Supporting Information for

3D Helical and 2D Rhomboidal Supramolecules: Stepwise Self-Assembly and Dynamic Transformation of Terpyridine-Based Metallo−architectures

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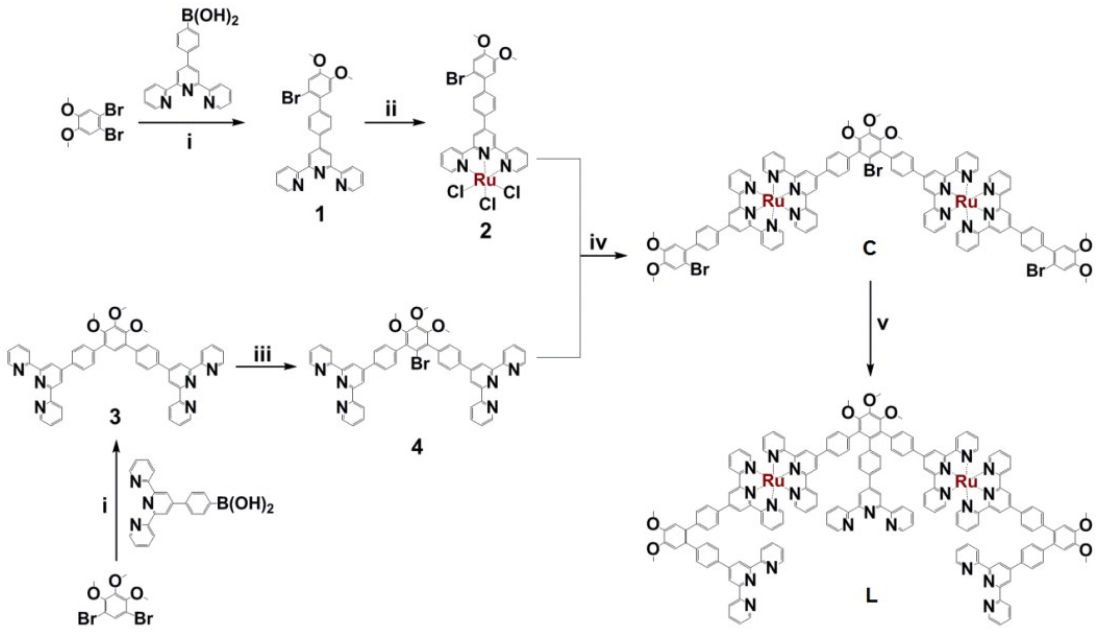
Materials and Methods:

NMR spectra were recorded on a Bruker ADVANCE 400 or 500 NMR Spectrometer. ^{1}H NMR chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard.

Mass spectra of complexes and ligands were determined on Waters Synapt G2 Mass Spectrometer with traveling wave ion mobility (TWIM) under the following conditions: ESI capillary voltage, 3.5 kV; cone voltage, 35 V; desolvation gas flow, 800 L/h. TWIM-MS was measured with IM traveling wave height, 25 V; and IM traveling wave velocity, 1000 m/s. Absorption spectra were measured with Hitachi (model U-3010) UV-Vis spectrophotometer in a 1-cm quartz cell.

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise specified.

Synthesis and characterization.



Scheme **S1**. Synthetic route to metal-organic ligand **L**.

Both 4'-(4-boronatophenyl)[2,2':6',2"]terpyridine and **3** were synthesized according to literature procedures.[S1]

1,5-Dibromo-2,3,4-trimethoxybenzene was synthesized according to literature procedure.[S2]

1: To a solution of 1,2-dibromo-4,5-dimethoxybenzene (444 mg, 1.5 mmol) and 4'-(4-boronato-phenyl)-[2,2':6',2"]terpyridine (565 mg, 1.6 mmol) in MeCN (100 mL), aqueous K_2CO_3 (2.0 mL, 1 M) was added. The system was pumped and backfilled with nitrogen; then, $Pd(PPh_3)_4$ (99 mg) was added. After refluxing for 24 h under argon, the mixture was cooled to 25 °C and evaporated *in vacuo*. The residue was washed with MeOH (100 mL), then the precipitate was dried *in vacuo* at 50 °C and purified by flash column chromatography (Al_2O_3), eluting with $CHCl_3$/n-hexane to give **1**, as a white solid: 413 mg (52%); ^{1}H NMR (500 MHz, 298 K, $CDCl_3$, ppm) δ = 8.81 (s, 2H), 8.75 (d, 2H), 8.69 (d, 2H), 7.98 (d, 2H), 7.89 (t, 2H), 7.57 (d, 2H), 7.36 (t, 2H), 7.16 (s, 1H), 6.90 (s, 1H), 3.94 (s, 3H), 3.91 (s, 3H); ^{13}C NMR (500 MHz, 298 K, $CDCl_3$, ppm):156.23, 155.98, 149.86, 149.15, 148.94, 148.34, 141.82, 137.60, 136.86, 134.08, 130.11, 126.98, 123.84, 121.34, 118.84, 115.84, 113.74, 112.43, 56.26, 56.15; ESI/MS (*m/z*): Calcd. for $[C_{29}H_{22}BrN_3O_2+H]^+$: 524.1, Found: 524.2.

2: To a round bottom flask, a mixture of **1** (262 mg, 0.5 mmol), $RuCl_3•H_2O$ (157 mg, 0.6 mmol), absolute EtOH (30 mL) was added. After refluxing at 80 °C for 12 h, the solution was cooled to 25 °C, then filtered *in vacuo* to give a dark precipitate, which was washed with copious amounts of MeOH and dried *in vacuo* at 50 °C to afford **2** (254 mg, 65.0%), as a dark solid that was used directly for next step without further purification: m.p. >250 °C. Anal. Calcd. for $C_{29}H_{22}BrN_3O_2RuCl_3•3H_2O$: C, 44.32; H, 3.59; N, 5.35. Found: C, 43.98; H, 3.62; N, 5.31.

4: To a solution of **3**[S1] (391 mg, 0.5 mmol) in $CHCl_3$ (50 mL), Br_2 in $CHCl_3$ (2.0 mL, 1 M) was added dropwise at 25 °C, then the solution was stirred at 80 °C for 10 h. After cooled to 25 °C, a saturated $NaHSO_3$ solution was slowly added until the reddish brown solution become colorless.

The solution was extracted with CH_2Cl_2 and organic phase was washed with a saturated NaCl solution and dried ($MgSO_4$). Removal the solvent *in vacuo* gave **4**, as a white solid: 371mg (86%); ^{1}H NMR (500 MHz, 298 K, $CDCl_3$, ppm) δ = 9.04 (s, 2H), 8.81 (s, 4H), 8.76 (m, 8H), 8.69 (d, 4H), 8.15 (d, 2H), 8.05 (d, 4H), 7.89 (m, 6H), 7.83 (d, 4H), 7.37 (t, 4H), 7.08 (d, 2H), 4.23 (t, 2H), 3.92 (t, 2H), 3.78 (t, 2H), 3.72 (t, 2H), 3.69 (t, 2H), 3.58 (t, 2H), 3.40 (s, 3H); ^{13}C NMR (500 MHz, 298 K, $CDCl_3$, ppm): 159.80, 156.19, 156.06, 155.57, 155.46, 149.71, 149.43, 149.17, 147.51, 138.31, 138.25, 136.91, 135.72, 135.08, 130.91, 128.54, 128.08, 127.55, 123.90, 121.40, 121.37, 118.71, 118.35, 115.05 71.97, 70.91, 70.70, 70.61, 69.75, 67.56, 59.07; ESI/MS (*m/z*): Calcd. for $[C_{15}H_{37}BrN_6O_3+H]^+$: 862.8, Found: 863.2.

C: A mixture of **2** (88 mg, 0.12 mmol) and **4** (43 mg, 0.05 mmol) was added to a 50 mL flask, then MeOH (10 mL) and $CHCl_3$ (10 mL) were added. After adding 4 drops *N*-ethylmorpholine, the suspension was stirred at 80 °C for 24 hours. After cooling to 25 °C, the mixture was filtered under reduced pressure. The solution was evaporated *in vacuo* generating a residue that was purified by flash column chromatography (Al_2O_3), eluting with CH_2Cl_2/MeOH to give a red solid, which was dissolved in MeOH and precipitated with NH_4PF_6 to afford complex **5**, as a dark red solid: 121 mg (90 %); m.p. >300 °C; ^{1}H NMR (500 MHz, 298 K, CD_3CN, ppm) δ = 9.16 (s, 2H), 8.88 (s, 4H), 8.77 (m, 6H), 8.69 (d, 4H), 8.45 (m, 8H), 8.33 (d, 4H), 8.18 (d, 2H), 8.14 (t, 2H), 7.98 (m, 3H), 7.82 (d, 2H), 7.76 (t, 4H), 7.65 (d, 4H), 7.54 (t, 4H), 7.47 (d, 4H), 7.41 (t, 2H), 7.36 (d, 2H), 7.33 (d, 4H), 7.04 (t, 4H), 7.00 (d, 2H), 6.92 (t, 4H), 6.38 (d, 4H), 4.23 (t, 2H), 1.91 (m, 2H), 1.57 (m, 2H), 1.39 (m, 14H), 0.93 (t, 3H); ^{13}C NMR (400 MHz, 298 K, CD_3CN, ppm): 157.93, 157.91, 155.25, 155.20, 152.17, 152.17, 152.15, 151.89, 149.40, 148.62, 147.49, 147.47, 146.26, 142.90, 140.04, 137.78, 135.77, 135.45, 133.06, 132.43, 131.16, 130.58, 127.22, 127.20, 127.13, 124.29, 121.32, 115.87, 114.04, 111.54, 99.67; ESI/MS (m/z): $[\mathbf{M}\text{-}4Cl^-]^{4+}$ 528.05 (calcd 528.07), $[\mathbf{M}\text{-}Cl^-]^{3+}$ 716.39 (calcd 716.42).

L: To a mixture of **C** (54 mg, 0.02 mmol) and 4'-(4-boronatophenyl)[2,2':6',2'']terpyridine (42 mg, 0.12 mmol) in MeCN (20 mL), aqueous K_2CO_3 (0.24 mL, 1 M) was added. The system was pumped and backfilled with nitrogen; then $Pd(PPh_3)_4$ (6.6 mg) was added. After refluxing for 24 h under Argon, the mixture was cooled to 25 °C and evaporated *in vacuo* to afford a residue that was washed with MeOH (100 mL). The precipitate was dried *in vacuo* at 50 °C and purified by flash column chromatography (Al_2O_3), eluting with CH_2Cl_2/MeOH to give **6**, as a red solid: 22 mg (40%); m.p. >300 °C; ^{1}H NMR (500 MHz, 298 K, CD_3CN, ppm) δ = 9.15 (s, 2H), 9.00 (s, 4H), 8.90 (d, 2H), 8.88 (d, 2H), 8.79 (d, 4H), 8.67 (d, 4H), 8.63 (d, 2H), 8.54 (m, 5H), 8.45 (t, 2H), 8.42 (d, 2H), 8.33 (d, 2H), 8.26 (d, 4H), 8.03 (t, 2H), 7.96 (m, 8H), 7.74 (d, 4H), 7.65 (m, 4H), 7.41 (m, 10H), 7.31 (t, 2H), 7.20 (m, 8H), 4.37 (t, 2H), 3.95 (t, 2H), 3.75 (t, 2H), 3.68 (t, 2H), 3.65 (t, 2H), 3.56 (t, 2H), 3.37 (s, 3H); ESI/MS (m/z): $[\mathbf{M}\text{-}4PF_6^-]^{4+}$ 699.48 (calcd 699.45), $[\mathbf{M}\text{-}3PF_6^-]^{3+}$ 980.94 (calcd 980.92).

H: L (10.6 mg, 0.0031 mmol) in 10 mL CH_3CN was added into 50 mL flask, then $Zn(NO_3)_2 \cdot 4H_2O$ (1.4 mg, 0.0047 mmol) in 2 mL CH_3OH was added. The solution was stirred at 85 ℃ for 10 hours. Followed by counterion exchange with NH_4PF_6 and washed with copious amounts of MeOH, then dried *in vacuo* to give **H** as a red solid. Yield: (11.5 mg, 95%). ^{1}H NMR (500 MHz, CD_3CN): *δ* (ppm) 8.97 (s, 8H), 8.95 (s, 8H), 8.94 (s, 8H), 8.79 (s, 4H), 8.68 (d, 8H), 8.60 (m, 20H), 8.14 (m, 24H), 8.08 (t, 8H), 7.94 (m, 8H), 7.85 (m, 16H), 7.78 (dd, 8H), 7.63 (m, 28H), 7.49 (d, 4H), 7.36 (tt, 16H), 7.32 (t, 8H), 7.21 (s, 4H), 7.20 (s, 4H), 7.07 (m, 20H), 4.13 (s,

6H), 4.00 (s, 12H),and 3.82 (s, 12H). ESI-MS (*m/z*): 1810.611 $[M\text{-}4PF_6^-]^{4+}$ (calcd. *m/z* = 1810.509), 1419.513 $[M\text{-}5PF_6^-]^{5+}$ (calcd. *m/z* = 1419.414), 1158.850 $[M\text{-}6PF_6^-]^{6+}$ (calcd. *m/z* = 1158.685), 972.474 $[M\text{-}7PF_6^-]^{7+}$ (calcd. *m/z* = 972.449), 832.809 $[M\text{-}8PF_6^-]^{8+}$ (calcd. *m/z* = 832.772), 724.160 $[M\text{-}9PF_6^-]^{9+}$ (calcd. *m/z* = 724.135), and 637.260 $[M\text{-}10PF_6^-]^{10+}$ (calcd. *m/z* = 637.225).

R: L (11.2 mg, 0.0033 mmol), **T** (3.6 mg, 0.0033 mmol) and 10 mL CH_3CN was added into 50 mL flask, then $Zn(NO_3)_2 \cdot 4H_2O$ (2.9 mg, 0.0099 mmol) in 2 mL CH_3OH was added. The solution was stirred at 85 ℃ for 10 hours. Followed by counterion exchange with NH_4PF_6 and washed with copious amounts of MeOH, then dried *in vacuo* to give **R** as a red solid. Yield: (17.7 mg, 97%). ^1H NMR (500 MHz, CD_3CN): δ (ppm) 9.02 (s, 4H), 9.01 (s, 4H), 9.00 (s, 4H), 8.97 (s, 4H), 8.76 (s, 2H), 8.73 (s, 2H), 8.71 (m, 8H), 8.65 (m, 8H), 8.60 (d, 2H), 8.58 (d, 2H), 8.04-8.17 (m, 24H), 7.82-7.92 (m, 24H), 7.69 (m, 4H), 7.62-7.66 (m, 16H), 7.40-7.47 (m, 12H), 7.37 (t, 4H), 7.32 (t, 4H), 7.28 (s, 2H), 7.27 (s, 2H), 7.14-7.20 (m, 8H), 7.10 (t, 4H), 4.20 (s, 3H), 4.17 (s, 3H), 4.05 (ss, 12H), 3.90 (s, 6H), and 3.87 (s, 6H). ESI-MS (*m/z*): 1699.243 $[M\text{-}3PF_6^-]^{3+}$ (calcd. *m/z* = 1699.917), 1238.669 $[M\text{-}4PF_6^-]^{4+}$ (calcd. *m/z* = 1238.697), 961.789 $[M\text{-}5PF_6^-]^{5+}$ (calcd. *m/z* = 961.964), 777.511 $[M\text{-}6PF_6^-]^{6+}$ (calcd. *m/z* = 777.476), 645.730 $[M\text{-}7PF_6^-]^{7+}$ (calcd. *m/z* = 645.699), 546.766 $[M\text{-}8PF_6^-]^{8+}$ (calcd. *m/z* = 546.866) and 469.967 $[M\text{-}9PF_6^-]^{9+}$ (calcd. *m/z* = 469.996).

Reference:

S1. J.-L. Wang, X. P. Li, X. C. Lu, I-F. Hsieh, Y. Cao, C. N. Moorefield, C. Wesdemiotis, S. Z. D. Cheng and G. R. Newkome, *J. Am. Chem. Soc.*, 2011, **133**, 11450.

S2. A. Bugarin, B. T. Connell, *Organometallics* 2008, **27**, 4357.

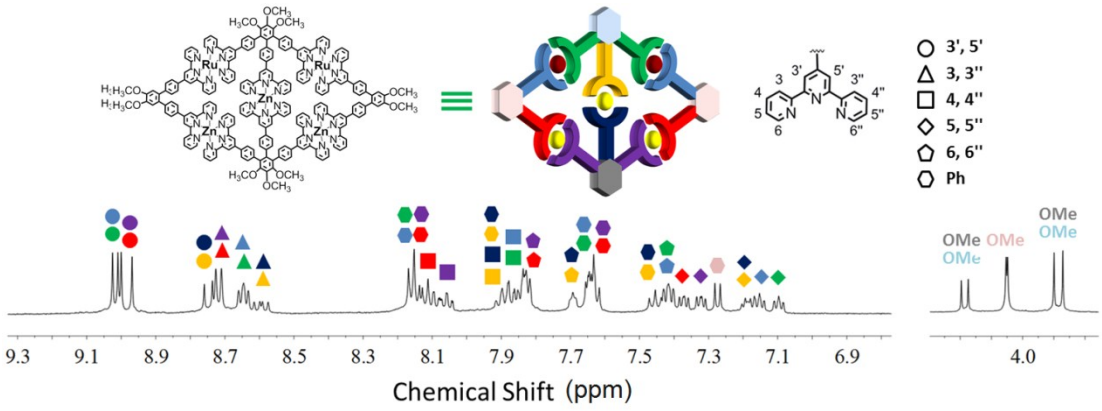


Figure S1. ^{1}H NMR spectra (500 MHz) of Rhomboidal structure **R** in CD_3CN at 298 K.

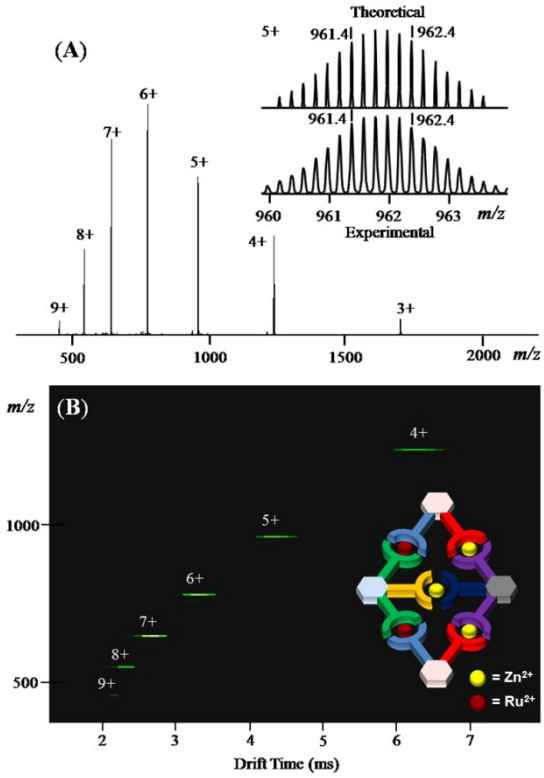


Figure S2. A) Illustration of ESI mass spectrum of **R**; B) 2D ESI-TWIM-MS plots (*m/z* vs drift time) for **R**. The charge states of intact assemblies are marked.

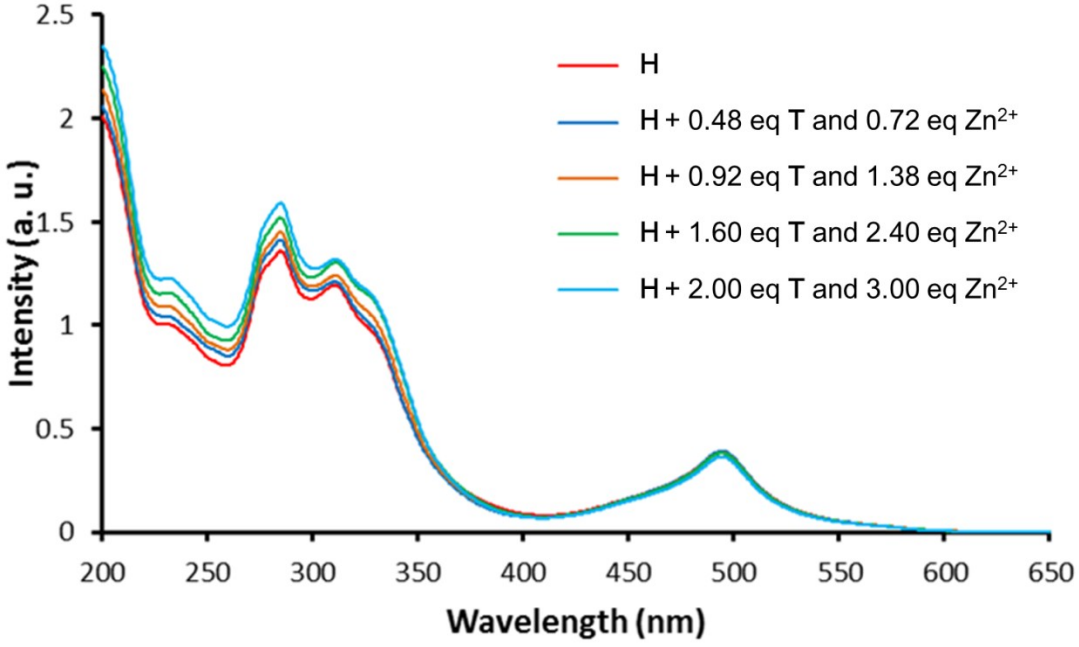


Figure S3. UV-vis spectra of helical structure **H** with (a) 0.00; (b) 0.48 eq **T** and 0.72 eq Zn^{2+}; (c)

0.92 eq **T** and 1.38 eq Zn^{2+}; (d) 1.60 eq **T** and 2.40 eq Zn^{2+}; (e) 2.00 eq **T** and 3.00 eq Zn^{2+}.

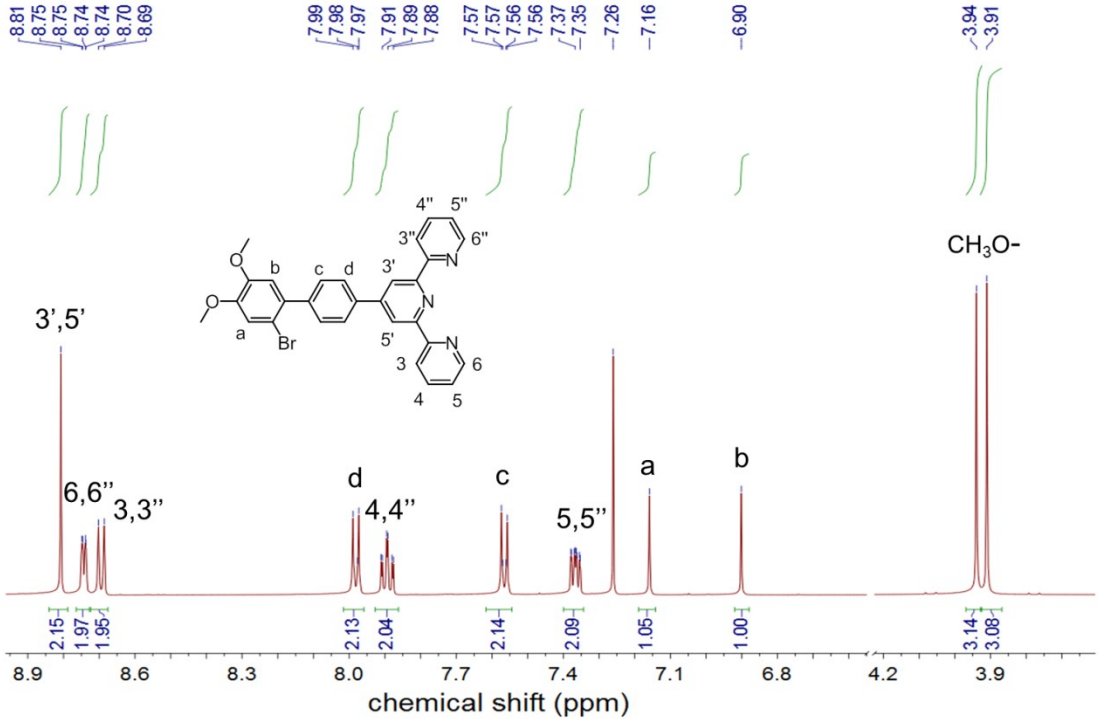


Figure S4. ^{1}H NMR spectrum of **1** in $CDCl_3$.

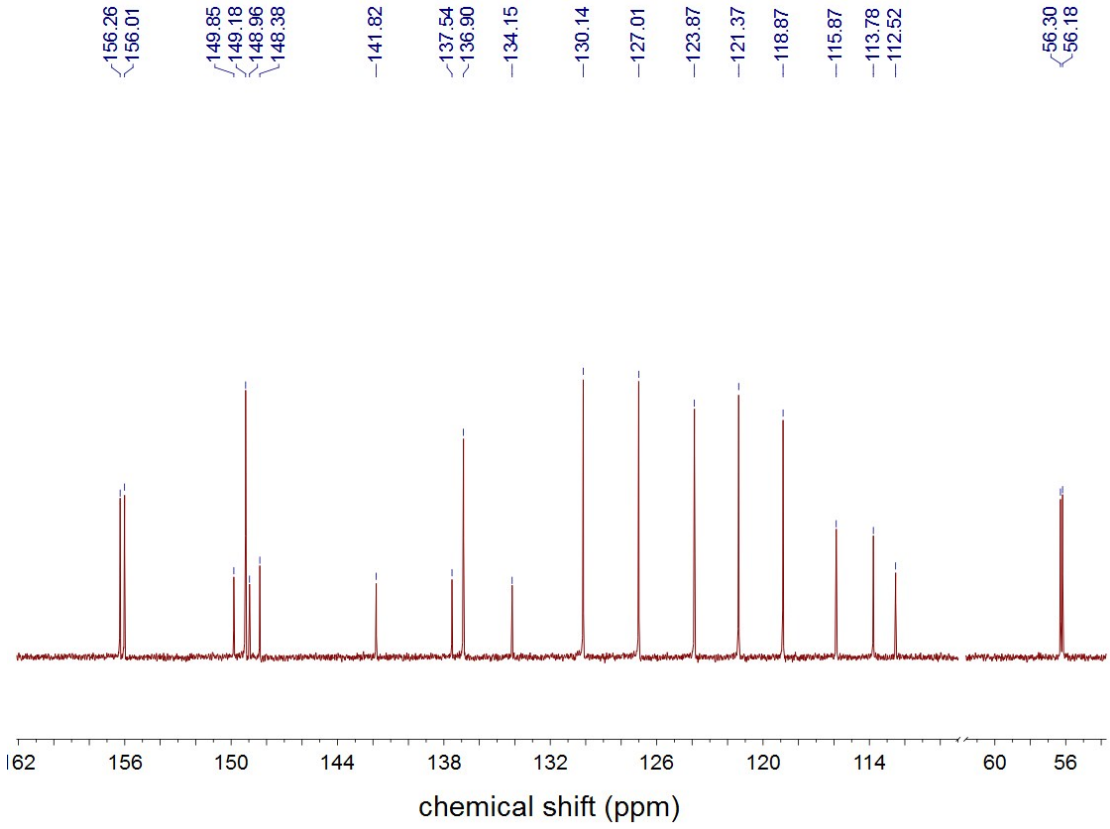


Figure S5. ^{13}C NMR spectrum of **1** in $CDCl_3$.

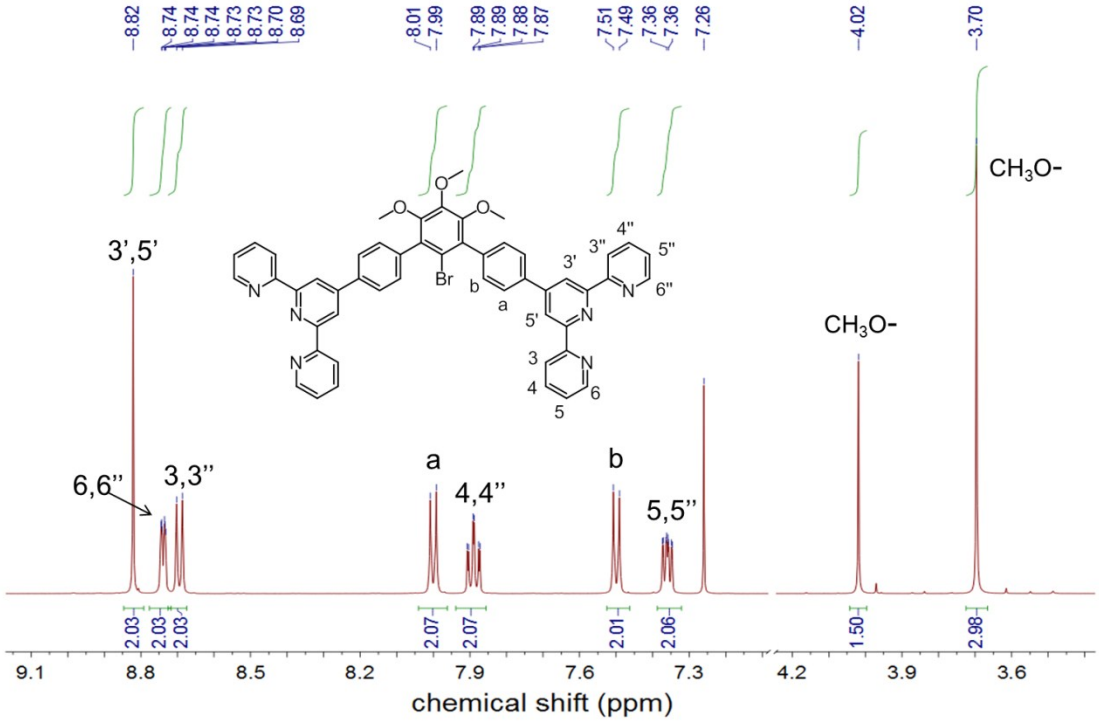


Figure S6. ^{1}H NMR spectrum of **4** in $CDCl_3$.

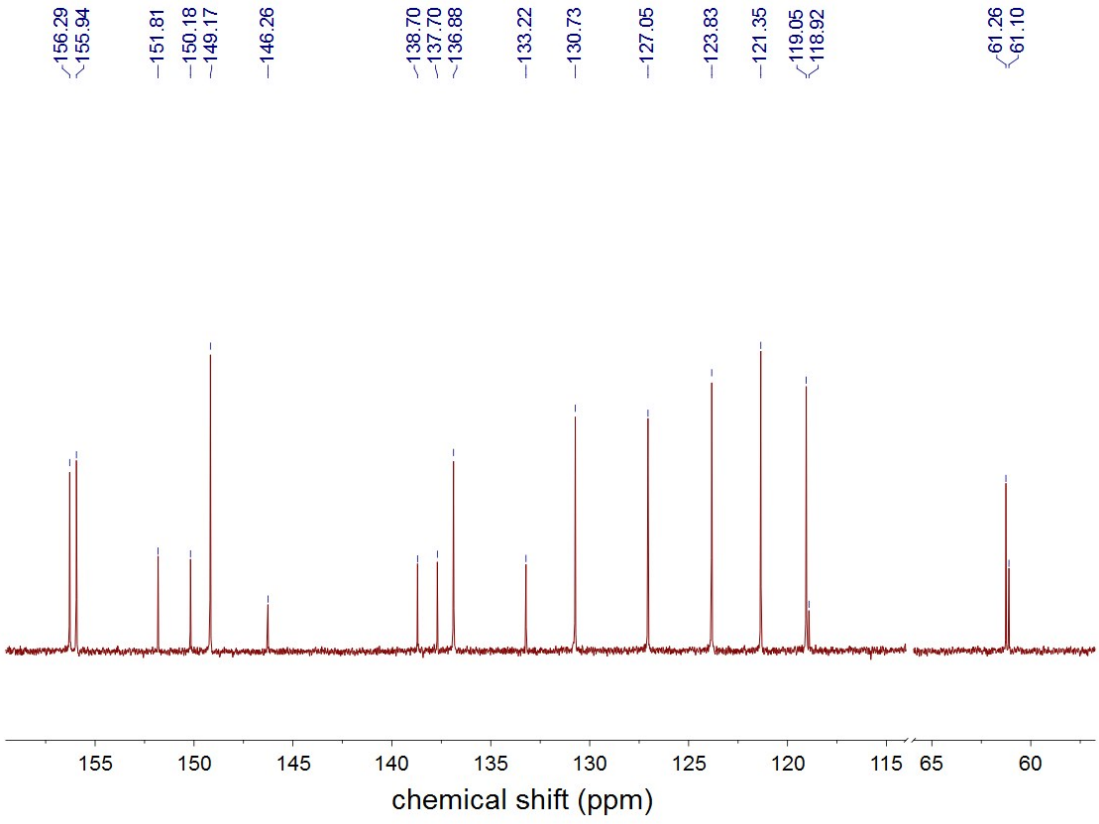


Figure S7. ^{13}C NMR spectrum of **4** in $CDCl_3$.

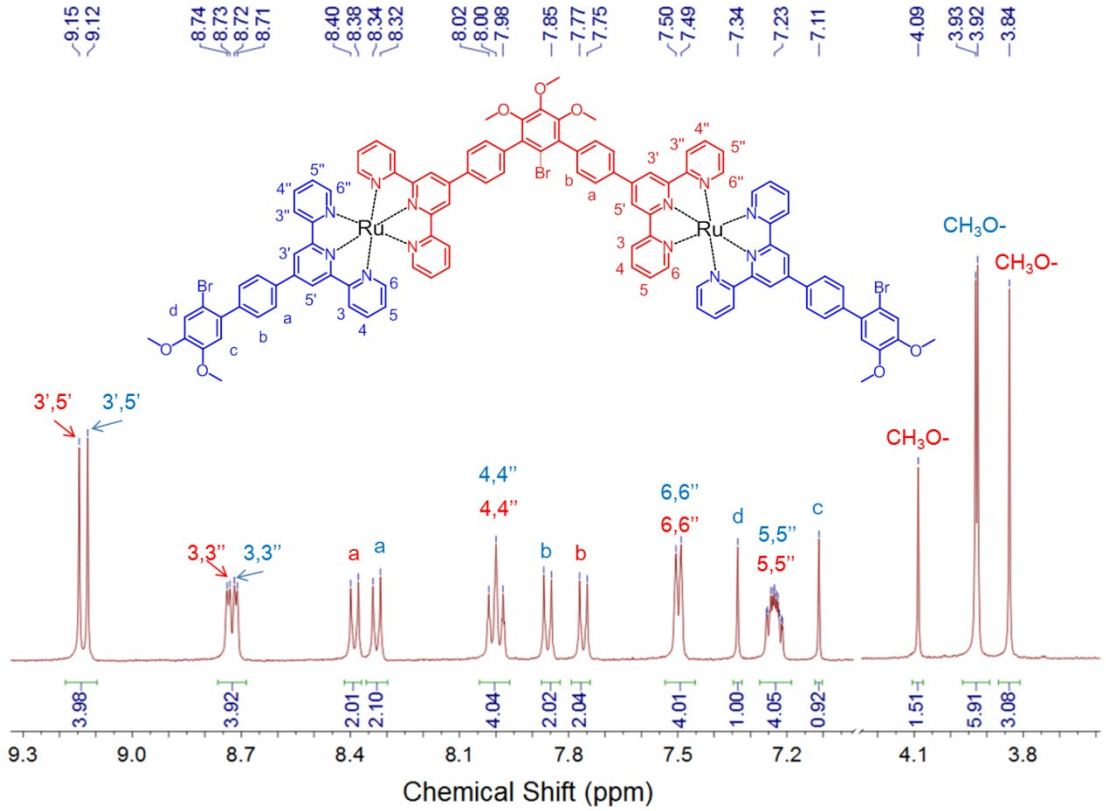


Figure S8. ^{1}H NMR spectrum of complex **C** in CD_3CN.

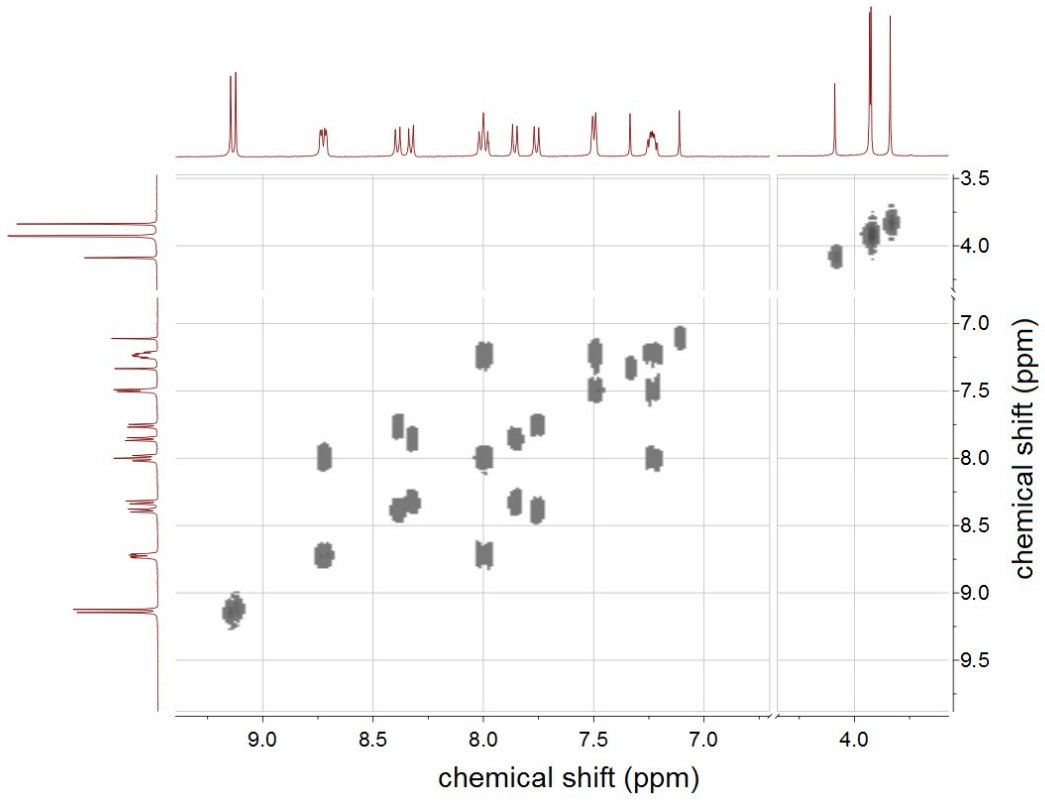


Figure S9. ^{1}H-^{1}H COSY spectrum of complex **C** in CD_3CN.

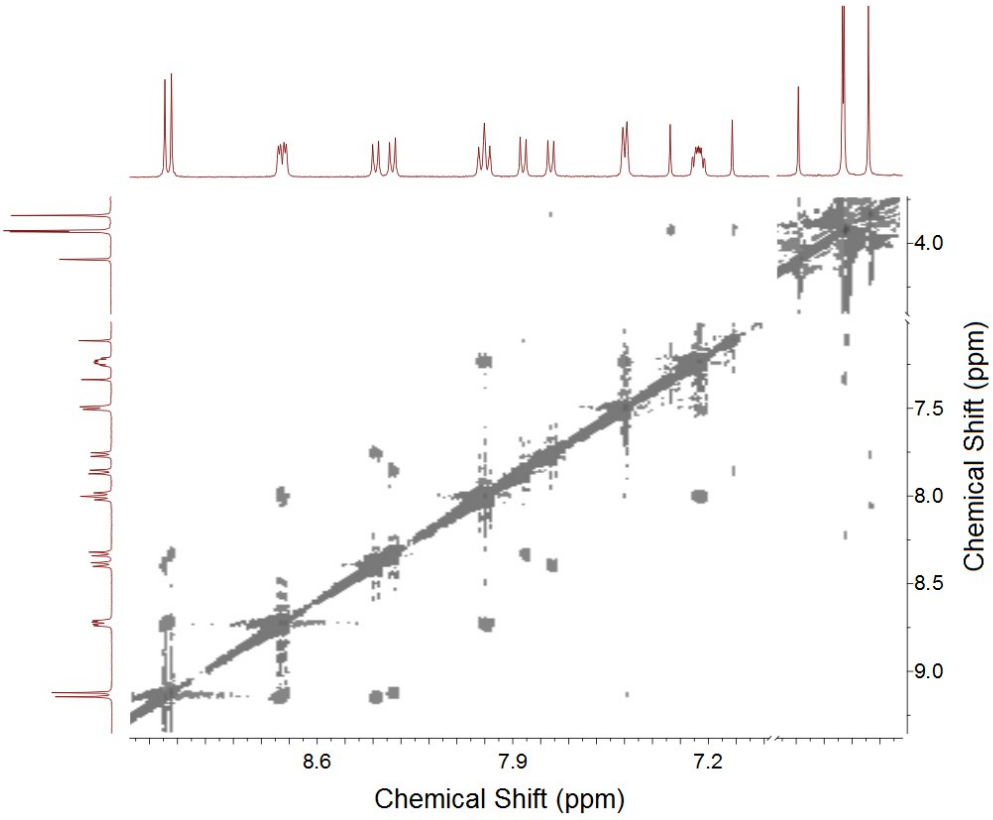


Figure S10. ^{1}H-^{1}H ROESY spectrum of complex **C** in CD_3CN.

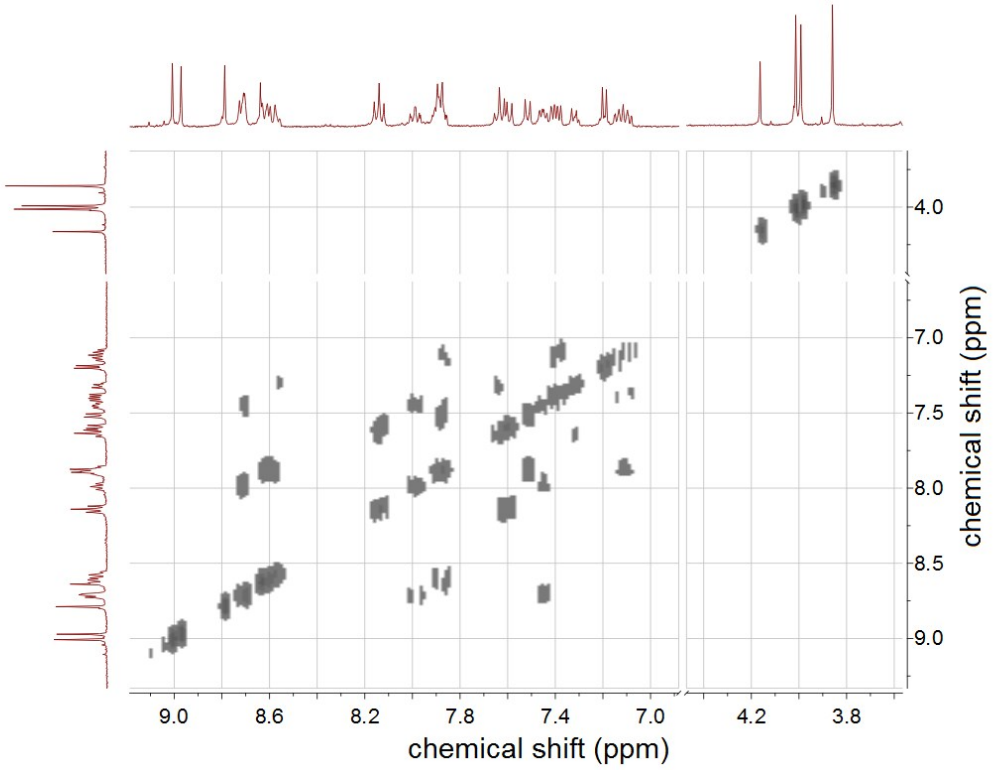


Figure S11. ^{1}H-^{1}H COSY spectrum of metal-organic ligand **L** in CD_3CN.

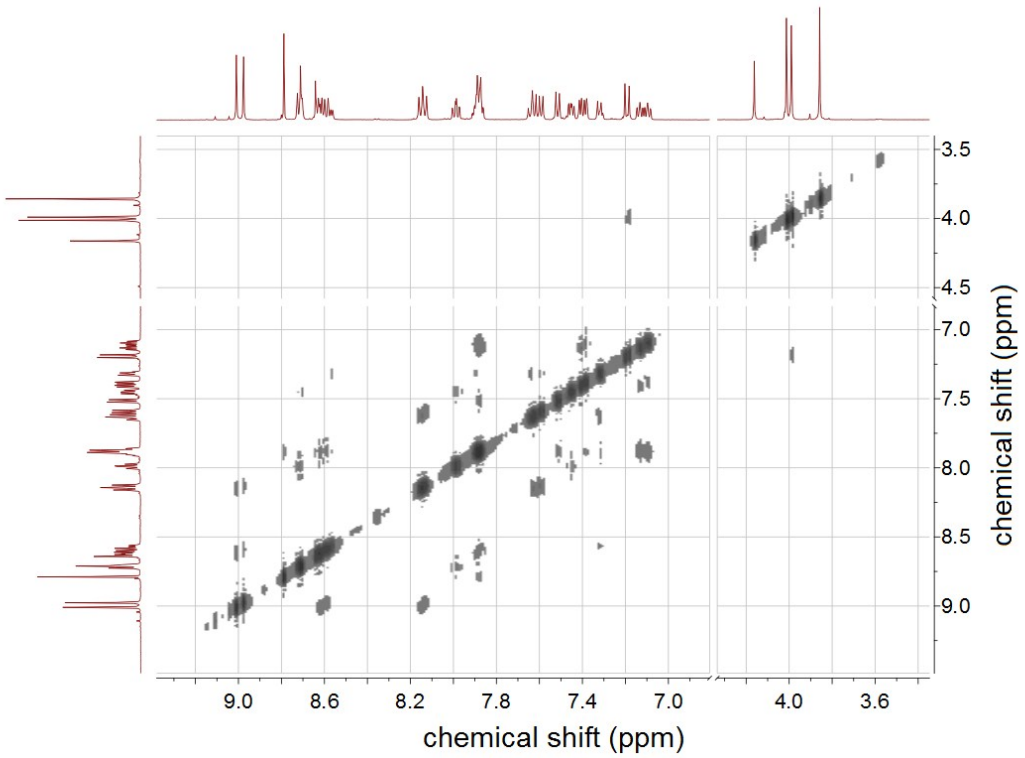


Figure S12. ^{1}H-^{1}H ROESY spectrum of metal-organic ligand **L** in CD_3CN.

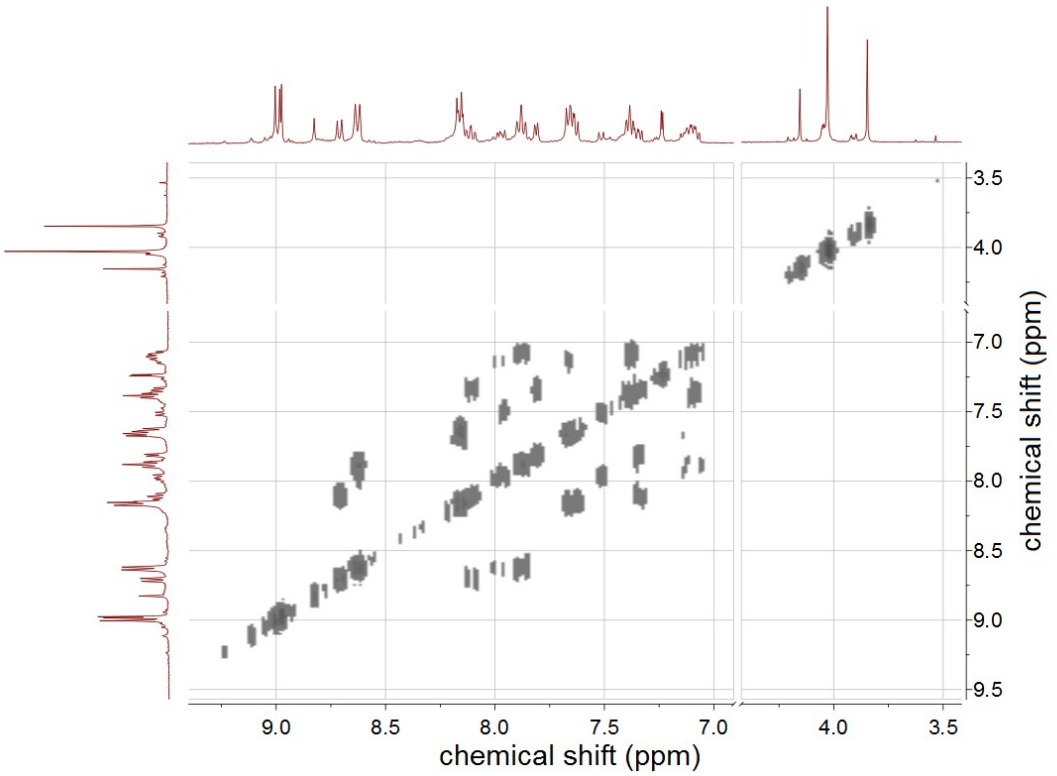


Figure S13. ^{1}H-^{1}H COSY spectrum of **H** in CD_3CN.

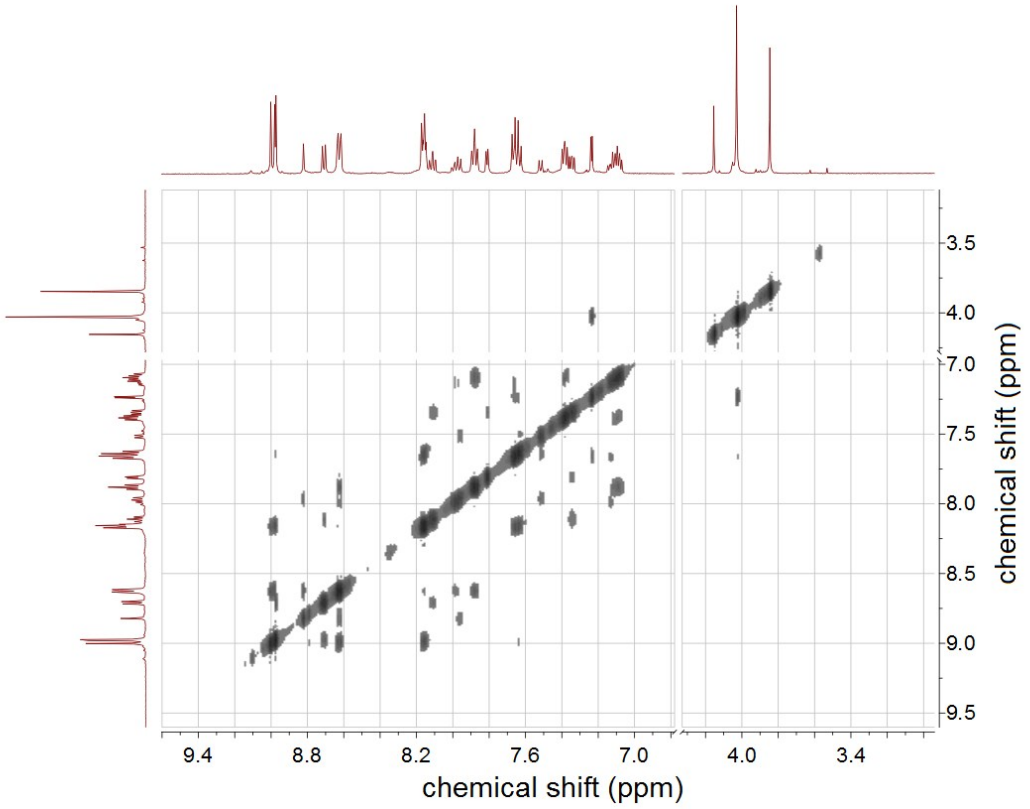


Figure S14. ^{1}H-^{1}H ROESY spectrum of **H** in CD_3CN.

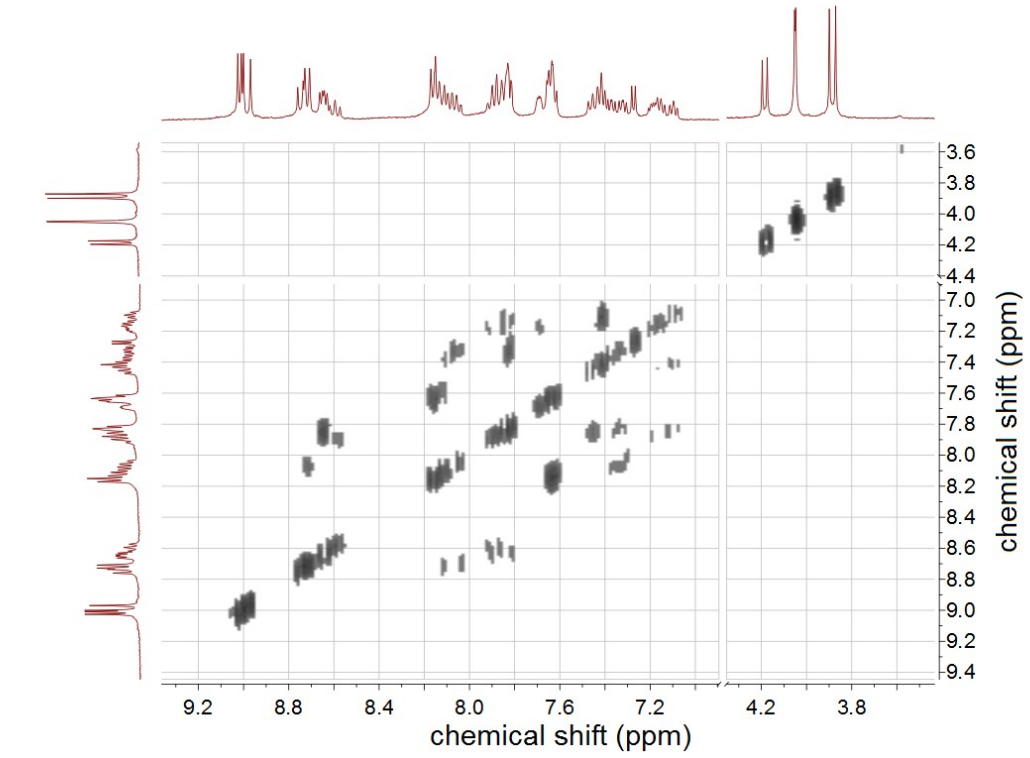


Figure S15. ^{1}H-^{1}H COSY spectrum of **R** in CD_3CN.

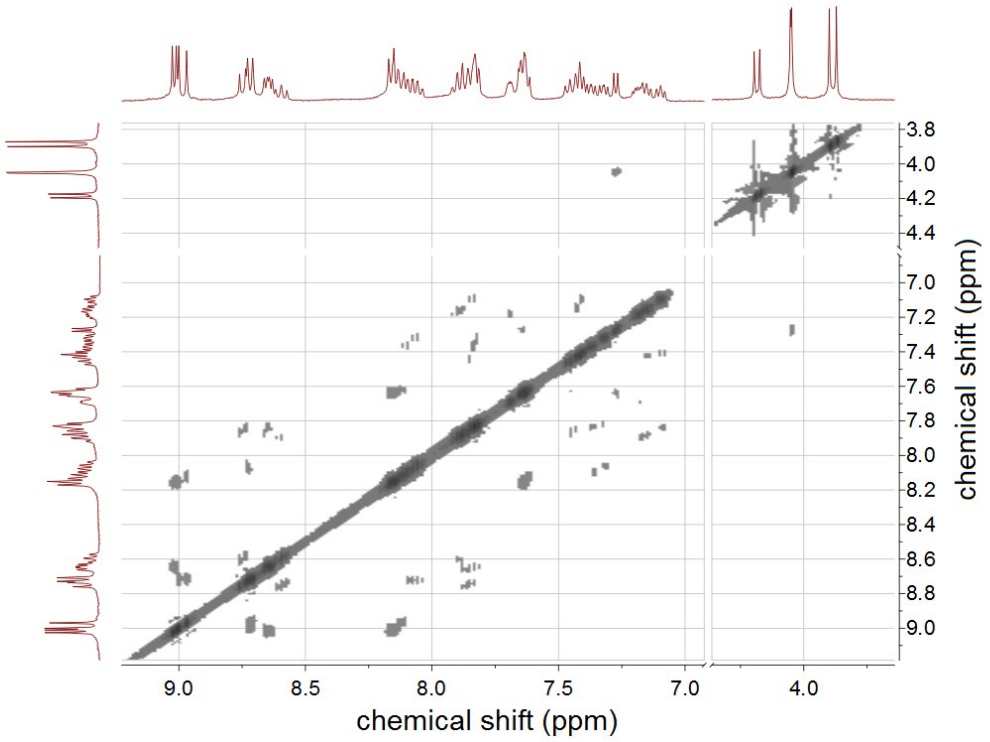


Figure S16. ^{1}H-^{1}H ROESY spectrum of **R** in CD_3CN.

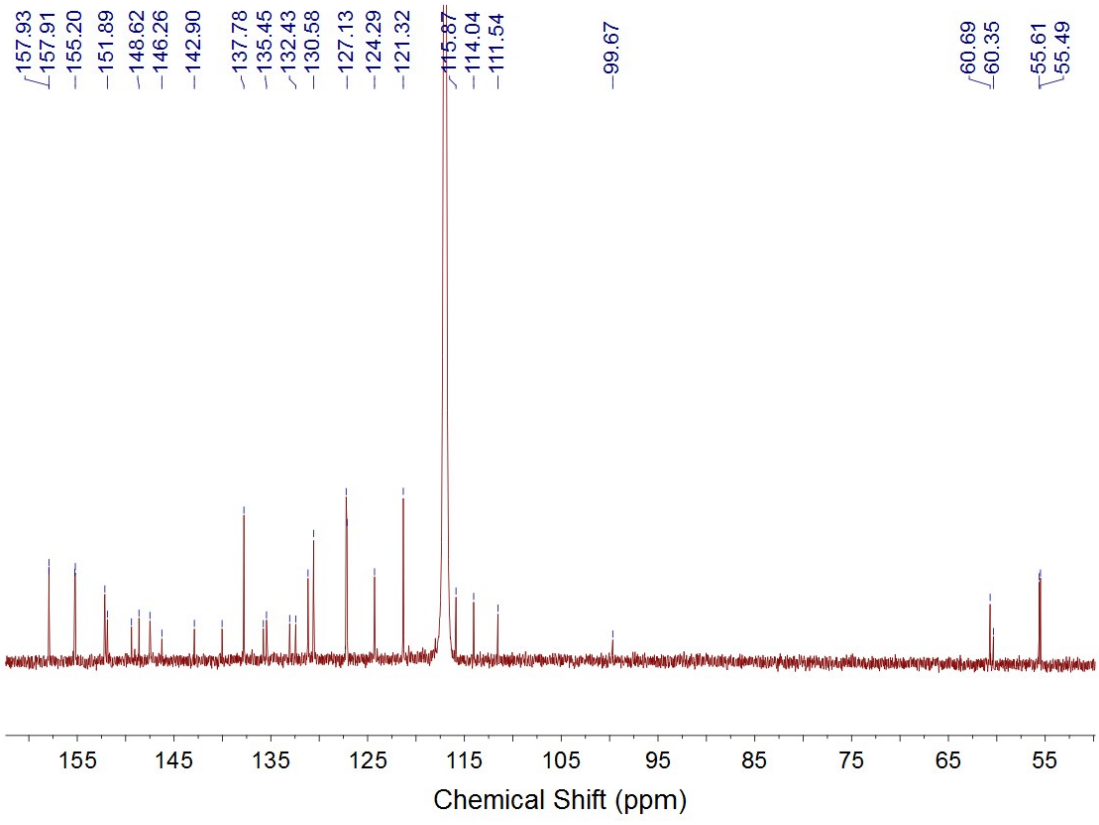


Figure S17. ^{13}C NMR spectrum of complex **C** in CD_3CN.