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Supplementary Information

Fluorescence Emission Enhancement of a T-Shaped Benzimidazole with a Mechanically-Interlocked 'Suit'

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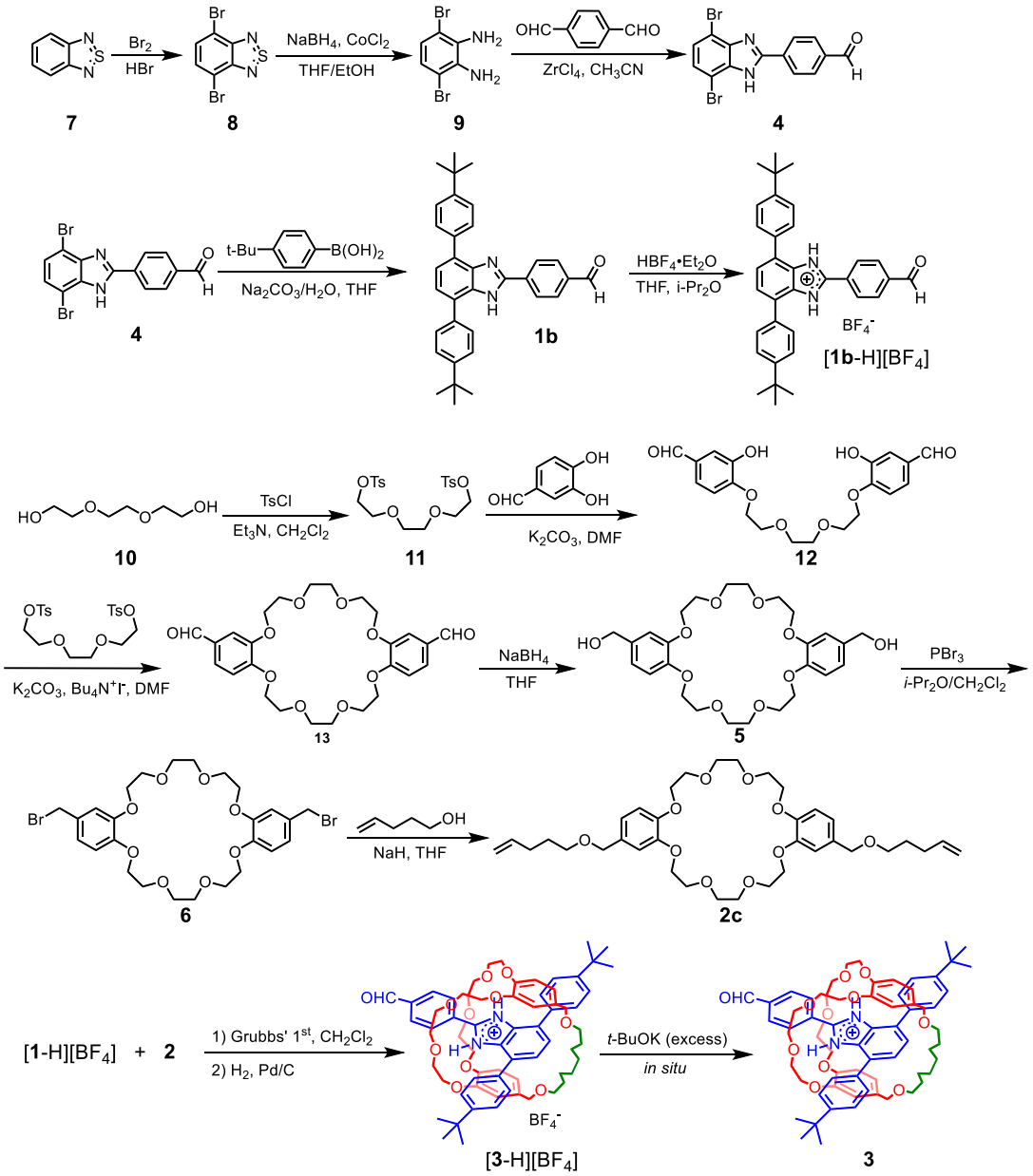
Table of Contents

General Comments

Chemicals were purchased from commercial suppliers and used without further purification unless stated otherwise. Tetrahydrofuran (THF), dichloromethane (DCM) and N, N-dimethylacetamide (DMF) were degassed and dried under nitrogen by passing them through a Vigor VSGS-5 Solvent Purification System. Reaction progress was monitored by thin layer chromatography (TLC) or on an Advion Plate Express® Automated TLC plate reader (TLC/CMS). Flash column chromatography was performed over silica gel (200-300 mesh). NMR spectra were recorded on a JEOL 400YH instrument. NMR spectra were internally referenced to tetramethylsilane (^{1}H) or alternatively, to the residual proton solvent signal (^{13}C). All ^{13}C NMR spectra were recorded with complete proton decoupling. UV-vis absorbance spectra were recorded on a Shimadzu UV-2600 spectrophotometer. Fluorescence spectra were recorded on a Shimadzu RF-6000 fluorescence spectrometer. The fluorescence quantum yields of liquid samples were determined by a Hamamatsu C9920 quantum efficiency measurement system. The fluorescence quantum yields of solid powders were measured on a spectrometer (FLS980) from Edinburgh Instruments Ltd. with an integrating sphere (φ 150 mm). ESI-MS data were recorded either on an Advion Expression LCMS instrument or a Thermo Fisher Scientific LTQ Orbitrap Elite LC/MS (ESI). HR-ESI-MS data were recorded on a Bruker timsTOF™ mass spectrometer.

Synthetic Methods



Scheme S1 Synthetic steps of compounds in this work.

Synthesis of 8

Compounds **8** was synthesized using a reported literature method.[1] Benzothiodiazole (**5**, 10.00 g, 73.4 mmol) was dissolved in a aqueous solution of HBr (150 mL, 48%). A solution of Br_2 (35.20 g, 11.3 mL) in HBr (100 mL, 48%) was added dropwise to form a mixture, which was stirred, heated to 100 °C and refluxed for 6 hours. An orange solid should precipitate during the reaction. After the mixture was cooled to room temperature, a saturated solution of $NaHSO_3$ was added dropwise to quench the excess Br_2. The mixture was then filtered, with the filtrate washed with water (5 × 100 mL), and dried under vacuum to give **8** as a yellow crystalline solid. Yield: 20.48 g, 95 %. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.71 (s, 2H).

Synthesis of 9

To a solution of 4,7-dibromobenzothiodiazole (**9**) (5.000 g, 17.0 mmol) in THF/EtOH (1 : 3) (250 mL), $NaBH_4$ (1.930 g, 51.0 mmol) was added in portions. After addition, $CoCl_2 \cdot 6H_2O$ (405 mg, 1.70 mmol) was added. The resulting black mixture was refluxed for 30 min, cooled to room temperature and then filtered. The filtrate was concentrated and partitioned between brine (100 mL) and CH_2Cl_2 (3 × 100 mL). The combined organic phase was dried over anhydrous Na_2SO_4. Removal of the solvent under vacuum gave **7** as a black tar. Yield: 4.306 g, 95%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 6.85 (s, 2H).

Synthesis of 4

9 (4.306 g, 16.2 mmol) was dissolved in 120 mL of CH_3CN. Terephthalaldehyde (21.72 g, 162 mmol), and $ZrCl_4$ (377 mg, 1.62 mmol) were added to the solution. The mixture was stirred at room temperature for 24 h and filtered. The solids were washed with CH_3CN (3 × 50 mL). A pale yellow solid (**7**) was obtained after air drying. Yield: 3.380 g, 55 %. ^{1}H NMR (400 MHz, CD_3SOCD_3, 298 K): δ = 13.52 (b, 1H), 10.10 (s, 1H), 8.55 (d, J = 8.1 Hz, 2H), 8.10 (d, J = 8.1 Hz, 2H), 7.43 (s, 2H).

Synthesis of 1b

In a Schlenk flask, **4** (500 mg, 1.32 mmol), *p*-(*t*-butyl)phenyl boronic acid (515 mg, 2.89 mmol), palladium *tetrakis* (triphenylphosphine) (152 mg, 0.132 mmol) was added. After the flask was degassed and backfilled with N_2, A degassed solution of Na_2CO_3 (30 mL) and degassed THF (30 mL) was added. The reaction mixture was heated to 80 °C, stirred for 24 h under nitrogen, and then cooled to room temperature. Ethyl acetate (50 mL) was added and the phases were separated. The aqueous phase was extracted with ethyl acetate (2 × 50 mL) and the combined organic phases were washed once with brine (50 mL), dried on sodium sulphate and concentrated under reduced pressure. The crude compound was further purified by column chromatography on silica gel (elutes with PE:EA = 4:1), affording a pale yellow solid. Yield: 610 mg, 94 %. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) δ = 10.03 (s, 1H), 8.24(d, 2H, J = 8.4 Hz), 7.98 (d, 2H, J = 8.4 Hz), 7.90-7.80 (m, 4H), 7.59 (d, 2H, J = 8.1 Hz), 7.47 (s, 2H), 1.41 (s, 18H).

Synthesis of [1b-H][BF_4]

To a solution of **1b** (100 mg, 0.205 mmol, 1 eq) in diisopropyl ether (50 mL), tetrafluoroboric acid diethyl ether complex (39.9 mg, 0.247 mmol, 1.2 eq) was added dropwise. The resulting yellow solid was filtered, washed with diisopropyl ether and air dried. Yield: 112 mg, 95 %. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 9.53 (s, 1H), 8.13 (d, 2H, J = 8.5 Hz), 7.69 (m, 8H), 7.56 (d, 2H, J = 8.0 Hz), 1.43 (s, 18H).

Synthesis of 11

Triethyleneglycol (33.00 g, 220 mmol) and triethylamine (53.37 g, 527 mmol) were dissolved in CH_2Cl_2 (250 mL) and the solution was cooled down to 0 °C. A solution of tosyl chloride (100.6 g, 527 mmol) and were added through a dropping funnel. The resulting mixture was stirred for 16h at room temperature. The solution was washed with 5% HCl (aq) (50 mL), saturated $NaHCO_3$ (50 mL), H_2O (50 mL) in sequence. The organic layer was dried over Na_2SO_4. After evaporation of solvent, the crude product was purified via recrystallization in MeOH, affording a white to transparent crystalline powder. Yield: 93.10 g, 92 %. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ =7.78 (d, J = 8.0 Hz, 4H), 7.33 (d, J = 8.0 Hz, 4H), 4.13 (t, J = 4.8 Hz, 4H), 3.65 (t, J = 4.8 Hz, 4H), 3.52 (s, 4H), 2.44 (s, 6H).

Synthesis of 12

The synthesis of **12** and **13** was carried out according to a literature method reported by Stoddart et al.[2] A solution of **11** (19.00 g, 0.0414 mol), 3,4-dihydroxybenzaldehyde (11.45 g, 0.0829 mol), and K_2CO_3 (11.45 g, 0.0829 mol) in 120 mL of DMF was heated at 60 °C for 5 h under N_2. Removal of the solvent in vacuo afforded a black tar, which was partitioned between H_2O (250 mL) and CH_2Cl_2 (3 × 150 mL). The aqueous layer was extracted with H_2O (100 mL) and CH_2Cl_2 (3 × 200 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was evaporated to yield a black tar which was purified by flash chromatography (SiO_2: EtOAc) to afford **12** as a white solid. Yield: 4.362 g, 27 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.82 (s, 2H), 7.42 (d, 2H, J = 2.0 Hz), 7.39 (d, 2H, J = 2.0 Hz), 7.37 (d, 2H, J = 2.0 Hz), 6.96 (d, 2H, J = 8.3 Hz), 4.28-4.24 (m, 4H), 3.93-3.89 (m, 4H), 3.79 (s, 4H).

Synthesis of 13

11 (3.520 g, 7.68 mmol) and diol **12** (3.000 g, 7.68 mmol) were dissolved in DMF (250 mL). K_2CO_3 (10.62 g, 76.8 mmol), and *n*-Bu_4NI (TBAI, 284 mg, X 0.768 mmol) were added to the solution. The temperature of the reaction was raised to 60 °C and stirred for 72 hours and then cooled to room temperature. The reaction mixture was filtered and the solid washed with DMF (50 mL). Removal of the solvent *in vacuo* afforded a yellow residue, which was partitioned between H_2O (150 mL) and CH_2Cl_2 (3 × 150 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was evaporated off to obtain a residue which was purified by flash chromatography (SiO_2: EtOAc) to give **13** as a white solid. Yield: 2.071 g, 53 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = δ = 9.91 (s, 2H), 7.43 (d, 2H J = 1.9 Hz), 7.40 (d, 2H J = 1.9 Hz), 7.36 (d, 2H J = 1.9 Hz), 6.92 (d, 2H, J = 8.2 Hz), 4.23-4.17 (m, 8H), 3.97-3.91 (m, 8H), 3.86-3.81 (m, 8H).

Synthesis of 5

A solution of **13** (1.880 g, 3.72 mmol) in THF (50 mL) was cooled down to 0 °C. $NaBH_4$(283 mg, 7.45 mmol) was added, and the solution was stirred under N_2 for 24 hours. HCl was added dropwise to quench the reaction. After addition of saturated solution of NaCl (20 mL), the mixture was extracted with EtOAc (4 × 20 mL). The organic phase was dried with Na_2SO_4 and removed of its solvent in *vacuo*, affording **5** as a transparent solid, which was used in the next step without further purification. Yield: 1.535 g, 82 %. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 6.91-6.79 (m, 6H), 4.58 (s, 4H), 4.17-4.12 (m, 8H), 3.92-3.88 (s, 8H), 3.82 (s, 8H).

Synthesis of 6

To a sealed flask containing a solution of **5** (1.500 g, 2.95 mmol) in CH_2Cl_2/Diisopropyl ether (1:1, 100 mL), phosphorus tribromide (4.79 g, 1.66 mL, 17.7 mmol) was added dropwise with an injector. After stirring for 24 h at room temperature under N_2 protection, CH_2Cl_2 (50 mL) was added to the mixture and then the solution carefully poured on to ice-water (100 g). The organic phase was separated, washed with saturated $NaHCO_3$ solution (30 mL) and brine (30 mL). After drying over anhydrous $NaSO_4$, the solvent was removed on a rotary evaporator. The oily residue solidified after the addition of ethyl acetate (10 mL). The solid was collected by filtration, rinsed with ether and air dried. Yield: 1.843 g, 98 %. The product was utilised in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 6.94-6.90 (m, 4H), 6.79 (d, 2H, J = 8.1 Hz), 4.46 (s, 4H), 4.19-4.13 (m, 8H), 3.93-3.89 (m, 8H), 3.81-3.79 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 149.09 and 148.88, 130.91, 122.28, 114.82, 113.68, 71.19, 69.77 and 69.74, 69.44, 34.29, 29.78.

Synthesis of 2c

Sodium hydride (60% in mineral oil, 631 mg, 15.8 mmol) was dissolved in a minimum amount of THF in a Schlenk flask under N_2 atmosphere. A solution of 4-penten-1-ol (1358 mg, 15.8 mmol) in THF (10 mL) was added dropwise to the mixture. After cessation of bubbling, the mixture was allowed to stir for 1 h at room temperature. A solution of **6** (1000 mg, 1.58 mmol) in THF (60 mL) was then introduced to the mixture in portions by syringe. The mixture was further stirred at room temperature for 24 hours and quenched by carefully addition of water dropwise. After ethyl acetate (30 mL) and brine (30 mL) were added, the organic layer was extracted with ethyl acetate (4 × 30 mL) and dried over anhydrous magnesium sulphate. Removal of the solvent gave a viscous oil which was purified by column chromatography (SiO_2, ethyl acetate / PE = 1:4) as a colorless oil. Yield: 691 mg, 68 %. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 6.88-6.79 (m, 6H), 5.85-5.74 (m, 2H), 5.03-4.91 (m, 4H), 4.39 (s, 4H), 4.16-4.11 (m, 8H), 3.92-3.88 (m, 8H), 3.81 (m, 8H), 3.43 (t, 4H, J = 6.6 Hz), 2.15-3.08 (m, 4H), 1.72-1.64 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 149.02, 148.46, 138.37, 131.91, 120.82, 114.80, 113.88, 113.70, 72.75, 71.32, 69.99, 69.61,

69.56 and 69.45, 30.43, 29.02. HR-MS (ESI): 667.3458 calcd for $C_{36}H_{53}O_{10}$ $[M+Na]^+$, found: 667.3453; 662.3904 calcd for $C_{36}H_{53}O_{10}$ $[M+NH_4]^+$, found: 662.3901.

Synthesis of [3-H][BF_4]

A mixture of [**1b**-H][BF_4] (307 mg, 0.533 mmol, 1.5 eq) and **2c** (230 mg, 0.357 mmol, 1.0 eq) in CH_2Cl_2 (5 mL) was stirred at room temperature for 30 min. Grubbs' 1st gen catalyst (30 mg, 0.0365 mmol, 0.1 eq) was added subsequently, the mixture was heated at 43 ºC for 24 hours. An additional portion of catalyst (15 mg, 0.0182 mmol, 0.05 eq) was added and heated at 43 ºC for another 24 hours. After saturated $NaHCO_3$ (aq) (10 mL) was added, the organic phase was extracted and removed of its solvent in *vacuo*. The dark oily residue [**3**-H][BF_4] was purified by column chromatography (SiO_2, CH_2Cl_2). There are tautomers of [**3**-H][BF_4], which were very difficult to furtherly separate. The residue was dissolved in CH_2Cl_2 (10 mL) and was added to a Schlenk flask which was equipped with 5% Pd/C (760 mg, 0.357 mmol) under N_2 atmosphere. The flask was slightly degassed and flushed and H_2 introduced via a balloon. The mixture was stirred overnight under ambient conditions. After being filtered, the mixture was evaporated on a rotary evaporator to give the dark residue, which was subsequently purified through recrystallization. Yield: 187 mg, 44 %. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 13.09 (s, 1H), 13.00 (s, 1H), 10.32 (s, 1H), 8.51 (d, 2H, J = 8.3 Hz), 8.39 (d, 2H, J = 8.3 Hz), 7.76 (d, 2H, J = 8.4 Hz), 7.62-7.58 (m, 4H), 7.45 (d, 2H, J = 8.4 Hz), 6.86 (dd, 2H, J1 = 7.8 Hz, J2 = 18.8 Hz), 6.49-6.44 (m, 2H), 6.21-6.12 (m, 4H), 4.24 (d, 2H, J = 11.6 Hz), 4.16 (d, 2H, J = 11.6 Hz), 3.80-3.25 (m, 24H), 3.22-3.15 (m, 4H), 2.97-2.8 4(m, 4H), 1.45-1.42 (m, 18H), 1.37-1.29 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 192.85, 152.41, 149.37, 147.59, 146.89, 139.08, 132.79, 132.38, 130.64, 130.10, 129.92, 129.30, 128.69, 128.47, 126.12, 125.73, 125.56, 125.09, 124.77, 121.80, 113.58, 111.82, 73.39, 70.26, 69.99, 69.72, 67.79, 67.69, 34.96, 32.01, 31.62, 31.56, 30.25, 29.78, 29.44, 28.86, 25.62, 22.77, 14.20. HR-MS (ESI): 1105.6148 calcd for $C_{68}H_{85}N_2O_{11}^+$ $[M+H]^+$, found: 1105.6156.

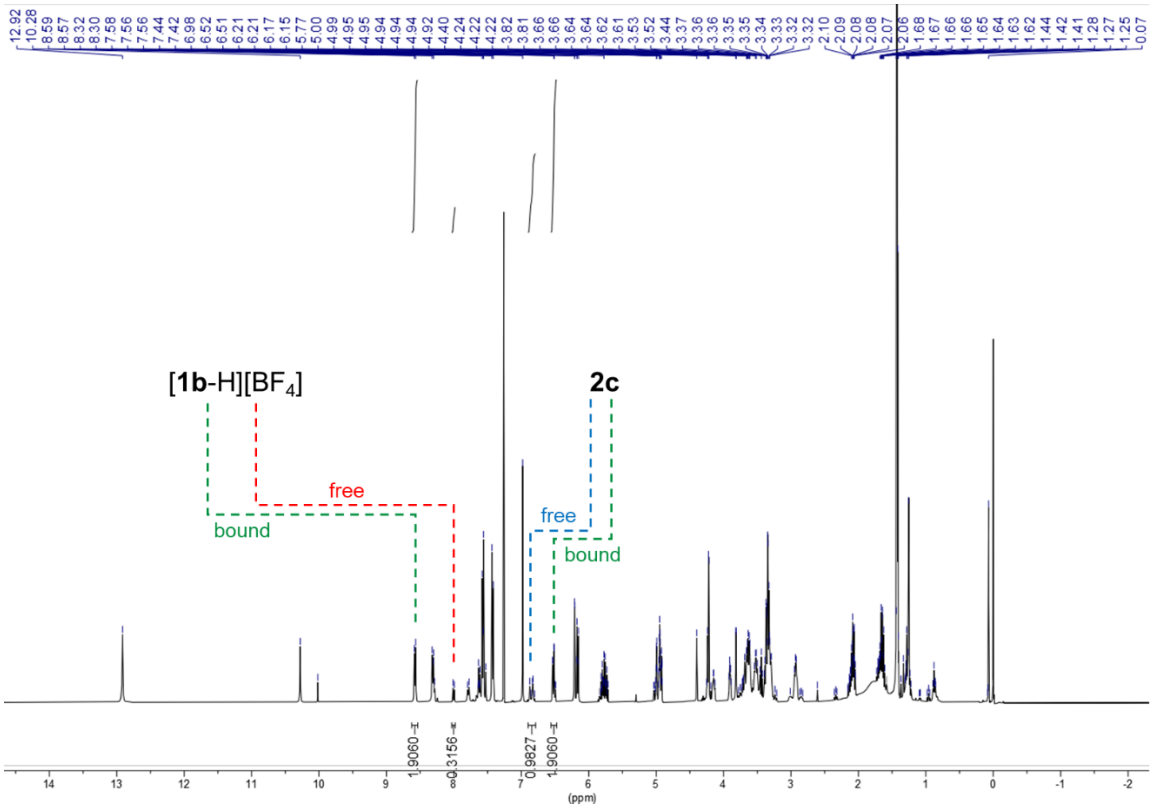
Synthesis of 3

20 equivalents of *t*-BuOK was added to a solution of [**3**-H][BF_4] in either THF or CD_2Cl_2 to give **3** *in situ*. The resultant product was used without further separation. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) δ = 11.74 (s, 1H), 10.15 (m, 1H), 8.90 (m, 2H), 8.04 (m, 2H), 7.88 (m, 2H), 7.75 (m, 2H), 7.59 (m, 2H), 7.46 (m, 2H), 6.79 (s, 2H), 6.34 (m, 2H), 5.98 (m, 4H), 4.15 (m, 2H), 4.00 (m, 4H), 3.87-3.16 (m, 22H), 3.09 (m, 2H), 2.95 (m, 2H), 1.44 (m, 26H). HR-MS (ESI): 1105.6148 calcd for $C_{68}H_{85}N_2O_{11}^+$ $[M+H]^+$, found: 1105.6145.

Determination of Association Constant between [1b-H][BF_4] and 2c

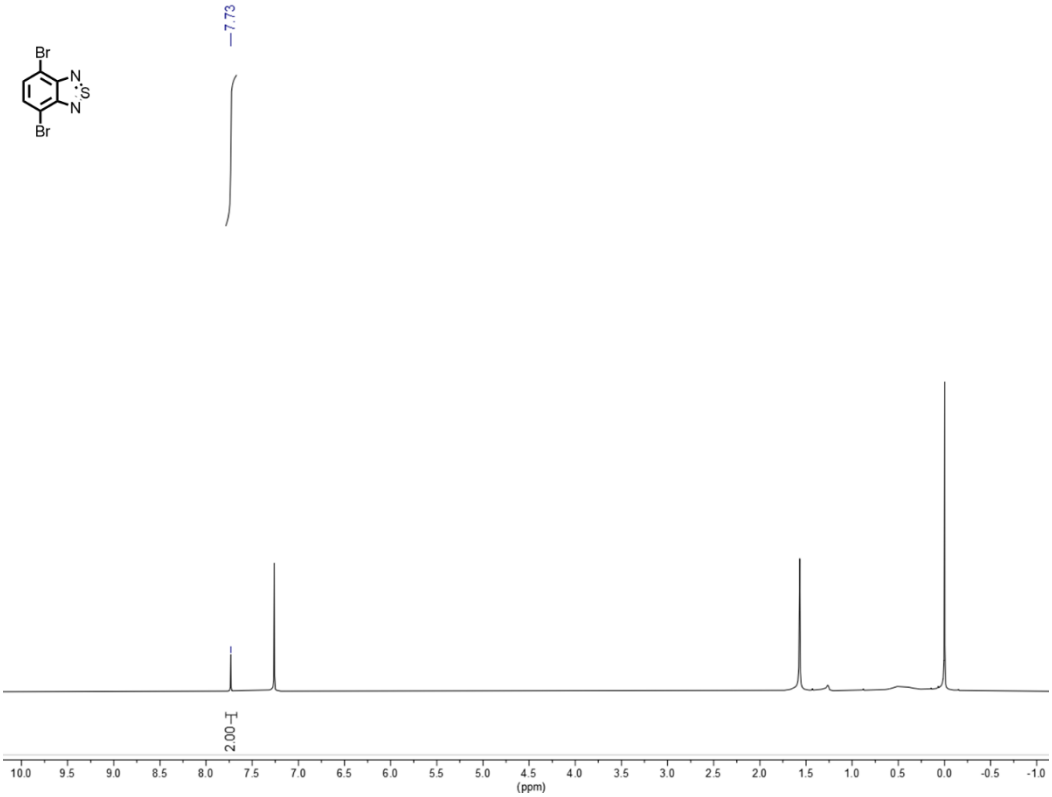
[**1b**-H][BF_4] (3.41 mg, 5.925 µmol), **2c** (3.81 mg, 5.908 µmol), were dissolved in 0.590 mL of $CDCl_3$ and ^{1}H NMR spectrum of this solution was collected

subsequently. According to integration of peaks, the ratio of the concentration of the complex to [**1b**-H][BF_4] is 6.0393, while the ratio of the concentration of the complex to **2c** is 5.8181. The association constant K_A can be therefore determined as 4.073 × 10^3 L·mol^{-1}. Errors are estimated to be less than 10%.

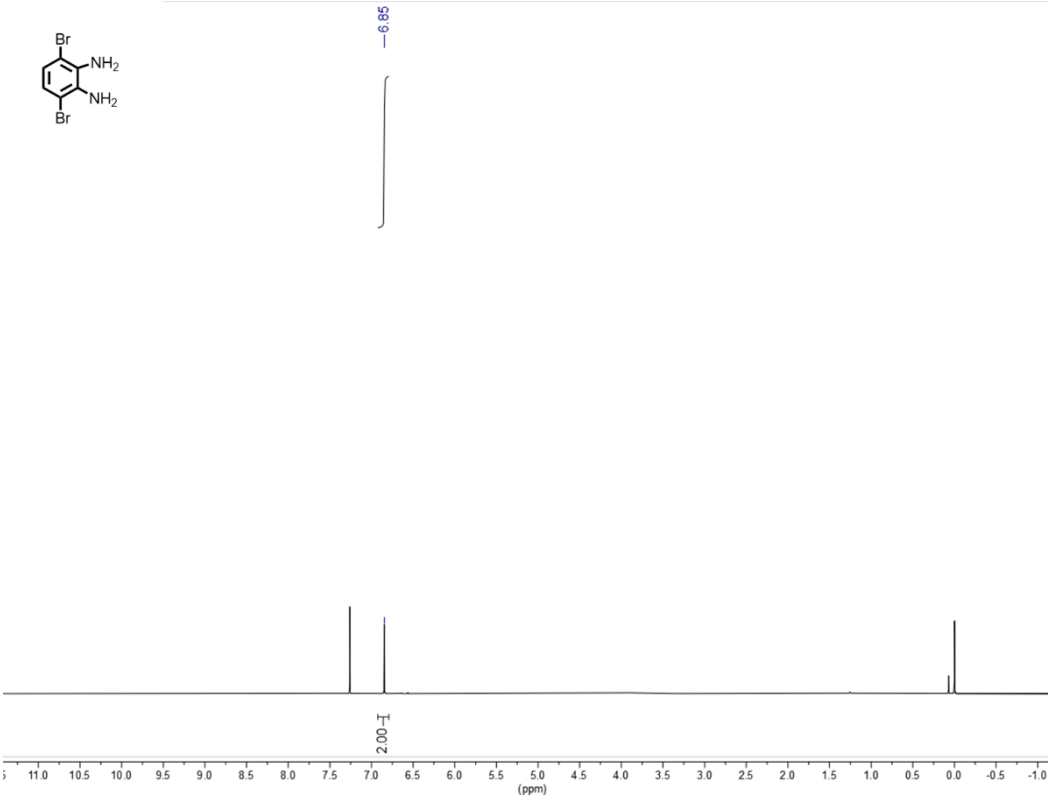


Supplementary Figure 1. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$, 298K) of a 1:1 mixture of [**1b**-H][BF_4] and **2c** in $CDCl_3$.

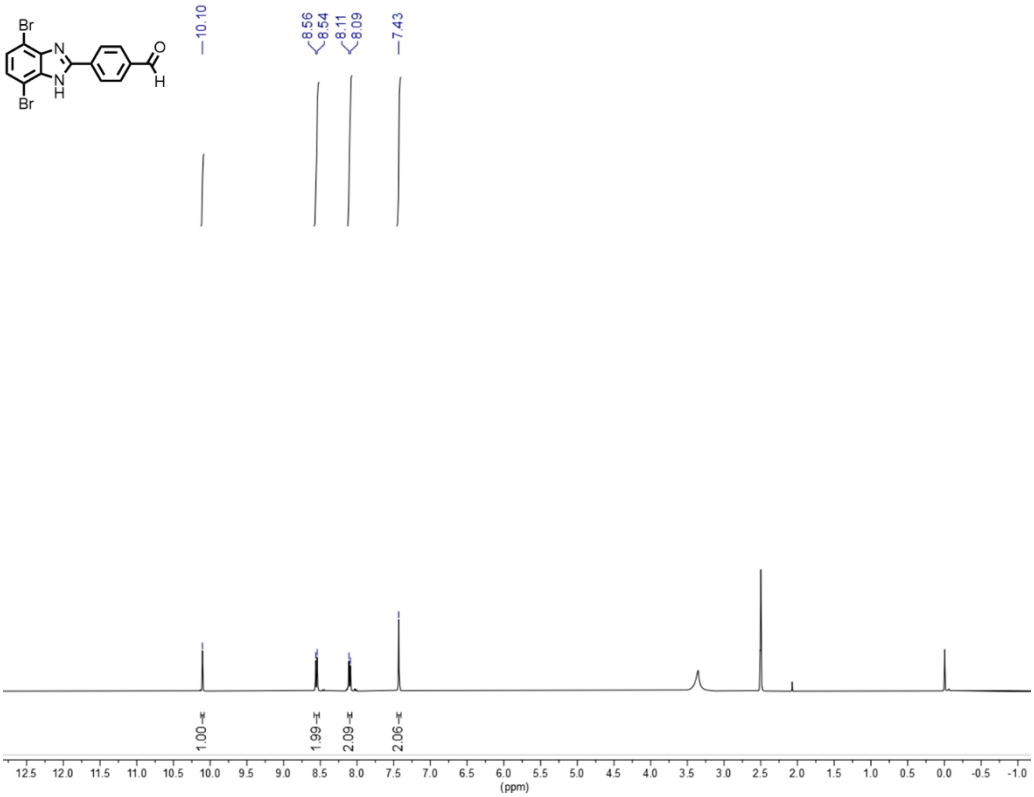
NMR Spectra of Compounds



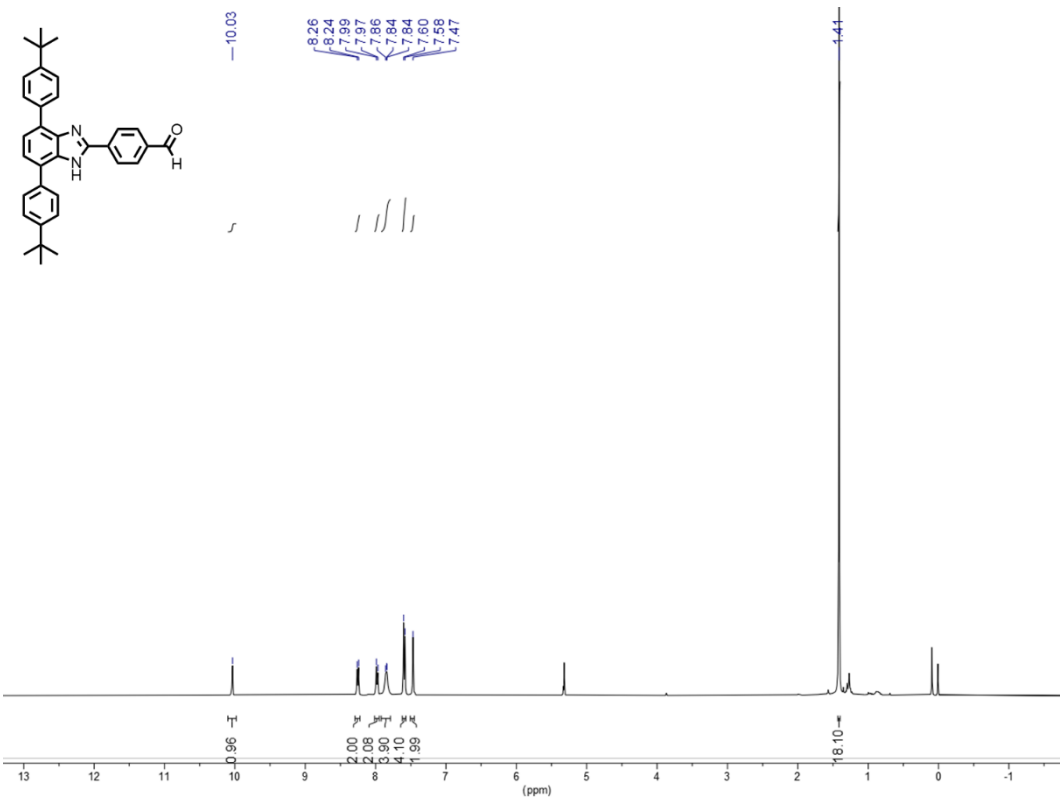
Supplementary Figure 2. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$, 298K) of **8**.



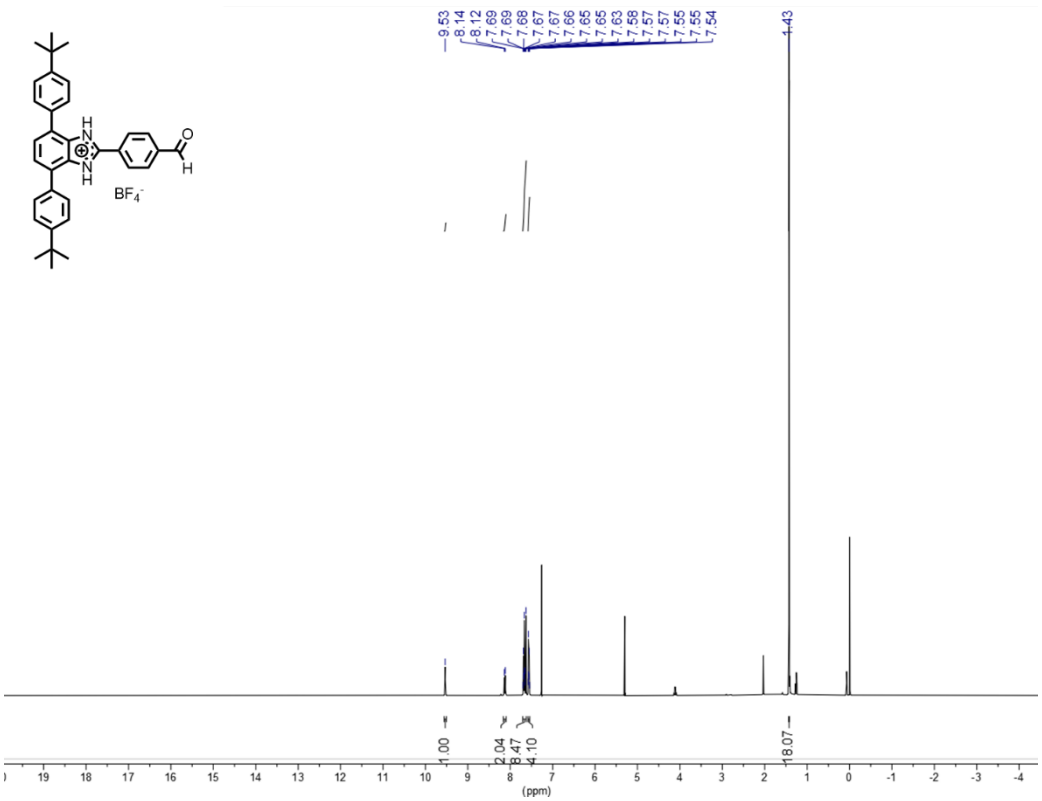
Supplementary Figure 3. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$, 298K) of **9**.



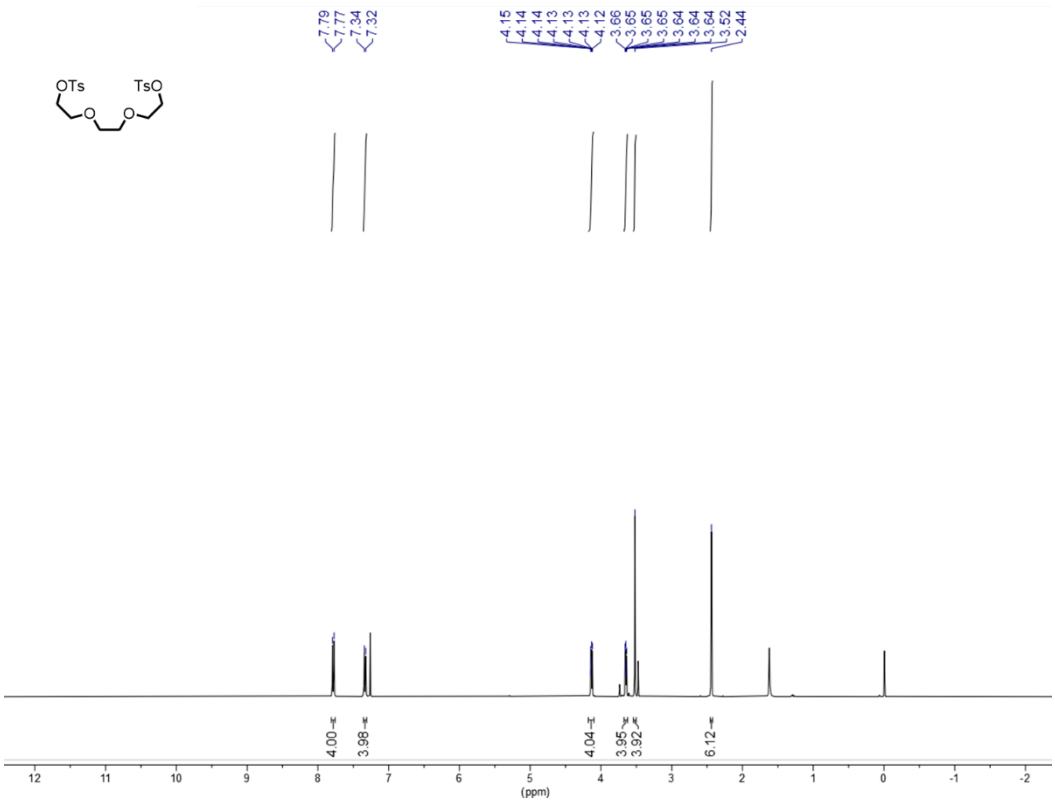
Supplementary Figure 4. ^{1}H NMR Spectrum (400 MHz, CD_3SOCD_3, 298K) of **4**.



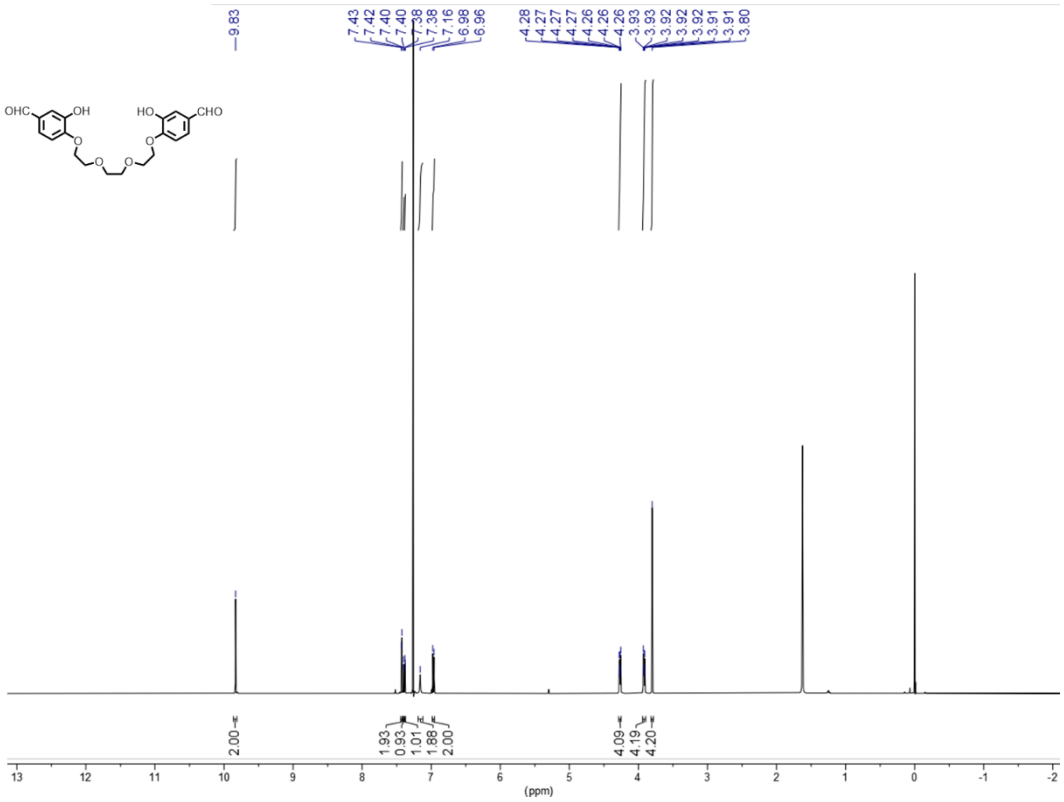
Supplementary Figure 5. ^{1}H NMR Spectrum (400 MHz, CD_2Cl_2, 298K) of **1b**.



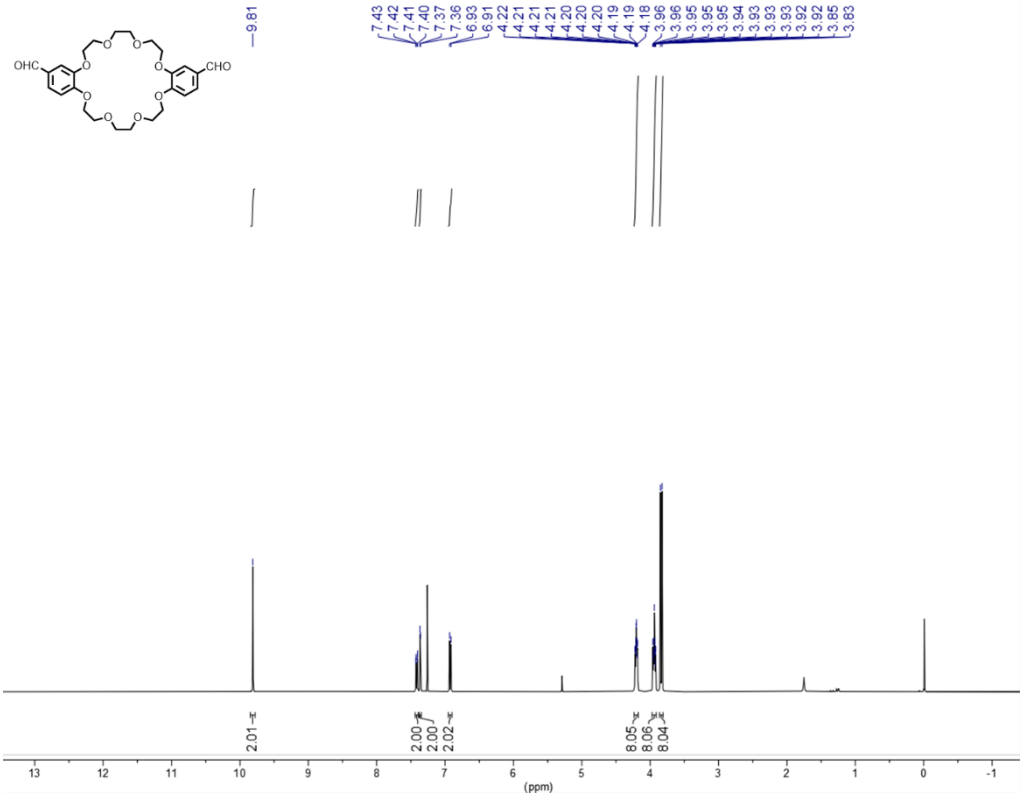
Supplementary Figure 6. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$, 298K) of [**1b**-H][BF_4].



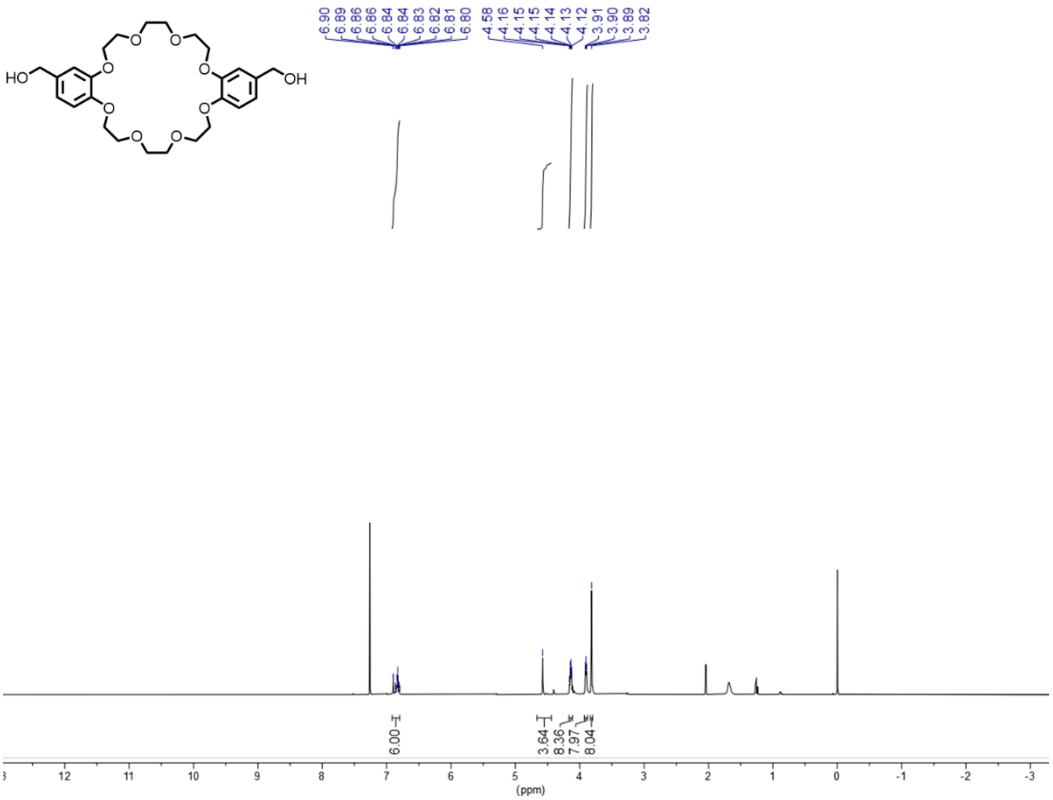
Supplementary Figure 7. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$, 298K) of **11**.



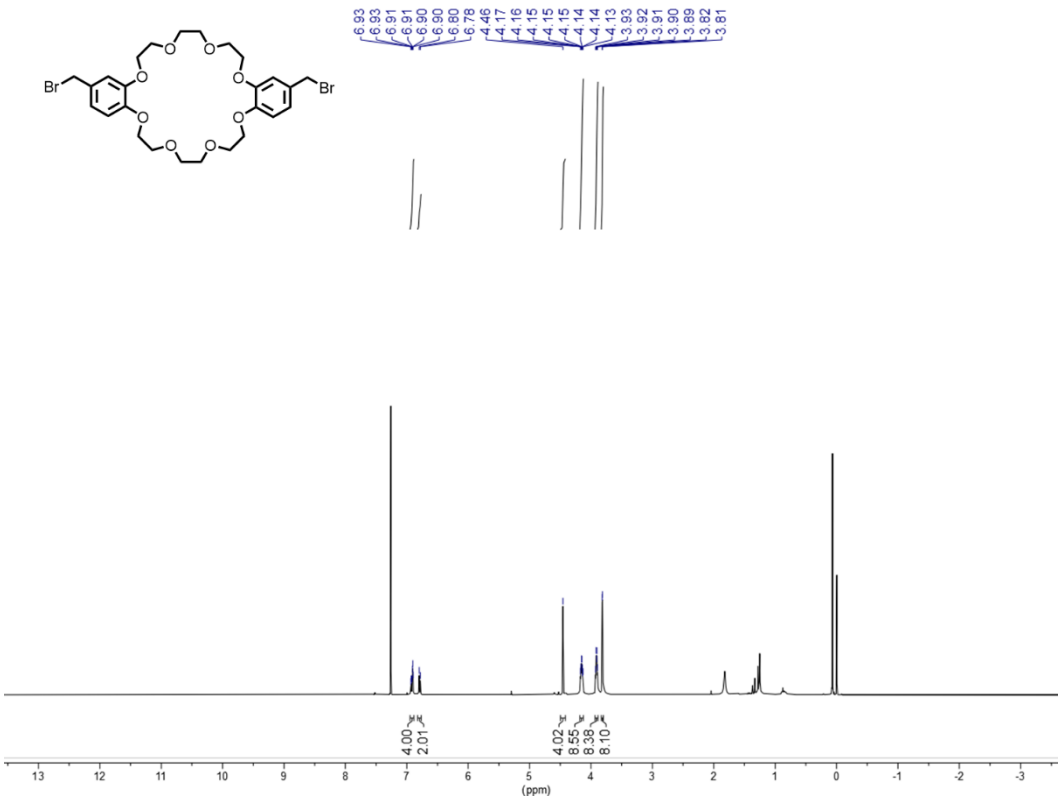
Supplementary Figure 8. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$, 298K) of **12**.



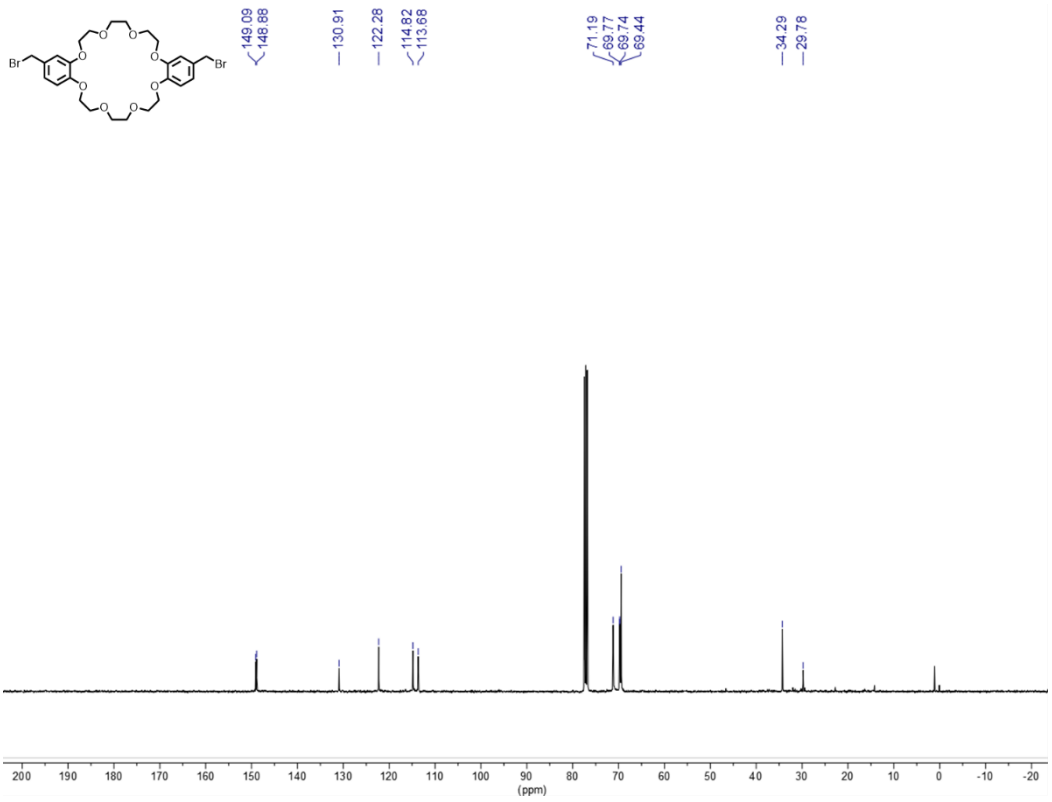
Supplementary Figure 9. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$, 298K) of **13**.



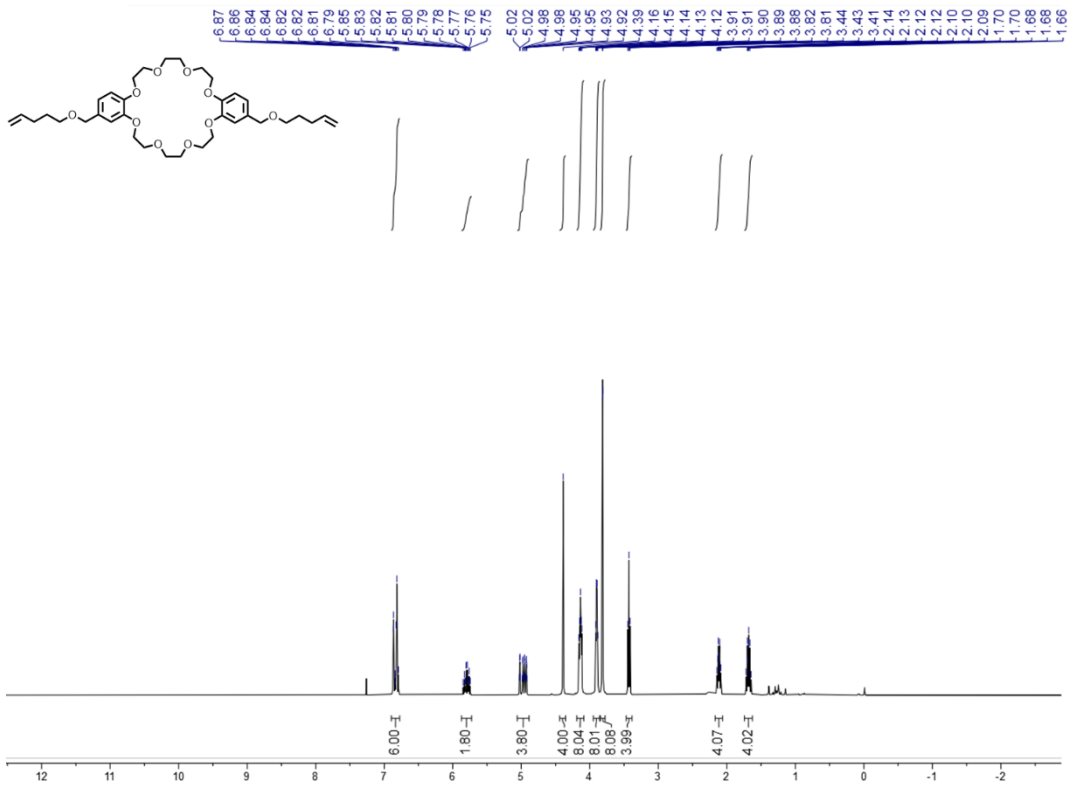
Supplementary Figure 10. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$, 298K) of **5**.



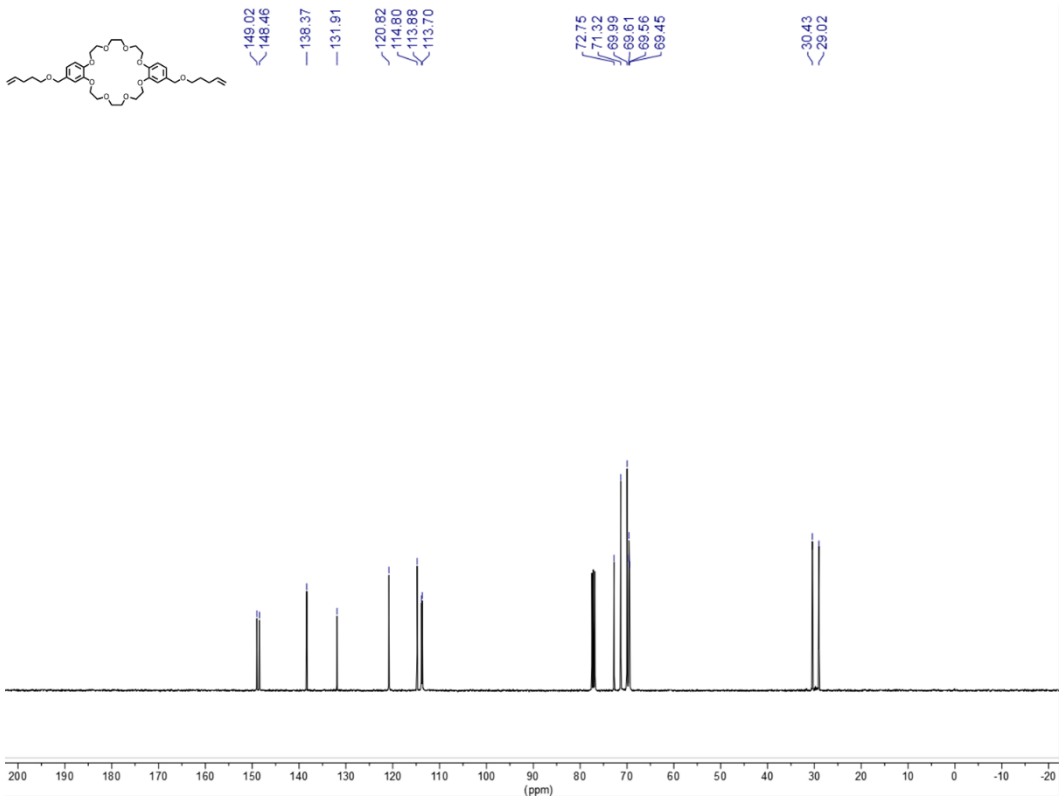
Supplementary Figure 11. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$, 298K) of **6**.



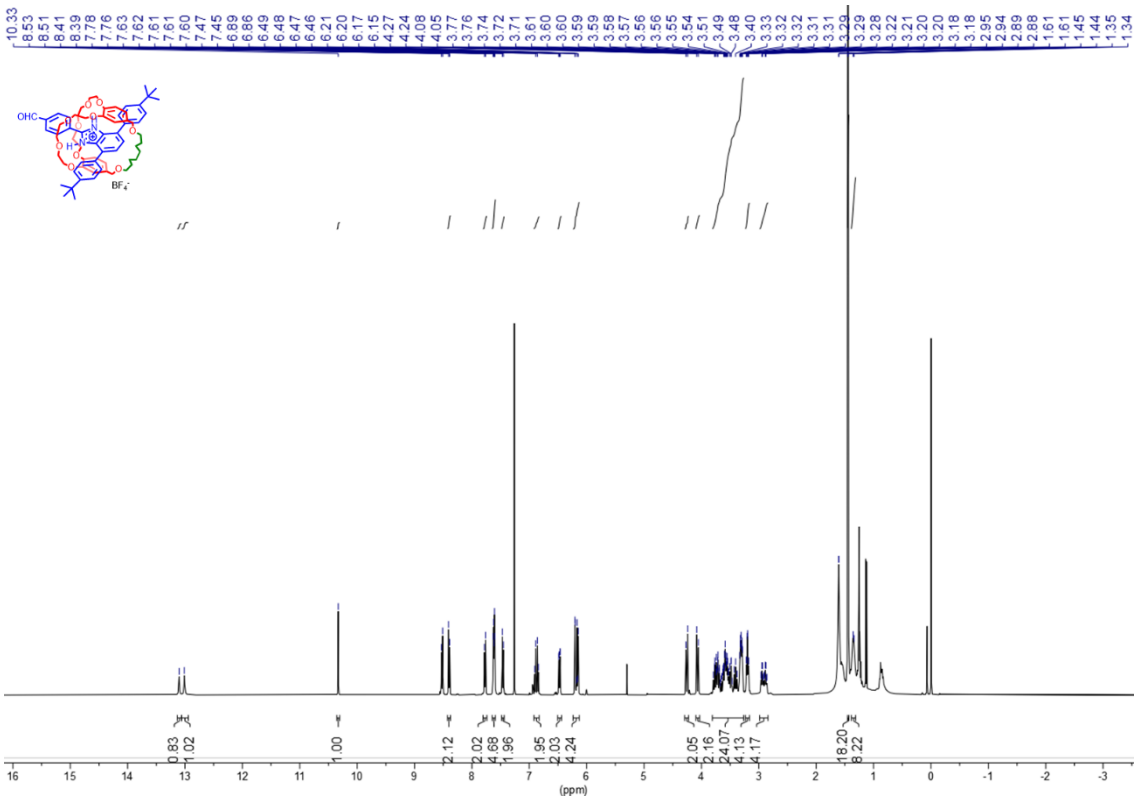
Supplementary Figure 12. ^{13}C NMR Spectrum (400 MHz, $CDCl_3$, 298K) of **6**.



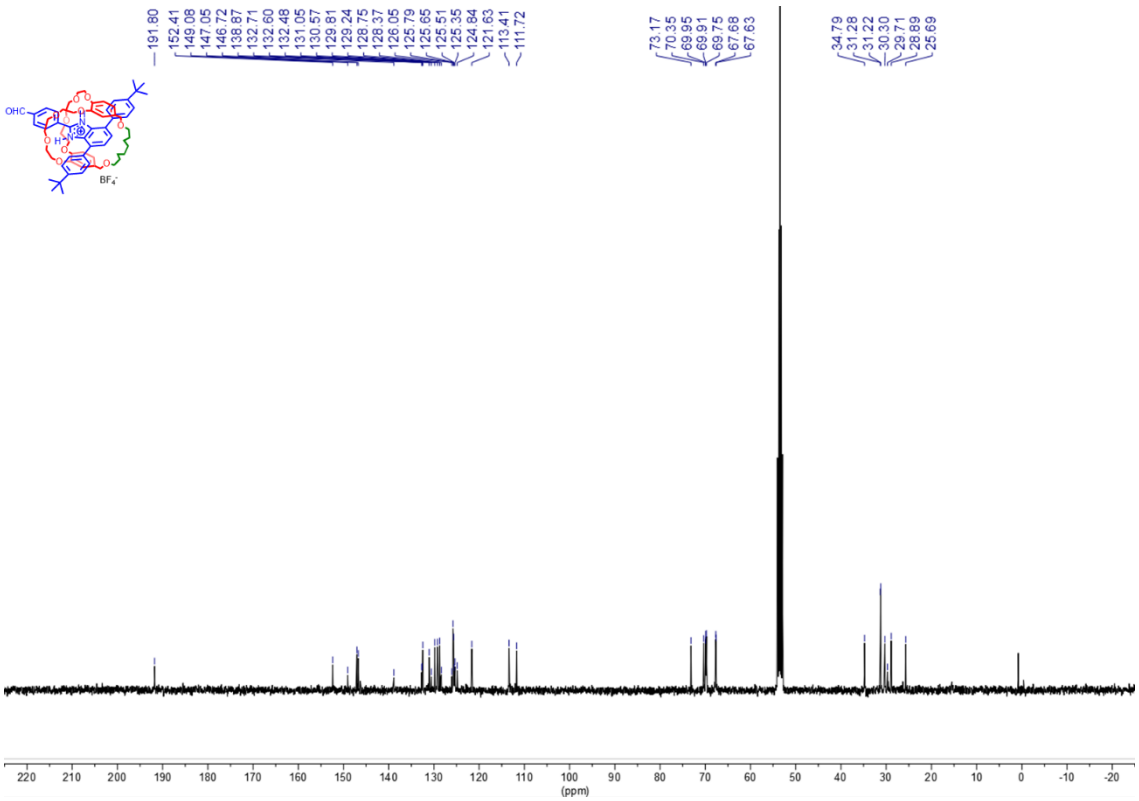
Supplementary Figure 13. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$, 298K) of **2c**.



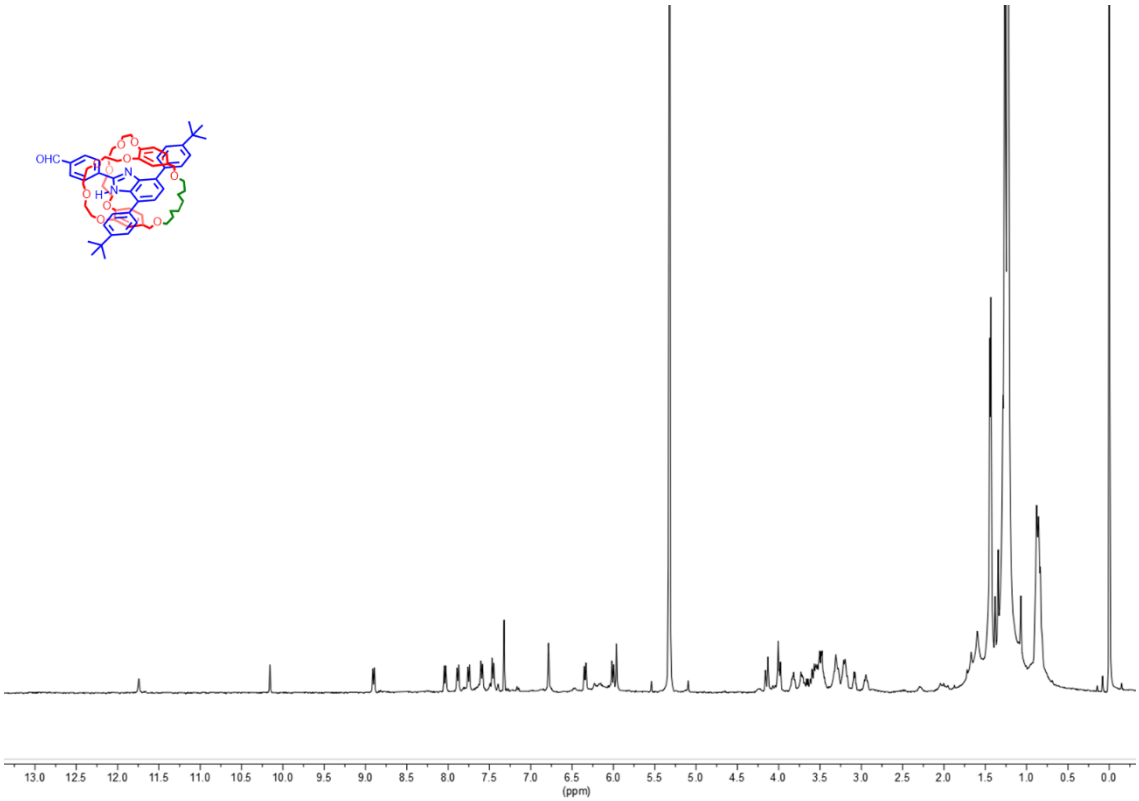
Supplementary Figure 14. ^{13}C NMR Spectrum (100 MHz, $CDCl_3$, 298K) of **2c**.



Supplementary Figure 15. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$, 298K) of [**3**-H][BF_4].

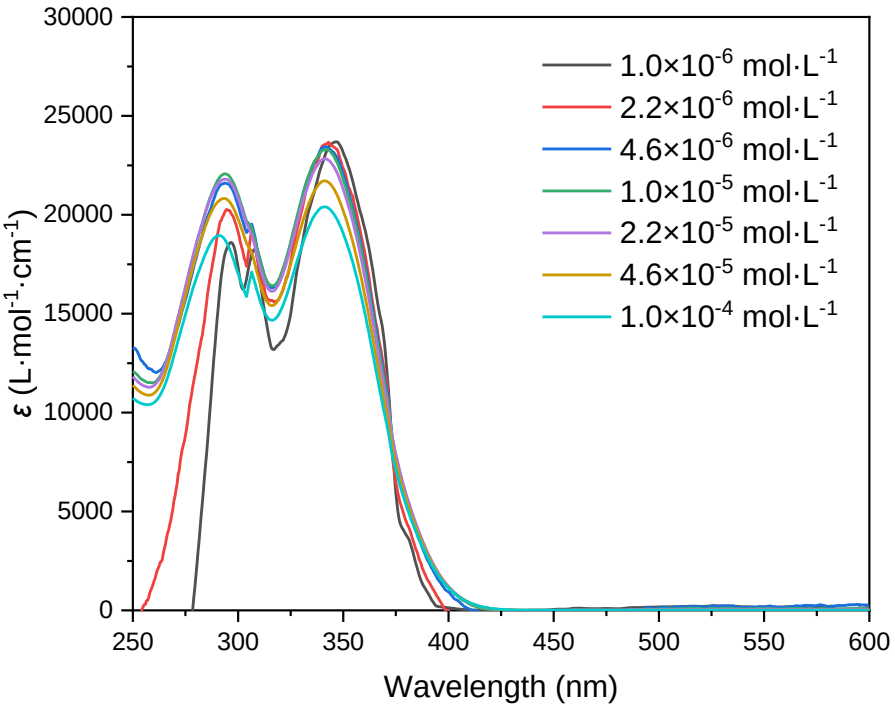


Supplementary Figure 16. ^{13}C NMR Spectrum (400 MHz, $CDCl_3$, 298K) of [**3**-H][BF_4].

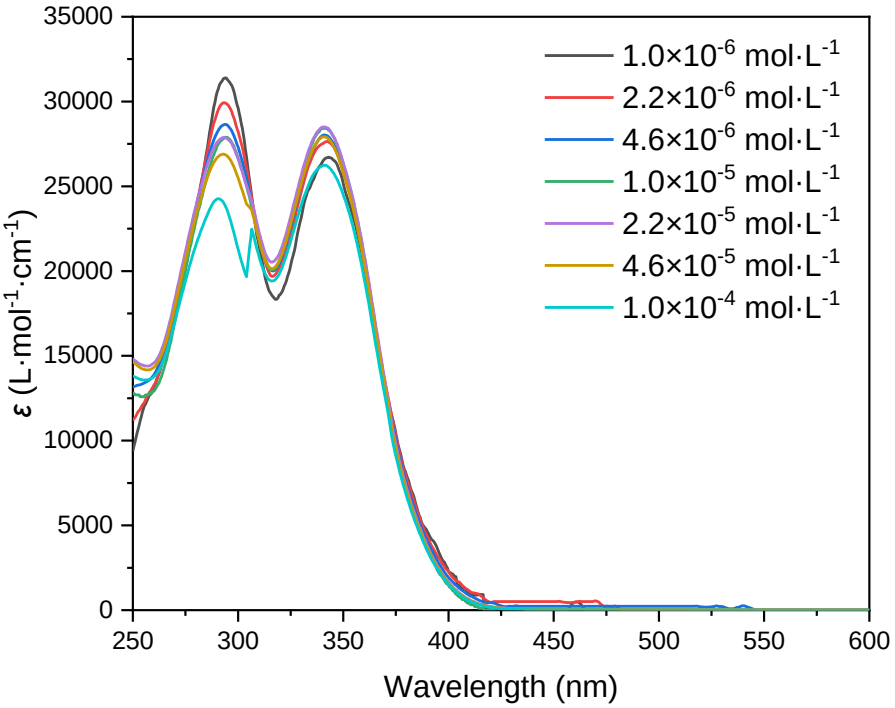


Supplementary Figure 17. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$, 298K) of **3** with excess *t*-BuOK.

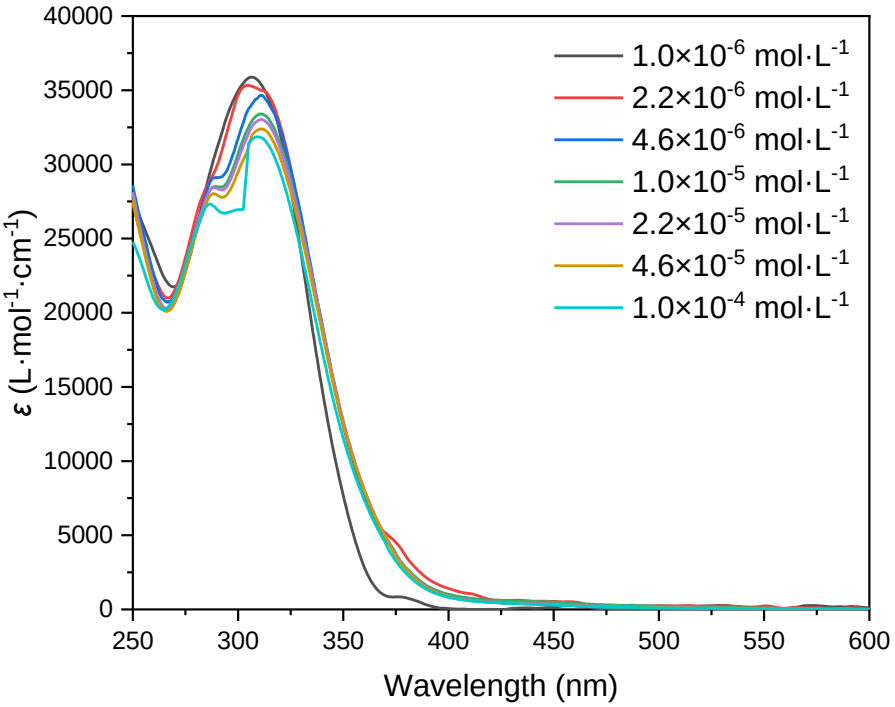
UV-Vis Spectra



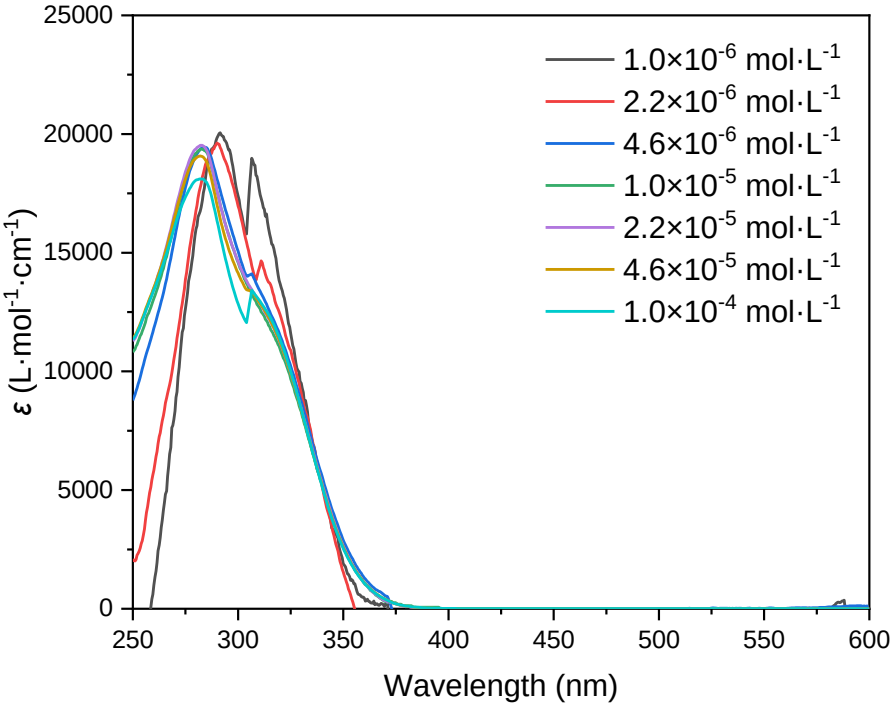
Supplementary Figure 18. UV-Vis absorption spectra of **1b** in THF from 1.0 μM to 1.0×10^2 μM.



Supplementary Figure 19. UV-Vis absorption spectra of [**1b**-H][BF_4] in THF from 1.0 μM to 1.0×10^2 μM.

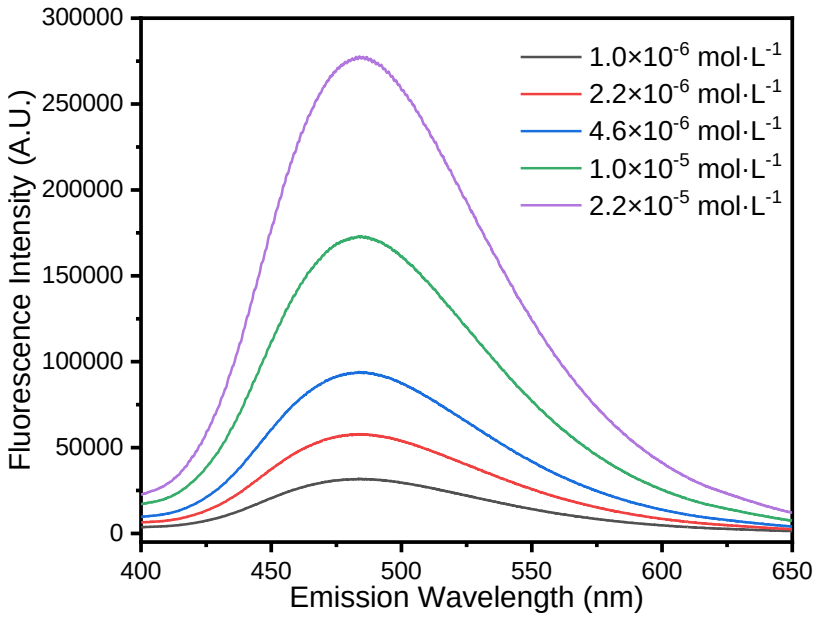


Supplementary Figure 20. UV-Vis absorption spectra of **3** in THF from 1.0 μM to 1.0×10^2 μM.

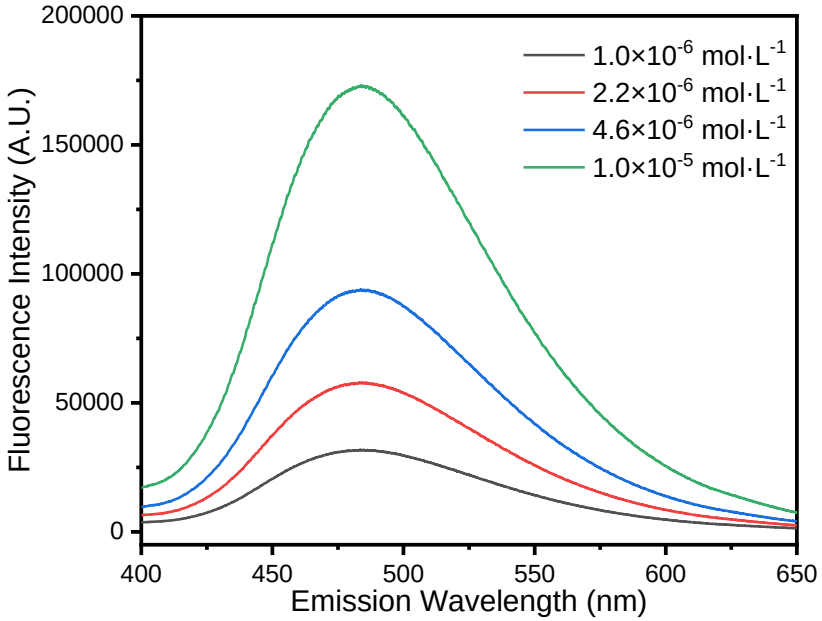


Supplementary Figure 21. UV-Vis absorption spectra of [**3**-H][BF_4] in THF from 1.0 μM to 1.0×10^2 μM.

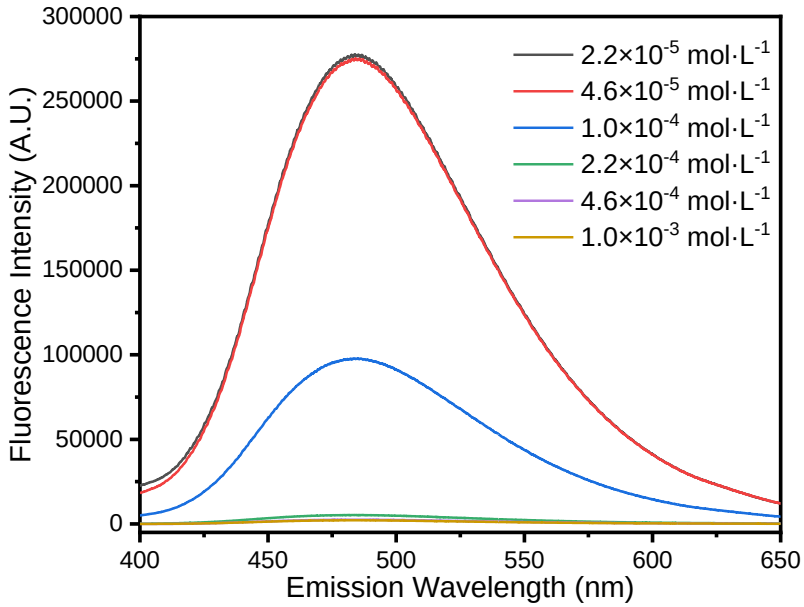
Fluorescence Emission Spectra



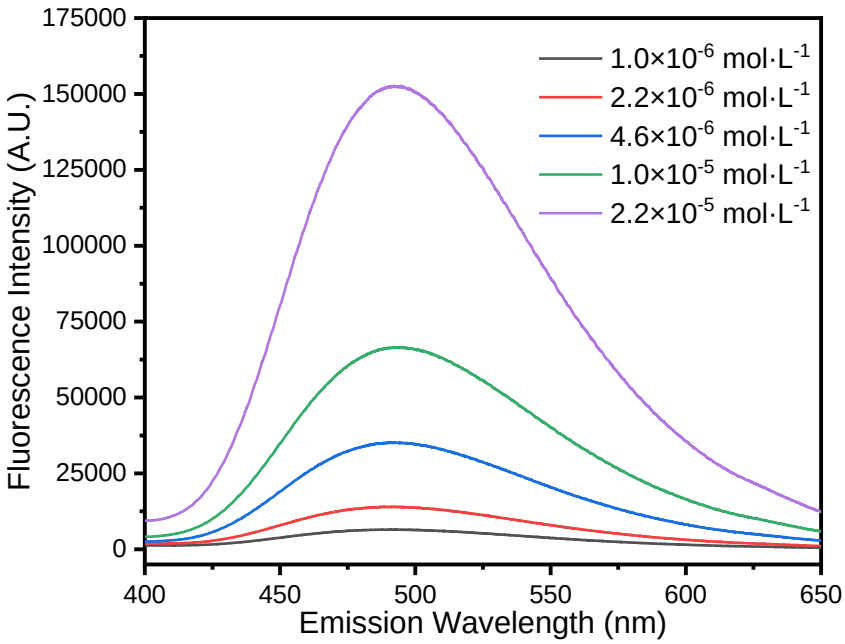
Supplementary Figure 22. Fluorescence emission spectra of **1b** (1.0 μM to 22 μM) in THF, when excited at 342 nm.



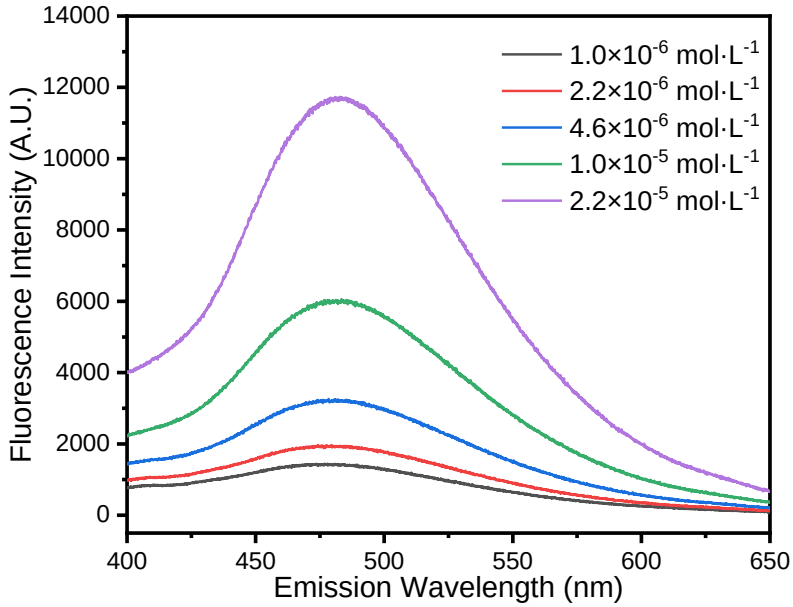
Supplementary Figure 23. Fluorescence emission spectra of [**1b**-H][BF_4] (1.0 μM to 22 μM) in THF, when excited at 342 nm.



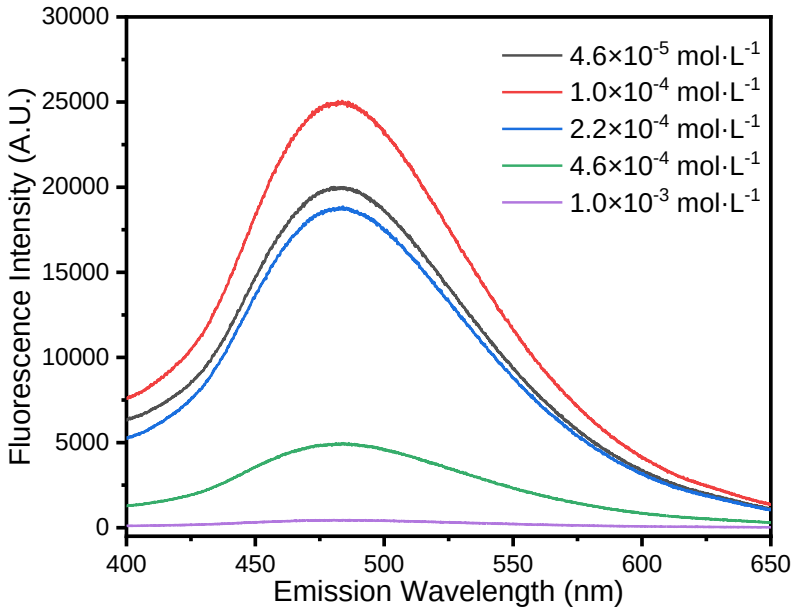
Supplementary Figure 24. Fluorescence emission spectra of [**1b**-H][BF_4] (46 μM to 1.0×10^3 μM) in THF, when excited at 342 nm.



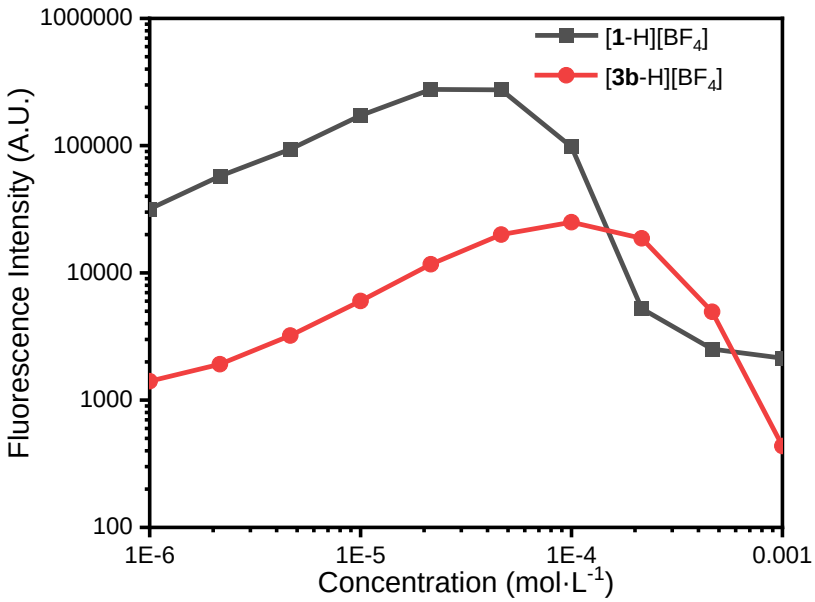
Supplementary Figure 25. Fluorescence emission spectra of **3** (1.0 μM to 46 μM) in THF, when excited at 342 nm.



Supplementary Figure 26. Fluorescence emission spectra of [**3**-H][BF_4] (1.0 μM to 22 μM) in THF, when excited at 342 nm.



Supplementary Figure 27. Fluorescence emission spectra of [**3**-H][BF_4] (46 μM to 1.0×10^3 μM) in THF, when excited at 342 nm.



Supplementary Figure 28. Fluorescent intensities of [**1b**-H][BF_4] and [**3**-H][BF_4] as a function of concentration in THF, when excited at 342 nm.

Details of Fluorescence Quantum Yields

The fluorescence emission quantum yields of solution samples were measured on a Hamamatsu C9920-02G absolute PL quantum yield measurement system. Quantum yields were recorded with samples of solutions with a concentration of 1×10^{-5} mol·L^{-1}. Excitation wavelength was 342 nm for solutions with DCM or THF as solvents, 341 nm for solutions with DMF as solvent.

Table S1. Quantum yields (Φ_e) of Solutions Used in This Study

Sample	**1b**	[**1b**-H][BF_4]	**3**	[**3**-H][BF_4]
Φ_e in DCM	0.494	0.490	0.124	0.032
Φ_e in THF	0.457	0.439	0.332	0.158
Φ_e in DMF	0.425	0.427	0.123	0.118

The fluorescence quantum yields of solid powders were measured on a spectrometer (FLS980) from Edinburgh Instruments Ltd. with an integrating sphere (φ 150 mm).

Table S2. Quantum yields (Φ_e) of Solid Powders Used in This Study

Sample	**1b**	[**1b**-H][BF_4]	**3**	[**3**-H][BF_4]
Φ_e	0.025	0.221	0.217	0.198

Details of X-ray Crystallography

Reflection data for [**3**-H][BF_4] were collected on a Rigaku SuperNova, Dual, AtlasS2 diffractometer using monochromatized Cu Kα radiation. Crystals were frozen in paratone oil inside a cryoloop under a cold stream of N_2. Diffraction data and unit-cell parameters were consistent with assigned space groups. Lorentzian polarization corrections and empirical absorption corrections, based on redundant data at varying effective azimuthal angles, were applied to the data sets. The structures were solved using OLEX^2 crystallography software with SHELX programs.[3,4] When practical, non-hydrogen atoms were refined anisotropically and hydrogen atoms placed in idealized positions and refined using a riding model.

Table S3. Crystal Data, Solution and Refinement Parameters

	[**3**-H][BF_4]	**1b**
CCDC number	2043996	2043995
formula	$C_{68}H_{85}N_2O_{11}BF_4$	$C_{34}H_{34}N_2O$
Formula weight	1193.23	486.63
Crystal system	Monoclinic	Triclinic
Space group	*P*21/m	*P*-1
T (K)	100.0	149.99(10)
a (Å)	15.4345(8)	11.6578(3)
b (Å)	27.2605(16)	12.4438(3)
c (Å)	18.4100(11)	13.0555(4)
α (°)	90	63.465(3)
β (°)	115.234(2)	72.555(2)
γ (°)	90	65.144(3)
V (Å^3)	7006.9(7)	1522.76(9)
Z	1	2
ρ (g·cm^{-3})	0.163	1.061
μ (mm^{-1})	0.080	0.490
reflections used	74132	18924
variables	1182	369
restraints	88	0

$R_1[I > 2\sigma(I)]$[a]	0.0872	0.0410
R_1 (all data)	0.2377	0.1133
R_2w $[I > 2\sigma(I)]$[b]	0.1069	0.0459
R_2w (all data)	0.2542	0.1180
GoF on F^2	1.028	1.056

[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma |F_o|$; [b] $R_2w = [\Sigma w(F_o^2 - F_c^2)^2 / w(F_o^2)^2]]^{1/2}$, where $w = q[\sigma^2(Fo^2) + (aP)^2 + bP]^{-1}$

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4. G.M. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112−122.