

## Supporting Information

### A Molecular Trefoil Knot From a Trimeric Circular Helicate

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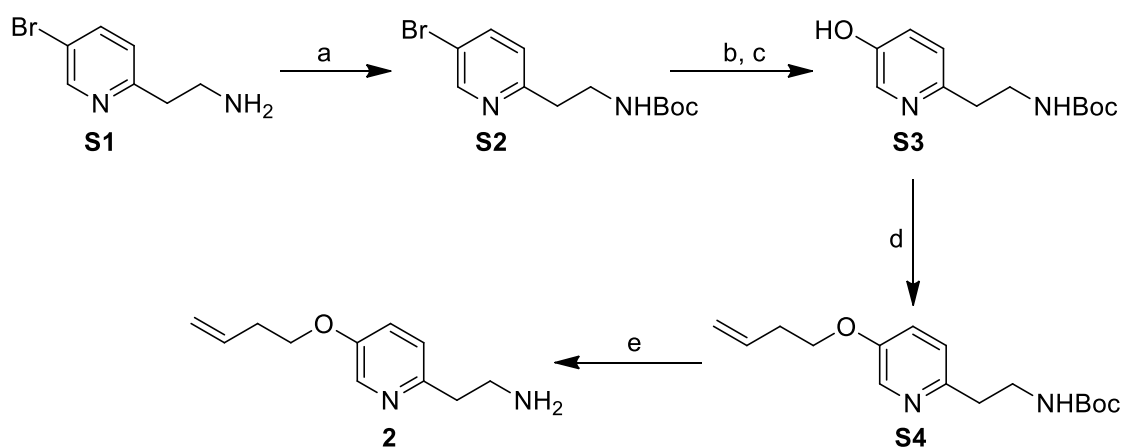
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## 1. General Experimental Section

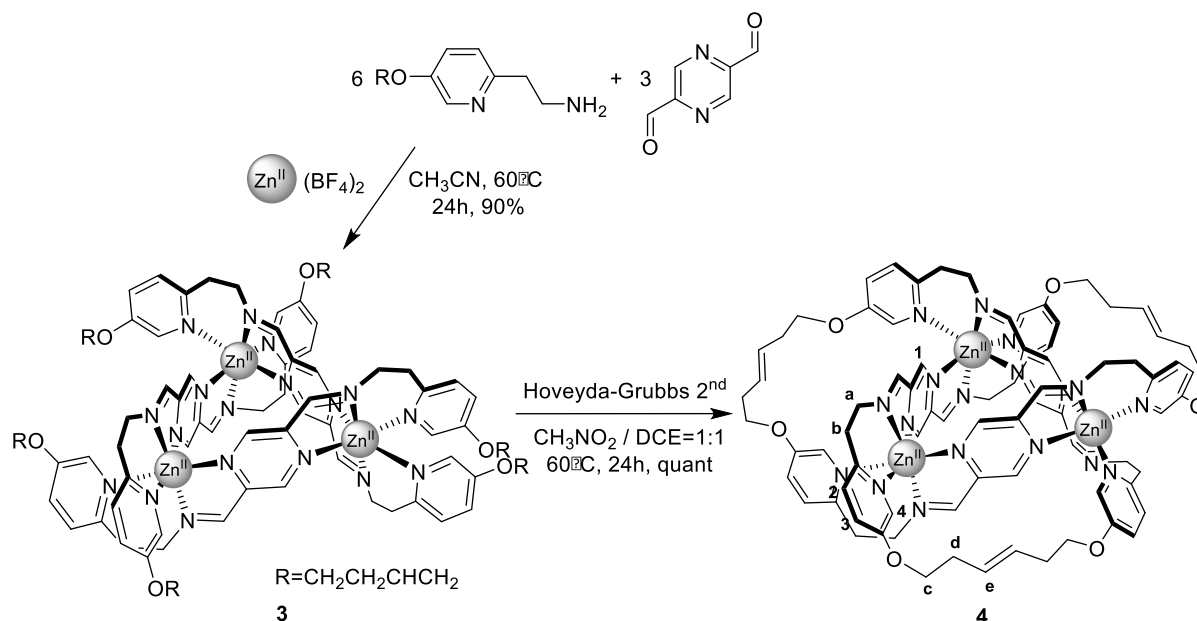
Unless stated otherwise, all reagents and solvents were purchased from Sigma-Aldrich Chemicals and used without further purification. Compound **1** was prepared according to literature procedures.<sup>S1</sup> All procedures were carried out using dry solvents unless otherwise stated and dry solvents were obtained by passing through an activated alumina column on a Phoenix SDS solvent drying system (JC Meyer Solvent Systems, CA, USA). NMR spectra were recorded on a BrukerAvance III (equipped with a cryoprobe) instrument with an Oxford AS600 magnet. Chemical shifts are reported in parts per million (ppm) from high to low frequency and referenced to the residual solvent resonance. N<sup>th</sup> order coupling constants (<sup>n</sup>J) are reported in Hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, br = broad. <sup>1</sup>H assignments were made using 2D NMR methods (COSY, HSQC, HMBC). Low resolution ESI mass spectrometry was performed with a Thermo Scientific LCQ Fleet or an Agilent Technologies 1200 LC system with 6130 single quadrupole MS detector mass spectrometer. High resolution ESI (electrospray ionization) and mass spectrometry were carried out by the mass spectrometry services at the University of Manchester

## 2. Synthetic Overview



**Scheme S1. Synthesis of Compound 2<sup>a</sup>**

<sup>a</sup>Reagents and conditions: a) Boc<sub>2</sub>O, DCM, rt, 12 h, 100% ; b) B<sub>2</sub>pin<sub>2</sub>, Pd(dppf)Cl<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>, KOAc, dioxane, 110 °C, 12 h; c) H<sub>2</sub>O<sub>2</sub>, DCM, 0 °C to rt, 24 h, two steps 68%; d) 4-Bromo-1-butene, Cs<sub>2</sub>CO<sub>3</sub>, DMF, 80 °C, 24 h, 63 %; e) TFA, DCM, 0 °C to rt, 24 h, 100%.

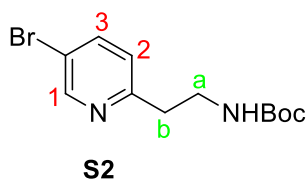


**Scheme S2. Synthesis of molecular trefoil knot **4**<sup>a</sup>**

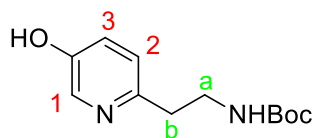
<sup>a</sup> Reagents and conditions: (a) Zn(BF<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, acetonitrile, 60 °C, 24 h, 90 %; (b) Hoveyda-Grubbs second generation catalyst, 1,2-dichloroethane/nitromethane (1:1), 60 °C, 24 h, quantitative.

### 3 Synthetic procedures and characterization details

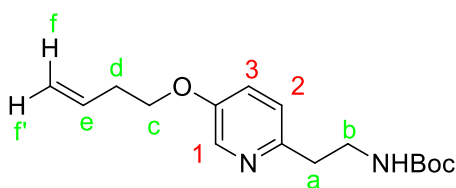
#### 3.1 Synthesis of Compound **2**



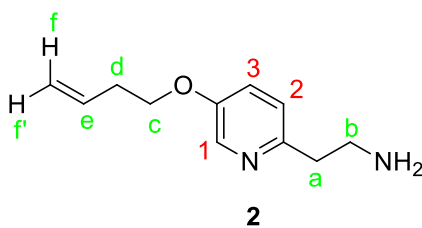
To a stirred solution of 2-(5-bromopyridin-2-yl)ethanamine (**S1**, 1.0 g, 4.97 mmol) in CH<sub>2</sub>Cl<sub>2</sub>, (Boc)<sub>2</sub>O (1.3 g, 5.97 mmol) was added under N<sub>2</sub>. The reaction mixture was stirred at room temperature for 12 hours. The reaction was diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed with water and brine, dried over MgSO<sub>4</sub>, and concentrated to get a solid (**S2**, 1.50 g, 100%) of sufficient purity for further steps. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.59 (d, *J* = 2.4 Hz, 1H, H<sup>1</sup>), 7.72 (dd, *J* = 8.4, 2.4 Hz, 1H, H<sup>3</sup>), 7.07 (d, *J* = 8.4 Hz, 1H, H<sup>2</sup>), 5.02 (br, 1H, NH), 3.52 (m, 2H, H<sup>a</sup>), 2.94 (t, *J* = 6.6 Hz, 2H, H<sup>b</sup>), 1.42 (s, 9H, Boc). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 158.2, 156.0, 150.5, 139.2, 124.9, 118.6, 79.4, 39.8, 37.4, 28.5. HRESI-MS *m/z* = 323.0353 [M+Na]<sup>+</sup> (calcd. for C<sub>12</sub>H<sub>17</sub>O<sub>2</sub>N<sub>2</sub>BrNa, 323.0366).

**S3**

**S2** (280 mg, 0.93 mmol), Pd(dppf)Cl<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub> (30 mg, 0.037 mmol), bis(pinacolato)diboron (283 mg, 1.12 mmol) and KOAc (273 mg, 2.79 mmol) were added to a microwave vial with a stirrer bar, the vial was evacuated and filled with N<sub>2</sub> for 3 cycles. 1,4-dioxane (9 mL) was added under a N<sub>2</sub> atmosphere. The resulting reaction mixture was stirred at 110 °C for 12 hours. The mixture was then diluted with Et<sub>2</sub>O, filtered through silica gel with copious washings (Et<sub>2</sub>O) and concentrated to give a solid. The solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (9 mL), and H<sub>2</sub>O<sub>2</sub> (30%, 332 μL, 3.26 mmol) was added at 0 °C. The resulting mixture was allowed to warm to room temperature and stirred for 24 hours. After this time, the solution was cooled to 0 °C and aqueous sodium thiosulfate added. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 x 15 mL), dried with Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The residue was purified by flash chromatography, eluting with CH<sub>2</sub>Cl<sub>2</sub>/MeOH (20:1/15:1) to give **S3** (150 mg, 68%) as a solid. <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>OD) δ 7.97 (d, 1H, *J* = 2.4 Hz, H<sup>1</sup>), 7.24-7.06 (m, 2H, H<sup>3</sup>, H<sup>2</sup>), 3.29 (t, 2H, *J* = 7.2 Hz, H<sup>a</sup>), 2.80 (t, 2H, *J* = 7.2 Hz, H<sup>b</sup>), 1.37 (s, 9H, Boc). <sup>13</sup>C NMR (151 MHz, CD<sub>3</sub>OD) δ 158.3, 154.2, 150.6, 137.2, 125.6, 125.4, 75.8, 41.6, 37.7, 28.7. HRESI-MS *m/z* = 239.1383 [M+H]<sup>+</sup> (calcd. for C<sub>12</sub>H<sub>19</sub>O<sub>3</sub>N<sub>2</sub>, 239.1389).

**S4**

**S3** (360 mg, 1.51 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (1.97 g, 6.04 mmol) were added to a microwave vial with a stirrer bar, the vial was evacuated and filled with N<sub>2</sub> for 3 cycles. DMF (8 mL) was added under N<sub>2</sub> atmosphere and the resulting reaction mixture was stirred at room temperature for 1 hour. Then 4-bromo-1-butene (460 μL, 4.53 mmol) was added under a N<sub>2</sub> atmosphere. The resulting mixture was then heated to 80 °C for 24 hours. After cooling to room temperature, the resulting mixture was filtered through celite with EtOAc washings and the combined organic layers were washed with 5 % LiCl solution (3 x 5 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to dryness. The residue was purified by flash chromatography, eluting with CH<sub>2</sub>Cl<sub>2</sub>/MeOH (20:1-to-15:1 gradient) to give **S4** (282 mg, 63%) as a solid. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.22 (d, *J* = 3.0 Hz, 1H, H<sup>1</sup>), 7.13 (dd, *J* = 8.4, 3.0 Hz, 1H, H<sup>3</sup>), 7.07 (d, 1H, *J* = 8.4, H<sup>2</sup>), 5.89 (ddt, *J* = 17.4, 10.2, 6.6 Hz, 1H, H<sup>e</sup>), 5.18 (m, 1H, H<sup>f</sup>), 5.12 (m, 1H, H<sup>f'</sup>), 5.06 (br, 1H, NH), 4.04 (t, *J* = 6.6 Hz, 2H, H<sup>c</sup>), 3.49 (m, 2H, H<sup>b</sup>), 2.91 (t, *J* = 6.6 Hz, 2H, H<sup>a</sup>), 2.55 (m, 2H, H<sup>d</sup>), 1.42 (s, 9H, Boc). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 156.1, 153.7, 151.6, 137.3, 134.2, 123.6, 122.2, 117.5, 79.2, 67.8, 40.3, 37.0, 33.7, 28.6. HRESI-MS *m/z* = 315.1679 [M+Na]<sup>+</sup> (calcd. for C<sub>16</sub>H<sub>24</sub>O<sub>3</sub>N<sub>2</sub>Na, 315.1679).



To a stirred solution of **S4** (200 mg, 0.68 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (6.8 mL) at 0 °C,  $\text{CF}_3\text{CO}_2\text{H}$  (1.36 mL) was added. The resulting mixture was stirred at room temperature for 2 h. After this time, the resulting mixture was concentrated to dryness, diluted with EtOAc and partitioned with saturated  $\text{NaHCO}_3$  solution (5 mL). The aqueous phase was extracted with EtOAc (4 x 5 mL) and the combined organic phase was dried ( $\text{Na}_2\text{SO}_4$ ), filtered and concentrated under reduced pressure to give a brown oil **2** in quantitative yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  8.48 (d,  $J$  = 3.0 Hz, 1H,  $\text{H}^1$ ), 8.02 (dd,  $J$  = 9.0, 3.0 Hz, 1H,  $\text{H}^3$ ), 7.82 (d, 1H,  $J$  = 9.0,  $\text{H}^2$ ), 5.92 (ddt,  $J$  = 17.4, 10.2, 6.6 Hz, 1H,  $\text{H}^e$ ), 5.21 (m, 1H,  $\text{H}^f$ ), 5.12 (m, 1H,  $\text{H}^{f'}$ ), 4.24 (t,  $J$  = 6.6 Hz, 2H,  $\text{H}^c$ ), 3.42-3.32 (m, 4H,  $\text{H}^a$ ,  $\text{H}^b$ ), 2.60 (m, 2H,  $\text{H}^d$ ).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  157.8, 146.2, 135.0, 132.0, 131.7, 128.8, 118.0, 70.2, 39.5, 34.2, 31.8. HRESI-MS  $m/z$  = 193.1328  $[\text{M}+\text{H}]^+$  (calcd. for  $\text{C}_{11}\text{H}_{17}\text{ON}_2$ , 193.1335).

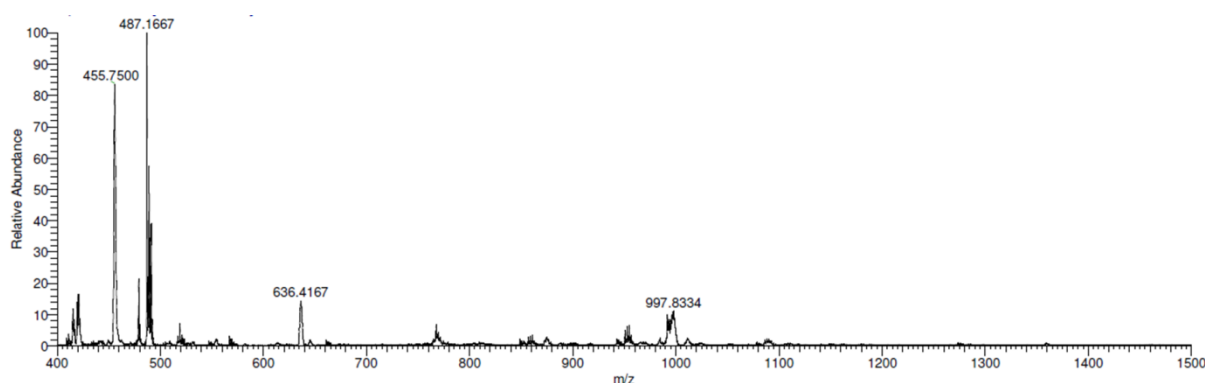
### 3.2 Synthesis of Circular Trimeric Helicate **3**

To a solution of **1** (10 mg, 73.5  $\mu\text{mol}$ ) in  $\text{CH}_3\text{CN}$  (5 mL), was added a solution of **2** (28 mg, 147  $\mu\text{mol}$ ) in  $\text{CH}_3\text{CN}$  (5 mL) and the mixture stirred at room temperature for 30 minutes. A solution of  $\text{Zn}(\text{BF}_4)_2 \cdot \text{H}_2\text{O}$  (19 mg, 73.5  $\mu\text{mol}$ ) in  $\text{CH}_3\text{CN}$  (1 mL) was added and the solution heated to 60 °C for 24 hours in a capped vial. After cooling to room temperature, the solvent was removed from the reaction and the residue was dissolved in a small amount of fresh dichloromethane, diethyl ether was added until a precipitate formed, which was collected by filtration onto a bed of celite, washed with excess diethyl ether and taken up in fresh acetonitrile to afford **3** as a light brown solid after evaporation of the solvent (47.7 mg, 22.1  $\mu\text{mol}$ , 90 %).  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  8.80 (s, 6H,  $\text{H}^b$ ), 8.35 (s, 6H,  $\text{H}^a$ ), 7.62 (d,  $J$  = 2.8 Hz, 6H,  $\text{H}^g$ ), 7.56 (dd,  $J$  = 8.8, 2.8 Hz, 6H,  $\text{H}^f$ ), 7.48 (d,  $J$  = 8.8 Hz, 6H,  $\text{H}^e$ ), 5.83 – 5.75 (m, 6H,  $\text{H}^i$ ), 5.11 – 4.99 (dd,  $J$  = 35.7, 10.6 Hz, 12H,  $\text{H}^{k,k'}$ ), 4.71 – 4.62 (m, 6H,  $\text{H}^c$ ), 4.49 – 4.40 (m, 6H,  $\text{H}^{c'}$ ), 4.02 – 3.91 (m, 12H,  $\text{H}^h$ ), 3.36 – 3.28 (m, 6H,  $\text{H}^d$ ), 3.15 – 3.03 (m, 6H,  $\text{H}^{d'}$ ), 2.42 – 2.35 (m, 12H,  $\text{H}^j$ ).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  164.3, 156.6, 153.2, 147.1, 145.7, 137.7, 135.0, 128.6, 126.7, 117.8, 69.3, 58.0, 33.8, 33.8. LRESI-MS:  $m/z$  = 997.8  $[\text{M}-2\text{BF}_4]^{2+}$  requires 998.3; 636.4  $[\text{M}-3\text{BF}_4]^{3+}$  requires 636.5; 455.8  $[\text{M}-4\text{BF}_4]^{4+}$  requires 455.6. HRESI-MS:  $m/z$  = 636.5257  $[\text{M}-3\text{BF}_4]^{3+}$  (calcd. for  $\text{C}_{84}\text{H}_{96}\text{N}_{18}\text{O}_6\text{Zn}_3\text{B}_3\text{F}_{12}$ , 636.5232).

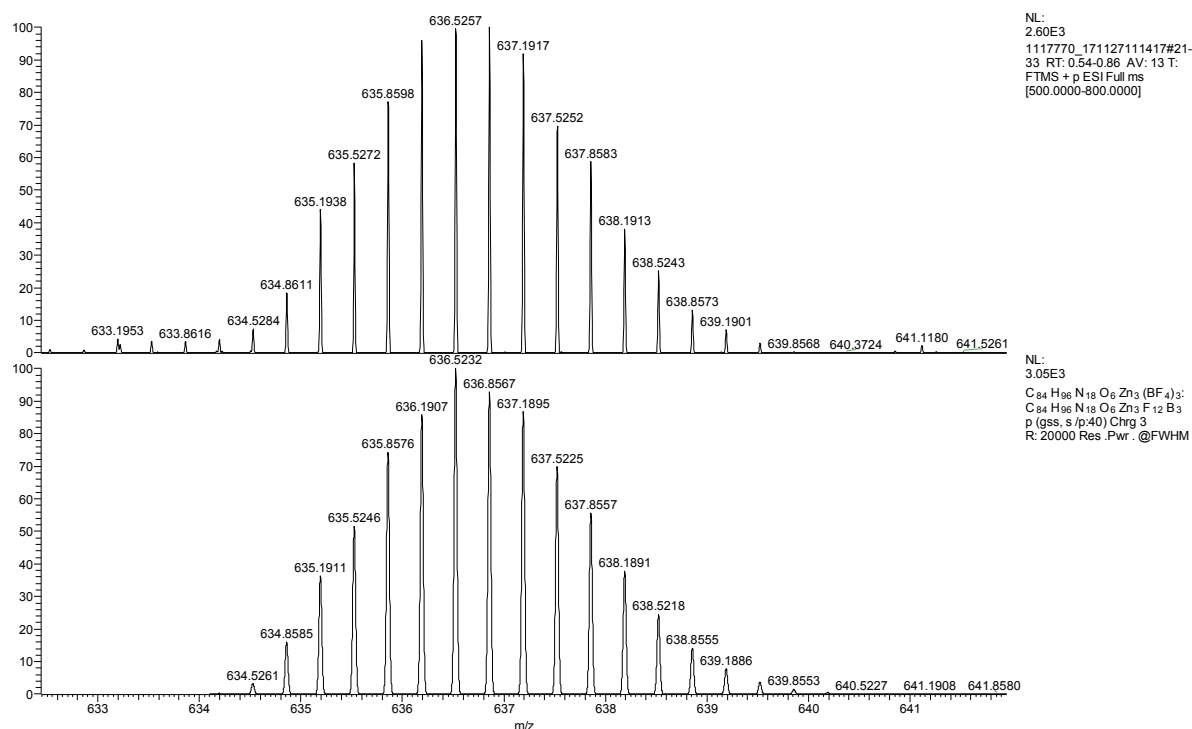
### 3.3 Synthesis of Trefoil Knot **4**

A solution of **3** (20 mg, 9.2  $\mu\text{mol}$ ) in degassed anhydrous nitromethane (1.8 mL) was added to an oven dried flask equipped with a stirrer bar under  $\text{N}_2$ . Hoveyda-Grubbs 2<sup>nd</sup> generation catalyst ( $\text{H}_2\text{IMes}(\text{Cl})_2\text{RuCH}(\text{o-OiPrC}_6\text{H}_4)$ ) (2.9 mg, 4.6  $\mu\text{mol}$ , 50 mol%) in degassed anhydrous 1,2-dichloroethane (1.8 mL) was added, and the reaction heated to 60 °C for 24 hours with stirring. After cooling to room temperature, the catalyst was quenched with excess ethylvinyl ether (0.4 mL) and stirred for 30 minutes. The solvent was removed under reduced pressure and the resulting solid sonicated in dichloromethane for 15 minutes, filtered onto celite, washed thoroughly with fresh

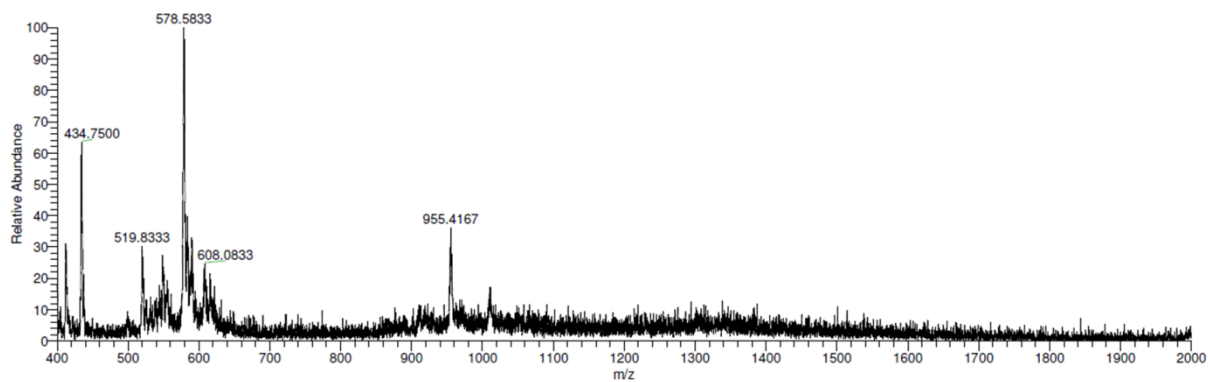
dichloromethane and taken up in acetonitrile. The solvent was removed to afford **4** as a light brown solid in a quantitative yield (19.1 mg, 9.2  $\mu\text{mol}$ ).  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  8.80 (s, 6H,  $\text{H}^b$ ), 8.30 (s, 6H,  $\text{H}^a$ ), 7.59 (dd,  $J = 8.8, 2.8$  Hz, 6H,  $\text{H}^f$ ), 7.52 (d,  $J = 8.8$  Hz, 6H,  $\text{H}^e$ ), 7.46 (d,  $J = 2.8$  Hz, 6H,  $\text{H}^g$ ), 5.46 – 5.41 (m, 6H,  $\text{H}^i$ ), 4.68 – 4.55 (m, 6H,  $\text{H}^c$ ), 4.36 – 4.24 (m, 6H,  $\text{H}^{c'}$ ), 4.05 – 3.96 (m, 6H,  $\text{H}^h$ ), 3.91 – 3.82 (m, 6H,  $\text{H}^j$ ), 3.30 – 3.22 (m, 6H,  $\text{H}^{d'}$ ), 3.09 – 2.99 (m, 6H,  $\text{H}^d$ ), 2.41 – 2.25 (m, 12H,  $\text{H}^i$ ).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  164.3, 156.9, 153.5, 146.9, 145.4, 136.9, 129.4, 128.4, 127.5, 69.6, 57.3, 34.2, 32.4. LRESI-MS:  $m/z = 955.4$   $[\text{M}-2\text{BF}_4]^{2+}$  requires 956.2; 608.1  $[\text{M}-3\text{BF}_4]^{4+}$  requires 608.5; 434.8  $[\text{M}-4\text{BF}_4]^{4+}$  requires 434.6. HRESI-MS:  $m/z = 956.2474$   $[\text{M}-2\text{BF}_4]^{2+}$  (calcd. for  $\text{C}_{78}\text{H}_{84}\text{N}_{18}\text{O}_6\text{Zn}_3\text{B}_4\text{F}_{16}$ , 956.2402).



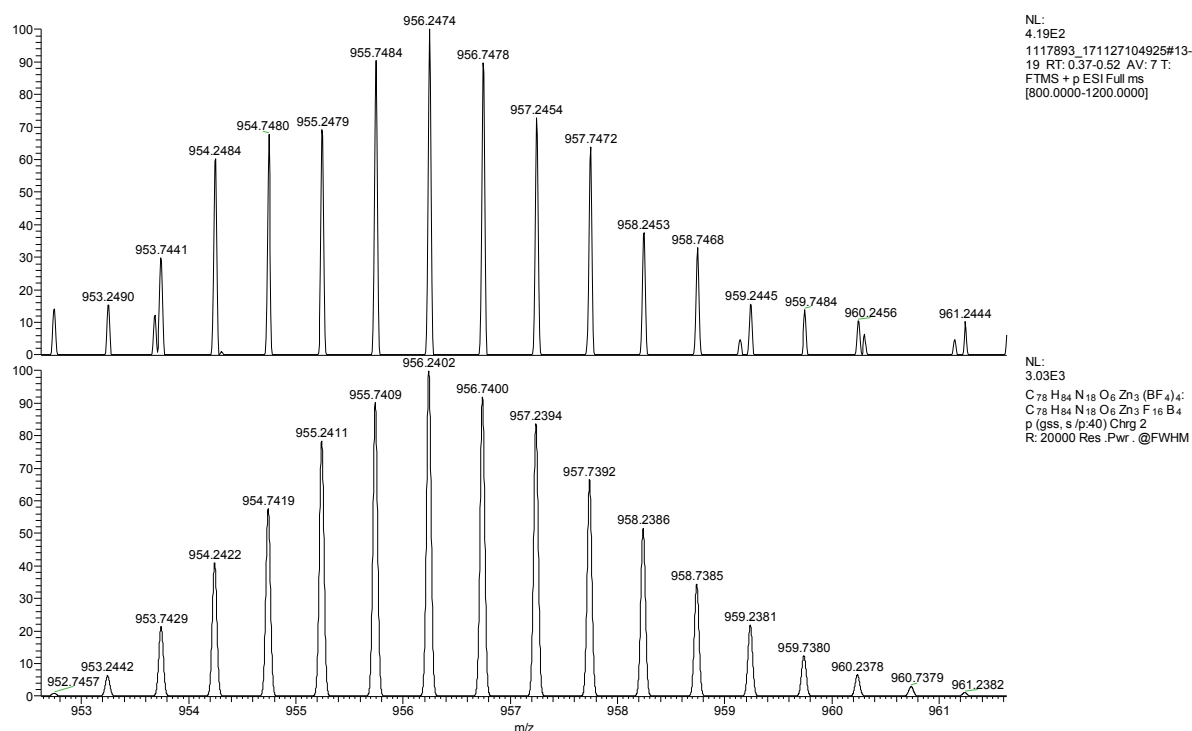
**Figure S1:** Low-resolution ESI-MS of circular trimeric helicate **3**. Calculated peaks ( $m/z$ ): 998.3  $[\text{M}-2\text{BF}_4]^{2+}$ ; 636.5  $[\text{M}-3\text{BF}_4]^{3+}$ ; 455.6  $[\text{M}-4\text{BF}_4]^{4+}$ .



**Figure S2:** High-resolution ESI-MS of the  $[M-3BF_4]^{3+}$  peak of circular trimeric helicate **3**. Experimental spectrum (top) and calculated spectrum (bottom).



**Figure S3:** Low-resolution ESI-MS of trefoil knot **4**. Calculated peaks ( $m/z$ ): 956.2  $[M-2BF_4]^{2+}$ ; 608.5  $[M-3BF_4]^{3+}$ ; 434.6  $[M-4BF_4]^{4+}$ .



**Figure S4:** High-resolution ESI-MS of the  $[M-2BF_4]^{2+}$  peak of trefoil knot **4**. Experimental spectrum (top) and calculated spectrum (bottom).

#### 4. X-Ray Crystallography

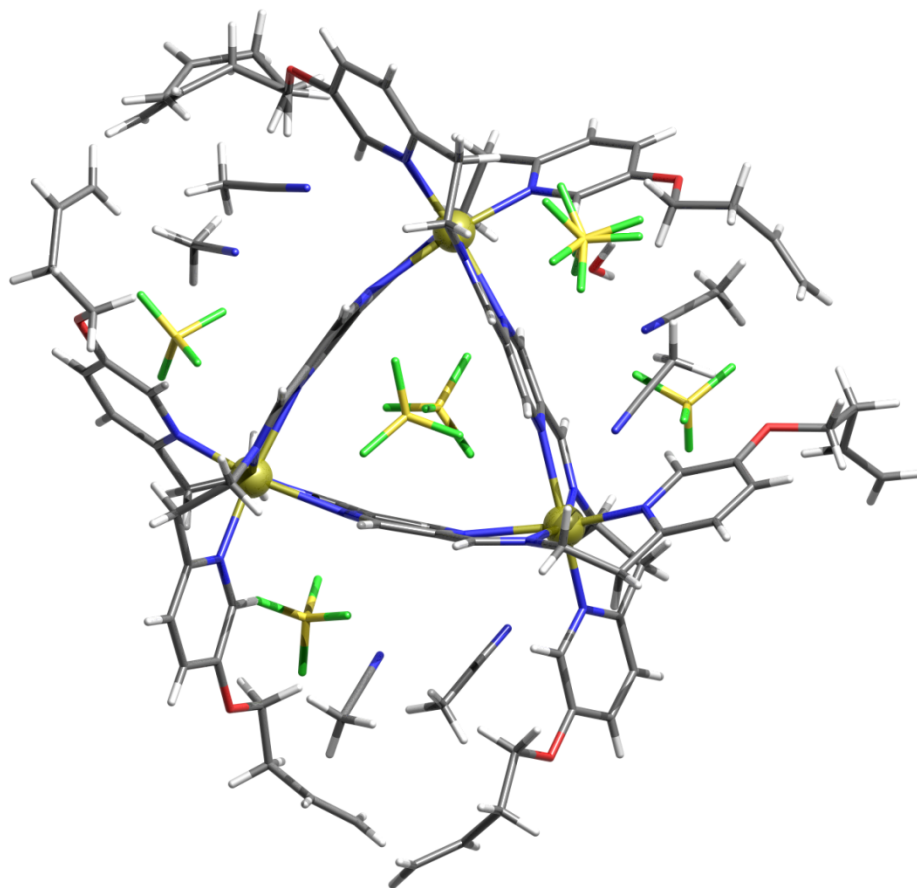
**Data Collection.** X-Ray data for trimeric circular helicate **3** were collected at a temperature of 150 K with  $CuK_{\alpha}$  wavelength radiation ( $\lambda = 1.54184 \text{ \AA}$ ) using a dual source Rigaku FR-X rotating anode diffractometer equipped with a HyPix 6000 HE detector and an Oxford Cryostream 700 plus. Data for trefoil knot **4** were collected at a temperature of 100 K with Zr L-edge wavelength radiation ( $\lambda = 0.6889 \text{ \AA}$ ) using the synchrotron source at single crystal X-ray diffraction beamline I19 in Diamond light Source,<sup>S2</sup> equipped with an Pilatus 2M detector and an Oxford Cryosystems Cryostream nitrogen flow gas system using GDA suite of programs. Both sets of data were reduced using CrysAlisPro 171.39.30c and absorption correction was performed using empirical methods (SCALE3 ABSPACK) based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles.<sup>S3</sup> The structures for both were solved and refined against all  $F^2$  values using Shelx-2016 implemented through Olex2 v1.2.x.<sup>S4</sup>



**Table S1.** Crystallographic information for sample trimetric circular helicate **3**

Identification code	Tri
Empirical formula	C <sub>96</sub> H <sub>116</sub> B <sub>6</sub> F <sub>24</sub> N <sub>24</sub> O <sub>7</sub> Zn <sub>3</sub>
Formula weight	2435.09
Temperature/K	150.05(10)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	19.5521(8)
b/Å	18.7147(9)
c/Å	32.1206(16)
$\alpha$ /°	90
$\beta$ /°	105.355(5)
$\gamma$ /°	90
Volume/Å <sup>3</sup>	11333.7(9)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.427
$\mu/\text{mm}^{-1}$	1.625
F(000)	5008.0
Crystal size/mm <sup>3</sup>	0.146 × 0.07 × 0.02
Radiation	CuK $\alpha$ ( $\lambda$ = 1.54184)
2 $\Theta$ range for data collection/°	4.686 to 143.268
Index ranges	-21 ≤ h ≤ 23, -23 ≤ k ≤ 22, -38 ≤ l ≤ 39
Reflections collected	112675
Independent reflections	21604 [ $R_{\text{int}}$ = 0.0916, $R_{\text{sigma}}$ = 0.0611]
Data/restraints/parameters	21604/488/1515

Goodness-of-fit on $F^2$	1.101
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0722$ , $wR_2 = 0.1969$
Final R indexes [all data]	$R_1 = 0.1018$ , $wR_2 = 0.2297$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.83/-1.19



**Figure S5.** Graphical representation of trimeric circular helicate **3** in the crystal. Light yellow = zinc, blue = nitrogen, grey = carbon, red = oxygen, green = fluorine, yellow = boron white = hydrogen

**Table S2.** Crystallographic information for sample trefoil knot **4**

Identification code	Tk
Empirical formula	$C_{78}H_{84}B_6F_{24}N_{18}O_6Zn_3$
Formula weight	2086.60
Temperature/K	100
Crystal system	trigonal
Space group	R-3c
$a/\text{\AA}$	18.4482(7)
$b/\text{\AA}$	18.4482(7)
$c/\text{\AA}$	52.7913(18)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	120
Volume/ $\text{\AA}^3$	15559.7(13)
Z	6
$\rho_{\text{calc}}/\text{cm}^3$	1.336
$\mu/\text{mm}^{-1}$	0.721
F(000)	6372.0
Crystal size/ $\text{mm}^3$	$0.03 \times 0.025 \times 0.01$
Radiation	synchrotron ( $\lambda = 0.6889$ )
$2\Theta$ range for data collection/ $^\circ$	3.88 to 36.496
Index ranges	$-16 \leq h \leq 16, -16 \leq k \leq 16, -47 \leq l \leq 47$
Reflections collected	12438
Independent reflections	1367 [ $R_{\text{int}} = 0.0618, R_{\text{sigma}} = 0.0339$ ]
Data/restraints/parameters	1367/58/125

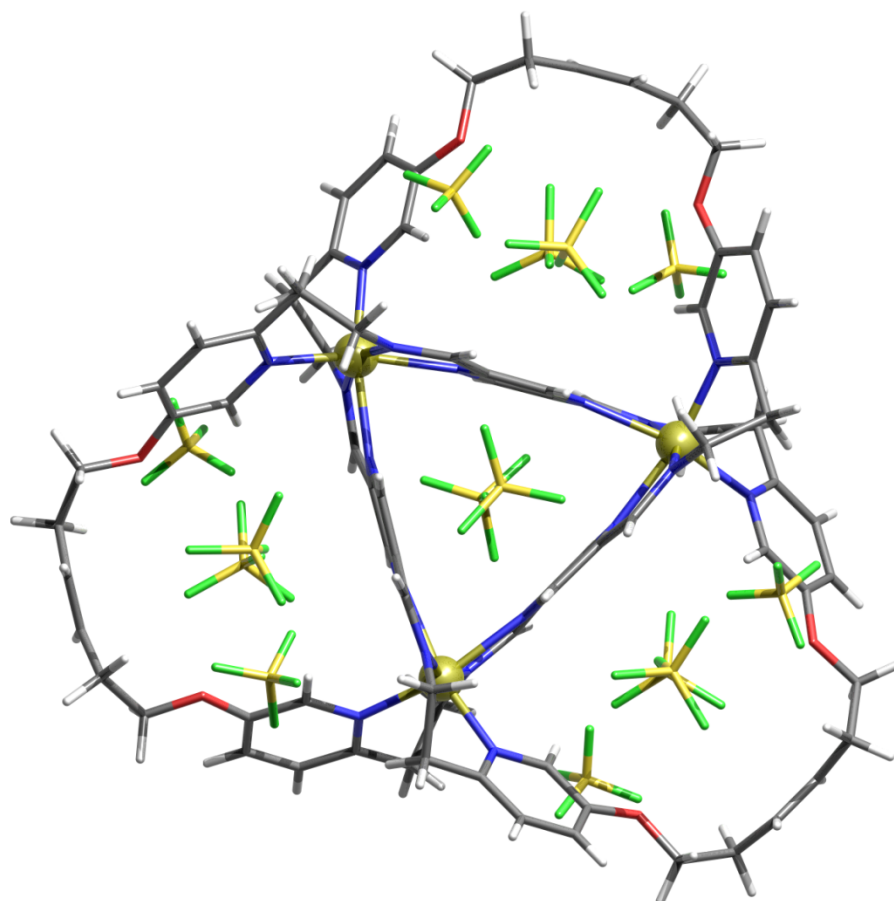
Goodness-of-fit on  $F^2$  2.108

Final R indexes [ $I \geq 2\sigma(I)$ ]  $R_1 = 0.1657$ ,  $wR_2 = 0.4580$

Final R indexes [all data]  $R_1 = 0.1796$ ,  $wR_2 = 0.4733$

Largest diff. peak/hole /  $e \text{ \AA}^{-3}$  0.96/-0.54

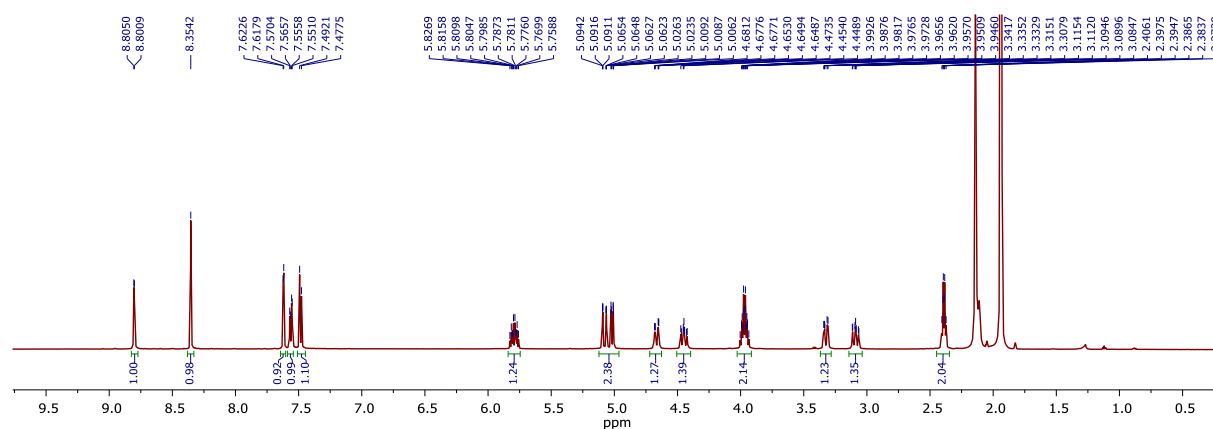
Despite the use of synchrotron radiation, crystals of **4** only diffracted to 1.1 Å resolution and the data were trimmed accordingly. In addition, due to the poor resolution obtained, the refinement of the model was based on a poorly defined electron density map, resulting in high values of  $R_1$  and  $wR_2$  and in order to maintain a reasonable data to parameter ratio. Carbon, boron and fluorine atoms were refined isotropically. Fixed distance and same distance restraints were applied to maintain sensible geometries in the model. Similar neighbouring thermal parameter and rigid bond restraints were also applied.



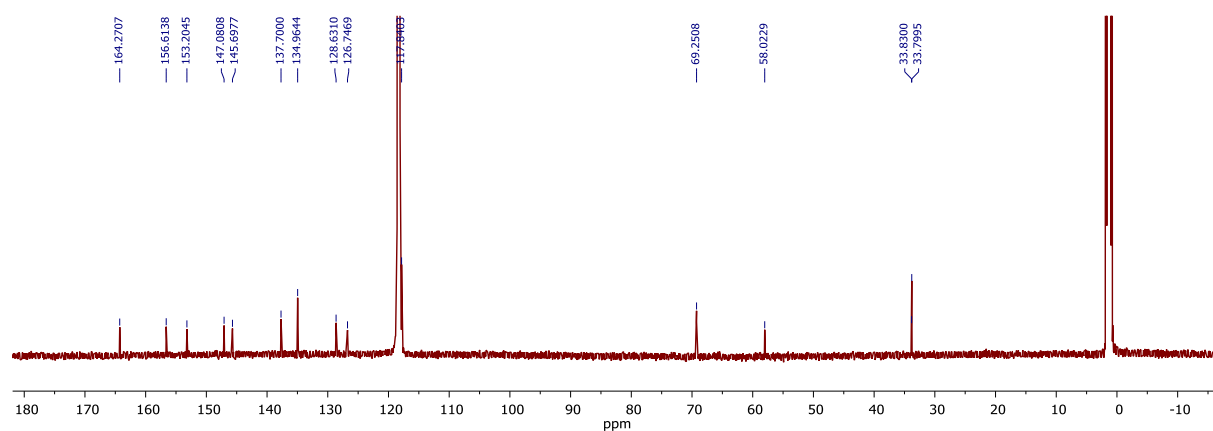
**Figure S6.** Graphical representation of trefoil knot **4** in the crystal. Light yellow = zinc, blue = nitrogen, grey = carbon, red = oxygen, green = fluorine, yellow = boron white = hydrogen.

CCDC 1815058 and 1815059 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

## 5. NMR Spectra



**Figure S7.** <sup>1</sup>H NMR (600 MHz, 298 K, CD<sub>3</sub>CN) of trimeric circular helicate **3**.



**Figure S8.** <sup>13</sup>C NMR (151 MHz, 298 K, CD<sub>3</sub>CN) of trimeric circular helicate **3**.

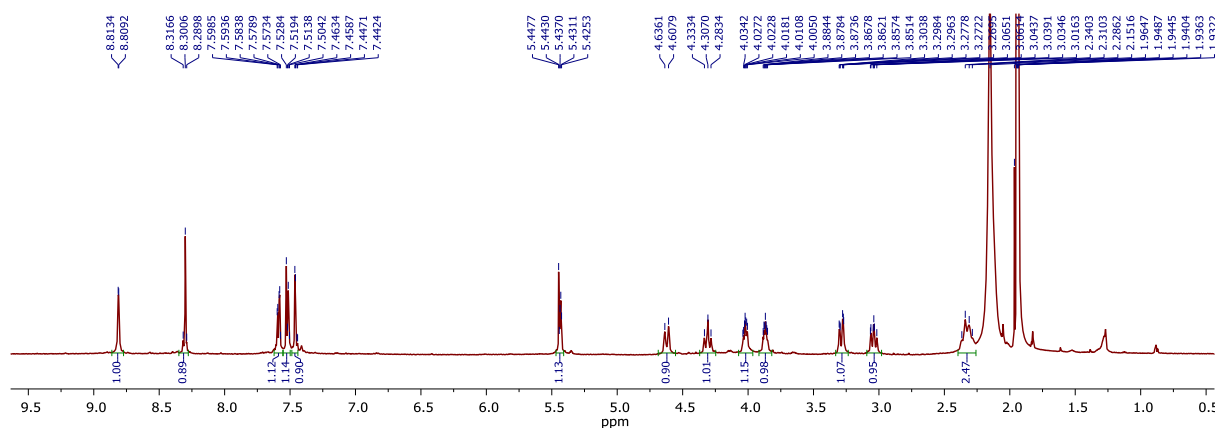


Figure S9.  $^1\text{H}$  NMR (600 MHz, 298 K,  $\text{CD}_3\text{CN}$ ) of trefoil knot **4**.

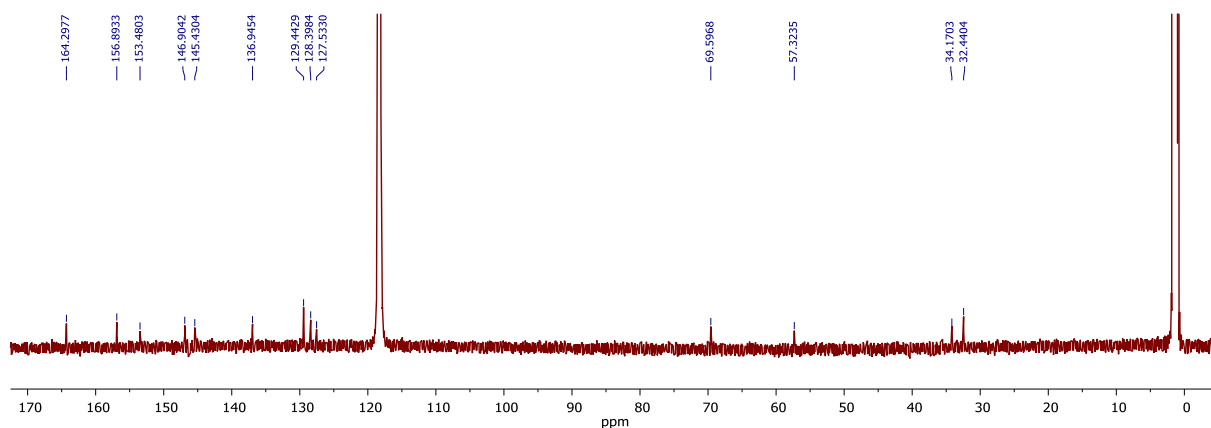


Figure S10.  $^{13}\text{C}$  NMR (151 MHz, 298 K,  $\text{CD}_3\text{CN}$ ) of trefoil knot **4**.

## 6. References

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