Electronic Supplementary Information (ESI) for

Lithium halide ion-pair recognition with halogen bonding and chalcogen bonding heteroditopic macrocycles

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S1 Synthesis and Characterisation

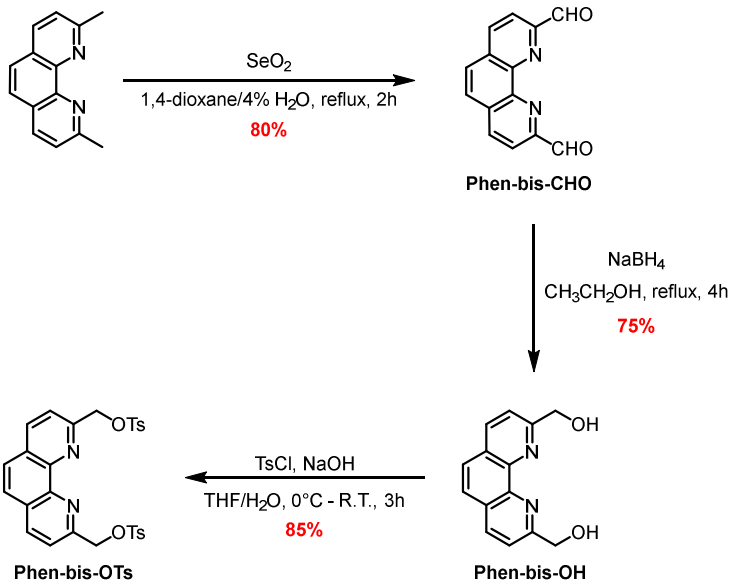
General Information

All solvents and reagents were purchased from commercial suppliers and used as received unless otherwise stated. Dry solvents were obtained by purging with nitrogen and then passing through an MBraun MPSP-800 column. H_2O was de-ionized and micro filtered using a Milli-Q ® Millipore machine. Column chromatography was carried out on Merck® silica gel 60 under a positive pressure of nitrogen. Routine NMR spectra were recorded on either a Varian Mercury 300, a Bruker AVIII 400 or a Bruker AVIII 500 spectrometer with ^{1}H NMR titrations recorded on a Bruker AVIII 500 spectrometer. TBA salts were stored in a vacuum desiccator containing phosphorus pentoxide prior to use. Where mixtures of solvents were used, ratios are reported by volume. Chemical shifts are quoted in parts per million relative to the residual solvent peak. Mass spectra were recorded on a Bruker µTOF spectrometer. Triethylamine was distilled from and stored over potassium hydroxide.

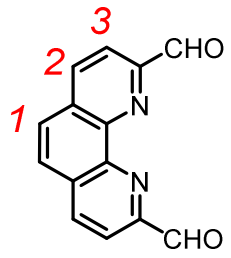
Tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine (TBTA)[1] and MOM-protected azide precursor (**4**)[2] were prepared according to literature procedures.

Synthetic Procedures and Characterisation

Synthesis of phenanthroline precursor



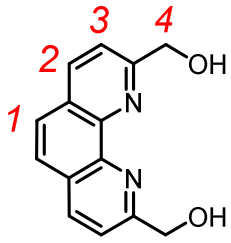
Scheme S1. Synthesis of phenanthroline precursor **Phen-bis-OTs**.



Phen-bis-CHO

Phen-bis-CHO was prepared according to a modified procedure.[3] Selenium dioxide (5.62 g, 50.6 mmol, 2.11 equiv) was added to a mixture of 1,4-dioxane (200 mL) and H_2O (10 mL) and heated to reflux to give a black solution. A solution of neocuproine (5 g, 24.0 mmol, 1 equiv) in 1,4-dioxane (50 mL) was then added dropwise over 2 hours and the reaction mixture was heated for 2 hours. The mixture was then filtered while hot and washed with warm 1,4-dioxane (20 mL). The orange filtrate was allowed to cool overnight and the yellow precipitate formed was filtered off, washed with Et_2O (100 mL) and allowed to air-dry for 1 day. The product was used in the next step without further purification.

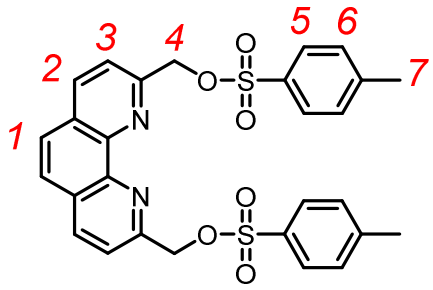
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 10.57 (s, 2H, CHO), 8.52 (d, J = 8.2, 2H, H_3), 8.39 (d, J = 8.2 Hz, 2H, H_2), 8.05 (s, 2H, H_1).



Phen-bis-OH

Phen-bis-OH was prepared according to a modified procedure.[3] **Phen-bis-CHO** (1.82 g, 7.70 mmol, 1 equiv) was suspended in EtOH (180 mL). $NaBH_4$ (729 mg, 19.3 mmol, 2.5 equiv) was then added and the reaction mixture was heated at reflux for 4 hours. The solvent was removed *in vacuo* and the product was further purified by recrystallization in H_2O to give the product as pale brown solid (1.39 g, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.21 (d, J = 8.2 Hz, 2H, H_3), 7.76 (s, 2H, H_1), 7.60 (d, J = 8.2 Hz, 2H, H_2), 5.26 (s, 4H, H_4), 5.10 (brs, 2H, OH).

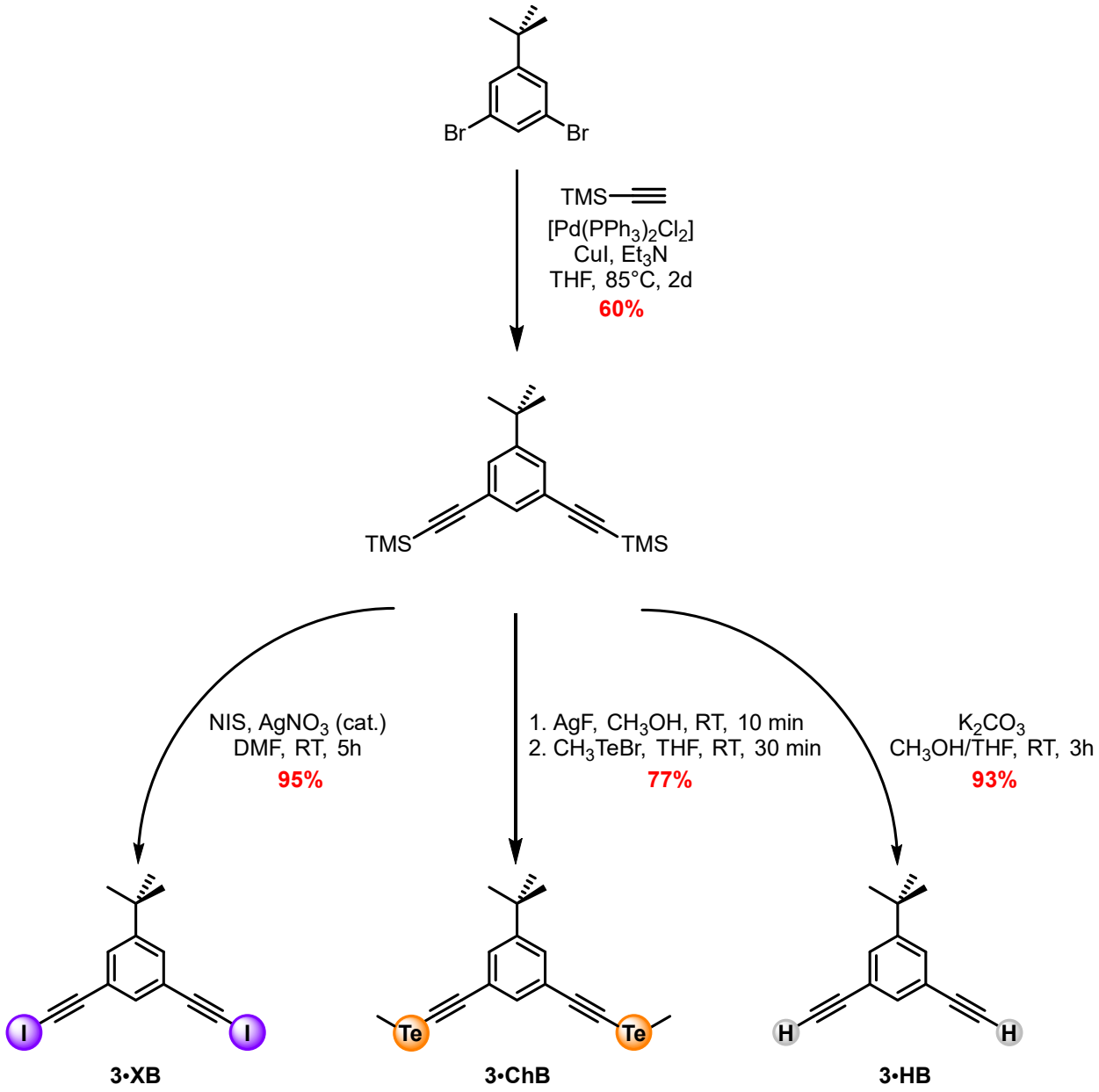


Phen-bis-OTs

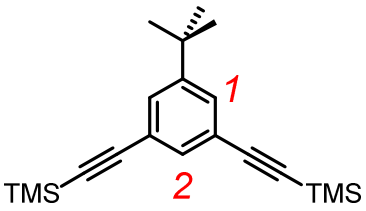
According to literature procedure,[4] **Phen-bis-OH** (1 g, 4.16 mmol, 1 equiv) was dissolved in THF (6 mL). An aqueous solution of NaOH (0.50 g, 12.5 mmol, 3 equiv) in H_2O (5 mL) was added in one portion. The mixture was then cooled to 0 ˚C and a solution of TsCl (1.98 g, 10.4 mmol, 2.5 equiv) in THF (30 mL) was added over 2 hours. The reaction mixture was then allowed to warm back to room temperature and stir for a further 1 hour. Iced water (20 mL) was then added to quench the reaction and the product was extracted with CH_2Cl_2 (30 mL x 3). The combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated on rotary evaporator. Further purification with silica gel column chromatography (20–80% EtOAc in *n*-hexane) gave the product as white solid (1.93 g, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.30 (d, J = 8.2 Hz, 2H, H_3), 7.87 (d, J = 8.3 Hz, 4H, H_5), 7.86 (d, J = 8.2 Hz, 2H, H_2), 7.81 (s, 2H, H_1), 7.34 (d, J = 8.3 Hz, 4H, H_6), 5.51 (s, 4H, H_4), 2.43 (s, 6H, H_7)

Synthesis of bis-alkyne precursors

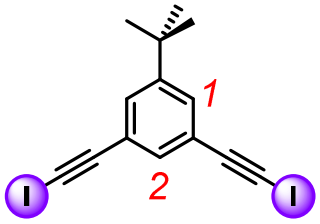


Scheme S2. Synthesis of bis-alkyne precursors **3•XB**, **3•ChB** and **3•HB**.



1,3-Dibromo-5-*tert*-butylbenzene (1 g, 3.42 mmol, 1 equiv), $Pd(PPh_3)_2Cl_2$ (120 mg, 0.17 mmol, 5 mol%) and CuI (65 mg, 0.34 mmol, 10 mol%) were dissolved in dry THF (5 mL) in a sealed flask. Distilled Et_3N (15 mL) was added and the content was then degassed by purging with N_2 for 10 minutes. Ethynyltrimethylsilane (1.21 mL, 8.56 mmol, 2.5 equiv) was added and the mixture was degassed for 2 minutes. The reaction mixture was then heated at 85°C overnight. A second portion of ethynyltrimethylsilane (1.21 mL, 8.56 mmol, 2.5 equiv) was added and the mixture was heated at 85°C overnight. The resulting black mixture was allowed to cool down to room temperature and filtered through a pad of celite while eluting with EtOAc. The volatile was removed *in vacuo* and the crude solid was redissolved in CH_2Cl_2 (50 mL) and washed with H_2O (50 mL) and brine (50 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated on rotary evaporator. Further purification with silica gel column chromatography (neat *n*-hexane) gave the product as yellow oil (0.67 g, 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.42 (m, 3H, $H_{1,2}$), 1.29 (s, 9H, *tert*-butyl H), 0.24 (s, 18H, TMS H)



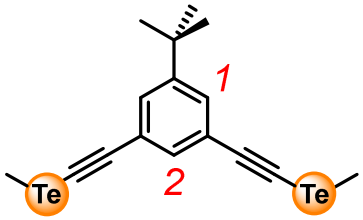
3•XB

1,3-bis[(trimethylsilyl)ethynyl]-5-*tert*butylbenzene (770 mg, 2.36 mmol, 1 equiv) was dissolved in dry DMF (15 mL). NIS (1.33 g, 5.89 mmol, 2.5 equiv) and $AgNO_3$ (60 mg, 0.35 mmol, 0.15 equiv) were added to the solution and the reaction mixture was stirred at room temperature in dark for 6 hours. H_2O (100 mL) was added and the product was extracted with Et_2O (30 mL x 3), washed with H_2O (50 mL) and brine (50 mL). Further purification with silica gel column chromatography (neat 40-60°C petroleum ether) gave the product as off-white solid (954 mg, 93%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.50 (t, J = 1.6 Hz, 1H, H_2), 7.37 (d, J = 1.6 Hz, 2H, H_1), 1.54 (s, 9H, *tert*-butyl H)

^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 151.66, 133.23, 130.14, 123.35, 93.80, 31.14

HRMS (EI) m/z: 433.9028 ($[M\bullet]^+$, $C_{14}H_{12}I_2$ requires 433.9023)



3•ChB

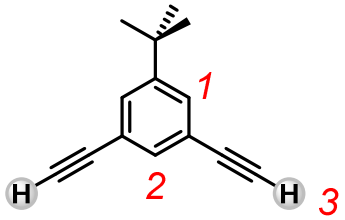
1,3-bis[(trimethylsilyl)ethynyl]-5-*tert*butylbenzene (200 mg, 0.61 mmol, 1 equiv) was dissolved in CH_3OH (3 mL) and a suspension of AgF (159 mg, 1.25 mmol, 2.05 equiv) in CH_3OH (12 mL) was added dropwise. The mixture was stirred for 10 minutes at room temperature to give the silver acetylide, to which dry THF (12 mL) was added to form a suspension. In a separate flask, dimethyl ditelluride (175 mg, 0.61 mmol, 1 equiv) was added to dry THF (4 mL) and cooled to 0°C. 1M Br_2 in CH_2Cl_2 (0.61 mL) was then added at 0°C to generate CH_3TeBr. After warming to room temperature, CH_3TeBr solution was added to silver acetylide suspension slowly and the reaction mixture was stirred for 30 minutes. The crude was then filtered through celite, and solvent was removed *in vacuo*. Product was purified by silica gel column chromatography (10% CH_2Cl_2 in *n*-hexane) to give the product as yellow oil (219 mg, 77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.35 (d, J = 1.5 Hz, 2H, H_1), 7.29 (t, J = 1.5 Hz, 1H, H_2), 2.21 (s, 6H, $TeCH_3$), 1.28 (s, 9H, *tert*-butyl H)

^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm): 151.33, 132.19, 128.98, 123.34, 110.30, 44.81, 34.73, 31.09, -14.42

^{125}Te NMR (126 MHz, $CDCl_3$) δ(ppm): 165.27

HRMS (MALDI-TOF) m/z: 495.942 ($[M\bullet]^+$, $C_{16}H_{18}Te_2$ requires 465.950)

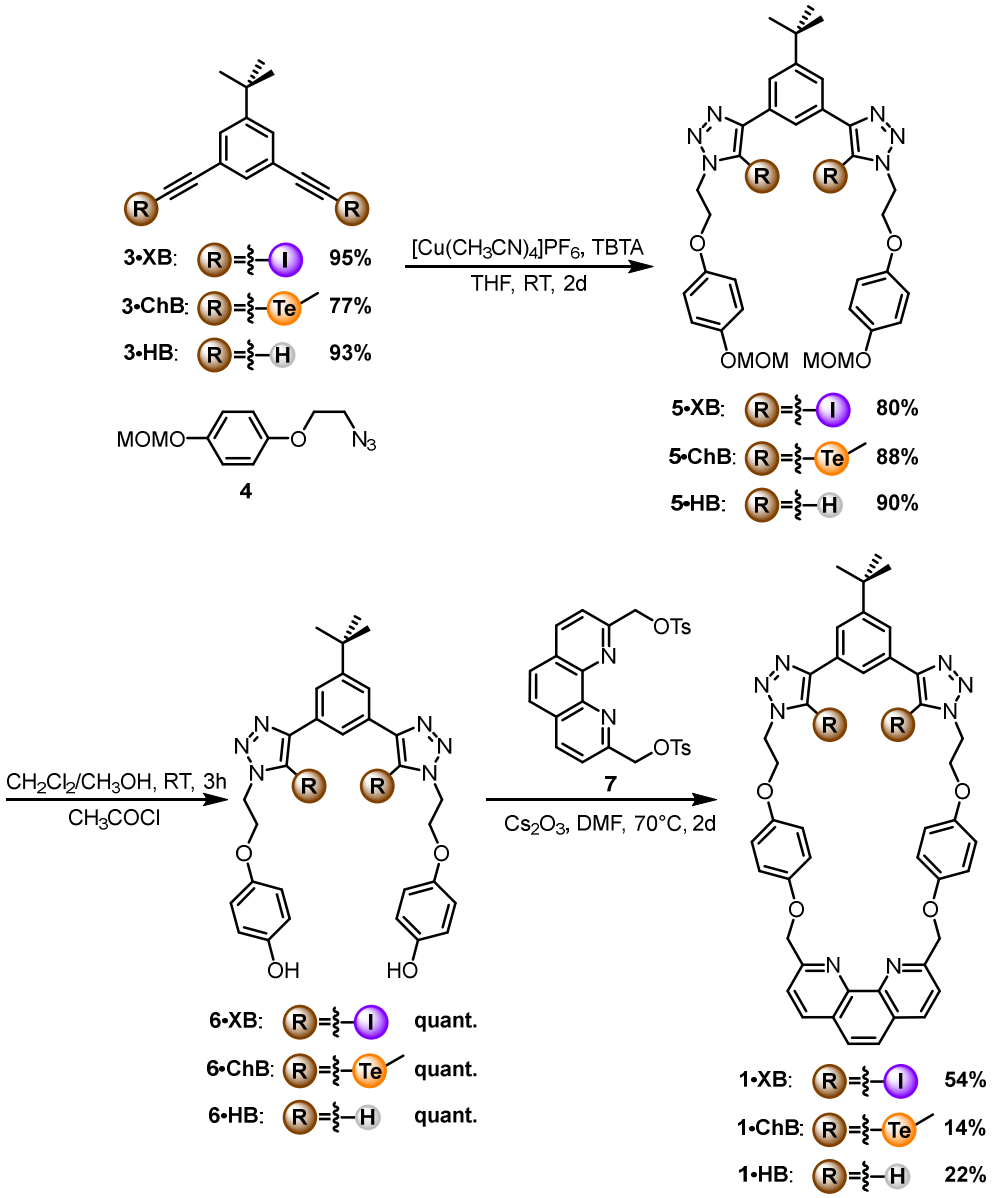


3•HB

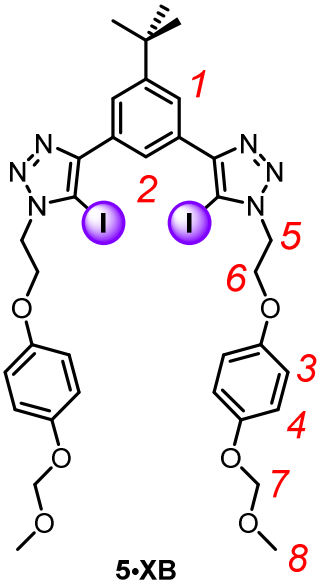
3,5-Bis(trimethylsilylethynyl)-1-(*tert*-butyl)benzene (**2**) (500 mg, 1.53 mmol, 1 equiv) was dissolved in a mixture of CH_3OH (15 mL) and THF (2 mL). Anhydrous K_2CO_3 (423 mg, 3.06 mmol, 2 equiv) was added and the reaction mixture was stirred at room temperature for 3 hours. The crude was concentrated on rotary evaporator to dryness and then redissolved in $CHCl_3$ (50 mL) and washed with H_2O (20 mL) and brine (20 mL). The combined organic layer was dried over anhydrous $MgSO_4$, filtered and the organic solvent was removed *in vacuo* to give bis-protoalkyne **3•HB** as yellow oil (0.266 g, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.50 (d, J = 1.3 Hz, 2H, H_1), 7.44 (t, J = 1.3 Hz, 1H, H_2), 3.06 (s, 2H, H_3), 1.30 (s, 9H, *tert*-butyl H)

Synthesis of heteroditopic macrocycles



Scheme S3. Synthesis of heteroditopic macrocycles **1•XB**, **1•ChB** and **1•HB**.



5•XB

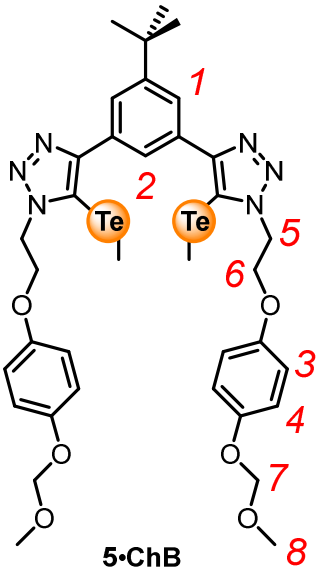
General Procedure for CuAAC Click Reaction

$[Cu(CH_3CN)_4]PF_6$ (52 mg, 0.14 mmol, 0.2 equiv) and TBTA (74 mg, 0.14 mmol, 0.2 equiv) were added to dry and degassed THF (2 mL) and stirred at room temperature for 15 minutes until all solid dissolved. A solution of azide **4** (386 mg, 1.73 mmol, 2.5 equiv) in dry THF (1.5 mL) was added, followed by a solution of bis-iodoalkyne **3•XB** (300 mg, 0.69 mmol, 1 equiv) in dry THF (1.5 mL). The resulting green solution was stirred at room temperature in dark for 2 days. The crude was then diluted with $CHCl_3$ (30 mL) and washed with basic EDTA (30 mL x 2). The combined organic layer was washed with brine (30 mL) and dried over anhydrous $MgSO_4$, filtered and concentrated on rotary evaporator. Further purification with silica gel column chromatography (10% EtOAc in CH_2Cl_2) gave the product **5•XB** as white solid (488 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.32 (t, J = 1.6 Hz, 1H, H_2), 8.02 (d, J = 1.6 Hz, 2H, H_1), 6.96 (d, J = 9.0 Hz, 4H, H_3), 6.82 (d, J = 9.0 Hz, 4H, H_4), 5.09 (s, 4H, H_7), 4.84 (t, J = 5.8 Hz, 4H, H_5), 4.44 (t, J = 5.8 Hz, 4H, H_6), 3.45 (s, 6H, H_8), 1.43 (s, 9H, *tert*-butyl H)

^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 153.13, 152.06, 152.02, 150.16, 130.28, 125.38, 123.75, 117.73, 115.73, 95.30, 78.07, 66.88, 56.01, 50.01, 35.34, 31.50

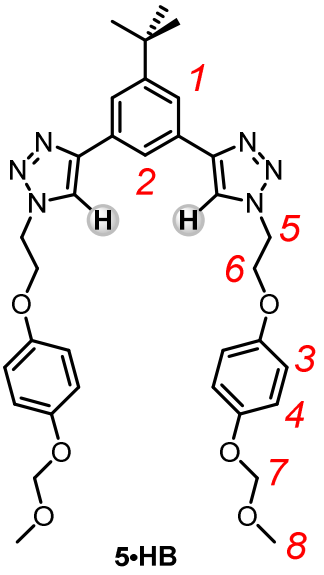
HRMS (ESI +ve) m/z: 881.1006 ($[M+H]^+$, $C_{34}H_{39}I_2N_6O_6$ requires 881.1015)



5•ChB

Following general procedure for CuAAC click reaction between azide **4** (126 mg, 0.56 mmol, 2.5 equiv) and bis-telluroalkyne **3•ChB** (105 mg, 0.23 mmol, 1 equiv), the product was purified by silica gel column chromatography (20% EtOAc in CH_2Cl_2) to give **5•ChB** as yellow solid (182 mg, 88%). Due to instability of **5•ChB**, only the ^{1}H NMR spectrum was recorded and the compound was used immediately in the next step without any further characterisation.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.47 (t, J = 1.6 Hz, 1H, H_2), 8.11 (d, J = 1.6 Hz, 2H, H_1), 6.95 (d, J = 9.0Hz, 4H, H_3), 6.80 (d, J = 9.0 Hz, 4H, H_4), 5.08 (s, 4H, H_7), 5.08 (t, J = 5.4 Hz, 4H, H_3) 4.39 (t, J = 5.4 Hz, 4H, H_4), 3.45 (s, 6H, H_8), 1.95 (s, 6H, $TeCH_3$ H), 1.43 (s, 9H, *tert*-butyl H).



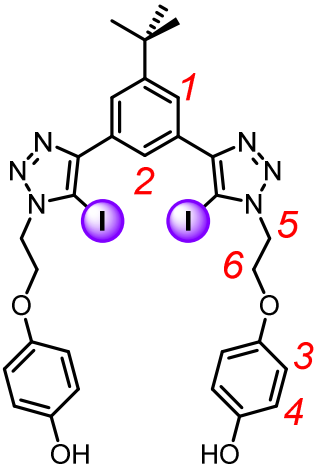
5•HB

Following general procedure for CuAAC click reaction between azide **4** (396 mg, 1.78 mmol, 2.5 equiv) and bis-protoalkyne **3•HB** (110 mg, 0.71 mmol, 1 equiv), the product was purified by silica gel column chromatography (10-20% EtOAc in CH_2Cl_2) to give **5•ChB** as white foam (342 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.03 (2H, s, triazole H), 8.02 (1H, t, J = 1.6 Hz, H_2), 7.89 (2H, d, J=1.6 Hz, H_1), 6.97 (4H, d, J=9.0 Hz, H_3), 6.83 (4H, d, J=9.0 Hz, H_4), 5.09 (4H, s, H_7), 4.80 (4H, t, J=5.0 Hz, H_5), 4.37 (4H, t, J=5.0 Hz, H_6), 3.45 (6H, s, H_8), 1.41 (9H, s, *tert*-butyl H)

^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 153.07, 152.72, 152.21, 148.17, 130.96, 122.92, 121.18, 120.69, 117.81, 115.85, 95.27, 67.36, 56.03, 50.15, 35.13, 31.50

HRMS (ESI +ve) m/z: 629.3082 ($[M+H]^+$, $C_{34}H_{41}N_6O_6$ requires 629.3082)



6•XB

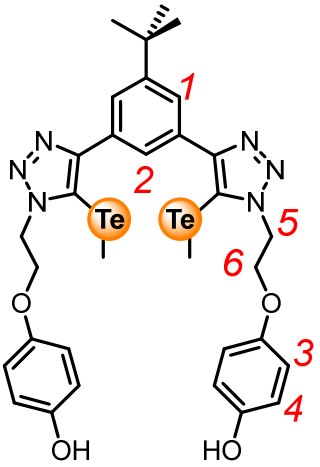
General Procedure for MOM-deprotection

Acetyl chloride (1.07 mL, 15.1 mmol, 30 equiv) was added to CH_3OH (5 mL) slowly at 0 ˚C. The solution was stirred at 0 ˚C for 5 minutes and stirred at room temperature for a further 15 minutes. A solution of **5•XB** (442 mg, 0.50 mmol, 1 equiv) in CH_2Cl_2 (5 mL) was added to the acidic methanol solution slowly and the reaction mixture was stirred at room temperature for 2 hours. After the reaction was complete (monitored by TLC 10% EtOAc in CH_2Cl_2), the crude mixture was concentrated on rotary evaporator and the product was dried on high vacuum for 1 day to yield the product **6•XB** as white powder in excellent purity (286 mg, quant.).

^{1}H NMR (400 MHz, d_6-acetone) δ (ppm): 8.45 (t, J = 1.6 Hz, 1H, H_2), 8.09 (d, J = 1.6 Hz, 2H, H_1), 6.81 (d, J = 9.0 Hz, 2H, H_3), 6.74 (d, J = 9.0 Hz, 2H, H_4), 4.91 (t, J = 5.4 Hz, 2H, H_5), 4.50 (t, J = 5.4 Hz, 2H, H_6), 2.85 (brs, 2H, hydroquinone OH), 1.45 (s, 9H, *tert*-butyl H)

^{13}C NMR (126 MHz, d_6-acetone) δ (ppm): 154.24, 152.65, 152.45, 150.09, 131.94, 125.28, 124.16, 116.65, 116.60, 79.99, 67.92, 50.94, 35.77, 31.66

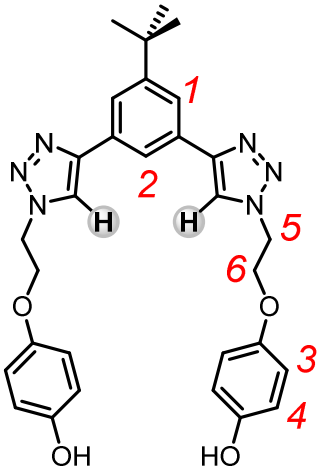
HRMS (ESI +ve) m/z: 793.0484 ($[M+H]^+$, $C_{30}H_{31}N_6O_4I_2$ requires 793.0491)



6•ChB

Following general procedure for MOM-deprotection of **5•ChB** (182 mg, 0.20 mmol, 1 equiv), the product bis-phenol **6•ChB** was isolated as yellow foam (164 mg, quant.). Due to instability of **6•ChB**, only the ^{1}H NMR spectrum was recorded and the compound was used immediately in the next step without any further characterisation.

^{1}H NMR (400 MHz, CD_3OD) δ (ppm): 8.16 (t, J = 1.6 Hz, 1H, H_2), 8.12 (d, J = 1.6 Hz, 2H, H_1), 6.73 (d, J = 8.7 Hz, 4H, H_3), 6.64 (d, J = 8.7 Hz, 4H, H_4), 5.16 (t, J = 4.9 Hz, 4H, H_5), 4.46 (t, J = 4.9 Hz, 4H, H_6), 1.97 (s, 6H, $TeCH_3$ H), 1.43 (s, 9H, *tert*-butyl H)



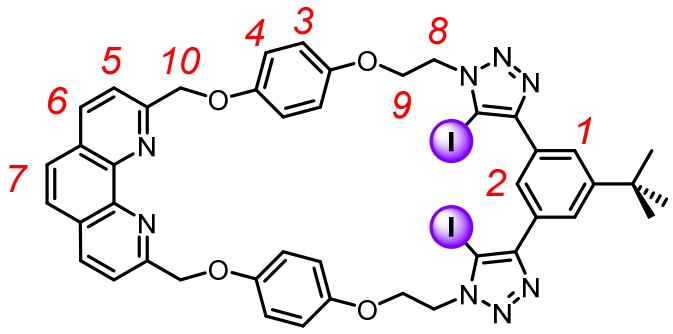
6•HB

Following general procedure for MOM-deprotection of **5•HB** (333 mg, 0.53 mmol, 1 equiv), the product bis-phenol **6•HB** was isolated as white foam (164 mg, quant.).

^{1}H NMR (400 MHz, d_6-acetone) δ(ppm): 8.65 (s, 2H, triazole H), 8.33 (t, J = 1.6 Hz, 1H, H_2), 8.01 (t, J = 1.6Hz, 2H, H_1), 6.83 (d, J = 9.0 Hz, 4H, H_3), 6.74 (d, J = 9.0 Hz, 4H, H_4), 4.89 (t, J = 5.1 Hz, 4H, H_5), 4.45 (t, J = 5.1 Hz, 4H, H_6), 3.30 (brs, 1H, hydroquinone OH), 1.41 (s, 9H, *tert*-butyl H)

^{13}C NMR (126 MHz, d_6-acetone) δ(ppm): 153.32, 152.73, 152.44, 147.57, 131.86, 123.27, 122.98, 121.18, 116.83, 116.61, 68.05, 51.02, 35.58, 31.59

HRMS (ESI +ve) m/z: 541.2554 ($[M+H]^+$, $C_{30}H_{33}N_6O_4$ requires 541.2558)



1•XB

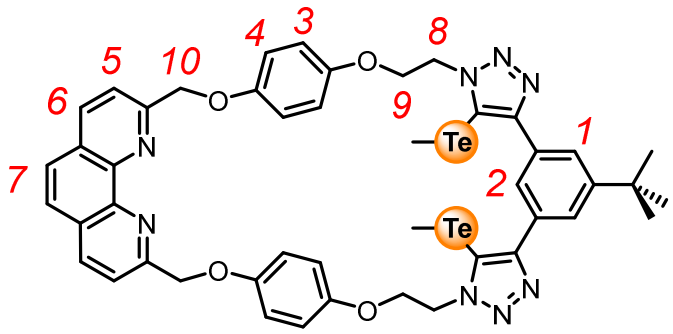
General Procedure for Macrocyclisation

Bis-phenol **5•XB** (398 mg, 0.50 mmol, 1 equiv.) and **Phen-bis-OTs** (276 mg, 0.50 mmol, 1 equiv.) were dissolved in dry DMF (502 mL) and Cs_2CO_3 (655 mg, 2.01 mmol, 4 equiv.) was added. The reaction mixture was heated at 70°C in dark under N_2 for 2 days. The solvent was removed *in vacuo* and the crude solid was redissolved in $CHCl_3$ (50 mL) and washed with H_2O (50 mL) and brine (50 mL). The organic solvent was dried with excess anhydrous $MgSO_4$, filtered and concentrated on rotary evaporator. Purification by iterative repeated silica gel column chromatography (5% CH_3OH in CH_2Cl_2, then 2% CH_3OH in CH_2Cl_2) gave the macrocycle **1•XB** as white powder (269 mg, 54%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.22 (t, J = 1.6 Hz, 1H, H_2), 8.21 (d, J = 8.3 Hz, 2H, H_5), 7.98 (d, J = 1.6 Hz, 2H, H_1), 7.83 (d, J = 8.3 Hz, 2H, H_6), 7.74 (s, 2H, H_7), 6.95 (d, J = 9.1 Hz, 4H, H_3), 6.77 (d, J = 9.1 Hz, 4H, H_4), 5.58 (s, 4H, H_{10}), 4.81 (t, J = 5.5 Hz, 4H, H_8), 4.39 (t, J = 5.5 Hz, 4H, H_9), 1.40 (s, 9H, *tert*-butyl H)

^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 158.61, 153.34, 152.31, 150.25, 145.44, 137.16, 130.17, 128.34, 126.50, 125.57, 123.42, 121.39, 116.45, 116.06, 78.32, 72.81, 67.36, 49.77, 35.29, 31.49, 22.50

HRMS (ESI +ve) m/z: 997.1165 ($[M+H]^+$, $C_{44}H_{39}I_2N_8O_4$ requires 997.1178)



1•ChB

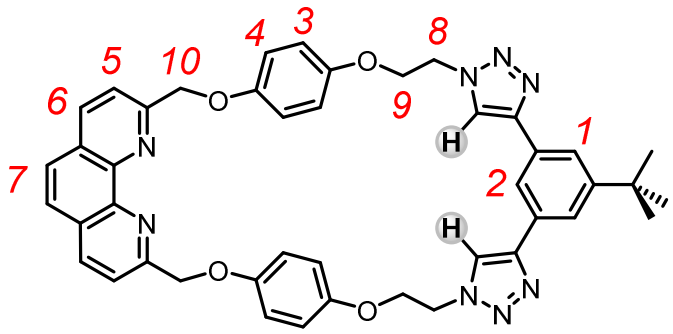
Following general procedure for macrocyclisation between bis-phenol **5•ChB** (164 mg, 0.20 mmol, 1 equiv.) and **Phen-bis-OTs** (109 mg, 0.20 mmol, 1 equiv.), the product was purified by iterative repeated preparative TLC (2% EtOH in CH_2Cl_2) to give the macrocycle **1•ChB** as white powder (45 mg, 22%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.46 (t, J = 1.6 Hz, 1H, H_b), 8.20 (d, J = 8.3 Hz, 2H, H_d), 7.99 (d, J = 1.6 Hz, 2H, H_a), 7.80 (d, J = 8.3 Hz, 2H, H_e), 7.73 (s, 2H, H_f), 6.96 (d, J = 8.6 Hz, 4H, hydroquinone ArH), 6.74 (d, J = 8.6 Hz, 4H, hydroquinone ArH), 5.58 (s, 4H, H_g), 4.95 (t, J = 5.4 Hz, 4H, H_h), 4.34 (t, J = 5.5 Hz, 4H, H_i), 1.90 (s, 6H, H_c), 1.39 (s, 9H, tert-butyl H)

^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 158.60, 153.31, 153.25, 152.39, 151.83, 137.23, 131.36, 128.32, 126.49, 125.55, 124.26, 121.39, 116.52, 115.93, 101.45, 72.60, 67.93, 50.22, 35.21, 31.49, 29.85

^{125}Te NMR (158 MHz, $CDCl_3$) δ (ppm): 113.50

HRMS (ESI +ve) m/z: 1029.1659 ($[M+H]^+$, $C_{46}H_{45}O_4N_8{}^{126}Te^{130}Te$ requires 1029.1654)



1•HB

Following general procedure for macrocyclisation between bis-phenol **5•HB** (286 mg, 0.53 mmol, 1 equiv.) and **Phen-bis-OTs** (291 mg, 0.53 mmol, 1 equiv.), the product was purified by iterative repeated preparative TLC (2% EtOH in CH_2Cl_2) to give the macrocycle **1•HB** as white powder (45 mg, 22%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.16 (d, J = 8.3 Hz, 2H, H_5), 8.02 (s, 2H, Triazole H), 7.91 (d, J = 1.6 Hz, 2H, H_1), 7.81 (t, J = 1.6 Hz, 1H, H_2), 7.77 (d, J = 8.3 Hz, 2H, H_6), 7.69 (s, 2H, H_7), 5.57 (s, 4H, H_{10}), 4.69 (t, J = 4.8 Hz, 4H, H_3), 4.23 (t, J = 4.8 Hz, 4H, H_4), 1.28 (s, 9H, *tert*-butyl H).

^{13}C NMR (126 MHz; $CDCl_3$) δ (ppm): 158.67, 153.36, 152.80, 152.30, 147.96, 145.43, 137.13, 130.84, 128.32, 126.46, 122.87, 121.43, 121.23, 120.51, 116.59, 116.30, 72.61, 67.96, 50.17, 35.10, 31.42.

HRMS (ESI +ve) m/z: 745.3245 ($[M+H]^+$, $C_{44}H_{41}O_4N_8$ requires 745.3237)

S2 Spectral Characterisation of Macrocycles

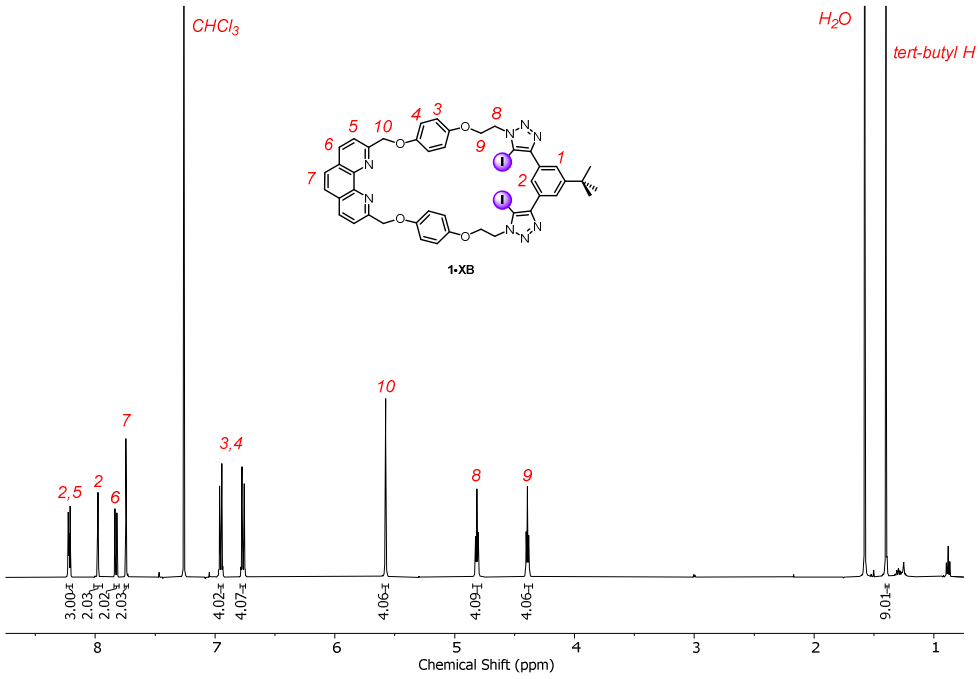


Figure S2-1. ^{1}H NMR spectrum of macrocycle **1•XB** (500 MHz, 298 K, $CDCl_3$).

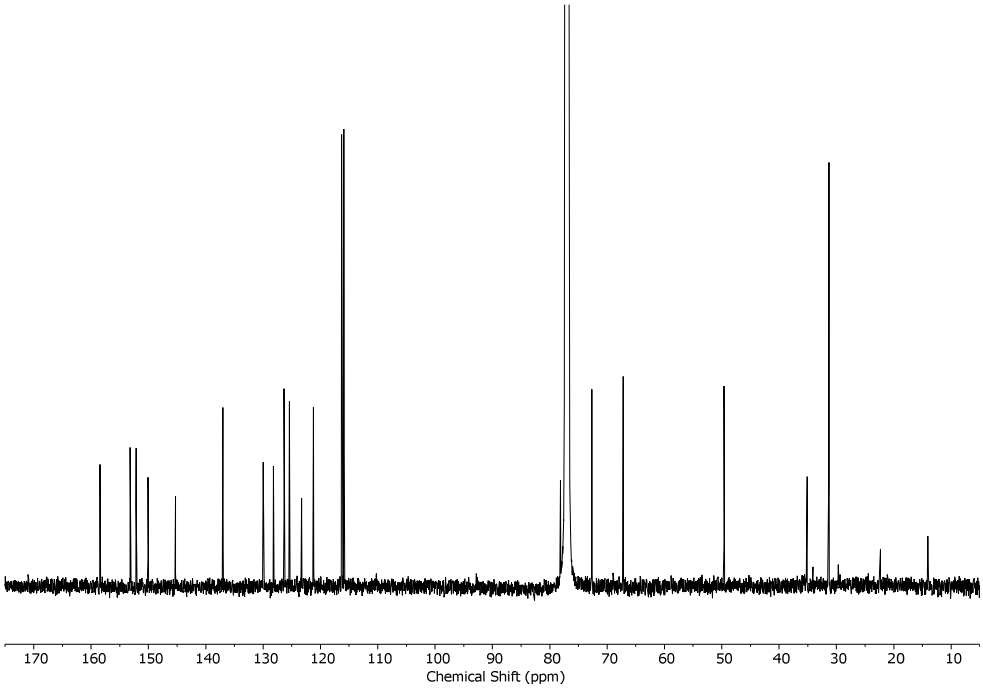


Figure S2-2. ^{13}C NMR spectrum of macrocycle **1•XB** (126 MHz, 298 K, $CDCl_3$).

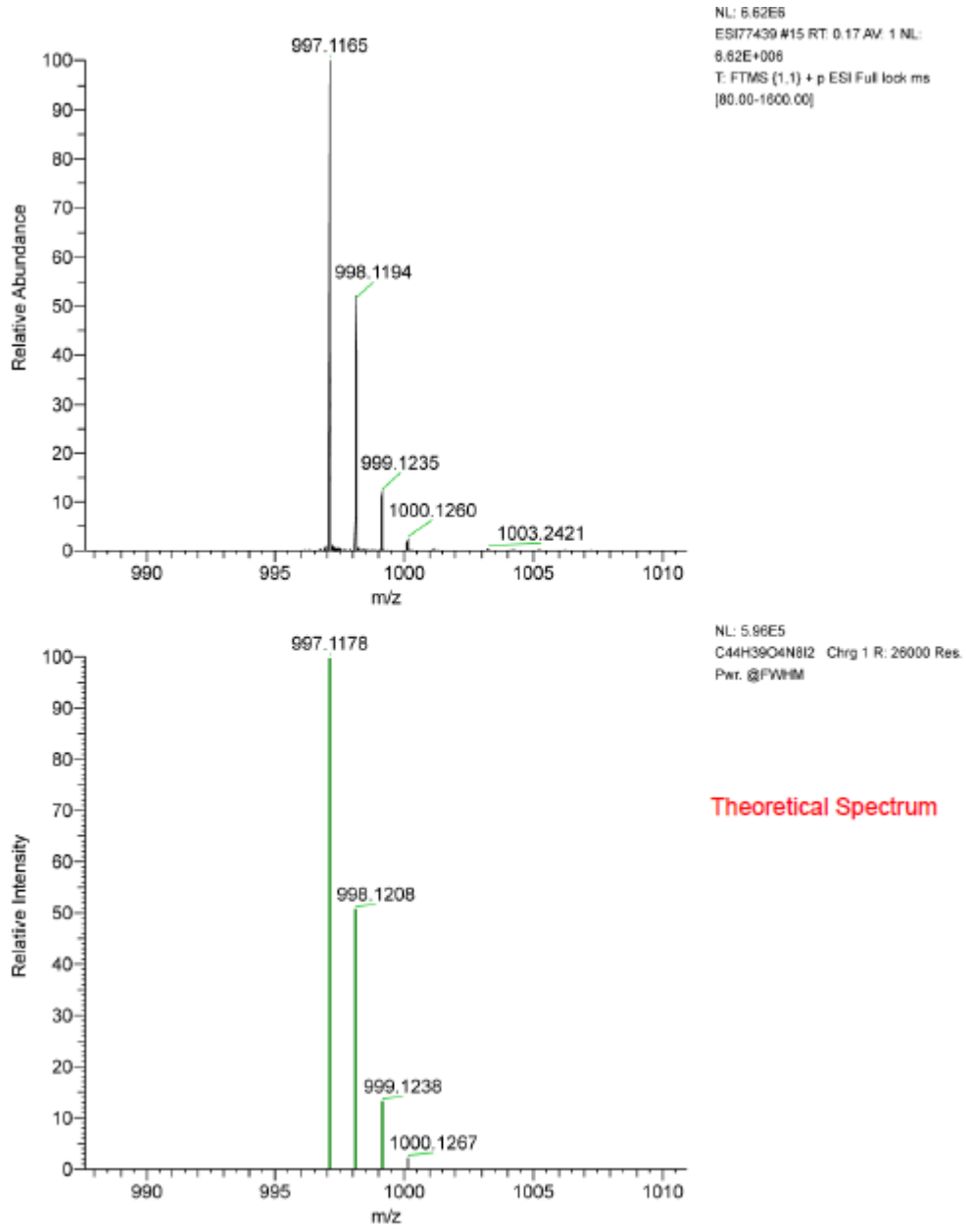


Figure S2-3. High resolution ESI mass spectrum of macrocycle **1•XB** (top) and its theoretical spectrum (bottom).

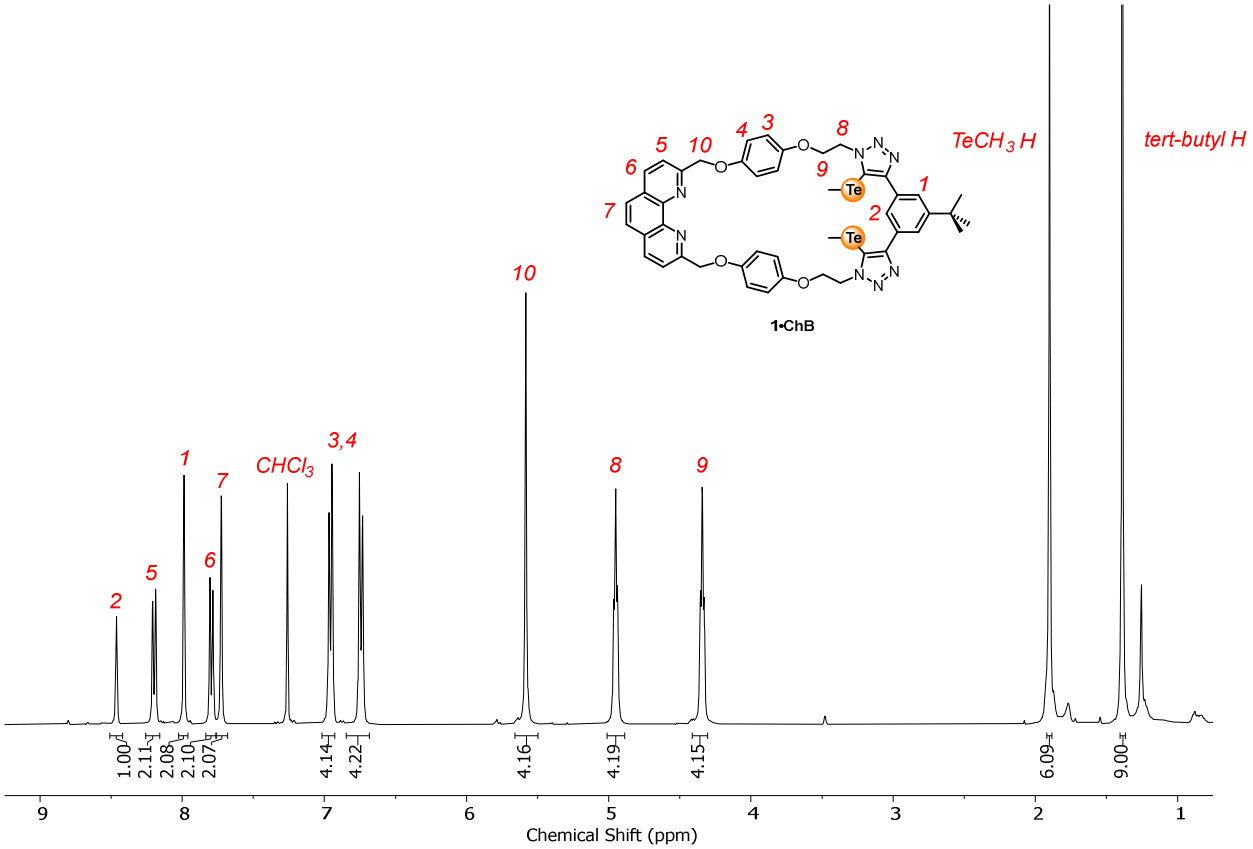


Figure S2-4. ^{1}H NMR spectrum of macrocycle **1•ChB** (500 MHz, 298 K, $CDCl_3$).

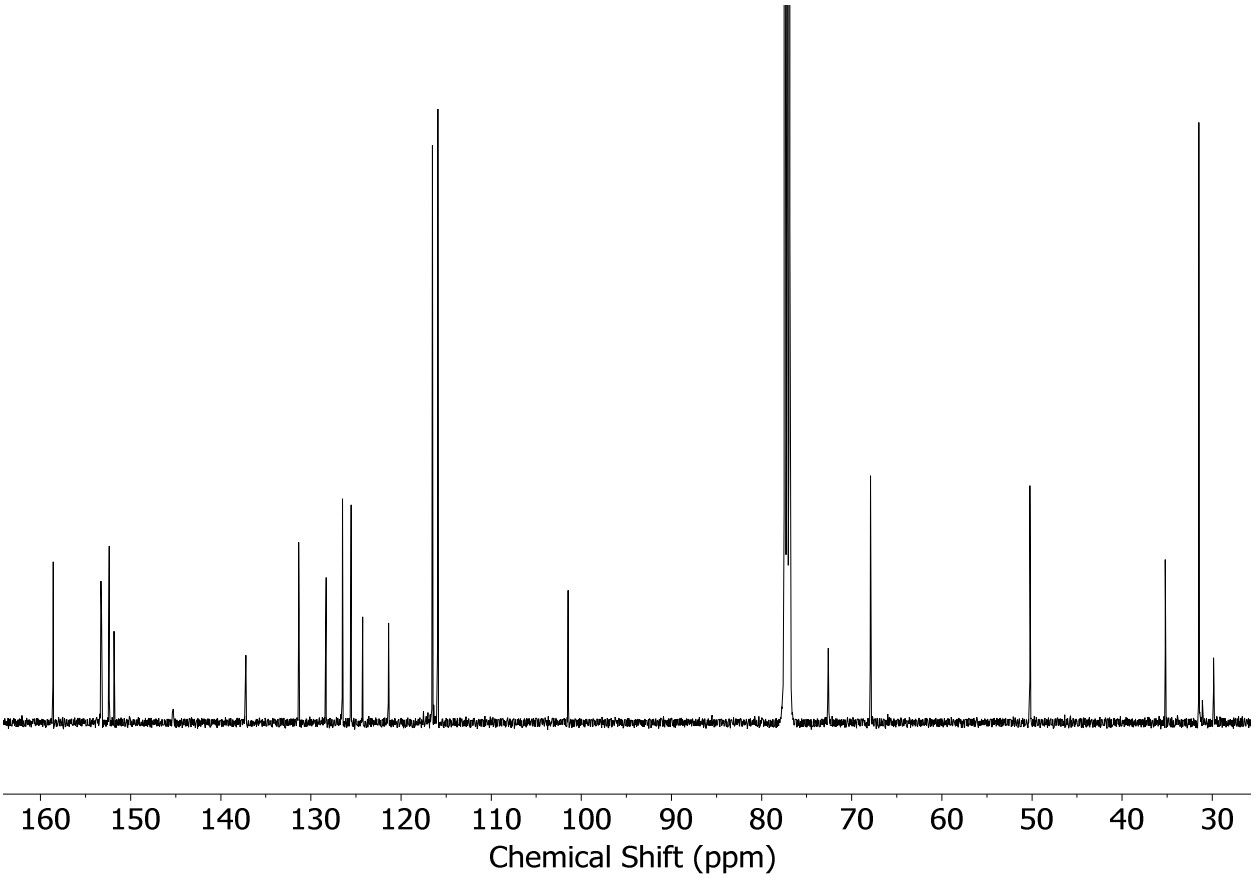


Figure S2-5. ^{13}C NMR spectrum of macrocycle **1•ChB** (126 MHz, 298 K, $CDCl_3$).

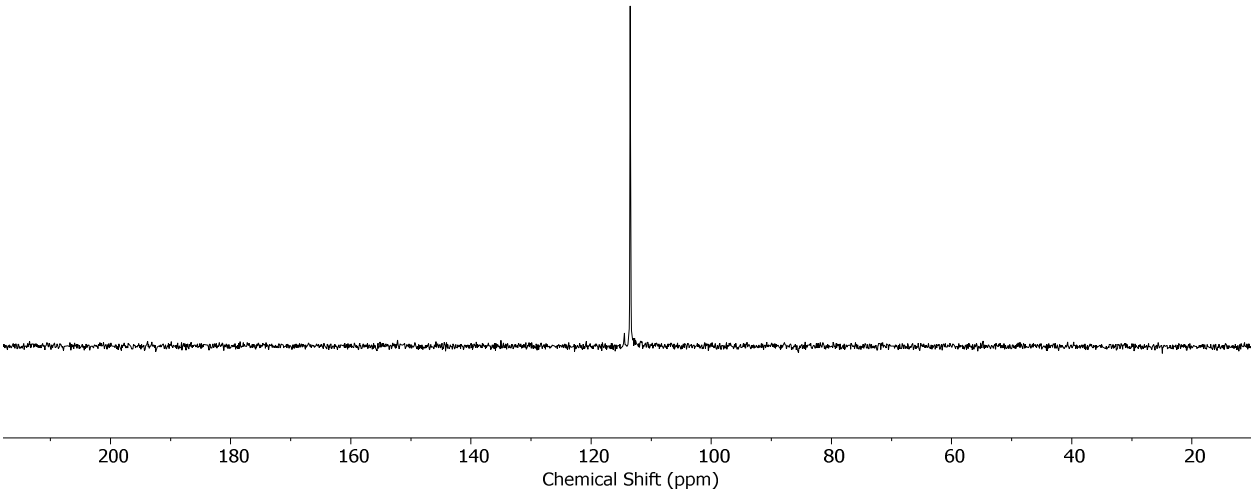
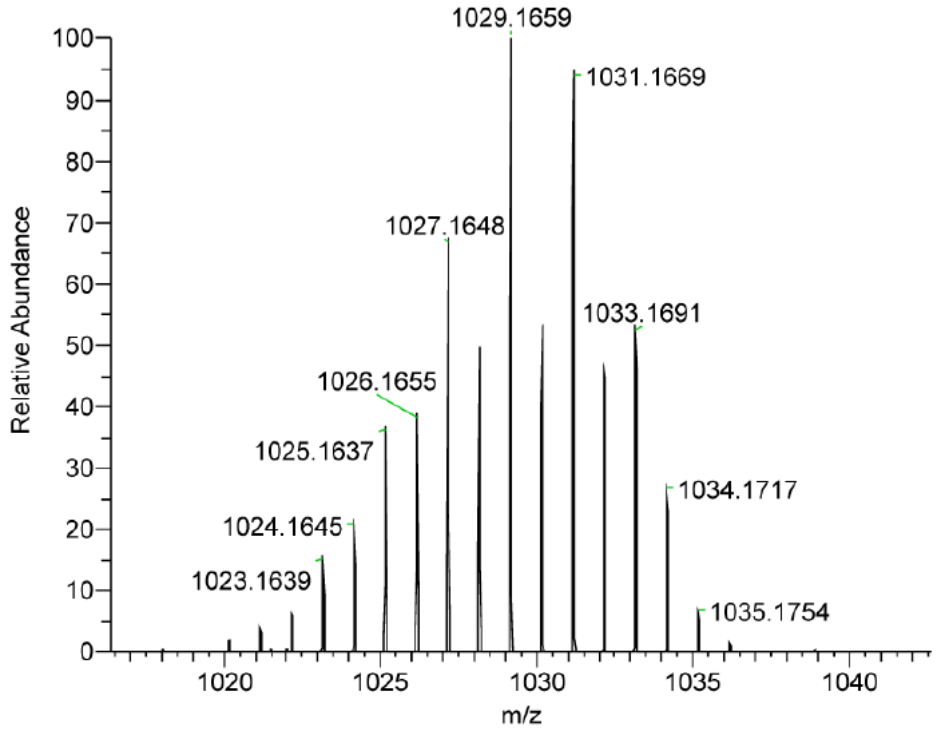


Figure S2-6. ^{125}Te NMR spectrum of macrocycle **1•ChB** (158 MHz, 298 K, $CDCl_3$).

Measured Spectrum



Theoretical Spectrum

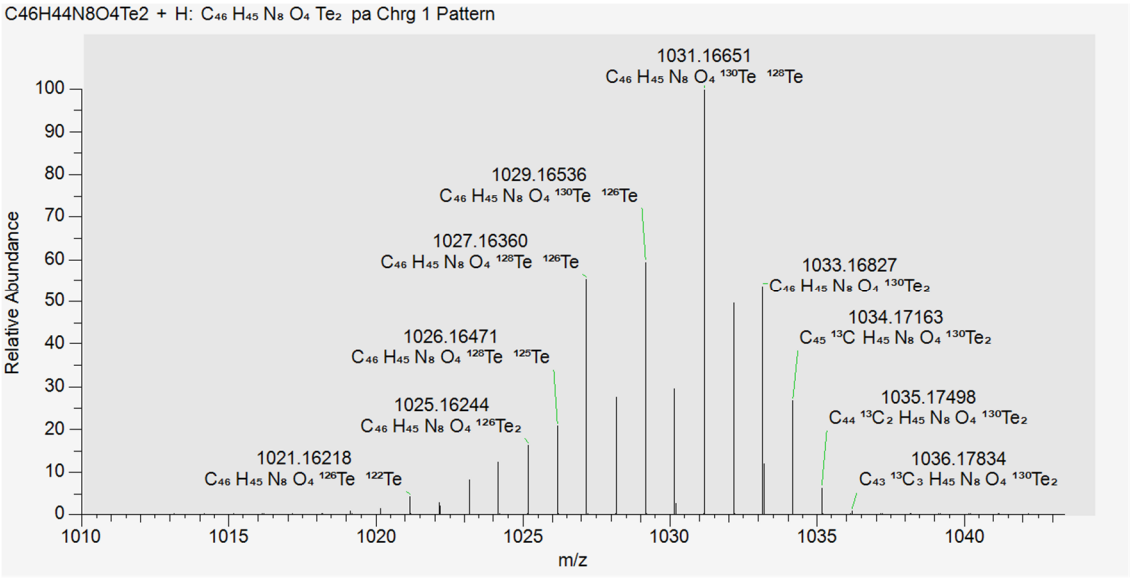


Figure S2-7. High resolution ESI mass spectrum of macrocycle **1•ChB** (top) and its theoretical spectrum (bottom).

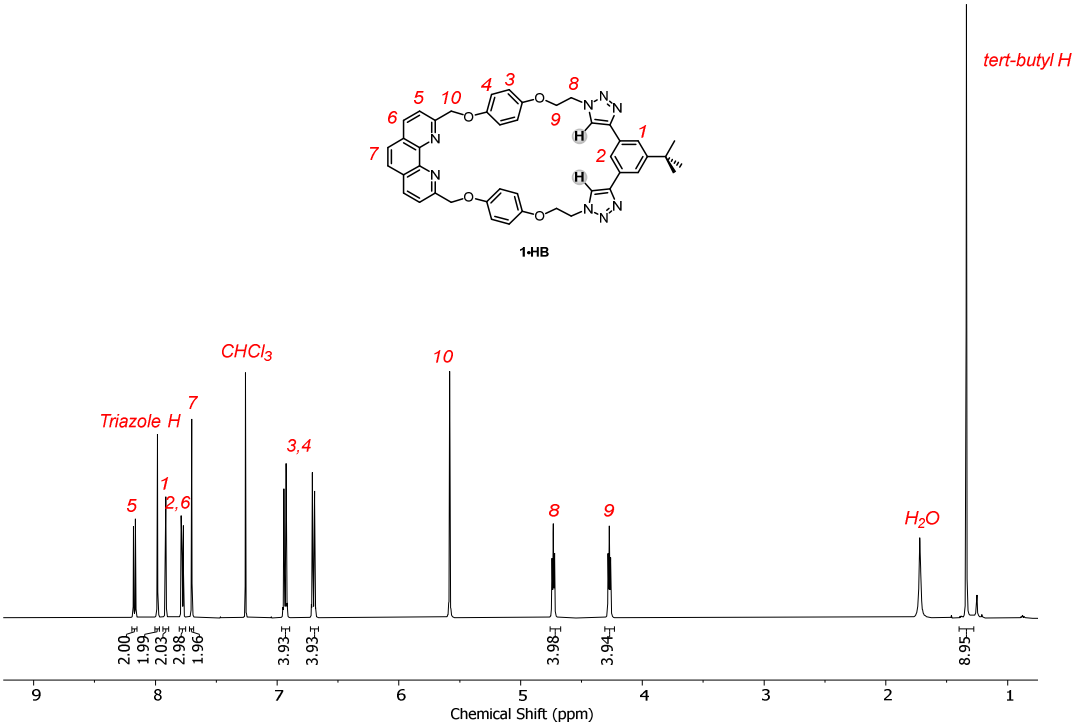


Figure S2-8. ^{1}H NMR spectrum of macrocycle **1•HB** (500 MHz, 298 K, $CDCl_3$).

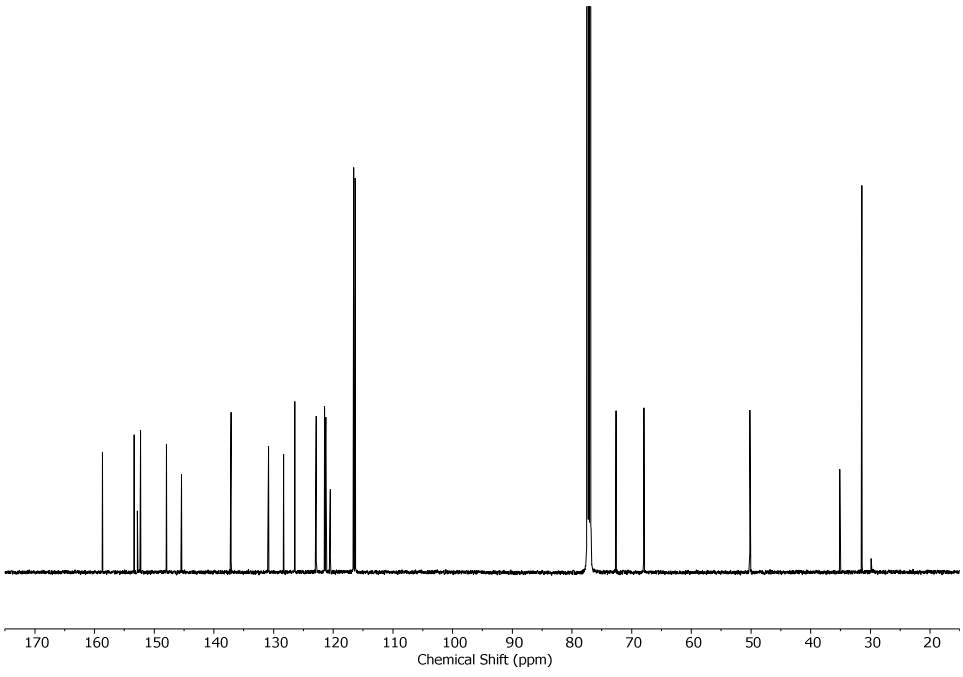


Figure S2-9. ^{13}C NMR spectrum of macrocycle **1•HB** (126 MHz, 298 K, $CDCl_3$).

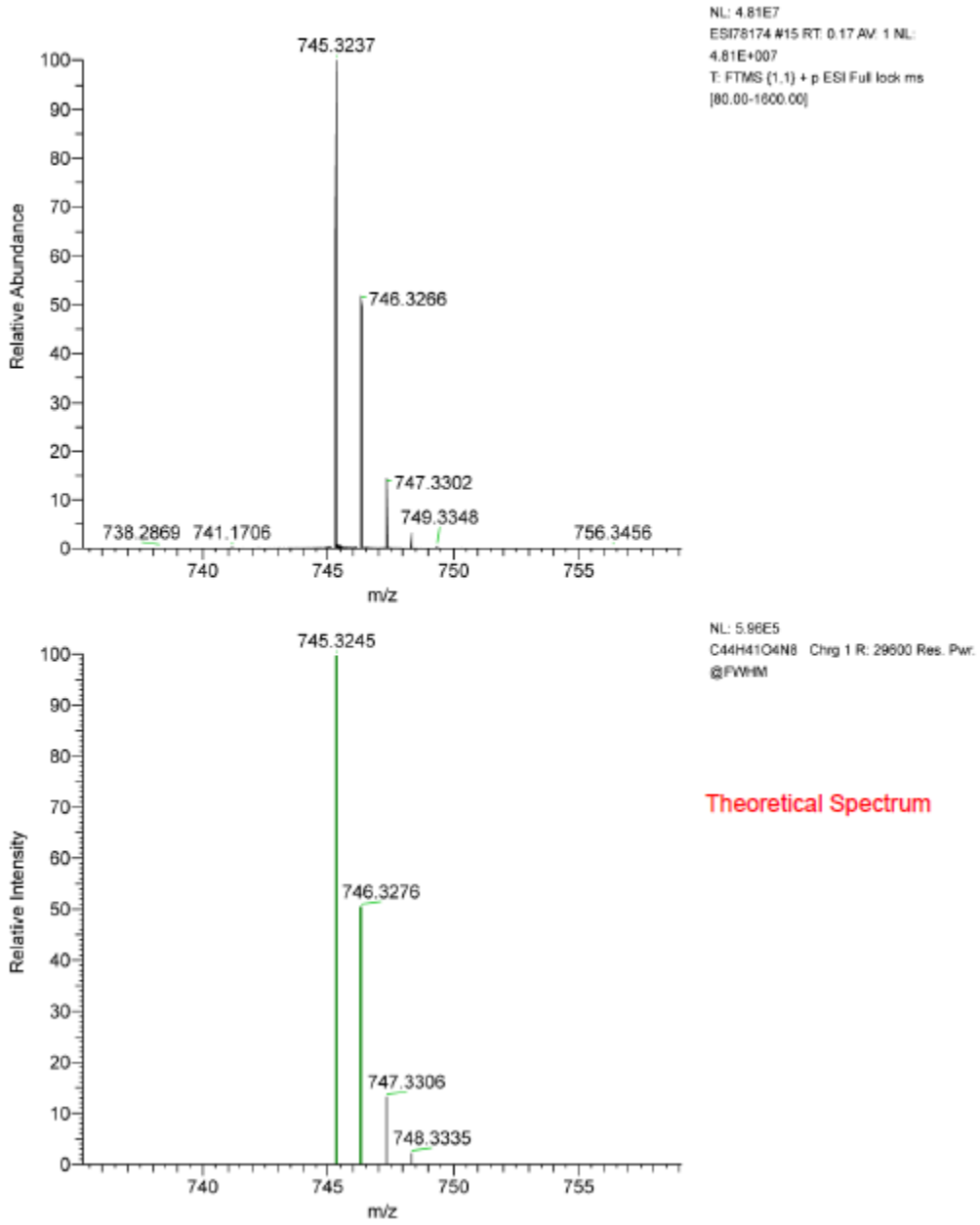


Figure S2-10. High resolution ESI mass spectrum of macrocycle **1•HB** (top) and its theoretical spectrum (bottom).

S3 Single Crystal X-ray Diffraction Studies

Single crystals of **1•XB** and **1•HB** suitable for X-ray analysis were each coated with Paratone-N oil, suspended in a small fiber loop, and placed in a cold gaseous nitrogen stream on a Oxford Diffraction Supernova X-ray diffractometer performing ϕ- and ω-scans at 150(2) K. Diffraction intensities were measured using graphite monochromated Mo *K*α and Cu Kα radiation (λ = 0.71073 and 1.54056 Å). Data collection, indexing, initial cell refinements, frame integration, final cell refinements and absorption corrections were accomplished using the program Crysalispro. Scattering factors and anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography*. All structures were solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXL following established refinement strategies.[5] [ref]= A short history of SHELX. G. M. Sheldrick, Acta Crystallogr A. 2008, 64, 112-22

All non-hydrogen atoms were refined anisotropically. All hydrogen atoms binding to carbon were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). Details of the data quality and a summary of the residual values for the refinements are listed in Table 1 and 2. Automatic structure evaluation performed with PLATON as implemented in the CheckCIF routine resulted in a few alerts for complexes **1•HB** for its restricted data quality, owing to loss of disordered solvents. Therefore Squeeze program was performed on data of **1•HB** to remove disordered solvents, based on all the relevant characterizations including NMR and HRMS.

Table 1. Crystal data and structure refinement for **1•XB**.

Identification code	rtmc	
Empirical formula	C45 H42 I2 N8 O6.20	
Formula weight	1047.86	
Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 25.3739(2) Å	α= 90°.
	b = 27.4143(2) Å	β= 105.1990(10)°.
	c = 14.36510(10) Å	γ = 90°.
Volume	9642.95(13) $Å^3$	
Z	8	
Density (calculated)	1.444 Mg/m^3	
Absorption coefficient	10.681 mm^{-1}	
F(000)	4189	
Crystal size	0.300 x 0.300 x 0.200 mm^3	
Theta range for data collection	3.606 to 76.207°.	
Index ranges	-31<=h<=25, -34<=k<=34, -18<=l<=17	
Reflections collected	59983	
Independent reflections	10028 [R(int) = 0.0334]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.08176 and 0.01028
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10028 / 6 / 561
Goodness-of-fit on F^2	1.099
Final R indices [I>2sigma(I)]	R1 = 0.0810, wR2 = 0.2274
R indices (all data)	R1 = 0.0830, wR2 = 0.2347
Extinction coefficient	n/a
Largest diff. peak and hole	3.051 and -0.462 e.$Å^{-3}$

Table 2. Crystal data and structure refinement for **1•HB**.

Identification code	rthmc	
Empirical formula	C45.67 H41.67 Cl5 N8 O4	
Formula weight	943.78	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 15.8391(5) Å	α= 96.663(3)°.
	b = 15.8758(4) Å	β= 102.548(3)°.
	c = 33.8664(12) Å	γ = 103.621(3)°.
Volume	7952.3(5) $Å^3$	
Z	6	
Density (calculated)	1.182 Mg/m^3	
Absorption coefficient	0.319 mm^{-1}	
F(000)	2932	
Crystal size	0.4 x 0.3 x 0.25 mm^3	
Theta range for data collection	2.876 to 30.411°.	
Index ranges	-21<=h<=21, -22<=k<=18, -44<=l<=48	
Reflections collected	101936	
Independent reflections	41553 [R(int) = 0.1030]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	1.00000 and 0.67982
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	41553 / 30 / 1722
Goodness-of-fit on F^2	1.106
Final R indices [I>2sigma(I)]	R1 = 0.1411, wR2 = 0.3578
R indices (all data)	R1 = 0.2966, wR2 = 0.4529
Extinction coefficient	n/a
Largest diff. peak and hole	2.008 and -1.184 e.$Å^{-3}$

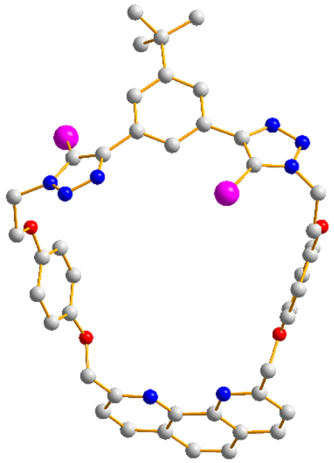


Figure S3-1 X-ray crystal structure of macrocyclic receptor **1•XB**. Hydrogen atoms are omitted for clarity. Gray = carbon, blue = nitrogen, red = oxygen and purple = iodine.

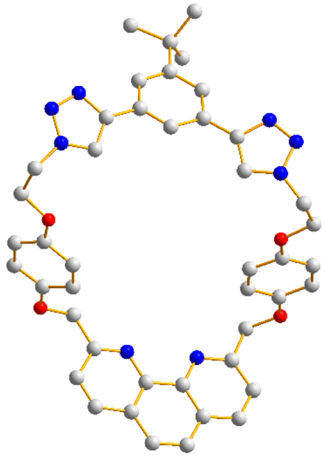


Figure S3-2 X-ray crystal structure of macrocyclic receptor **1•HB**. Hydrogen atoms are omitted for clarity. Gray = carbon, blue = nitrogen, red = oxygen and purple = iodine.

S4 NMR Binding Studies

S4.1 Lithium Binding Studies

General Procedure

In a typical experiment, a solution of the receptor dissolved in $CDCl_3$ was added slowly into a solution of $LiClO_4$ dissolved in an equal-volume of CD_3CN, and the mixture was then sonicated for 1 hour to form the lithium bound receptor.

For all receptors, a general downfield shift of phenanthroline proton signals $H_{5\text{-}7}$ was observed, suggestive of lithium complexation.[6–8] In the case of **1•ChB** and **1•HB**, downfield perturbation of $TeCH_3$ and triazole protons were also seen respectively, providing further evidence to the binding of lithium cation.

^{1}H NMR Spectra of Lithium Complexation

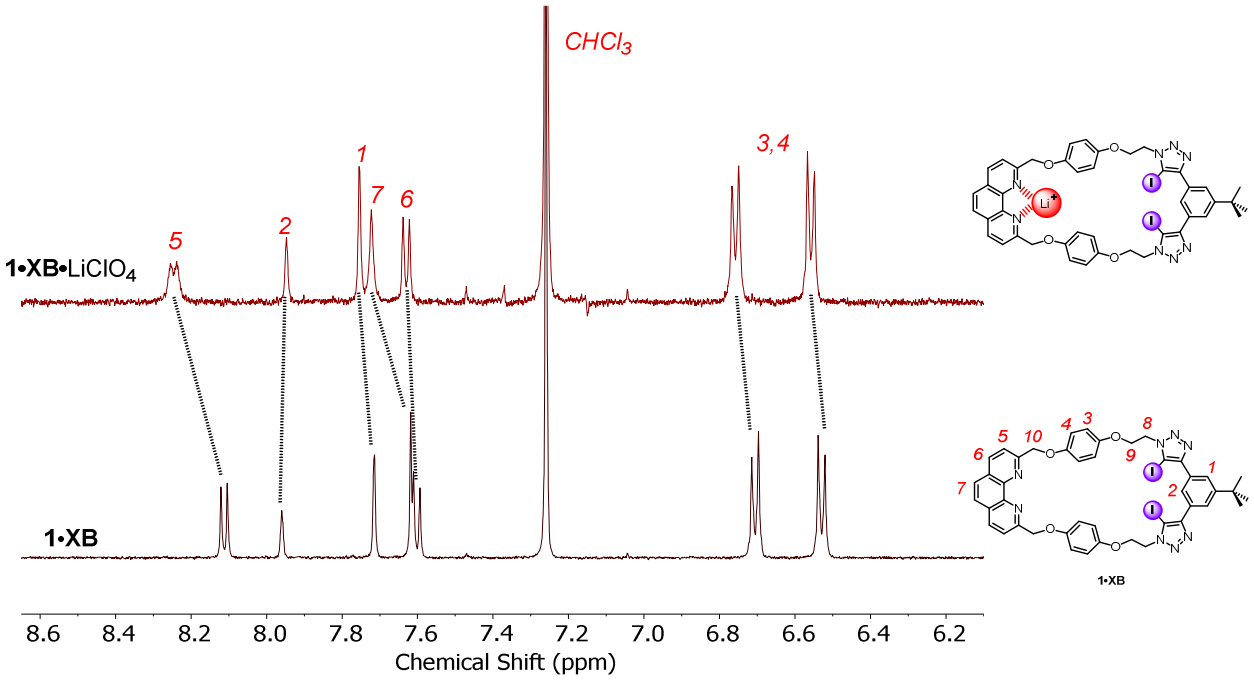


Figure S4-1. Truncated ^{1}H NMR spectra of receptor **1•XB** in the absence (bottom) and presence (top) of one equivalent of $LiClO_4$ (500 MHz, 298 K, 1:1 $CDCl_3$:CD_3CN).

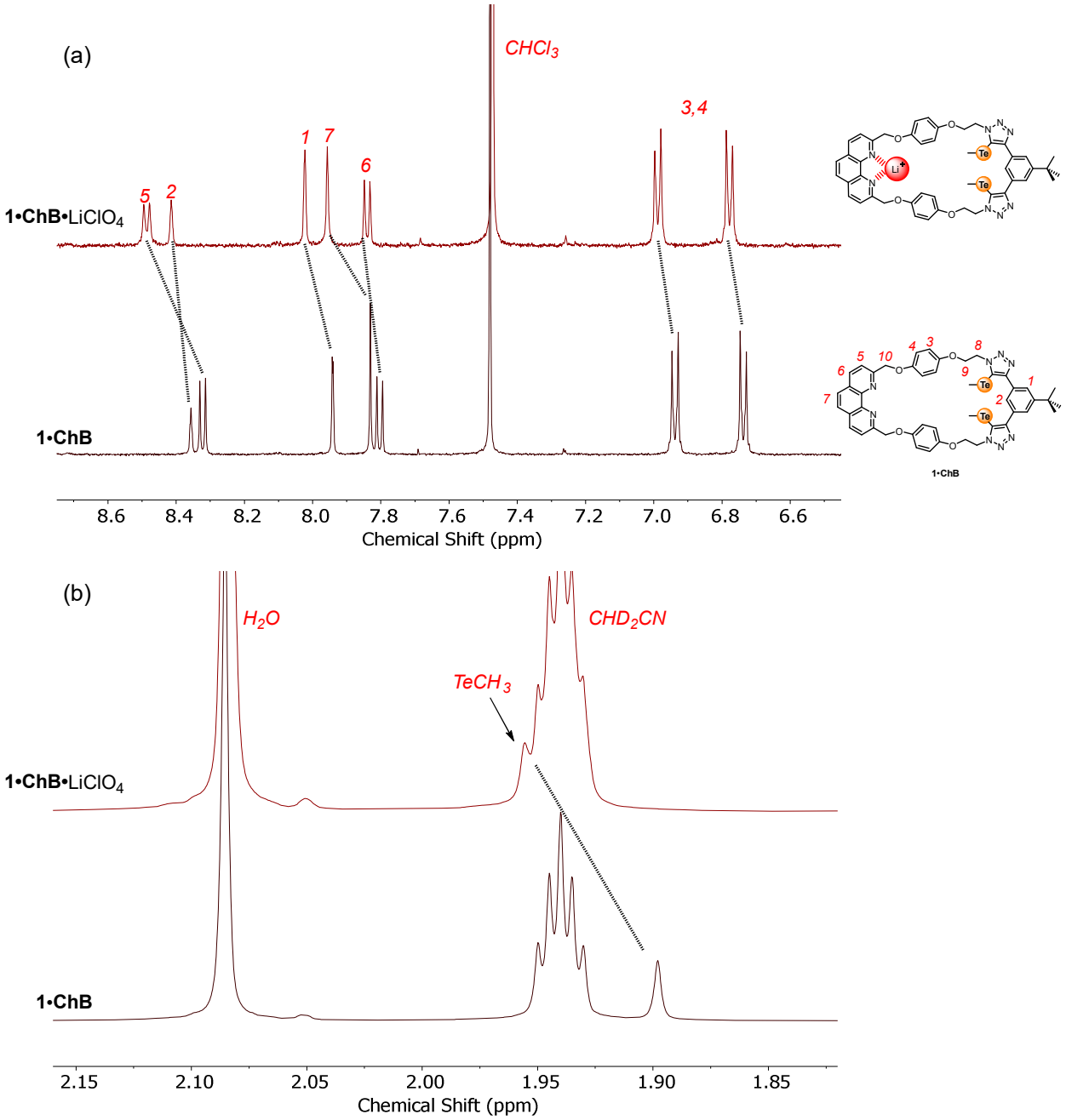


Figure S4-2. Truncated ^{1}H NMR spectra of receptor **1•ChB** showing changes in chemical shift of (a) the aromatic region and (b) $TeCH_3$ peak in the absence (bottom) and presence (top) of one equivalent of $LiClO_4$ (500 MHz, 298 K, 1:1 $CDCl_3$:CD_3CN).

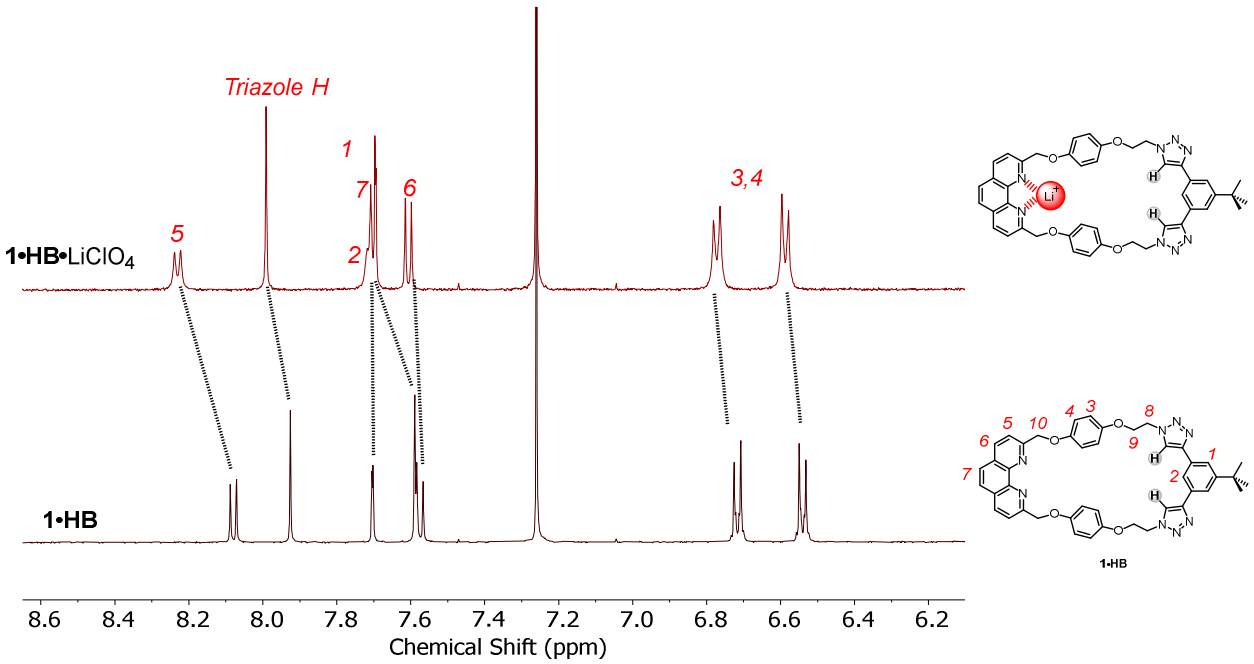


Figure S4-3. Truncated ^{1}H NMR spectra of receptor **1•HB** in the absence (bottom) and presence (top) of one equivalent of $LiClO_4$ (500 MHz, 298 K, 1:1 $CDCl_3$:CD_3CN).

S4.2 Ion-Pair Binding Studies

General Procedure

Preliminary ion-pair binding studies were conducted to assess the capability of the receptors to simultaneously recognise lithium cation and halide anion. In each experiment, a solution of the receptor dissolved in $CDCl_3$ was added slowly into a solution of $LiClO_4$ dissolved in an equal-volume of CD_3CN, and the mixture was then sonicated for 1 hour to form the lithium bound receptor. TBA halide salt dissolved in 1:1 $CDCl_3$:CD_3CN was added to the lithium-receptor complex and the mixture was shaken vigorously before recording the NMR spectra.

In all cases, the addition of anions caused little perturbations to the phenanthroline signals $H_{5\text{-}7}$, suggesting the lithium remained bound by the phenanthroline in the presence of competing anions. For **1•XB**•$LiClO_4$, downfield shift of internal benzene spacer proton H_2 was observed, which is indicative of halide binding at the XB donor site (Figure S4-4–S4-5). Addition of anions to **1•ChB**•$LiClO_4$ did not cause shift in the aromatic region but downfield shift was observed for the $TeCH_3$ proton, inferring the contribution of ChB in halide binding (Figure S4-6–S4-7). Lastly, triazole proton of **1•HB**•$LiClO_4$ shifted downfield in the presence of halides, in accordance with triazole CH HB interactions with anions.

^{1}H NMR Spectra of Preliminary Ion-pair Binding

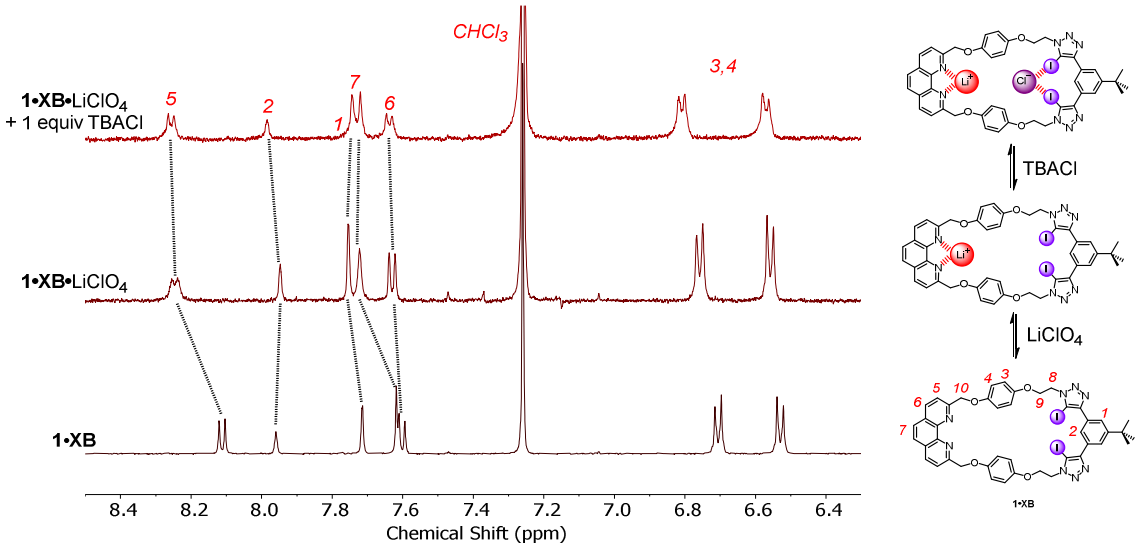


Figure S4-4. Truncated ^{1}H NMR spectra showing the aromatic regions of receptor **1•XB** (bottom), upon addition of 1 equivalent $LiClO_4$ (middle) and a further addition of 1 equivalent of TBACl (top) (500 MHz, 298 K, 1:1 $CDCl_3$:CD_3CN).

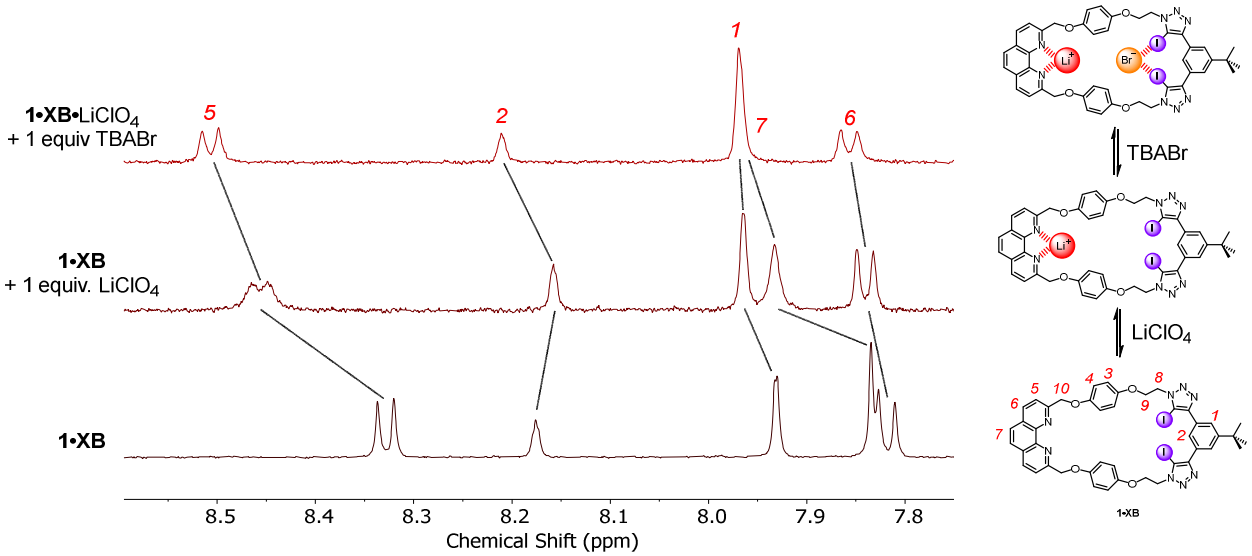


Figure S4-5. Truncated ^{1}H NMR spectra showing the aromatic regions of receptor **1•XB** (bottom), upon addition of 1 equivalent $LiClO_4$ (middle) and a further addition of 1 equivalent of TBABr (top) (500 MHz, 298 K, 1:1 $CDCl_3$:CD_3CN).

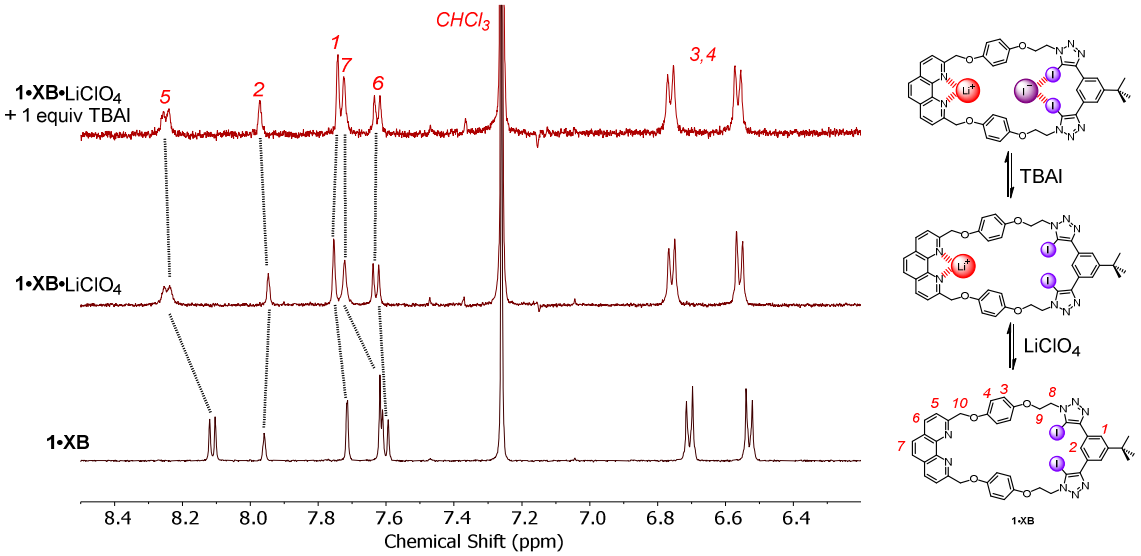


Figure S4-6. Truncated ^{1}H NMR spectra showing the aromatic regions of receptor **1•XB** (bottom), upon addition of 1 equivalent $LiClO_4$ (middle) and a further addition of 1 equivalent of TBAI (top) (500 MHz, 298 K, 1:1 $CDCl_3$:CD_3CN).

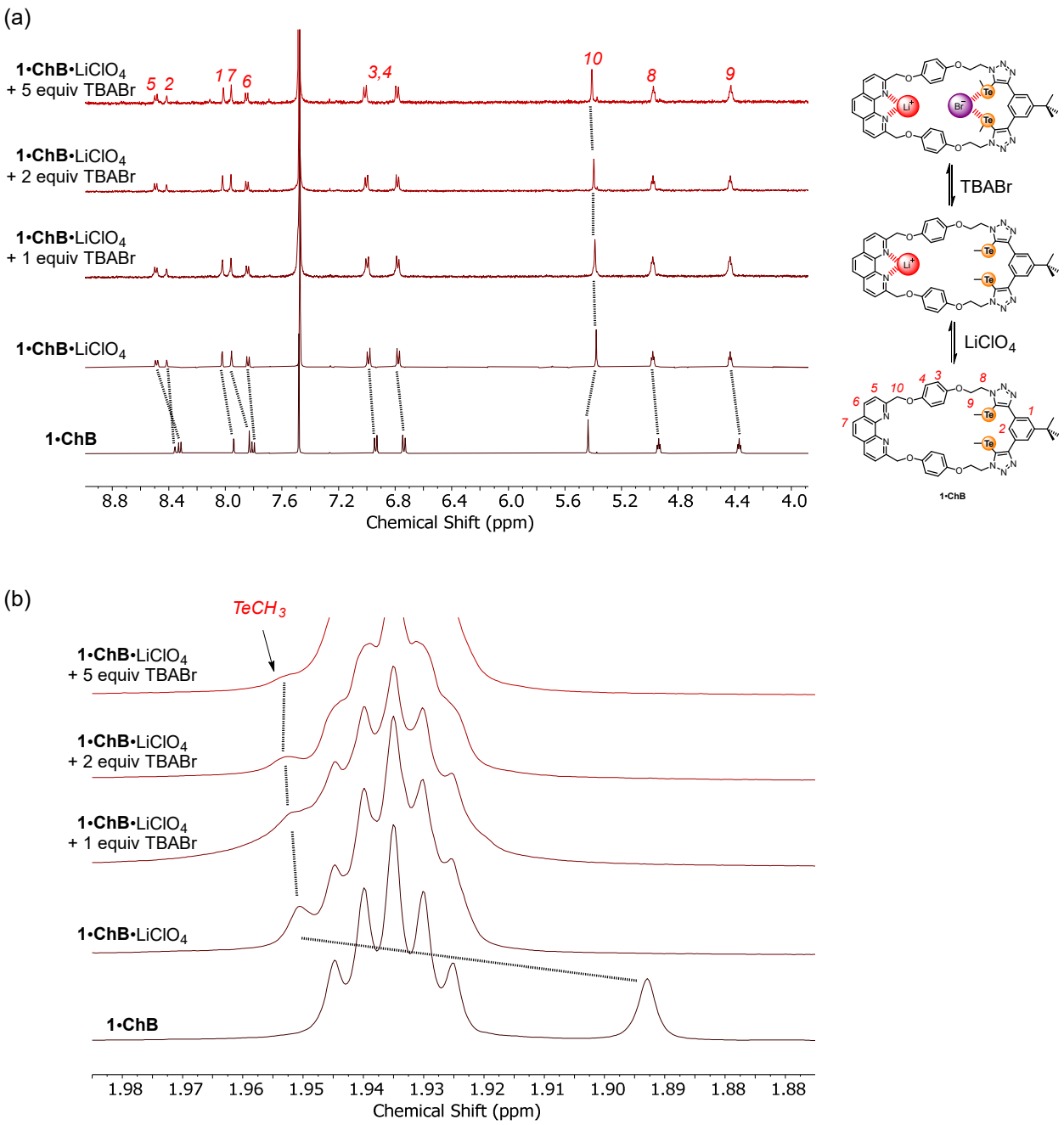


Figure S4-7. Truncated ^{1}H NMR spectra showing (a) the aromatic regions and (b) $TeCH_3$ peak of receptor **1•ChB** upon addition of 1 equivalent $LiClO_4$ and further addition of 1, 2 and 5 equivalents of TBABr (500 MHz, 298 K, 1:1 $CDCl_3$:CD_3CN).

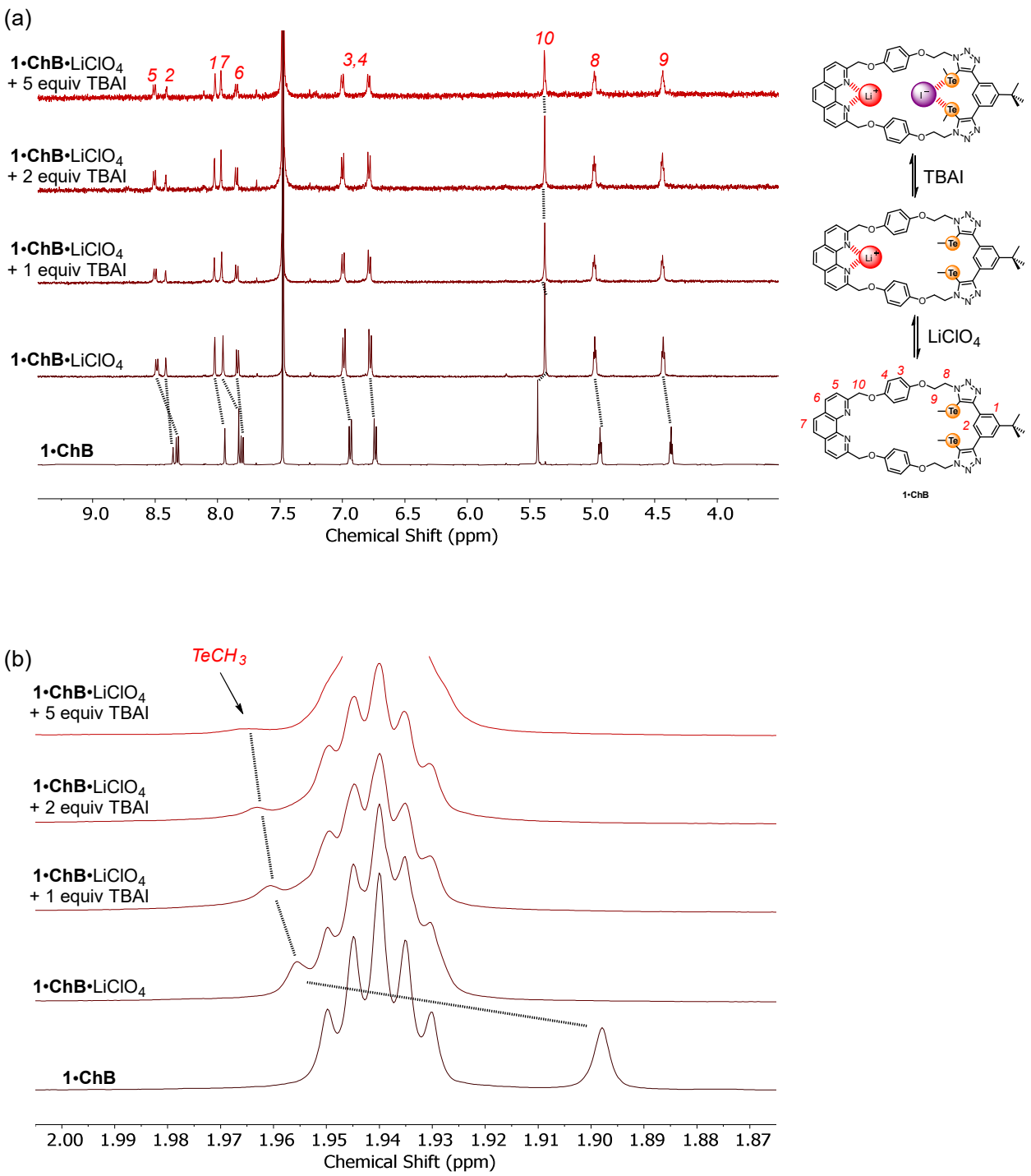


Figure S4-8. Truncated ^{1}H NMR spectra showing (a) the aromatic regions and (b) $TeCH_3$ peak of receptor **1•ChB** upon addition of 1 equivalent $LiClO_4$ and further addition of 1, 2 and 5 equivalents of TBAI (500 MHz, 298 K, 1:1 $CDCl_3$:CD_3CN).

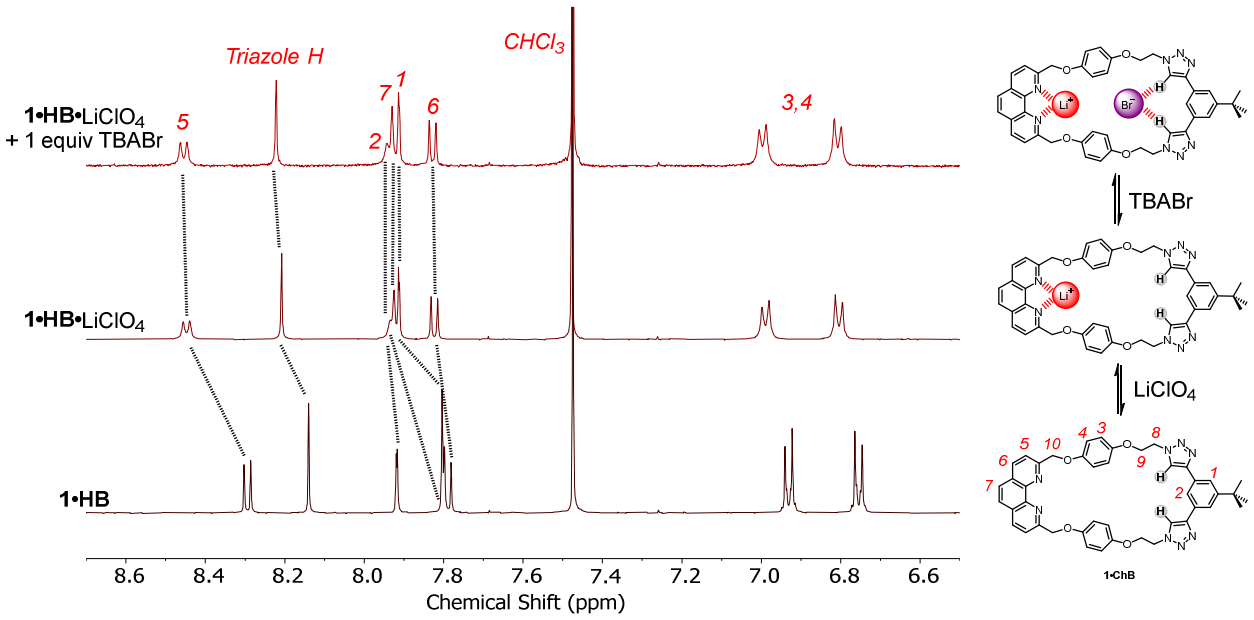


Figure S4-9. Truncated ^{1}H NMR spectra showing the aromatic regions of receptor **1•HB** (bottom), upon addition of 1 equivalent $LiClO_4$ (middle) and a further addition of 1 equivalent of TBABr (top) (500 MHz, 298 K, 1:1 $CDCl_3$:CD_3CN).

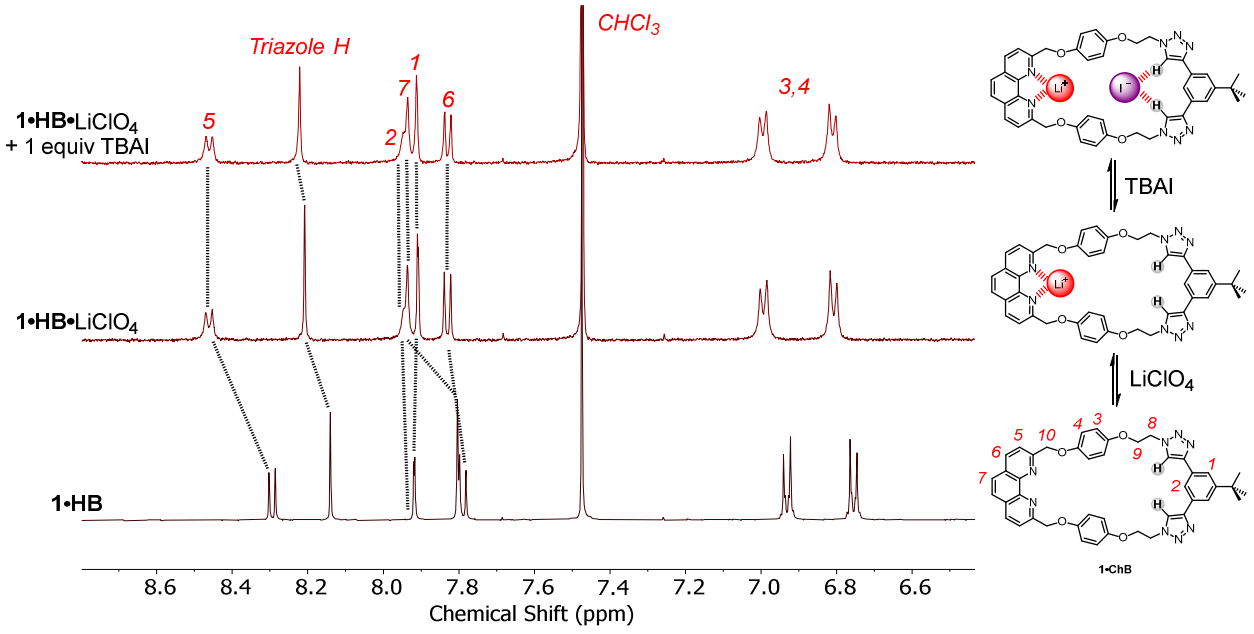


Figure S4-10. Truncated ^{1}H NMR spectra showing the aromatic regions of receptor **1•HB** (bottom), upon addition of 1 equivalent $LiClO_4$ (middle) and a further addition of 1 equivalent of TBAI (top) (500 MHz, 298 K, 1:1 $CDCl_3$:CD_3CN).

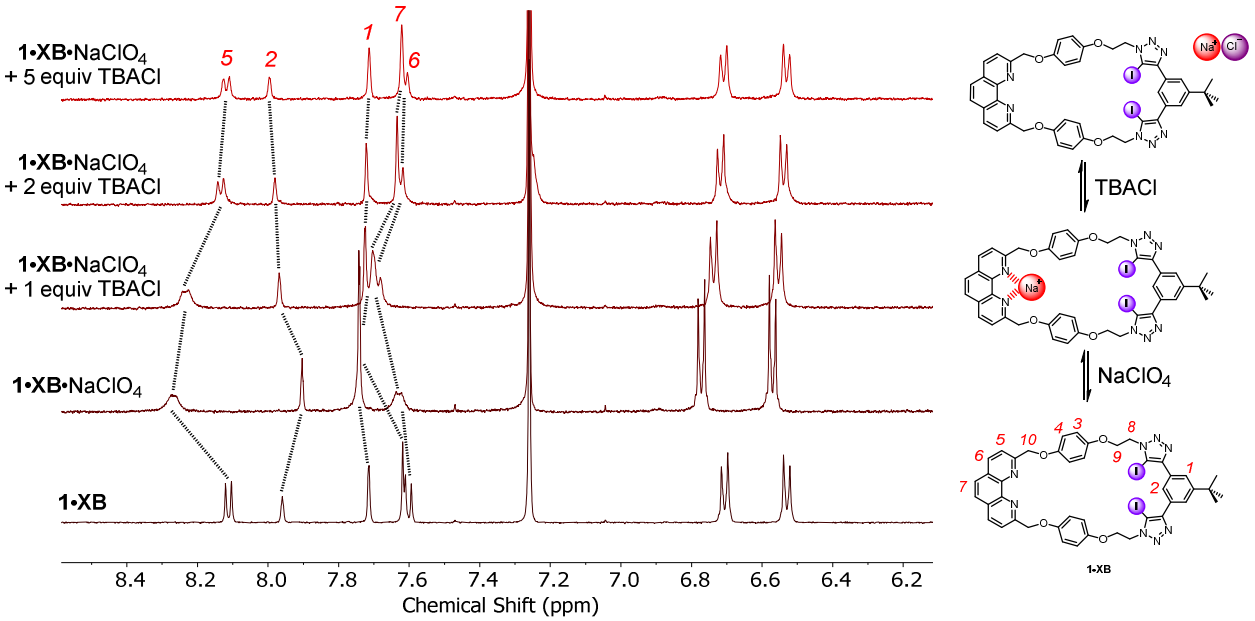


Figure S4-11. Truncated ^{1}H NMR spectra showing the aromatic regions of receptor **1•XB,** upon addition of 1 equivalent $NaClO_4$ and a further addition of 1, 2 and 5 equivalents of TBACl (500 MHz, 298 K, 1:1 $CDCl_3$:CD_3CN).

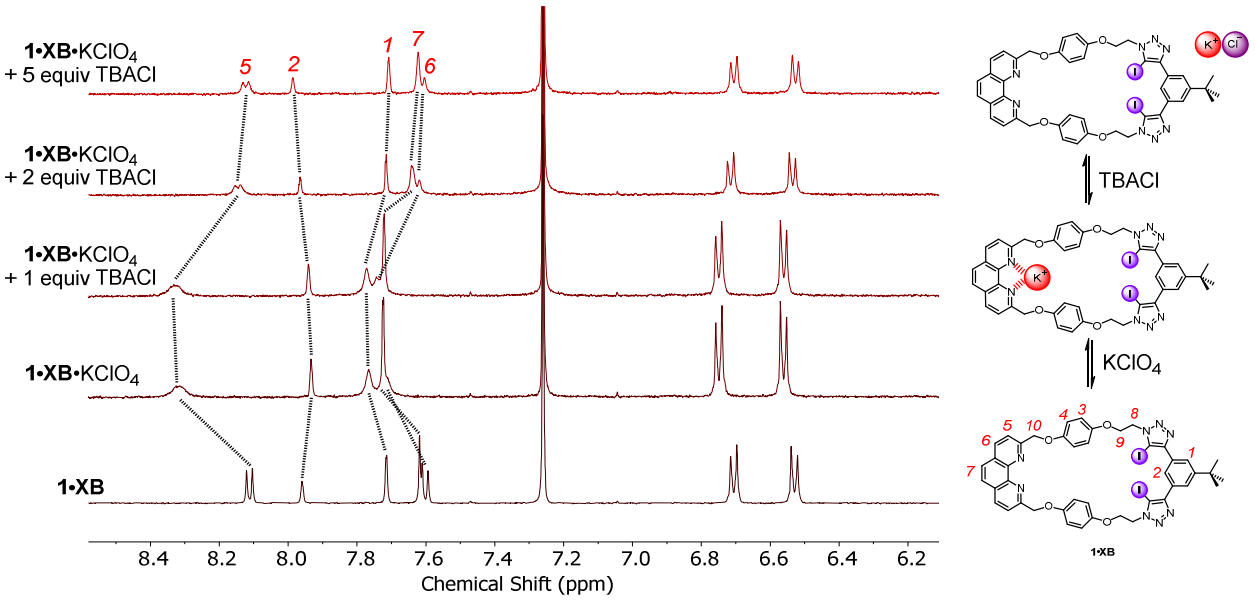


Figure S4-12. Truncated ^{1}H NMR spectra showing the aromatic regions of receptor **1•XB,** upon addition of 1 equivalent $KClO_4$ and a further addition of 1, 2 and 5 equivalents of TBACl (500 MHz, 298 K, 1:1 $CDCl_3$:CD_3CN).

S4.3 Anion Binding Titrations (in the presence of lithium cation)

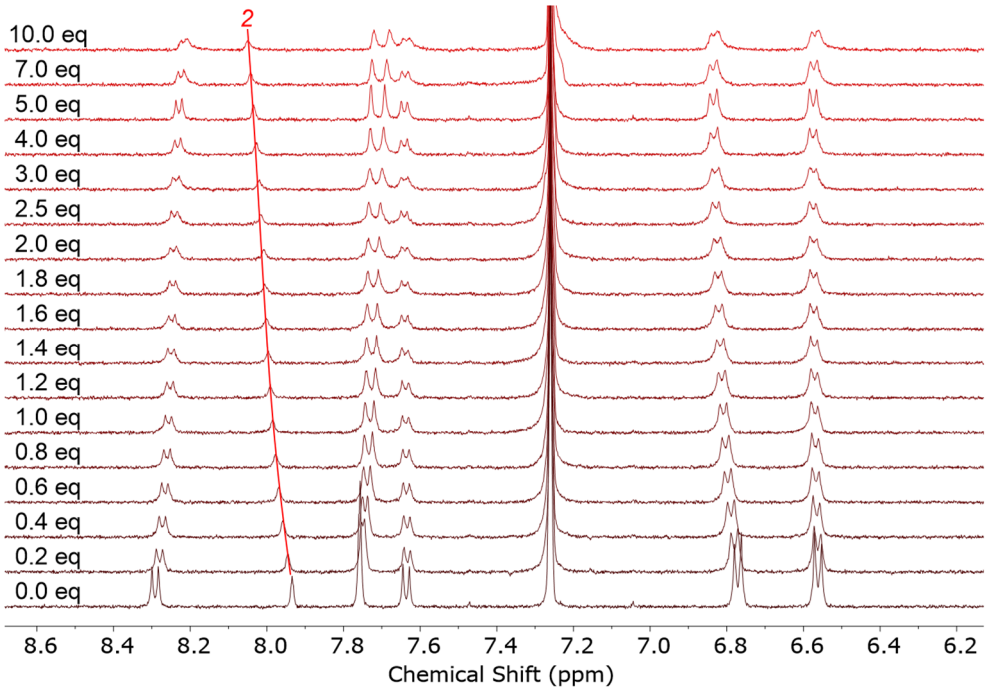
General Procedure

All ^{1}H NMR titration experiments were performed on a Bruker AVIII 500 MHz spectrometer. In a typical experiment with lithium bound receptor, uncomplexed receptor molecule was dissolved in 1:1 $CDCl_3$:CD_3CN containing an equimolar of $LiClO_4$. The receptor solution was then sonicated for 1 hour. A solution of appropriate tetrabutylammonium (TBA) salt in 1:1 $CDCl_3$:CD_3CN was added to the solution of lithium bound receptor at 298 K. A 50 mM solution of TBA salt was added in aliquots to a 1.0 mM solution of lithium bound receptor, where 1.0 equivalent of TBA salt added corresponds to 10.0 μL of the salt solution. 17 spectra were recorded at 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, 3.0, 4.0, 5.0, 7.0, 10.0 equivalents of added guest anion.

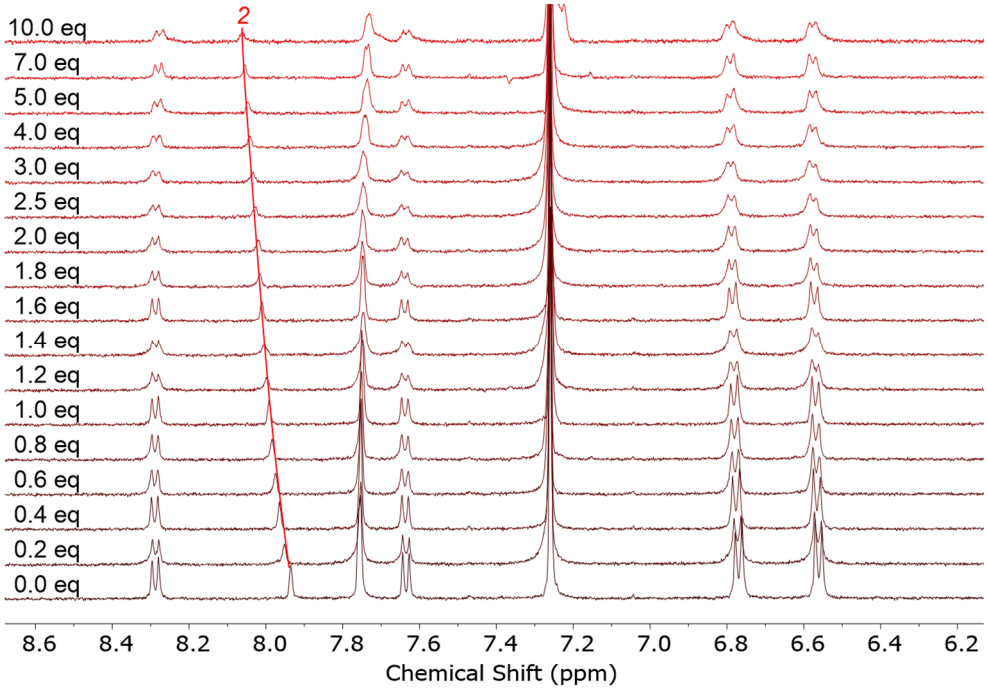
The binding of anions with all receptors were found to be fast on the NMR timescale. The values of the observed chemical shift and concentration of anion were entered into the Bindfit programme for every titration point. From initial estimates made of the binding constants and limiting chemical shifts, these parameters were refined using nonlinear 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.

[1]H NMR Titrations Spectra

(a)



(b)



(c)

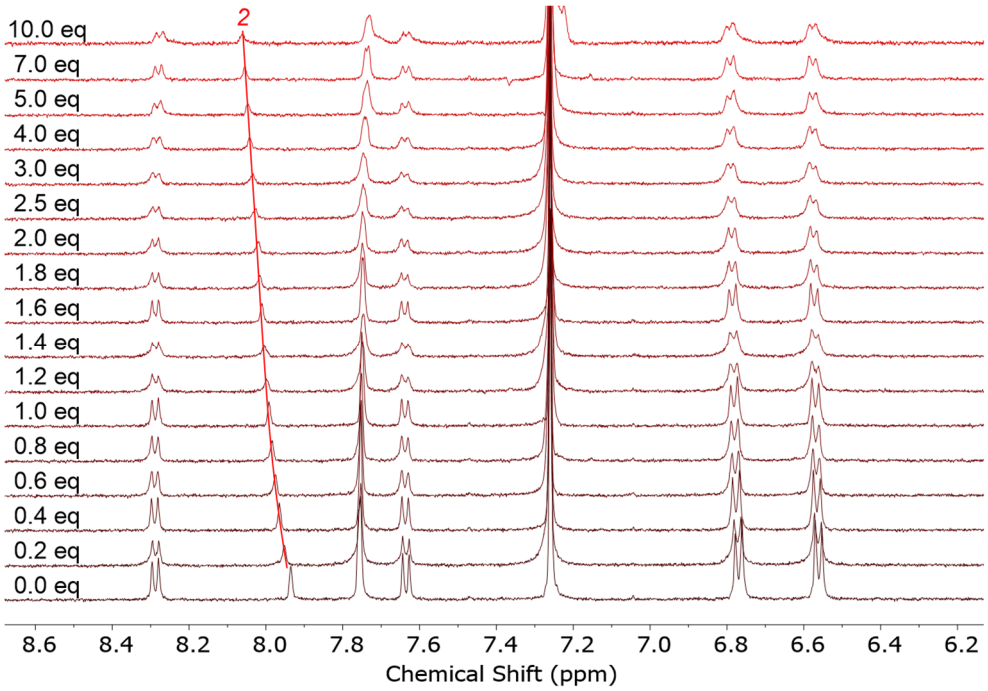
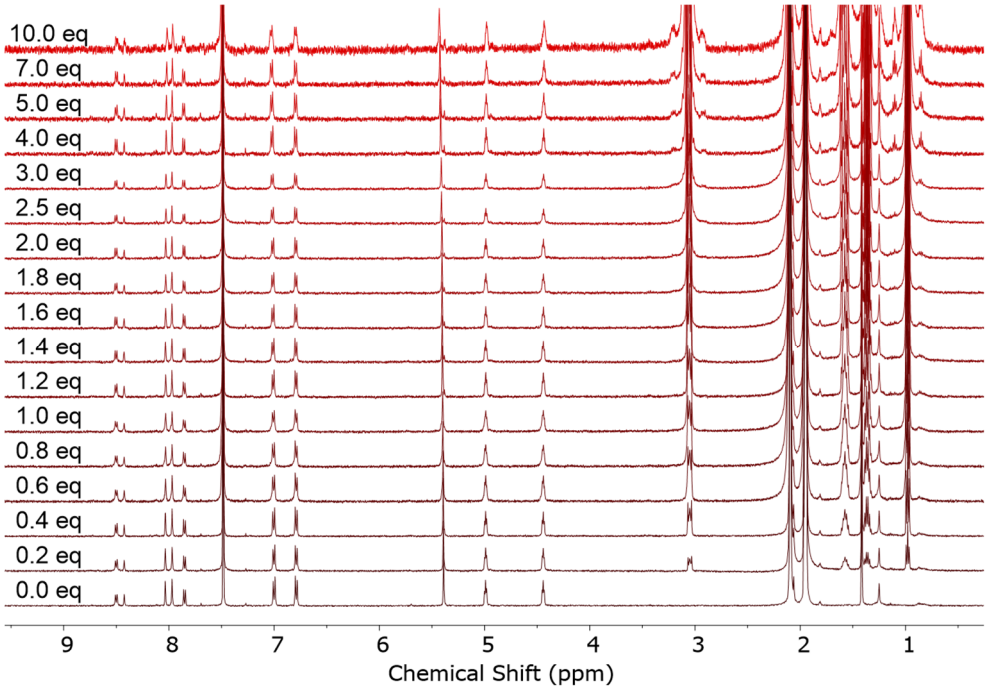


Figure S4-13. Truncated ^{1}H NMR titration spectra of **1•XB** upon addition of 10 equivalents of (a) TBACl, (b) TBABr and (c) TBAI (500 MHz, 298 K, 1:1 $CDCl_3$:CD_3CN, [**1•XB**] = 1.0 mM). (Connecting lines are to guide the eye only)

(a)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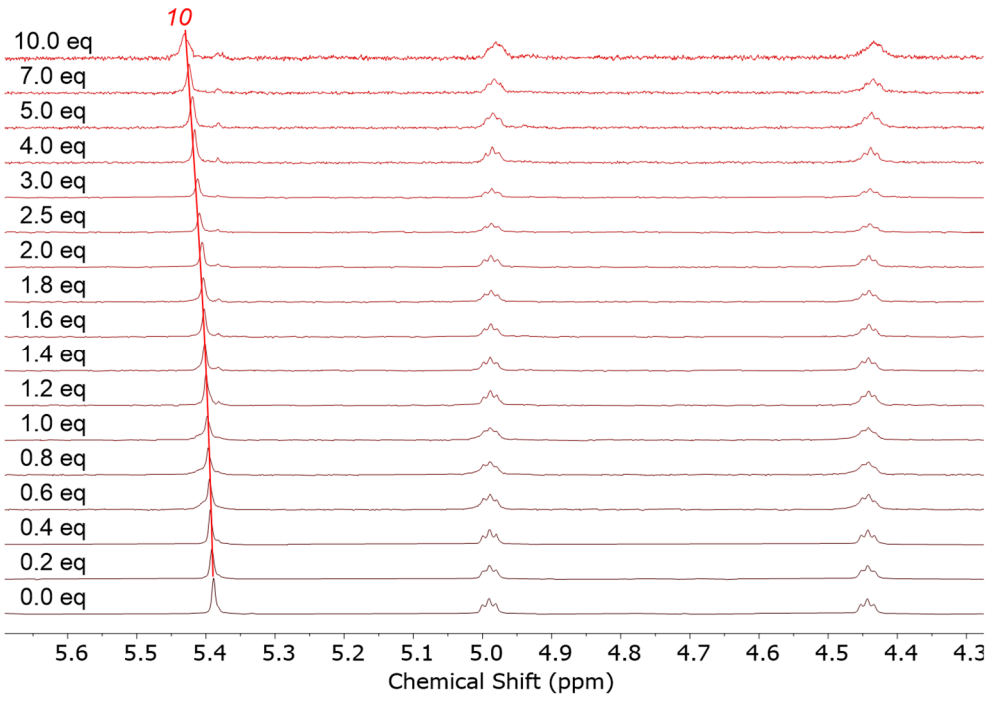
7.0 eq
5.0 eq
4.0 eq
3.0 eq
2.5 eq
2.0 eq
1.8 eq
1.6 eq
1.4 eq
1.2 eq
1.0 eq
0.8 eq
0.6 eq
0.4 eq
0.2 eq
0.0 eq
9
8
7
6
5
4
3
2
1
Chemical Shift (ppm)

(b)


10
10.0 eq
7.0 eq
5.0 eq
4.0 eq
3.0 eq
2.5 eq
2.0 eq
1.8 eq
1.6 eq
1.4 eq
1.2 eq
1.0 eq
0.8 eq
0.6 eq
0.4 eq
0.2 eq
0.0 eq
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
Chemical Shift (ppm)

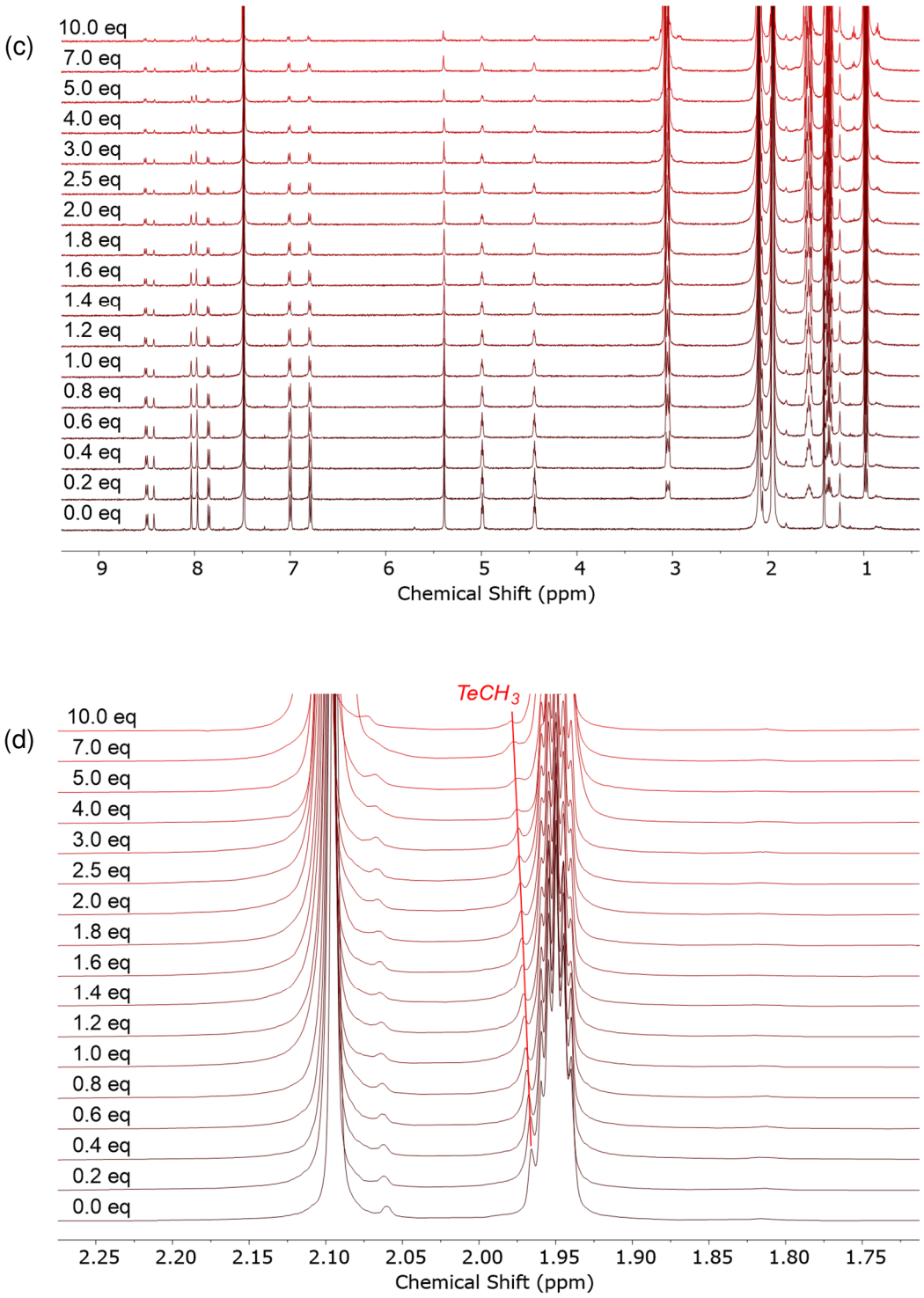


Figure S4-14. Full and truncated ^{1}H NMR titration spectra of **1•ChB** upon addition of 10 equivalents of (a-b) TBABr and (c-d) TBAI (500 MHz, 298 K, 1:1 $CDCl_3$:CD_3CN, [**1•ChB**] = 1.0 mM). (Connecting lines are to guide the eye only)

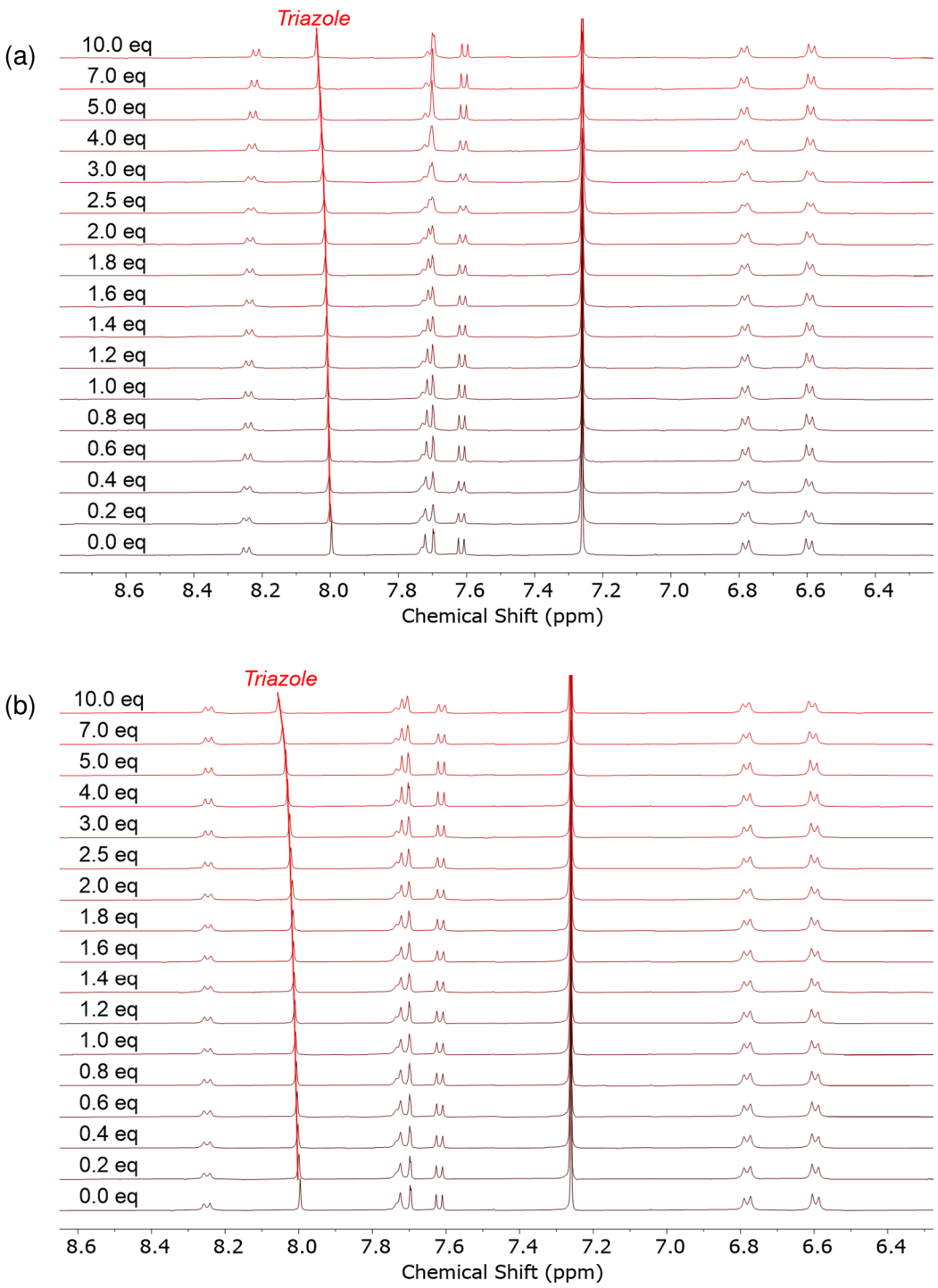


Figure S4-15. Full and truncated ^{1}H NMR titration spectra of **1•HB** upon addition of 10 equivalents of (a) TBABr and (b) TBAI (500 MHz, 298 K, 1:1 $CDCl_3$:CD_3CN, [**1•ChB**] = 1.0 mM). (Connecting lines are to guide the eye only)

Binding Isotherms

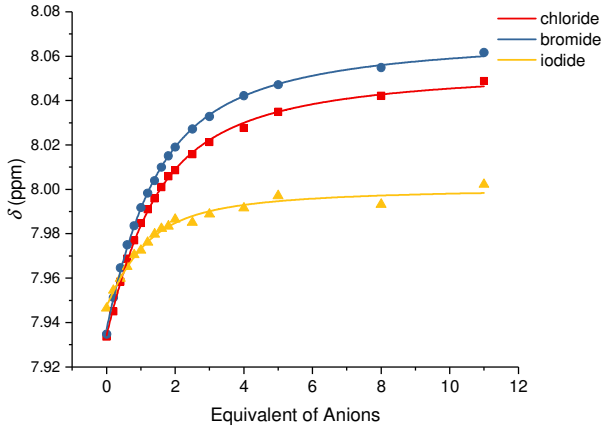


Figure S4-16. Binding isotherms of **1•XB•**$LiClO_4$ showing changes in chemical shift of internal benzene proton H_2 with increasing equivalents of anions. ([**1•XB•**$LiClO_4$] = 1.0 mM, 500 MHz, 298 K, 1:1 $CDCl_3$:CD_3CN)

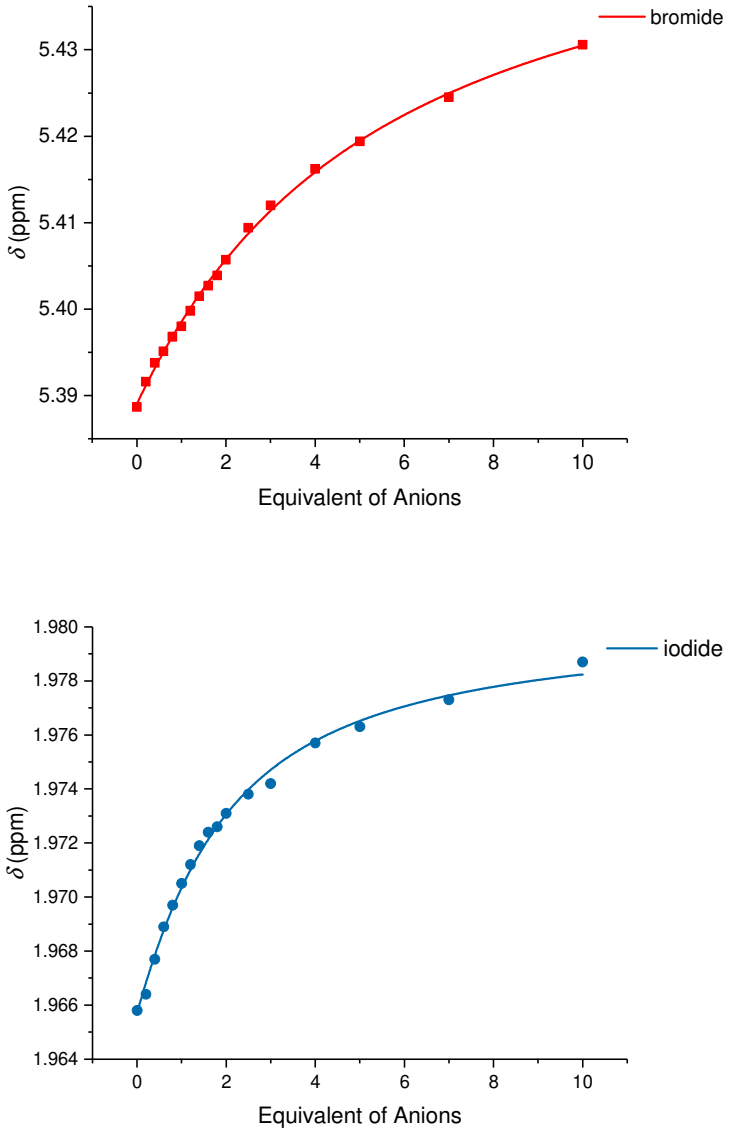


Figure S4-17. Binding isotherms of **1•ChB•**$LiClO_4$ showing changes in chemical shift of (a) methylene proton H_{10} and (b) $TeCH_3$ methyl proton with increasing equivalents of bromide and iodide respectively. ([**1•ChB•**$LiClO_4$] = 1.0 mM, 500 MHz, 298 K, 1:1 $CDCl_3$:CD_3CN)

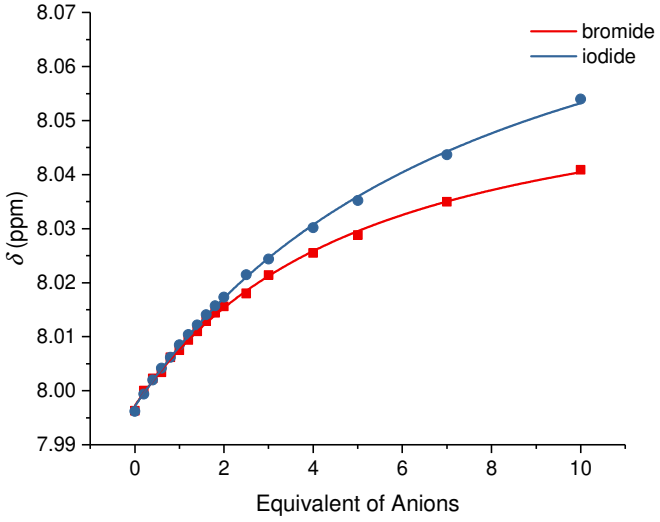


Figure S4-18. Binding isotherms of **1•HB•**$LiClO_4$ showing changes in chemical shift of triazole proton with increasing equivalents of bromide and iodide. ([**1•HB•**$LiClO_4$] = 1.0 mM, 500 MHz, 298 K, 1:1 $CDCl_3$:CD_3CN)

S5 Solid-liquid Extraction (SLE) Studies

General Procedure

The capability of the receptors to extract solid lithium halide salt into organic solvent was investigated by solid-liquid extraction (SLE) experiments In a typical experiment, excess solid lithium halide salt was added to a solution of macrocycle in $CDCl_3$ (600 μL) and the mixture was vigorously sonicated for 1 hour. The excess salt was subsequently filtered off and CD_3CN (200 μL) was added to improve the resolution of the post-extraction ^1H NMR spectra. The lithium halide salt used was LiCl, LiBr and LiI. The receptor concentration was 2.0 mM.

Inspection of the post-extraction ^1H NMR spectra (Figures S5-1–S5-3) of the receptors (**1•XB**, **1•ChB** and **1•HB**) confirmed the solubilisation of all three lithium halides as evidenced by significant downfield perturbations of the macrocycle's phenanthroline aromatic protons *5*–*7* and internal benzene proton *2*, analogous to the ^1H NMR spectra obtained from sequential addition of equimolar of $LiClO_4$ and TBA halide salt (Figure S4-4–S4-10). This suggests the successful solubilisation of solid lithium halide salt.

[1]H NMR Spectra of SLE

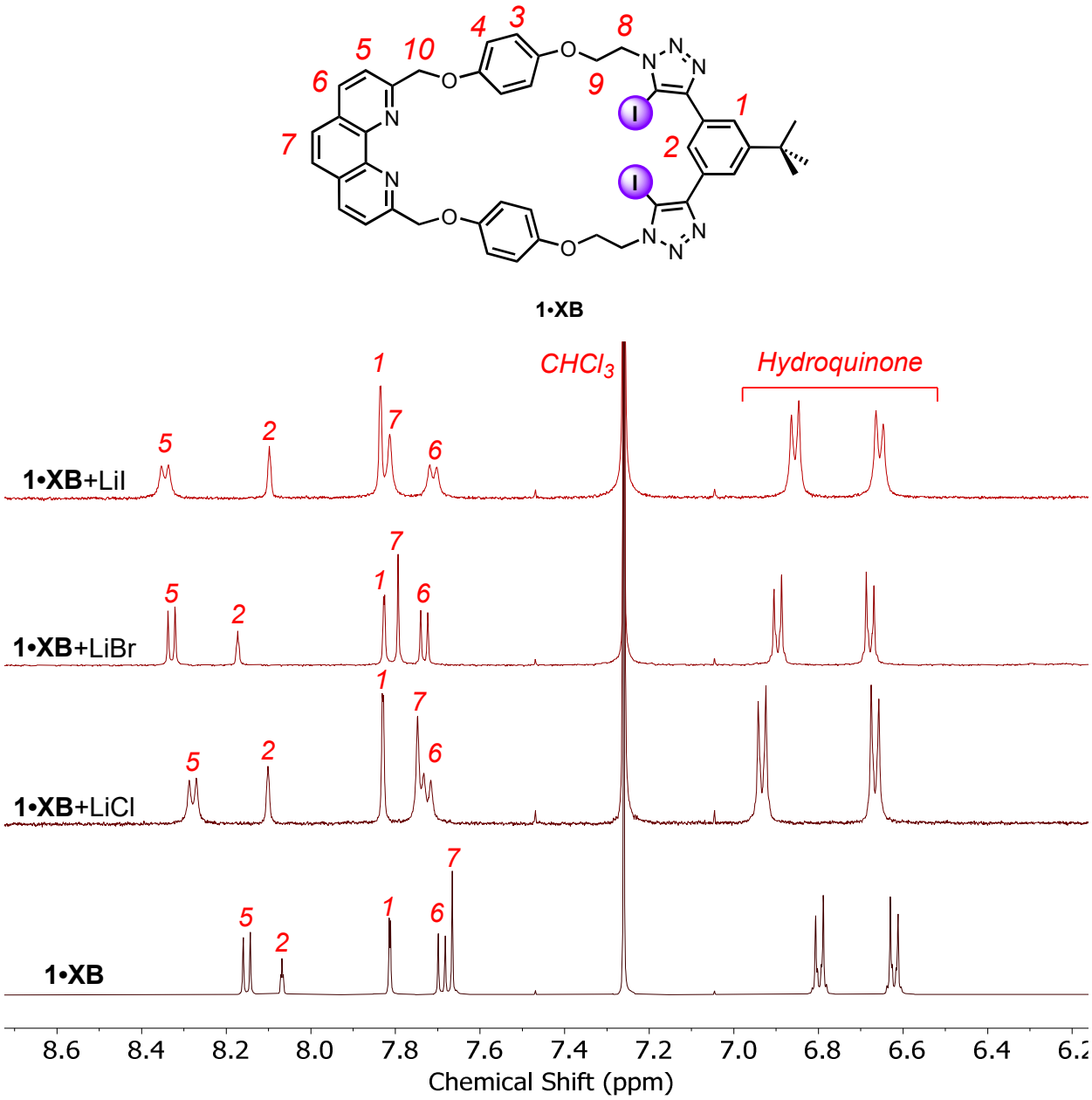


Figure S5-1. Comparative pre- and post-extraction [1]H NMR spectra of **1•XB** with excess solid LiCl, LiBr and LiI (500 MHz, 298 K, 3:1 $CDCl_3$:CD_3CN).

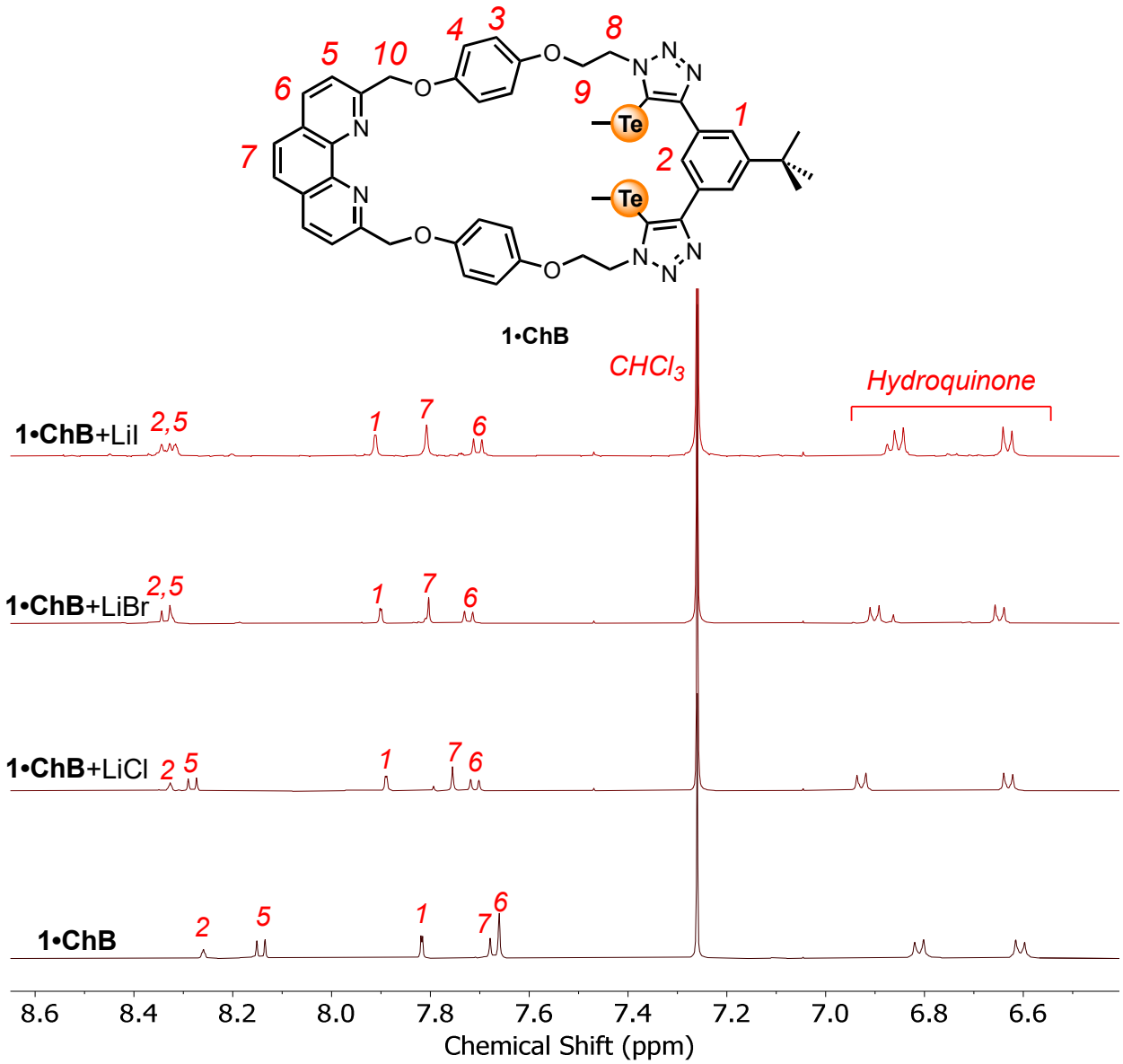


Figure S5-2. Comparative pre- and post-extraction ^{1}H NMR spectra of **1•ChB** with excess solid LiCl, LiBr and LiI (500 MHz, 298 K, 3:1 $CDCl_3$:CD_3CN).

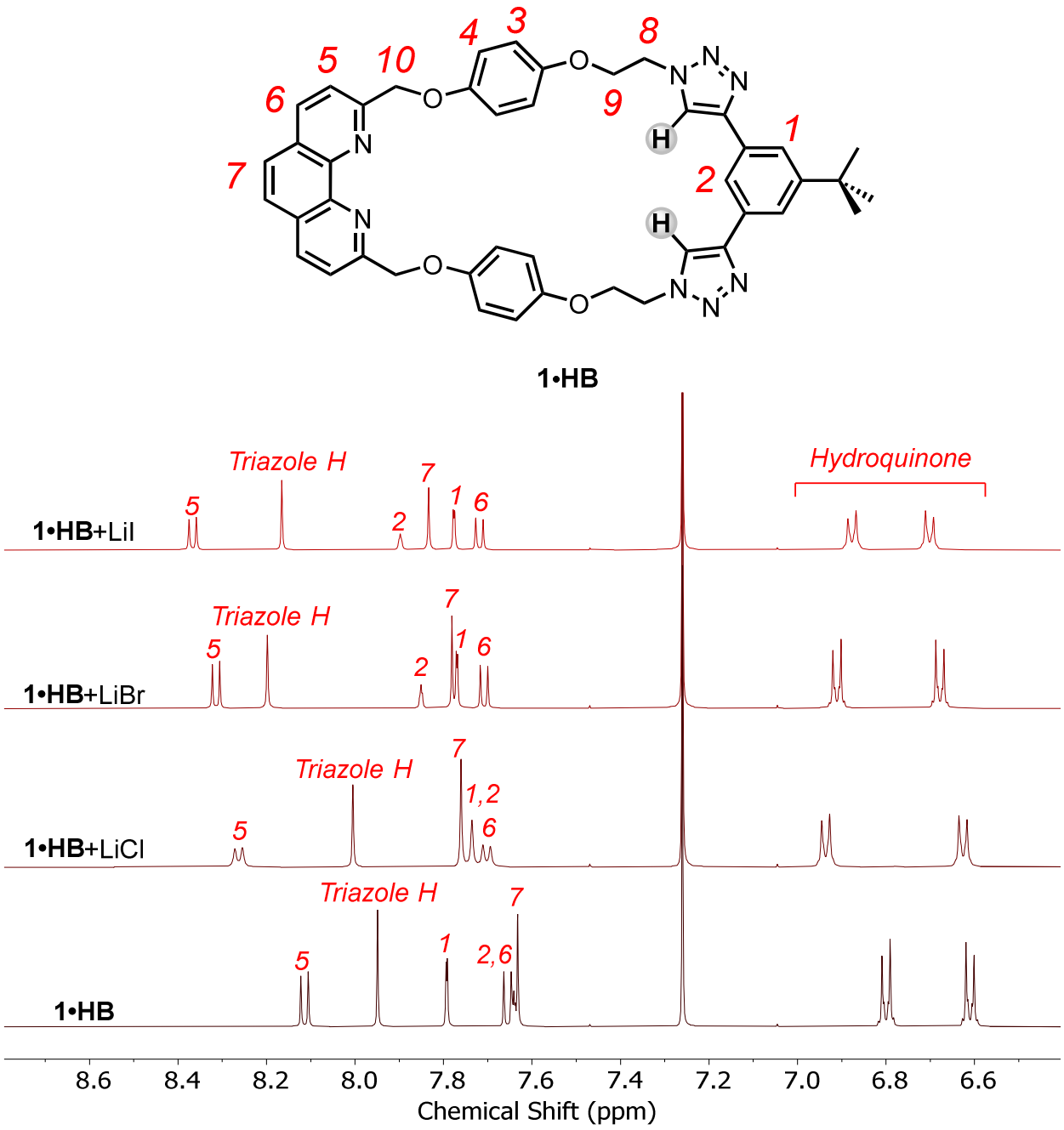


Figure S5-3. Comparative pre- and post-extraction ^{1}H NMR spectra of **1•HB** with excess solid LiCl, LiBr and LiI (500 MHz, 298 K, 3:1 $CDCl_3$:CD_3CN).

S6 References

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