Supporting Information for

Facile Syntheses of [3]-, [4]- and [6]Catenanes Templated by Orthogonal Supramolecular Interactions

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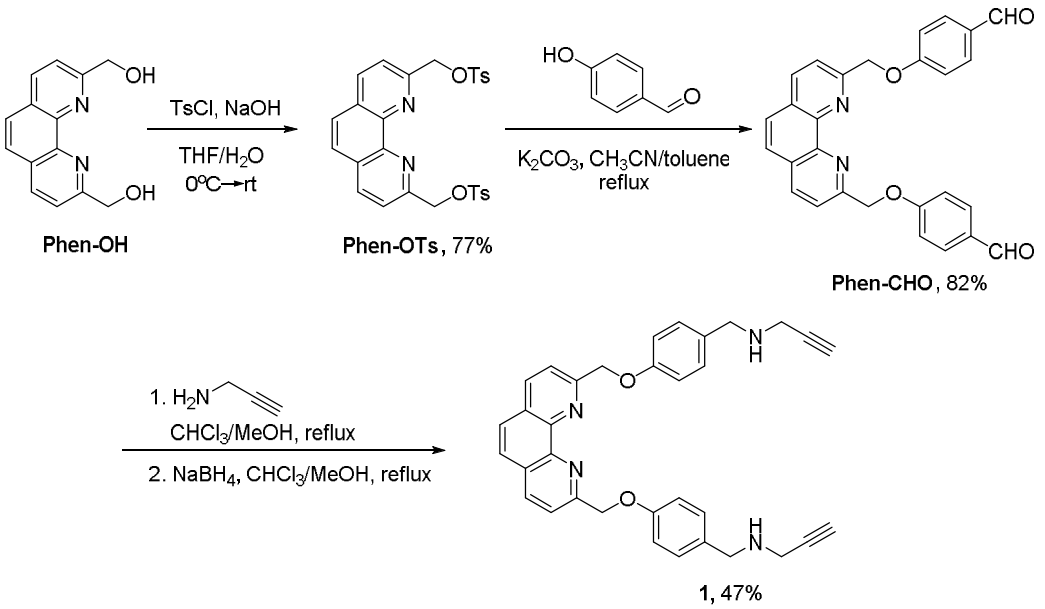
1. Synthesis

General: All reagents were purchased from commercial suppliers (Aldrich, Dkmchem and J & K) and used without further purification. All the solvents for synthesis were of analytical grade (ACI Labscan and Arkonic Scientific) and used without distillation. **Phen-OH**,[1] 2-azidoethylamine,[2] **DN-OTs**,[3] *N*-(4-hydroxylbenzyl)propargylamine,[4] **DN-N_3**,[5] cucurbit[6]uril (CB[6])[6] and cyclo*bis*paraquat(*p*-phenylene) ($CBPQT^{4+}$)[7] were synthesised according to literature procedures. Unless stated otherwise, all the reactions involving Cu^+ were carried out under an argon atmosphere, with all the solvents purged with argon for 30 min *in prior*.

Thin layer chromatography (TLC) was performed on silica gel 60 F254 (Merck, Germany, Aluminium sheet) and column chromatography was carried out on silica gel 60F (Silicycle, Canada). LCMS analyses were carried out using a Waters-Alliance e2695 system coupled to a 2489 UV/Vis detector and a QDa MS detector. NMR spectra were recorded on Brucker DPX spectrometers with working frequencies of 400 MHz for ^1H, 100 MHz for ^{13}C and 500 MHz for 2D NMR experiments (COSY, NOESY and DOSY), respectively. Chemical shifts are reported in ppm and referenced to solvent residues ($CDCl_3$: δ = 7.26 ppm, D_2O: δ = 4.69 ppm, CD_3CN: δ = 1.94 ppm and $(CD_3)_2SO$: δ = 2.50 ppm). UV-Vis spectra were recorded by a Perkin Elmer 19 UV/Vis spectrophotometer. High-resolution mass spectrometry of **C6** was performed on a Thermo Scientific LTQ Orbitrap Velos mass spectrometer, while that of **C3** and **C4** were performed on a Finnigan LCQ mass spectrometer. MS^2 and MS^3 experiments were carried out on a Finnigan LCQ mass spectrometer. Simulation of isotopic patterns of **C3**, **C4** and **C6** were conducted on IsoPro, version 3.1.



Phen-OH **Phen-OTs**, 77% **Phen-CHO**, 82%

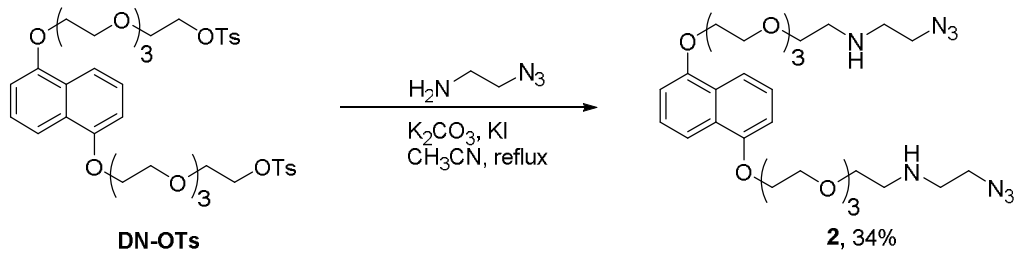
1, 47%

Scheme S1

Phen-OTs. To a suspension of **Phen-OH** (1.18 g, 4.9 mmol) in THF (6 mL) was added a solution of NaOH (0.59 g, 14.7 mmol) in water (5 mL). The mixture was cooled to 0°C and a THF solution of TsCl (2.33 g, 12.3 mmol, 30 mL) was added over 2 hrs. The reaction mixture was stirred for another 2 hrs at room temperature before iced water (10 mL) was added. The resulting aqueous solution was extracted with CH_2Cl_2 (3 × 30 mL). The organic fractions were combined, washed with brine, dried over $MgSO_4$ and concentrated. The resulting brown oil was purified by a silica column (ethyl acetate/hexanes = 2:1) to give the product as white solid. Yield = 2.10 g, 77 %. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 8.30 (d, *J* = 8.0 Hz, 2 H), 7.89−7.84 (m, 6 H), 7.81 (s, 2 H), 7.34 (d, *J* = 7.8 Hz, 4 H), 5.50 (s, 4 H), 2.43 (s, 6 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ = 154.8, 145.2, 144.8, 137.5, 132.5, 130.0, 128.5, 128.2, 126.8, 121.2, 72.4, 21.7. ESI-MS: 571.4 $[M+Na]^+$.

Phen-CHO. A mixture of **Phen-OTs** (1.50 g, 2.7 mmol), 4-hydroxybenzaldehyde (0.70 g, 5.7 mmol) and K_2CO_3 (0.95 g, 6.8 mmol) in CH_3CN/toluene (v/v 4:1, 30 mL) was heated to reflux for overnight. Solvents were removed using a rotary evaporator. The residue was partitioned between CH_2Cl_2 (40 mL) and water (20 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated to afford a yellow solid, which was used in the next step without further purification. Yield = 0.99 g, 82%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 9.91 (s, 2 H), 8.35 (d, *J* = 8.4 Hz, 2 H), 7.94 (d, *J* = 8.4 Hz, 2 H), 7.89−7.86 (m, 6 H), 7.19 (d, *J* = 8.8 Hz, 4 H), 5.73 (s, 4 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ = 190.2, 162.7, 156.6, 144.6, 136.8, 131.5, 129.9, 127.9, 126.0, 120.4, 114.7, 71.1. ESI-MS: 471.4 $[M+Na]^+$.

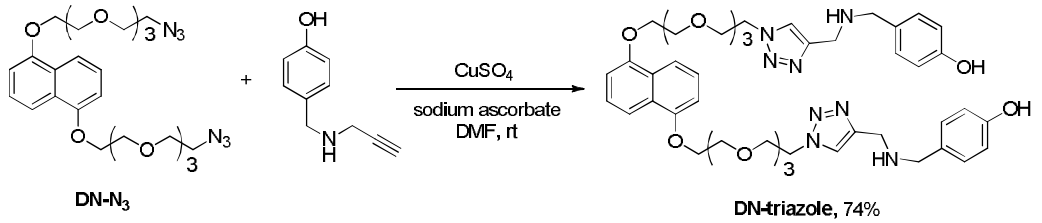
Compound **1**. A solution of **Phen-CHO** (990 mg, 2.2 mmol) and propargylamine (490 mg, 8.8 mmol) in $CHCl_3$/MeOH (v/v 3:1, 32 mL) was heated to reflux for one day. The reaction mixture was cooled to room temperature. $NaBH_4$ (340 mg, 8.8 mmol) was added and the mixture was heated to reflux for overnight. Solvents were removed under reduced pressure and the residue was partitioned in water (10 mL) and CH_2Cl_2 (20 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated to give a yellow solid, which was purified by a silica column (CH_2Cl_2/MeOH/Et_3N = 99:1:0.5) to afford a yellow solid. Yield = 540 mg, 47%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 8.31 (d, *J* = 8.4 Hz, 2 H), 7.95 (d, *J* = 8.4 Hz, 2 H), 7.82 (s, 2 H), 7.30 (d, *J* = 8.8 Hz, 4 H), 7.04 (d, *J* = 8.4 Hz, 4 H), 5.65 (s, 4 H), 3.84 (s, 4 H), 3.43 (d, *J* = 2.4 Hz, 4 H), 2.26 (t, *J* = 2.2 Hz, 2 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ = 158.5, 157.7, 145.2, 137.2, 132.1, 129.8, 128.3, 126.4, 120.9, 114.9, 71.6, 71.5, 51.6, 37.2. ESI-MS: 549.7 $[M+Na]^+$.



DN-OTs **2**, 34%

Scheme S2

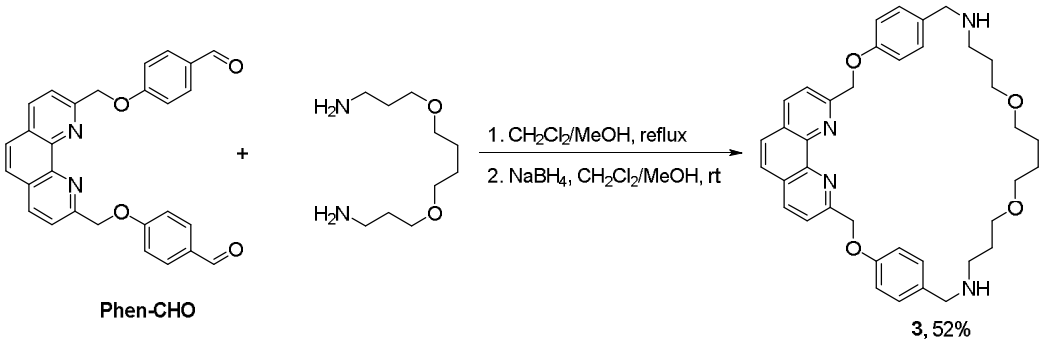
Compound **2**. To a refluxing mixture of 2-azidoethylamine (440 mg, 8.0 mmol), K_2CO_3 (690 mg, 5.0 mmol) and KI (30 mg, 0.2 mmol) in CH_3CN (8 mL) was added a CH_3CN solution of **DN-OTs** (1.64 g, 2.0 mmol, 30 mL) at a rate of 1.5 mL/hr by using a syringe pump. After the addition was completed, heating was continued for overnight. Insoluble materials were removed by filtration and the residue was washed with CH_2Cl_2 (30 mL). The combined filtrates were concentrated and purified by a silica column (CH_2Cl_2/MeOH/Et_3N = 99:3:0.5) to afford a brown oil. Yield = 440 mg, 34 %. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.86 (d, *J* = 8.4 Hz, 2 H), 7.34 (t, *J* = 8.0 Hz, 2 H), 6.84 (d, *J* = 7.8 Hz, 2 H), 4.29 (t, *J* = 4.8 Hz, 4 H), 4.00 (t, *J* = 4.6 Hz, 4 H), 3.82−3.79 (m, 4 H), 3.71−3.66 (m, 8 H), 3.63−3.61 (m, 4H), 3.57 (t, *J* = 5.2 Hz, 4 H) 3.38 (t, *J* = 5.8 Hz, 4 H), 2.80−2.77 (m, 8 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ = 153.7, 126.2, 124.5, 114.0, 105.1, 70.4, 70.1, 70.0, 69.8, 69.8, 69.2, 67.3, 50.8, 48.3, 47.8. ESI-MS: 649.5 $[M+H]^+$.



DN-N$_3$ **DN-triazole**, 74%

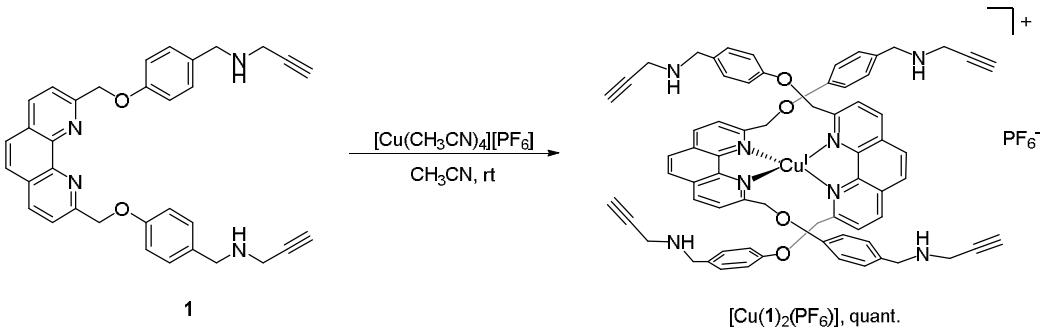
Scheme S3

DN-triazole. To a solution of *N*-(4-hydroxylbenzyl)propargylamine (90 mg, 0.6 mmol) and **DN-N$_3$** (140 mg, 0.25 mmol) in DMF (1 mL) was added anhydrous $CuSO_4$ (4 mg, 0.025 mmol) and sodium ascorbate (10 mg, 0.05 mmol). The resulting mixture was stirred at room temperature for overnight. Solvents were removed under reduced pressure and the residue was purified by a silica column (CH_2Cl_2/MeOH/Et_3N = 94:6:1) to afford a brown oil. Yield = 164 mg, 74%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.80 (d, *J* = 8.4 Hz, 2 H), 7.60 (s, 2 H), 7.26 (t, *J* = 8.0 Hz, 2 H), 6.96 (d, *J* = 8.4 Hz, 4 H), 6.76 (d, *J* = 8.0 Hz, 2 H), 6.61 (d, *J* = 8.4 Hz, 4 H), 4.39 (t, *J* = 4.8 Hz, 4 H), 4.21 (t, *J* = 4.6 Hz, 4 H), 3.92 (t, *J* = 4.6 Hz, 4 H), 3.80 (s, 4 H), 3.76−3.72 (m, 8 H), 3.62−3.52 (m, 16 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ = 156.5, 154.4, 145.9, 129.9, 126.9, 125.3, 123.5, 115.9, 114.7, 105.9, 71.1, 70.8, 70.6, 70.0, 69.5, 68.1, 52.7, 50.4, 46.1, 43.6. ESI-MS: 885.4 $[M+H]^+$.



Scheme S4

Compound **3**. A mixture of **Phen-CHO** (134 mg, 0.3 mmol) and 4,9-dioxa-1,12-dodecanediamine (60 mg, 0.3 mmol) in CH_2Cl_2/MeOH (v/v 1:1, 600 mL) was heated to reflux for overnight. The solution was cooled to room temperature and $NaBH_4$ (45 mg, 1.2 mmol) was added in portions. The resulting solution was stirred at room temperature for another overnight. Solvents were removed by a rotary evaporator and the residue was partitioned between CH_2Cl_2 (15 mL) and water (10 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The organic fractions were combined, washed with brine, dried over $MgSO_4$. Solvents were removed by a rotary evaporator and the residue was purified by a silica column (CH_2Cl_2/MeOH/Et_3N = 90:10:1) to give a yellow solid. Yield = 97 mg, 52%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 8.26 (d, *J* = 8.4 Hz, 2 H), 7.85 (d, *J* = 8.0 Hz, 2 H), 7.78 (s, 2 H), 7.35 (d, *J* = 8.8 Hz, 4 H), 7.10 (d, *J* = 8.8 Hz. 4 H), 5.60 (s, 4 H), 3.90 (s, 4 H), 3.44 (t, *J* = 5.8 Hz, 4 H), 3.33 (m, 4 H), 2.82 (t, *J* = 6.6 Hz, 4 H), 1.89 (m, 4 H), 1.49 (m, 4 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ = 158.9, 158.1, 145.5, 137.4, 131.0, 128.5, 126.7, 122.0, 115.9, 72.5, 70.9, 68.6, 51.6, 45.2, 27.8, 26.3. ESI-MS: 621.7 $[M+H]^+$.



Scheme S5

$[Cu(1)_2][(PF_6)]$. A mixture of **1** (26.3 mg, 0.05 mmol) and $Cu(CH_3CN)_4PF_6$ (9.3 mg, 0.025 mmol) in CH_3CN (3 mL) was stirred at room temperature for 1 hr under argon. The resulting dark red solution was concentrated in vacuum to give the product as red solid. Yield = 31 mg, quant. ^{1}H NMR (400 MHz, CD_3CN, 298 K) δ = 8.56 (d, *J* = 11.2 Hz, 4 H),

8.00−7.97 (m, 8 H), 6.69 (d, *J* = 10.8 Hz, 8 H), 6.07 (d, *J* = 11.2 Hz, 8 H), 4.92 (s, 8 H), 3.54 (s, 8 H), 3.24 (s, 8 H), 2.49 (s, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN, 298 K) δ = 157.6, 156.2, 144.0, 138.9, 133.4, 129.8, 127.6, 125.5, 114.1, 83.4, 72.5, 71.7, 51.7, 37.5. ESI-MS: 1115.6 $[M\text{-}PF_6]^+$.

Synthesis of C3

A mixture of **2** (32.4 mg, 0.05 mmol) and CB[6] (100 mg, 0.1 mmol) in 0.2 M HCl (40 mL) was heated to 90°C for 2 hrs. The resulting solution was cooled to 60°C and a solution of **1** (26.3 mg 0.05 mmol) in 0.2 M HCl (40 mL) was added dropwisely over 1 hour. The resulting mixture was kept at 60°C for overnight and cooled to room temperature. HPLC analysis showed that *ca.* 85% of the materials in the product mixture corresponds to **C3**. Pure **C3** was isolated from the crude mixture by preparative HPLC. ^1H NMR (400 MHz, D_2O, 298 K) δ = 8.39 (d, *J* = 8.4 Hz, 2 H), 7.93 (d, *J* = 8.4 Hz, 2 H), 7.85−7.82 (m, 4 H), 7.66 (d, *J* = 8.8 Hz, 4 H), 7.43 (t, *J* = 7.8 Hz, 2 H), 7.21 (d, *J* = 8.8 Hz, 4 H), 7.01 (d, *J* = 7.8 Hz, 2 H), 6.23 (s, 2 H), 5.54−5.37 (m, 28 H), 5.17−5.10 (m, 24 H), 4.29−4.27 (m, 8 H), 4.02−3.92 (m, 40 H), 3.75−3.71 (m, 16 H), 3.55 (t, *J* = 6.6 Hz, 4 H), 3.52−3.48 (m, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, D_2O, 298 K) δ = 158.9, 157.6, 156.5, 156.3, 154.3, 144.3, 139.2, 138.5, 132.8, 128.6, 126.9, 126.5, 124.1, 120.2, 116.1, 114.8, 107.3, 71.4, 70.4, 70.1, 70.0, 69.6, 68.3, 66.1, 52.2, 51.7, 51.4, 47.6, 46.0, 45.4, 42.3. Alternatively, **C3** can be precipitated as a PF_6^- salt from the product mixture by addition of saturated aq. NH_4PF_6. The white precipitates were collected by filtration, washed with water (3 × 5 mL) and dried in vacuum. Isolated yield = 120 mg, 66 %. ^1H NMR of the PF_6^- salt (400 MHz, DMSO-d_6, 353 K) δ = 8.59 (m, 2 H), 8.02 (m, 2 H), 7.91 (m, 2 H), 7.76−7.72 (m, 6 H), 7.37 (m, 2 H), 7.17 (m, 4 H), 6.99 (m, 2 H), 6.46 (s, 2 H), 5.61−5.51 (m, 28 H), 5.39−5.37 (m, 24 H), 4.26−4.23 (m, 40 H), 4.26−4.23 (m, 4 H), 3.96−3.90 (m, 8 H), 3.68−3.65 (m, 20 H), 3.47 (m, 4 H).

Synthesis of C4

A solution of **3** (12 mg, 0.019 mmol) in $CHCl_3$ (0.5 mL) was mixed with a solution of $Cu(CH_3CN)_4PF_6$ (7.1 mg, 0.019 mmol) in CH_3CN (1 mL) and stirred at room temperature for 1 hr, followed by the addition of **1** (10 mg, 0.019 mmol) in $CHCl_3$ (1 mL). The dark red solution was stirred at room temperature for overnight. Solvents were removed and the residue re-dissolved in DMF (20 mL). An aqueous solution of **2** and CB[6] in 0.2 M HCl (20 mL) was heated to 90°C under argon for 2 hrs and added to the DMF solution at 60°C. The reaction mixture was heated at 60°C for further 2 days. HPLC analysis showed that *ca.* 84% of the materials corresponds to **C4**. A pure sample of **C4** was obtained by preparative HPLC. For preparative HPLC, the product mixture was evaporated by a rotatory evaporator and re-dissolved in 10 ml of H_2O/CH_3CN (v/v 1:1). The solution was injected onto a semi-preparative column (see details below) and the peak corresponding to **C4** was collected. Solvents were evaporated to give a pure sample of **C4**. From 1.275 ml of the 10 ml H_2O/CH_3CN solution, 5.3 mg of **C4** was isolated, isolated yield = 54%. ^1H NMR (400 MHz, D_2O, 298 K) δ = 8.58 (d, *J* = 8.0 Hz, 2 H), 8.47 (d, *J* = 8.0 Hz, 2 H),

8.02−8.01 (m, 4 H), 8.00 (d, *J* = 2.8 Hz, 2 H), 7.84−7.83 (m, 4 H), 7.47 (t, *J* = 7.6 Hz, 2 H), 7.05 (d, *J* = 8.4 Hz, 6 H), 6.55 (d, *J* = 8.4 Hz, 4 H), 6.31 (s, 2 H), 6.13 (d, *J* = 8.8 Hz, 4 H), 5.91 (d, *J* = 8.8 Hz, 4 H), 5.60 (d, *J* = 15.6 Hz, 12 H), 5.49 (d, *J* = 15.6 Hz, 12 H), 5.31−5.24 (m, 24 H), 5.01 (s, 4 H), 4.93 (s, 4 H), 4.31 (m, 4 H), 4.13−4.03 (m, 36 H), 3.97−3.95 (m, 8 H), 3.84−3.82 (m, 4 H), 3.79−3.77 (m, 12 H), 3.74−3.72 (m, 4 H), 3.66−3.60 (m, 12 H), 3.55 (t, *J* = 4.8 Hz, 4 H), 2.99 (t, *J* = 6.8 Hz, 4 H), 1.99 (m, 4 H), 1.73 (m, 4 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, D_2O, 298 K) δ = 158.1, 156.7, 156.3, 154.6, 154.4, 153.8, 143.5, 143.4, 143.2, 139.1, 138.6, 138.2, 132.0, 130.7, 129.5, 129.0, 127.3, 126.8, 126.5, 125.6, 123.7, 122.7, 120.3, 114.9, 113.6, 112.8, 107.5, 72.1, 71.4, 71.1, 70.4, 67.0, 69.7, 68.5, 66.1, 60.7, 52.3, 51.7, 51.5, 49.6, 47.7, 47.5, 46.1, 45.4, 44.9, 42.8, 42.6, 34.8, 26.0, 25.6.

Synthesis of C6

A mixture of **1** (26.3 mg, 0.05 mmol) and $Cu(CH_3CN)_4PF_6$ (9.3 mg, 0.025 mmol) in CH_3CN (5 mL) was stirred at room temperature for 1 hr and diluted with 40 mL DMF and heated to 60^{o}C for a further hour. An aqueous solution of **2** (32.4 mg, 0.05 mmol) and CB[6] (100 mg, 0.1 mmol) in 45 mL of 0.2 M HCl heated at 90^{o}C for 2 hrs and was then added dropwise to the copper complex solution. The reaction mixture was heated at 60^{o}C for further 2 days. HPLC analysis showed that *ca.* 91% of the materials in the product mixture corresponds to **C6**. A pure sample of **C6** was obtained by preparative HPLC. For preparative HPLC, the crude mixture was first evaporated by a rotatory evaporator and re-dissolved in 9 ml of water. The concentrated solution was injected onto a semi-preparative column (see details below) and the peak corresponding to **C6** was collected. Solvents were evaporated to give a pure sample of **C6**. From 0.775 ml of the 9 ml re-dissolved mixture, 9.8 mg of **C6** was isolated, isolated yield = 69% (the formate residue observed in one of the ^{1}H NMR spectra of one batch of the sample (~3 mg) is estimated to contribute less than 1% error in the calculation of the total isolated yield). ^{1}H NMR (400 MHz, D_2O, 298 K) δ = 8.65 (d, *J* = 8.0 Hz, 4 H), 8.17−8.14 (m, 8 H), 7.85 (d, *J* = 8.0 Hz, 4 H), 7.44 (t, *J* = 7.6 Hz, 4H), 7.07 (d, *J* = 8.0 Hz, 8 H), 7.02 (d, *J* = 7.2 Hz, 4 H), 6.31 (s, 4 H), 6.07 (d, *J* = 8.0 Hz, 8 H), 5.54−5.42 (m, 28 H), 5.29−5.21 (m, 24 H), 4.29 (m, 8H), 4.08−3.94 (m, 88 H), 3.76−3.73 (m, 32 H), 3.61−3.52 (m. 16 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, D_2O, 298 K) δ = 157.7, 156.5, 156.3, 155.0, 154.3, 143.4, 139.0, 138.8, 131.4, 129.5, 127.4, 126.6, 126.4, 126.1, 123.7, 120.3, 114.9, 113.9, 107.5, 71.3, 70.4, 70.1, 70.0, 69.6, 68.4, 66.1, 52.1, 51.7, 51.5, 51.4, 47.6, 46.0, 45.3, 42.8.

2. HPLC analysis

HPLC and LCMS analyses were carried out using a Waters-Alliance e2695 system coupled to a 2489 UV/Vis detector and a QDa MS detector. HPLC grade water (Scharlau), MeCN (Arkonic Scientific) and formic acid (Fluka) were used without purification. Analytical HPLC analyses were performed by injecting 5 µL of the product crude mixture onto an XBridge analytical column (C18, 3.5 µm particle size, 2.1 × 50 mm), with a gradient elution using elution profiles described below at room temperature. Semi-preparative HPLC was performed with a SunFire preparative column (C18, 10 µm particle size, 4.6 × 250 mm) using the same elution profile as the analytical HPLC. UV-Vis absorbance was monitored as 254 nm and 280 nm.

Method 1.
Flow rate = 0.8 mL/min

Time/min	Water (with 0.05% formic acid)	MeCN
0	83%	17%
1	81%	19%
3	79%	21%
8	79%	21%
8.5	0%	100%
10	0%	100%

Method 2.
Flow rate = 0.8 mL/min

Time/min	Water (with 0.05% formic acid)	MeCN (0.05% formic acid)
0	85%	15%
1	80%	20%
10	70%	30%
10.5	0%	100%
13.5	0%	100%

Method 3.

Flow rate = 0.6 mL/min

Time/min	Water (0.05% formic acid)	MeCN
0	90%	10%
3	83%	17%
14	77%	23%
14.5	0%	100%
18.5	0%	100%

Method 4.

Flow rate = 0.6 mL/min

Time/min	Water	MeCN
0	95%	5%
1	95%	5%
10	0%	100%
12	0%	100%

Method 5.

Flow rate = 0.6 mL/min

Time/min	Water (0.05% formic acid)	MeCN
0	91%	9%
3	90%	10%
13	60%	40%
13.5	0%	100%
16	0%	100%

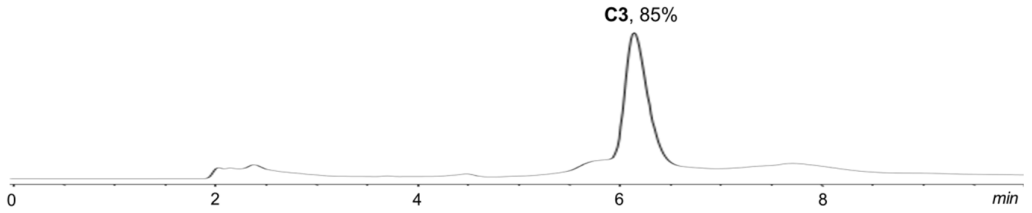


Fig. S1. HPLC chromatogram of the product mixture of **C3**. Separation was achieved using Method 1.

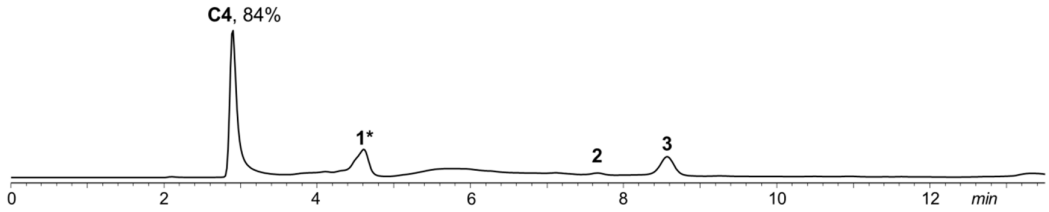


Fig. S2. HPLC chromatogram of the product mixture of **C4**. Separation was achieved using Method 2. ESI-MS showed **1*** as a minor oxidation product of **1**. Similar oxidation was observed in previous attempts of the assembly carried under aerobic conditions.

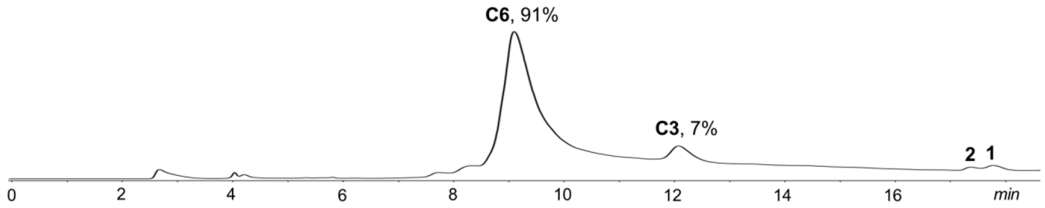


Fig. S3. HPLC chromatogram of the product mixture of **C6**. Separation was achieved using Method 3.

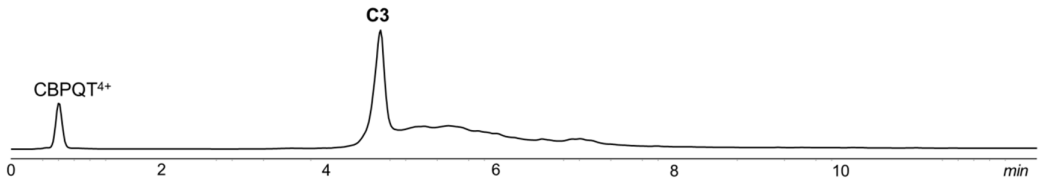


Fig. S4. HPLC chromatogram of the crude mixture of from the CB[6]-catalyzed click reaction of **1** and **2** in the presence of $CBPQT^{4+}$. Only **C3** was resulted. Separation was achieved using Method 4.

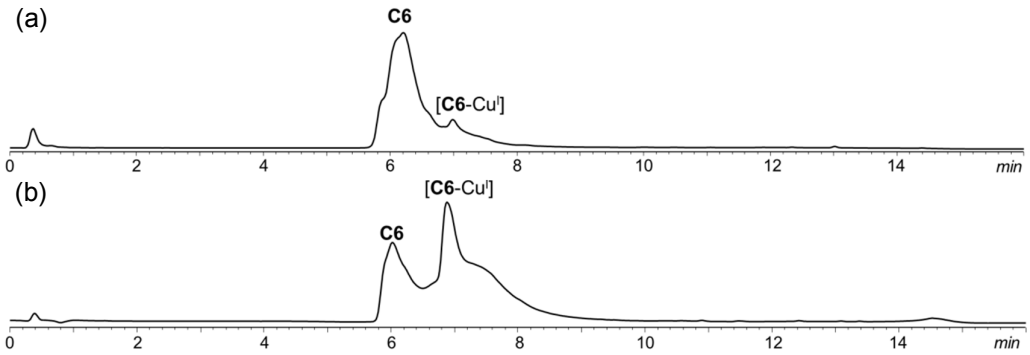


Fig. S5. HPLC chromatograms of **C6** that is (a) shortly after isolated from preparative HPLC, and (b) after storing at 4 ^{o}C for 4 months. Separation was achieved using Method 5.

Yields of **C3**, **C4** and **C6** were calculated from the relative peak areas in the respective chromatograms. Relative absorptivity of different components in the assembly mixture was estimated from the molar absorptivity of **1** (ε_{280nm} = 19,000 $M^{-1}cm^{-1}$), **2** (ε_{280nm} = 5000 $M^{-1}cm^{-1}$), and **3** (ε_{280nm} = 18,000 $M^{-1}cm^{-1}$), and the reference copper(I) complexes [Cu(**1**)$_2$][(PF_6)] (ε_{280nm} = 500,000 $M^{-1}cm^{-1}$) and [Cu(**1**)(**3**)][(PF_6)] (ε_{280nm} = 480,000 $M^{-1}cm^{-1}$) measured independently. Good correlation of the relative peak areas and the relative absorptivity has been observed for the residual **1** and **2** (and **3**) in the chromatograms of the **C4** and **C6** crude mixtures.

3. NMR data

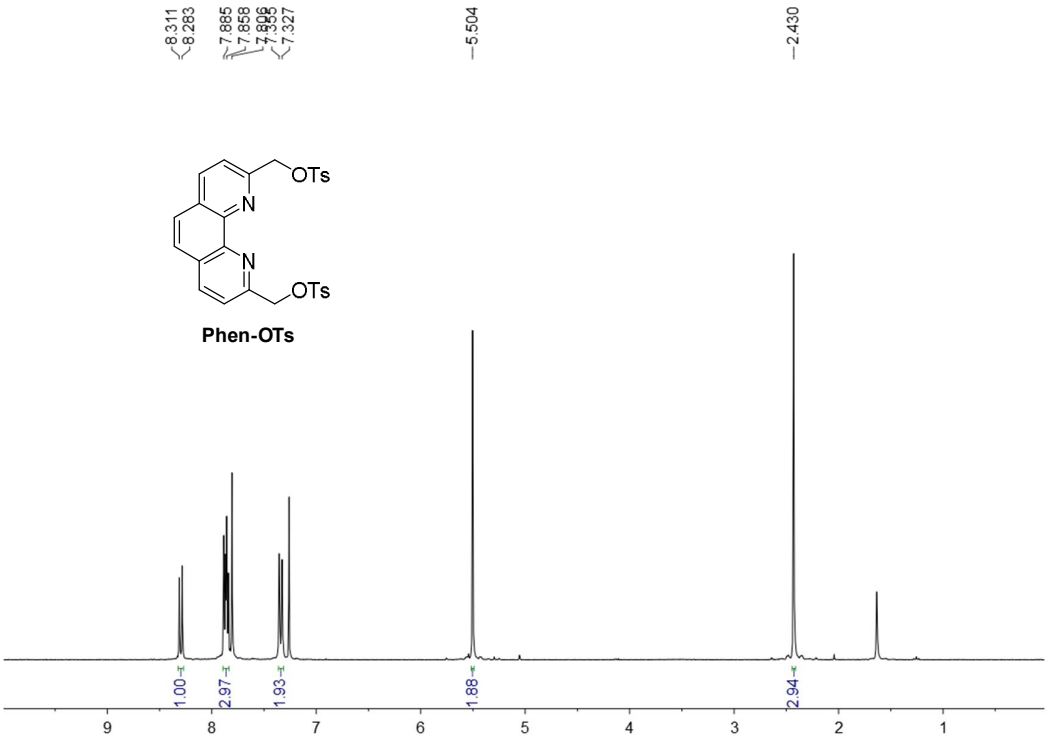


Fig. S6. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of **Phen-OTs**.

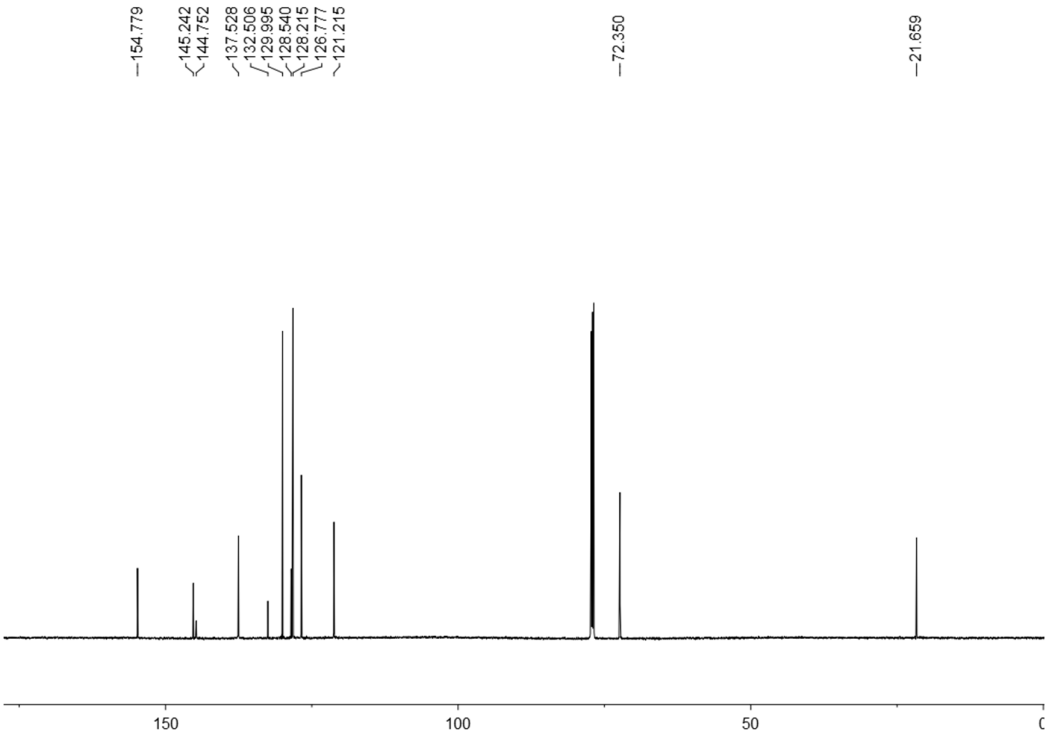


Fig. S7. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) of **Phen-OTs**.

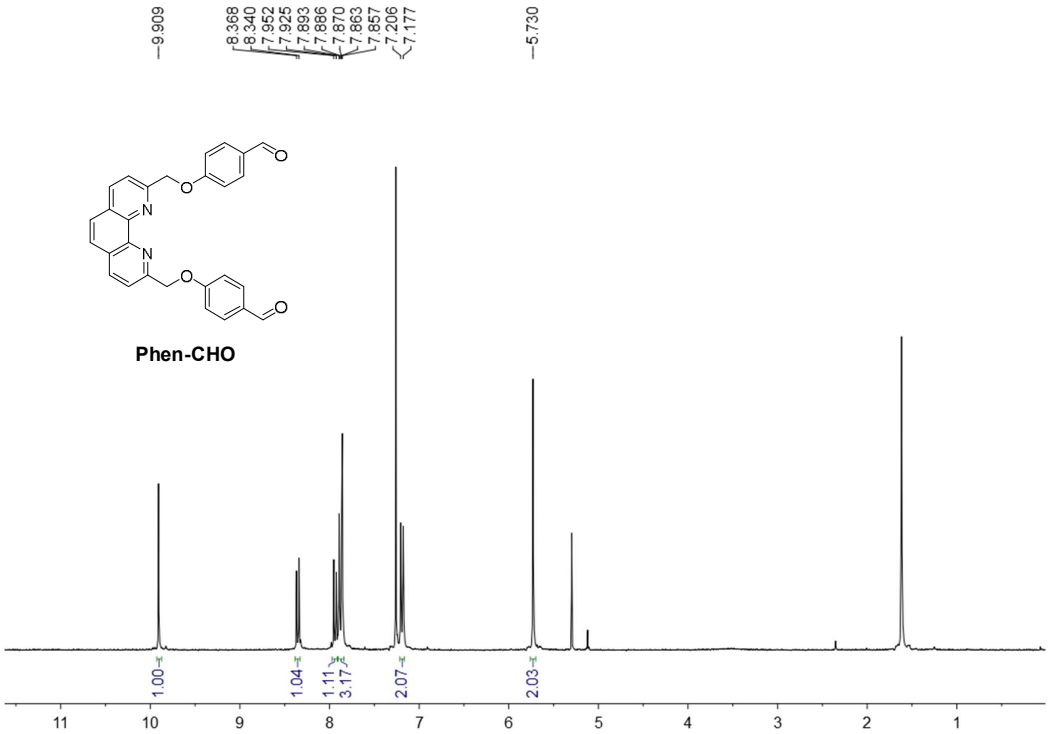


Fig. S8. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of **Phen-CHO**.

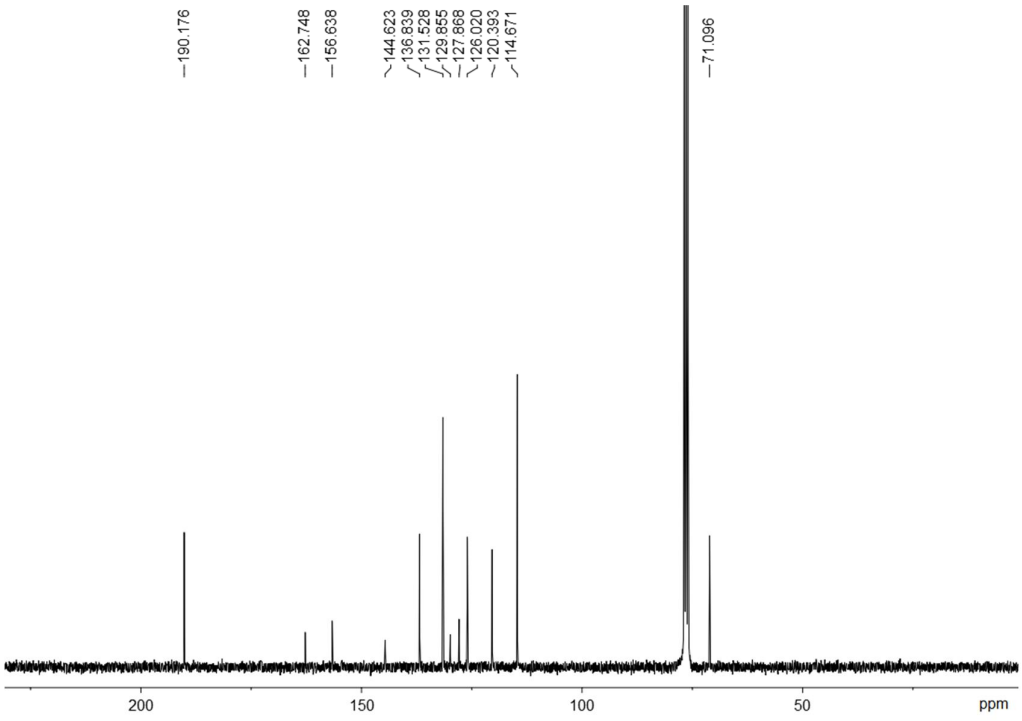


Fig. S9. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) of **Phen-CHO**.

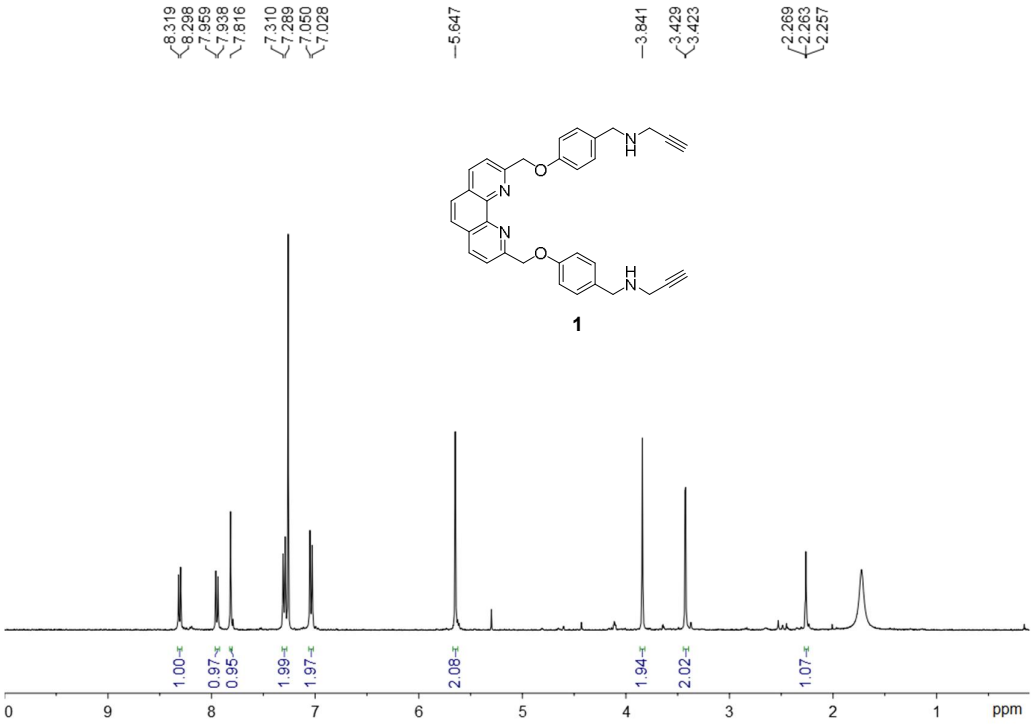


Fig. S10. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of **1**.

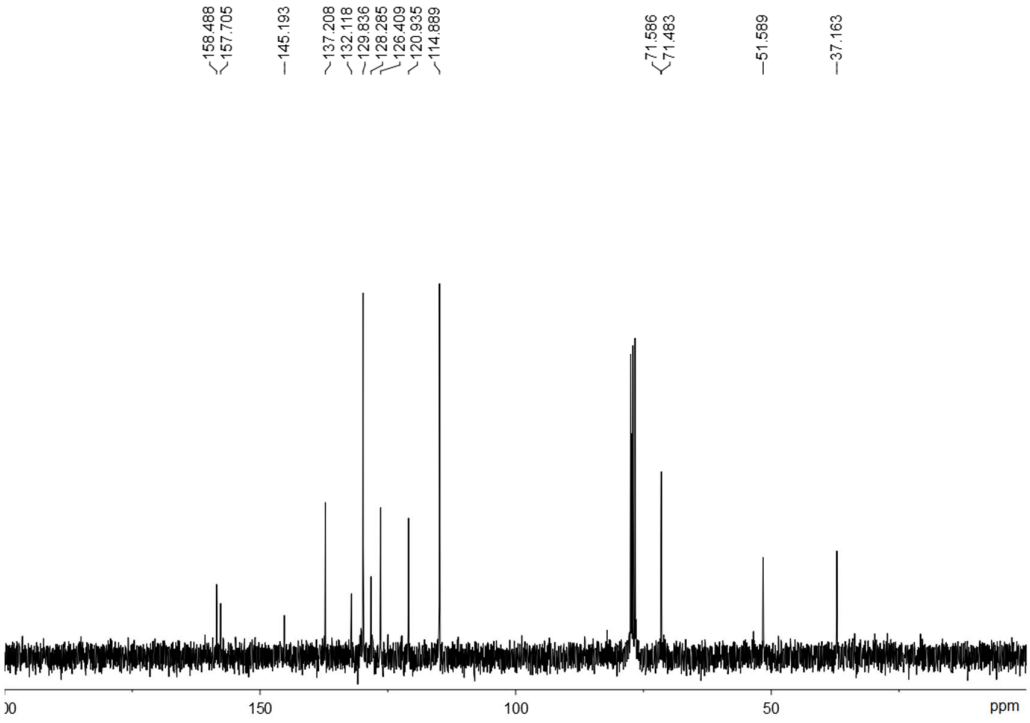


Fig. S11. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) of **1**.

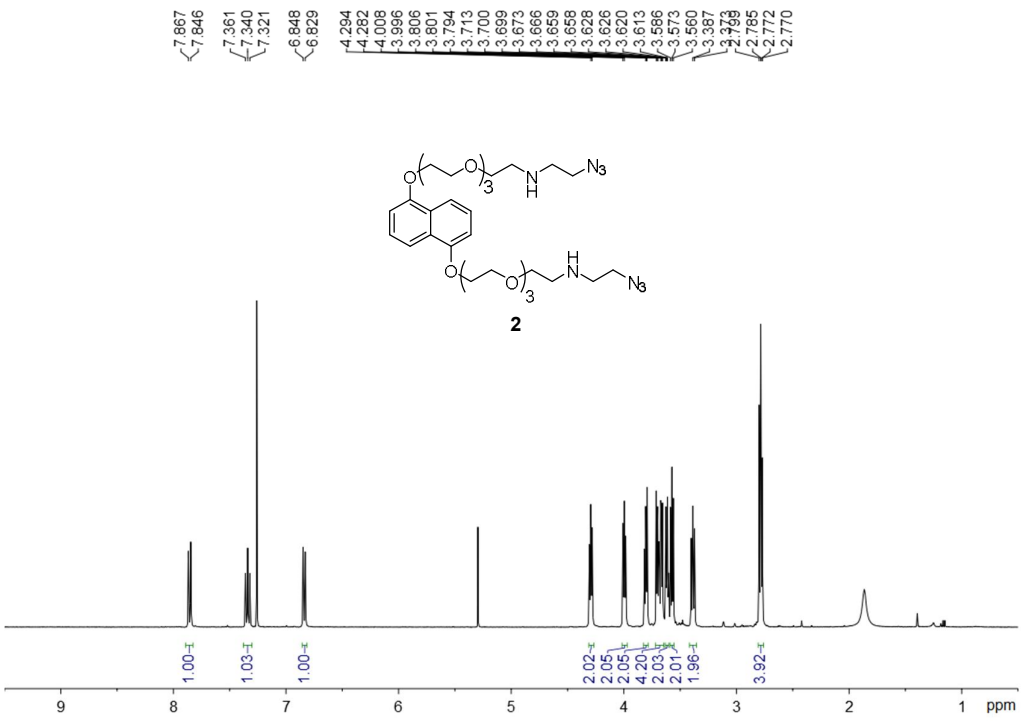


Fig. S12. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of **2**.

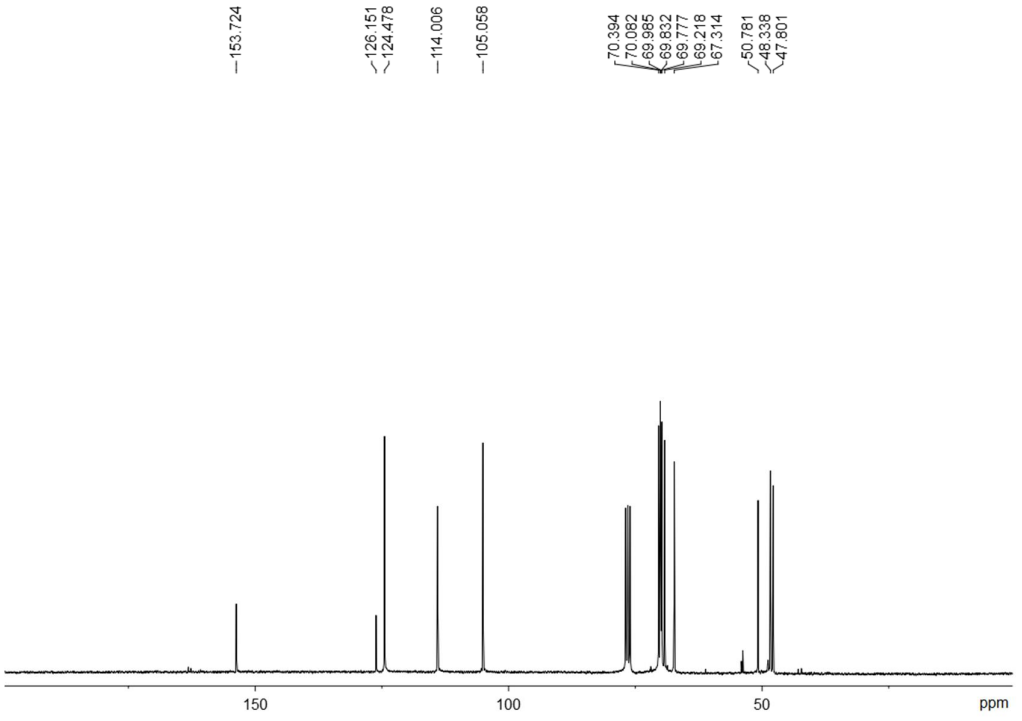
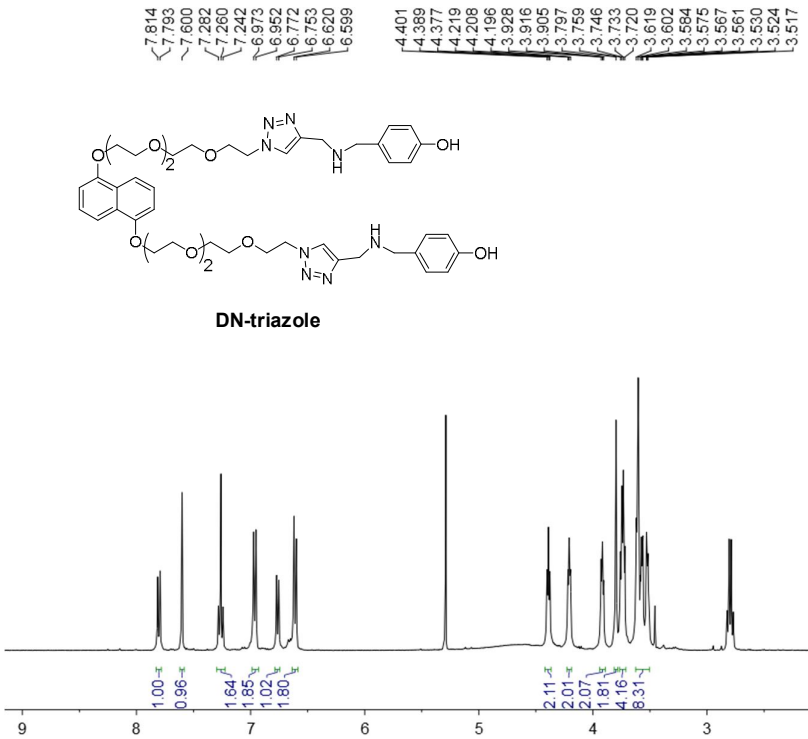


Fig. S13. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) of **2**.



DN-triazole

Fig. S14. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of **DN-triazole**.

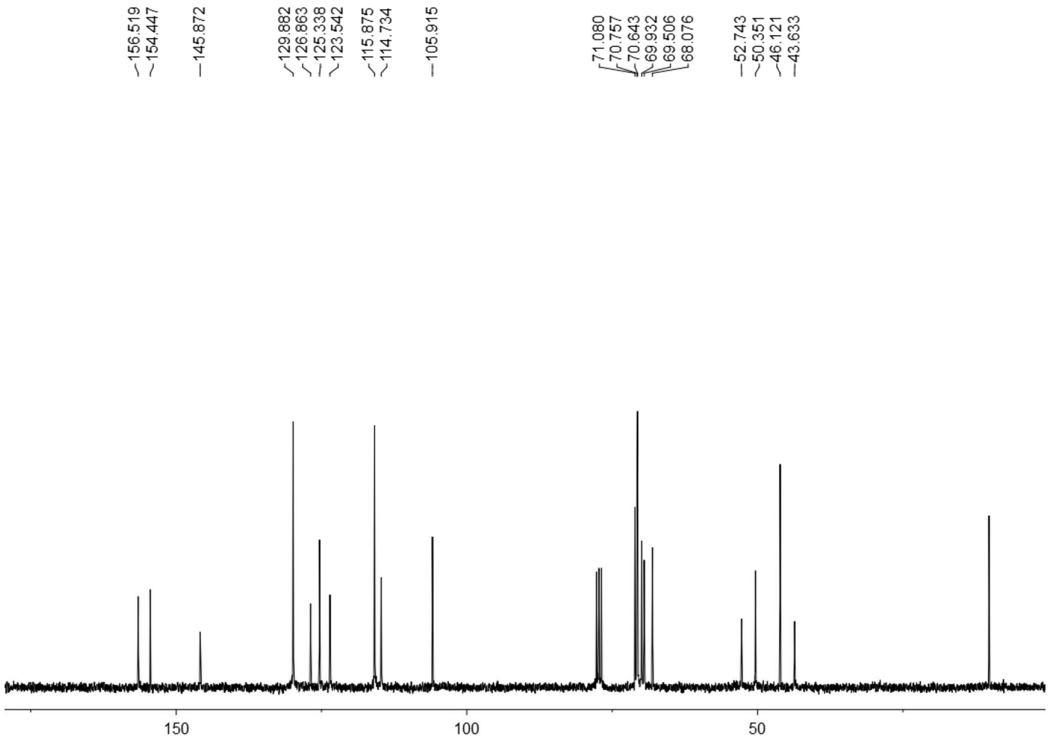


Fig. S15. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) of **DN-triazole**.

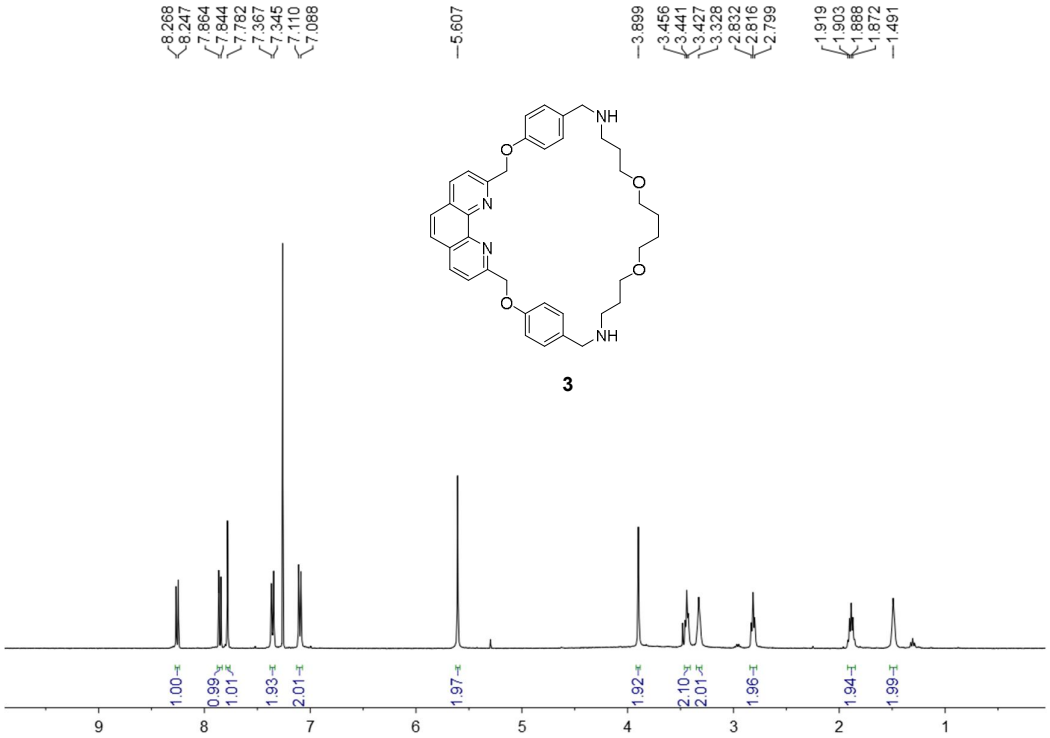


Fig. S16. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of **3**.

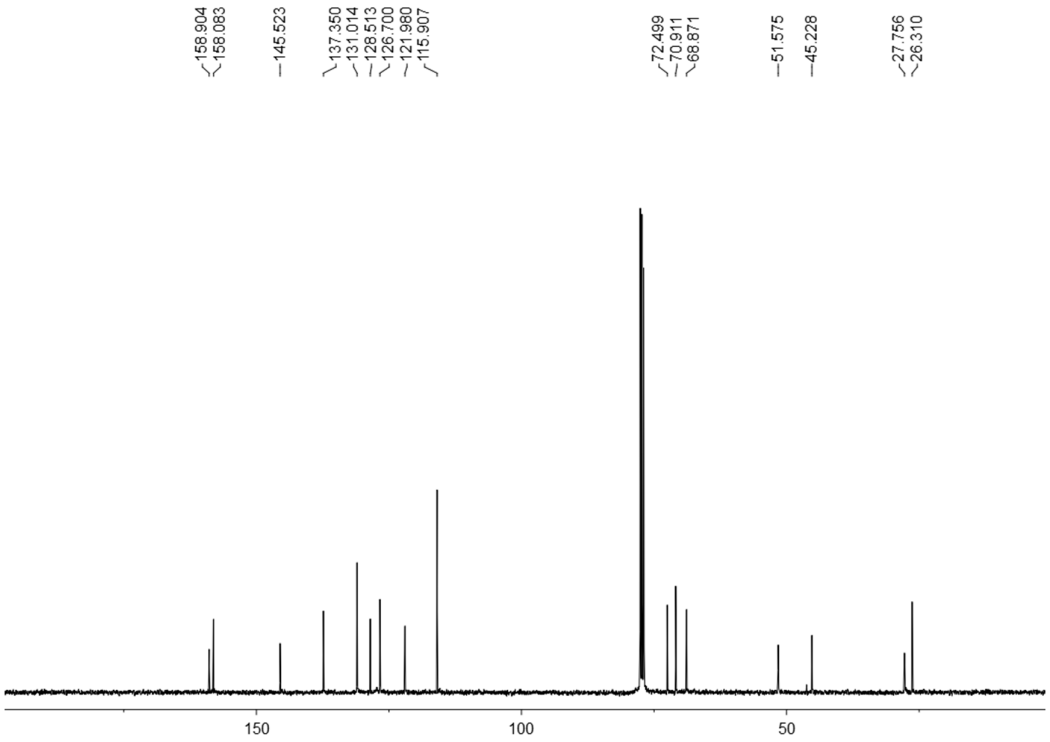


Fig. S17. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) of **3**.

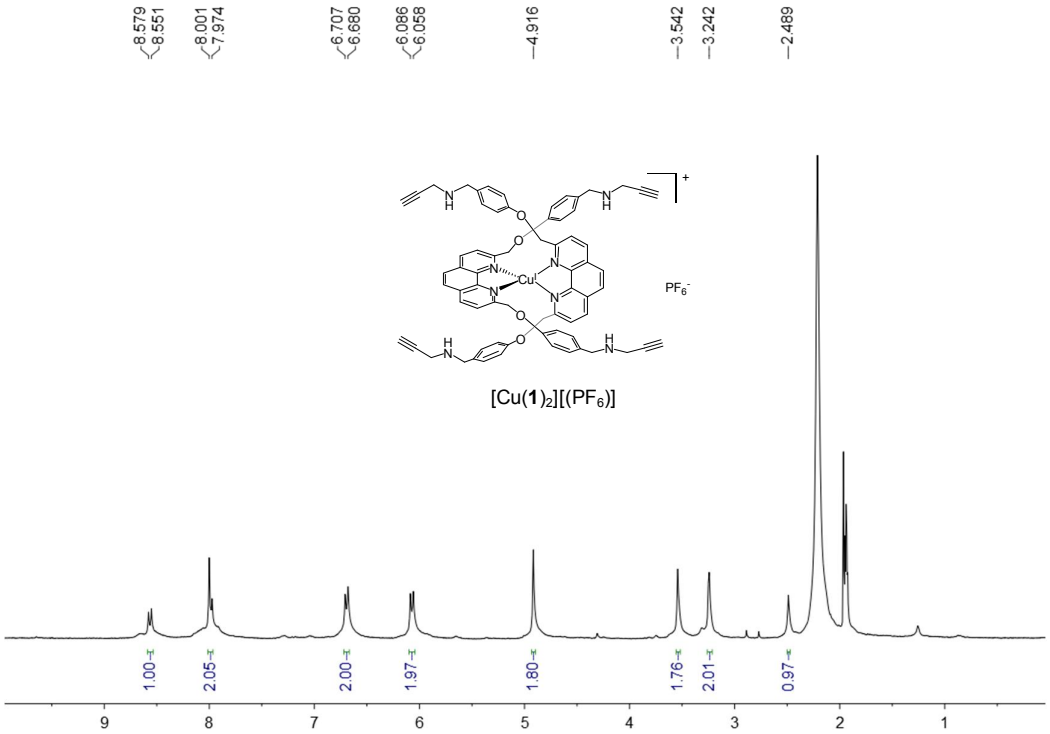


Fig. S18. ^{1}H NMR (400 MHz, CD_3CN, 298 K) of $[Cu(\mathbf{1})_2][(PF_6)]$.

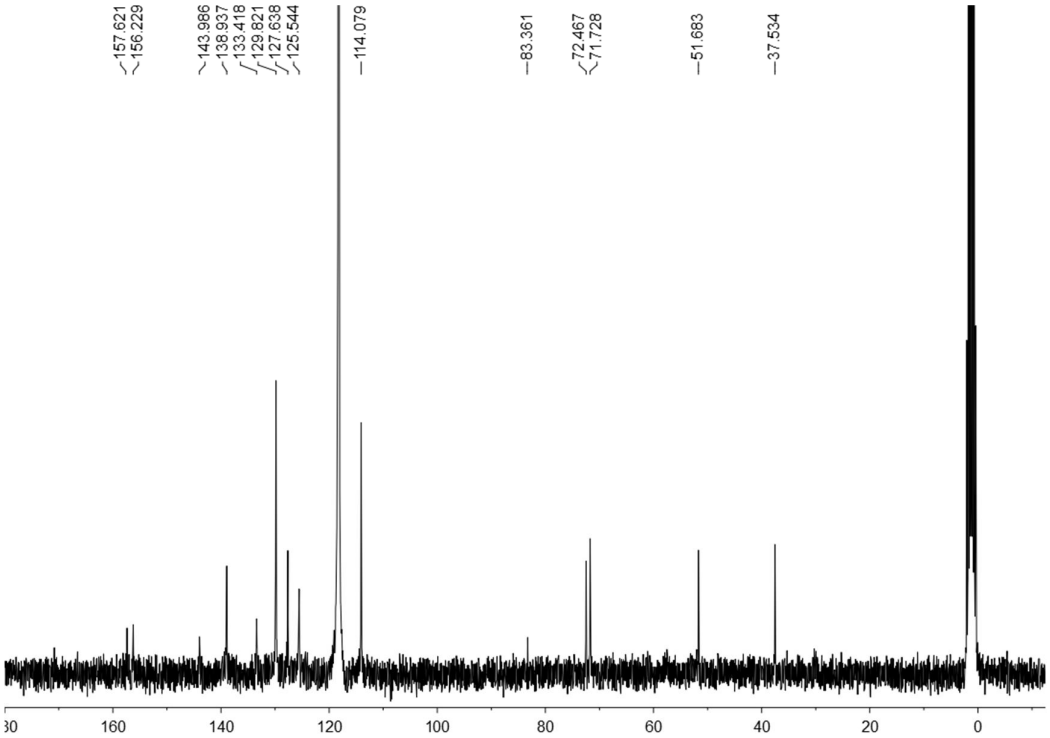


Fig. S19. $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_3CN, 298 K) of $[Cu(\mathbf{1})_2][(PF_6)]$.

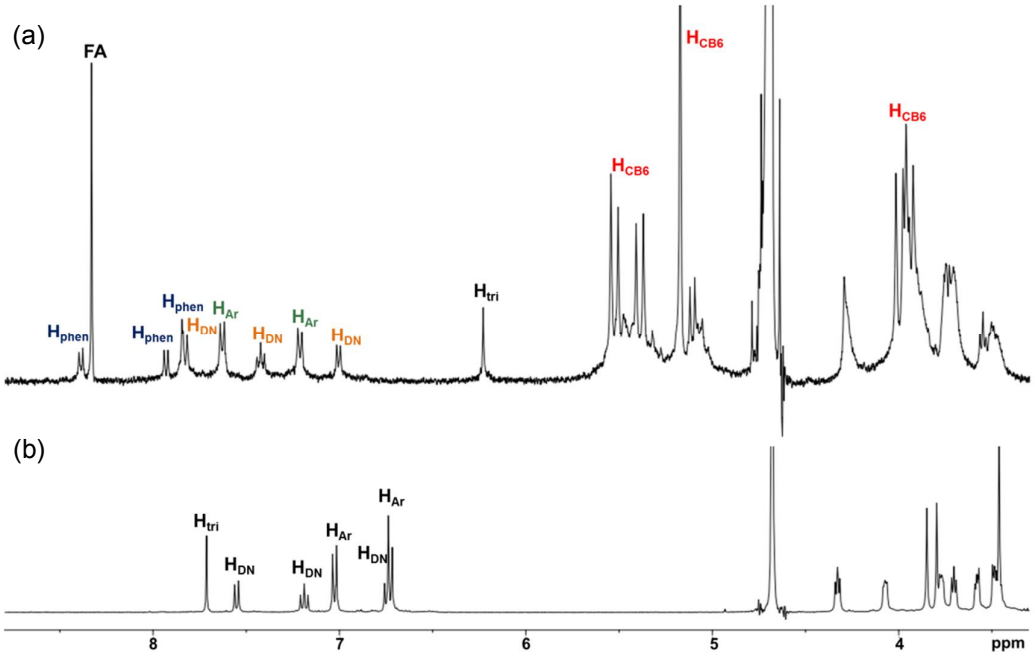


Fig. S20. Comparison of the ^{1}H NMR (400 MHz, D_2O, 298 K) of (a) **C3** (residual formic acid/formate (FA) is from preparative HPLC) and (b) **DN-triazole**. The triazole proton showed a significant upfield shift from 7. ppm of **DN-triazole** to 6. ppm of **C3** due to the inclusion of the triazole unit inside CB[6].

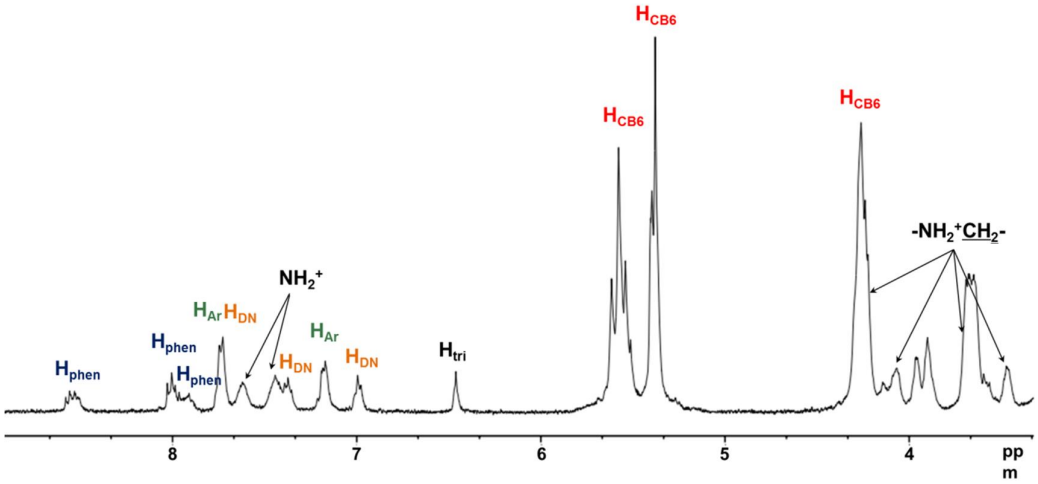


Fig. S21. ^{1}H NMR (400 MHz, DMSO-d_6, 353 K) of the PF_6^- salt of **C3**.

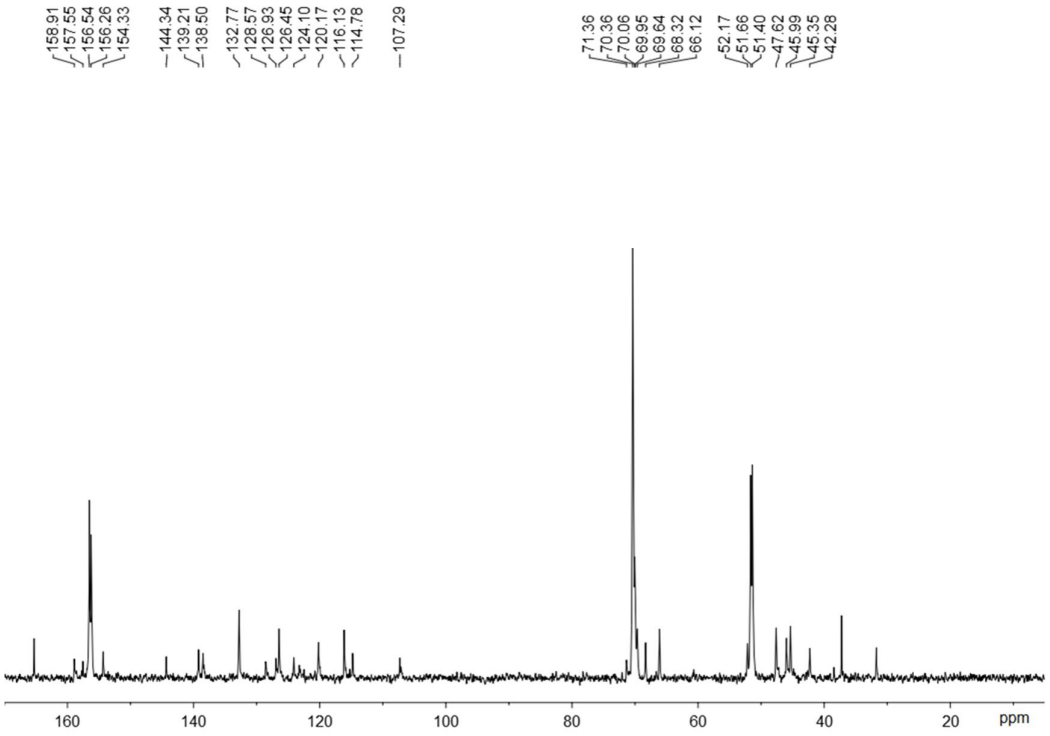


Fig. S22. $^{13}C\{^{1}H\}$ NMR (100 MHz, D_2O, 298 K) of **C3**.

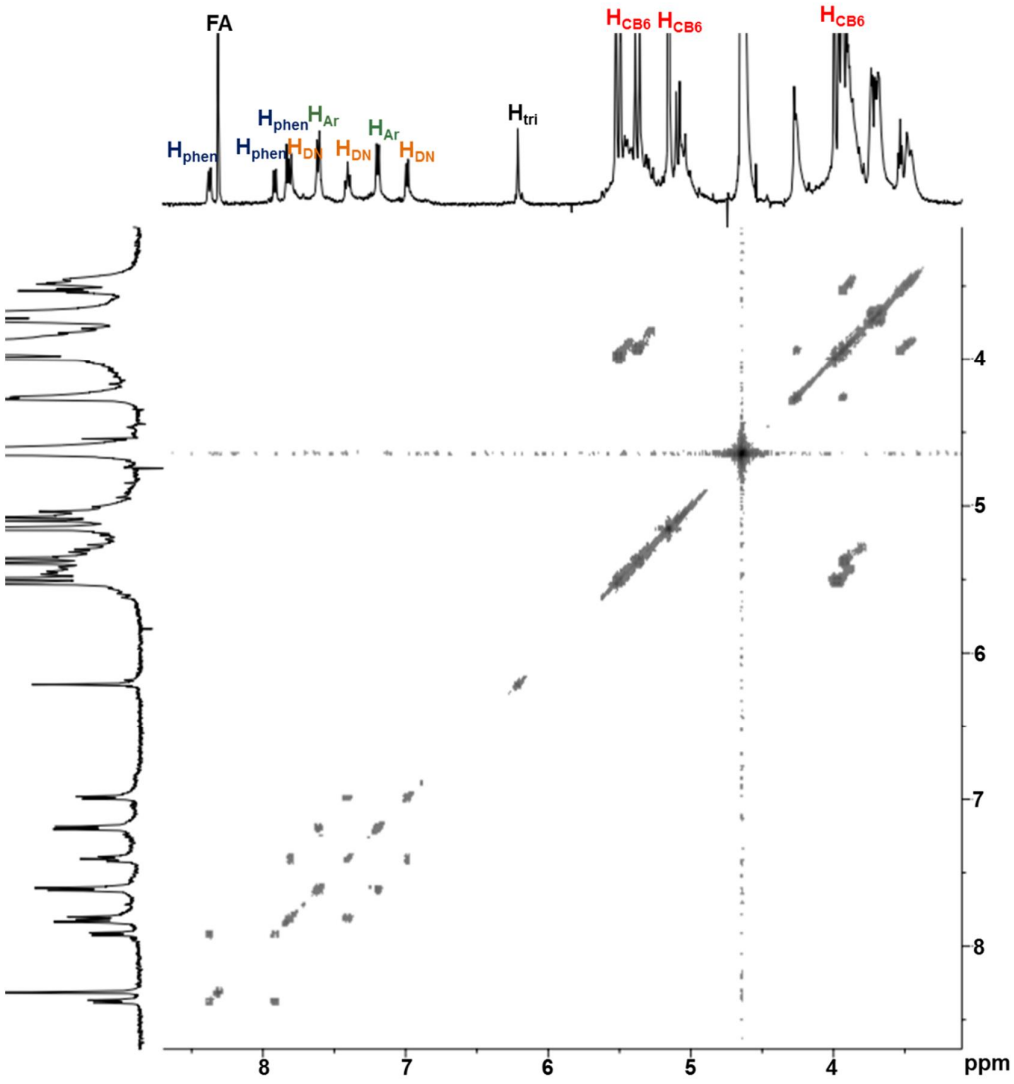


Fig. S23. ^{1}H-^{1}H COSY (500 MHz, D_2O, 298 K) of **C3**.

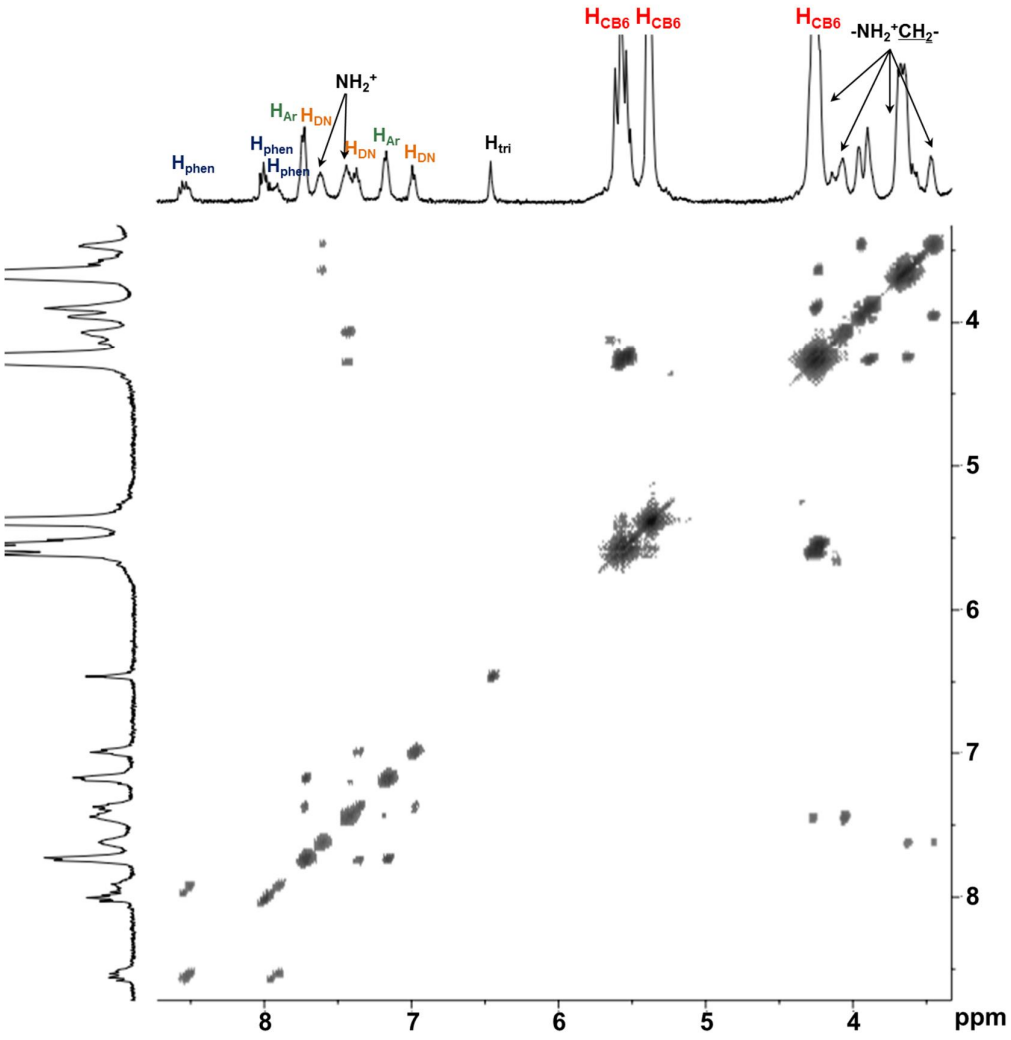


Fig. S24. ^{1}H-^{1}H COSY (500 MHz, DMSO-d_6, 353 K) of the PF_6^- salt of **C3**.

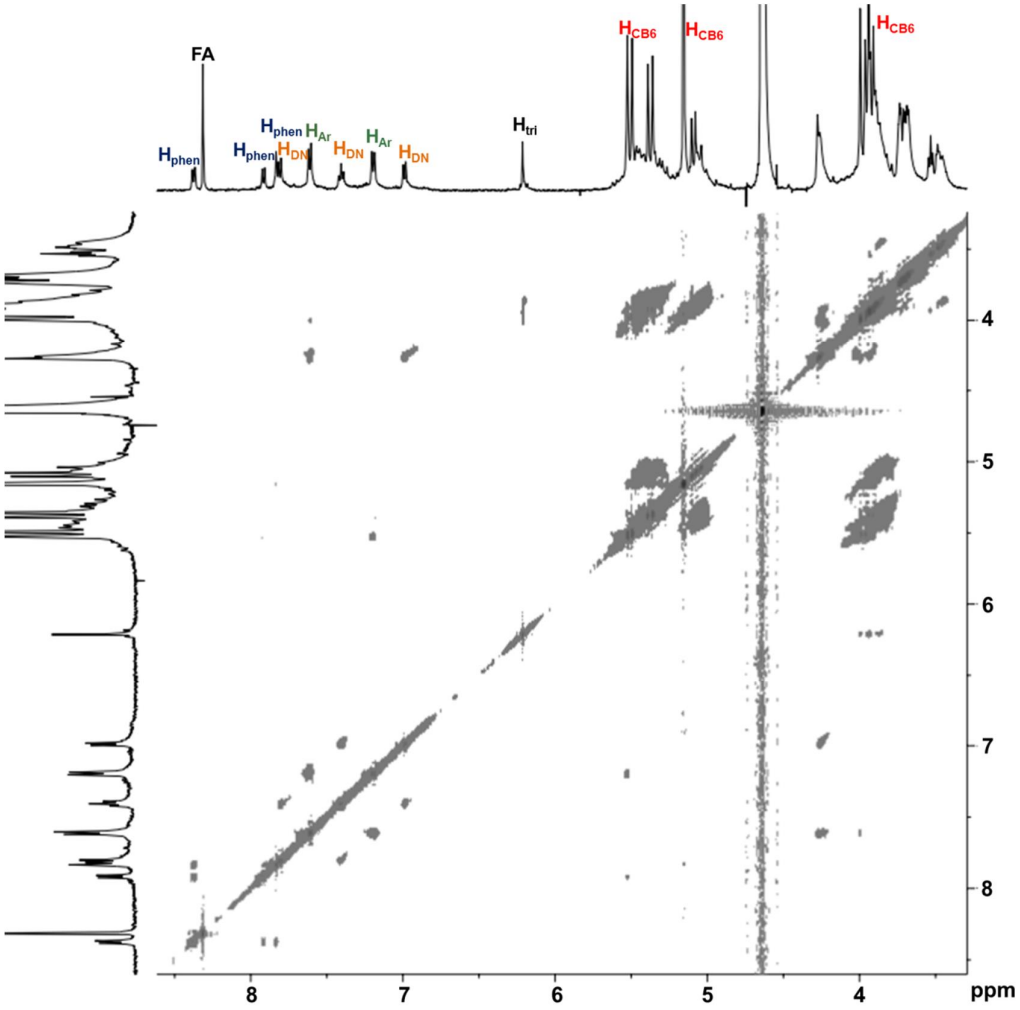


Fig. S25. 2D NOESY (500 MHz, D_2O, 298 K) of **C3**.

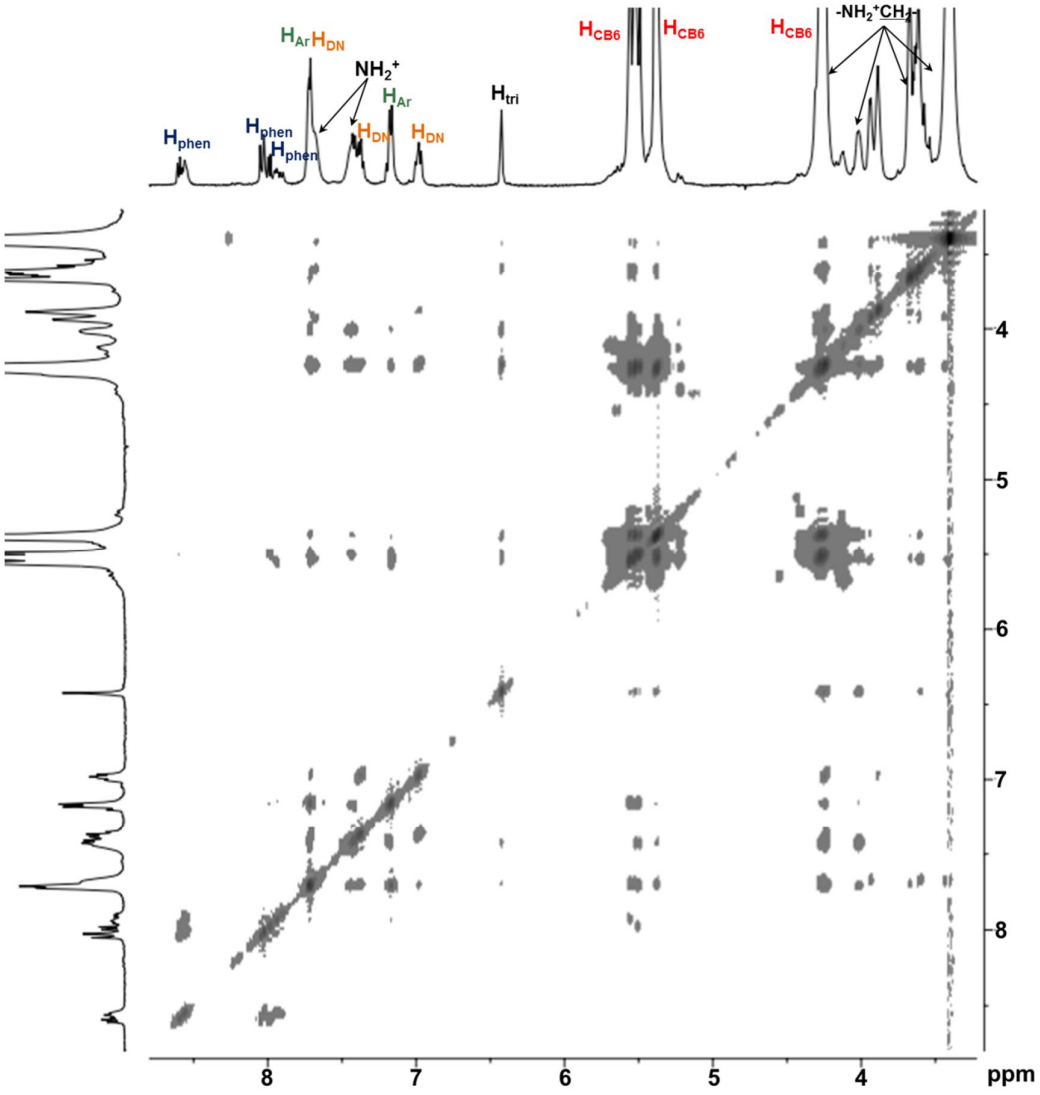


Fig. S26. 2D NOESY (500 MHz, DMSO-d_6, 298 K) of the PF_6^- salt of **C3**.

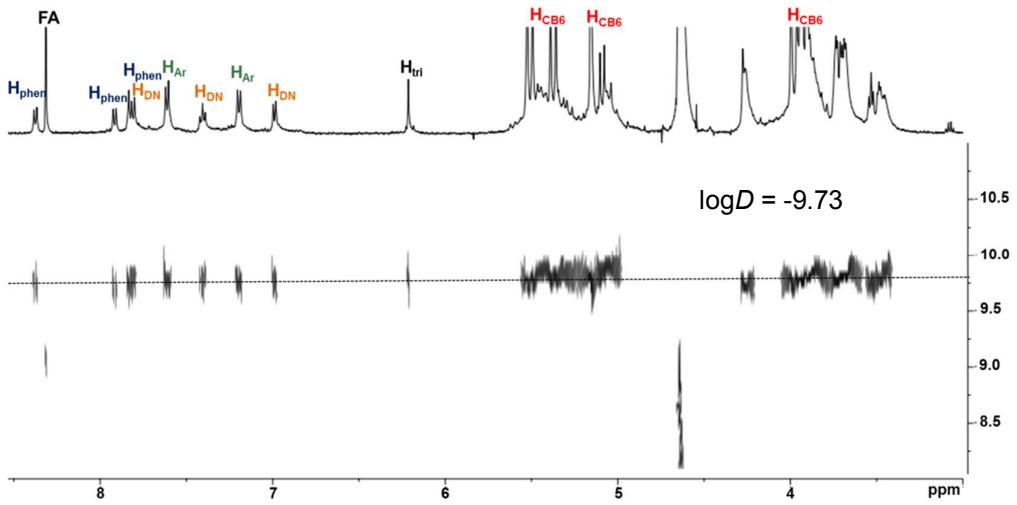


Fig. S27. DOSY (500 MHz, D_2O, 298 K) of **C3**.

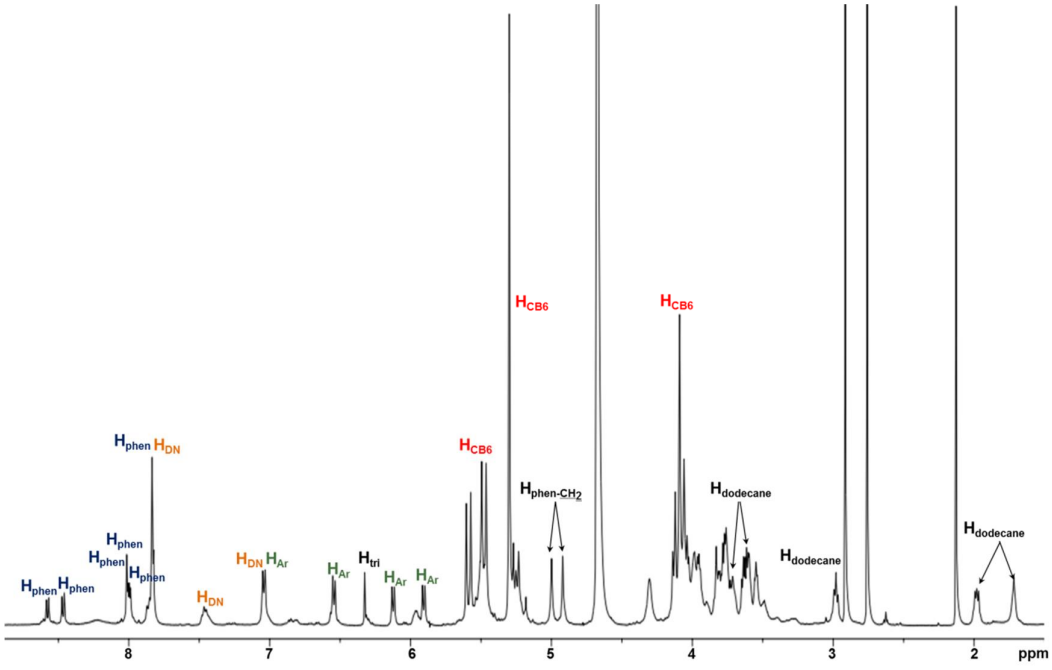


Fig. S28. ^{1}H NMR (400 MHz, D_2O, 298 K) of **C4**.

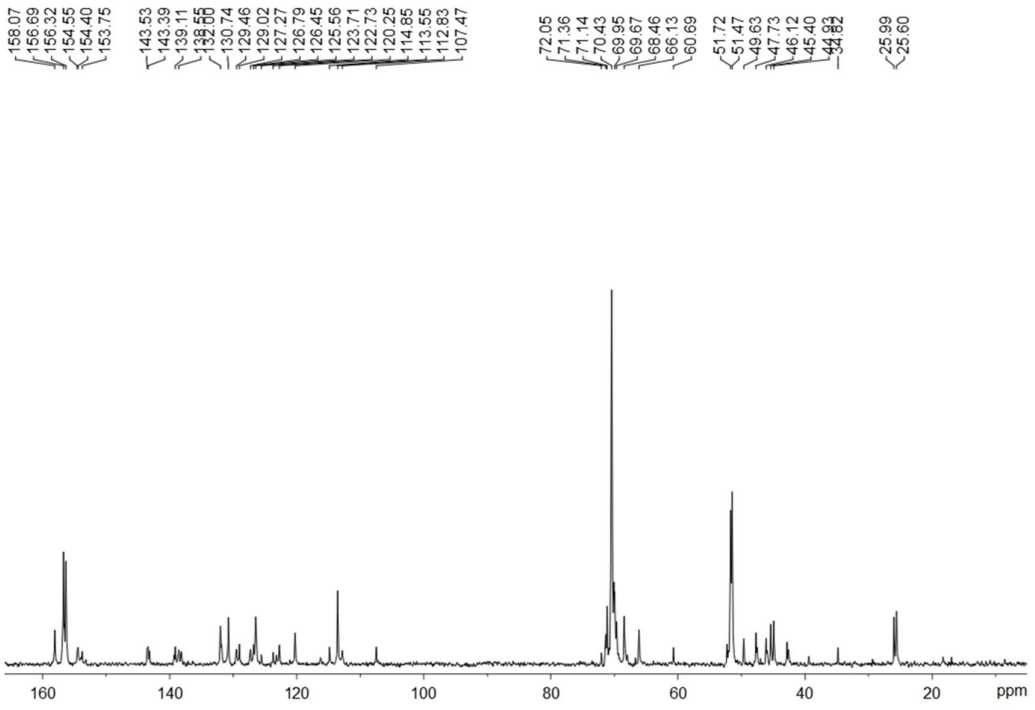


Fig. S29. $^{13}C\{^{1}H\}$ NMR (100 MHz, D_2O, 298 K) of **C4**.

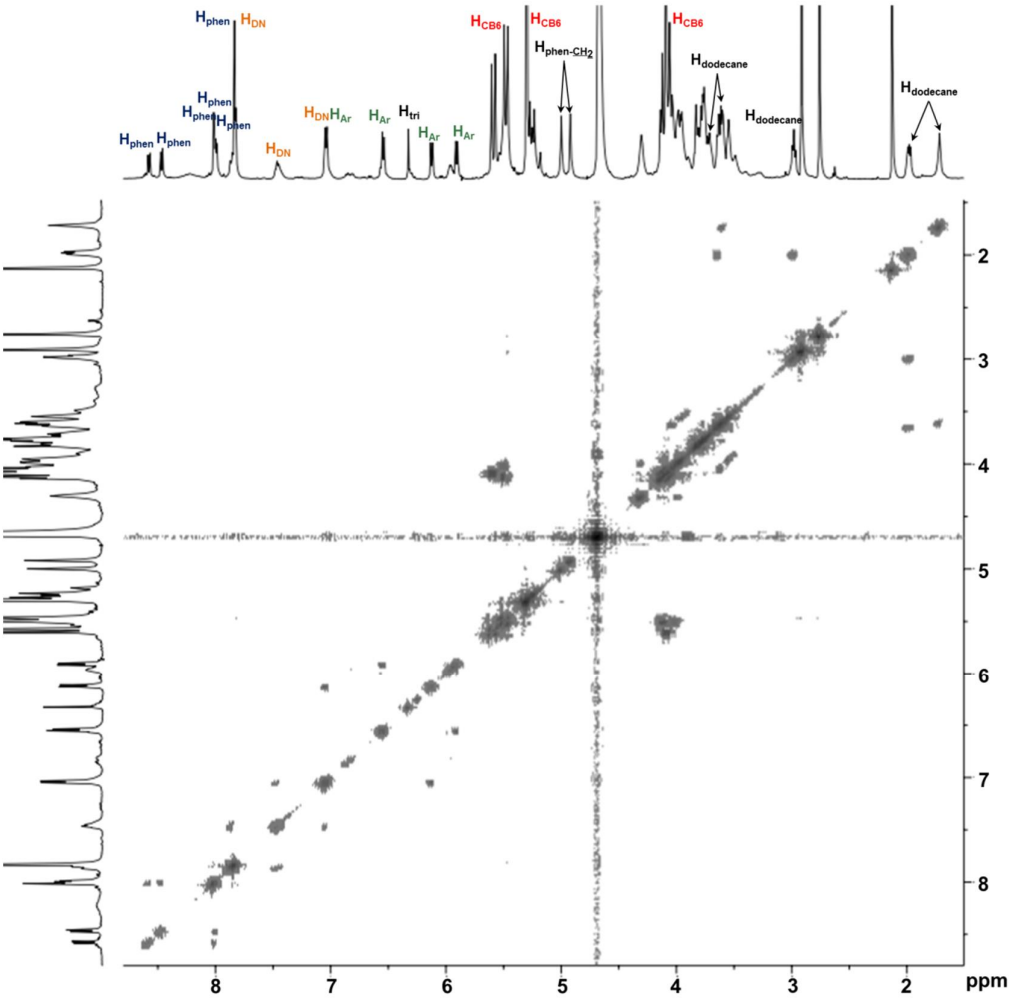


Fig. S30. ^{1}H-^{1}H COSY (500 MHz, D_2O, 298 K) of **C4**.

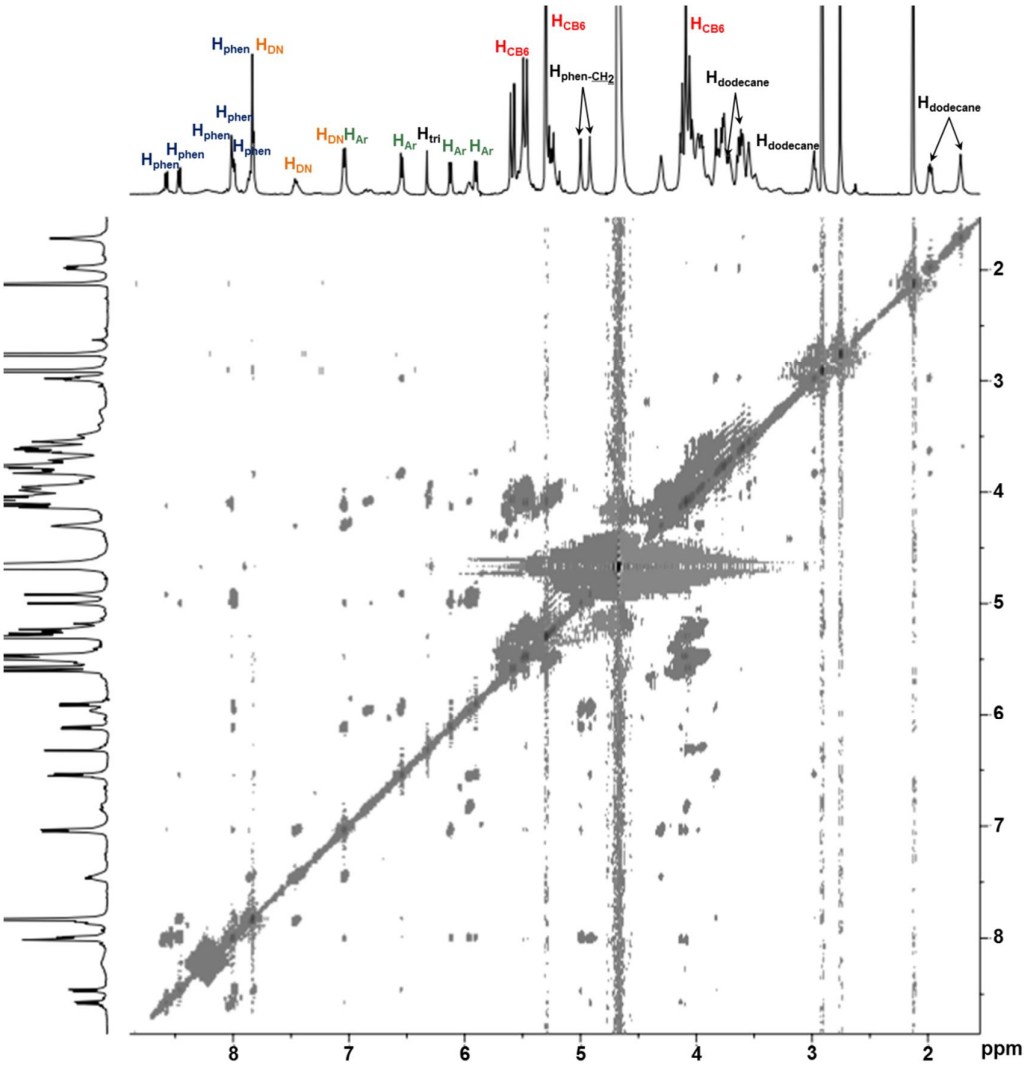


Fig. S31. 2D NOESY (500 MHz, D_2O, 298 K) of **C4**.

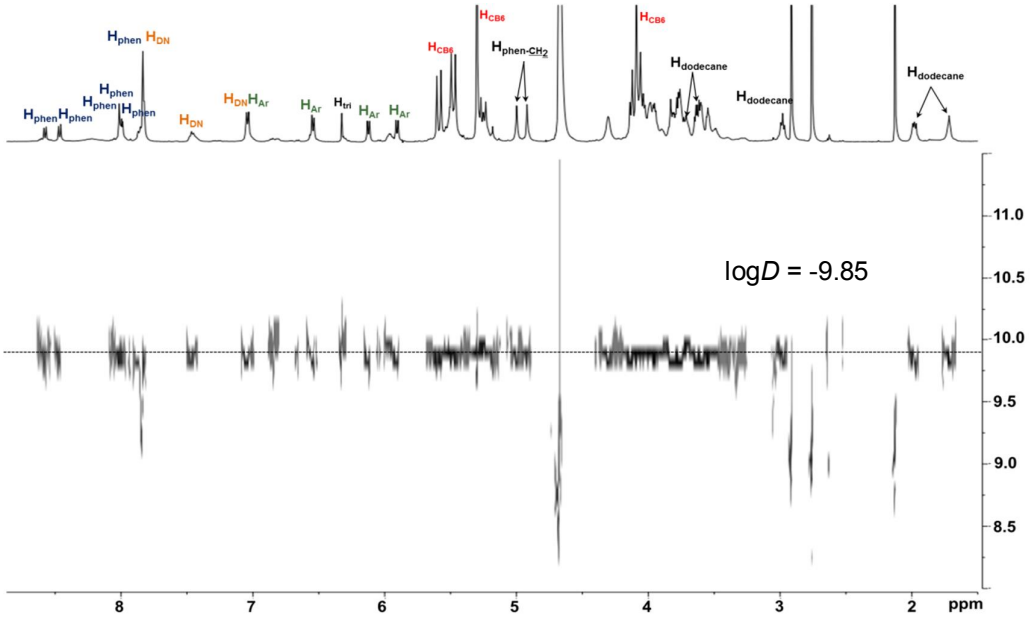


Fig. S32. DOSY (500 MHz, D_2O, 298 K) of **C4**.

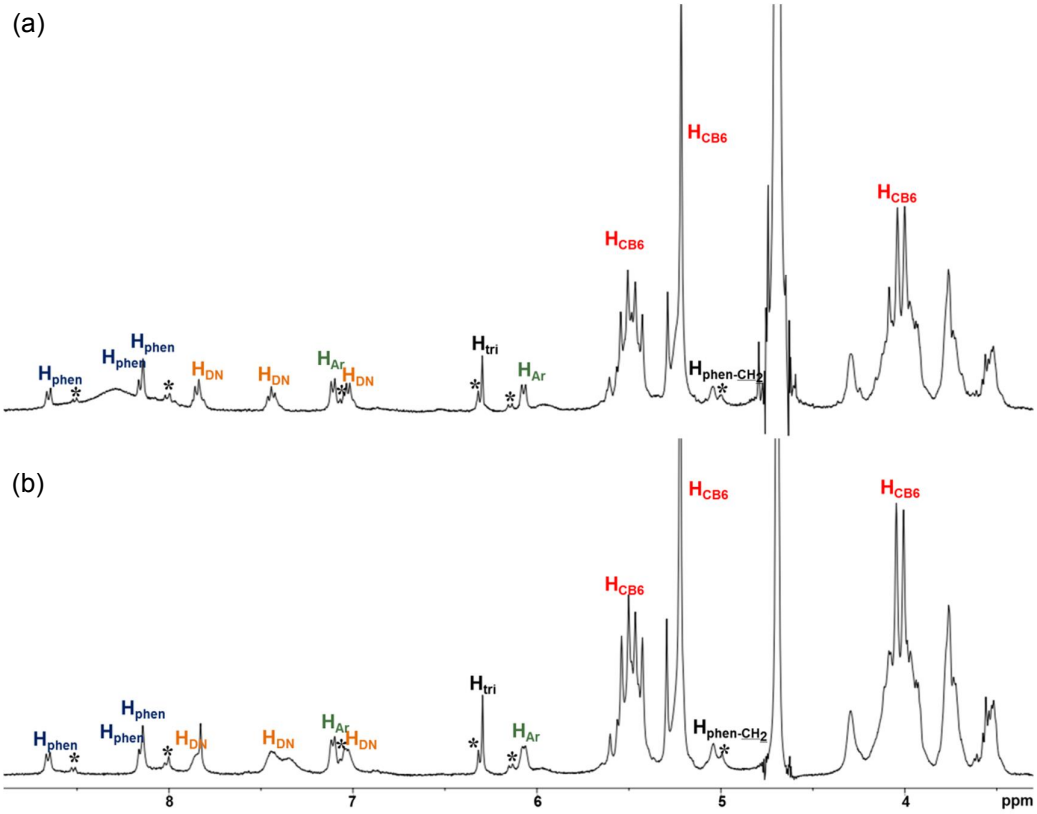


Fig. S33. (a) ^{1}H NMR (400 MHz, D_2O, 298 K) of **C6**. Resonances from copper-free **C6** are labeled with *. The broad peak at 8.3 ppm in (a) is presumably due to the formate residue from preparative HPLC that is in exchange between the multiple ammonium sites of **C6**. Another sample of **C6** obtained from another round of preparative HPLC gave a ^{1}H spectrum without this broad but all other resonances.

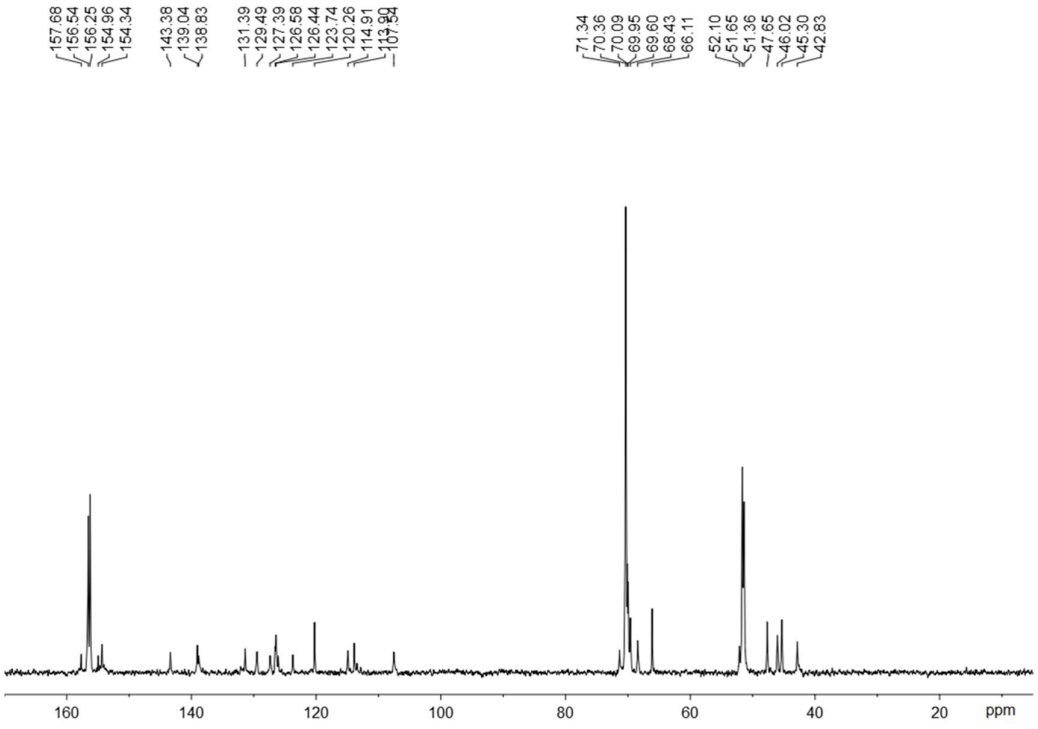


Fig. S34. $^{13}C\{^{1}H\}$ NMR (100 MHz, D_2O, 298 K) of **C6**.

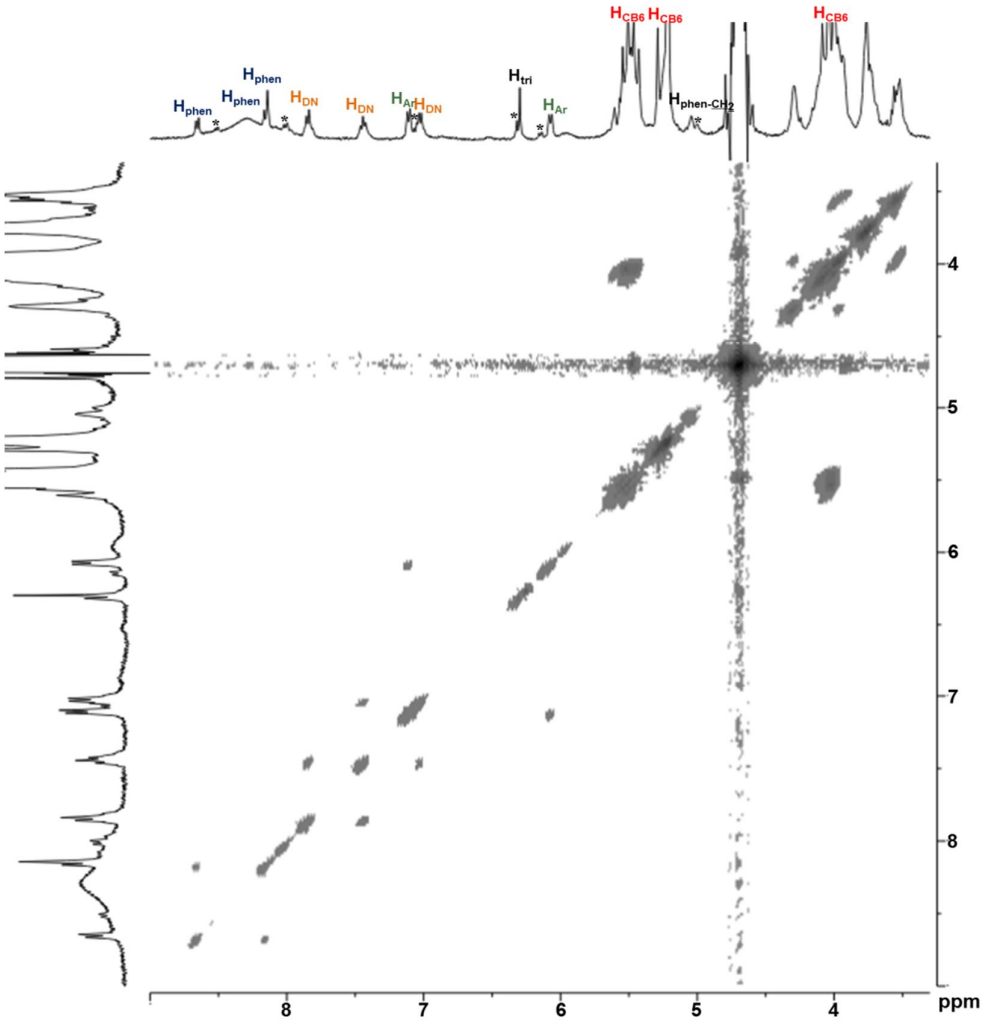


Fig. S35. ^{1}H-^{1}H COSY (500 MHz, D_2O, 298 K) of **C6**.

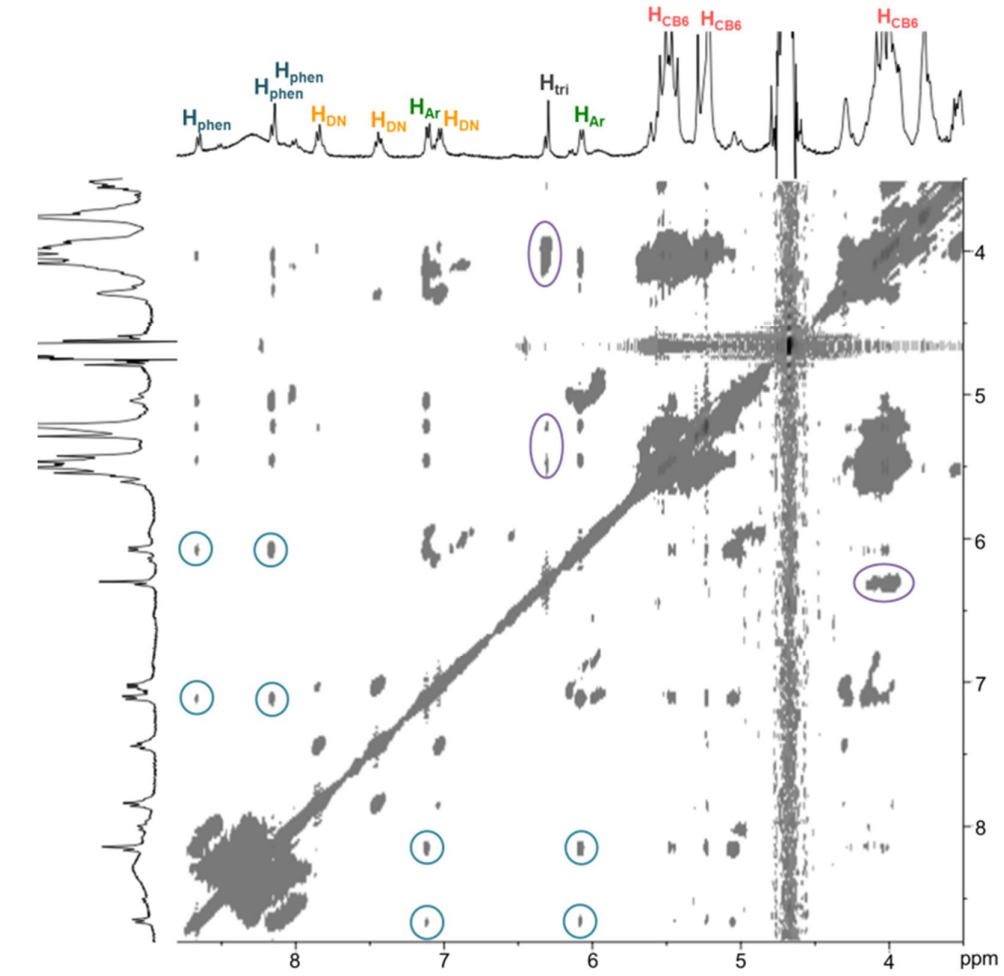


Fig. S36. Partial NOESY (500 MHz, D_2O, 298 K) of **C6**. Highlighted cross peaks indicated the close proximity between H_{phen} and H_{Ar}, and that between H_{tri} and CB[6].

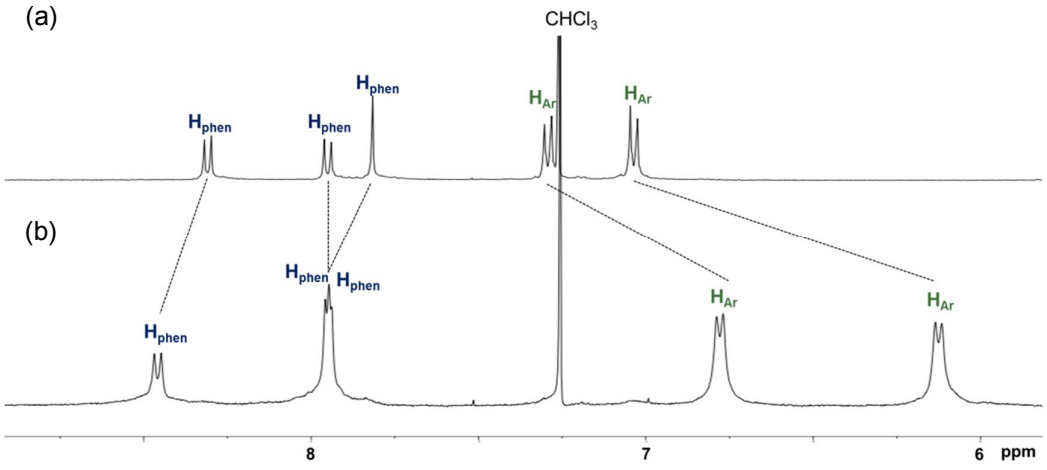


Fig. S37. Comparison of the partial ^1H NMR (400 MHz, $CDCl_3$, 298 K) of (a) **1** and (b) $[Cu(\mathbf{1})_2][(PF_6)]$.

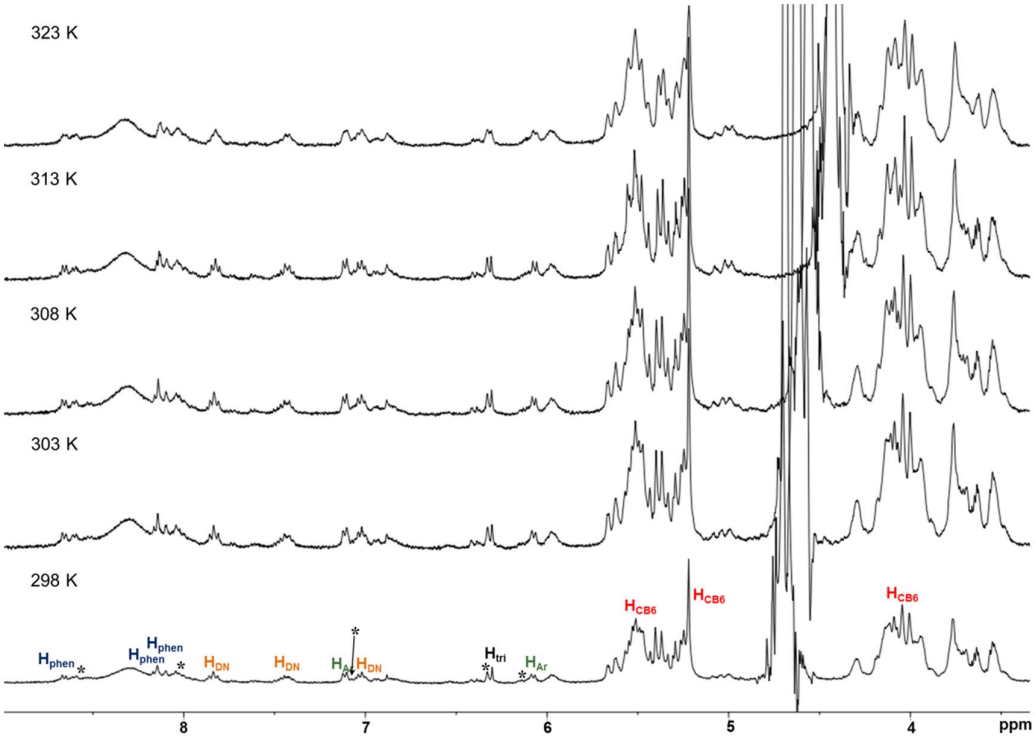


Fig. S38. ^{1}H NMR (400 MHz, D_2O) of **C6** obtained at 298-323 K. No significant spectral change was observed, indicating that **C6** is adopting a similar overall structure over the studied temperature range.

4. ESI-MS

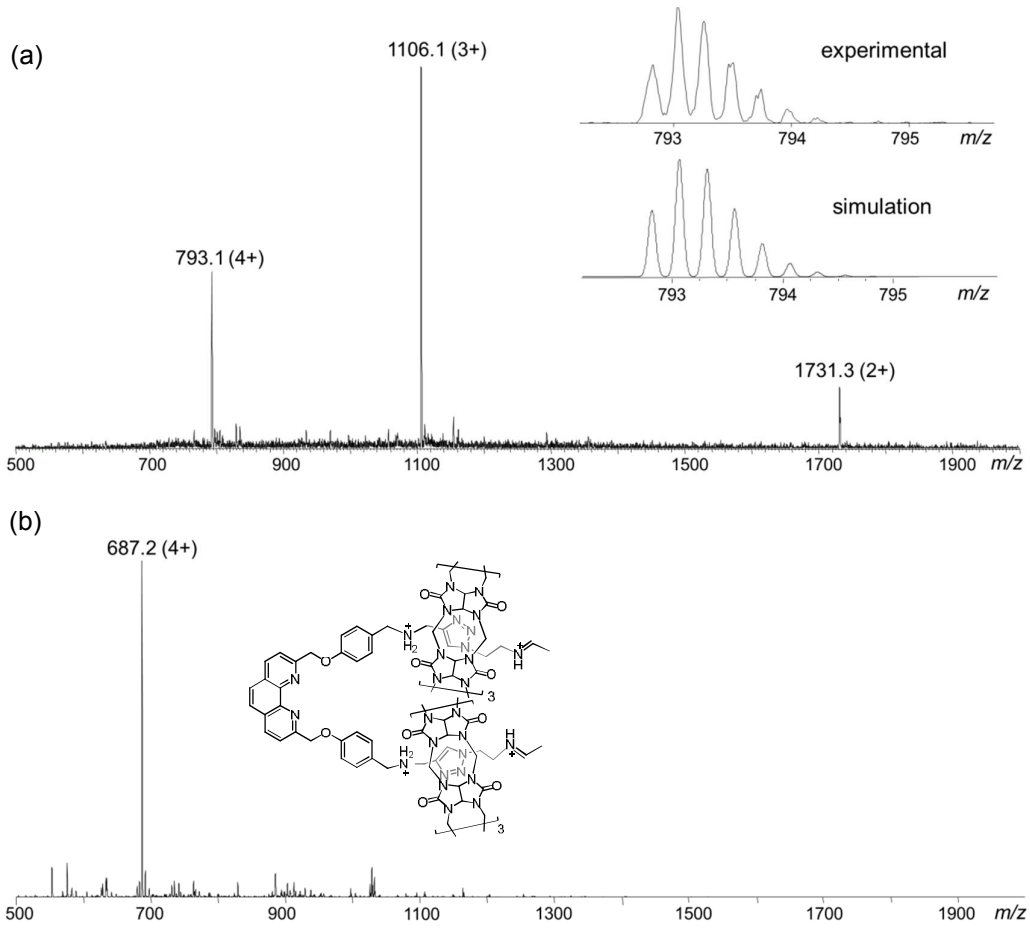


Fig. S39. ESI-MS analysis of **C3**. (a) MS spectrum of **C3**, expanded view of the peak at *m/z* = 793.1 is shown in the inset; (b) MS^2 spectrum of **C3** obtained from the fragmentation of peak at *m/z* = 793.1.

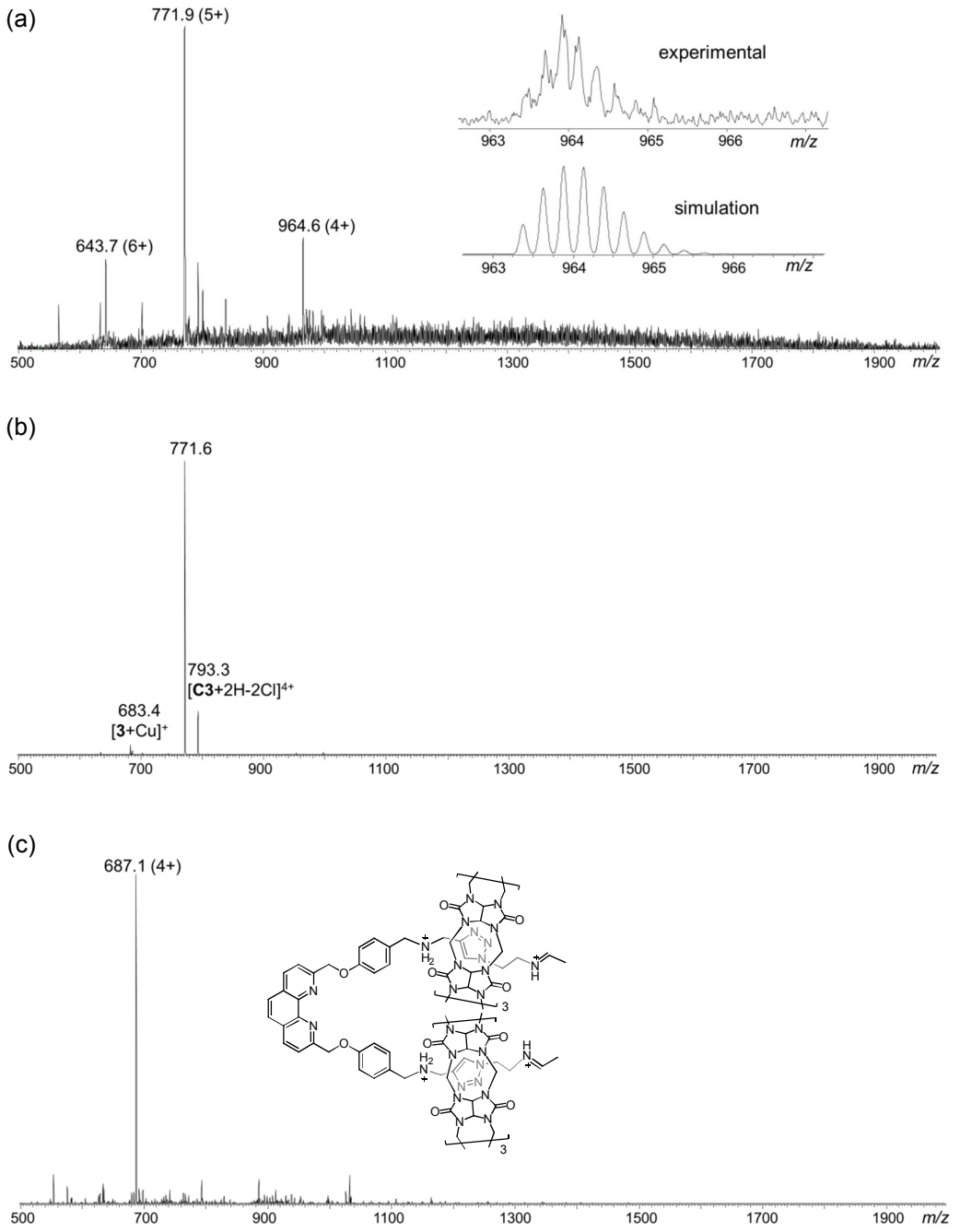


Fig. S40. ESI-MS analysis of **C4**. (a) MS spectrum of **C4**, expanded view of the peak at *m/z* = 964.6 is shown in the inset; (b) MS^2 spectrum of **C4** obtained from the fragmentation of peak at *m/z* = 771.9; (c) MS^3 spectrum of **C4** obtained from the fragmentation of peak at *m/z* = 793.3 in MS^2 spectrum.

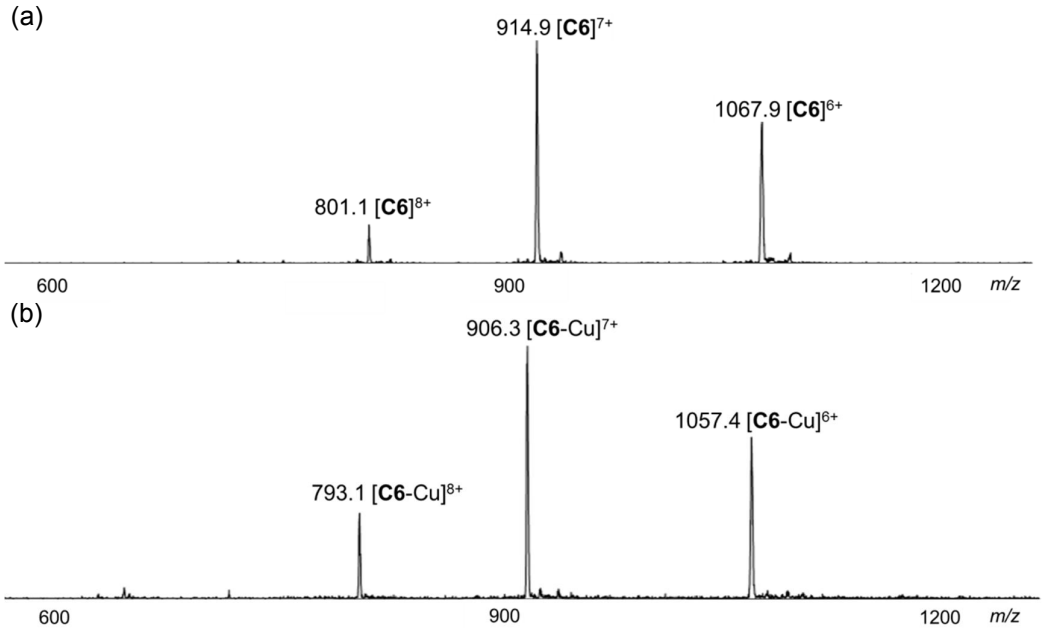
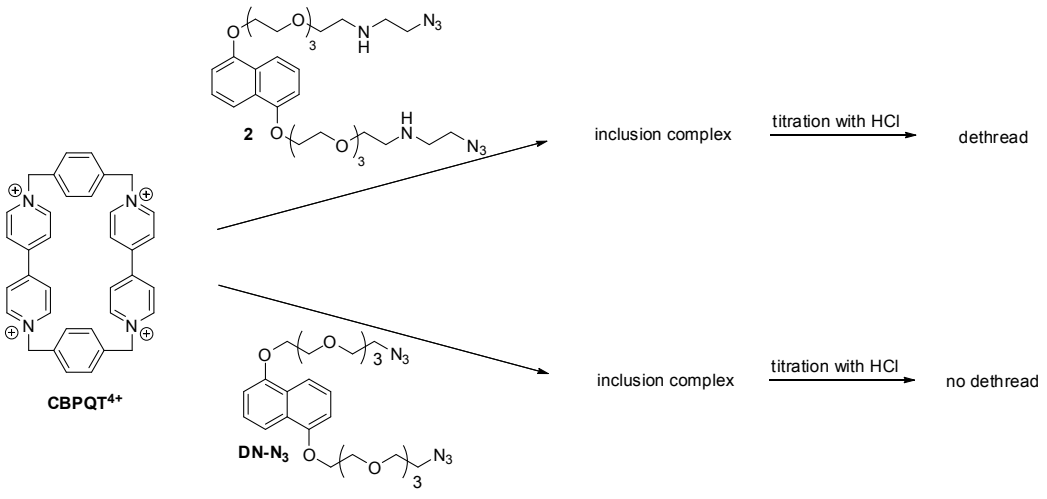


Fig. S41. ESI-MS spectra of (a) Cu^{+}-complexed **C6** and (b) copper-free **C6**.

5. UV-Vis

To investigate the effect of acid on the formation of the charge transfer complex between $CBPQT^{4+}$ and **2**, the inclusion complex [**2**⊂$CBPQT^{4+}$] was synthesised by mixing an equimolar amount of **2** and $CBPQT^{4+}$ and titrated against aq. HCl. Upon addition of the acid, a decrease of the intensity of the charge transfer band at 530 nm and a concomitant decolouration of the deep violet colour of the donor-acceptor complex was observed (Fig. S41a). On the other hand, no significant decrease in the intensity of the charge transfer band was observed when the titration was repeated with the control compound **DN-N_3** that lacks the secondary amine (Fig. S41b). These observations are consistent with the proposed protonation of **2** under the acidic reaction condition that dethreads the $CBPQT^{4+}$ due to Columbic repulsion.



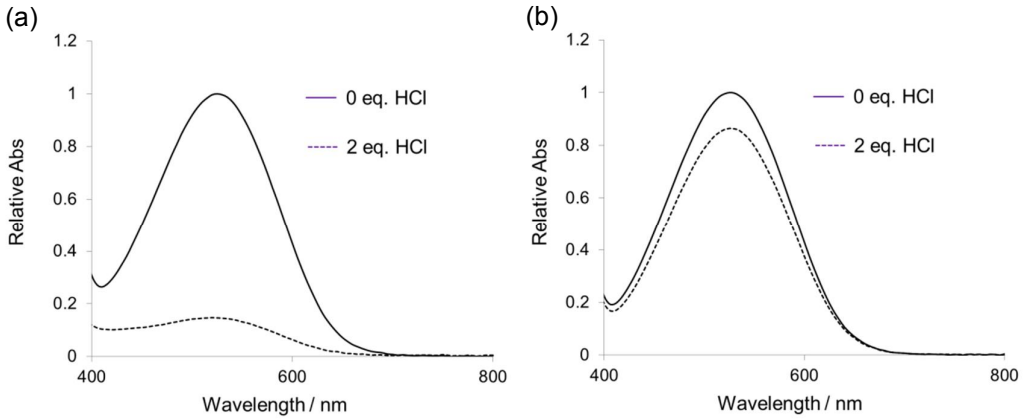


Fig. S42. UV-Vis absorption spectra of the inclusion complex (a) [**2**⊂$CBPQT^{4+}$] and (b) [**DN-N_3**⊂$CBPQT^{4+}$] in the presence and absence of 2 eq. of aq. HCl.

6. References

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