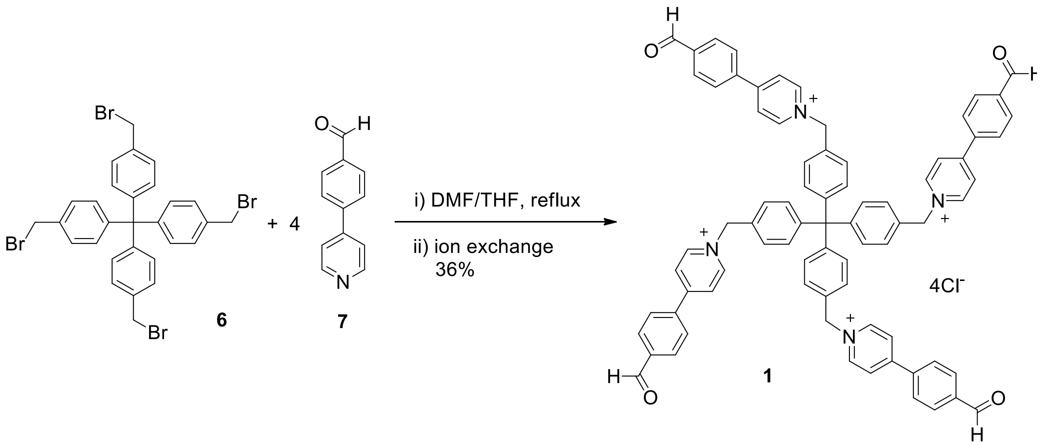
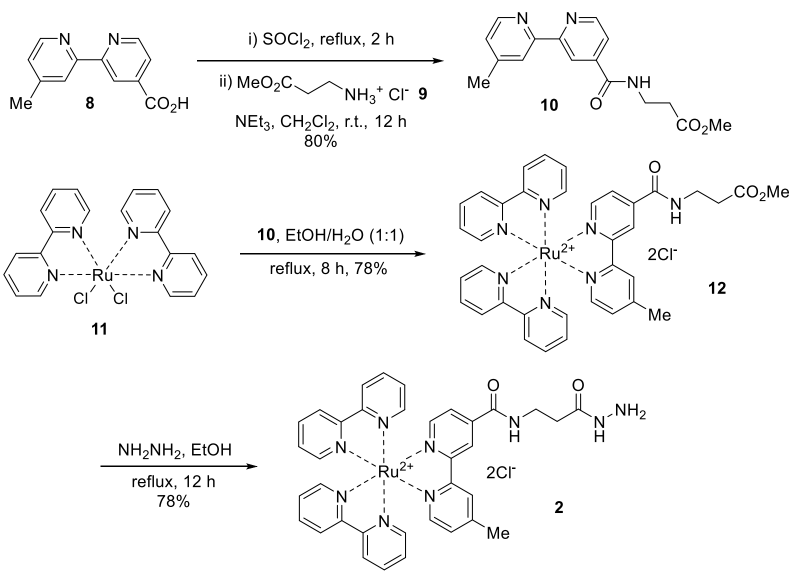
Electronic Supplementary Material (ESI) for ChemComm.



Compound 1. A mixture of compounds **6** (0.14 g, 0.20 mmol) and **7** (0.18 g, 1. 00 mmol) in THF (5 mL) and DMF (10 mL) was stirred under reflux for 12 h and then cooled to room temperature. To the mixture was added acetone (20 mL) and the precipitate formed thereafter was filtrated and washed with acetone and dried under vacuum. The resulting solid was further recrystallized from acetonitrile to give the crude product as bromide salt as a light yellow solid. The solid was then dissolved in water of least amount. To the solution was added dropwise saturated aqueous solution of potassium hexafluorophosphate until no precipitate was formed. The precipitate was filtrated and washed with cold water and then dissolved in acetonitrile of least amount. To the solution was added dropwise saturated aqueous solution of tetrabutylammonium chloride (TCA). The precipitate formed was filtrated and washed with cold acetonitrile and further dried in vacuo to give compound **1** as a pale yellow solid (0.093 g, 37%). M.p. > 300 °C (decomp). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 10.16 (s, 4H), 9.36 (d, J = 8.0 Hz, 8H), 8.64 (d, J = 8.0 Hz, 8H), 8.28 (d, J = 8.0 Hz, 8H), 8.14 (d, J = 8.0 Hz, 8H), 7.50 (d, J = 8.0 Hz, 8H), 7.23 (d, J = 8.0 Hz, 8H), 5.86 (s, 8H). ^{13}C NMR (400 MHz, DMSO-d$_6$): δ 193.2, 154.3, 147.1, 145.6, 139.1, 138.5, 132.7, 131.3, 130.7, 129.5, 128.8, 126.2, 64.5, 62.3. HRMS (ESI): Calcd for $C_{77}H_{60}N_4O_4$: 276.1153 [M-4Cl]$^{4+}$. Found: 276.1148.

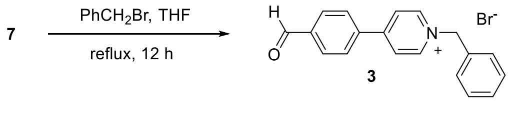


Compound 10. A mixture of compound **8** (0.21 g, 1.00 mmol) and thionyl chloride $SOCl_2$ (2 mL) was refluxed for 2 hours and then evaporated with a rotavapor. The resulting residue was dissolved in dichloromethane (3 mL). To the solution were added compound **9** (0.17 g, 1.2 mmol) and triethylamine

(0.5 mL) and the solution was stirred at room temperature for 12 hours. After workup, the resulting residue was subjected to column chromatography (CH_2Cl_2/petroleum ether 2:1) to give compound **10** as a white solid (0.24 g, 80%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.03 (s, 1H), 8.81 (d, *J* = 4.8 Hz, 1H), 8.74 (s, 1H), 8.59 (d, *J* = 4.7 Hz, 1H), 8.29 (s, 1H), 7.79 (d, *J* = 4.1 Hz, 1H), 7.36 (d, *J* = 4.0 Hz, 1H), 3.62 (s, 3H), 3.53 (d, *J* = 5.9 Hz, 3H), 2.64 (t, *J* = 6.8 Hz, 3H), 2.44 (s, 3H). ^{13}C NMR (400 MHz, DMSO): δ 172.1, 165.2, 156.5, 150.3, 149.6, 148.6, 143.0, 125.8, 121.9, 121.8, 118.4, 51.9, 40.2, 40.0, 39.8, 36.1, 33.7, 21.1. Calcd for $C_{16}H_{17}N_3O_3$: 300.1343. Found: 300.1358.

Compound 12. A mixture of compounds **10** (83 mg, 0.28 mmol) and **11** (0.12 g, 0.25 mmol) in ethanol and water (10 mL, 1:1) was heated under reflux for 8 hours and then evaporated with a rotavapor. The resulting residue was suspended in dichloromethane (5 mL) and the undissolved solid was filtrated off. To the filtrate was added ether (10 mL) and the resulting precipitate was filtrated off and washed with ether and dried in vacuo to give compound **12** as a red solid (0.14 g, 78%). ^{1}H NMR (400 MHz, CD_3OD): δ 9.03 (d, *J* = 1.4 Hz, 1H), 8.71 (d, *J* = 8.1 Hz, 4H), 8.67 (s, 1H), 8.14 (t, *J* = 7.9 Hz, 4H), 7.95 (d, *J* = 6.0 Hz, 1H), 7.85–7.80 (m, 4H), 7.78 (d, *J* = 5.9, 1.8 Hz, 1H), 7.64 (d, *J* = 5.8 Hz, 1H), 7.53–7.45 (m, 4H), 7.38 (d, *J* = 5.8 Hz, 1H), 3.75 (s, 2H), 3.69 (s, 3H), 2.70 (t, *J* = 6.6 Hz, 2H), 2.62 (s, 3H). ^{13}C NMR (400 MHz, CD_3OD): δ 149.5, 148.6, 148.5, 148.4, 148.43, 148.4, 147.6, 143.3, 142.7, 142.6, 142.6, 142.4, 141.8, 133.9, 129.3, 120.2, 119.0, 116.9, 116.1, 115.7, 115.6, 112.9, 42.3, 27.3, 24.3, 11.3. Calcd for $C_{36}H_{33}N_7O_3RuCl$: 748.1378. Found: 748.1378 $[M-Cl]^+$.

Compound 2. A mixture of **12** (83 mg, 0.28 mmol) and hydrazine hydrate (1 mL) in ethanol (5 mL) was heated under reflux for 12 hours and then evaporated with a rotavapor. The resulting residue was dissolved in dichloromethane (4 mL) and to the solution was added ether (5 mL). The precipitate formed was filtrated and washed with ether and dried in vacuo to give compound 2 as a red solid (0.14 g, 78%). ^{1}H NMR (400 MHz, CD_3OD): δ 9.10 (d, *J* = 1.4 Hz, 1H), 8.74 (d, *J* = 8.6 Hz, 5H), 8.15 (t, *J* = 7.8 Hz, 4H), 7.96 (d, *J* = 5.9 Hz, 1H), 7.87–7.77 (m, 5H), 7.65 (d, *J* = 5.8 Hz, 1H), 7.54–7.47 (m, 4H), 7.39 (d, *J* = 4.9 Hz, 1H), 3.71 (t, *J* = 6.8 Hz, 2H), 2.62 (s, 3H), 2.54 (t, *J* = 6.8 Hz, 2H). ^{13}C NMR (400 MHz, CD_3OD): δ 171.3, 164.3, 158.0, 157.1, 157.0, 157.0, 156.9, 156.1, 151.9, 151.3, 151.2, 151.1, 150.9, 150.3, 142.4, 137.9, 137.9, 137.8, 128.8, 127.6, 127.5, 125.6, 124.8, 124.3, 124.2, 124.2, 121.5, 36.5, 33.1, 19.9. Calcd for $C_{35}H_{33}ClN_9O_2Ru$: 748.1479. Found: 748.1490 $[M-Cl]^+$.



Compound 3. A mixture of benzyl bromide (85 mg, 0.50 mmol) and **7** (93 mg, 0.15 mmol) in THF (4 mL) was heated under reflux for 12 h and then cooled to room temperature. To the solution was added acetone (20 mL) and the precipitate formed thereafter was filtrated and washed with THF and dried in vacuum to afford compound **3** as a white solid (0.12 g, 50%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.13 (s, 1H), 9.32 (d, *J* = 8.0 Hz, 2H), 8.61 (d, *J* = 8.0 Hz, 2H), 8.26 (d, *J* = 8.0 Hz, 2H), 8.13 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 5.88 (s, 2H). ^{13}C NMR (400 MHz, DMSO-d_6): δ 193.3, 154.4, 145.5, 139.2, 138.4, 134.8, 130.7, 129.8, 129.7, 129.5, 129.2, 126.2, 63.1, 62.7. MS (ESI): *m/z* 274 $[M-Cl]^+$. HRMS (ESI): Calcd for $C_{19}H_{18}NO$: 274.1226 $[M-Cl]^+$. Found: 274.1230.

General procedures for reaction of SOF-CHO and 2. An aqueous solution (1 mL) of **SOF-CHO** ([**1**] = 1.0 mM) and **2** (0.5 mM) was stirred at 50 °C for 24 h and then used for the dialysis.

Dialysis experiment. To a dialysis bag (cutoff M_n = 1 kDa), which was immersed in water (25 mL), was added the above solution of **SOF-CH=N-[Ru(BPY)₃]** reaction mixture (2.0 mL, [**1**] = 1.0 mM).

The solution was subjected to a shaker for 24 hours and the outside water was renewed one time per 6 hours. The amount of **2** diffused into the outside water was determined by recording the adsorption of its bipyridine complex.

General procedure for the azide reduction reaction. For the reaction relating **2**, to a solution of Hantzsch ester (38 mg, 0.15 mmol, 1.5 equiv.), i-Pr_2NEt (0.18 mL, 1.0 mmol, 10 equiv.) and HCO_2H (37 µL, 1.0 mmol, 10 equiv.) in dichloromethane and n-hexane (5 mL, 1:1) was added azide **4** (17.7 mg, 0.10 mmol, 1.0 equiv.) and **2** (0.2 mg, 0.0003 mmol, 0.003 equiv.). The red solution was stirred at room temperature and irradiated with a 26 W CFL bulb at a distance of 20 cm until TLC indicated the complete consumption of the azide. The reaction mixture was then subjected to HPLC for analysis. For reactions relating **SOF-CH=N-[Ru(BPY)$_3$]**, to a mixture of Hantzsch ester (38 mg, 0.15 mmol, 1.5 equiv.), i-Pr_2NEt (0.18 mL, 1.0 mmol, 10 equiv.) and HCO_2H (37 µL, 1.0 mmol, 10 equiv.) in dichloromethane and n-hexane (5 mL, 1:1) was added azide **4** (17.7 mg, 0.1 mmol, 1.0 equiv.) and **SOF-CH=N-[Ru(BPY)$_3$]** (5 mg). The yellow solution was stirred at 25 ºC and irradiated with a 26 W CFL bulb at a distance of 20 cm. The reaction mixture was then subjected to HPLC for determining the content of amines **5X** by comparing with that of commercially available authentic samples.

Dynamic light scattering (DLS) measurement. DLS were determined on a Malvern Zetasizer Nano ZS90 using a monochromatic coherent He–Ne laser (633 nm) as the light source and a detector that performed the scattered light at an angle of 90°.

UV-Vis measurement procedure. UV-vis spectra were detected on a Perkin-Elmer 750s instrument. The UV-vis spectra of the solution were recorded.

Table S1. Estimated molecular orbital energy of the complex unit of **2**.

Compound	E_{gap}^{opt}(eV)[a]	$E_{1/2}^{ox}$ (V)[b]	LUMO(eV)[c]	HOMO(eV)[c]
2	2.38	1.54	–3.66	–6.04

[a]Optical band gap E_{gap}^{opt} =1240 / λ_{onset}^{abs}. The optical band gap estimated from the tangents of the absorption edges of their UV/Vis spectra.

[b]The oxidation potential was obtained from the cyclic voltammetry.

[c]HOMO and LUMO energies were calculated with reference to NHE (4.50 eV) LUMO = $-(4.50+E_{1/2}^{re})$; HOMO = $-(4.50 + E_{1/2}^{ox})$; HOMO = LUMO–E_{gap}^{opt}. Potentials versus normal hydrogen electrode (NHE).

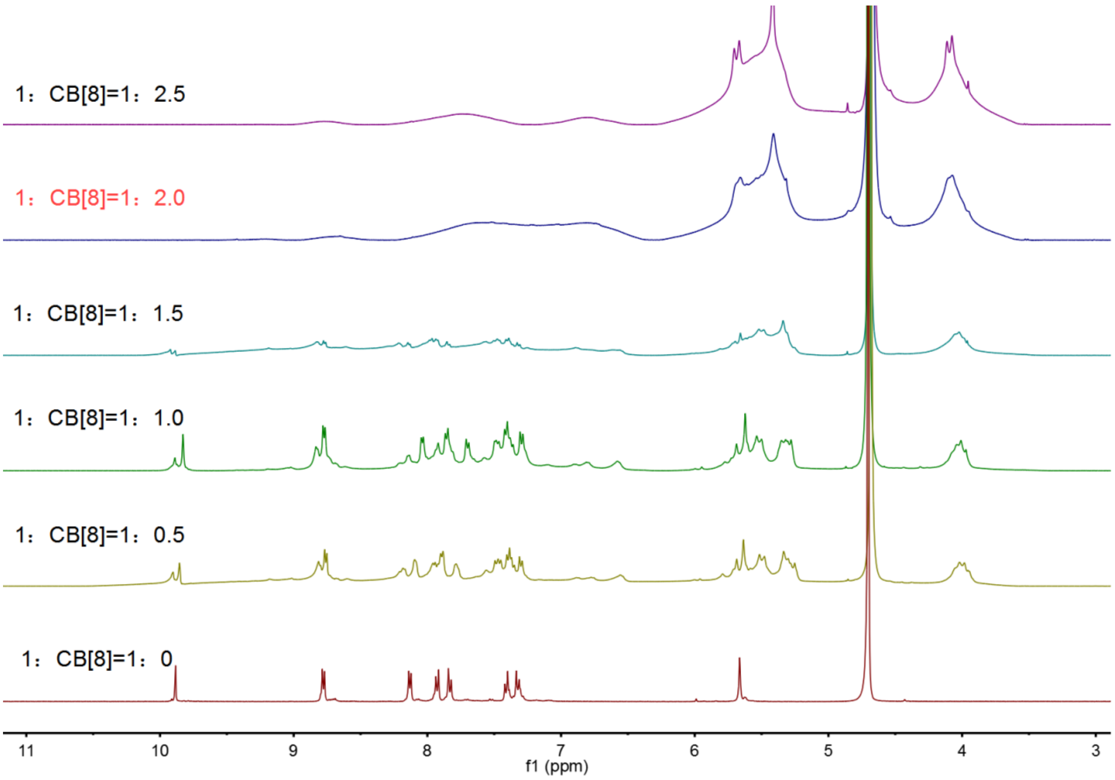


Fig. S1 ^{1}H NMR spectra of **1** and CB of varying molar amounts in D2O (400 MHz, 25 °C, [**1**] = 1.0 mM).

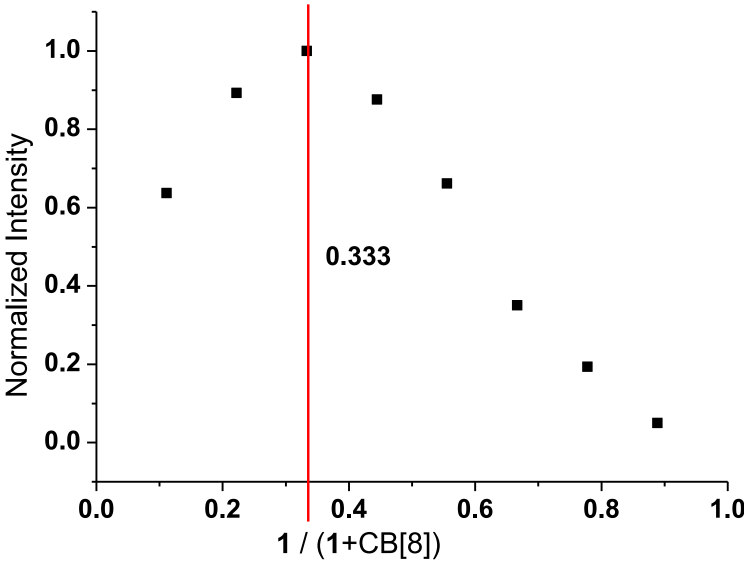


Fig. S2 Job's plot for the mixture solution of **1** and CB[8] in water at 25 °C (λ_{ex} = 300 nm, λ_{em} = 480 nm). [**1**] + CB[8] = 5.0 ×10^{-5} M.

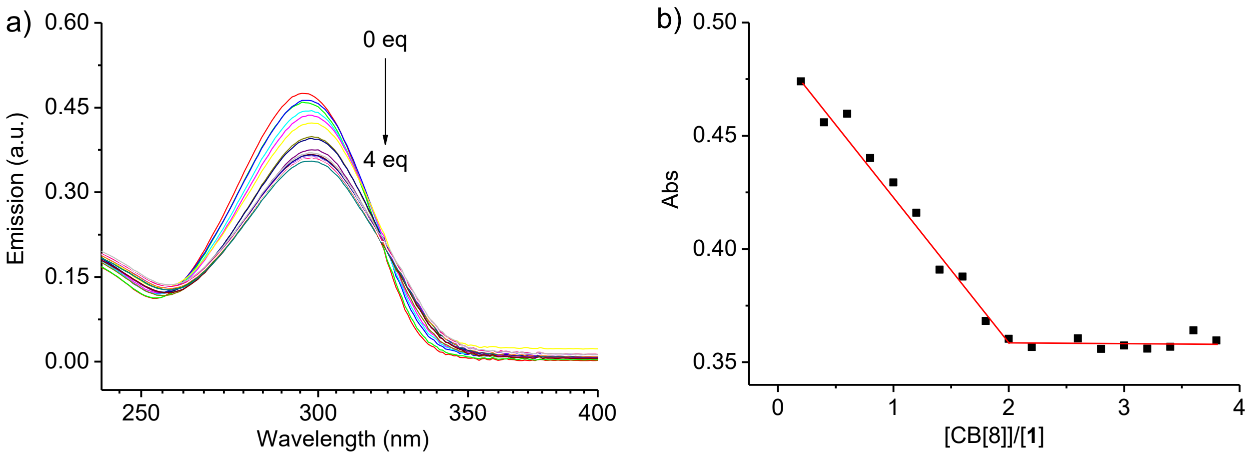


Fig. S3 a) Fluorescent spectra of **1** (0.05 mM) in the presence of CB[8] of incremental amounts. b) Emission at 296 nm versus [CB[8]]/[**1**].

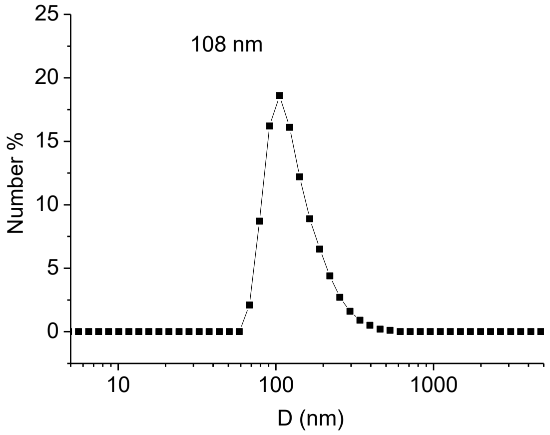


Fig. S4 The DLS profile of **SOF-CHO** in water ([**1**] =1 mM).

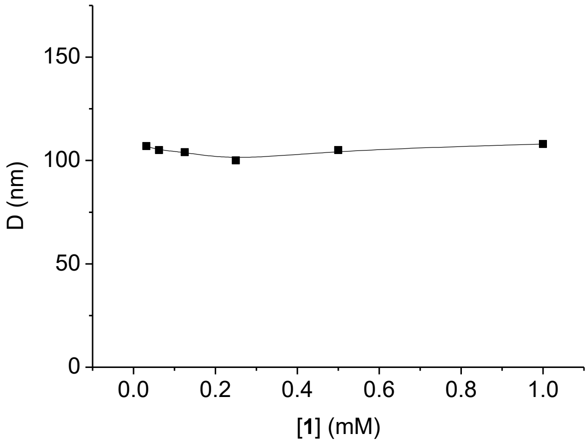


Fig. S5 The hydrodynamic diameter (D) of **SOF-CHO** versus [**1**] in water at 25 °C. The experiments were performed after the solutions were laid for 8 h.

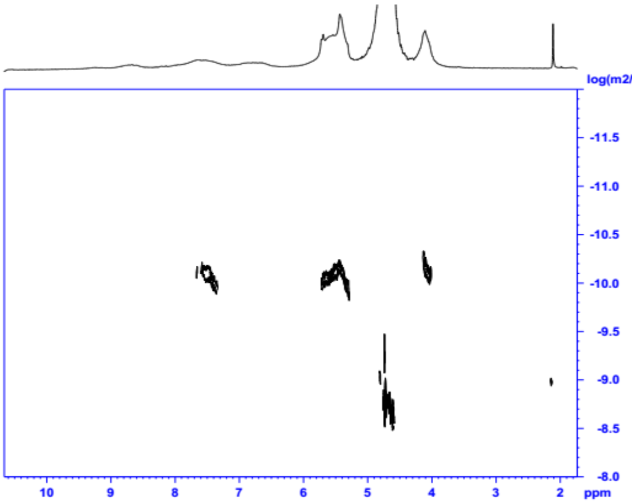


Fig. S6 DOSY ^{1}H NMR spectrum (400 MHz) of the solution of **1** (1 mM) and CB[8] (2 mM) in D2O. The ordinate represents the log value of the diffusion constant.

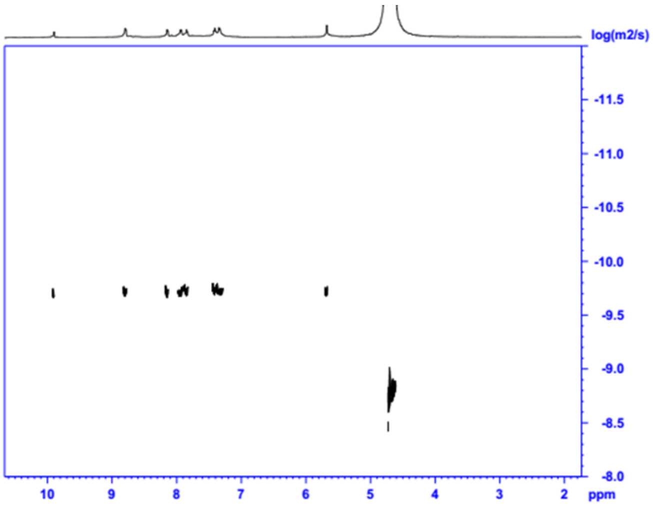


Fig. S7 DOSY ^{1}H NMR spectrum (400 MHz) of the solution of **1** (1 mM) in D2O. The ordinate represents the log value of the diffusion constant.

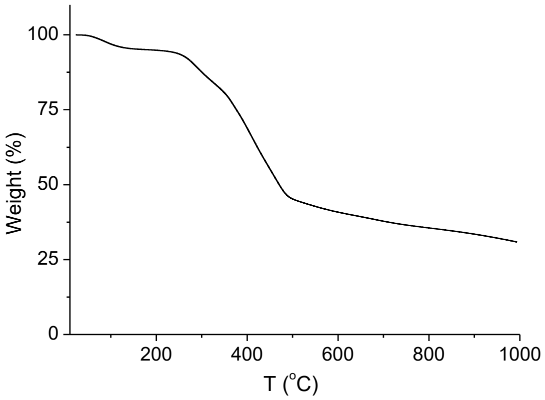


Fig. S8 TGA trace of solid of **SOF-CHO**.

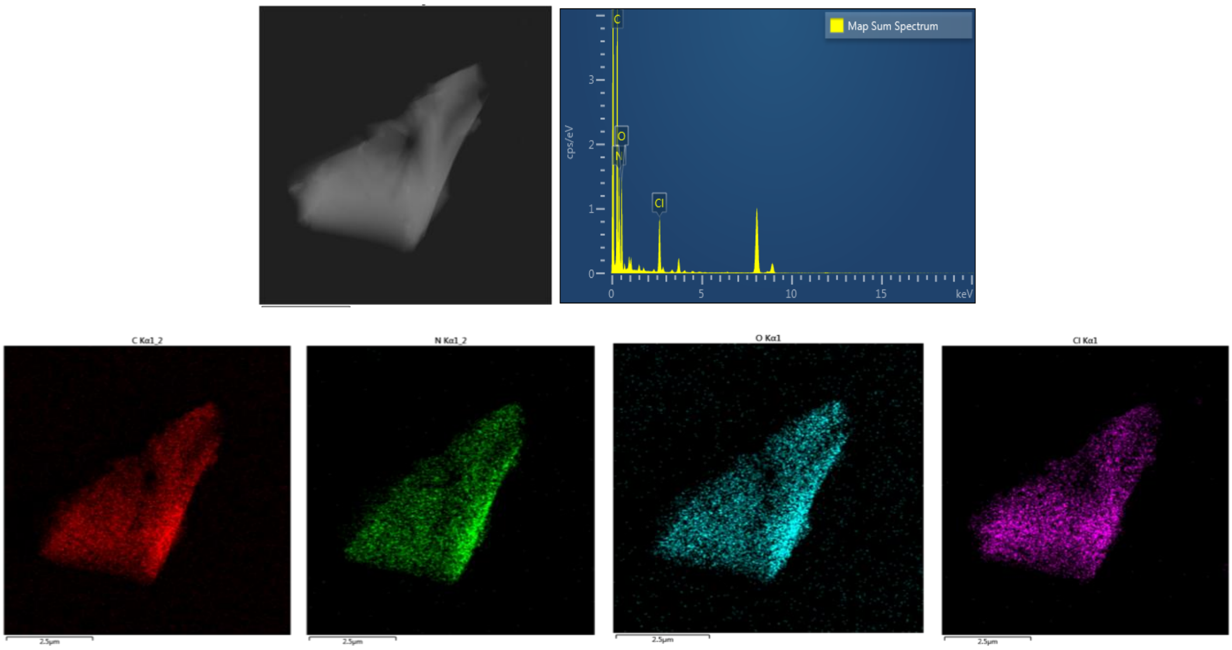


Fig. S9 The element distribution mapping images of **SOF-CHO**, confirming the compositions of the C, N, O and Cl elements by the energy-dispersive X-ray spectroscopy.

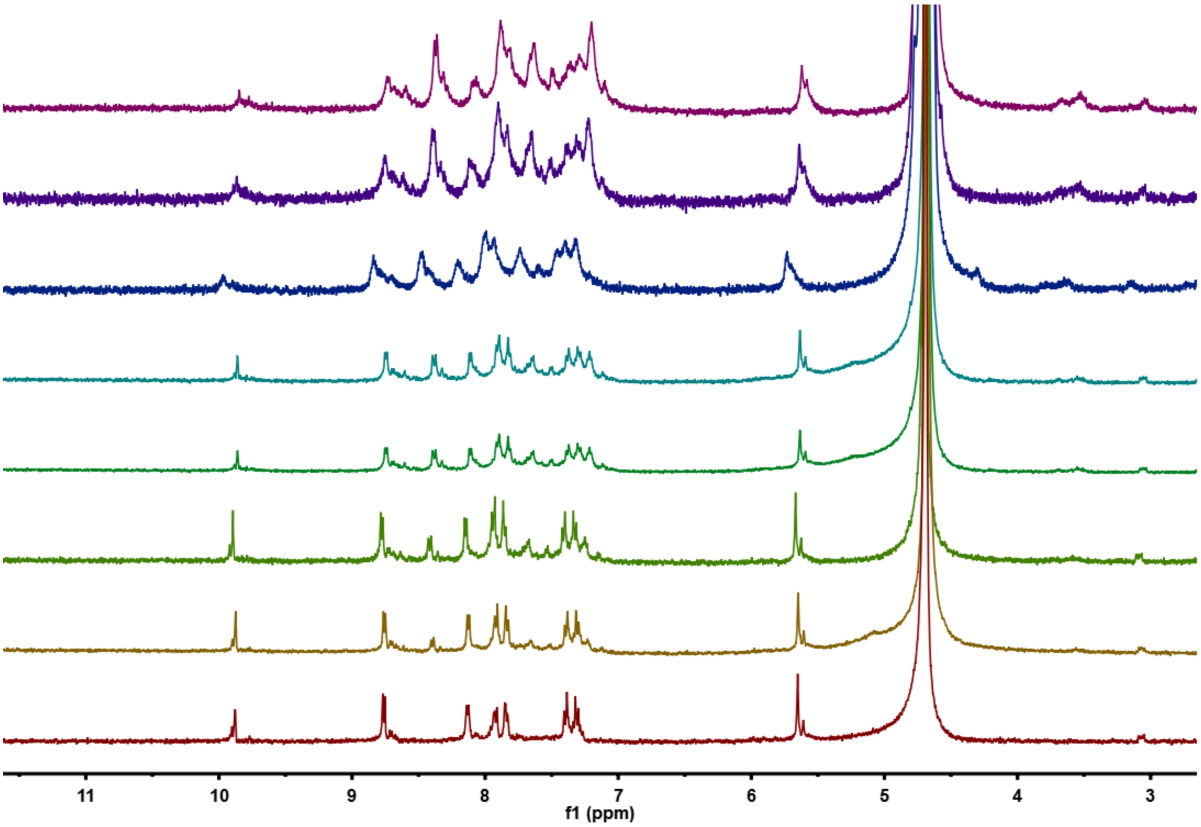


Fig. S10 ^{1}H NMR spectra (400 MHz) of the solution of **SOF-CHO** ([**1**] = 1.0 mM) and **2** of varying amount in D_2O at 25 °C.

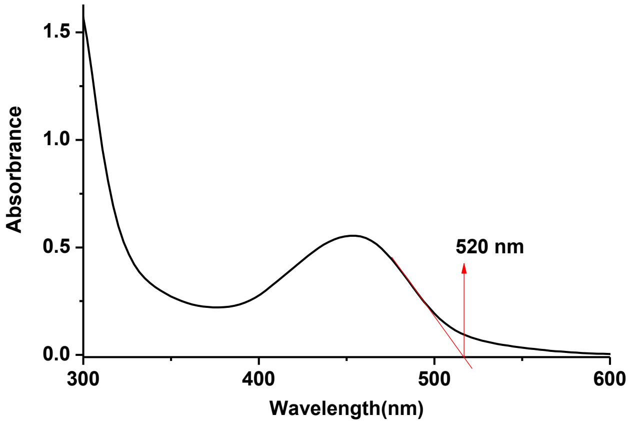


Fig. 11 UV-vis spectra of **2** in the aqueous solution of water (25 °C, [**2**] =0.02 mM).

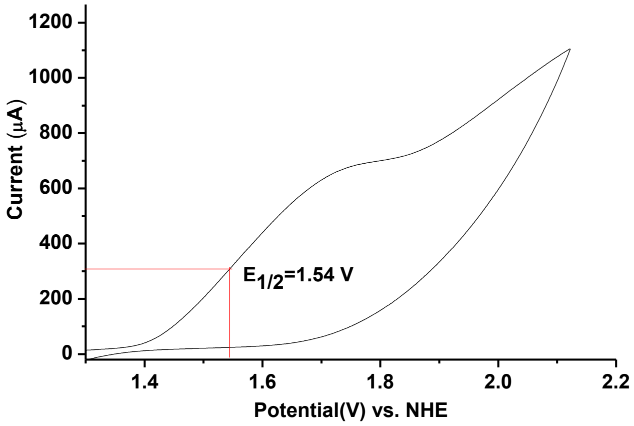


Fig. S12 Cyclic voltammetry of **2** (0.2 mM) in the aqueous solution of KCl (100 mM) with a scan rate of 100 mV/s. Working, reference, and counter electrodes are platinum disk electrode, Ag/AgCl, and Pt, respectively.

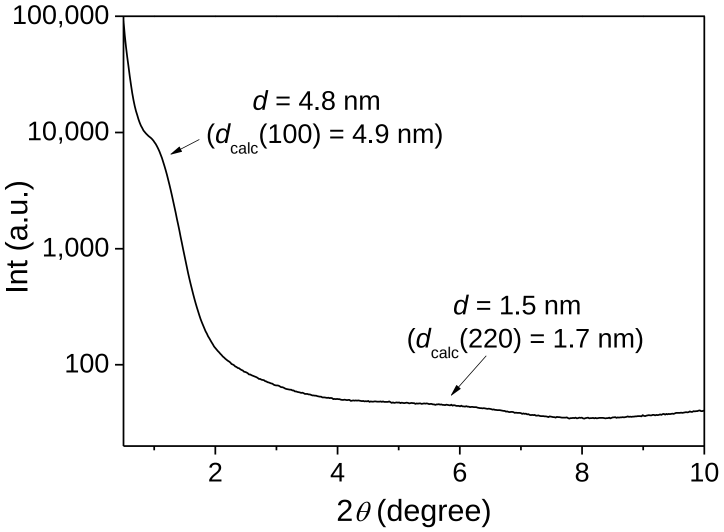


Fig. S13 XRD of solid-state **SOF-CH=N-[Ru(BPY)$_3$]** after 10 runs of the catalysis reaction.

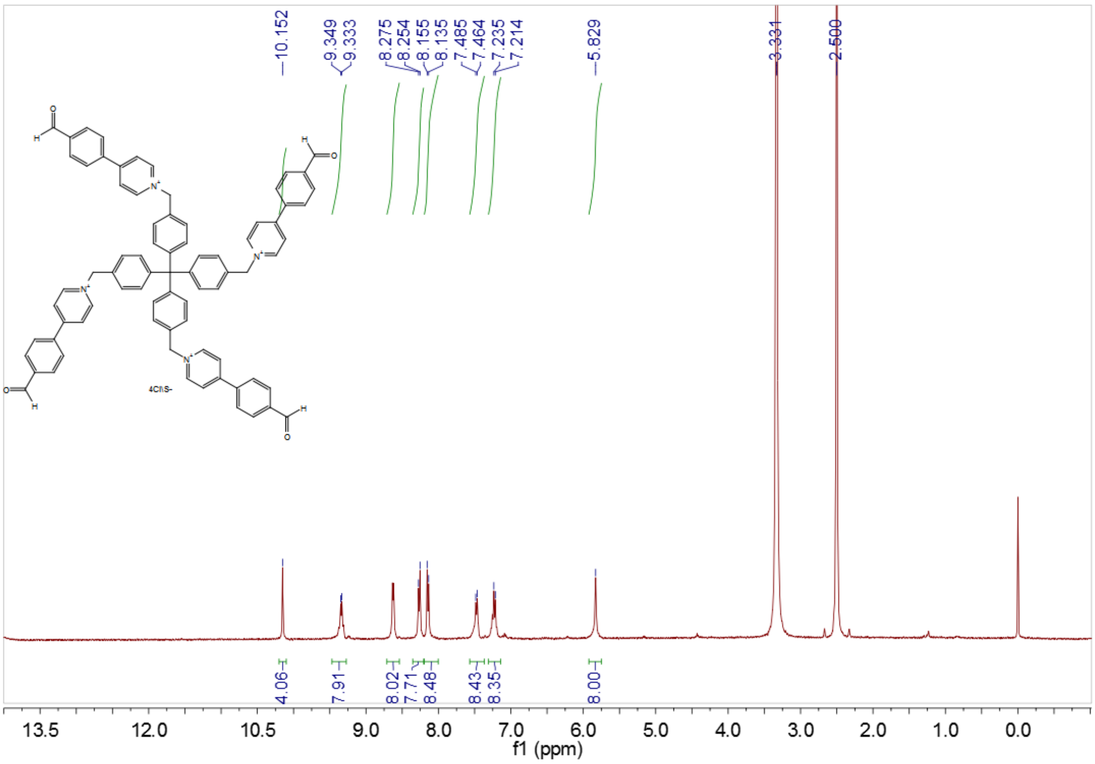


Fig. 14 ^{1}H NMR spectrum (400 MHz) of compound **1** (4mM) in DMSO-d_6.

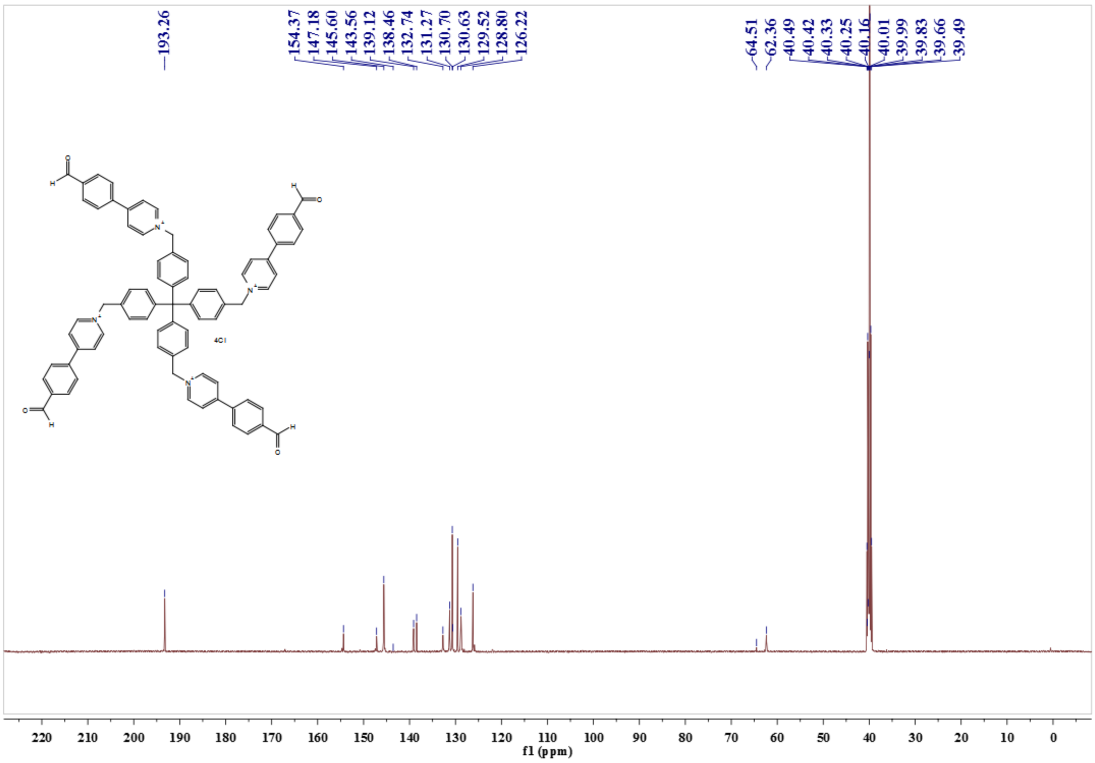


Fig. 15 ^{13}C NMR spectrum (400 MHz) of compound **1** (4 mM) in DMSO-d_6.

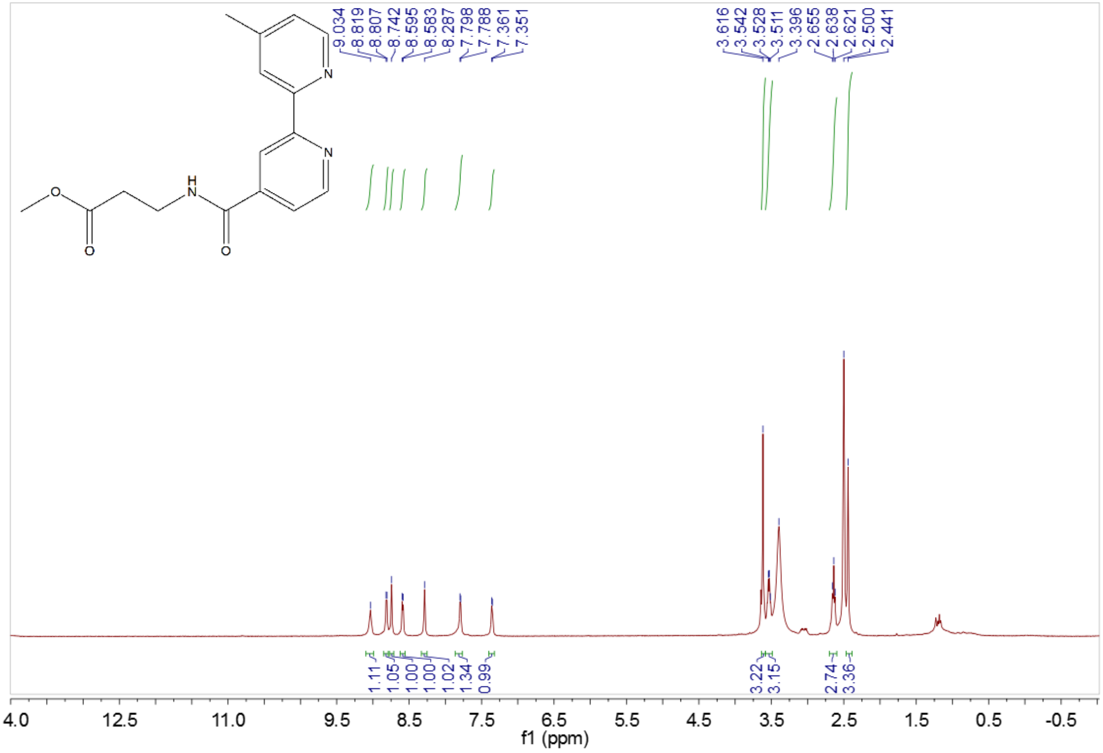


Fig. 16 ^{1}H NMR spectrum (400 MHz) of compound **3** (4 mM) in DMSO-d_6.

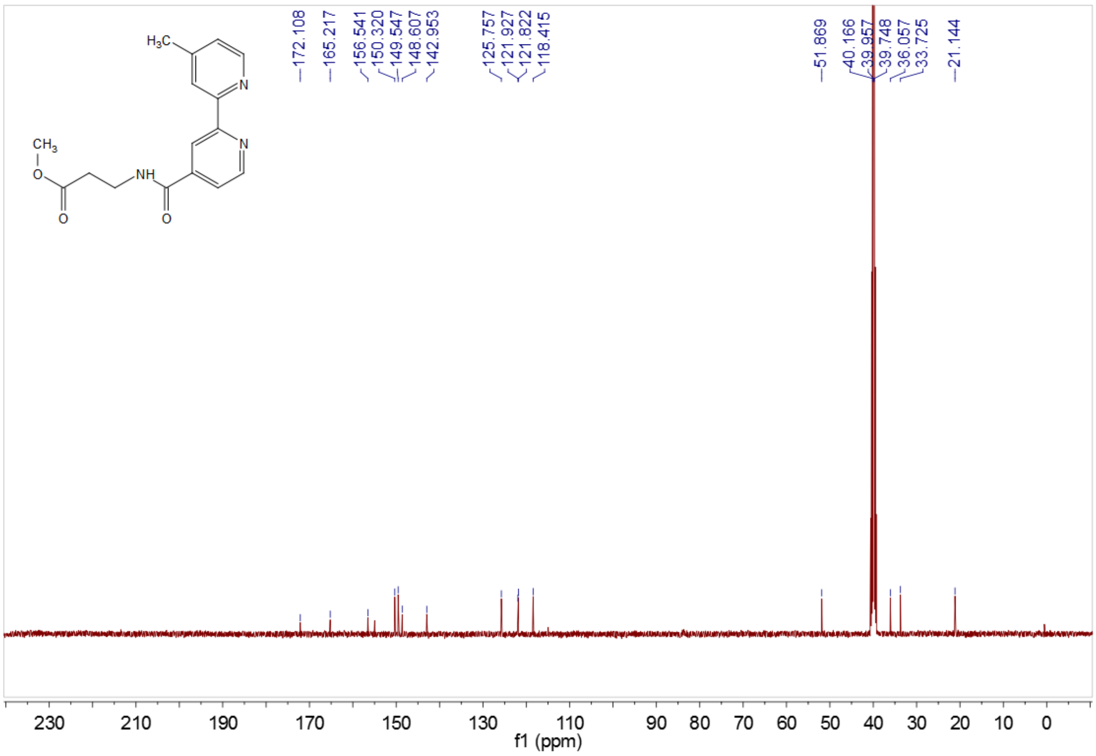


Fig. 17 ^{13}C NMR spectrum (400 MHz) of compound **1** (4 mM) in DMSO-d_6.

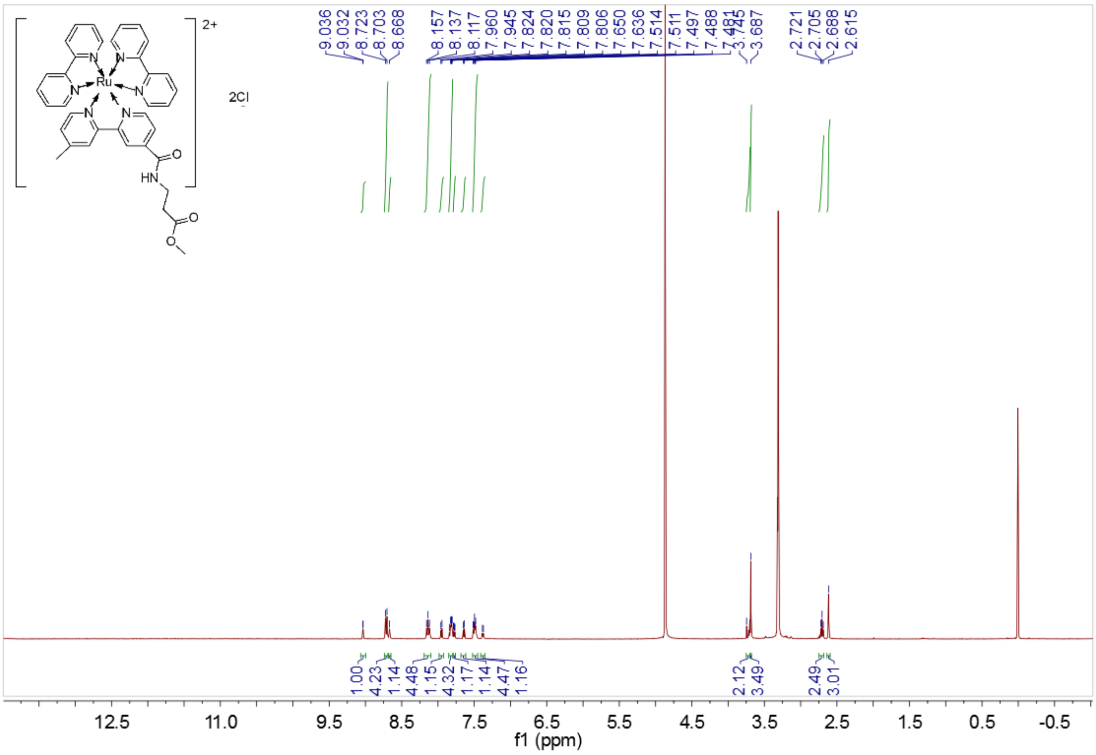


Fig. 18 ^{1}H NMR spectrum (400 MHz) of compound **4** (4 mM) in CD$_3$OD.

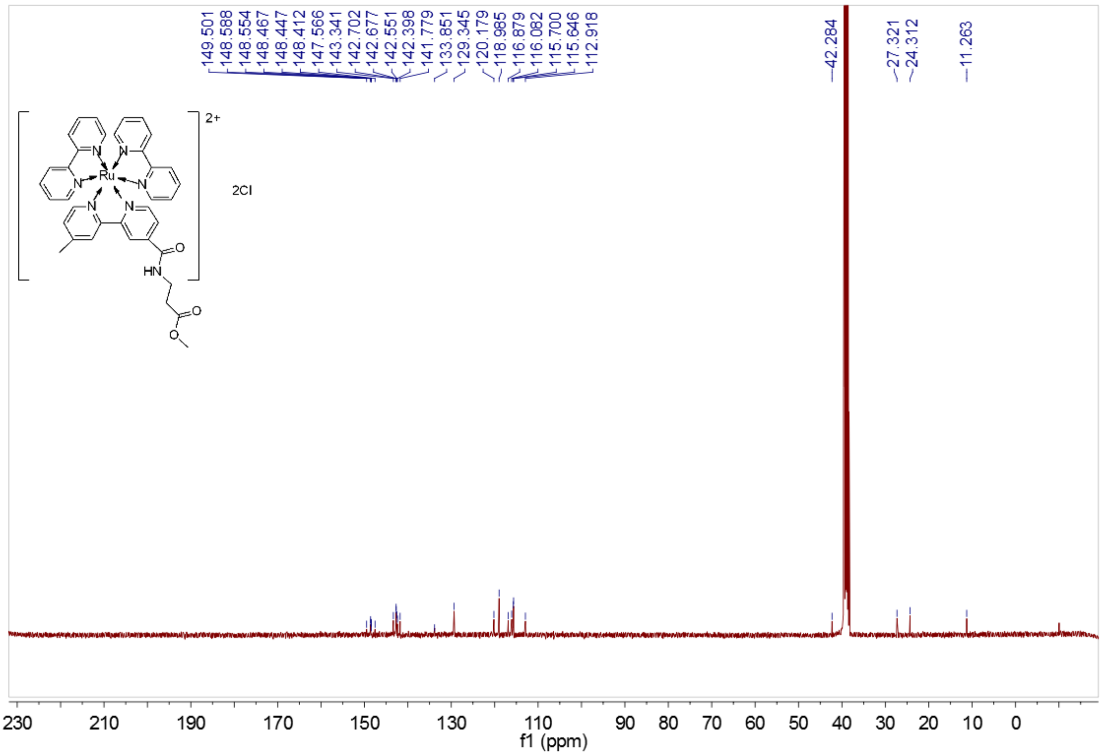


Fig. 19 ^{13}C NMR spectrum (400 MHz) of compound **4** (4 mM) in CD$_3$OD.

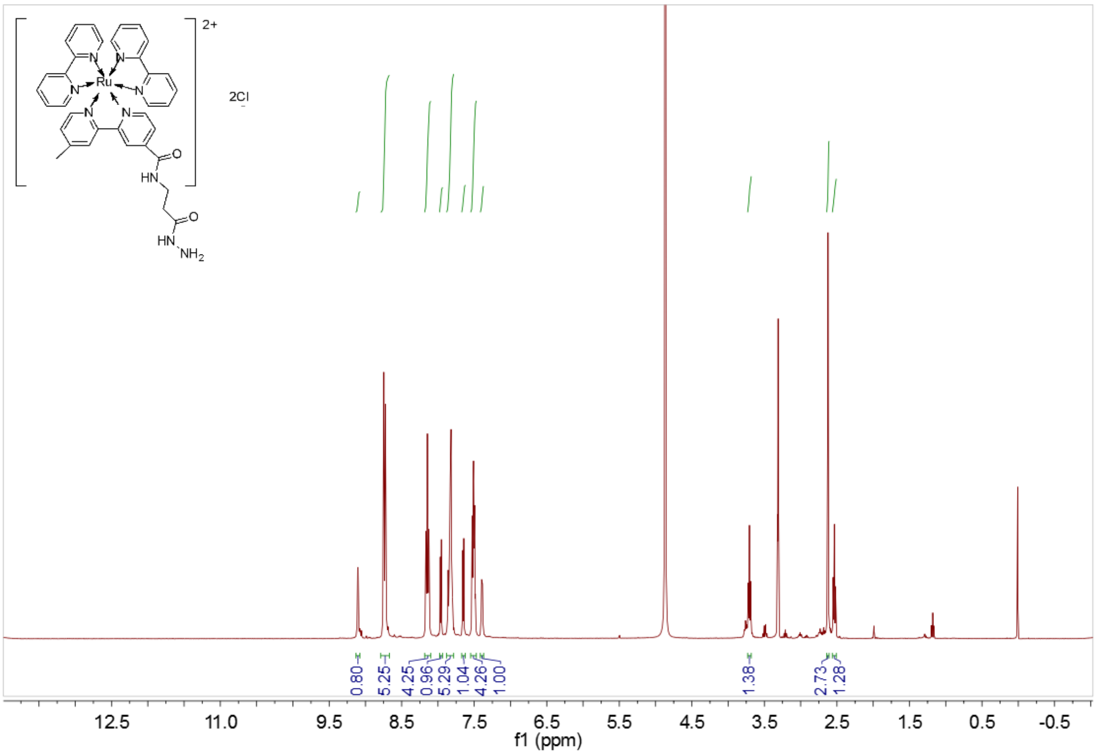


Fig. 20 ^{1}H NMR spectrum (400 MHz) of compound **J-2** (4 mM) in CD_3OD.

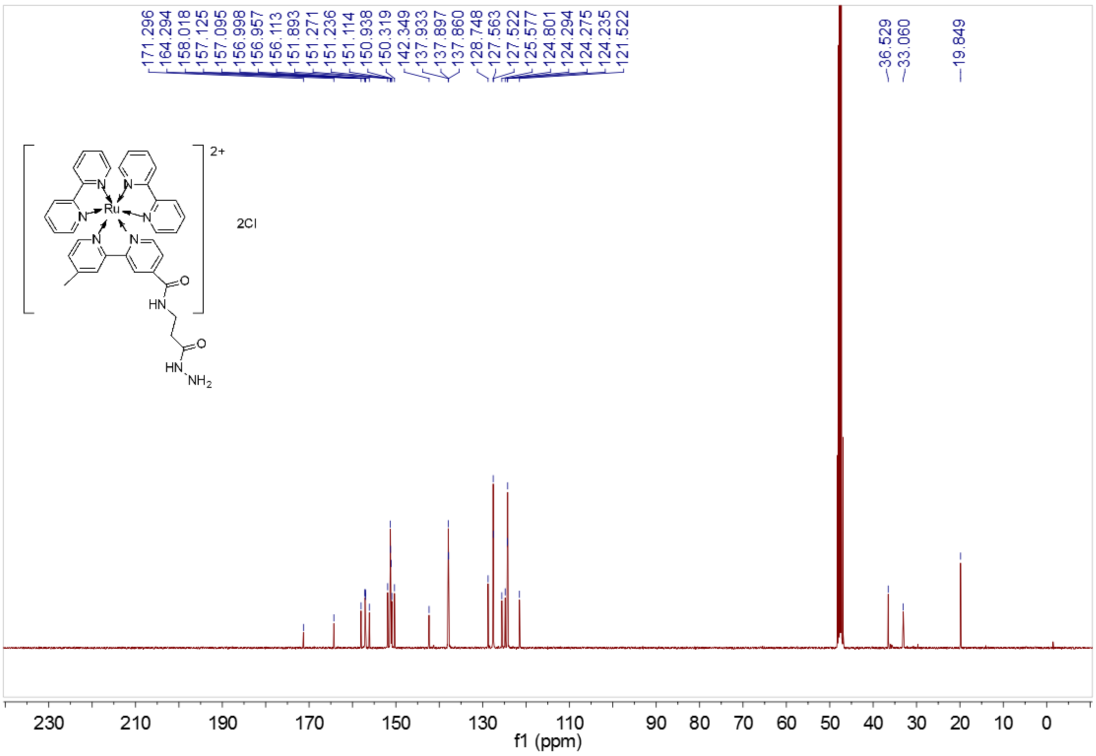


Fig. 21 ^{13}C NMR spectrum (400 MHz) of compound **2** (4 mM) in CD_3OD.