Supporting information
for
Photochemical resolution of a thermally inert cyclometalated Ru(phbpy)(N-N)(sulfoxide)$^{+}$ complex

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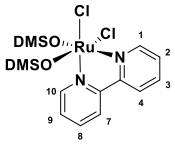
Synthesis

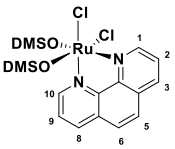
General

Reagents were purchased from Sigma-Aldrich and used without further purification. Dpq,[1] dppz,[1] dppn,[2] Hphbpy,[3] (*R*)-(+)-methyl *p*-tolyl sulfoxide[4] and *cis*-$Ru(DMSO)_4Cl_2$[5] were synthesized according to reported procedures. Dry solvents were collected from a Pure Solve MD5 solvent dispenser from Demaco Holland BV. For all inorganic reactions solvents were deoxygenated by bubbling argon through the solution for 30 minutes and carried out under an inert atmosphere in the dark, unless stated otherwise. Solvents were removed under vacuum with a rotary evaporator in the dark at 30 °C, unless stated otherwise. Flash chromatography was performed on silica gel (Screening devices B.V.) with a particle size of 40 - 64 µM and a pore size of 60 Å. HPLC for the separation of [**11-A**]HCO_2 and [**11-C**]$HCO_2$was performed on a Jupiter® 4µm Proteo 90 Å 3000 UHPLC (250 x 21.2 mm, flow rate 14 $mL \cdot min^{-1}$). TLC analysis was conducted on TLC aluminium foils with silica gel matrix (Supelco, silica gel 60, 56524) with detection by UV-absorption (254 nm). NMR spectra were recorded on a Bruker AV-400 or AV-500. ^1H NMR and ^{13}C NMR spectra were recorded in [D_6]acetone, [D_3]acetonitrile and [D_6]DMSO with chemical shifts (δ) relative to the solvent peak. High resolution mass spectra were recorded by direct injection (2 µl of 2 µM solution in water/acetonitrile; 50/50; v/v and 0.1% formic acid) in a mass spectrometer (Thermo Finnigan LTQ Orbitrap) equipped with an electrospray ion source in positive mode (source voltage 3.5 kV, sheath gas flow 10, capillary temperature 250 °C) with resolution R = 60000 at m/z 400 (mass range m/z = 150 – 2000) and dioctylphtalate (m/z = 391.28428) as a lock mass. The high-resolution mass spectrometer was calibrated prior to measurements with a calibration mixture (Thermo Finnigan).

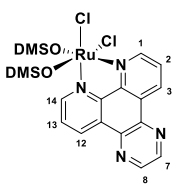
Compound preparation



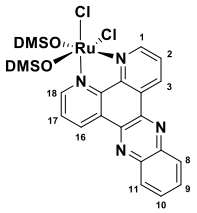
[Ru(bpy)(DMSO)$_2$Cl$_2$], [**12**]: *cis*-[$Ru(DMSO)_4Cl_2$] (200 mg, 0.410 mmol) and bpy (64.0 mg, 0.410 mmol) were dissolved in deoxygenated EtOH/DMSO (3.2 mL, 16:1) and heated at reflux for 2 h. After cooling to rt, the resulting precipitate was filtered, washed with cold ethanol (5 mL), diethyl ether (15 mL) and dried *in vacuo* affording the title compound as an orange powder (168 mg, 0.350 mmol, 86%). ^1H NMR (400 MHz, [D_6]DMSO) δ = 9.66 (d, *J* = 4.5 Hz, 1H, 1), 9.55 (d, *J* = 4.5 Hz, 1H, 10), 8.66 (d, *J* = 8.1 Hz, 1H, 7), 8.61 (d, *J* = 8.2 Hz, 1H, 4), 8.22 (td, *J* = 7.8, 1.6 Hz, 1H, 8), 8.10 (td, *J* = 7.8, 1.5 Hz, 1H, 3), 7.77 (dd, *J* = 7.2, 5.6 Hz, 1H, 9), 7.61 (dd, *J* = 7.4, 5.7 Hz, 1H, 2), 3.40 (s, 3H, CH_3), 3.36 (s, 3H, CH_3), 2.98 (s, 3H, CH_3), 2.28 (s, 3H, CH_3); HRMS: m/z calcd for $[C_{14}H_{20}Cl_2N_2O_2RuS_2 - Cl]^+$: 448.96982; found: 489.96900; elemental analysis calcd (%) for [**12**]: C 34.71, H 4.16, N 5.78; found: C 34.82, H 4.31, N 5.53.



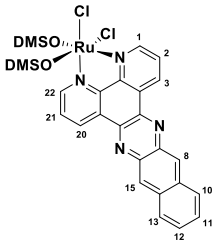
[Ru(phen)(DMSO)$_2$Cl$_2$], [**13**]: The procedure described for [**12**] was followed using [*cis*-$Ru(DMSO)_4Cl_2$] (100 mg, 0.210 mmol) and phen (38.0 mg, 0.210 mmol) yielding the product as an orange powder (82.0 mg, 0.160 mmol, 77%). ^1H NMR (400 MHz, [D_6]DMSO) δ = 9.96 (d, *J* = 5.4 Hz, 1H, 1), 9.83 (d, *J* = 5.2 Hz, 10), 8.87 (d, *J* = 8.2 Hz, 1H, 8), 8.74 (d, *J* = 8.3 Hz, 3), 8.34 – 8.22 (m, 2H, 5, 6), 8.17 (dd, 1H, *J* = 8.2, 5.4 Hz, 9), 8.01 (dd, *J* = 8.2, 5.4 Hz, 1H, 2), 3.48 (s, 3H, CH_3), 3.43 (s, 3H, CH_3), 2.94 (s, 3H, CH_3), 2.15 (s, 3H, CH_3); HRMS: m/z calcd for $[C_{16}H_{20}Cl_2N_2O_2RuS_2 - Cl]^+$: 472.96962; found: 472.96904; elemental analysis calcd (%) for [**13**]: C 37.80, H 3.97, N 5.51; found: C 37.64, H 4.03, N 5.58.



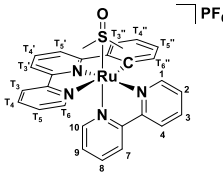
[Ru(dpq)(DMSO)$_2$Cl$_2$], [**14**]: The procedure described for [**12**] was followed using *cis*-$Ru(DMSO)_4Cl_2$ (200 mg, 0.410 mmol) and dpq (95.0 mg, 0.410 mmol) yielding the product as an orange brown powder (220 mg, 0.390 mmol, 95%). ^1H NMR (400 MHz, [D_6]DMSO) δ = 10.13 (d, *J* = 5.5 Hz, 1H, 1), 10.00 (d, *J* = 6.5 Hz, 1H, 14), 9.66 (d, *J* = 6.9 Hz, 1H, 12), 9.53 (d, *J* = 8.2 Hz, 1H, 3), 9.35 (m, 2H, 7, 8), 8.33 (dd, *J* = 8.2, 5.3 Hz, 1H, 13), 8.17 (dd, *J* = 8.2, 5.5 Hz, 1H, 2), 3.50 (s, 3H, CH_3), 3.45 (s, 3H, CH_3), 2.95 (s, 3H, CH_3), 2.28 (s, 3H, CH_3); HRMS: m/z calcd for $[C_{18}H_{20}Cl_2N_4O_2RuS_2 - Cl]^+$: 524.975969; found: 524.97535; elemental analysis calcd (%) for [**14**]: C 38.57, H 3.60, N 10.00 ; found: C 37.73; H 4.12, N 9.50.



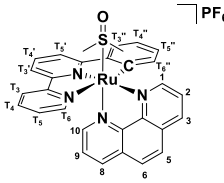
[Ru(dppz)(DMSO)$_2$Cl$_2$], [**15**]: [*cis*-[Ru(DMSO)$_4$Cl$_2$] (100 mg, 0.210 mmol) and dppz (60.0 mg, 0.210 mmol) in ethanol (3 mL) and DMSO (0.2 mL) were refluxed for 2 h. The reaction was cooled down to room temperature and the resulting precipitate was filtered, washed with cold ethanol (5 mL) and diethyl ether (15 mL). The crude was then redissolved in a minimal amount of acetone, and precipitated with Et$_2$O to afford the title compound as a light brown powder (110 mg, 0.18 mmol, 87%). ^{1}H NMR (400 MHz, [D$_6$]DMSO) δ = 10.10 (d, *J* = 4.2 Hz, 1H, 1), 9.98 (d, *J* = 3.9 Hz, 1H, 18), 9.73 (d, *J* = 8.0 Hz, 1H, 16), 9.61 (d, *J* = 7.7 Hz, 1H, 3), 8.54 – 8.46 (m, 2H, 8, 11), 8.36 – 8.29 (m, 1H, 17), 8.20 – 8.12 (m, 3H, 2, 9, 10), 3.49 (s, 3H, CH$_3$), 3.46 (s, 3H, CH$_3$), 2.95 (s, 3H, CH$_3$), 2.32 (s, 3H, CH$_3$); HRMS: m/z calcd for [C$_{22}$H$_{22}$Cl$_2$N$_4$O$_2$RuS$_2$ − Cl]$^+$: 574.99162; found: 574.99119; elemental analysis calcd (%) for [**15**].2H$_2$O: C 49.49, H 3.58, N 9.62; found: C 48.69, H 3.43, N 9.35.



[Ru(dppn)(DMSO)$_2$Cl$_2$], [**16**]: The same procedure was followed as described for [**15**] using *cis*-[Ru(DMSO)$_4$Cl$_2$] (100 mg, 0.206 mmol) and dppn (70.0 mg, 0.211 mmol) to afford the product as an light brown powder (131 mg, 0.198 mmol, 96%). ^{1}H NMR (400 MHz, [D$_6$]DMSO) δ = 10.09 (d, *J* = 5.5 Hz, 1H, 1), 9.96 (d, *J* = 4.3 Hz, 1H, 22), 9.72 (d, *J* = 6.9 Hz, 1H, 21), 9.60 (d, *J* = 7.9 Hz, 1H, 3), 9.23 (d, *J* = 2.4 Hz, 2H, 8, 15), 8.49 – 8.39 (m, 2H, 10, 13), 8.37 – 8.27 (m, 1H, 21), 8.19 – 8.10 (m, 1H, 2), 7.85 – 7.71 (m, 2H, 11, 12), 3.50 (s, 3H, CH$_3$), 3.46 (s, 3H, CH$_3$), 2.96 (s, 3H, CH$_3$), 2.35 (s, 3H, CH$_3$); HRMS: m/z calcd for [C$_{26}$H$_{24}$ClN$_4$O$_2$RuS$_2$ – Cl]$^+$: 625.00727; found: 625.00679; elemental analysis calcd (%) for [**16**]: C 47.27, H 3.66, N 8.48; found: C 47.47, H 3.79, N 8.36.

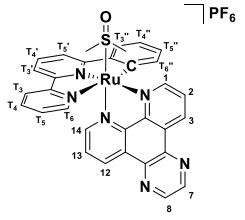


[Ru(phbpy)(bpy)(DMSO)]PF$_6$, [**1**]PF$_6$: [Ru(bpy)(DMSO)$_2$Cl$_2$] (122 mg, 0.250 mmol) and Hphbpy (58 mg 0.25 mmol) were dissolved in a mixture of MeOH/H$_2$O (15 mL, 5:1) and to this mixture were added 4 drops of *N*-methylmorpholine. After heating at reflux for 16 h, solvents were removed *in vacuo,* followed by purification over silica (0 – 15% MeOH in DCM) and salt metathesis using aqueous KPF$_6$. The resulting precipitate was filtered and washed with water (3x) affording the title compound as a red powder (116 mg, 0.16 mmol, 65%). *Rf* = 0.30 (10% MeOH in DCM); ^{1}H NMR (400 MHz, [D$_6$]acetone) δ = 10.32 (d, *J* = 5.9 Hz, 1H, 1), 8.72 (d, *J* = 8.2 Hz, 1H, 4), 8.64 (d, *J* = 8.2 Hz, 1H, T$_5$'), 8.58 (d, *J* = 8.2 Hz, 1H, 7), 8.46 (d, *J* = 7.9 Hz, 1H, T$_3$'), 8.30 (d, *J* = 5.4 Hz, 1H, T$_6$), 8.26 – 8.10 (m, 4H, 3, T$_5$', T$_4$' T$_3$), 7.90 (t, *J* = 7.9 Hz, 1H, 1H, 8), 7.84 (t, *J* = 7.5 Hz, 2H, 2, T$_3$''), 7.59 – 7.50 (m, 1H, T$_5$), 7.39 (d, *J* = 5.6 Hz, 1H, 10), 7.25 (t, *J* = 6.6 Hz, 1H, 9), 6.89 (t, *J* = 7.5 Hz, 1H, T$_4$"), 6.81 (t, *J* = 7.3 Hz, 1H, T$_5$"), 6.61 (d, *J* = 7.4 Hz, 1H, T$_6$"), 2.41 (s, 3H, CH$_3$), 2.25 (s, 3H, CH$_3$); ^{13}C NMR (101 MHz, [D$_6$]acetone) δ = 181.9 (C$_q$), 168.4 (C$_q$), 157.9 (C$_q$), 156.8 (C$_q$), 156.0 (C$_q$), 154.9 (C$_H$, 1), 153.1 (C$_H$, T$_6$), 149.0 (CH, 10), 148,0 (C$_q$), 139.7 (C$_H$, T$_4$), 138.4 (C$_H$, T$_6$"), 138.2 (C$_H$, T$_4$'), 137.7 (C$_H$, 8), 136.0 (C$_H$, 3), 130.9 (C$_H$, T$_5$"), 128.7 (C$_H$, T$_5$), 127.3 (C$_H$, 9), 127.2 (C$_H$, 2), 126.2 (C$_H$, T$_3$"), 124.9 (C$_H$, T$_3$), 124.7 (C$_H$, 4), 123.8 (C$_H$, 7), 123.2 (C$_H$, T$_4$"), 121.1 (C$_H$, T$_3$'), 120.4 (C$_H$, T$_5$'), 45.6 (CH$_3$), 43.5 (CH$_3$); HRMS: m/z calcd for [C$_{28}$H$_{25}$N$_4$ORuS − PF$_6$]: 567.07926; found: 567.07885; elemental analysis calcd (%) for [**1**]PF$_6$: C 47.26, H 3.54, N 7.87; found: C 46.54, H 4.19, N 7.35.

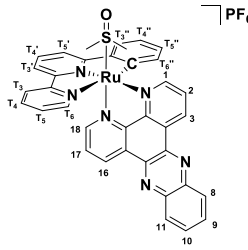


[Ru(phbpy)(phen)(DMSO)]PF$_6$, [**2**]PF$_6$: The same procedure was followed as described for [**6**]PF$_6$ using [Ru(phen)(DMSO)$_2$Cl$_2$] (114 mg, 0.22 mmol) and Hphbpy (51 mg, 0.22 mmol) to afford the product as a red powder (113 mg, 0.15 mmol, 68%). ^{1}H NMR (400 MHz, [D$_6$]acetone) δ = 10.67 (d, *J* = 5.4 Hz, 1H, 1), 8.82 (d, *J* = 8.2 Hz, 1H, 3), 8.64 (d, *J* = 8.1 Hz, 1H, T$_3$), 8.51 (dd, *J* = 8.2, 4.7 Hz, 2H, 8, T$_5$), 8.35 (d, *J* = 8.9 Hz, 1H, 5), 8.28 (d, *J* = 8.1 Hz, 1H, T$_5$'), 8.26 – 8.15 (m, 3H, 2, 6, T$_6$, T$_4$'), 8.11 (t, *J* = 7.9 Hz, 1H, T$_4$), 7.84 (d, *J* = 7.7 Hz, 1H, T$_3$"), 7.76 (d, *J* = 5.2 Hz, 1H, 10), 7.62 (dd, *J* = 8.3, 5.1 Hz, 1H, 9), 7.46 – 7.36 (m, 1H, T$_5$), 6.83 (t, *J* = 7.5 Hz, 1H, T$_4$"), 6.66 (t, *J* = 7.3 Hz, 1H, T$_5$"), 6.41 (d, *J* = 7.5 Hz, 1H, T$_6$"), 2.47 (s, 3H, CH$_3$), 2.35 (s, 3H, CH$_3$); ^{13}C NMR (101 MHz, [D$_6$]acetone) δ = 180.9 (C$_q$),

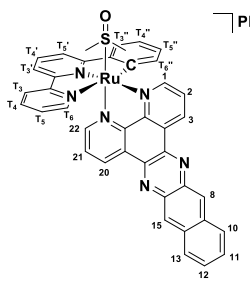
167.6 (C_q), 157.2 (C_q), 157.1 (C_q), 154.3 (CH, 1), 152.4 (C_H, T_4'), 148.6 (C_H, 10), 147.3 (C_q), 147.2 (C_q), 145.5 (C_q), 138.8 (C_H, T_4), 137.6 (CH, T_6"), 137.5 (C_H, T_6), 136.0 (C_H, T_5), 134.3 (C_H, 3), 131.3 (C_q), 130.2 (C_q), 129.8 (C_H, T_5"), 128.5 (C_H, 5), 127.7 (C_H, T_5), 127.4 (C_H, 6), 125.6 (C_H, 2), 125.3 (CH, T_3"), 125.0 (C_H, 9), 124.0 (C_H, T_2), 122.3 (C_H, T_4"), 120.3 (C_H, 8), 119.6 (C_H, T_5'), 44.7 (CH_3), 43.2 (CH_3). HRMS: m/z calcd for $[C_{30}H_{25}N_4ORuS - PF_6]^+$: 591.07926; found: 591.07887; elemental analysis calcd (%) for [**2**]PF_6: C 48.98, H 3.43, N 7.62; C 48.46, H 3.57, N 7.47.



[Ru(phbpy)(dpq)(DMSO)]PF_6, [**3**]PF_6: The same procedure was followed as described for [6]PF_6 using [Ru(dpq)$(DMSO)_2Cl_2$] (115 mg, 0.210 mmol) and Hphbpy (49.0 mg, 0.220 mmol) to afford the product as a red powder (120 mg 0.150 mmol 74%). ^{1}H NMR (400 MHz, [D_6]acetone) δ = 10.80 (d, *J* = 4.3 Hz, 1H, 1), 9.66 (d, *J* = 6.9 Hz, 1H, 3), 9.32 – 9.22 (m, 2H, 7, 12), 9.16 (d, *J* = 2.1 Hz, 1H, 8), 8.64 (d, *J* = 8.2 Hz, 1H, T_3), 8.50 (d, *J* = 6.9 Hz, 1H, T_3'), 8.38 – 8.26 (m, 3H, 2, T_5', T_6), 8.22 (t, *J* = 8.0 Hz, 1H, T_4'), 8.10 (t, *J* = 8.0 Hz, 1H, T_4), 7.96 – 7.82 (m, 2H, 14, T_3"), 7.72 – 7.57 (m, 1H, 13), 7.42 (t, *J* = 6.4 Hz, 1H, T_5), 6.84 (t, *J* = 6.8 Hz, 1H, T_4"), 6.68 (t, *J* = 6.7 Hz, 1H, T_5"), 6.55 (d, *J* = 6.3 Hz, 1H, T_6"), 2.48 (s, 3H, CH_3), 2.38 (s, 3H, CH_3). ^{13}C NMR (101 MHz, [D_6]acetone) δ = 181.1 (C_q), 168.0 (C_q), 157.7 (C_q), 157.5 (C_q), 156.1 (CH, 1), 153.1 (C_H, T_6), 150.6 (C_H, 14), 149.2 (C_q), 147.8 (C_q), 147.7 (C_q), 147.4 (C_H, 7), 147.1 (C_H, 8), 140.8 (C_q), 140.1 (C_q), 139.5 (CH, T_4), 138.3 (CH, T_4'), 138.3 (C_H, T_6"), 132.8 (C_H, 12), 131.2 (C_H, 3), 130.7 (C_q), 130.5 (C_H, T_5"), 129.3 (C_q), 128.3 (C_H, T_5), 127.0 (C_H, 2), 126.6 (C_H, 13), 126.0 (C_H, T_3"), 124.7 (C_H, T_3), 123.0 (C_H, T_4"), 121.0 (C_H, T_3'), 120.3 (C_H, T_5'), 45.1 (CH_3), 43.7 (CH_3). ESI-MS: m/z calcd for $[C_{32}H_{25}N_6ORuS - PF_6]^+$: 643.1; found: 643.1; elemental analysis calcd (%) for [**3**]PF_6.$4H_2O$: C 44.71, H 3.87, N 9.78; found: C 43.90, H 3.48, N 9.40.

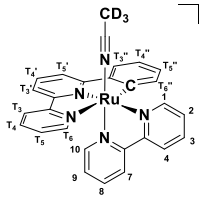


[Ru(phbpy)(dppz)(DMSO)]PF_6, [**4**]PF_6: The same procedure was followed as described for [**6**]PF_6 using [Ru(dppz)$(DMSO)_2Cl_2$] (160 mg, 0.26 mmol) and Hphbpy (60 mg, 0.26 mmol) to afford the product as a dark red powder (161 mg, 0.190 mmol, 73%). A racemic mixture was obtained but only one enantiomer is shown. ^{1}H NMR (400 MHz, [D_6]acetone) δ = 10.79 (d, *J* = 6.3 Hz, 1H, 1), 9.75 (d, *J* = 8.1 Hz, 1H, 3), 9.37 (d, *J* = 8.1 Hz, 1H, 16), 8.67 (d, *J* = 8.1 Hz, 1H, T_3), 8.53 (d, *J* = 7.9 Hz, 1H, 8), 8.48 (d, *J* = 8.3 Hz, 1H, T_3'), 8.41 – 8.29 (m, 4H, 7, 2, T_5', T_6), 8.24 (t, *J* = 8.1 Hz, 1H, T_4'), 8.20 – 8.08 (m, 3H, T_4, 9, 10), 7.87 (dd, *J* = 14.5, 6.9 Hz, 2H, 18, T_3"), 7.68 (t, *J* = 7.1 Hz, 1H, 17), 7.46 (t, *J* = 6.8 Hz, 1H, T_5), 6.88 (t, *J* = 7.5 Hz, 1H, T_4"), 6.74 (t, *J* = 7.4 Hz, 1H, T_5"), 6.66 (d, *J* = 7.5 Hz, 1H, T_6"), 2.50 (s, 3H, CH_3), 2.39 (s, 3H, CH_3). ^{13}C NMR (101 MHz, [D_6]acetone) δ = 180.3 (C_q), 167.2 (C_q), 156.8 (C_q), 156.8 (C_q), 155.4 (C_H, 1), 152.3 (C_H, T_6), 149.9 (C_H, 18), 149.4 (C_q), 148.0 (C_q), 147.1 (C_q), 142.6 (C_q), 142.4 (C_q), 140.1 (C_q), 139.5 (C_q), 138.7 (C_H, T_4), 137.7 (C_H, T_4'), 137.4 (C_H, T_6"), 132.2 (C_H, 16), 132.1 (C_H, 10), 132.1 (C_H, 11), 130.7 (C_H, 3), 130.3 (C_q), 129.8 (C_H, T_5"), 129.6 (C_H, 8), 129.5 (C_H, 9), 128.9 (C_q), 127.5 (CH, T_4), 126.3 (C_H, 2), 125.9 (C_H, 17), 125.2 (C_H, T_3"), 123.9 (C_H, T_2), 122.3 (C_H, 8), 120.2 (C_H, T_3'), 119.6 (C_H, 2), 44.3 (CH_3), 42.9 (CH_3). HRMS: m/z calcd for $[C_{36}H_{27}N_6ORuS - PF_6]^+$: 693.10105; found: 693.10113; elemental analysis calcd (%) for [**4**]PF_6: C 51.61, H 3.25, N 10.03; found: C 48.86, H 3.52, N 9.05.

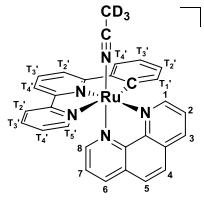


[Ru(phbpy)(dppn)(DMSO)]PF_6, [**5**]PF_6: The same procedure was followed as described for [6]PF_6 using [Ru(dppn)$(DMSO)_2Cl_2$] (100 mg, 0.15 mmol) and Hphbpy (35 mg, 0.15 mmol) to afford the product as a dark red powder (88 mg 0.10 mmol 65%). A racemic mixture was obtained but only one enantiomer is shown. ^{1}H NMR (500 MHz, [D_6]acetone) δ = 10.80 (d, *J* = 5.5 Hz, 1H, 1), 9.53 (d, *J* = 8.0 Hz, 1H, 3), 9.00 (d, *J* = 8.0 Hz, 1H, 20), 8.87 (s, 1H, 3), 8.71 (s, 1H, 15), 8.68 (d, *J* = 8.2 Hz, 1H, T_3), 8.54 (d, *J* = 8.0 Hz, 1H, T_3'), 8.37 (d, *J* = 7.4 Hz, 2H, T_5', T_6), 8.35 – 8.23 (m, 3H, 2, 10, T_4'), 8.14 (t, *J* = 7.9 Hz, 1H, T_4), 8.05 (d, *J* = 8.5 Hz, 1H, 13), 7.97 (d, *J* = 7.7 Hz, 1H, 3), 7.72 (d, *J* = 5.5 Hz, 1H, 22), 7.67 (t, *J* = 7.4 Hz, 1H, 12), 7.64 – 7.58 (m, 1H, 11), 7.51 – 7.44 (m, 1H, T_5), 7.38 (dd, *J* = 8.0, 5.4 Hz, 1H, 21), 6.95 (t, *J* = 7.3 Hz, 1H, T_4"), 6.87 (dt, *J* = 14.3, 7.3 Hz, 2H, T_6", T_5"), 2.52 (s, 3H, CH_3), 2.41 (s, 3H,

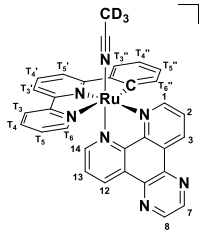
CH_3). ^{13}C NMR (126 MHz, [D-6]acetone) δ 181.3 (C_q), 168.2 (C_q), 157.8 (C_q), 157.8 (C_q), 156.5 (C_H, 1), 153.3 (C_H, 21), 150.9 (C_q), 150.8 (C_H, 22), 149.5 (C_q), 148.1 (C_q), 141.9 (C_q), 141.3 (C_q), 139.7 (C_H, T_4), 139.3 (C_q), 139.3 (C_q), 138.9 (C_H, T_6"), 138.4 (C_H, 1), 135.9 (C_q), 135.8 (C_q), 133.0 (C_H, 20), 131.8 (C_H, 3), 131.6 (C_q), 130.9 (C_H, T_5"), 130.1(C_q) , 129.6 (C_H, 10), 129.6 (C_H, 13), 129.0 (C_H, 8), 129.0 (C_H, 15), 128.8 (C_H, 12), 128.7 (C_H, 11), 128.5 (C_H, T_5), 127.3 (C_H, 2), 126.8 (C_H, 21), 126.3 (C_H, T_3"), 124.9 (C_H, T_3), 123.4 (C_H, T_4"), 121.2 (C_H, T_3'), 120.6 (C_H, T_5'), 45.2 (CH_3), 43.9 (CH_3). HRMS: m/z calcd for $[C_{40}H_{29}N_6ORuS - PF_6]^+$: 743.11670; found: 743.11680; elemental analysis calcd (%) for [**5**]PF_6: C 54.12, H 3.29, N 9.47; found: C 52.67, H 3.82, N 8.78.



[Ru(phbpy)(bpy)(CD₃CN)]PF₆ [**6**]PF_6: [**1**]PF_6 (3.0 mg, 4.0 µmol) was dissolved in 0.6 mL deoxygenated CD_3CN and irradiated for 7 h at 1 cm from a Xenon Arc (1000 W) lamp fitted with IR (> 700 nm) and UV-cutoff (< 400 nm) filter at 298 K, while maintaining the temperature at 25 °C. After completion of the reaction, the sample was concentrated *in vacuo* to afford the title compound as a dark purple solid (2.7 mg, 4.0 µmol, quant.). ^1H NMR (500 MHz, [D_3]acetonitrile) δ = 9.55 (d, *J* = 5.8 Hz, 1H, 1), 8.40 (d, *J* = 8.2 Hz, 1H, 4), 8.33 (d, *J* = 8.1 Hz, 1H, T_3), 8.18 (d, *J* = 8.1 Hz, 1H, T_3'), 8.14 (d, *J* = 8.0 Hz, 1H, T_4'), 8.03 – 7.96 (m, 3H, 3, T_6), 7.95 – 7.87 (m, 2H, T_4, T_5'), 7.74 (dd, *J* = 7.6, 1.4 Hz, 1H, T_3"), 7.68 (ddd, *J* = 7.3, 5.7, 1.4 Hz, 1H, 2), 7.58 (ddd, *J* = 8.2, 7.4, 1.5 Hz, 1H, 8), 7.36 (ddd, *J* = 5.8, 1.5, 0.8 Hz, 1H, 10), 7.32 (ddd, *J* = 7.5, 5.3, 1.2 Hz, 1H, T_5), 6.91 (ddd, *J* = 7.3, 5.8, 1.4 Hz, 1H, 9), 6.81 (td, *J* = 7.5, 1.3 Hz, 1H, T_4"), 6.73 (td, *J* = 7.3, 1.4 Hz, 1H, T_5"), 6.36 (ddd, *J* = 7.4, 1.4, 0.6 Hz, 1H, T_6"). ^{13}C NMR (126 MHz, [D_3]acetonitrile) δ = 184.8 (C_q), 167.0 (C_q), 157.2 (C_q), 156.7 (C_q), 156.7 (C_q), 154.9 (C_q), 151.0 (C_H, 1), 150.6 (C_H, T_6), 149.6 (C_H, 10), 147.8 (C_q), 137.6 (C_H, T_4), 136.3 (C_H, T_6"), 135.0 (CH, 1), 133.4 (C_H, 8), 132.5 (C_H, 3), 128.9 (C_H, T_5"), 126.7 (C_H, T_5), 125.9 (C_H, 2), 125.2 (C_H, 9), 124.4 (C_H, T_3"), 123.2 (C_H, 3), 122.8 (C_H, T_3), 122.2 (C_H, 7), 121.2 (C_H, T_4"), 118.7 (C_H, T_3'), 117.8 (C_H, 2). ESI-MS m/z calcd for $[C_{28}H_{22}N_5Ru_6 - PF_6]^+$: 530.1; found: 530.0.

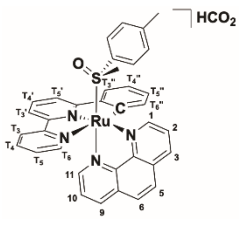


[Ru(phbpy)(phen)(CD₃CN)]PF₆, [**7**]PF_6: The same procedure was followed as described for [**6**]PF_6 using [Ru(phbpy)(bpy)(DMSO)]PF_6 (1.9 mg, 3.0 µmol) to afford the product as a dark red solid (1.8 mg 3.0 µmol, quant.). A racemic mixture was obtained but only one enantiomer is shown. ^1H NMR (500 MHz, [D_3]acetonitrile) δ 9.91 (d, *J* = 4.2 Hz, 1H, 1), 8.58 (d, *J* = 7.0 Hz, 1H, 3), 8.37 (d, *J* = 7.4 Hz, 1H, T_3), 8.22 – 8.17 (m, 2H, 5, T_3'), 8.15 (d, *J* = 6.8 Hz, 1H, 8), 8.11 – 8.05 (m, 2H, 2, T_5'), 8.02 – 7.95 (m, 2H, 6, T_4'), 7.94 – 7.89 (m, 2H, T_4, T_6), 7.77 (d, *J* = 6.4 Hz, 1H, T_3"), 7.72 (d, *J* = 4.1 Hz, 1H, 10), 7.30 (dd, *J* = 8.1, 5.4 Hz, 1H, 9), 7.23 (t, *J* = 7.8, 1H, T_5), 6.78 (t, *J* = 6.8 Hz, 1H, T_4"), 6.60 (t, *J* = 7.3 Hz, 1H, T_5"), 6.17 (d, *J* = 6.2 Hz, 1H, T_6"). ^{13}C NMR (126 MHz, [D_3]acetonitrile) δ = 184.7 (C_q), 167.2 (C_q), 157.2 (C_q), 156.9 (C_q), 151.2 (C_H, 1), 150.7 (C_H, T_6), 150.1 (C_H, 10), 147.8 (C_q), 147.4 (C_q), 146.7 (C_q), 137.6 (C_H, T_4), 136.3 (C_H, T_6"), 135.1 (C_H, T_4'), 132.5 (C_H, 8), 131.5 (C_H, 3), 130.8 (C_q), 129.7 (C_q), 128.7 (C_H, T_5"), 127.7 (C_H, 5), 127.2 (C_H, 6), 126.6 (C_H, T_5), 125.2 (C_H, 2), 124.4 (C_H, T_3"), 124.1 (C_H, 9), 122.8 (C_H, T_3), 121.2 (C_H, T_4"), 118.7 (C_H, T_3'), 117.9 (C_H, 2). ESI-MS $[C_{30}H_{19}D_3N_5Ru_6 - PF_6]^+$: 559.1; found: 559.1.



[Ru(phbpy)(dpq)(CD₃CN)]PF₆, [**8**]PF_6: The same procedure was followed as described for [**6**]PF_6 using $[Ru(dpq)(DMSO)_2Cl_2]$ (2.4 mg, 3.0 µmol) to afford the product as a dark red solid (2.2 mg, 3.0 µmol, quant.). A racemic mixture was obtained but only one enantiomer is shown. ^1H NMR (500 MHz, [D_3]acetonitrile) δ = 9.99 (d, *J* = 4.2 Hz, 1H, 1), 9.47 (d, *J* = 8.1 Hz, 1H, 3), 9.16 (d, *J* = 2.1 Hz, 1H, 7), 9.08 (d, *J* = 2.1 Hz, 1H, 8), 9.05 (d, *J* = 8.0 Hz, 1H, 12), 8.36 (d, *J* = 8.1 Hz, 1H, T_3), 8.22 – 8.15 (m, 2H, 2, T_3), 8.07 (d, *J* = 7.2 Hz, 1H, T_5'), 7.99 – 7.94 (m, 2H, 1, T_6), 7.91 (ddd, *J* = 8.1, 7.5, 1.6 Hz, 1H, T_4), 7.82 (d, *J* = 6.8 Hz, 1H, 14), 7.77 (d, *J* = 6.4 Hz, 1H, 3), 7.39 (dd, *J* = 8.1, 5.5 Hz, 1H, 13), 7.22 (ddd, *J* = 7.5, 5.3, 1.2 Hz, 1H, T_5), 6.77 (t, *J* = 7.3 Hz, 1H, T_4"), 6.60 (t, *J* = 7.3 Hz, 1H, T_5"), 6.28 (d, *J* = 7.4 Hz, 1H, T_6"). ^{13}C NMR (126 MHz, [D_3]acetonitrile) δ = 184.1 (C_q), 167.0 (C_q), 157.2 (C_q), 156.8 (C_q), 152.0 (C_H, 1), 151.5 (CH, T_6), 151.3 (C_H, 14), 149.1 (C_q), 148.1 (C_q), 147.8 (C_q), 146.2

(C_H, 7), 146.0 (C_H, 8), 140.4 (C_q), 140.0 (C_q), 137.8 (C_H, T_4), 136.5 (C_H, T_6''), 135.4 (C_H, T_4'), 129.8 (C_q), 129.0 (C_H, 12), 128.8 (C_H, T_5''), 128.6 (C_q), 127.9 (C_H, 3), 126.6 (C_H, T_5), 126.0 (C_H, 2), 125.1 (C_H, 13), 124.5 (C_H, T_3''), 122.9 (C_H, T_3), 121.4 (C_H, T_4''), 118.8 (C_H, T_3'), 118.0 (C_H, T_5'). ESI-MS m/z calcd for $[C_{32}H_{22}N_7Ru_6 - PF_6]^+$: 606.1; found: 606.1.



A* and *C*-[Ru(phbpy)(phen)(*R*-methyl *p*-tolylsulfoxide)]PF_6**, [**11-*A]HCO_2 **and** [**11-*A***] HCO_2: [**2**]PF_6 (13.6 mg, 18.5 µmol) was dissolved in deoxygenated MeCN (3 mL) and irradiated for 3 h in a custom built photo-cell 1 cm from a Xenon Arc (1000 W) lamp fitted with IR (>700 nm) and UV-cutoff (<410 nm) filter, while maintaining the temperature at 25 °C. After concentrating the reaction *in vacuo,* the resulting solid was redissolved in deoxygenated MeOH (10 mL), followed by the addition of (*R*)-(+)-methyl *p*-tolyl sulfoxide (10.3 mg, 66.8 µmol). The mixture was allowed to stir at reflux for 16 h, after it was purified over reverse-phase HPLC (0.1% HCO_2H, 30 to 35% MeCN in H_2O, 20 min) affording both [**11-C**]HCO_2 (R_f = 12.184 min, 0.80 mg, 1.0 µmol, 5%) and [**11-A**]HCO_2 (R_f = 12.984 min, 0.50 mg, 0.65 µmol, 4%) as their respective diastereomers, [**11-A**]HCO_2: ^{1}H NMR (850 MHz, [D_3]acetonitrile) δ = 10.75 (d, *J* = 5.3 Hz, 1H, 1), 8.67 (d, *J* = 8.2 Hz, 1H, 3), 8.32 (d, *J* = 7.9 Hz, 1H, T_2'), 8.20 (d, *J* = 8.8 Hz, 1H, 5), 8.16 (dd, *J* = 8.2, 5.2 Hz, 1H, 2), 8.03 (d, *J* = 8.8 Hz, 1H, 6), 8.00 (d, *J* = 8.1 Hz, 1H, 11), 7.89 – 7.86 (m, 2H, 10, T_5), 7.84 (d, *J* = 5.3 Hz, 1H, T_2), 7.80 – 7.75 (m, 2H, T_4'', T_4), 7.72 (d, *J* = 8.0 Hz, 1H, 9), 7.47 (d, *J* = 5.4 Hz, 1H, T_4'), 7.40 (dd, *J* = 8.1, 5.2 Hz, 1H, T_3'), 7.14 (dd, *J* = 7.3, 5.4 Hz, 1H, T_3), 6.89 (t, *J* = 7.3 Hz, 1H, T_3''), 6.81 (d, *J* = 8.1 Hz, 2H, 2 x CH *m*-tolyl), 6.71 (t, *J* = 7.2 Hz, 1H, T_2''), 6.44 (d, *J* = 7.5 Hz, 1H, T_1''), 6.43 (d, *J* = 12.9, 7.8 Hz, 2H, 2 x CH *o*-tolyl), 2.77 (s, 3H). ESI-MS m/z calcd for $[C_{36}H_{29}N_4ORuS - PF_6]^+$: 667.1; found: 667.1.

Single Crystal X-ray Crystallography

All reflection intensities were measured at 110(2) K using a SuperNova diffractometer (equipped with Atlas detector) either with Mo *K*α radiation (λ = 0.71073 Å) for **[1]**PF_6 or with Cu *K*α radiation (λ = 1.54178 Å) for **[2]**PF_6, **[3]**PF_6, and **[4]**PF_6 under the program CrysAlisPro (Version 1.171.36.32 Agilent Technologies, 2013 or Version 1.171.38.43 Agilent Technologies, 2015). The same program was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXS-2014/7 (Sheldrick, 2015) and was refined on F^2 with SHELXL-2014/7 (Sheldrick, 2015). Numerical absorption (based on Gaussian integration) or analytical numeric absorption corrections using a multifaceted crystal model based were applied using CrysAlisPro. The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions using the instructions AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 *U*eq of the attached C atoms.

[1]PF_6: The structure is ordered.

[2]PF_6: The structure is partly disordered. The PF_6^- counterion is disordered over 2 orientations, and the occupancy factor of the major component of the disorder refines to 0.721(8). The crystal lattice includes a mixture of disordered lattice solvent molecules (DCM/Hexane) located on a special position (inversion center). Their contribution has been removed from the final refinement using the Squeeze procedure in Platon (Squeeze, 2009).

[3]PF_6: The structure is mostly ordered. There are four crystallographically independent formula units (4 Ru complexes + 4 PF_6^- counterions) in the asymmetric unit. Two of the four PF_6^- counterions are found to be disordered over two orientations, and the occupancy factors of the major components of the disorder refine to 0.803(5) and 0.510(6). The crystal was found to be non-merohedrally twinned, and the twin relationship corresponds to a twofold axis along −0.4078**a*** + 0.4089**b*** + 0.8164**c***. The BASF scale factor refines to 0.5243(5).

[4]PF_6: The structure is significantly disordered. The ligand C1→C16, the coordinated DMSO molecule, and the counterions are found to be disordered over 2 orientations. All occupancy factors can be retrieved from the .cif file. Both counterions are found at special positions (twofold axial symmetry). The PF_6^- counterion P2/F7→F12 is constrained to have an occupancy factor of 0.5. The other counterion corresponds to a mixture of another PF_6^- (major) and Cl^- (minor, from DCM). The sum of the occupancy factors for the mixture is also constrained to be 0.5. The contribution of some unresolved electron density (disordered lattice solvent molecule) has been removed from the final refinement using the Squeeze procedure in Platon (Squeeze, 2009).

Computer programs:
CrysAlis PRO, Agilent Technologies, Version 1.171.36.32 (release 02-08-2013 CrysAlis171 .NET) (compiled Aug 2 2013, 16:46:58), *SHELXS2014*/7 (Sheldrick, 2015), *SHELXL2014*/7 (Sheldrick, 2015), *SHELXTL* v6.10 (Sheldrick, 2008).

Reference:
Sheldrick, G. M. (2015). Acta Cryst. C71, 3-8
Spek A.L. (2009) Acta Cryst. D65, 148-155

Table S1. Crystallographic data for [1]PF_6

	[1]PF_6
Crystal data	
Chemical formula	$C_{28}H_{25}N_4ORuS \cdot F_6P$
M_r	711.62
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	110
a, b, c (Å)	16.4880 (5), 10.0475 (3), 18.4299 (6)
β (°)	116.276 (4)
V (Å^3)	2737.68 (17)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.78
Crystal size (mm)	0.52 × 0.27 × 0.07
Data collection	
Diffractometer	SuperNova, Dual, Cu at zero, Atlas
Absorption correction	Gaussian *CrysAlis PRO*, Agilent Technologies, Version 1.171.36.32 (release 02-08-2013 CrysAlis171 .NET) (compiled Aug 2 2013,16:46:58) Numerical absorption correction based on gaussian integration over a multifaceted crystal model
T_{min}, T_{max}	0.397, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	21572, 6271, 5597
R_{int}	0.028
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.028, 0.066, 1.03
No. of reflections	6271
No. of parameters	381
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.37, -0.60

Table S2. Crystallographic data for [2]PF_6

	[2]PF_6
Crystal data	
Chemical formula	$C_{30}H_{25}N_4ORuS \cdot F_6P$
M_r	735.64
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	110
a, *b*, *c* (Å)	9.1748 (3), 12.0308 (3), 15.1510 (4)
α, β, γ (°)	95.641 (2), 98.831 (3), 109.006 (3)
V (Å^3)	1542.65 (8)
Z	2
Radiation type	Cu *K*α
μ (mm^{-1})	5.84
Crystal size (mm)	0.31 × 0.09 × 0.08
Data collection	
Diffractometer	SuperNova, Dual, Cu at zero, Atlas
Absorption correction	Analytical *CrysAlis PRO*, Agilent Technologies, Version 1.171.36.32 (release 02-08-2013 CrysAlis171 .NET) (compiled Aug 2 2013,16:46:58) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897)
T_{min}, T_{max}	0.296, 0.685
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19662, 6033, 5760
R_{int}	0.023
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.616
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.026, 0.064, 1.05
No. of reflections	6033
No. of parameters	463
No. of restraints	237
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.90, -0.99

Table S3. Crystallographic data for [3]PF_6

	[3]PF_6
Crystal data	
Chemical formula	$C_{32}H_{25}N_6ORuS \cdot F_6P$
M_r	787.68
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	110
a, *b*, *c* (Å)	15.1228 (4), 16.8679 (4), 25.1053(4)
α, β, γ (°)	100.2336 (18), 90.1903 (18), 104.221 (2)
V (Å^3)	6101.7 (12)
Z	8
Radiation type	Cu *K*α
μ (mm^{-1})	5.98
Crystal size (mm)	0.39 × 0.11 × 0.06
Data collection	
Diffractometer	SuperNova, Dual, Cu at zero, Atlas
Absorption correction	Analytical *CrysAlis PRO* 1.171.38.43 (Rigaku Oxford Diffraction, 2015) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.309, 0.730
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	73586, 25508, 19051
R_{int}	0.040
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.616
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.036, 0.092, 0.89
No. of reflections	25508
No. of parameters	1851
No. of restraints	483
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.87, -0.69

Table S4. Crystallographic data for [4]PF_6

	[4]PF_6
Crystal data	
Chemical formula	$C_{36}H_{27}N_6ORuS \cdot 0.755(F_6P) \cdot 0.245(Cl)$
M_r	810.97
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	110
a, *b*, *c* (Å)	15.6544 (3), 38.0206 (6), 14.7943 (3)
β (°)	116.312 (2)
V (Å^3)	7893.1 (3)
Z	8
Radiation type	Cu *K*α
μ (mm^{-1})	4.64
Crystal size (mm)	0.55 × 0.18 × 0.09
Data collection	
Diffractometer	SuperNova, Dual, Cu at zero, Atlas
Absorption correction	Analytical *CrysAlis PRO*, Agilent Technologies, Version 1.171.36.32 (release 02-08-2013 CrysAlis171 .NET) (compiled Aug 2 2013,16:46:58) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897)
T_{min}, T_{max}	0.182, 0.701
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	25819, 7765, 6677
R_{int}	0.027
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.616
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.061, 0.187, 1.04
No. of reflections	7765
No. of parameters	787
No. of restraints	1371
H-atom treatment	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + (0.105P)^2 + 27.6141P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.65, -2.07

Photochemistry

Electronic absorption spectra

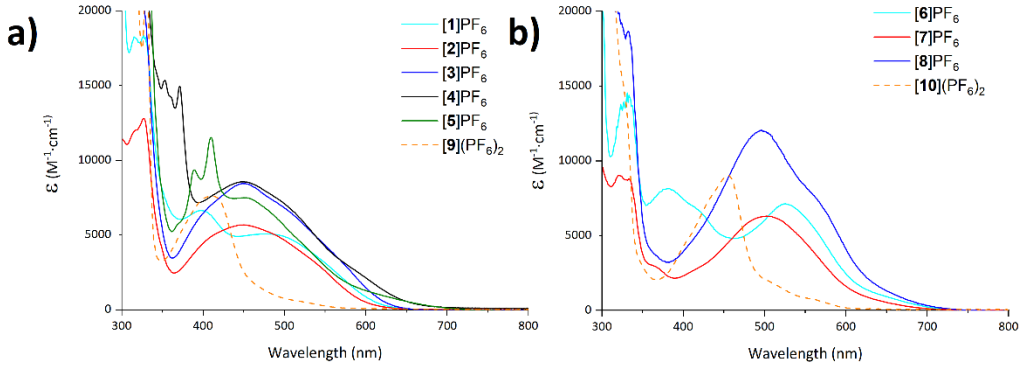


Figure S1. a) Electronic absorption spectra for [**1**]PF_6 – [**5**]PF_6 and b) [**6**]PF_6 – [**8**]PF_6 in acetonitrile. Dashed lines represent the non-cyclometalated analogons [**9**]$(PF_6)_2$ (a) and [**10**]$(PF_6)_2$ (b), respectively.

Photosubstitution quantum yield

3.00 mL of [**1**]PF_6 (6.83 x 10^{-5} M), [**2**]PF_6 (4.10 x 10^{-5} M), [**3**]PF_6 (4.10 x 10^{-5} M) or [**9**]$(PF_6)_2$ (6.52 x 10^{-5} M) in acetonitrile was transferred to a 1 cm wide quartz fluorescence cuvette with stirring bar and deoxygenated for 15 minutes with dinitrogen after which it was irradiated with a Roithner LaserTechnik H2A1-H450 LED (λ_{exc} 450 nm, FWHM 35 nm) with photon flux $\Phi = 1.68 \cdot 10^{-7}$ mol s^{-1}) while the solution was kept at constant temperature (25° C). During this period UV-vis spectra were recorded on a Varian Inc. Cary 50 UV-vis spectrometer with an interval of 10 minutes for 24 h and ESI-MS spectra were recorded after the irradiation experiment to confirm the formation of the solvent species $[Ru(phbpy)(N\text{-}N)(MeCN)]^+$. Photosubstitution quantum yields were determined as described earlier.[6] `

NMR irradiation experiments

^{1}H NMR irradiation experiments were carried out as follows: 2.0 mg of either [**1**]PF_6, [**2**]PF_6 or [**3**]PF_6 were dissolved in 0.6 mL [D_3]acetonitrile and irradiated 1 cm from a Xenon-Arc 1000 W fitted with IR (>700 nm) and UV-cutoff (<410 nm) filters, while maintaining the temperature at 25 °C during the irradiation period spectra were recorded every h on a Bruker AV-400 until completion.

Singlet oxygen quantum yield

Singlet oxygen measurements were carried out as described before.[7]

Electrochemistry

Cyclic voltammetry experiments were performed using a cell with a platinum working electrode, a silver wire as pseudo-reference electrode, and a platinum wire as auxiliary electrode. 0.1 M Bu_4NPF_6 in MeCN was used as the supporting electrolyte. 1 mM solutions of each complex were purged with argon prior to the experiment, and was measured at room temperature using Autolab PGSTAT10 and GPES 4.9 by Eco Chemie. Each experiment was calibrated against ferrocene with a scan rate of 100 mV s^{-1}. For [**4**]PF_6, [**6**]PF_6**,** [**7**]PF_6**,** [**8**]PF_6 a scan rate of 200 mV s^{-1} was used.

Circular Dichroism

Measurements were performed on a BioLogic Science Instruments MOS-500 Circular Dichroism Spectrometer, using stock solutions of 4.9 x 10^{-5} M for both [**11-A**] and [**11-C**] in acetonitrile.

DFT and TDDFT

The structures of [**1**]$^+$ - [**5**]$^+$ were minimized by DFT using the ADF program from SCM (version 2016) using the TZP basis set, the PBE0 functional, and COSMO to simulate solvent effects in water. When available the X-ray structure was used as starting x,y,z coordinates. The HOMO and LUMO orbitals of the converged geometries are shown in Figures S2 to S6, and their X,Y,Z coordinates are given in Table S5-S9.

For TDDFT the first 20 excited singlet states energies were calculated at the same level of theory (PBE0/TZP/COSMO) using the Davidson method.

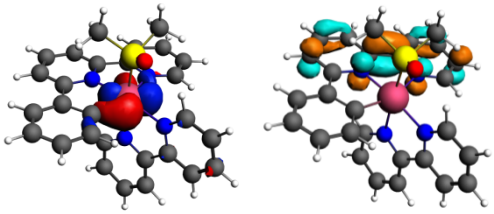


Figure S2. HOMO (left) and LUMO (right) of [**1**]$^+$ optimized by DFT (COSMO).

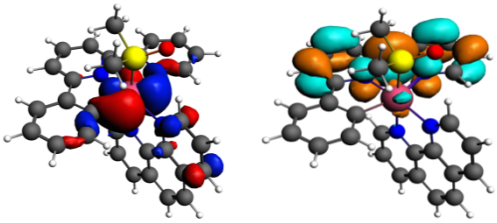


Figure S3. HOMO (left) and LUMO (right) of [**2**]$^+$ optimized by DFT (COSMO).

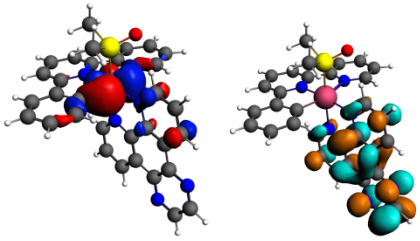


Figure S4. HOMO (left) and LUMO (right) of [**3**]$^+$ optimized by DFT (COSMO).

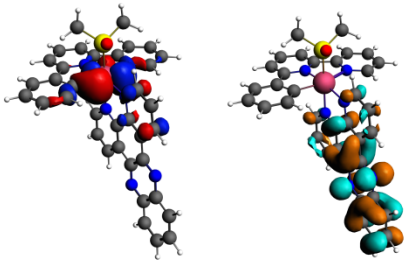


Figure S5. HOMO (left) and LUMO (right) of [**4**]$^+$ optimized by DFT (COSMO).

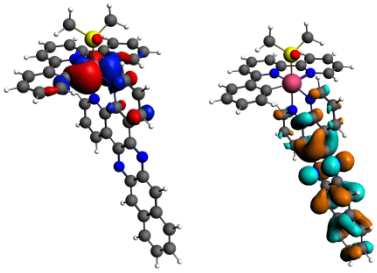


Figure S6. HOMO (left) and LUMO (right) of [**5**]$^+$ optimized by DFT (COSMO).

Table S5. Nuclear coordinates (Å) of $[1]^+$ minimized at the DFT/PBE0/TZP/COSMO level in water.

C	-3.092059918703469	-2.953763541996143	-0.3623755067135818
C	-2.267799373623135	-1.835611857219086	-0.3579493067222426
N	-0.9530330856692046	-1.929159366293118	-0.6656841469902909
C	-0.44644420728757	-3.126462363744916	-0.9604509235630987
C	-1.207454729453378	-4.283007498994305	-0.9789808395030694
C	-2.55652746851154	-4.191101086478097	-0.6782782809241547
C	-2.762586002878201	-0.4864446943794763	-0.008847867606422961
N	-1.839189850733144	0.4885195061657225	-0.07483469779203257
C	-2.106148195630574	1.765568510204425	0.2718717872582969
C	-3.395119216663364	2.102075368510701	0.6799306416882837
C	-4.367139720559663	1.117590979496853	0.7301373589578873
C	-4.058431602577763	-0.1927833087946576	0.3915510957252279
C	-0.9433939044569928	2.655263904187933	0.171537972779341
C	0.2722356643345686	2.056268122090429	-0.2587725696921889
C	1.3842237571414	2.895589582321745	-0.3619612617686954
C	1.310772945697677	4.250429465745696	-0.05534839904154751
C	0.1086248753609154	4.816388590381196	0.3619822522092387
C	-1.017904432120712	4.017634364182936	0.4737533437663844
Ru	0.07201450889055687	0.04251999853342155	-0.5964979859051032
N	2.120979284160034	-0.4581505741172647	-0.8031395335591798
C	2.748357531538665	-0.8100145058703875	0.3450772458878791
C	4.081697678177355	-1.205488974224543	0.3571791248046064
C	4.797454186783784	-1.243329422781619	-0.8239045902330494
C	4.157094412315669	-0.8740136262639554	-1.995787122505422
C	2.831103086936372	-0.4893265502960352	-1.940721192169548
C	1.936766823814543	-0.7381507616185101	1.564555276899486
N	0.6557690335531026	-0.3524200085816733	1.391541891863963
C	-0.1394942304009864	-0.2522128470627395	2.461319759667911
C	0.291629116553009	-0.5297423293338656	3.743729067363296
C	1.605799649992916	-0.9280465211583667	3.930319194443967
C	2.434739991662856	-1.032143975873053	2.829667132812931
H	2.333670826639179	2.485115997598028	-0.6934100069623688
H	2.196048655963822	4.873000282532714	-0.1455832429630024
H	0.05081954652540108	5.873595236084944	0.5962920069274305
H	-1.954176442582344	4.460998733415038	0.7965959415666398
H	-3.633396422553741	3.119815849686566	0.959126576433333
H	-5.373120630336593	1.367671180688004	1.044974294598611
H	-4.813189898269619	-0.964606722923069	0.44870181242151
H	-4.14239004063643	-2.86008861215177	-0.1227557219368028
H	-3.18775794892966	-5.071416356666486	-0.6872290008668716
H	-0.7444040202297085	-5.229026182758319	-1.228083766486775
H	0.6116359156675872	-3.153929937394199	-1.194644479129663
H	2.310464763725883	-0.1656626434596486	-2.831881254924877
H	4.669251946731791	-0.8771364435334424	-2.949412724691424
H	5.835549223975058	-1.552224980048198	-0.8264439829679374
H	4.558115684089822	-1.482741727313771	1.286741923350429
H	3.463585917677309	-1.337540479974417	2.955432953459277
H	1.983837867979463	-1.152746633919174	4.920194536096048
H	-0.3972527739635251	-0.429848016835303	4.572309131124366
H	-1.157690422601773	0.06358657198071946	2.27983398624253
S	-0.3263499772429871	0.5277821140449679	-2.794718217236126
O	0.7832213965164273	1.15417037704699	-3.582728891746056
C	-1.754025134209319	1.56971587368819	-3.060187024673313
C	-0.8499934528863713	-0.8908084859382438	-3.7507793157594
H	-1.016831740738188	-0.5598125208759763	-4.775030839656535
H	-1.761662078318002	-1.30232128386564	-3.31987392733556

H	-0.04677561320506909	-1.624745873545554	-3.710948063387591
H	-1.565109866573011	2.512978153150039	-2.551736473993619
H	-2.641182319705258	1.085228268264819	-2.655566458642154
H	-1.849902244900364	1.721467800862641	-4.134208238458328

Table S6. Nuclear coordinates (Å) of [2]$^+$ minimized at the DFT/PBE0/TZP/COSMO level in water.

Ru	1.153618881383357	0.9180183002164338	10.77986131303118
S	0.1900247727944037	-0.08489704462042774	8.964682908312158
N	0.3059123962117131	2.88073717261768	10.17590692488239
C	-0.8881361378106207	3.399865169304758	10.45989026363197
H	-1.548107452081619	2.780542493770891	11.05610813091861
C	-1.286044573996403	4.653898819869442	10.02675128112145
H	-2.268012638593357	5.027652950108116	10.28735475150532
C	-0.4040635925739154	5.400261263886597	9.263083118861976
H	-0.6766233867823361	6.385448340801878	8.903895060069702
C	0.8386051086156285	4.869583935033737	8.959902761421059
H	1.540457839333376	5.435873815962367	8.362889204957151
C	1.17130340688171	3.604972848513057	9.428852289682011
C	2.477659528464976	2.972733187338158	9.146083160520307
C	3.500660180482625	3.555282729414	8.411432691438936
H	3.387991702341096	4.540844328995506	7.981672590455352
C	4.681405530267512	2.84544512248719	8.239610624009703
H	5.490878487154226	3.28055075198442	7.665703260283003
C	4.83334531230107	1.591607131226064	8.805060163969555
H	5.759193308234455	1.045175211287658	8.682539893638987
C	3.782422811806318	1.043897306412588	9.538272153571645
C	3.762277078646553	-0.2463033354406663	10.23547526246765
C	4.858144341793778	-1.113058911932681	10.22819881021573
H	5.760668887060493	-0.8575537204506121	9.682356870823156
C	4.801628365819626	-2.309350933776176	10.9249105849848
H	5.651670037825477	-2.982853300118962	10.91941034456392
C	3.648038321204865	-2.634105389636439	11.63442274404997
H	3.601682143923966	-3.567734795016918	12.18731500302323
C	2.555768946063747	-1.772522953390207	11.63831252610722
H	1.669833661716849	-2.060235850216233	12.19837598668935
C	0.523445613531465	-1.831319324208858	8.802827683692211
H	0.1572553501145873	-2.320202382567235	9.703836266703986
H	1.597723938876199	-1.98079276556983	8.711235853981789
H	-0.008590203096254528	-2.188396593949448	7.921902876103717
C	0.8557563091726985	0.461789736512136	7.39870416350515
H	0.3341924399307157	-0.07945688865941393	6.610598783876808
H	1.925682936938519	0.2600641030903453	7.369192763139626
H	0.6643424162145861	1.530107383358355	7.315897715783988
C	2.947568808391554	2.53476503013434	12.7372019877141
H	3.481533819920258	2.825129611852993	11.84162285529689
C	3.371588822536208	2.989403996485632	13.98770390952985
H	4.237681474927085	3.636101258031776	14.04603592964799
C	2.685158857169217	2.605372442534988	15.11272736426126
H	2.99083968280479	2.93970613659932	16.09774590353529
C	1.569004385816105	1.765132044609631	14.97917769307318
C	1.210815466598207	1.355816125739131	13.68218153557003
C	0.08038040645854289	0.5106777360757601	13.48537056613145
C	-0.6715687056781555	0.08887922749155969	14.59708228103351
C	-1.785907175562477	-0.7305987146247515	14.36100787949432
H	-2.384483970019577	-1.079766773873475	15.19463852261514
C	-2.098910308064583	-1.063975742390276	13.0670604687525
H	-2.955584625192253	-1.683618598686522	12.8345316148754

C	-1.301964472759577	-0.5964148501890109	12.02002698391813
H	-1.557568498374436	-0.8292592813605291	10.99404362276108
C	0.7923402318353826	1.315088067661209	16.08964327959557
H	1.08249022989048	1.634880617722844	17.08411850810457
C	-0.2809170358905422	0.5096875272127825	15.90542412474271
H	-0.8699545998379951	0.1703960459801973	16.75004515953664
N	2.635813827599621	1.743935014480283	9.66802468228844
C	2.56848037266093	-0.5616062484652293	10.94090404816376
N	-0.2263564922299481	0.1615874132604901	12.20509713753056
N	1.898993365152706	1.741131038653506	12.5795227852313
O	-1.298488685811243	0.06302259417035619	8.856410239945719

Table S7. Nuclear coordinates (Å) of $[3]^+$ minimized at the DFT/PBE0/TZP/COSMO level in water.

Ru	10.6207256833375	9.295233007968479	7.262573765262218
S	8.370011482732028	9.141632158477744	7.666467004008378
N	10.80984678441878	7.085352710903147	7.339329643078129
C	10.6407970843447	6.197689007531256	6.360144059133822
H	10.37253158616282	6.600850563992569	5.39081809171783
C	10.79163508729395	4.833680713910531	6.547357605142531
H	10.64488133112537	4.155800376041853	5.716298540712426
C	11.12819091180582	4.372622613417835	7.809423546996983
H	11.25289267837091	3.313082126044224	7.997786577684955
C	11.30300370058517	5.286704912219491	8.835070632943122
H	11.56186591420812	4.94836983747091	9.828954152264799
C	11.13975306973114	6.641213018029336	8.57403950391461
C	11.30841431165543	7.676689442705658	9.61608718417372
C	11.66678353119138	7.427837339967875	10.93328341665688
H	11.84386195515079	6.419723137395541	11.28162283188168
C	11.79652081669137	8.504808985975641	11.7998741161382
H	12.07248636890153	8.331908633370647	12.8331933973153
C	11.58414011561652	9.796360496906921	11.34987481365386
H	11.69621561832902	10.63533833731856	12.02374217854446
C	11.22869689788322	10.00337130526458	10.01856440640583
C	10.98937631140329	11.28726935859079	9.349491907581013
C	11.07601687095539	12.50787202938395	10.02416634413014
H	11.31212391674918	12.53828677752333	11.0828825622697
C	10.86093331117874	13.69484408623345	9.342543848005075
H	10.92496771971256	14.64194215801047	9.866682857431789
C	10.56696171310691	13.65976607759504	7.981956966061568
H	10.40390794370477	14.58794516302166	7.44244213677592
C	10.47782331340559	12.4444680656739	7.310995834506863
H	10.239890694559	12.45335884748803	6.250589426420211
C	7.504348616460628	10.70246458772832	7.681749844339286
H	7.660518985134081	11.17291733492947	6.712572748232679
H	7.91503929692708	11.33124297337576	8.469309500322826
H	6.448669224041882	10.48937234007581	7.845734414218828
C	7.965126186353581	8.589709760356454	9.316458730465408
H	6.879694022402982	8.569232092575136	9.401221233162072
H	8.401085704381913	9.273105350530102	10.04369274949879
H	8.374602983611974	7.588483129701374	9.437079598152673
C	13.71038402074536	9.401506514412306	7.463434551268935
H	13.53590547531059	9.136452115032299	8.497886216194853
C	15.0039753755154	9.610036665659296	6.996549658231518
H	15.83650576836136	9.50201348899496	7.679330133996196
C	15.1970970226167	9.951971013135966	5.678360433650473
H	16.1883218018532	10.1239443036744	5.27968464866055
C	14.0856587507726	10.07531999246378	4.841007910851894

C	12.81781971458143	9.848048210314698	5.387247523468301
C	11.63578052020674	9.943432627545112	4.574456795317032
C	11.73598045092237	10.25571080257667	3.21376277572543
C	10.56317119560392	10.30370438507537	2.45667647072246
H	10.61428848811327	10.54561841131857	1.403223854088821
C	9.366465113590893	10.02608145475171	3.075172102249142
H	8.433336630822614	10.03560637399471	2.5270676724332
C	9.349800124833232	9.724960679625816	4.433010679509516
H	8.419876610619982	9.477254363922157	4.928437312977538
C	14.1972960545429	10.42133439928836	3.437185743605487
C	13.04449640110569	10.5088059435822	2.638767573701518
C	15.47722769548334	10.95715534431511	1.646528428302875
H	16.45642965479959	11.14484443408487	1.218385283444001
C	14.32846814363281	11.04507477047086	0.8502883354841143
H	14.40925944685463	11.30137046391011	-0.2010330074992666
N	11.08987384660908	8.937622568409273	9.202268048371153
C	10.67348067930038	11.2251313620792	7.964100982854689
N	12.6397553339432	9.515187571455252	6.685781880195239
N	10.44854164072089	9.695949708770131	5.186621449236729
N	15.41616475312045	10.64891562972157	2.925040396067837
N	13.12530425210134	10.82390626774583	1.337021734618786
O	7.604606345874031	8.254941364982322	6.730580556039137

Table S8. Nuclear coordinates (Å) of [4]$^{+}$ minimized at the DFT/PBE0/TZP/COSMO level in water.

Ru	2.229963416438115	4.078474027365608	1.261085207691187
N	1.786489859213788	4.39124509597966	3.418561200182987
C	1.562890580693166	3.482570190312146	4.367983166071152
H	1.605334707014311	2.445320812691067	4.056266907774295
C	1.285757919654191	3.818920537646991	5.682168818226002
H	1.109605605159452	3.039622697520192	6.412334473886094
C	1.237517858583027	5.160199555729562	6.024965827036887
H	1.018524593738451	5.465343888134492	7.041194275672937
C	1.477040116533242	6.112577927977239	5.048928238820829
H	1.448431283340686	7.164794391784963	5.296981761624942
C	1.754154607709133	5.702677166933367	3.750775447792996
C	2.049983721129078	6.659664013284616	2.662883058389963
C	2.129051244420022	8.037115759044882	2.812810591858166
H	1.935662227403134	8.506701931237091	3.767099091899019
C	2.476252992996486	8.805827832468577	1.710148796553368
H	2.5449342543992	9.882661728339585	1.807156004764732
C	2.748665938191489	8.203943506496023	0.4939423097662431
H	3.037403955701237	8.802191498421584	-0.359980727423715
C	2.650202404084589	6.818392189101369	0.383185981689698
C	2.907702231492518	6.001972625585262	-0.8083341156949931
C	3.283665739952134	6.564979104443254	-2.030225256432773
H	3.404087883158646	7.638713890131042	-2.130490401517271
C	3.504650969097781	5.751709365126158	-3.130320619716742
H	3.796208119770915	6.188243817006398	-4.079196077033333
C	3.347473829868838	4.373779229037491	-3.006428600056408
H	3.516993329354464	3.733182366247404	-3.866871904657614
C	2.971779792900881	3.81282763597351	-1.789652177885765
H	2.851683051226654	2.734940417454103	-1.727611075708026
N	2.285182866867604	6.096851401873852	1.464485022116281
C	2.742637420268089	4.597892974512718	-0.6579120212647583
C	5.127653722448527	4.858103238307378	2.028395836074483
H	4.710424664937687	5.852886954709161	2.107931550800804
C	6.480631509796499	4.640979097531362	2.255918993667442

H	7.114802092969768	5.47796120104817	2.517459314022676
C	6.985734084574746	3.365426009272404	2.138414372306015
H	8.035032028371461	3.155369831296881	2.301120118286518
C	6.120730068410324	2.322926908495468	1.804486958599383
C	4.771127907263359	2.62284096479825	1.599602754775628
C	3.820055742447506	1.591061109374133	1.267267832826505
C	4.22999332661067	0.2589500691978912	1.158397077899038
C	3.26952000902472	-0.7075693519161139	0.8586206220602551
H	3.563865926623526	-1.745428771819826	0.7723419558967591
C	1.965398398757948	-0.3079178699662181	0.6761099466278151
H	1.185398721321261	-1.020643076233856	0.4410506722881631
C	1.638884397328304	1.038414481935269	0.7849986151877453
H	0.6290782995944495	1.382318261624068	0.6047074140344485
C	6.576968733180783	0.9471841297286105	1.663718006279023
C	5.634176368926958	-0.08022997942318122	1.352196273454986
C	8.249148611524809	-0.5948220251690907	1.695901839526384
C	7.306279804972078	-1.622911597512019	1.391584262394221
C	9.614547556774843	-0.9317132573716194	1.856428055359604
H	10.31731533097851	-0.1384800215639333	2.085046450717026
C	7.755868947243528	-2.958552368631796	1.260033847963872
H	7.026593180608407	-3.726911415185167	1.029700238823547
C	10.01614622861287	-2.229988417783146	1.720352534803011
H	11.06171968563456	-2.489021818798254	1.841961279045583
C	9.080273544330149	-3.250385729443859	1.421203623243585
H	9.425808677717248	-4.272656422173705	1.318664138046039
N	4.287210397020733	3.87892786683836	1.706014061715912
N	2.535554779066389	1.982877072538931	1.073817430920521
N	7.856757324171733	0.6829761813768269	1.830416525501984
N	6.004094576953108	-1.337954237613775	1.223900928674023
S	0.03294212178066588	4.118815112631885	0.6110552919649468
C	-0.4512430663298825	5.628930611365771	-0.2118839161095055
H	0.1518048323888075	5.714758945832227	-1.113127907510561
H	-0.2778594120502489	6.47788948326402	0.4475413199143135
H	-1.508249499794365	5.536949118298446	-0.4568694163490417
C	-1.108307008029155	4.187003552583933	1.985931606269184
H	-2.118672844100666	4.231498420461438	1.581160149860236
H	-0.8933748318344561	5.066190980280632	2.592092587527202
H	-0.9675086039918116	3.279766693655257	2.570745753682812
O	-0.454201383654823	3.006650454589574	-0.2663083509925832

Table S9. Nuclear coordinates (Å) of $[5]^+$ minimized at the DFT/PBE0/TZP/COSMO level in water.

Ru	2.225848252831929	4.087661898753039	1.251657018396513
N	1.763530708360145	4.417956647548603	3.402406215539751
C	1.531329453041901	3.517093817694045	4.357197888864984
H	1.57469985209412	2.477424110572406	4.054263910417902
C	1.243710301412094	3.864293275890017	5.666336136940187
H	1.060777366986573	3.091084127618009	6.401080157961451
C	1.194619321452045	5.208396551160556	5.997987836502104
H	0.9679005362791919	5.522000046917414	7.009767983880237
C	1.442856615209925	6.152737902661566	5.016242906071697
H	1.413350455622538	7.206857993363196	5.255495490352065
C	1.729687130871923	5.732040456585351	3.723648364396654
C	2.033954675684763	6.679923261366979	2.630220238391987
C	2.110014779314597	8.058639748075132	2.769298544016062
H	1.907989942937175	8.535734629898998	3.717951765898779
C	2.465642843778993	8.818453602081055	1.66312925900512
H	2.532107299720538	9.896009168234595	1.751508223046998

C	2.748538854382408	8.206774958823576	0.4541543069452232
H	3.04314296577244	8.798244982856311	-0.4023341479676421
C	2.653095430342739	6.820185842973233	0.3543127740333533
C	2.922553500139061	5.993693720014308	-0.8276574858976137
C	3.311254763853213	6.546305337095845	-2.050382277354367
H	3.432032397127352	7.619051778243849	-2.158762256772632
C	3.545167045056802	5.723407435194232	-3.140596065076643
H	3.846757601929235	6.151648792575731	-4.089930668908677
C	3.388434705523931	4.346379990847542	-3.006072740170111
H	3.568784301305081	3.698552996797905	-3.858666247929718
C	2.999618621649768	3.795758443239416	-1.788685725861543
H	2.880288834245543	2.718527962785568	-1.717676245077831
N	2.280026777444306	6.107317640549849	1.438655088672647
C	2.756957914254285	4.590808232290637	-0.6668359596947461
C	5.119984287890549	4.871524126283474	2.023857961763388
H	4.705655024944745	5.869171562837231	2.076019061162522
C	6.469127506247939	4.654864688972893	2.268534187434693
H	7.104573868694214	5.494778178345644	2.516637884265593
C	6.969778544923758	3.374229821137814	2.185119760002403
H	8.016279890998403	3.163420503221915	2.363395355469732
C	6.104213613721433	2.328519406073787	1.866177018777589
C	4.758474425530714	2.628599776882763	1.640515033405461
C	3.804594431751447	1.59313961694121	1.317262133037847
C	4.205590754054427	0.2564322003839285	1.244718420783696
C	3.242998794711123	-0.7093584804234285	0.9533553673488446
H	3.531409767234102	-1.750697550666	0.8948084093306008
C	1.943732968238333	-0.3054032631293137	0.7429220352035721
H	1.162551525943034	-1.018043742641236	0.5123763660743661
C	1.625902985117522	1.0443643748689	0.8171355486156872
H	0.6216743876086822	1.392166820004464	0.6155994442550818
C	6.559805035043621	0.9468485972991426	1.762785047364061
C	5.606010287483906	-0.09160675394325946	1.464637653647827
C	8.223169403084599	-0.6071097956760023	1.851567577833137
C	7.27120351988527	-1.643548532603713	1.565257985732064
C	9.565435351498941	-0.9348302836928243	2.034021253634718
H	10.27256257052414	-0.1411658781892709	2.248781656356447
C	7.699512508956356	-2.966729475331125	1.475246762236336
H	6.969365833679626	-3.738738571941945	1.258516235740963
C	9.993862615667556	-2.254358177956161	1.941148415336051
C	11.36178318641884	-2.612138196701385	2.120353965105711
C	9.038595900677675	-3.294233614078035	1.656236564871987
C	9.499124291044016	-4.639789023923686	1.564598830082601
N	4.278562004891853	3.887620464425434	1.715497076675683
N	2.526535945177413	1.988905233609816	1.097886148059817
N	7.828335087133643	0.684861765827077	1.948036724401624
N	5.96349552646971	-1.347044462546467	1.374693289398288
S	0.03542990536666932	4.124272674099972	0.57928857162859
C	-0.4449029787896993	5.633869490009357	-0.2467112997603526
H	0.1672728626838114	5.72296507882489	-1.141421443261288
H	-0.2815149826388723	6.48243934689803	0.4156880621869872
H	-1.498752943656293	5.539334345405199	-0.5041864632922269
C	-1.119221057333176	4.187986893365191	1.942839969509047
H	-2.12614206220284	4.227671989058448	1.529153499257443
H	-0.9130472251694087	5.067803003407596	2.550892892299282
H	-0.9803712037725043	3.281354801176515	2.528946487461564
O	-0.4389868011736154	3.011350140038378	-0.303321559661705
C	10.81522152868249	-4.937343446537255	1.742288558015232

C	11.75857894400404	-3.910504498232734	2.023526368588769
H	8.777079216219215	-5.420431626323957	1.350402622346344
H	11.15482581806377	-5.964478183525976	1.669458974915277
H	12.8017974874205	-4.172120764574426	2.161292541695308
H	12.0790926291452	-1.827021817302171	2.334466787143834

Chiral HPLC trace of [11-C]HCO_2 and [11-A]HCO_2

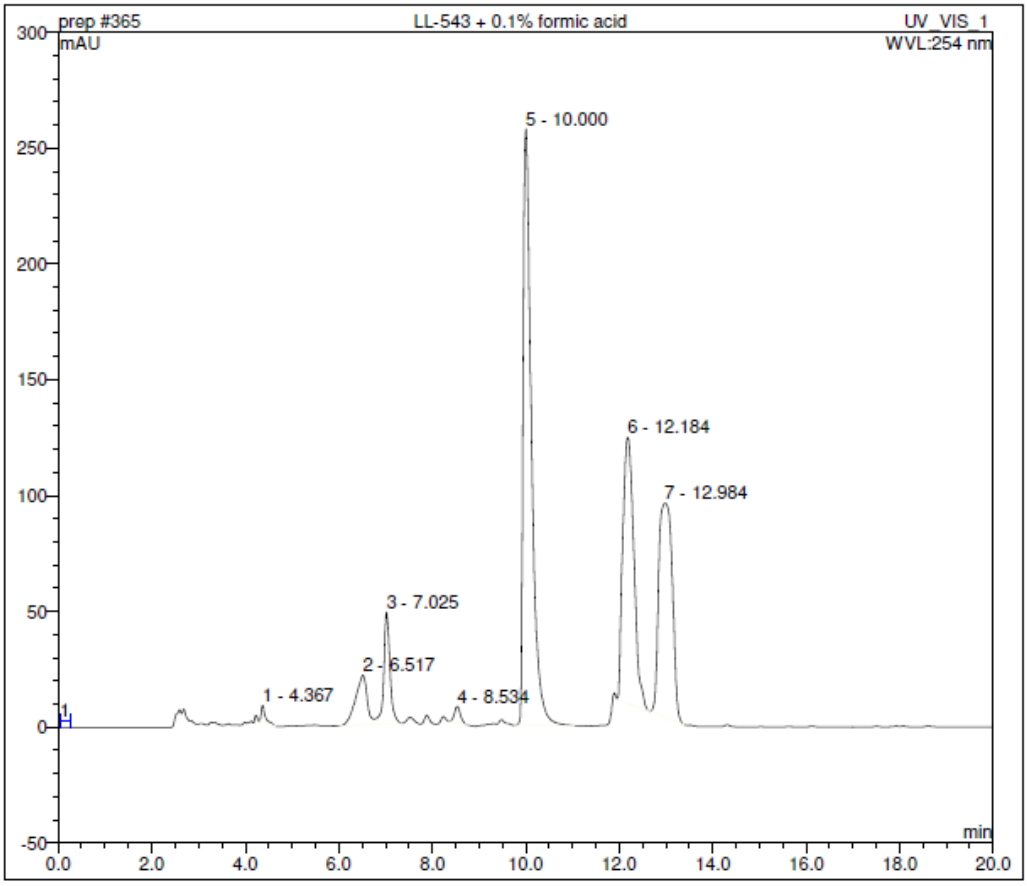


Figure S7. HPLC trace of [**11-C**]PF_6 (6, R_f = 12.184 min) and [**11-A**]PF_6 (7, R_f = 12.984 min).

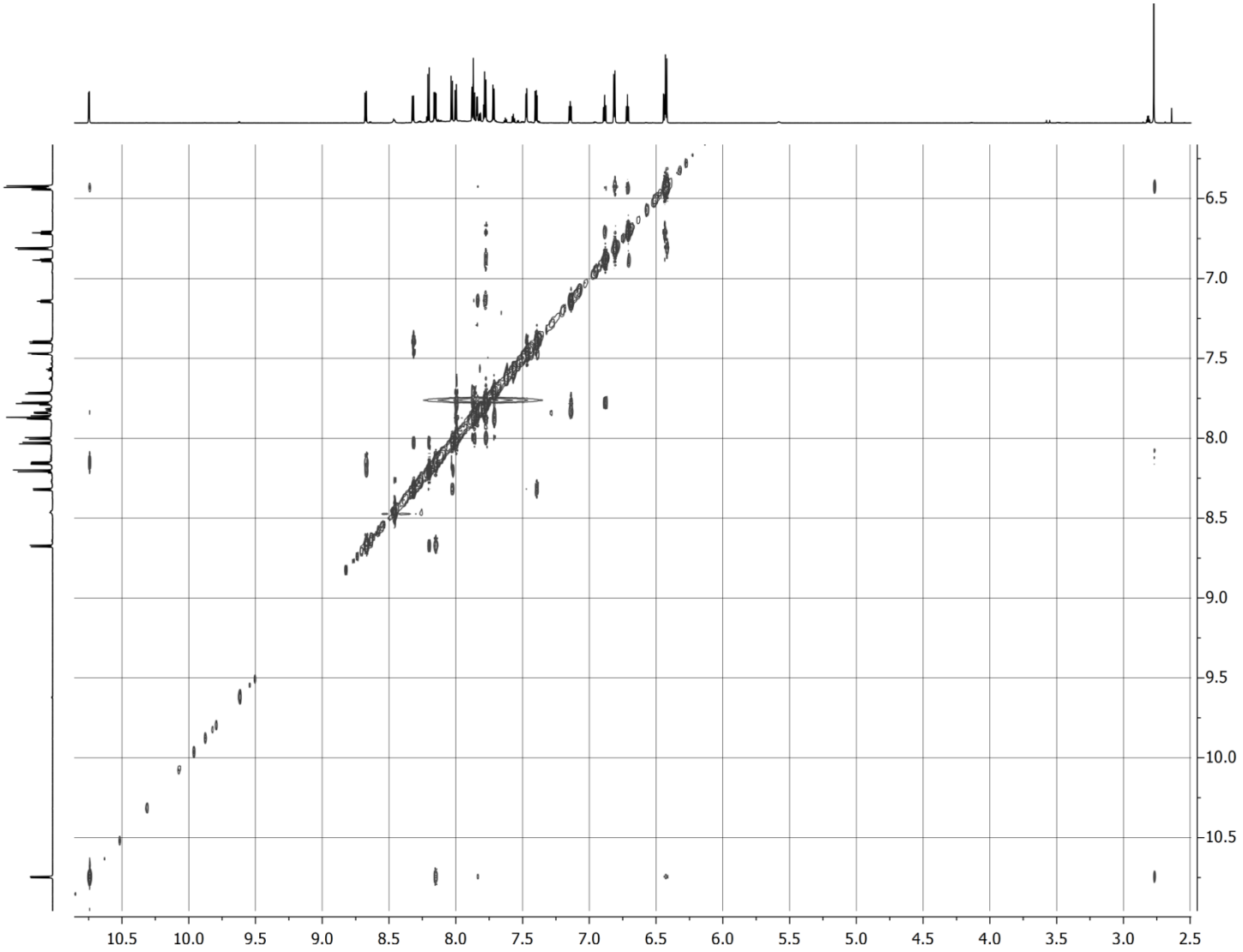


Figure S8. NOESY of [**11-A**]HCO_2 measured in CD_3CN

References

1. van der Tol, E. B.; van Ramesdonk, H. J.; Verhoeven, J. W.; Steemers, F. J.; Kerver, E. G.; Verboom, W.; Reinhoudt, D. N., Tetraazatriphenylenes as extremely efficient antenna chromophores for luminescent lanthanide ions. *Chem. Eur. J.* **1998,** *4* (11), 2315-2323.
2. Molphy, Z.; Prisecaru, A.; Slator, C.; Barron, N.; McCann, M.; Colleran, J.; Chandran, D.; Gathergood, N.; Kellett, A., Copper phenanthrene oxidative chemical nucleases. *Inorg. Chem.* **2014,** *53* (10), 5392-404.
3. Constable, E. C.; Henney, R. P.; Leese, T. A.; Tocher, D. A., Cyclometallation reactions of 6-phenyl-2, 2′-bipyridine; a potential C, N, N-donor analogue of 2, 2′: 6′, 2 ″-terpyridine. Crystal and molecular structure of dichlorobis (6-phenyl-2, 2′-bipyridine) ruthenium (II). *Dalton Trans.* **1990,** (2), 443-449.
4. Bode, M. L.; Gates, P. J.; Gebretnsae, S. Y.; Vleggaar, R., Structure elucidation and stereoselective total synthesis of pavettamine, the causal agent of gousiekte. *Tetrahedron* **2010,** *66* (11), 2026-2036.
5. Evans, I. P.; Spencer, A.; G, W., Dichlorotetrakis(Dimethyl Sulphoxide)Ruthenium(Ii) and Its Use as a Source Material for Some New Ruthenium(Ii) Complexes. *Dalton Trans.* **1973,** (2), 204-209.
6. Bahreman, A.; Cuello-Garibo, J. A.; Bonnet, S., Yellow-light sensitization of a ligand photosubstitution reaction in a ruthenium polypyridyl complex covalently bound to a rhodamine dye. *Dalton Trans.* **2014,** *43* (11), 4494-505.
7. Lameijer, L. N.; Hopkins, S. L.; Breve, T. G.; Askes, S. H.; Bonnet, S., d- Versus l-Glucose Conjugation: Mitochondrial Targeting of a Light-Activated Dual-Mode-of-Action Ruthenium-Based Anticancer Prodrug. *Chem. Eur. J.* **2016,** *22* (51), 18484-18491.