

Electronic Supporting Information (ESI)

Same knot, longer rope: altering ligand geometry provides control over nuclearity in self-assembled trefoil knots

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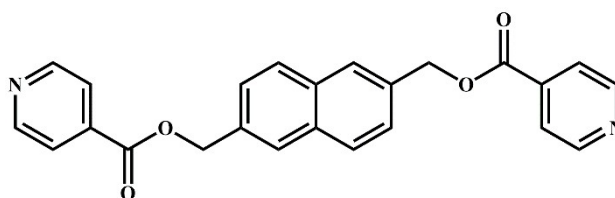
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1. Materials and methods

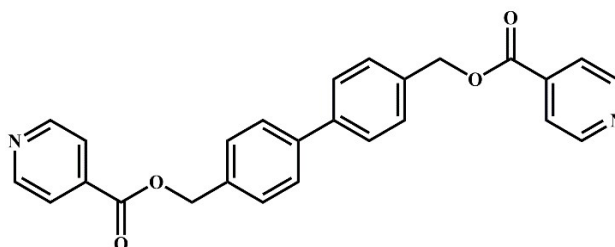
All reagents and solvents were purchased from commercial sources and used as supplied unless otherwise mentioned. The starting materials $[\text{Cp}^*\text{MCl}_2]_2$ ($\text{M}=\text{Rh}$), 2,2'-bisbenzimidazole (**Bibzm**), 2,5-dihydro-3,6-di-2-pyridinylpyrrolo[3,4-*c*]pyrrole-1,4-dione (**Dpdpd**), (2,7-dihydroxybenzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetrone) (**Dhndi**), **L_a** and **L_b**, were prepared by literature method. NMR spectra were recorded on Bruker AVANCE I 400 spectrometer.

NMR spectra were recorded at room temperature and referenced to the residual protonated solvent.^{S1} Proton chemical shift $\delta \text{H} = 1.94$ ppm (CD_3CN) is reported relative to the solvent residual peak. Coupling constants are expressed in hertz. Elemental analysis was performed with an Elementar Vario EL III analyzer. The full $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for some complexes could not be obtained due to limited solubility even after 24 h of measuring time.

2.1 Synthesis of ligand **L_b** and **L_a**



Scheme S1. Chemical structure of ligand **L_a**



Scheme S2. Chemical structure of ligand **L_b**

The ligand **L_b** was synthesized according to previously reported literature procedures.^{S2} The ligand **L_a** was synthesized as following process. Dimethyl 2,6-Naphthalenedicarboxylate (500 mg, 2.05 mmol) was added into 15 mL anhydrous THF. Then LiAlH_4 (389 mg, 10.24 mmol) was carefully added into the solution under nitrogen protection at 0 °C. The mixture was stirred at 66 °C for 24 h. The mixture was extracted by ethyl acetate, and got naphthalene-2,6-diyldimethanol as a white solid in 77.8% yield.^{S3} The following procedures were familiar to the synthesis of **L_b**.

2.2 Synthesis of complex 1

AgOTf (25.7 mg, 0.10 mmol) was added to a solution of $[\text{Cp}^*\text{RhCl}_2]_2$ (15.5 mg, 0.025 mmol) in CH_3OH (10 mL) at room temperature. The reaction mixture was stirred in the dark at room temperature overnight and then filtered. **Bibzm** (5.85 mg, 0.025 mmol) and NaOH (2 mg, 0.05

mmol) were mixed in CH₃OH (10 mL) at room temperature for 5 h. Then mixed the two kinds of solution above and added **L_b** (10.6 mg, 0.025 mmol) to the mixture. The reaction mixture was stirred at room temperature for 24 h to give a light yellow solution. The solvent was concentrated to about 6 mL in a rotary evaporator. Then added about 0.3 mL CH₃CN into the solvent. After extraction with isopropyl ether, a yellow solid was precipitated and collected. The product was dried under vacuum (68% yield). ¹H NMR (400 MHz, Acetonitrile-*d*₃) δ 8.23 (d, *J* = 5.8 Hz, 14H, pyridyl-H), 8.02 (dd, *J* = 6.1, 3.3 Hz, 16H, pyridyl-H), 7.52 – 7.36 (m, 52H, pyridyl-H and phenyl-H), 7.21 (d, *J* = 7.9 Hz, 14H, phenyl-H), 5.08 (s, 16H, -CH₂-), 1.76 (s, 120H, Cp*-H); elemental analysis (%) calcd for C₂₄₈H₂₃₂F₂₄Rh₈N₂₄O₄₀S₈: C 52.04, H 4.06, N 5.87; found: C 51.89, H 4.10, N 5.95.

2.3 Synthesis of complex 2

The synthesis of **2** was carried out similarly to that of **1**, with the use of **L_a** (9.96 mg, 0.025 mmol) instead of **L_b**, which was obtained as a yellow solid in 78.4% yield. ¹H NMR (400 MHz, Acetonitrile-*d*₃) δ 8.14 (d, *J* = 5.8 Hz, 12H, pyridyl-H), 8.02 (dd, *J* = 6.2, 3.5 Hz, 18H, naphthyl-H), 7.77 (s, 8H, pyridyl-H), 7.49 (d, *J* = 11.3 Hz, 28H, pyridyl-H and phenyl-H), 5.47 (s, 4H, -CH₂-), 5.11 (s, 8H, -CH₂-), 1.77 (s, 90H, Cp*-H); elemental analysis (%) calcd for C₁₈₀H₁₆₈F₁₈Rh₆N₁₈O₃₀S₆: C 51.29, H 3.99, N 5.98; found: C 51.13, H 4.12, N 6.12.

2.4 Synthesis of complex 3

AgOTf (25.7 mg, 0.10 mmol) was added to a solution of [Cp*RhCl₂]₂ (15.5 mg, 0.025 mmol) in CH₃OH (10 mL) at room temperature. The reaction mixture was stirred in the dark at room temperature overnight and then filtered. **Dpdpd** (7.20 mg, 0.025 mmol) and NaOH (2 mg, 0.05 mmol) were mixed in CH₃OH (10 mL) at room temperature for 5 h. Then mixed the two kinds of solution above and added **L_a** (9.96 mg, 0.025 mmol) to the mixture. The reaction mixture was stirred at room temperature for 24 h to give a dark blue solution. The solvent was concentrated to about 6 mL in a rotary evaporator. Upon addition of diethyl ether, a dark blue solid was precipitated and collected. The product was recrystallized from a methanol/diethyl ether mixture in 71.1% yield. ¹H NMR (400 MHz, Acetonitrile-*d*₃) δ 9.00 (d, *J* = 5.6 Hz, 4H, pyridyl-H), 8.92 (d, *J* = 7.9 Hz, 4H, pyridyl-H), 8.77 (s, 2H, pyridyl-H), 8.61 (d, *J* = 6.1 Hz, 6H, pyridyl-H), 8.21 (t, *J* = 7.7 Hz, 4H, pyridyl-H), 7.85 – 7.74 (m, 10H, naphthyl-H), 7.69 (t, *J* = 8.6 Hz, 10H, pyridyl-H and naphthyl-H), 7.49 (d, *J* = 8.5 Hz, 4H, pyridyl-H), 5.68 (d, *J* = 11.4 Hz, 4H, -CH₂-), 5.35 (d, *J* = 11.5 Hz, 4H, -CH₂-), 1.63 (s, 60H, Cp*-H); elemental analysis (%) calcd for C₁₂₄H₁₁₂F₁₂Rh₄N₁₂O₂₄S₄: C 50.48, H 3.80, N 5.70; found: C 50.28, H 3.93, N 5.87.

2.5 Synthesis of complex 4

The synthesis of **4** was carried out similarly to that of **3**, with the use of **Dhndi** (7.45 mg, 0.025 mmol) instead of **Dpdpd**, which was obtained as a dark brown solid in 49.2% yield. ¹H NMR (400 MHz, Acetonitrile-*d*₃) δ 8.66 (d, *J* = 5.7 Hz, 4H, pyridyl-H), 8.46 (s, 4H, pyridyl-H), 7.85 (d, *J* = 22.6 Hz, 6H, naphthyl-H), 7.70 (d, *J* = 8.4 Hz, 2H, pyridyl-H), 7.50 (d, *J* = 8.4 Hz, 2H, pyridyl-H), 5.52 (s, 4H, -CH₂-), 1.70 (s, 30H, Cp*-H); elemental analysis (%) calcd for C₆₀H₅₂F₆Rh₂N₄O₁₆S₂: C 49.05, H 3.54, N 3.82; found: C 49.21, H 3.47, N 3.95.

3. Single-Crystal Structure Determination

X-ray Crystallography Details. Single crystals of complex **1** suitable for X-ray diffraction study was collected at 170 K, **2** was collected at 154 K, **3** at and **4** at 173 K on a Bruker D8 VENTURE system. The structures of **1**, **2**, **3** and **4** were solved by direct methods, using Fourier techniques, and refined on F^2 by a full-matrix least-squares method.^{S5,S6} In these data, the disordered solvent molecules which could not be restrained properly were removed using the SQUEEZE route.

In asymmetric unit of **1**, there were disordered anions and solvents (seven triflate anions, ten methanol and eleven water molecules) which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit them. 21 ISOR and 8 DFIX instructions were used to restrain ligands and Cp* fragments so that there were 134 restraints in the data. Hydrogen of water molecules could not be found and others were put in calculated positions.

In asymmetric unit of **2**, there were disordered anion and solvents (one triflate anion, seven methanol and twelve water molecules) which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit them. Two metallo-angle (Rh4, Rh6 and coordinated Cp* fragments) and one triflate anion were disordered and they were divided into two parts (61:39, 59:41 for metallo-angle and 46:54 for anion). 66 ISOR, 3 SIMU and 23 DFIX instructions were used to restrain anions, solvent molecule and Cp* fragments so that there were 599 restraints in the data. Hydrogen of methanol and water molecules could not be found and others were put in calculated positions.

In asymmetric unit of **3**, there were disordered anions and solvents (two triflate anions, two N,N-dimethylformamide, seven methanol and five water molecules) which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit them. 18 ISOR, 10 DELU and 12 DFIX instructions were used to restrain anions, ligands and solvent molecules so that there were 131 restraints in the data. Hydrogen of one water molecule could not be found and others were put in calculated positions.

In asymmetric unit of **4**, there were disordered solvent molecules (one diethyl ether, two methanol and one water molecules) which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit them. One triflate anion was disordered and it was divided into two parts (75:25). 12 ISOR and 7 DFIX instructions were used to restrain anion and solvent molecule so that there were 87 restraints in the data. Hydrogen of water molecule could not be found and others were put in calculated positions.

4. X-Ray crystal structure parameters of complexes 1, 2, 3, and 4

Table S1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{258}H_{300}F_{24}N_{24}O_{64}Rh_8S_8$	
Formula weight	6296.96	
Temperature	170(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$C2/c$	
Unit cell dimensions	$a = 71.010(4)$ Å	$\alpha = 90^\circ$.
	$b = 16.0851(10)$ Å	$\beta = 99.200(5)^\circ$.
	$c = 49.267(2)$ Å	$\gamma = 90^\circ$.
Volume	55549(5) Å ³	
Z	8	
Density (calculated)	1.506 Mg/m ³	
Absorption coefficient	5.143 mm ⁻¹	
F(000)	25856	
Crystal size	0.250 × 0.220 × 0.180 mm ³	
Theta range for data collection	2.039 to 70.000°.	
Index ranges	-86 ≤ h ≤ 86, -19 ≤ k ≤ 19, -58 ≤ l ≤ 60	
Reflections collected	414239	
Independent reflections	52659 [R(int) = 0.1766]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.753 and 0.475	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	52659 / 134 / 2724	
Goodness-of-fit on F^2	1.067	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1040$, $wR_2 = 0.2942$	
R indices (all data)	$R_1 = 0.1506$, $wR_2 = 0.3509$	
Extinction coefficient	0.000018(3)	
Largest diff. peak and hole	2.502 and -1.628 e.Å ⁻³	

[a] $R_1 = \sum ||F_o| - |F_c||$ (based on reflections with $F_o^2 > 2\sigma F^2$). $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$; $w = 1 / [\sigma^2(F_o^2) + (0.095P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2] / 3$ (also with $F_o^2 > 2\sigma F^2$)

Table S2. Crystal data and structure refinement for **2**.

Empirical formula	$C_{194}H_{240}F_{18}N_{18}O_{52}Rh_6S_6$	
Formula weight	4807.85	
Temperature	154(2) K	
Wavelength	1.34138 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	$a = 23.6578(11)$ Å	$\alpha = 119.776(2)^\circ$.
	$b = 23.6790(11)$ Å	$\beta = 98.285(2)^\circ$.
	$c = 23.8109(11)$ Å	$\gamma = 91.895(2)^\circ$.
Volume	11371.5(9) Å ³	
Z	2	
Density (calculated)	1.404 Mg/m ³	
Absorption coefficient	3.174 mm ⁻¹	
F(000)	4948	
Crystal size	0.180 × 0.140 × 0.060 mm ³	
Theta range for data collection	3.249 to 55.042°.	
Index ranges	-28 ≤ h ≤ 28, -28 ≤ k ≤ 28, -28 ≤ l ≤ 29	
Reflections collected	157195	
Independent reflections	43046 [R(int) = 0.0873]	
Completeness to theta = 53.594°	99.7 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.751 and 0.493	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	43046 / 599 / 2600	
Goodness-of-fit on F^2	1.056	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0810$, $wR_2 = 0.2032$	
R indices (all data)	$R_1 = 0.1039$, $wR_2 = 0.2139$	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.944 and -1.217 e.Å ⁻³	

[a] $R_1 = \sum ||F_o| - |F_c||$ (based on reflections with $F_o^2 > 2\sigma F_o^2$). $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$; $w = 1 / [\sigma^2(F_o^2) + (0.095P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2] / 3$ (also with $F_o^2 > 2\sigma F_o^2$)

Table S3. Crystal data and structure refinement for **3**.

Empirical formula	$C_{138}H_{172}F_{12}N_{14}O_{41}Rh_4S_4$	
Formula weight	3450.77	
Temperature	173.0 K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	$a = 18.7640(13)$ Å	$\alpha = 111.167(4)^\circ$.
	$b = 20.0235(12)$ Å	$\beta = 104.102(4)^\circ$.
	$c = 23.0409(15)$ Å	$\gamma = 94.488(4)^\circ$.
Volume	7696.2(9) Å ³	
Z	2	
Density (calculated)	1.489 Mg/m ³	
Absorption coefficient	4.742 mm ⁻¹	
F(000)	3556	
Crystal size	0.25 × 0.22 × 0.18 mm ³	
Theta range for data collection	2.150 to 67.499°.	
Index ranges	-22 ≤ h ≤ 22, -23 ≤ k ≤ 23, -27 ≤ l ≤ 27	
Reflections collected	93371	
Independent reflections	27676 [R(int) = 0.1710]	
Completeness to theta = 67.499°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.5089	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	27676 / 131 / 1539	
Goodness-of-fit on F ²	1.000	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1095$, $wR_2 = 0.2902$	
R indices (all data)	$R_1 = 0.1772$, $wR_2 = 0.3584$	
Extinction coefficient	0.00114(10)	
Largest diff. peak and hole	1.300 and -1.137 e.Å ⁻³	

[a] $R_1 = \sum ||F_o| - |F_c||$ (based on reflections with $F_o^2 > 2\sigma F^2$). $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$; $w = 1 / [\sigma^2(F_o^2) + (0.095P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2] / 3$ (also with $F_o^2 > 2\sigma F^2$)

Table S4. Crystal data and structure refinement for **4**.

Empirical formula	$C_{70}H_{84}F_6N_4O_{22}Rh_2S_2$	
Formula weight	1717.35	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	$a = 11.7168(9)$ Å	$\alpha = 68.846(4)^\circ$.
	$b = 16.8296(12)$ Å	$\beta = 87.425(4)^\circ$.
	$c = 20.3839(14)$ Å	$\gamma = 87.035(4)^\circ$.
Volume	3742.1(5) Å ³	
Z	2	
Density (calculated)	1.524 Mg/m ³	
Absorption coefficient	4.877 mm ⁻¹	
F(000)	1768	
Crystal size	0.250 × 0.220 × 0.180 mm ³	
Theta range for data collection	2.325 to 69.496°.	
Index ranges	-14 ≤ h ≤ 14, -20 ≤ k ≤ 20, -23 ≤ l ≤ 24	
Reflections collected	77977	
Independent reflections	14061 [R(int) = 0.0644]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.753 and 0.469	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14061 / 79 / 914	
Goodness-of-fit on F^2	1.046	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0447$, $wR_2 = 0.1269$	
R indices (all data)	$R_1 = 0.0517$, $wR_2 = 0.1320$	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.217 and -1.196 e.Å ⁻³	

[a] $R_1 = \sum ||F_o| - |F_c||$ (based on reflections with $F_o^2 > 2\sigma F_o^2$). $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$; $w = 1 / [\sigma^2(F_o^2) + (0.095P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2] / 3$ (also with $F_o^2 > 2\sigma F_o^2$)

5. NMR spectra

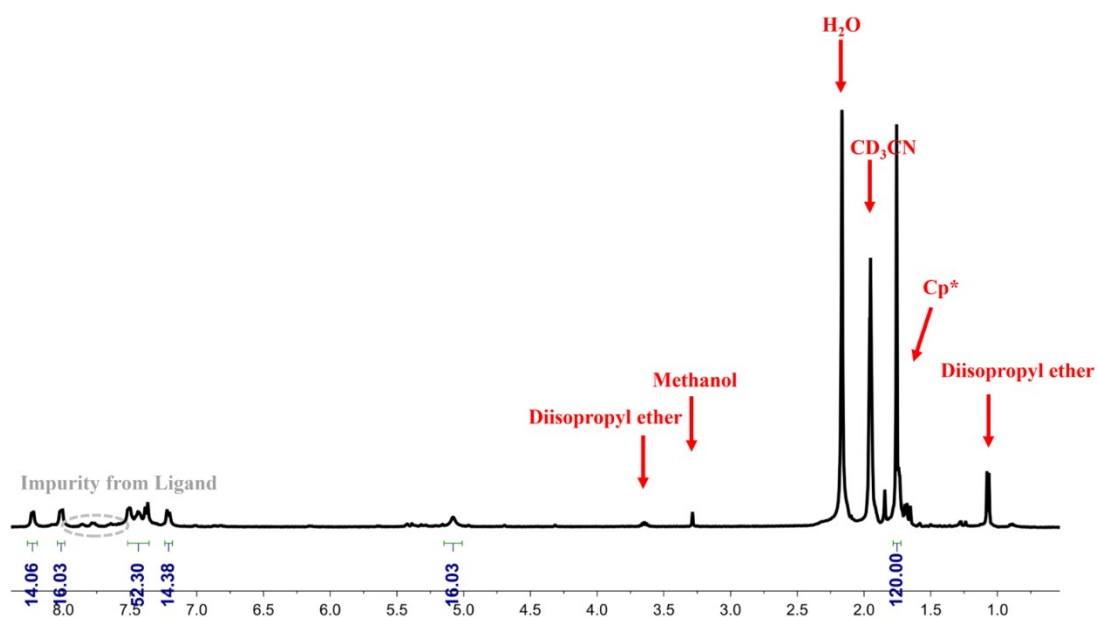


Fig. S1. ^1H NMR (400 MHz, CD_3CN , ppm) spectrum of **1**.

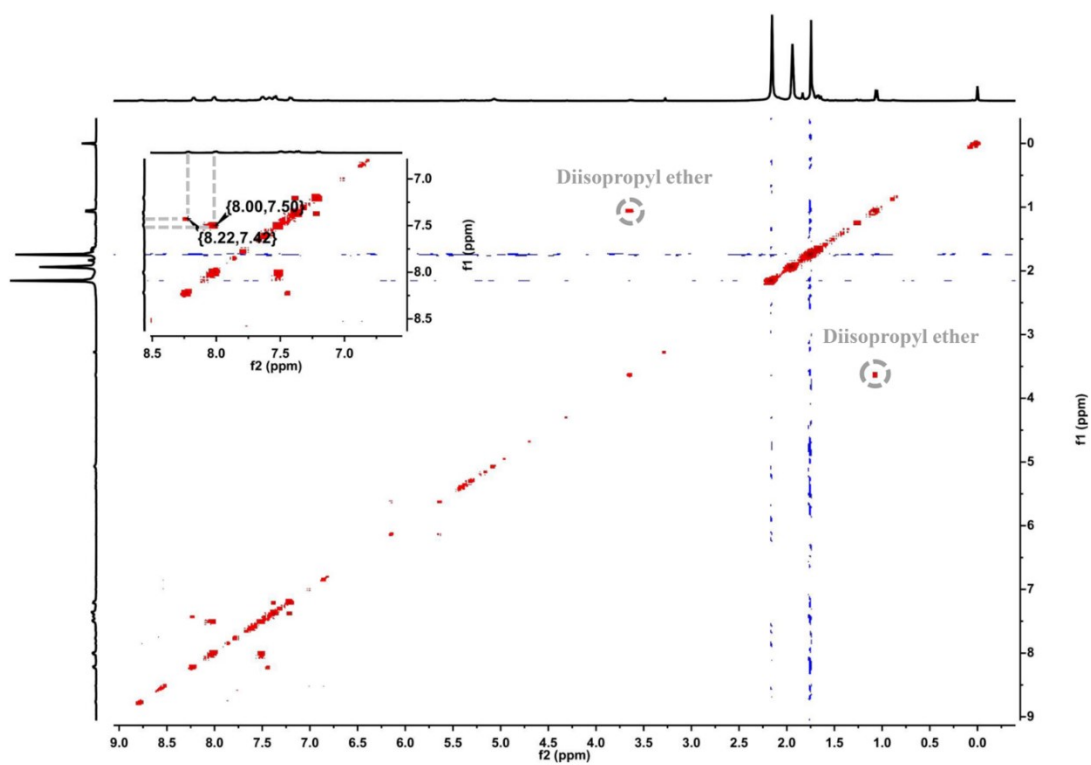


Fig. S2. ^1H - ^1H COSY NMR (400 MHz, CD_3CN , ppm) spectrum of **1**.

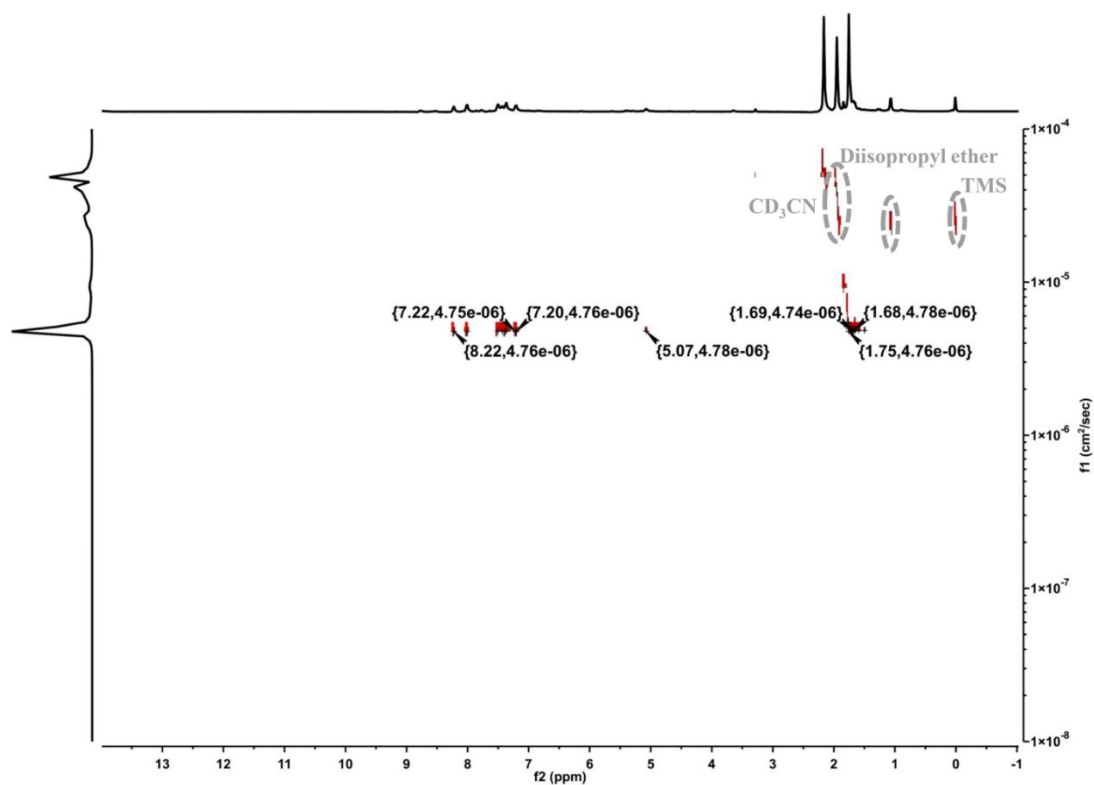


Fig. S3. ^1H DOSY NMR (400 MHz, CD_3CN , ppm) spectrum of **1**.

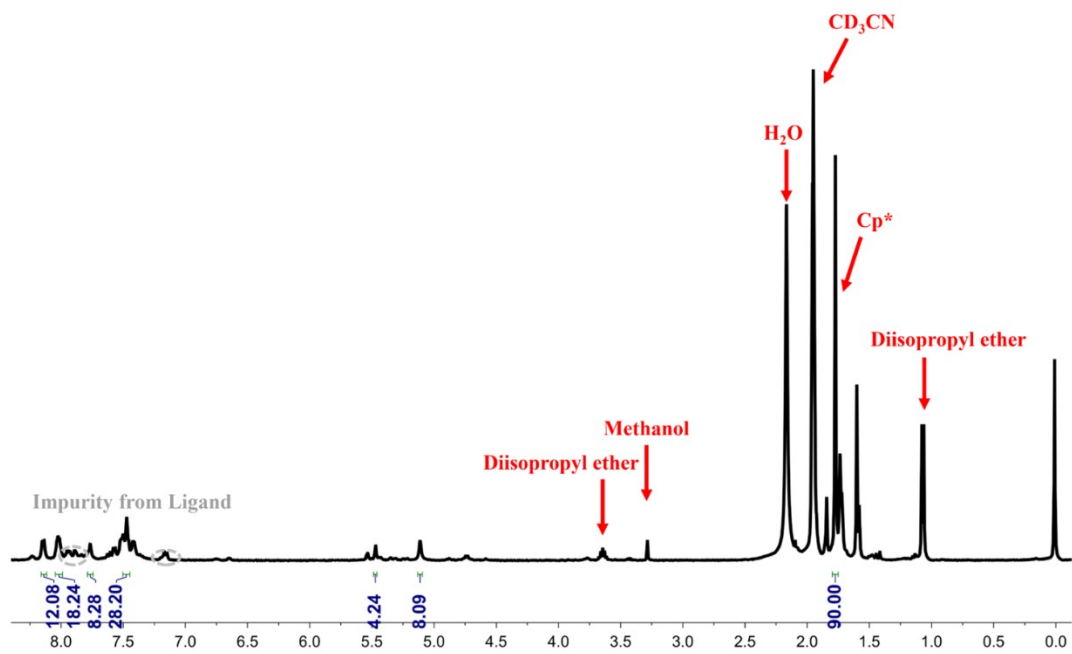


Fig. S4. ^1H NMR (400 MHz, CD_3CN , ppm) spectrum of **2**.

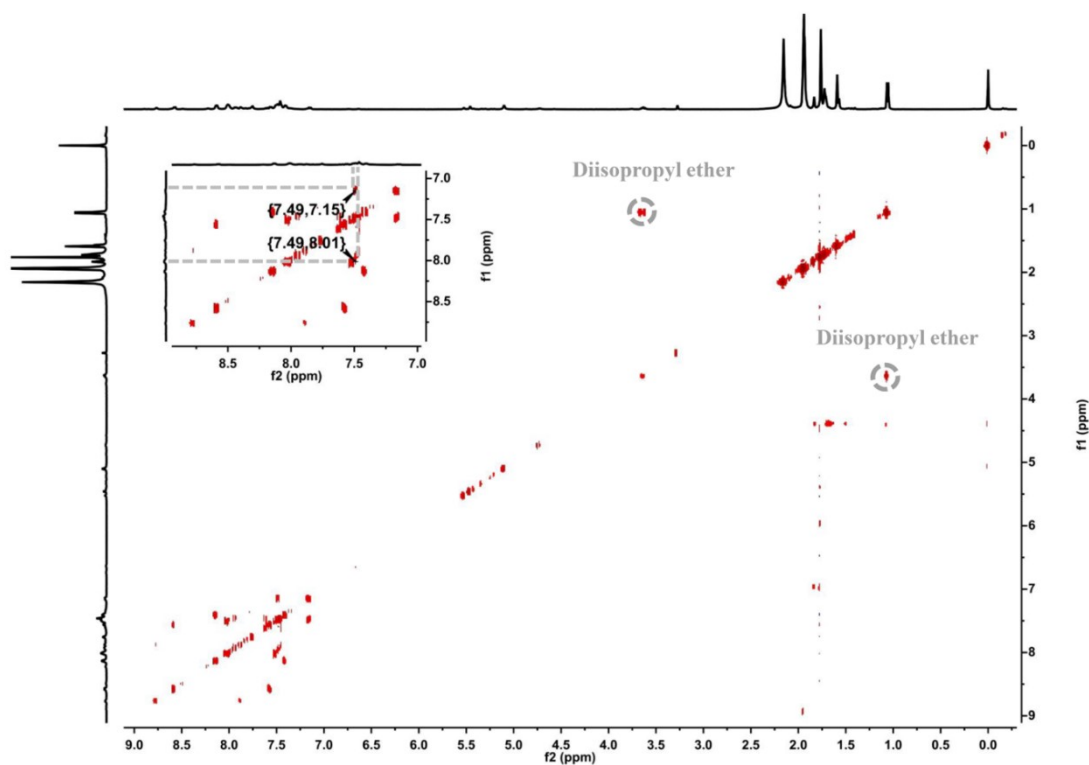


Fig. S5. ^1H - ^1H COSY NMR (400 MHz, CD_3CN , ppm) spectrum of **2**.

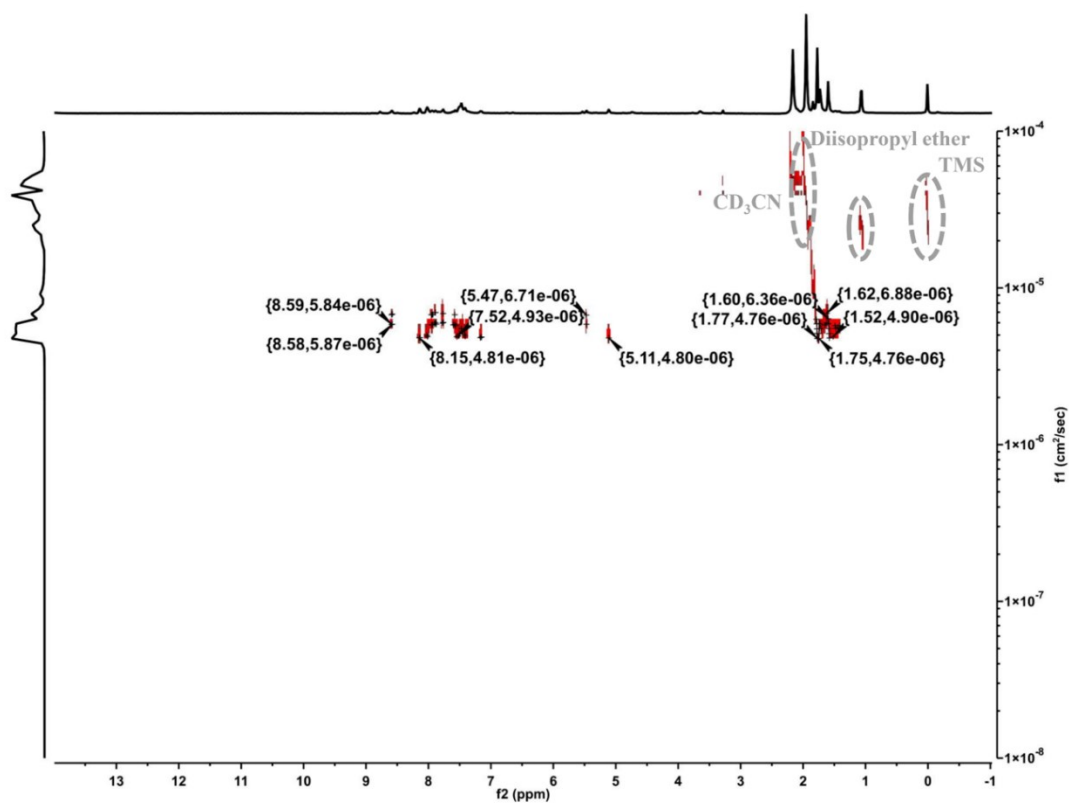


Fig. S6. ^1H DOSY NMR (400 MHz, CD_3CN , ppm) spectrum of **2**.

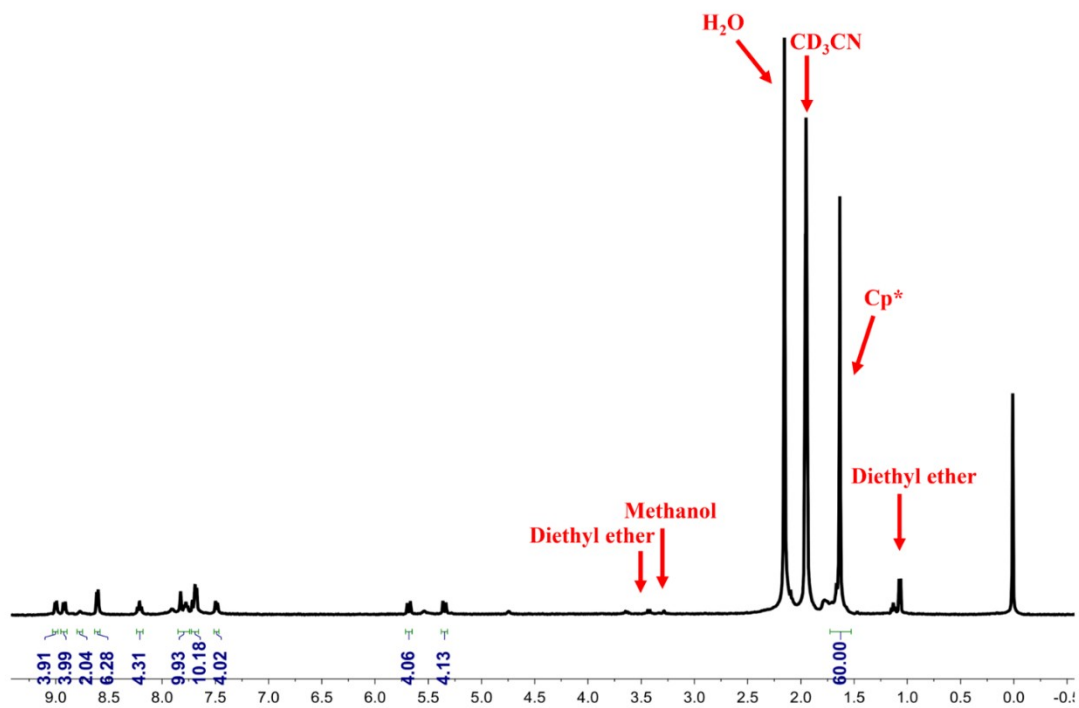


Fig. S7. ^1H NMR (400 MHz, CD_3CN , ppm) spectrum of **3**.

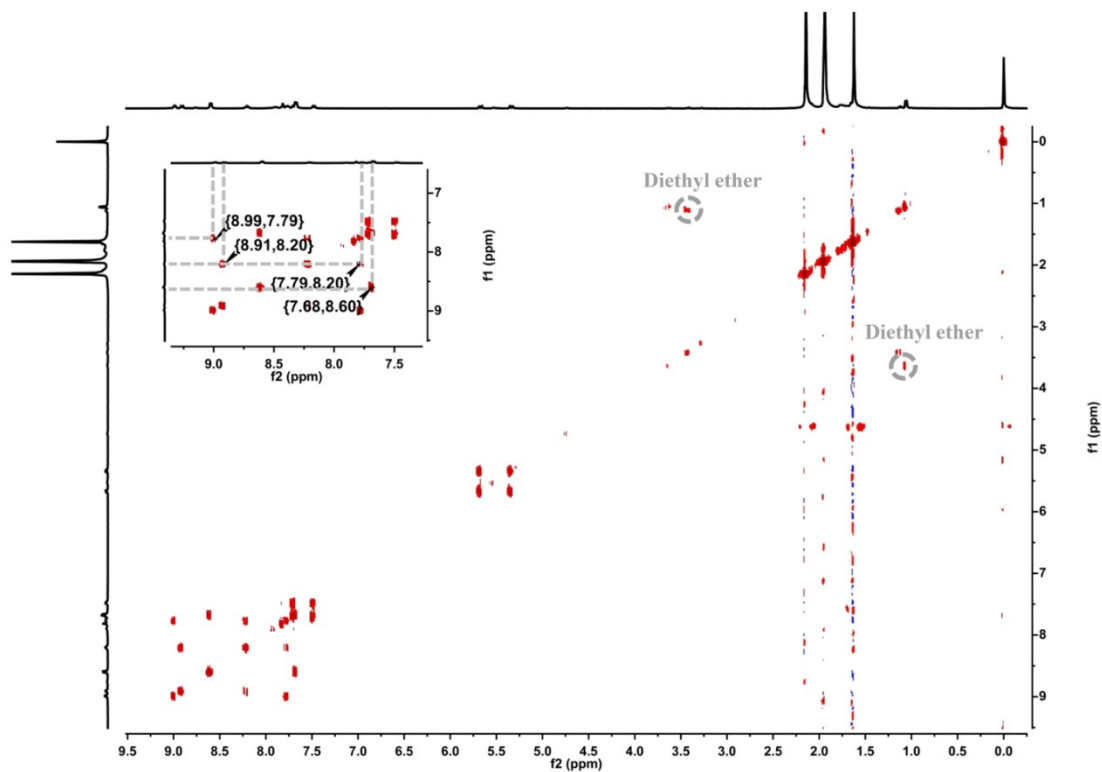


Fig. S8. ^1H - ^1H COSY NMR (400 MHz, CD_3CN , ppm) spectrum of **3**.

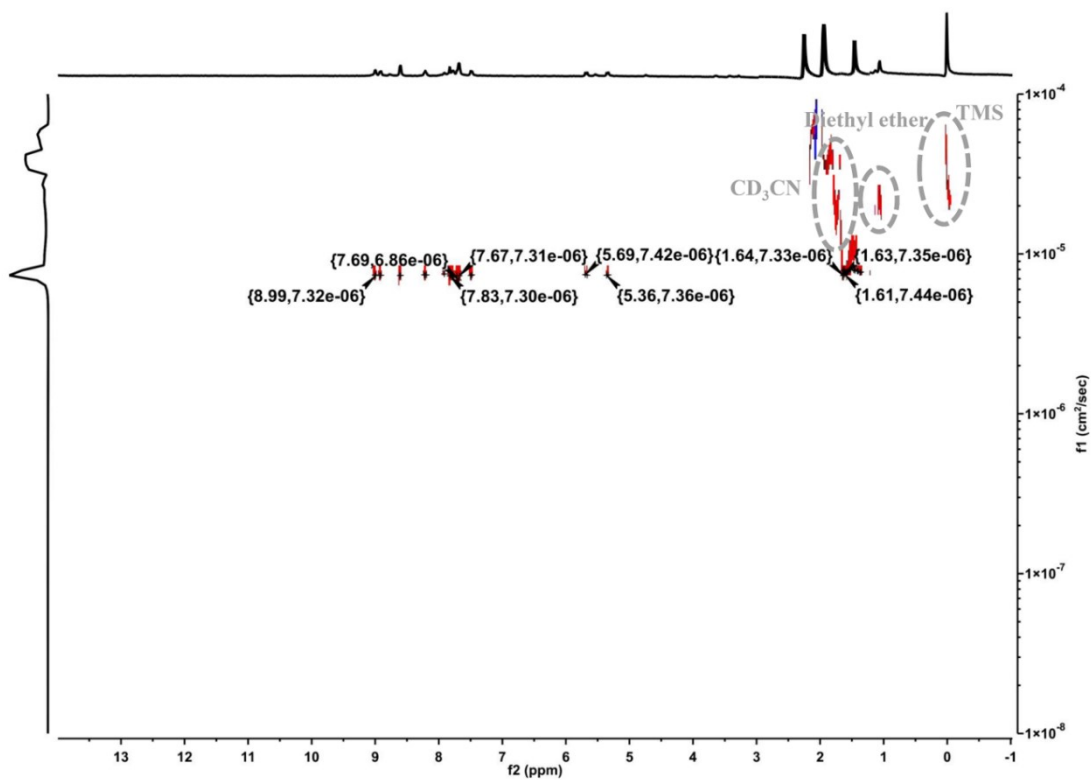


Fig. S9. ^1H DOSY NMR (400 MHz, CD_3CN , ppm) spectrum of **3**.

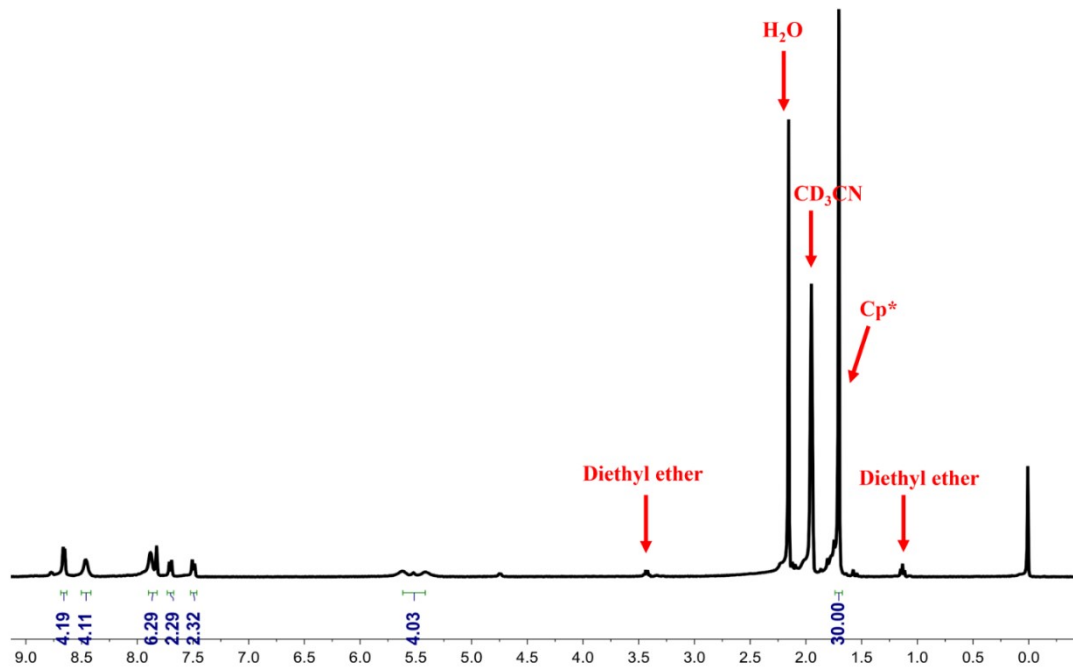


Fig. S10. ^1H NMR (400 MHz, CD_3CN , ppm) spectrum of **4**.

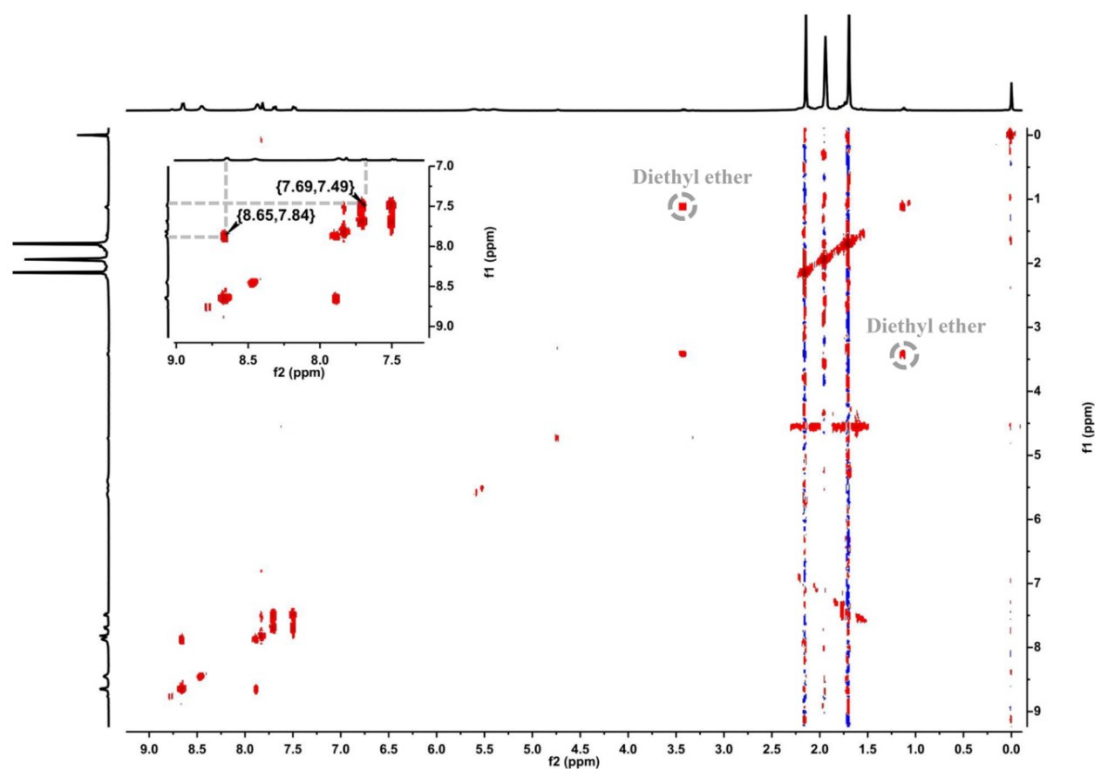


Fig. S11. ¹H-¹H COSY NMR (400 MHz, CD₃CN, ppm) spectrum of 4.

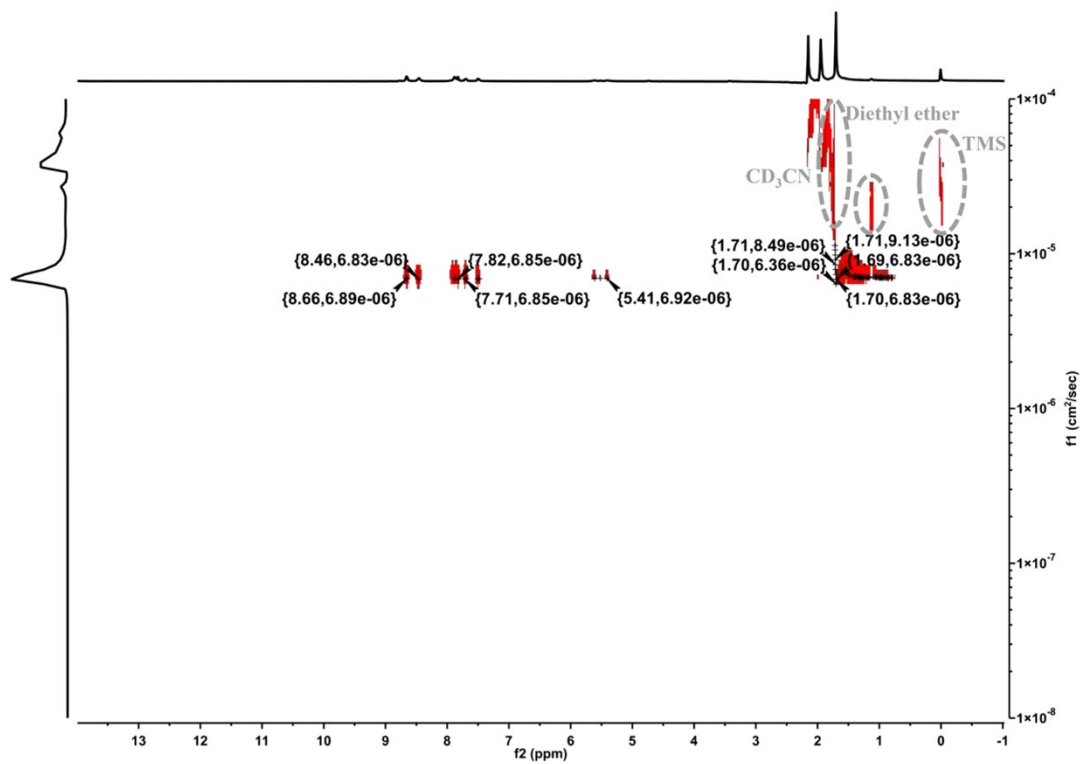


Fig. S12. ¹H DOSY NMR (400 MHz, CD₃CN, ppm) spectrum of 4.

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