Unlocking reactivity: synthetic, structural and catalytic exploration of ruthenium(II) complexes featuring pdc and NHC ligands

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SUPPLEMENTARY INFORMATION

1. Synthetic details of complexes **C2**-**C12**.
2. NMR spectra of complexes **C2**-**C12** (Figures S1-S21)
3. Crystallographic details of **C2**-**C6**, **C8**-**C12** (Tables S1-S3)
4. Electrochemical details (Figure S22)
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1. Synthetic details of complexes **C2**-**C12**.

C2. The ligand (0.27g, 1.5 eq) and Ag_2O (0.18g, 1 eq) were stirred in DCM (10 mL) at 45 °C under an argon atmosphere in a Schlenk tube for 1 h. Complex **C1** (0.30, 1 eq) was added to the mixture and allowed to stir overnight. The reaction mixture was filtered. The product was purified by gravity silica gel column chromatography using acetone as eluent. Yield: 39%. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.11 (d, *J* = 7.7 Hz, 2H, CH of pdc), 7.89 (dd, *J* = 8.0, 7.4 Hz, 1H, CH of pdc), 6.61 (s, 2H, CH of imidazole), 4.69-4.68 (m, 2H, CH of COD), 3.88-3.87 (m, 2H, CH of COD), 3.68 (s, 6H, CH_3 of imidazole), 2.80-2.60 (m, 4H CH_2 of COD), 2.37-2.28 (m, 2H, CH_2 of COD), 2.19-2.12 (m, 2H, CH_2 of COD). ^{13}C NMR (400 MHz, $CDCl_3$) δ_C 170.9 (CO of pdc), 169.5 (NCN of imidazole), 149.8 (*C*CH of pdc), 135.8 (CH of pdc), 127.0 (CH of pdc), 124.5 (CH of imidazole), 117.5 (CH of COD), 86.2 (CH of COD), 39.8 (CH_3 of imidazole), 31.7 (CH_2 of COD), 27.5 (CH_2 of COD). HR-MS (ESI) m/z 472.1004 calcd 470.4910 (M^++2H). Elemental Analysis: calcd (**C2**.2H_2O): C, 47.43; H, 5.37; N, 8.30; found: C, 47.82, H, 5.30, N, 8.45.

C3. The ligand (0.16g, 1.5 eq) and Ag_2O (0.15g, 1 eq) were refluxed in DCM (10 mL) under an argon atmosphere in a Schlenk tube for 1 h. Complex **C1** (0.24g, 1 eq) was added to the mixture and allowed to stir overnight. The reaction mixture was filtered. The product was purified by gravity silica gel column chromatography using acetone as eluent. Yield: 16%. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.04 (dd, *J* = 18.2, 7.7 Hz, 2H, CH of pdc), 7.86 (dd, *J* = 10.4, 5.0 Hz, 1H, CH of pdc), 6.66 (d, *J* = 1.9 Hz, 1H, CH of imidazole), 6.61 (d, *J* = 1.9 Hz, 1H, CH of imidazole), 5.28-4.87 (m, 2H, CH_2 of alkenyl tether), 4.72 (d, *J* = 3 Hz, 2H, CH of COD), 4.49-4.48 (m, 1H, CH of alkenyl tether), 3.90-3.80 (m, 2H, CH of COD), 3.76 (s, 3H, CH_3 of imidazole), 3.73 (s, 1H, CH of alkenyl tether), 2.78-2.62 (m, 4H, CH_2 of COD), 2.36-2.30 (m, 2H, CH_2 of COD), 2.19-2.17 (m, 2H, CH_2 of COD), 1.71 (s, 3H, CH_3 of alkenyl tether). ^{13}C NMR (400 MHz, $CDCl_3$) δ_C 171.0 (NCN of imidazole), 169.7 (CO of pdc), 143.6 (*C*CH of pdc), 135.7 (CH of pdc), 126.9 (CH of pdc), 125.1 (CH of imidazole), 123.6 (CH of imidazole), 117.7 (CH of COD), 111.0 (=CH_2 of alkenyl tether), 86.4 (CH of COD), 55.2 (CH_2 of alkenyl tether), 40.1 (CH_3 of imidazole), 31.8 (CH_2 of COD), 27.4 (CH_2 of COD), 20.3 (CH_3 of alkenyl tether). HR-MS (ESI) m/z 512.4423 calcd 510.5560 (M^++2H). Elemental Analysis: calcd (**C3**.0.6CH_2Cl_2): C, 50.48; H, 5.06; N, 7.48; found: C, 50.67, H, 4.99, N, 7.82.

C4. The ligand (0.20g, 1.5 eq) and Ag_2O (0.12g, 1 eq) were stirred in DCM (10 mL) at 45 °C under an argon atmosphere in a Schlenk tube for 1 h. Complex **C1** (0.21, 1 eq) was added to the mixture and allowed to stir overnight. The reaction mixture was filtered. The product was purified by gravity silica gel column chromatography using acetone as eluent. Yield: 32%. ^{1}H

NMR (400 MHz, $CDCl_3$) δ_H 7.80-7.78 (m, 2H, CH of pdc), 7.35 (s, 1H, CH of pdc), 7.18-7.10 (m, 3H, CH of benzyl), 6.69-6.66 (m, 3H, CH of benzyl and imidazole), 6.54 (d, *J* = 1.9 Hz, 1H, CH of imidazole), 5.62-5.20 (m, 2H, CH_2 of benzyl), 4.81-4.80 (m, 2H, CH of COD), 3.82-3.80 (m, 5H, CH_3 of imidazole and CH of COD), 2.74-2.64 (m, 4H, CH_2 of COD), 2.37-2.27 (m, 2H, CH_2 of COD), 2.19-2.11 (m, 2H, CH_2 of COD). ^{13}C NMR (300 MHz, $CDCl_3$) δ_C 170.8 (NCN of imidazole), 170.2 (CO of pdc), 149.7 (*C*CH of pdc), 137.8 (*C*CH of benzyl), 135.7 (CH of pdc), 128.5 (CH of benzyl), 127.2 (CH of benzyl), 126.8 (CH of pdc), 126.2 (CH of benzyl), 125.3 (CH of imidazole) 123.5 (CH of imidazole), 117.5 (CH of COD), 86.5 (CH of COD), 53.2 (CH_2 of benzyl), 40.0 (CH_3 of imidazole), 31.6 (CH_2 of COD), 27.4 (CH_2 of COD). HR-MS (ESI) m/z 548.1398 calcd 546.5890 (M^++2H). Elemental Analysis: calcd (**C4**.H_2O): C, 55.31; H, 5.18; N, 7.44; found: C, 55.18, H, 4.90, N, 7.42.

C5. Yield: 30%. The sensitive nature of this complex in solution precluded the use of ^{13}C NMR spectroscopy as it degraded *in situ* over the time range required for a spectrum with a high signal-to-noise ratio. Similarly, mass spectrometry, CHN analysis, and cyclic voltammetry could not be utilised in this case. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.06-7.49 (m, 8H), 7.02 (s 1H, CH of imidazole), 6.73 (s, 1H, CH of imidazole), 4.43-4.41 (m, 2H, CH of COD), 3.58 (s, 3H, CH_3 of imidazole), 3.51-3.49 (m, 2H, CH of COD), 2.61-2.15 (m, 12H, CH_2 of COD and CH_2 ethyl).

C6. The ligand (0.24g, 1.5 eq) and Ag_2O (0.13g, 1 eq) were stirred in DCM (10 mL) at 45 °C under an argon atmosphere in a Schlenk tube for 1 h. Complex **C1** (0.23, 1 eq) was added to the mixture and allowed to stir overnight. The reaction mixture was filtered. The product was purified by gravity silica gel column chromatography using a mixture of ethyl acetate/acetone as eluent (1:4). Yield: 38%. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.11-7.80 (m, 3H, CH of pdc and 2H of benzyl), 7.85-7.76 (m, 2H, CH of pdc), 6.79-6.76 (m, 2H, CH of benzyl and 1H, CH of imidazole), 6.57-6.56 (d, *J* = 1.6 Hz, 1H, CH of imidazole), 6.01 (m, 1H, CH_2 of benzyl), 5.32 (m, CH_2 of benzyl), 4.76-4.71 (m, 2H, CH of COD), 3.86-3.68 (m, 5H, CH_3 of imidazole and CH of COD), 2.74-2.50 (m, 4H, CH_2 of COD), 2.40-2.07 (m, 4H, CH_2 of COD). ^{13}C NMR (300 MHz, $CDCl_3$) δ_C 171.9 (CO of pdc), 170.8 (NCN of imidazole), 149.9 (*C*CH of pdc), 147.5 (*C*CH of benzyl), 136.0 (CH of pdc), 127.0 (CH of pdc), 126.8 (CH of benzyl), 126.2 (CH of imidazole), 123.8 (CH of benzyl), 125.3 (CH of imidazole) 123.5 (CH of imidazole), 117.9 (CH of COD), 86.6 (CH of COD), 52.8 (CH_2 of benzyl), 40.3 (CH_3 of imidazole), 31.7 (CH_2 of COD), 27.5 (CH_2 of COD). HR-MS (ESI) m/z 593.0369 calcd 591.5900 (M^++H). Elemental Analysis: calcd (**C6**.0.5H_2O): C, 52.00, H, 4.53, N, 9.33; found: C, 52.15, H, 4.31, N, 8.98.

C7. The ligand (0.14g, 1.5 eq) and Ag_2O (0.08g, 1 eq) were stirred in DCM (10 mL) at 42 °C under an argon atmosphere in a Schlenk tube for 1 h. Complex **C1** (0.13, 1 eq) was added to the mixture and allowed to stir overnight. The reaction mixture was filtered. The product was purified by gravity silica gel column chromatography with a mixture of acetone/ethyl acetate as eluent. Yield: 61%. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.17-7.99 (d, *J* = 8.7 Hz, 2H, CH of pdc), 7.87-7.70 (m, 3H, CH of pdc and benzyl), 7.31-7.21 (m, 4.6 Hz, 3H, CH of benzyl), 6.88 (d, *J* = 8 Hz, 2H, CH of benzyl), 6.81-6.70 (m, 1H, CH of benzyl), 6.69-6.62 (m, 1H, CH of imidazole), 6.61-6.60 (d, *J* = 3Hz, 1H, CH of imidazole), 6.04 (d, J = 12.6Hz, 1H, CH_2 of benzyl), 5.72-5.45 (m, 3H, CH_2 of benzyl), 4.95-4.79 (m, 2H, CH of COD), 3.80-3.74 (m, 2H, CH of COD), 2.73-2.71 (m, 2H, CH_2 of COD), 2.58 (m, 2H, CH_2 of COD), 2.38-2.29 (m, 4H, CH_2 of COD). ^{13}C NMR (300 MHz, $CDCl_3$) δ_C 172.4 (CO of pdc), 170.7 (NCN of imidazole), 147.2 (*C*CH of pdc), 145.3 (*C*CH of benzyl), 137.5 (*C*CH of benzyl), 135.8 (CH of pdc), 128.8 (CH of benzyl), 127.6 (CH of pdc), 126.8 (CH of benzyl), 126.5 (CH of benzyl), 125.0 (CH of benzyl), 124.2 (CH of imidazole), 123.8 (CH of imidazole), 117.9 (CH of COD), 86.7 (CH of COD), 53.8 (CH_2 of benzyl), 53.0 (CH_2 of benzyl), 31.6(CH_2 of COD), 28.0-27.5 (4H, CH_2 of COD) . HR-MS (ESI) m/z 669.1622 calcd 667.6840 (M^++2H). Elemental Analysis: calcd (**C7**.0.3CH_2Cl_2): C, 55.97; H, 4.45; N, 8.08; found: C, 55.74, H, 4.23, N, 7.99.

C8. The ligand (0.31g, 1.5 eq) and Ag_2O (0.12g, 1 eq) were stirred in DCM (10 mL) at 45 °C under an argon atmosphere in a Schlenk tube for 1 h. Complex **C1** (0.21g, 1 eq) was added to the mixture and allowed to stir overnight. The reaction mixture was filtered. The product was purified by gravity silica gel column chromatography a mixture of acetone/ethyl acetate as eluent. Yield: 25%. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.13-7.74 (m, 6H, CH of pdc and phenyl), 7.50-6.91 (m, 8H, CH of pdc and phenyl), 6.73-6.70 (m, 3H, CH of phenyl and imidazole), 6.53 (d, *J* = 1.9 Hz, 1H, CH of imidazole), 6.10-5.94 (m, 1H, CH_2), 5.60-5.30 (m, 1H, CH_2), 4.90-4.60 (m, 3H, CH of COD and CH_2 of ethyl), 4.35 (m, 1H, CH_2 of ethyl), 3.83-3.70 (m, 2H, CH of COD), 3.21-3.18 (m, 1H, CH_2 of ethyl), 2.80-2.11 (m, 9H, CH_2 of COD and ethyl). ^{13}C NMR (300 MHz, $CDCl_3$) δ_C 171.3 (CO of pdc), 170.7 (NCN of imidazole), 149.6 (CCH of pdc), 147.1 (*C*CH of benzyl), 145.5 (*C*CH of benzyl), 137.8 (*C*CH of benzyl), 135.9 (CH of pdc), 129.1 (CH of benzyl), 128.7 (CH of benzyl), 127.2 (CH of pdc), 127.0 (CH of benzyl), 126.9 (CH of benzyl), 126.9 (CH of imidazole), 126.6 (CH of benzyl), 124.9 -123.7 (CH of benzyl and imidazole), 118.2-117.8 (CH of COD), 86.7 (CH of COD), 52.9 (CH_2 of benzyl), 52.0 (CH_2 of ethylbn) 38.3 (CH_2 of ethylbn), 31.8-31.4 (CH_2 of COD), 27.4 (CH_2 of COD. HR-MS (ESI) m/z 683.1798 calcd 681.7110 (M^++2H). Elemental Analysis: calcd (**C8.**0.5H_2O): C, 57.38; H, 4.82; N, 8.11; found: C, 56.88, H, 4.37, N, 8.24.

C9. The ligand (0.14g, 1.5 eq) and Ag_2O (0.08g, 1 eq) were stirred in DCM (10 mL) at 42 °C under an argon atmosphere in a Schlenk tube for 1 h. Complex **C1** (0.13, 1 eq) was added to the mixture and allowed to stir overnight. The reaction mixture was filtered. The product was purified by gravity silica gel column chromatography with a mixture of acetone/ethyl acetate as eluent. Yield: 8%. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.08-8.05 (d, *J* = 8 Hz, 4H, CH of benzyl), 7.81-7.78 (m, 3H, CH of pdc), 6.92 (d, *J* = 8 Hz, 4H, CH of benzyl), 6.71 (s, 2H, CH of imidazole), 6.05 (d, *J* = 17.4 Hz, 2H, CH_2 of benzyl), 5.53 (d, *J* = 17.0 Hz, 2H, CH_2 of benzyl), 4.77 (m, 2H, CH of COD), 3.73 (m, 2H, CH of COD), 2.74-2.10 (m, 8H, CH_2 of COD). ^{13}C NMR (300 MHz, $CDCl_3$) δ_C 173.4 (NCN of imidazole), 170.6 (CO of pdc), 149.6 (*C*CH of pdc), 147.4 (*C*CH of benzyl), 144.9 (*C*CH of benzyl), 136.1 (CH of pdc), 127.0 (CH of pdc) 127.0 (CH of benzyl), 124.9 (CH of imidazole), 124.0 (CH of benzyl), 118.2 (CH of COD), 86.7 (CH of COD), 53.2 (CH_2 of benzyl), 31.6 (CH_2 of COD), 27.4 (CH_2 of COD). HR-MS (ESI) m/z 714.1472 calcd 712.6810 (M^++2H). Elemental Analysis: calcd (**C9**): C, 53.93; H, 4.10; N, 9.83; found: C, 54.01, H, 4.01, N, 9.53.

C10. The imidazolium ligand (0.16g, 2eq) and Ag_2O (0.12g, 1eq) were stirred in DMF at 90°C under an argon atmosphere in a Schlenk tube for 1 h. C1 (0.20, 1 eq) was added to the mixture and allowed to stir overnight. The crude was filtered through silica; methanol was added and concentrated under vacuo. The product was recrystallised with diethyl ether/DMF-MeOH. The product was then washed with ethyl acetate. Yield: 69%. ^{1}H NMR (300 MHz, MeOD) δ_H 8.30-8.27 (m, 2H, CH of pdc), 8.14-8.11 (m, 1H, CH of pdc), 7.35 (s, 1H, CH of imidazole), 6.76 (s, 1H, CH of imidazole), 4.80-4.40 (m, 3H, CH and CH_2 of alkenyl tether), 4.19-3.69 (m, 5H, CH and CH_2 of alkenyl tether), 2.10 (s, 3H CH_3 of alkenyl tether), 1.27 (s, 3H, CH_3 of alkenyl tether). ^{13}C NMR (75 MHz, MeOD) δ_C 175.8 (NCN of imidazole), 174.1 (CO of pdc), 153.3 (*C*CH of pdc), 151.3 (*C*CH of pdc) 143.0 (*C*=CH_2 of alkenyl tether), 138.2 (CH of pdc), 128.9 (CH of pdc), 128.5 (CH of pdc), 124.6 (CH of imidazole), 121.4 (CH of imidazole), 110.8 (=CH_2 of alkenyl tether), 94.9 (-CCH_2 of imidazole), 65.3 (=CH_2 of alkenyl tether), 55.3 (CH_2 of alkenyl tether), 54.0 (CH_2 of alkenyl tether), 22.2 (CH_3 of imidazole), 19.8 (CH_3 of imidazole). HR-MS (ESI) m/z 462.9854 calcd 460.4500 (M^++2H). Elemental Analysis: calcd (**C10.**0.5$CHCl_3$): C, 42.72, H, 4.17, N, 8.08; found: C, 42.93, H, 4.22, N, 7.72.

C11. The imidazolium ligand (0.20g, 2eq) and Ag_2O (0.13g, 1eq) were stirred in DMF at 120°C under an argon atmosphere in a Schlenk tube for 1 h. Complex [Ru(pdc)(COD)(N-methylimidazole)] (0.25, 1 eq) was added to the mixture and allowed to stir for about 2 days. Diethyl ether was added to the reaction mixture and was purified column chromatography using acetone as eluent. Yield: 13%. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.12-8.09 (m, 2H, CH of pdc),

7.90-7.86 (m, 1H, CH of pdc), 7.09 (s, 1H, CH of methylimidazole), 6.95 (d, *J* = 1.9 Hz, 1H, CH of methylimidazole), 6.61-6.59 (m, 2H, CH of alkenyl tether), 6.44 (d, *J* = 1.9 Hz, 1H, CH of methylimidazole), 4.59 (d, J = 9 Hz, 1H, CH_2 of alkene), 4.21 (d, *J* = 9 Hz, 1H, CH_2 of alkene), 3.80 (d, *J* = 5 Hz, 2H, CH_2 of alkenyl tether), 3.53 (s, 3H, CH_3 of methylimidazole), 2.86 (s, 3H, CH_3 of imidazole), 1.70 (s, 3H, CH_3 of alkenyl tether). ^{13}C NMR (400 MHz, $CDCl_3$) δ_C 181.0 (NCN of imidazole), 172.1 (CO of pdc), 150.8 (*C*CH of pdc), 149.9 (*C*CH of pdc), 137.3 (CH of imidazole), 134.9, 127.9 (CH of pdc), 127.1 (CH of pdc), 126.7 (CH of imidazole), 122.8 (CH of imidazole), 120.4 (CH of imidazole), 118.7 (CH of imidazole), 91.1 (-CCH_2 of alkenyl tether), 65.4 (CH_2 of alkene), 55.0 (CH_2 of alkenyl tether), 34.9 (CH_3 of methylimidazole), 34.2 (CH_3 of alkenyl tether), 22.4 (CH_3 of alkenyl tether). HR-MS (ESI) m/z 485.0881 calcd 484.4780 (M^++1H). Elemental Analysis: calcd (**C11**.CH_2Cl_2) C, 42.19, H, 4.07, N, 12.30 found; C, 42.08, H, 4.28, N, 12.15.

C12. The imidazolium ligand (0.16g, 2eq) and Ag_2O (0.11g, 1eq) were stirred in DMF at 120°C under an argon atmosphere in a Schlenk tube for 1 h. Complex [Ru(pdc)(COD)(4-phenylpyridine)] (0.25, 1 eq) was added to the mixture and allowed to stir for about 2 days.Diethyl ether was added and the crude was washed with diethyle ether. Further purification was done by solvent wash using water, followed by diethyl ether and ethyl acetate. The product was also redissolved using DCM, filtered and concentrated under vacuo. Yield: 61%. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.15-8.05 (m, 4H, CH of pdc and CH of 4-Phpy), 7.92 (t, *J* = 7.7 Hz, 1H, CH of pdc), 7.52-7.35 (m, 7H, CH of 4-Phpy), 6.98 (d, *J* = 1.9 Hz, 1H, CH of imidazole), 6.48 (d, *J* = 1.9 Hz, 1H, CH of imidazole), 4.60 (d, *J* = 12.4 Hz, 1H, =CH_2 of alkenyl tether), 4.24 (d, *J* = 12.4 Hz, 1H, =CH_2 of alkenyl tether), 3.85 (d, *J* = 44.4 Hz, 2H, CH_2 of alkenyl tether), 2.88 (s, 3H, CH_3 of imidazole), 1.65 (s, 3H, CH_3 of alkenyl tether). ^{13}C NMR (300 MHz, $CDCl_3$) δ 179.2 (NCN of imidazole), 172.0 (CO of pdc), 150.5 (*C*CH of 4-Phpy), 150.2 (*C*CH of pdc), 149.7 (*C*CH of 4-Phpy), 148.8 (CH of 4-Phpy), 136.4 (CH of pdc), 135.5 (CH of 4-Phpy), 129.8 (CH of 4-Phpy), 129.3 (CH of 4-Phpy), 127.4 (CH of pdc), 126.9 (CH of 4-Phpy), 123.2 (CH of imidazole), 122.3 (CH of 4-Phpy), 119.0 (CH of imidazole), 91.3 (-CCH_2 of imidazole), 65.7 (CH_2 of alkenyl tether), 54.8 (=CH_2 of alkenyl tether), 35.0 (CH_3 of imidazole), 22.5 (CH_3 of alkenyl tether). HR-MS (ESI) m/z 559.1176 calcd 557.5720 (M^++2H). Elemental Analysis: calcd (**C12**.CH_2Cl_2) C, 50.47, H, 4.08, N, 8.72; found; C, 50.51, H, 3.78, N, 9.33.

2. NMR spectra of complexes **C2**-**C12** (Figures S1-S20)

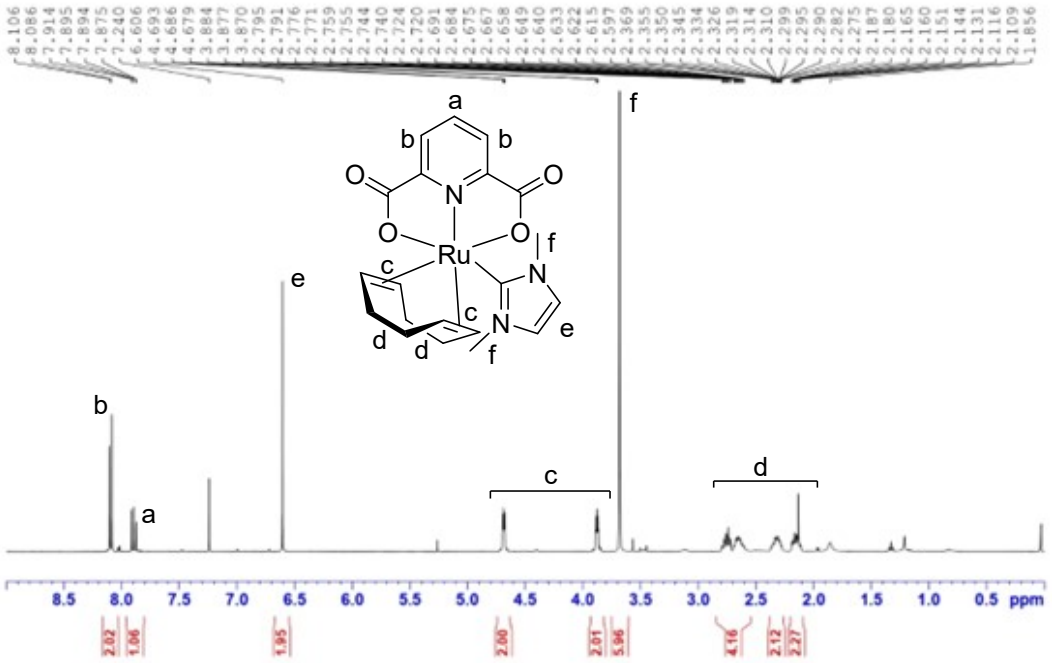


Figure S1 C2: ^{1}H NMR spectrum

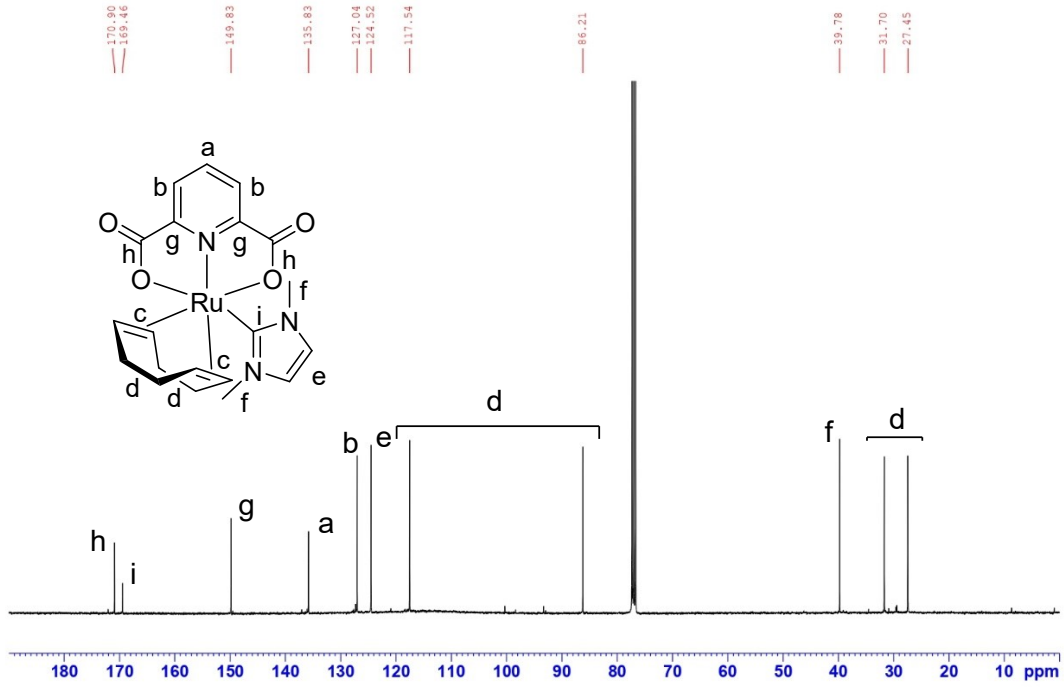


Figure S2 C2: ^{13}C NMR spectrum

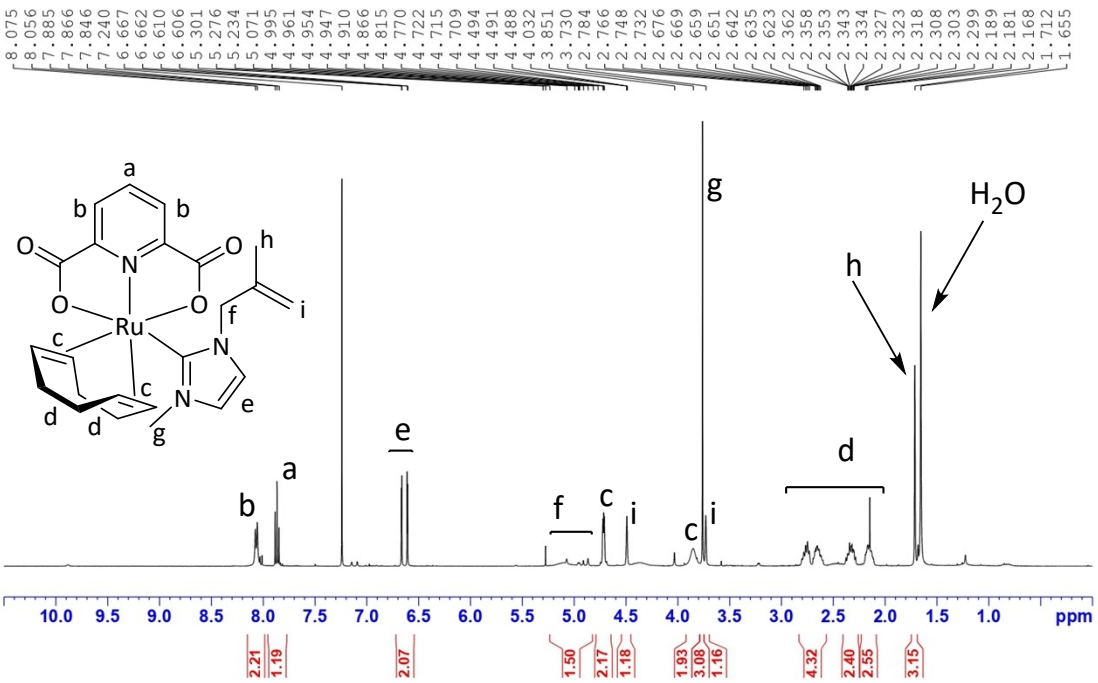
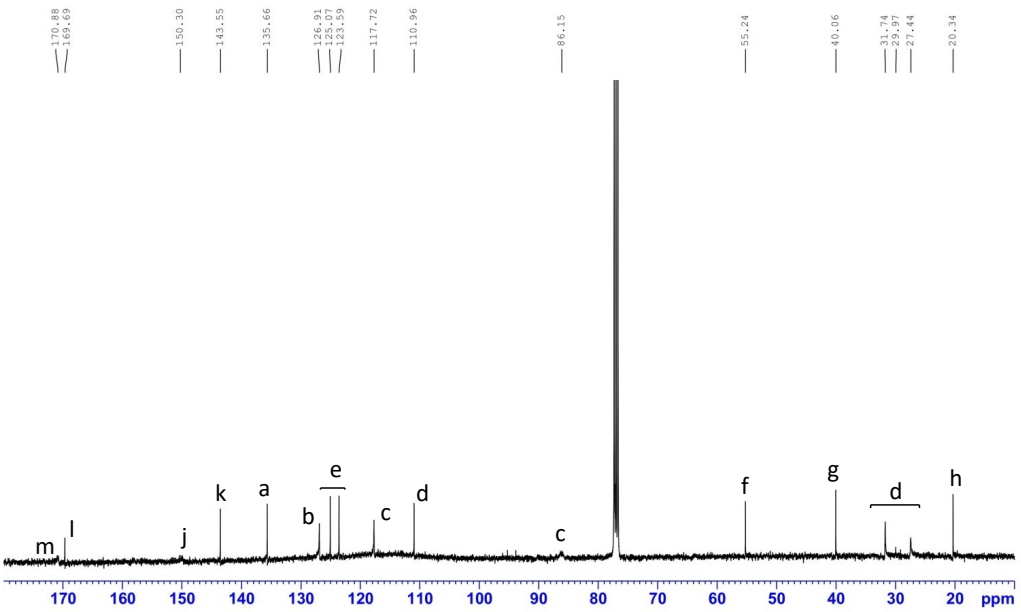


Figure S3 C3: ^{1}H NMR spectrum



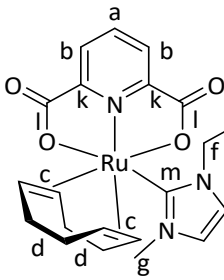


Figure S4 C3: ^{13}C NMR spectrum

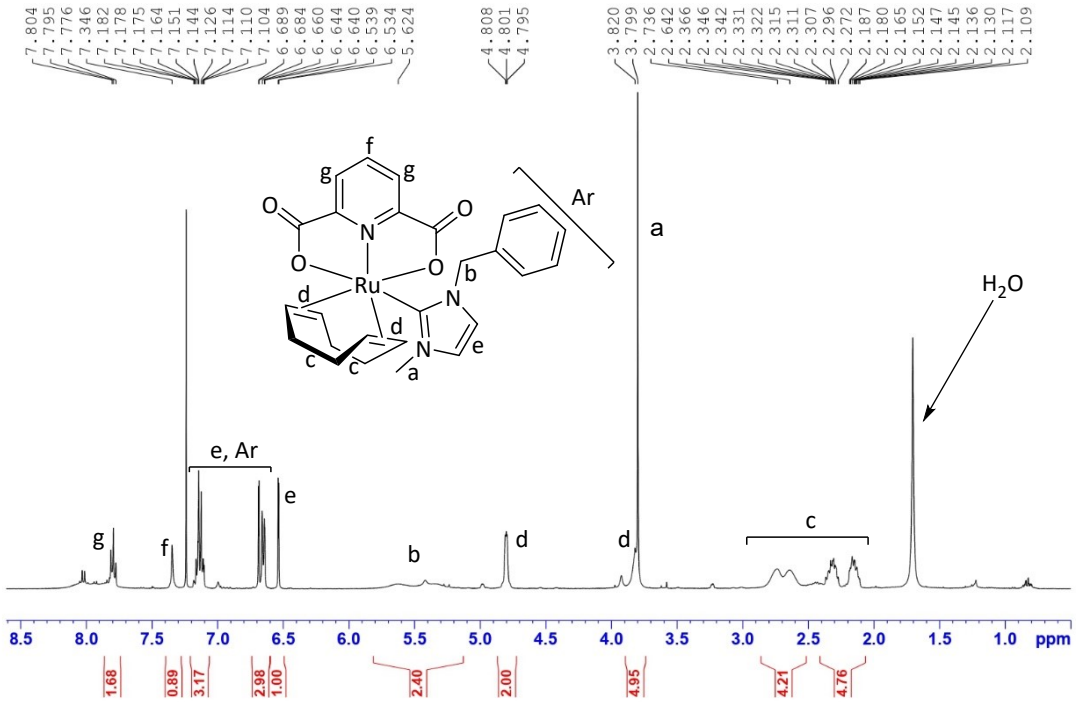


Figure S5 C4: ^{1}H NMR spectrum

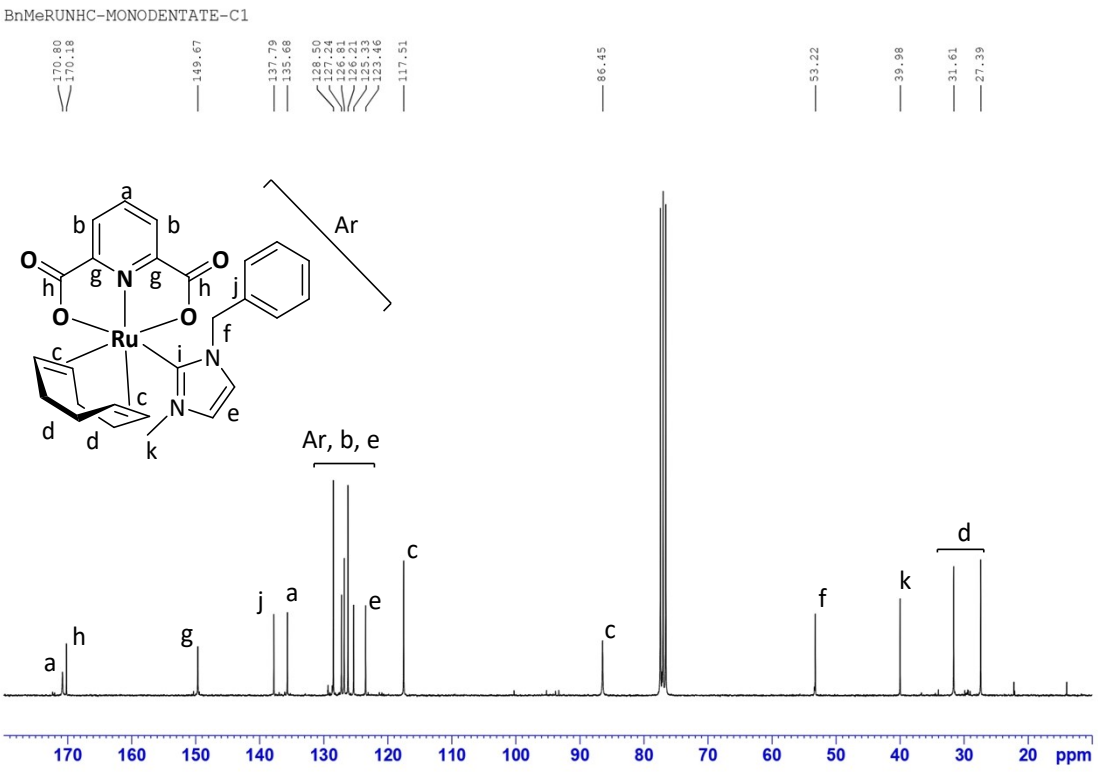


Figure S6 C4: ^{13}C NMR spectrum

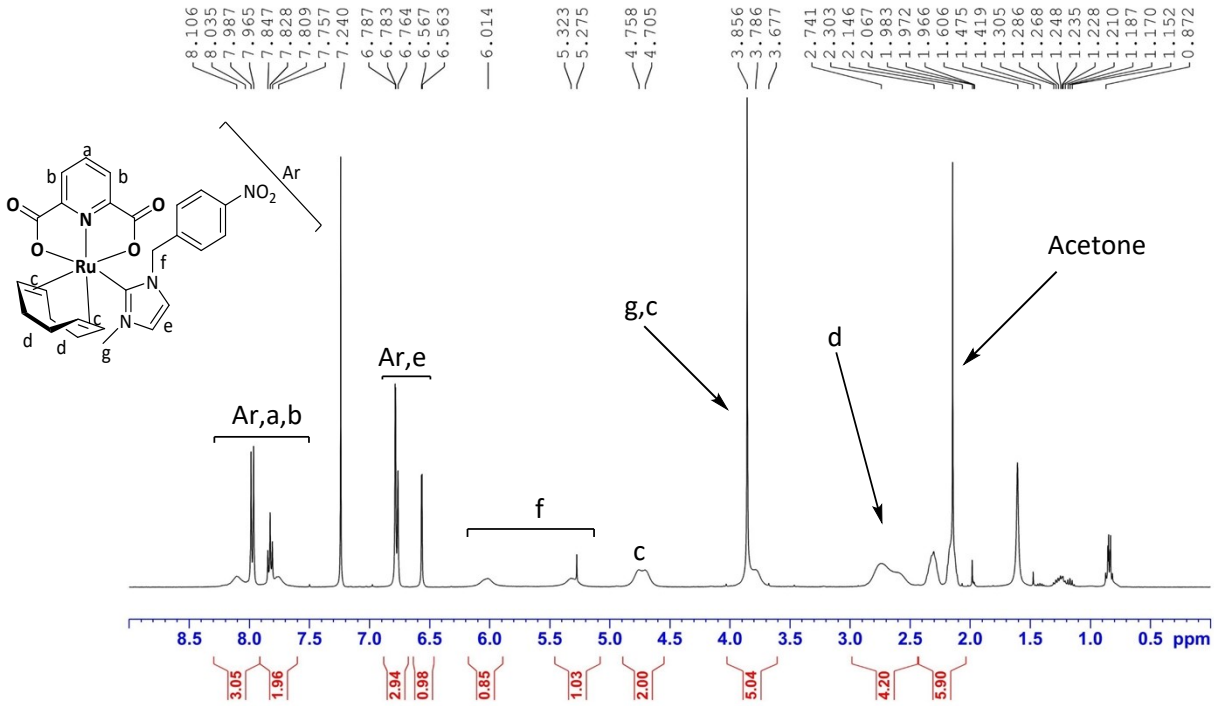


Figure S7 C6: ^{1}H NMR spectrum

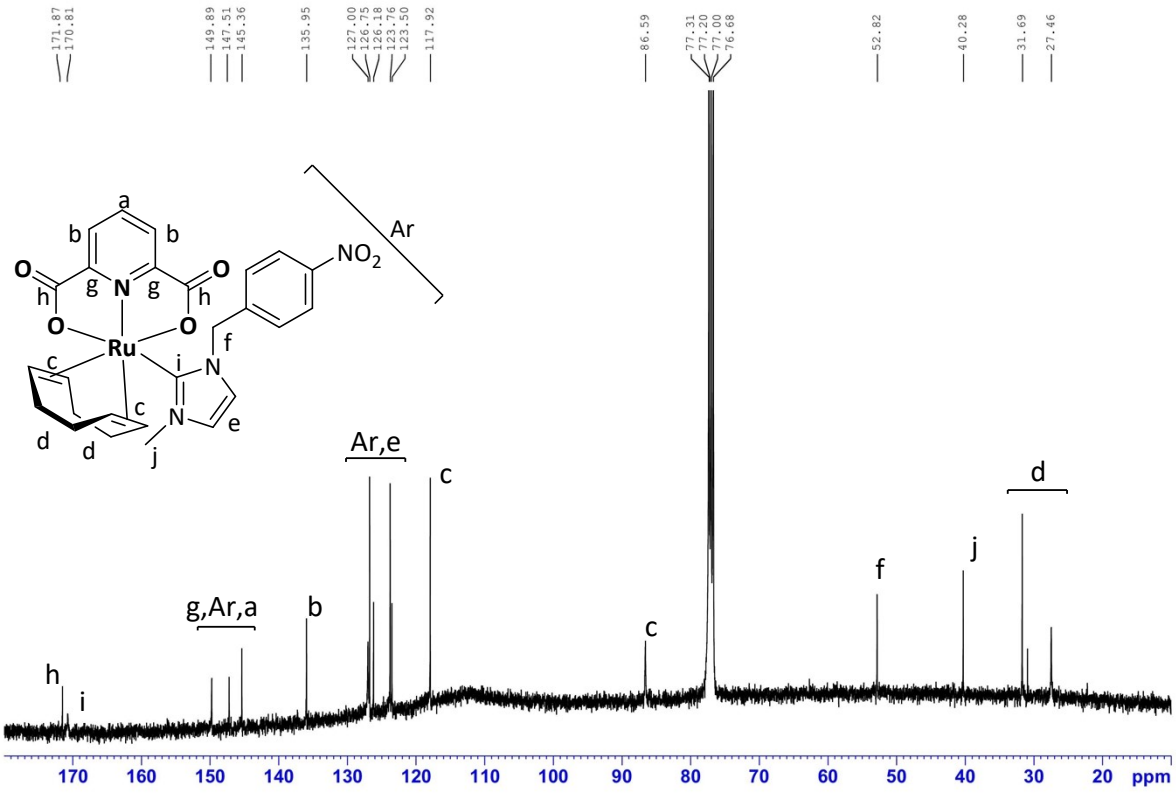


Figure S8 C6: ^{13}C NMR spectrum

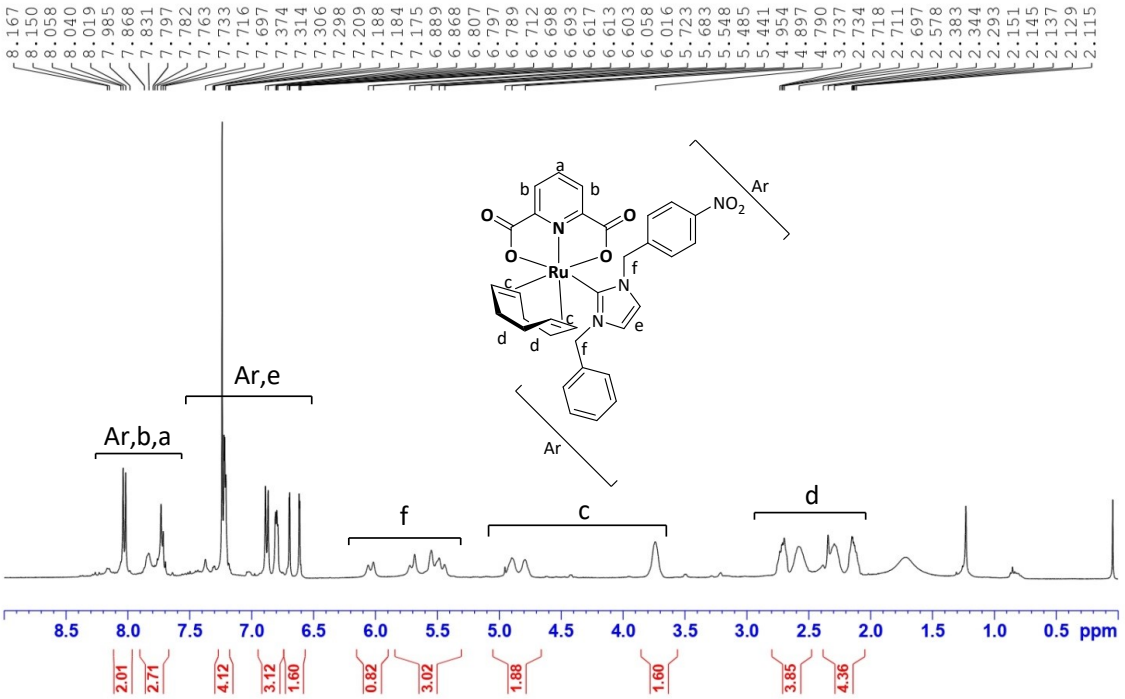


Figure S9 C7: ^{1}H NMR spectrum

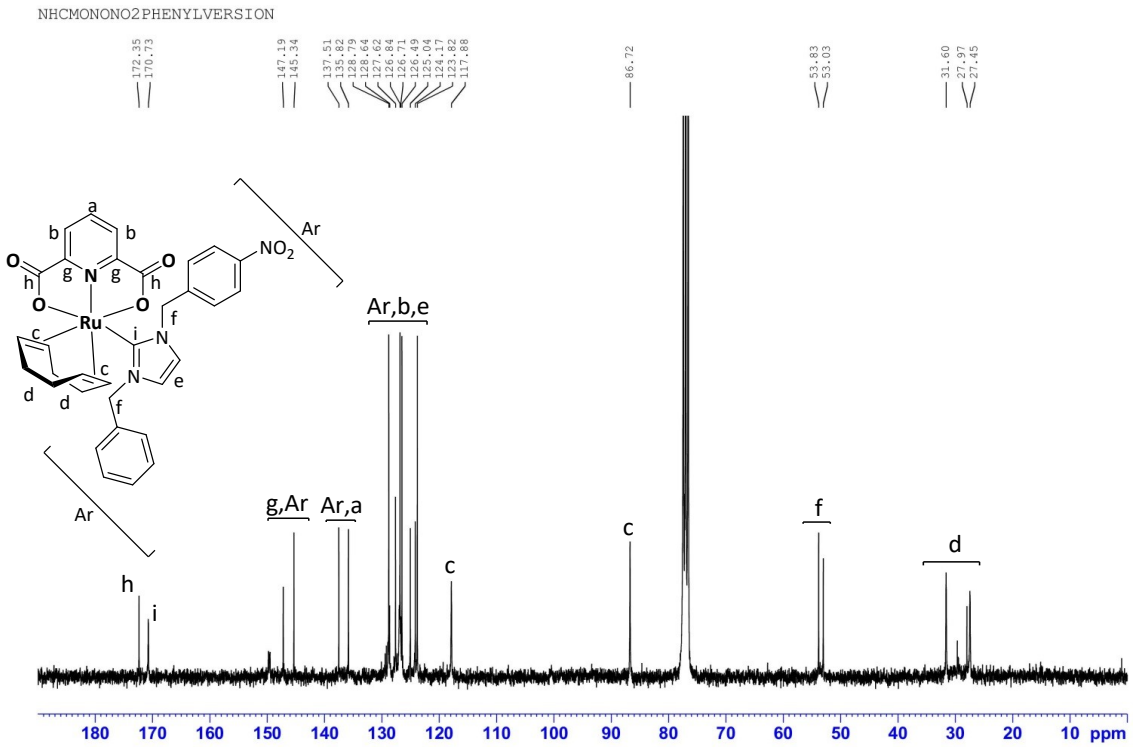


Figure S10 C7: ^{13}C NMR spectrum

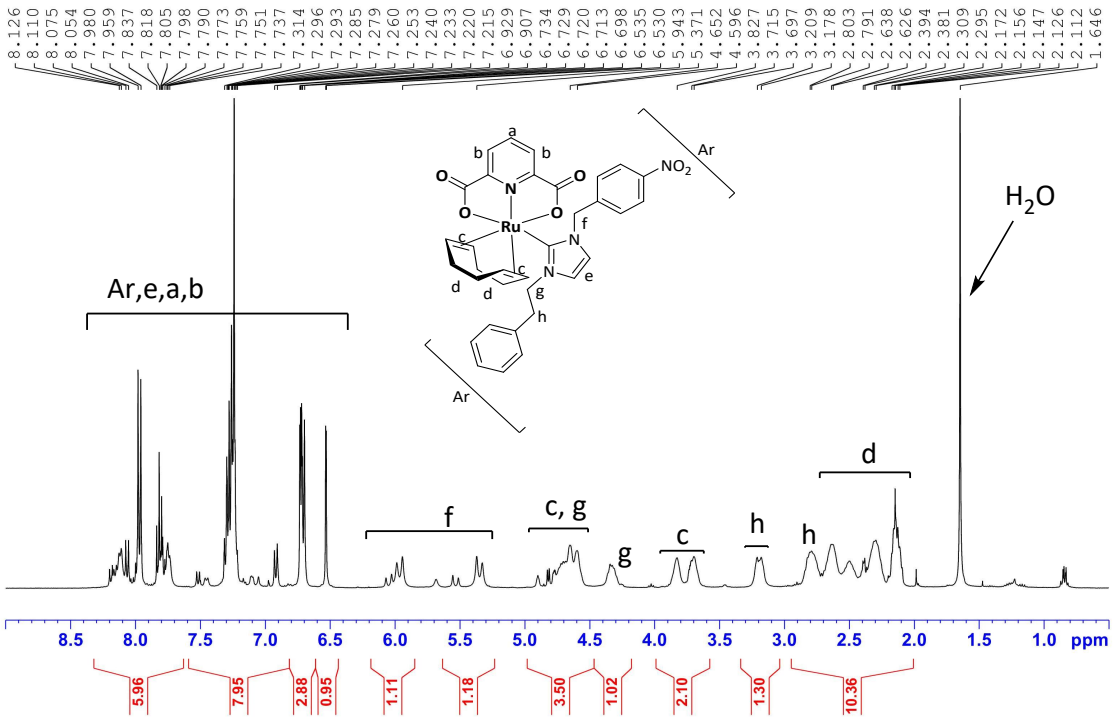


Figure S11 C8: ^{1}H NMR spectrum

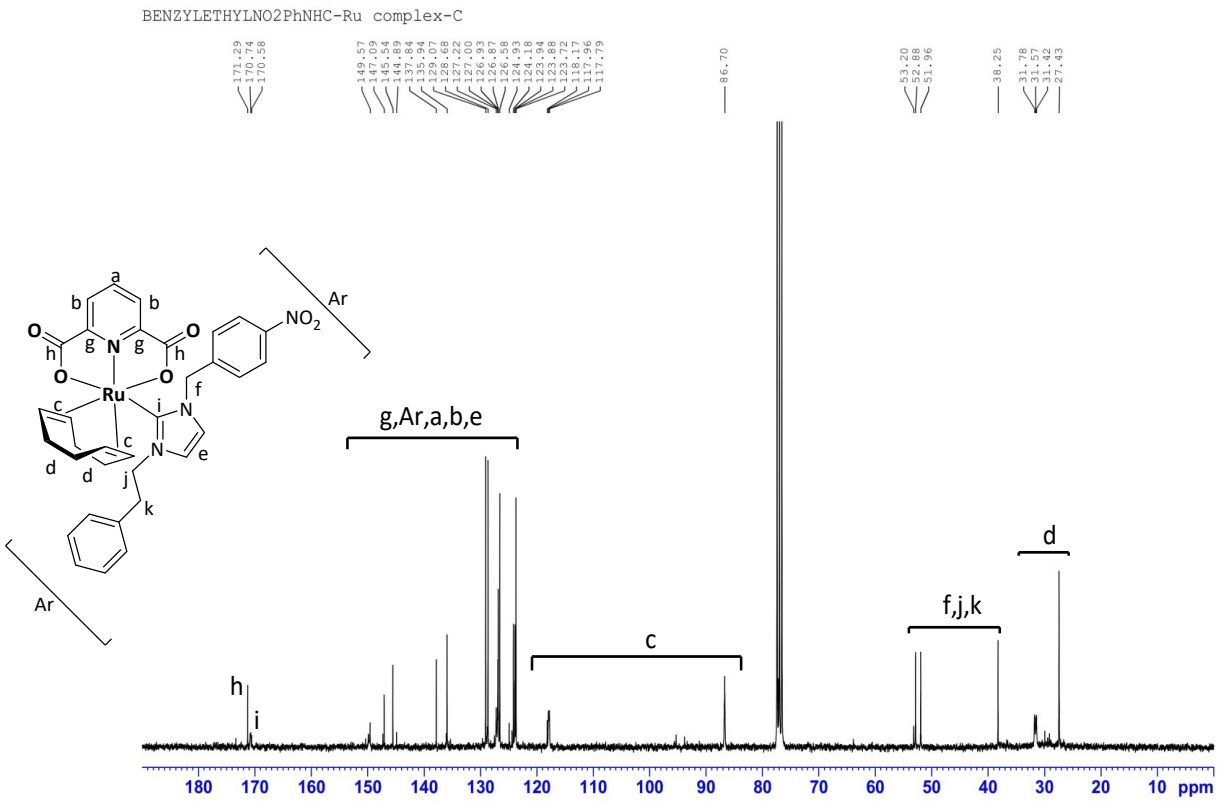


Figure S12 C8: ^{13}C NMR spectrum

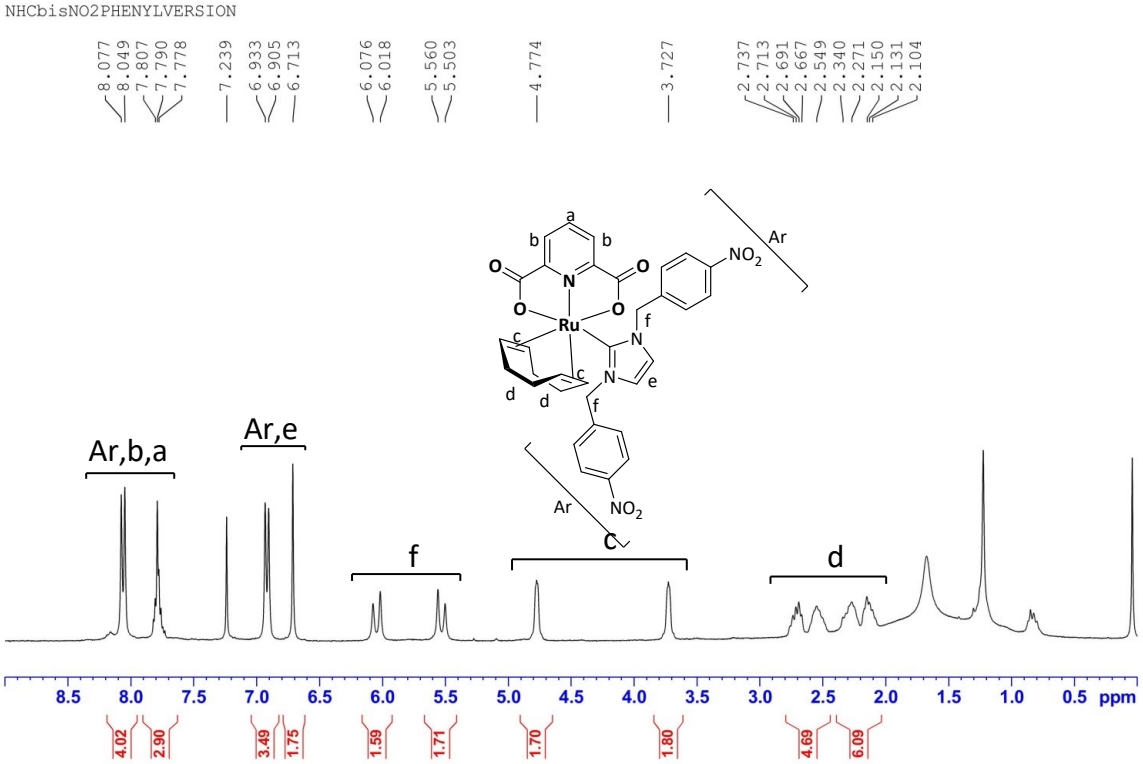


Figure S13 C9: ^{1}H NMR spectrum

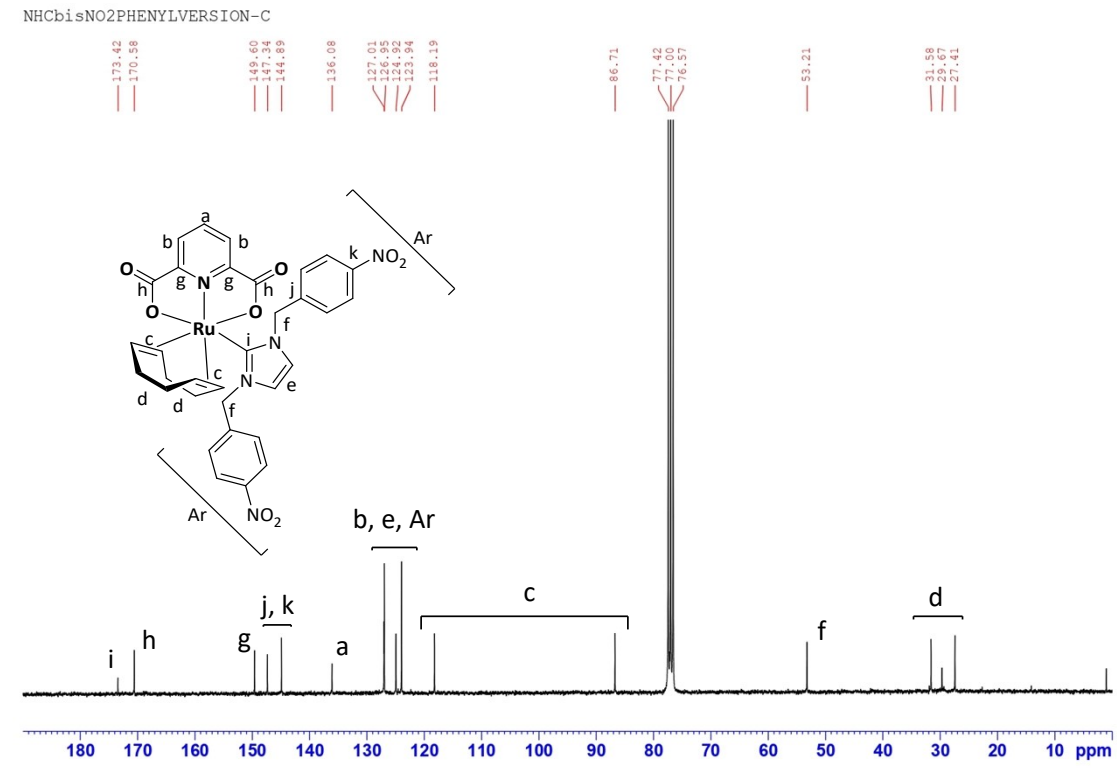


Figure S14 C9: ^{13}C NMR spectrum

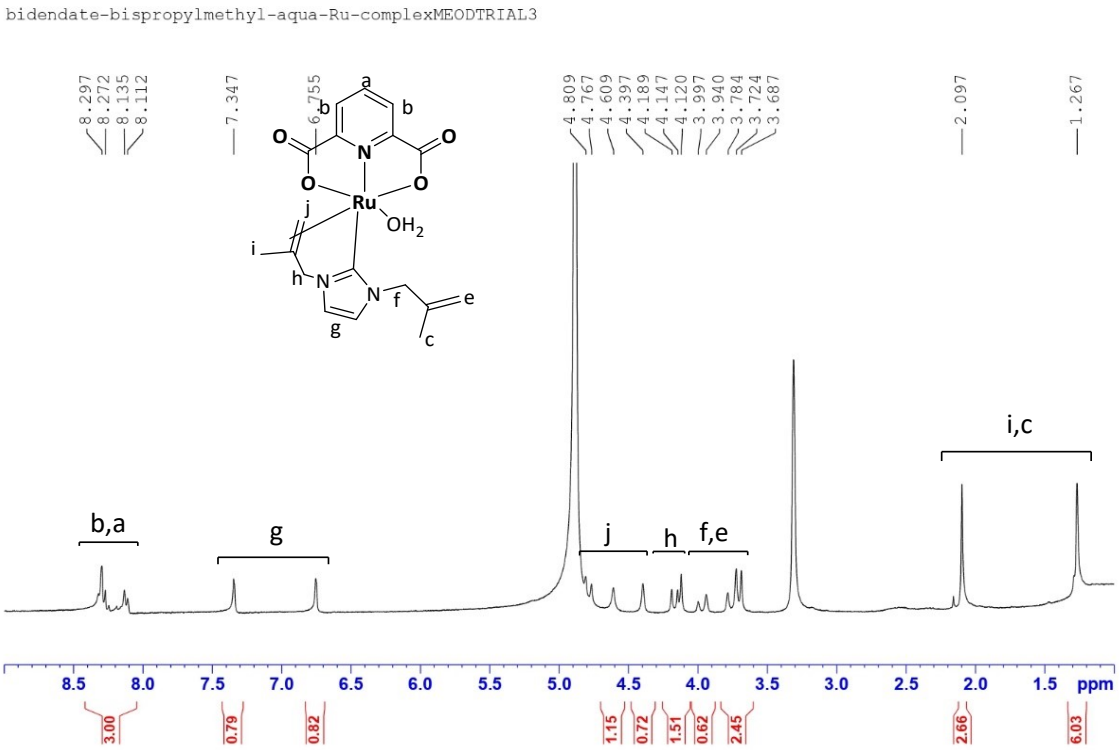


Figure S15 C10: ^{1}H NMR spectrum

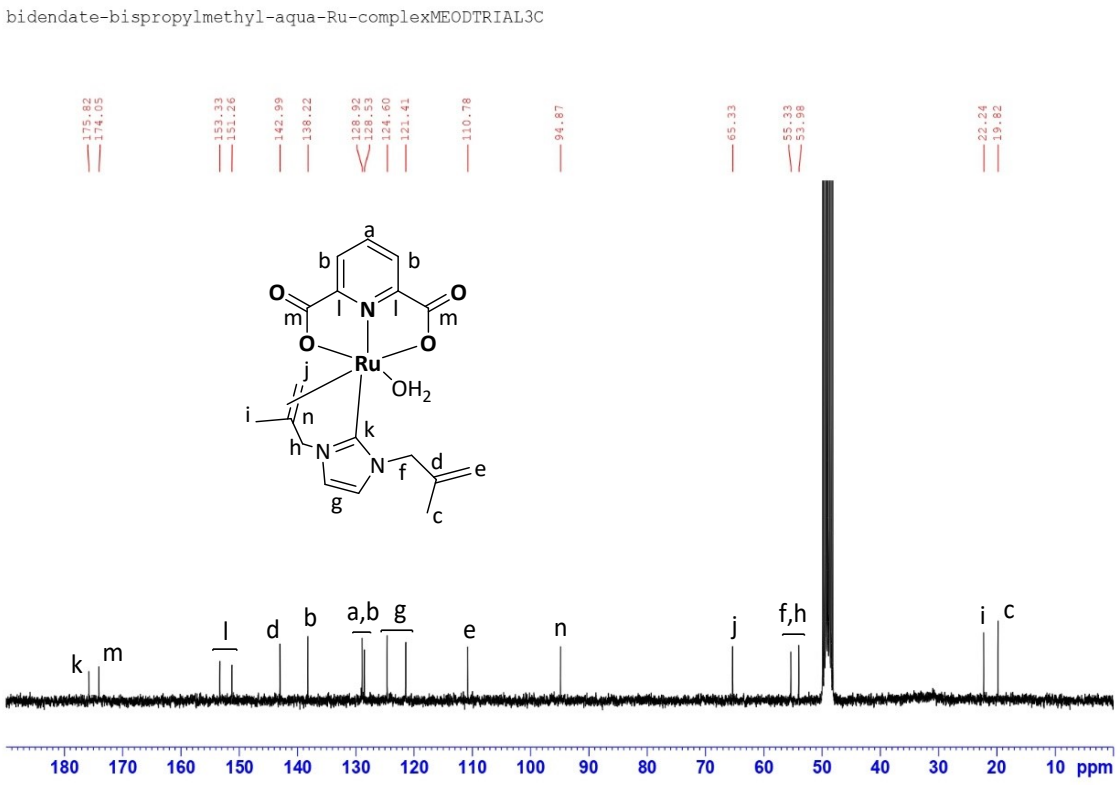


Figure S16 C10: ^{13}C NMR spectrum

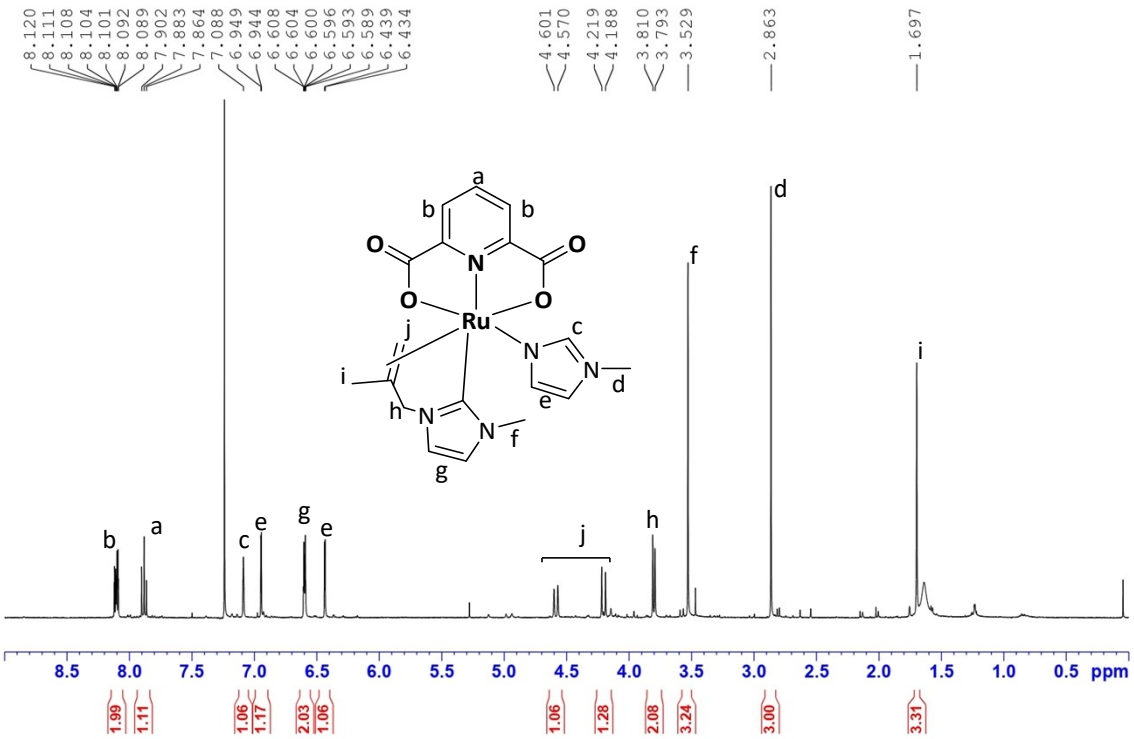


Figure S17 C11: ^{1}H NMR spectrum

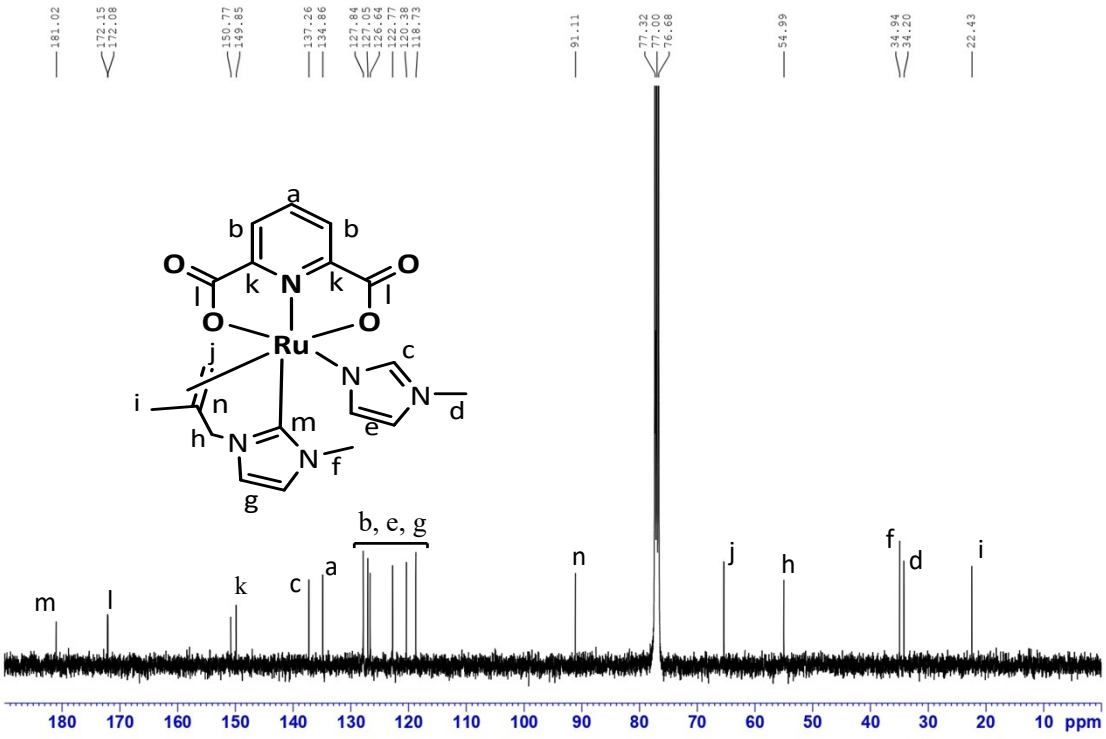


Figure S18 C11: ^{13}C NMR spectrum

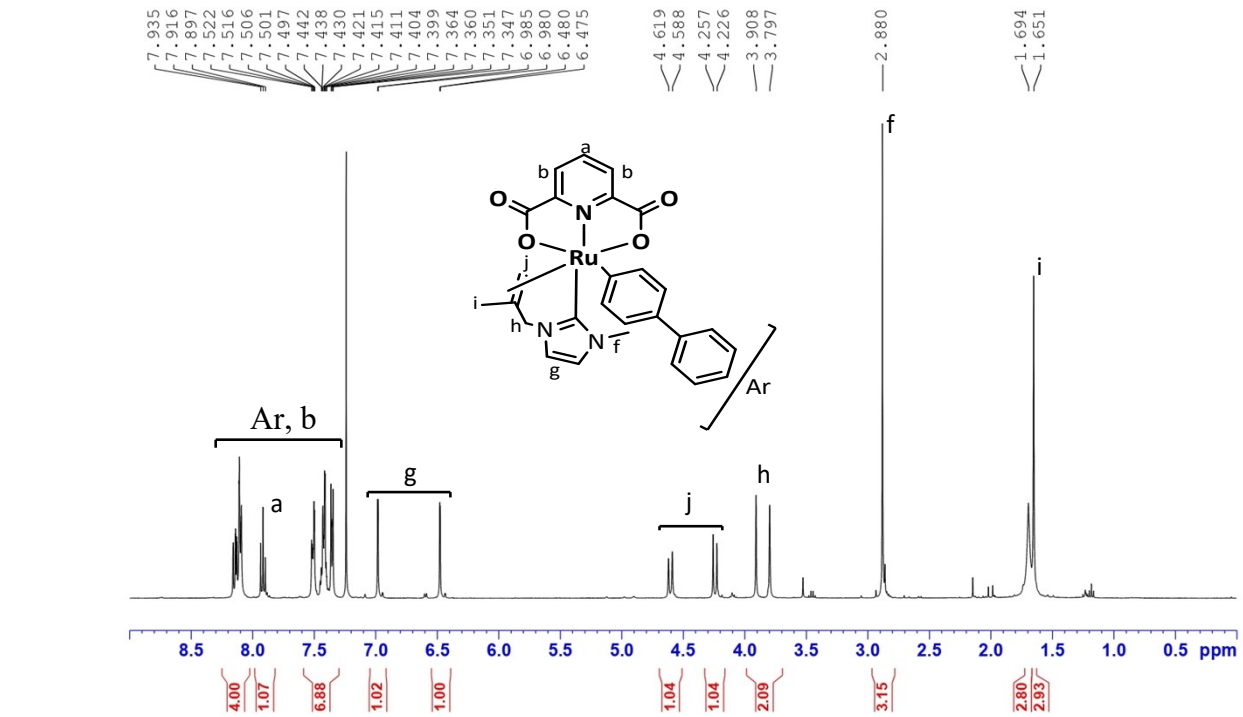


Figure S19 C12: ^{1}H NMR spectrum

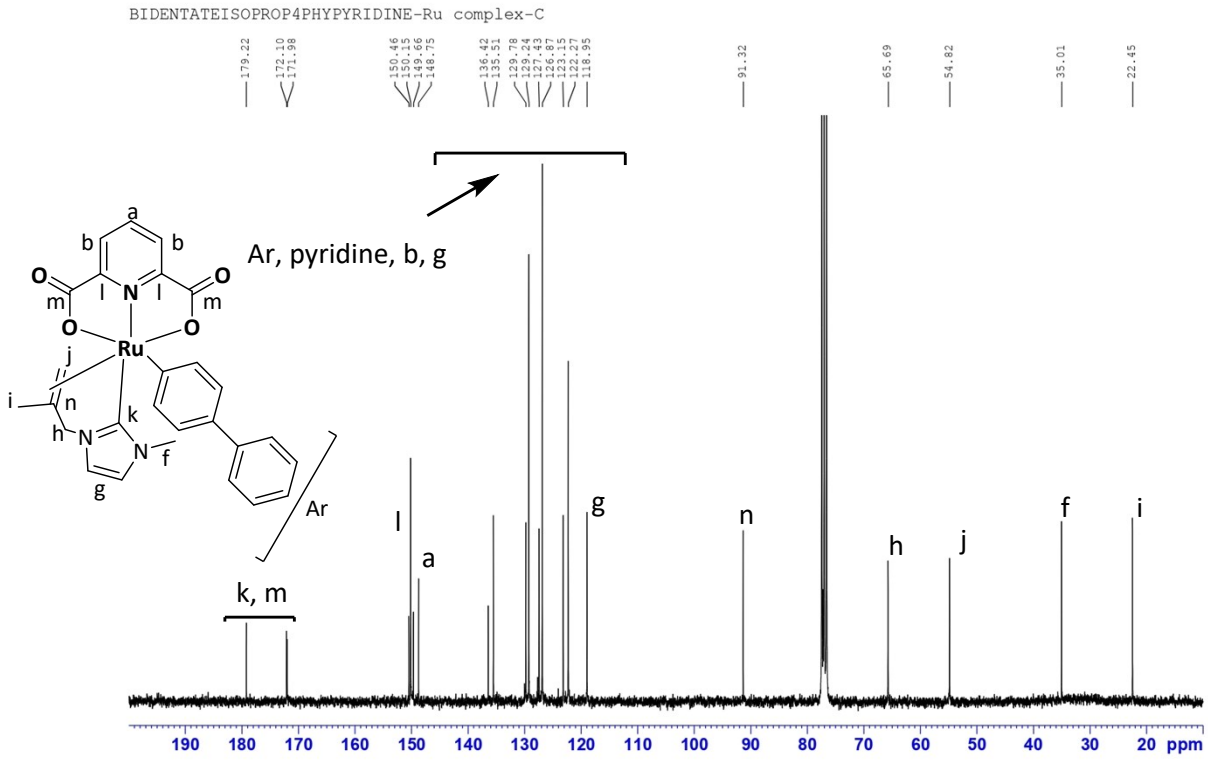


Figure S20 C12: ^{13}C NMR spectrum

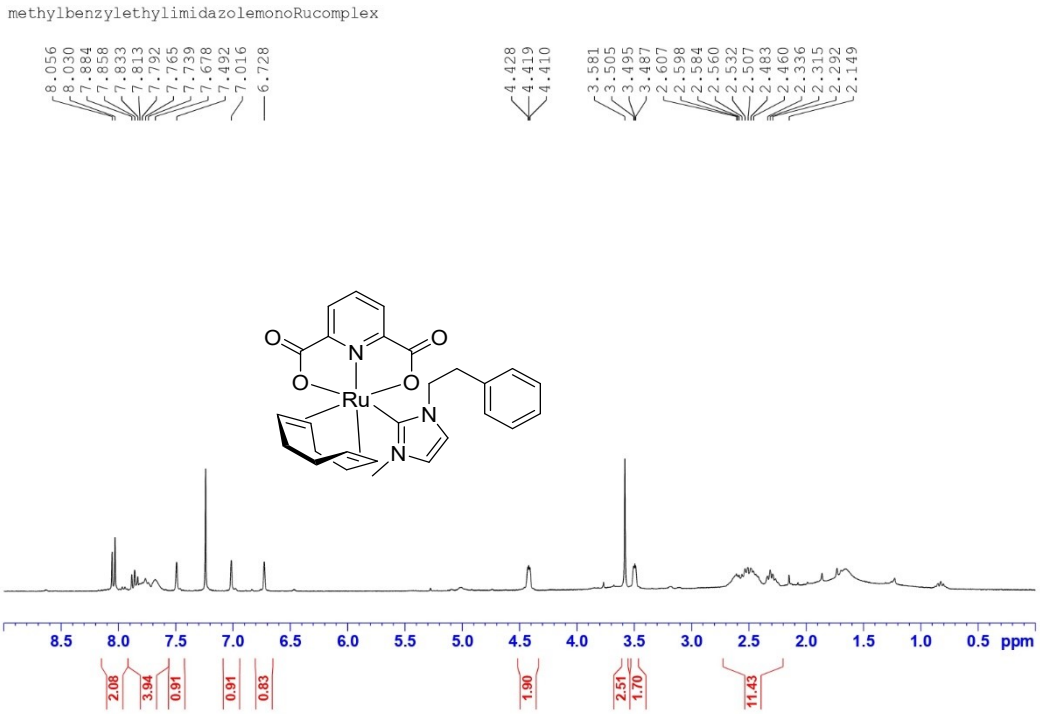


Figure S21 C5: ^{1}H NMR spectrum

3. Crystallographic details of **C2**-**C6**, **C8**-**C12** (Tables S1-S3)

Table S1: Crystallographic parameters for NHC Complexes.

Description	C2	C3	C4	C5	C6
Empirical formula	$C_{20}H_{25}N_3O_5Ru$	$C_{46}H_{53}N_6O_8Ru_2$	$C_{26}H_{27}N_3O_4Ru$	$C_{27}H_{29}N_3O_4Ru$	$C_{26}H_{26}N_4O_6Ru$
Formula weight	488.50	1020.08	546.58	560.60	591.58
Temperature (K)	149.99(10)	149.99(10)	149.99(10)	150.00(10)	150.00(10)
Crystal system	orthorhombic	monoclinic	orthorhombic	monoclinic	orthorhombic
Space group	$P2_12_12_1$	$C2/m$	$Pca2_1$	$P2_1/c$	$Pca2_1$
a (Å)	7.82300(10)	13.30480(10)	17.24420(10)	17.23840(10)	12.99141(15)
b (Å)	15.2957(2)	13.5619(2)	12.15900(10)	14.09470(10)	14.05629(16)
c (Å)	16.3651(2)	12.14960(10)	22.0006(2)	9.53400(10)	12.95619(16)
α (°)	90	90	90	90	90
β (°)	90	96.6700(10)	90	93.4940(10)	90
γ (°)	90	90	90	90	90
Volume (Å^3)	1958.22(4)	2177.42(4)	4612.92(6)	2312.17(3)	2365.94(5)
Z	4	2	8	4	4
ρ_{calc}g (cm^3)	1.657	1.556	1.574	1.610	1.661
μ (mm^{-1})	6.813	6.121	5.825	5.827	5.811
F(000)	1000.0	1046.0	2240.0	1152.0	1220.0
Radiation (λ, Å)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
Reflections collected	23077	23298	50019	49229	31519
Independent reflections	3988	2421	9577	4891	4799
R_{int}	0.0413	0.0381	0.0419	0.0312	0.0483
Data/restraints/parameters	3988/0/268	2421/30/192	9577/1/616	4891/0/318	4799/1/335
Goodness-of-fit on F^2	1.113	1.139	1.124	1.099	1.156
Final R indexes [all data]	R_1 = 0.0253, wR_2 = 0.0628	R_1 = 0.0367, wR_2 = 0.0799	R_1 = 0.0324, wR_2 = 0.0794	R_1 = 0.0276, wR_2 = 0.0719	R_1 = 0.0415, wR_2 = 0.1186
Largest diff. peak/hole (e Å^{-3})	0.43/-0.92	0.84/-1.15	0.55/-0.59	0.56/-0.82	0.55/-1.00

Description	C8	C9	C10	C11	C12
Empirical formula	$C_{35}H_{34}N_4O_6Cl_6Ru$	$C_{136}H_{136.2}Cl_{17.37}N_{20}O_{35.2}Ru_4$	$C_{18}H_{21}N_3O_5Ru$	$C_{19}H_{25}N_5O_6Ru$	$C_{26}H_{24}N_4O_4Ru$
Formula weight	920.43	3634.17	460.45	520.51	557.56
Temperature (K)	149.99(10)	149.98(10)	150.00(2)	149.99(10)	149.99(10)
Crystal system	triclinic	monoclinic	triclinic	triclinic	orthorhombic
Space group	*P*-1	$P2_1/n$	*P*-1	*P*-1	$P2_12_12_1$
a (Å)	9.9781(2)	9.9817(5)	9.7789(8)	8.2408(2)	12.9825(3)
b (Å)	12.8763(2)	14.0691(8)	10.0997(9)	10.3384(3)	13.1403(2)
c (Å)	15.9233(3)	26.5049(15)	10.8427(9)	14.7449(4)	13.4427(3)
α (°)	81.329(2)	90	74.531(3)	109.197(2)	90
β (°)	75.973(2)	93.040(4)	64.202(3)	91.635(2)	90
γ (°)	72.202(2)	90	79.030(3)	112.158(2)	90
Volume (Å^3)	1883.32(7)	3716.9(4)	925.81(14)	1081.90(5)	2293.24(8)
Z	2	1	2	2	4
ρcalcg (cm^3)	1.623	1.624	1.652	1.598	1.615
μ (mm^{-1})	0.893	6.803	0.882	0.770	0.726
F(000)	932.0	1845.0	468.0	532.0	1136.0
Radiation (λ, Å)	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
Reflections collected	45900	21596	41333	23445	38524
Independent reflections	9100	7101	3832	5671	6431
R_{int}	0.0334	0.0772	0.1304	0.0381	0.0499
Data/restraints/parameters	9100/438/637	7101/3/512	3832/0/259	5671/0/305	6431/0/318
Goodness-of-fit on F^2	1.047	1.066	1.061	1.061	1.024
Final R indexes [all data]	R_1 = 0.0287, wR_2 = 0.0758	R_1 = 0.1017, wR_2 = 0.2764	R_1 = 0.0437, wR_2 = 0.1030	R_1 = 0.0322, wR_2 = 0.0804	R1 = 0.0299, wR2 = 0.0713
Largest diff. peak/hole (e Å^{-3})	0.61/-0.56	1.76/-1.54	0.77/-0.81	1.10/-0.96	1.08/-0.52

Table S2: Bond lengths (SC-XRD) for **2**-**6**, **8**-**12**.

C2		**C3**		**C4**		**C5**		**C6**	
Atoms	**Length (Å)**	**Atoms**	**Length (Å)**	**Atoms**	**Length (Å)**	**Atoms**	**Length (Å)**	**Atoms**	**Length (Å)**
Ru1-O1	2.124(3)	Ru1-O1	2.123(2)	Ru1-O1	2.113(4)	Ru1-O1	2.0991(15)	Ru1-O1	2.113(4)
Ru1-O3	2.127(3)	Ru1-O1'	2.123(2)	Ru1-O3	2.123(4)	Ru1-O3	2.1394(15)	Ru1-O3	2.128(3)
Ru1-N1	2.021(3)	Ru1-N1	2.022(4)	Ru1-N1	2.013(5)	Ru1-N1	2.0124(18)	Ru1-N1	2.019(5)
Ru1-C8	2.116(4)	Ru1-C5	2.104(5)	Ru1-C8	2.126(6)	Ru1-C8	2.124(2)	Ru1-C8	2.110(6)
Ru1-C13	2.190(4)	Ru1-C11	2.187(3)	Ru1-C19	2.332(6)	Ru1-C20	2.175(2)	Ru1-C19	2.181(5)
Ru1-C14	2.206(4)	Ru1-C11'	2.187(3)	Ru1-C20	2.312(6)	Ru1-C21	2.194(2)	Ru1-C20	2.179(5)
Ru1-C17	2.320(4)	Ru1-C14	2.313(3)	Ru1-C23	2.194(6)	Ru1-C24	2.337(2)	Ru1-C23	2.308(6)
Ru1-C18	2.343(5)	Ru1-C14'	2.313(3)	Ru1-C24	2.177(7)	Ru1-C25	2.324(2)	Ru1-C24	2.321(6)
C8		**C9**		**C10**		**C11**		**C12**	
Atoms	**Length (Å)**	**Atoms**	**Length (Å)**	**Atoms**	**Length (Å)**	**Atoms**	**Length (Å)**	**Atoms**	**Length (Å)**
Ru1-O1	2.1332(12)	Ru1-O1	2.141(7)	Ru1-O1	2.102(3)	Ru1-O1	2.1075(15)	Ru1-O1	2.121(2)
Ru1-O3	2.1325(12)	Ru1-O3	2.081(7)	Ru1-O3	2.131(3)	Ru1-O3	2.1324(16)	Ru1-O3	2.116(2)
Ru1-N1	2.0173(15)	Ru1-N1	2.003(9)	Ru1-O5	2.199(3)	Ru1-N4	2.1630(17)	Ru1-N4	2.169(3)
Ru1-C8	2.1185(16)	Ru1-C8	2.161(10)	Ru1-N1	2.008(3)	Ru1-N1	1.9977(18)	Ru1-N1	2.007(3)
Ru1-C26	2.1849(18)	Ru1-C25	2.175(10)	Ru1-C8	1.974(4)	Ru1-C8	2.012(2)	Ru1-C8	2.022(3)
Ru1-C27	2.2095(17)	Ru1-C26	2.161(10)	Ru1-C13	2.153(4)	Ru1-C13	2.182(2)	Ru1-C13	2.201(4)
Ru1-C30	2.3075(17)	Ru1-C29	2.341(9)	Ru1-C12	2.193(4)	Ru1-C14	2.157(2)	Ru1-C14	2.163(3)
Ru1-C31	2.3182(17)	Ru1-C30	2.308(9)	C12-C13	1.398(6)	C13-C14	1.392(4)	C12-C13	1.405(5)

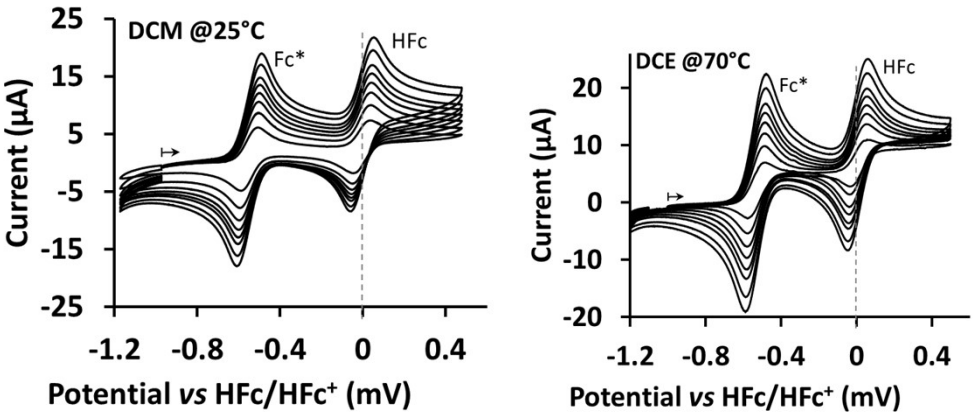
Table S3: Bond angles (SC-XRD) for **2**-**6**, **8**-**12**.

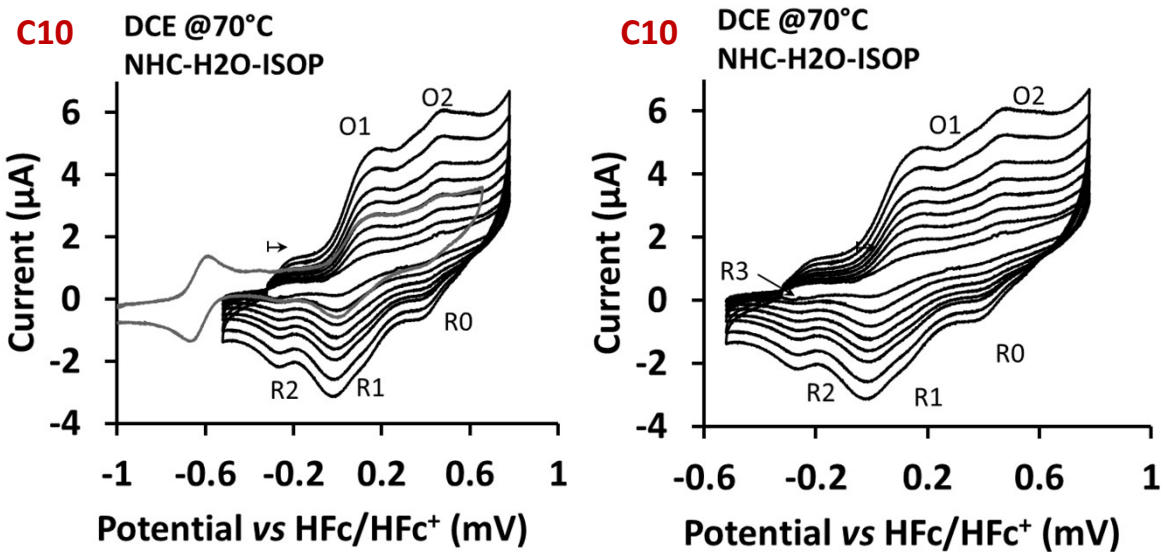
C2		C3		C4		C5		C6	
Atoms	**Angle (˚)**	**Atoms**	**Angle (˚)**	**Atoms**	**Angle (˚)**	**Atoms**	**Angle (˚)**	**Atoms**	**Angle (˚)**
O3-Ru1-C13	122.95(15)	**O1-Ru1-C11**	121.78(11)	**O3-Ru1-C23**	119.3(2)	**O3-Ru1-C21**	89.23(7)	**O3-Ru1-C19**	121.31(19)
N1-Ru1-C18	95.37(15)	**N1-Ru1-C11**	161.27(9)	**N1-Ru1-C19**	93.1(2)	**N1-Ru1-C24**	95.57(8)	**N1-Ru1-C19**	161.8(2)
O3-Ru1-C8	88.26(14)	**O1-Ru1-C5**	89.94(7)	**O3-Ru1-C8**	94.4(2)	**O3-Ru1-C8**	87.02(7)	**O3-Ru1-C8**	91.6(2)
O3-Ru1-C17	75.56(14)	**O1-Ru1-C14**	107.70(11)	**O3-Ru1-C19**	75.4(2)	**O3-Ru1-C24**	76.78(7)	**O3-Ru1-C20**	84.32(19)
N1-Ru1-C8	95.88(15)	**N1-Ru1-C5**	92.33(15)	**N1-Ru1-C8**	96.3(2)	**N1-Ru1-C8**	92.36(8)	**N1-Ru1-C8**	94.9(2)
O1-Ru1-C8	92.67(14)	**O1-Ru1-C8**	89.94(7)	**O1-Ru1-C8**	85.8(2)	**O1-Ru1-C8**	90.46(7)	**O1-Ru1-C8**	90.1(2)
C17-Ru1-C18	34.01(16)	**C11-Ru1-C11'**	37.15(18)	**C19-Ru1-C20**	33.9(3)	**C24-Ru1-C25**	34.10(8)	**C19-Ru1-C20**	37.3(2)
C8-Ru1-C14	88.57(16)	**O1-Ru1-C11'**	84.62(11)	**C8-Ru1-C24**	87.8(2)	**C8-Ru1-C21**	89.37(8)	**C8-Ru1-C24**	159.1(2)
O3-Ru1-C14	86.31(18)	**O1-Ru1-C11**	121.78(11)	**O3-Ru1-C24**	82.5(2)	**O3-Ru1-C25**	107.26(7)	**O3-Ru1-C24**	108.5(2)
N1-Ru1-O3	76.81(13)	**N1-Ru1-O1**	76.81(6)	**N1-Ru1-O3**	76.61(18)	**N1-Ru1-O3**	76.13(7)	**N1-Ru1-O3**	76.92(18)
N1-Ru1-O1	76.21(13)	**N1-Ru1-O1'**	76.82(6)	**N1-Ru1-O1**	77.0(2)	**N1-Ru1-O1**	77.86(7)	**N1-Ru1-O1**	76.80(18)
O1-Ru1-O3	152.96(12)	**O1-Ru1-O1'**	153.60(12)	**O1-Ru1-O3**	153.44(18)	**O1-Ru1-O3**	153.73(6)	**O1-Ru1-O3**	153.72(14)
C8		**C9**		**C10**		**C11**		**C12**	
O3-Ru1-C27	88.17(6)	**O3-Ru1-C26**	85.3(4)	**O3-Ru1-C12**	122.76(13)	**O3-Ru1-C13**	122.37(8)	**O3-Ru1-C14**	122.05(12)
N1-Ru1-C30	90.60(6)	**N1-Ru1-C25**	161.5(4)	**N1-Ru1-C12**	159.89(14)	**N1-Ru1-C13**	160.16(9)	**N1-Ru1-C13**	161.52(11)
O3-Ru1-C8	87.09(6)	**O3-Ru1-C8**	92.7(4)	**O3-Ru1-C8**	95.45(14)	**O3-Ru1-C8**	96.57(7)	**O3-Ru1-C8**	87.23(11)
O1-Ru1-C31	74.59(6)	**O3-Ru1-C25**	121.3(4)	**O3-Ru1-O5**	87.15(12)	**O3-Ru1-N4**	88.69(6)	**O3-Ru1-N4**	91.20(10)
N1-Ru1-C8	96.74(6)	**N1-Ru1-C8**	94.3(4)	**N1-Ru1-C8**	99.18(15)	**N1-Ru1-C8**	94.73(8)	**N1-Ru1-C8**	96.59(12)
O1-Ru1-C8	93.64(6)	**O1-Ru1-C26**	121.4(4)	**N1-Ru1-O5**	87.13(13)	**N1-Ru1-N4**	88.90(7)	**N1-Ru1-N4**	90.10(10)
C26-Ru1-C27	36.98(7)	**C26-Ru1-C25**	36.3(4)	**C12-Ru1-C13**	37.51(16)	**C13-Ru1-C14**	37.42(10)	**C13-Ru1-C14**	37.55(14)
C8-Ru1-C27	89.19(6)	**C8-Ru1-C26**	88.5(4)	**C8-Ru1-C12**	79.90(16)	**C8-Ru1-C13**	80.52(8)	**C8-Ru1-C13**	79.16(14)
O3-Ru1-C26	124.76(6)	**O3-Ru1-C29**	74.9(4)	**O3-Ru1-C13**	85.35(13)	**O3-Ru1-C14**	85.14(8)	**O3-Ru1-C13**	84.64(11)
N1-Ru1-O3	76.70(5)	**N1-Ru1-O3**	76.5(3)	**N1-Ru1-O3**	77.36(12)	**N1-Ru1-O3**	77.17(7)	**N1-Ru1-O3**	77.16(9)
N1-Ru1-O1	76.37(5)	**N1-Ru1-O1**	77.0(3)	**N1-Ru1-O1**	77.26(12)	**N1-Ru1-O1**	77.50(7)	**N1-Ru1-O1**	77.29(10)
O1-Ru1-O3	152.96(5)	**O3-Ru1-O1**	153.4(3)	**O3-Ru1-O1**	154.49(11)	**O3-Ru1-O1**	154.62(6)	**O3-Ru1-O1**	154.44(9)

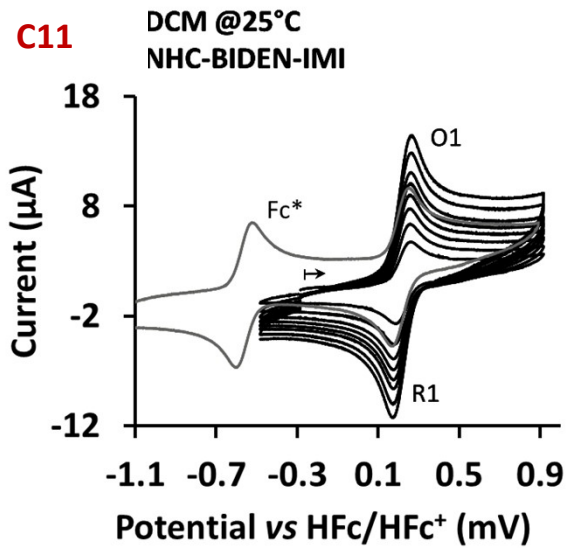
4. Electrochemical details (Figure S22)

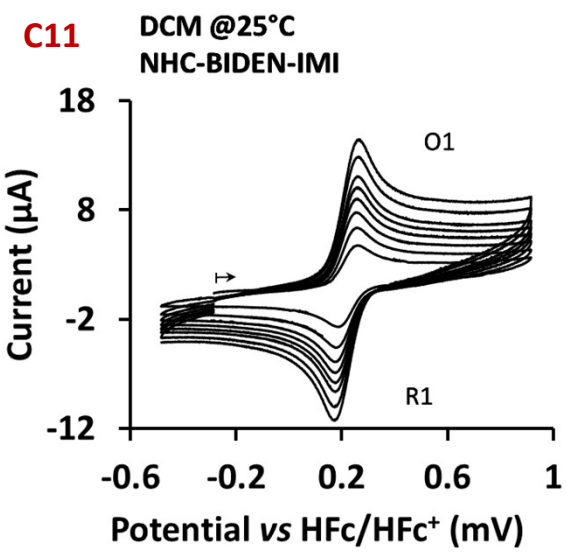
DCM @ 25°C (150 mV/s) Fc* vs HFc = -0.553 V

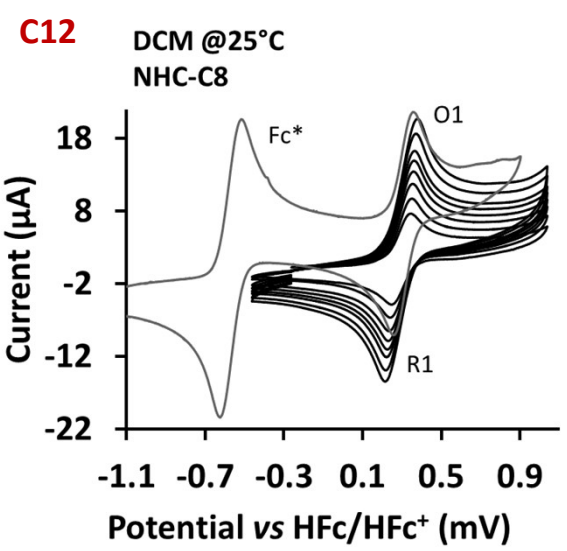
DCE @ 70°C (150 mV/s) Fc* vs HFc = -0.544 V

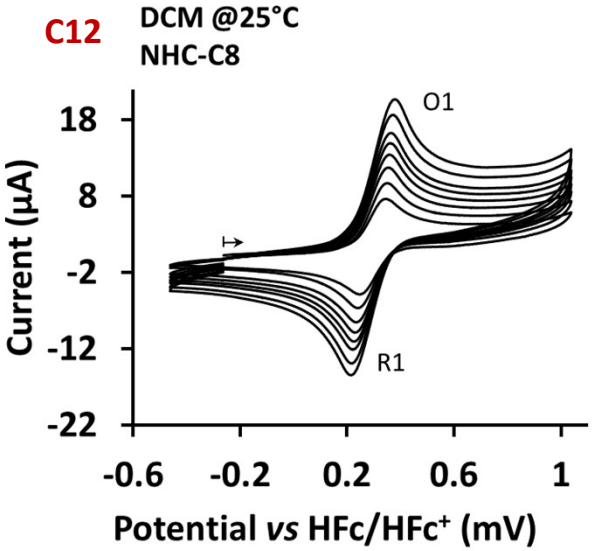


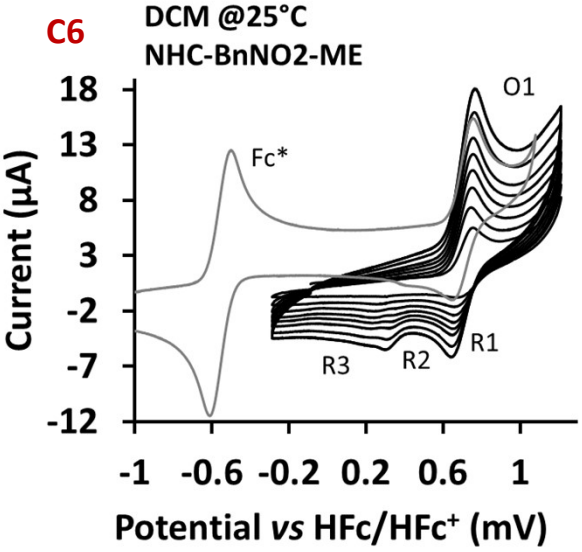


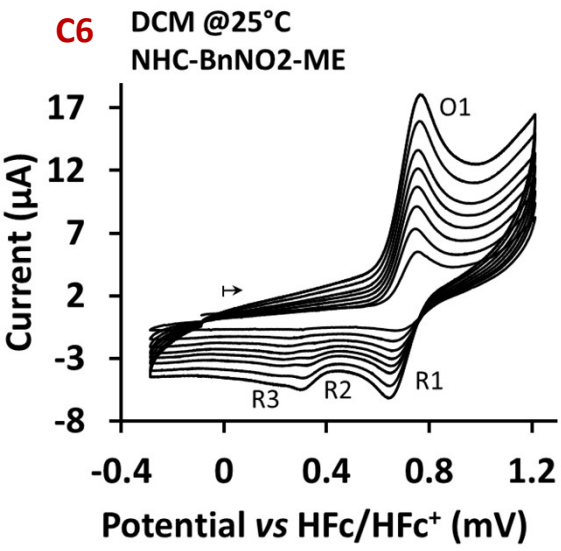

C11
DCM @25°C
NHC-BIDEN-IMI
Current (µA)
18
8
-2
-12
Fc*
O1
R1
-1.1 -0.7 -0.3 0.1 0.5 0.9
Potential vs HFc/HFc+ (mV)

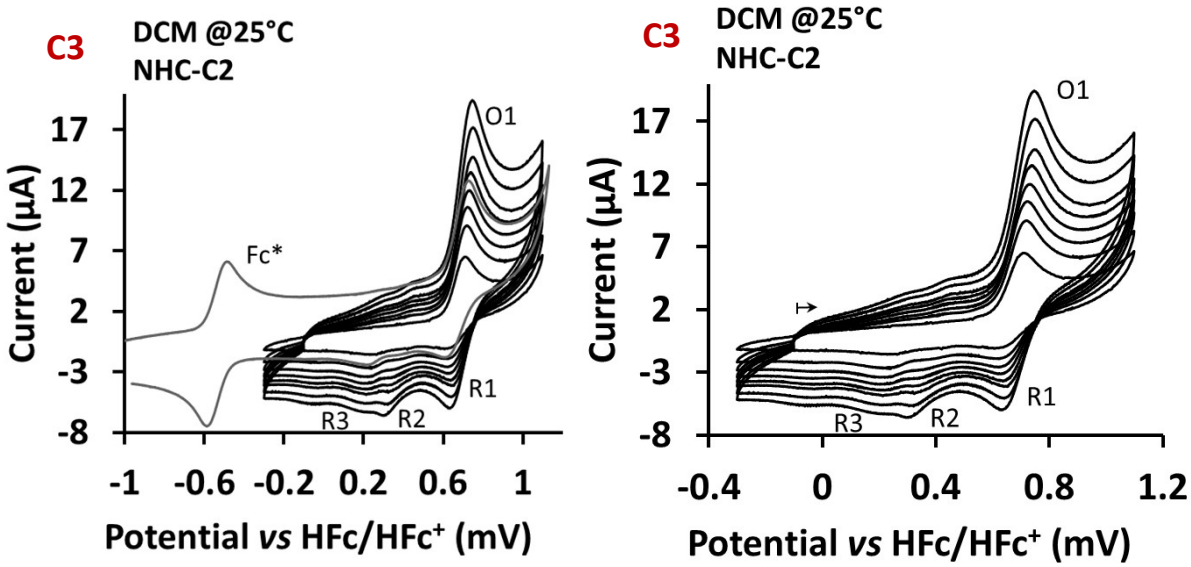

C11
DCM @25°C
NHC-BIDEN-IMI
Current (µA)
18
8
-2
-12
O1
R1
-0.6 -0.2 0.2 0.6 1
Potential vs HFc/HFc+ (mV)


C12
DCM @25°C
NHC-C8
Current (µA)
18
8
-2
-12
-22
Fc*
O1
R1
-1.1 -0.7 -0.3 0.1 0.5 0.9
Potential vs HFc/HFc+ (mV)

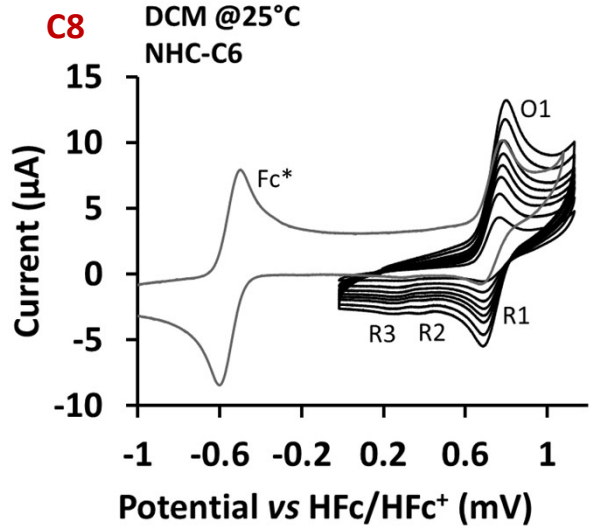

C12
DCM @25°C
NHC-C8
Current (µA)
18
8
-2
-12
-22
O1
R1
-0.6 -0.2 0.2 0.6 1
Potential vs HFc/HFc+ (mV)

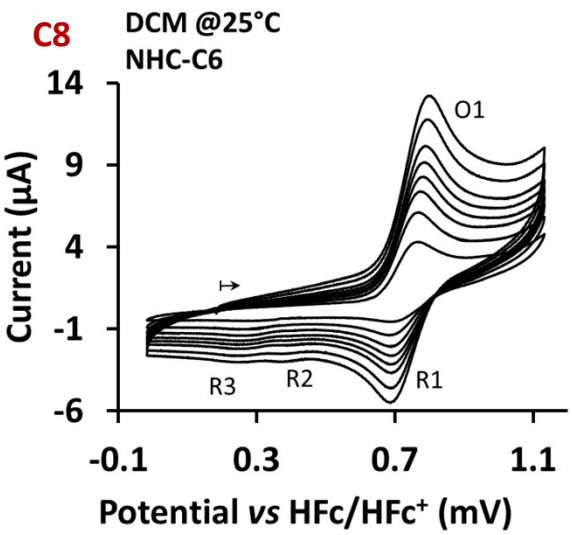

C6
DCM @25°C
NHC-BnNO2-ME
Current (µA)
18
13
8
3
-2
-7
-12
Fc*
O1
R1
R2
R3
-1 -0.6 -0.2 0.2 0.6 1
Potential vs HFc/HFc+ (mV)

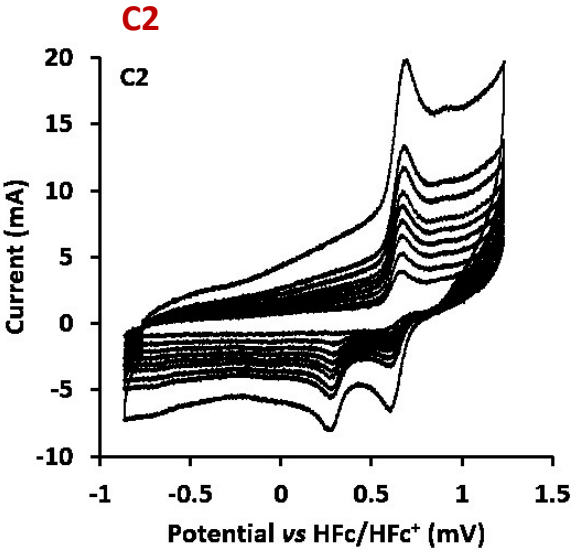

C6
DCM @25°C
NHC-BnNO2-ME
Current (µA)
17
12
7
2
-3
-8
O1
R1
R2
R3
-0.4 0 0.4 0.8 1.2
Potential vs HFc/HFc+ (mV)

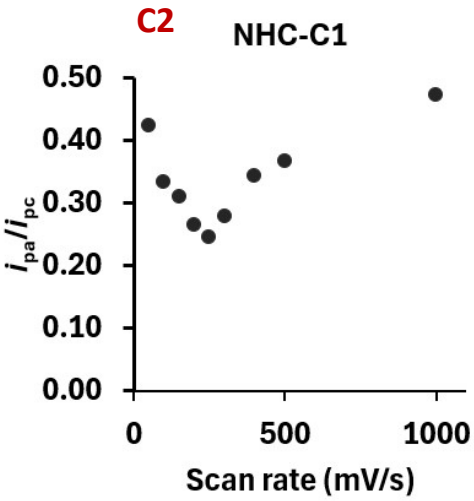

C3
DCM @25°C
NHC-C2
Current (µA)
17
12
7
2
-3
-8
Fc*
O1
R1
R2
R3
-1
-0.6
-0.2
0.2
0.6
1
Potential vs HFc/HFc+ (mV)

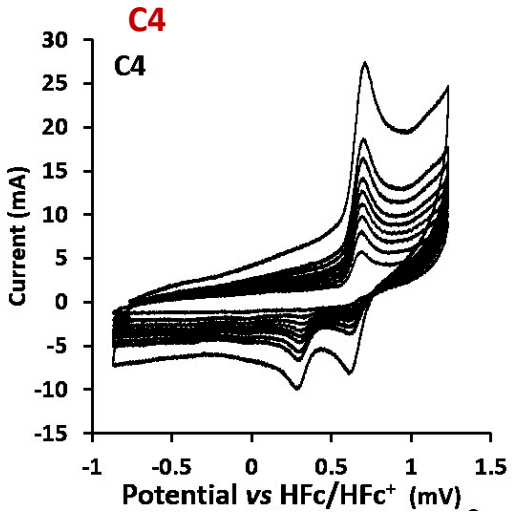
C3
DCM @25°C
NHC-C2
Current (µA)
17
12
7
2
-3
-8
O1
R1
R2
R3
-0.4
0
0.4
0.8
1.2
Potential vs HFc/HFc+ (mV)

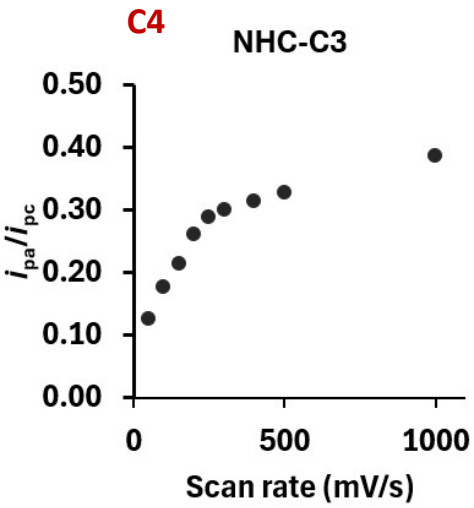

C8
DCM @25°C
NHC-C6
Current (µA)
15
10
5
0
-5
-10
Fc*
O1
R1
R2
R3
-1
-0.6
-0.2
0.2
0.6
1
Potential vs HFc/HFc+ (mV)

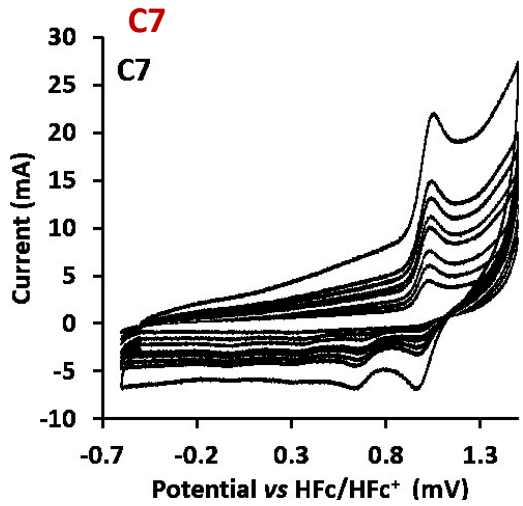

C8
DCM @25°C
NHC-C6
Current (µA)
14
9
4
-1
-6
O1
R1
R2
R3
-0.1
0.3
0.7
1.1
Potential vs HFc/HFc+ (mV)

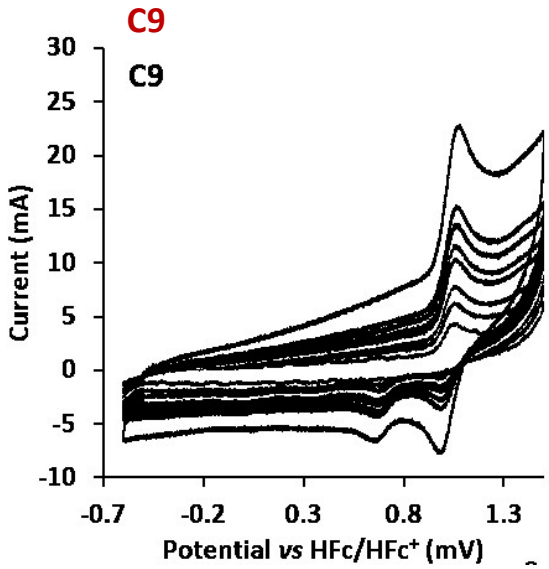

C2
C2
Current (mA)
20
15
10
5
0
-5
-10
-1
-0.5
0
0.5
1
1.5
Potential vs HFc/HFc+ (mV)

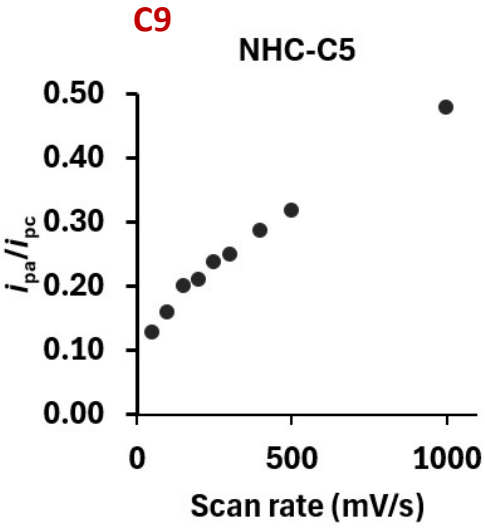

C2
NHC-C1
ipa/ipc
0.50
0.40
0.30
0.20
0.10
0.00
0
500
1000
Scan rate (mV/s)

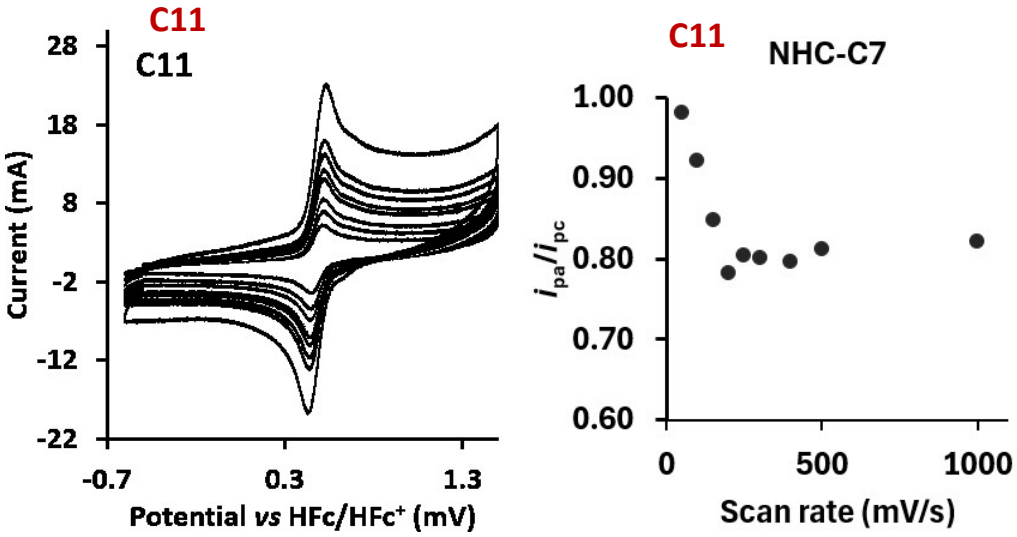

C4
C4
Current (mA)
Potential vs HFc/HFc+ (mV)


C4
NHC-C3
ipa/ipc
Scan rate (mV/s)


C7
C7
Current (mA)
Potential vs HFc/HFc+ (mV)


C9
C9
Current (mA)
Potential vs HFc/HFc+ (mV)


C9
NHC-C5
ipa/ipc
Scan rate (mV/s)



Additional discussion (Electrochemical analysis):

Complexes **C10**-**C12** exhibit a chemically reversible Ru^{II}/Ru^{III} redox process (O1/R1) across all scan rates (i_{pa}/i_{pc} = 1.0), occurring at increasingly positive potentials: 0.085 V (**C10**), 0.215 V (**C11**), and 0.288 V (**C12**). This trend contradicts expectations based on the electron-donating abilities of the ligands, which follow the order: aqua < imidazole-containing ligand < pyridine-containing ligand. Instead, the observed redox potential sequence (C10 < C11 < C12) suggests that factors beyond simple electron donation influence the redox behaviour of these carbene-containing Ru complexes. One key factor is the stabilisation of the Ru^{3+} state. The aqua ligand, through intermolecular hydrogen bonding and solvation effects (considering DCE was used instead of DCM), may lower the oxidation potential by stabilising the oxidised species. Additionally, proton-coupled electron transfer (PCET) in the aqua complex could further facilitate oxidation.[51] In contrast, pyridine, a stronger donor, can also act as a π-acceptor, potentially destabilise Ru^{3+} and increasing the oxidation potential. Moreover, subtle structural reorganisations upon oxidation may play a role. The aqua complex may undergo favourable structural adjustments that ease oxidation,[52] while the more rigid coordination of pyridine could resist such changes, making oxidation more challenging.[53,54] These combined effects could potentially explain why the aqua complex exhibits the lowest oxidation potential, despite being the weakest donor, while pyridine, its electronic and structural influences, results in the highest oxidation potential.

5. Catalysis details (Table S4)

Table S4: Alcohol Oxidation Optimization Process

Complex	Benzyl alcohol (mmol)	Oxidant (mmol)	KOH	Solvent (mL)	Cat. (mol%)	Time (hr)	Conversion (%)	TOF (h^{-1})
C0	1	^{t}BuOOH: 2	-	Acet:2	2	0.5	94	94
C0	1	^{t}BuOOH: 2	-	Acet:2	2	1	89	45
C0	1	^{t}BuOOH: 2	-	Acet:2	2	2	79	20
C0	1	^{t}BuOOH: 2	-	Acet:2	3	1	71	24
C0	1	^{t}BuOOH: 2	-	Acet:2	3	2	90	15
C0	1	H_2O_2: 2	-	Acet:2	3	2	19	3
C0	1	^{t}BuOOH: 2	-	-	3	2	78	13
C0	1	^{t}BuOOH: 2	-	Acet:2	1	0.5	57	114
C0	1	^{t}BuOOH: 2	-	Acet:2	1	1	55	55
C0	1	^{t}BuOOH: 2	-	Acet:2	1	2	66	33
C0	1	^{t}BuOOH: 1.5	-	Acet:2	3	0.5	29	19
C0	1	^{t}BuOOH: 1.5	-	Acet:2	3	1	32	11
C0	1	^{t}BuOOH: 1.5	-	Acet:2	3	2	46	8
C0	1	^{t}BuOOH: 2	-	Acet:2	3	3	95	11
C0	1	^{t}BuOOH: 2	-	Acet:2	3	4	97	8
C0	1	^{t}BuOOH: 2	5 mol%	Acet:2 H_2O: 0.5	3	2	93	16
C0	1	^{t}BuOOH: 2	1 mmol	Acet:2 H_2O: 0.5	3	2	74	12
C0	1	^{t}BuOOH: 1	-	Acet:2	3	1	36	12
C0	1	^{t}BuOOH: 2[a]	-	Acet:2	3	2	87	15
C0	1	^{t}BuOOH: 1	-	Acet:2	3	2	53	9

[a] Batch addition, 1hr interval

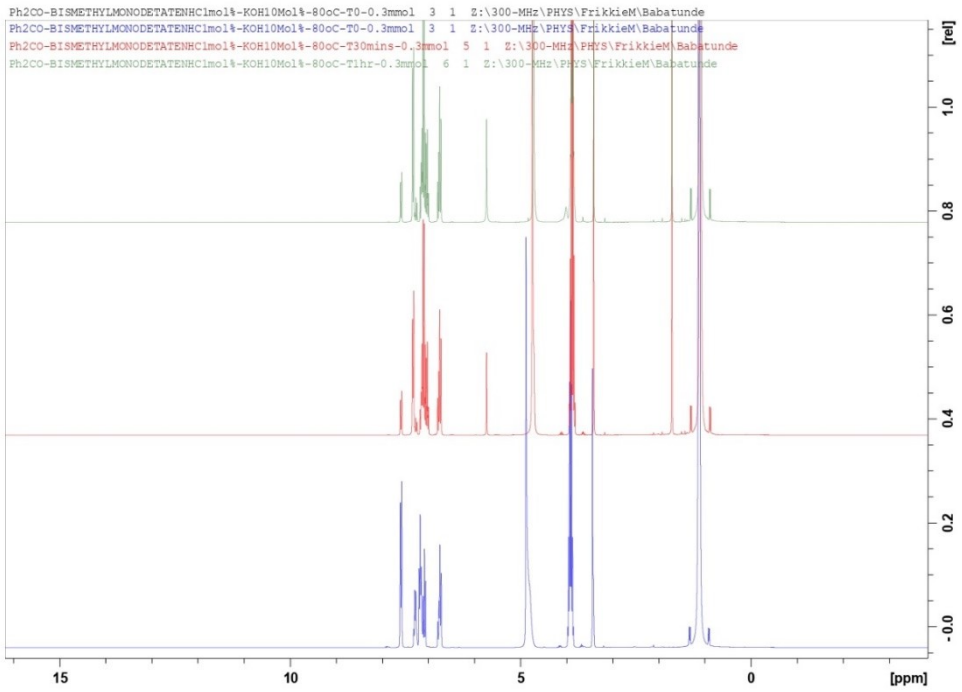


Figure S23: Stacked NMR spectra of transfer hydrogenation of benzophenone using **C2** at time; 0, 0.5 h and 1 h. Ph_2CO (0.3 mmol), anisole (0.3 mmol), ^{i}PrOH (300 µL), catalyst (1 mol %), C_6D_6, 80 °C, KOH (10 mol%).

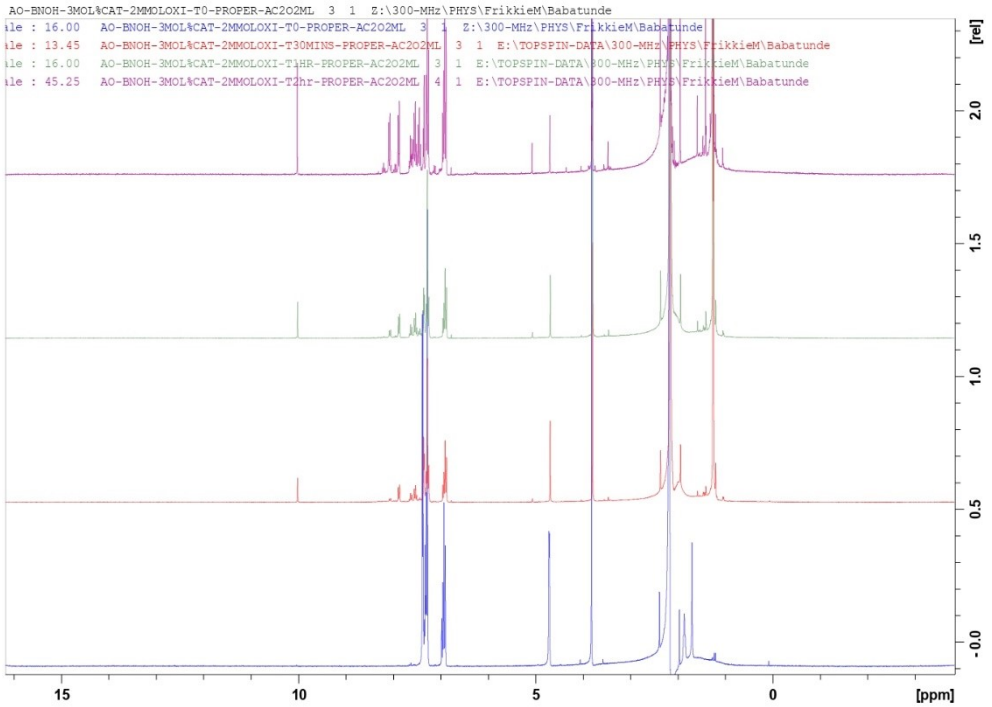


Figure S24: Stacked NMR spectra of alcohol oxidation of benzyl alcohol using **C1** at time; 0, 0.5 h, 1 h and 2 h. General conditions: substrate (1 mmol), catalytic loading (3 mol%), anisole (1 mmol), acetone (2 mL), ^{t}BuOOH (2 mmol), RT.

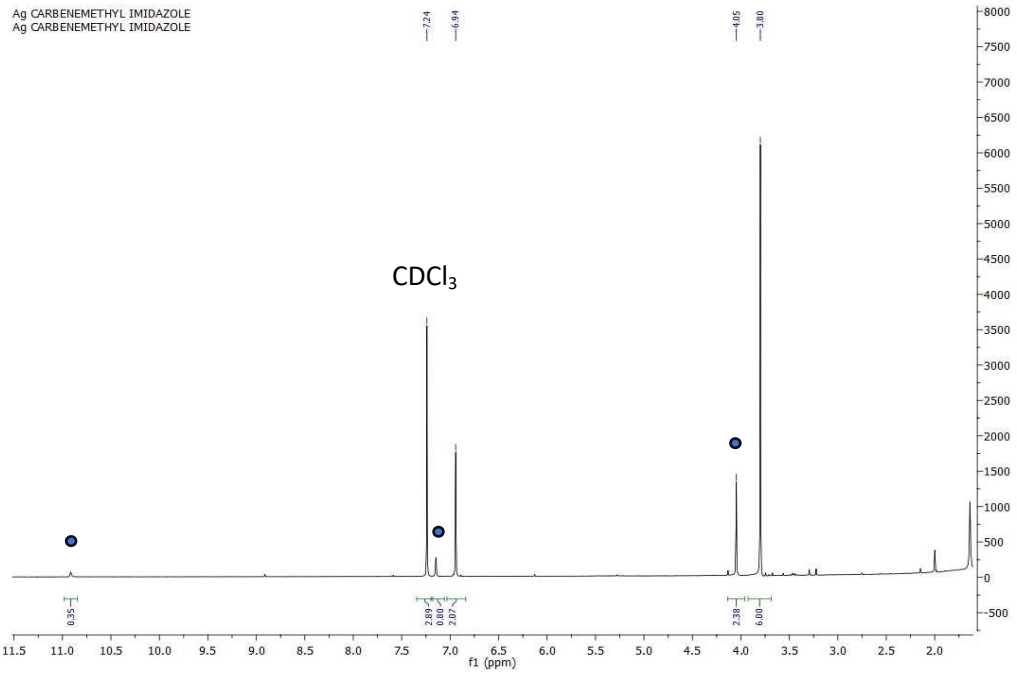


Figure S25: ^{1}H NMR spectrum of the reaction mixture containing the bis-carbene silver(I) intermediate using **L2** after 1 hour. Signals related to unreacted [H**L2**]Cl is indicated by blue dots (≈35%).

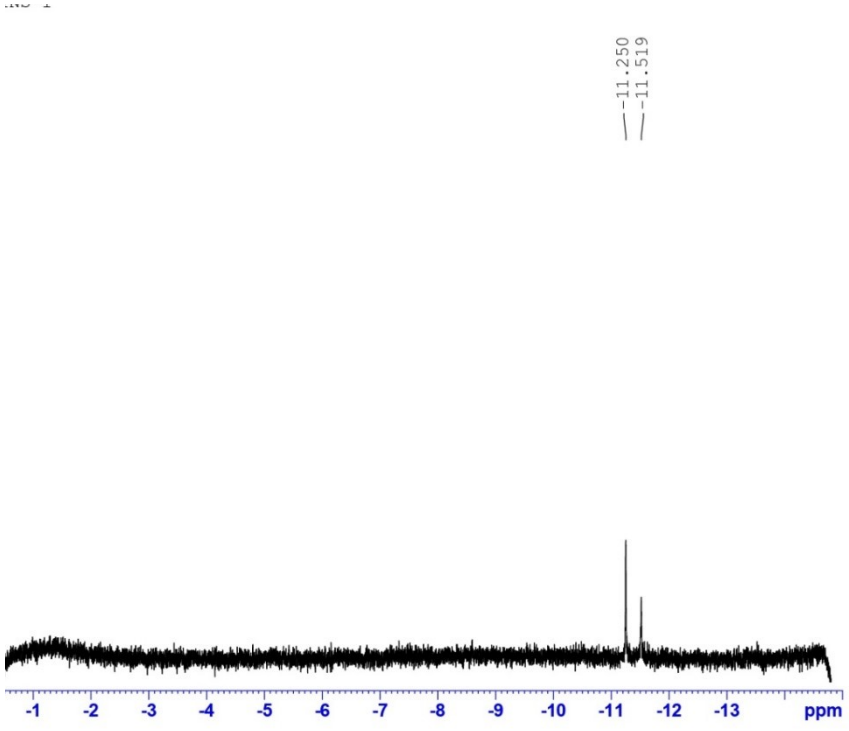
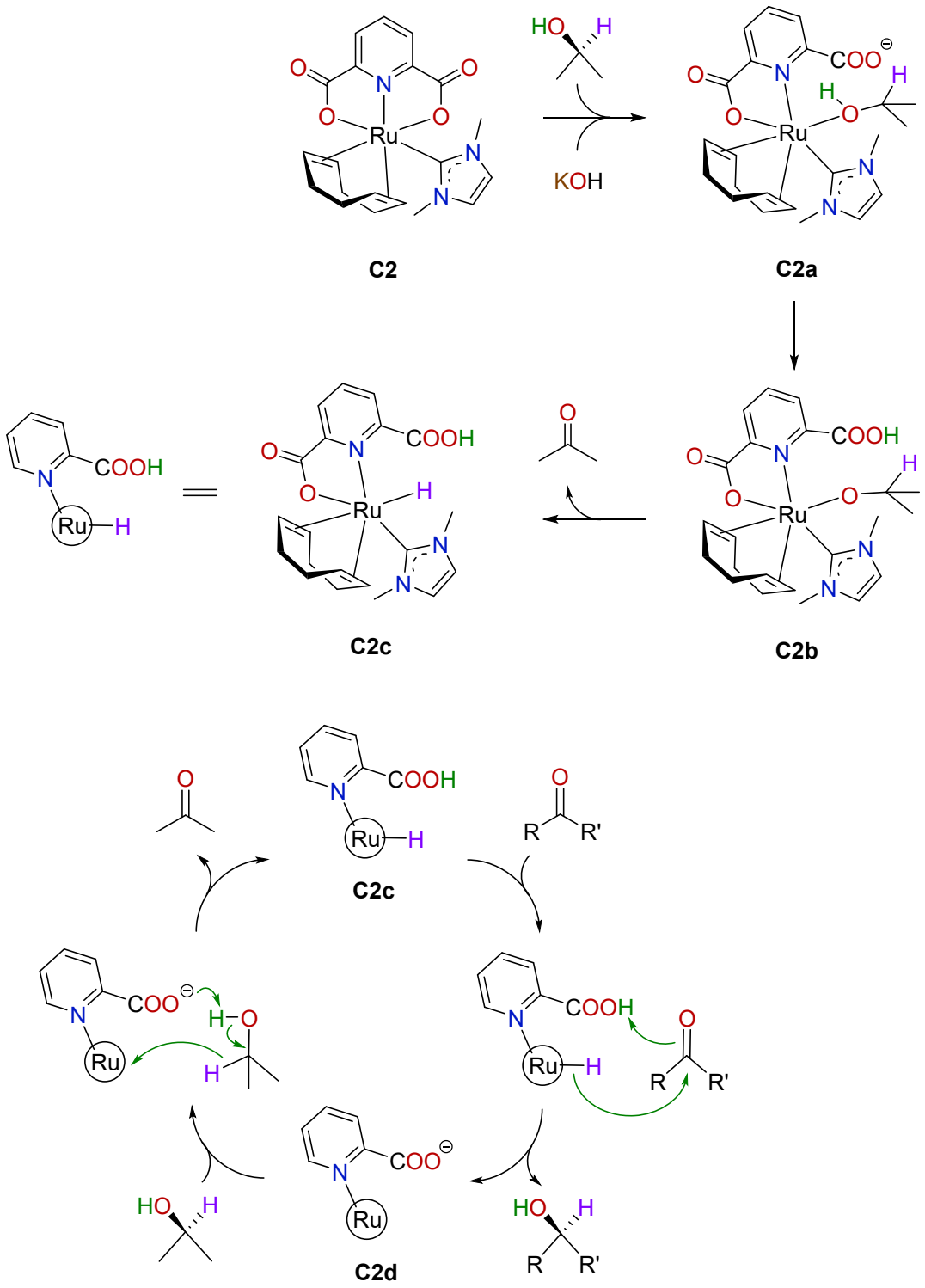


Figure S26: ^{1}H NMR spectrum of the hydride region of a transfer hydrogenation sample taken after 4 hours using **C2** as catalyst.

General conditions: substrate (2 mmol), catalytic loading (3 mol%), anisole (2 mmol), acetone (2 mL), ^{t}BuOOH (4 mmol), RT.



Scheme S1: Proposed mechanism for the catalysed transfer hydrogenation reaction using **C2**.