

Supporting Information for

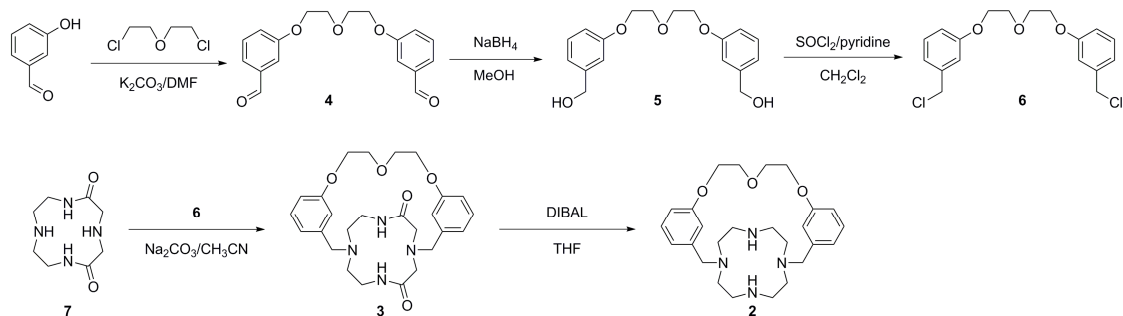
Selective Retention of Methanol over Ethanol by Cyclen-Based Cryptand/Cu(II) Complex

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Scheme S1. Synthetic scheme.

Synthesis

Compounds **4**¹ and **7**² were prepared according a literature previously reported.

3,3'-[Oxybis(ethane-2,1-diylxy)]dibenzaldehyde (**4**)

A mixture of 3-hydroxybenzaldehyde (7.460 g, 61.087 mmol), K₂CO₃ (8.676 g) and 2,2'-dichloroethyl ether (3.5 mL, 29.858 mmol) in DMF (65 mL) was heated to 80-85 °C while stirring under argon atmosphere. After two days of heating, reaction mixture was cooled to room temperature and poured into ice cold water (~750 mL) while stirring. The resultant solid product was filtered, washed with cold water and air dried. The crude product was recrystallized from boiling ethanol to result in the pure product.

Yield: 7.680 g (82%). Mp 82.0–83.0 °C. Anal. Calcd. for C₁₈H₁₈O₅: C, 68.78; H, 5.77. Found: C, 68.66; H, 5.83. FAB mass (m/z): 315 ([M+H]⁺, 100%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.97 (s, 2H), 7.53-7.51 (m, 4H), 7.48-7.44 (m, 2H), 7.37-7.25 (m, 2H), 4.22 (t, *J*=4.5 Hz, 4H), 3.86 (t, *J*=4.5 Hz, 4H).

[Oxybis(ethane-2,1-diylxybenzene-3,1-diyl)]dimethanol (**5**)

To a stirring suspension of 1,7-bis(3'-formylphenyl)-1,4,7-trioxahheptane (**4**; 1.897 g, 6.035 mmol) in methanol (35 mL), NaBH₄ (0.545 g, 14.407 mmol) was added pinch wise. The reaction mixture was stirred at room temperature till the reduction was complete (about 6 h) and the solvent was evaporated to result in a pasty mass. Water (20 mL) was added to that and the resultant suspension was extracted with ethylacetate (30 mL x 3), dried over Na₂SO₄, filtered and evaporated till dryness. The residue was diluted with dichloromethane (5 mL) and stored at room temperature to result in 1st crop of solid product (1.370 g), which was isolated by filtration. Storage of filtrate at 4 °C resulted in 2nd crop of solid product (0.380 g).

Yield: 1.750 g (91%). Mp 81.0–81.5 °C. Anal. Calcd. for C₁₈H₂₂O₅: C, 67.91; H, 6.97. Found: C, 67.59; H, 7.01. Cold ESI-MS (m/z): 340.435 [M + Na]⁺. ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.21 (t, *J*=7.8 Hz, 2H), 6.88–6.87 (m, 4H), 6.79 (dd, *J*₁=8.0 Hz, *J*₂=2.4 Hz, 2H), 5.17 (t, *J*=5.8 Hz, 2H), 4.46 (d, *J*=5.7 Hz, 4H), 4.10 (t, *J*=5.4 Hz, 4H), 3.81 (t, 4.5 Hz, 4H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 158.4, 144.3, 129.1, 118.6, 112.7, 112.4, 69.1, 67.0, 62.7.

1,1'-[Oxybis(ethane-2,1-diyloxy)]bis[3-(chloromethyl)benzene] (6)

To a suspension of **5** (2.554 g, 8.022 mmol) and pyridine (0.6 mL) in dichloromethane (40 mL), SOCl₂ (13 mL) dissolved in dichloromethane (10 mL) was added drop wise while stirring. The reaction mixture was stirred for a day at room temperature and extracted with saturated NaHCO₃ solution. The organic phase was dried over Na₂SO₄, filtered and evaporated till dryness to result in viscous liquid. The product was purified by silica gel column chromatography using dichloromethane as eluting solvent.

Yield: 2.729 g (95%). Mp 60.0–61.0 °C. Anal. Calcd. for C₁₈H₂₀Cl₂O₃·1/4H₂O: C, 60.09; H, 5.75. Found: C, 60.31; H, 5.74. FAB mass (m/z): 355 ([M+H]⁺, 26%), 357 ({[M+H]+2}⁺, 16%), 359 ({[M+H]+4}⁺, 5%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.28 (t, *J*=7.8 Hz, 2H), 7.01–6.99 (m, 4H), 6.91 (dd, *J*₁=8.2 Hz, *J*₂=2.5 Hz, 2H), 4.71 (s, 4H), 4.12 (t, *J*=4.7 Hz, 4H), 3.82 (t, *J*=4.5 Hz, 4H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 158.4, 139.0, 129.7, 121.0, 114.9, 114.3, 68.9, 67.1, 45.9.

8,11,14-Trioxa-1,21,24,29-tetraazatetracyclo[19.5.5.1^{3,7}.1^{15,19}]tritiaconta-3(33),4,6,15(32),16,18-hexaene-23,30-dione (3)

A suspension of 2,6-dioxocyclen (1.285 g, 6.417 mmol) and Na₂CO₃ (5.174 g) in MeCN (1.35 L) was heated to reflux while stirring under argon atmosphere. To the refluxing mixture, 1,7-bis(3'-chloromethylphenyl)-1,4,7-trioxahexane (2.527 g, 7.024 mmol) solution in MeCN (50 mL) was added drop wise and the heating was continued for 5 days. The reaction mixture was cooled to room temperature, filtered and evaporated to result in yellowish viscous liquid. The crude product was column chromatographed over silica gel using a mixed solvent (AcOEt:MeOH = 85:15) as eluent. The third fraction was collected, evaporated till dryness and diluted with small amount of dichloromethane. Addition of diethyl ether to the dichloromethane solution and storage at room temperature resulted in the crystals of the pure product.

Yield: 1.350 g (42%). Mp 186–186.5 °C. Anal. Calcd. for $C_{26}H_{34}N_4O_5 \cdot 1/4CH_2Cl_2$: C, 62.58; H, 6.90; N, 11.12. Found: C, 62.60; H, 7.34; N, 11.10. FAB mass (m/z): 483 ($[M+H]^+$, 100%). 1H NMR (400 MHz, CD_2Cl_2): δ 7.26 (td, $J_1=7.7$ Hz, $J_2=2.2$ Hz, 2H), 7.09-7.02 (m, 4H), 6.87 (d, $J=8.30$ Hz, 2H), 6.80 (d, $J=7.6$ Hz, 2H), 4.18-4.11 (m, 4H), 3.89-3.85 (m, 4H), 3.72 (s, 2H), 3.59 (s, 2H), 3.52 (br, 2H), 3.36 (d, $J=14.9$ Hz, 2H), 2.94 (d, $J=14.9$ Hz, 2H), 2.79 (br, 2H), 2.58 (br, 4H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 170.2, 160.0, 159.8, 141.2, 139.6, 130.0, 129.8, 123.1, 122.6, 117.2, 117.2, 113.8, 113.0, 70.1, 70.0, 68.4, 68.2, 63.6, 61.5, 60.6, 53.4, 37.9.

8,11,14-Trioxa-1,21,24,29-tetraazatetracyclo[19.5.5.1^{3,7}.1^{15,19}]tritriaconta-3(33),4,6,15(32),16,18-hexaene (2)

The flask containing **3** (1.280 g, 2.541 mmol) was cooled in an ice bath under argon atmosphere and a THF solution of DIBAL-H (52 mL 1(M); 52 mmol) was added to that drop wise while stirring. The reaction mixture was brought to room temperature and stirring was continued for a day. After 24 h, reaction mixture was again cooled in ice bath and benzene (140 mL), NaF (8.500 g) and water (2.5 mL) was added to that successively. The reaction mixture was again brought to rt and stirring was continued for another one day followed by filtration and evaporation of the filtrate. The resultant residue was diluted with small amount of CH_3CN and stored at RT to afford the crystals of the pure product.

Yield: 0.372 g (32%). Mp 178.0–179.0 °C. Anal. Calcd. for $C_{26}H_{38}N_4O_3 + 0.9 CH_3CN$: C, 67.93; H, 8.35; N, 13.96. Found: C, 67.64; H, 8.18; N, 13.80. FAB mass (m/z): 455 (M^+). 1H NMR (400 MHz, CD_2Cl_2): δ 7.19 (t, $J=7.8$ Hz, 2H), 7.08 (t, $J=1.8$ Hz, 2H), 6.81-6.78 (m, 4H), 4.16 (t, $J=4.4$ Hz, 4H), 3.89 (t, $J=4.4$ Hz, 4H), 3.46 (s, 4H), 2.72-2.52 (m, 12H), 2.40-2.30 (m, 4H), 2.26 (broad s, 2H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 159.7, 141.9, 129.2, 122.6, 117.0, 112.6, 69.8, 68.4, 61.0, 52.0, 45.6.

General procedure for 2/Cu(CF₃SO₃)₂ complexes

Compound **2** (0.0151 mmol) in alcohol (1 mL) was added to corresponding $Cu(OTf)_2$ in methanol (1 mL). Crystals were obtained quantitatively on evaporation of the solvent.

2/Cu(CF₃SO₃)₂/MeOH

Anal. Calcd. for $C_{28}H_{38}N_4O_9S_2F_6Cu + CH_3OH$: C, 41.06; H, 4.99; N, 6.60. Found: C, 41.09; H, 4.94; N, 6.66.

2/Cu(CF₃SO₃)₂/EtOH

Anal. Calcd. for C₂₈H₃₈N₄O₉S₂F₆Cu+CH₃CH₂OH: C, 41.79; H, 5.14; N, 6.50. Found: C, 41.85; H, 5.05; N, 6.55.

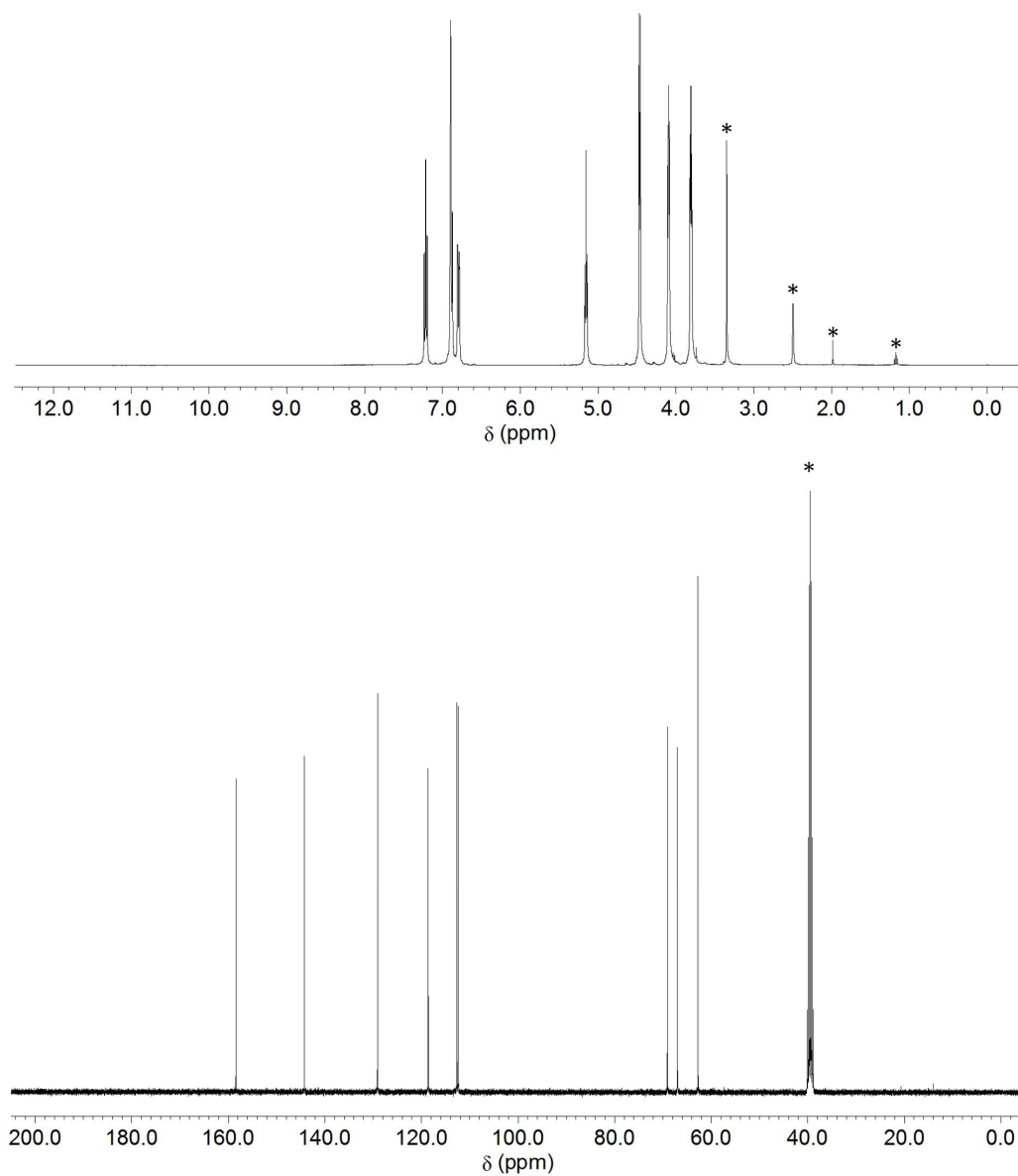
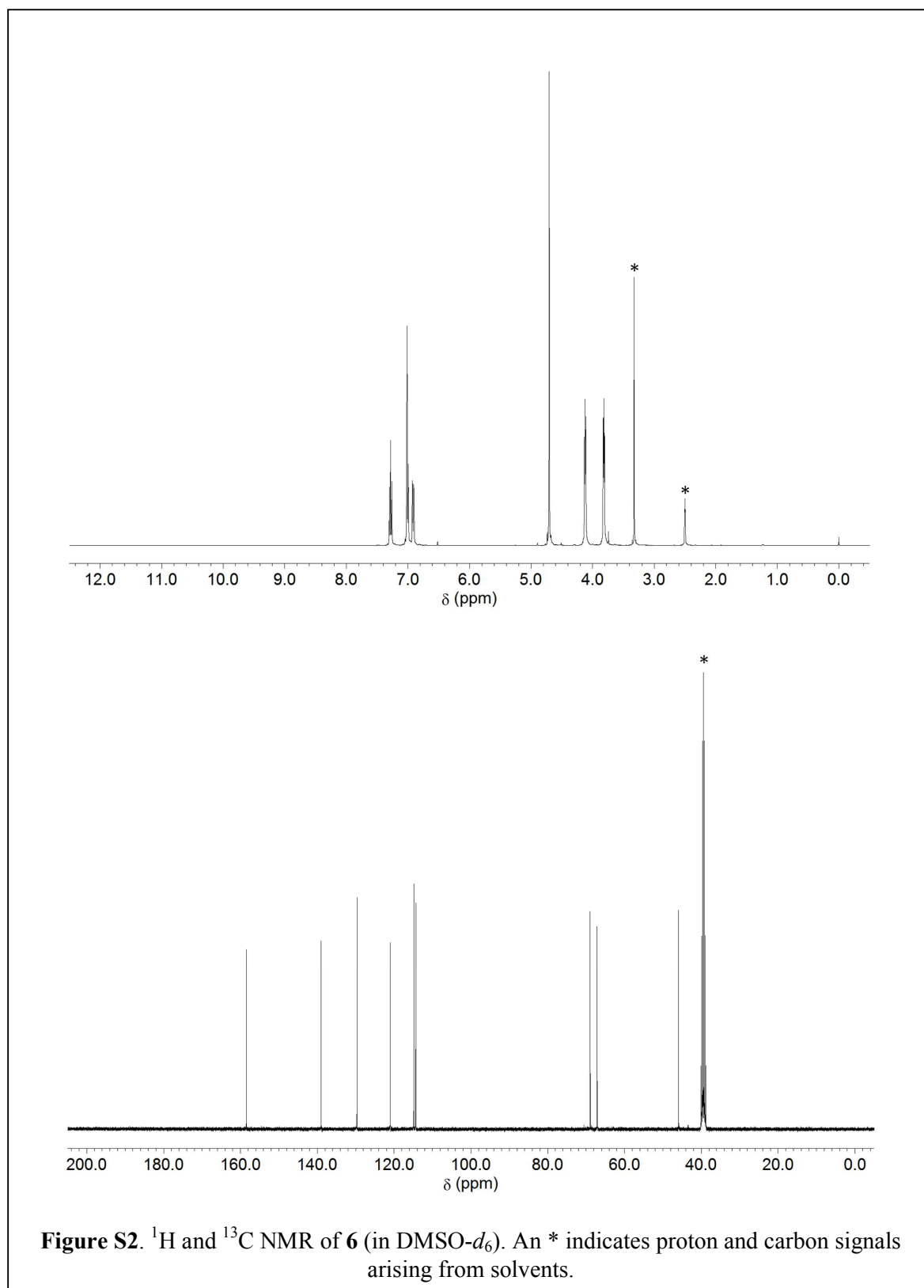


Figure S1. ¹H and ¹³C NMR of **5** (in DMSO-*d*₆). An * indicates proton and carbon signals arising from solvents.



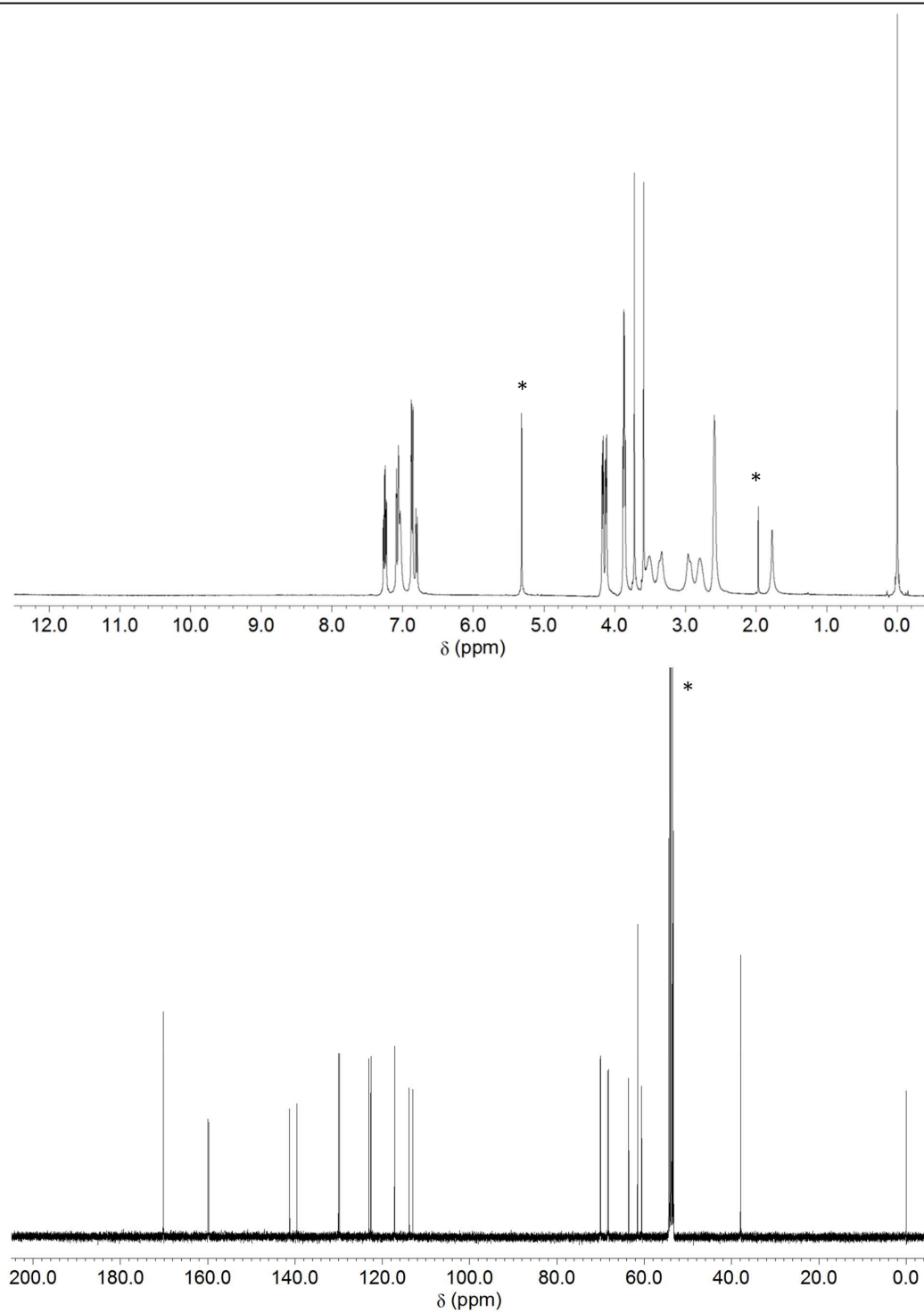


Figure S3. ^1H and ^{13}C NMR of **3** (in CD_2Cl_2). An * indicates proton and carbon signals arising from solvents.

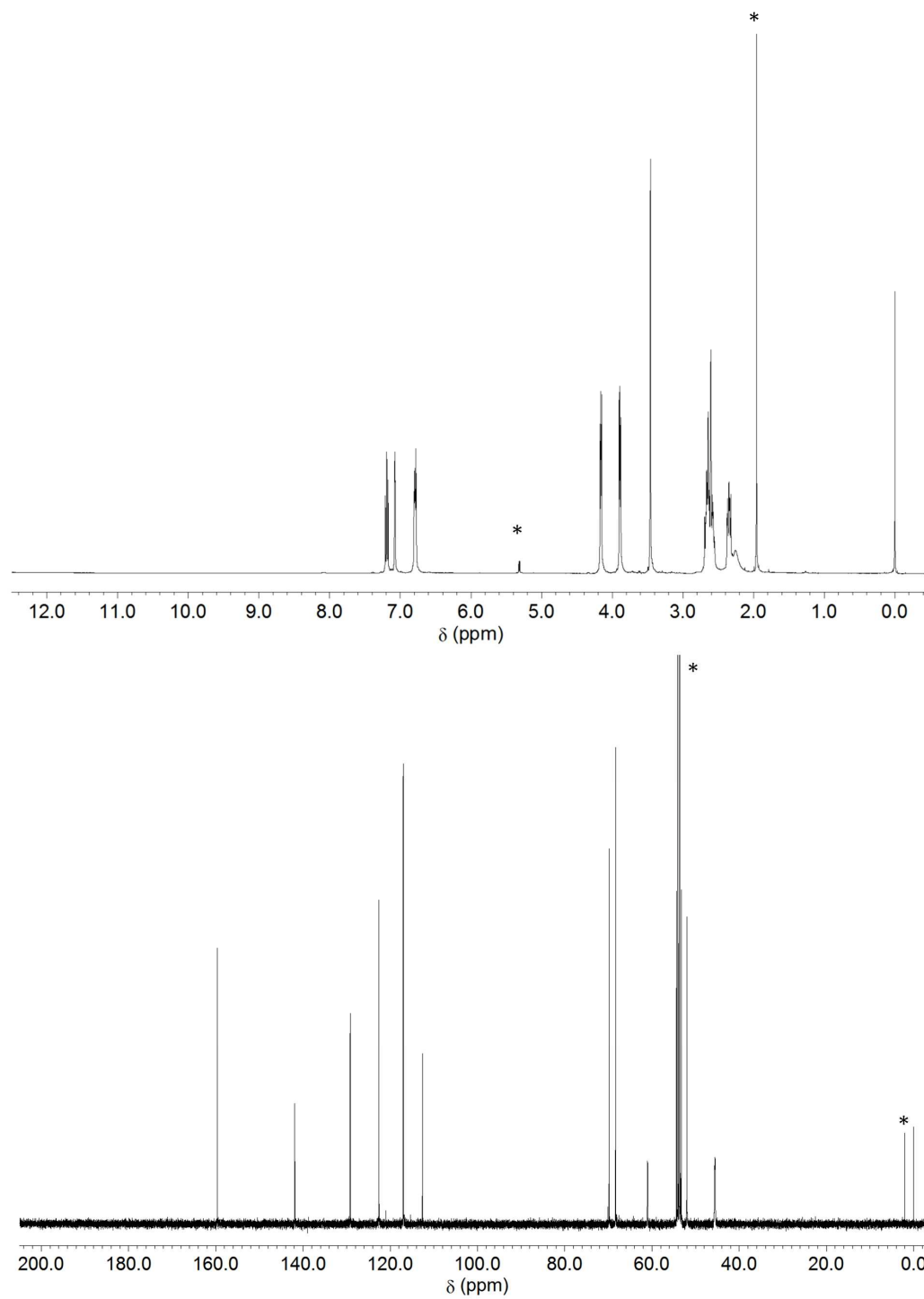


Figure S4. ^1H and ^{13}C NMR of **2** (in CD_2Cl_2). An * indicates proton and carbon signals arising from solvents.

X-ray crystallography

Crystals of **2**, **3**, **2**/Cu(CF₃SO₃)₂/MeOH, and **2**/Cu(CF₃SO₃)₂/EtOH were mounted on top of a glass fiber, and data collections were performed using a Bruker SMART CCD area diffractometer at 123–223 K. Data were corrected for Lorentz and polarization effects, and absorption corrections were applied using the SADABS³ program. Structures were solved by a direct method and subsequent difference-Fourier syntheses using the program SHELEX.⁴ All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at calculated positions and then refined using $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The crystallographic refinement parameters of the complexes are summarized in Table S1.

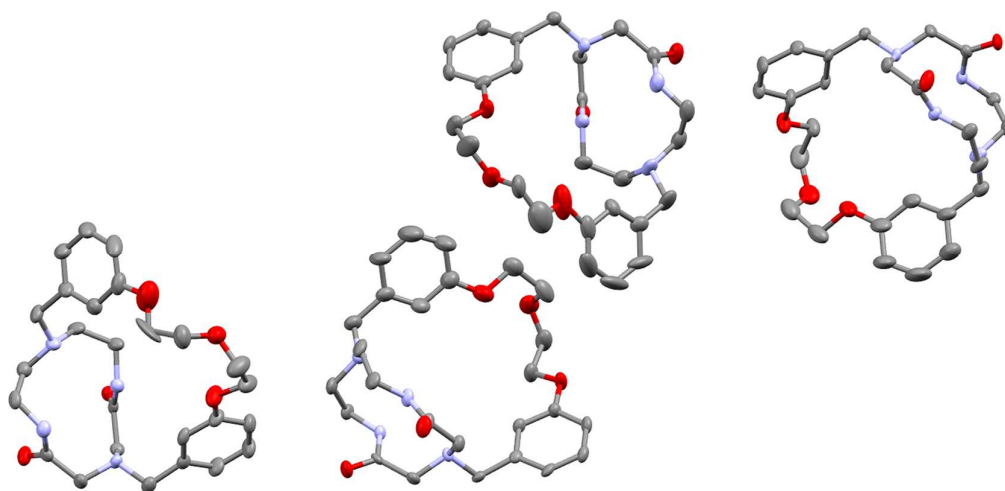


Figure S5. Ellipsoid displays of **3**. Hydrogen atoms and solvent are omitted.

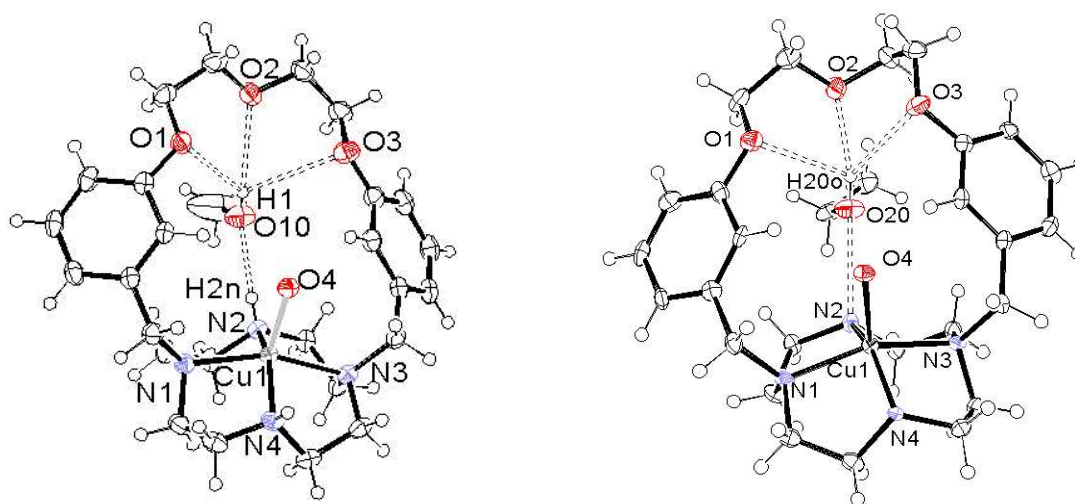


Figure S6. ORTEP diagrams of **2**/Cu(CF₃SO₃)₂/MeOH (right) and **2**/Cu(CF₃SO₃)₂/EtOH (left).

Table S1. Crystal data of **3**, **2**, **2**/Cu(CF₃SO₃)₂/MeOH, and **2**/Cu(CF₃SO₃)₂/EtOH.

Compound	3	2	2 /Cu(CF ₃ SO ₃) ₂ /MeOH	2 Cu(CF ₃ SO ₃) ₂ /EtOH
Formula	C ₂₆ H ₃₄ N ₄ O ₅	C ₂₈ H ₄₁ N ₅ O ₃	C ₂₉ H ₄₂ CuF ₆ N ₄ O ₁₀ S ₂	C ₆₀ H ₈₈ Cu ₂ F ₁₂ N ₈ O ₂₀ S ₄
<i>M</i>	482.57	495.66	848.33	1724.7
<i>T</i> /K	173	223	173	123
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	Cc	P2(1)/c	P2(1)/c	P2(1)
<i>a</i> /Å	39.522(4)	16.2485(12)	8.8773(4)	8.9164(6)
<i>b</i> /Å	12.4506(11)	8.5811(6)	22.1125(10)	18.4649(12)
<i>c</i> /Å	23.074(2)	22.2768(13)	18.5199(8)	22.3975(15)
α /°				
β /°	118.076(2)	119.362(4)	92.5300(10)	97.1080(10)
γ /°				
<i>U</i> /Å ³	10018.0(16)	2707.0(3)	3631.9(3)	3659.2(4)
<i>Z</i>	16	4	4	2
<i>D_c</i> /g cm ⁻³	1.280	1.216	1.551	1.565
μ /mm ⁻¹	0.090	0.080	0.806	0.801
Data / restraints / parameters	11395/22/1289	6458/0/334	9021/13/482	11048/47/987
No. reflns used [$> 2\sigma(I)$]	11395 [R(int) = 0.0400]	6458 [R(int) = 0.0753]	9021 [R(int) = 0.0293]	11048 [R(int) = 0.0551]
<i>R</i> ₁ , <i>wR</i> ₂ [$I > 2\sigma(I)$]	0.0611, 0.1537	0.0595, 0.1107	0.0386, 0.0963	0.0501, 0.1062
<i>R</i> ₁ , <i>wR</i> ₂ [all data]	0.0780, 0.1687	0.1552, 0.1397	0.0491, 0.1023	0.0746, 0.1282
GOF	1.021	0.937	1.031	0.968

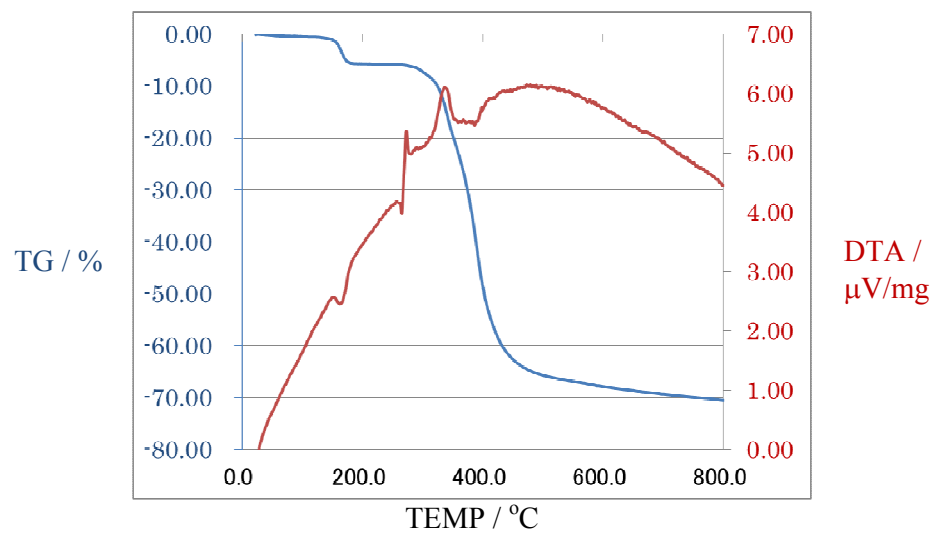


Figure S7a. TG-DTA of 2/Cu(II)/EtOH complex.

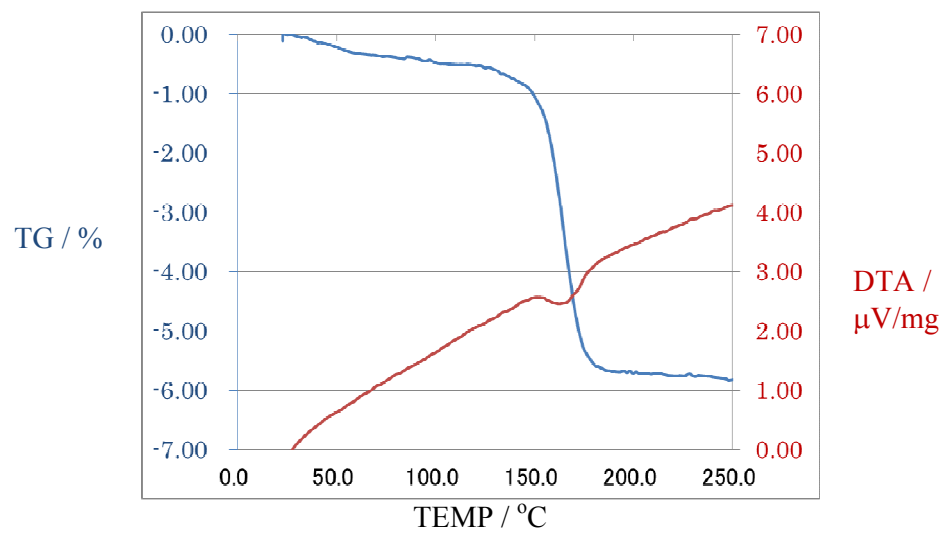


Figure S7b. TG-DTA of 2/Cu(II)/EtOH complex (magnified).

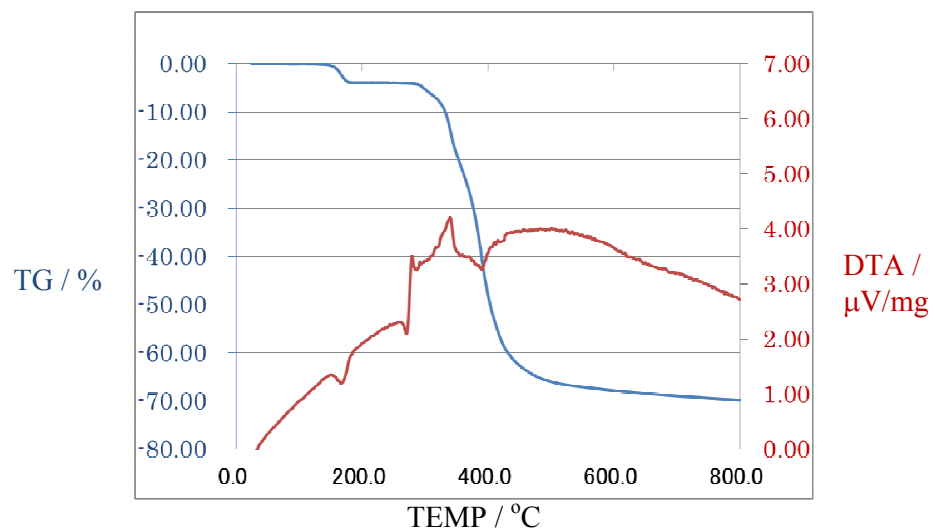


Figure S8a. TG-DTA of 2/Cu(II)/MeOH complex.

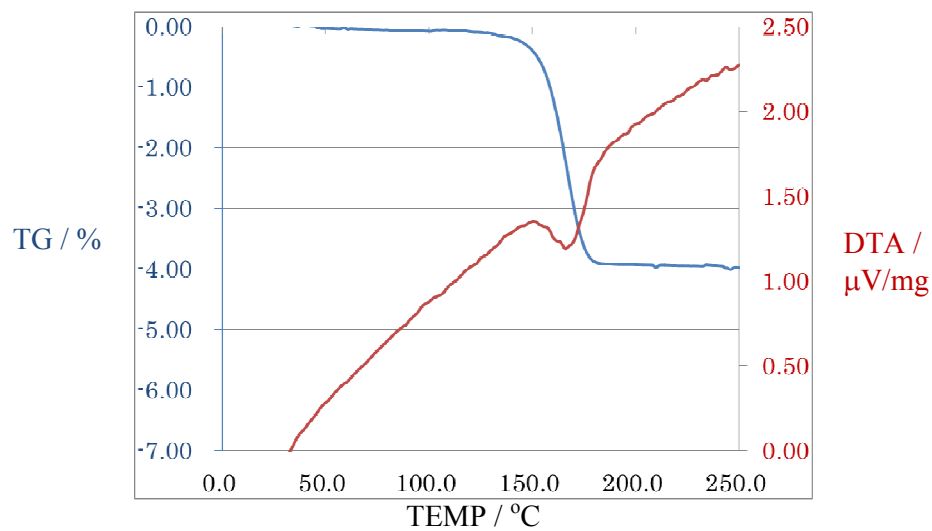


Figure S8b. TG-DTA of 2/Cu(II)/MeOH complex (magnified).

Table S2. The binding energies and binding-energy-differences between **2**/Cu(II)/MeOH and **2**/Cu(II)/EtOH.

		E_{alcohol} (au)	E_{host} (au)	E_{complex} (au)	ΔE_{ROH} (au) ^a	ΔE_{ROH} (kcal/mol)
B ₃ LYP/ 6-31G*	2 /Cu(II)/MeOH	-115.6799668	-3097.7113869	-3213.4259201	-0.0345664 (ΔE_{MeOH})	-21.69
	2 /Cu(II)/EtOH	-154.9591746	-3097.0870604	-3252.0760031	-0.0297681 (ΔE_{EtOH})	-18.68
	$\Delta \Delta E (= E_{\text{MeOH}} - E_{\text{EtOH}})^b$				-0.0047983	-3.01
EDF2/ 6-31G*	2 /Cu(II)/MeOH	-115.6054831	-3096.9676761	-3212.6099139	-0.0367547 (ΔE_{MeOH})	-23.06
	2 /Cu(II)/EtOH	-154.8495459	-3096.3538631	-3251.2314742	-0.0280652 (ΔE_{EtOH})	-17.61
	$\Delta \Delta E (= E_{\text{MeOH}} - E_{\text{EtOH}})$				-0.0086895	-5.45

a) Binding energies ($\Delta E_{\text{ROH}} = E_{\text{2/Cu(II)/ROH}} - E_{\text{2/Cu(II)}} - E_{\text{ROH}}$).

b) Binding energy differences ($\Delta \Delta E = \Delta E_{\text{MeOH}} - \Delta E_{\text{EtOH}}$) between **2**/Cu(II)/MeOH and **2**/Cu(II)/EtOH.

CSI-MS conditions

Ring lens: 10 V

Orifice1 voltage: 20 V

Orifice 2 voltage: 5V

Needle voltage: 1000V

Data correction interval: 5 μ s

Spray temperature: 273 K

References

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- (2) Habata, Y.; Taniguchi, A.; Ikeda, M.; Hiraoka, T.; Matsuyama, N.; Otsuka, S.; Kuwahara, S. *Inorg. Chem.* **2013**, *52*, 2542–2549.
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- (4) SHELXTLTM, version 5.1, Bruker AXS, Inc., Madison, WI, 1997.