Electronic Supplementary Information for Dalton Transactions

INDOLPhos: Novel hybrid phosphine-phosphoramidite ligands for asymmetric hydrogenation and hydroformylation

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Supplementary Material

I General remarks

General Procedures. All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. THF, pentane, hexane and diethyl ether were distilled from sodium benzophenone ketyl; CH_2Cl_2, isopropanol and methanol were distilled from CaH_2 and toluene was distilled from sodium under nitrogen. NMR spectra (^1H, ^{31}P and ^{13}C) were measured on a Varian INOVA 500 MHz. High resolution mass spectra were recorded on a JEOL JMS SX/SX102A four sector mass spectrometer; for FAB-MS 3-nitrobenzyl alcohol was used as matrix. Gas chromatographic analyses were run on a Shimadzu GC-17A apparatus (split/splitless, equipped with a FID detector and a BPX35 column, internal diameter of 0.22 mm, film thickness 0.25 μm, carrier gas 70 kPa He). Chiral GC separations were conducted on an Interscience Trace GC Ultra (FID detector) with a ph Megadex column (internal diameter 0.1 mm, 5 m column, film thickness 0.1 μm) and an Interscience Focus GC (FID detector) with a Supelco BETA DEX column (0.25 mm x 30 m).

Materials. With exception of the compounds given below, all reagents were purchased from commercial suppliers and used without further purification. The following compounds were synthesized according to published procedures: phosphorochloridite of (*S*)-(-)-2,2'-bisnaphthol,[1] phosphorochloridite of (*S*)-(-)-3,3'-bis(trimethylsilyl)-2,2'-bisnaphthol,[1] phosphorchloridite of (*S*)-(-)-3,3'-dimethyl-2,2'-bisnaphtol.[2]

II Synthesis of ligands and complexes

Diphenyl(3-methyl-2-indolyl)phosphine (1a).[3] To a solution of 3-methylindole (2.46 g, 18.8 mmol) in THF (50 mL) was added dropwise 7.9 mL of *n*-BuLi (2.5 M in hexanes) at -70 °C. The resulting suspension was stirred at -70 °C for 20 min. Carbon dioxide was bubbled through the suspension for 30 min allowing the mixture to warm to room temperature after which the solvent was removed *in vacuo*. The resulting white residue was dissolved in THF (50 mL) to give a clear yellow solution which was cooled to -70 °C. To this solution 11.6 mL of *t*-BuLi (1.7 M in pentanes) was added and the resulting orange solution was stirred at -70 °C for 1 h. Chlorodiphenylphosphine (3.37 mL, 18.8 mmol) was added dropwise and the reaction mixture was stirred for 16 h allowing to warm to room temperature. The resulting yellow solution was washed with 50 mL degassed sat. aq. NH_4Cl. The organic layer was dried over $MgSO_4$, filtered and the solvent was removed *in vacuo*. The crude pale yellow residue was recrystallised from MeOH to yield the product as a white powder. Yield: 4.01 g (68 %). ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ (ppm) 7.63 (d, J = 8.0 Hz, 1H), 7.48 (bs, 1H), 7.38-7.33 (m, 10H), 7.24 (d, J = 8.0 Hz, 1H), 7.21 (dt, J = 7.0 Hz, 1.0 Hz, 1H), 7.13 (dt, J = 7.0 Hz, 1.0 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR ($CDCl_3$, 125.5 MHz, 298 K): δ (ppm) 138.25, 136.43, 136.36, 133.32, 133.17, 129.52, 129.47, 129.07, 129.05, 129.01, 127.41, 127.26, 123.31, 122.49, 122.27, 119.56, 119.44, 111.16, 10.05. ^{31}P{^{1}H} NMR ($CDCl_3$, 202.3 MHz, 298 K): δ (ppm) -32.08 (s). HRMS (FAB) calcd for $[M + H]^+$ $C_{21}H_{19}NP$, 316.1255; found, 316.1242.

Diisopropyl(3-methyl-2-indolyl)phosphine (1b). To a solution of 3-methylindole (3.55 g, 27.1 mmol) in THF (70 mL) was added dropwise 11.4 mL of *n*-BuLi (2.5 M in hexanes) at -70 °C. The resulting suspension was stirred at -70 °C for 20 min. Carbon dioxide was bubbled through the suspension for 30 min allowing the mixture to warm to room temperature after which the solvent was removed *in vacuo*. The resulting white residue was dissolved in THF (70 mL) to give a clear yellow solution which was cooled to -70 °C. To this solution 18.9 mL of *t*-BuLi (1.5 M in pentanes) was added and the resulting orange solution was stirred at -70 °C for 1 h. Chlorodiisopropylphosphine (4.31 mL, 27.1 mmol) was added dropwise and the reaction mixture was stirred for 16 h allowing to warm to room temperature. The resulting yellow solution was washed with 50 mL degassed sat. aq. NH_4Cl. The organic layer was dried over $MgSO_4$, filtered and the solvent was removed *in vacuo*. The crude pale yellow residue was dissolved in 60% EtOAc/Hexanes and filtered through a pad of SiO_2 to obtain the product as an off white powder. Yield: 5.23 g (78 %). ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ (ppm) 7.91 (br s, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 7.5 Hz, 1H), 7.23 (t, J = 7.5 Hz, 1H), 7.13 (t, J = 7.5 Hz, 1H), 2.48 (s, 3H), 2.18 (septet, J = 7.0 Hz, 2H), 1.16 (dd, J_{HH} = 7.0 Hz, J_{PH} = 16.0 Hz, 6H), 1.01 (dd, J_{HH} = 7.0 Hz, J_{PH} = 11.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 125.5 MHz, 298 K): δ (ppm) 137.96, 129.16, 129.11, 127.91, 127.68, 123.54, 123.35, 122.96, 119.24, 119.22, 110.74, 23.88, 23.81, 20.62, 20.46, 19.89, 19.83, 10.41, 10.31. ^{31}P{^{1}H} NMR ($CDCl_3$, 202.3 MHz, 298 K): δ (ppm) -17.70 (s). HRMS (FAB) calcd for $[M + H]^+$ $C_{15}H_{23}NP$, 248.1568; found, 248.1561.

Diphenyl{1-[(*S*)-3,5-dioxa-4-phospha-cyclohepta(2,1-*a*;3,4-*a*')dinaphtalen-4-yl]-3-methyl-2-indolyl}phosphine (2a). To a solution of **1a** (1.05 g, 3.3 mmol) in THF

(15 mL) was added dropwise 1.33 mL of *n*-BuLi (2.5 M in hexanes) at -70 °C. The resulting yellow-orange solution was stirred for 0.5 h at -70 °C and allowed to warm to room temperature. This solution was added dropwise to a solution of (*S*)-(-)-2,2'-bisnaphtol phosphorochloridite (1.17 g, 3.3 mmol) in THF (10 mL) at -70 °C. The reaction mixture was stirred for 15 h allowing to warm to room temperature. The resulting pale yellow solution was filtered through a pad of SiO_2 which was rinsed twice with THF (2 x 10 mL). The solvent was removed *in vacuo*. Co-evaporation with pentanes gave the product as a white powder. Yield: 2.08 g (99 %). ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ (ppm) 7.97 (d, J = 9.0 Hz, 1H), 7.94 (d, J = 8.5 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.56-7.31 (m, 18H), 7.28 (m, 1H), 6.89 (t, J = 7.3 Hz, 1H), 6.75 (d, J = 8.5 Hz, 1H), 6.53 (d, J = 8.5 Hz, 1H), 6.24 (t, J = 7.8 Hz, 1H), 2.04 (s, 3H). ^{13}C NMR ($CDCl_3$, 125.5 MHz, 298 K): δ (ppm) 150.38, 148.74, 140.64, 135.73, 135.06, 133.16, 132.87, 132.78, 132.20, 131.96, 131.51, 130.88, 130.62, 128.86, 128.81, 128.76, 128.68, 128.64, 128.62, 128.58, 128.47, 128.11, 127.33, 126.93, 126.62, 126.55, 125.50, 125.13, 124.72, 123.83, 122.97, 121.91, 121.53, 121.24, 118.64, 116.34, 10.78. ^{31}P{^{1}H} NMR ($CDCl_3$, 202.3 MHz, 298 K): δ (ppm) 143.43 (d, J_{PP} = 165.7 Hz), -27.95 (d, J_{PP} = 165.7 Hz). HRMS (FAB) calcd for $[M + H]^+$ $C_{41}H_{30}NO_2P_2$, 630.1752; found, 630.1743.

Diisopropyl{1-[(*S*)-3,5-dioxa-4-phospha-cyclohepta(2,1-*a*;3,4-*a*')dinaphtalen-4-yl]-3-methyl-2-indolyl}phosphine (2b). To a solution of **1b** (298 mg, 1.2 mmol) in THF (10 mL) was added dropwise 0.48 mL of *n*-BuLi (2.5 M in hexanes) at -70°C. The resulting pale yellow solution was stirred for 1 h at -70 °C and allowed to warm to room temperature. This solution was added dropwise to a solution of (*S*)-(-)-2,2'-bisnaphtol phosphorochloridite (422 mg, 1.2 mmol) in THF (5 mL) at -70 °C. The reaction mixture was stirred for 1 h at -70 °C and then allowed to warm to room temperature. The resulting pale yellow solution was filtered through a pad of SiO_2 which was rinsed twice with THF (2 x 10 mL). The solvent was removed *in vacuo*. The crude off-white solid was purified by SiO_2 column chromatography (5 % EtOAc/Hexanes) to obtain the product as a white powder. Yield: 598 mg (89 %). ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ (ppm) 8.06 (d, J = 9.0 Hz, 1H), 7.99 (d, J = 8.5 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 9.0 Hz, 1H), 7.55 (d, J = 8.5 Hz, 1H), 7.51-7.45 (m, 4H), 7.40 (d, J = 7.5 Hz, 1H), 7.37-7.31 (m, 2H), 6.87 (t, J = 7.5 Hz, 1H), 6.79 (d, J = 9.0 Hz, 1H), 6.52 (br d, J = 6.5 Hz, 1H), 6.18 (t, J = 8.5 Hz, 1H), 2.75 (br m, 1H), 2.67 (m, 1H), 2.50 (s, 3H), 1.33-1.27 (m, 6H), 1.18-0.99 (m, 6H). ^{13}C NMR ($CDCl_3$, 125.5 MHz, 298 K): δ (ppm) 150.56, 148.85, 140.44, 133.16, 132.91, 132.02, 131.52, 130.99, 130.69, 128.67, 128.59, 127.36, 126.96. 126.71, 126.59, 125.57, 125.16, 124.87, 123.41, 122.97, 122.94, 121.89, 121.55, 121.15, 119.24, 118.62, 116.42, 110.73, 26.22, 25.60, 23.88, 23.81, 22.35, 22.14, 21.61, 21.54, 21.45, 20.62, 20.47, 19.89, 19.83, 11.52, 11.41. ^{31}P{^{1}H} NMR ($CDCl_3$, 202.3 MHz, 223 K): δ (ppm) 143.61 (d, J_{PP} = 249.2 Hz, 0.5P), 142.17 (s, 0.5P), -10.39 (d, J_{PP} = 247.8 Hz, 0.5P), -11.52 (s, 0.5P). HRMS (FAB) calcd for $[M + H]^+$ $C_{35}H_{34}NO_2P_2$, 562.2065; found, 562.2070.

Diphenyl{1-[(*S*)-2,6-bis-trimethylsilyl-3,5-dioxa-4-phospha-cyclohepta(2,1-*a*;3,4-*a*')dinaphtalen-4-yl]-3-methyl-2-indolyl}phosphine (2c). To a solution of **1a** (218 mg, 0.69 mmol) in THF (5 mL) was added dropwise 0.276 mL of *n*-BuLi (2.5 M in hexanes) at -70 °C. The resulting yellow-orange solution was stirred for 0.5 h at -70 °C and allowed to warm to room temperature. This solution was added dropwise to a

solution of (*S*)-(-)-3,3'-bis(trimethylsilyl)-2,2'-bisnaphtol phosphorochloridite (343 mg, 0.69 mmol) in THF (5 mL) at -70°C. The reaction mixture was stirred for 1 h at -70 °C and then allowed to warm to room temperature. The resulting red solution was filtered through a pad of SiO_2 which was rinsed twice with THF (3 x 5 mL). The solvent was removed *in vacuo*. Co-evaporation with CH_2Cl_2 gave the product as an off white powder. Yield: 493 mg (92 %). ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ (ppm) 8.05 (s, 1H), 7.92 (d, J = 7.5 Hz, 1H), 7.89 (s, 2H), 7.52-7.22 (m, 17H), 6.90 (t, J = 7.5 Hz, 1H), 6.42 (d, J = 8.5 Hz, 1H), 6.28 (t, J = 7.75 Hz, 1H), 1.70 (s, 3H), 0.05 (s, 9H), 0.01 (s, 9H). ^{13}C NMR ($CDCl_3$, 125.5 MHz, 298 K): δ (ppm) 154.91, 153.04, 139.66, 137.90. 137.48, 134.21, 134.15, 134.03, 133.99, 132.90, 132.79, 132.64, 131.99, 131.47, 130.85, 129.21, 129.13, 129.08, 128.71, 128.66, 128.59, 128.47, 128.38, 127.22, 127.11, 126.78, 126.72, 125.26, 124.91, 123.88, 123.62, 121.86, 121.15, 118.23, 116.46, 10.58, -0.14, -0.26. ^{31}P{^{1}H} NMR ($CDCl_3$, 202.3 MHz, 298 K): δ (ppm) 133.73 (d, J_{PP} = 250.4 Hz), -25.82 (d, J_{PP} = 253.3 Hz). HRMS (FAB) calcd for $[M + H]^+$ $C_{47}H_{45}NO_2P_2Si_2$, 774.2542; found, 774.2532.

Diisopropyl{1-[(*S*)-2,6-dimethyl-3,5-dioxa-4-phospha-cyclohepta(2,1-*a*;3,4-*a*')di-naphtalen-4-yl]-3-methyl-2-indolyl}phosphine (2d). To a solution of **1b** (314 mg, 1.3 mmol) in THF (8 mL) was added dropwise 1.07 mL of *sec*-BuLi (1.3 M in cyclohexane/hexanes) at -70°C. The resulting pale yellow solution was stirred for 1 h at -70 °C and allowed to warm to room temperature. This solution was added dropwise to a solution of (*S*)-(-)-3,3'-dimethyl-2,2'-bisnaphtol phosphorochloridite (481 mg, 1.3 mmol) in THF (5 mL) at -70 °C. The reaction mixture was stirred for 1 h at -70 °C and then allowed to warm to room temperature. The solvent was removed *in vacuo* and the reddish-brown residue was redissolved in a 20:80 mixture of EtOAc/Hexanes (20 mL). The resulting suspension was filtered through a pad of SiO_2 which was rinsed with a 20:80 mixture of EtOAc/Hexanes (20 mL). The solvent was removed *in vacuo* to obtain the product as a white powder. Yield: 695 mg (93 %). ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ (ppm) 7.90 (m, 2H), 7.80 (d, J = 8.0 Hz, 1H), 7.47-7.39 (m, 6H), 7.29-7.23 (m, 2H), 6.93 (t, J = 7.5 Hz, 1H), 6.51 (d, J = 8.5 Hz, 1H), 6.24 (t, J = 7.5 Hz, 1H), 2.75 (m, 2H), 2.62 (s, 3H), 2.54 (s, 3H), 1.69 (s, 3H), 1.33-1.27 (m, 6H), 1.17-1.07 (m, 3H), 1.05-1.00 (m, 3H). ^{13}C NMR ($CDCl_3$, 125.5 MHz, 298 K): δ (ppm) 150.77, 148.06, 140.17, 132.16, 132.02, 131.89, 131.61, 131.46, 130.55, 130.41, 130.35, 130.25, 127.84, 127.76, 127.29, 127.18, 127.08, 125.73, 125.56, 125.34, 125.29, 125.08, 123.44, 122.97, 122.59, 121.35, 119.24, 118.60, 116.49, 110.72, 30.30, 30.20, 26.87, 26.79, 26.74, 26.66, 23.88, 23.80, 22.13, 21.94, 21.44, 20.62, 20.47, 19.89, 19.83, 17.40, 17.24, 11.57, 11.44. ^{31}P{^{1}H} NMR ($CDCl_3$, 202.3 MHz, 223 K): δ (ppm) 137.65 (d, J_{PP} = 239.7 Hz, 0.25P), 136.34 (s, 0.75P), -9.80 (d, J_{PP} = 239.7 Hz, 0.25P), -11.25 (s, 0.75P). HRMS (FAB) calcd for $[M + H]^+$ $C_{37}H_{37}NO_2P_2$, 590.2378; found, 590.2356.

[Rh(2c)(cod)]BF_4. A suspension of $[Rh(cod)Cl]_2$ (56 mg, 0.11 mmol) and $AgBF_4$ (44 mg, 0.23 mmol) in THF (4 mL) was stirred for 45 minutes protected from light. The resulting yellow mixture was filtered over a short pad of Celite which was rinsed with THF (4 mL). To this solution, **2c** (176 mg, 0.23 mmol) in THF (8 mL) was added dropwise and the resulting orange solution was stirred for 1 h, filtered, and the solution was concentrated *in vacuo* to ca. 0.5 mL. Pentanes (20 mL) was added to precipitate an orange solid which was washed with pentanes (20 mL) and dried *in vacuo*. Yield: 203 mg (83 %). ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ (ppm) 8.21 (s,

1H), 8.04 (d, J = 8.5 Hz, 1H), 7.99 (m, 3H), 7.67-7.54 (m, 8H), 7.44 (m, 4H), 7.36 (m, 2H), 7.23 (d, J = 8.5 Hz, 1H), 7.08 (t, J = 7.5 Hz, 2H), 6.50 (t, J = 8.0 Hz, 1H), 6.02 (d, J = 8.5 Hz, 1H), 5.76 (br s, 1H), 5.44 (br s, 2H), 4.08 (br s, 1H), 2.48-2.05 (m, 8H), 1.94 (s, 3H), 0.29 (s, 9H), 0.12 (s, 9H). ^{13}C NMR ($CDCl_3$, 125.5 MHz, 298 K): δ (ppm) 153.81, 153.68, 139.05, 138.41, 137.67, 137.44, 134.05, 133.84, 133.73, 133.64, 132.86, 132.39, 131.68, 131.64, 131.55, 131.45, 130.70, 130.44, 130.36, 129.97, 129.88, 129.05, 128.81, 128.77, 128.32, 128.17, 127.89, 127.07, 126.94, 126.85, 126.83, 126.45, 126.35, 126.07, 125.95, 123.62, 121.95, 120.60, 120.51, 115.51, 111.63, 108.89, 97.12, 31.31, 30.17, 30.00, 29.02, 10.36, 1.00, -0.94. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202.3 MHz, 298 K): δ (ppm) 137.83 (dd, J_{PRh} = 257.3 Hz, J_{PP} = 45.9 Hz), 24.94 (dd, J_{PRh} = 140.2 Hz J_{PP} = 45.9 Hz). HRMS (FAB) calcd for $[M - BF_4]^+$ $C_{55}H_{57}NO_2P_2Si_2Rh$, 984.2458; found, 984.2459.

III Catalysis: Rh catalysed hydrogenation and hydroformylation

General procedure for the asymmetric hydrogenation. The hydrogenation experiments were carried out in a stainless steel autoclave (150 mL) charged with an insert suitable for 5 reaction vessels (including Teflon mini stirring bars) for conducting parallel reactions. In a typical experiment, the reaction vessels were charged with 2.5 μmol of $[Rh(nbd)_2]BF_4$, 2.75 μmol of ligand and 0.25 mmol of alkene substrate in 2.5 mL of CH_2Cl_2. In case of ligand **2c** the corresponding rhodium complex [Rh(**2c**)(cod)]BF_4 was used instead of the *in situ* generated catalyst because the free ligand **2c** proved to be very unstable towards hydrolysis by moisture. Before starting the catalytic reactions, the charged autoclave was purged three times with 15 bar of dihydrogen and then pressurised at 10 bar H_2. The reaction mixtures were stirred at 25 °C for the appropriate reaction time. After catalysis the pressure was reduced to 1.0 bar and the conversion and enantiomeric purity was determined by chiral GC (dimethyl itaconate: Supelco BETA DEX, isothermal at 68 °C, t_R (*R*) = 43.1 min. and t_R (*S*) = 43.7 min.; methyl 2-acetamidoacrylate: ph Megadex column, initial temperature = 70 °C and ΔT = 7 °C min^{-1}; t_R (*S*) = 3.32 min. and t_R (*R*) = 4.05 min.).

General procedure for the asymmetric hydroformylation of styrene. The reactions were performed in a stainless steel autoclave containing a 15 mL glass beaker equipped with a Teflon stirring bar. The substrate styrene was filtered freshly over basic alumina to remove possible peroxide impurities. The autoclave was charged with 3.0 μmol of $[Rh(acac)(CO)_2]$, 12.0 μmol of ligand, 344 μl of styrene and 193 μl of decane in 3.0 ml of toluene. Before starting the catalytic reactions, the charged autoclave was purged three times with 15 bar of syngas (CO/H_2=1/1) and then pressurized at 10 bar (CO/H_2 = 1/1). The reaction mixtures were stirred at 40 °C or 60 °C for the appropriate reaction time. After catalysis the pressure was reduced to 1.0 bar and the conversion was checked by GC. The enantiomeric purity was determined by chiral GC (ph Megadex column; initial temperature = 40 °C and ΔT = 25 °C min^{-1}; t_R (*R*) = 4.51 min. and t_R (*S*) = 4.64 min.).

IV NMR spectroscopy study of rhodium complexes

NMR spectroscopy study of [Rh(2a)$_2$]BF$_4$ and [Rh(2a)(nbd)]BF$_4$. [Rh(nbd)$_2$]BF$_4$ (6.44 mg, 17.2 μmol) and **2a** (10.76 mg, 17.1 μmol) were dissolved in $CDCl_3$ (1 mL) and stirred for 3 h to allow complex formation. A 4:1 mixture of [Rh(**2a**)$_2$]BF$_4$ and [Rh(**2a**)(nbd)]BF$_4$ was obtained.
[Rh(**2a**)$_2$]BF$_4$: ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ (ppm) 7.93-7.14 (m, 42 H), 7.01 (d, J = 8.5 Hz, 1H), 6.93 (t, J = 7.5 Hz, 1H), 6.85 (m, 2H), 6.75 (t, J = 7.3 Hz, 1H), 6.61 (t, J = 8.3 Hz, 2H), 6.17 (t, J = 8.0 Hz, 1H), 5.80 (d, J = 9.0 Hz, 1H), 5.46 (d, J = 9.0 Hz, 1H), 1.80 (s, 3H), 1.29 (s, 3H). ^{31}P{^{1}H} NMR ($CDCl_3$, 202.3 MHz, 298 K): δ (ppm) 157.05 (m, $J_{PN,Rh}$ = 225.2 Hz, $J_{PN,PCtrans}$ = 388.7 Hz, $J_{PN,PCcis}$ = -61.8 Hz, $J_{PN,PN'}$ = 25.7 Hz), 24.83 (m, $J_{PC,Rh}$ = 124.0 Hz, $J_{PC,PNtrans}$ = 388.7 Hz, $J_{PC,PNcis}$ = -61.8 Hz, $J_{PC,PC'}$ = 16.9 Hz).
[Rh(**2a**)(nbd)]BF$_4$*: ^{31}P{^{1}H} NMR ($CDCl_3$, 202.3 MHz, 298 K): δ (ppm) 147.06 (dd, $J_{PN,Rh}$ = 270.9 Hz, $J_{PN,PC}$ = 56.6 Hz), 26.51 (dd, $J_{PC,Rh}$ = 144.2, $J_{PC,PN}$ = 55.2 Hz).

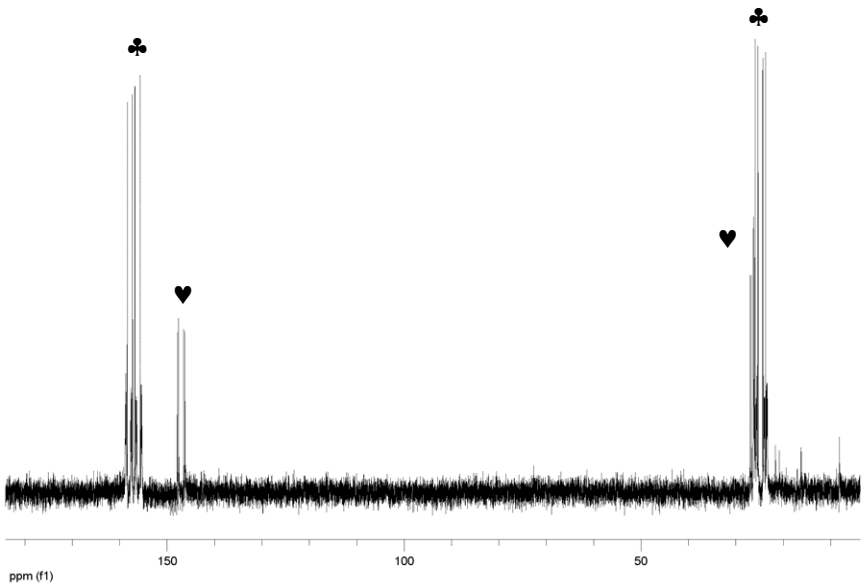

Fig. S1 ^{31}P{^{1}H} NMR spectrum of complex study with ligand **2a**. ♣ [Rh(**2a**)$_2$]BF$_4$, ♥ [Rh(**2a**)(nbd)]BF$_4$.

NMR spectroscopy study of [Rh(2b)(nbd)]BF$_4$. [Rh(nbd)$_2$]BF$_4$ (5.26 mg, 14.0 μmol) and **2b** (7.15 mg, 12.7 μmol) were dissolved in $CDCl_3$ (1 mL) and stirred for 1 h to allow complex formation. ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ (ppm) 8.23 (d, J = 8.5 Hz, 1H), 8.07 (d, J = 8.5 Hz, 1H), 7.90 (d, J = 8.5 Hz, 1H), 7.81 (d, J = 9.0 Hz, 1H), 7.66 (d, J = 8.5 Hz, 1H), 7.60-7.53 (m, 2H), 7.45-7.35 (m, 5H), 6.99 (t, J = 7.5 Hz, 1H), 6.83 (d, J = 9.0 Hz, 1H), 6.62 (br s, 1H), 6.48 (br s, 1H), 6.26 (t, J = 7.8 Hz, 1H), 5.98 (d, J = 8.5 Hz, 1H), 5.48 (br s, 2H), 4.39 (br s, 1H), 4.13 (br s, 1H), 3.01 (m, 2H), 2.47 (s, 3H), 1.72 (br s, 2H), 1.54-1.34 (m, 12H). ^{31}P{^{1}H} NMR ($CDCl_3$, 202.3 MHz, 298 K): δ (ppm) 146.05 (dd, $J_{PN,Rh}$ = 272.1 Hz, $J_{PN,PC}$ = 51.2 Hz), 53.23 (dd, $J_{PC,Rh}$ = 142.8 Hz, $J_{PC,PN}$ = 52.6 Hz).

* Not all ^{1}H NMR shifts could be identified because many are obscured by signals stemming from [Rh(**2a**)$_2$BF$_4$] and are therefore omitted.

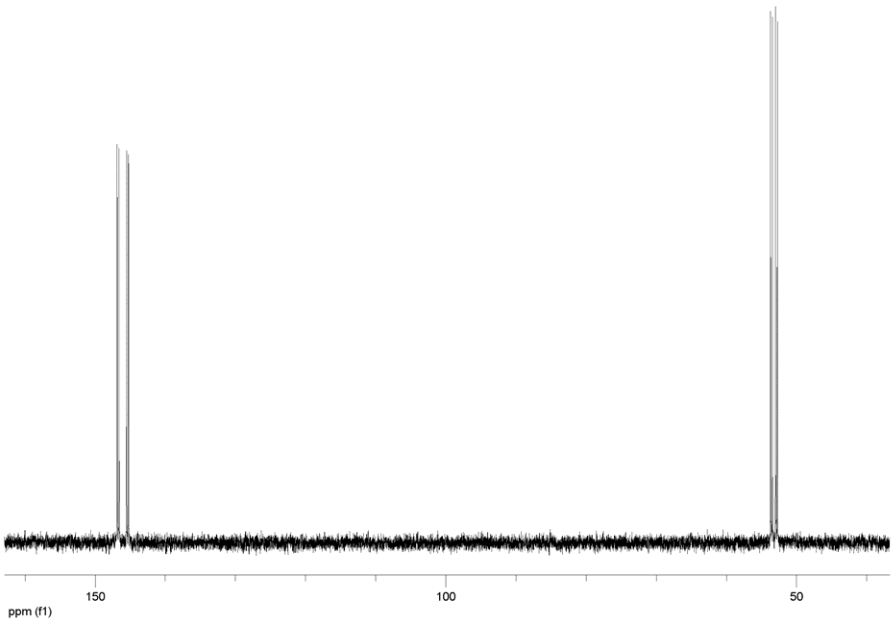

Fig. S2 $^{31}P\{^{1}H\}$ NMR spectrum of complex study with ligand **2b**.

NMR spectroscopy study of [Rh(2c)(nbd)]BF_4. $[Rh(nbd)_2]BF_4$ (4.97 mg, 13.3 μmol) and **2c** (10.22 mg, 13.2 μmol) were dissolved in $CDCl_3$ (1 mL) and stirred for 0.5 h to allow complex formation. ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ (ppm) 8.26 (s, 1H), 8.06 (d, J = 8.5 Hz, 1H), 7.99 (d, J = 8.5 Hz, 1H), 7.98 (s, 1H), 7.89 (d, J = 6.5 Hz, 1H), 7.86 (d, J = 7.0 Hz, 1H), 7.63 (m, 6H), 7.57 (m, 2H), 7.47 (d, J = 8.0 Hz, 1H), 7.36 (t, J = 8.0 Hz, 2H), 7.30 (m, 2H), 7.20 (d, J = 9.0 Hz, 1H), 7.15 (d, J = 8.5 Hz, 1H), 7.10 (t, J = 7.0 Hz, 1H), 6.52 (t, J = 8.0 Hz, 1H), 5.97 (d, J = 8.0 Hz, 1H), 5.82 (br s, 1H), 5.76 (br s, 1H), 5.69 (br s, 1H), 4.17 (br s, 1H), 4.09 (br s, 1H), 4.04 (br s, 1H), 1.92 (s, 3H), 1.80 (d, J = 9.5 Hz, 1H), 1.60 (d, J = 9.0 Hz, 1H), 0.31 (s, 9H), -0.07 (s, 9H). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202.3 MHz, 298 K): δ (ppm) 139.58 (dd, $J_{PN,Rh}$ = 268.0 Hz, $J_{PN,PC}$ = 53.8 Hz), 25.04 (dd, $J_{PC,Rh}$ = 145.5 Hz, $J_{PC,PN}$ = 53.8 Hz).

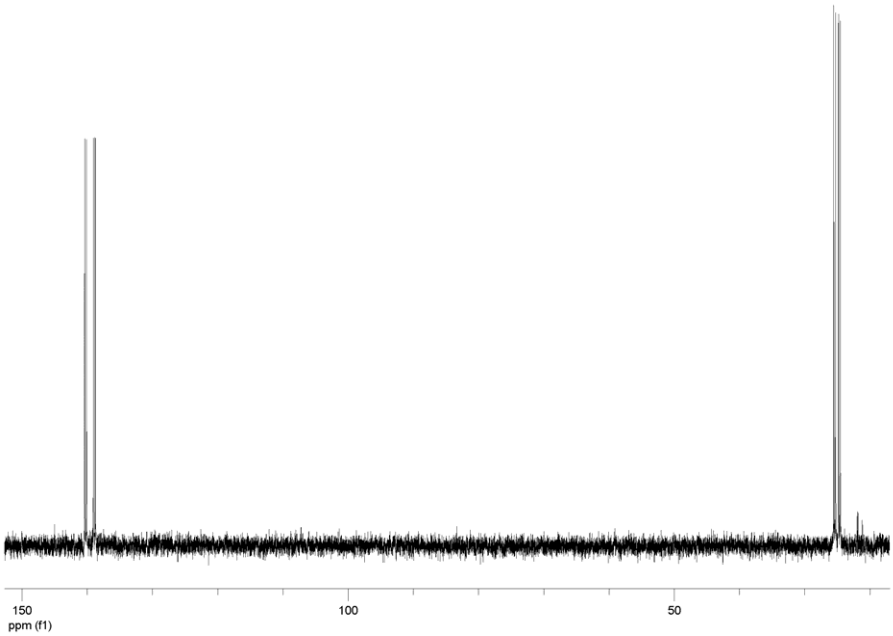

Fig. S3 $^{31}P\{^{1}H\}$ NMR spectrum of complex study with ligand **2c**.

NMR spectroscopy study of [Rh(2d)(nbd)]BF_4. $[Rh(nbd)_2]BF_4$ (4.27 mg, 11.4 µmol) and **2d** (7.50 mg, 12.7 µmol) were dissolved in $CDCl_3$ (1 mL) and stirred for 1h to allow complex formation. ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ (ppm) 8.04 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.60 (s, 1H), 7.56-7.50 (m, 2H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.35-7.28 (m, 3H), 7.22 (d, *J* = 8.5 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.72 (br s, 1H), 6.56 (br s, 1H), 6.36 (t, *J* = 8.0 Hz, 1H), 5.85 (d, *J* = 8.5 Hz, 1H), 5.60 (br s, 1H), 4.75 (br s, 1H), 4.30 (br s, 1H), 4.17 (br s, 1H), 3.08 (m, 1H), 2.96 (m, 1H), 2.80 (s, 3H), 2.49 (s, 3H), 1.90 (br d, *J* = 6.0 Hz, 1H), 1.82 (s, 3H), 1.66 (br d, *J* = 7.5 Hz, 1H), 1.53-1.44 (m, 6H), 1.36 (dd, *J* = 19.0, 7.0 Hz, 3H), 1.14 (dd, *J* = 22.0, 6.5 Hz, 3H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202.3 MHz, 298 K): δ (ppm) 141.67 (dd, $J_{PN,Rh}$ = 272.1 Hz, $J_{PN,PC}$ = 52.4 Hz), 55.36 (dd, $J_{PC,Rh}$ = 142.8 Hz, $J_{PC,PN}$ = 52.6 Hz).

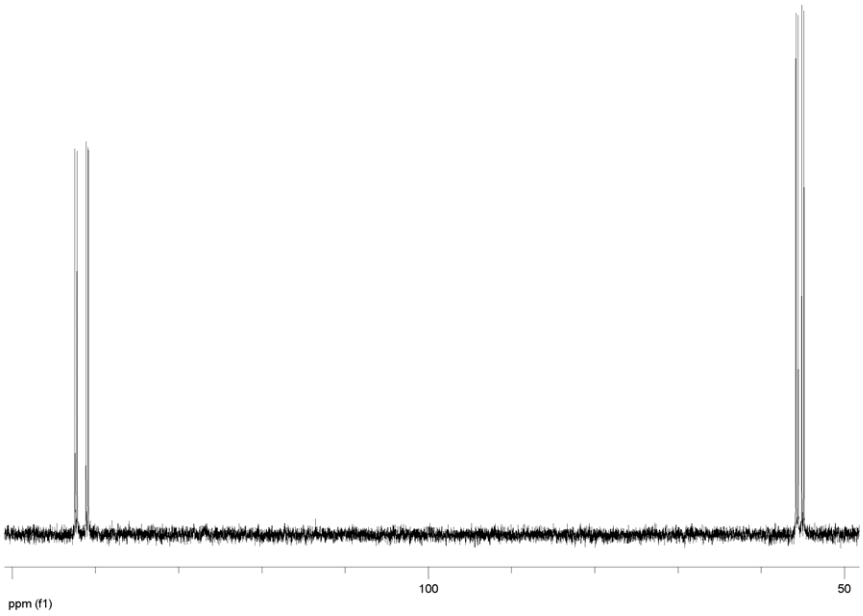

Fig. S4 $^{31}P\{^1H\}$ NMR spectrum of complex study with ligand **2d**.

V ^{1}H and ^{13}C NMR spectra of new compounds

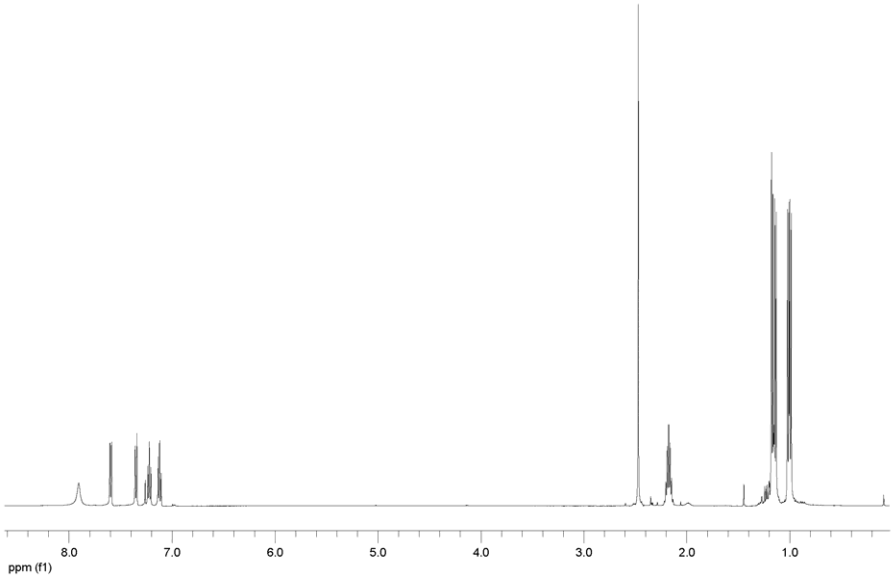

Fig. S5 ^{1}H NMR spectrum of **1b**

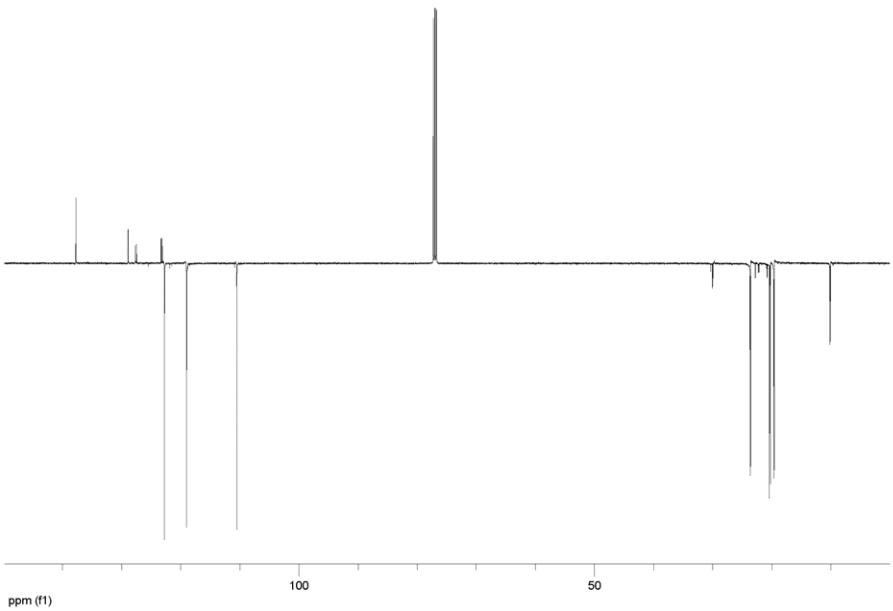

Fig. S6 ^{13}C NMR spectrum of **1b**

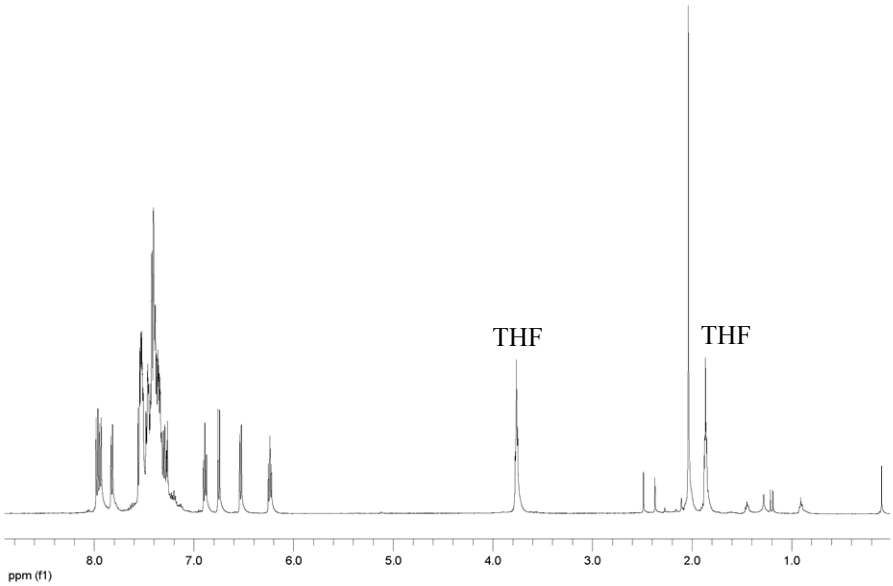

Fig. S7 ^{1}H NMR spectrum of **2a**

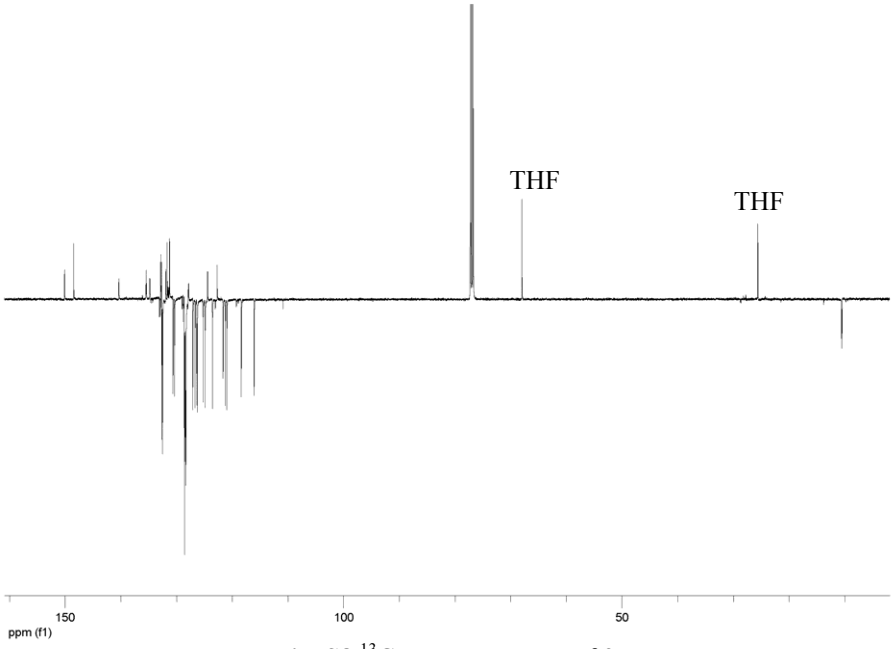

Fig. S8 ^{13}C NMR spectrum of **2a**

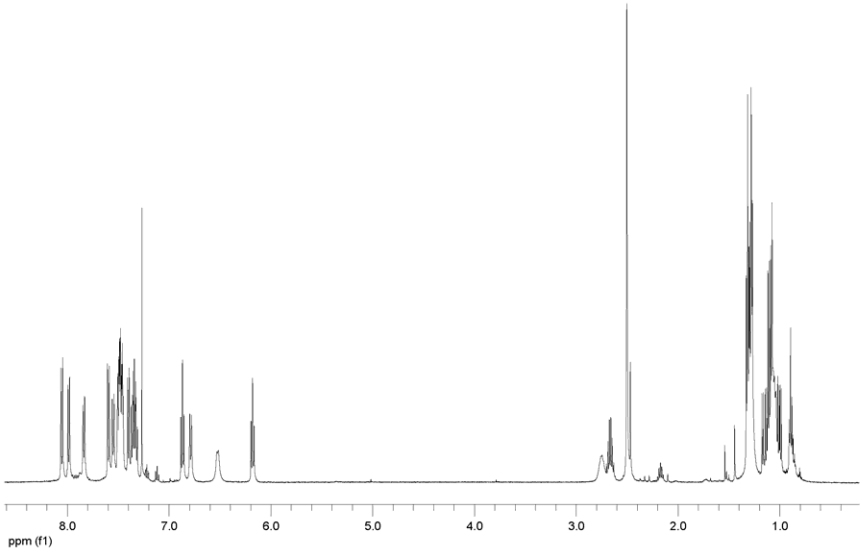

Fig. S9 ^{1}H NMR spectrum of **2b**

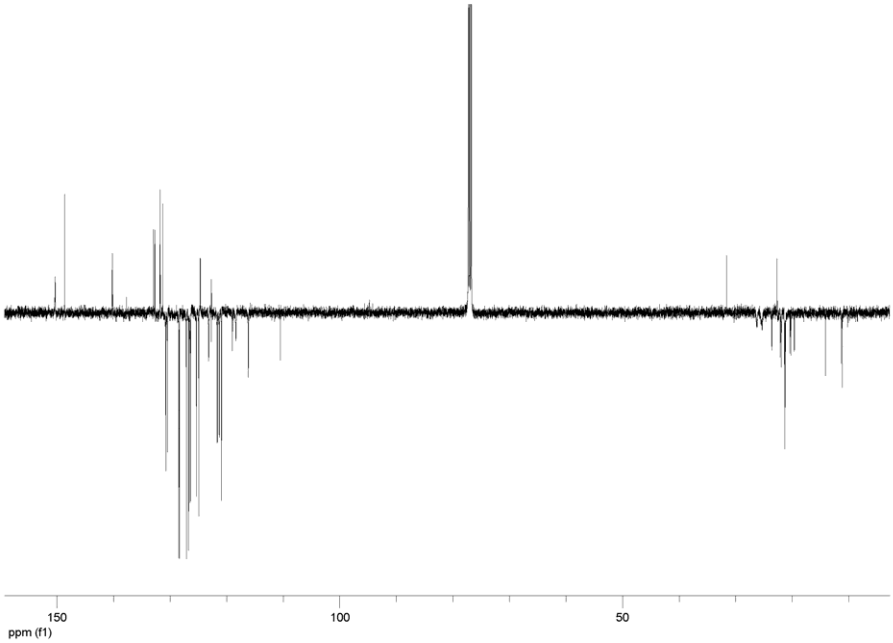

Fig. S10 ^{13}C NMR spectrum of **2b**

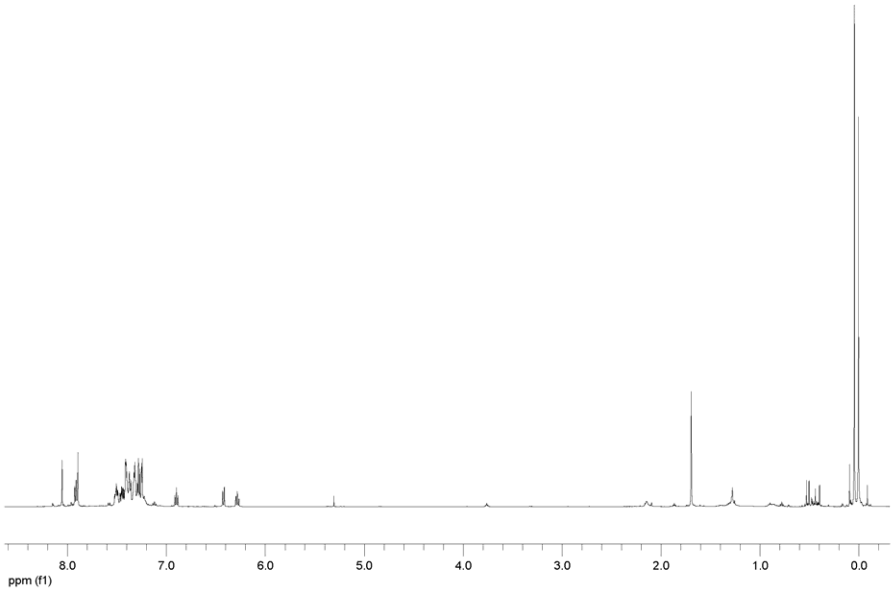

Fig. S11 ^{1}H NMR spectrum of **2c**

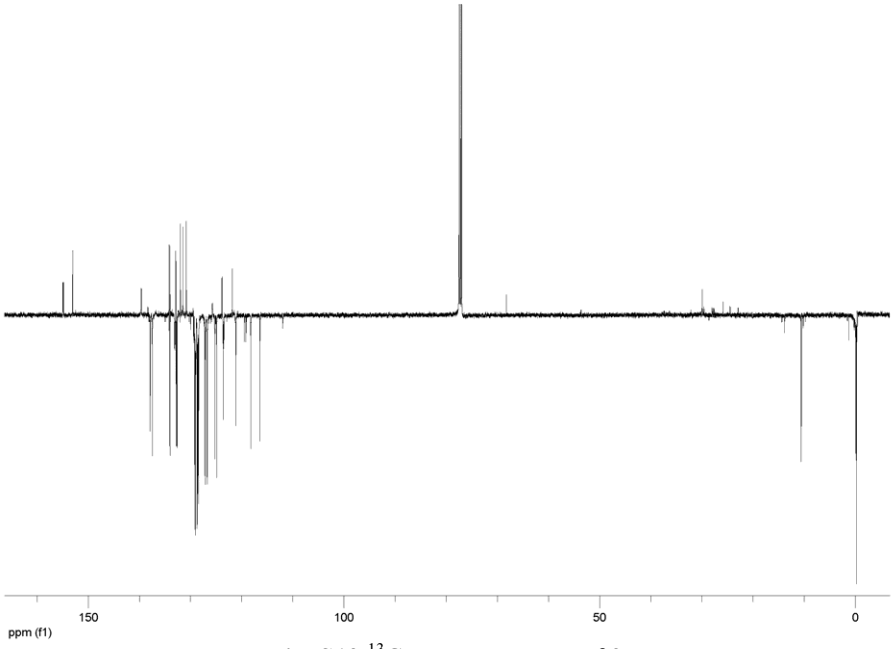

Fig. S12 ^{13}C NMR spectrum of **2c**

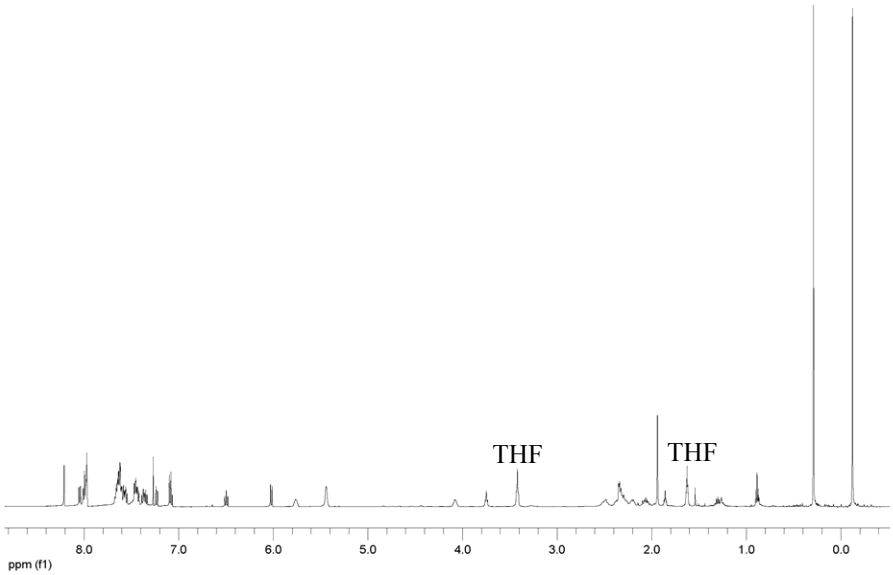

Fig. S13 ^{1}H NMR spectrum of [Rh(**2c**)(cod)]BF_4

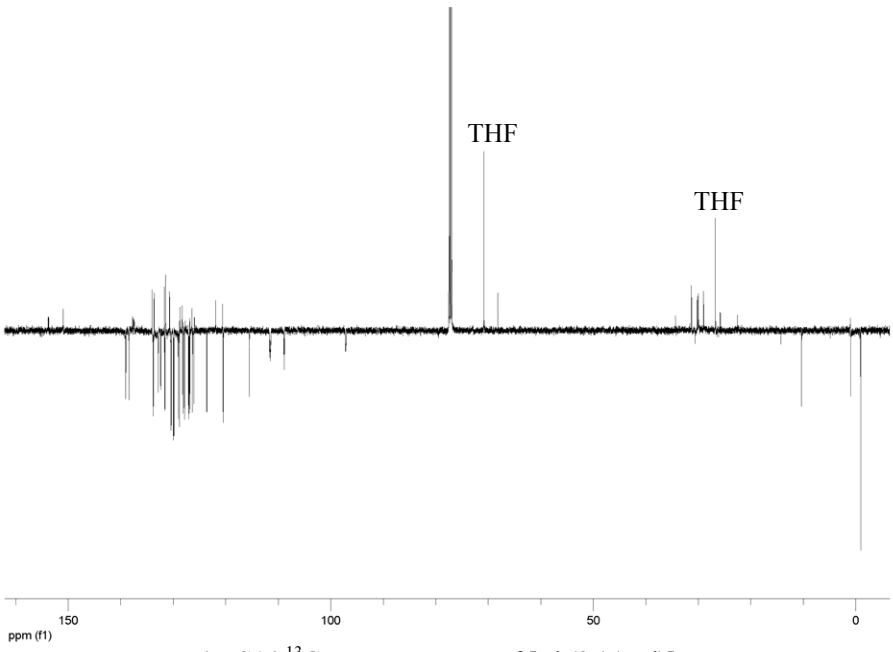

Fig. S14 ^{13}C NMR spectrum of [Rh(**2c**)(cod)]BF_4

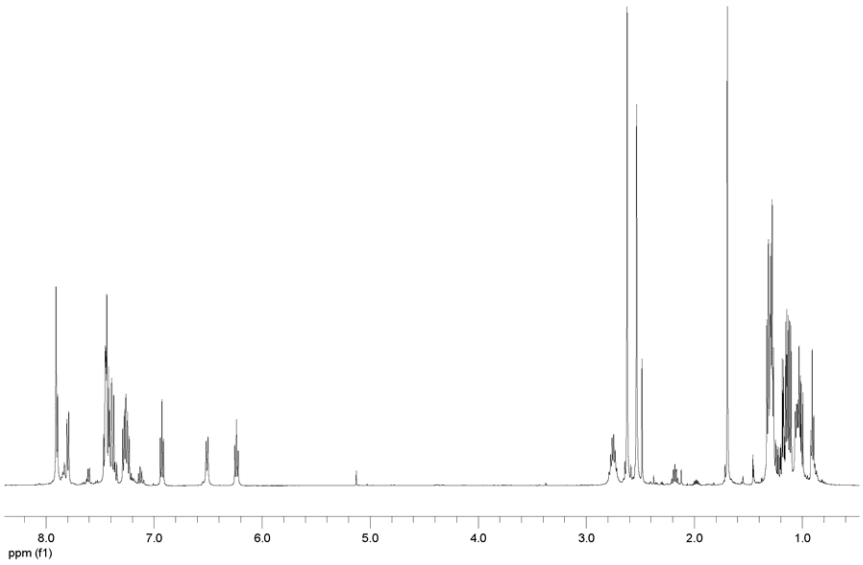

Fig. S15 ^{1}H NMR spectrum of **2d**

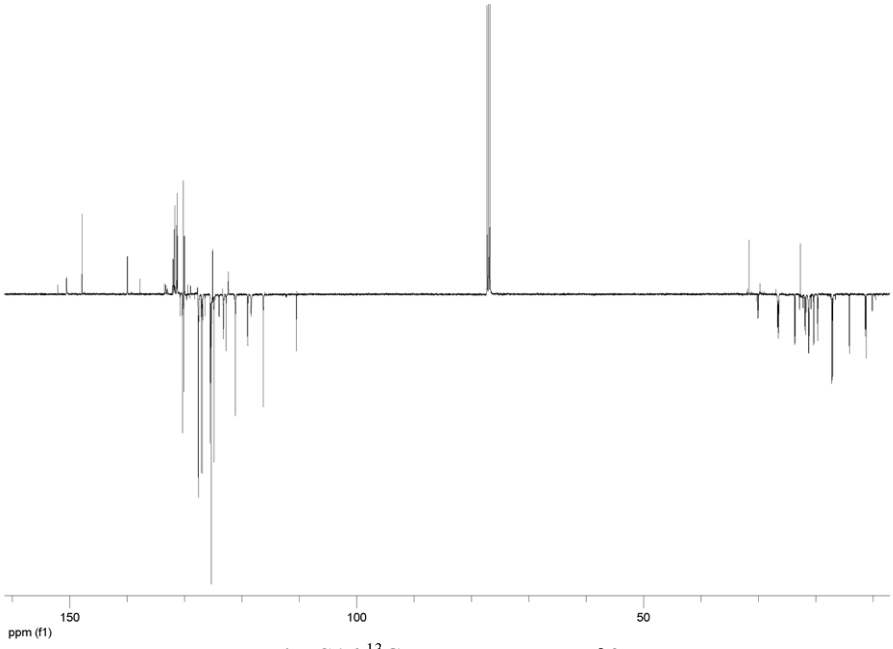

Fig. S16 ^{13}C NMR spectrum of **2d**

VI References

[1] (*a*) G. J. H. Buisman, L. A. van der Veen, A. Klootwijk, W. G. J. de Lange, P. C. J. Kamer, P. W. N. M. van Leeuwen and D. Vogt, *Organometallics*, 1997, **16**, 2929; (*b*) Joost Nicolaas Hendrik Reek, Ruifang Chen, Paul Clemens Jozef Kamer, Vincent Friso Slagt and Petrus Wilhelmus Nicolaas Maria van Leeuwen, EP 1479439, 2004; (*c*) V. F. Slagt, P. W. N. M. van Leeuwen and J. N. H. Reek, *Chem. Commun.*, 2003, 2474.

[2] L. A. Arnold, R. Imbos, A. Mandoli, A. H. M. de Vries, R. Naasz, B. L. Feringa, *Tetrahedron* 2000, **56**, 2865.

[3] Also prepared by Browning *et al.* following a different route in J. O. Yu, E. Lam, J. L. Sereda, N. C. Rampersad, A. J. Lough, C. S. Browning and D. H. Farrar, *Organometallics*, 2005, **24**, 37.