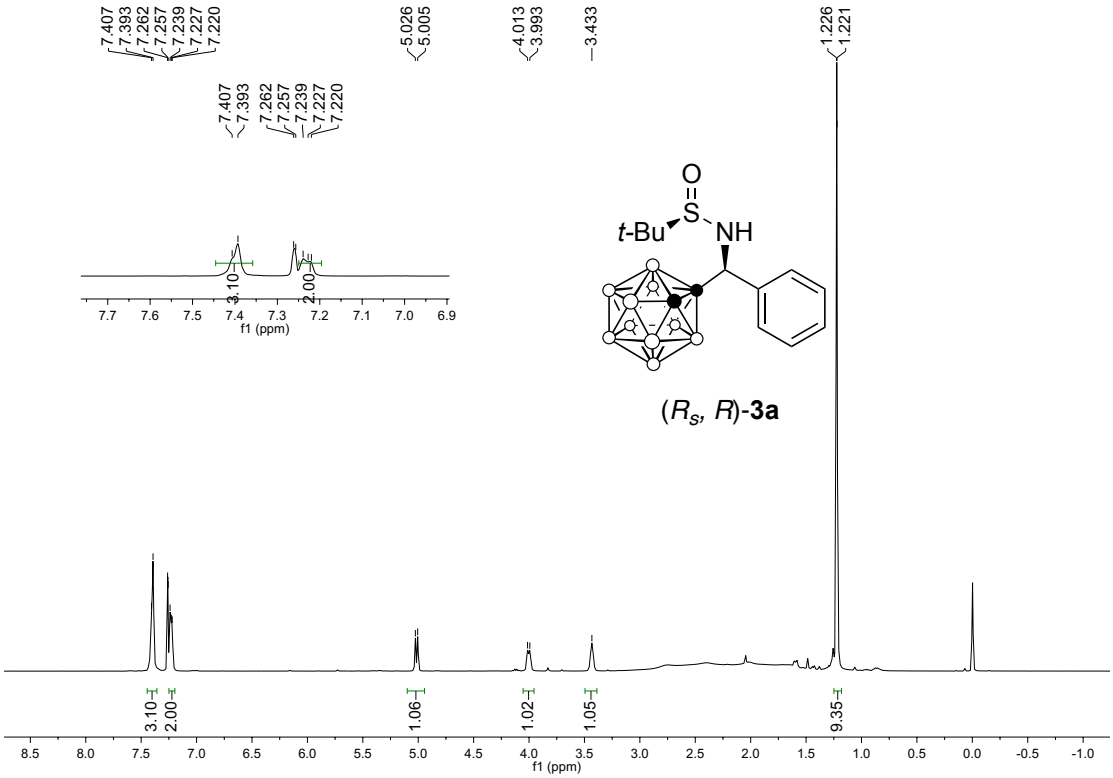
7. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R.J; Howard, J. A. K.; and Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.

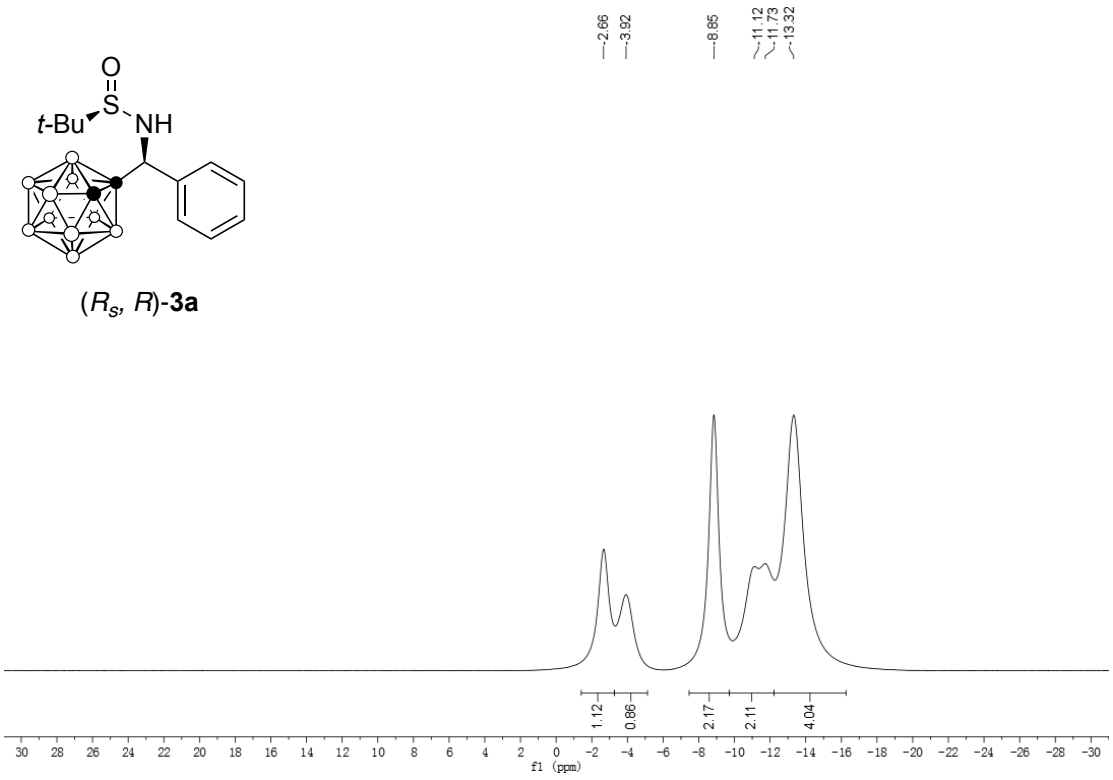
8. Copies of NMR spectra

^{1}H NMR spectrum of (*Rs, R*)**-3a**



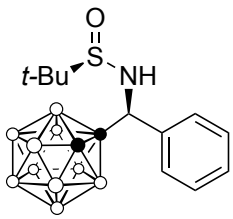
(R_S, *R*)-**3a**

^{11}B{^{1}H} NMR spectrum of (*Rs, R*)**-3a**



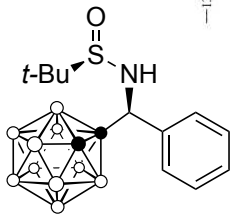
(R_S, *R*)-**3a**

^{11}B NMR spectrum of (*Rs, R*)**-3a**



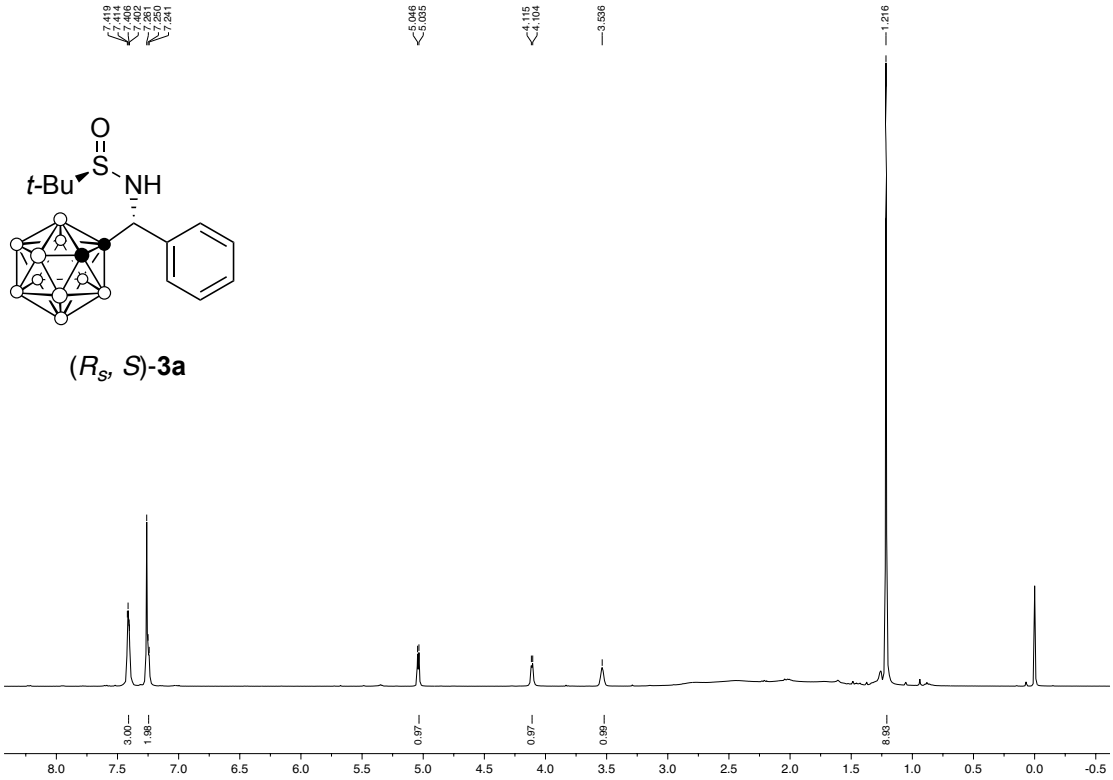
(R_s, *R*)-**3a**

^{13}C NMR spectrum of (*Rs, R*)**-3a**



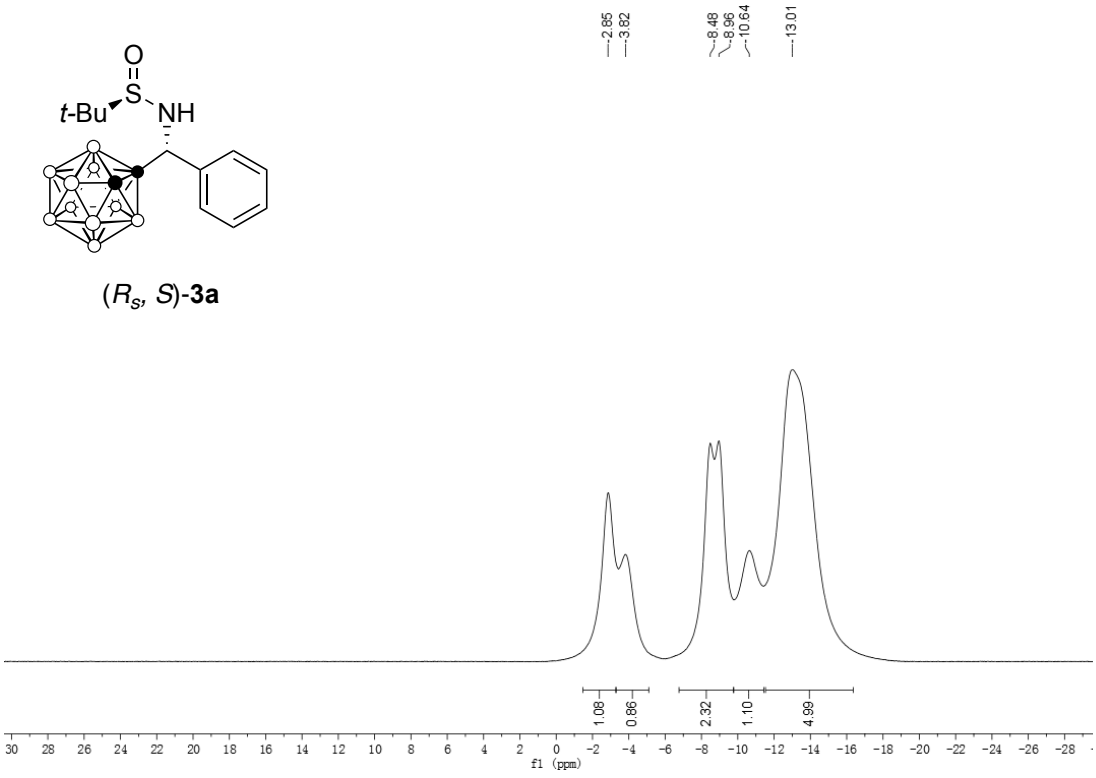
(R_s, *R*)-**3a**

^{1}H NMR spectrum of (R_S, S)-**3a**



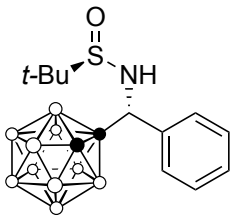
(R_S, S)-**3a**

^{11}B{^{1}H} NMR spectrum of (R_S, S)-**3a**



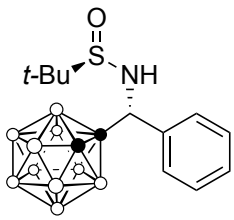
(R_S, S)-**3a**

^{11}B NMR spectrum of (R_S, S)-**3a**



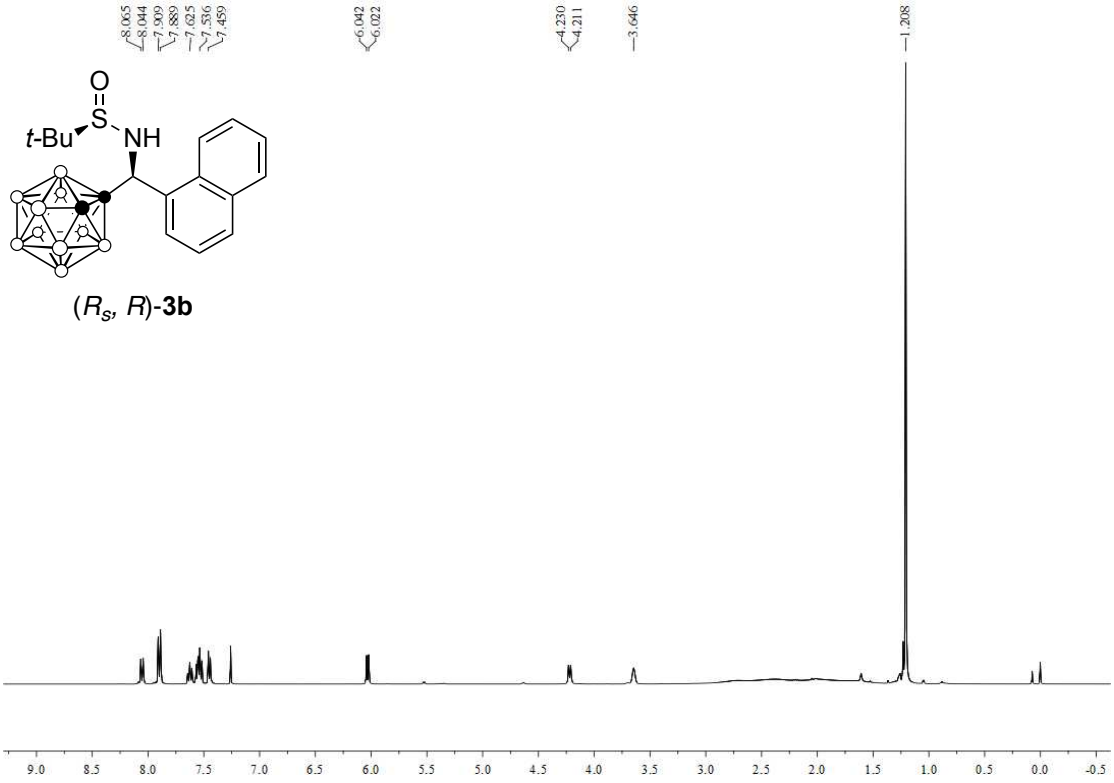
(R_s, S)-**3a**

^{13}C NMR spectrum of (R_S, S)-**3a**



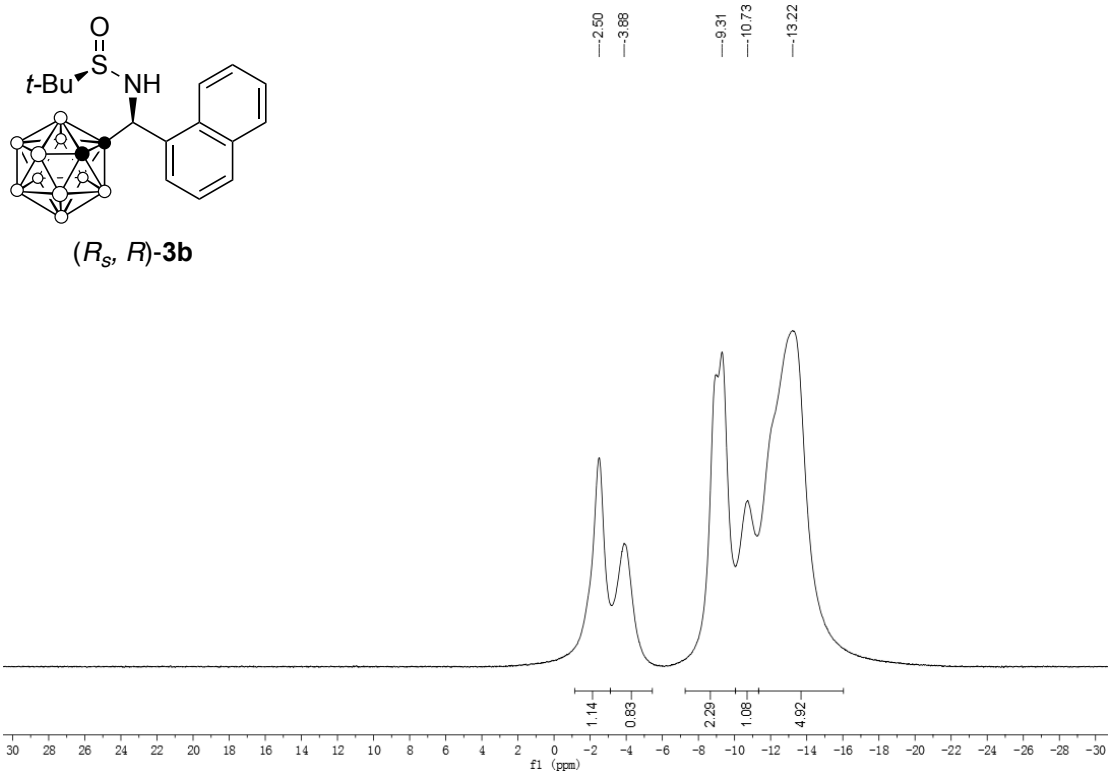
(R_s, S)-**3a**

^{1}H NMR spectrum of (*Rs, R*)-**3b**



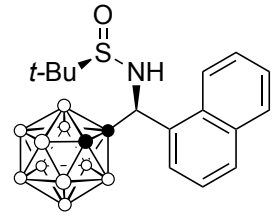
(R_s, *R*)-**3b**

^{11}B{^{1}H} NMR spectrum of (*Rs, R*)-**3b**



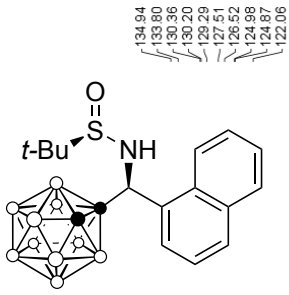
(R_s, *R*)-**3b**

^{11}B NMR spectrum of (*Rs, R*)-**3b**



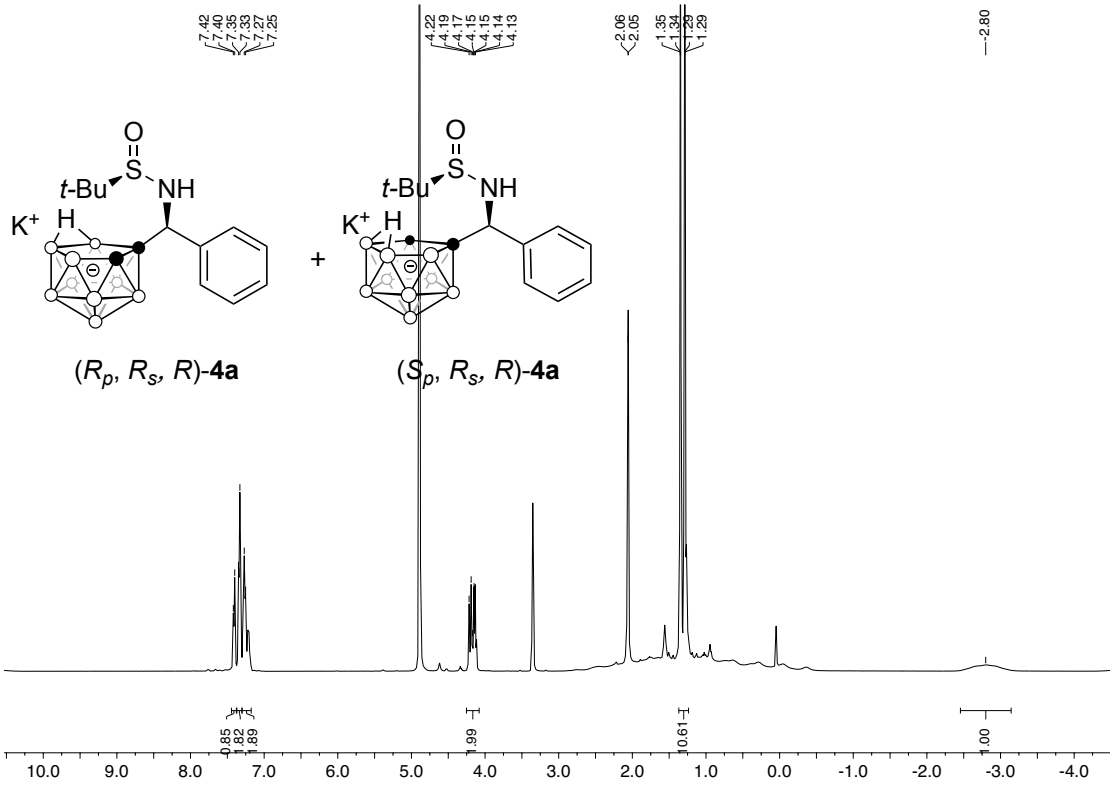
(R_s, *R*)-**3b**

^{13}C NMR spectrum of (*Rs, R*)-**3b**

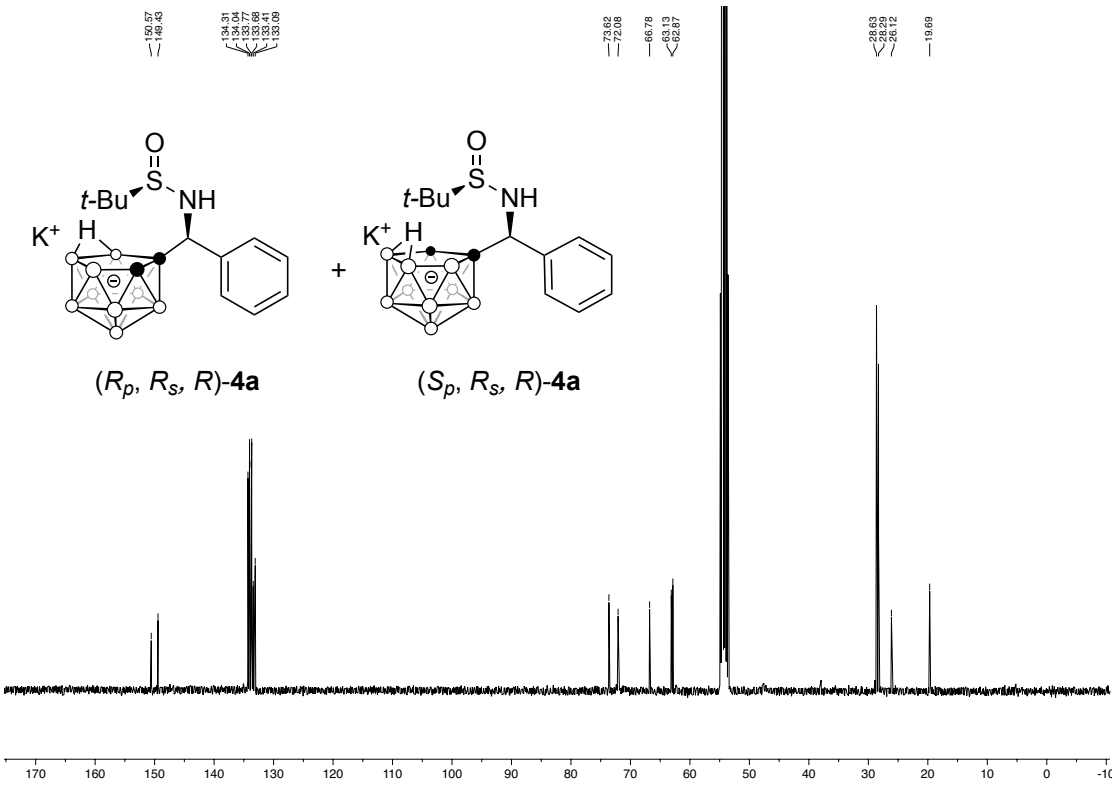


(R_s, *R*)-**3b**

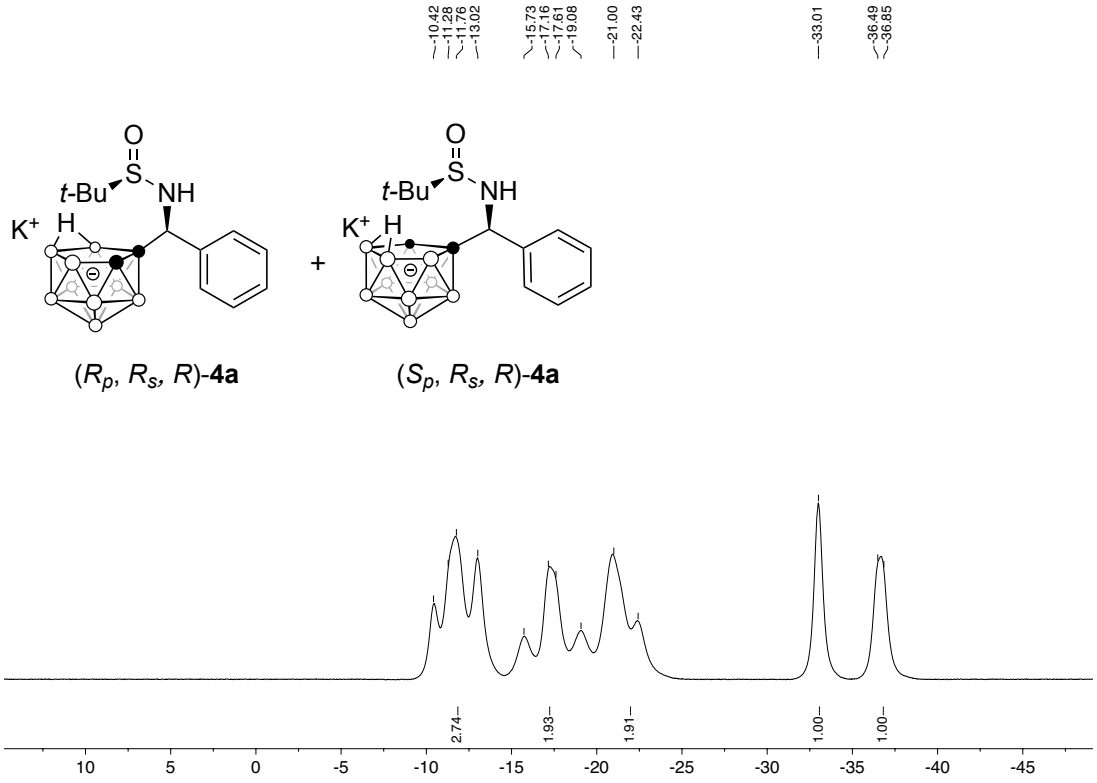
^{1}H NMR spectrum of **4a**



^{13}C NMR spectrum of **4a**

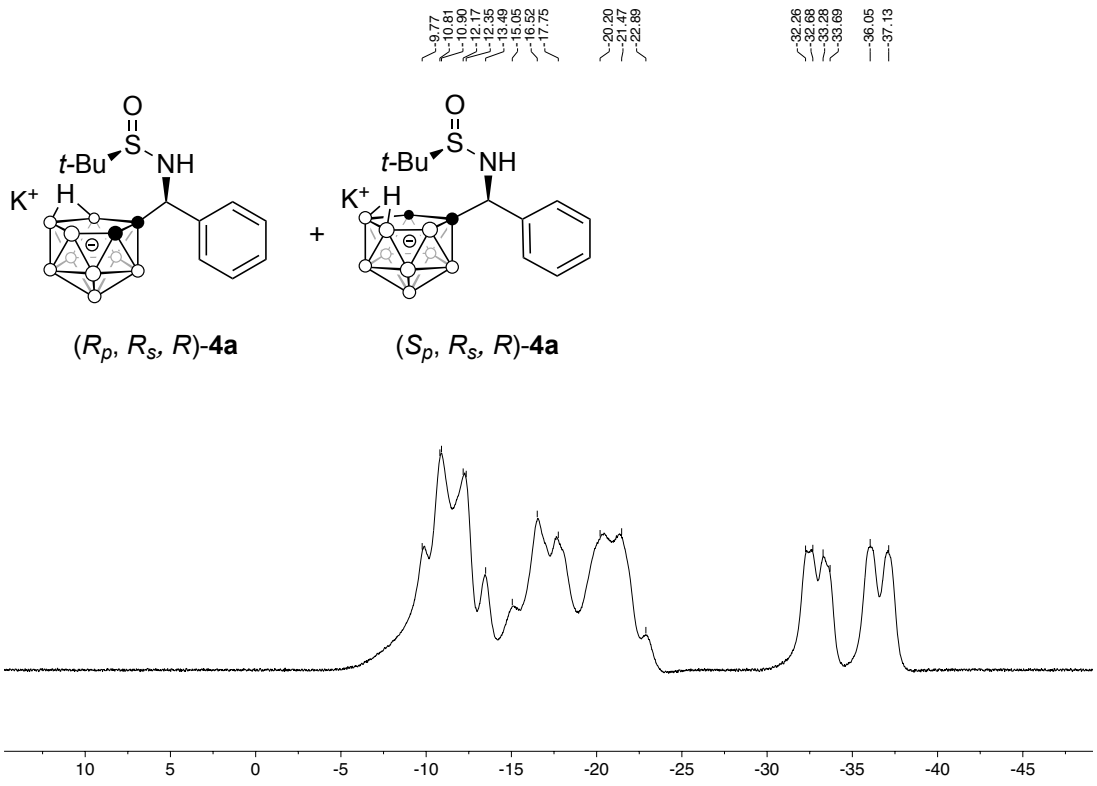


$^{11}B\{^{1}H\}$ NMRspectrum of **4a**



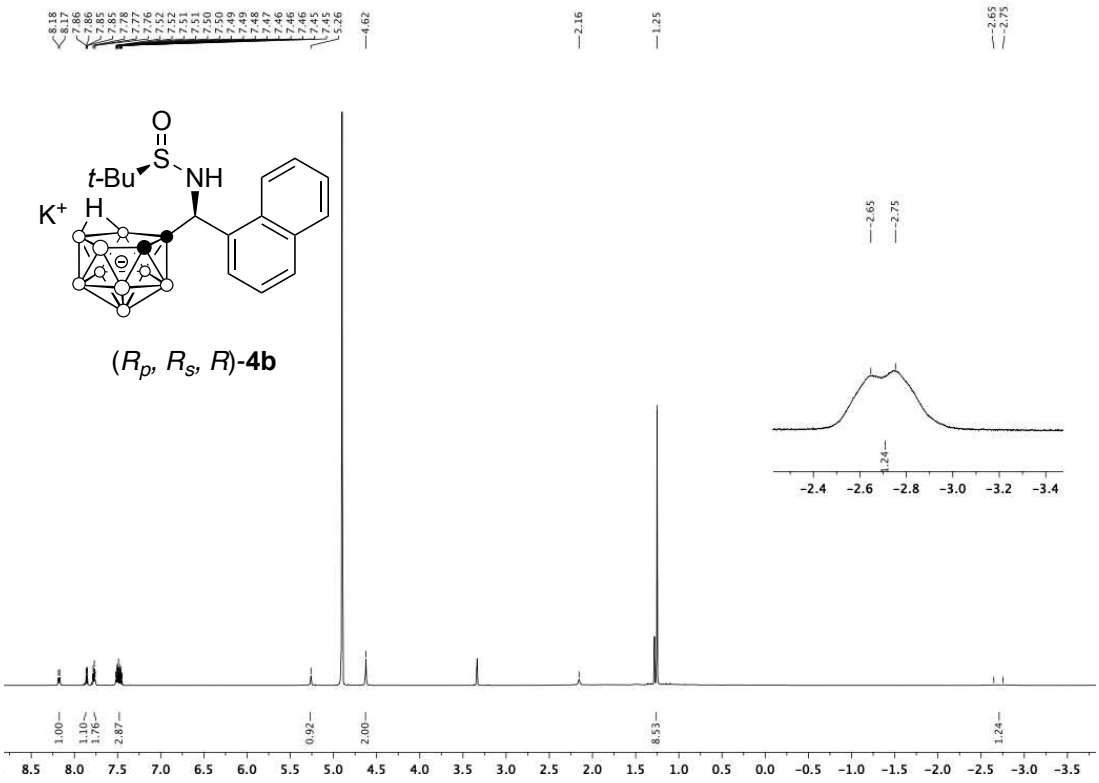
(R_p, R_s, R)-**4a** + (S_p, R_s, R)-**4a**

^{11}B NMR spectrum of **4a**

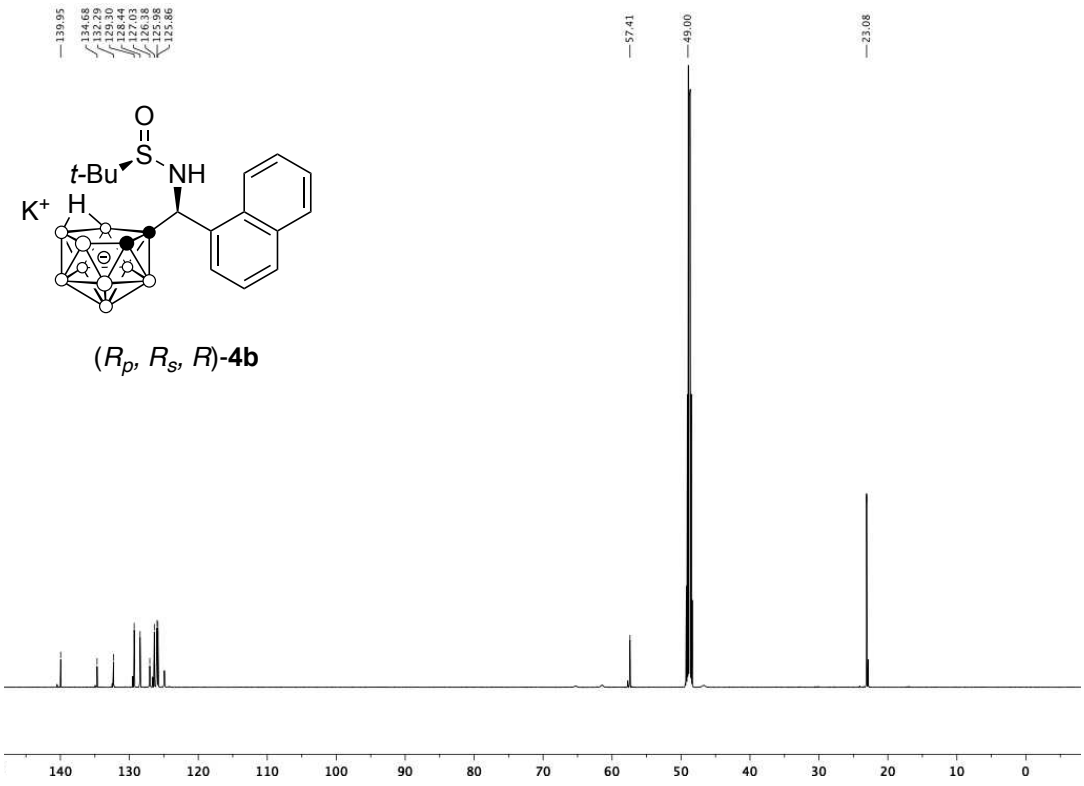


(R_p, R_s, R)-**4a** + (S_p, R_s, R)-**4a**

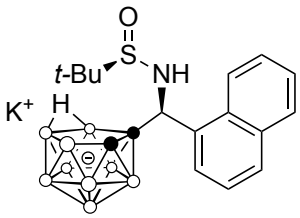
^{1}H NMR spectrum of (R_p, R_s, R)-**4b**



^{13}C NMR spectrum of (R_p, R_s, R)-**4b**

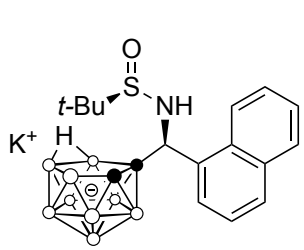


$^{11}B\{^{1}H\}$ NMR spectrum of (R_p, R_s, R)-**4b**



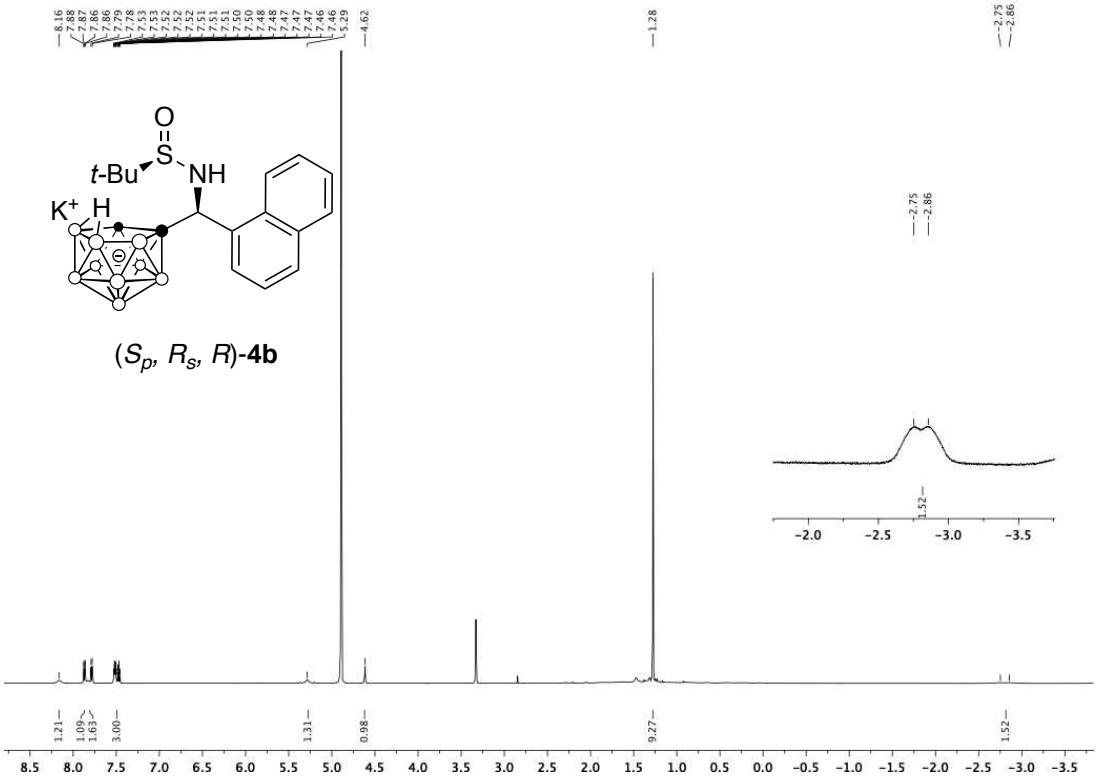
(R_p, R_s, R)-**4b**

^{11}B NMR spectrum of (R_p, R_s, R)-**4b**

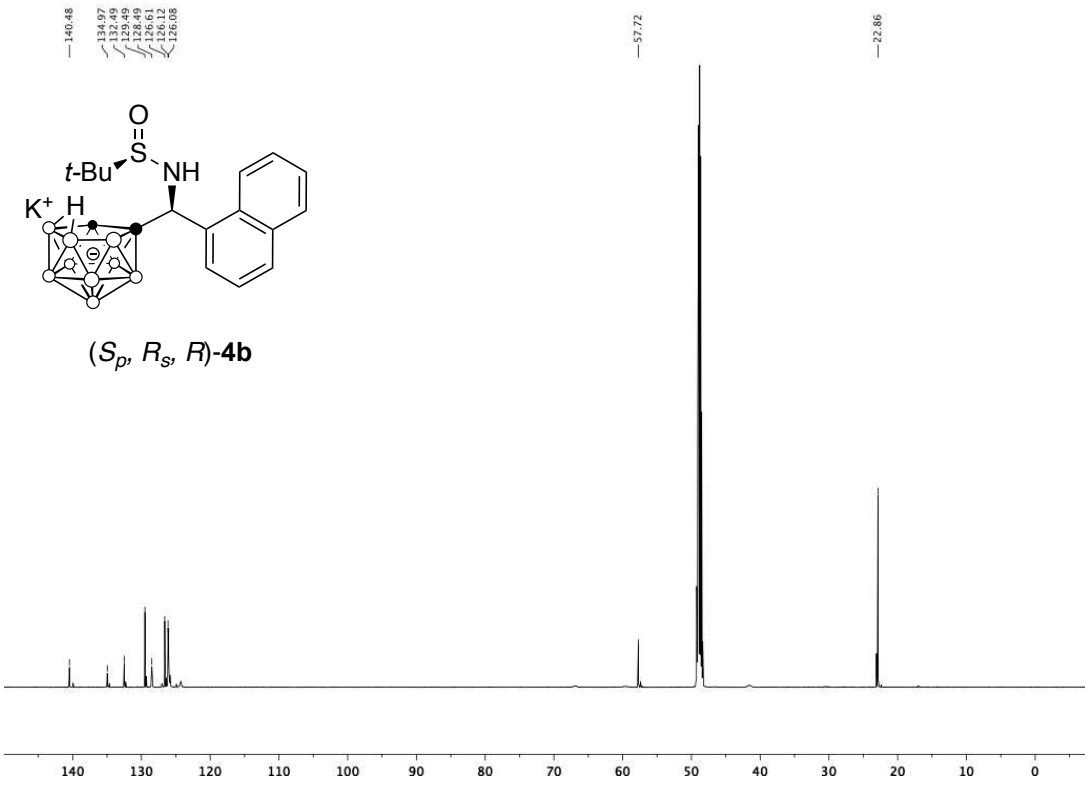


(R_p, R_s, R)-**4b**

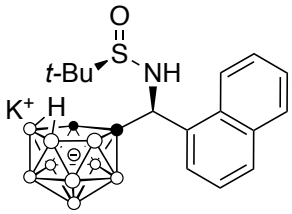
^{1}H NMR spectrum of (S_p, R_s, R)-**4b**



^{13}C NMR spectrum of (S_p, R_s, R)-**4b**

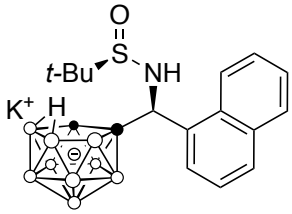


$^{11}B\{^{1}H\}$ NMR spectrum of (S_p, R_s, R)-**4b**



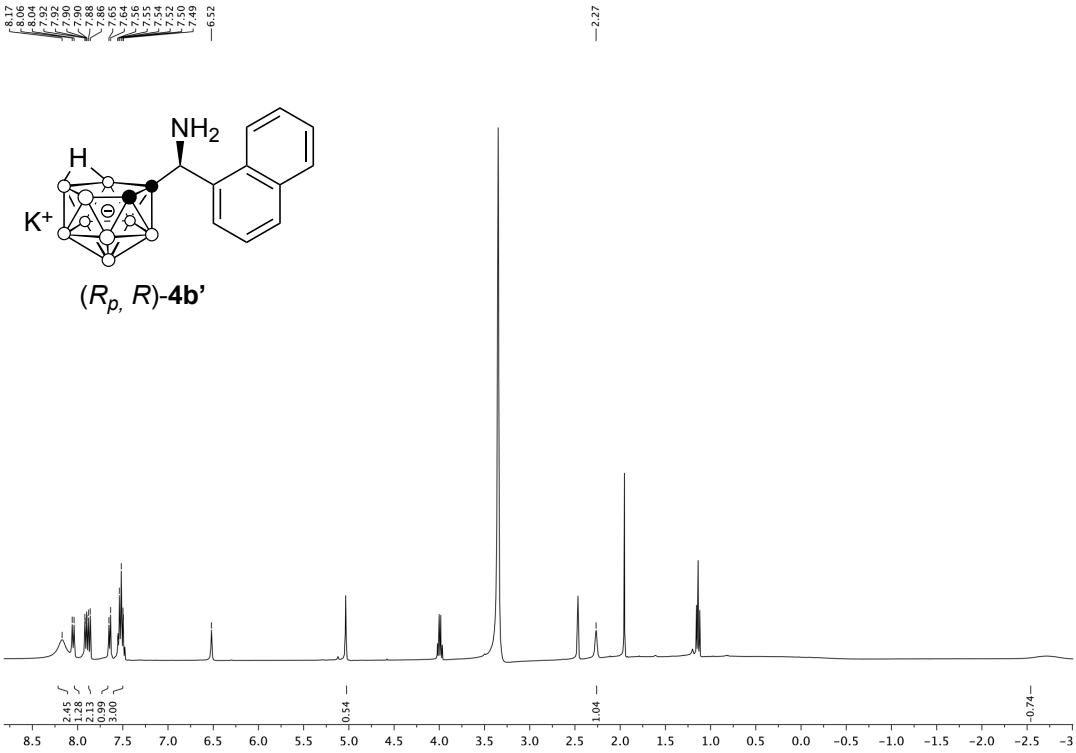
(S_p, R_s, R)-**4b**

^{11}B NMR spectrum of (S_p, R_s, R)-**4b**



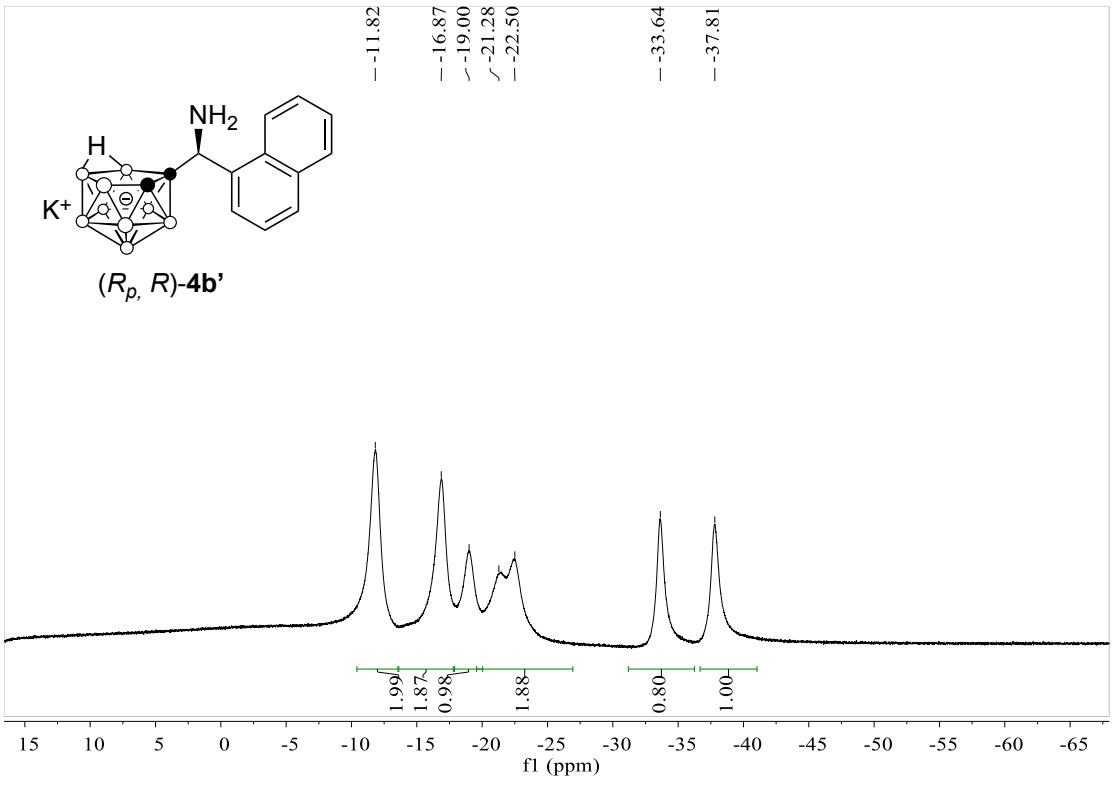
(S_p, R_s, R)-**4b**

^{1}H NMR spectrum of (R_p, R)-**4b**



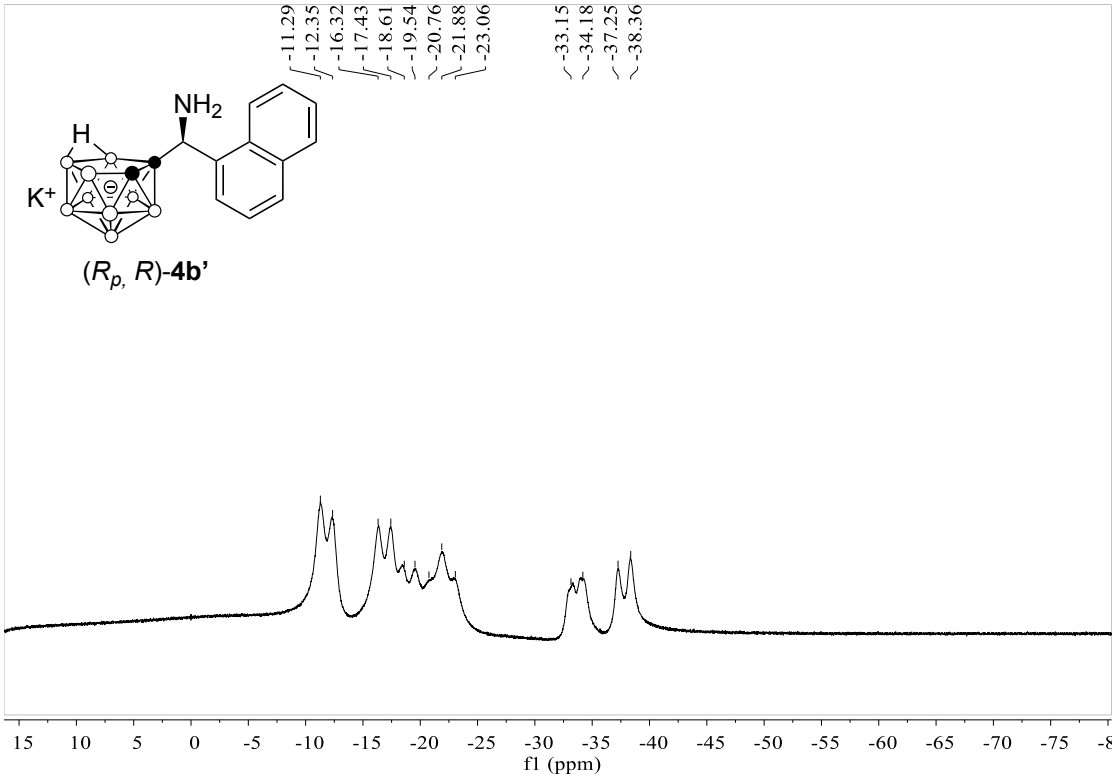
(R_p, R)-**4b'**

^{11}B{^{1}H} NMR spectrum of (R_p, R)-**4b'**



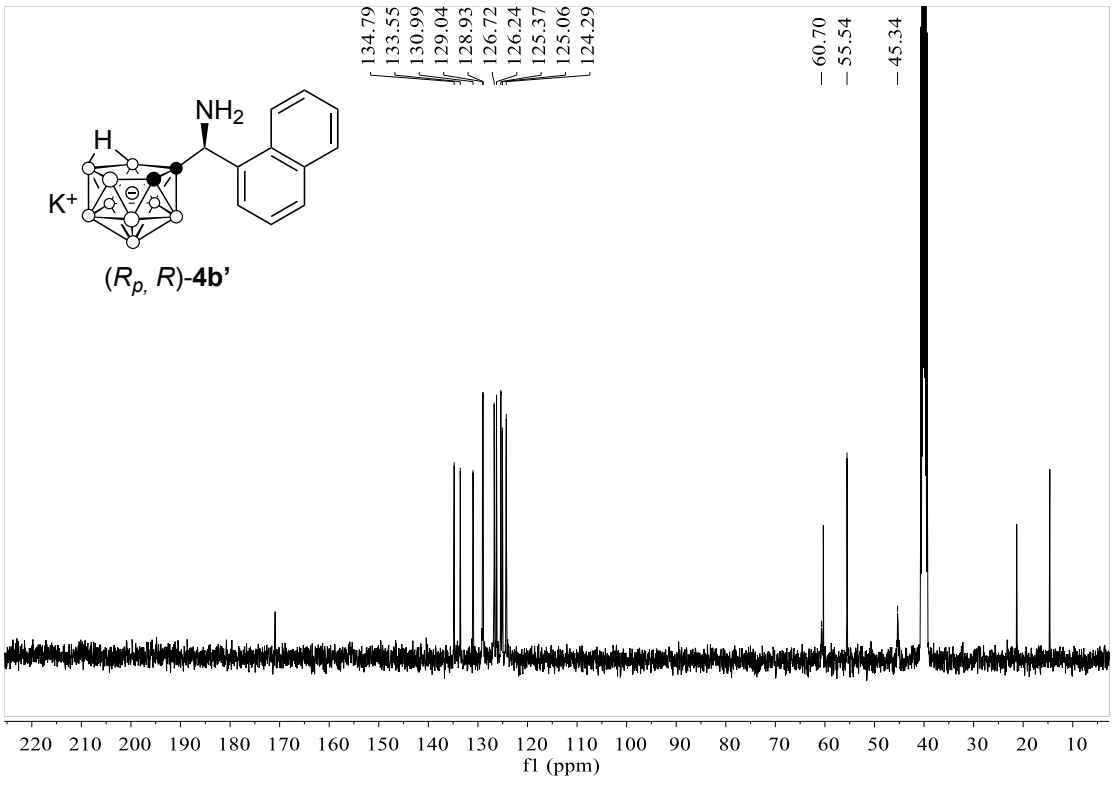
(R_p, R)-**4b'**

^{11}B NMR spectrum of (R_p, R)-**4b'**



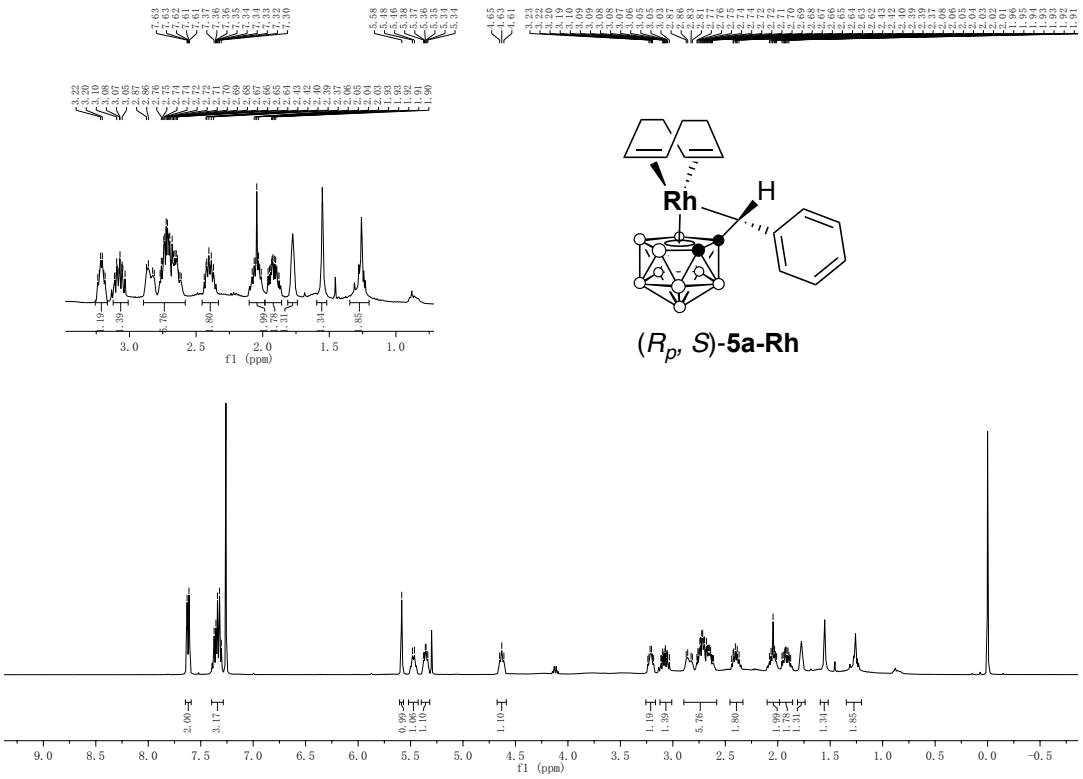
(R_p, R)-**4b'**

^{13}C NMR spectrum of (R_p, R)-**4b'**



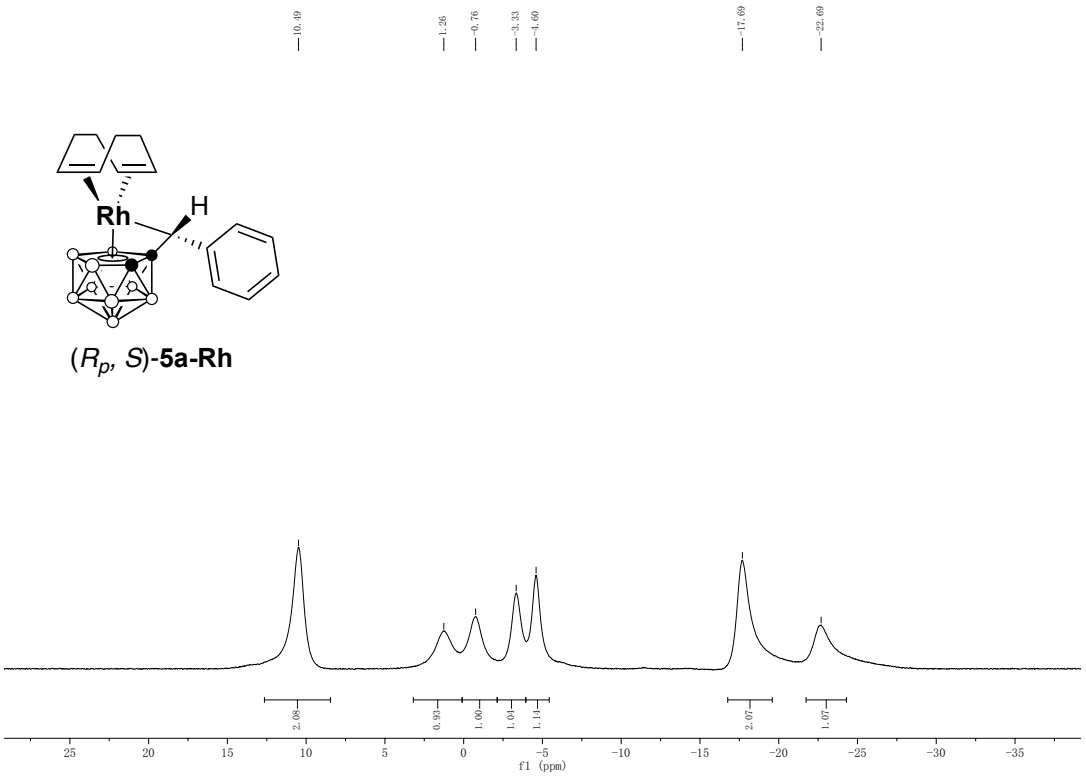
(R_p, R)-**4b'**

^{1}H NMR spectrum of (R_p, S)-**5a-Rh**



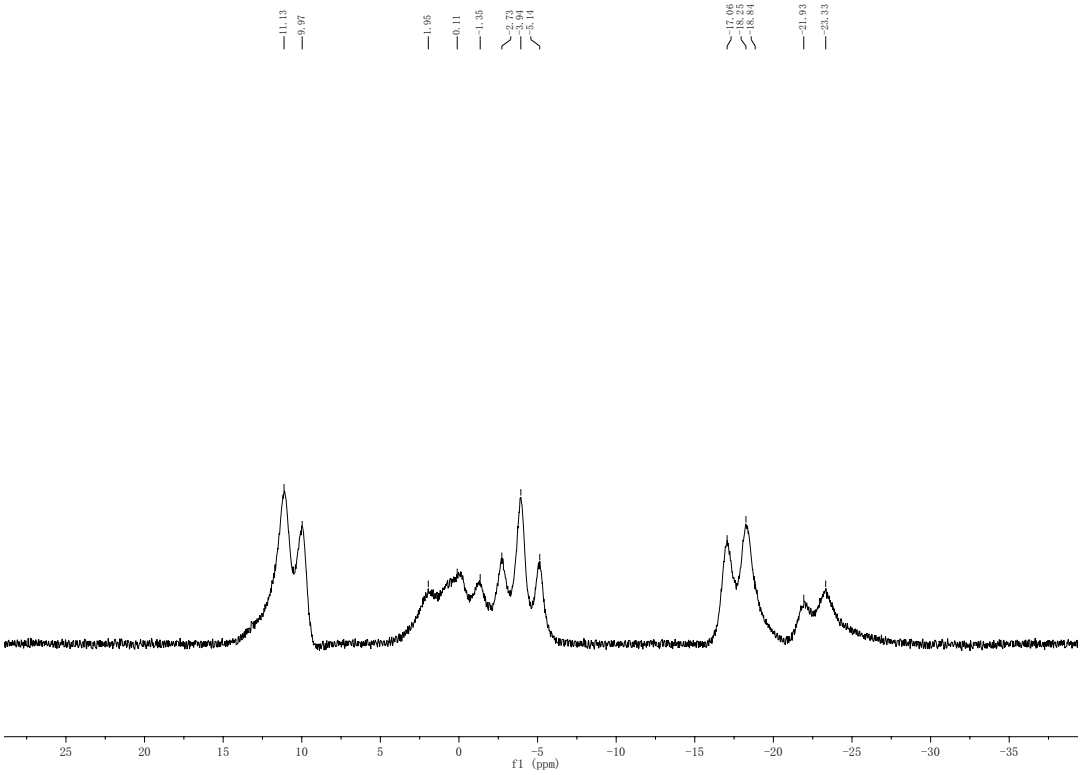
(R_p, S)-**5a-Rh**

^{11}B{^{1}H} NMR spectrum of (R_p, S)-**5a-Rh**

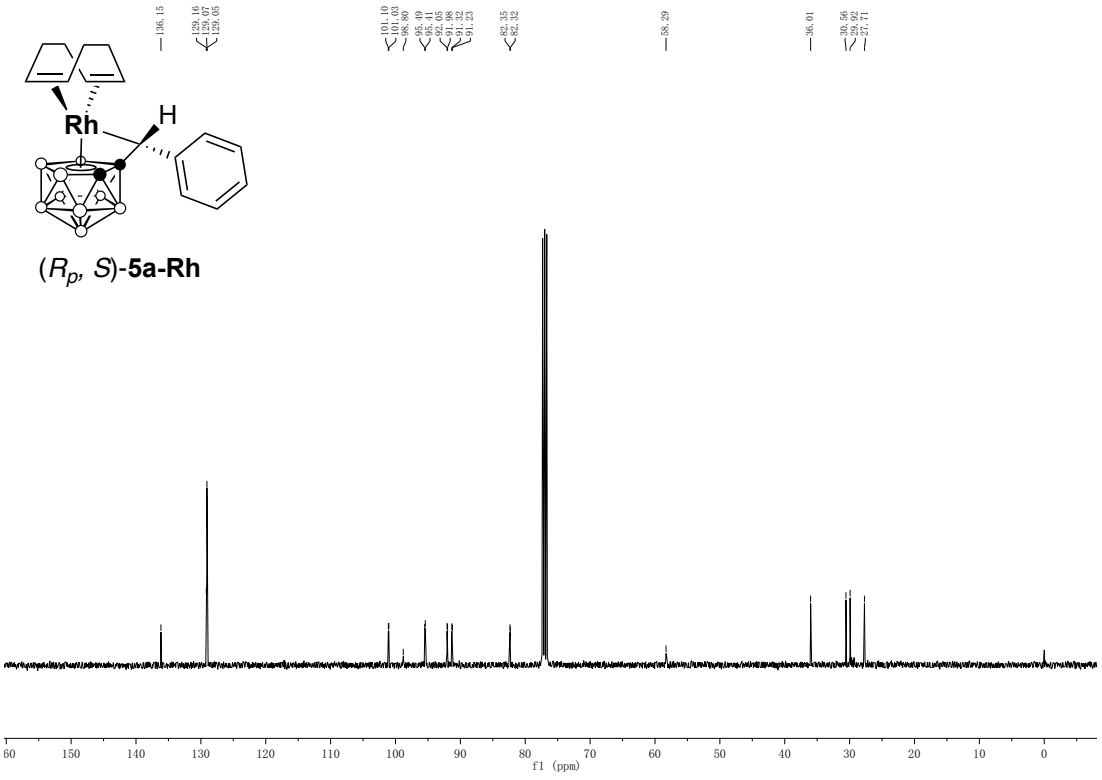


(R_p, S)-**5a-Rh**

^{11}B NMR spectrum of (R_p, S)-**5a-Rh**

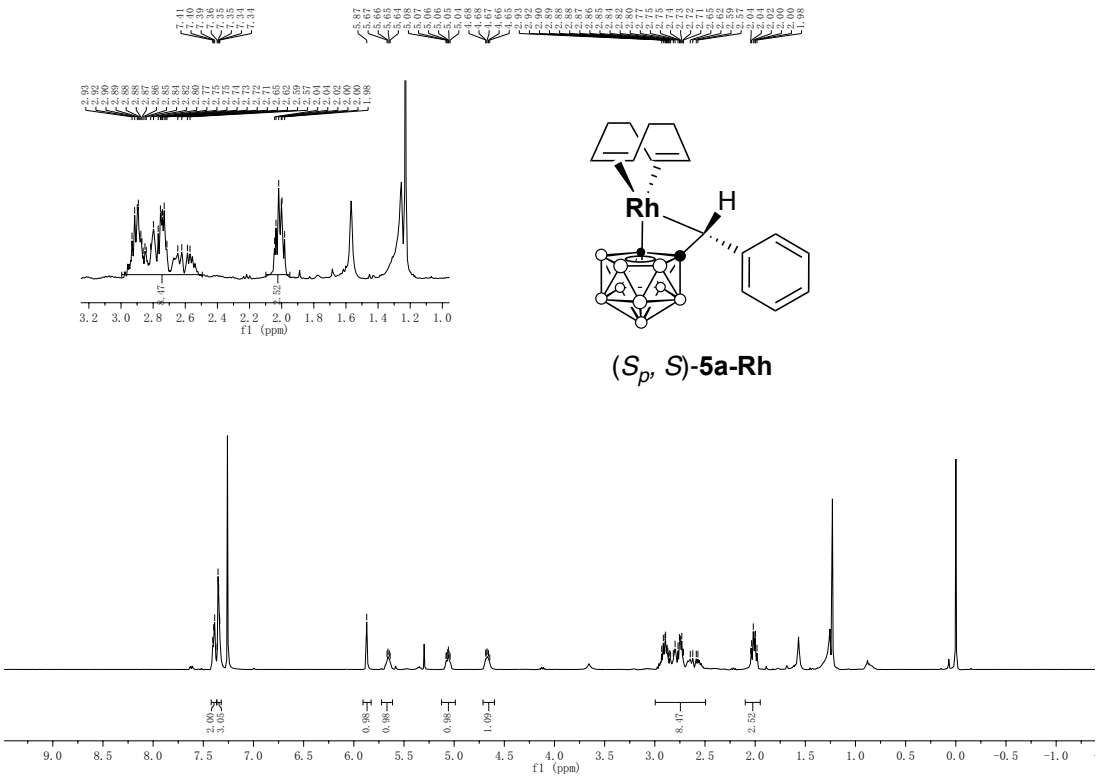


^{13}C NMR spectrum of (R_p, S)-**5a-Rh**



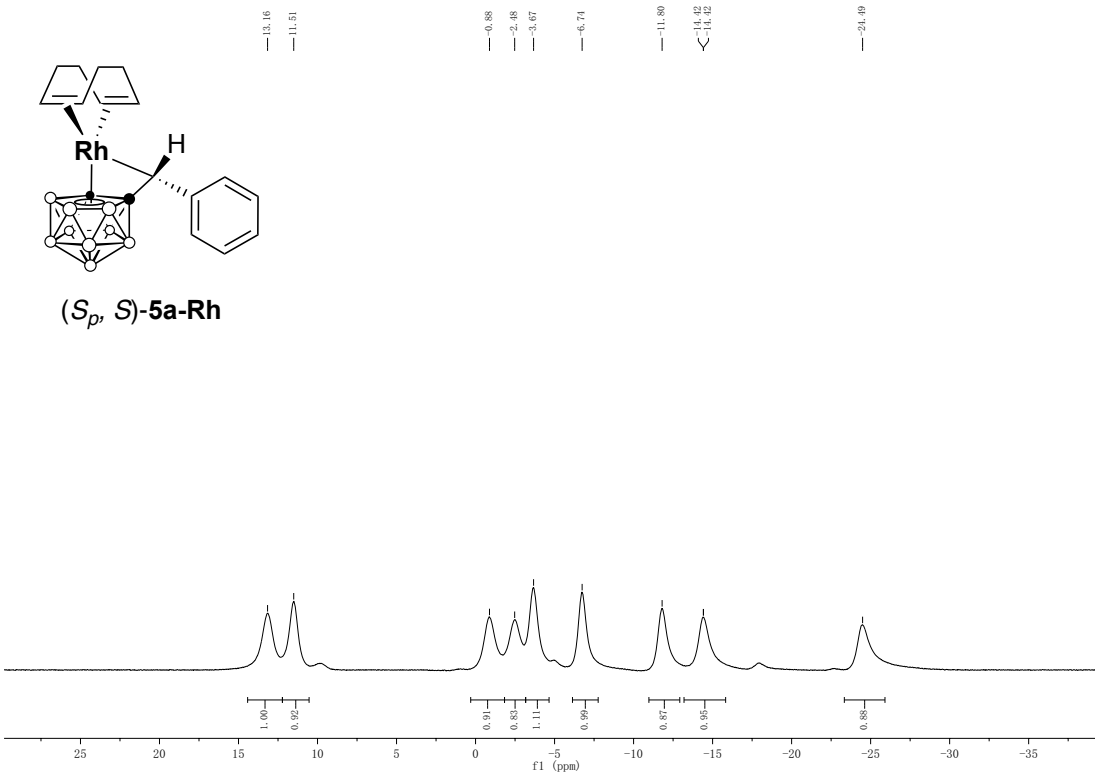
(R_p, S)-**5a-Rh**

^{1}H NMR spectrum of (S_p, S)-**5a-Rh**



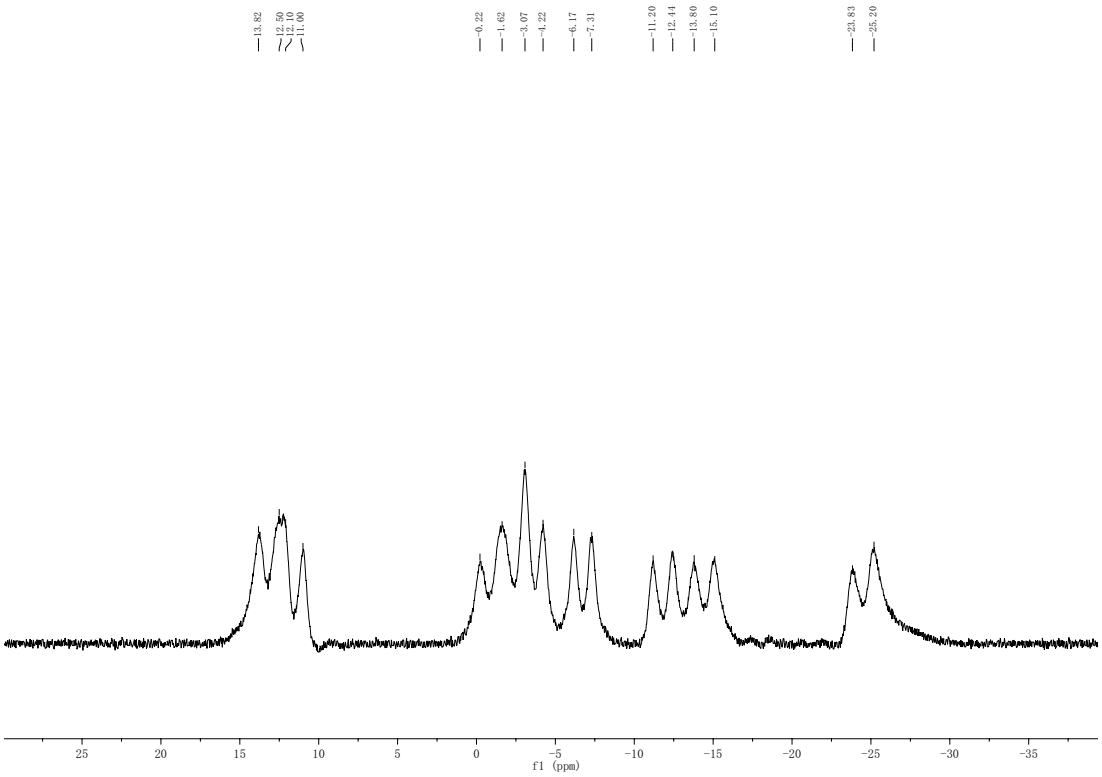
(S_p, S)-**5a-Rh**

^{11}B{^{1}H} NMR spectrum of (S_p, S)-**5a-Rh**

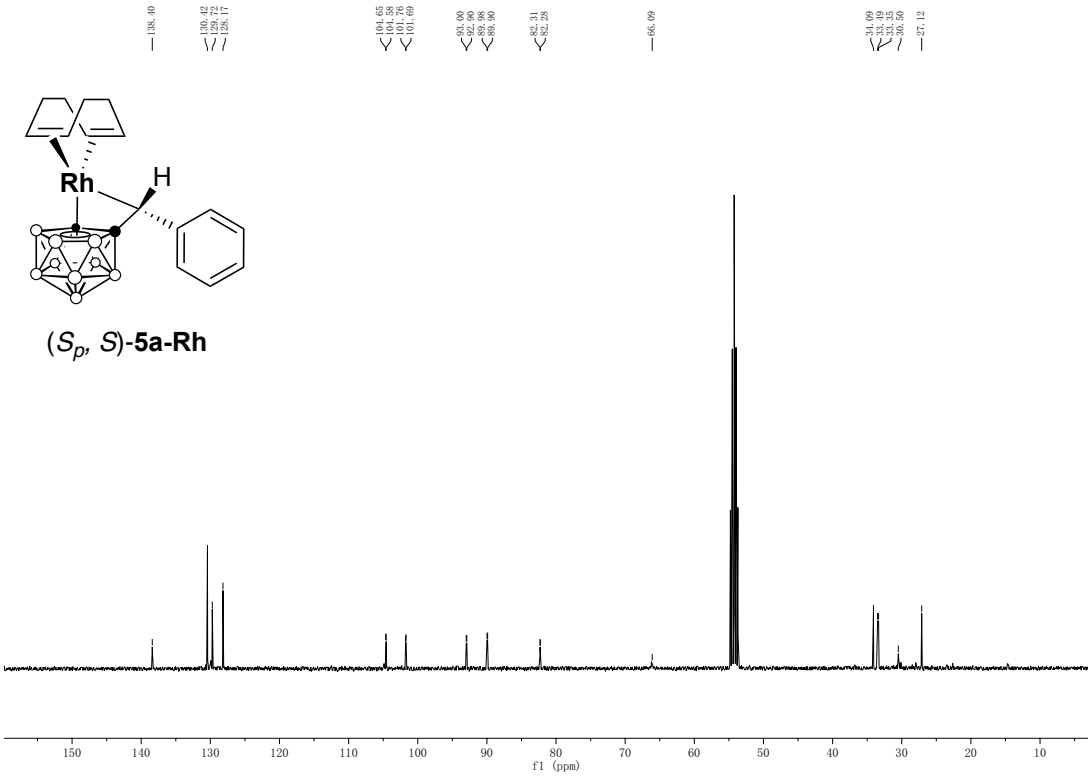


(S_p, S)-**5a-Rh**

^{11}B NMR spectrum of (S_p, S)-**5a-Rh**

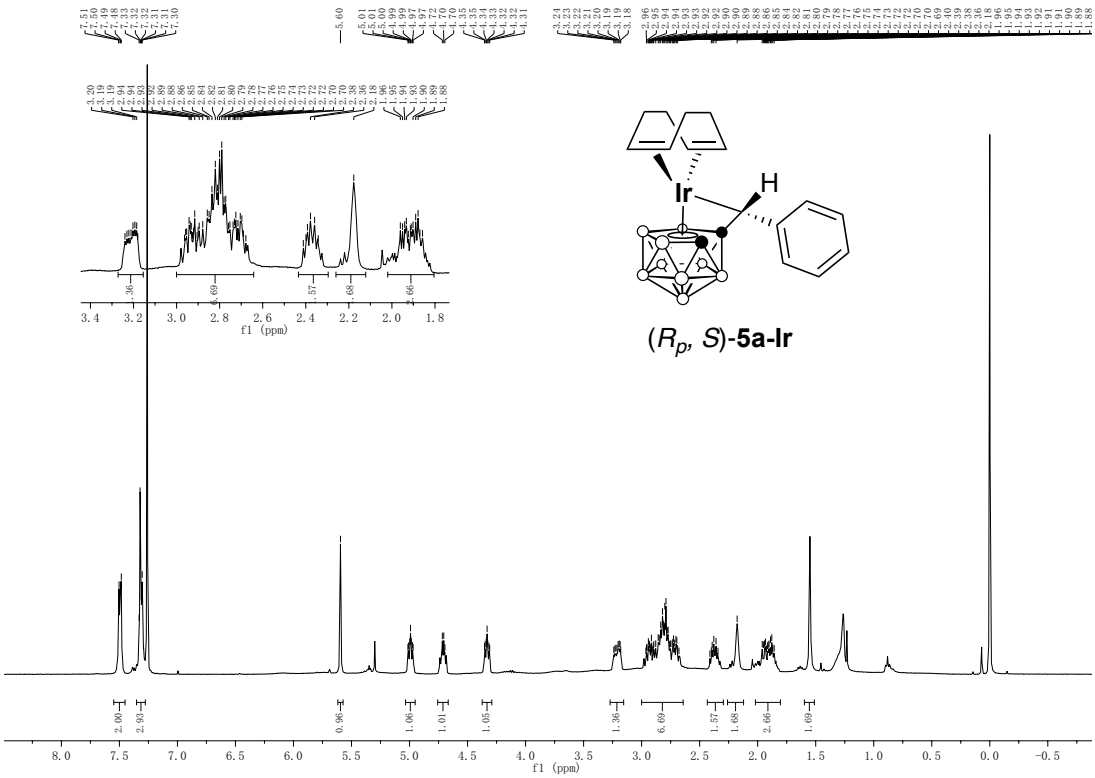


^{13}C NMR spectrum of (S_p, S)-**5a-Rh**



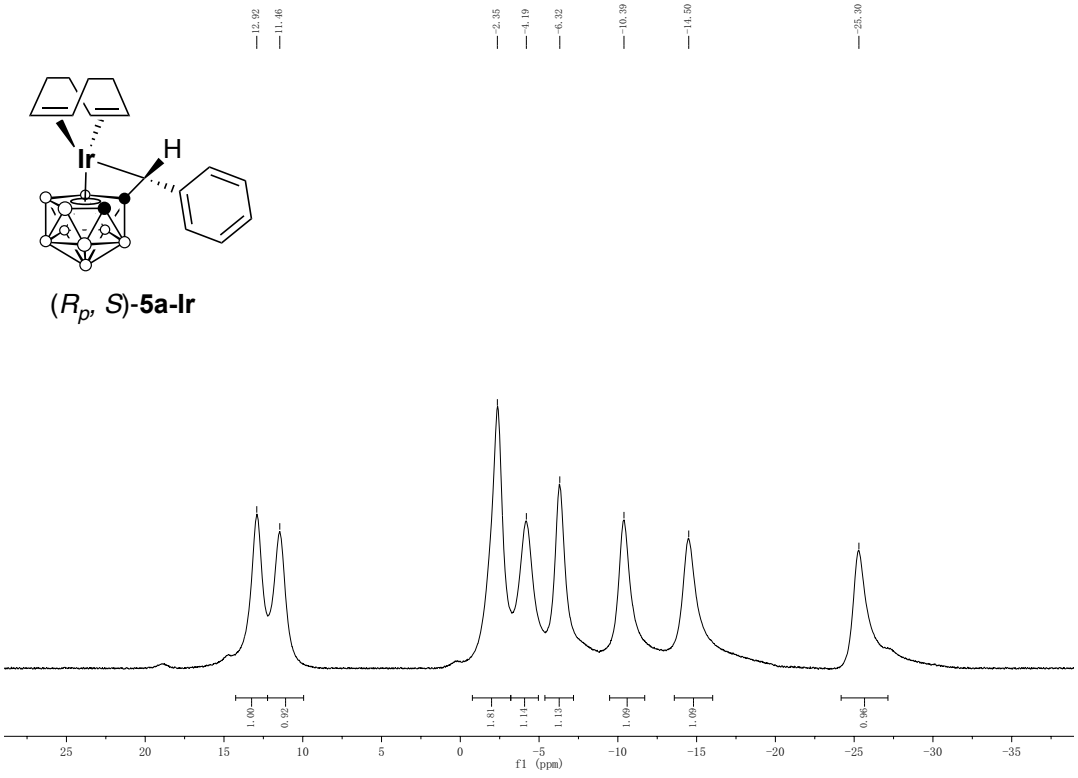
(S_p, S)-**5a-Rh**

^{1}H NMR spectrum of (R_p, S)-**5a-Ir**



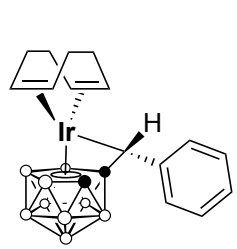
(R_p, S)-**5a-Ir**

^{11}B{^{1}H} NMR spectrum of (R_p, S)-**5a-Ir**



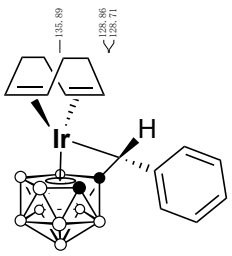
(R_p, S)-**5a-Ir**

^{11}B NMR spectrum of (R_p, S)-**5a-Ir**



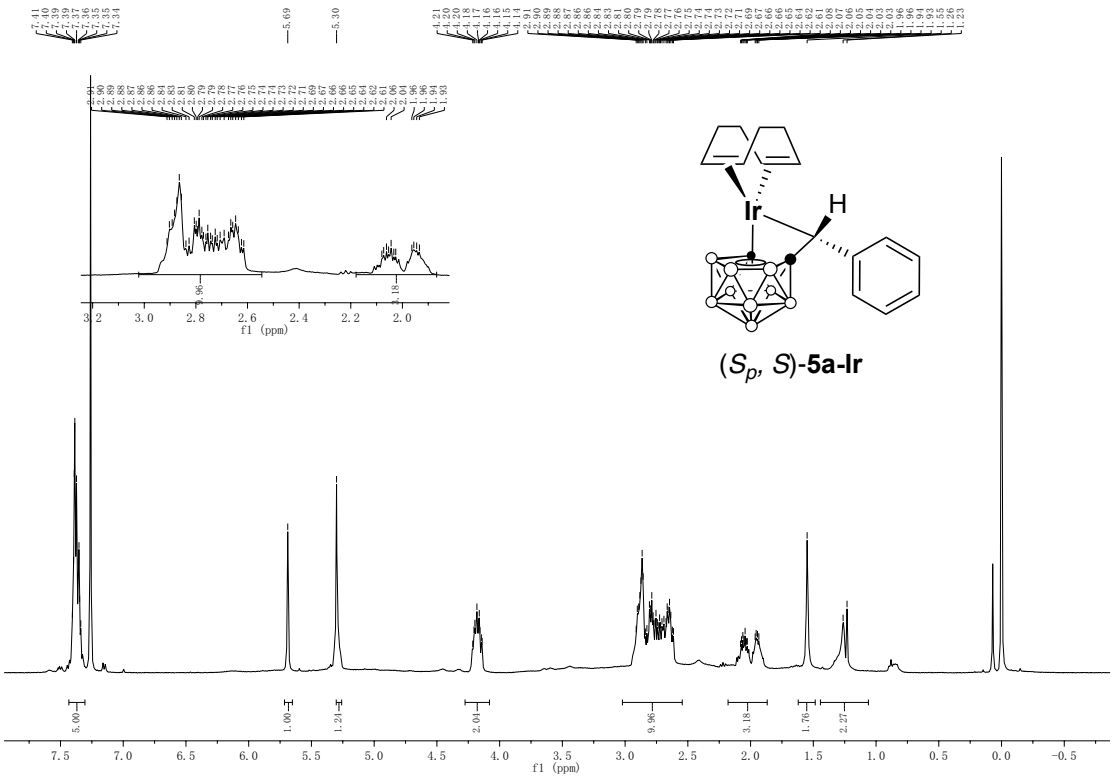
(R_p, S)-**5a-Ir**

^{13}C NMR spectrum of (R_p, S)-**5a-Ir**

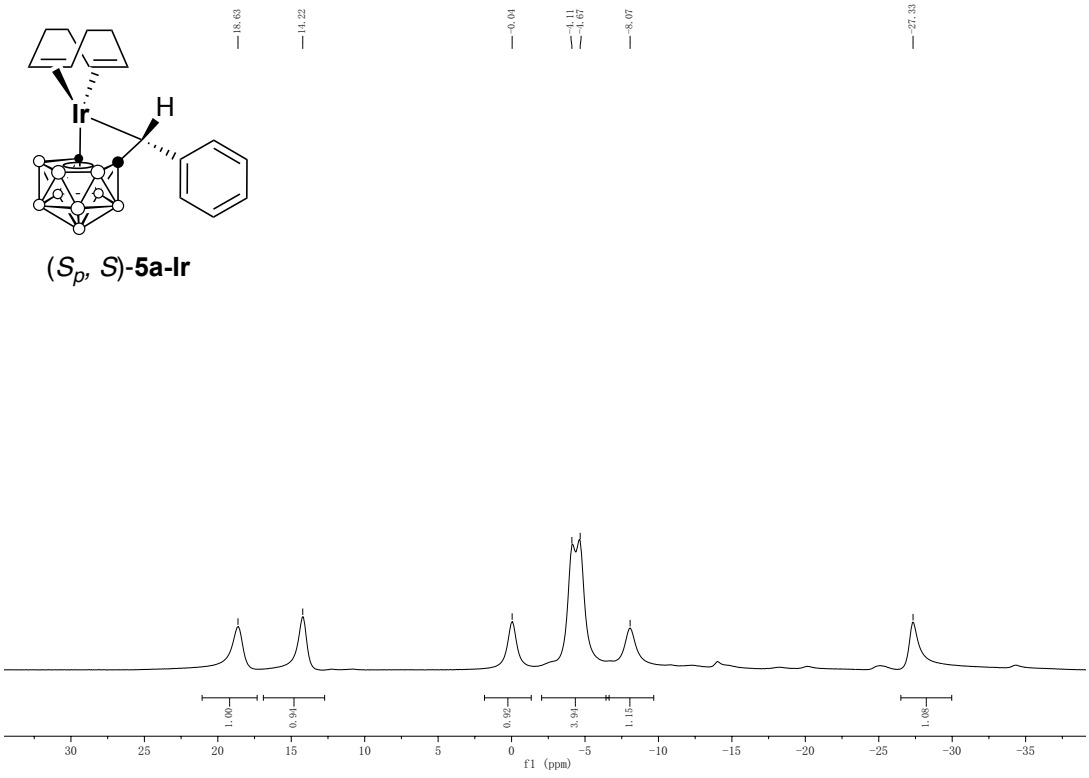


(R_p, S)-**5a-Ir**

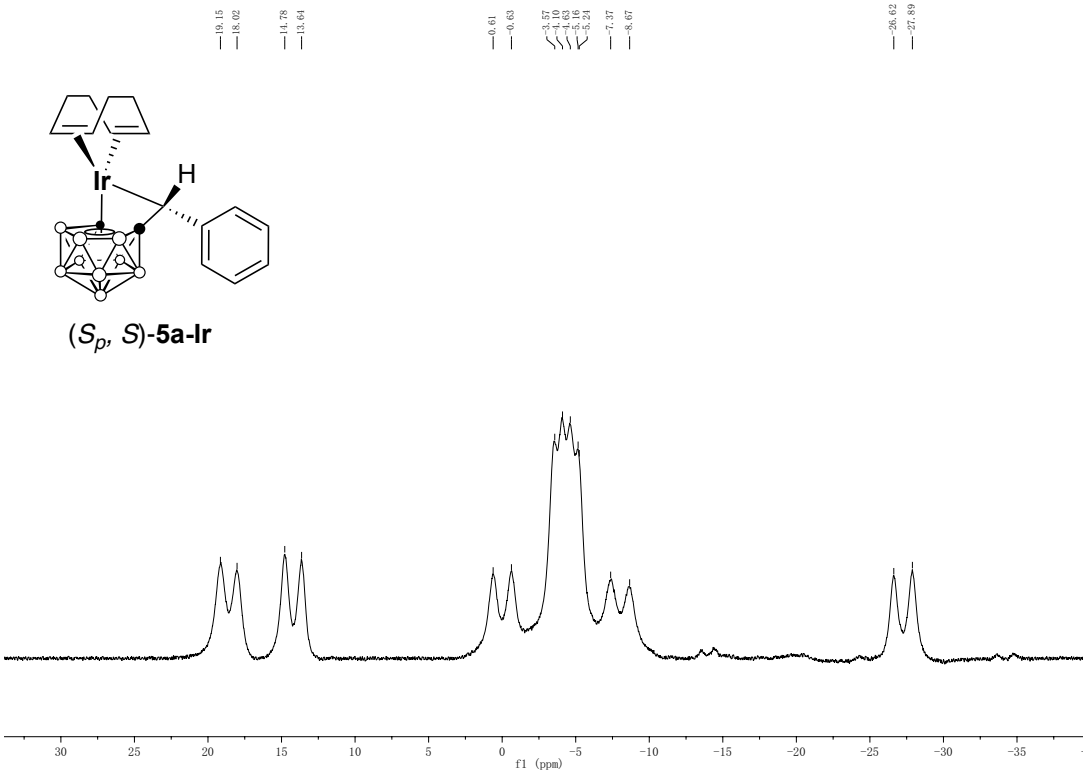
^{1}H NMR spectrum of (S_p, S)-**5a-Ir**



^{11}B{^{1}H} NMR spectrum of (S_p, S)-**5a-Ir**

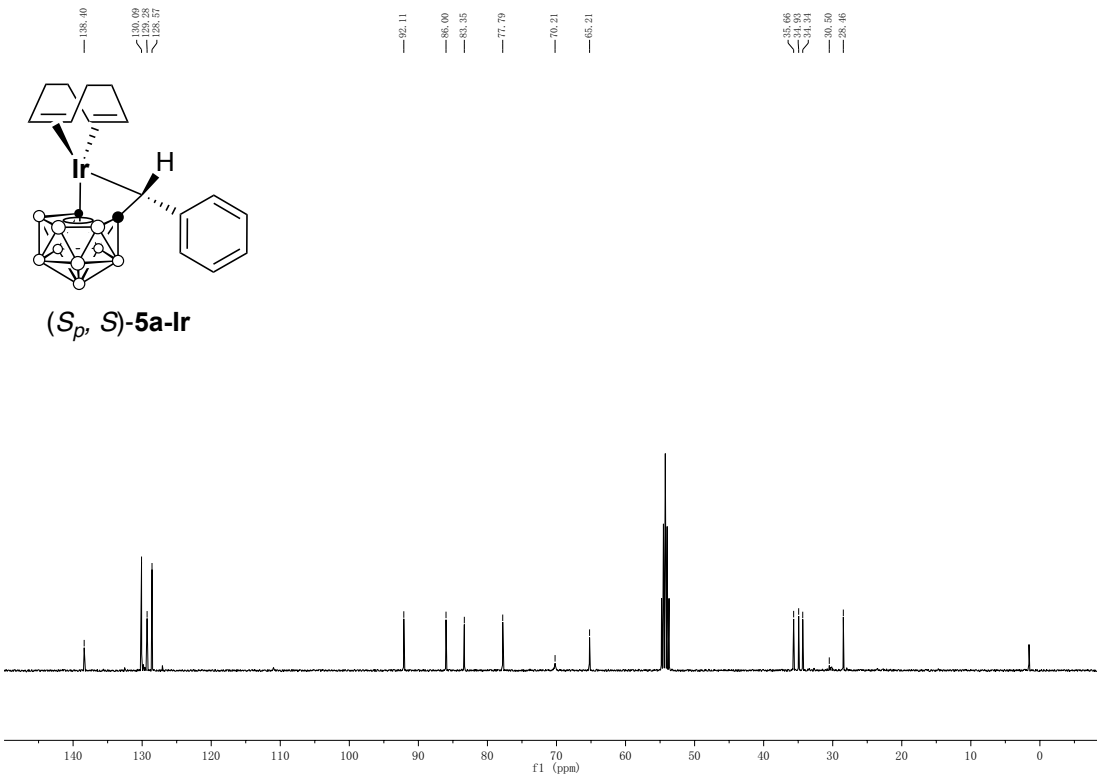


^{11}B NMR spectrum of (S_p, S)-**5a-Ir**



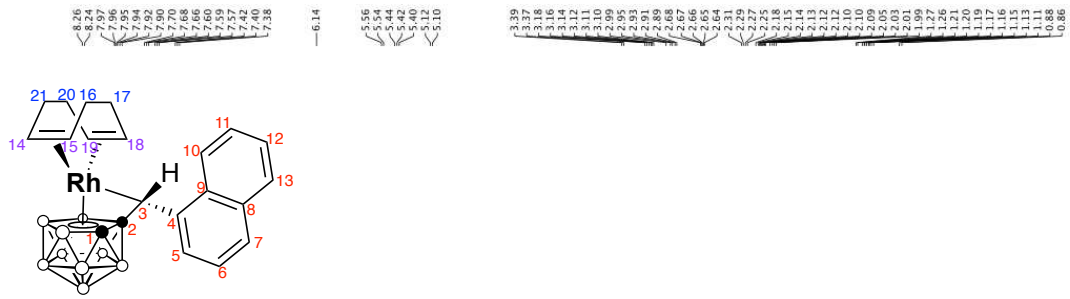
(S_p, S)-**5a-Ir**

^{13}C NMR spectrum of (S_p, S)-**5a-Ir**

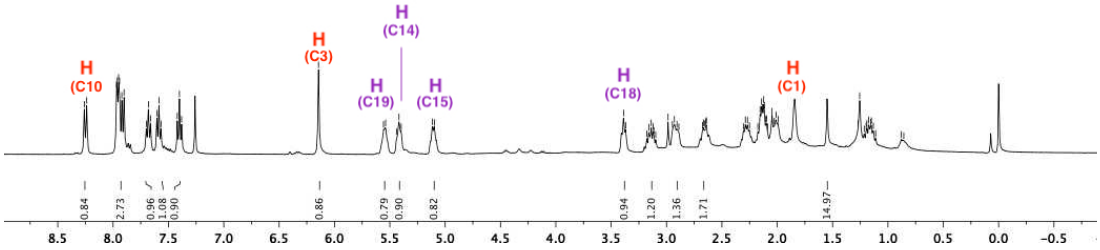


(S_p, S)-**5a-Ir**

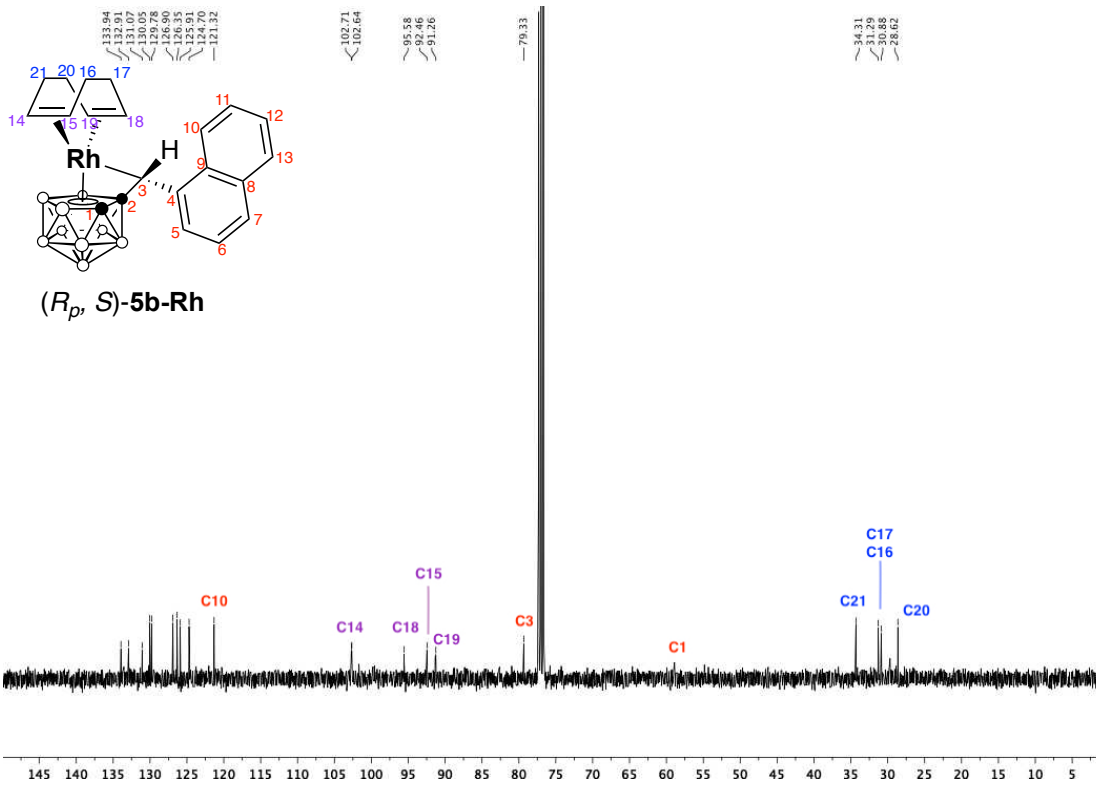
^{1}H NMR spectrum of (R_p, S)-**5b-Rh**



(R_p, S)-**5b-Rh**

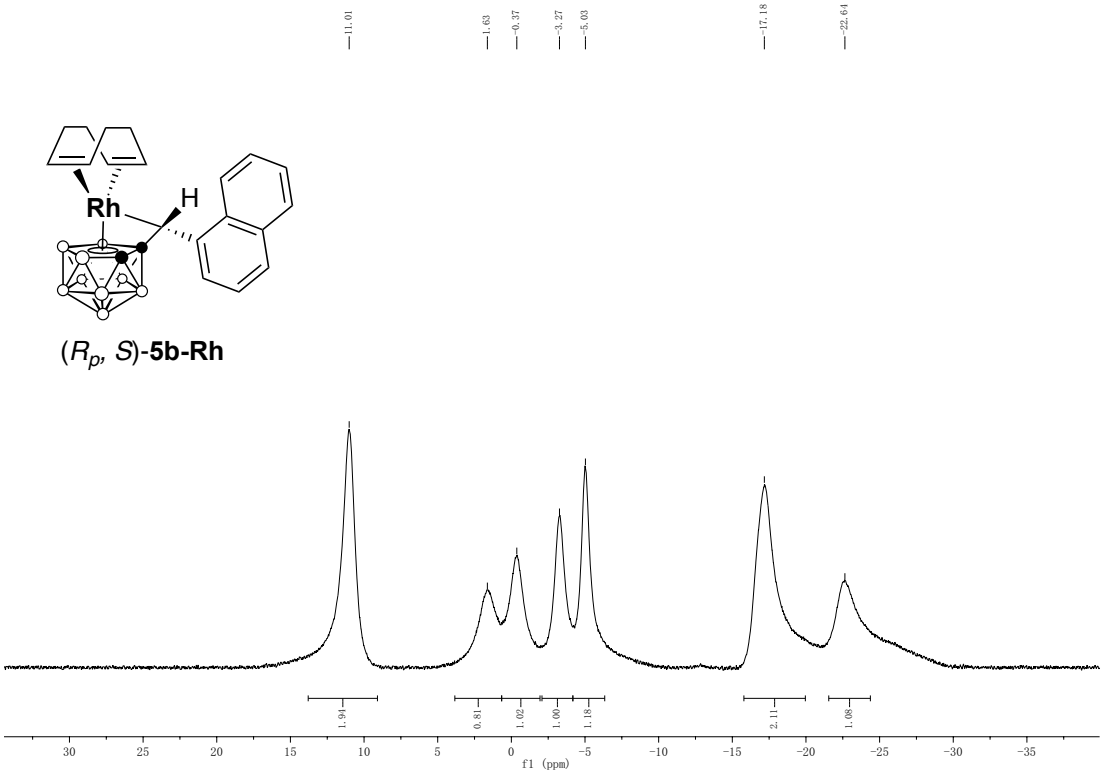


^{13}C NMR spectrum of (R_p, S)-**5b-Rh**



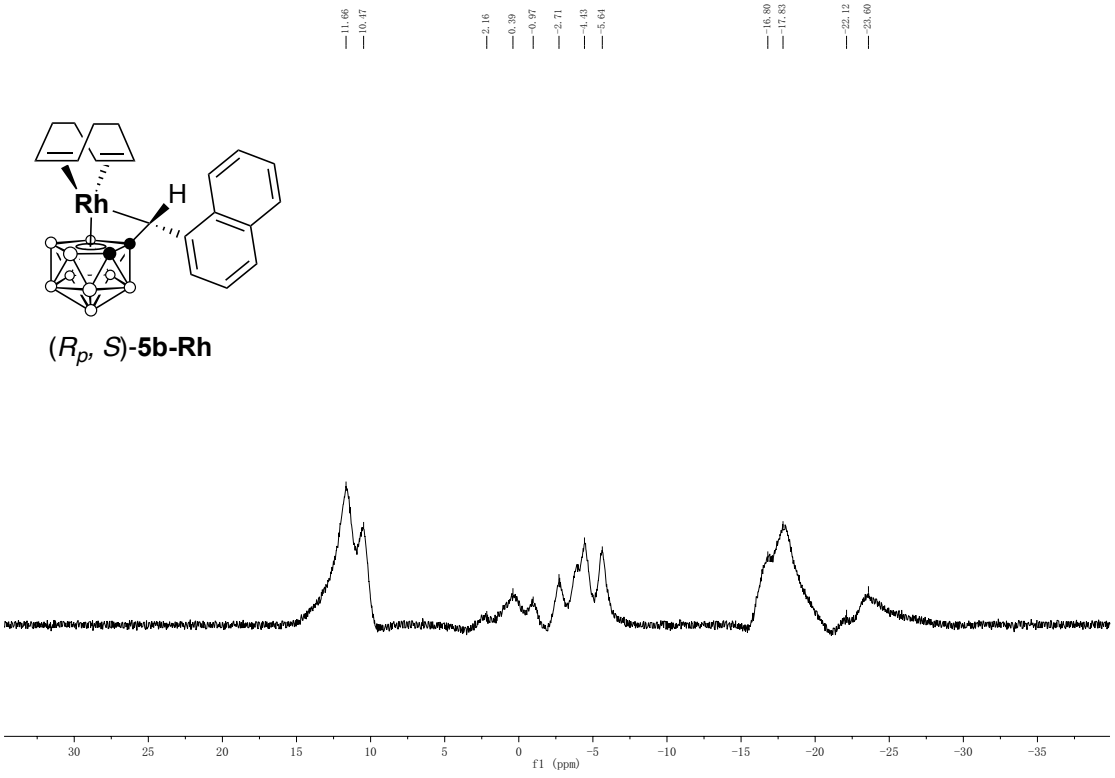
(R_p, S)-**5b-Rh**

$^{11}B\{^{1}H\}$ NMR spectrum of (R_p, S)-**5b-Rh**



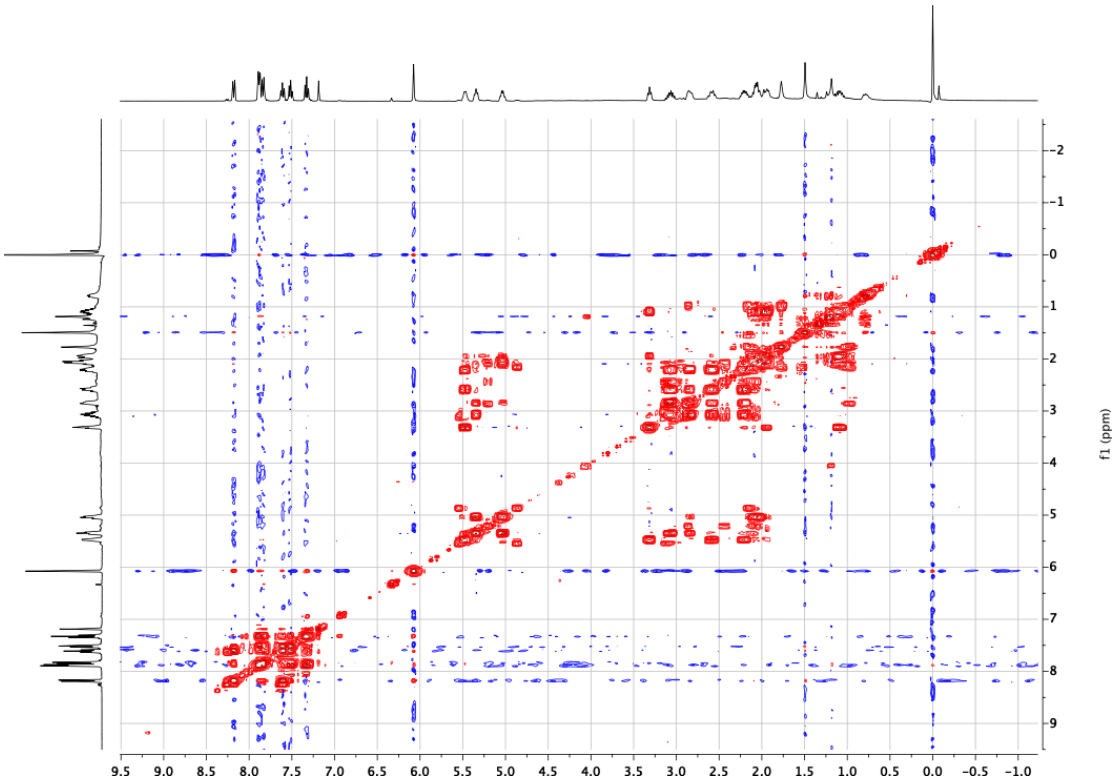
(R_p, S)-**5b-Rh**

^{11}B NMR spectrum of (R_p, S)-**5b-Rh**

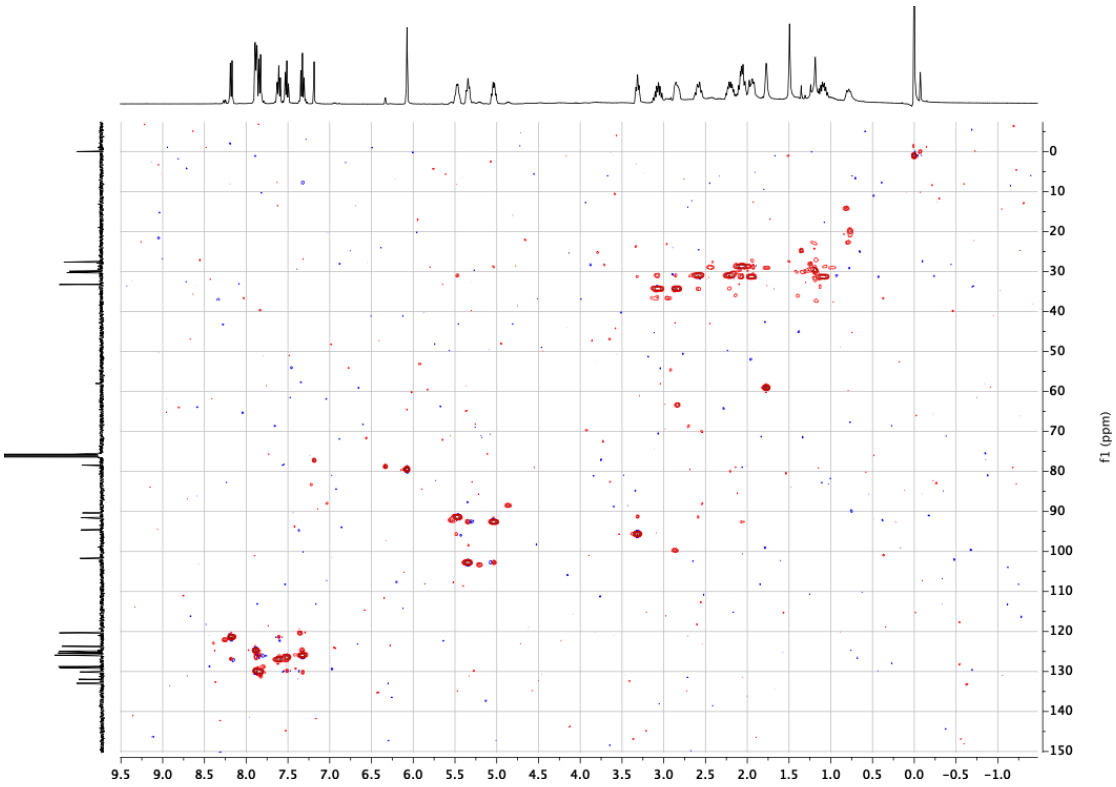


(R_p, S)-**5b-Rh**

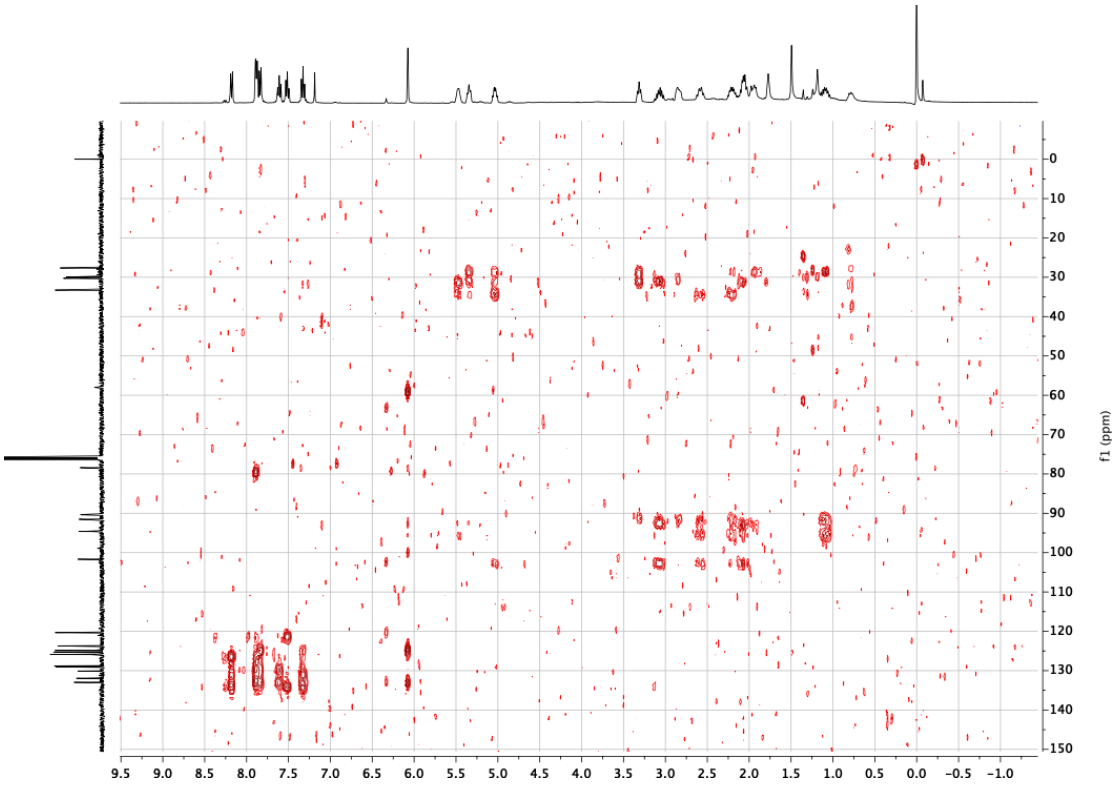
H-H COSY spectrum of (R_p, S)-**5b-Rh**



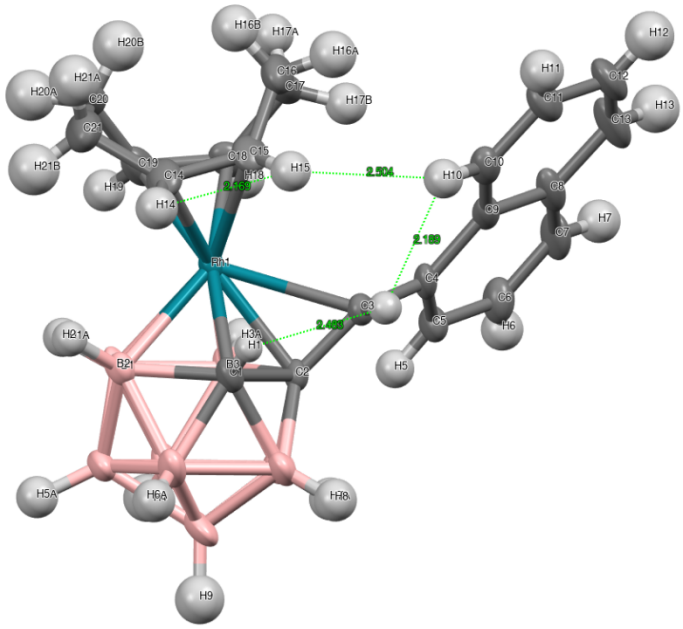
HSQC spectrum of (R_p, S)-**5b-Rh**

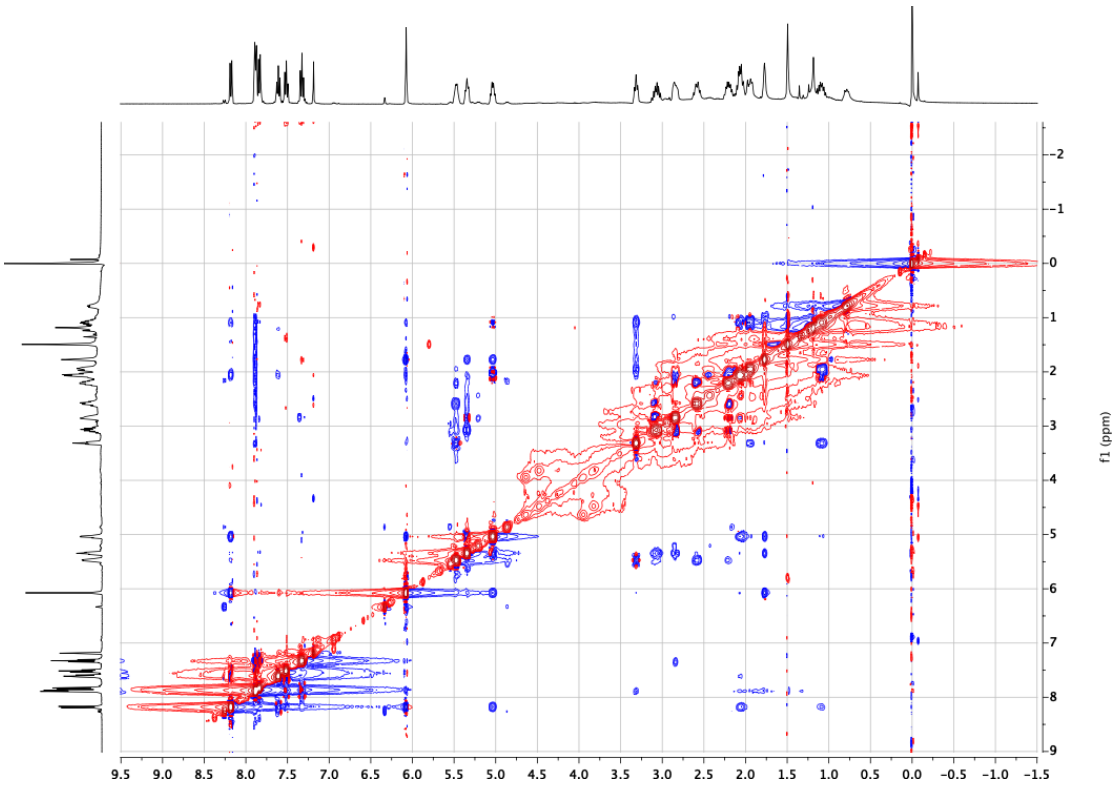


HMBC spectrum of (R_p, S)-**5b-Rh**

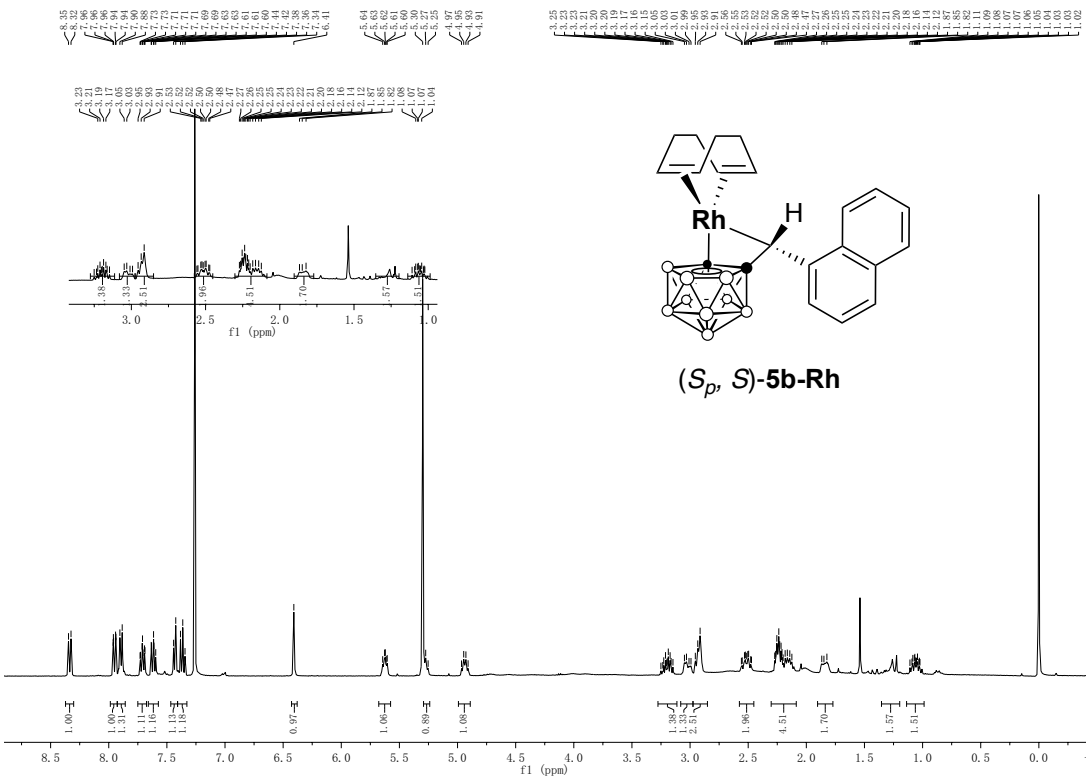


NOE spectrum of (R_p, S)-**5b-Rh**



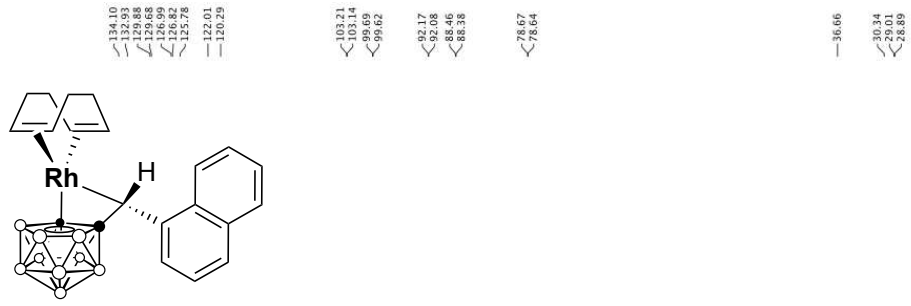


^{1}H NMR spectrum of (S_p, S)-**5b-Rh**

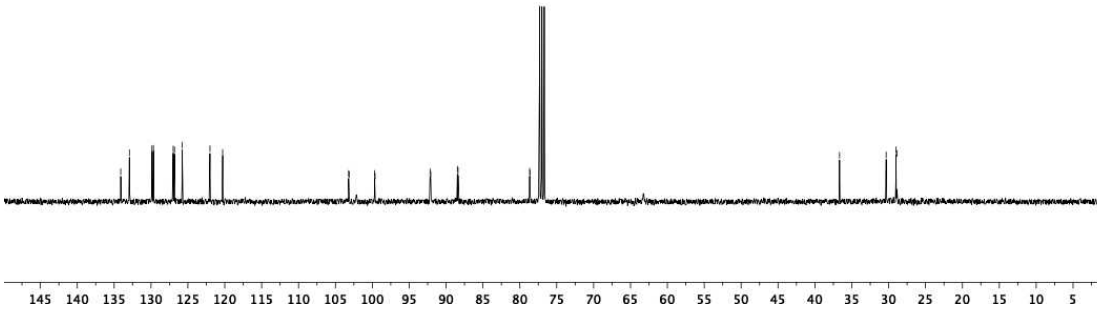


(S_p, S)-**5b-Rh**

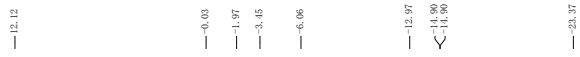
^{13}C NMR spectrum of (S_p, S)-**5b-Rh**

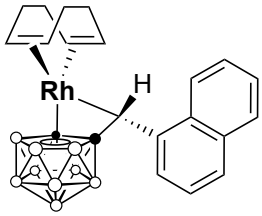


(S_p, S)-**5b-Rh**

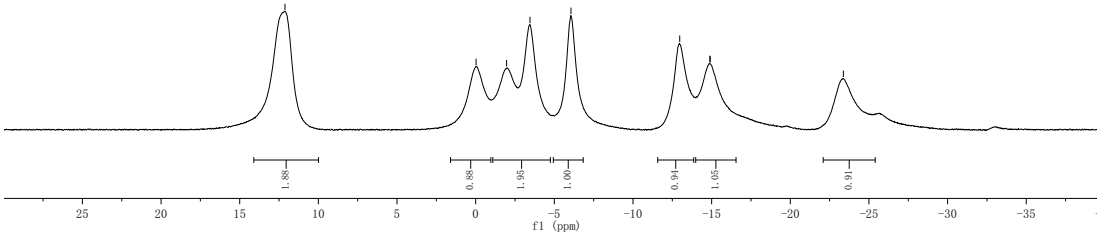


^{11}B{^{1}H} NMR spectrum of (S_p, S)-**5b-Rh**

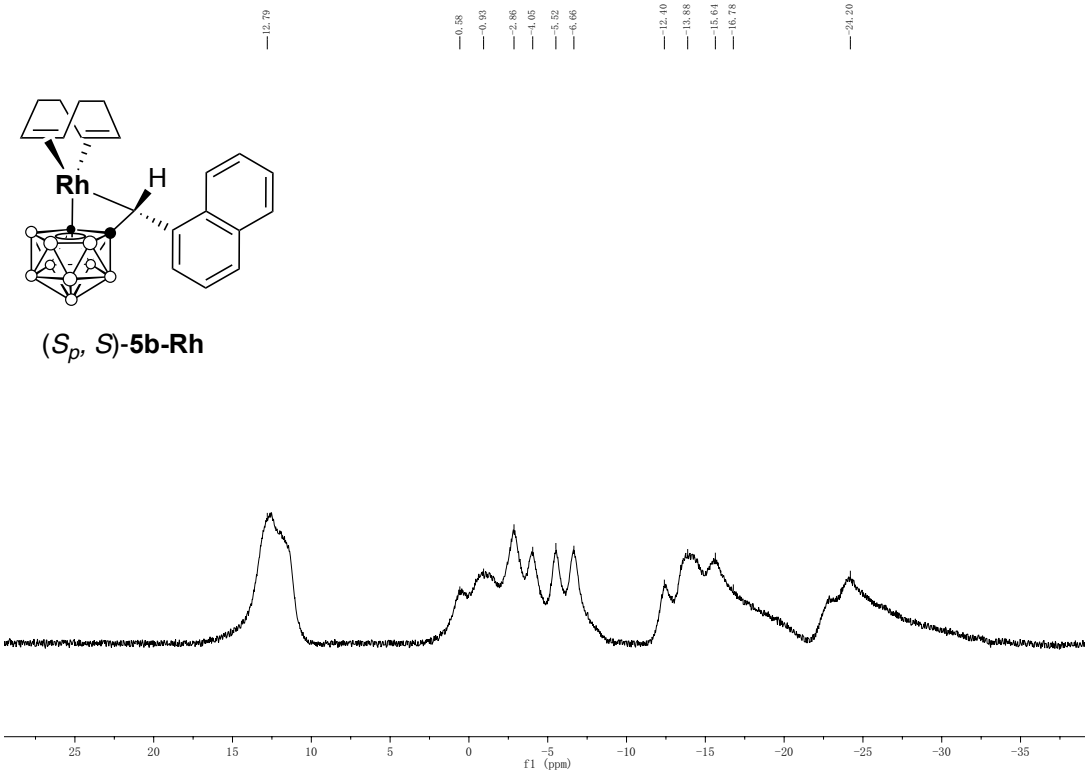




(S_p, S)-**5b-Rh**

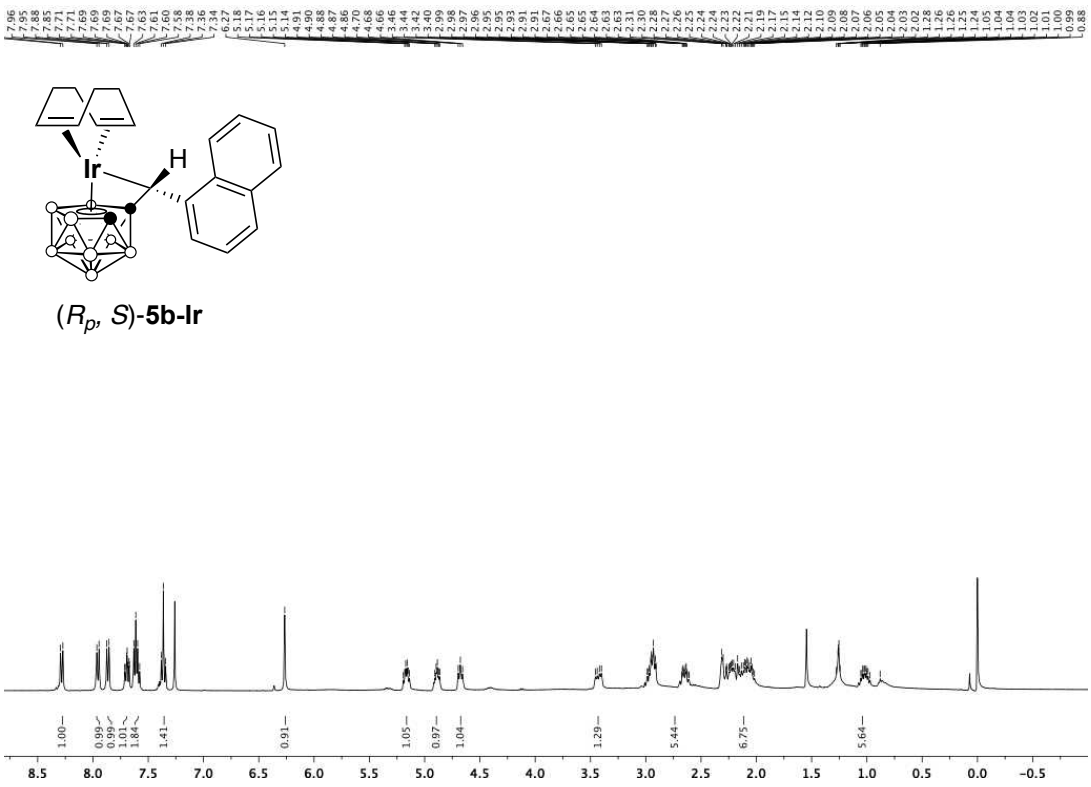


^{11}B NMR spectrum of (S_p, S)-**5b-Rh**



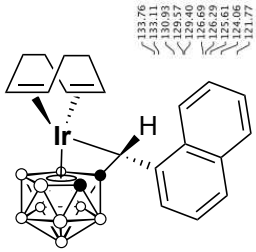
(S_p, S)-**5b-Rh**

^{1}H NMR spectrum of (R_p, S)-**5b-Ir**



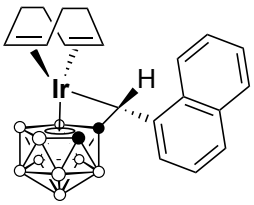
(R_p, S)-**5b-Ir**

^{13}C NMR spectrum of (R_p, S)-**5b-Ir**



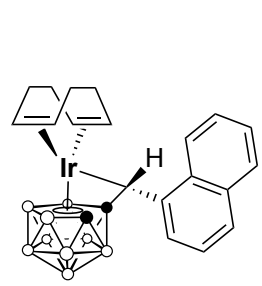
(R_p, S)-**5b-Ir**

^{11}B{^{1}H} NMR spectrum of (R_p, S)-**5b-Ir**



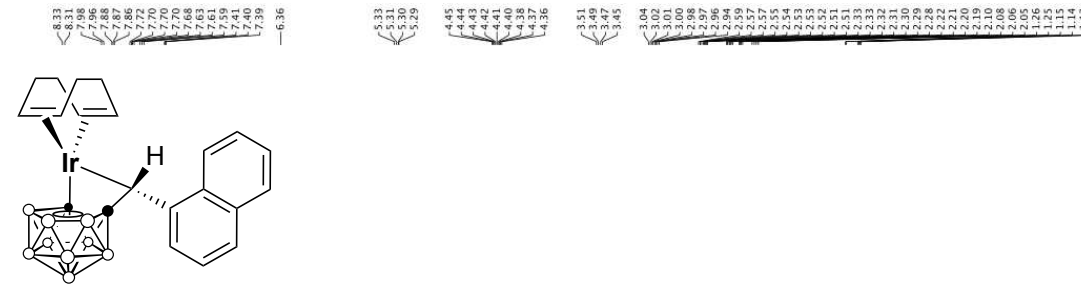
(R_p, S)-**5b-Ir**

^{11}B NMR spectrum of (R_p, S)-**5b-Ir**

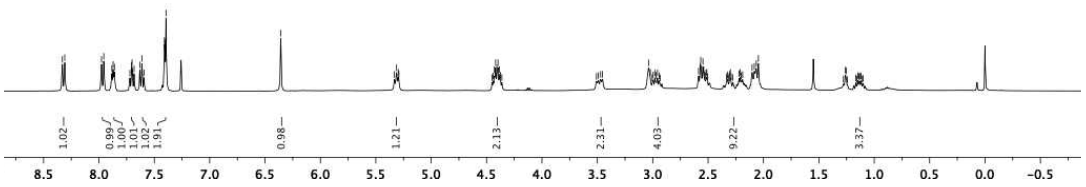


(R_p, S)-**5b-Ir**

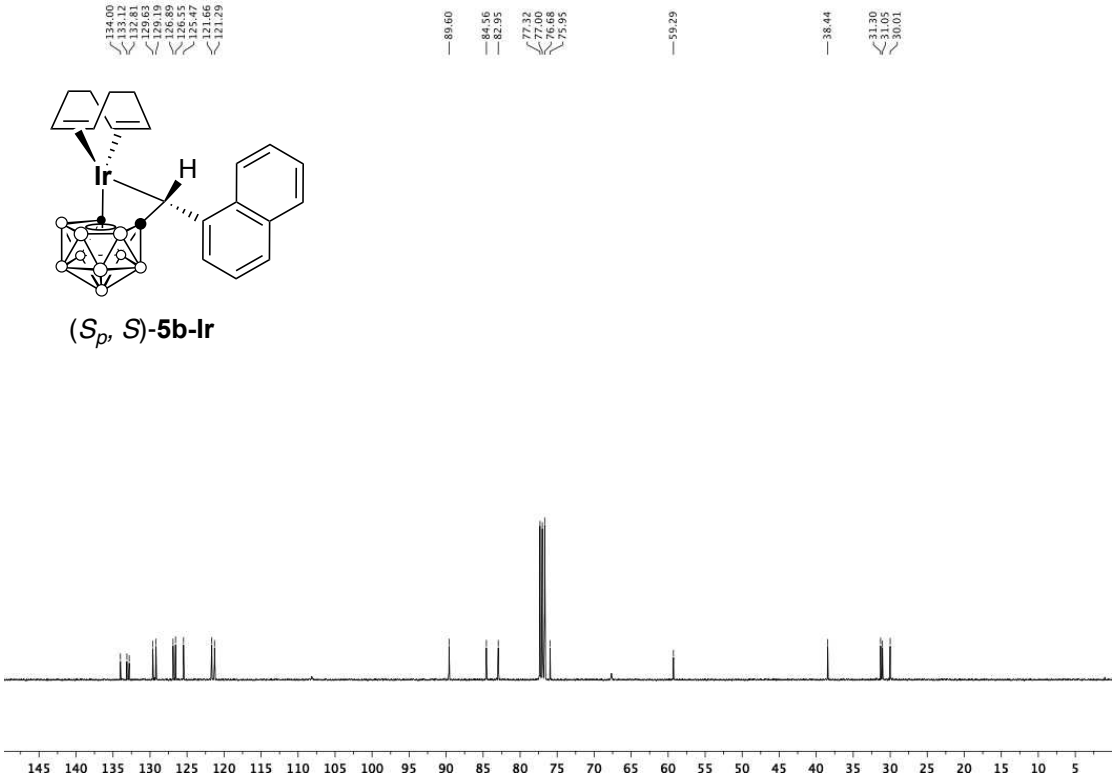
^{1}H NMR spectrum of (S_p, S)-**5b-Ir**



(S_p, S)-**5b-Ir**

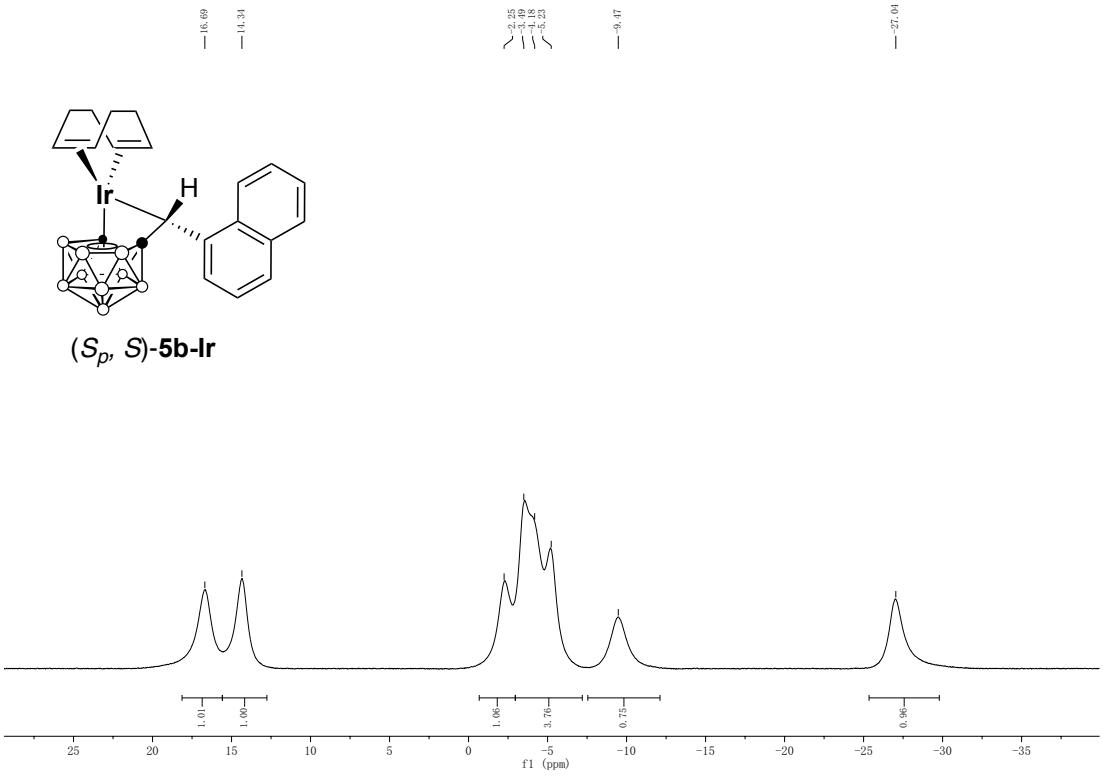


^{13}C NMR spectrum of (S_p, S)-**5b-Ir**



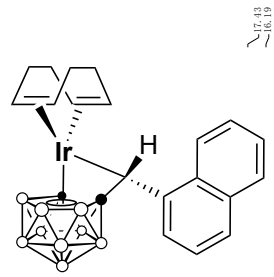
(S_p, S)-**5b-Ir**

^{11}B{^{1}H} NMR spectrum of (S_p, S)-**5b-Ir**



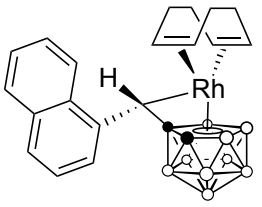
(S_p, S)-**5b-Ir**

^{11}B NMR spectrum of (S_p, S)-**5b-Ir**

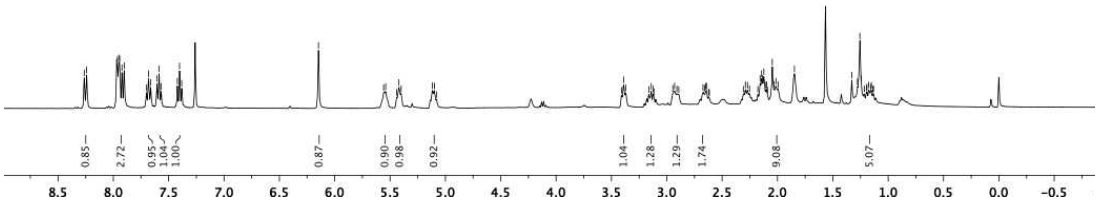


(S_p, S)-**5b-Ir**

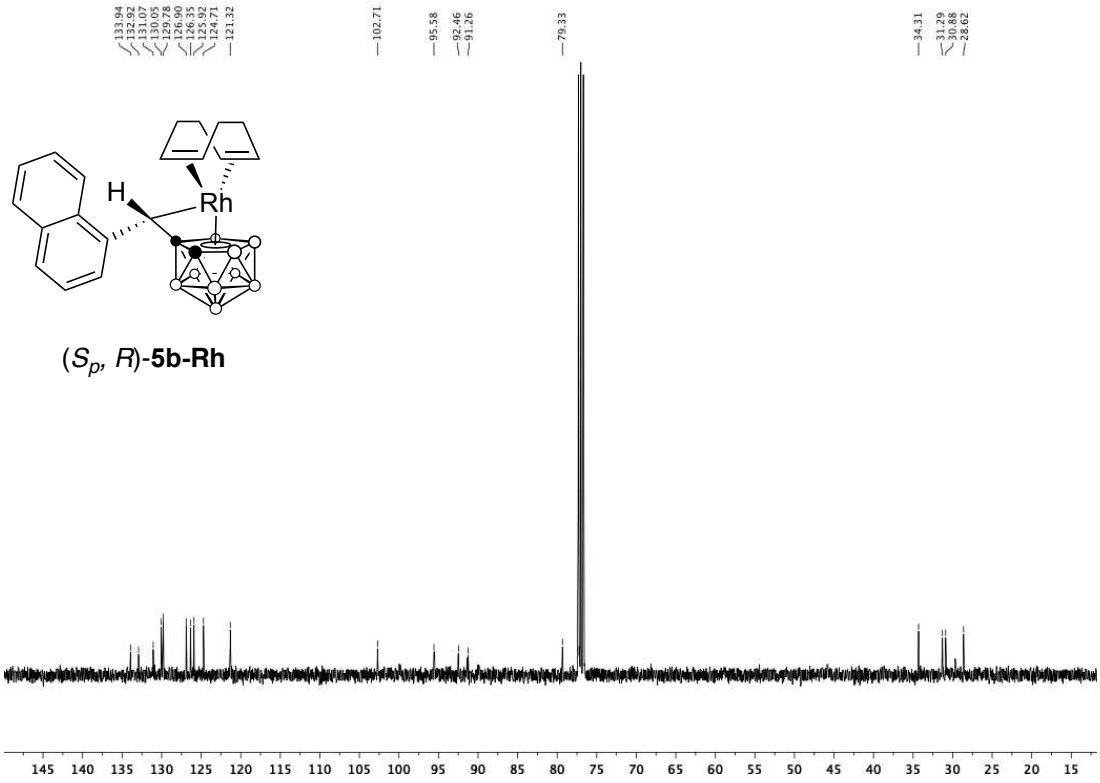
^{1}H NMR spectrum of (S_p, R)-**5b-Rh**



(S_p, R)-**5b-Rh**

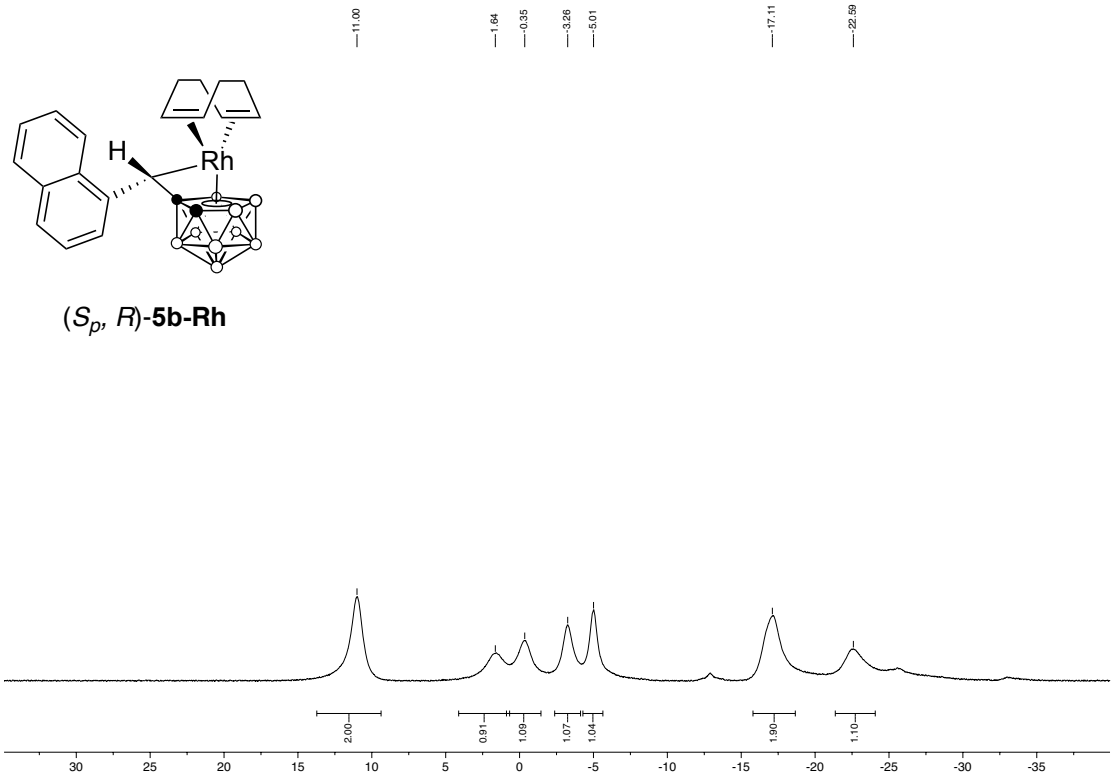


^{13}C NMR spectrum of (S_p, R)-**5b-Rh**



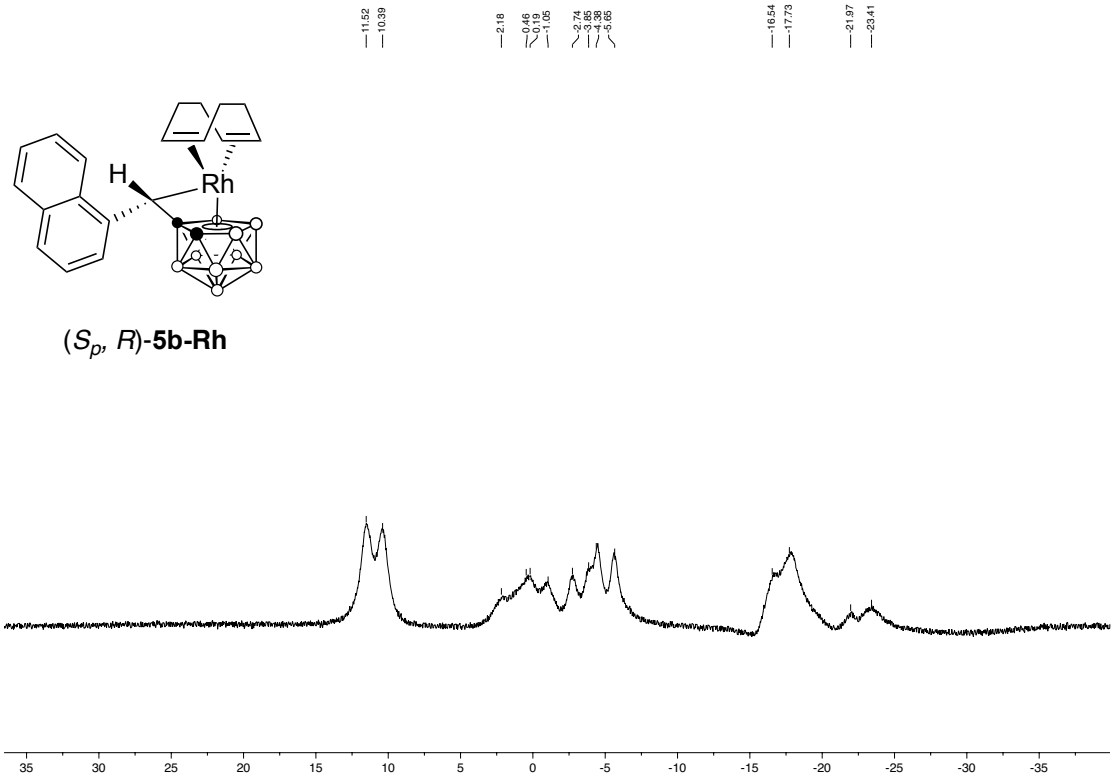
(S_p, R)-**5b-Rh**

^{11}B{^{1}H} NMR spectrum of (S_p, R)-**5b-Rh**



(S_p, R)-**5b-Rh**

^{11}B NMR spectrum of (S_p, R)-**5b-Rh**



(S_p, R)-**5b-Rh**