Carbazole-fused calixarene cavities: single and mixed AIEgen systems for NO detection

Varun Rawat,[a] Abhishek Baheti[a], Om Shanker Tiwari[b], and Arkadi Vigalok*[a]

[a]School of Chemistry, The Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv 69978, Israel. [b] The Shmunis School of Biomedicine and Cancer Research, George S. Wise Faculty of Life Sciences, Tel Aviv University, Tel Aviv 6997801, Israel

Electronic Supporting Information

1. General Information

The synthetic manipulations involving air-sensitive compounds were performed in a nitrogen-filled Innovative Technology or Vigor glove box. All solvents were degassed and stored under high-purity nitrogen and activated 4Å molecular sieves. All deuterated solvents were stored under high-purity nitrogen on 3Å molecular sieves. Commercially available reagents (Aldrich, Strem and Fluka) were used as received. The NMR spectra were recorded on Bruker Avance 400MHz spectrometer. ^{1}H and ^{13}C NMR signals are reported in ppm downfield from TMS. All measurements were performed at 22 °C in $CDCl_3$/CD_2Cl_2 unless stated otherwise. Mass Spectra were recorded on a VG-Autospec M-250 instrument. UV and Fluorescence spectra were recorder on Vernier fluorescence/UV-Vis spectrophotometer and Hitachi F-2710 fluorescence spectrophotometer.

2. Experimental section

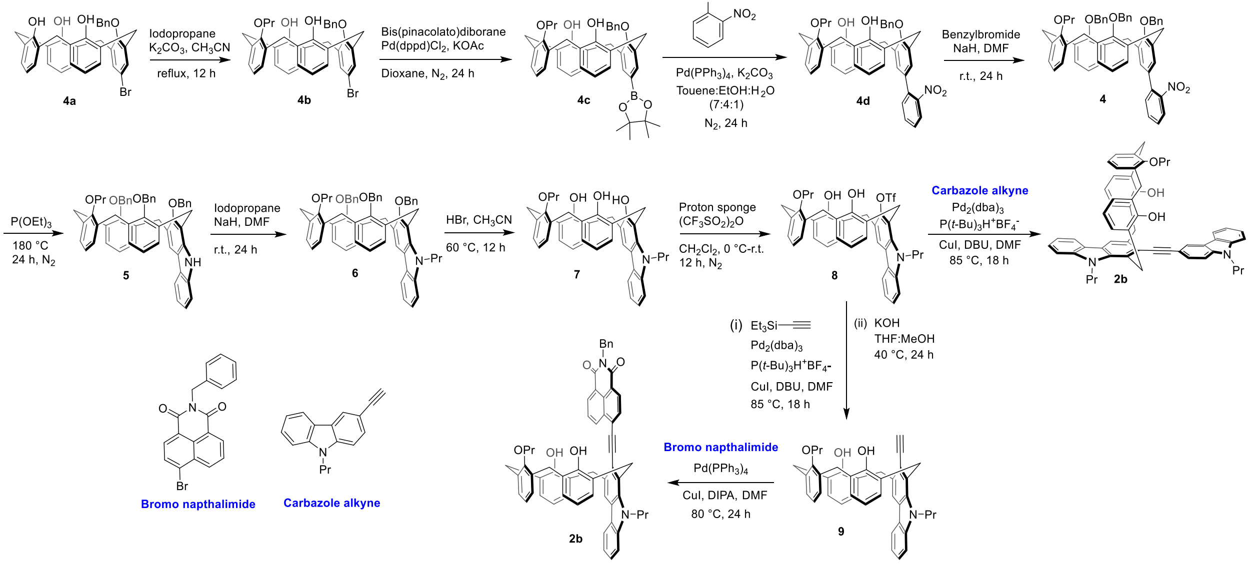
2.1 NO detection experiments using NO gas.

NO gas was generated by a slow addition of 5M nitric acid to copper turnings under a dinitrogen atmosphere. The stream of NO was passed through the nitrogen degassed 10% NaOH to remove higher oxides. The gas was passed briskly through a stirred 10 μM solution of the calixarene compounds in a septum-fitted vial, sealed in the glovebox, for about a 5 min and the fluorescence changes were recorded.

2.2 Quantitative detection using DEA NONOate as NO source.

The solutions of calixarene compounds (10 μM) were prepared in a glove box using degassed Millipore water and DMF. The calixarene solution was treated with a freshly prepared solution of diethylammonium (*Z*)-1-(*N*,*N*-diethylamino)diazen-1-ium-1,2-diolate (DEA NONOate, **10**) (10^{-2} M) in degassed Millipore water. After adding the aliquots (1.5, 3.75 or 7.5 equiv.), the mixture was stirred under nitrogen at RT for 24h and fluorescence changes were recorded.

2.3 Synthesis of the new compounds.



Scheme S1. General synthesis of compounds **2a,b**.

Synthesis of compound 4b

To compound **4a** (0.592 g, 1.0 mmol) dissolved in MeCN (50 mL), 1-iodopropane (0.34 g, 2.0 mmol) and K_2CO_3 (0.167 g, 1.2 mmol) were added. The mixture was refluxed for 12 h and evaporated in vacuum. The residue was dissolved in CH_2Cl_2 (50 mL) and 1 N HCl (50 mL) was added. The organic layer was separated, washed with brine (2 x 150 mL), dried over $MgSO_4$ and evaporated in vacuum. The residue was precipitated with DCM/methanol and filtered. White solid, Yield = 0.47 g (74%). ^1H NMR ($CDCl_3$, 400MHz): δ 8.08 (s, 2H), 7.71 (d, *J* = 6.8 Hz, 2H), 7.38-7.47 (m, 3H), 7.04-7.08 (m, 4H), 7.00-7.02 (m, 2H), 6.95 (d, *J* = 7.6 Hz, 2H), 6.80 (t, *J* = 8.0 Hz, 1H), 6.65 (t, *J* = 7.6 Hz, 2H), 5.03 (s, 2H), 4.41 (d, *J* = 6.0 Hz, 2H), 4.27 (d, *J* = 6.0 Hz, 2H), 3.96 (t, *J* = 6.4 Hz, 2H), 3.39 (d, *J* = 13.2 Hz, 2H), 3.32 (d, *J* = 12.8 Hz, 2H), 2.04 (sext, *J* = 6.8 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100MHz): δ 153.5, 151.9, 151.2, 136.5, 135.8, 133.4, 132.1, 132.0, 129.2, 128.9, 128.8, 128.6, 128.4, 128.2, 127.7, 127.2, 125.6, 119.3, 118.1, 78.61, 78.55, 31.6, 31.5, 23.6, 11.2 HRMS (ESI-TOF) *m/z* $[M-H]^-$ calcd for $C_{38}H_{34}BrO_4$ 633.1640, found 633.1644.

Synthesis of compound 4c

A pressure tube was charged with Pd(dppf)Cl_2 (115 mg, 0.15 mmol), KOAc (926 mg, 9.45 mmol), and Bis(pinacolato)diborane (956 mg, 3.78 mmol) under nitrogen. Dioxane (6 mL) and **4b** (2.0 g, 3.15 mmol) were added. After stirring at 90 °C for 24 h, the solvent was evaporated and product was extracted with ethyl acetate, washed with water, and dried over anhydrous magnesium sulfate. Solvent was evaporated and the residue was subjected to column chromatography (DCM-hexane, 1:2). White solid, Yield = 1.28 g (60%). ^{1}H NMR ($CDCl_3$, 400MHz): δ 8.29 (s, 2H), 7.76 (d, *J* = 7.2 Hz, 1H), 7.39-7.52 (m, 4H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.12-7.14 (m, 2H), 7.05 (dd, *J* = 7.6 Hz, 1.6 Hz, 2H), 6.95 (d, *J* = 7.6 Hz, 2H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.65 (t, *J* = 7.6 Hz, 2H), 5.05 (s, 2H), 4.29-4.37 (m, 4H), 3.96 (t, *J* = 6.4 Hz, 2H), 3.45 (d, *J* = 12.8 Hz, 2H), 3.37 (d, *J* = 12.8 Hz, 2H), 2.03-2.08 (m, 2H), 1.23-1.30 (m, 15H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100MHz): δ 154.5, 153.4, 151.9, 136.7, 131.1, 135.8, 133.6, 132.9, 129.4, 129.2, 129.0, 128.9, 128.7, 128.5, 128.2, 128.0, 127.9, 127.7, 127.3, 127.0, 126.2, 125.5, 121.1, 119.2, 83.7, 78.5, 78.4, 31.6, 25.0, 23.6, 11.1. HRMS (ESI-TOF) *m/z* $[M-H]^-$ calcd for $C_{44}H_{46}BO_6$ 680.3424, found 680.3417.

Synthesis of compound 4d

A two-neck R.B. flask was charged with **4c** (3.4 g, 5.0 mmol), 1-iodo-2-nitrobenzene (1.89 g, 7.6 mmol), K_2CO_3 (2.07 mg, 15.0 mmol) under nitrogen. A mixture of toluene : ethanol : water (7:4:1, 60 mL) was added. Then, Pd(PPh_3)$_4$ (289 mg, 0.25 mmol) was added and the mixture was heated at 100 °C for 24 h, under nitrogen. After the completion of the reaction, the solvent was evaporated and product was extracted with ethyl acetate, washed with water, and dried over anhydrous magnesium sulfate. Solvent was evaporated and the residue was subjected to column chromatography (DCM-hexane, 1:1). Yellow solid, Yield = 2.1 g (62 %). ^{1}H NMR ($CDCl_3$, 400MHz): δ 8.18 (s, 2H), 7.74 (d, *J* = 7.2 Hz, 1H), 7.54-7.59 (m, 3H), 7.40-7.49 (m, 3H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.22-7.24 (m, 2H), 6.72 (d, *J* = 7.2 Hz, 2H), 6.68 (d, *J* = 6.4 Hz, 2H), 6.64 (d, *J* = 7.2 Hz, 2H), 6.57 (s, 2H), 6.27 (d, *J* = 7.2 Hz, 2H), 5.12(s, 2H), 4.34 (d, *J* = 12.0 Hz, 2H), 4.25 (d, *J* = 12.8 Hz, 2H), 3.94 (t, *J* = 6.4 Hz, 2H), 3.30 (dd, *J* = 12.8 Hz, 3.2 Hz, 4H), 2.07 (quad, *J* = 6.8 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100MHz): δ 153.5, 152.0, 134.8, 133.7, 133.0, 131.8, 130.1, 129.0, 128.9, 128.8, 128.7, 128.0, 127.9, 127.7, 127.8, 123.1, 119.2, 78.5, 31.6, 31.5, 23.6, 11.2. HRMS (ESI-TOF) *m/z* $[M-H]^-$ calcd for $C_{37}H_{38}NO_6$ 676.2699, found 676.2695.

Synthesis of compound 4

To compound **4d** (1.72 g, 2.55 mmol) dissolved in DMF (100 mL), benzyl bromide (2.62 g, 1.82 mL, 15.33 mmol) was added and the mixture was stirred for 5 min at room temperature under nitrogen. Then, oil-dispersed NaH (0.368 g, 15.33 mmol) was added slowly and the mixture was stirred for 24 h at room temperature. The organic solvent was evaporated in vacuum. A small amount of water was added carefully to destroy the excess of NaH and 10% HCl (100 mL) was added. To the aq. residue, CH_2Cl_2 was added and the organic layer separated, washed with 10% HCl (100 mL) and then water, and dried over $MgSO_4$. The solvent was evaporated in vacuum. The crude product was purified by column chromatography (DCM-hexane, 1:2). Yellow solid, Yield = 1.57 g (72 %). ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.26-7.41 (m, 13H), 7.15-7.18 (m, 5H), 6.71 (d, *J* = 7.6 Hz, 2H), 6.45-6.60 (m, 8H), 4.89-4.94 (m, 6H), 4.41 (d, *J* = 13.2 Hz, 2H), 4.15 (d, *J* = 13.6 Hz, 2H), 3.87 (t, *J* = 8.0 Hz, 2H), 3.10 (d, *J* = 13.6 Hz, 2H), 2.90 (d, *J* = 13.6 Hz, 2H), 1.82-1.92 (m, 2H), 0.85 (t, *J* = 7.6 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100MHz): δ 157.1, 155.9, 155.3, 149.6, 138.0, 137.4, 136.6, 136.4, 135.8, 135.2, 134.8, 132.2, 131.9, 131.1, 130.1, 129.6, 128.44, 128.37, 128.33, 128.28, 128.2, 128.1, 127.9, 127.6, 123.9, 122.7, 122.0, 76.9, 76.8, 76.5, 31.5, 31.4, 23.4, 10.3. HRMS (ESI-TOF) *m/z* $[M-H]^-$ calcd for $C_{58}H_{50}NO_6$ 856.3638, found 856.3630.

Synthesis of compound 5

A solution of **4** (1.2 g, 1.39 mmol) and $P(OEt)_3$ (10 mL) was heated at 180 °C with vigorous stirring for 24 h under nitrogen, during which time the color changed from colorless to yellowish green. At that time, the reaction was cooled to room temperature and concentrated under high vacuum. The green residue was purified by column chromatography (DCM-hexane, 1:1). White solid, Yield = 0.75 g (65 %). ^{1}H NMR (CD$_2$Cl$_2$, 400MHz): δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.65 (s, 1H), 7.38-7.44 (m, 5H), 7.22-7.35 (m, 10H), 7.08-7.16 (m, 4H), 6.45-6.58 (m, 7H), 6.26-6.28 (m, 1H), 5.88 (t, *J* = 7.6 Hz, 1H), 4.90-5.02 (m, 6H), 4.30-4.40 (m, 4H), 3.83 (t, *J* = 8.0 Hz, 2H), 3.29 (d, *J* = 14.4 Hz, 1H), 3.19 (d, *J* = 13.6 Hz, 1H), 2.99-3.07 (m, 2H), 1.83-1.92 (m, 2H), 0.85 (t, *J* = 7.6 Hz, 3H). ^{13}C {^{1}H} NMR (CD$_2$Cl$_2$, 100MHz): δ 156.8, 155.7, 155.6, 154.5, 140.0, 138.7, 138.2, 138.04, 137.99, 136.0, 135.6, 135.5, 134.4, 129.9, 129.6, 129.4, 128.6, 128.3, 128.2, 128.1, 128.04, 127.96, 127.93, 127.88, 127.7, 127.4, 124.44, 124.41, 122.5, 122.2, 121.8, 119.6, 119.1, 118.8, 118.2, 110.3, 77.0, 76.8, 76.7, 76.4, 31.8, 31.4, 31.2, 27.3, 23.4, 10.1. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd for $C_{58}H_{52}NO_4$ 826.3896, found 826.3893.

Synthesis of compound 6

To compound **5** (700 mg, 0.85 mmol) dissolved in DMF (30 mL), was added oil-dispersed NaH (31 mg, 1.27 mmol) and the mixture was stirred for 15 min at room temperature under nitrogen. Then, 1-iodopropane (289 mg, 165 μL, 1.7 mmol) was added and the mixture was stirred for 24 h at room temperature. The organic solvent was evaporated in vacuum. A small amount of water was added carefully to destroy the excess NaH. To the aq. residue CH$_2$Cl$_2$ was added and the organic layer separated, washed with 10% HCl (100 mL) and then water and dried over MgSO$_4$. The solvent was evaporated in vacuum. The crude product was purified by column chromatography (DCM-hexane, 1:2). White solid, Yield = 657 mg (89 %). ^{1}H NMR (CDCl$_3$, 400MHz): δ 8.08 (d, *J* = 7.6 Hz, 1H), 7.88 (s, 1H), 7.55 (d, *J* = 6.8 Hz, 2H), 7.35-7.48 (m, 10H), 7.13-7.24 (m, 4H), 6.92-7.03 (m, 5H), 6.18 (d, *J* = 4.0 Hz, 2H), 6.06-6.09 (m, 3H), 5.77 (t, *J* = 4.4 Hz, 1H), 5.14 (d, *J* = 12.0 Hz, 1H), 4.93 (d, *J* = 12.0Hz, 1H), 4.72-4.83 (m, 4H), 4.47-4.53 (m, 3H), 4.26-4.31 (m, 2H), 4.16 (d, *J* = 14.8 Hz, 1H), 3.96-4.10 (m, 2H), 3.28-3.37 (m, 2H), 3.15 (t, *J* = 12.8 Hz, 2H), 2.02 (sext, *J* = 7.6 Hz, 2H), 1.64-1.73 (m, 2H), 0.83 (t, *J* = 7.6 Hz, 3H), 0.78 (t, *J* = 7.6 Hz, 3H). ^{13}C {^{1}H} NMR (CDCl$_3$, 100MHz): δ 157.9, 155.5, 154.6, 142.1, 138.8, 138.13, 138.08, 137.44, 137.36, 134.3, 133.7, 133.4, 133.2, 130.7, 129.3, 129.2, 128.9, 128.7, 128.6, 128.5, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4, 126.9, 124.6, 123.4, 122.8, 122.5, 122.0, 121.6, 120.0, 119.43, 119.37, 118.9, 108.9, 77.1, 76.5, 76.3, 46.5, 31.6, 31.4, 31.2, 24.5, 23.3, 23.0, 11.4, 9.8. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd for $C_{61}H_{58}NO_4$ 868.4366, found 868.4374.

Synthesis of compound 7

Compound **6** (650 mg, 0.75 mmol) was suspended in CH_3CN (15 mL), and after the addition of HBr 48% (10 mL) the mixture was stirred at 60 °C for 12 h. The resulting suspension was diluted with DCM and neutralized with diluted $NaHCO_3$ solution. The organic phase was separated and washed with water and brine, dried over $MgSO_4$ and evaporated. The residue was subjected to column chromatography (DCM-hexane, 1:1). White solid, Yield = 402 mg (90 %). ^{1}H NMR (CD_2Cl_2, 400MHz): δ 10.00 (s, 1H), 9.84 (s, 1H), 8.94 (s, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.76 (s, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.03-7.17 (m, 5H), 7.87 (t, *J* = 7.6 Hz, 1H), 6.75 (t, *J* = 7.6 Hz, 1H), 6.57 (t, *J* = 7.6 Hz, 1H), 4.83-4.90 (m, 1H), 4.47-4.62 (m, 3H), 4.18-4.34(m, 4H), 4.08-4.14 (m, 1H), 3.70 (d, *J* = 14.4 Hz, 1H), 3.56 (d, *J* = 13.6 Hz, 1H), 3.45 (d, *J* = 12.8 Hz, 1H), 2.22-2.29 (m, 2H), 1.76-1.79 (m, 1H), 1.61-1.69 (m, 1H), 1.31 (t, *J* = 7.6 Hz, 3H), 0.83 (t, *J* = 7.6 Hz, 3H). ^{13}C {^{1}H} NMR (CD_2Cl_2, 100MHz): δ 151.9, 151.6, 150.3, 150.1, 142.9, 138.0, 135.6, 133.9, 130.0, 129.7, 129.3, 129.2, 128.9, 128.8, 128.4, 128.3, 128.2, 126.1, 124.6, 123.7, 121.5, 121.2, 120.7, 119.8, 119.5, 119.3, 119.0, 112.3, 109.5, 79.3, 48.8, 32.1, 31.1, 24.2, 23.4, 23.2, 11.1, 10.6. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{40}H_{40}NO_4$ 598.2957, found 598.2966.

Synthesis of compound 8

To a suspension of **7** (400 mg, 0.67 mmol) and 1,8-bis(dimethylamino)naphthalene (proton sponge) (287 mg, 1.34 mmol) in dry DCM (50 ml) at 0 °C trifluoromethanesulfonic anhydride (0.168 mL, 1.00 mmol) was added under nitrogen. After 12 hours of stirring at room temperature, the organic layer was washed twice with HCl 10% and once with water, dried over $MgSO_4$ and evaporated. The residue was washed with MeOH to remove the residual proton sponge giving **8** as a white solid. Yield = 342 mg (70 %). ^{1}H NMR (CD_2Cl_2, 400MHz): δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 5.6 Hz, 2H), 7.35-7.41 (m, 4H), 7.04-7.12 (m, 3H), 6.94 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 6.87 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 6.80 (t, *J* = 7.6 Hz, 1H), 6.71 (dt, *J* = 7.6 Hz, 2.0 Hz, 2H), 6.57 (s, 1H), 4.80-4.91 (m, 2H), 4.57 (d, *J* = 13.6 Hz, 1H), 4.39-4.47 (m, 1H), 4.00-4.15 (m, 5H), 3.57-3.63 (m, 3H), 2.12 (sext, *J* = 7.2 Hz, 2H), 1.60-1.69 (m, 1H), 1.46-1.55 (m, 1H), 1.28 (t, *J* = 7.6 Hz, 3H), 0.74 (t, *J* = 7.6 Hz, 3H). ^{13}C {^{1}H} NMR (CD_2Cl_2, 100MHz): δ 151.1, 153, 150.6, 144.3, 142.7, 138.9, 132.8, 132.2, 130.1, 129.9, 129.7, 129.5, 129.3, 129.0, 126.9, 126.6, 126.45, 126.41, 126.3, 126.2, 125.5, 123.3, 121.1, 120.3, 120.0, 119.7, 118.3, 117.8, 110.6, 79.8, 47.6, 32.7, 32.1, 31.8, 28.2, 23.4, 22.2, 11.4, 10.6. HRMS (ESI-TOF) *m/z* $[M-H]^-$ calcd for $C_{41}H_{37}F_3NO_6S$ 728.2294, found 728.2297.

Synthesis of compound 2a

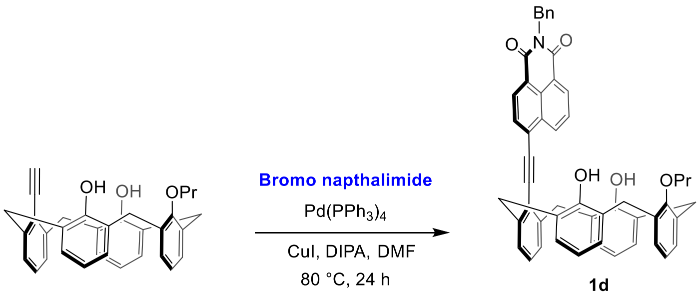
To a mixture of $P(t\text{-}Bu)_3H^+$ BF_4^- (6.8 mg, 0.024 mmol) and Pd_2dba_3 (5.4 mg, 0.06 mmol) dissolved in 20 ml of dry DMF, CuI (56 mg, 0.29 mmol), DBU (70 µl, 0.47 mmol), 3-ethynyl-9-propyl-9*H*-carbazole (273 mg, 1.17 mmol) and **8** (175 mg, 0.24 mmol) were added, and the mixture was heated at 85 °C for 13 hours in an oil bath. The solvent was evaporated and the resulting crude product was dissolved in DCM and washed with brine several times. Drying the DCM extract over $MgSO_4$ followed by solvent removal under vacuum gave the crude product. The residue was subjected to column chromatography (hexane-DCM, 1:2). White solid, Yield = 40.0 mg (21%). ^{1}H NMR (CD_2Cl_2, 400MHz): δ 8.49 (d, *J* = 1.6 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 7.85-7.89 (m, 1H), 7.71 (d, *J* = 4.8 Hz, 1H), 7.66-7.70 (m, 1H), 7.49-7.51 (m, 2H), 7.36-7.46(m, 5H), 7.27-7.31 (m, 2H), 7.07-7.13 (m, 3H), 6.91 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 6.84 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 6.80 (t, *J* = 7.6 Hz, 1H), 6.75 (t, *J* = 7.6 Hz, 1H), 6.69 (t, *J* = 7.6 Hz, 1H), 6.38 (s, 1H), 5.29 (d, *J* = 14.8 Hz, 1H), 5.09 (d, *J* = 12.8 Hz, 1H), 4.82-4.89 (m, 1H), 4.34-4.46 (m, 5H), 4.11-4.19 (m, 3H), 3.82-3.90 (m, 3H), 3.49 (dd, *J* = 14.0 Hz, 3.2 Hz, 2H), 1.98 (quad, *J* = 7.2 Hz, 2H), 1.74 (quad, *J* = 7.2 Hz, 2H), 1.01 (t, *J* = 7.6 Hz, 3H), 0.85 (t, *J* = 7.6 Hz, 3H), 0.78 (t, *J* = 7.6 Hz, 3H). ^{13}C {^{1}H} NMR (CD_2Cl_2, 100MHz): δ 154.6, 153.7, 152.3, 143.5, 143.0, 141.1, 140.4, 137.4, 134.6, 133.3, 132.9, 130.5, 130.2, 129.7, 129.5, 129.2, 129.1, 129.04, 128.97, 128.8, 128.4, 126.9, 126.3, 126.1, 126.0, 125.6, 125.4, 125.3, 123.9, 123.8, 123.4, 122.9, 122.6, 122.2, 120.6, 120.0, 119.7, 119.6, 119.32, 119.28, 119.1, 114.2, 109.9, 109.2, 109.0, 100.1, 87.8, 77.9, 46.9, 44.8, 36.0, 33.3, 32.9, 32.0, 23.3, 22.4, 22.2, 14.0, 11.6, 11.1, 10.3. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{57}H_{53}N_2O_3$ 813.4056, found 813.4071.

Synthesis of compound 9

To a mixture of $P(t\text{-}Bu)_3H^+$ BF_4^- (6.8 mg, 0.024 mmol) and Pd_2dba_3 (5.4 mg, 0.06 mmol) dissolved in 20 ml of dry DMF, CuI (56 mg, 0.29 mmol), DBU (70 µl, 0.47 mmol), triethylsilylacetylene (420 µl, 2.34 mmol) and **8** (175 mg, 0.24 mmol) were added, and the mixture was heated at 85 °C for 13 hours in an oil bath. The solvent was evaporated and the resulting crude product was dissolved in DCM and washed with brine several times. Drying the DCM extract over $MgSO_4$ followed by solvent removal under vacuum gave the crude product. The residue was subjected to column chromatography (hexane-DCM, 1:1). Obtained white solid was treated with KOH (69 mg, 1.23 mmol) in dry THF (2.5 ml) and methanol (7.5 ml) under nitrogen, and stirred at 40 °C on oil bath for 24 hours or until there was a full conversion. The reaction was quenched with water and DCM was added. The organic layer was separated and washed twice with water and then with brine. Drying the organic layer over MgSO4 followed by solvent removal under vacuum gave the crude product. Precipitation from DCM/hexane afforded the pure product **9**. White solid, yield: 25.0 mg (17%).^{1}H NMR (CD_2Cl_2, 400MHz): δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.60 (s, 1H), 7.41 (s, 1H), 7.30-7.36 (m, 4H), 7.07 (t, *J* = 6.4 Hz, 3H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.72-6.79 (m, 3H), 6.62 (t, *J* = 7.6 Hz, 1H), 5.88 (s, 1H), 5.07 (d, *J* = 15.2 Hz, 1H), 4.73-4.84 (m, 2H), 4.07-4.15 (m, 2H), 3.91-4.00 (m, 2H), 3.70-3.76 (m, 2H), 3.46-3.52 (m, 2H), 1.97 (quad, *J* = 7.2 Hz, 2H), 1.58-1.73 (m, 2H), 1.19 (t, *J* = 7.6 Hz, 3H), 0.79 (t, *J* = 7.6 Hz, 3H). ^{13}C {^{1}H} NMR (CD_2Cl_2, 100MHz): δ 154.7, 153.8, 152.6, 143.8, 137.5, 135.3, 133.5, 133.2, 131.7, 130.4, 130.2, 130.0, 129.5, 129.41, 129.37, 129.1, 129.0, 128.7, 128.6, 128.5, 128.2, 127.1, 126.7, 126.6, 126.5, 126.0, 125.7, 125.5, 123.5, 121.3, 121.0, 120.7, 120.5, 120.0, 119.9, 119.7, 119.6, 119.5, 110.2, 109.6, 87.8, 86.1, 83.8, 78.3, 47.2, 46.8, 40.6, 36.0, 34.7, 33.4, 33.3, 32.6, 32.2, 24.0, 23.6, 23.0, 22.5, 11.4, 10.8, 9.8. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{42}H_{40}NO_3$ 606.3008, found 606.3007.

Synthesis of compound 2b

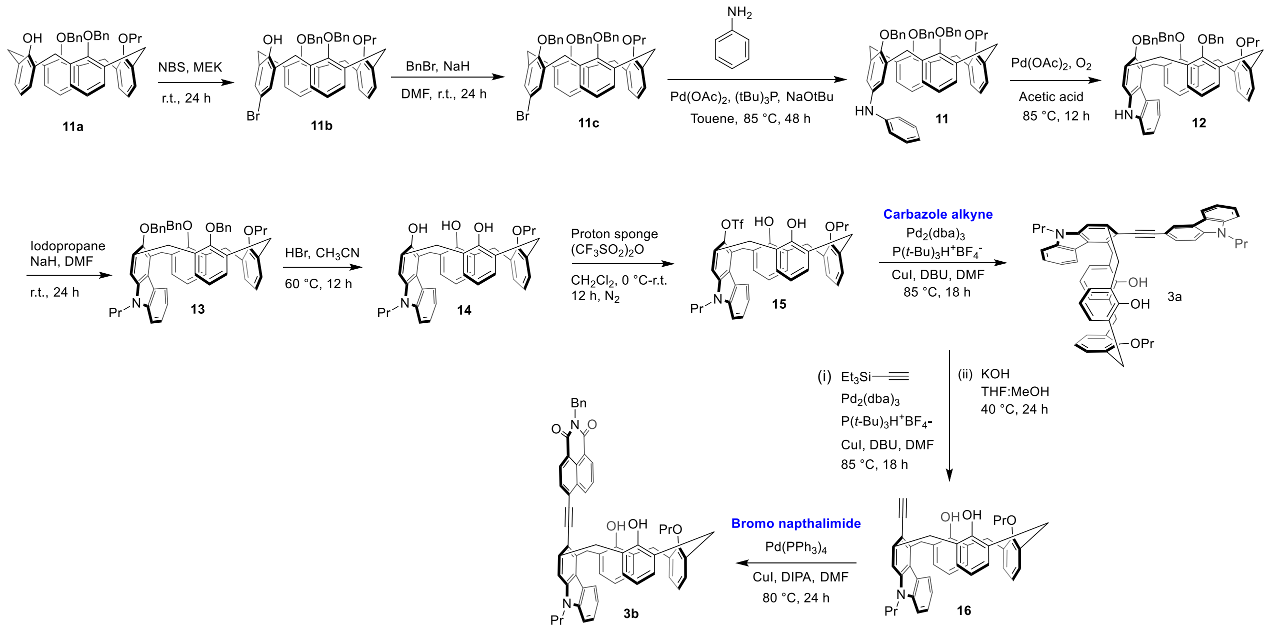
2-benzyl-6-bromo-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (38 mg, 0.10 mmol) was added to a solution of $Pd(PPh_3)_4$ (3.0 mg, 0.0027 mmol), CuI (0.59 mg, 0.003 mmol) and iPr_2NH (1 mL) in 5 ml dry DMF. To this mixture **9** (31 mg, 0.052 mmol) in 2 mL DMF was added slowly under nitrogen atmosphere. The reaction mixture was stirred at 80 °C on oil bath for 24h. The solvent was evaporated and the resulting crude was dissolved in DCM followed by washing with brine several times. The organic layer was dried over $MgSO_4$. Further, the solvent was evaporated and the crude product was subjected to column chromatography over silica gel (Hexane -DCM, 1:4). Yellow solid, Yield = 20.0 mg (43%). ^{1}H NMR (CD_2Cl_2, 400MHz): δ 9.20 (d, *J* = 8.0 Hz, 1H), 8.63 (dd, *J* = 16.0 Hz, 7.6 Hz, 1H), 8.16 (d, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.73 (s, 1H), 7.66 (s, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.37-7.41 (m, 3H), 7.26-7.34 (m, 3H), 7.03-7.09 (m, 5H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.80 (t, *J* = 7.6 Hz, 1H), 6.67-6.75 (m, 3H), 6.10 (s, 1H), 5.38 (s, 2H), 5.11 (d, *J* = 12.8 Hz, 1H), 4.82-4.93 (m, 1H), 4.49 (d, *J* = 14.8 Hz, 1H), 4.38 (d, *J* = 13.2 Hz, 1H), 4.16 (t, *J* = 8.0 Hz, 1H), 3.98 (d, *J* = 13.2 Hz, 2H), 3.85-3.88 (m, 1H), 3.49-3.60 (m, 3H), 3.35 (d, *J* = 13.2 Hz, 1H), 2.16 (quad, *J* = 7.2 Hz, 2H), 1.66-1.73 (m, 1H), 1.57-1.65 (m, 1H), 0.82 (t, *J* = 7.6 Hz, 3H), 0.54 (t, *J* = 7.6 Hz, 3H). ^{13}C {^{1}H} NMR (CD_2Cl_2, 100MHz): δ 164.6, 164.3, 154.5, 153.8, 153.2, 151.7, 150.4, 144.2, 143.2, 139.3, 138.1, 137.8, 135.5, 134.4, 134.1, 133.24, 133.16, 132.0, 131.2, 131.0, 130.5, 130.3, 129.9, 129.8, 129.4, 129.13, 129.06, 128.9, 128.8, 127.7, 127.2, 127.0, 126.7, 126.4, 126.0, 125.8, 123.6, 123.2, 121.8, 121.6, 120.6, 120.2, 120.1, 120.0, 119.7, 110.4, 109.5, 102.0, 94.7, 80.8, 78.7, 47.5, 43.9, 36.4, 33.4, 32.2, 32.0, 31.9, 23.5, 23.3, 22.5, 11.4, 10.6, 10.5. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{61}H_{51}N_2O_5$ 891.3798, found 891.3806.



Scheme S2. Synthesis of **1d**

Synthesis of compound 1d

2-benzyl-6-bromo-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (22.0 mg, 0.06 mmol) was added to a solution of $Pd(PPh_3)_4$ (12.0 mg, 0.010 mmol), CuI (2.36 mg, 0.012 mmol) and iPr_2NH (3 mL) in 10 ml dry DMF. To this mixture, the calixarene (24.0 mg, 0.05 mmol) in 2 mL DMF was added slowly under nitrogen atmosphere. The reaction mixture was stirred at 80 °C on oil bath for 24h. The solvent was evaporated and the resulting crude was dissolved in DCM followed by washing with brine several times. The organic layer was dried over $MgSO_4$. Further the solvent was evaporated and the crude product was subjected to column chromatography over silica gel (Hexane-DCM, 1:3). Yellow solid, Yield = 19.7 mg (52%). ^{1}H NMR ($CDCl_3$, 400MHz): δ 9.20 (d, *J* = 8.4 Hz, 1H), 8.66 (d, *J* = 7.2 Hz, 1H), 8.61 (d, *J* = 7.6 Hz, 1H), 8.13 (d, *J* = 7.6 Hz, 1H), 7.83 (t, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.20-7.23 (m, 4H), 7.06 (d, *J* = 7.2 Hz, 2H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.83-6.87 (m, 3H), 6.74 (t, *J* = 7.6 Hz, 2H), 5.41 (s, 2H), 4.96 (d, *J* = 12.8 Hz, 1H), 3.93-3.98 (m, 4H), 3.69 (d, *J* = 12.8 Hz, 2H), 3.52 (d, *J* = 14.0 Hz, 2H), 1.61 (quad, *J* = 7.2 Hz, 2H), 0.60 (t, *J* = 7.6 Hz, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100MHz): δ 164.4. 164.2, 153.4, 150.3, 142.6, 138.8, 137.5, 134.2, 133.9, 132.8, 132.0, 131.9, 131.6, 130.9, 130.2, 129.9, 129.7, 129.2, 128.8, 128.6, 128.5, 127.6, 127.44, 127.37, 127.1, 126.8, 126.3, 122.8, 122.4, 121.2, 119.8, 100.6, 92.5, 79.6, 43.8, 36.7, 31.8, 23.1, 10.5. HRMS (ESI-TOF) *m/z* $[M-H]^-$ calcd for $C_{52}H_{40}NO_5$ 758.2906, found 758.2911.



Scheme S3. Synthetic sequence for calixarene **3a** and **3b**

Synthesis of compound 11b

A solution of calixarene **11a** (6.46 g, 10.00 mmol) and NBS (1.80 g, 10.00 mmol) in methyl ethyl ketone (260 mL) was stirred at room temperature for 24 h. The reaction solution was evaporated to afford a yellow residue, which was the re-precipitated in MeOH and filtered. Yellowish solid, Yield = 6.97 g (96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, J = 7.9, 1.6 Hz, 4H), 7.47 – 7.34 (m, 6H), 7.26 (s, 2H), 7.19 (d, J = 7.5 Hz, 2H), 7.00 (t, J = 7.5 Hz, 1H), 6.50 (d, J = 5.1 Hz, 4H), 6.46 (d, J = 4.7 Hz, 2H), 4.87 (d, J = 11.0 Hz, 2H), 4.82 (d, J = 11.0 Hz, 2H), 4.75 (s, 3H), 4.42 (d, J = 3.3 Hz, 2H), 4.39 (d, J = 2.7 Hz, 2H), 3.69 – 3.59 (m, 2H), 3.26 (d, J = 13.8 Hz, 2H), 3.19 (d, J = 13.3 Hz, 2H), 1.94 – 1.80 (m, 2H), 0.44 (t, J = 7.5 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 156.88, 154.04, 152.59, 137.13, 137.04, 133.86, 133.21, 131.98, 130.92, 129.31, 128.79, 128.60, 128.49, 128.25, 128.01, 123.62, 123.14, 111.50, 78.04, 76.53, 30.99, 30.84, 22.41, 9.36. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd for $C_{45}H_{41}O_4NaBr$ 747.2086, found 747.2090.

Synthesis of compound 11c

To compound **11b** (6.57 g, 9.30 mmol) dissolved in DMF (250 mL), benzyl bromide (7.90 g, 5.50 mL, 46.50 mmol) was added and the mixture was stirred for 5 min at room temperature under nitrogen. Then oil-dispersed NaH (1.20 g, 46.50 mmol) was added slowly and the mixture was stirred for 24 h at room temperature. The organic solvent was evaporated in vacuum. To the crude residue CH_2Cl_2 was added and the organic layer washed with 10% HCl (100 mL) and then water and dried over $MgSO_4$. The solvent was evaporated in vacuum. The crude product was purified by column chromatography (CH_2Cl_2/Hexane, 1:4 v/v). White solid, Yield = 7.36 g (97%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.15 (m, 15H), 6.83 – 6.41 (m, 11H), 5.02 (d, J = 2.5 Hz, 4H), 4.84 (s, 2H), 4.43 (d, J = 13.6 Hz, 2H), 4.13 (d, J = 13.6 Hz, 2H), 3.94 – 3.79 (m, 2H), 3.16 (d, J = 13.6 Hz, 2H), 2.88 (d, J = 13.7 Hz, 2H), 1.91 (m, 2H), 0.95 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.53, 155.44, 154.60, 137.82, 137.70, 137.31, 135.83, 135.01, 134.86, 130.82, 129.74, 129.70, 128.82, 128.22, 128.13, 128.01, 122.56, 122.30, 115.07, 76.80, 76.56, 76.50, 31.38, 31.20, 23.43, 10.43. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd for $C_{52}H_{47}O_4NaBr$ 837.2555, found 837.2563.

Synthesis of compound 11

The reaction was carried out under an inert atmosphere of pure nitrogen. To a stirred suspension of $Pd(OAc)_2$ (0.030 g, 0.13 mmol), $P(t\text{-}Bu)_3$ (0.053 g, 0.26 mmol) and sodium tert-butoxide (0.312 g, 3.25 mmol), in toluene (20 mL) were added aniline (0.2 mL, 2.60 mmol) and compound **11c** (1.00 g, 1.30 mmol dissolved in 10 mL toluene). The reaction mixture was then stirred at 85 ^oC for 48 h. The solvent was evaporated and the resulting crude product was dissolved in CH_2Cl_2 (50 mL), washed with water (5 ml x 2), brine and dried over $MgSO_4$. Removal of solvent under reduced pressure and column chromatographic purification with CH_2Cl_2/Hexane (1:3 v/v) gave pure compound **11d**. Off-white solid, Yield = 0.920 g (85%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.39 (m, 5H), 7.39 – 7.05 (m, 14H), 6.75 (m, 4H), 6.72 – 6.57 (m, 7H), 6.47 (m, 3H), 5.09 (s, 4H), 4.86 (s, 2H), 4.44 (d, J = 13.4 Hz, 2H), 4.20 (d, J = 12.7 Hz, 2H), 3.93 – 3.80 (m, 2H), 3.16 (d, J = 13.5 Hz, 2H), 2.91 (d, J = 12.9 Hz, 2H), 1.92 (dd, J = 15.2, 7.5 Hz, 2H), 0.96 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.54, 155.46, 138.03, 135.90, 134.94, 129.81, 128.51, 128.39, 128.32, 128.16, 128.10, 127.95, 122.47, 122.19, 76.88, 76.85, 76.41, 31.44, 23.40, 10.43. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd for $C_{58}H_{53}NO_4Na$ 850.3872, found 850.3876.

Synthesis of compound 12

Toluene (4 mL) and acetic acid (16 mL) was added to a flask containing calixarene **11** (0.828 g, 1 mmol) and $Pd(OAc)_2$ (10 mol%). An oxygen balloon was connected to the reaction vessel, then the reaction mixture was stirred at 80 °C for 24 h. After cooling, the reaction mixture was diluted with ethyl acetate, washed with saturated $NaHCO_3$, dried over $MgSO_4$, and concentrated in vacuo. The crude material was purified by flash chromatography (CH_2Cl_2/Hexane, 1:2 v/v) to give the carbazole calixarene **12**. Brown solid, Yield = 0.504 g (61%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.28 (d, J = 8.0 Hz, 1H), 8.15 (s, 1H), 7.62 – 7.57 (m, 4H), 7.54 – 7.39 (m, 9H), 7.28 – 7.13 (m, 7H), 7.07 (t, J = 7.6 Hz, 2H), 6.99 (t, J = 7.4 Hz, 1H), 6.29 – 6.02 (m, 6H), 5.17 (s, 1H), 5.16 (d, J = 11.0 Hz, 1H), 5.05 (d, J = 11.0 Hz, 1H), 4.89 (d, J = 11.1 Hz, 1H), 4.79 – 4.83 (m, 3H), 4.57 (d, J = 11.2 Hz, 2H), 4.46 (d, J = 11.2 Hz, 1H), 4.42 (d, J = 11.2 Hz, 1H), 4.08 – 3.17 (m, 3H), 3.20 (dd, J = 13.3, 5.0 Hz, 3H), 2.07 (q, J = 16.2, 7.9 Hz, 2H), 0.84 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 154.85, 138.00, 137.44, 137.24, 136.31, 133.43, 133.24, 132.10, 130.63, 129.72, 128.99, 128.87, 128.36, 127.95, 127.60, 127.49, 127.43, 126.78, 124.79, 122.28, 122.13, 121.93, 121.57, 119.08, 110.66, 109.96, 77.45, 76.32, 76.05, 32.03, 31.28, 31.12, 29.78, 26.02, 23.26, 9.61. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd for $C_{58}H_{51}NO_4Na$ 848.3716, found 848.3720.

Synthesis of compound 13

To compound **12** (0.500 g, 0.61 mmol) dissolved in DMF (30 mL), was added oil-dispersed NaH (0.030 g, 1.22 mmol) and the mixture was stirred for 15 min at room temperature under nitrogen. Then 1-iodopropane (0.415 g, 0.24 mL, 2.44 mmol) was added and the mixture was stirred for 24 h at room temperature. The organic solvent was evaporated in vacuum. A small amount of water was added carefully to destroy the excess NaH. To the aq. residue CH_2Cl_2 was added and the organic layer separated, washed with 10% HCl (10 mL), water and dried over $MgSO_4$. The solvent was evaporated in vacuum. The crude product was purified by column chromatography (CH_2Cl_2/Hexane, 1:2 v/v). White solid, Yield = 0.487 g (92 %). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.32 (d, J = 8.0 Hz, 1H), 7.65 – 7.56 (m, 4H), 7.54 – 7.39 (m, 8H), 7.30 – 7.13 (m, 7H), 7.09 (t, J = 7.6 Hz, 2H), 7.00 (t, J = 7.4 Hz, 1H), 6.31 – 6.04 (m, 6H), 5.18 (d, J = 12.0 Hz, 1H), 5.08 (d, J = 12.0 Hz, 1H), 4.93 (d, J = 11.0 Hz, 1H), 4.84 (m, 3H), 4.60 (dd, J = 13.2, 3.2 Hz, 2H), 4.52 (d, J = 13.5 Hz, 1H), 4.44 (d, J = 13.5 Hz, 1H), 4.38 (t, J = 7.3 Hz, 2H), 4.24 – 4.01 (m, 3H), 3.33 – 3.12 (m, 3H), 2.18 – 1.96 (m, 4H), 1.13 (t, J = 7.4 Hz, 3H), 0.86 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 157.85, 154.92, 154.86, 149.24, 141.02, 138.17, 137.52, 137.30, 137.04, 135.93, 133.63, 133.54, 133.44, 133.38, 132.16, 130.65, 129.03, 128.93, 128.44, 128.41, 128.02, 127.99, 127.65, 127.54, 127.47, 126.89, 124.56, 123.57, 122.34, 122.21, 121.97, 121.63, 120.33, 118.40, 108.77, 108.21, 77.53, 77.48, 76.34, 76.20, 44.77, 32.34, 31.35, 31.20, 26.05, 23.30, 22.41, 11.77, 9.69. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd for $C_{61}H_{57}NO_4Na$ 890.4185, found 890.4191.

Synthesis of compound 14

Compound **13** (0.434 g, 0.50 mmol) was suspended in CH_3CN (20 mL), and after the addition of 48% HBr (10 mL) the mixture was stirred at 55 °C for 24 h. The resulting suspension was diluted with DCM and neutralized with diluted $NaHCO_3$ solution. The organic phase was separated and washed with water, dried over $MgSO_4$ and evaporated. The residue was subjected to column chromatography (CH_2Cl_2/Hexane, 1:1 v/v). White solid, Yield = 0.266 g (89 %).

^1H NMR (400 MHz, CD_2Cl_2) δ 9.90 (s, 1H), 9.80 (s, 1H), 9.58 (s, 1H), 8.70 (d, J = 8.0 Hz, 1H), 7.42 –7.51 (m, 3H), 7.29 (ddd, J = 8.1, 7.0, 1.2 Hz, 1H), 7.23 (dd, J = 7.6, 1.6 Hz, 1H), 7.20 – 7.12 (m, 4H), 7.09 (dd, J = 7.6, 1.5 Hz, 1H), 6.91 (t, J = 7.6 Hz, 1H), 6.79 (t, J = 7.6 Hz, 1H), 6.56 (t, J = 7.6 Hz, 1H), 4.78 (d, J = 14.2 Hz, 1H), 4.59 (d, J = 4.0 Hz, 1H), 4.55 (d, J = 5.6 Hz, 1H), 4.48 (d, J = 13.8 Hz, 1H), 4.42 (d, J = 13.1 Hz, 1H), 4.28 – 4.16 (m, 4H), 3.75 (d, J = 13.8 Hz, 1H), 3.59 (d, J = 13.0 Hz, 1H), 3.52 (d, J = 13.0 Hz, 1H), 2.39 (q, J = 14.6, 7.3 Hz, 2H), 1.86 (q, J = 14.6, 7.3 Hz, 2H), 1.38 (t, J = 7.4 Hz, 3H), 0.97 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 151.78, 151.25, 150.65, 143.47, 141.30, 136.42, 135.14, 134.25, 129.47, 129.05, 128.89, 128.69, 128.53, 127.66, 125.90, 124.94, 122.79, 122.45, 122.16, 121.23, 120.59, 118.13, 108.98, 107.91, 79.23, 44.44, 32.88, 31.73, 31.22, 26.56, 23.40, 22.15, 11.62, 10.56. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd for $C_{40}H_{39}NO_4Na$ 620.2777, found 620.2775.

Synthesis of compound 15

To a suspension of **14** (0.200 g, 0.32 mmol) and 1,8-bis(dimethylamino)naphthalene (proton sponge) (0.206 g, 0.96 mmol) in dry DCM (60 ml) at 0 °C trifluoromethanesulfonic anhydride (0.12 mL, 0.64 mmol) was added under nitrogen. After 4 hours of stirring at room temperature, the organic layer was washed twice with 10% HCl and once with water, dried over $MgSO_4$ and evaporated. The residue was washed with MeOH to remove proton sponge. White solid, Yield = 0.182 g (78 %).

^1H NMR (400 MHz, CD_2Cl_2) δ 8.63 (d, J = 8.0 Hz, 1H), 7.79 (s, 1H), 7.69 (d, J = 7.7 Hz, 1H), 7.45 (t, J = 7.9 Hz, 1H), 7.39 – 7.24 (m, 3H), 7.13 (dd, J = 7.6, 1.6 Hz, 1H), 7.10 (s, 1H), 7.05 (dd, J = 7.5, 1.5 Hz, 1H), 6.92 (dd, J = 7.6, 1.4 Hz, 1H), 6.82 (t, J = 7.5 Hz, 2H), 6.70 – 6.59 (m, 3H), 4.85 (d, J = 14.1 Hz, 1H), 4.69 (d, J = 13.2 Hz, 1H), 4.60 (d, J = 14.1 Hz, 1H), 4.16 (td, J =

6.6, 2.1 Hz, 2H), 4.09 – 4.01 (m, 4H), 3.68 (d, J = 13.2 Hz, 1H), 3.60 (d, J = 14.0 Hz, 1H), 3.56 (d, J = 14.3 Hz, 1H), 2.18 (q, J = 14.2, 6.9 Hz, 2H), 1.75 (q, J = 14.7, 7.4 Hz, 2H), 1.33 (t, J = 7.4 Hz, 3H), 0.89 (t, J = 7.4 Hz, 3H). 13C NMR (100 MHz, CD_2Cl_2) δ 153.82, 152.98, 150.26, 141.37, 139.63, 136.88, 134.57, 132.76, 132.48, 132.20, 132.11, 130.08, 129.72, 129.67, 129.56, 129.26, 129.19, 128.77, 128.67, 126.69, 126.46, 126.33, 126.05, 125.95, 125.59, 123.23, 122.46, 122.13, 122.08, 120.67, 120.63, 119.67, 119.27, 119.05, 118.32, 109.58, 108.86, 80.28, 79.66, 44.42, 32.20, 32.01, 31.76, 29.73, 23.13, 22.05, 11.54, 10.38. ^{19}F NMR (400 MHz, CD_2Cl_2) δ -74.66. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd for $C_{41}H_{38}NO_6NaSF_3$ 752.2270, found 752.2275.

Synthesis of compound 16

TES-acetylene calixarene data:

To a mixture of $P(t\text{-}Bu)_3H^+$ BF_4^- (4.0 mg, 0.0137 mmol) and Pd_2dba_3 (7.0 mg, 0.007 mmol) dissolved in 20 ml of dry DMF, CuI (33 mg, 0.17 mmol), DBU 0.04 mL, 0.27 mmol), triethylsilylacetylene (0.15 mL, 0.82 mmol) and **15** (100 mg, 0.14 mmol) were added, and the mixture was heated at 85 °C for 12 hours in an oil bath. The solvent was evaporated and the resulting crude product was dissolved in CH_2Cl_2 and washed with brine several times. Drying the CH_2Cl_2 extract over $MgSO_4$ followed by solvent removal under vacuum gave the crude product. The residue was subjected to column chromatography (CH_2Cl_2/Hexane, 1:4 v/v).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.50 (d, J = 8.0 Hz, 1H), 7.60 (dd, J = 7.6, 1.1 Hz, 1H), 7.44 (s, 1H), 7.43 – 7.38 (m, 1H), 7.34 (dd, J = 7.4, 1.3 Hz, 1H), 7.30 – 7.21 (m, 2H), 7.12 (dd, J = 7.5, 1.5 Hz, 1H), 7.07 (d, J = 6.5 Hz, 1H), 6.96 (s, 1H), 6.82 (t, J = 7.5 Hz, 1H), 6.70 (t, J = 7.5 Hz, 1H), 6.65 (dd, J = 7.5, 1.2 Hz, 1H), 6.57 – 6.52 (m, 1H), 6.37 (m, 2H), 5.19 (d, J = 14.5 Hz, 1H), 5.05 (d, J = 13.0 Hz, 1H), 4.69 (d, J = 14.5 Hz, 1H), 4.31 (d, J = 13.4 Hz, 1H), 4.18 (d, J = 13.7 Hz, 1H), 4.06 – 3.87 (m, 4H), 3.77 (d, J = 13.1 Hz, 1H), 3.45 (d, J = 13.8 Hz, 1H), 3.32 (d, J = 13.4 Hz, 1H), 2.04 (m, 2H), 1.69 (q, J = 14.6, 7.3 Hz, 2H), 1.23 (m, 12H), 0.90 (q, J = 7.9 Hz, 6H), 0.73 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 154.67, 153.77, 152.64, 141.26, 140.95, 136.61, 133.47, 131.98, 130.73, 129.87, 128.94, 128.90, 128.83, 128.66, 128.42, 127.07, 125.16, 124.76, 123.10, 121.97, 118.95, 118.42, 118.28, 114.72, 108.75, 108.70, 105.27, 100.49, 78.36, 44.15, 36.29, 35.00, 31.87, 31.81, 23.43, 22.01, 11.43, 10.91, 7.61, 4.78.

Obtained white solid was treated with KOH (78 mg, 1.4 mmol) in dry THF (2.5 ml) and methanol (7.5 ml) under nitrogen, and stirred at 40 °C on oil bath for 24 hours or until there was a full conversion. The reaction was quenched with water and CH_2Cl_2 was added. The organic layer was separated and washed twice with water and then with brine. Drying the organic layer over $MgSO_4$ followed by solvent removal under vacuum gave the crude product. Precipitation from CH_2Cl_2/MeOH afforded the pure product **16**.

White solid, yield: 30.5 mg (36% over two steps). ^1H NMR (400 MHz, CD_2Cl_2) δ 8.51 (d, J = 8.0 Hz, 1H), 7.64 – 7.55 (m, 2H), 7.40 – 7.44 (m, 1H), 7.35 (dd, J = 9.1, 4.5 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.27 – 7.21 (m, 1H), 7.13 (dd, J = 7.5, 1.6 Hz, 1H), 7.09 – 7.04 (m, 1H), 7.02 (s, 1H), 6.82 (t, J = 7.3 Hz, 1H), 6.77 – 6.68 (m, 2H), 6.65 (dd, J = 7.6, 1.4 Hz, 1H), 6.48 (t, J = 7.6 Hz, 1H), 6.17 (s, 1H), 5.10 (d, J = 14.5 Hz, 1H), 4.96 (d, J = 13.0 Hz, 1H), 4.74 (d, J = 14.5 Hz, 1H), 4.22 (d, J = 13.8 Hz, 1H), 4.14 (d, J = 13.8 Hz, 1H), 4.08 – 3.92 (m, 4H), 3.81 (s, 1H), 3.79 (d, J = 10.2 Hz, 1H), 3.49 (d, J = 13.8 Hz, 1H), 3.42 (d, J = 13.9 Hz, 1H), 2.05 (q, J = 14.1, 7.0 Hz, 2H), 1.71 (q, J = 14.6, 7.3 Hz, 2H), 1.27 (t, J = 7.4 Hz, 3H), 0.77 (t, J = 7.4 Hz, 4H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 154.36, 153.48, 152.25, 141.44, 141.04, 137.24, 133.51, 132.41, 130.78, 129.89, 129.14, 128.89, 128.82, 128.72, 128.61, 128.46, 127.00, 125.75, 125.26, 125.12, 123.11, 121.94, 119.26, 118.68, 118.51, 108.75, 84.70, 83.17, 78.04, 44.22, 36.25, 34.72, 32.45, 31.88, 31.70, 23.35, 22.76, 22.03, 13.98, 11.46, 10.54. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd for $C_{42}H_{39}NO_3Na$ 628.2828, found 628.2826.

Synthesis of compound 3a

To a mixture of $P(t\text{-}Bu)_3H^+\ BF_4^-$ (6.8 mg, 0.024 mmol) and Pd_2dba_3 (5.4 mg, 0.06 mmol) dissolved in 20 ml of dry DMF, CuI (56 mg, 0.29 mmol), DBU (70 µl, 0.47 mmol), 3-ethynyl-9-propyl-9*H*-carbazole (273 mg, 1.17 mmol) and **15** (0.175 g, 0.24 mmol) were added and the mixture was heated at 85 °C for 12 hours on oil bath. The solvent was evaporated and the resulting crude product was dissolved in DCM and washed with brine several times. Drying the DCM extract over $MgSO_4$ followed by solvent removal under vacuum gave the crude product. The residue was subjected to column chromatography (CH_2Cl_2/Hexane, 1:2 v/v). Off-white solid, Yield = 72.0 mg (37%).

^1H NMR (400 MHz, CD_2Cl_2) δ 8.59 (d, J = 7.9 Hz, 1H), 8.53 (s, 1H), 8.22 (d, J = 7.7 Hz, 1H), 7.95 – 7.88 (m, 2H), 7.66 (d, J = 7.4 Hz, 1H), 7.54 (t, J = 6.5 Hz, 3H), 7.46 (dd, J = 16.6, 9.8 Hz, 1H), 7.28 – 7.45 (m, 5H), 7.10 – 7.13 (m, 2H), 7.09 (d, J = 7.3 Hz, 1H), 6.90 (d, J = 7.4 Hz, 1H), 6.83 (d, J = 7.6 Hz, 1H), 6.74 (s, 1H), 6.69 (q, J = 12.8, 7.5 Hz, 2H), 5.26 (d, J = 14.5 Hz, 1H), 5.19 (d, J = 12.9 Hz, 1H), 4.87 (d, J = 14.5 Hz, 1H), 4.40 (t, J = 7.1 Hz, 2H), 4.27 (d, J = 13.7 Hz, 1H), 4.21 – 4.08 (m, 4H), 3.94 – 3.83 (m, 2H), 3.52 (d, J = 13.7 Hz, 1H), 3.44 (d, J = 13.6

Hz, 1H), 2.01 (q, J = 14.5, 7.2 Hz, 2H), 1.76 – 1.83 (m, 4H), 1.05 (t, J = 7.4 Hz, 3H), 0.85 (q, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 154.51, 153.75, 140.99, 136.17, 133.81, 132.73, 130.56, 129.94, 129.43, 129.24, 128.91, 128.69, 128.54, 127.06, 126.05, 125.89, 125.17, 125.01, 123.61, 123.04, 121.18, 120.57, 119.27, 118.65, 118.46, 114.35, 109.14, 108.93, 108.76, 77.99, 44.80, 44.35, 37.41, 36.55, 34.78, 33.86, 32.41, 32.00, 23.35, 22.40, 22.09, 11.58, 11.52, 10.36. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd for $C_{57}H_{52}N_2O_3Na$ 835.3876, found 835.3872.

Synthesis of compound 3b

2-benzyl-6-bromo-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (38 mg, 0.10 mmol) was added to a solution of $Pd(PPh_3)_4$ (3.0 mg, 0.0027 mmol), CuI (0.59 mg, 0.003 mmol) and iPr_2NH (1 mL) in 5 ml dry DMF. To this mixture **16** (31.5 mg, 0.052 mmol) in 2 mL DMF was added slowly under nitrogen atmosphere. The reaction mixture was stirred at 80 °C in an oil bath for 24h. The solvent was evaporated and the resulting crude was dissolved in DCM followed by washing with brine several times. The organic layer was dried over $MgSO_4$. Further, the solvent was evaporated and the crude product was subjected to column chromatography over silica gel (CH_2Cl_2/Hexane, 1:1 v/v). Orange solid, Yield = 28.2 mg (61%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.24 (d, J = 8.3 Hz, 1H), 8.67 (d, J = 7.3Hz, 1H), 8.63 (d, J = 7.7 Hz, 1H), 8.58 (d, J = 7.9 Hz, 1H), 8.20 – 8.14 (m, 1H), 7.87 (t, J = 13.4 Hz, 1H), 7.79 (s, 1H), 7.68 (d, J = 7.7 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.47 – 7.25 (m, 7H), 7.18 – 7.07 (m, 2H), 7.06 – 7.00 (m, 1H), 6.86 (d, J = 7.5 Hz, 1H), 6.80 (t, J = 6.9 Hz, 1H), 6.75 – 6.62 (m, 2H), 6.52 (t, J = 12.4 Hz, 1H), 6.37 (s, 1H), 5.42 (s, 2H), 5.30 (d, J = 14.2 Hz, 1H), 5.25 (d, J = 12.8 Hz, 1H), 4.90 (d, J = 14.0 Hz, 1H), 4.09 – 3.96 (m, 4H), 3.94 (d, J = 12.9 Hz, 1H), 3.87 – 3.83 (m, 2H), 3.51 (d, J = 13.9 Hz, 1H), 3.44 (d, J = 14.2 Hz, 1H), 1.76 (q, J = 14.6, 7.3 Hz, 2H), 1.51 (q, J = 14.0, 7.0 Hz, 2H), 0.85 (t, J = 7.4 Hz, 3H), 0.56 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 164.23, 163.94, 154.24, 153.46, 151.30, 141.49, 141.15, 137.83, 137.77, 134.01, 133.76, 133.04, 132.60, 131.77, 131.54, 130.95, 130.67, 130.57, 130.49, 130.25, 130.08, 129.91, 129.44, 129.18, 128.91, 128.85, 128.64, 128.44, 128.22, 127.89, 127.39, 127.24, 127.11, 126.62, 126.35, 125.76, 125.43, 123.19, 122.82, 122.10, 120.87, 119.72, 119.61, 118.96, 118.75, 114.64, 108.87, 101.83, 93.71, 78.42, 44.37, 43.53, 36.73, 34.83, 32.55, 31.85, 31.70, 23.00, 22.76, 22.08, 13.98, 11.51, 10.15. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd for $C_{61}H_{50}N_2O_5Na$ 913.3617, found 913.3622.

3. NMR Spectra

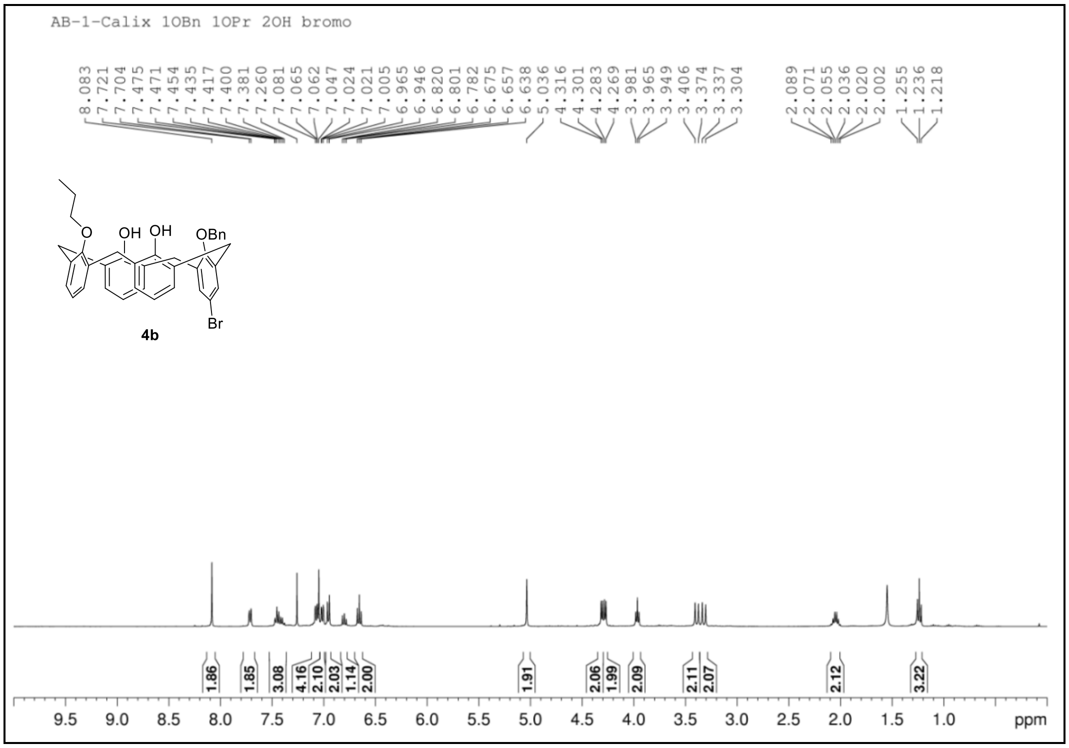


Figure S1. ^{1}H NMR (400 MHz) spectra of **4b** in $CDCl_3$.

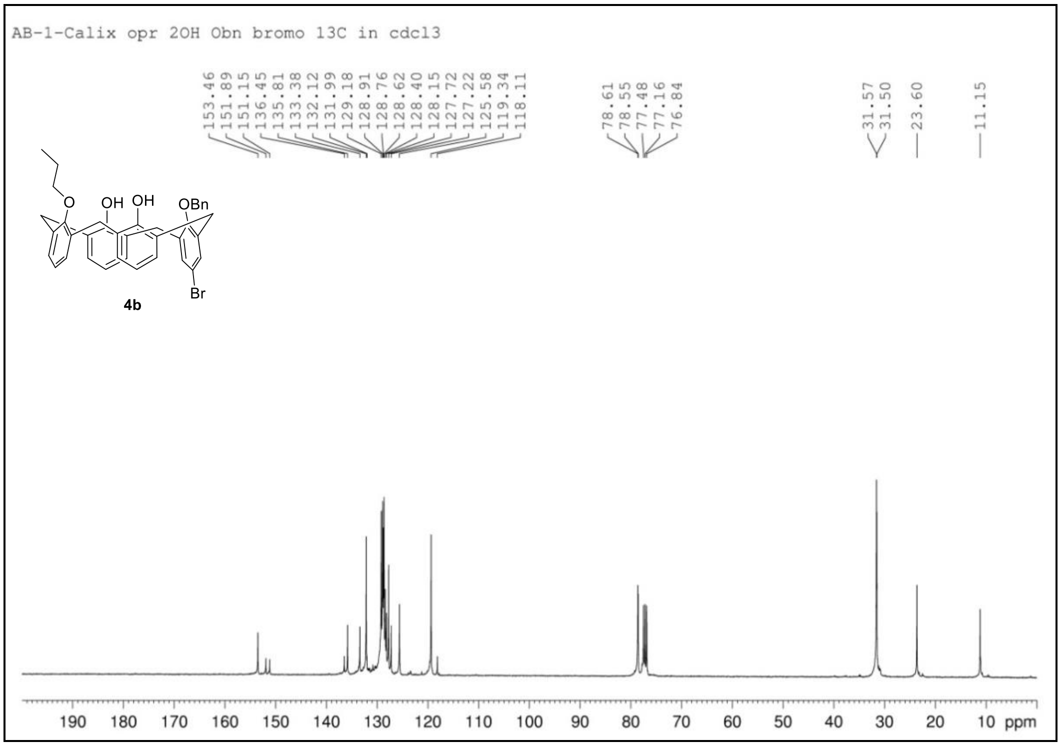


Figure S2. ^{13}C {^{1}H} NMR (100 MHz) spectra of **4b** in $CDCl_3$.

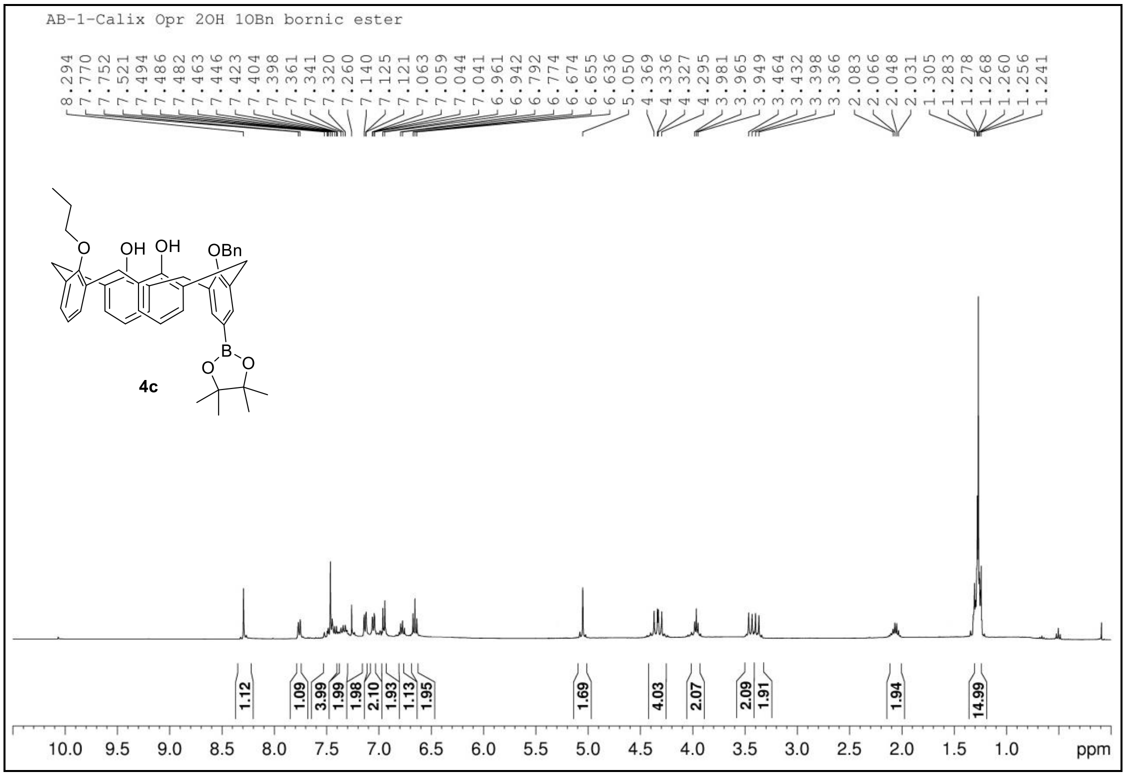


Figure S3. ^{1}H NMR (400 MHz) spectra of **4c** in CDCl$_3$.

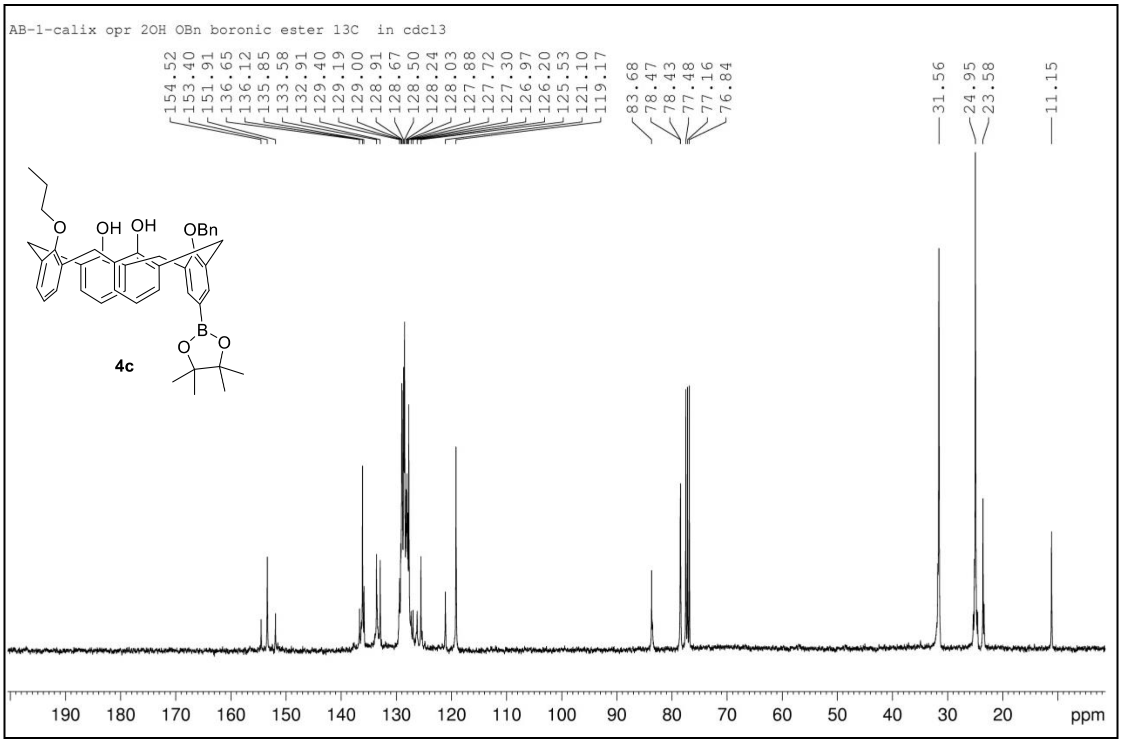


Figure S4. ^{13}C {^{1}H} NMR (100 MHz) spectra of **4c** in CDCl$_3$.

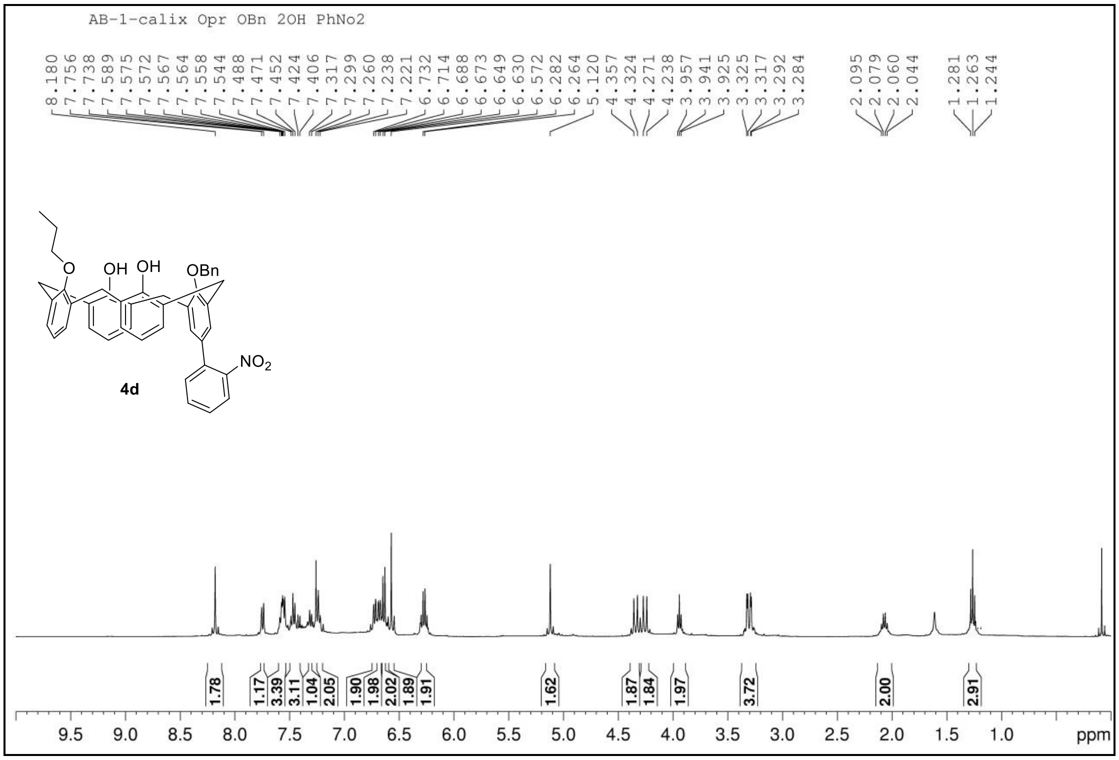


Figure S5. ^{1}H NMR (400 MHz) spectra of **4d** in CDCl$_3$.

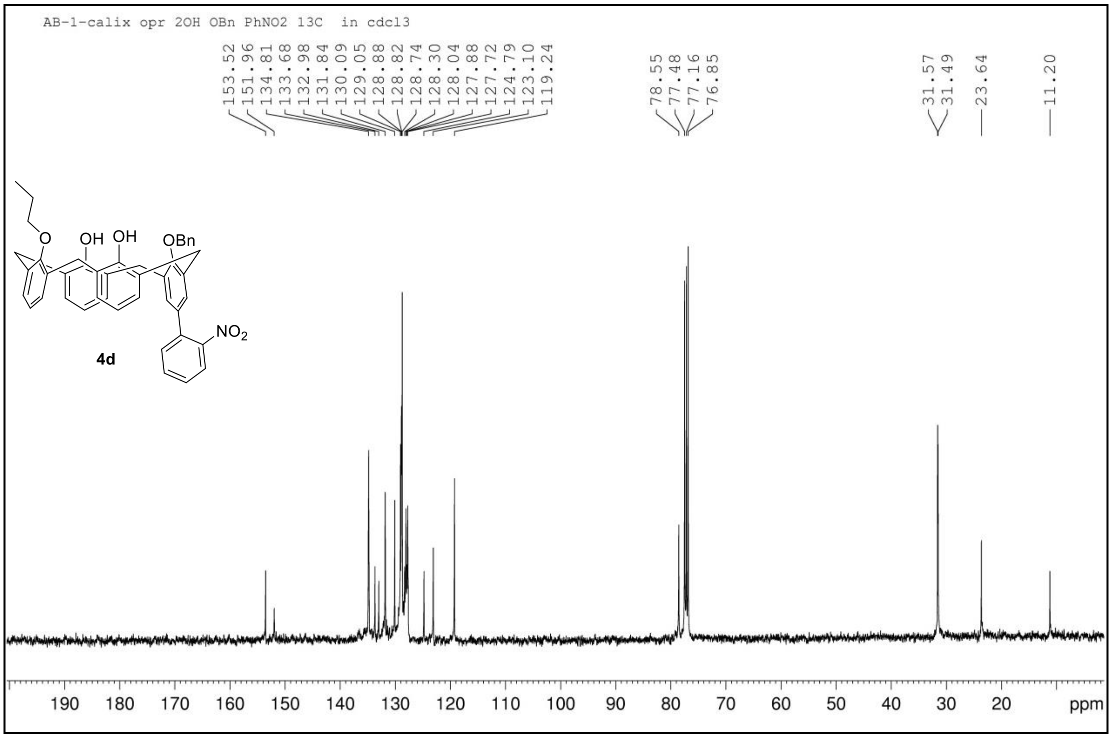


Figure S6. ^{13}C {^{1}H} NMR (100 MHz) spectra of **4d** in CDCl$_3$.

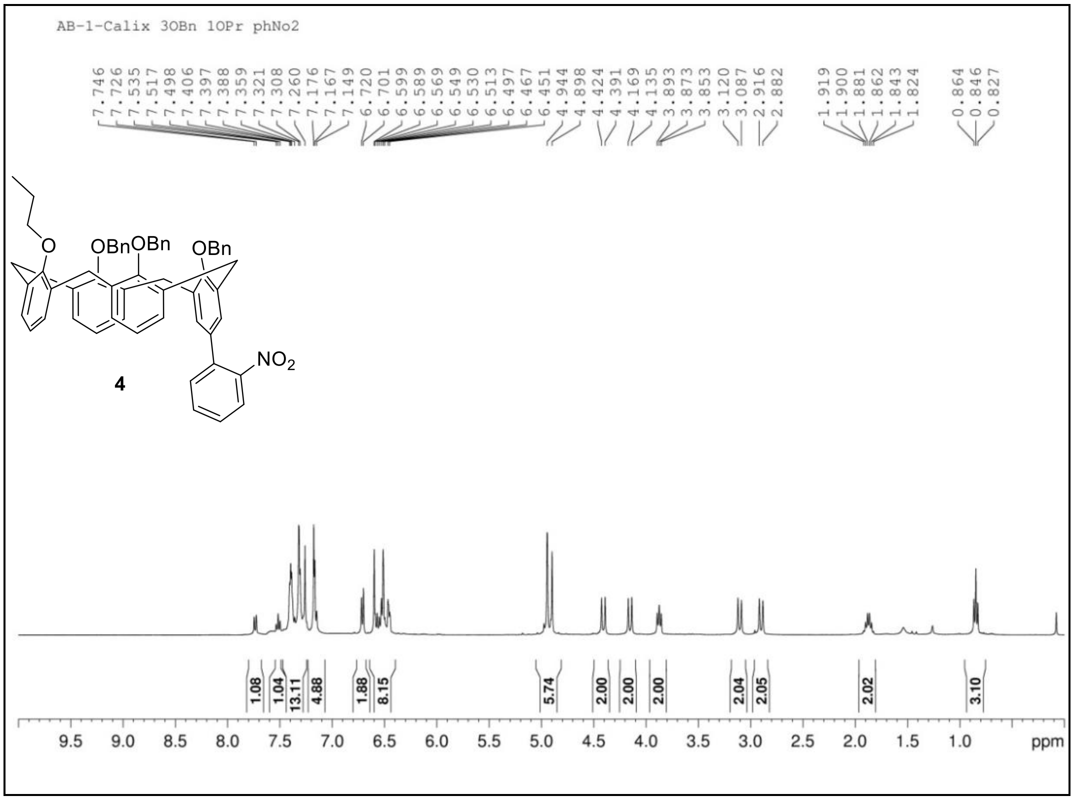


Figure S7. ^{1}H NMR (400 MHz) spectra of **4** in CDCl$_3$.

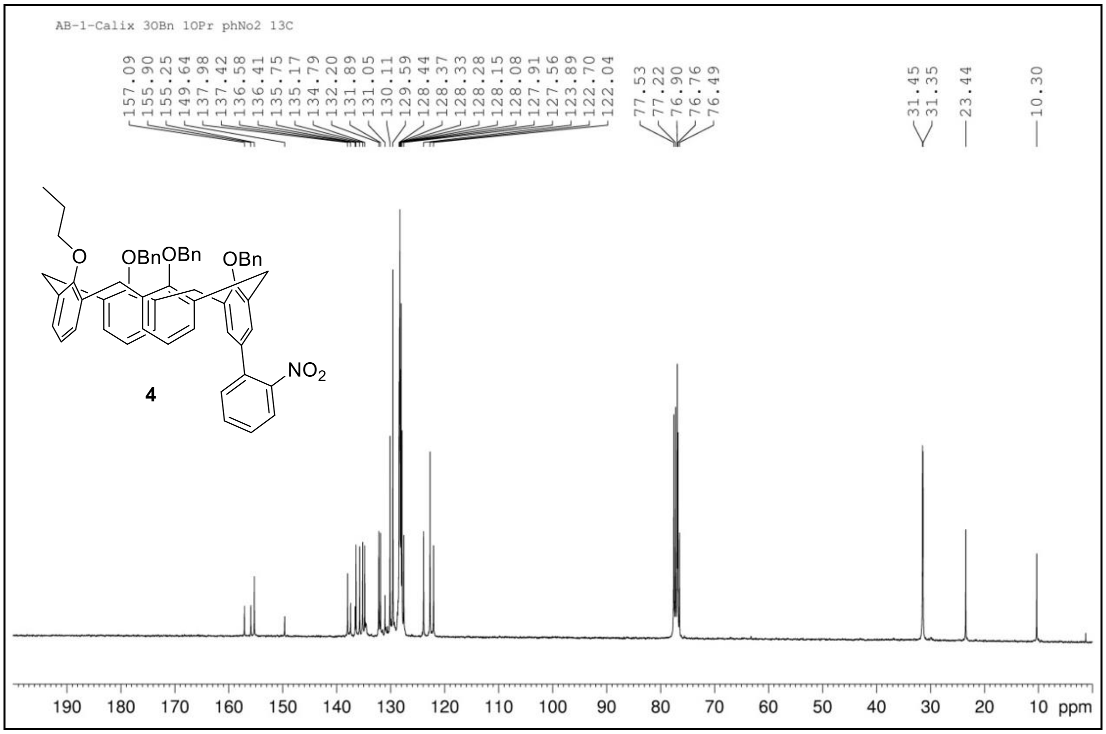


Figure S8. ^{13}C {^{1}H} NMR (100 MHz) spectra of **4** in CDCl$_3$.

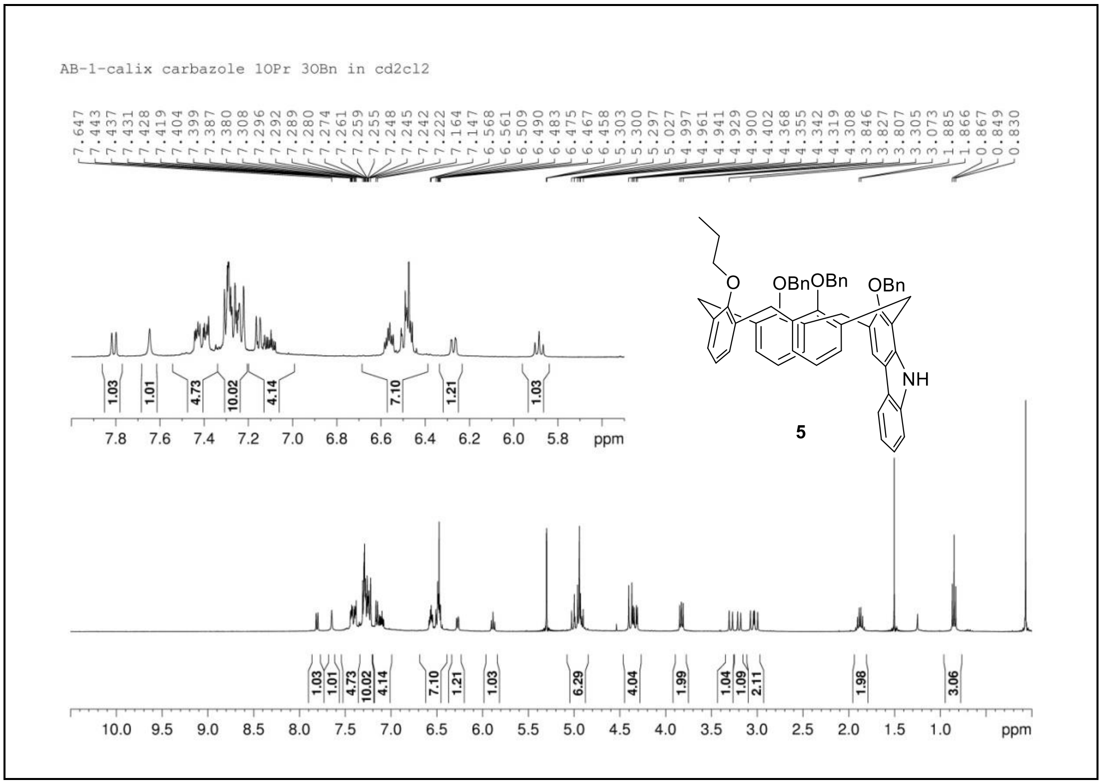


Figure S9. ^{1}H NMR (400 MHz) spectra of **5** in CD_2Cl_2.

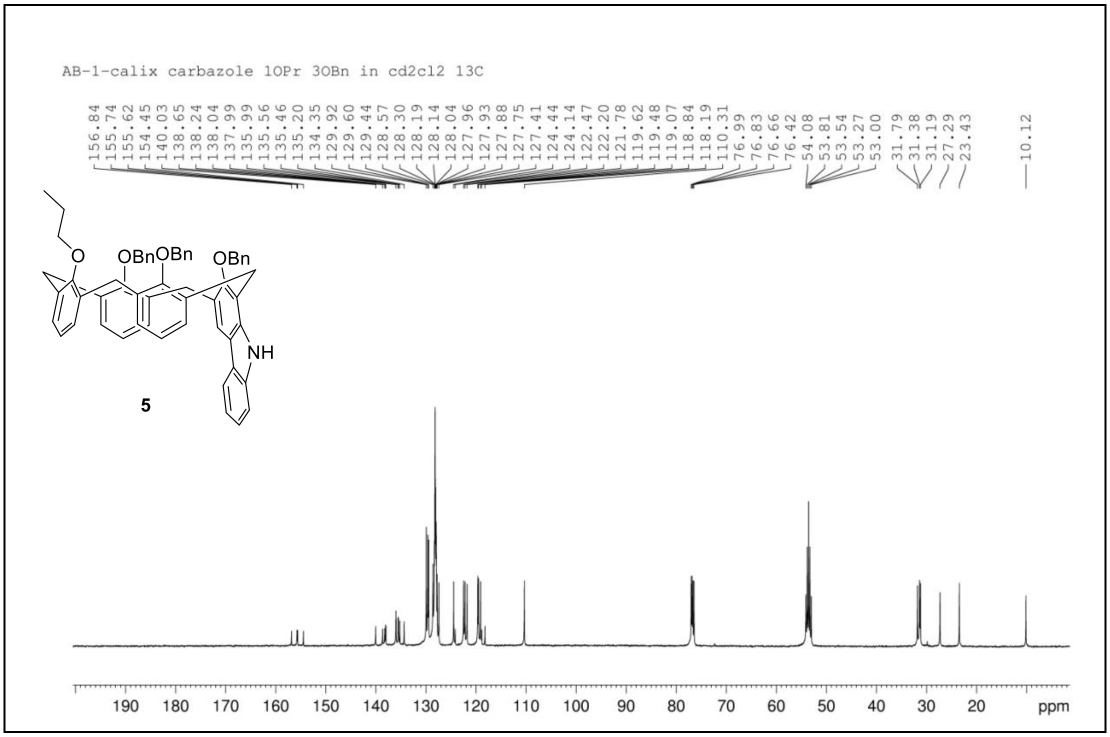


Figure S10. ^{13}C {^{1}H} NMR (100 MHz) spectra of **5** in CD_2Cl_2.

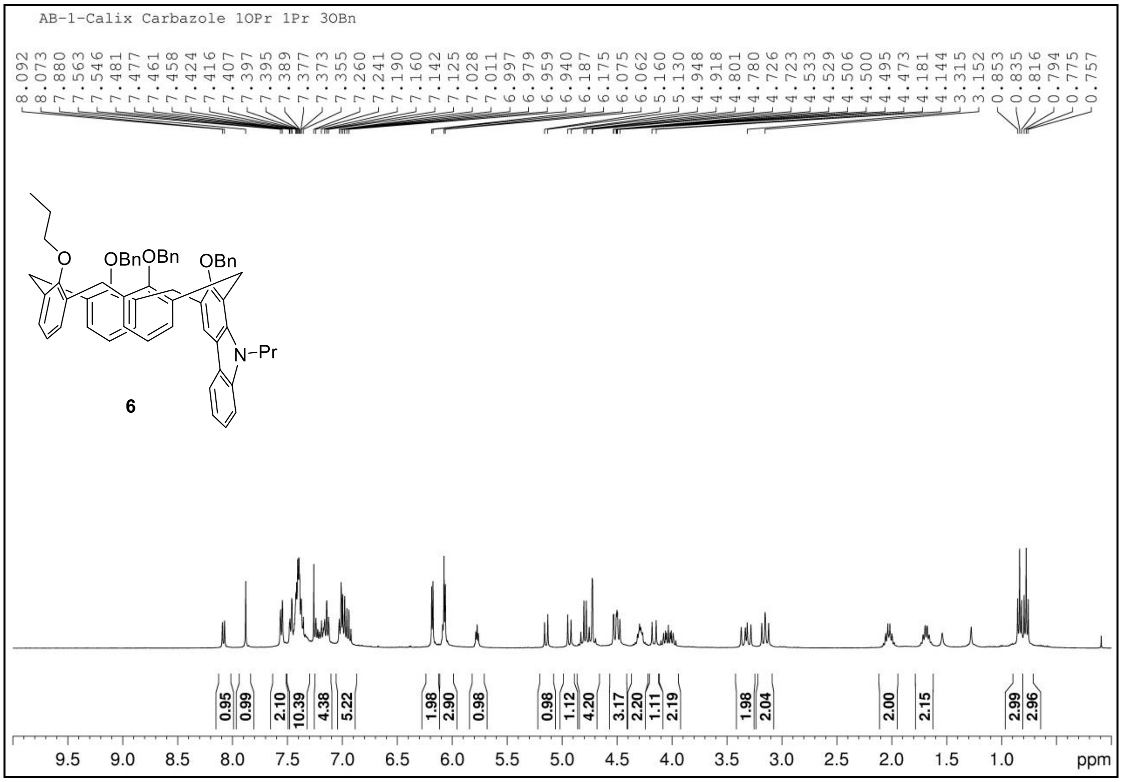


Figure S11. ^{1}H NMR (400 MHz) spectra of **6** in CD_2Cl_2.

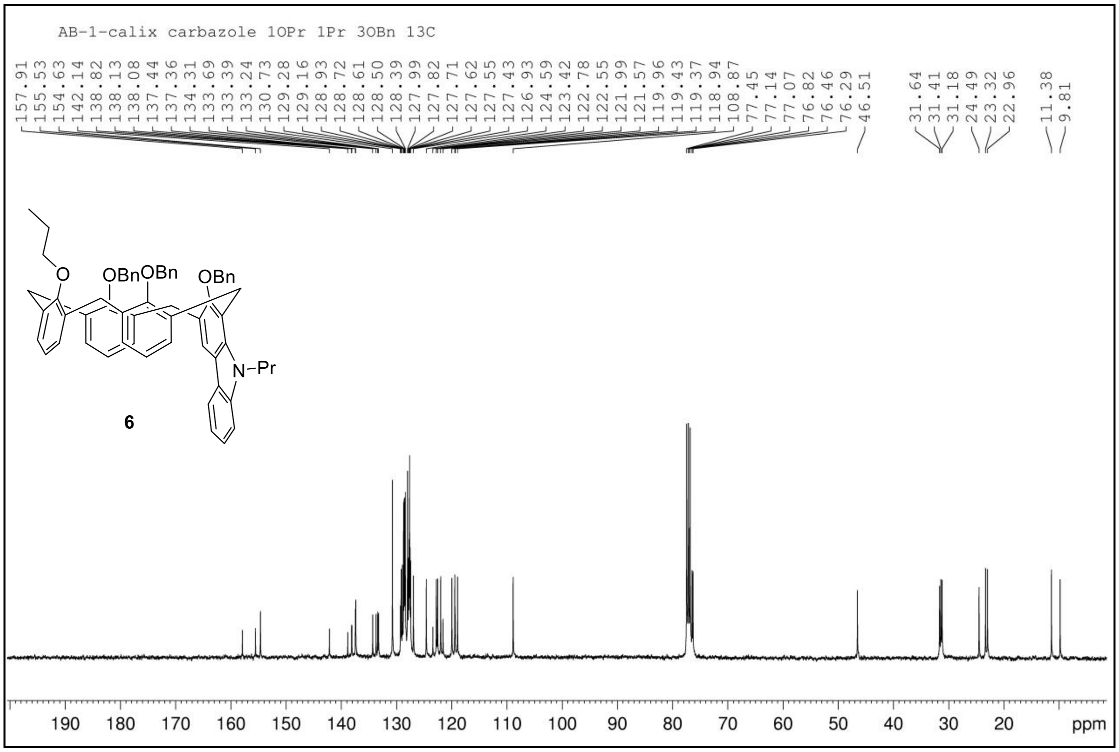


Figure S12. ^{13}C {^{1}H} NMR (100 MHz) spectra of **6** in CD_2Cl_2.

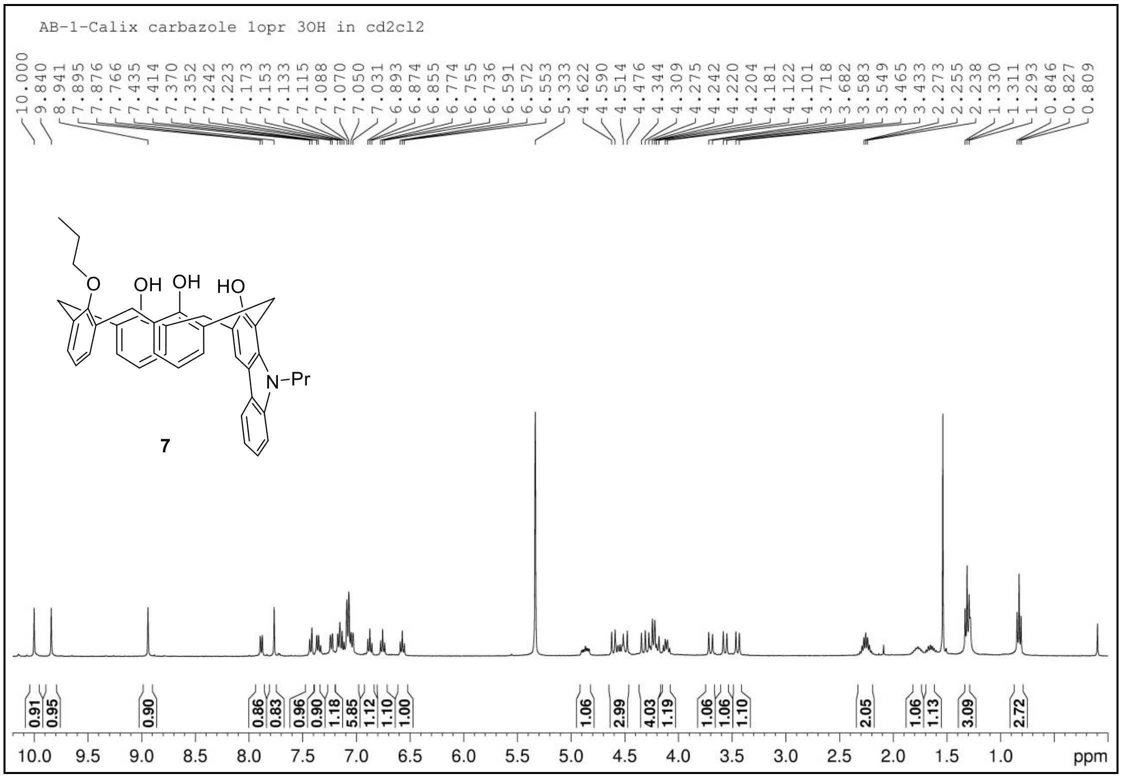


Figure S13. ^{1}H NMR (400 MHz) spectra of **7** in CD_2Cl_2.

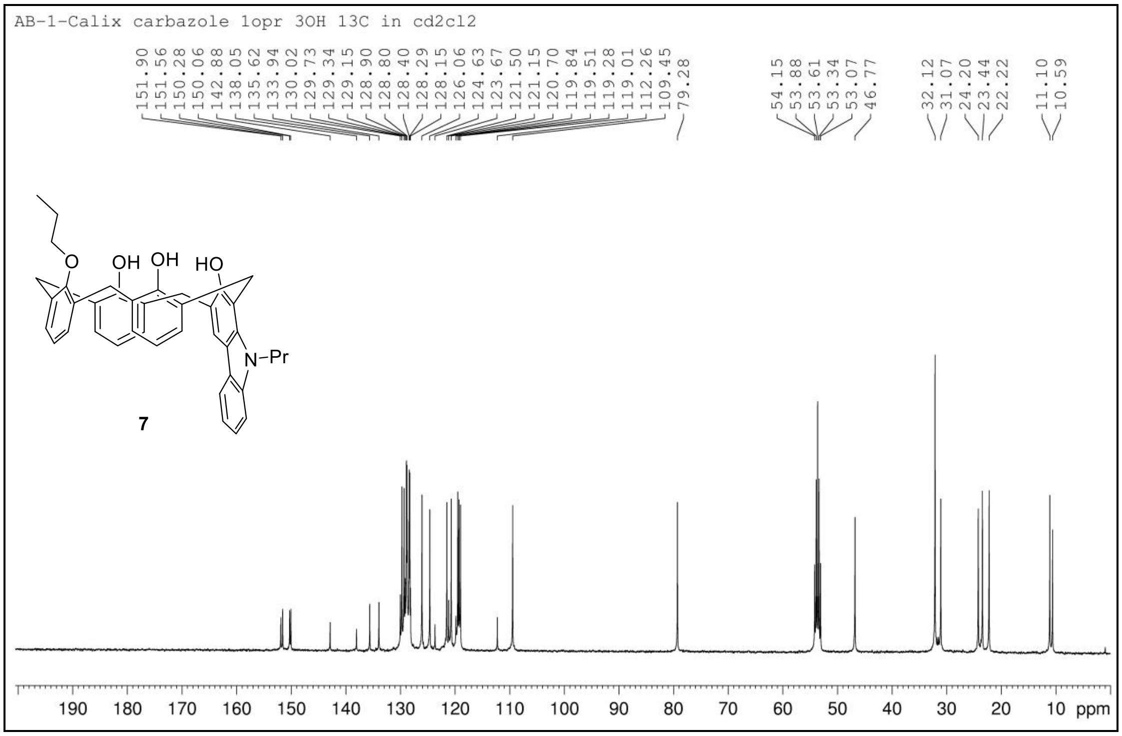


Figure S14. $^{13}C\{^1H\}$ NMR (100 MHz) spectra of **7** in CD_2Cl_2.

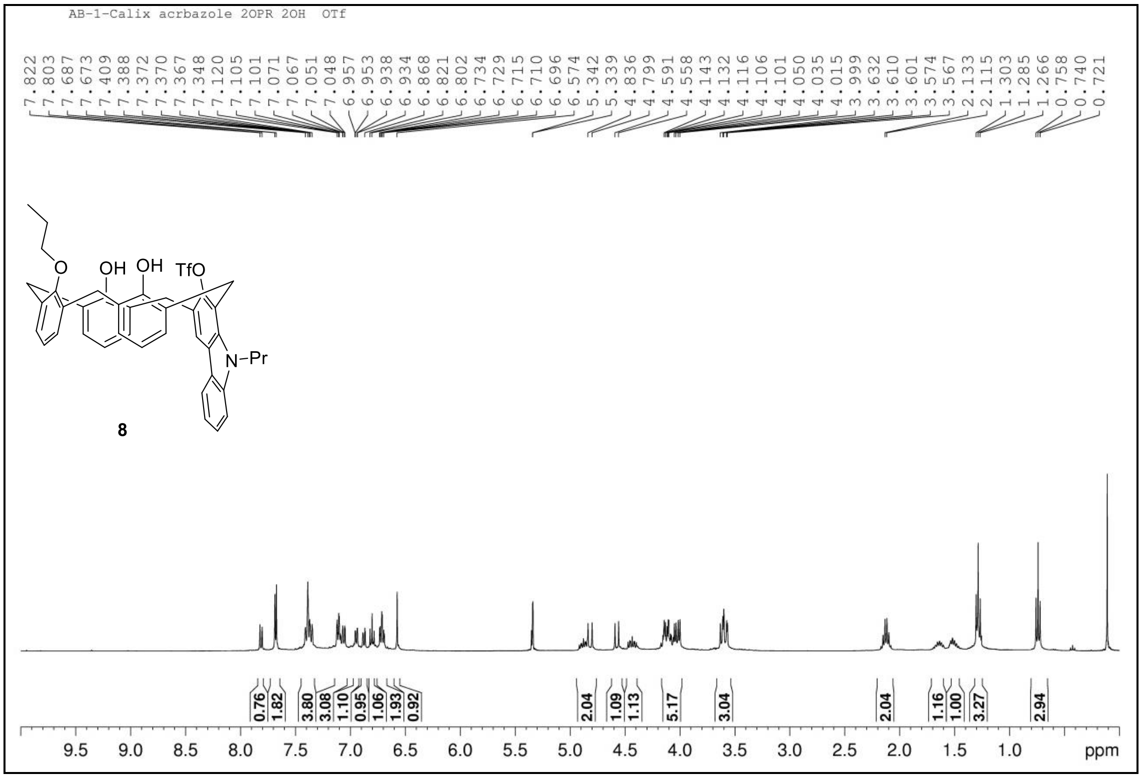


Figure S15. ^{1}H NMR (400 MHz) spectra of **8** in CD_2Cl_2.

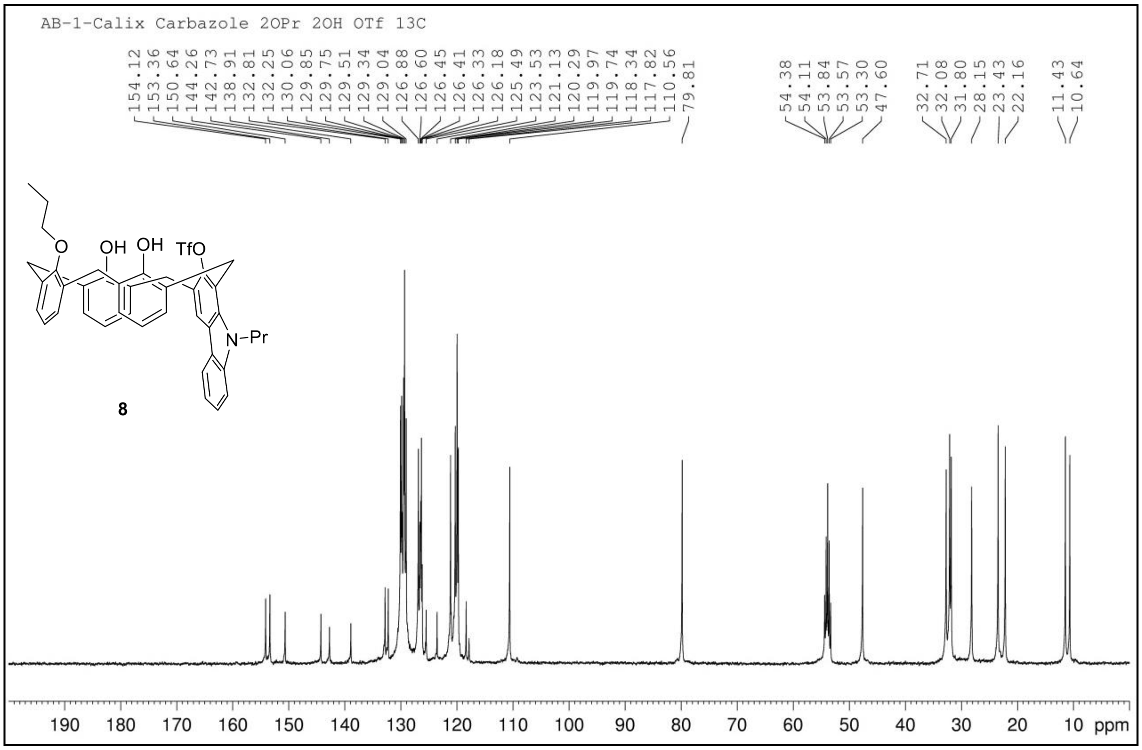


Figure S16. ^{13}C {^{1}H} NMR (100 MHz) spectra of **8** in CD_2Cl_2.

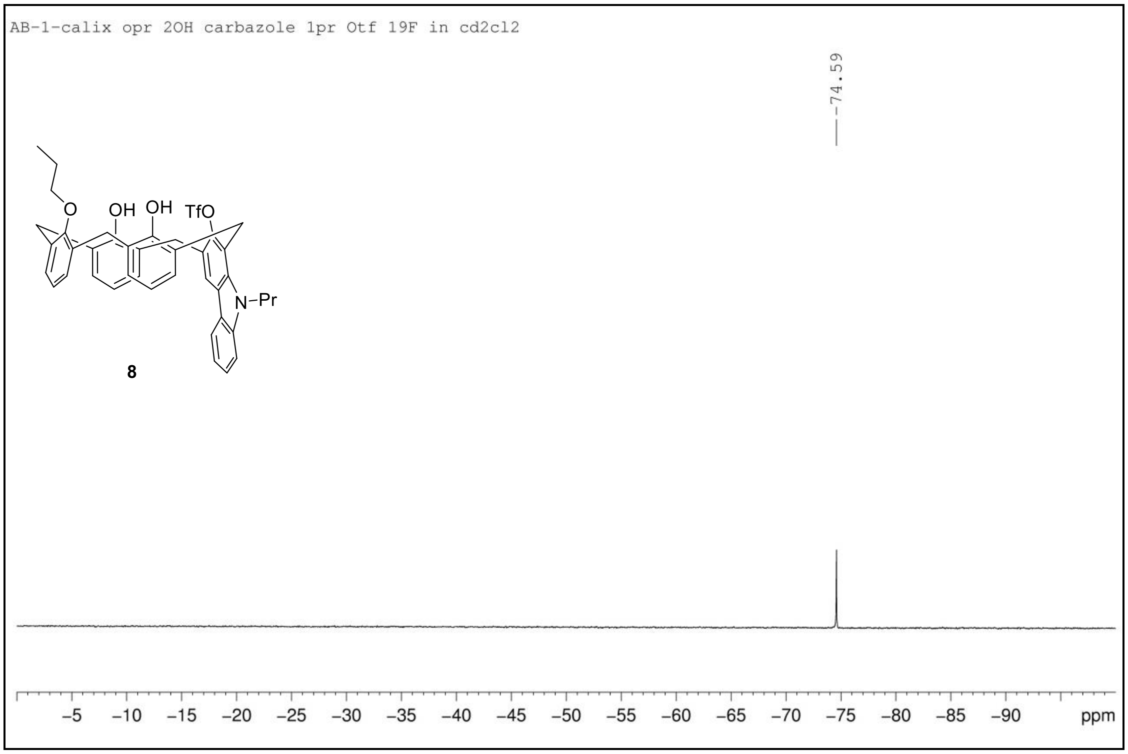


Figure S17. ^{19}F NMR (400 MHz) spectra of **8** in CD_2Cl_2.

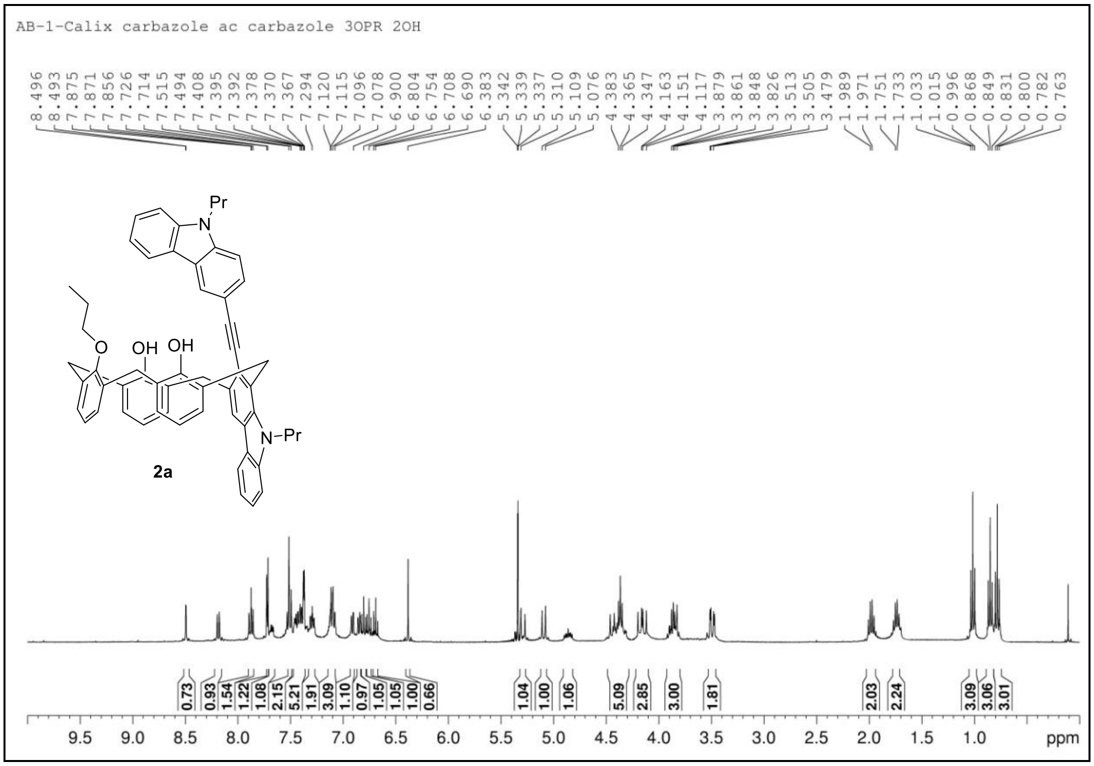


Figure S18. ^{1}H NMR (400 MHz) spectra of **2a** in CD_2Cl_2.

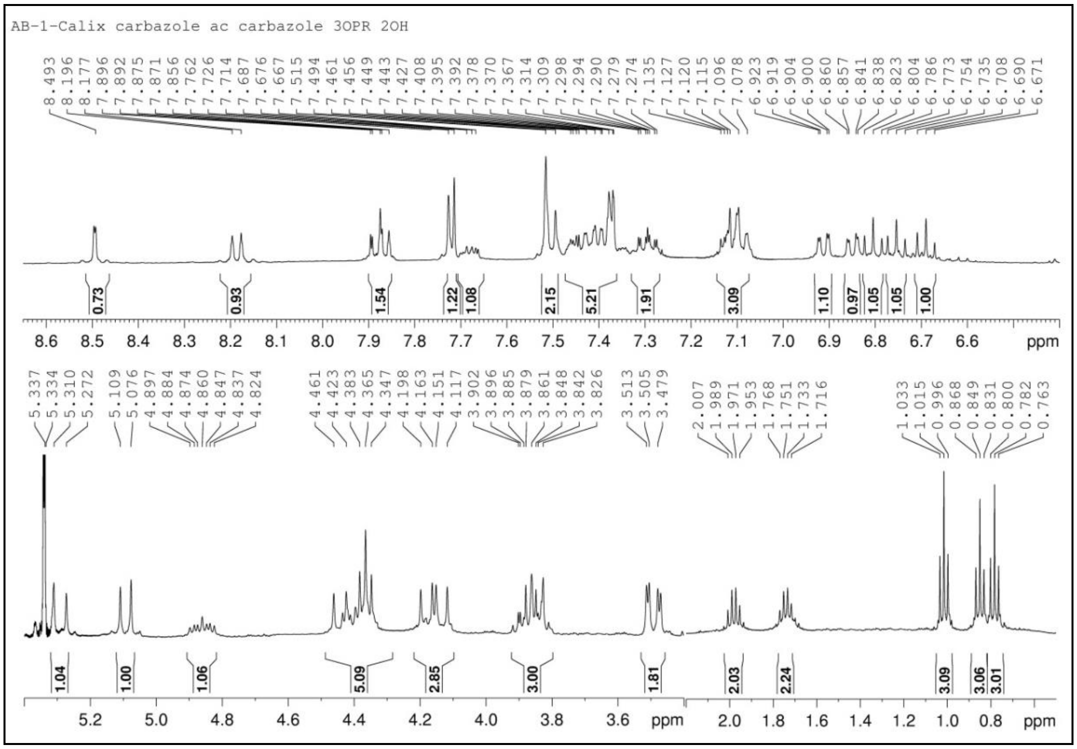


Figure S18. Partial ^{1}H NMR (400 MHz) spectra (0.5-2.2 ppm, 3.4-5.4 ppm and 6.4-8.65 ppm) of **2a** in CD_2Cl_2.

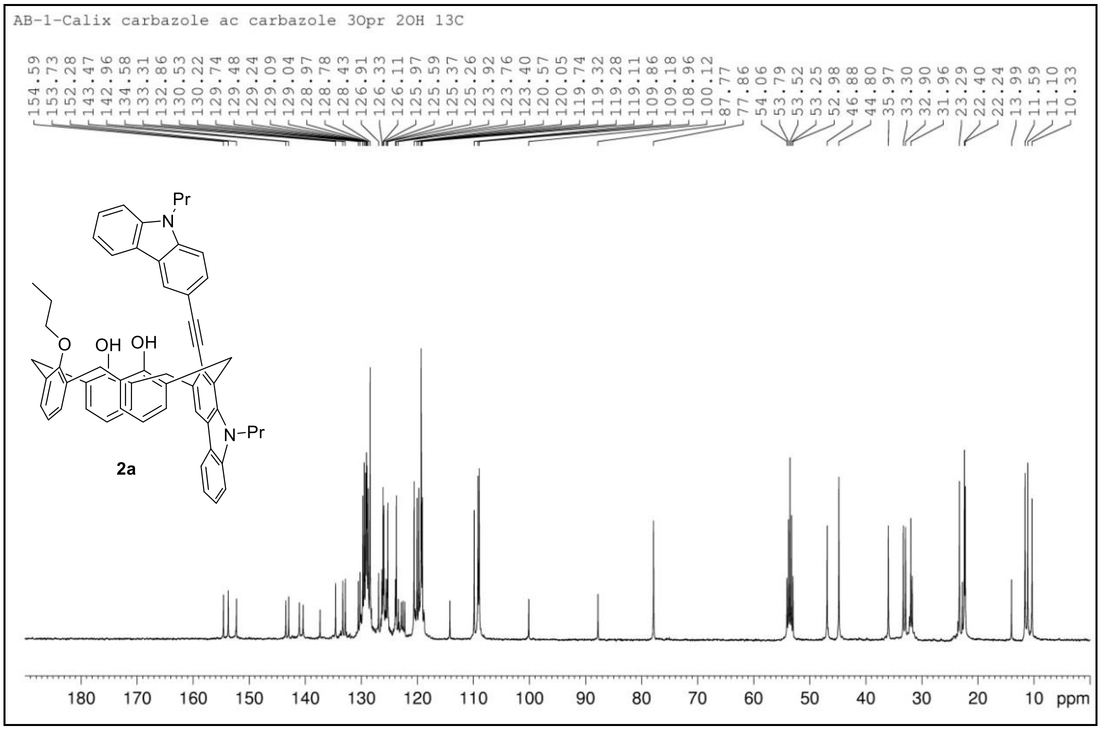


Figure S19. ^{13}C {^{1}H} NMR (100 MHz) spectra of **2a** in CD_2Cl_2.

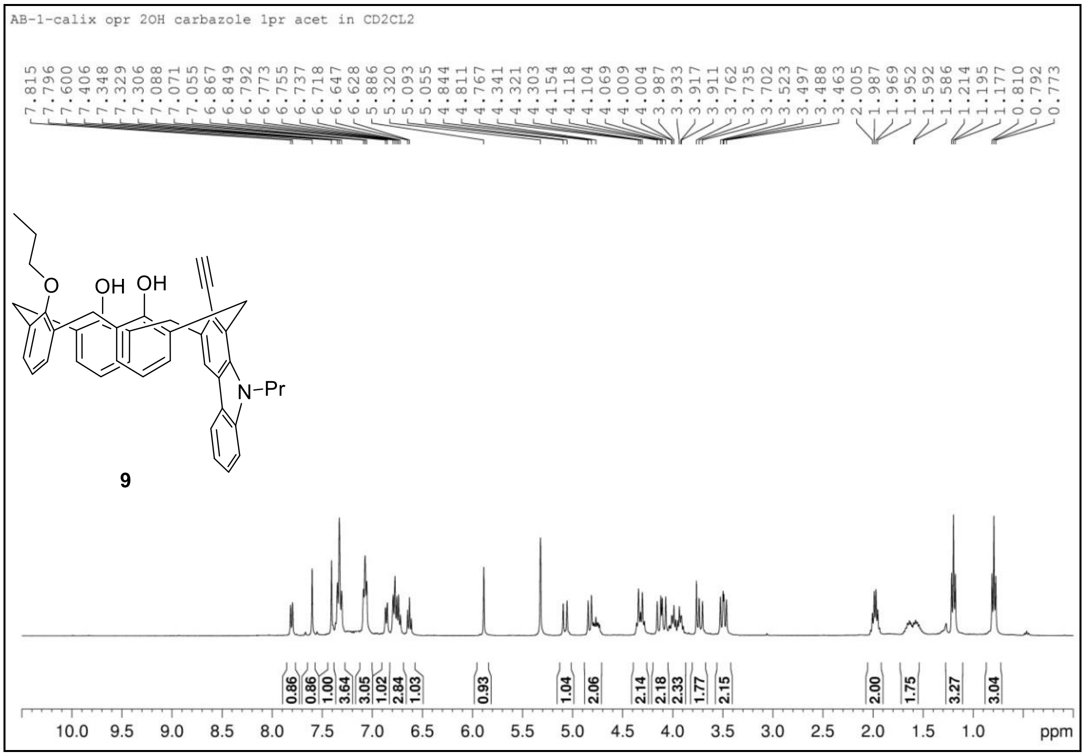


Figure S20. ^{1}H NMR (400 MHz) spectra of **9** in CD_2Cl_2.

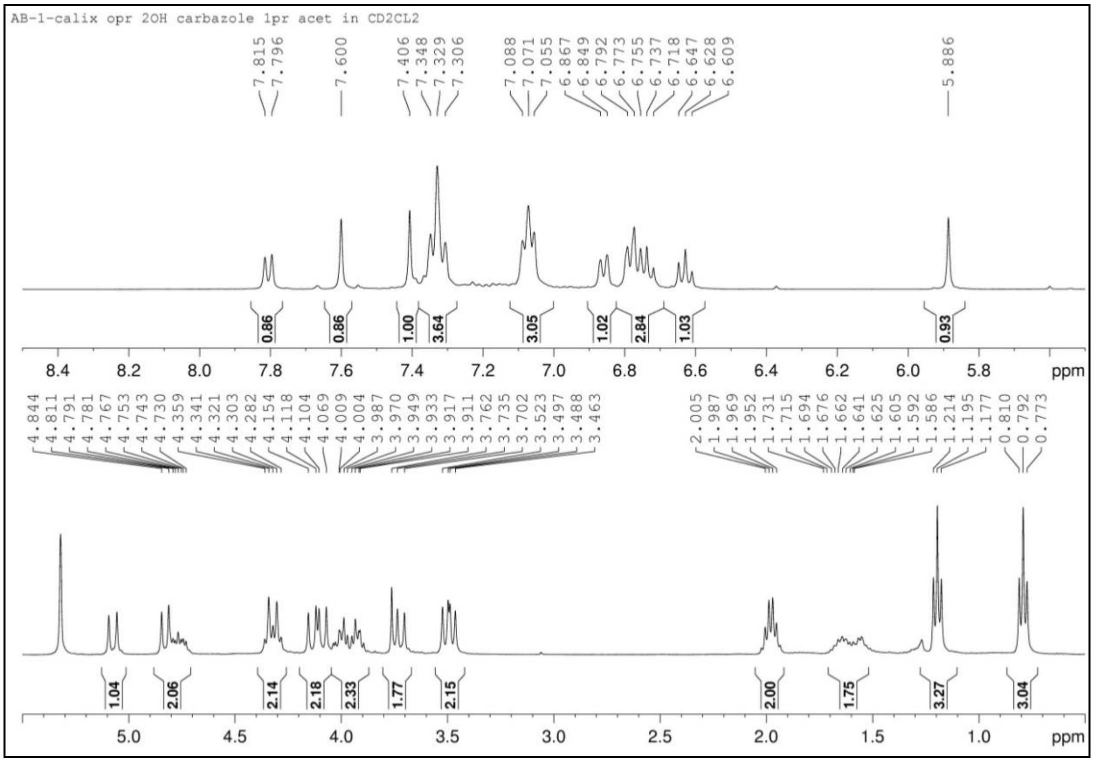


Figure S21. Partial ^{1}H NMR (400 MHz) spectra (0.5-5.5 ppm and 5.7-8.4 ppm) of **9** in CD_2Cl_2.

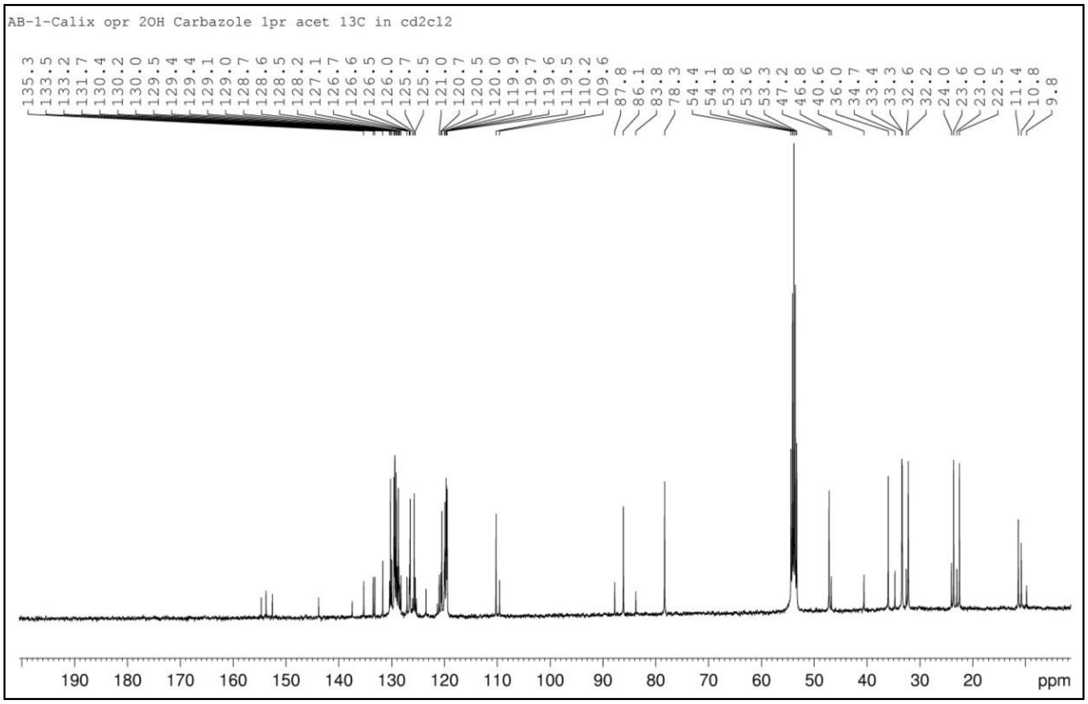


Figure S22. ^{13}C {^{1}H} NMR (100 MHz) spectra of **9** in CD_2Cl_2.

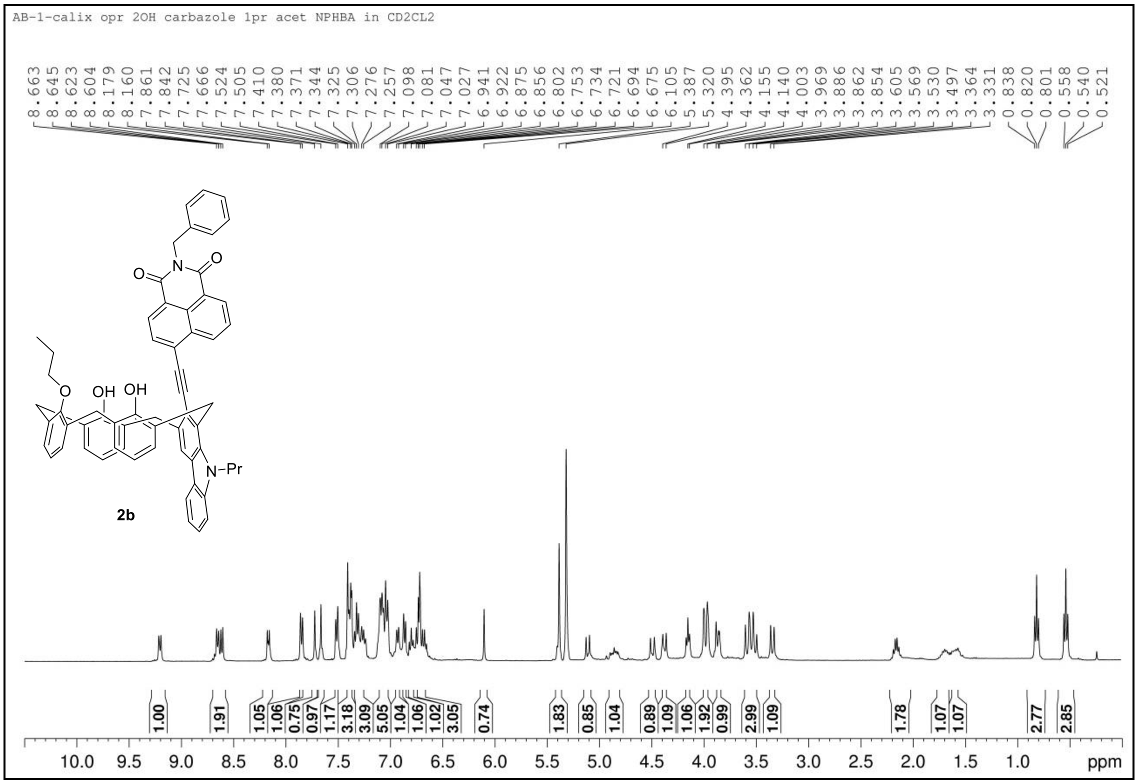


Figure S23. ^{1}H NMR (400 MHz) spectra of **2b** in CD_2Cl_2.

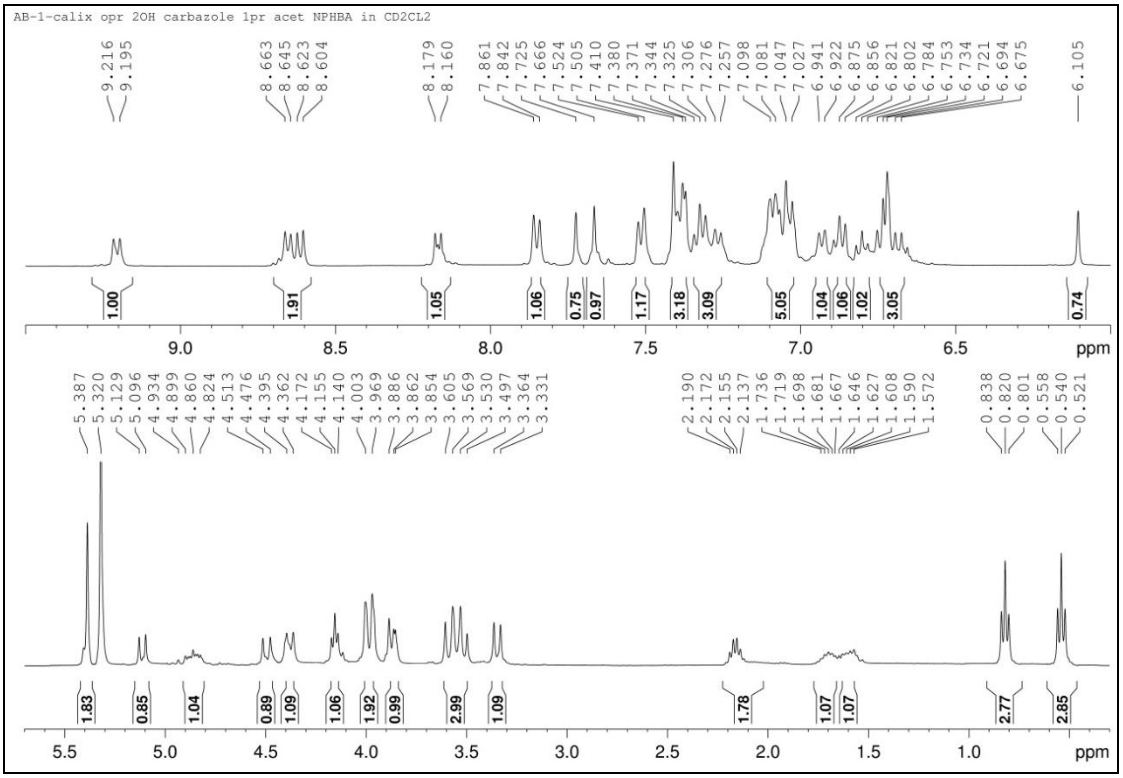


Figure S24. Partial ^{1}H NMR (400 MHz) spectra (0.3-5.7 ppm and 6.0-9.5 ppm) of **2b** in CD_2Cl_2.

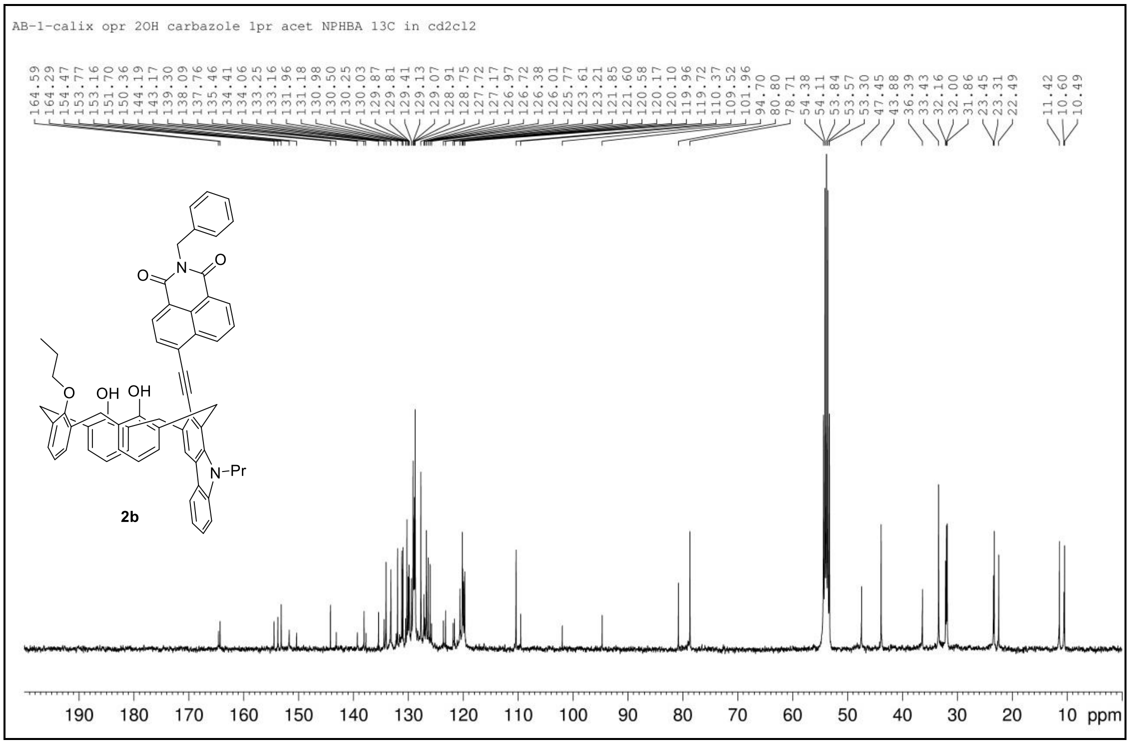


Figure S25. ^{13}C {^{1}H} NMR (100 MHz) spectra of **2b** in CD_2Cl_2.

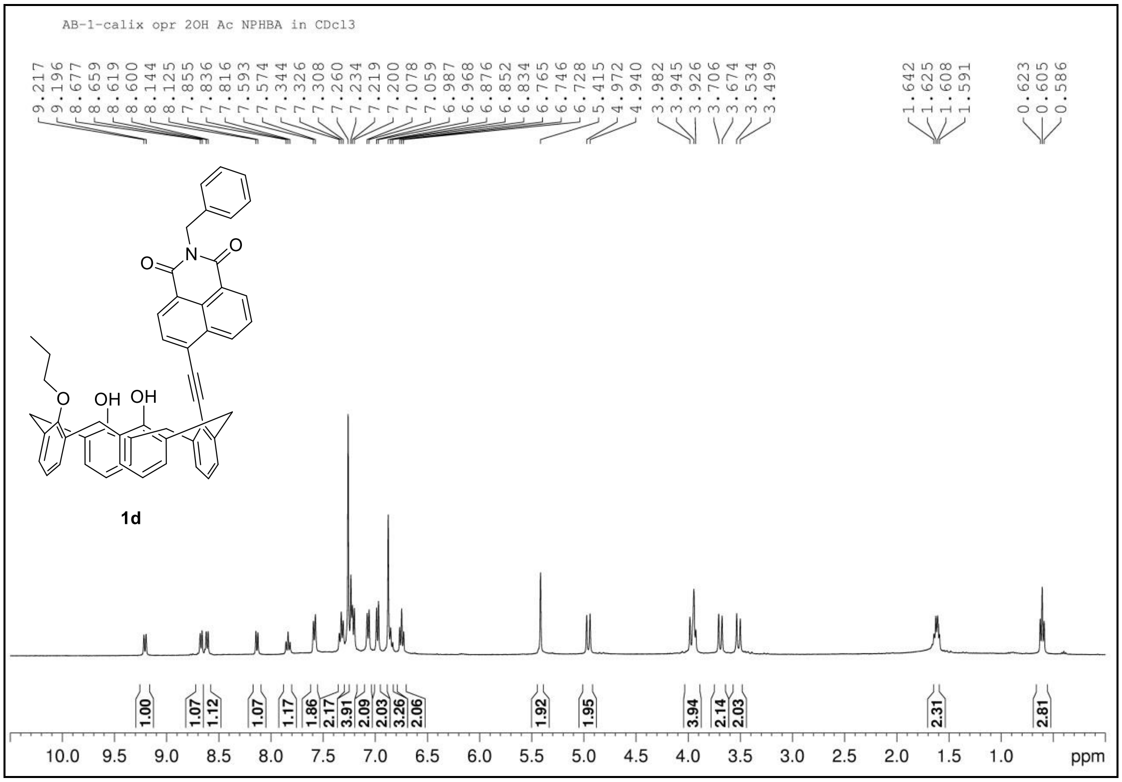


Figure S26. ^{1}H NMR (400 MHz) spectra of **1d** in CDCl$_3$.

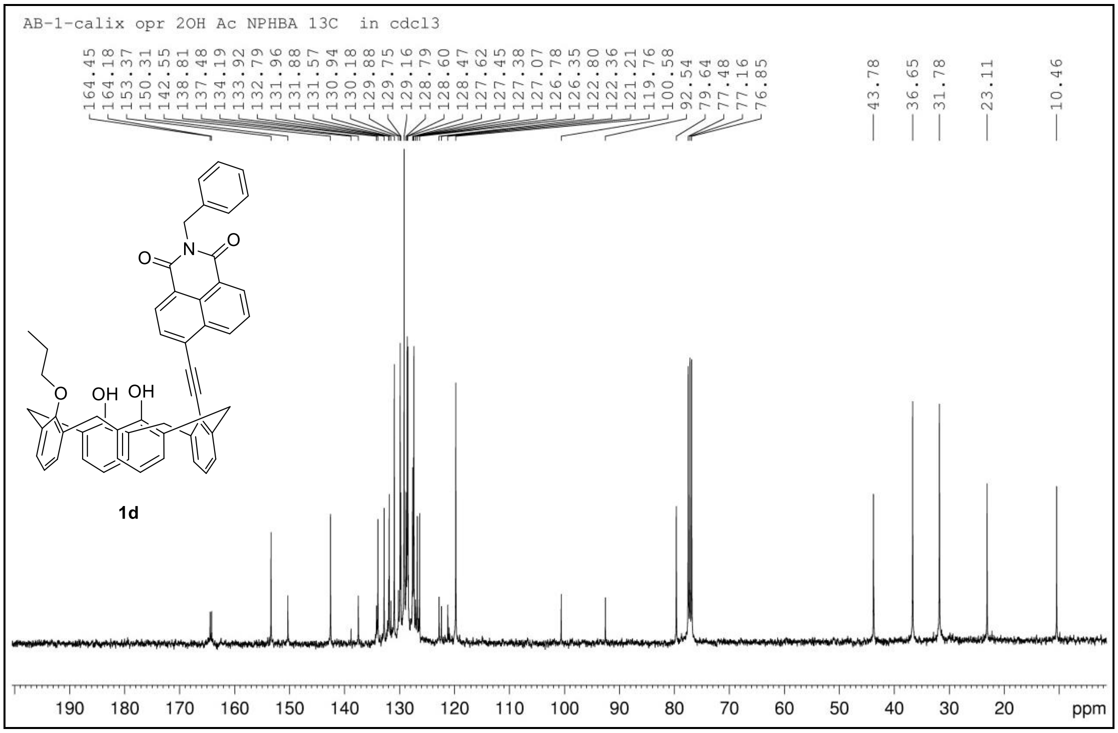


Figure S27. ^{13}C {^{1}H} NMR (100 MHz) spectra of **1d** in CDCl$_3$.

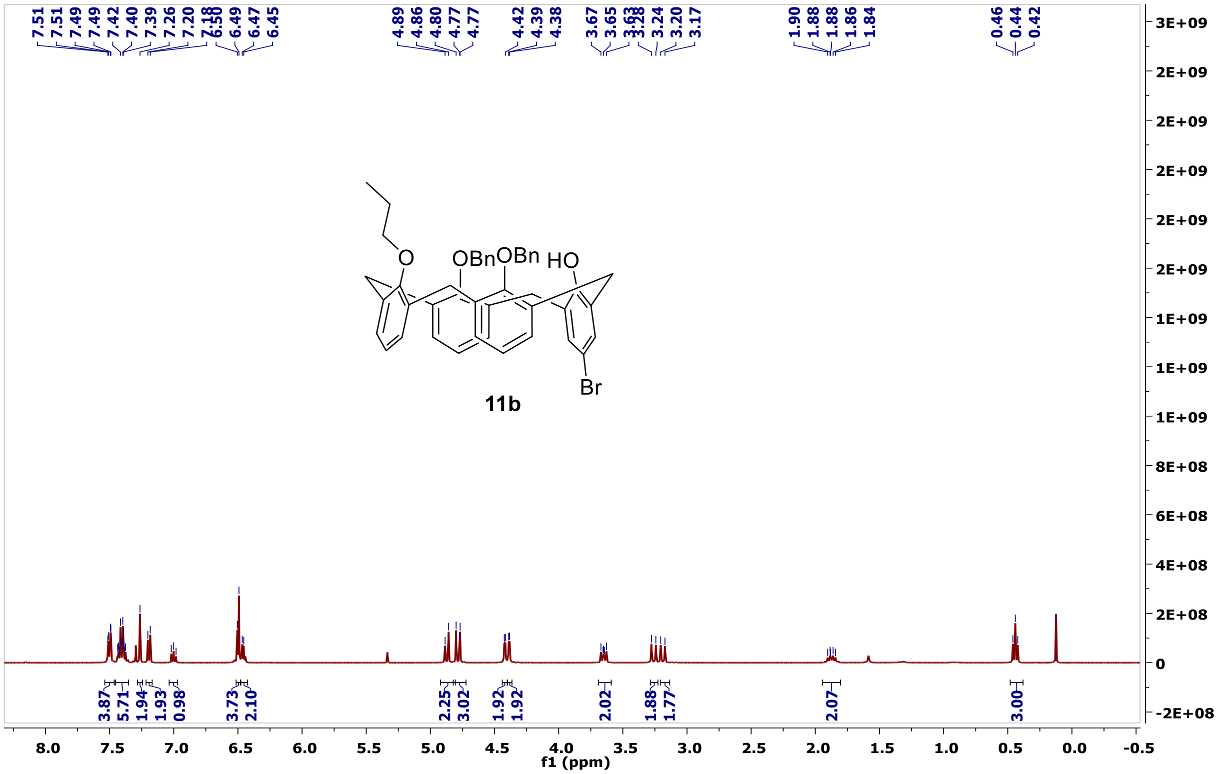


Figure S28. ^{1}H NMR (400 MHz) spectra of **11b** in CDCl$_3$.

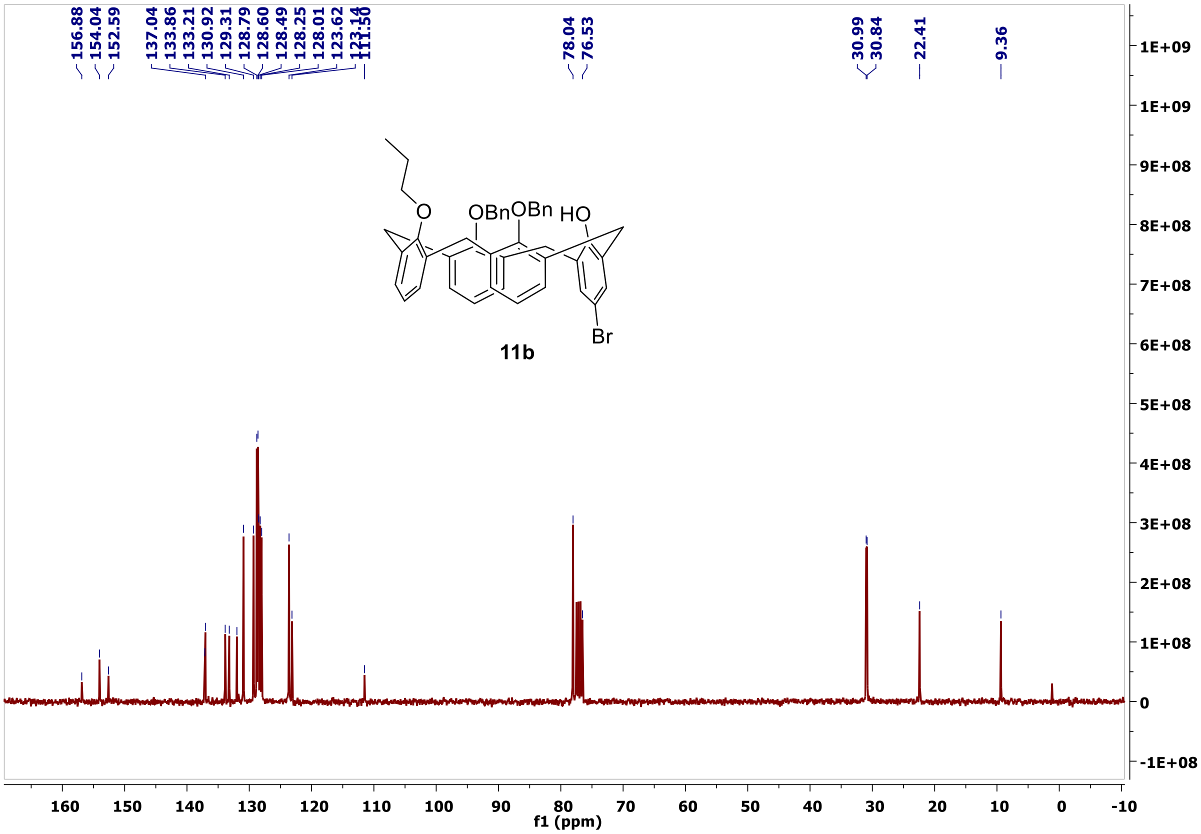


Figure S29. ^{13}C {^{1}H} NMR (100 MHz) spectra of **11b** in CDCl$_3$.

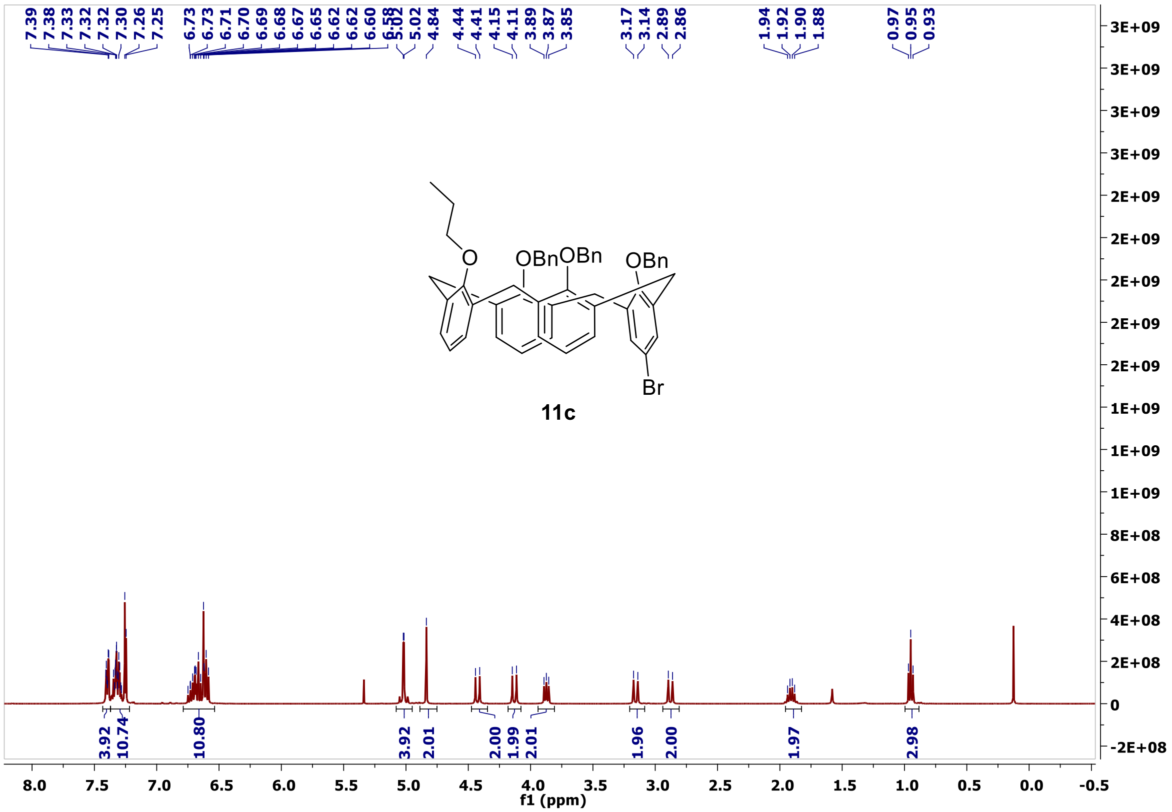


Figure S30. ^{1}H NMR (400 MHz) spectra of **11c** in $CDCl_3$.

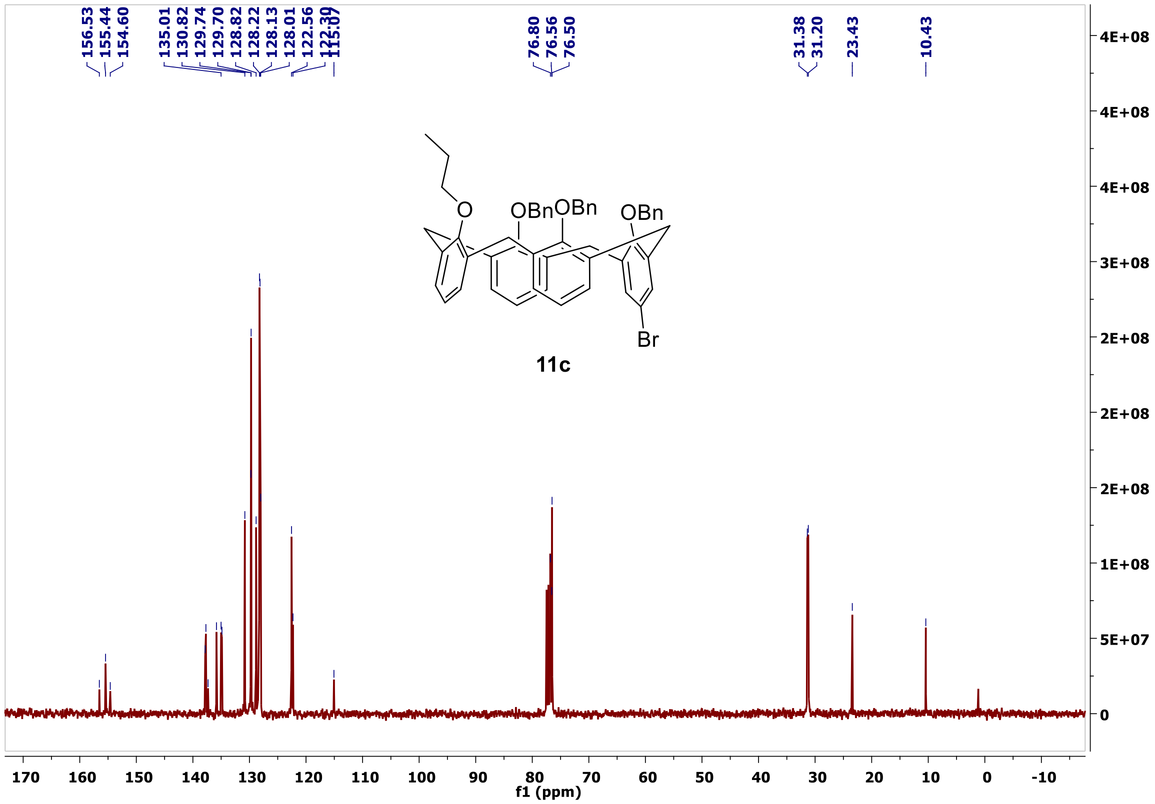


Figure S31. ^{13}C {^{1}H} NMR (100 MHz) spectra of **11c** in $CDCl_3$.

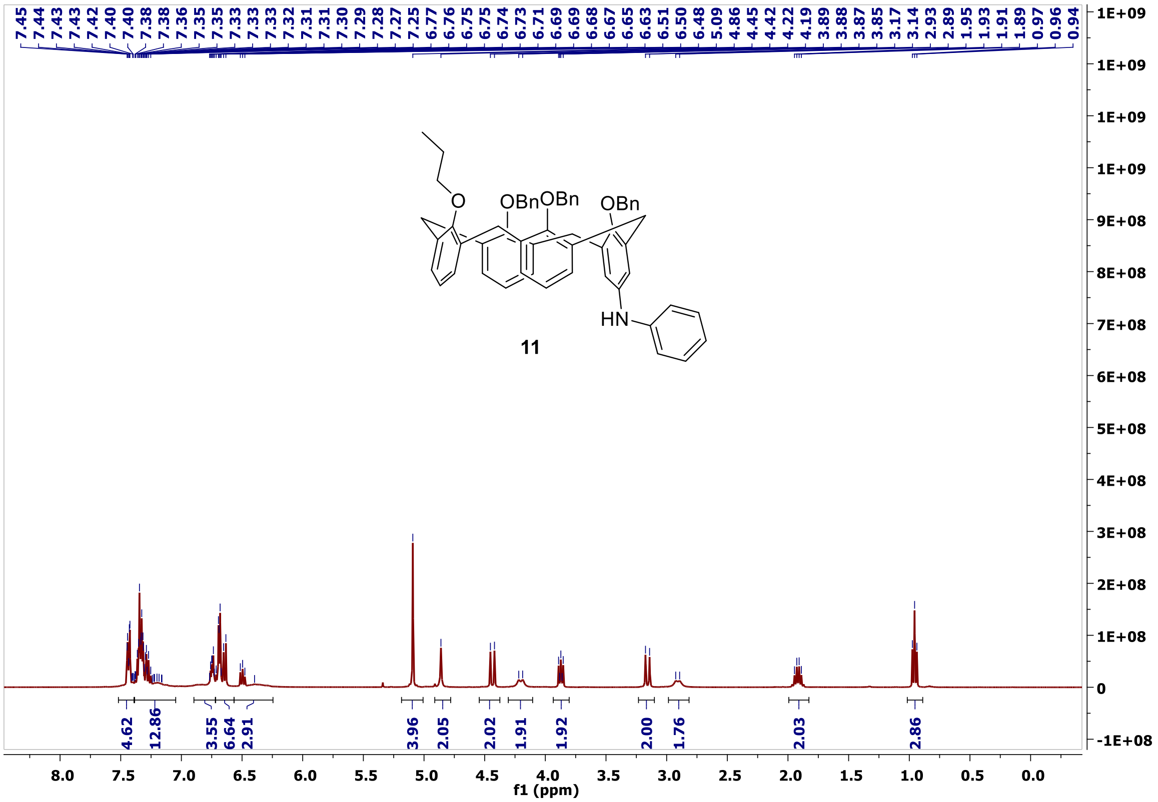


Figure S32. ^{1}H NMR (400 MHz) spectra of **11** in CDCl$_3$.

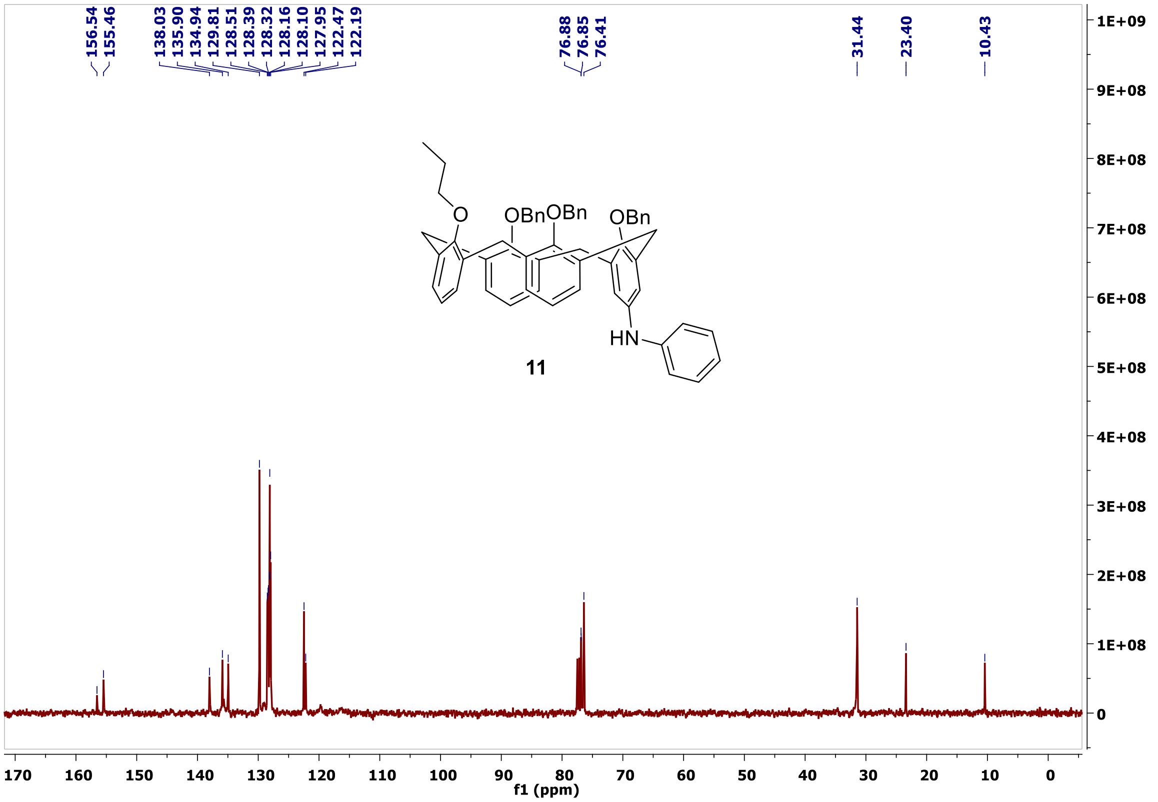


Figure S33. ^{13}C {^{1}H} NMR (100 MHz) spectra of **11** in CDCl$_3$.

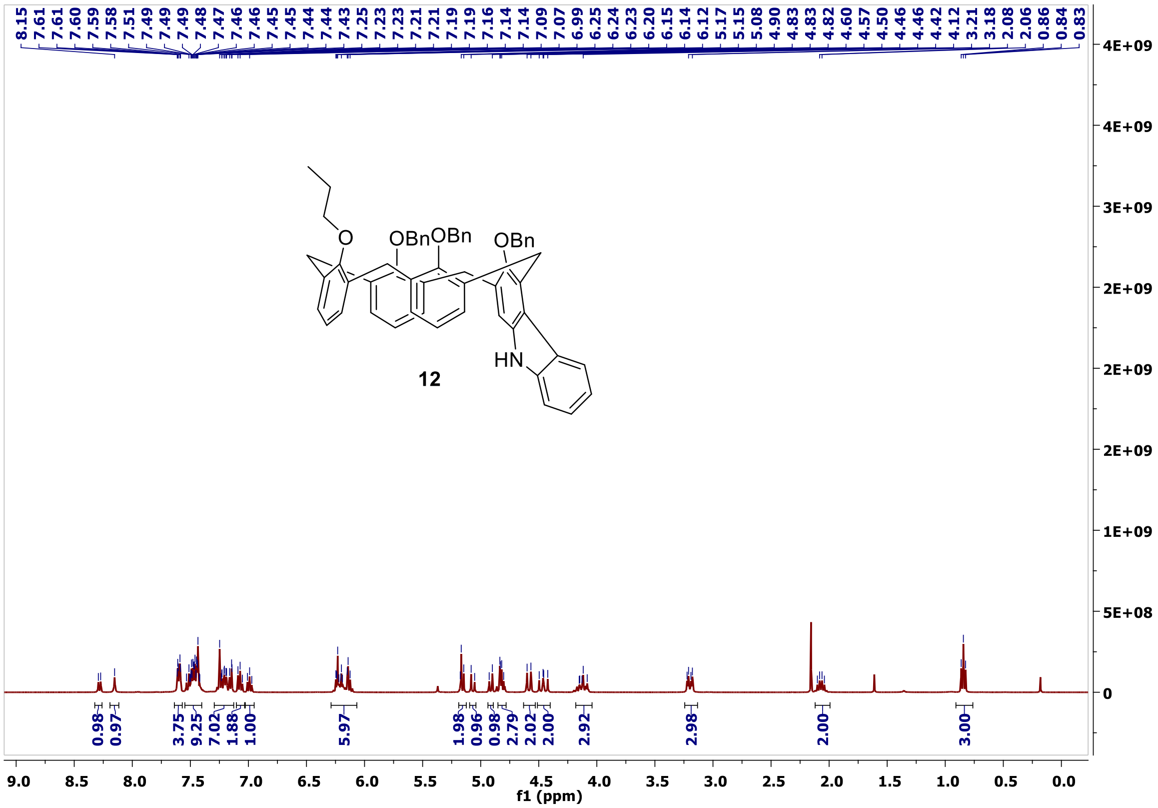


Figure S34. ^{1}H NMR (400 MHz) spectra of **12** in CD_2Cl_2.

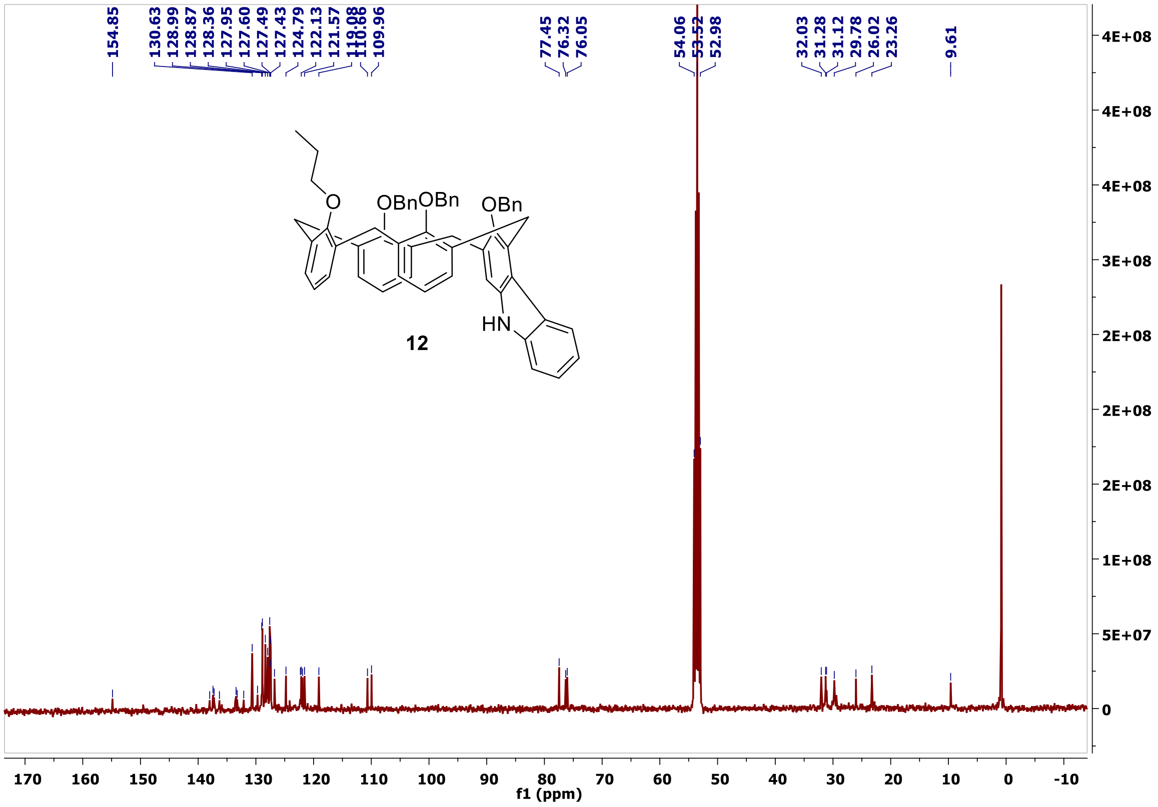


Figure S35. ^{13}C {^{1}H} NMR (100 MHz) spectra of **12** in CD_2Cl_2.

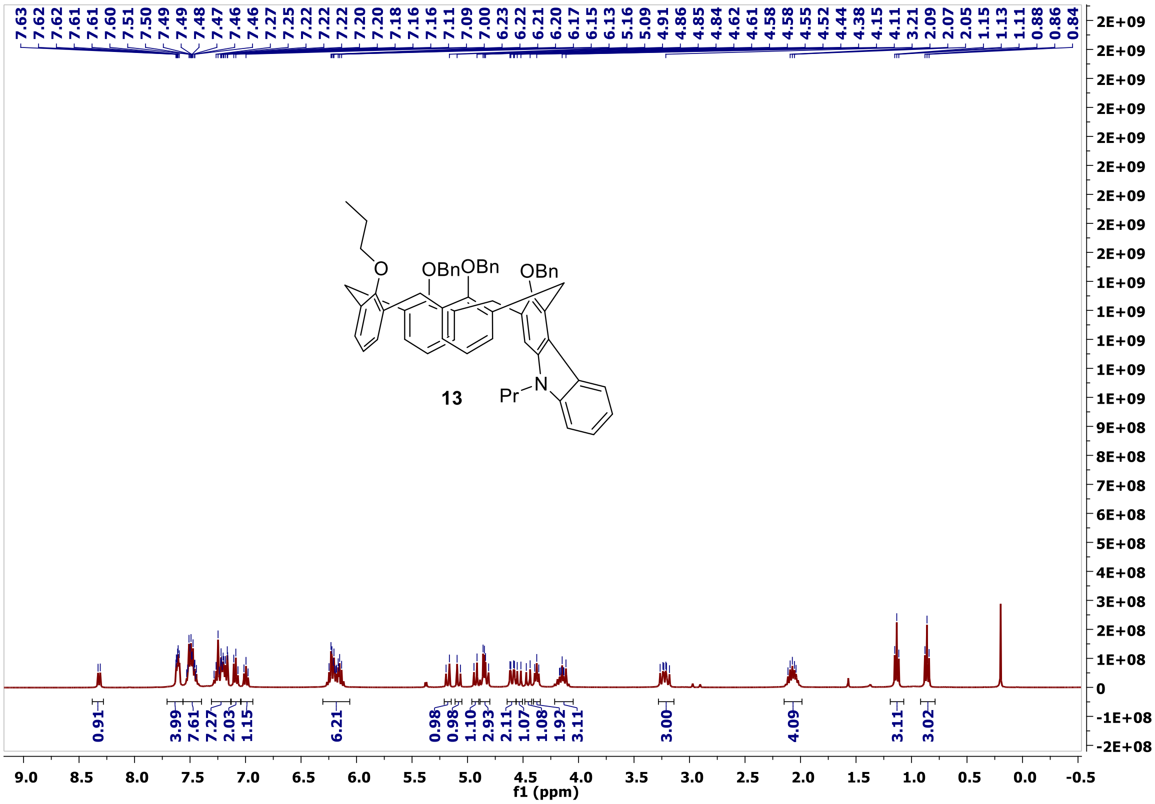


Figure S36. ^{1}H NMR (400 MHz) spectra of **13** in CD_2Cl_2.

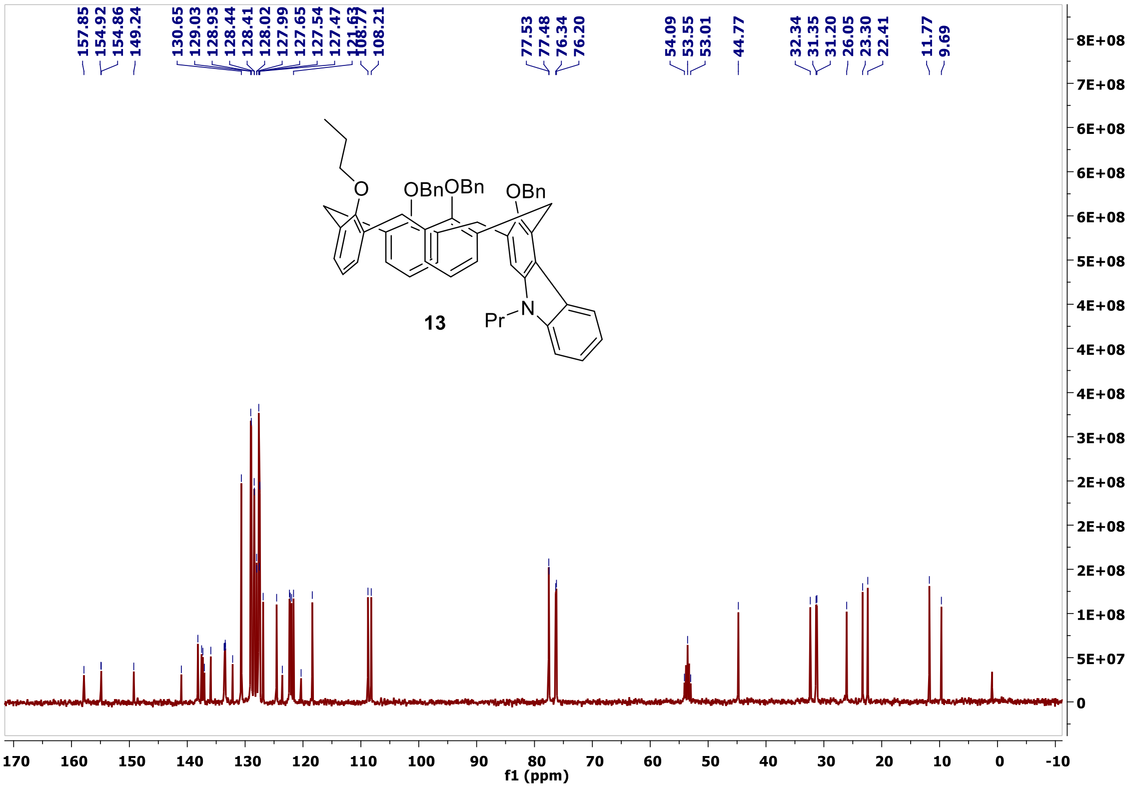


Figure S37. ^{13}C {^{1}H} NMR (100 MHz) spectra of **13** in CD_2Cl_2.

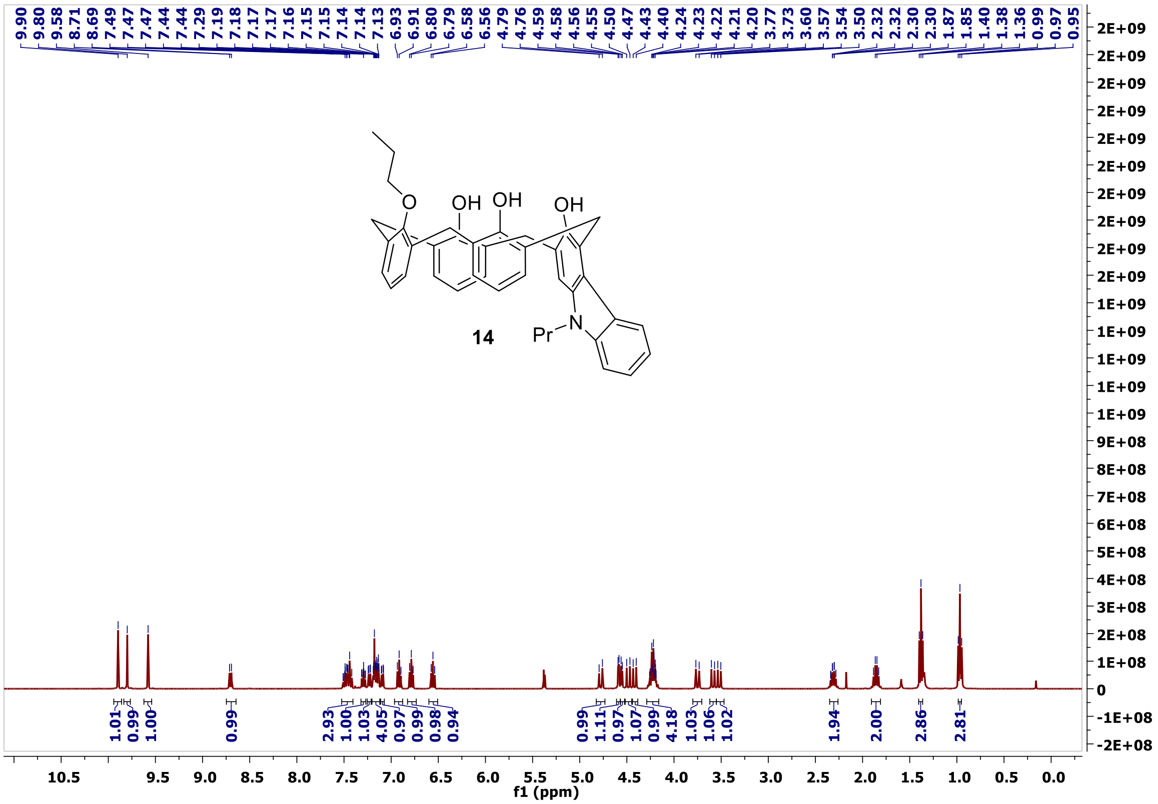


Figure S38. ^{1}H NMR (400 MHz) spectra of **14** in CD_2Cl_2.

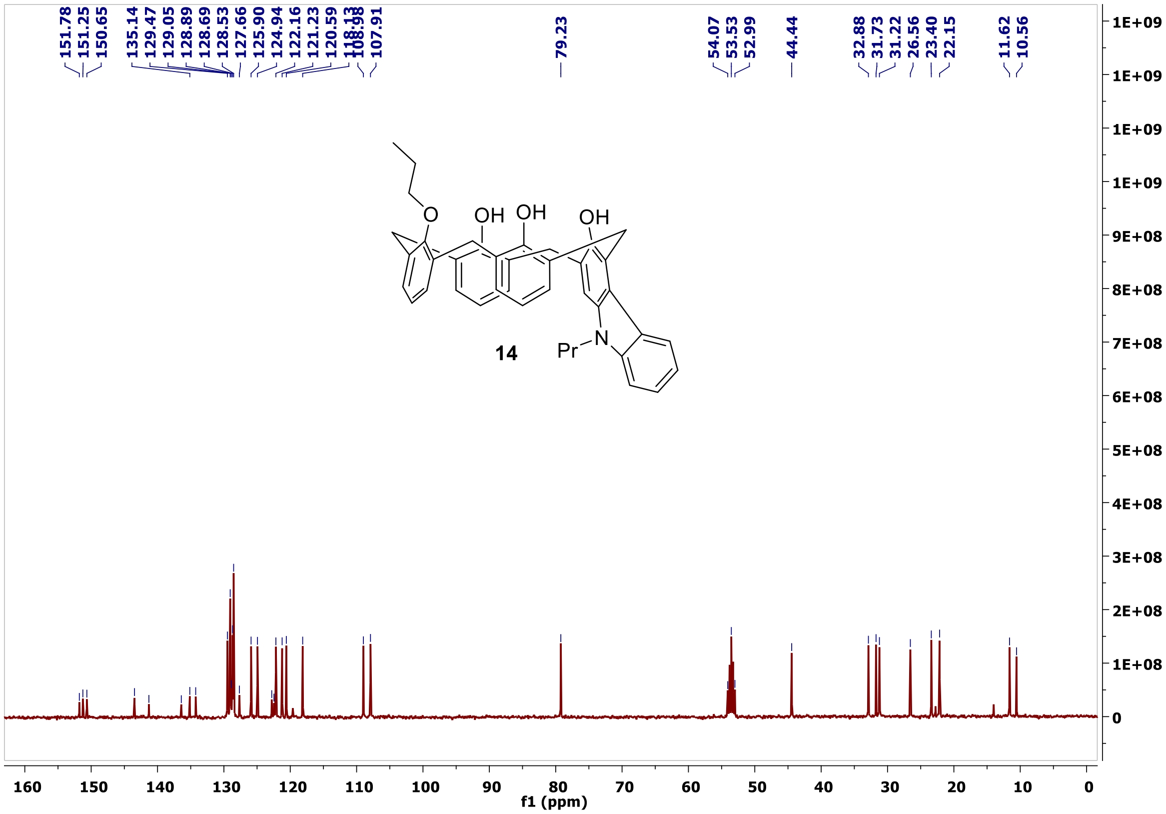


Figure S39. ^{13}C {^{1}H} NMR (100 MHz) spectra of **14** in CD_2Cl_2.

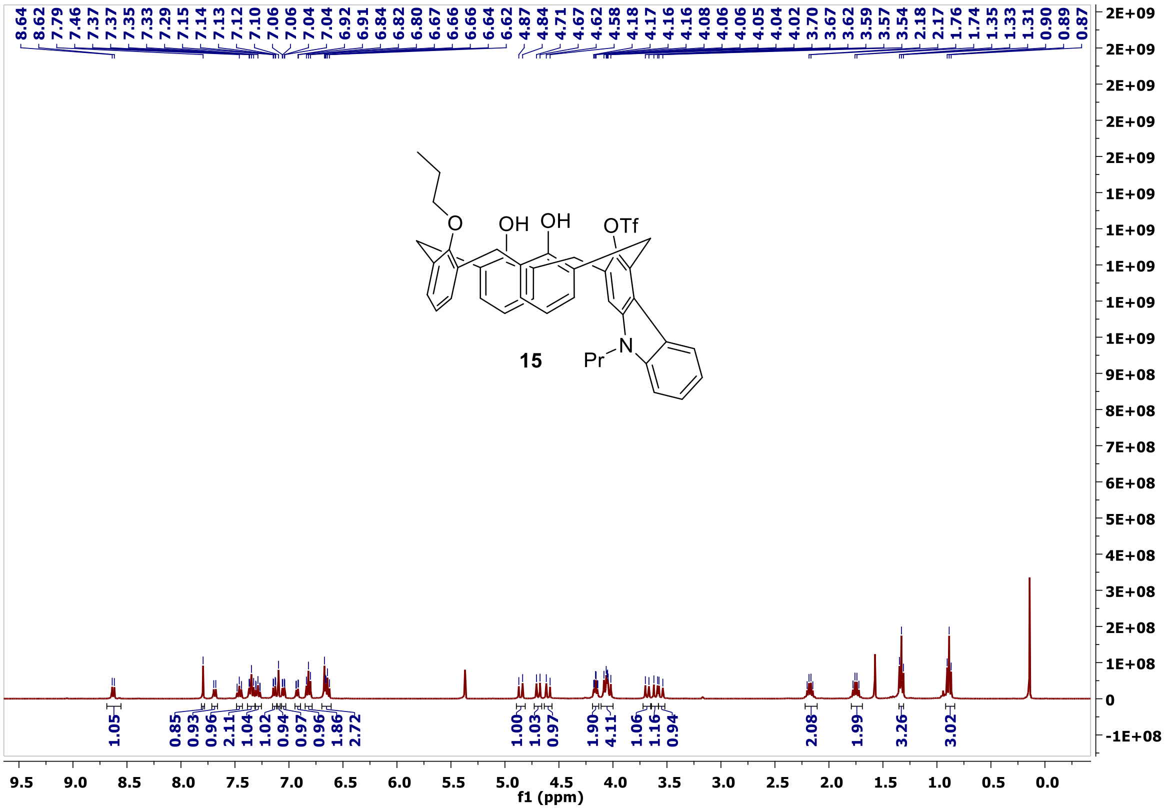


Figure S40. ^{1}H NMR (400 MHz) spectra of **15** in CD_2Cl_2.

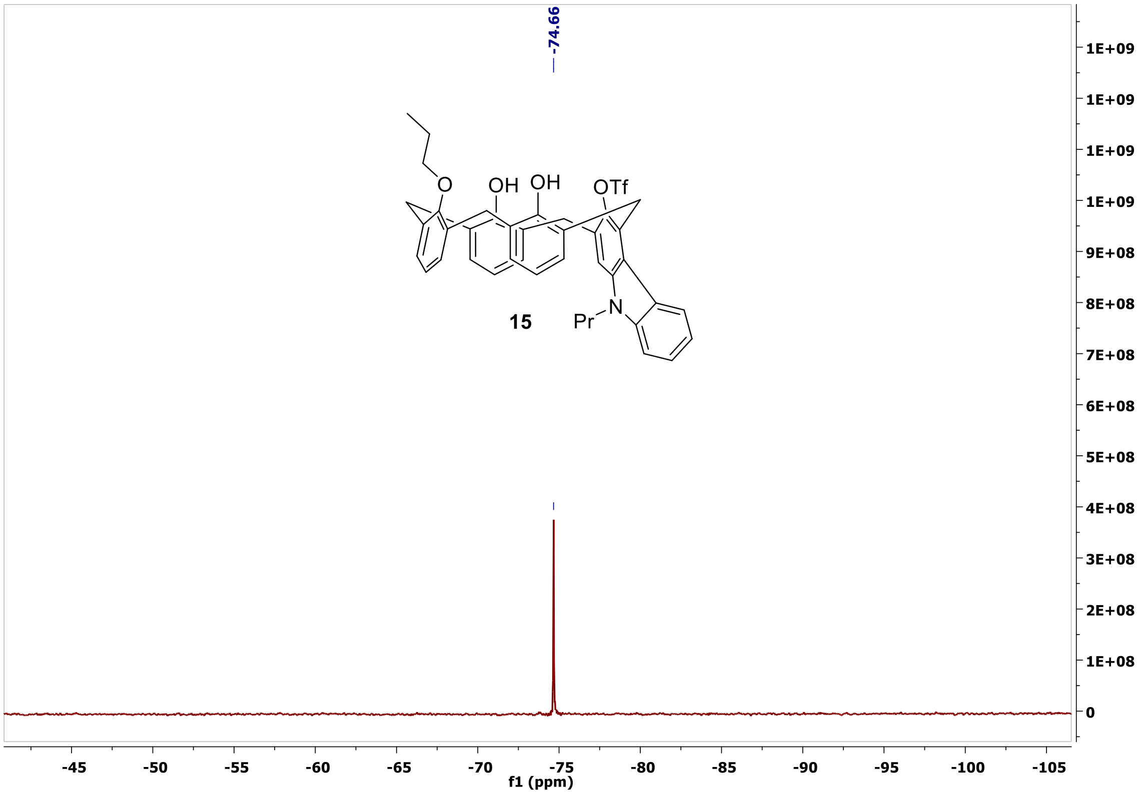


Figure S41. ^{19}F NMR (400 MHz) spectra of **15** in CD_2Cl_2.

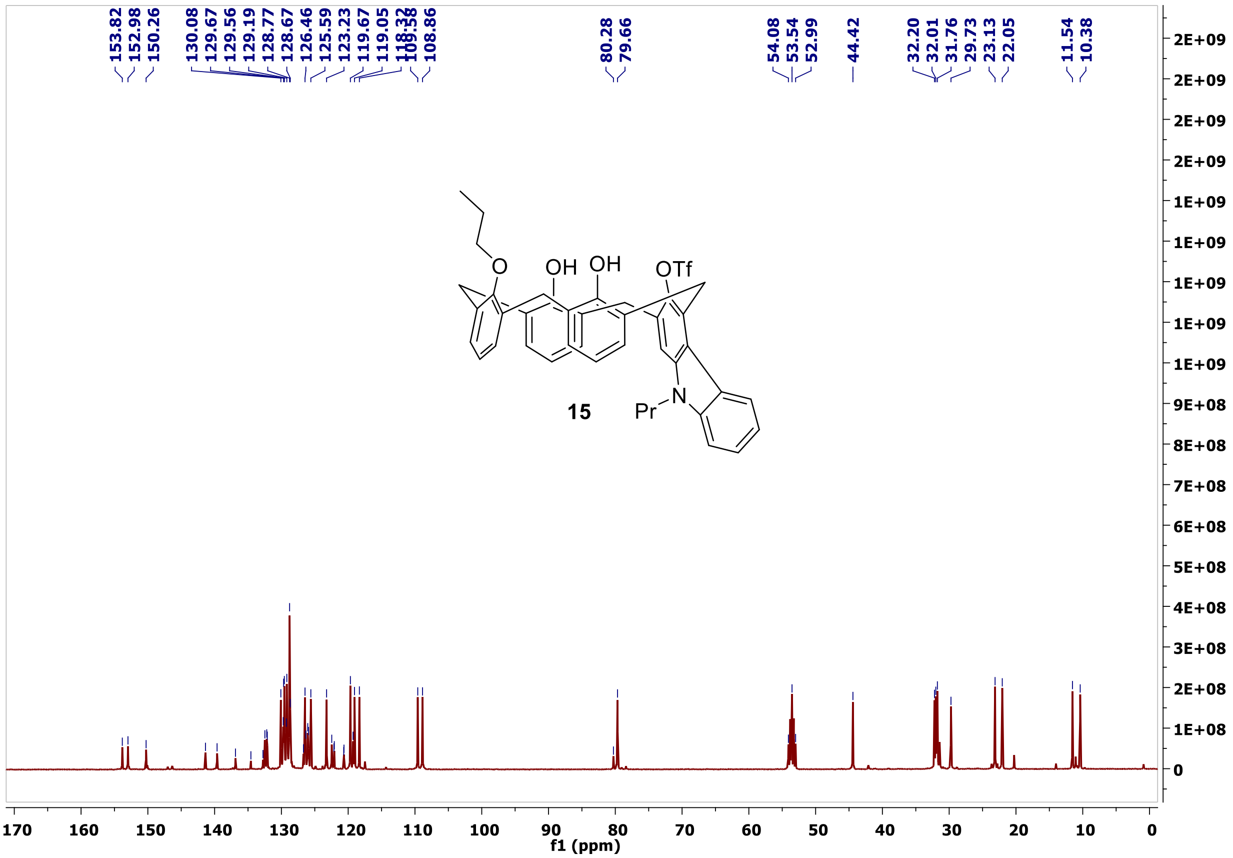


Figure S42. ^{13}C {^{1}H} NMR (100 MHz) spectra of **15** in CD$_2$Cl$_2$.

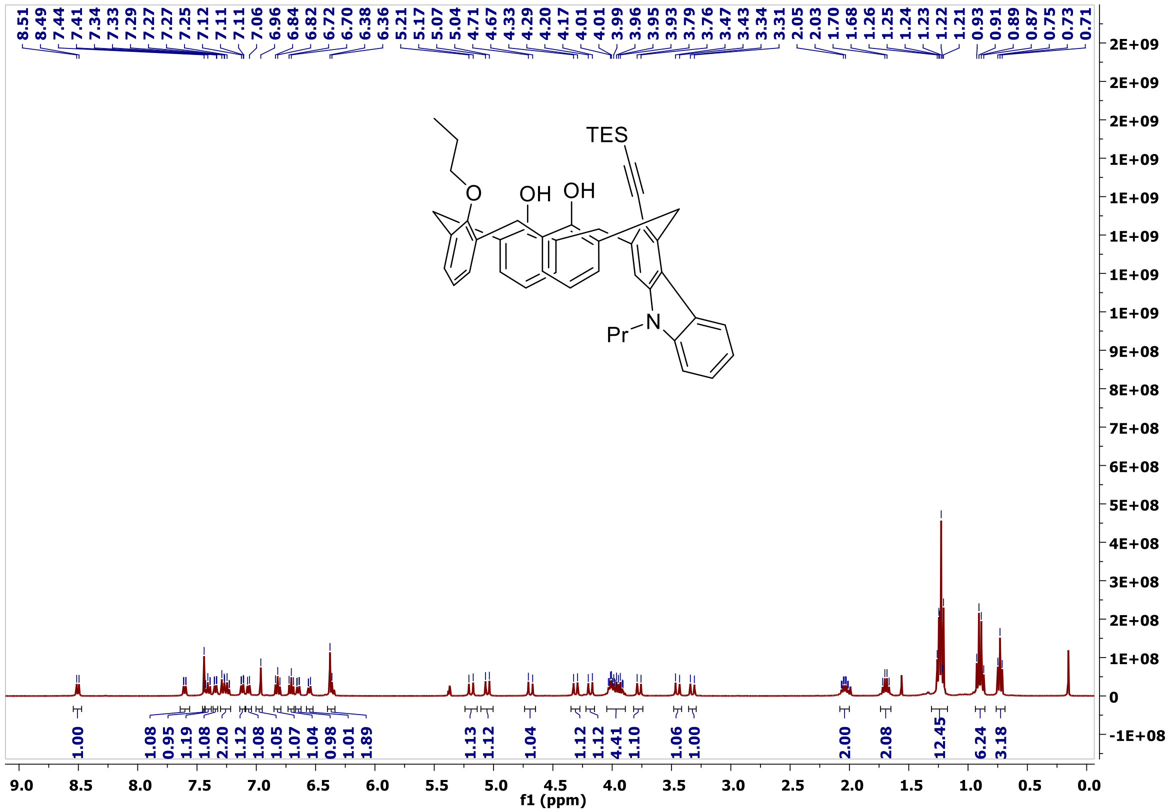


Figure S43. ^{1}H NMR (400 MHz) spectra of **TES-acetylene calixarene** in CD_2Cl_2.

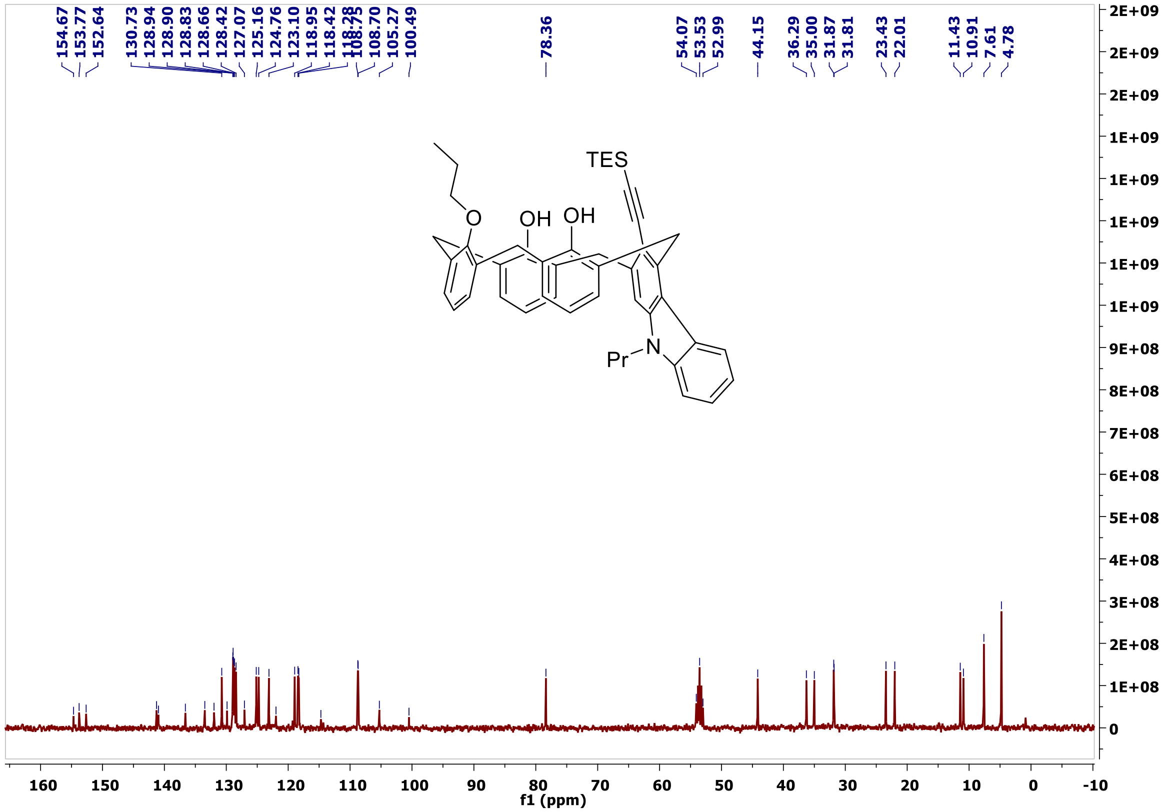


Figure S44. ^{13}C {^{1}H} NMR (100 MHz) spectra of **TES-acetylene calixarene** in CD_2Cl_2.

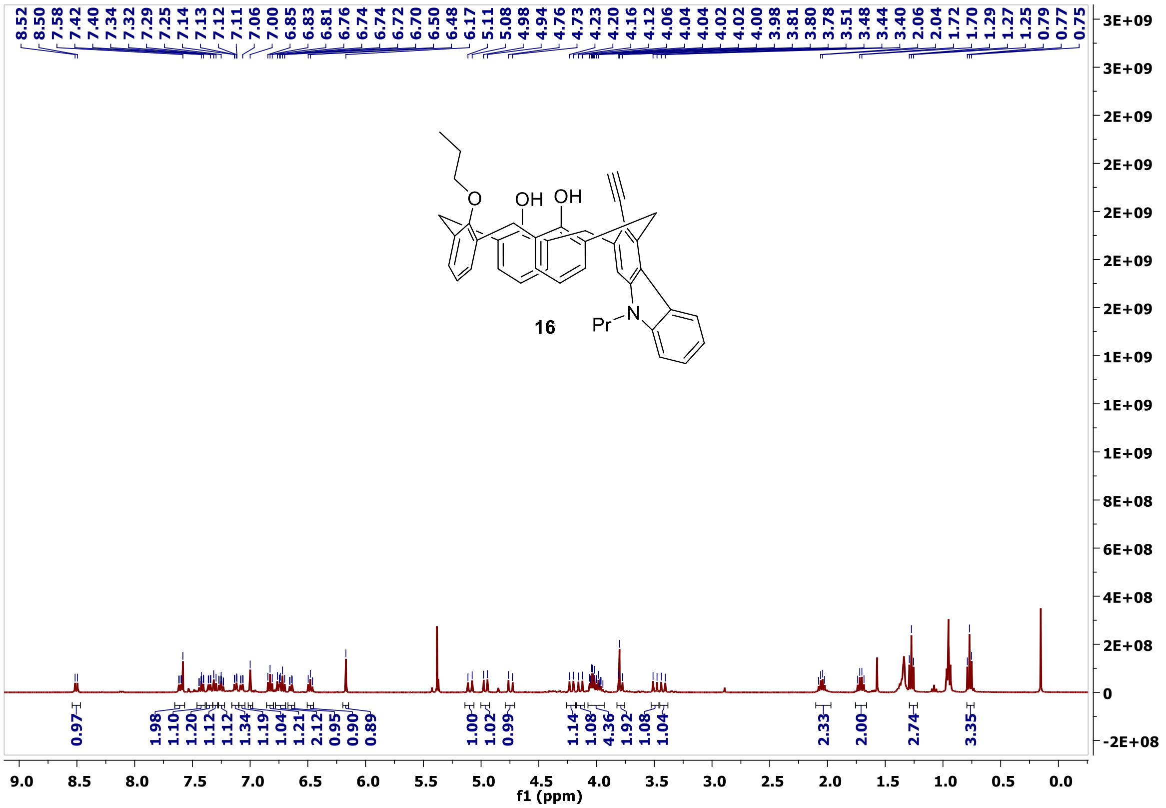


Figure S45. ^{1}H NMR (400 MHz) spectra of **16** in CD_2Cl_2.

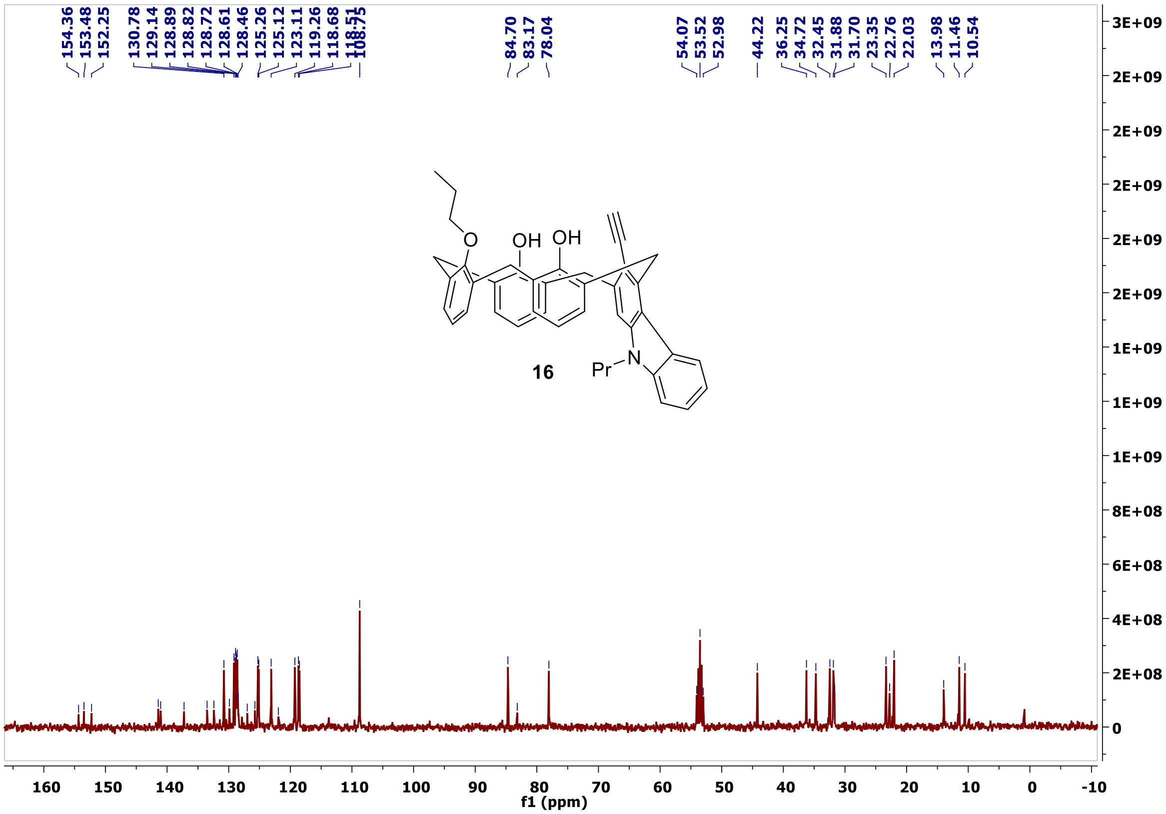


Figure S46. ^{13}C {^{1}H} NMR (100 MHz) spectra of **16** in CD_2Cl_2.

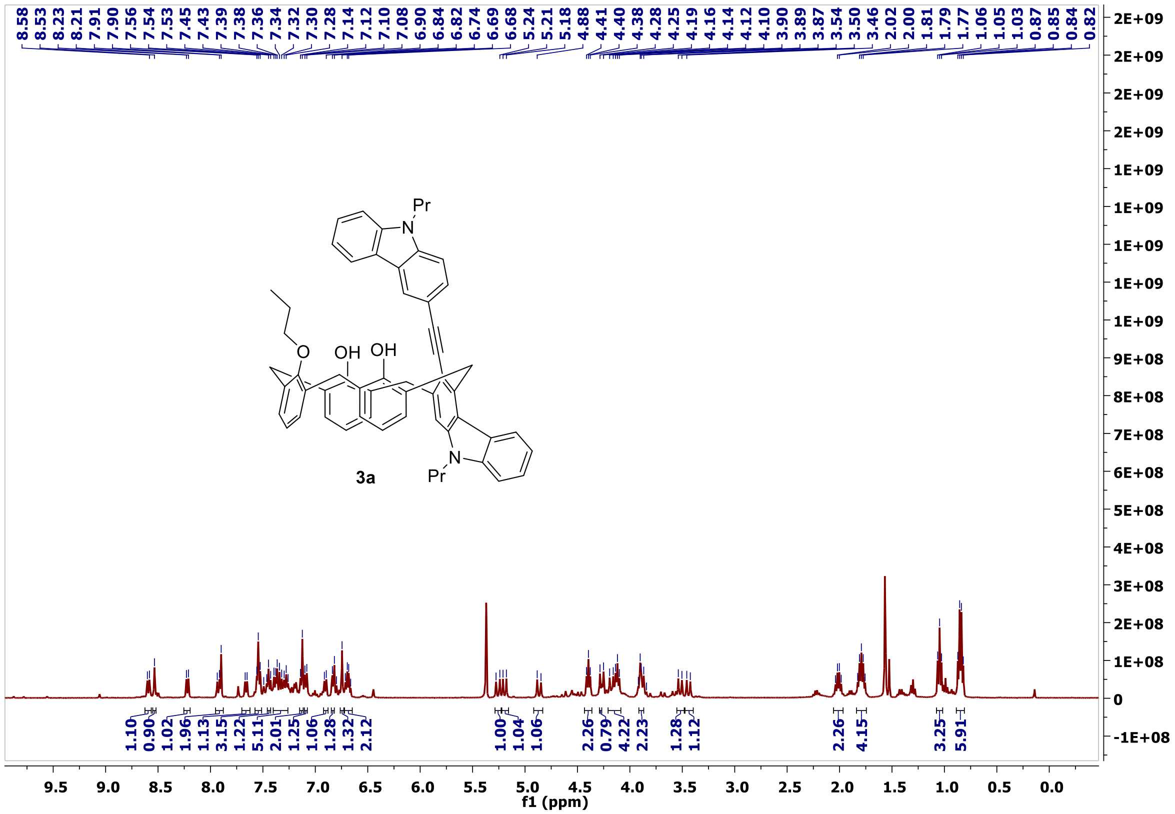


Figure S47. ^{1}H NMR (400 MHz) spectra of **3a** in CD_2Cl_2.

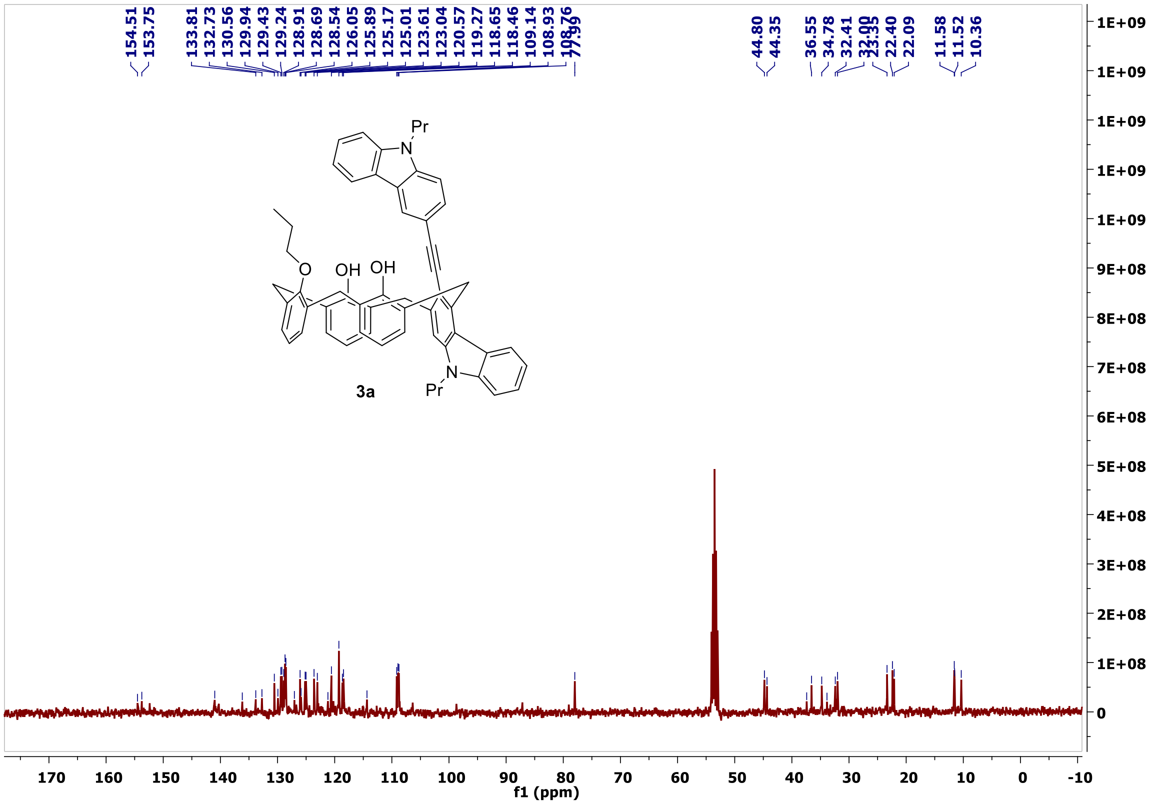


Figure S48. ^{13}C {^{1}H} NMR (100 MHz) spectra of **3a** in CD_2Cl_2.

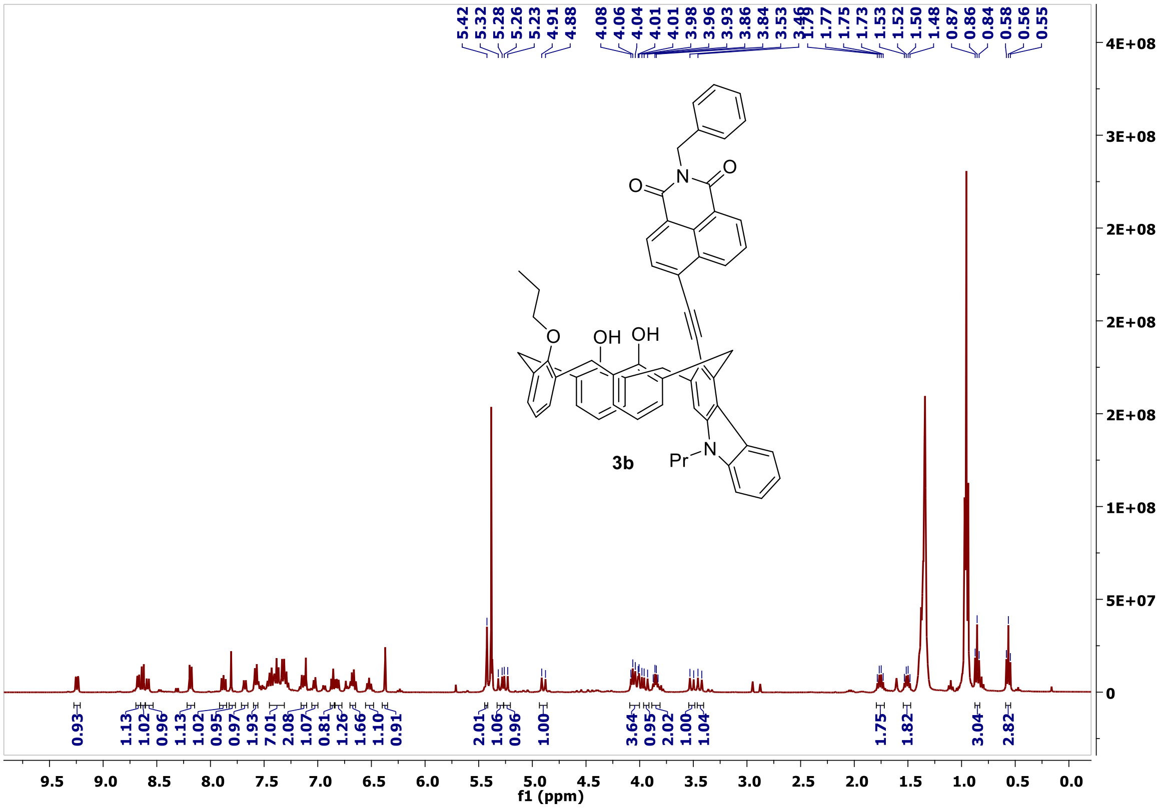


Figure 49. ^{1}H NMR (400 MHz) spectra of **3b** in CD_2Cl_2.

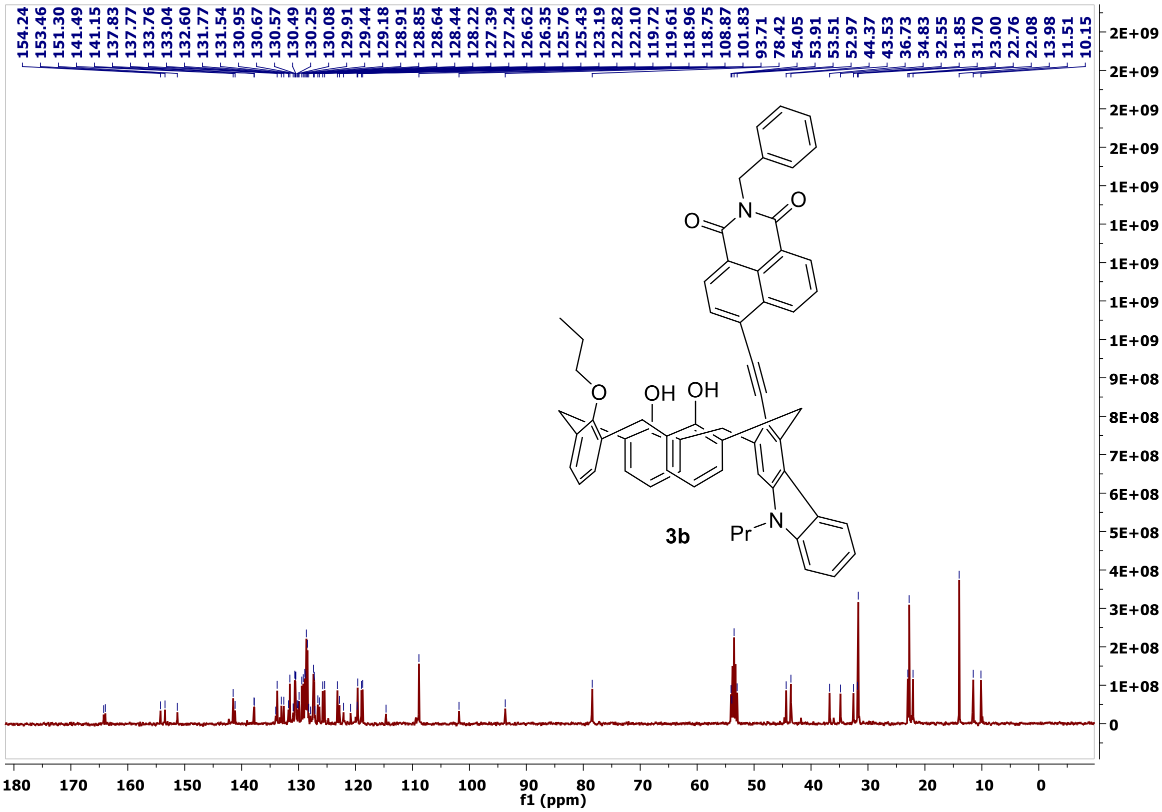


Figure S50. $^{13}C\ \{^1H\}$ NMR (100 MHz) spectra of **3b** in CD_2Cl_2.

4. Absorption and Emission Spectra

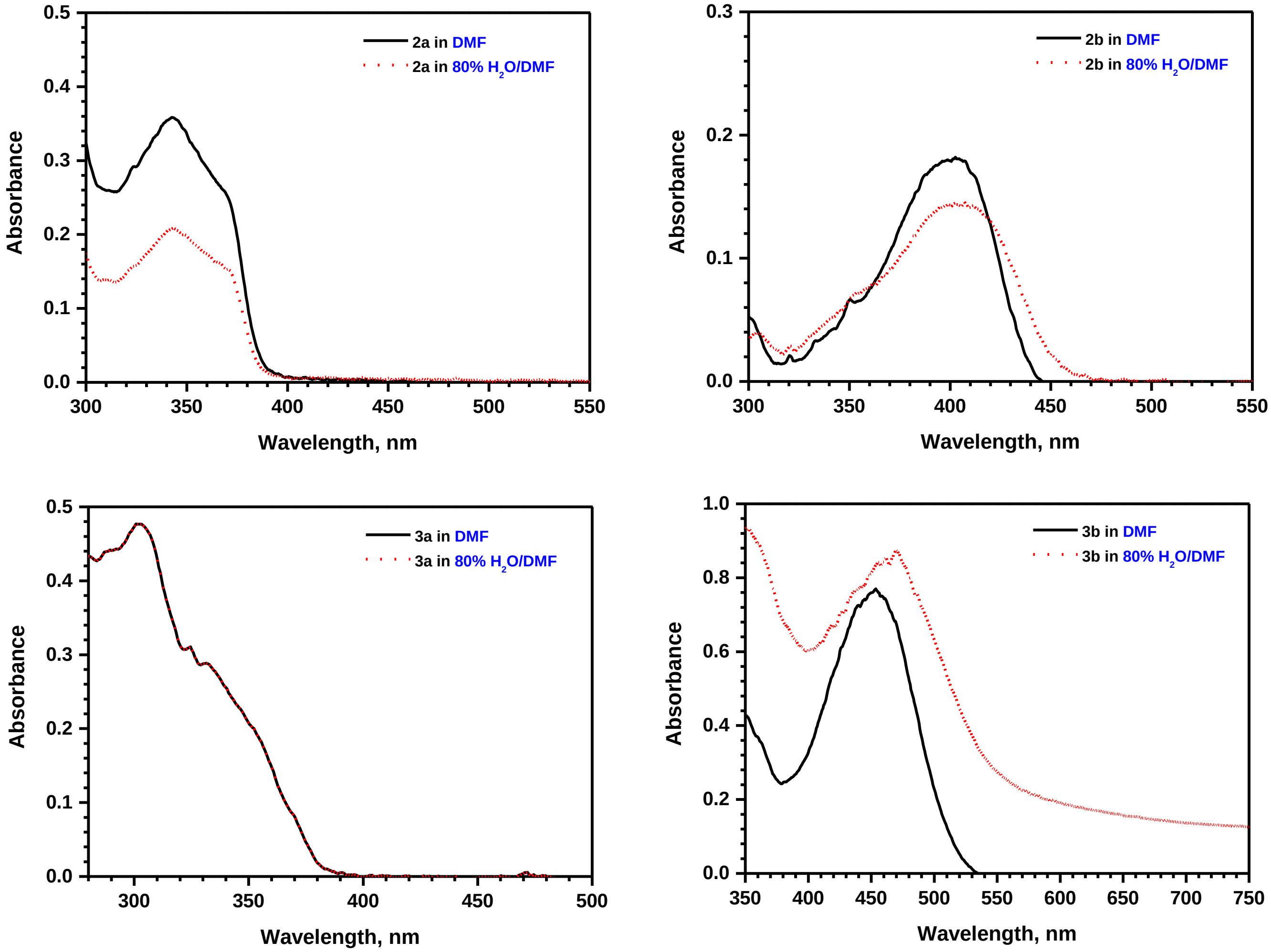


Figure S51. Absorption spectra of compounds **2** and **3** (10 μM).

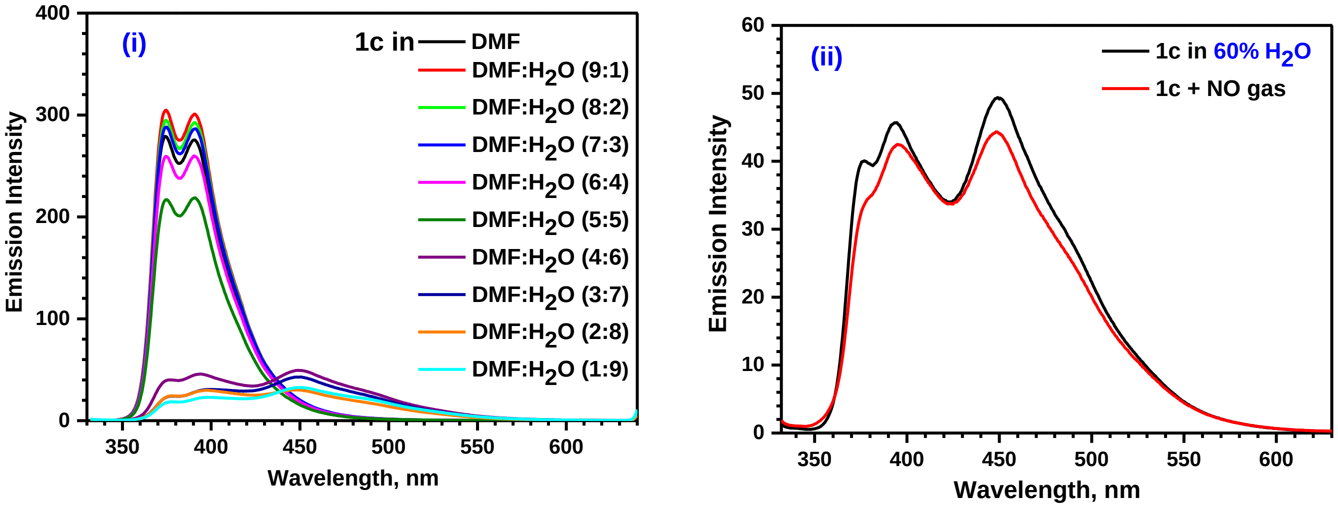


Figure S52. Emission spectra of compounds **1c** (10 μM) in water-DMF solution: (i) at different H_2O:DMF ratios; (ii) in 60% H_2O/DMF, before and after passing NO gas.

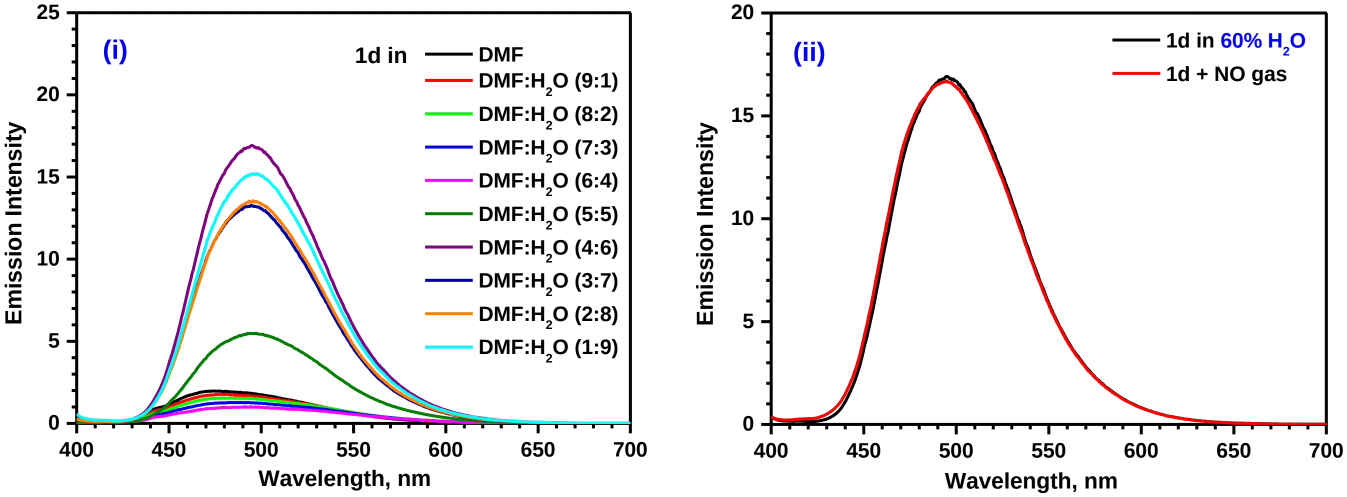


Figure S53. Emission spectra of compounds **1d** (10 μM) in water-DMF solution: (i) at different H_2O:DMF ratios; (ii) in 60% H_2O/DMF, before and after passing NO gas. .

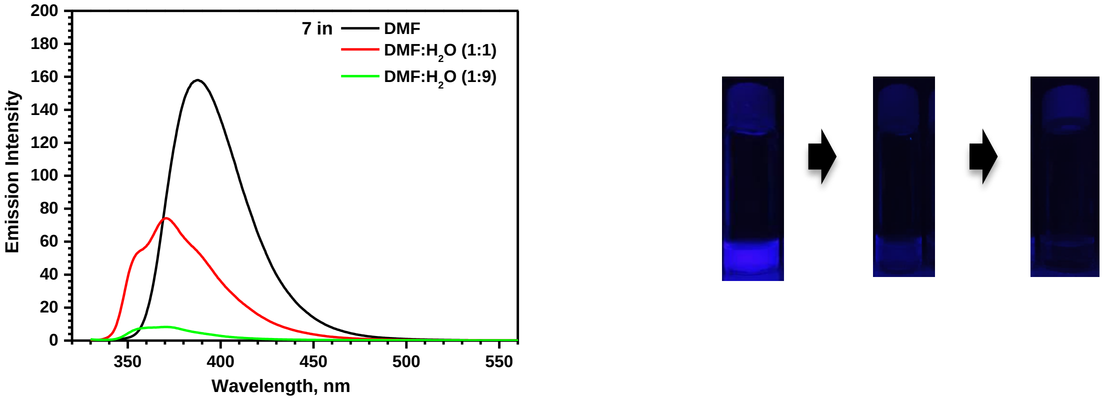


Figure S54. Emission spectra of compounds **7** (10 μM) in H_2O/DMF at different ratios.

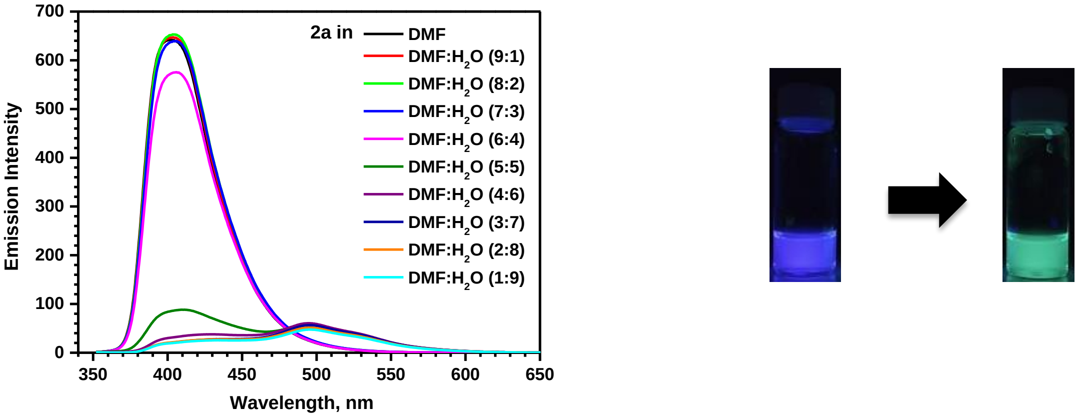


Figure S55. Emission spectra of compounds **2a** (10 μM) in H_2O/DMF at different ratios.

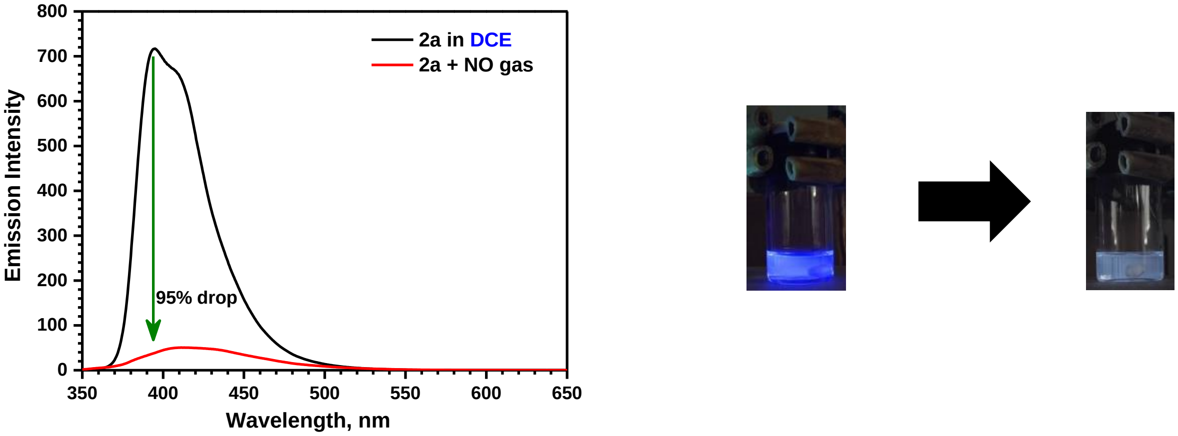


Figure S56. Emission spectra of compounds **2a** (10 μM) in DCE before and after passing NO gas.

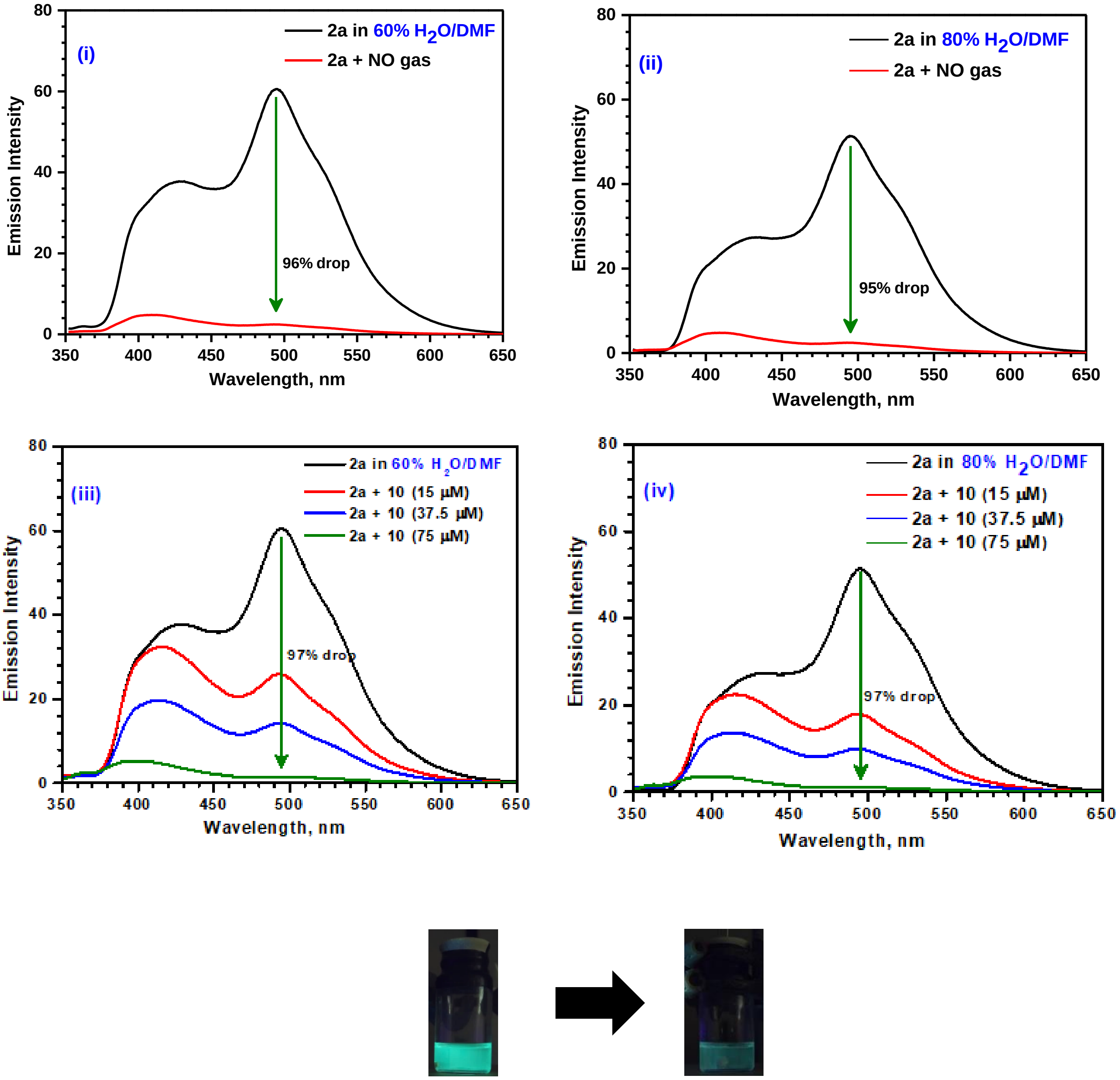


Figure S57. Emission spectra of **2a** (i) before and after passing NO gas in 60% H_2O/DMF; (ii) before and after passing NO gas in 80% H_2O/DMF; (iii) before and after adding various amounts of **10** in 60% H_2O/DMF; (iv) before and after adding various amounts of **10** in 80% H_2O/DMF.

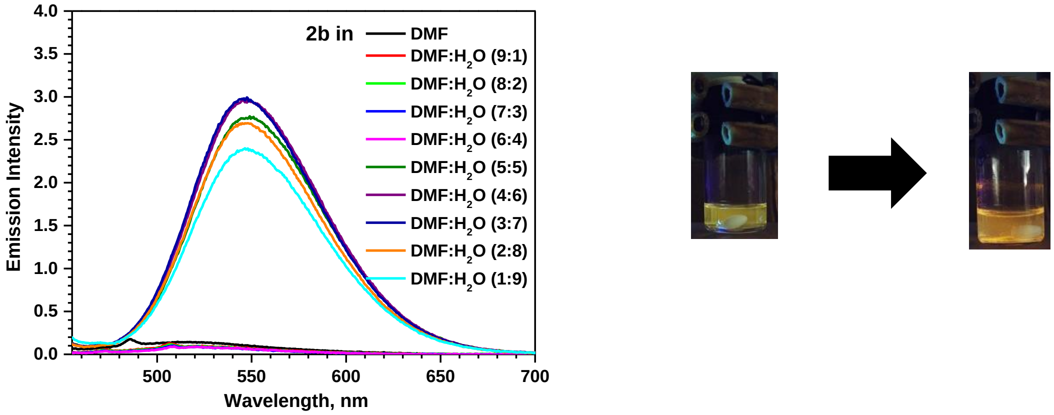


Figure S58. Emission spectra of compound **2b** (10 μM) in H_2O/DMF at different ratios.

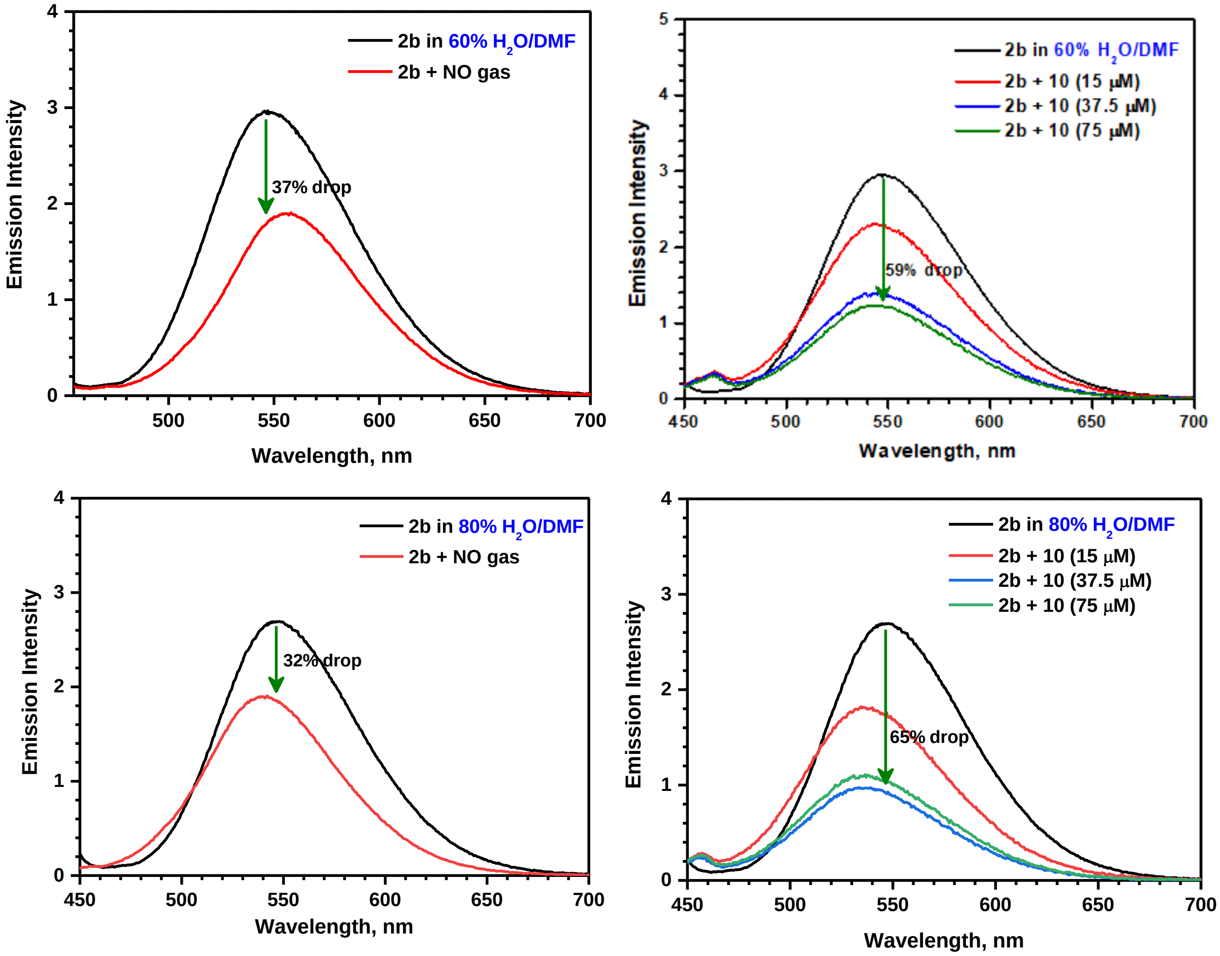


Figure S59. Emission spectra of **2b** (i) before and after passing NO gas in 60% H_2O/DMF; (ii) before and after adding various amounts of **10** in 60% H_2O/DMF; (iii) before and after adding different equivalents of **10** in 80% H_2O/DMF; (iv) before and after adding various amounts of **10** in 60% H_2O/DMF.

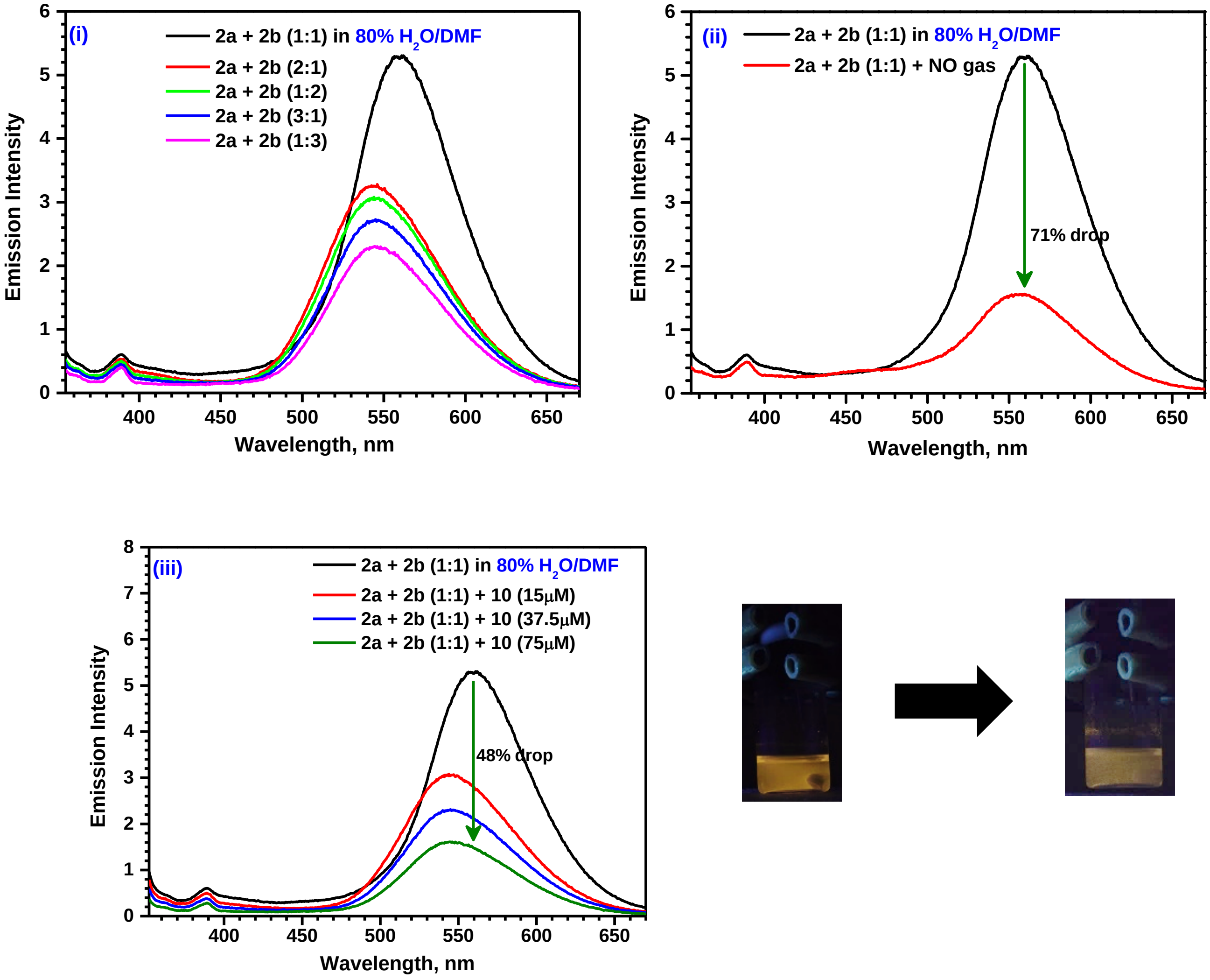


Figure S60. Emission spectra of (i) **2a + 2b** in 80% H_2O/DMF at different raios; (ii) **2a + 2b** (1:1) before and after passing NO gas in 80% H_2O/DMF; (iii) **2a + 2b** (1:1) before and after adding various amounts of **10** in 80% H_2O/DMF.

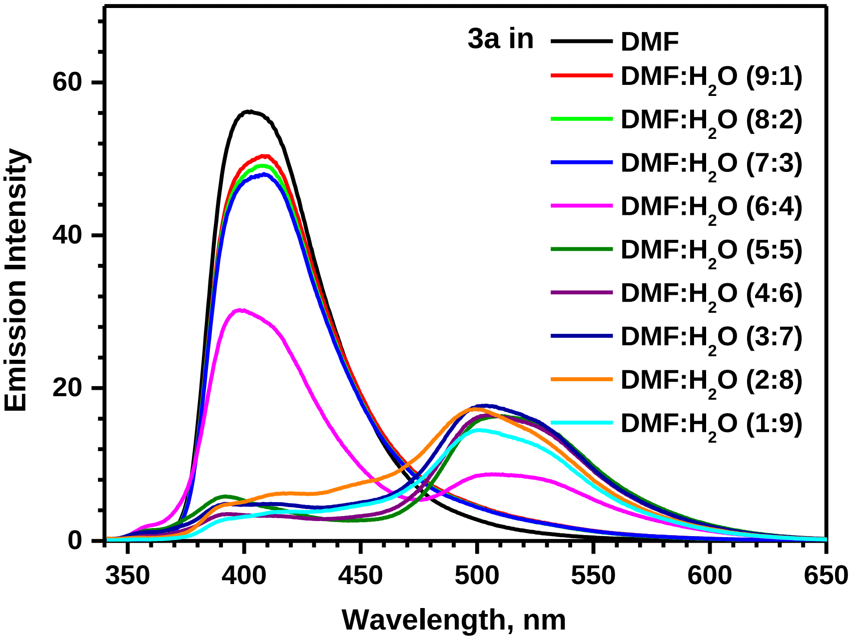


Figure S61. Emission spectra of compound **3a** (10 μM) in H_2O/DMF at different ratios.

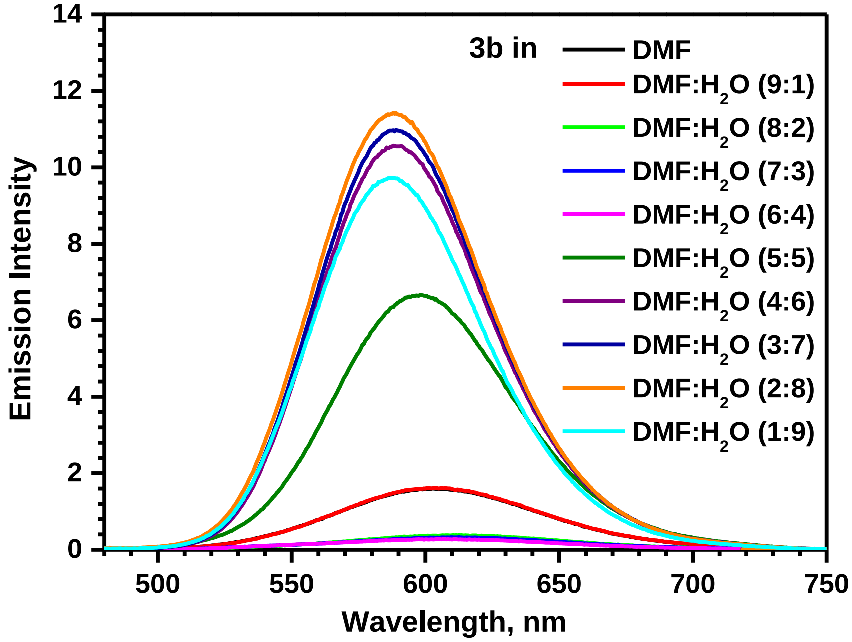


Figure S62. Emission spectra of compound **3b** (10 μM) in H_2O/DMF at different ratios.

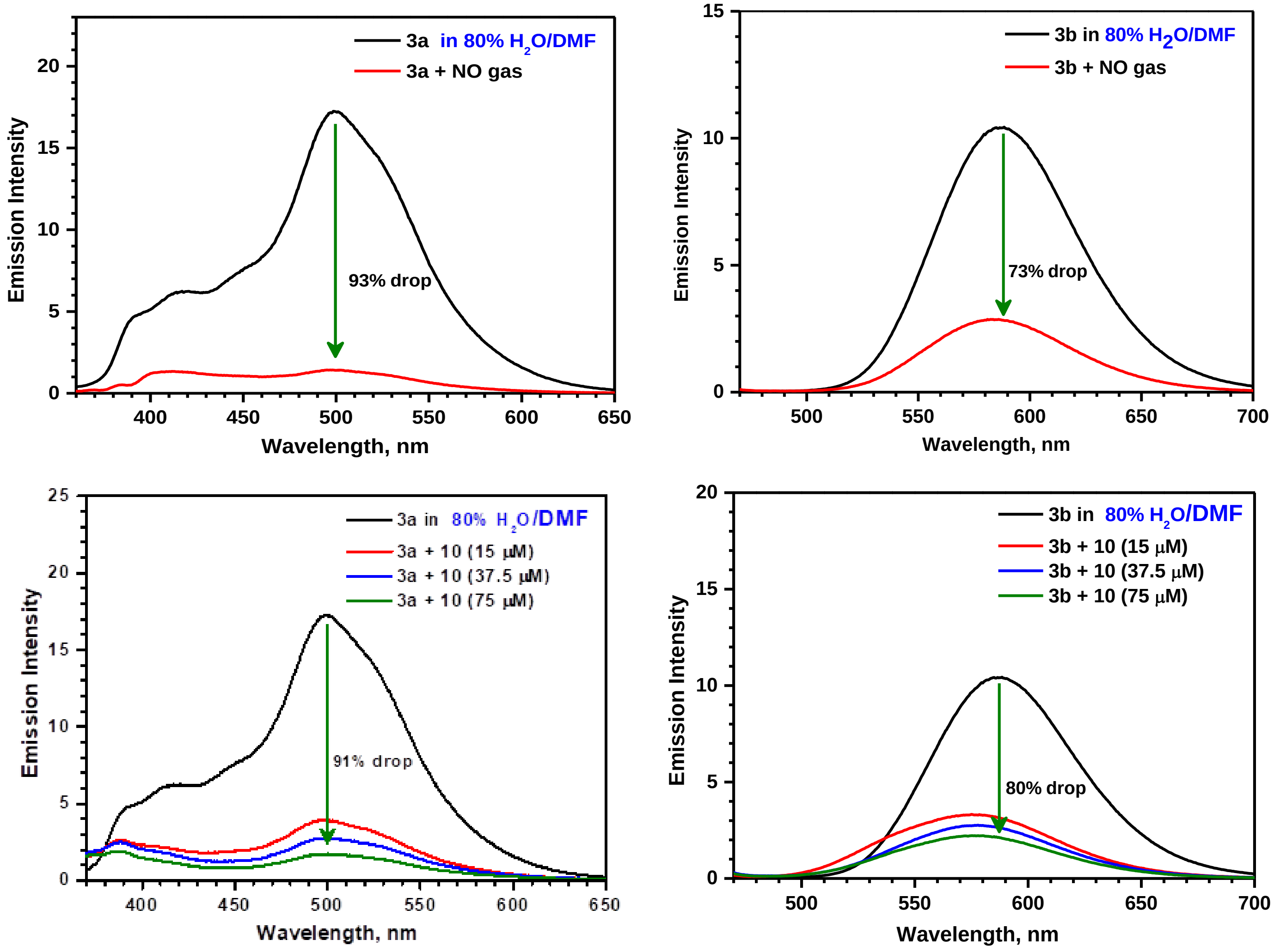


Figure S63. Emission spectra of (i) **3a** before and after passing NO gas in 80% H_2O/DMF; (ii) **3b** before and after passing NO gas in 80% H_2O/DMF; (iii) **3a** before and after adding various amounts of **10** in 80% H_2O/DMF; (iv) **3b** before and after adding various amounts of **10** in 60% H_2O/DMF.

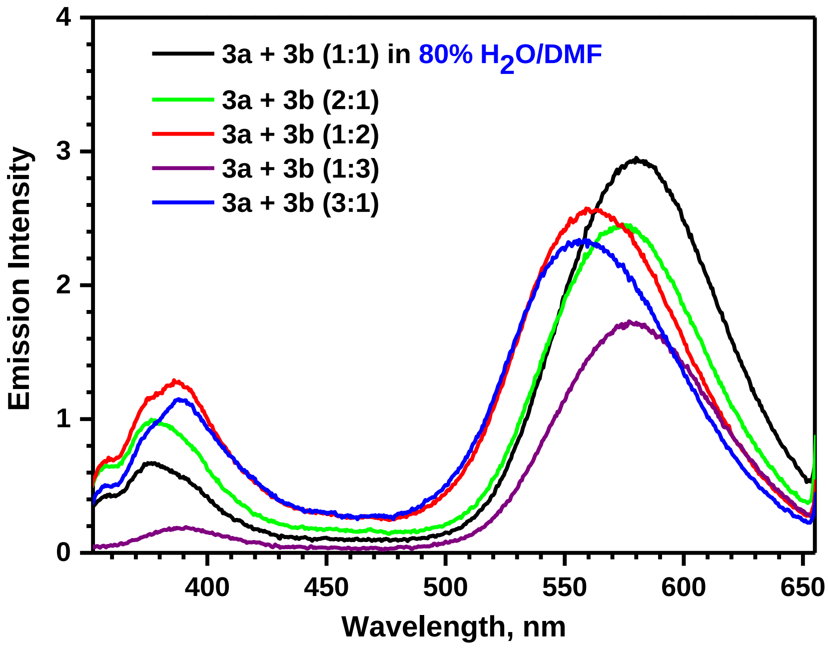


Figure S64. Emission spectra of **3a + 3b** at different ratios (in 80% H_2O/DMF).

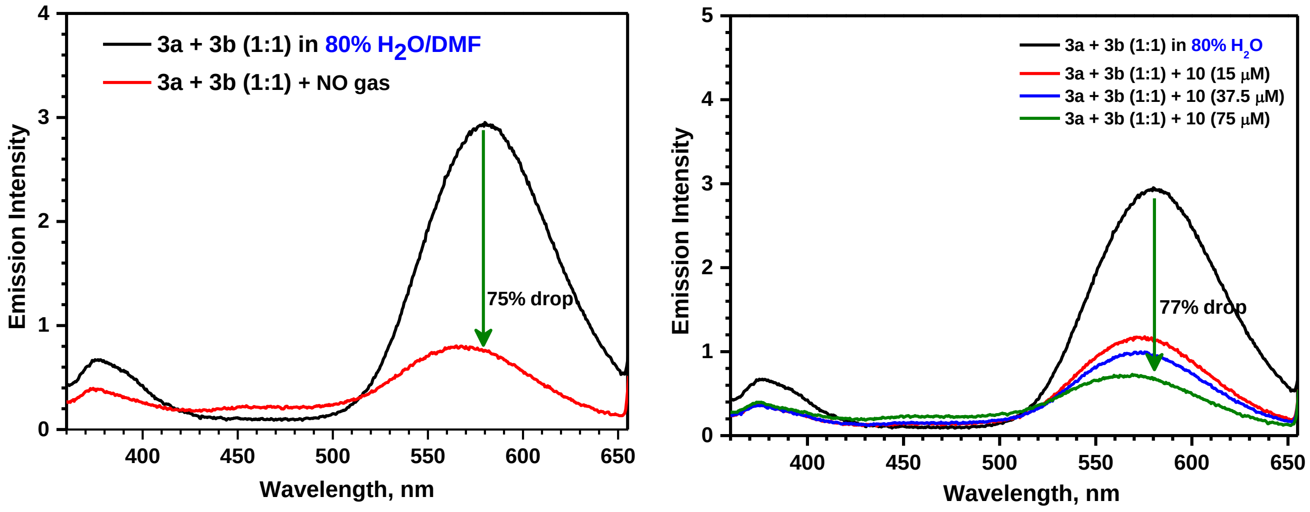


Figure S65. Emission spectra of (i) **3a + 3b** (1:1) before and after passing NO gas in 80% H_2O/DMF; (ii) **3a + 3b** (1:1) before and after adding various amount of **10** in 80% H_2O/DMF.

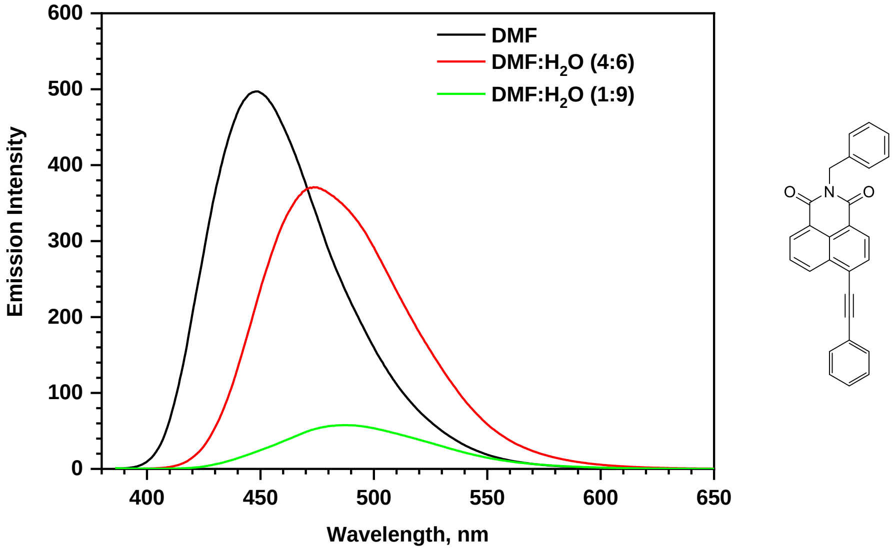


Figure S66. Emission spectra of a linear naphthalimide (10 μM) in H_2O/DMF at various ratios.

5. Scanning Electron Microscopy (SEM)

Powders were dissolved in 80 % H_2O/DMF and in 100 % DMF at a concentration of 10 µM, followed by a vortex to obtain a clear solution. A 10 µL aliquot was allowed to dry on a silicon wafer at ambient conditions overnight and coated with Au. After deposition on the silicon surface, samples were dried at room temperature and imaged. SEM images were collected using a Zeiss Gemini 300 (Zeiss, Germany) with an operating voltage of 3 kV.

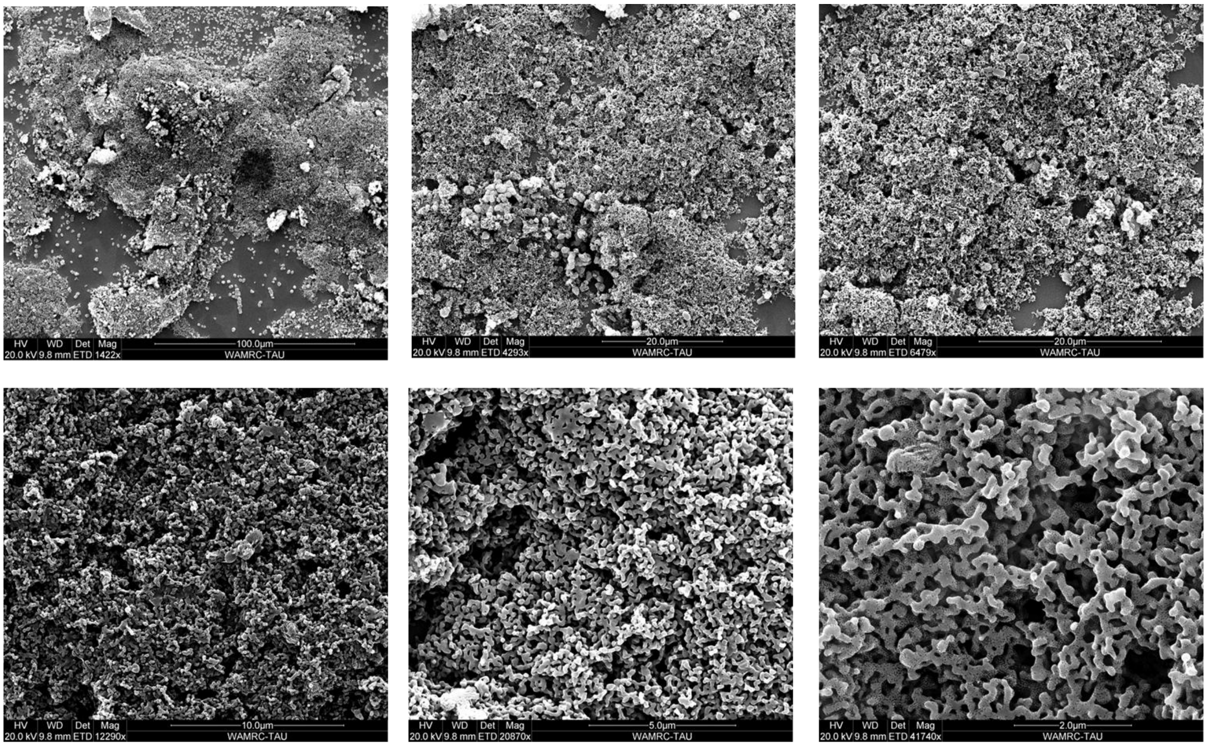


Figure S67. SEM images of **3b** in 80% H_2O/DMF solvent at a concentration of 10 µM.

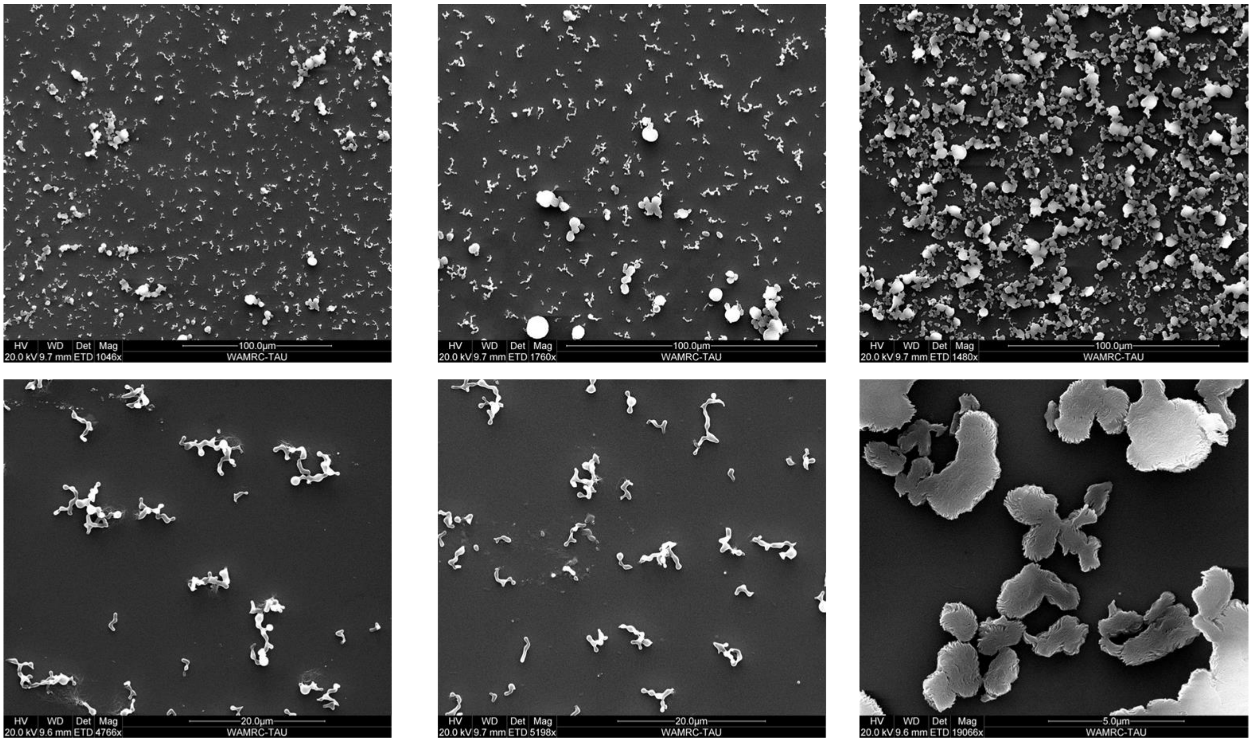


Figure S68. SEM images of **3b** in 100% DMF solvent at a concentration of 10 μM.

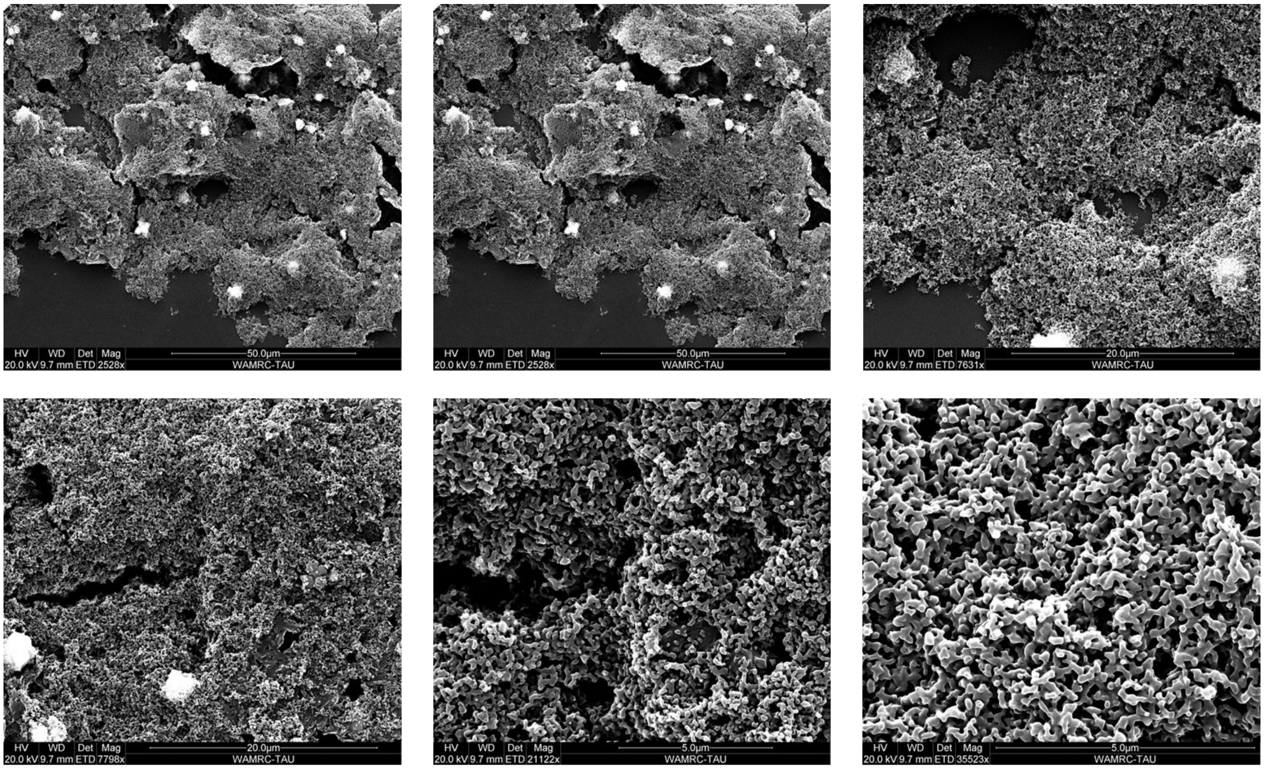


Figure S69. SEM images of **3a** in 80% H_2O/DMF solvent at a concentration of 10 μM.

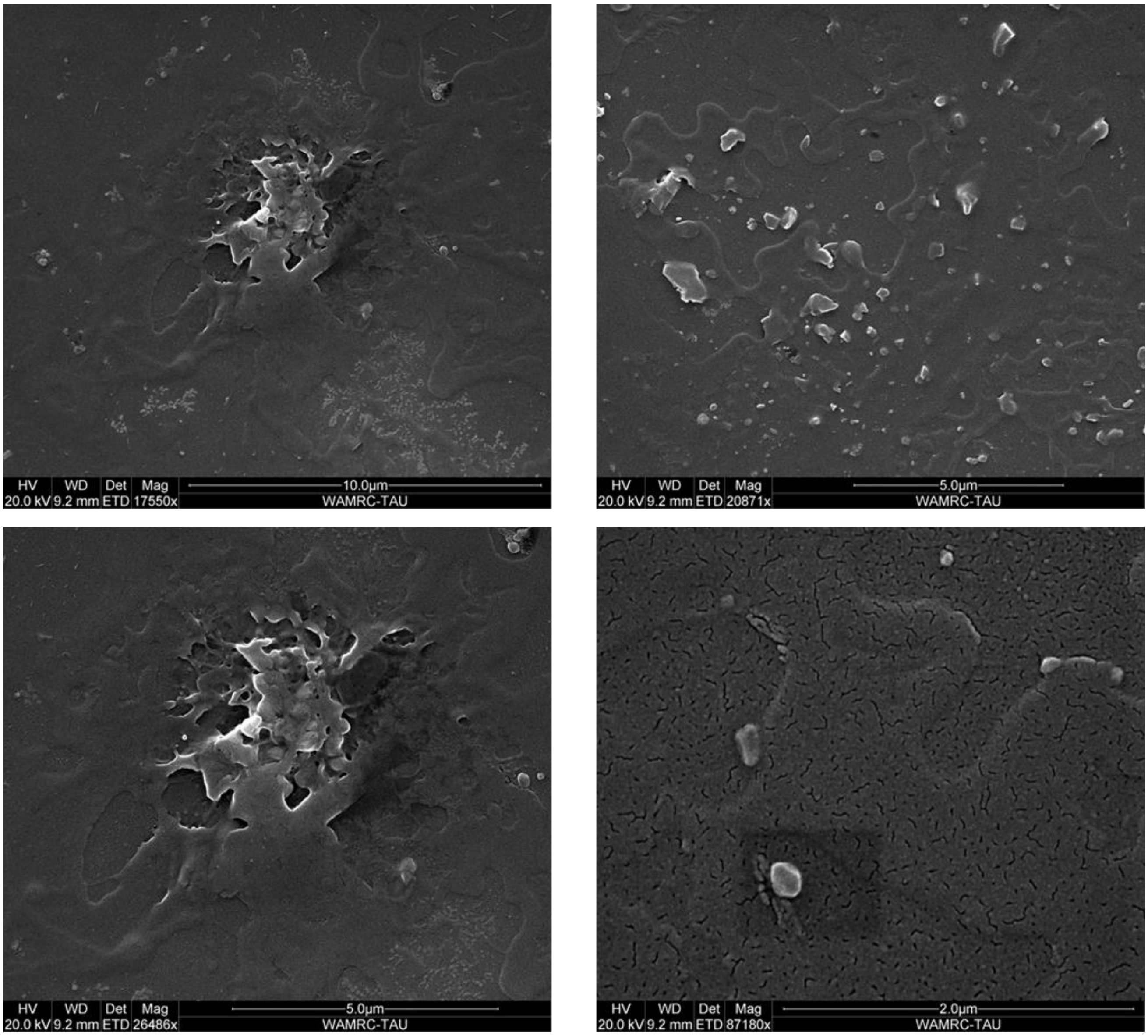


Figure S70. SEM images of **3a** in 100% DMF solvent at a concentration of 10 μM.