Supporting Information

Selective and quantitative synthesis of a linear [3]catenane by two component coordination-driven self-assembly

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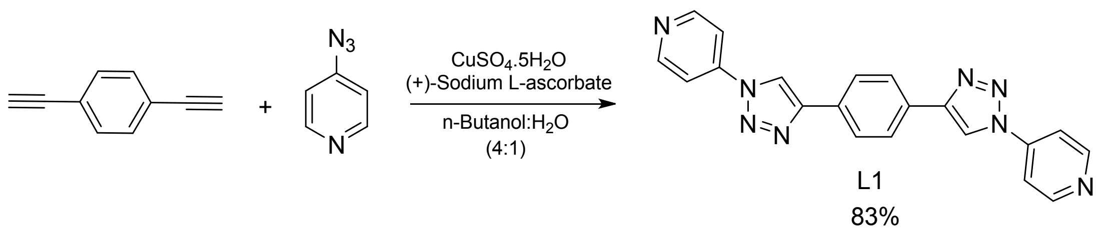
1. Materials and methods

Arene-ruthenium acceptors **A1** and **A2** were prepared according to the reported methods.[S1] Deuterated NMR solvents were purchased from Cambridge Isotope Laboratory (Andover, MA, USA). NMR spectra were recorded on Bruker 300, 400, 800 and 900 MHz spectrometers (University of Ulsan and Korea Basic Science Institute, Ochang). ^{1}H NMR chemical shifts are reported relative to the residual protons of deuterated CD_3OD (3.31 ppm) and deuterated CD_3NO_2 (4.33 ppm). ESI-MS data of all compounds were recorded on Synapt G2 quadrupole time-of flight (TOF) mass spectrometer equipped with an electrospray ion source (Waters, Milford, MA, USA) and analyzed with the MassLynx software suite system at the Korea Basic Science Institute, Ochang).

Single crystal X-ray diffraction

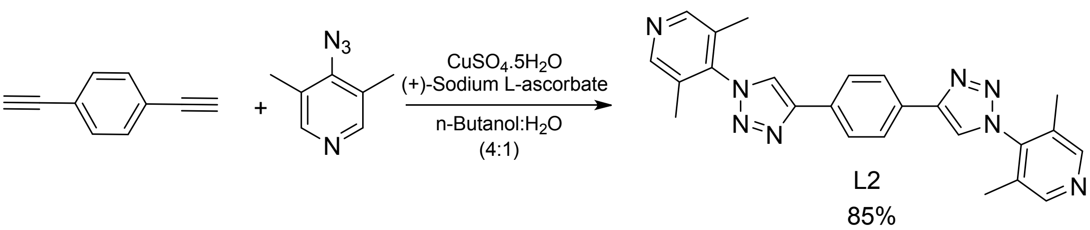
Diffraction data of **2** was collected at 100 K on an ADSC Quantum 210 CCD diffractometer with synchrotron radiation (λ = 0.70000 Å) at the Supramolecular Crystallography Beamline 2D, Pohang Accelerator Laboratory (PAL), Pohang, Korea. The raw data were processed and scaled using the program HKL3000. The structure was solved by direct methods, and the refinements were carried out with full-matrix least-squares on F^2 with appropriate software implemented in the SHELXTL program package.[S2] All the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added to their geometrically ideal positions. The contributions of the most disordered solvent molecules were removed from the diffraction data using the SQUEEZE routine of PLATON software,[S3] and then final refinements were carried out. X-ray crystallographic data is provided in Table S1.

Synthesis of ligand L1 [1,4-bis(1-(pyridin-4-yl)-1H-1,2,3-triazol-4-yl)benzene]



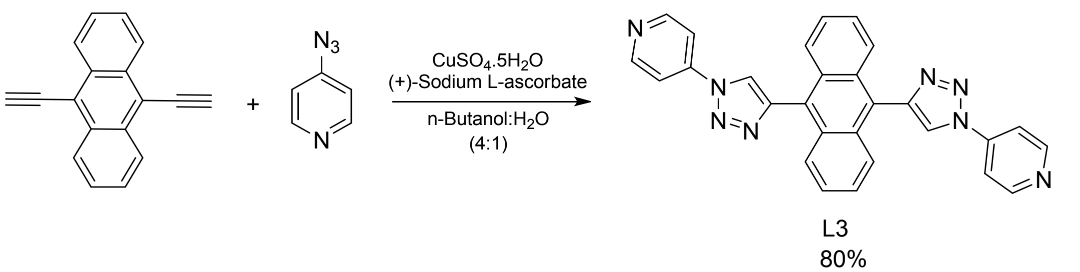
4-Azidopyridine (10.56 mg, 0.088 mmol), 1,4-bis(ethynyl)benzene (50.0 mg, 0.040 mmol), $CuSO_4{\cdot}5H_2O$ (0.53 mg, 0.002 mmol) and (+)-sodium L-ascorbate (0.85 mg, 0.004 mmol) were added to a 4:1 (v/v) solution of n-butanol and water and stirred at 50^{o}C for 24 h. The precipitated product was filtered and washed several times with methanol and water. The pale yellow powder obtained was characterized as ligand **L1**. Yield: (41.5 mg, Yield: 83 %), Mp: > 300 ℃. Anal. Calcd for $C_{20}H_{14}N_8$: C, 65.56; H, 3.85; N, 30.58. Found: C, 65.44; H, 3.86; N, 30.47. ^{1}H NMR (400 MHz, CF_3COOD) δ 8.63 (dd, *J* = 4.6, 1.6 Hz, 2H), 7.73 (s, 1H), 7.50 (dd, *J* = 4.6, 1.6 Hz, 2H); ^{13}C NMR (100 MHz, CF_3COOD) δ 150.55, 142.97, 142.48, 141.31, 131.55, 119.51, 118.93; ESI-HRMS calcd for $C_{20}H_{15}N_8$ (**L1**+H^+): 367.1420; found 367.1420.

Synthesis of ligand L2 [1,4-bis(1-(3,5-dimethylpyridin-4-yl)-1H-1,2,3-triazol-4-yl)benzene]



4-Azido-3,5-dimethylpyridine (12.84 mg, 0.088 mmol), 1,4-bis(ethynyl)benzene (50.0 mg, 0.040 mmol), $CuSO_4{\cdot}5H_2O$ (0.53 mg, 0.002 mmol) and (+)-sodium L-ascorbate (0.85 mg, 0.004 mmol) were added to a 4:1 (v/v) solution of n-butanol and water and stirred at 50°C for 24 h. The precipitated product was filtered and washed several times with methanol and water. The pale yellow powder obtained was characterized as ligand **L2**. Yield: (42.3 mg, Yield: 85 %), Mp: 286 ℃ (dec.) Anal. Calcd for $C_{24}H_{22}N_8$: C, 68.23; H, 5.25; N, 26.52. Found: C, 68.01; H, 5.26; N, 26.42. ^{1}H NMR (400 MHz, CD_3OD+$CDCl_3$ (1:1)) δ 8.54 (s, 2H), 8.46 (s, 2H), 8.07 (s, 4H), 2.20 (s, 12H); ^{13}C NMR (100 MHz, CD_3OD+$CDCl_3$ (1:1)) δ 150.12, 148.35, 144.02, 131.08, 130.60, 127.05, 122.65, 14.62; ESI-HRMS calcd for $C_{24}H_{23}N_8$ (**L2**+H^+): 423.2046; found 423.2040.

Synthesis of ligand L3 [9,10-bis(1-(pyridin-4-yl)-1H-1,2,3-triazol-4-yl)anthracene]



4-Azidopyridine (11.35 mg, 0.094 mmol), 1,4-bis(ethynyl)anthracene (20.0 mg, 0.043 mmol), $CuSO_4{\cdot}5H_2O$ (0.53 mg, 0.002 mmol) and (+)-sodium L-ascorbate (0.85 mg, 0.004 mmol) were added to a 4:1 (v/v) solution of n-butanol and water and stirred at 50°C for 24 h. The precipitated product was filtered and washed several times with methanol and water. The light brown powder obtained was characterized as ligand

L3. Yield: (16 mg, Yield: 80 %), Mp: > 300 ℃. Anal. Calcd for $C_{28}H_{18}N_8$: C, 72.09; H, 3.89; N, 24.02. Found: C, 71.81; H, 3.90; N, 23.95. ^{1}H NMR (400 MHz, CD_3OD+$CDCl_3$ (1:1)) δ 9.01 (s, 2H), 8.85 (d, *J* = 6.3 Hz, 4H), 8.18 (dd, *J* = 4.7, 1.6 Hz, 4H), 7.90 (dd, *J* = 6.8, 3.2 Hz, 4H), 7.52 (dd, *J* = 6.8, 3.2 Hz, 4H); ^{13}C NMR (100 MHz, CD_3OD+$CDCl_3$ (1:1)) δ 151.87, 145.80, 140.24, 134.39, 131.60, 127.40, 126.53, 126.22, 114.88; ESI-HRMS calcd for $C_{28}H_{19}N_8$ (**L3**+H^+): 467.1733; found 467.1727.

2. Coordination-driven self-assembly of 1, 2, 4, 5, 6 and 7

Coordination-driven self-assembly of monoreactangle 1

The arene-Ru(II) acceptor **A1** (1.91 mg, 2.0 μmol) and donor **L1** (0.73 mg, 2.0 μmol) were stirred in CD_3OD (4.0 mL) at room temperature for 12 h to produce a green solution. ^{1}H NMR (900 MHz, CD_3OD) δ 8.93 (s, 4H), 8.60 (d, *J* = 6.3 Hz, 8H), 7.96 (d, *J* = 5.4 Hz, 8H), 7.82 (s, 8H), 7.33 (s, 8H), 5.90 (d, *J* = 6.0 Hz, 8H), 5.67 (d, *J* = 6.0 Hz, 8H), 2.87 (dt, *J* = 14.0, 7.0 Hz, 4H), 2.15 (s, 12H), 1.37 (d, *J* = 7.0 Hz, 24H); ^{13}C NMR (225 MHz, CD_3OD) δ 170.95, 153.46, 148.17, 145.06, 137.32, 129.47, 125.81, 118.26, 115.09, 111.32, 103.67, 99.79, 84.40, 82.59, 30.64, 21.08, 15.99; ESI-MS for **1** ($C_{104}H_{92}F_{12}N_{16}O_{20}Ru_4S_4$): m/z = 733.4337 [**1**-3OTf]$^{3+}$.

Coordination-driven self-assembly of 2

The arene-Ru(II) acceptor **A1** (16.9 mg, 20 μmol) and donor **L1** (7.33 mg, 20 μmol) were stirred in CD_3OD (1.0 mL) at room temperature for 12 h to produce a dark green solution. The products were precipitated and isolated by dropwise addition of diethyl ether into this solution, and washed twice with diethyl ether using centrifugation method. The dark-green powder was characterized as **2**. Yield: (22.6 mg, Yield: 93 %), Anal. Calcd for $C_{312}H_{276}F_{36}N_{48}O_{60}Ru_{12}S_{12}\cdot 2H_2O$: C 46.99; H 3.54; N 8.58. Found: C 46.82; H 3.55; N 8.55. ^{1}H NMR (900 MHz, CD_3OD) δ 9.24 (s, 2H), 9.13 (s, 2H), 8.77 (s, 2H), 8.75 (s, 6H), 8.69 (s, 12H), 8.43 (s, 8H), 8.24 (s, 4H), 8.20 (s, 2H), 8.17 (s, 5H), 8.14 (s, 3H), 8.07 (s, 4H), 7.94 (s, 10H), 7.76 (s, 8H), 7.72 (s, 4H), 7.64 (s, 4H), 7.59 (d, *J* = 13.0 Hz, 2H), 7.52 (s, 6H), 7.49 (d, *J* = 12.4 Hz, 2H), 7.43 (d, *J* = 12.9 Hz, 8H), 7.40 (d, *J* = 9.9 Hz, 6H), 7.17 (s, 8H), 6.11 (s, 4H), 6.05 (d, *J* = 5.3 Hz, 2H), 6.01 (s, 3H), 5.97 (d, *J* = 10.2 Hz, 7H), 5.93 (s, 4H), 5.90 (s, 3H), 5.86 (s, 5H), 5.81 (s, 3H), 5.76 (d, *J* = 13.9 Hz, 5H), 5.70 (s, 4H), 5.67 (s, 3H), 5.59 (s, 5H), 3.26 – 3.20 (m, 2H), 3.09 (dt, *J* = 13.4, 6.5 Hz, 2H), 2.96 (s, 2H), 2.91 (s, 2H), 2.89 – 2.83 (m, 4H), 2.51 (s, 4H), 2.45 (d, *J* = 12.7 Hz, 3H), 2.39 (d, *J* = 11.5 Hz, 8H), 2.28 (d, *J* = 18.0 Hz, 4H), 2.23 (d, *J* = 12.9 Hz, 6H), 2.22 – 2.19 (m, 3H), 2.18 (s, 4H), 2.15 (s, 3H), 2.12 (s, 5H), 2.05 (s, 8H), 1.62 (s, 2H), 1.60 (s, 3H), 1.56 (s, 8H), 1.53 (s, 3H), 1.51 (d, *J* = 5.6 Hz, 6H), 1.48 (d, *J* = 5.2 Hz, 6H), 1.43 (s, 16H), 1.39 (s, 15H), 1.35 (s, 18H), 1.31 (d, *J* = 9.3 Hz, 10H), 1.25 (s, 5H), 1.13 (s, 4H); ^{13}C NMR (225 MHz, CD_3OD) δ 171.63, 171.38, 171.14, 170.96, 170.76, 153.56, 153.34, 147.97, 147.63, 147.49, 147.16, 147.05, 146.64, 146.15, 145.26, 145.12, 144.89, 144.13, 143.86, 143.57, 138.90, 138.68, 138.48, 137.56, 137.37, 134.72, 129.48, 129.39, 128.95, 128.87, 128.83, 128.67, 128.46, 125.93, 125.76, 125.59, 125.23, 125.07, 124.72, 124.25, 122.58, 121.17, 119.76, 118.35, 117.14, 115.52, 115.34, 114.19, 113.27, 111.33, 111.31, 111.23, 111.20, 111.13, 111.11, 104.50, 104.05, 103.68, 103.58, 103.46, 99.89, 99.55, 99.45, 98.64, 84.61, 84.51, 84.36, 83.30, 82.64, 82.43, 35.13, 34.40, 33.54, 31.65, 30.87, 30.71, 30.62, 30.55, 30.25, 29.42, 29.19, 29.04, 28.91, 28.83, 26.72, 25.51, 23.15, 22.33, 21.88, 21.50, 21.44, 21.24, 21.18, 21.10, 21.06, 20.62, 19.61, 18.61, 17.90, 16.70, 16.35, 16.03, 15.93; ESI-MS for **2** ($C_{312}H_{276}F_{36}N_{48}O_{60}Ru_{12}S_{12}$): m/z = 1835.9700 [**2**-4OTf]$^{4+}$, 1438.9819 [**2**-5OTf]$^{5+}$.

Coordination-driven self-assembly of 4

The arene-Ru(II) acceptor **A1** (7.65 mg, 8.0 μmol) and donor **L2** (3.38 mg, 8.0 μmol) were stirred in CD_3OD (1.0 mL) at room temperature for 12 h to produce a dark brown solution. The products were precipitated and isolated by dropwise addition of diethyl ether into this solution, and washed twice with diethyl ether using centrifugation method. The dark-green powder was characterized as **4**. Yield: (9.9 mg, Yield: 90%), Anal. Calcd for $C_{112}H_{108}F_{12}N_{16}O_{20}Ru_4S_4\cdot 2H_2O$: C, 48.13; H, 4.04; N, 8.02. Found: C, 48.07; H, 4.05; N, 8.02. ^{1}H NMR (400 MHz, CD_3OD) δ 8.63 (s, 4H), 8.48 (s, 8H), 8.15 (s, 8H), 7.31 (s, 8H), 5.93 (d, *J* = 6.4 Hz, 8H), 5.70 (d, *J* = 6.3 Hz, 8H), 2.88 (dt, *J* = 13.6, 6.9 Hz, 4H), 2.15 (s, 12H), 2.09 (s, 24H), 1.35 (d, *J* = 6.9 Hz, 24H); ^{13}C NMR (100 MHz, CD_3OD) δ 172.53 (s), 153.38 (s), 149.41 (s), 148.37 (s), 139.01 (s), 135.07 (s), 131.56 (s), 127.92 (s), 127.12 (s), 112.93 (s), 105.34 (s), 101.82 (s), 86.31 (s), 84.24 (s), 32.35 (s), 22.81 (s), 17.77 (s), 15.07 (s). ESI-MS for **4** ($C_{112}H_{108}F_{12}N_{16}O_{20}Ru_4S_4$): m/z = 770.8080 [**4**-3OTf]$^{3+}$.

Coordination-driven self-assembly of 5

The arene-Ru(II) acceptor **A1** (7.65 mg, 8.0 μmol) and donor **L3** (3.73 mg, 8.0 μmol) were stirred in CD_3OD (1.0 mL) at room temperature for 12 h to produce a dark green solution. The products were precipitated and isolated by dropwise addition of diethyl ether into this solution, and washed twice with diethyl ether using centrifugation method. The dark-green powder was characterized as **5**. Yield: (10.4 mg, Yield: 91%), Anal. Calcd for $C_{120}H_{100}F_{12}N_{16}O_{20}Ru_4S_4\cdot 2H_2O$: C, 50.00; H, 7.91; N, 7.77. Found: C, 49.89; H, 7.91; N, 7.76. ^{1}H NMR (300 MHz, CD_3OD) δ 9.06 (s, 4H), 8.67 (d, *J* = 6.8 Hz, 8H), 8.11 (d, *J* = 6.8 Hz, 8H), 7.59 (dd, *J* = 6.9, 3.2 Hz, 8H), 7.29 (s, 8H), 6.95 (dd, *J* = 6.9, 3.2 Hz, 8H), 5.93 (d, *J* = 6.3 Hz, 8H), 5.70 (d, *J* = 6.3 Hz, 8H), 2.88 (dt, *J* = 13.7, 6.7 Hz, 4H), 2.14 (s, 12H), 1.36 (d, *J* = 6.9 Hz, 24H); ^{13}C NMR (75 MHz, CD_3NO_2) δ 172.62 (s), 155.24 (s), 146.65 (s), 146.37 (s), 138.71 (s), 131.97 (s), 127.67 (s), 127.10 (s), 125.03 (s), 117.06 (s), 112.94 (s), 105.14 (s), 101.09 (s), 85.62 (s), 84.25 (s), 32.05 (s), 22.49 (s), 17.58 (s). ESI-MS for **5** ($C_{120}H_{100}F_{12}N_{16}O_{20}Ru_4S_4$): m/z = 800.1315 [**5**-3OTf]$^{3+}$.

Coordination-driven self-assembly of 6

The arene-Ru(II) acceptor **A1** (7.65 mg, 8.0 μmol) and donor **L4** (2.24 mg, 8.0 μmol) were stirred in CD_3OD (1.0 mL) at room temperature for 12 h to produce a dark brown solution. The products were precipitated and isolated by dropwise addition of diethyl ether into this solution, and washed twice with diethyl ether using centrifugation method. The dark-green powder was characterized as **6**. Yield: (9.2 mg, Yield: 93%), ^{1}H NMR (300 MHz, CD_3OD) δ 8.42 (d, *J* = 6.7 Hz, 8H), 7.48 (s, 8H), 7.46 (d, J = 6.7 Hz, 8H), 7.24 (s, 8H), 5.85 (d, *J* = 6.3 Hz, 8H), 5.61 (d, *J* = 6.3 Hz, 8H), 2.82 (dt, *J* = 13.8, 6.9 Hz, 4H), 2.09 (s, 12H), 1.32 (d, *J* = 6.9 Hz, 24H); ^{13}C NMR (75 MHz, CD_3OD) δ 170.95 (s), 138.40 (s), 137.24 (s), 134.98 (s), 128.00 (s), 122.46 (s), 119.76 (s), 118.23 (s), 112.26 (s), 107.17 (s), 103.69 (s), 99.99 (s), 84.52 (s), 78.82 (s), 30.61 (s), 21.21 (s), 16.02 (s). ESI-MS for **6** ($C_{112}H_{108}F_{12}N_{16}O_{20}Ru_4S_4$): m/z = 676.0780 [**6**-3OTf]$^{3+}$.

Coordination-driven self-assembly of 7

The arene-Ru(II) acceptor **A2** (6.85 mg, 8.0 μmol) and donor **L1** (3.38 mg, 8.0 μmol) were stirred in CD_3OD (1.0 mL) at room temperature for 12 h to produce a yellow solution. The products were precipitated and isolated by dropwise addition of diethyl ether into this solution, and washed twice with diethyl ether using centrifugation method. The dark-green powder was characterized as **7**. Yield: (8.4 mg, Yield: 83 %), Anal. Calcd for $C_{88}H_{84}F_{12}N_{16}O_{20}Ru_4S_4 \cdot 2H_2O$: C, 42.58; H, 3.57; N,9.03. Found: C, 42.75; H, 3.59; N, 9.06. ^{1}H NMR (300 MHz, CD_3OD) δ 8.85 (s, 1H), 8.26 (d, *J* = 6.0 Hz, 2H), 7.96 (d, *J* = 6.0 Hz, 2H), 7.69 (s, 2H), 5.98 (d, *J* = 6.0 Hz, 2H), 5.81 (d, *J* = 5.9 Hz, 2H), 2.87 (dt, *J* = 13.6, 7.0 Hz, 1H), 2.26 (s, 3H), 1.39 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (75 MHz, CD_3OD) δ 154.35 (s), 148.55 (s), 147.32 (s), 125.89 (s), 114.89 (s), 103.20 (s), 102.53 (s), 99.99 (s), 97.61 (s), 82.06 (s), 81.52 (s), 31.10 (s), 21.07 (s), 16.65 (s); ESI-MS for **7** ($C_{88}H_{84}F_{12}N_{16}O_{20}Ru_4S_4$): m/z = 666.4131 [**7**-3OTf]$^{3+}$.

3. ^{1}H, ^{13}C NMR and ESI-MS spectra of L1 and L2

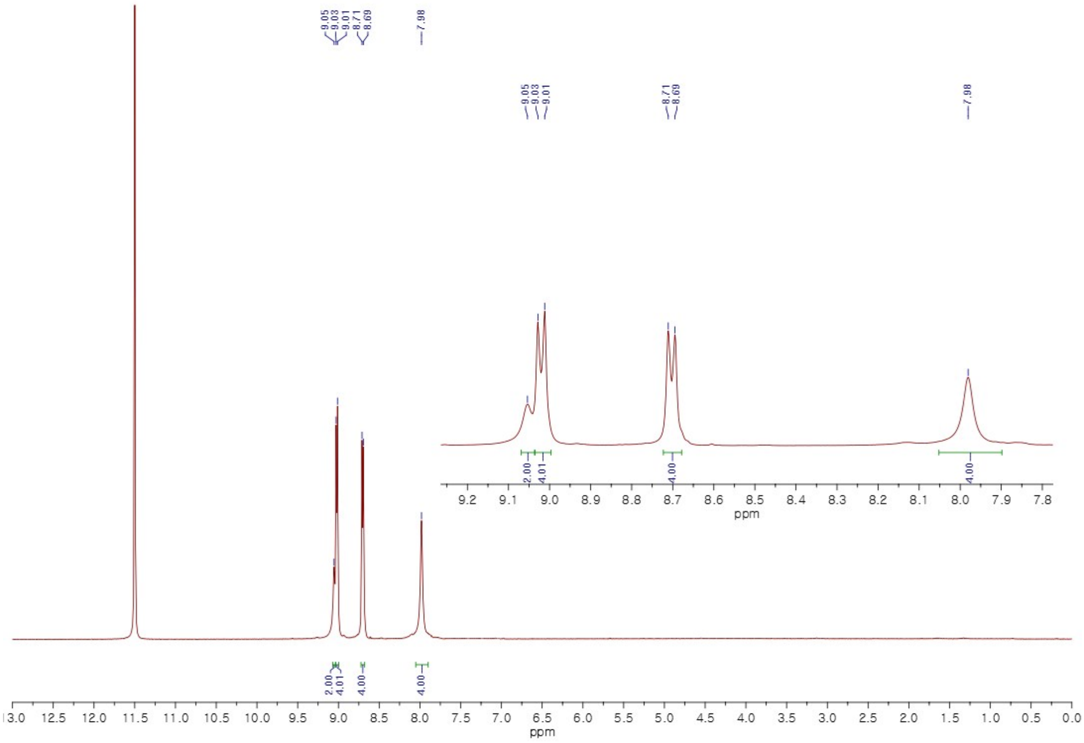


Figure S1. ^{1}H NMR spectrum of **L1** (CF_3COOD, 400 MHz)

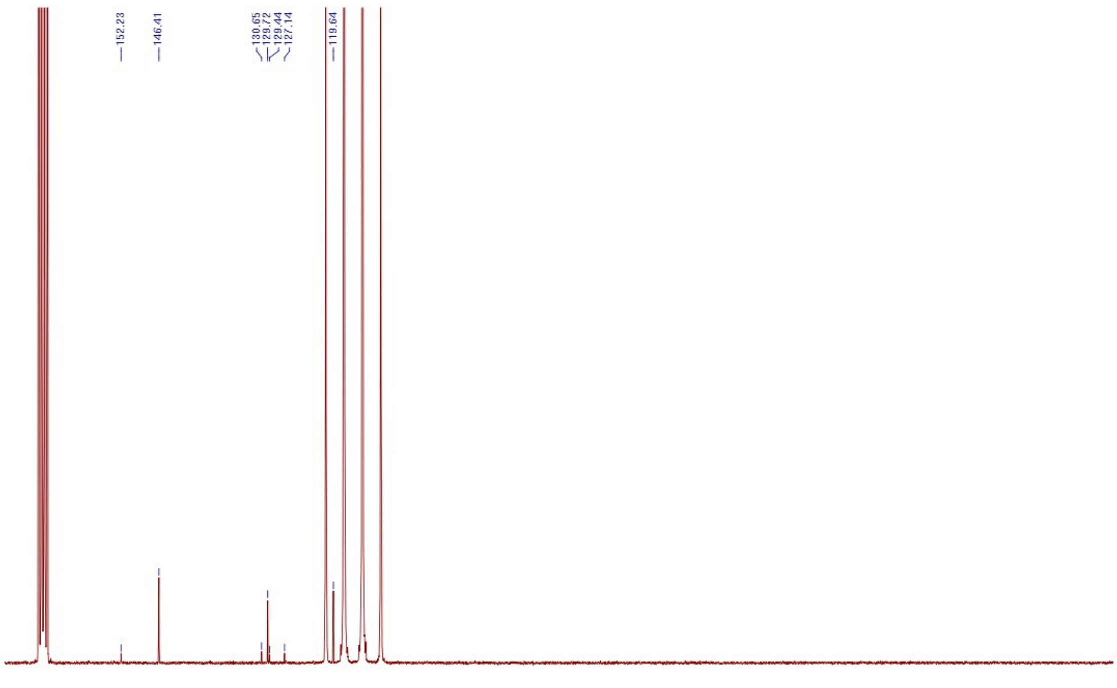


Figure S2. ^{13}C NMR spectrum of **L1** (CF_3COOD, 100 MHz)

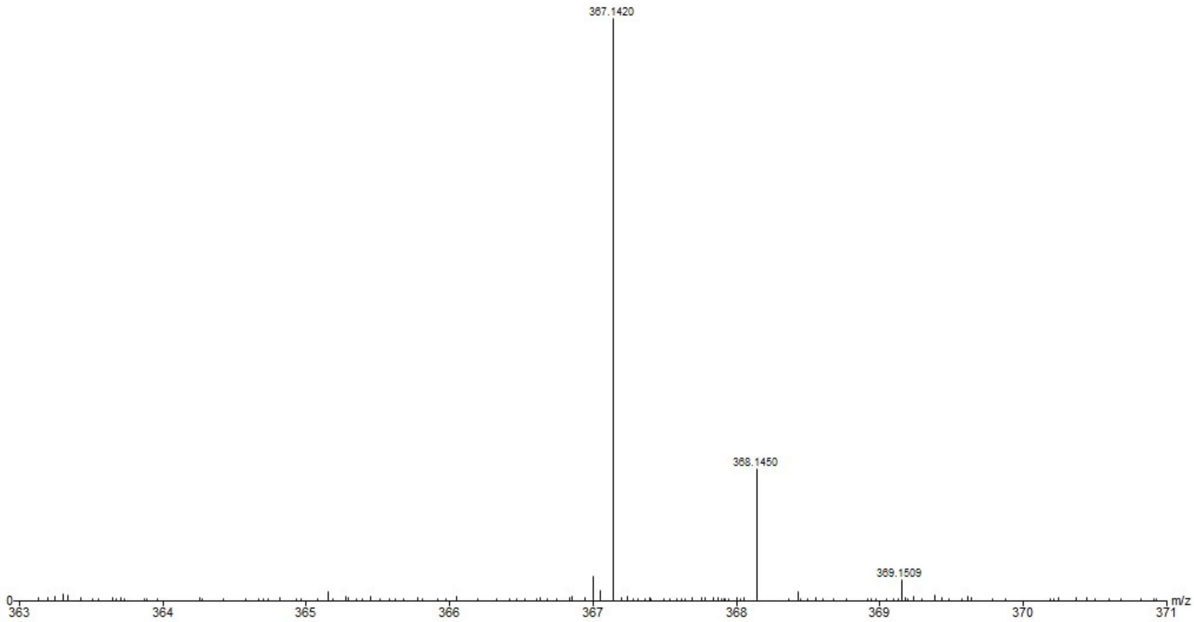


Figure S3. ESI-HRMS spectrum of **L1** ($C_{20}H_{15}N_8$ ($L+H^+$))

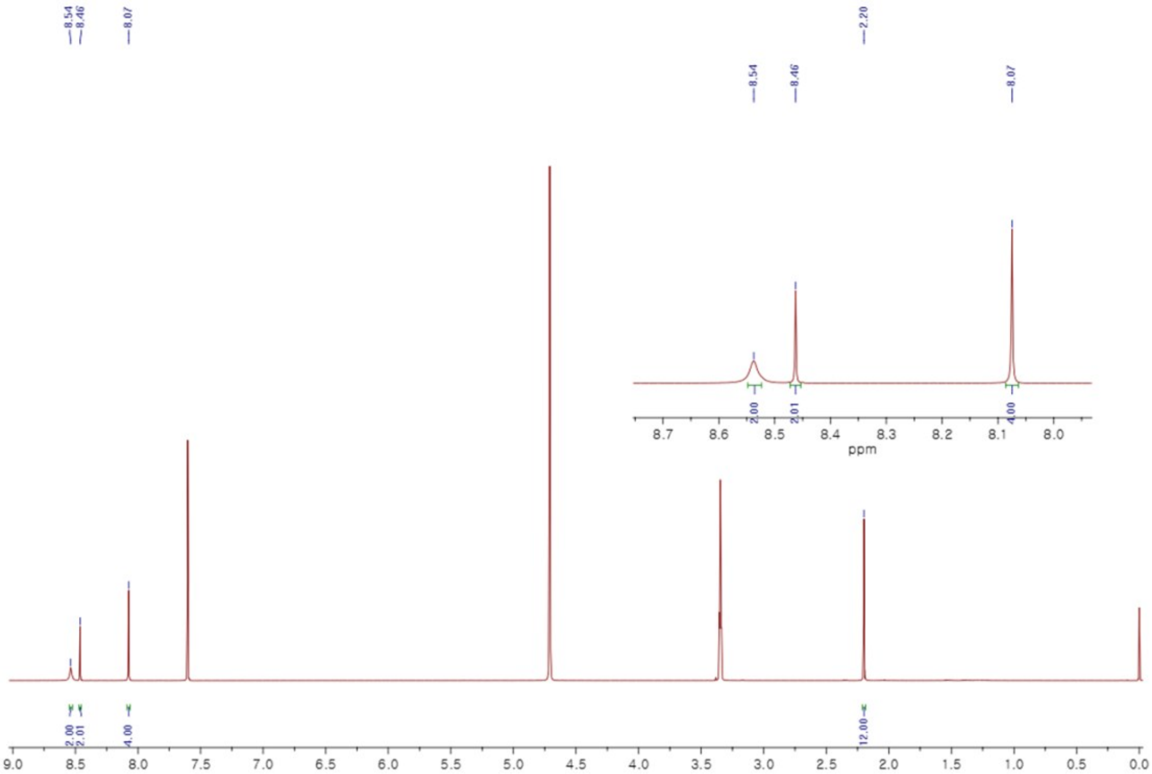


Figure S4. ^1H NMR spectrum of **L2** ($CD_3OD+CDCl_3$ (1:1), 400 MHz)

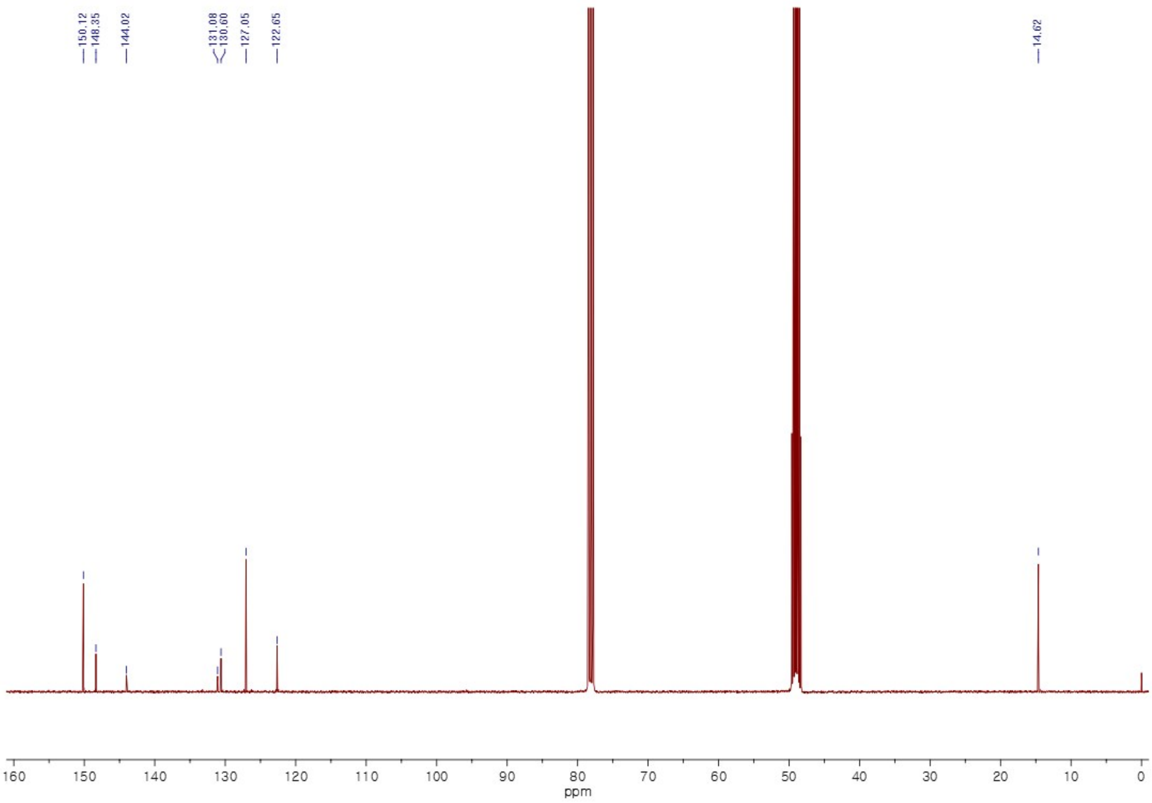


Figure S5. ^{13}C NMR spectrum of **L2** (CD_3OD+$CDCl_3$ (1:1), 100 MHz)

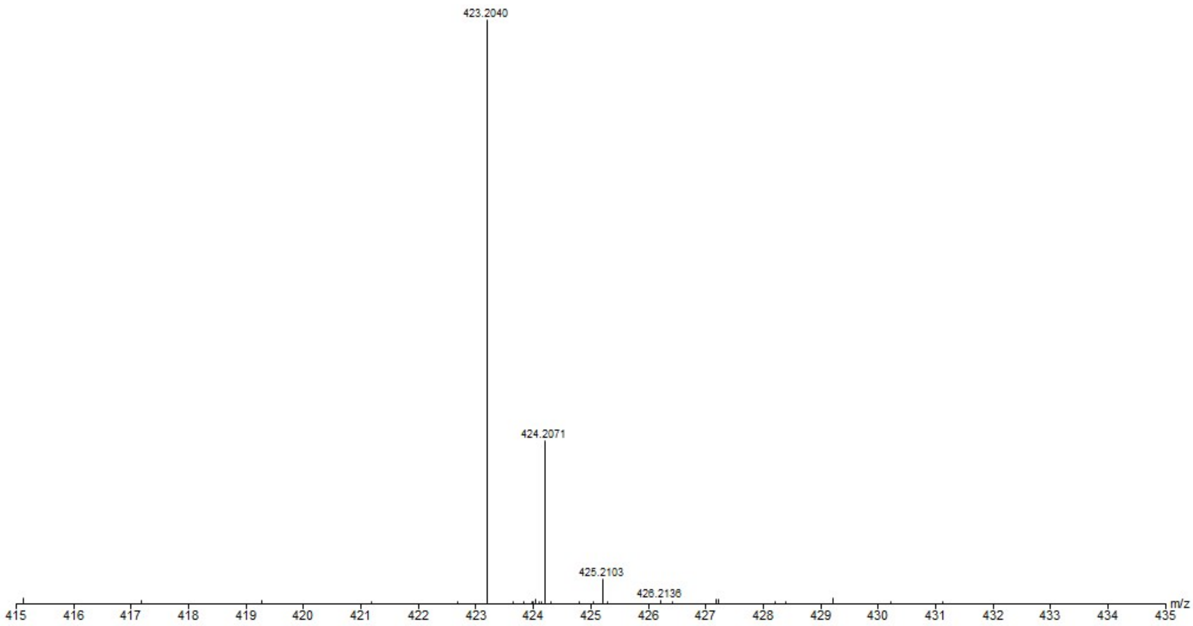


Figure S6. ESI-HRMS spectrum of **L2** ($C_{24}H_{23}N_8$ (L2+H^+))

4. ^{1}H, ^{13}C NMR and ESI-MS spectra of 1 and 2

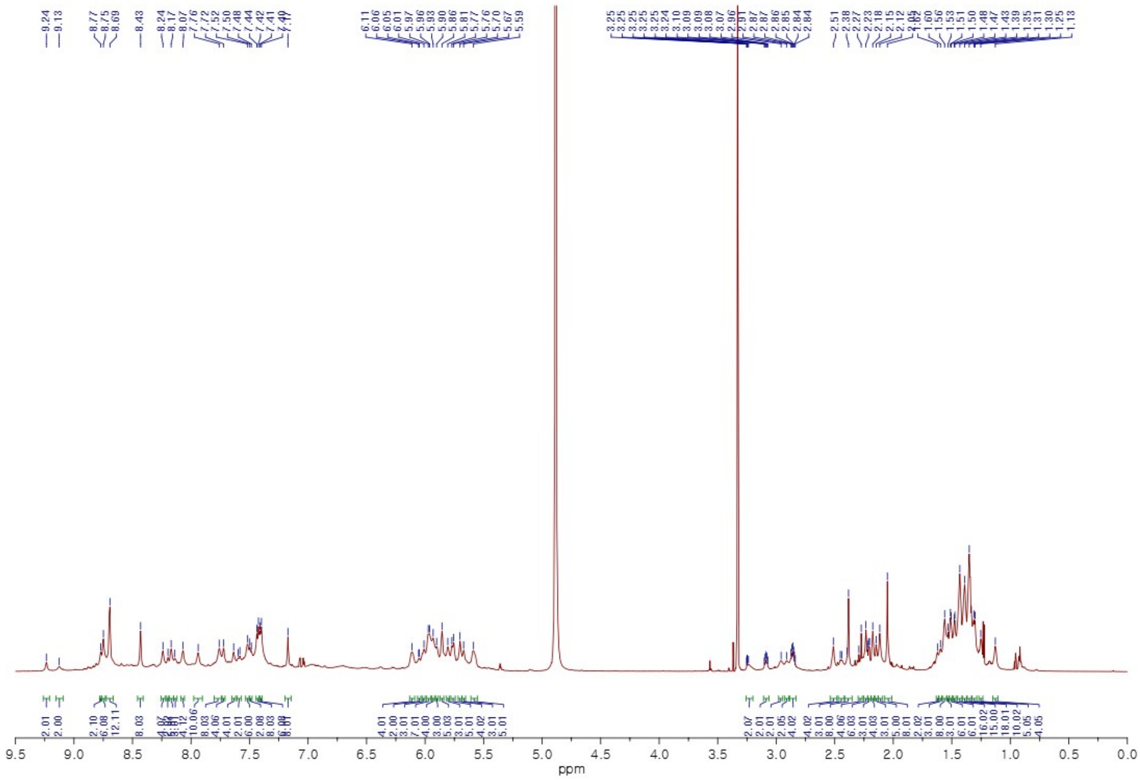


Figure S7. ^{1}H NMR spectrum of **2** (CD_3OD [20 mM], 900 MHz)

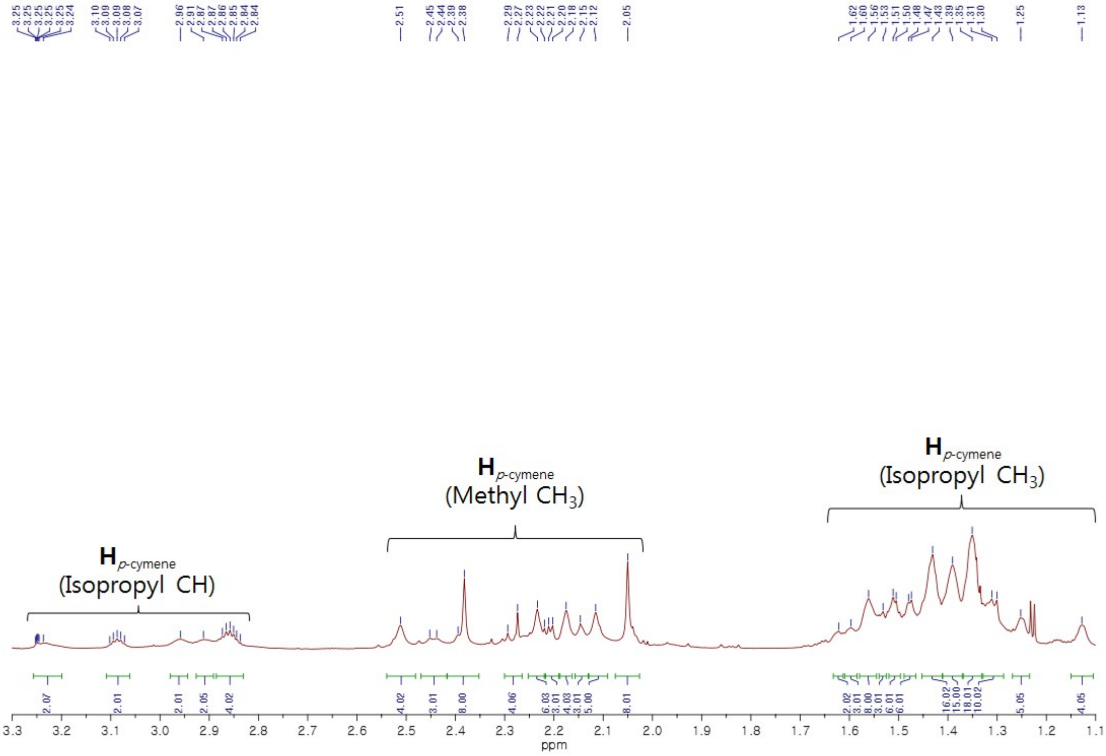


Figure S8. Expanded ^{1}H NMR spectrum of **2** (CD_3OD [20 mM], 900 MHz)

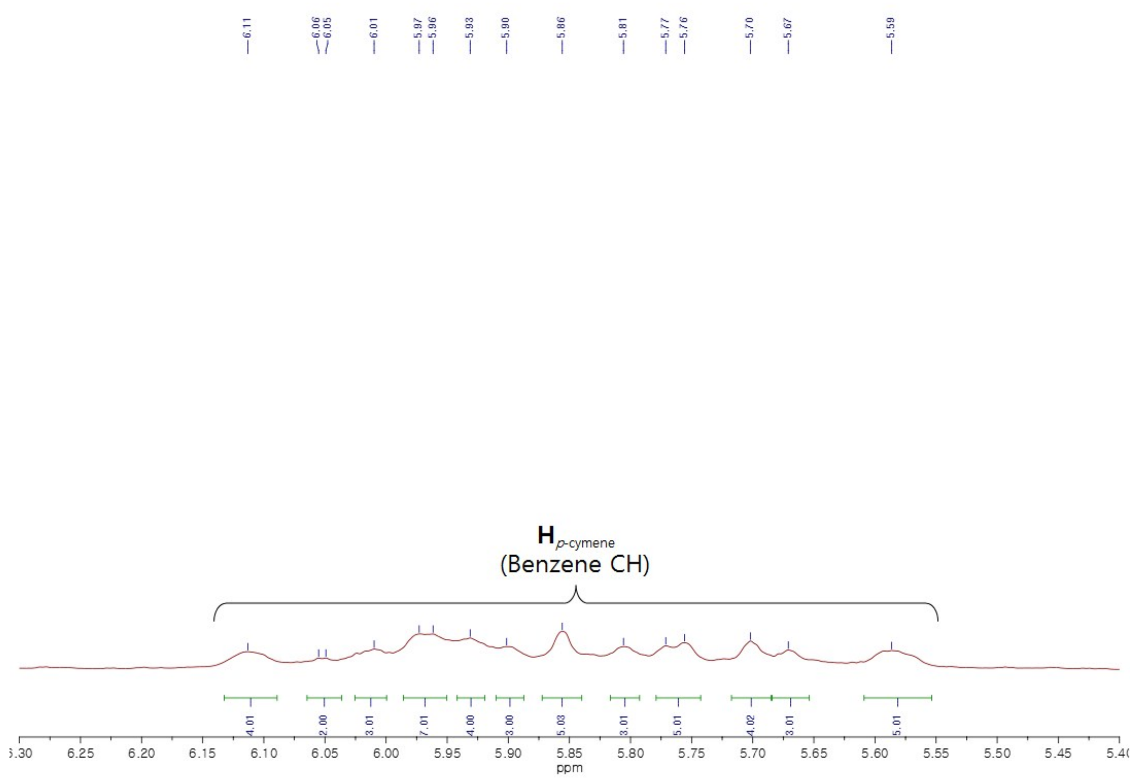


Figure S9. Expanded ^{1}H NMR spectrum of **2** (CD_3OD [20 mM], 900 MHz)

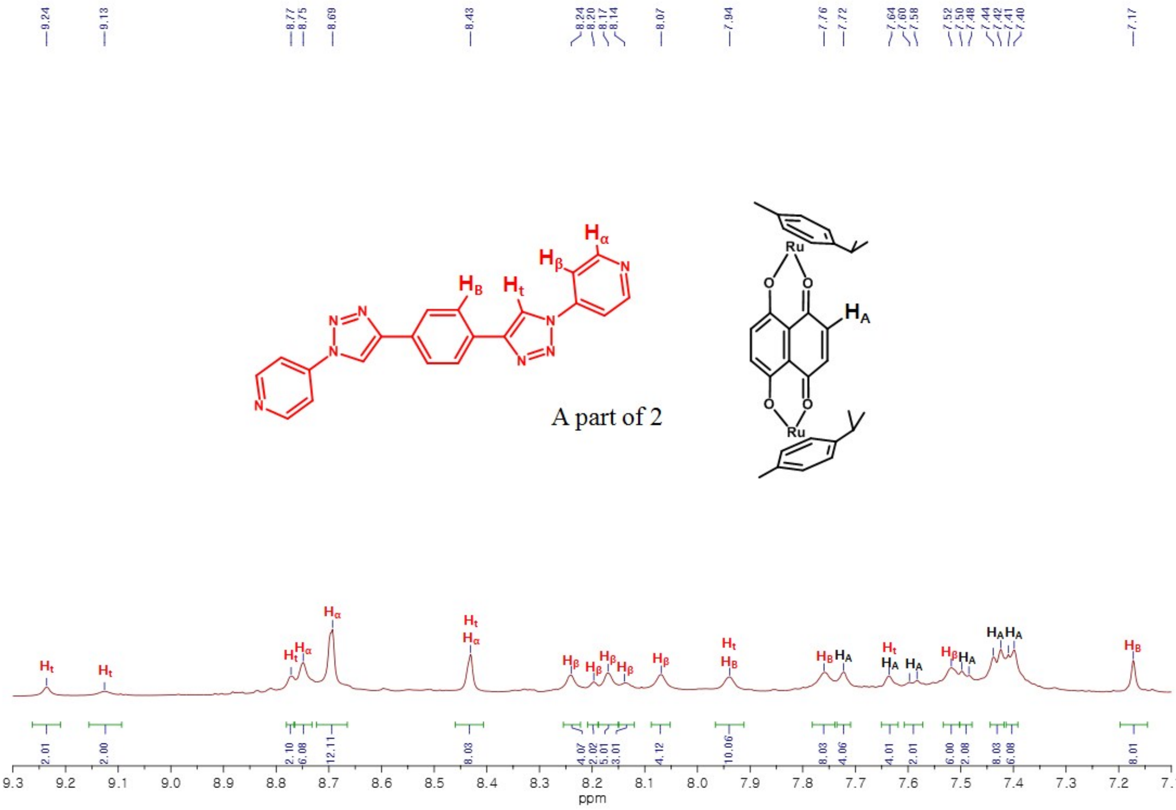


Figure S10. Expanded ^{1}H NMR spectrum of **2** (CD_3OD [20 mM], 900 MHz)

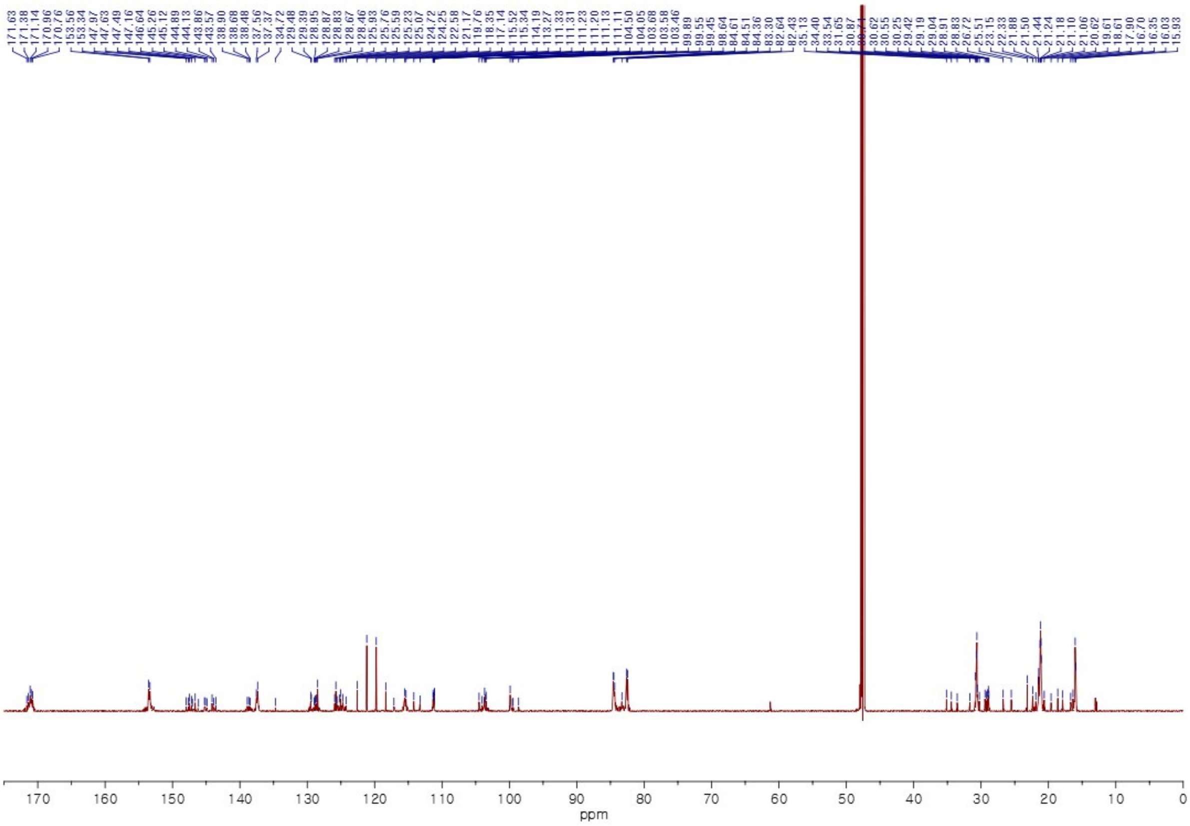


Figure S11. ^{13}C NMR spectrum of **2** (CD_3OD [20 mM], 225 MHz)

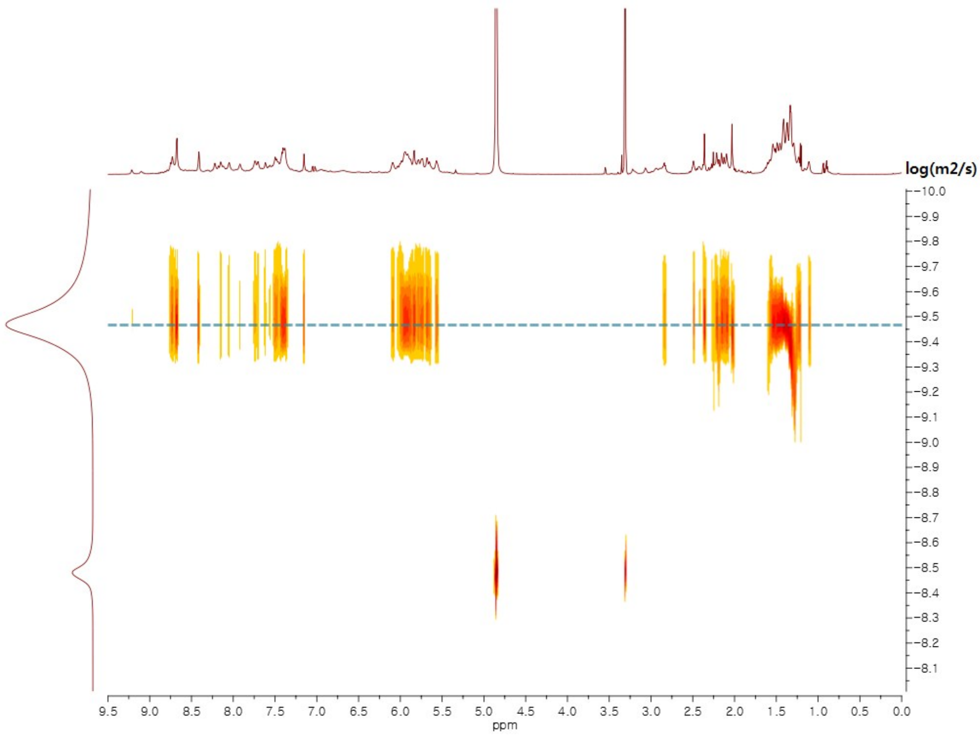


Figure S12. ^{1}H-DOSY NMR spectrum of **2** (CD_3OD [20 mM], 298 K, 800 MHz)

Diffusion coefficient: 3.4×10^{-10} m^2/sec

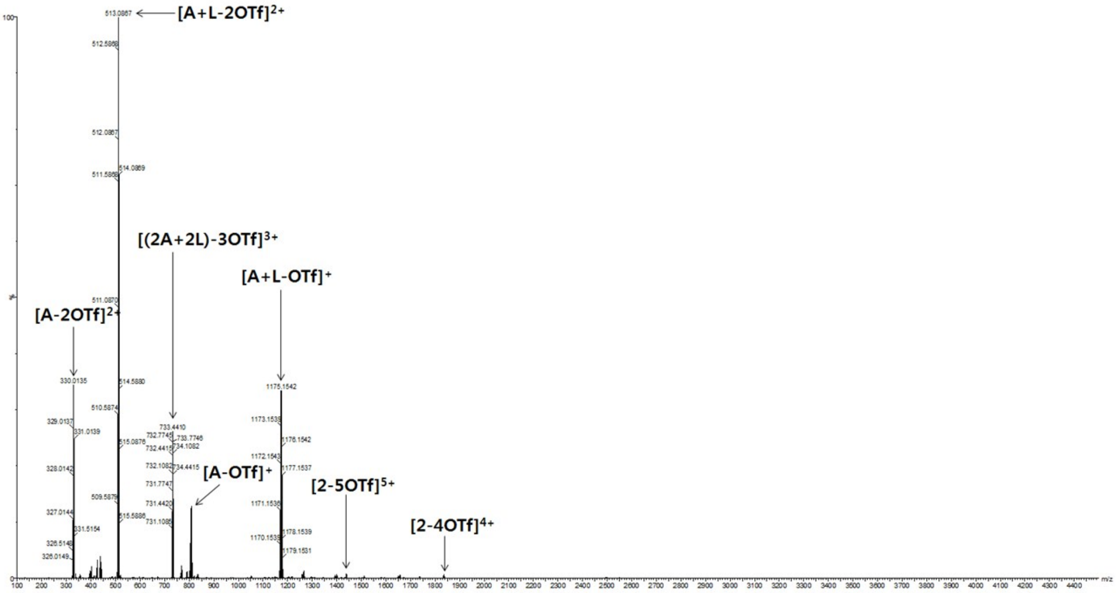


Figure S13. Full ESI mass spectrum of **2**. (Reaction in CD_3OD [20 mM])

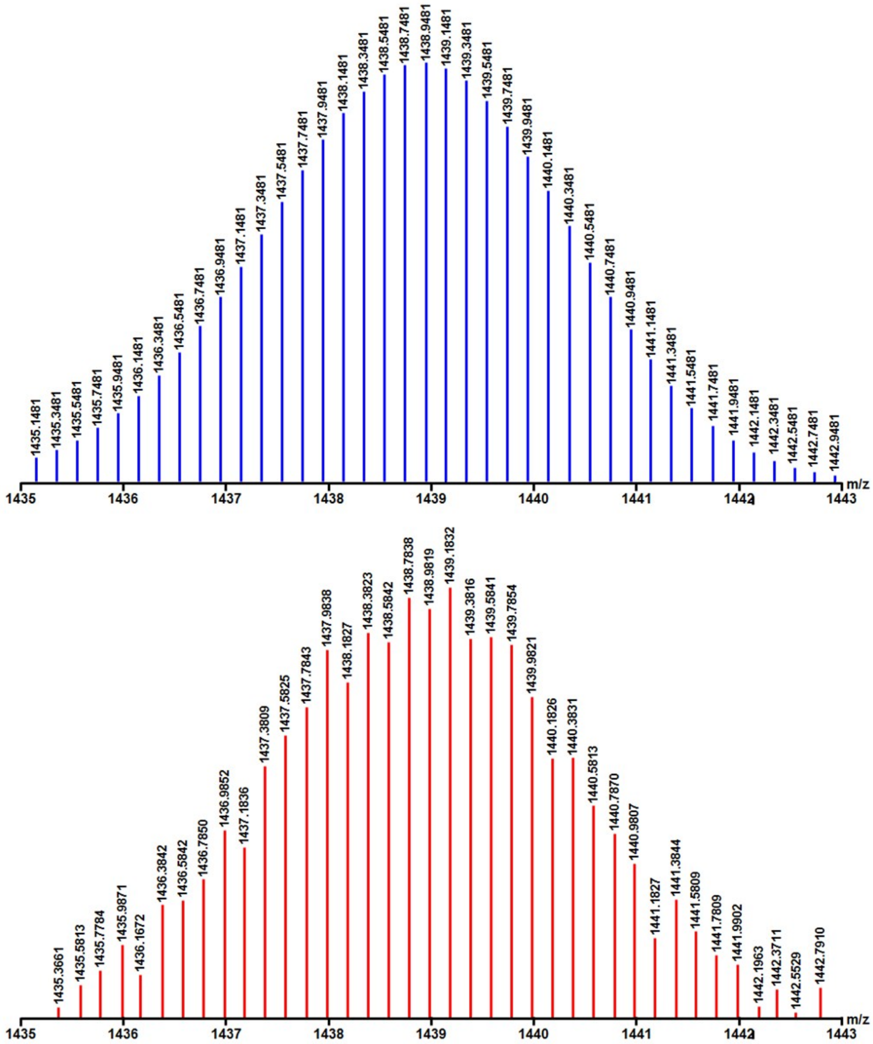


Figure S14. Calculated (blue) and experimental (red) ESI mass spectra of [**2**-5OTf]$^{5+}$.(Reaction in CD_3OD [20 mM])

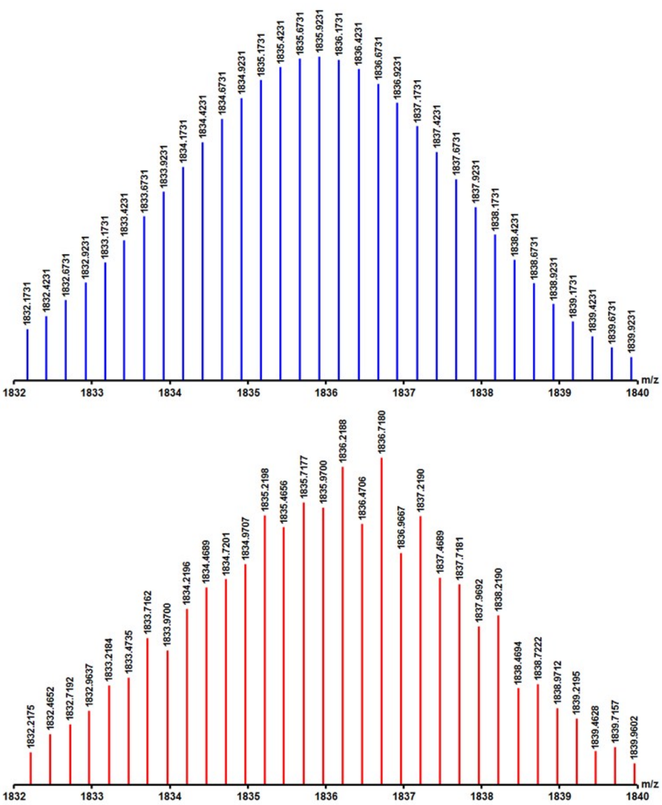


Figure S15. Calculated (blue) and experimental (red) ESI mass spectra of [**2**-4OTf]$^{4+}$.(Reaction in CD_3OD [20 mM])

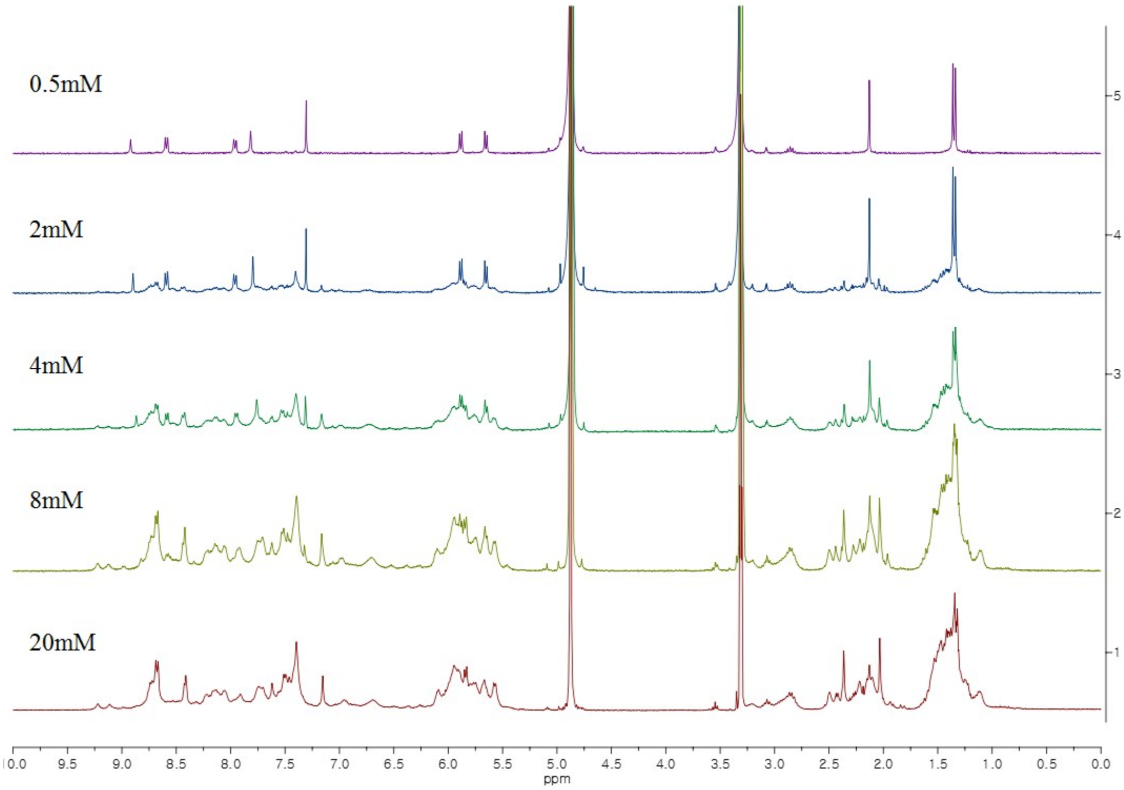


Figure S16. ^{1}H NMR spectra showing increasing of proportion of **2** upon sequentially increasing the concentration from 0.5 mM to 20 mM (CD_3OD, 300 MHz).

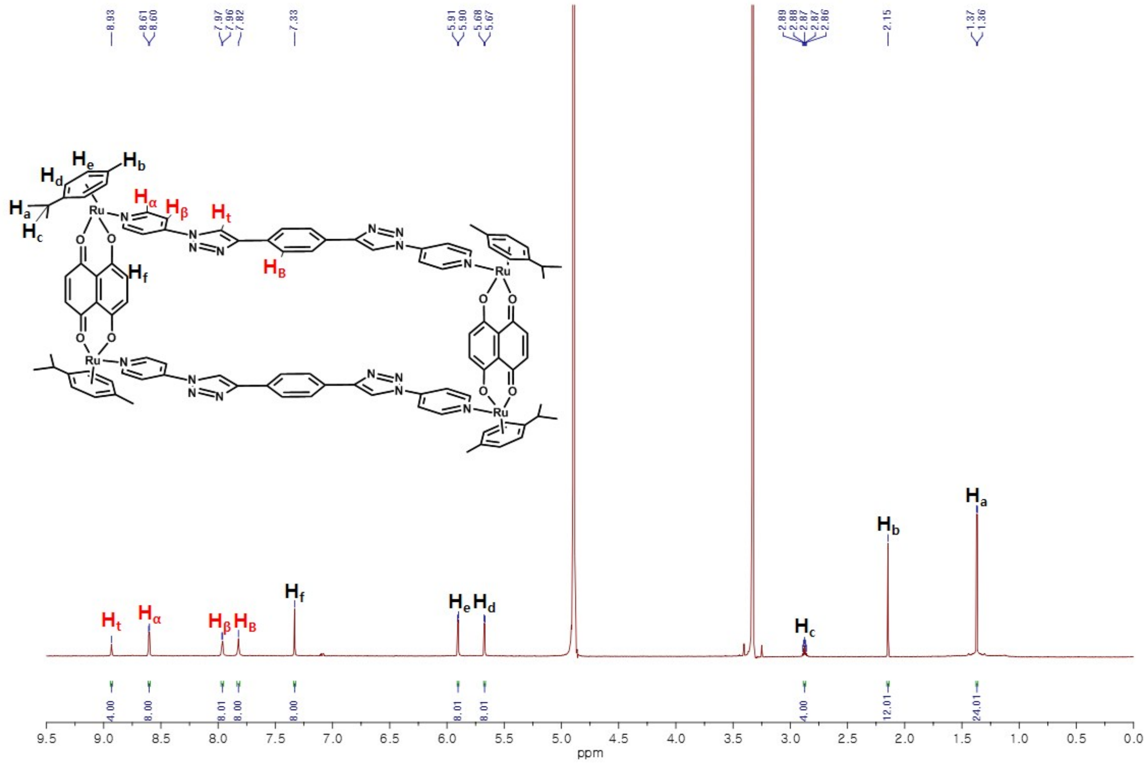


Figure S17. ^{1}H NMR spectrum of **1** (CD_3OD [0.5 mM], 900 MHz)

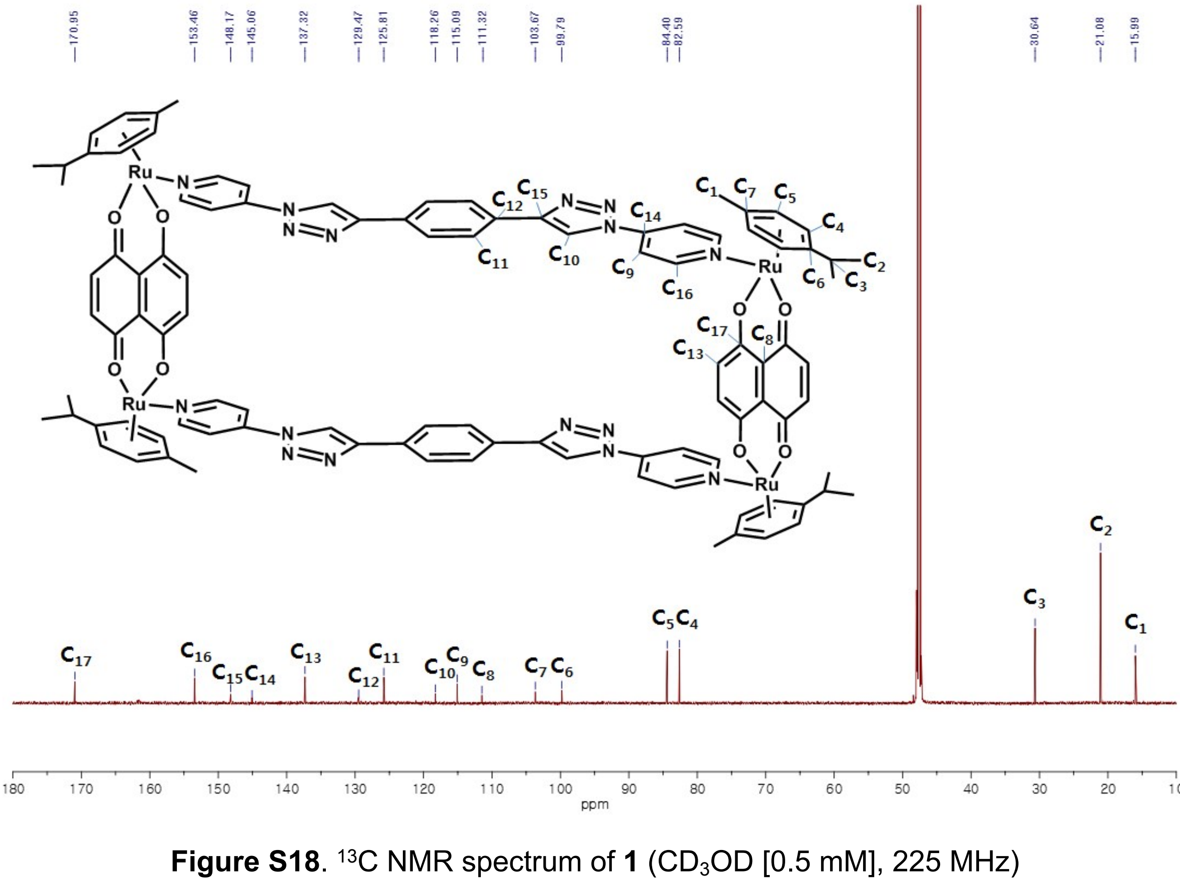


Figure S18. ^{13}C NMR spectrum of **1** (CD_3OD [0.5 mM], 225 MHz)

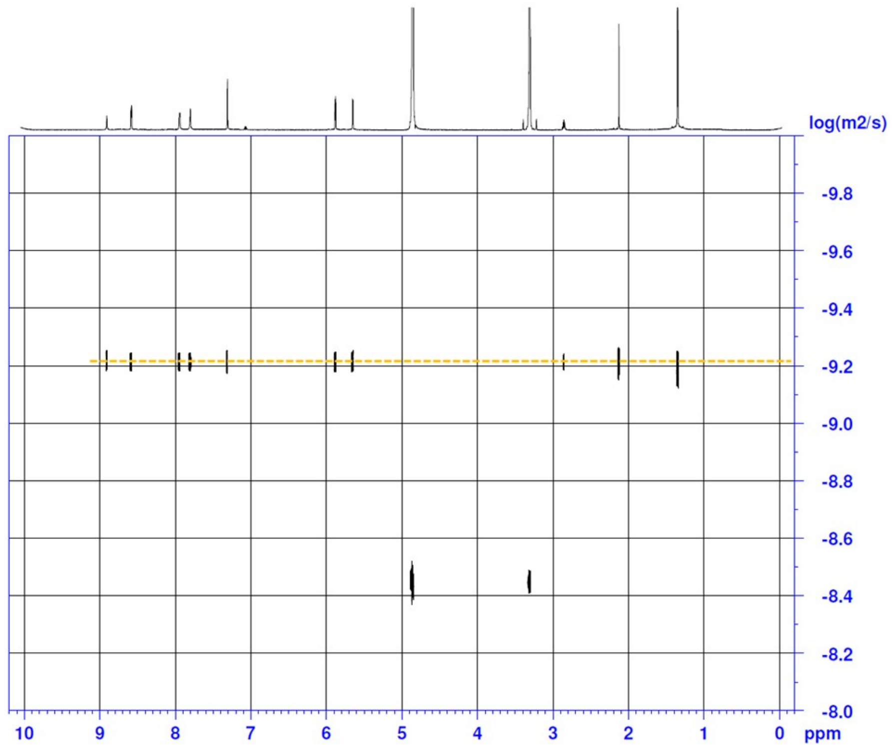


Figure S19.^{1}H-DOSY NMR spectrum of **1** (CD_3OD [0.5 mM], 298 K, 800 MHz)

Diffusion coefficient: 6.1×10^{-10} m^2/sec

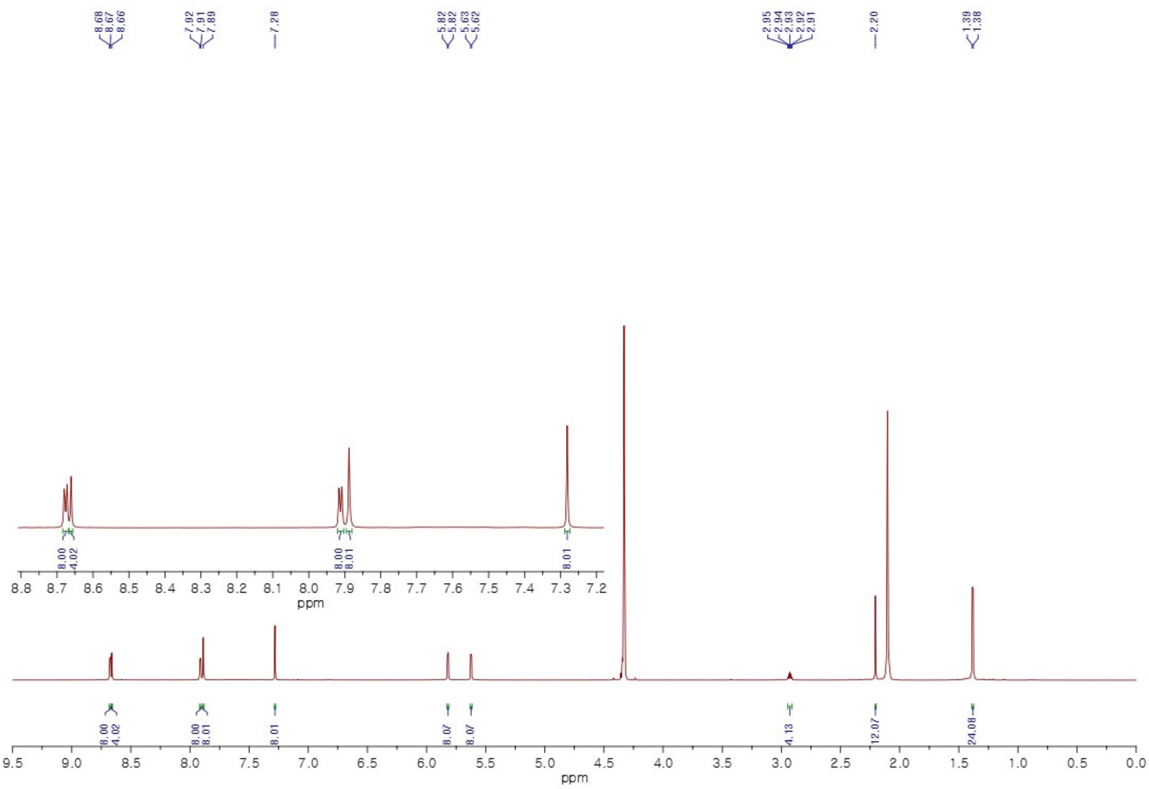


Figure S20. ^{1}H NMR spectrum of **1** (CD_3NO_2 [8.0 mM], 900 MHz)

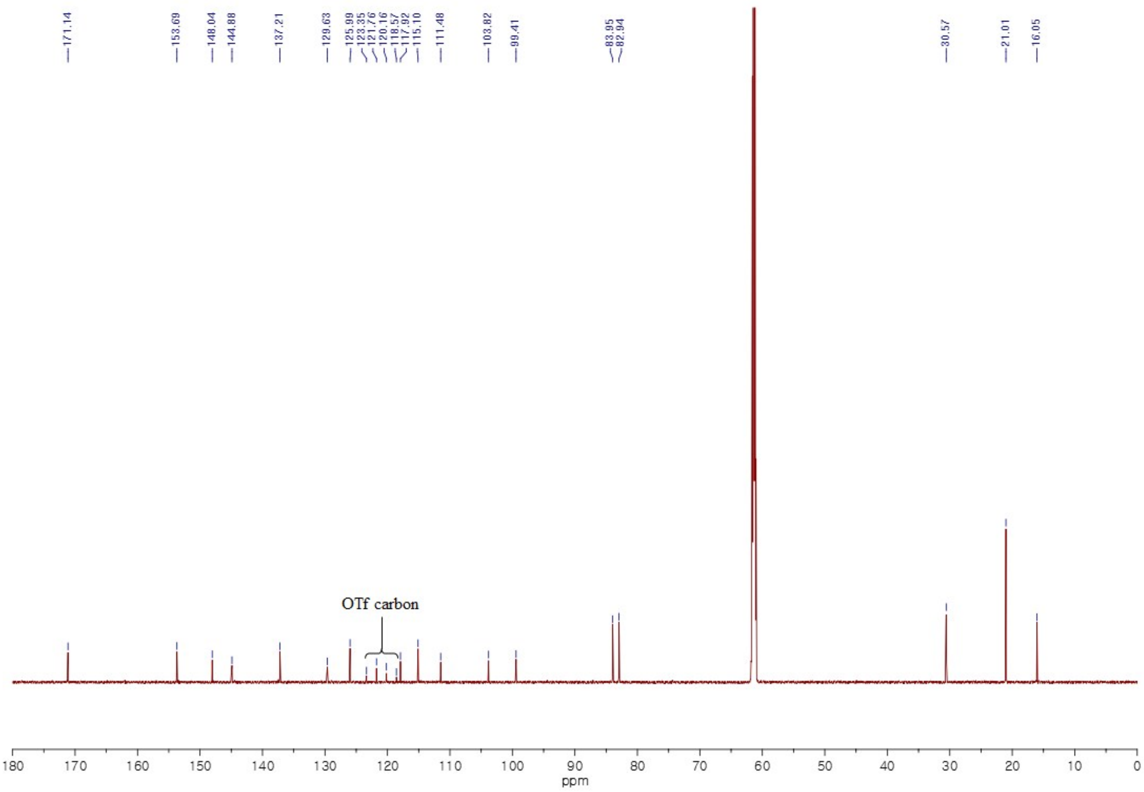


Figure S21. ^{13}C NMR spectrum of **1** (CD_3NO_2 [8.0 mM], 225 MHz)

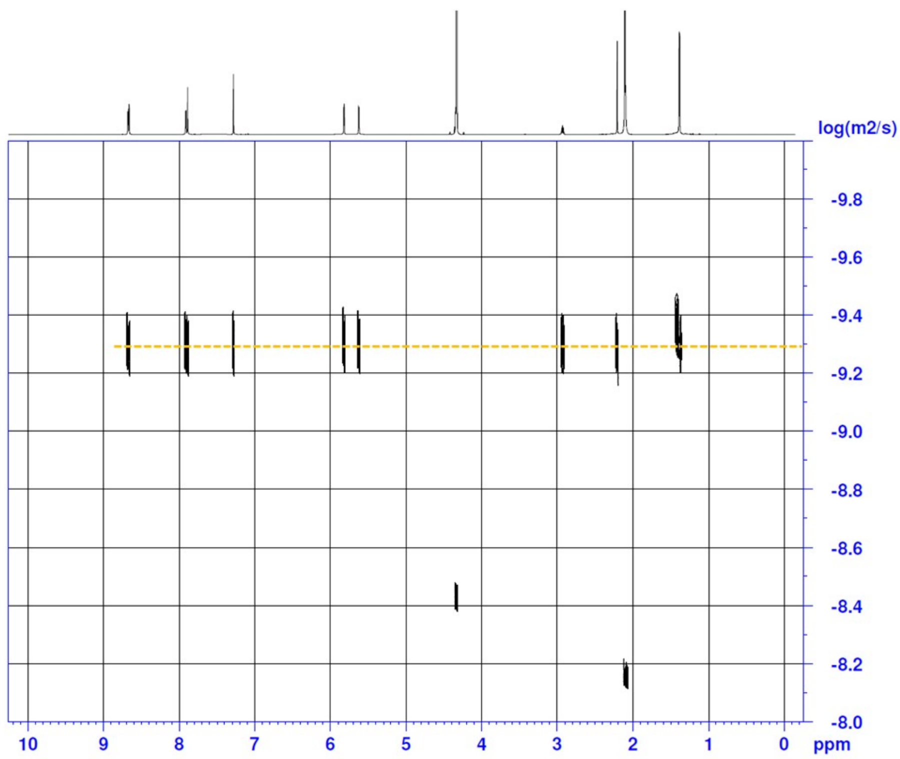


Figure S22.^{1}H-DOSY NMR spectrum of **1** (CD_3NO_2 [8.0 mM], 298 K, 800 MHz)

Diffusion coefficient: 5.1×10^{-10} m^2/sec

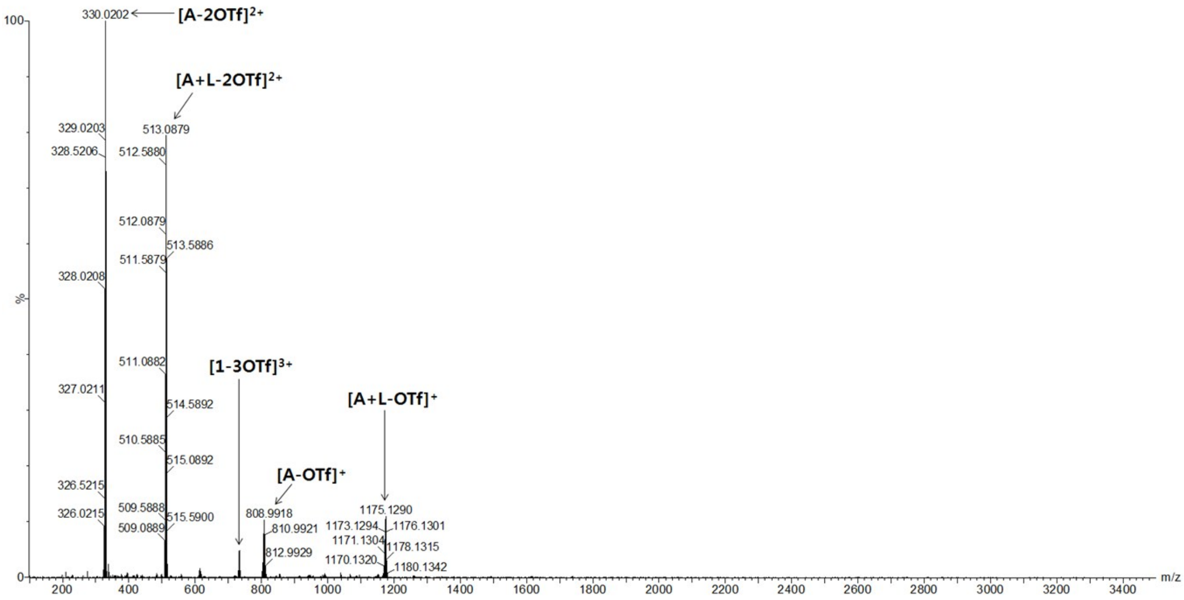


Figure S23. Full ESI mass spectrum of **1**. (Reaction in CD_3OD [0.5 mM])

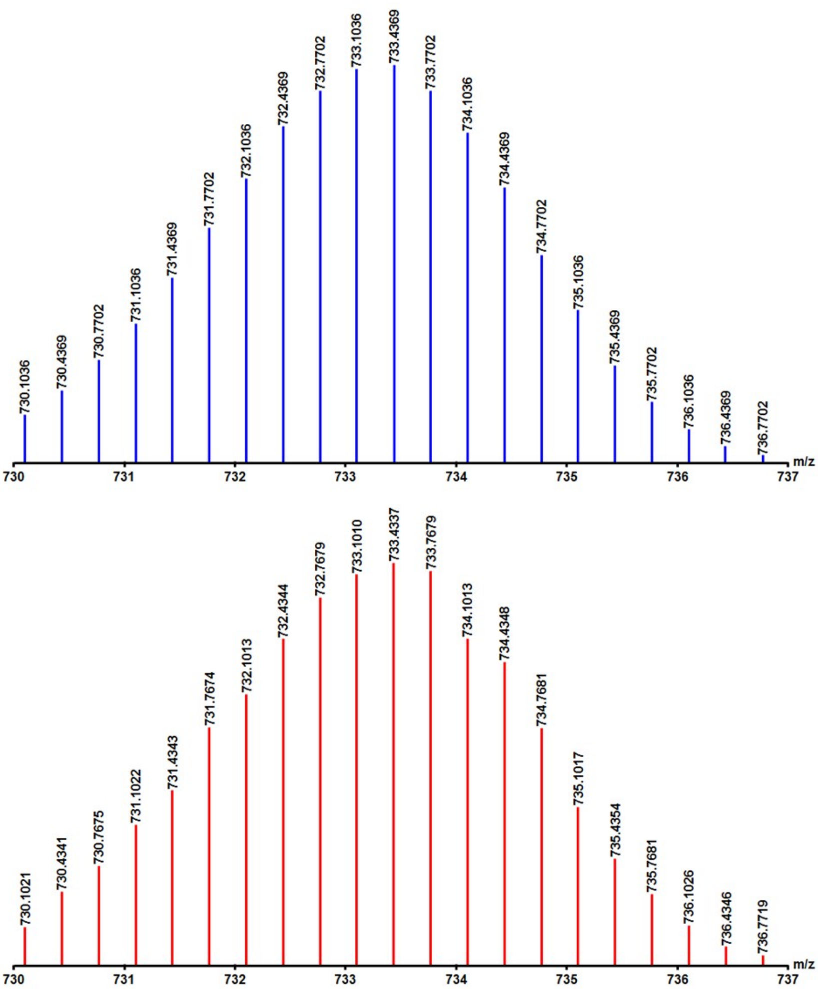


Figure S24. Calculated (blue) and experimental (red) ESI mass spectra of [**1**-3OTf]$^{3+}$

(Reaction in CD_3OD [0.5 mM])

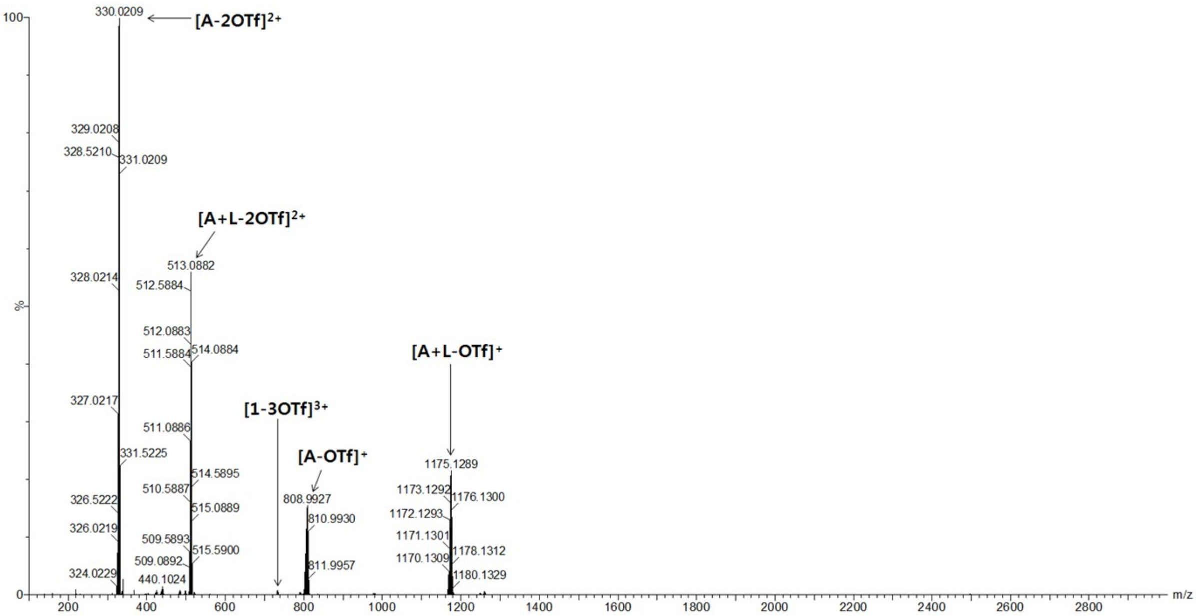
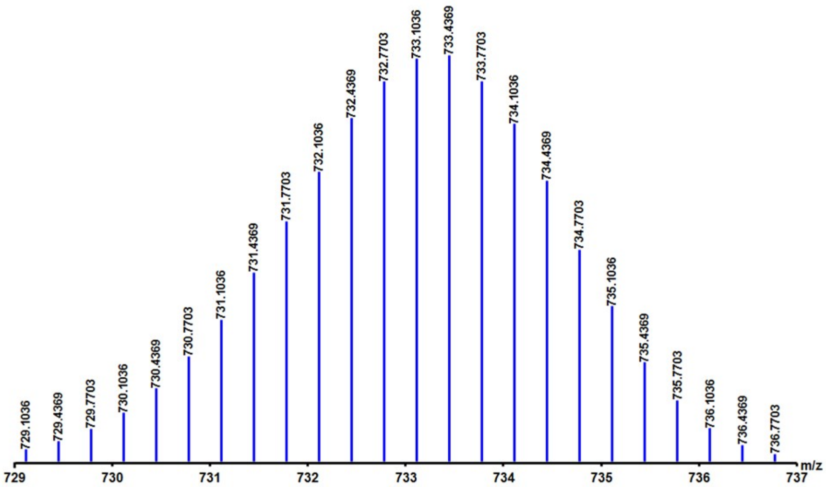


Figure S25. Full ESI mass spectrum of **1**. (Reaction in CD_3NO_2 [8.0 mM])



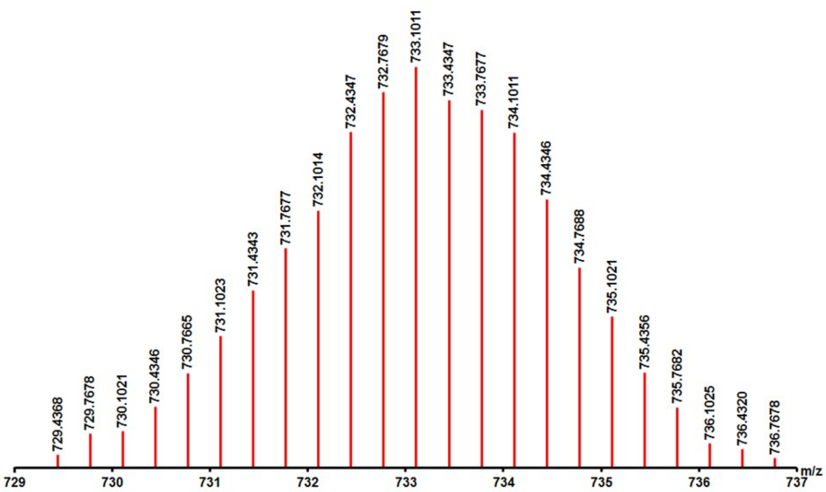


Figure S26. Calculated (blue) and experimental (red) ESI mass spectra of [**1**-3OTf]$^{3+}$ (Reaction in CD_3NO_2 [8.0 mM])

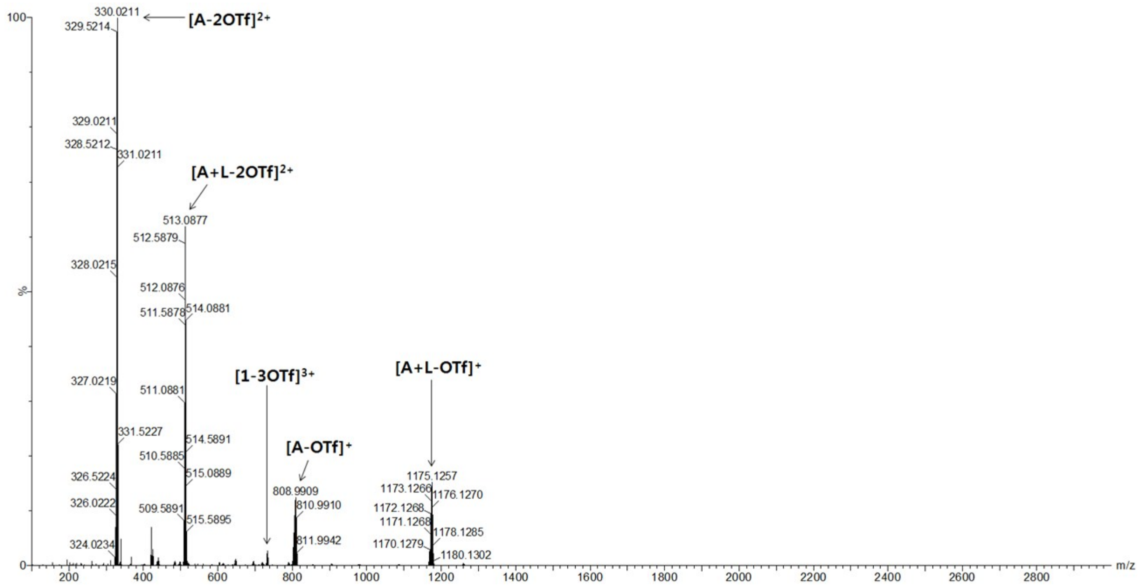


Figure S27. Full ESI mass spectrum of **1** (Reaction was carried out in the presence of pyrene [2.0 eq] in CD_3OD [8.0 mM])

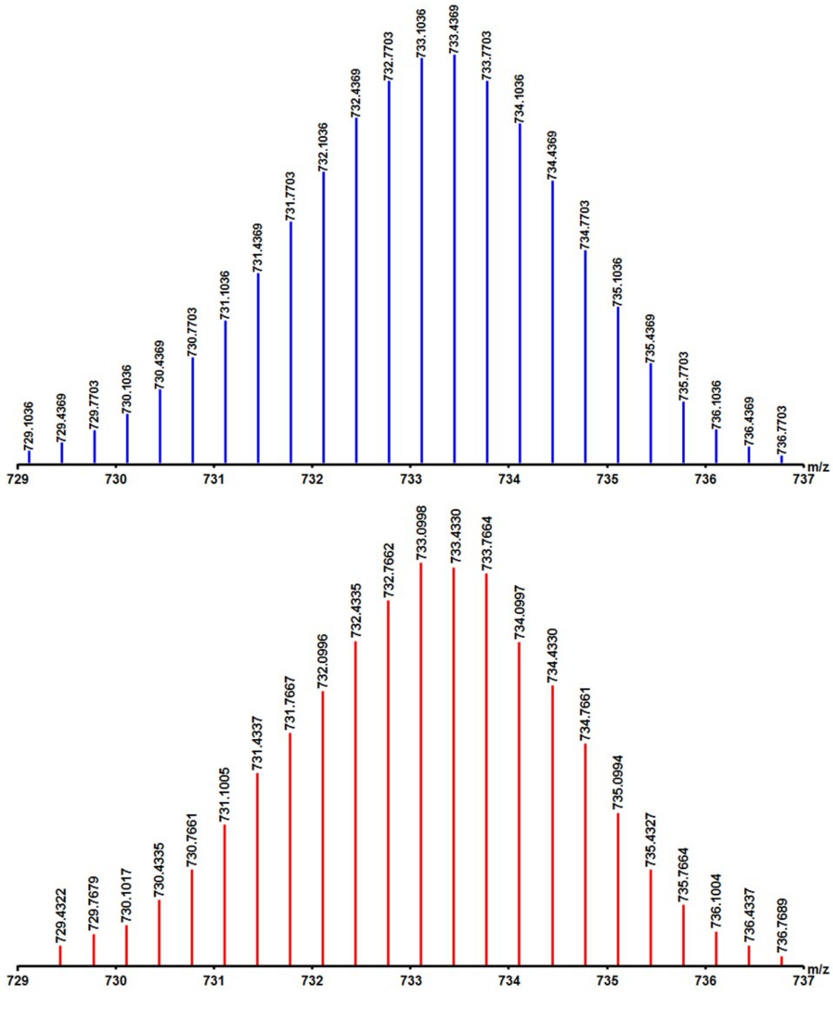


Figure S28. Calculated (blue) and experimental (red) ESI mass spectra of [**1**-3OTf]$^{3+}$ (Reaction was carried out in the presence of pyrene [2.0 eq] in CD_3OD [8.0 mM]

5. 2D NMR analysis (COSY, ROESY, HSQC and HMBC) of 1 and 2

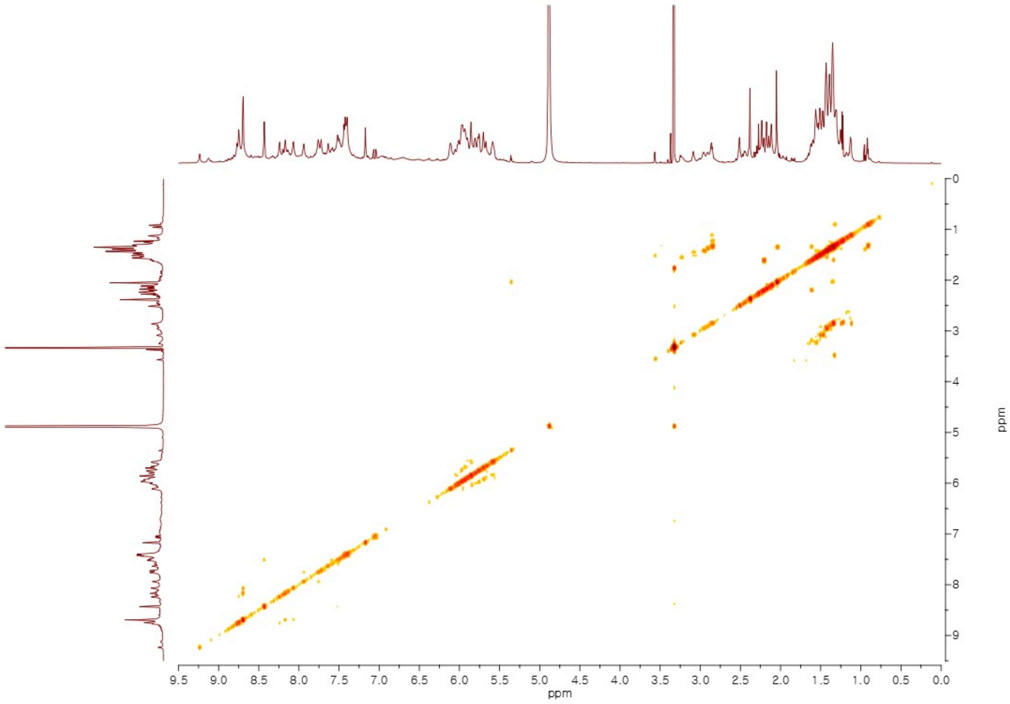


Figure S29. ^{1}H-^{1}H COSY NMR spectrum of **2** (CD_3OD [20 mM], 298 K, 900 MHz)

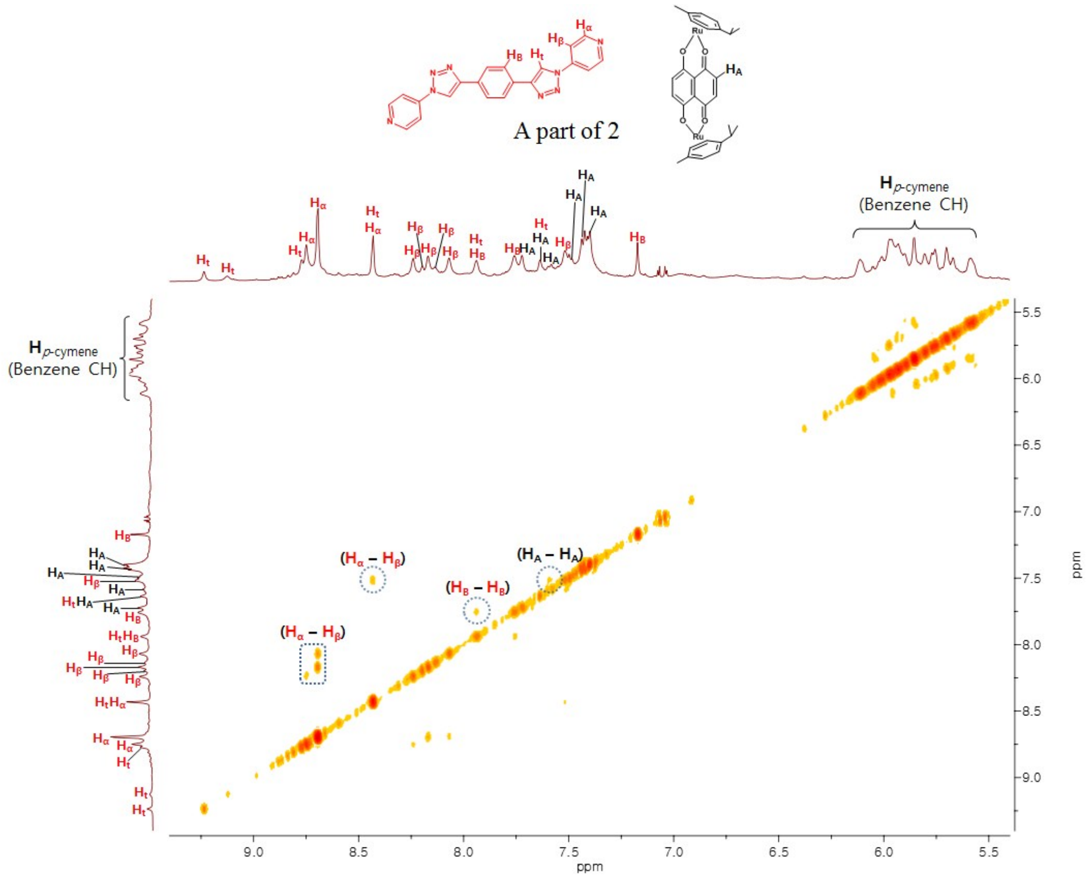


Figure S30. Expanded ^{1}H-^{1}H COSY NMR spectrum of **2** (CD_3OD [20 mM], 298 K, 900 MHz)

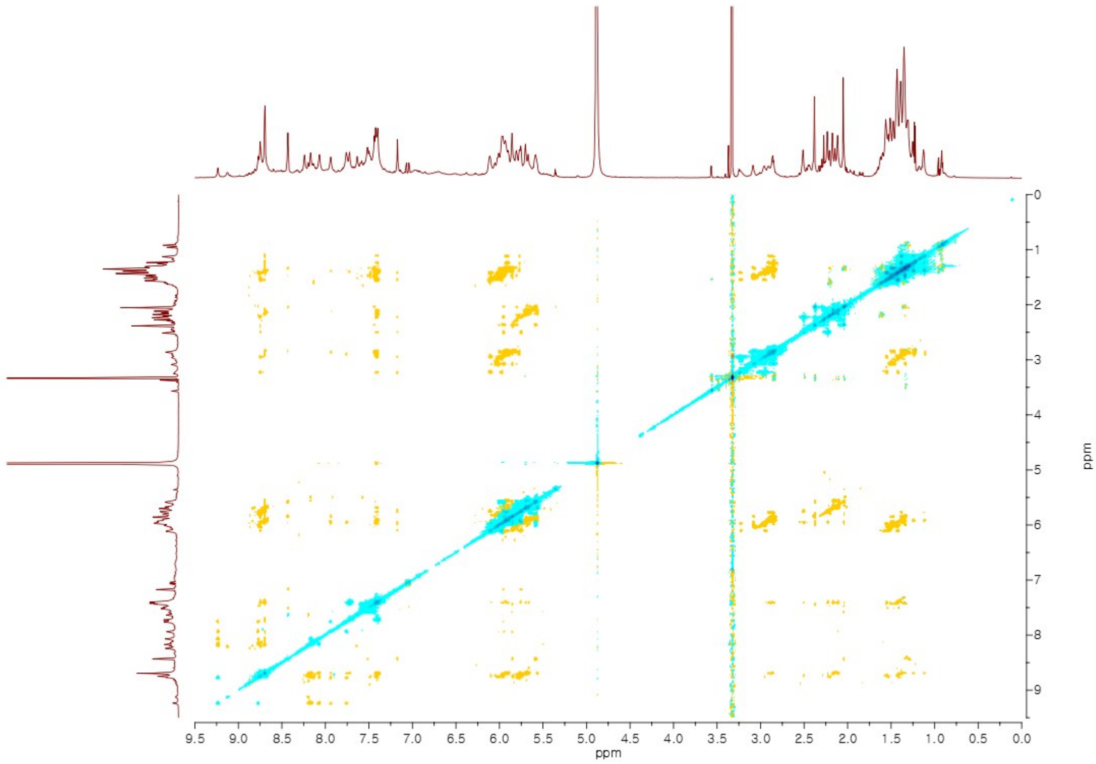


Figure S31.[1]H-[1]H ROESY NMR spectrum of **2** (CD_3OD [20 mM], 298 K, 900 MHz)

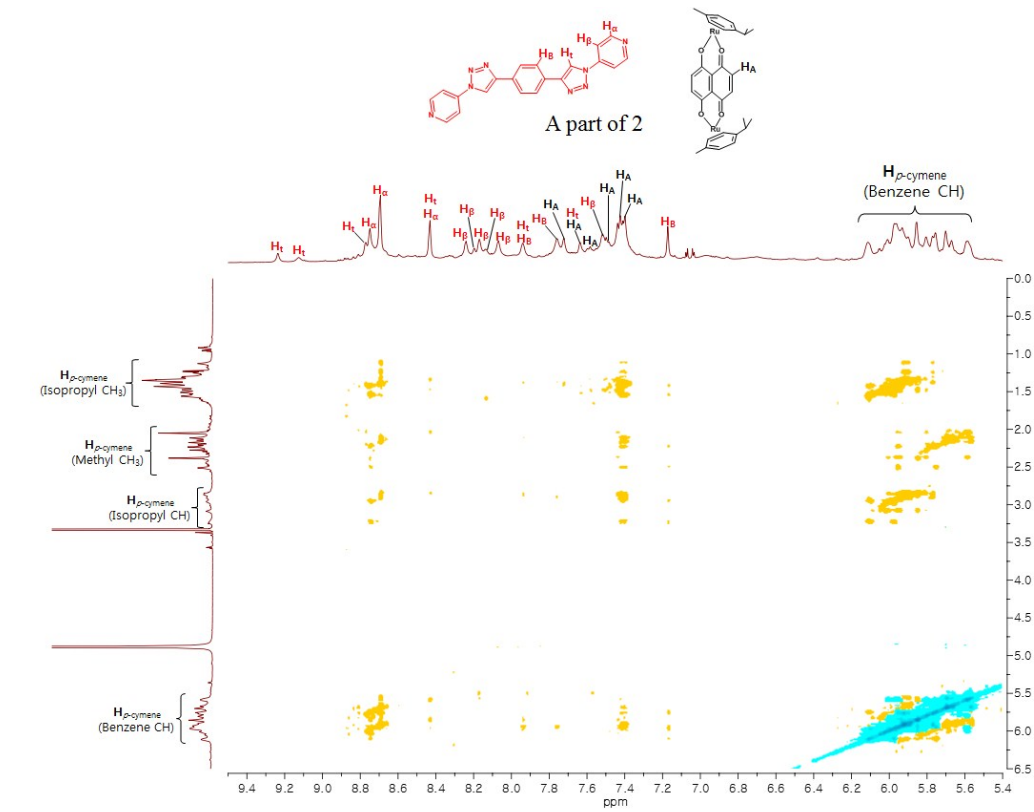


Figure S32. Expanded [1]H-[1]H ROESY NMR spectrum of **2** (CD_3OD [20 mM], 298 K, 900 MHz)

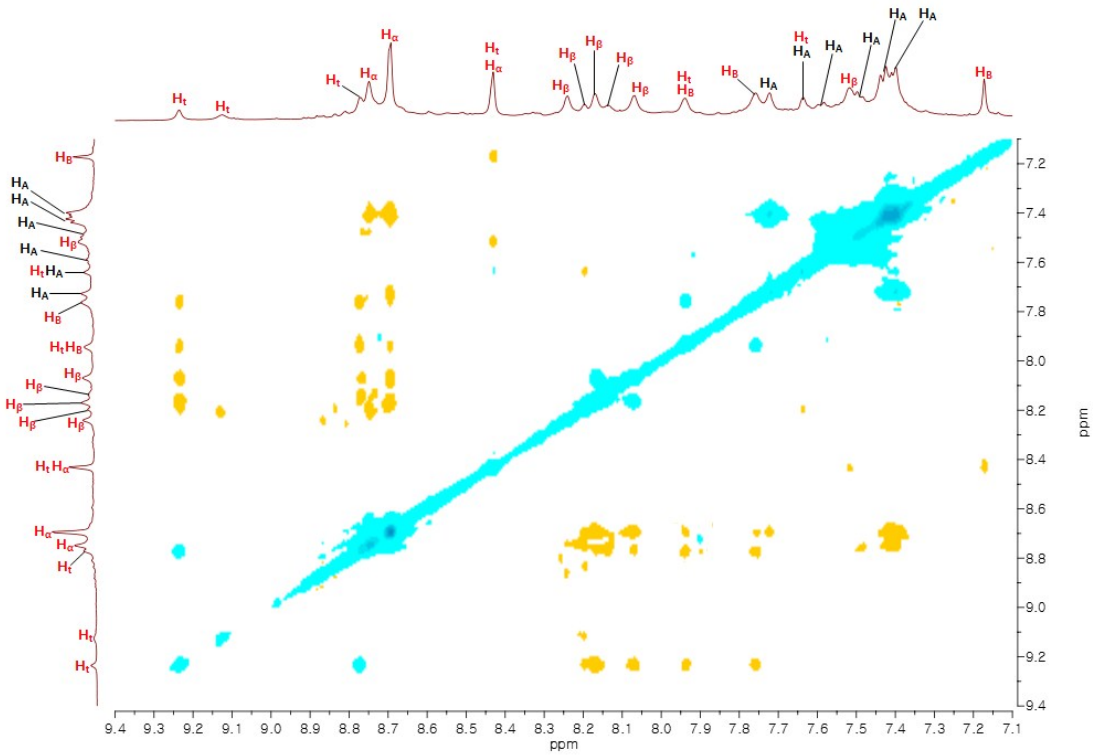


Figure S33. Expanded ^{1}H-^{1}H ROESY NMR spectrum of **2** (CD_3OD [20 mM], 298 K, 900 MHz)

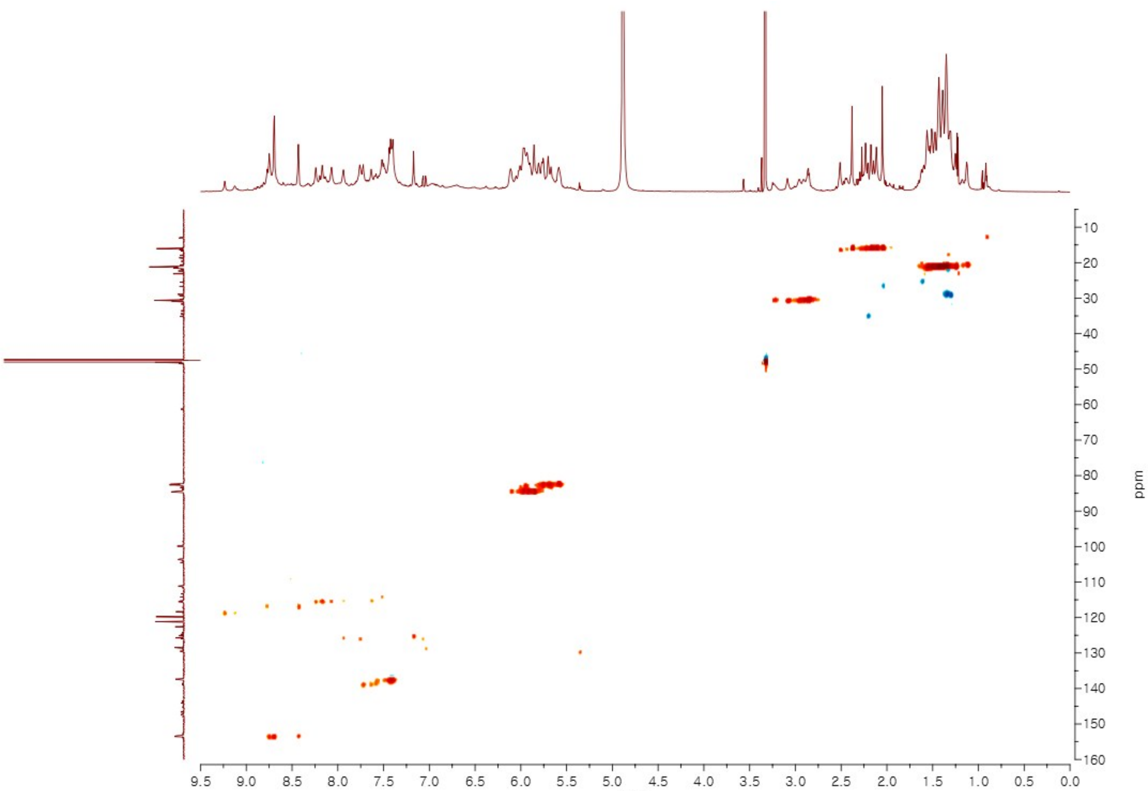


Figure S34. ^{1}H-^{13}C HSQC NMR spectrum of **2** (CD_3OD [20 mM], 298 K, 900 MHz)

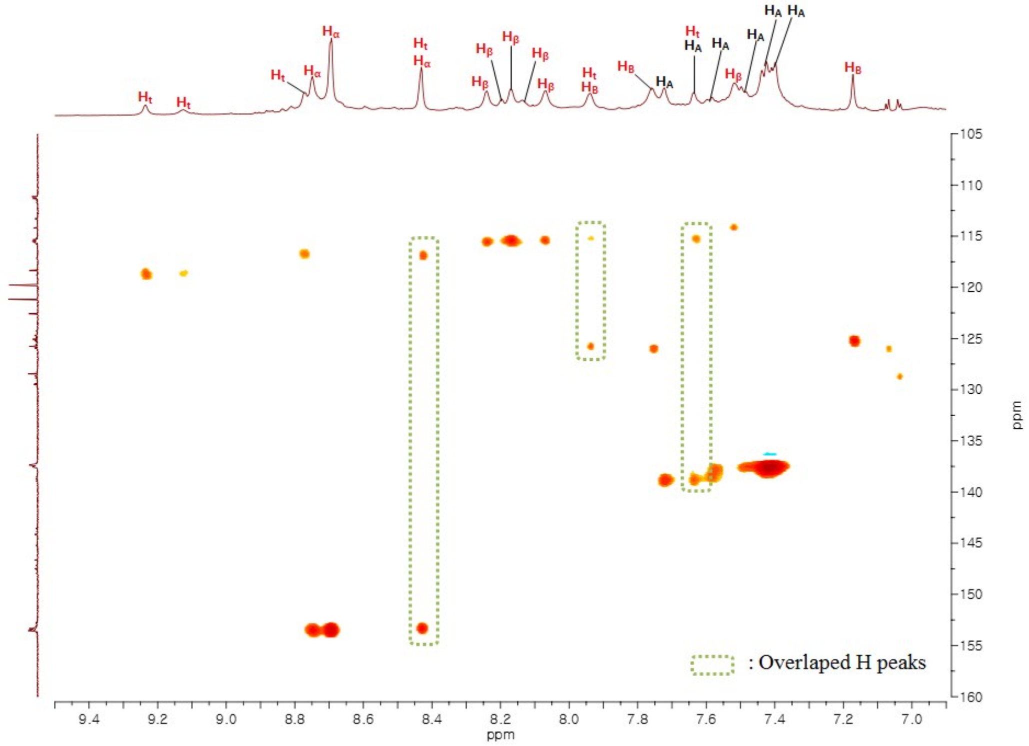


Figure S35. Expanded ^{1}H-^{13}C HSQC NMR spectrum of **2** (CD_3OD [20 mM], 298 K, 900 MHz)

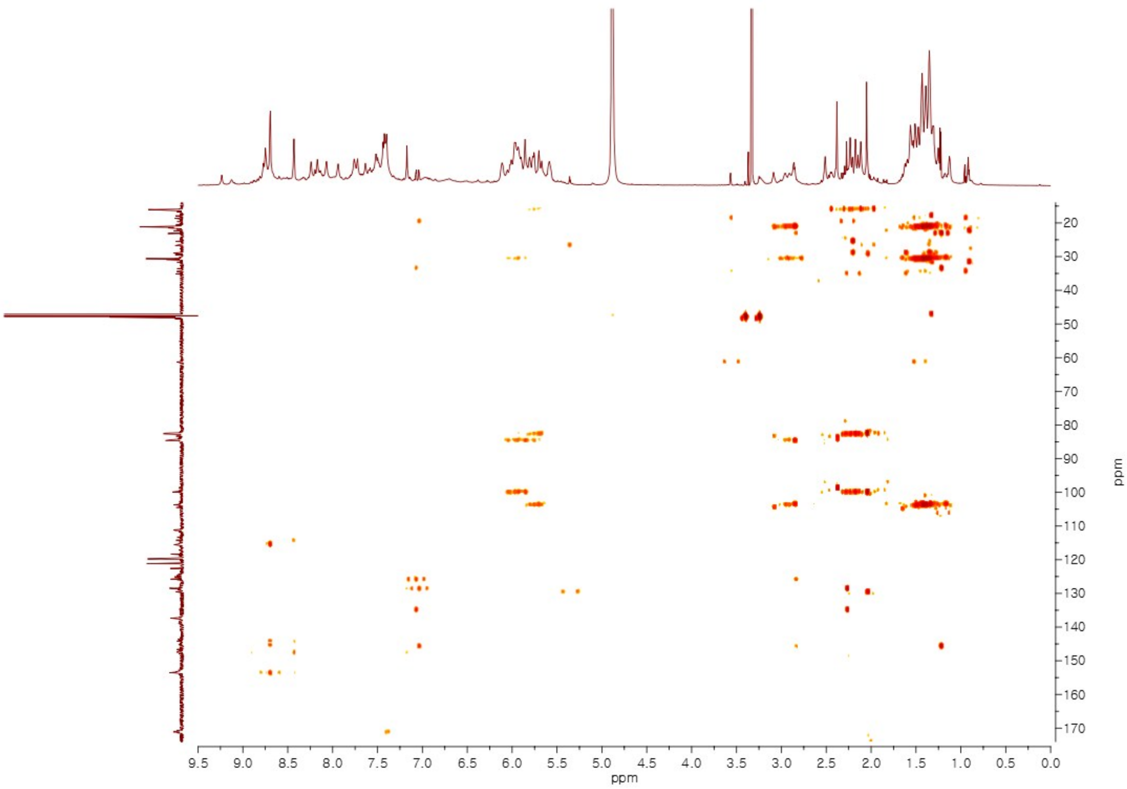


Figure S36. ^{1}H-^{13}C HMBC NMR spectrum of **2** (CD_3OD [20 mM], 298 K, 900 MHz)

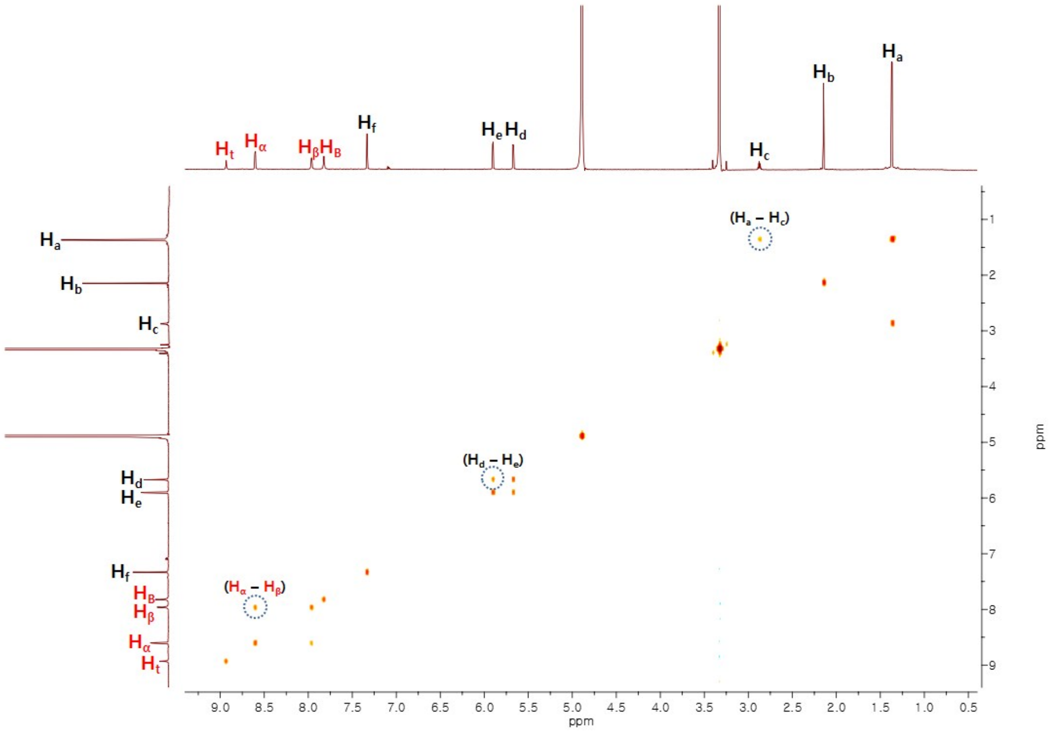


Figure S37.[1]H-[1]H COSY NMR spectrum of **1** (CD_3OD [0.5 mM], 298 K, 900 MHz)

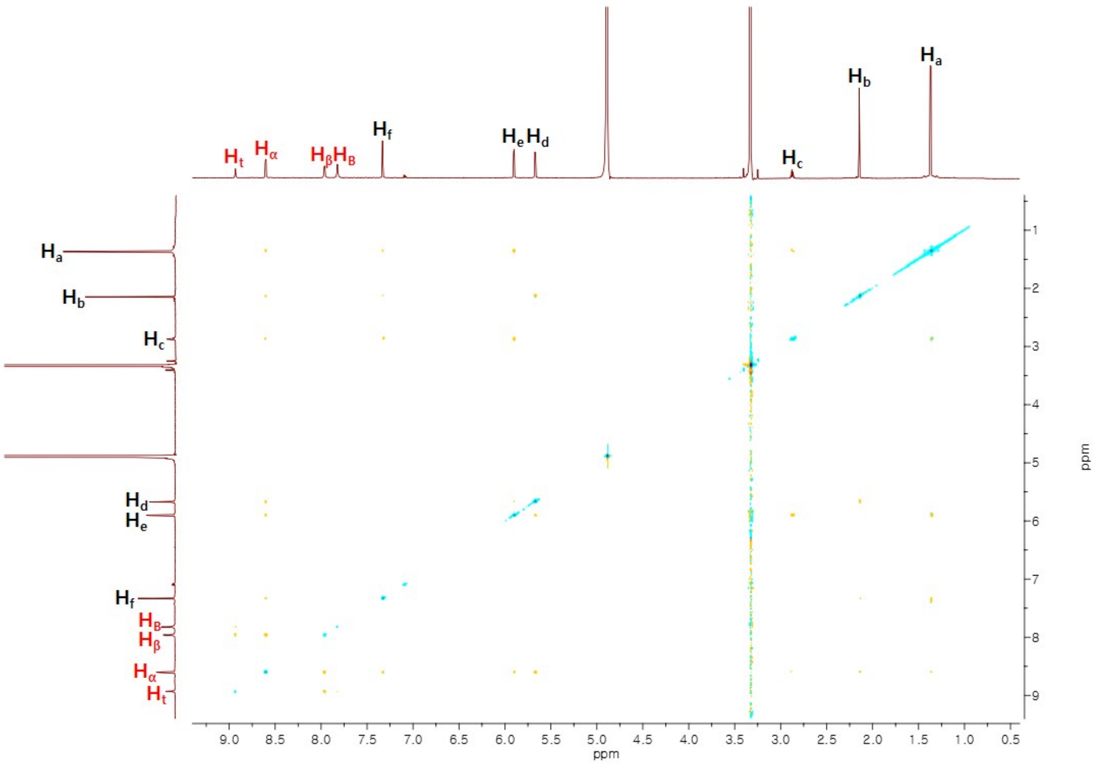


Figure S38.[1]H-[1]H ROESY NMR spectrum of **1** (CD_3OD [0.5 mM], 298 K, 900 MHz)

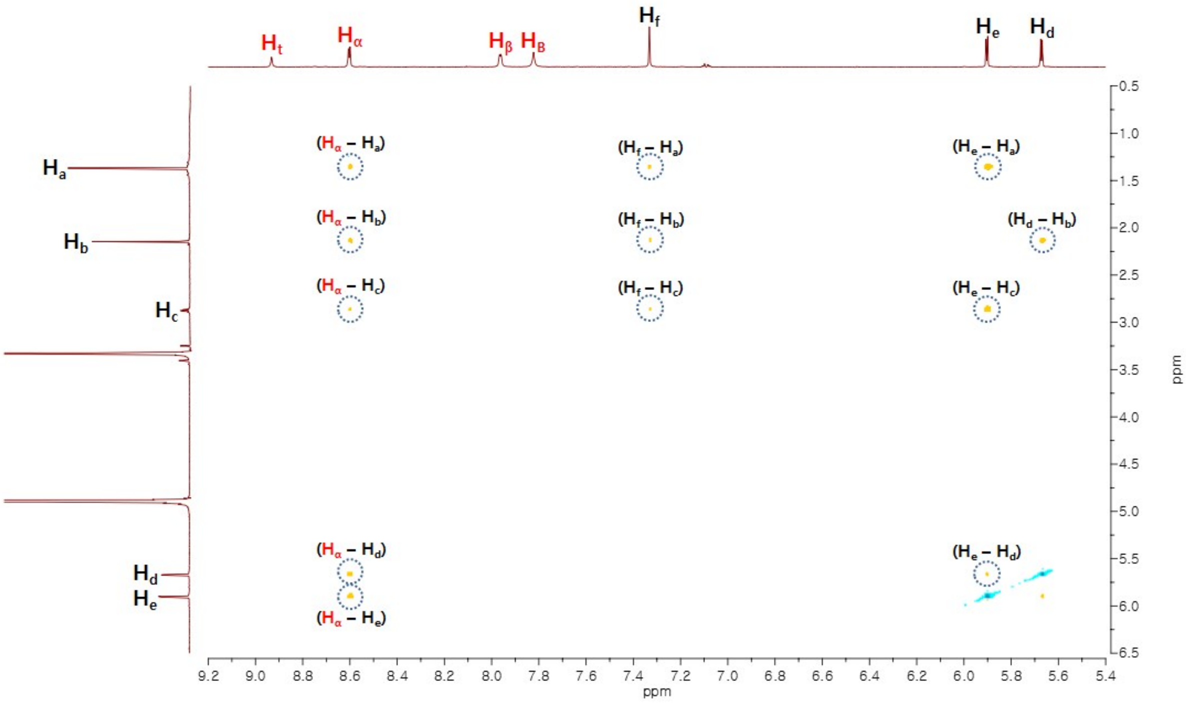


Figure S39. Expanded ^{1}H-^{1}H ROESY NMR spectrum of **1** (CD_3OD [0.5 mM], 298 K, 900 MHz)

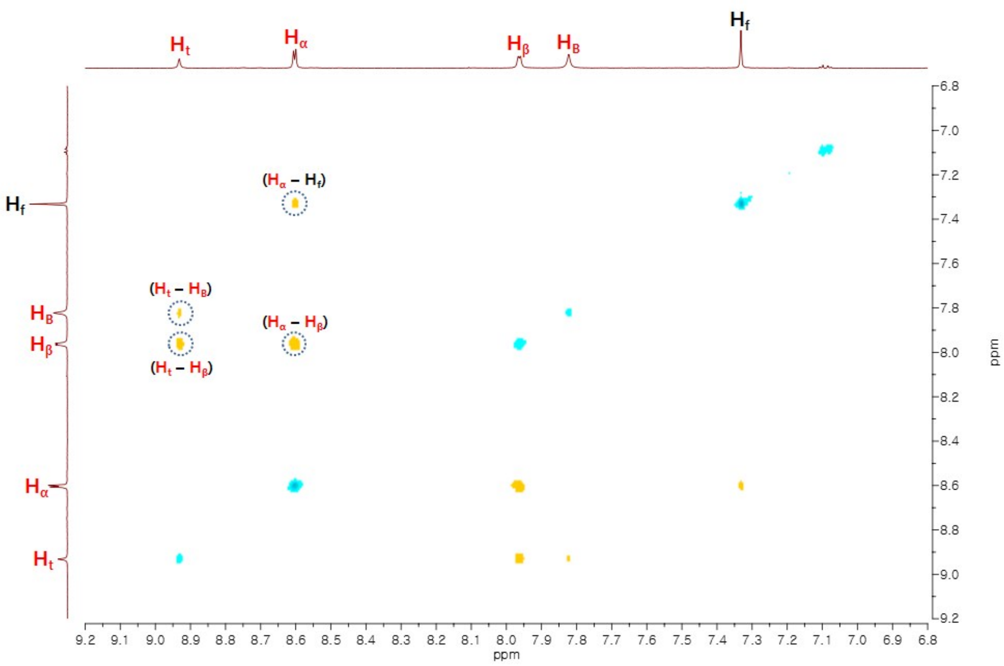


Figure S40. Expanded ^{1}H-^{1}H ROESY NMR spectrum of **1** (CD_3OD [0.5 mM], 298 K, 900 MHz)

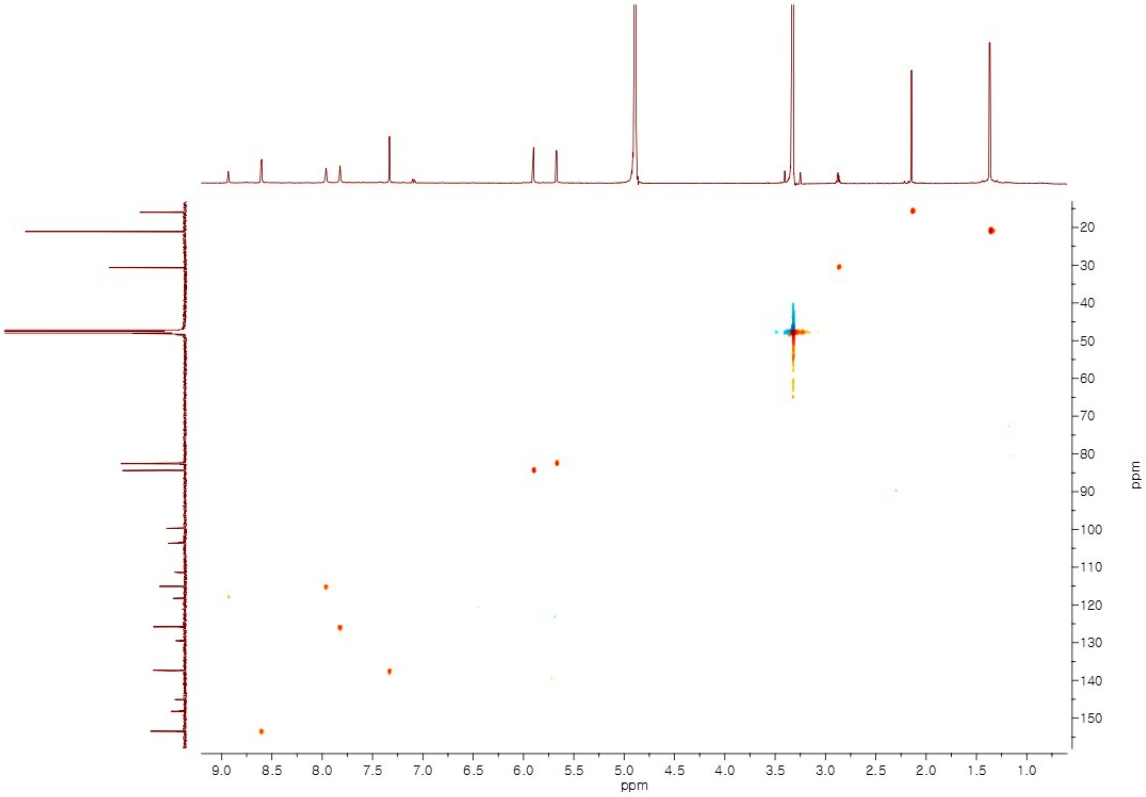


Figure S41. ^{1}H-^{13}C HSQC NMR spectrum of **1** (CD_3OD [0.5 mM], 298 K, 900 MHz)

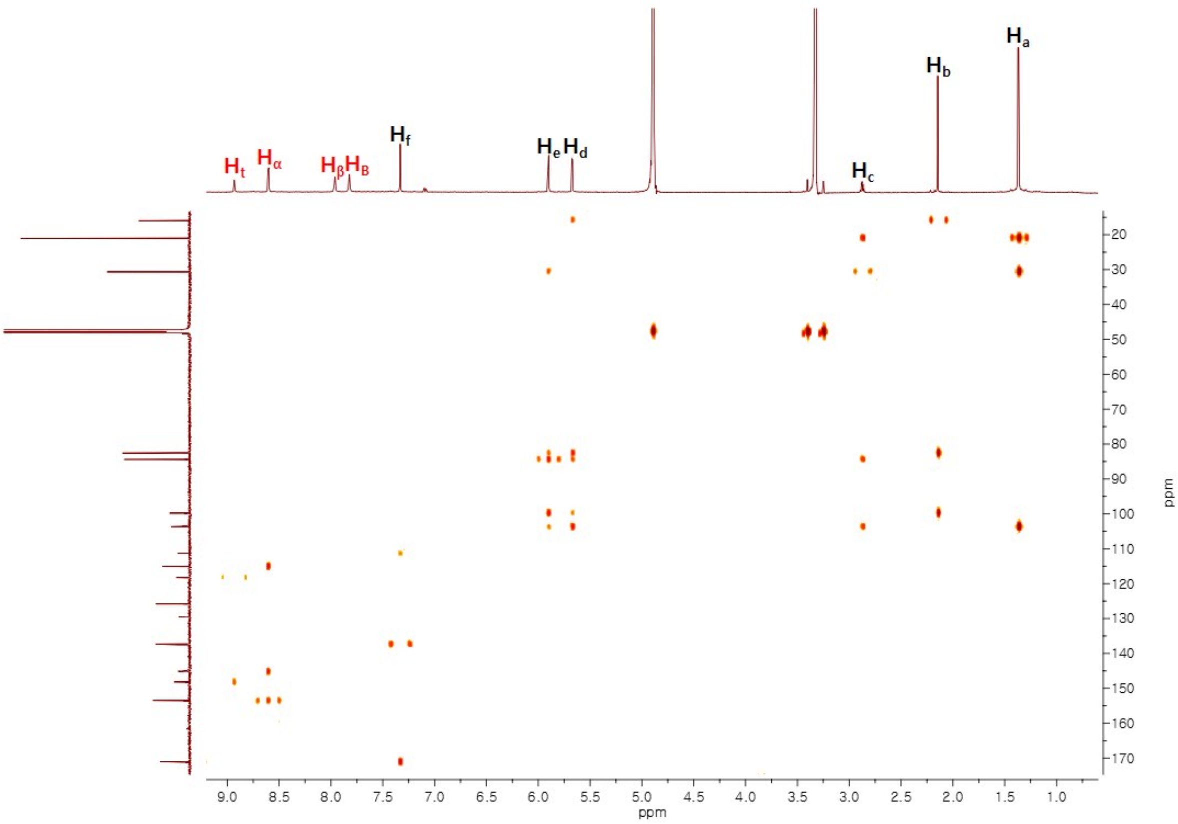


Figure S42. ^{1}H-^{13}C HMBC NMR spectrum of **1** (CD_3OD [0.5 mM], 298 K, 900 MHz)

6. NMR titrations of 2

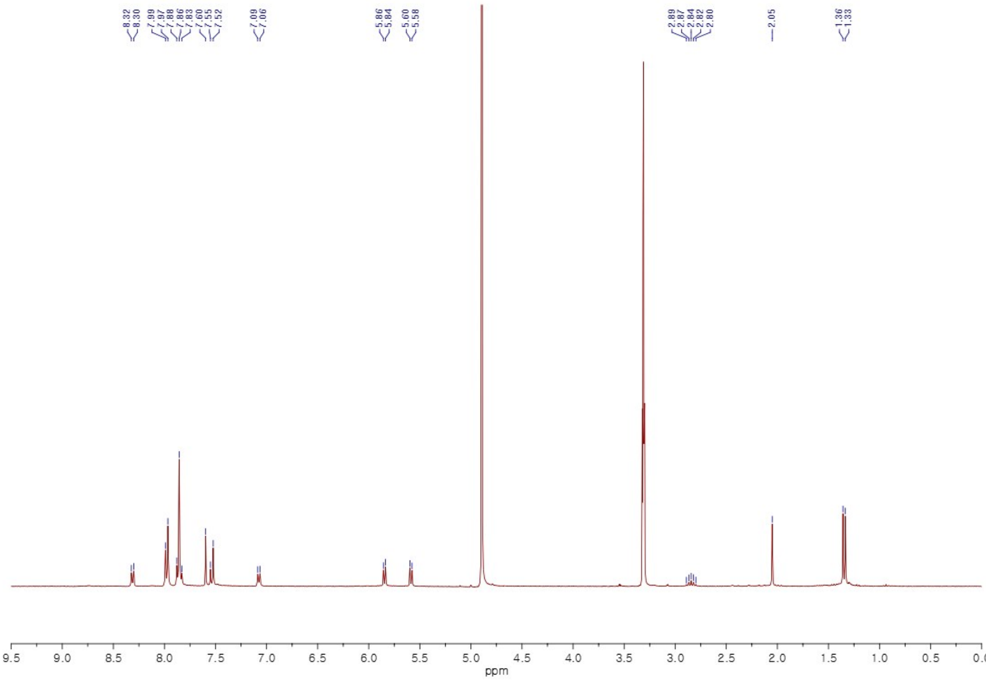


Figure S43. ^{1}H NMR spectrum showing formation of only **1** when reaction was carried out in the presence of pyrene (2.0 eq) (CD_3OD [4.0 mM], 300 MHz)

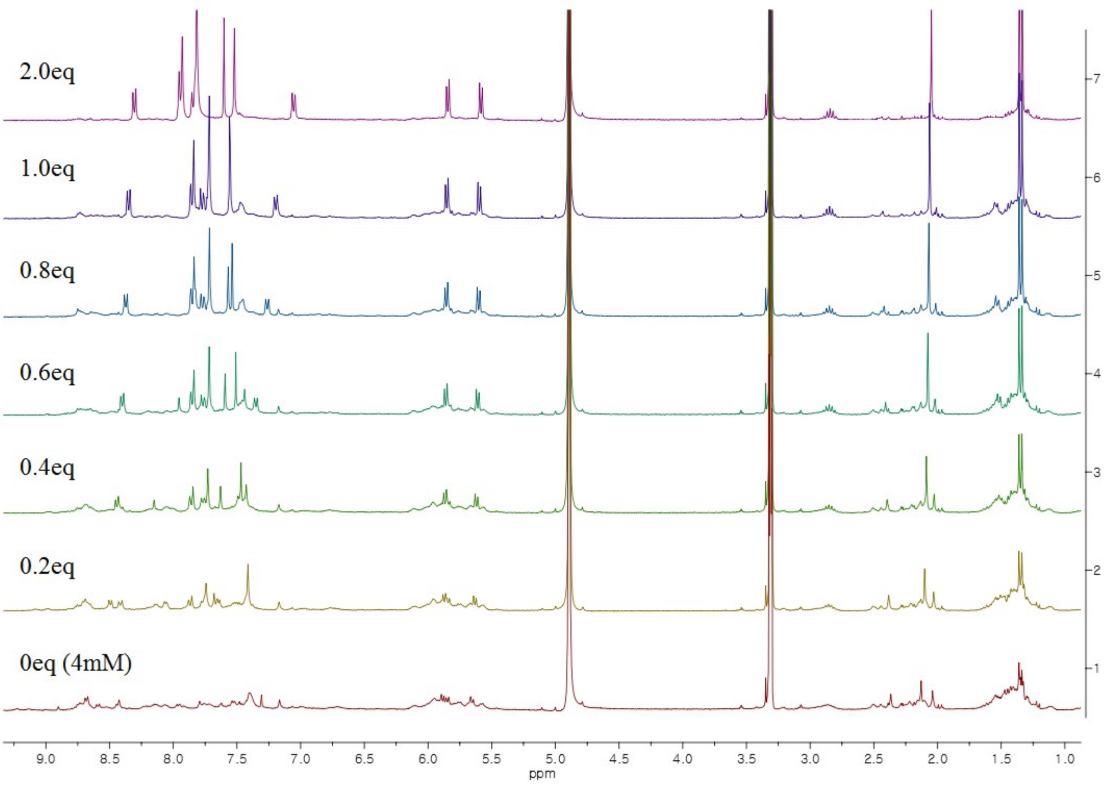


Figure S44. ^{1}H NMR spectra of mixture **1+2** showing increasing proportion of monomeric macrocycle **1** upon addition of pyrene from 0 eq to 2.0 eq (CD_3OD [4.0 mM], 300 MHz)

7. ^{1}H, 13C NMR and ESI-MS spectra of 4, 5, 6 and 7

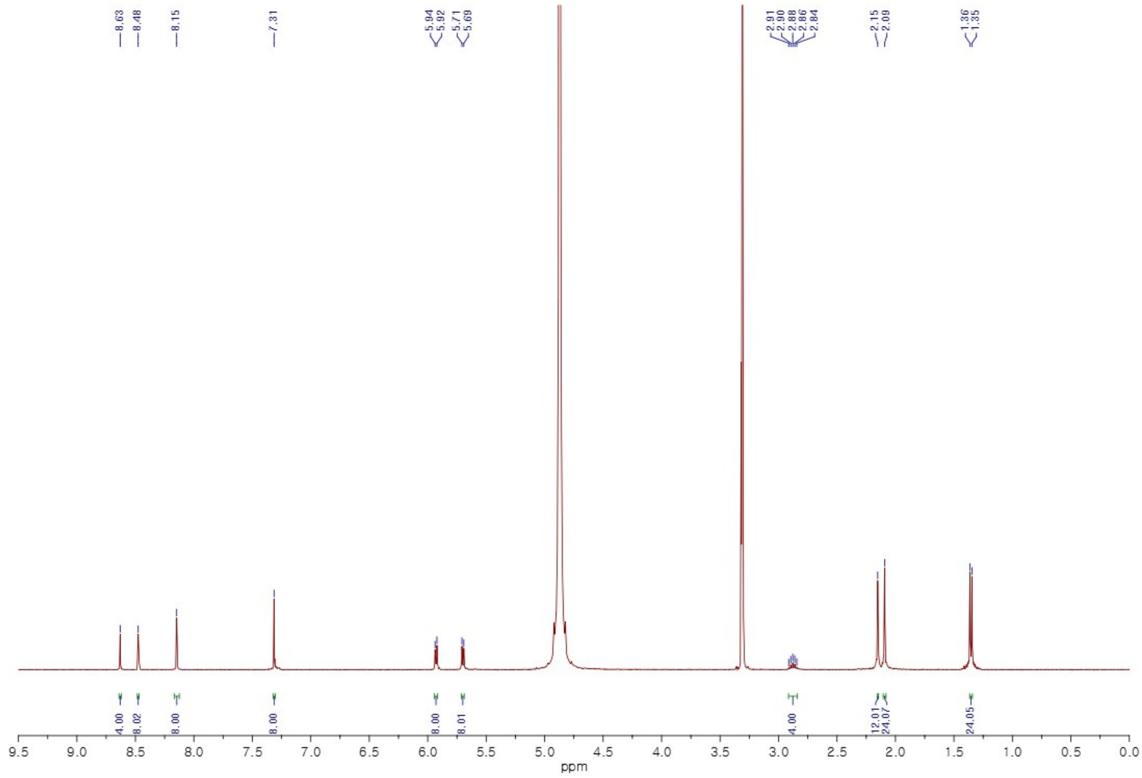


Figure S45. ^{1}H NMR spectrum of **4** (CD_3OD [8.0 mM], 400 MHz)

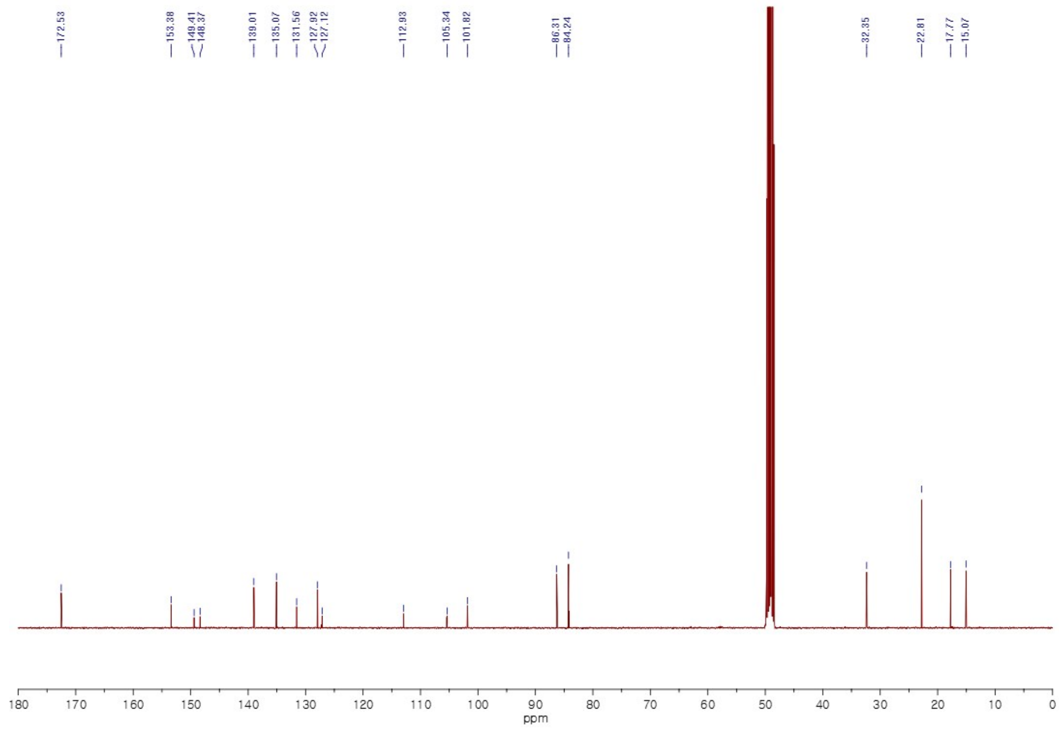


Figure S46. ^{13}C NMR spectrum of **4** (CD_3OD [8.0 mM], 100 MHz)

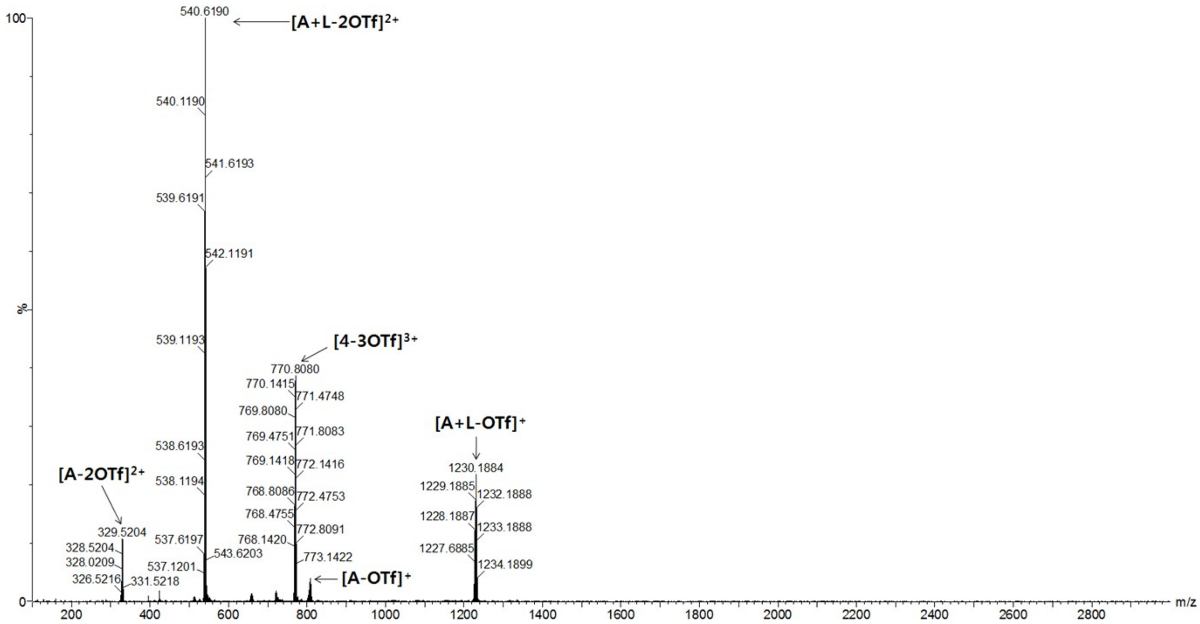


Figure S47. Full ESI mass spectrum of **4**

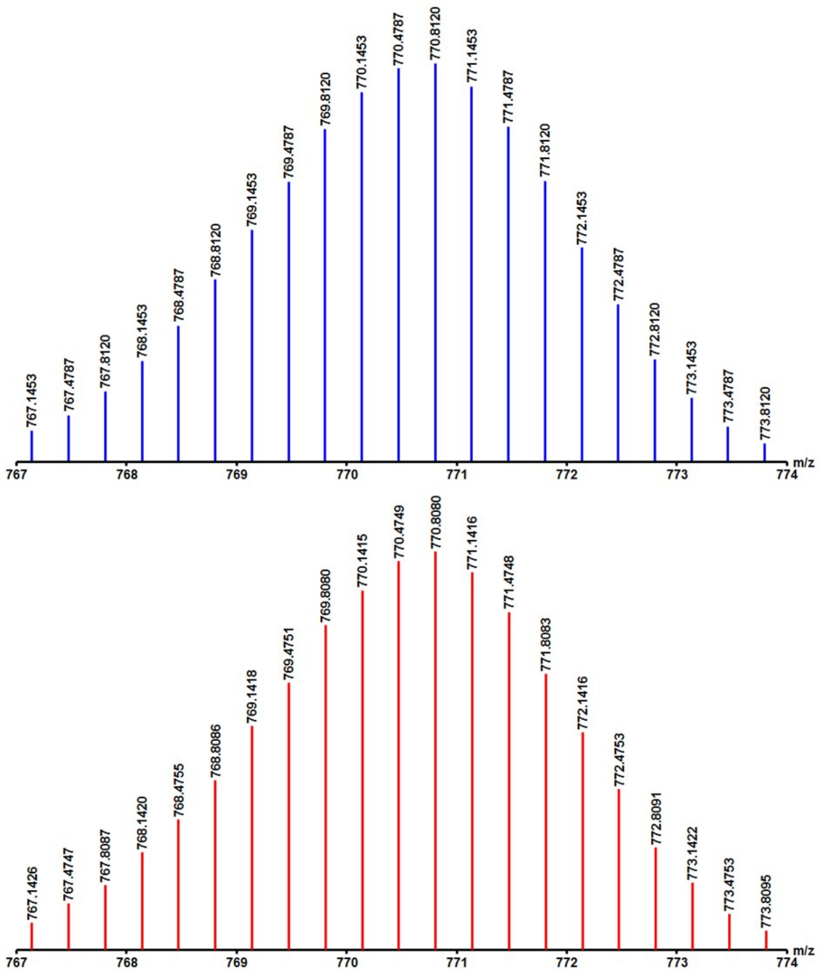


Figure S48. Calculated (blue) and experimental (red) ESI mass spectra of [**4**-3OTf]$^{3+}$

(Reaction in CD_3OD [8.0 mM])

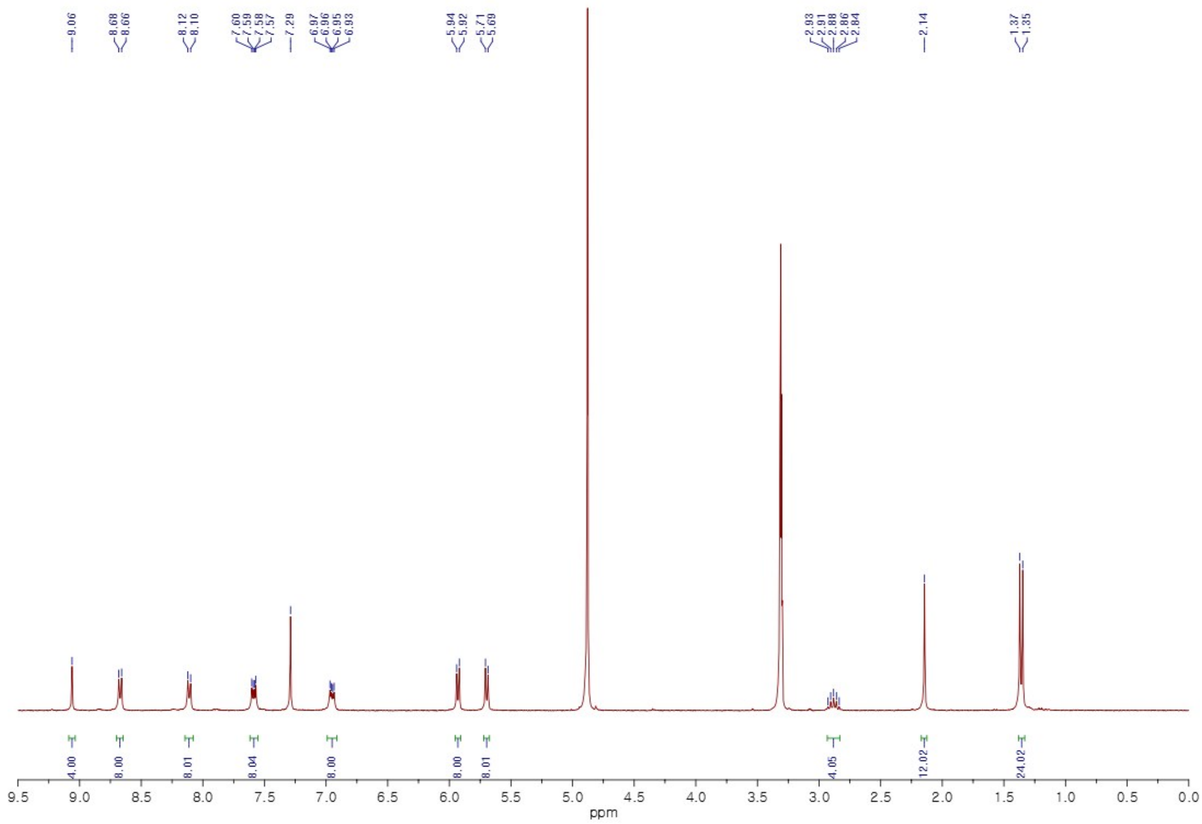


Figure S49. ^{1}H NMR spectrum of **5** (CD_3OD [8.0 mM], 300 MHz)

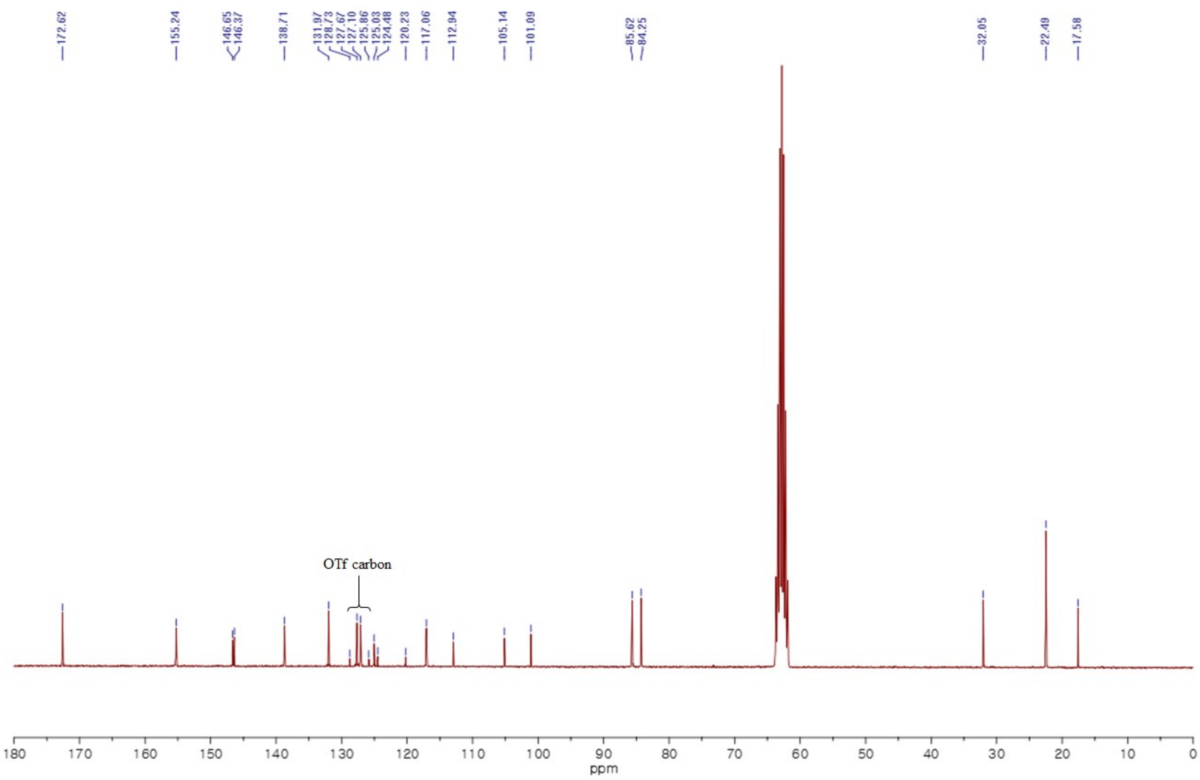


Figure S50. ^{13}C NMR spectrum of **5** (CD_3NO_2 [8.0 mM], 75 MHz)

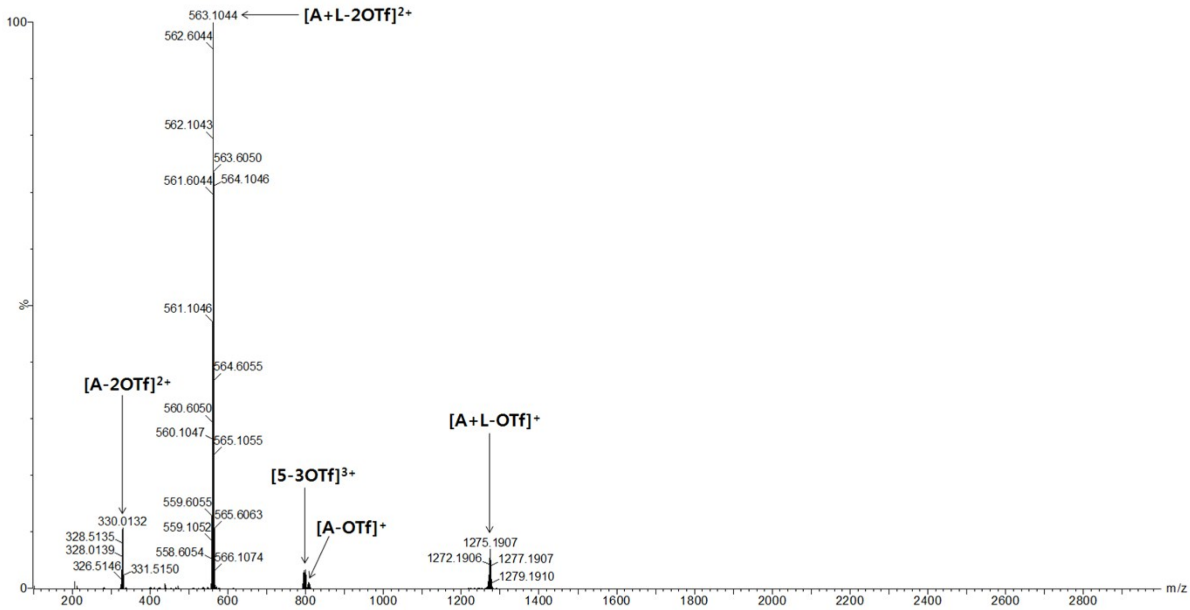


Figure S51. Full ESI mass spectrum of **5**

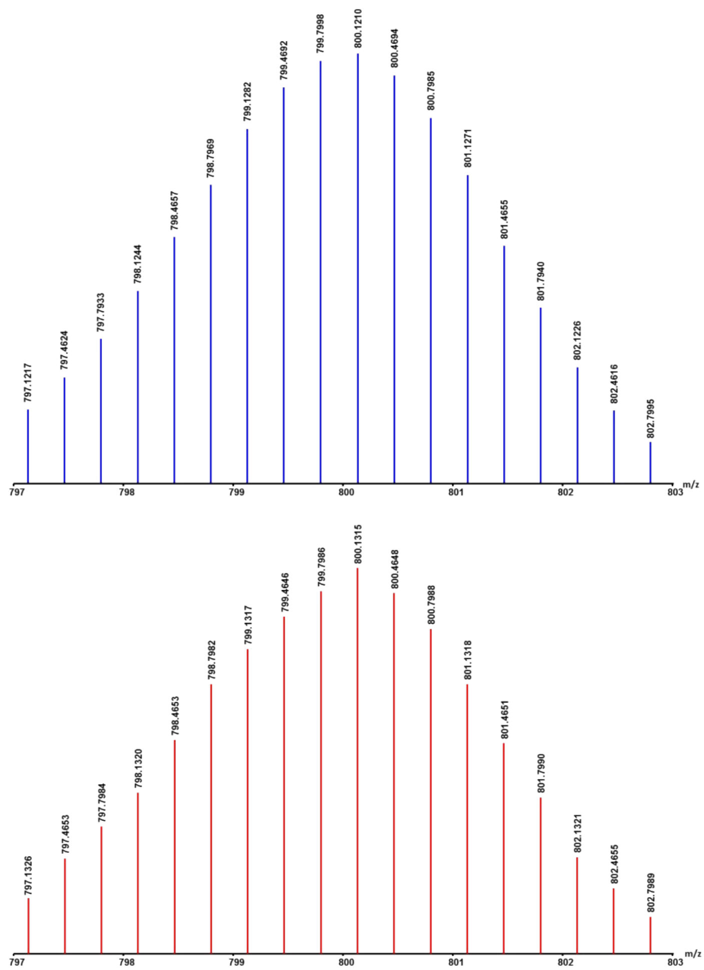


Figure S52. Calculated (blue) and experimental (red) ESI mass spectra of [**5**-3OTf]$^{3+}$

(Reaction in CD_3OD [8.0 mM])

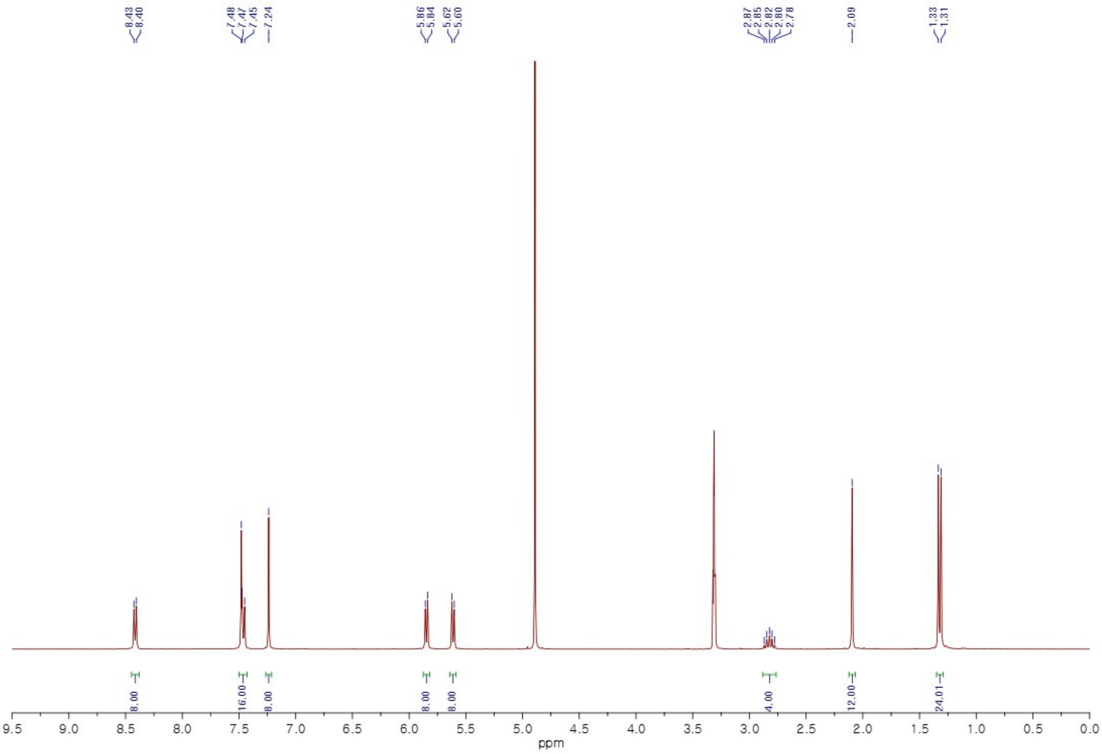


Figure S53. ^{1}H NMR spectrum of **6** (CD_3OD [8.0 mM], 400 MHz)

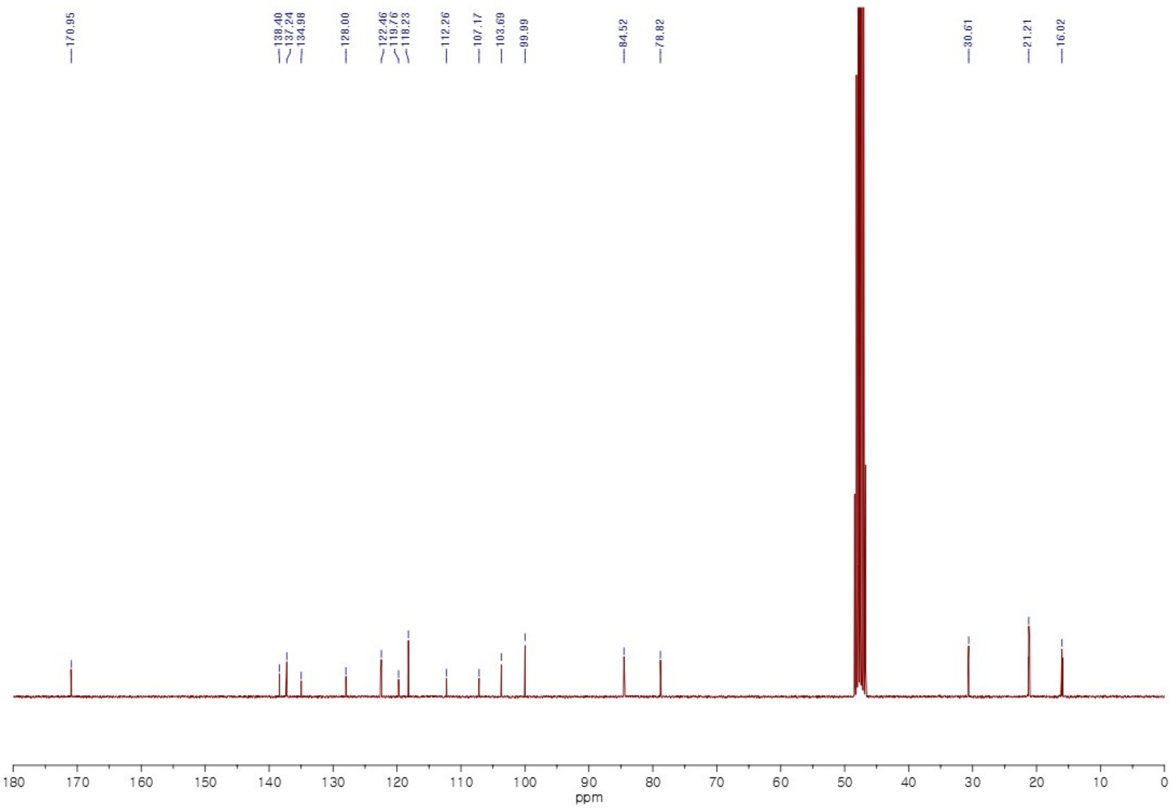


Figure S54. ^{13}C NMR spectrum of **6** (CD_3OD [8.0 mM], 100 MHz)

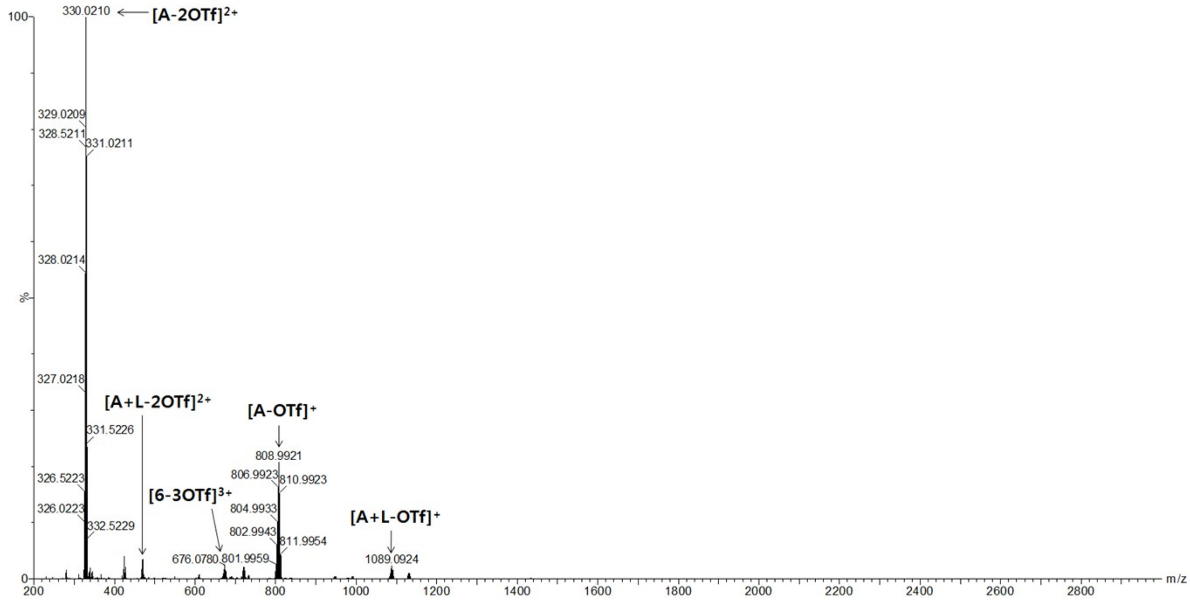


Figure S55. Full ESI mass spectrum of **6**

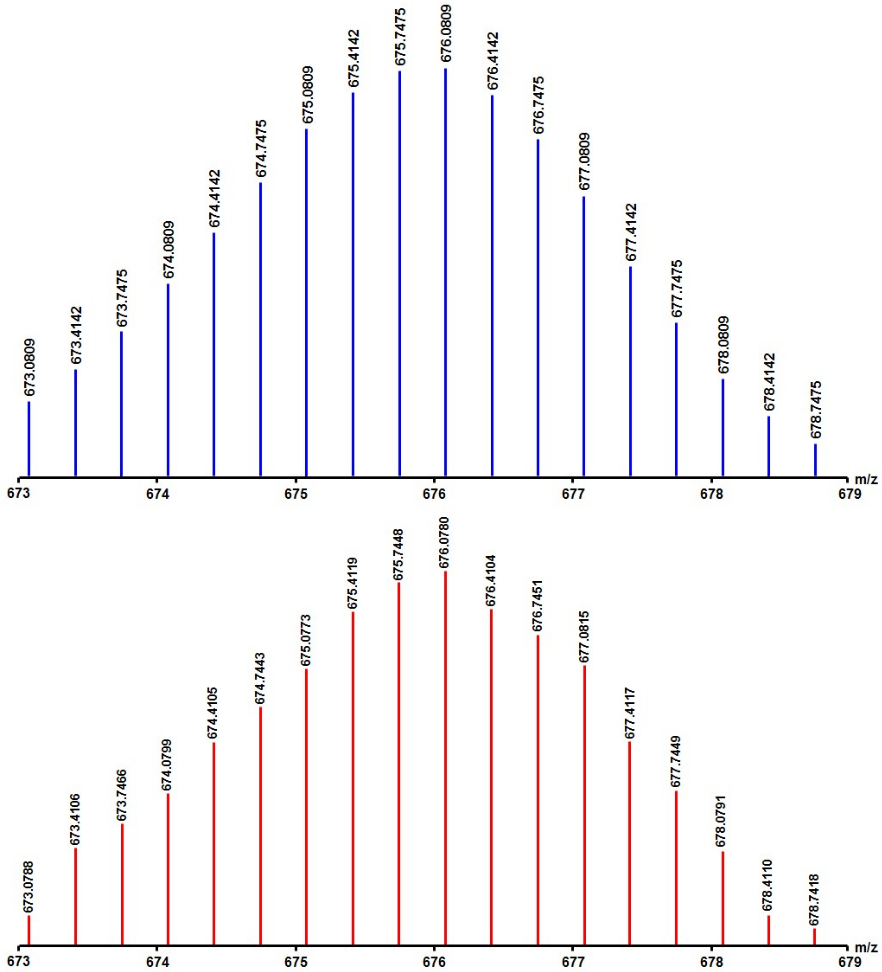


Figure S56. Calculated (blue) and experimental (red) ESI mass spectra of [**6**-3OTf]$^{3+}$

(Reaction in CD_3OD [8.0 mM])

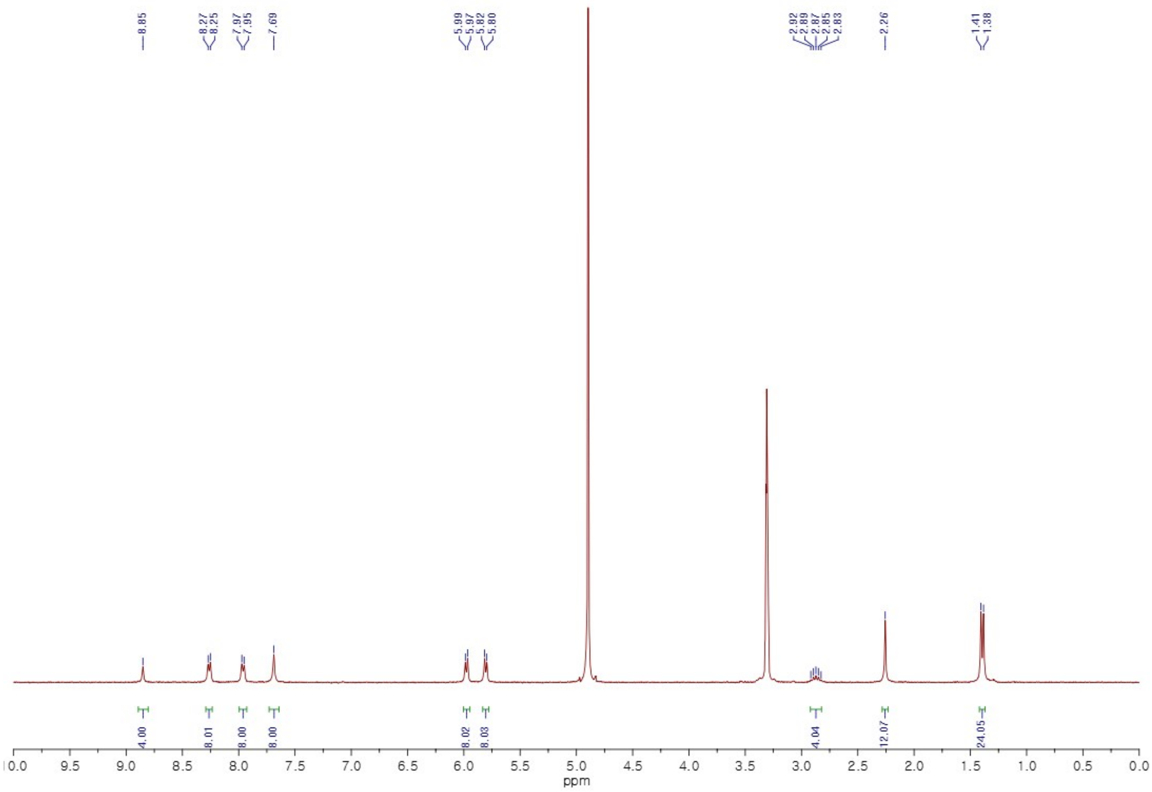


Figure S57. ^{1}H NMR spectra of **7** (CD_3OD [8.0 mM], 300 MHz)

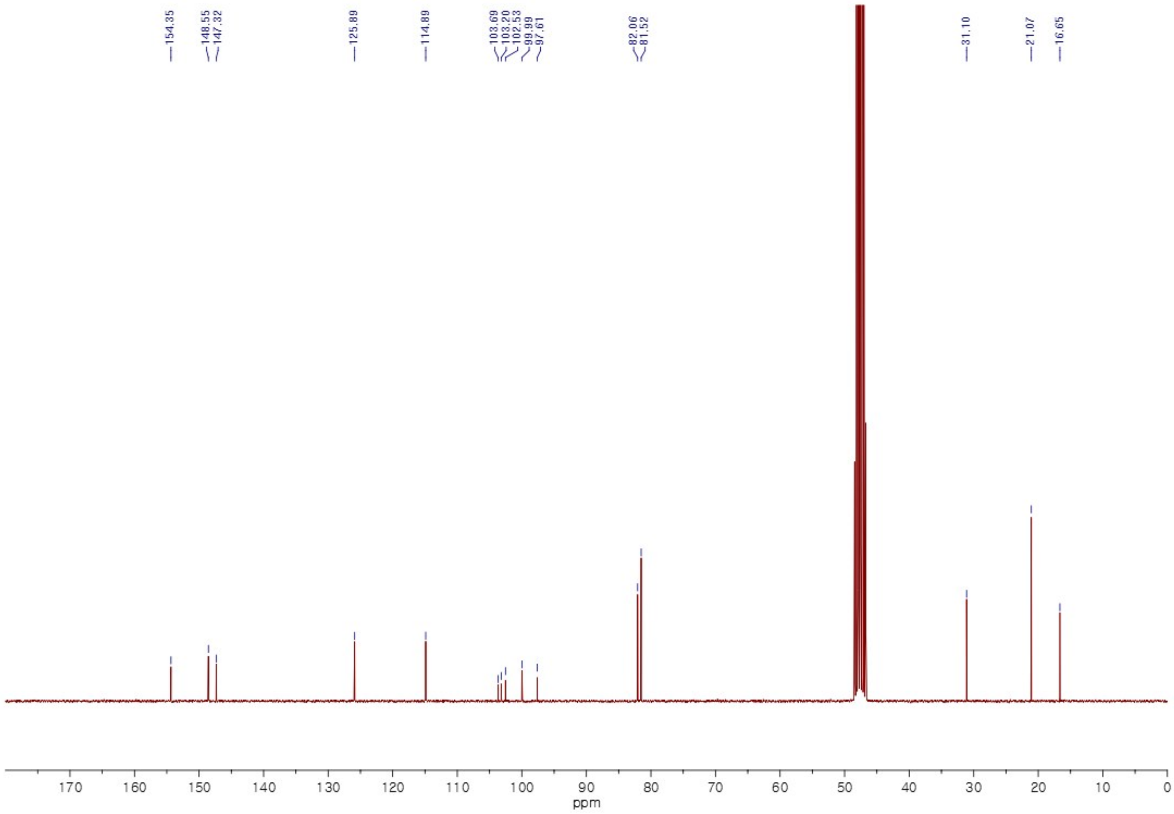


Figure S58. ^{13}C NMR spectra of **7** (CD_3OD [8.0 mM], 75 MHz)

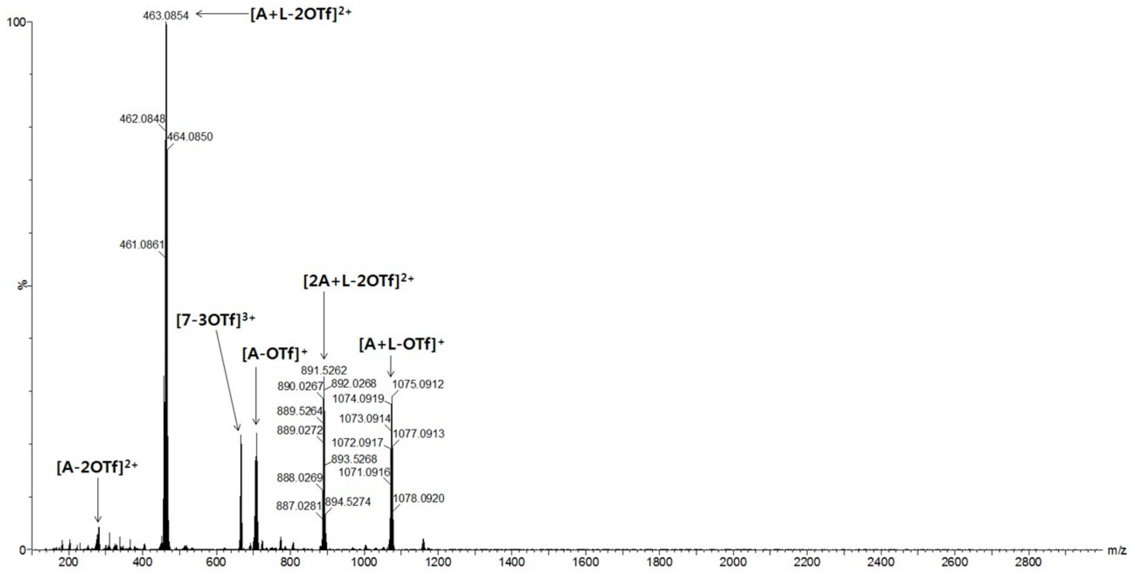


Figure S59. Full ESI mass spectrum of **7**

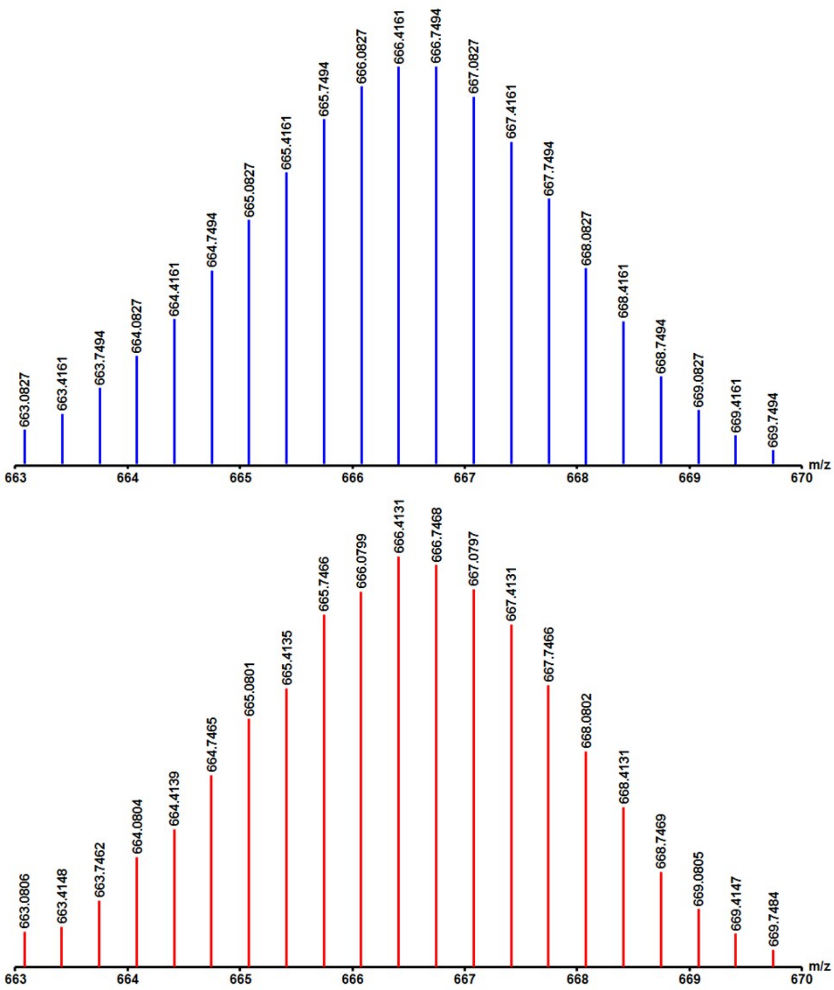


Figure S60. Calculated (blue) and experimental (red) ESI mass spectra of [**7**-3OTf]$^{3+}$

(Reaction in CD_3OD [8.0 mM])

8. Computational details and discussion

The computational study using the combination of semi-empirical and density functional theory (DFT) methods was carried out in order to explain the formation of linear [3]catenane **2**. The structure of **2** is linearly interlocked with three [2+2] mono-rectangular rings (**1**) which are composed of two acceptor **A1** moieties and two donor **L1** moieties (see Scheme 1 in the main text). Due to the huge size of **2**, the geometry optimizations for linear [3]catenane **2** and a mono-rectangular ring **1** were performed using semi-empirical PM7 method[S4] implemented in MOPAC2016 software package,[S5] which was developed to take the non-covalent interactions (NCI), such as hydrogen bonding and van der Waals (vdW) interaction, into account (Figure S1). The conductor-like screening model (COSMO) technique was employed to consider the contribution of the methanol medium (dielectric constant, $\varepsilon = 32.613$) to the geometry optimization.[S6] The methyl and isopropyl groups in arene ligand of Ru(II) were omitted for structural simplicity in the geometry optimization. All the molecular structures were optimized with no symmetry constraints. The main intermolecular interactions can be divided into $\pi \ldots \pi$ stacking (black dotted lines), CH…π (red dotted lines), and CH…N (blue dotted lines) interactions as shown in Figure S1. While single crystal X-ray diffraction (scXRD) data were obtained from a well-packed single-crystal solid sample, the geometry optimizations were performed considering the influence from solvent medium in an approximated manner. Nevertheless, PM7-optmized geometries for **2** represents qualitatively well the experimentally measured geometric characteristics (see Figure 4 in the main text). The evaluated center to center distances between stacked triazole moieties are ranging from ~3.5 to ~3.9 Å except only one pair (4.2 Å), which clearly indicates the π-π interactions between the π-conjugated moieties of **L1**. The CH…π distances between naphthalene moiety of **A1** and phenyl moieties of **L1** are ranging from were found to be in the range of ~2.5 to ~2.9 Å. Lastly, CH…N interactions between two outer mono-rectangular rings were also observed, and their distances are ranging from ~2.4 to ~2.7 Å. (To provide detailed geometric information, the Cartesian coordinates of PM7-opimized geometries for linear [3]catenane **2** and a [2+2] mono-rectangular ring **1** are provided in this Supporting Information.) The spatial distribution of NCI among [2+2] mono-rectangular rings is analyzed by plotting the iso-surface of reduced density gradient (RDG, $s = 1/(2(3\pi^2)^{1/3} \cdot |\nabla\rho(\mathrm{r})|/\rho(\mathrm{r})^{4/3})$,[S7] for which we utilized MULTIWFN program (Figure S2).[S8] The green-colored iso-surfaces clearly show a variety of intermolecular interactions not only between donor moieties but also donor and acceptor moieties. Therefore, our computational results indicate that the intermolecular non-bonding interactions among mono-rectangular rings play a pivotal role in the formation of linear [3]catenane **2**.

To get a more insight into the formation of **2**, the binding energy for the formation of **2** from three [2+2] mono-rectangular rings (**1**) was evaluated by means of density functional theory (DFT) calculations. We employed three hybrid density functional methods, PBE0,[S9] M06-2X,[S10] and ωB97X-D,[S11] for single-point electronic energy calculations with the geometries optimized by the semi-empirical PM7 method. The influence of solvent medium (methanol, $\varepsilon = 32.613$) on the electronic energy was accounted using the polarizable continuum model with the integral equation formalism variant (IEFPCM)[S12] implemented in Gaussian 16 software package.[S13] The LanL2DZ effective pseudo-potential was used for the basis set for Ru,[S14] and the 6-31G(d,p) was used for other elements. Figure S3 shows the binding energies per one [2+2] mono-rectangular ring **1** (BE/[2+2]) for the linear

[3]catenane **2** evaluated using three hybrid DFT methods, PBE0, M06-2X, and ωB97X-D. Whereas PBE0 cannot describe vdW interactions, both M06-2X and ωB97X-D were designed to effectively deal with weakly interacting systems. The numerical values of BE/[2+2] for **2** obtained with PBE0, M06-2X, and ωB97X-D methods are +4.08, –13.20, and –26.52 kcal/mol, respectively. Whereas PBE0 methods indicate that the formation of 2 is unfavorable due to the lack of capability to describe NCI, M06-2X and ωB97X-D methods suggests that the formation of 2 is thermodynamically feasible process. Therefore, our computational results strongly suggest that NCI is of great importance in the formation of linear [3]catenane **2**. The higher BE obtained with ωB97X-D compared to that with M06-2X can be explained with the poor performance of M06-2X out of equilibrium relative to ωB97X-D, because the DFT calculations were carried out with the PM7-optimized geometry.[S15]

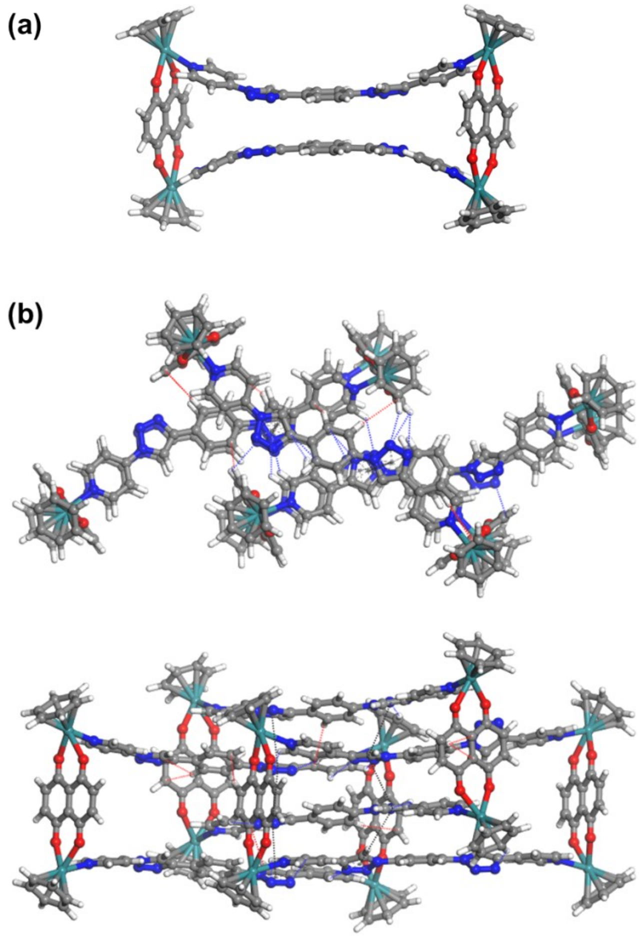


Figure S61. The PM7-optimized geometries for (a) [2+2] mono-rectangular ring **1** and (b) top- and side-views of linear [3]catenane **2**. The as π…π, CH…π and CH…N interactions are indicated by black, red, and blue dotted lines, respectively.

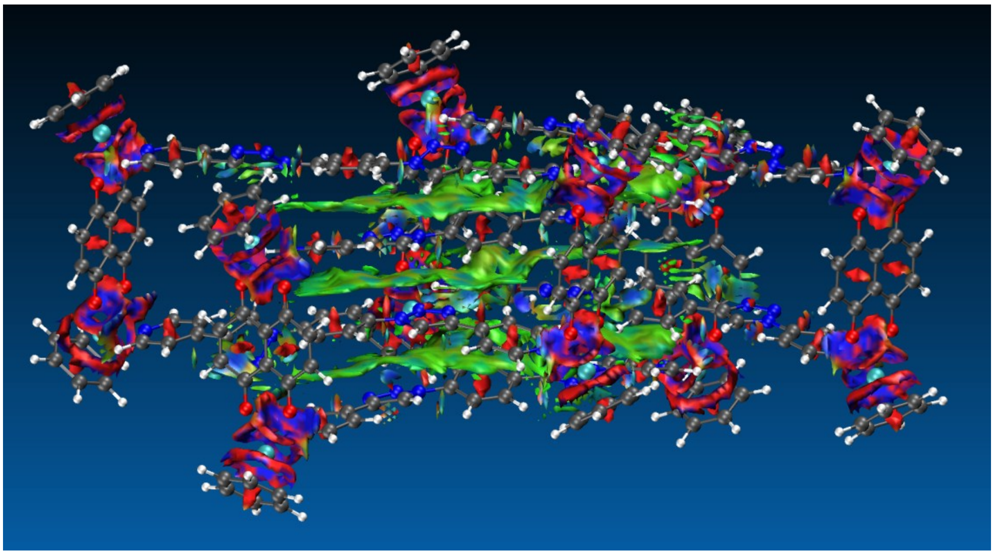


Figure S62. Reduced density gradient iso-surfaces (s = 0.65 au) for linear [3]catenane **2**. The iso-surfaces are colored on a blue-green-red scale according to the values of sign(λ_2)ρ, ranging from –0.02 to +0.02 au. The $\pi\ldots\pi$ interactions between **L1** moieties and the CH…π distances between **A1** and **L1** moieties are indicated by green-colored iso-surfaces. The CH…N interactions mainly between two outer mono-rectangular rings are indicated by blue-colored iso-surfaces. The strong electrostatic interactions and steric contributions indicated by blue- and red-colored iso-surfaces, respectively, are observed near transition metal cation, Ru(II).

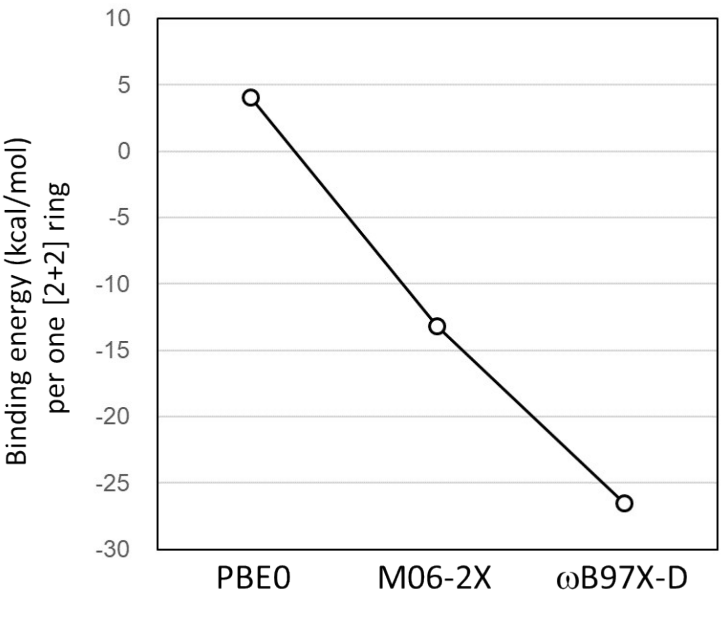


Figure S63. Binding energies per one [2+2] mono-rectangular ring **1**, BE = [E(**2**) – 3 × E(**1**)] / 3, for the formation of linear [3]catenane **2** evaluated using PBE0, M06-2X, and ωB97X-D methods.

Cartesian coordinates of compounds 1 and 2 optimized by PM7 method

[2+2] mono-rectangular ring 1

Ru	-10.542488	4.564255	0.644364
Ru	10.919029	4.418434	-0.605352
Ru	10.559584	-4.482816	0.968431
Ru	-10.903895	-4.325022	-0.946712
O	10.679232	2.808486	0.953630
N	-8.622611	3.412043	0.792095
O	-10.879358	2.529014	1.541551
O	-10.462233	2.947589	-0.914670
N	3.123870	-1.957711	-2.003926
O	11.133463	2.360997	-1.494680
O	10.489807	-2.428648	1.878428
C	-7.818962	3.311438	-0.294159
N	3.110548	1.504094	-2.300697
C	11.399131	0.182930	-2.314142
C	10.889903	-0.739617	0.335485
N	-2.888940	1.547400	2.255376
N	-4.156275	1.704243	2.405538
N	-4.729382	1.911825	1.173711
C	10.938713	0.669278	0.085568
N	4.378764	1.693269	-2.448091
C	11.353312	-1.140686	-2.079139
N	8.926946	3.412108	-0.802058
C	10.728522	1.574232	1.146941
O	-10.756406	-2.277317	-1.863828
C	4.962556	1.999974	-1.212423
C	8.101877	3.361917	0.271117
N	-4.668405	-2.016606	1.931527
C	2.633224	-1.887909	-0.690161
O	-11.192019	-2.702645	0.587266
N	4.842830	-2.111490	-0.696572
C	-6.076989	2.326307	1.032935
C	-6.541459	2.757509	-0.217235
N	8.666298	-3.423728	0.401628
C	11.157398	1.139526	-1.224545
C	-4.016982	-1.950023	-0.224749
C	6.572077	-2.404541	0.994304
C	-2.540014	1.657397	0.899199
C	7.214352	2.413341	-2.157360
C	-0.111025	1.481909	1.319421
N	4.403499	-2.097971	-1.996818
C	12.378256	-5.818926	0.944201
C	-11.517840	5.937276	2.141204
N	-5.110767	-2.056854	0.631995
C	-11.397977	-0.942283	2.120673
C	-6.440650	-2.412158	0.295977
C	8.495540	2.940312	-1.996378
C	7.826796	-2.911739	1.332761
C	0.262858	-1.705862	-1.371960
C	-6.925381	2.380237	2.146650
C	-11.021618	1.315681	1.269783
C	7.056417	-2.946886	-1.318830
C	-10.886317	0.835575	-0.048170
C	3.927778	1.964819	-0.260440
C	6.169862	-2.464798	-0.346347
C	10.540186	1.068456	2.514766
C	10.492187	-0.254497	2.749012
C	-9.771343	6.692371	0.592500
C	-1.177645	1.603752	0.419176
C	-3.733867	1.883708	0.199895
C	9.751712	-6.423127	1.812289
H	-11.882967	5.774588	3.165588
C	-1.492015	-1.798800	0.288780
N	-3.388576	-1.886961	1.932017
C	-11.975936	6.049565	-0.271492
C	-0.527124	-1.883964	1.299726
C	10.629652	-1.208720	1.639807
C	3.748949	-1.974580	0.154586
C	-10.629079	1.724410	-1.112776
C	-8.191553	2.943566	1.988199
C	12.888336	5.509383	-0.552960
C	1.226806	-1.818177	-0.363272
C	-11.192149	-1.462775	0.762404
N	-8.953832	-3.355995	-0.413897
C	8.295760	-3.430208	-0.902132
C	-0.921962	1.702368	-0.954340
C	10.120638	-6.648685	0.459188
C	-10.791377	-1.051472	-1.618473
C	-2.899499	-1.851012	0.615446
C	6.810396	2.844308	0.179792
C	1.200523	1.481822	0.861036
C	0.823971	-1.895248	0.975995
C	0.384750	1.704682	-1.426655
H	-10.332974	6.781425	-1.516386
C	10.689030	-5.895550	2.724680
C	-6.853042	-2.371691	-1.042281
C	12.112028	5.942629	0.549818
C	-10.201234	-6.464603	-1.102341
C	-10.647012	6.510178	-0.498902
C	1.440943	1.607221	-0.512716
C	-12.408902	5.767012	1.039978
N	2.784431	1.659360	-0.980283
C	10.292776	6.555349	-0.978697
C	-10.971880	-0.569860	-0.304884
C	-1.089011	-1.696489	-1.048277
C	12.366757	5.596066	-1.872535
C	12.013017	-5.597692	2.287133
C	-10.529899	1.214497	-2.487993
C	-7.320566	-2.875927	1.283377
C	-11.313707	0.378181	2.362870
C	11.075191	6.132407	-2.083200
C	-12.429241	-5.845613	-0.281446
C	-8.116438	-2.870094	-1.360838
C	-11.141669	-6.390602	-0.046714
O	10.954417	-2.880945	-0.561194
C	11.063133	-1.644911	-0.730195
C	-8.567961	-3.353580	0.885717
C	6.343530	2.391113	-1.060840
C	-10.210838	6.416630	1.914608
C	10.816330	6.477697	0.333685
C	-10.609732	-0.105597	-2.728725
C	11.424009	-6.337631	0.019446
C	-12.778129	-5.397208	-1.579745
H	12.758214	-5.246977	3.015962
H	10.690761	6.254709	-3.105569
H	9.400353	-7.114149	-0.229183
C	-11.837562	-5.479933	-2.642406
H	12.541088	5.937280	1.562188
C	-10.555622	-6.027859	-2.403255
H	-9.843784	-6.143355	-3.233053
H	-13.179946	-5.843962	0.522488
H	-8.231991	3.726511	-1.235508
H	11.606444	0.612261	-3.300202
H	11.517022	-1.895011	-2.855749
H	8.514166	3.781161	1.208634
H	-5.928599	2.700557	-1.120878
H	-4.095681	-1.956989	-1.301190
H	5.929756	-1.996822	1.779557
H	6.894553	2.043768	-3.134983
H	-0.308397	1.383438	2.391362
H	13.411362	-5.638667	0.612974
H	-11.607315	-1.682787	2.899859
H	9.217709	3.026077	-2.830060
H	8.189968	-2.949093	2.378686
H	0.571791	-1.624071	-2.416702

H	-6.607984	2.018424	3.130197
H	6.787452	-2.977232	-2.379420
H	3.944721	2.141199	0.804711
H	10.438502	1.820998	3.303357
H	10.345534	-0.683790	3.745668
H	-8.769324	7.117655	0.431253
H	-3.920998	2.019461	-0.854517
H	8.751830	-6.722502	2.159144
H	-12.676228	5.974627	-1.116416
H	-0.836529	-1.940241	2.345843
H	3.825747	-1.953417	1.230630
H	-8.900845	3.066235	2.831501
H	13.908863	5.135321	-0.392912
H	9.033099	-3.875035	-1.602045
H	-1.748560	1.781289	-1.665764
H	6.177677	2.820065	1.069378
H	2.021757	1.381642	1.574449
H	1.566669	-1.968298	1.772548
H	0.577133	1.782463	-2.500464
H	10.428683	-5.776885	3.785600
H	-6.212367	-1.984047	-1.839249
H	-9.228398	-6.950529	-0.936182
H	-13.446713	5.455527	1.226530
H	9.317174	7.031875	-1.151388
H	-1.832333	-1.607935	-1.842371
H	13.001147	5.329512	-2.730002
H	-10.384468	1.961819	-3.275273
H	-7.040857	-2.893067	2.341529
H	-11.447095	0.816439	3.357953
H	-8.490843	-2.919561	-2.402874
H	-10.888293	-6.790407	0.944974
H	-9.300908	-3.784538	1.598726
H	-9.542362	6.621724	2.763369
H	10.236869	6.864456	1.183215
H	-10.536106	-0.539495	-3.731709
H	11.733525	-6.567003	-1.010361
H	-13.789852	-5.015810	-1.775907
H	-12.136897	-5.198670	-3.662569

linear [3]catenane 2

Ru	-2.960829	-8.384403	0.314303
Ru	17.192494	-0.941369	-5.845687
Ru	-3.880359	-0.996172	5.413524
Ru	16.452040	5.737887	0.159777
N	-1.158369	-7.139248	-0.112809
N	2.502239	-5.110999	-3.025800
N	3.713525	-4.775631	-3.310970
N	4.505262	-5.015427	-2.222503
N	10.981150	-4.662189	-1.661778
N	12.160631	-4.232729	-1.942943
N	12.054971	-3.094002	-2.704771
N	15.415771	-1.499372	-4.624689
C	0.013418	-7.340344	0.533268
C	-1.188738	-6.359534	-1.221364
C	1.211604	-6.799103	0.063487
C	-0.028446	-5.794804	-1.745330
C	1.197451	-6.048386	-1.116877
C	2.429890	-5.588676	-1.709907
C	3.735445	-5.538935	-1.194862
C	5.890419	-4.695823	-2.203964
C	6.775819	-5.568638	-1.562227
C	6.336104	-3.522302	-2.820188
C	8.129369	-5.261623	-1.553748
C	7.693732	-3.225447	-2.799522
C	8.596250	-4.098726	-2.182003
C	10.013359	-3.827108	-2.240543
C	10.710946	-2.806463	-2.906507
C	13.192857	-2.495946	-3.303932
C	13.029794	-1.619828	-4.384683
C	14.479544	-2.833412	-2.861333
C	14.172696	-1.145911	-5.028872
C	15.571889	-2.321784	-3.559470
N	-1.945866	-0.943382	4.273511
N	2.150236	0.359082	1.648095
N	3.391566	0.622502	1.468775
N	4.119262	0.035397	2.474091
N	10.666324	0.328264	3.105647
N	11.821381	0.820268	2.823611
N	11.664133	1.853631	1.929156
N	14.815946	4.312921	0.675325
C	-0.880221	-1.228129	5.062259
C	-1.743045	-0.586548	2.984258
C	0.430788	-1.133193	4.597538
C	-0.458495	-0.475461	2.454006
C	0.647621	-0.713040	3.281180
C	1.977568	-0.414882	2.806793
C	3.260447	-0.636321	3.334184
C	5.517121	0.275594	2.550129
C	6.385535	-0.690731	3.063896
C	5.992826	1.501681	2.064411
C	7.754386	-0.441231	3.036175
C	7.357781	1.738634	2.051247
C	8.247652	0.758867	2.512242
C	9.664267	1.023393	2.414727
C	10.312307	2.005743	1.649036
C	12.743882	2.652344	1.479439
C	12.519573	3.635735	0.506126
C	14.024169	2.491121	2.027128
C	13.582864	4.457885	0.134875
C	15.036441	3.351262	1.604003
C	18.289550	6.618965	1.120649
C	18.157402	7.165727	-0.184901
C	16.956433	7.810568	-0.570410
C	15.888340	7.923898	0.356605
C	16.017169	7.374840	1.654024
C	17.223934	6.740152	2.042884
C	-5.852203	0.085045	5.590149
C	-5.804419	-0.937053	6.574967
C	-4.729104	-0.991370	7.498211
C	-3.706569	-0.012491	7.442890
C	-3.751310	1.006729	6.458778
C	-4.834501	1.068490	5.549975
C	19.239184	-1.718049	-6.375415
C	19.009274	-0.520666	-7.104062
C	17.861114	-0.394293	-7.926214
C	16.950266	-1.475464	-8.034186
C	17.175215	-2.666780	-7.303638
C	18.328184	-2.795566	-6.489836
O	-2.238342	-7.337840	2.172552
O	-3.526563	-6.202740	0.322575
O	-2.913558	-3.023888	5.254670
O	-4.171489	-1.900845	3.376761
O	17.493895	-0.382518	-3.676922
O	15.999312	0.885185	-5.264495
O	17.099888	3.592062	-0.138505
O	15.559416	4.828571	-1.703205
C	-2.417956	-6.309804	2.872109
C	-3.724678	-5.244289	1.095872
C	-1.847871	-6.266238	4.223672
C	-3.152431	-5.214072	2.390369
C	-4.580864	-4.137041	0.647214

C	-2.022242	-5.180681	5.002893
C	-3.335244	-4.060563	3.218903
C	-4.768858	-3.061829	1.432157
C	-2.778563	-4.026483	4.507467
C	-4.083395	-2.961919	2.730761
C	17.385261	0.570190	-2.872514
C	15.930844	1.797700	-4.412167
C	18.082748	0.488696	-1.581148
C	16.605365	1.703941	-3.176567
C	15.117910	2.985099	-4.714450
C	17.984526	1.491354	-0.689569
C	16.494224	2.767117	-2.223785
C	15.007062	3.980079	-3.816574
C	17.174638	2.679883	-0.992893
C	15.699578	3.893972	-2.522260
C	-4.810070	-9.258702	-0.629362
C	-3.741739	-9.413883	-1.548238
C	-2.550165	-10.060937	-1.143982
C	-2.433413	-10.582131	0.169345
C	-3.496201	-10.427519	1.091841
C	-4.690353	-9.773695	0.685908
C	-9.728637	0.607048	-7.277077
C	-9.273177	1.748163	-7.978860
C	-10.080283	2.914619	-8.037837
C	-11.346359	2.927608	-7.403886
C	-11.804671	1.780686	-6.697243
C	-11.002344	0.616747	-6.654464
Ru	-9.798476	2.384044	-5.871593
Ru	8.391318	-6.580363	3.054926
Ru	-9.473833	9.435176	-0.294560
Ru	8.056669	-0.029794	9.237437
N	-8.344584	1.690704	-4.324063
N	-5.247426	-0.719084	-1.072837
N	-4.103073	-1.151057	-0.674705
N	-3.113626	-0.554289	-1.411154
N	3.366609	-1.486835	-1.328629
N	4.469573	-1.917394	-0.837096
N	4.197045	-2.646908	0.299217
N	7.154391	-4.941414	2.155236
C	-7.075588	1.888440	-4.758954
C	-8.559447	1.066012	-3.143711
C	-5.971360	1.460494	-4.026757
C	-7.500052	0.594460	-2.369718
C	-6.186950	0.774330	-2.826172
C	-5.072343	0.197556	-2.118188
C	-3.686065	0.310639	-2.329297
C	-1.744911	-0.887618	-1.211817
C	-0.745019	0.002332	-1.617043
C	-1.434924	-2.115152	-0.610954
C	0.585948	-0.345156	-1.411842
C	-0.103492	-2.450385	-0.411691
C	0.906922	-1.564926	-0.805888
C	2.283163	-1.913575	-0.541566
C	2.817710	-2.670933	0.505517
C	5.197598	-3.359968	0.991702
C	6.549821	-3.031192	0.834420
C	4.829476	-4.452044	1.791073
C	7.505854	-3.851315	1.436248
C	5.840655	-5.234835	2.336225
N	-8.128520	7.879153	0.578230
N	-5.405552	4.564842	3.410258
N	-4.298347	4.028287	3.798845
N	-3.277630	4.498735	3.016814
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C	-3.784630	5.386121	2.083253
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C	-0.300321	2.576751	4.083810
C	0.720709	3.472902	3.750872
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C	2.590539	2.197939	4.979477
C	4.942446	1.763010	5.789588
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C	5.495152	0.445532	7.712624
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C	9.724850	-7.587257	1.519323
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C	10.189454	-2.659784	4.587608
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C	10.133874	-1.677432	5.504007
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C	5.929959	-3.624782	7.337514
C	9.017081	-1.609063	6.460386
C	6.977057	-2.596135	7.384926
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C	-18.645728	-6.292010	-2.438761
C	-18.635454	-5.533678	-3.637045
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C	1.984471	3.347258	0.160745
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N	-9.369305	-2.398379	-5.467383
N	-8.702514	-2.563521	-4.281891
N	-3.108533	-2.566177	-4.192523
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C	-14.572726	-3.151264	-3.640667
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C	-10.859705	-2.892830	-3.919007
C	-9.609696	-2.876823	-3.279914
C	-7.283707	-2.519610	-4.222925
C	-6.616016	-3.268431	-3.246272
C	-6.582268	-1.761775	-5.170073
C	-5.228356	-3.277687	-3.233131
C	-5.194626	-1.767032	-5.153815
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C	0.374131	-1.722627	-4.826701
C	1.492910	-2.202110	-4.136554
C	0.565076	-0.849807	-5.903359
C	2.766966	-1.862134	-4.588661
C	1.867869	-0.554978	-6.306904
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C	6.863131	-0.699021	-7.839318

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C	4.882150	-2.716301	-7.946489
C	5.973443	-2.846626	-7.055510
C	-18.994506	1.681096	4.675366
C	-17.970835	2.577218	5.064371
C	-16.948946	2.147394	5.948224
C	-16.970901	0.833863	6.474100
C	-17.996677	-0.067411	6.089597
C	-19.012343	0.360710	5.198824
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C	4.976634	6.075036	1.612380
C	3.812407	6.849196	1.411065
C	3.712543	7.708130	0.283513
C	4.762339	7.765731	-0.659886
C	5.934557	6.981226	-0.456906
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O	-17.144216	0.496812	1.962409
O	-15.828876	-4.687507	-0.530124
O	-16.864561	-2.980302	-2.074986
O	4.565102	3.422197	-0.797327
O	3.593451	4.992750	-2.532844
O	5.125417	-0.367111	-4.480027
O	4.053967	1.141404	-6.211499
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C	-17.059676	-0.342871	1.038030
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C	-17.558042	0.023614	-0.295476
C	-15.381981	-4.203137	1.717463
C	-16.433189	-2.555764	0.168154
C	-17.485833	-0.851953	-1.313828
C	-15.891750	-3.839387	0.386812
C	-16.914513	-2.190986	-1.105817
C	4.750137	2.590610	-1.705305
C	3.707314	4.057598	-3.368515
C	5.471925	1.347535	-1.392413
C	4.288927	2.828597	-3.026468
C	3.222865	4.276463	-4.734121
C	5.630598	0.398322	-2.328457
C	4.427484	1.802629	-4.015420
C	3.338596	3.305735	-5.661957
C	5.049768	0.576229	-3.669198
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H	-0.077247	-5.182356	-2.652836
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H	6.413480	-6.485947	-1.088853
H	5.632410	-2.838321	-3.311832
H	8.836869	-5.936865	-1.059967
H	8.043832	-2.302728	-3.274816
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H	12.044260	-1.320267	-4.746707
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H	-2.646271	-0.366037	2.388202
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H	-4.731265	-1.743598	8.302403
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H	-3.004796	1.814768	6.481512
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H	19.740949	0.299228	-7.055224
H	17.720308	0.504613	-8.544963
H	16.090343	-1.400741	-8.714578
H	16.504891	-3.527787	-7.443219
H	18.532004	-3.745468	-5.975071
H	-1.287365	-7.149537	4.547358
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H	-1.616153	-5.099330	6.016043
H	-5.421285	-2.222633	1.160973
H	18.671554	-0.418164	-1.403489
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H	18.485802	1.481450	0.284330
H	14.413478	4.883003	-3.991872
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H	-3.855091	-9.057292	-2.582745
H	-1.750384	-10.243492	-1.878109
H	-1.529030	-11.136869	0.460485
H	-3.433418	-10.886503	2.090477
H	-5.534623	-9.692400	1.385043
H	-9.147020	-0.324782	-7.310333
H	-8.314077	1.716528	-8.515524
H	-9.753245	3.776132	-8.639783
H	-11.993450	3.813819	-7.482631
H	-12.818073	1.767288	-6.268513
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H	-6.991554	2.393537	-5.748562
H	-9.616685	0.942883	-2.847763
H	-4.963134	1.646972	-4.403422
H	-7.691221	0.074857	-1.427331
H	-3.123696	0.916122	-3.022315
H	-0.991223	0.963204	-2.072290
H	-2.227106	-2.799978	-0.302727
H	1.383302	0.341113	-1.712743
H	0.150534	-3.405999	0.048971
H	2.341298	-3.159882	1.337234
H	6.857370	-2.165917	0.239224
H	3.783796	-4.707843	1.988654
H	8.591013	-3.662212	1.339952
H	5.640936	-6.161870	2.929703
H	-6.608582	8.838143	-0.482848
H	-9.564245	6.875939	1.713853
H	-4.795170	7.336995	0.458400
H	-7.854648	5.334238	2.783423
H	-3.184056	5.899278	1.351157
H	-1.141650	5.991060	2.406522
H	-2.423833	2.188697	4.069469
H	1.216707	5.383322	2.857406
H	-0.063796	1.620595	4.556263
H	2.085279	1.461765	5.580003
H	6.657972	2.626686	4.755961
H	3.471754	0.724166	7.038700
H	8.311358	1.624284	6.404926
H	5.245455	-0.157169	8.616499
H	6.660950	-9.016750	2.201269
H	7.961524	-8.017322	0.306438
H	10.316794	-7.202586	0.677556
H	11.376775	-7.424172	2.940475
H	10.069891	-8.425763	4.850900
H	7.722352	-9.259738	4.468217
H	-7.966897	12.067109	-0.958135
H	-10.032260	11.700030	-2.336600
H	-12.106623	10.744001	-1.267777
H	-12.106382	10.158460	1.175821
H	-10.034291	10.543716	2.558639
H	-7.975866	11.500378	1.497206
H	9.763732	2.498351	9.814275
H	10.986635	0.333474	10.196661
H	9.781802	-1.623430	11.229383
H	7.380544	-1.388362	11.947548
H	6.165631	0.781804	11.568635
H	7.359527	2.723803	10.512308
H	-6.675015	5.872848	-5.270926
H	-12.206179	3.550284	-2.052263
H	-6.621071	7.893832	-3.730884
H	-12.190777	5.602603	-0.540162
H	10.998573	-2.749929	3.854675
H	5.223472	-5.388684	6.331743
H	10.891058	-0.888868	5.582580
H	5.128708	-3.542284	8.079564
H	-17.603724	-5.165047	-5.526944
H	-15.754035	-6.797712	-5.047849
H	-15.764206	-8.125727	-2.915985
H	-17.640827	-7.843358	-1.266472
H	-19.484099	-6.193433	-1.733857
H	-19.483961	-4.876584	-3.881057
H	-13.943904	-0.270356	4.217117
H	-16.096524	2.686891	2.211353
H	-11.775480	0.442132	3.109871
H	-13.982879	3.546956	1.057194
H	-10.126820	0.865629	0.877551
H	-7.853394	1.089100	1.856041
H	-7.951174	4.412095	-0.939742
H	-5.403387	0.913352	1.567331
H	-5.491291	4.242571	-1.227466
H	-3.261858	4.135418	-1.237591
H	0.574734	1.837297	0.782990
H	-0.961008	5.162373	-1.527908
H	2.868565	2.892025	0.639247
H	1.410617	6.068255	-1.629938
H	-13.799603	-5.527409	-1.458466
H	-15.517824	-2.770996	-4.077586
H	-11.458758	-4.704369	-1.999727
H	-13.230959	-1.845545	-4.724365
H	-9.338582	-3.040094	-2.247926
H	-7.168037	-3.853523	-2.501313
H	-7.117813	-1.176857	-5.930020
H	-4.689436	-3.877499	-2.490594
H	-4.640387	-1.189848	-5.904435
H	-2.507151	-0.674102	-5.105076
H	1.375179	-2.855992	-3.269525
H	-0.282482	-0.422433	-6.441411
H	3.683677	-2.235069	-4.103756
H	2.094287	0.084288	-7.181507
H	7.846017	-1.959237	-6.355195
H	7.651537	0.065327	-7.822205
H	5.743820	0.272890	-9.448410

H	3.982522	-1.527384	-9.545796
H	4.154174	-3.536612	-8.043859
H	6.088299	-3.757356	-6.453157
H	-19.821377	2.031594	4.039350
H	-17.987711	3.617785	4.711684
H	-16.193404	2.864444	6.299916
H	-16.215033	0.522192	7.208264
H	-18.048788	-1.066195	6.548333
H	-19.833857	-0.321184	4.934504
H	6.971443	5.586810	0.866344
H	5.089272	5.472402	2.525152
H	3.026902	6.865254	2.179860
H	2.831278	8.356636	0.171746
H	4.718568	8.473481	-1.500989
H	6.772597	7.060444	-1.162302
H	-15.063977	-3.537963	3.736763
H	-17.979431	1.029199	-0.396731
H	-14.976858	-5.214509	1.822960
H	-17.842177	-0.628115	-2.324963
H	5.868396	1.255029	-0.379696
H	2.771211	5.251771	-4.941465
H	6.178720	-0.531804	-2.150570
H	2.988800	3.420597	-6.693062

9. X-ray crystal structure parameters of 2

Table S1. X-ray crystal structure parameters of **2**

Empirical formula	C104 H120.33 F8 N16 O20.50 Ru4 S2.67	
Formula weight	2564.26	
Temperature	100(2) K	
Wavelength	0.700 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	*a* = 28.000(6) Å	α = 90°
	b = 48.956(10) Å	β = 105.96(3)°
	c = 30.810(6) Å	γ = 90°
Volume	40605 (15) $Å^3$	
Z	12	
Density (calculated)	1.258 g/cm^3	
Absorption coefficient	0.522 mm^{-1}	
F(000)	15732	
Crystal size	0.200 × 0.200 × 0.100 mm^3	
Theta range for data collection	1.354 to 32.637°	
Index ranges	-35≤*h*≤37, -62≤*k*≤65, -38≤*l*≤34	
Reflections collected	107465	
Independent reflections	58400 [R(int) = 0.0296]	
Completeness to theta = 25.000°	80.0%	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.880	
Refinement method	Full-matrix-block least-squares on F^2	
Data / restraints / parameters	58400 / 2505 / 4116	
Goodness-of-fit on F^2	1.082	

Final R indices [I>2sigma(I)]	R_1 = 0.1086, wR_2 = 0.2818
R indices (all data)	R_1 = 0.1521, wR_2 = 0.3209
Absolute structure parameter	0.80(4)
Largest diff. peak and hole	0.875 and -0.512 e.Å^{-3}

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