Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Contents

S1. Experimental

S1.1 General Information

All commercially available chemicals and solvents were used as received without further purification. All dry solvents were thoroughly degassed with N_2, dried through a Mbraun MPSP-800 column and used immediately. Water used was deionized and passed through a Milli-Q® Millipore machine for microfiltration. Chromatography was performed using silica gel (particle size: 40-63 μm) or preparative TLC plates (20 x 20 cm, 1 cm silica thickness).

NMR spectra were recorded on Bruker AVIII HD Nanobay 400 MHz, Bruker AVIII 500 MHz and Bruker AVIII 500 MHz (with ^{13}C cryoprobe) spectrometers. Low resolution electrospray ionisation mass spectrometry (ESI-MS) was performed using the Waters Micromass LCT for characterisation of compounds previously reported in the literature, and high resolution ESI-MS was recorded using Bruker microTOF spectrometer for novel compounds.

S1.2 Synthesis and Characterisation

TBTA (tris(benzyltriazolemethyl)amine), stopper azide (Fig. S1-1),[1] 2-(4-amino-3-nitrophenyl)-4-bromo-1,8-naphthalimide,[2] isophthalamide macrocycle **5**[3] and stopper alkyne **6**[1] were prepared according to literature procedures.

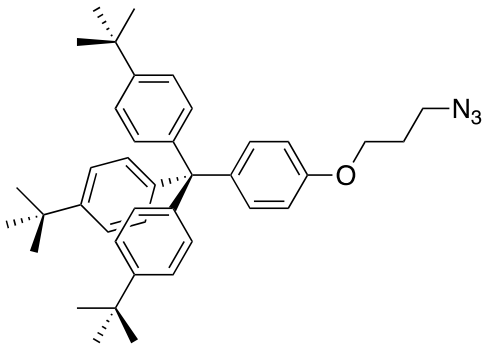
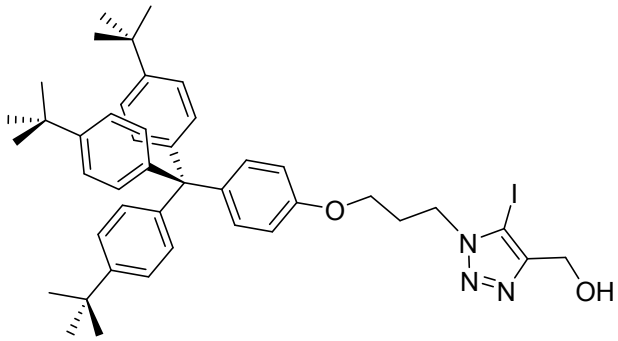


Figure S1 – 1 Structure of stopper azide[1]

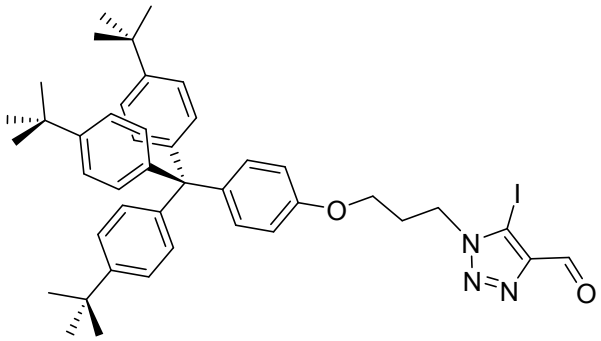
Stopper iodotriazole alcohol



Stopper azide[1] (0.200 g, 0.340 mmol), NaI (0.188 g, 1.34 mmol) and $Cu(ClO_4)_2.6H_2O$ (0.240 g, 0.642 mmol) were dissolved in dry THF (5 mL) and stirred for 5 minutes in the dark. TBTA (cat.), DBU (47.8 µL, 0.335 mmol) in dry CH_3CN (5 mL) and finally propargyl alcohol (18.2 mL, 0.324 mmol) were added and the reaction was stirred for 16 hours in the dark. The solvent was removed *in vacuo* and the residue was taken up in CH_2Cl_2 (30 mL). The organics were washed with EDTA/NH_4OH solution (3x15 mL), H_2O (15 mL) and brine (15 mL), dried over $MgSO_4$ and the solvent removed *in vacuo*. Purification was achieved via column chromatography (silica, 95:5 CH_2Cl_2/CH_3OH) to afford the product as a white solid (0.146 g, 56%).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.20 – 7.26 (m, 6H, Ar*H*), 7.05 – 7.12 (m, 8H, Ar*H*), 6.71 – 6.78 (m, 2H, Ar*H*), 4.72 (d, *J* = 6.2 Hz, 2H, OH-C*H*$_2$-C), 4.59 (t, *J* = 7.0 Hz, 2H, O-C*H*$_2$-CH$_2$), 3.99 (t, *J* = 5.8 Hz, 2H, N-C*H*$_2$-CH$_2$), 2.40 (tt, *J* = 7.0 Hz, *J* = 5.8 Hz, 2H, CH$_2$-*CH*$_2$-CH$_2$), 2.03 (t, *J* = 6.3 Hz, 1H, -O*H*), 1.30 (s, 27H, ^{t}Bu); **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm) 156.29, 148.49, 144.21, 132.45, 130.84, 124.21, 113.20, 63.98, 63.20, 56.88, 47.91, 34.45, 31.53, 29.81; **HRMS (ESI):** *m/z* 770.31766 $[M+H]^+$ ($[C_{43}H_{52}IN_3O_2 \cdot H]$ calc. 770.31770).

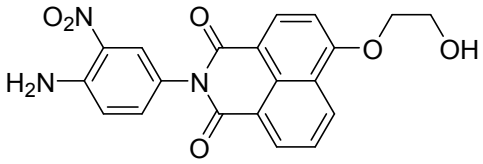
Stopper iodotriazole aldehyde (1)



Oxalyl chloride (0.137 mL, 1.6 mmol) and dry DMSO (0.23 mL, 3.25 mmol) were dissolved in CH_2Cl_2 (20 mL) at -78°C and the mixture stirred for 15 minutes. Stopper iodotriazole alcohol (250 mg, 0.325 mmol) in CH_2Cl_2 (20 mL) was added, and after 15 minutes this was followed by NEt_3 (0.680 mL, 4.85 mmol). After stirring for 1 hour the solution was quenched with 1M $HCl_{(aq.)}$ (20 mL) and extracted with CH_2Cl_2 (3x20 mL). The organics were dried over $MgSO_4$ and the solvent removed *in vacuo*. Purification was achieved via column chromatography (silica, 98:2 CH_2Cl_2/CH_3OH) to afford **1** as an off-white solid (138 mg, 55%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.13 (s, 1H, C*H*O), 7.29 – 7.19 – 7.25 (m, 6H, Ar*H*), 7.04 – 7.13 (m, 8H, Ar*H*), 6.71 – 6.78 (m, 2H, Ar*H*), 4.68 (t, *J* = 7.0 Hz, 2H, N-CH_2), 4.01 (t, *J* = 5.6 Hz, 2H, O-CH_2), 2.40 – 2.48 (m, 2H, CH_2), 1.30 (s, 27H, -CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) 184.34, 156.15, 148.51, 147.45, 144.18, 140.39, 132.48, 130.83, 124.21, 113.16, 82.18, 63.82, 63.21, 47.71, 34.45, 31.53, 29.61; **HRMS (ESI):** *m/z* 790.28418 $[M+Na]^+$ ($[C_{43}H_{50}IN_3O_2{\cdot}Na]^+$ calc. 790.28399).

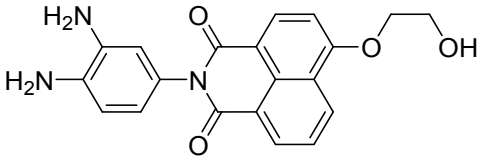
Amino-nitrophenyl-naphthalimide alcohol



K_2CO_3 (1.70 g, 12.2 mmol) and 2-(4-amino-3-nitrophenyl)-4-bromo-1,8-naphthalimide[2] (500 mg, 1.22) were mixed in ethylene glycol (20 mL) and stirred at 150°C for 6 hours. The reaction was cooled to RT, added to ice-cold H_2O (100 mL) and the precipitate collected by filtration whereupon it was washed with H_2O (3x50 mL) and Et_2O (5x50 mL) to afford the product as a yellow solid (289.1 mg, 61%).

^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm) 8.72 (dd, *J* = 8.4, 1.2 Hz, 1H, Ar*H*), 8.51 (dd, *J* = 7.2, 1.2 Hz, 1H, Ar*H*), 8.45 (d, *J* = 8.3 Hz, 1H, Ar*H*), 8.02 (d, *J* = 2.4 Hz, 1H, Ar*H*), 7.86 (dd, *J* = 8.4, 7.3 Hz, 1H, Ar*H*), 7.62 (s, 2H, -NH_2), 7.33 – 7.43 (m, 2H, Ar*H*), 7.12 (d, *J* = 8.9 Hz, 1H, Ar*H*), 5.13 (t, *J* = 5.8 Hz, 1H, -O*H*), 4.37 (t, *J* = 4.7 Hz, 2H, O-CH_2), 3.96 – 3.89 (m, 2H, OH-CH_2); **^{13}C NMR** (126 MHz, DMSO-d_6) δ (ppm) 164.07, 163.40, 159.98, 145.92, 136.88, 133.36, 131.16, 129.72, 129.13, 128.87, 126.24, 125.86, 123.50, 123.08, 122.47, 119.27, 114.62, 106.87, 71.07, 59.40; **HRMS (ESI):** *m/z* 394.10333 $[M+H]^+$ ($[C_{20}H_{15}N_3O_6{\cdot}H]^+$ calc. 394.10336).

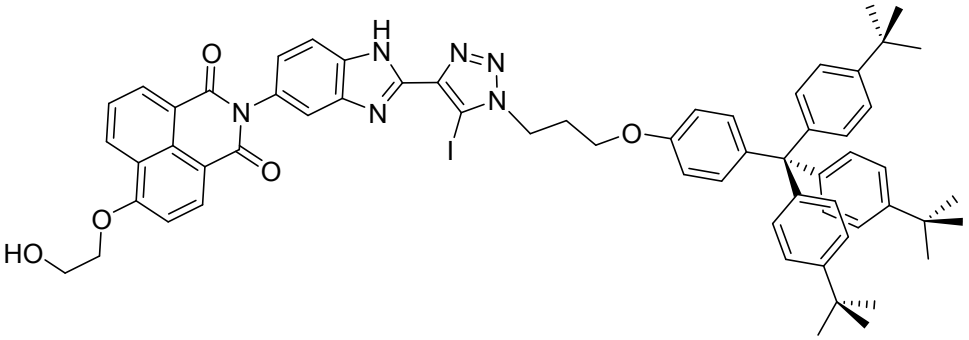
***o*-Phenylenediamine naphthalimide alcohol (2)**



Amino-nitrophenyl-naphthalimide alcohol (630 mg, 1.60 mmol), Zn powder (2.09 g, 32.0 mmol), 1M $NH_4Cl_{(aq.)}$ solution (15 mL) and $CuSO_4.5H_2O$ (10 crystals) were heated in ethanol (15 mL) at reflux for 5 hours. The mixture was filtered through Celite® whilst hot and the filtrate concentrated *in vacuo*. The resulting solid was washed with H_2O (5x30 mL) to afford **2** as a yellow powder (524 mg, 90%).

^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.66 (dd, *J* = 8.4, 1.2 Hz, 1H, Ar*H*), 8.36 – 8.49 (m, 2H, Ar*H*), 7.81 (dd, *J* = 8.4, 7.3 Hz, 1H, Ar*H*), 7.30 (d, *J* = 8.4 Hz, 1H, Ar*H*), 6.54 (d, *J* = 8.1 Hz, 1H, Ar*H*), 6.36 (d, *J* = 2.3 Hz, 1H, Ar*H*), 6.26 (dd, *J* = 8.1, 2.3 Hz, 1H, Ar*H*), 5.09 (t, *J* = 5.8 Hz, 1H, -O*H*), 4.46 – 4.64 (s, 4H, -NH_2), 4.32 (t, *J* = 4.7 Hz, 2H, OH-CH_2), 3.89 (t, *J* = 5.0 Hz, 2H, O-CH_2); **^{13}C NMR** (126 MHz, DMSO) δ (ppm) 164.07, 163.44, 159.79, 135.13, 134.82, 133.23, 131.08, 128.99, 128.64, 126.24, 125.31, 123.06, 122.55, 117.26, 114.75, 114.68, 113.93, 106.88, 71.02, 59.41, 54.92; **HRMS (ESI):** *m/z* 364.12910 $[M+H]^+$ ($[C_{20}H_{17}N_3O_4{\cdot}H]^+$ calc. 364.12918).

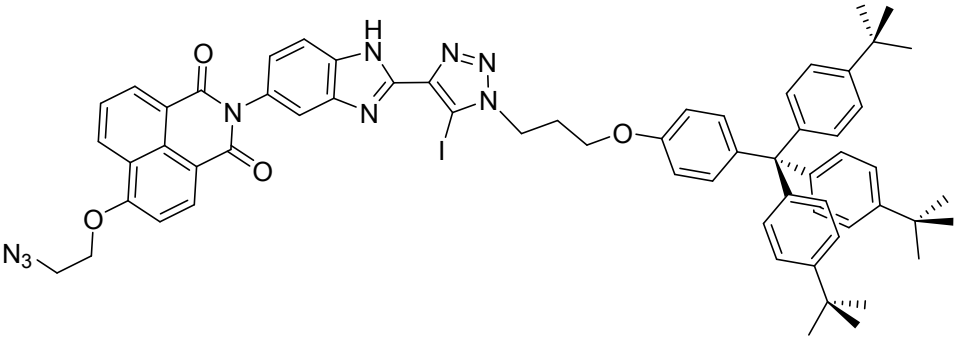
Benzimidazole-iodotriazole naphthalimide alcohol (3)



Stopper iodotriazole aldehyde **1** (130 mg, 0.17 mmol), *o*-phenylenediamine **2** (68 mg, 0.19 mmol), and NH_4OAc (13 mg, 0.17 mmol) were dissolved in 1:1 $CHCl_3$/EtOH (10 mL) and stirred at 65°C for 4 hours. After cooling to RT and removing the solvent *in vacuo* the product was purified by preparative TLC (silica, 95:5 CH_2Cl_2/CH_3OH) to afford **3** as a yellow solid (92.2 mg, 49%).

^{1}H NMR (400 MHz, 1:1 $CDCl_3$/CH_3OD) δ (ppm) 8.74 (d, *J* = 8.4 Hz, 1H, Ar*H*), 8.49 – 8.59 (m, 2H, Ar*H*), 7.67 – 7.77 (m, 2H, Ar*H*), 7.58 (s, 1H, Ar*H*), 7.09 – 7.19 (m, 8H, Ar*H* & stopper-Ar*H*), 6.96 – 7.05 (m, 8H, stopper-Ar*H*), 6.68 – 6.75 (m, 2H, stopper-Ar*H*), 4.68 (t, *J* = 7.0 Hz, 2H, N-CH_2), 4.35 (t, *J* = 4.6 Hz, 2H, OH-CH_2), 4.05 (t, *J* = 4.4 Hz, O-CH_2), 4.00 (t, *J* = 5.6 Hz, O-CH_2), 2.41 (t, *J* = 6.3 Hz, 2H, CH_2), 1.22 (s, 27H, -CH_3); **^{13}C NMR** (126 MHz, 1:1 $CDCl_3$/CH_3OD) δ (ppm) 165.46, 164.88, 160.95, 156.25, 148.25, 144.14, 140.01, 134.17, 132.16, 132.03, 130.61, 129.86, 129.72, 126.00, 123.95, 123.82, 122.23, 114.77, 113.03, 106.27, 70.55, 63.96, 63.00, 60.14, 34.07, 31.00, 29.49; **HRMS (ESI):** *m/z* 1111.39605 $[M+H]^+$ ($[C_{63}H_{63}IN_6O_5 \cdot H]^+$ calc. 1111.39774).

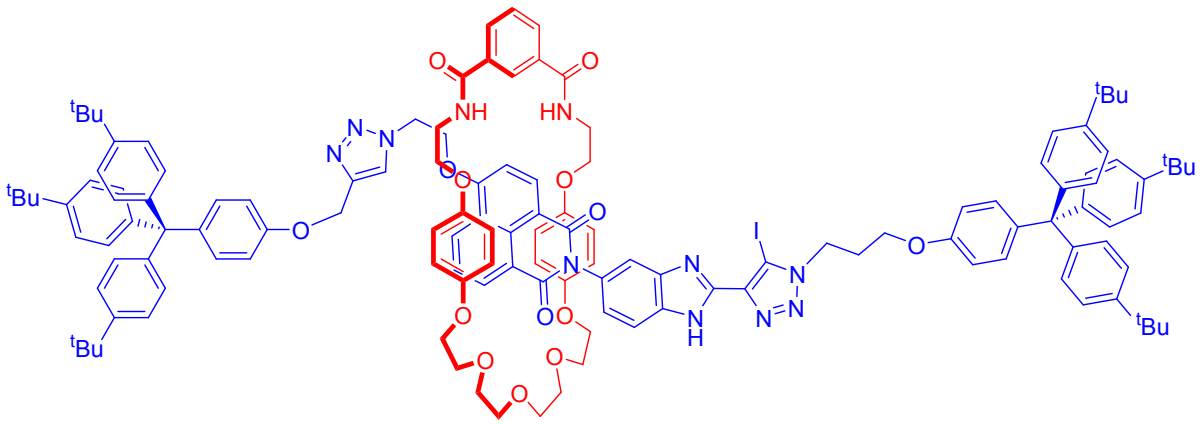
Benzimidazole-iodotriazole naphthalimide azide (4)



Naphthalimide alcohol **3** (50 mg, 0.089 mmol) and NEt_3 (40 µL, 0.19 mmol) were dissolved in dry CH_2Cl_2 (5 mL) and stirred for 5 minutes at 0 °C. MsCl (20 mL, 0.18 mmol) in dry CH_2Cl_2 (5 mL) was added dropwise and the reaction stirred for 3 hours at RT. The reaction mixture was washed with water (2x10 mL), 1M $HCl_{(aq.)}$ (3x10 mL) and brine (3x10 mL) and dried over $MgSO_4$. The solvent was removed *in vacuo* to afford a yellow oil. This was dissolved in dry, degassed DMSO (10 mL) containing NaN_3 (19.9 mg, 0.356 mmol) and the mixture was heated at 85 °C for 16 hours under N_2. The solution was cooled to RT and partitioned between water (50 mL) and EtOAc (50 mL). The aqueous layer was washed with EtOAc (2x15 mL). The combined organics were washed with brine (3x15 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Purification was achieved via preparative TLC (silica, 98:2 CH_2Cl_2/CH_3OH) to afford **4.18** as a yellow solid (28.1 mg, 55%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.55 – 8.74 (m, 3H, Ar*H*), 7.79 (t, *J* = 7.8 Hz, 1H, Ar*H*), 7.18 – 7.25 (m, 8H, Ar*H* & stopper-Ar*H*), 7.02 – 7.13 (m, 10H, Ar*H* & stopper-Ar*H*), 6.73 – 6.81 (m, 2H, stopper-Ar*H*), 4.73 (t, *J* = 7.0 Hz, 2H, N-CH_2), 4.49 (t, *J* = 4.8 Hz, 2H, O-CH_2), 4.00 – 4.08 (m, 2H, O-CH_2), 3.83 (t, *J* = 4.8 Hz, 2H, N_3-CH_2), 2.43 – 2.42 (m, 2H, CH_2), 1.30 (s, 27H, -CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) 171.24, 148.39, 144.14, 132.38, 130.75, 124.15, 123.58, 63.12, 62.66, 60.48, 50.28, 41.00, 34.96, 34.37, 32.00, 31.46, 29.77, 29.43, 22.76, 21.13, 18.99; **HRMS (ESI):** *m/z* 1136.40198 $[M+H]^+$ ($[C_{63}H_{62}IN_9O_4 \cdot H]^+$ calc. 1136.40422).

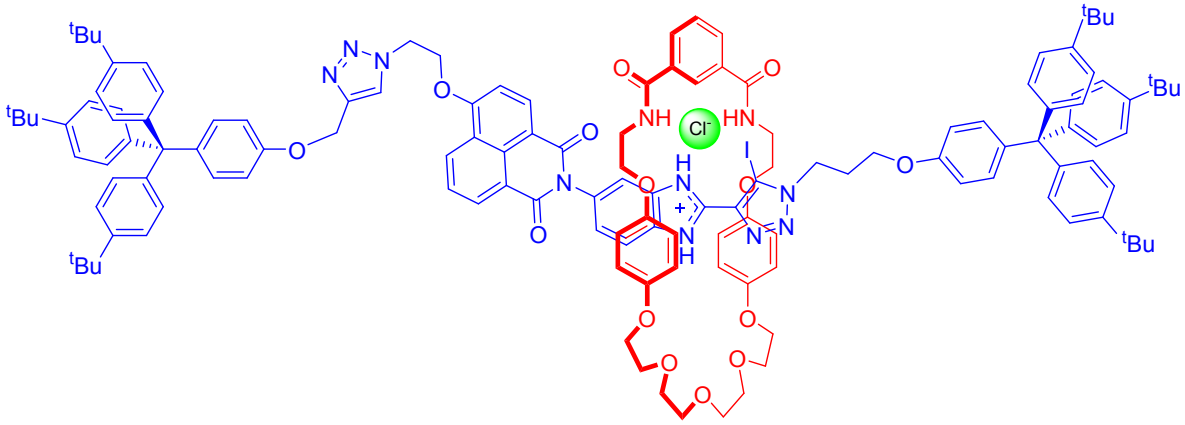
Benzimidazole-iodotriazole neutral [2]rotaxane (7)



Naphthalimide azide **4** (50 mg, 0.044 mmol) was dissolved in dry, degassed CH_2Cl_2 (2 mL) and 2M HCl in Et_2O (2 drops) was added and the mixture stirred for 5 minutes. The solvent was removed *in vacuo* and the resulting solid dissolved in dry CH_2Cl_2 (2 mL). Isophthalamide macrocycle **5** (39.3 mg, 0.067 mmol) was added and the solution stirred for 5 minutes. $[Cu(CH_3CN)_4][PF_6]$ (16.4 mg, 0.044 mmol), and stopper alkyne **6** (36.0 mg, 0.067 mmol) were added and the reaction stirred for 2 days. The solution was diluted with CH_2Cl_2 (20 mL), washed with EDTA/NH_4OH solution (2x20 mL), brine (2x20 mL) and H_2O (20 mL), the combined organics dried over $MgSO_4$ and the solvent removed *in vacuo*. Purification was achieved via preparative TLC (silica, 95:5 CH_2Cl_2/CH_3OH, 92.5:7.5 CH_2Cl_2/CH_3OH) and the resulting solid washed with H_2O (5x10 mL) to afford yellow powder **7** (21.6 mg, 22%).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 10.58 (s, 1H, axle N*H*8.46 (d, *J* = 8.1 Hz, 2H, ext. mac. Ar*H*), 8.10 (s, 1H, int. mac. Ar*H*), 7.94 – 8.06 (m, 2H, Ar*H*), 7.89 (s, 1H, Ar*H*), 7.81 (s, 1H, Ar*H*), 7.68 – 7.75 (m, 2H, Ar*H*), 7.66 (s, 1H, Ar*H*), 7.50 – 7.60 (m, 3H, trz*H* & Ar*H*), 7.18 – 7.25 (m, 15H, Ar*H* & stopper-Ar*H*), 7.02 – 7.14 (m, 19H, Ar*H* & stopper-Ar*H*), 6.80 – 6.86 (m, 4H, stopper-Ar*H* & mac. N*H*), 6.75 (s, 1H, Ar*H*), 5.95 – 6.08 (m, 4H, hydroquinone CH_2), 5.76 – 5.85 (m, 4H, hydroquinone CH_2), 5.23 (s, 2H, O-CH_2-C), 5.02 – 5.11 (m, 4H, N-CH_2 & O-CH_2), 4.73 – 4.80 (m, 2H, N-CH_2), 4.07 – 4.12 (m, 2H, O-CH_2), 3.43 – 3.94 (m, 20H, crown ether CH_2 & mac. CH_2), 3.28 – 3.38 (m, 2H, mac. CH_2), 2.47 – 2.55 (m, 2H, CH_2), 1.27 – 1.32 (m, 27H, -CH_3); **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm) 156.38, 156.28, 151.92, 148.58, 148.46, 144.24, 144.11, 132.51, 130.87, 130.81, 124.21, 113.96, 113.25, 71.30, 71.00, 70.18, 63.19, 34.45, 31.54, 31.52, 29.85; **HRMS (ESI):** *m/z* 2274.01859 $[M+H]^+$ ($[C_{138}H_{155}IN_{11}O_{14}]^+$ calc. 2274.02017).

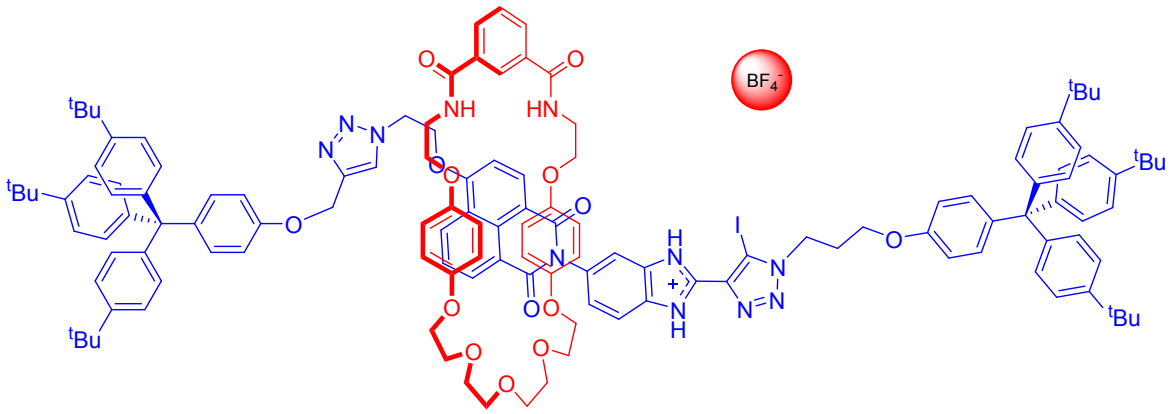
Benzimidazolium-iodotriazole chloride [2]rotaxane (7·HCl)



Rotaxane **7** (22 mg, 0.0097 mmol) was taken up in CH_2Cl_2 (20 mL) and washed with 3M $HCl_{(aq.)}$ (5x15 mL). The organics were dried and the solvent removed *in vacuo* to afford **7·HCl** as a yellow powder (22 mg, quant.).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 9.28 (s, 1H, int. mac. Ar*H*), 8.85 – 8.96 (m, 2H, ext. mac. Ar*H*), 8.63 (d, *J* = 7.1 Hz, 1H, Ar*H*), 8.59 (d, *J* = 7.8 Hz, 1H, Ar*H*), 8.51 (d, *J* = 8.4 Hz, 1H, Ar*H*), 8.10 – 8.19 (m, 2H, axle Ar*H* & ext. mac. Ar*H*), 7.96 - 8.07 (m, 2H, mac. N*H*), 7.92 (s, 1H, trz*H*), 7.74 (t, *J* = 7.8 Hz, 1H, Ar*H*), 7.40 (d, 1H, *J* = 8.7 Hz, Ar*H*), 7.16 – 7.26 (m, 12H, stopper-Ar*H*), 7.02 – 7.14 (m, 17H, Ar*H* & stopper-Ar*H*), 6.85 – 6.91 (m, 2H, stopper-Ar*H*), 6.78 – 6.82 (m, 2H, stopper-Ar*H*), 6.76 (s, 1H, Ar*H*), 6.20 (d, *J* = 8.5 Hz, 4H, hydroquinone CH_2), 5.87 (d, *J* = 8.6 Hz, 4H, hydroquinone CH_2), 5.23 (s, 2H, O-CH_2-C), 5.01 – 5.06 (m, 2H, N-CH_2), 4.76 – 4.81 (m, 2H, O-CH_2), 4.60 (t, *J* = 7.0 Hz, 2H, N-CH_2), 4.32 – 4.39 (m, 2H, mac. CH_2), 4.00 – 4.08 (m, 6H, mac. N-CH_2, axle O-CH_2), 3.64 – 3.87 (m, 16H, *crown ether*), 3.53 (m, 2H, mac. CH_2), 2.44 (t, *J* = 6.4 Hz, 2H, axle CH_2), 1.29 (d, *J* = 5.3 Hz, 54H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm) 166.41, 156.33, 156.24, 152.96, 151.61, 148.56, 148.52, 144.16, 144.14, 140.55, 133.93, 132.56, 130.86, 124.23, 124.20, 114.62, 113.76, 113.34, 113.19, 70.76, 70.51, 66.96, 66.27, 63.23, 63.21, 40.37, 34.46, 34.44, 31.53.

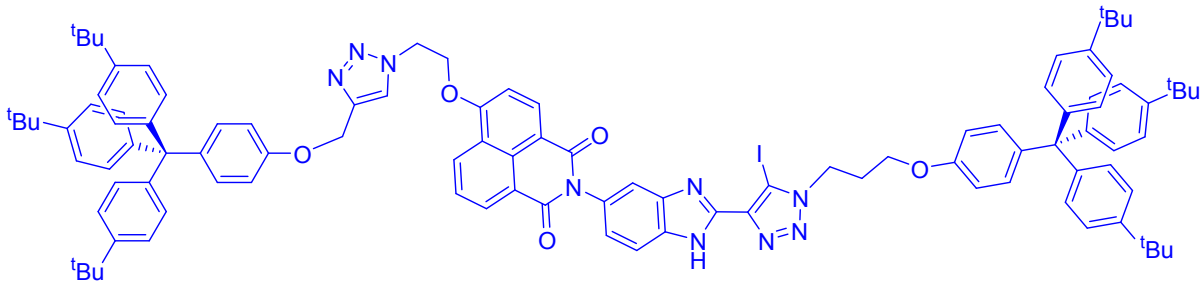
Benzimidazolium-iodotriazole tetrafluoroborate [2]rotaxane (7·HBF_4)



Rotaxane **7** (5 mg, 0.0022 mmol) was taken up in CH_2Cl_2 (20 mL) and HBF_4 acid diethyl ether complex was added. The solvent was removed *in vacuo* to afford **7·HBF$_4$** as a yellow powder (5.19 mg, quant.).

Due to the low solubility of **7·HBF$_4$** in $CDCl_3$ the obtained NMR spectra were too broad to accurately interpret.

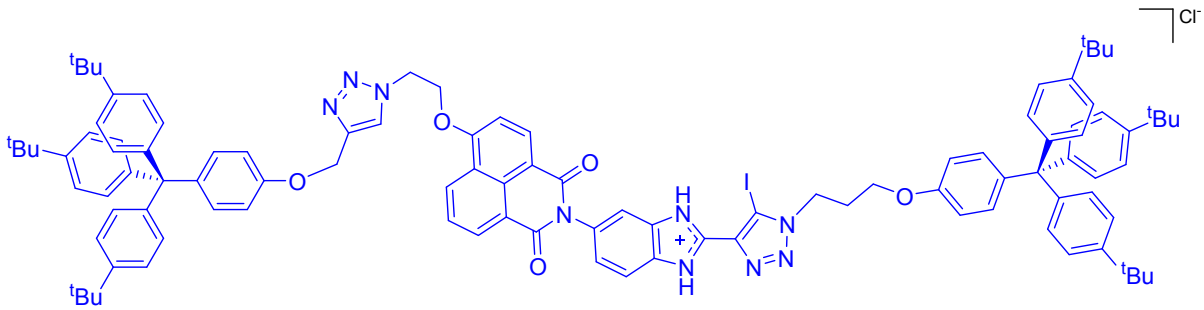
Free benzimidazole-iodotriazole axle (8)



Naphthalimide azide **4** (39 mg, 0.034 mmol), TBTA (1.81 mg, 0.0034 mmol), $[Cu(CH_3CN]_4PF_6]$ (1.27 mg, 0.0034 mmol) were dissolved in dry, degassed CH_2Cl_2 (10 mL). Stopper alkyne **6** (18 mg, 0.034 mmol) was added and the reaction stirred for 2 days. The solution was diluted with CH_2Cl_2 (20 mL), washed with EDTA/NH_4OH solution (2x20 mL), brine (2x20 mL) and H_2O (20 mL), the combined organics dried over $MgSO_4$ and the solvent removed *in vacuo*. Purification was achieved via preparative TLC (silica, 96:4 CH_2Cl_2/CH_3OH) to afford **8** as a yellow solid (3 mg, 5%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.25 – 10.32 (m, 1H, N*H*), 8.65 (d, *J* = 7.3 Hz, 1H, Ar*H*), 8.59 (d, *J* = 8.2 Hz, 1H, Ar*H*), 8.49 (d, *J* = 8.4 Hz, 1H, Ar*H*), 7.99 (d, *J* = 8.7 Hz, 1H, Ar*H*), 7.88 (s, 1H, trz*H*), 7.82 (s, 1H, Ar*H*), 7.72 (t, *J* = 7.8 Hz, 1H, Ar*H*), 7.63 (d, *J* = 8.6 Hz, 1H, Ar*H*), 7.48 (s, 1H, Ar*H*), 7.18 – 7.25 (m, 12H, stopper-Ar*H*), 7.03 – 7.14 (m, 17H, Ar*H* & stopper-Ar*H*), 6.86 (d, *J* = 8.3 Hz, 2H, stopper-Ar*H*), 6.75 – 6.81 (m, 2H, stopper-Ar*H*), 5.21 (s, 2H, O-CH_2-C), 4.97 – 5.03 (m, 2H, CH_2), 4.69 – 4.77 (m, 4H. CH_2), 4.02 – 4.08 (m, 2H, CH_2), 2.44 – 2.51 (m, 2H, CH_2), 1.23 – 1.32 (m, 54H, stopper-CH_2); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) 156.20, 148.55, 148.47, 144.22, 144.15, 140.52, 132.54, 132.47, 130.85, 124.22, 123.60, 113.31, 113.21, 77.48, 77.36, 77.16, 76.84, 63.21, 62.14, 34.45, 31.53, 29.86, 22.85; **HRMS (ESI)**: *m/z* 1679.76447 $[M+H]^+$ ($[C_{103}H_{108}IN_9O_5·H]^+$ calc. 1679.76244).

Free benzimidazolium-iodotriazole chloride axle (8·HCl)



Benzimidazole-iodotriazole axle **8** (3 mg, 0.0018 mmol) was taken up in $CHCl_3$ (20 mL) and washed with 3M $HCl_{(aq.)}$ solution (3x20 mL). The organic layer was dried over $MgSO_4$ and concentrated *in vacuo* to afford **8·HCl** (3 mg, quant.).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 – 8.68 (m, 1H, Ar*H*), 8.56 – 8.62 (m, 1H, Ar*H*), 8.46 – 8.53 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.88 (s, 1H, trz*H*), 7.78 – 7.84 (m, 1H, Ar*H*), 7.68 – 7.77 (s, 1H, Ar*H*), 7.60 – 7.67 (m, 1H, Ar*H*), 7.19 – 7.25 (m, 12H, stopper-Ar*H*), 7.03 – 7.14 (m, 17H, Ar*H* & stopper-Ar*H*), 6.86 (d, *J* = 8.5 Hz, 2H, stopper-Ar*H*), 6.74 – 6.80 (m, 2H, Ar*H*), 5.21 (s, 2H, O-CH_2-C), 5.01 (s, 2H, CH_2), 4.70 – 4.79 (m, 4H, CH_2), 4.03 – 4.09 (m, 2H, CH_2), 2.44 – 2.52 (m, 2H, CH_2), 1.23 – 1.33 (m, 54H, stopper-CH_2).

S2. UV-vis data for free axle 8

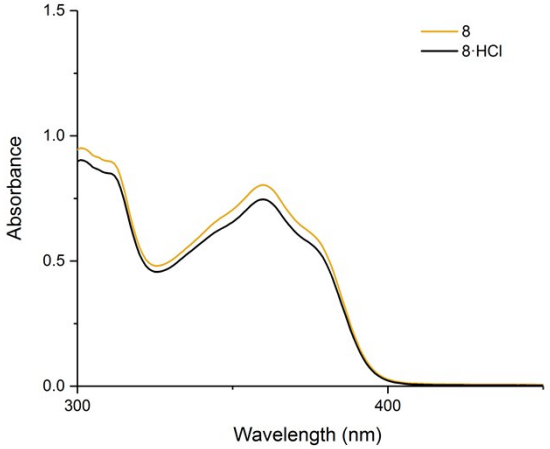


Figure S2 – 1 UV-vis spectra of free axle **8** (yellow) and **8·HCl** (black) in $CHCl_3$. Identical shape suggests no co-conformational change between neutral axle and after protonation with coordinating chloride anion ($2.5x10^{-5}$ M, 298 K)

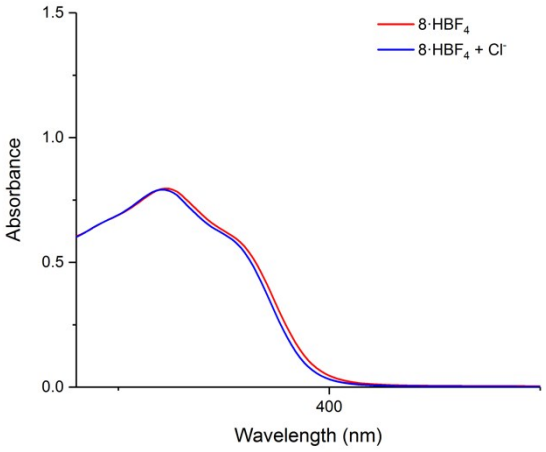


Figure S2 – 2 UV-vis spectra of protonated axle **8·HBF$_4$** (red) and **8·HBF$_4$** upon addition of TBACl (blue) in $CHCl_3$. Identical shape suggests no co-conformational change upon addition of coordinating anion ($2.5x10^{-5}$ M, 298 K)

S3. Spectral data for novel compounds

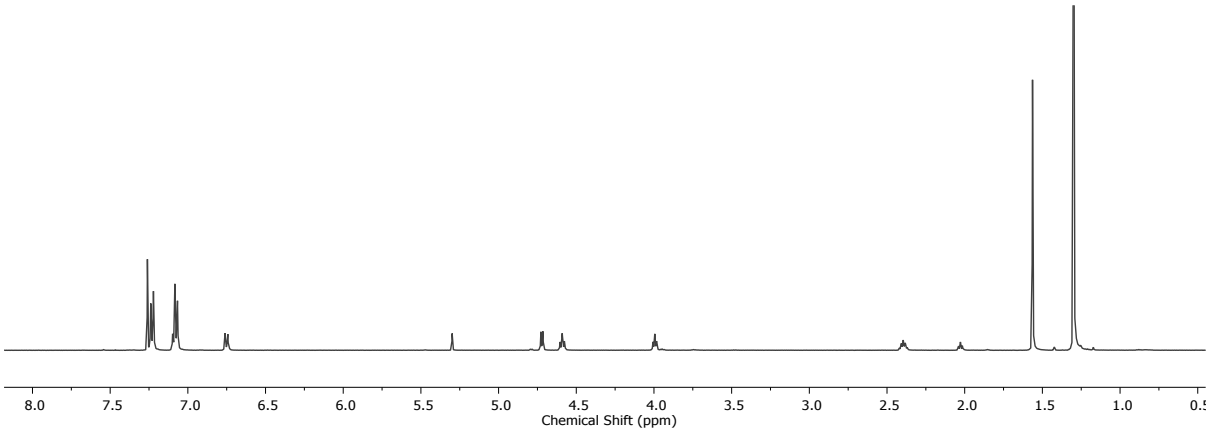


Figure S3 – 1 ^{1}H NMR spectrum of stopper iodotriazole alcohol ($CDCl_3$, 298 K, 500 MHz)

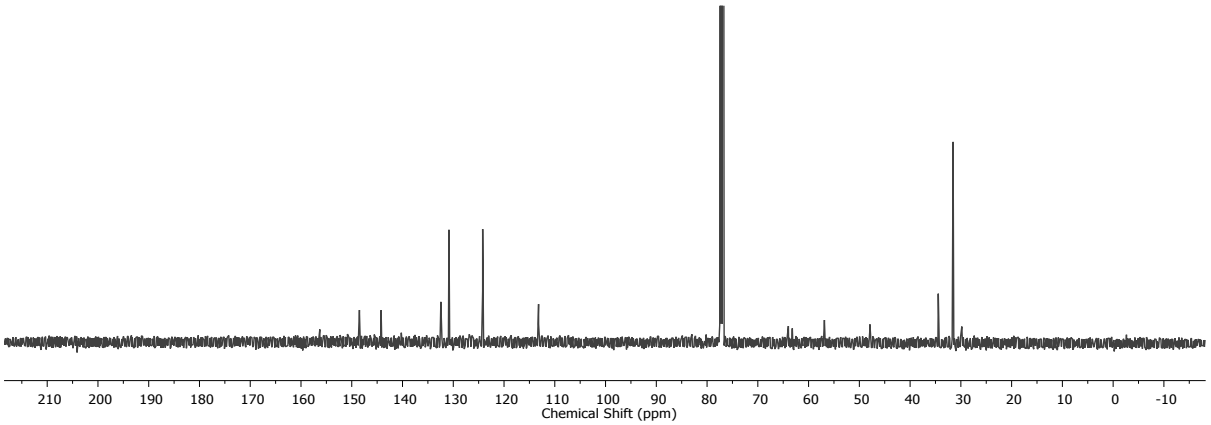


Figure S3 – 2 ^{13}C NMR spectrum of stopper iodotriazole alcohol ($CDCl_3$, 298 K, 126 MHz)

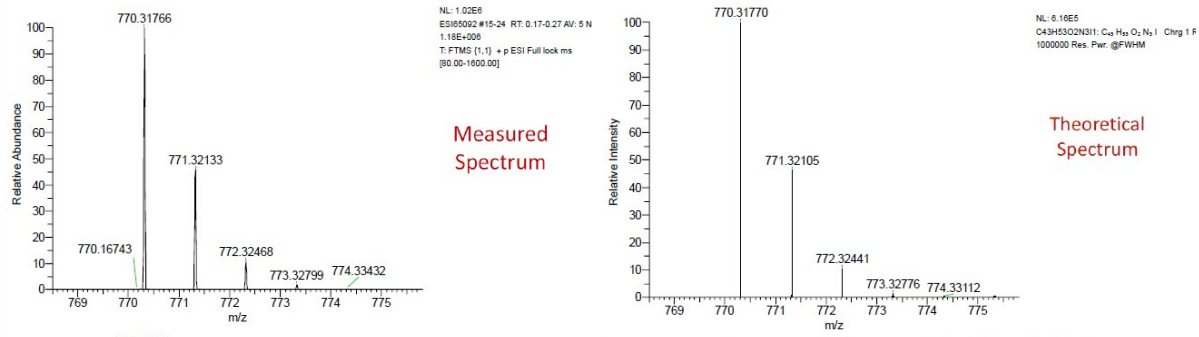


Figure S3 – 3 High-resolution ESI mass spectrum of stopper iodotriazole alcohol (left) with theoretical isotope model (right)

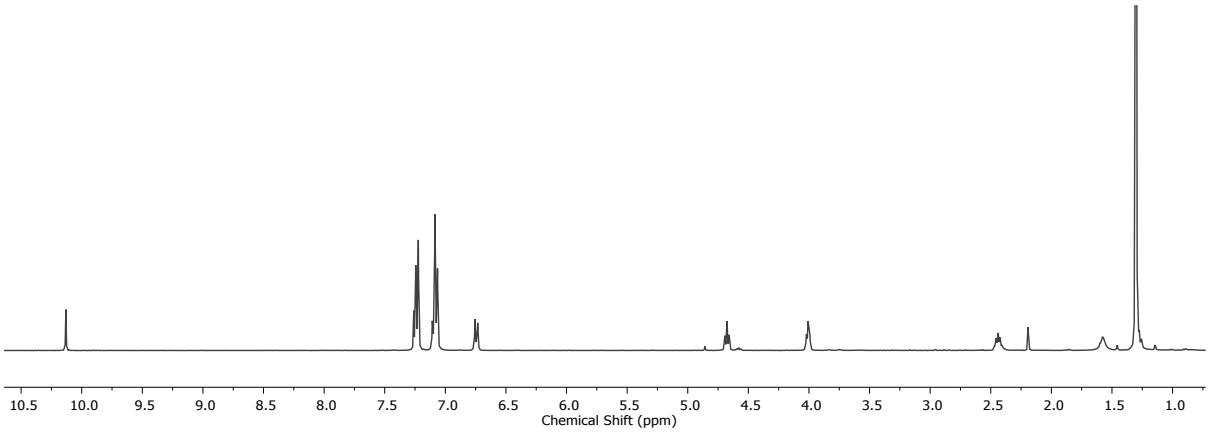


Figure S3 – 4 ^{1}H NMR spectrum of stopper iodotriazole aldehyde **1** ($CDCl_3$, 298 K, 400 MHz)

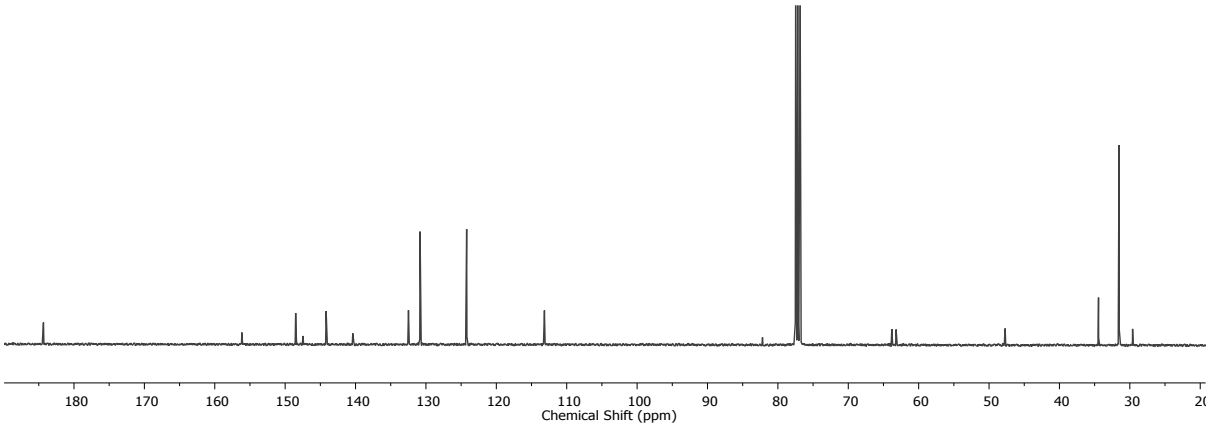


Figure S3 – 5 ^{13}C NMR spectrum of stopper iodotriazole aldehyde **1** ($CDCl_3$, 298 K, 101 MHz)

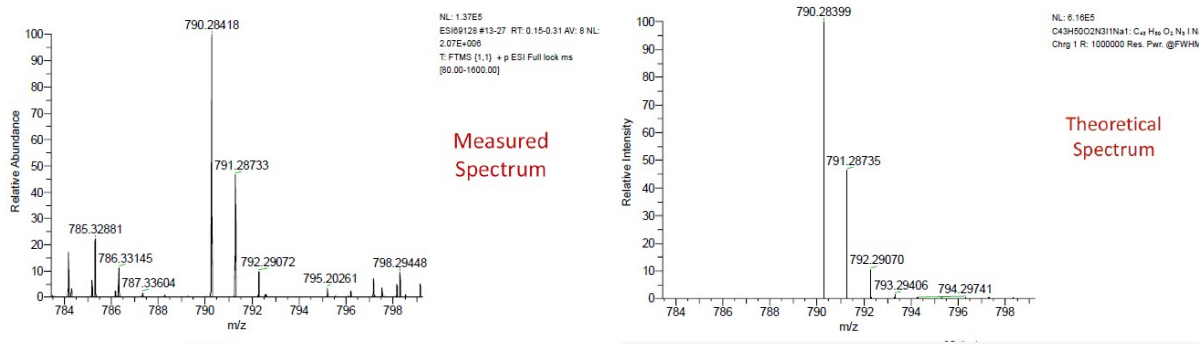


Figure S3 – 6 High-resolution ESI mass spectrum of stopper iodotriazole aldehyde **1** (left) with theoretical isotope model (right)

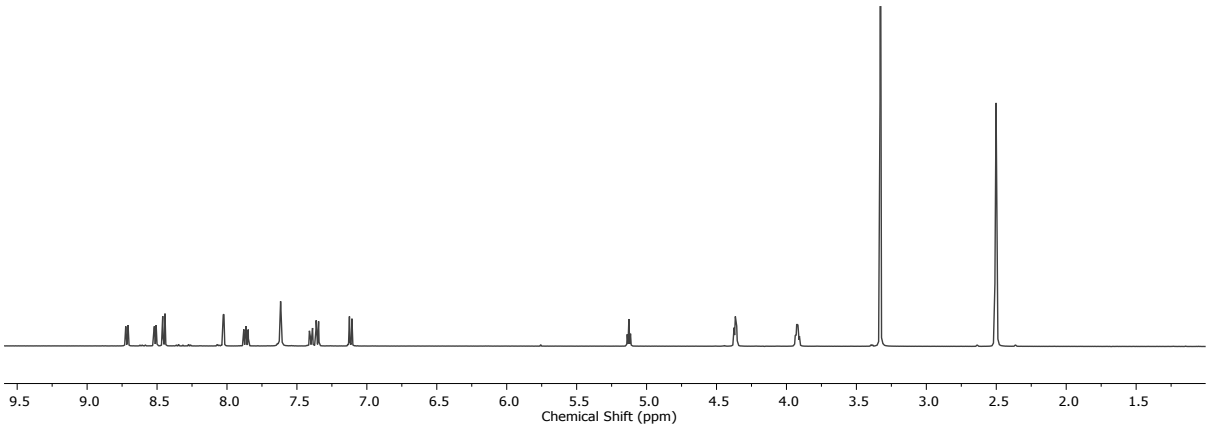


Figure S3 – 7 ^{1}H NMR spectrum of amino-nitrophenyl-naphthalimide alcohol (DMSO-d_6, 298 K, 500 MHz)

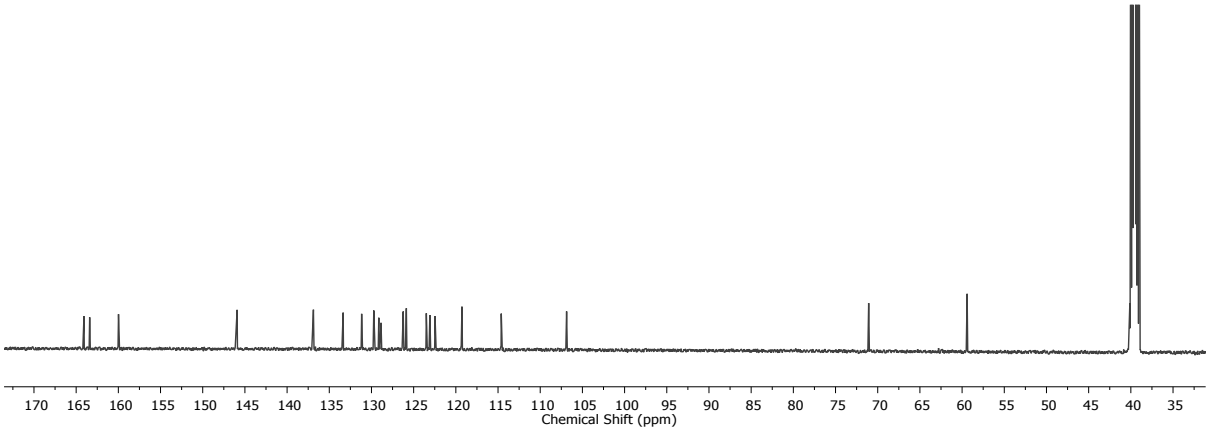


Figure S3 – 8 ^{13}C NMR spectrum of amino-nitrophenyl-naphthalimide alcohol (DMSO-d_6, 298 K, 126 MHz)

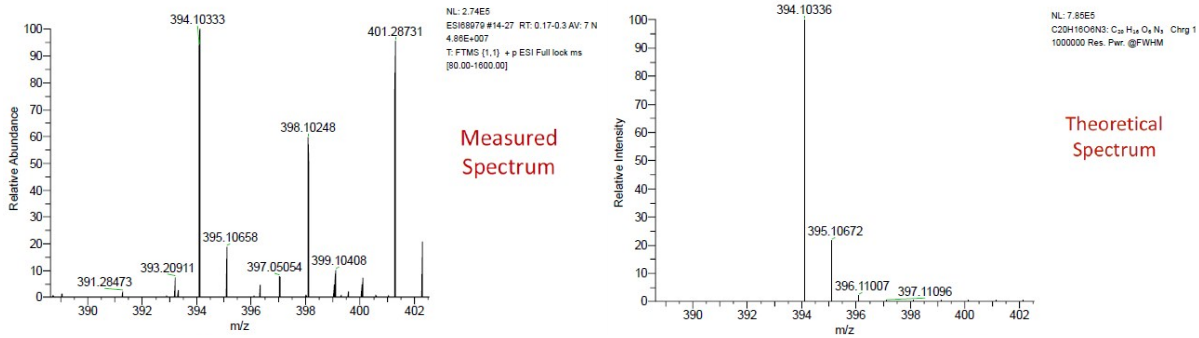


Figure S3 – 9 High-resolution ESI mass spectrum of amino-nitrophenyl-naphthalimide alcohol (left) with theoretical isotope model (right)

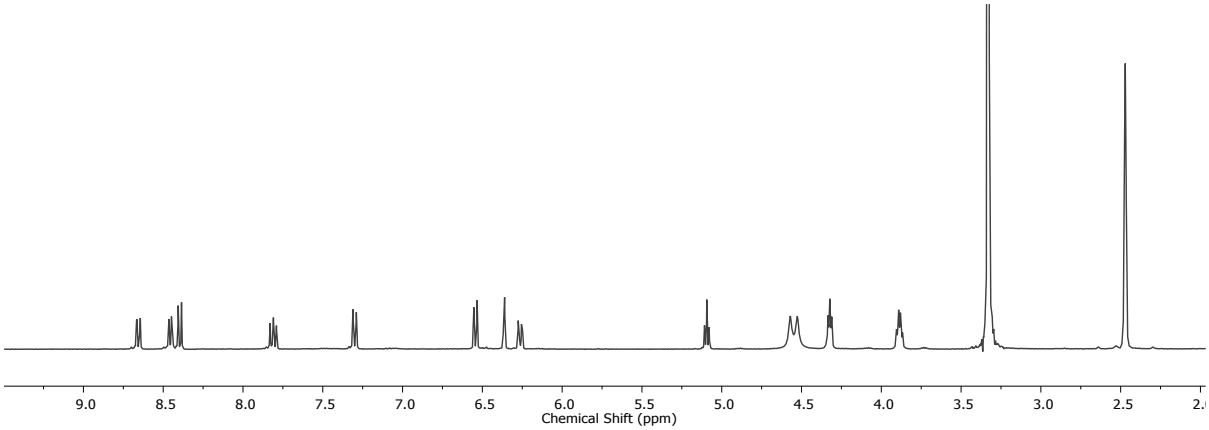


Figure S3 – 10 ^{1}H NMR spectrum of *o*-phenylenediamine naphthalimide alcohol **2** (DMSO-d_6, 298 K, 400 MHz)

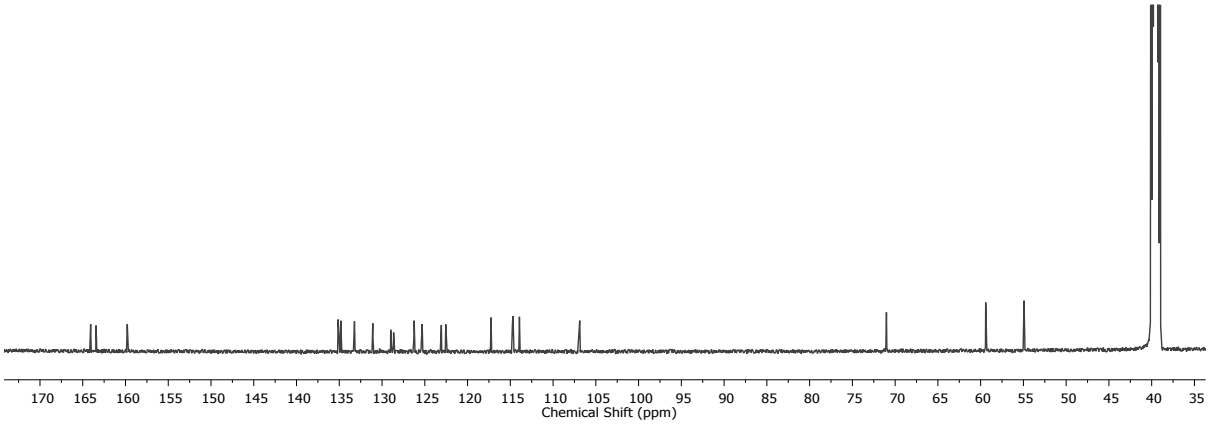


Figure S3 – 11 ^{13}C NMR spectrum of *o*-*p*henylenediamine naphthalimide alcohol **2** (DMSO-d_6, 298 K, 126 MHz)

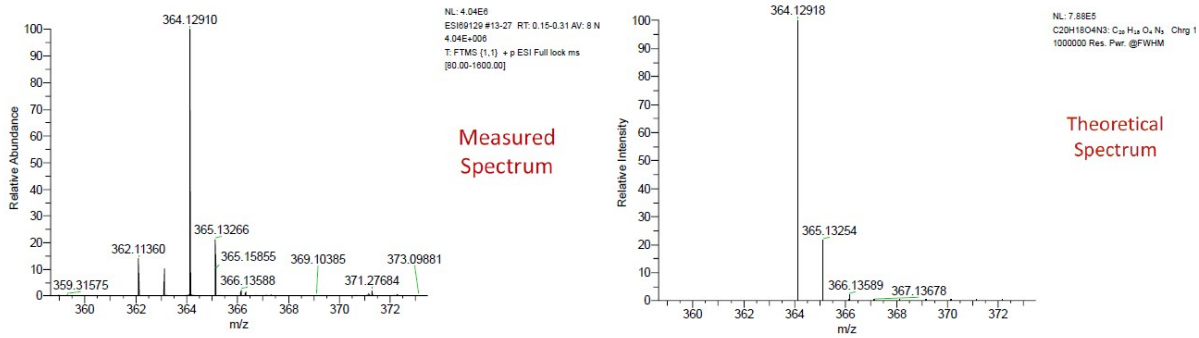


Figure S3 – 12 High-resolution ESI mass spectrum of amino-nitrophenyl-naphthalimide alcohol **2** (left) with theoretical isotope model (right)

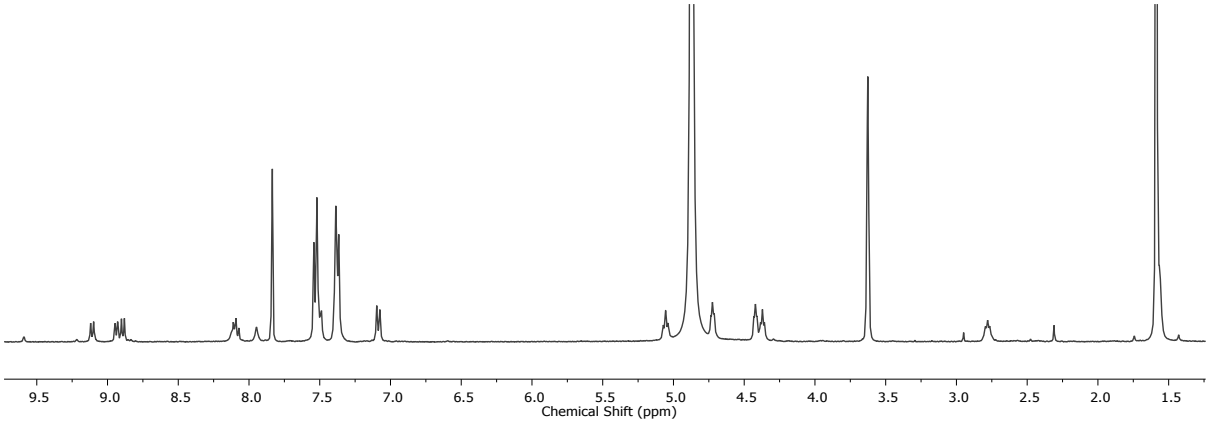


Figure S3 – 13 ^{1}H NMR spectrum of benzimidazole-iodotriazole naphthalimide alcohol **3** (1:1 $CDCl_3/CD_3OD$, 298 K, 400 MHz)

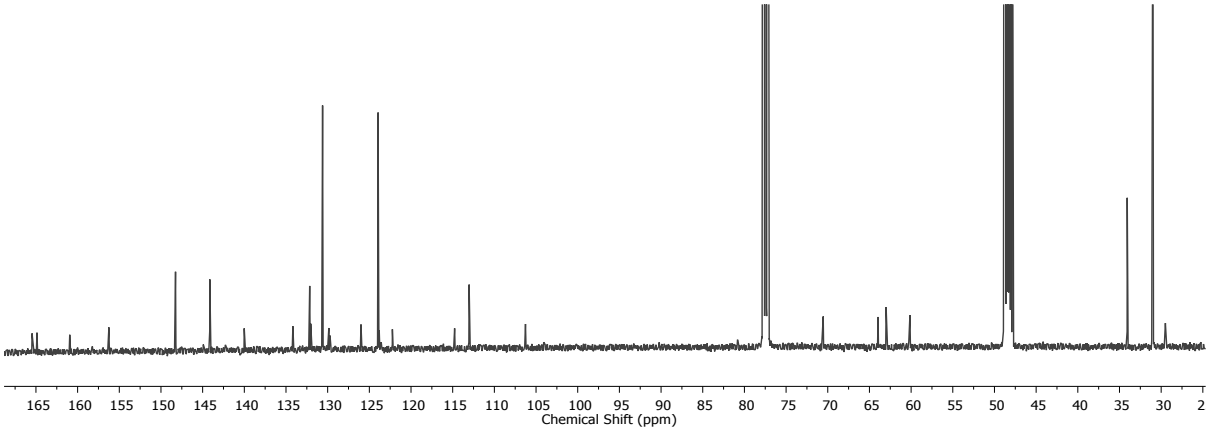


Figure S3 – 14 ^{13}C NMR spectrum of benzimidazole-iodotriazole naphthalimide alcohol **3** (1:1 $CDCl_3/CD_3OD$, 298 K, 126 MHz)

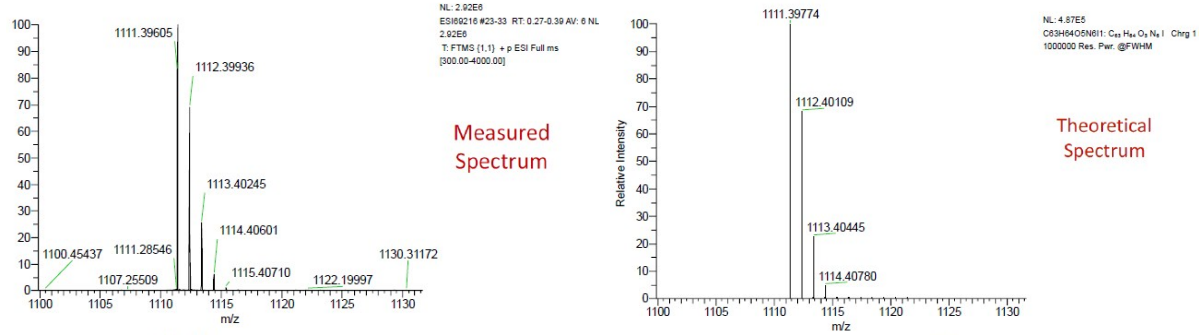


Figure S3 – 15 High-resolution ESI mass spectrum of benzimidazole-iodotriazole naphthalimide alcohol **3** (left) with theoretical isotope model (right)

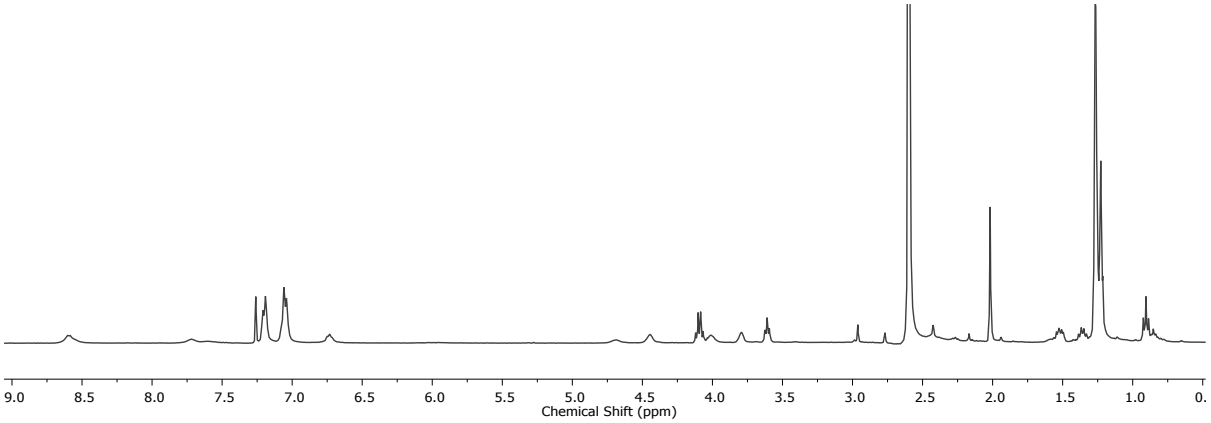


Figure S3 – 16 ^{1}H NMR spectrum of benzimidazole-iodotriazole naphthalimide azide **4** ($CDCl_3$, 298 K, 400 MHz)

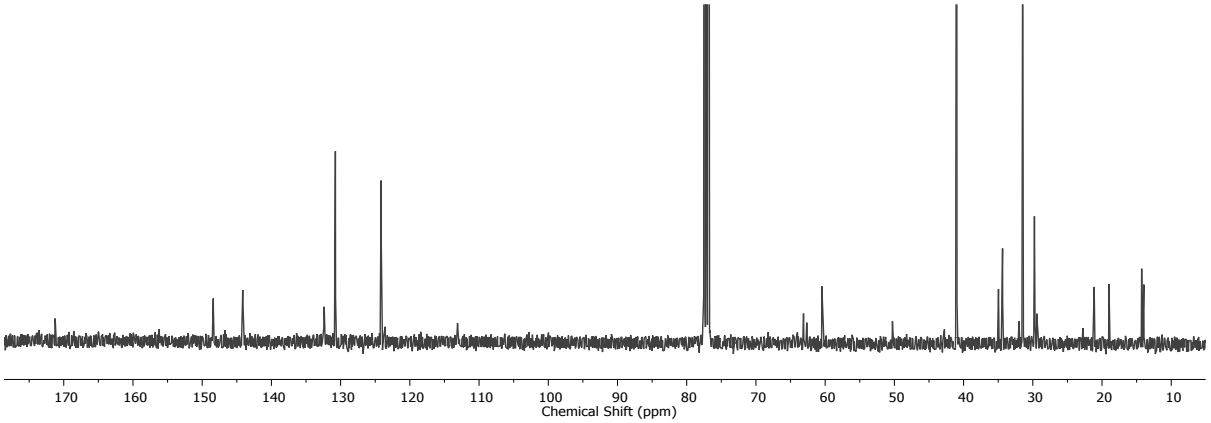


Figure S3 – 17 ^{1}H NMR spectrum of benzimidazole-iodotriazole naphthalimide azide **4** ($CDCl_3$, 298 K, 101 MHz)

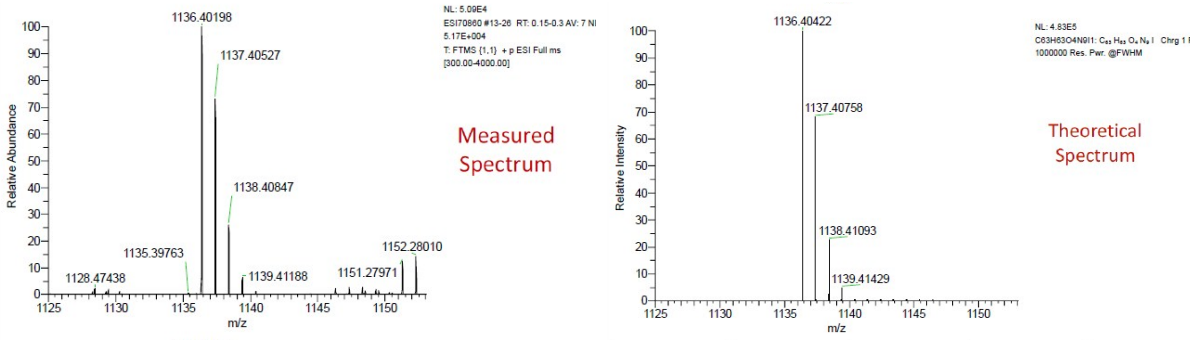


Figure S3 – 18 High-resolution ESI mass spectrum of benzimidazole-iodotriazole naphthalimide azide **4** (left) with theoretical isotope model (right)

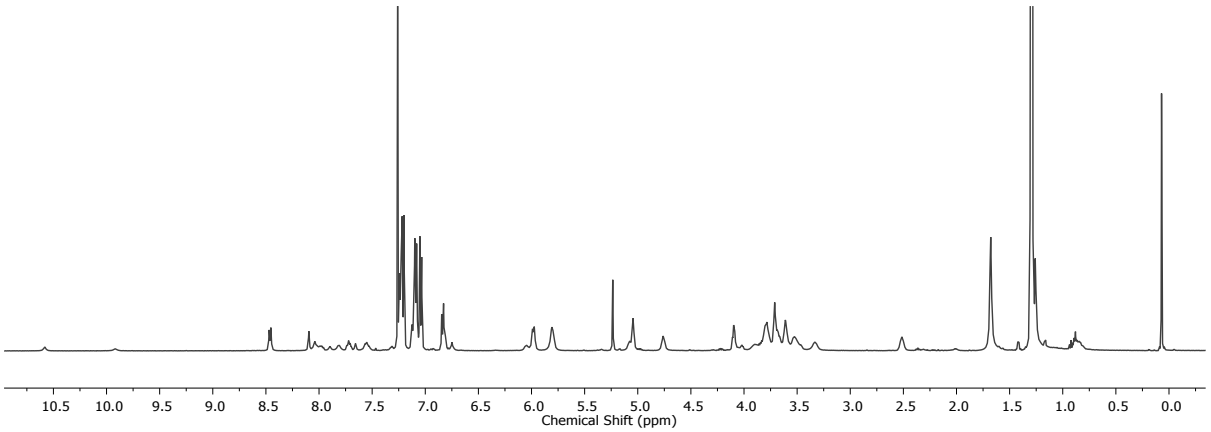


Figure S3 – 19 ^{1}H NMR spectrum of benzimidazole-iodotriazole naphthalimide neutral [2]rotaxane **7** ($CDCl_3$, 298 K, 500 MHz)

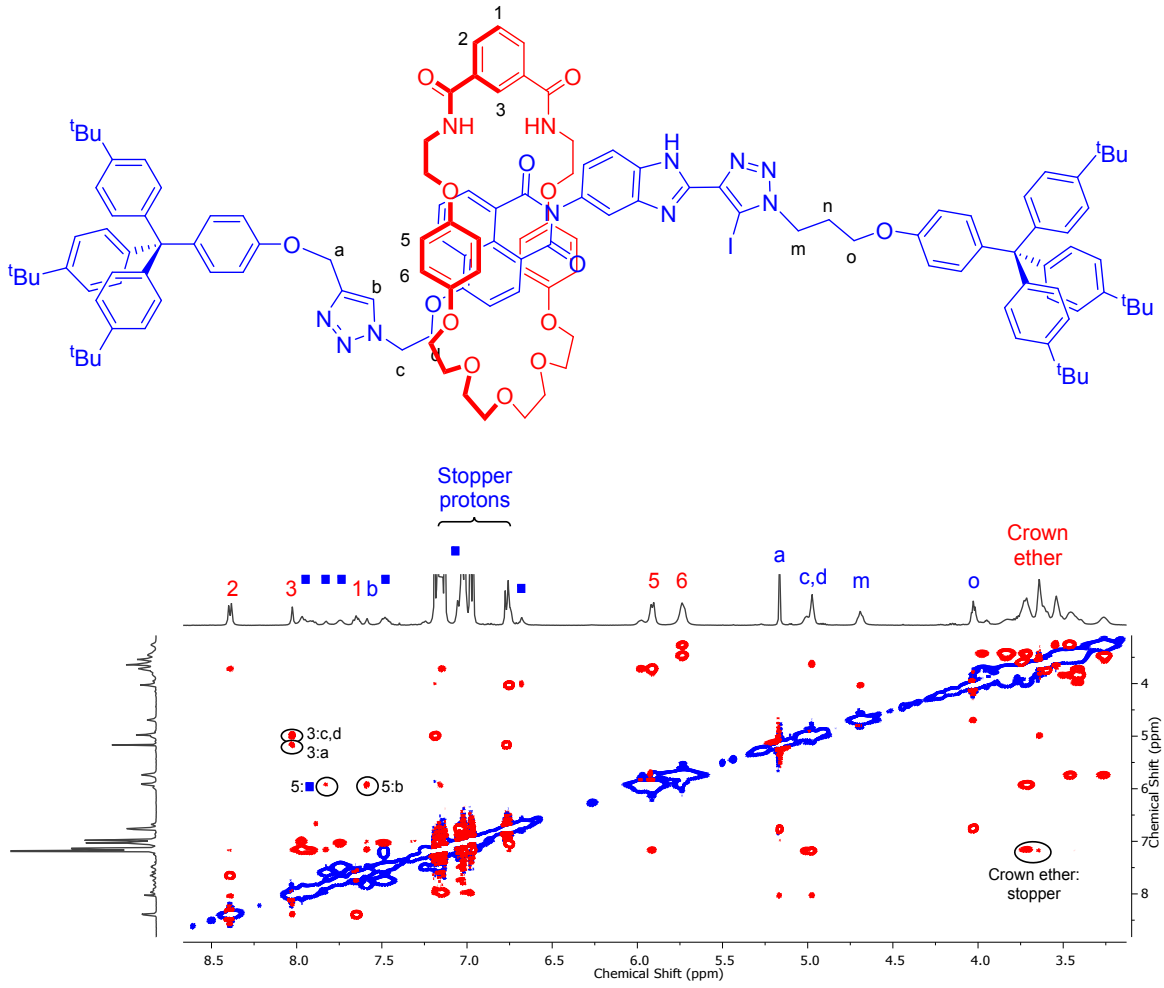


Figure S3 – 20 Truncated ^{1}H-^{1}H ROESY spectrum of neutral [2]rotaxane **7** ($CDCl_3$, 298 K, 500 MHz). Axle-based naphthalimide and benzyl protons shown as squares, key cross-peak interactions highlighted.

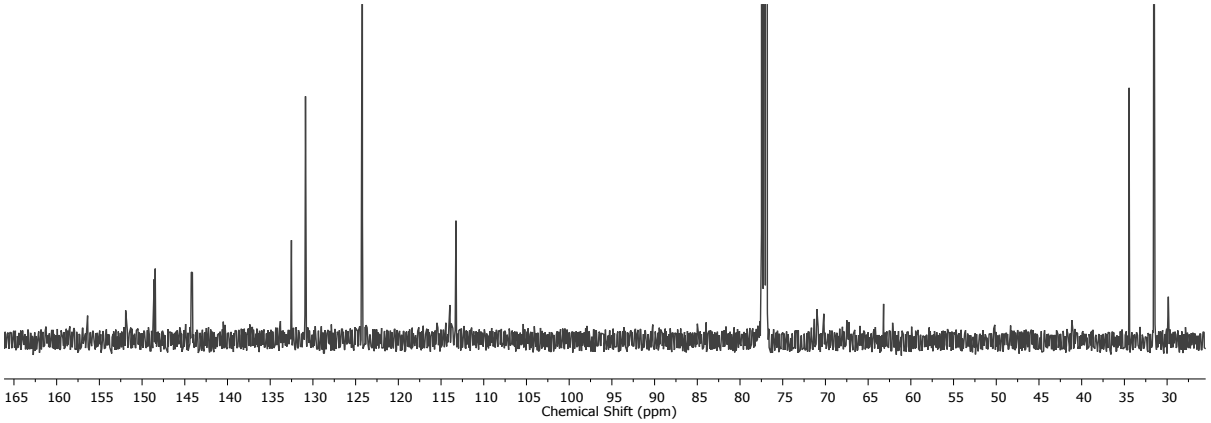


Figure S3 – 21 ^{13}C NMR spectrum of benzimidazole-iodotriazole naphthalimide neutral [2]rotaxane **7** ($CDCl_3$, 298 K, 126 MHz)

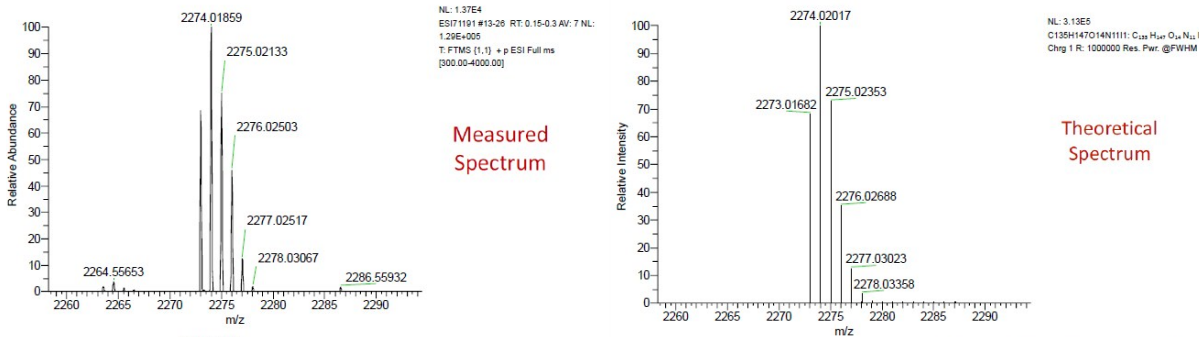


Figure S3 – 22 High-resolution ESI mass spectrum of benzimidazole-iodotriazole naphthalimide neutral [2]rotaxane **7** (left) with theoretical isotope model (right)

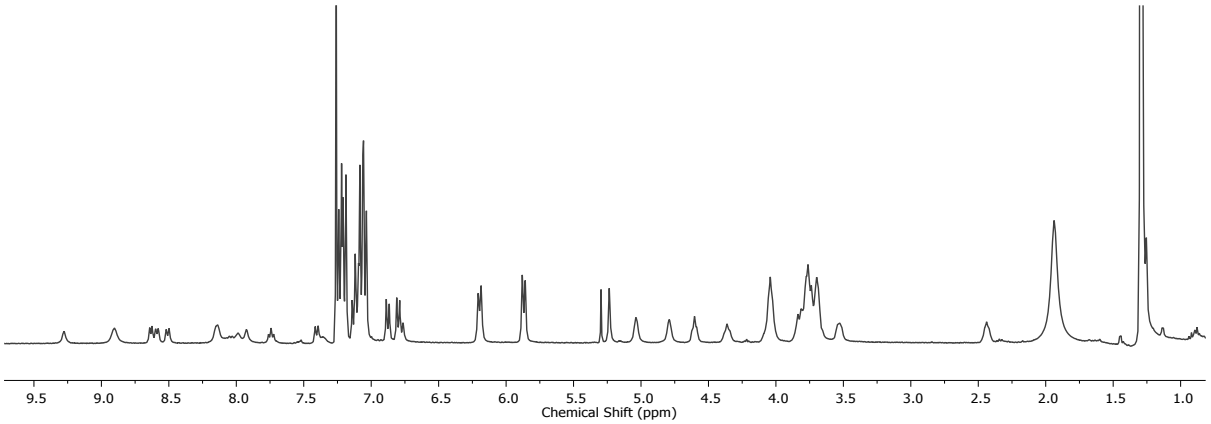


Figure S3 – 23 ^{1}H NMR spectrum of benzimidazole-iodotriazole naphthalimide chloride [2]rotaxane **7·HCl** ($CDCl_3$, 298 K, 500 MHz)

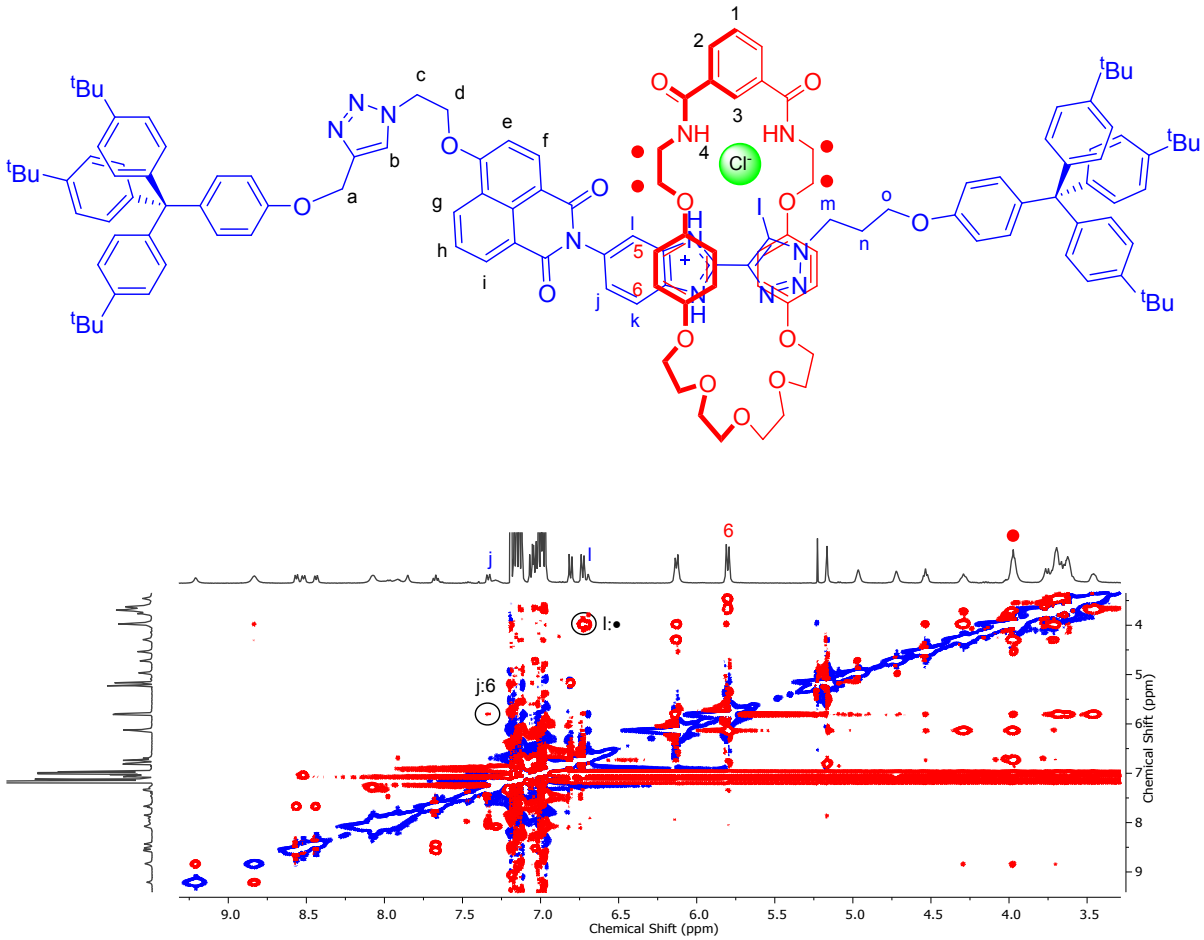


Figure S3 – 24 Truncated ^{1}H-^{1}H ROESY spectrum of chloride [2]rotaxane **7·HCl** ($CDCl_3$, 298 K, 500 MHz). Macrocycle alkyl peaks shown as circles, key cross-peak interactions highlighted.

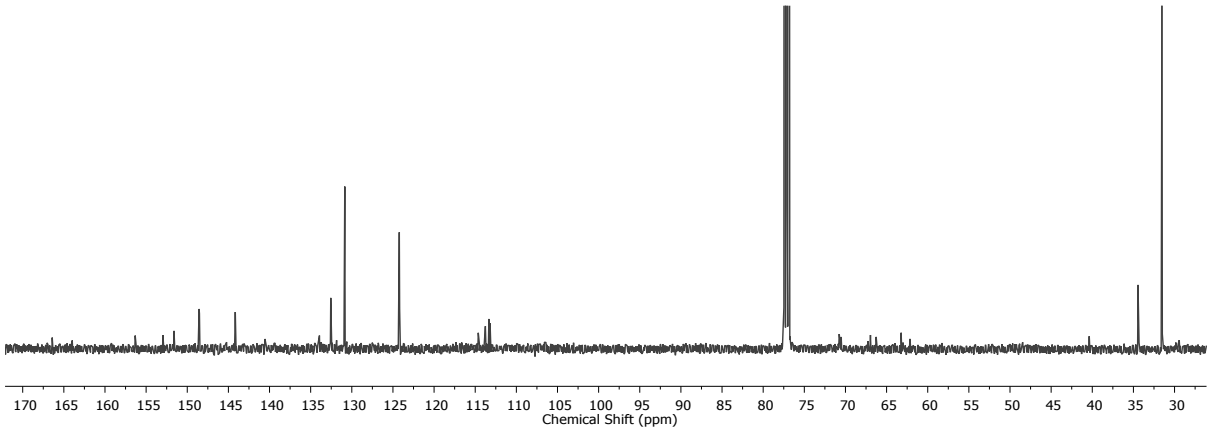


Figure S3 – 25 ^{13}C NMR spectrum of benzimidazole-iodotriazole naphthalimide chloride [2]rotaxane **7·HCl** ($CDCl_3$, 298 K, 126 MHz)

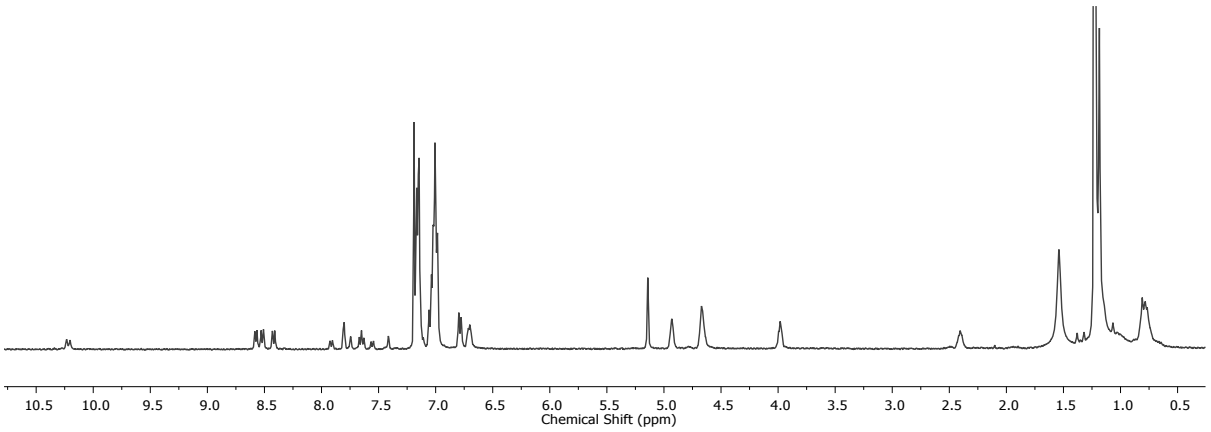


Figure S3 – 26 ^{1}H NMR spectrum of benzimidazole-iodotriazole naphthalimide axle **8** ($CDCl_3$, 298 K, 400 MHz)

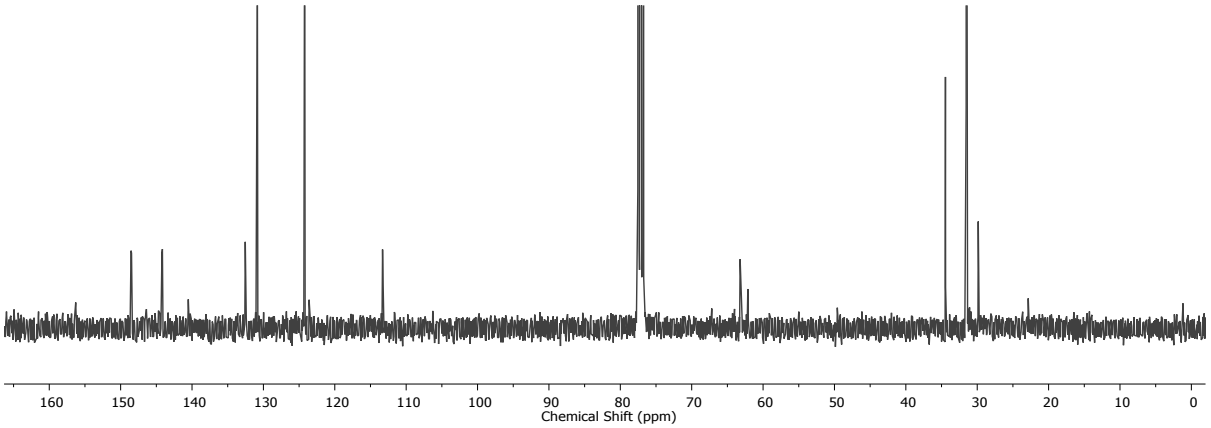


Figure S3 – 27 ^{13}C NMR spectrum of benzimidazole-iodotriazole naphthalimide axle **8** ($CDCl_3$, 298 K, 101 MHz)

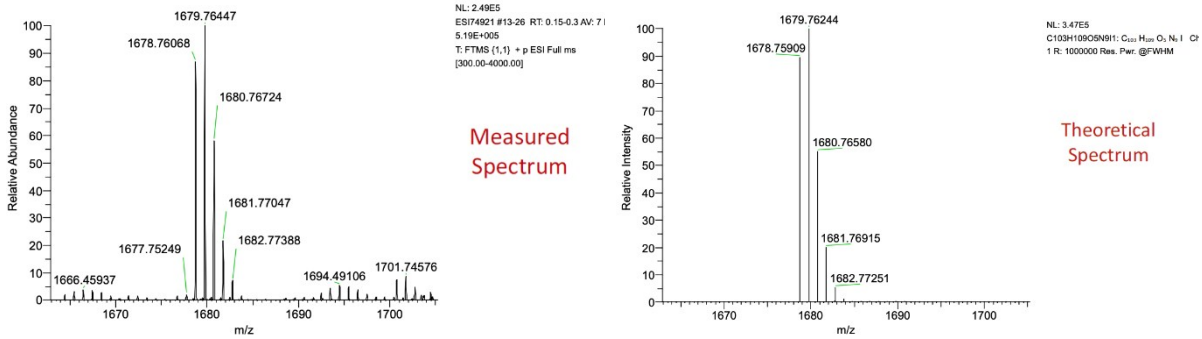


Figure S3 – 28 High-resolution ESI mass spectrum of benzimidazole-iodotriazole naphthalimide neutral [2]rotaxane **8** (left) with theoretical isotope model (right)

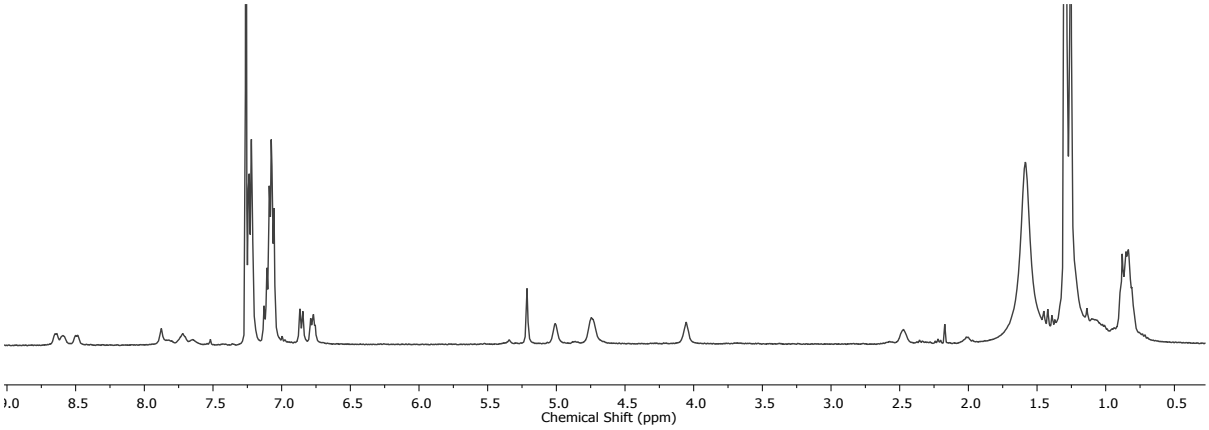


Figure S3 – 29 ^{1}H NMR spectrum of benzimidazolium-iodotriazole naphthalimide chloride axle **8·HCl** ($CDCl_3$, 298 K, 400 MHz)

S4. References

1 V. Aucagne, K. D. Hänni, D. A. Leigh, P. J. Lusby and D. B. Walker, *J. Am. Chem. Soc.*, 2006, **128**, 2186-2187.

2 T. Tang, Y. Zhou, Y. Chen, M. Li, Y. Feng, C. Wang, S. Wang and X. Zhou, *Anal. Methods*, 2015, **7**, 2386-2390.

3 J. A. Wisner, P. D. Beer and M. G. B. Drew, *Angew. Chem. Int. Ed.*, 2001, **40**, 3606-3609.