

Supporting information for

# Halogen bonding rotaxanes for nitrate recognition in aqueous media

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## S1. GENERAL CONSIDERATIONS

All solvents and reagents were purchased from commercial suppliers and used as received unless otherwise stated. Dry solvents were obtained by purging with nitrogen and then passing through an MBraun MPSP-800 column. H<sub>2</sub>O was de-ionized and micro filtered using a Milli-Q® Millipore machine. Column chromatography was carried out on Merck® silica gel 60 under a positive pressure of nitrogen. Routine NMR spectra were recorded on either a Varian Mercury 300, a Bruker AVIII 400 or a Bruker AVIII 500 spectrometer with <sup>1</sup>H NMR titrations recorded on a Bruker AVIII 500 spectrometer. TBA salts were stored in a vacuum desiccator containing phosphorus pentoxide prior to use. Where mixtures of solvents were used, ratios are reported by volume. Chemical shifts are quoted in parts per million relative to the residual solvent peak. Mass spectra were recorded on a Bruker μTOF spectrometer. Triethylamine was distilled from and stored over potassium hydroxide. Brine refers to a saturated aqueous solution of NaCl, NH<sub>4</sub>OH<sub>(aq.)</sub> refers to a 28–30% solution of NH<sub>3</sub> in water. Petrol refers to the fraction of petroleum ether boiling between 40 and 60 °C. Column chromatography was carried out on Merck® silica gel 60 under a positive pressure of nitrogen, preparative TLC was performed on 20 × 20 cm plates, with a silica layer of thickness 1 mm. Amberlite® was “loaded” by washing the resin with NaOH<sub>(aq.)</sub> (10%), water, and either NH<sub>4</sub>Cl<sub>(aq.)</sub> (1 M), NaOTf<sub>(aq.)</sub> (1 M) or NH<sub>4</sub>PF<sub>6(aq.)</sub> (0.1 M), followed by further water, and the solvent to be used in the anion exchange.

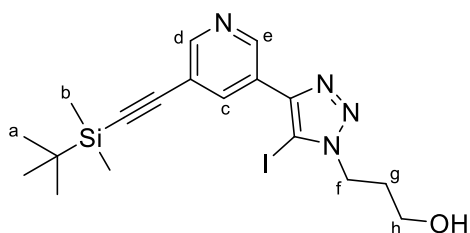
The following compounds were prepared according to literature procedures: hydroxypropyl-ethynyl bromopyridine **1**,<sup>S1</sup> asymmetrically protected diethynyl pyridine **2**,<sup>S1</sup> mono-protected diethynyl pyridine **3**,<sup>S1</sup> 3-azido propan-1-ol **4**,<sup>S2</sup> TMS-ethynyl bromopyridine **6**,<sup>S3</sup> terphenyl-propyl azide **9**,<sup>S4</sup> terphenyl-aryl azide **10**,<sup>S5</sup> permethyl-β-cyclodextrin azide **11**,<sup>S6-9</sup> 3-azido-1-mesypropyl-propane **14**,<sup>S10</sup> isophthalamide macrocycle **18**,<sup>S11</sup> pyridine bis-amide macrocycle precursor **S1**<sup>S12</sup> and the hydrogen bonding [2]rotaxane<sup>S13</sup> **28**·PF<sub>6</sub> has been previously reported.

### Safety note

**CAUTION:** Low molecular weight organic azides, sodium azide and 1,2,3-triazole and triazolium groups are potentially explosive. While no problems were encountered in the course of this work, they should be handled in small quantities and with appropriate care.

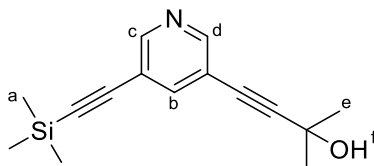
## S2. EXPERIMENTAL PROCEDURES & CHARACTERISATION DATA

### 3-(hydroxypropyl-iodotriazolyl)-5-(TBDMS-ethynyl)pyridine, **5**



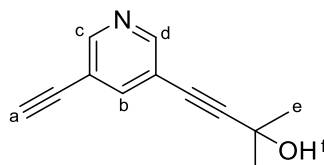
**4** (0.10 g, 1.0 mmol) was dissolved in dry, degassed THF (1.0 mL) and covered in foil. NaI (0.50 g, 3.3 mmol) and Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.62 g, 1.7 mmol) were added and the mixture was stirred for 5 mins under N<sub>2</sub>. TBTA (0.006 g, 11 μmol), DBU (0.13 g, 0.83 mmol, 0.5 mL THF) and **3** (0.20 g, 0.84 mmol, 0.5 mL THF) were added and the mixture was stirred under N<sub>2</sub> for 16 h. The reaction was diluted with DCM (80 mL) and washed with NH<sub>4</sub>OH (2 × 40 mL) and brine (2 × 40 mL) and dried over MgSO<sub>4</sub>. The solvent was removed *in vacuo*. Purification by silica gel column chromatography (5% MeOH in DCM) afforded **5** (0.375 g, 96%). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>) δ (ppm): 9.12 (1H, d, <sup>4</sup>J<sub>c</sub> = 2.1 Hz, H<sub>e</sub>), 8.69 (1H, d, <sup>4</sup>J<sub>d</sub> = 1.8 Hz, H<sub>d</sub>), 8.31 (1H, t, <sup>4</sup>J<sub>c</sub> = 2.1 Hz, H<sub>c</sub>), 4.64 (2H, t, J<sub>fg</sub> = 6.8 Hz, H<sub>f</sub>), 3.73 (2H, q, J<sub>hg,i</sub> = 5.6 Hz, H<sub>h</sub>), 2.21 (2H, quin, J<sub>gf,h</sub> = 6.4 Hz, H<sub>g</sub>), 1.79 (1H, t, J<sub>ih</sub> = 5.3 Hz, H<sub>i</sub>), 1.01 (9H, s, H<sub>a</sub>), 0.21 (6H, s, H<sub>b</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz; CDCl<sub>3</sub>) δ (ppm): 152.2, 150.5, 146.9, 146.6, 146.1, 137.5, 137.1, 125.9, 120.4, 101.6, 97.5, 58.9, 47.9, 32.1, 26.1, 16.7, 1.0, -4.7. HRESI-MS (pos.): 469.09090, calc. for [C<sub>18</sub>H<sub>25</sub>IN<sub>4</sub>O<sub>2</sub>Si·H]<sup>+</sup> = 469.09151.

### 3-(TMS-ethynyl)-5-(hydroxypropyl-ethynyl)pyridine, **7**



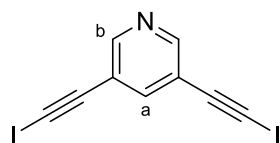
**6** (0.10 g, 0.40 mmol), CuI (0.02 g, 0.09 mmol), PPh<sub>3</sub> (0.02 g, 0.09 mmol) and Pd<sub>2</sub>(dba)<sub>3</sub> (0.02 g, 0.02 mmol) were suspended in Et<sub>3</sub>N and deoxygenated with N<sub>2</sub>. 2-Methylbut-3-yn-2-ol (62 μL, 0.64 mmol) was added and the mixture was stirred overnight at 75 °C under N<sub>2</sub>. The mixture was cooled to room temperature and filtered through Celite<sup>®</sup> and washed with EtOAc (3 × 10 mL). The solvent was removed *in vacuo*. Purification by preparative thin layer chromatography (3% MeOH in DCM) afforded **7** (0.093 g, 91%). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>) δ (ppm): 8.56 (2H, br. s., H<sub>c,d</sub>), 7.77 (1H, s, H<sub>b</sub>), 1.61 (6H, s, H<sub>e</sub>), 0.25 (9H, s, H<sub>a</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz; CDCl<sub>3</sub>) δ (ppm): 151.1, 150.9, 141.3, 119.9, 119.5, 100.4, 99.2, 98.1, 78.0, 65.4, 31.3, 1.0. HRESI-MS (pos.): 258.13110, calc. for [C<sub>15</sub>H<sub>19</sub>NOSi·H]<sup>+</sup> = 258.13087.

### 3-ethynyl-5-(hydroxypropyl-ethynyl)pyridine, **8**



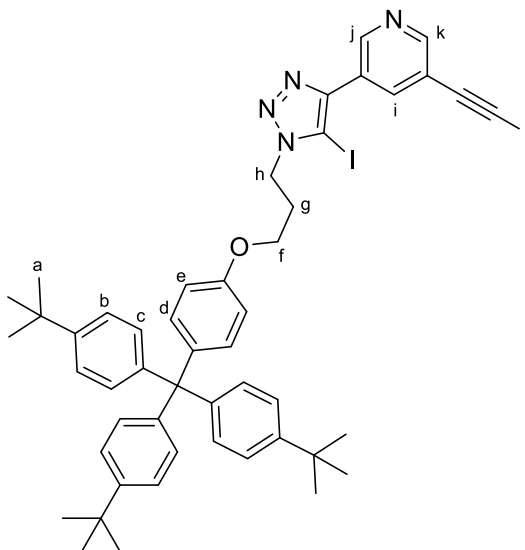
**7** (0.48 g, 1.9 mmol) was dissolved in MeOH (2.3 mL) and KOH (0.11 g, 1.9 mmol) was added. The mixture was stirred at room temperature, overnight under N<sub>2</sub>. Thereafter, H<sub>2</sub>O (10 mL) and HCl (1 M aq., 5 mL) was added and the mixture was extracted with DCM (4 × 20 mL). The combined organics were dried over MgSO<sub>4</sub>. The solvent was removed *in vacuo* to afford **8** (0.344 g, quant.). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>) δ (ppm): 8.60 (2H, d, <sup>4</sup>J<sub>c,d|b</sub> = 3.4 Hz, H<sub>c,d</sub>), 7.80 (1H, t, <sup>4</sup>J<sub>b|c,d</sub> = 2.0 Hz, H<sub>b</sub>), 3.23 (1H, s, H<sub>a</sub>), 1.62 (6H, s, H<sub>e</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz; CDCl<sub>3</sub>) δ (ppm): 151.3, 141.5, 132.0, 128.5, 119.7, 119.0, 98.5, 81.4, 79.4, 77.7, 65.3, 31.3. HRESI-MS (pos.): 186.09116, calc. for [C<sub>12</sub>H<sub>11</sub>NO·H]<sup>+</sup> = 186.09134.

### 3,5-diiodoethynyl pyridine, **12**



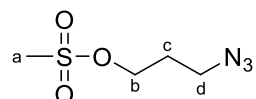
Previously prepared diethynyl pyridine<sup>S14</sup> (0.128 g, 1.00 mmol) was dissolved in THF (10 mL). CuI (0.034 g, 0.18 mmol) and *N*-iodomorpholine (0.751 g, 2.20 mmol) were added to this solution and stirred at room temperature for 2 h after which a white precipitate had formed. The suspension was poured onto a pad of neutral alumina. The filtrate was collected under vacuum and the solid phase washed with DCM (4 × 20 mL). The combined organic fractions were washed with saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (40 mL), dried over MgSO<sub>4</sub> and the solvent removed under reduced pressure. The residue was taken up in 10% EtOAc in hexane and the solution poured onto a pad of silica. The filtrate was collected under vacuum and the solid phase washed with 10% EtOAc in hexane (4 × 20 mL). The organic fractions were combined and the solvent removed *in vacuo*. Purification by recrystallisation from hexane yielded **12** as shiny, feathery white crystals. Yield: 0.254 g (65%). <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>) δ (ppm): 8.59 (2H, d, <sup>4</sup>J<sub>b|a</sub> = 2 Hz, H<sub>b</sub>), 7.75 (1H, t, <sup>4</sup>J<sub>a|b</sub> = 2 Hz, H<sub>a</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz; CDCl<sub>3</sub>) δ (ppm): 151.9, 142.3, 120.2, 89.8. HRESI-MS (pos.): 379.8421, calc. for [C<sub>9</sub>H<sub>3</sub>I<sub>2</sub>N·H]<sup>+</sup> = 379.8428.

### 3-iodoethynyl-5-(terphenyl-propyl-iodotriazolyl) pyridine, **13**



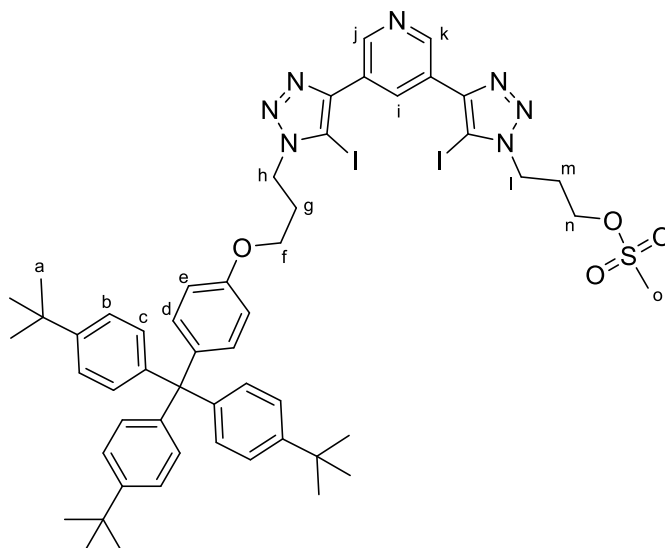
[Cu(MeCN)<sub>4</sub>][PF<sub>6</sub>] (15 mg, 40 μmol) and TBTA (cat.) were dissolved in dry degassed THF (3 mL). **9** (0.13 g, 0.20 mmol) and **12** (82 mg, 0.20 mmol) were added. The mixture was stirred overnight, at room temperature under N<sub>2</sub>. The solvent was removed *in vacuo*. The residue was redissolved in DCM (40 mL) and washed with NH<sub>4</sub>OH (2 × 10 mL) and brine (2 × 10 mL). The organics were dried over MgSO<sub>4</sub>. The solvent was removed *in vacuo*. Purification by preparative thin layer chromatography (0.5% MeOD in DCM) afforded **13** (66 mg, 34%). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>) δ (ppm): 9.16 (1H, s, H<sub>j</sub>), 8.68 (1H, s, H<sub>k</sub>), 8.36 (1H, s, H<sub>i</sub>), 7.17–7.25 (6H, m, H<sub>b</sub>), 7.03–7.17 (8H, m, H<sub>c,d</sub>), 6.77 (2H, d, J<sub>e|d</sub> = 8.8 Hz, H<sub>e</sub>), 4.68 (2H, t, J<sub>h|g</sub> = 7.0 Hz, H<sub>h</sub>), 4.05 (2H, t, J<sub>f|g</sub> = 5.6 Hz, H<sub>f</sub>), 2.46 (2H, quin, J<sub>g|f,h</sub> = 6.5 Hz, H<sub>g</sub>), 1.30 (27H, s, H<sub>a</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz; CDCl<sub>3</sub>) δ (ppm): 156.1, 152.5, 148.3, 147.4, 146.3, 144.0, 140.1, 137.6, 132.3, 130.7, 126.0, 124.0, 120.4, 113.0, 90.4, 63.8, 63.0, 53.4, 48.1, 34.3, 31.4, 29.6, 11.9. HRESI-MS (pos.): 989.21199, calc. for [C<sub>49</sub>H<sub>52</sub>ON<sub>4</sub>I<sub>2</sub>·Na]<sup>+</sup> = 989.21227.

### 3-azido-1-mesyl-propane, **14**<sup>S10</sup>



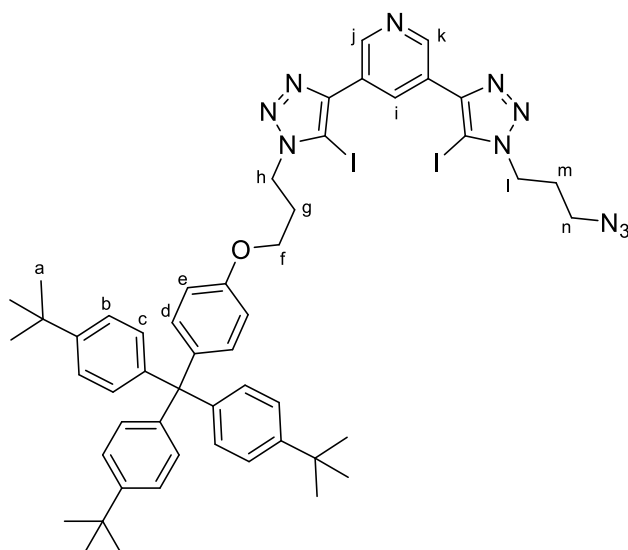
**4** (1.4 g, 14 mmol) and Et<sub>3</sub>N (4.0 mL, 29 mmol) were dissolved in dry degassed THF (150 mL). The solution was cooled to 0 °C. MsCl (1.5 mL, 19 mmol) was added and the mixture was stirred at room temperature, overnight under N<sub>2</sub>. The solvent was removed *in vacuo*. The residue was taken up in DCM (100 mL) and washed with H<sub>2</sub>O (3 × 100 mL) and NaHCO<sub>3</sub> (5% aq., 3 × 100 mL). The organics were dried over MgSO<sub>4</sub>. The solvent was removed *in vacuo* to afford **14** (2.1 g, 87%). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>) δ (ppm): 4.32 (2H, t, J<sub>d|c</sub> = 6.0 Hz, H<sub>d</sub>), 3.49 (2H, t, J<sub>b|c</sub> = 6.4 Hz, H<sub>b</sub>), 3.03 (3H, s, H<sub>a</sub>), 2.01 (2H, quin, J<sub>c|b,d</sub> = 6.2 Hz, H<sub>c</sub>).

### 3-(mesyl-propyl-iodotriazolyl)-5-(terphenyl-propyl-iodotriazolyl) pyridine, 15



[Cu(MeCN)<sub>4</sub>][PF<sub>6</sub>] (14 mg, 40 μmol) and TBTA (cat.) were dissolved in dry degassed THF (6 mL), and the flask was covered in tin foil. **14** (0.22 g, 1.3 mmol) and **13** (0.16 g, 0.16 mmol) were added. The mixture was stirred at room temperature, overnight under N<sub>2</sub>. The mixture was diluted with CHCl<sub>3</sub> (60 mL) and washed with NH<sub>4</sub>OH (2 × 10 mL) and brine (2 × 10 mL). The organics were dried over MgSO<sub>4</sub>. The solvent was removed *in vacuo*. Purification by silica gel column chromatography (0–0.5% MeOH in DCM) afforded **15** (0.165 g, 86%) as a brown solid. **<sup>1</sup>H NMR** (500 MHz; CDCl<sub>3</sub>) δ (ppm): 9.33 (2H, s, H<sub>j,k</sub>), 9.23 (1H, s, H<sub>i</sub>), 7.23 (6H, d, J<sub>b|c</sub> = 8.5 Hz, H<sub>b</sub>), 7.02–7.14 (8H, m, H<sub>c,d</sub>), 6.77 (2H, d, J<sub>e|d</sub> = 8.7 Hz, H<sub>e</sub>), 4.71 (2H, t, J<sub>l|m</sub> = 6.4 Hz, H<sub>l</sub>), 4.65 (2H, t, J<sub>h|g</sub> = 6.4 Hz, H<sub>h</sub>), 4.33 (2H, t, J<sub>n|m</sub> = 5.6 Hz, H<sub>n</sub>), 4.06 (2H, t, J<sub>f|g</sub> = 5.6 Hz, H<sub>f</sub>), 3.08 (3H, s, H<sub>o</sub>), 2.47 (4H, quin, J<sub>f,h,l,n|g,m</sub> = 6.3 Hz, H<sub>g,m</sub>), 1.29 (27H, s, H<sub>a</sub>). **<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz; CDCl<sub>3</sub>) δ (ppm): 156.2, 148.3, 148.0, 147.9, 147.1, 146.8, 144.0, 140.1, 132.8, 132.3, 130.6, 126.3, 126.1, 124.0, 113.0, 66.0, 63.9, 63.0, 53.4, 48.1, 47.2, 37.5, 34.2, 31.3, 29.6, 29.2. **HRESI-MS** (pos.): 1168.2486, calc. for [C<sub>53</sub>H<sub>61</sub>I<sub>2</sub>N<sub>7</sub>O<sub>4</sub>S·Na]<sup>+</sup> = 1168.2487.

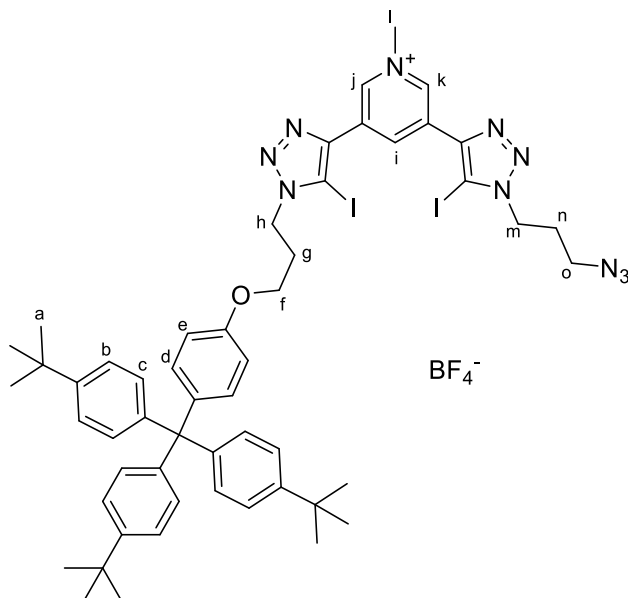
### 3-(azido-propyl-iodotriazolyl)-5-(terphenyl-propyl-iodotriazolyl) pyridine, 16



**15** (0.16 g, 0.14 mmol) and NaN<sub>3</sub> (39 mg, 0.59 mmol) were dissolved in dry degassed DMF (6 mL) and stirred at 85 °C overnight under N<sub>2</sub>. Thereafter, the mixture was cooled to room temperature, and partitioned between H<sub>2</sub>O (20 mL) and EtOAc (20 mL). The aqueous layer was washed with further EtOAc (2 × 20 mL). The combined organics were washed with brine (3 × 10 mL) and dried over MgSO<sub>4</sub>. The solvent was removed *in vacuo* afforded **16** (0.137 g, 87%) as a brown solid. **<sup>1</sup>H NMR** (400 MHz; CDCl<sub>3</sub>) δ (ppm): 9.26 (2H, s, H<sub>j,k</sub>), 8.87 (1H, s, H<sub>i</sub>), 7.23 (6H, d, J<sub>b|c</sub> = 8.0 Hz, H<sub>b</sub>), 7.05–7.14 (8H, m, H<sub>c,d</sub>), 6.78 (2H, d, J<sub>e|d</sub> = 8.7

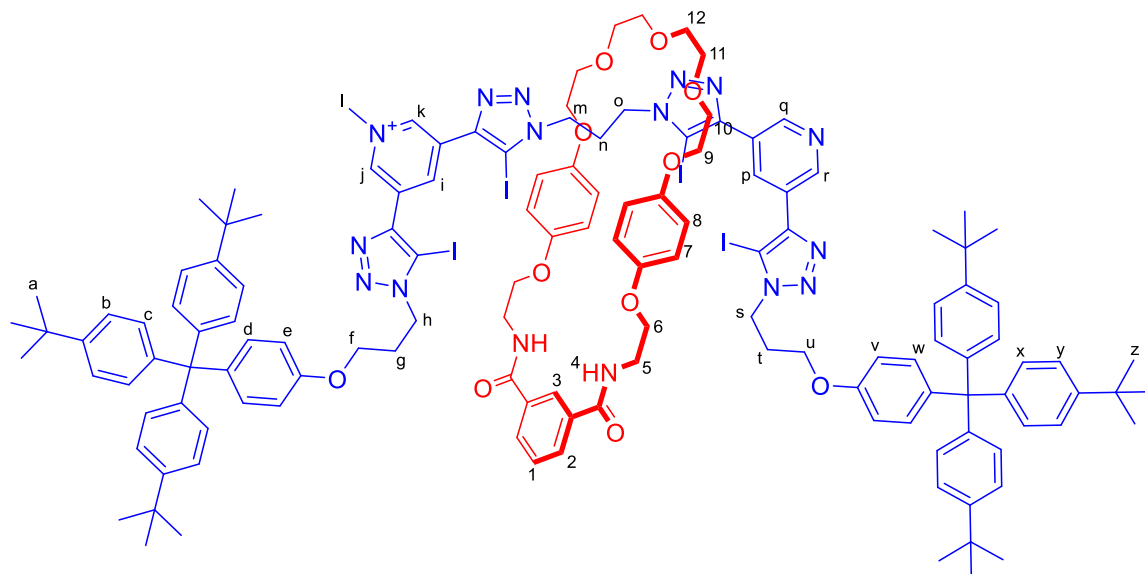
Hz, H<sub>e</sub>), 4.70 (2H, t,  $J_{lm} = 6.8$  Hz, H<sub>l</sub>), 4.58 (2H, t,  $J_{hg} = 6.8$  Hz, H<sub>h</sub>), 4.06 (2H, t,  $J_{nm} = 5.6$  Hz, H<sub>n</sub>), 3.47 (2H, t,  $J_{fg} = 6.4$  Hz, H<sub>f</sub>), 2.47 (2H, quin,  $J_{ml,n} = 6.4$  Hz, H<sub>m</sub>), 2.25 (2H, quin,  $J_{gl,h} = 6.4$  Hz, H<sub>g</sub>), 1.30 (27H, s, H<sub>a</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz; CDCl<sub>3</sub>) δ (ppm): 156.1, 148.3, 148.2, 147.9, 147.8, 147.0, 146.8, 144.0, 140.1, 133.0, 132.4, 132.3, 130.7, 129.0, 128.9, 128.5, 128.2, 126.4, 126.2, 125.3, 124.0, 124.0, 113.0, 63.9, 63.0, 48.2, 48.1, 48.0, 34.3, 31.3, 29.6, 29.0, 21.4. **HRESI-MS** (pos.): 1115.27745, calc. for [C<sub>52</sub>H<sub>58</sub>I<sub>2</sub>N<sub>10</sub>O·Na]<sup>+</sup> = 1115.27766.

**3-(azido-propyl-iodotriazolyl)-5-(terphenyl-propyl-iodotriazolyl) pyridinium tetrafluoroborate, 17·BF<sub>4</sub>**



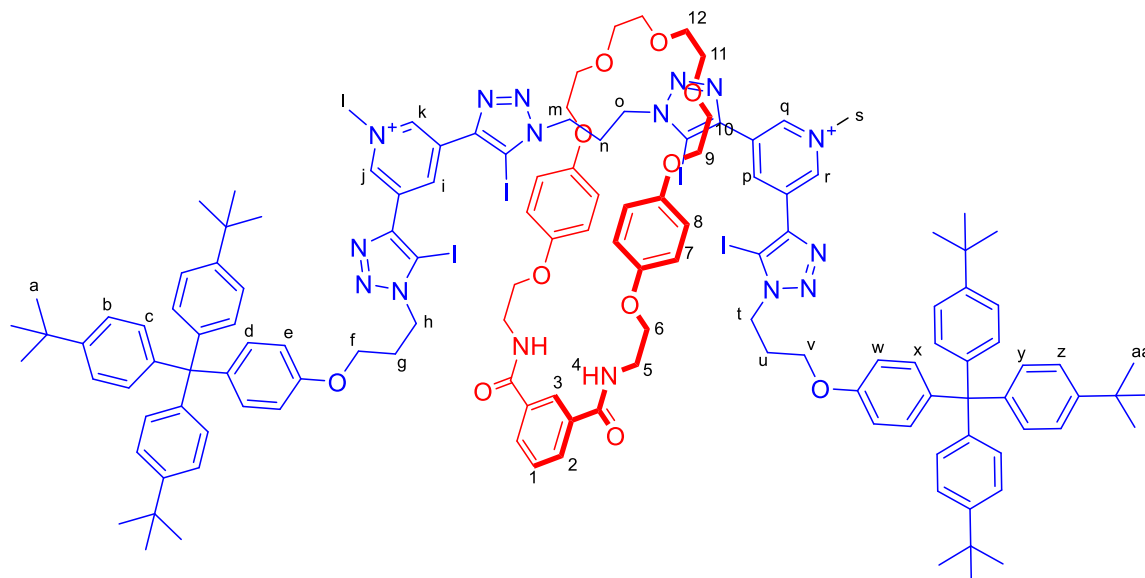
Initially, **16** (38 mg, 35 μmol) was dissolved in CH<sub>3</sub>I (2 mL) and stirred at 35 °C overnight under N<sub>2</sub>. The solvent was removed *in vacuo* but afforded an insoluble powder that could not be anion exchanged to a more soluble anion. Consequently, in a second method, **16** (60 mg, 55 μmol) was dissolved in dry DCM (5 mL). [Me<sub>3</sub>O][BF<sub>4</sub>] (8.8 mg, 60 μmol) was added and the mixture was stirred at room temperature overnight under N<sub>2</sub>. Thereafter, the reaction was quenched with MeOH (1 mL) and the solvent was removed *in vacuo*. Purification by preparative thin layer chromatography (3% MeOH in DCM) afforded **17·BF<sub>4</sub>** (30.0 mg, 46%) as a white powder. <sup>1</sup>H NMR (400 MHz; CD<sub>3</sub>OD) δ (ppm): 9.75 (1H, s, H<sub>i</sub>), 9.30–9.51 (2H, m, H<sub>j,k</sub>), 7.15–7.25 (6H, m, H<sub>b</sub>), 6.99–7.10 (8H, m, H<sub>c,d</sub>), 6.74 (2H, d,  $J_{e|d} = 8.9$  Hz, H<sub>e</sub>), 4.73 (2H, t,  $J_{on} = 6.9$  Hz, H<sub>o</sub>), 4.61 (2H, t,  $J_{hg} = 6.6$  Hz, H<sub>h</sub>), 4.58 (3H, s, H<sub>l</sub>), 4.04 (2H, t,  $J_{mn} = 5.6$  Hz, H<sub>m</sub>), 3.45 (2H, t,  $J_{fg} = 6.3$  Hz, H<sub>f</sub>), 2.46 (2H, quin,  $J_{nl,m,o} = 6.1$  Hz, H<sub>n</sub>), 2.23 (2H, quin,  $J_{gl,h} = 6.4$  Hz, H<sub>g</sub>), 1.26 (27H, s, H<sub>a</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz; CD<sub>3</sub>OD) δ (ppm): 148.4, 144.1, 140.2, 132.3, 130.6, 124.0, 113.0, 63.9, 63.0, 42.2, 34.2, 31.1, 28.8. <sup>19</sup>F NMR (377 MHz; CD<sub>3</sub>OD) δ (ppm): -153.84 (s, BF<sub>4</sub>). **HRESI-MS** (pos.): 1107.31149, calc. for [C<sub>53</sub>H<sub>61</sub>I<sub>2</sub>N<sub>10</sub>O]<sup>+</sup> = 1107.31137.

**Asymmetric rotaxane: pyridinium/pyridine bis-iodotriazole axle–isophthalamide 5-O-polyether macrocycle, 19•PF<sub>6</sub>**



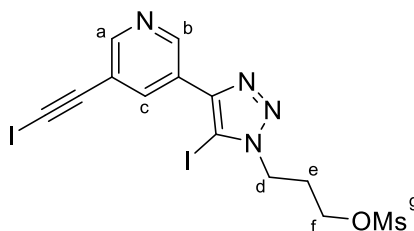
**18** (13 mg, 20  $\mu\text{mol}$ ), **17**•BF<sub>4</sub> (12 mg, 10  $\mu\text{mol}$ ) and TBA•Cl (2.5 mg, 10  $\mu\text{mol}$ ) were dissolved in dry, degassed THF (1 mL), and the flask was covered in tin foil. The mixture was stirred for 30 mins, and thereafter, [Cu(MeCN)<sub>4</sub>][PF<sub>6</sub>] (cat.), TBTA (cat.) and **13** (10.5 mg, 10  $\mu\text{mol}$ ) were added. The mixture was stirred at room temperature, overnight under N<sub>2</sub>. The mixture was diluted with CHCl<sub>3</sub> (20 mL), and washed with NH<sub>4</sub>OH (2  $\times$  10 mL) and brine (2  $\times$  10 mL). The solvent was removed *in vacuo*. Purification by preparative thin layer chromatography (3% MeOH in DCM) afforded **19**•Cl which was anion exchanged to the hexafluorophosphate salt by washing with NH<sub>4</sub>PF<sub>6</sub> (0.1 M aq., 8  $\times$  10 mL) and H<sub>2</sub>O (2  $\times$  10 mL). The solvent was removed *in vacuo* to afford **19**•PF<sub>6</sub> (9.0 mg, 32%). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>)  $\delta$  (ppm): 9.57 (1H, br. s., H<sub>j</sub>), 9.33 (1H, br. s., H<sub>k</sub>), 9.27 (3H, br. s., H<sub>p,q,r</sub>), 8.91 (1H, s, H<sub>3</sub>), 8.48 (2H, br. s., H<sub>4</sub>), 8.40 (1H, s, H<sub>i</sub>), 8.35 (2H, d,  $J_{2|1} = 7.8$  Hz, H<sub>2</sub>), 7.53 (1H, t,  $J_{1|2} = 7.8$  Hz, H<sub>1</sub>), 7.17–7.24 (12H, m, H<sub>b,y</sub>), 7.02–7.12 (16H, m, H<sub>c,d,w,x</sub>), 6.78 (4H, d,  $J_{e,v|d,w} = 7.5$  Hz, H<sub>e,v</sub>), 6.31 (4H, d,  $J_{8|7} = 9.0$  Hz, H<sub>8</sub>), 5.79 (4H, d,  $J_{7|8} = 8.9$  Hz, H<sub>7</sub>), 4.69 (2H, t,  $J = 6.9$  Hz, H<sub>h</sub>), 4.59 (3H, s, H<sub>1</sub>), 3.46–4.56 (36H, m, H<sub>f,m,o,s,u,5,6,9,10,11,12</sub>), 2.30–2.53 (6H, m, H<sub>g,n,t</sub>), 1.29 (54H, s, H<sub>a,z</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz; CDCl<sub>3</sub>)  $\delta$  (ppm): 148.4, 132.3, 130.7, 129.1, 128.2, 124.1, 113.1, 69.5, 34.3, 31.4 (several peaks were too weak to be detected). <sup>31</sup>P NMR (162 MHz; CDCl<sub>3</sub>)  $\delta$  (ppm): –144:20 (spt,  $J = 714.0$  Hz, PF<sub>6</sub>). <sup>19</sup>F NMR (377 MHz; CDCl<sub>3</sub>)  $\delta$  (ppm): –71:08 (d,  $J = 714.0$  Hz, PF<sub>6</sub>). HRESI-MS (pos.): 2669.80135, calc. for [C<sub>134</sub>H<sub>151</sub>L<sub>4</sub>N<sub>16</sub>O<sub>11</sub>]<sup>+</sup> = 2669.80333.

**Dicationic rotaxane: bis-(3,5-bis-iodotriazole pyridinium) axle–isophthalamide 5-O-polyether macrocycle, 20•(PF<sub>6</sub>)<sub>2</sub>**



**19•PF<sub>6</sub>** (7.6 mg, 2.7 μmol) was dissolved in dry CHCl<sub>3</sub> (1 mL) and CH<sub>3</sub>I (10 μL) was added. The mixture was stirred overnight at room temperature under N<sub>2</sub>. However, no evidence of product formation was observed by mass spectrometric analysis. A further portion of CH<sub>3</sub>I (0.1 mL) was added and the mixture was stirred for 3 days. Thereafter, the solvent was removed *in vacuo* and rotaxane was anion exchanged to the hexafluorophosphate salt by washing a CHCl<sub>3</sub> solution (25 mL) of the crude mixture with NH<sub>4</sub>PF<sub>6</sub> (0.1 M, 8 × 10 mL) and H<sub>2</sub>O (2 × 10 mL). The solvent was removed *in vacuo* to afford the target rotaxane **20•(PF<sub>6</sub>)<sub>2</sub>** (2.9 mg, 36%). <sup>1</sup>H NMR (500 MHz; 45:45:10 CDCl<sub>3</sub>:CD<sub>3</sub>OD:D<sub>2</sub>O) δ (ppm): 9.44 (2H, s, H<sub>j,k</sub>), 9.38 (2H, s, H<sub>q,r</sub>), 9.19 (1H, br. s., H<sub>3</sub>), 8.66 (1H, br. s., H<sub>i</sub>), 8.26 (2H, br. s., H<sub>p,1</sub>), 8.05 (2H, d, H<sub>4</sub>), 8.01 (2H, d, H<sub>2</sub>), 7.15–7.26 (12H, m, H<sub>b,z</sub>), 6.98–7.14 (16H, m, H<sub>c,d,x,y</sub>), 6.74–6.86 (12H, m, H<sub>e,w,7,8</sub>), 3.56–4.16 (42H, m, H<sub>f,h,l,m,o,s,t,v,5,6,9,10,11,12</sub>), 2.54 (2H, br. s., H<sub>n</sub>), 2.44 (4H, br. s., H<sub>g,u</sub>), 1.18–1.36 (54H, m, H<sub>aa,aa</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz; CDCl<sub>3</sub>) δ (ppm): 155.6, 148.1, 130.9, 129.6, 124.2, 115.8, 115.6, 95.9, 70.9, 69.9, 60.0, 39.9, 34.4, 31.5, 29.2, 18.3 (several resonances were too weak to detect). <sup>31</sup>P NMR (162 MHz; CDCl<sub>3</sub>) δ (ppm): –144:36 (spt, *J* = 714.0 Hz, PF<sub>6</sub>). <sup>19</sup>F NMR (377 MHz; CDCl<sub>3</sub>) δ (ppm): –70:82 (d, *J* = 714.0 Hz, PF<sub>6</sub>). **HRESI-MS** (pos.): 1341.90639, calc. for [C<sub>135</sub>H<sub>154</sub>I<sub>4</sub>N<sub>16</sub>O<sub>11</sub>]<sup>+</sup> = 1341.90922.

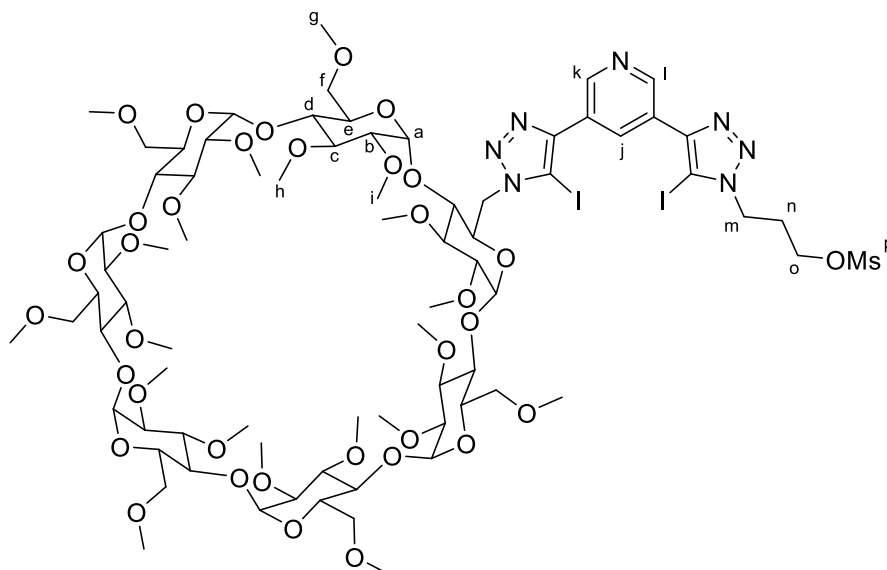
**3-(mesyl-propyl-iodotriazolyl)-5-(iodoethynyl)pyridine, 21**



[Cu(MeCN)<sub>4</sub>][PF<sub>6</sub>]<sub>2</sub> (23 mg, 62 μmol) and TBTA (cat.) were dissolved in dry, degassed THF, and the flask was covered in foil. **14** (56 mg, 0.30 mmol) and **12** (0.12 g, 0.30 mmol) were added, and the mixture was stirred at room temperature, overnight under N<sub>2</sub>. Thereafter, the mixture was diluted with CDCl<sub>3</sub> (50 mL), and washed with NH<sub>4</sub>OH (2 × 10 mL) and brine (2 × 10 mL). The organics were dried over MgSO<sub>4</sub>. The solvent was removed *in vacuo*. Purification by silica gel column chromatography (0.75% MeOH in DCM) afforded **21** (47 mg, 27%). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>) δ (ppm): 9.13 (1H, s, H<sub>b</sub>), 8.69 (1H, s, H<sub>a</sub>), 8.28 (1H, t, <sup>4</sup>*J*<sub>ca,b</sub> = 2.0 Hz, H<sub>c</sub>), 4.63 (2H, t, *J*<sub>d,e</sub> = 6.7 Hz, H<sub>d</sub>), 4.32 (2H, t, *J*<sub>f,e</sub> = 5.7 Hz, H<sub>f</sub>), 3.07 (3H, s, H<sub>g</sub>), 2.45 (2H, quin, *J*<sub>e|d,f</sub> = 6.1 Hz, H<sub>e</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz; 5:1 CDCl<sub>3</sub>:CD<sub>3</sub>OD) δ (ppm): 152.4, 151.2, 147.1, 146.8, 138.5, 126.7, 66.7, 47.8, 37.6, 29.6. **HRESI-MS** (pos.): 558.87936, calc. for [C<sub>13</sub>H<sub>12</sub>I<sub>2</sub>N<sub>4</sub>O<sub>3</sub>S•H]<sup>+</sup> = 558.87922.

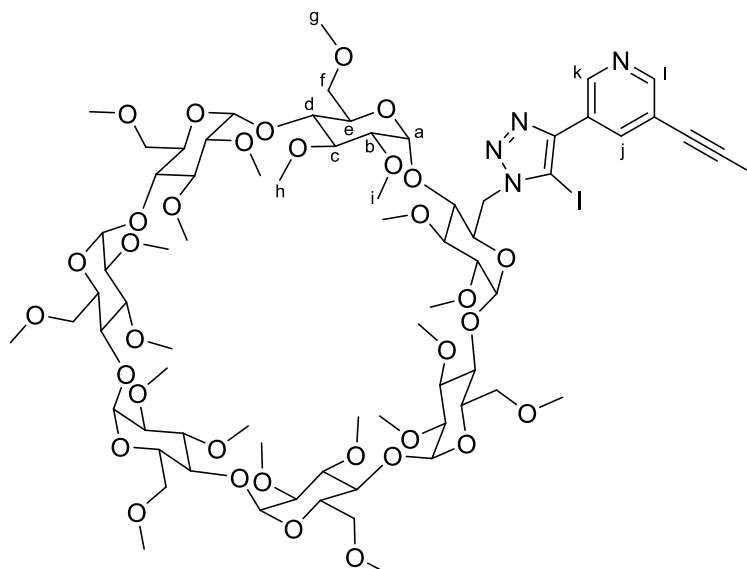


### 3-(mesyl-propyl-iodotriazolyl)-5-(permethyl- $\beta$ -cyclodextrin-iodotriazolyl)pyridine, 22



**21** (14 mg, 26  $\mu\text{mol}$ ), **11** (43 mg, 29  $\mu\text{mol}$ ),  $[\text{Cu}(\text{MeCN})_4][\text{PF}_6]$  (cat.) and TBTA (cat.) were dissolved in dry, degassed THF (1.5 mL), and the flask was covered in foil. The mixture was stirred at room temperature, overnight under  $\text{N}_2$ . The mixture was diluted with  $\text{CHCl}_3$  (20 mL) and washed with  $\text{NH}_4\text{OH}$  ( $2 \times 10$  mL) and brine ( $2 \times 10$  mL). The organics were dried over  $\text{MgSO}_4$ . The solvent was removed *in vacuo*. Purification by preparative thin layer chromatography (3% MeOH in DCM) afforded **22** (10.2 mg, 20%).  $^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ )  $\delta$  (ppm): 9.24 (2H, d,  $^4J_{k,lj} = 2.0$  Hz,  $\text{H}_{k,l}$ ), 8.85 (1H, t,  $^4J_{jik,l} = 2.0$  Hz,  $\text{H}_j$ ), 4.94–5.26 (7H, m,  $\text{H}_a$ ), 4.62 (2H, t,  $J_{mn} = 6.7$  Hz,  $\text{H}_m$ ), 4.32 (2H, t,  $J_{on} = 5.7$  Hz,  $\text{H}_o$ ), 3.06 (3H, s,  $\text{H}_p$ ), 2.84–4.12 (102H, m,  $\text{H}_{b,c,d,e,f,g,h,i}$ ), 2.45 (2H, quin,  $J_{nm,o} = 6.1$  Hz,  $\text{H}_n$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz;  $\text{CDCl}_3$ )  $\delta$  (ppm): 148.0, 147.1, 146.2, 132.8, 126.5, 126.2, 124.8, 99.8–98.2, 84.2, 82.3–79.8, 71.4–70.3, 65.9, 61.9–58.4, 51.8, 47.2, 37.6, 29.7, 29.2. HRESI-MS (pos.): 1998.56222, calc. for  $[\text{C}_{75}\text{H}_{121}\text{O}_{37}\text{N}_7\text{I}_2\text{S}\cdot\text{H}]^+ = 1998.56847$ .

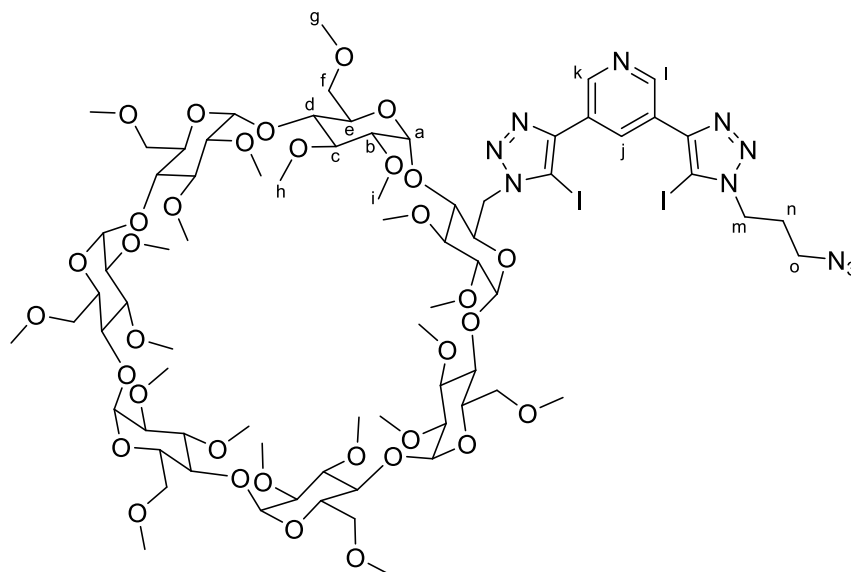
### 3-(permethyl- $\beta$ -cyclodextrin-iodotriazolyl)-5-(iodoethynyl)pyridine, 23



$[\text{Cu}(\text{MeCN})_4][\text{PF}_6]$  (10 mg, 27  $\mu\text{mol}$ ) and TBTA (cat.) were dissolved in dry degassed THF (1 mL). **11** (0.10 g, 69  $\mu\text{mol}$ ) and **12** (26 mg, 69  $\mu\text{mol}$ ) were added. The mixture was stirred overnight, at room temperature under  $\text{N}_2$ . The solvent was removed *in vacuo*. The residue was redissolved in DCM (40 mL) and washed with  $\text{NH}_4\text{OH}$  ( $2 \times 10$  mL) and brine ( $2 \times 10$  mL). The organics were dried over  $\text{MgSO}_4$ . The solvent was removed *in vacuo*. Purification by preparative thin layer chromatography (3% MeOH in DCM) afforded **23** (6.4 mg, 5%).  $^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ )  $\delta$  (ppm): 9.17 (1H, d,  $^4J_{kij} = 1.6$  Hz,  $\text{H}_k$ ), 8.68 (1H, s,  $\text{H}_l$ ), 8.30 (1H, s,  $\text{H}_j$ ), 4.96–5.29 (7H, m,  $\text{H}_a$ ), 2.80–4.16 (102H, m,  $\text{H}_{b,c,d,e,f,g,h,i}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz;  $\text{CDCl}_3$ )  $\delta$

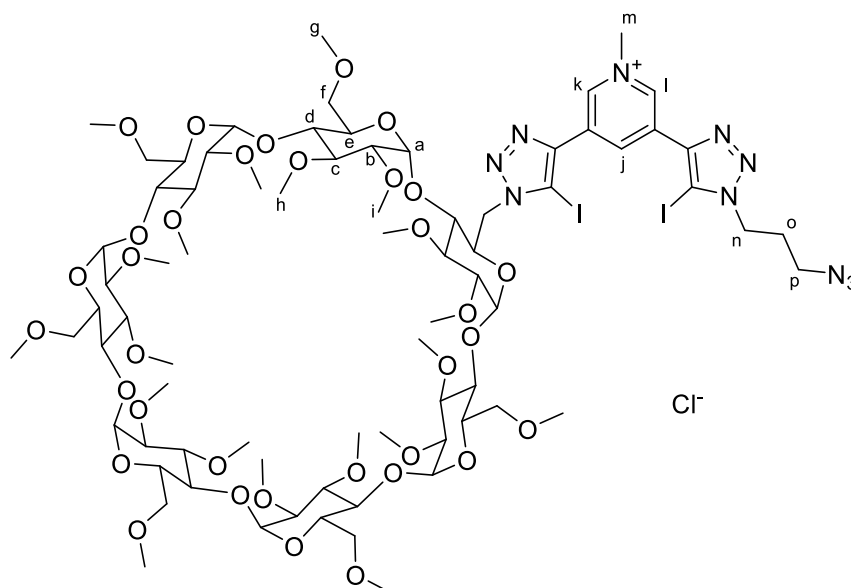
(ppm): 147.1, 145.6, 137.4, 134.2, 127.3, 126.1, 104.4, 99.8–98.2, 84.1–79.9, 71.5–70.5, 61.8–58.4, 51.9, 29.7. **HRESI-MS** (pos.): 1819.52786, calc. for  $[C_{71}H_{112}O_{34}N_4I_2 \cdot H]^+$  = 1819.53201.

**3-(azido-propyl-iodotriazolyl)-5-(permethyl- $\beta$ -cyclodextrin-iodotriazolyl)pyridine, 24**



**22** (64 mg, 32  $\mu$ mol) and  $NaN_3$  (11 mg, 0.16 mmol) were dissolved in dry, degassed DMF (2 mL), and the mixture was stirred at 85 °C, overnight under  $N_2$ . The mixture was cooled to room temperature and partitioned between  $H_2O$  (10 mL) and EtOAc (10 mL). The aqueous layer was washed with EtOAc ( $2 \times 10$  mL). The combined organics were washed with brine ( $3 \times 10$  mL), and dried over  $MgSO_4$ . The solvent was removed *in vacuo* to afford **24** (62 mg, quant.).  **$^1H$  NMR** (400 MHz;  $CDCl_3$ )  $\delta$  (ppm): 9.22 (2H, s,  $H_{k,l}$ ), 8.85 (1H, s,  $H_j$ ), 4.90–5.36 (7H, m,  $H_a$ ), 4.55 (2H, t,  $J_{min} = 6.8$  Hz,  $H_m$ ), 3.01–3.97 (104H, m,  $H_{b,c,d,e,f,g,h,i,o}$ ), 2.22 (1H, quin,  $J_{nlm,o} = 6.5$  Hz,  $H_n$ ).  **$^{13}C\{^1H\}$  NMR** (101 MHz;  $CDCl_3$ )  $\delta$  (ppm): 147.8, 147.7, 146.8, 146.1, 132.8, 130.8, 128.7, 126.4, 126.3, 99.7–98.7, 84.1, 82.2, 81.9–79.7, 71.3–70.1, 61.7–61.1, 59.1–58.3, 51.8, 48.0, 48.0, 29.6, 29.0. **HRESI-MS** (pos.): 1945.59012, calc. for  $[C_{74}H_{118}O_{34}N_{10}I_2 \cdot H]^+$  = 1945.59850.

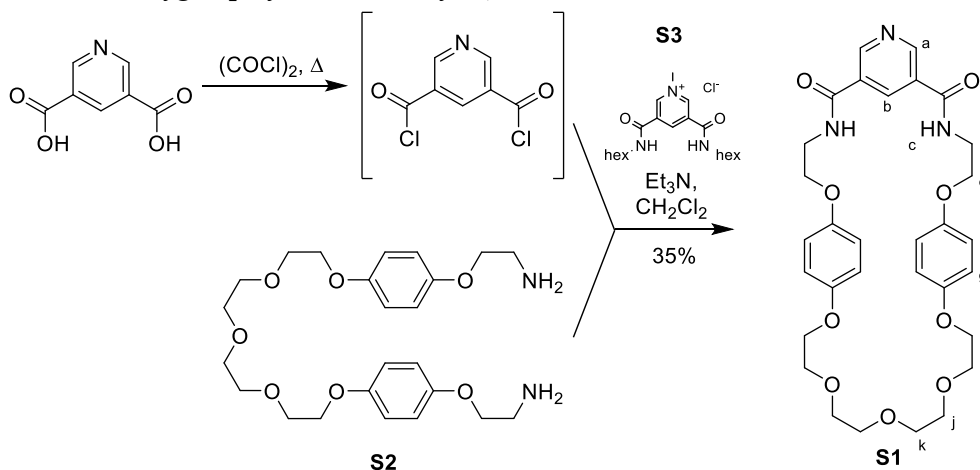
**3-(azido-propyl-iodotriazolyl)-5-(permethyl- $\beta$ -cyclodextrin-iodotriazolyl)pyridinium chloride, 25·Cl**



**24** (80 mg, 41  $\mu$ mol) was dissolved in  $CHCl_3$  (0.2 mL) and  $CH_3I$  (0.1 mL 1.0 mmol) was added. The mixture was stirred overnight at 40 °C under  $N_2$ . The solvent was removed *in vacuo*. The residue was taken up in  $CHCl_3$  (1.5 mL) and passed through a chloride-loaded Amberlite® column to afford the desired product **25·Cl** (56.6 mg, 69%).  **$^1H$  NMR** (400 MHz;  $CDCl_3$ )  $\delta$  (ppm): 10.17 (1H, s,  $H_j$ ), 9.40 (2H, s,  $H_{k,l}$ ), 4.88–5.29

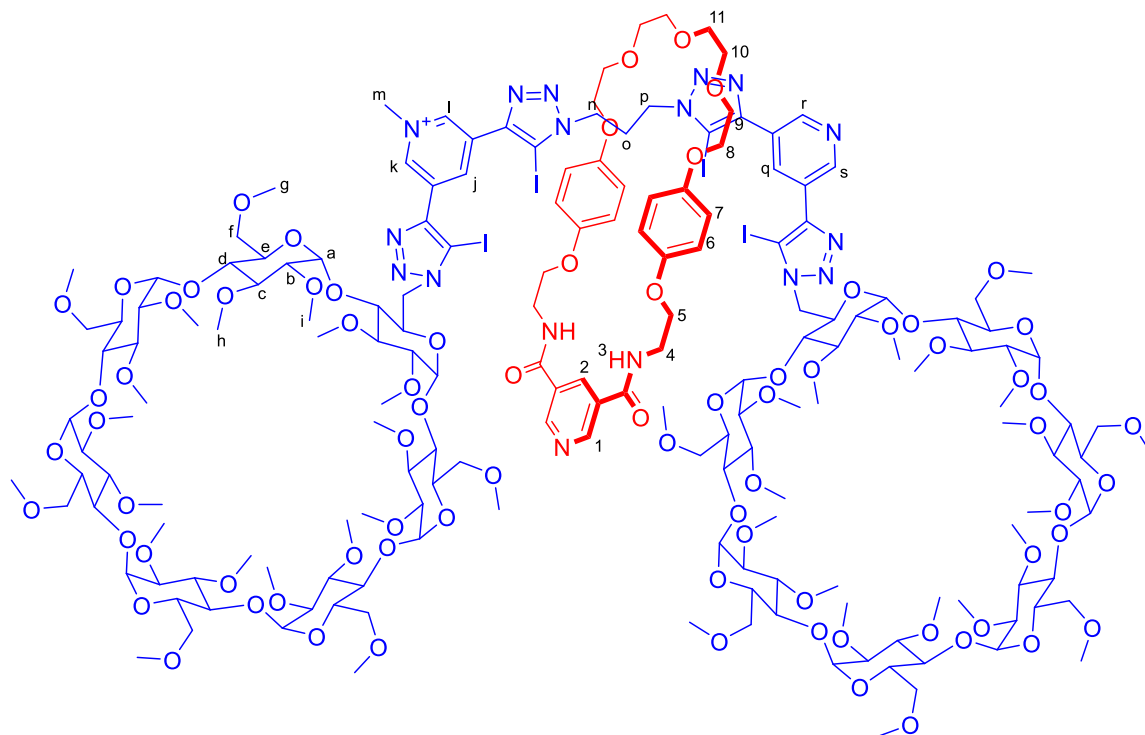
(7H, m, H<sub>a</sub>), 4.67 (3H, s, H<sub>m</sub>), 2.88–4.49 (106H, m, H<sub>b,c,d,e,f,g,h,i,n,p</sub>), 2.05 (2H, quin, J<sub>o,n,p</sub> = 6.8 Hz, H<sub>o</sub>).  
<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz; CDCl<sub>3</sub>) δ (ppm): 141.7, 141.1, 140.2, 140.1, 133.3, 133.0, 132.2, 131.9, 130.9, 128.8, 99.1–97.7, 83.0–81.1, 80.5–78.7, 71.3–69.5, 61.9–57.9, 53.7, 50.4, 48.2, 48.1, 31.7, 29.6, 29.2, 28.9.  
**HRESI-MS** (pos.): 1959.60753, calc. for [C<sub>75</sub>H<sub>121</sub>O<sub>34</sub>N<sub>10</sub>I<sub>2</sub>]<sup>+</sup> = 1959.61305.

**Pyridine-bis-amide 5-oxygen-polyether macrocycle, S1<sup>S12</sup>**



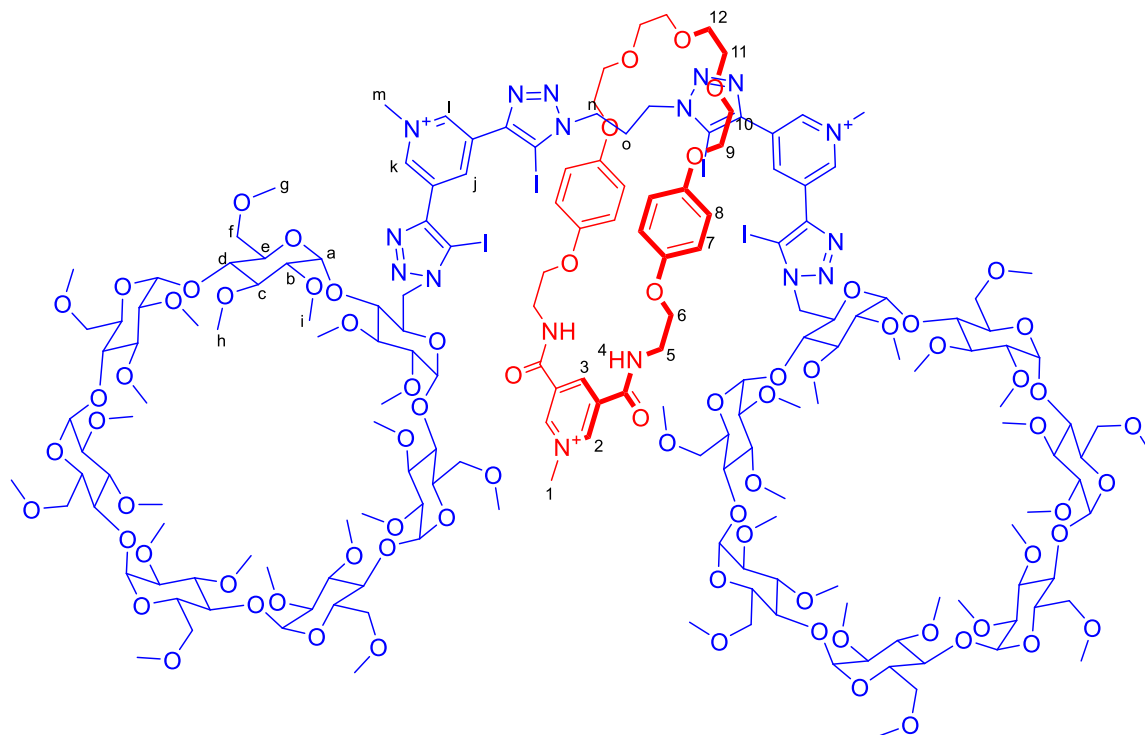
Pyridine-3,5-dicarboxylic acid (0.19 g, 1.0 mmol) was suspended in DCM (4 mL), and  $(\text{COCl})_2$  (0.4 mL) was added. The mixture was refluxed overnight under  $\text{N}_2$ . The solvent was removed *in vacuo*, and the residue was redissolved in dry DCM (20 mL). This was added dropwise to a solution of **S2**<sup>S12</sup> (0.54 g, 1.0 mmol), **S3**·**Cl**<sup>S12</sup> (0.38 g, 1.0 mmol) and  $\text{Et}_3\text{N}$  (3.3 mL, 23 mmol) dissolved in dry DCM (50 mL). The mixture was stirred at room temperature for 1 h under  $\text{N}_2$ . Thereafter, the mixture was washed with HCl (10% aq., 2 × 50 mL) and  $\text{H}_2\text{O}$  (2 × 50 mL). The organics were dried over  $\text{MgSO}_4$ . The solvent was removed *in vacuo*. Purification by silica gel column chromatography (3% MeOH in  $\text{CHCl}_3$ ) afforded **S1** (0.25 g, 43%) as a white powder. <sup>1</sup>H NMR (400 MHz; CD<sub>3</sub>OD) δ (ppm): 9.08 (2H, d, <sup>4</sup>J<sub>alb</sub> = 2.2 Hz, H<sub>a</sub>), 8.39–8.51 (1H, m, H<sub>b</sub>), 6.77 (8H, s, H<sub>f,g</sub>), 4.07 (4H, t, J<sub>dle</sub> = 4.9 Hz, H<sub>d</sub>), 3.97–4.03 (4H, m, H<sub>e</sub>), 3.75–3.82 (8H, m, H<sub>h,i</sub>), 3.62–3.70 (8H, m, H<sub>j,k</sub>). **LRESI-MS** (pos.): 596.28, calc. for [C<sub>31</sub>H<sub>37</sub>N<sub>3</sub>O<sub>9</sub>·H]<sup>+</sup> = 596.26.

**Water-soluble asymmetric monocationic [2]rotaxane: permethyl- $\beta$ -cyclodextrin-stoppered pyridinium/pyridine bis-iodotriazole axle with pyridine bis-amide 5-O-polyether macrocycle, S4·Cl**



**S1**<sup>S12</sup> (8.0 mg, 13  $\mu$ mol), **25·Cl** (7.3 mg, 3.5  $\mu$ mol) and **23** (6.4 mg, 3.5  $\mu$ mol) were dissolved in dry, degassed THF (0.1 mL). The flask was covered in foil and the mixture was stirred for 30 mins. Thereafter, a solution of [Cu(MeCN)<sub>4</sub>][PF<sub>6</sub>] (cat.) and TBTA (cat.) in dry, degassed THF (0.1 mL) was added, and the mixture was stirred overnight at room temperature under N<sub>2</sub>. The mixture was then diluted with CHCl<sub>3</sub> (20 mL) and washed with NH<sub>4</sub>OH (10 mL) and brine (10 mL). The solvent was removed *in vacuo* and the organics were dried over MgSO<sub>4</sub>. Purification by preparative thin layer chromatography (8% MeOH in DCM) afforded the monocationic [2]rotaxane precursor **S4·Cl** (1.7 mg, 9%). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>)  $\delta$  (ppm): 9.81 (1H, br. s., H<sub>k</sub>), 9.73 (1H, br. s., H<sub>i</sub>), 9.50 (2H, d, H<sub>r,s</sub>), 9.28 (2H, d, H<sub>l</sub>), 9.10 (1H, br. s., H<sub>j</sub>), 8.94 (1H, br. s., H<sub>2</sub>), 8.62 (2H, br. s., H<sub>3</sub>), 8.26 (1H, br. s., H<sub>q</sub>), 6.27–6.44 (8H, m, H<sub>6,7</sub>), 4.98–5.33 (14H, m, H<sub>a</sub>), 2.79–4.83 (235H, m, H<sub>b,c,d,e,f,g,h,i,m,n,p,4,5,8,9,10,11</sub>), 2.21–2.47 (2H, m, H<sub>o</sub>). HRESI-MS (pos.): 2188.20672, calc. for [C<sub>177</sub>H<sub>270</sub>O<sub>77</sub>N<sub>17</sub>I<sub>4</sub>·H]<sup>2+</sup> = 2188.20236.

**Water-soluble symmetric tricationic [2]rotaxane: permethyl- $\beta$ -cyclodextrin-stoppered bis-(3,5-bis-iodotriazole pyridinium) axle with pyridinium bis-amide 5-O-polyether macrocycle, **27**·(OTf)<sub>3</sub>**



The monocationic [2]rotaxane precursor **S4**·Cl (4.0 mg, 0.9  $\mu$ mol) was dissolved in CHCl<sub>3</sub> (1.5 mL) and CH<sub>3</sub>I (0.5 mL) was added. The solution was stirred at room temperature overnight, under N<sub>2</sub>. The solvent was removed *in vacuo*. Anion exchange to the triflate (OTf)<sup>-</sup> salt was achieved by passing a solution of the [2]rotaxane through a triflate-loaded Amberlite<sup>®</sup> column to afford **27**·(OTf)<sub>3</sub> (4.0 mg, 99%). <sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>)  $\delta$  (ppm): 9.74–10.33 (6H, m, H<sub>j,k,l</sub>), 9.24 (2H, br. s., H<sub>2</sub>), 8.46 (1H, br. s., H<sub>3</sub>), 6.14 (8H, br. s., H<sub>7,8</sub>), 5.00–5.25 (14H, m, H<sub>a</sub>), 2.78–4.99 (241H, m, H<sub>b,c,d,e,f,g,h,i,m,n,1,5,6,9,10,11,12</sub>), 2.25–2.43 (2H, m, H<sub>o</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz; CDCl<sub>3</sub>)  $\delta$  (ppm): 167.8, 159.7, 152.0, 137.2, 132.4, 130.9, 130.0, 129.9, 129.7, 128.8, 99.2–98.5, 90.8, 82.0–80.0, 71.2–68.0, 61.6–58.2, 45.9, 38.7–35.9, 32.7, 32.2, 31.9, 31.4, 30.3, 30.3, 30.0, 29.7, 29.7, 29.5, 29.4, 29.2, 28.9, 27.2, 27.1, 26.4, 25.6, 24.8, 24.3, 23.7, 23.4, 23.0, 22.7, 14.1, 14.0, 10.9. <sup>19</sup>F NMR (377 MHz; CDCl<sub>3</sub>)  $\delta$  (ppm): –78:28 (s, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>). HRESI-MS (pos.): 1468.47832, calc. for [C<sub>179</sub>H<sub>276</sub>I<sub>4</sub>N<sub>17</sub>O<sub>77</sub>]<sup>3+</sup> = 1468.48110.

### S3. $^1\text{H}$ NMR TITRATION PROTOCOL & DATA

#### Organic and aqueous–organic solvents

Spectra for  $^1\text{H}$  NMR titrations were recorded at 293 K on a Varian Unity Plus 500 spectrometer with  $^1\text{H}$  operating at 500 MHz. Initial sample volumes were 0.50 mL and concentrations were  $1.0\text{ mmol L}^{-1}$  of host. Solutions ( $50\text{ mmol L}^{-1}$ ) of anions as their tetrabutylammonium salts were added in aliquots, the samples thoroughly shaken and spectra recorded. Spectra were recorded at 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, 3.0, 4.0, 5.0, 7.0 and 10 equivalents of anion. Stability constants were obtained by analysis of the resulting data using the WinEQNMR2<sup>S15</sup> computer program; In all cases where association constants were calculated, bound and unbound species were found to be in fast exchange on the NMR timescale.

#### Aqueous titrations

A solution of the tricationic [2]rotaxane **27**·(OTf)<sub>3</sub> (1 mM) was titrated with anions as the sodium salts (0.5 M) in 9:1 D<sub>2</sub>O:acetone-*d*<sub>6</sub> at 293 K; all spectra were referenced to the acetone-*d*<sub>6</sub> resonance at 2.10 ppm. The chemical shift of protons b, 2 and 3, as appropriate, were monitored. Spectra were recorded at 0, 1, 2, 3, 5, 7, 10, 15, 20, 25, 30, 40, 50, 60, 80, 100 and 120 equivalents of anion. Stability constants were obtained by analysis of the resulting data using the WinEQNMR2<sup>S15</sup> computer program; In all cases where association constants were calculated, bound and unbound species were found to be in fast exchange on the NMR timescale.

Binding Isotherms for Anion Association of **19**·PF<sub>6</sub>

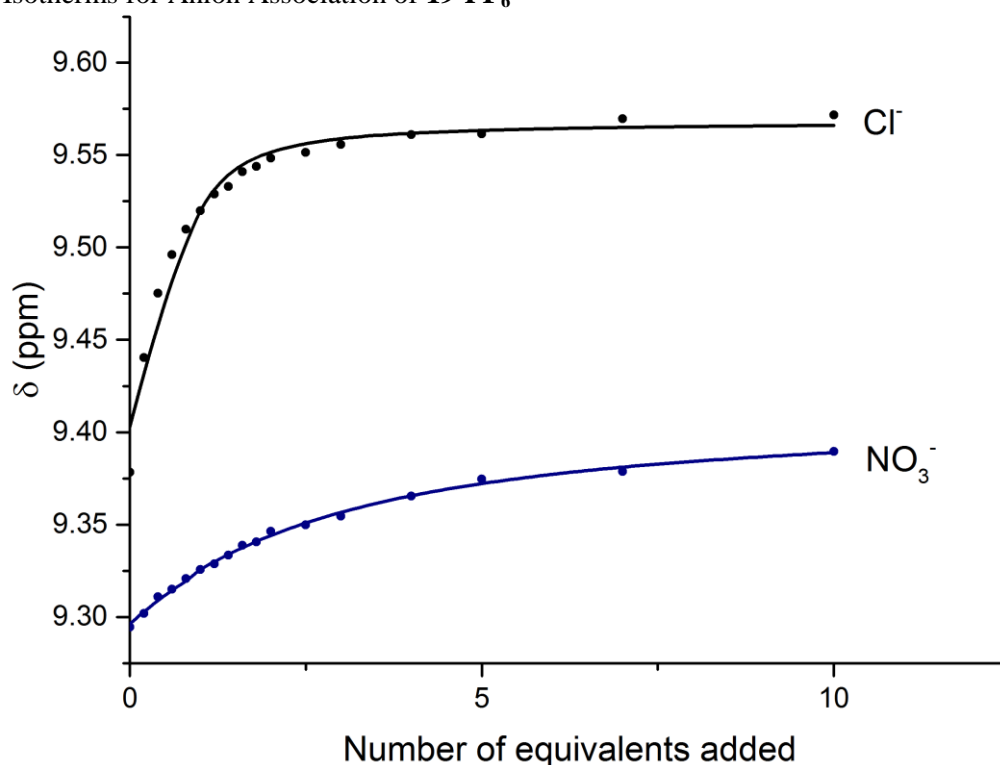


Figure S1: Observed data (solid points) and fitted isotherms<sup>S15</sup> (lines) for addition of anions as their TBA salts to **19**·PF<sub>6</sub> (293 K, 1:1 CDCl<sub>3</sub>:CD<sub>3</sub>OD, 500 MHz).

Binding Isotherms for Anion Association of  $20 \cdot (\text{PF}_6)_2$

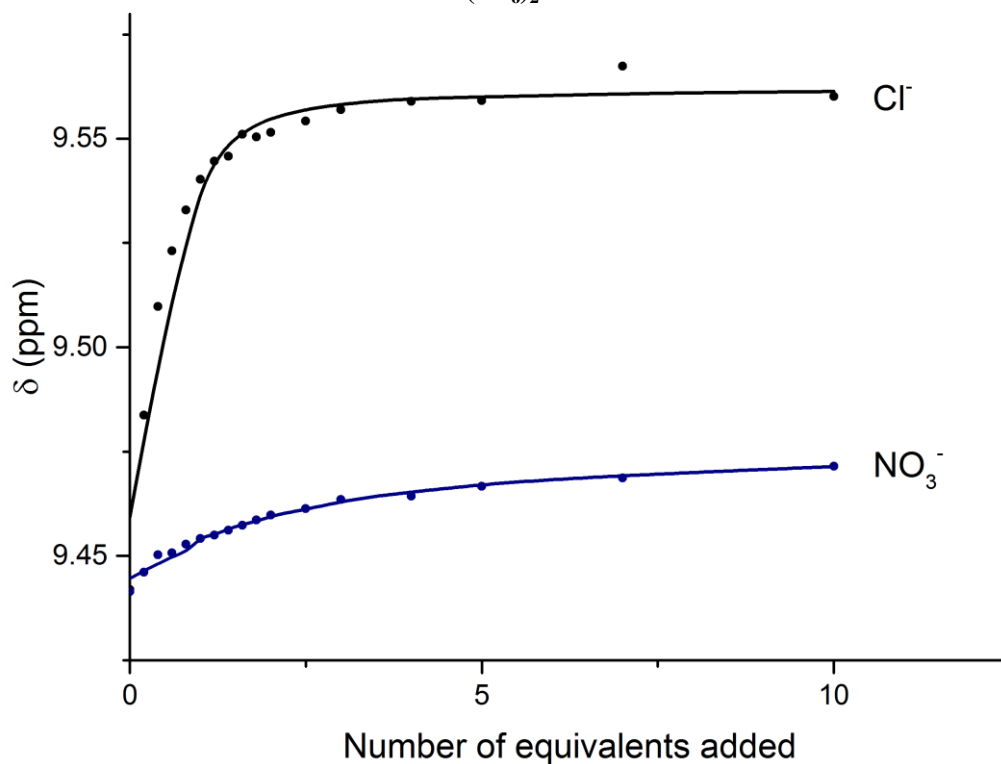


Figure S2: Observed data (solid points) and fitted isotherms<sup>S15</sup> (lines) for addition of anions as their TBA salts to  $20 \cdot (\text{PF}_6)_2$  (293 K, 45:45:10  $\text{CDCl}_3$ : $\text{CD}_3\text{OD}$ : $\text{D}_2\text{O}$ , 500 MHz).

Binding Isotherms for Anion Association of  $27 \cdot (\text{OTf})_3$

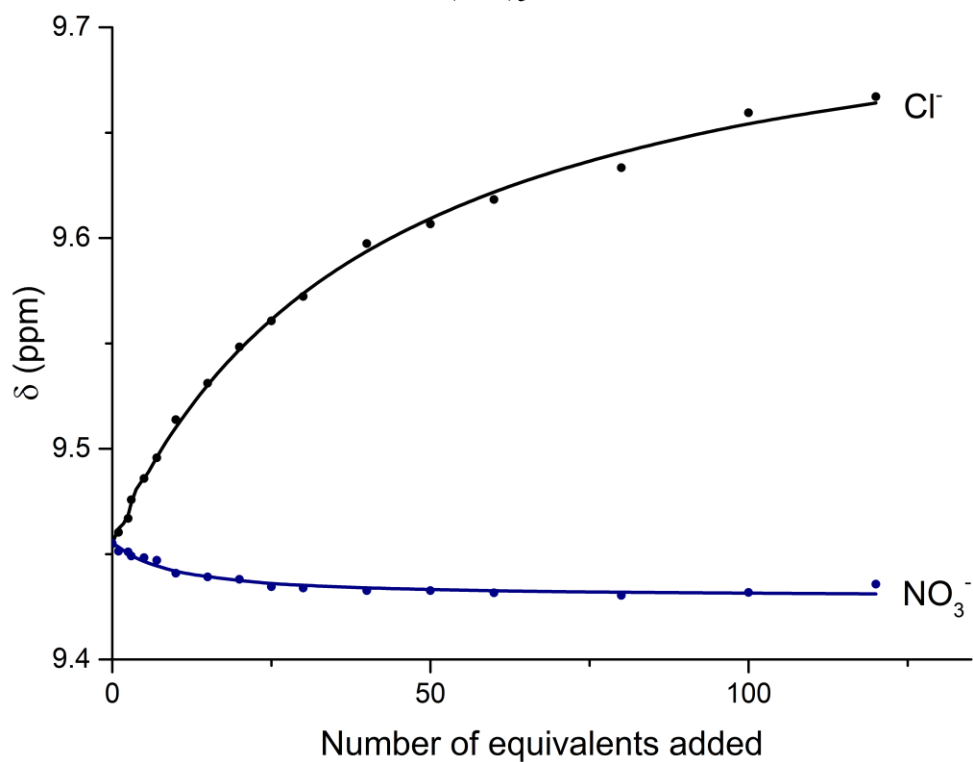


Figure S3: Observed data (solid points) and fitted isotherms<sup>S15</sup> (lines) for addition of anions as their sodium salts to  $27 \cdot (\text{OTf})_3$  (293 K, 9:1  $\text{D}_2\text{O}$ :acetone- $d_6$ , 500 MHz).

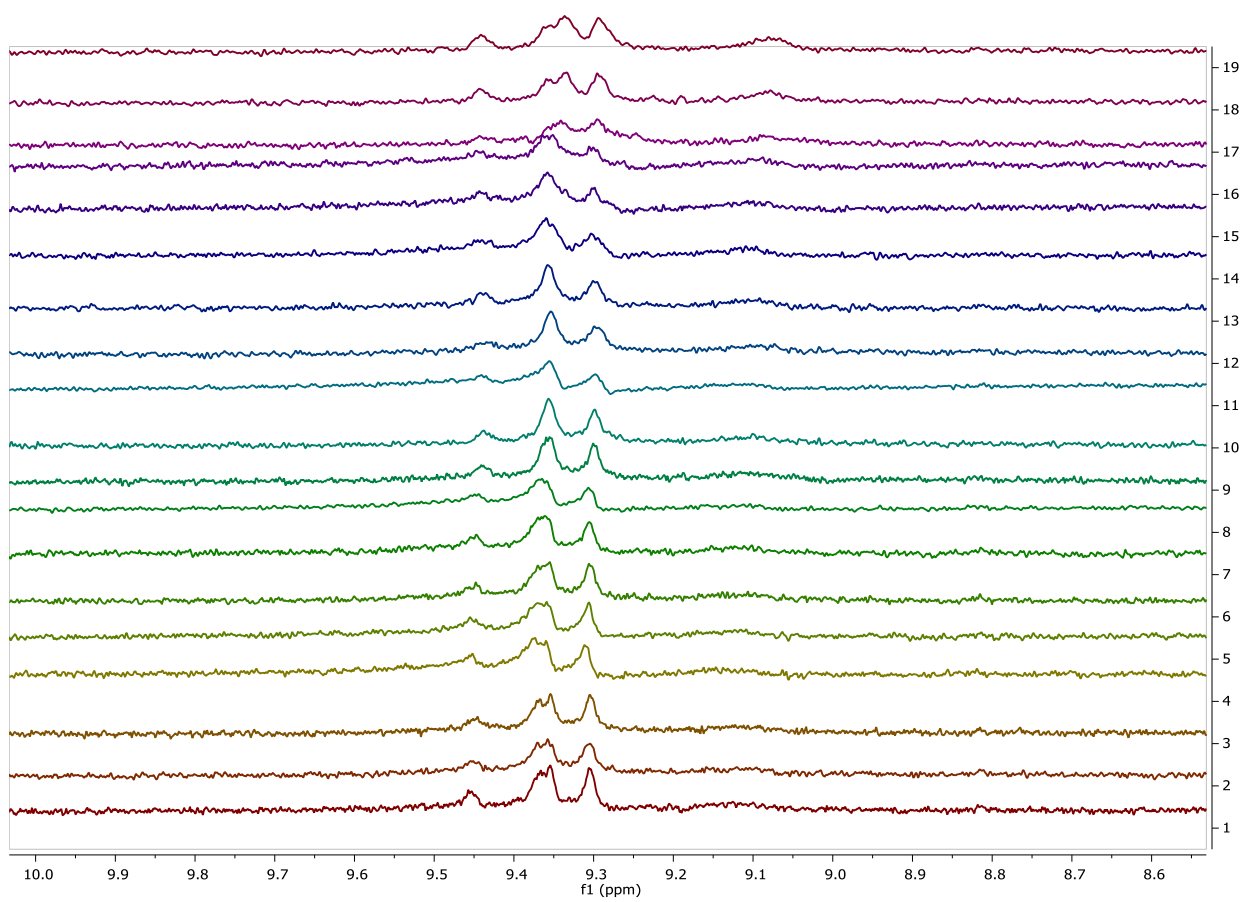


Figure S4: Representative  $^1\text{H}$  NMR spectra for the titration of  $27\cdot(\text{OTf})_3$  with  $\text{NO}_3^-$  in 9:1  $\text{D}_2\text{O}:\text{acetone-}d_6$ .



## S4. NUCLEAR MAGNETIC RESONANCE ( $^1\text{H}$ , $^{13}\text{C}$ , $^{31}\text{P}$ , $^{19}\text{F}$ AND 2D $^1\text{H}$ - $^1\text{H}$ ROESY) SPECTRA

### 3-(hydroxypropyl-iodotriazolyl)-5-(TBDMS-ethynyl)pyridine, **5**

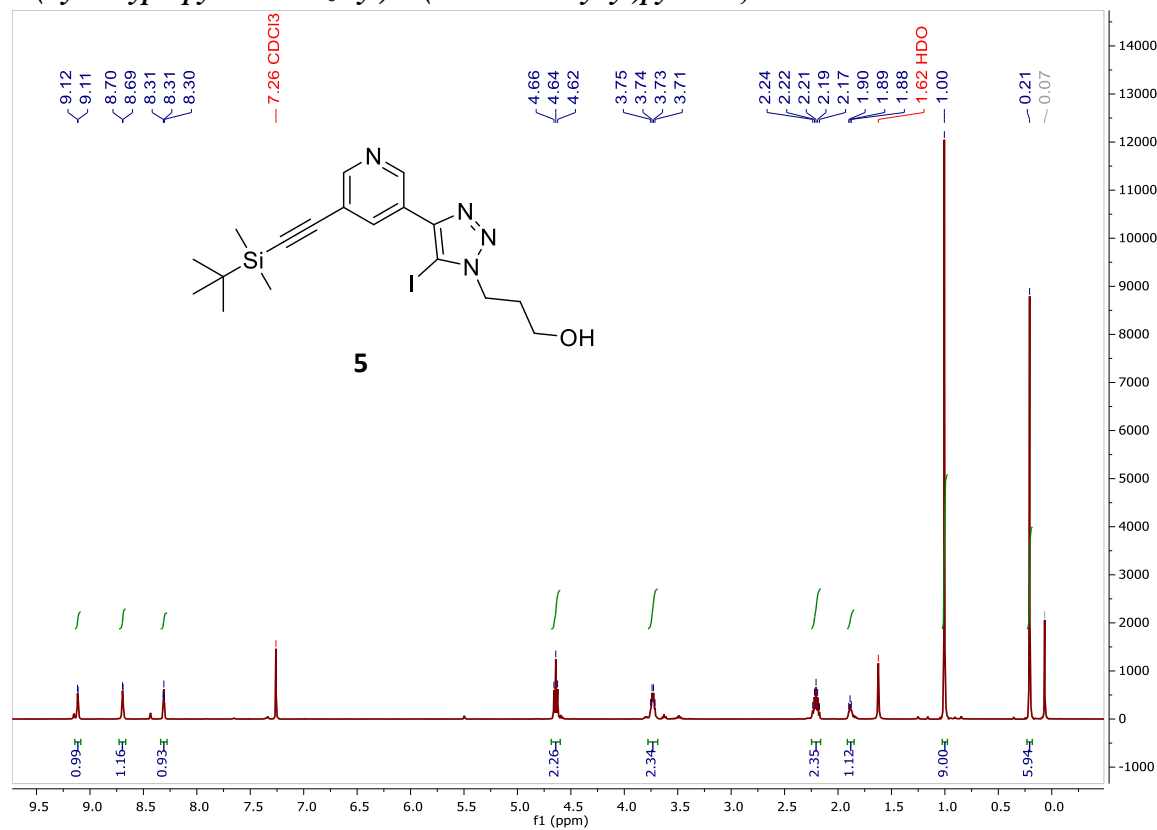


Figure S5:  $^1\text{H}$  NMR spectrum of 3-(hydroxypropyl-iodotriazolyl)-5-(TBDMS-ethynyl)pyridine, **5** (400 MHz,  $\text{CDCl}_3$ )

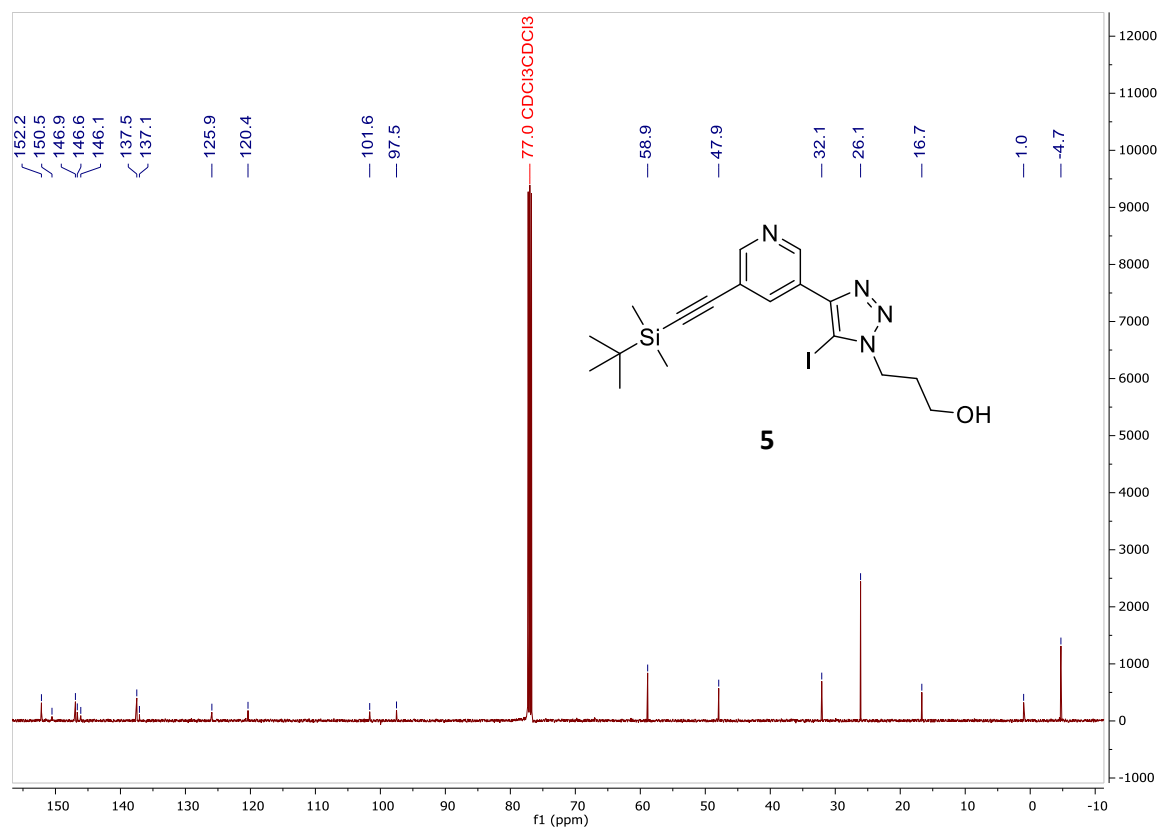


Figure S6:  $^{13}\text{C}$  NMR spectrum of 3-(hydroxypropyl-iodotriazolyl)-5-(TBDMS-ethynyl)pyridine, **5** (126 MHz,  $\text{CDCl}_3$ )

3-(TMS-ethynyl)-5-(hydroxypropyl-ethynyl)pyridine, **7**

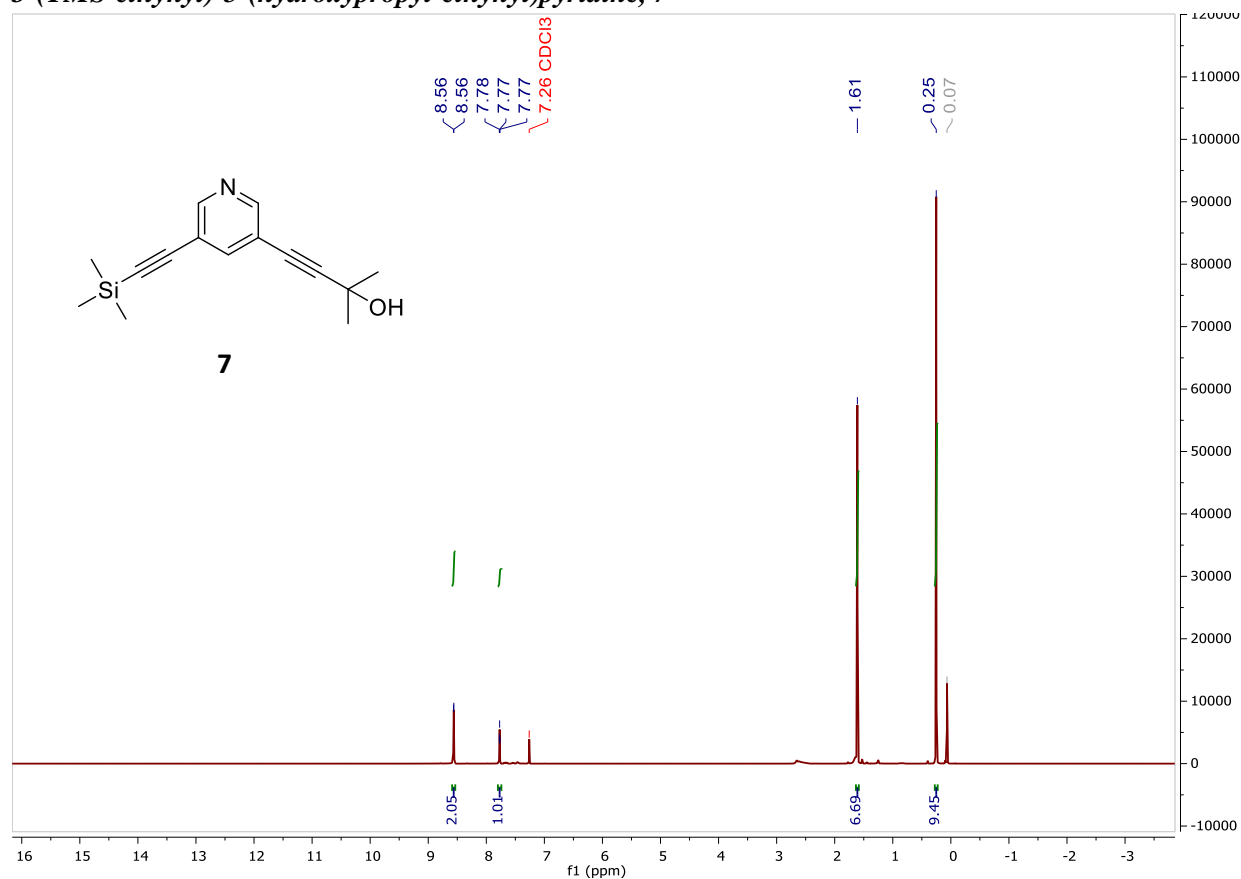


Figure S7: <sup>1</sup>H NMR spectrum of 3-(TMS-ethynyl)-5-(hydroxypropyl-ethynyl)pyridine, **7** (400 MHz, CDCl<sub>3</sub>)

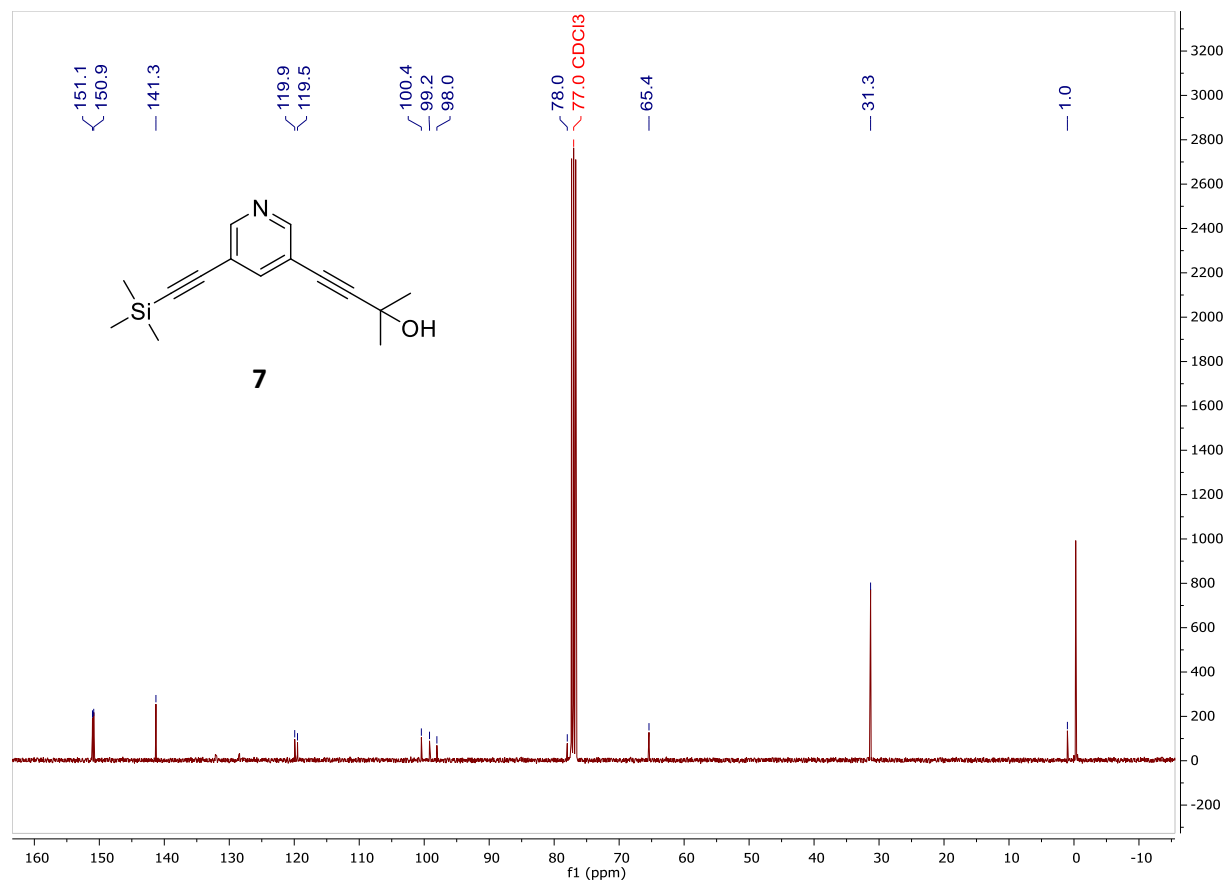


Figure S8: <sup>13</sup>C NMR spectrum of 3-(TMS-ethynyl)-5-(hydroxypropyl-ethynyl)pyridine, **7** (100 MHz, CDCl<sub>3</sub>)

3-ethynyl-5-(hydroxypropyl-ethynyl)pyridine, 8

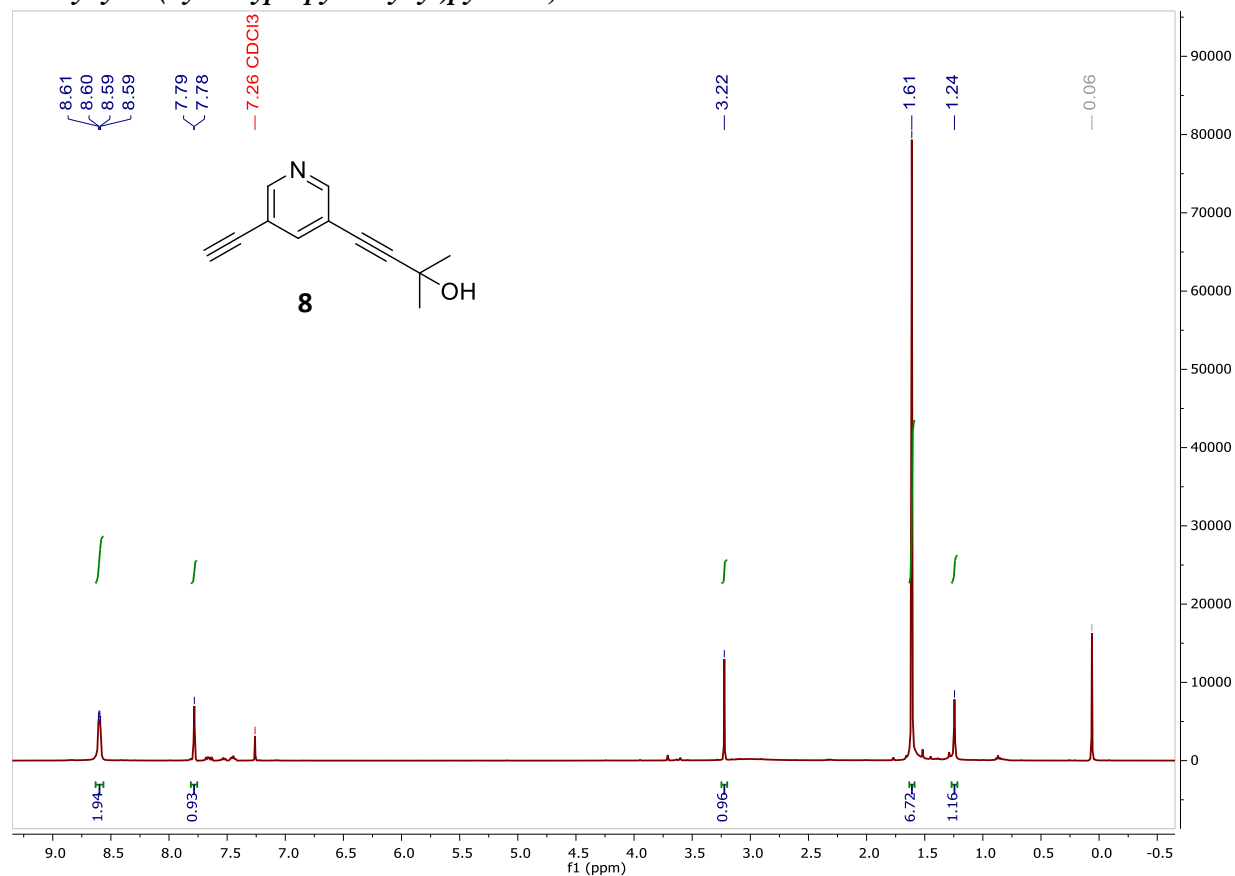


Figure S9: <sup>1</sup>H NMR spectrum of 3-ethynyl-5-(hydroxypropyl-ethynyl)pyridine, 8 (400 MHz, CDCl<sub>3</sub>)

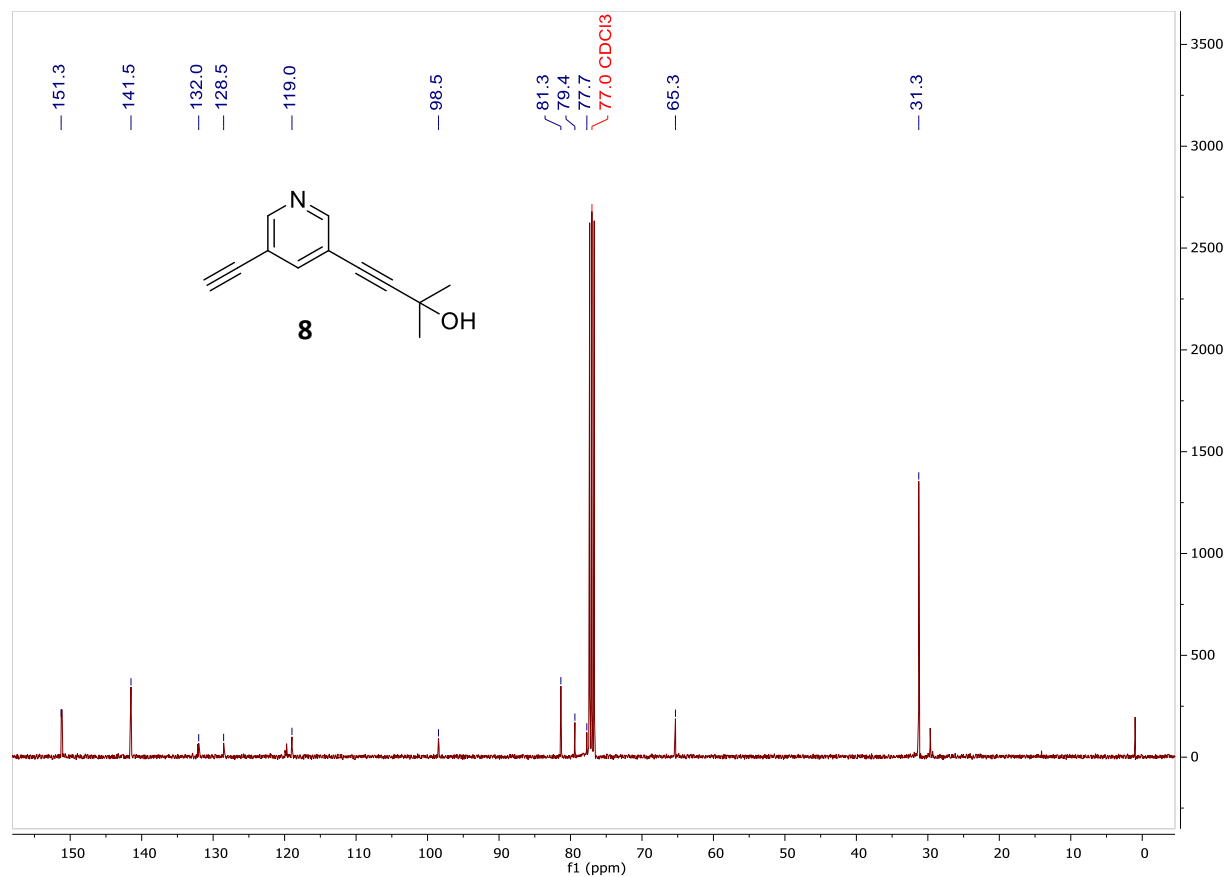


Figure S10: <sup>13</sup>C NMR spectrum of 3-ethynyl-5-(hydroxypropyl-ethynyl)pyridine, 8 (100 MHz, CDCl<sub>3</sub>)

3,5-diiodoethynyl pyridine, **12**

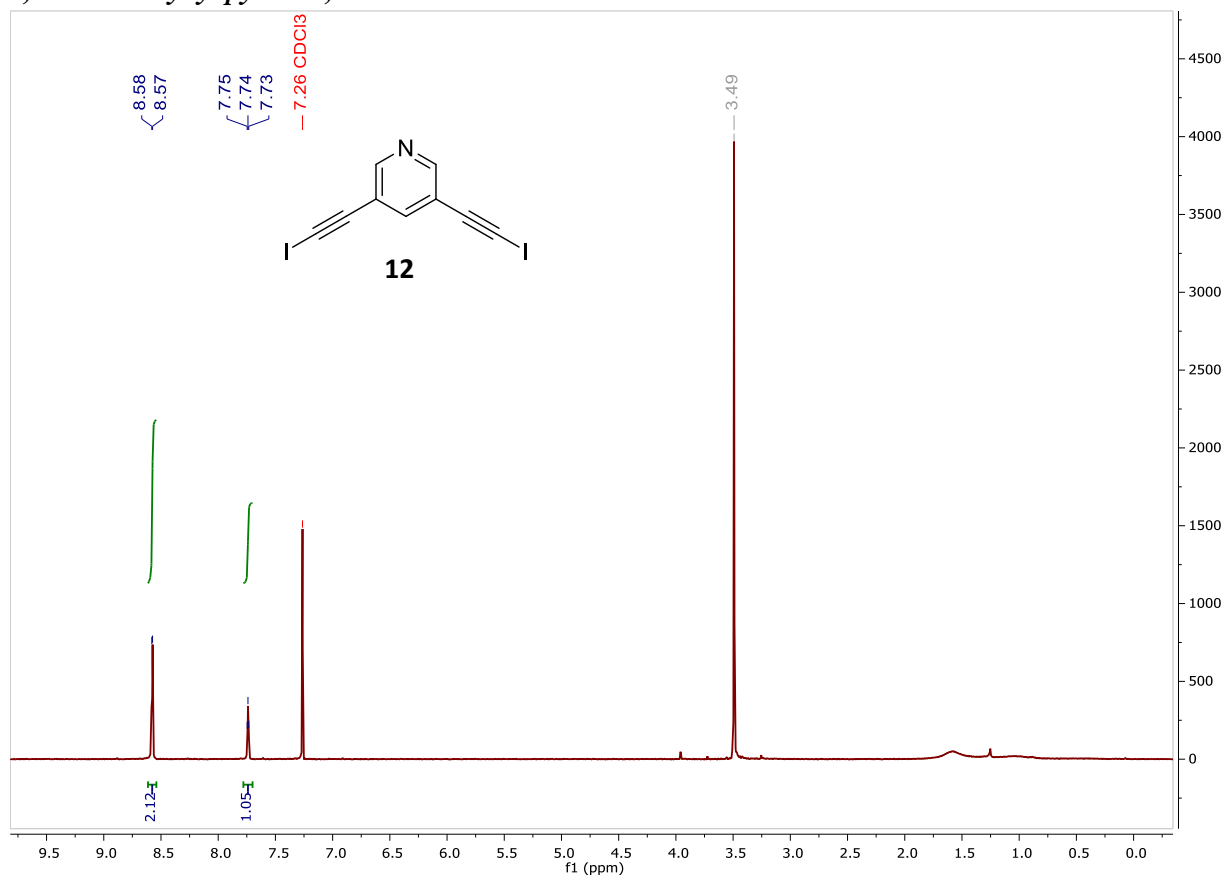


Figure S11:  $^1\text{H}$  NMR spectrum of 3,5-diiodoethynyl pyridine, **12** (300 MHz,  $\text{CDCl}_3$ )

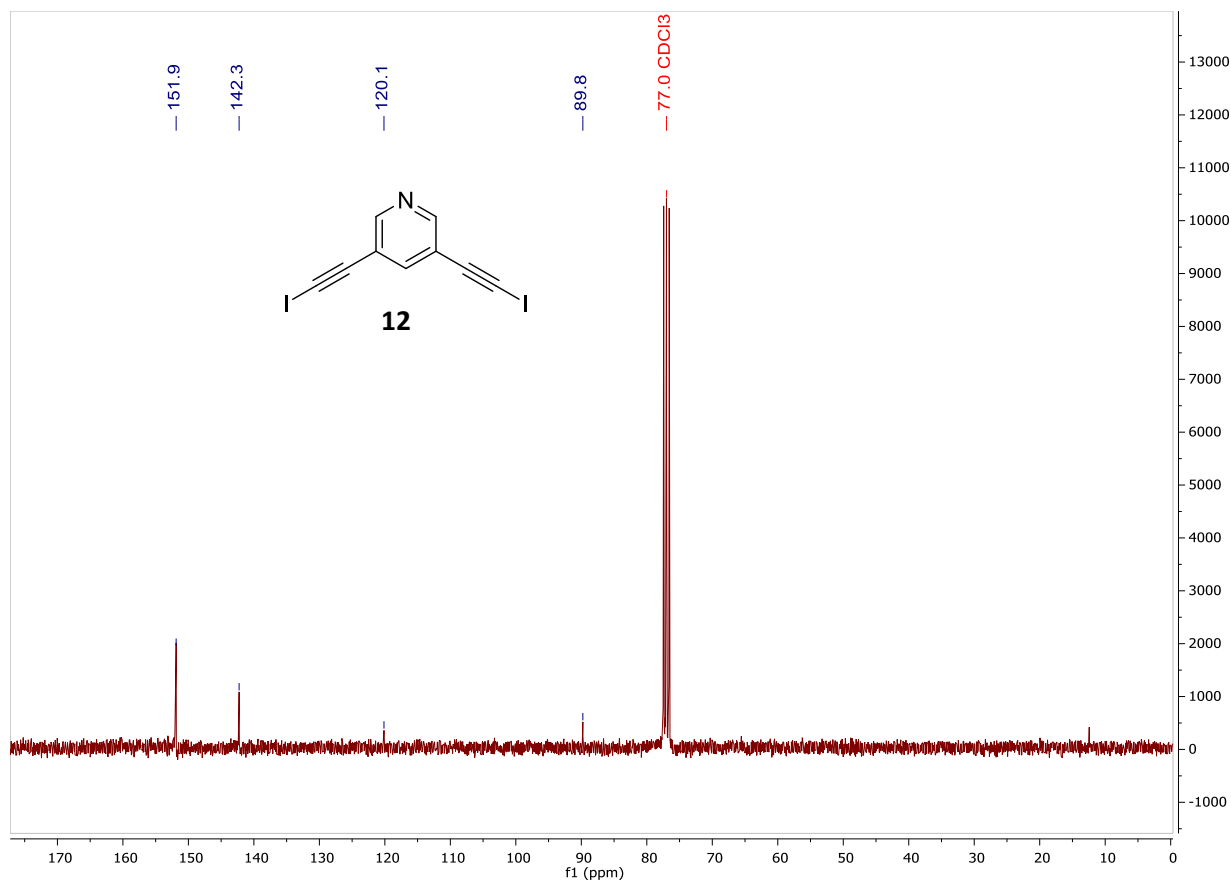
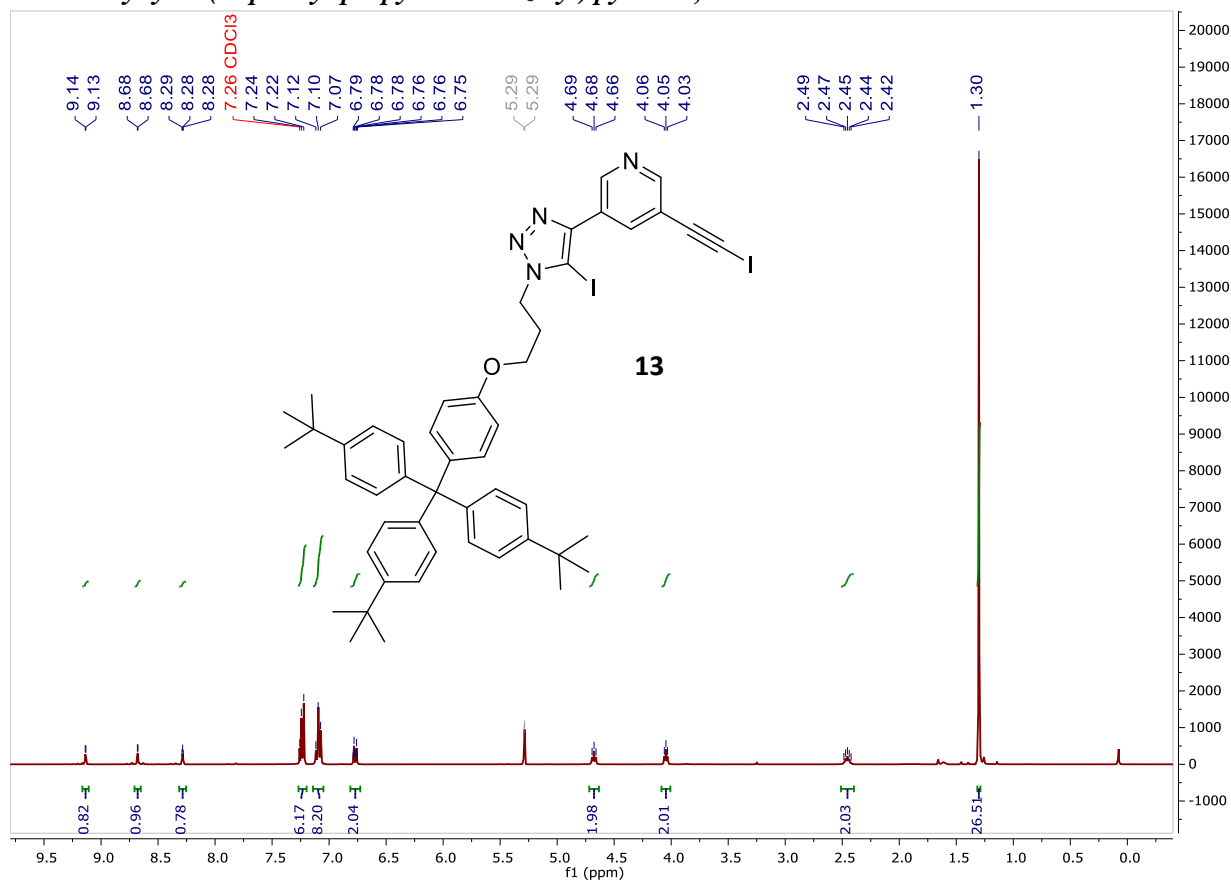
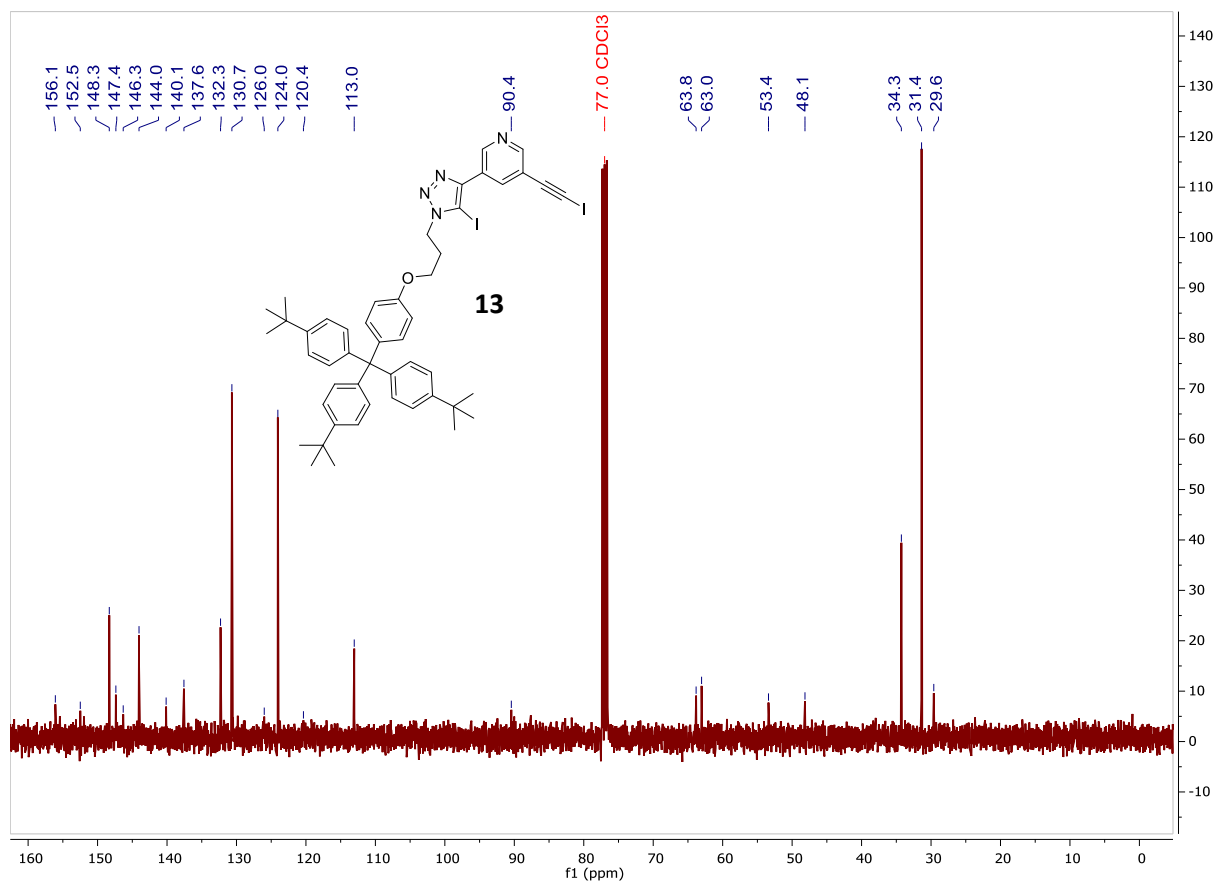


Figure S12:  $^{13}\text{C}$  NMR spectrum of 3,5-diiodoethynyl pyridine, **12** (76 MHz,  $\text{CDCl}_3$ )

**3-iodoethynyl-5-(terphenyl-propyl-iodotriazolyl) pyridine, 13**



**Figure S13:** <sup>1</sup>H NMR spectrum of 3-iodoethynyl-5-(terphenyl-propyl-iodotriazolyl) pyridine, **13** (400 MHz, CDCl<sub>3</sub>)



**Figure S14:** <sup>13</sup>C NMR spectrum of 3-iodoethynyl-5-(terphenyl-propyl-iodotriazolyl) pyridine, **13** (100 MHz, CDCl<sub>3</sub>)

3-(mesyl-propyl-iodotriazolyl)-5-(terphenyl-propyl-iodotriazolyl) pyridine, 15

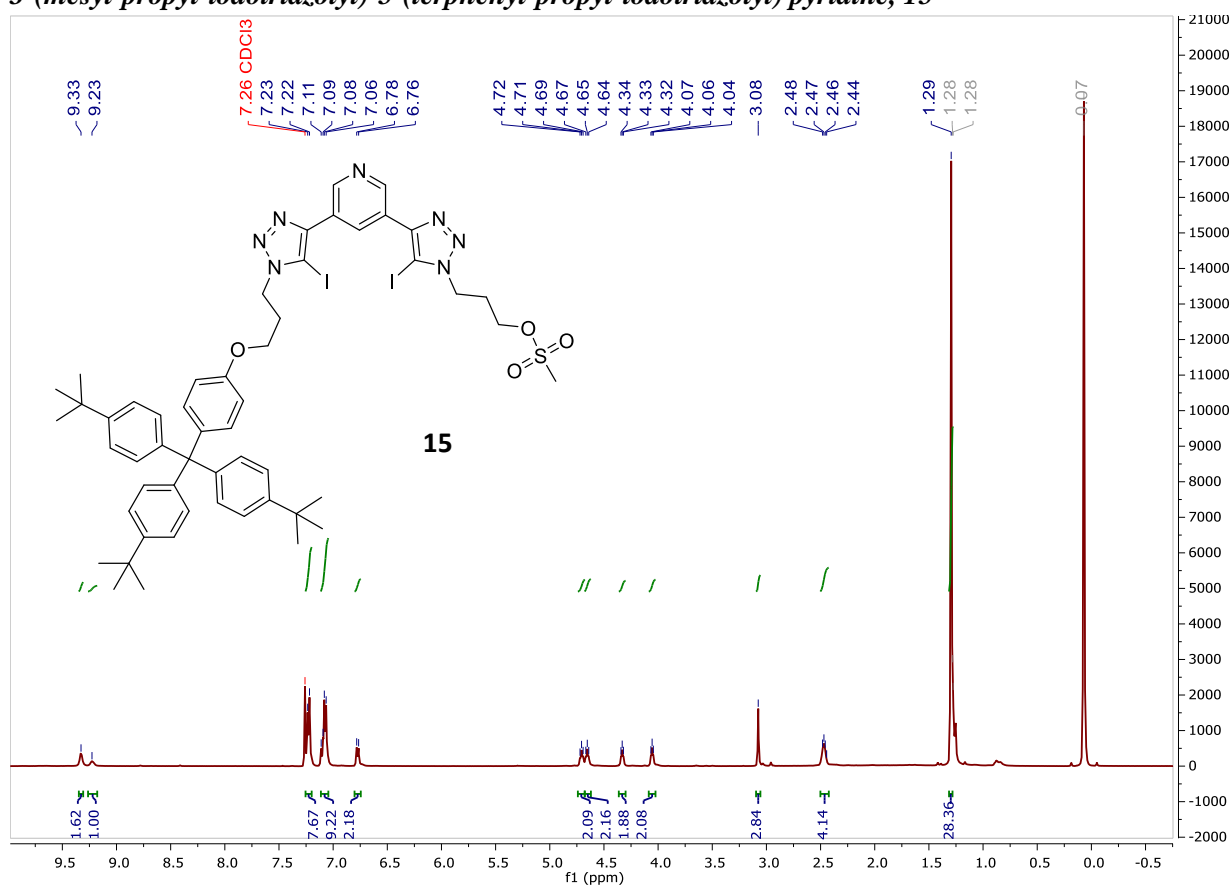


Figure S15: <sup>1</sup>H NMR spectrum of 3-(mesyl-propyl-iodotriazolyl)-5-(terphenyl-propyl-iodotriazolyl) pyridine, 15 (500 MHz, CDCl<sub>3</sub>)

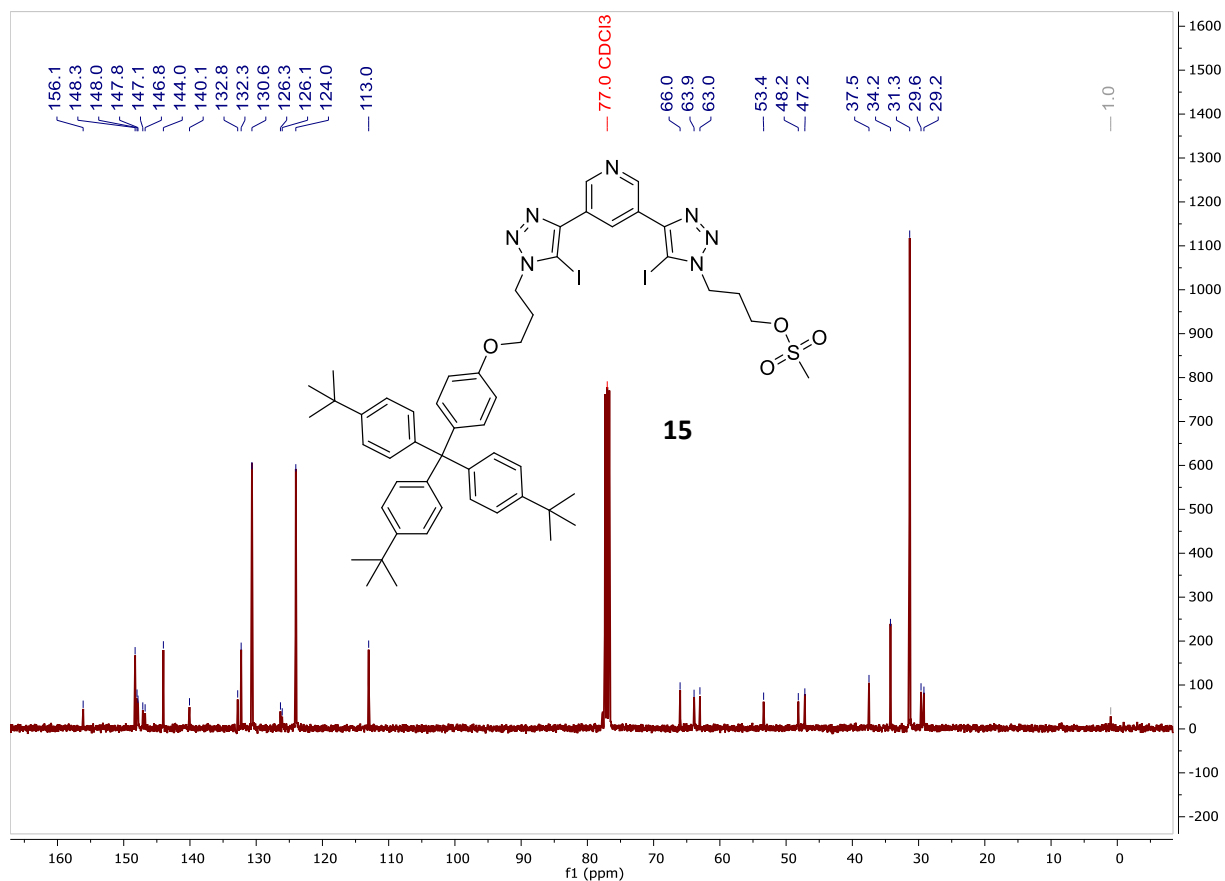


Figure S16: <sup>13</sup>C NMR spectrum of 3-(mesyl-propyl-iodotriazolyl)-5-(terphenyl-propyl-iodotriazolyl) pyridine, 15 (100 MHz, CDCl<sub>3</sub>)

**3-(azido-propyl-iodotriazolyl)-5-(terphenyl-propyl-iodotriazolyl) pyridine, 16**

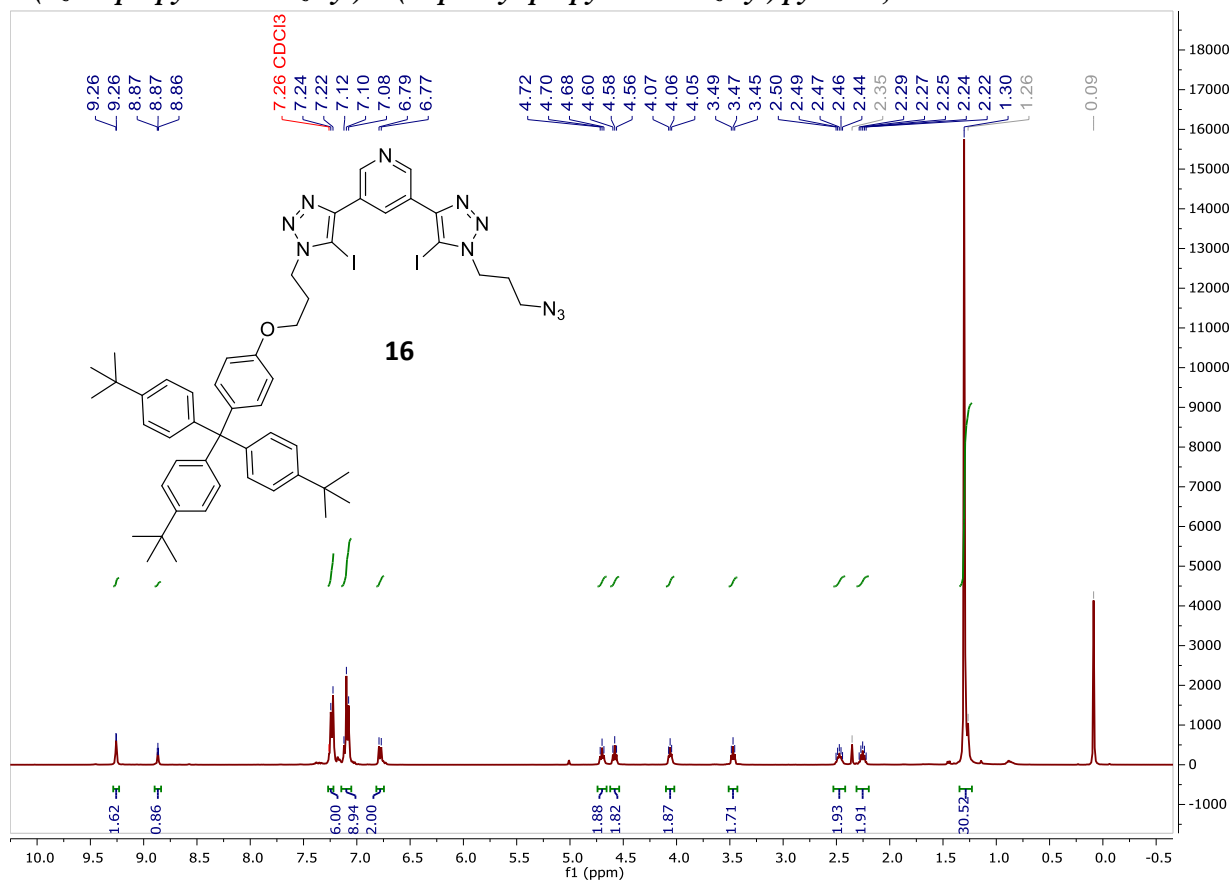


Figure S17: <sup>1</sup>H NMR spectrum of 3-(azido-propyl-iodotriazolyl)-5-(terphenyl-propyl-iodotriazolyl) pyridine, 16 (400 MHz, CDCl<sub>3</sub>)

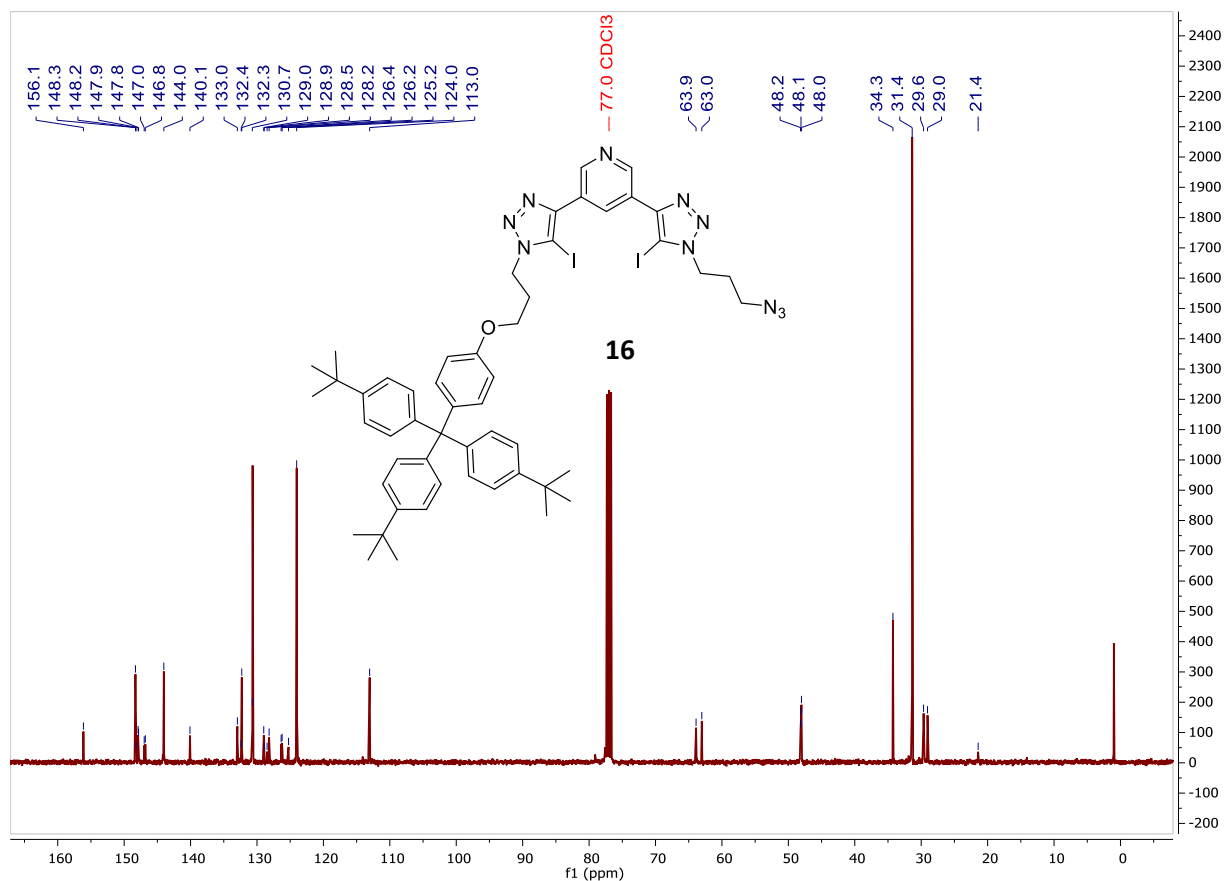
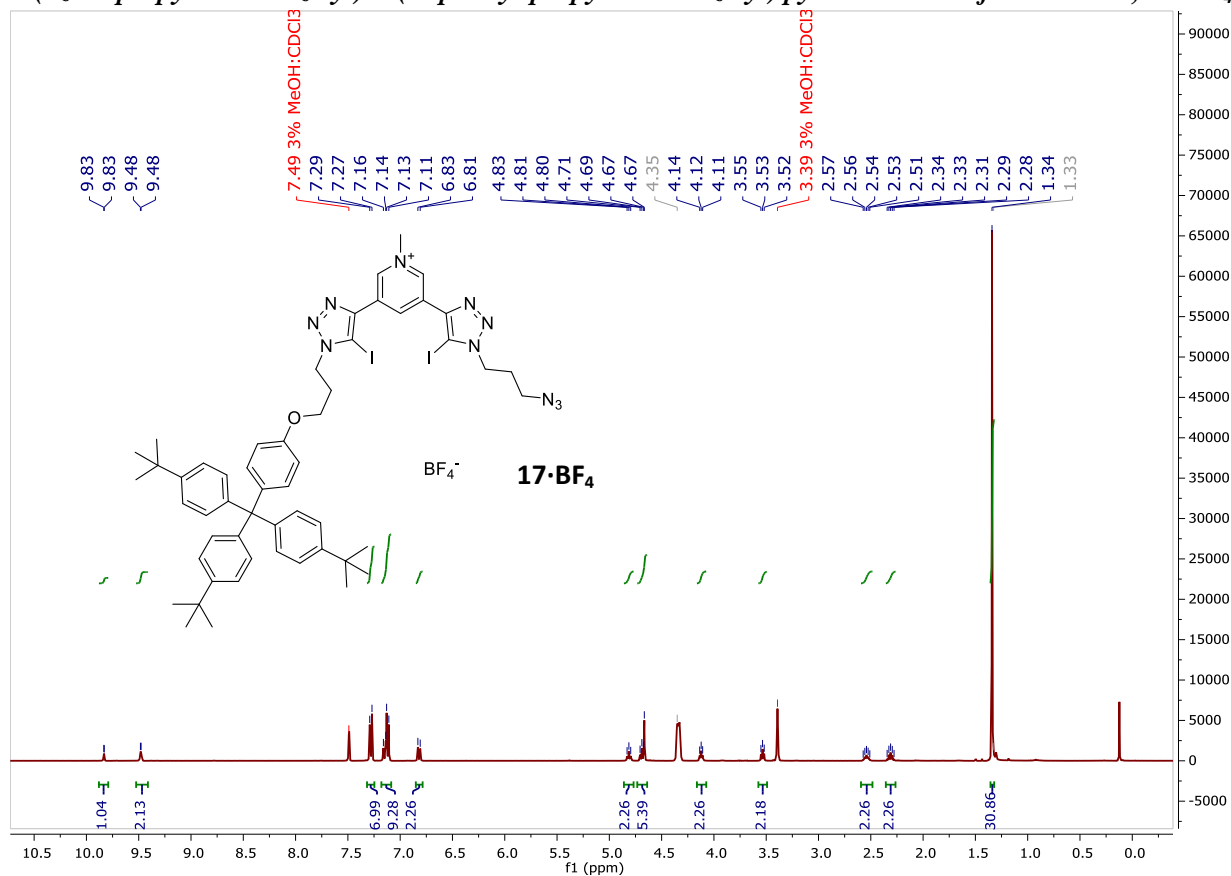
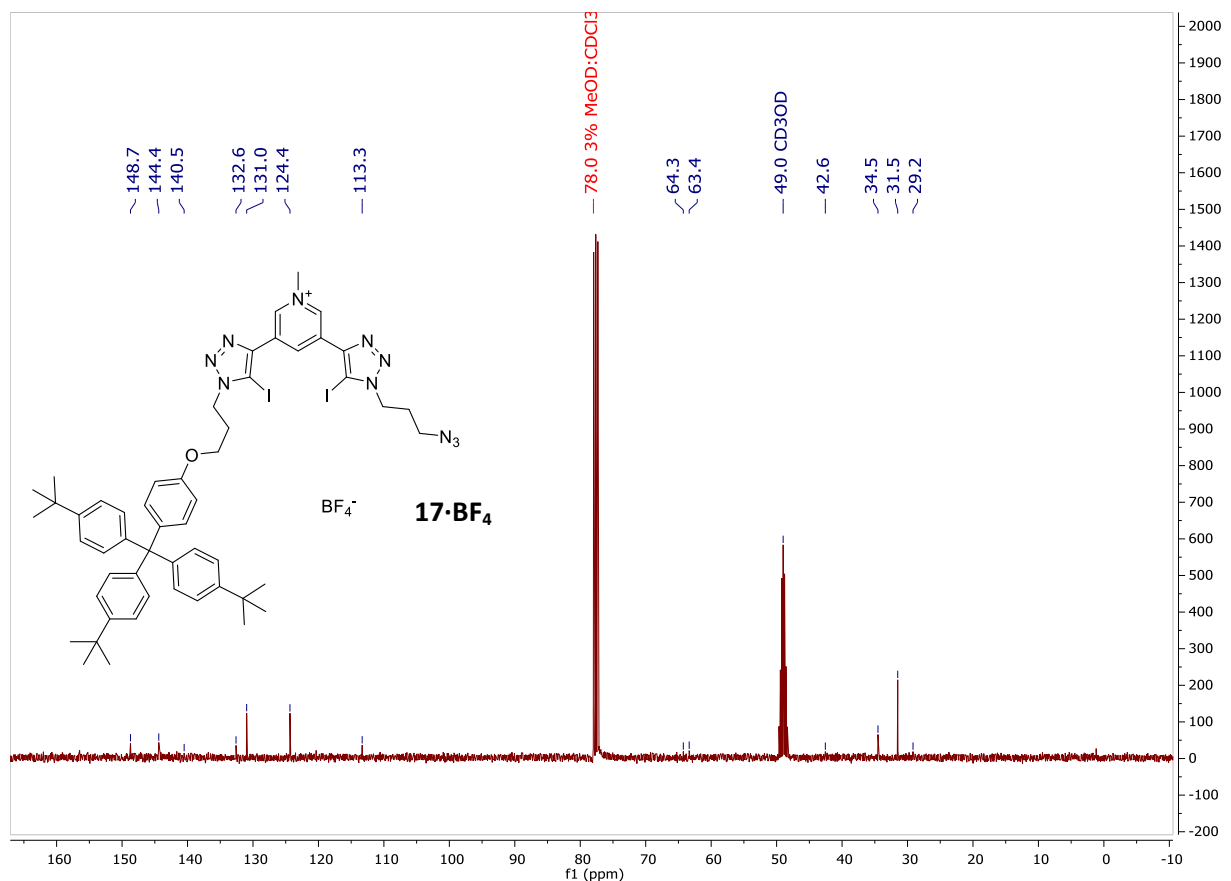


Figure S18: <sup>13</sup>C NMR spectrum of 3-(azido-propyl-iodotriazolyl)-5-(terphenyl-propyl-iodotriazolyl) pyridine, 16 (100 MHz, CDCl<sub>3</sub>)

**3-(azido-propyl-iodotriazolyl)-5-(terphenyl-propyl-iodotriazolyl) pyridinium tetrafluoroborate, 17·BF<sub>4</sub>**



**Figure S19:** <sup>1</sup>H NMR spectrum of 3-(azido-propyl-iodotriazolyl)-5-(terphenyl-propyl-iodotriazolyl) pyridinium tetrafluoroborate, 17·BF<sub>4</sub> (400 MHz, 3% MeOD:CDCl<sub>3</sub>)



**Figure S20:** <sup>13</sup>C NMR spectrum of 3-(azido-propyl-iodotriazolyl)-5-(terphenyl-propyl-iodotriazolyl) pyridinium tetrafluoroborate, 17·BF<sub>4</sub> (100 MHz, 3% MeOD:CDCl<sub>3</sub>)



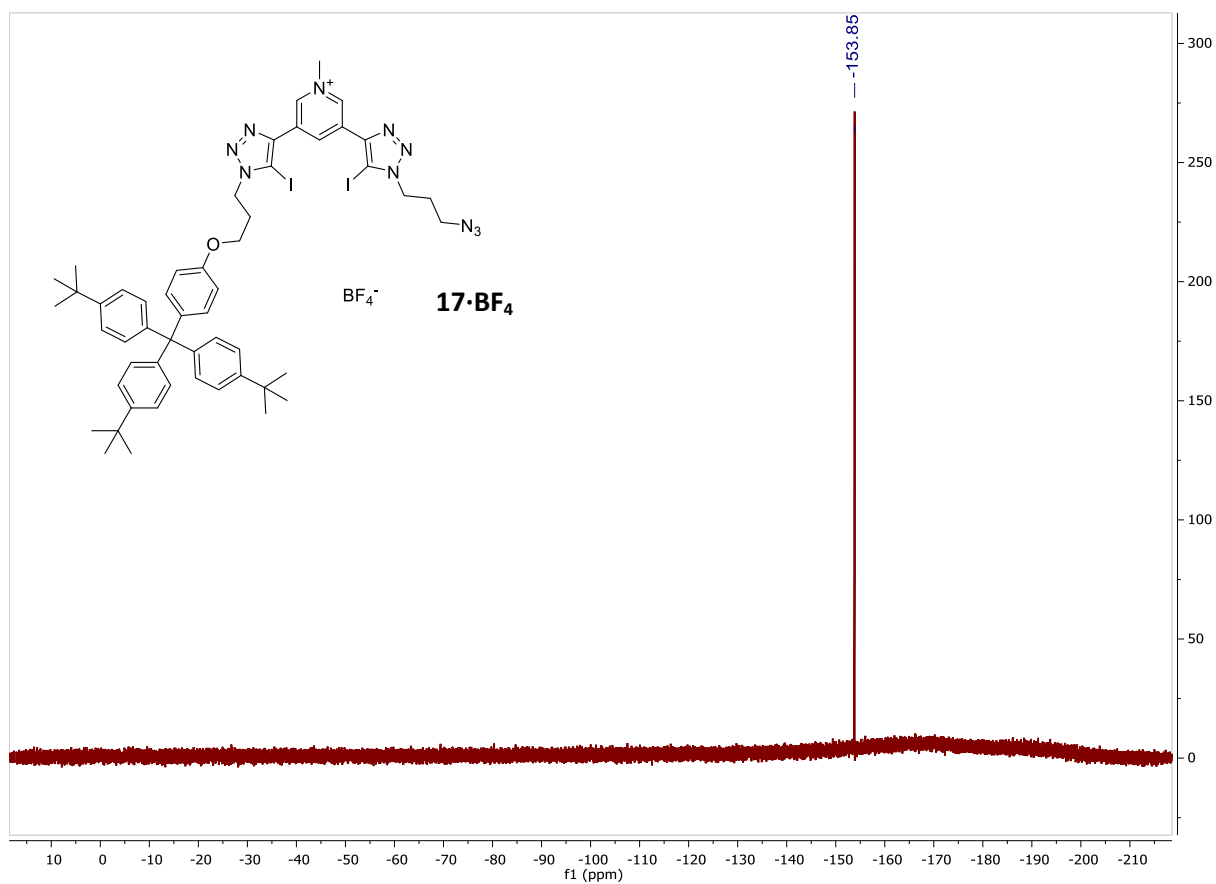
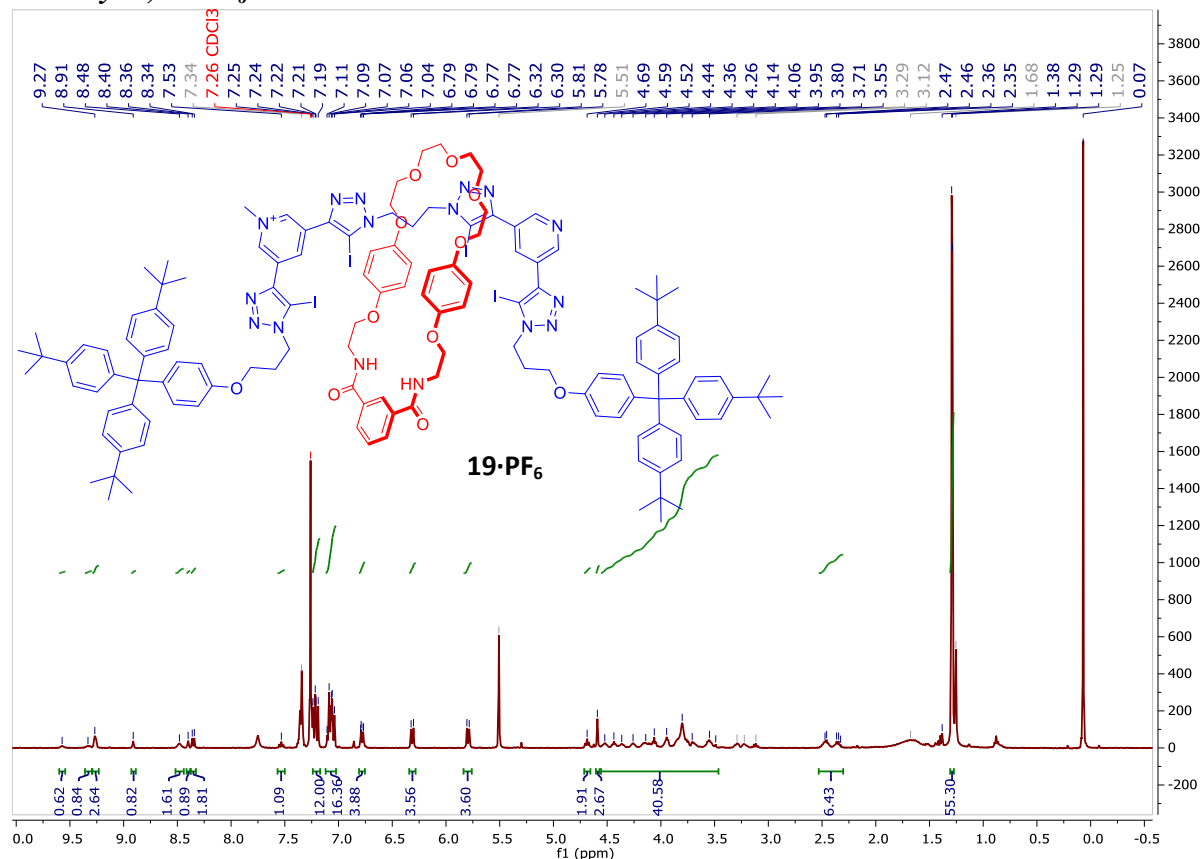
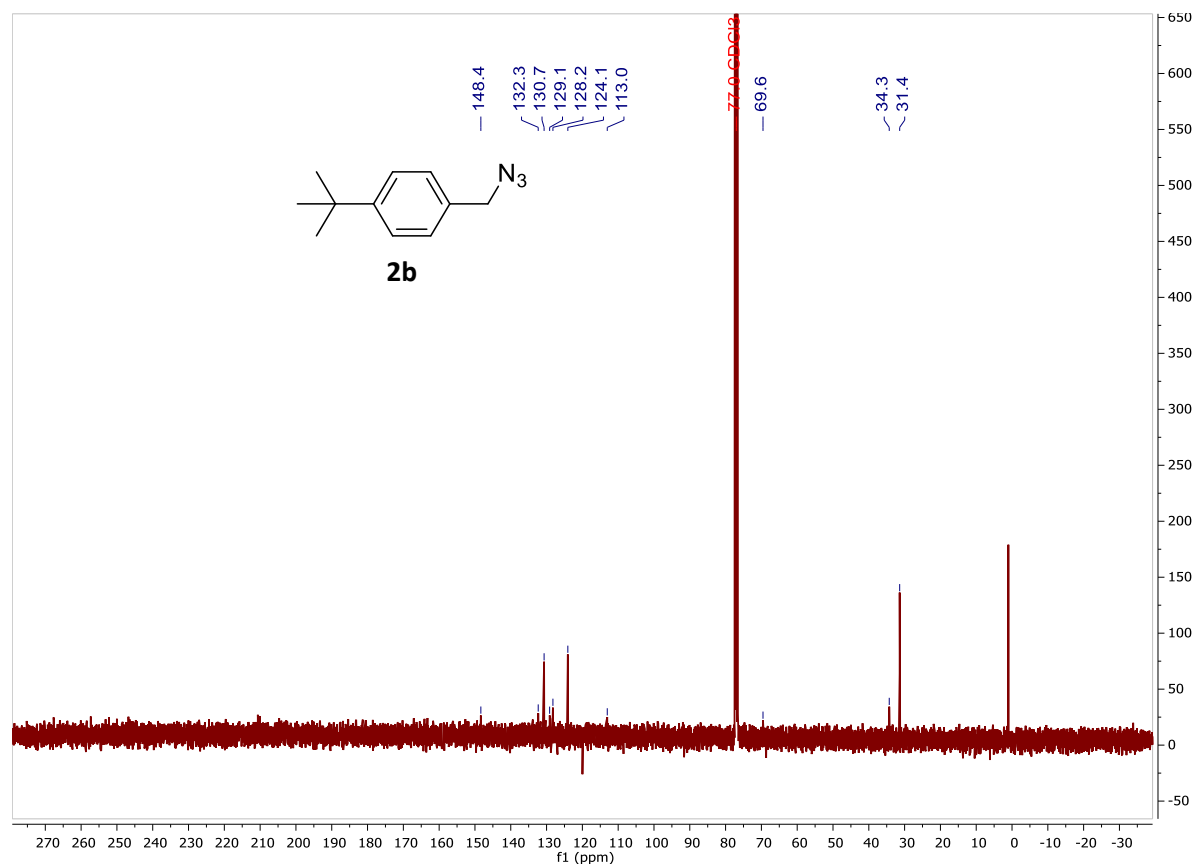


Figure S21: <sup>19</sup>F NMR spectrum of 3-(azido-propyl-iodotriazolyl)-5-(terphenyl-propyl-iodotriazolyl) pyridinium tetrafluoroborate, **17·BF<sub>4</sub>** (376 MHz, 3% MeOD:CDCl<sub>3</sub>)

**Asymmetric rotaxane: pyridinium/pyridine bis-iodotriazole axle–isophthalamide 5-O-polyether macrocycle, 19·PF<sub>6</sub>**



**Figure S22:** <sup>1</sup>H NMR spectrum of Asymmetric rotaxane: pyridinium/pyridine bis-iodotriazole axle–isophthalamide 5-O-polyether macrocycle, 19·PF<sub>6</sub> (400 MHz, CDCl<sub>3</sub>)



**Figure S23:** <sup>13</sup>C NMR spectrum of Asymmetric rotaxane: pyridinium/pyridine bis-iodotriazole axle–isophthalamide 5-O-polyether macrocycle, 19·PF<sub>6</sub> (100 MHz, CDCl<sub>3</sub>)

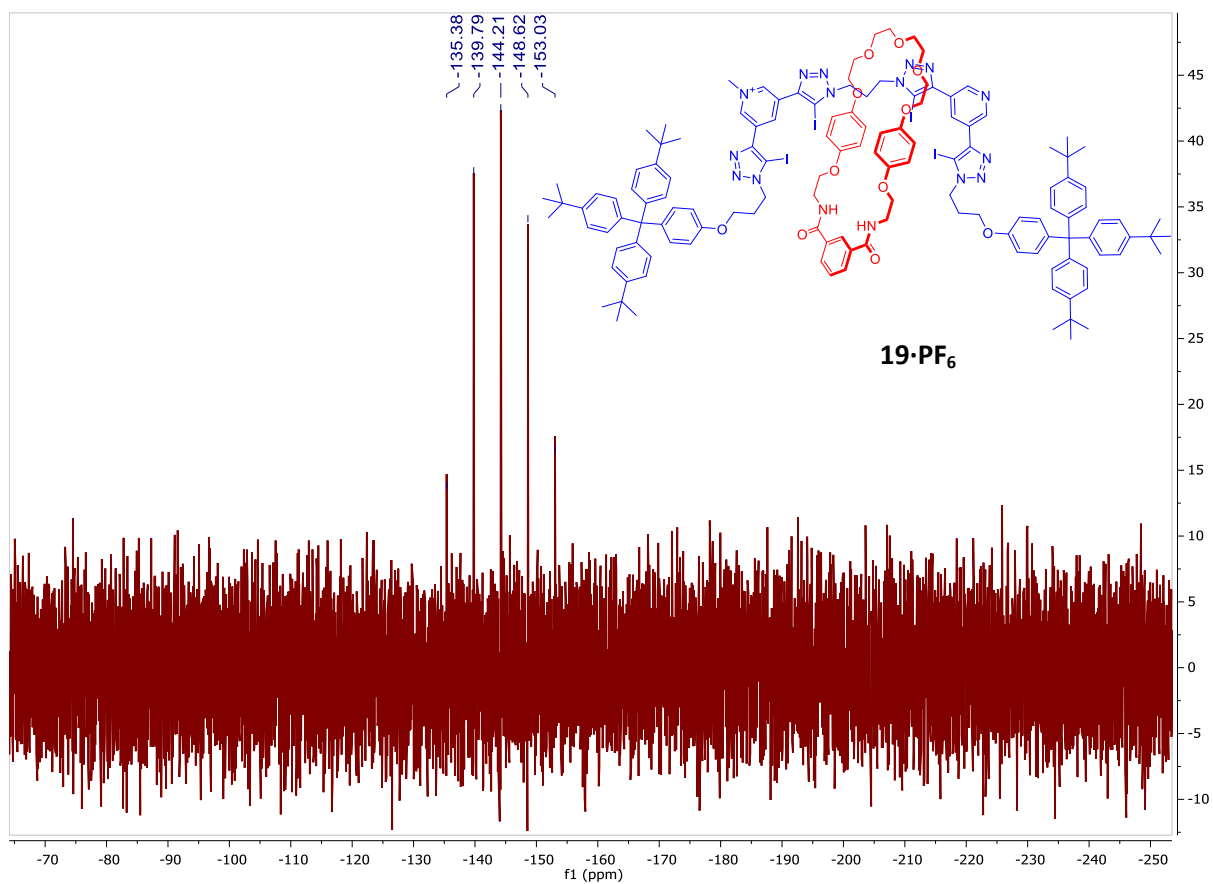


Figure S24: <sup>31</sup>P NMR spectrum of Asymmetric rotaxane: pyridinium/pyridine bis-iodotriazole axle–isophthalamide 5-O-polyether macrocycle, **19-PF<sub>6</sub>** (162 MHz, CDCl<sub>3</sub>)

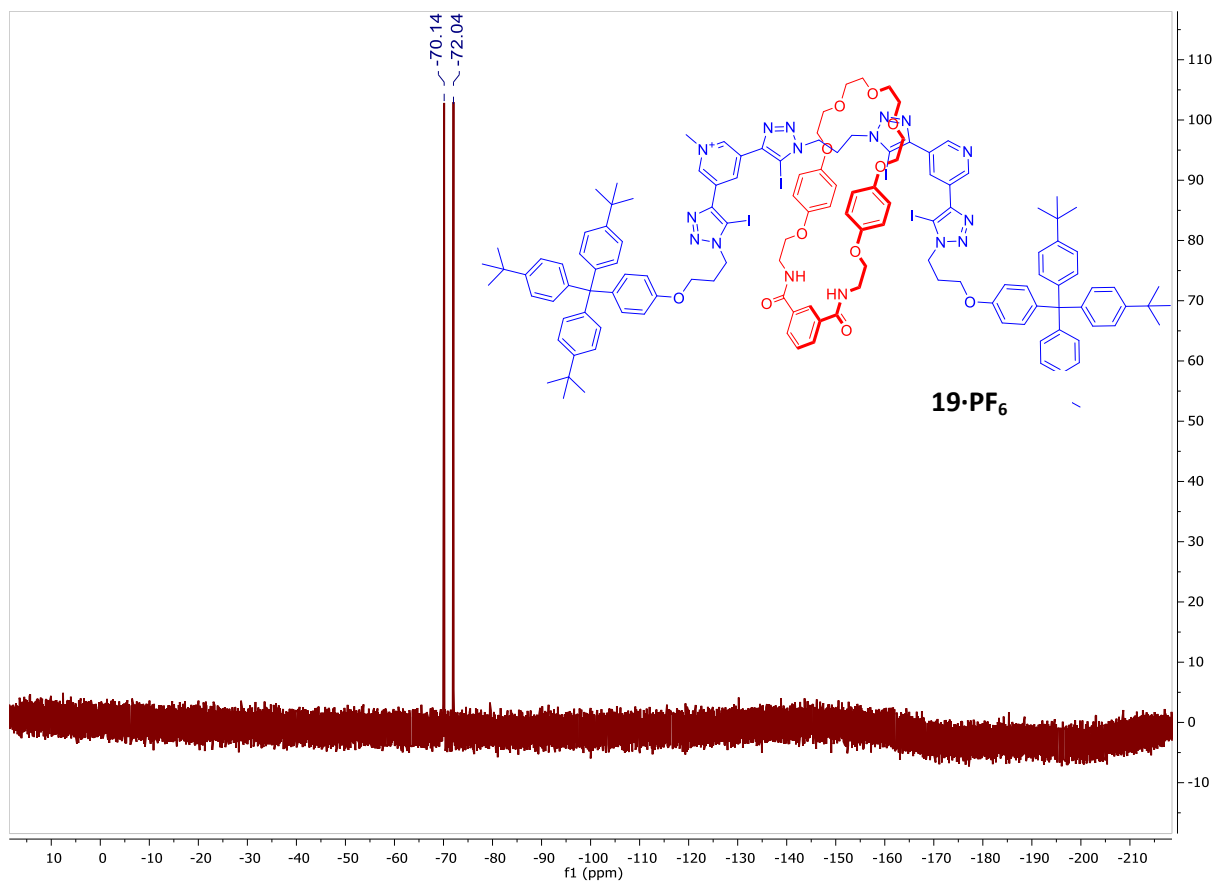
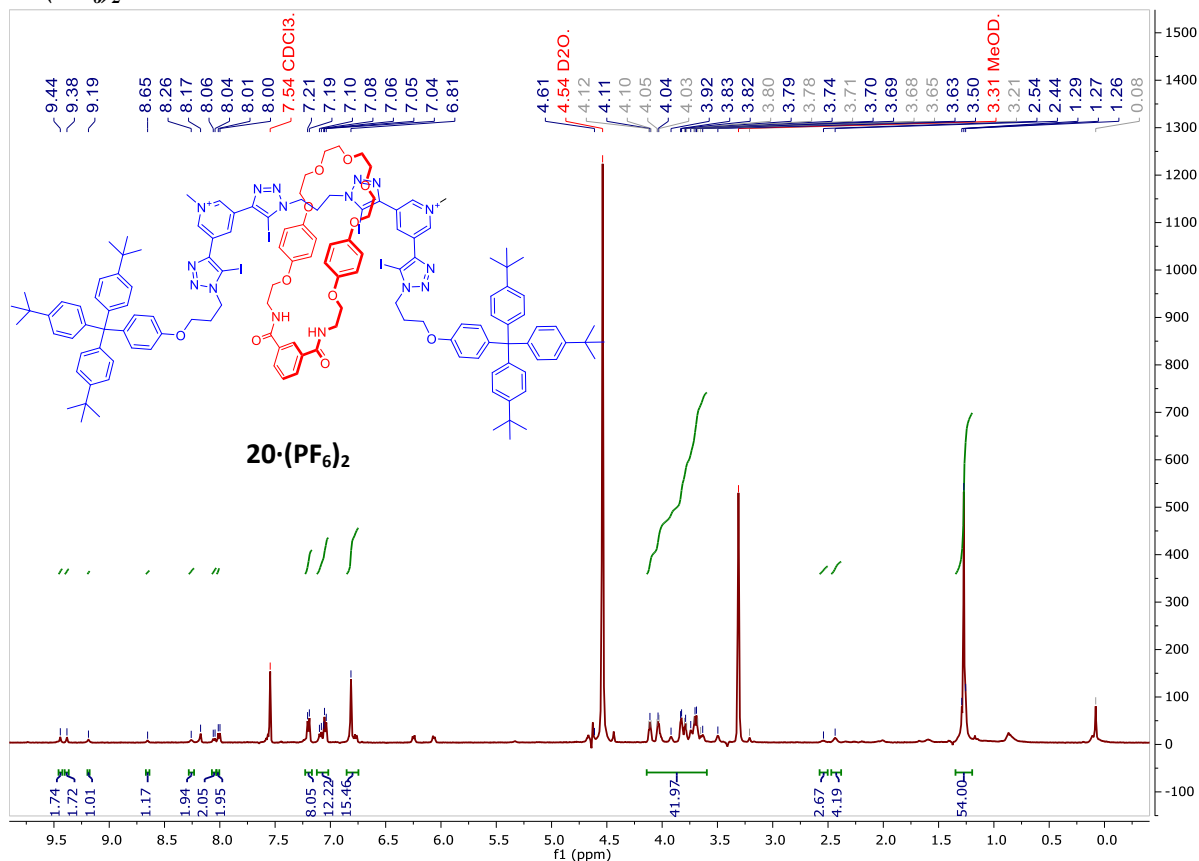
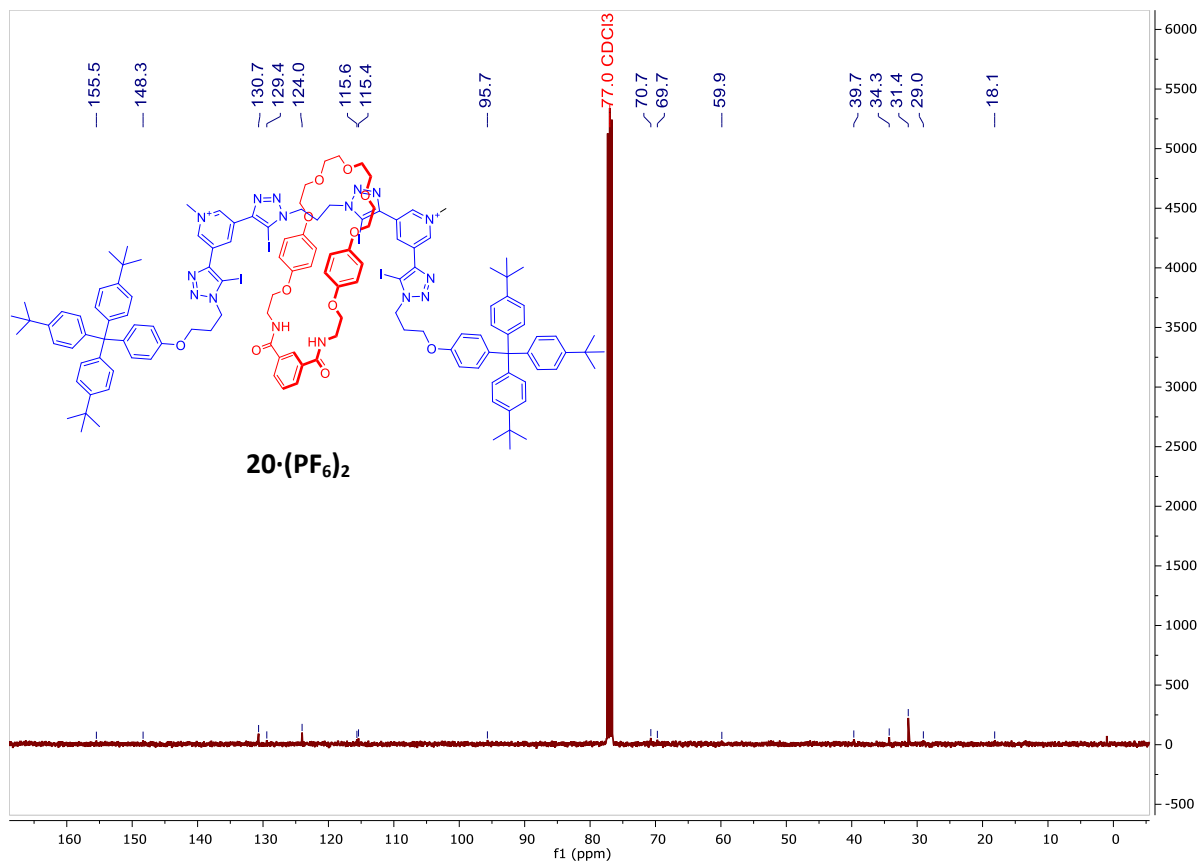


Figure S25: <sup>19</sup>F NMR spectrum of Asymmetric rotaxane: pyridinium/pyridine bis-iodotriazole axle–isophthalamide 5-O-polyether macrocycle, **19-PF<sub>6</sub>** (376 MHz, CDCl<sub>3</sub>)

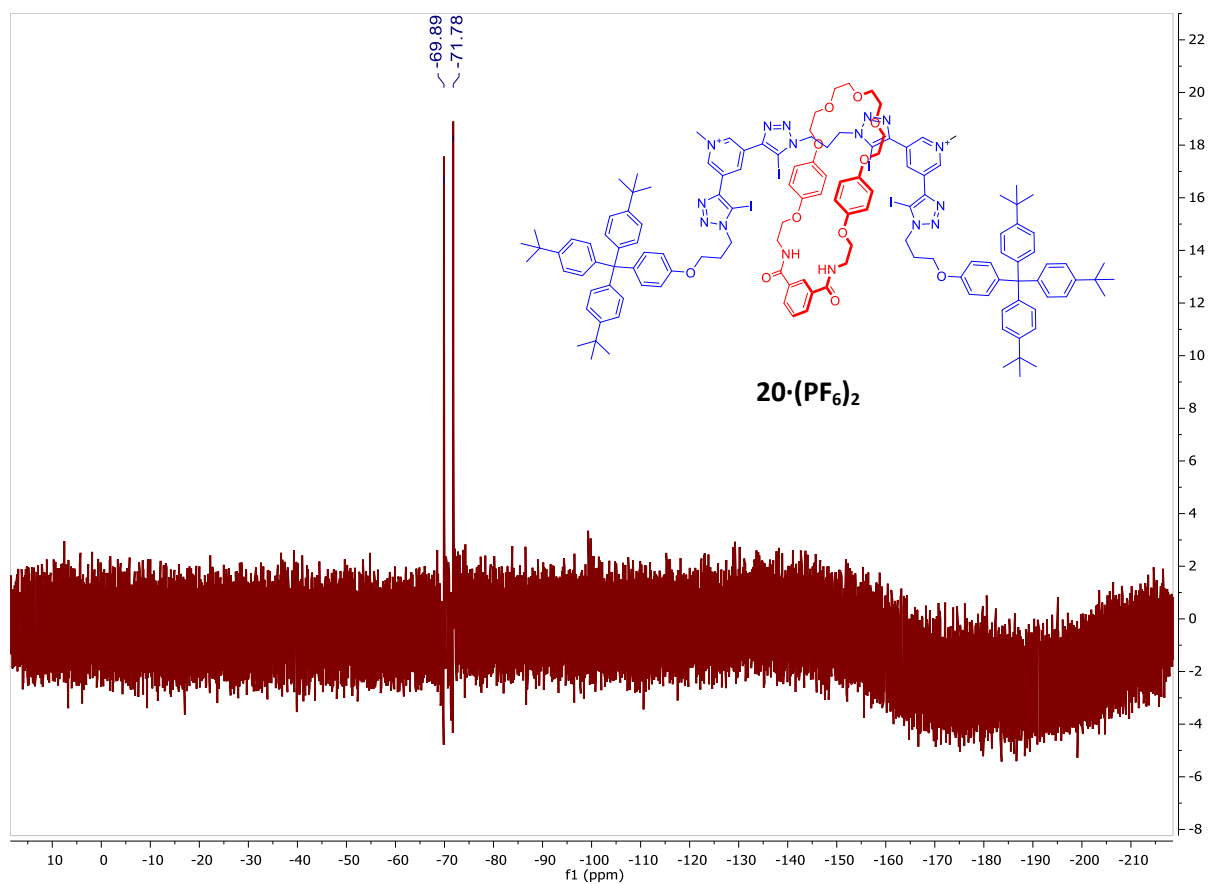
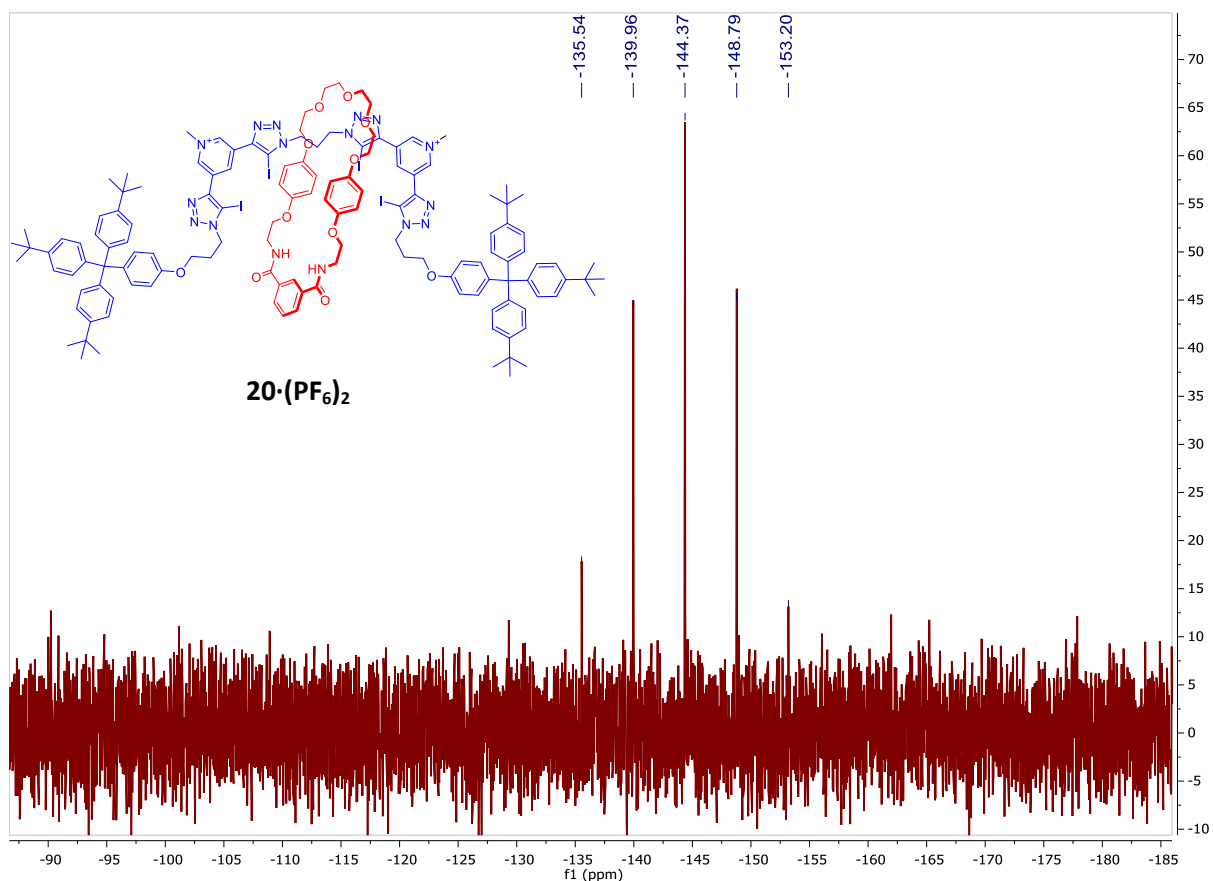
**Dicationic rotaxane: bis-(3,5-bis-iodotriazole pyridinium) axle-isophthalamide 5-O-polyether macrocycle, 20·(PF<sub>6</sub>)<sub>2</sub>**



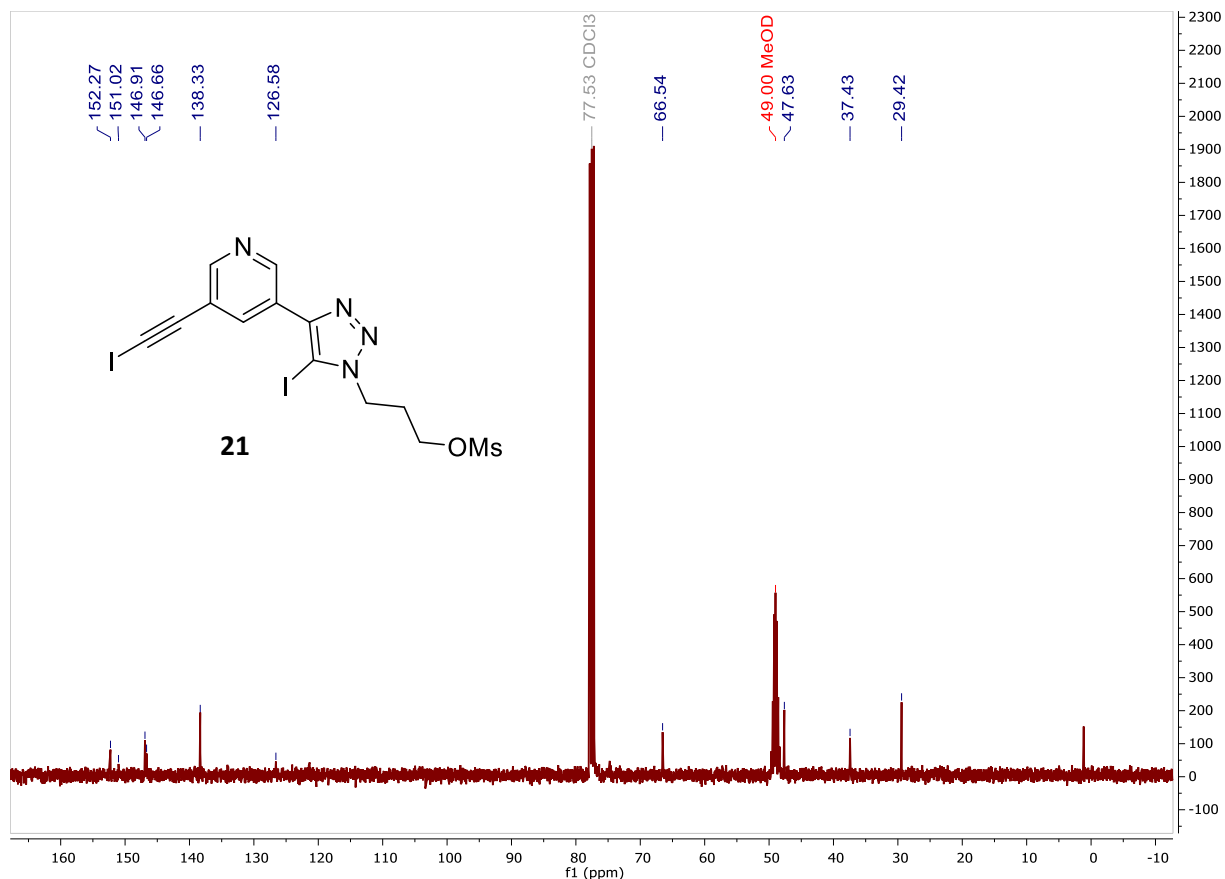
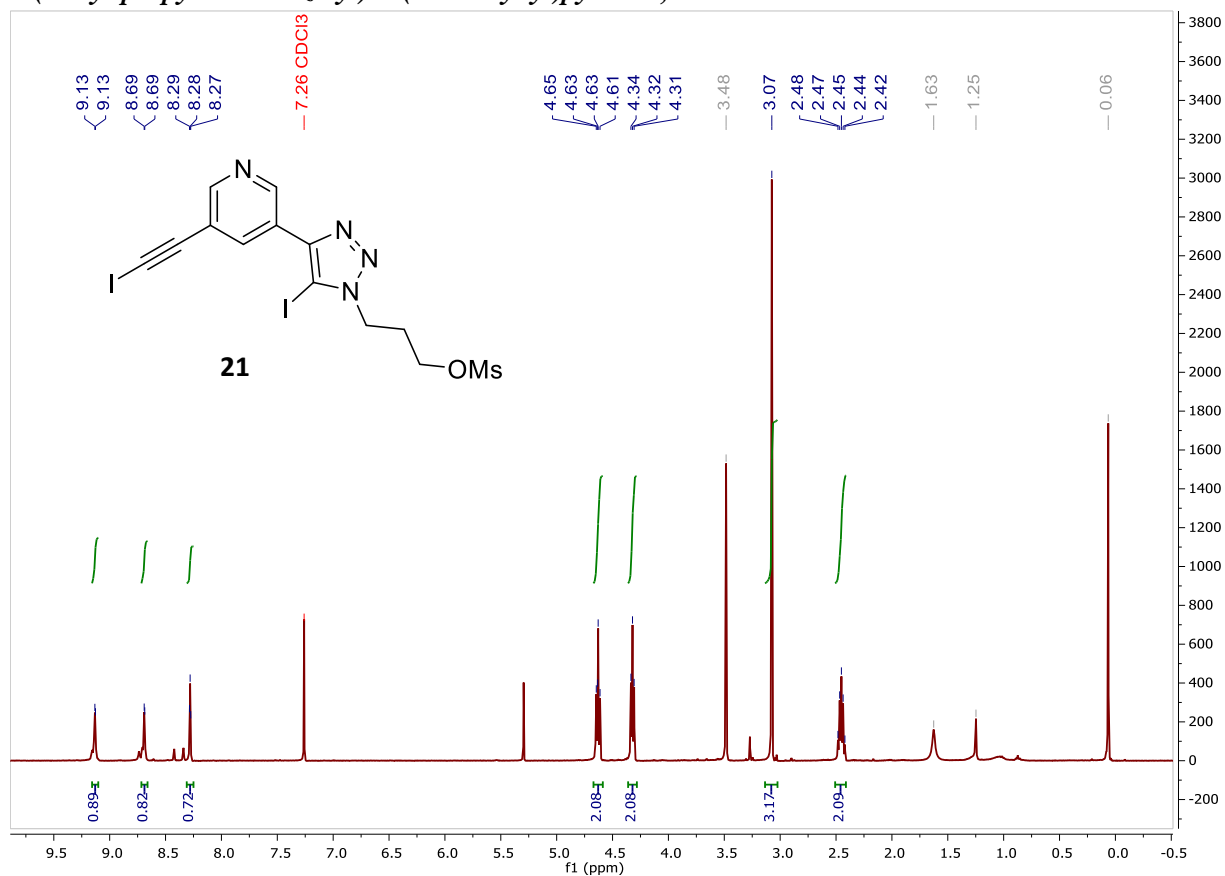
**Figure S26:** <sup>1</sup>H NMR spectrum of Dicationic rotaxane: bis-(3,5-bis-iodotriazole pyridinium) axle-isophthalamide 5-O-polyether macrocycle, 20·(PF<sub>6</sub>)<sub>2</sub> (500 MHz, 45:45:10 CDCl<sub>3</sub>:CD<sub>3</sub>OD:D<sub>2</sub>O)



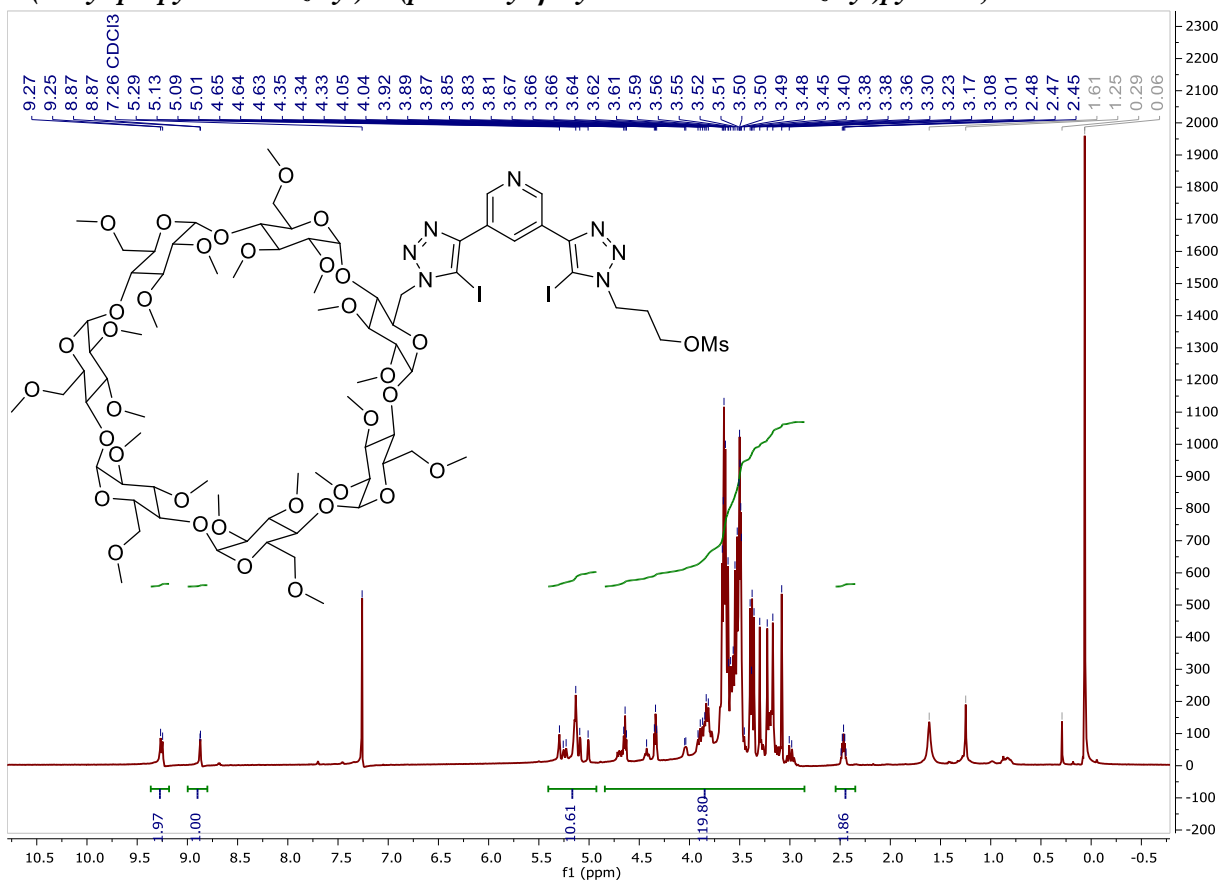
**Figure S27:** <sup>13</sup>C NMR spectrum of Dicationic rotaxane: bis-(3,5-bis-iodotriazole pyridinium) axle-isophthalamide 5-O-polyether macrocycle, 20·(PF<sub>6</sub>)<sub>2</sub> (100 MHz, CDCl<sub>3</sub>)



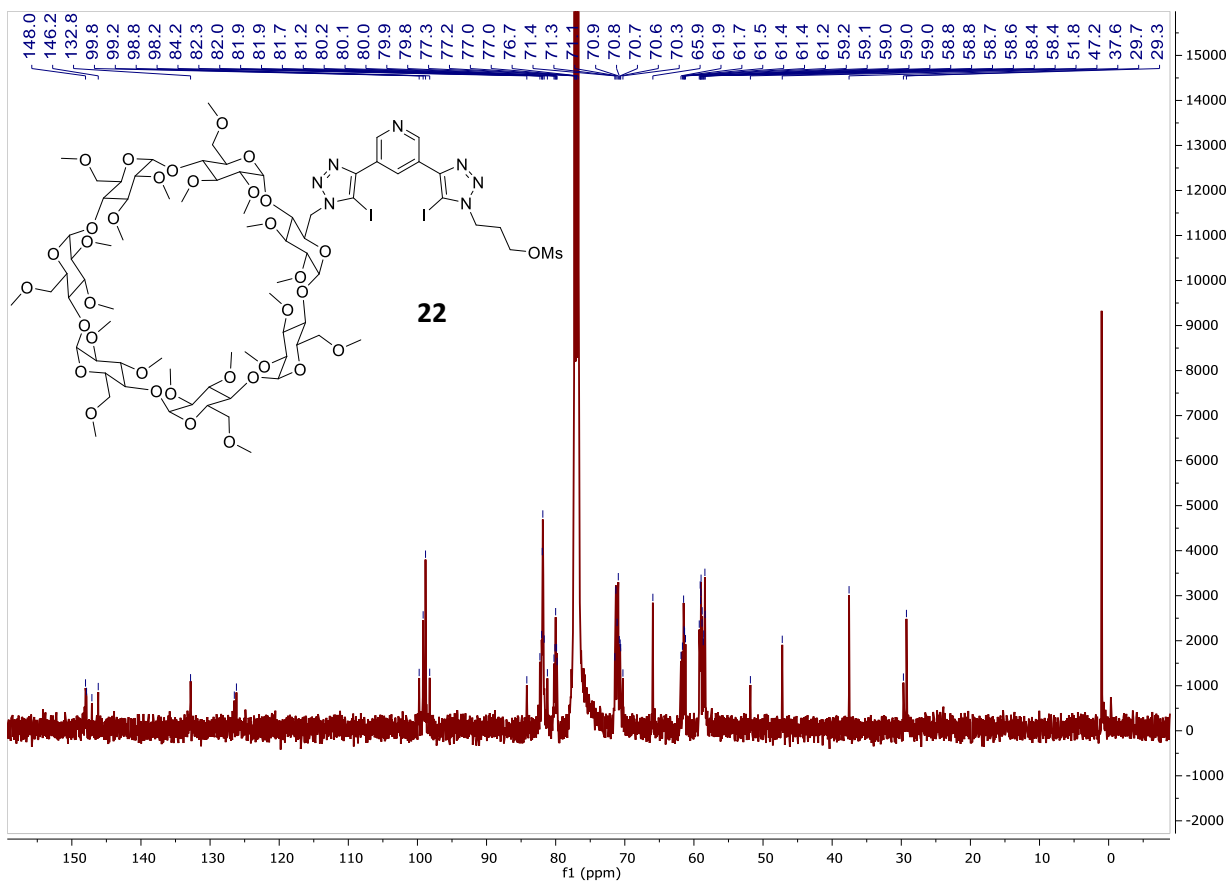
**3-(mesyl-propyl-iodotriazolyl)-5-(iodoethyl)pyridine, 21**



**3-(mesyl-propyl-iodotriazolyl)-5-(permethyl- $\beta$ -cyclodextrin-iodotriazolyl)pyridine, 22**

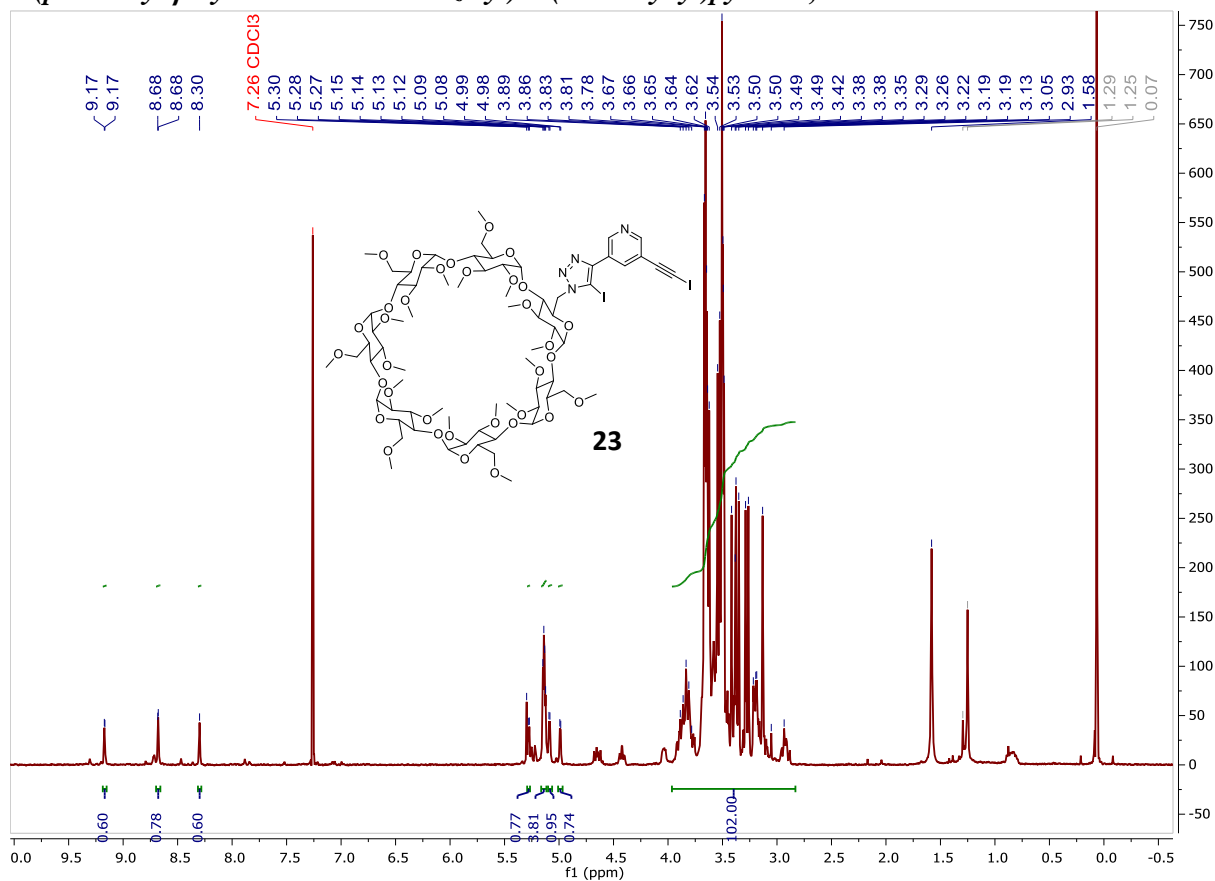


**Figure S32:**  $^1\text{H}$  NMR spectrum of 3-(mesyl-propyl-iodotriazolyl)-5-(permethyl- $\beta$ -cyclodextrin-iodotriazolyl)pyridine, 22 (500 MHz,  $\text{CDCl}_3$ )

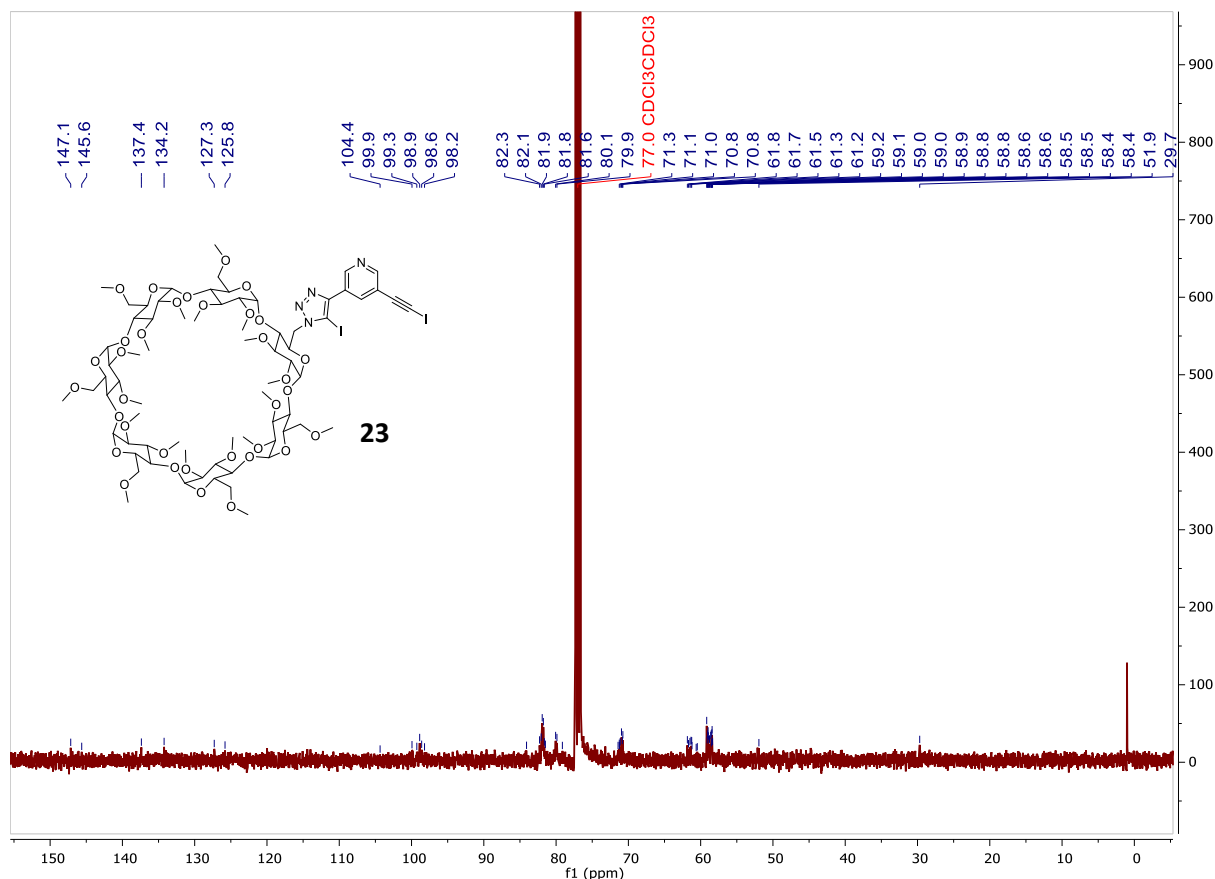


**Figure S33:**  $^{13}\text{C}$  NMR spectrum of 3-(mesyl-propyl-iodotriazolyl)-5-(permethyl- $\beta$ -cyclodextrin-iodotriazolyl)pyridine, 22 (126 MHz,  $\text{CDCl}_3$ )

**3-(permethy- $\beta$ -cyclodextrin-iodotriazolyl)-5-(iodoethynyl)pyridine, 23**



**Figure S34:** <sup>1</sup>H NMR spectrum of 3-(permethyl- $\beta$ -cyclodextrin-iodotriazolyl)-5-(iodoethynyl)pyridine, 23 (400 MHz, CDCl<sub>3</sub>)

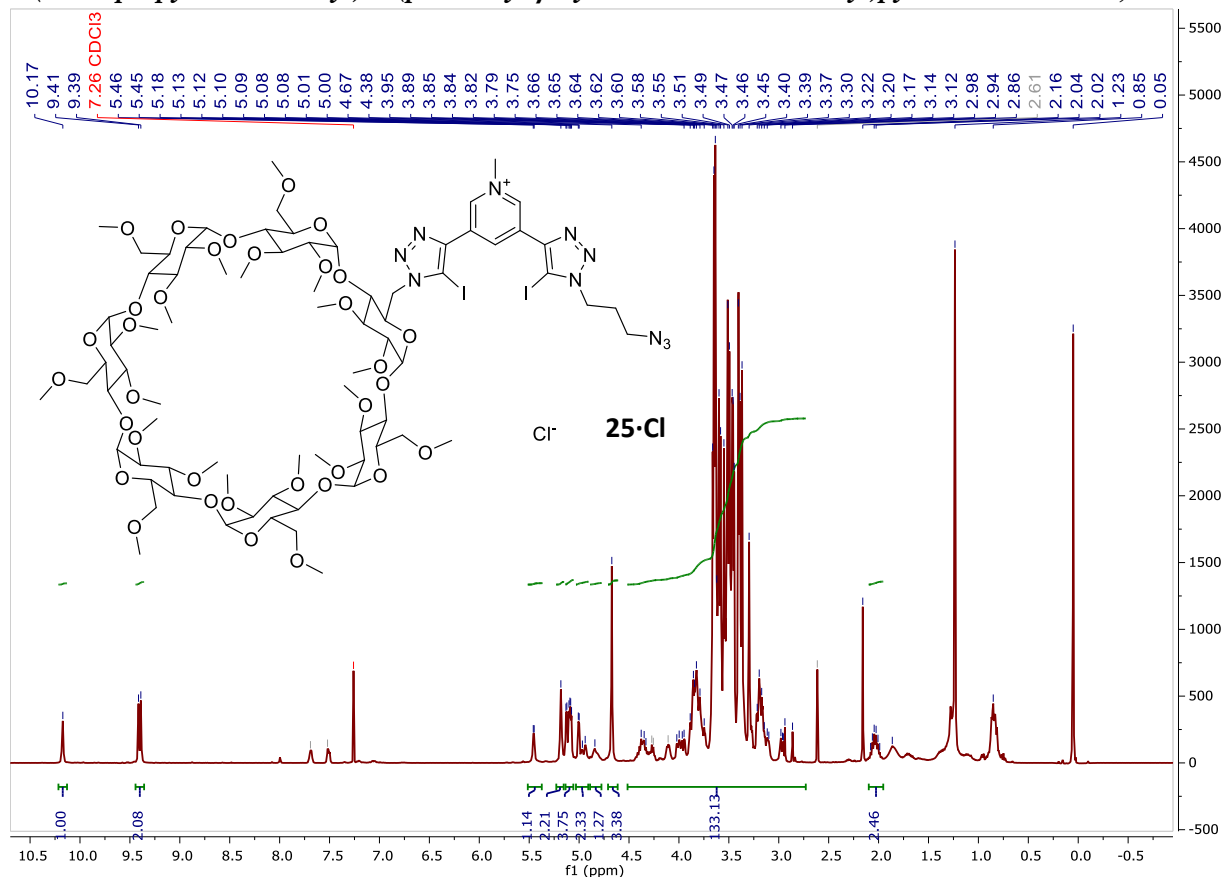


**Figure S35:** <sup>13</sup>C NMR spectrum of 3-(permethyl- $\beta$ -cyclodextrin-iodotriazolyl)-5-(iodoethynyl)pyridine, 23 (100 MHz, CDCl<sub>3</sub>)

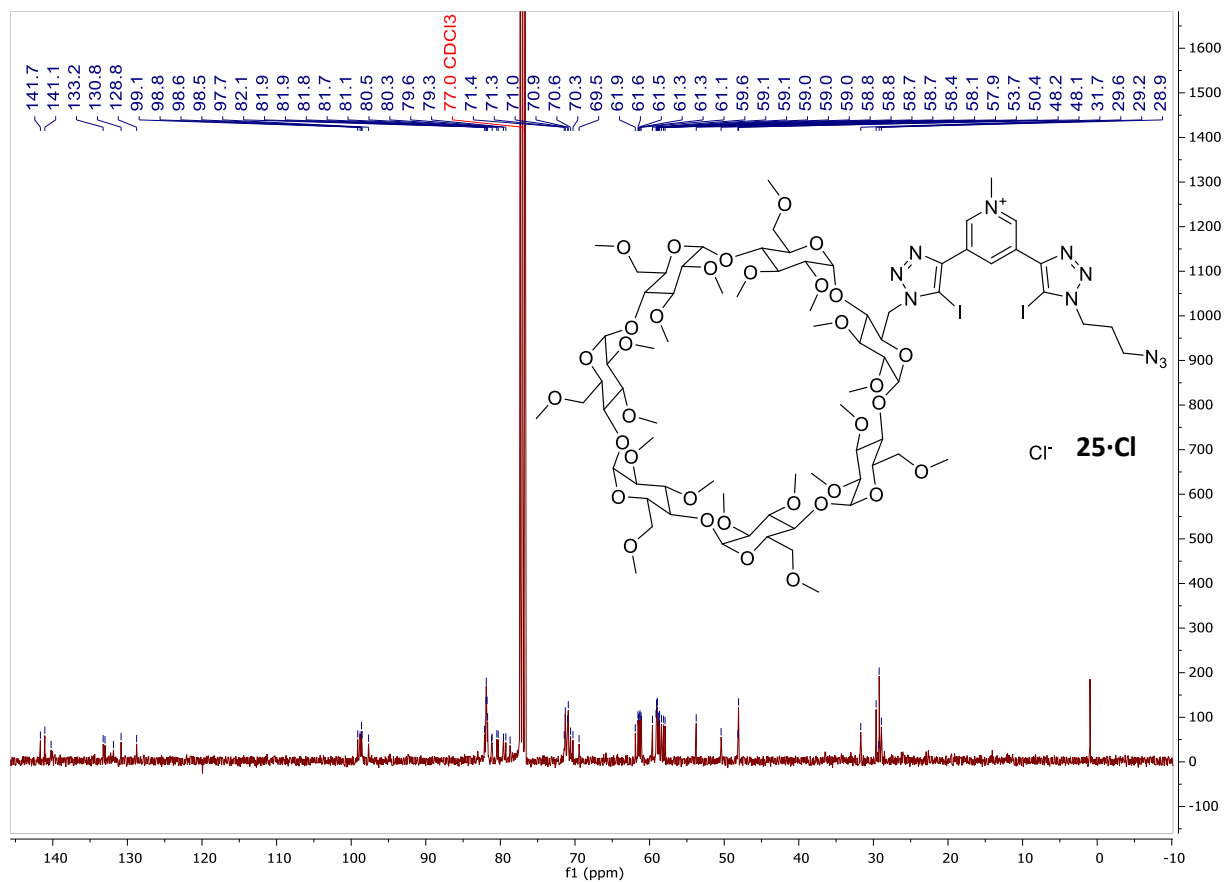




**3-(azido-propyl-iodotriazolyl)-5-(permethyl- $\beta$ -cyclodextrin-iodotriazolyl)pyridinium chloride, 25-Cl**

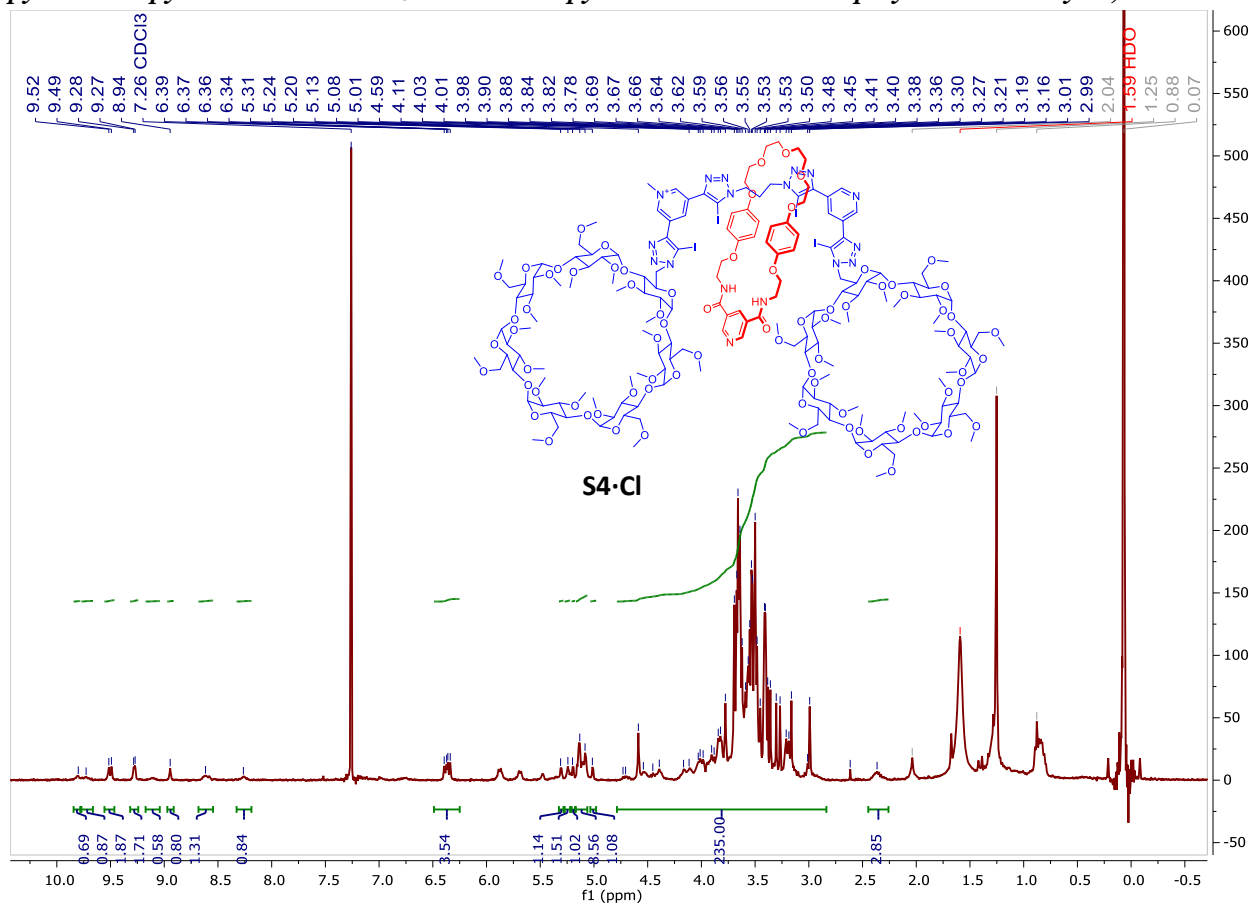


**Figure S38:  $^1\text{H}$  NMR spectrum of 3-(azido-propyl-iodotriazolyl)-5-(permethyl- $\beta$ -cyclodextrin-iodotriazolyl)pyridinium chloride, 25-Cl (400 MHz,  $\text{CDCl}_3$ )**



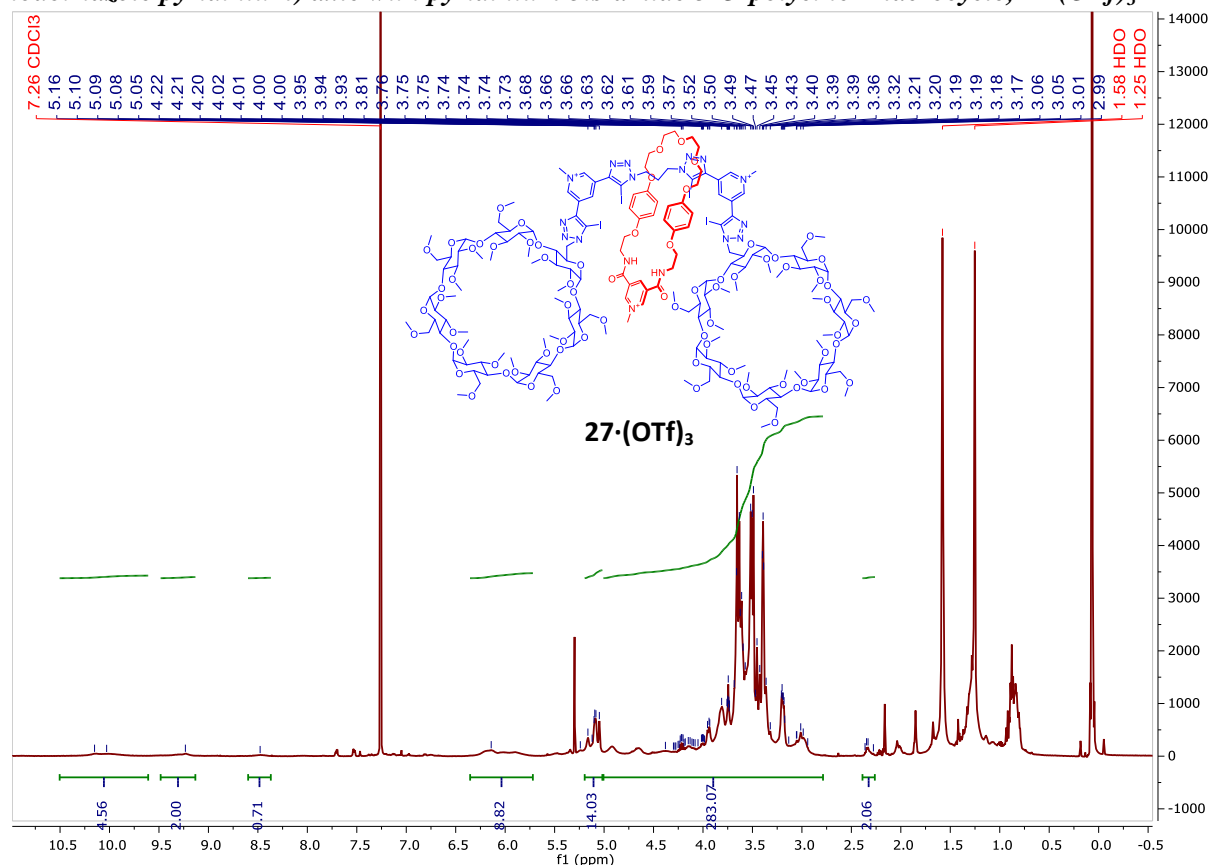
**Figure S39:  $^{13}\text{C}$  NMR spectrum of 3-(azido-propyl-iodotriazolyl)-5-(permethyl- $\beta$ -cyclodextrin-iodotriazolyl)pyridinium chloride, 25-Cl (100 MHz,  $\text{CDCl}_3$ )**

**Water-soluble asymmetric monocationic [2]rotaxane: permethyl- $\beta$ -cyclodextrin-stoppered pyridinium/pyridine bis-iodotriazole axle with pyridine bis-amide 5-O-polyether macrocycle, S4-Cl**



**Figure S40:**  $^1\text{H}$  NMR spectrum of Water-soluble asymmetric monocationic [2]rotaxane: permethyl- $\beta$ -cyclodextrin-stoppered pyridinium/pyridine bis-iodotriazole axle with pyridine bis-amide 5-O-polyether macrocycle, S4-Cl (400 MHz,  $\text{CDCl}_3$ )

**Water-soluble symmetric tricationic [2]rotaxane: permethyl- $\beta$ -cyclodextrin-stoppered bis-(3,5-bis-iodotriazole pyridinium) axle with pyridinium bis-amide 5-O-polyether macrocycle, 27·(OTf)<sub>3</sub>**



**Figure S41: <sup>1</sup>H NMR spectrum of Water-soluble symmetric tricationic [2]rotaxane: permethyl- $\beta$ -cyclodextrin-stoppered bis-(3,5-bis-iodotriazole pyridinium) axle with pyridinium bis-amide 5-O-polyether macrocycle, 27·(OTf)<sub>3</sub> (500 MHz, CDCl<sub>3</sub>)**

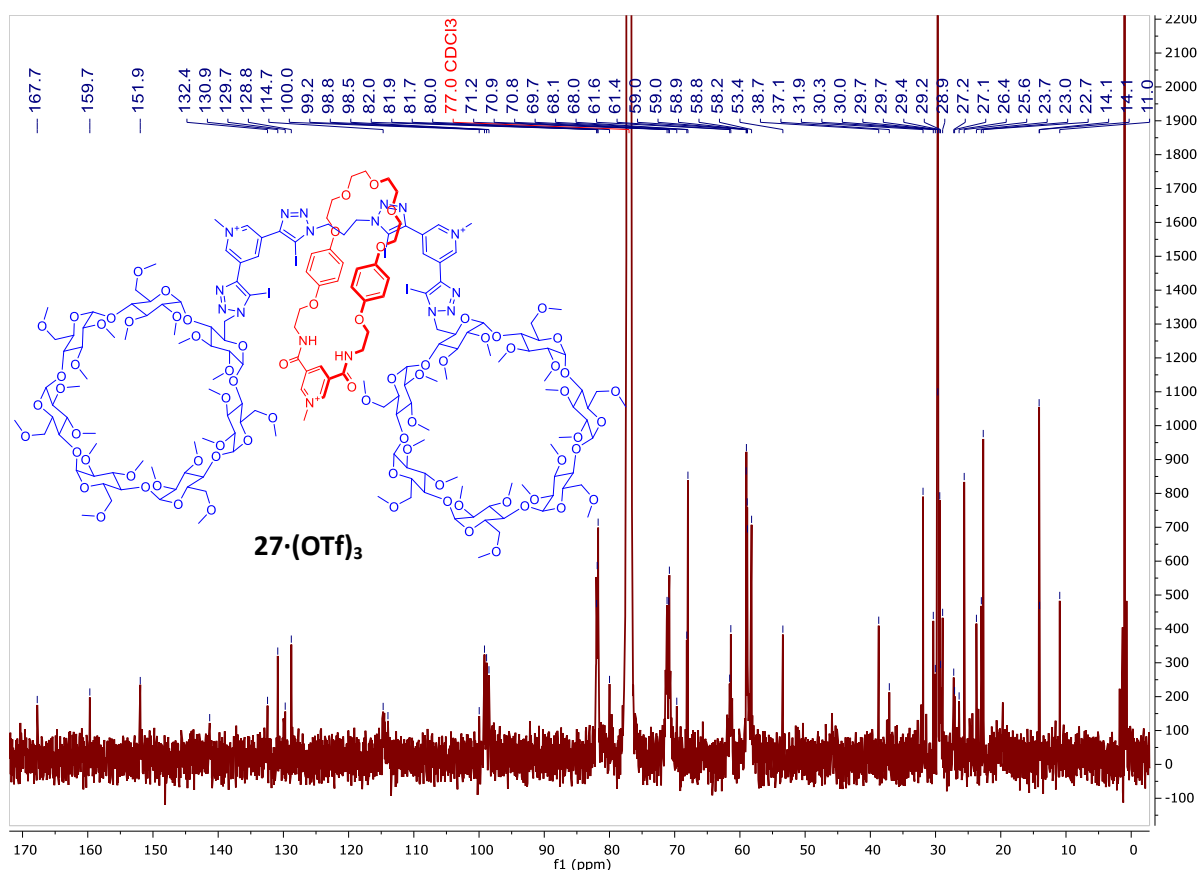


Figure S42:  $^{13}\text{C}$  NMR spectrum of Water-soluble symmetric tricationic [2]rotaxane: permethyl- $\beta$ -cyclodextrin-stoppered bis-(3,5-bis-iodotriazole pyridinium) axle with pyridinium bis-amide 5-O-polyether macrocycle,  $27\cdot(\text{OTf})_3$  (125 MHz,  $\text{CDCl}_3$ )

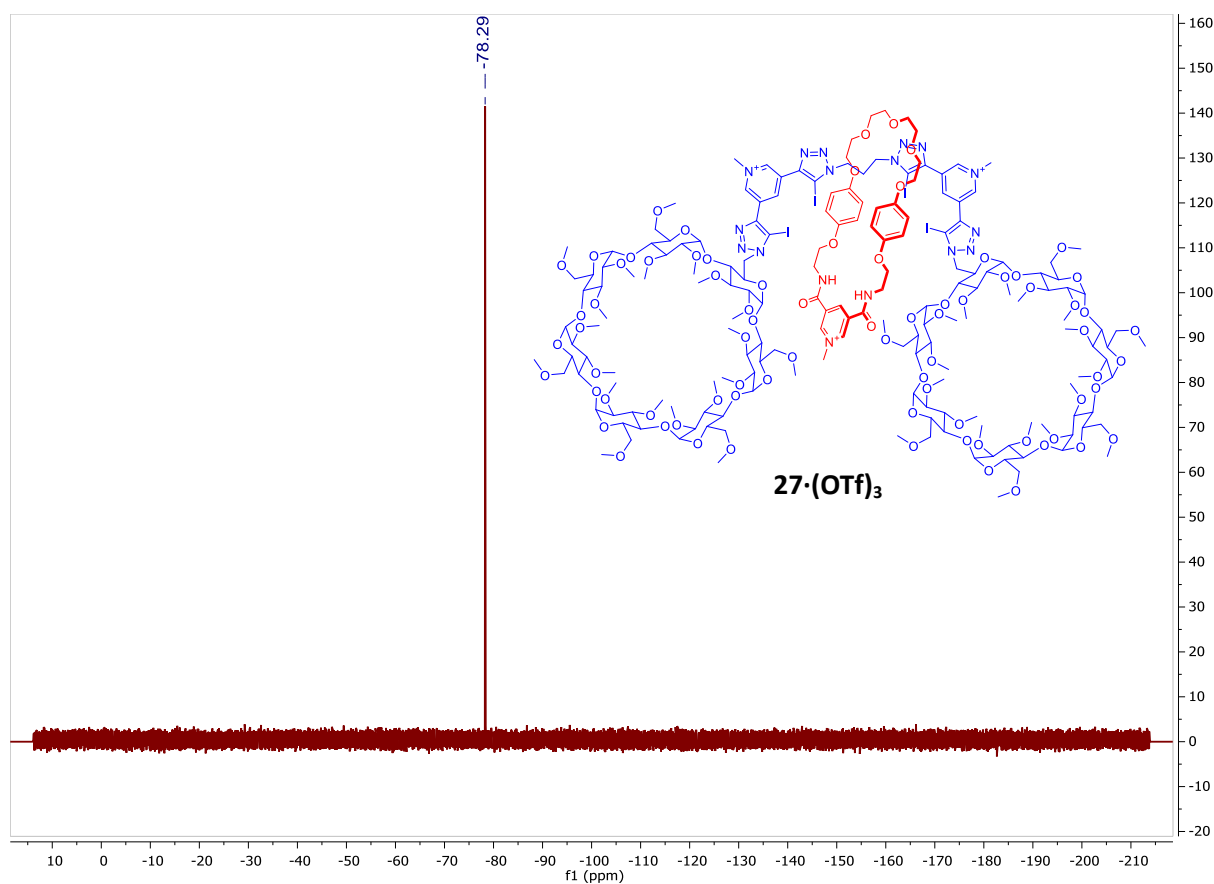


Figure S43:  $^{19}\text{F}$  NMR spectrum of Water-soluble symmetric tricationic [2]rotaxane: permethyl- $\beta$ -cyclodextrin-stoppered bis-(3,5-bis-iodotriazole pyridinium) axle with pyridinium bis-amide 5-O-polyether macrocycle,  $27\cdot(\text{OTf})_3$  (376 MHz,  $\text{CDCl}_3$ )

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