Mechanistic insights into catalytic carboxylic ester hydrogenation with cooperative Ru(II)-bis1,2,3-triazolylidene pyridine pincer complexes

Sluijter, S.N.; Korstanje, T.J.; van der Vlugt, J.I.; Elsevier, C.J.

DOI
10.1016/j.jorganchem.2017.01.003

Publication date
2017

Document Version
Other version

Published in
Journal of Organometallic Chemistry

SUPPORTING INFORMATION

Mechanistic Insights into Catalytic Carboxylic Ester Hydrogenation with Cooperative Ru(II)-bis{1,2,3-Triazolylidene}pyridine Pincer Complexes

Soraya N. Sluijter, Ties J. Korstanje, Jarl Ivar van der Vlugt* and Cornelis J. Elsevier*

Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, PO Box 94157, 1090 GD, Amsterdam, The Netherlands. E-mail: j.i.vandervlugt@uva.nl; c.j.elsevier@uva.nl

Contents

General experimental details S2

Synthesis procedures and NMR spectra of intermediate **A**, ligand **L1**, **L2** and complexes **1**-**5** S2

Catalytic ester hydrogenation experiments S16

NMR reactivity experiments S17

DFT investigation *fac*/*mer* coordination of CNC ligand S20

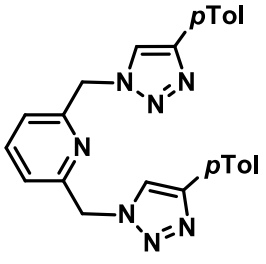
References S20

Experimental

General experimental details

All reactions were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. Solvents were dried and distilled according to standard methods.[5] Methyl benzoate was degassed and dried over 4Å molsieves. All other chemicals were purchased from commercial suppliers and used without further purification. The NMR spectra were recorded on Varian Mercury 300 MHz, Bruker DRX Avance 300 and Bruker AMX 400 MHz spectrometers. ^{19}F NMR was used to confirm the (non-coordinating nature of the) BF_4 anion (-152 ppm). ^{1}H-^{1}H COSY and/or ^{1}H-^{13}C HSQC NMR spectroscopy was used to assign the signals of several compounds. High resolution mass spectrometry was performed on a Bruker MicrOTOF-Q (ESI^+) GC analysis for esters was performed on a Thermo Scientific Trace GC Ultra equipped with a Restek RTX-200 column (30 m x 0.25 mm x 0.5 µm). Temperature program: Initial temperature 50 °C, hold for 4 min, heat to 130 °C with 30 °C/min, hold for 2 min, heat to 250 °C with 50 °C/min, hold for 9 min. Inlet temperature 200 °C, split ratio of 60, 1 mL/min carrier flow, FID temperature 250 °C. GC analysis for fatty esters and benzoic acid was performed on a Thermo Scientific Trace GC Ultra equipped with a Restek Stabilwax-DA column (30 m x 0.25 mm x 0.25 µm). Temperature program: initial temperature 40 °C, heat to 175 °C with 6 °C/min, heat to 250°C with 50 °C/min, hold for 18 minutes. Inlet temperature 280 °C, split ratio of 40, 1.5 mL/min carrier flow, FID temperature 250 °C. Conversion of trifluoroacetic acid and methyl trifluoroacetate were determined by ^{19}F NMR spectroscopy using 1,3-bis(trifluoromethane)benzene as internal standard.

Synthesis procedures and NMR spectra of intermediate A, ligand L1, L2 and complexes 1-5 .



Synthesis of 3,3-[pyridine-2,6-diylbis(methylene)]bis(4-para-tolyl-1,2,3-triazole); intermediate **A**. To a solution of 2,6-bis(bromomethyl)pyridine (397 mg, 1.5 mmol) in DMF/H_2O (7.5 mL, 4:1) was added NaN_3 (205 mg, 3.1 mmol), *para*-tolylacetylene (357 mg, 3.1 mmol), Na_2CO_3 (159 mg, 1.5 mmol), $CuSO_4 \cdot 5H_2O$ (150 mg, 0.6 mmol) and sodium ascorbate (238 mg, 1.2 mmol). The reaction mixture was stirred at room temperature for 16 h, after which the

suspension was poured into an EDTA/NH_4OH solution (100 mL, 0.5 M). CAUTION: The treatment with ammonium hydroxide before extraction is essential to avoid the possible formation of potentially explosive organic azides. The product was extracted with dichloromethane (3 x 15 mL) and washed with water (2 x 50 mL) and brine (50 mL). The organic phase was dried over $MgSO_4$ and concentrated *in vacuo* to yield the product as a white solid (480 mg, 1.1 mmol, 76%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (s, 2H, NC*H*C), 7.75-7.65 (m, 6H, pyr-C*H*, Tol-C*H*), 7.22 (m, 8H, Pyr-C*H*, Tol-C*H*), 5.71 (s, 4H, CH_2), 2.40 (s, 6H, Tol-CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 155.0 (C_q), 139.0 (Pyr-*C*H), 138.3 (C_q), 136.1 (C_q), 129.8 (Tol-*C*H), 127.7 (C_q), 125.9 (Tol-*C*H), 122.2 (pyr-*C*H), 120.1 (tz-*C*H), 55.51(CH_2), 21.51 (CH_3). MS(EI^+) for $C_{25}H_{23}N_7$: *m/z* calculated 421.2009 $[M]^+$, observed 421.2013.

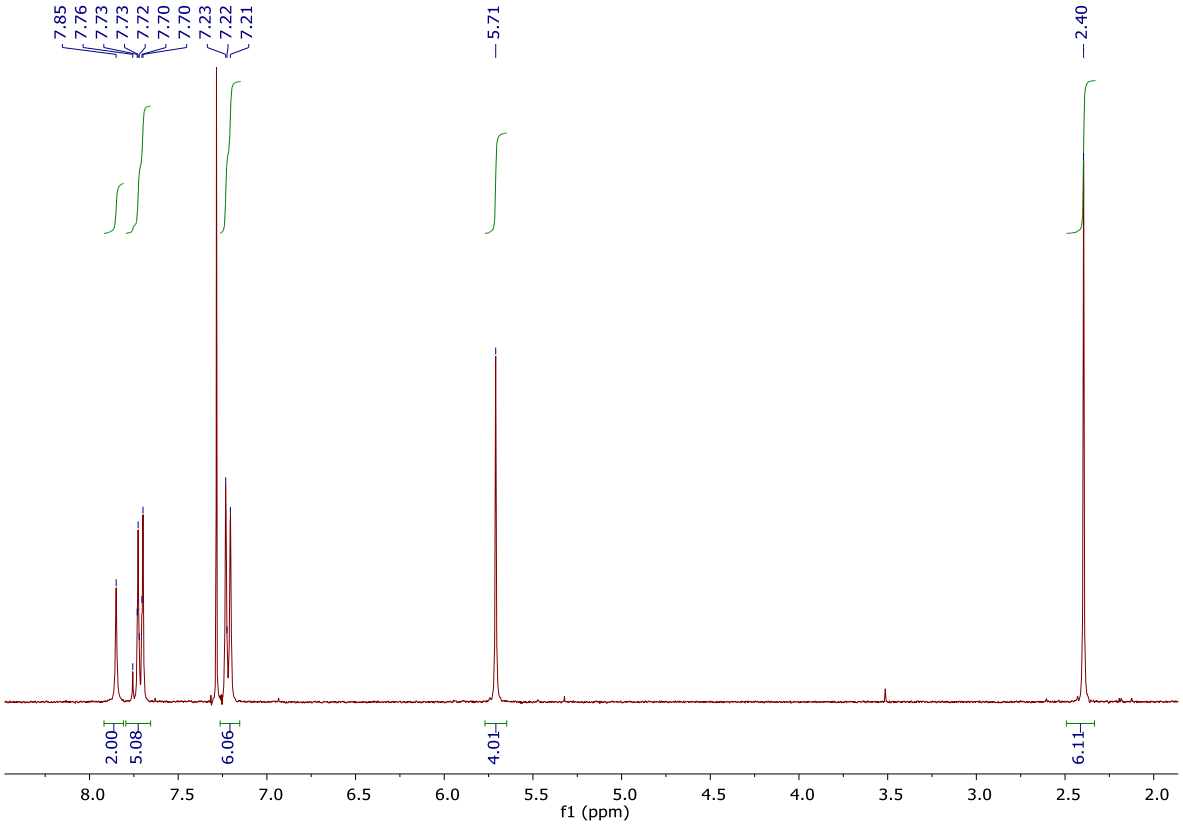


Figure S1: ^{1}H NMR spectrum of intermediate **A** in $CDCl_3$.

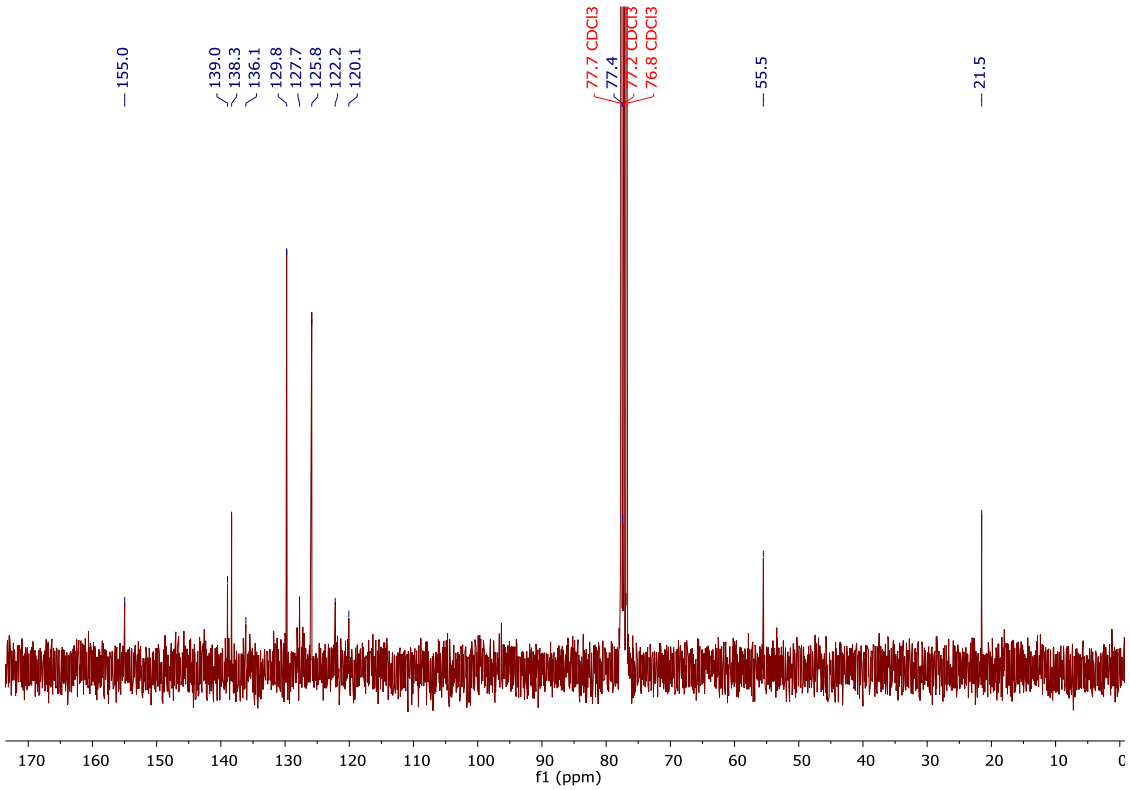
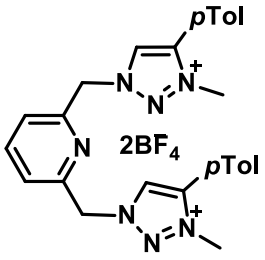


Figure S2: $^{13}C\{^{1}H\}$ NMR spectrum of intermediate **A** in $CDCl_3$.



Synthesis of 3,3-[pyridine-2,6-diylbis(methylene)]bis(3-methyl-4-para-tolyl-1,2,3-triazolium) bistetrafluoroborate; Ligand **L1**. Meerweins' salt $Me_3O.BF_4$, 137 mg, 0.92 mmol) was added to a solution of intermediate **A** (155 mg, 0.37 mmol) in dichloromethane (10 mL) and the reaction mixture was stirred at room temperature for 16 h. A few drops of methanol were added to quench the reaction. The precipitate was collected on a glass frit and washed with small amounts of DCM and Et_2O, yielding the product as a white solid (185 mg, 0.30 mmol, 81%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.19 (s, 2H, NC*H*C), 8.08 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H, Pyr-C*H*), 7.70 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H, Pyr-C*H*), 7.54 (d, $^{3}J_{HH}$ = 8.0 Hz, 4H, Tol-C*H*), 7.37 (d, $^{3}J_{HH}$ = 8.0 Hz, 4H, Tol-C*H*), 6.07 (s, 4H, CH_2), 4.22 (s, 6H, N-CH_3), 2.40 (s, 6H, Tol-CH_3); $^{13}C\{^{1}H\}$ NMR (75 MHz, acetonitrile-d_3) δ 152.6, 144.2, 143.4 (C_q), 140.7 (pyr-*C*H), 131.0, 130.1 (Tol-*C*H), 130.0 (tz-*C*H), 124.9 (Pyr-*C*H), 120.1 (C_q), 58.2 (CH_2), 39.6 (N-CH_3), 21.5 (CH_3). MS(CSI$^+$) for $C_{27}H_{29}N_7BF_4$: *m/z* calculated 538.2513 $[M\text{-}BF_4]^+$, observed 538.2482.

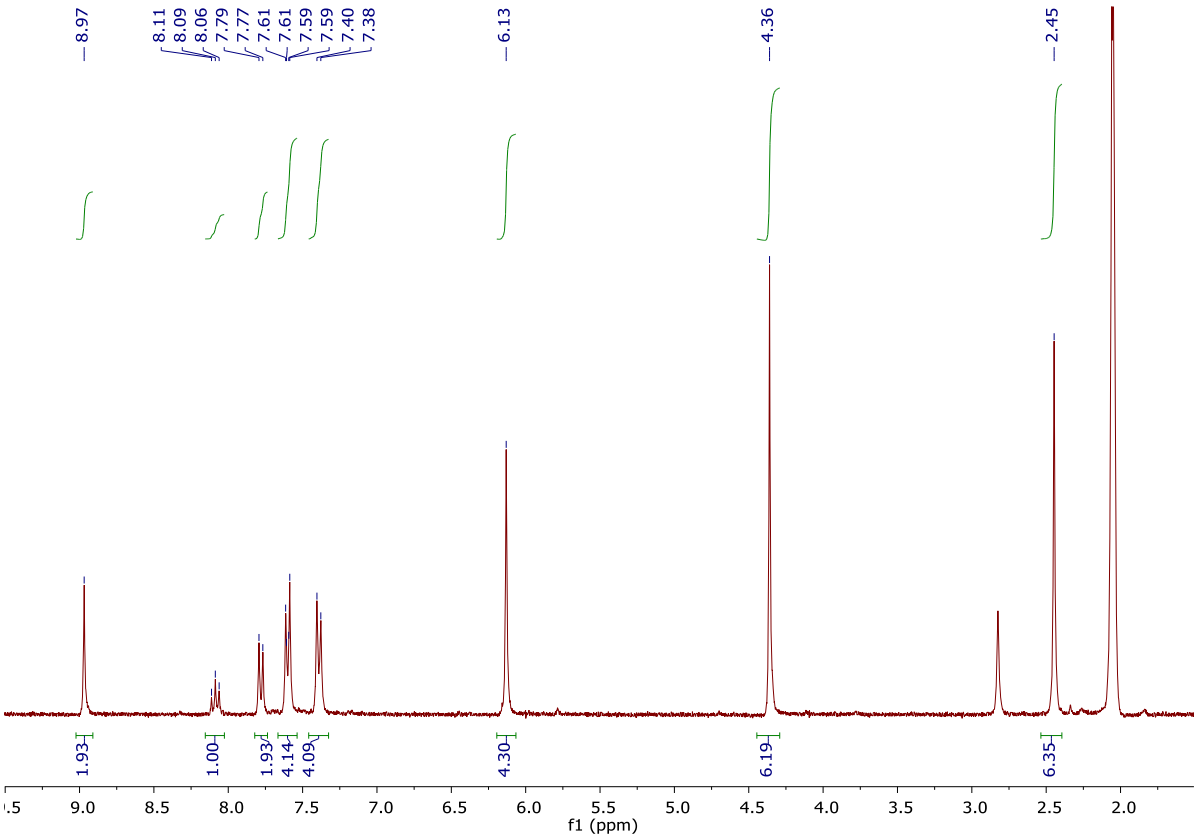


Figure S3: ^{1}H NMR spectrum of ligand **L1** in acetone-d_6.

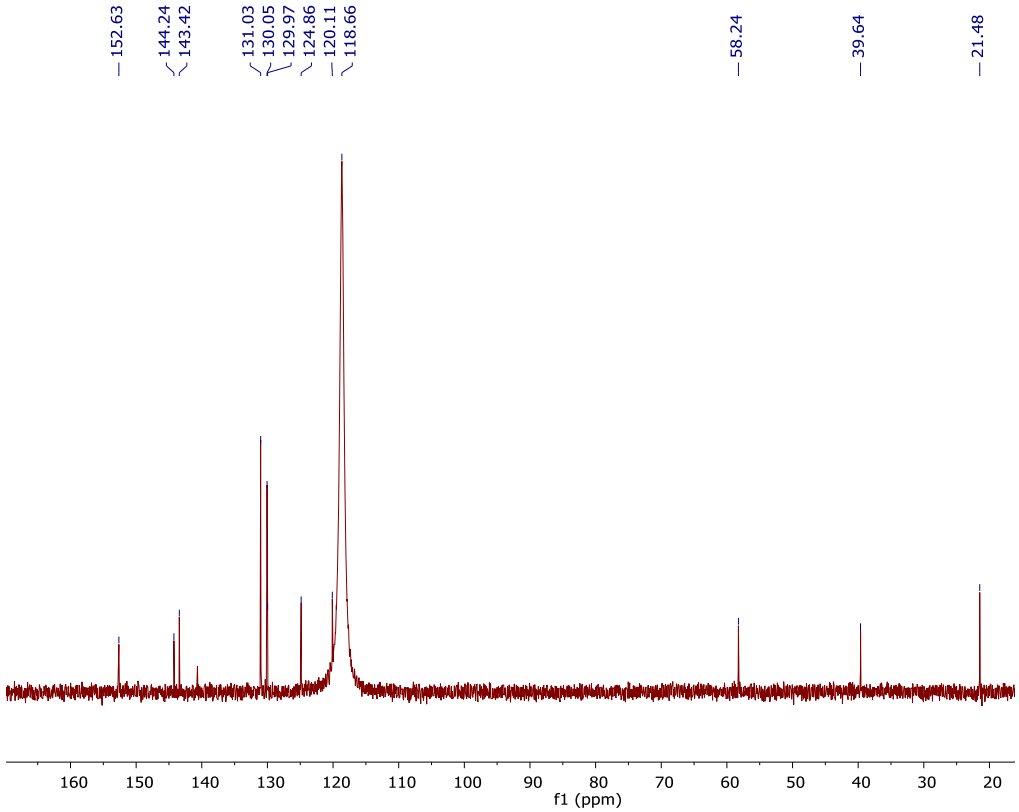
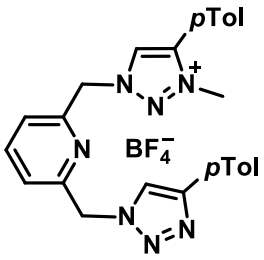


Figure S4: ^{13}C{^{1}H} NMR of ligand **L1** in acetonitrile-d_3.



Synthesis of 3,3-[pyridine-2,6-diylbis(methylene)](4-para-tolyl-1,2,3-triazolyl)(3-methyl-4-para- tolyl-1,2,3-triazolium) tetrafluoroborate; Ligand **L2**. Meerweins' salt $Me_3O.BF_4$, 126 mg, 0.85 mmol) was added to a solution of intermediate **A** (360 mg, 0.85 mmol) in DCM (30 mL) and the reaction mixture was stirred at room temperature for 16 h. A few drops of methanol were added to quench the reaction. After the solvent was removed under reduced pressure, the product was purified by column chromatography (SiO_2, DCM:acetone = 1:1) yielding the product (151 mg, 0.29 mmol, 34%) as a white powder.^{1}H NMR (300 MHz, DMSO-d_6) δ 9.10 (s, 1H, tz-C*H*), 8.48 (s, 1H, tz-C*H*), 8.00 (t, $^3J_{HH}$ = 7.7 Hz, 1H, Pyr-C*H*), 7.63 (d, $^3J_{HH}$ = 8.1 Hz, 2H, Tol-C*H*), 7.60 – 7.53 (m, 3H, Pyr-C*H* and Tol-C*H* overlapping), 7.46 (d, $^3J_{HH}$ = 7.7 Hz, 1H, Pyr-C*H*), 7.40 (d, $^3J_{HH}$ = 7.9 Hz, 2H, Tol-C*H*), 7.17 (d, $^3J_{HH}$ = 7.8 Hz, 2H, Tol-C*H*), 6.05 (s, 2H, CH_2), 5.75 (s, 2H, CH_2), 4.18 (s, 3H, N-CH_3), 2.43 (s, 3H, CH_3), 2.32 (s, 3H, CH_3); ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 155.1, 151.9, 146.3, 142.4 (C_q), 141.5 (Pyr-*C*H), 138.9, 137.1(tz-*C*H), 129.8 (Tol-*C*H), 129.3 (Tol-*C*H), 129.2, 129.1 (Tol-*C*H), 127.7, 124.9 (Tol-*C*H), 122.4, 122.4 (Pyr-*C*H), 121.7, 119.5 (C_q), 56.8, 54.0 (*C*H_2), 38.9 (N-*C*H_3), 21.0, 20.8 (*C*H_3). MS(CSI$^+$) for $C_{26}H_{26}N_7$: *m/z* calculated 436.2250 $[M\text{-}BF_4]^+$, observed 436.2323.

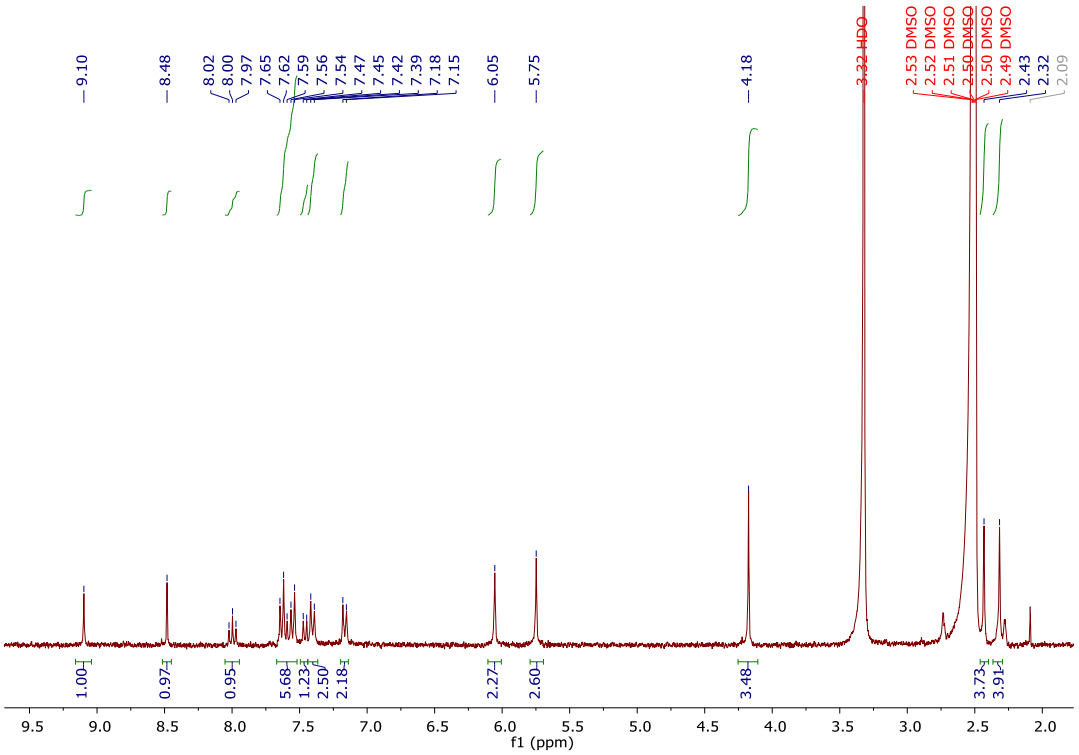


Figure S5: ^{1}H NMR spectrum of ligand **L2** in DMSO-d_6.

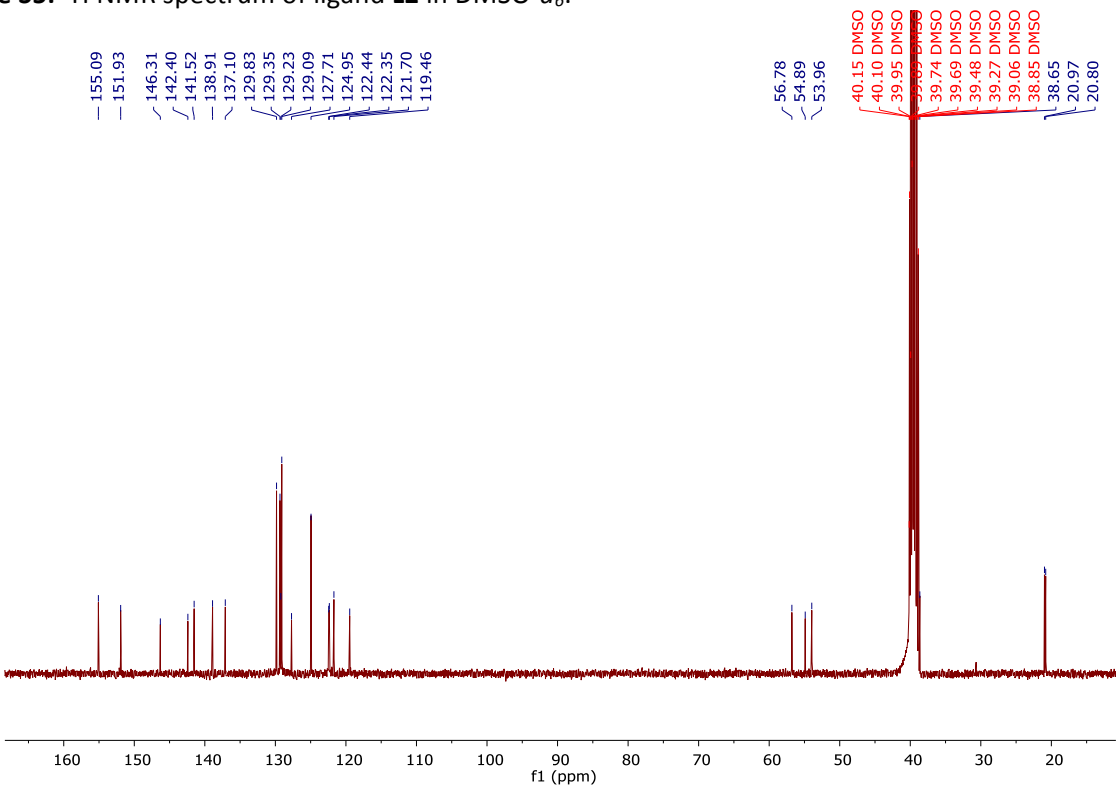


Figure S6: ^{13}C{^{1}H} NMR of ligand **L2** in DMSO-d_6.

Synthesis of [Ag(CNC)]BF_4; **1**. Ag_2O (87 mg, 0.3 mmol) was added to a solution of ligand **L1** (95 mg, 0.15 mmol) in MeOH (10 mL) in a Schlenk flask charged with 4Å molsieves. The resulting suspension was stirred for 2 days at room temperature during which it changed color to pale grey/brown. The mixture was filtered over Celite (to obtain good yields the filtrate was thoroughly flushed with MeOH and acetone) and dried *in vacuo* yielding the product (87 mg, 0.13 mmol, 90%) as a pale yellow solid. The compound was stored under nitrogen and with exclusion of light. ^{1}H NMR (300 MHz, acetone-d_6) δ 7.93 (t, $^3J_{HH}$ = 7.7 Hz, 1H, Pyr-C*H*), 7.55 (d, $^3J_{HH}$ = 7.7 Hz, 2H, Pyr-C*H*), 7.47 (d, $^3J_{HH}$ = 7.8, 4H, Tol-C*H*), 7.23 (d, $^3J_{HH}$ = 7.8 Hz, 4H, Tol-C*H*), 5.84 (s, 4H, CH_2), 4.09 (s, 6H, N-CH_3), 2.44 (s, 6H, CH_3); ^{13}C{^{1}H} NMR (75 MHz, acetone-d_6) δ 155.3, 149.8, 148.3, 140.8, 130.5, 129.9, 125.8 (Ar-*C*), 60.7 (*C*H_2), 37.9 (N-*C*H_3), 21.3 (*C*H_3). MS(CSI$^+$) for $C_{27}H_{29}{}^{107}AgN_7$: *m/z* calculated 556.1379 $[M\text{-}BF_4]^+$, observed 556.1342 and for $C_{27}H_{29}{}^{109}AgN_7$: *m/z* calculated 558.1379 $[M\text{-}BF_4]^+$, observed 558.1377.

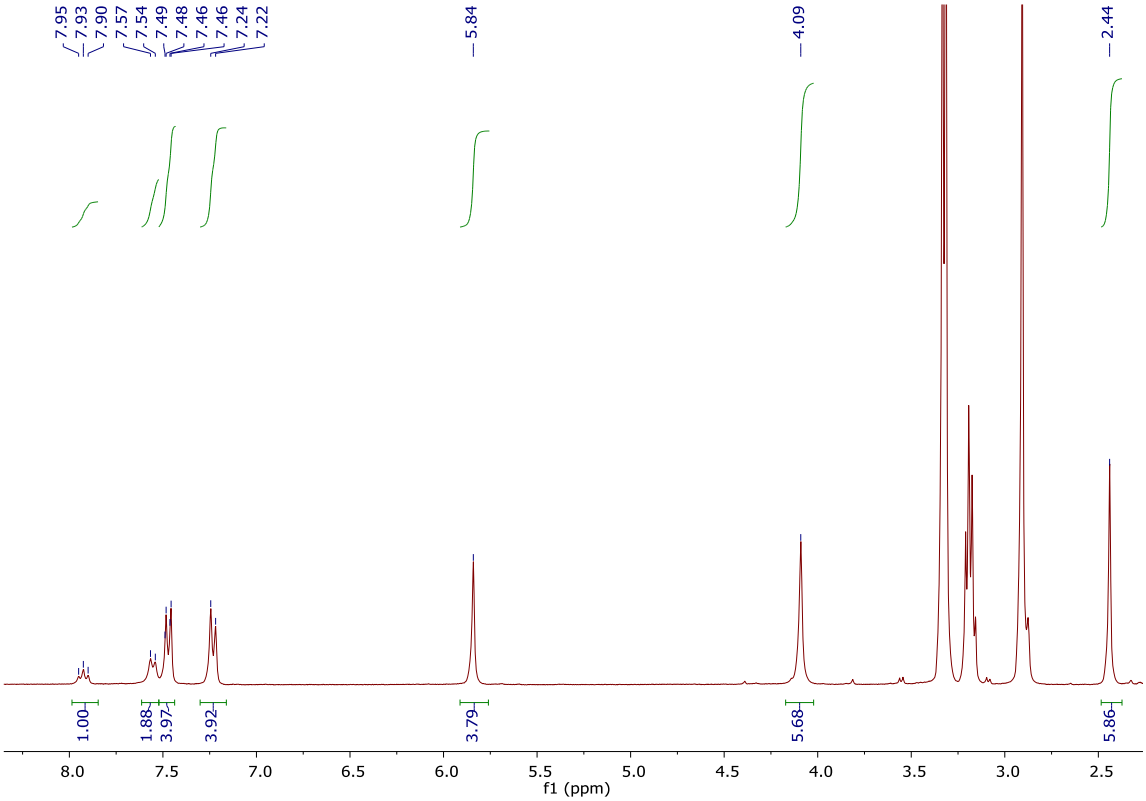


Figure S7: ^{1}H NMR spectrum of Ag^I complex **1** in acetone-d_6.

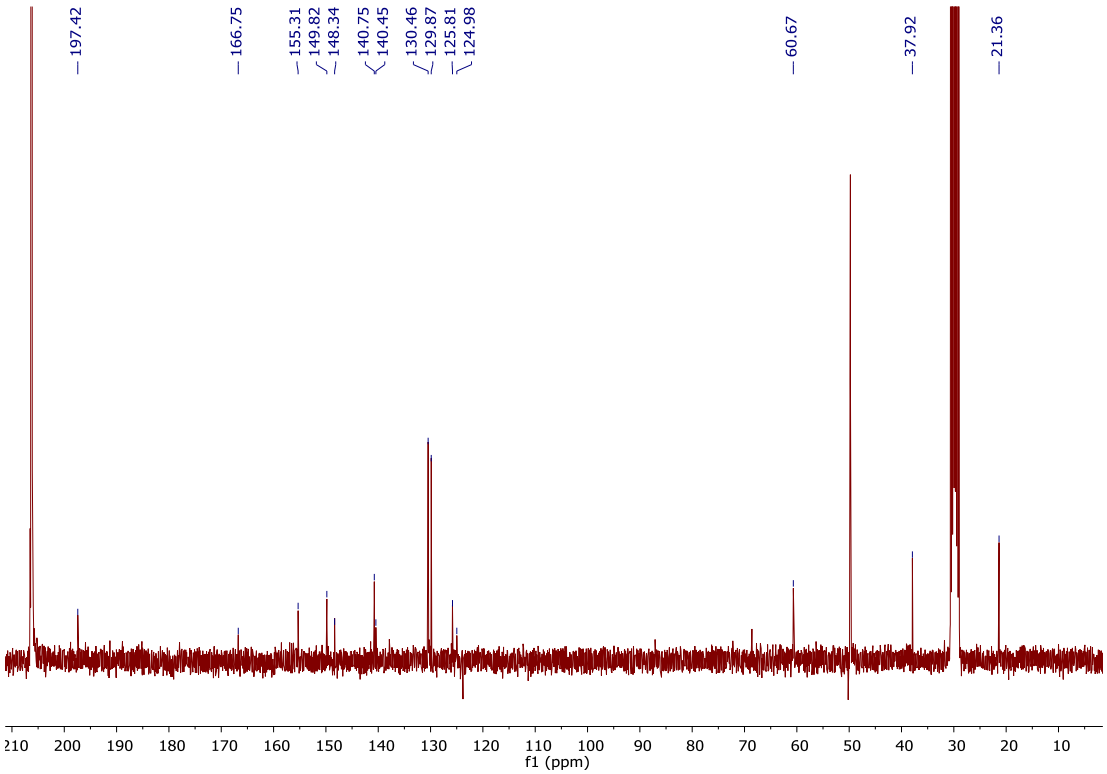
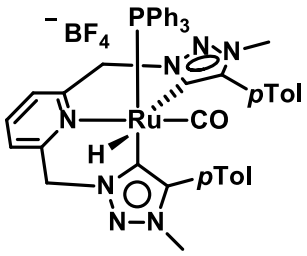


Figure S8: $^{13}C\{^{1}H\}$ NMR spectrum of Ag^{I} complex **1** in acetone-d_6.



Synthesis of [Ru(CO)(H)(PPh$_3$)(CNC)]BF$_4$; **2**. A mixture of silver complex **1** (78,2 g, 0.12 mmol) and [RuHCl(CO)(PPh$_3$)$_3$] (115 g, 0.12 mmol) in THF (8 mL) was heated at 55 °C for 2 days. The resulting pale brown suspension was filtered, evaporated to dryness and extracted with MeOH (2 × 5 mL). The solvent was evaporated, and the product was obtained by precipitation from DCM with Et_2O as pale beige powder (76.2 mg, 0.08 mmol, 68%). IR ν(CO) 1926 cm^{-1}. $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) δ 46.7; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.94 (t, $^{3}J_{HH}$ = 7.7 Hz, 1H, Pyr-C*H*), 7.76 (d, $^{3}J_{HH}$ = 7.5 Hz, 1H, Pyr-C*H*), 7.58 – 7.12 (m, 16H, PPh$_3$ & Pyr-C*H*), 6.97 (d, $^{3}J_{HH}$ = 2.8 Hz, 4H, Tol-C*H*), 6.90 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H, Tol-C*H*), 6.53 – 6.44 (m, 3H, Tol-C*H* & CH_2) 6.05 (d, $^{2}J_{HH}$ = 13.8 Hz, 2H, CH_2), AB system centered at $\delta_{A:}$ 5.51 (d, $^{2}J_{HH}$ = 15.7 Hz, 1H, CH_2) & δ_B: 4.82 (d, $^{2}J_{HH}$ = 15.7 Hz, 1H, CH_2), 3.73 (s, 3H, N-CH_3), 3.54 (s, 3H, N-CH_3), 2.46 (s, 3H, Tol-CH_3), 2.40 (s, 3H, Tol-CH_3), -7.04 (d, $^{2}J_{PH}$ = 28.9 Hz, 1H, Ru-H); $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) δ 208.51 (d, $^{2}J_{CP}$ = 14.8 Hz, Ru-*C*O), 172.2 (d, $^{2}J_{CP}$ = 7.2 Hz, C_{tzNHC}), 164.9 (d, $^{2}J_{CP}$ = 75.7 Hz, C_{tzNHC}) 155.4 & 155.2 (Pyr-C_q), 148.7 (Pyr-*C*H), 148.3 (d, J_{CP} = 7.1 Hz, PPh$_3$-C_q), 139.6 (d, J_{CP} = 6.0 Hz, PPh$_3$-*C*H) 138.1 (Pyr-*C*H), 136.7 (d, J_{CP} = 38.0 Hz, PPh$_3$-*C*H), 136.2, 134.3, 133.7, 133.5,

132.61, 131.8, 131.8, 131.7, 130.2 (Tol-*C*H), 129.4 (Tol-*C*H), 129.3, 129.2, 129.1, 128.9, 128.4 (d, J_{CP} = 7.7 Hz, 6 *C*H arom, PPh3), 128.3, 128.1, 128.0, 127.9, 127.4, 127.4, 125.3, 125.1, 125.0, 124.3, 124.1, 61.5 (CH_2), 58.3 (CH_2), 37.0, 36.8 (N-CH_3), 21.4, 21.1 (Tol-CH_3). MS(CSI^+) for $C_{46}H_{43}N_7OPRu$: *m/z* calculated 842.2323 $[M\text{-}H\text{-}BF_4]^+$, observed 842.2233.

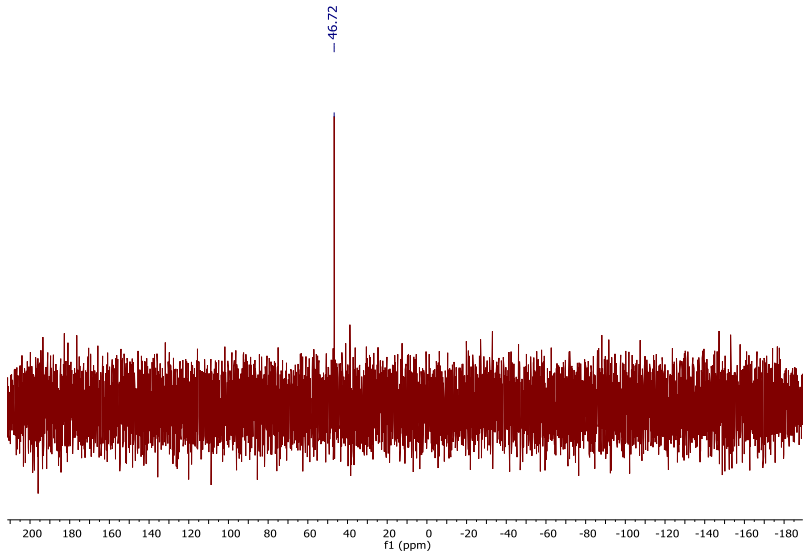


Figure S9: $^{31}P\{^1H\}$ NMR spectrum of Ru^{II} complex **2** in CD_2Cl_2.

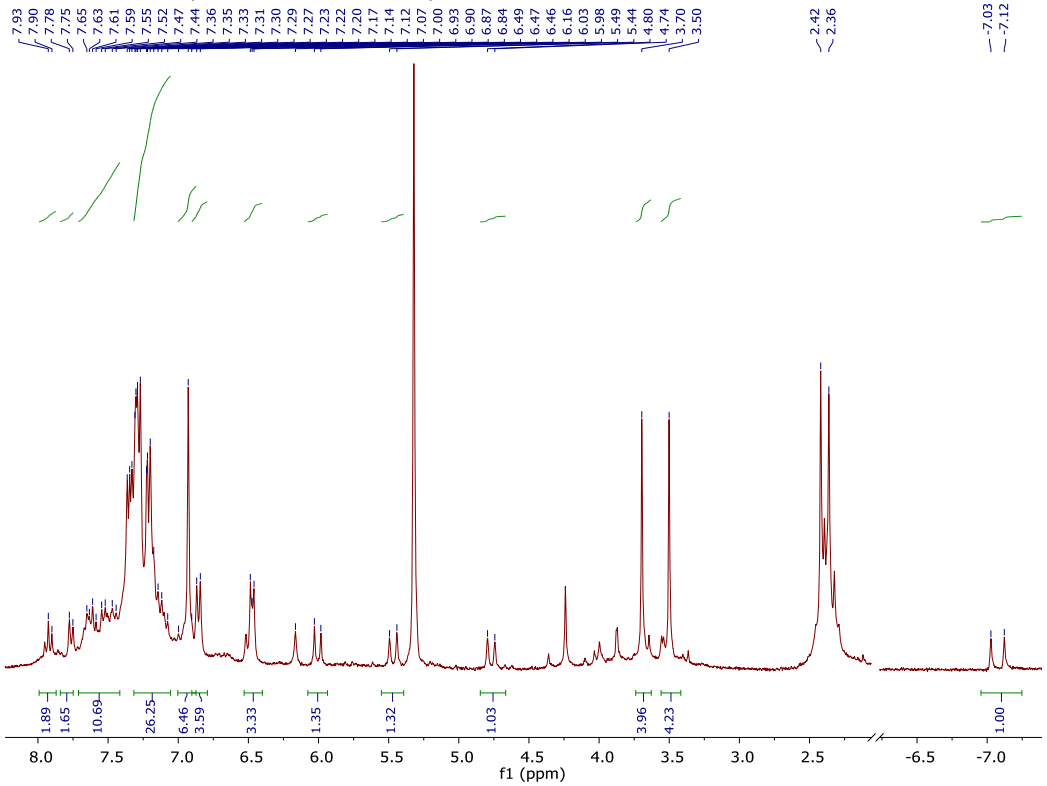


Figure S10: ^1H NMR spectrum of Ru^{II} complex **2** in CD_2Cl_2.

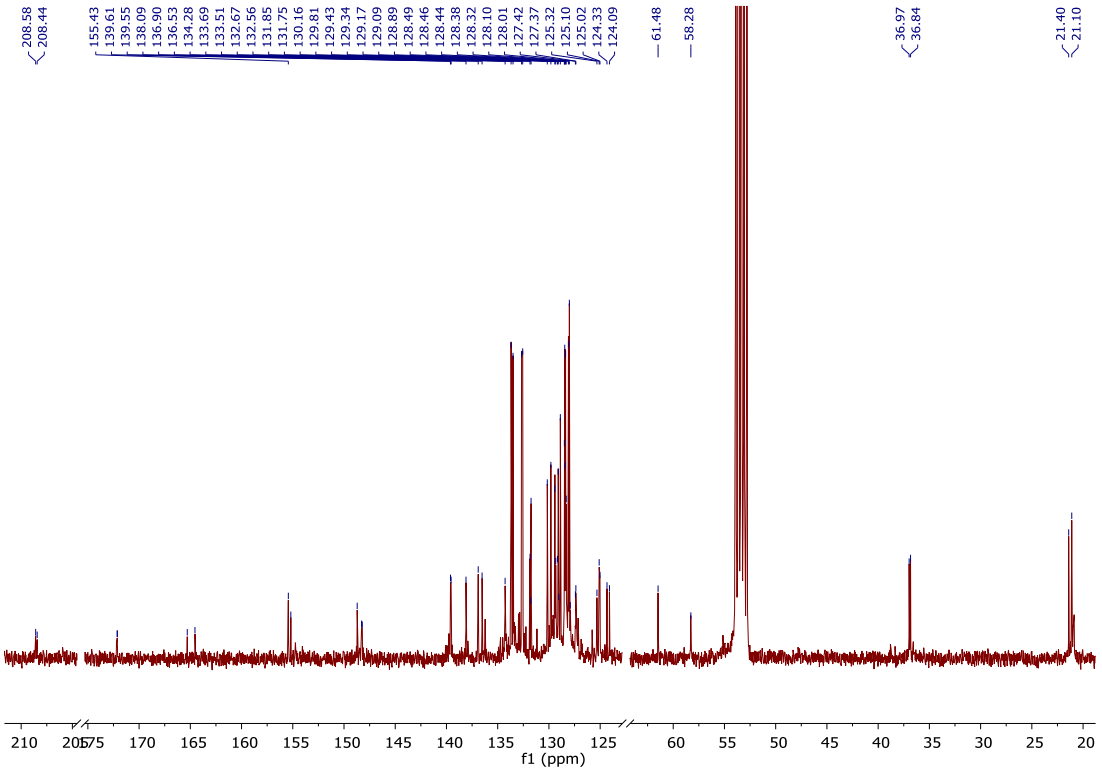
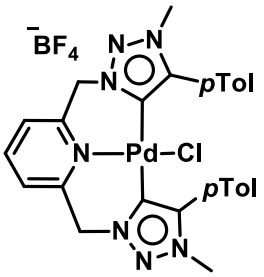


Figure S11: $^{13}C\{^{1}H\}$ NMR spectrum of Ru^{II} complex **2** in CD_2Cl_2.



Synthesis of [Pd(CNC)(Cl)]BF$_4$; **3***.* To a solution of complex **1** (75 mg, 0.12 mmol) in MeCN (7 mL) was added $[Pd(NCPh)_2Cl_2]$ (45 mg, 0.12 mmol) and the resulting mixture was stirred for 2 h. The resulting suspension was filtered over Celite and the solvent was removed under reduced pressure. The product was precipitated from DCM with pentane to obtain the product as a yellow solid (72 mg, 0.11 mmol, 92%). ^{1}H NMR (300 MHz, acetone-d_6) δ 8.40 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H, Pyr-C*H*), 8.22 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H, Pyr-C*H*), 7.61 (d, $^{3}J_{HH}$ = 7.9 Hz, 4H, Tol-C*H*), 7.24 (d, $^{3}J_{HH}$ = 7.9 Hz, 4H, Tol-C*H*), 6.26 (s, 3H, CH_2), 4.16 (s, 6H, N-CH_3), 2.35 (s, 6H, CH_3); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.27 (t, $^{3}J_{HH}$ = 7.7 Hz, 1H, Pyr-C*H*), 7.97 (d, $^{3}J_{HH}$ = 7.7 Hz, 2H, Pyr-C*H*), 7.48 (d, $^{3}J_{HH}$ = 7.8 Hz, 4H, Tol-C*H*), 7.29 (d, $^{3}J_{HH}$ = 7.8 Hz, 4H, Tol-C*H*), AB system centered at δ_A 6.10 (d, $^{2}J_{HH}$ = 15.1 Hz, 1H, CH_2) & δ_B: 5.98 (d, $^{2}J_{HH}$ = 14.8 Hz, 1H, CH_2), 4.02 (s, 6H, N-CH_3), 2.42 (s, 6H, CH_3); $^{13}C\{^{1}H\}$ NMR (75 MHz, CD_2Cl_2) δ 168.0 (C_{tzNHC}), 154.2, 148.3, 146.5 (C_q), 142.5 (Pyr-*C*H), 140.9 (C_q), 130.9, 129.4 (Tol-*C*H), 127.24 (Pyr-*C*H), 123.7 (C_q), 59.38 (*C*H_2), 37.65 (N-*C*H_3), 21.61 (*C*H_3). MS(CSI$^+$) for $C_{27}H_{27}ClN_7Pd$: *m/z* calculated 590.1058 $[M\text{-}BF_4]^+$, observed 590.1012.

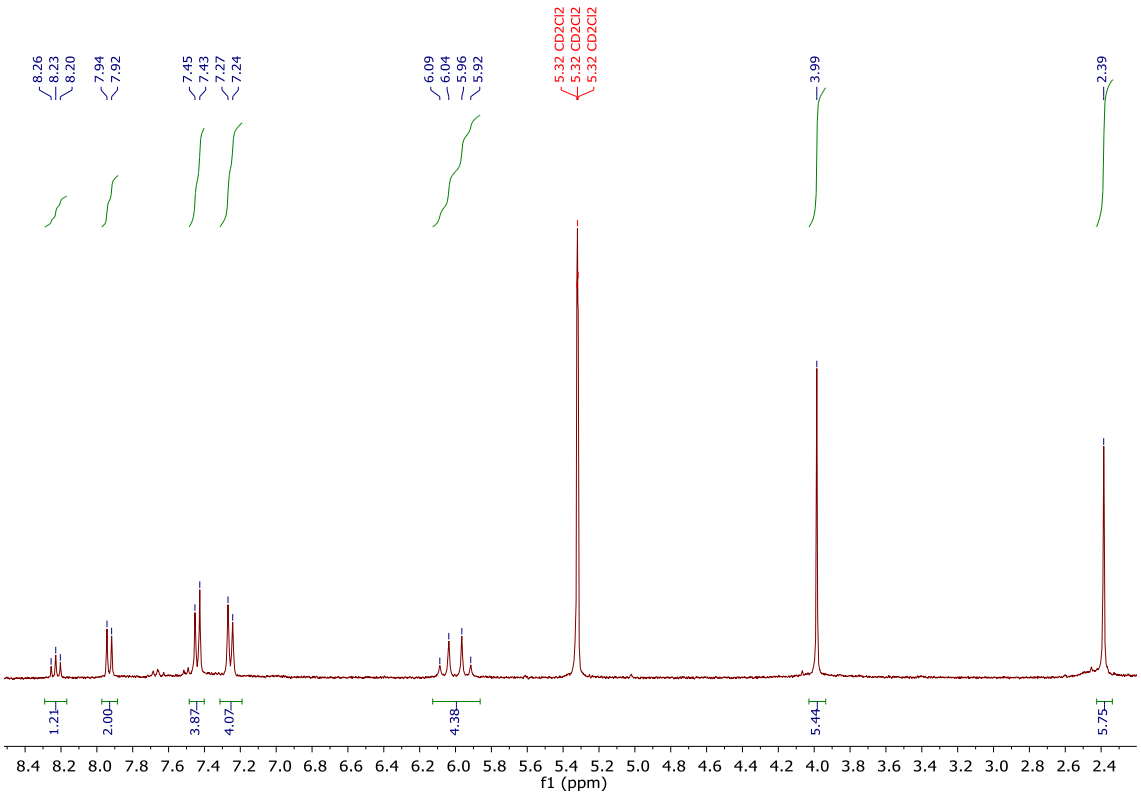


Figure S12: ^{1}H NMR spectrum of Pd^{II} complex **3** in CD_2Cl_2.

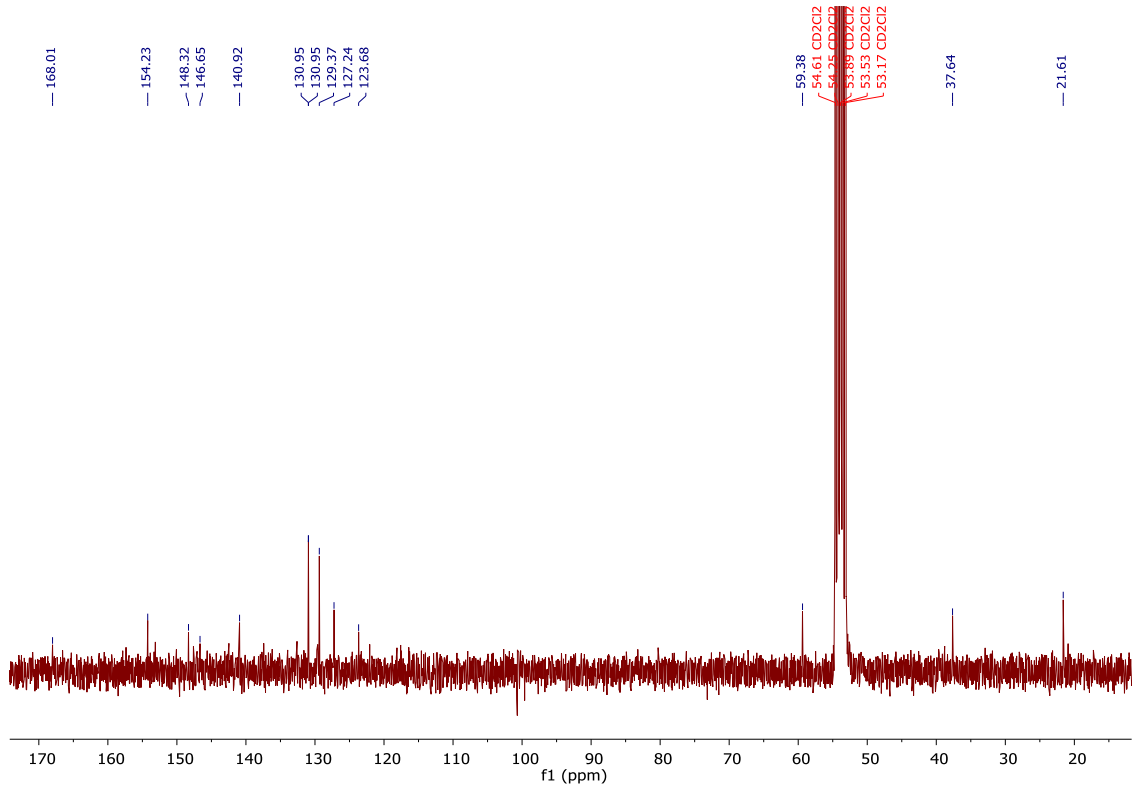
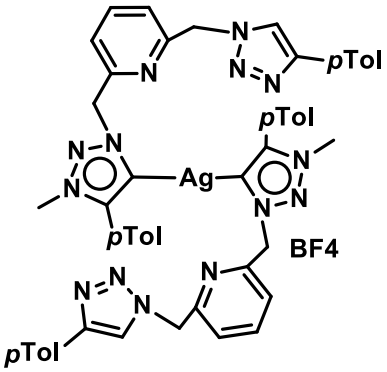


Figure S13: $^{13}C\{^{1}H\}$ NMR spectrum of Pd^{II} complex **3** in CD_2Cl_2.

Synthesis of [Ag(CNN)]BF_4; **4**. This complex was synthesized in analogy to complex **1** from ligand **L2**. Pale beige solid (58 mg, 0.05 mmol, 78%) ^{1}H NMR (300 MHz, methanol-d_4) δ 7.99 (s, 1H), 7.72 (t, $^3J_{HH}$ = 7.7 Hz, 1H, Pyr-C*H*), 7.43 (d, $^3J_{HH}$ = 7.9 Hz, 1H, Pyr-C*H*), 7.34 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Tol-C*H*), 7.28 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Tol-C*H*), 7.20 (d, $^3J_{HH}$ = 7.9 Hz, 1H, Pyr-C*H*), 7.16 (d, $^3J_{HH}$ = 7.8 Hz, 2H, Tol-C*H*), 6.96 (d, $^3J_{HH}$ = 7.8 Hz, 2H, Pyr-C*H*), 5.61 (s, 2H, CH_2), 5.38 (s, 2H, CH_2), 4.01 (s, 3H, N-CH_3), 2.45 (s, 3H, Tol-CH_3), 2.30 (s, 3H, Tol-CH_3); ^{13}C{^{1}H} NMR (101 MHz, methanol-d_4) δ 154.2, 154.1, 148.4 (C_q), 139.6 (Pyr-*C*H), 138.6 (Tol-*C*H), 138.2 (Tol-*C*H), 137.6, 131.7, 129.7, 129.1, 128.9, 128.9, 127.0, 124.9, 124.8, 124.5, 122.0, 121.8 (C_q), 47.9, 47.5 (*C*H_2), 36.2 (N-*C*H_3), 19.9 (Tol-*C*H_3), 19.7 (Tol-*C*H_3). MS(CSI$^+$) for $C_{52}H_{50}{}^{109}AgN_{14}$: *m/z* calculated 979.3390 $[L_2Ag\text{-}BF_4]^+$, observed 979.3445.



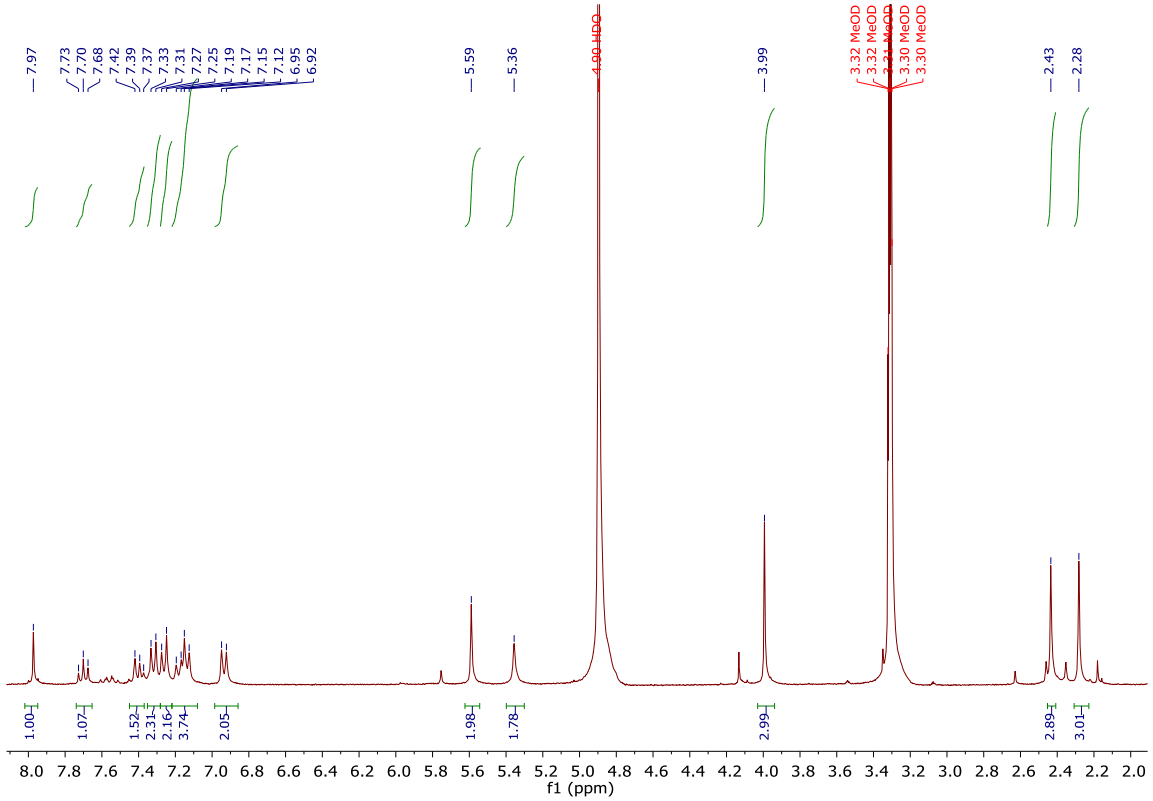


Figure S14: ^{1}H NMR spectrum of Ag^I complex **4** in MeOD.

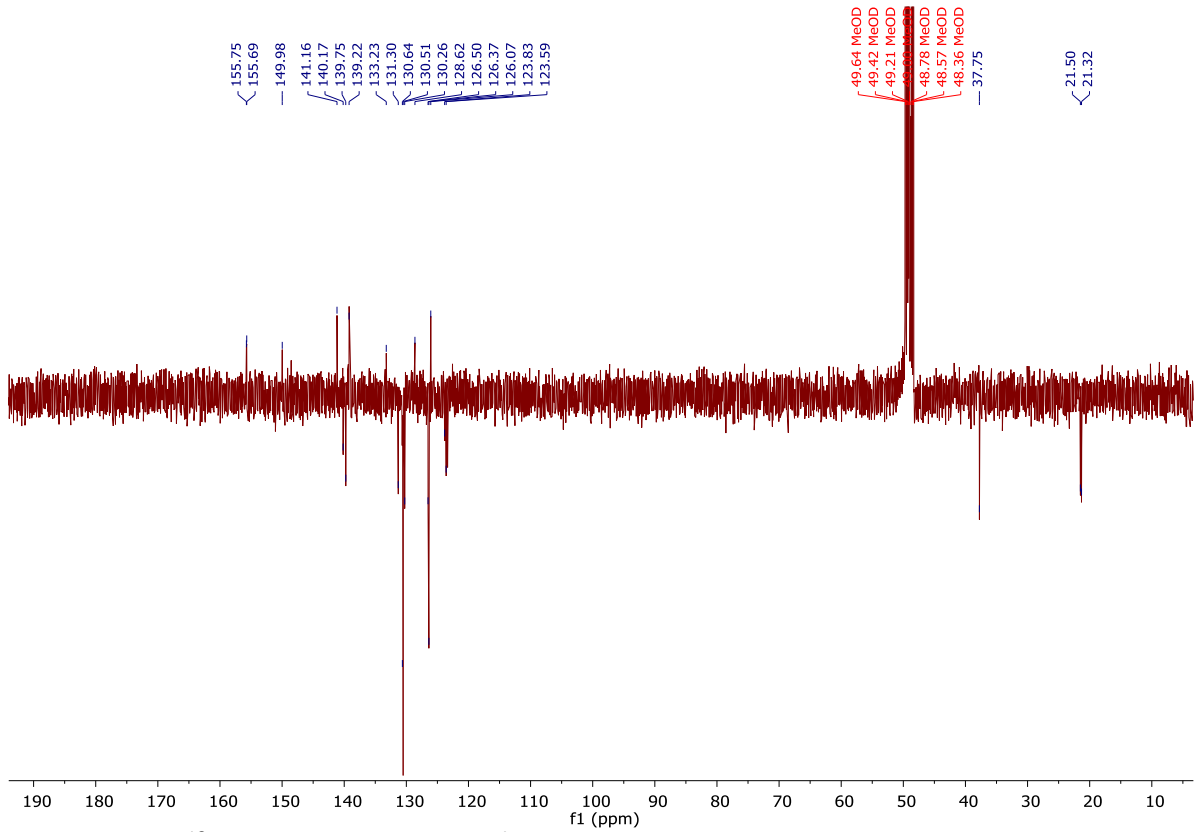
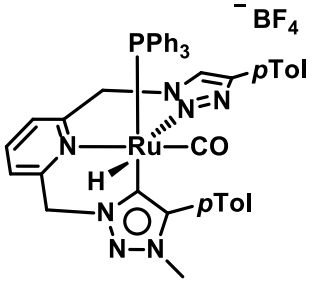


Figure S15: APT ^{13}C NMR spectrum of Ag^{I} complex **4** in MeOD.



Synthesis of [Ru(CO)(H)(PPh$_3$)(CNN)]BF$_4$; **5**. This complex was synthesized in analogy to complex **2** from Ag(I) complex **4 (**0.5 equiv.). Pale beige powder (23 mg, 0.025 mmol, 64%) IR ν(CO) 1949 cm^{-1}. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 40.9; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.59 (s, 1H, tz-C*H*), 7.90 (t, $^{3}J_{HH}$ = 7.7 Hz, 1H, Pyr-C*H*), 7.78 – 7.64 (m, 4H, Tol-C*H*), 7.59 – 7.14 (m, 20H, Tol-C*H*, PPh_3 and Pyr-C*H* overlapping), 7.07 – 6.95 (m, 1H, Pyr-C*H*), 6.18 (d, $^{3}J_{HH}$ = 13.7 Hz, 1H, CH_2), 6.07 (d, $^{2}J_{HH}$ = 15.4 Hz, 1H, CH_2), 5.90 (d, $^{2}J_{HH}$ = 14.1 Hz, 1H, CH_2), 4.82 (d, $^{2}J_{HH}$ = 15.8 Hz, 1H, CH_2), 3.79 (s, 3H, CH_3), 2.60 (s, 3H, CH_3), 2.46 (s, 3H, CH_3), -12.96 (d, $^{2}J_{PH}$ = 27.9 Hz, 1H, Ru-*H*); ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 166.7 (d, $^{2}J_{CP}$ = 76.9 Hz, C_{tzNHC}), 156.4 & 154.9 (Pyr-C_q), 149.2, 149.0, 140.5 (d, J_{CP} = 3.7 Hz, PPh_3), 139.0, 134.4, 134.2, 133.6, 133.4, 131.8, 130.3, 130.0, 129.8, 129.8, 129.2, 129.1, 128.9, 128.8, 128.8, 128.7, 127.7, 127.3, 126.4, 125.4, 125.0, 124.4 (tz-*C*H), 61.4 & 55.0 (*C*H$_2$), 37.2 (N-*C*H$_3$), 21.9 (Tol-*C*H$_3$), 21.6 (Tol-*C*H$_3$, Ru-CO not observed. MS(FD^{+}) for $C_{45}H_{42}N_7OPRu$: *m/z* calculated 828.22104 [M-BF_4]$^{+}$, observed 828.21537.

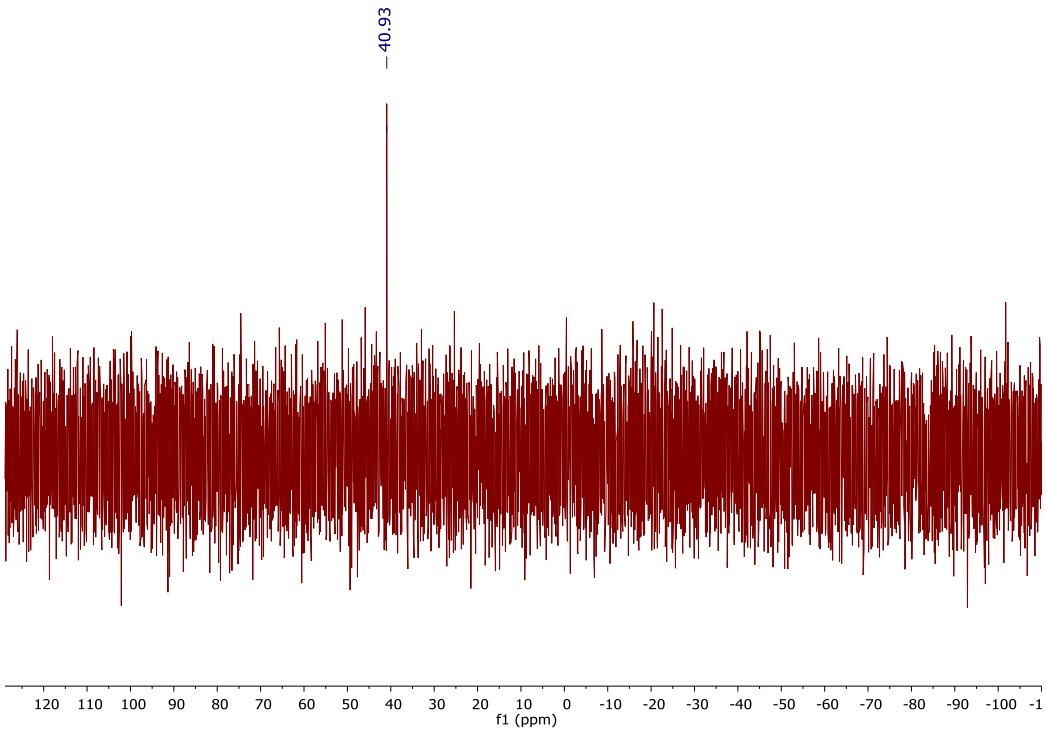


Figure S16: $^{31}P\{^{1}H\}$ NMR spectrum of Ru^{II} complex **5** in CD_2Cl_2.

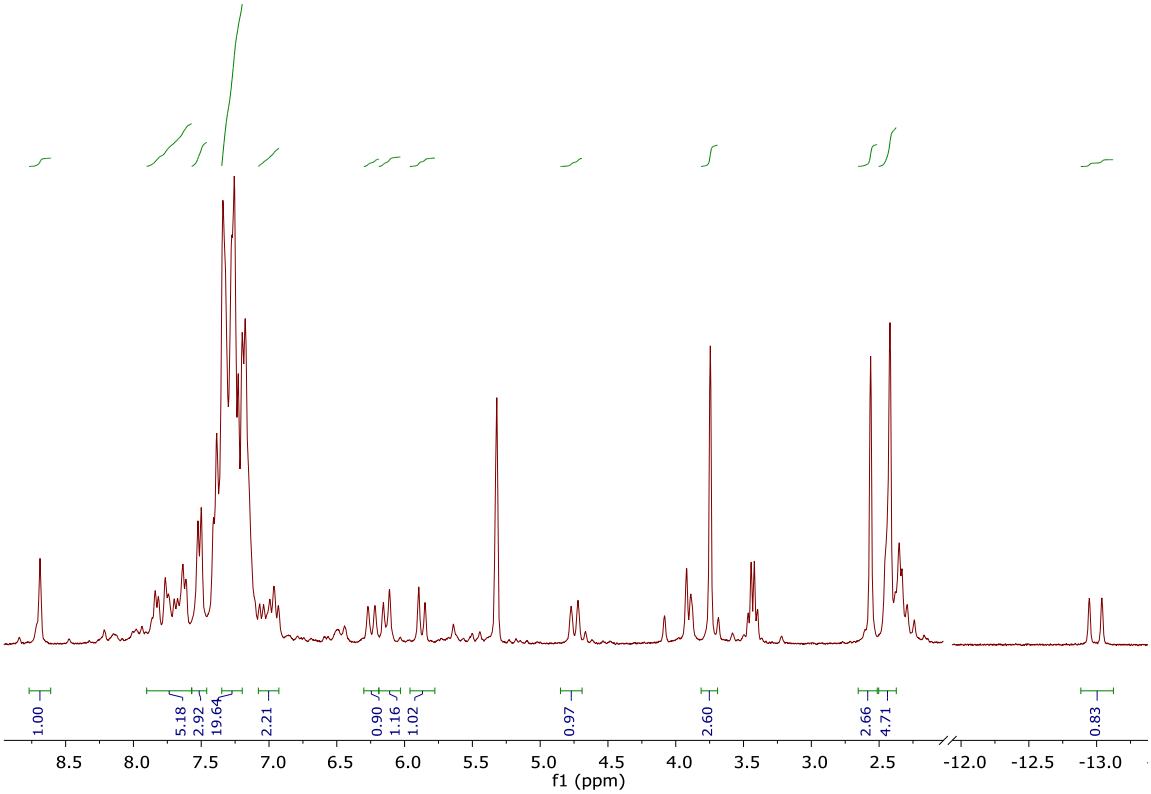


Figure S17: ^{1}H NMR spectrum of Ru^{II} complex **5** in CD_2Cl_2.

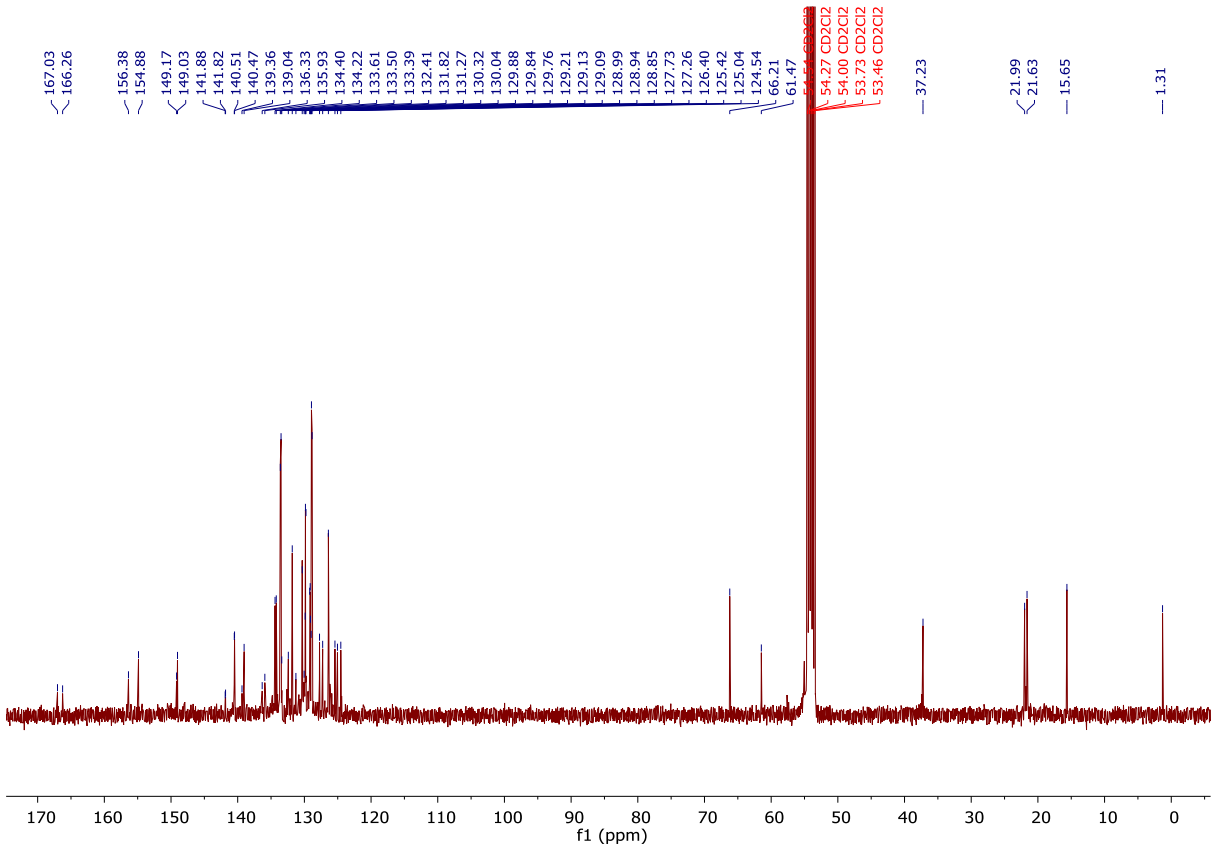


Figure S18: $^{13}C\{^{1}H\}$ NMR spectrum of Ru^{II} complex **5** in CD_2Cl_2.

Catalytic ester hydrogenation experiments

General procedure for catalytic ester hydrogenation reactions: The catalyst (3,75 µmol), KO*t*Bu (11 mg, 0.1 mmol for 20 mol%), Me_3NO (if applicable, 1.9 mg) and the substrate (if solid; 0.5 mmol) were weighed in a 4 mL GC-vial with a septum screw-cap charged with a stirring bar under an N_2 atmosphere. Subsequently, *p*-xylene (23.2 µL), the substrate (if liquid; 0.5 mmol) and THF (2 mL) were added. A needle was used to puncture the cap and a set of four vials was placed in a stainless steel autoclave (200 mL) under argon gas. The autoclave was flushed 2 times with 10 bar of H_2 and then pressurized to the desired pressure (5 or 50 bar), after which it was placed in a preheated oil bath (140 °C; built-in thermometer indicated 100 °C as the internal temperature of the autoclave). After allowing the autoclave to warm up (approximately 30 min.) the mixture was stirred for 2h after which the autoclave was cooled in an ice bath and the pressure was released. The conversions were determined by GC analysis as described in the general experimental details above.

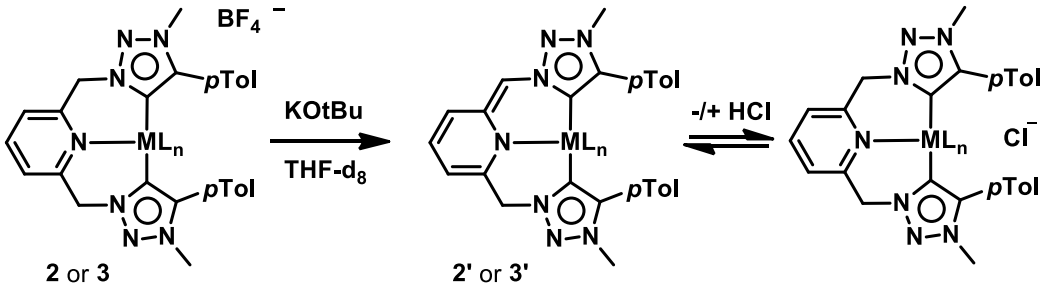
Table S1: The influence of additives on the catalytic hydrogenation of methyl benzoate.

	t (h)	p (bar)	mol% KOtBu	Conv. (%)	Yield (%)	Additive
1	2	50	20	62	49	-
2	2	50	20	67	66	Me_3NO
3	2	50	10	57	56	Me_3NO
4	2	50	2	0	0	Me_3NO

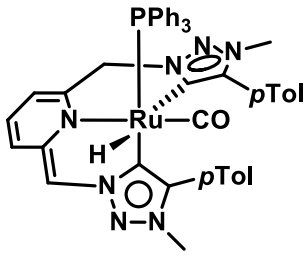
Conditions: 0.5 mmol ester, 0.5 mol% of **2**, 0.5 mol% of Me_3NO for entry 2-4, indicated amount of KO*t*Bu and H_2 pressure in 1,4-dioxane at 100 °C for 2 hours. The yield and conversion was determined by GC analysis with *p*-xylene as internal standard.

NMR reactivity experiments

General procedure for deprotonation/dearomatization of complexes:



To a solution of the CNC complex (1 equiv.) in THD-d_8 was added KO*t*Bu (1 equiv.) upon which an immediate color change to dark-red was observed. Low stability of the complexes prevented their isolation and full characterization.



[(CNC)Ru(CO)(H)(PPh_3)]*; **2'**. Dark-red solution. $^{31}P\{^1H\}$ NMR (162 MHz, THF-d_8) δ 55.3; ^1H NMR (300 MHz, THF-d_8) δ 7.74 – 7.04 (m, 19H, PPh_3 & 4H Tol-C*H*), 6.93 (d, $^3J_{HH}$ = 7.8 Hz, 2H, Tol-C*H*), 6.64 (d, $^3J_{HH}$ = 7.7 Hz, 2H, Tol-C*H*), 6.12 (d, $^2J_{HH}$ = 13.1 Hz, 1H, CH_2), 5.90 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Pyr-C*H*), 5.57 – 5.43 (m, 2H, C*H* and Pyr-C*H* overlapping), 5.13 (d, $^2J_{HH}$ = 13.1 Hz, 1H, CH_2), 4.90 (d, $^3J_{HH}$ = 8.8 Hz, 1H, Pyr-C*H*), 4.02 (s, 3H, N-CH_3), 3.17 (s, 3H, N-CH_3), 2.42 (s, 3H, Tol-CH_3), 2.39 (s, 3H, Tol-CH_3), -7.19 (d, $^2J_{PH}$ = 21.9 Hz, 1H, Ru-*H*); $^{13}C\{^1H\}$ NMR (75 MHz, THF) δ 138.8 (C_q), 137.6 (d, J_{CP} =12.1 Hz, PPh_3), 134.8, 133.8, 133.7, 133.7, 133.6, 133.4,

131.8 (d, J_{CP} = 9.5 Hz, PPh_3), 131.3, 130.6 (pyr-*C*H), 130.3, 129.4, 128.7, 128.4, 128.3, 128.2, 128.2, 128.0, 127.5, 127.4 (d, J_{PH} = 4,5 Hz, PPh_3), 126.9, 126.7, 116.8 (Pyr-*C*H), 100.4 (Pyr-*C*H), 94.5 (*C*H), 64.1 (CH_2), 35.6 (N-CH_3, 34.5 (N-CH_3), 20.4 (Tol-CH_3), 20.3 (Tol-CH_3).

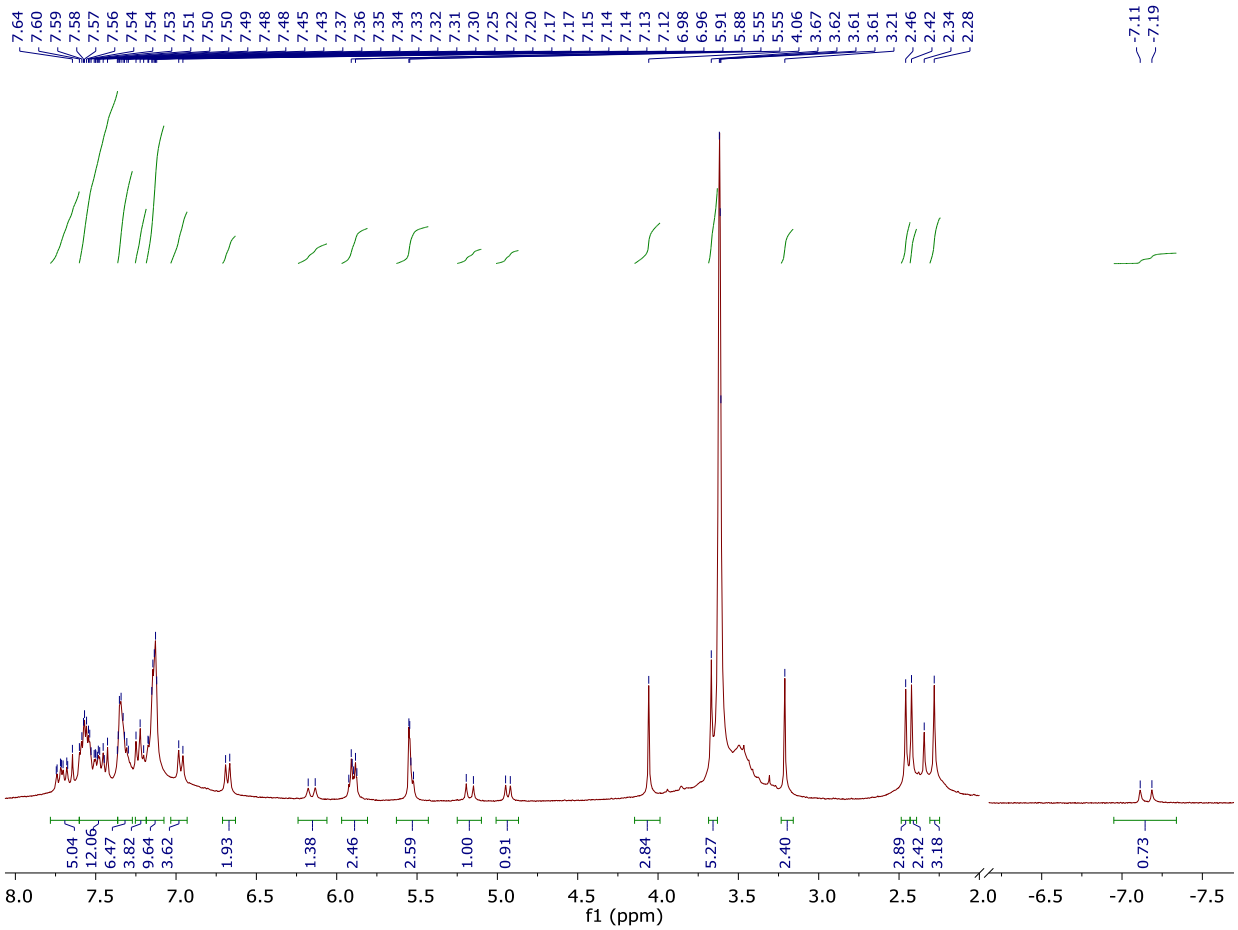
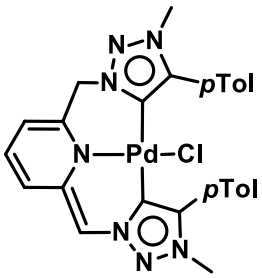


Figure S19: ^{1}H NMR spectrum of Ru^{II} complex **2'** in THF-d_8.

[(CNC)Pd(Cl)];* **3'**. Dark-red solution. ^{1}H NMR (300 MHz, THF-d_8) δ 7.44 (d, $^{3}J_{HH}$ = 8.0 Hz, 2H, Tol-C*H*), 7.35 (d, $^{3}J_{HH}$ = 8.0 Hz, 2H, Tol-C*H*), 7.15 – 7.01 (m, 4H, Tol-C*H*), 6.45 (dd, $^{3}J_{HH}$ = 9.0, 6.1 Hz, 1H, Pyr-C*H*), 6.27 (s, 1H, C*H*), 6.10 (d, $^{3}J_{HH}$ = 9.0 Hz, 1H, Pyr-C*H*), 5.70 (d, $^{3}J_{HH}$ = 6.2 Hz, 1H, Pyr-C*H*), AB system centered at δ_A 5.28 (d, $^{2}J_{HH}$ = 14.2 Hz, 1H, CH_2) & δ_B: 5.11 (d, $^{2}J_{HH}$ = 12.7 Hz, 1H, CH_2), 3.96 (s, 3H, 1H, NCH_3), 3.80 (s, 3H, NCH_3), 2.32 (s, 6H, CH_3). 467



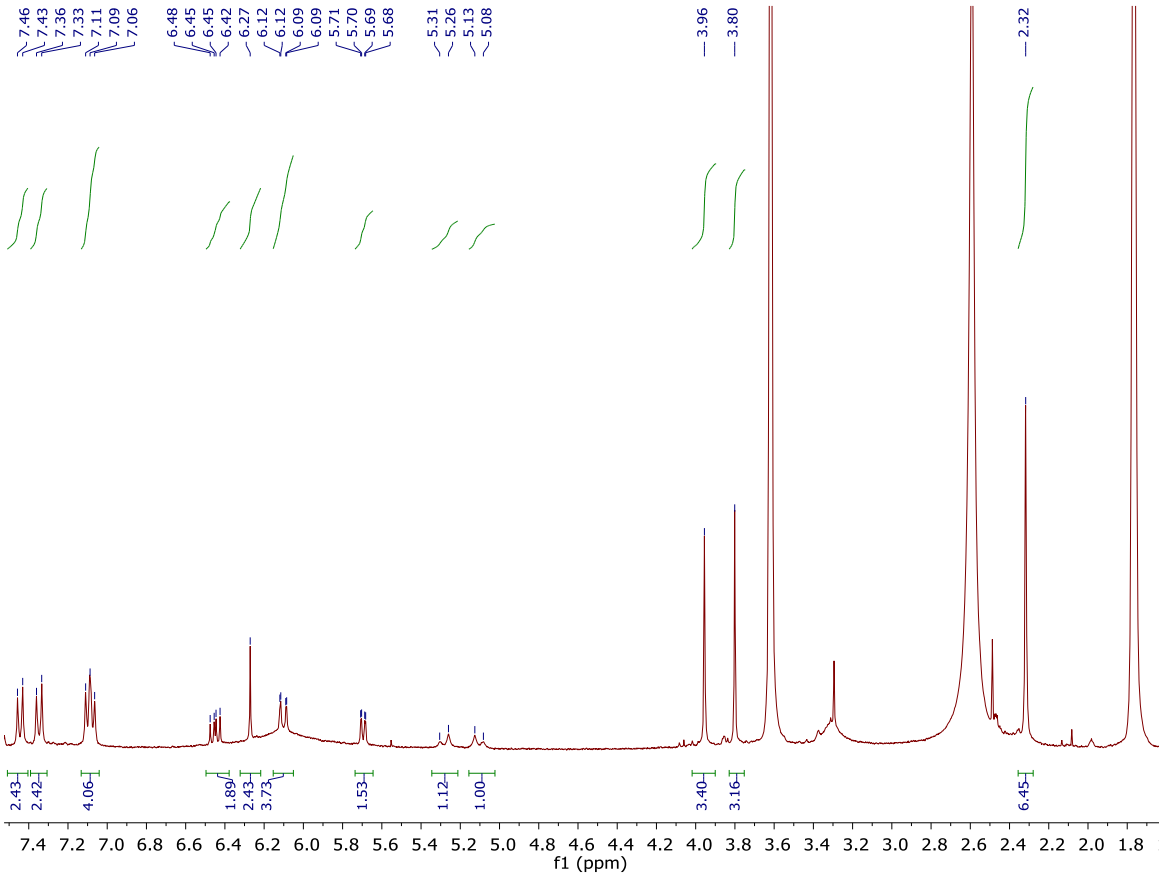


Figure S20: ^{1}H NMR spectrum of Pd^{II} complex **3'** in THF-d_8.

NMR experiment on the effect of possible vacant sites on Ru in the hydrogenolysis of esters. Trimethylamine *N*-oxide (Me_3NO; 5 mg, 0.07 mmol) was added to a solution of complex **2** (10 mg, 0.01 mmol) was dissolved in CD_2Cl_2 (1 mL) under N_2 atmosphere and stirred for 18 hours. The resulting solution was characterized by NMR spectroscopy as is described above.

NMR experiments under near-catalytic conditions: Complex **5** (~20 mg) was dissolved in THF-d_8 (0.6 mL) and KO*t*Bu was added (0, 10 or 20 equiv.) under nitrogen atmosphere. The mixture was transferred to a J.Young NMR pressure tube and pressurized with 5 bar H_2, after which a ^{1}H NMR spectrum was recorded. The tube was subsequently heated in an oil bath at 100 °C for two hours and analyzed by multinuclear NMR spectroscopy at room temperature.

DFT investigation *fac*/*mer* coordination of CNC ligand

Most lutidine-based pincer complexes, including those with more flexible six-membered chelate rings, adopt a meridional (*mer*) conformation.[1] However, a recent DFT and experimental study has shown that for [Ru(PNP)($PhCOO)_2$] the *fac* coordination mode was significantly more stable (yet inactive in direct insertion of CO_2 into the C-H bonds of arenes).[2] To gain insight in the reason for *fac* coordination in our case, we performed DFT calculations. The *mer* conformation turned out to be more thermodynamically favorable by 2.2 kcal/mol at the BP86/def2-TZVP level (Figure S1). This points to the *fac* configuration being the kinetic product, produced by these specific reaction conditions. Attempts to obtain the *mer* analogue synthetically have not been successful to date (combinations of various bases mentioned above or Ag(I) complex **4** and several ruthenium precursors ([($RuCl_2(MeCN)_4$,], [RuCl(CO)(H)($PPh_3)_3$], [$RuCl_2(PPh_3)_4$] and [Ru(*p*-cym)($CO)Cl_2$]) in various solvents (THF/DCM/MeCN) and temperatures (25-70 °C).[3,4]

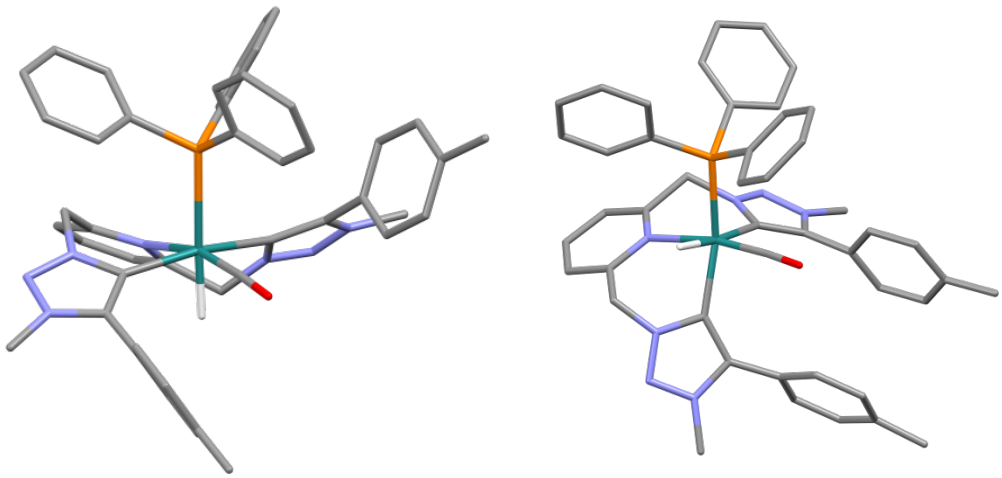


Figure S21: Computed DFT (BP86/def2-TZVP) structures of Ru CNC complexes with meridional (left) and facial (right) coordination. Hydrogen atoms, except for hydride and CH_2, are omitted for clarity.

References

(1) Gunanathan, C.; Milstein, D. *Chem. rev.* **2014**, *114*, 12024–12087.

(2) Stoychev, S. D.; Conifer, C. M.; Uhe, A.; Hölscher, M.; Leitner, W. *Dalton trans.***2014**, *43*, 11180–11189.

(3) Filonenko, G. A.; Cosimi, E.; Lefort, L.; Conley, M. P.; Copéret, C.; Lutz, M.; Hensen, E. J. M.; Pidko, E. A. *ACS Catal.* **2014**, *4*, 2667–2671.
(4) Fogler, E.; Balaraman, E.; Ben-David, Y.; Leitus, G.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2011**, *30*, 3826–3833.
(5) Armarego, W.; Perrin, D. D. *Purification of Laboratory Chemicals*; Fourth.; Pergamon, Oxford, 1997.