Electronic Supporting Information for:

A convenient method for the generation of {Rh(PNP)}$^+$ and {Rh(PONOP)}$^+$ fragments: reversible formation of vinylidene derivatives

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1. General methods

All manipulations were performed under an atmosphere of argon using Schlenk and glove box techniques unless otherwise stated. Dinitrogen and dihydrogen were dried by passage through a stainless steel column of activated 3 Å molecular sieves. Glassware was oven dried at 150 °C overnight and flame-dried under vacuum prior to use. Molecular sieves were activated by heating at 300 °C *in vacuo* overnight. 1,2-$C_6H_4F_2$ was pre-dried over Al_2O_3, distilled from calcium hydride and dried twice over 3 Å molecular sieves. CD_2Cl_2 was freeze-pump-thaw degassed and dried over 3 Å molecular sieves. Other anhydrous solvents were purchased from Acros Organics or Sigma-Aldrich, freeze-pump-thaw degassed and stored over 3 Å molecular sieves. Na[BAr^F_4],[1] PONOP,[2] PNP,[3] HCCAr'[4] and [$Rh(COD)_2$][BAr^F_4][5] were synthesised according to published procedures. All other reagents are commercial products and were used as received. NMR spectra were recorded on Bruker spectrometers under argon at 298 K unless otherwise stated. Chemical shifts are quoted in ppm and coupling constants in Hz. NMR spectra in 1,2-$C_6H_4F_2$ were recorded using an internal capillary of C_6D_6. Microanalyses were performed at the London Metropolitan University by Stephen Boyer.

2. NMR scale reactions: Synthesis and reactivity of [Rh(pincer)(COD)][BAr^F_4] 1

General procedure

A 0.02 mol [Rh] L^{-1} solution of **1** was generated *in situ* from [$Rh(COD)_2$][BAr^F_4] and PONOP or PNP in 1,2-$C_6H_4F_2$ in an NMR tube fitted with a J. Young's valve. For reactions with gases, the solution was freeze-pump-thaw degassed and then placed under an atmosphere of dihydrogen, carbon monoxide or dinitrogen. Liquid reagents were added directly by syringe under an atmosphere of argon. Reactions were then followed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, with constant mixing when not in the spectrometer.

Reaction between [$Rh(COD)_2$][BAr^F_4] and pincer ligands

1. PNP

Following the general procedure and using [$Rh(COD)_2$][BAr^F_4] (11.8 mg, 10.0 μmol), PNP (4.0 mg, 10 μmol) and 1,2-$C_6H_4F_2$ (0.50 mL) gave a mixture of monomeric **1a-CH_2** and dimeric **1b-CH_2** in an approximate 2:1 ratio (based on integration of ^{1}H NMR data, using the CH=CH resonances). Structural dynamics of **1a-CH_2** is apparent from comparison of the ^{31}P{^{1}H} NMR spectrum recorded at 121 MHz and 162 MHz.

1a-CH_2:

^{1}H NMR (300 MHz, 1,2-$C_6H_4F_2$, selected data): *δ* 5.58 (br, 2H, CH), 4.88 (br, 2H, RhCH).

^{31}P{^{1}H} NMR (121 MHz, 1,2-$C_6H_4F_2$): *δ* 63.4 (vbr dd, $^2J_{PP}$ ~ 320, $^1J_{RhH}$ ~ 140), 52.6 (vbr dd, $^2J_{PP}$ ~ 320, $^1J_{RhH}$ ~ 130).

^{31}P{^{1}H} NMR (162 MHz, 1,2-$C_6H_4F_2$): *δ* 63.4 (br dd, $^2J_{PP}$ ~ 320, $^1J_{RhH}$ ~ 140), 52.6 (br dd, $^2J_{PP}$ ~ 320, $^1J_{RhH}$ ~ 130).

1b-CH_2:

^{1}H NMR (300 MHz, 1,2-$C_6H_4F_2$, selected data): *δ* 4.96 (br, 4H, RhCH).

^{31}P{^{1}H} NMR (121 MHz, 1,2-$C_6H_4F_2$): *δ* 66.0 (br d, $^1J_{RhH}$ ~ 120).

^{31}P{^{1}H} NMR (162 MHz, 1,2-$C_6H_4F_2$): *δ* 66.0 (br d, $^1J_{RhH}$ ~ 120).

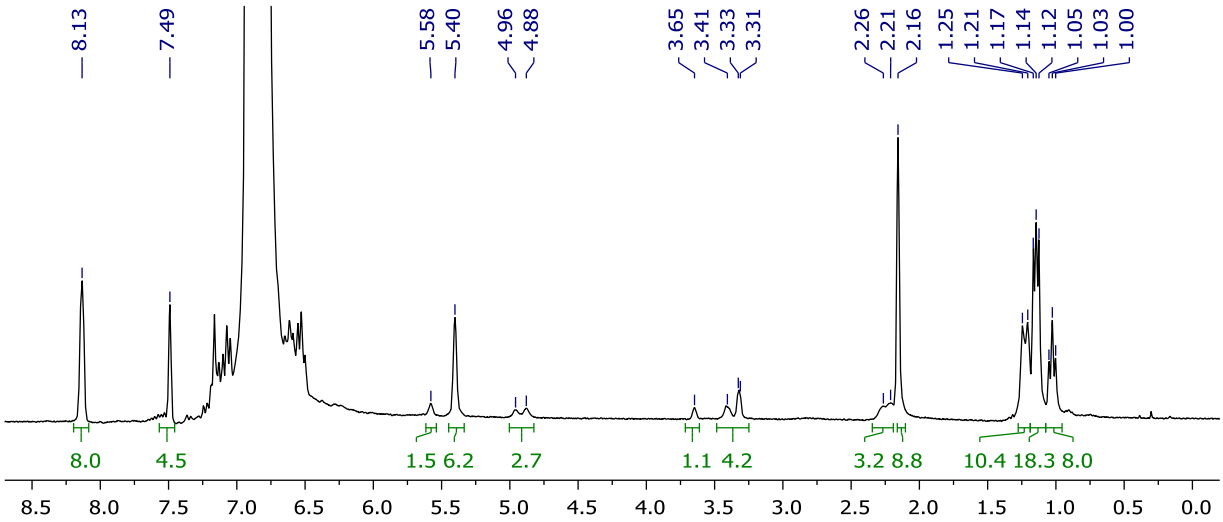

Figure S1. ^{1}H NMR spectrum of the reaction between $[Rh(COD)_2][BAr^F{}_4]$ and PNP (1,2-$C_6H_4F_2$, 300 MHz).

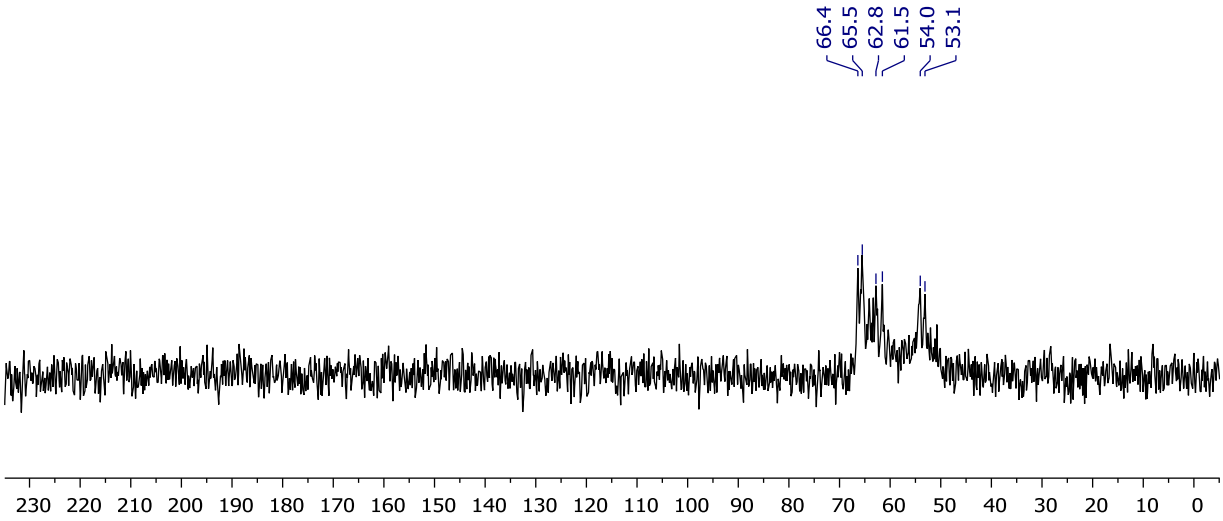

Figure S2. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction between $[Rh(COD)_2][BAr^F{}_4]$ and PNP (1,2-$C_6H_4F_2$, 121 MHz).

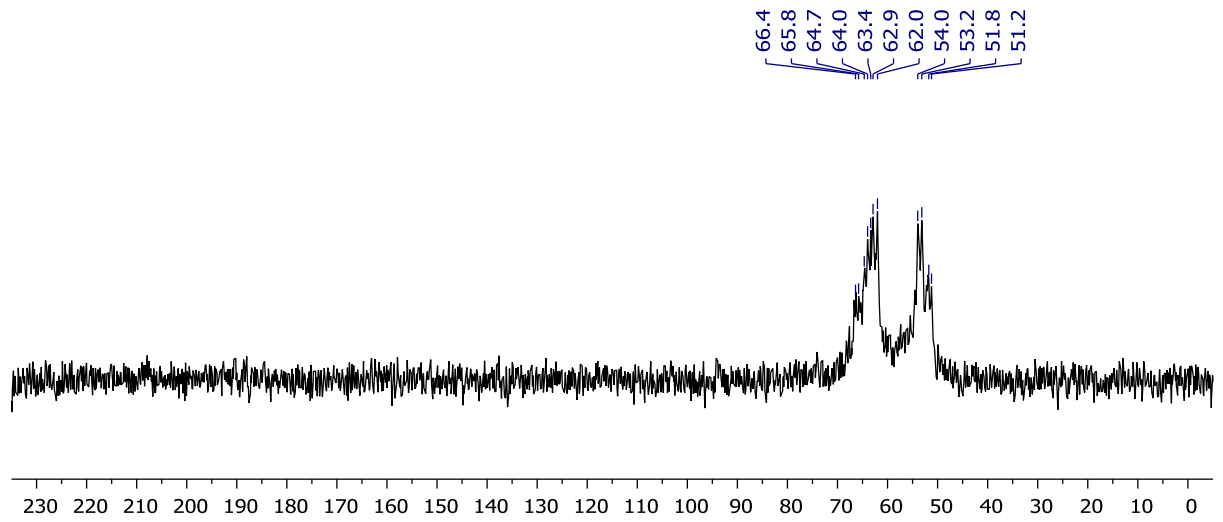

Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction between $[Rh(COD)_2][BAr^F{}_4]$ and PNP (1,2-$C_6H_4F_2$, 162 MHz).

2. PONOP

Following the general procedure and using $[Rh(COD)_2][BAr^F{}_4]$ (12.4 mg, 10.5 μmol), PONOP (4.2 mg, 10 μmol) and 1,2-$C_6H_4F_2$ (0.53 mL) gave a mixture of monomeric **1a-O** and dimeric **1b-O** in an approximate 5:1 ratio (based on integration of $^{31}P\{^1H\}$ NMR data).

1a-O:

^{1}H NMR (300 MHz, 1,2-$C_6H_4F_2$, selected data): *δ* 5.54 (br, 2H, CH), 5.13 (br, 2H, RhCH),

$^{31}P\{^1H\}$ NMR (121 MHz, 1,2-$C_6H_4F_2$): *δ* 202.5 (d, $^1J_{RhP}$ = 134).

1b-O:

^{1}H NMR (300 MHz, 1,2-$C_6H_4F_2$, selected data): *δ* 4.92 (br, 4H, RhCH).

$^{31}P\{^1H\}$ NMR (121 MHz, 1,2-$C_6H_4F_2$): *δ* 202.2 (d, $^1J_{RhP}$ = 132).

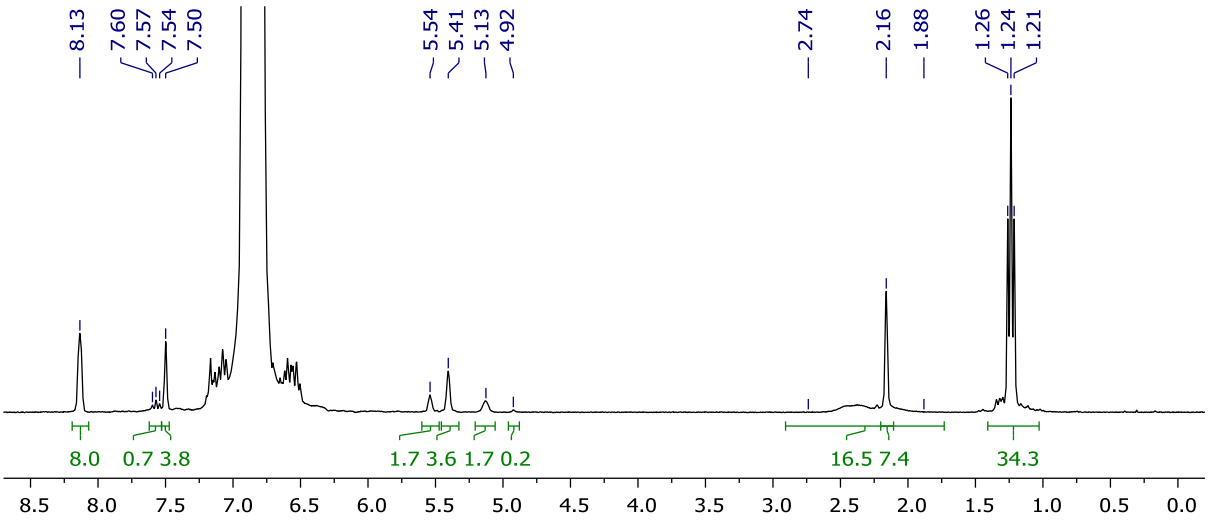

Figure S4. ^{1}H NMR spectrum of the reaction between $[Rh(COD)_2][BAr^F{}_4]$ and PONOP (1,2-$C_6H_4F_2$, 300 MHz).

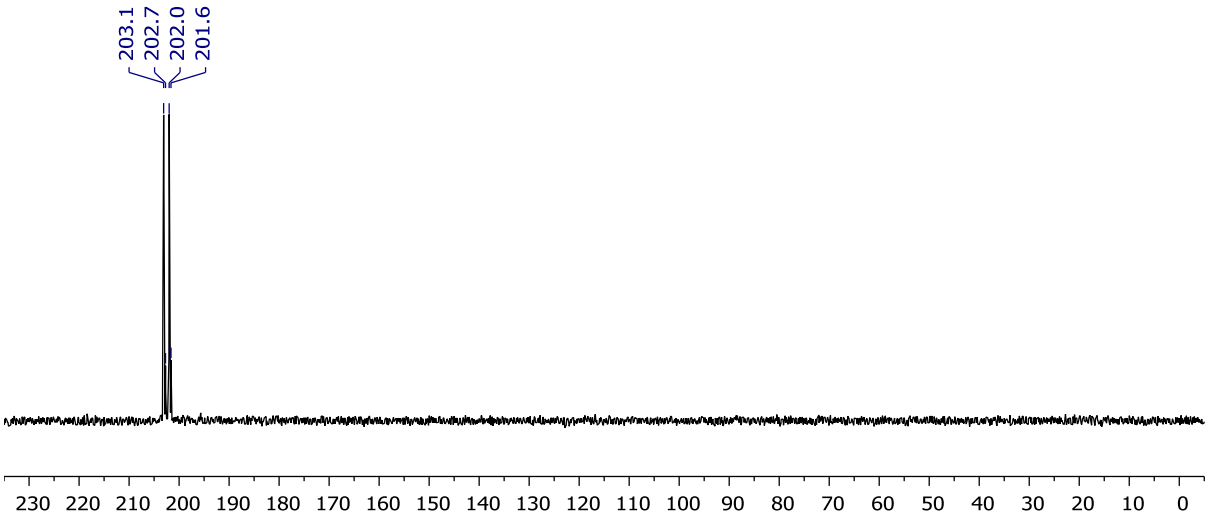

Figure S5. $^{31}P\{^1H\}$ NMR spectrum of the reaction between $[Rh(COD)_2][BAr^F{}_4]$ and PONOP (1,2-$C_6H_4F_2$, 121 MHz).

Addition of 1,5-cyclooctadiene

1. PNP

Following the general procedure and using [Rh(COD)$_2$][BAr$^F_4$] (11.8 mg, 10.0 μmol), PNP (4.0 mg, 10 μmol), 1,2-$C_6H_4F_2$ (0.50 mL) and 1,5-cyclooctadiene (12.9 μL, 105 μmol) gave **1a-CH$_2$**, which was subsequently characterised *in situ*. Under these conditions, **1a-CH$_2$** is highly dynamic on the ^{31}P NMR time scale. These dynamics are considerably less pronounced in the absence of excess 1,5-cyclooctadiene (*vide supra*).

^{1}H NMR (500 MHz, 1,2-$C_6H_4F_2$): *δ* 8.09 – 8.15 (m, 8H, Ar^F), 7.53 (t, $^3J_{HH}$ = 8.1, 1H, py), 7.49 (br, 4H, Ar^F), 5.56 – 5.60 (m, 2H, CH), 4.88 (br, 2H, RhCH), 3.30 – 3.35 (m, 4H, PCH$_2$), 2.22 – 2.33 (m, 4H, CH$_2$), 1.16 – 1.27 (m, 4H, CH$_2$), 1.10 – 1.19 (m, 36H, *t*Bu).

^{13}C{^{1}H} NMR (126 MHz, 1,2-$C_6H_4F_2$): *δ* 162.3 (q, $^1J_{BC}$ = 50, Ar^F), 161.8 (vt, J_{PC} = 3, py), 140.0 (s, py), 134.8 (s, Ar^F), 129.9 (s, CH), 129.5 (qq, $^1J_{FC}$ = 32, $^1J_{BC}$ = 3, Ar^F), 125.1 (q, $^1J_{FC}$ = 272, Ar^F), 120.5 (br, py), 117.3 (sept, $^3J_{FC}$ = 4, Ar^F), 70.4 (d, $^1J_{RhC}$ = 12, RhCH), 36.5 (s, CH$_2$), 36 (HMBC, *t*Bu{C}), 36 (HSQC, PCH$_2$), 29.7 (s, CH$_2$), 29.4 (br, *t*Bu{CH$_3$}),

^{31}P{^{1}H} NMR (300 MHz, 1,2-$C_6H_4F_2$): *δ* 57.6 (br, fwhm = 1700 Hz).

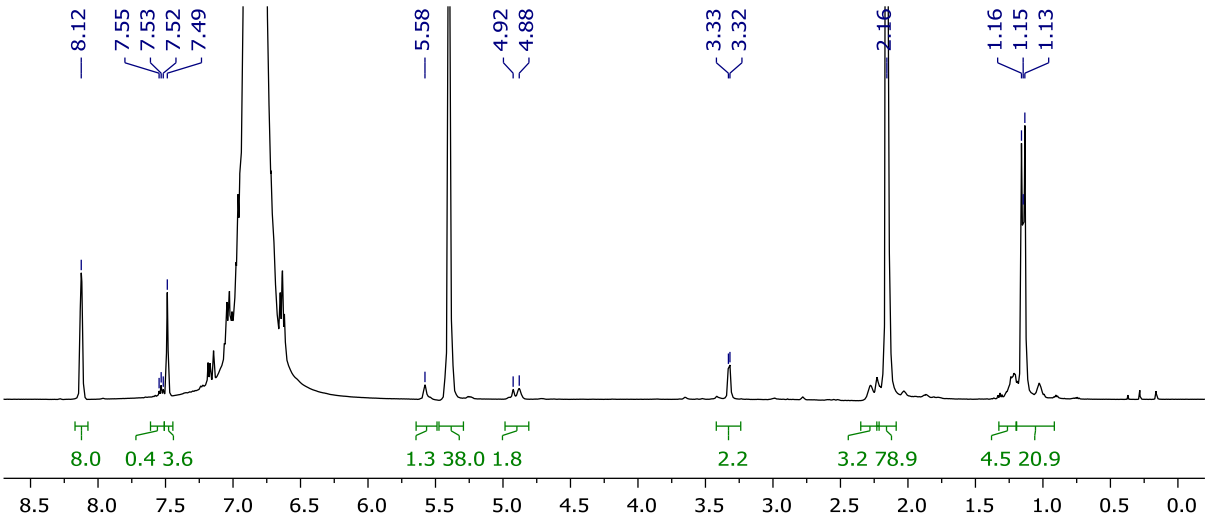

Figure S6. ^{1}H NMR spectrum of **1a-CH$_2$** generated *in situ* from the reaction between [Rh(COD)$_2$][BAr$^F_4$] and PNP in the presence of excess 1,5-cyclooctadiene (1,2-$C_6H_4F_2$, 500 MHz).

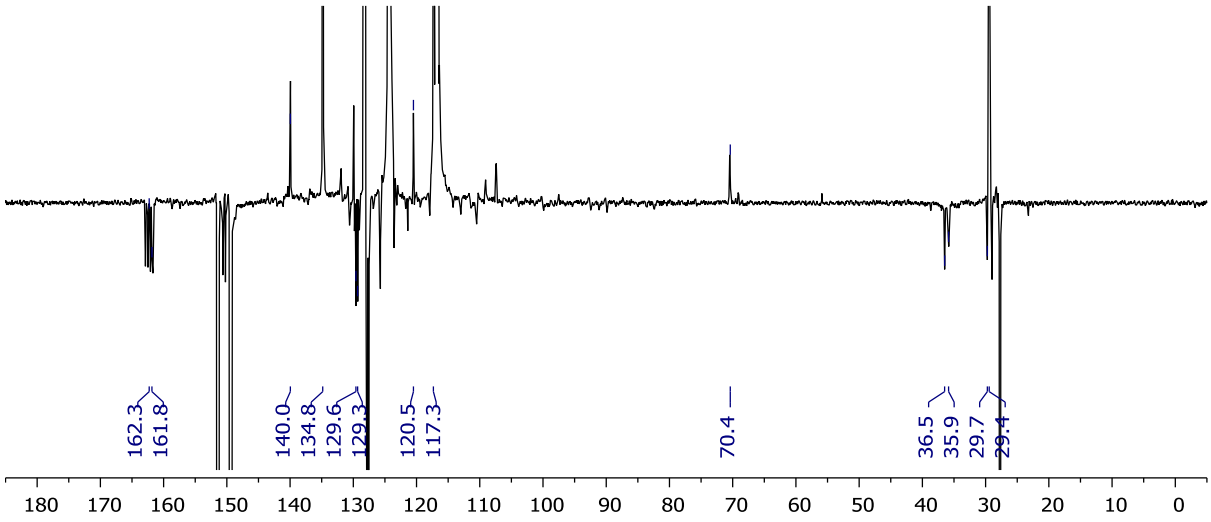

Figure S7. ^{1}H NMR spectrum of **1a-CH$_2$** generated *in situ* from the reaction between [Rh(COD)$_2$][BAr$^F_4$] and PNP in the presence of excess 1,5-cyclooctadiene (1,2-C$_6$H$_4$F$_2$, 126 MHz).

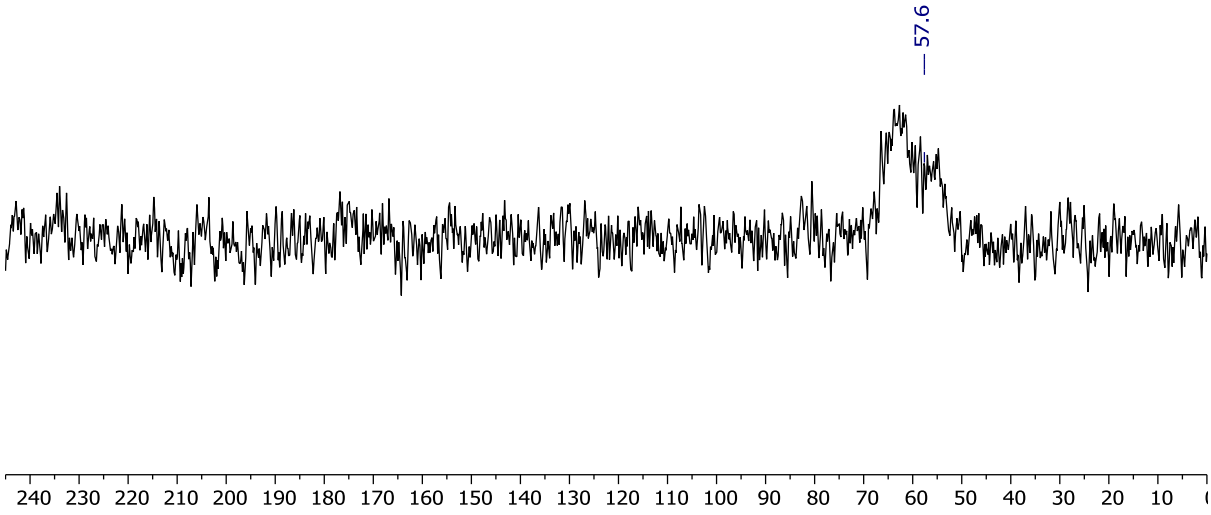

Figure S8. ^{31}P{^{1}H} NMR spectrum of **1a-CH$_2$** generated *in situ* from the reaction between [Rh(COD)$_2$][BAr$^F_4$] and PNP in the presence of excess 1,5-cyclooctadiene (1,2-C$_6$H$_4$F$_2$, 121 MHz).

2. PONOP

Following the general procedure and using [Rh(COD)$_2$][BAr$^F_4$] (12.4 mg, 10.5 μmol), PONOP (4.2 mg, 10 μmol), 1,2-C$_6$H$_4$F$_2$ (0.53 mL) and 1,5-cyclooctadiene (12.9 μL, 105 μmol) gave **1a-CH$_2$**, which was subsequently characterised *in situ*.

^{1}H NMR (500 MHz, 1,2-C$_6$H$_4$F$_2$): *δ* 8.03 – 8.09 (m, 8H, Ar^F), 7.57 (t, $^{3}J_{HH}$ = 8.1, 1H, py), 7.49 (br, 4H, Ar^F), 6.58 (d, $^{3}J_{HH}$ = 8.0, 2H, py), 5.49 – 5.59 (m, 2H, CH), 5.12 (br, 2H, RhCH), 1.96 – 2.69 (m, 8H, CH$_2$), 1.23 (vt, J_{PH} = 7, 36H, *t*Bu).

^{13}C{^{1}H} NMR (126 MHz, 1,2-C$_6$H$_4$F$_2$): *δ* 163.4 (vt, J_{PC} = 3, py), 162.6 (q, $^{1}J_{BC}$ = 50, Ar^F), 145.2 (s, py), 135.1 (s, Ar^F), 129.7 (qq, $^{1}J_{FC}$ = 32, $^{1}J_{BC}$ = 3, Ar^F), 129.5 (s, CH), 124.9 (q, $^{1}J_{FC}$ = 272, Ar^F), 117.6 (sept, $^{3}J_{FC}$ = 4, Ar^F), 102.3 (vt, J_{PC} = 2, py), 77.6 (d, $^{1}J_{RhC}$ = 11, RhCH), 41.5 (vtd, J_{PC} = 5, $^{2}J_{RhC}$ = 2, *t*Bu{C}), 35.7 (s, CH$_2$), 30.1 (s, CH$_2$), 27.5 (vt, J_{PC} = 3, *t*Bu{CH$_3$}).

^{31}P{^{1}H} NMR (121 MHz, 1,2-C$_6$H$_4$F$_2$): *δ* 202.6 (d, $^{1}J_{RhP}$ = 134).

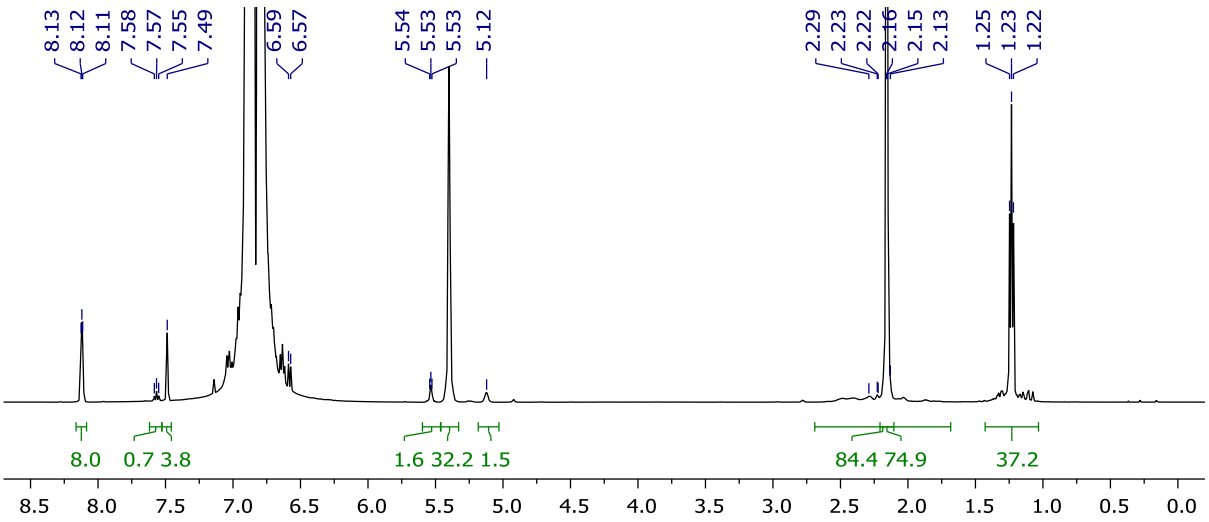

Figure S9. ^{1}H NMR spectrum of **1a-O** generated *in situ* from the reaction between $[Rh(COD)_2][BAr^F{}_4]$ and PONOP in the presence of excess 1,5-cyclooctadiene (1,2-$C_6H_4F_2$, 500 MHz).

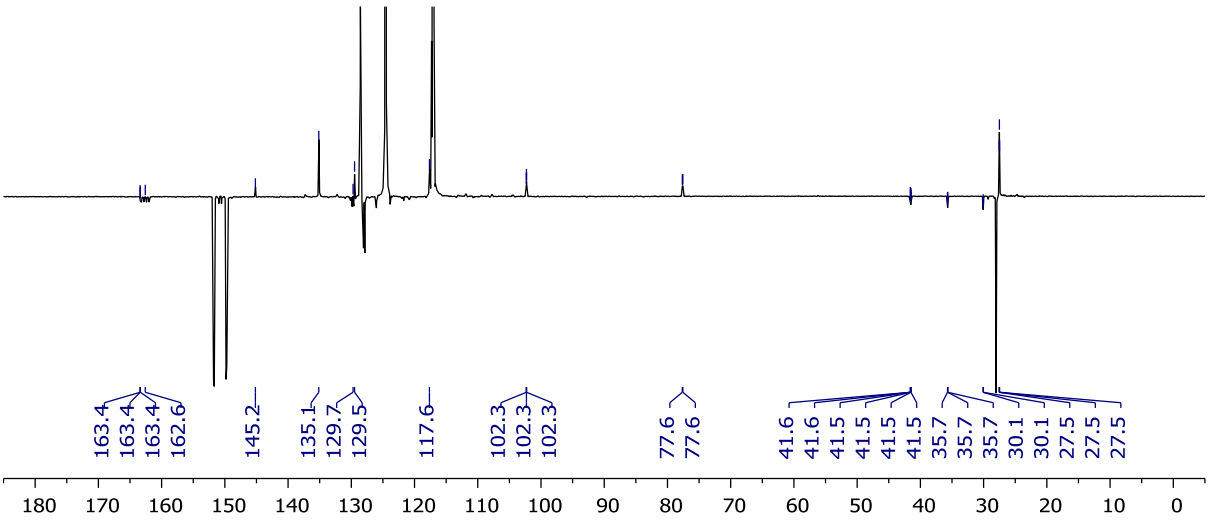

Figure S10. $^{13}C\{^{1}H\}$ APT NMR spectrum of **1a-O** generated *in situ* from the reaction between $[Rh(COD)_2][BAr^F{}_4]$, and PONOP in the presence of excess 1,5-cyclooctadiene (1,2-$C_6H_4F_2$, 126 MHz).

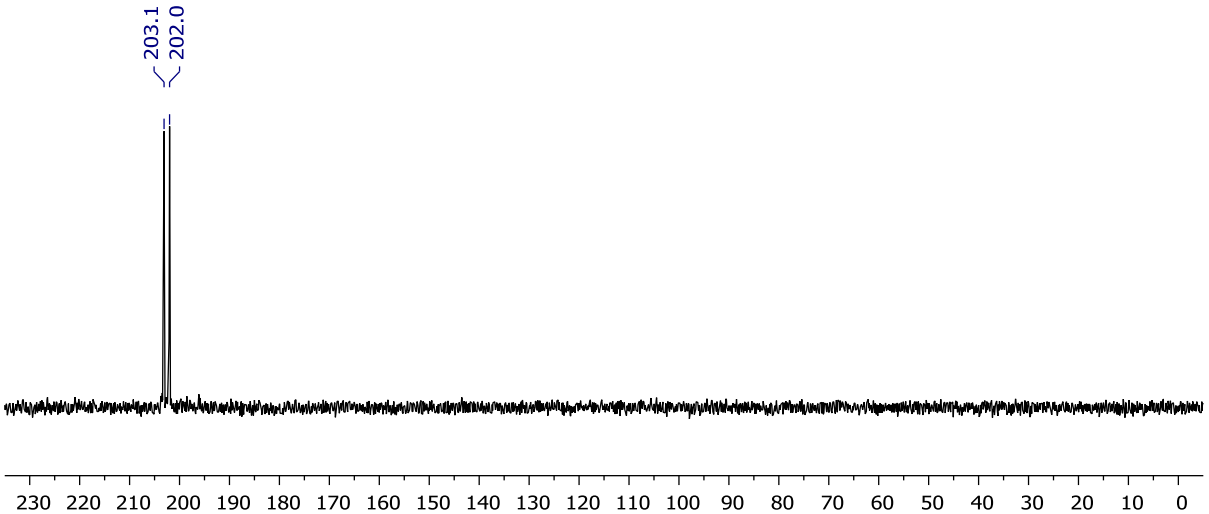

Figure S11. $^{31}P\{^{1}H\}$ NMR spectrum of **1a-O** generated *in situ* from the reaction between $[Rh(COD)_2][BAr^F{}_4]$ and PONOP in the presence of excess 1,5-cyclooctadiene (1,2-$C_6H_4F_2$, 121 MHz).

Carbon monoxide

1. PNP

Following the general procedure using $[Rh(COD)_2][BAr^F{}_4]$ (11.8 mg, 10.0 μmol), PNP (4.0 mg, 10 μmol), 1,2-$C_6H_4F_2$ (0.50 mL), and carbon monoxide (1 atm) gave **2a-CH₂** in < 5 min. Data are consistent with the literature.[6,7]

$^{31}P\{^1H\}$ NMR (121 MHz, 1,2-$C_6H_4F_2$): δ 78.1 (d, $^1J_{RhP}$ = 121).

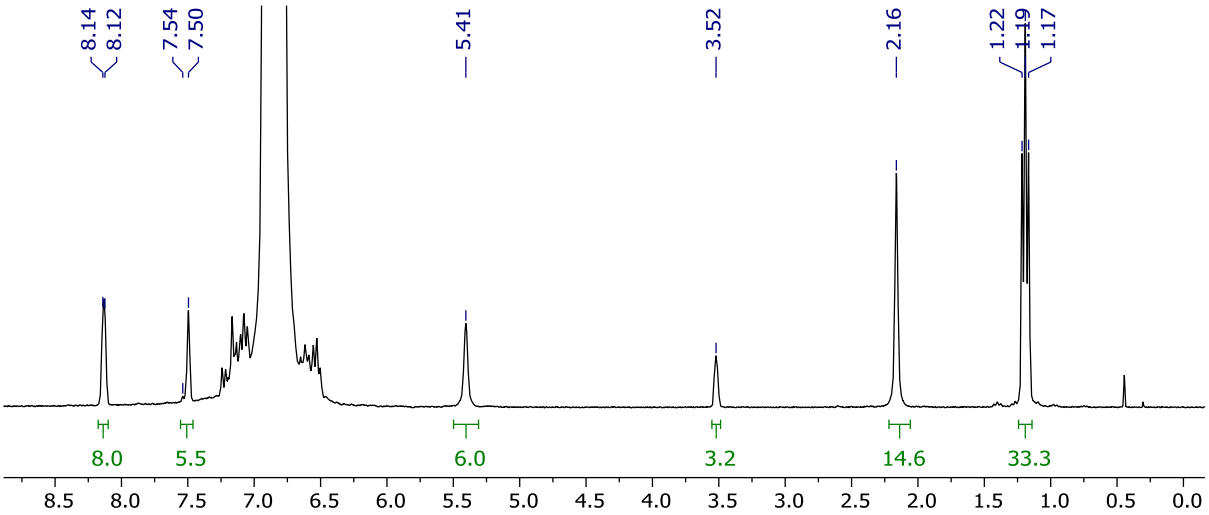

Figure S12. ^1H NMR spectrum of the reaction between **1-CH₂** and carbon monoxide (1,2-$C_6H_4F_2$, 300 MHz).

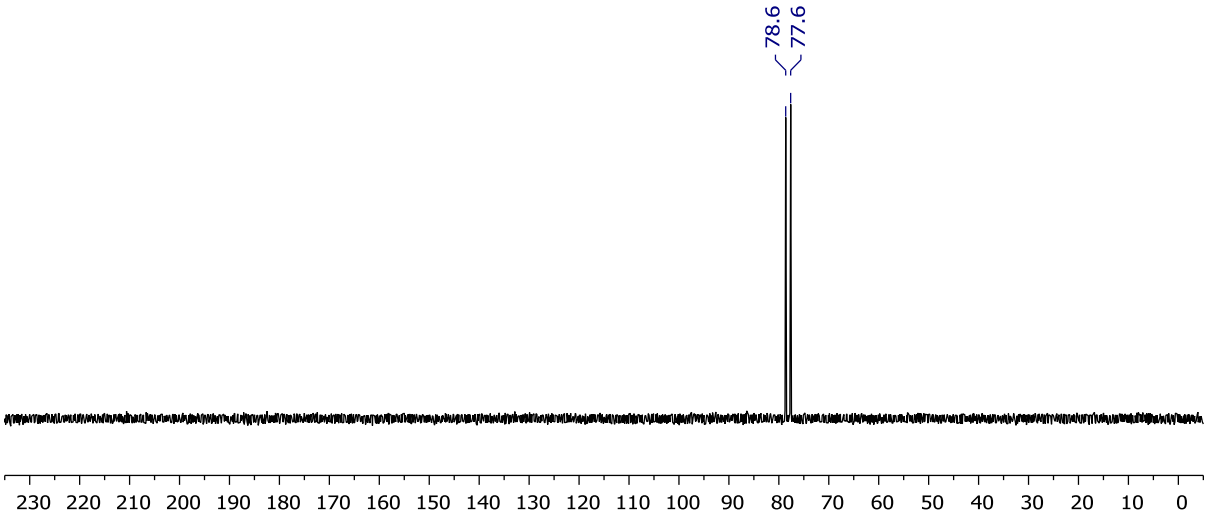

Figure S13. $^{31}P\{^1H\}$ NMR spectrum of the reaction between **1-CH₂** and carbon monoxide (1,2-$C_6H_4F_2$, 121 MHz).

2. PONOP

Following the general procedure and using $[Rh(COD)_2][BAr^F{}_4]$ (13.0 mg, 11.0 μmol), PONOP (4.4 mg, 11 μmol), 1,2-$C_6H_4F_2$ (0.55 mL) and carbon monoxide (1 atm) gave **2a-O** in < 5 min. Data are consistent with the literature.[8]

$^{31}P\{^1H\}$ NMR (121 MHz, 1,2-$C_6H_4F_2$): δ 219.5 (d, $^1J_{RhP}$ = 127).

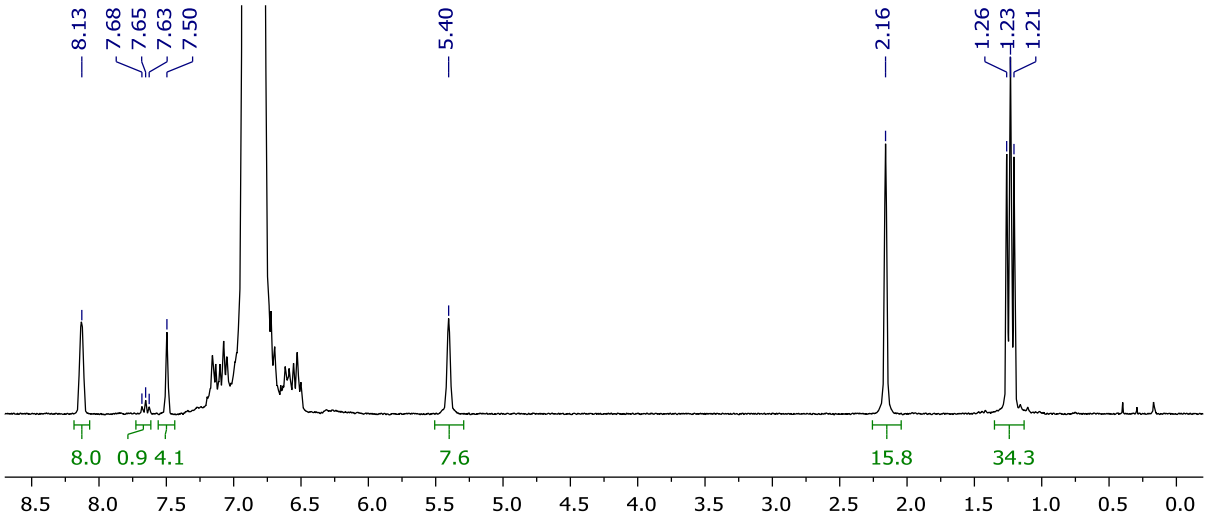

Figure S14. ^1H NMR spectrum of the reaction between **1-O** and carbon monoxide (1,2-$C_6H_4F_2$, 300 MHz).

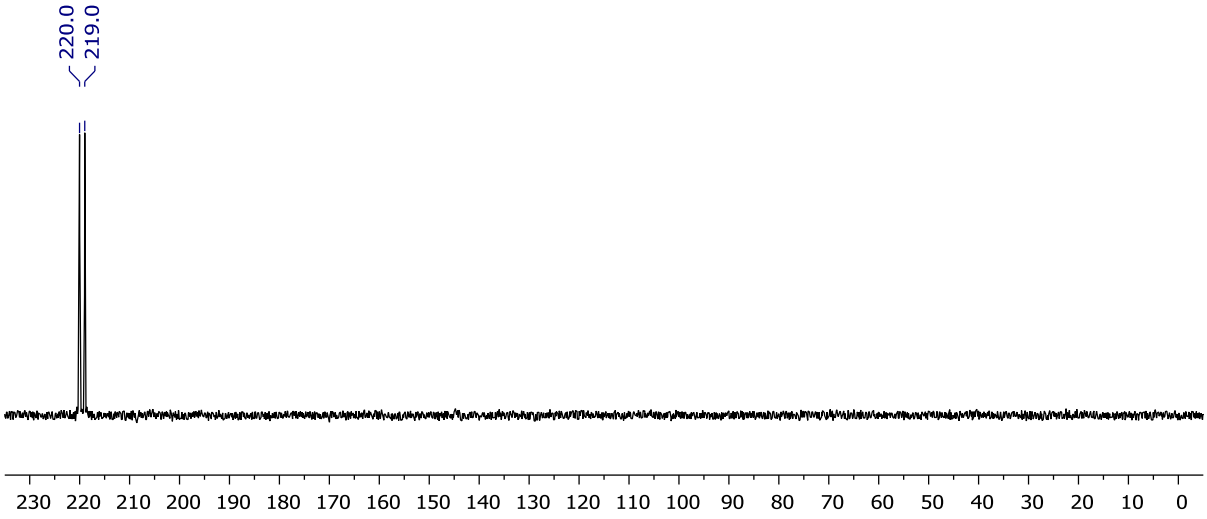

Figure S15. $^{31}P\{^1H\}$ NMR spectrum of the reaction between **1-O** and carbon monoxide (1,2-$C_6H_4F_2$, 121 MHz).

Dihydrogen

1. PNP

Following the general procedure using $[Rh(COD)_2][BAr^F{}_4]$ (11.8 mg, 10.0 μmol), PNP (4.0 mg, 10 μmol), 1,2-$C_6H_4F_2$ (0.50 mL), and dihydrogen (1 atm) gave **2b-CH_2**, alongside cyclooctadiene, cyclooctene and cyclooctane, in < 5 min. Data are consistent with the literature.[7]

$^{31}P\{^1H\}$ NMR (121 MHz, 1,2-$C_6H_4F_2$): δ 81.7 (d, $^1J_{RhP}$ = 120).

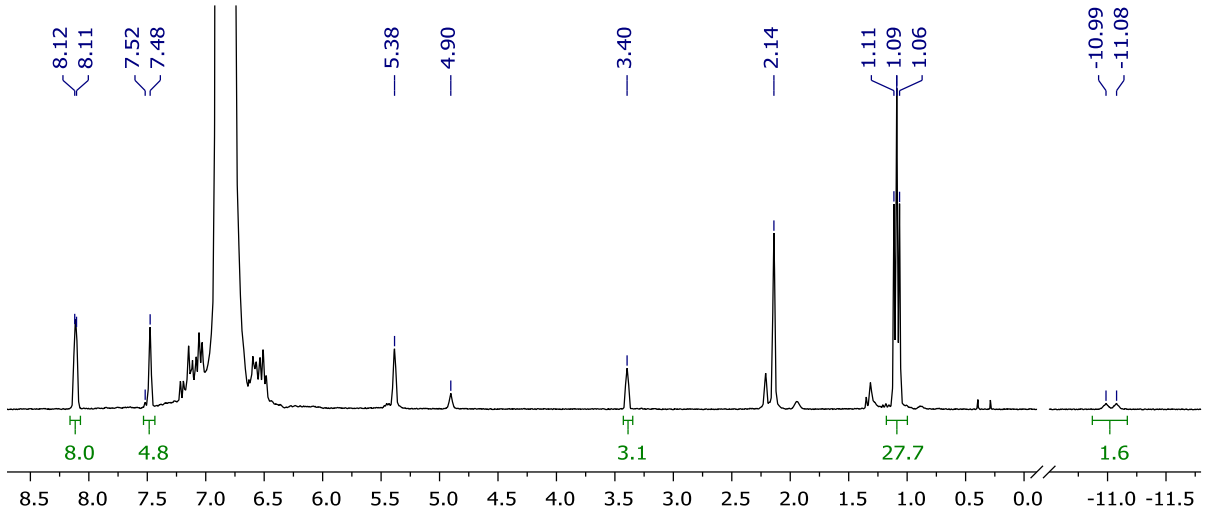

Figure S16**.** ^1H NMR spectrum of the reaction between **1-CH_2** and dihydrogen (1,2-$C_6H_4F_2$, 300 MHz).

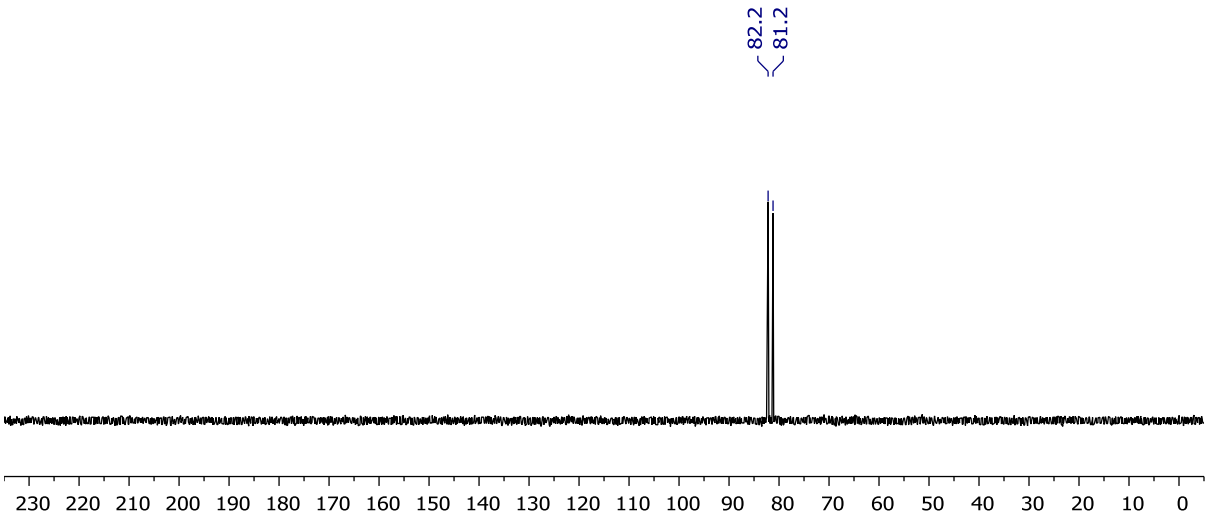

Figure S17. $^{31}P\{^1H\}$ NMR spectrum of the reaction between **1-CH_2** and dihydrogen (1,2-$C_6H_4F_2$, 121 MHz).

2. PONOP

Following the general procedure and using [Rh(COD)$_2$][BAr$^F{}_4$] (13.0 mg, 11.0 μmol), PONOP (4.4 mg, 11 μmol), 1,2-$C_6H_4F_2$ (0.55 mL) and dihydrogen (1 atm) gave **2b-O**, alongside cyclooctane after 2 days. Data are consistent with the literature.[9]

$^{31}P\{^1H\}$ NMR (121 MHz, 1,2-$C_6H_4F_2$): δ 224.5 (d, $^1J_{RhP}$ = 126).

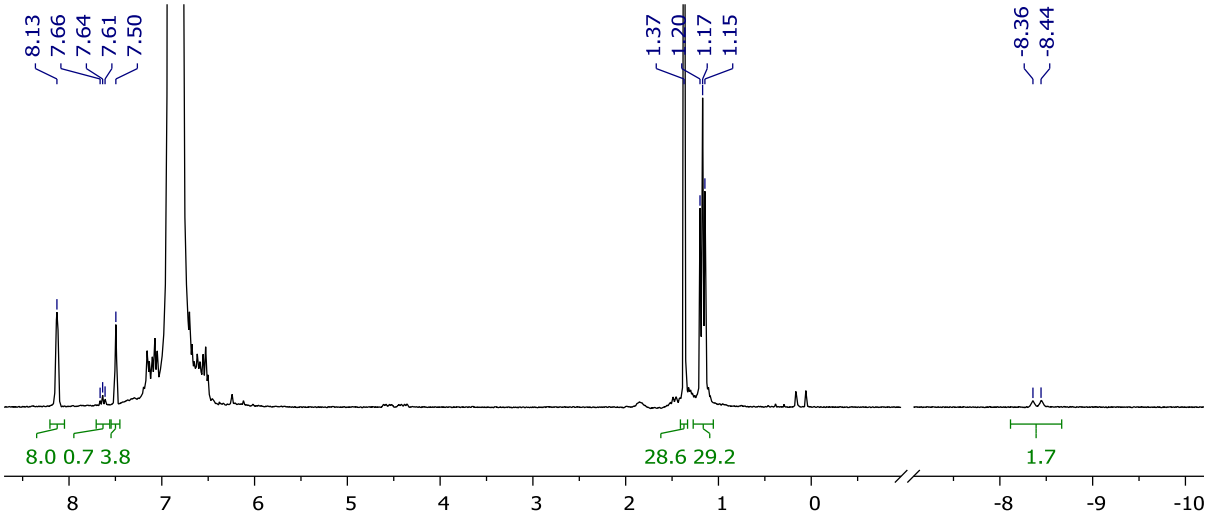

Figure S18. ^{1}H NMR spectrum of the reaction between **1-O** and dihydrogen (1,2-$C_6H_4F_2$, 300 MHz).

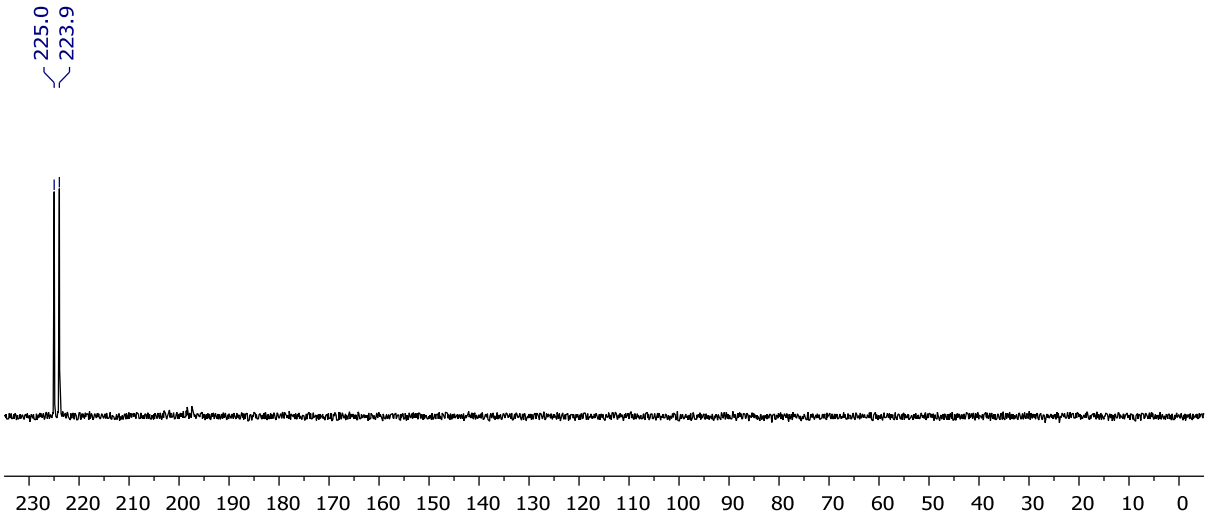

Figure S19. $^{31}P\{^1H\}$ NMR spectrum of the reaction between **1-O** and dihydrogen (1,2-$C_6H_4F_2$, 121 MHz).

Dinitrogen

1. PNP

Following the general procedure using $[Rh(COD)_2][BAr^F{}_4]$ (11.8 mg, 10.0 μmol), PNP (4 mg, 10 μmol), 1,2-$C_6H_4F_2$ (0.50 mL), and dinitrogen (1 atm) gave **2c-CH$_2$** after 3 h. The data are consistent with the literature.[7,10]

$^{31}P\{^1H\}$ NMR (121 MHz, 1,2-$C_6H_4F_2$): δ 70.5 (d, $^1J_{RhP}$ = 126).

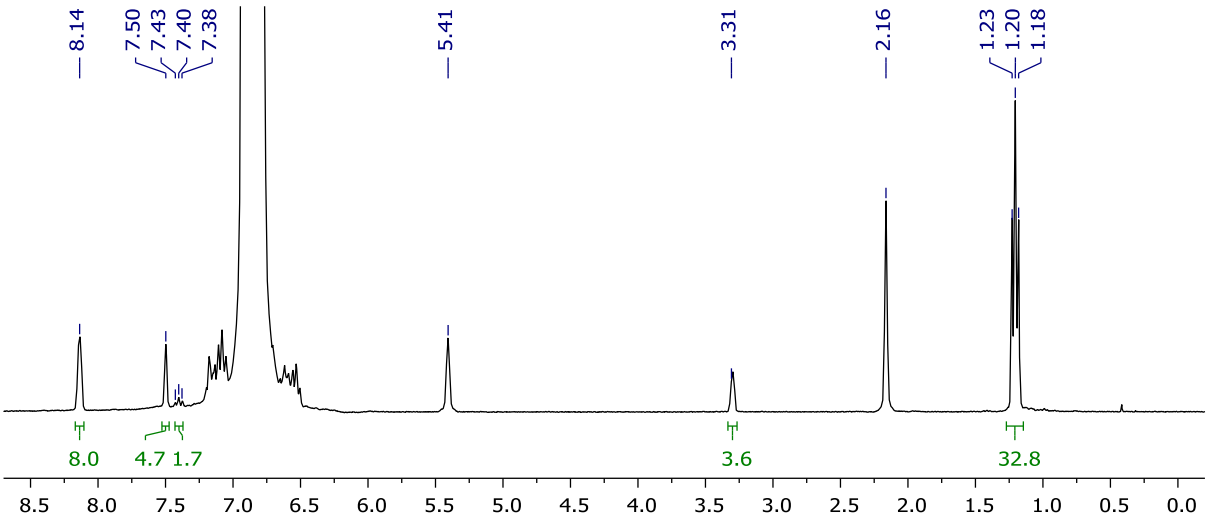

Figure S20. ^1H NMR spectrum of the reaction between **1-CH$_2$** and dinitrogen (1,2-$C_6H_4F_2$, 300 MHz).

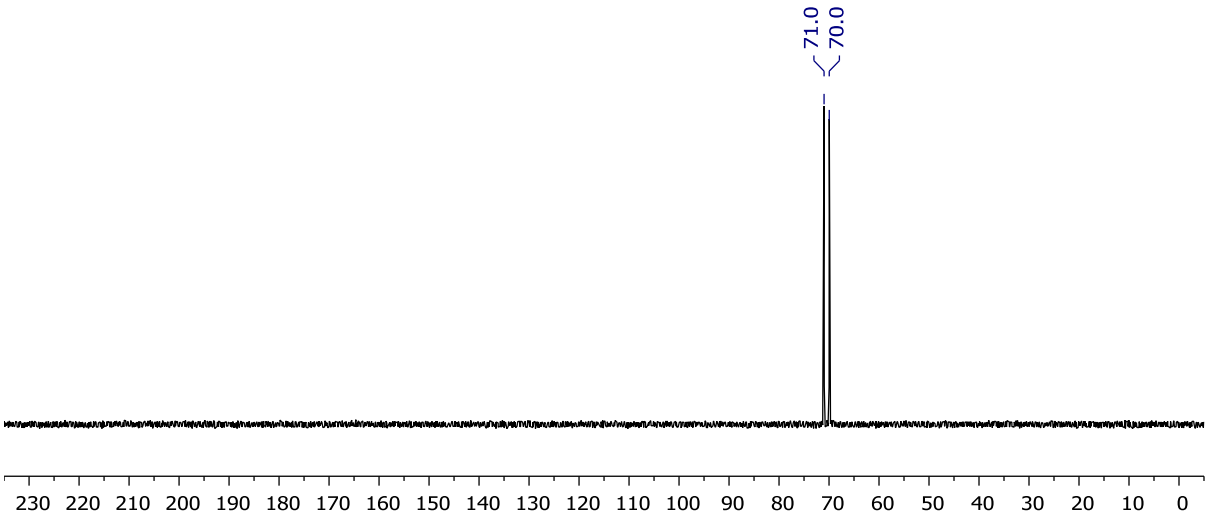

Figure S21. $^{31}P\{^1H\}$ NMR spectrum of the reaction between **1-CH$_2$** and dinitrogen (1,2-$C_6H_4F_2$, 121 MHz).

2. PONOP

Following the general procedure and using $[Rh(COD)_2][BAr^F{}_4]$ (11.7 mg, 9.89 µmol), PONOP (4.0 mg, 10 µmol), 1,2-$C_6H_4F_2$ (0.55 mL) and dinitrogen (1 atm) gave **2c-O** with 95% conversion after 2 days. Data are consistent with the literature.[8]

$^{31}P\{^1H\}$ NMR (121 MHz, 1,2-$C_6H_4F_2$): δ 210.6 (d, $^1J_{RhP}$ = 133).

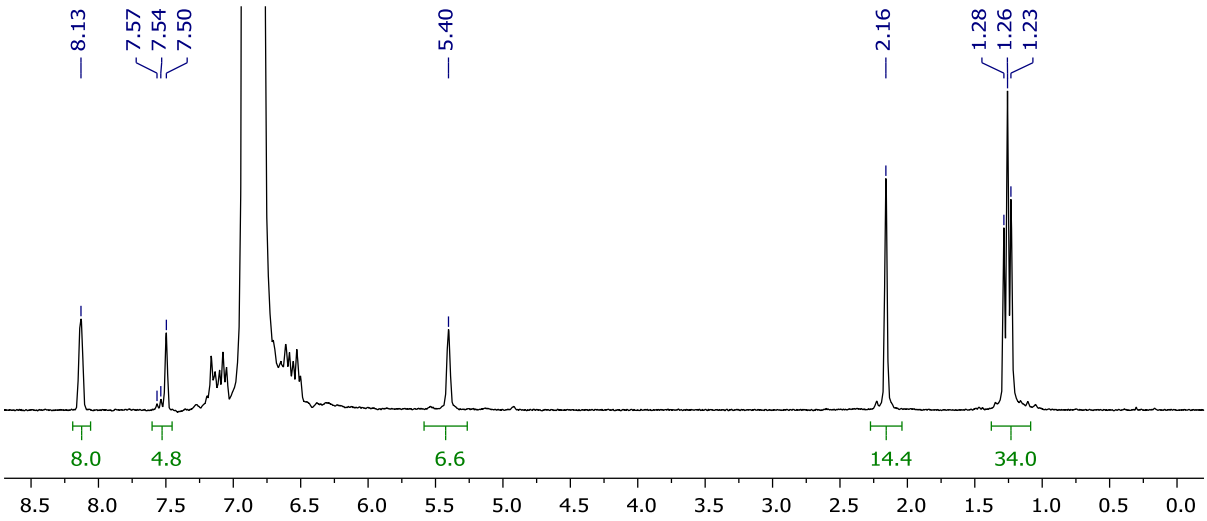

Figure S22. ^1H NMR spectrum of the reaction between **1-O** and dinitrogen (1,2-$C_6H_4F_2$, 300 MHz).

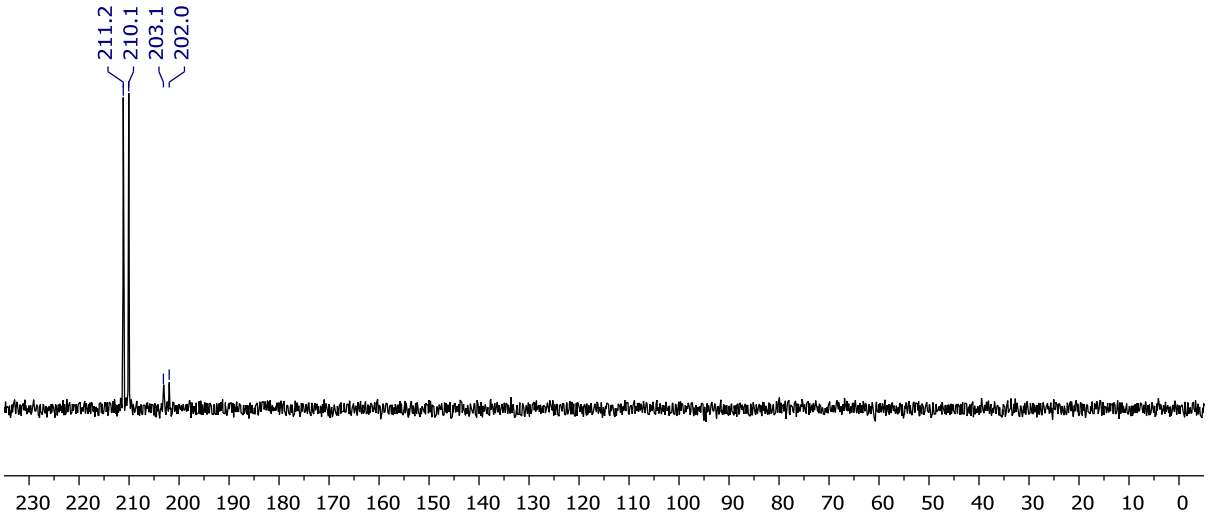

Figure S23. $^{31}P\{^1H\}$ NMR spectrum of the reaction between **1-O** and dinitrogen (1,2-$C_6H_4F_2$, 121 MHz).

Water

1. PNP

Following the general procedure and using $[Rh(COD)_2][BAr^F{}_4]$ (11.8 mg, 10.0 μmol), PNP (4.0 mg, 10 μmol), 1,2-$C_6H_4F_2$ (0.50 mL) and water (7.2 μL, 400 μmol) gave **2d-CH_2** after 3 h.

$^{31}P\{^1H\}$ NMR (121 MHz, 1,2-$C_6H_4F_2$): δ 63.1 (d, $^1J_{RhP}$ = 144).

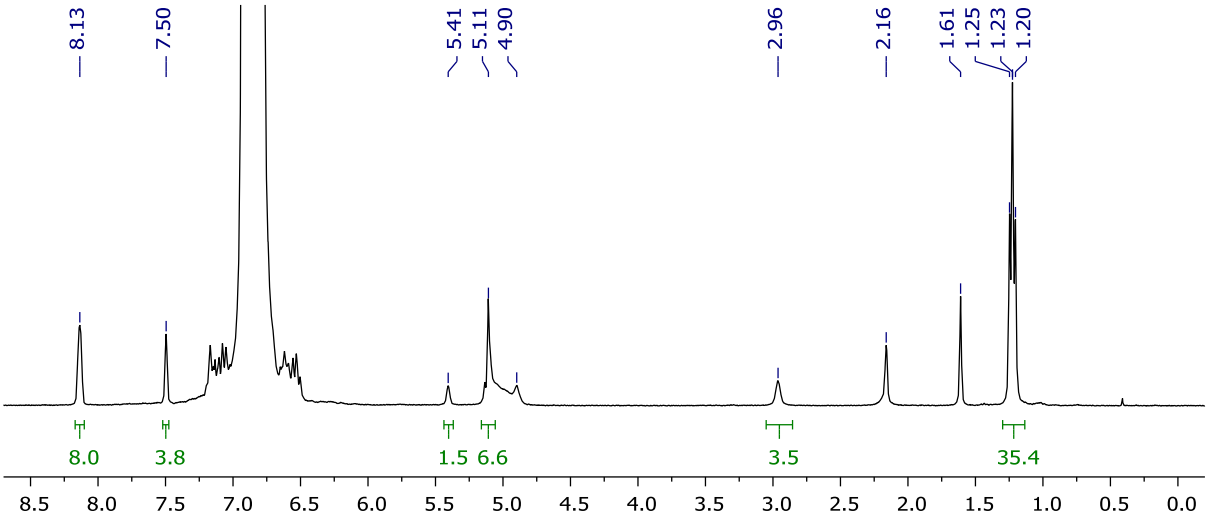

Figure S24. ^1H NMR spectrum of the reaction between **1-CH_2** and water (1,2-$C_6H_4F_2$, 300 MHz).

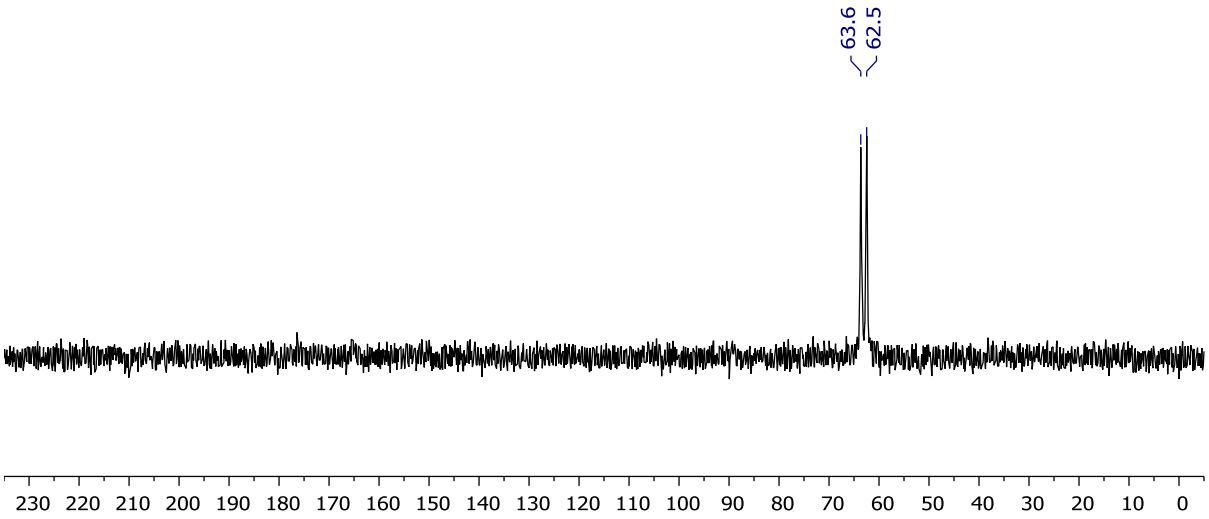

Figure S25. $^{31}P\{^1H\}$ NMR spectrum of the reaction between **1-CH_2** and water (1,2-$C_6H_4F_2$, 121 MHz).

2. PONOP

Following the general procedure and using $[Rh(COD)_2][BAr^F{}_4]$ (11.7 mg, 9.89 μmol), PONOP (4.0 mg, 10 μmol), 1,2-$C_6H_4F_2$ (0.55 mL) and water (7.2 μL, 400 μmol) gave **2d-O** with 88% conversion after 3 days.

$^{31}P\{^1H\}$ NMR (121 MHz, 1,2-$C_6H_4F_2$): δ 199.1 (d, $^1J_{RhP}$ = 150).

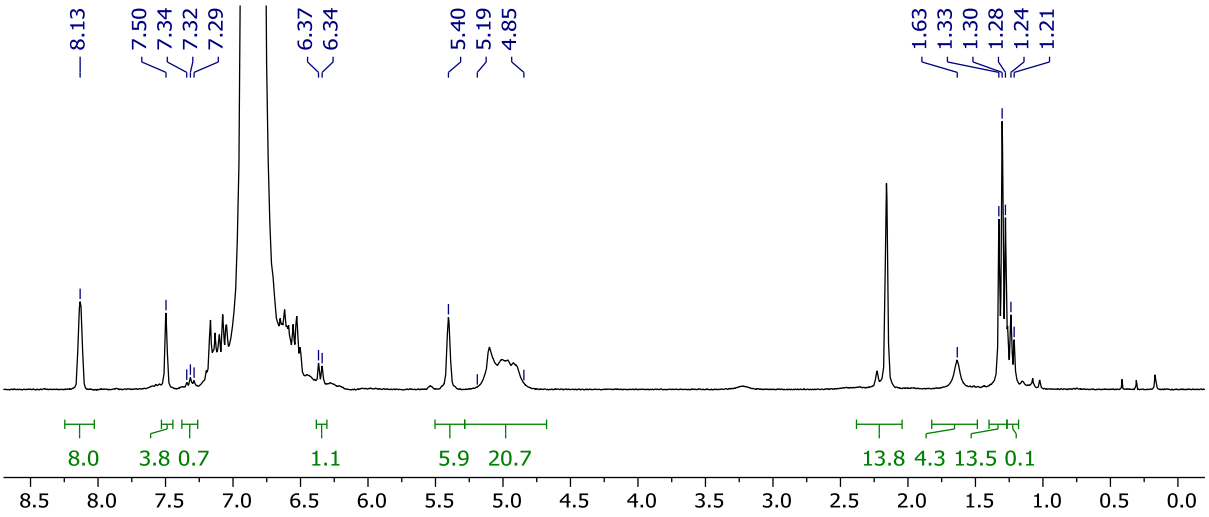

Figure S26. ^1H NMR spectrum of the reaction between **1-O** and water (1,2-$C_6H_4F_2$, 300 MHz).

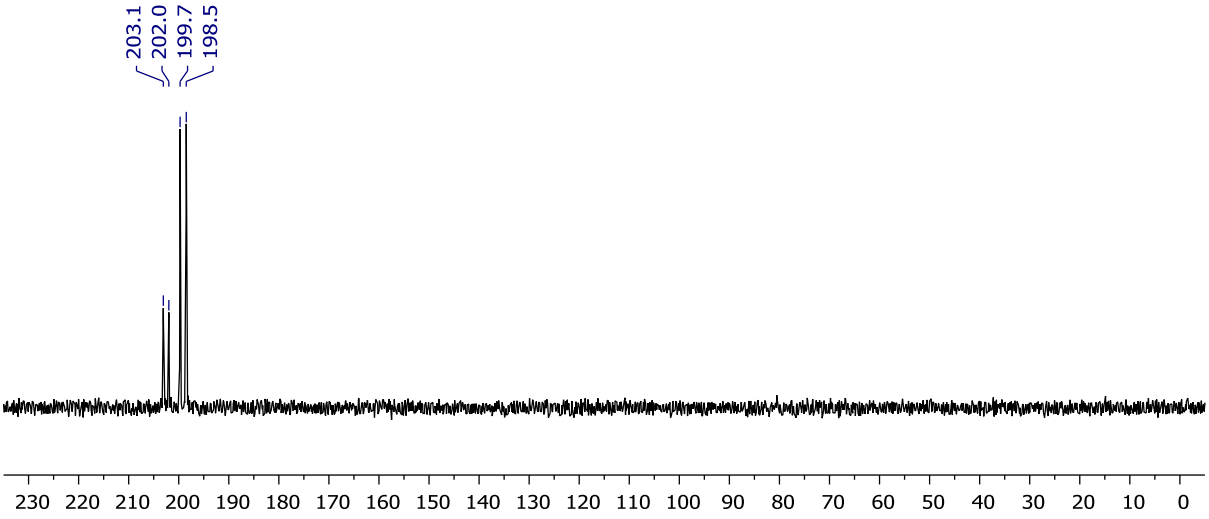

Figure S27. $^{31}P\{^1H\}$ NMR spectrum of the reaction between **1-O** and water (1,2-$C_6H_4F_2$, 121 MHz).

3. Preparation of [{Rh(PNP)}$_2$(COD)][BAr$^F{}_4$]$_2$ 1b-CH$_2$

A solution of [Rh(COD)$_2$][BAr$^F{}_4$] (206 mg, 174 μmol) and PNP (69.0 mg, 174 μmol) in 1,2-$C_6H_4F_2$ (*ca*. 5 mL) was mixed at ambient temperature for 5 mins and then layered with excess hexane (*ca*. 50 mL). Storage at ambient temperature afforded **1b-CH$_2$** as a mixture of red rods and yellow orange powder. Yield: 221 mg (90%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a solution in 1,2-$C_6H_4F_2$ at ambient temperature.

Anal. Calcd for $C_{118}H_{122}B_2F_{48}N_2P_4Rh_2$ (2831.5 gmol^{-1}): C, 50.05; H, 4.34; N, 0.99. Found: C, 50.14; H, 4.21; N, 0.94.

4. Preparation of [{Rh(PONOP)}$_2$(COD)][BAr$^F{}_4$]$_2$ 1b-O

A solution of [Rh(COD)$_2$][BAr$^F{}_4$] (240 mg, 203 μmol) and PONOP (80.9 mg, 203 μmol) in 1,2-$C_6H_4F_2$ (*ca*. 5 mL) was mixed at ambient temperature for 5 mins and then layered with excess hexane (*ca*. 50 mL). Storage at ambient temperature afforded **1b-O** as a mixture of red rods and yellow orange powder. Yield: 277 mg (96%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a solution in 1,2-$C_6H_4F_2$ at ambient temperature.

Anal. Calcd for $C_{114}H_{114}B_2F_{48}N_2O_4P_4Rh_2$ (2839.43 gmol^{-1}): C, 48.22; H, 4.05; N, 0.99. Found: C, 48.50; H, 4.07; N, 0.95.

5. Preparation of [Rh(PNP)(OH$_2$)][BAr$^F{}_4$] 2d-CH$_2$

A mixture of [Rh(COD)$_2$][BAr$^F{}_4$] (29.6 mg, 25.0 μmol), PNP (9.9 mg, 25 μmol), 1,2-$C_6H_4F_2$ (*ca*. 0.5 mL) and H_2O (0.12 mL, 6.3 mmol) was vigorously stirred at ambient temperature for 2 h. Excess hexane (*ca*. 40 mL) was added and the suspension cooled to -78 °C with vigorous stirring. The supernatant was filtered away, washed with hexane (2 x 2 mL), the solid dried redissolved in 1,2-$C_6H_4F_2$ (*ca*. 1 mL) layered with excess hexane (*ca*. 50 mL) and stored at ambient temperature to afford **2d-CH$_2$** as orange rods. Yield: 24.7 mg (71%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a solution in 1,2-$C_6H_4F_2$ at ambient temperature.

^{1}H NMR (500 MHz, 1,2-$C_6H_4F_2$, selected data): δ 8.12 – 8.15 (m, 8H, Ar^F), 7.49 (br, 4H, Ar^F), 7.16 (obsc. t, $^3J_{HH}$ = 7.8, 1H, py), 2.96 (vt, J_{PH} = 3.8, 4H, PCH$_2$), 1.44 (s, 2H, RhOH$_2$), 1.22 (vt, J_{PH} = 7, 36H, *t*Bu).
^{13}C{^{1}H} NMR (126 MHz, 1,2-$C_6H_4F_2$): δ 166.2 (vt, J_{PC} = 6, py), 162.5 (q, $^1J_{BC}$ = 50, Ar^F), 135.1 (s, Ar^F), 134.3 (s, py), 129.8 (qq, $^1J_{FC}$ = 32, $^1J_{BC}$ = 3, Ar^F), 125.1 (q, $^1J_{FC}$ = 272, Ar^F), 120.3 (vt, J_{PC} = 5, py), 117.6 (sept, $^3J_{FC}$ = 4, Ar^F), 34.5 (vt, J_{PC} = 7, *t*Bu{C}), 34.4 (vt, J_{PC} = 7, PCH$_2$), 28.4 (vt, J_{PC} = 4, *t*Bu{CH$_3$}).
^{31}P{^{1}H} NMR (121 MHz, 1,2-$C_6H_4F_2$): δ 63.1 (d, $^1J_{RhP}$ = 144).
Anal. Calcd for $C_{55}H_{57}BF_{24}NOP_2Rh$ (1379.69 gmol^{-1}): C, 47.88; H, 4.16; N, 1.02. Calcd for $C_{55}H_{57}BF_{24}NOP_2Rh{\cdot}H_2O$ (1397.71 gmol^{-1}): C, 47.26; H, 4.25; N, 1.00. Found: C, 47.89; H, 4.07; N, 0.98.

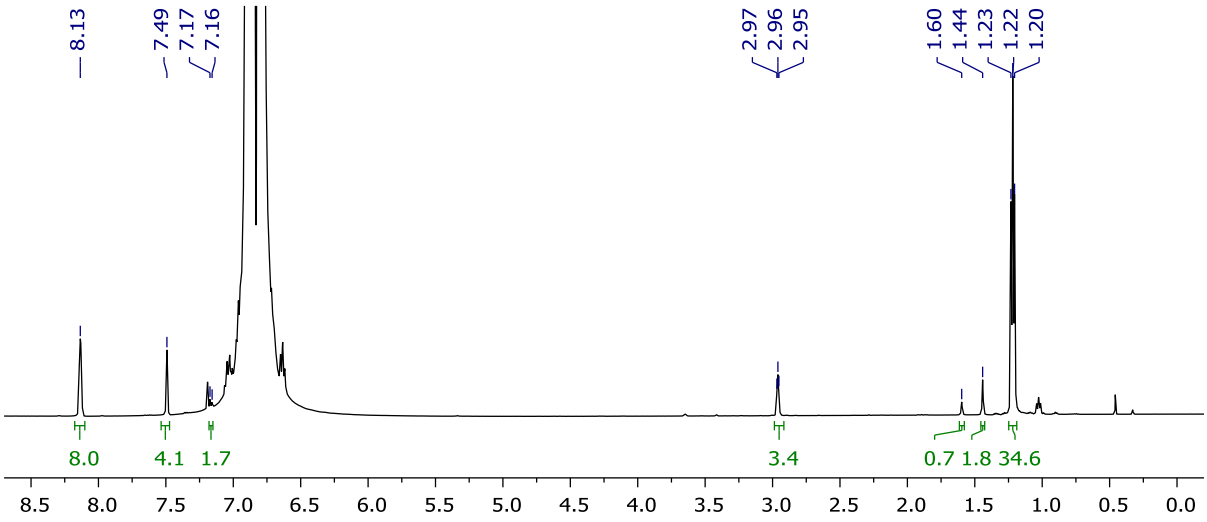

Figure S28. ^{1}H NMR spectrum of **2d-CH$_2$** (500 MHz, 1,2-$C_6H_4F_2$).

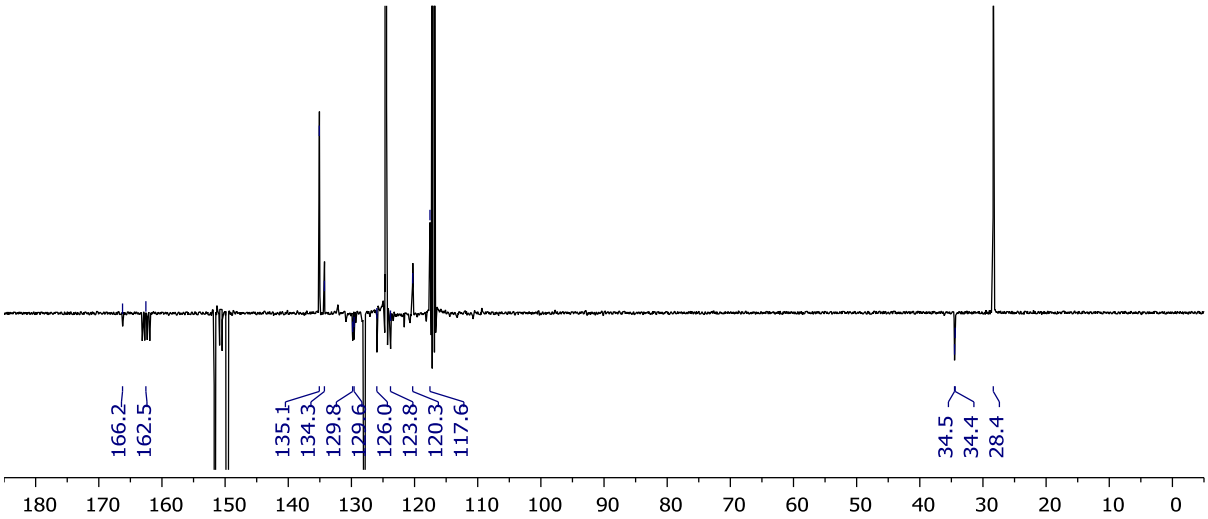

Figure S29. $^{13}C\{^{1}H\}$ APT NMR spectrum of **2d-CH$_2$** (126 MHz, 1,2-$C_6H_4F_2$).

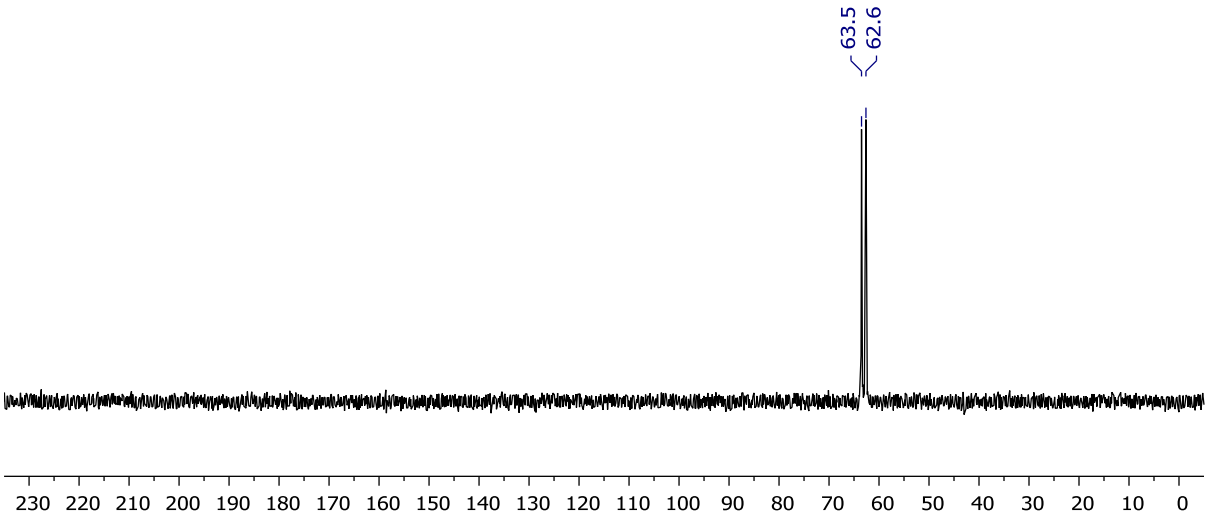

Figure S30. $^{31}P\{^{1}H\}$ NMR spectrum of **2d-CH$_2$** (121 MHz, 1,2-$C_6H_4F_2$).

6. Preparation of [Rh(PONOP)(OH$_2$)][BAr$^F_4$] 2d-O

A mixture of [{Rh(PONOP)}$_2$(COD)][BAr$^F_4$]$_2$ (35.2 mg, 12.4 μmol), 1,2-$C_6H_4F_2$ (*ca*. 0.5 mL) and H_2O (0.12 mL, 6.3 mmol) was vigorously stirred at ambient temperature for 2 h. Excess hexane (ca. 40 mL) was added and the suspension cooled to -78 °C with vigorous stirring. The supernatant was filtered away. The solid dried redissolved in 1,2-$C_6H_4F_2$ (*ca*. 1 mL) layered with excess hexane (*ca*. 50 mL) and stored at ambient temperature to afford **2d-O** as orange rods. Yield: 16.9 mg (49%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a solution in 1,2-$C_6H_4F_2$ at ambient temperature.

^{1}H NMR (500 MHz, 1,2-$C_6H_4F_2$): δ 8.10 – 8.17 (m, 8H, Ar^F), 7.49 (br, 4H, Ar^F), 7.33 (t, $^3J_{HH}$ = 8.1, 1H, py), 6.37 (d, $^3J_{HH}$ = 8.1, 1H, py), 2.13 (s, 2H, RhOH$_2$), 1.30 (vt, J_{PH} = 7, 36H, *t*Bu).

^{13}C{^{1}H} NMR (126 MHz, 1,2-$C_6H_4F_2$): δ 165.8 (vt, J_{PC} = 4, py), 162.6 (q, $^1J_{BC}$ = 50, Ar^F), 140.3 (s, py), 135.1 (Ar^F), 129.7 (qq, $^1J_{FC}$ = 32, $^1J_{BC}$ = 3, Ar^F), 125.4 (q, $^1J_{FC}$ = 272, Ar^F), 117.6 (sept, $^3J_{FC}$ = 4, Ar^F), 102.1 (vt, J_{PC} = 3, py), 39.8 (vtd, J_{PC} = 6, $^2J_{RhC}$ = 2, *t*Bu{C}), 26.8 (vt, J_{PC} = 4, *t*Bu{CH$_3$}).

^{31}P{^{1}H} NMR (121 MHz, 1,2-$C_6H_4F_2$): δ 199.4 (d, $^1J_{RhP}$ = 148).

Anal. Calcd for $C_{53}H_{53}BF_{24}NO_3P_2Rh$ (1383.64 gmol^{-1}): C, 46.01; H, 3.86; N, 1.01. $C_{53}H_{53}BF_{24}NO_3P_2Rh{\cdot}H_2O$ (1401.65 gmol^{-1}) C, 45.42; H, 3.96 N; 1.00. Found: C, 45.79; H, 3.68; N, 1.10.

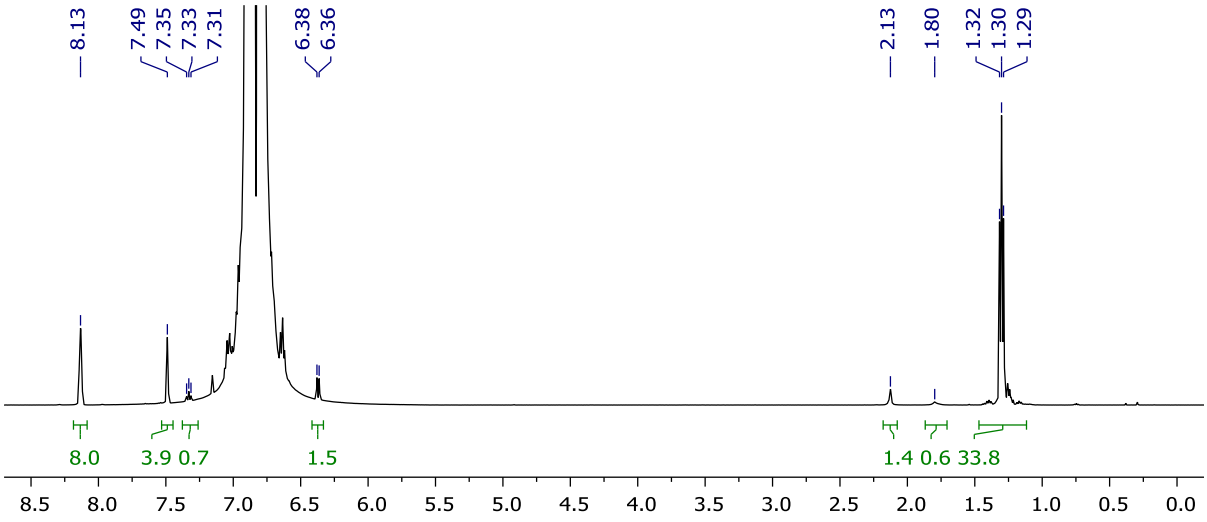

Figure S31. ^{1}H NMR spectrum of **2d-O** (500 MHz, 1,2-$C_6H_4F_2$).

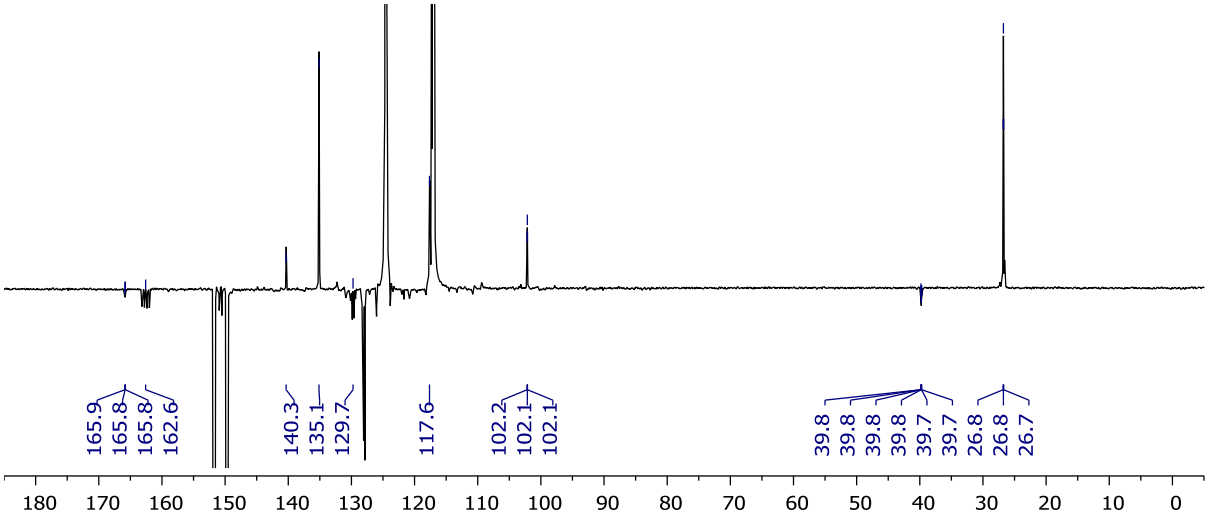

Figure S32. ^{13}C{^{1}H} APT NMR spectrum of **2d-O** (126 MHz, 1,2-$C_6H_4F_2$).

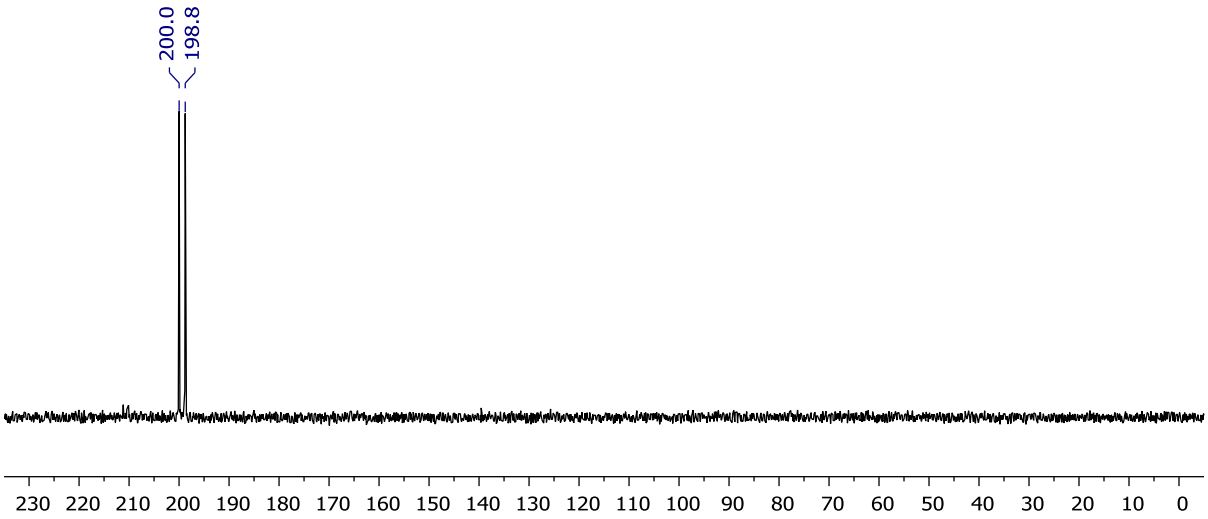

Figure S33. $^{31}P\{^{1}H\}$ NMR spectrum of **2d-O** (121 MHz, 1,2-$C_6H_4F_2$).

7. NMR scale reactions of isolated [{Rh(pincer)}$_2$(COD)][BAr$^F{}_4$]$_2$ 1b

General procedure

A 0.02 mol [Rh] L^{-1} solution of **1b** in 1,2-$C_6H_4F_2$ was either freeze-pump-thaw degassed and placed under an atmosphere of dinitrogen, or treated with three equivalents of terminal alkyne in an NMR tube fitted with a J. Young's valve and followed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, with constant mixing when not in the spectrometer.

Dinitrogen

1. [{Rh(PONOP)}$_2$(COD)][BAr$^F{}_4$]$_2$ (**1b-O**)

Following the general procedure and using **1b-O** (14.2 mg, 5.00 μmol), 1,2-$C_6H_4F_2$ (0.50 mL) and dinitrogen gave **2c-O** after 2 days. Data are consistent with the literature.[8]

^{31}P{^{1}H} NMR (121 MHz, 1,2-$C_6H_4F_2$): δ 210.6 (d, $^1J_{RhP}$ = 133).

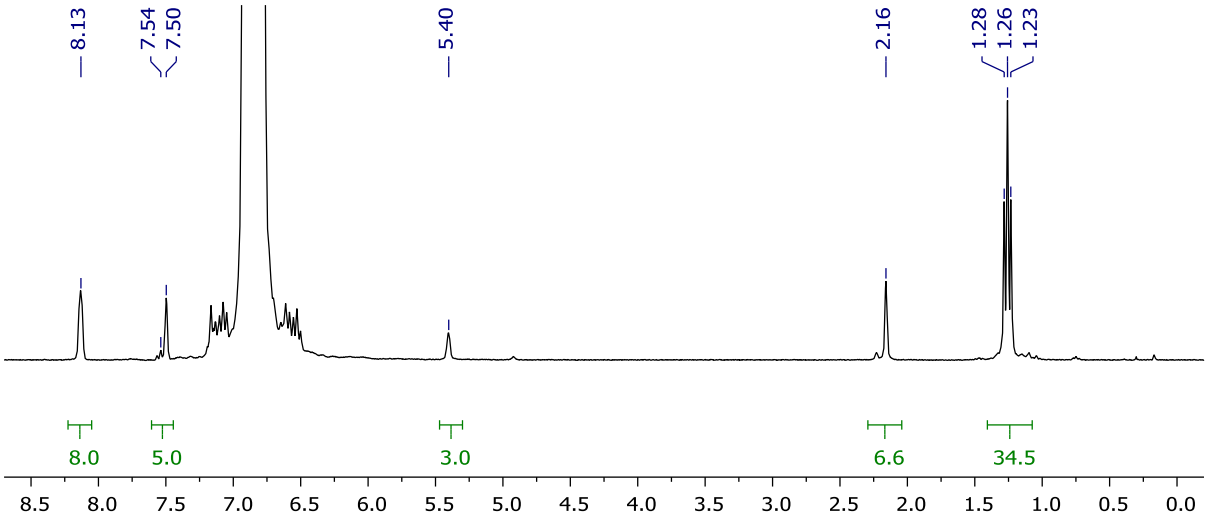

Figure S34. ^{1}H spectrum of the reaction between **1b-O** and dinitrogen (1,2-$C_6H_4F_2$, 300 MHz).

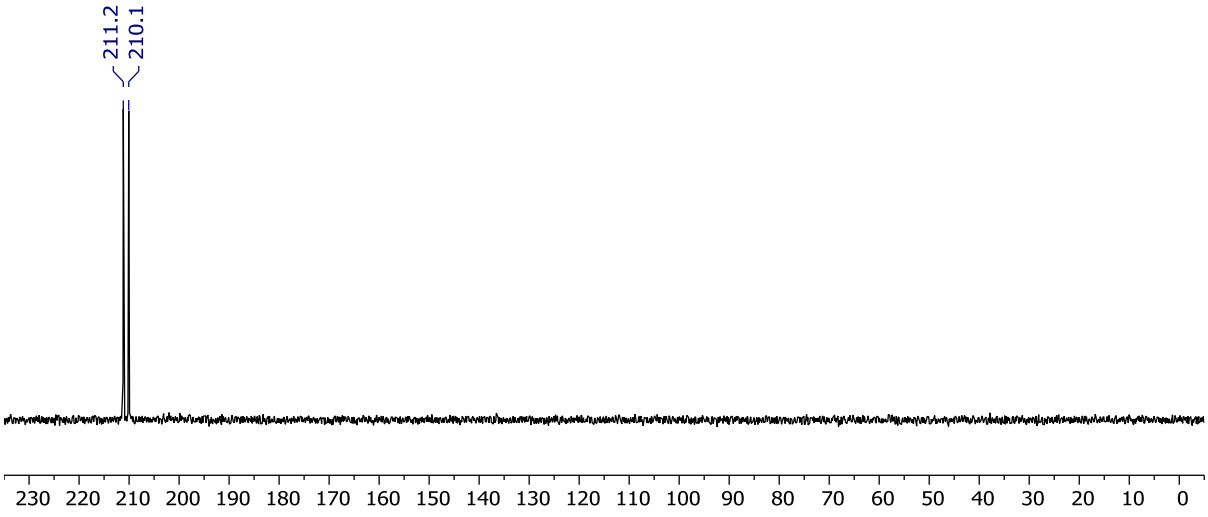

Figure S35. ^{31}P{^{1}H} spectrum of the reaction between **1b-O** and dinitrogen (1,2-$C_6H_4F_2$, 121 MHz).

HCC*t*Bu

1. [{Rh(PNP)}$_2$(COD)][BAr$^F{}_4$]$_2$ (**1b-CH$_2$**)

Following the general procedure and using **1b-CH$_2$** (14.2 mg, 5.0 μmol), 1,2-$C_6H_4F_2$ (0.50 mL) and HCC*t*Bu (0.2 mol L^{-1} solution, 73 μL, 15 μmol) gave **3a-CH$_2$** in < 5 mins.

$^{31}P\{^1H\}$ NMR (121 MHz, 1,2-$C_6H_4F_2$): δ 65.6 (d, $^1J_{RhP}$ = 139).

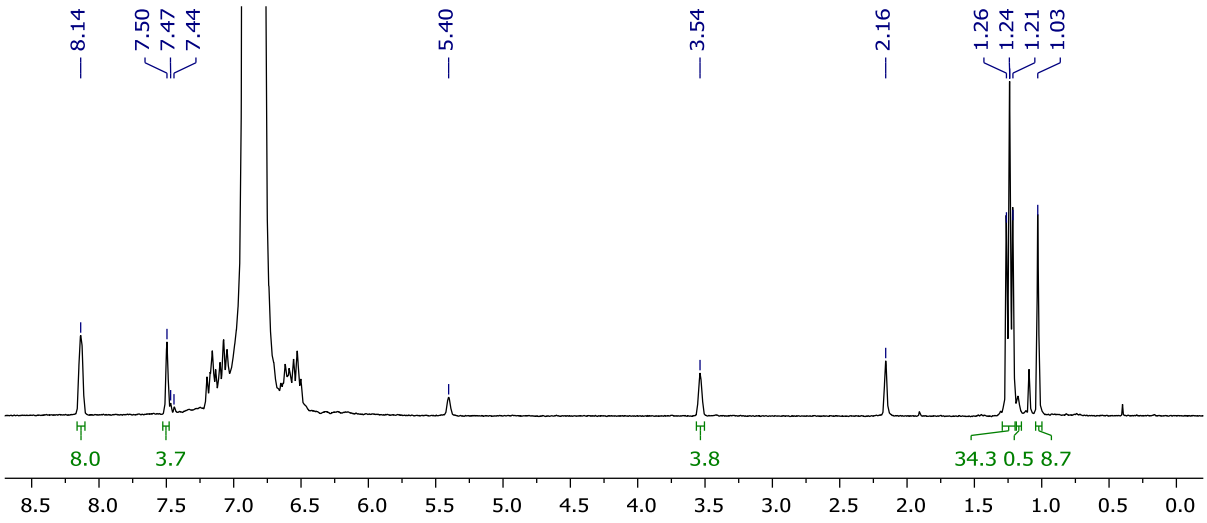

Figure S36. ^1H NMR spectrum of the reaction between **1b-CH$_2$** and HCC*t*Bu (1,2-$C_6H_4F_2$, 300 MHz).

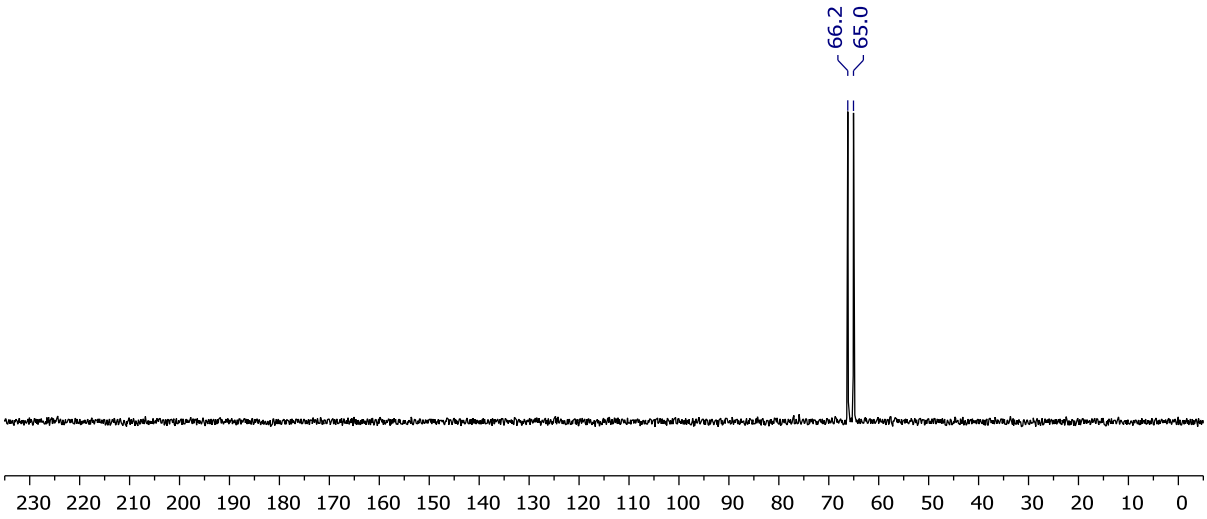

Figure S37. $^{31}P\{^1H\}$ NMR spectrum of the reaction between **1b-CH$_2$** and HCC*t*Bu (1,2-$C_6H_4F_2$, 121 MHz).

2. [{Rh(PONOP)}$_2$(COD)][BAr$^F{}_4$]$_2$ (**1b-O**)

Following the general procedure and using **1b-O** (13.8 mg, 4.86 μmol), 1,2-$C_6H_4F_2$ (0.50 mL) and HCC*t*Bu (0.20 mol L^{-1} solution, 73 μL, 15 μmol) gave **3a-O** after 18 h.

$^{31}P\{^1H\}$ NMR (121 MHz, 1,2-$C_6H_4F_2$): δ 206.5 (d, $^1J_{RhP}$ = 144).

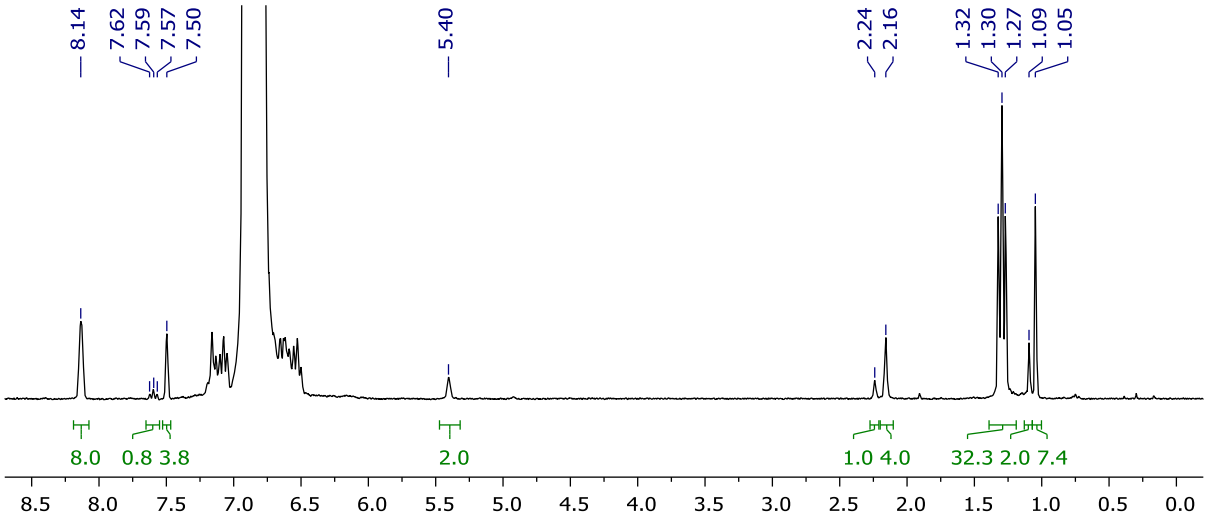

Figure S38. ^{1}H NMR spectrum of the reaction between **1b-O** and HCC*t*Bu (1,2-$C_6H_4F_2$, 300 MHz).

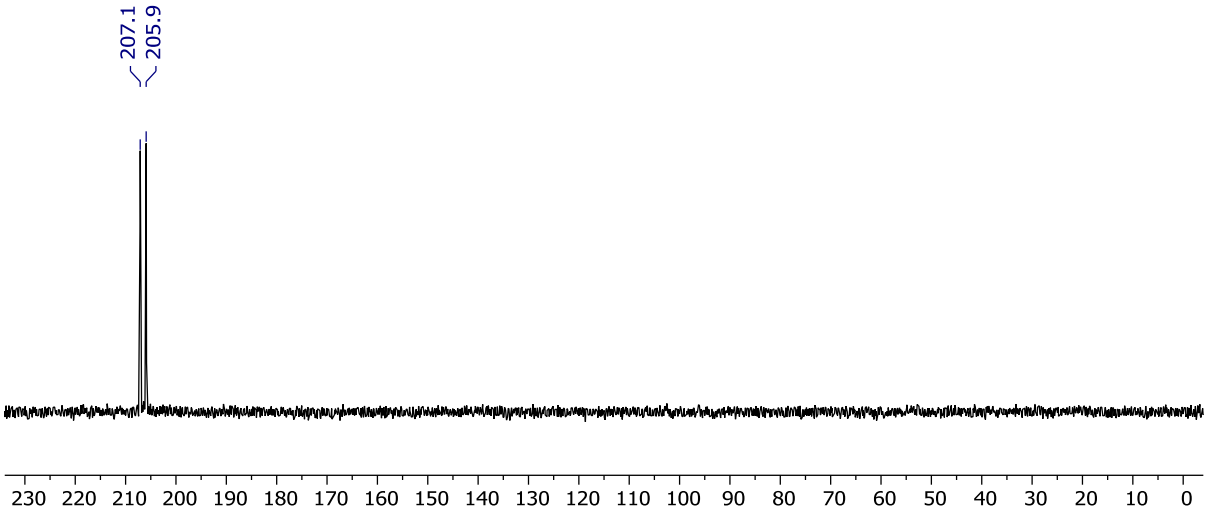

Figure S39. $^{31}P\{^1H\}$ NMR spectrum of the reaction between **1b-O** and HCC*t*Bu (1,2-$C_6H_4F_2$, 121 MHz).

HCCAr'

1. [{Rh(PNP)}$_2$(COD)][BAr$^F{}_4$]$_2$ (**1b-CH$_2$**)

Following the general procedure and using **1b-CH$_2$** (14.2 mg, 5.0 μmol), 1,2-$C_6H_4F_2$ (0.50 mL) and HCCAr' (3.2 mg, 15 μmol) gave **3b-CH$_2$** in < 5 mins.

^{31}P{^{1}H} NMR (121 MHz, 1,2-$C_6H_4F_2$): δ 65.9 (d, $^1J_{RhP}$ = 137).

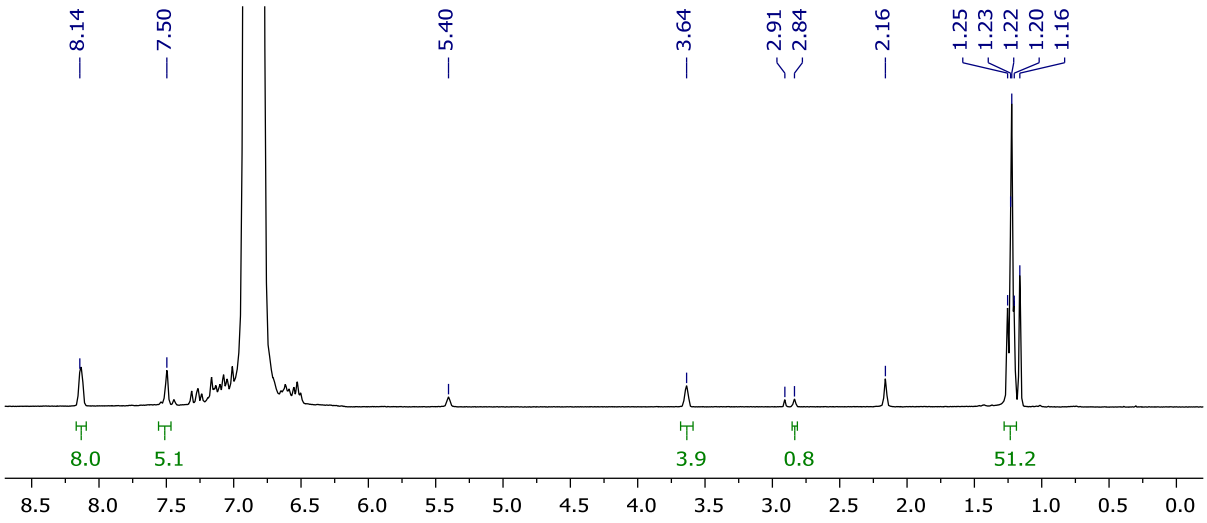

Figure S40. ^{1}H NMR spectrum of the reaction between **1b-CH$_2$** and HCCAr' (1,2-$C_6H_4F_2$, 300 MHz).

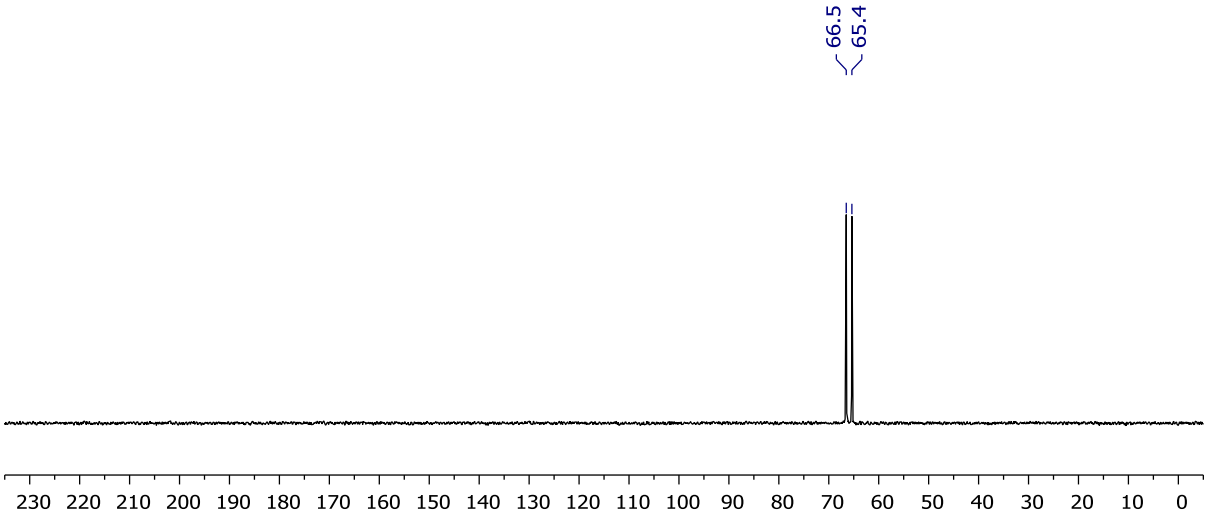

Figure S41. ^{31}P{^{1}H} NMR spectrum of the reaction between **1b-CH$_2$** and HCCAr' (1,2-$C_6H_4F_2$, 121 MHz).

2. [{Rh(PONOP)}$_2$(COD)][BAr$^F{}_4$]$_2$ (**1b-O**)

Following the general procedure and using **1b-O** (14.6 mg, 5.14 μmol), 1,2-$C_6H_4F_2$ (0.51 mL) and HCCAr' (3.3 mg, 15 μmol) gave a mixture of **2e-O** and **3b-O** in an approximate 7:3 ratio after 2 days.

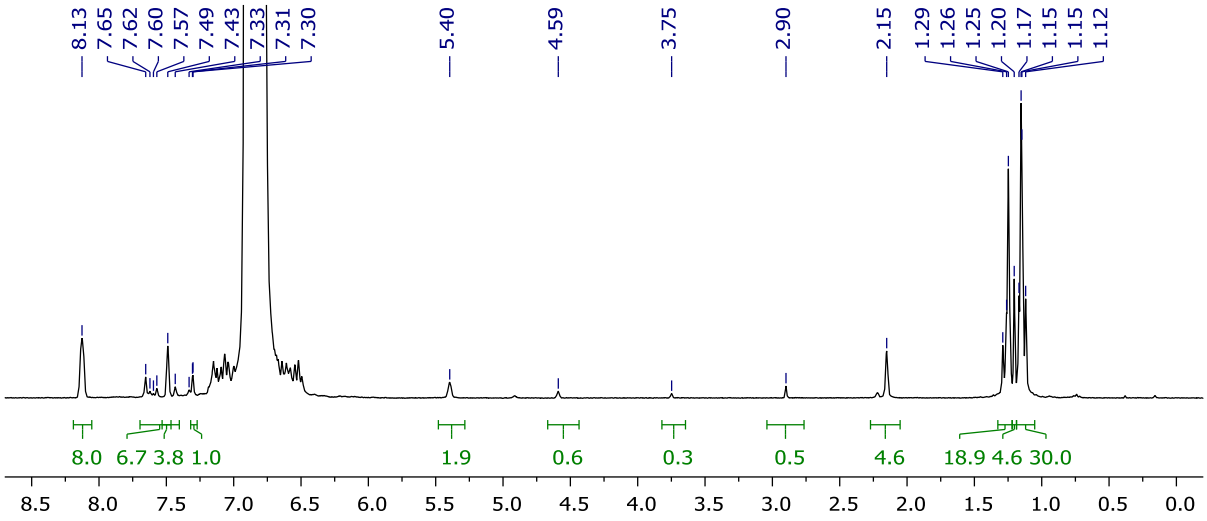

Figure S42. ^{1}H NMR spectrum of the reaction between **1b-O** and HCCAr' (1,2-$C_6H_4F_2$, 300 MHz).

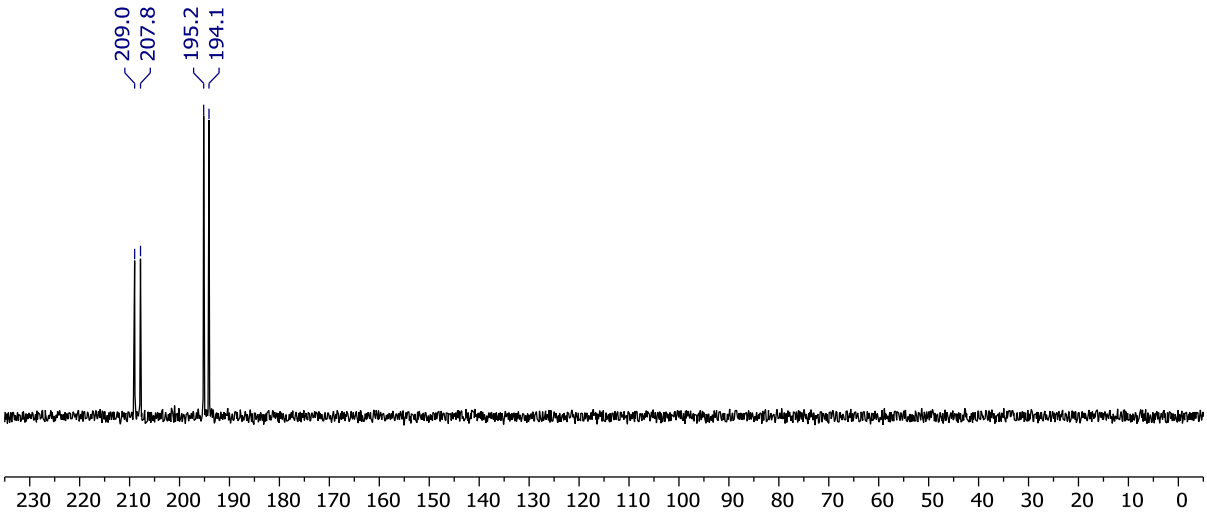

Figure S43. ^{31}P{^{1}H} NMR spectrum of the reaction between **1b-O** and HCCAr' (1,2-$C_6H_4F_2$, 121 MHz).

8. Preparation of [Rh(PNP)(CCH*t*Bu)][BAr$^F_4$] 3a-CH$_2$

A solution of HCC^{t}Bu (0.20 mol L^{-1}, 0.37 mL, 74 µmol) in 1,2-$C_6H_4F_2$ was added at ambient temperature to a solution of **1b-CH$_2$** (70.7 mg, 25.2 µmol) in 1,2-$C_6H_4F_2$ (2 mL) and stirred for 1 h. The resulting solution was layered with excess hexane (*ca*. 20 mL) and stored at ambient temperature to afford **3a-CH$_2$** as green blocks. Yield: 69.8 mg (96%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a solution in 1,2-$C_6H_4F_2$ at ambient temperature.

^{1}H NMR (500 MHz, 1,2-$C_6H_4F_2$): δ 8.09 – 8.16 (m, 8H, Ar^F), 7.48 (br, 4H, Ar^F), 7.45 (t, $^3J_{HH}$ = 7.9, 1H, py), 7.17 (d, $^3J_{HH}$ = 7.9, 2H, py), 3.52 (vt, J_{PH} = 3.6, 4H, PCH$_2$), 1.22 (vt, J_{PH} = 7, 36H, P*t*Bu), 1.16 (s, 1H, RhCCH*t*Bu), 1.01 (s, 9H, RhCCH*t*Bu).

^{13}C{^{1}H} NMR (126 MHz, 1,2-$C_6H_4F_2$): δ 317.5 (HMBC, RhCCH*t*Bu), 164.9 (vtd, J_{PC} = 5, $^2J_{RhC}$ = 2, py), 162.5 (q,$^1J_{BC}$ = 50, Ar^F), 141.1 (s, py), 135.1 (Ar^F), 129.7 (qq, $^1J_{FC}$ = 32, $^1J_{BC}$ = 3, Ar^F), 125.1 (q, $^1J_{FC}$ = 272, Ar^F), 120.9 (vt, J_{PC} = 5, py), 120.7 (dt, $^2J_{RhC}$ = 15, $^3J_{PC}$ = 5, RhCCH*t*Bu), 117.6 (sept, $^3J_{FC}$ = 4, Ar^F), 36.2 (vt, J_{PC} = 8, PCH$_2$), 35.8 (vtd, J_{PC} = 8, $^2J_{RhC}$ = 2, P*t*Bu{C}), 31.7 (s, RhCCH*t*Bu{CH$_3$}), 29 (obscured, RhCCH*t*Bu{C}), 28.8 (vt, J_{PC} = 3, P*t*Bu{CH$_3$}).

^{31}P{^{1}H} NMR (121 MHz, 1,2-$C_6H_4F_2$): δ 65.6 (d, $^1J_{RhP}$ = 139).

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 65.7 (d, $^1J_{RhP}$ = 139).

Anal. Calcd for $C_{59}H_{61}BF_{24}NO_2P_2Rh$ (1443.82 gmol^{-1}): C, 50.75; H, 4.54; N, 0.97. Found: C, 50.62; H, 4.39; N, 0.97.

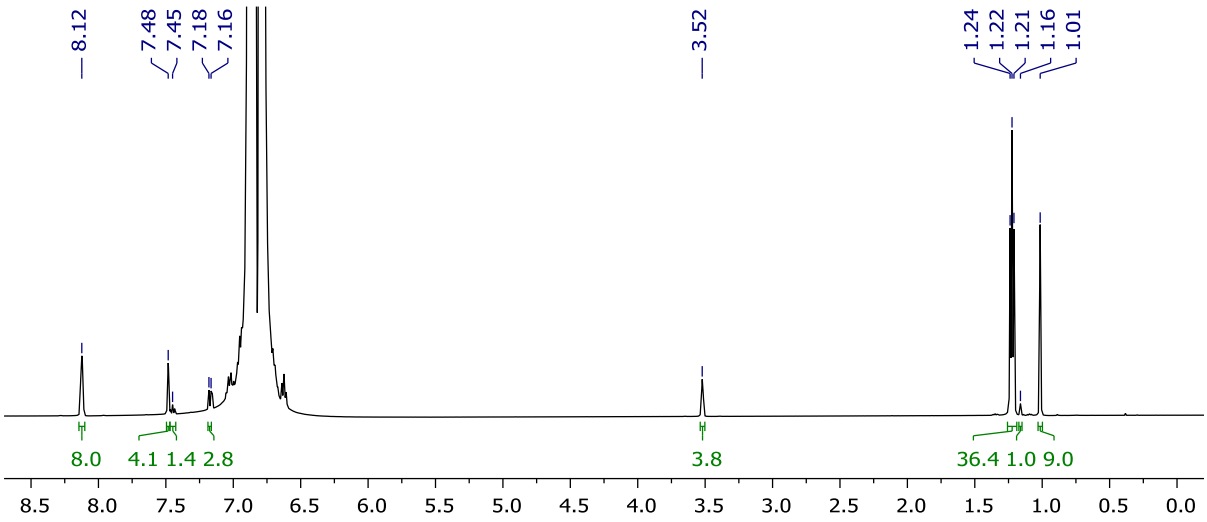

Figure S44. ^{1}H NMR spectrum of **3a-CH$_2$** (1,2-$C_6H_4F_2$, 500 MHz).

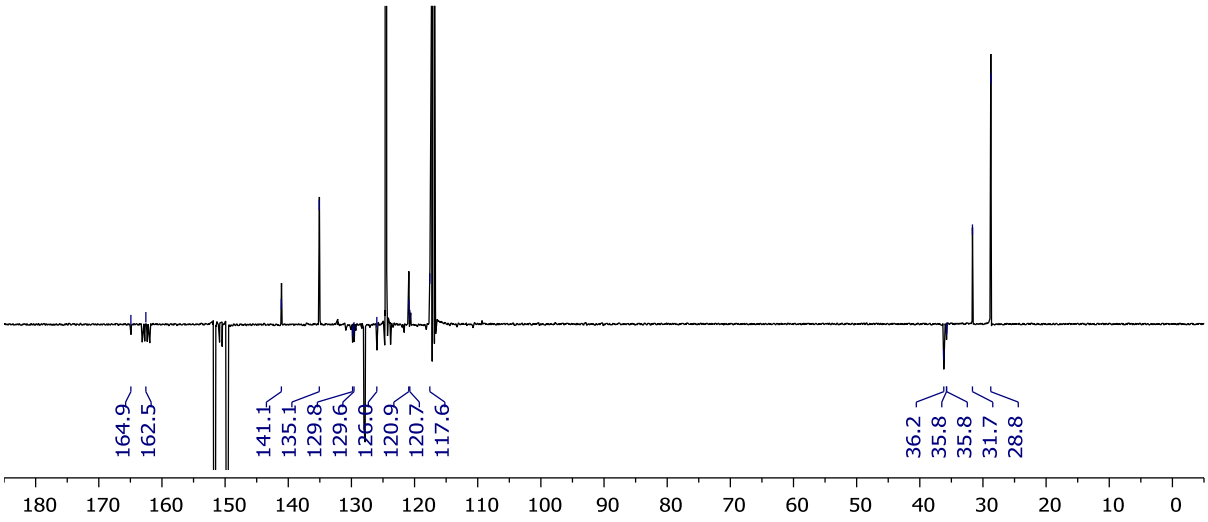

Figure S45. $^{13}C\{^{1}H\}$ APT NMR spectrum of **3a-CH$_2$** (1,2-$C_6H_4F_2$, 126 MHz).

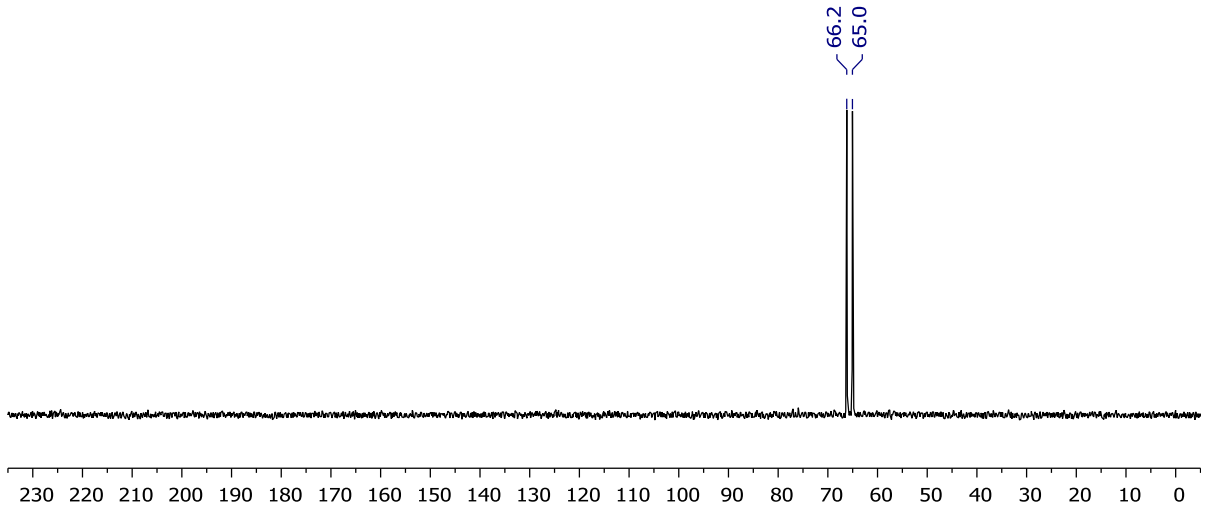

Figure S46. $^{31}P\{^{1}H\}$ NMR spectrum of **3a-CH$_2$** (1,2-$C_6H_4F_2$, 121 MHz).

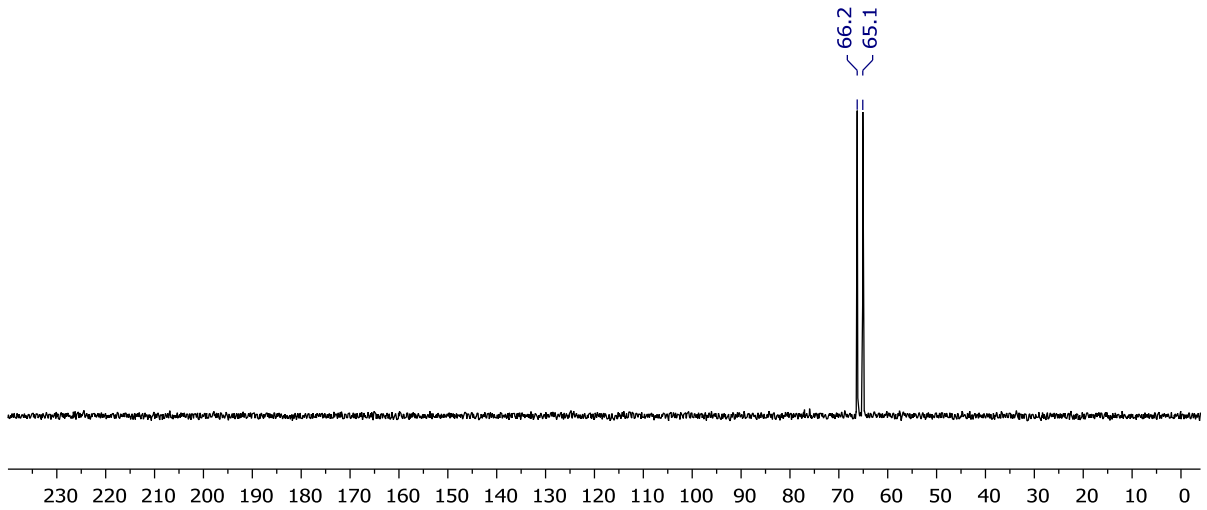

Figure S47. $^{31}P\{^{1}H\}$ NMR spectrum of **3a-CH$_2$** (CD_2Cl_2, 162 MHz).

9. Preparation of [Rh(PONOP)(CCH*t*Bu)][BAr$^F_4$] 3a-O

A solution of HCC*t*Bu (0.20 mol L^{-1}, 0.37 mL, 74 µmol) in 1,2-$C_6H_4F_2$ was added at ambient temperature to a solution of **1b-O** (71.6 mg, 25.2 µmol) in 1,2-$C_6H_4F_2$ (2 mL) and stirred for 18 h. The resulting solution was layered with excess hexane (*ca*. 20 mL) and stored at ambient temperature to afford **3a-O** as indigo blocks. Yield: 62.5 mg (86%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a solution in 1,2-$C_6H_4F_2$ at ambient temperature.

^{1}H NMR (500 MHz, 1,2-$C_6H_4F_2$, selected data): *δ* 8.07 – 8.18 (m, 8H, Ar^F), 7.59 (t, $^3J_{HH}$ = 8.2, 1H, py), 7.49 (br, 4H, Ar^F), 2.24 (s, 1H, RhCCH*t*Bu), 1.29 (vt, J_{PH} = 8, 36H, P*t*Bu), 1.04 (s, 9H, RhCCH*t*Bu).
^{13}C{^{1}H} NMR (126 MHz, 1,2-$C_6H_4F_2$): *δ* 330.0 (HMBC run in CD_2Cl_2, RhCCH*t*Bu), 163.5 (vt, J_{PC} = 3, py), 162.6 (q, $^1J_{BC}$ = 50, Ar^F), 147.7 (s, py), 135.1 (s, Ar^F), 129.7 (qq, $^1J_{FC}$ = 32, $^1J_{BC}$ = 3, Ar^F), 125.1 (q, $^1J_{FC}$ = 272, Ar^F), 121.6 (dt, $^2J_{RhC}$ = 15, $^3J_{PC}$ = 4, RhCCH*t*Bu), 117.6 (sept, $^3J_{FC}$ = 4, Ar^F), 103.0 (t,$^3J_{RhC}$ = 3, py), 40.9 (vtd, J_{PC} = 6, J_{RhC} = 3, P*t*Bu{C}), 31.6 (s, RhCCH*t*Bu{CH_3}), 30.7 (s, RhCCH*t*Bu{C}), 26.9 (t, $^2J_{PC}$ = 4, P*t*Bu{CH_3}).
^{31}P{^{1}H} NMR (121 MHz, 1,2-$C_6H_4F_2$): *δ* 206.5 (d, $^1J_{RhP}$ = 144).
^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2): *δ* 206.8 (d, $^1J_{RhP}$ = 144).
Anal. Calcd for $C_{59}H_{61}BF_{24}NO_2P_2Rh$ (1447.77 gmol^{-1}): C, 48.95; H, 4.25; N, 0.97. Found: C, 48.84; H, 4.07; N, 0.95.

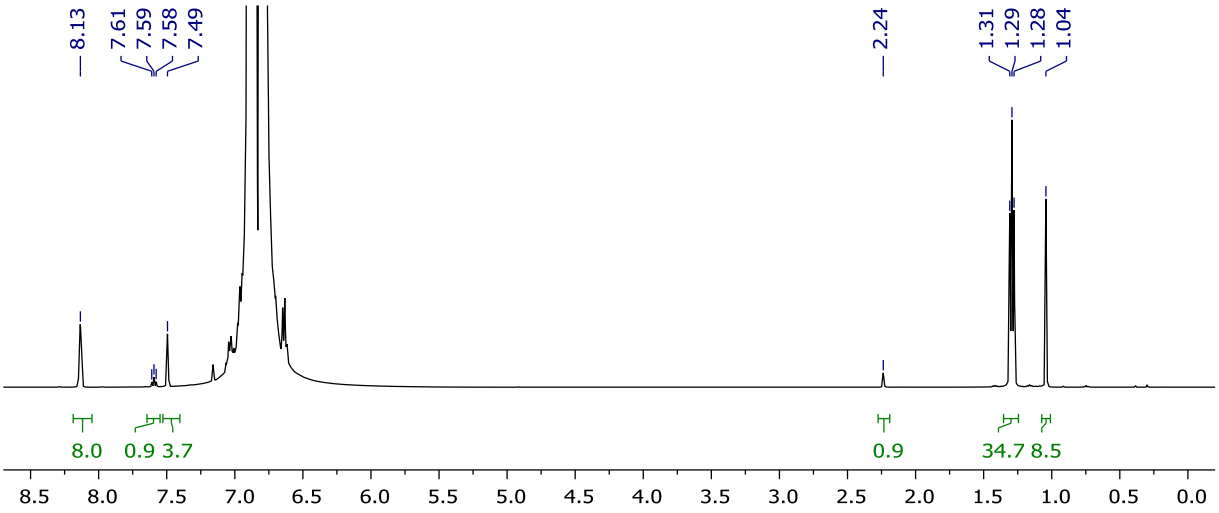

Figure S48. ^{1}H NMR spectrum of **3a-O** (1,2-$C_6H_4F_2$, 500 MHz).

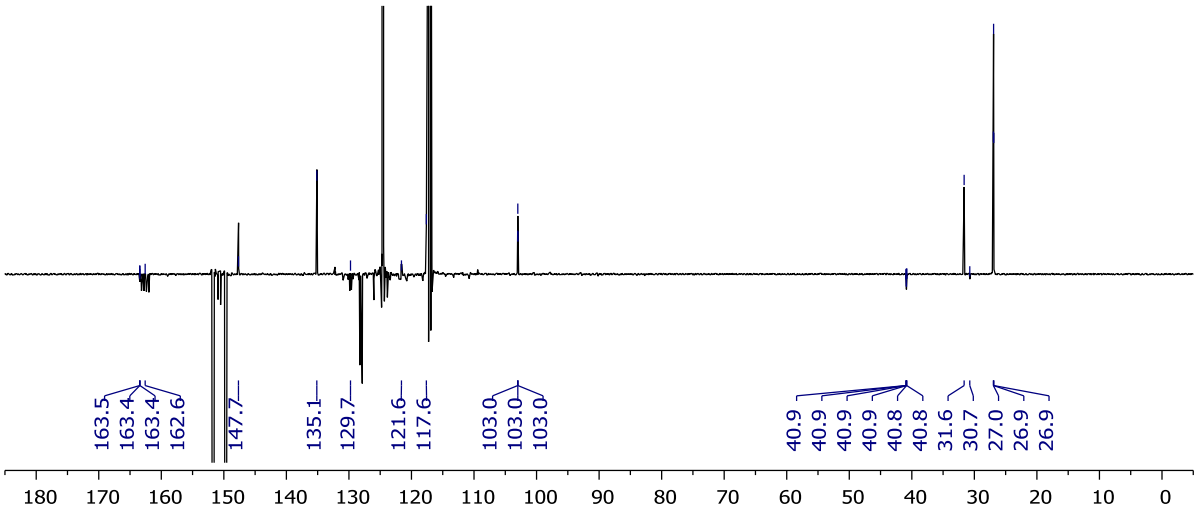

Figure S49. $^{13}C\{^{1}H\}$ APT NMR spectrum of **3a-O** (1,2-$C_6H_4F_2$, 126 MHz).

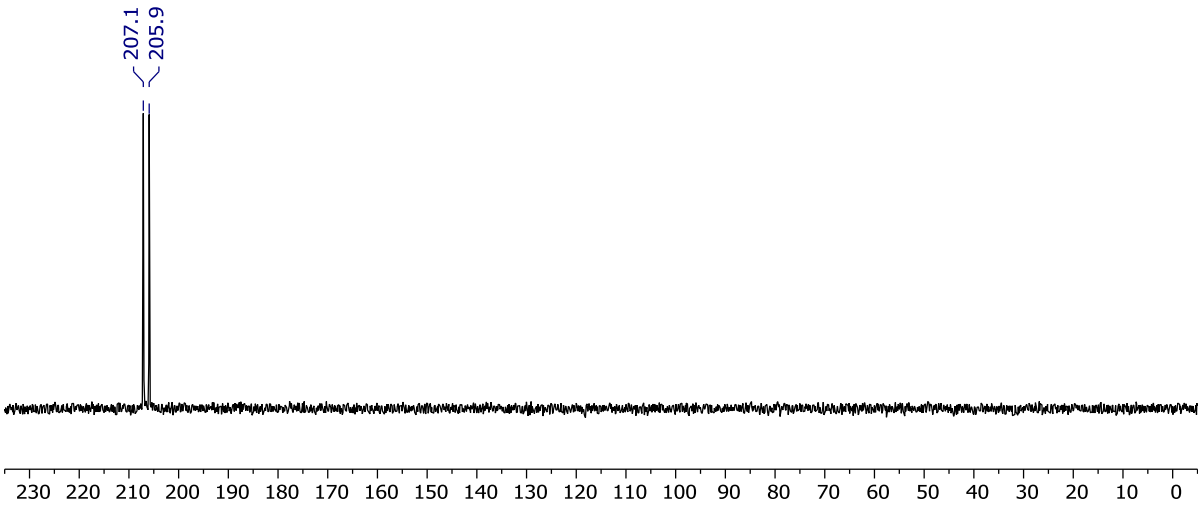

Figure S50. $^{31}P\{^{1}H\}$ NMR spectrum of **3a-O** (1,2-$C_6H_4F_2$, 121 MHz).

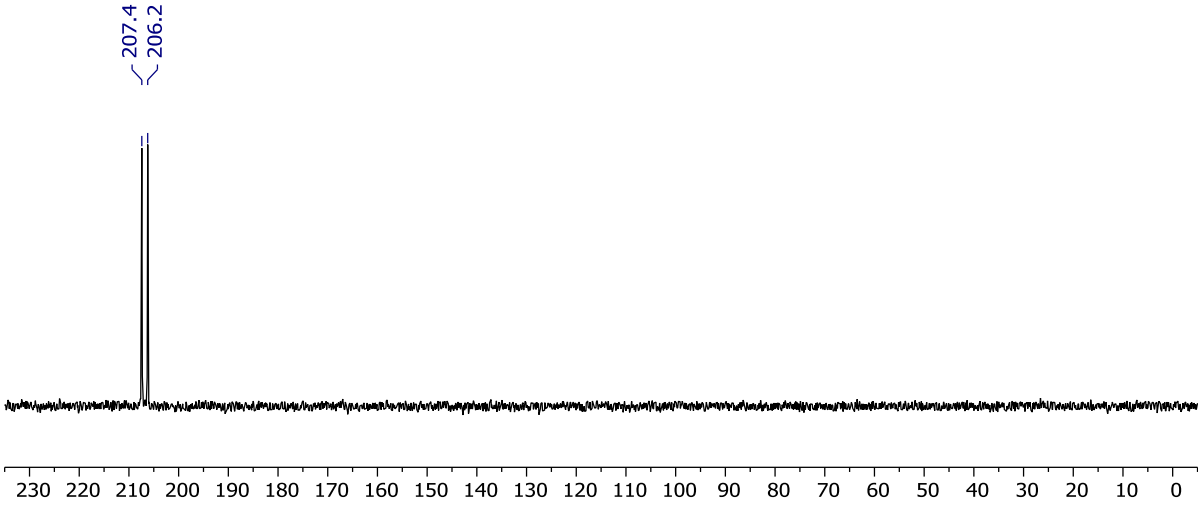

Figure S51. $^{31}P\{^{1}H\}$ NMR spectrum of **3a-O** (CD_2Cl_2, 121 MHz).

10. Preparation of [Rh(PNP)(CCHAr')][BAr$^{F}_{4}$] 3b-CH_2

A solution of **1b-CH_2** (70.7 mg, 25 μmol) and HCCAr' (8.0 mg, 75 μmol) in 1,2-$C_6H_4F_2$ (*ca*. 1mL) was stirred at ambient temperature for 1 h. The dark green solution was layered with excess hexane (*ca*. 40 mL) to afford **3b-CH_2** as malachite rods. Yield: 71.4 mg (90%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a solution in 1,2-$C_6H_4F_2$ at ambient temperature.

^{1}H NMR (500 MHz, 1,2-$C_6H_4F_2$): *δ* 8.07 – 8.18 (m, 8H, Ar^F), 7.50 (obsc. t, $^{3}J_{HH}$ = 7.8, 1H, py), 7.49 (br, 4H, Ar^F), 7.26 (br, 1H, Ar'-H), 7.25 (d, $^{3}J_{HH}$ = 7.8, 2H, py), 7.00 (s, 2H, Ar'-H), 3.63 (vt, J_{PH} = 3.6, 4H, PCH_2), 2.82 (s, 1H, RhCCHAr'), 1.24 (s, Ar'-*t*Bu, 9H), 1.22 (s, Ar'-*t*Bu, 9H),1.22 (vt, J_{PH} = 7.1, 36H, P*t*Bu).
^{13}C{^{1}H} NMR (126 MHz, 1,2-$C_6H_4F_2$): *δ* 326.9 (HMBC, RhCCHAr'), 165.0 (vt, J_{PC} = 5, py), 162.5 (q,$^{1}J_{BC}$ = 50, Ar^F), 141.4 (s, py), 135.0 (s, Ar^F), 129.6 (qq, $^{1}J_{FC}$ = 32, $^{1}J_{BC}$ = 3, Ar^F), 125.1 (q, $^{1}J_{FC}$ = 272, Ar^F), 121.6 (s, Ar'{CH}), 121.1 (vt, J_{PC} = 5, py), 121.1 (s, Ar'{CH}), 117.1 (sept, $^{3}J_{FC}$ = 4, Ar^F), 115.2 (dt, $^{2}J_{RhC}$ = 16, $^{3}J_{PC}$ = 5, RhCCHAr'), 36.1 (vt, J_{PC} = 8, PCH_2), 35.6 (vtd, J_{PC} = 8, $^{2}J_{RhC}$ = 2, P*t*Bu{C}), 34.7 (s, Ar'-*t*Bu{C}), 30.8 (s, Ar'-*t*Bu{CH_3}), 28.6 (vt, J_{PC} = 3, P*t*Bu{CH_3}). The Ar'{C} resonances were not unambiguously located.
^{31}P{^{1}H} NMR (121 MHz, 1,2-$C_6H_4F_2$): *δ* 65.9 (d, $^{1}J_{RhP}$ = 137).
^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 65.7 (d, $^{1}J_{RhP}$ = 139).
Anal. Calcd for $C_{71}H_{77}BF_{24}NP_2Rh$ (1576.03 gmol^{-1}): C, 54.11; H, 4.92; N, 0.89. Found: C, 53.95; H, 4.81; N, 0.83.

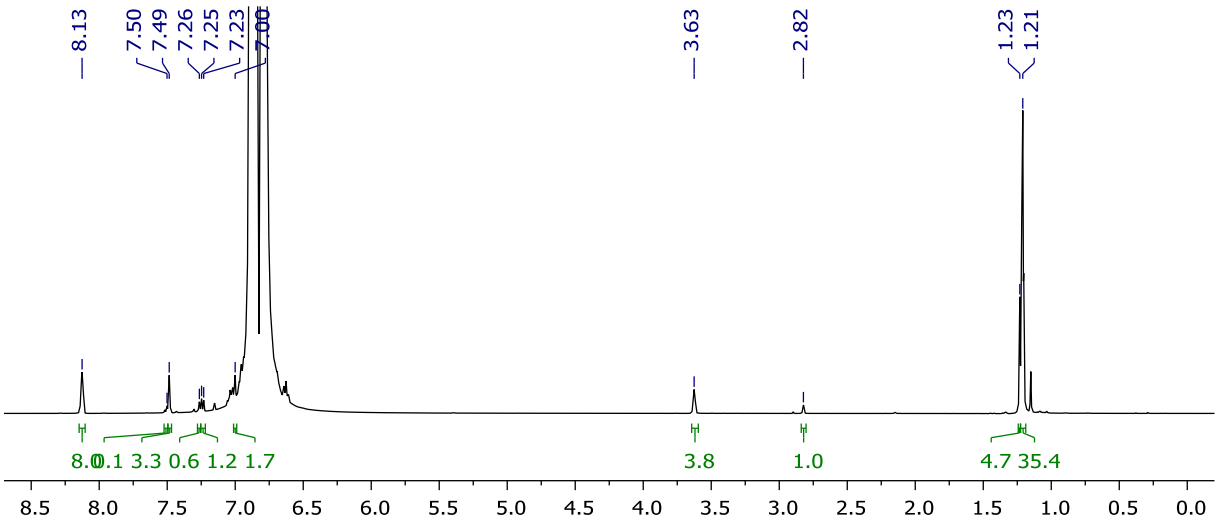

Figure S52. ^{1}H NMR spectrum of **3b-CH_2** (1,2-$C_6H_4F_2$, 500 MHz).

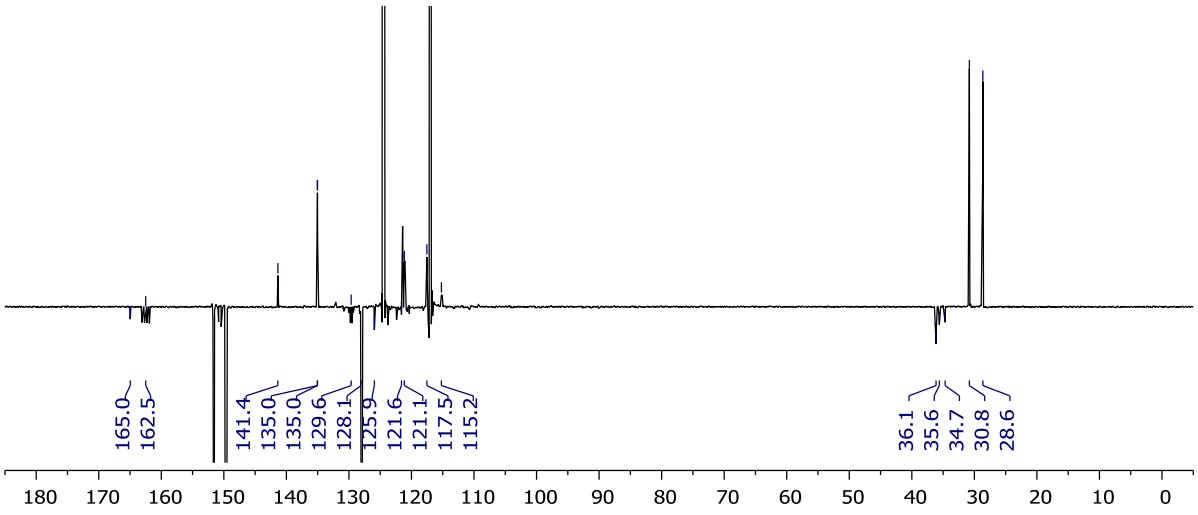

Figure S53. $^{13}C\{^{1}H\}$ APT NMR spectrum of **3b-CH_2** (1,2-$C_6H_4F_2$, 126 MHz).

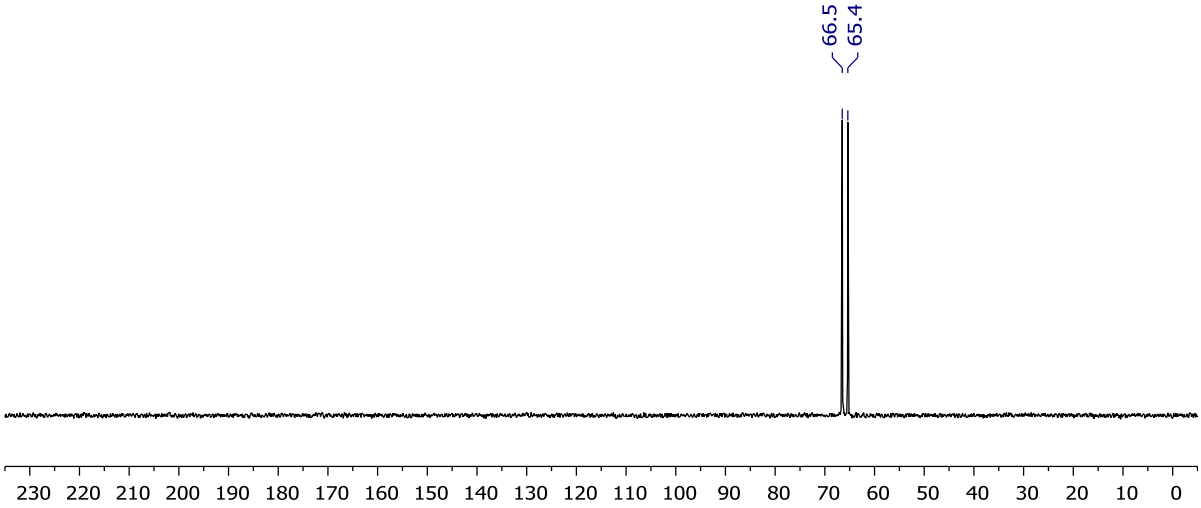

Figure S54. $^{31}P\{^{1}H\}$ NMR spectrum of **3b-CH_2** (1,2-$C_6H_4F_2$, 121 MHz).

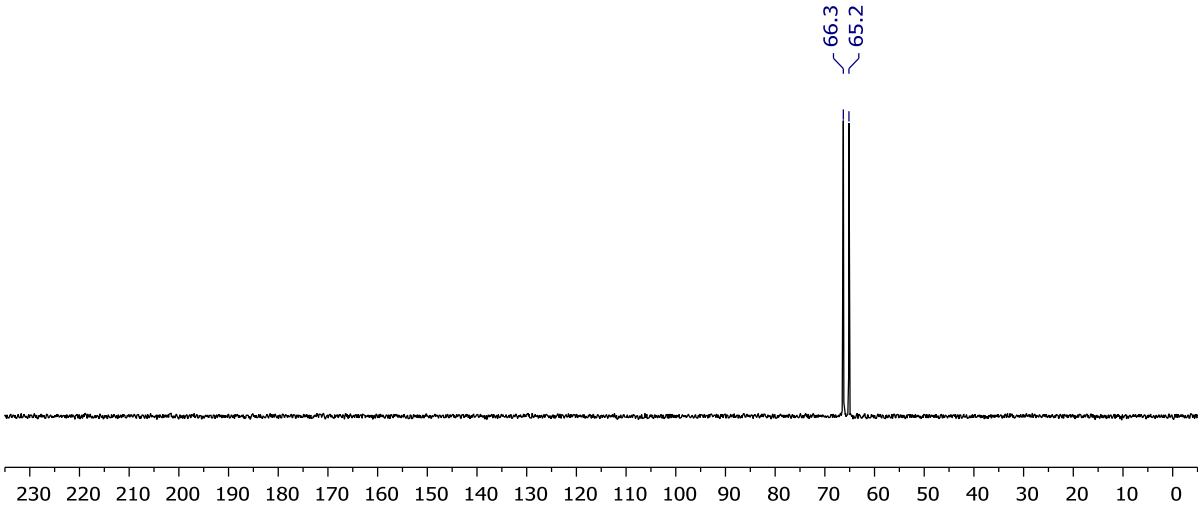

Figure S55. $^{31}P\{^{1}H\}$ NMR spectrum of **3b-CH_2** (CD_2Cl_2, 162 MHz).

11. Preparation of an inseparable mixture of 2e-O and 3b-O

A solution of **1b-O** (35.7 mg, 12.6 µmol) and HCCAr' (8.1 mg, 37.8 µmol) in 1,2-$C_6H_4F_2$ (*ca*. 1mL) was stirred at ambient temperature for 18 h. The dark green solution was layered with excess hexane (*ca*. 50 mL) and stored at -30 °C to afford a 7:3 mixture of **2e-O** and **3b-O** as malachite rods. Yield: 20.2 mg (51%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a solution in 1,2-$C_6H_4F_2$ at ambient temperature.

2e-O:

^{1}H NMR (500 MHz, 1,2-$C_6H_4F_2$, selected data): δ 7.66 (s, 2H, Ar'-H), 7.63 (obscured t, $^{3}J_{HH}$ = 8, 1H, py), 7.58 (s, 1H, Ar'-H), 4.59 (s, 1H, HCCAr'), 1.25 (s, 18H, Ar'-*t*Bu}), 1.15 (vt, J_{PH} = 8, 36H,P*t*Bu).

^{13}C{^{1}H} NMR (126 MHz, 1,2-$C_6H_4F_2$, selected data): δ 75.9 (d, $^{1}J_{RhC}$ = 12, HCCAr'), 67.6 (d, $^{1}J_{RhC}$ = 13, HCCAr'),

^{31}P{^{1}H} NMR (121 MHz, 1,2-$C_6H_4F_2$): δ 194.6 (d, $^{1}J_{RhP}$ = 129).

3b-O:

^{1}H NMR (500 MHz, 1,2-$C_6H_4F_2$, selected data): δ 7.63 (obscured t, $^{3}J_{HH}$ = 8, 1H, py), 7.34 (s, 1H, Ar'), 7.18 (s, 2H, Ar'), 3.75 (s, 1H, CCHAr'),1.27 (vt, J = 8, 36H, *t*Bu), 1.21 (s, 18H, Ar'-*t*Bu).

^{13}C{^{1}H} NMR (126 MHz, 1,2-$C_6H_4F_2$, selected data): δ 339.5 (HMBC, RhCCHAr'), 128 (obscured, RhCCHAr').

^{31}P{^{1}H} NMR (121 MHz, 1,2-$C_6H_4F_2$): δ 208.4 (d, $^{1}J_{RhP}$ = 143).

Anal. Calcd for $C_{69}H_{73}BF_{24}NO_2P_2Rh$ (1579.97 gmol^{-1}): C, 52.45; H, 4.66; N, 0.89. Found: C, 52.53; H, 4.77; N, 0.90.

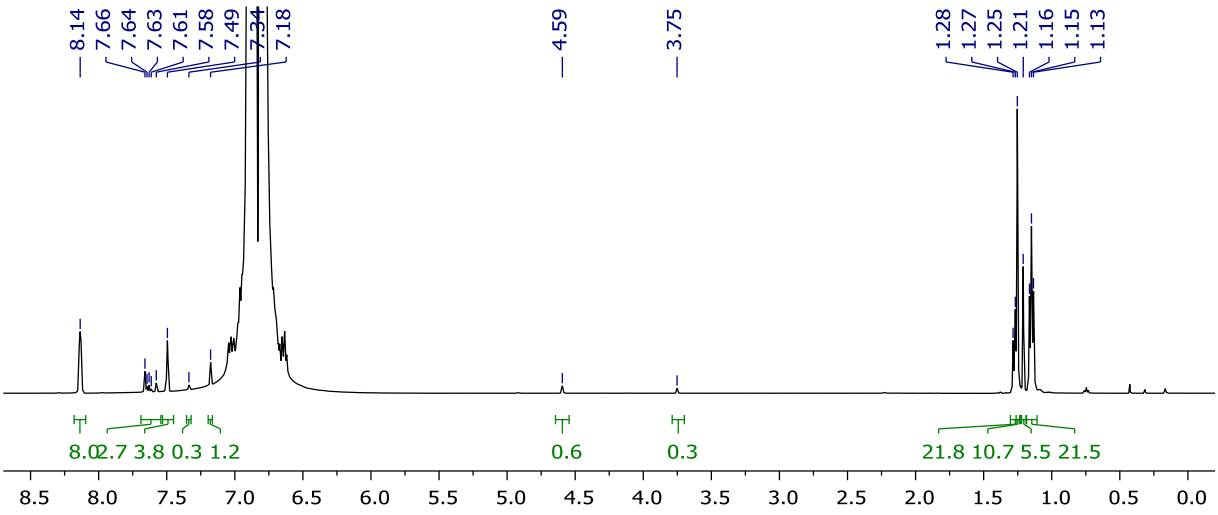

Figure S56. ^{1}H NMR spectrum of 7:3 mixture of **2e-O** and **3b-O** (1,2-$C_6H_4F_2$, 500 MHz).

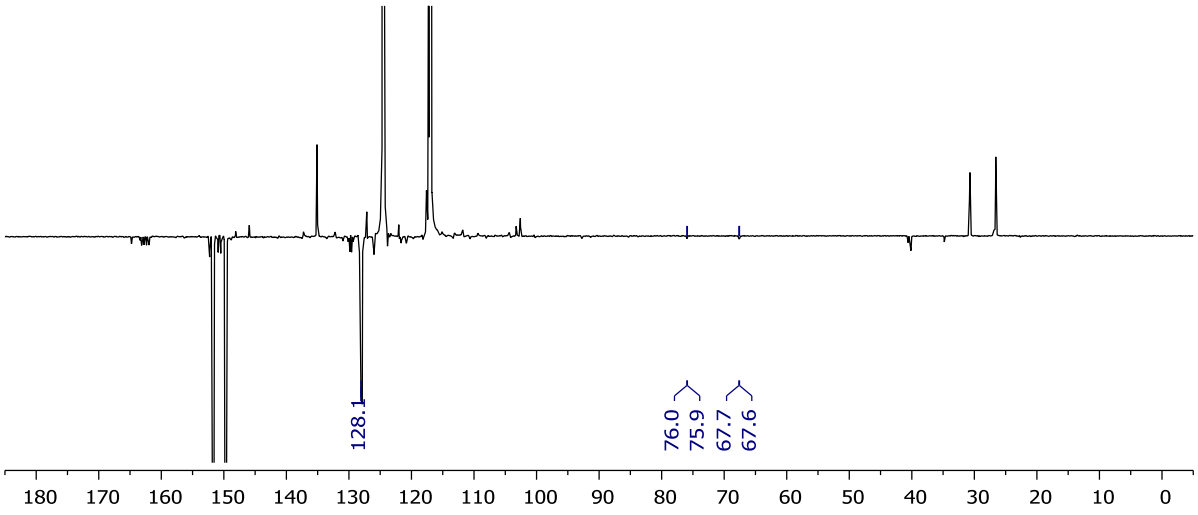

Figure S57. $^{13}C\{^{1}H\}$ APT NMR spectrum 7:3 mixture of **2e-O** and **3b-O** (1,2-$C_6H_4F_2$, 126 MHz).

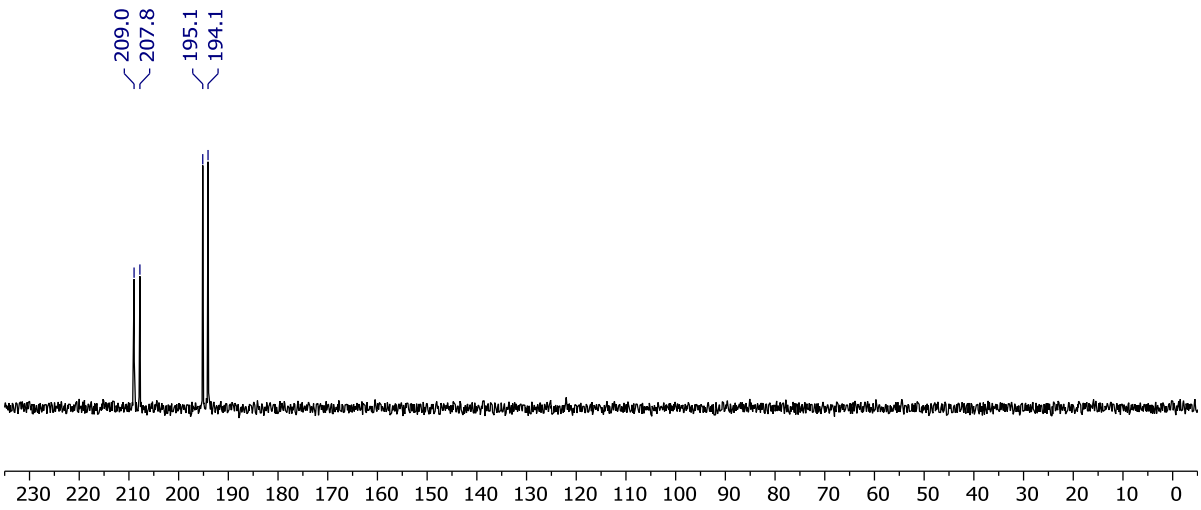

Figure S58. $^{31}P\{^{1}H\}$ NMR spectrum of 7:3 mixture of **2e-O** and **3b-O** (1,2-$C_6H_4F_2$, 121 MHz).

12. NMR scale reactions of [Rh(pincer)(CCHR)][BAr$^F_4$] (3) with carbon monoxide

[Rh(PNP)(CCH*t*Bu)][BAr$^F_4$] (3a-CH$_2$)

A solution of **3a-CH$_2$** (6.0 mg, 4.2 µmol) in 1,2-$C_6H_4F_2$ (0.50 mL) was freeze-pump-thaw degassed and placed under an atmosphere of carbon monoxide to afford **2a-CH$_2$** in < 5 mins.

^{31}P{^{1}H} NMR (121 MHz, 1,2-$C_6H_4F_2$): δ 78.1 (d, $^1J_{RhP}$ = 121).

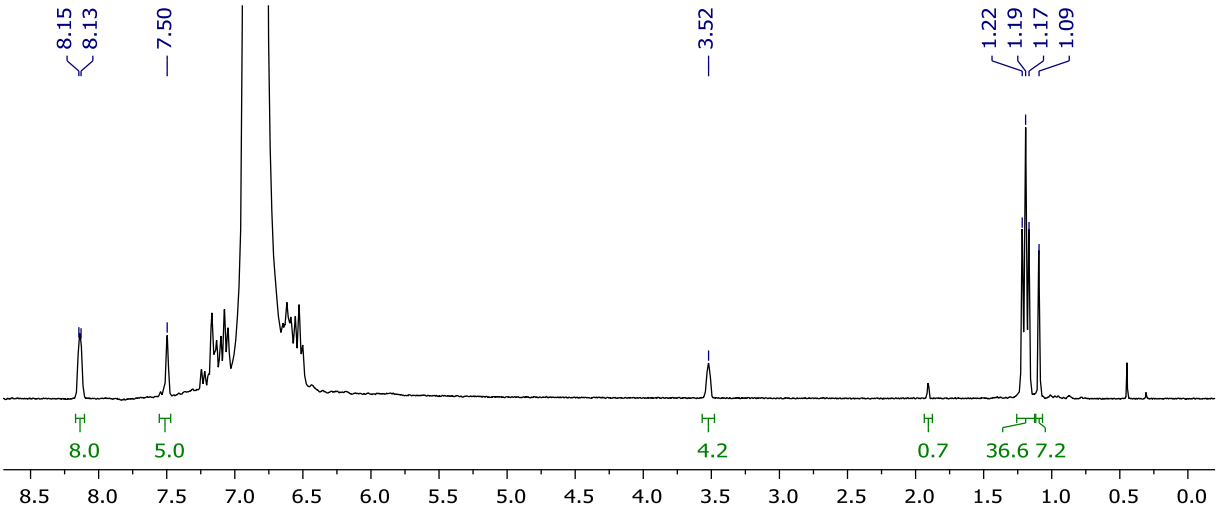

Figure S59. ^{1}H spectrum of the reaction between **3a-CH$_2$** and carbon monoxide (1,2-$C_6H_4F_2$, 300 MHz).

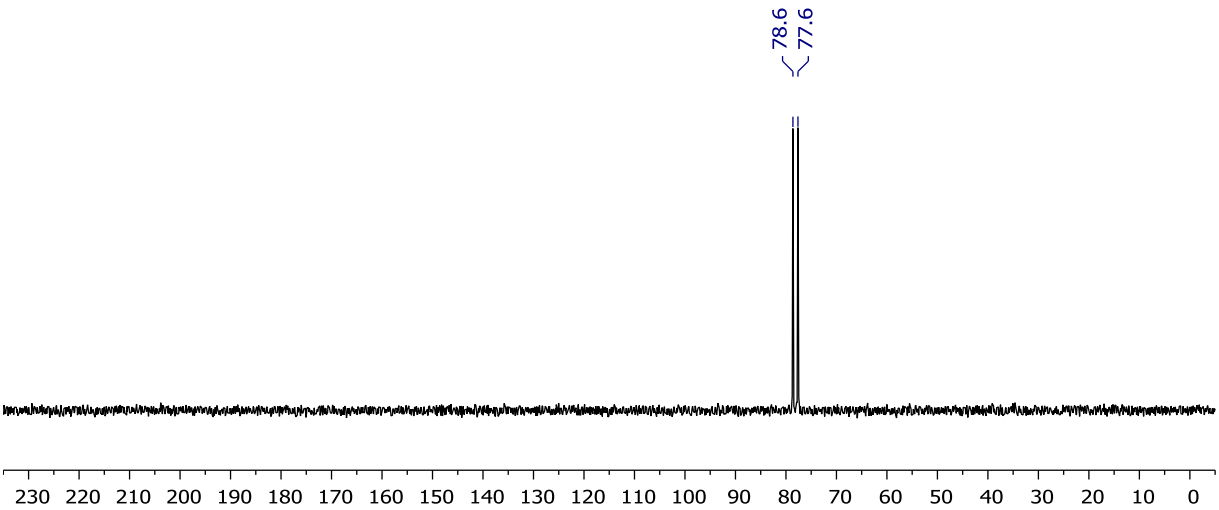

Figure S60. ^{31}P{^{1}H} NMR spectrum of the reaction between **3a-CH$_2$** and carbon monoxide (1,2-$C_6H_4F_2$, 121 MHz).

[Rh(PONOP)(CCH*t*Bu)][BAr$^F_4$] (3a-O)

A solution of **3a-O** (14.5 mg, 10.0 µmol) in 1,2-$C_6H_4F_2$ (0.50 mL) was freeze-pump-thaw degassed and placed under an atmosphere of carbon monoxide to afford **2a-O** in < 5 mins.

$^{31}P\{^1H\}$ NMR (121 MHz, 1,2-$C_6H_4F_2$): δ 219.5 (d, $^1J_{RhP}$ = 127).

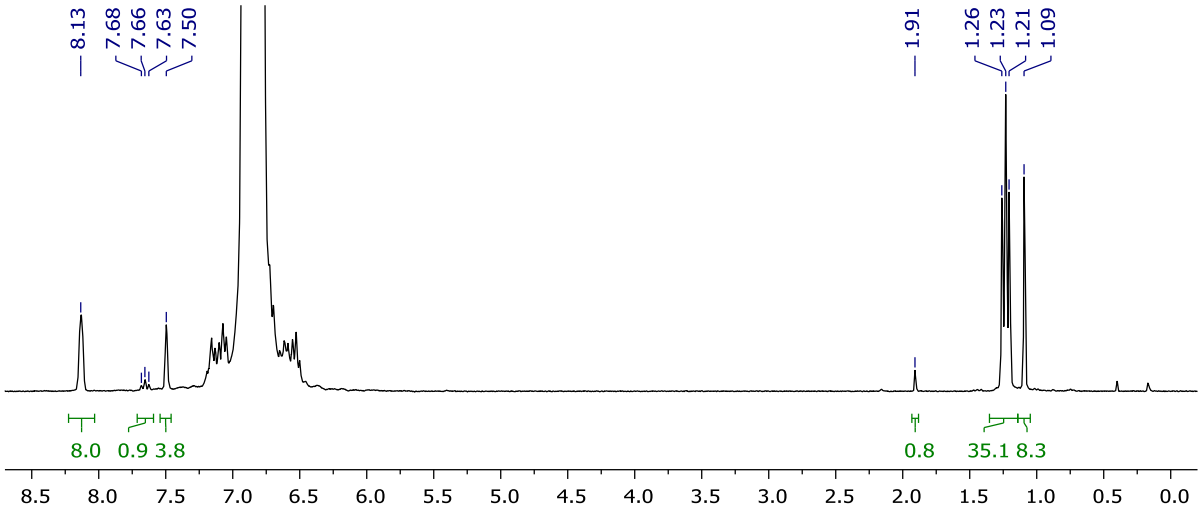

Figure S61. ^1H spectrum of the reaction between **3a-O** and carbon monoxide (1,2-$C_6H_4F_2$, 300 MHz).

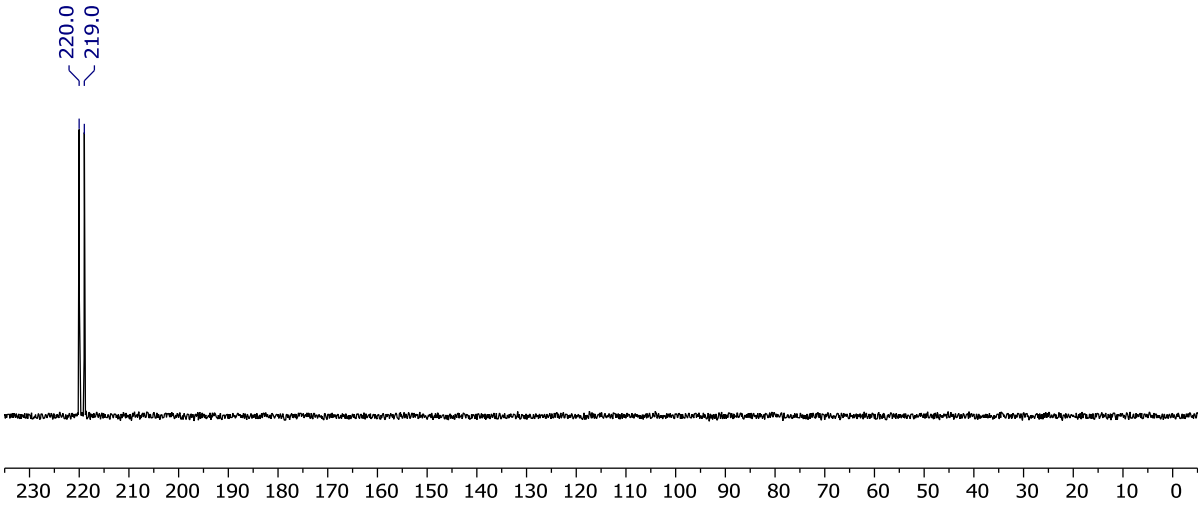

Figure S62. $^{31}P\{^1H\}$ NMR spectrum of the reaction between **3a-O** and carbon monoxide (1,2-$C_6H_4F_2$, 121 MHz).

[Rh(PNP)(CCHAr')][BAr$^{F}_{4}$] (3b-CH$_2$)

A solution of **3b-CH$_2$** (14.9 mg, 9.45 µmol) in 1,2-$C_6H_4F_2$ (0.47 mL) was freeze-pump-thaw degassed and placed and under an atmosphere of carbon monoxide to afford **2a-CH$_2$** after 90 min.

$^{31}P\{^{1}H\}$ NMR (121 MHz, 1,2-$C_6H_4F_2$): δ 78.1 (d, $^{1}J_{RhP}$ = 121).

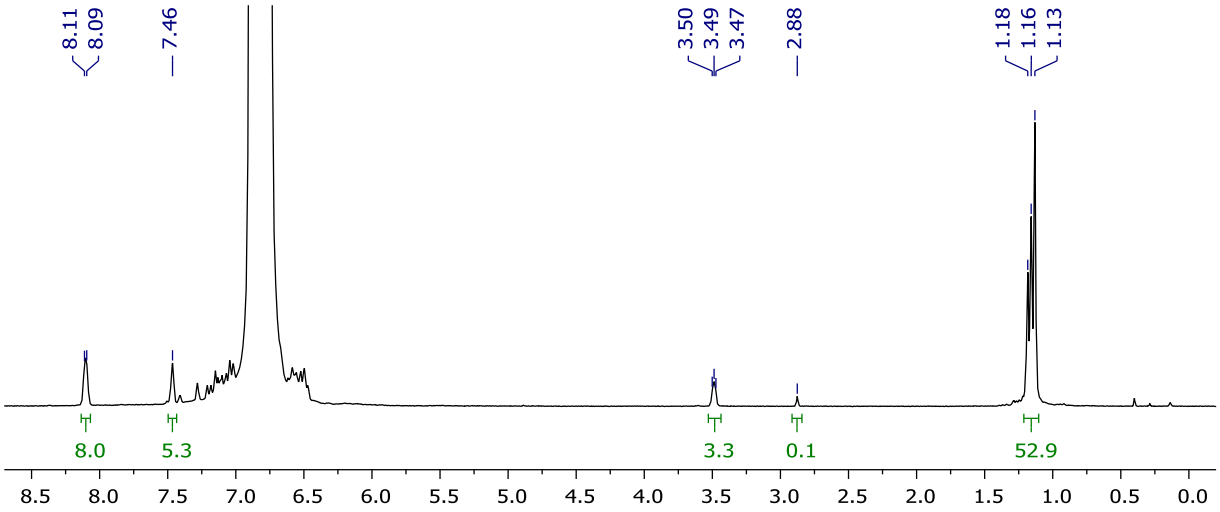

Figure S63. ^{1}H spectrum of the reaction between **3b-CH$_2$** and carbon monoxide (1,2-$C_6H_4F_2$, 300 MHz).

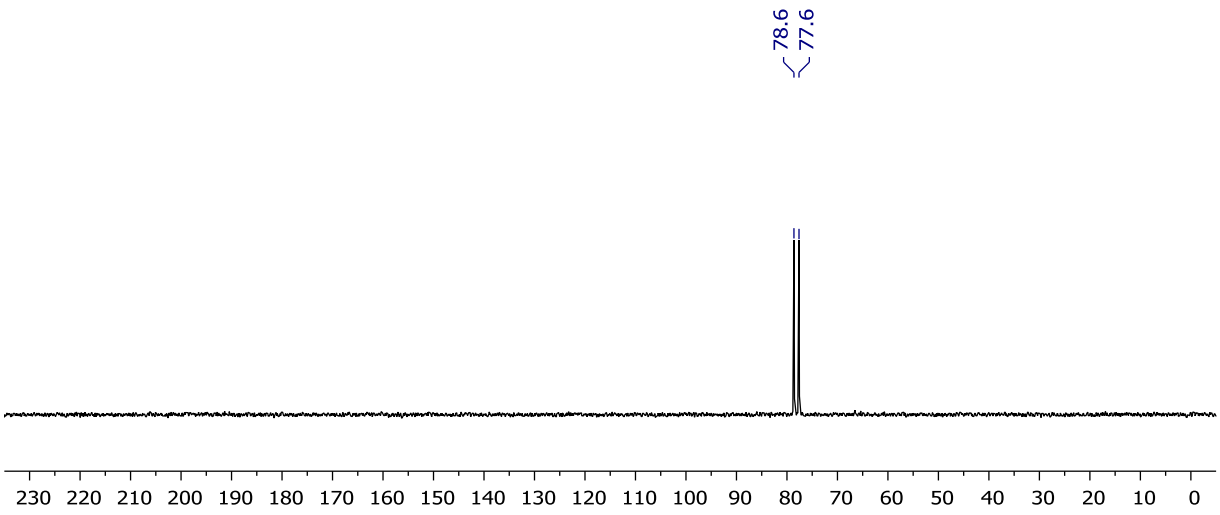

Figure S64. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction between **3b-CH$_2$** and carbon monoxide (1,2-$C_6H_4F_2$, 121 MHz).

Mixture of [Rh(PONOP)(HCCAr')][BAr$^F_4$] (2e-O) and [Rh(PONOP)(CCHAr')][BAr$^F_4$] (3b-O)

A 7:3 mixture of **2e-O** and **3b-O** (6.8 mg, 4.3 µmol) was dissolved in 1,2-$C_6H_4F_2$ (0.35 mL), freeze-pump-thaw degassed and placed under an atmosphere of carbon monoxide to afford **2a-O** in < 5 mins.

$^{31}P\{^1H\}$ NMR (121 MHz, 1,2-$C_6H_4F_2$): δ 219.5 (d, $^1J_{RhP}$ = 127).

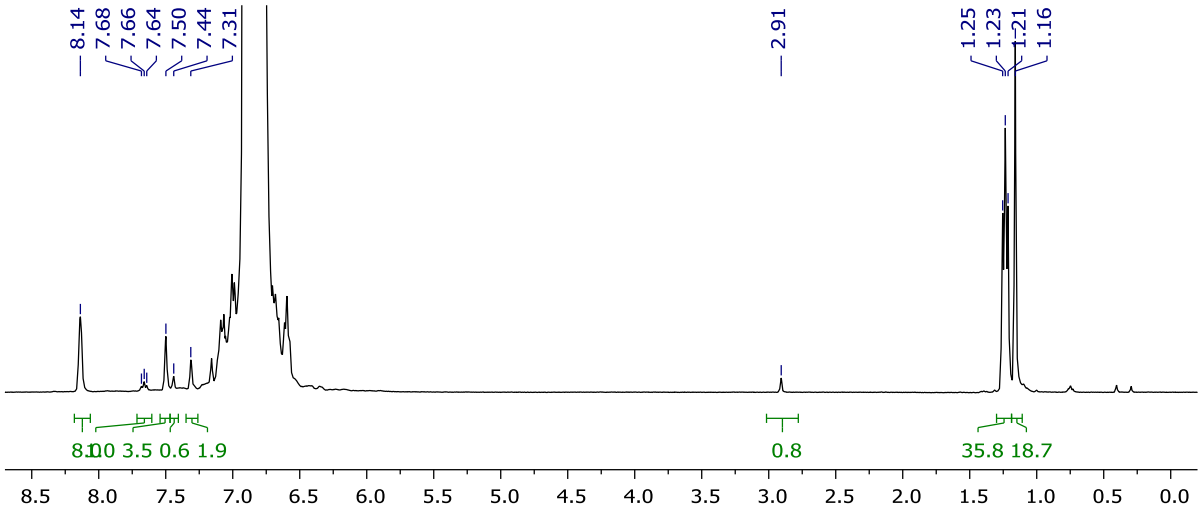

Figure S65. ^1H NMR spectrum of the reaction between a 7:3 mixture of **2e-O** and **3b-O** and carbon monoxide (1,2-$C_6H_4F_2$, 300 MHz).

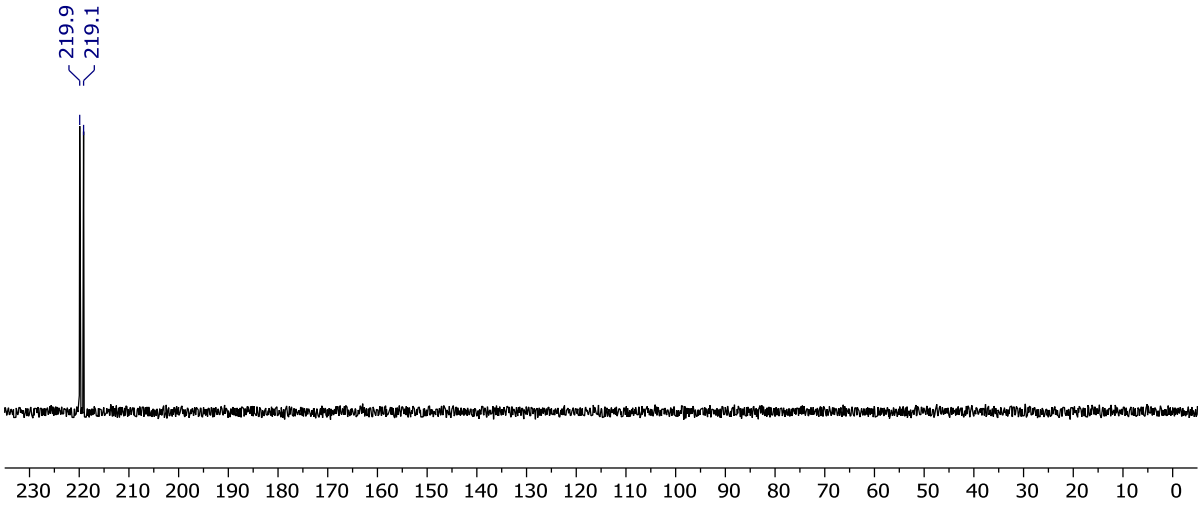

Figure S66. $^{31}P\{^1H\}$ NMR spectrum of the reaction between a 7:3 mixture of **2e-O** and **3b-O** and carbon monoxide (1,2-$C_6H_4F_2$, 121 MHz).

13. References

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