

Supplementary Material

for

Antimicrobial properties of mono- and di- *fac*-rhenium tricarbonyl 2-pyridyl-1,2,3-triazole complexes

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1. General experimental

Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. A CEM S-class microwave reactor was used to carry out microwave enhanced reactions. ^1H and ^{13}C NMR were recorded on either a 400 MHz Varian MR or 500 MHz Varian AR spectrometer at 298 K. Chemical shifts (δ) are reported in parts per million (ppm) and referenced to residual solvent peaks (CDCl_3 : ^1H δ 7.26, ^{13}C δ 77.16 ppm; d_6 -DMSO: ^1H δ 2.50 ppm, ^{13}C δ 39.50 ppm). Coupling constants (J) are reported in Hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: m = multiplet, q = quartet, p = pentet, ddd = doublet of doublet of doublets, dt = doublet of triplet, dd = doublet of doublet, t = triplet, d = doublet, s = singlet. IR spectra were recorded on a Bruker ALPHA FT-IR spectrometer with an attached ALPHA-P measurement module. Microanalyses were performed at the Campbell Microanalytical Laboratory, University of Otago. High resolution electrospray mass spectra (HR-ESMS) were collected on a Bruker micrOTOF-Q spectrometer. UV-visible absorption spectra were acquired with a Perkin Elmer Lambda-950 spectrophotometer in DMF (10^{-5} M concentrations). Melting points were determined using a Leica VMHB melting bar. Bidentate 2-pyridyl-1,2,3-triazole ligands (**5a** and **5b**),¹ di-(2-pyridyl-1,2,3-triazole) ligands (**6a** and **6b**)² and rhenium complexes (**7a_{Cl}** and **7b_{Cl}**)³ were prepared by previously reported procedures.

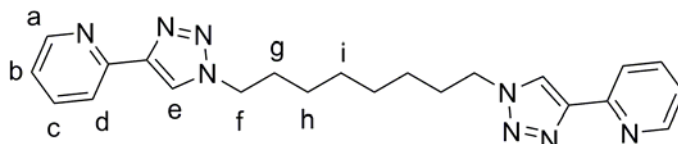
Safety Note: Whilst no problems were encountered during the course of this work, azide compounds are potentially explosive and appropriate precautions should be taken when working with them.

2. General procedure for the synthesis of the ligands

A dibromoalkane (1 eq.) and sodium azide (3 eq.) were dissolved in 4:1 DMF/ H_2O (15 mL). The mixture was irradiated in a CEM microwave reactor at 125 °C (200 W, 200 PSI) for three hours. The reaction mixture was then cooled to room temperature and 2-ethynyl pyridine (2 eq.), sodium ascorbate (0.5 eq.), and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.4 eq.) were added to the reaction mixture. The mixture was stirred for 12 hours. The suspension was partitioned between

aqueous 0.1 M NH₄OH/EDTA (100 mL) and CH₂Cl₂ (100 mL) and the layers were separated. The organic phase was washed with water (100 mL) and brine (100 mL), dried over MgSO₄ and the solvent was removed under reduced pressure to obtain the ligand as an off-white solid.

2.1 Synthesis of 1,8-bis{4-(2-pyridyl)-1H-1,2,3-triazol-1-yl}octane (**6c**)



The ligand was prepared by the general procedure described above. 1,8-Dibromooctane (0.528 g, 1.90 mmol, 1 eq.), sodium azide (0.378 g, 5.82 mmol, 3 eq.), 2-ethynylpyridine (0.400 g, 3.88 mmol, 2 eq.), sodium ascorbate (0.192 g, 0.97 mmol, 0.5 eq.) and CuSO₄·5H₂O (0.194 g, 0.77 mmol, 0.4 eq.) were used in the reaction. The product (**6c**) was obtained as an off-white solid after recrystallization from acetonitrile and diisopropyl ether. Yield: 0.670 g, 85%. Mp 158-160 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.58 (d, *J* = 4.9 Hz, 2H, H_a), 8.24-8.15 (m, H_d and H_e), 7.79 (t, *J* = 7.8 Hz, 2H, H_c), 7.26-7.19 (m, 2H, H_b), 4.41 (t, *J* = 7.1 Hz, 4H, H_f), 1.96-1.83 (m, 4H, H_g), 1.33-1.25 (m, 8H, H_h and H_i). ¹³C NMR (100 MHz, CDCl₃) δ 150.52, 149.50, 148.53, 137.02, 122.93, 121.89, 120.34, 50.54, 30.27, 28.85, 26.42. ATR-IR: ν (cm⁻¹) 3128, 2926, 2849, 1604, 1595, 1568, 1545, 1415, 1257, 1230, 1190, 1135, 1091, 1075, 1049, 1037, 996, 978, 846, 784, 756, 744. HR-ESMS (DMF) *m/z* = 425.2176 [**6c**+Na]⁺ (calc. for C₂₂H₂₆N₈Na⁺ 425.2173). Anal. calcd. for C₂₂H₂₆N₈: C 65.65, H 6.51, N 27.84%; found: C 65.55, H 6.40, N 27.93%.

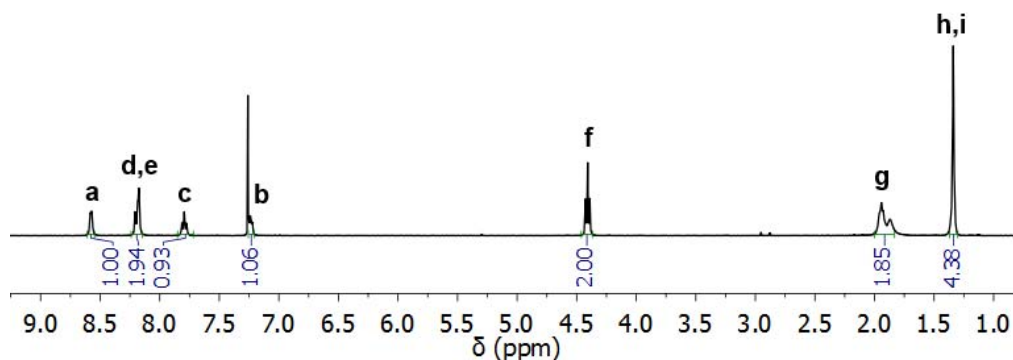
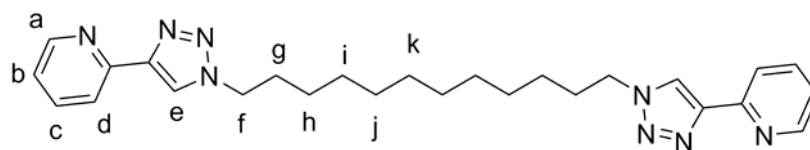


Figure S1: ¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **6c**.

2.2 Synthesis of 1,12-bis{4-(2-pyridyl)-1H-1,2,3-triazol-1-yl}dodecane (6d)



The ligand was prepared by the general procedure describe above. 1,12-Dibromodecane (0.398 g, 1.20 mmol, 1 eq.), sodium azide (0.236 g, 3.60 mmol, 3 eq.), 2-ethynylpyridine (0.250 g, 2.40 mmol, 2 eq.), sodium ascorbate (0.120 g, 0.60 mmol, 0.5 eq.) and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.121 g, 0.48 mmol, 0.4 eq.) were used in the reaction. The product (**6d**) was obtained as an off-white solid after recrystallization from dichloromethane and diisopropyl ether. Yield: 0.440 g, 79%. Mp 168-170 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.58 (d, $J = 4.6$ Hz, 2H, H_a), 8.23-8.14 (m, 4H, H_d and H_e), 7.79 (t, $J = 7.7$ Hz, 2H, H_c), 7.24 (dd, $J = 7.5, 4.9$ Hz, 2H, H_b), 4.41 (t, $J = 7.2$ Hz, 4H, H_f), 1.94 (p, $J = 7.2$ Hz, 4H, H_g), 1.38-1.18 (m, 16H, H_h - H_k). ^{13}C NMR (100 MHz, CDCl_3) δ 150.88, 149.81, 148.80, 137.35, 123.23, 122.19, 120.66, 50.96, 30.67, 29.82, 29.73, 29.40, 26.88. ATR-IR: ν (cm^{-1}) 3129, 2978, 1599, 1568, 1547, 1416, 1319, 1225, 1188, 1137, 1077, 1045, 996, 895, 847, 785, 745. HR-ESMS (CH_2Cl_2) $m/z = 481.2788$ [**6d**+ Na] $^+$ (calc. for $\text{C}_{26}\text{H}_{34}\text{N}_8\text{Na}^+$ 481.2799). Anal. calcd. for $\text{C}_{26}\text{H}_{34}\text{N}_8$: C 68.09, H 7.47, N 24.43%; found: C 68.00, H 7.61, N, 24.36%.

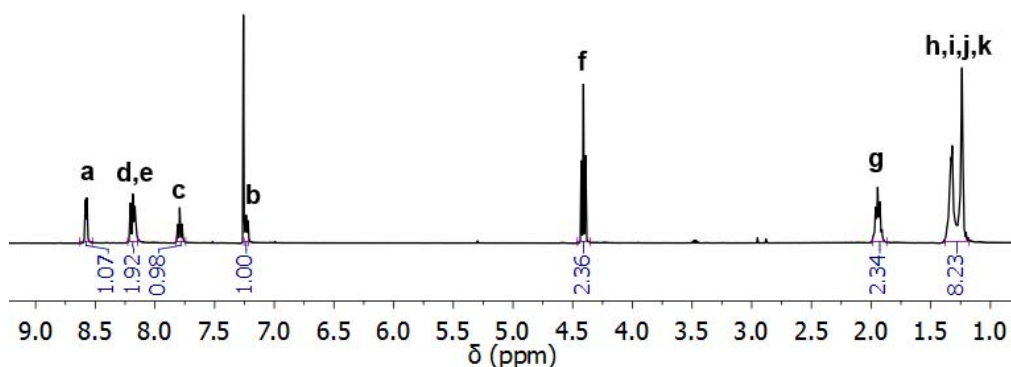
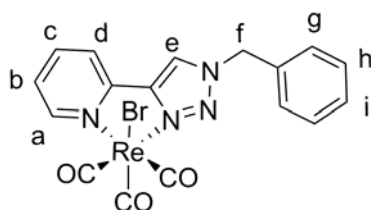


Figure S2: ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of **6d**.

3 General procedure for the synthesis of the neutral rhenium(I) complexes

Either pentacarbonylrhenium(I) chloride or pentacarbonylrhenium(I) bromide (1.0 eq./2.0 eq.) and a 2-pyridyl-1,2,3-triazole or a di-(2-pyridyl-1,2,3-triazole) ligand (1.0 eq.) were dissolved in ethanol (15 mL). The resultant mixture was refluxed at 78 °C for 24 hours in the absence of light. The suspension was cooled to room temperature and the solvent volume was reduced by half using rotary evaporation. Addition of diethyl ether led to the precipitation of the rhenium(I) complexes as yellow solids, which were collected by filtration and washed with diethyl ether and petroleum ether and vacuum dried.

3.1 Synthesis of **7a_{Br}**



The complex was prepared by the general procedure described above. Pentacarbonylrhenium(I) bromide (0.250 g, 0.616 mmol, 1.0 eq.) and **5a** (0.145 g, 0.616 mmol, 1.0 eq.) were used in the reaction. Crystals suitable for X-ray crystallographic analysis were obtained by vapour diffusion of diisopropyl ether into an acetonitrile solution of the complex. Yield: 0.359 g, 99%. Mp > 230 °C. ^1H NMR (400 MHz, d_6 -DMSO) δ 9.29 (s, 1H, H_e), 9.00-8.95 (m, 1H, H_a), 8.32 (d, $J = 7.8$ Hz, 1H, H_d), 8.26 (td, $J = 7.8, 1.4$ Hz, 1H, H_c), 7.36 (ddd, $J = 7.3, 5.5, 1.5$ Hz, 1H, H_b), 7.49-7.40 (m, 5H, H_g-H_i), 5.92 (s, 2H, H_f). ^{13}C NMR (100 MHz, d_6 -DMSO) δ 197.08, 196.30, 188.91, 153.16, 148.62, 148.50, 140.54, 134.12, 129.10, 128.88, 128.50, 126.44, 125.96, 122.77, 54.77. ATR-IR: ν (cm^{-1}) 3083, 2024, 1886, 1867, 1615, 1571, 1458, 1341, 1263, 1120, 1051, 997, 852, 784, 685, 643, 531, 485. HR-ESMS (DMF) $m/z = 608.9532$ [**7a_{Br}**+Na]⁺ (calc. for C₁₇H₁₂BrN₄O₃Re⁺ 608.9543). UV-vis (DMF) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{L mol}^{-1} \text{cm}^{-1}$): 330 (0.4×10^4), 290 (1.1×10^4), 275 (1.5×10^4). Anal. calcd. for C₁₇H₁₂BrN₄O₃Re: C 34.82, H 2.06, N 9.55%; found: C 35.08, H 2.05, N 9.58%.

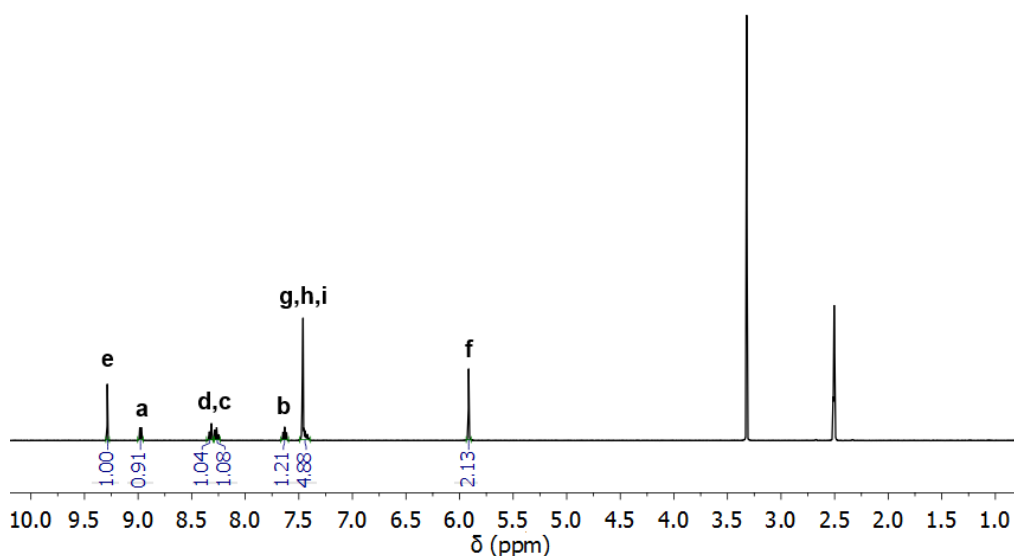
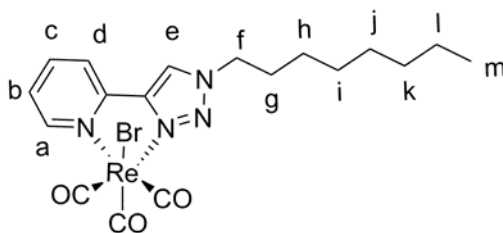


Figure S3: ^1H NMR spectra (400 MHz, d_6 -DMSO, 298 K) of rhenium complex **7a_{Br}**.

3.2 Synthesis of **7b_{Br}**



The complex was prepared by the general procedure described above. Pentacarbonylrhenium(I) bromide (0.157 g, 0.387 mmol, 1.0 eq.) and **5b** (0.100 g, 0.387 mmol, 1.0 eq.) were used in the reaction. Yield: 0.224 g, 94%. Mp 148-150 °C. ^1H NMR (400 MHz, d_6 -DMSO) δ 9.29 (s, 1H, H_e), 8.98 (d, J = 5.5 Hz, 1H, H_a), 8.30-8.26 (m, 2H, H_d and H_c), 7.63 (td, J = 5.4, 3.5 Hz, 1H, H_b), 4.62 (t, J = 7.2 Hz, 2H, H_f), 1.93 (p, 2H, J = 7.1 Hz, H_g), 1.34-1.19 (m, 10H, H_h-H_l), 0.90-0.77 (m, 3H, H_m). ^{13}C NMR (100 MHz, d_6 -DMSO) δ 197.15, 196.31, 188.95, 153.20, 148.75, 148.15, 140.53, 126.36, 125.71, 122.56, 51.57, 31.09, 29.08, 28.43, 28.19, 25.56, 22.04, 13.93. ATR-IR: ν (cm^{-1}) 3095, 2956, 2923, 2856, 2021, 1920, 1885, 1618, 1456, 1371, 1270, 1243, 1114, 1052, 868, 787, 630, 533, 486. HR-ESMS (DMF) m/z = 529.1235 [**7b_{Br}**-Br]⁺ (calc. for C₁₈H₂₂N₄O₃Re 529.1244). UV-vis (DMF) λ_{max} /nm ($\epsilon/\text{L mol}^{-1} \text{cm}^{-1}$): 330 (0.2×10^4), 290 (0.6×10^4), 275 (0.8×10^4). Anal. calcd. for C₁₈H₂₂BrN₄O₃Re•0.5H₂O: C 35.01, H 3.75, N 9.07%; found: C 34.77, H 3.39, N 9.07%.

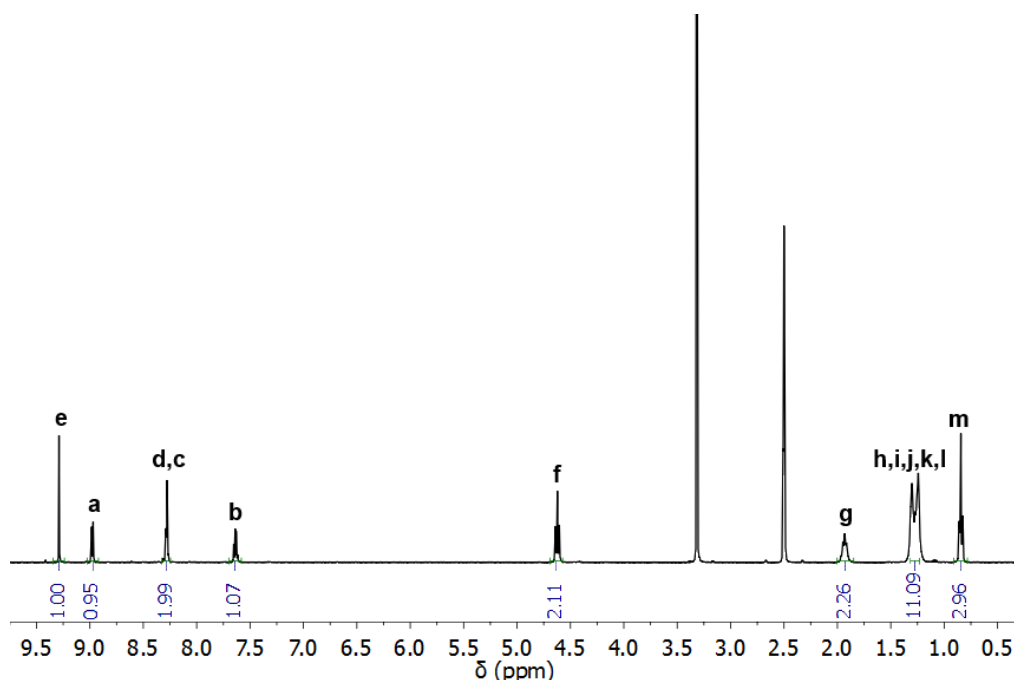
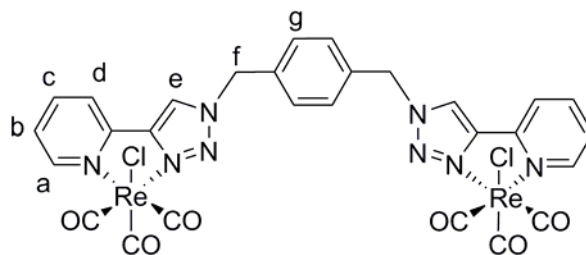


Figure S4: ^1H NMR spectra (400 MHz, d_6 -DMSO, 298 K) of rhenium complex **7b_{Br}**.

3.3 Synthesis of **8a_{Cl}**



The complex was prepared by the general procedure described above. Pentacarbonylrhenium(I) chloride (0.183 g, 0.507 mmol, 2.0 eq.) and **6a** (0.100 g, 0.254 mmol, 1.0 eq.) were used in the reaction. Crystals suitable for X-ray crystallographic analysis were obtained by vapour diffusion of diethyl ether into dimethylformamide solution of the complex. Yield: 0.230 g, 90%. Mp > 230 °C. ^1H NMR (500 MHz, d_6 -DMSO) δ 9.29 (s, 2H, H_e), 8.99-8.89 (m, 2H, H_a), 8.34-8.17 (m, 4H, H_d and H_c), 7.66-7.59 (m, 2H, H_b), 7.54 (s, 4H, H_g), 5.93 (s, 4H, H_f). ^{13}C NMR (125 MHz, d_6 -DMSO) δ 197.37, 196.54, 189.30, 152.80, 148.42, 148.37, 140.44, 134.67, 129.09, 126.32, 125.91, 122.60, 54.13. ATR-IR: ν (cm^{-1}) 3120, 3029, 2936, 2021, 1892, 1859, 1616, 1581, 1467, 1454, 1422, 782, 483. HR-ESMS (DMF) m/z = 971.0151 [**8a_{Cl}**-Cl]⁺ (calc. for C₂₈H₁₈ClN₈O₆Re₂⁺ 971.0144). UV-vis (DMF) λ_{max} /nm ($\epsilon/\text{L mol}^{-1} \text{cm}^{-1}$): 330 (0.4×10^4), 290 (1.1×10^4), 275 (1.3×10^4). Anal. calcd. for C₂₈H₁₈Cl₂N₈O₆Re₂: C 33.44, H 1.80, N 11.14%; found: C 33.82, H 1.91, N 11.17%.

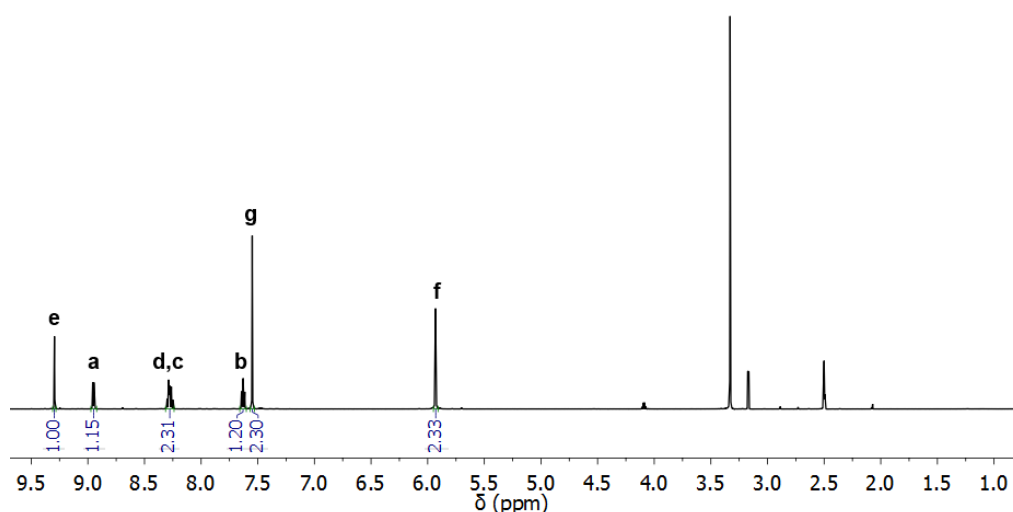
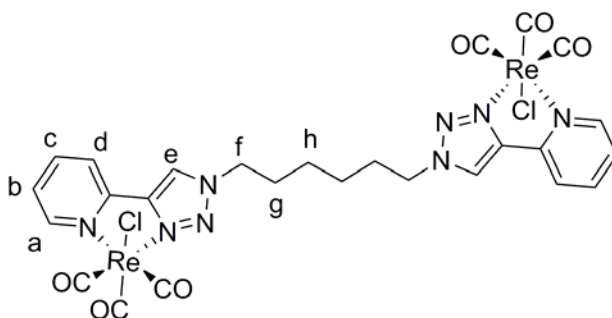


Figure S5: ^1H NMR spectrum (500 MHz, d_6 -DMSO, 298 K) of rhenium complex **8a_{Cl}**.

3.4 Synthesis of **8b_{Cl}**



The complex was prepared by the general procedure described above. Pentacarbonylrhenium(I) chloride (0.150 g, 0.415 mmol, 2.0 eq.) and **6b** (0.078 g, 0.207 mmol, 1.0 eq.) were used in the reaction. Yield: 0.178 g, 86%. Mp > 230 °C. ¹H NMR (500 MHz, *d*₆-DMSO) δ 9.26 (s, 2H, H_e), 8.95 (dd, *J* = 5.5, 1.3 Hz, 2H, H_a), 8.34-8.20 (m, 4H, H_d and H_c), 7.63 (ddd, *J* = 7.3, 5.5, 1.8 Hz, 2H, H_b), 4.62 (t, *J* = 7.3 Hz, 4H, H_f), 2.00-1.92 (m, 4H, H_g), 1.44-1.36 (m, 4H, H_h). ¹³C NMR (125 MHz, *d*₆-DMSO) δ 197.60, 196.75, 189.55, 153.00, 148.72, 148.15, 140.64, 126.41, 125.69, 122.54, 51.46, 28.80, 24.99. ATR-IR: *ν* (cm⁻¹) 3138, 2938, 2022, 1894, 1652, 1617, 1580, 1456, 1426, 784, 479. HR-ESMS (DMF) *m/z* = 951.0420 [**8b_{Cl}**-Cl]⁺ (calc. for C₂₆H₂₂ClN₈O₆Re₂⁺ 951.0456). UV-vis (DMF) λ_{max}/nm (ε/L mol⁻¹ cm⁻¹): 330 (0.7 × 10⁴), 290 (1.7 × 10⁴), 275 (2.3 × 10⁴). Anal. calcd. for C₂₆H₂₂Cl₂N₈O₆Re₂: C 31.68, H 2.25, N 11.37%; found: C 31.84, H 2.33, N 11.28%.

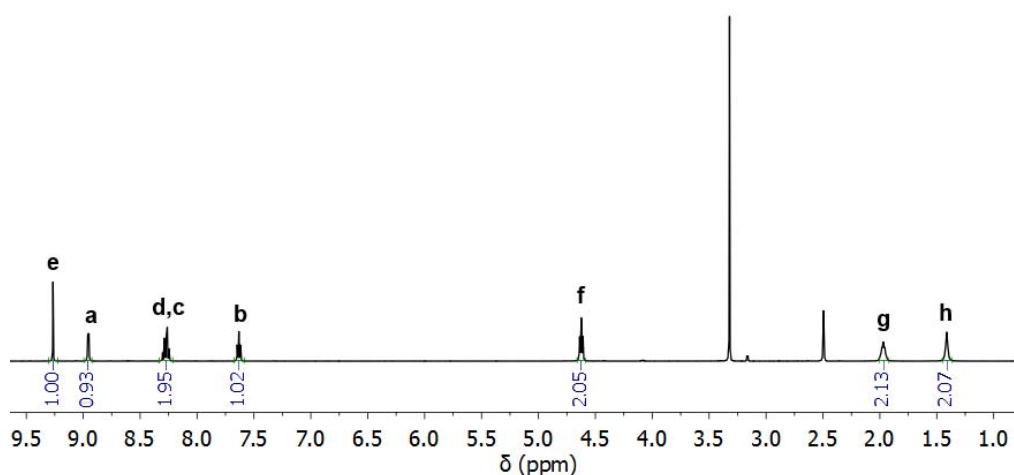
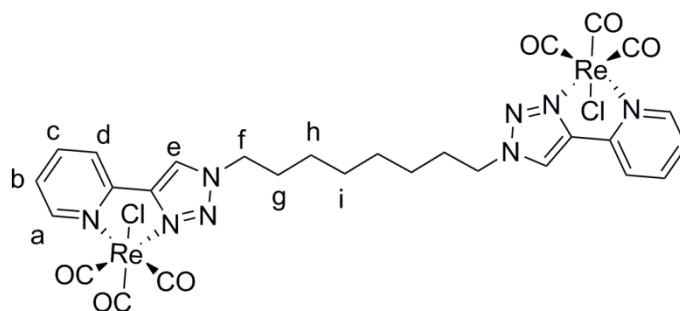


Figure S6: ¹H NMR spectra (500 MHz, *d*₆-DMSO, 298 K) of rhenium complex **8b_{Cl}**.

3.5 Synthesis of **8**_{Cl}



The complex was prepared by the general procedure described above. Pentacarbonylrhenium(I) chloride (0.180 g, 0.497 mmol, 2.0 eq.) and **6c** (0.100 g, 0.248 mmol) were used in the reaction. Yield: 0.210 g, 83%. Mp > 230 °C. ¹H NMR (400 MHz, *d*₆-DMSO) δ 9.25 (s, 2H, H_e), 8.95 (d, *J* = 5.3 Hz, 2H, H_a), 8.32-8.23 (m, 4H, H_d and H_c), 7.63 (ddd, *J* = 7.3, 5.6, 2.2 Hz, 2H, H_b), 4.60 (t, *J* = 7.2 Hz, 4H, H_f), 1.94 (p, *J* = 6.9 Hz, 4H, H_g), 1.32-1.25 (m, 8H, H_h and H_i). ¹³C NMR (100 MHz, *d*₆-DMSO) δ 197.84, 196.99, 189.78, 153.23, 148.95, 148.37, 140.87, 126.64, 125.88, 122.76, 51.76, 29.24, 28.24, 25.72. ATR-IR: ν (cm⁻¹) 3128, 2921, 2024, 1983, 1978, 1652, 1615, 1580, 1467, 1453, 1427, 1363, 1331, 1272, 1156, 1094, 998, 974, 894, 781, 754, 492. HR-ESMS (DMF) *m/z* = 979.0707 [**8**_{Cl}-Cl]⁺ (calc. for C₂₈H₂₆ClN₈O₆Re₂⁺ 979.0770). UV-vis (DMF) λ_{max} /nm (ϵ /L mol⁻¹ cm⁻¹): 330 (0.7 × 10⁴), 290 (2.0 × 10⁴), 275 (2.4 × 10⁴). Anal. calcd. for C₂₈H₂₆Cl₂N₈O₆Re₂: C 33.17, H 2.58, N 11.05%; found: C 33.30, H 2.78, N 11.01%.

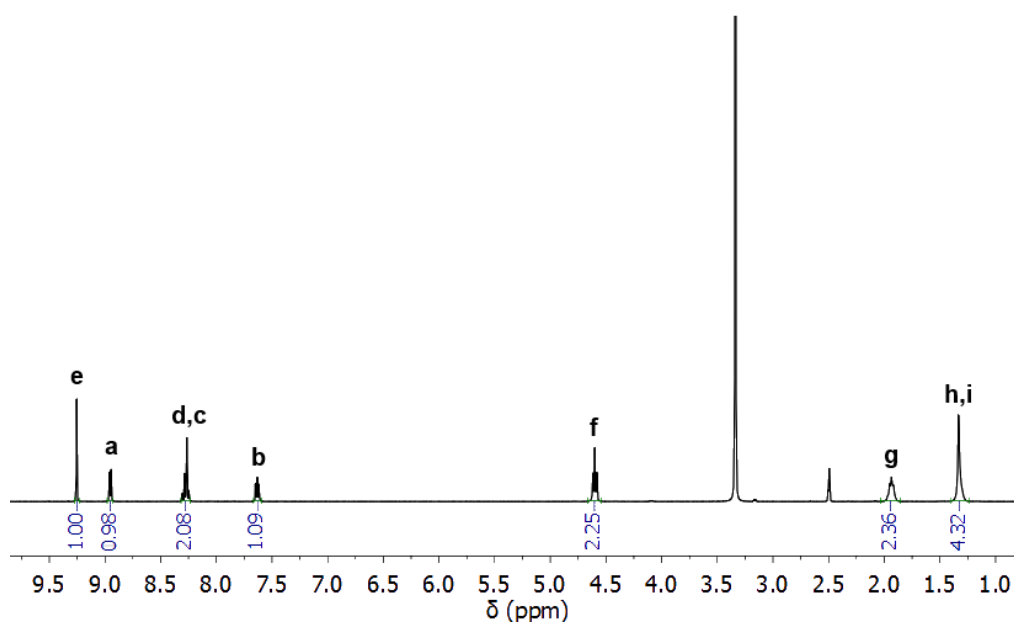
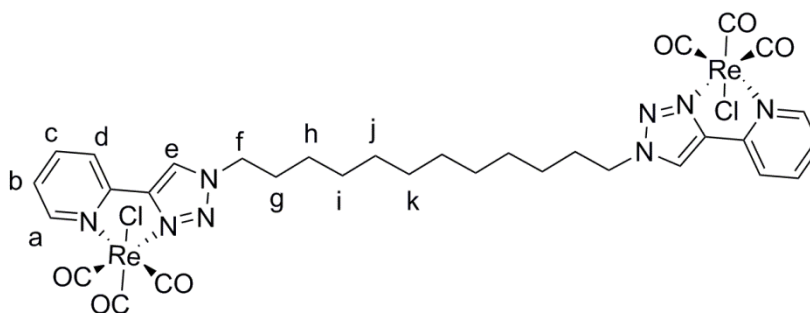


Figure S7: ¹H NMR spectra (400 MHz, *d*₆-DMSO, 298 K) of rhenium complex **8**_{Cl}.

3.6 Synthesis of **8d_{Cl}**



The complex was prepared by the general procedure described above. Pentacarbonylrhenium(I) chloride (0.100 g, 0.276 mmol, 2.0 eq.) and **6d** (0.064 g, 0.138 mmol, 1.0 eq.) were used in the reaction. Yield: 0.130 g, 87%. Mp > 190 °C. ^1H NMR (400 MHz, d_6 -DMSO) δ 9.27 (s, 2H, H_e), 8.96 (d, J = 5.4 Hz, 2H, H_a), 8.29-8.21 (m, 4H, H_d and H_c), 7.64 (ddd, J = 7.3, 5.6, 2.1 Hz, 2H, H_b), 4.61 (t, J = 7.2 Hz, 4H, H_f), 1.97-1.86 (m, 4H, H_g), 1.35-1.17 (m, 16H, H_h-H_k). ^{13}C NMR (100 MHz, d_6 -DMSO) δ 198.06, 197.18, 189.97, 153.43, 149.15, 148.56, 141.07, 126.83, 126.10, 122.96, 51.98, 29.46, 29.24, 29.17, 28.66, 26.01. ATR-IR: ν (cm^{-1}) 3300, 3087, 2925, 2853, 2022, 1908, 1887, 1618, 1582, 1456, 1432, 1371, 1269, 1160, 1130, 1100, 1054, 998, 895, 781, 488. HR-ESMS (DMF) m/z = 1035.1404 [**8d_{Cl}**-Cl]⁺ (calc. for C₃₂H₃₄ClN₈O₆Re₂⁺ 1035.1396). UV-vis (DMF) λ_{max} /nm ($\epsilon/\text{L mol}^{-1} \text{cm}^{-1}$): 330 (0.9×10^4), 290 (2.5×10^4), 275 (3.0×10^4). Anal. calcd. for C₃₂H₃₄Cl₂N₈O₆Re₂•H₂O: C 35.33, H 3.34, N 10.30%; found: C 35.09, H 3.24, N, 10.20%.

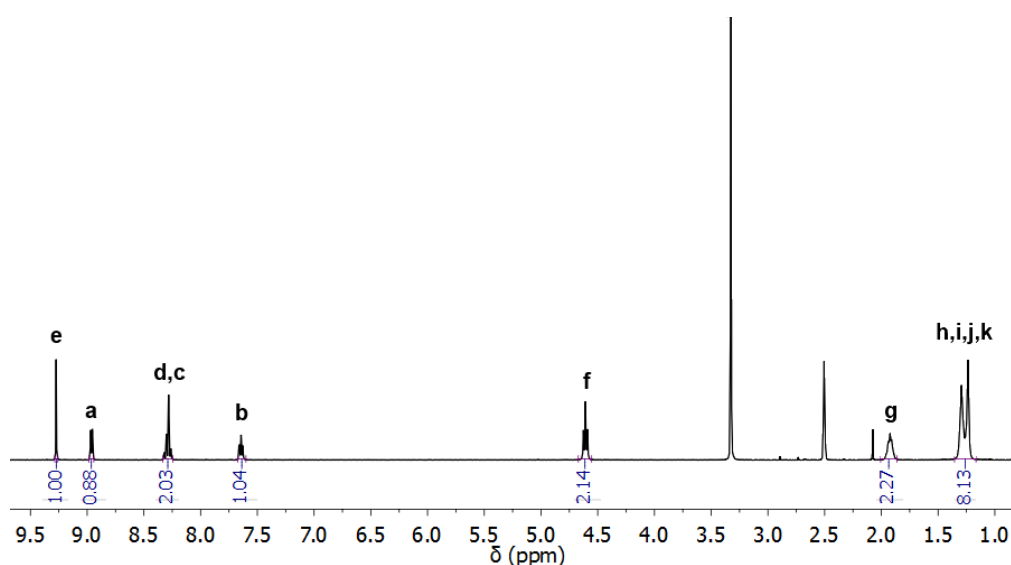
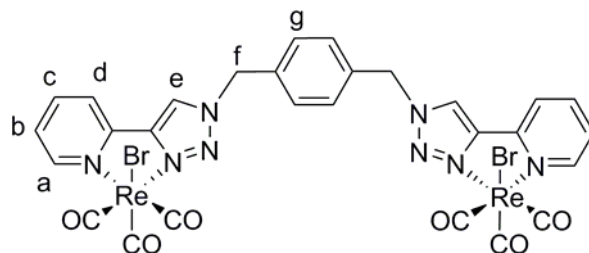


Figure S8: ^1H NMR spectra (400 MHz, d_6 -DMSO, 298 K) of rhenium complex **8d_{Cl}**.

3.7 Synthesis of **8a_{Br}**



The complex was prepared by the general procedure described above. Pentacarbonylrhenium(I) bromide (0.124 g, 0.304 mmol, 2.0 eq.) and **6a** (0.060 g, 0.152 mmol, 1.0 eq.) were used in the reaction. Yield: 0.141 g, 85%. Mp > 230 °C. ¹H NMR (400 MHz, *d*₆-DMSO) δ 9.30 (s, 2H, H_e), 8.97 (d, *J* = 5.5 Hz, 2H, H_a), 8.32-8.21 (m, 4H, H_d and H_c), 7.62 (ddd, *J* = 7.4, 5.4, 1.7 Hz, 2H, H_b), 7.53 (s, 4H, H_g), 5.94 (s, 4H, H_f). ¹³C NMR (100 MHz, *d*₆-DMSO) δ 197.06, 196.29, 188.89, 153.15, 148.59, 148.55, 140.55, 134.86, 129.15, 126.46, 126.11, 122.77, 54.29. ATR-IR: *ν* (cm⁻¹) 3108, 2927, 2852, 2021, 1887, 1616, 1582, 1455, 1454, 1423, 1271, 1122, 1052, 782, 752, 643, 533, 483. HR-ESMS (DMSO) *m/z* = 1014.9601 [**8a_{Br}**-Br]⁺ (calc. for C₂₈H₁₈BrN₈O₆Re₂⁺ 1014.9600). UV-vis (DMF) λ_{max}/nm (ε/L mol⁻¹ cm⁻¹): 330 (0.5 × 10⁴), 290 (1.8 × 10⁴), 275 (2.3 × 10⁴). Anal. calcd. for C₂₈H₁₈Br₂N₈O₆Re₂•0.5(CH₃CH₂OH): C 31.16, H 1.89, N 10.02%; found: C 31.55, H 1.61, N 10.38%.

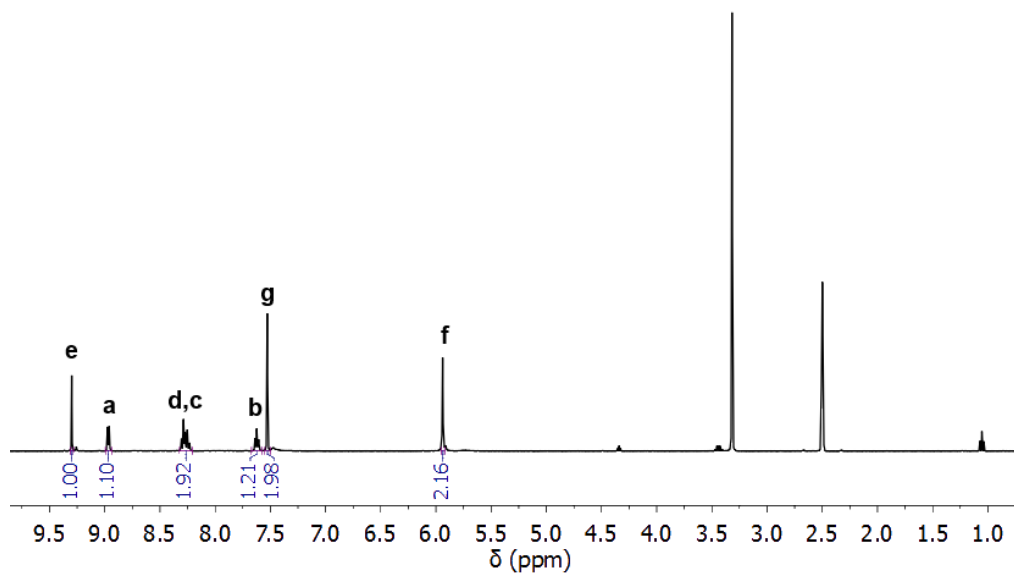
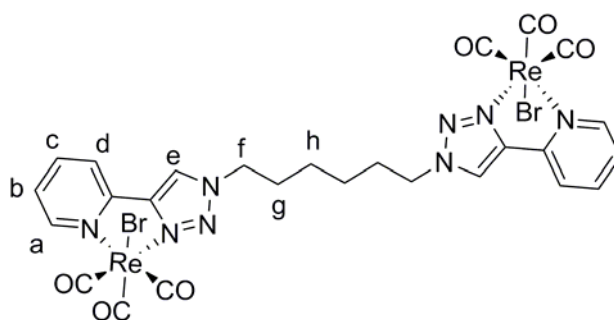


Figure S9: ¹H NMR spectra (400 MHz, *d*₆-DMSO, 298 K) of rhenium complex **8a_{Br}**.

3.8 Synthesis of **8b_{Br}**



The complex was prepared by the general procedure described above. Pentacarbonylrhenium(I) bromide (0.195 g, 0.481 mmol, 2.0 eq.) and **6b** (0.090 g, 0.240 mmol, 1.0 eq.) were used in the reaction. Yield: 0.254 g, 98%. Mp > 230 °C. ^1H NMR (400 MHz, d_6 -DMSO) δ 9.28 (s, 2H, H_e), 8.98 (d, J = 5.4 Hz, 2H, H_a), 8.27 (m, 4H, H_d and H_c), 7.63 (td, J = 5.8, 3.0 Hz, 2H, H_b), 4.63 (t, J = 7.2 Hz, 4H, H_f), 1.97 (p, J = 7.2 Hz, 4H, H_g), 1.46-1.34 (m, 4H, H_h). ^{13}C NMR (100 MHz, d_6 -DMSO) δ 197.13, 196.33, 188.94, 153.18, 148.73, 148.15, 140.58, 126.37, 125.74, 122.58, 51.47, 28.83, 24.95. ATR-IR: ν (cm^{-1}) 3136, 2928, 2856, 2017, 1897, 1859, 1617, 1457, 1365, 1271, 1157, 1123, 1052, 1000, 784, 629, 531, 479. HR-ESMS (DMF) m/z = 994.9914 [**8b_{Br}**-Br]⁺ (calc. for C₂₆H₂₂BrN₈O₆Re₂⁺ 994.9931). UV-vis (DMF) λ_{max} /nm ($\epsilon/\text{L mol}^{-1} \text{cm}^{-1}$): 330 (0.7×10^4), 290 (2.1×10^4), 275 (2.7×10^4). Anal. calcd. for C₂₆H₂₂Br₂N₈O₆Re₂: C 29.06, H 2.06, N 10.43%; found: C 29.12, H 2.07, N 10.23%.

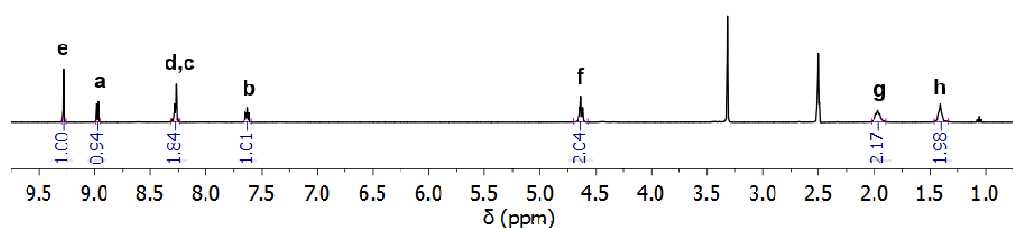
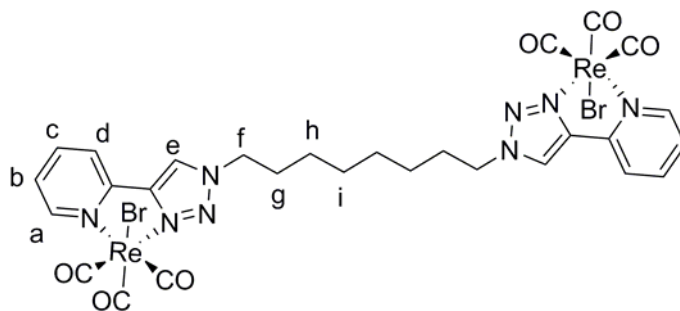


Figure S10: ^1H NMR spectra (400 MHz, d_6 -DMSO, 298 K) of rhenium complex **8b_{Br}**.

3.9 Synthesis of **8c_{Br}**



The complex was prepared by the general procedure described above. Pentacarbonylrhenium(I) bromide (0.151 g, 0.373 mmol, 2.0 eq.) and **6c** (0.075 g, 0.186 mmol, 1.0 eq.) were used in the reaction. Yield: 0.190 g, 92%. Mp > 230 °C. ^1H NMR (400 MHz, d_6 -DMSO) δ 9.28 (s, 2H, H_e), 8.97 (d, J = 5.5 Hz, 2H, H_a), 8.30-8.24 (m, 4H, H_d and H_c), 7.63 (td, J = 5.5, 3.5 Hz, 2H, H_b), 4.61 (t, J = 7.2 Hz, 4H, H_f), 1.94 (p, J = 7.1 Hz, 4H, H_g), 1.32 (m, 8H, H_h and H_i). ^{13}C NMR (100 MHz, d_6 -DMSO) δ 197.14, 196.34, 188.94, 153.18, 148.73, 148.14, 140.58, 126.36, 125.68, 122.54, 51.54, 29.04, 28.00, 25.45. ATR-IR.: ν (cm⁻¹) 3127, 2923, 2856, 2025, 1898, 1616, 1580, 1432, 1270, 1240, 1157, 1122, 997, 778, 642, 626, 532, 480. HR-ESMS (DMF) m/z = 1023.0288 [**8c_{Br}**-Br]⁺ (calc. for C₂₈H₂₆BrN₈O₆Re₂⁺ 1023.0226). UV-vis (DMF) λ_{max} /nm (ϵ /L mol⁻¹ cm⁻¹): 330 (0.6 × 10⁴), 290 (1.7 × 10⁴), 275 (2.3 × 10⁴). Anal. calcd. for C₂₈H₂₆Br₂N₈O₆Re₂: C 30.50, H 2.38, N 10.16%; found: C 30.79, H 2.34, N 10.27%.

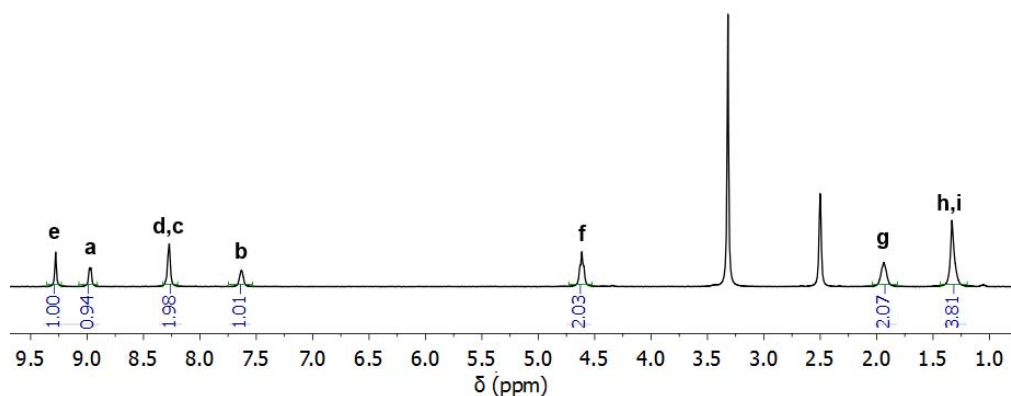
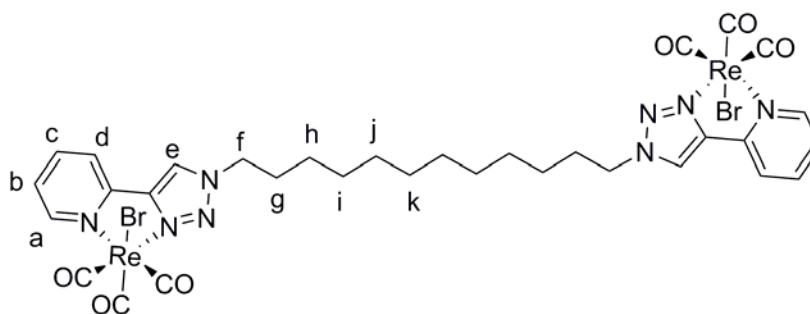


Figure S11: ^1H NMR spectra (400 MHz, d_6 -DMSO, 298 K) of rhenium complex **8c_{Br}**.

3.10 Synthesis of **8d_{Br}**



The complex was prepared by the general procedure described above. Pentacarbonylrhenium(I) bromide (0.354 g, 0.872 mmol, 2.0 eq) and ligand **6d** (0.200 g, 0.436 mmol, 1.0 eq.) were used in the reaction. Yield: 0.480 g, 95%. Mp 218-220 °C. ¹H NMR (400 MHz, *d*₆-DMSO) δ 9.28 (s, 2H, H_e), 8.97 (d, *J* = 5.5 Hz, 2H, H_a), 8.32-8.25 (m, 4H, H_d and H_c), 7.63 (td, *J* = 5.5, 3.5 Hz, 2H, H_b), 4.61 (t, *J* = 7.1 Hz, 4H, H_f), 1.91 (p, *J* = 6.9 Hz, 4H, H_g), 1.32-1.19 (m, 16H, H_h-H_k). ¹³C NMR (100 MHz, *d*₆-DMSO) δ 197.15, 196.34, 188.93, 153.18, 148.74, 148.13, 140.58, 126.37, 125.70, 122.54, 51.57, 29.06, 28.81, 28.75, 28.22, 25.55. ATR-IR: *ν* (cm⁻¹) 3088, 2899, 2850, 2020, 1910, 1889, 1618, 1583, 1463, 1432, 1369, 780, 484. HR-ESMS (methanol) *m/z* = 1079.1021 [**8d_{Br}**-Br]⁺ (calc. for C₃₂H₃₄BrN₈O₆Re₂⁺ 1079.0871). UV-vis (DMF) λ_{max}/nm (ε/L mol⁻¹ cm⁻¹): 330 (0.8 × 10⁴), 290 (2.3 × 10⁴), 275 (2.9 × 10⁴). Anal. calcd. for C₃₂H₃₄Br₂N₈O₆Re₂: C 33.17, H 2.96, N 9.67%; found: C 32.93, H 2.87, N 9.48%.

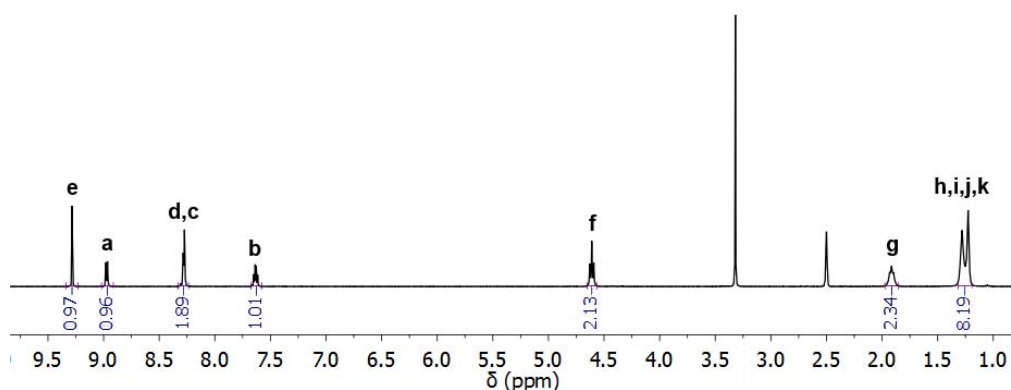
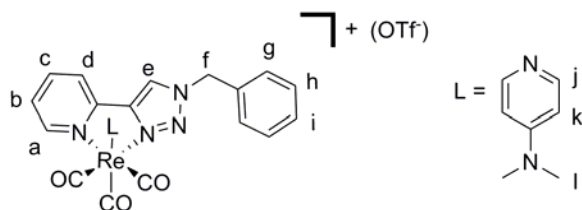


Figure S12: ¹H NMR spectra (400 MHz, *d*₆-DMSO, 298 K) of rhenium complex **8d_{Br}**.

4 General procedure for the synthesis of the cationic rhenium(I) complexes

One of the neutral mono- or di-rhenium bromide complexes and silver triflate (1.25 eq. or 2.5 eq.) were dissolved in dry CH_2Cl_2 (10 mL) and stirred at room temperature in the absence of light, for 12 hours. The reaction mixture was filtered through cotton wool and the solvent volume was removed under reduced pressure. The resultant golden yellow oil was re-dissolved in dry THF (8 mL), 4-dimethylaminopyridine (1 eq. or 2 eq.) was then added and the mixture was irradiated in a CEM microwave reactor at 100 °C (200 W, 200 PSI) for 1 hour. Removal of the solvent under reduced pressure and subsequent purification by silica gel column chromatography (10% MeOH in CH_2Cl_2), followed by recrystallization afforded the complexes as pale yellow solids.

4.1 Synthesis of **7a**_{DMAP}



The complex was prepared by the general procedure described above. **5a**_{Br} (0.054 g, 0.091 mmol, 1 eq.), silver triflate (0.035 g, 0.136 mmol, 1.5 eq.) and 4-dimethylaminopyridine (0.011 g, 0.091 mmol, 1 eq.) were used in the reaction. Purification via column chromatography, followed by recrystallization from acetonitrile and diisopropyl ether led to the isolation of the product as a pale yellow solid. Crystals suitable for X-ray crystallographic analysis were obtained by vapour diffusion of diisopropyl ether into an acetonitrile solution of the complex. Yield: 0.055 g, 78%. Mp 220-222 °C. ¹H NMR (400 MHz, *d*₆-DMSO) δ 9.28 (s, 1H, H_e), 9.25 (d, *J* = 5.5 Hz, 1H, H_a), 8.34 (td, *J* = 7.8, 1.4 Hz, 1H, H_c), 8.26 (d, *J* = 7.9 Hz, 1H, H_d), 7.77 (ddd, *J* = 7.3, 5.5, 1.4 Hz, 1H, H_b), 7.64-7.57 (m, 2H, H_j), 7.51-7.41 (m, 5H, H_g-H_i), 6.45-6.40 (m, 2H, H_k), 6.01-5.86 (m, 2H, H_l), 2.90 (s, 6H, H_l). ¹³C NMR (125 MHz, *d*₆-DMSO) δ 195.93, 195.08, 192.09, 154.15, 153.92, 149.86, 148.92, 148.32, 141.65, 134.13, 129.14, 128.97, 128.48, 127.56, 126.79, 123.29, 108.16, 55.19, 38.69. ATR-IR: *ν* (cm⁻¹) 3127, 2927, 2848, 2025, 1902, 1617, 1580, 1563, 1542, 1467, 1396, 1271, 1157, 1122, 1029, 899, 778, 735, 627, 532, 480. HR-ESMS (DMF) *m/z* = 629.1267 [**7a**_{DMAP}]⁺ (calc. for C₂₄H₂₂N₆O₃Re⁺ 629.1306). UV-vis (DMF) λ_{max}/nm (ε/L mol⁻¹ cm⁻¹): 330 (0.1 × 10⁴), 290 (1.2 × 10⁴), 275 (1.4 × 10⁴). Anal. calcd. for C₂₅H₂₂F₃N₆O₆ReS: C 38.61, H 2.85, N 10.81%; found: C 38.87, H 2.79, N 10.84%.

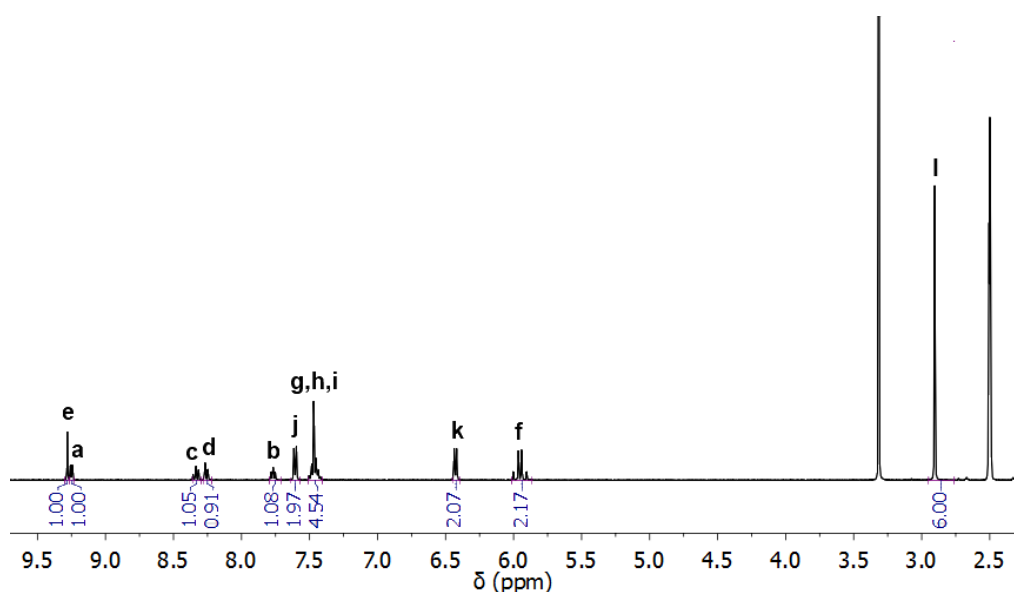


Figure S13: Partial ¹H NMR spectra (400 MHz, *d*₆-DMSO, 298 K) of rhenium complex **7a**_{DMAP}.

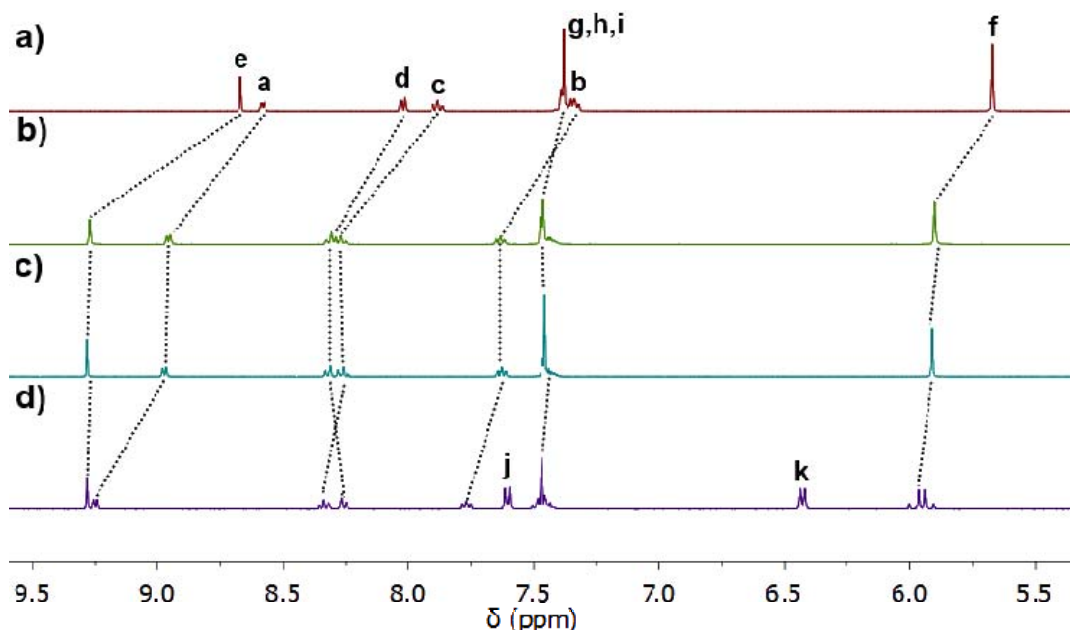
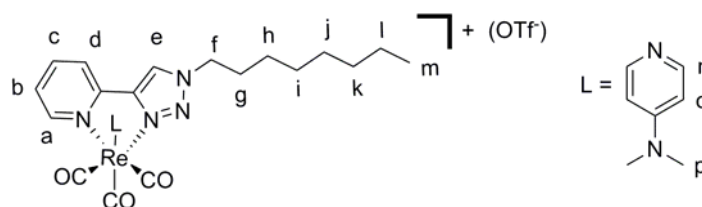


Figure S14: Partial stacked ^1H NMR spectra (400 MHz, d_6 -DMSO, 298 K) of a) ligand **5a**, rhenium complexes b) **7a_{Cl}**, c) **7a_{Br}** and d) **7a_{DMAP}**.

4.2 Synthesis of **7b_{DMAP}**



The complex was prepared by the general procedure described above. **7b_{Br}** (0.050 g, 0.082 mmol, 1 eq.), silver triflate (0.032 g, 0.123 mmol, 1.5 eq.) and 4-dimethylaminopyridine (0.010 g, 0.082 mmol, 1 eq.) were used in the reaction. Purification via column chromatography, followed by recrystallization from dichloromethane and diethyl ether led to the isolation of the product as a pale yellow solid. Yield: 0.048, 73%. Mp 146-148 °C. ^1H NMR (400 MHz, d_6 -DMSO) δ 9.31 (s, 1H, H_e), 9.26 (d, J = 5.5 Hz, 1H, H_a), 8.37 (td, J = 7.8, 1.4 Hz, 1H, H_c), 8.24 (d, J = 7.9 Hz, 1H, H_d), 7.78 (ddd, J = 7.3, 5.5, 1.3 Hz, 1H, H_b), 7.69-7.61 (m, 2H, H_n), 6.53-6.45 (m, 2H, H_o), 4.68 (td, J = 7.0, 2.1 Hz, 2H, H_f), 2.91 (s, 6H, H_p), 1.95 (p, J = 6.1, 4.8 Hz, 2H, H_g), 1.43-1.11 (m, 10H, H_h-H_i), 0.89-0.74 (m, 3H, H_m). ^{13}C NMR (125 MHz, d_6 -DMSO) δ 195.95, 195.18, 192.07, 154.20, 153.95, 149.95, 148.53, 148.45, 141.71, 127.52, 126.67, 123.05, 108.23, 52.02, 38.66, 31.09, 28.97, 28.46, 28.16, 25.50, 22.02, 13.90. ATR-IR: ν (cm⁻¹) 3082, 2928,

2852, 2025, 1915, 1628, 1618, 1545, 1455, 1398, 1271, 1259, 1224, 1154, 1021, 815, 785, 757, 644, 517, 482. HR-ESMS (MeOH) $m/z = 651.2125$ [**7b**_{DMAP}]⁺ (calc. for C₂₅H₃₂N₆O₃Re⁺ 651.2089). UV-vis (DMF) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{L mol}^{-1} \text{cm}^{-1}$): 330 (0.4×10^4), 290 (3.7×10^4), 275 (3.4×10^4). Anal. calcd. for C₂₆H₃₂F₃N₆O₆ReS: C 39.04, H 4.03, N 10.51%; found: C 38.95, H 3.98, N 10.27%.

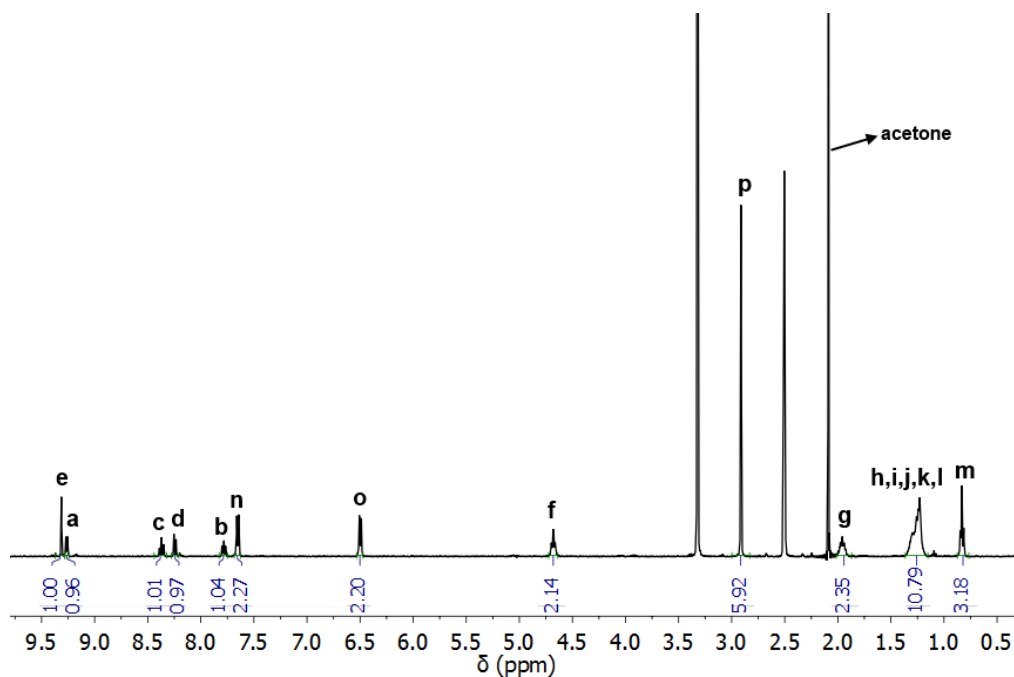
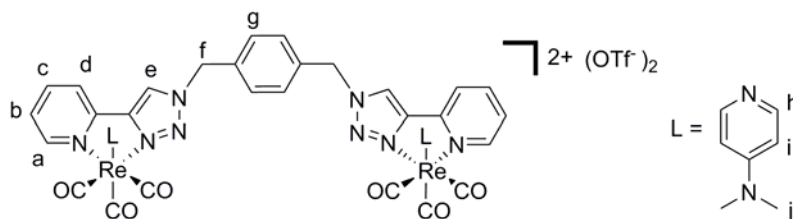


Figure S15: ¹H NMR spectra (400 MHz, *d*₆-DMSO, 298 K) of rhenium complex **7b**_{DMAP}.

4.3 Synthesis of **8a_{DMAP}**



The complex was prepared by the general procedure described above. **8a_{Br}** (0.070 g, 0.061 mmol, 1 eq.), silver triflate (0.040 g, 0.153 mmol, 2.5 eq.) and 4-dimethylaminopyridine (0.015 g, 0.123 mmol, 2 eq.) were used in the reaction. Purification via column chromatography, followed by recrystallization from acetonitrile and diisopropyl ether led to the isolation of the product as a pale yellow solid. Crystals suitable for X-ray crystallographic analysis were obtained by vapour diffusion of diisopropyl ether into an acetonitrile solution of the complex. Yield: 0.050 g, 53%. Mp > 230 °C. ¹H NMR (400 MHz, *d*₆-DMSO) δ 9.31 (s, 2H, H_e), 9.25 (d, *J* = 5.6 Hz, 2H, H_a), 8.35 (t, *J* = 7.8 Hz, 2H, H_c), 8.26 (d, *J* = 7.9 Hz, 2H, H_d), 7.78 (dd, *J* = 7.8, 5.9 Hz, 2H, H_b), 7.64-7.59 (m, 4H, H_h), 7.55 (s, 4H, H_g), 6.47-6.41 (m, 4H, H_i), 5.99 (s, 4H, H_f), 2.89 (s, 12H, H_j). ¹³C NMR (125 MHz, *d*₆-DMSO) δ 195.86, 195.12, 192.05, 154.16, 154.00, 149.94, 148.87, 148.28, 141.72, 134.85, 129.14, 127.65, 126.98, 123.27, 108.19, 54.72, 38.70. ATR-IR: ν (cm⁻¹) 3105, 2960, 2027, 1901, 1617, 1542, 1446, 1397, 1257, 1222, 1152, 1028, 949, 908, 818, 782, 754, 635, 572, 481. HR-ESMS (MeOH) *m/z* = 528.0667 [**8a_{DMAP}**-DMAP]²⁺ (calc. for C₃₅H₂₈N₁₀O₆Re₂²⁺ 528.0635). UV-vis (DMF) λ_{max} /nm (ϵ /L mol⁻¹ cm⁻¹): 330 (0.6 × 10⁴), 290 (6.8 × 10⁴), 275 (6.5 × 10⁴). Anal. calcd. for C₄₄H₃₈F₆N₁₂O₁₂Re₂S₂•H₂O: C 36.01, H 3.09, N 10.95%; found: C 35.64, H 2.99, N 10.56%.

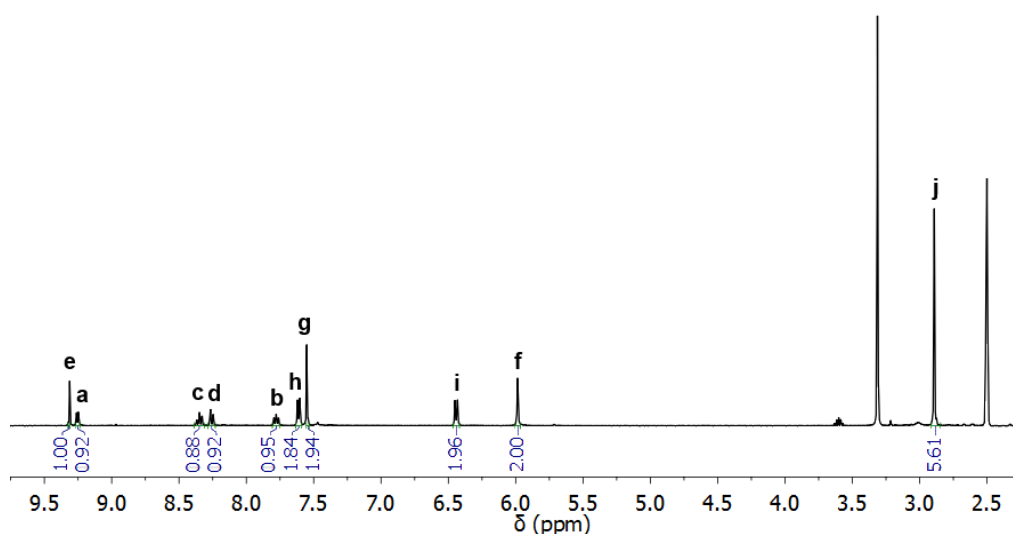


Figure S16: Partial ¹H NMR spectra (400 MHz, *d*₆-DMSO, 298 K) of rhenium complex **8a_{DMAP}**.

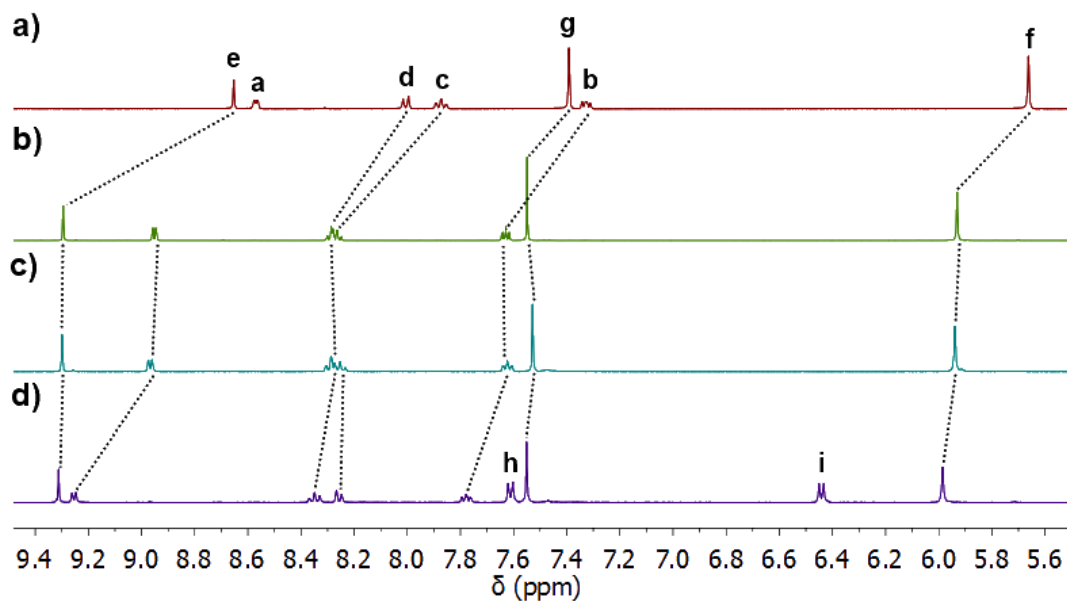
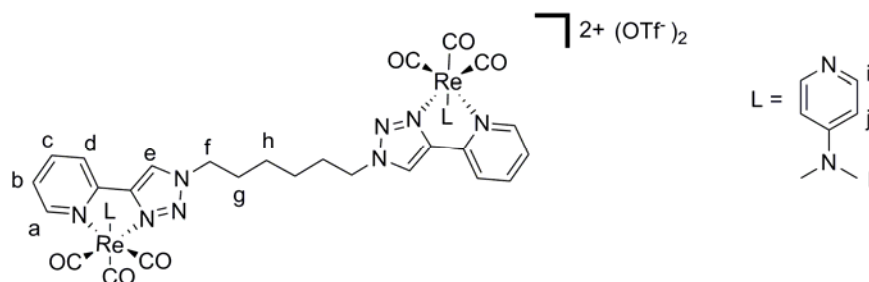


Figure S17: Partial stacked ^1H NMR spectra (400 MHz, d_6 -DMSO, 298 K) of a) ligand **6a**, rhenium complexes b) **8a_{Cl}**, c) **8a_{Br}** and d) **8a_{DMAP}**.

4.4 Synthesis of **8b**_{DMAP}



The complex was prepared by the general procedure described above. **8b**_{Br} (0.070 g, 0.065 mmol, 1eq.), silver triflate (0.042 g, 0.163 mmol, 2.5 eq.) and 4-dimethylaminopyridine (0.016 g, 0.130 mmol, 2 eq.) were used in the reaction. Purification via column chromatography, followed by recrystallization from dichloromethane and diethyl ether led to the isolation of the product as a pale yellow solid. Yield: 0.050 g, 52%. Mp 133-135 °C. ¹H NMR (400 MHz, *d*₆-DMSO) δ 9.30 (s, 2H, H_e), 9.26 (d, *J* = 5.5 Hz, 2H, H_a), 8.37 (td, *J* = 7.9, 1.4 Hz, 2H, H_c), 8.24 (d, *J* = 7.9 Hz, 2H, H_d), 7.78 (ddd, *J* = 7.3, 5.5, 1.4 Hz, 2H, H_b), 7.67-7.62 (m, 4H, H_i), 6.50-6.46 (m, 4H, H_j), 4.69 (t, *J* = 7.1 Hz, 4H, H_f), 2.88 (s, 12H, H_k), 2.00 (p, *J* = 7.2 Hz, 4H, H_g), 1.38-1.30 (m, 4H, H_h). ¹³C NMR (125 MHz, *d*₆-DMSO) δ 195.91, 195.19, 192.05, 154.18, 154.00, 149.97, 148.53, 148.41, 141.76, 127.54, 126.67, 123.05, 108.24, 51.92, 38.66, 28.87, 24.95. ATR-IR: *ν* (cm⁻¹) 3113, 2917, 2852, 2025, 1894, 1617, 1542, 1457, 1395, 1255, 1222, 1153, 1019, 948, 908, 816, 785, 754, 636, 572, 481. HR-ESMS (MeOH) *m/z* = 518.0802 [**8b**_{DMAP}-DMAP]²⁺ (calc. for C₃₃H₃₂N₁₀O₆Re₂²⁺ 518.0792). UV-vis (DMF) λ_{max}/nm (ε/L mol⁻¹ cm⁻¹): 330 (0.7 × 10⁴), 290 (6.9 × 10⁴), 275 (6.4 × 10⁴). Anal. calcd. for C₄₂H₄₂F₆N₁₂O₁₂Re₂S₂ : C 34.61, H 2.90, N 11.53%; found: C 34.90, H 2.78, N 11.43%.

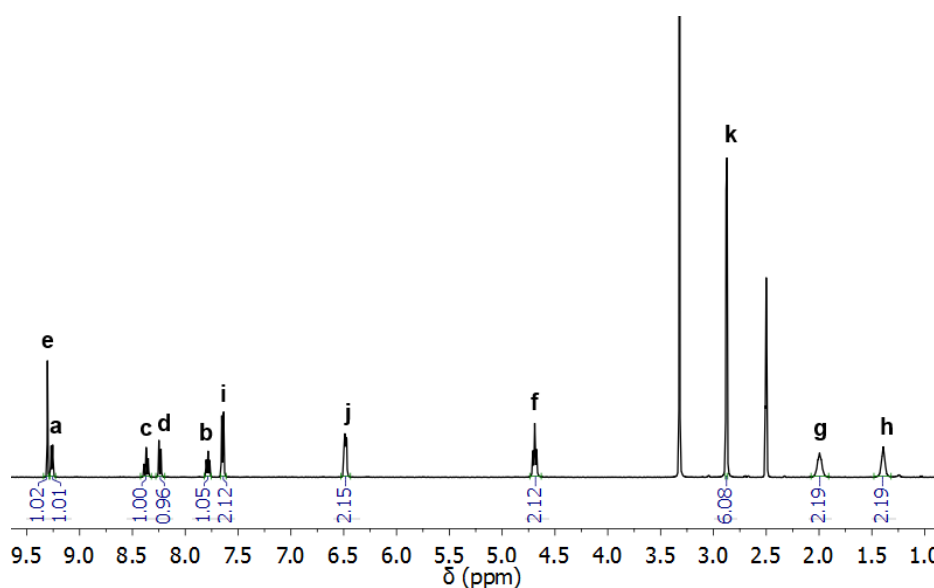
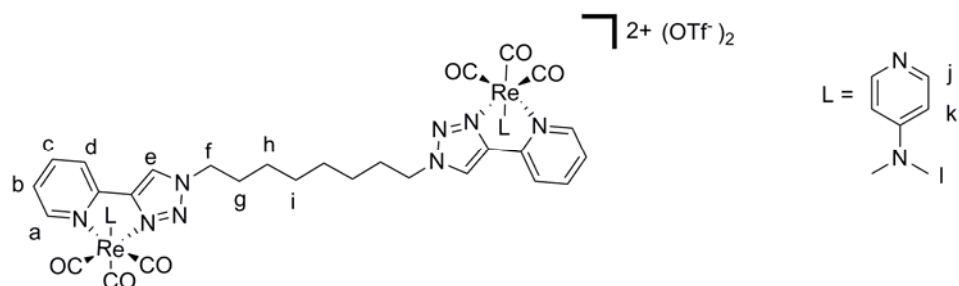


Figure S18: ¹H NMR spectra (400 MHz, *d*₆-DMSO, 298 K) of rhenium complex **8b**_{DMAP}.

4.5 Synthesis of **8c_{DMAP}**



The complex was prepared by the general procedure described above. **8c_{Br}** (0.040 g, 0.038 mmol, 1eq.), silver triflate (0.025 g, 0.094 mmol, 2.5 eq.) and 4-dimethylaminopyridine (0.010 g, 0.075 mmol, 2 eq.) were used in the reaction. Purification via column chromatography, followed by recrystallization from dichloromethane and diethyl ether led to the isolation of the product as a pale yellow solid. Yield: 0.025 g, 46%. Mp 87-89 °C. ¹H NMR (500 MHz, *d*₆-DMSO) δ 9.30 (s, 2H, H_e), 9.26 (d, *J* = 5.6 Hz, 2H, H_a), 8.37 (td, *J* = 7.8, 1.5 Hz, 2H, H_c), 8.24 (d, *J* = 7.9 Hz, 2H, H_d), 7.78 (ddd, *J* = 7.3, 5.5, 1.4 Hz, 2H, H_b), 7.66-7.61 (m, 4H, H_j), 6.51- 6.46 (m, 4H, H_k), 4.67 (t, *J* = 7.1 Hz, 4H, H_f), 2.90 (s, 12H, H_i), 2.01-1.90 (m, 4H, H_g), 1.36-1.30 (m, 8H, H_h and H_i). ¹³C NMR (125 MHz, *d*₆-DMSO) δ 195.90, 195.20, 192.07, 154.19, 153.98, 149.95, 148.52, 148.41, 141.75, 127.55, 126.65, 123.06, 108.22, 51.98, 38.67, 29.02, 28.16, 25.56. ATR-IR: ν (cm⁻¹) 3108, 2928, 2861, 2027, 1902, 1623, 1543, 1457, 1395, 1258, 1223, 1153, 1019, 812, 783, 755, 636, 573, 516, 484. HR-ESMS (MeOH) *m/z* = 532.0911 [**8c_{DMAP}**-DMAP]²⁺ (calc. for C₃₅H₃₆N₁₀O₆Re₂²⁺ 532.0948). UV-vis (DMF) λ_{max} /nm (ϵ /L mol⁻¹ cm⁻¹): 330 (0.6 × 10⁴), 290 (5.4 × 10⁴), 275 (5.2 × 10⁴). Anal. calcd. for C₄₄H₄₆F₆N₁₂O₁₂Re₂S₂•1.5H₂O•0.5 (CH₃CH₂OCH₂CH₃): C 35.66, H 3.51, N 10.85%; found: C 35.85, H 3.42, N 10.49%.

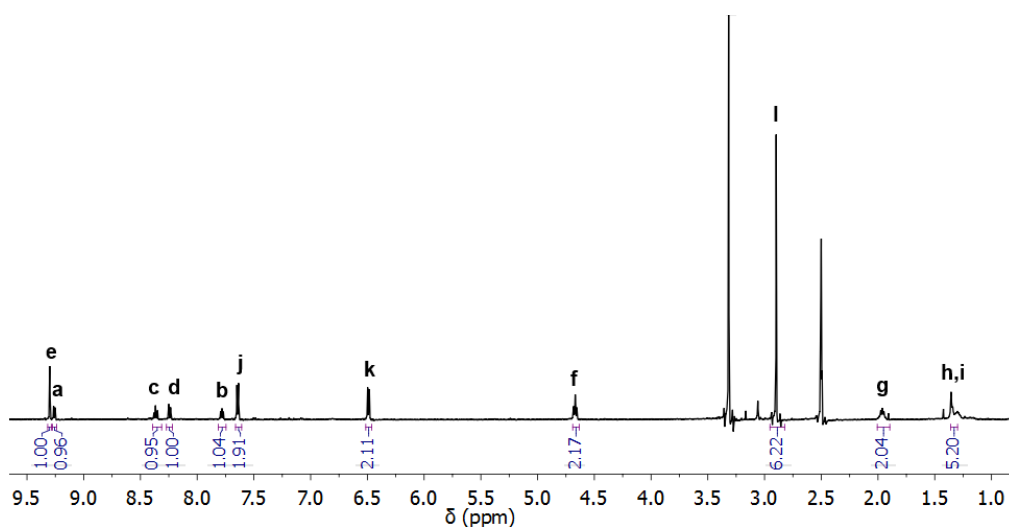
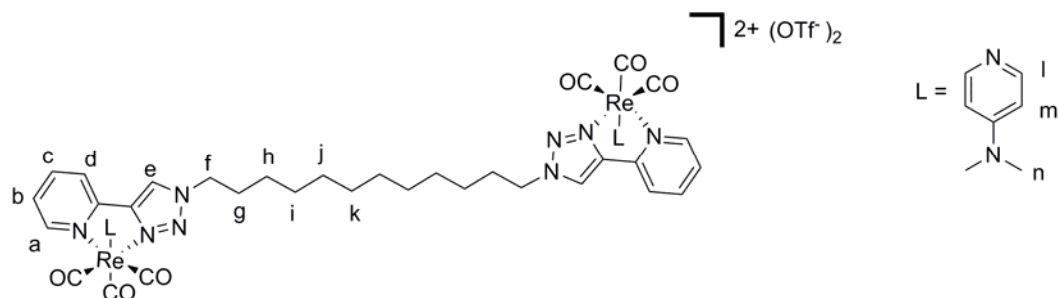


Figure S19: ¹H NMR spectra (400 MHz, *d*₆-DMSO, 298 K) of rhenium complex **8c_{DMAP}**.

4.6 Synthesis of **8d**_{DMAP}



The complex was prepared by the general procedure described above. **8d**_{Br} (0.095 g, 0.082 mmol, 1eq.), silver triflate (0.053 g, 0.205 mmol, 2.5 eq.) and 4-dimethylaminopyridine (0.020 g, 0.164 mmol, 2 eq.) were used in the reaction. Purification via column chromatography, followed by recrystallization from dichloromethane and hexane led to the isolation of the product as a pale yellow solid. Yield: 0.060 g, 47%. Mp 78-80 °C. ¹H NMR (400 MHz, *d*₆-DMSO) δ 9.32 (s, 2H, H_e), 9.26 (d, *J* = 5.6 Hz, 2H, H_a), 8.41-8.31 (m, 2H, H_c), 8.25 (d, *J* = 7.9 Hz, 2H, H_d), 7.78 (dd, *J* = 7.5, 5.8 Hz, 2H, H_b), 7.67-7.60 (m, 4H, H_i), 6.51-6.46 (m, 4H, H_m), 4.67 (t, *J* = 7.0 Hz, 4H, H_f), 2.90 (s, 12H, H_n), 1.94 (p, *J* = 7.1 Hz, 4H, H_g), 1.25-1.17 (m, 16H, H_h-H_k). ¹³C NMR (100 MHz, *d*₆-DMSO) δ 195.95, 195.19, 192.05, 154.20, 153.96, 149.96, 148.53, 148.45, 141.75, 127.53, 126.68, 123.08, 108.24, 52.02, 38.67, 29.00, 28.92, 28.89, 28.26, 25.55. ATR-IR: *ν* (cm⁻¹) 3112, 2926, 2854, 2024, 1980, 1897, 1616, 1543, 1445, 1394, 1254, 1222, 1150, 1064, 1028, 812, 781, 754, 635, 572, 515, 481. HR-ESMS (MeOH) *m/z* = 621.1709 [**8d**_{DMAP}]²⁺ (calc. for C₄₆H₅₄N₁₂O₆Re₂²⁺ 621.1683). UV-vis (DMF) λ_{max}/nm (ε/L mol⁻¹ cm⁻¹): 330 (0.7 × 10⁴), 290 (7.0 × 10⁴), 275 (6.4 × 10⁴). Anal. calcd. for C₄₈H₅₄F₆N₁₂O₁₂Re₂S₂•4.5CH₂Cl₂: C 37.31, H 3.91, N 10.34%; found: C 37.21, H 3.89, N 10.19%.

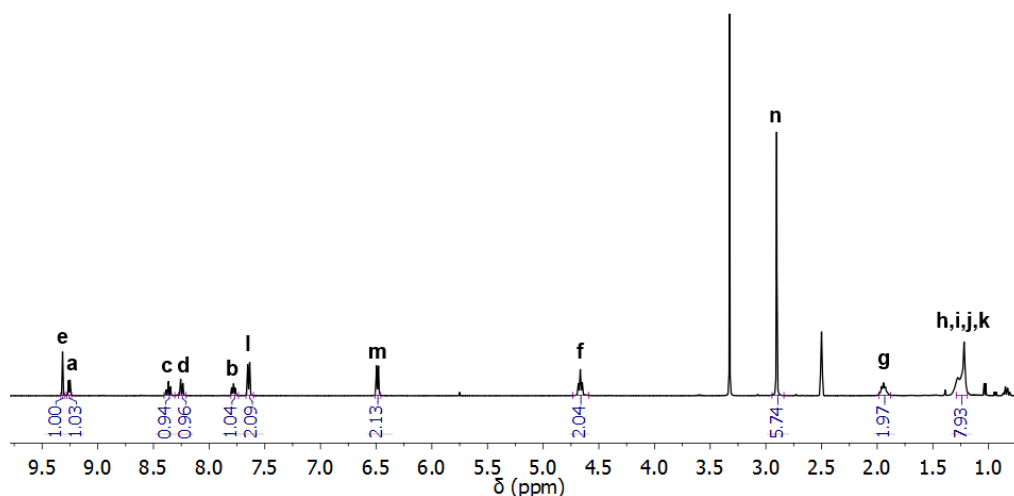


Figure S20: ¹H NMR spectra (400 MHz, *d*₆-DMSO, 298 K) of rhenium complexes **8d**_{DMAP}.

5 Kinetic stability of the rhenium(I) complexes versus histidine

Histidine competition experiment for the rhenium complex **8a_{Cl}**

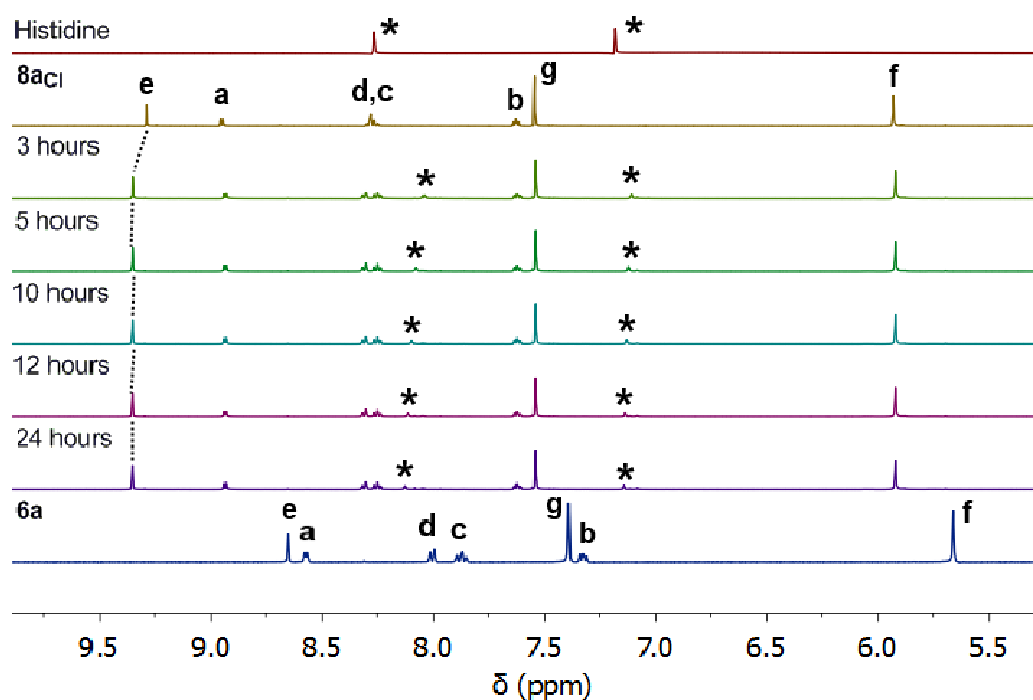


Figure S21: Partial stacked ¹H NMR spectra (500 MHz, *d*₆-DMSO, 313 K) of mixtures containing the rhenium complex **8a_{Cl}** (1 eq.), DL-histidine hydrochloride monohydrate (6 eq.) and NaHCO₃ (6 eq.).

Histidine competition experiment for the rhenium complex $8\mathbf{c}_{\text{DMAP}}$

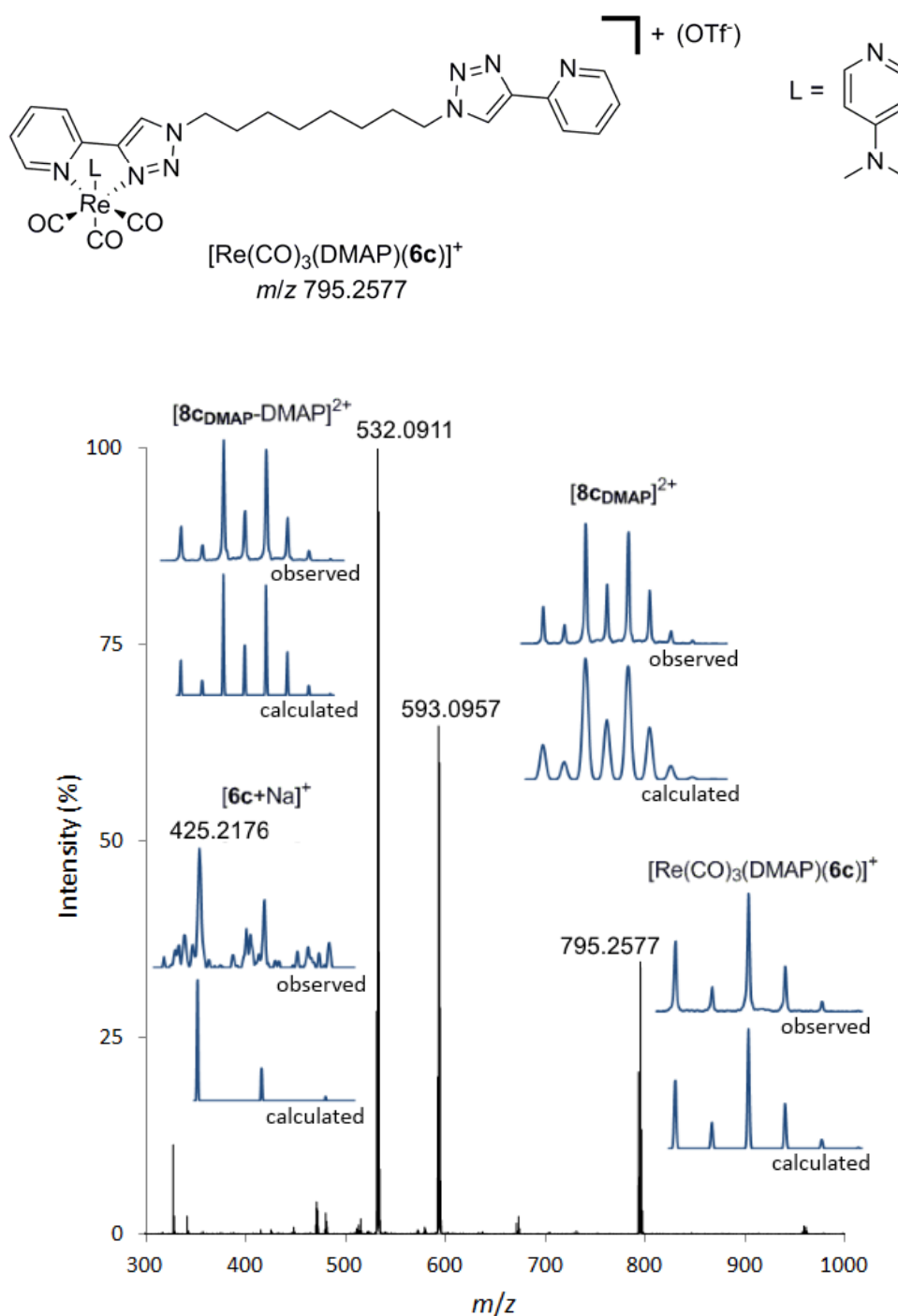


Figure S22: Chemical structure of the mono-cationic rhenium complex $[\text{Re}(\text{CO})_3(\text{DMAP})(\mathbf{6c})]^+$ and HR-ES mass spectrum of reaction mixture containing $\mathbf{8c}_{\text{DMAP}}$ (1 eq.), DL-histidine hydrochloride monohydrate (6 eq.) and NaHCO_3 (6 eq.).

6 X-ray Crystallography

Table 6.1. SQUEEZE results for **8a_{DMAP}**

Platon squeeze void number	1
Platon squeeze void average x	-0.004
Platon squeeze void average y	0.012
Platon squeeze void average z	-0.001
Platon squeeze void volume	624
Platon squeeze void count electrons	241
Platon squeeze details	Disordered acetonitrile, diisopropyl ether and triflate molecules and triflate molecules

Table 6.2. X-ray crystallographic data collected in this work

compound	7a_{Br}	8a_{Cl}	7a_{DMAP}	8a_{DMAP}
CCDC number	1402800	1402802	1402801	1402803
Chemical formula	C ₁₇ H ₁₂ BrN ₄ O ₃ Re	C ₃₄ H ₃₂ Cl ₂ N ₁₀ O ₈ Re ₂	C ₂₅ H ₂₂ F ₃ N ₆ O ₆ ReS	C ₄₂ H ₃₈ N ₁₂ O ₆ Re ₂
Formula weight	586.42	1152.00	777.75	1179.24
Temperature, K	94.0(2)	90(2)	90(2)	100.0(1)
Wavelength, Å	0.71073	0.71073	0.71073	1.54180
Crystal system	Orthorhombic	Orthorhombic	Triclinic	Triclinic
Space group	<i>Pbcn</i>	<i>Pbca</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> , Å	10.7506(10)	17.4365(10)	8.4002(11)	10.5925(4)
<i>b</i> , Å	10.3184(9)	11.3085(6)	11.0403(15)	11.4645(5)
<i>c</i> , Å	32.139(3)	20.1644(13)	14.7650(17)	12.9089(4)
α , deg	90	90	86.022(6)	89.794(3)
β , deg	90	90	86.798(6)	82.874(3)
γ , deg	90	90	87.350(6)	82.860(4)
Volume, Å ³	3565.2(6)	3976.0(4)	1362.7(3)	1543.34(10)
<i>Z</i>	8	4	2	1
D _{calcd} , Mg/m ³	2.185	1.931	1.913	1.269
μ , mm ⁻¹	9.083	6.283	4.609	7.911
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0539 <i>wR</i> ₂ = 0.1087	<i>R</i> ₁ = 0.0314 <i>wR</i> ₂ = 0.0705	<i>R</i> ₁ = 0.0443 <i>wR</i> ₂ = 0.0817	<i>R</i> ₁ = 0.0693 <i>wR</i> ₂ = 0.2121
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0692 <i>wR</i> ₂ = 0.1200	<i>R</i> ₁ = 0.0332 <i>wR</i> ₂ = 0.0717	<i>R</i> ₁ = 0.0443 <i>wR</i> ₂ = 0.0817	<i>R</i> ₁ = 0.0745 <i>wR</i> ₂ = 0.2237

7 UV-vis spectra of the rhenium(I) complexes

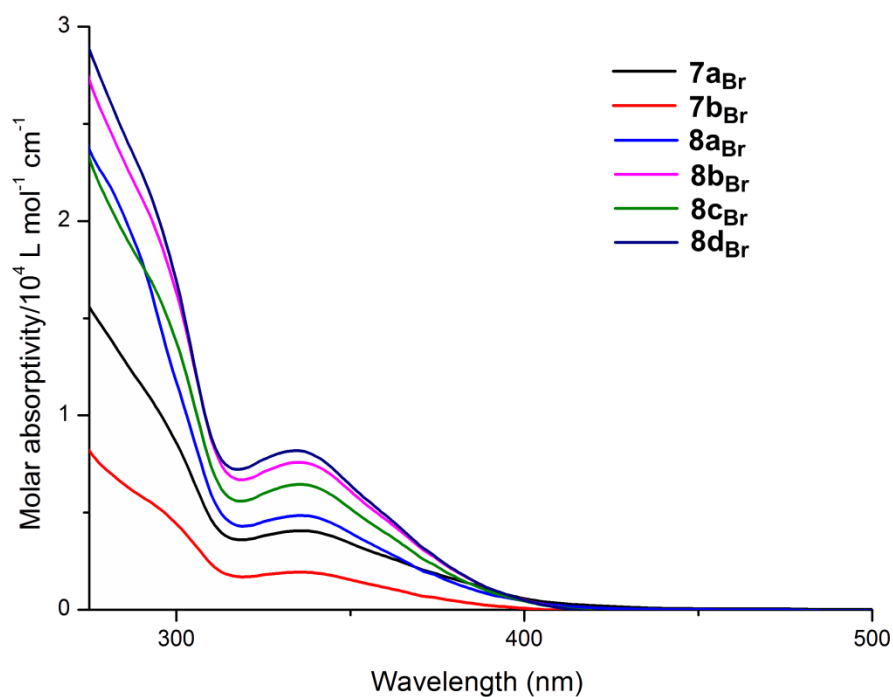


Figure S23: Electronic absorption spectra (UV-vis, DMF, 10⁻⁵ M) of the neutral rhenium(I) bromide complexes.

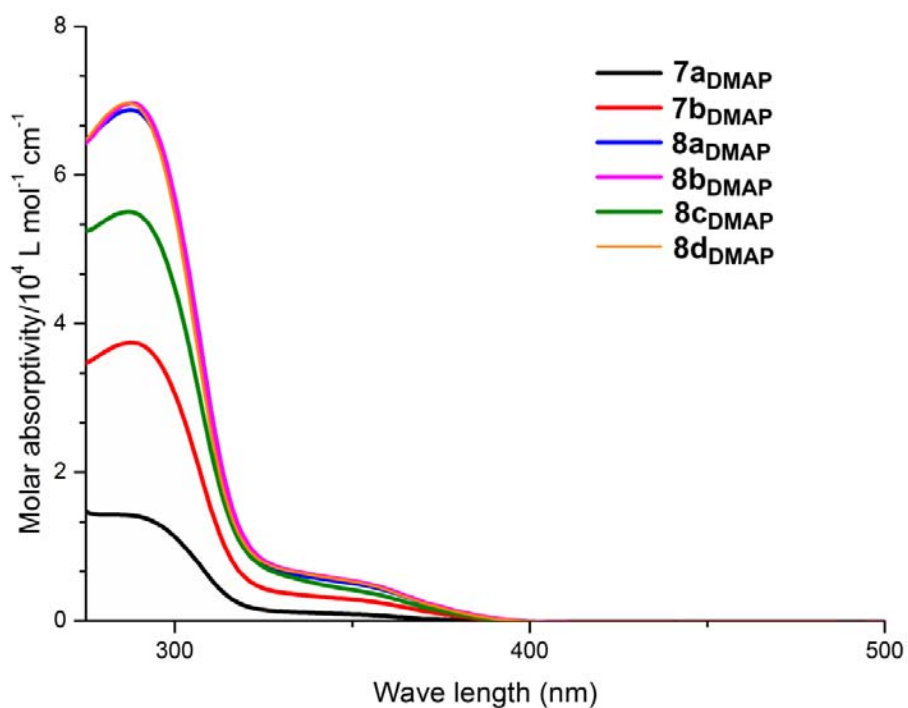


Figure S24: Electronic absorption spectra (UV-vis, DMF, 10⁻⁵ M) of the cationic rhenium(I) complexes.

8 Molecular models of stereoisomers of $8a_{\text{DMAP}}$ and $7a_{\text{DMAP}}$

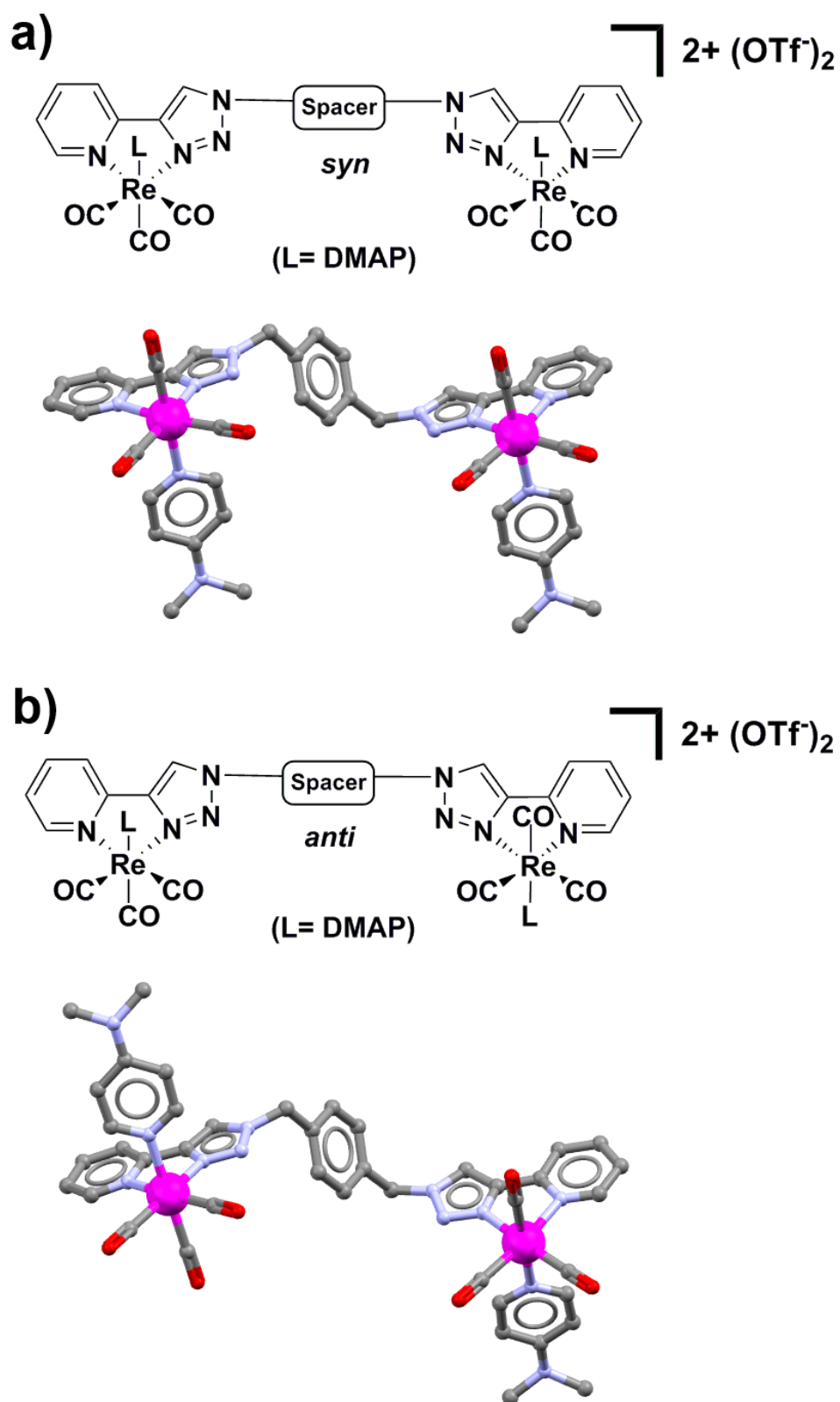


Figure S25: Spartan14⁴ molecular models of the *syn* and *anti* isomers of di-rhenium(I) complex $8a_{\text{DMAP}}$.

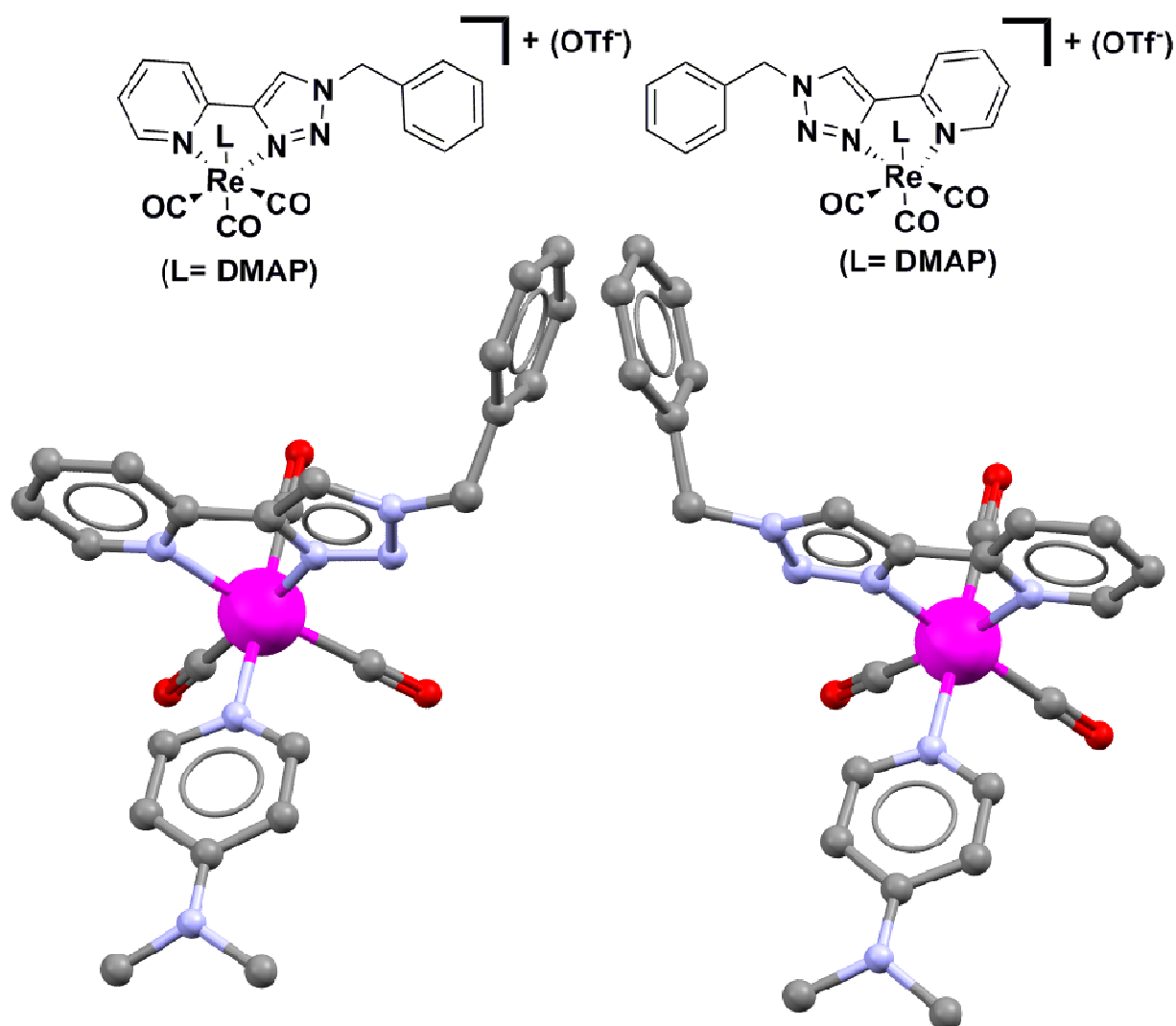


Figure S26: Spartan14⁴ molecular models of the Λ and Δ enantiomers of the mono-rhenium complex **7a**_{DMAP}.

References

- (1) Crowley, J. D.; Bandeen, P. H.; Hanton, L. R. *Polyhedron* **2010**, *29*, 70.
- (2) Crowley, J. D.; Bandeen, P. H. *Dalton Trans.* **2010**, *39*, 612.
- (3) Kim, T. Y.; Elliott, A. B. S.; Shaffer, K. J.; McAdam, C. J.; Gordon, K. C.; Crowley, J. D. *Polyhedron* **2013**, *52*, 1391.
- (4) Spartan 14, Wavefunction Inc. Irvine, CA 92,612, USA **2014**.