

Carbon dioxide reduction by mononuclear ruthenium polypyridyl complexes

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S1. Experimental section:

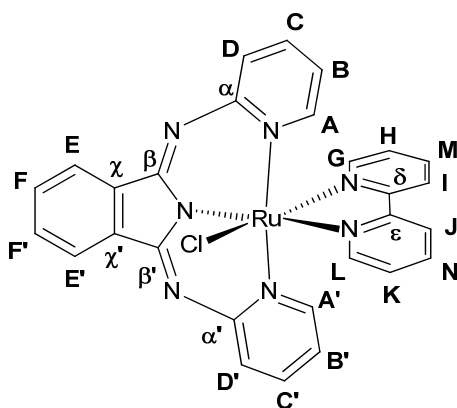
Materials

All reagents used in present work were obtained from Aldrich Chemical Co., Alfa Aesar or Carbosynth Ltd. and were used without further purification. Synthesis grade organic solvents were obtained from SDS and were routinely degassed with Argon. Ethanol was dried with 3.5 Å molecular sieve and DCM, hexane and diethyl ether were used from the SPS. 2,2,2-Trifluoroethanol (TFE) was obtained from Alfa Aesar and was used without further purification. 4,4'-Dimethoxy-2,2'-bipyridine and NaBH₄ were purchased from Aldrich Chemical Co. and 4,4'-Bis(ethoxycarbonyl)-2,2'-bipyridine were purchased from Carbosynth Ltd. and used without further purification. Carbon dioxide and hydrogen gases were obtained from Carbueros Metálicos S. A..

Preparations

[Ru^{III}(Hbid)Cl₃]¹, [Ru^{II}Cl(bpy)(trpy)]PF₆², were prepared as described in the literature. All synthetic manipulations were routinely performed under argon/nitrogen atmosphere using Schlenck and vacuum line techniques.

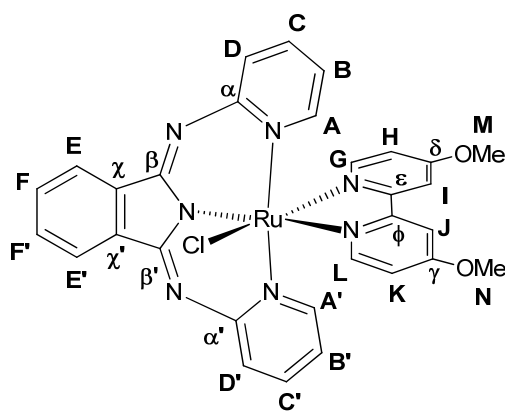
Synthesis of Ru^{II}(bid)(bpy)Cl·0.5LiCl·0.5Et₂O (1)



100 mg (0.197 mmol) of Ru(Hbid)Cl₃ were solved in 50 mL of ethanol. 37 mg (0.237 mmol) of 2,2'-bipyridine were added. The mixture was heated to reflux for 1h. 42 mg (0.986 mmol) of LiCl and 0.1 mL (0.790 mmol) of triethylamine were added. The mixture was heated to reflux for 4h. Complex **1** was separated by filtration and cleaned with diethylether Yield 50.0 mg (0.0846 mmol) 42.9%. Anal. Calc. for C₃₀H₂₅Cl_{1.5}Li_{0.5}N₇O_{0.5}Ru: C, 55.49; H, 3.88; N, 15.10. Found: C, 55.23; H, 3.91; N,

14.73. ^1H NMR (500 MHz, DMF- d_7 , 298 K): δ 10.31 (d, 1H, $J_{\text{LK}} = 5.4$ Hz, H_{L}), 8.84 (d, 1H, $J_{\text{JN}} = 7.6$ Hz, H_{J}), 8.55 (d, 1H, $J_{\text{IM}} = 8.0$ Hz, H_{I}), 8.31 (td, 1H, $J_{\text{NJ}} = J_{\text{NK}} = 7.6$ Hz, $J_{\text{NL}} = 1.5$ Hz, H_{N}), 8.18 (dd, 2H, $J_{\text{EF}} = J_{\text{E'F'}} = 5.4$ Hz, $J_{\text{EF'}} = J_{\text{E'F}} = 3.0$ Hz, H_{E} , $\text{H}_{\text{E'}}$), 8.06 (ddd, 1H, $J_{\text{KL}} = 7.6$ Hz, $J_{\text{KN}} = 5.4$ Hz, $J_{\text{KJ}} = 1.2$ Hz, H_{K}), 7.72 (dd, 2H, $J_{\text{FE}} = J_{\text{F'E'}} = 5.4$ Hz, $J_{\text{FE'}} = J_{\text{F'E}} = 3.0$ Hz, H_{F} , $\text{H}_{\text{F'}}$), 7.65 (ddd, 1H, $J_{\text{MI}} = 7.2$ Hz, $J_{\text{MH}} = 8.0$ Hz, $J_{\text{MG}} = 1.4$ Hz, H_{M}), 7.61-7.56 (m, 4H, H_{A} , $\text{H}_{\text{A'}}$, H_{C} , $\text{H}_{\text{C'}}$), 7.55-7.49 (m, 3H, H_{G} , H_{D} , $\text{H}_{\text{D'}}$), 7.06 (ddd, 1H, $J_{\text{HG}} = 7.2$ Hz, $J_{\text{HM}} = 5.9$ Hz, $J_{\text{HI}} = 1.3$ Hz, H_{H}), 6.55 (td, 2H, $J_{\text{BA}} = J_{\text{BC}} = 6.6$ Hz, $J_{\text{BD}} = 1.7$ Hz, H_{B} , $\text{H}_{\text{B'}}$). ^{13}C NMR (125 MHz, DMF- d_7 , 298 K): δ 160.5 (C_{δ}), 160.2 (C_{ϵ}), 158.2 (C_{α} , $\text{C}_{\alpha'}$), 154.5 (C_{L}), 153.0 (C_{A} , $\text{C}_{\text{A'}}$), 152.4 (C_{β} , $\text{C}_{\beta'}$), 150.9 (C_{G}), 142.1 (C_{χ} , $\text{C}_{\chi'}$), 136.4 (C_{N}), 135.0 (C_{M}), 134.6 (C_{C} , $\text{C}_{\text{C'}}$), 130.0 (C_{F} , $\text{C}_{\text{F'}}$), 128.4 (C_{K}), 128.2 (C_{D} , $\text{C}_{\text{D'}}$), 126.2 (C_{H}), 124.5 (C_{J}), 124.2 (C_{I}), 121.1 (C_{E} , $\text{C}_{\text{E'}}$), 117.1 (C_{B} , $\text{C}_{\text{B'}}$). UV-vis (CH_2Cl_2) [λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 299 (43312), 374 (28149), 428 (10584), 586 (5719), 658 (5020). MALDI(+)-MS (DCM): 556 [$\text{M}-\text{Cl}$] $^+$. $E_{1/2}(\text{CH}_2\text{Cl}_2, \text{V vs SSCE})$: 0.295 ($E_{\text{p,a}} = 404$ mV, $E_{\text{p,c}} = 185$ mV, $\Delta E = 219$ mV).

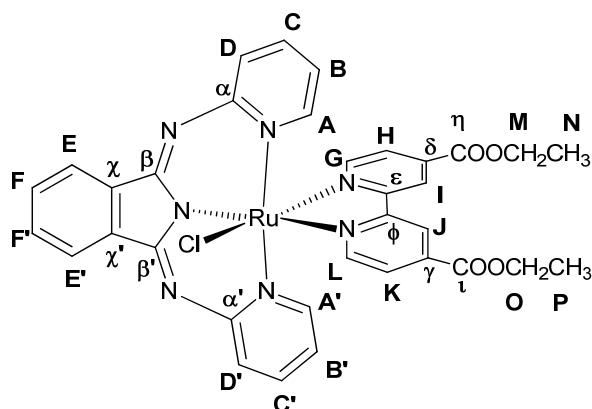
Synthesis of $\text{Ru}^{\text{II}}(\text{bid})(4,4'\text{-(MeO)}_2\text{bpy})\text{Cl}\cdot 1.5\text{H}_2\text{O}$ (**1d**)



To a mixture of 50.0 mg (0.0987 mmol) of $\text{Ru}(\text{HBid})\text{Cl}_3$ and 25.6 mg (0.237 mmol) of 4,4'-methoxy-2,2'-bipyridine were dissolved in 20 mL of ethanol. After the mixture was heated to reflux for 1 h, 21.8 mg (0.495 mmol) of LiCl and 50.0 μL (0.359 mmol) of triethylamine were added. The mixture was heated to reflux for 4 h. Upon cooling to room temperature, the precipitate appeared which was separated by filtration and cleaned with diethylether. Yield. 50.3 mg (0.0773 mmol) 77.8%. Anal. Calc. for $\text{C}_{30}\text{H}_{27}\text{ClN}_7\text{O}_{3.5}\text{Ru}$: C, 53.14; H, 4.01; N, 14.46. Found: C, 53.22; H, 3.56; N, 14.23. ^1H NMR (500 MHz, DMF- d_7 , 298 K): δ 9.99 (d, 1H, $J_{\text{LK}} = 6.4$ Hz, H_{L}), 8.52 (d, 1H, $J_{\text{JK}} = 2.7$ Hz, H_{J}), 8.23 (d, 1H, $J_{\text{IH}} = 2.8$ Hz, H_{I}), 8.18 (dd, 2H, $J_{\text{EF}} = J_{\text{E'F'}} = 5.4$ Hz, $J_{\text{EF'}} = J_{\text{E'F}}$

= 3.0 Hz, H_E, H_{E'}), 7.79 (dd, 1H, $J_{DC} = 6.5$ Hz, $J_{DB} = 1.6$ Hz, H_D, H_{D'}), 7.73 (dd, 2H, $J_{KL} = 6.4$ Hz, $J_{KJ} = 2.7$ Hz, H_K), 7.70 (dd, 2H, $J_{FE} = J_{F'E'} = 5.4$ Hz, $J_{FE'} = J_{F'E} = 3.0$ Hz, H_F, H_{F'}), 7.58 (ddd, 2H, $J_{BA} = 7.8$ Hz, $J_{BC} = 6.5$ Hz, $J_{BD} = 1.6$ Hz, H_B, H_{B'}), 7.54 (dd, 2H, $J_{AB} = 7.8$ Hz, $J_{AC} = 1.6$ Hz, H_A, H_{A'}), 7.09 (d, 1H, $J_{GH} = 6.7$ Hz, H_G), 6.71 (dd, 1H, $J_{HG} = 6.7$ Hz, $J_{HI} = 2.8$ Hz, H_H), 6.55 (td, 2H, $J_{CB} = J_{CD} = 6.5$ Hz, $J_{CA} = 1.6$ Hz, H_C, H_{C'}), 4.23 (s, 3H, H_N), 3.84 (s, 3H, H_M). ¹³C NMR (125 MHz, DMF-*d*₇, 298 K): δ 166.9 (C_γ), 165.9 (C_δ), 161.1 (C_ε), 160.9 (C_φ), 158.4 (C_α, C_{α'}), 154.9 (C_L), 153.4 (C_D, C_{D'}), 151.3 (C_G), 151.3 (C_β, C_{β'}), 142.4 (C_χ, C_{χ'}), 133.8 (C_B, C_{B'}), 129.6 (C_F, C_{F'}), 128.3 (C_A, C_{A'}), 120.8 (C_E, C_{E'}), 116.5 (C_C, C_{C'}), 115.6 (C_K), 112.9 (C_H), 111.0 (C_J), 111.0 (C_I), 57.1 (C_N), 56.7 (C_M). UV-vis (CH₂Cl₂) [λ_{max} , nm (ϵ , M⁻¹cm⁻¹): 277 (35529), 294 (36432), 312 (30846), 378 (33530), 416 (12894), 601 (4706), 668 (5517)]. MALDI(+)-MS (DCM): 651 M⁺, 616 [M-Cl]⁺. E_{1/2}(CH₂Cl₂, V vs SSCE): 0.168 (E_{p,a} = 224 mV, E_{p,c} = 95 mV, $\Delta E = 129$ mV).

Synthesis of Ru^{II}(bid)(4,4'-(EtOCO)₂bpy)Cl·LiCl (1w)



To a mixture of 100 mg (0.197 mmol) of Ru(HBid)Cl₃ and 71.2 mg (0.237 mmol) of 4,4'-ethoxycarbonyl-2,2'-bipyridine were dissolved in 20 mL of ethanol. After the mixture was heated to reflux for 1 h, 45.6 mg (1.08 mmol) of LiCl and 100 μ L (0.718 mmol) of triethylamine were added. The mixture was heated to reflux for 4 h. After cooling to room temperature the resulting solution was kept in the freezer overnight. The precipitate obtained was separated by filtration and cleaned with diethylether. Yield. 65.2 mg (0.0887 mmol) 45.0%. Anal. Calc. for C₃₄H₂₈Cl₂LiN₇O₄Ru: C, 52.52, H, 3.63; N, 12.61. Found: C, 52.34; H, 3.64; N, 12.48. ¹H NMR (400 MHz, DMF-*d*₇, 298 K): δ 10.56 (d, 1H, $J_{LK} = 5.9$ Hz, H_L), 9.32 (s, 1H, H_J), 9.01 (s, 1H, H_I), 8.50 (d, 1H, $J_{KL} = 5.9$ Hz, H_K), 8.16 (dd, 2H, $J_{EF} = J_{E'F'} = 5.4$ Hz, $J_{EF'} = J_{E'F} = 3.0$ Hz, H_E, H_{E'}), 8.04 (d,

^1H , $J_{\text{GH}} = 6.2$ Hz, H_{G}), 7.74 (dd, 2H, $J_{\text{FE}} = J_{\text{F'E'}} = 5.4$ Hz, $J_{\text{FE'}} = J_{\text{F'E}} = 3.0$ Hz, H_{F} , $\text{H}_{\text{F'}}$), 7.61 (ddd, 2H, $J_{\text{BA}} = 7.8$ Hz, $J_{\text{BC}} = 6.3$ Hz, $J_{\text{BD}} = 1.3$ Hz, H_{B} , $\text{H}_{\text{B'}}$), 7.53 (d, 1H, $J_{\text{HG}} = 6.2$ Hz, H_{H}), 7.48 (dd, 2H, $J_{\text{AB}} = 7.8$ Hz, $J_{\text{AC}} = 1.4$ Hz, H_{A} , $\text{H}_{\text{A'}}$), 7.42 (dd, 2H, $J_{\text{DC}} = 6.3$ Hz, $J_{\text{DB}} = 1.3$ Hz, H_{D} , $\text{H}_{\text{D'}}$), 6.58 (td, 2H, $J_{\text{CB}} = J_{\text{CD}} = 6.3$ Hz, $J_{\text{CA}} = 1.4$ Hz, H_{C} , $\text{H}_{\text{C'}}$), 4.58 (q, 2H, $J_{\text{OP}} = 7.1$, H_{O}), 4.31 (q, 2H, $J_{\text{MN}} = 7.1$, H_{M}), 1.50 (t, 3H, $J_{\text{PO}} = 7.1$, H_{P}), 1.29 (t, 3H, $J_{\text{NM}} = 7.1$, H_{N}). ^{13}C NMR (100 MHz, $\text{DMF-}d_7$, 298 K): δ 165.1 (C_{I}), 164.5 (C_{N}), 161.6 (C_{E}), 161.2 (C_{O}), 158.0 (C_{α} , $\text{C}_{\alpha'}$), 155.6 (C_{L}), 153.7 (C_{β} , $\text{C}_{\beta'}$), 153.0 (C_{D} , $\text{C}_{\text{D'}}$), 152.2 (C_{G}), 141.9 (C_{γ} , $\text{C}_{\gamma'}$), 136.3 (C_{γ}), 135.7 (C_{B} , $\text{C}_{\text{B'}}$), 135.1 (C_{δ}), 130.3 (C_{F}), 128.2 (C_{A} , $\text{C}_{\text{A'}}$), 127.4 (C_{K}), 125.1 (C_{H}), 124.0 (C_{J}), 123.4 (C_{I}), 121.3 (C_{E}), 118.0 (C_{C} , $\text{C}_{\text{C'}}$), 62.9 (C_{O}), 62.5 (C_{M}), 14.4 (C_{P}), 14.2 (C_{N}). UV-vis (CH_2Cl_2) [λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$)]: 257 (31693), 306 (39071), 320 (35552), 360 (23322), 434 (16728), 562 (7656), 610 (12979). MALDI(+)-MS (DCM): 735 M^+ , 700 $[\text{M}-\text{Cl}]^+$. $E_{1/2}(\text{CH}_2\text{Cl}_2, \text{V vs SSCE})$: 0.407 ($E_{\text{p,a}} = 452$ mV, $E_{\text{p,c}} = 362$ mV, $\Delta E = 90$ mV).

Standard procedure for catalytic CO_2 hydrogenation.

Method A. HEL multi reactor: Catalytic reactions were run with a HEL multireactor autoclave which consists on a cylindrical vessel (7.5 cm of diameter and 15 cm high in 316ss), it has drilled holes to take 24 vials (10 mm diameter x 75 mm high). A cover is placed over the 24 vials, acting as a condenser to prevent solvent loss. This cover has fittings to allow active flow of coolant and also “cold fingers” to ensure refluxing (All wetted parts are made of 316ss). This cover is secured to the base with a screw-on ring. In each vial of the reactor 0.8 mL of complex solution were added and in the cases using 0.1 mL of amine. After having all the solvents and reagents distributed in all the tubes, the multireactor was closed and degassed three times with nitrogen gas. After that, the autoclave's lid was cooled to 5 °C (and was kept at this temperature during the reaction with an oil circulation bath) and the reactor was introduced to an oil bath previously heated at the desired temperature. At that moment stirring at 500 rpm also started and was considered to be the initial time of the reaction. To stop the reaction the multireactor was cooled with an ice bath and the temperature of the reactor's lid warmed to 25 °C. The whole reactor was depressurized and this was considered the final time of the reaction. The samples were analyzed by ^1H NMR, taking 0.2 mL of the reaction solution and mixing with them with 0.25 mL of D_2O containing DMF as

internal standard (120 μL in 10 mL). Three replicates were performed for each measurement.

Method B. SPR16 Slurry Phase Reactor (parallel autoclave system): Catalytic reactions were run with an SPR16 Slurry Phase Reactor which is a completely automated reactor system consisting 16 autoclaves (15 mL). Once programme started, firstly leak test for each autoclave was done and then each reactor was purged with nitrogen gas. Afterwards, into each autoclave of the reactor 4.0 mL (solvent/amine = 9/1) of complex solution were added from top of the vessel under flow of nitrogen gas. After having all the solvents and reagents distributed in all the vessels, stirring at 1000 rpm started, followed by pressurizing with CO_2 gas and then H_2 gas at the desired pressures. After this, temperature was increased to the desired temperature. When reached at desired temperature, that moment was considered to be the initial time. After the reaction time, each reactor was cooled down to room temperature and depressurized. When started cooling, that moment was considered to be the final time of the reaction. . The samples were analyzed by ^1H NMR, taking 0.3 mL of the reaction solution and mixing with them with 0.2 mL of D_2O containing DMF as internal standard (120 μL in 10 mL). Two replicates were performed for each measurement.

Generation of ruthenium hydride (1-H) species and ruthenium formate species (1-OCHO). To a gas tight NMR tube 0.3 mL of 16.9 mM dry $\text{DMF-}d_7$ solution of complex **1** (5.0 μmol), 0.2 mL of 250 mM dry $\text{DMF-}d_7$ solution of NaBH_4 (50 μmol , 10 eq.) and 0.1 mL of 54.6 mM $\text{DMF-}d_7$ solution of Cp_2Fe (5.5 μmol , as internal standard) were added. This reaction was monitored every 10 min for 130 min by ^1H NMR spectroscopy at 65 $^\circ\text{C}$. After 130 min, reaction mixture was cooled down to room temperature and 1 bar of CO_2 was introduced. The colour of reaction mixture immediately turned dark green to dark blue green. ^1H NMR (500 MHz, $\text{DMF-}d_7$, 338 K) for Ru-H species (**1-H**): δ 10.11 (d, 1H), 8.65 (d, 1H), 8.48 (d, 1H), 8.16 (br, 2H), 8.03 (overlapped with the signal of DMF, 1H), 7.91 (br d, 2H), 7.68- (m, 2H), 7.55 (br, 2H), 7.45 (t, 2H), 7.36 (br, 2H), 7.17 (br d, 1H), 7.11 (br t, 1H), 6.18 (td, 1H), -8.48 (s, 1H, Ru-H). ^1H NMR (500 MHz, $\text{DMF-}d_7$, 298 K) for Ru-O-CHO species (**1-O-CHO**): δ 9.76 (d, 1H), 8.90 (d, 1H), 8.59 (d, 1H), 8.37 (overlapped with unknown product derived from NaBH_4 with CO_2 , 1H), 8.21 (dd, 2H), 8.11 (t, 1H), 7.75 (dd, 2H), 7.7-7.6 (m, 5H), 7.57 (d, 2H), 7.45 (d, 1H), 7.25 (s, 1H, Ru-OCHO), 7.06 (t, 1H), 6.63 (td, 2H).

Alternate method for the direct generation of ruthenium formate species (1-O-CHO) from complex 1. To a gas tight NMR 2.0 mg (3.4 μmol) of complex **1**, 1.1 mg (17 μmol) of NaOCHO and 0.6 mL of DMF- d_7 were added. This reaction mixture was heated to 80 °C for 20 hours. 18% of complex **1** converted to formate species (1-O-CHO).

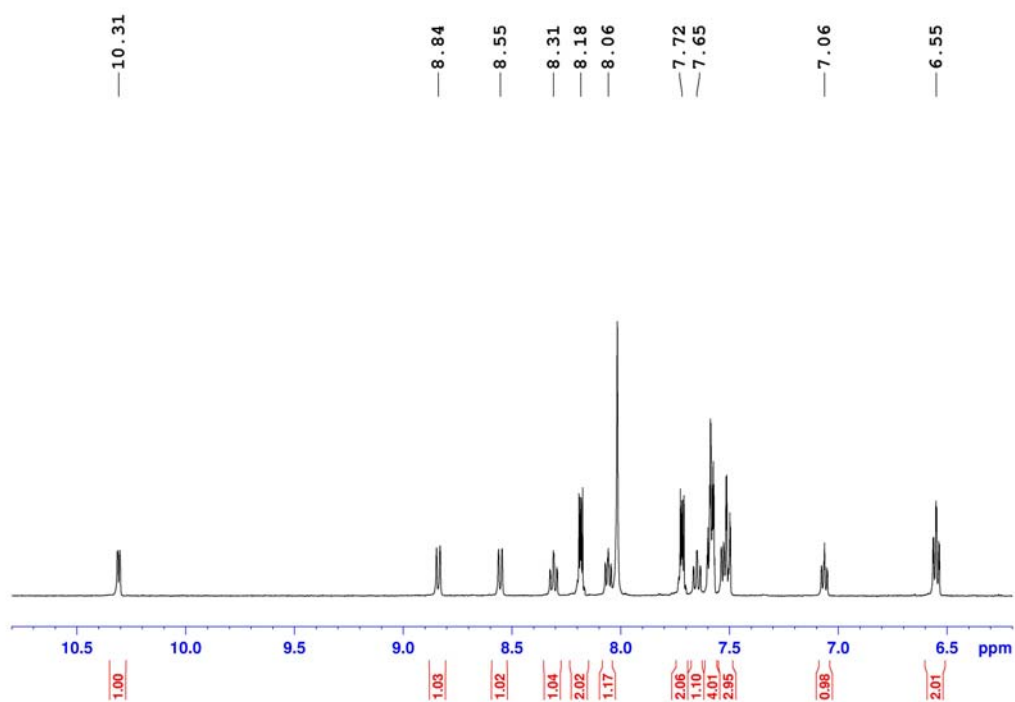
Instrumentation and measurements

Cyclic voltammetric (CV) experiments were performed in a IJ-Cambria IH-660 potentiostat, using a three electrode cell. Glassy carbon disk electrodes (3 mm diameter) from BAS were used as working electrode, platinum wire as auxiliary and SSCE as the reference electrode. Cyclic voltammograms were recorded at 100 mV/s scan rate under nitrogen atmosphere. The complexes were dissolved in previously degassed dichloromethane containing the necessary amount of (*n*-Bu₄N)(PF₆), used as supporting electrolyte, to yield a 0.1 M ionic strength solution. All $E_{1/2}$ values reported in this work were estimated from cyclic voltammetry as the average of the oxidative and reductive peak potentials $(E_{p,a}+E_{p,c})/2$. Unless explicitly mentioned the concentration of the complexes were approximately 1 mM. The NMR spectroscopy was performed on bruker avance 400 MHz bruker avance II and bruker avance 500 MHz. Samples were run in DMF- d_7 . The ESI mass spectroscopy experiments were performed on a Waters Micromass LCT Premier equipment, respectively. UV-Vis spectroscopy was performed on a Cary bio 50 UV-vis spectrophotometer with 1 cm quartz cells.

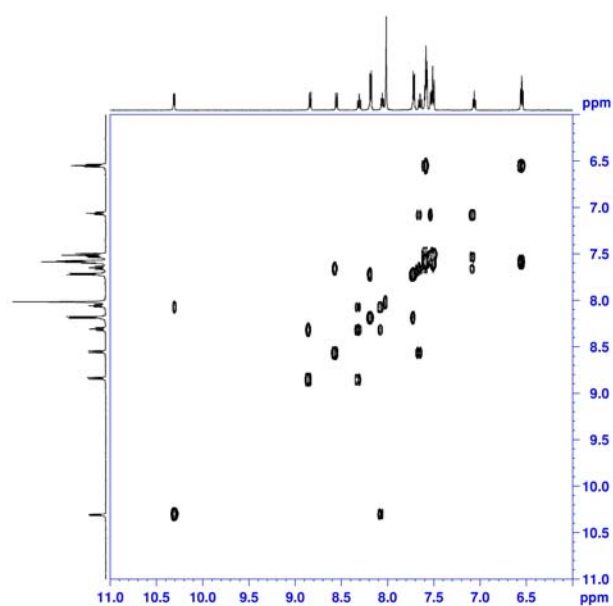
S2. NMR:

Figure S1. 1D and 2D NMR spectra (500 MHz, 298K, DMF-*d*₇) for complex **1**: (a) ¹H-NMR, (b) COSY, (c) NOESY (d) DEPTQ135 (e) HSQC and (f) HMBC.

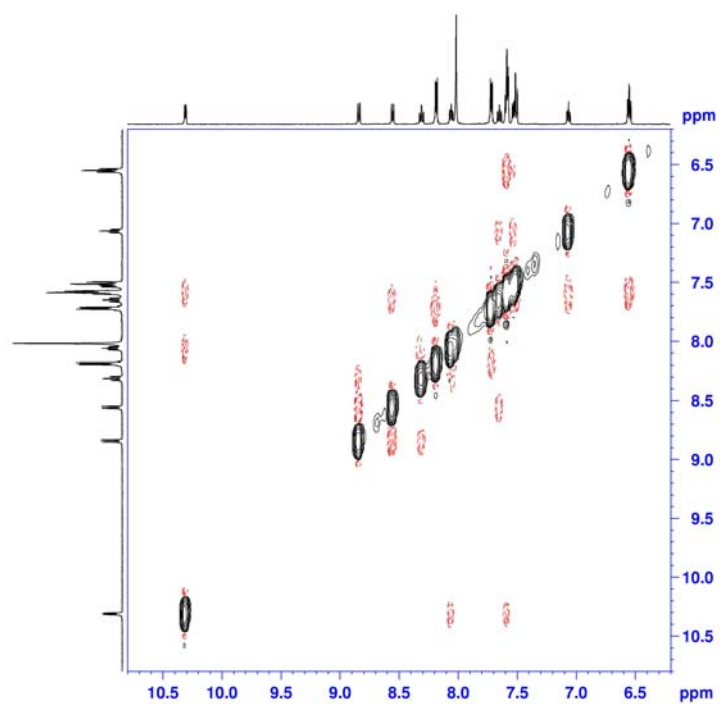
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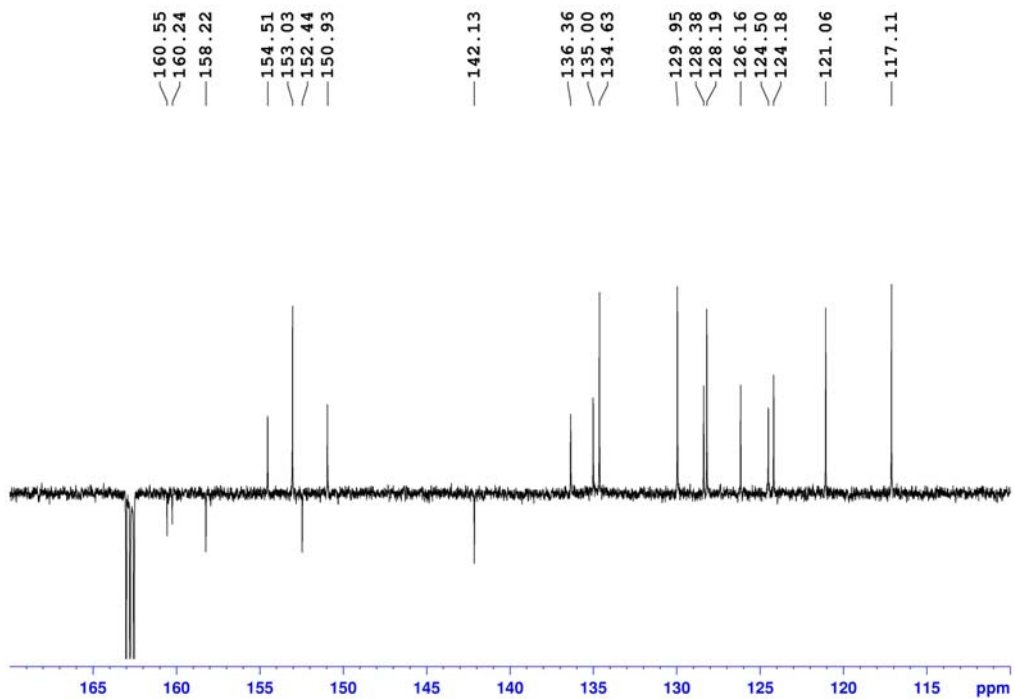
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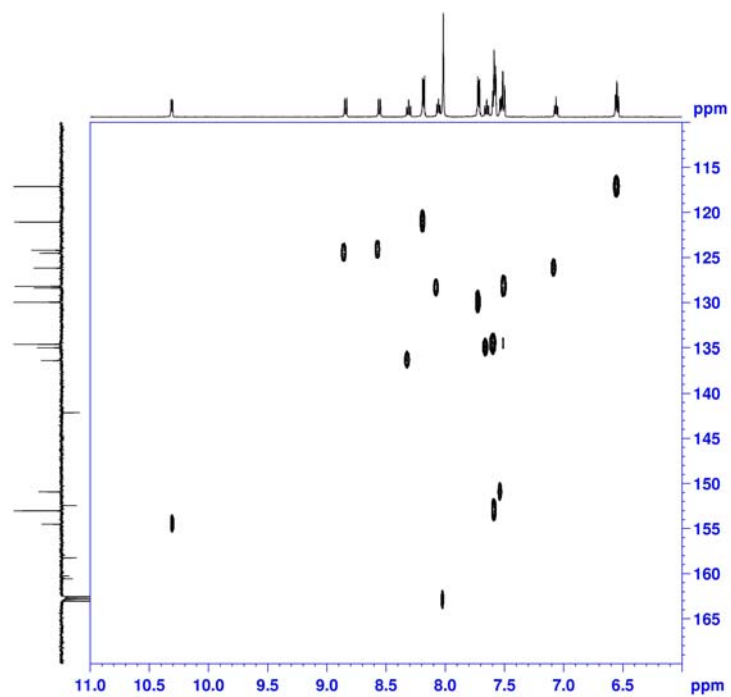
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(d)



(e)



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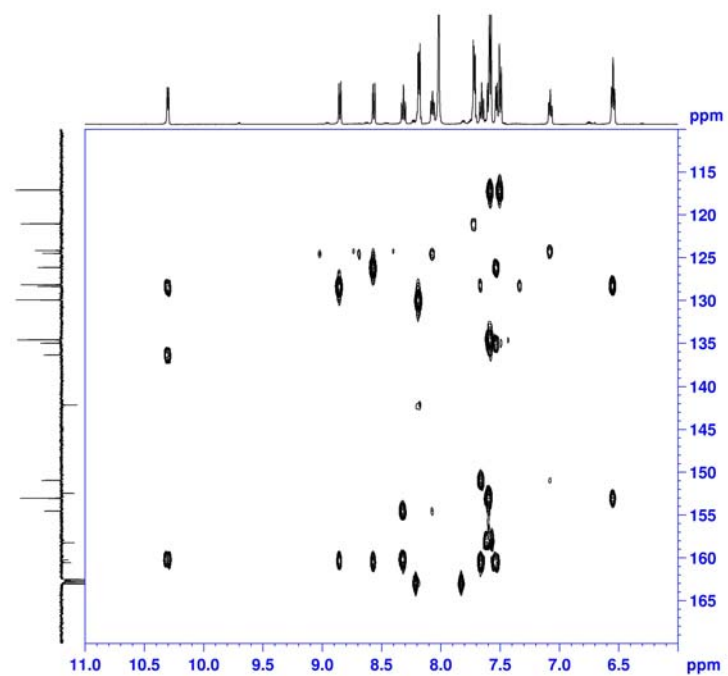
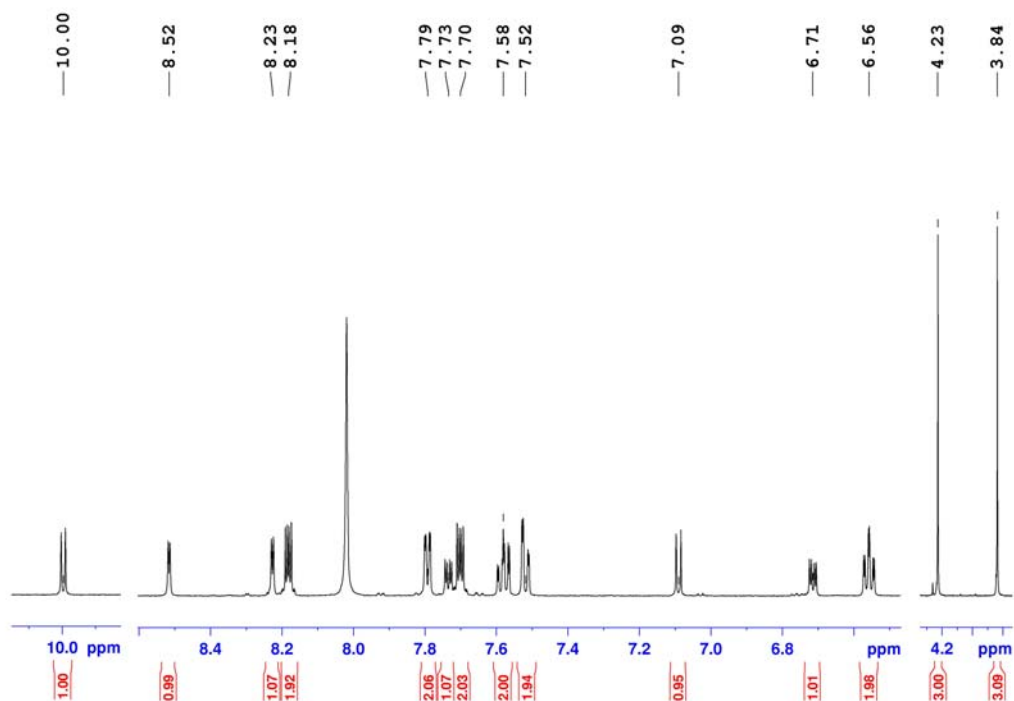
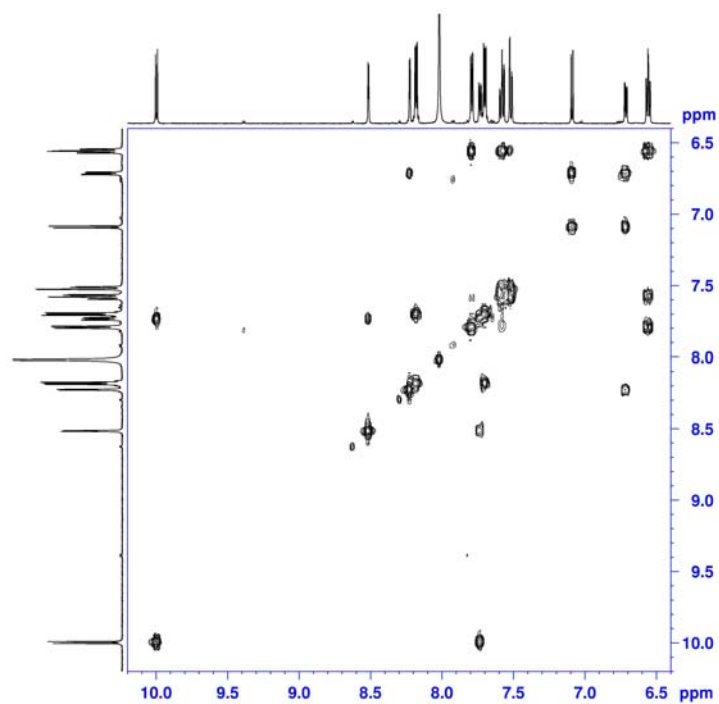


Figure S2. 1D and 2D NMR spectra (500 MHz, 298K, DMF-*d*₇) for complex **1d**: (a) ¹H-NMR, (b) COSY, (c) NOESY (d) DEPTQ135 (e) HSQC and (f) HMBC.

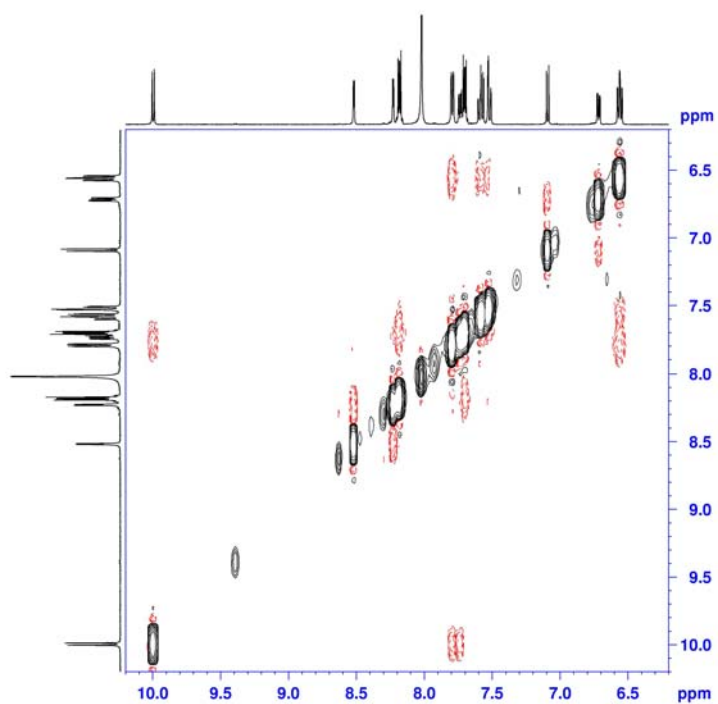
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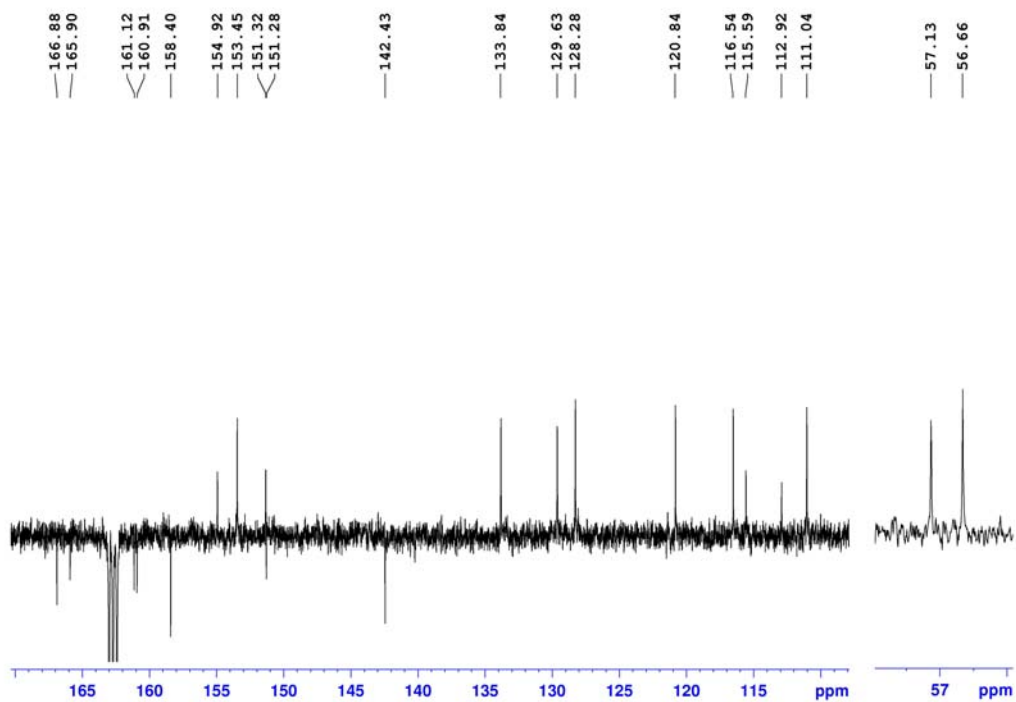
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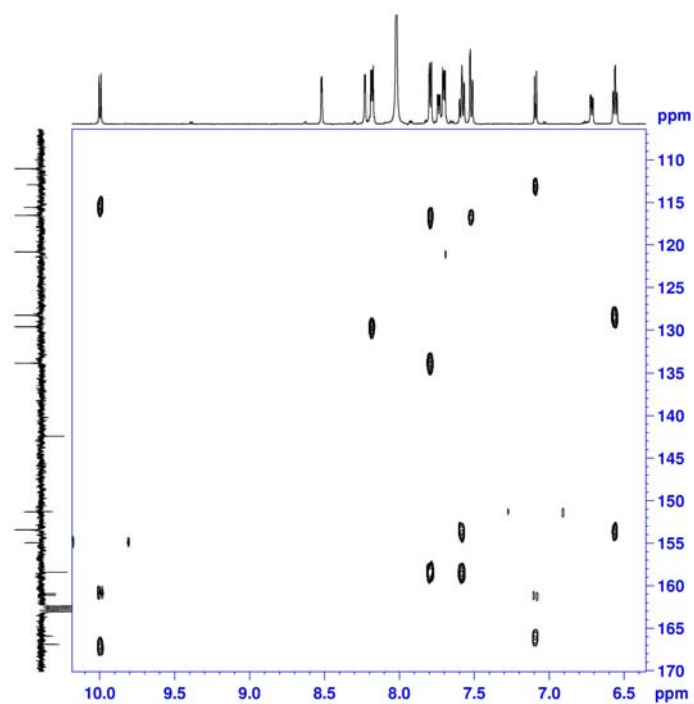
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(d)



(e)



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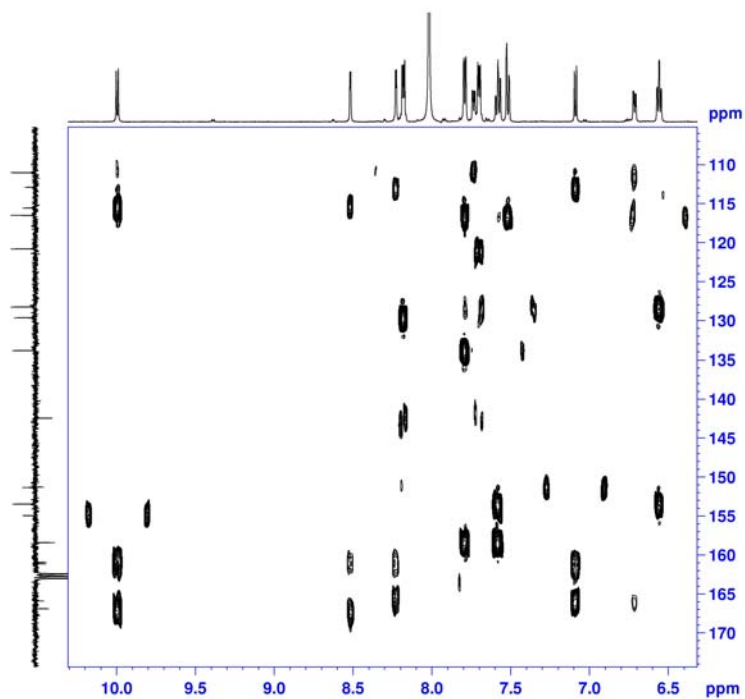
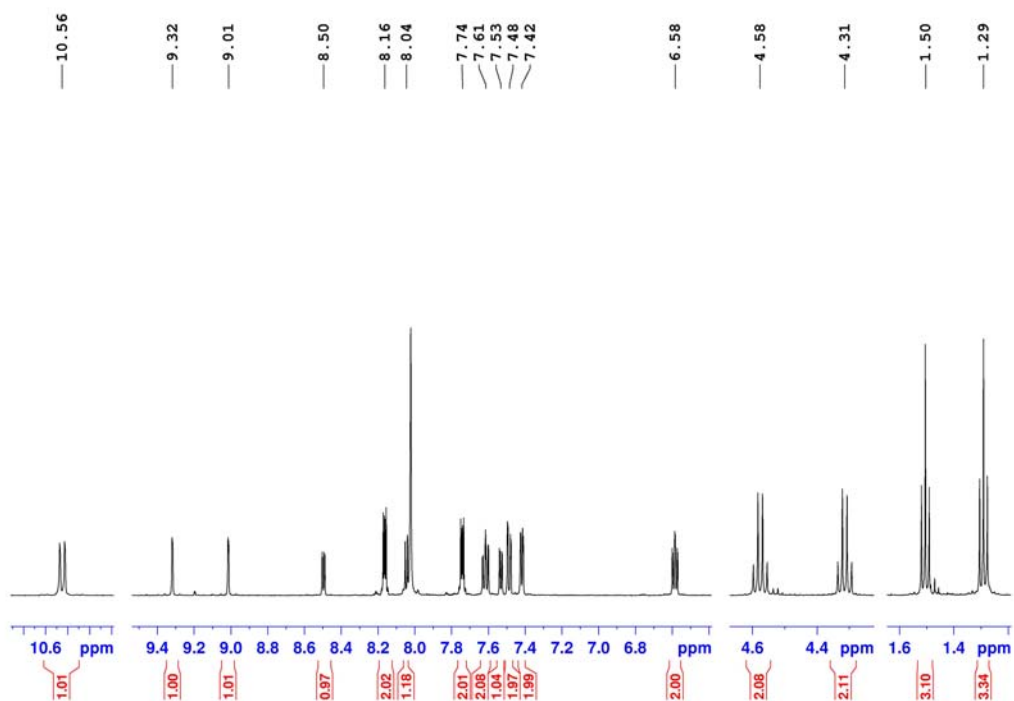
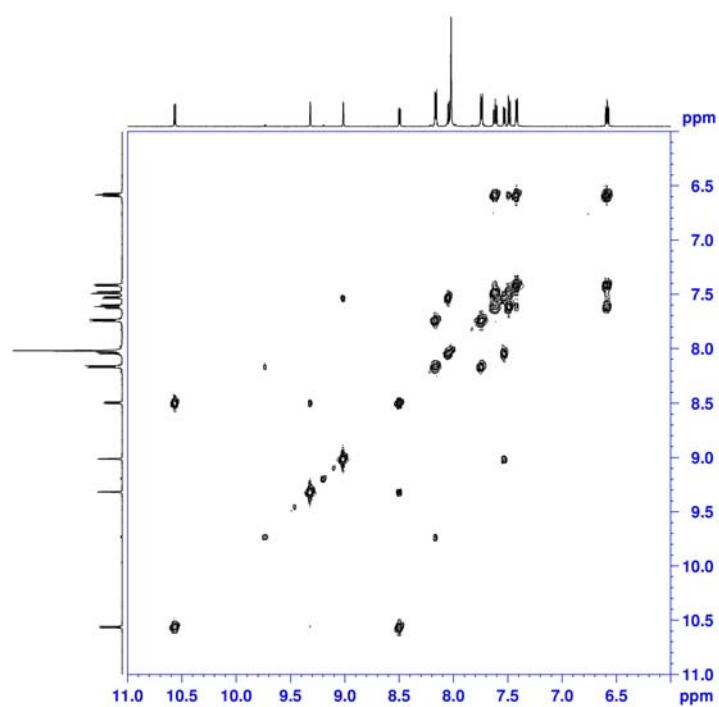


Figure S3. 1D and 2D NMR spectra (400 MHz, 298K, DMF-*d*₇) for complex **1w**: (a) ¹H-NMR, (b) COSY, (c) NOESY (d) DEPTQ135 (e) HSQC and (f) HMBC.

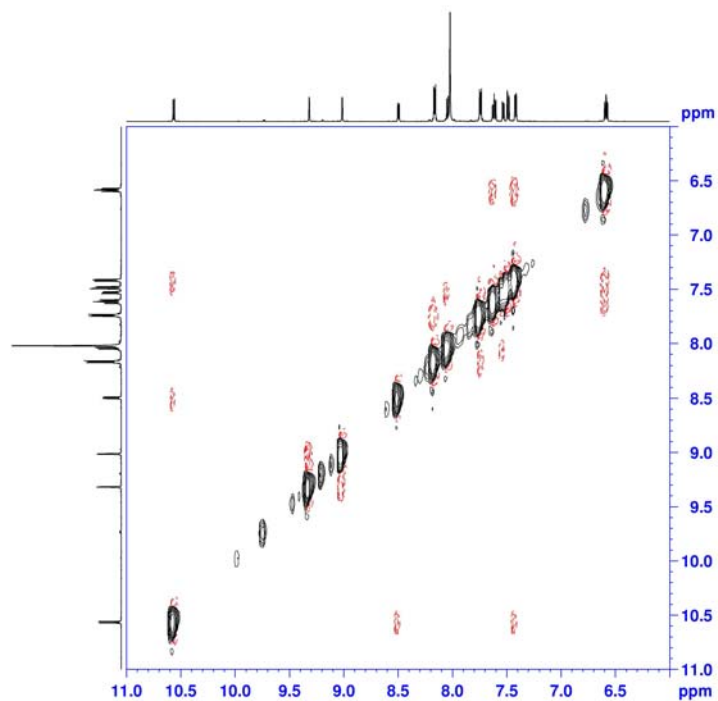
(a)



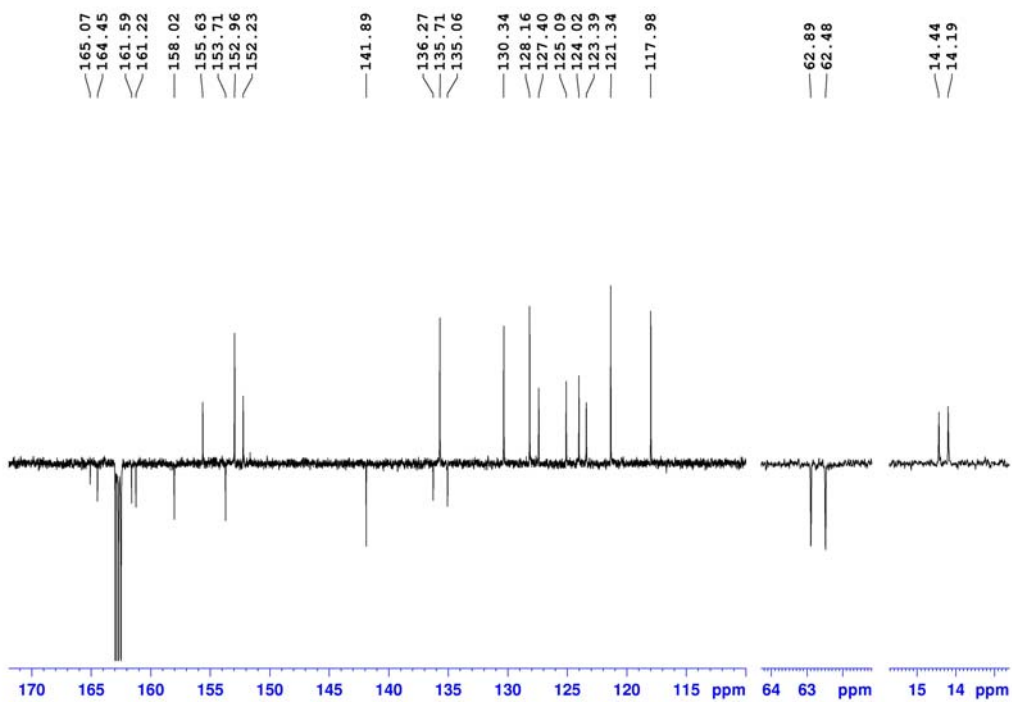
(b)



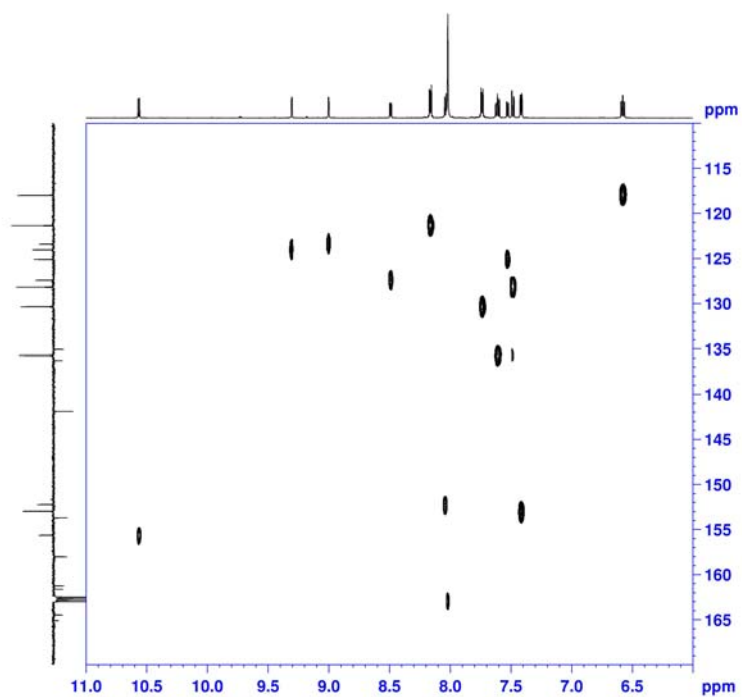
(c)



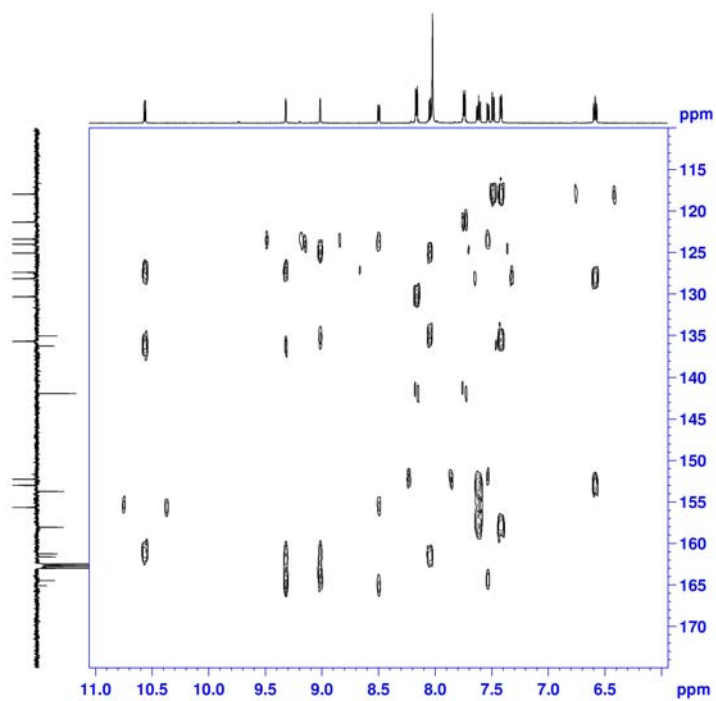
(d)

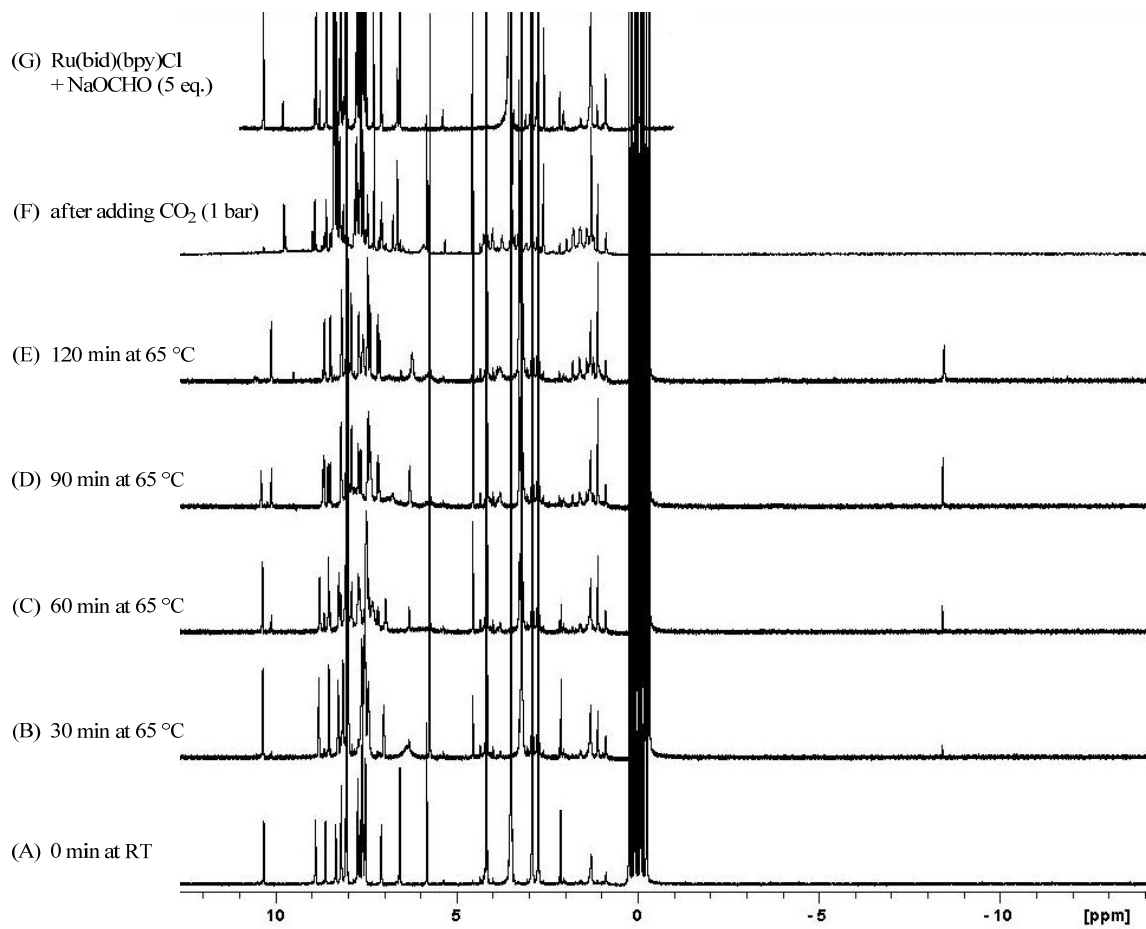


(e)



(f)





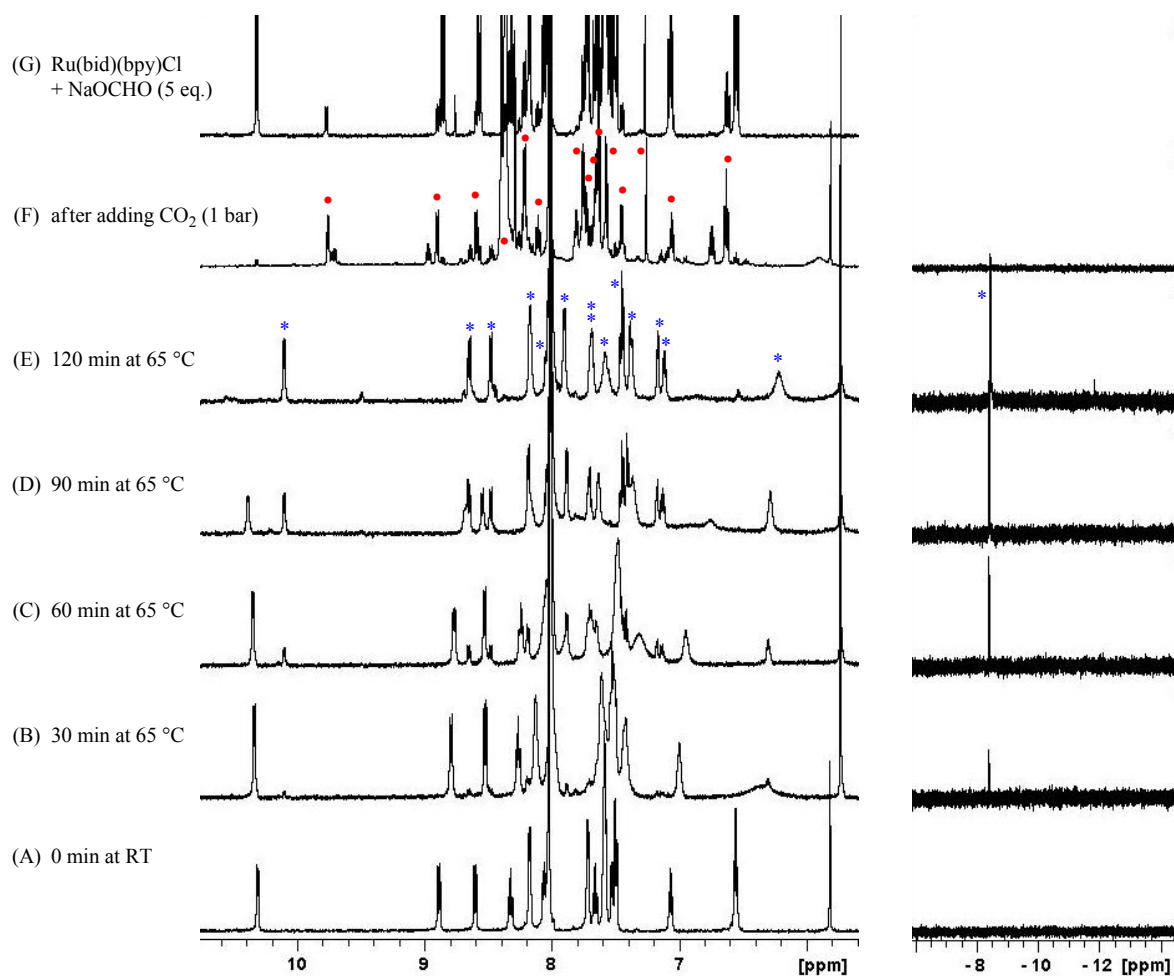


Figure S4. ^1H NMR spectra of reaction mixture of $[\text{Ru}(\text{bid})(\text{bpy})\text{Cl}]$ with NaBH_4 in $\text{DMF-}d_7$. Top: from 13 ppm to -15 ppm, bottom: aromatic region and hydride region. (A) 0 min at RT. (B) 30 min at 65 °C. (C) 60 min at 65 °C. (D) 90 min at 65 °C. (E) 120 min at 65 °C. *: $\text{Ru}(\text{bid})(\text{bpy})\text{H}$ (F) after adding CO_2 (1 bar) at RT. ●: $\text{Ru}(\text{bid})(\text{bpy})(\text{OCHO})$ (G) $\text{Ru}(\text{bid})(\text{bpy})\text{Cl}$ with NaOCHO in $\text{DMF-}d_7$. See experimental section for further experimental details.

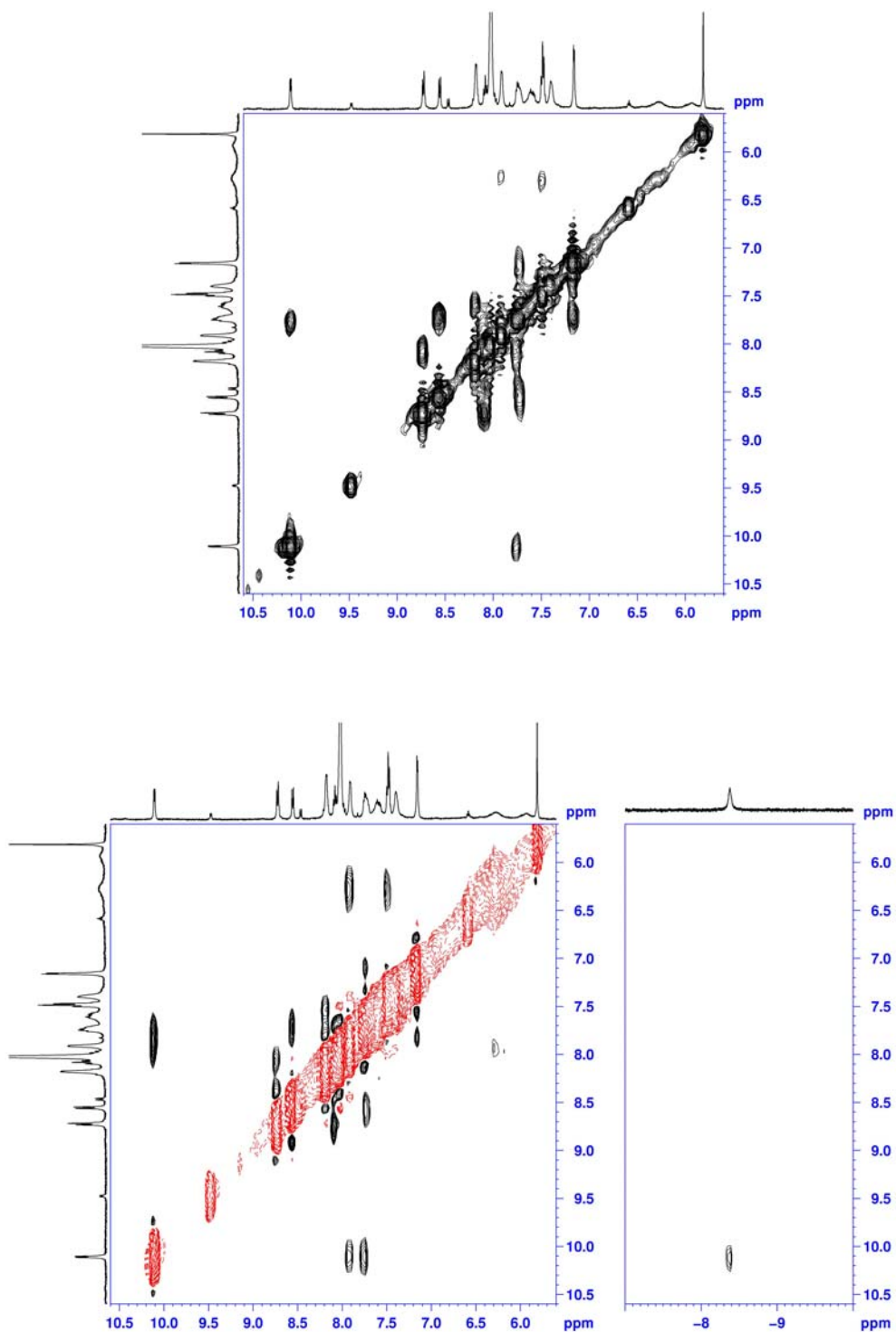


Figure S5. COSY spectrum (top) and NOESY spectrum (bottom) of reaction mixture after 130 min reaction time.

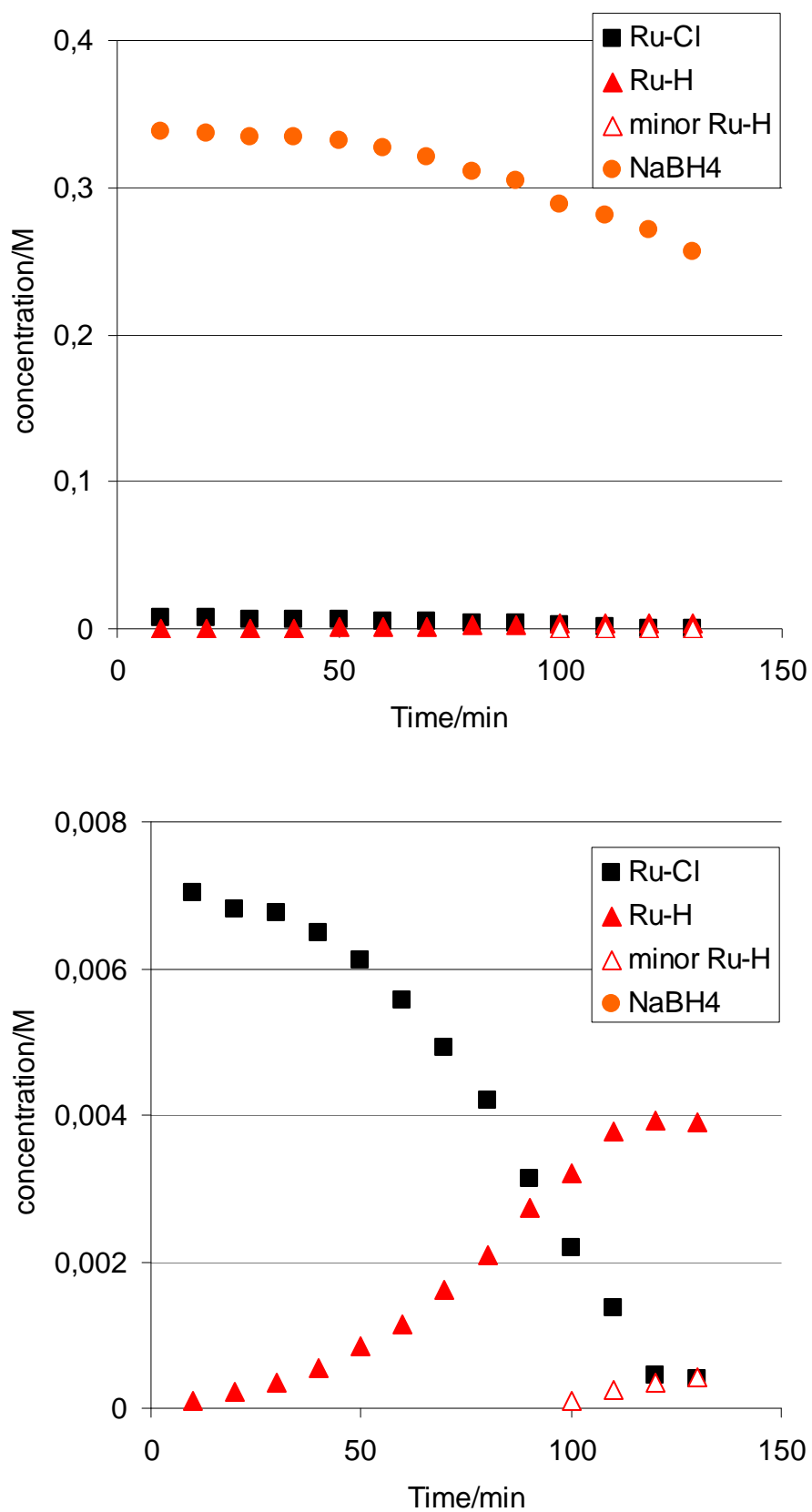


Figure S6. Time profiles of ruthenium species and NaBH₄. ■: [Ru(bid)(bpy)Cl], ▲: [Ru(bid)(bpy)H], △: minor Ru-H species ●: NaBH₄

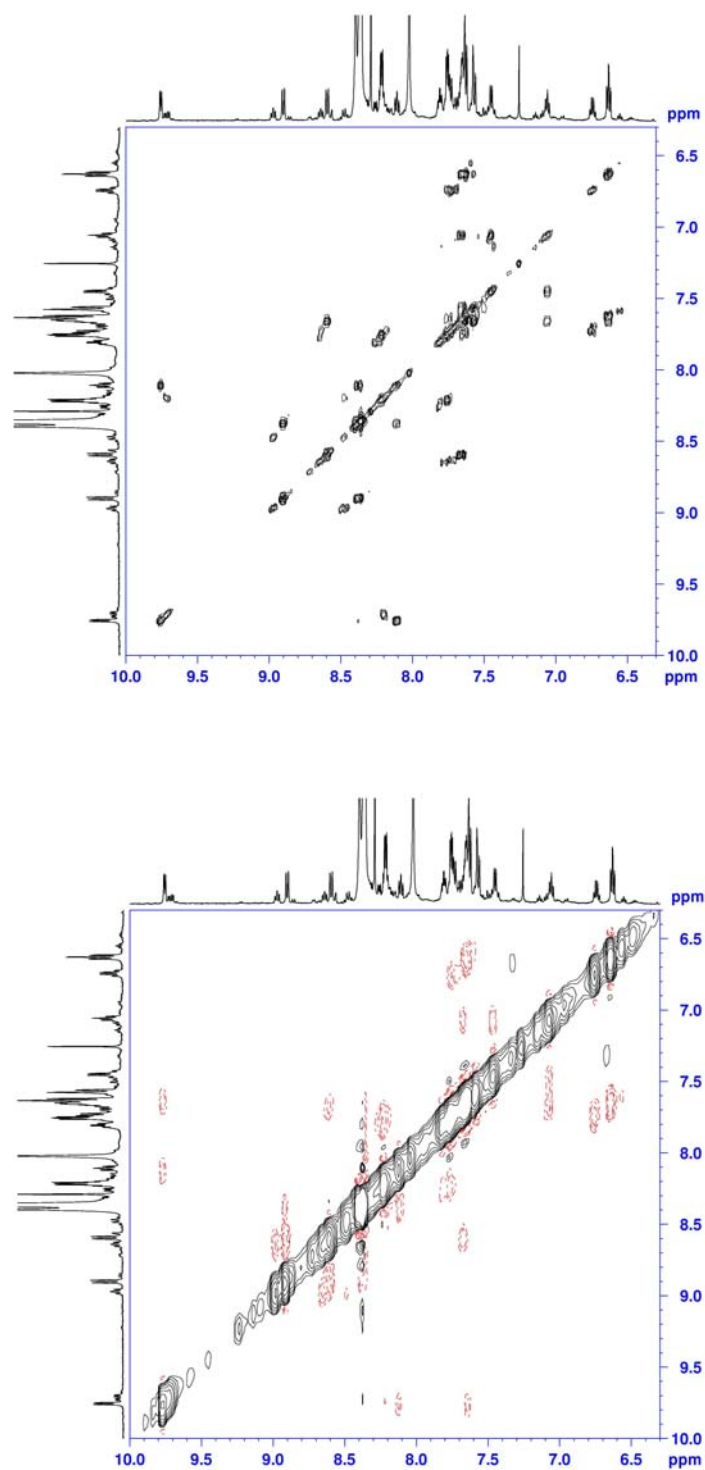


Figure S7. COSY spectrum (top) and NOESY spectrum (bottom) of reaction mixture after adding CO₂ (1 bar).

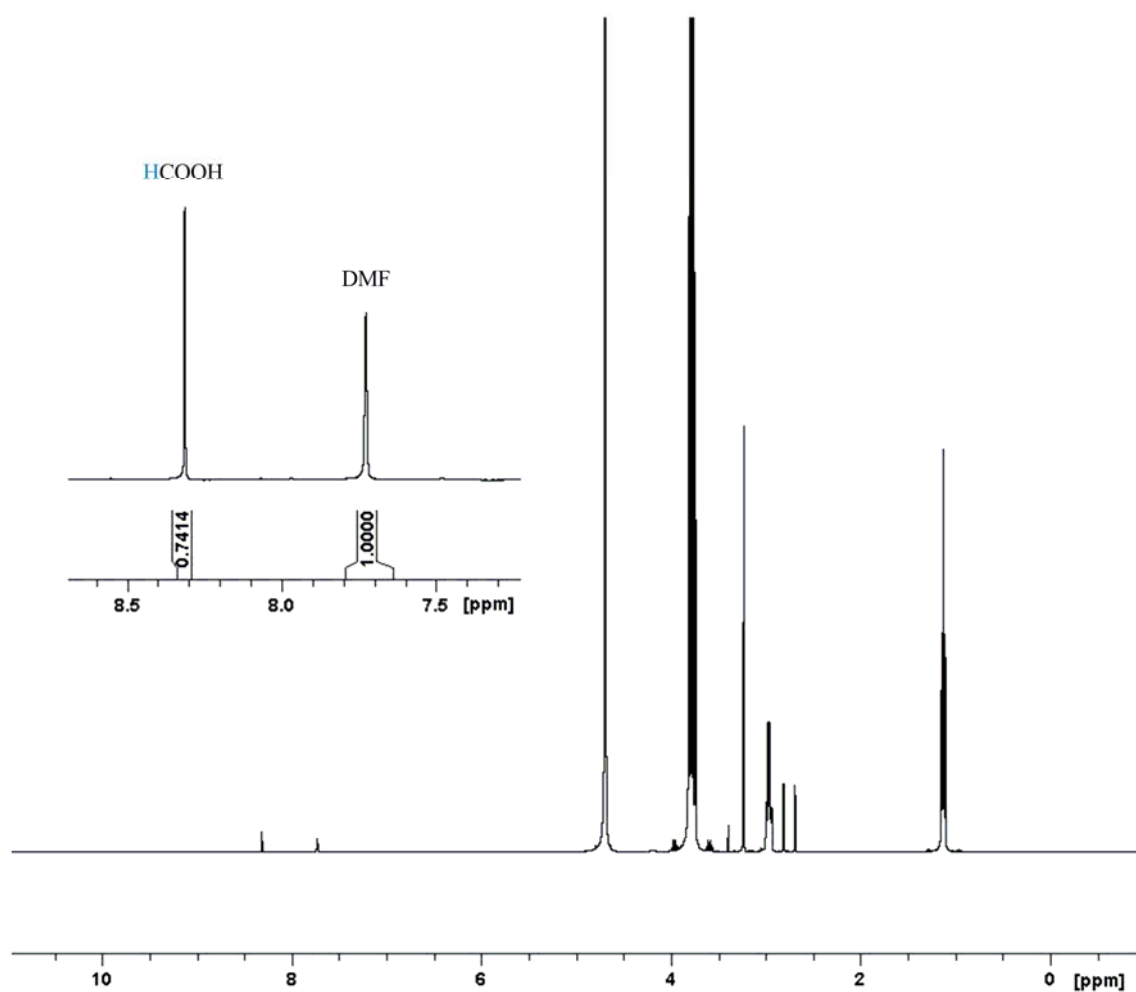


Figure S8. Catalytic example: ^1H NMR spectrum of aliquot solution in D_2O after catalytic reaction (using 0.3 mM of complex **1**, CO_2 25 bar and H_2 25 bar at 100 °C for 20 min).

S3. Kinetic measurements:

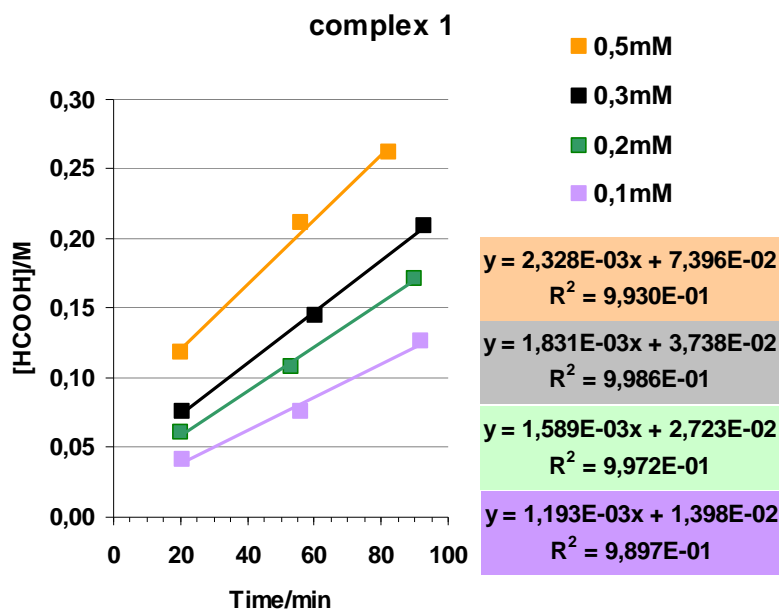


Figure S9. Formation of formic acid at different pre-catalyst concentrations with respect to time (complex **1**, 25 bar of CO₂, 25 bar of H₂, 100 °C)

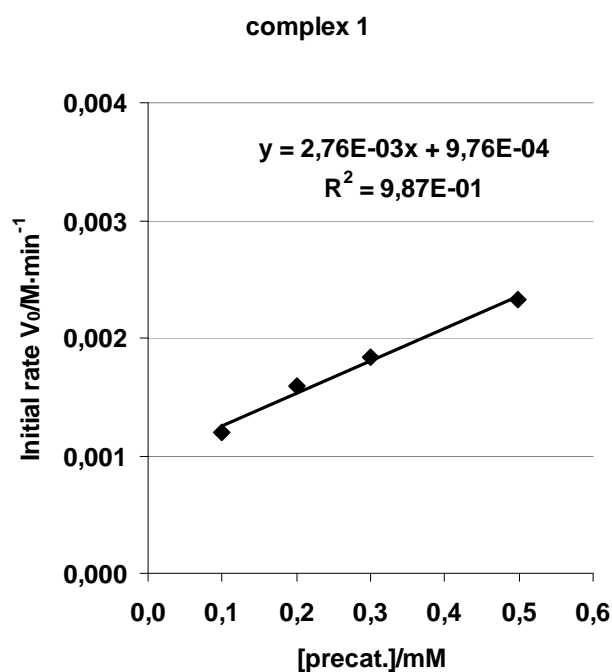


Figure S10. Initial rates with respect to pre-catalyst concentration. (complex **1**, 25 bar of CO₂, 25 bar of H₂, 100 °C)

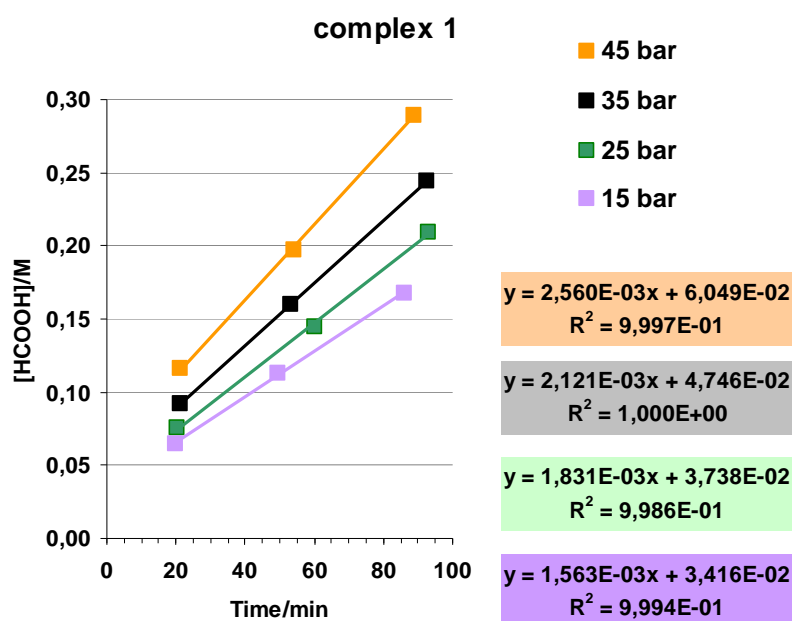


Figure S11. Formation of formic acid at different H₂ pressures with respect to time (0.3 mM of complex **1**, 25 bar of CO₂, 100 °C). ■: 15 bar of H₂, ■: 25 bar of H₂, ■: 35 bar of H₂, ■: 45 bar of H₂

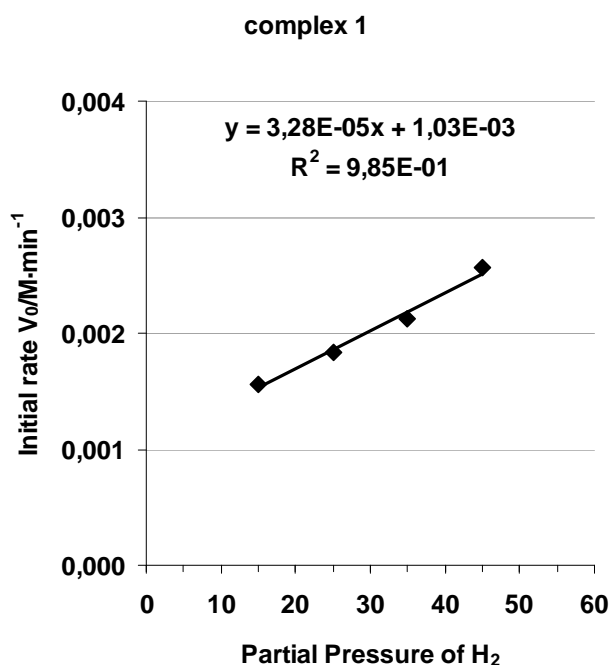


Figure S12. Initial rates with respect to partial pressure of H₂. (0.3 mM of complex **1**, 25 bar of CO₂, 100 °C)

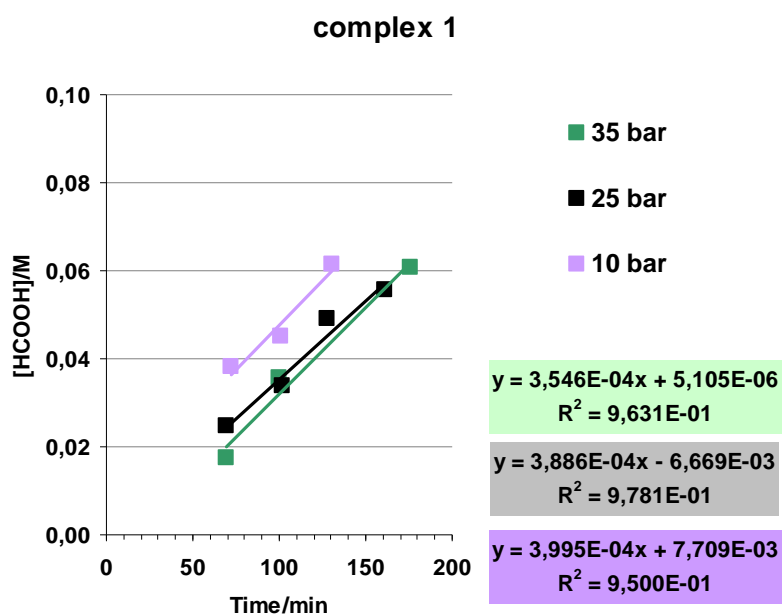


Figure S13. Formation of formic acid at different CO₂ pressures with respect to time (0.3 mM of complex **1**, 25 bar of H₂, 100 °C). ■: 10 bar of CO₂, ■: 25 bar of CO₂, ■: 35 bar of CO₂.

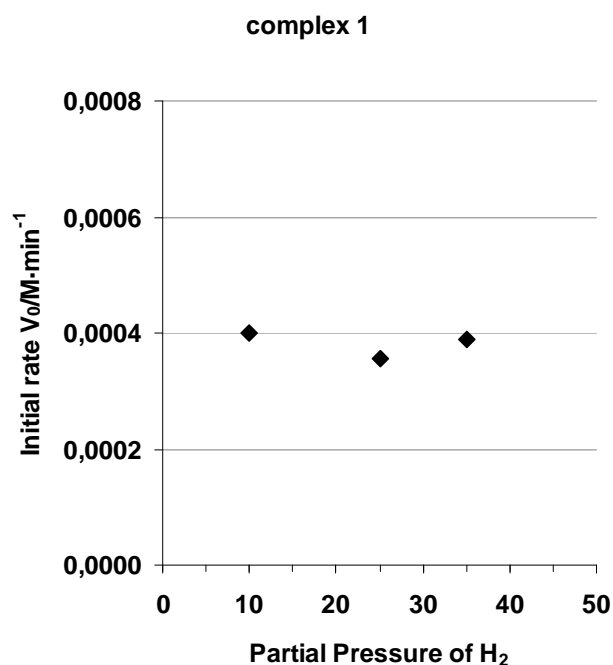


Figure S14. Initial rates with respect to partial pressure of CO₂. (0.3 mM of complex **1**, 25 bar of H₂, 100 °C)

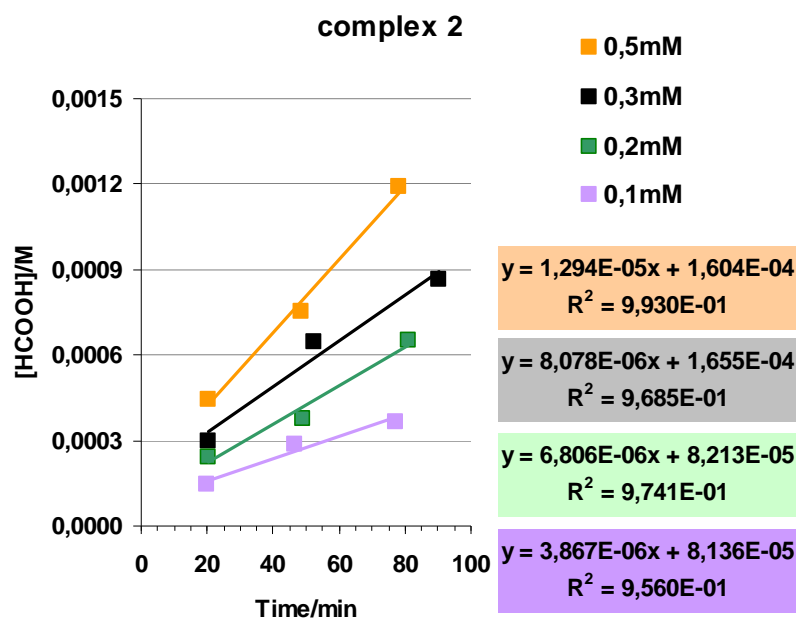


Figure S15. Formation of formic acid at different pre-catalyst concentrations with respect to time (complex 2, 25 bar of CO₂, 25 bar of H₂, 100 °C). ■: 0.1 mM, ■: 0.2 mM, ■: 0.3 mM, ■: 0.5 mM

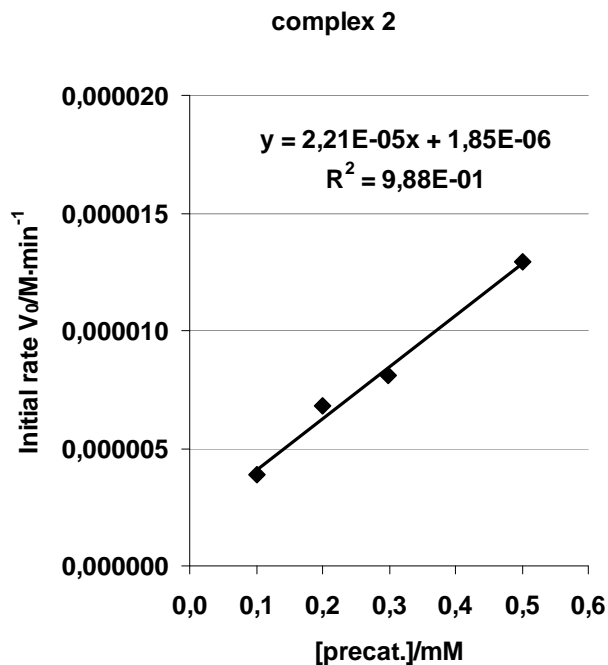
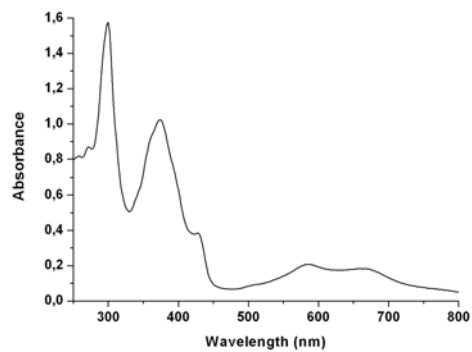


Figure S16. Initial rates with respect to pre-catalyst concentration. (complex 2, 25 bar of CO₂, 25 bar of H₂, 100 °C)

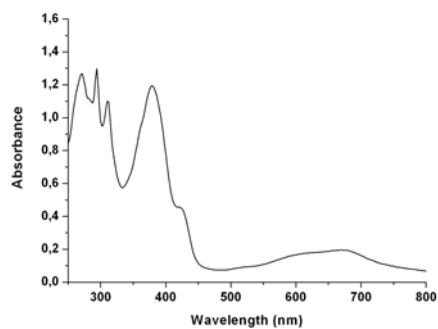
S4. UV-vis:

Figure S17. UV-vis, 0.036 mM in DCM, of complexes (a) **1** (b) **1d**, (c) **1w**, (d) **2**.

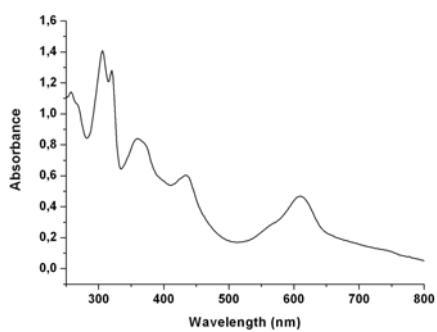
(a)



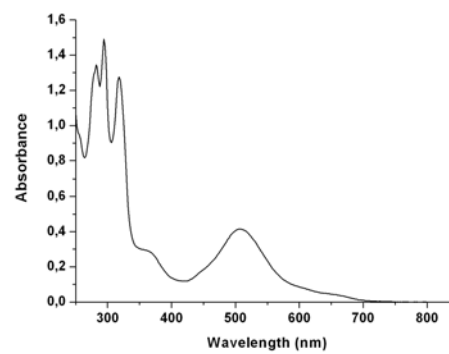
(b)



(c)



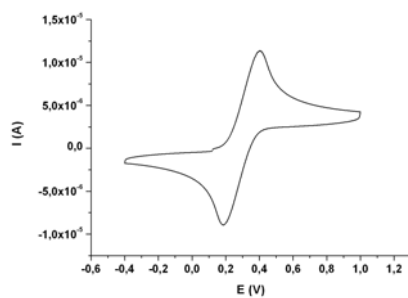
(d)



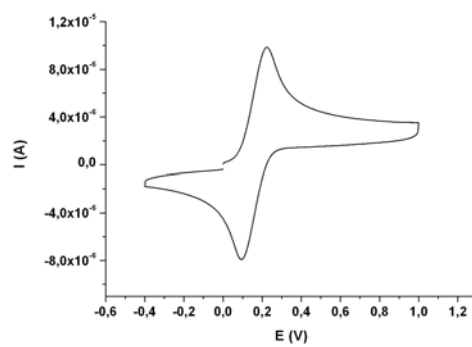
S5. Electrochemistry:

Figure S18. Cyclic voltammograms vs SSCE at a scan rate 100 mV/s in DCM-TBAH (0.1 M), of complex (a) **1**, (b) **1d**, (c) **1w**, (d) **2**.

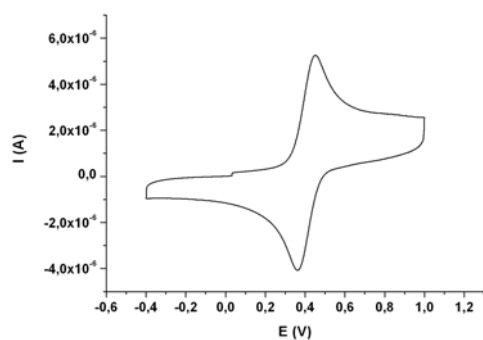
(a)



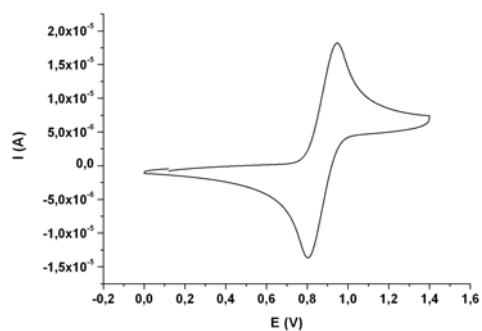
(b)



(c)



(d)



S6. X-ray:

X-Ray structure determination

Crystals for complex **1** were grown by slow diffusion of diethyl ether into a solution of complex **1** in dichloromethane. CCDC 833745 contains the supplementary crystallographic data for complex **1**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The measured crystals were prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation. The measured crystals were mounted using a nylon loop directly from the crystallization solution to the diffractometer equipped with an APPEX 2 4K CCD area detector, a FR591 rotating anode with MoK $_{\alpha}$ radiation, Montel mirrors as monochromator and a Kryoflex low temperature device ($T = -173$ °C). Full-sphere data collection was used with ω and φ scans. *Programs used:* Data collection Apex-2³; data reduction, Bruker Saint V/.60 A⁴; absorption correction, SADABS⁵; structure solution and refinement, SHELXTL⁶.

S7. References:

- 1.a) R. R. Gagne, W. A. Marritt, D. N. Marks, W. O. Siegl, *Inorg. Chem.* **1981**, *20*, 3260-7. b) D. N. Marks, W. O. Siegl, R. R. Gagne, *Inorg. Chem.* **1982**, *21*, 3140-7.
2. S. C. Rasmussen, S. E. Ronco, D. A. Mlsna, M. A. Billadeau, W. T. Pennington, J. W. Kolis, J. D. Petersen, *Inorg. Chem.* **1995**, *34*, 821-829.
3. Data collection with APEX II v2009.1-02. Bruker (2007). Bruker AXS Inc., Madison, Wisconsin, USA.
4. Data reduction with Bruker SAINT V7.60A. Bruker (2007). Bruker AXS Inc., Madison, Wisconsin, USA.
5. SADABS: V2008/1 Bruker (2001). Bruker AXS Inc., Madison, Wisconsin, USA.
6. SHELXTL V6.14, Structure solution and refinement. G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122.