

# **Ammonia borane and hydrazine bis(borane) dehydrogenation mediated by an unsymmetrical (PNN) ruthenium pincer hydride: metal-ligand cooperation for hydrogen production**

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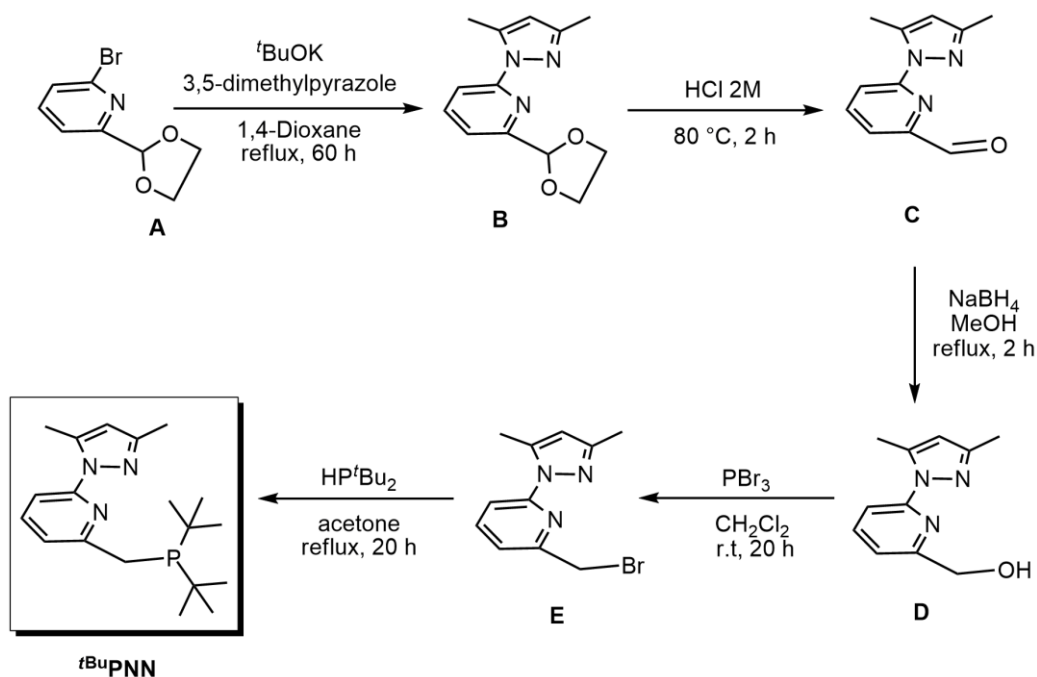
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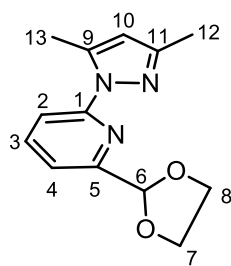
## **Supporting Information**

## <sup>t</sup>BuPNN Ligand Synthesis



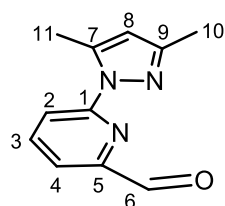
**Scheme S1.** Synthetic steps to the unsymmetrical pincer ligand <sup>t</sup>BuPNN.

**Synthesis of B.** 3,5-dimethylpyrazole (0.97 g, 10.12 mmol, 1.02 eq.) and potassium *tert*-butoxide (1.33 g, 12.00 mmol, 1.2 eq.) were added in sequence to a solution of **A** (2.29 g, 9.92 mmol) in dry and degassed 1,4-dioxane (40 mL) under nitrogen. The resulting mixture was heated at reflux for 60 h, then cooled to room temperature and quenched by a few drops of water. The solvent was removed and the residue was extracted with ethyl acetate (3 x 15 mL). The collected organic phase was dried over  $\text{Na}_2\text{SO}_4$ . Filtration, removal the solvent *in vacuo* and drying gave the crude product that was purified by flash chromatography (silica gel: petroleum ether : AcOEt = 80 : 20) to give **B** as a pale yellow oil (1.82 g, yield 74.6%).



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 293K):  $\delta$  2.29 (s, 3H,  $\text{CH}_3$ ,  $\text{H}^{12}$ ), 2.66 (s, 3H,  $\text{CH}_3$ ,  $\text{H}^{13}$ ), 4.18-4.04 (m, 4H,  $\text{H}^{7,8}$ ), 5.82 (s, 1H,  $\text{H}^{10}$ ), 5.97 (s, 1H,  $\text{H}^6$ ), 7.35 (m, 1H,  $\text{CH Ar}$ ,  $\text{H}^4$ ), 7.88-7.77 (2H,  $\text{CH Ar}$ ,  $\text{H}^{2,3}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 293 K):  $\delta$  13.6 ( $\text{CH}_3$ ,  $\text{C}^{13}$ ), 14.7 ( $\text{CH}_3$ ,  $\text{C}^{12}$ ), 65.6 ( $\text{C}^{7,8}$ ), 103.6 ( $\text{C}^6$ ), 109.2 ( $\text{CH Ar}$ ,  $\text{C}^{10}$ ), 115.9 ( $\text{CH Ar}$ ,  $\text{C}^2$ ), 117.4 ( $\text{CH Ar}$ ,  $\text{C}^4$ ), 139.1 ( $\text{CH Ar}$ ,  $\text{C}^3$ ), 142.0 ( $\text{C Ar}$ ,  $\text{C}^9$ ), 149.9 ( $\text{C Ar}$ ,  $\text{C}^1$ ), 153.0 ( $\text{C Ar}$ ,  $\text{C}^{11}$ ), 155.4 ( $\text{C Ar}$ ,  $\text{C}^5$ ). Anal. Calcd (%) for  $\text{C}_{13}\text{H}_{15}\text{N}_3\text{O}_2$  (245.28): C 63.66, H 6.16, N 17.13; found C 63.71, H 6.20 N 17.10.

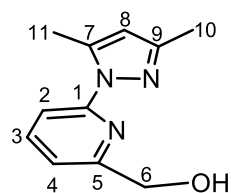
**Synthesis of C.** Compound **B** (1.23 g, 5.00 mmol) was treated with  $\text{CF}_3\text{COOH}$  (30 mL) and the resulting mixture was stirred at reflux for 3 h. After that time, the mixture was allowed to warm to room temperature and the acid was removed under reduced pressure. The mixture was diluted with water (30 mL) and the pH was adjusted to 7 with a saturated solution of  $\text{NaHCO}_3$ . The organic product was extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 20 mL) and collected organic extracts were dried over  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated under reduced pressure to give the crude product that was purified by flash chromatography (silica gel: petroleum ether :  $\text{AcOEt}$  = 85 : 15) to give **C** as white solid (0.925 g, yield 92.0%).



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 293K):  $\delta$  2.30 (s, 3H,  $\text{CH}_3$ ,  $\text{H}^{10}$ ), 2.74 (s, 3H,  $\text{CH}_3$ ,  $\text{H}^{11}$ ), 6.04 (s, 1H,  $\text{CH Ar}$ ,  $\text{H}^8$ ), 7.79 (m, 1H,  $\text{CH Ar}$ ,  $\text{H}^2$ ), 7.94 (m, 1H,  $\text{CH Ar}$ ,  $\text{H}^3$ ), 8.16 (m, 1H,  $\text{CH Ar}$ ,  $\text{H}^4$ ), 10.00 (s, 1H,  $\text{CHO}$ ,  $\text{H}^6$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 293 K):  $\delta$  13.7 ( $\text{CH}_3$ ,  $\text{C}^{11}$ ), 15.1 ( $\text{CH}_3$ ,  $\text{C}^{10}$ ), 109.2 ( $\text{CH Ar}$ ,  $\text{C}^8$ ), 118.3 ( $\text{CH Ar}$ ,  $\text{C}^2$ ), 119.9 ( $\text{CH Ar}$ ,  $\text{C}^4$ ), 139.4 ( $\text{CH Ar}$ ,  $\text{C}^3$ ), 142.3 ( $\text{C Ar}$ ,  $\text{C}^7$ ), 150.6 ( $\text{C Ar}$ ,  $\text{C}^1$ ), 150.8 ( $\text{C Ar}$ ,  $\text{C}^5$ ), 153.9 ( $\text{C Ar}$ ,  $\text{C}^9$ ), 192.7 ( $\text{C}^6$ ). Anal. Calcd (%) for  $\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}$  (201.22): C 65.66, H 5.51, N 20.88; found C 65.71, H 5.60 N 20.87.

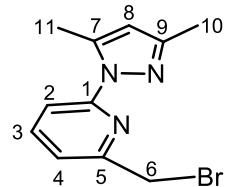
**Synthesis of D.**  $\text{NaBH}_4$  (0.19 g, 5.00 mmol) was added to a solution of **C** (0.90 g, 4.5 mmol) in dry and degassed  $\text{EtOH}$  (40 mL). The resulting mixture was stirred at reflux for 2 h. The mixture was then allowed to warm to room temperature and quenched by a few drops of water. The solvent was removed and the residue was extracted with ethyl acetate (3 x 15 mL). The collected organic phase was dried over  $\text{Na}_2\text{SO}_4$ .

Filtration, removal the solvent *in vacuo* and drying gave the crude product that was purified by flash chromatography (silica gel: petroleum ether : AcOEt = 70 : 30) to give **4** as white solid (0.82 g, yield 90.0%).



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 293K):  $\delta$  2.23 (s, 3H,  $\text{CH}_3$ ,  $\text{H}^{10}$ ), 2.54 (s, 3H,  $\text{CH}_3$ ,  $\text{H}^{11}$ ), 4.67 (s, 2H,  $\text{CH}_2\text{OH}$ ,  $\text{H}^6$ ), 5.94 (s, 1H,  $\text{CH}$  Ar,  $\text{H}^8$ ), 7.02 (m, 1H,  $\text{CH}$  Ar,  $\text{H}^4$ ), 7.71-7.64 (2H,  $\text{CH}$  Ar,  $\text{H}^{2,3}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 293 K):  $\delta$  13.4 ( $\text{CH}_3$ ,  $\text{C}^{11}$ ), 14.7 ( $\text{CH}_3$ ,  $\text{C}^{10}$ ), 64.1 ( $\text{CH}_2\text{OH}$ ,  $\text{C}^6$ ), 109.3 ( $\text{CH}$  Ar,  $\text{C}^8$ ), 114.3 ( $\text{CH}$  Ar,  $\text{C}^2$ ), 117.4 ( $\text{CH}$  Ar,  $\text{C}^4$ ), 139.2 ( $\text{CH}$  Ar,  $\text{C}^3$ ), 141.5 ( $\text{C}$  Ar,  $\text{C}^7$ ), 149.9 ( $\text{C}$  Ar,  $\text{C}^1$ ), 152.0 ( $\text{C}$  Ar,  $\text{C}^9$ ), 157.9 ( $\text{C}$  Ar,  $\text{C}^5$ ). Anal. Calcd (%) for  $\text{C}_{11}\text{H}_{13}\text{N}_3\text{O}$  (203.24): C 65.01, H 6.45, N 20.68; found C 65.10, H 6.50 N 20.75.

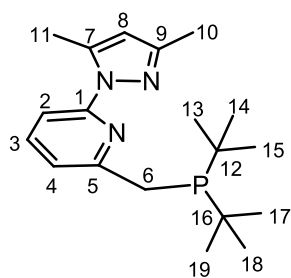
**Synthesis of E.**  $\text{PBr}_3$  (0.74 mL, 7.86 mmol) was added dropwise to a solution of **D** (0.80 g, 3.93 mmol) in dry and degassed  $\text{CH}_2\text{Cl}_2$  (20 mL) cooled to 0 °C. The solution was stirred at room temperature for 24 h. Afterwards, the mixture was treated with a saturated aqueous solution of  $\text{Na}_2\text{CO}_3$  to reach pH = 8. The aqueous phase was separated, and extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 15 mL). The collected organic phase was dried over  $\text{Na}_2\text{SO}_4$ . Filtration, removal the solvent *in vacuo* and drying gave the final product **E** as a colorless oil (1.02 g, yield 98.0%).



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 293K):  $\delta$  2.31 (s, 3H,  $\text{CH}_3$ ,  $\text{H}^{10}$ ), 2.69 (s, 3H,  $\text{CH}_3$ ,  $\text{H}^{11}$ ), 4.53 (s, 2H,  $\text{CH}_2\text{Br}$ ,  $\text{H}^6$ ), 6.01 (s, 1H,  $\text{CH}$  Ar,  $\text{H}^8$ ), 7.26 (m, 1H,  $\text{CH}$  Ar,  $\text{H}^4$ ), 7.82-7.77 (2H,  $\text{CH}$  Ar,  $\text{H}^{2,3}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , 293 K):  $\delta$  13.5 ( $\text{CH}_3$ ,  $\text{C}^{11}$ ), 14.8 ( $\text{CH}_3$ ,  $\text{C}^{10}$ ), 33.5 ( $\text{CH}_2\text{Br}$ ,  $\text{C}^6$ ), 109.3 ( $\text{CH}$  Ar,  $\text{C}^8$ ), 114.9 ( $\text{CH}$  Ar,  $\text{C}^2$ ), 119.9 ( $\text{CH}$  Ar,  $\text{C}^4$ ), 139.2 ( $\text{CH}$  Ar,  $\text{C}^3$ ), 142.1 ( $\text{C}$  Ar,  $\text{C}^7$ ), 150.0 ( $\text{C}$  Ar,  $\text{C}^1$ ), 153.0 ( $\text{C}$  Ar,  $\text{C}^9$ ), 154.6 ( $\text{C}$  Ar,  $\text{C}^5$ ). Anal. Calcd (%) for  $\text{C}_{11}\text{H}_{12}\text{N}_3$  (266.14): C 49.64, H 4.54, N 15.79; found C 49.71, H 4.65 N 15.67.

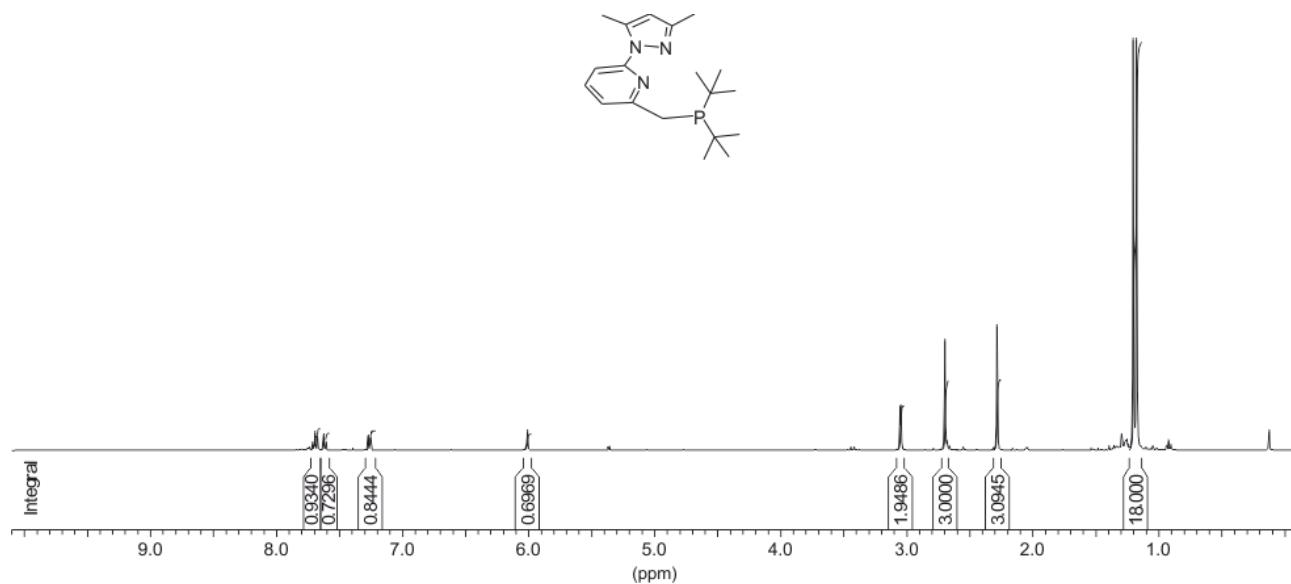
**Synthesis of  $^t\text{BuPNN}$ .** A solution of **E** (0.60 g, 2.25 mmol) in dry and degassed acetone (10 mL) was treated with an acetone solution (5 mL) of  $^t\text{Bu}_2\text{PH}$  (0.52 mL, 2.80 mmol). The resulting mixture was

refluxed under N<sub>2</sub> atmosphere for 12 h. Afterwards, the solution previously cooled to room temperature was treated with 30 mL of dry and degassed pentane causing the precipitation of the HBr phosphine adduct (**6**-HBr). The collected white solid was washed with degassed pentane (3 x 15 mL) before being dissolved in 15 mL of degassed H<sub>2</sub>O and treated with 15 mL of a saturated NaOAc solution. The aqueous phase was then extracted with dry and degassed Et<sub>2</sub>O (3 x 20 mL) and the collected (colourless) organic phases were dried over Na<sub>2</sub>SO<sub>4</sub>. Solvent removal gave <sup>t</sup>BuPNN in the form of an analytically pure white solid (0.54 g, yield 72.0%).

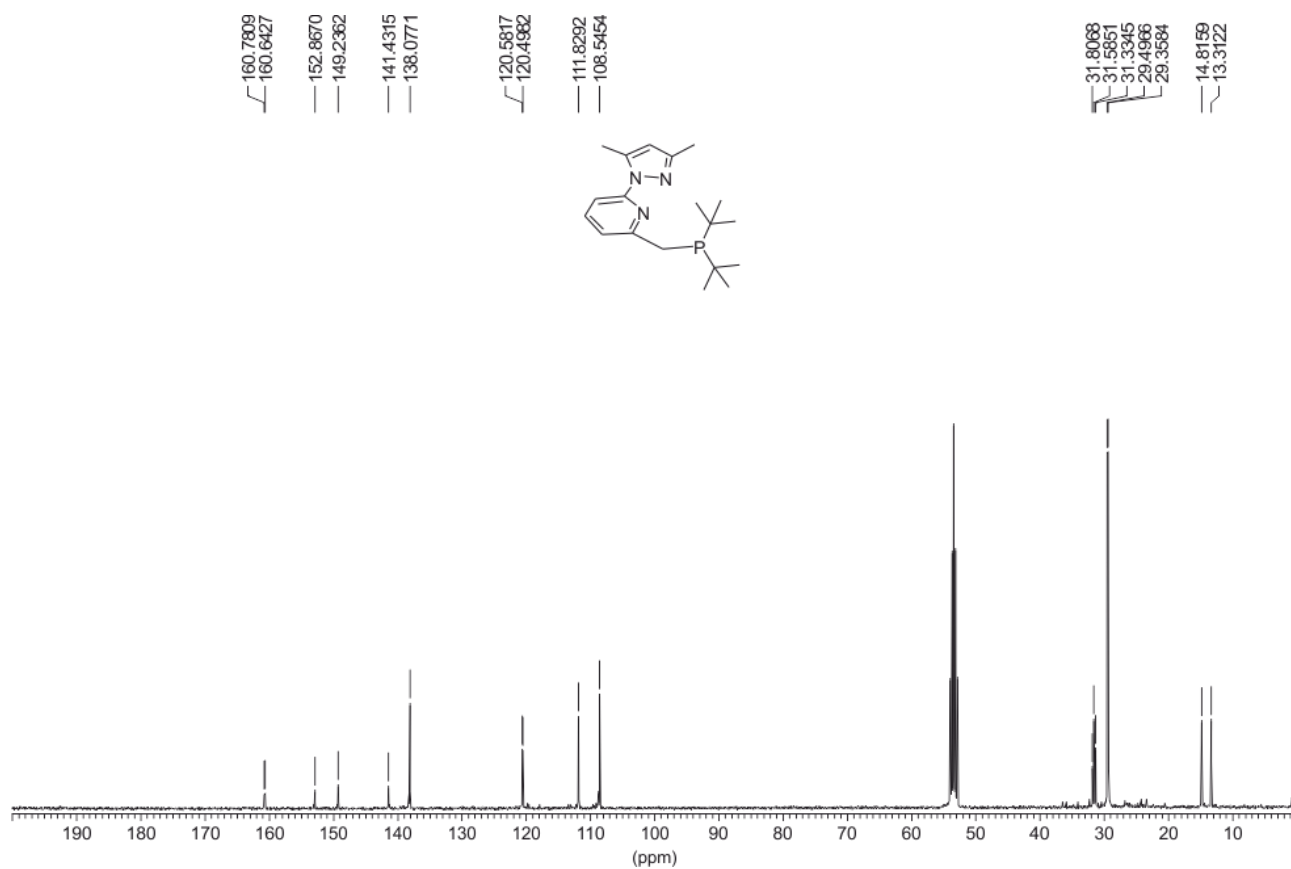


<sup>31</sup>P{<sup>1</sup>H} NMR (161 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 293K):  $\delta$  36.8 (s). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 293K):  $\delta$  1.18 (d, <sup>3</sup>J<sub>PH</sub> = 10.8 Hz, 18H, P-C(CH<sub>3</sub>)<sub>3</sub>, H<sup>13,14,15,17,18,19</sup>), 2.28 (s, 3H, CH<sub>3</sub>, H<sup>10</sup>), 2.69 (s, 3H, CH<sub>3</sub>, H<sup>11</sup>), 3.05 (d, <sup>3</sup>J<sub>PH</sub> = 3.0 Hz, 2H, ArCH<sub>2</sub>P, H<sup>6</sup>), 6.00 (s, 1H, CH Ar, H<sup>8</sup>), 7.26 (m, 1H, CH Ar, H<sup>4</sup>), 7.61 (m, 1H, CH Ar, H<sup>2</sup>),

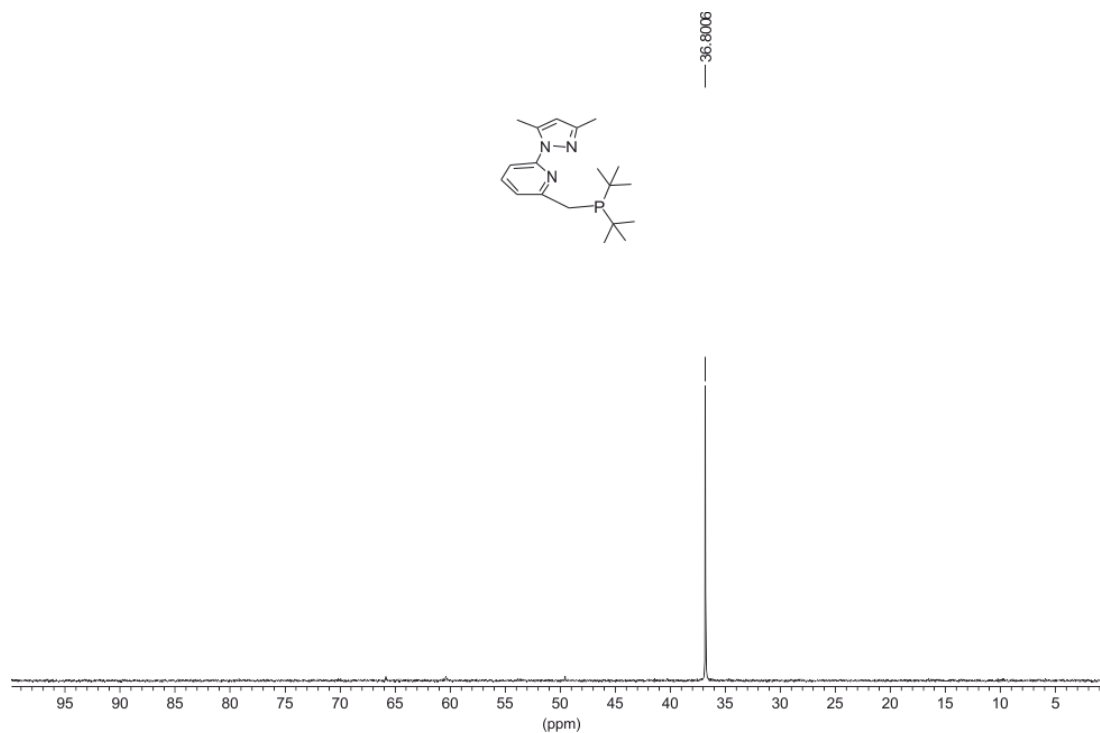
7.69 (m, 1H, CH Ar, H<sup>3</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 293 K):  $\delta$  13.3 (CH<sub>3</sub>, C<sup>11</sup>), 14.8 (CH<sub>3</sub>, C<sup>10</sup>), 29.5 (d, <sup>2</sup>J<sub>PC</sub> = 13.5 Hz, P-C(CH<sub>3</sub>)<sub>3</sub>, C<sup>13,14,15,17,18,19</sup>), 31.4 (d, <sup>1</sup>J<sub>PC</sub> = 24.9 Hz, ArCH<sub>2</sub>P, C<sup>6</sup>), 31.7 (d, <sup>1</sup>J<sub>PC</sub> = 21.9 Hz, P-C(CH<sub>3</sub>)<sub>3</sub>, C<sup>12,16</sup>), 108.5 (CH Ar, C<sup>8</sup>), 111.8 (CH Ar, C<sup>2</sup>), 120.5 (d, J<sub>PC</sub> = 8.0 Hz, CH Ar, C<sup>4</sup>), 138.0 (CH Ar, C<sup>3</sup>), 141.4 (C Ar, C<sup>7</sup>), 149.2 (C Ar, C<sup>1</sup>), 152.8 (C Ar, C<sup>9</sup>), 160.7 (d, J<sub>PC</sub> = 14.0 Hz, C Ar, C<sup>5</sup>). Anal. Calcd (%) for C<sub>19</sub>H<sub>30</sub>N<sub>3</sub>P (331.44): C 68.85, H 9.12, N 12.68; found C 68.87, H 9.20 N 12.70.



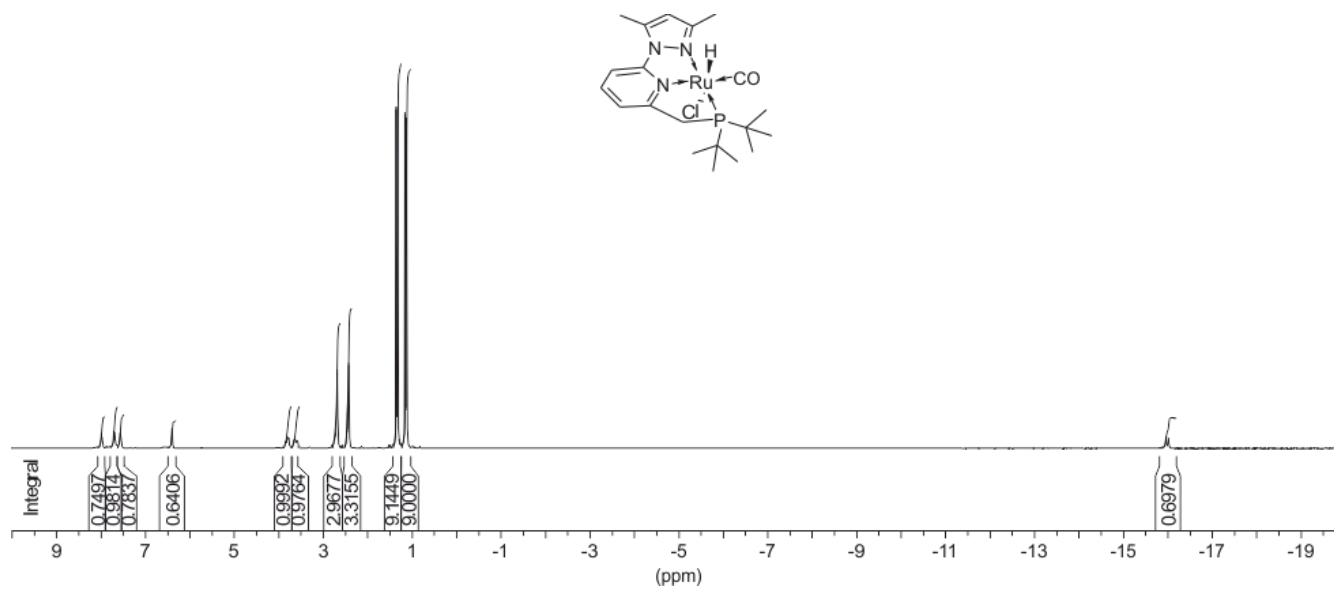
**Figure S1.** <sup>1</sup>H NMR spectrum (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298K) of *t*BuPNN.



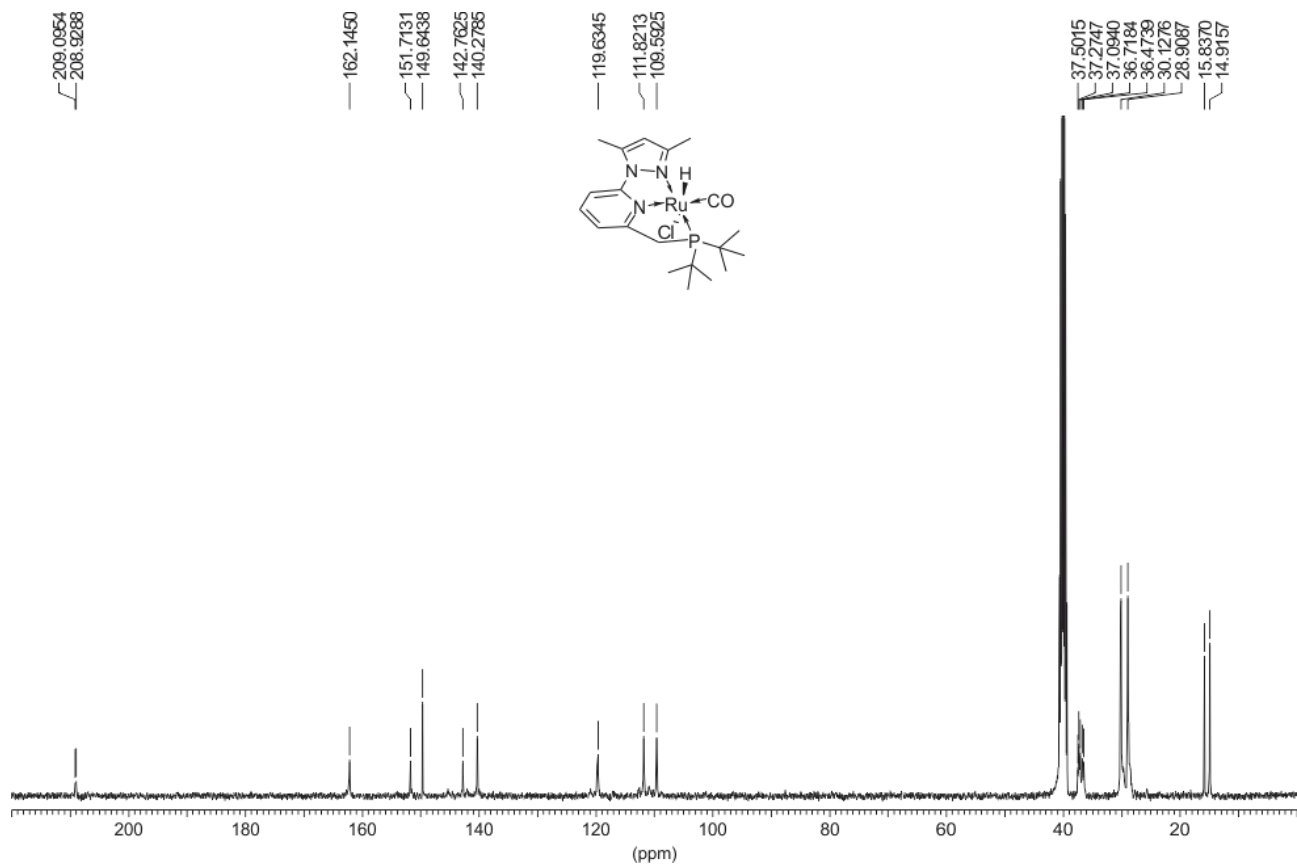
**Figure S2.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298K) of *t*BuPNN.



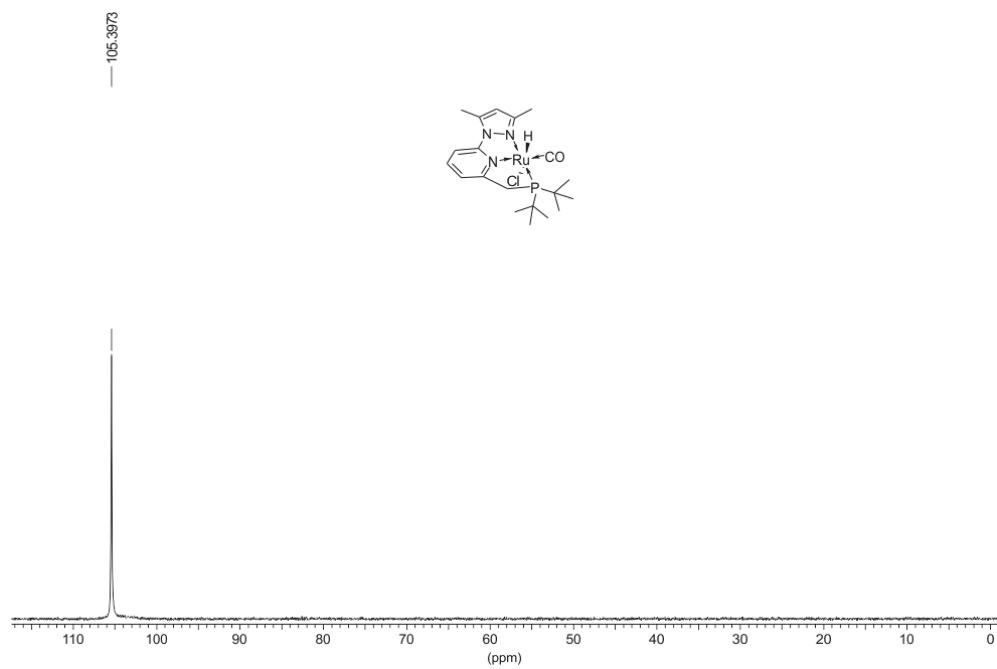
**Figure S3.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 298K) of *t*BuPNN.



**Figure S4.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{DMSO}-d_6$ , 298K) of **1**.

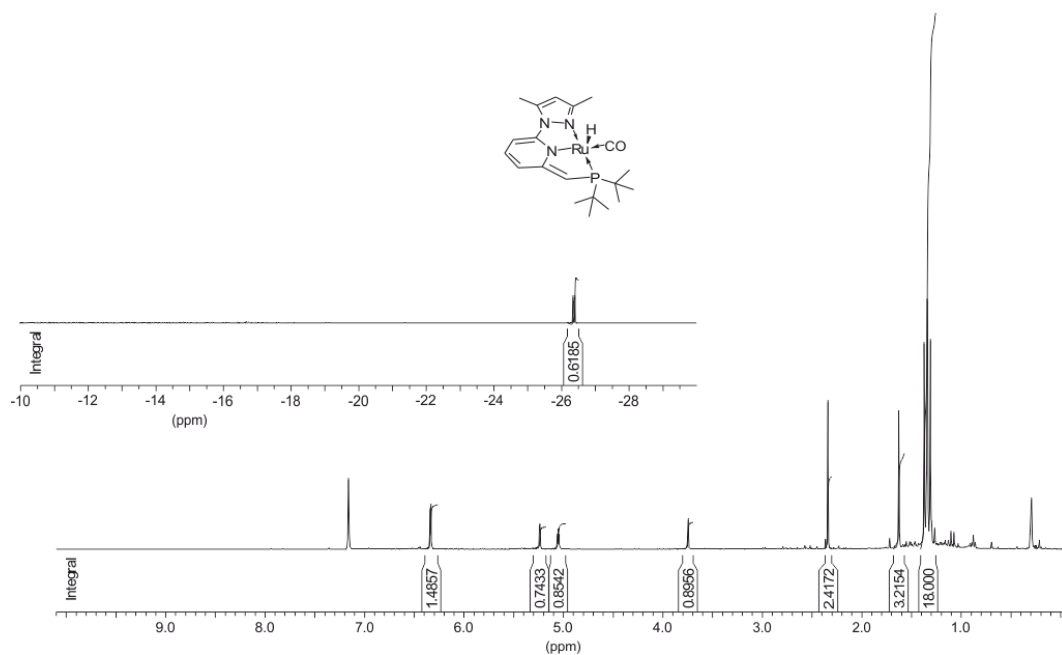


**Figure S5.**  $^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{DMSO-}d_6$ , 298K) of **1**.

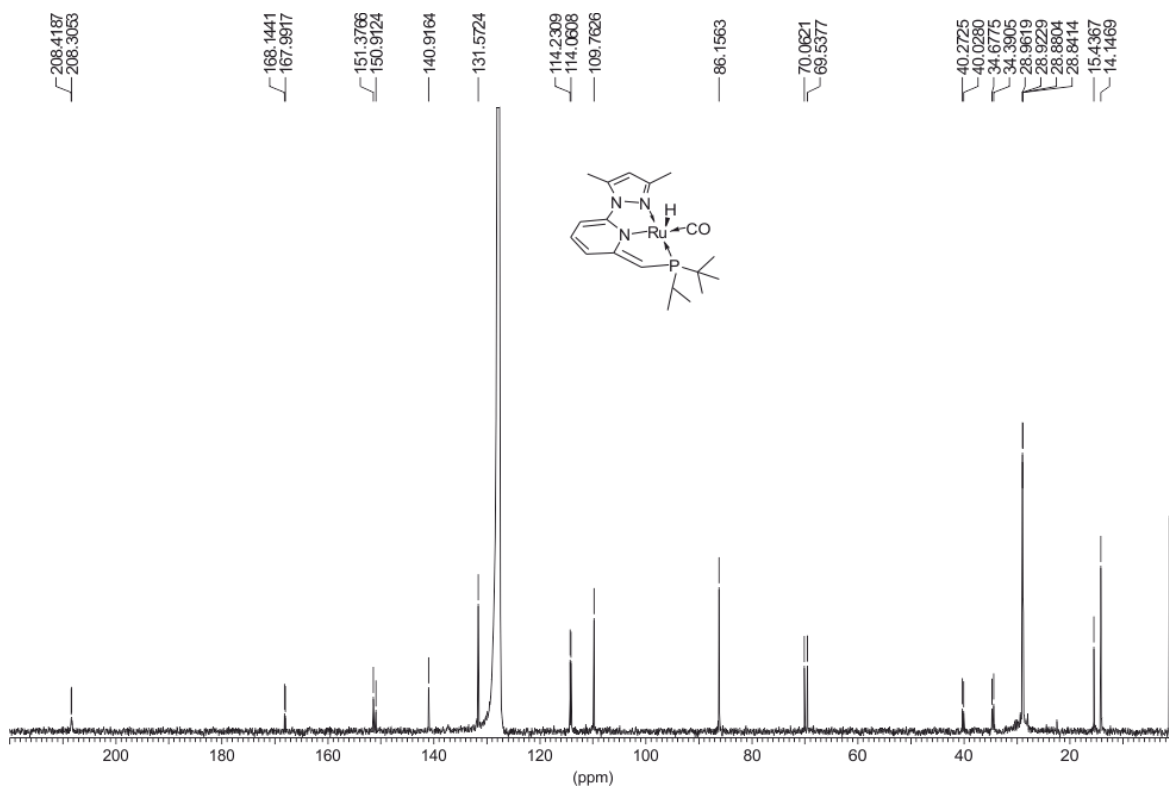


**Figure S6.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (161 MHz,  $\text{DMSO-}d_6$ , 298K) of **1**.

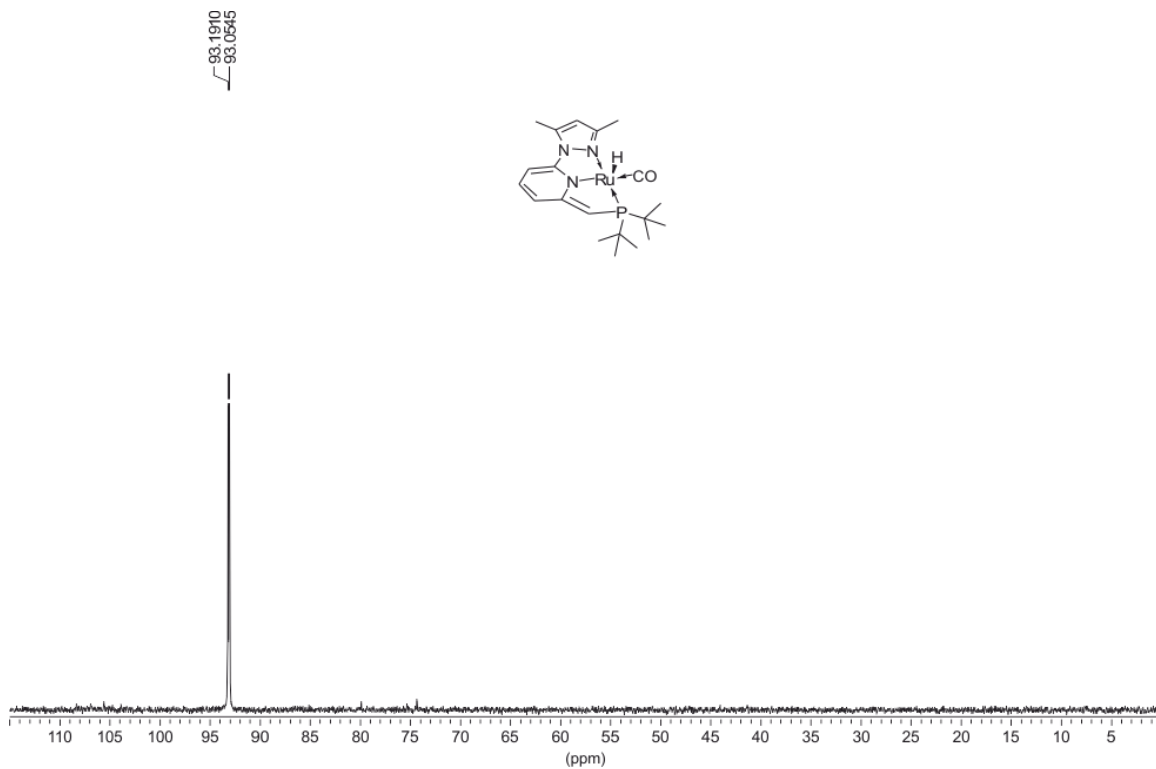




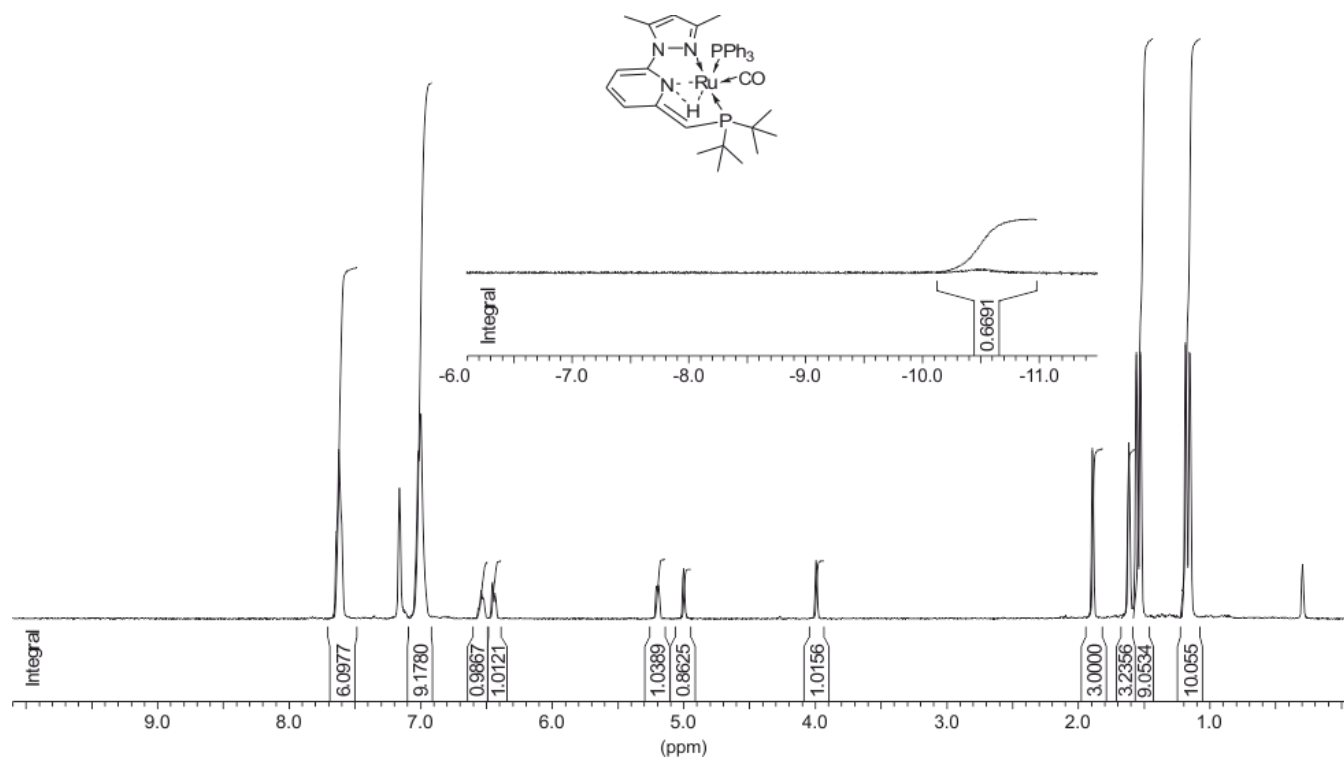
**Figure S7.**  $^1\text{H}$  NMR spectrum (400 MHz, Benzene- $d_6$ , 298K) of 2.



**Figure S8.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (100 MHz, Benzene- $d_6$ , 298K) of 2.



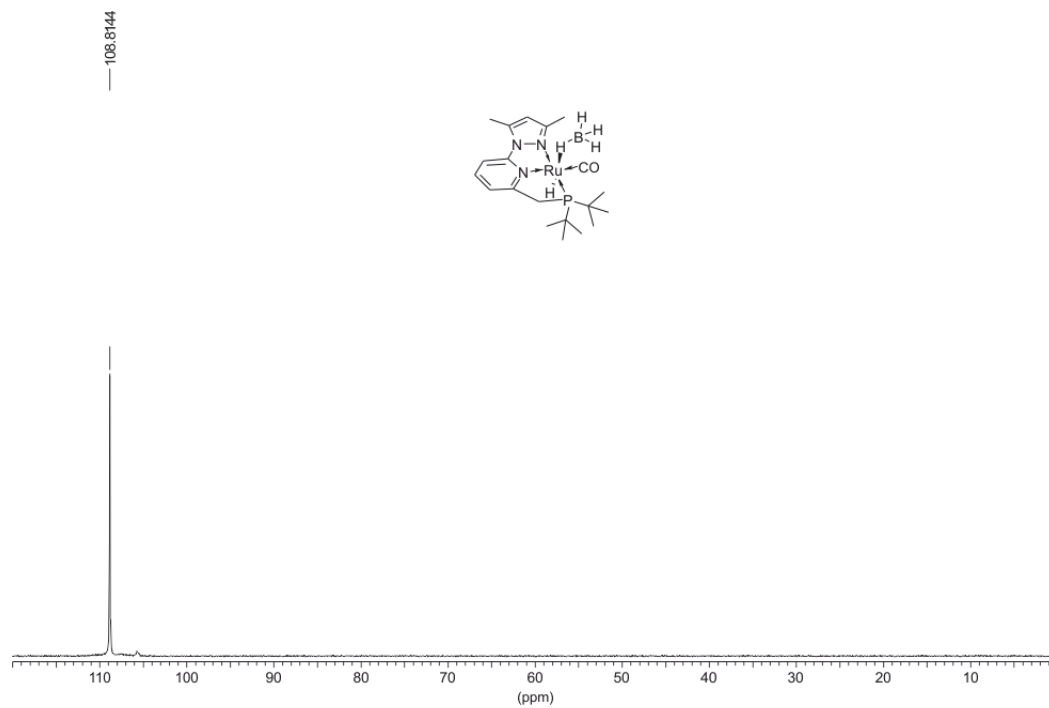
**Figure S9.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (161 MHz, benzene- $d_6$ , 298K) of **2**.



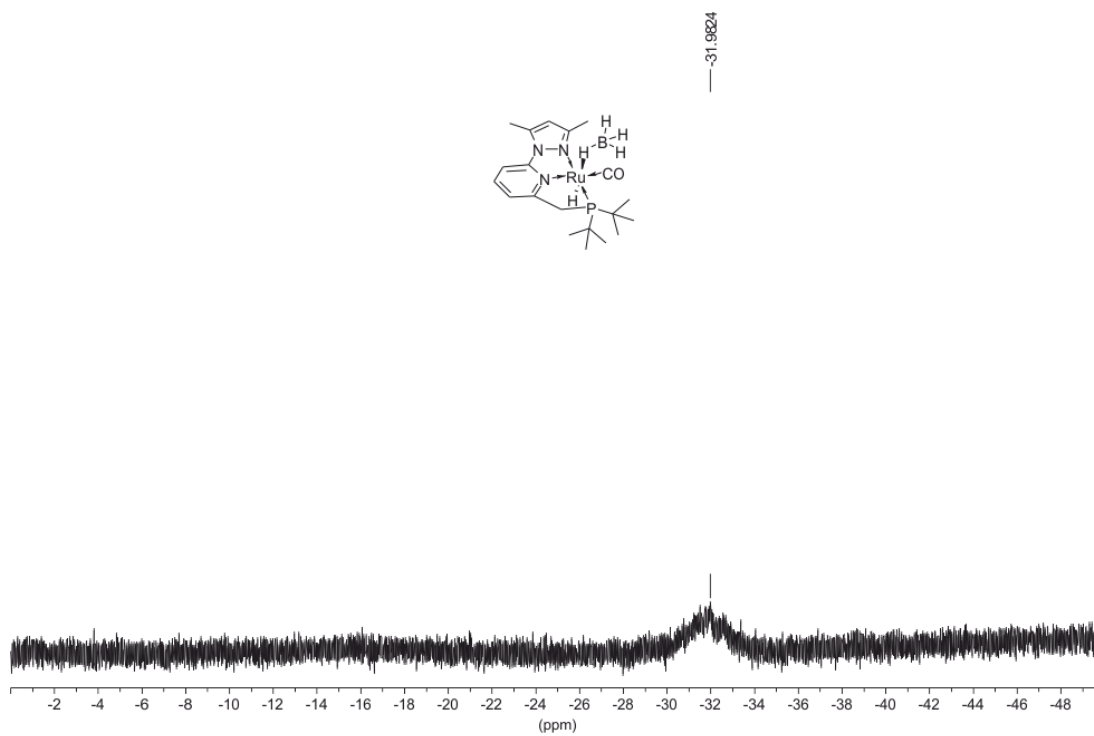
**Figure S10.**  $^1\text{H}$  NMR spectrum (400 MHz, Benzene- $d_6$ , 298K) of **2 · PPh<sub>3</sub>**.



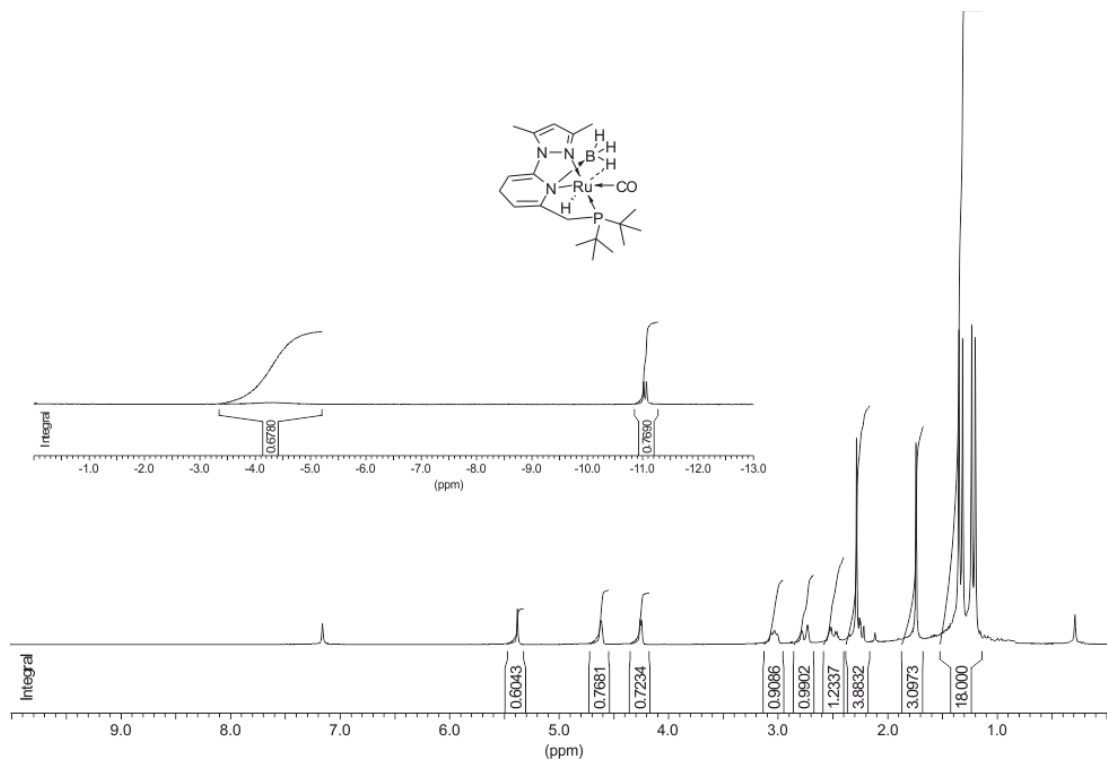




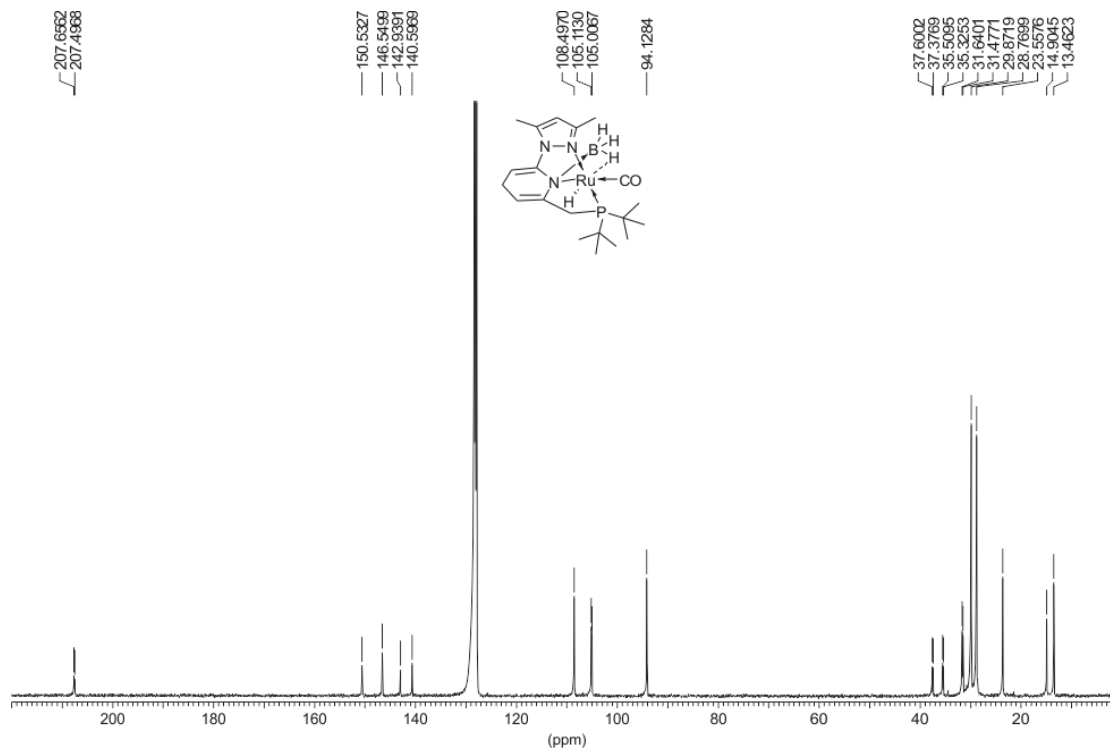
**Figure S15.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 298K) of **3**.



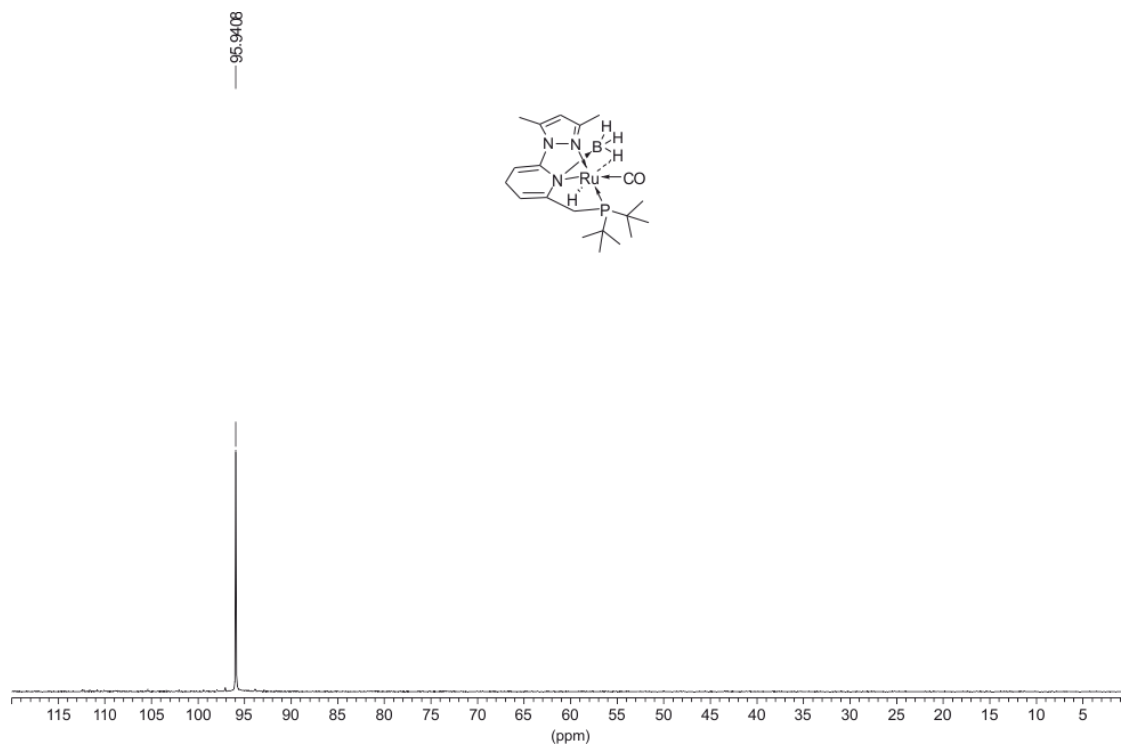
**Figure S16.**  $^{11}\text{B}$  NMR spectrum (128 MHz,  $\text{CD}_2\text{Cl}_2$ , 298K) of **3**.



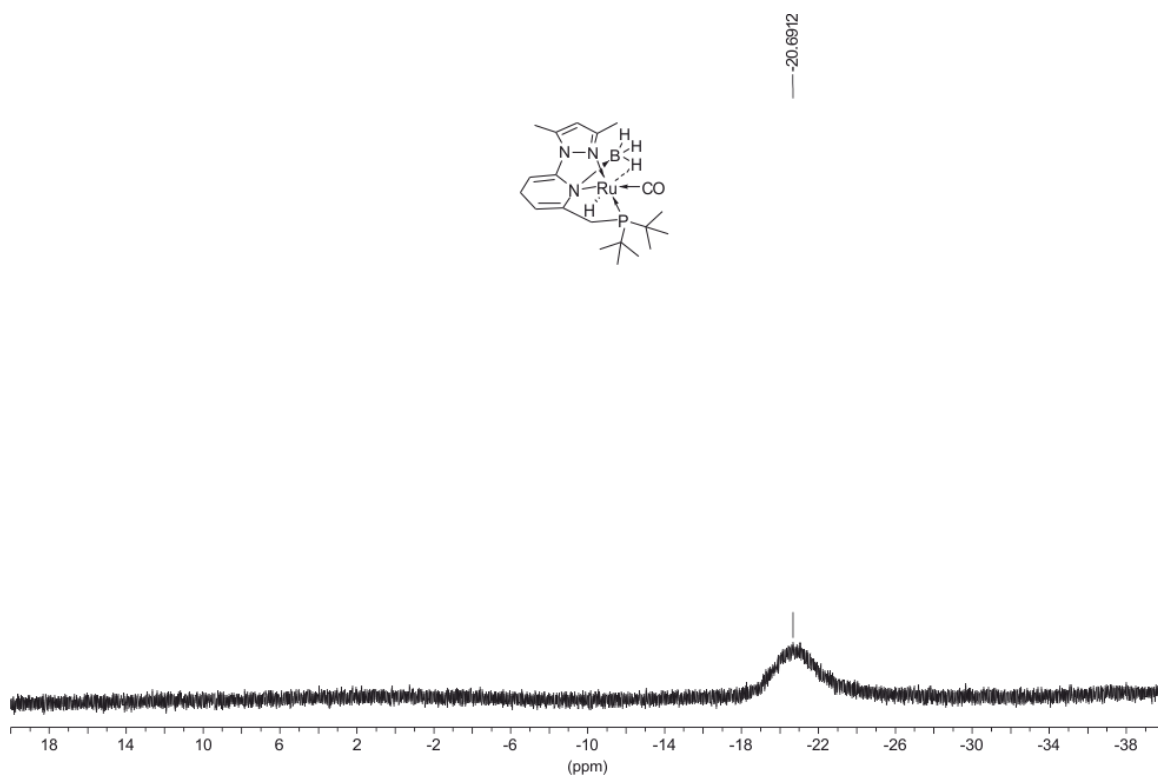
**Figure S17.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{C}_6\text{D}_6$ , 298K) of **4**.



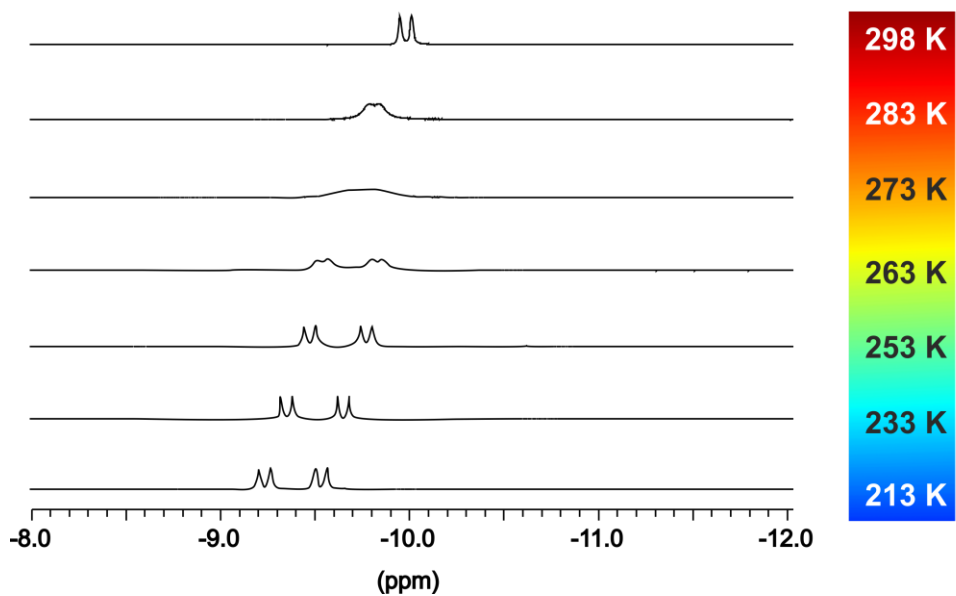
**Figure S18.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (100 MHz,  $\text{C}_6\text{D}_6$ , 298K) of **4**.



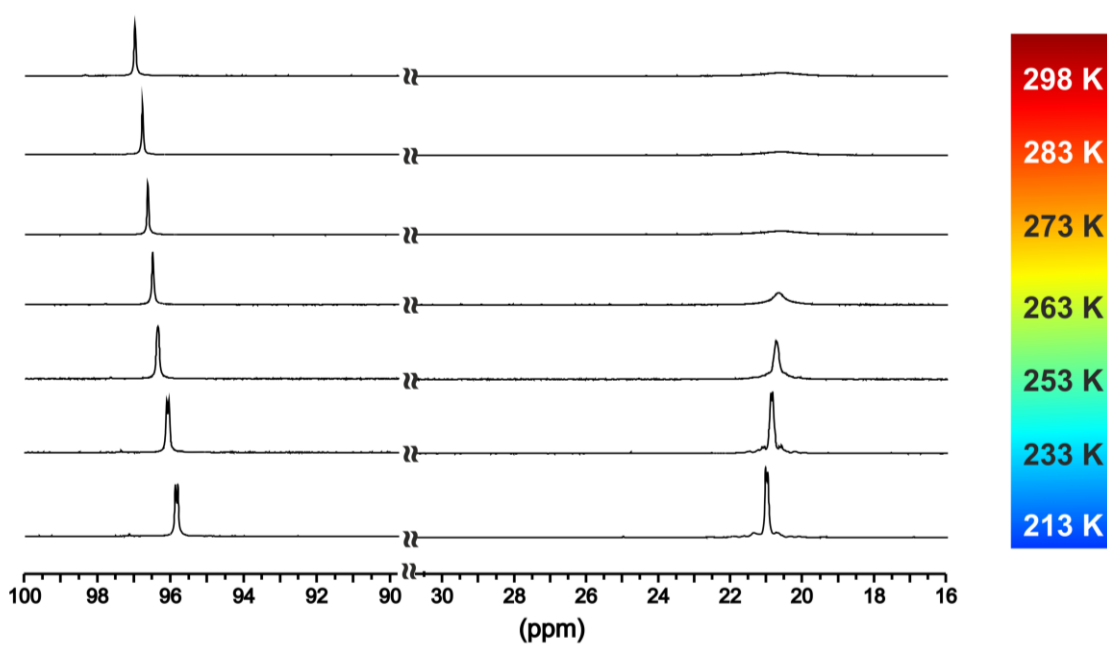
**Figure S19.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 298K) of **4**.



**Figure S20.**  $^{11}\text{B}$  NMR spectrum (128 MHz,  $\text{CD}_2\text{Cl}_2$ , 298K) of **4**.



**Figure S21.** Variable-temperature  $^1\text{H}$  NMR spectra (400 MHz, toluene- $d_8$ , hydride region) of  $2 \cdot \text{PPh}_3$ .



**Figure S22.** Variable-temperature  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra (161 MHz, toluene- $d_8$ ) of  $2 \cdot \text{PPh}_3$ .





**Figure S23.** “Man of the moon” device during a catalytic run.

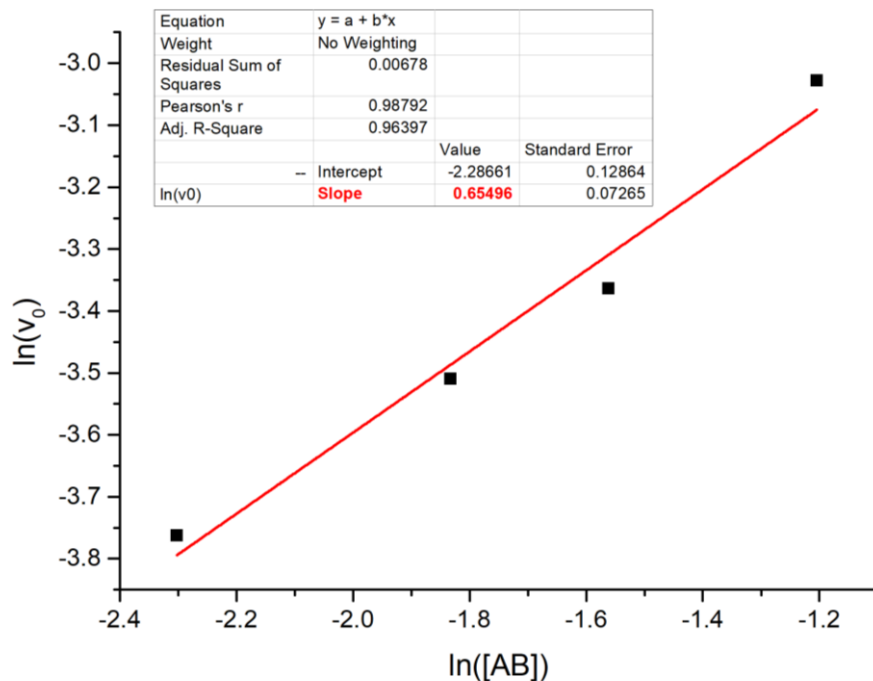
*Man of the moon X102* is a device conceived by the University of Zaragoza (Spain) for monitoring the progress of reactions that evolve gases by measuring the pressure variation vs. time in closed reaction systems. More information about the features of the kit can be found at the following link:

<http://www.manonthemoontech.com/x102-gas-evolution.html>.

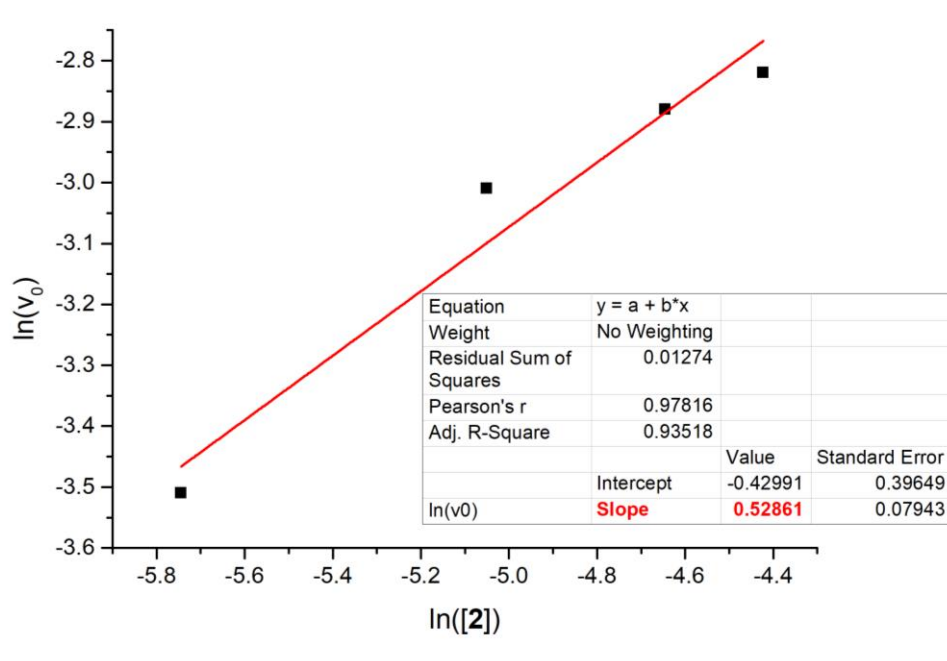
**Table S1.** Selected bond distances (Å) and angles (°) for complexes **2** · MeCN, **2** · PPh<sub>3</sub> and **4**. See Figures 1, 2 and 3 in the main text for atom numbering.

	<b>2</b> · MeCN	<b>2</b> · PPh <sub>3</sub>	<b>4</b>
Ru(1)-N(1)	2.094(3)	2.129(10)	2.1454(18)
Ru(1)-N(3)	2.113(3)	2.125(7)	2.1069(19)
Ru(1)-N(4)	2.211(3)	-	-
Ru(1)-P(1)	2.290(8)	2.330(3)	2.2756(6)
Ru(1)-P(2)	-	2.484(3)	-
Ru(1)-C(20)	1.833(3)	1.824(12)	1.828(2)
Ru(1)-H(100)	1.463(4)	2.314	1.56(2)
Ru(1)-B(1)	-	-	2.460(3)
B(1)-N(1)	-	-	1.593(3)
N(1)-H(100)	-	2.370	-
C(1)-C(6)	1.376(5)	1.385(15)	1.501(3)
P(1)-Ru(1)-N(3)	158.56(8)	152.6(3)	159.70(5)
P(1)-Ru(1)-N(1)	83.27(7)	81.4(3)	86.11(5)
C(20)-Ru(1)-N(1)	172.05(13)	171.2(5)	172.43(9)
H(100)-Ru(1)-N(1)	86.6(15)	64.3	101.6(9)
H(100)-Ru(1)-N(4)	171.9(13)	-	-
H(100)-Ru(1)-P(1)	84.2(13)	92.8	85.6(9)
H(100)-Ru(1)-P(2)	-	147.1	-
Ru(1)-H(100)-N(1)	-	54.0	-
H(100)-Ru(1)-H(103)	-	-	170.0(12)

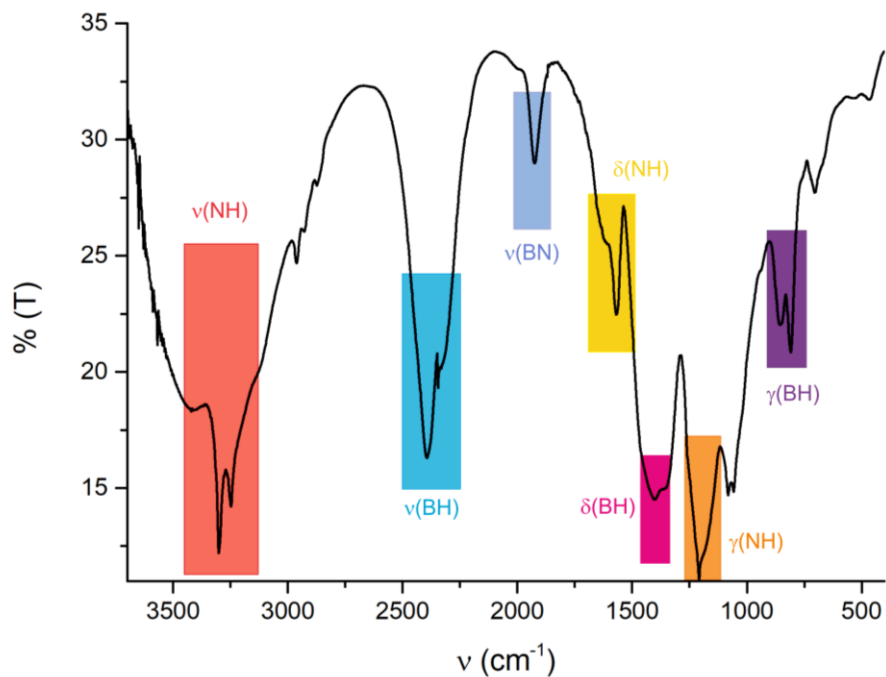
**Initial rate experiments on the catalytic dehydrogenation of AB by 2:** the evaluation of the reaction order with respect to [AB] was performed through an initial rate experiment at T = 298 K at four different initial AB concentrations (0.30, 0.21, 0.16 and 0.10 M) while keeping the catalyst concentration constant ([**2**] = 3.2 · 10<sup>-3</sup> M).<sup>[S1]</sup> A mean rate value was calculated from the first collected points, and the results were used to infer the reaction order in [AB]. An analogous procedure was followed for the determination of the rate order with respect to the catalyst, using four different concentrations ([**2**] = 3.2 · 10<sup>-3</sup> / 6.4 · 10<sup>-3</sup> / 9.6 · 10<sup>-3</sup> / 1.2 · 10<sup>-2</sup> M) while keeping AB concentration constant ([AB] = 0.16 M). A linear ln(v<sub>0</sub>) vs. ln([**2**]) plot leads to the determination of the reaction rate dependence from [**2**].



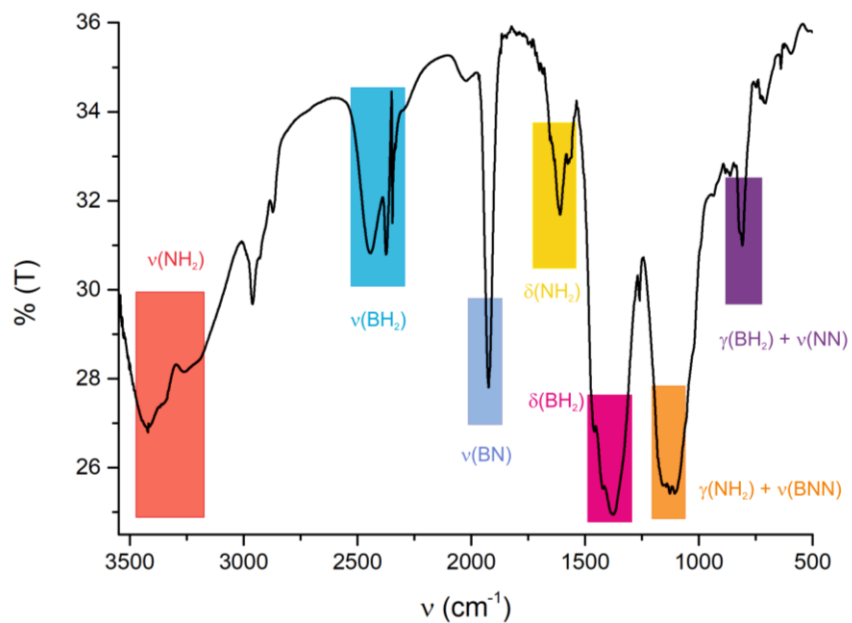
**Figure S24.**  $\ln(v_0)$  vs.  $\ln([AB])$  plot for the determination of the AB dehydrogenation reaction kinetic order with respect to AB concentration.



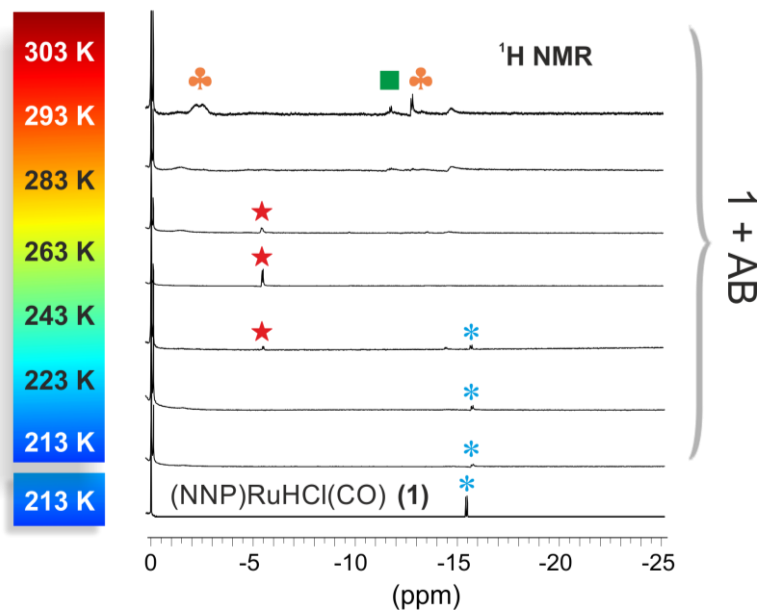
**Figure S25.**  $\ln(v_0)$  vs.  $\ln([2])$  plot for the determination of the AB dehydrogenation reaction kinetic order with respect to the catalyst concentration.



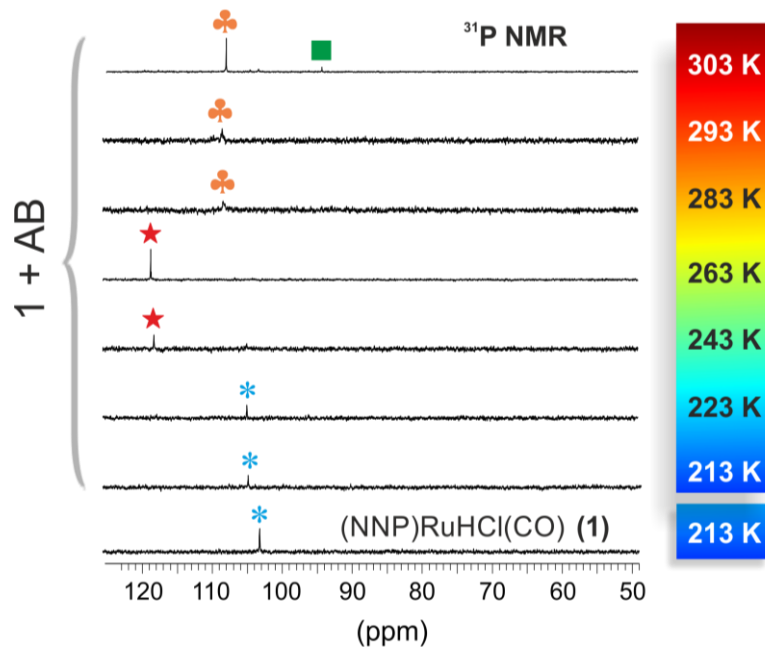
**Figure S26.** FTIR spectrum (KBr pellet) of the off-white solid precipitate formed during the reaction between **1** and AB (2 mol%, THF, RT).



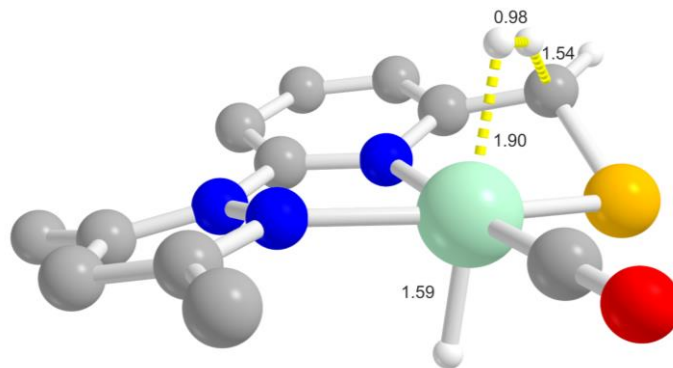
**Figure S27.** FTIR spectrum (KBr pellet) of the off-white solid precipitate formed during the reaction between **1** and HBB (2 mol%, THF, RT).



**Figure S28.** Variable-temperature  $^1\text{H}$  NMR spectra (400 MHz, hydride region) of **1** and its mixture with AB (1:10 ratio) in  $\text{THF-}d_8$ . Light blue asterisk: **1**. Red star: evidence of putative  $(^t\text{BuPNN})\text{Ru}(\text{H})_2(\text{CO})$  as intermediate. Orange clover: **3**. Green square: **4** as catalyst spent form.



**Figure S29.** Variable-temperature  $^{31}\text{P}$  NMR spectra (161 MHz) of **1** and its mixture with AB (1:10 ratio) in  $\text{THF-}d_8$ . Light blue asterisk: **1**. Red star: evidence of putative  $(^t\text{BuPNN})\text{Ru}(\text{H})_2(\text{CO})$  as intermediate. Orange clover: **3**. Green square: **4** as catalyst spent form.



**Figure S30.** Optimized structure of **TS<sub>2</sub>**. Selected optimized bond lengths reported (Å). H atoms on the pincer ligand not relevant for the discussion and *tert*-butyl groups on P omitted for clarity. Atom color code: white, H; gray, C; orange, P; blue, N; red, O; aquamarine, Ru.

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[S1] For further details on this method, see the website:

<http://www.chm.davidson.edu/vce/kinetics/MethodOfInitialRates.html>