Chiral MOP-phosphonite ligands: synthesis, characterisation and interconversion of η^1,η^6-(σ-P, π-arene) chelated rhodium(I) complexes

Supporting Information

Arne Ficks, Ross W. Harrington and Lee J. Higham*

School of Chemistry, Bedson Building, Newcastle University,

*Newcastle upon Tyne, NE1 7RU, UK; *Email: lee.higham@newcastle.ac.uk*

Table of Contents

1 General Supporting Information

Table S1: Selected ^{13}C NMR resonances of **4a** and **5**.

	4a		**5**	
	$^{13}C(\eta^1,\eta^6)$ [ppm][a]	$^{13}C(\eta^1)$ [ppm][a]	$^{13}C(\eta^1,\eta^6)$ [ppm][a]	$^{13}C(\eta^1)$ [ppm][a]
C1’	100.5	121.9	93.6	118.7
C2’	149.1	153.8	141.4	154.3
C3’	87.5	114.2	89.5	112.4
C4’	95.8	128.1	92.3	130.7
C10’	112.8	128.2	120.2	128.6
C9’	118.7	134.6	123.1	134.2

[a] Solution NMR analysis (126 MHz, CD_2Cl_2, 21 °C).

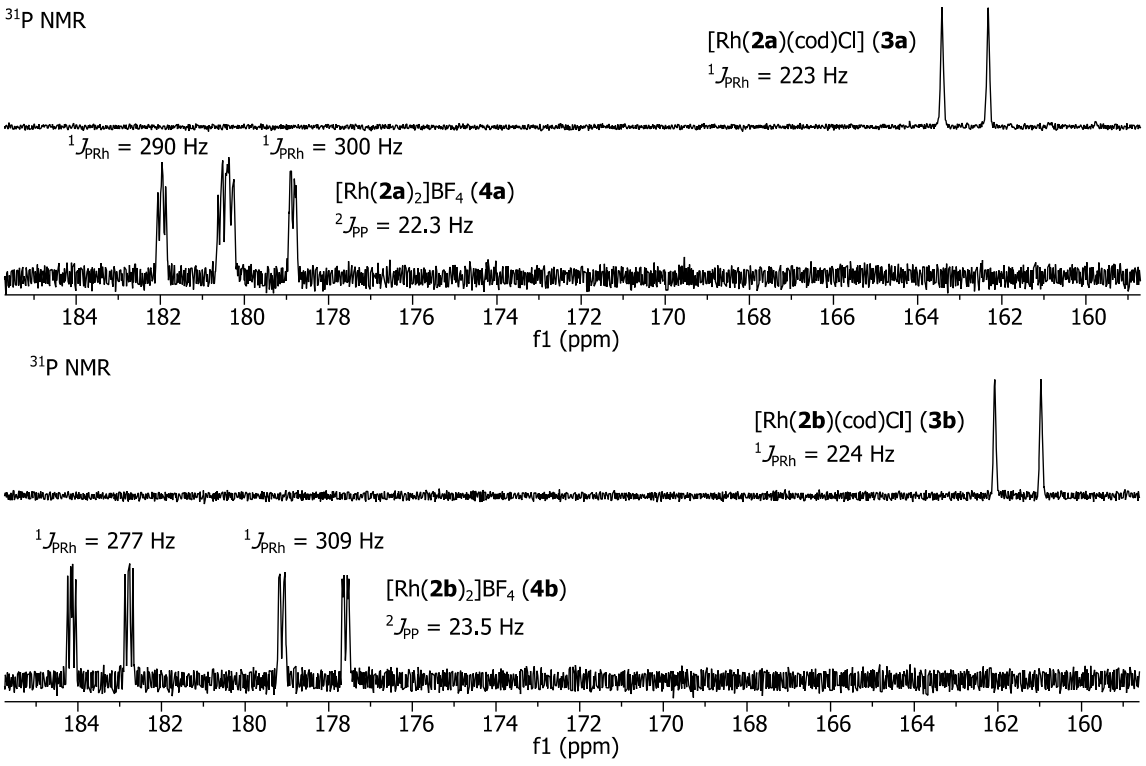


Fig. S1: ^{31}P NMR (202 MHz) spectra of **3a,b** and **4a,b**. Note that in the case of **4a,b**, coupling to the hydrogen atoms in 3-position of the ligands is also resolved in the spectra.

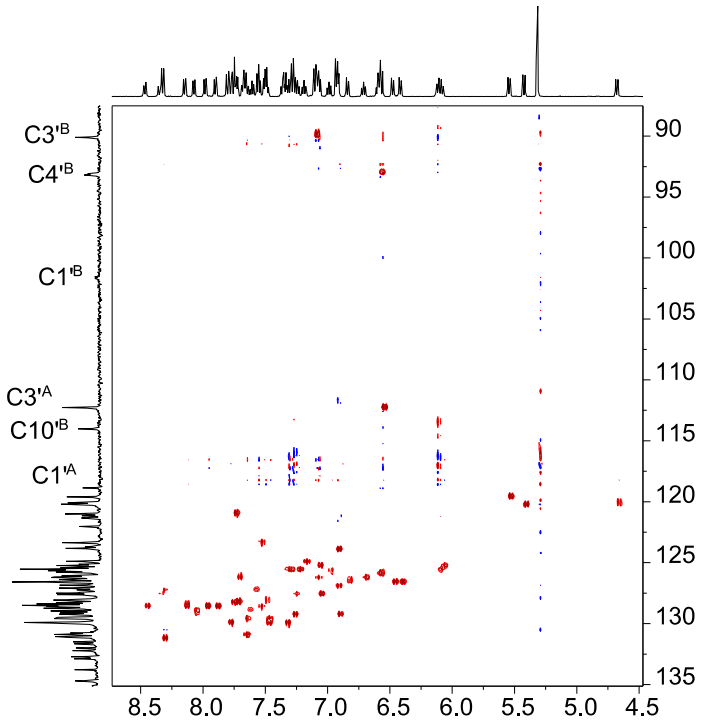


Fig. S2: Section of the ^{13}C–^{1}H HSQC spectrum of **4b** in CD_2Cl_2 at 21 °C using a 400 MHz spectrometer. Metal coordinated carbons (labelled B) are shifted to higher field compared to their non-coordinated counterparts (labelled A).

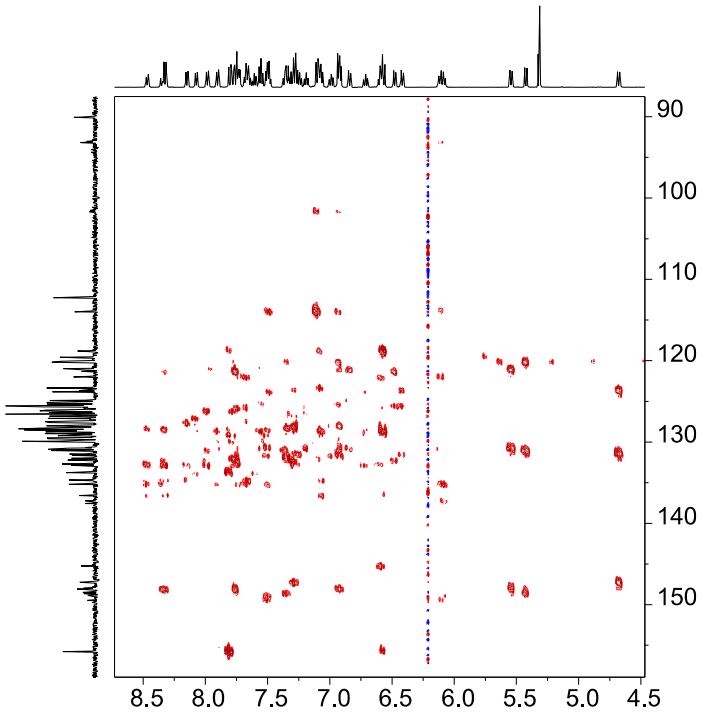


Fig. S3: Section of the ^{13}C–^{1}H HMBC spectrum of **4b** in CD_2Cl_2 at 21 °C using a 400 MHz spectrometer.

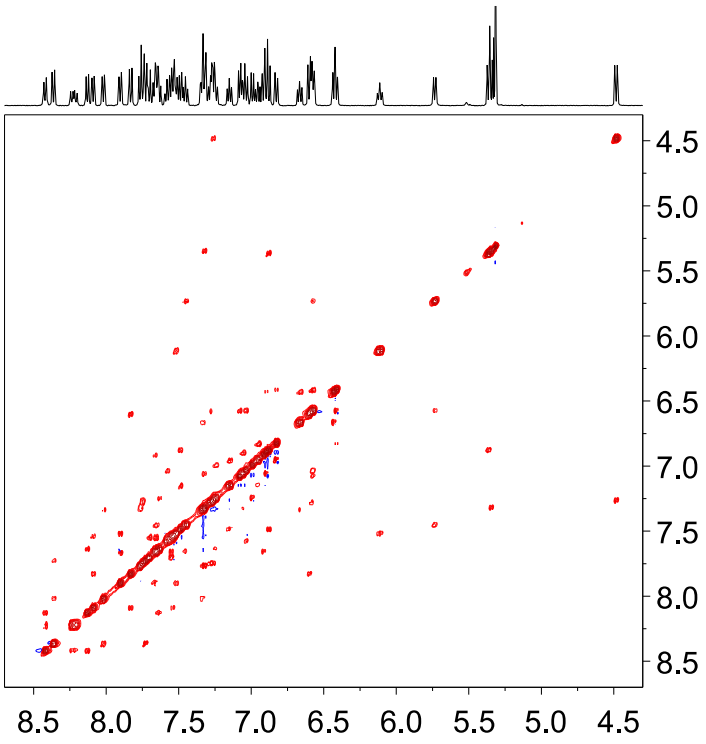


Fig. S4: Section of the ^{1}H-NOESY spectrum of **4b** in CD_2Cl_2 at –50 °C. Positive NOE correlations are shown in red; exchange was not observed at this temperature. The spectrum was acquired with 2048 × 512 data points and a spectral width of 9 ppm using a 500 MHz spectrometer with a mixing time of 500 ms.

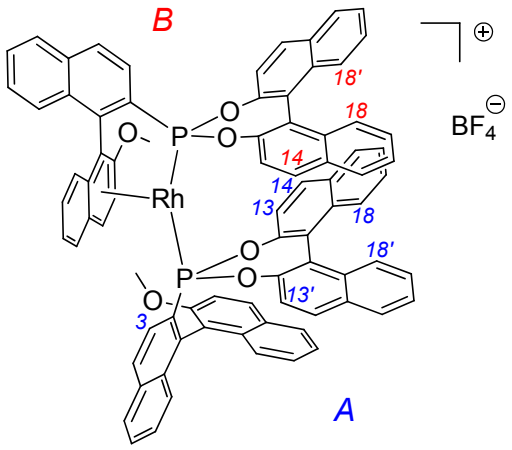


Fig. S5: Structure of **4a** based on NOE correlations in the ^{1}H-NOESY NMR. The η^1 ligand is coined *A*, the η^1,η^6-(σ-P, π-arene) ligand is coined *B*. Selected NOE contacts: $H18^{A}$–$H18^{B}$, $H13^{A}$–OCH_3^{B}, $H3^{A}$–$H13'^{A}$, $H14^{B}$–$H13'^{A}$, $H18^{A}$–$H18'^{A}$, $H18^{B}$–$H18'^{B}$.

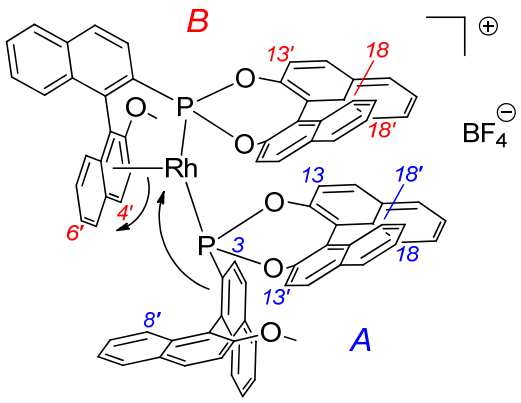


Fig. S6: Dynamic behaviour observed in solution for **4b** (arrows). The η^1 ligand is labelled *A*, the η^1,η^6-(σ-P, π-arene) ligand is labelled *B*. Selected NOE contacts: $H13'^{B}$–OCH_3^{B}, $H3^{A}$–$H13'^{B}$, $H3^{A}$–$H13^{A}$, $H4'^{B}$–$H8'^{A}$, $H18^{B}$–$H18'^{B}$, $H18^{A}$–$H18'^{A}$, $H13'^{A}$–$H6'^{B}$.

The Eyring equation relates the rate constant k and the activation free energy $\Delta G^{\ddagger}$.[1] The most common form of the Eyring equation is:

$$k = \frac{\kappa T}{h} \cdot e^{-\Delta G^{\ddagger}/RT} \quad (1)$$

where κ is the Boltzmann constant, h is Planck's constant, T is the temperature in Kelvin and R is the universal gas constant. The equation can be rewritten as:

$$\Delta G^{\ddagger} = -\ln\left(\frac{k\,h}{\kappa\,T}\right) RT \quad (2)$$

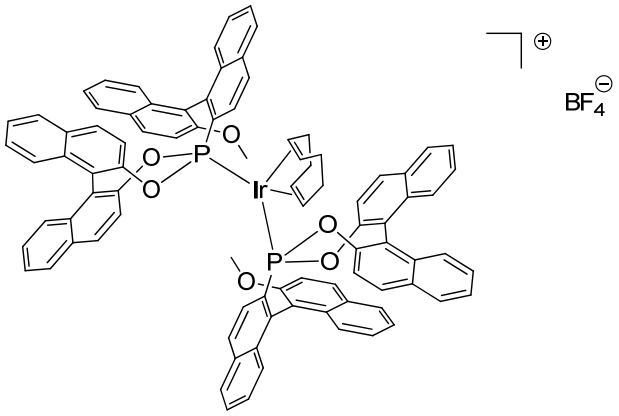


Fig. S7: Structure of **7a** based on NMR and HRMS analysis.

2 Experimental Procedures and Analytical Data

2.1 General Considerations

All air and/or water sensitive reactions were performed under a nitrogen atmosphere using standard Schlenk line techniques. Tetrahydrofuran and dichloromethane were dried over sodium/benzophenone and calcium hydride respectively, and distilled prior to use. MOP-phosphonite ligands **2a**,**b** were synthesised according to literature procedures.[2] All other chemicals were used as purchased without further purification.

2.2 Chemical Analysis

General Procedures. Infrared spectra were recorded on a Varian 800 FT-IR spectrometer. Mass spectrometry was carried out by the EPSRC National Mass Spectrometry Service Centre Swansea. Analytical high performance liquid chromatography (HPLC) was performed on a Varian Pro Star HPLC equipped with a variable wavelength detector.

X-ray Diffraction. All data were collected on an Oxford Diffraction Gemini A Ultra diffractometer at 150 K, using Mo Kα (λ = 0.71073Å; **3a** and **6a**), or Cu Kα (λ = 1.54178 Å; **4b**) radiation. Semi-empirical absorption corrections were applied based on symmetry-equivalent and repeated reflections. Structures were solved by direct methods and refined on all unique F^2 values, with anisotropic non-H atoms and constrained riding isotropic H atoms. CrysAlisPro software was used for data collection, integration, and absorption corrections.[3] Structure solution, refinement, and graphics were made with the SHELXTL program.[4] The disordered dichloromethane solvent molecule in the asymmetric unit of **6a** was treated using the PLATON/SQUEEZE routine.[5] A summary of key crystallographic experimental information is provided in Table S2.

NMR Spectroscopy. ^{1}H NMR, ^{11}B{^{1}H} NMR, ^{13}C{^{1}H} NMR, ^{19}F NMR, and ^{31}P{^{1}H} NMR spectra were recorded on a JEOL Lambda 500 (^{1}H 500.16 MHz) or JEOL ECS-400 (^{1}H 399.78 MHz) spectrometer at room temperature (21°C) if not otherwise stated, using the indicated solvent as internal reference. Two-dimensional NMR experiments (COSY, NOESY, HSQC, HMBC) were used for the assignment of proton and carbon resonances; the labelling scheme is shown in Fig. S8. Full range NOESY spectra were acquired with 512 × 1024 data points and a spectral width of 9.0 ppm; mixing times were chosen between 10 and 500 ms. For the measurement of exchange rate constants in **4a**,**b** the proton resonances of the methoxy group were used. Peak volumes were determined manually from the NOESY spectrum using MestReNova 8, and the rate constants were calculated with an estimated error of 10% using EXSYCalc.[6]

Table S2: Summary of X-Ray Crystallographic Data for **3a**, **4b** and **6a**.

	3a	**4b**	**6a**
Formula	$C_{53}H_{49}ClO_4PRh$	$C_{90}H_{74}BF_4O_8P_2Rh$	$C_{50}H_{41}Cl_3IrO_3P$
formula wt	919.25	1535.15	1019.35
cryst syst	orthorhombic	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a, Å; *α*, deg	9.5919(3); 90	14.0434(4); 90	9.3945(2); 90
b, Å; *β*, deg	19.2348(5); 90	20.3321(6); 90	19.2373(5); 90
c, Å; *γ*, deg	23.6141(6); 90	25.7605(6); 90	23.8082(5); 90
V, Å^3	4356.8(2)	7355.4(3)	4302.73(17)
Z	4	4	4
ρ_{calc}, g cm^{-3}	1.401	1.386	1.574
μ, mm^{-1}	0.537	2.864	3.369
F(000)	1904	3176	2032
T_{min}/T_{max}	0.85566/1.00000	0.71860/1.00000	0.4314/0.5522
hkl range	–11 to 12, –25 to 24, –24 to 31	–14 to 14, –21 to 21, –27 to 27	–11 to 12, –24 to 20, –31 to 28
θ range, deg	3.0 to 28.5	1.7 to 62.4	3.0 to 28.6
no. of measd rflns	25484	19157	24836
no. of unique rflns (R_{int})	9385 (0.0321)	8935 (0.0542)	9076 (0.0256)
no. of obsd rflns, $I > 2\sigma(I)$	8683	8181	8788
refined params/restraints	542/0	961/0	496/0
goodness of fit	1.081	1.027	1.075
Abs. structure param.	–0.03(2)	–0.037(7)	–0.009(4)
R1/wR2 ($I > 2\sigma(I)$)	0.0330/0.0757	0.0401/0.0986	0.0218/0.0562
R1/wR2 (all data)	0.0388/0.0795	0.0461/0.1031	0.0234/0.0573
resid electron dens, e Å^{-3}	0.74/–0.45	0.80/–0.50	0.84/–0.91

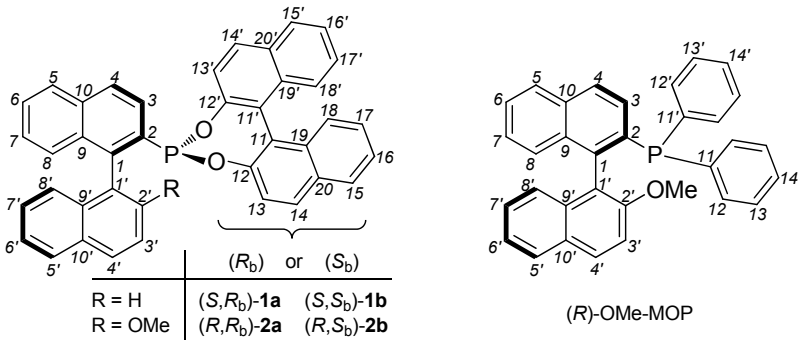
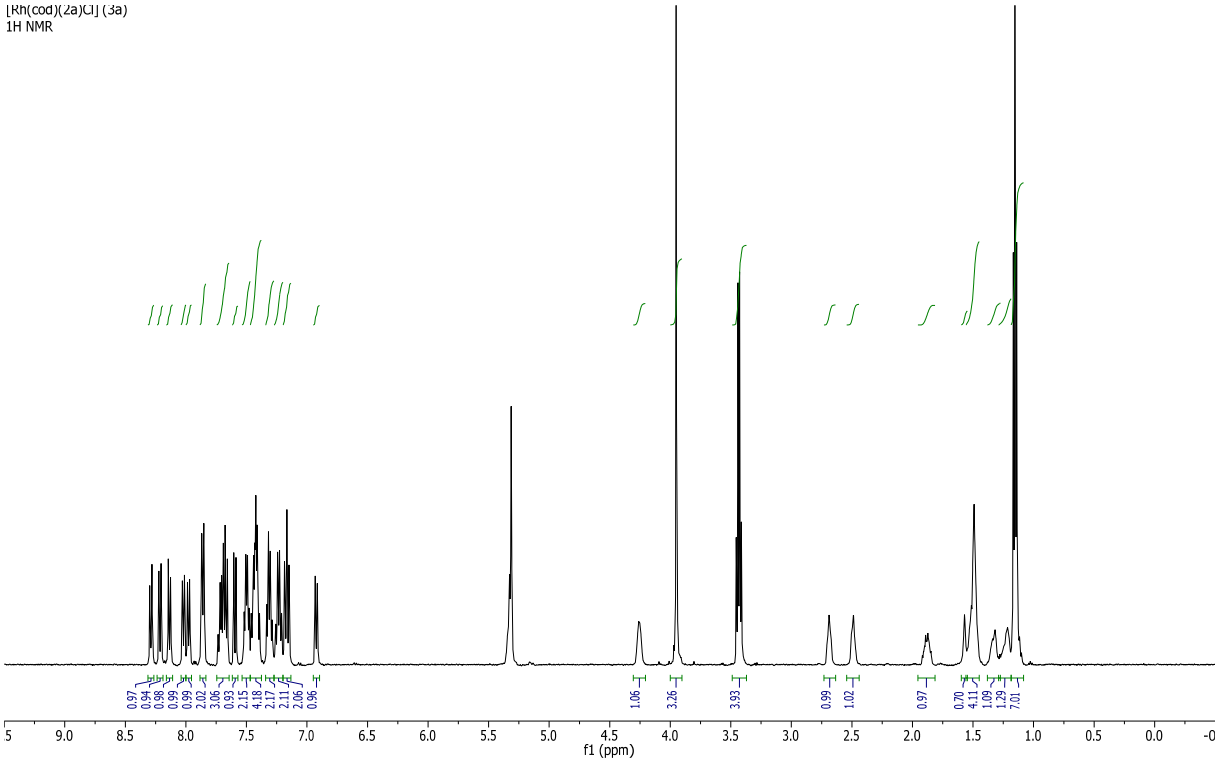


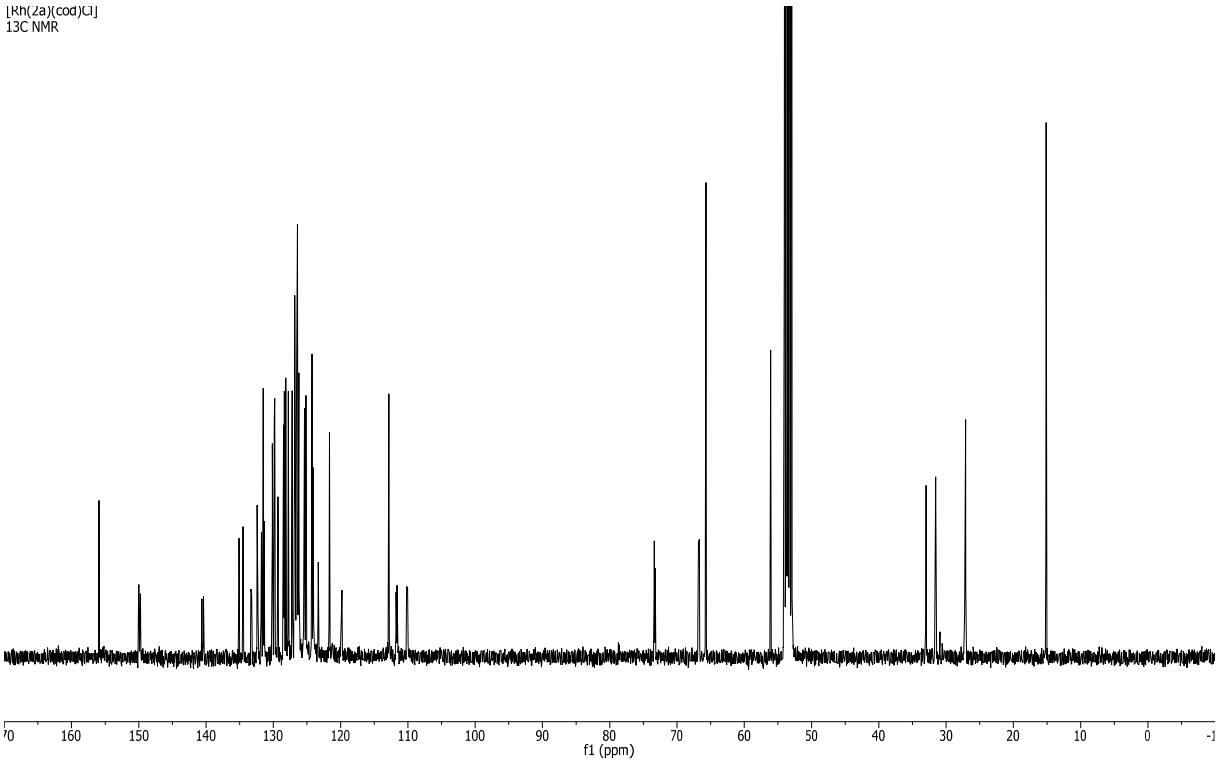
Fig. S8: Numbering scheme used in this study.

2.3 [RhCl(**2a**)(η⁴-cod)] (**3a**)

2a (21.0 mg, 35.0 µmol) and [Rh(η⁴-cod)Cl]$_2$ (8.6 mg, 17.5 µmol) were dissolved in dichloromethane (1 mL) and stirred for 30 minutes. The solution was filtered and layered with diethyl ether. Dark orange crystals suitable for X-ray analysis were formed overnight.

^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.29 (d, $^3J_{HH}$ = 8.8 Hz, 1H, *H*13), 8.21 (d, $^3J_{HH}$ = 9.1 Hz, 1H, *H*4'), 8.14 (d, $^3J_{HH}$ = 8.8 Hz, 1H, *H*14), 8.02 (d, $^3J_{HH}$ = 8.3 Hz, 1H, *H*15), 7.98 (d, $^3J_{HH}$ = 8.2 Hz, 1H, *H*5'), 7.86 (m, 2H, *H*5/*H*15'), 7.73-7.65 (m, 3H, *H*3/*H*4/*H*14'), 7.60 (d, $^3J_{HH}$ = 9.1 Hz, 1H, *H*3'), 7.52-7.48 (m, 2H, *H*6/*H*16), 7.46-7.39 (m, 4H, *H*16'/*H*18/*H*18'/*H*6'), 7.33-7.29 (m, 2H, *H*17/*H*17'), 7.26-7.21 (m, 2H, *H*7'/*H*7), 7.18 (d, $^3J_{HH}$ = 8.8 Hz, 1H, *H*8'), 7.16 (d, $^3J_{HH}$ = 8.8 Hz, 1H, *H*13'), 6.92 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *H*8), 5.31 (br s, 1H, cod-C*H*), 4.26 (br s, 1H, cod-C*H*), 3.95 (s, 3H, OCH_3), 2.69 (br s, 1H, cod-C*H*), 2.49 (br s, 1H, cod-C*H*), 1.88 (m, 1H, cod-CH_2), 1.50 (m, 4H, cod-CH_2), 1.32 (m, 1H, cod-CH_2), 1.21 (m, 1H, cod-CH_2), 1.13 (m, 1H, cod-CH_2) ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): δ = 155.9 (*C*2'), 150.0 (d, $^2J_{CP}$ = 5.4 Hz, *C*12), 149.8 (d, $^2J_{CP}$ = 12.6 Hz, *C*12'), 140.5 (d, $^2J_{CP}$ = 24.6 Hz, *C*1), 135.1 (*C*9), 134.5 (*C*9'), 133.3 (d, $^1J_{CP}$ = 11.2 Hz, *C*2), 132.4 (m, *C*19/*C*19'), 131.8 (*C*20), 131.5 (*C*4'), 131.4 (*C*20'), 130.2 (*C*14), 129.9 (*C*14'), 129.8 (*C*8'), 129.4 (*C*10'), 128.5 (*C*15'), 128.4 (*C*15), 128.2 (*C*5), 127.8 (*C*6), 127.2 (*C*5'), 126.8 (*C*18'), 126.7 (*C*4/*C*18), 126.6 (*C*7), 126.5 (*C*7'/*C*8), 126.3 (*C*17), 126.2 (*C*17'), 125.5 (d, $^2J_{CP}$ = 2.5 Hz, *C*3), 125.4 (*C*16), 125.2 (*C*16'), 124.3 (d, $^3J_{CP}$ = 3.6 Hz, *C*11), 124.3 (*C*6'), 124.1 (d, $^3J_{CP}$ = 2.5 Hz, *C*13), 123.4 (d, $^3J_{CP}$ = 2.5 Hz, *C*11'), 121.7 (*C*13'), 119.9 (d, $^3J_{CP}$ = 7.6 Hz, *C*1'), 112.9 (*C*3'), 111.7 (dd, *J* = 15.9 Hz, *J* = 6.5 Hz, cod-*C*H), 110.1 (dd, *J* = 14.4 Hz, *J* = 5.4 Hz, cod-*C*H), 73.3 (d, *J* = 13.8 Hz, cod-*C*H), 66.8 (d, *J* = 13.6 Hz, cod-*C*H), 56.1 (O*C*H_3), 33.0 (d, *J* = 2.9 Hz, cod-*C*H_2), 31.6 (d, *J* = 2.0 Hz, cod-*C*H_2), 27.2 (m, cod-*C*H_2) ppm. The resonance for *C*10 was obscured. **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2): δ = 162.9 (d, $^1J_{PRh}$ = 223 Hz) ppm. **IR** (neat): $\tilde{\nu}$ = 3050.3 (w), 2971.5 (w), 1620.3 (w), 1589.3 (m), 1508.5 (m), 1462.2 (m), 1430.9 (w), 1326.8 (w), 1249.5 (w), 1224.1 (s), 1152.6 (w), 1073.9 (m), 944.9 (s), 868.8 (w), 807.3 (s), 746.6 (s), 695.6 (w), 673.9 (w), 636.5 (m), 598.5 (w), 559.3 (w) cm^{-1}. **HRMS** (NSI$^+$, MeOH): Found: *m*/*z* = 867.1257. Calculated for [M + Na]$^+$: *m*/*z* = 867.1273.

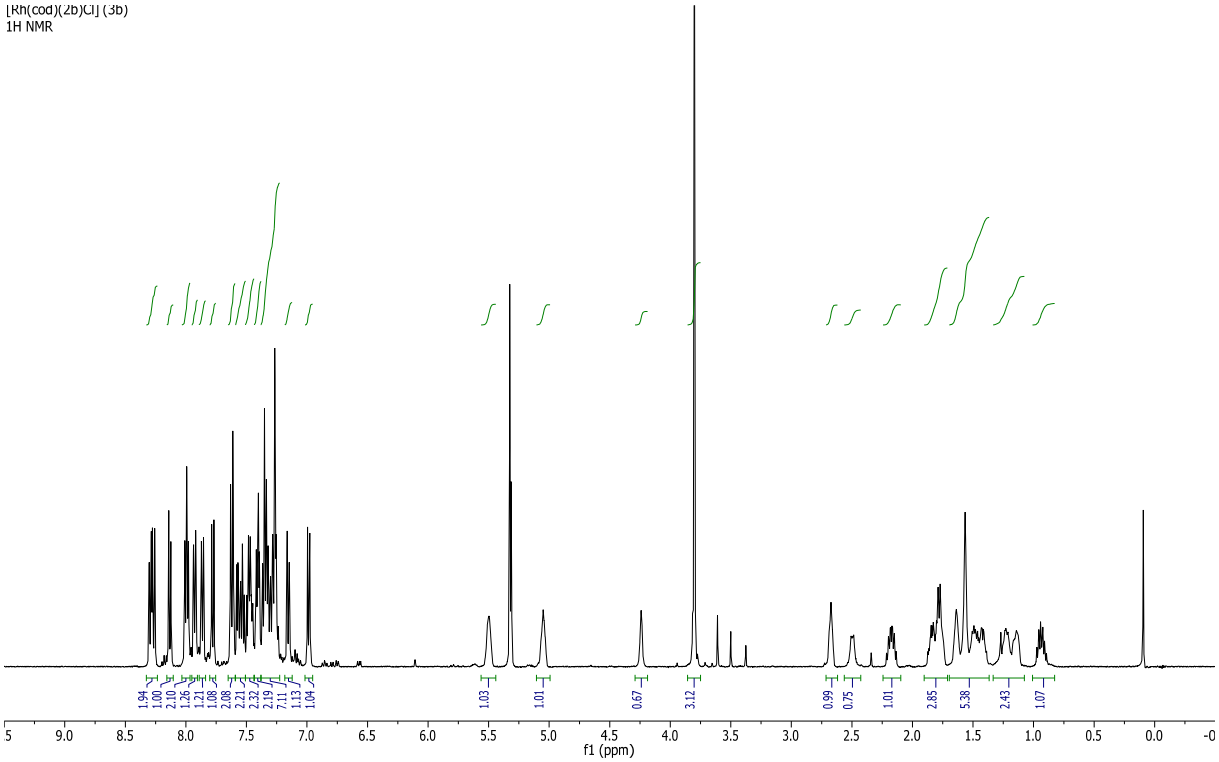


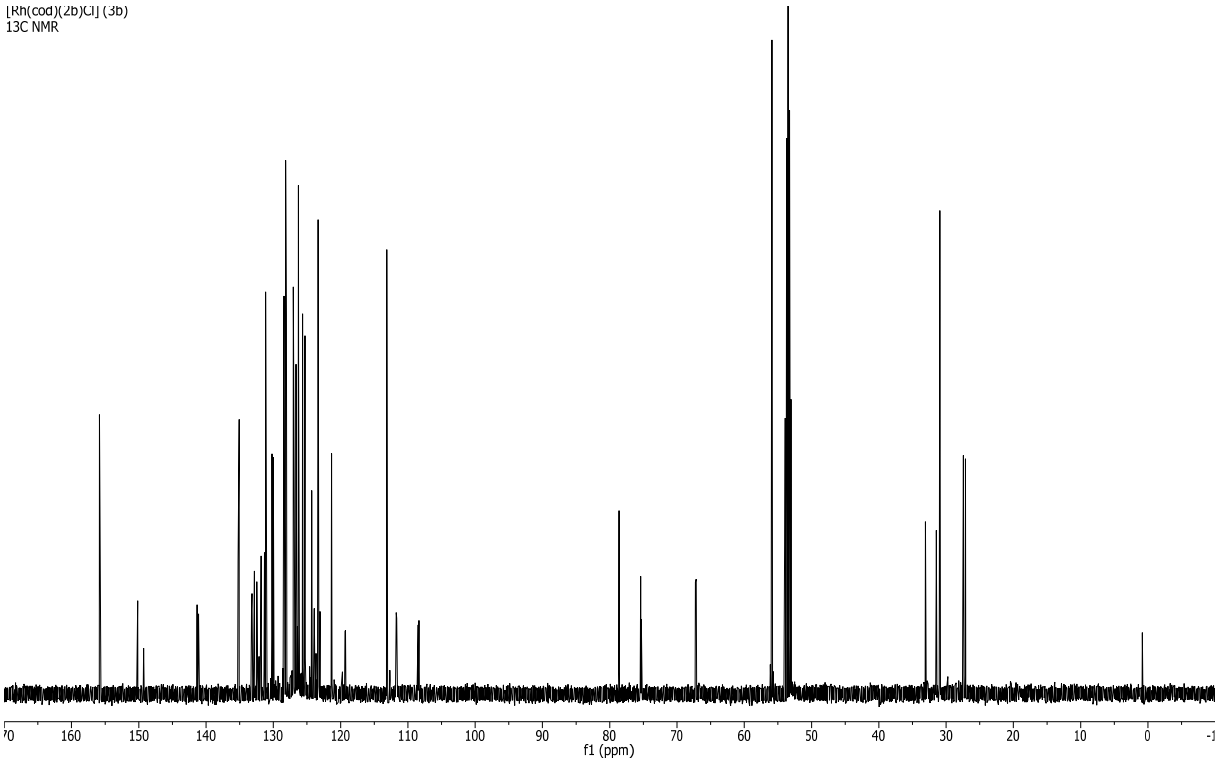


2.4 [RhCl(**2b**)(η⁴-cod)] (**3b**)

2b (21.0 mg, 35.0 µmol) and [Rh(η^4-cod)Cl]$_2$ (8.6 mg, 17.5 µmol) were dissolved in dichloromethane (1 mL) and stirred for 30 minutes. The solution was filtered and layered with diethyl ether to precipitate the product as a yellow solid overnight.

^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.29 (d, $^3J_{HH}$ = 8.8 Hz, 1H, *H*13'), 8.27 (d, $^3J_{HH}$ = 9.2 Hz, 1H, *H*4'), 8.13 (d, $^3J_{HH}$ = 8.8 Hz, 1H, *H*14'), 8.00 (d, $^3J_{HH}$ = 8.5 Hz, 1H, *H*15'), 7.99 (d, $^3J_{HH}$ = 8.5 Hz, 1H, *H*5'), 7.93 (d, $^3J_{HH}$ = 8.2 Hz, 1H, *H*15), 7.86 (d, $^3J_{HH}$ = 8.2 Hz, 1H, *H*5), 7.78 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *H*14), 7.62 (m, 2H, *H*3'/*H*4), 7.58-7.52 (m, 2H, *H*3/*H*6), 7.50-7.44 (m, 2H, *H*16/*H*16'), 7.42-7.39 (m, 2H, *H*18/*H*7'), 7.37-7.23 (m, 6H, *H*6'/*H*8'/*H*17/*H*7/*H*17'/*H*18'), 7.15 (d, $^3J_{HH}$ = 8.5 Hz, 1H, *H*8), 6.99 (d, $^3J_{HH}$ = 8.8 Hz, 1H, *H*13), 5.50 (br s, 1H, cod-C*H*), 5.05 (br s, 1H, cod-C*H*), 3.80 (s, 3H, OCH_3), 2.67 (br s, 1H, cod-C*H*), 2.17 (m, 1H, cod-CH_2), 1.83 (m, 1H, cod-CH_2), 1.78 (m, 1H, cod-CH_2), 1.63 (br s, 1H, cod-C*H*), 1.49 (m, 1H, cod-CH_2), 1.42 (m, 1H, cod-CH_2), 1.22 (m, 1H, cod-CH_2), 1.14 (m, 1H, cod-CH_2), 0.94 (m, 1H, cod-CH_2) ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): δ = 155.9 (*C*2'), 150.2 (d, $^2J_{CP}$ = 5.6 Hz, *C*12'), 149.3 (d, $^2J_{CP}$ = 12.6 Hz, *C*12), 141.2 (d, $^2J_{CP}$ = 26.4 Hz, *C*1), 135.2 (d, $^1J_{CP}$ = 1.4 Hz, *C*2), 135.1 (*C*9'), 133.2 (d, $^3J_{CP}$ = 11.2 Hz, *C*9), 132.8 (d, $^4J_{CP}$ = 1.4 Hz, *C*19), 132.5 (d, $^4J_{CP}$ = 2.1 Hz, *C*19'), 131.8 (d, $^5J_{CP}$ = 1.4 Hz, *C*20'), 131.3 (d, $^5J_{CP}$ = 0.9 Hz, *C*20), 131.1 (*C*4'), 130.2 (d, $^4J_{CP}$ = 1.4 Hz, *C*14'), 130.0 (d, $^4J_{CP}$ = 1.1 Hz, *C*14), 128.5 (*C*15'), 128.4 (*C*15), 128.2 (*C*5), 128.1 (*C*5'), 128.1 (*C*6), 127.0 (*C*18/*C*8), 126.9 (*C*4), 126.7 (*C*7), 126.6 (*C*17'), 126.4 (*C*17), 126.3 (*C*18'), 126.2 (*C*7'), 125.7 (*C*8'), 125.4 (*C*16'), 125.3 (*C*3), 125.3 (*C*16), 124.3 (d, $^3J_{CP}$ = 2.1 Hz, *C*13'), 123.9 (d, $^3J_{CP}$ = 4.0 Hz, *C*11'), 123.3 (*C*6'), 123.1 (d, $^3J_{CP}$ = 2.5 Hz, *C*11), 121.4 (*C*13), 119.3 (d, $^3J_{CP}$ = 8.3 Hz, *C*1'), 113.2 (*C*3'), 111.7 (dd, *J* = 15.3 Hz, *J* = 6.7 Hz, cod-*C*H), 108.4 (dd, *J* = 14.9 Hz, *J* = 5.5 Hz, cod-*C*H), 75.4 (d, *J* = 13.6 Hz, cod-*C*H), 67.2 (d, *J* = 13.0 Hz, cod-*C*H), 55.9 (O*C*H_3), 33.1 (d, *J* = 2.5 Hz, cod-*C*H_2), 31.5 (d, *J* = 2.4 Hz, cod-*C*H_2), 27.4 (d, *J* = 1.5 Hz, cod-*C*H_2), 27.1 (d, *J* = 1.9 Hz, cod-*C*H_2) ppm; resonances for *C*10 and *C*10' were obscured. **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2): δ = 161.5 (d, $^1J_{PRh}$ = 224 Hz) ppm. **HRMS** (NSI$^+$, MeCN): Found: *m*/*z* = 809.1672. Calculated for [M – Cl]$^+$: *m*/*z* = 809.1686.





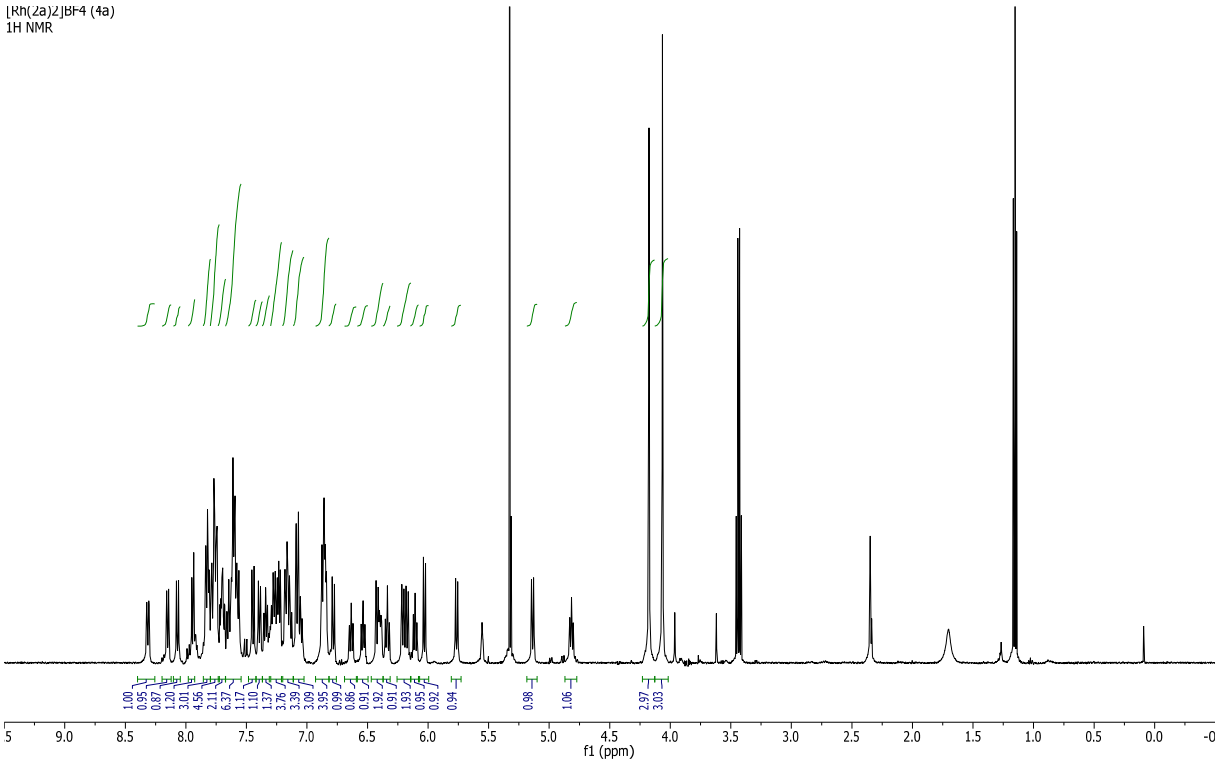
2.5 [Rh(**2a**)$_2$]BF$_4$ (**4a**)

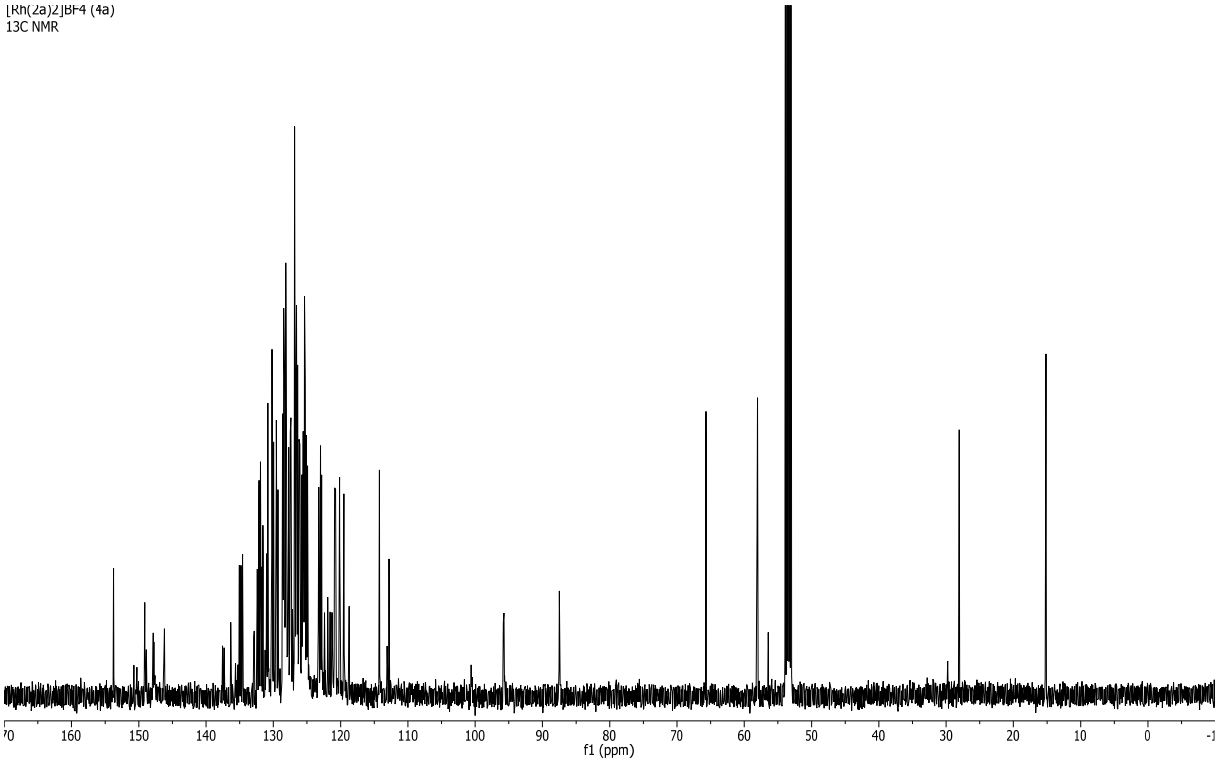
Method A: **2a** (30 mg, 50 µmol) and [Rh(η^4-cod)$_2$]BF$_4$ (10 mg, 25 µmol) were dissolved in dichloromethane (1 mL) and stirred for 30 minutes. The solution was filtered and layered with diethyl ether to precipitate the product as a yellow solid overnight.

Method B: **3a** (21 mg, 25 µmol) was dissolved in dichloromethane (1 mL), AgBF$_4$ (4.8 mg, 25 µmol) and **2a** (15 mg, 25 µmol) were then added and stirred for 30 minutes. The solution was filtered and concentrated *in vacuo*. The crude product was washed with diethyl ether to give the product as a yellow solid.

^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.31 (d, $^3J_{HH}$ = 8.3 Hz, 1H, *H*4^A), 8.15 (d, $^3J_{HH}$ = 8.3 Hz, 1H, *H*5^A), 8.07 (d, $^3J_{HH}$ = 8.8 Hz, 1H, *H*14^B), 7.94 (d, $^3J_{HH}$ = 8.3 Hz, 1H, *H*5^B), 7.83 (m, 1H, *H*15^B), 7.83 (m, 1H, *H*8^B), 7.80 (m, 1H, *H*6'^{B}), 7.78 (m, 1H, *H*15'^{B}), 7.76 (m, 1H, *H*15^A), 7.75 (m, 1H, *H*4'^{A}), 7.75 (m, 1H, *H*14^A), 7.70 (m, 1H, *H*7'^{B}), 7.69 (m, 1H, *H*6^B), 7.64 (m, 1H, *H*6^A), 7.61 (m, 1H, *H*4^B), 7.61 (m, 1H, *H*7^B), 7.60 (m, 1H, *H*3'^{A}), 7.58 (m, 1H, *H*3^A), 7.57 (m, 1H, *H*15'^{A}), 7.45 (d, $^3J_{HH}$ = 8.9 Hz, 1H, *H*14'^{B}), 7.39 (d, $^3J_{HH}$ = 8.3 Hz, 1H, *H*5'^{B}), 7.34 (pt, J_{HH} = 7.3 Hz, 1H, *H*16'^{B}), 7.28 (m, 1H, *H*7^A), 7.24 (m, 1H, *H*16'^{A}), 7.23 (m, 1H, *H*3'^{B}), 7.17 (m, 1H, *H*16^B), 7.17 (m, 1H, *H*5'^{A}), 7.15 (m, 1H, *H*16^A), 7.08 (m, 1H, *H*14'^{A}), 7.08 (m, 1H, *H*8^A), 7.06 (m, 1H, *H*17'^{B}), 6.87 (m, 1H, *H*18'^{B}), 6.86 (m, 1H, *H*17'^{A}), 6.85 (m, 1H, *H*8'^{B}), 6.85 (m, 1H, *H*13^B), 6.78 (d, $^3J_{HH}$ = 8.6 Hz, 1H, *H*13^A), 6.63 (pt, J_{HH} = 7.9 Hz, 1H, *H*17^B), 6.54 (pt, J_{HH} = 7.9 Hz, 1H, *H*17^A), 6.42 (d, $^3J_{HH}$ = 8.6 Hz, 1H, *H*18^B), 6.39 (br d, $^3J_{HH}$ = 8.0 Hz, 1H, *H*4'^{B}), 6.34 (pt, *J* = 8.1 Hz, 1H, *H*3^B), 6.21 (d, $^3J_{HH}$ = 8.6 Hz, 1H, *H*18^A), 6.17 (d, $^3J_{HH}$ = 8.6 Hz, 1H, *H*18'^{A}), 6.17 (pt, J_{HH} = 8.6 Hz, 1H, *H*6'^{A}), 6.03 (d, $^3J_{HH}$ = 8.9 Hz, 1H, *H*13'^{B}), 5.76 (d, $^3J_{HH}$ = 8.9 Hz, 1H, *H*13'^{A}), 5.14 (d, $^3J_{HH}$ = 8.6 Hz, 1H, *H*8'^{A}), 4.82 (pt, J_{HH} = 7.7 Hz, 1H, *H*7'^{A}), 4.18 (s, 3H, OC*H*$_3^B$), 4.07 (s, 3H, OC*H*$_3^A$) ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): δ = 153.8 (*C*2'^{A}), 150.5 (d, $^1J_{CP}$ = 53.0 Hz, *C*2^B), 149.1 (*C*2'^{B}), 148.9 (d, $^2J_{CP}$ = 15.5 Hz, *C*12'^{B}), 147.9 (d, $^2J_{CP}$ = 7.6 Hz, *C*12^B), 147.7 (d, $^2J_{CP}$ 13.2 Hz, *C*12'^{A}), 146.2 (d, $^2J_{CP}$ = 6.7 Hz, *C*12^A), 137.4 (d, $^2J_{CP}$ = 33.7 Hz, *C*1^B), 136.4 (*C*2^A), 135.6 (*C*1^A), 135.3 (*C*9^B), 135.0 (*C*10^B), 134.8 (*C*10^A), 134.6 (*C*9'^{A}), 132.8 (*C*9^A), 132.4 (*C*19^B/*C*19^A), 132.1 (*C*7'^{B}/*C*20^B), 131.9 (*C*19'^{B}), 131.7 (*C*19'^{A}), 131.5 (*C*20^A), 131.0 (*C*20'^{B}), 130.8 (*C*14^B/*C*20'^{A}), 130.2 (*C*4^B/*C*14'^{B}), 129.9 (*C*14^A), 129.6 (*C*6^B), 129.3 (*C*14'^{A}), 128.7 (*C*7^B), 128.5 (*C*5^B/*C*6^A), 128.4 (*C*15^B), 128.3 (*C*5^A), 128.2 (*C*6'^{B}/*C*15'^{B}/*C*15^A/*C*10'^{A}), 128.1 (*C*4'^{A}), 127.9 (d, *J* = 13.5 Hz, *C*4^A), 127.7 (*C*15'^{A}), 127.5 (*C*7^A), 127.4 (*C*8^A), 126.9 (*C*18'^{B}/*C*18^B), 126.6 (*C*18'^{A}/*C*3^A), 126.6 (*C*5'^{B}), 126.5 (*C*18^A), 126.4 (*C*8^B), 126.2 (*C*17'^{B}), 126.1 (*C*5'^{A}), 125.8 (*C*17^B), 125.6 (*C*17^A), 125.5 (*C*17'^{A}), 125.4 (*C*16^B), 125.3 (*C*16'^{B}/*C*16^A/*C*7'^{A}), 125.1 (*C*3^B), 124.9 (*C*16'^{A}), 123.3 (*C*8'^{B}), 123.0 (*C*6'^{A}), 122.8 (*C*8'^{A}), 122.4 (*C*11^A), 121.9 (*C*1'^{A}), 121.6 (*C*11^B), 121.3 (*C*11'^{A}), 120.9 (*C*13^B), 120.7 (*C*13^A), 120.1 (*C*13'^{B}), 120.1 (*C*11'^{B}), 119.5 (*C*13'^{A}), 118.7 (*C*9'^{B}) 114.2 (*C*3'^{A}), 112.8 (*C*10'^{B}), 100.5 (d, *J* = 14.3 Hz, *C*1'^{B}), 95.8 (d, *J* = 11.3 Hz, *C*4'^{B}), 87.5 (*C*3'^{B}), 58.1 (OCH$_3^B$), 58.1 (OCH$_3^A$) ppm. **^{31}P NMR** (202 MHz, CD_2Cl_2): δ = 181.3 (ddd, $^1J_{PRh}$ = 290 Hz, $^2J_{PP}$ = 22.3 Hz, $^3J_{PH}$ = 16.6 Hz, *P*^{A}), 179.6 (ddd, $^1J_{PRh}$ = 300 Hz, $^2J_{PP}$ = 22.3 Hz, $^3J_{PH}$ = 6.6 Hz, *P*^{B}) ppm. **IR** (neat): $\tilde{\nu}$ = 3058.4 (w), 1621.3

(w), 1590.9 (w), 1506.2 (m), 1463.6 (m), 1324.4 (w), 1277.9 (w), 1222.9 (s), 1154.4 (w), 1069.0 (s), 956.8 (s), 837.3 (s), 810.1 (m), 746.4 (m), 696.2 (w) cm^{-1}. **HRMS** (NSI^+, MeOH): Found: m/z = 1299.2432. Calculated for $[M - BF_4]^+$: m/z = 1299.2445.

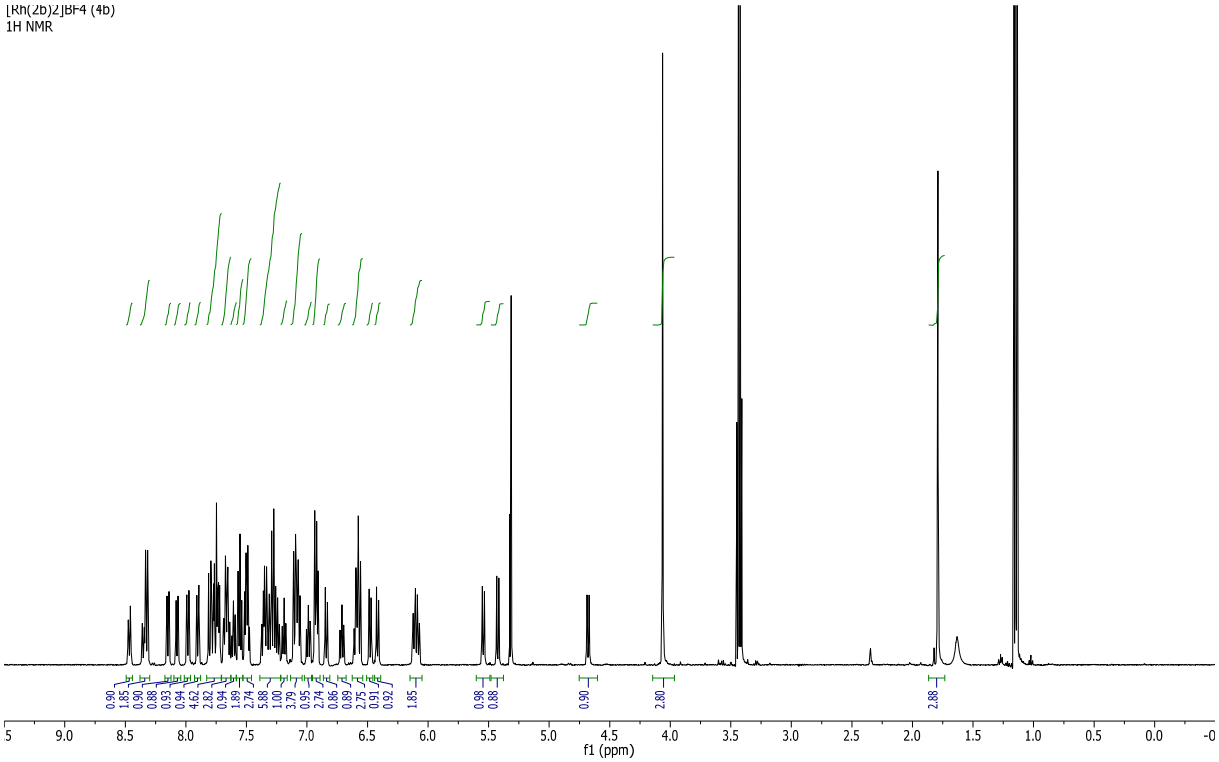


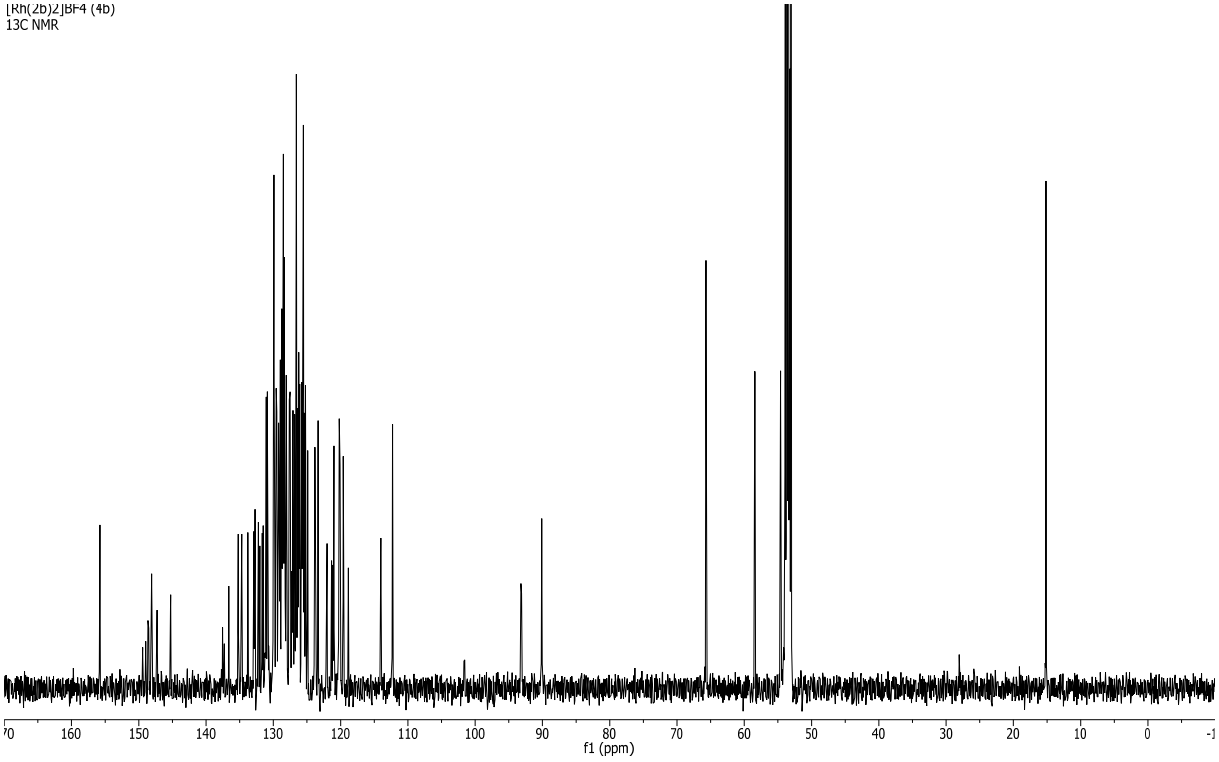


2.6 [Rh(**2b**)$_2$]BF$_4$ (**4b**)

The same procedures as described for the synthesis of **4a** were utilised using **2b** as ligand. Yellow crystals suitable for X-ray analysis were formed overnight from slow diffusion of diethyl ether into a dichloromethane solution.

^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.47 (dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HP}$ = 1.1 Hz, 1H, $H4^A$), 8.34 (dd, $^3J_{HP}$ = 13.7 Hz, $^3J_{HH}$ = 8.6 Hz, 1H, $H3^A$), 8.32 (d, $^3J_{HH}$ = 8.6 Hz, 1H, $H14'^B$), 8.15 (d, $^3J_{HH}$ = 8.2 Hz, 1H, $H5^A$), 8.07 (d, $^3J_{HH}$ = 8.2 Hz, 1H, $H5'^A$), 7.98 (d, $^3J_{HH}$ = 8.2 Hz, 1H, $H15'^B$), 7.90 (d, $^3J_{HH}$ = 8.2 Hz, 1H, $H5^B$), 7.80 (d, $^3J_{HH}$ = 9.1 Hz, 1H, $H4'^A$), 7.78 (d, $^3J_{HH}$ = 8.2 Hz, 1H, $H15^B$), 7.75 (m, 1H, $H13'^B$), 7.74 (m, 1H, $H15'^A$), 7.73 (m, 1H, $H8^B$), 7.67 (m, 3H, $H6^A$/$H6^B$/$H7'^B$), 7.61 (m, 1H, $H7'^A$), 7.55 (m, 2H, $H6'^A$/$H7^B$), 7.51 (m, 1H, $H15^A$), 7.50 (m, 1H, $H4^B$), 7.49 (m, 1H, $H6'^B$), 7.36 (m, 1H, $H16^B$), 7.34 (m, 1H, $H14^B$), 7.31 (m, 1H, $H16'^B$), 7.28 (m, 1H, $H14'^A$), 7.27 (m, 1H, $H7^A$), 7.24 (m, 1H, $H16'^A$), 7.19 (pt, J_{HH} = 7.5 Hz, 1H, $H16^A$), 7.10 (m, 1H, $H3'^B$), 7.09 (m, 1H, $H17^B$), 7.08 (m, 1H, $H8'^A$), 7.06 (m, 1H, $H8^A$), 6.99 (ddd, $^3J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, $H17^A$), 6.93 (m, 2H, $H8'^B$/$H18^B$), 6.92 (d, $^3J_{HH}$ = 8.2 Hz, 1H, $H14^A$), 6.84 (d, $^3J_{HH}$ = 8.6 Hz, 1H, $H18^A$), 6.71 (ddd, $^3J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, $H17'^B$), 6.60 (m, 1H, $H4'^B$), 6.59 (m, 1H, $H17'^A$), 6.57 (m, 1H, $H3'^A$), 6.48 (d, $^3J_{HH}$ = 8.6 Hz, 1H, $H18'^B$), 6.42 (d, $^3J_{HH}$ = 8.6 Hz, 1H, $H18'^A$), 6.11 (d, $^3J_{HH}$ = 8.8 Hz, 1H, $H5'^B$), 6.09 (dd, $^3J_{HH}$ = 8.3 Hz, $^3J_{HP}$ = 8.3 Hz, 1H, $H3^B$), 5.54 (d, $^3J_{HH}$ = 8.6 Hz, 1H, $H13^A$), 5.42 (d, $^3J_{HH}$ = 8.6 Hz, 1H, $H13^B$), 4.68 (d, $^3J_{HH}$ = 8.6 Hz, 1H, $H13'^A$), 4.06 (s, 3H, OCH_3^B), 1.79 (s, 3H, OCH_3^A) ppm. **^{11}B NMR** (128 MHz, CD_2Cl_2): δ = –2.0 (s) ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): δ = 155.8 ($C2'^A$), 149.2 (d, $^1J_{CP}$ = 56.2 Hz, $C2^B$), 148.6 (d, $^2J_{CP}$ = 12.5 Hz, $C12^B$), 148.1 (m, $C12^A$/$C12'^B$), 147.3 (d, $^2J_{CP}$ = 5.7 Hz, $C12'^A$), 145.3 ($C2'^B$), 137.4 (d, $^2J_{CP}$ = 32.0 Hz, $C1^B$), 136.6 ($C1^A$), 135.2 ($C10^B$), 134.9 (d, $^1J_{CP}$ = 44.1 Hz, $C2^A$), 134.7 ($C10^A$), 133.8 ($C9'^A$), 132.9 ($C19'^B$), 132.8 ($C9^A$), 132.7 ($C19'^A$), 132.2 ($C20'^B$), 132.0 ($C19^B$), 131.7 ($C19^A$), 131.5 ($C20'^A$), 131.1 ($C20^B$), 131.0 ($C14'^B$), 130.9 ($C7'^B$), 130.8 ($C20^A$), 130.7 ($C9^B$), 129.9 ($C4'^A$/$C4^B$/$C16^A$), 129.6 ($C6^B$), 129.5 ($C6'^B$), 129.2 ($C14'^A$), 129.1 ($C14^A$), 129.0 ($C5'^A$), 128.7 ($C6^A$/$C10'^A$), 128.6 ($C7^B$), 128.5 ($C4^A$, $C15'^B$, $C5^B$), 128.4 ($C5^A$), 128.3 ($C15^B$), 128.1 ($C15'^A$), 128.0 ($C15^A$), 127.6 ($C7^A$), 127.5 ($C8^A$), 127.3 (d, $^2J_{CP}$ = 26.0 Hz, $C3^A$), 127.1 ($C7'^A$), 126.8 ($C18^A$), 126.6 ($C18'^B$, $C18'^A$), 126.4 ($C18^B$), 126.2 ($C17^A$), 126.2 ($C17'^B$), 126.1 ($C8^B$), 125.8 ($C17'^A$), 125.7 ($C17^B$), 125.5 ($C5'^B$, $C14^B$, $C16'^A$, $C16'^B$), 125.2 ($C3^B$), 125.1 ($C8'^A$), 124.9 ($C16^B$), 123.8 ($C8'^B$), 123.7 ($C11'^A$), 123.3 ($C6'^A$), 122.0 ($C9'^B$), 121.3 ($C11'^B$), 121.1 ($C11^A$), 121.0 ($C13'^B$), 120.2 ($C13'^A$, $C11^B$), 120.1 ($C13^B$), 119.6 ($C13^A$), 118.9 ($C1'^A$), 114.0 ($C10'^B$), 112.3 ($C3'^A$), 101.6 (d, J = 13.1 Hz, $C1'^B$), 93.1 (d, J = 12.3 Hz, $C4'^B$), 90.1 ($C3'^B$), 58.4 (OCH_3^B), 54.6 (OCH_3^A) ppm. **^{19}F NMR** (376 MHz, CD_2Cl_2): δ = –152.9 (s) ppm. **^{31}P NMR** (202 MHz, CD_2Cl_2): δ = 183.5 (ddd, $^1J_{PRh}$ = 277 Hz, $^2J_{PP}$ = 23.5 Hz, $^3J_{PH}$ = 13.7 Hz, P^A), 178.4 (ddd, $^1J_{PRh}$ = 309 Hz, $^2J_{PP}$ = 23.5 Hz, $^3J_{PH}$ = 8.3 Hz, P^B) ppm. **IR** (neat): $\tilde{\nu}$ = 3063.2 (w), 1621.2 (w), 1591.7 (w), 1506.3 (m), 1463.7 (m), 1324.2 (w), 1274.0 (m), 1223.7 (s), 1153.8 (w), 1068.9 (s), 956.1 (s), 837.0 (w), 810.1 (s), 746.6 (s), 696.3 (m) cm^{-1}. **HRMS** (NSI$^+$, MeOH): Found: m/z = 1299.2440. Calculated for $[M - BF_4]^+$: m/z = 1299.2445.



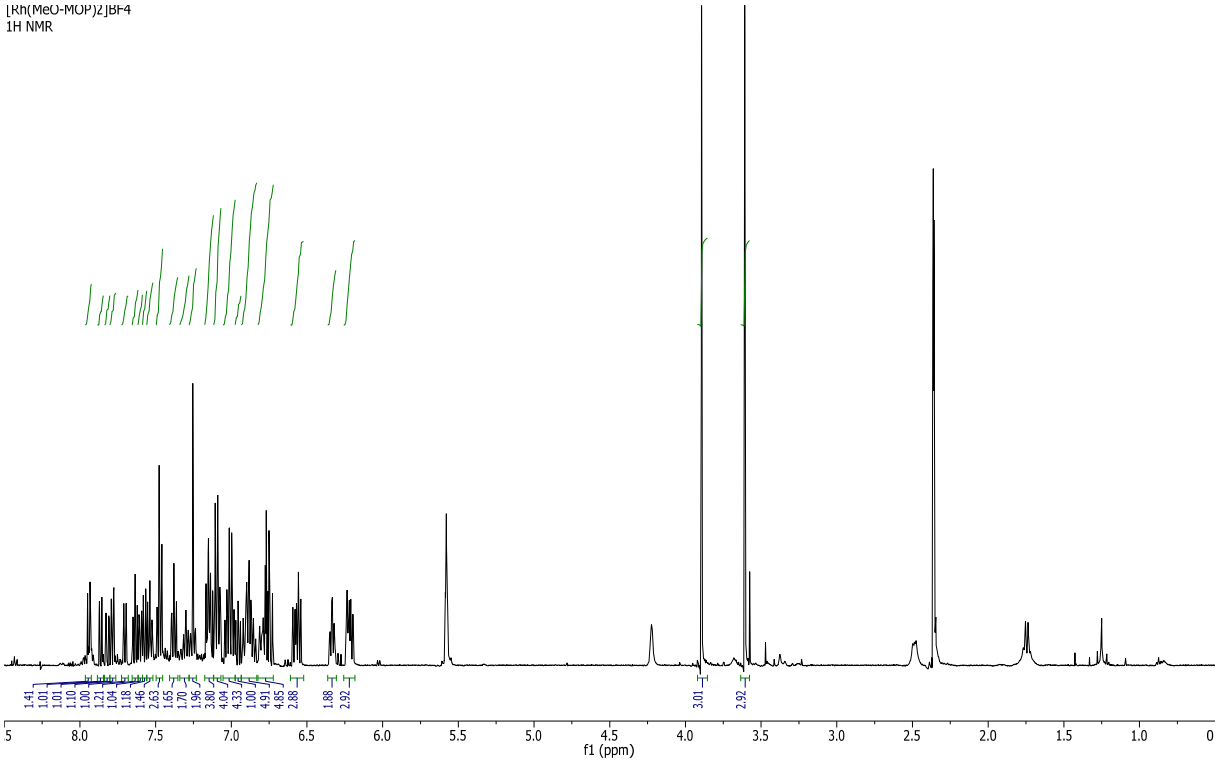


2.7 $[Rh(OMe\text{-}MOP)_2]BF_4$ (**5**)

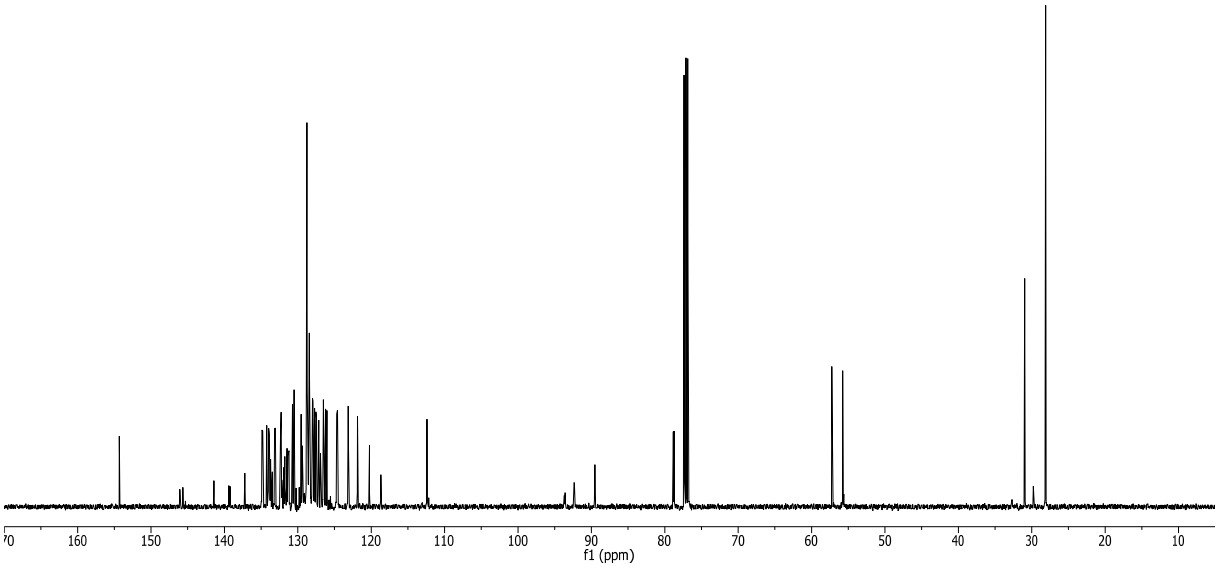
The same procedures as described for the synthesis of **4a** were utilised using OMe-MOP as ligand. The solution was filtered and layered with hexane to precipitate the product as an orange solid overnight.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.94 (d, $^3J_{HH}$ = 8.2 Hz, 1H, $H5^B$), 7.86 (d, $^3J_{HH}$ = 8.0 Hz, 1H, $H5^A$), 7.82 (dd, $^3J_{HH}$ = 9.0 Hz, $^4J_{HP}$ = 1.3 Hz, 1H, $H4^B$), 7.78 (dd, $^3J_{HH}$ = 8.3 Hz, $^5J_{HP}$ = 0.8 Hz, 1H, $H8^B$), 7.70 (d, $^3J_{HH}$ = 7.5 Hz, 1H, $H3'^B$), 7.64 (ddd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, $H6^B$), 7.60 (d, $^3J_{HH}$ = 8.7 Hz, 1H, $H4^A$), 7.57 (d, $^3J_{HH}$ = 8.2 Hz, 1H, $H5'^A$), 7.54 (ddd, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, $H7^B$), 7.49-7.46 (m, 2H, $H6^A/H4'^A$), 7.38 (ddd, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, $H7'^B$), 7.30 (m, 1H, $H14'^B$), 7.25 (m, 1H, $H14^B$), 7.17-7.12 (m, 3H, $H6'^B/H6'^A/H7^A$), 7.11-7.07 (m, 4H, $H3^B/H13'^B/H14'^A$), 7.04-6.98 (m, 4H, $H3^A/H5'^B/H13^B$), 6.96 (ddd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, $H7'^A$), 6.92-6.84 (m, 5H, $H12'^B/H13'^A/H14^A$), 6.81-6.73 (m, 5H, $H12'^A/H8'^B/H3'^A/H8^A$), 6.60-6.54 (m, 3H, $H12^B/H8'^A$), 6.33 (m, 2H, $H13^A$), 6.24-6.19 (m, 3H, $H4'^B/H12^A$), 3.89 (s, 3H, OCH_3^B), 3.61 (s, 3H, OCH_3^A) ppm. **^{11}B NMR** (128 MHz, CD_2Cl_2): δ = –1.6 (s) ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): δ = 154.3 ($C2'^A$), 145.9 (d, $^1J_{CP}$ = 50.3 Hz, $C2^B$), 141.4 ($C2'^B$), 139.3 (d, $^2J_{CP}$ = 21.6 Hz, $C1^B$), 137.2 ($C1^A$), 134.9 (d, $^2J_{CP}$ = 13.1 Hz, $C12'^A$), 134.2 ($C9^B/C9'^A$), 133.9 (d, $^2J_{CP}$ = 13.1 Hz, $C12^A$), 133.7 ($C10^A$), 133.5 ($C9^A$), 133.1 (d, $^2J_{CP}$ = 12.2 Hz, $C12'^B$), 132.3 (d, $^2J_{CP}$ = 11.7 Hz, $C12^B$), 132.3 ($C11^B$), 131.9 ($C11^A$), 131.4 (m, $C3^A$), 131.3 ($C14'^B$), 130.7 ($C4'^A$), 130.6 ($C4^B/C14^B/C14'^A$), 130.0 (d, $^1J_{CP}$ = 49.8 Hz, $C11'^A$), 129.6 ($C7'^B$), 129.4 ($C14^A$), 128.8 ($C6^B$), 128.7 (d, $^3J_{CP}$ = 3.7 Hz, $C13'^B$), 128.6 (d, $^3J_{CP}$ = 10.8 Hz, $C13^B$), 128.6 ($C10'^A$), 128.4 ($C5^B/C7^B$), 128.3 ($C6'^A$), 128.0 ($C5^A/C3^B$), 127.9 ($C5'^A$), 127.7 ($C6^A$), 127.5 ($C13'^A$), 127.1 ($C7^A$), 126.9 (d, $^3J_{CP}$ = 14.0 Hz, $C4^A$), 126.5 ($C8^A$), 126.5 (d, $^3J_{CP}$ = 3.4 Hz, $C13^A$), 126.2 ($C8^B$), 126.0 ($C7'^A$), 124.7 ($C5'^B$), 124.6 ($C8'^A$), 123.2 ($C6'^B$), 123.1 ($C9'^B$), 121.9 ($C8'^B$), 120.2 ($C10'^B$), 118.7 ($C1'^A$), 112.4 ($C3'^A$), 93.6 (d, J = 13.1 Hz, $C1'^B$), 92.3 (d, J = 9.2 Hz, $C4'^B$), 89.5 ($C3'^B$), 57.2 (OCH_3^B), 55.8 (OCH_3^A) ppm; resonances for $C2^A$, $C10^B$ and $C11'^B$ were obscured. **^{19}F NMR** (376 MHz, CD_2Cl_2): δ = –153.3 (s) ppm. **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$): δ = 50.0 (dd, $^1J_{PRh}$ = 217 Hz, $^2J_{PP}$ = 32.1 Hz, P^B), 37.2 (dd, $^1J_{PRh}$ = 197 Hz, $^2J_{PP}$ = 32.1 Hz, P^A) ppm.

[Rh(MeO-MOP)2]BF4
1H NMR



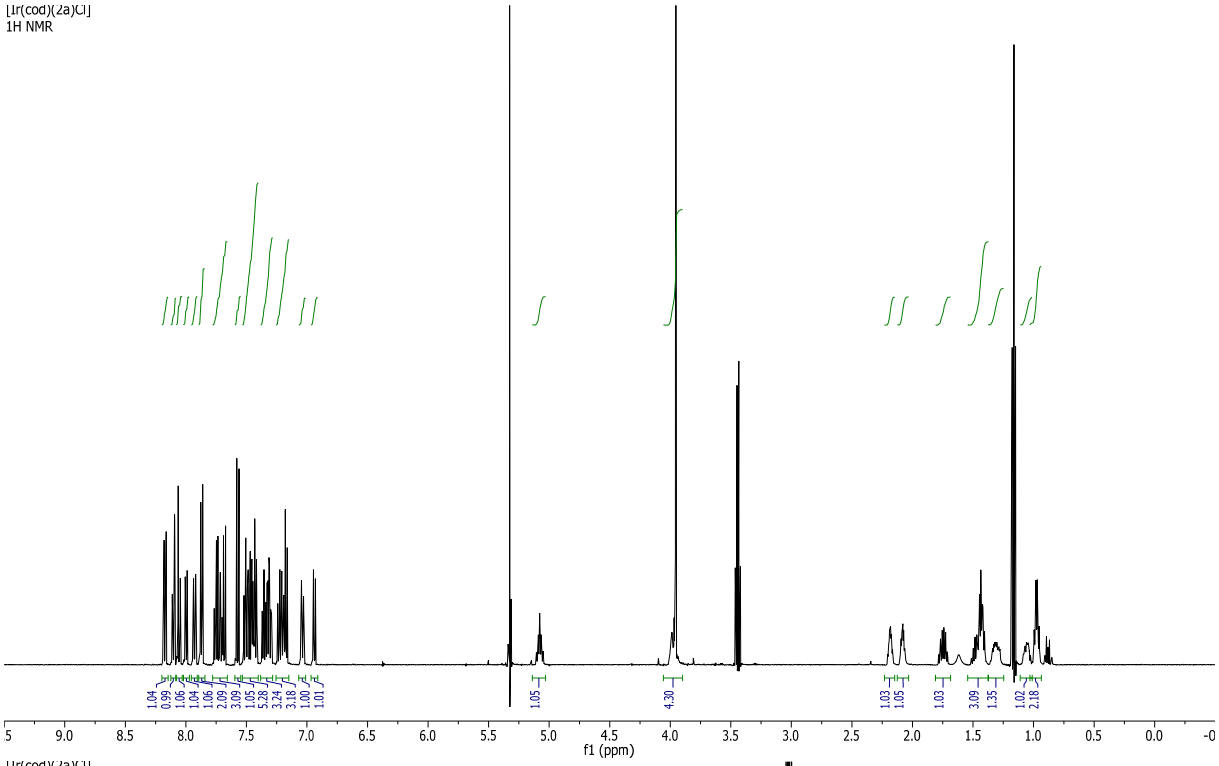
[Rh(MeO-MOP)2]BF4
13C NMR

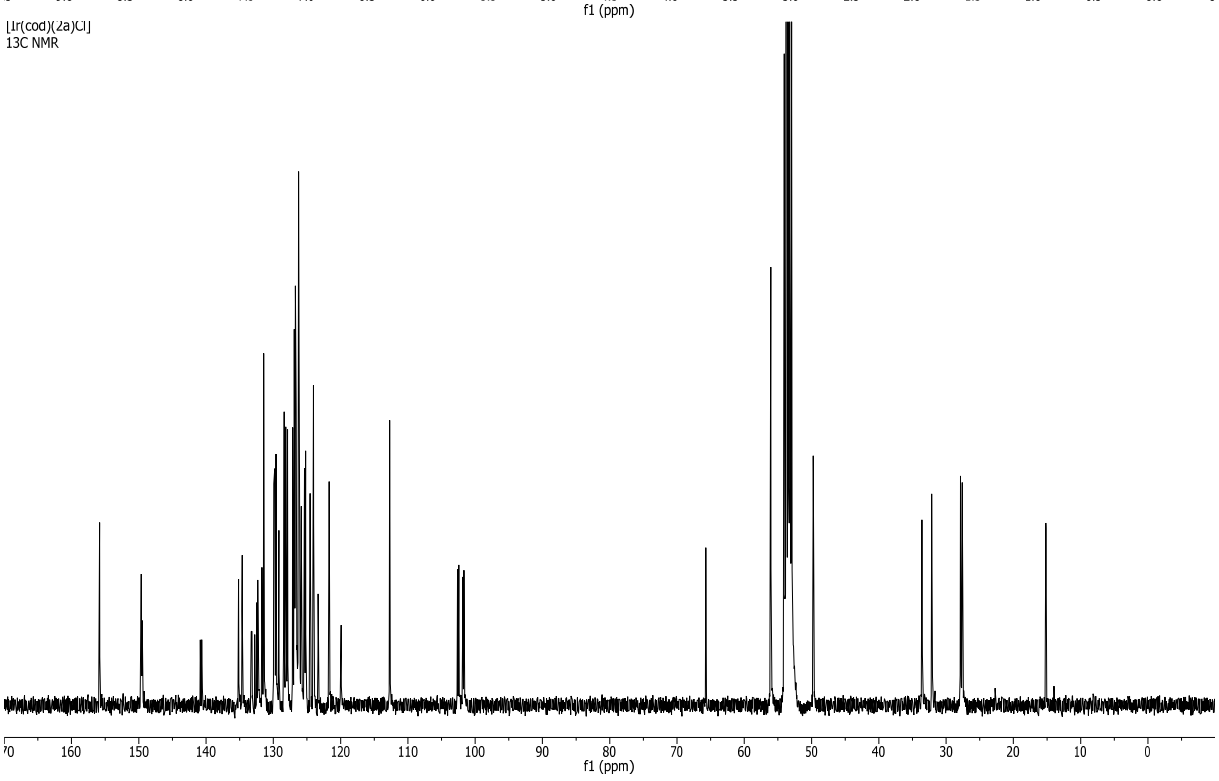


2.8 [IrCl(**2a**)(η⁴-cod)] (**6a**)

2a (21.0 mg, 35.0 µmol) and $[Ir(\eta^4\text{-cod})Cl]_2$ (11.8 mg, 17.5 µmol) were dissolved in dichloromethane (1 mL) and stirred for 30 minutes. The solution was filtered and layered with diethyl ether. Red crystals suitable for X-ray analysis were formed overnight.

^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.17 (d, $^3J_{HH}$ = 9.1 Hz, 1H, *H*4'), 8.10 (d, $^3J_{HH}$ = 8.8 Hz, 1H, *H*13), 8.05 (d, $^3J_{HH}$ = 8.8 Hz, 1H, *H*14), 8.00 (d, $^3J_{HH}$ = 8.9 Hz, 1H, *H*15), 7.93 (d, $^3J_{HH}$ = 8.2 Hz, 1H, *H*5'), 7.87 (d, $^3J_{HH}$ = 8.1 Hz, 1H, *H*15'), 7.87 (d, $^3J_{HH}$ = 8.1 Hz, 1H, *H*5), 7.75 (dd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HP}$ = 6.3 Hz, 1H, *H*3), 7.71 (dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HP}$ = 6.3 Hz, 1H, *H*4), 7.68 (d, $^3J_{HH}$ = 8.9 Hz, 1H, *H*14'), 7.57 (d, $^3J_{HH}$ = 9.1 Hz, 1H, *H*3'), 7.52-7.41 (m, 5H, *H*6/*H*16/*H*16'/*H*18'/*H*18), 7.37-7.29 (m, 3H, *H*6'/*H*17/*H*17'), 7.24-7.18 (m, 2H, *H*7/*H*7'), 7.17 (d, $^3J_{HH}$ = 8.9 Hz, 1H, *H*13'), 7.04 (d, $^3J_{HH}$ = 8.5 Hz, 1H, *H*8'), 6.94 (d, $^3J_{HH}$ = 8.5 Hz, 1H, *H*8), 5.08 (m, 1H, cod-C*H*), 3.98 (m, 1H, cod-C*H*), 3.96 (s, 3H, OCH_3), 2.18 (m, 1H, cod-C*H*), 2.08 (m, 1H, cod-C*H*), 1.75 (m, 1H, cod-CH_2), 1.51-1.40 (m, 3H, cod-CH_2), 1.31 (m, 1H, cod-CH_2), 1.05 (m, 1H, cod-CH_2), 1.00-0.95 (m, 2H, cod-CH_2) ppm. **^{13}C{^{1}H} NMR** (101 MHz, CD_2Cl_2): δ = 155.8 (*C*2'), 149.7 (d, $^2J_{CP}$ = 4.3 Hz, *C*12), 149.6 (d, $^2J_{CP}$ = 10.9 Hz, *C*12'), 140.7 (d, $^2J_{CP}$ = 22.4 Hz, *C*1), 135.1 (*C*2), 134.6 (*C*9'), 133.2 (d, *J* = 11.7 Hz), 132.8, 132.4 (d, *J* = 1.3 Hz), 132.3 (d, *J* = 2.2 Hz), 132.2, 131.7, 131.4 (*C*4'), 129.9 (*C*14'), 129.8 (*C*14), 129.6 (*C*8'), 129.2 (*C*10'), 128.4 (*C*15), 128.4 (*C*15'), 128.1 (*C*5), 127.9 (*C*6), 127.1 (*C*5'), 126.9 (*C*4), 126.7 (*C*18), 126.7 (*C*18'), 126.6 (*C*7), 126.6 (*C*8), 126.3 (*C*17/*C*17'), 126.2 (*C*7'), 125.8 (d, $^2J_{CP}$ = 3.3 Hz, *C*3), 125.4 (*C*16), 125.2 (*C*16'), 124.5 (*C*13), 124.0 (*C*6'/*C*11), 123.3 (d, $^3J_{CP}$ = 2.7 Hz, *C*11'), 121.7 (*C*13'), 120.0 (d, $^3J_{CP}$ = 7.8 Hz, *C*1'), 112.7 (*C*3'), 102.5 (d, $^2J_{CP}$ = 18.5 Hz, cod-*C*H), 101.8 (d, $^2J_{CP}$ = 15.9 Hz, cod-*C*H), 56.1 (cod-*C*H), 56.0 (O*C*H_3), 49.7 (cod-*C*H), 33.6 (d, $^3J_{CP}$ = 3.9 Hz, cod-*C*H_2), 32.1 (d, $^3J_{CP}$ = 2.7 Hz, cod-*C*H_2), 27.9 (d, $^3J_{CP}$ = 2.3 Hz, cod-*C*H_2), 27.6 (d, $^3J_{CP}$ = 2.6 Hz, cod-*C*H_2) ppm; resonances for *C*9, *C*19, *C*19', *C*20 and *C*20' could not be specifically assigned. **^{31}P {^{1}H} NMR** (202 MHz, CD_2Cl_2): δ = 140.4 ppm. **HRMS** (NSI^+, MeCN): Found: *m*/*z* = 897.2214. Calculated for $[M - Cl]^+$: *m*/*z* = 897.2237.

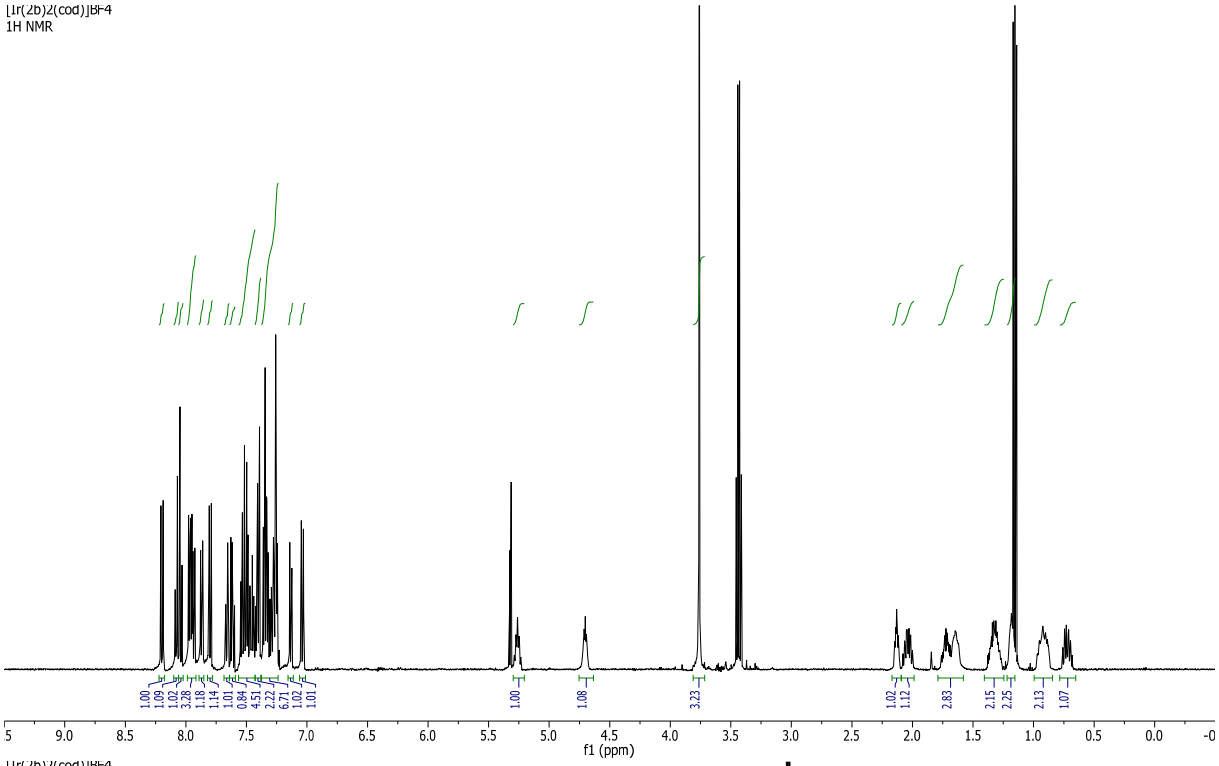


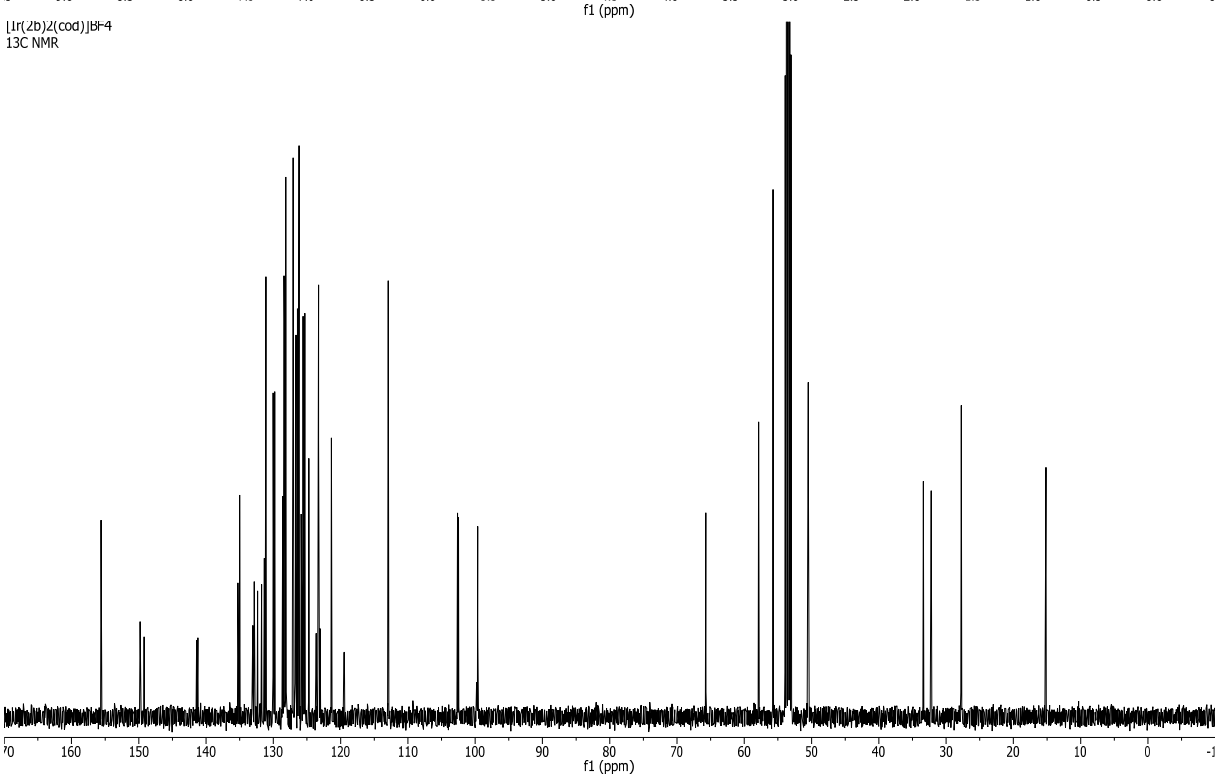


2.9 [IrCl(**2b**)(η⁴-cod)] (**6b**)

2b (30.0 mg, 50.0 µmol) and $[Ir(\eta^4\text{-cod})Cl]_2$ (16.8 mg, 25.0 µmol) were dissolved in dichloromethane (2 mL) and stirred for 30 minutes. The solution was filtered and layered with diethyl ether to precipitate the product as a yellow solid overnight.

^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.20 (d, $^3J_{HH}$ = 9.2 Hz, 1H, *H*4'), 8.08 (d, $^3J_{HH}$ = 8.8 Hz, 1H, *H*13'), 8.04 (d, $^3J_{HH}$ = 8.8 Hz, 1H, *H*14'), 7.97-7.92 (m, 3H, *H*15'/*H*5'/*H*15), 7.87 (d, $^3J_{HH}$ = 8.3 Hz, 1H, *H*5), 7.80 (d, $^3J_{HH}$ = 8.9 Hz, 1H, *H*14), 7.66 (d, $^3J_{HH}$ = 8.8 Hz, 1H, *H*4), 7.61 (dd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HP}$ = 6.3 Hz, 1H, *H*3), 7.53 (ddd, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, *H*6), 7.51 (d, $^3J_{HH}$ = 9.2 Hz, 1H, *H*3'), 7.49 (ddd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, *H*16), 7.46-7.39 (m, 4H, *H*16'/*H*7'/*H*18/*H*8'), 7.36-7.30 (m, 2H, *H*6'/*H*17), 7.29-7.23 (m, 3H, *H*7/*H*17'/*H*18'), 7.13 (d, $^3J_{HH}$ = 8.6 Hz, 1H, *H*8), 7.04 (d, $^3J_{HH}$ = 8.9 Hz, 1H, *H*13), 5.26 (m, 1H, cod-C*H*), 4.70 (m, 1H, cod-C*H*), 3.76 (s, 3H, OCH_3), 2.13 (m, 1H, cod-C*H*), 2.04 (m, 1H, cod-CH_2), 1.72 (m, 1H, cod-CH_2), 1.65 (m, 1H, cod-CH_2), 1.36-1.26 (m, 2H, cod-CH_2), 1.18 (m, 1H, cod-C*H*), 0.96-0.86 (m, 2H, cod-CH_2), 0.73 (m, 1H, cod-CH_2) ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): δ = 155.6 (*C*2'), 149.8 (d, $^2J_{CP}$ = 5.8 Hz, *C*12'), 149.2 (d, $^2J_{CP}$ = 12.8 Hz, *C*12), 141.3 (d, $^2J_{CP}$ = 24.1 Hz, *C*1), 135.3 (d, $^1J_{CP}$ = 1.8 Hz, *C*2), 135.0 (*C*9'), 133.1 (d, $^3J_{CP}$ = 11.6 Hz, *C*9), 132.8 (d, $^4J_{CP}$ = 7.4 Hz, C19), 132.4 (d, $^4J_{CP}$ = 1.6 Hz, *C*19'), 131.7 (d, $^5J_{CP}$ = 1.6 Hz, *C*20'), 131.4 (d, $^5J_{CP}$ = 0.9 Hz, *C*20), 131.1 (*C*4'), 130.0 (*C*14'), 129.8 (*C*14), 128.4 (*C*15'), 128.4 (*C*15), 128.2 (*C*5'), 128.1 (*C*5), 128.1 (*C*6), 127.1 (d, $^4J_{CP}$ = 2.0 Hz, *C*8), 127.1 (*C*4), 127.0 (*C*8'/*C*18), 126.7 (*C*18'), 126.4 (*C*7), 126.3 (*C*17'), 126.2 (*C*7'), 125.8 (d, $^2J_{CP}$ = 3.1 Hz, *C*3), 125.6 (*C*17), 125.3 (*C*16'), 125.3 (*C*16), 124.7 (d, $^3J_{CP}$ = 2.7 Hz, *C*13'), 123.6 (d, $^3J_{CP}$ = 3.7 Hz, *C*11'), 123.3 (*C*6'), 123.0 (d, $^3J_{CP}$ = 2.5 Hz, *C*11), 121.4 (d, $^3J_{CP}$ = 1.4 Hz, *C*13), 119.5 (d, $^3J_{CP}$ = 8.0 Hz, *C*1'), 112.9 (*C*3'), 102.6 (d, $^2J_{CP}$ = 18.5 Hz, cod-*C*H), 99.7 (d, $^2J_{CP}$ = 17.0 Hz, cod-*C*H), 57.9 (d, $^2J_{CP}$ = 1.5 Hz, cod-*C*H), 55.7 (O*C*H_3), 50.5 (cod-*C*H), 33.4 (d, $^3J_{CP}$ = 3.5 Hz, cod-*C*H_2), 32.2 (d, $^3J_{CP}$ = 3.0 Hz, cod-*C*H_2), 27.8 (d, $^3J_{CP}$ = 2.4 Hz, cod-*C*H_2), 27.7 (d, $^3J_{CP}$ = 2.9 Hz, cod-*C*H_2) ppm; resonances for *C*10 and *C*10' were obscured. **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2): δ = 139.6 ppm. **HRMS** (NSI^+, MeCN): Found: *m*/*z* = 897.2226. Calculated for $[M - Cl]^+$: *m*/*z* = 897.2237.



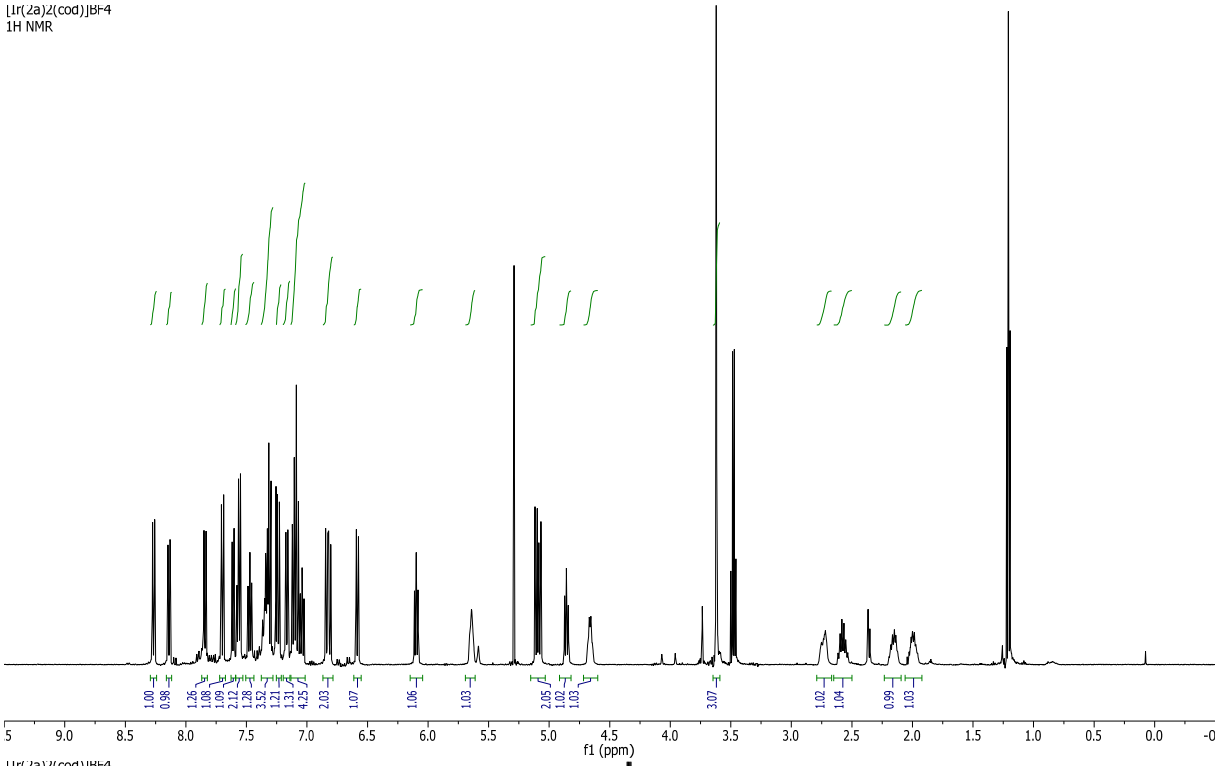


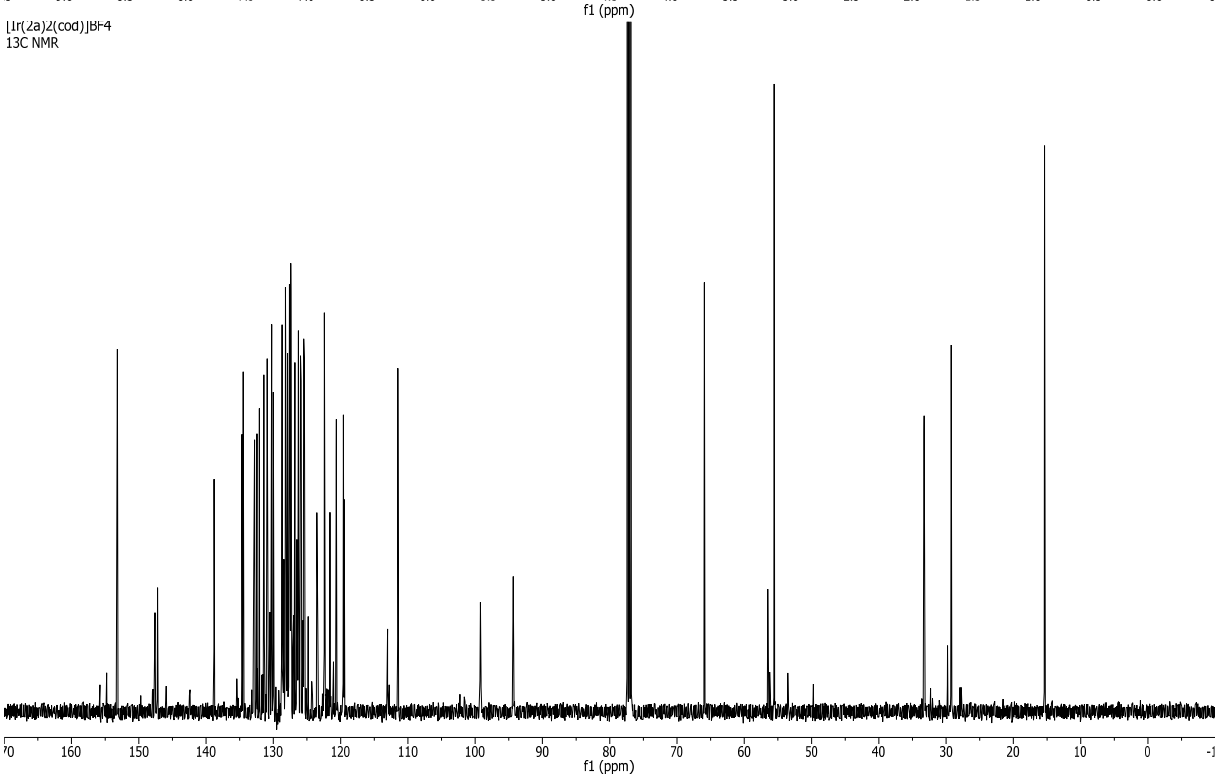
2.10 [Ir(**2a**)$_2$(η^4-cod)]BF$_4$ (**7a**)

Method A: **2a** (30.0 mg, 50 µmol) and [Ir(η^4-cod)$_2$]BF$_4$ (12.4 mg, 25 µmol) were dissolved in dichloromethane (1 mL) and stirred for 30 minutes. The solution was filtered and layered with diethyl ether to precipitate the product as a green solid.

Method B: **6a** (24.6 mg, 25 µmol) was dissolved in dichloromethane (1 mL), AgBF$_4$ (4.8 mg, 25 µmol) and **2a** (15.0 mg, 25 µmol) were added and stirred for 30 minutes. The solution was filtered and concentrated *in vacuo*. The crude product was washed with diethyl ether to give the product as a green solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.27 (d, $^3J_{HH}$ = 8.8 Hz, 2H, *H*14), 8.14 (d, $^3J_{HH}$ = 8.2 Hz, 2H, *H*15), 7.85 (d, $^3J_{HH}$ = 8.3 Hz, 2H, *H*5), 7.69 (d, $^3J_{HH}$ = 9.1 Hz, 2H, *H*4'), 7.61 (d, $^3J_{HH}$ = 8.1 Hz, 2H, *H*15'), 7.58-7.54 (m, 4H, *H*4/*H*16), 7.83 (pt, J_{HH} = 7.5 Hz, 2H, *H*6), 7.37-7.30 (m, 6H, *H*3/*H*16'/*H*3'), 7.24 (d, $^3J_{HH}$ = 8.8 Hz, 2H, *H*13), 7.16 (d, $^3J_{HH}$ = 8.2 Hz, 2H, *H*5'), 7.12-7.02 (m, 8H, *H*17/*H*7/*H*14'/*H*17'), 6.84 (d, $^3J_{HH}$ = 8.6 Hz, 2H, *H*8), 6.81 (d, $^3J_{HH}$ = 8.6 Hz, 2H, *H*18), 6.58 (d, $^3J_{HH}$ = 8.6 Hz, 2H, *H*18'), 6.10 (pt, J_{HH} = 7.5 Hz, 2H, *H*6'), 5.64 (m, 2H, cod-C*H*), 5.10 (d, $^3J_{HH}$ = 8.8 Hz, 2H, *H*13'), 5.08 (d, $^3J_{HH}$ = 8.5 Hz, 2H, *H*8'), 4.86 (pt, J_{HH} = 7.6 Hz, 2H, *H*7'), 4.67 (m, 2H, cod-C*H*), 3.62 (s, 6H, OCH_3), 2.73 (m, 2H, cod-CH_2), 2.57 (m, 2H, cod-CH_2), 2.15 (m, 2H, cod-CH_2), 2.00 (m, 2H, cod-CH_2) ppm. **^{11}B NMR** (128 MHz, CD_2Cl_2): δ = –1.6 (s) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ = 153.2 (*C*2'), 147.6 (pt, J_{CP} = 12.2 Hz, *C*12'), 147.2 (pt, J_{CP} = 7.0 Hz, *C*12), 138.8 (*C*1), 134.7 (*C*10), 134.5 (*C*9'), 132.9 (pt, J_{CP} = 8.4 Hz, *C*9), 132.8 (*C*19), 132.4 (*C*19'), 132.1 (*C*20), 131.4 (*C*20'), 130.9 (*C*14), 130.2 (*C*4'), 130.0 (*C*14'), 128.7 (*C*15), 128.6 (*C*6), 128.2 (*C*5), 128.1 (*C*4), 127.9 (*C*15'), 127.6 (*C*8), 127.6 (*C*18), 127.5 (*C*18'), 127.4 (*C*10'), 127.4 (*C*7), 126.8 (*C*17), 126.3 (*C*5'), 126.0 (*C*17'), 125.9 (*C*16), 125.5 (*C*16'), 125.4 (*C*7'), 123.5 (*C*11), 122.4 (*C*6'), 122.3 (*C*8'), 121.6 (*C*11'), 120.6 (*C*13), 119.6 (*C*13'), 119.5 (*C*1'), 111.5 (*C*3'), 99.2 (pt, J_{CP} = 14.8 Hz, cod-*C*H), 94.3 (pt, J_{CP} = 10.2 Hz, cod-*C*H), 55.6 (O*C*H$_3$), 33.3 (cod-*C*H$_2$), 29.3 (cod-*C*H$_2$) ppm; resonances for *C*2 and *C*3 were obscured. **^{19}F NMR** (376 MHz, CD_2Cl_2): δ = –153.5 (s) ppm. **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$): δ = 156.3 ppm. **HRMS** (NSI$^+$, MeOH): Found: *m*/*z* = 1495.3935. Calculated for [M – BF$_4$]$^+$: *m*/*z* = 1495.3935.





2.11 Asymmetric Addition of Phenylboronic Acid to 1-Naphthaldehyde

[Rh(acac)(η^2-C_2H_4)$_2$] (2.6 mg, 10 µmol) and ligand **2a** (12 mg, 20 µmol) were dissolved in THF (4 mL) and left to stir for 20 minutes. Phenylboronic acid (122 mg, 1.0 mmol), base (2.5 M aqueous solution, 1.0 mmol) and 1-naphthaldehyde (68 µl, 0.5 mmol) were added subsequently. The reaction mixture was heated to 60 °C and the conversion was followed by TLC analysis. After 8 hours reaction time the solvent was evaporated and the crude product was purified by column chromatography (hexane/EtOAc, 10:1) on silica media (h = 15 cm, d = 2 cm) to give the product as a colourless oil; 85% yield, 34% *ee* (*R*). The enantiomeric excess was measured by chiral HPLC (Column Daicel Chiralpak OD; flow rate: 1.0 mL/min; hexane/2-propanol, 80:20; retention times: (*S*) t_1 = 10.1 min, (*R*) t_2 = 19.4 min).[7]

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