Electronic Supplementary Information for

# Neutral iodotriazole foldamers as tetradentate halogen bonding anion receptors

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## S1. Synthesis and Characterisation

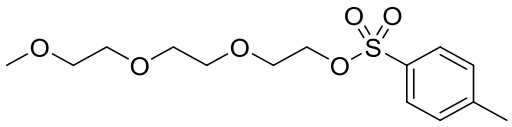
### S1.1 General Procedures

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. TBTA (tris(benzyltriazolemethyl)amine) and BTA (benzyltriazolemethyl)amine) were prepared according to reported procedures.[1]

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. Electrospray ionisation mass spectrometry (ESI-MS) was performed using the Waters Micromass LCT and Bruker microTOF spectrometers.

### S1.2 Synthesis of Compounds

2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate

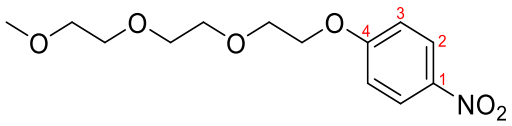


**14**

Triethylene glycol monomethyl ether (4.80 ml, 30 mmol) and dry triethylamine (6.27 ml, 45 mmol) were dissolved in dry DCM (60 ml) and *p*-toluenesulfonyl chloride (6.863 g, 36 mmol) was added. The reaction was stirred for 20 h at rt. The final mixture was washed with sat. aq. $NaHCO_3$, dried with anhydrous $Na_2SO_4$ and concentrated under vacuum. Crude material was purified by column chromatography (1.5% MeOH/DCM) to afford 8.870 g (27.86 mmol, 93%) of product as a colourless oil.

$\delta_H$ (400 MHz, $CDCl_3$): 7.73 (d, J = 8.3 Hz, 2H, Ar*H*), 7.29 (d, J = 8.1 Hz, 2H, Ar*H*), 4.15 – 4.04 (m, 2H, TEG-C$H_2$), 3.67 – 3.56 (m, 2H, TEG-C$H_2$), 3.58 – 3.50 (m, 6H, TEG-C$H_2$), 3.47 (m, 2H, TEG-C$H_2$), 3.30 (s, 3H, TEG-C$H_3$), 2.39 (s, 3H, ArC$H_3$); $\delta_C$ (100 MHz, $CDCl_3$): 13C NMR (101 MHz, CDCl3) δ 144.75 (Ar*C*), 132.92 (Ar*C*), 129.77 (Ar*C*), 127.86 (Ar*C*), 71.81 (TEG-*C*$H_2$), 70.63 (TEG-*C*$H_2$), 70.45 (TEG-*C*$H_2$), 70.44 (TEG-*C*$H_2$), 69.23 (TEG-*C*$H_2$), 68.56 (TEG-*C*$H_2$), 58.91 (TEG-*C*$H_3$), 21.55 (Ar*C*$H_3$); ESI-MS m/z 341.1 $[M+Na]^+$.

1-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-4-nitrobenzene

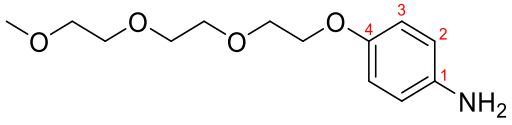



**15**

*p*-Nitrophenol (835 mg, 6 mmol) and **14** (1.592 g, 5 mmol) were added to dry MeCN (30 ml). $K_2CO_3$ (829 mg, 6 mmol) was added and the mixture was heated at reflux for 2.5 days. The solvent was then removed under vacuum and the residue suspended in water. The mixture was extracted with EtOAc and the combined organic phases were washed with water and brine, dried with anhydrous $Na_2SO_4$ and concentrated under vacuum. The crude product was purified by silica column chromatography (1.5% MeOH/DCM, $R_f$ 0.37 in 2% MeOH/DCM) to afford 1.335 g (4.68 mmol, 94%) of **15** as a yellowish oil.

$\delta_H$ (400 MHz, $CDCl_3$): 8.16 (m, 2H, $H^2$), 6.95 (m, 2H, $H^3$), 4.21 (m, 2H, TEG-C$H_2$), 3.88 (m, 2H, TEG-C$H_2$), 3.80 – 3.58 (m, 6H, TEG-C$H_2$), 3.53 (m, 2H, TEG-C$H_2$), 3.35 (m, 3H, TEG-C$H_3$). $\delta_C$ (100 MHz, $CDCl_3$): 163.90 ($C^1$), 141.58 ($C^4$), 125.86 ($C^2$), 114.62 ($C^3$), 71.92 (TEG-$C$H$_2$), 70.91 (TEG-$C$H$_2$), 70.64 (TEG-$C$H$_2$), 70.57 (TEG-$C$H$_2$), 69.41 (TEG-$C$H$_2$), 68.23 (TEG-$C$H$_2$), 59.03 (TEG-$C$H$_3$); ESI-MS m/z 308.1 $[M+Na]^+$.

4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)aniline

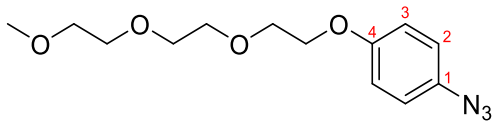



**16**

Compound **15** (1.300 g, 4.56 mmol) was dissolved in MeOH (50 ml). Hydrazine hydrate (2.2 ml, 45.6 mmol) and 10% Pd/C (60 mg) were added. The mixture was heated at reflux overnight. It was then filtered through Celite, concentrated under reduced pressure and dried under high vacuum. The crude product was purified by column chromatography on silica (1-5% MeOH/DCM) to afford 1.035 g (4.05 mmol, 89%) of **16** as a yellowish oil.

$\delta_H$ (400 MHz, $CDCl_3$): 6.70 – 6.62 (m, 2H, $H^3$), 6.57 – 6.51 (m, 2H, $H^2$), 3.96 (m, 2H, TEG-C$H_2$), 3.72 (m, 2H, TEG-C$H_2$), 3.67 – 3.61 (m, 2H, TEG-C$H_2$), 3.61 – 3.54 (m, 4H, TEG-C$H_2$), 3.50 – 3.44 (m, 2H, TEG-C$H_2$), 3.29 (s, 3H, TEG-C$H_3$), 3.19 (br s, 2H, N$H_2$). $\delta_C$ (100 MHz, $CDCl_3$): 151.70 ($C^4$), 140.27 ($C^1$), 116.19 ($C^2$), 115.77 ($C^3$), 71.81 (TEG-$C$H$_2$), 70.63 (TEG-$C$H$_2$), 70.51 (TEG-$C$H$_2$), 70.41 (TEG-$C$H$_2$), 69.79 (TEG-$C$H$_2$), 68.05 (TEG-$C$H$_2$), 58.90 (TEG-$C$H$_3$); ESI-MS m/z 256.2 $[M+H]^+$.

1-azido-4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene

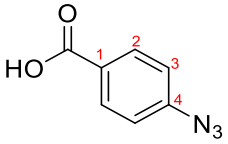


**5**

Compound **16** (1.005 g, 3.94 mmol) was dissolved in 17% aqueous HCl (26 ml) and the solution was cooled down to 0 °C. $NaNO_2$ (435 mg, 6.30 mmol) was added in small portions, causing the reaction mixture to become purple and then change colour to light brown. After strirring for 15 min at 0 °C, $NaN_3$ (410 mg, 6.30 mmol) was added portionwise, resulting in immediate evolution of gas. The reaction was stirred for 20 min at 0 °C and allowed to warm up to rt over 1 h. It was then diluted with water (25 ml) and neutralised with $Na_2CO_3$. The resulting solution was extracted with EtOAc, the organic fractions were dried with anhydrous $Na_2SO_4$ and concentrated under vacuum. The crude product was purified by silica column chromatography (1-1.5% MeOH/DCM, $R_f$ 0.29 in 2% MeOH/DCM), giving 776 mg (2.76 mmol, 67%) of **5** as a brown oil.

$\delta_H$ (400 MHz, $CDCl_3$): 6.97 – 6.83 (m, 4H, Ar*H*), 4.09 (m, 2H, TEG-C$H_2$), 3.83 (m, 2H, TEG-C$H_2$), 3.75 – 3.69 (m, 2H, TEG-C$H_2$), 3.69 – 3.60 (m, 4H, TEG-C$H_2$), 3.56 – 3.51 (m, 2H, TEG-C$H_2$), 3.36 (s, 3H, TEG-C$H_3$). $\delta_C$ (100 MHz, $CDCl_3$): 156.29 ($C^4$), 132.58 ($C^1$), 120.02 ($C^2$), 116.02 ($C^3$), 72.02 (TEG-*C*$H_2$), 70.92 (TEG-*C*$H_2$), 70.74 (TEG-*C*$H_2$), 70.65 (TEG-*C*$H_2$), 69.80 (TEG-*C*$H_2$), 67.94 (TEG-*C*$H_2$), 59.10 (TEG-*C*$H_3$); high resolution ESI-MS calcd for $C_{13}H_{19}N_3NaO_4$ $[M+Na]^+$: 304.12678, found: 304.12669.

4-azidobenzoic acid

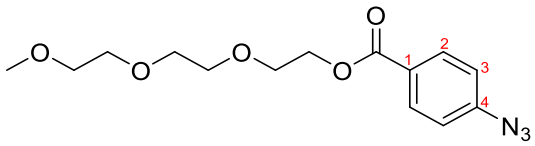


**17**

A literature procedure was used.[2] Sodium 4-aminobenzoate (1.591 g, 10 mmol) and *para*-toluenesulfonic acid monohydrate (7.600 g, 40 mmol) were added to water (50 ml). $NaNO_2$ (2.760 g, 40 mmol) was then added portionwise. The mixture was stirred for 20 min at rt and $NaN_3$ (975 mg, 15 mmol) was added portionwise, resulting in release of gas and heavy frothing. The resulting mixture was stirred for 30 min at rt. It was then filtered, the collected solid was washed with water and recrystallised in water/EtOH to afford **17** as a beige solid (820 mg, 5.03 mmol, 50%).

$\delta_H$ (400 MHz, $CDCl_3$): 8.01 – 7.87 (m, 1H, $H^2$), 7.03 – 6.88 (m, 1H, $H^3$); $\delta_C$ (100 MHz, $CDCl_3$): 167.66 (*C*$O_2$H), 144.26 ($C^1$), 131.50 ($C^2$), 127.44 ($C^4$), 118.61 ($C^3$); ESI-MS m/z 162.1 $[M-H]^-$.

2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-azidobenzoate

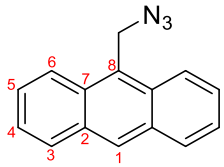



**6**

Compound **17** (820 mg, 5.03 mmol) was added to dry DCM (50 ml) and the solution was cooled to 0 °C. Dicyclohexylcarbodiimide (DCC, 1.038 g, 5.03 mmol) was thed added, followed by 4-(dimethylamino)pyridine (DMAP, 61 mg, 0.5 mmol) and triethylene glycol monomethyl ether (0.885 ml, 5.53 mmol). The mixture was allowed to warm up to rt and stirred overnight. It was then filtered, concentrated and the product was isolated by silica chromatography (7:3 hexanes/acetone) to afford **6** (730 mg, 2.36 mmol, 47%) as a yellow oil.

$\delta_H$ (400 MHz, $CDCl_3$): 8.11 – 7.98 (m, 2H, *H*$^2$), 7.12 – 6.99 (m, 2H, *H*$^3$), 4.53 – 4.36 (m, 2H, TEG-C*H*$_2$), 3.90 – 3.78 (m, 2H, TEG-C*H*$_2$), 3.78 – 3.61 (m, 6H, TEG-C*H*$_2$), 3.59 – 3.47 (m, 2H, TEG-C*H*$_2$), 3.37 (s, 3H, TEG-C*H*$_3$); $\delta_C$ (100 MHz, $CDCl_3$): 165.86 (*C*=O), 144.93 (*C*$^1$), 131.67 (*C*$^2$), 126.80 (*C*$^4$), 118.93 (*C*$^3$), 72.07 (TEG-*C*H$_2$), 70.84 (TEG-*C*H$_2$), 70.79 (TEG-*C*H$_2$), 70.74 (TEG-*C*H$_2$), 69.36 (TEG-*C*H$_2$), 64.34 (TEG-*C*H$_2$), 59.18 (TEG-*C*H$_3$); high resolution ESI-MS m/z calcd for $C_{14}H_{19}O_5N_3Na$ $[M+Na]^+$: 332.12169, found: 332.12151.

9-azidomethylanthracene

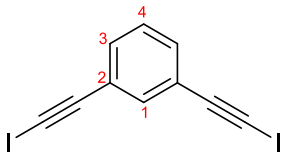



**7**

A literature procedure was used.[3] 9-hydroxymethylanthracene (1.54 g, 7.40 mmol) was added to DCM (30 ml) and the solution was cooled to 0 °C. $SOCl_2$ (810 µl, 11.10 mmol) was then added slowly and the reaction was allowed to warm up to rt while being stirred for 1 h. Solvent was removed under vacuum and the residue redissolved in DMF (10 ml). $NaN_3$ (777 mg, 11.95 mmol) was added and the reaction was stirred at 50 °C for 1 h. It was then allowed to cool down, diluted with water and extracted with EtOAc. The combined organic phases were washed with brine, dried with anhydrous $MgSO_4$, filtered and concentrated under vacuum. The crude product was purified by silica column (1:19 EtOAc:petrol) to afford 980 mg (4.20 mmol, 57%) of **7** as a yellow crystalline solid.

$\delta_H$ (400 MHz, $CDCl_3$): 8.51 (s, 1H, *H*$^1$), 8.29 (dd, J = 8.9, 1.1 Hz, 2H, *H*$^6$), 8.05 (dd, J = 8.4, 1.2 Hz, 2H, *H*$^3$), 7.60 (ddd, J = 8.9, 6.5, 1.4 Hz, 2H, *H*$^5$), 7.52 (ddd, J = 7.8, 6.5, 1.0 Hz, 2H, *H*$^4$), 5.33 (s, 2H, C*H*$_2$). $\delta_C$ (100 MHz, $CDCl_3$): 131.50 (*C*$^2$), 130.83 (*C*$^7$), 129.42 (*C*$^3$), 129.12 (*C*$^1$), 126.97 (*C*$^5$), 125.90 (*C*$^8$), 125.33 (*C*$^4$), 123.64 (*C*$^6$), 46.49 (*C*H$_2$); EI-MS m/z 233.0949 $[M]^+$.

1,3-bis(iodoethynyl)benzene

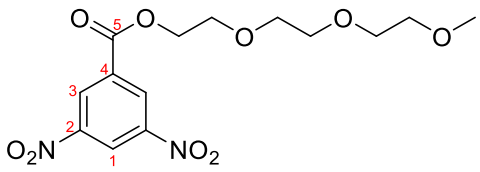


**8b**

1,3-Diethynylbenzene (378 mg, 3 mmol) was added to dry THF (10 ml). The solution was cooled to -78 °C under $N_2$ atmosphere and 2.5M *n*-BuLi solution in hexanes (6 ml, 15 mmol) was added slowly, resulting in formation of a clumped precipitate. The reaction was strirred for 30 min at -78 °C. $I_2$ (3.807 g, 15 mmol) was separately dissolved in dry THF (12 ml) and the resulting solution was slowly added to the reaction mixture. The reaction was then allowed to warm to rt, diluted with water and extracted with $CHCl_3$. Sodium thiosulfate was added to the biphasic mixture during extraction to remove excess $I_2$. The organic layer was then washed with brine, dried with anhydrous $MgSO_4$ and concentrated under vacuum. The residue was dry-loaded onto a silica column from DCM and eluted with petrol to afford **8b** (1.078 g, 2.85 mmol, 95%) as a white crystalline solid.

$\delta_H$ (400 MHz, $CDCl_3$): 7.42 (d, J = 1.8 Hz, 1H, $H^1$), 7.30 (dd, J = 7.8, 1.6 Hz, 2H, $H^3$), 7.18 (t, J = 7.7 Hz, 1H, $H^4$). $\delta_C$ (100 MHz, $CDCl_3$): δ 136.20 ($C^1$), 132.65 ($C^3$), 128.41 ($C^4$), 123.78 ($C^2$), 93.22 ($C$≡CI), 7.80 (C≡$C$I); EI-MS m/z 377.8398 $[M]^+$.

2-(2-(2-methoxyethoxy)ethoxy)ethyl 3,5-dinitrobenzoate

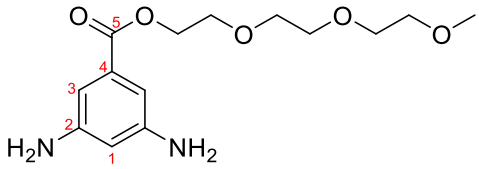


**18**

3,5-Dinitrobenzoic acid (1.061 g, 5 mmol) was added to dry DCM (100 ml) and the solution was cooled to 0 °C. DCC (1.032 g, 5 mmol) and DMAP (61 mg, 0.5 mmol) were dissolved separately in small volumes of dry DCM and added to the reaction mixture, followed by triethylene glycol monomethyl ether (0.880 ml, 5.5 mmol). The reaction was allowed to warm up to rt overnight. The mixture was then filtered, concentrated under vacuum and separated by silica column chromatography (1-1.5% MeOH/DCM) to afford **18** as a clear oil (1.483 g, 4.14 mmol, 83%).

$\delta_H$ (400 MHz, $CDCl_3$): 9.20 (t, J = 2.2 Hz, 1H, $H^1$), 9.16 (d, J = 2.1 Hz, 2H, $H^3$), 4.63 – 4.55 (m, 2H, TEG-C$H_2$), 3.92 – 3.84 (m, 2H, TEG-C$H_2$), 3.75 – 3.69 (m, 2H, TEG-C$H_2$), 3.67 (dd, J = 6.2, 3.5 Hz, 2H, TEG-C$H_2$), 3.63 (dd, J = 5.7, 3.6 Hz, 2H, TEG-C$H_2$), 3.55 – 3.48 (m, 2H, TEG-C$H_2$), 3.33 (s, 3H, TEG-C$H_3$). $\delta_C$ (100 MHz, $CDCl_3$): 162.62 ($C^5$), 148.73 ($C^2$), 133.92 ($C^4$), 129.64 ($C^3$), 122.49 ($C^1$), 72.00 (TEG-$C$H$_2$), 70.77 (TEG-$C$H$_2$), 70.74 (TEG-$C$H$_2$), 70.70 (TEG-$C$H$_2$), 68.85 (TEG-$C$H$_2$), 65.89 (TEG-$C$H$_2$), 59.10 (TEG-$C$H$_2$). ESI-MS m/z 381.1 $[M+Na]^+$.

2-(2-(2-methoxyethoxy)ethoxy)ethyl 3,5-diaminobenzoate

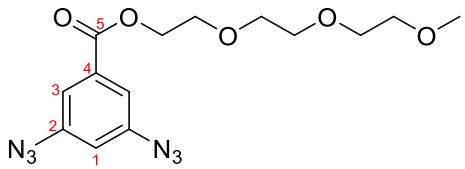


**19**

A modified literature procedure was used.[4] **18** (1.250 g, 3.49 mmol) was dissolved in EtOAc (15 ml) and 10% Pd/C (100 mg) was added. The mixture was flushed with $H_2$ and stirred overnight under $H_2$ atmosphere at atmospheric pressure and rt. It was then filtered through Celite and concentrated to afford **19** as a brownish oil (1.044 g, 3.49 mmol, quant.).

$\delta_H$ (400 MHz, $CDCl_3$): 6.76 (d, J = 2.1 Hz, 2H, $H^3$), 6.15 (t, J = 2.1 Hz, 1H, $H^1$), 4.43 – 4.35 (m, 2H, TEG-C$H_2$), 3.78 (m, 2H, TEG-C$H_2$), 3.72 (br s, 4H, N$H_2$), 3.70 – 3.58 (m, 6H, TEG-C$H_2$), 3.52 (m, 2H, TEG-C$H_2$), 3.35 (s, 3H, TEG-C$H_3$); $\delta_C$ (100 MHz, $CDCl_3$): 166.96 ($C^5$), 147.66 ($C^2$), 131.98 ($C^4$), 106.99 ($C^3$), 105.79 ($C^1$), 71.98 (TEG-*C*$H_2$), 70.76 (TEG-*C*$H_2$), 70.66 (TEG-*C*$H_2$), 70.63 (TEG-*C*$H_2$), 69.32 (TEG-*C*$H_2$), 64.03 (TEG-*C*$H_2$), 59.06 (TEG-*C*$H_3$); ESI-MS m/z 299.2 $[M+H]^+$.

2-(2-(2-methoxyethoxy)ethoxy)ethyl 3,5-diazidobenzoate

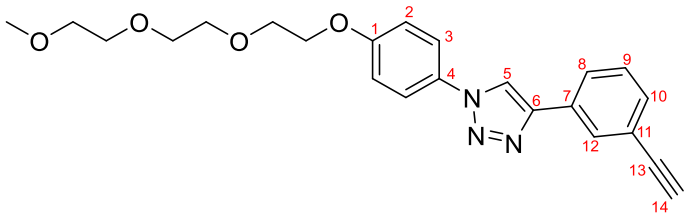


**12**

A literature procedure was used.[4] **19** (994 mg, 3.33 mmol) was added to 37% aq HCl (50 ml) and the solution was cooled to 0 °C. $NaNO_2$ (781 mg, 11.33 mmol)) was added in small portions and the mixture was stirred at 0 °C for 15 min. $NaN_3$ (737 mg, 11.33 mmol) was then added portionwise, resulting in release of gas. After stirring for another 15 min at 0 °C the reaction was allowed to warm to rt and stirred at rt for 20 min. It was then poured into cold water (150 ml) and extracted with EtOAc (4x). The extracts were washed with sat. aq. $NaHCO_3$ and brine, dried with anhydrous $Na_2SO_4$ and concentrated under vacuum. The crude product was purified by silica chromatography (1-2% MeOH/DCM) to afford **12** as a yellow oil (785 mg, 2.24 mmol, 67%).

$\delta_H$ (400 MHz, $CDCl_3$): 7.48 (d, J = 2.2 Hz, 2H, $H^3$), 6.79 (t, J = 2.1 Hz, 1H, $H^1$), 4.55 – 4.43 (m, 2H, TEG-C$H_2$), 3.82 (m, 2H, TEG-C$H_2$), 3.75 – 3.59 (m, 6H, TEG-C$H_2$), 3.53 (m, 2H, TEG-C$H_2$), 3.36 (s, 3H, TEG-C$H_3$). $\delta_C$ (100 MHz, $CDCl_3$): 164.95 ($C^5$), 142.33 ($C^2$), 133.37 ($C^4$), 116.55 ($C^3$), 113.95 ($C^1$), 72.05 (TEG-*C*$H_2$), 70.82 (TEG-*C*$H_2$), 70.77 (TEG-*C*$H_2$), 70.73 (TEG-*C*$H_2$), 69.15 (TEG-*C*$H_2$), 64.88 (TEG-*C*$H_2$), 59.15 (TEG-*C*$H_2$); high resolution ESI-MS m/z calcd for $C_{14}H_{18}N_6NaO_5$ $[M+Na]^+$: 373.12309, Found: 373.12336.

1-(3-ethynylphenyl)-4-(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)-1H-1,2,3-triazole



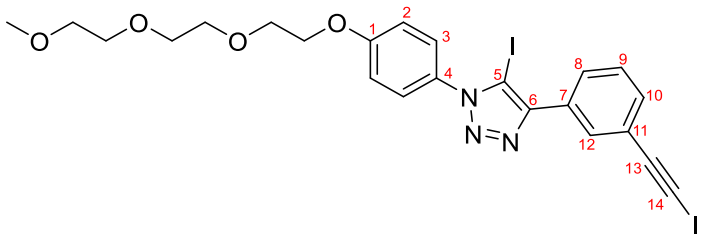
**9a**

*General procedure for azide-alkyne cycloaddition*

Compound **5** (281 mg, 1.00 mmol), diethynylbenzene **8a** (266 µl, 2.00 mmol) and DIPEA (17 µl, 0.10 mmol) were added to dry, degassed DCM (10 ml) under Ar atmosphere. Then $Cu(MeCN)_4PF_6$ (19 mg, 0.05 mmol) and TBTA (27 mg, 0.05 mmol) were added simultaneously. The mixture was stirred overnight at rt and under Ar. It was then diluted with DCM, washed with 2% aqueous $NH_3$, dried with anhydrous $Na_2SO_4$ and concentrated. The product was isolated by silica column chromatography (3-10% acetone/DCM) to provide **9a** as a white solid (280 mg, 0.69 mmol, 69%).

$\delta_H$ (400 MHz, $CDCl_3$): 8.12 (s, 1H, $H^5$), 7.97 (t, J = 1.7 Hz, 1H, $H^{12}$), 7.87 (dt, J = 7.7, 1.5 Hz, 1H, $H^8$), 7.67 – 7.57 (m, 2H, $H^3$), 7.43 (dt, J = 7.6, 1.4 Hz, 1H, $H^{10}$), 7.36 (t, J = 7.7 Hz, 1H, $H^9$), 7.03 – 6.95 (m, 2H, $H^2$), 4.14 (m, 2H, TEG-C$H_2$), 3.85 (m, 2H, TEG-C$H_2$), 3.72 (m, 2H, TEG-C$H_2$), 3.69 – 3.59 (m, 4H, TEG-C$H_2$), 3.52 (m, 2H, TEG-C$H_2$), 3.34 (s, 3H, TEG-C$H_3$), 3.11 (s, 1H, $H^{14}$); $\delta_C$ (100 MHz, $CDCl_3$): 159.13 ($C^1$), 147.21 ($C^6$), 131.81 ($C^{10}$), 130.69 ($C^7$), 130.48 ($C^4$), 129.36 ($C^{12}$), 128.98 ($C^9$), 126.15 ($C^8$), 122.78 ($C^{11}$), 122.05 ($C^3$), 118.19 ($C^5$), 115.51 ($C^2$), 83.29 ($C^{13}$), 77.81 ($C^{14}$), 71.94 (TEG-$C$H$_2$), 70.89 (TEG-$C$H$_2$), 70.67 (TEG-$C$H$_2$), 70.59 (TEG-$C$H$_2$), 69.63 (TEG-$C$H$_2$), 67.90 (TEG-$C$H$_2$), 59.04 (TEG-$C$H$_3$); high resolution ESI-MS m/z calcd for $C_{23}H_{26}N_3O_4$ $[M+Na]^+$: 408.19178, Found: 408.19153.

5-iodo-4-(3-(iodoethynyl)phenyl)-1-(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)-1H-1,2,3-triazole



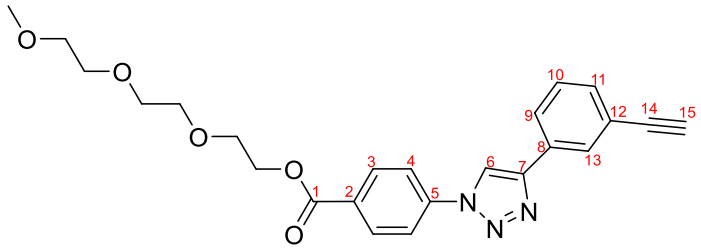
**9b**

*General procedure for azide-iodoalkyne cycloaddition*

Compound **5** (141 mg, 0.5 mmol) and **8b** (227 mg, 0.6 mmol) were added to dry, degassed THF (5 ml) under Ar atmosphere. Then $Cu(MeCN)_4PF_6$ (19 mg, 0.05 mmol) and TBTA (27 mg, 0.05 mmol) were added simultaneously and the reaction was stirred for 4 h under Ar. The reaction mixture was diluted with DCM and washed with 2% aqueous $NH_3$. The DCM layer was dried with anhydrous $Na_2SO_4$, and concentrated. The product was isolated by silica column chromatography (5-10% acetone/DCM) to afford **9b** (152 mg, 0.23 mmol, 46%) as an off-white solid.

$\delta_H$ (400 MHz, $CDCl_3$): 8.08 (s, 1H, $H^{12}$), 7.97 (dt, J = 7.6, 1.7 Hz, 1H, $H^8$), 7.51 – 7.37 (m, 4H, $H^3$, $H^9$, $H^{10}$), 7.13 – 7.01 (m, 2H, $H^2$), 4.21 (t, J = 4.8 Hz, 2H, TEG-C$H_2$), 3.90 (t, J = 4.7 Hz, 2H, TEG-C$H_2$), 3.80 – 3.73 (m, 2H, TEG-C$H_2$), 3.73 – 3.63 (m, 4H, TEG-C$H_2$), 3.55 (m, 2H, TEG-C$H_2$), 3.38 (s, 3H, TEG-C$H_3$). $\delta_C$ (100 MHz, $CDCl_3$): δ 160.21 ($C^1$), 149.15 ($C^6$), 132.52 ($C^{10}$), 131.41 ($C^{12}$), 130.55 ($C^{11}$), 130.00 ($C^4$), 128.71 ($C^9$), 128.12 ($C^8$), 127.94 ($C^3$), 123.87 ($C^7$), 115.21 ($C^2$), 93.85 ($C^{13}$), 78.99 ($C^5$), 72.05 (TEG-$C$H$_2$), 71.02 (TEG-$C$H$_2$), 70.79 (TEG-$C$H$_2$), 70.71 (TEG-$C$H$_2$), 69.70 (TEG-$C$H$_2$), 68.01 (TEG-$C$H$_2$), 59.17 (TEG-$C$H$_3$), 7.39 ($C^{14}$). high resolution ESI-MS m/z calcd for $C_{23}H_{24}I_2N_3O_4$ $[M+H]^+$: 659.98507, Found: 659.98486.

2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-(4-(3-(ethynyl)phenyl)-1H-1,2,3-triazol-1-yl)benzoate

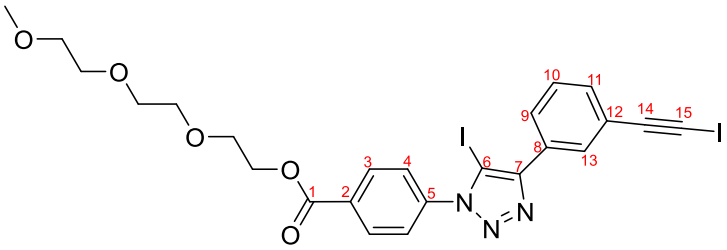


**10a**

General procedure for azide-alkyne cycloaddition was used to couple azide **6** (155 mg, 0.5 mmol) and 1,3-diethynylbenzene **8a** (133 µl, 1 mmol). The product was isolated by silica column (5-10% acetone/DCM) to afford **10a** (113 mg, 0.26 mmol, 69%) as a yellowish solid.

$\delta_H$ (400 MHz, $CDCl_3$): 8.30 (s, 1H, $H^6$), 8.24 – 8.17 (m, 2H, $H^3$), 7.99 (td, J = 1.7, 0.6 Hz, 1H, $H^{13}$), 7.93 – 7.84 (m, 3H, $H^4$, $H^9$), 7.46 (dt, J = 7.7, 1.4 Hz, 1H, $H^{11}$), 7.39 (td, J = 7.7, 0.6 Hz, 1H, $H^{10}$), 4.54 – 4.45 (m, 2H, TEG-C$H_2$), 3.90 – 3.80 (m, 2H, TEG-C$H_2$), 3.74 – 3.69 (m, 2H, TEG-C$H_2$), 3.69 – 3.61 (m, 4H, TEG-C$H_2$), 3.55 – 3.49 (m, 2H, TEG-C$H_2$), 3.34 (s, 3H, TEG-C$H_3$), 3.13 (s, 1H, $H^{15}$); $\delta_C$ (100 MHz, $CDCl_3$): 165.40 ($C^1$), 147.85 ($C^7$), 140.04 ($C^2$), 132.19 ($C^{11}$), 131.56 ($C^3$), 130.31 ($C^5$/$C^8$/$C^{12}$), 130.23 ($C^5$/$C^8$/$C^{12}$), 129.50 ($C^{13}$), 129.11 ($C^{10}$), 126.27 ($C^9$), 122.93 ($C^8$/$C^{12}$), 119.83 ($C^4$), 117.75 ($C^6$), 83.17 ($C^{14}$), 77.98 ($C^{15}$), 71.98 (TEG-$C$H$_2$), 70.76 (TEG-$C$H$_2$), 70.72 (TEG-$C$H$_2$), 70.67 (TEG-$C$H$_2$), 69.20 (TEG-$C$H$_2$), 64.61 (TEG-$C$H$_2$), 59.12 (TEG-$C$H$_3$); high resolution ESI-MS m/z calcd for $C_{24}H_{26}O_5N_3$ $[M+H]^+$: 436.18670, found: 436.18667.

2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-(5-iodo-4-(3-(iodoethynyl)phenyl)-1H-1,2,3-triazol-1-yl)benzoate

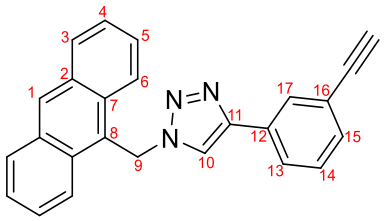


**10b**

General procedure for azide-iodoalkyne cycloaddition was used to couple compounds **6** (62 mg, 0.20 mmol) and **8b** (83 mg, 0.22 mmol). The product was isolated by silica chromatography (25-50% acetone/hexanes) to afford **10b** (66 mg, 0.096 mmol, 53%) as a white solid.

$\delta_H$ (400 MHz, $CDCl_3$): 8.30 – 8.22 (m, 2H, $H^3$), 8.05 (m, 1H, $H^{13}$), 7.94 (dt, J = 7.5, 1.6 Hz, 1H, $H^9$), 7.69 – 7.61 (m, 2H, $H^4$), 7.50 – 7.36 (m, 2H, $H^{10}$, $H^{11}$), 4.58 – 4.45 (m, 2H, TEG-C$H_2$), 3.91 – 3.80 (m, 2H, TEG-C$H_2$), 3.74 – 3.69 (m, 2H, TEG-C$H_2$), 3.69 – 3.59 (m, 4H, TEG-C$H_2$), 3.56 – 3.46 (m, 2H, TEG-C$H_2$), 3.34 (s, 3H, TEG-C$H_3$); $\delta_C$ (100 MHz, $CDCl_3$): 165.29 ($C^1$), 149.86 ($C^7$), 140.24 ($C^2$), 132.66 ($C^{11}$), 131.77 ($C^5$), 131.44 ($C^{13}$), 130.92 ($C^3$), 130.11 ($C^8$/$C^{12}$), 128.72 ($C^{10}$), 128.14 ($C^9$), 126.37 ($C^4$), 123.87 ($C^8$/$C^{12}$), 93.65 ($C^{14}$), 77.61 ($C^6$), 71.95 (TEG-$C$H$_2$), 70.73 (TEG-$C$H$_2$), 70.68 (TEG-$C$H$_2$), 70.64 (TEG-$C$H$_2$), 69.14 (TEG-$C$H$_2$), 64.72 (TEG-$C$H$_2$), 59.11 (TEG-$C$H$_3$), 7.96 ($C^{15}$); high resolution ESI-MS calcd. for $C_{24}H_{24}O_5N_3I_2$ $[M+H]^+$: 687.97998, found: 687.97973.

1-(anthracen-9-ylmethyl)-4-(3-ethynylphenyl)-1H-1,2,3-triazole

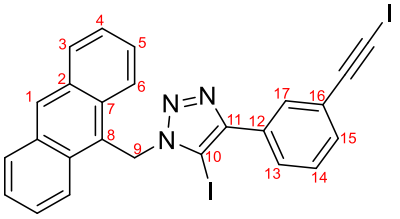


**11a**

General procedure for azide-alkyne cycloaddition was used to couple **7** (233 mg, 1 mmol) and 1,3-diethynylbenzene **8a** (266 µl, 2 mmol). The product was purified by silica column (20% EtOAc/hexanes) to afford **11a** (283 mg, 0.79 mmol, 79%) as a yellow solid.

**$\delta_H$** (400 MHz, $CDCl_3$): 8.59 (s, 1H, $H^1$), 8.32 (d, J = 8.9, 2H, $H^6$), 8.09 (d, J = 8.4, 2H, $H^3$), 7.71 – 7.66 (m, 2H, $H^{17}$, $H^{13}$), 7.61 (ddd, J = 8.9, 6.6, 1.4 Hz, 2H, $H^5$), 7.54 (ddd, J = 7.8, 6.6, 1.1 Hz, 2H, $H^4$), 7.33 (dt, J = 7.7, 1.4 Hz, 1H, $H^{15}$), 7.28 (s, 1H, $H^{10}$), 7.27 – 7.22 (m, 1H, $H^{14}$), 6.56 (s, 2H, C$H_2$), 3.00 (s, 1H, C≡C*H*); **$\delta_C$** (100 MHz, $CDCl_3$): 147.00 ($C^{11}$), 131.65 ($C^{15}$), 131.59 ($C^2$), 130.95 ($C^7$), 130.83 ($C^{12}$), 130.13 ($C^1$), 129.66 ($C^3$), 129.24 ($C^{17}$), 128.84 ($C^{14}$), 127.93 ($C^5$), 126.07 ($C^{13}$), 125.60 ($C^4$), 123.68 ($C^8$), 123.00 ($C^6$), 122.57 ($C^{16}$), 119.45 ($C^{10}$), 83.32 (*C*≡CH), 77.54 (C≡*C*H), 46.68 (*C*$H_2$); high resolution ESI-MS m/z calcd for $C_{25}H_{18}N_3$ $[M+H]^+$: 360.14952, found: 360.14965.

1-(anthracen-9-ylmethyl)-5-iodo-4-(3-(iodoethynyl)phenyl)-1H-1,2,3-triazole

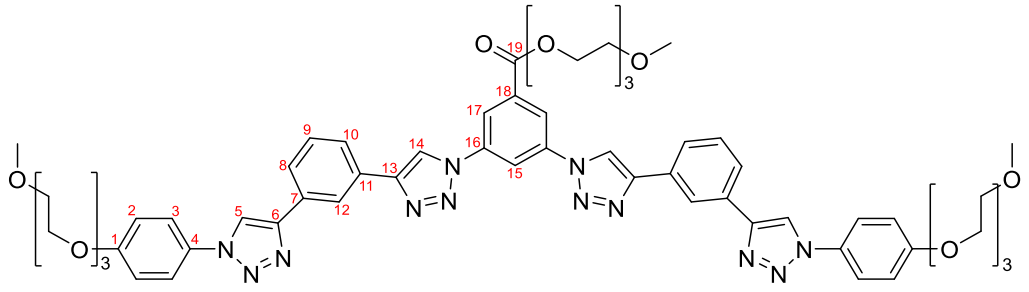


**11b**

General procedure for azide-iodoalkyne cycloaddition was used to couple **7** (233 mg, 1 mmol) and **8b** (454 mg, 1.2 mmol). The product was isolated by silica column chromatography (1:1 DCM/hexanes) to provide **11b** (385 mg, 0.63 mmol, 63%) as a yellow solid.

**$\delta_H$** (400 MHz, $CDCl_3$): 8.43 (s, 1H, $H^1$), 8.10 (d, J = 8.9 Hz, 2H, $H^6$), 7.92 (dd, J = 8.3, 1.5 Hz, 2H, $H^3$), 7.83 (t, J = 1.9 Hz, 1H, $H^{17}$), 7.72 (dt, J = 7.4, 1.8 Hz, 1H, $H^{13}$), 7.42 (m, 2H, $H^5$), 7.36 (m, 2H, $H^4$), 7.31 – 7.19 (m, 2H, $H^{14}$, $H^{15}$), 6.30 (d, J = 2.3 Hz, 2H, C$H_2$); **$\delta_C$** (100 MHz, $CDCl_3$): 148.34 ($C^{11}$), 131.90 ($C^{15}$), 131.14 (Ar *C*), 130.97 (Ar *C*), 130.83 (Ar *C*), 130.41 ($C^8$), 129.52 ($C^1$), 129.14 ($C^3$), 128.30 ($C^{14}$), 127.58 ($C^{13}$), 126.93 ($C^5$), 124.96 ($C^4$), 123.6 ($C^{12}$), 123.46 ($C^6$), 93.13 (*C*≡CI), 77.36 ($C^{10}$), 47.86 (*C*$H_2$), 9.45 (C≡*C*I); high resolution ESI-MS m/z calcd for $C_{25}H_{15}I_2N_3$ $[M+Na]^+$: 633.92475, found: 633.92458.

Phenylene-centered, ether-terminated HB receptor **1a**

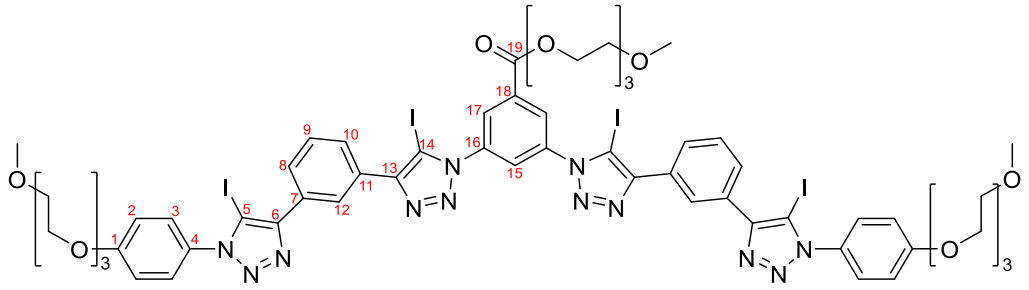


**1a**

General procedure for azide-alkyne cycloaddition was used to couple **12** (35 mg, 0.1 mmol) and **9a** (90 mg, 0.22 mmol). The product was separated by silica column chromatography (20% acetone/DCM then 3% MeOH/DCM) followed by PTLC (preparative thin layer chromatography 2.5-3% MeOH/DCM) to afford the product as a colorless amorphous solid (75 mg, 0.064 mmol, 64%).

**$\delta_H$** (400 MHz, $CDCl_3$): 8.57 (s, 2H, $H^{14}$), 8.42 (s, 1H, $H^{15}$), 8.26 (s, 2H, $H^{17}$), 8.24 (s, 2H, $H^{5}$), 8.22 (s, 2H, $H^{12}$), 7.74 (m, 4H, $H^{8}$, $H^{10}$), 7.59 (d, J = 8.4 Hz, 4H, $H^{3}$), 7.30 (t, J = 8.0 Hz, 2H, $H^{9}$), 6.90 (d, J = 8.4 Hz, 4H, $H^{2}$), 4.41 (s, 2H, TEG-C$H_2$), 4.07 (t, J = 4.6 Hz, 4H, TEG-C$H_2$), 3.81 (m, 6H, TEG-C$H_2$), 3.75 – 3.56 (m, 18H, TEG-C$H_2$), 3.52 (m, 4H, TEG-C$H_2$), 3.45 (m, 2H, TEG-C$H_2$), 3.33 (s, 6H, TEG-C$H_3$), 3.22 (s, 3H, TEG-C$H_3$); **$\delta_C$** (100 MHz, $CDCl_3$): 163.99 ($C^{19}$), 158.91 ($C^{1}$), 148.19 ($C^{6}$/$C^{13}$), 147.48 ($C^{6}$/$C^{13}$), 137.77 ($C^{16}$), 133.11 ($C^{18}$), 130.95 ($C^{7}$/$C^{11}$), 130.42 ($C^{4}$), 130.24 ($C^{7}$/$C^{11}$), 129.40 ($C^{9}$), 125.65 ($C^{8}$/$C^{10}$), 125.45 ($C^{8}$/$C^{10}$), 122.90 ($C^{12}$), 121.69 ($C^{3}$), 119.85 ($C^{17}$), 118.34 ($C^{5}$/$C^{14}$), 118.30 ($C^{5}$/$C^{14}$), 115.35 ($C^{2}$), 114.76 ($C^{15}$), 71.96 (TEG-$C$H$_2$), 71.88 (TEG-$C$H$_2$), 70.88 (TEG-$C$H$_2$), 70.73 (TEG-$C$H$_2$), 70.69 (TEG-$C$H$_2$), 70.64 (TEG-$C$H$_2$), 70.60 (TEG-$C$H$_2$), 70.54 (TEG-$C$H$_2$), 69.63 (TEG-$C$H$_2$), 68.90 (TEG-$C$H$_2$), 67.83 (TEG-$C$H$_2$), 65.11 (TEG-$C$H$_2$), 59.04 (TEG-$C$H$_3$), 58.90 (TEG-$C$H$_3$); high resolution ESI-MS m/z calcd for $C_{60}H_{68}N_{12}O_{13}$ $[M+Na]^+$: 1165.51016, found: 1165.51083.

Phenylene-centered, ether-terminated XB receptor **1b**

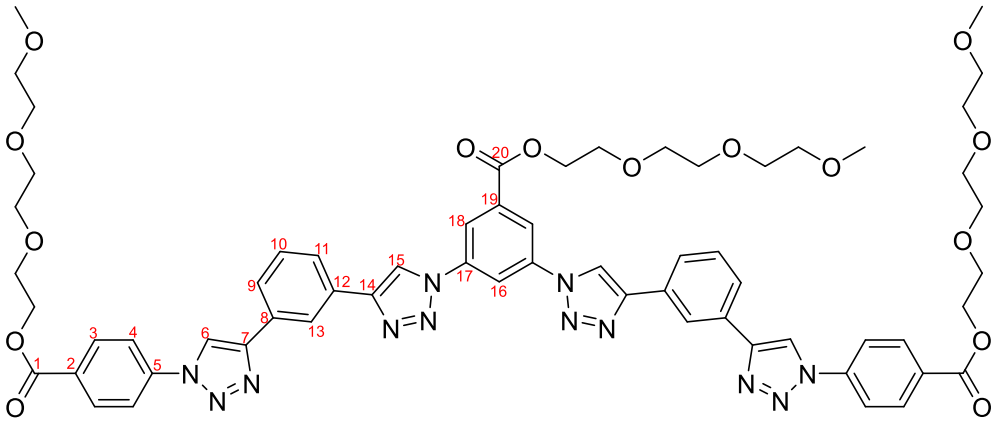


**1b**

General procedure for azide-iodoalkyne cycloaddition was used to couple **12** (35 mg, 0.1 mmol) and **9b** (145 mg, 0.22 mmol). The product was isolated by silica column chromatography (25-30% hexanes/acetone) to afford **1b** as a white solid foam (103 mg, 0.062 mmol, 62%).

**$\delta_H$** (400 MHz, $CDCl_3$): δ 8.68 (t, J = 1.8 Hz, 2H, $H^{12}$), 8.55 (d, J = 2.0 Hz, 2H, $H^{17}$), 8.15 (t, J = 2.0 Hz, 1H, $H^{15}$), 8.11 (dt, J = 7.8, 1.4 Hz, 2H, $H^8/H^{10}$), 8.07 (dt, J = 7.9, 1.4 Hz, 2H, $H^8/H^{10}$), 7.64 (t, J = 7.8 Hz, 2H, $H^9$), 7.47 – 7.41 (m, 4H, $H^3$), 7.11 – 7.03 (m, 4H, $H^2$), 4.61 – 4.53 (m, 2H, TEG-C$H_2$), 4.21 (t, J = 4.8 Hz, 4H, TEG-C$H_2$), 3.88 (dt, J = 13.7, 4.8 Hz, 6H, TEG-C$H_2$), 3.78 – 3.58 (m, 18H, TEG-C$H_2$), 3.55 (dd, J = 5.8, 3.5 Hz, 4H, TEG-C$H_2$), 3.49 (dd, J = 5.7, 3.5 Hz, 2H, TEG-C$H_2$), 3.37 (s, 6H, TEG-C$H_3$), 3.31 (d, J = 4.0 Hz, 3H, TEG-C$H_3$); **$\delta_C$** (100 MHz, $CDCl_3$): 163.82 ($C^{19}$), 160.18 ($C^1$), 150.91 ($C^6/C^{13}$), 149.66 ($C^6/C^{13}$), 137.94 ($C^{16}$), 133.06 ($C^{18}$), 130.86 ($C^7/C^{11}$), 130.11 ($C^4/C^7/C^{11}$), 130.06 ($C^4/C^7/C^{11}$), 129.24 ($C^9$), 128.87 ($C^{17}$), 128.41 ($C^8/C^{10}$), 128.34 ($C^{15}$), 128.14 ($C^8/C^{10}$), 127.97 ($C^3$), 126.69 ($C^{12}$), 115.20 ($C^2$), 79.14 ($C^5/C^{14}$), 78.03 ($C^5/C^{14}$), 72.04 (TEG-$C$H$_2$), 71.99 (TEG-$C$H$_2$), 71.00 (TEG-$C$H$_2$), 70.83 (TEG-$C$H$_2$), 70.78 (TEG-$C$H$_2$), 70.70 (TEG-$C$H$_2$), 69.69 (TEG-$C$H$_2$), 69.02 (TEG-$C$H$_2$), 67.99 (TEG-$C$H$_2$), 65.52 (TEG-$C$H$_2$), 59.16 (TEG-$C$H$_3$), 59.13 (TEG-$C$H$_3$); high resolution ESI-MS m/z calcd for $C_{60}H_{64}I_4N_{12}O_{13}$ $[M+Na]^+$: 1691.07977, found: 1691.08228.

Phenylene-centered, ester-terminated HB receptor **2a**

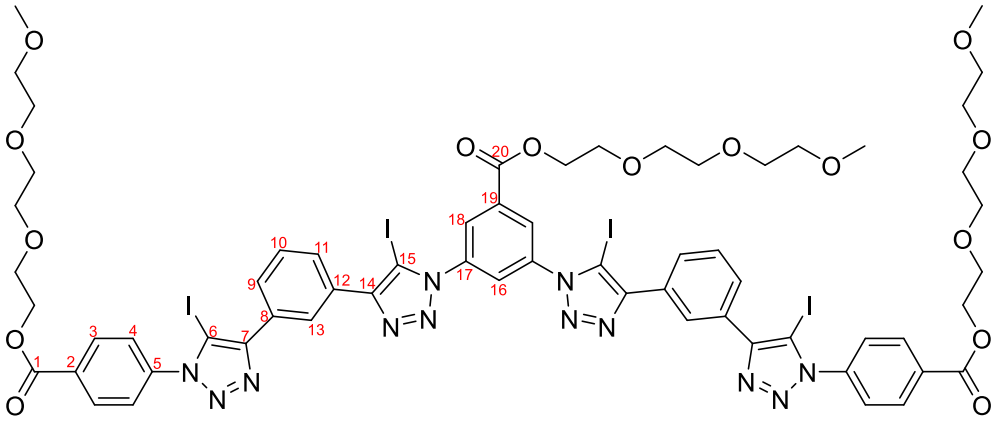


**2a**

General procedure for azide-alkyne cycloaddition was used to couple compounds **10a** (154 mg, 0.35 mmol) and **12** (56 mg, 0.16 mmol) using BTA (6.7 mg, 0.035 mmol) as catalyst instead of TBTA. The product was isolated by silica chromatography (2-3% MeOH/DCM followed by PTLC (2.5% MeOH/DCM) to afford **2a** (130 mg, 0.106 mmol, 67%) as a white solid.

**$\delta_H$** (400 MHz, $CDCl_3$): 8.58 (s, 2H, $H^{15}$), 8.56 (s, 1H, $H^{16}$), 8.45 (s, 2H, $H^{6}$), 8.37 (s, 2H, $H^{18}$), 8.34 (s, 2H, $H^{13}$), 8.16 (d, J = 8.2 Hz, 4H, $H^{3}$), 7.87 (m, 8H, $H^{4}$, $H^{9}$, $H^{11}$), 7.44 (t, J = 7.8 Hz, 2H, $H^{10}$), 4.60 – 4.40 (m, 6H, TEG-C$H_2$), 3.87 (m, 6H, TEG-C$H_2$), 3.70 (m, 19H, TEG-C$H_2$), 3.51 (m, 7H, TEG-C$H_2$), 3.35 (s, 6H, TEG-C$H_3$), 3.26 (s, 3H, TEG-C$H_3$); **$\delta_C$** (100 MHz, $CDCl_3$): 165.43 ($C^{1}$), 164.13 ($C^{20}$), 148.41 ($C^{7}$/$C^{14}$), 148.18 ($C^{7}$/$C^{14}$), 140.06 ($C^{2}$), 138.03 ($C^{17}$), 133.55 ($C^{19}$), 131.53 ($C^{3}$), 130.70 ($C^{8}$/$C^{12}$), 130.41 ($C^{8}$/$C^{12}$), 130.21 ($C^{5}$), 129.72 ($C^{10}$), 126.01 ($C^{9}$/$C^{11}$), 125.92 ($C^{9}$/$C^{11}$), 123.16 ($C^{13}$), 120.10 ($C^{18}$), 119.74 ($C^{4}$), 118.24 ($C^{15}$), 118.03 ($C^{6}$), 115.14 ($C^{16}$), 72.05 (TEG-$C$H$_2$), 72.00 (TEG-$C$H$_2$), 70.88 (TEG-$C$H$_2$), 70.83 (TEG-$C$H$_2$), 70.80 (TEG-$C$H$_2$), 70.74 (TEG-$C$H$_2$), 70.70 (TEG-$C$H$_2$), 69.26 (TEG-$C$H$_2$), 69.07 (TEG-$C$H$_2$), 65.33 (TEG-$C$H$_2$), 64.63 (TEG-$C$H$_2$), 59.16 (TEG-$C$H$_3$), 59.01 (TEG-$C$H$_3$); high resolution ESI-MS calcd. for $C_{62}H_{68}N_{12}O_{15}Na$ $[M+Na]^+$: 1243.48193, found: 1243.48171.

Phenylene-centered, ester-terminated XB receptor **2b**

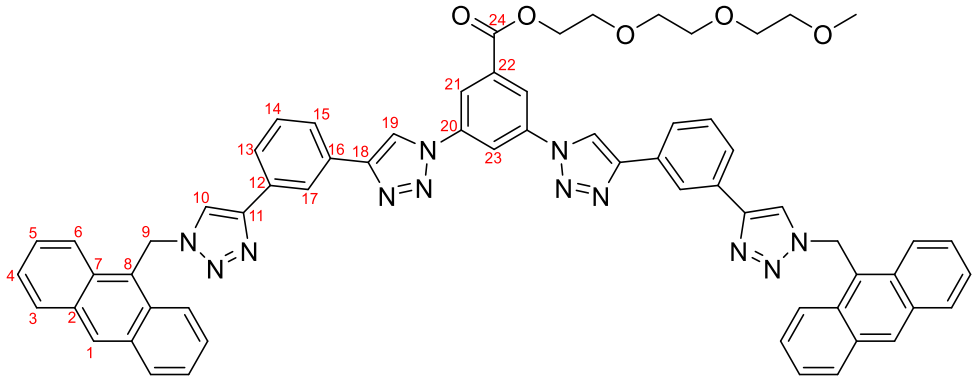


**2b**

General procedure for azide-iodoalkyne cycloaddition was used to couple compounds **10b** (136 mg, 0.20 mmol) and **12** (31 mg, 0.089 mmol). The product was isolated by silica column chromatography (1.5-2.5% MeOH/DCM) to afford **2b** (90 mg, 0.052 mmol, 58%) as a white foam.

**$\delta_H$** (400 MHz, $CDCl_3$): 8.69 (t, J = 1.8 Hz, 2H, $H^{13}$), 8.59 – 8.53 (m, 2H, $H^{18}$), 8.29 (d, J = 8.3 Hz, 4H, $H^3$), 8.18 – 8.15 (m, 1H, $H^{16}$), 8.14 – 8.08 (m, 4H, $H^9$, $H^{11}$), 7.71 (d, J = 8.3 Hz, 4H, $H^4$), 7.67 (t, J = 7.9 Hz, 2H, $H^{10}$), 4.58 (m, 2H, TEG-C$H_2$), 4.54 (m, 4H, TEG-C$H_2$), 3.94 – 3.82 (m, 6H, TEG-C$H_2$), 3.77 – 3.58 (m, 18H, TEG-C$H_2$), 3.52 (m, 6H, TEG-C$H_2$), 3.36 (s, 6H, TEG-C$H_3$), 3.32 (s, 3H, TEG-C$H_3$); **$\delta_C$** (100 MHz, $CDCl_3$): 165.41 ($C^1$), 163.83 ($C^{20}$), 150.87 ($C^7$/$C^{14}$), 150.51 ($C^7$/$C^{14}$), 140.42 ($C^2$), 137.96 ($C^{17}$), 133.10 ($C^{19}$), 131.88 ($C^5$), 131.01 ($C^3$), 130.55 ($C^8$/$C^{12}$), 130.21 ($C^8$/$C^{12}$), 129.33 ($C^{10}$), 128.90 ($C^{18}$), 128.56 ($C^9$/$C^{11}$), 128.36 ($C^9$/$C^{11}$), 128.34 ($C^{16}$), 126.88 ($C^{13}$), 126.49 ($C^4$), 77.93 ($C^6$/$C^{15}$), 77.63 ($C^6$/$C^{15}$), 72.06 (TEG-$C$H$_2$), 72.02 (TEG-$C$H$_2$), 70.86 (TEG-$C$H$_2$), 70.84 (TEG-$C$H$_2$), 70.81 (TEG-$C$H$_2$), 70.79 (TEG-$C$H$_2$), 70.75 (TEG-$C$H$_2$), 70.74 (TEG-$C$H$_2$), 69.24 (TEG-$C$H$_2$), 69.05 (TEG-$C$H$_2$), 65.57 (TEG-$C$H$_2$), 64.81 (TEG-$C$H$_2$), 59.20 (TEG-$C$H$_3$), 59.16 (TEG-$C$H$_3$); high resolution ESI-MS calcd. for $C_{62}H_{64}N_{12}O_{15}I_4Na$ $[M+Na]^+$: 1747.06850, found: 1747.06899.

Phenylene-centered, anthryl-terminated HB receptor **3a**

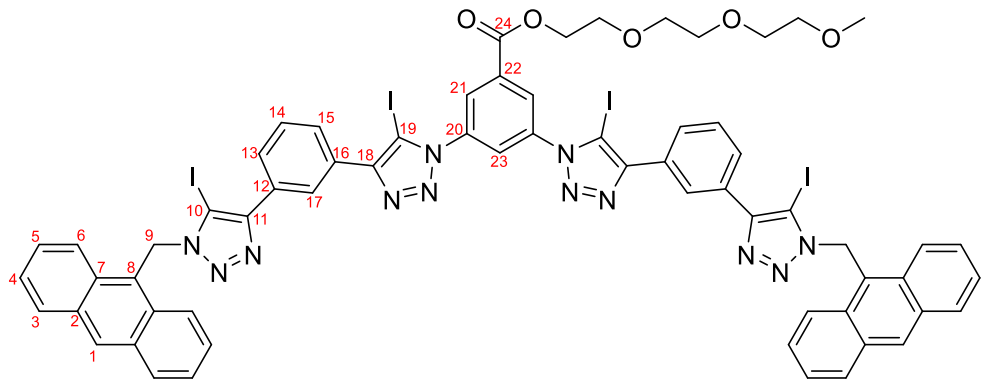


**3a**

General procedure for azide-alkyne cycloaddition was used to couple **11a** (79 mg, 0.22 mmol) and **12** (35 mg, 0.1 mmol). The product was isolated by silica column chromatography (1-1.5% MeOH/DCM) to provide **3a** (88 mg, 0.082 mmol 82%) as a yellow solid.

**$\delta_H$** (400 MHz, $CDCl_3$): 8.53 (s, 2H, $H^1$), 8.38 – 8.29 (m, 8H, $H^6$, $H^{19}$, $H^{21}$), 8.27 (t, J = 2.1 Hz, 1H, $H^{23}$), 8.07 (t, J = 1.7 Hz, 2H, $H^{17}$), 8.05 – 7.98 (d, J = 8.4 Hz, 4H, $H^3$), 7.77 (dt, J = 7.7, 1.4 Hz, 2H, $H^{15}$), 7.69 (dt, J = 7.8, 1.4 Hz, 2H, $H^{13}$), 7.54 (ddd, J = 8.7, 6.6, 1.4 Hz, 4H, $H^5$), 7.50 (s, 2H, $H^{10}$), 7.46 (ddd, J = 7.7, 6.6, 1.0 Hz, 4H, $H^4$), 7.33 (t, J = 7.8 Hz, 2H, $H^{14}$), 6.54 (s, 4H, $H^9$), 4.54 – 4.42 (m, 2H, TEG-C$H_2$), 3.87 – 3.78 (m, 2H, TEG-C$H_2$), 3.69 – 3.63 (m, 2H, TEG-C$H_2$), 3.63 – 3.58 (m, 2H, TEG-C$H_2$), 3.58 – 3.51 (m, 2H, TEG-C$H_2$), 3.45 – 3.39 (m, 2H, TEG-C$H_2$), 3.21 (s, 3H, TEG-C$H_3$); **$\delta_C$** (100 MHz, $CDCl_3$): 164.17 ($C^{24}$), 148.52 ($C^{18}$), 147.38 ($C^{11}$), 138.01 ($C^{20}$), 133.47 ($C^{22}$), 131.53 ($C^7$), 131.30 ($C^{12}$), 130.92 ($C^2$), 130.16 ($C^{16}$), 130.05 ($C^1$), 129.60 ($C^3$), 129.49 ($C^{14}$), 127.85 ($C^5$), 125.89 ($C^{13}$), 125.54 ($C^4$), 125.50 ($C^{15}$), 123.75 ($C^8$), 123.03 ($C^6$), 122.98 ($C^{17}$), 120.26 ($C^{21}$), 119.83 ($C^{10}$), 118.02 ($C^{19}$), 115.28 ($C^{23}$), 71.93 (TEG-$C$H$_2$), 70.81 (TEG-$C$H$_2$), 70.69 (TEG-$C$H$_2$), 70.62 (TEG-$C$H$_2$), 68.99 (TEG-$C$H$_2$), 65.24 (TEG-$C$H$_2$), 58.96 (TEG-$C$H$_3$), 46.71 ($C^9$); high resolution ESI-MS m/z calcd for $C_{64}H_{53}N_{12}O_5$ $[M+Na]^+$: 1091.40758, found: 1091.40832.

Phenylene-centered, anthryl-terminated XB receptor **3b**

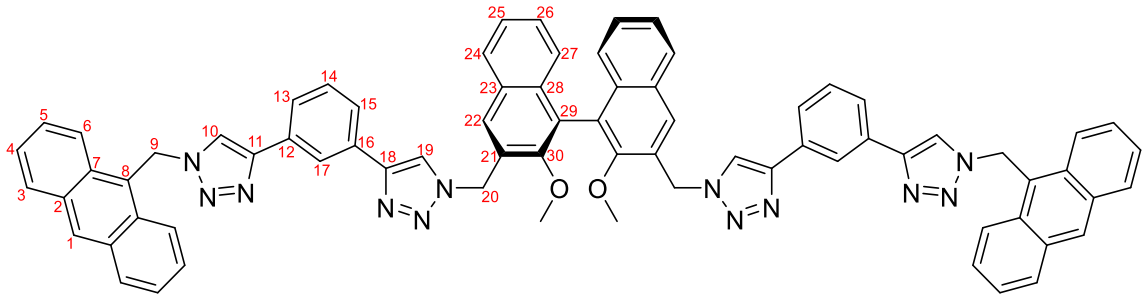


**3b**

General procedure for azide-iodoalkyne cycloaddition was used to couple **11b** (136 mg, 0.22 mmol) and **12** (35 mg, 0.1 mmol). The product was isolated by silica column chromatography (4-10% acetone/DCM) followed by PTLC (1% MeOH/DCM) to provide **3b** (84 mg, 0.053 mmol, 53%) as a yellow solid.

**$\delta_H$** (400 MHz, $CDCl_3$): 8.59 (t, J = 1.8 Hz, 2H, $H^{17}$), 8.55 (s, 2H, $H^{1}$), 8.51 (d, J = 2.0 Hz, 2H, $H^{21}$), 8.32 – 8.23 (d, J = 8.8 Hz, 4H, $H^{6}$), 8.07 (t, J = 2.0 Hz, 1H, $H^{23}$), 8.03 (m, 8H, $H^{3}$, $H^{13}$, $H^{15}$), 7.63 – 7.52 (m, 6H, $H^{5}$, $H^{14}$), 7.48 (ddd, J = 7.7, 6.6, 1.0 Hz, 4H, $H^{4}$), 6.46 (s, 4H, $H^{9}$), 4.62 – 4.52 (m, 2H, TEG-C$H_2$), 3.91 – 3.81 (m, 2H, TEG-C$H_2$), 3.75 – 3.68 (m, 2H, TEG-C$H_2$), 3.67 – 3.62 (m, 2H, TEG-C$H_2$), 3.62 – 3.56 (m, 2H, TEG-C$H_2$), 3.53 – 3.44 (m, 2H, TEG-C$H_2$), 3.30 (s, 3H, TEG-C$H_3$); **$\delta_C$** (125 MHz, $CDCl_3$): 163.84 ($C^{24}$), 150.90 ($C^{11}$/$C^{18}$), 149.36 ($C^{11}$/$C^{18}$), 137.91 ($C^{20}$), 133.06 ($C^{22}$), 131.56 ($C^{2}$/$C^{7}$), 131.43 ($C^{2}$/$C^{7}$), 130.94 ($C^{12}$/$C^{16}$), 130.02 ($C^{1}$), 129.54 ($C^{3}$), 129.19 ($C^{14}$), 128.87 ($C^{21}$), 128.30 ($C^{13}$/$C^{15}$, $C^{23}$), 128.04 ($C^{13}$/$C^{15}$), 127.29 ($C^{5}$), 126.59 ($C^{17}$), 125.29 ($C^{4}$), 123.89 ($C^{6}$), 123.86 ($C^{8}$), 77.97 ($C^{19}$), 76.54 ($C^{10}$), 72.01 (TEG-$C$H$_2$), 70.85 (TEG-$C$H$_2$), 70.80 (TEG-$C$H$_2$), 70.73 (TEG-$C$H$_2$), 69.04 (TEG-$C$H$_2$), 65.53 (TEG-$C$H$_2$), 59.15 (TEG-$C$H$_3$), 48.36 ($C^{9}$); high resolution ESI-MS m/z calcd for $C_{64}H_{49}I_4N_{12}O_5$ $[M+H]^+$: 1573.01221; found: 1573.01348.

Binaphthol-centered, anthryl-terminated HB receptor **4a**

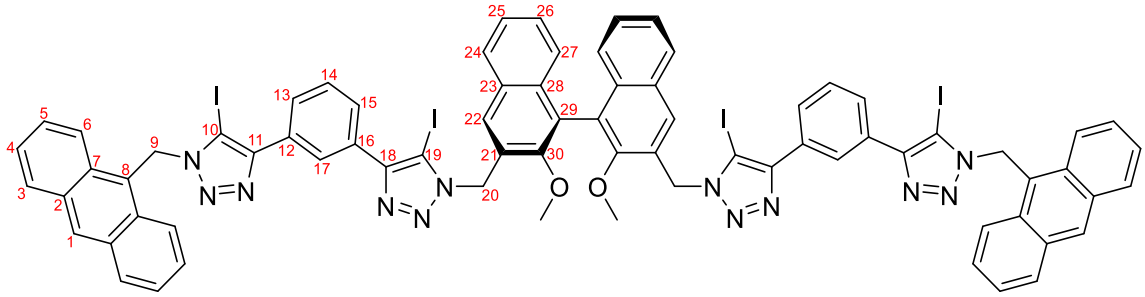


**4a**

General procedure for azide-iodoalkyne cycloaddition was used to couple **11a** (108 mg, 0.3 mmol) and (*S*)-3,3'-bis(azidomethyl)-2,2'-dimethoxy-1,1'-binaphthalene **13** (57 mg, 0.135 mmol). The product was isolated by silica column chromatography (1-1.5% MeOH/DCM) to provide **4a** (136 mg, 0.119 mmol, 88%) as a yellow solid.

**$\delta_H$** (400 MHz, $CDCl_3$): 8.52 (s, 2H, $H^1$), 8.26 (d, J = 8.8 Hz, 4H, $H^6$), 8.04 – 7.97 (m, 6H, $H^3$, $H^{17}$), 7.91 (s, 2H, $H^{19}$), 7.78 (m, 4H, $H^{22}$, $H^{27}$), 7.65 (dt, J = 7.8, 1.4 Hz, 2H, $H^{15}$), 7.59 – 7.49 (m, 6H, $H^5$, $H^{13}$), 7.45 (ddd, J = 7.7, 6.6, 1.0 Hz, 4H, $H^4$), 7.36 (ddd, J = 8.1, 6.8, 1.2 Hz, 2H $H^{25}$), 7.32 (s, 2H, $H^{10}$), 7.29 – 7.20 (m, 4H, $H^{14}$, $H^{26}$), 7.17 – 7.11 (m, 2H, $H^{24}$), 6.49 (s, 4H, $H^9$), 5.88 – 5.69 (m, 4H, $H^{20}$), 3.06 (s, 6H, $OCH_3$); **$\delta_C$** (100 MHz, $CDCl_3$): 154.43 ($C^{30}$), 147.69 ($C^{18}$), 147.53 ($C^{11}$), 134.48 (BINOL quat *C*), 131.56 ($C^7$), 131.14 (Ar quat *C*), 131.12 (Ar quat *C*), 130.92 ($C^2$), 130.41 (Ar quat *C*), 130.37 ($C^{22}$), 130.09 ($C^1$), 129.63 ($C^3$), 129.35 ($C^{14}$), 128.43 ($C^{27}$), 128.39 (BINOL quat *C*), 127.87 ($C^5$), 127.56 ($C^{26}$), 125.64 ($C^{25}$), 125.63 ($C^{24}$), 125.54 ($C^4$), 125.37 ($C^{13}$), 125.25 ($C^{15}$), 124.31 (BINOL quat *C*), 123.68 ($C^8$), 123.00 ($C^6$), 122.70 ($C^{17}$), 120.55 ($C^{19}$), 119.56 ($C^{10}$), 61.09 ($OCH_3$), 50.29 ($C^{20}$), 46.65 ($C^9$); high resolution ESI-MS m/z calcd for $C_{74}H_{55}N_{12}O_2$ $[M+H]^+$: 1143.45655, found: 1143.45547; $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ +48.2° (c 1.00, $CHCl_3$).

Binaphthol-centered, anthryl-terminated XB receptor **4b**



**4b**

General procedure for azide-iodoalkyne cycloaddition was used to couple **11b** (136 mg, 0.22 mmol) and *(S)*-3,3'-bis(azidomethyl)-2,2'-dimethoxy-1,1'-binaphthalene **13** (42 mg, 0.1 mmol). The product was isolated by silica column chromatography (2% MeOH/DCM) followed by PTLC (1% MeOH/DCM) to provide **4b** (140 mg, 0.085 mmol, 85%) as a yellow solid.

**$\delta_H$** (500 MHz, $CDCl_3$): 8.61 (s, 2H, $H^{17}$), 8.55 (s, 2H, $H^{1}$), 8.27 (d, J = 8.9 Hz, 4H, $H^{6}$), 8.07 (d, J = 7.9 Hz, 2H, $H^{13}$/$H^{15}$), 8.04 (d, J = 8.4 Hz, 4H, $H^{3}$), 7.98 (d, J = 7.9 Hz, 2H, $H^{13}$/$H^{15}$), 7.76 (d, J = 8.2 Hz, 2H, $H^{27}$), 7.55 (m, 6H, $H^{5}$, $H^{14}$), 7.47 (t, J = 7.5 Hz, 4H, $H^{4}$), 7.40 (s, 2H, $H^{22}$), 7.36 (t, J = 7.5 Hz, 2H, $H^{26}$), 7.25 (t, J = 6.9, 5.8 Hz, 2H, $H^{25}$), 7.17 (d, J = 8.6 Hz, 2H, $H^{24}$), 6.45 (s, 4H, $H^{9}$), 5.93 (s, 4H, $H^{20}$), 3.28 (s, 6H, $OCH_3$); **$\delta_C$** (125 MHz, $CDCl_3$): 153.93 ($C^{30}$), 149.94 ($C^{11}$/$C^{18}$), 149.52 ($C^{11}$/$C^{18}$), 134.25 (BINOL quat *C*), 131.55 ($C^{2}$/$C^{7}$), 131.41 ($C^{2}$/$C^{7}$), 130.82 (Ar quat *C*), 130.69 (Ar quat *C*), 130.39 (Ar quat *C*), 129.98 ($C^{1}$), 129.51 ($C^{3}$), 129.04 ($C^{14}$), 128.67 ($C^{22}$), 128.39 ($C^{27}$), 128.24 (BINOL quat *C*), 127.90 ($C^{13}$/$C^{15}$), 127.70 ($C^{13}$/$C^{15}$), 127.28 ($C^{25}$), 127.25 ($C^{5}$), 126.36 ($C^{17}$), 125.68 ($C^{24}$), 125.49 ($C^{26}$), 125.27 ($C^{4}$), 123.90 ($C^{8}$), 123.87 ($C^{6}$), 77.60 ($C^{19}$), 76.49 ($C^{10}$), 61.05 ($OCH_3$), 50.45 ($C^{20}$), 48.32 ($C^{9}$); high resolution ESI-MS m/z calcd for $C_{74}H_{51}I_4N_{12}O_2$ $[M+H]^+$: 1647.04312; found: 1647.04339; $[\alpha]_D^{25}$ +27.3° (c 1.00, $CHCl_3$).

## S1.3 Spectral characterisation

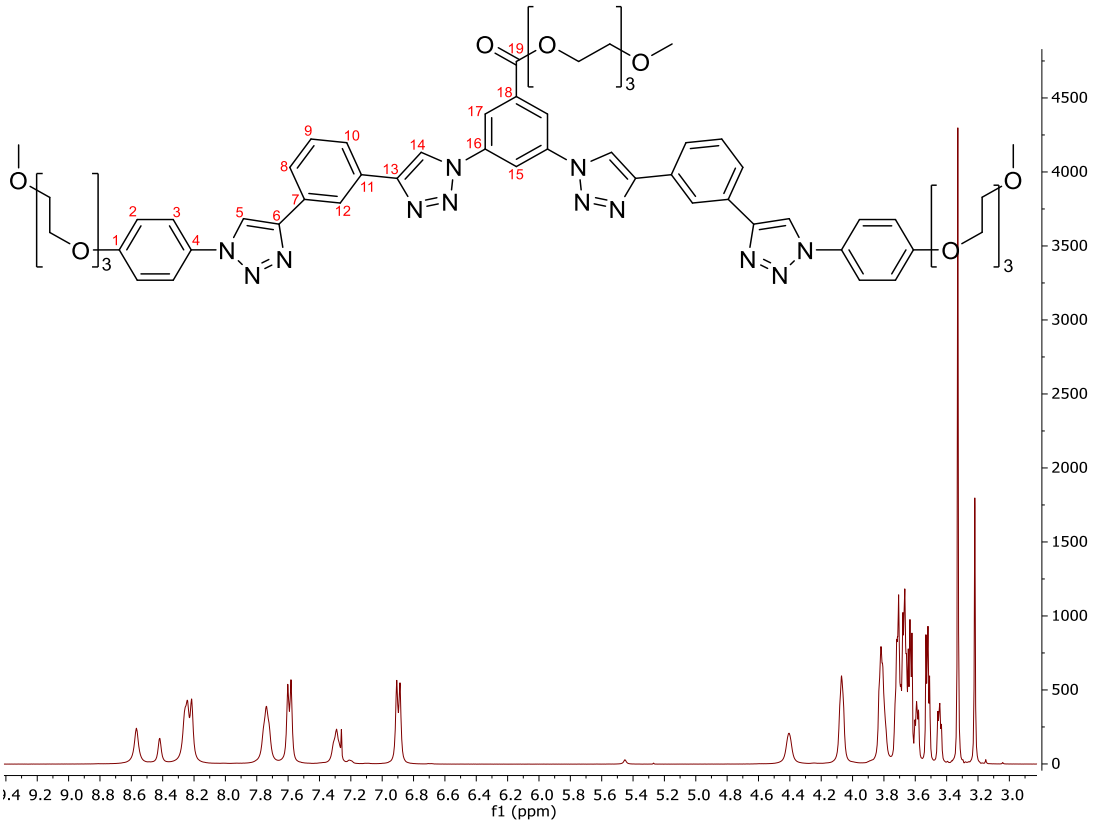



**Fig. 1-1** $^{1}$H NMR spectrum of **1a** (400 MHz, $CDCl_3$).

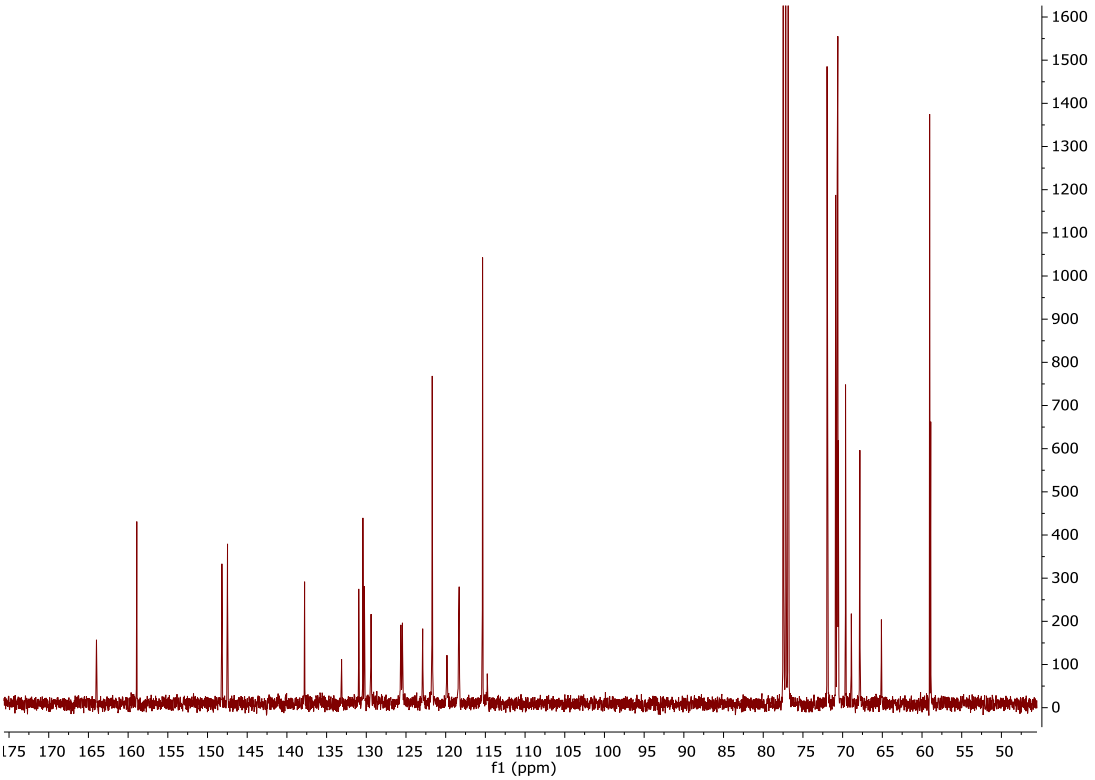
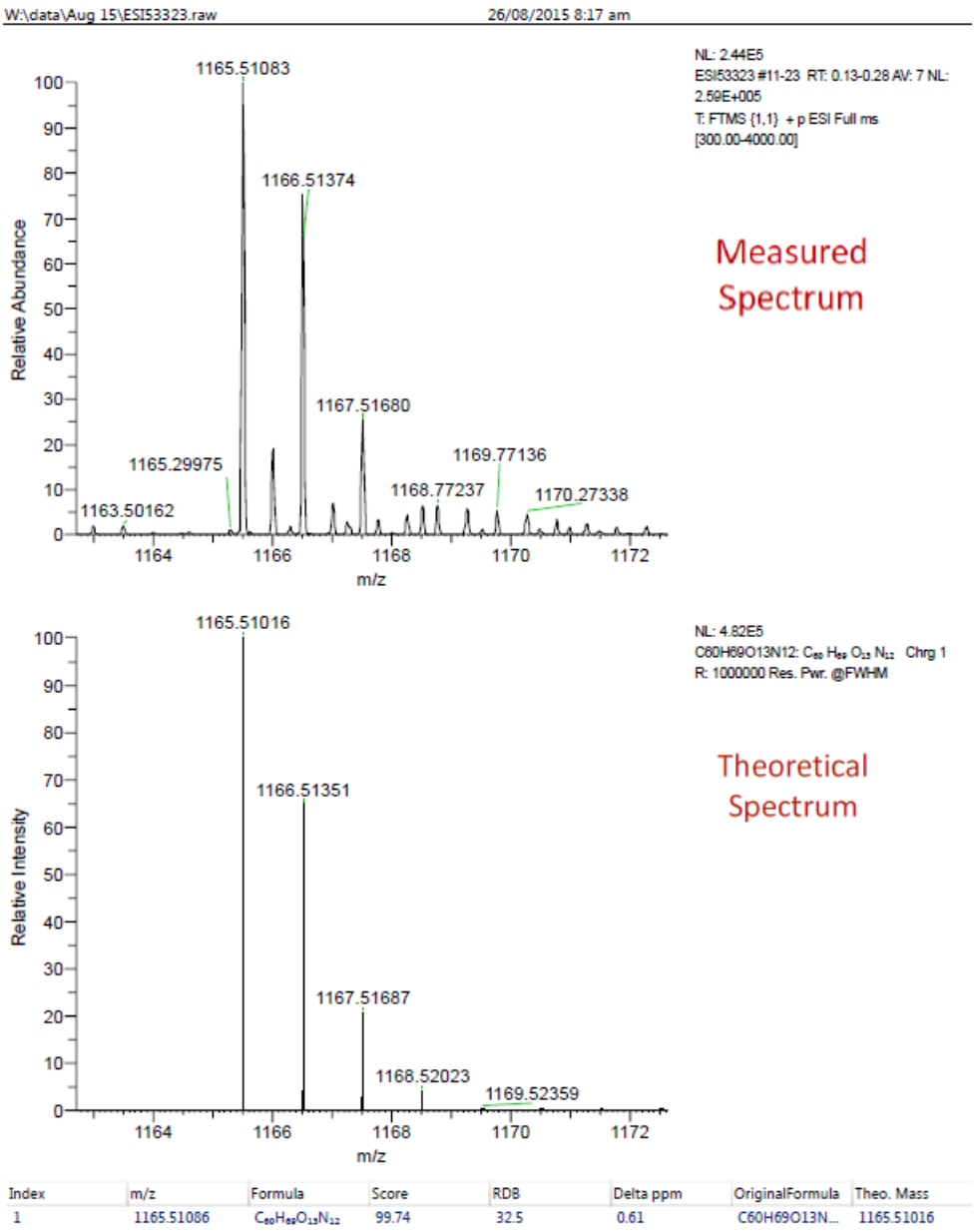



**Fig. 1-2** $^{13}$C NMR spectrum of **1a** (100 MHz, $CDCl_3$).




| Index | m/z | Formula | Score | RDB | Delta ppm | OriginalFormula | Theo. Mass |
|---|---|---|---|---|---|---|---|
| 1 | 1165.51086 | $C_{60}H_{69}O_{13}N_{12}$ | 99.74 | 32.5 | 0.61 | C60H69O13N... | 1165.51016 |

**Fig 1-3** High resolution ESI mass spectrum of **1a**.

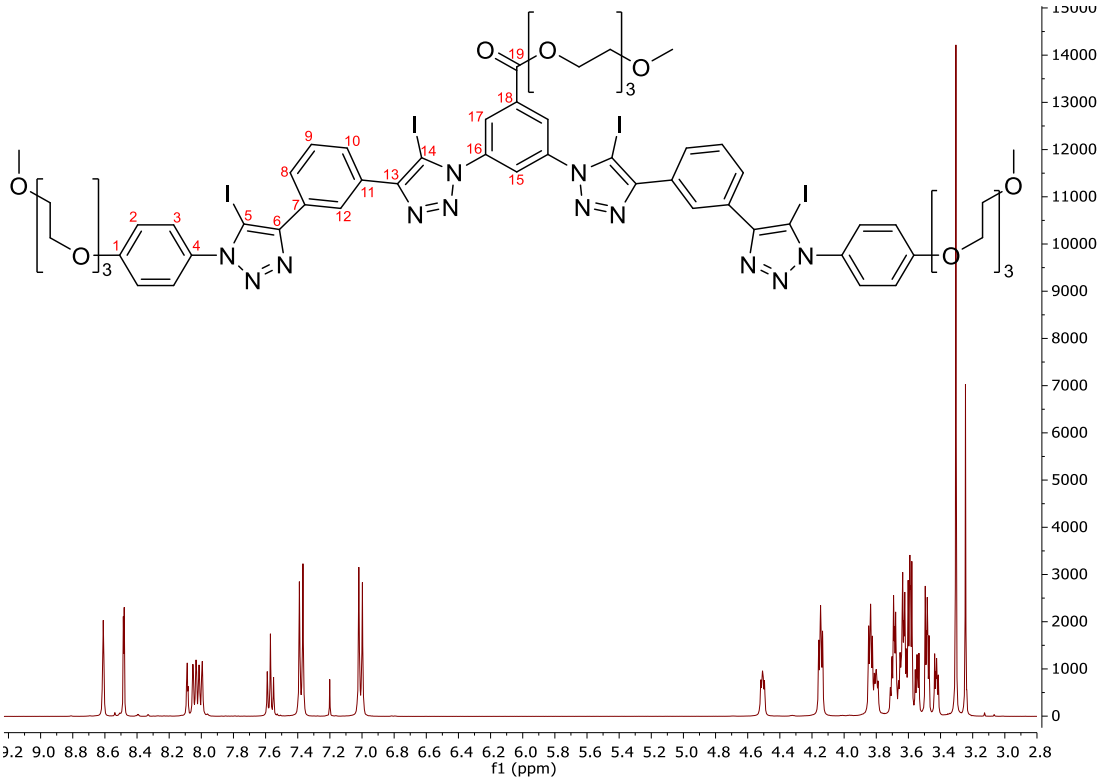



**Fig. 1-4** $^{1}$H NMR spectrum of **1b** (400 MHz, $CDCl_3$).

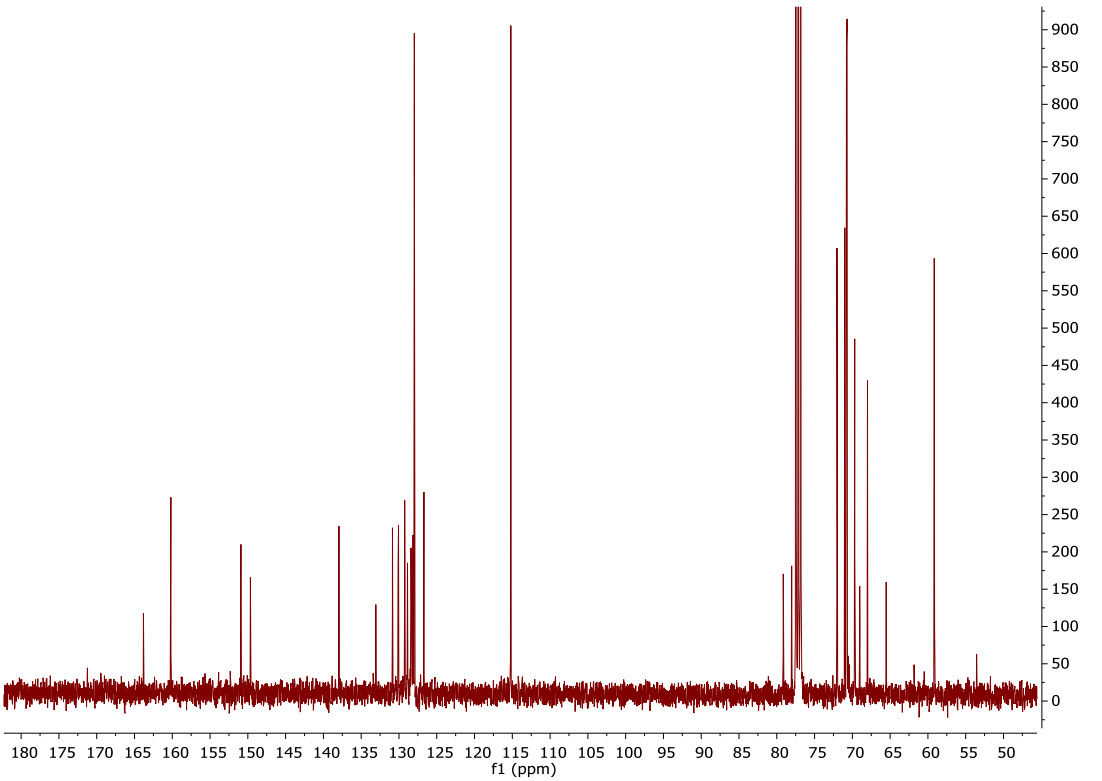



**Fig. 1-5** $^{13}$C NMR spectrum of **1b** (100 MHz, $CDCl_3$).

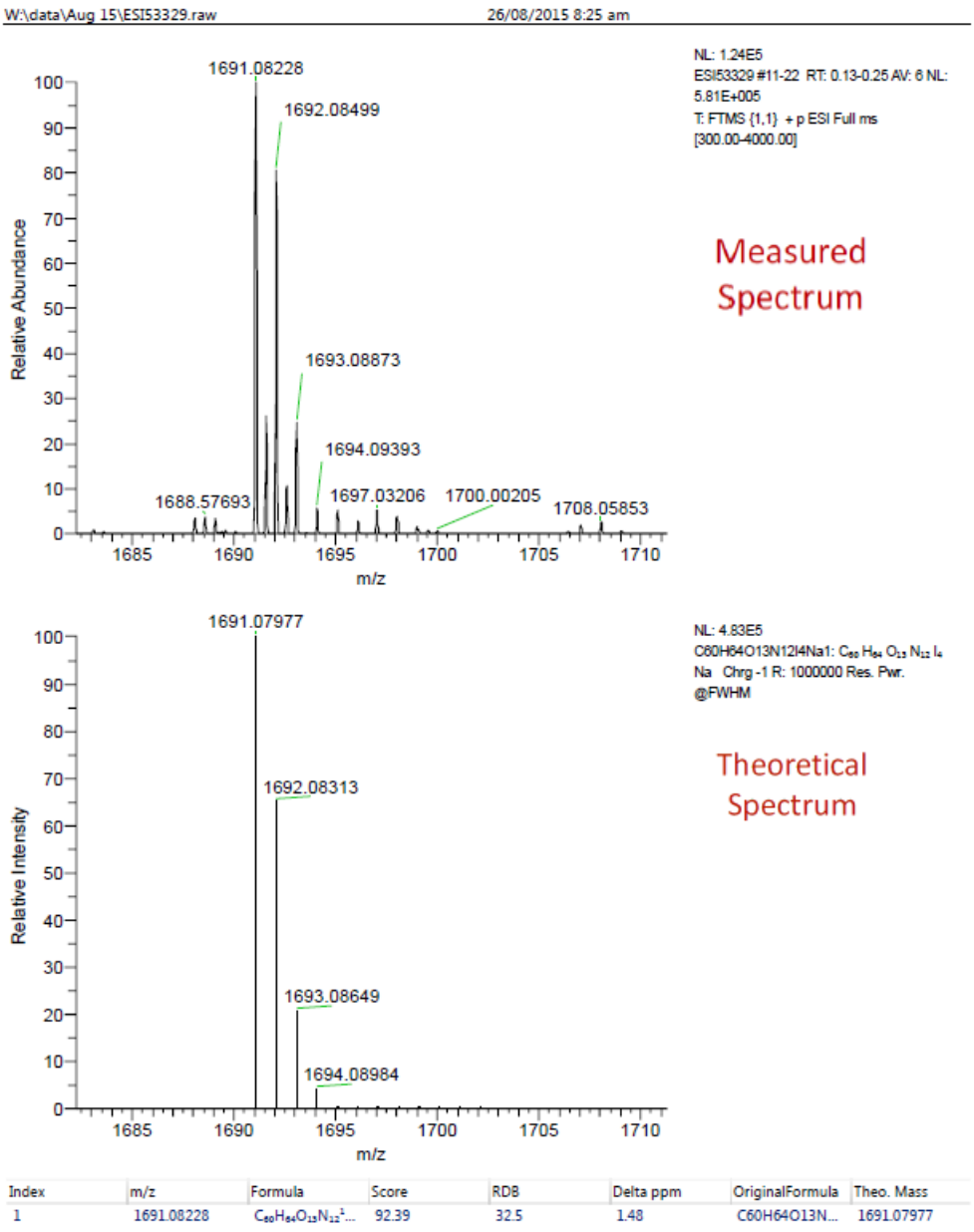



**Fig 1-6** High resolution ESI mass spectrum of **1b**.

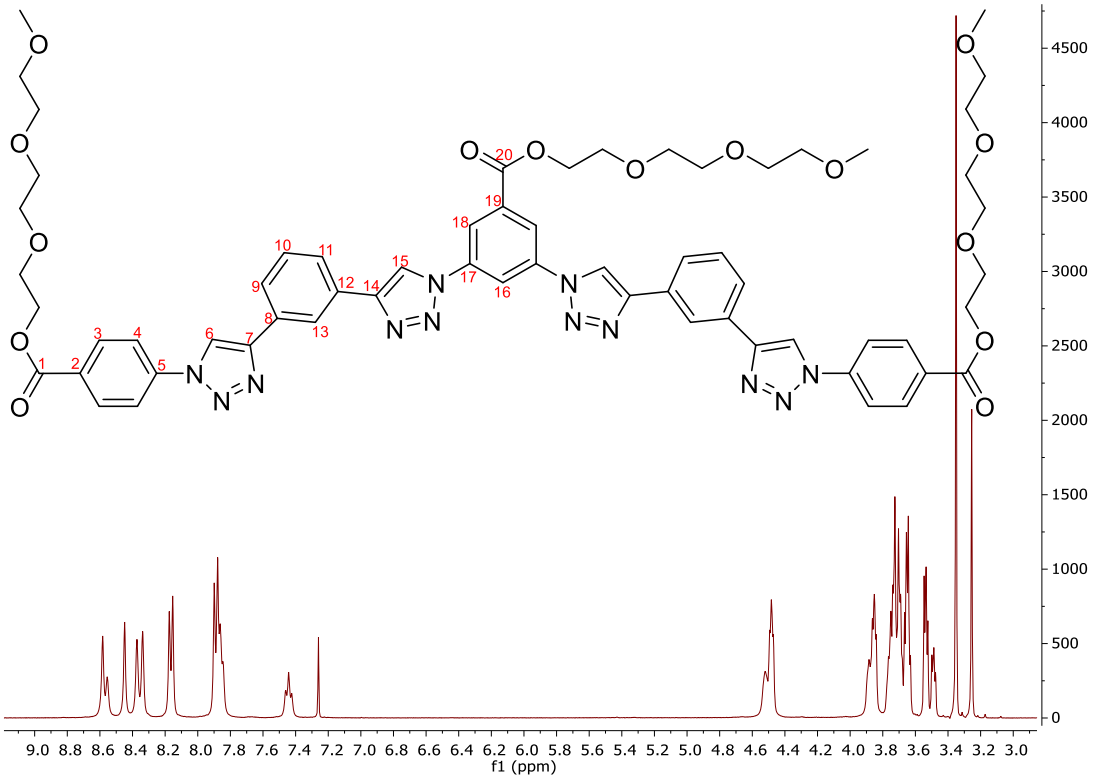



**Fig. 1-7** $^{1}$H NMR spectrum of **2a** (400 MHz, $CDCl_3$).

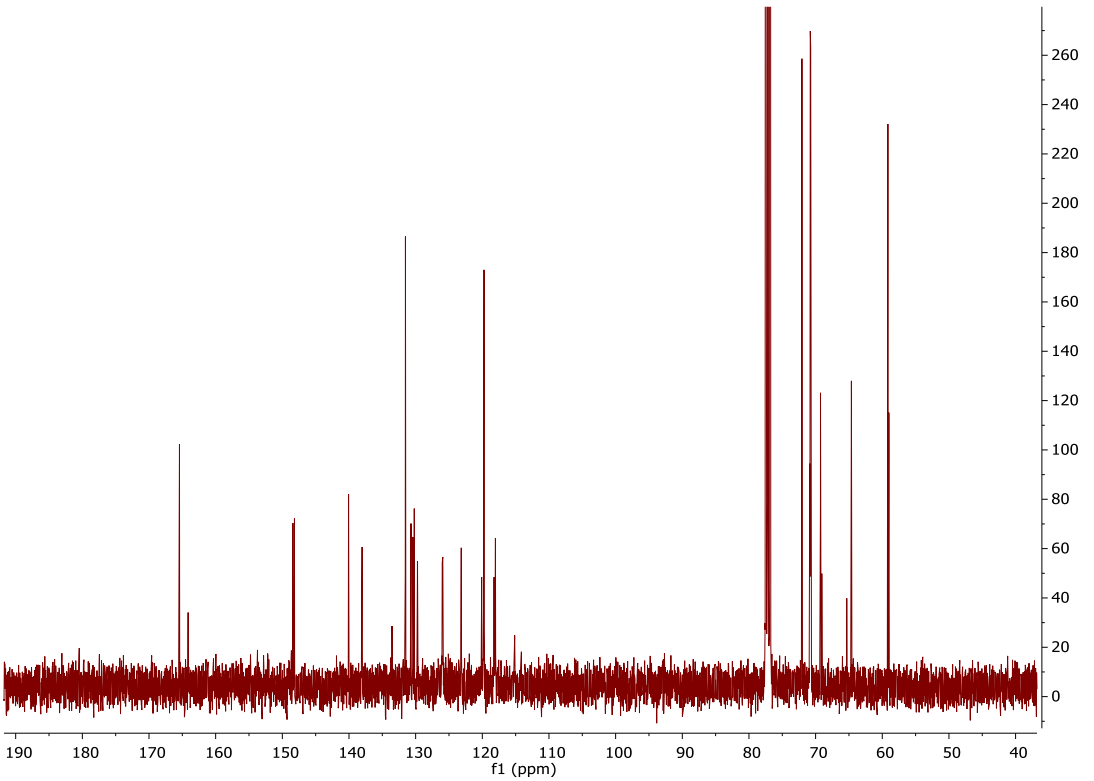



**Fig. 1-8** $^{13}$C NMR spectrum of **2a** (100 MHz, $CDCl_3$).

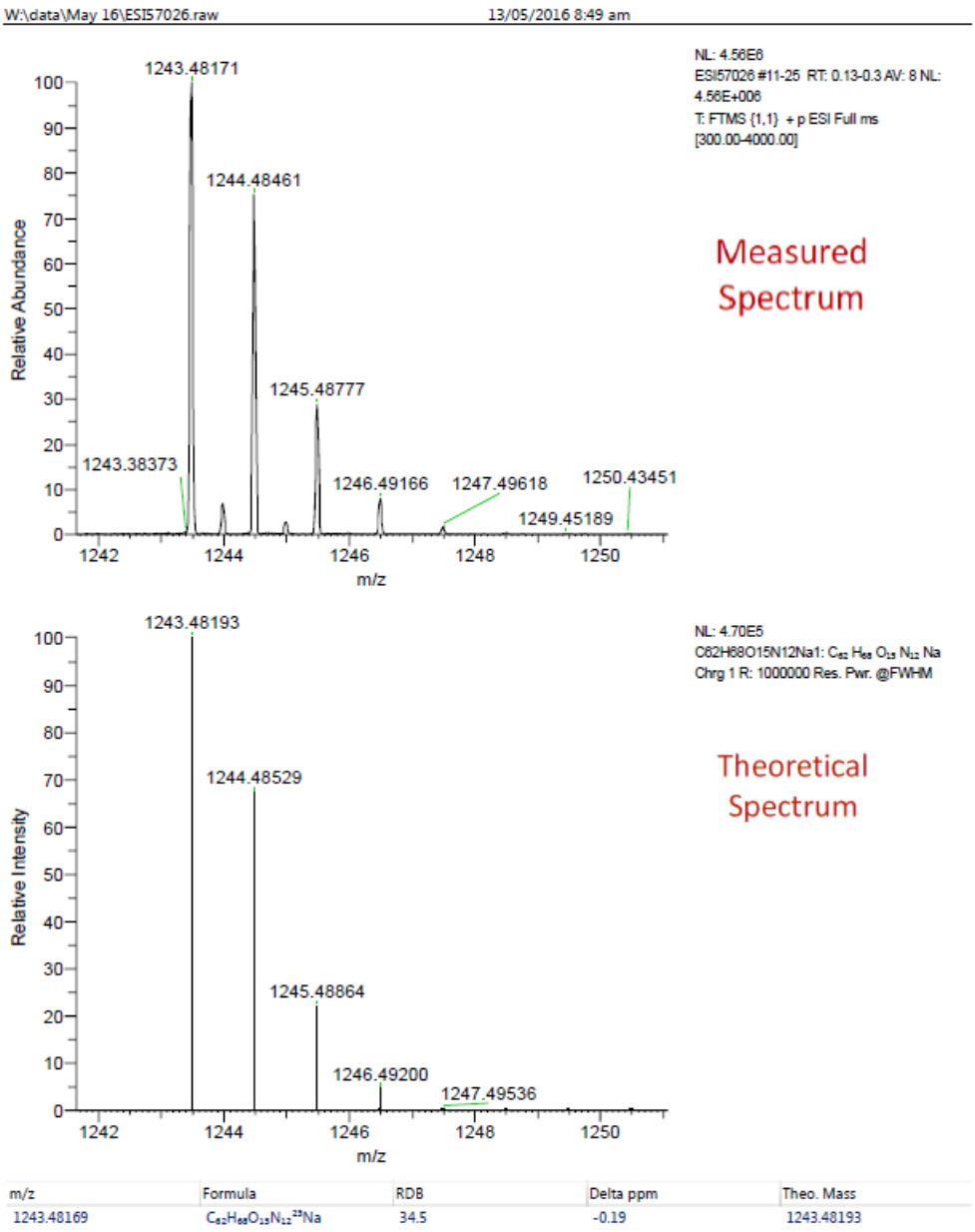



**Fig 1-9** High resolution ESI mass spectrum of **2a**.

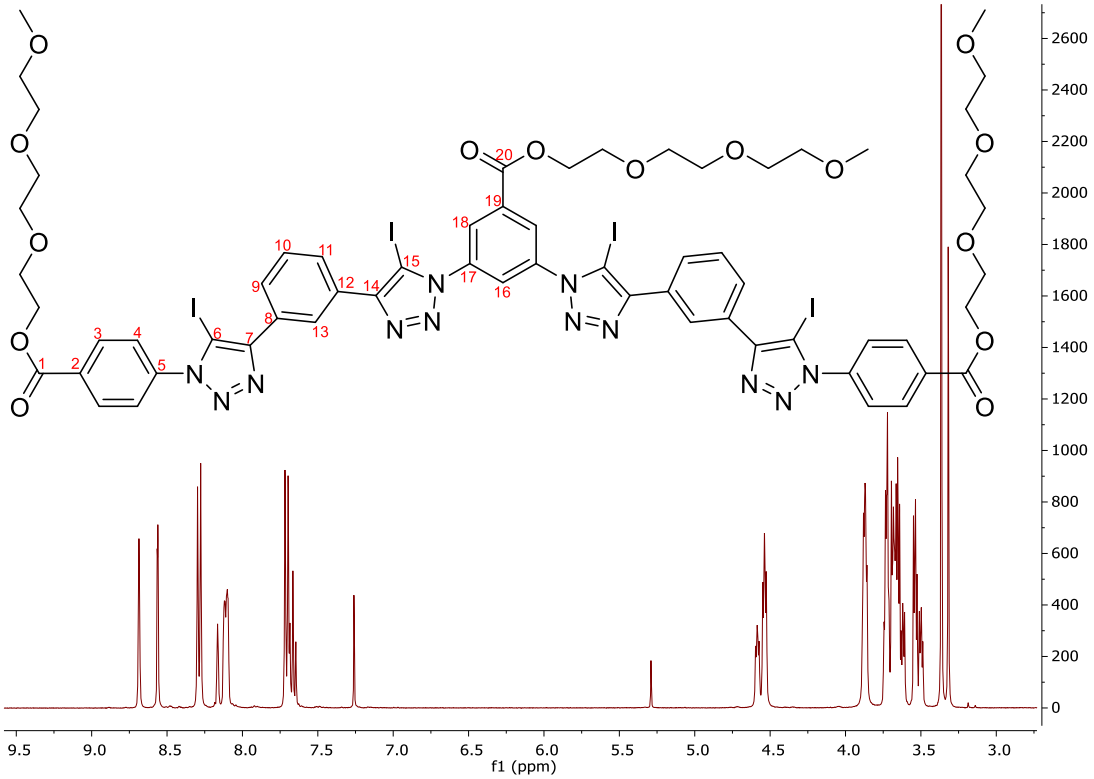



**Fig. 1-10** $^{1}$H NMR spectrum of **2b** (400 MHz, $CDCl_3$).

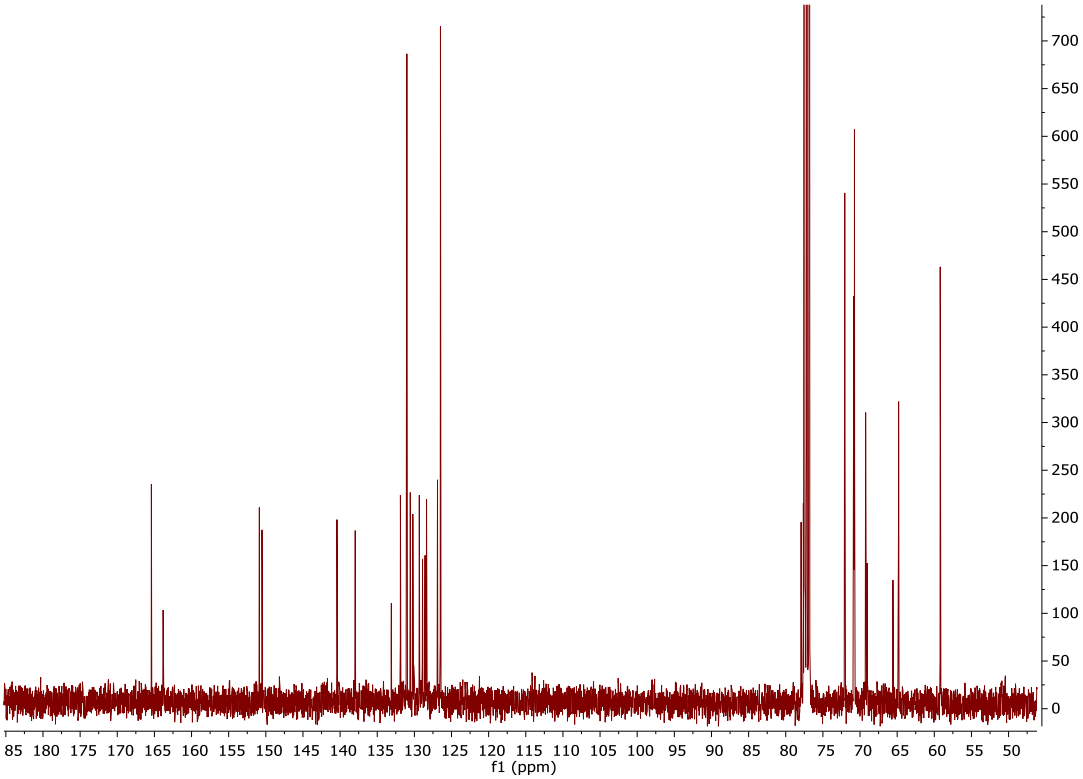



**Fig. 1-11** $^{13}$C NMR spectrum of **2b** (100 MHz, $CDCl_3$).

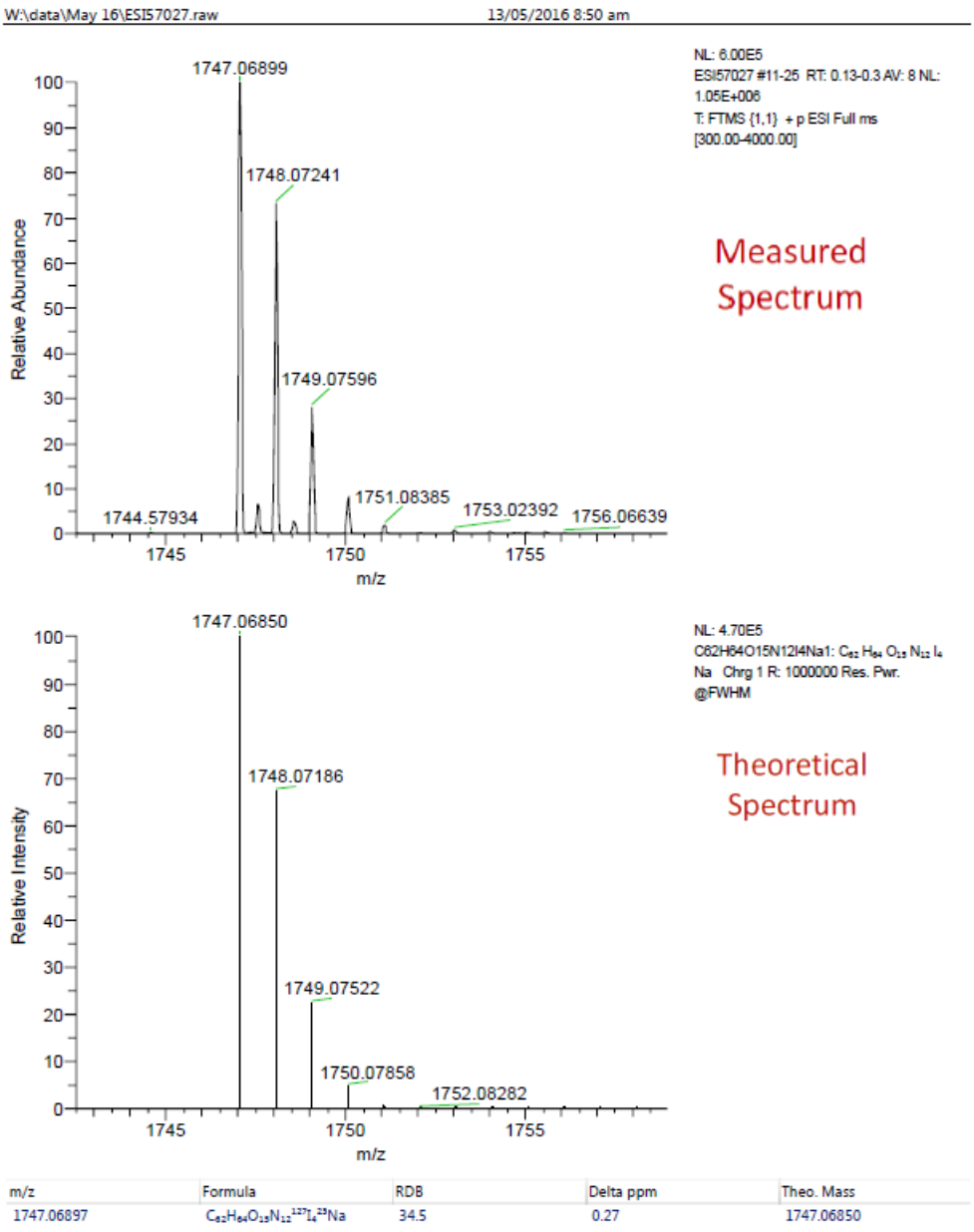



**Fig 1-12** High resolution ESI mass spectrum of **2b**.

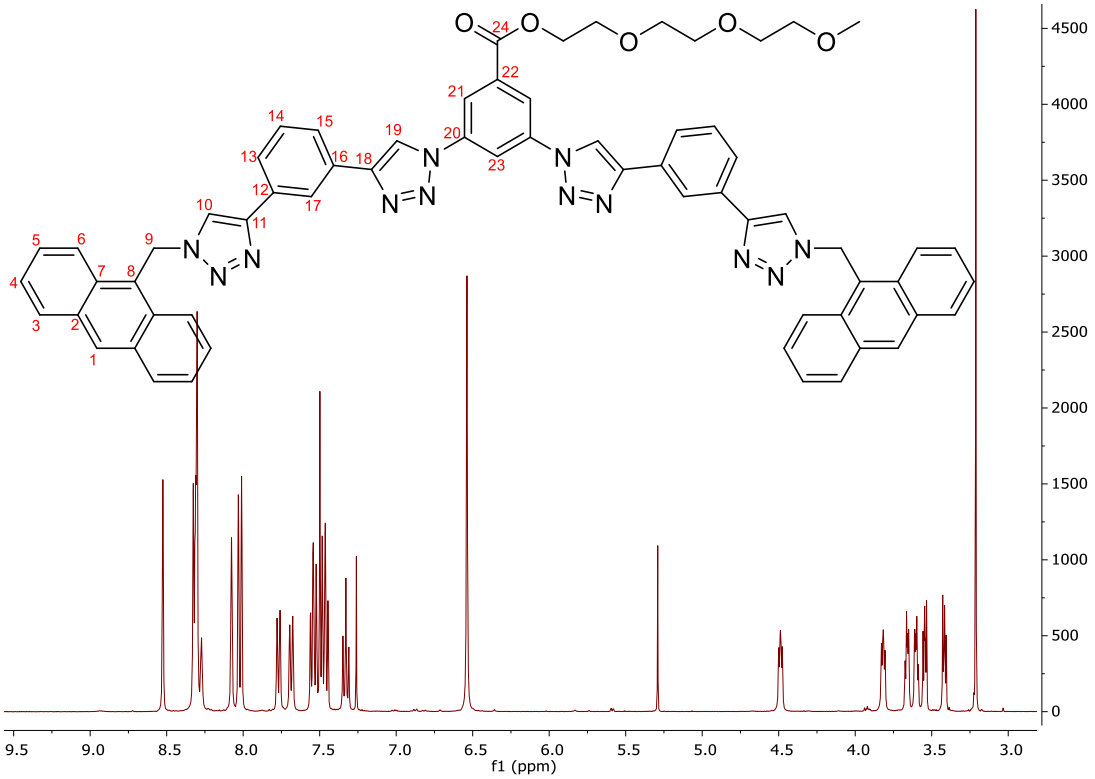



**Fig. 1-13** $^{1}$H NMR spectrum of **3a** (400 MHz, $CDCl_3$).

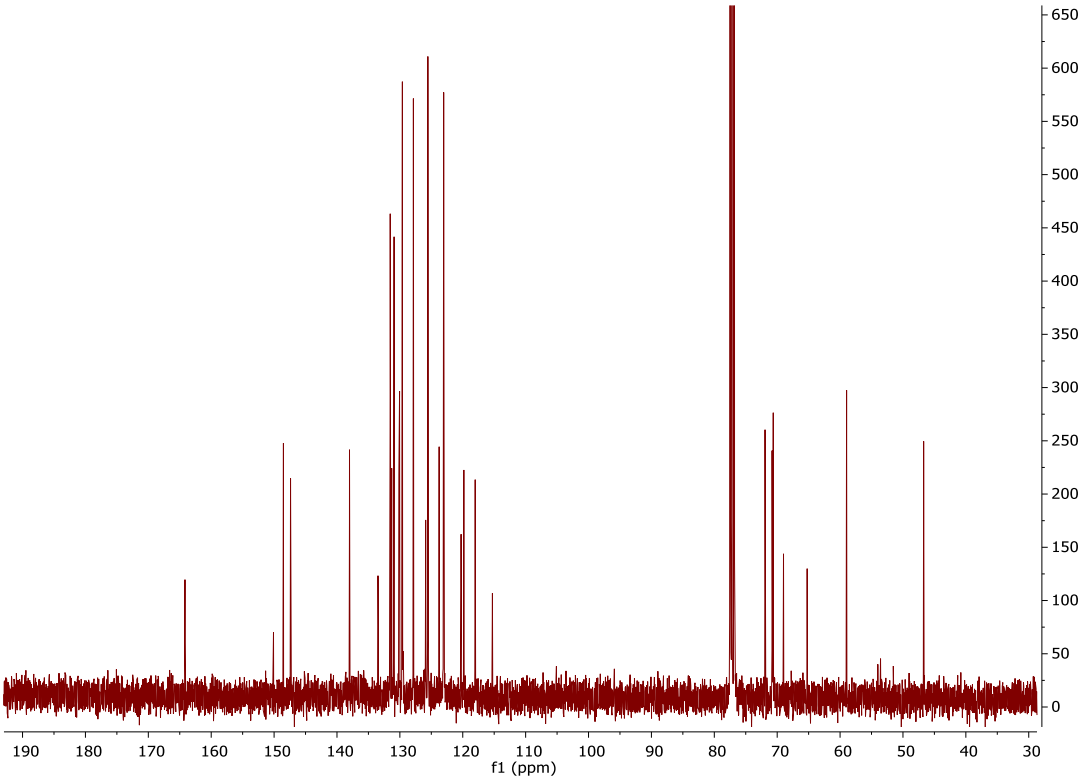



**Fig. 1-14** $^{13}$C NMR spectrum of **3a** (100 MHz, $CDCl_3$).

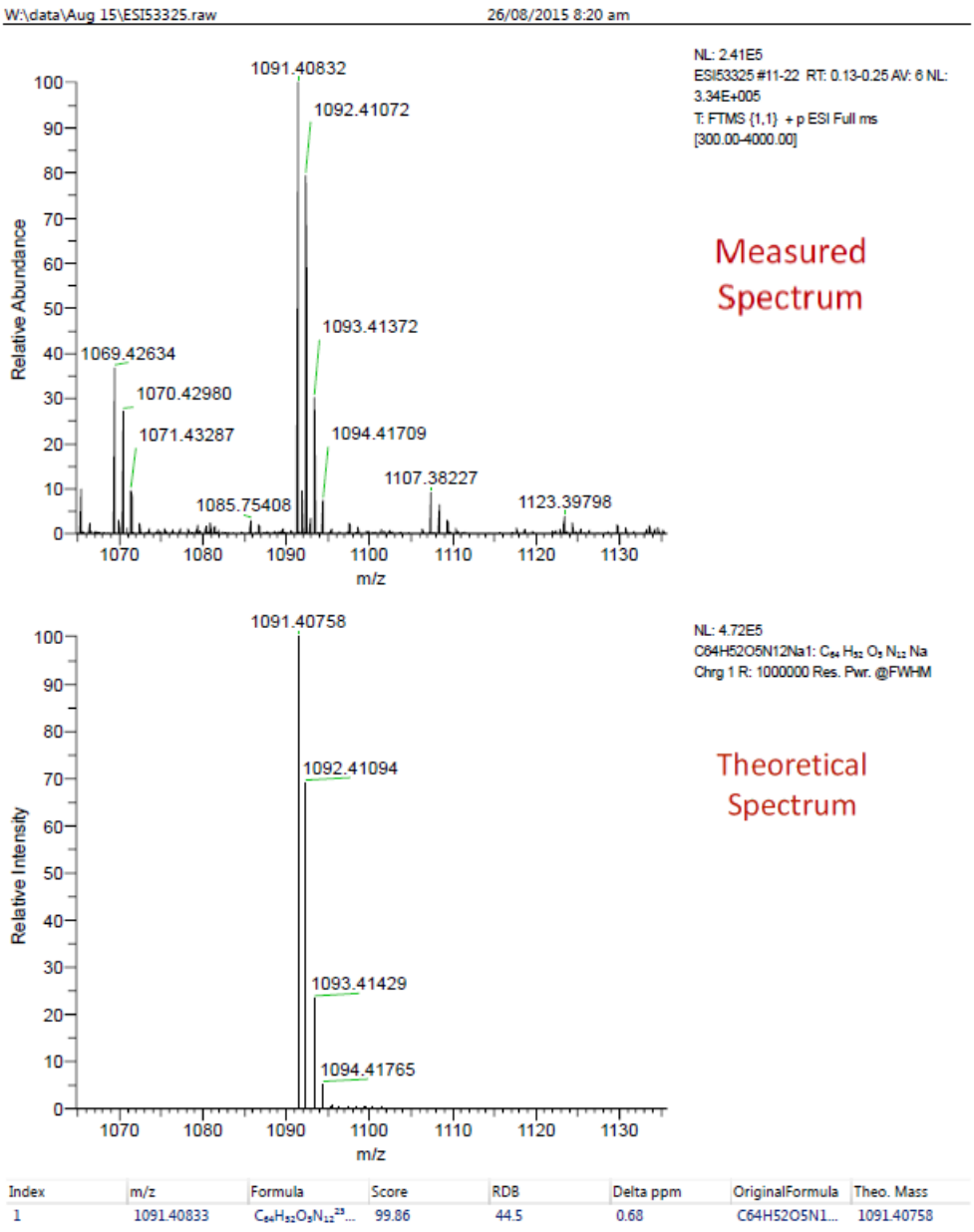



**Fig 1-15** High resolution ESI mass spectrum of **3a**.

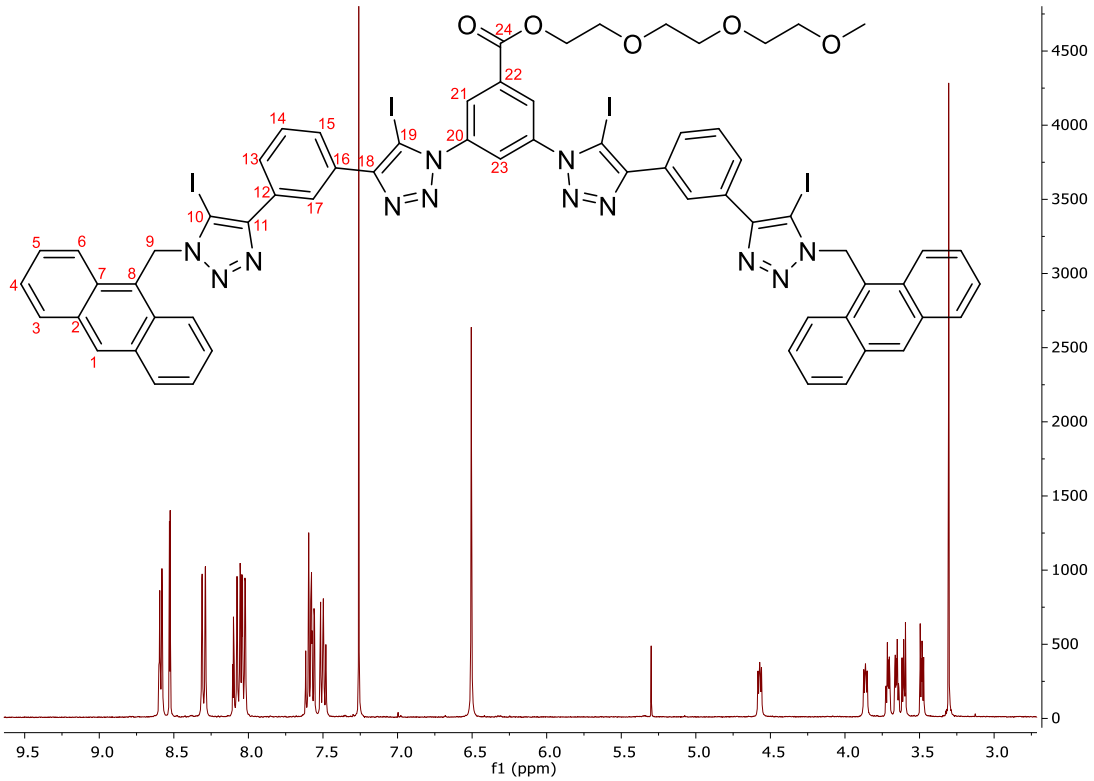



**Fig. 1-16** $^{1}$H NMR spectrum of **3b** (400 MHz, $CDCl_3$).

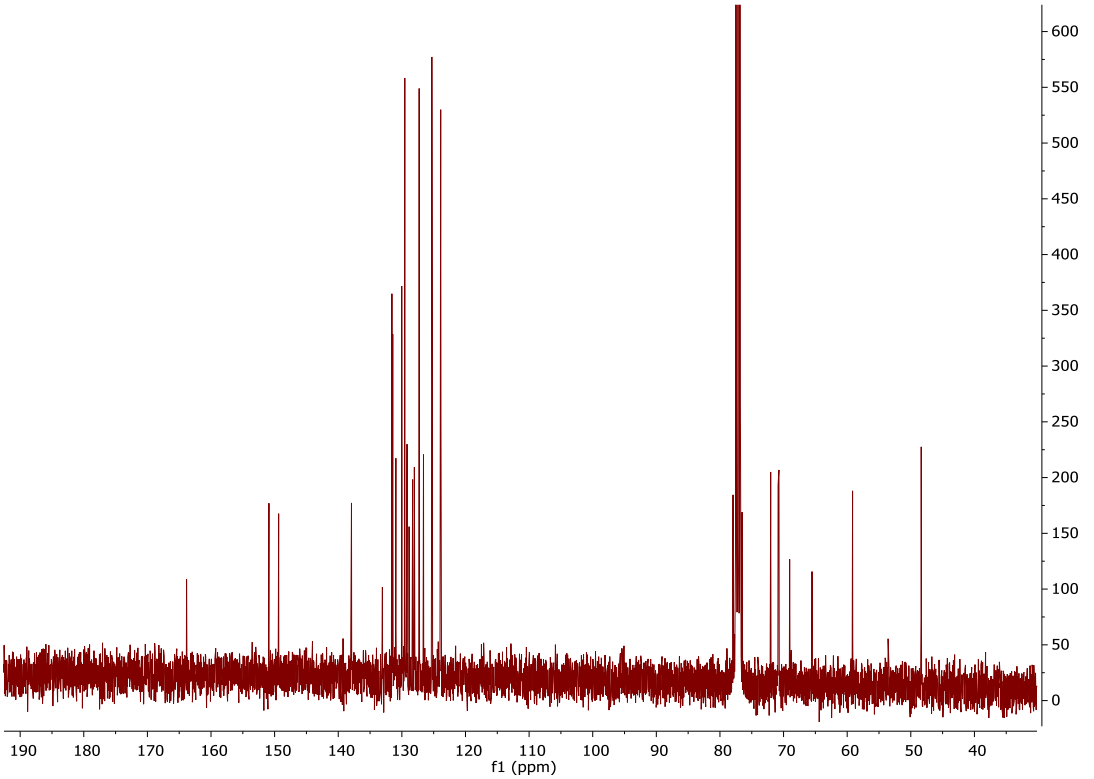



**Fig. 1-17** $^{13}$C NMR spectrum of **3b** (100 MHz, $CDCl_3$).

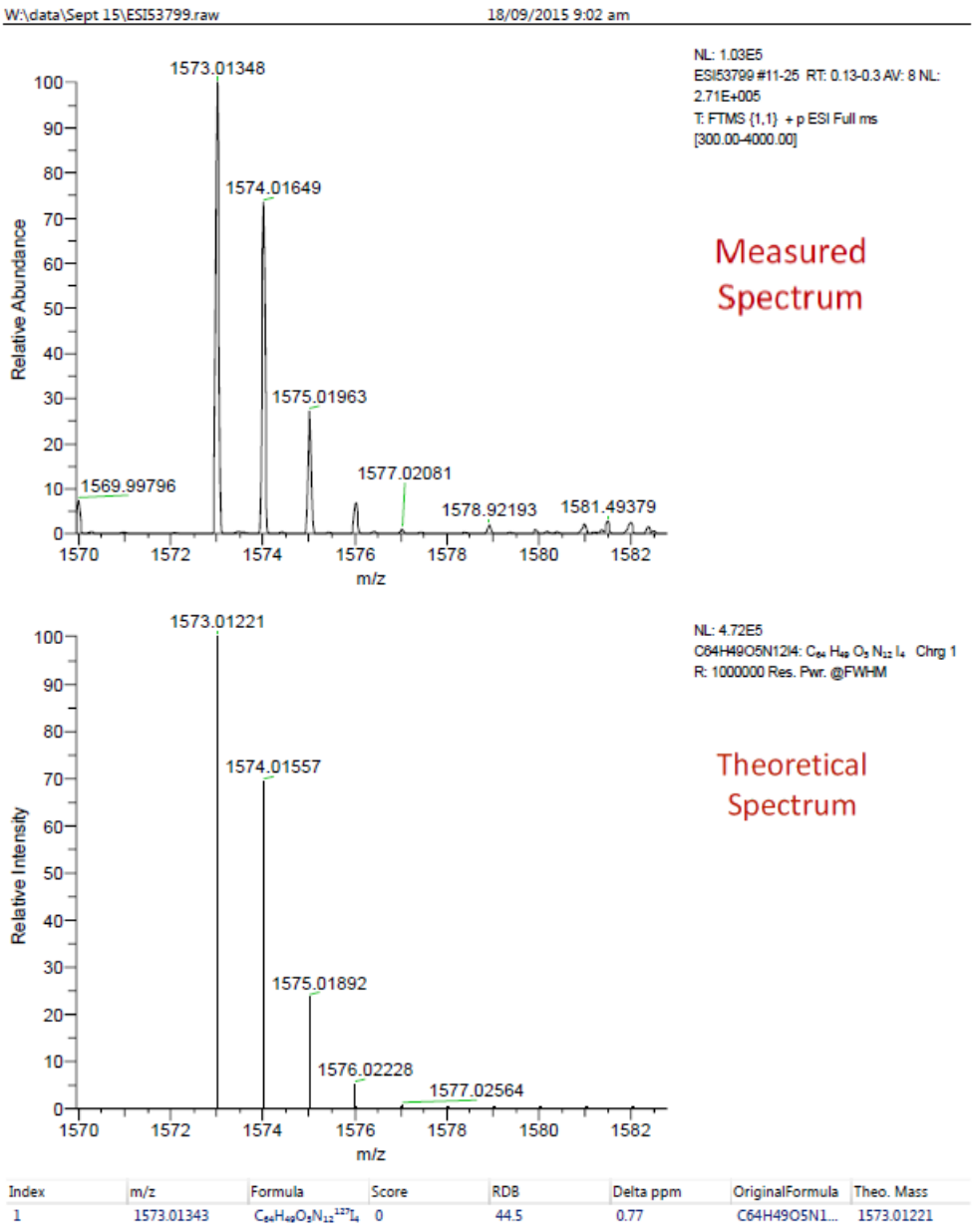



**Fig 1-18** High resolution ESI mass spectrum of **3b**.

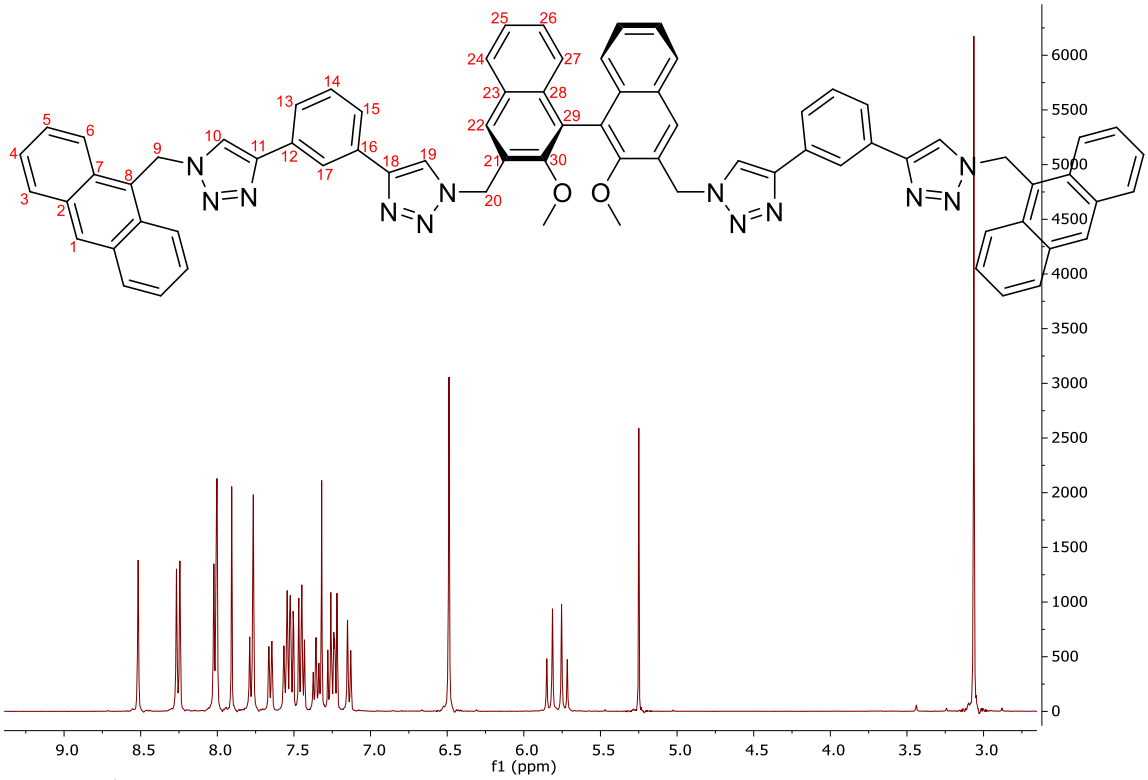



**Fig. 1-19** $^{1}$H NMR spectrum of **4a** (400 MHz, $CDCl_3$).

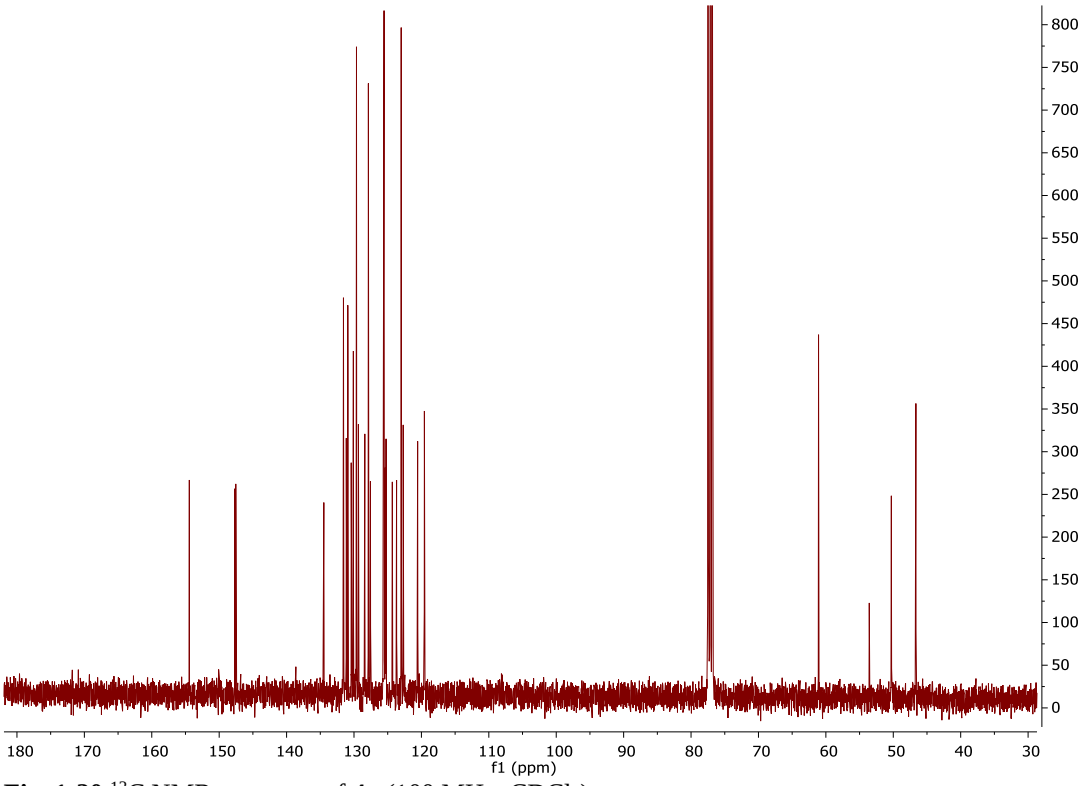
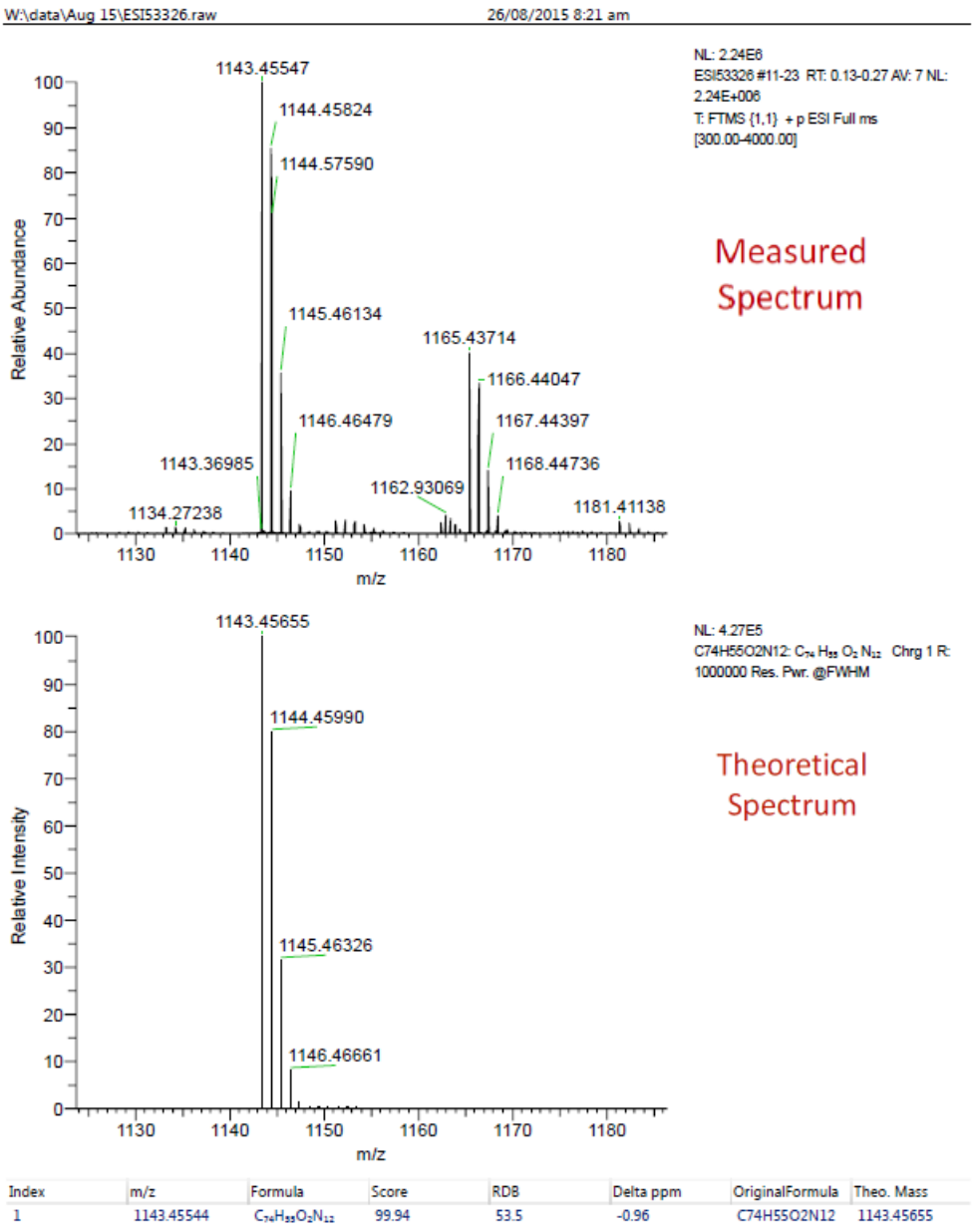



**Fig. 1-20** $^{13}$C NMR spectrum of **4a** (100 MHz, $CDCl_3$).




| Index | m/z | Formula | Score | RDB | Delta ppm | OriginalFormula | Theo. Mass |
|---|---|---|---|---|---|---|---|
| 1 | 1143.45544 | $C_{74}H_{55}O_2N_{12}$ | 99.94 | 53.5 | -0.96 | C74H55O2N12 | 1143.45655 |

**Fig 1-21** High resolution ESI mass spectrum of **4a**.

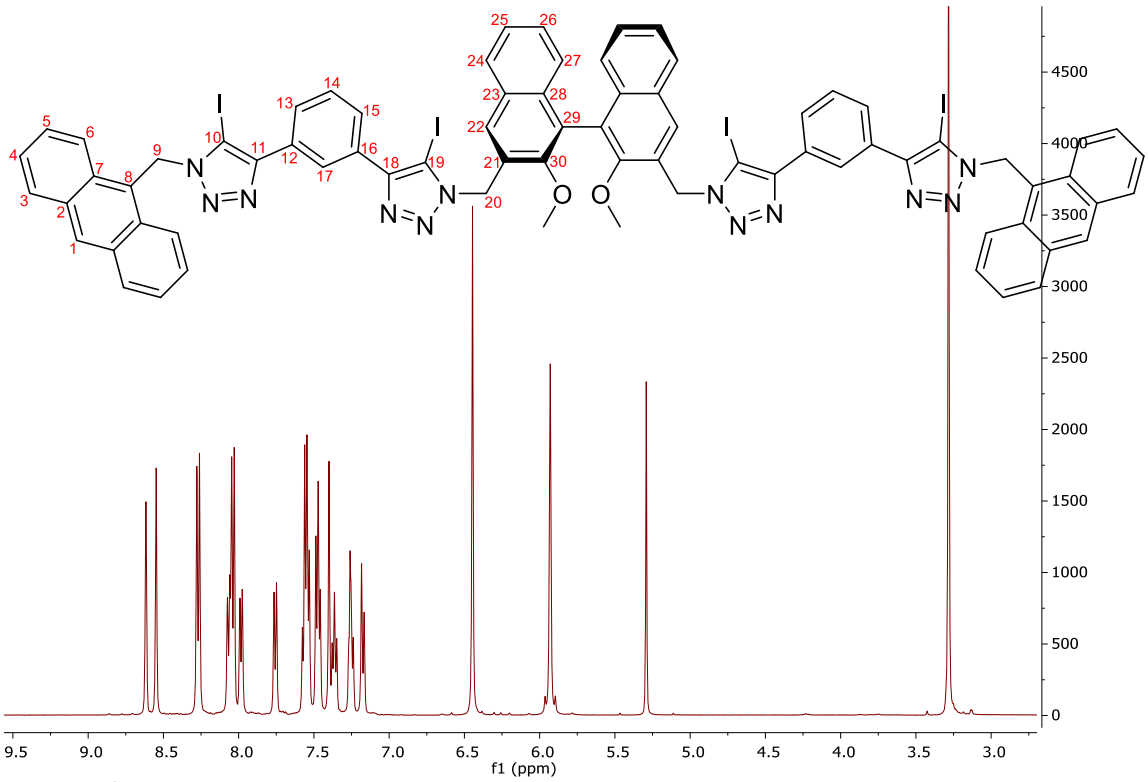



**Fig. 1-22** $^{1}$H NMR spectrum of **4b** (400 MHz, $CDCl_3$).

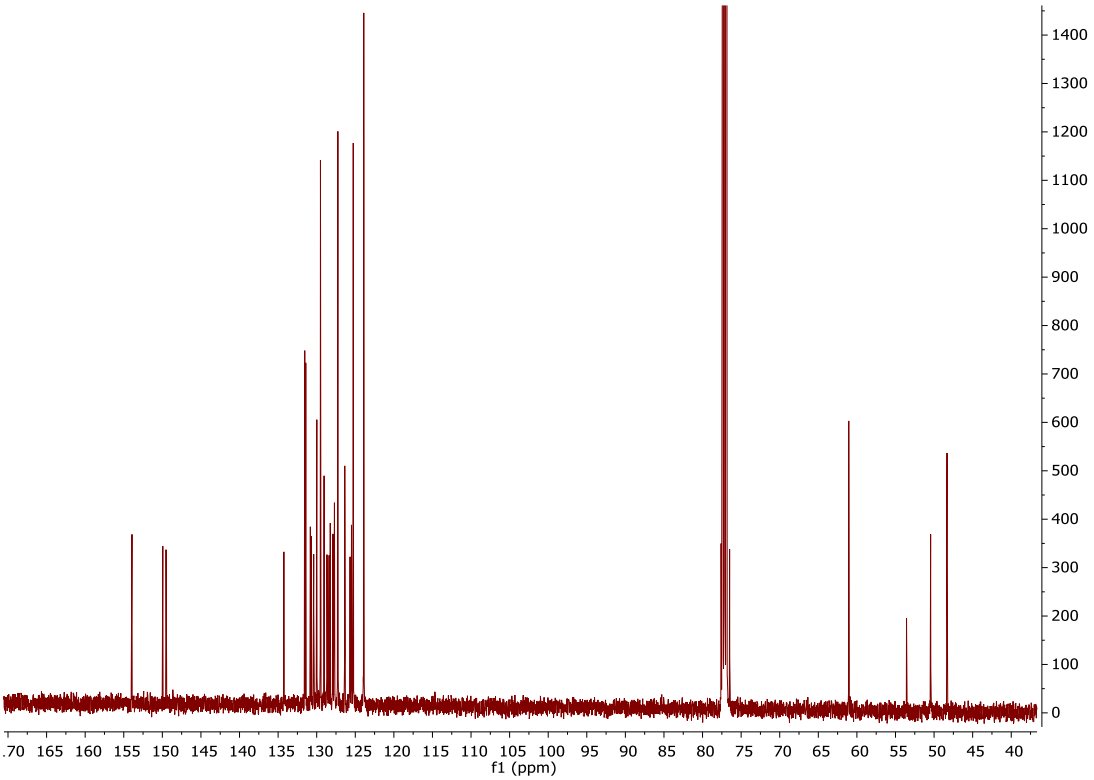
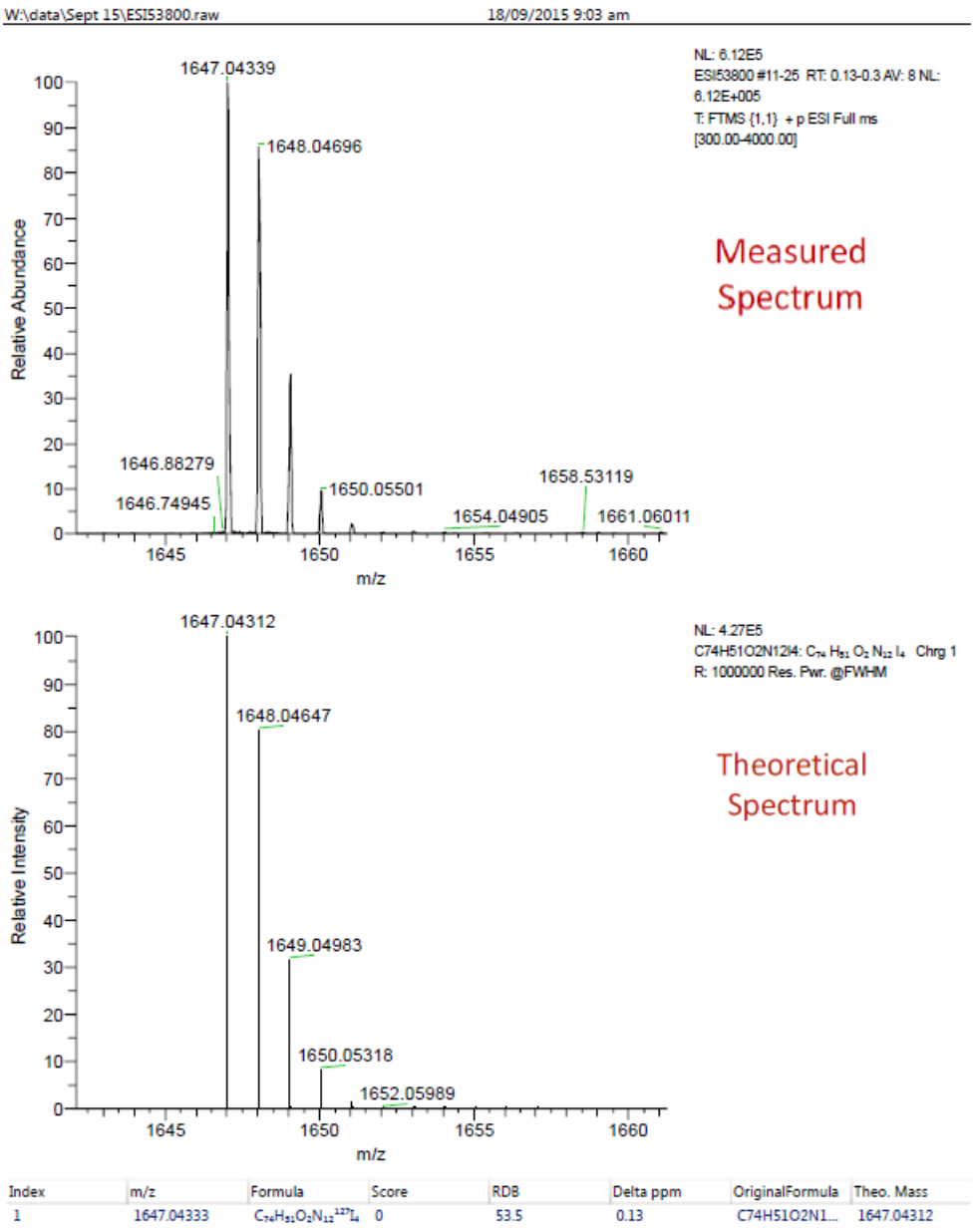



**Fig. 1-23** $^{13}$C NMR spectrum of **4b** (100 MHz, $CDCl_3$).




| Index | m/z | Formula | Score | RDB | Delta ppm | OriginalFormula | Theo. Mass |
|---|---|---|---|---|---|---|---|
| 1 | 1647.04333 | $C_{74}H_{51}O_2N_{12}{}^{127}I_4$ | 0 | 53.5 | 0.13 | C74H51O2N1... | 1647.04312 |

**Fig 1-24** High resolution ESI mass spectrum of **4b**.

## S2. Anion binding studies by $^1$H NMR titrations

### S2.1 General Protocol

$^1$H NMR titration experiments were performed on a Bruker AVIII 500 MHz spectrometer. NMR tube was loaded with 0.5 ml of 0.0015 M solution of the test compound in the solvent of choice ($CDCl_3$ or 1:1 $CDCl_3$/acetone-$d_6$). The sample was titrated with 0.075 M solution of the appropriate anion introduced as tetrabutylammonium (TBA) salt. The titration curve was built from 17 data points corresponding to 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 2.0, 2.5, 3.0, 4.0, 5.0, 7.0, 10.0 equivalents of titrant added. Unless otherwise stated, the inner triazole proton signal ($H_A$) was monitored for hydrogen bonding receptors **1a**-**4a**. For the iodotriazole receptor **4b** the titration curves were derived from $H_C$. In chiral recognition experiments with **4b** methylene protons $H_D$ were also followed. Iodotriazole receptors **1b**, **2b** and **3b** showed small changes in chemical shift upon titration (0.05 – 0.15 ppm) and provided unreliable binding constant information. To obtain good quality binding data for these compounds the host-host competition method was used (see section S3).

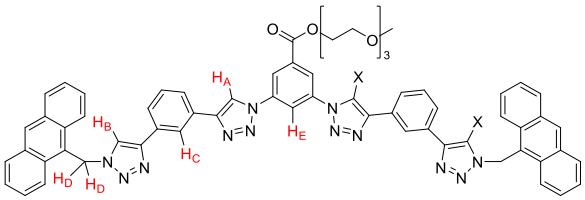



**Fig. S2-1** Labeling of protons that were monitored to generate titration curves. This nomenclature is consistent for all receptors **1**-**4**.

The binding of anions with all receptors was found to be fast on the NMR timescale. The values of the observed chemical shift and concentration of anion were entered into the WinEQNMR2[5] program for every titration point. From initial estimates made of the binding constants and limiting chemical shifts, these parameters were refined using non-linear least-squares analyses to obtain the best fit between empirical and calculated chemical shifts based on a 1:1 binding stoichiometry. The input parameters were varied till convergence of the best fit values of the binding constants and their errors were obtained. The observed titration curves were consistent with 1:1 binding stoichiometry.

### S2.2 $^1$H NMR titration data for receptors 1-4

All titrations of compounds **1-3** were carried out in $CDCl_3$ (500 MHz, 298 K) whereas **4** was titrated in 1:1 $CDCl_3$/acetone-$d_6$. In Figures S2-2 – S2-10 observed chemical shifts are represented by the markers, while continuous lines represent the calculated binding curves.

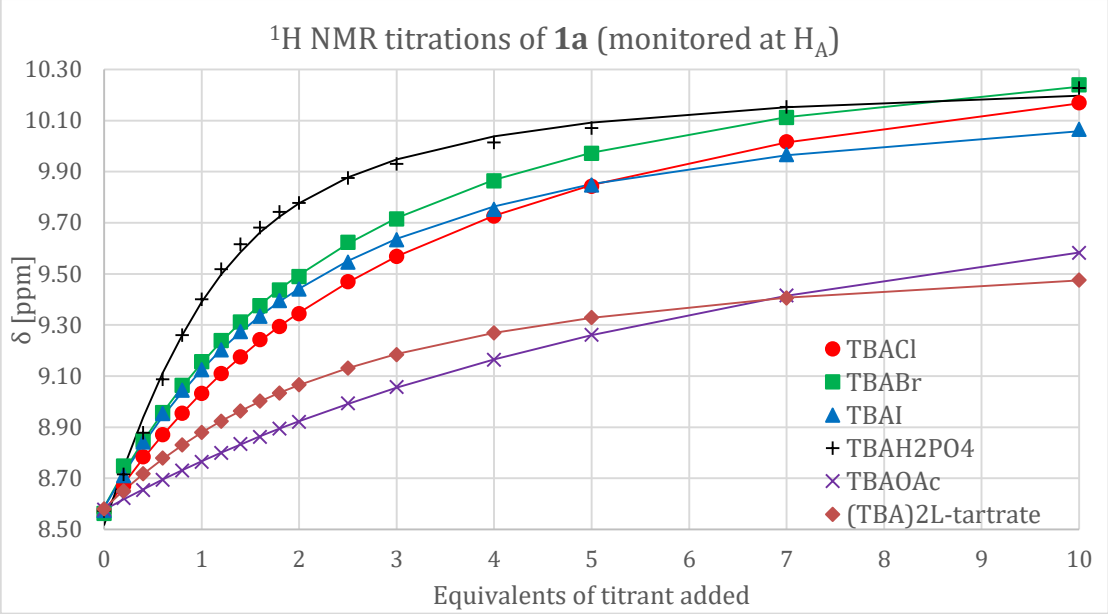



**Fig. S2-2** $^{1}$H NMR titrations of **1a** (monitored at $H_A$).

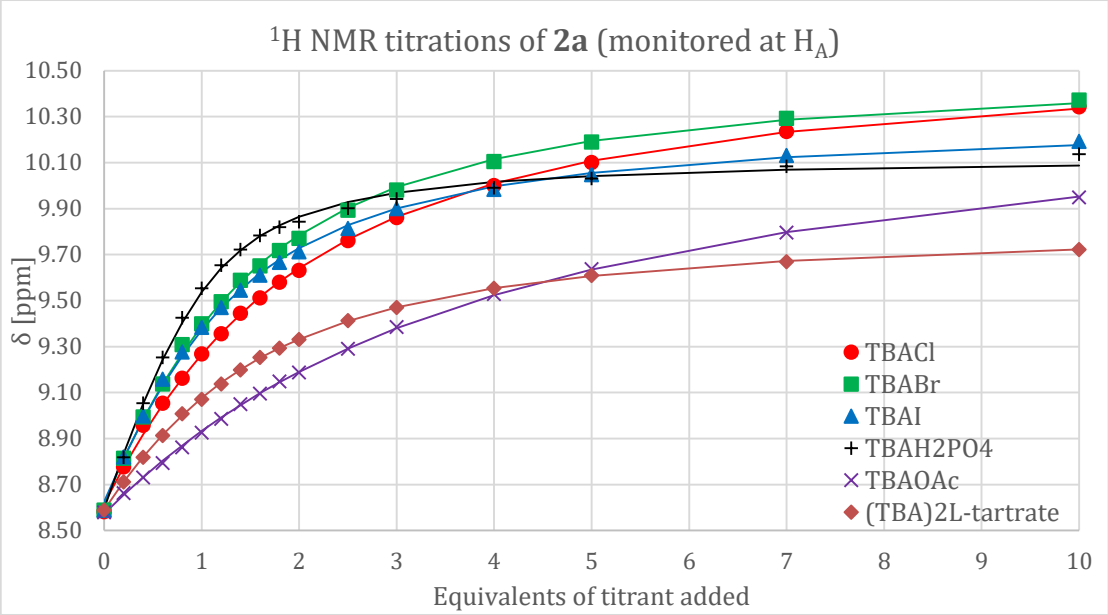



**Fig. S2-3** $^{1}$H NMR titrations of **2a** (monitored at $H_A$).

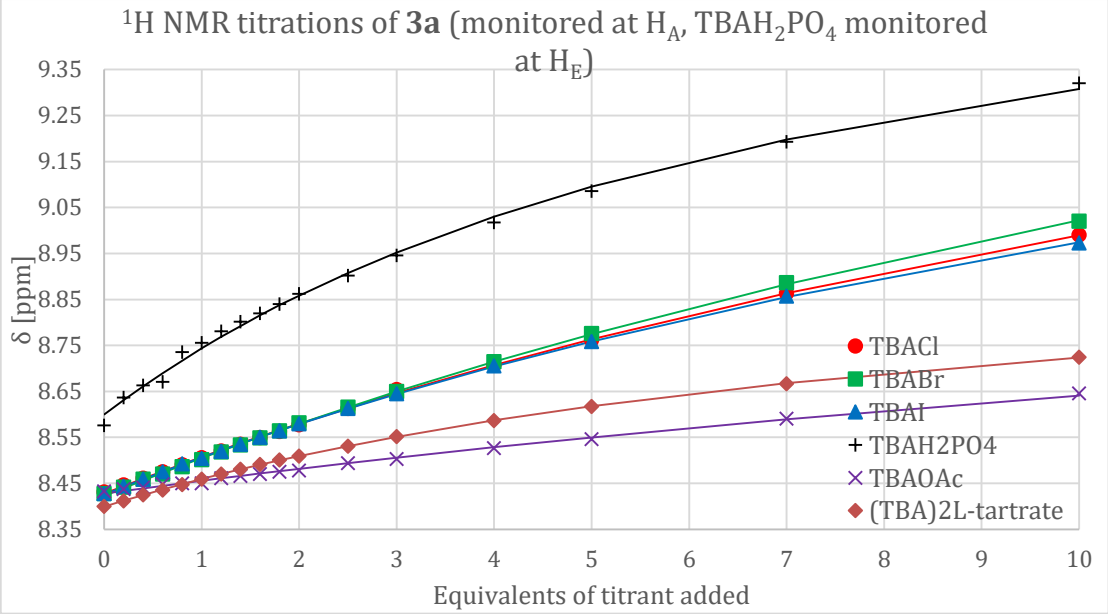



**Fig S2-4** $^1$H NMR titrations of **3a** (monitored at $H_A$, for $TBAH_2PO_4$ monitored at $H_E$).

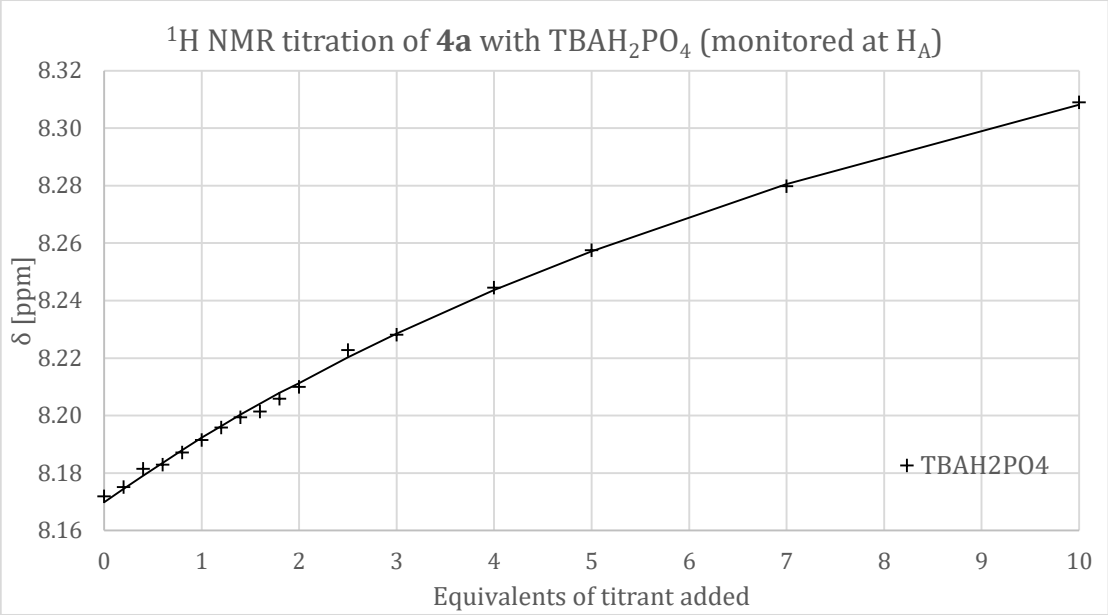



**Fig S2-5** $^1$H NMR titration of **4a** with $TBAH_2PO_4$ (monitored at $H_A$).

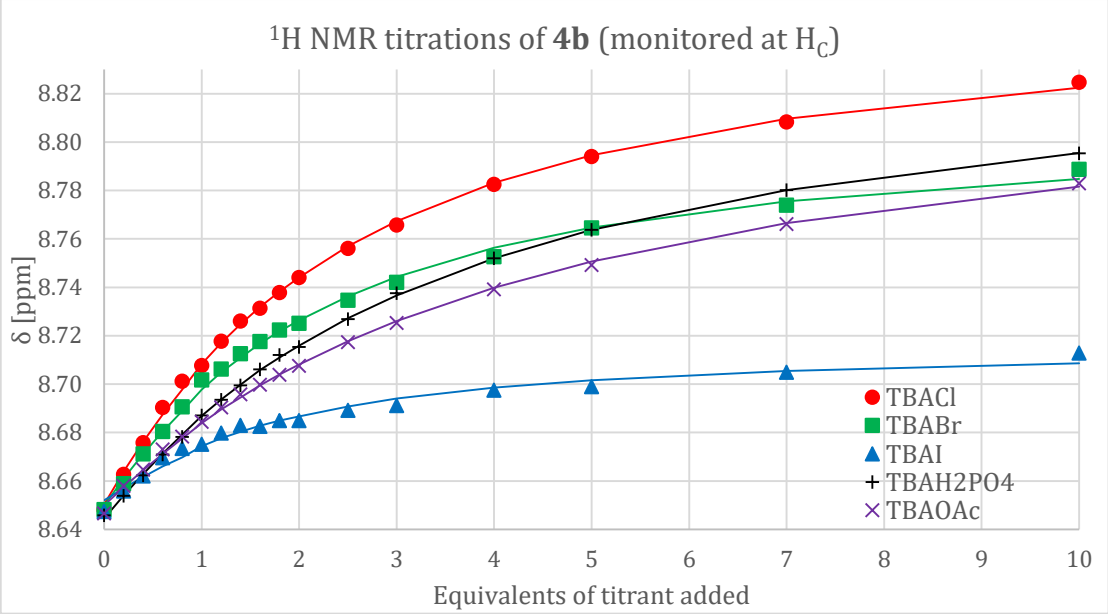



**Fig S2-6** $^{1}$H NMR titrations of **4b** (monitored at $H_C$).

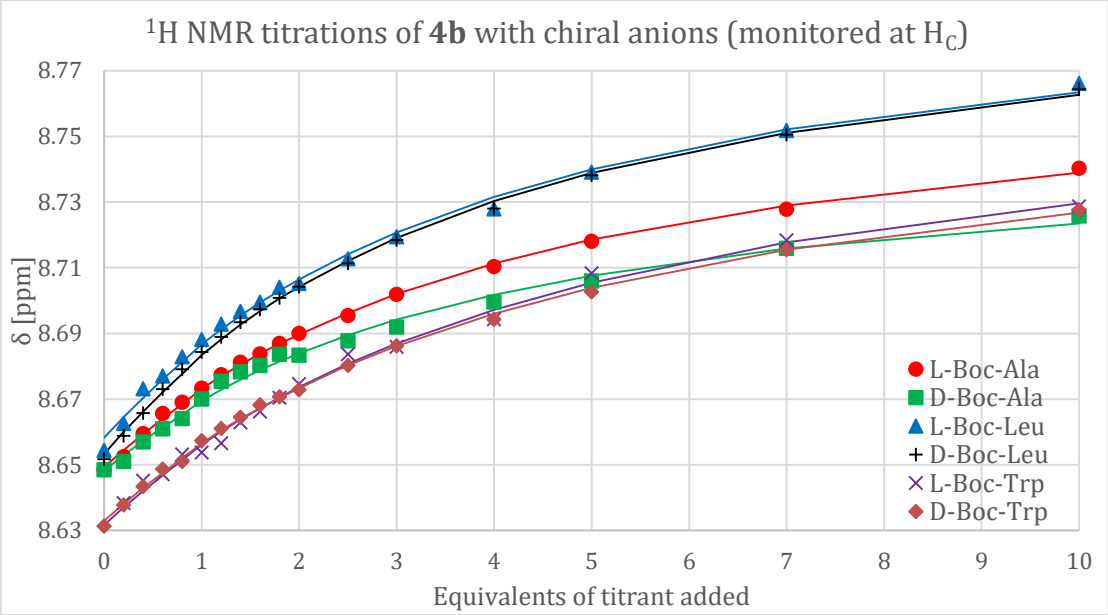



**Fig S2-7** $^{1}$H NMR titrations of **4b** with chiral anions (monitored at $H_C$). All anions were introduced as tetrabutylammonium salts.

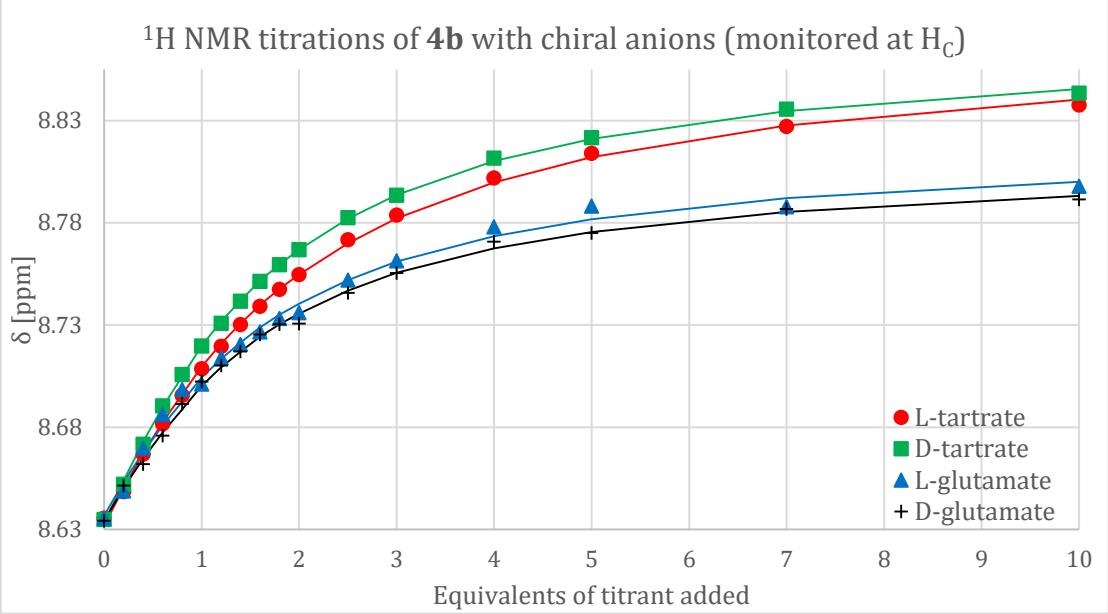



**Fig S2-8** $^{1}$H NMR titrations of **4b** with chiral dicarboxylates (monitored at $H_C$). All anions were introduced as tetrabutylammonium salts.

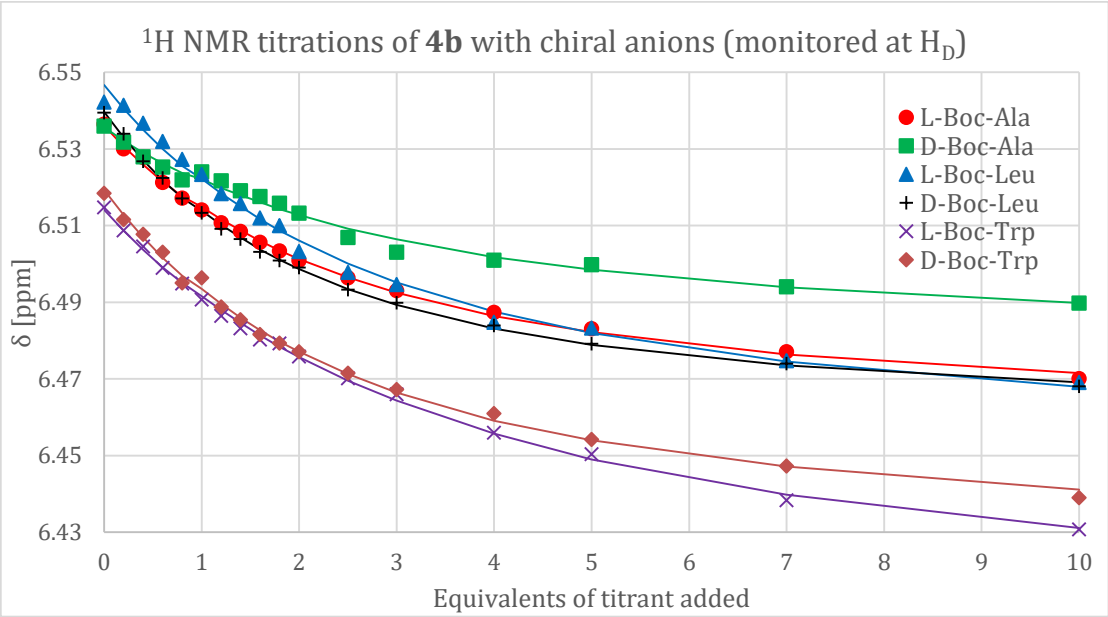



**Fig S2-9** $^{1}$H NMR titrations of **4b** with chiral anions (monitored at $H_D$). All anions were introduced as tetrabutylammonium salts.

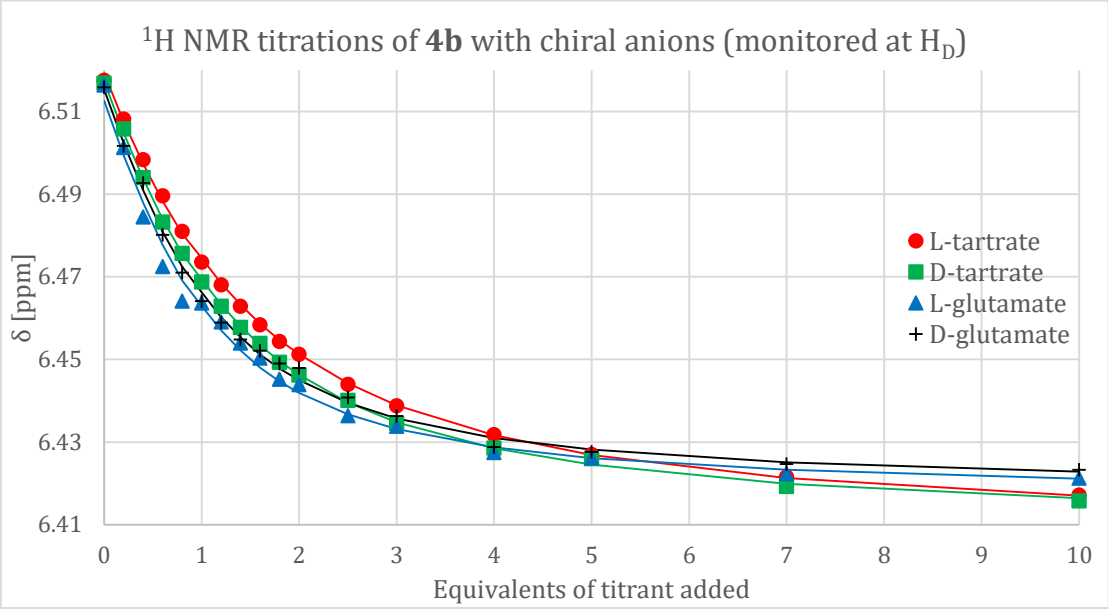



**Fig S2-10** $^{1}$H NMR titrations of **4b** with chiral dicarboxylates (monitored at $H_D$). All anions are introduced as tetrabutylammonium salts.

## S3 Anion binding studies by $^1$H NMR host-host competition method

### S3.1 General protocol

Host-host competition method was used to determine anion binding constants for iodotriazole receptors **1b**, **2b** and **3b**. In a typical experiment, 0.5 ml of 0.0015 M solution of the test compound is loaded into an NMR tube and combined with 0.025 ml of 0.0015 M solution of a reference compound (**2a** was generally used as reference). The resulting mixture was titrated with 0.015 M solution of anion introduced as tetrabutylammonium salt. A spectrum was recorded before titrant addition, followed by at least three data points, typically with 1, 1.5, 2 equivalents of titrant. Finally, 0.1 ml of 0.15 M titrant solution was added to a total of 22 equivalents and another spectrum recorded. Signal of the inner triazole ($H_A$, see Fig. S2-1) protons in the reference compound was monitored to extract binding constant information. All spectra were recorded on a Bruker AVIII 500 MHz spectrometer at 298 K in $CDCl_3$. Techniques similar but not identical to the one described here were used in some studies to measure association constants between crown ethers and alkaline metal cations.[6]

### S3.2 Data analysis

Nomenclature:

| | |
|---|---|
| $\delta$ | observed chemical shift of the reference compound |
| $\delta_R$ | chemical shift of the free reference compound |
| $\delta_{RX}$ | chemical shift of the reference compound bound to the anion |
| $C_R$ | analytical concentration of the reference compound |
| $C_A$ | analytical concentration of the test compound |
| $C_X$ | analytical concentration of the titrant (anion) |
| [R] | concentration of the free reference compound |
| [RX] | concentration of the reference compound bound to the anion |
| [A] | concentration of the free test compound |
| [AX] | concentration of the test compound bound to the anion |
| $K_R$ | anion binding constant of the reference compound |
| $K_A$ | anion binding constant of the test compound |

Under fast exchange conditions the observed chemical shift of the reference compound is a weighted average of the chemical shifts of free and bound reference (1). Using this and the expression for analytical concentration of reference (2) we can derive the concentrations of free (3) and bound (4) reference.

$$\delta = \frac{\delta_R[R] + \delta_{RX}[RX]}{C_R} \quad (1)$$

$$C_R = [R] + [RX] \quad (2)$$

$$[R] = C_R \frac{\delta - \delta_{RX}}{\delta_R - \delta_{RX}} \quad (3)$$

$$[RX] = C_R - [R] \quad (4)$$

Rearranging the reference binding constant equation (5) we can now derive the free anion concentration (6).

$$K_R = \frac{[RX]}{[R][X]} \qquad (5)$$

$$[X] = \frac{[RX]}{K_R[R]} \qquad (6)$$

Knowing the analytical concentrations of anion and the test compound it is possible to obtain the concentrations of bound (7) and free (8) test compound. This gives all components of the test compound binding constant equation (9).

$$[AX] = C_X - [\mathrm{X}] - [\mathrm{RX}] \qquad (7)$$

$$[A] = C_A - [AX] \qquad (8)$$

$$K_A = \frac{[AX]}{[A][X]} \qquad (9)$$

While $\delta_R$ can be obtained directly from a spectrum taken before addition of titrant, $\delta_{RX}$ can be calculated from an overtitrated spectrum taken with 22 eq of anion. As most analyte and reference is bound under these conditions, we can assume that $[X] \approx C_X - C_A - C_R$. It is then possible to derive concentrations of bound (10) and free (11) reference from (2) and (5).

$$[RX] = \frac{K_R[X]C_R}{1 + K_R[X]} \qquad (10)$$

$$[R] = C_R - [RX] \qquad (11)$$

Knowing these, we can now rearrange (1) to subtract the contribution of the small amount of free reference from the observed chemical shift and obtain $\delta_{RX}$ (12).

$$\delta_{RX} = \frac{\delta C_R - [R]\delta_R}{[RX]} \qquad (12)$$

In practice it is necessary to simultaneously determine $K_R$ and $K_A$ from the competition experiment rather than use separately obtained $K_R$ to calculate $K_A$. This is because binding affinity of the reference compound can be affected by the test compound and thus it is necessary to know *system-specific* $K_R$ to determine $K_A$. In order to do this, we can find a relationship (13) between $K_R$ and $K_A$ from (6) – (9).

$$K_A = \frac{C_X - [RX] - \frac{[RX]}{K_R[R]}}{\left(C_A - C_X + [RX] + \frac{[RX]}{K_R[R]}\right)\frac{[RX]}{K_R[R]}} \qquad (13)$$

Three data points taken with different amounts of titrant provide three versions of equation (13) with different sets of concentration parameters. These equations can be arranged into three pairs of equations, where solution of each pair will provide $K_A$ and $K_R$. The most convenient way of solving this system is to plot $K_A(K_R)$ for each data point as shown in Fig S3-1. Each intersection of two plots is a graphic solution of one of the aforementioned pairs of equations. Point of closest approach of all three plots (determined as the point of lowest standard deviation between data points) is then found which signifies that for the respective $K_R$ all data points are in best agreement. The x-value of this point is then taken as the system-specific $K_R$.

It is necessary to note that $K_R$ obtained from the $K_A(K_R)$ plot feeds into the calculation of $\delta_{RX}$, and the new value of $\delta_{RX}$ feeds back into the determination of $K_R$. In practice this loop leads to stable values of $\delta_{RX}$ and $K_R$ after a small number of iterations. Prior to doing the simultaneous determination of $K_R$ and $K_A$ an initial value of $\delta_{RX}$ can be calculated using a reasonable estimate of $K_R$ (for example, a value from a separate NMR titration of the reference compound).

Finally, a mean value of $K_A$ is calculated from the three data points using $K_R$ and $\delta_{RX}$ determined as above. Data points can be omitted from inclusion into the mean if they have a high uncertainty.

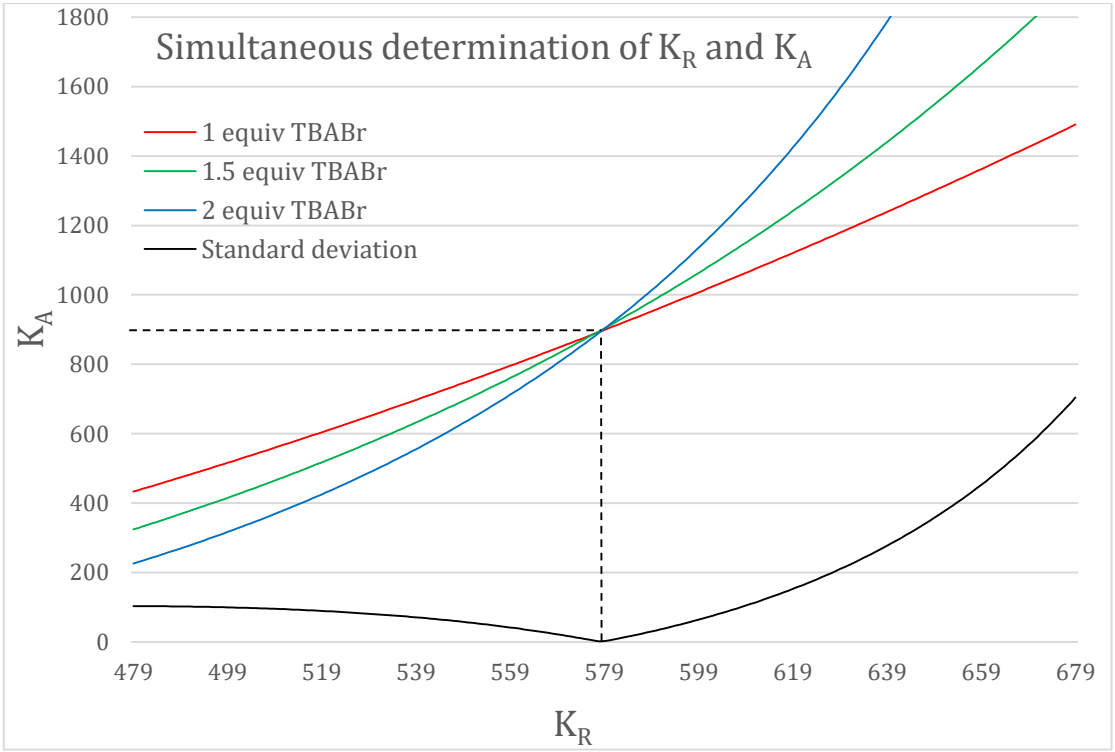



**Fig S3-1** $K_A(K_R)$ plot for a host-host competition experiment with **2b** as test compound and **2a** as reference, titrated with TBABr. Lowest standard deviation of data points is for $K_R$ = 579 $M^{-1}$. At this $K_R$, the $K_A$ values for the three data points are: 899 $M^{-1}$ (1 eq), 904 $M^{-1}$ (1.5 eq), 903 $M^{-1}$ (2 eq) which gives an average $K_A$ = 902 $M^{-1}$.

### S3-3 Uncertainty analysis

Uncertainties of $K_A$ values were estimated by assuming certain errors of sample preparation and propagating them through equations (3) – (9). Errors were not propagated onto $\delta_{RX}$ for simplicity.

Assumptions:

- Relative uncertainty of a weighing: $\xi_1$ = 0.004 (weighing 5 mg with ±0.02 mg accuracy)
- Relative uncertainty of solvent volume measurement: $\xi_2$ = 0.005 (dispensing 1 ml with ±5 µl accuracy); this applies to addition of solvent to weighings of test compound, reference and titrant as well as to the transfer of test compound solution into NMR tube.
- Uncertainties in volume of reference solution and titrant added to the sample are neglected as relatively dilute (0.0015-0.015 M) solutions are added via a precision microsyringe, making these additions highly accurate.

- Uncertainty in chemical shift measurement is neglected as well; all spectra are referenced to residual solvent peak to ensure the accuracy of observed chemical shifts.

Error propagation was done as follows:

$\Delta Y$ absolute uncertainty of value Y

$\frac{\Delta Y}{Y}$ relative uncertainty of value Y

$$\frac{\Delta C_A}{C_A} = \sqrt{{\xi_1}^2 + {\xi_2}^2} \quad (14)$$

$$\frac{\Delta[R]}{[R]} = \frac{\Delta C_X}{C_X} = \frac{\Delta C_R}{C_R} = \sqrt{{\xi_1}^2 + 2{\xi_2}^2} \quad (15)$$

$$\Delta[RX] = \sqrt{{\Delta C_R}^2 + \Delta[R]^2} \quad (16)$$

$$\frac{\Delta[X]}{[X]} = \sqrt{\left(\frac{\Delta[R]}{[R]}\right)^2 + \left(\frac{\Delta[RX]}{[RX]}\right)^2} \quad (17)$$

$$\Delta[AX] = \sqrt{{\Delta C_X}^2 + \Delta[X]^2 + \Delta[RX]^2} \quad (18)$$

$$\Delta[A] = \sqrt{{\Delta C_A}^2 + \Delta[AX]^2} \quad (19)$$

$$\Delta K_A = K_A \sqrt{\left(\frac{\Delta[AX]}{[AX]}\right)^2 + \left(\frac{\Delta[A]}{[A]}\right)^2 + \left(\frac{\Delta[X]}{[X]}\right)^2} \quad (20)$$

## S4. Luminescence spectroscopy

Luminescence titrations were performed using a HORIBA Fluorolog, and the data was processed using the FluorEssence software. A cuvette was initially loaded with 2.5 ml of 1 µM solution of XB receptor **3b** or **4b**. The sample was then titrated with 0.05 M solution of TBABr containing 1 µM of the respective receptor (to keep the receptor concentration constant throughout the titration). Receptor **3b** was studied in $CHCl_3$ and **4b** in 1:1 $CHCl_3$/acetone. An excitation wavelength of $\lambda_{ex}$ = 350 nm was used for both receptors **3b** and **4b**.

## S5. X-Ray crystallography

Single crystals of compound **3b·NaI** were grown by combining **3b** and excess NaI in 6:4 $CHCl_3$/acetone. Crystal growth was initiated by vapour diffusion of acetone into the resulting supersaturated solution of **3b·NaI**. Diffraction data were collected at 100(2) K using a custom-built Crystal Logic diffractometer with synchrotron radiation ($\lambda$ = 0.6889 Å) at Diamond Light Source, beamline I19.[7] Unit cell parameter determination and data reduction were carried out using CrysAlisPro.[8]. The structures were solved by charge-flipping using SUPERFLIP[9] and refined by full matrix least squares on $F^2$ using the CRYSTALS[10] suite. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were initially positioned geometrically and their positions and displacement parameters refined using restraints prior to their inclusion in the final model using riding constraints.[11]

The crystals were small and weakly diffracting and, despite the use of synchrotron radiation, the diffraction was still weak and the data which were obtained were of relatively low quality. Where appropriate, restraints to bond lengths and angles were therefore applied to ensure a physically reasonable model, and thermal and vibrational restraints were applied to maintain sensible displacement ellipsoids. Enlarged displacement ellipsoids suggested the presence of disorder in the non-coordinating acetone solvent molecules; however, attempts to model this disorder using two sites did not produce a satisfactory model. An area of residual electron density, presumably arising from diffuse disordered solvent molecules, was also present and since this electron density could not be modelled sensibly it was included in refinement by treating the discrete Fourier transform of the void region as contributions to the calculated structure factors with PLATON/SQUEEZE[12, 13] (125 Å containing 51 electrons). Full refinement details are given in the CIF. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 1529410).

## S6. References


1 B.-Y. Lee, S. R. Park, H. B. Jeon and K. S. Kim, *Tetrahedron Lett.*, 2006, **47**, 5105-5109.
2 K. V. Kutonova, M. E. Trusova, P. S. Postnikov, V. D. Filimonov and J. Parello, *Synthesis-Stuttgart*, 2013, **45**, 2706-2710.
3 D. Lu, J. Lei, Z. Tian, L. Wang and J. Zhang, *Dyes and Pigments*, 2012, **94**, 239-246.
4 R. M. Meudtner and S. Hecht, *Angewandte Chemie-International Edition*, 2008, **47**, 4926-4930.
5 M. J. Hynes, *Journal of the Chemical Society-Dalton Transactions*, 1993, 311-312.
6 J. M. Daniel, S. D. Friess, S. Rajagopalan, S. Wendt and R. Zenobi, *International Journal of Mass Spectrometry*, 2002, **216**, 1-27.
7 H. Nowell, S. A. Barnett, K. E. Christensen, S. J. Teat and D. R. Allan, *Journal of Synchrotron Radiation*, 2012, **19**, 435-441.
8 *Journal*.
9 L. Palatinus and G. Chapuis, *J. Appl. Crystallogr.*, 2007, **40**, 786-790.
10 P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl. Crystallogr.*, 2003, **36**, 1487-1487.
11 R. I. Cooper, A. L. Thompson and D. J. Watkin, *J. Appl. Crystallogr.*, 2010, **43**, 1100-1107.
12 P. Vandersluis and A. L. Spek, *Acta Crystallographica Section A*, 1990, **46**, 194-201.
13 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7-13.