

SUPPORTING INFORMATION

Binary Catalyst System of Cationic Ru-CNC Pincer Complex with an Alkali Metal Salt for Selective Hydroboration of Carbon Dioxide

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Note added after first publication: This Supplementary Information file replaces that originally published on 15th September 2016, in which inaccurate crystal structure data were presented.

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S1. General considerations

All preparations and manipulations were performed using standard Schlenk techniques under a nitrogen atmosphere unless specified. Solvents were dried using a MBraun SPS column. Chemicals were purchased from commercial suppliers and used as received without further purification. CD₂Cl₂ was purchased from Cambridge Isotopes and stored under N₂ and 3 Å molecular sieves.

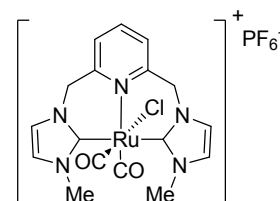
Ligands **1**, **2**, **3** and silver complexes^{1b,2} **4**, **5** and **6** were synthesized according to literature procedures. Complex **10** was prepared according to modified literature using dichloromethane as solvent under room temperature for 24h³. [Ru(CO)₂Cl₂]_n⁴ and RuHCl(CO)(PPh₃)₃⁵ were also prepared via literature procedures. NMR spectra were measured at 25°C using a Bruker ACF 500 MHz and JEOL Resonance 500MHz NMR spectrometer. Chemical shifts are expressed with a positive sign, in parts per million, relative to residual ¹H and ¹³C solvent signals, and external BF₃.OEt₂ for ¹¹B NMR. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration.

Flash column chromatography was generally performed using Silica Gel. Elemental analyses were performed on a VarioMICRO Elementar system. IR spectra were recorded using a Varian 3100 FT-IR spectrometer using KBr pellets. ESI-MS measurements were performed on Finnigan LCQ mass spectrometer, isotope distribution patterns were used as a composition proof in addition to m/z signal. Diffraction measurements were conducted at 100(2) K on a Bruker AXS D8 Venture diffractometer by using Mo-K α radiation ($\lambda = 0.71073$ Å). The data were corrected for absorption effects using the multi-scan method implemented in the program SADABS.⁶ Structure solutions and refinements were performed by using the programs SHELXT⁷, SHELXL-version 2014/6⁸ and SHELXL-2014/7.⁹ For complex **12**, the atomic position of the hydride coordinated to the ruthenium was calculated with the aid of the program XHydex.¹⁰ The method employed was a potential energy minimization, the search for a terminal H-atom on Ru1 was attempted on a hole location with a radius of 3.00 Å and a Metal-H bond length of 1.600(0.050) Å. The U[iso] of the hydride H1 and fractional coordinates were fixed. CCDC No.: 1479629 (complex **12**), 1479630 (complex **14**)

S2. Synthetic procedures and characterization details

Complex 7

In the dark, a mixture of silver complex **4** (0.582 g, 1.05 mmol) and $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ (0.228 g, 1.00 mmol) in CH_3OH (40 mL) was heated under reflux for 24 h. After cooling to room temperature, the solution was filtered through Celite. NH_4PF_6 (0.408 g, 2.50 mmol, 5 equiv.) was added and stirred at room temperature for 2 h.



The resultant solution was evaporated and extracted with CH_3CN (4×10 mL). The solvent was removed under vacuum and the crude residue was purified by column chromatography ($\text{CH}_2\text{Cl}_2 : \text{CH}_3\text{CN}$, 10:1). The complex was subsequently dissolved in some CH_3CN and triturated with Et_2O to afford complex **7** as a pale yellow solid (0.162 g, 27%). A meaningful $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for complex **7** could not be obtained due to low solubility of the product in common organic solvents and significant line broadening.

^1H NMR (500MHz, $\text{DMSO}-d_6$): δ 8.27 (t, $J = 7.7$ Hz, 1H, py-H4), 7.88 (d, $J = 7.2$ Hz, 2H, 2 py-H3), 7.70 (s, 2H, 2 imi-H3), 7.61 (s, 2H, 2 imi-H4), 6.38 (br s, 1H, py-CHH), 5.93 (br s, 1H, py-CHH), 5.63 (br s, 1H, py-CHH), 5.21 (br s, 1H, py-CHH), 3.98 (s, 6H, 2 NCH_3).

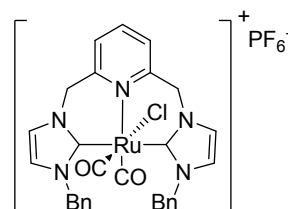
IR (KBr): $\nu(\text{CO})$ 2053, 1989 cm^{-1}

MS [ESI]: m/z (%) = 459.94 $[\text{Ru}(\text{CNC}_{\text{Me}})(\text{CO})_2(\text{Cl})]^+$ (75), 431.96 $[\text{Ru}(\text{CNC}_{\text{Me}})(\text{CO})(\text{Cl})]^+$ (15), 404.11 $[\text{Ru}(\text{CNC}_{\text{Me}})(\text{Cl})]^+$ (100).

EA: Calcd. $\text{C}_{17}\text{H}_{19}\text{ClF}_6\text{N}_3\text{O}_2\text{PRu} \cdot 0.25\text{Et}_2\text{O}$: C 34.57, H 3.47, N 11.20%. Found: C 34.68, H 3.38, N 11.28%.

Complex 8

In the dark, a mixture of silver complex **5** (0.741 g, 1.05 mmol) and $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ (0.228 g, 1.00 mmol) in dry CH_3CN (40 mL) was heated under reflux for 2 h. After cooling to room temperature, the solution was filtered through Celite and evaporated. NH_4PF_6 (0.408 g, 2.50 mmol, 5 equiv.) and CH_3OH (20 mL) was added and stirred at room temperature for 2 h. The resultant solution was evaporated and extracted with CH_3CN (4×5 mL). The solvent was removed under vacuum and the crude residue was purified by column chromatography ($\text{CH}_2\text{Cl}_2 : \text{CH}_3\text{CN}$, 10:1). The complex was subsequently dissolved in some CH_3CN and triturated with Et_2O to afford complex **8** as a pale yellow solid (0.502 g, 66%).



^1H NMR (500MHz, $\text{DMSO}-d_6$): δ 8.30 (t, $J = 7.7$ Hz, 1H, py-H4), 7.93 (br d, $J = 10.2$ Hz, 2H, 2 py-H3), 7.79 (s, 1H, imi-H3), 7.78 (s, 1H, imi-H3), 7.39 – 7.29 (m, 8H, 2 imi-H4 + 6 Ar-H), 7.21 – 7.17 (m, 4H, 4 Ar-H), 6.57 (d, $J = 13.7$ Hz, 1H, py-CHH), 5.98 (d, $J = 16.1$ Hz, 1H, py-CHH), 5.75 – 5.43 (m, 5H, py-CHH + 2 NCH_2), 5.33 (d, $J = 15.9$ Hz, 1H, py-CHH).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, $\text{DMSO}-d_6$): δ 197.30 (s, CO), 192.10 (s, CO), 172.52 (s, Ru-C), 170.20 (s, Ru-C), 156.36 (s, py C2), 155.94 (s, py C2), 141.86 (s, py C4), 136.66 (s, Ar C1), 136.29 (s, Ar C1), 128.75 (s, 4 Ar C3), 127.96 (s, 2 Ar C2), 127.81 (s, 2 Ar C2), 127.41 (s, 2 Ar C4), 126.90 (s, py C3), 126.78 (s, py C3), 126.70 (s, imi-C4), 124.53 (s, imi-C4), 123.49 (s, imi-C3), 123.30 (s, imi-C3), 55.55 (s, py- CH_2), 53.57 (s, py- CH_2), 53.09 (s, NCH_2), 52.45 (s, NCH_2).

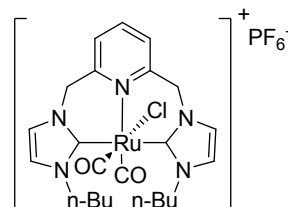
IR (KBr): $\nu(\text{CO})$ 2057, 1989 cm^{-1}

MS [ESI]: m/z (%) = 612.03 $[\text{Ru}(\text{CNC}_{\text{Bn}})(\text{CO})_2(\text{Cl})]^+$ (100), 556.04 $[\text{Ru}(\text{CNC}_{\text{Bn}})(\text{Cl})]^+$ (25), 520.24 $[\text{Ru}(\text{CNC}_{\text{Bn}})]^+$ (45).

EA: Calcd. $\text{C}_{29}\text{H}_{27}\text{ClF}_6\text{N}_5\text{O}_2\text{PRu}$: C 45.89, H 3.59, N 9.23%. Found: C 46.25, H 3.49, N 9.41%.

Complex 9

In the dark, a mixture of silver complex **6** (0.670 g, 1.05 mmol) and $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ (0.228 g, 1.00 mmol) in dichloroethane (40 mL) and CH_3OH (10 mL) was heated under reflux for 4 h. After cooling to room temperature, the solution was filtered through Celite and evaporated. NH_4PF_6 (0.408 g, 2.50 mmol, 5 equiv.) and CH_3OH (20 mL) was added and stirred at room temperature for 2 h. The resultant solution was evaporated and extracted with CH_3CN (4×5 mL). The solvent was removed under vacuum and the crude residue was purified by column chromatography (CH_2Cl_2 : CH_3CN , 10:1). The complex was subsequently dissolved in some CH_3CN and triturated with Et_2O to afford complex **9** as a pale yellow solid (0.394 g, 57%).



^1H NMR (500MHz, $\text{DMSO}-d_6$): δ 8.26 (t, $J = 7.7$ Hz, 1H, py-H4), 7.87 (br d, $J = 14.5$ Hz, 2H, 2 py-H3), 7.74 – 7.61 (m, 4H, 2 imi-H3 + 2 imi-H4), 6.46 (d, $J = 15.6$ Hz, 1H, py-CHH), 5.89 (d, $J = 16.4$ Hz, 1H, py-CHH), 5.63 (d, $J = 13.8$ Hz, 1H, py-CHH), 5.21 (d, $J = 15.8$ Hz, 1H, py-CHH), 4.48 (br-s, 1H, NCHH) 4.16 (m, 3H, 3 NCHH), 1.86 (br-s, 4H, 2 CH_2), 1.41 (br-s, 4H, 2 CH_2), 0.94 (t, $J = 7.4$ Hz, 6H, 2 CH_3).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, $\text{DMSO}-d_6$): 198.61 (s, CO), 192.46 (s, CO), 171.29 (s, Ru-C), 168.76 (s, Ru-C), 156.35 (s, py C2), 155.95 (s, py C2), 141.79 (s, py C4), 126.66 (s, py C3), 126.42 (s, py C3), 124.08 (s, imi-C4), 122.95 (s, imi-C4), 122.79 (s, imi-C3), 122.34 (s, imi-C3), 55.38 (s, py- CH_2), 53.41 (s, py- CH_2), 49.89 (s, NCH_2), 49.27 (s, NCH_2), 32.92 (s, 2 CH_2), 19.31 (s, 2 CH_2), 13.57 (s, 2 CH_3).

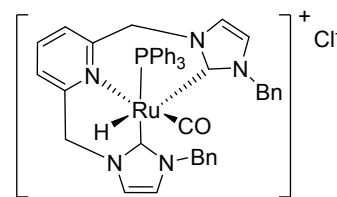
IR (KBr): $\nu(\text{CO})$ 2048, 1983 cm^{-1}

MS [ESI]: m/z (%) = 544.06 $[\text{Ru}(\text{CNC}_{n\text{-Bu}})(\text{CO})_2(\text{Cl})]^+$ (100), 516.02 $[\text{Ru}(\text{CNC}_{n\text{-Bu}})(\text{CO})(\text{Cl})]^+$ (15), 488.02 $[\text{Ru}(\text{CNC}_{n\text{-Bu}})(\text{Cl})]^+$ (45), 450.21 $[\text{Ru}(\text{CNC}_{n\text{-Bu}}) - 2\text{H}]^+$ (55).

EA: Calcd. $\text{C}_{23}\text{H}_{31}\text{ClF}_6\text{N}_5\text{O}_2\text{PRu} \cdot 0.25\text{Et}_2\text{O}$: C 40.63, H 4.76, N 9.87%. Found: C 40.80, H 4.51, N 10.10%.

Complex 10

In the dark, a mixture of silver complex **5** (0.071 g, 0.10 mmol) and $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (0.095 g, 0.10 mmol) in CH_2Cl_2 (5 mL) was stirred under room temperature for 24 h. The solution was filtered through Celite and the solvent was removed under vacuum. The crude residue was purified by column chromatography. Elution with CH_2Cl_2 : CH_3OH (10:1) afforded complex **10** as a yellow solid (0.068 g, 80%).



^1H NMR (500MHz, $\text{DMSO}-d_6$): δ 7.97 (t, $J = 7.6$ Hz, 1H, py-H4), 7.77 (d, $J = 7.6$ Hz, 1H, py-H3), 7.68 (s, 1H, imi-H3), 7.39 – 7.08 (m, 27H, py-H3 + imi-H3 + 15H arom PPh_3 + 10 Ar-H), 6.85 (s, 1H, imi-H4), 6.84 (s, 1H, imi-H4), 5.86 (d, $J = 14.3$ Hz, 1H, py-CHH), 5.74 – 5.61 (m, 3H, py-CHH + NCH_2), 5.38 (d, $J = 15.6$ Hz, 1H, py-CHH), 5.28 – 5.21 (m, 2H, 2 NCH_2), 4.17 (d, $J = 15.3$ Hz, 1H, py-CHH), -7.15 (d, $J_{\text{HP}} = 28.8$ Hz, 1H, Ru-H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, $\text{DMSO}-d_6$): 208.65 (d, $^2J_{\text{CP}} = 14.0$ Hz, CO), 189.06 (d, $^2J_{\text{CP}} = 8.2$ Hz, Ru-C), 182.32 (d, $^2J_{\text{CP}} = 81.5$ Hz, Ru-C), 156.92 (s, py C2), 156.11 (d, $^3J_{\text{CP}} = 2.2$ Hz, py C2), 139.73 (s, py C4), 136.61 (s, Ar

C1), 136.08 (s, Ar C1), 135.59 (d, $^1J_{CP} = 39.2$ Hz, 3 C_q arom, PPh₃), 132.35 (d, $^3J_{CP} = 10.9$ Hz, 6 CH arom, PPh₃), 129.62 (d, $^4J_{CP} = 1.5$ Hz, 3 CH arom, PPh₃), 128.83 (s, 4 Ar C3), 128.50 (s, 2 Ar C2), 128.22 (d, $^2J_{CP} = 8.0$ Hz, 6 CH arom, PPh₃), 127.63 (s, 2 Ar C2), 126.60 (s, 2 Ar C4), 124.50 (s, py C3), 124.32 (s, py C3), 123.52 (s, imi-C4), 123.02 (s, imi-C4), 122.18 (s, imi-C3), 121.69 (s, imi-C3), 57.64 (s, py-CH₂), 54.91 (s, py-CH₂), 53.36 (s, NCH₂), 52.82 (s, NCH₂).

$^31P\{^1H\}$ NMR (202 MHz, DMSO-*d*₆): δ 44.60 (s, PPh₃)

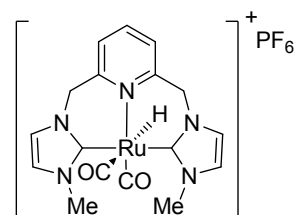
IR (KBr): $\nu(CO)$ 1916 cm⁻¹

MS [ESI]: m/z (%) = 811.99 [Ru(CNC_{Bn})(CO)(PPh₃)(H)]⁺ (25), 550.14 [Ru(CNC_{Bn})(CO)(H)]⁺ (100), 520.26 [Ru(CNC_{Bn})]⁺ (15).

EA: Calcd. C₄₆H₄₂ClN₅OPRu*3H₂O: C 61.22, H 5.36, N 7.76%. Found: C 61.97, H 5.32, N 7.98%.

Complex 11

A mixture of ruthenium complex **7** (0.121 g, 0.20 mmol) and NaBH₄ (0.010 g, 0.25 mmol) in CH₃CH₂OH (15 mL) and CH₃CN (3 mL) was stirred under room temperature for 1 h. NH₄PF₆ (0.160 g, 1.00 mmol, 5 equiv.) was then added to the resultant solution and stirred at room temperature for another 1 h. The resultant solution was evaporated and extracted with CH₃CN (3 × 5 mL). The solvent was removed under vacuum and the crude residue was purified by column chromatography (CH₂Cl₂ : CH₃CN, 10:1). The complex was subsequently dissolved in some CH₃CN and triturated with Et₂O to afford complex **11** as a pale yellow solid (0.080 g, 70%).



1H NMR (500MHz, DMSO-*d*₆): δ 8.15 (t, $J = 7.7$ Hz, 1H, py-H4), 7.80 (d, $J = 6.5$ Hz, 2H, 2 py-H3), 7.65 (s, 1H, imi-H3), 7.63 (s, 1H, imi-H3), 7.51 (s, 1H, imi-H4), 7.44 (s, 1H, imi-H4), 5.87 (d, $J = 15.8$ Hz, 1H, py-CHH), 5.73 (d, $J = 14.5$ Hz, 1H, py-CHH), 5.10 (d, $J = 15.8$ Hz, 1H, py-CHH), 4.87 (d, $J = 14.4$ Hz, 1H, py-CHH), 3.86 (s, 3H, NCH₃), 3.77 (s, 3H, NCH₃), -5.10 (s, 1H, Ru-H).

$^{13}C\{^1H\}$ NMR (125 MHz, DMSO-*d*₆): δ 203.68 (s, CO), 193.46 (s, CO), 178.82 (s, Ru-C), 177.70 (s, Ru-C), 156.75 (s, py C2), 155.95 (s, py C2), 140.46 (s, py C4), 125.23 (s, 2 py C3), 123.43 (s, imi-C4), 123.35 (s, imi-C4), 122.10 (s, imi-C3), 121.77 (s, imi-C3), 56.36 (s, py-CH₂), 55.82 (s, py-CH₂), 38.25 (s, NCH₃), 37.20 (s, NCH₃).

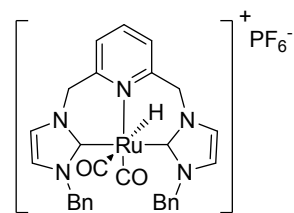
IR (KBr): $\nu(CO)$ 2032, 1973 cm⁻¹

MS [ESI]: m/z (%) = 425.81 [Ru(CNC_{Me})(CO)₂(H)]⁺ (10), 398.10 [Ru(CNC_{Me})(CO)(H)]⁺ (100), 370.16 [Ru(CNC_{Me})(H)]⁺ (20).

EA: Calcd. C₁₇H₂₀F₆N₅O₂PRu: C 35.67, H 3.52, N 12.23%. Found: C 35.72, H 3.33, N 12.27%.

Complex 12

A mixture of ruthenium complex **8** (0.152 g, 0.20 mmol) and NaBH₄ (0.010 g, 0.25 mmol) in CH₃CH₂OH (15 mL) and CH₃CN (3 mL) was stirred under room temperature for 1 h. NH₄PF₆ (0.160 g, 1.00 mmol, 5 equiv.) was then added to the resultant solution and stirred at room temperature for another 1 h. The resultant solution was evaporated and extracted with CH₃CN (3 × 5 mL). The solvent was removed under vacuum and the crude residue was purified by column chromatography (CH₂Cl₂ : CH₃CN, 20:1).



The complex was subsequently dissolved in some CH₃CN and triturated with Et₂O to afford complex **12** as a pale yellow solid (0.117 g, 80%).

¹H NMR (500MHz, DMSO-*d*₆): δ 8.19 (t, *J* = 7.7 Hz, 1H, py-H4), 7.85 (d, *J* = 7.7 Hz, 2H, 2 py-H3), 7.73 (s, 1H, imi-H3), 7.71 (s, 1H, imi-H3), 7.37 – 7.28 (m, 8H, 2 imi-H4 + 6 Ar-H), 7.16 – 7.14 (m, 4H, 4 Ar-H), 5.92 (d, *J* = 16.0 Hz, 1H, py-CHH), 5.80 (d, *J* = 14.6 Hz, 1H, py-CHH), 5.41 – 5.34 (m, 4H, 2 NCH₂), 5.21 (d, *J* = 15.9 Hz, 1H, py-CHH), 4.97 (d, *J* = 14.3 Hz, 1H, py-CHH), -4.99 (s, 1H, Ru-H).

¹³C{¹H} NMR (125 MHz, DMSO-*d*₆): 202.85 (s, CO), 193.28 (s, CO), 179.13 (s, Ru-C), 178.31 (s, Ru-C), 156.92 (s, py C2), 156.08 (s, py C2), 140.54 (s, py C4), 136.78 (s, Ar C1), 136.46 (s, Ar C1), 128.68 (s, 2 Ar C3), 128.62 (s, 2 Ar C3), 127.81 (s, 2 Ar C2), 127.59 (s, 2 Ar C2), 126.88 (s, py C3), 126.68 (s, py C3), 125.32 (s, 2 Ar C4), 123.25 (s, imi-C4), 123.03 (s, imi-C4), 122.39 (s, imi-C3), 122.35 (s, imi-C3), 56.54 (s, py-CH₂), 55.95 (s, py-CH₂), 53.35 (s, NCH₂), 52.88 (s, NCH₂).

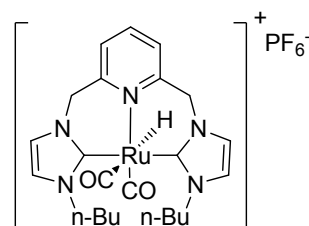
IR (KBr): ν(CO) 2042, 1956 cm⁻¹

MS [ESI]: *m/z* (%) = 577.87 [Ru(CNC_{Bn})(CO)₂(H)]⁺ (5), 550.13 [Ru(CNC_{Bn})(CO)(H)]⁺ (100), 520.25 [Ru(CNC_{Bn}) - H]⁺ (45).

EA: Calcd. C₂₉H₂₈F₆N₅O₂PRu: C 48.07, H 3.89, N 9.67%. Found: C 48.04, H 3.63, N 9.71%.

Complex 13

A mixture of ruthenium complex **9** (0.138 g, 0.20 mmol) and NaBH₄ (0.010 g, 0.25 mmol) in CH₃CH₂OH (15 mL) and CH₃CN (3 mL) was stirred under room temperature for 1 h. NH₄PF₆ (0.160 g, 1.00 mmol, 5 equiv.) was then added to the resultant solution and stirred at room temperature for another 1 h. The resultant solution was evaporated and extracted with CH₃CN (3 × 5 mL). The



solvent was removed under vacuum and the crude residue was purified by column chromatography (CH₂Cl₂ : CH₃CN, 20:1). The complex was subsequently dissolved in some CH₃CN and triturated with Et₂O to afford complex **13** as a pale yellow solid (0.096 g, 73%).

¹H NMR (500MHz, DMSO-*d*₆): δ 8.15 (t, *J* = 7.3 Hz, 1H, py-H4), 7.80 (s, 2H, 2 py-H3), 7.69 (s, 1H, imi-H3), 7.65 (s, 1H, imi-H3), 7.60 (s, 1H, imi-H4), 7.50 (s, 1H, imi-H4), 5.85 (d, *J* = 15.9 Hz, 1H, py-CHH), 5.72 (d, *J* = 14.5 Hz, 1H, py-CHH), 5.12 (d, *J* = 15.8 Hz, 1H, py-CHH), 4.89 (d, *J* = 14.3 Hz, 1H, py-CHH), 4.13 – 4.06 (m, 4H, 2 NCH₂), 1.83 – 1.72 (m, 4H, 2 CH₂), 1.42 – 1.36 (m, 4H, 2 CH₂), 0.93 – 0.91 (m, 6H, 2 CH₃), -5.08 (s, 1H, Ru-H).

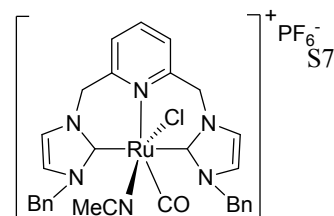
¹³C{¹H} NMR (125 MHz, DMSO-*d*₆): δ 203.90 (s, CO), 193.66 (s, CO), 177.468 (s, Ru-C), 176.85 (s, Ru-C), 156.90 (s, py C2), 156.05 (s, py C2), 140.46 (s, py C4), 125.17 (s, 2 py C3), 122.81 (s, imi-C4), 122.34 (s, imi-C4), 121.89 (s, imi-C3), 121.53 (s, imi-C3), 56.41 (s, py-CH₂), 55.81 (s, py-CH₂), 50.168 (s, NCH₂), 49.63 (s, NCH₂), 32.45 (s, CH₂), 32.39 (s, CH₂), 19.37 (s, CH₂), 19.29 (s, 2 CH₂), 13.48 (s, 2 CH₃).

IR (KBr): ν(CO) 2024, 1963 cm⁻¹

MS [ESI]: *m/z* (%) = 509.88 [Ru(CNC_{n-Bu})(CO)₂(H)]⁺ (5), 482.17 [Ru(CNC_{n-Bu})(CO)(H)]⁺ (100), 450.22 [Ru(CNC_{n-Bu}) - 2H]⁺ (35).

EA: Calcd. C₂₃H₃₂F₆N₅O₂PRu*0.25Et₂O: C 42.70, H 5.15, N 10.37%. Found: C 42.48, H 4.97, N 10.00%.

Complex 14



A mixture of ruthenium complex **8** (0.152 g, 0.20 mmol) and trimethylamine *N*-oxide (0.016 g, 0.22 mmol) in CH₃CN (6 mL) was stirred under reflux for 12 h. After cooling to room temperature, the solution was filtered through Celite and the solvent was removed under vacuum. The crude residue was purified by column chromatography (CH₂Cl₂ : CH₃CN, 20:1). The complex was subsequently dissolved in some CH₃CN and triturated with Et₂O to afford complex **14** as a yellow solid (0.130 g, 84%).

¹H NMR (500MHz, DMSO-*d*₆): δ 8.26 (t, *J* = 7.7 Hz, 1H, py-H4), 7.90 – 7.86 (m, 2H, 2 py-H3), 7.70 (s, 1H, imi-H3), 7.68 (s, 1H, imi-H3), 7.41 - 7.20 (m, 12H, 2 imi-H4 + 10Ar-H), 6.52 (d, *J* = 15.1 Hz, 1H, py-CHH), 5.76 – 5.44 (m, 7H, 3 py-CHH + 2 NCH₂), 2.21 (s, 3H, coordinated CH₃CN).

¹³C {¹H} NMR (125 MHz, DMSO-*d*₆): δ 204.39 (s, CO), 179.83 (s, Ru-C), 179.06 (s, Ru-C), 157.38 (s, py C2), 156.80 (s, py C2), 141.06 (s, py C4), 137.31 (s, 2 Ar C1), 129.15 (s, coordinated CH₃CN), 128.72 (s, 2 Ar C3), 128.59 (s, 2 Ar C3), 127.74 (s, 2 Ar C2), 127.64 (s, 2 Ar C2), 127.41 (s, 2 Ar C4), 127.07 (s, py C3), 126.89 (s, py C3), 125.93 (s, imi-C4), 123.65 (s, imi-C4), 123.10 (s, imi-C3), 122.24 (s, imi-C3), 53.72 (s, py-CH₂), 53.50 (s, py-CH₂), 52.45 (s, 2 NCH₂), 3.99 (s, coordinated CH₃CN).

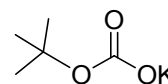
IR (KBr): ν(CO) 1962 cm⁻¹

MS [ESI]: *m/z* (%) = 624.93 [Ru(CNC_{Bn})(CO)(Cl)(MeCN)]⁺ (60), 583.97 [Ru(CNC_{Bn})(CO)(Cl)]⁺ (100), 556.05 [Ru(CNC_{Bn})(Cl)]⁺ (65), 520.24 [Ru(CNC_{Bn})]⁺ (80).

EA: Calcd. C₃₀H₂₉ClF₆N₆OPRu: C 46.73, H 3.79, N 10.90%. Found: C 46.49, H 3.51, N 10.88%.

Potassium tert-butyl carbonate (KOCO₂tBu)¹¹

A mixture of potassium *tert*-butoxide (2.24 g, 20.0 mmol) and dry THF (120 mL) were added to a flame-dried 250 mL two-necked round bottom flask under an argon atmosphere. The mixture was stirred vigorously until all the potassium *tert*-butoxide was dissolved. 150 g of dry ice (solid CO₂) was added slowly in small portions (~15 g). The slurry was stirred vigorously for 1 h under an argon atmosphere. The solvent was removed under vacuum to afford KOCO₂tBu as an off-white solid (2.66 g, 85%)



¹H NMR (500MHz, D₂O): δ 1.23 (s, 9H, t-Bu)

¹³C {¹H} NMR (125 MHz, D₂O): δ 30.34 (s, C(CH₃)₃), 70.01 (s, C(CH₃)₃), 161.19 (s, KOCO₂tBu)

S3. Selected crystal data, data collection, and refinement parameters for complex 12 and 14

	Complex 12	Complex 14
Empirical formula	C ₃₁ H ₃₀ Cl ₄ F ₆ N ₅ O ₂ PRu	C ₃₁ H ₃₀ Cl ₃ F ₆ N ₆ OPRu
Formula weight	892.44	855.00
Temperature of data collection	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal size	0.097 x 0.156 x 0.226 mm ³	0.092 x 0.147 x 0.322 mm ³
Crystal system	Orthorhombic	Triclinic
Space group	P b c a	P -1
Unit cell dimensions	a = 16.6675(5) Å α = 90° b = 11.1422(3) Å β = 90° c = 38.2172(12) Å γ = 90°	a = 10.630(4) Å α = 77.336(14)° b = 12.402(5) Å β = 74.113(10)° c = 14.118(5) Å γ = 79.124(10)°
Volume	7097.4(4) Å ³	1730.1(11) Å ³
Z	8	2
Density (calculated)	1.670 g/m ³	1.641 g/m ³
F(000)	3584	860
Theta range for data collection	2.26 to 27.10°	2.21 to 28.23°
Reflections collected	16701	42950
Independent reflections	7823 [R(int) = 0.0520]	8519 [R(int) = 0.0524]
Goodness-of-fit on F ²	1.096	1.036
Final R indices [I>2σ(I)]	R1 = 0.0630, wR2 = 0.1284	R1 = 0.0413, wR2 = 0.0949
R indices (all data)	R1 = 0.0973, wR2 = 0.1407	R1 = 0.0539, wR2 = 0.0994
Largest diff. peak and hole	1.443 and -1.154 eÅ ⁻³	1.228 and -1.320 eÅ ⁻³

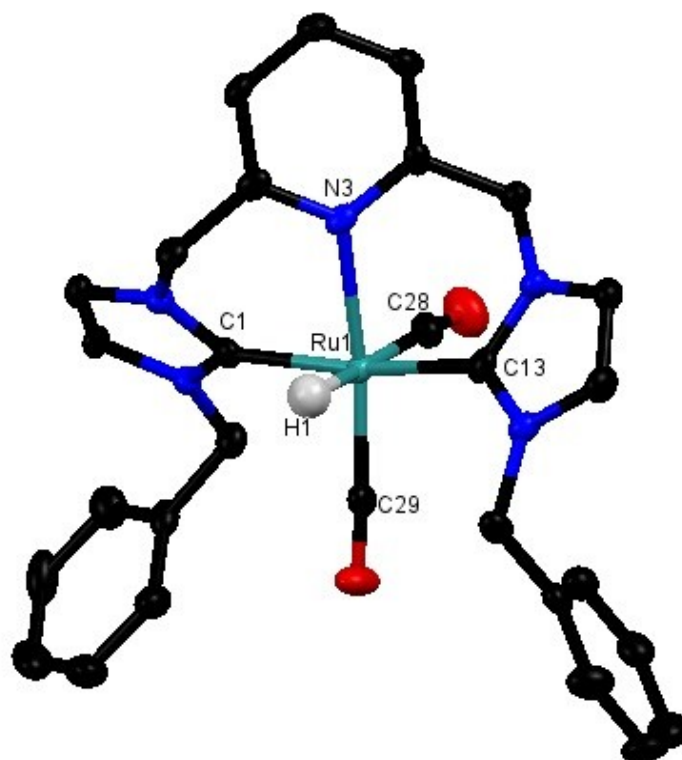


Figure S1. Crystal structure of complex **12**. (50% probability ellipsoids, Hydrogen atoms, with exception of the hydrido ligand, solvent molecules and PF₆ anions have been omitted for clarity)

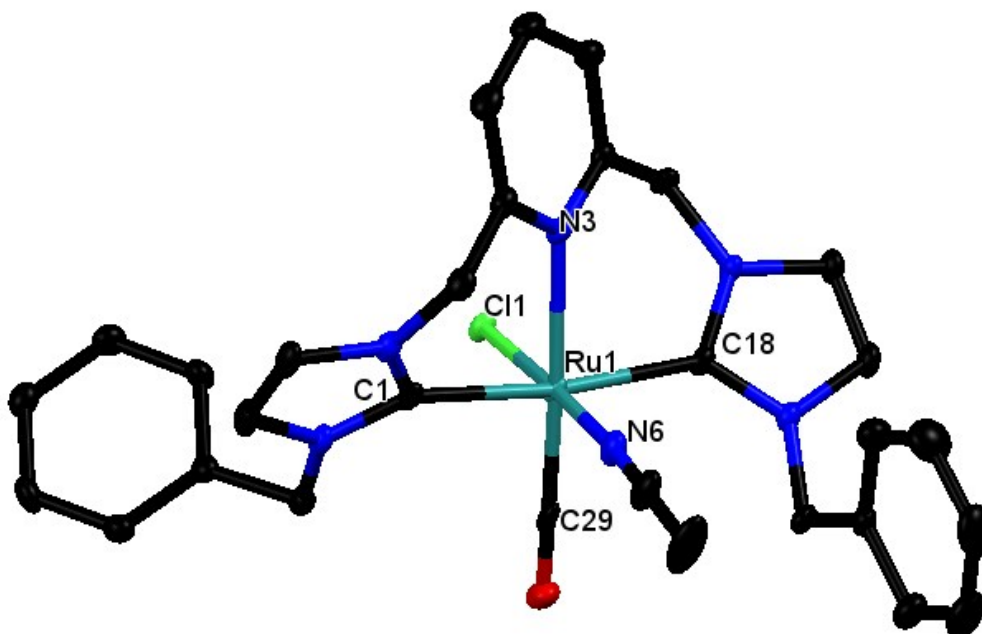
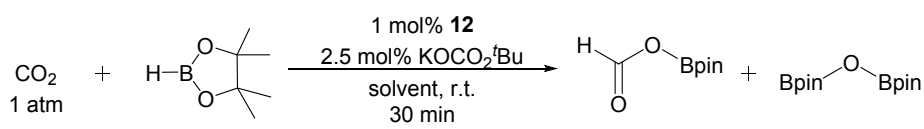


Figure S2. Crystal structure of complex **14**. (50% probability ellipsoids, Hydrogen atoms, solvent molecules and PF₆ anions have been omitted for clarity)

S4. Hydroboration procedures

Typical procedure for the hydroboration of CO₂ (Table 1, 2 and S3). In a 25 mL oven-dried Schlenk tube, the alkali metal salt (0.030 mmol, 2.5 mol%) and 1,3,5-trimethoxybenzene (0.050 mmol, 8.4 mg, internal standard) was added under 1 atm of carbon dioxide. 2 mL of CD₂Cl₂ was added followed by HBpin (1 equivalent, 1.2 mmol, 153.6 mg) and the reaction mixture was stirred vigorously at room temperature. The Ru-CNC catalyst (0.012 mmol, 1 mol%) was subsequently added. 0.4 mL aliquots of the reaction mixture was transferred to a NMR tube at 30 and 60 min intervals for analysis. The formation of HCOOBpin was monitored over time using ¹H NMR and ¹¹B {¹H} NMR spectroscopy.

Table S3. Screening of solvents for the Hydroboration of CO₂^a



Entry	Solvent	Yield of	
		HCOOBpin (%) ^b	(Bpin) ₂ O (%) ^b
1	CD ₂ Cl ₂	76	10
2	DMF- <i>d</i> ₇	67	7
3	THF- <i>d</i> ₈	56	23
4	DMSO- <i>d</i> ₆	45	7
5	CD ₃ CN	8	n.d. ^c

^aHBpin (1.2 mmol), solvent (2 mL), complex **12** (1 mol%), KOCO₂tBu (2.5 mol%), 1,3,5-trimethoxybenzene (0.05 mmol, internal standard), 1 atm CO₂, r.t.. ^bDetermined using ¹H NMR spectroscopy by integration against an internal standard, 1,3,5-trimethoxybenzene. ^cn.d.: not detected in the ¹H NMR spectra of the crude mixtures.

S5. ^1H NMR and ESI-MS of reactions

Reaction of complex 12 with KO^tBu under CO₂ and N₂. In a 25 mL oven-dried Schlenk tube, complex 12 (0.012 mmol, 8.8 mg) and KO^tBu (2.5 equiv, 3.4 mg) was added under 1 atm of carbon dioxide or nitrogen. 0.60 mL of THF-*d*₈ was then added and the reaction mixture was stirred vigorously at room temperature for 1 h. The reaction mixtures were then transferred to NMR tubes for analysis. Complex 12 decomposed in nitrogen into intractable mixtures in the presence of KO^tBu but remained unchanged in carbon dioxide in the presence of KO^tBu.

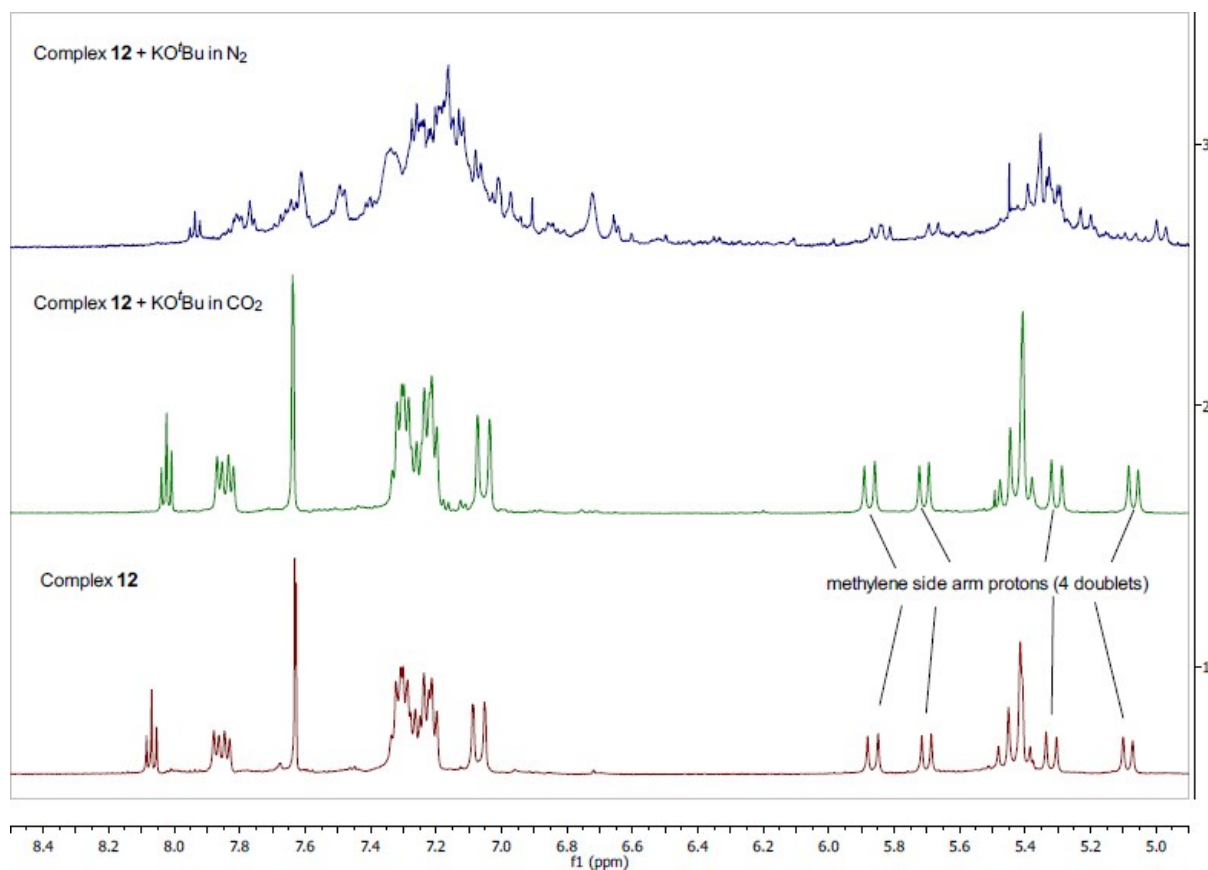


Figure S4. ^1H NMR of complex 12 with KO^tBu in CO₂ and N₂ atmospheres

Reaction of complex **14 with HBpin.** Complex **14** (0.005 mmol, 3.9 mg), HBpin (0.5 mmol, 72.6 μ L) and 0.60 mL of DCM- d_2 was added into a J Young NMR tube in a glovebox. The reaction mixture was shaken occasionally at room temperature for 1 h and then analysed by ^1H NMR. The formation of a Ru-H species can be seen by the peak at -5.04 ppm.

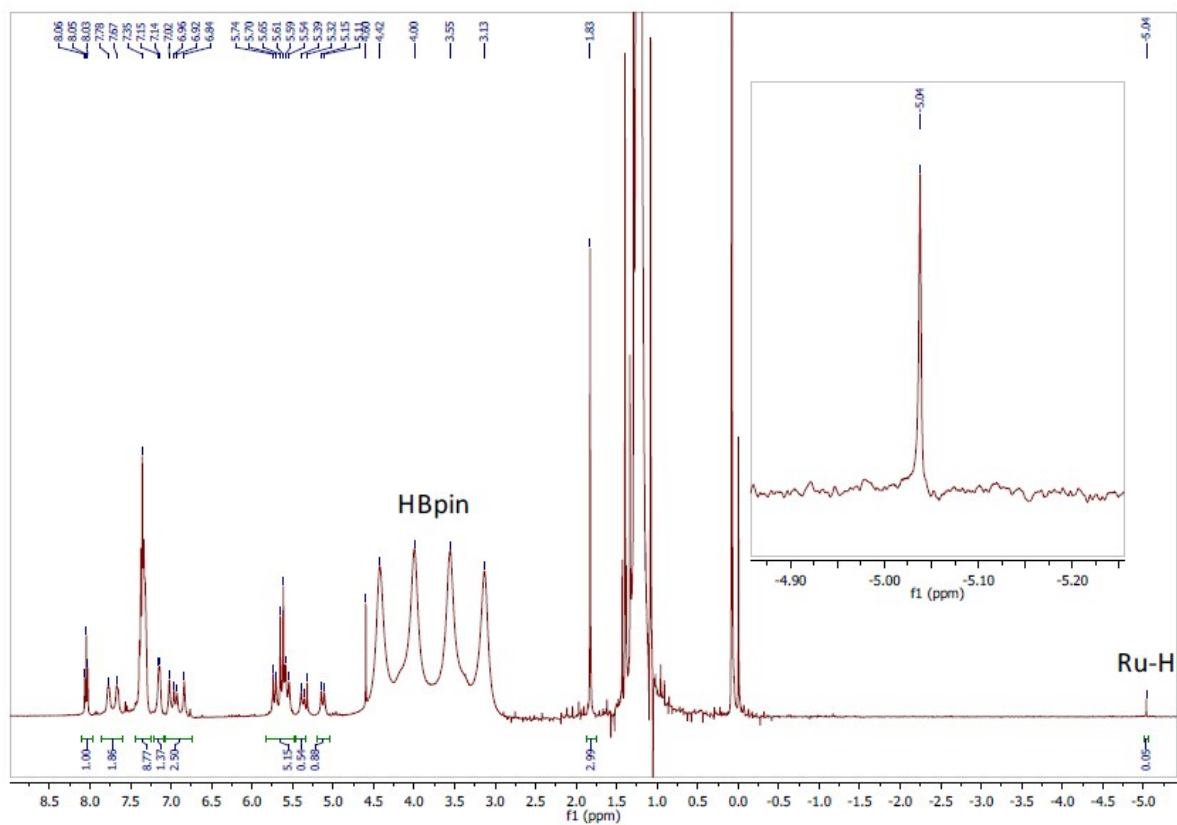


Figure S5. ^1H NMR of the reaction between **14** and excess HBpin in CD_2Cl_2

Stoichiometric reaction of complex **12 with HBpin (1:1 ratio).** In a 25 mL oven-dried Schlenk tube, complex **12** (0.01 mmol, 7.3 mg), HBpin (0.01 mmol, 1.41 mg, 1.45 μ L) and 0.6 mL of CD_2Cl_2 were added and the reaction mixture was stirred vigorously at room temperature for 1 h. The reaction mixture was then transferred to an NMR tube for analysis. No changes were observed in the ^1H NMR of **12**. This observation is consistent with our proposed mechanism that it is more likely for **12** to react with CO_2 rather than HBpin.

Some HBpin hydrolysed due to adventitious moisture to give Bpin-OH and H_2 .¹² However, upon addition of an excess of HBpin to **12** (100:1 ratio), only a trace amount of HBpin was observed to be hydrolysed in ^{11}B $\{^1\text{H}\}$ NMR analysis.

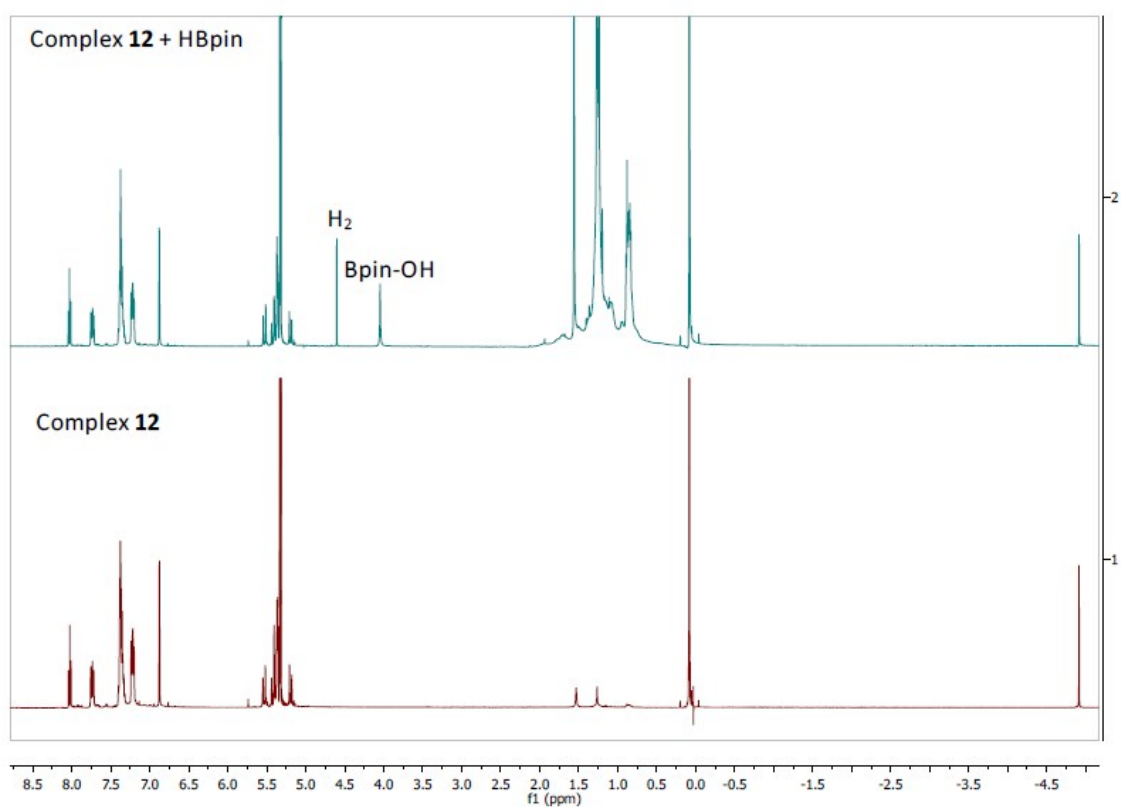


Figure S6. ^1H NMR of complex **12** and the stoichiometric reaction of complex **12** with HBpin (1:1 ratio) at r.t. in CD_2Cl_2

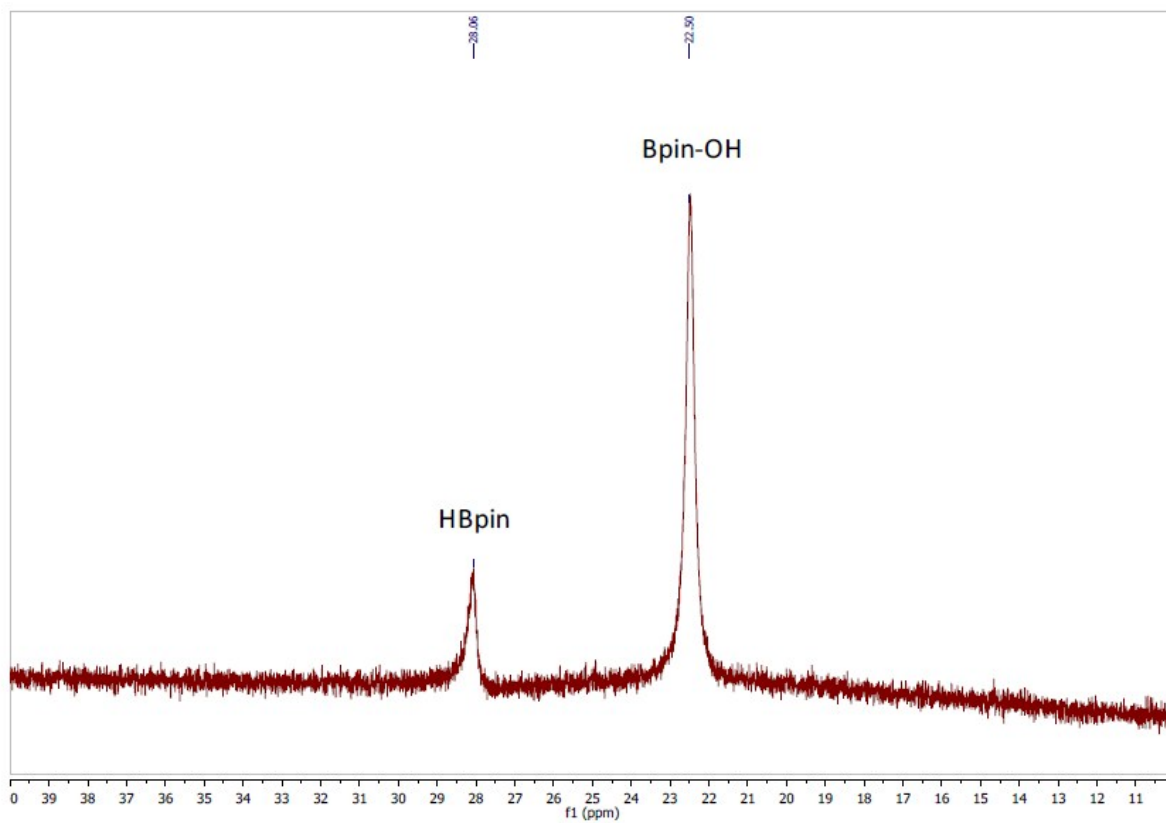


Figure S7. ^1H NMR of the stoichiometric reaction of complex **12** with HBpin (1:1 ratio) at r.t. in CD_2Cl_2

Reaction of excess HBpin with complex 12 (100:1 ratio). In a 25 mL oven-dried Schlenk tube, complex **12** (0.01 mmol, 7.3 mg), HBpin (1 mmol, 130 mg) and 0.6 mL of CD₂Cl₂ were added and the reaction mixture was stirred vigorously at room temperature for 1 h. The reaction mixture was then transferred to an NMR tube for analysis. Only a trace amount of HBpin was observed to be hydrolysed via ¹¹B {¹H} NMR.

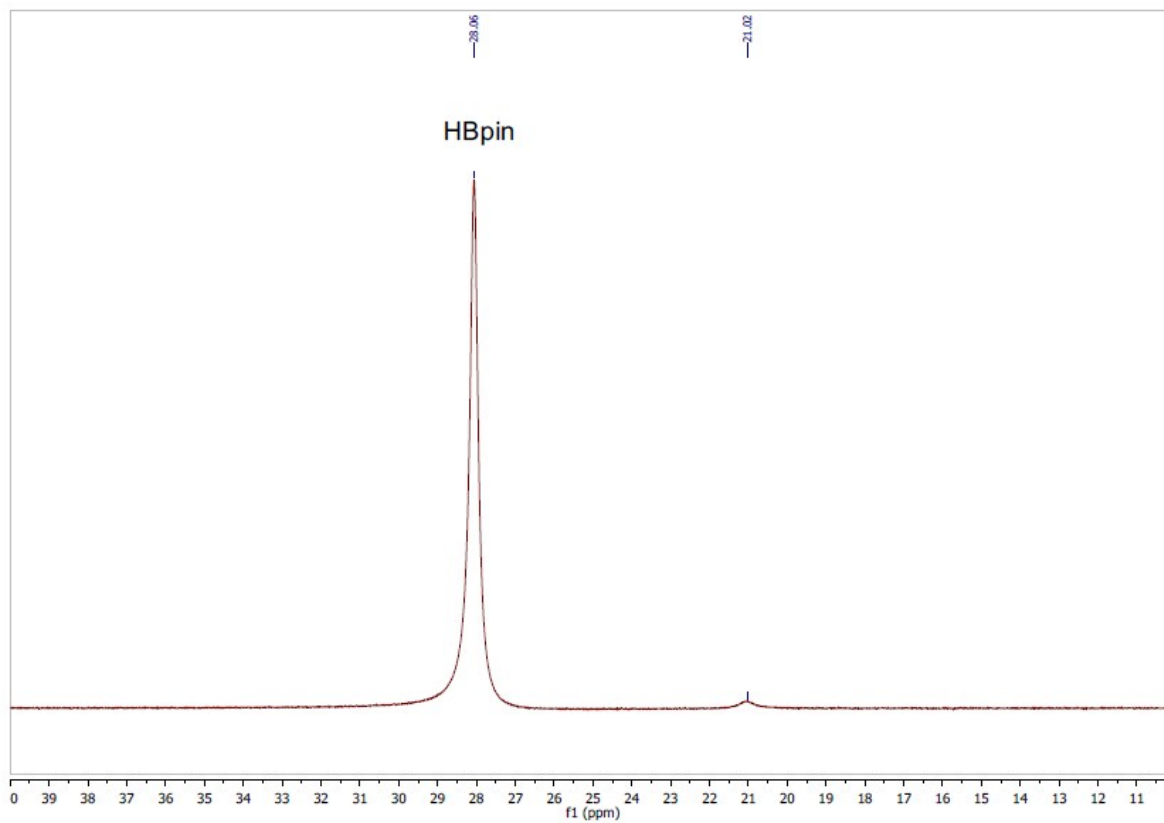


Figure S8. ¹¹B {¹H} NMR of the reaction of excess HBpin with complex **12** (100:1 ratio) at r.t. in CD₂Cl₂

Reaction of excess HBpin with KOCO₂tBu (40:1 ratio). In a 25 mL oven-dried Schlenk tube, KOCO₂tBu (0.03 mmol, 4.7 mg), HBpin (1.2 mmol, 153.6 mg) and 1.5 mL of THF-*d*₈ were added and the reaction mixture was stirred vigorously at room temperature for 1 h. 0.5 mL of the reaction mixture was then transferred to an NMR tube for analysis. A broad peak appeared in the ¹¹B {¹H} NMR at ~2.7 ppm which may suggest the formation of boron “ate” species similar to **B**.

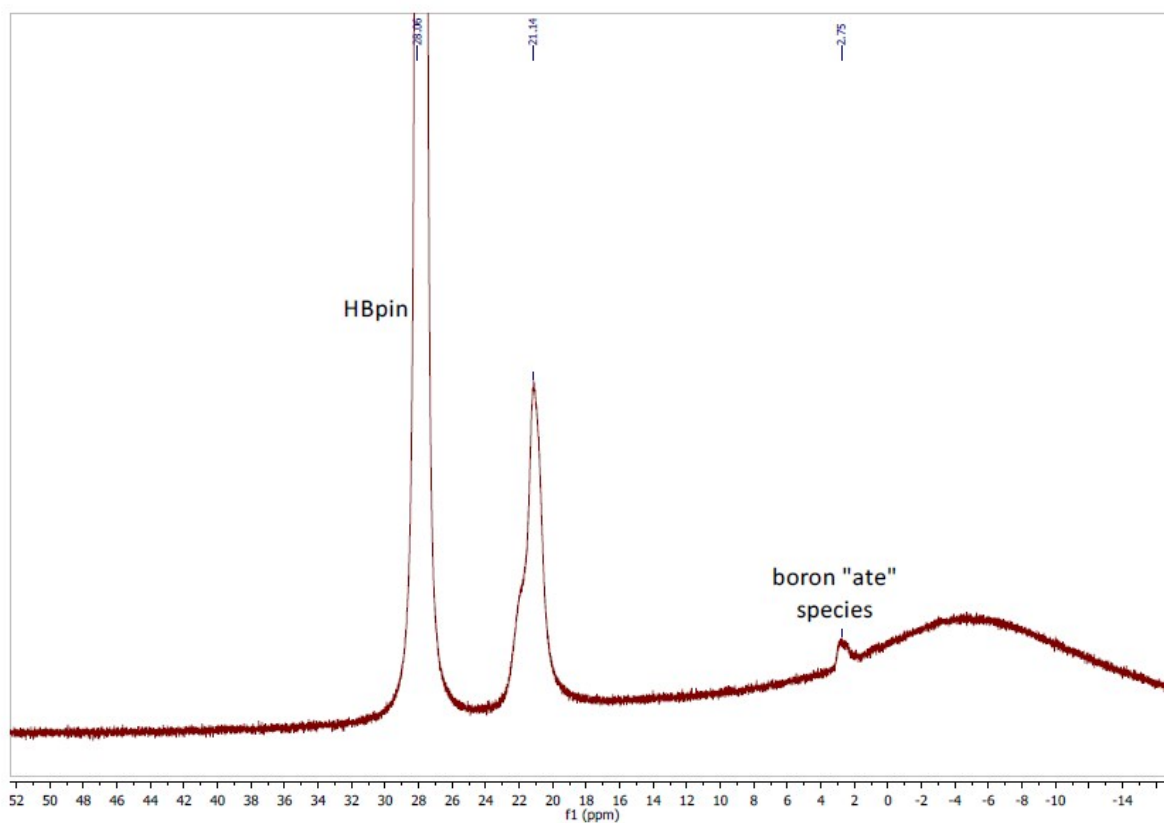


Figure S9. ¹¹B {¹H} NMR of the reaction of excess HBpin with KOCO₂tBu (40:1 ratio) at r.t. in THF-*d*₈

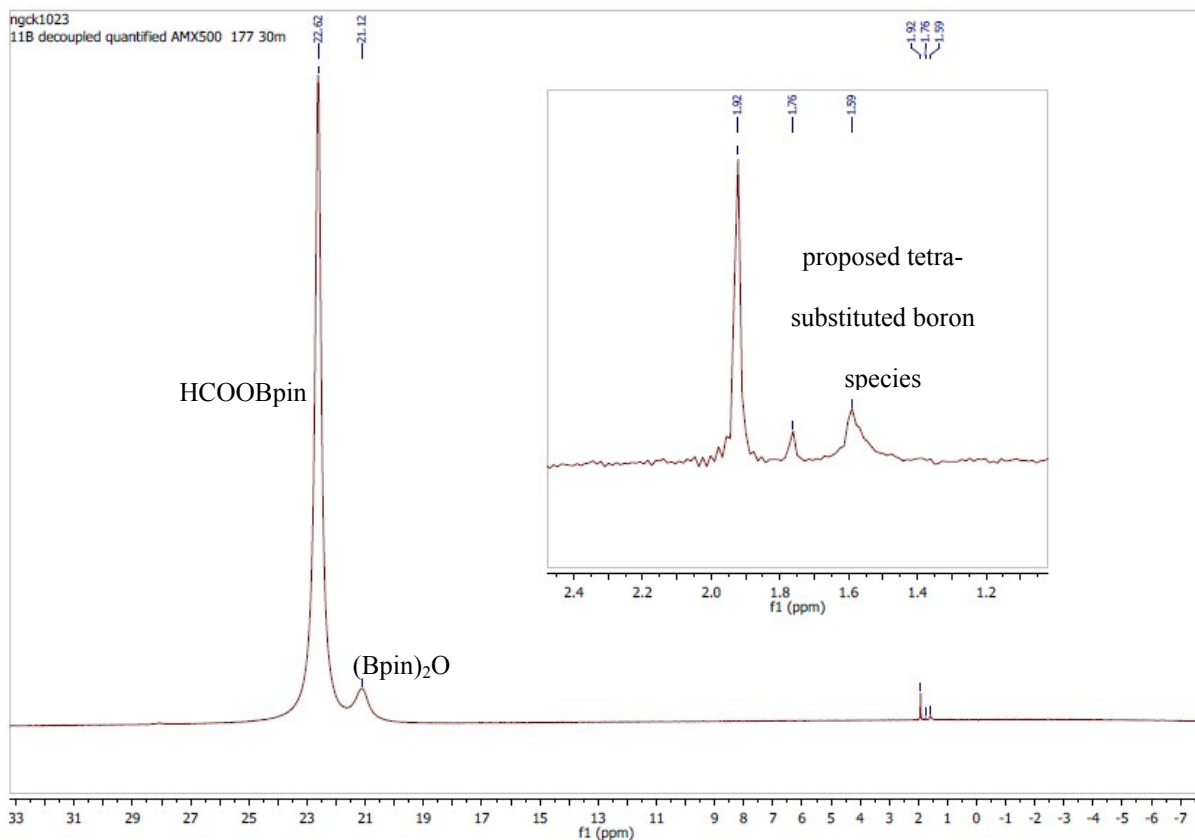


Figure S10. ^{11}B $\{^1\text{H}\}$ NMR of the reaction mixture using complex **12** as catalyst and KOCO_2^tBu as alkali metal salt after 0.5 h

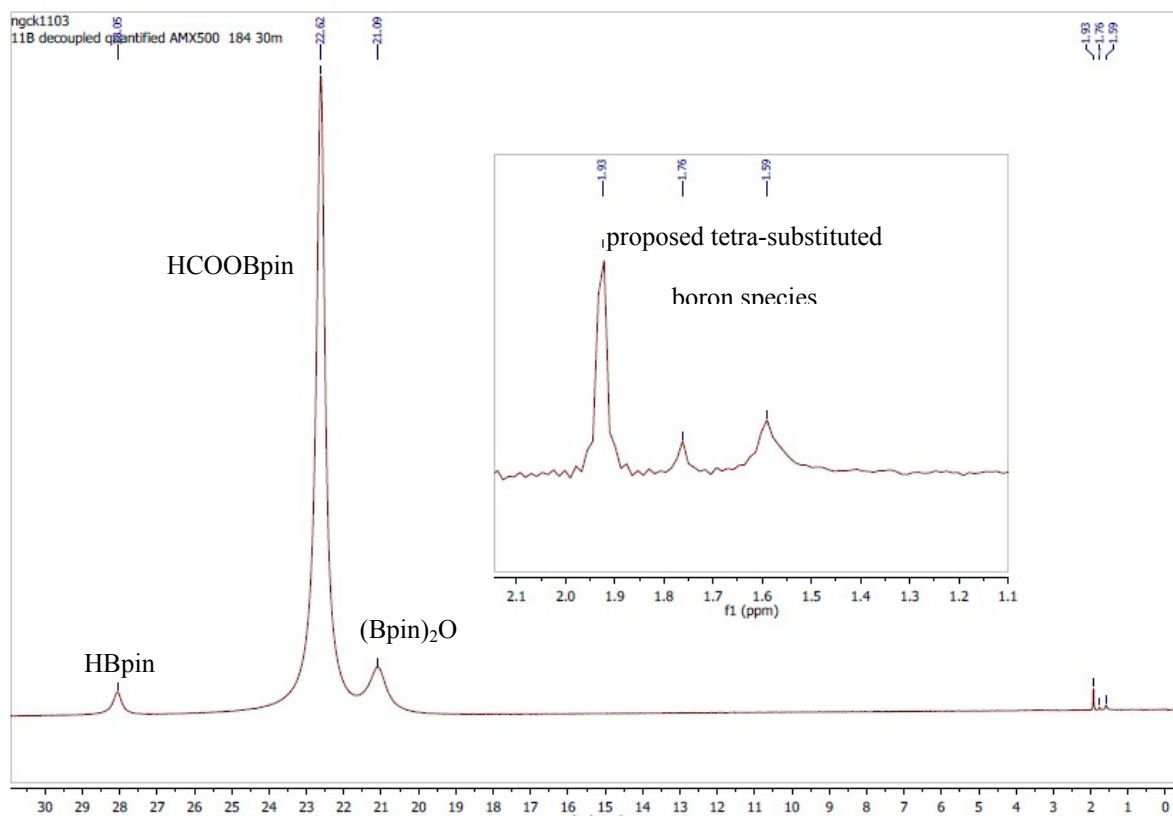


Figure S11. $^{11}\text{B} \{^1\text{H}\}$ NMR of the reaction mixture using complex **12** as catalyst and KHCO_3 as alkali metal salt after 0.5 h

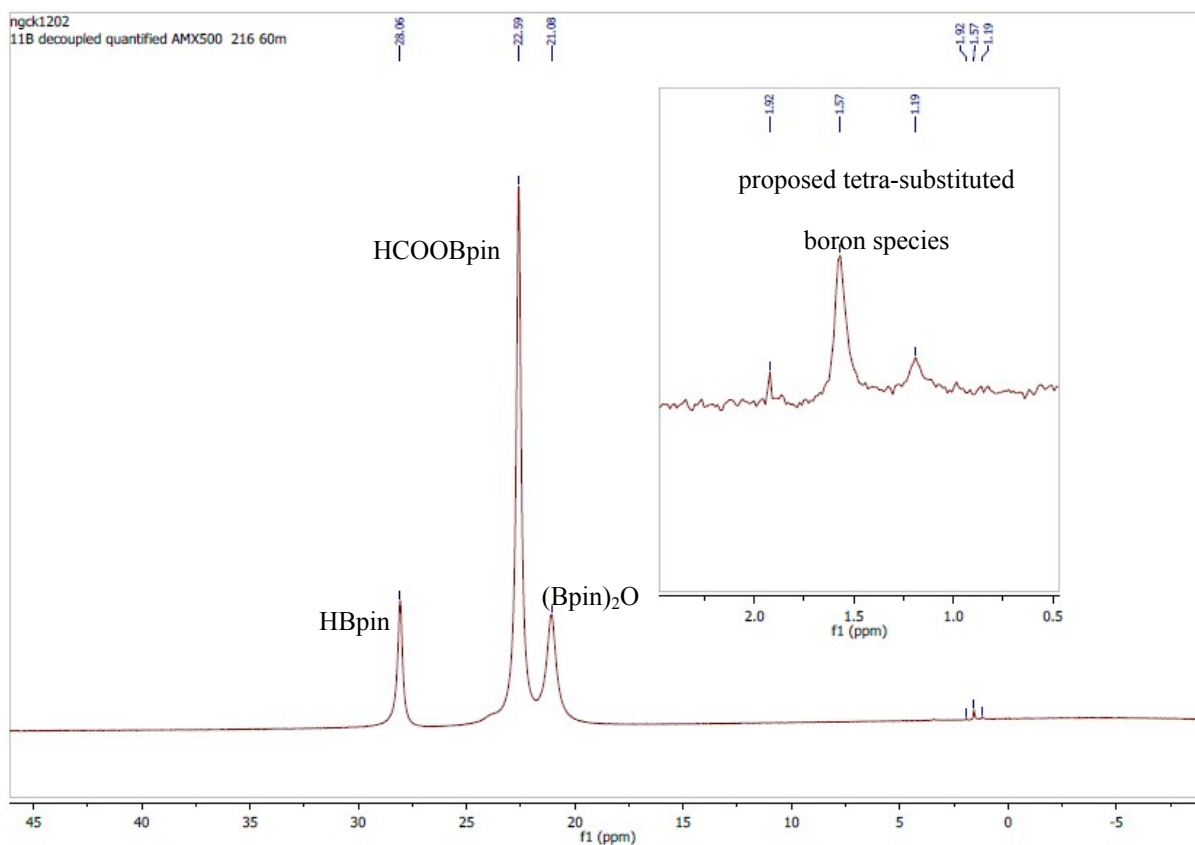


Figure S12. ^{11}B $\{^1\text{H}\}$ NMR of the reaction mixture using complex **12** as catalyst and potassium phthalimide as alkali metal salt after 1 h

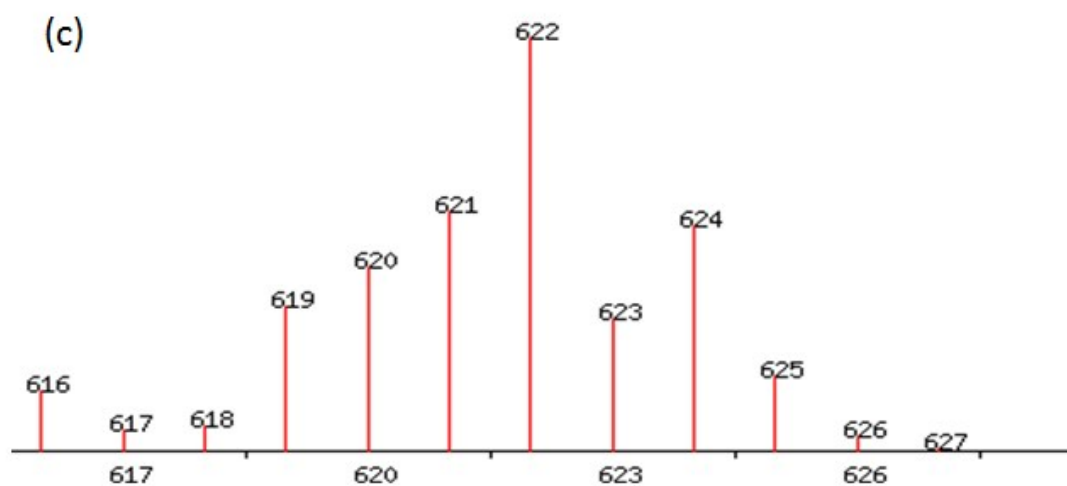
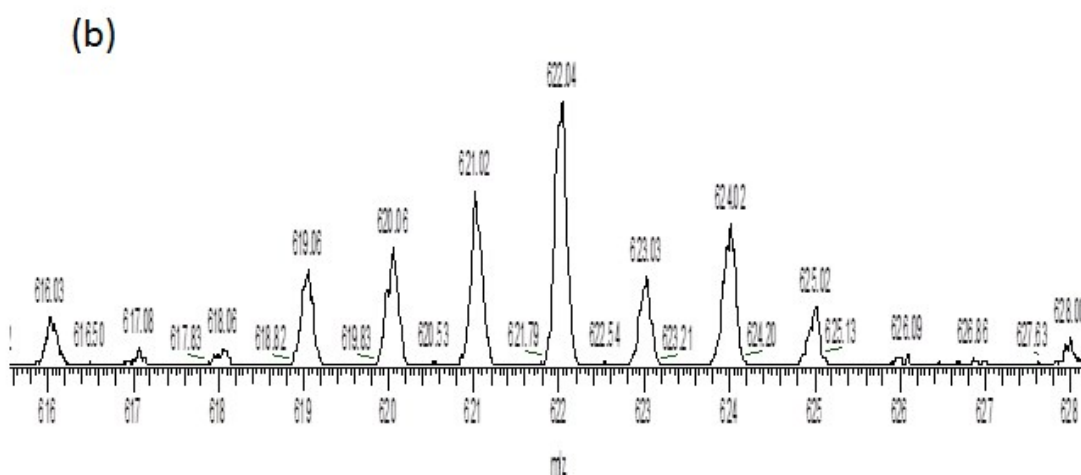
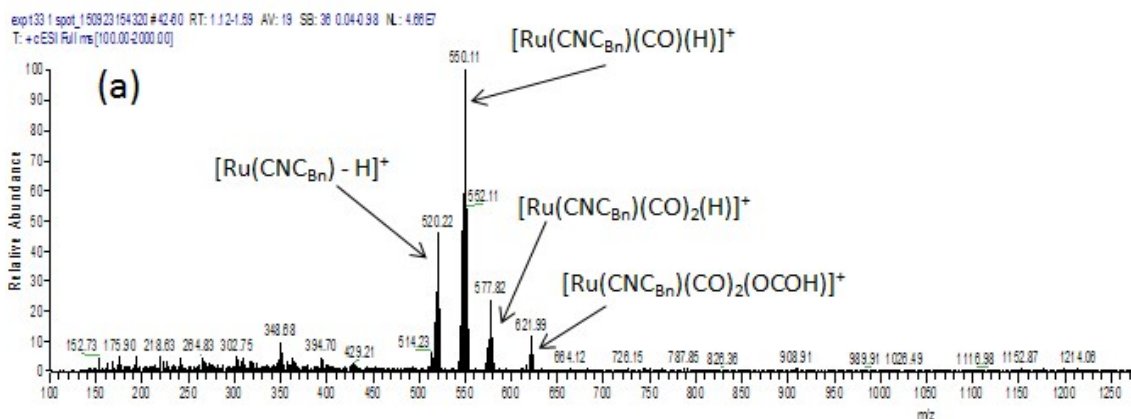


Figure S13.

(a) ESI-MS of the reaction mixture using complex **12** $[\text{Ru}(\text{CNC}_{\text{Bn}})(\text{CO})_2(\text{H})]^+$ as catalyst and KO^tBu as the alkali metal salt under catalytic hydroboration conditions.

(b) experimental isotopic distribution pattern of $[\text{Ru}(\text{CNC}_{\text{Bn}})(\text{CO})_2(\text{OCOH})]^+$

(c) predicted isotopic distribution for $[\text{Ru}(\text{CNC}_{\text{Bn}})(\text{CO})_2(\text{OCOH})]^+$

S6. NMR Spectra of synthesized compounds

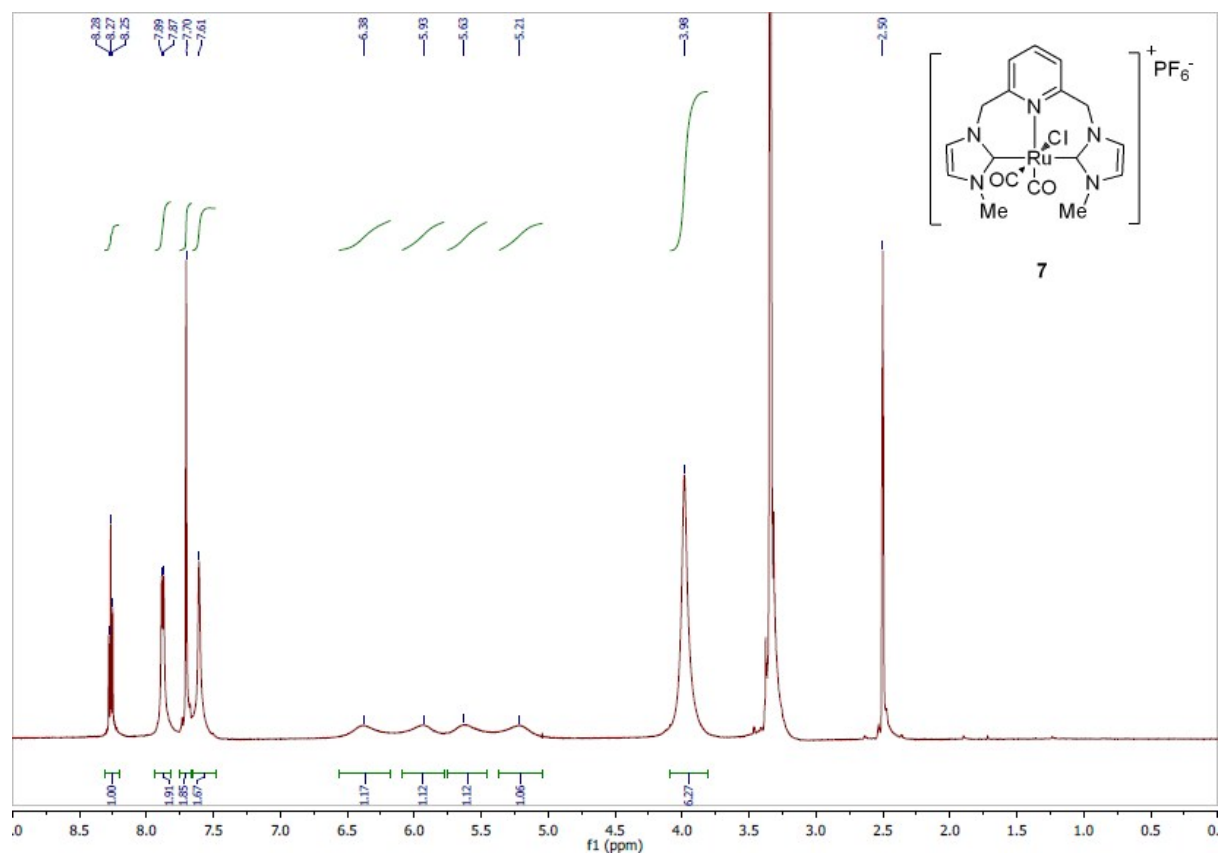


Figure S14. ^1H NMR spectrum of **7** in $\text{DMSO-}d_6$

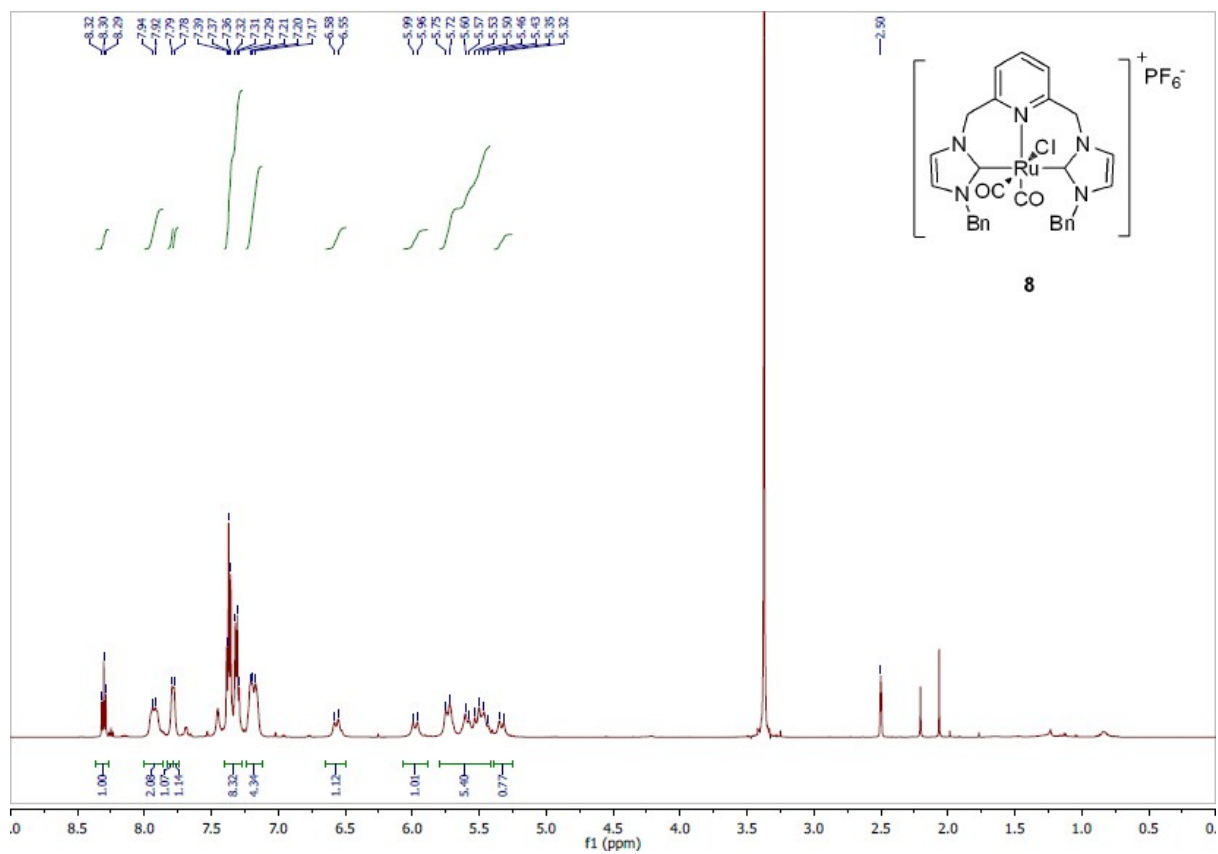


Figure S15. ^1H NMR spectrum of **8** in $\text{DMSO-}d_6$

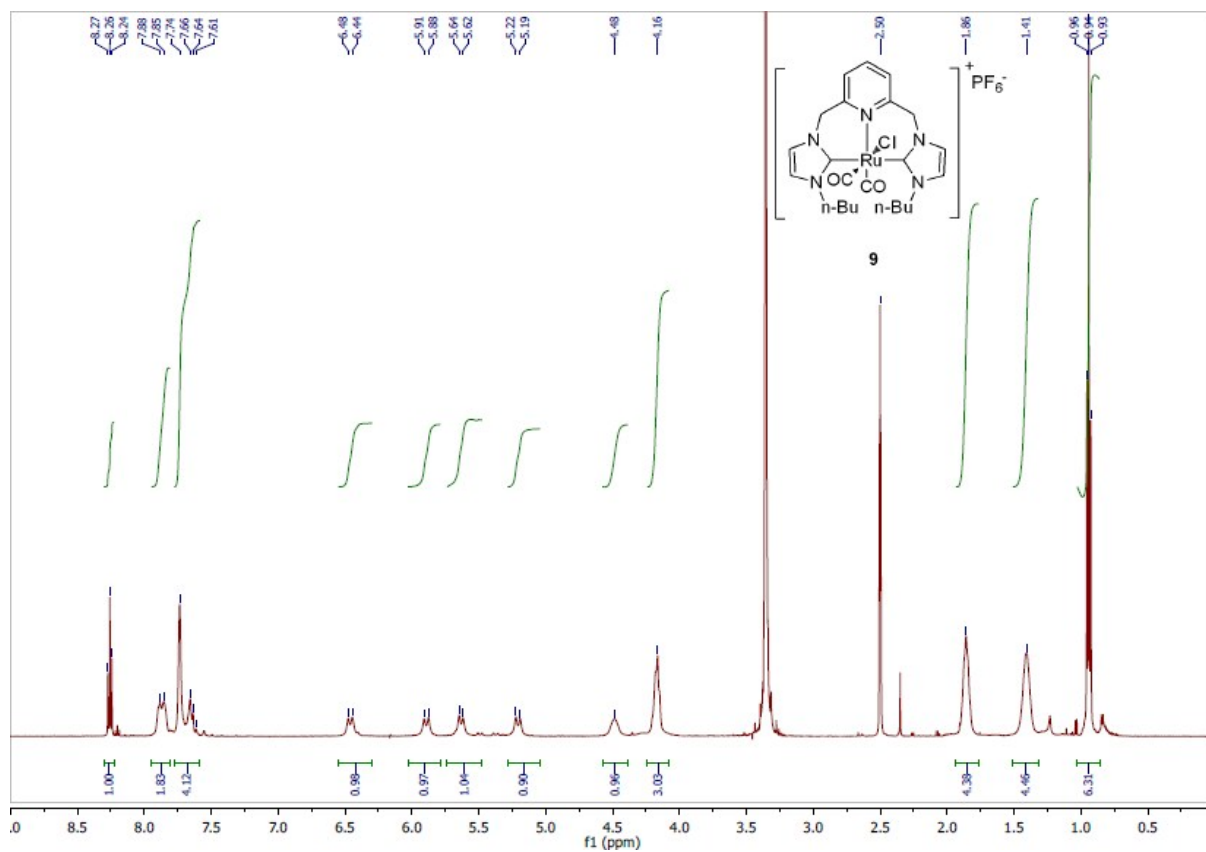


Figure S17. ¹H NMR spectrum of **9** in DMSO-*d*₆

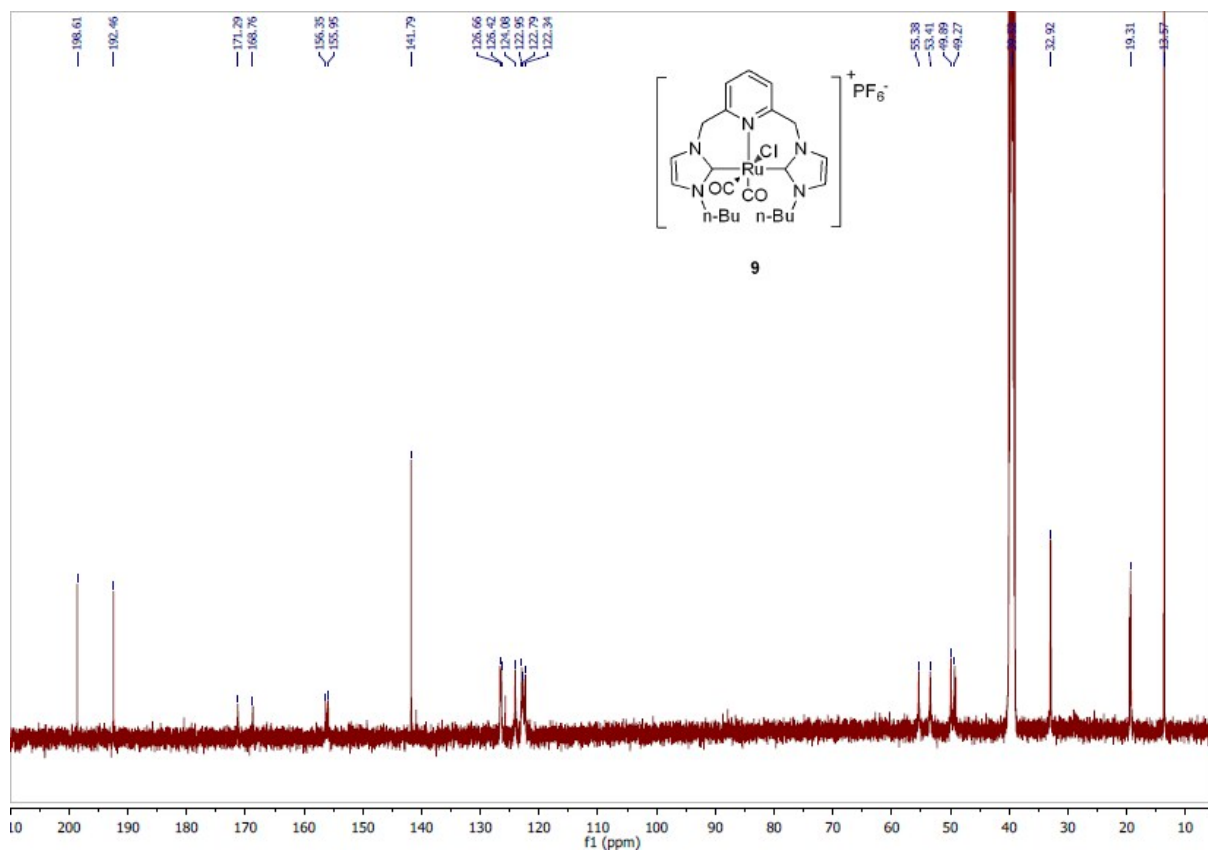


Figure S18. ¹³C NMR spectrum of **9** in DMSO-*d*₆

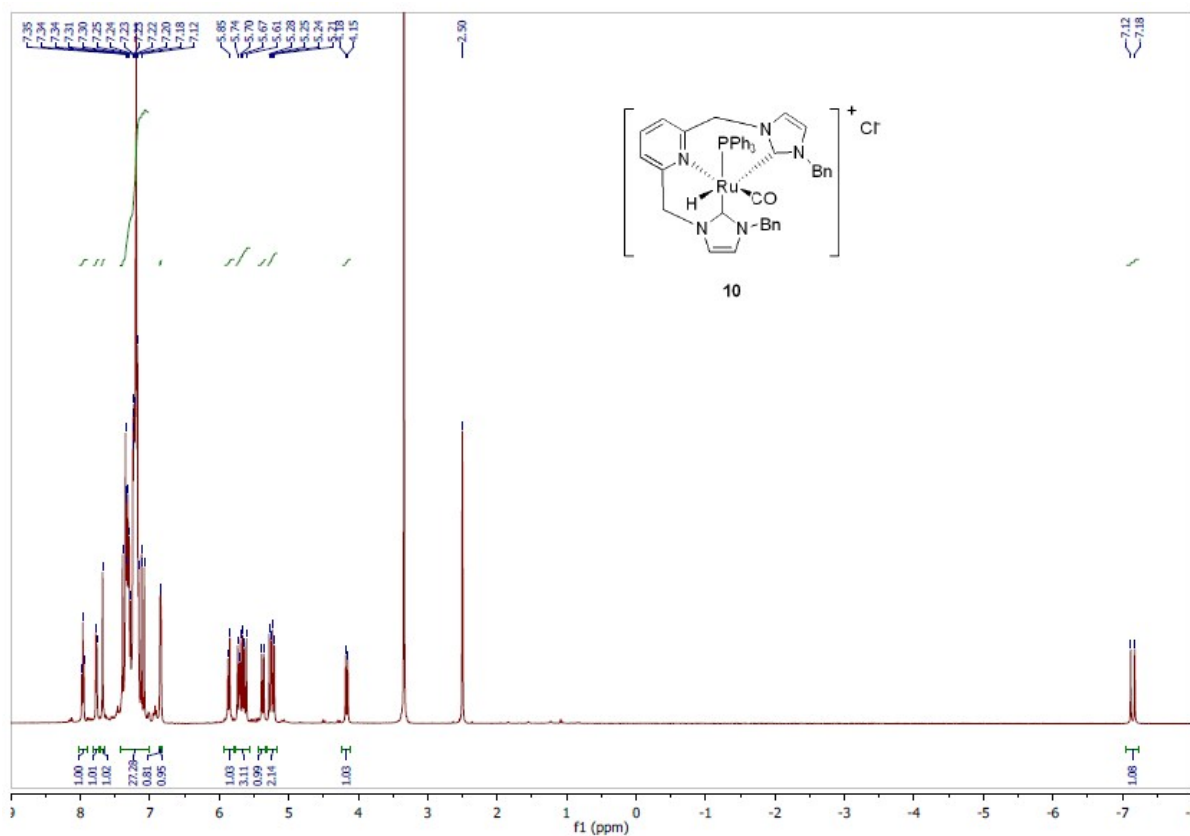


Figure S19. ^1H NMR spectrum of **10** in $\text{DMSO-}d_6$

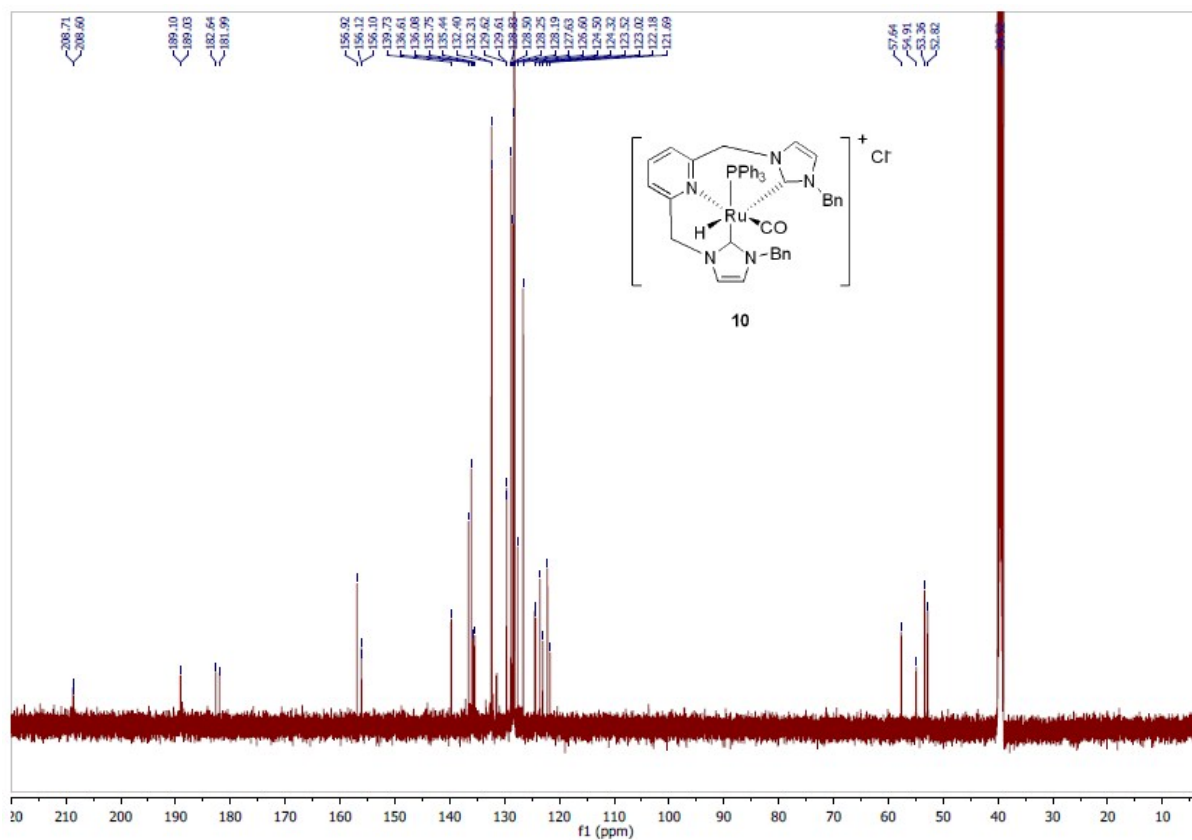


Figure S20. ¹³C NMR spectrum of **10** in DMSO-*d*₆

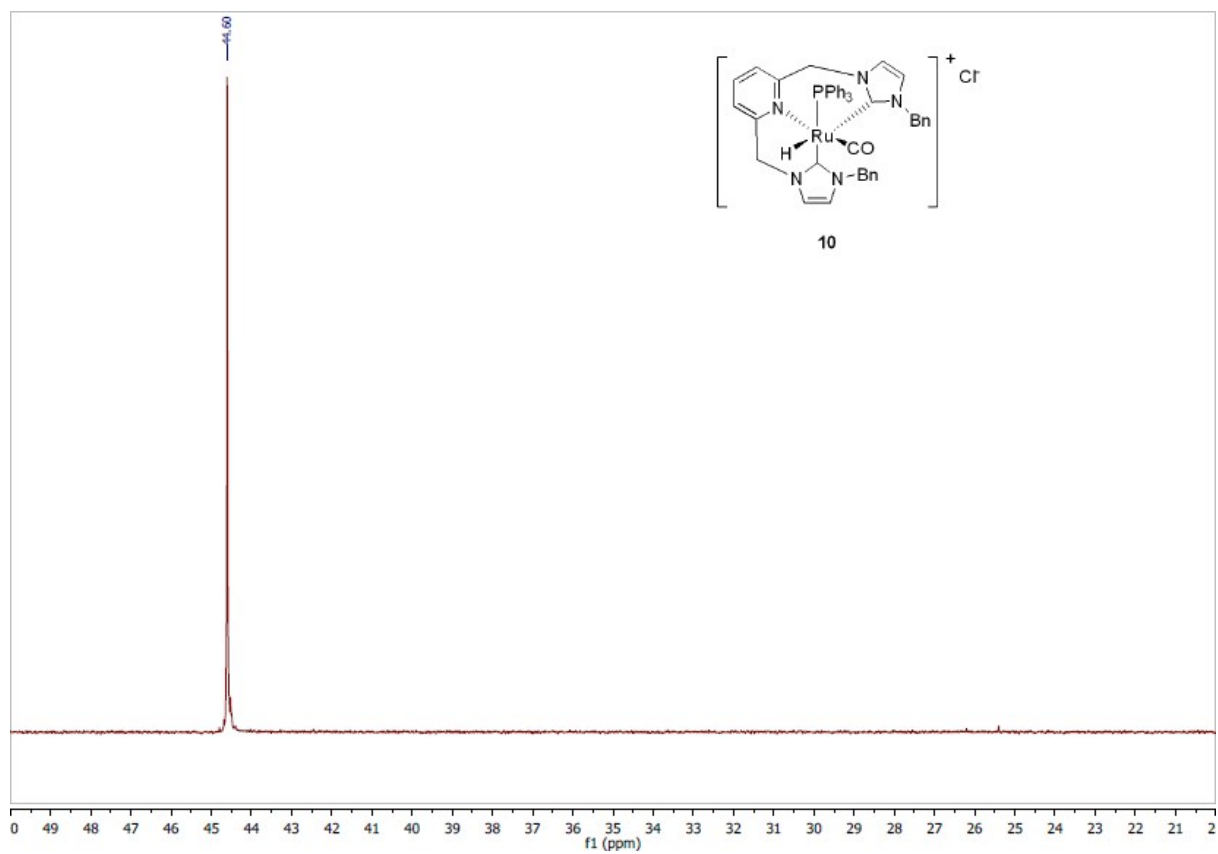


Figure S21. ^{31}P NMR spectrum of **10** in $\text{DMSO-}d_6$

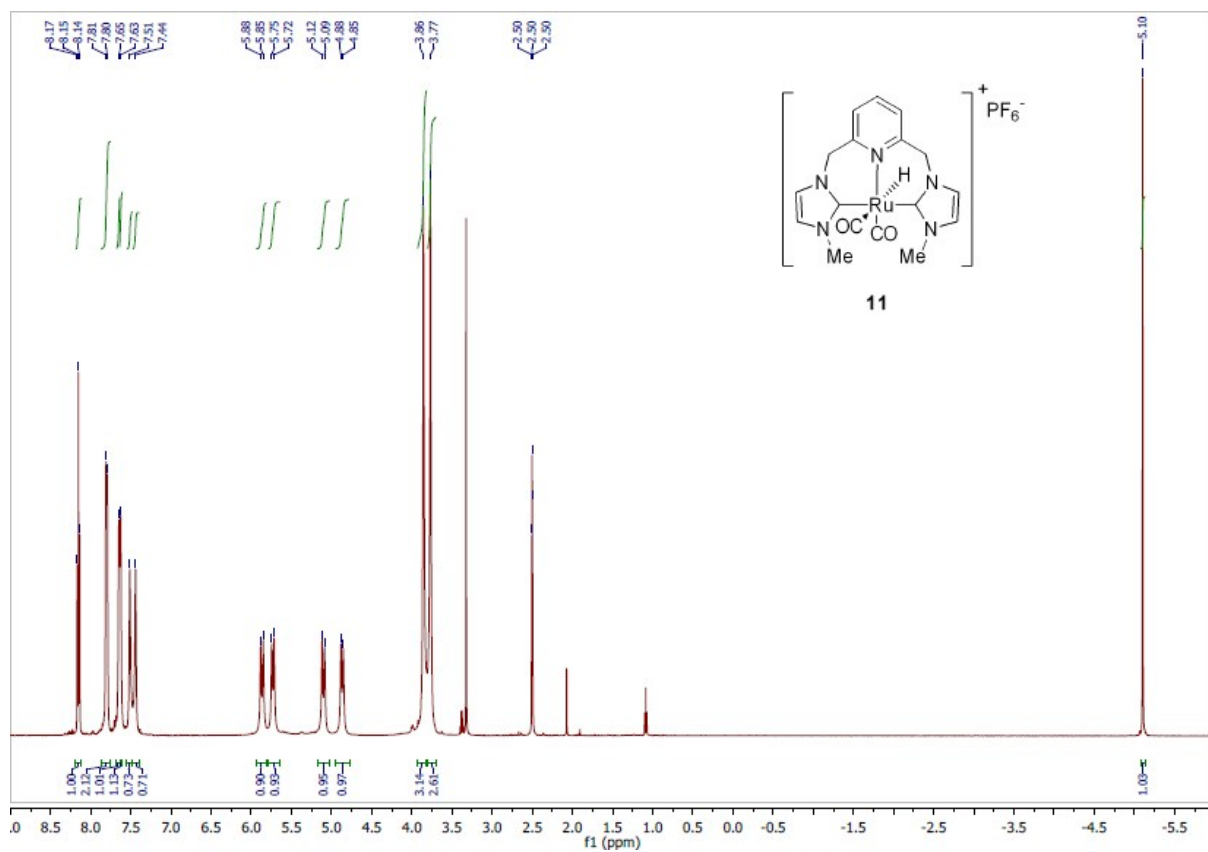


Figure S22. ^1H NMR spectrum of **11** in $\text{DMSO-}d_6$

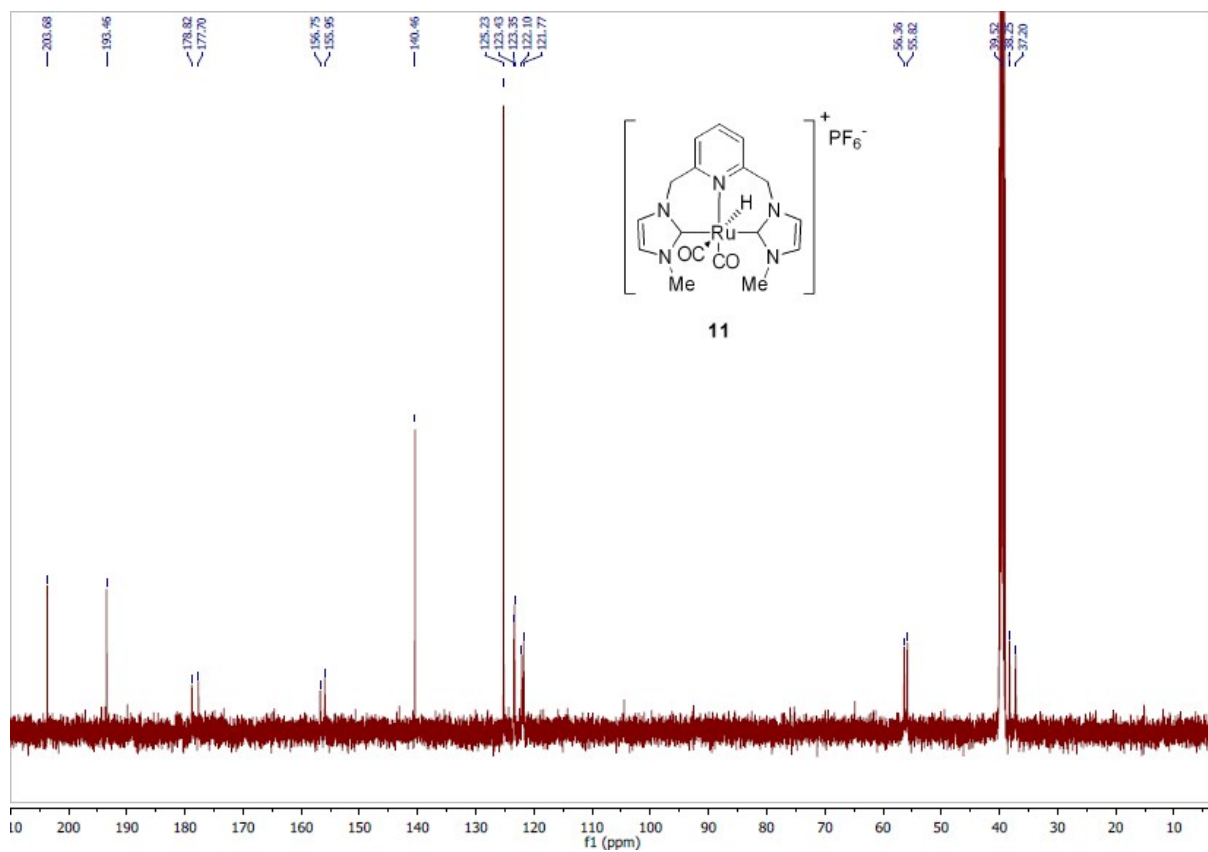


Figure S23. ^{13}C NMR spectrum of **11** in $\text{DMSO-}d_6$

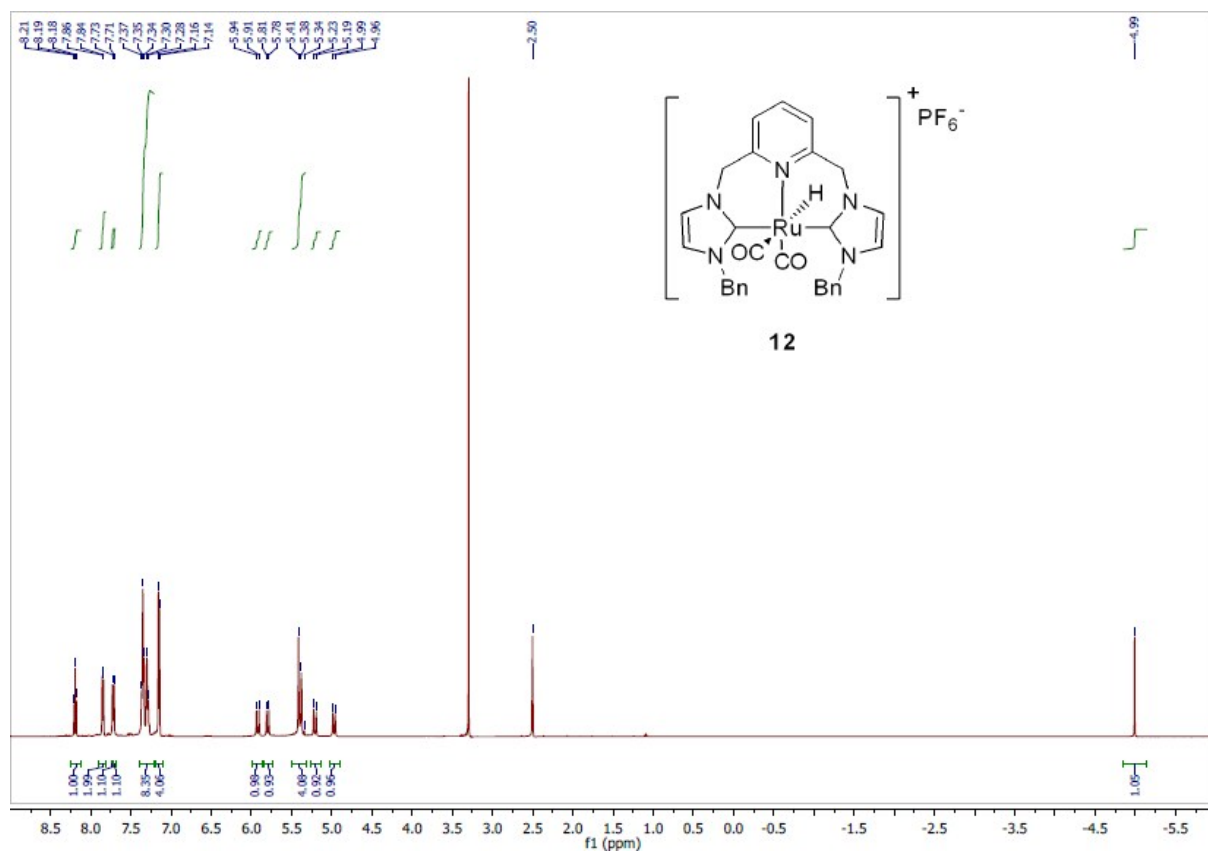


Figure S24. ^1H NMR spectrum of **12** in $\text{DMSO-}d_6$

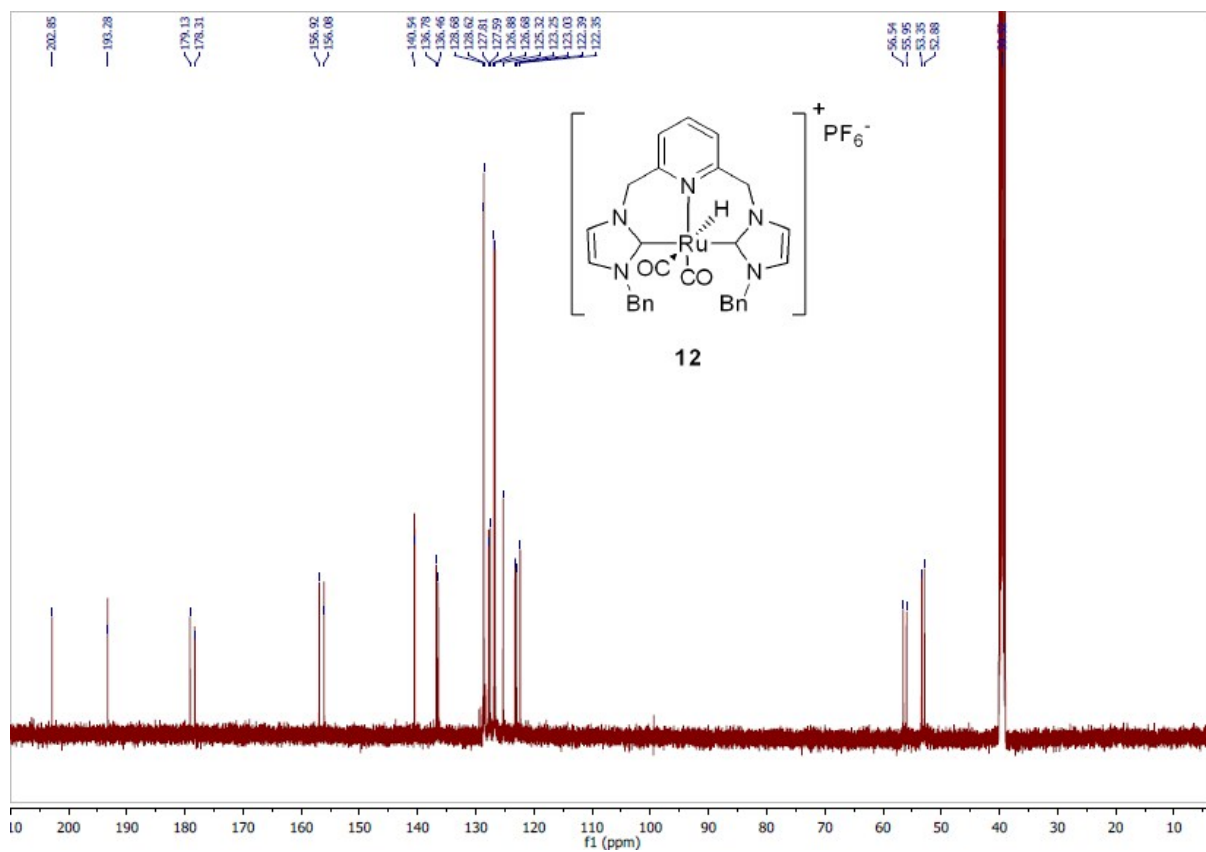


Figure S25. ^{13}C NMR spectrum of **12** in $\text{DMSO-}d_6$

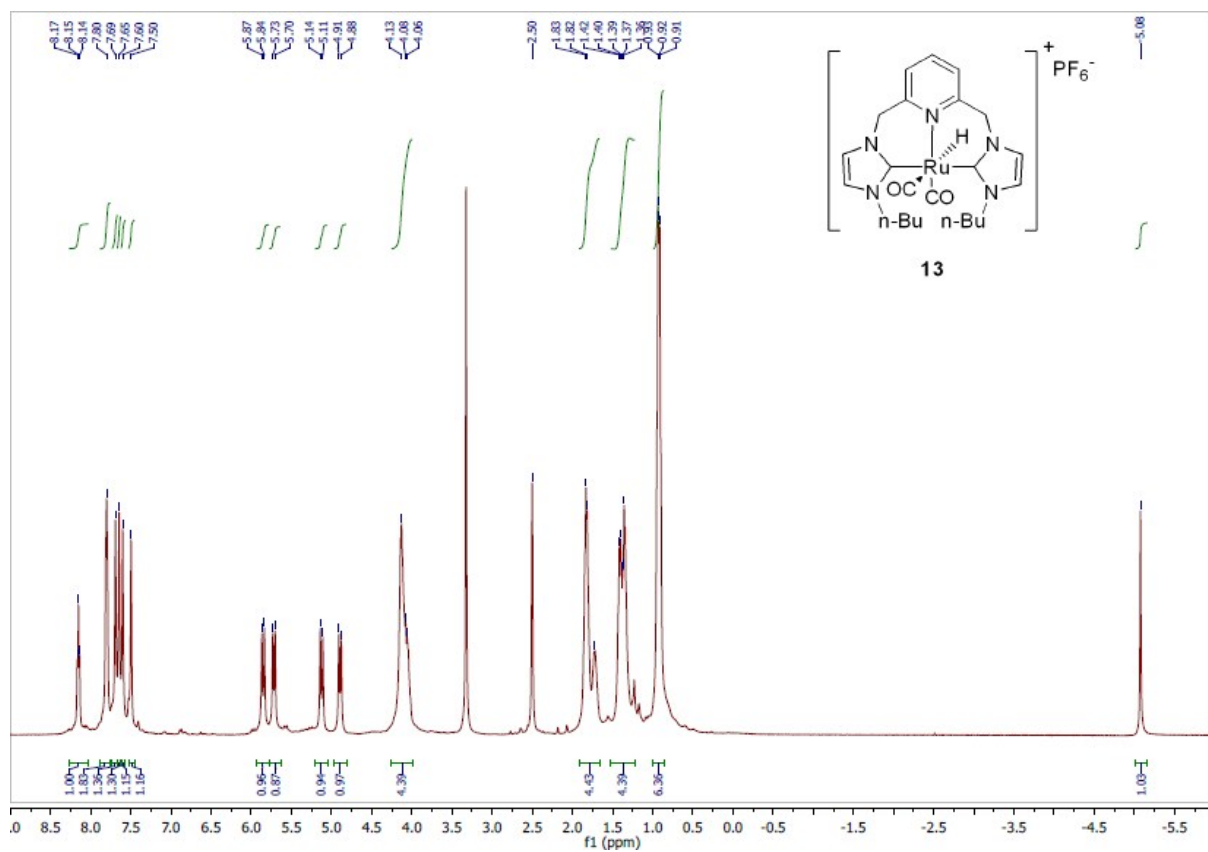


Figure S26. ^1H NMR spectrum of **13** in $\text{DMSO-}d_6$

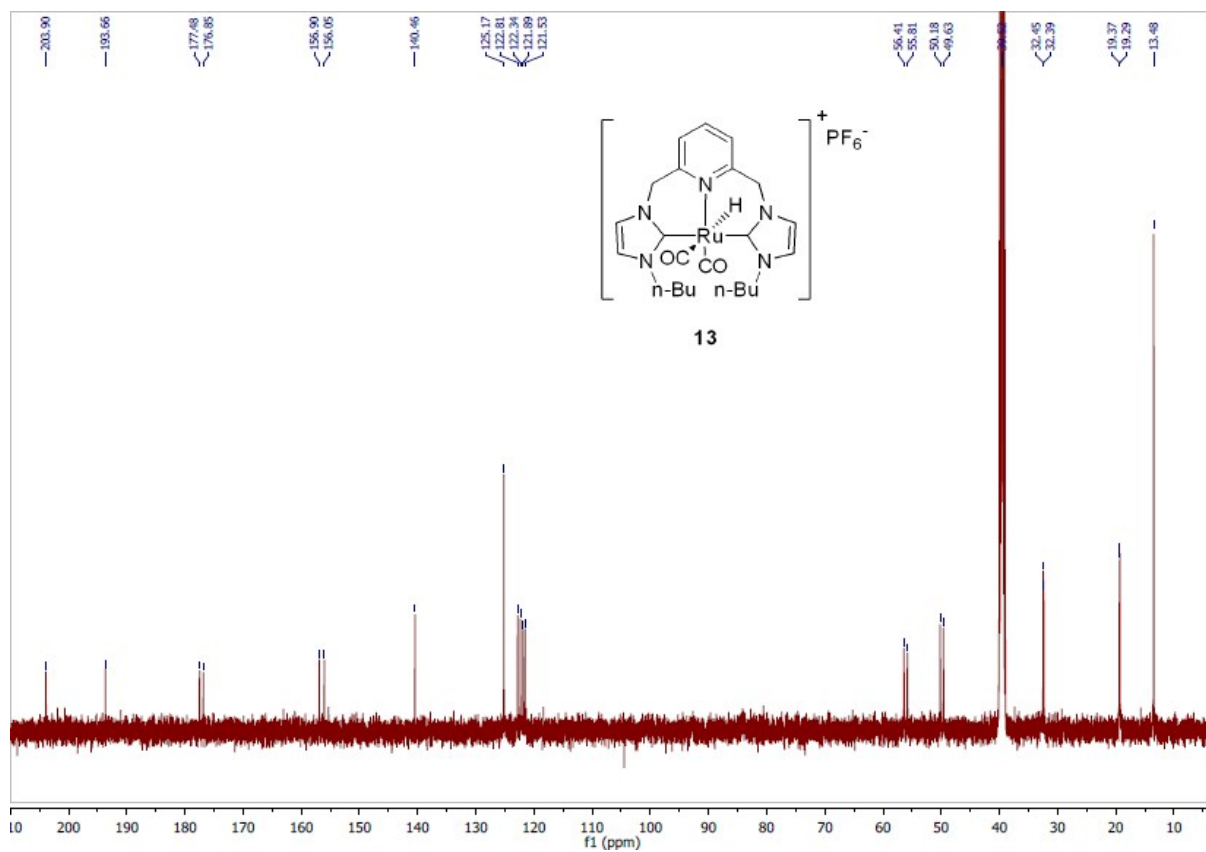


Figure S27. ¹³C NMR spectrum of **13** in DMSO-*d*₆

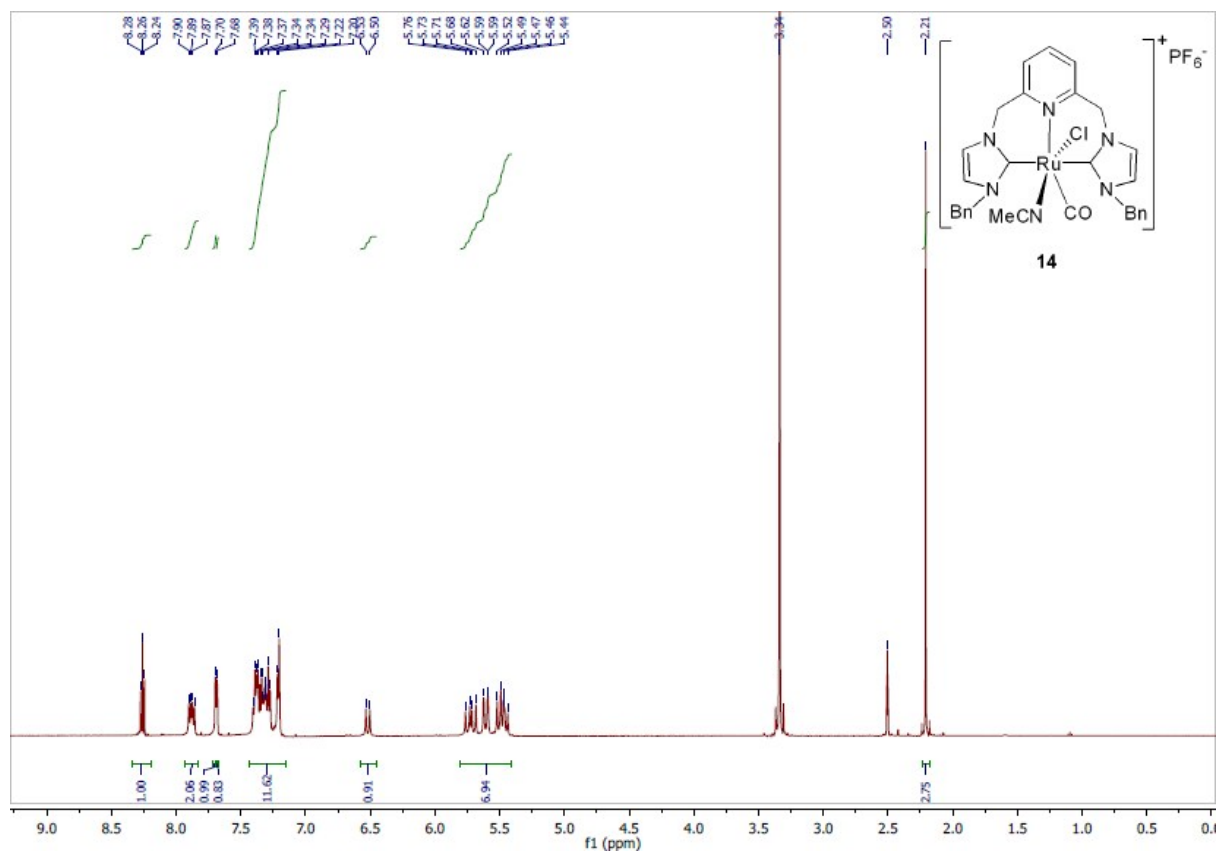


Figure S28. ^1H NMR spectrum of **14** in $\text{DMSO-}d_6$

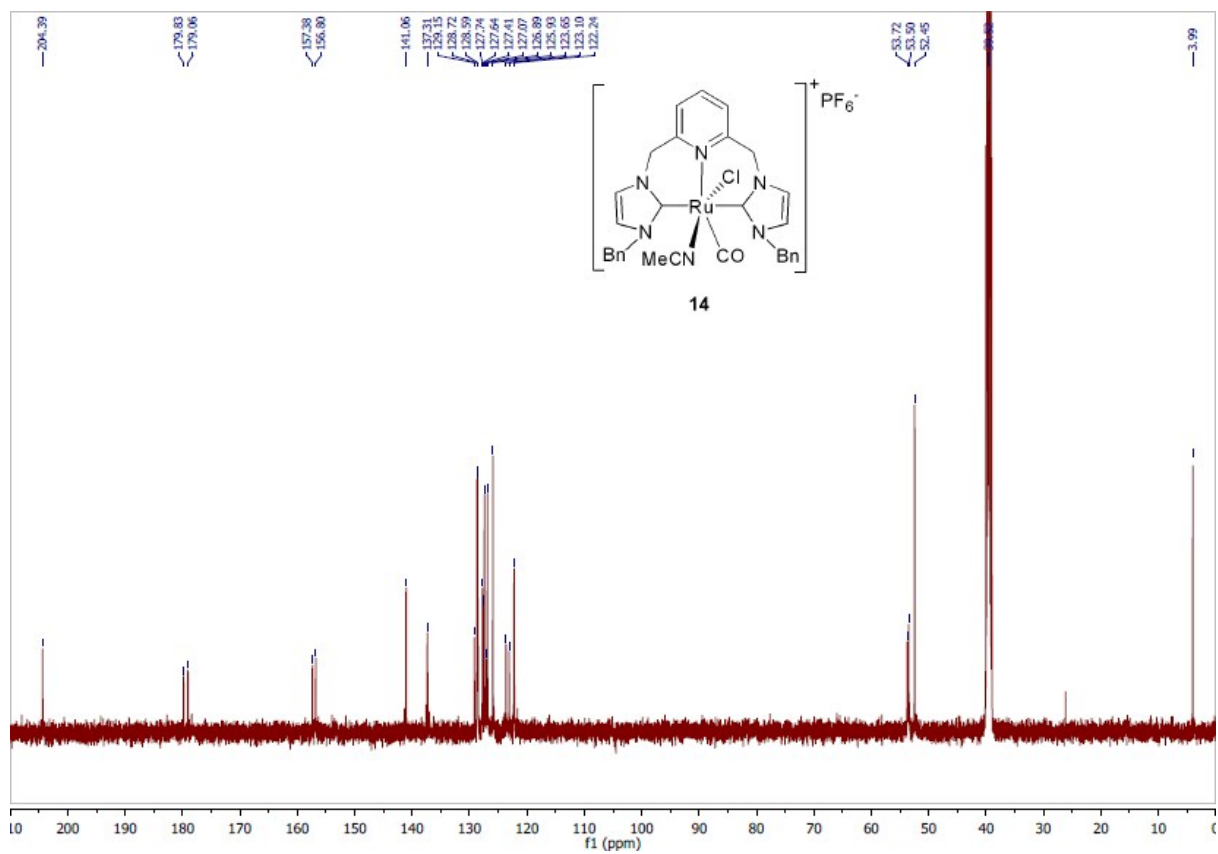


Figure S29. ^{13}C NMR spectrum of **14** in $\text{DMSO-}d_6$

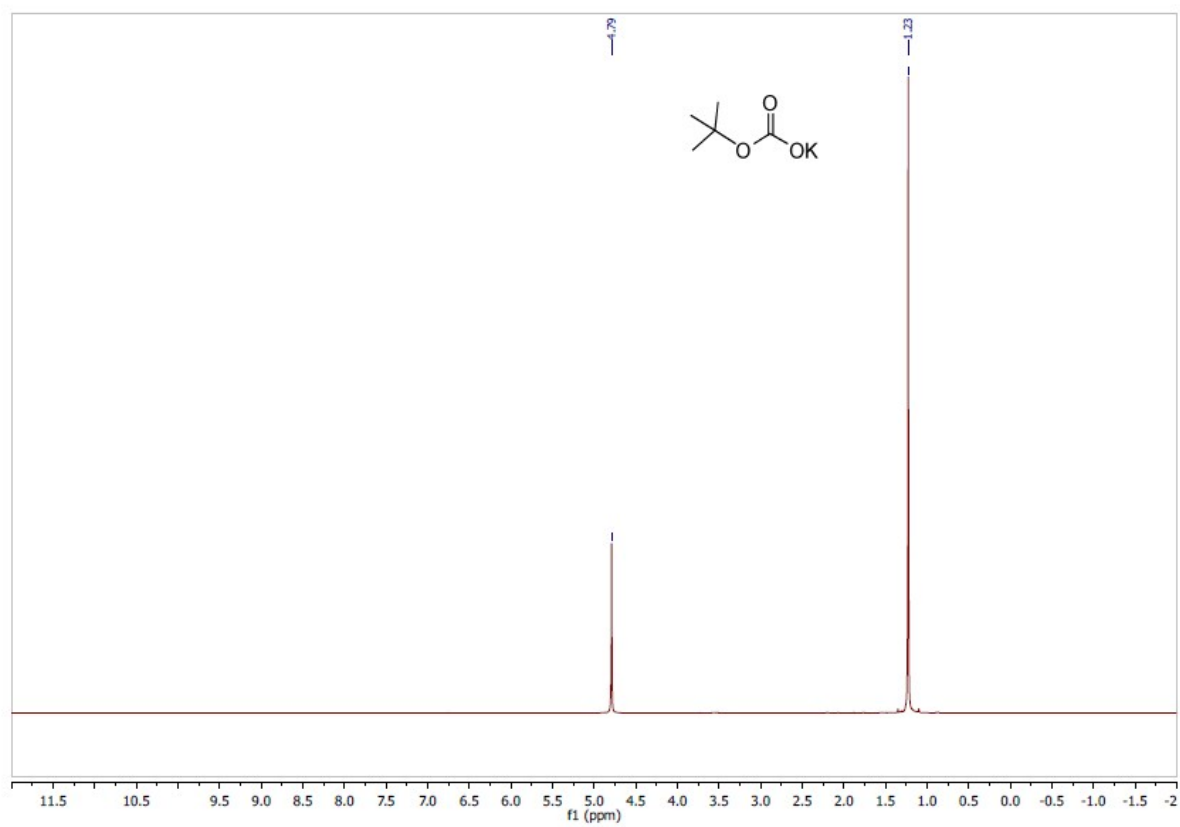


Figure S30. ^1H NMR spectrum of KOCOC_2tBu in D_2O

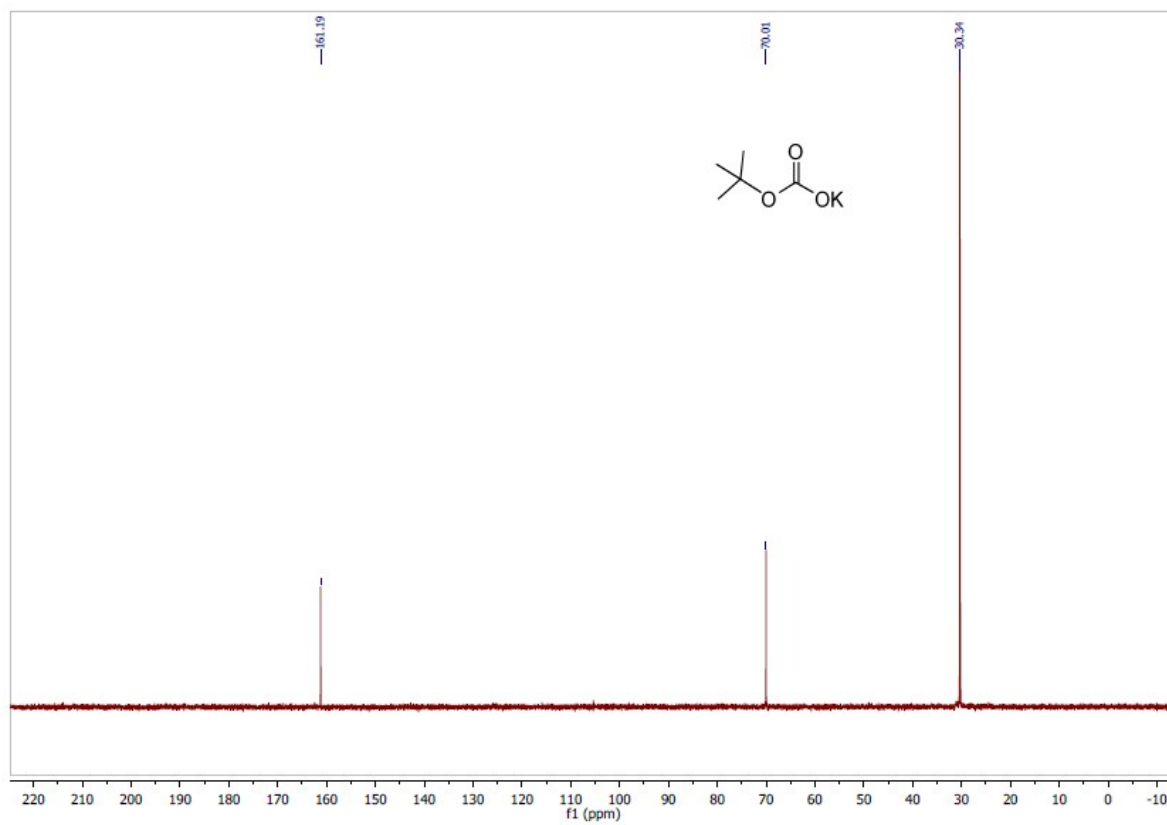


Figure S31. ^{13}C NMR spectrum of KOCO_2tBu in D_2O

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