Supplementary Information

Hydrogenation of imines catalysed by ruthenium(II) complexes based on lutidine-derived CNC pincer ligands

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1. Synthetic Procedures

1.1 General Procedures. All reactions and manipulations were performed under nitrogen or argon, either in a Braun Labmaster 100 glovebox or using standard Schlenk-type techniques. All solvents were distilled under nitrogen with the following desiccants: sodium-benzophenone-ketyl for diethyl ether (Et_2O) and tetrahydrofuran (THF); sodium for hexane and toluene; CaH_2 for dichloromethane and acetonitrile (CH_2Cl_2, CH_3CN); and NaOMe for methanol (MeOH). 1-Isopropyl-1*H*-imidazole, 1-hexyl-1*H*-imidazole, 1-(2,2´-dimethylpropyl)-1*H*-imidazole and 1-(3,5-dimethylphenyl)-1*H*-imidazole were prepared as previously described.[1] $RuHCl(CO)(PPh_3)_3$ was synthesized according to a literature procedure.[2] Imines (entries 9−15, Table 1) were prepared by previously reported methods.[3] All other reagents were purchased from commercial suppliers and used as received. NMR spectra were obtained on Bruker DPX-300, DRX-400, or DRX-500 spectrometers. $^{31}P\{^1H\}$ NMR shifts were referenced to external 85% H_3PO_4, while $^{13}C\{^1H\}$ and ^1H shifts were referenced to the residual signals of deuterated solvents. All data are reported in ppm downfield from Me_4Si. All NMR measurements were carried out at 25 °C, unless otherwise stated. HRMS data were obtained on a JEOL JMS-SX 102A mass spectrometer at the Instrumental Services of Universidad de Sevilla (CITIUS). ESI-MS experiments were carried out in a Bruker 6000 apparatus by the Mass Spectrometry Service of the Instituto de Investigaciones Químicas. Elemental analyses were run by the Analytical Service of the Instituto de Investigaciones Químicas in a Leco CHNS-932 elemental analyzer. IR spectra were acquired on a Bruker Tensor 27 instrument.

1.2 Synthesis of imidazolium salts 1

***2,6-Bis[(3-Isopropylimidazolium-1-yl)methyl]pyridine dichloride*, 1a(Cl):** A solution of 2,6-bis(chloromethyl)pyridine (2.00 g, 11.4 mmol) and 1-isopropyl-1*H*-imidazole (2.69 g, 24.4 mmol) in THF (40 mL) was refluxed for 7 days. The precipitate is filtered off and washed with Et_2O (3 × 10 mL). White solid (3.11 g, 69%). Anal. Calcd for $C_{19}H_{27}Cl_2N_5$ (%): C 57.6; H 6.9; N 17.7. Found: C 57.7; H 6.9; N 17.5. ^1H NMR (DMSO-d_6, 400 MHz): δ 1.50 (d, $^3J_{HH}$ = 6.8 Hz, 12H, 4 CH_3), 4.73 (h, $^3J_{HH}$ = 6.4 Hz, 2H, 2 C*H*$(CH_3)_2$), 5.57 (s, 4H, 2 py-CH_2), 7.51 (d, $^3J_{HH}$ = 7.6 Hz, 2H, 2 H-3 pyr), 7.80

(s, 2H, 2 H imid), 7.97 (t, $^3J_{HH}$ = 7.6 Hz, 1H, H-4 pyr), 8.00 (s, 2H, 2 H imid), 9.66 (s, 2H, H-2 imid). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 101 MHz): δ 22.3 (4 CH_3), 52.2 (2 $CH(CH_3)_2$), 52.6 (2 pyr-CH_2), 120.4 (2 CH imid), 122.2 (2 CH imid), 123.3 (2 C-3 py), 135.7 (2 C-2 imid), 138.8 (C-4 py), 153.7 (2 C-2 py).

2,6-Bis[(3-Isopropylimidazolium-1-yl)methyl]pyridine dibromide, **1a(Br):** Compound **1a(Br)** was prepared as described for **1a(Cl)** using 2,6-bis(bromomethyl)pyridine. White solid (1.05 g, 58%). Anal. Calcd for $C_{19}H_{27}Br_2N_5$ (%): C 47.0; H 5.6; N 14.4. Found: C 47.0; H 5.7; N 14.6. ^1H NMR (DMSO-d_6, 400 MHz): δ 1.50 (d, $^3J_{HH}$ = 6.8 Hz, 12H, 4 CH_3), 4.71 (h, $^3J_{HH}$ = 6.7 Hz, 2H, 2 $CH(CH_3)_2$), 5.56 (s, 4H, 2 py-CH_2), 7.50 (d, $^3J_{HH}$ = 7.5 Hz, 2H, 2 H-3 py), 7.78 (s, 2H, 2 H imid), 7.98 (s, 2H, 2 H imid), 7.99 (t, $^3J_{HH}$ = 7.6 Hz, 1H, H-4 py), 9.49 (s, 2H, H-2 imid). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 101 MHz): δ 22.3 (4 CH_3), 52.3 (2 $CH(CH_3)_2$), 52.7 (2 py-CH_2), 120.4 (2 CH imid), 122.2 (2 CH imid), 123.3 (2 C-3 py), 135.5 (2 C-2 imid), 138.9 (C-4 py), 153.6 (2 C-2 py).

2,6-Bis[(3-Hexylimidazolium-1-yl)methyl]pyridine dichloride, **1b(Cl):** This product was prepared as described for **1a(Cl)**. White oil (0.894 g, 65%). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.65 (t, $^3J_{HH}$ = 6.9 Hz, 6H, 2 CH_3), 1.06 (m, 12H, 6 CH_2), 1.66 (m, 4H, 2 CH_2), 4.22 (t, $^3J_{HH}$ = 7.2 Hz, 4H, 2 CH_2), 5.60 (s, 4H, 2 py-CH_2), 7.25 (s, 2H, 2 H imid), 7.49 (t, $^3J_{HH}$ = 7.5 Hz, 1H, H-4 py), 7.62 (d, $^3J_{HH}$ = 7.6 Hz, 2H, 2 H-3 py), 8.14 (s, 2H, 2 H imid), 10.64 (s, 2H, H-2 imid). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 13.7 (2 CH_3), 22.1 (2 CH_2), 25.6 (2 CH_2), 30.1 (2 CH_2), 30.8 (2 CH_2), 49.7 (2 CH_2), 53.2 (2 py-CH_2), 121.1 (2 CH imid), 123.7 (2 CH imid + 2 C-3 py), 137.4 (2 C-2 imid), 138.8 (C-4 py), 153.2 (2 C-2 py). HRMS (FAB): *m/z* 408.3130 $[M-H-2Cl]^+$ (exact mass calculated for $C_{22}H_{38}N_5$: 408.3127).

2,6-Bis[(3,5-dimethylphenylimidazolium-1-yl)methyl]pyridine dichloride, **1d(Cl):** A solution of 2,6-bis(chloromethyl)pyridine (0.200 g, 1.14 mmol) and 1-(3,5-dimethylphenyl)imidazole (0.489 g, 2.84 mmol) in MeCN (40 mL) was refluxed for 8 days. Solvent was removed under reduced pressure, and the mixture was dissolved in CH_2Cl_2 (25 mL) and Et_2O was added to precipitate the product. The solid was separated by filtration and washed with Et_2O (3 × 10 mL). White solid (0.518 g, 88%). Anal. Calcd for $C_{29}H_{31}Cl_2N_5$ (%): C 66.9; H 6.0; N 13.5. Found: C 66.8; H 6.2; N 13.3. ^1H NMR ($CDCl_3$, 500 MHz): δ 2.34 (s, 12H, 4 *Ar*-CH_3), 5.99 (s, 4H, 2 py-CH_2), 7.03 (s,

2H, 2 H imid), 7.24 (s, 4H, 4 H arom), 7.53 (s, 2 H arom), 7.70 (t, $^{3}J_{HH}$ = 7.5 Hz, 1H, H-4 py), 7.83 (d, $^{3}J_{HH}$ = 7.5 Hz, 2H, 2 H-3 py), 8.34 (s, 2H, 2 H imid), 11.24 (s, 2H, H-2 imid). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ 21.3 (4 *Ar*-CH_3), 53.2 (2 py-CH_2), 119.4 (4 CH arom), 120.5 (2 CH imid), 124.4 (4 C_q arom), 124.7 (2 CH imid), 132.0 (2 CH arom), 134.4 (2 C-3 py), 136.6 (2 C-2 imid), 139.8 (2 C_q arom), 140.9 (C-4 py), 152.8 (2 C-2 py).

1.3. Synthesis of silver complexes 2

2a(Cl): In the dark, to a solution of **1a(Cl)** (1.53 g, 3.86 mmol) in CH_2Cl_2 (50 mL) was added Ag_2O (1.02 g, 4.40 mmol). The suspension was stirred for 24 h, and filtered. Solvent was evaporated, and the solid washed with Et_2O (3 × 15 mL). The product was isolated as a white solid after evaporation of the solvent (2.08 g, 88%). Anal. Calcd for $C_{19}H_{25}Ag_2Cl_2N_5$ (%): C 37.4; H 4.1; N 11.5. Found: C 37.2; H 4.1; N 11.4. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.47 (d, $^{3}J_{HH}$ = 6.8 Hz, 12H, 4 CH_3), 4.72 (h, $^{3}J_{HH}$ = 6.7 Hz, 2H, 2 C*H*(CH_3)$_2$), 5.37 (s, 4H, 2 py-CH_2), 7.04 (s, 2H, 2 H imid), 7.19 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H, 2 H-3 py), 7.33 (s, 2H, 2 H imid), 7.69 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H, H-4 py). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ 23.9 (4 CH_3), 54.8 (2 *C*H(CH_3)$_2$), 57.2 (2 py-CH_2), 117.7 (2 CH-3 py), 122.3 (2 CH imid), 122.7 (2 CH imid), 138.9 (CH-4 py), 156.2 (2 C-2 py), 179.7 (2 C-2 imid).

2a(Br): This product was prepared as described for **2a(Cl)**. White solid (1.28 g, 89%). Anal. Calcd for $C_{19}H_{25}Ag_2Br_2N_5$ (%): C 32.6; H 3.6; N 10.0. Found: C 32.6; H 3.7; N 9.8. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.45 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, 4 CH_3), 4.71 (h, $^{3}J_{HH}$ = 6.7 Hz, 2H, 2 C*H*(CH_3)$_2$), 5.37 (s, 4H, 2 py-CH_2), 7.02 (s, 2H, 2 H imid), 7.17 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H, 2 H-3 py), 7.29 (s, 2H, 2 H imid), 7.68 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H, H-4 py). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz): δ 23.9 (4 CH_3), 54.2 (2 *C*H(CH_3)$_2$), 56.8 (2 py-CH_2), 117.5 (2 CH-3 py), 122.2 (2 CH imid), 122.4 (2 CH imid), 138.7 (CH-4 py), 155.7 (2 C-2 py), 180.4 (2 C-2 imid).

2b(Cl): To a solution of bis-imidazolium salt **1b(Cl)** (0.450 g, 0.94 mmol) in CH_2Cl_2 (15 mL) was added Ag_2O (0.228 g, 0.98 mmol). The suspension was stirred in the dark for 24 h, and filtered through a short pad of celite. The product is isolated as a brown

solid after evaporation of the solvent (0.335 g, 51%). Anal. Calcd for $C_{25}H_{37}Ag_2Cl_2N_5$ (%): C 43.2; H 5.4; N 10.1. Found: C 43.1; H 5.3; N 10.1. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 0.85 (t, $^3J_{HH}$ = 6.9 Hz, 6H, 2 CH_3), 1.28 (m, 12H, 6 CH_2), 1.78 (m, 4H, 2 CH_2), 4.06 (t, $^3J_{HH}$ = 7.2 Hz, 4H, 2 CH_2), 5.35 (s, 4H, py-CH_2), 7.00 (d, $^3J_{HH}$ = 1.7 Hz, 2H, 2 H imid), 7.15 (d, $^3J_{HH}$ = 7.7 Hz, 2H, 2 H-3 py), 7.30 (d, $^3J_{HH}$ = 1.7 Hz, 2H, 2 H imid), 7.65 (t, $^3J_{HH}$ = 7.7 Hz, 1H, H-4 py). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75 MHz): δ 13.9 (2 CH_3), 22.5 (2 CH_2), 26.1 (2 CH_2), 31.3 (2 CH_2), 31.4 (2 CH_2), 52.3 (2 CH_2), 56.8 (2 py-CH_2), 121.1 (2 CH imid), 121.9 (2 CH imid), 122.4 (2 CH-3 py), 138.7 (CH-4 py), 155.7 (2 C-2 py), 179.8 (2 C-2 imid).

2c(Br): A solution of 2,6-bis(bromomethyl)pyridine (0.062 g, 0.23 mmol) and 1-(2,2′-dimethylpropyl)-1*H*-imidazole (0.077 g, 0.56 mmol) in THF (5 mL) was refluxed for 6 days. To the resulting mixture, Et_2O (20 mL) was added to precipitate the bis-imidazolium salt, and the solid was filtered off and washed with Et_2O (2 × 15 mL). The bis-imidazolium salt was used directly to prepare the Ag-NHC complex. The solid was taken up in CH_2Cl_2 (5 mL) and Ag_2O (0.060 g, 0.26 mmol) was added. The resulting mixture was stirred in the dark for 16 h, filtered through a short pad of celite, and brought to dryness. The obtained solid was washed with Et_2O (3 × 10 mL). The product is obtained as a yellow solid (0.175 g, 99%). Anal. Calcd for $C_{23}H_{33}Ag_2Br_2N_5$ (%): C 36.5; H 4.2; N 9.2. Found: C 36.6; H 4.4, N 9.3. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 1.15 (s, 18H, 2 $C(CH_3)_3$), 4.10 (s, 4H, 2 $CH_2C(CH_3)$), 5.58 (s, 4H, py-CH_2), 7.18 (d, $^3J_{HH}$ = 1.6 Hz, 2H, 2 H imid), 7.34 (d, $^3J_{HH}$ = 7.8 Hz, 2H, 2 H-3 py), 7.44 (d, $^3J_{HH}$ = 1.6 Hz, 2H, 2 H imid), 7.83 (t, $^3J_{HH}$ = 7.7 Hz, 1H, H-4 py). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75 MHz): δ 28.1 (6 CH_3), 32.9 (2 $C(CH_3)_3$), 57.0 (2 $CH_2C(CH_3)_3$), 63.8 (2 py-CH_2), 122.0 (2 CH imid), 122.1 (2 CH imid), 123.1 (2 CH-3 py), 139.0 (CH-4 py), 156.2 (2 C-2 py), 183.4 (2 C-2 imid).

2d(Cl): This product was prepared as described for **2a(Cl)**. Brown solid (0.168 g, 49%). Anal. Calcd for $C_{29}H_{29}Ag_2Cl_2N_5$ (%): C 47.4; H 4.0; N 9.5. Found: C 47.4; H 4.0; N 9.6. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 2.37 (s, 12H, 4 *Ar*-CH_3), 5.51 (s, 4H, 2 py-CH_2), 7.10 (s, 2 H arom) 7.17 (s, 4H, 4 H arom), 7.29 (d, $^3J_{HH}$ = 2.0 Hz, 2H, 2 H imid), 7.33 (d, $^3J_{HH}$ = 7.5 Hz, 2H, 2 H-3 py), 7.46 (d, $^3J_{HH}$ = 2.0 Hz, 2H, 2 H imid), 7.77 (t, $^3J_{HH}$ = 7.5 Hz, 1H, H-4 py). ^{13}C{^{1}H} NMR ($CDCl_3$, 202 MHz): δ 21.3 (4 *Ar*-CH_3), 57.0 (2 py-CH_2), 122.1 (4 CH arom), 122.3 (2 CH imid), 122.6 (2 CH imid), 123.1 (2 C-3 py),

129.1 (2 CH arom), 138.9 (2 C_q arom), 139.8 (2 C_q arom + C-4 py), 155.5 (2 C-2 py), 179.8 (br s, 2 C-2 imid).

1.4. Synthesis of ruthenium complexes 3

3a(Cl): A mixture of silver complex **2a(Cl)** (0.150 g, 0.25 mmol) and RuHCl(CO)(PPh_3)$_3$ (0.234 g, 0.25 mmol) in THF (8 mL) was heated at 55 ^oC for 24 h. The resulting solution was filtered, brought to dryness and extracted with MeOH (2 × 5 mL). Solvent was evaporated, and the obtained solid was recrystallised from MeOH/toluene. Yellow solid (0.120 g, 65%). Anal. Calcd for $C_{38}H_{41}ClN_5OPRu$ (%): C 60.7; H 5.5; N 9.3. Found: C 60.7; H 5.7; N 9.3. IR (nujol mull, cm^{-1}): 1921 (s), 1878 (m), 1840 (m) (ν_{RuH}, ν_{CO}). ^1H NMR (CD_2Cl_2, 400 MHz): δ −7.30 (d, $^2J_{HP}$ = 30.5 Hz, 1H, RuH), 1.22 (d, $^3J_{HH}$ = 6.5 Hz, 3H, CH_3), 1.30 (d, $^3J_{HH}$ = 6.5 Hz, 3H, CH_3), 1.59 (d, $^3J_{HH}$ = 6.5 Hz, 3H, CH_3), 1.61 (d, $^3J_{HH}$ = 6.5 Hz, 3H, CH_3), 4.29 (d, $^2J_{HH}$ = 15.5 Hz, 1H, py-C*H*H), 5.04 (h, $^3J_{HH}$ = 6.5 Hz, 1H, C*H*(CH_3)$_2$), 5.44 (h, $^3J_{HH}$ = 6.5 Hz, 1H, C*H*(CH_3)$_2$), 5.71 (d, $^2J_{HH}$ = 14.0 Hz, 1H, py-C*H*H), 5.82 (d, $^2J_{HH}$ = 15.5 Hz, 1H, py-C*H*H), 5.91 (d, $^2J_{HH}$ = 14.0 Hz, 1H, py-C*H*H), 7.01 (s, 1H, H imid), 7.15 (m, 18H, 15 H arom PPh_3+2 H-3 py+H-4 py), 7.49 (s, 1H, H imid), 7.89 (s, 1H, H imid), 8.05 (s, 1H, H imid). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz): δ 42.4. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 126 MHz): δ 23.0 (CH_3), 24.2 (CH_3), 25.0 (CH_3), 24.9 (CH_3), 51.7 (C*H*(CH_3)$_2$), 52.3 (C*H*(CH_3)$_2$), 55.6 (py-CH_2), 58.5 (py-CH_2), 116.7 (CH imid), 117.8 (CH imid), 123.5 (CH imid), 124.6 (CH imid), 125.0 (C-3 py), 125.1 (C-3 py), 128.5 (d, $^4J_{CP}$ = 9 Hz, 6 CH arom, PPh_3), 129.9 (3 CH arom, PPh_3), 133.2 (d, $^3J_{CP}$ = 11 Hz, 6 CH arom, PPh_3), 136.7 (br d, $^1J_{CP}$ = 39 Hz, 3 C_q arom, PPh_3), 138.7 (C-4 py), 156.9 (C-2 py), 157.0 (C-2 py), 181.5 (d, $^2J_{CP}$ = 81 Hz, C-2 imid), 189.0 (d, $^2J_{CP}$ = 7 Hz, C-2 imid), 209.2 (d, $^2J_{CP}$ = 15 Hz, CO). MS (ESI, DMSO/MeCN): *m/z* 716 ($[M-Cl]^+$, 100). Fragmentation of ion *m/z* = 716: 454 ($[M-Cl-PPh_3]^+$, 100).

3a(BF_4): A mixture of silver complex **2a(Br)** (0.050 g, 0.07 mmol) and RuHCl(CO)(PPh_3)$_3$ (0.068 g, 0.07 mmol) in THF (2 mL) was heated at 55 ^oC for 16 h. The resulting solution was filtered, brought to dryness and extracted with MeOH (2 × 2 mL). Solvent was removed, and the obtained solid was dissolved in CH_2Cl_2 (2 mL) and treated with $NaBF_4$ (0.008 g, 0.07 mmol) for 16 h. The resulting mixture was filtered

through a short pad of Celite, and solvent was evaporated. Complex **3a(BF$_4$)** was isolated as a yellow solid after recrystallisation from CH_2Cl_2/Et_2O (0.037 g, 65%).

IR (nujol mull, cm^{-1}): 1909 (s), 1878 (m), 1840 (m) (ν_{RuH}, ν_{CO}). ^{1}H NMR (DMSO-d_6, 400 MHz): δ −7.38 (d, $^2J_{HP}$ = 30.4 Hz, 1H, RuH), 1.20 (d, $^3J_{HH}$ = 6.4 Hz, 3H, CH_3), 1.29 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3), 1.48 (d, $^3J_{HH}$ = 6.4 Hz, 3H, CH_3), 1.57 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3), 4.18 (d, $^2J_{HH}$ = 15.2 Hz, 1H, py-C*H*H), 4.94 (h, $^3J_{HH}$ = 6.4 Hz, 1H, C*H*(CH_3)$_2$), 5.25 (d, $^2J_{HH}$ = 15.6 Hz, 1H, py-C*H*H), 5.31 (h, $^3J_{HH}$ = 6.4 Hz, 1H, C*H*(CH_3)$_2$), 5.56 (d, $^2J_{HH}$ = 13.6 Hz, 1H, py-C*H*H), 5.67 (d, $^2J_{HH}$ = 14.4 Hz, 1H, py-C*H*H), 7.06 (dd, $^3J_{HP}$ = 9.2 Hz, $^3J_{HH}$ = 9.2 Hz, 6H, 6 H arom, PPh_3), 7.14 (d, $^3J_{HH}$ = 7.2 Hz, 1H, H-3 py), 7.20 (t, $^3J_{HH}$ = 7.6 Hz, 6H, 6 H arom, PPh_3), 7.28 (t, $^3J_{HH}$ = 7.6 Hz, 3H, 3 H arom, PPh_3), 7.46 (d, $^3J_{HH}$ = 2.0 Hz, 1H, H imid), 7.51 (d, $^3J_{HH}$ = 1.6 Hz, 1H, H imid), 7.61 (d, $^3J_{HH}$ = 1.6 Hz, 1H, H imid), 7.66 (m, 2H, H imid + H-3 py), 7.86 (t, $^3J_{HH}$ = 7.6 Hz, 1H, H-4 py). ^{31}P{^{1}H} NMR (DMSO-d_6, 162 MHz): δ 42.9. ^{13}C{^{1}H} NMR (DMSO-d_6, 101 MHz): δ 23.2 (CH_3), 24.2 (CH_3), 24.7 (CH_3), 24.9 (CH_3), 51.9 (C*H*(CH_3)$_2$), 52.7 (C*H*(CH_3)$_2$), 55.8 (py-CH_2), 58.5 (py-CH_2), 118.7 (CH imid),120.0 (CH imid), 123.8 (CH imid), 124.7 (CH imid), 125.2 (C-3 py), 125.4 (C-3 py), 129.1 (d, $^4J_{CP}$ = 9 Hz, 6 CH arom, PPh_3), 130.5 (3 CH arom, PPh_3), 133.3 (d, $^3J_{CP}$ = 11 Hz, 6 CH arom, PPh_3), 136.7 (br d, $^1J_{CP}$ = 40 Hz, 3 C_q arom, PPh_3), 140.5 (C-4 py), 156.6 (C-2 py), 157.6 (C-2 py), 180.4 (d, $^2J_{CP}$ = 81 Hz, C-2 imid), 187.9 (d, $^2J_{CP}$ = 8 Hz, C-2 imid), 209.5 (d, $^2J_{CP}$ = 15 Hz, CO). HRMS (FAB): *m/z* 716.2108 [M−BF_4]$^+$ (exact mass calculated for $C_{38}H_{41}N_5OP^{102}Ru$: 716.2029).

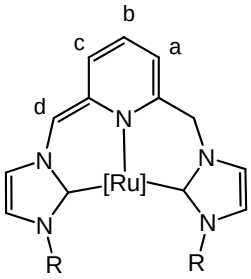
3b(Cl): This complex was prepared as described for **3a(Cl)**. Yellow solid (0.056 g, 47%). Anal. Calcd for $C_{44}H_{53}ClN_5OPRu$ (%): C 63.3; H 6.4; N 8.4. Found: C 63.3; H 6.4; N 8.3. IR (CH_2Cl_2 solution, cm^{-1}): 1924 (s, ν_{CO}). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ -7.14 (d, $^2J_{HP}$ = 28.8 Hz, 1H, RuH), 0.87 (m, 6H, 2 CH_3), 1.36 (m, 12H, 6 CH_2), 1.74 (m, 4H, 2 CH_2), 4.06 (m, 2H, 2 C*H*H), 4.26 (d, $^2J_{HH}$ = 15.2 Hz, 1H, py-C*H*H), 4.41 (m, 1H, C*H*H), 4.75 (m, 1H, C*H*H), 5.76 (m, 2H, 2 py-C*H*H), 5.95 (d, $^2J_{HH}$ = 14.0 Hz, 1H, py-C*H*H), 6.95 (br s, 1H, H imid), 7.08 (d, $^3J_{HH}$ = 1.6 Hz, 1H, H imid), 7.19−7.29 (m, 17H, 15 H arom PPh_3+2 H-3 py), 7.53 (t, $^3J_{HH}$ = 4.4 Hz, 1H, H-4 py), 7.85 (br s, 1H, H imid), 7.96 (d, $^3J_{HH}$ = 1.6 Hz, 1H, H imid). ^{31}P{^{1}H} NMR (CD_2Cl_2, 75 MHz): δ 43.3. ^{13}C{^{1}H} NMR (CD_2Cl_2, 101 MHz): δ 14.0 (2 CH_3), 22.8 (2 CH_2), 26.7 (CH_2), 26.9 (CH_2), 31.2 (CH_2), 31.7 (2 CH_2), 31.9 (CH_2), 50.7 (CH_2), 51.7 (CH_2), 55.6 (py-CH_2), 58.6 (py-CH_2),

120.2 (CH imid), 121.2 (CH imid), 122.8 (CH imid), 124.5 (CH imid+C-3 pyr), 125.0 (C-3 py), 128.4 (d, $^4J_{CP}$ = 8 Hz, 6 CH arom, PPh_3), 129.8 (3 CH arom, PPh_3), 133.1 (d, $^3J_{CP}$ = 10 Hz, 6 CH arom, PPh_3), 136.6 (d, $^1J_{CP}$ = 39 Hz, 3 C_q arom, PPh_3), 138.6 (C-4 py), 157.1 (2 C-2 py), 182.3 (d, $^2J_{CP}$ = 81 Hz, C-2 imid), 189.9 (d, $^2J_{CP}$ = 8 Hz, C-2 imid), 209.4 (d, $^2J_{CP}$ = 15 Hz, CO). MS (ESI, DMSO/MeOH): *m/z* 800 ($[M-Cl]^+$, 100). Fragmentation of ion *m/z* = 800: 538 ($[M-Cl-PPh_3]^+$, 100).

3c(Br): A mixture of silver complex **2c(Br)** (0.175 g, 0.23 mmol) and $RuHCl(CO)(PPh_3)_3$ (0.233 g, 0.23 mmol) in THF (8 mL) was heated at 55 °C for 24 h. The resulting solution was filtered, brought to dryness and extracted with MeOH (3 × 5 mL). Solvent was evaporated, and the residue was dissolved in THF and treated with NaBr (0.023 g, 0.23 mmol) for 24 h. Solvent was removed under vacuum, and the solid was extracted in CH_2Cl_2 (3 × 5 mL). The resulting solution was brought to dryness, and the solid was recrystallised from MeOH/toluene. Yellow solid (0.042 g, 22%). Anal. Calcd for $C_{42}H_{49}BrN_5OPRu$ (%): C 59.2; H 5.8; N 8.2. Found: C 59.3; H 5.9; N 8.2. IR (CH_2Cl_2 solution, cm^{-1}): 1919 (s, ν_{CO}). ^1H NMR (CD_2Cl_2, 500 MHz): δ −7.52 (d, $^2J_{HP}$ = 31.5 Hz, 1H, RuH), 1.07 (s, 9H, $C(CH_3)_3$), 1.21 (s, 9H, $C(CH_3)_3$), 3.81 (d, $^2J_{HH}$ = 13.5 Hz, 1H, C*H*HC(CH_3)), 3.93 (d, $^2J_{HH}$ = 13.5 Hz, 1H, C*H*HC(CH_3)), 4.52 (d, $^2J_{HH}$ = 15.0 Hz, 1H, py-C*H*H), 4.84 (d, $^2J_{HH}$ = 13.5 Hz, 1H, C*H*HC(CH_3)), 5.12 (d, $^2J_{HH}$ = 13.5 Hz, 1H, C*H*HC(CH_3)), 5.47 (d, $^2J_{HH}$ = 14.0 Hz, 1H, py-C*H*H), 5.73 (d, $^2J_{HH}$ = 15.0 Hz, 1H, py-C*H*H), 5.85 (d, $^2J_{HH}$ = 14.0 Hz, 1H, py-C*H*H), 7.05 (d, $^3J_{HH}$ = 1.6 Hz, 1H, H imid), 7.07 (t, $^3J_{HH}$ = 6.5 Hz, 1H, H-4 py), 7.12 (d, $^3J_{HH}$ = 8.5 Hz, 1H, H-3 py), 7.17 (dd, $^3J_{HP}$ = 8.0 Hz, $^3J_{HH}$ = 8.0 Hz, 6H, 6 H arom, PPh_3), 7.23 (d, $^3J_{HH}$ = 1.6 Hz, 1H, H imid), 7.26 (m, 9H, 9 H arom, PPh_3), 7.39 (d, $^3J_{HH}$ = 7.5 Hz, 1H, H-3 py), 7.85 (d, $^3J_{HH}$ = 1.6 Hz, 1H, H imid), 8.07 (d, $^3J_{HH}$ = 1.6 Hz, 1H, H imid). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz): δ 44.2. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 126 MHz): δ 28.4 (3 CH_3), 29.0 (3 CH_3), 34.0 (*C*(CH_3)$_3$), 34.1 (*C*(CH_3)$_3$), 56.0 (py-CH_2), 58.5 (py-CH_2), 61.7 (2 *C*H_2C(CH_3)$_3$), 63.1 (2 *C*H_2C(CH_3)$_3$), 121.2 (CH imid), 121.7 (CH imid), 123.2 (CH imid), 124.1 (CH imid), 124.2 (C-3 py), 124.8 (C-3 py), 128.5 (d, $^4J_{CP}$ = 9 Hz, 6 CH arom, PPh_3), 130.0 (3 CH arom, PPh_3), 133.5 (d, $^3J_{CP}$ = 11 Hz, 6 CH arom, PPh_3), 136.5 (br d, $^1J_{CP}$ = 40 Hz, 3 C_q arom, PPh_3), 138.7 (C-4 py), 157.0 (C-2 py), 157.3 (C-2 py), 185.2 (d, $^2J_{CP}$ = 82 Hz, C-2 imid), 190.3 (br s, C-2 imid), 211.0 (d, $^2J_{CP}$ = 16 Hz, CO). MS (ESI, DMSO/MeOH): *m/z* 772 ($[M-Br]^+$, 100). Fragmentation of ion *m/z* = 772: 510 ($[M-Br-PPh_3]^+$, 100).

3d(Cl): A mixture of **2d(Cl)** (0.092 g, 0.13 mmol) and $RuHCl(CO)(PPh_3)_3$ (0.120 g, 0.13 mmol) in CH_2Cl_2 (8 mL) was stirred for 6 h. The resulting solution was filtered, brought to dryness and extracted with MeOH (2 × 5 mL). Solvent was evaporated and the obtained solid was recrystallized from MeOH/toluene. Yellow solid (0.056 g, 51%). Complex **3d(Cl)**, while stable under inert atmosphere in the solid state, decomposes in solution (CH_2Cl_2, MeOH, MeCN, THF). Hence, spectroscopically pure samples could not be obtained. Signals of the complex in the ^1H and $^{13}C\{^1H\}$ NMR spectra were assigned with the help of ^1H-^{13}C HMQC and ^1H-^{13}C HMBC experiments. IR (CH_2Cl_2 solution, cm^{-1}): 1934 (s, ν_{CO}). ^1H NMR (CD_2Cl_2, 500 MHz): δ −7.56 (d, $^2J_{HP}$ = 27.5 Hz, 1H, RuH), 2.11 (s, 6 H, 2 *Ar*-CH_3), 2.36 (br s, 6H, 2 *Ar*-CH_3), 4.51 (d, $^2J_{HH}$ = 15.5 Hz, 1H, py-C*H*H), 5.94 (d, $^2J_{HH}$ = 15.5 Hz, 1H, py-C*H*H), 5.96 (d, $^2J_{HH}$ = 14.0 Hz, 1H, py-C*H*H), 6.14 (d, $^2J_{HH}$ = 14.0 Hz, 1H, py-C*H*H), 6.29 (s, 2H, 2 H arom), 6.62 (s, 1H, H imid), 6.75 (s, 1H, H arom), 6.86 (s, 1H, H arom), 7.00 (s, 1H, H imid), 7.18 (m, 13H, 12 H arom PPh_3+H arom), 7.27 (m, 4H, 3 H arom PPh_3+H arom), 7.36 (m, 2H, H-3 py+H-4 py), 7.67 (d, $^3J_{HH}$ = 6.5 Hz, 1H, H-3 py), 7.76 (s, 1H, H imid), 8.11 (s, 1H, H imid). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz): δ 43.4. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 126 MHz): δ 21.4 (br, 2 *Ar*-CH_3), 21.4 (2 *Ar*-CH_3), 56.0 (py-CH_2), 59.3 (py-CH_2), 121.9 (CH imid), 122.5 (2 CH arom), 124.4 (C-3 py), 124.5 (CH arom), 125.0 (CH imid), 125.2 (CH imid), 125.6 (CH imid), 128.6 (d, $^4J_{CP}$ = 9 Hz, 6 CH arom, PPh_3), 128.8 (CH arom), 129.8 (3 CH arom, PPh_3), 130.8 (CH arom), 133.2 (d, $^3J_{CP}$ = 10 Hz, 6 CH arom, PPh_3), 136.6 (2 C_q arom), 136.9 (2 C_q arom), 137.9 (C-3 py), 138.4 (br, CH arom), 138.7 (C-4 py), 140.2 (C_q arom), 140.6 (C_q arom), 157.4 (C-2 py), 158.0 (C-2 py), 182.3 (d, $^2J_{CP}$ = 81 Hz, C-2 imid), 191.3 (d, $^2J_{CP}$ = 7 Hz, C-2 imid), 208.9 (d, $^2J_{CP}$ = 15 Hz, CO). MS (ESI, DMSO/MeOH): *m/z* 840 ($[M-Cl]^+$, 100). Fragmentation of ion *m/z* = 840: 578 ($[M-Cl-PPh_3]^+$, 100). HRMS (FAB): *m/z* 840.2350 $[M-Cl]^+$ (exact mass calculated for $C_{48}H_{45}N_5OP^{102}Ru$: 840.2405).

1.5. NMR characterisation of 4



4a: In a NMR tube, a suspension of **3a(Cl)** (0.018 g, 0.024 mmol) in THF-d_8 (0.7 mL) was treated with Bu^{t}OK (0.003 g, 0.027 mmol) forming a dark-red solution. Low stability of the product has precluded its isolation and full characterization. ^{1}H NMR (THF-d_8, 500 MHz): δ −7.32 (d, $^2J_{HP}$ = 23.0 Hz, 1H, RuH), 0.43 (d, $^3J_{HH}$ = 6.5 Hz, 3H, CH_3), 1.23 (d, $^3J_{HH}$ = 7.0 Hz, 3H, CH_3), 1.39 (d, $^3J_{HH}$ = 6.5 Hz, 3H, CH_3), 1.55 (d, $^3J_{HH}$ = 6.5 Hz, 3H, CH_3), 4.43 (d, $^2J_{HH}$ = 13.5 Hz, 1H, py-C*H*H), 4.60 (d, $^3J_{HH}$ = 9.0 Hz, 1H, H^c), 4.77 (s, 1H, H^d), 5.04 (h, $^3J_{HH}$ = 7.0 Hz, 1H, C*H*$(CH_3)_2$), 5.13 (d, $^3J_{HH}$ = 5.5 Hz, 1H, H^a), 5.18 (h, $^3J_{HH}$ = 6.5 Hz, 1H, C*H*$(CH_3)_2$), 5.42 (d, $^2J_{HH}$ = 14.0 Hz, 1H, py-C*H*H), 5.46 (dd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 5.5 Hz, 1H, H^b), 6.72 (d, $^3J_{HH}$ = 1.6 Hz, 1H, H imid), 6.88 (d, $^3J_{HH}$ = 1.6 Hz, 1H, H imid), 7.10 (m, 10H, H imid+9 H arom, PPh_3), 7.21 (d, $^3J_{HH}$ = 1.6 Hz, 1H, H imid), 7.41 (dd, $^3J_{HP}$ = 8.0 Hz, $^3J_{HH}$ = 8.0 Hz, 6H, 6 H arom, PPh_3). ^{31}P{^{1}H} NMR (THF-d$_8$, 202 MHz): δ 47.9. ^{13}C{^{1}H} NMR (THF-d_8, 126 MHz): δ 22.6 (CH_3), 23.7 (CH_3), 24.1 (CH_3), 24.4 (CH_3), 50.9 (C*H*$(CH_3)_2$), 51.4 (C*H*$(CH_3)_2$), 60.6 (py-CH_2), 93.8 (C^d), 98.4 (C^b), 114.3 (C^c), 115.1 (CH imid), 116.4 (CH imid), 119.0 (CH imid), 121.8 (CH imid), 127.5 (C^a), 128.0 (d, $^4J_{CP}$ = 9 Hz, 6 CH arom, PPh_3), 128.1 (3 CH arom, PPh_3), 134.8 (d, $^3J_{CP}$ = 11 Hz, 6 CH arom, PPh_3), 139.5 (d, $^1J_{CP}$ = 36 Hz, 3 C_q arom, PPh_3), 148.1 (C-2 py), 152.9 (C-2 py), 181.2 (d, $^2J_{CP}$ = 9 Hz, C-2 imid), 187.4 (d, $^2J_{CP}$ = 96 Hz, C-2 imid), 210.6 (d, $^2J_{CP}$ = 14 Hz, CO).

4d: In situ generation of **4d** has been carried out as described for **4a**. Low stability of the product has precluded full characterization. ^{1}H NMR (THF-d_8, 400 MHz): δ −7.67 (d, $^2J_{HP}$ = 23.0 Hz, 1H, RuH), 1.98 (s, 6H, 2 CH_3), 2.06 (br m, 6H, 2 CH_3), 4.52 (d, $^2J_{HH}$ = 13.6 Hz, 1H, py-C*H*H), 4.73 (d, $^3J_{HH}$ = 8.5 Hz, 1H, H^c), 4.74 (s, 1H, H^d), 5.22 (d, $^3J_{HH}$ = 6.0 Hz, 1H, H^a), 5.60 (m, 2H, py-C*H*H + H^b), 5.78 (s, 2H, 2 H arom), 6.60 (s, 1H, H arom), 6.68 (s, 1H, H imid), 6.73 (s, 1H, H imid), 6.77 (s, 1H, H imid), 6.91 (s, 1H, H arom), 7.10−7.34 (m, 18H, H imid+15 H arom, PPh_3 + 2 H arom). ^{31}P{^{1}H} NMR (THF-

d_8, 162 MHz): δ 46.8. $^{13}C\{^1H\}$ NMR (THF-d_8, 101 MHz): δ 21.3 (2 CH_3), 21.4 (br, 2 CH_3), 61.2 (py-CH_2), 93.9 (C^d), 98.7 (C^b), 113.7 (C^c), 118.9 (CH), 121.0 (CH), 123.8 (C^a), 123.9 (CH), 124.7 (2 CH), 127.8 (CH), 128.0 (d, $^4J_{CP}$ = 8 Hz, 6 CH arom, PPh_3), 128.3 (CH), 128.7 (3 CH arom, PPh_3), 130.4 (CH), 134.8 (d, $^3J_{CP}$ = 11 Hz, 6 CH arom, PPh_3), 137.4 (CH), 139.5 (d, $^1J_{CP}$ = 34 Hz, 3 C_q arom, PPh_3), 141.9 (C_q arom), 142.6 (C_q arom), 147.8 (C-2 py), 153.4 (C-2 py), 186.3 (br, C-2 imid), 188.3 (d, $^2J_{CP}$ = 95 Hz, C-2 imid), 210.1 (d, $^2J_{CP}$ = 13 Hz, CO). Signals for one aromatic CH and four quaternary carbons could not be unambiguously assigned.

1.6. Procedure for Catalytic Hydrogenation Reactions

In a glovebox, a Fischer-Porter vessel was charged with a solution of complex **3b(Cl)** (1.2 mg, 1.4 μmol), ^{t}BuOK (1.6 mg, 14.0 μmol) and the corresponding imine (1.4 mmol) in 2-methyltetrahydrofuran (1.0 mL). The reactor was purged three times with H_2, and finally pressurized to 5 bar and heated to 70 ^{o}C. After 6 h, the reactor was slowly cooled down to room temperature and depressurized. The reaction solution was evaporated, and conversion was determined by ^{1}H NMR.

2. X-Ray Structure Determination.

Single crystals of **3a(BF_4)** were obtained by slow diffusion of Et_2O into a saturated solution of dichloromethane. A suitable single crystal coated with dry perfluoropolyether was mounted on glass fiber and fixed in a cold nitrogen stream. Intensity data were collected on a Bruker-Nonius X8Apex-II CCD diffractometer using graphite-monochromated Mo K_α radiation (λ = 0.71073 Å). The data were reduced (SAINT) and corrected for Lorentz−polarization and absorption effects by a multiscan method (SADABS).[4] Structures were solved by direct methods (SIR-2002)[5] and refined against all F^2 data by full-matrix least-squares techniques (SHELXTL-6.12)[6] minimising $w[F^2o\text{-}F^2c]^2$. All the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included from calculated positions and refined riding on their respective carbon atoms with isotropic displacement

parameters. A summary of cell parameters, data collection, structure solution, and refinement is given in Table S1. CCDC 894892 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic data and structure refinement for **3a(BF$_4$)**.

Formula	$C_{38}H_{41}BF_4N_5OPRu$
M_r	802.61
T [K]	173(2)
Crystal size [mm^3]	0.14 × 0.12 × 0.11
Crystal system	monoclinic
Space group	P 2_1/n
a [Å]	27.171(4)
b [Å]	10.1791(13)
c [Å]	30.812(4)
α [°]	90
β [°]	113.210(4)
γ [°]	90
V [Å^3]	7832.2(18)
Z	8
$D_{calcd.}$ [g cm^{-3}]	1.361
Absorption coefficient [mm^{-1}]	0.496
F(000)	3296
θ range [°]	1.44 to 25.25
Measured reflections	58525
Data/restraints/parameters	14122 / 0 / 927
Goodness-of-fit on F^2	1.085
Final R indices [I>2σ(I)]	R_1 = 0.0770,
	wR_2 = 0.1583
R indices (all data)	R_1 = 0.0970,
	wR_2 = 0.1924
Largest diff. peak/hole [eÅ^{-3}]	1.499 / −1.042

3. Bibliography

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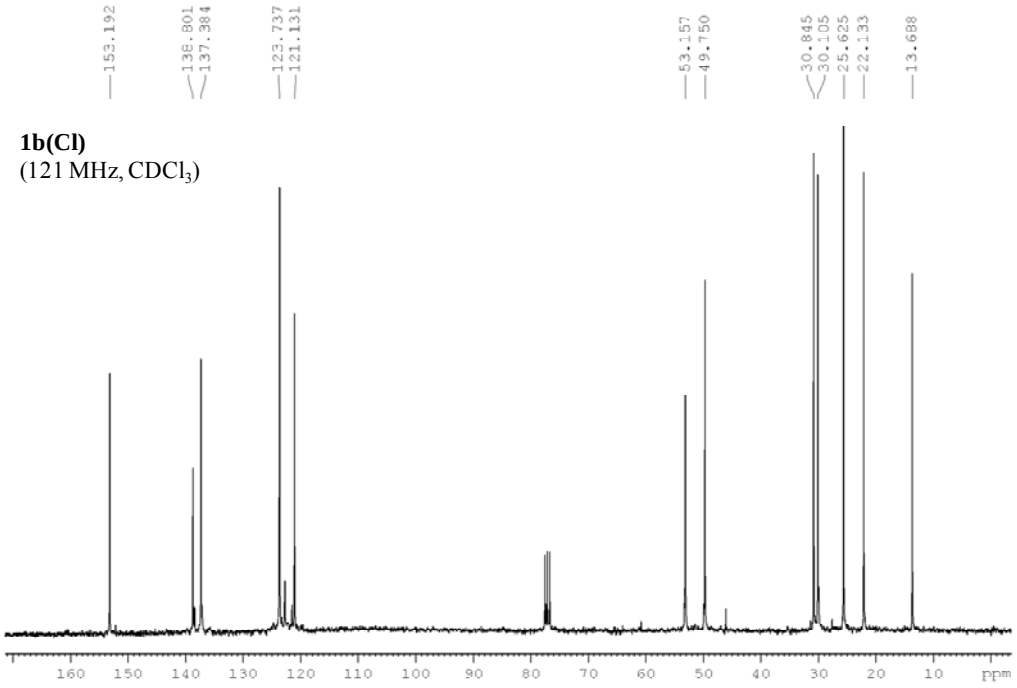

Figure S1. $^{13}C\{^{1}H\}$ NMR spectrum of **1b(Cl)** (121 MHz) in $CDCl_3$.

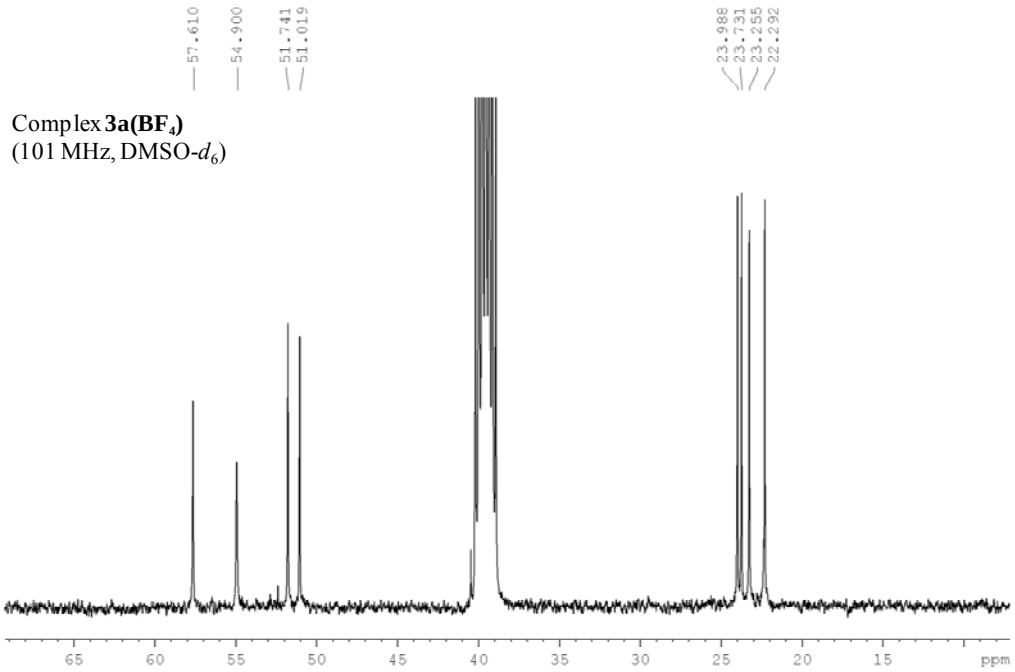

Figure S2a. $^{13}C\{^{1}H\}$ NMR spectrum of **3a(BF$_4$)** (101 MHz) in DMSO-d_6 (10−65 ppm region).

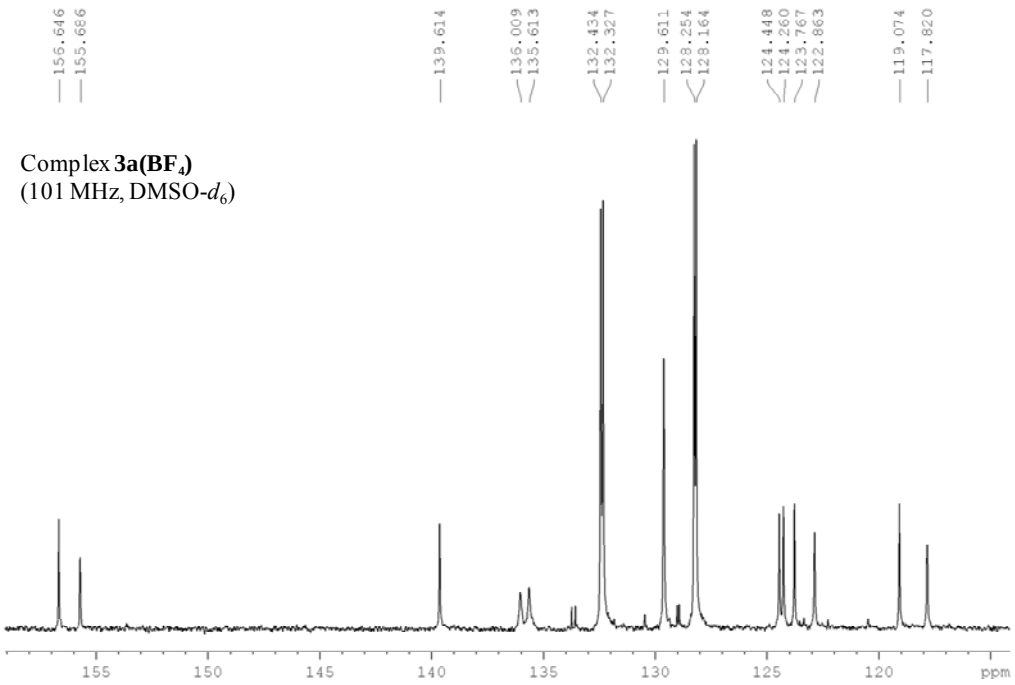

Figure S2b. $^{13}C\{^{1}H\}$ NMR spectrum of **3a(BF$_4$)** (101 MHz) in DMSO-d_6 (115-160 ppm region).

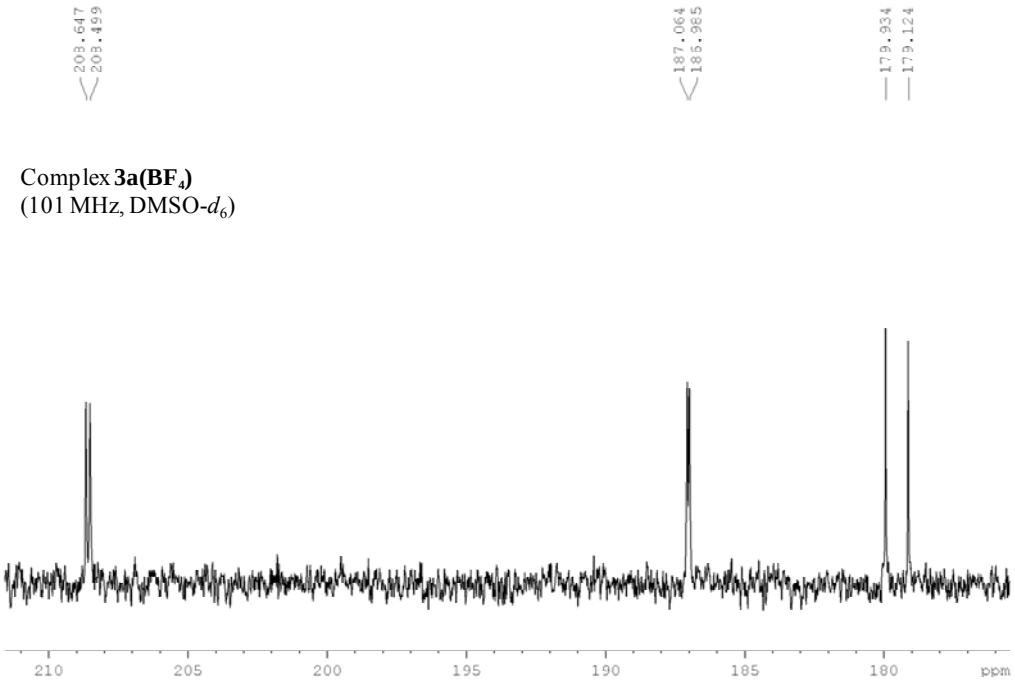

Figure S2c. $^{13}C\{^{1}H\}$ NMR spectrum of **3a(BF$_4$)** (101 MHz) in DMSO-d_6 (175-210 ppm region).

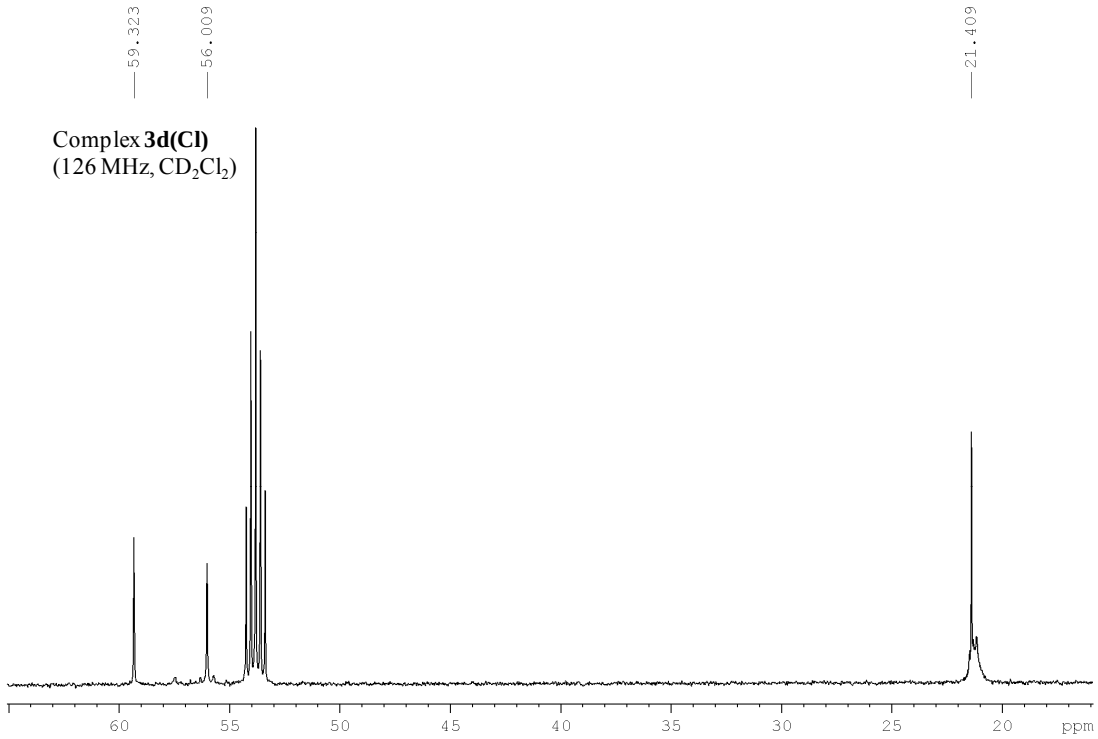

Figure S3a. $^{13}C\{^{1}H\}$ NMR spectrum of **3d(Cl)** (126 MHz) in CD_2Cl_2 (15-65 ppm region).

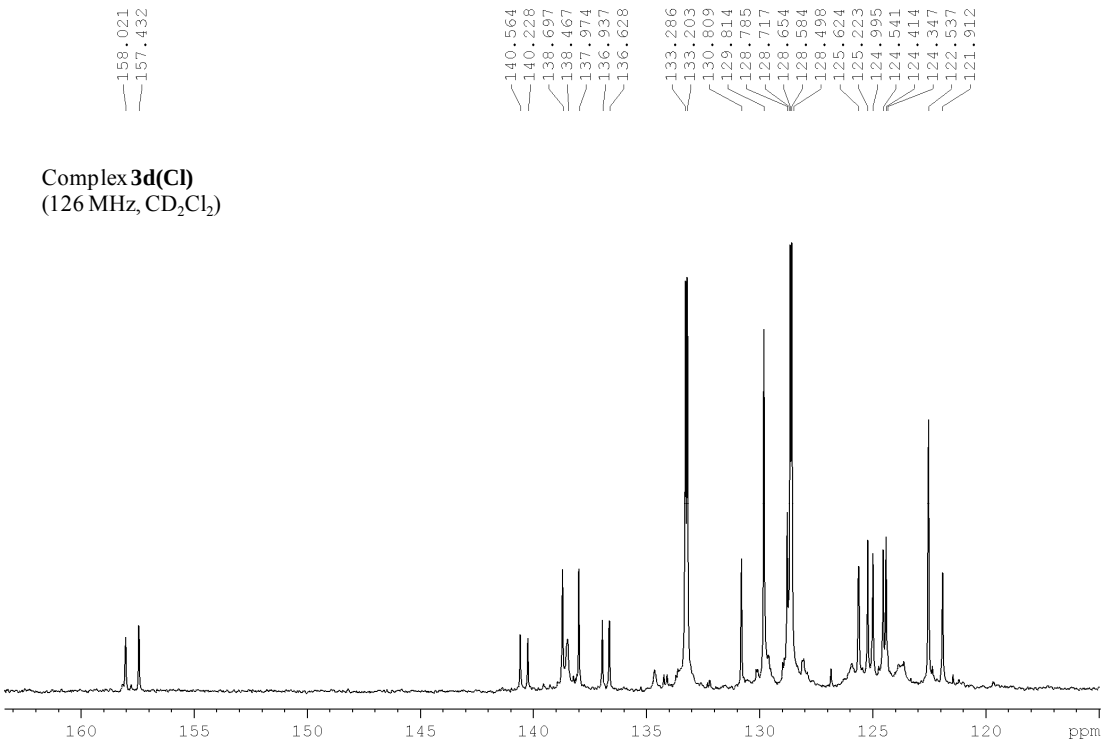

Figure S3b. $^{13}C\{^{1}H\}$ NMR spectrum of **3d(Cl)** (126 MHz) in CD_2Cl_2 (110-160 ppm region).

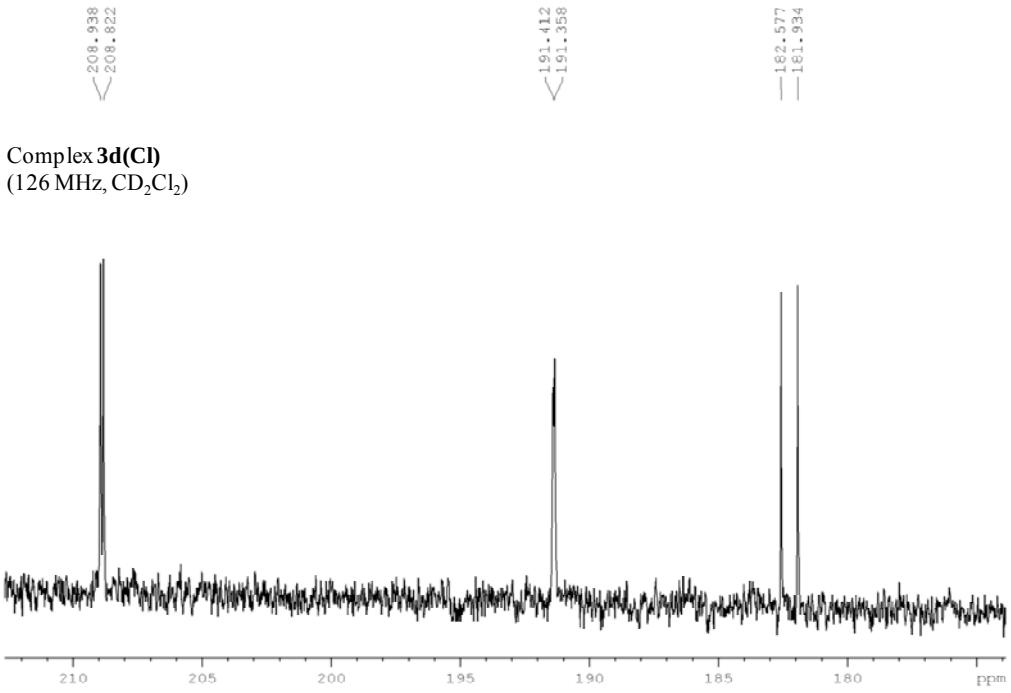

Figure S3c. $^{13}C\{^{1}H\}$ NMR spectrum of **3d(Cl)** (126 MHz) in CD_2Cl_2 (175-210 ppm region).

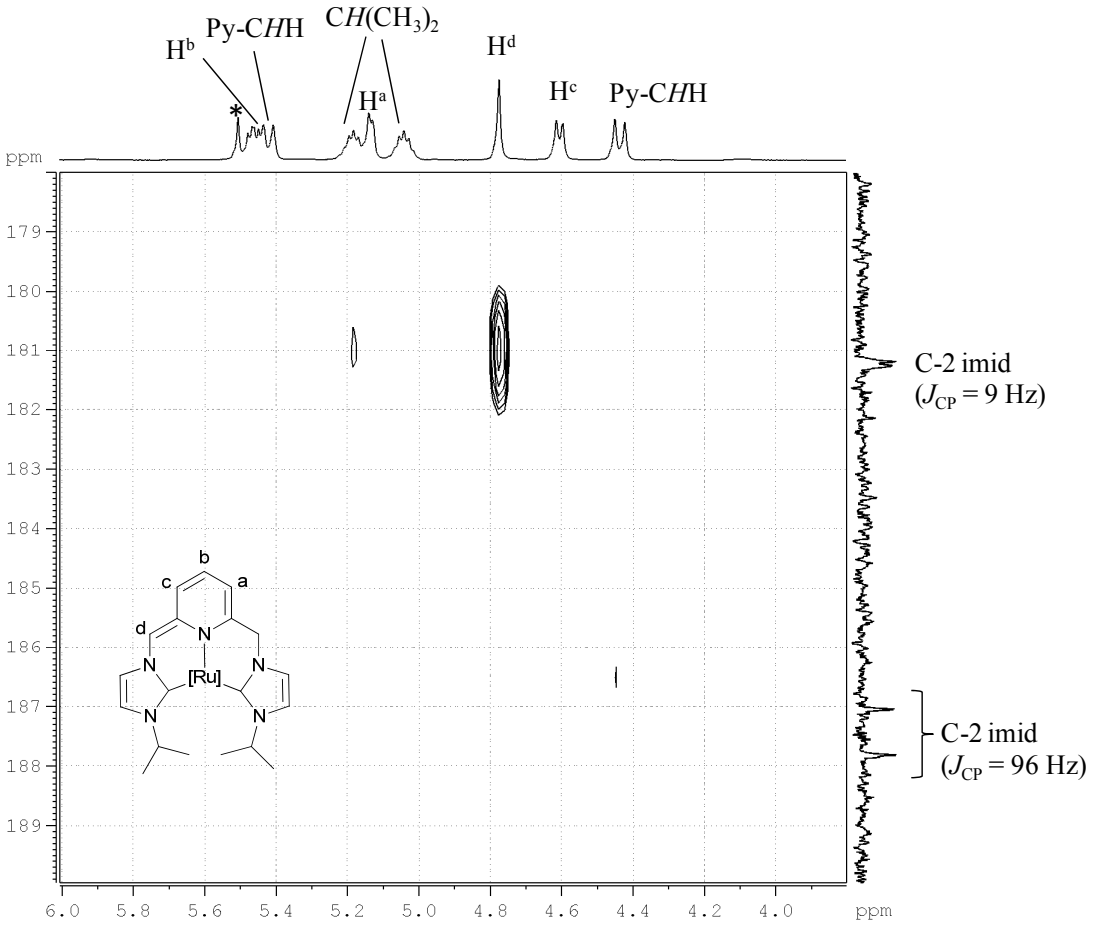

Figure S4. Region of the ^{1}H-^{13}C HMBC experiment of **4a** in THF-d_8 (* denotes residual CH_2Cl_2 solvent).