Electronic Supplementary Information

Triptycene-derived calix[6]resorcinarene-like hosts: synthesis, structure and self-assemblies in the solid state

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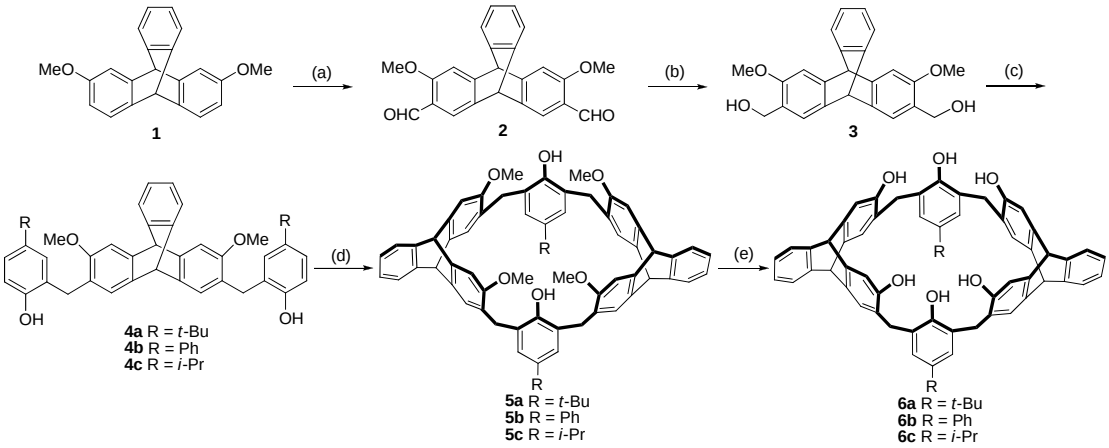
Content

1. Synthesis and characterization data of new compounds

General methods: Melting points, taken on an electrothermal melting point apparatus, are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a DMX300 NMR. MALDI-TOF mass spectra were obtained on a BIFLEXIII mass spectrometer. Elemental analyses were performed by the Analytical Laboratory of Institute of Chemistry, CAS. High Resolution Mass Spectra (HRMS) were recorded on a Mass Spectrometer operating in negative ESI mode. Materials obtained commercially were used without further purification. Column chromatography was performed on 100-200 mesh silica gel.



Scheme S1. Synthesis of the macrocycles **5a-c** and **6a-c**. Reagents and conditions: (a) hexamethylenamine, CF_3CO_2H, reflux, 75%; (b) $NaBH_4$, MeOH, 98%; (c) *p*-substituted-phenol, *p*-TsOH, PhMe; (d) *p*-TsOH, *o*-dichlorobenzene; (e) BBr_3, dichloromethane.

2,7-Dimethoxyltriptycene-3,6-dialdehyde (2).

2,7-Dimethoxyltriptycene **1**[S1] (2.0 g, 6.4 mmol) and hexamethylenetetramine (2.7 g, 19 mmol) were taken in trifluoroacetic acid (100 mL). The reaction mixture was refluxed overnight under an Ar atmosphere. After cooling to room temperature, the mixture was quenched with saturated aqueous sodium carbonate solution in ice water and extracted with dichloromethane (DCM). The organic layer was washed with water and dried with $MgSO_4$. The solvent was evaporated under reduced pressure, and the residue was submitted to silica gel column chromatography. Elution with

DCM/EtOAc (20:1, v/v) gave **2** (1.77 g, 75 %, R_f = 0.58) as a white solid. Mp: 317-319 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.32 (s, 2H), 7.78 (s, 2H), 7.41-7.36 (m, 2H), 7.10 (s, 2H), 7.08-7.00 (m, 2H), 5.44 (s, 1H), 5.43 (s, 1H), 3.90 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.1, 160.7, 151.9, 144.8, 142.0, 137.4, 126.3, 125.6, 123.9, 123.7, 122.6, 121.9, 108.4, 55.9, 55.3, 51.8. EI-MS: *m/z* 370 $[M]^+$. Anal. Calcd for $C_{24}H_{18}O_4 \cdot 0.05CH_2Cl_2$: C 77.10, H 4.87; found: C 77.10, H 4.85.

2,7-Dimethoxyl-3,6-dihydroxymethyltriptycene (3).

To a solution of **2** (1.0 g, 2.7 mmol) in 1:1 (v/v) MeOH/THF (50 mL) was added sodium borohydride (0.2 g, 5.3 mmol). The mixture was stirred for 15 min at room temperature. Until the consumption of starting material, 2 N HCl was added to quench the reaction and extracted with DCM. The organic phase was dried with $MgSO_4$, and concentrated to give pure alcohol **3** (0.99 g, 98 %) as a white solid. Mp: 248-250 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33 (m, 2H), 7.26 (s, 2H), 6.99 (s, 2H), 6.98 -6.92 (m, 2H), 5.33 (s, 1H), 5.30 (s, 1H), 4.54 (s, 4H), 3.77 (s, 6H), 2.19 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.8, 146.3, 146.1, 144.9, 138.2, 125.4, 125.2, 124.9, 124.0, 123.4, 123.3, 107.2, 61.7, 55.6, 54.7, 52.5. EI-MS: *m/z* 374 $[M]^+$. Anal. calcd. for $C_{24}H_{22}O_4 \cdot 0.5CH_2Cl_2$: C 70.58, H, 5.56; found: C 70.58, H 5.58.

General procedure for the synthesis of 4a-c.

A mixture of 2,7-dimethoxyl-3,6-dihydroxymethyltriptycene **3** (1.0 mmol), *p*-substituted phenol **3** (10.0 mmol) and a catalytic amount of *p*-toluenesulfonic acid (0.1 mmol) in toluene (50 mL) was heated at reflux for 4 h. After cooling to room temperature, the solvent was removed in vacuo. And the residue was submitted to column chromatography.

4a. Elution with petroleum ether/ EtOAc (5:1, v/v) gave **4a** (R_f = 0.18) in 54 % yield as a white solid. Mp: 124-126 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34 -7.24 (m, 2H), 7.21-7.19 (m, 5H), 7.10-7.06 (m, 2H), 6.97 (s, 2H), 6.94-6.91 (m, 2H), 6.77 (s, 2H), 6.72 (s, 1H), 6.69 (s, 1H), 5.27 (s, 1H), 5.26 (s, 1H), 3.87 (s, 6H), 3.82-3.71 (ABq, *J* = 15 Hz ,4H), 1.28 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.6, 151.9, 145.8, 145.0,

144.9, 143.0, 139.1, 127.4, 125.7, 125.5, 125.3, 125.02, 124.95, 124.5, 123.4, 123.3, 115.9, 107.5, 56.1, 54.3, 52.4, 34.0, 31.7, 31.1. MALDI-TOF MS: *m/z* 638 $[M]^+$, 661 $[M+Na]^+$. Anal. Calcd for $C_{44}H_{46}O_4 \cdot 0.82CH_2Cl_2$: C 75.98, H 6.78; found: C 75.97, H 6.78.

4b. Elution with petroleum ether/ EtOAc (5:1, v/v) gave **4b** (R_f = 0.16) in 78 % yield as a white solid. Mp: 138-140 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57-7.48 (m, 4H), 7.43-7.37 (m, 6H), 7.35-7.23 (m, 8H), 7.09 (s, 2H), 6.98 (s, 2H), 6.92-6.91 (m, 2H), 6.84 (s, 1H), 6.81 (s, 1H), 5.26 (s, 1H), 5.23 (s, 1H), 3.90 (s, 6H), 3.88-3.76 (ABq, *J* = 15 Hz ,4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.0, 152.3, 145.6, 145.2, 144.7, 141.2, 139.2, 133.5, 129.3, 128.7, 126.9, 126.8, 126.8, 126.5, 125.8, 125.4, 125.1, 124.2, 123.6, 123.3, 116.8, 107.6, 56.2, 54.3, 52.3, 30.8. MALDI-TOF MS: *m/z* 678 $[M]^+$, 701 $[M+Na]^+$, 717 $[M+K]^+$. Anal. Calcd for $C_{48}H_{38}O_4 \cdot 0.2CH_2Cl_2$: C 83. 20, H 5.56; found: C 83.53, H 5.85.

4c. Elution with petroleum ether/EtOAc (5:1, v/v) gave **4c** (R_f = 0.20) in 59 % yield as a white solid. Mp: 110-112 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32-7.29 (m, 2H), 7.21 (s, 2H), 7.03 (s, 2H), 6.97 (s, 2H), 6.96-6.86 (m, 4H), 6.77 (s, 2H), 6.72 (s, 1H), 6.69 (s, 1H), 5.26 (s, 2H), 3.88 (s, 6H), 3.81-3.70 (ABq, *J* = 15 Hz, 4H), 2.81 (q, *J* = 6.9 Hz, 2H), 1.20 (d, *J* = 6.9 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.5, 152.2, 145.8, 145.0, 144.9, 140.7, 139.1, 128.6, 127.5, 126.1, 125.7, 125.6, 125.3, 125.0, 124.5, 123.4, 123.3, 116.2, 115.1, 107.5, 56.1, 54.3, 52.4, 33.3, 30.8, 24.3. MALDI-TOF MS: *m/z* 610 $[M]^+$, 633 $[M+Na]^+$, 649 $[M+K]^+$. Anal. Calcd for $C_{42}H_{42}O_4 \cdot 0.25CH_2Cl_2$: C 80.29, H 6.78; found: C 80.25, H 6.92.

General procedure for the synthesis of 5a-c.

To a solution of catalytic amount of TsOH (0.02 mmol) in *o*-dichlorobenzene (25 mL) was slowly added a solution of **3** (0.1 mmol) and **4** (0.1 mmol) in *o*-dichlorobenzene (25 mL) at 100 °C under argon atmosphere. After that, the mixture heated for an additional 24 h. The brown solution was evaporated in vacuo, then the mixture was separated by column chromatography over silica gel with petroleum

ether/DCM/EtOAc (10: 5: 1, v/v) as the eluent to afford **5a-c**. Compound **5a-c** could be further crystallized from CH_2Cl_2/MeOH.

5a. R_f = 0.27. White solid, 21 % yield. Mp>300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.10 (s, 5H), 7.08 (s, 5H), 6.99-6.82 (m, 10H), 5.18 (s, 2H), 5.12 (s, 2H), 4.23 (d, *J* = 14.8 Hz, 4H), 3.82 (s, 12H), 3.24 (d, *J* = 14.9 Hz, 4H), 1.35 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.2, 150.7, 146.9, 146.0, 143.9, 141.5, 138.0, 126.7, 125.5, 125.4, 125.1, 124.71, 124.65, 123.2, 122.9, 107.6, 56.1, 54.3, 52.5, 33.9, 31.8, 29.6. MALDI-TOF MS: *m/z* 976 $[M]^+$, 999 $[M+Na]^+$, 1015 $[M+K]^+$. HRMS-ESI Calcd for $C_{68}H_{63}O_6$: 975.4625. Found: 975.4639.

5b. R_f = 0.24. White solid, 22 % yield. Mp>300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58 (s, 2H), 7.55 (s, 2H), 7.41-7.34 (m, 8H), 7.27-7.23 (m, 8H), 7.13 (s, 4H), 6.90 (s, 8H), 5.18 (s, 2H), 5.13 (s, 2H), 4.28 (d, *J* = 14.6 Hz, 4H), 3.83 (s, 12H), 3.28 (d, *J* = 14.7 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.1, 152.7, 146.8, 145.9, 144.1, 141.5, 138.2, 128.6, 128.5, 127.0, 126.8, 126.2, 125.6, 125.1, 124.7, 124.4, 123.1, 123.0, 107.8, 56.2, 54.3, 52.3, 29.5. MALDI-TOF MS: *m/z* 1017 $[M]^+$, 1039 $[M+Na]^+$. HRMS-ESI Calcd for $C_{72}H_{55}O_6$: 1015.3999. Found: 1015.4011.

5c. R_f = 0.29. White solid, 20 % yield. Mp>300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27 (s, 2H), 7.08 (s, 4H), 6.96 (s, 4H), 6.94-6.90 (m, 4H), 6.89 (s, 4H), 5.18 (s, 2H), 5.11 (s, 2H), 4.22 (d, *J* = 14.8 Hz, 4H), 3.82 (s, 12H), 3.23 (d, *J* = 14.8 Hz, 4H), 2.87 (q, *J* = 6.9 Hz, 2H), 1.28 (d, *J* = 6.9 Hz, 12H).^{13}C NMR (75 MHz, $CDCl_3$): δ 153.2, 150.9, 146.9, 146.0, 144.0, 138.0, 127.6, 125.9, 125.4, 125.1, 124.7, 124.6, 123.1, 122.9, 107.7, 56.1, 54.3, 53.4, 52.5, 51.9, 33.1, 29.4, 24.4. MALDI-TOF MS: *m/z* 948 $[M]^+$, 971 $[M+Na]^+$, 987 $[M+K]^+$. Anal. Calcd for $C_{66}H_{60}O_6 \cdot 0.3CH_2Cl_2$: C 81.70, H 6.27; found: C 81.74, H 6.47.

General procedure for the preparation of 6a-c.

To a solution of **5** (0.10 mmol) in dichloromethane (5 mL), boron tribromide (47 uL, 0.5 mmol) in dichloromethane (5 mL) was added upon cooling with ice. The mixture was stirred at room temperature overnight. 2 N HCl was then added to

quench the reaction under 0°C. A white solid was precipitated, filtrated and washed with water to give a crude product. The crude product was submitted to column chromatography with petroleum ether/EtOAc (1: 2, v/v) as the eluent to give the target product.

6a. R_f = 0.46. White solid, 90 % yield. Mp>300 °C. ^{1}H NMR (300 MHz, acetone-d_6): δ 8.95 (s, 2H), 8.81 (s, 3H), 7.32-7.27 (m, 4H), 7.20 (s, 4H), 7.10 (s, 4H), 6.94-6.87 (m, 4H), 6.77 (s, 4H), 5.16 (s, 2H), 5.15 (s, 2H), 3.95 (d, J = 13.8 Hz, 4H), 3.33 (d, J = 14.0 Hz, 4H), 1.31 (s, 18H). ^{13}C NMR (75 MHz, acetone-d_6): δ 150.5, 148.9, 147.9, 146.8, 145.5, 144.4, 138.9, 127.5, 126.7, 126.0, 125.6, 125.3, 124.1, 123.7, 123.5, 113.1, 54.0, 53.0, 34.6, 32.1, 32.0. MALDI-TOF MS: *m/z* 943 $[M+Na]^+$. HRMS-ESI Calcd for $C_{64}H_{55}O_6$: 919.3999. Found: 919.3994.

6b. R_f = 0.43. White solid, 95 % yield. Mp>300 °C. ^{1}H NMR (300 MHz, acetone-d_6) δ 7.56 (d, J = 7.2 Hz, 4H), 7.47-7.39 (m, 8H), 7.35 (d, J = 7.1 Hz, 2H), 7.33-7.25 (m, 5H), 7.22 (s, 4H), 6.97-6.86 (m, 5H), 6.81 (s, 4H), 5.27 (s, 2H), 5.18 (s, 2H), 4.00 (d, J = 13.9 Hz, 4H), 3.45 (d, J = 13.8 Hz, 4H). ^{13}C NMR (75 MHz, acetone-d_6) δ 155.2, 151.9, 147.9, 145.7, 141.7, 139.3, 138.9, 133.6, 130.2, 129.6, 128.8, 128.5, 127.5, 127.3, 126.3, 124.1, 123.1, 116.6, 113.2, 112.4, 54.0, 52.9, 31.5. MALDI-TOF MS: *m/z* 983 $[M+Na]^+$. HRMS-ESI Calcd for $C_{68}H_{47}O_6$: 959.3373. Found: 959.3376.

6c. R_f = 0.36. White solid, 92 % yield. Mp>300 °C. ^{1}H NMR (300 MHz, acetone-d_6) δ 8.95 (s, 2H), 8.84 (s, 4H), 7.33-7.27 (m, 4H), 7.11 (s, 4H), 7.03 (s, 4H), 6.94-6.90 (m, 4H), 6.77 (s, 4H), 5.18 (s, 2H), 5.15 (s, 2H), 3.94 (d, J = 13.9 Hz, 4H), 3.31 (d, J = 16.4 Hz, 4H), 1.22 (d, J = 6.9 Hz, 12H). ^{13}C NMR (75 MHz, CD_3CN) δ 150.1, 148.4, 147.3, 146.4, 145.9, 139.2, 131.2, 130.2, 128.9, 126.2, 125.8, 124.4, 124.0, 118.4, 113.1, 53.7, 52.8, 31.4, 29.6, 20.5. MALDI-TOF MS: *m/z* 915 $[M+Na]^+$. HRMS-ESI Calcd for $C_{62}H_{51}O_6$: 891.3686. Found: 891.3693.

Reference:

S1. C. Zhang and C.-F. Chen, *J. Org. Chem.*, 2007, **72**, 3880-3888.

2. Copies of ^{1}H NMR and ^{13}C NMR spectra of new compounds

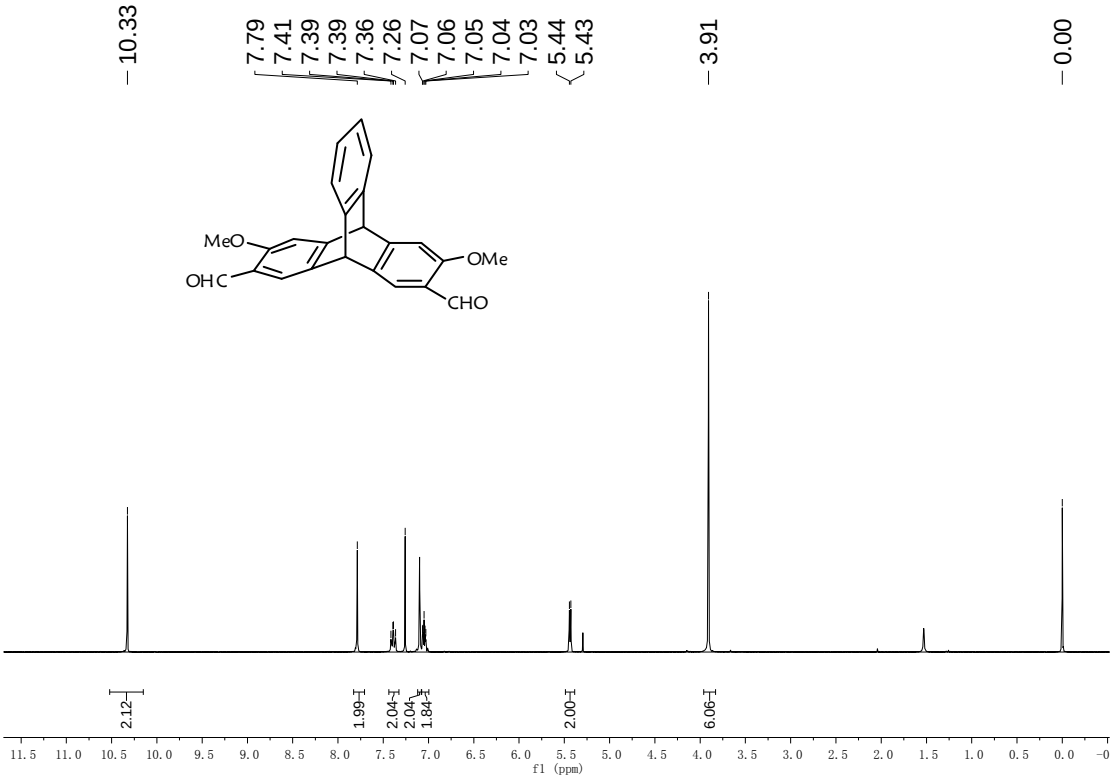


Fig. S1 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **2**.

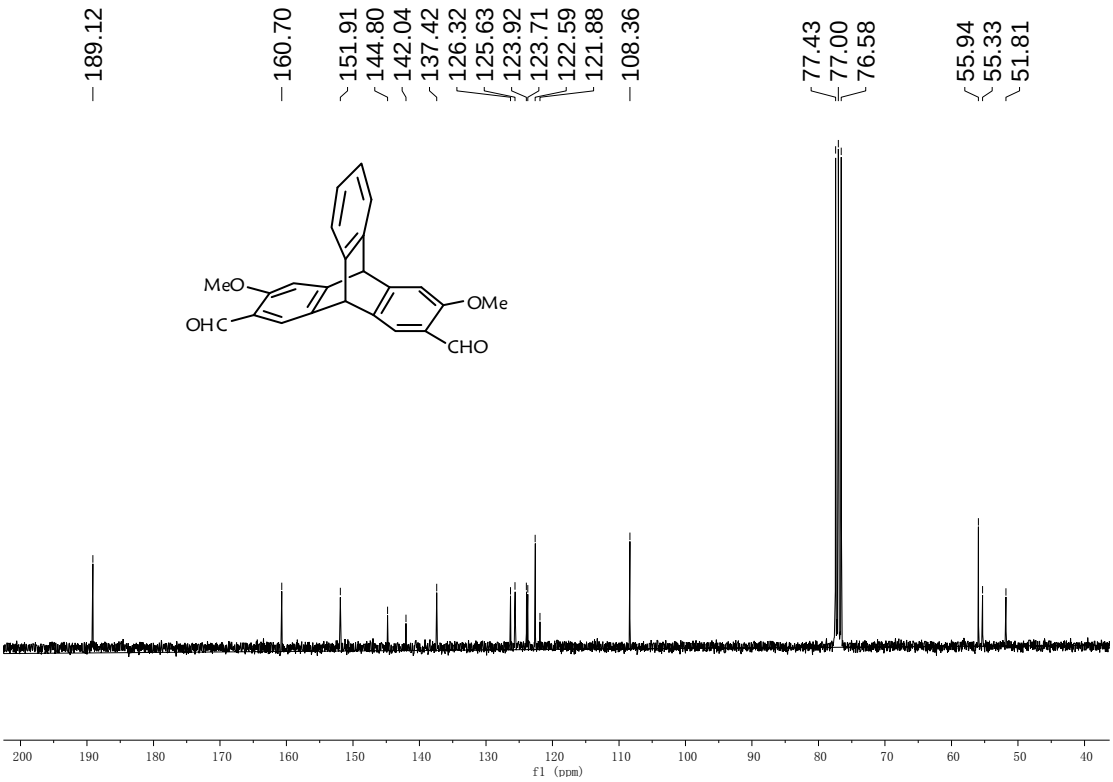


Fig. S2 ^{13}C NMR spectrum (300 MHz, $CDCl_3$) of **2**.

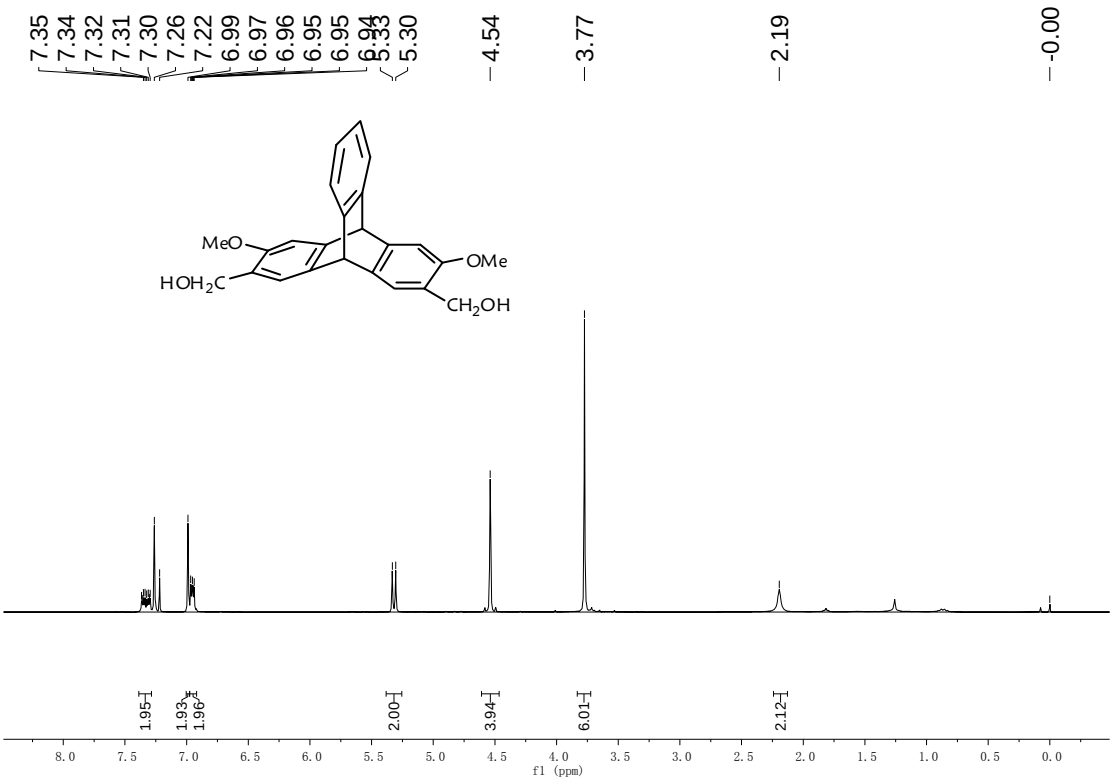


Fig. S3 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3**.

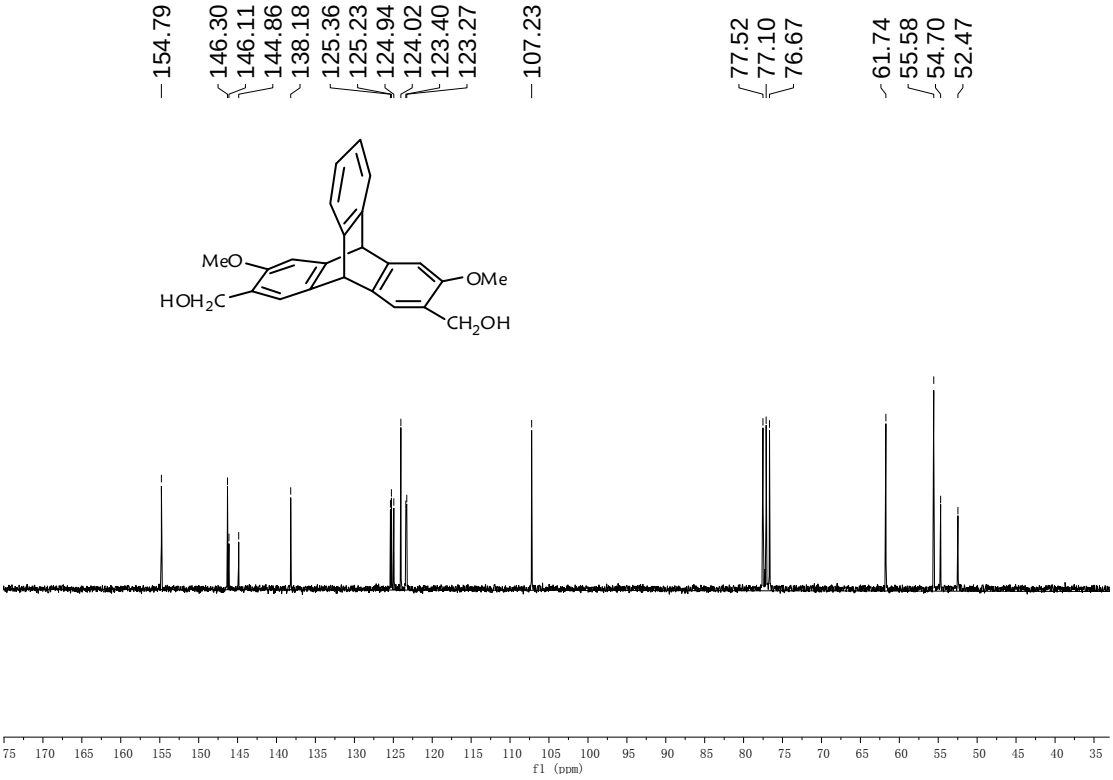


Fig. S4 ^{13}C NMR spectrum (300 MHz, $CDCl_3$) of **3**.

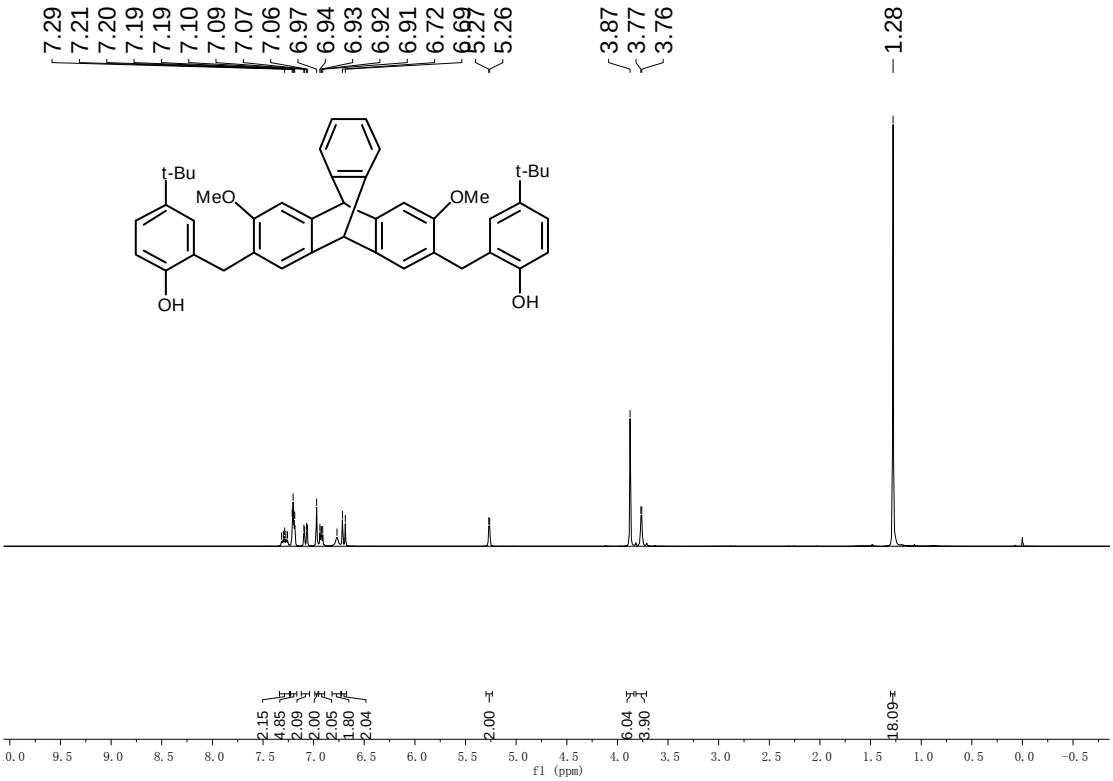


Fig. S5 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **4a**.

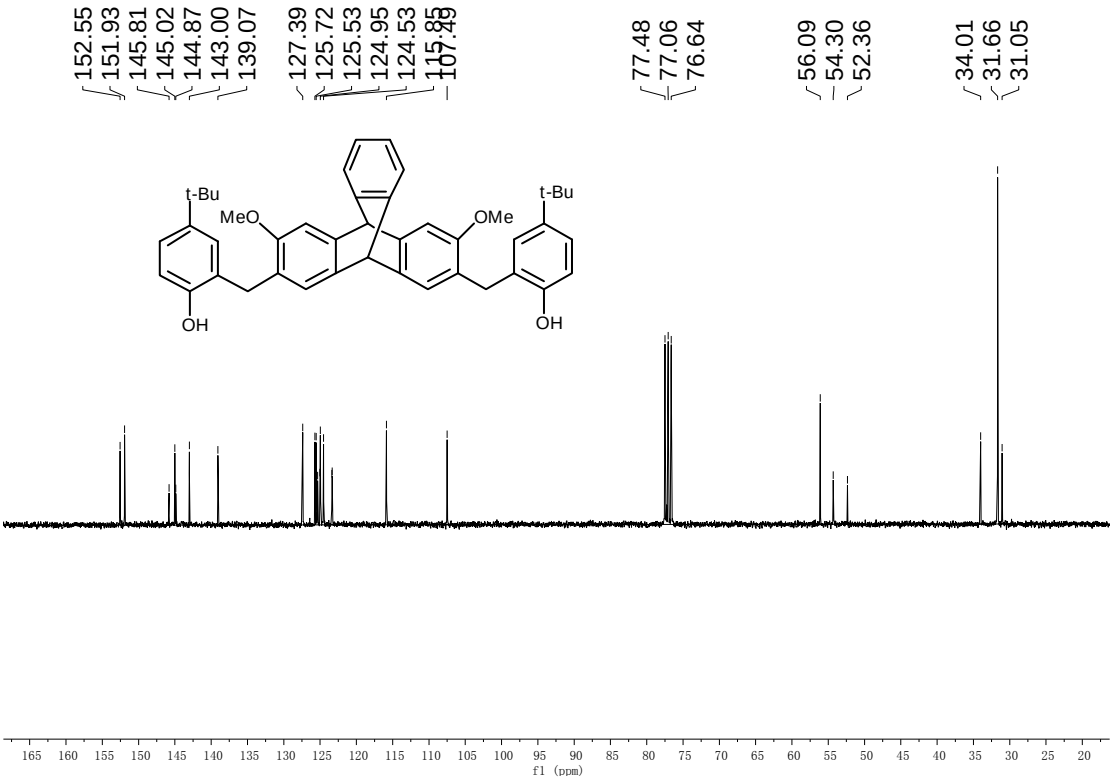


Fig. S6 ^{13}C NMR spectrum (300 MHz, $CDCl_3$) of **4a**.

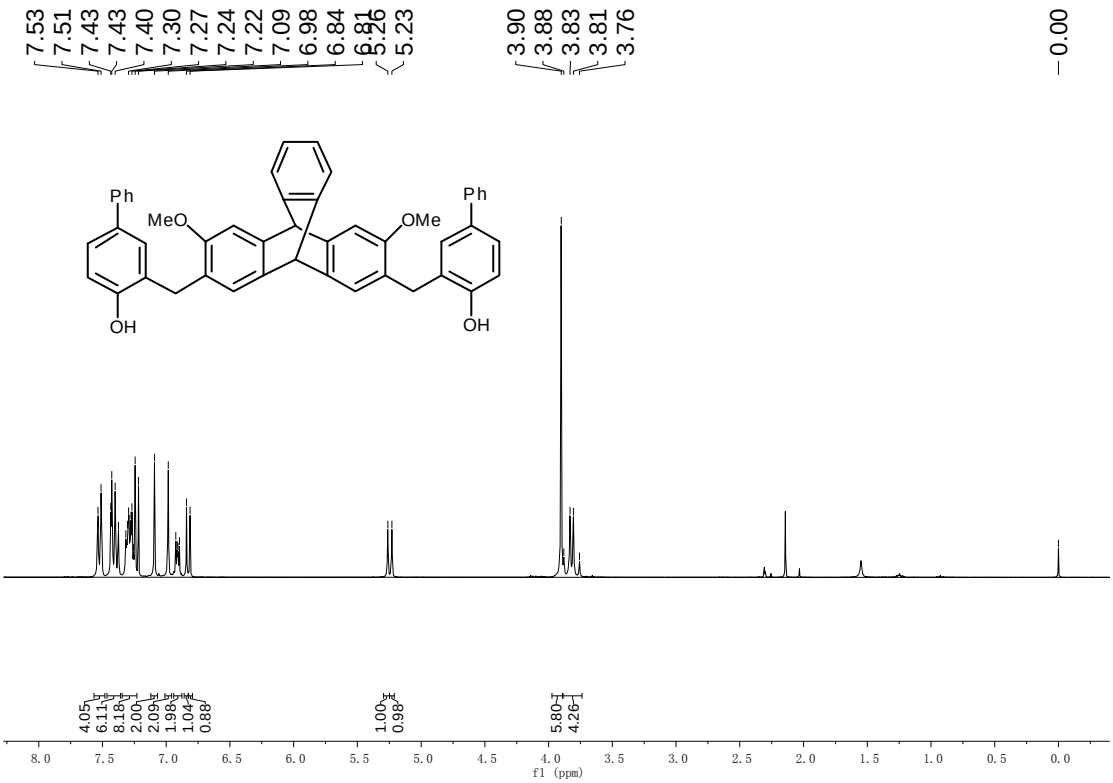


Fig. S7 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **4b**.

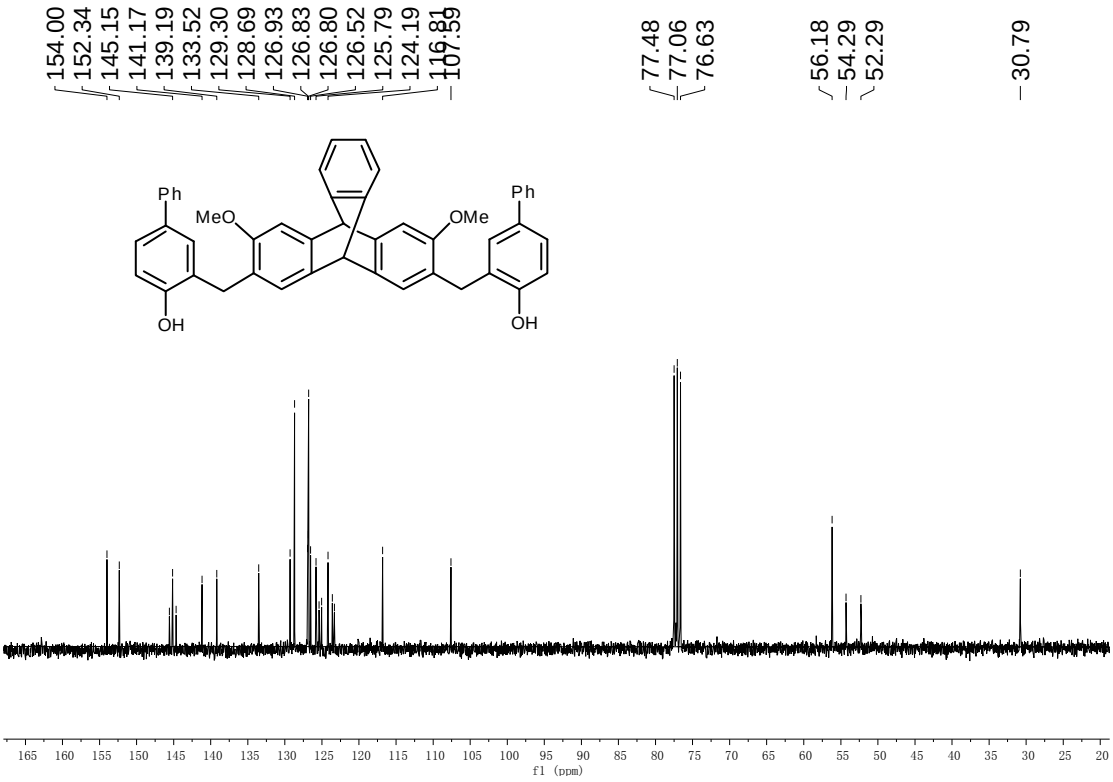


Fig. S8 ^{13}C NMR spectrum (300 MHz, $CDCl_3$) of **4b**.

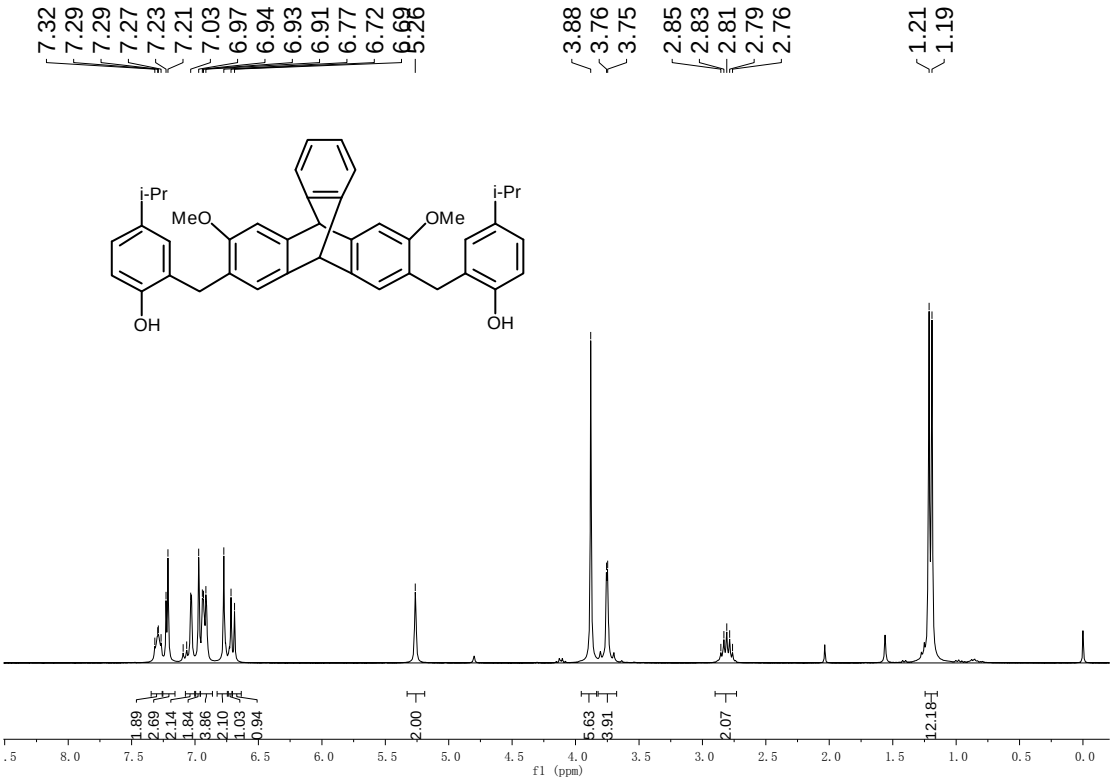


Fig. S9 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **4c**.

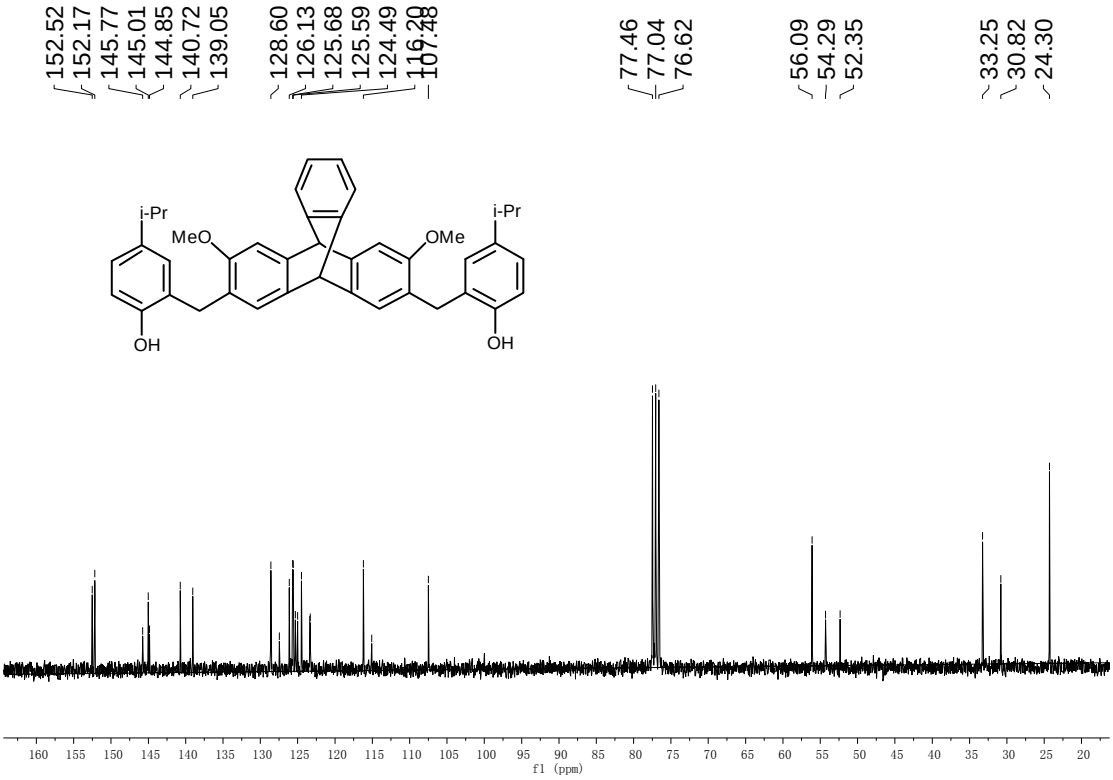


Fig. S10 ^{13}C NMR spectrum (300 MHz, $CDCl_3$) of **4c**.

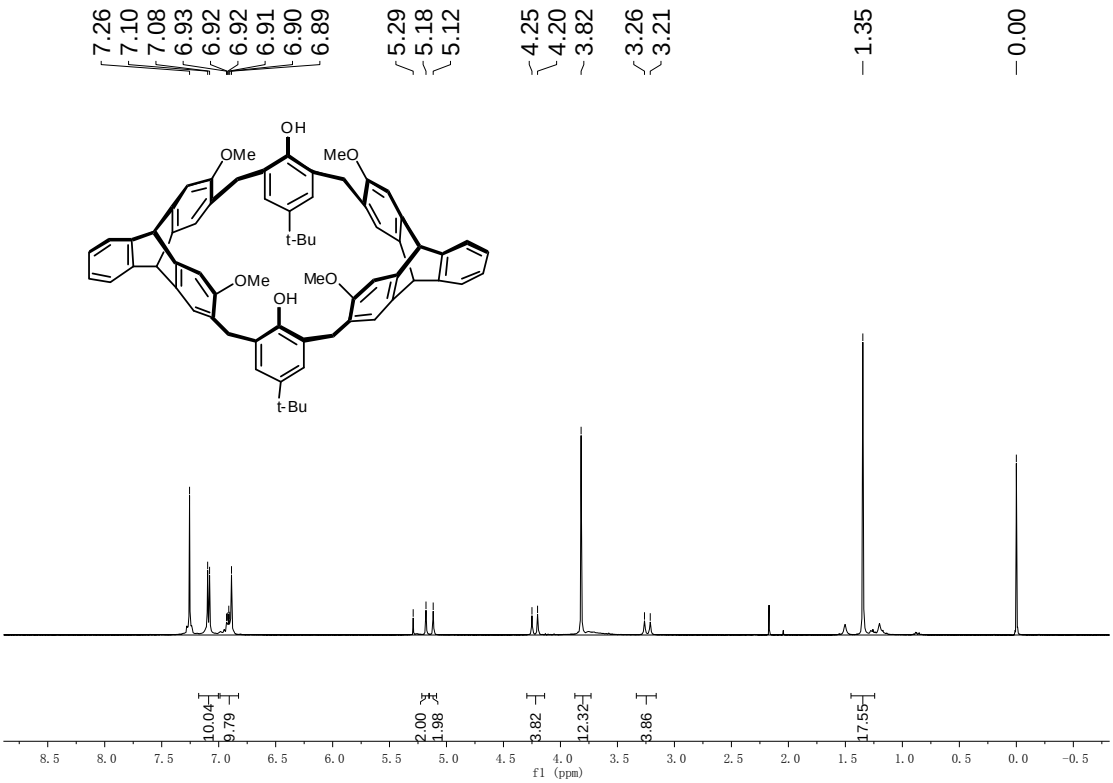


Fig. S11 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **5a**.

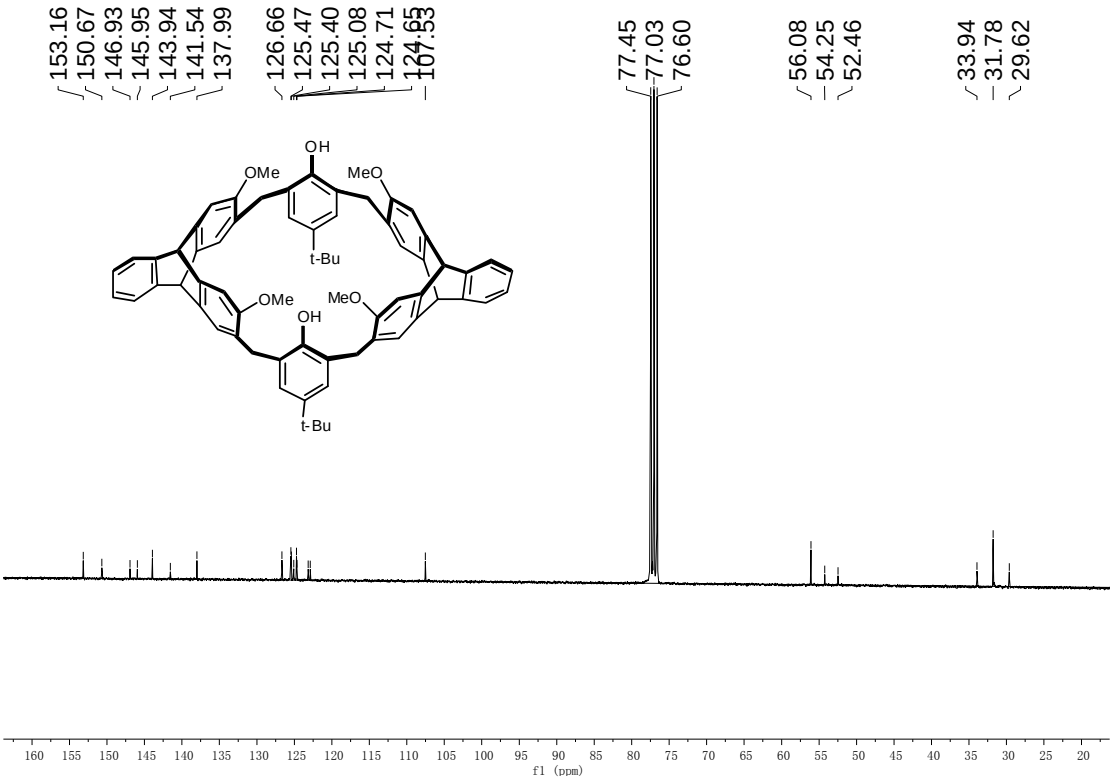


Fig. S12 ^{13}C NMR spectrum (300 MHz, $CDCl_3$) of **5a**.

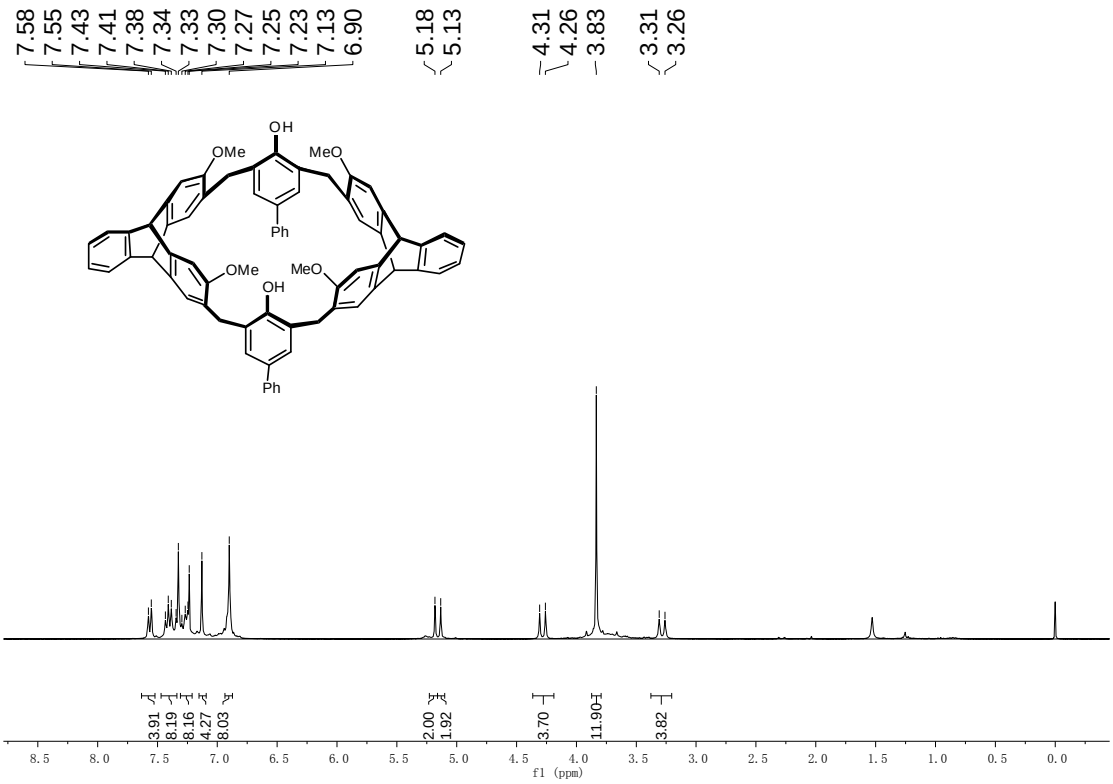


Fig. S11 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **5b**.

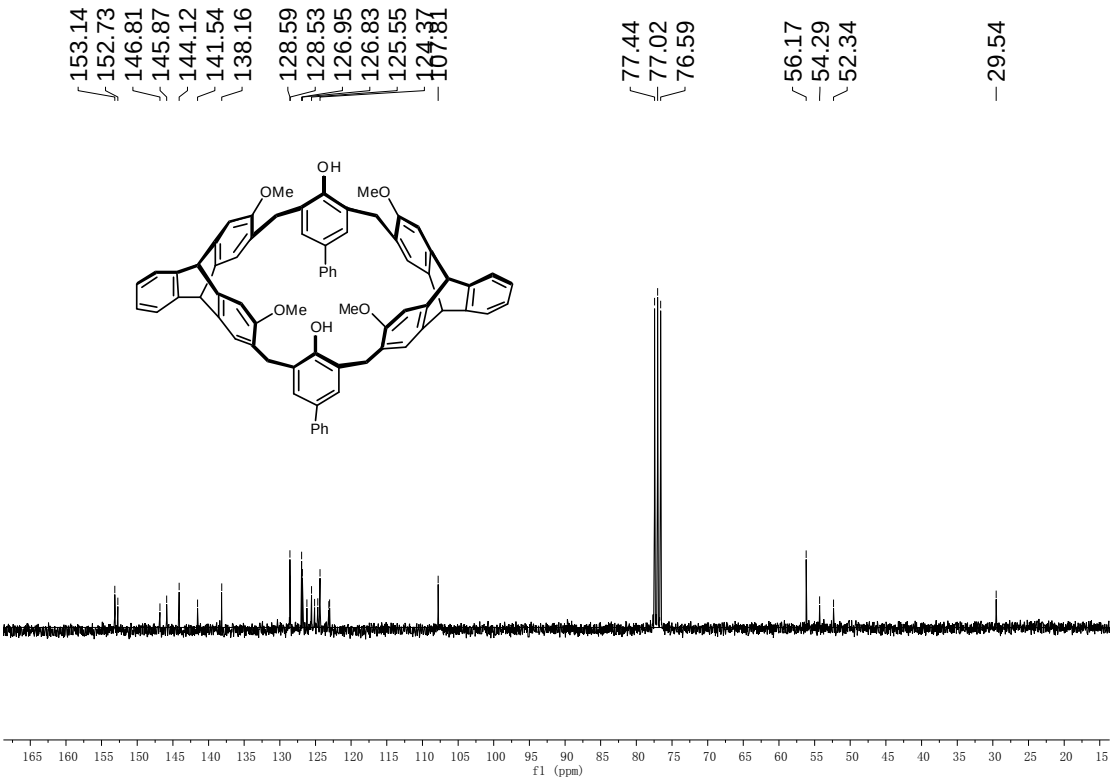


Fig. S12 ^{13}C NMR spectrum (300 MHz, $CDCl_3$) of **5b**.

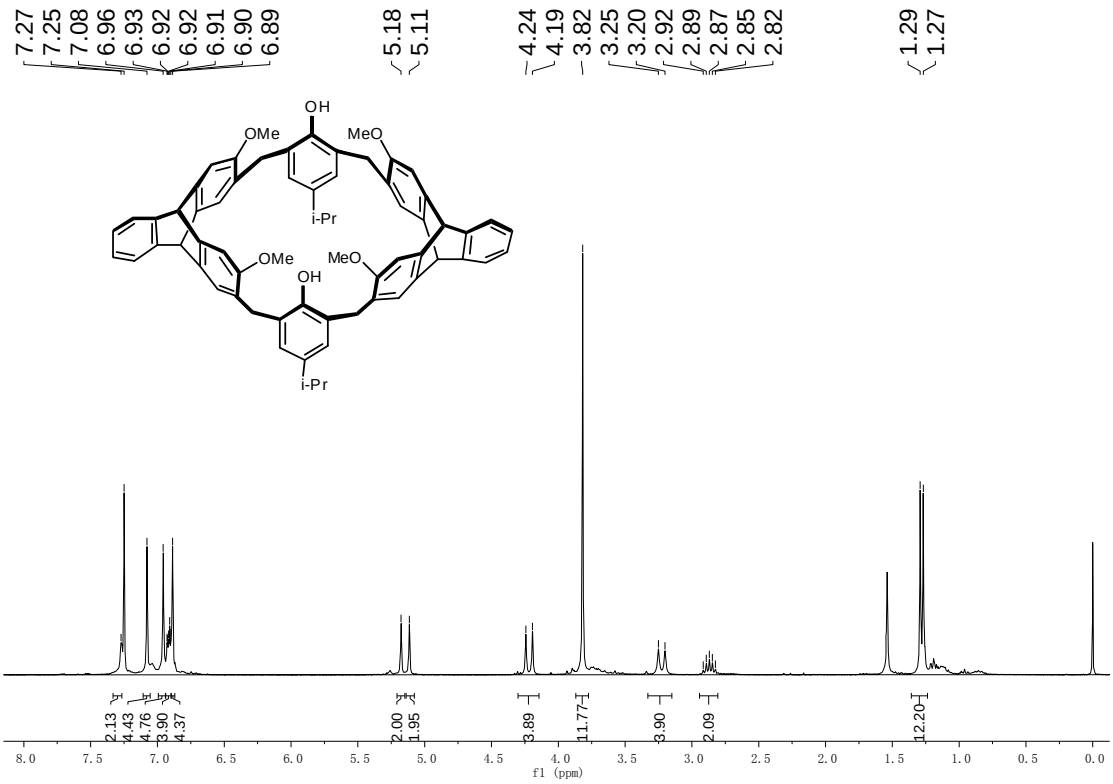


Fig. S13 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **5c**.

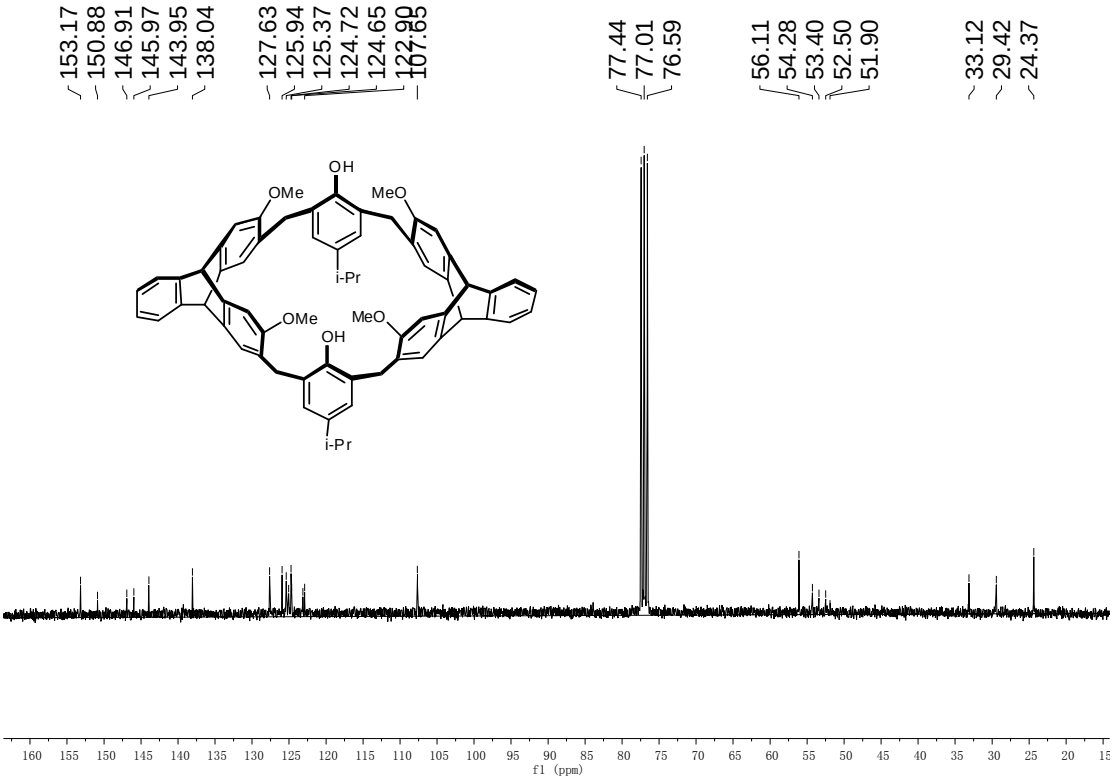


Fig. S14 ^{13}C NMR spectrum (300 MHz, $CDCl_3$) of **5c**.

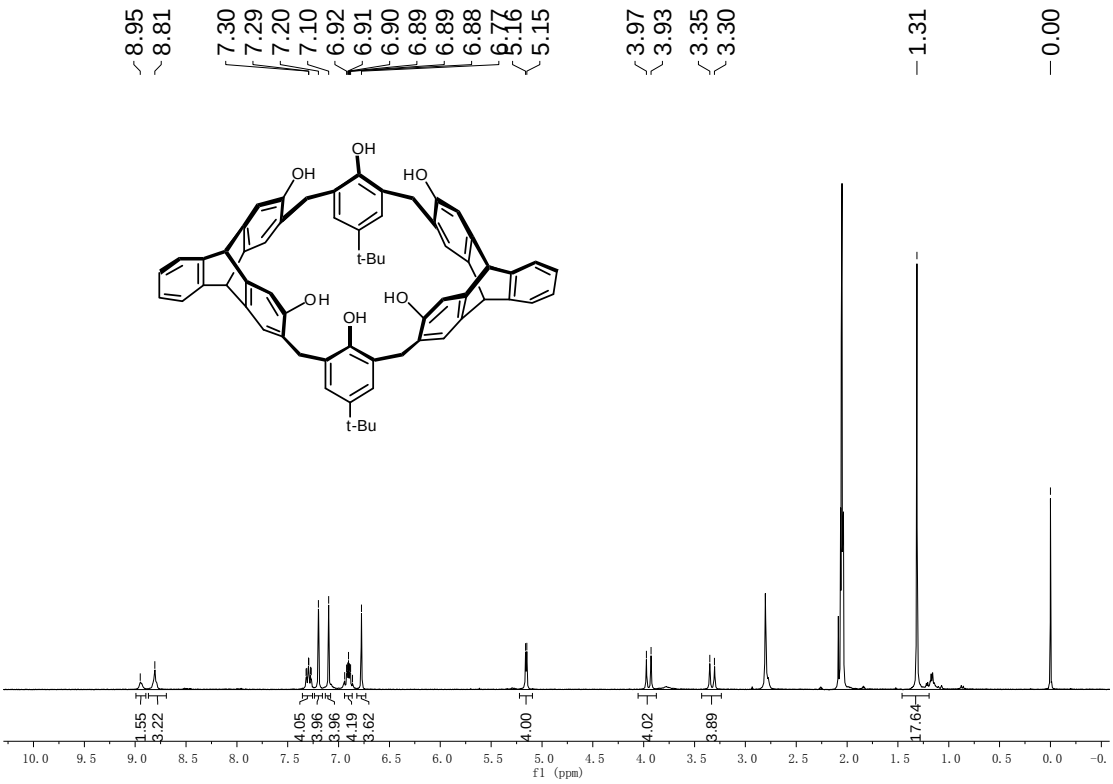


Fig. S15 ^{1}H NMR spectrum (300 MHz, acetone-d_6) of **6a**.

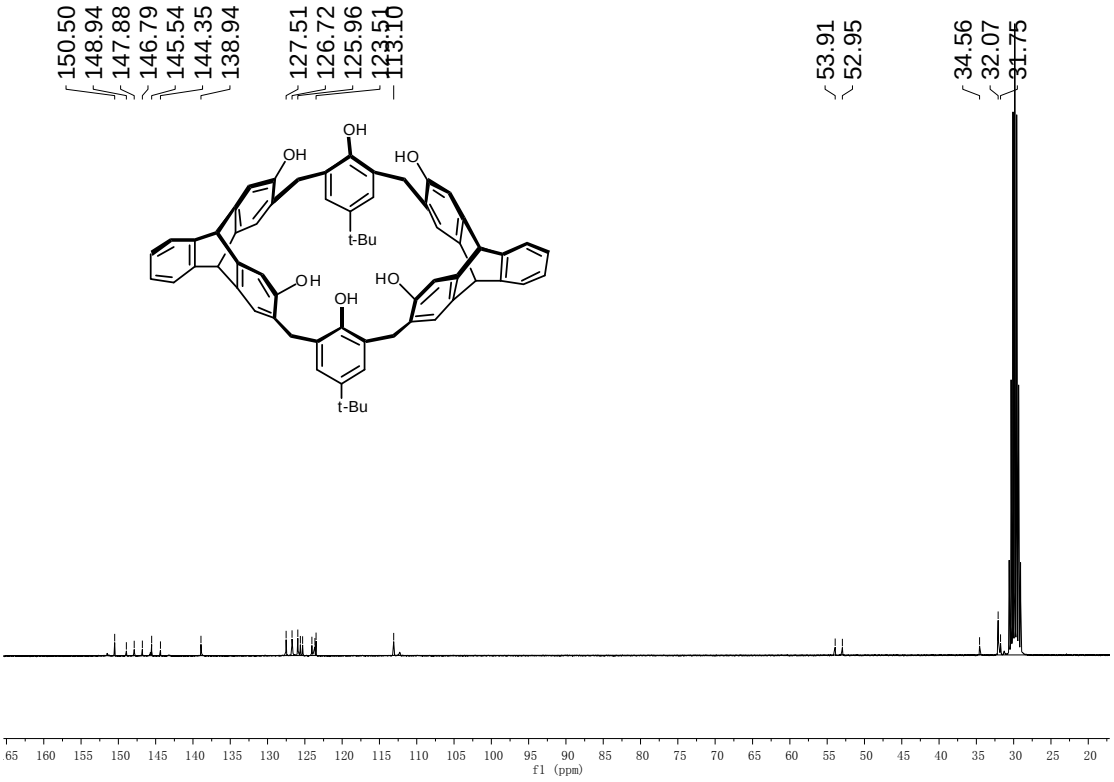


Fig. S16 ^{13}C NMR spectrum (300 MHz, acetone-d_6) of **6a**.

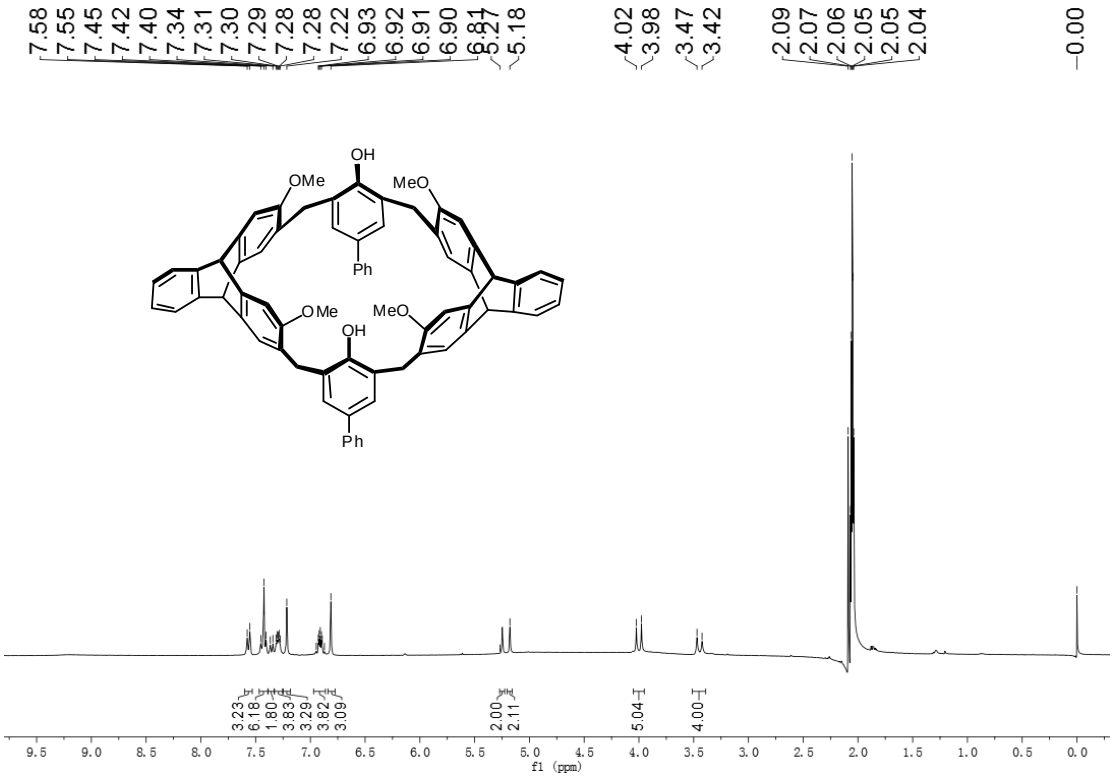


Fig. S17 ^{1}H NMR spectrum (300 MHz, acetone-d_6) of **6b**.

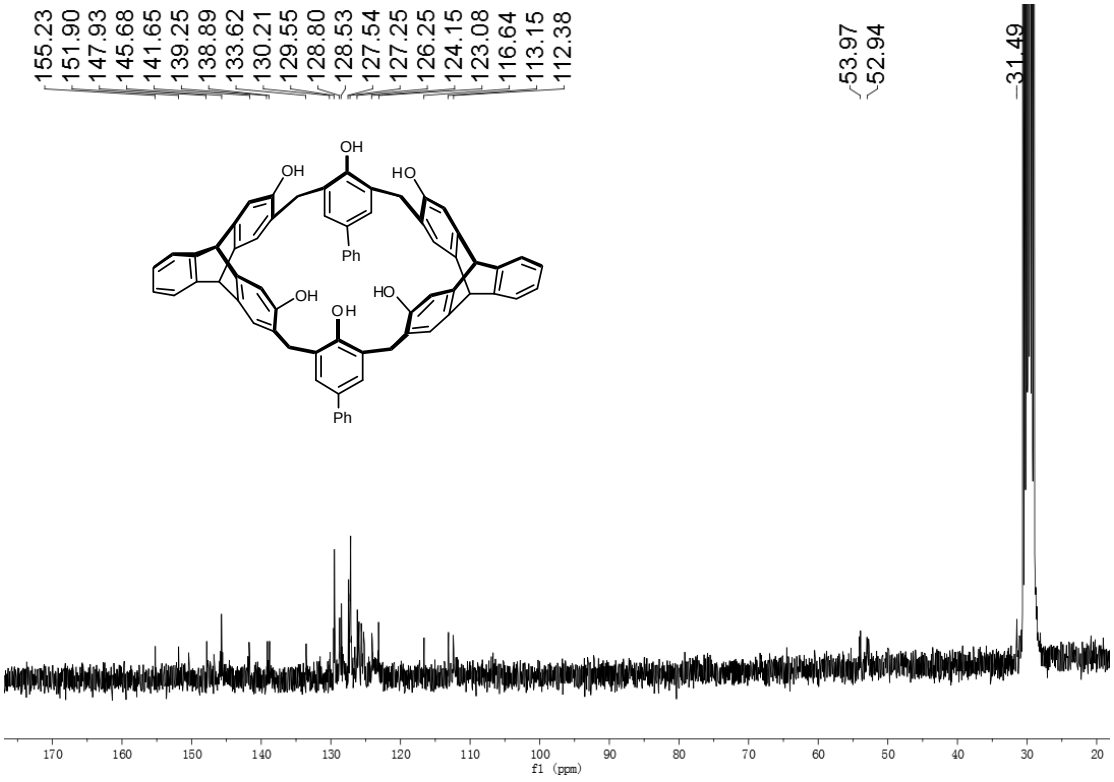


Fig. S18 ^{13}C NMR spectrum (300 MHz, acetone-d_6) of **6b**.

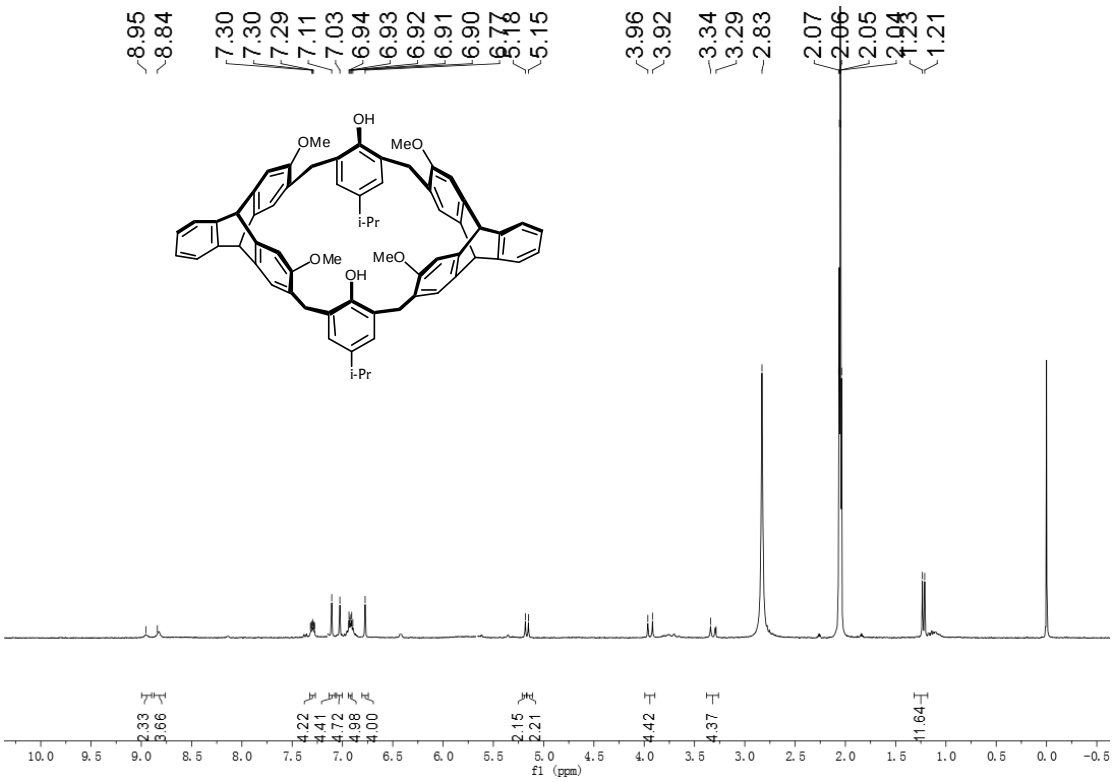


Fig. S19 ^{1}H NMR spectrum (300 MHz, acetone-d_6) of **6c**.

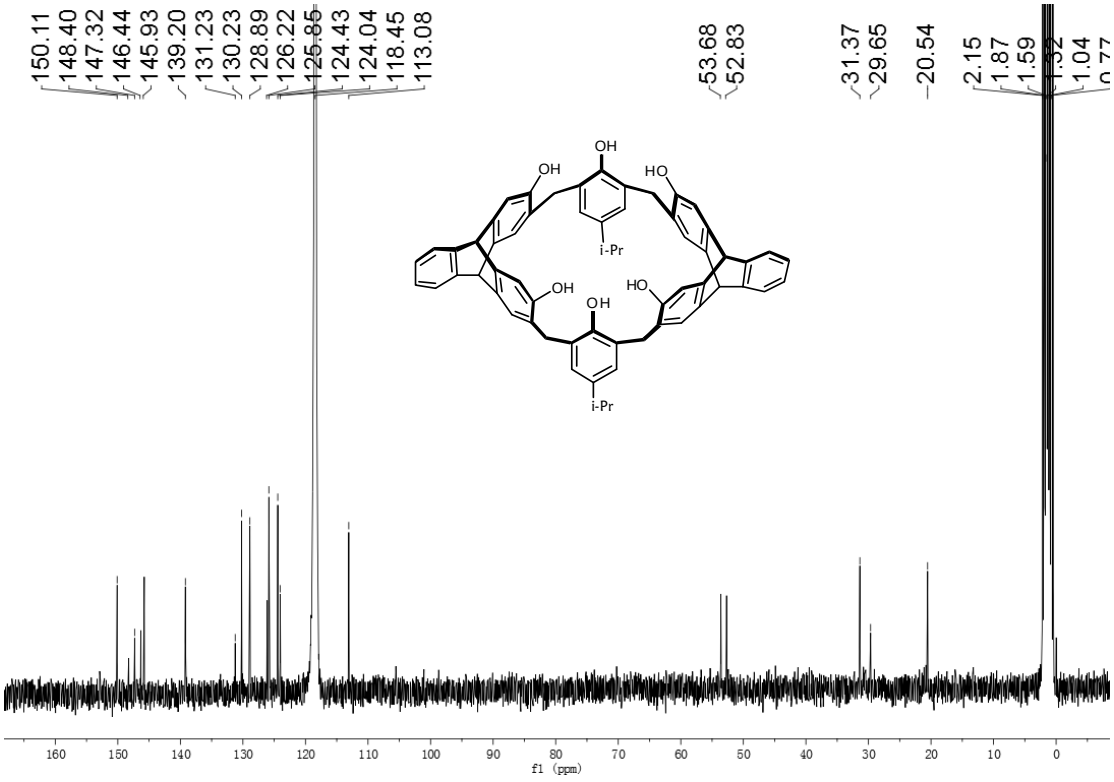


Fig. S20 ^{13}C NMR spectrum (300 MHz, CD_3CN) of **6c**.

3. Variable-temperature ^{1}H NMR experiments of macrocycle 5a

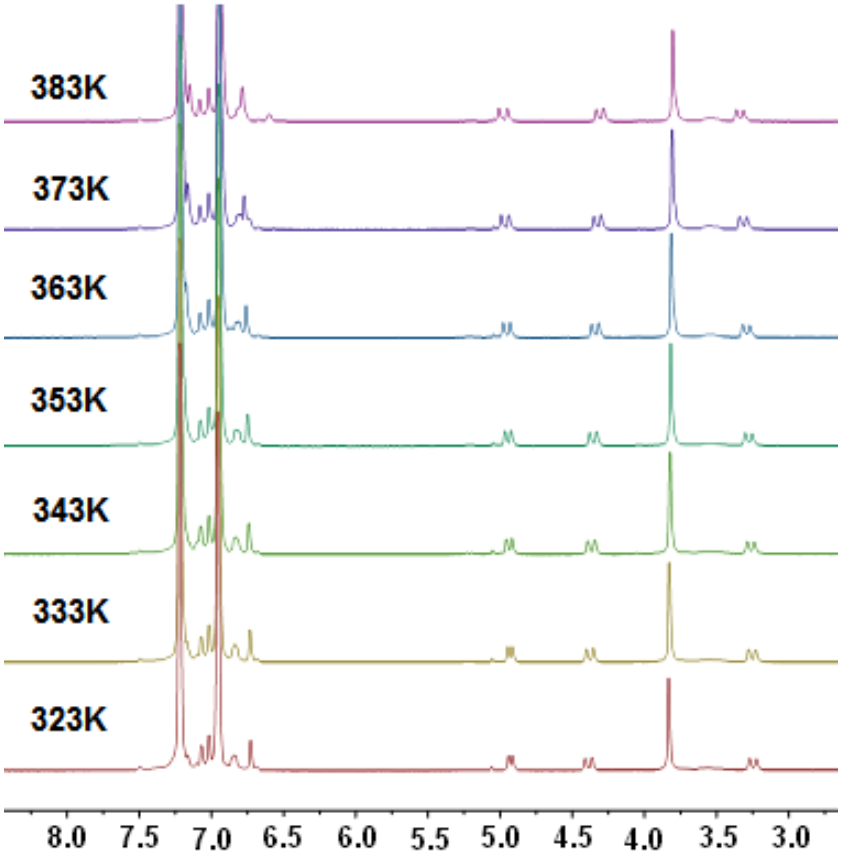


Fig. S21 Partial ^{1}H NMR spectra of **5a** (*o*-dichlorobenzene-d_4, 300 MHz) at various temperatures.

4. X-ray crystal data and crystal packing of 5a and 6a

The X-ray measurements were carried on a Saturn724 CCD diffractometer with graphite-monochromator Mo-Kα radiation (λ = 0.71073 Å) at 173 K. Intensities were collected using CrystalClear (Rigaku Inc., 2008) technique and absorption effects were collected using the multi-scan technique. The structures of **5a** and **6a** were all solved by direct methods and refined by a full matrix least squares technique based on F^2 using SHELXL 97 program. Application of the restraints is for confining the thermal vibration parameters of the disordered solvent molecules, which can make them be isotropic.

Because highly disordered solvent molecules in **5a** were difficult to be determined, they can be deleted with SQUEEZE program. Thus, crystal data for **5a** were given two times: **5a** (CCDC 842676) with disordered solvents of dichloromethane was provided in ESI, and **5a**-solvents squeezed (previous **5a**-solvent free, CCDC 842677) was depicted in article with the solvents of dichloromethane squeezed (ref. 11). For **6a** (CCDC 842678), its data were also provided in reference 11.

Crystal data for **5a**•6CH_2Cl_2: $C_{74}H_{76}Cl_{12}O_6$, M_w = 1486.74, crystal size 0.30×0.26×0.24 mm, triclinic, space group $P\bar{1}$, a = 12.717(3) Å, b = 17.240(3) Å, c = 18.924(4) Å, α = 109.86(3)°, β = 100.40(3)°, γ = 107.82(3)°, V = 3523(2) Å^3, T = 173(2) K, Z = 2, μ = 0.524 mm^{-1}, 31373 reflections measured, 12871 unique (R_{int} = 0.071), final R indices [($I > 2\sigma(I)$)]: R = 0.182, wR = 0.430, R indices (all data): R = 0.203, wR = 0.443.

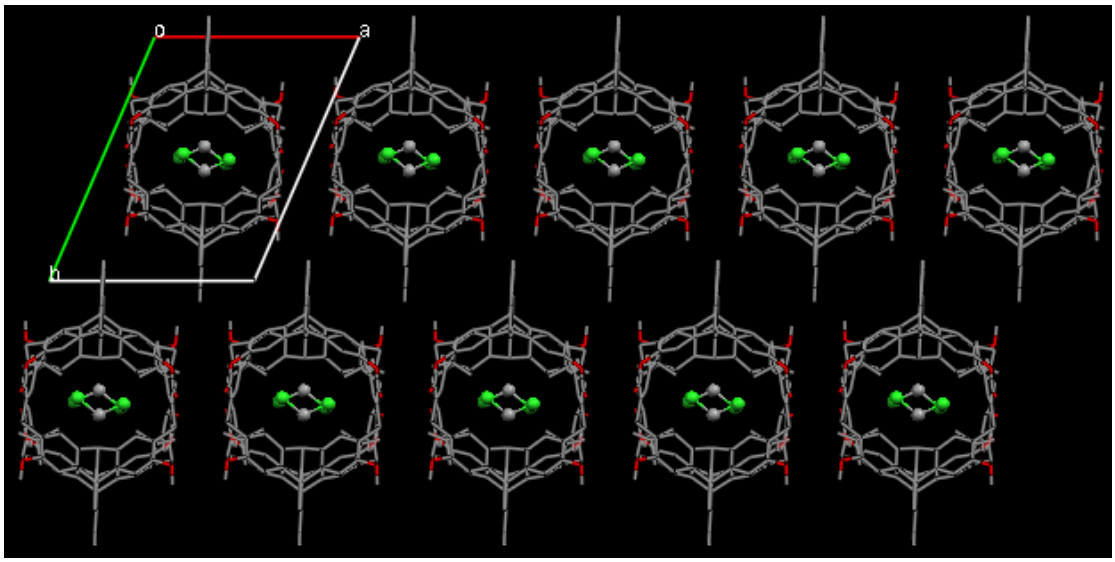


Fig. S22 Microporous architecture with the CH_2Cl_2 molecules located inside each channel viewed along the *c*-axis. Some solvent molecules and hydrogen atoms are omitted for clarity.

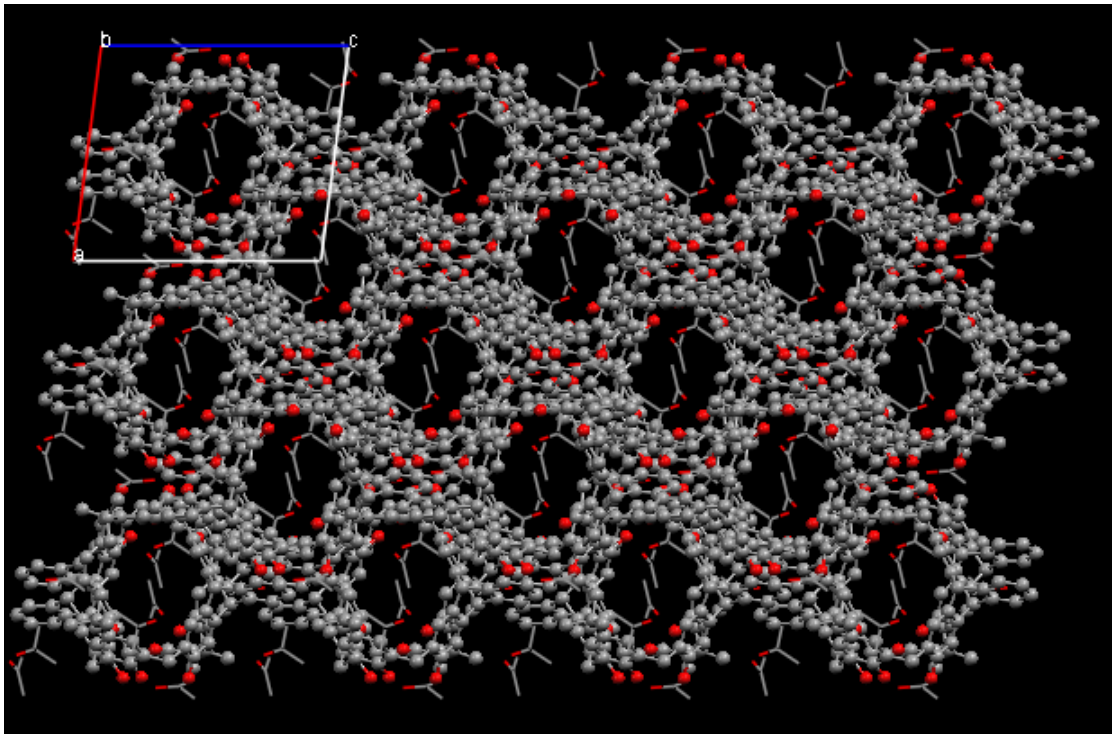


Fig. S23 Microporous architecture with the acetone molecules located inside each channel viewed along the *b*-axis. Hydrogen atoms are omitted for clarity.