Electronic Supplementary Information (ESI)

A Remote Coordination Booster Enhances Catalytic Efficiency by Accelerating the Generation of Active Catalyst

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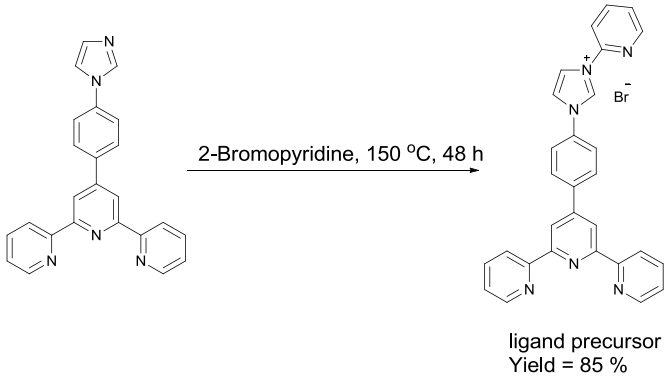
General information

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on Bruker AVANCE III 400 and 500 MHz NMR spectrometers at room temperature unless mentioned otherwise. Chemical shifts (δ) are expressed in ppm using the residual proton resonance of the solvent as an internal standard ($CHCl_3$: δ = 7.26 ppm for ^{1}H spectra, 77.2 ppm for $^{13}C\{^{1}H\}$ spectra; CH_3COCH_3: δ = 2.05 ppm for ^{1}H spectra, 29.8 ppm for $^{13}C\{1H\}$ spectra); CH_3CN: δ = 1.94 ppm for ^{1}H spectra, 118.3 ppm and 1.3 ppm for $^{13}C\{^{1}H\}$ spectra). All coupling constants (J) are expressed in hertz (Hz) and only given for ^{1}H-^{1}H couplings unless mentioned otherwise. The following abbreviations were used to indicate multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), dt (doublet of triplet), m (multiplet). ESI mass spectroscopy was performed on a Bruker microTOF QII spectrometer. GCMS analysis was performed on a Agilent 7890A GC/5975C MS system. The UV-Visible absorption studies were carried out on Cary 100 UV-Vis spectrophotometer using 1.0 cm quartz cuvettes at room temperature. The electrochemical measurements (cyclic voltammetry, CV and differential pulse voltammogram, DPV) were carried out using a CHI 620E Electrochemical Analyzer at room temperature. Dry solvents and reagents were obtained from commercial suppliers and used without further purification. $RuCl_3.xH_2O$ and deuterated solvents were purchased from Aldrich. $[Ru(para\text{-cymene})Cl_2]_2$ was prepared by following a reported method[S1]. All the alkenes and alkynes are purchased from Aldrich. The products were previously reported and the identity of the products was verified by GC and GCMS with known samples. ^{1}H NMR spectroscopy was also used to match the products with the known samples.

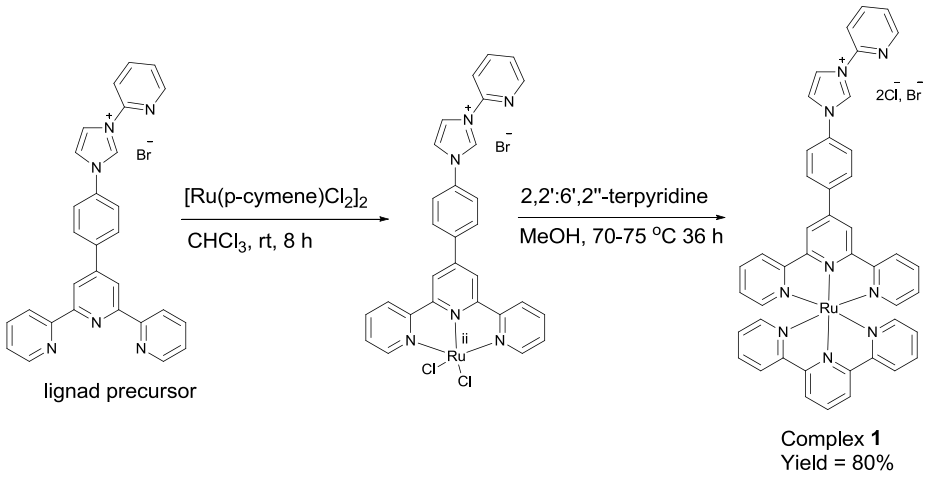
Synthesis of ligand precursor and complexes



Scheme S1. Synthesis of ligand precursor

Ligand precursor: 4′-[4-(Imidazol-1-yl)phenyl]- 2,2′:6′,2″-terpyridine (0.75 g, 2.0 mmol) and 2-bromopyridine (1 mL) were mixed in a pressure tube and stirred for 40 h at 140−150 °C in neat conditions. After that, the reaction mixture was cooled to room temperature and 15 mL of THF was added to this reaction mixture. The resulting solid was filtered and washed with 30 mL of THF to give desired product. (Scheme S1). Yield: = 910 mg (85%). ^{1}H NMR (500 MHz, DMSO–d_6, 300K): δ 10.76 (s, 1H), 8.85 – 8.77 (m, 5H), 8.78 – 8.69 (m, 4H), 8.34 – 8.27 (m, 3H), 8.24 (d, *J* = 8.2 Hz, 1H), 8.20 (d, *J* = 8.7 Hz, 2H), 8.12 (ddd, *J* = 9.2, 6.7, 2.8 Hz, 2H), 7.72 (ddd, *J* = 7.4, 4.9, 0.9 Hz, 1H), 7.60 (dd, *J* = 6.6, 4.9 Hz, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (125 MHz, DMSO–d_6, 300K): δ 155.4, 154.3, 149.3, 149.0, 148.1, 146.3, 140.6, 138.9, 138.2, 135.3, 134.4,

128.8, 125.6, 124.9, 122.9, 122.1, 121.4, 120.1, 118.5, 114.8 ppm. HRMS (ESI, positive ion): *m/z* = 453.1862 (calculated for $[C_{29}H_{21}N_6]^+$ = 453.1822).

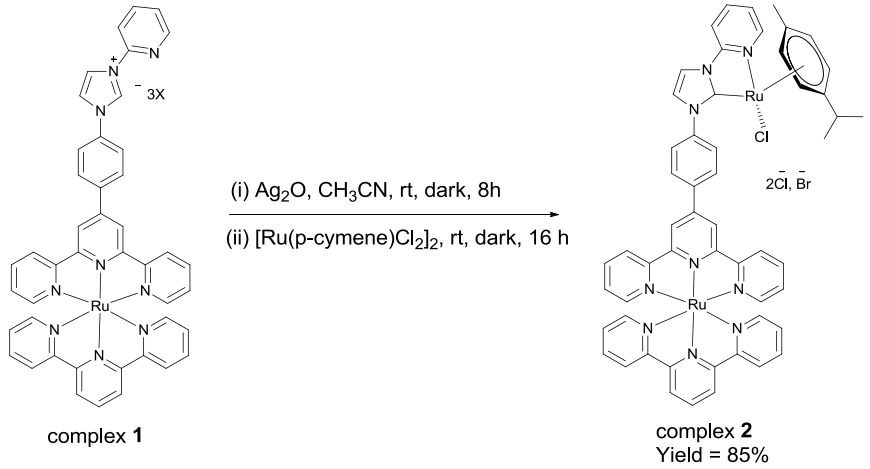


Scheme S2. Synthesis of complex **1**.

Complex1

Step I: Ligand precursor (267.0 mg, 0.5 mmol) and [Ru(*para*-cym)Cl_2]$_2$ (154.0 mg, 0.25 mmol) were mixed in chloroform (8 mL) in a Schlenk tube. The reaction mixture was stirred for 8 h at room temperature which resulted into dark blue precipitate (Scheme S2). The dark blue precipitate was filtered and washed with chloroform. This dark blue complex was further used for the synthesis of complex **1** without any further purification.

Step II: The blue compound formed in *step I* (142.0 mg, 0.2 mmol) and 2,2':6',2''-terpyridine (51.0 mg, 0.22 mmol) were mixed in methanol (15 mL) in a Schlenk tube. The reaction mixture was stirred at 70–75 ˚C for 36 h. After this, the reaction mixture was allowed to cool down to room temprature. The reaction mixture was filtered and the solvent was removed in rotavapor. The solid compound was washed with chloroform to afford the desired compound (Scheme S2). Yield: = 150.0 mg (80%). ^{1}H NMR (500 MHz, DMSO–d_6, 300K): δ 11.11 (s, 1H), 9.71 (s, 2H), 9.28 (d, J = 8.0 Hz, 2H), 9.16 (d, J = 8.2 Hz, 2H), 8.92–8.90 (m, 6H), 8.76 (d, J = 4.8 Hz, 1H), 8.57 (t, J = 8.1 Hz, 1H), 8.48 (d, J = 8.6 Hz, 2H), 8.43 (d, J = 8.0 Hz, 1H), 8.33 (dd, J = 11.0, 4.6 Hz, 1H), 8.10 (t, J = 7.9 Hz, 2H), 8.07 – 8.02 (m, 2H), 7.75 (dd, J = 7.4, 4.9 Hz, 1H), 7.57 (d, J = 5.6 Hz, 2H), 7.47 (d, J = 5.2 Hz, 2H), 7.33–7.270 (m, 4H). ^{13}C{^{1}H} NMR (125 MHz, DMSO–d_6, 300K): δ 158.0, 157.8, 155.3, 154.7, 152.2, 152.1, 149.3, 146.3, 144.8, 140.7, 138.2, 138.1, 136.0, 135.8, 134.5, 129.4, 127.9, 127.7, 125.6, 125.1, 124.7, 124.1, 122.4, 121.9, 121.2, 120.1, 115.0 ppm. HRMS (ESI, positive ion): *m/z* = 262.7270 (calculated for $[C_{44}H_{32}N_9Ru]^{3+}$ = 262.7273).



Scheme S3. Synthesis of complex **2**.

Complex 2: Silver(I) oxide (9.3 mg, 0.04 mmol) and complex **1** (47.0 mg, 0.05 mmol) were mixed in acetonitrile (5 mL) in a Schlenk tube. The reaction mixture was stirred for 8 h at room temperature under dark conditions. $[Ru(para\text{-}cym)Cl_2]_2$ (15.2 mg, 0.025 mmol) was added to the reaction mixture. This reaction mixture was again stirred for 16 h under dark conditions. The resulting red solution was filtered through Celite plug. The Celite plug was further washed with 10 mL of methanol. The collected filtrate was reduced to a 0.5 mL under vacuum. Addition of diethylether to this concentrated solution resulted into a large amount of precipitate. This precipitate was filtered and washed with diethylether to afford the desired product (Scheme S3). Yield: = 51.5 mg (85%). ^{1}H NMR (500 MHz, DMSO–d_6, 300K): δ 9.80 (s, 2H), 9.45 (d, J = 4.5 Hz, 1H), 9.32 (d, J = 7.4 Hz, 1H), 9.17 (d, J = 7.4 Hz, 2H), 8.97 (d, J = 7.5 Hz, 2H), 8.94 – 8.87 (m, 3H), 8.57 (t, J = 7.8 Hz, 1H), 8.47 – 8.30 (m, 4H), 8.11 (t, J = 7.4 Hz, 2H), 8.07 – 8.02 (m, 3H), 7.65 – 7.62 (d, J = 5.7 Hz, 1H), 7.58 (d, J = 5.3 Hz, 2H), 7.48 (d, J = 5.3 Hz, 2H), 7.34 – 7.26 (m, 5H), 6.13 (d, J = 4.7 Hz, 1H), 5.97 (d, J = 5.7 Hz, 1H), 5.35 (d, J = 5.3 Hz, 1H), 5.11 (d, J = 5.8 Hz, 1H), 2.41 – 2.33 (m, 1H), 2.21 (s, 3H), 0.86 (dd, J = 16.7, 6.8 Hz, 6H) ppm. HRMS (ESI, positive ion): *m/z* = 352.7181 (calculated for $[C_{54}H_{45}N_9ClRu_2]^{3+}$ = 352.7191), *m/z* = 546.5618 (calculated for $[C_{54}H_{45}N_9ClRu_2 + Cl]^{2+}$ = 546.5632).

The halide ($2Cl^-$ and Br^-) salt was converted to hexafluorophosphate salt by anion metathesis.[S2] ^{1}H NMR (500 MHz, CD_3CN, 300K): δ 9.24 (d, J = 5.6 Hz, 1H), 9.11 (s, 2H), 8.78 (d, J = 8.2 Hz, 2H), 8.70 (d, J = 8.1 Hz, 2H), 8.54 – 8.50 (m, 4H), 8.44 (t, J = 8.2 Hz, 1H), 8.29 (d, J = 8.4 Hz, 2H), 8.23 (t, J = 8.0 Hz, 1H), 8.18 (d, J = 2.2 Hz, 1H), 8.01 – 7.91 (m, 5H), 7.88 (d, J = 2.2 Hz, 1H), 7.56 – 7.52 (m, 1H), 7.45 (d, J = 5.5 Hz, 2H), 7.39 (d, J = 5.5 Hz, 2H), 7.23 – 7.17 (m, 4H), 5.84 (d, J = 6.2 Hz, 1H), 5.65 (d, J = 6.2 Hz, 1H), 5.37 (d, J = 6.1 Hz, 1H), 4.95 (d, J = 6.1 Hz, 1H), 2.43 (dt, J = 13.8, 6.9 Hz, 1H), 2.21 (s, 3H), 0.97 (d, J = 6.9 Hz, 3H), 0.92 (d, J = 6.9 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 300K): δ 186.4, 159.0, 156.7, 156.6, 156.3, 153.6, 153.4, 152.5, 147.5, 142.7, 141.5, 139.4, 139.1, 139.1, 136.9, 130.3, 128.5, 128.4, 128.3, 127.0, 125.5, 125.4, 124.7, 124.61, 122.8, 118.5, 114.1, 110.4, 108.2, 93.0, 89.5, 88.4, 84.2, 32.0, 22.8, 22.1, 19.3 ppm. Anal. Found: C, 42.03; H, 3.22; N, 8.58. Calcd for $C_{54}H_{45}N_9ClRu_2P_3F_{18}.2H_2O$: C, 42.38; H, 3.23; N, 8.24.

Complex 3: This complex was synthesised by following a reported procedure and the synthesis of the complex was confirmed by matching the NMR chemical shift values with proper integration ration (Figure S19).[S3]. ^{1}H NMR (400 MHz, DMSO–d_6, 300K): 9.33 (d, *J* = 5.2 Hz, 1H), 8.40 (d, *J* = 2.1 Hz, 1H), 8.28 – 8.21 (m, 1H), 8.15 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 2.1 Hz, 1H), 7.52 (dd, *J* = 9.6, 3.5 Hz, 1H), 6.40 (d, *J* = 5.9 Hz, 1H), 6.36 (d, *J* = 6.2 Hz, 1H), 6.17 (d, *J* = 6.2 Hz, 1H), 5.74 (d, *J* = 5.9 Hz, 1H), 4.10 (s, 3H), 2.52 – 2.47, 2.41 – 2.30 (m, 1H), 2.12 (s, 3H), 0.84 (t, *J* = 7.1 Hz, 6H) ppm.

Complex 4: Hexafluorophosphate salt of complex **2** (75.0 mg, 0.05 mmol) and silver triflate (16.0 mg, 0.06 mmol) were mixed in acetonitrile (5 mL) in a Shlenk tube. The reaction mixture was refluxed for 60 h under dark conditions. After this, the reaction mixture was allowed to cool down to room temprature. This reaction mixture was filtered through a Celite plug. The filtrate was reduced to a minimum volume of 0.5 mL. Addition of 10 mL of diethylether resulted into a solid product. Crystallization (MeCN/Et_2O) of this solid product resulted into the analytically pure product (Scheme XX, main article). Yield: = 74.0 mg (90 %).^{1}H NMR (500 MHz, CD_3CN, 300K): δ 9.09 (s, 2H), 8.94 (d, *J* = 5.6 Hz, 1H), 8.77 (d, *J* = 8.2 Hz, 2H), 8.72 (d, *J* = 8.1 Hz, 2H), 8.53 – 8.49 (m, 4H), 8.43 (t, *J* = 8.1 Hz, 1H), 8.28 (d, *J* = 2.1 Hz, 1H), 8.20 (t, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.5 Hz, 2H), 7.98 (d, *J* = 4.0 Hz, 1H), 7.97 – 7.91 (m, 4H), 7.70 (d, *J* = 2.1 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.44 (d, *J* = 5.4 Hz, 2H), 7.38 (d, *J* = 5.5 Hz, 2H), 7.22 – 7.16 (m, 4H), 2.89 (s, 3H), 2.77 (s, 3H), 2.23 (s, 3H), 2.04 (s, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, CD_3CN, 300K): δ 190.7, 159.1, 159.0, 156.8, 156.3, 155.7, 154.04, 153.5, 153.4, 147.4, 141.7, 141.6, 139.1, 139.1, 136.9, 130.0, 129.6, 128.6, 128.5, 127.2, 126.1, 125.8, 125.7, 125.5, 124.8, 123.6, 123.4, 122.6, 120.9, 118.7, 113.0, 4.1, 4.1, 1.8 ppm. Anal. Found: C, 39.48; H, 2.87; N, 11.42. Calcd for $C_{53}H_{43}N_{13}Ru_2P_3F_{21}SO_3.CH_3CN$: C, 39.33; H, 2.76; N, 11.68.

Single crystal X-ray diffraction studies

Hexafluorophosphate salt of complex **1** and complex **4** were crystallized by diffusion of diethylether into the concentrated acetonitrile solution of the respected complexes. Complex **4** showed distorted octahedral geometries around the ruthenium centre. The C_{NHC}–Ru^{II}–$Cp_{yridine}$ bite angle was 88.9(2)˚ and C_{NHC}–Ru^{II} bond length 1.975(6) Å. The Ru–N_{MeCN} bond trans to the carbene was found to be larger than the other Ru–N_{MeCN} bonds, due to the strong trans influence of carbene ligand.[xx] The triflate anion of complex **4** was found to be highly disordered. Other bond lengths and bond angles were found to be in good agreement with the reported values for similar type of complexes in the literature.

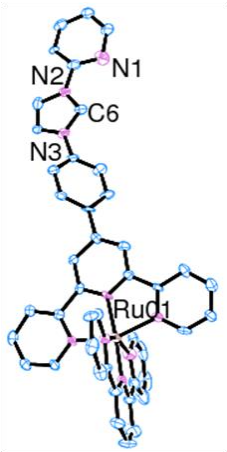


Figure S1. X-ray crystal structure of complex **1** (30% ellipsoids probability level). Hydrogen atoms, and counteranions are removed for clarity. Selected bond lengths (Å) and bond angles (°): N(2)-C(6) = 1.354(14), N(3)-C(6) = 1.370(13), N(2)-C(6)-N(3) = 105.1(10).

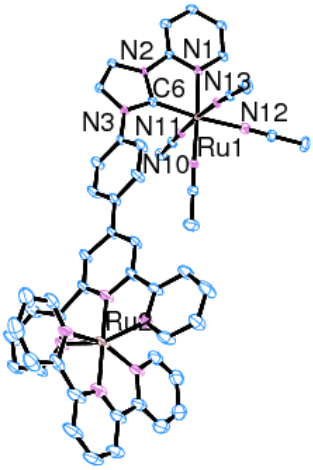


Figure S2. X-ray crystal structure of **4** (30% ellipsoids probability level). Hydrogen atoms, solvent molecule and counteranions are removed for clarity. Selected bond lengths (Å) and bond angles (°): Ru(1)-C(6) = 1.975(6), Ru(1)-N(1) = 2.077(5), Ru(1)-N10(1) = 2.039(5), Ru(1)-N(11) = 2.020(6), Ru(1)-N(12) = 2.096(5), Ru(1)-N(13) = 2.025(5), N(2)-C(6) = 1.364(2), N(3)-C(6) = 1.356(8), C(6)-Ru(1)-N(1) = 88.9(2), N(3)-C(6)-N(2) = 103.0(5), C(6)-Ru(1)-N(12) = 173.6(2).

NMR and mass spectra of the complexes

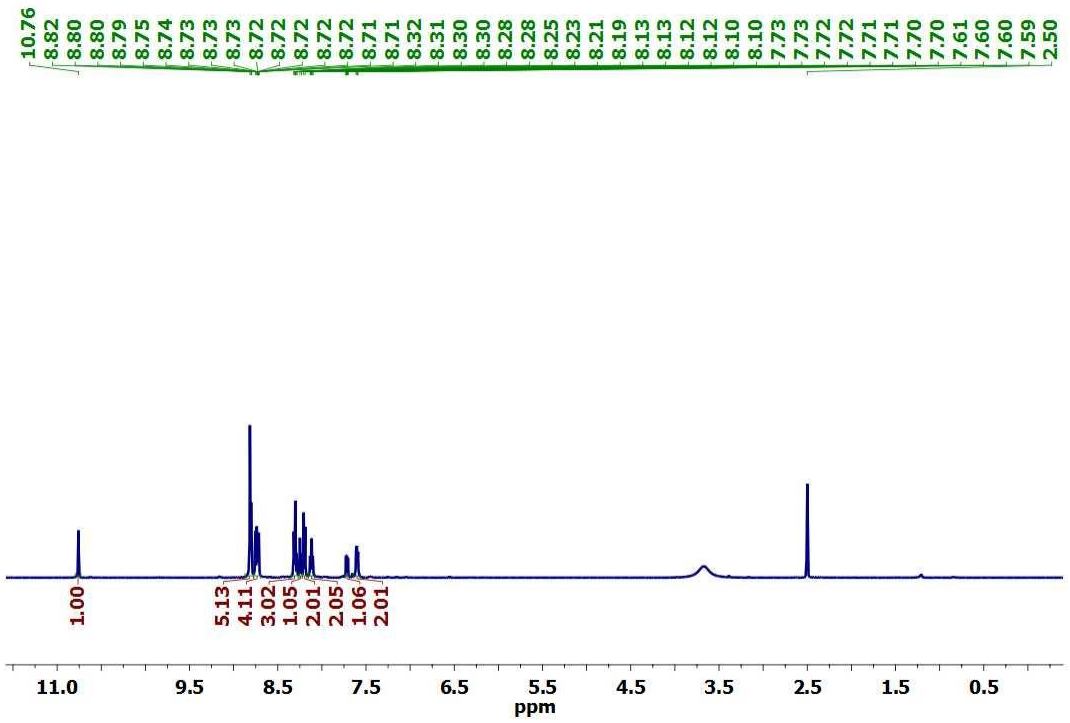


Figure S3. ^{1}H NMR spectrum of ligand precursor (500 MHz, DMSO–d_6, 300 K).

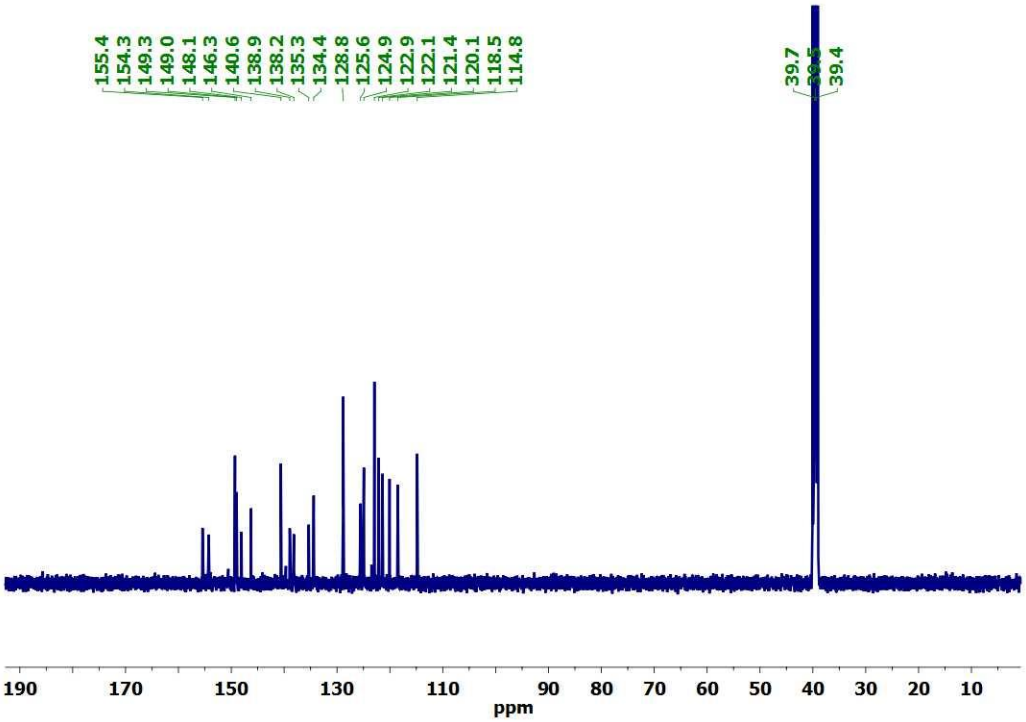


Figure S4. ^{13}C{^{1}H} NMR spectrum of ligand precursor (500 MHz, DMSO–d_6, 300 K).

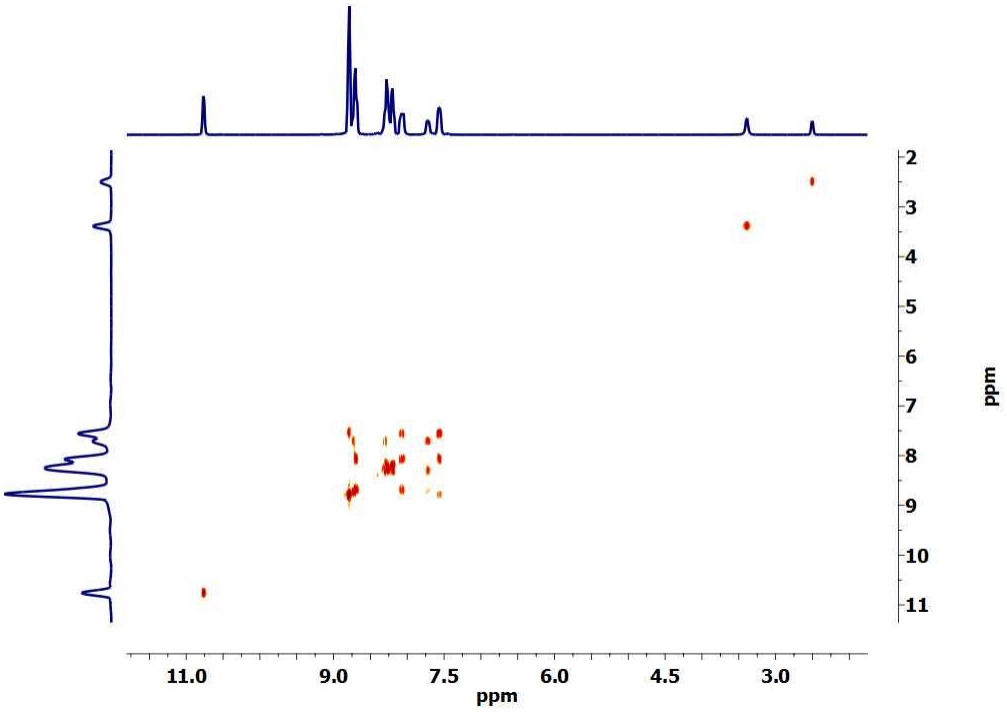


Figure S5. $^{1}H–^{1}H$ COSY NMR spectrum of ligand precursor.

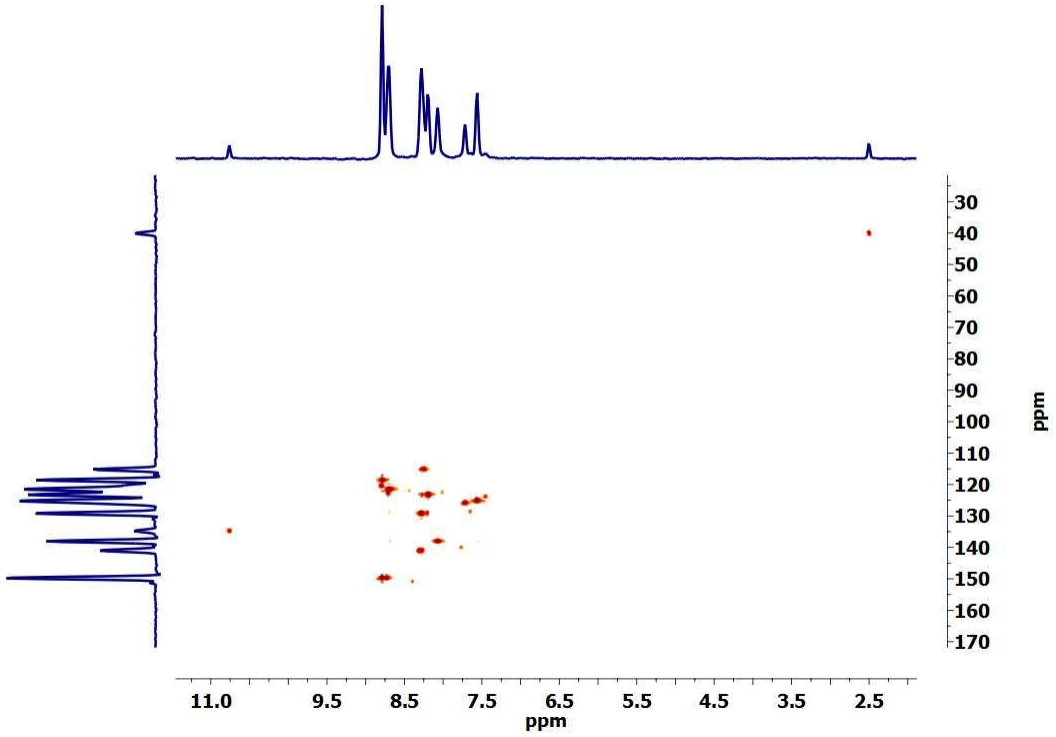


Figure S6. $^{1}H–^{13}C$ HSQC NMR spectrum of ligand precursor.

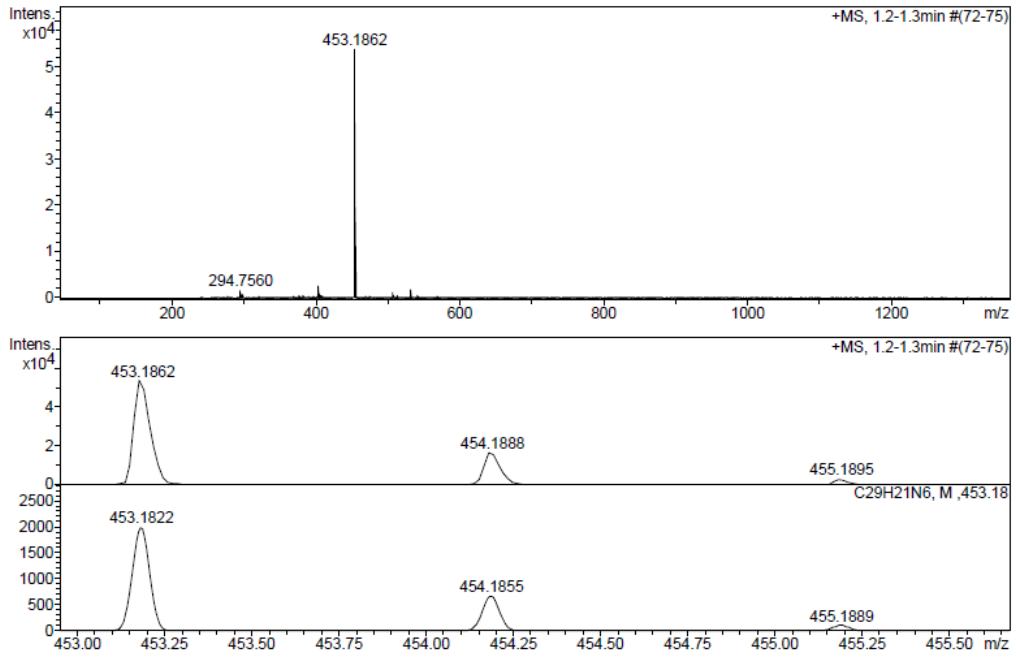


Figure S7. ESI–MS (positive ion mode) spectrum of ligand precursor**.**

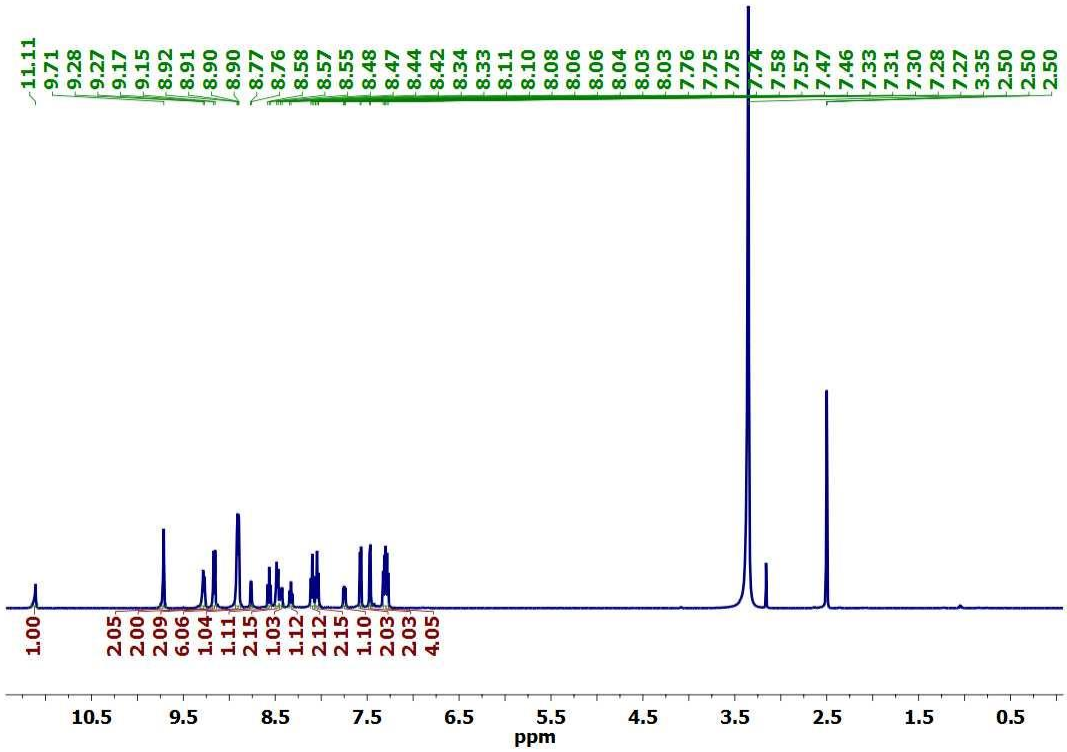


Figure S8. ^{1}H NMR spectrum of complex **1** (500 MHz, DMSO–d_6, 300 K).

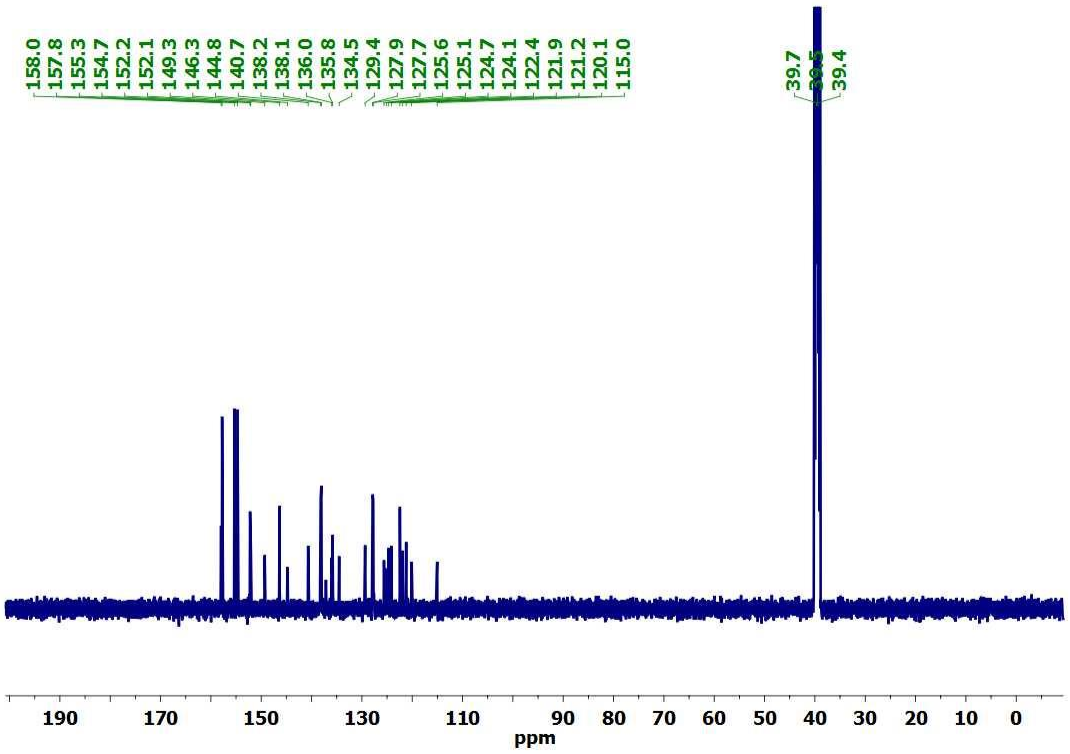


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of complex **1** (500 MHz, DMSO–d_6, 300 K).

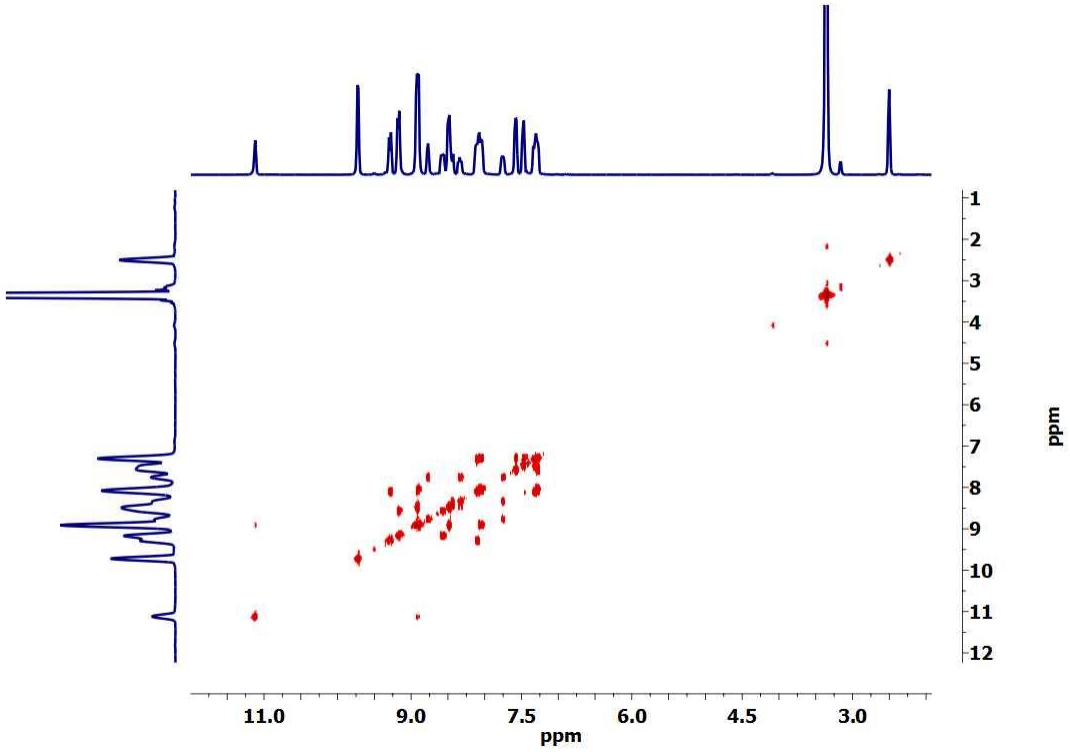


Figure S10. $^{1}H–^{1}H$ COSY NMR spectrum of complex **1**.

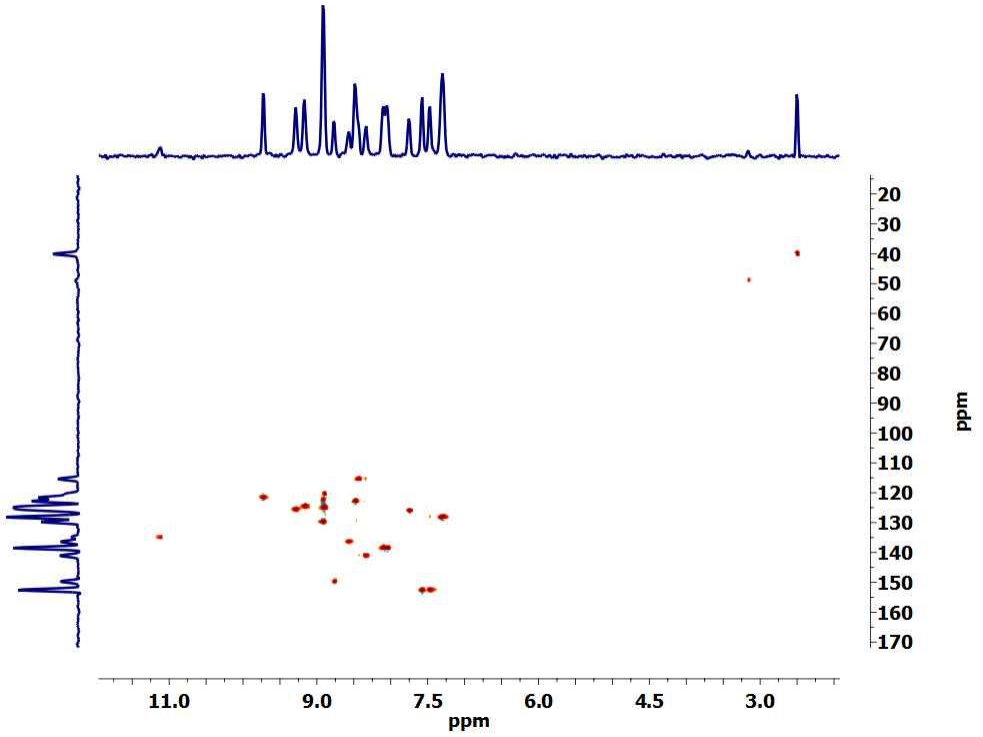


Figure S11. $^{1}H–^{13}C$ HSQC NMR spectrum of complex **1**.

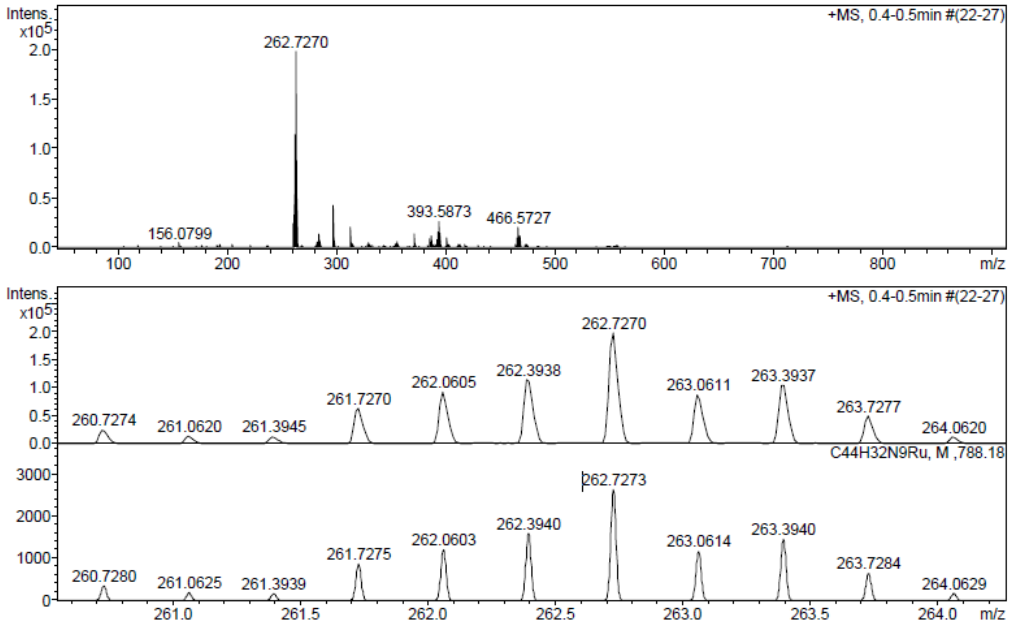


Figure S12. ESI–MS (positive ion mode) spectrum of complex **1.**

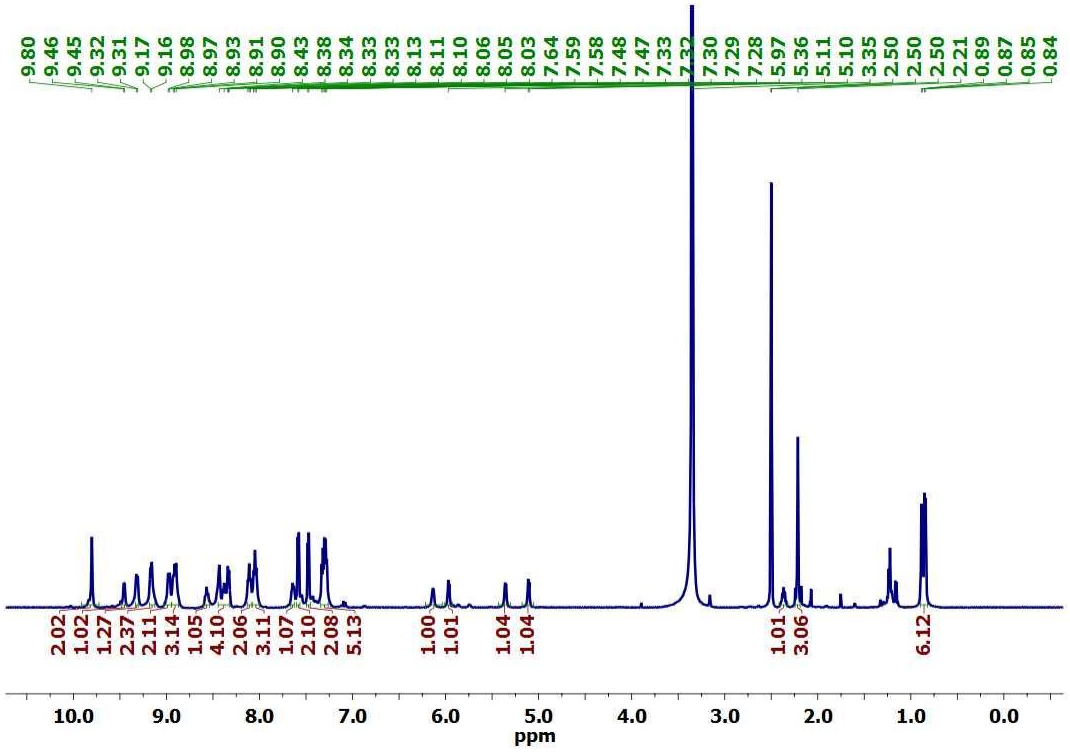


Figure S13. ^{1}H NMR spectrum of halide ($2Cl^{-}$ and Br^{-}) salt of complex **2** (500 MHz, DMSO–d_6, 300 K).

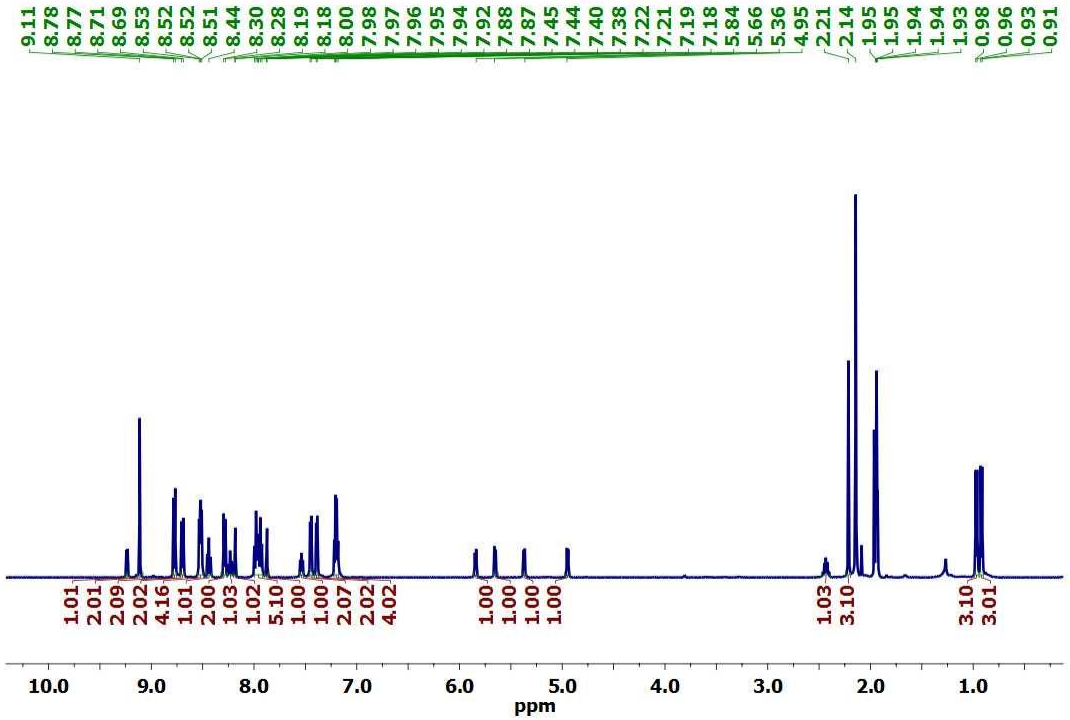


Figure S14. ^{1}H NMR spectrum of PF_6 salt of complex **2** (500 MHz, CD_3CN, 300 K).

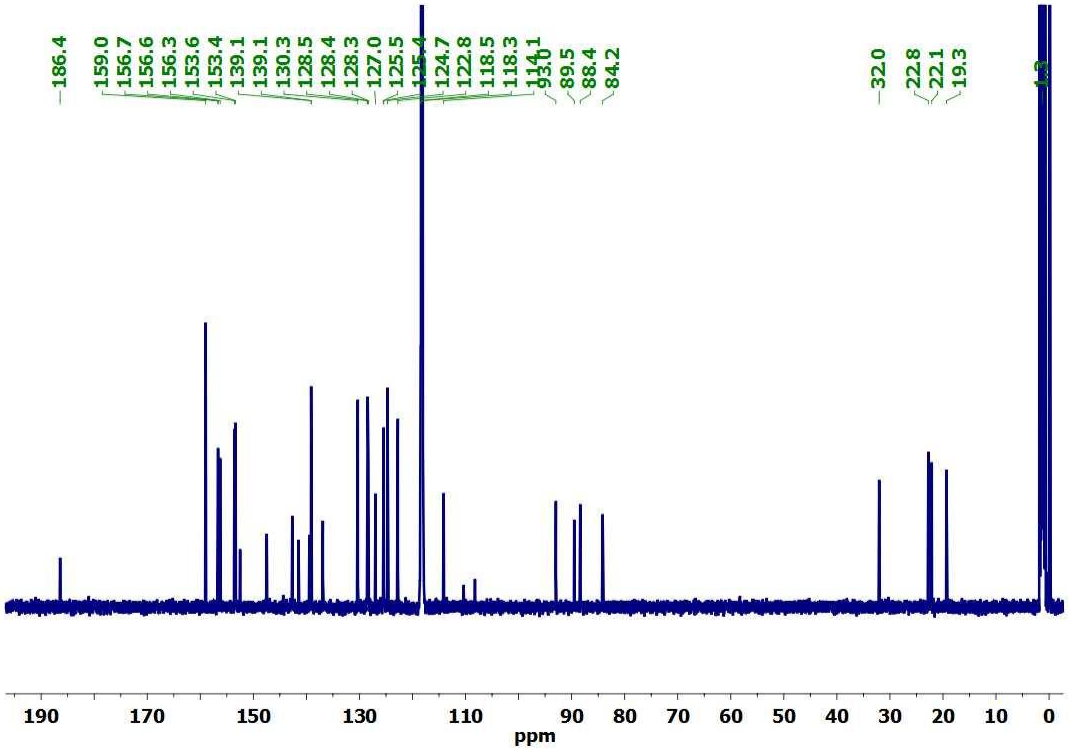


Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of PF_6 salt of complex **2** (125 MHz, CD_3CN, 300 K).

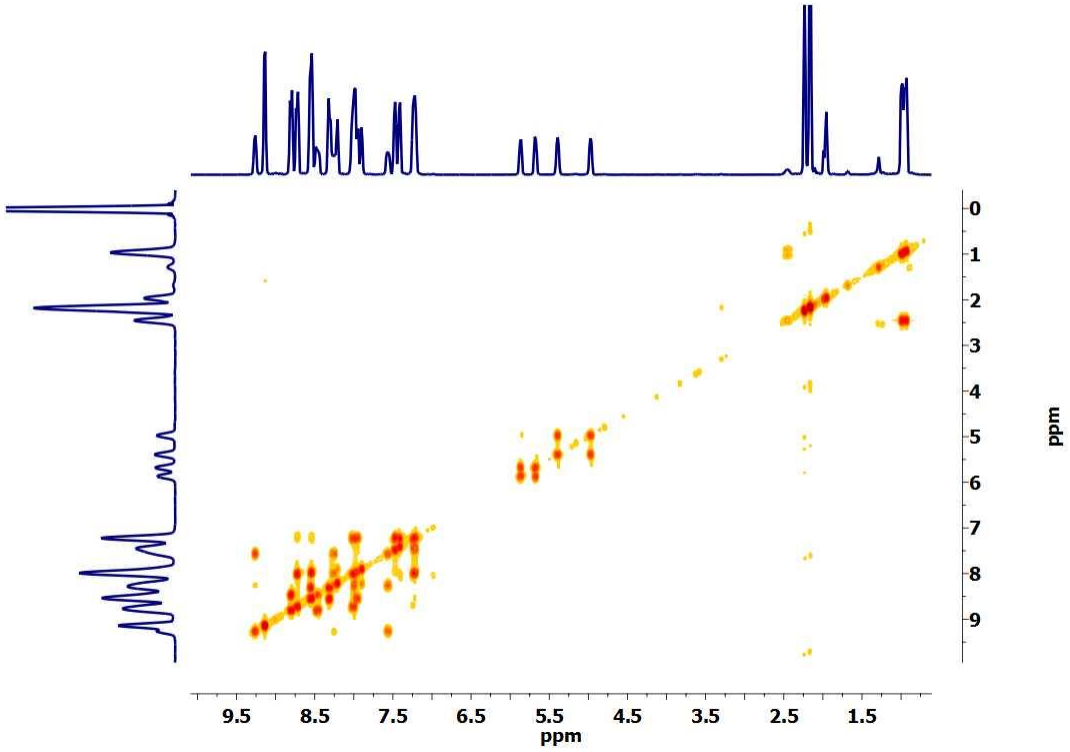


Figure S16. ^{1}H-^{1}H COSY NMR spectrum of PF_6 salt of complex **2**.

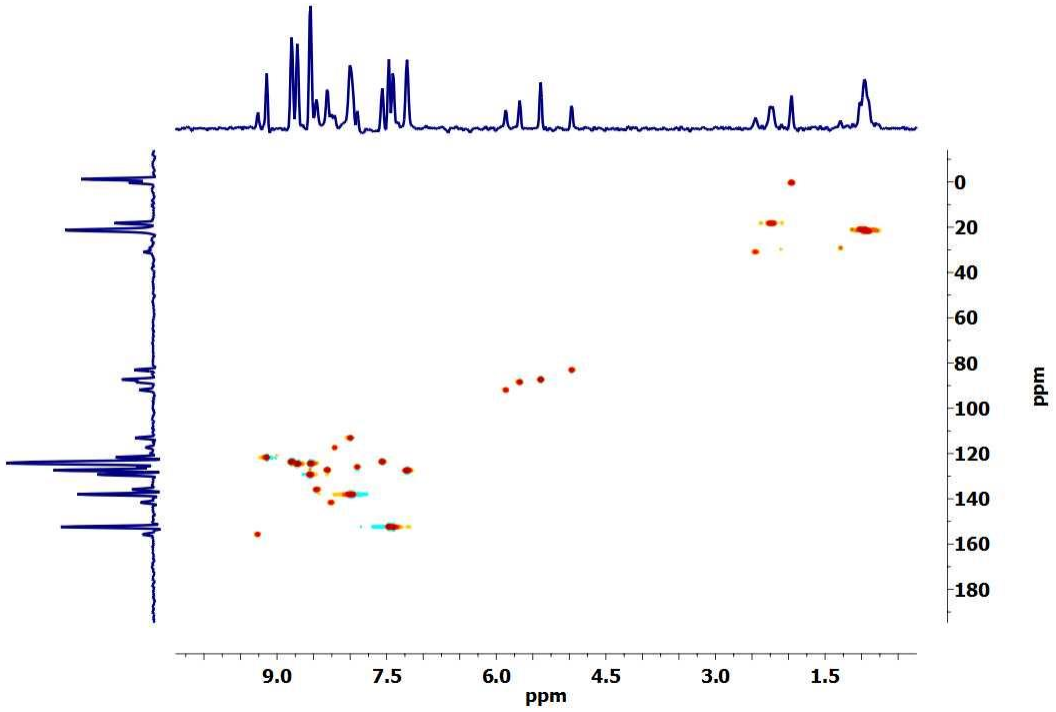
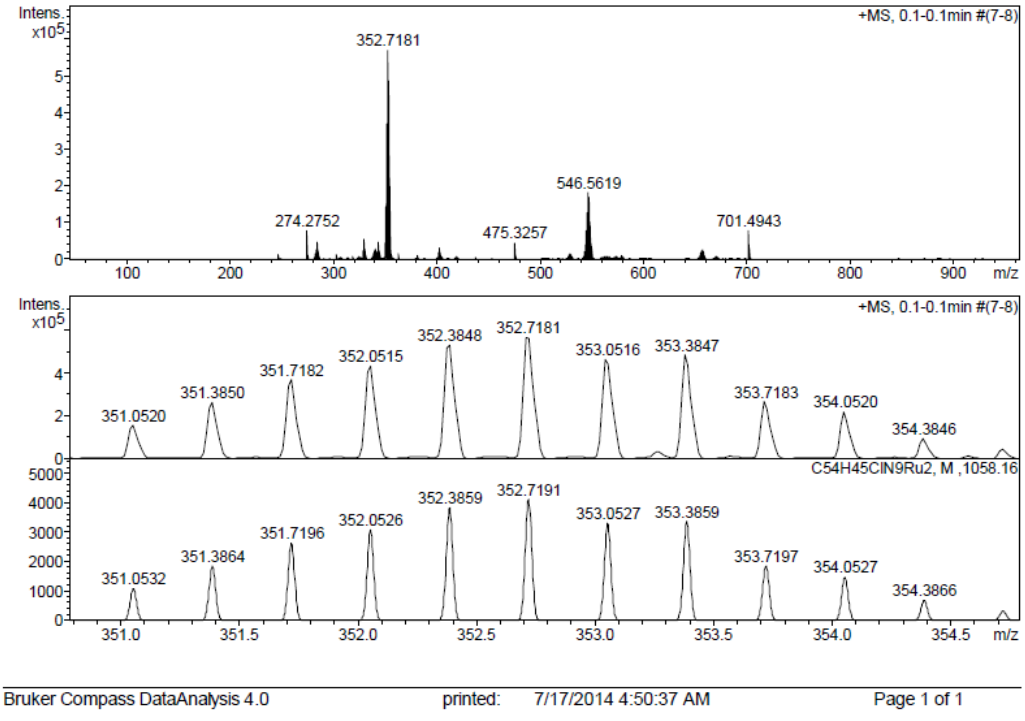


Figure S17. ^{1}H-^{13}C HSQC NMR spectrum of PF_6 salt of complex **2**.



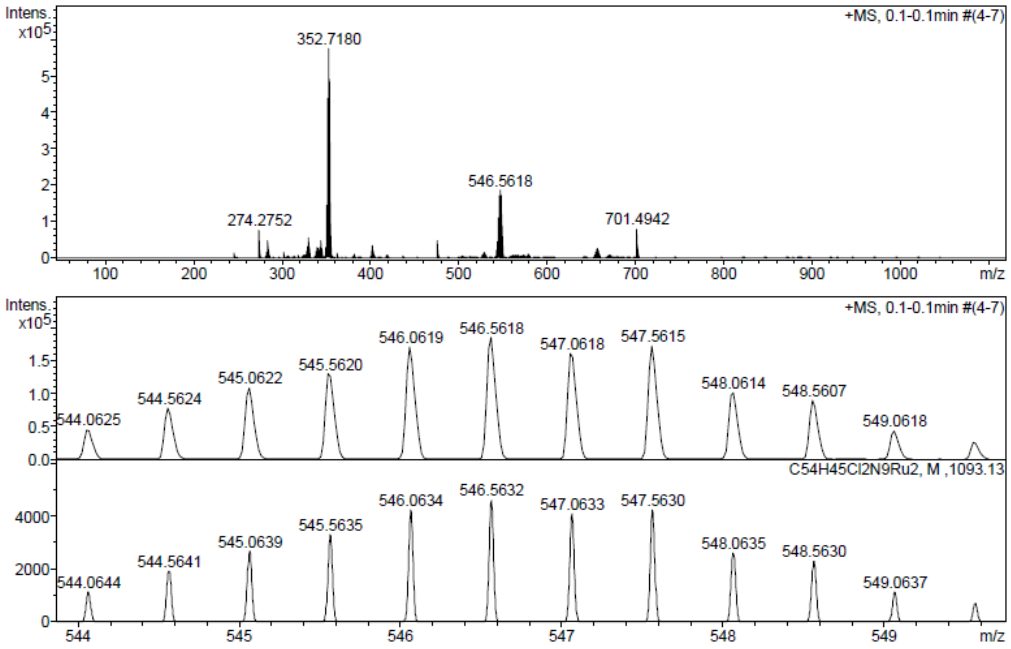


Figure S18. ESI-MS (positive ion mode) spectrum of halide ($2Cl^-$ and Br^-) salt of complex **2**.

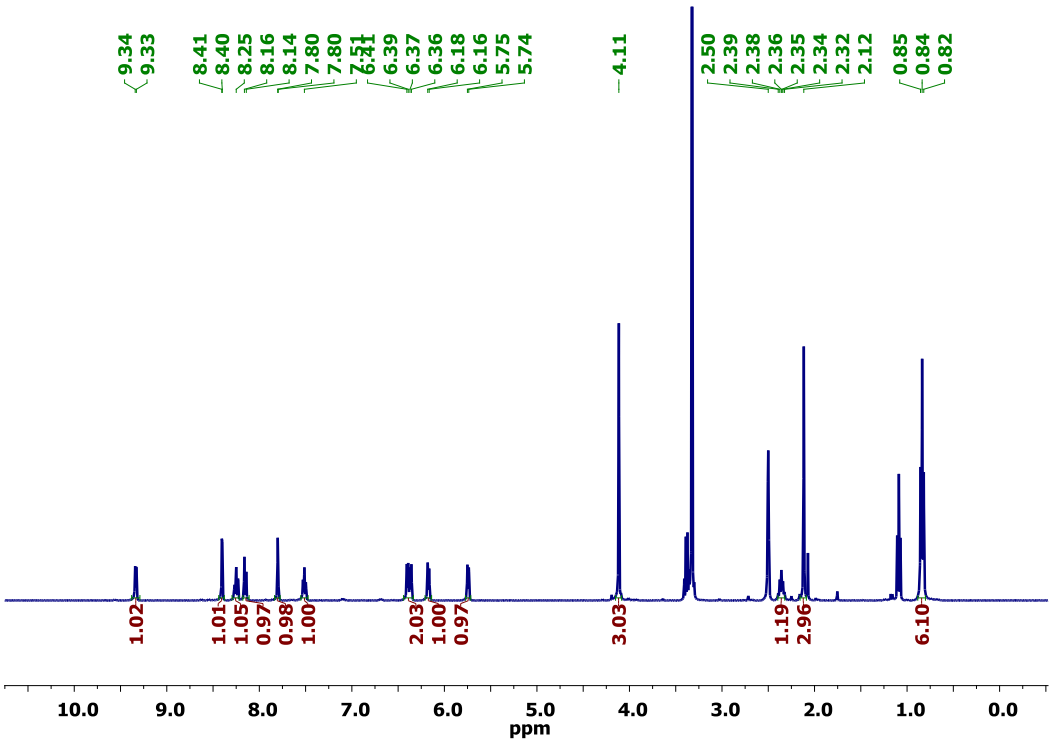


Figure S19. ^{1}H NMR spectrum of of complex **3** (400 MHz, DMSO-d_6, 300 K).

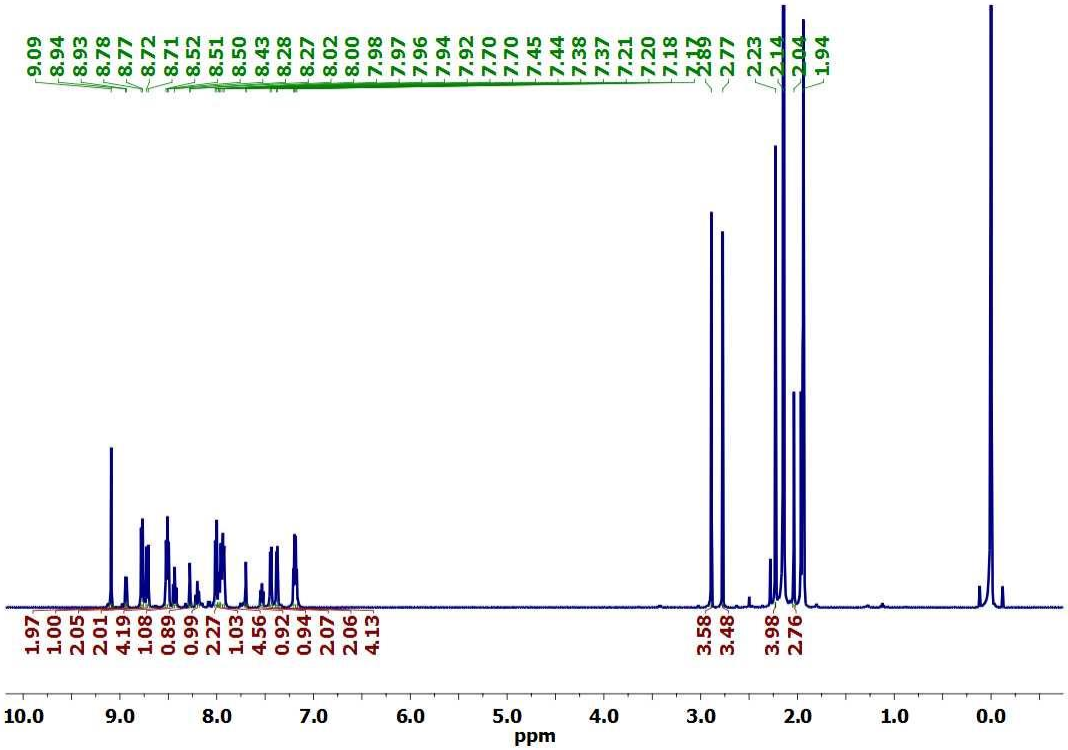


Figure S20. ^{1}H NMR spectrum of of complex **4** (500 MHz, CD_3CN, 300 K).

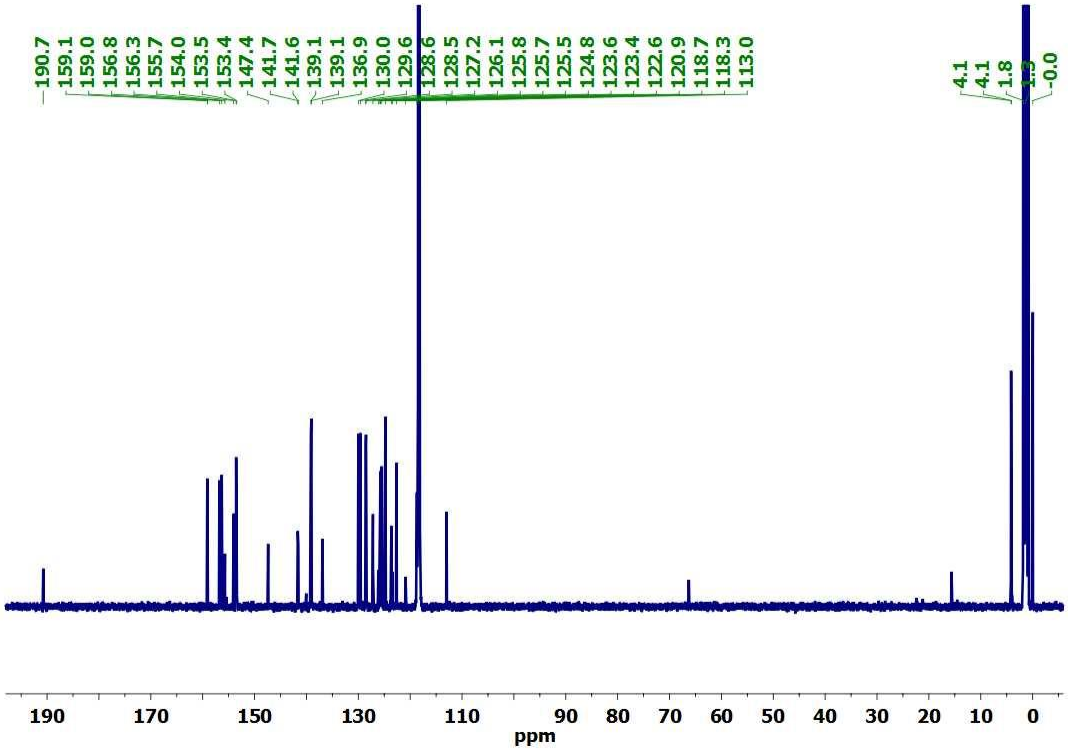


Figure S21. ^{13}C{^{1}H} NMR spectrum of complex **4** (125 MHz, CD_3CN, 300 K).

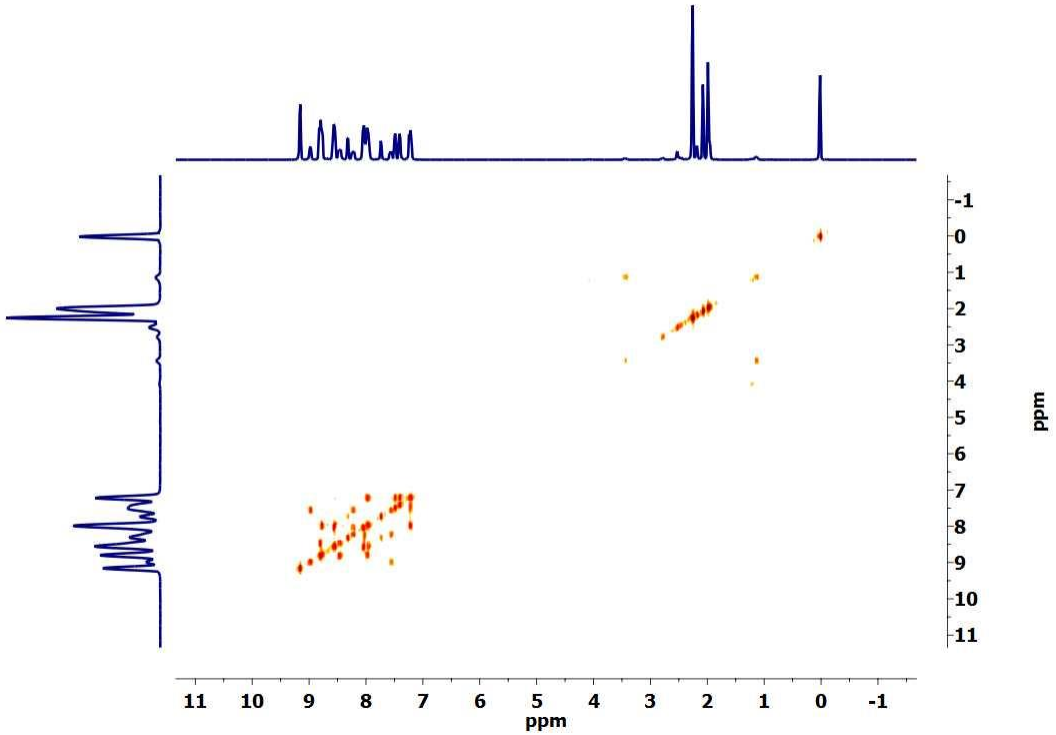


Figure S22. ^{1}H-^{1}H COSY NMR spectrum of complex **4**.

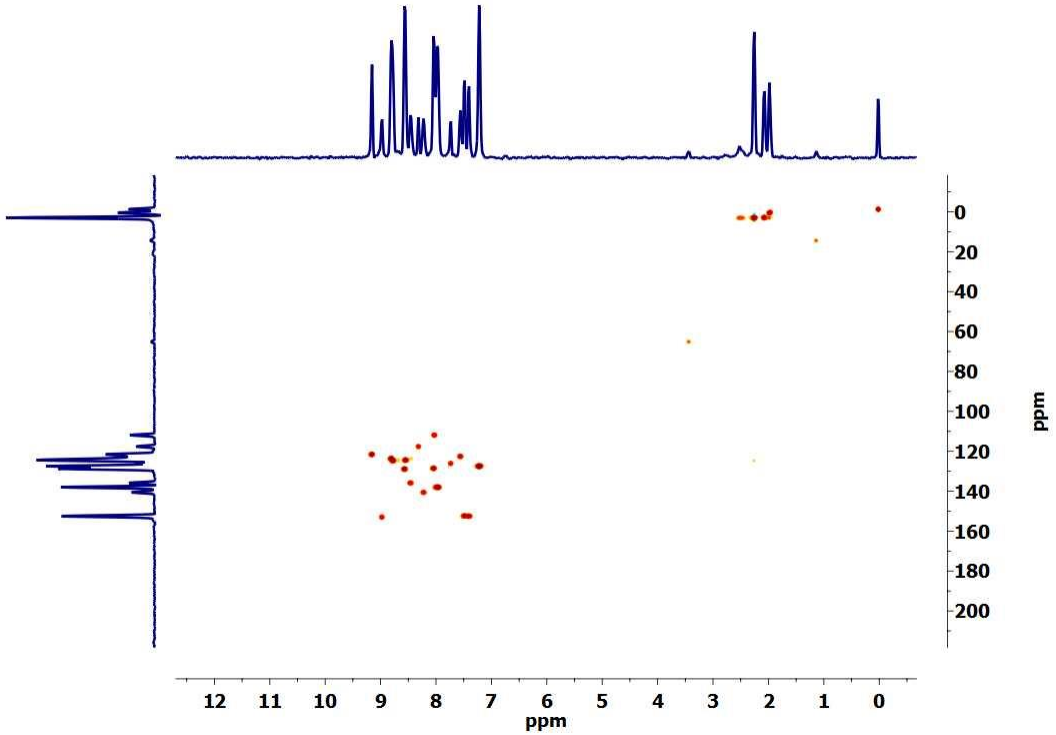


Figure S23. ^{1}H-^{13}C HSQC NMR spectrum of complex **4**.

UV-Vis spectroscopic studies

UV-Vis spectroscopic studies were carried out on a Cary 100 UV-Vis spectrophotometer using 1.0 cm quartz cuvettes at room temperature. Hexafluorophosphate salts of complex **1** and complex **2** were used for this study. Stock solutions of both the complexes were made in acetonitrile. The total volume of each sample was kept constant to 2.5 mL.

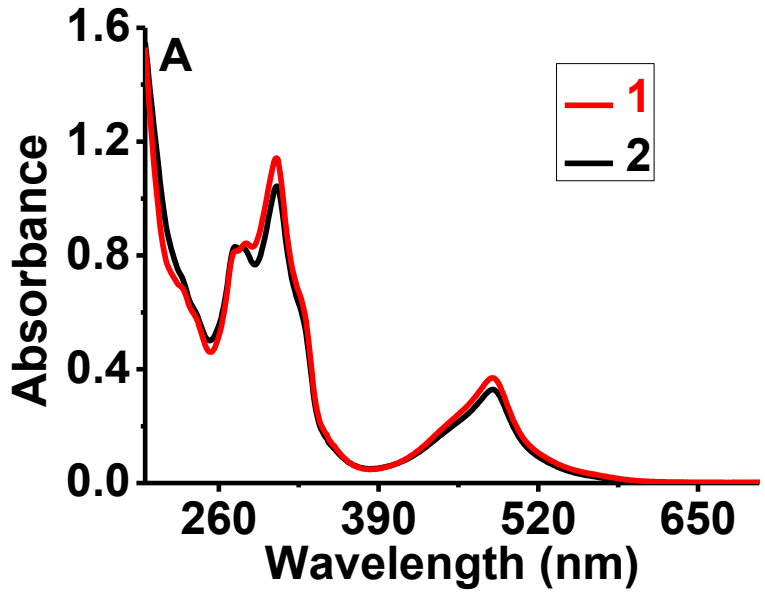


Figure S24. UV-Vis spectra of complex **1** and complex **2**

Electrochemical analysis of the complexes

Electrochemical studied (CV and DPV) were carried out by three electrode configuration. Working electrode: Pt disk (1 mm diameter); counter electrode: a Pt wire; reference electrode: saturated calomel electrode, SCE. Hexafluorophosphate salts of complex **1** and complex **2** were used to avoid any interference arising from halide oxidation processes. $[NBu_4]PF_6$ (0.1 M) in acetonitrile was used as the supporting electrolyte. Ferrocene ($E_{1/2}$, Fc/Fc^+ = 0.37 volts vs. SCE) was used as an external calibration standard for all the experiments.

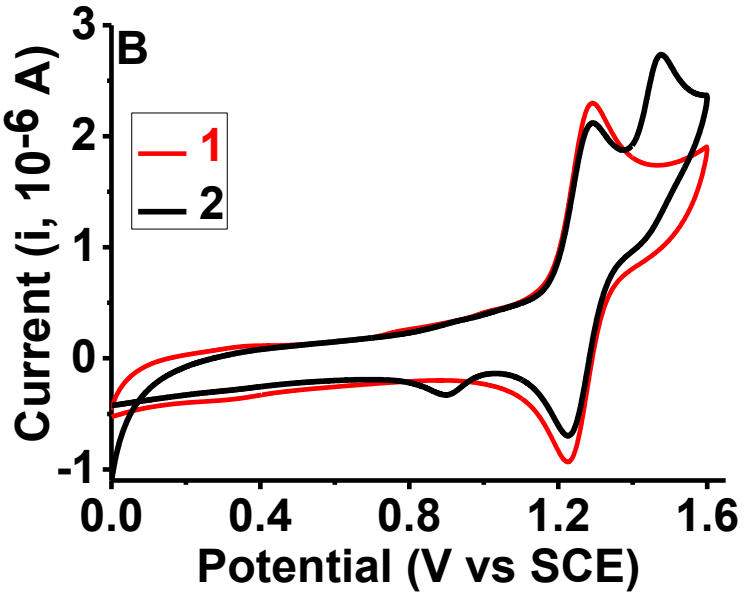


Figure S25. Cyclic voltammogram of complex **1** and complex **2**.

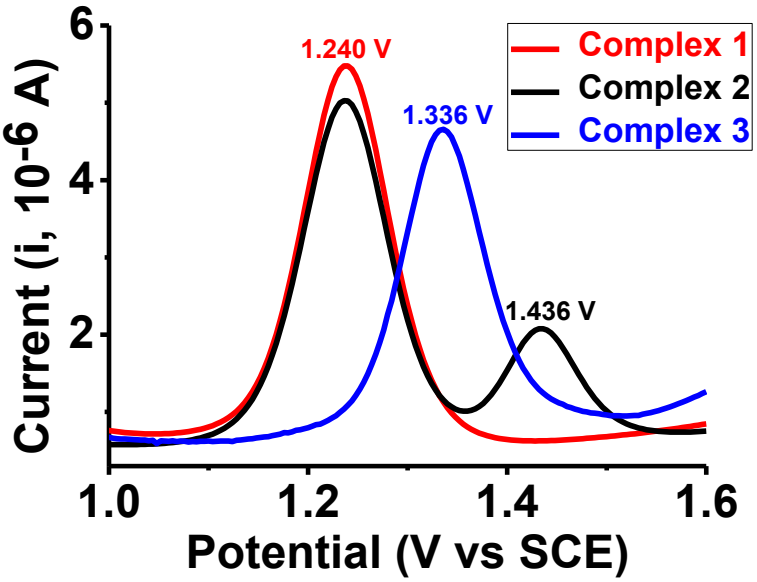


Figure S26. Differential pulse voltammogram of complexes **1**, **2** and **3**.

^{1}HNMR studies to check the fate of *para*–cymene under oxidative conditions

^{1}HNMR studies were carried out to check the fate of *para*–cymene under oxidative conditions. Hexafluorophosphate salt of complex **2** (6.0 mg, 0.004 mmol) was dissolved in 0.3 mL of

acetone–d_6. 10 equivalents of $NaIO_4$ were dissolved in 0.2 mL of D_2O and transferred to acetone–d_6 solution of complex **2** . The fate of *para*–cymene was monitored upto 30 min by ^{1}HNMR spectroscopy (Figure 3, main article). Presence of free *para*–cymene was confirmed by comparing the resonance peaks with authentic *para*–cymene sample. Similar studies were also carried out with complex **3** to compare the rate of *para*–cymene loss under the similar conditions (Figure 3, main article).

General procedure for the catalysis studies

Substrate (0.4 mmol) in 1 mL of acetone and catalyst (0.5 mol%, halide salt; $2Cl^-$ and Br^-} of complex **2** or PF_6^- salt of complex **2** or complex **3** or complex **4**) were taken in a round bottom flask. 2 mL of acetone and 2 mL of H_2O were added to it. $NaIO_4$ (213 mg, 1.0 mmol) was dissolved in 1 mL of H_2O and transferred to the reaction mixture. The reaction mixture was stirred at room temprature for ~15 min–240 min. After this time, Na_2SO_3 (2.0 mmol) was added to the reaction mixture followed by addition of 2 mL of DCM and 3 mL of H_2O. The reaction mixture was further stirred for 10 min. Standard (ethylbenzene or mesitylene or stilbene or acetophenone) was added as a reference and the reaction mixture was again stirred for 5 min. It was then transferred to a separating funnel with the help of 3 mL of H_2O and 8 mL of DCM. The organic layer was separated and aqueous layer was again extracted with 5 mL of DCM (two times). The combined organic layer was washed with 20 mL of brine solution. Products and unreacted substrates were analyzed by GCMS. The yields of the products were calculated by GC analyses.

All the products (with yields >20%) were isolated in pure form by silica gel column chromatography. ^{1}H NMR spectrum of each product was recorded to further confirm their identity and purity level (see below).

Styrene. Yield of benzaldehyde = 25.5 mg (60%) with complex **2** (halide salt; $2Cl^-$ and Br^-), 4.3 mg (10%) with complex **3** and 17.4 mg (41%) with complex **4**.

^{1}H NMR (400 MHz, $CDCl_3$, 300K): δ 10.03 (s, 1H), 7.92–7.83 (m, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.5 Hz, 2H) ppm.

4-Methylstyrene. Yield of 4-methylbenzaldehyde = 29.3 mg (61%) with complex **2** (halide salt; $2Cl^-$ and Br^-), 3.4 mg (7%) with complex **3** and 14.4 mg (30%) with complex **4**.

^{1}H NMR (400 MHz, $CDCl_3$, 300K): δ 9.96 (s, 1H), 7.77 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 7.9 Hz, 2H), 2.44 (s, 3H) ppm.

4-Chlorostyrene. Yield of 4-chlorobenzaldehyde = 36.0 mg (64%) with complex **2** (halide salt; $2Cl^-$ and Br^-) and 31.5 mg (56%) with complex **4**.

^{1}H NMR (400 MHz, $CDCl_3$, 300K): δ 9.99 (s, 1H), 7.83 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H) ppm.

4-Fluorostyrene. Yield of 4-fluorobenzaldehyde = 29.8 mg (60%) with complex **2** (halide salt; $2Cl^-$ and Br^-) and 25.3 mg (51%) with complex **4**.

^{1}H NMR (400 MHz, $CDCl_3$, 300K): δ 9.96 (s, 1H), 7.90 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.20 (t, *J* = 8.5 Hz, 2H) ppm.

α-Methylstyrene. Yield of acetophenone = 34.6 mg (72%) with complex **2** (halide salt; $2Cl^-$ and Br^-), 10.6 mg (22%) with complex **3** and 13.5 mg (28%) with complex **4**.

^{1}H NMR (400 MHz, $CDCl_3$, 300K): δ 8.01–7.90 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 2.60 (s, 3H) ppm.

4-Vinylanisole. Yield of 4-methoxybenzaldehyde = 23.4 mg (43%) with complex **2** (halide salt; $2Cl^-$ and Br^-), 9.3 mg (17%) with complex **3** and 22.3 mg (41%) with complex **4**.

^{1}H NMR (400 MHz, $CDCl_3$, 300K): δ 9.88 (s, 1H), 7.83 (d, *J* = 8.7 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 3.88 (s, 3H) ppm.

4-Bromostyrene. Yield of 4-bromobenzaldehyde = 44.4 mg (60%) with complex **2** (halide salt; $2Cl^-$ and Br^-) and 47.4 mg (64%) with complex **4**.

^{1}H NMR (400 MHz, $CDCl_3$, 300K): δ 9.98 (s, 1H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H) ppm.

***Trans*-stilbene.** Yield of benzaldehyde = 56.9 mg (67%) with complex **2** (halide salt; $2Cl^-$ and Br^-), 34.0 mg (40%) with complex **3** and 55.2 mg (65%) with complex **4**.

***Cis*-stilbene.** Yield of benzaldehyde = 62 mg (73%) with complex **2** (halide salt; $2Cl^-$ and Br^-), 39.9 mg (47%) with complex **3** and 57.7 mg (68%) with complex **4**.

Allylbenzene. Yield of 2-phenylacetaldehyde = 20.7 mg (43%) with complex **2** (halide salt; $2Cl^-$ and Br^-) and 24.5 mg (51%) with complex **4**.

^{1}H NMR (400 MHz, $CDCl_3$, 300K): δ 9.76 (t, *J* = 2.4 Hz, 1H), 7.38 (m, 2H), 7.32 (m, 1H), 7.23 (m, 2H), 3.69 (d, *J* = 2.3 Hz, 2H) ppm.

***Trans*-α-methylstilbene.** Yield of acetophenone = 36.0 mg (75%) with complex **2** (halide salt; $2Cl^-$ and Br^-), 24.0 mg (50%) with complex **3** and 33.6 mg 70% with complex **4**.

Diphenylacetylene. Yield of benzil = 50.5 mg (60%) with complex **2** (halide salt; $2Cl^-$ and Br^-), 21.0 mg (25%) with complex **3** and 54.6 mg (65%) with complex **4**.

^{1}H NMR (400 MHz, $CDCl_3$, 300K): δ 8.06–7.89 (m, 4H), 7.66 (t, *J* = 7.4 Hz, 2H), 7.52 (t, *J* = 7.8 Hz, 4H) ppm.

1-Phenyl1butyne. Yield of 1-Phenylbutane-1,2-dione = 41.5 mg (64%) with complex **2** (halide salt; $2Cl^-$ and Br^-), 15.6 mg (24%) with complex **3** and 34.4 mg (53%) with complex **4**.

^{1}H NMR (400 MHz, $CDCl_3$, 300K): δ 8.04–7.92 (m, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 2.92 (q, *J* = 7.3 Hz, 2H), 1.20 (t, *J* = 7.3 Hz, 3H) ppm.

1-Phenyl1propyne. Yield of 1-Phenylpropane-1,2-dione = 39.7 mg (67%) with complex **2** (halide salt; $2Cl^-$ and Br^-), 11.3 mg (19%) with complex **3** and 30.2 mg (51%) with complex **4**.

^{1}H NMR (400 MHz, $CDCl_3$, 300K): δ 8.04–7.97 (m, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 2.53 (s, 3H) ppm.

^{1}H NMR spectra of the products obtained by oxidative scission of carbon-carbon multiple bonds.

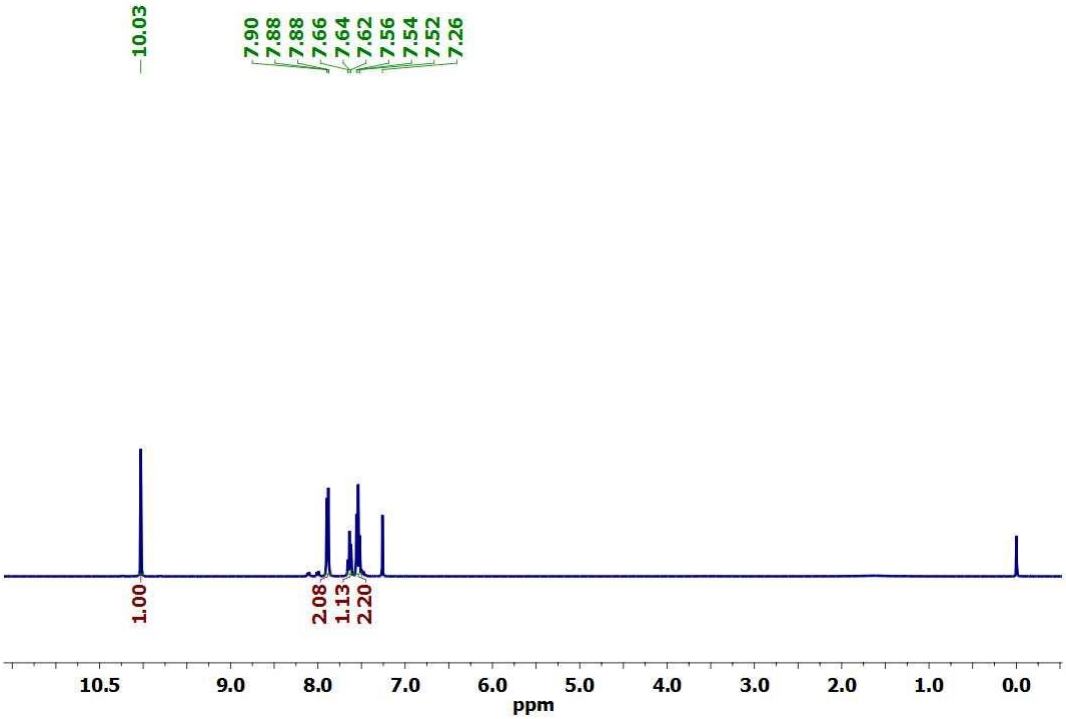


Figure S27. ^{1}H NMR spectrum of **Benzaldehyde** (400 MHz, $CDCl_3$, 300 K).

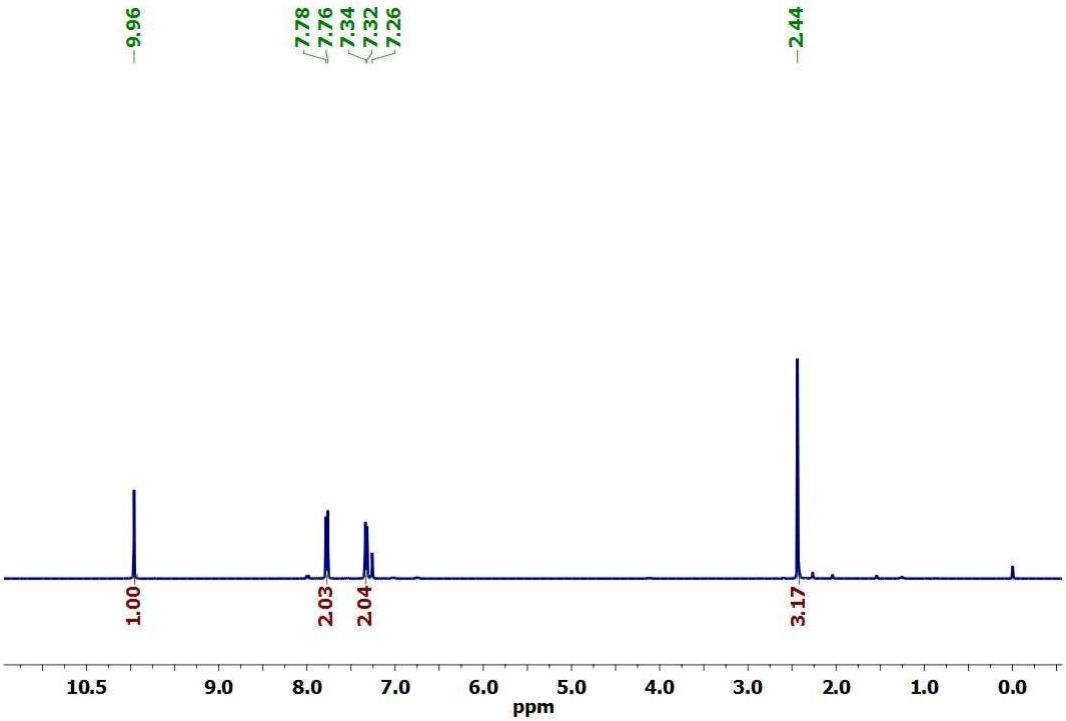


Figure S28. ^{1}H NMR spectrum of **4-Methylbenzaldehyde** (400 MHz, $CDCl_3$, 300 K).

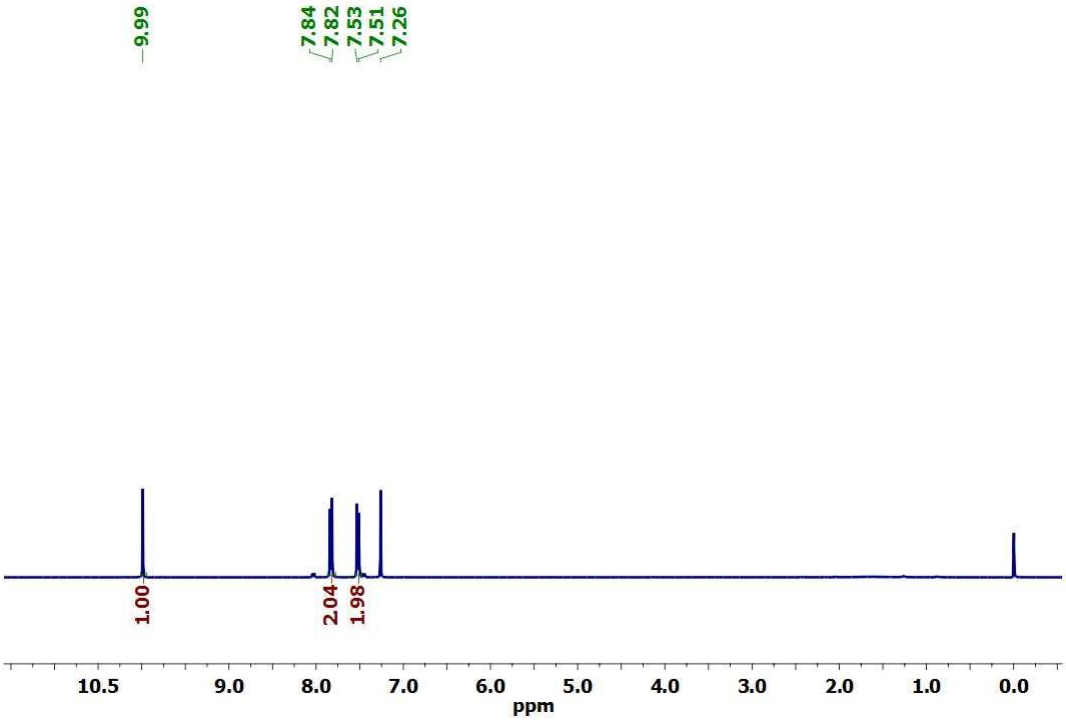


Figure S29. ^{1}H NMR spectrum of **4-Chlorobenzaldehyde** (400 MHz, $CDCl_3$, 300 K).

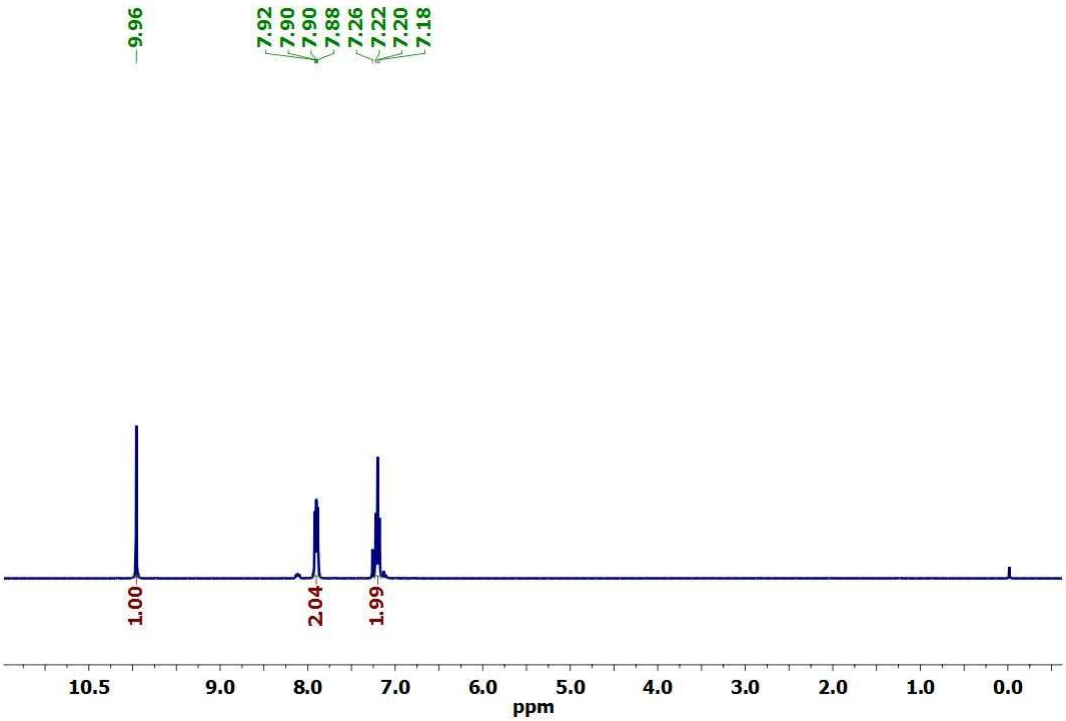


Figure S30. ^{1}H NMR spectrum of **4-Fluorobenzaldehyde** (400 MHz, $CDCl_3$, 300 K).

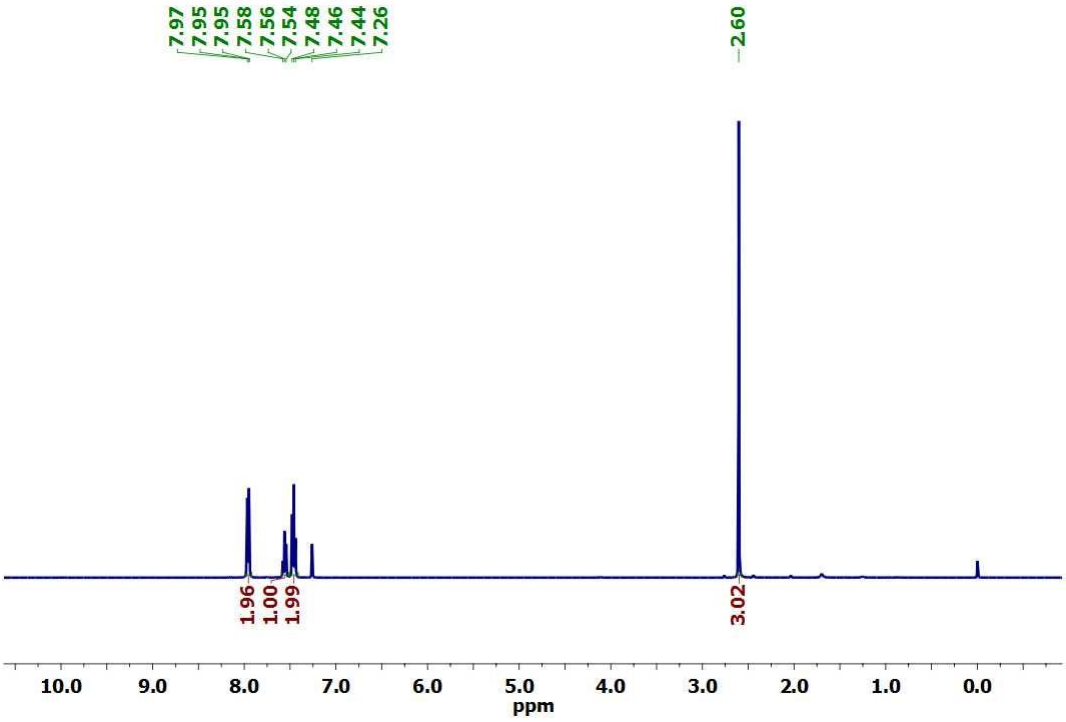


Figure S31. ^{1}H NMR spectrum of **Acetophenone** (400 MHz, $CDCl_3$, 300 K).

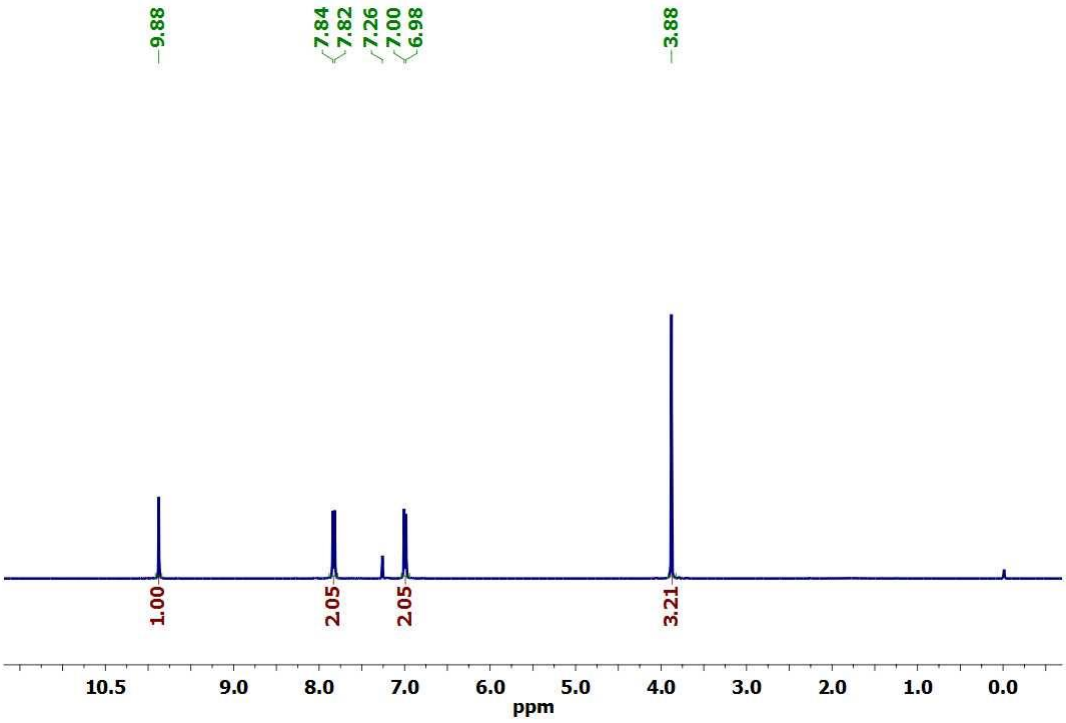


Figure S32. ^{1}H NMR spectrum of **4-Methoxybenzaldehyde** (400 MHz, $CDCl_3$, 300 K).

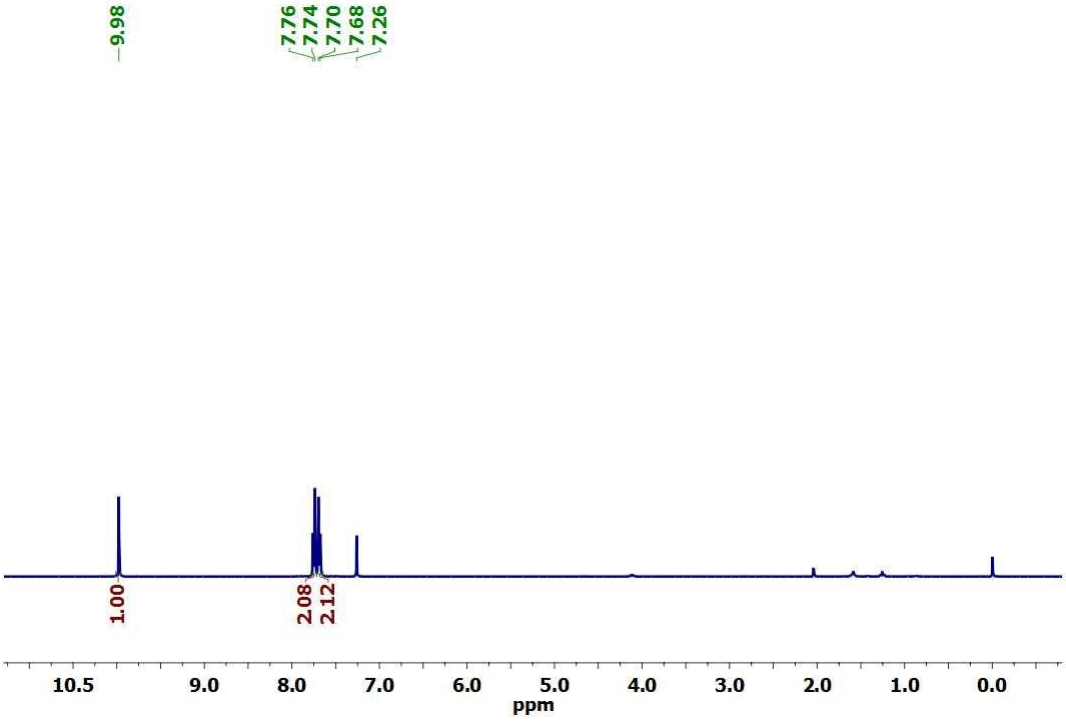


Figure S33. ^{1}H NMR spectrum of **4-Bromobenzaldehyde** (400 MHz, $CDCl_3$, 300 K).

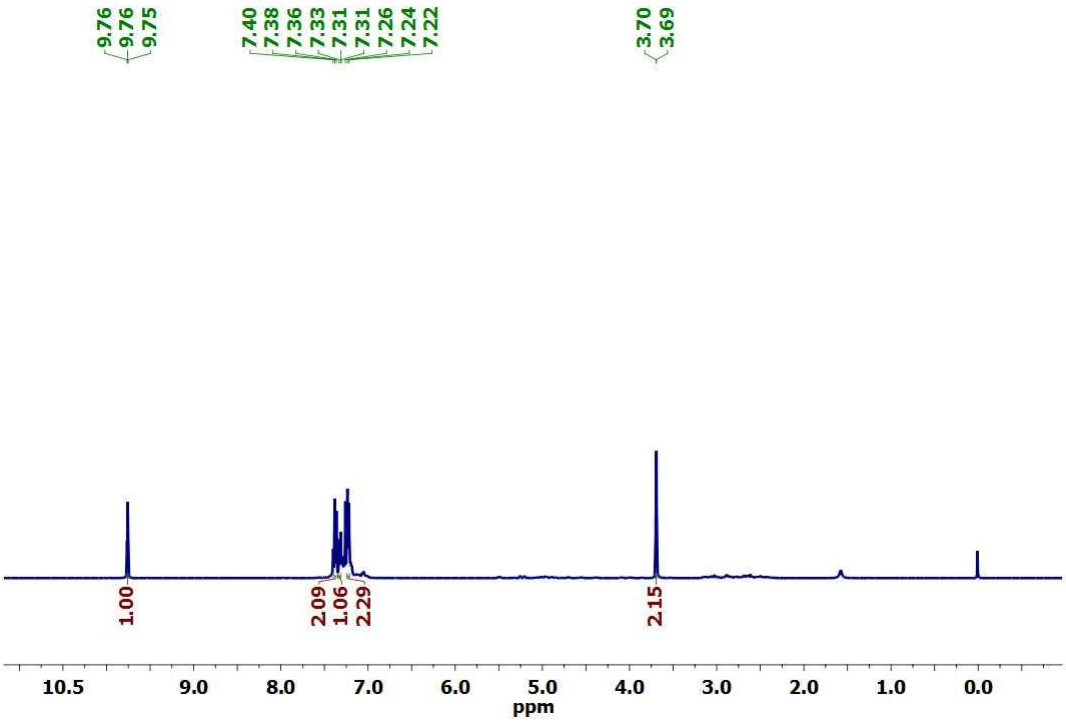


Figure S34. ^{1}H NMR spectrum of **2-Phenylactaldehyde** (400 MHz, $CDCl_3$, 300 K).

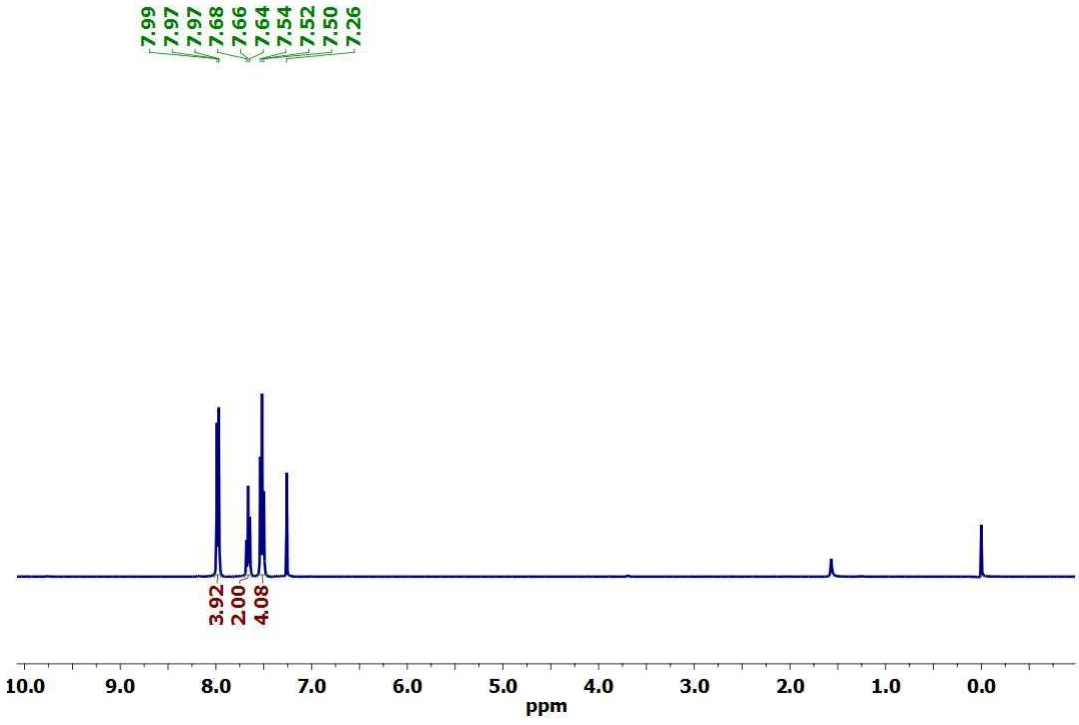


Figure S35. ^{1}H NMR spectrum of **Benzil** (400 MHz, $CDCl_3$, 300 K).

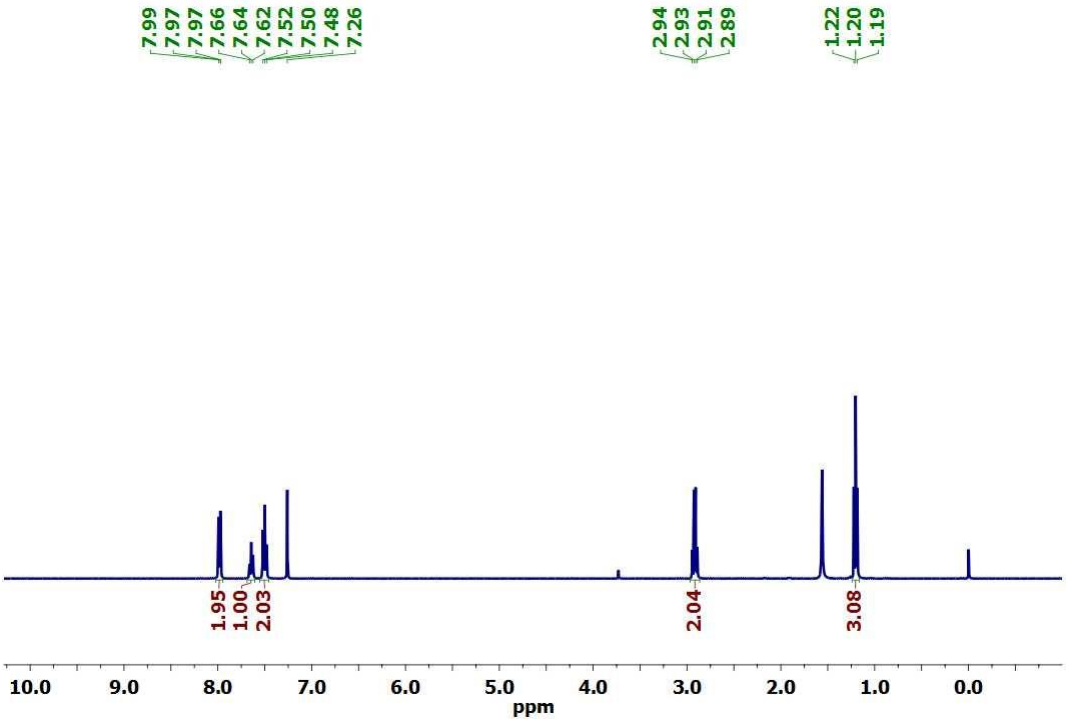


Figure S36. ^{1}H NMR spectrum of **1-Phenylbutane-1,2-dione** (400 MHz, $CDCl_3$, 300 K).

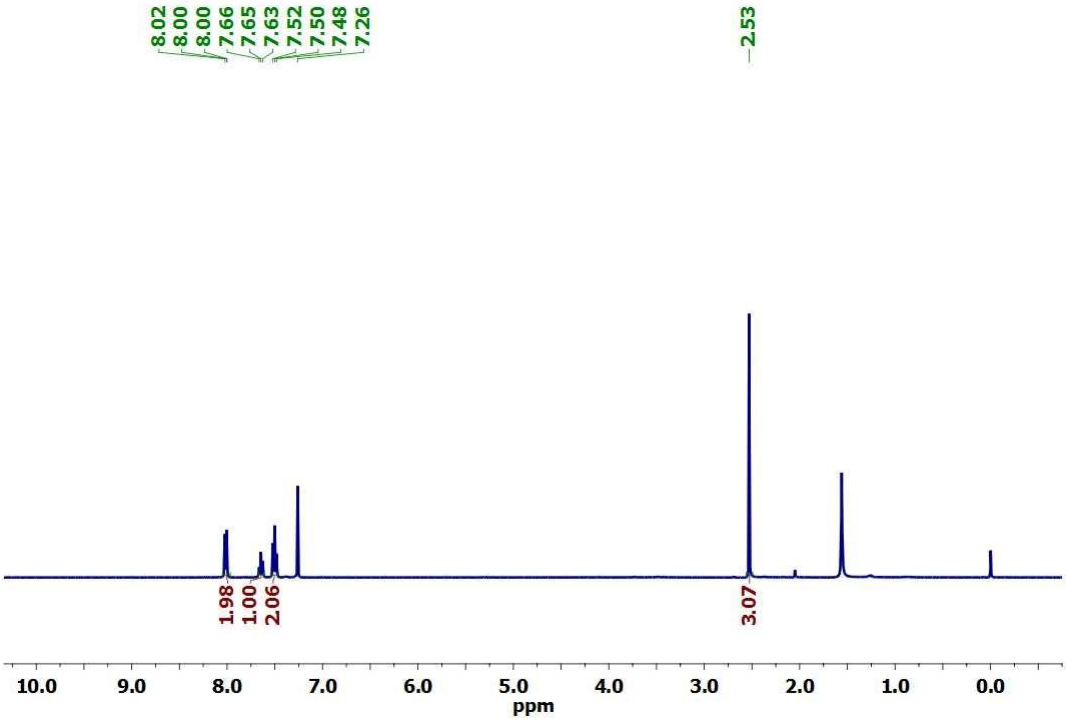


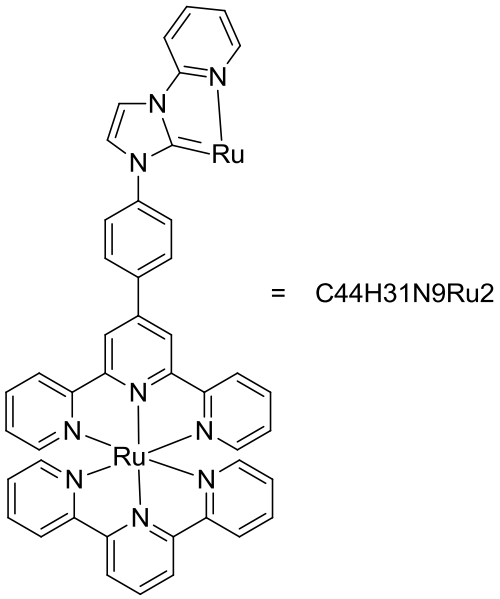
Figure S37. ^{1}H NMR spectrum of **1-Phenylpropane-1,2-dione** (400 MHz, $CDCl_3$, 300 K).

General procedure for studying the kinetic profile of the catalytic reactions with complex 2 and complex 3

For these experiments, catalyst (0.5 mol%, hexafluorophosphate salt), 4–methylstyrene (47.3 mg, 0.4 mmol), mesitylene (used as an internal standard) and $NaIO_4$ (213 mg, 1.0 mmol) were mixed in the solvent system, acetone-water (6 mL, v/v, 1:1). The reactions were carried out at room temperature and the yields of the product (4–methylbenzaldehyde) were determined by GC after different time intervals upto 60 min. The results were plotted as shown in Figure 4 (main article).

Oxidation of 4–methylstyrene under substoichiometric reaction conditions monitored by mass spectrometry

This experiment was carried out to check the specieses present in the reaction mixture during the catalysis. Catalyst (0.005 mmol, PF_6 salt of complex **2**), 4–methylstyrene (0.05 mmol) and $NaIO_4$ (0.125 mmol) were taken in a solvent system (acetone + water; 3 mL, v/v, 1:1) in a round bottom flask. Reaction was carried out for 30 min at room temprature. After this, GC analysis of the reaction mixture showed the formation of product (substrate:product, 1:3). ESI-HRMS analysis of the same reaction mixture showed a number cluster peaks related to different ruthenium specieses present in the solution during the catalysis (Figure S38).



= C44H31N9Ru2

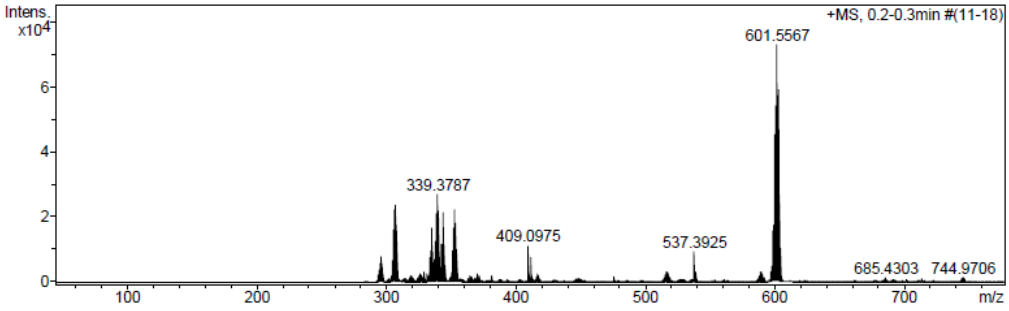
$[C_{44}H_{31}N_9Ru_2\text{-}H]^{3+}$ = 296

$[C_{44}H_{31}N_9Ru_2\text{-}H + O2]^{3+}$ =306

$[C_{44}H_{31}N_9Ru_2(CH_3COCH_3)(H_2O)_2Cl]^{3+}$ = 339

$[C_{54}H_{45}N_9Ru_2Cl]^{3+}$ = 352 (mother complex)

$[C_{54}H_{45}N_9Ru_2ClPF_6]^{2+}$ = 601 (mother complex)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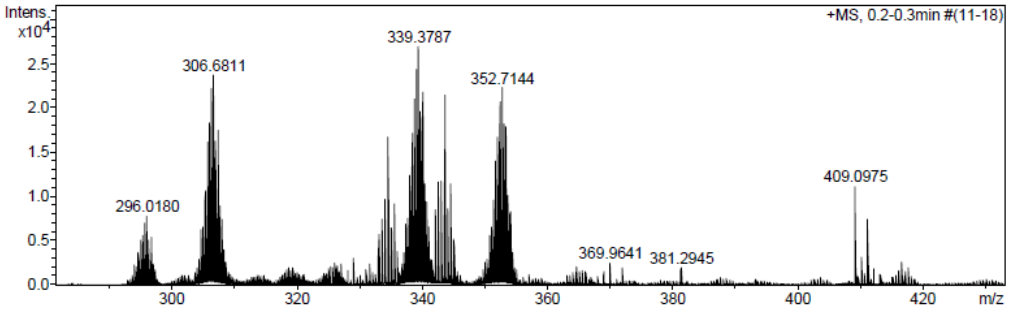
m/z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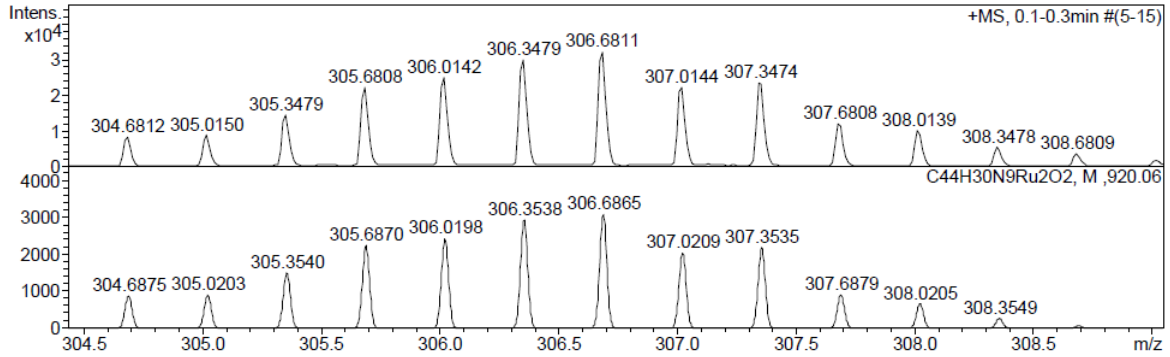
m/z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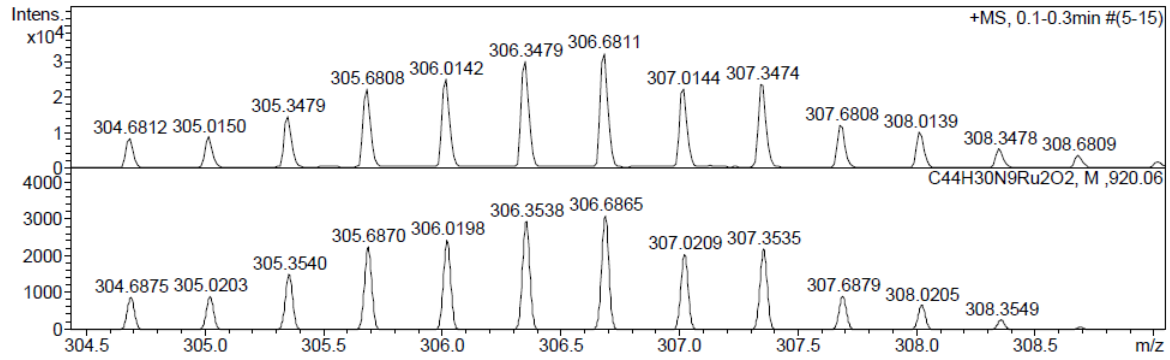
m/z


Intens.
x10^4
+MS, 0.1-0.3min #(5-15)
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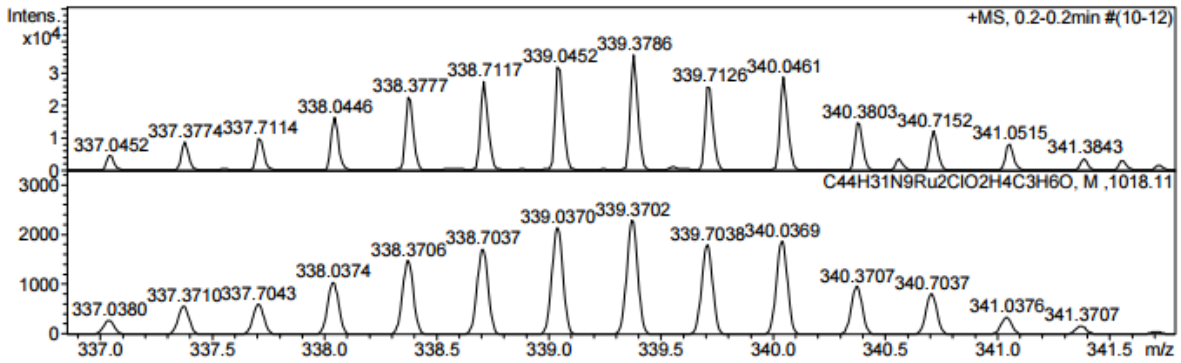


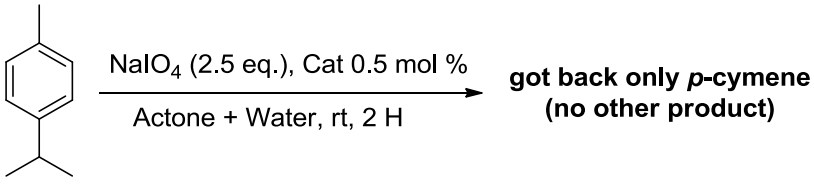
Scheme S38. Substoichiometric reaction of 4–methylstyrene (complex **2**:$NaIO_4$:4–methystyrene; 1:25:10).

Effect of added *para*–cymene and different arenes

For these experiments, the amounts of catalyst (0.5 mol%) (halide; $2Cl^-$ and Br^- salt of complex), 4–methylstyrene (47.3 mg, 0.4 mmol) and $NaIO_4$ (213 mg, 1.0 mmol) were kept constant in a fixed volume of solvent (acetone + water; 6 mL, v/v, 1:1). The amount of added *para*–cymene to the reaction mixture was varied from 0 to 80 equivalents with respect to catalyst precursor. The reactions were carried out at room temperature for 25 min (in a similar fashion as described for catalysis). The yields of 4–methylbenzaldehyde were determined by GC analysis (using *trans*-stilbene as an internal standard) (Figure 5, main article). To check the effect of different arenes (both electron deficient and electron rich arenes), similar procedure was adopted and ~40 equivalents of different arenes were added to the reaction mixture (Figure 5, main article).

Para-cymene as a starting material

To check whether decoordinated *para*–cymene is getting transformed under the catalytic conditions, catalysis with *para*–cymene as a substrate was performed with halide ($2Cl^-$ and Br^-) salt of complex **2** (in a similar fashion as described in general catalysis procedure). GCMS analysis showed that *para*–cymene was not transforming to other products (Scheme S4) and only *para*–cymene peak appeared when analyzed by GC and GCMS (confirmed by authentic *para*–cymene sample).



Scheme S4. Catalytic reaction with *para*-cymene as substrate with complex–**2** as catalyst (monitored by GC and GCMS analysis).

References

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