Electronic Supplementary Information

Effects of Alkyl Chain Length of Oxatub[4]arene on Its Conformational Interconversion, Molecular Recognition and Macroscopic Self-Assembly

Liu-Pan Yang,[a] Fei Jia,[a,d] Fangfang Pan,[b] Zhi-Sheng Pan,[a] Kari Rissanen[c] and Wei Jiang*[a]

[a] *Department of Chemistry, South University of Science and Technology of China, No. 1088 Xueyuan Blvd, Nanshan District, Shenzhen, 518055, P. R. China.*
E-mail: jiangw@sustc.edu.cn
[b] *College of Chemistry, Central China Normal University Wuhan, 430079, China*
[c] *Department of Chemistry and Nanoscience Center, University of Jyvaskyla, Jyvaskyla, P.O. Box 3540014, Finland*
[d] *Institut für Chemie und Biochemie, Freie Universität Berlin, Takustraße 3, 14195 Berlin, Germany*

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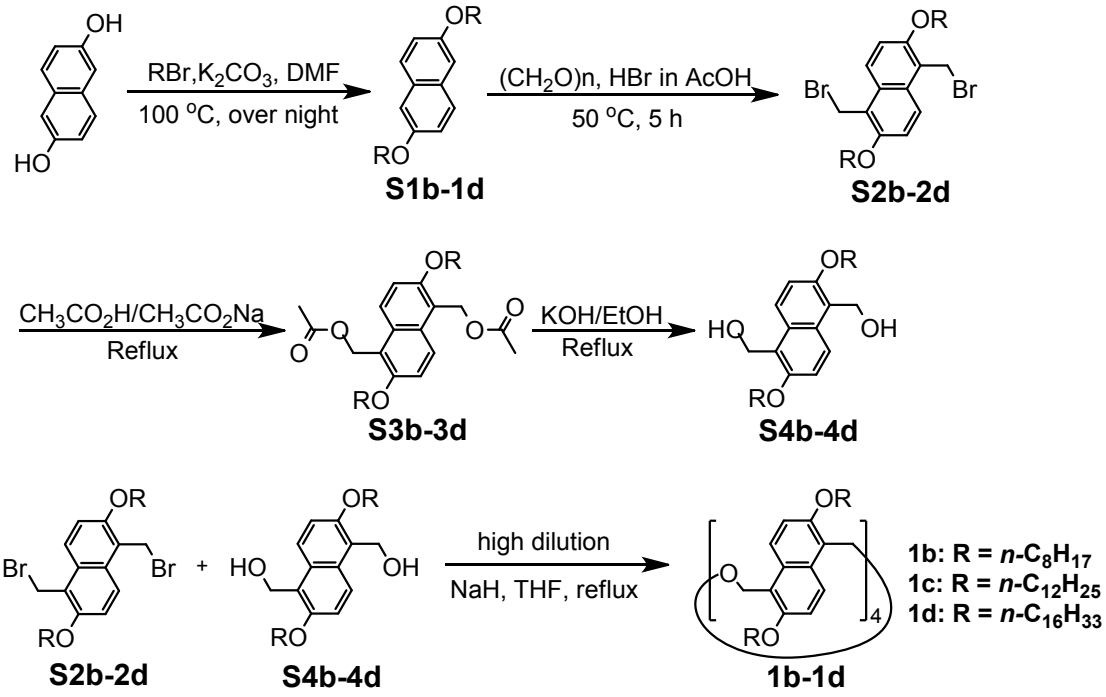
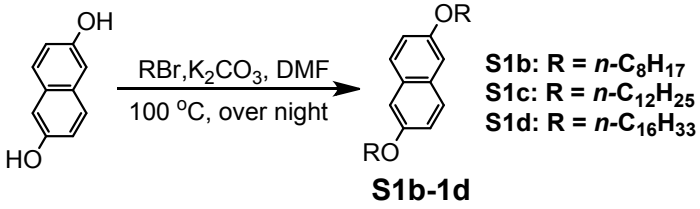
1. Experimental Section

1.1 General Method. All the reagents involved in this research were commercially available and used without further purification unless otherwise noted. Solvents were either employed as purchased or dried prior to use by standard laboratory procedures. ^{1}H NMR, ^{13}C NMR, and ^{1}H-^{1}H ROESY NMR spectra were recorded on Bruker Avance-400 or 500 spectrometers. All chemical shifts are reported in *ppm* with residual solvents or TMS (tetramethylsilane) as the internal standards. Electrospray-ionization time-of-flight high-resolution mass spectrometry (ESI-TOF-HRMS) experiments were conducted on an applied Q EXACTIVE mass spectrometry system. Molecular simulations were performed at the Semi-Empirical PM6 level of theory by using Spartan'14 (Wavefunction, Inc.). Isothermal Titration Calorimetry (ITC) titration experiments were carried out in 1,2-dichloroethane/CH_3CN 3 : 2 (v/v) at 25 °C on a NanoITC LV – 190 μL (Waters GmbH, TA Instruments, Eschborn, Germany).[1] Scanning electron microscope (SEM) images were obtained from the field emission SEM (FESEM, ZEISS Merlin). Transmission electron microscopy investigations were carried out on a HITACHI HT-7700 instrument. Powder XRD measurement was performed on a Smartlab (9 kW, Rigaku, Japan). The synthesis of **1a** has been reported.[1]

1.2 Synthetic Procedures



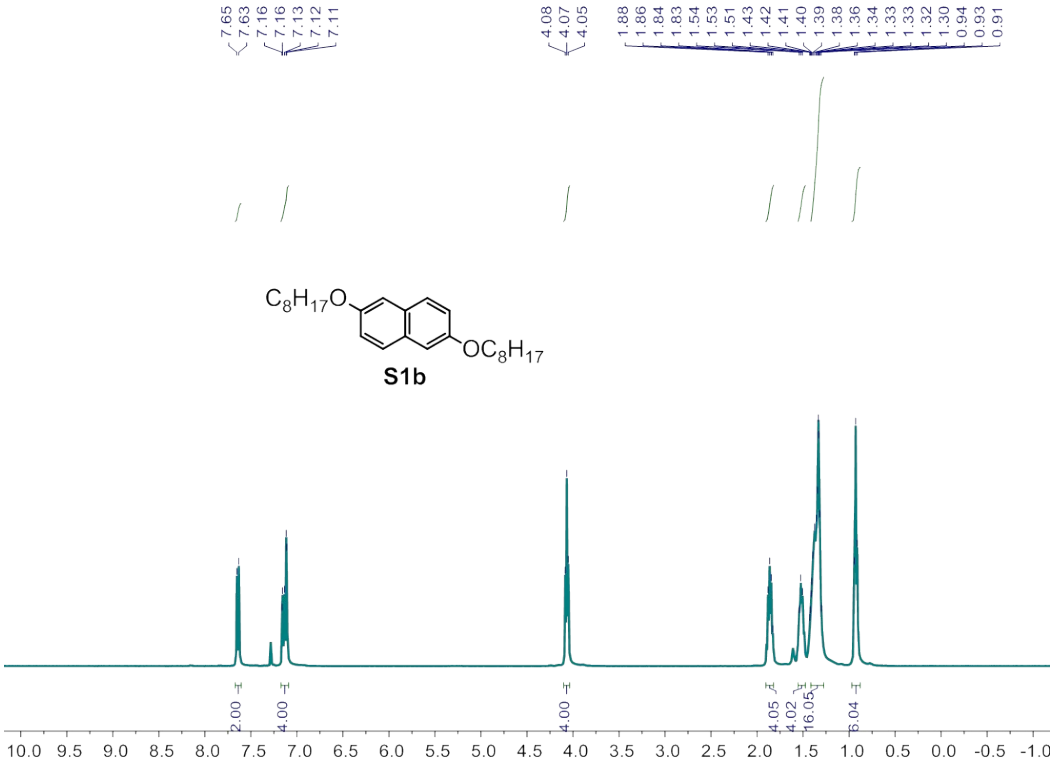
Compounds S1b-1d



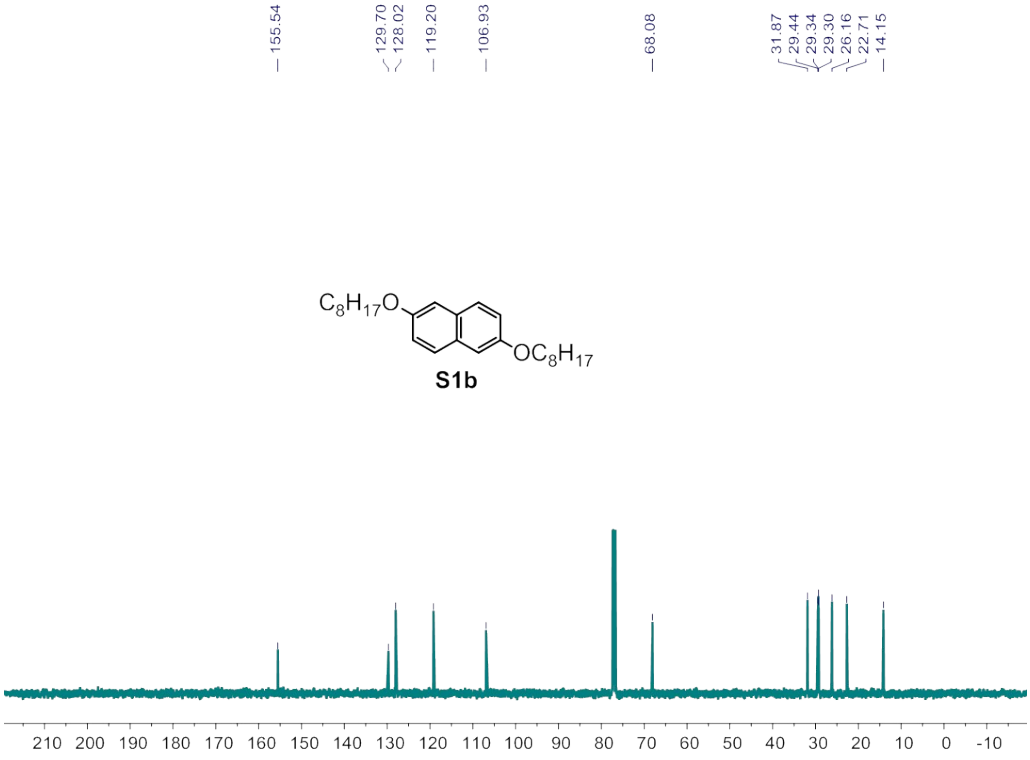
General procedure for S1b-1d: The mixture of 2,6-dihydroxynaphthalene (16.0 g, 100 mmol), 1-bromo-hydrocarbon (300 mmol), and K_2CO_3 (69.0 g, 500 mmol) in dry DMF (300 mL) were stirred overnight at 100 °C under Argon protection. After cooling to room temperature, the mixture was poured into water (500 mL). The precipitate was filtered and washed with copious H_2O and MeOH. The filter cake was collected and dried in vacuum to give the target compound.

S1b was obtained in 62% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ [ppm] = 7.64 (d, J = 8.8 Hz, 2H), 7.17 – 7.09 (m, 4H), 4.07 (t, J = 6.6 Hz, 4H), 1.85 (q, J = 7.1 Hz, 4H), 1.52 (t, J = 7.7 Hz, 4H), 1.41 – 1.27 (m, 16H), 0.97 – 0.88 (m,

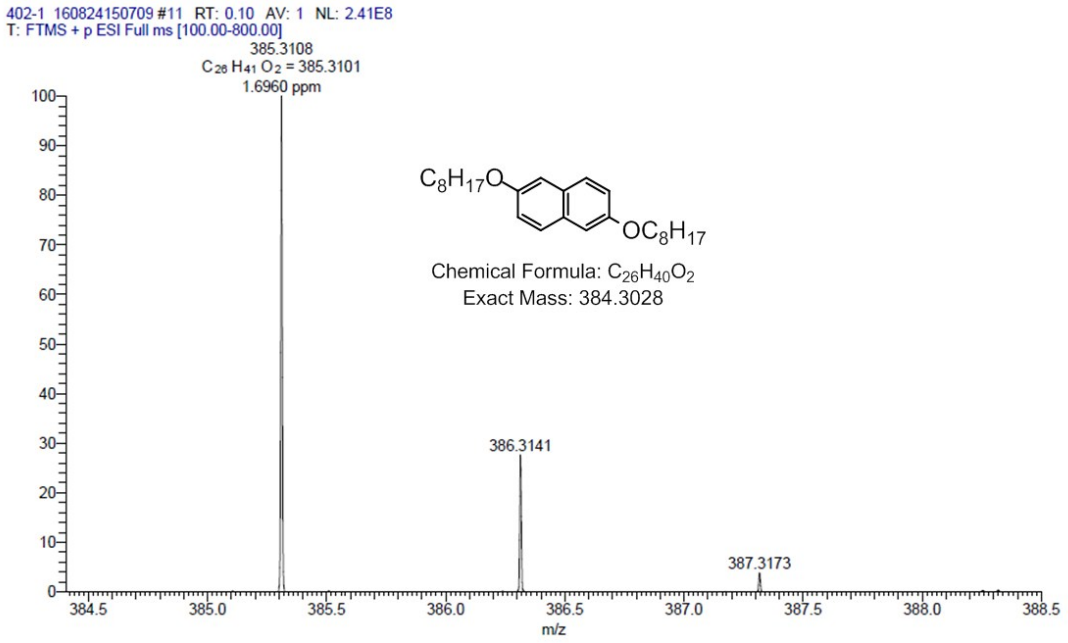
6H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ [ppm] = 155.54, 129.70, 128.02, 119.20, 106.93, 68.08, 31.87, 29.44, 29.34, 29.30, 26.16, 22.71, 14.15. ESI-HRMS: m/z calcd for $[M+H]^+$ $C_{26}H_{41}O_2$, 385.3101; found 385.3808 (error = 1.7 ppm).



^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of compound **S1b**

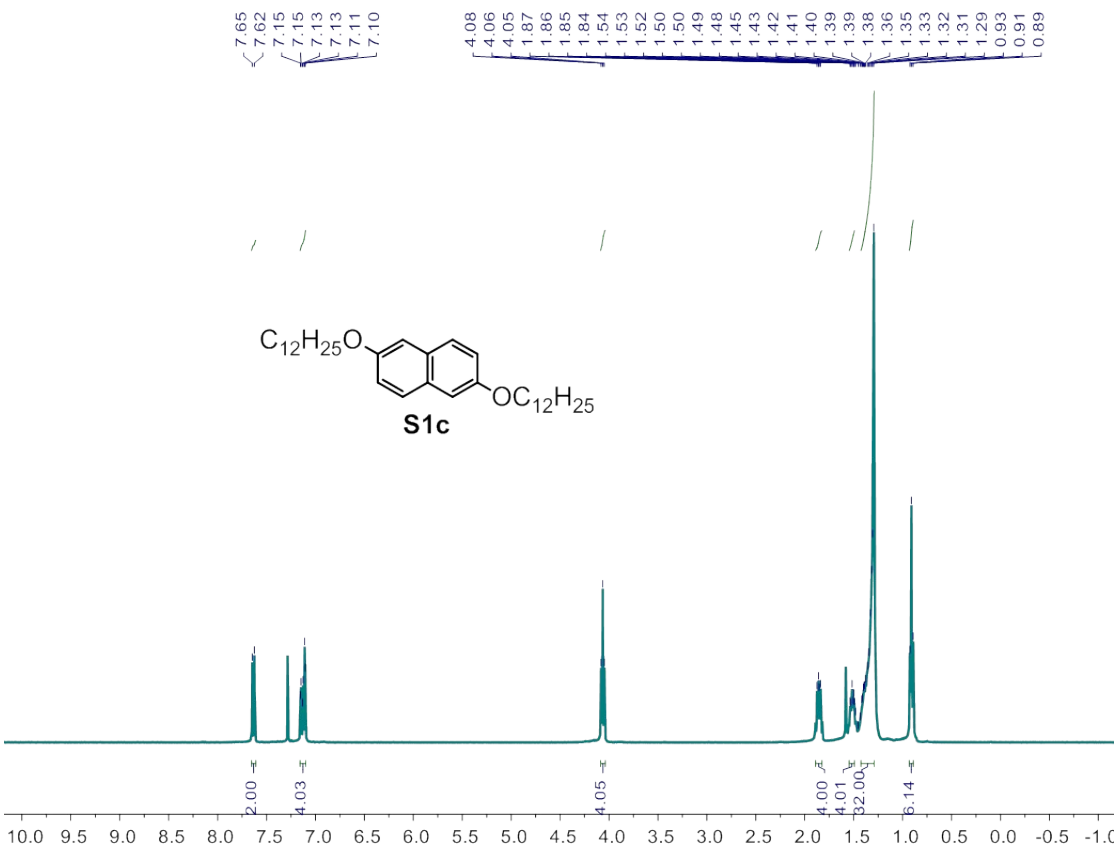


^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 ^{o}C) of compound **S1b**

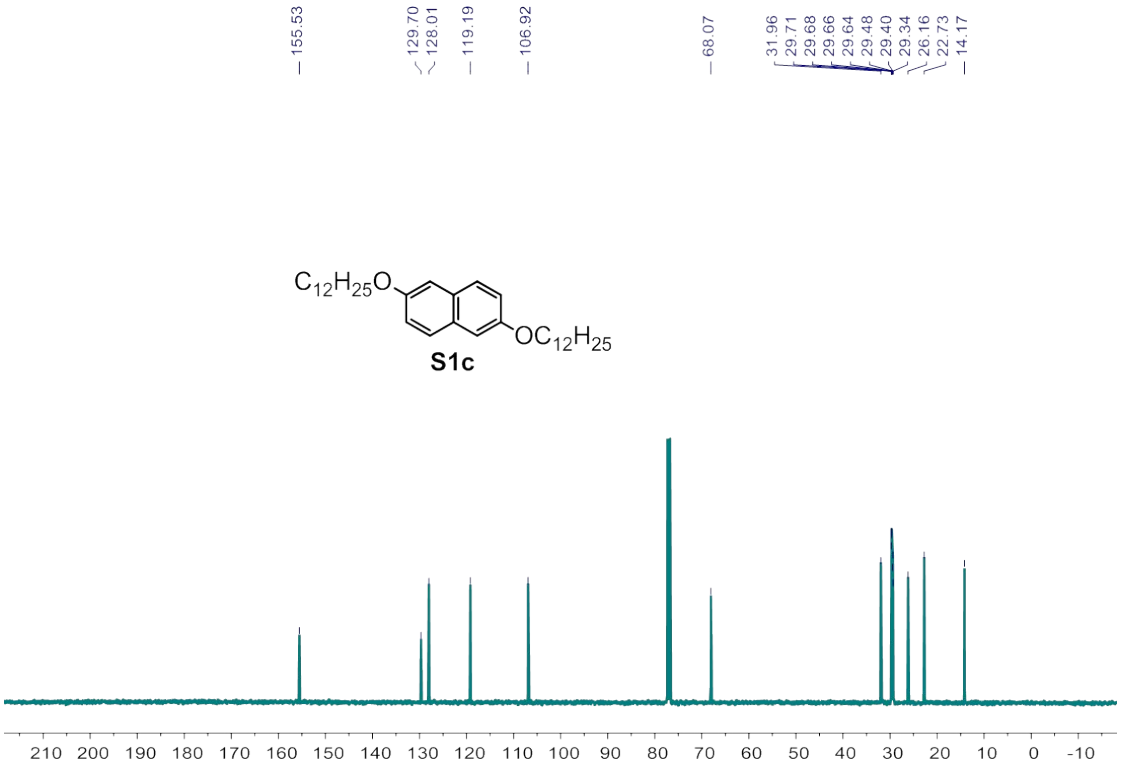


ESI mass spectrum of compound **S1b**

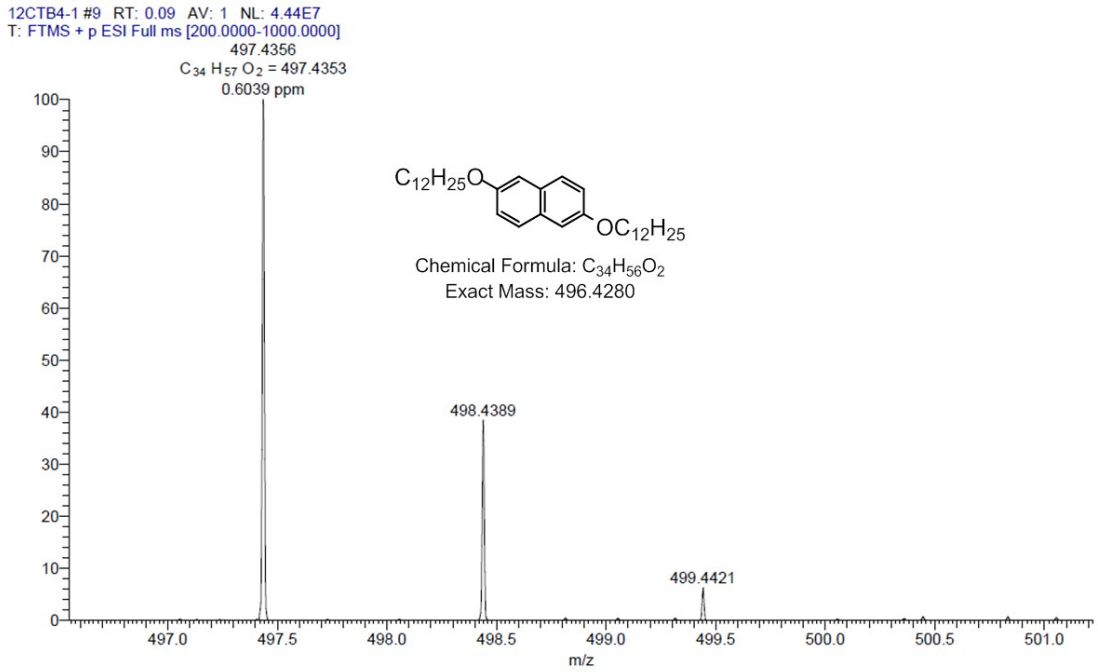
S1c was obtained in 92% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ [ppm] = δ 7.64 (d, *J* = 8.8 Hz, 2H), 7.16 – 7.10 (m, 4H), 4.06 (t, *J* = 6.6 Hz, 4H), 1.86 (dd, *J* = 8.3, 6.5 Hz, 4H), 1.55 – 1.49 (m, 4H), 1.43 – 1.29 (m, 32H), 0.91 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ [ppm] = 155.54, 129.70, 128.02, 119.20, 106.93, 68.08, 31.87, 29.44, 29.34, 29.30, 26.16, 22.71, 14.15. ESI-HRMS: m/z calcd for $[M+H]^+$ $C_{34}H_{57}O_2$, 497.4353; found 497.4356 (error = 0.6 ppm).



^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of compound **S1c**

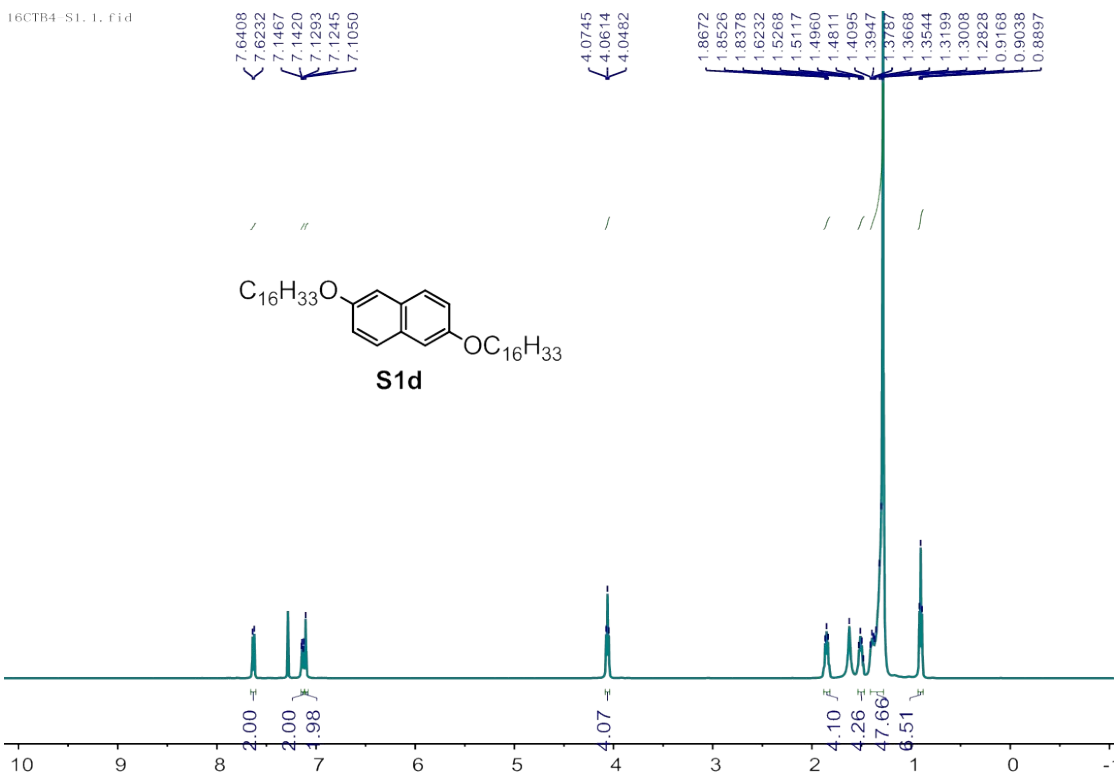


^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 °C) of compound **S1c**

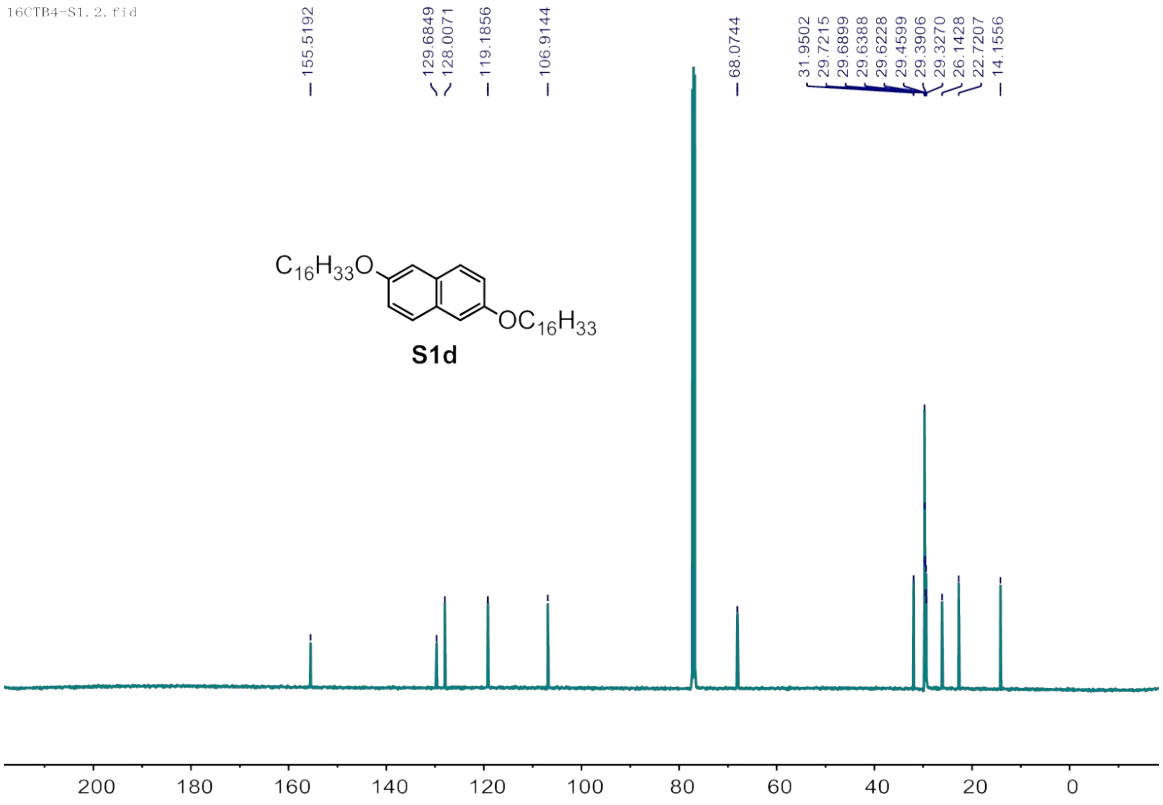


ESI mass spectrum of compound **S1c**

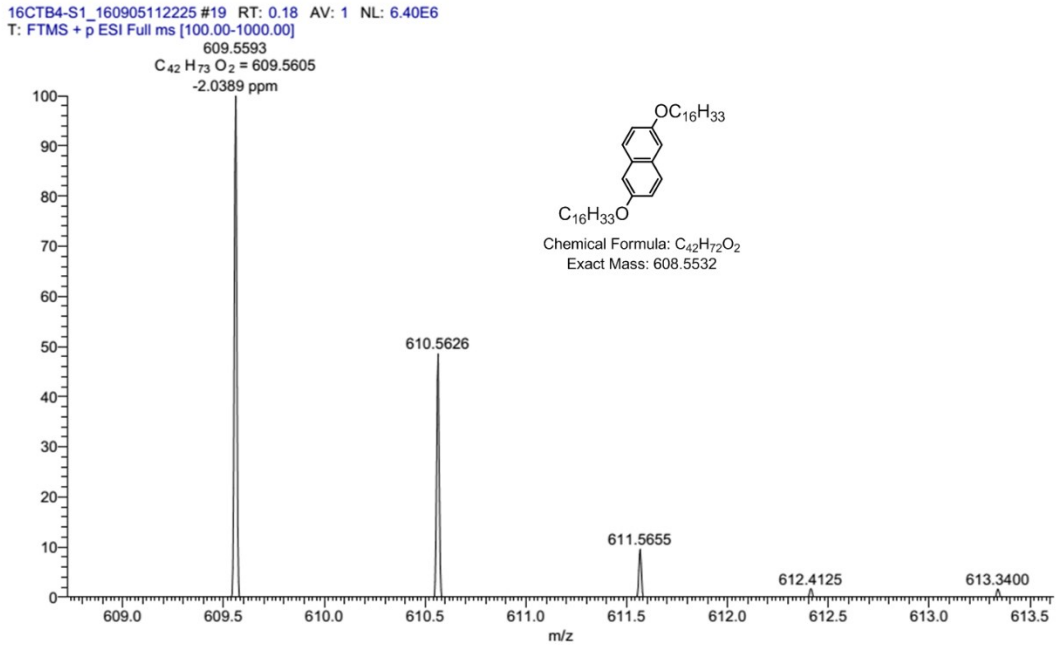
S1d was obtained in **94%** yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C): δ [ppm] = 7.63 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 8.7, 2.4 Hz, 2H), 7.10 (s, 2H), 4.06 (t, *J* = 6.6 Hz, 4H), 1.88 – 1.82 (m, 4H), 1.50 (q, *J* = 7.5 Hz, 4H), 1.41 – 1.28 (m, 48H), 0.90 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C): δ [ppm] = 155.52, 129.68, 128.01, 119.19, 106.91, 68.07, 31.95, 29.72, 29.69, 29.64, 29.62, 29.46, 29.39, 29.33, 26.14, 22.72, 14.16. ESI-HRMS: m/z calcd for $[M+H]^+$ $C_{42}H_{73}O_2$, 609.5605; found 609.5593 (error = -2.0 ppm).



^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 °C) of compound **S1d**

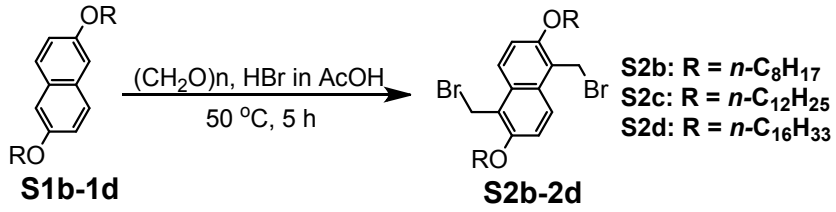


^{13}C NMR spectrum (126 MHz, $CDCl_3$, 25 °C) of compound **S1d**



ESI mass spectrum of compound **S1d**

Dibromides S2b-2d

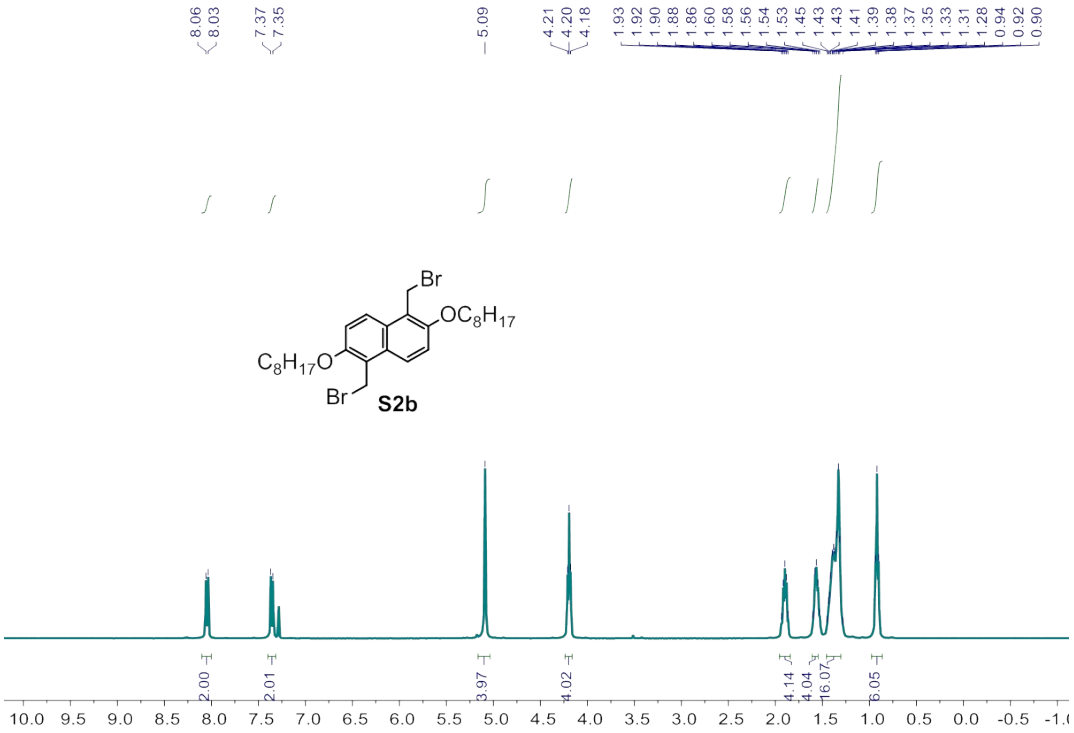


S1b-1d **S2b-2d**

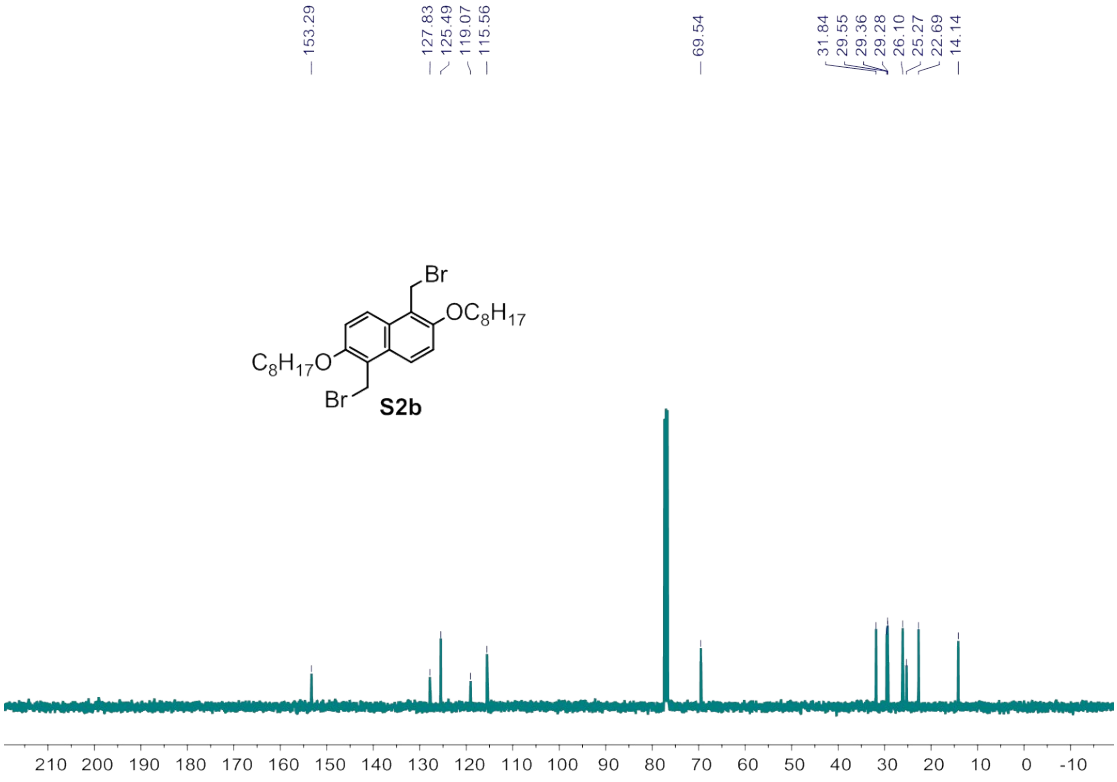
General procedure for S2b-2d: the corresponding compound **S1** (30 mmol) and paraformaldehyde (6.0 g, 300 mmol) were dissolved in HBr/AcOH (30% w/w, 400 mL). The resulting mixture was heated to 50 °C and stirred for 5h. The solution was cooled to room temperature. The light purple precipitate was filtered off and washed with copious AcOH and MeOH, and then dried to afford the target product.

S2b was obtained in 61% yield as an off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ [ppm] = 8.05 (d, *J* = 9.3 Hz, 2H), 7.36 (d, *J* = 9.4 Hz, 2H), 5.09 (s, 4H), 4.20 (t, *J* = 6.5 Hz, 4H), 1.90 (p, *J* = 6.8 Hz, 4H), 1.57 (d, *J* = 6.6 Hz, 4H), 1.36 (dt, *J* = 26.9, 6.5 Hz, 16H), 0.98 – 0.86 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ [ppm] = 153.29, 127.83, 125.49, 119.07, 115.56, 69.54, 31.84, 29.55, 29.36, 29.28, 26.10,

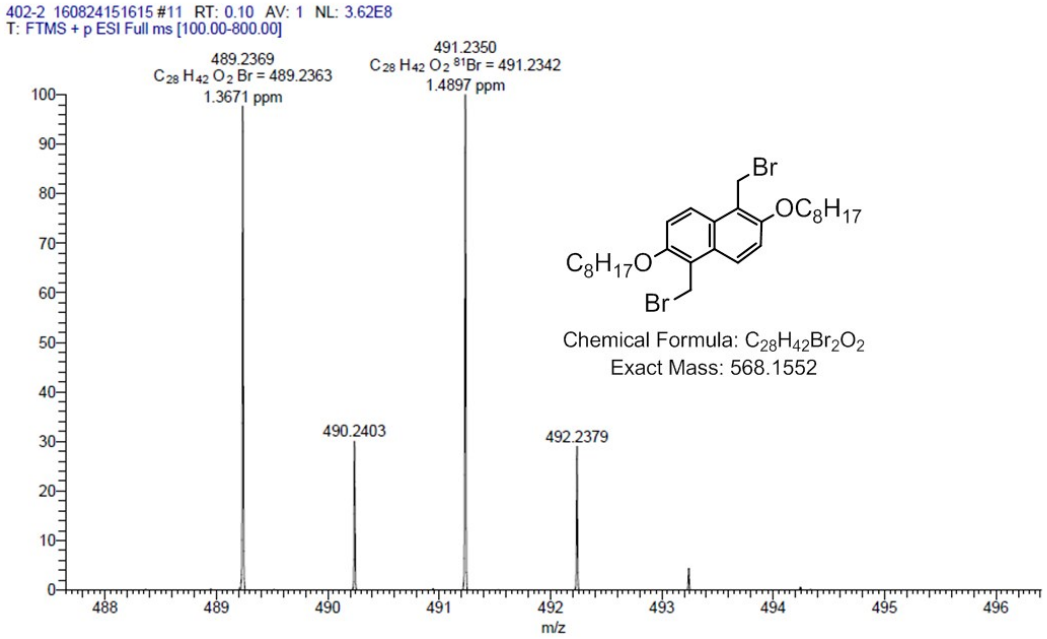
25.27, 22.69, 14.14. ESI-HRMS: m/z calcd for $[M-Br]^+$ $C_{28}H_{42}O_2Br$, 489.2363; found 489.2369 (error = 1.4 ppm).



^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of dibromide **S2b**

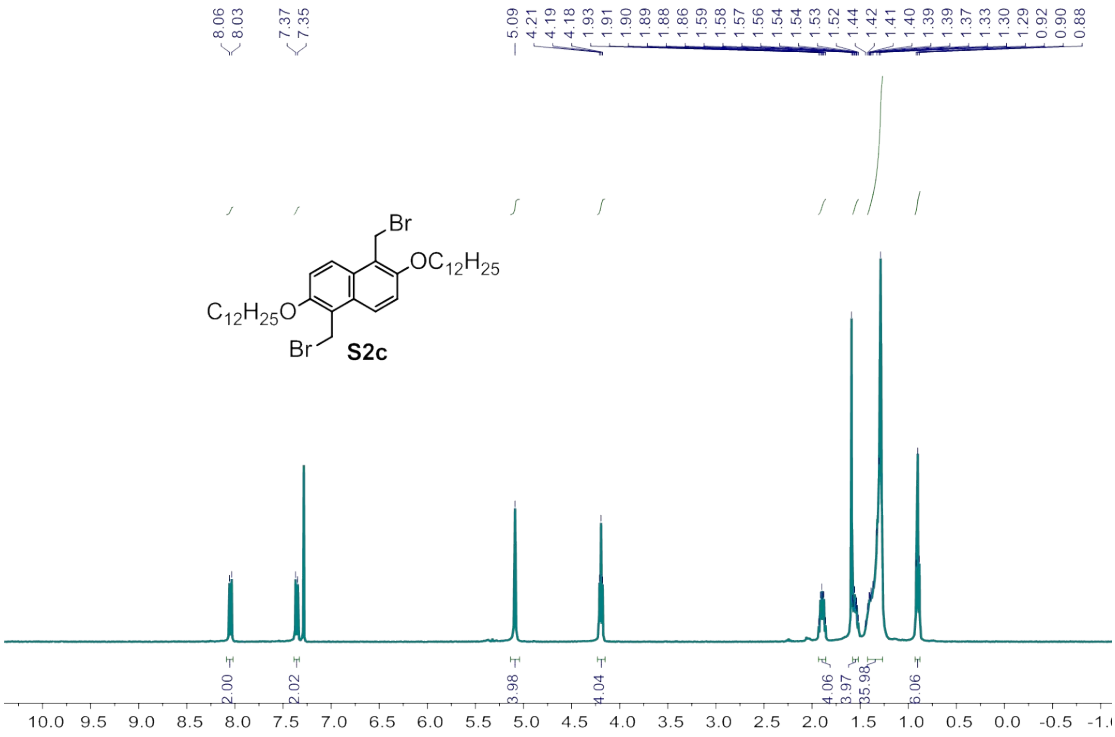


^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 °C) of dibromide **S2b**

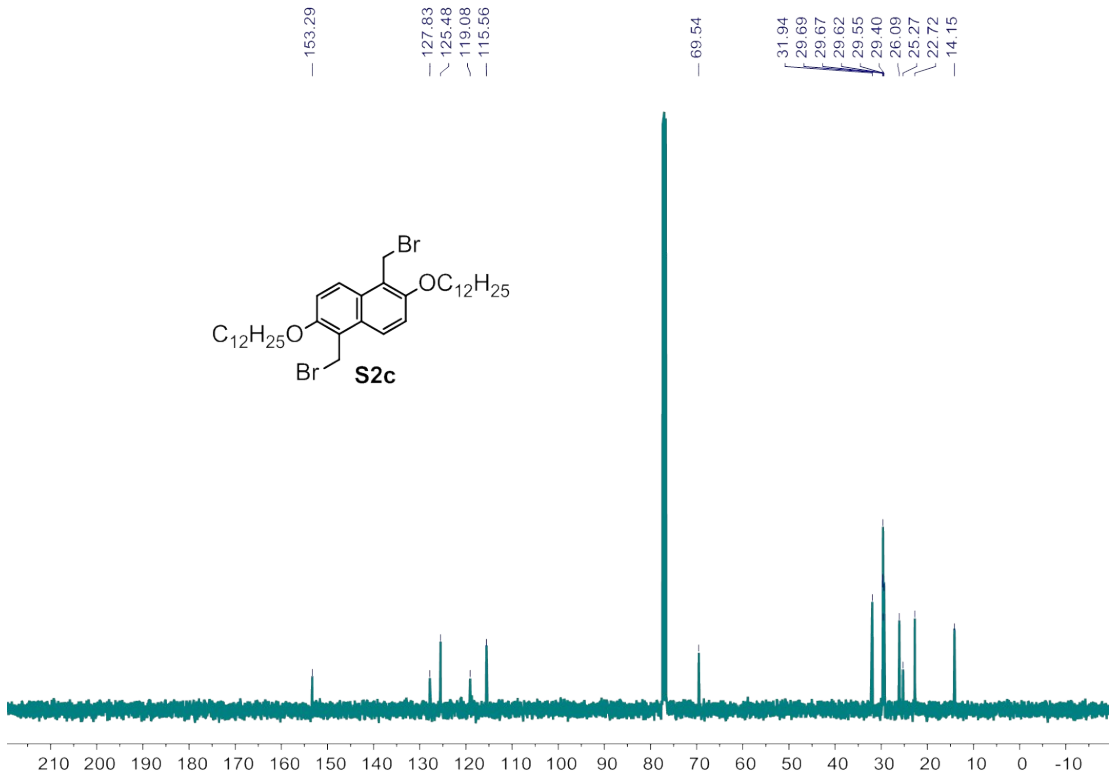


ESI mass spectrum of dibromide **S2b**

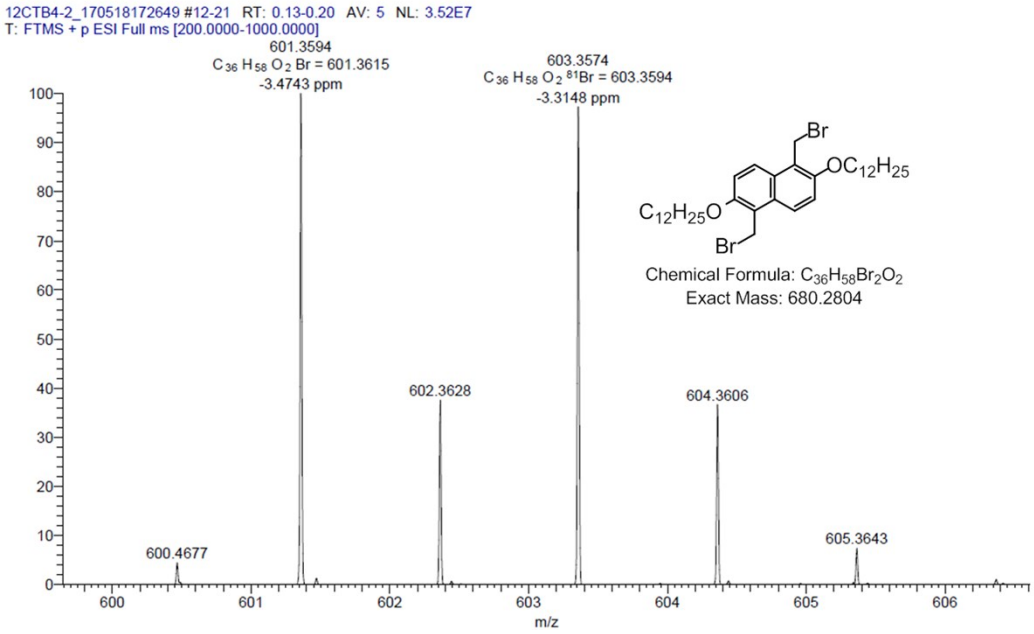
S2b was obtained in 62% yield as an off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ [ppm] = 8.05 (d, *J* = 9.3 Hz, 2H), 7.36 (d, *J* = 9.4 Hz, 2H), 5.09 (s, 4H), 4.20 (t, *J* = 6.5 Hz, 4H), 1.90 (p, *J* = 6.8 Hz, 4H), 1.57 (d, *J* = 6.6 Hz, 4H), 1.36 (dt, *J* = 26.9, 6.5 Hz, 16H), 0.98 – 0.86 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ [ppm] = 153.29, 127.83, 125.49, 119.07, 115.56, 69.54, 31.84, 29.55, 29.36, 29.28, 26.10, 25.27, 22.69, 14.14. ESI-HRMS: m/z calcd for $[M-Br]^+$ $C_{36}H_{58}O_2Br$, 601.3615; found 601.3594 (error = -3.5 ppm).



^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of dibromide **S2c**

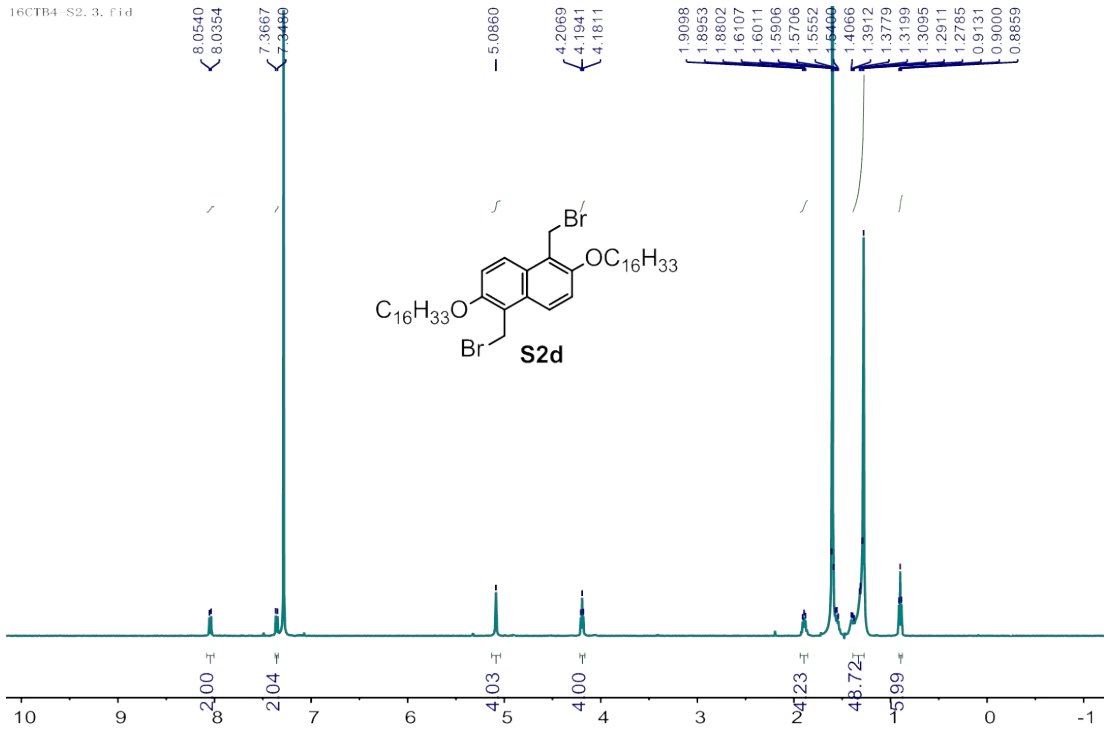


^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 °C) of dibromide **S2c**

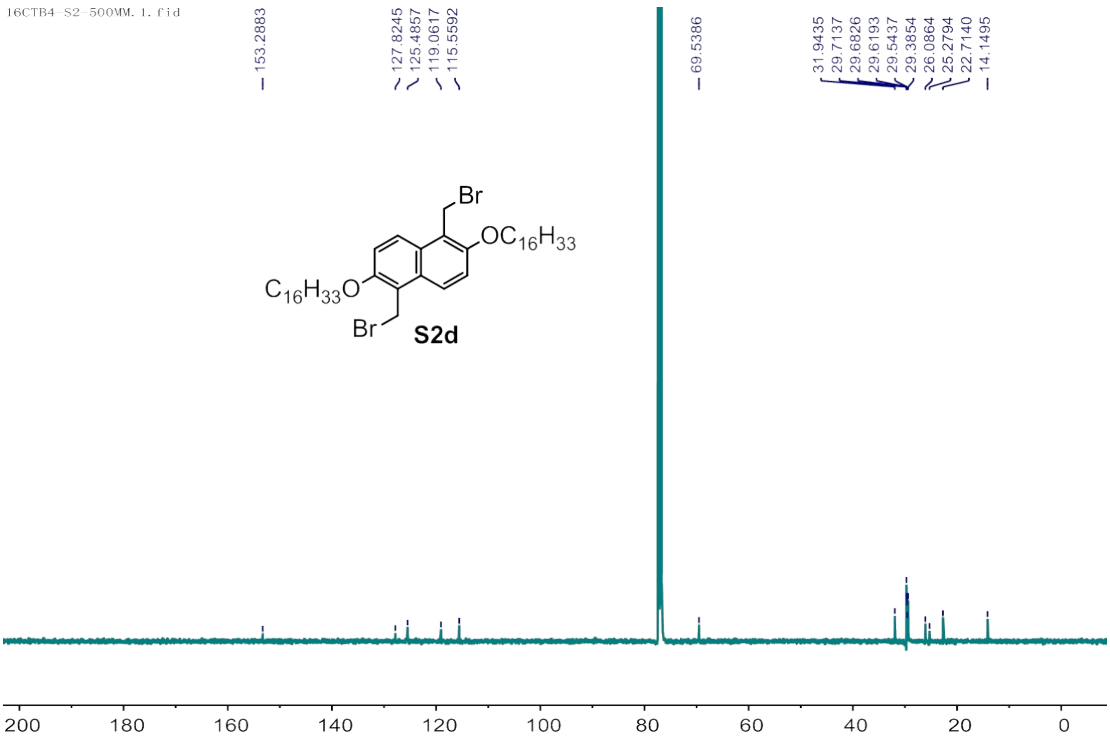


ESI mass spectrum of dibromide **S2c**

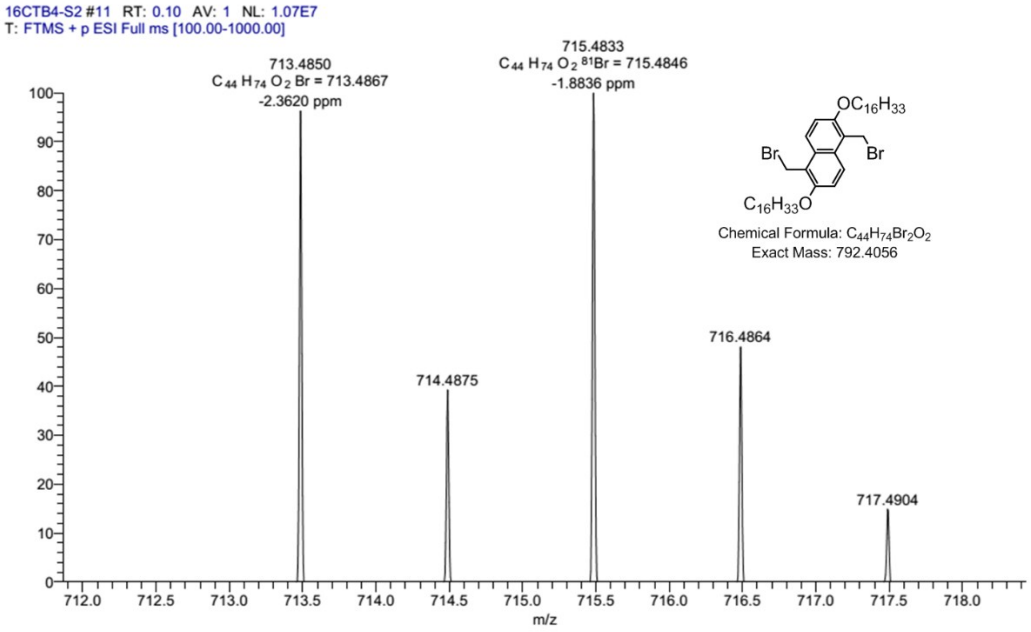
S2d was obtained in 56% yield as an off-white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C): δ [ppm] = 8.04 (d, J = 9.3 Hz, 2H), 7.36 (d, J = 9.4 Hz, 2H), 5.09 (s, 4H), 4.19 (t, J = 6.5 Hz, 4H), 1.94 – 1.86 (m, 4H), 1.28 (s, 48H), 0.90 (t, J = 6.8 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C): δ [ppm] = 153.29, 127.82, 125.49, 119.06, 115.56, 69.54, 31.94, 29.71, 29.68, 29.62, 29.54, 29.39, 26.09, 25.28, 22.71, 14.15. ESI-HRMS: *m/z* calcd for $[M\text{-}Br]^+$ $C_{44}H_{74}BrO_2$, 713.4872; found 713.4850 (error = -2.3 ppm).



^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 °C) of dibromide **S2d**

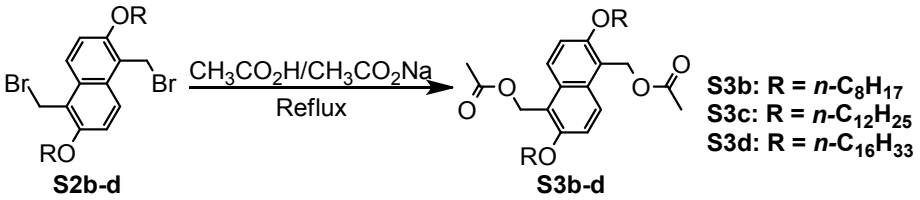


^{13}C NMR spectrum (126 MHz, $CDCl_3$, 25 °C) of dibromide **S2d**



ESI mass spectrum of dibromide **S2d**

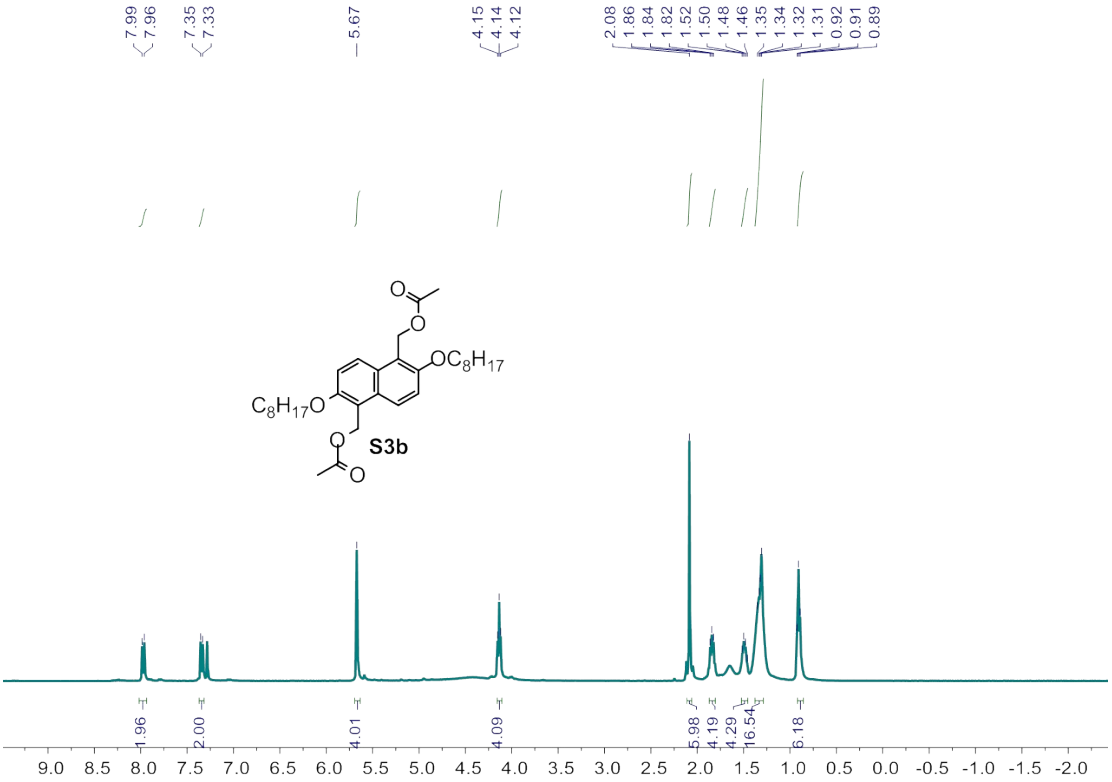
Compounds S3b-3d



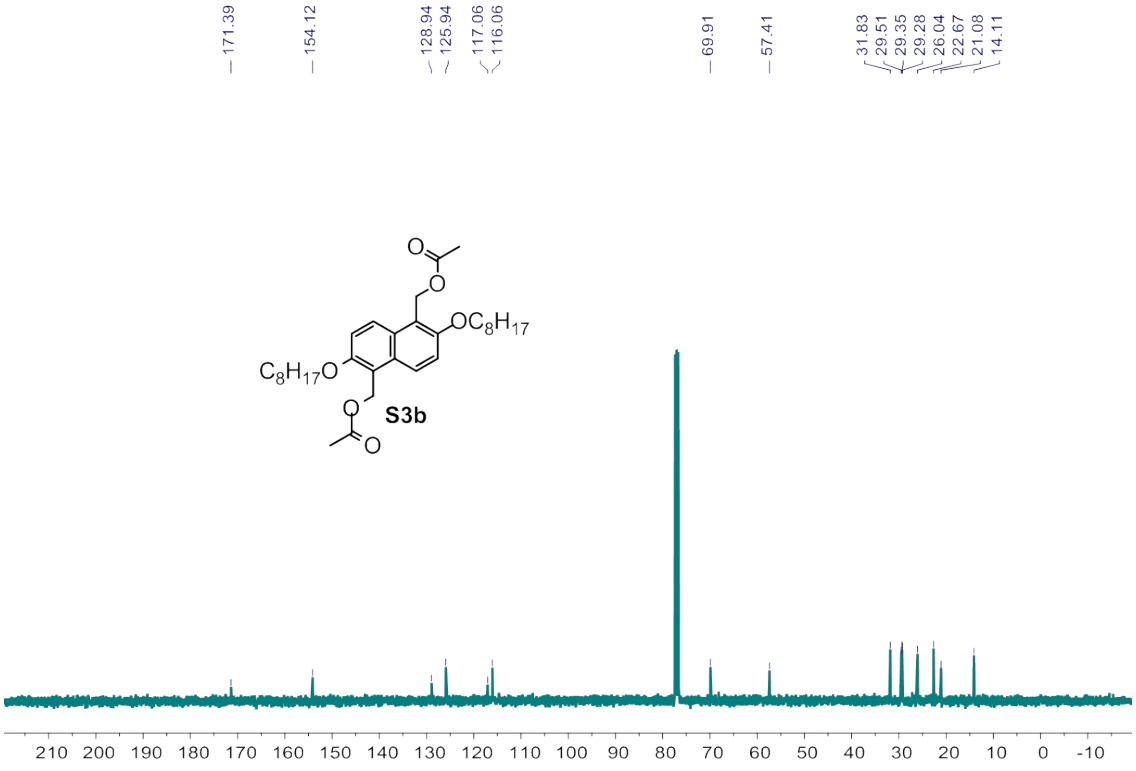
General procedure for S3b-3d: To a stirred mixture of corresponding dibromide **S2** (10 mmol) in CH_3COOH (250 mL), CH_3COONa (3.3 g, 40 mmol) was added. The reaction mixture was stirred and heated at 110℃ for 5h. The reaction mixture was cooled to room temperature and the resulting precipitate was washed with ethanol and dried to afford the target compound.

S3b was obtained in 91% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ [ppm] = 7.97 (d, J = 9.3 Hz, 2H), 7.34 (d, J = 9.3 Hz, 2H), 5.67 (s, 4H), 4.14 (t, J = 6.5 Hz, 4H), 2.08 (s, 6H), 1.87 – 1.81 (m, 4H), 1.49 (q, J = 7.3 Hz, 4H), 1.33 (m, 16H) 0.90 (d, J = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ [ppm] = 171.39, 154.12, 128.94, 125.94, 117.06, 116.06, 69.91, 57.41, 31.83, 29.51, 29.35,

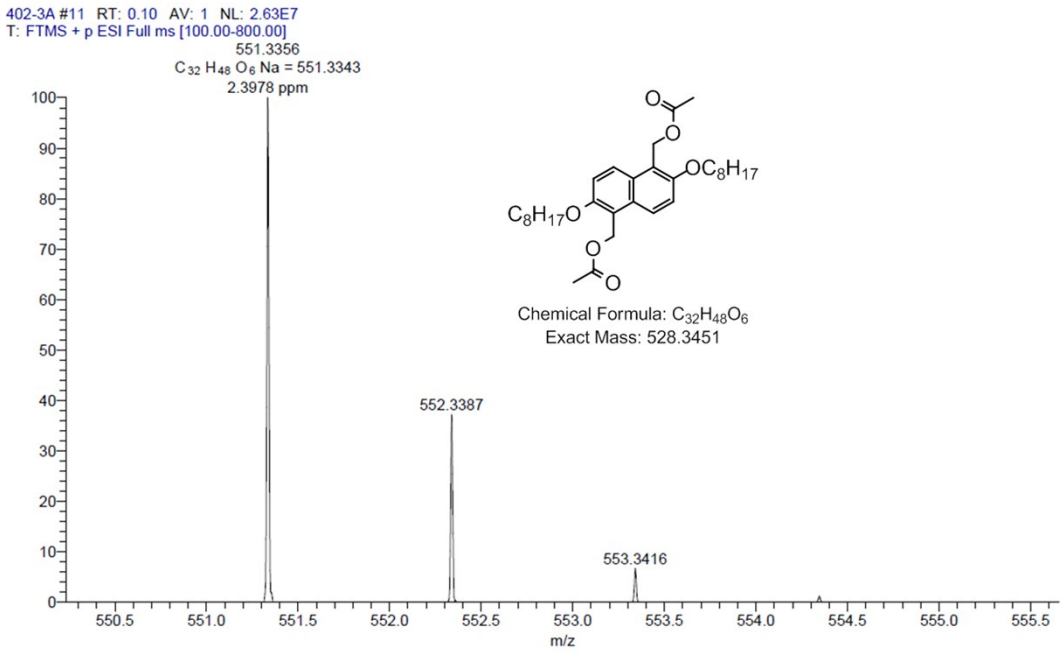
29.28, 26.04, 22.67, 21.08, 14.11. ESI-HRMS: m/z calcd for $[M+Na]^+$ $C_{32}H_{48}O_6Na$, 551.3343; found 551.3356 (error = 2.4 ppm).



^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of compound **S3b**

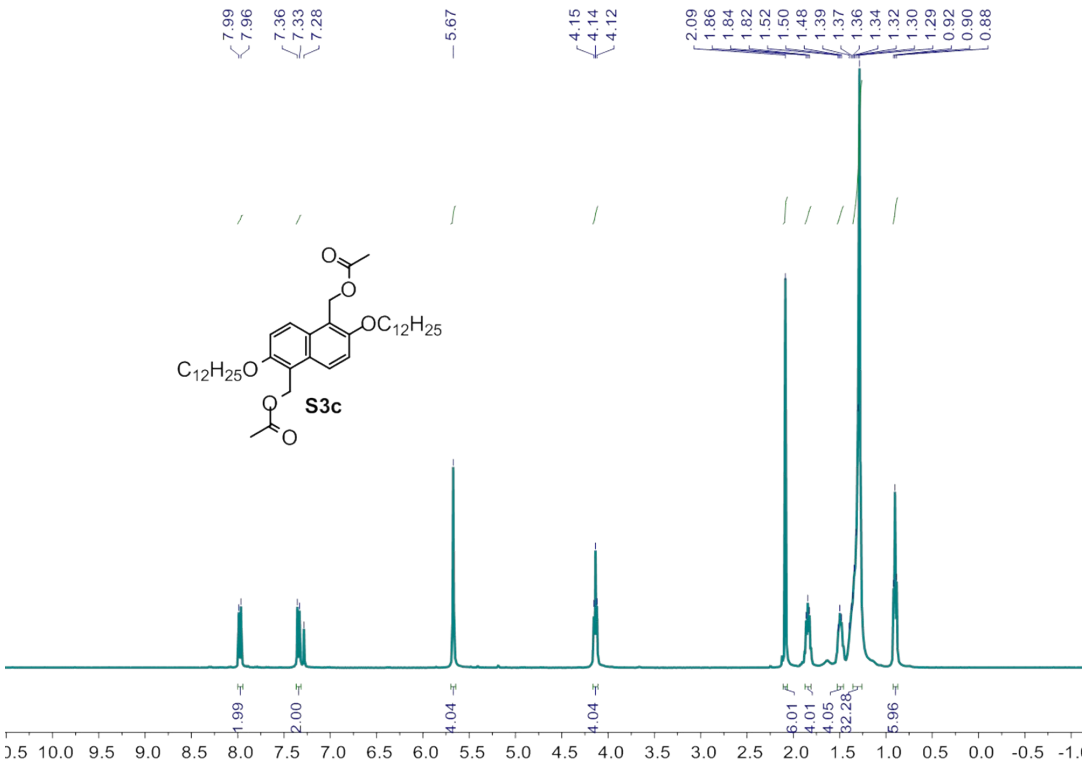


^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 ^{o}C) of compound **S3b**

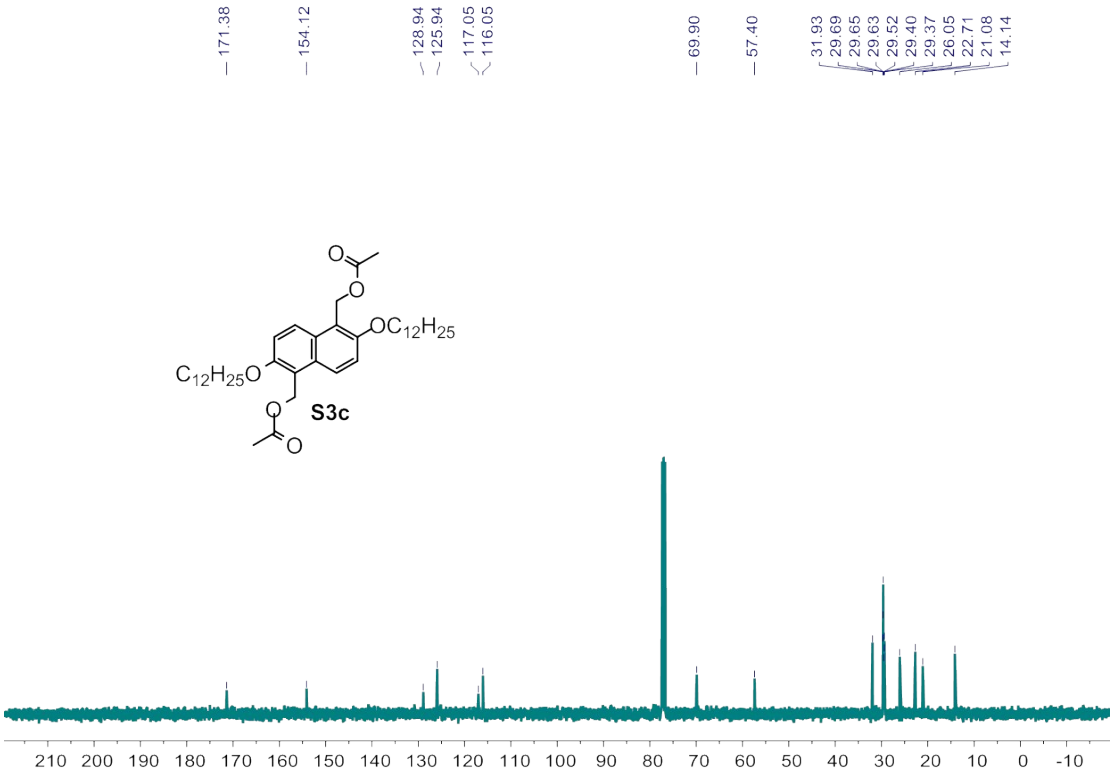


ESI mass spectrum of compound **S3b**

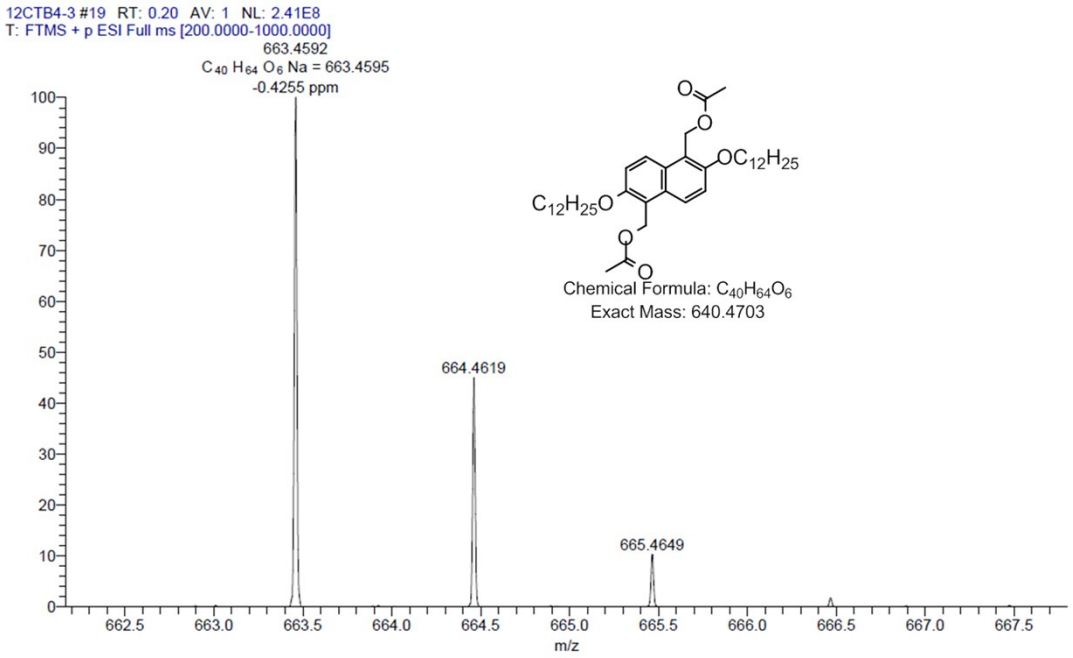
S3c was obtained in 94% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ [ppm] = 7.97 (d, *J* = 9.3 Hz, 2H), 7.34 (d, *J* = 9.3 Hz, 2H), 5.67 (s, 4H), 4.14 (t, *J* = 6.5 Hz, 4H), 2.09 (s, 6H), 1.87 – 1.81 (m, 4H), 1.49 (q, *J* = 7.3 Hz, 4H), 1.32 (m, 32H), 0.90 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ [ppm] = 171.39, 154.12, 128.94, 125.94, 117.06, 116.06, 69.91, 57.41, 31.83, 29.51, 29.35, 29.28, 26.04, 22.67, 21.08, 14.11. ESI-HRMS: m/z calcd for $[M+Na]^+$ $C_{40}H_{64}O_6Na$, 663.4595; found 663.4592 (error = -0.4 ppm).



^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of compound **S3c**

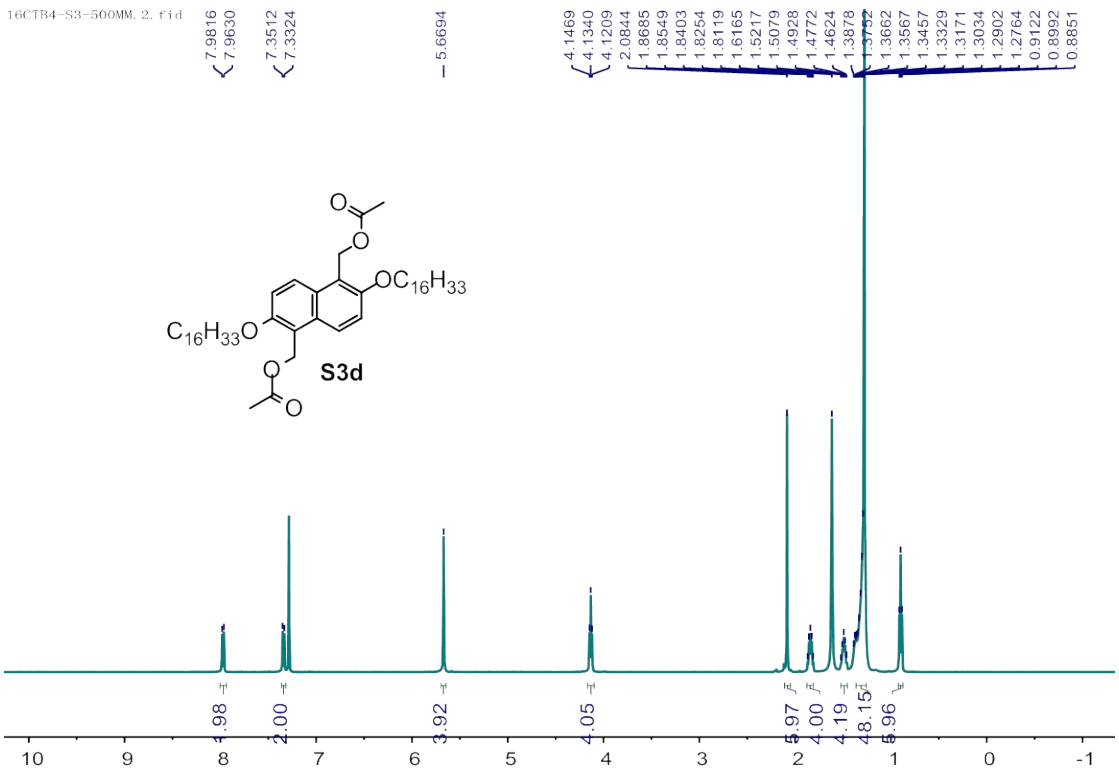


^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 °C) of compound **S3c**

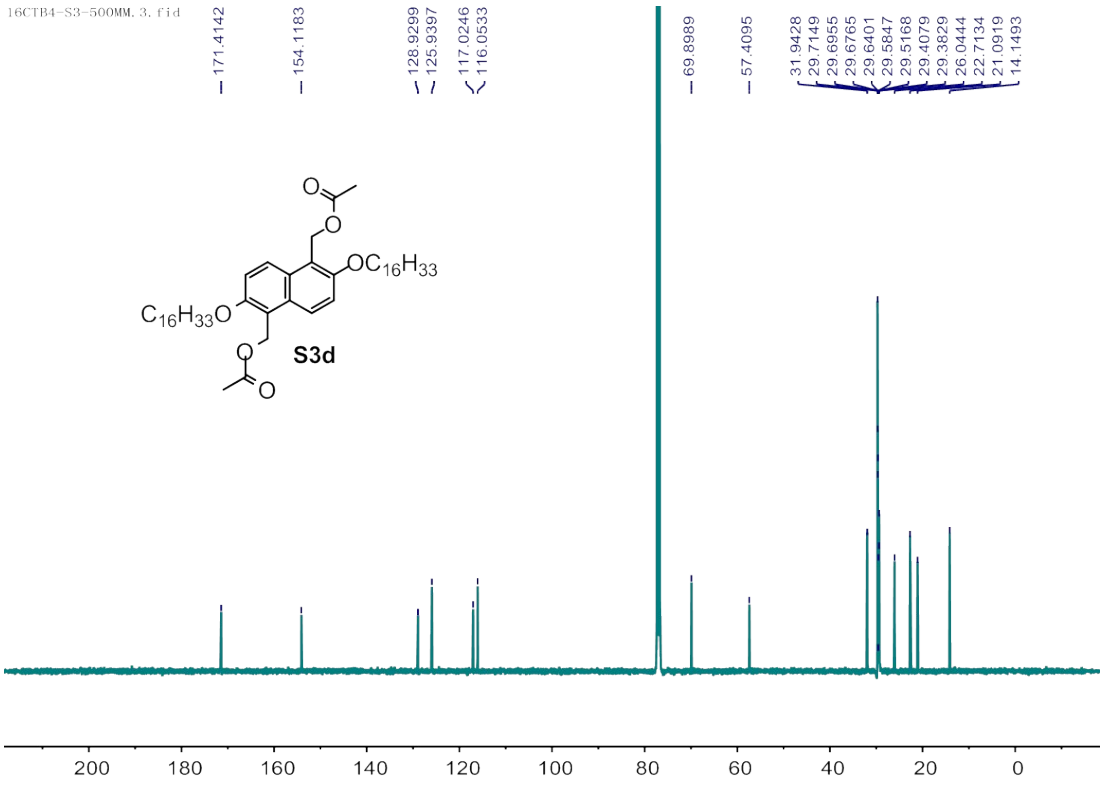


ESI mass spectrum of compound **S3c**

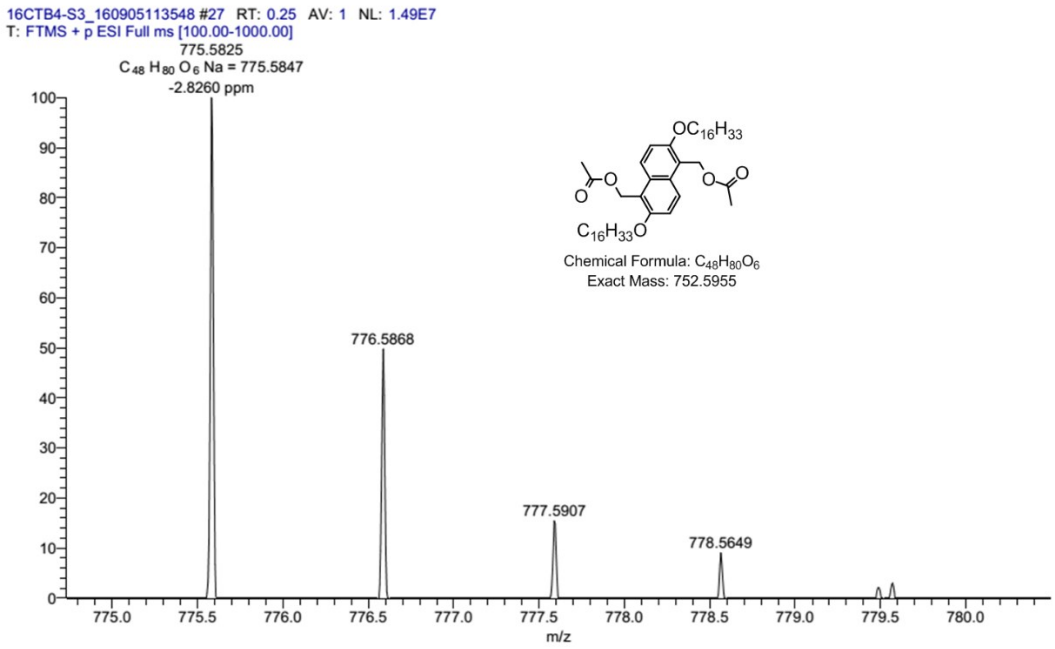
S3d was obtained in 98% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C): δ [ppm] = 7.97 (d, *J* = 9.3 Hz, 2H), 7.34 (d, *J* = 9.4 Hz, 2H), 5.67 (s, 4H), 4.13 (t, *J* = 6.5 Hz, 4H), 2.08 (s, 6H), 1.84 (p, *J* = 6.8 Hz, 4H), 1.49 (p, *J* = 7.1 Hz, 4H), 1.28 (s, 48H), 0.90 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ [ppm] = 171.41, 154.12, 128.93, 125.94, 117.02, 116.05, 69.90, 57.41, 31.94, 29.71, 29.70, 29.68, 29.64, 29.58, 29.52, 29.41, 29.38, 26.04, 22.71, 21.09, 14.15. ESI-HRMS: *m/z* calcd for $[M+Na]^+$ $C_{48}H_{80}O_6Na$, 775.5853; found 775.5825 (error = -2.8 ppm).



^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 °C) of compound **S3d**

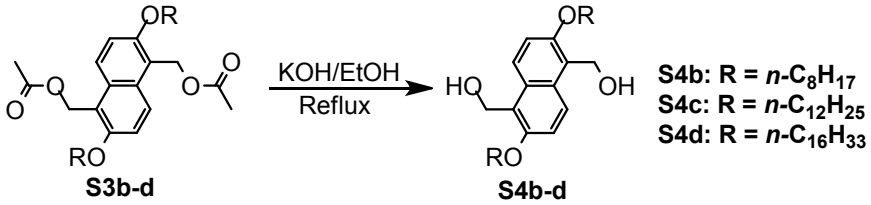


^{13}C NMR spectrum (126 MHz, $CDCl_3$, 25 °C) of compound **S3d**



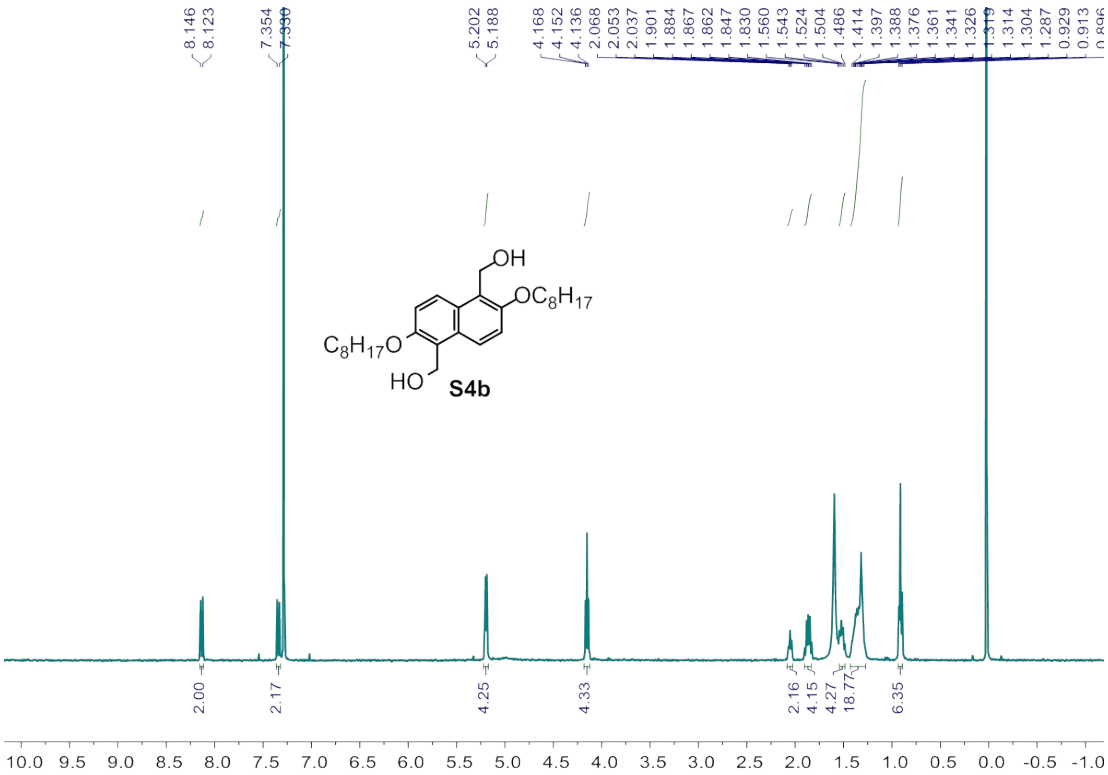
ESI mass spectrum of compound **S3d**

Diol S4b-4d

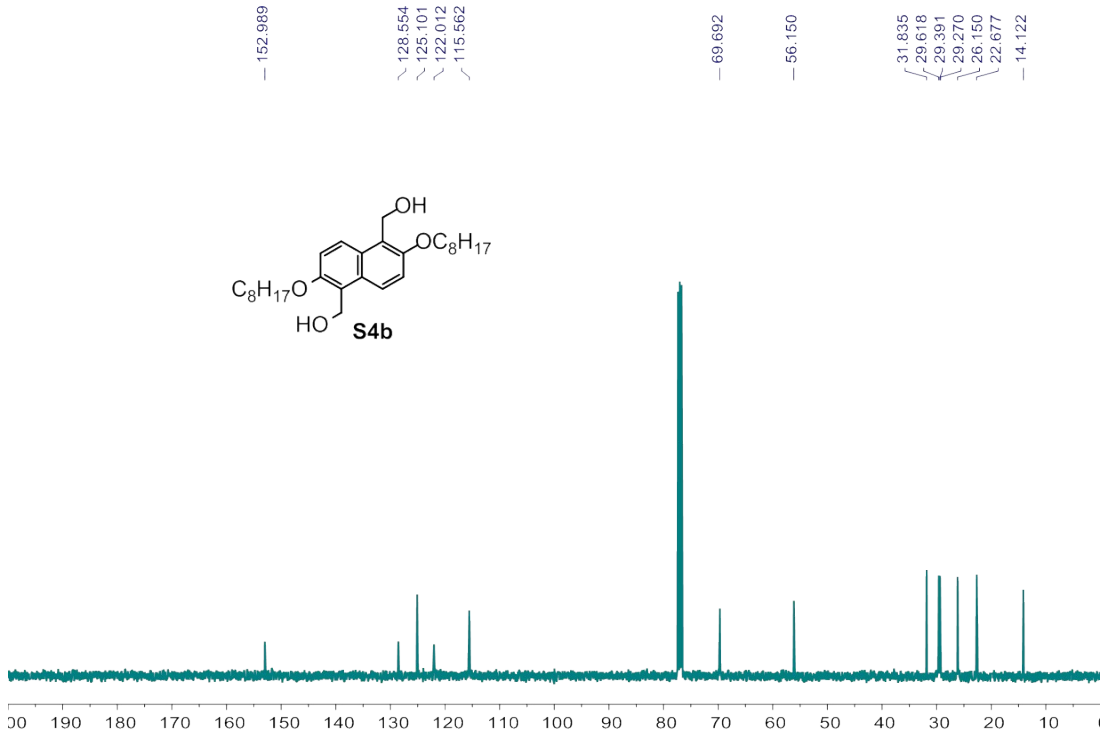


General procedure for S4b-4d: the corresponding compound S3 (10 mmol) was added to a solution of 3.9 g potassium hydroxide in 250 mL ethanol and refluxed for 2 h. Upon cooling, the product precipitates and was filtered off and dried in vacuum to give the target product.

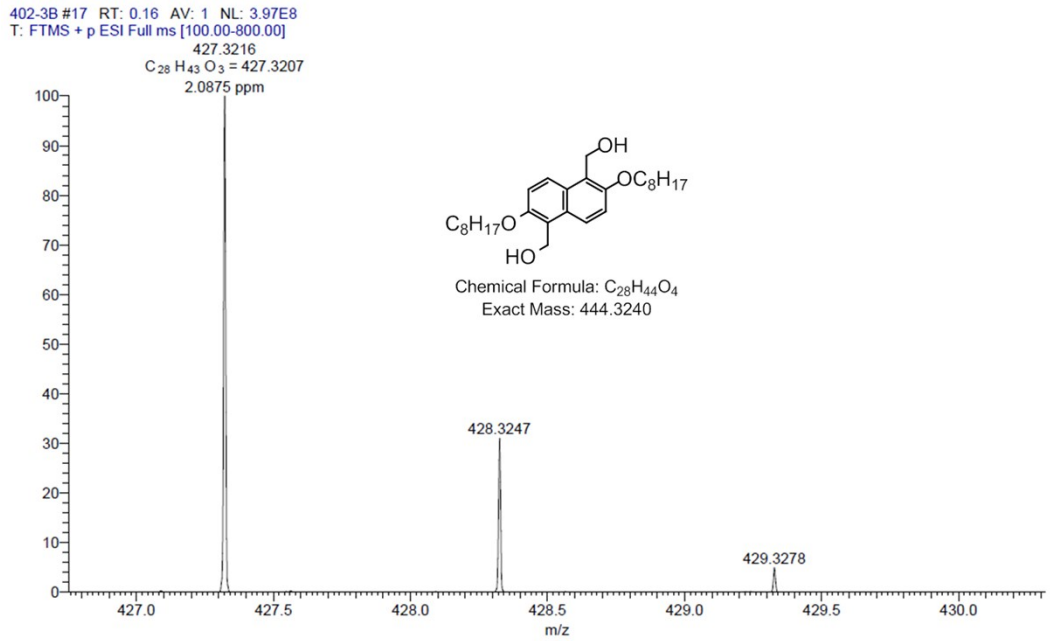
S4b was obtained in 92% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ [ppm] = 8.13 (d, *J* = 9.4 Hz, 2H), 7.34 (d, *J* = 9.4 Hz, 2H), 5.20 (d, *J* = 5.8 Hz, 4H), 4.15 (t, *J* = 6.5 Hz, 4H), 2.05 (t, *J* = 6.2 Hz, 2H), 1.90 – 1.83 (m, 4H), 1.54 – 1.48 (m, 4H), 1.43 – 1.27 (m, 16H), 0.94 – 0.89 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ [ppm] = 152.99, 128.55, 125.10, 122.01, 115.56, 69.69, 56.15, 31.84, 29.62, 29.39, 29.27, 26.15, 22.68, 14.12. ESI-HRMS: m/z calcd for $[M\text{-}OH]^+$ $C_{28}H_{43}O_3$, 423.3207; found 427.3216 (error = 2.1 ppm).



^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of diol **S4b**

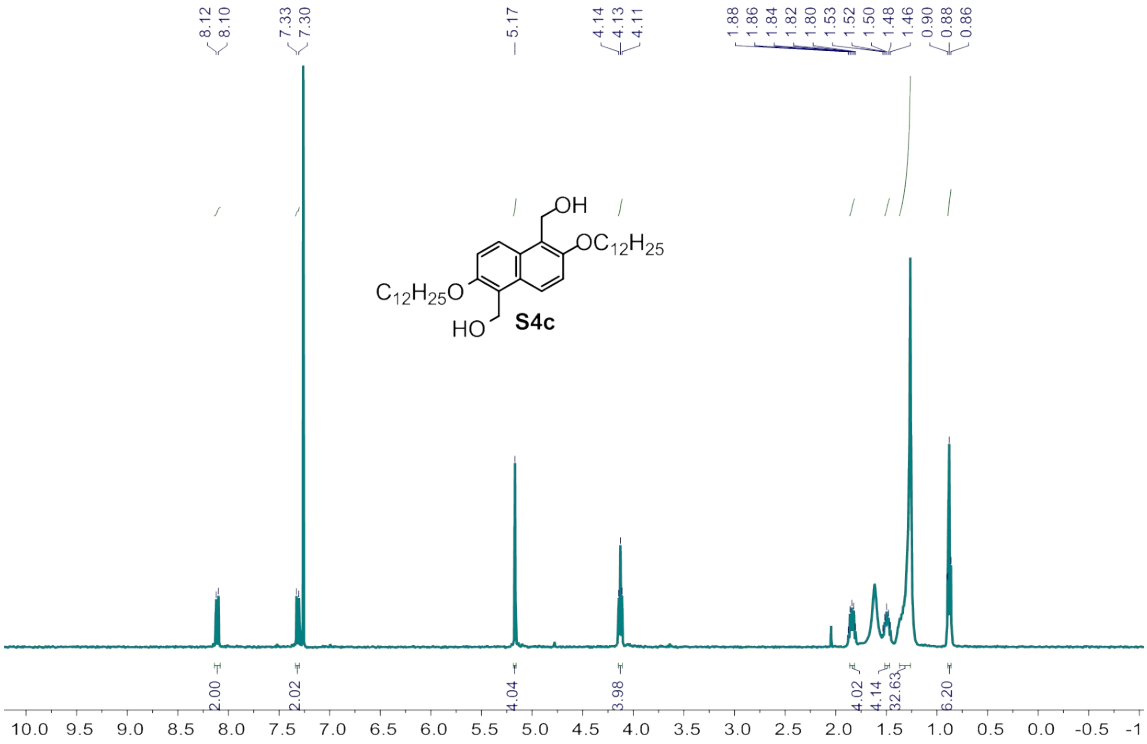


^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 °C) of diol **S4b**

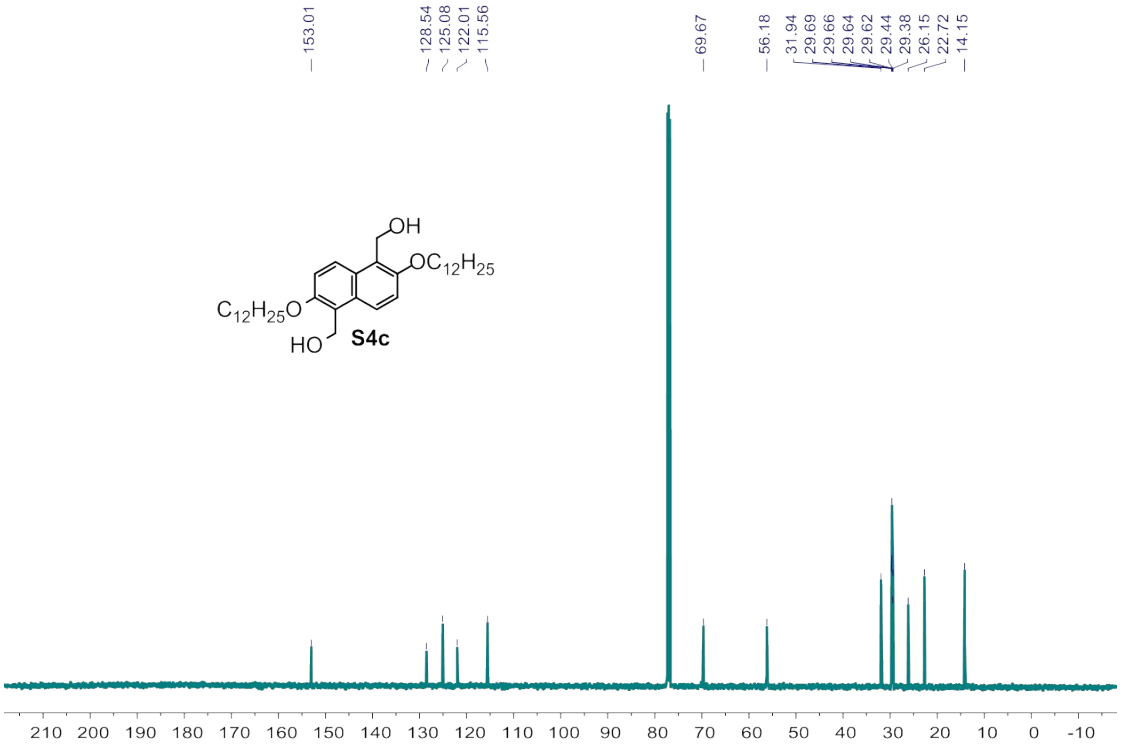


ESI mass spectrum of diol **S4b**

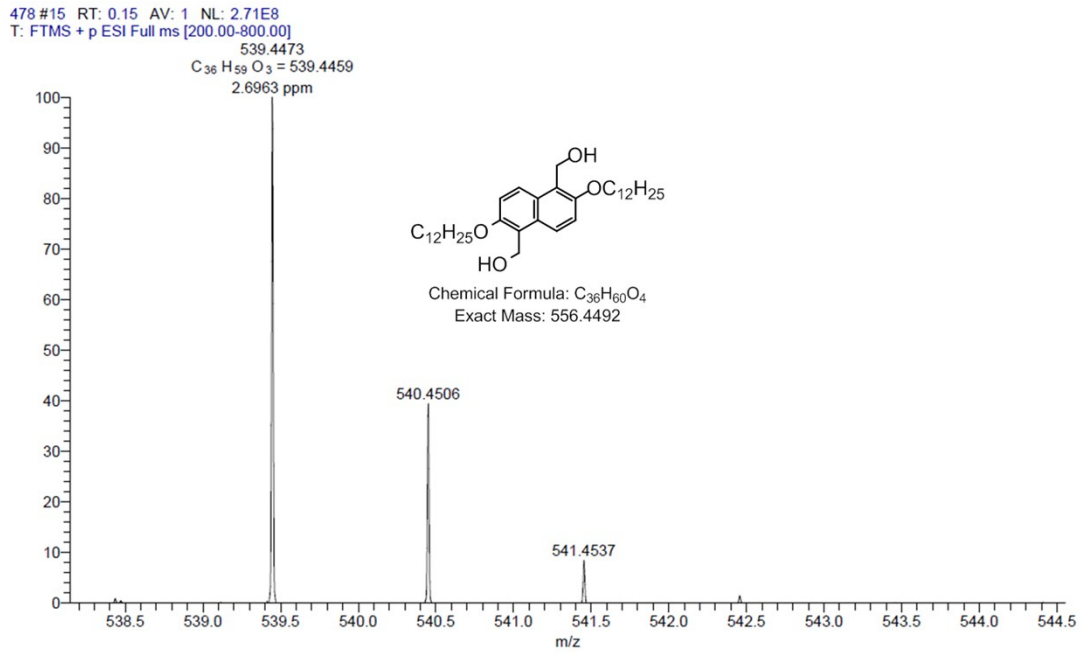
S4c was obtained in 98% yield as a white solid. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 ^{o}C): δ [ppm] = 8.11 (d, *J* = 9.3 Hz, 2H), 7.32 (d, *J* = 9.3 Hz, 2H), 5.17 (s, 4H), 4.13 (t, *J* = 6.5 Hz, 4H), 1.86 – 1.81 (m, 4H), 1.49 (d, *J* = 7.9 Hz, 4H), 1.26 (s, 32H), 0.87 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ [ppm] = 153.01, 128.54, 125.08, 122.01, 115.56, 69.67, 56.18, 31.94, 29.69, 29.66, 29.64, 29.62, 29.44, 29.38, 26.15, 22.72, 14.15. ESI-HRMS: *m/z* calcd for $[M\text{-}OH]^+$ $C_{36}H_{59}O_3$, 539.4459; found 539.4473 (error = 2.7 ppm).



^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of diol **S4c**

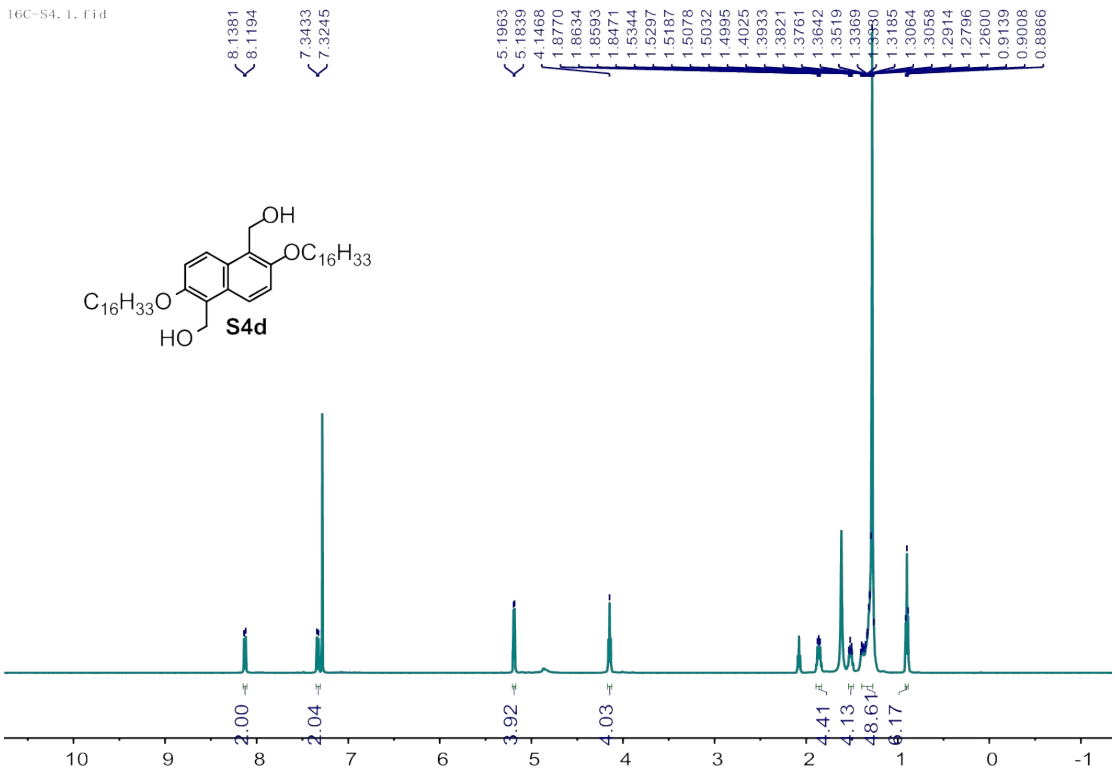


^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 °C) of diol **S4c**

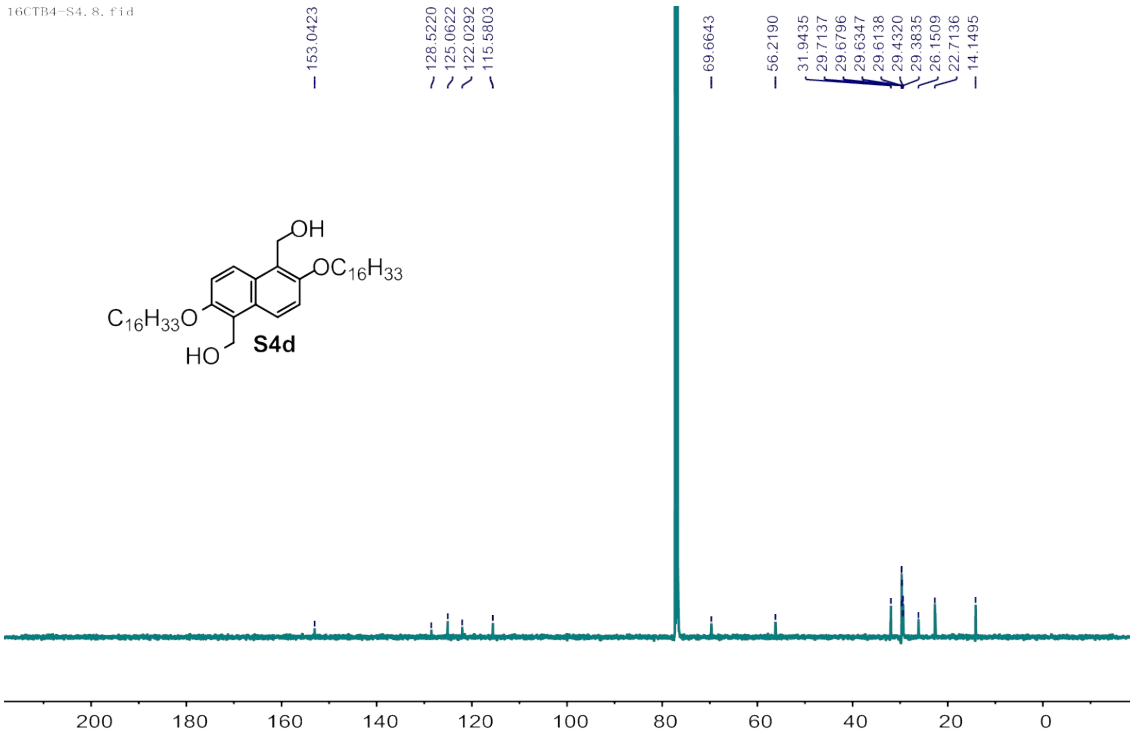


ESI mass spectrum of diol **S4c**

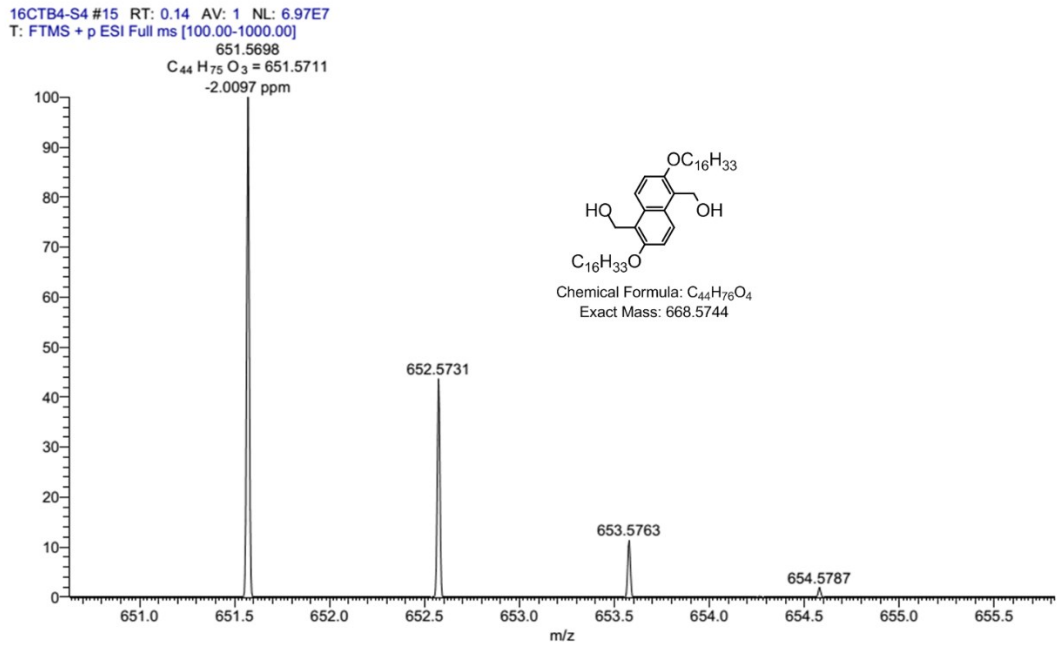
S4c was obtained in 82% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C): δ [ppm] = 8.13 (d, *J* = 9.3 Hz, 2H), 7.33 (d, *J* = 9.4 Hz, 2H), 5.19 (d, *J* = 6.2 Hz, 4H), 4.15 (s, 4H), 1.86 (dd, *J* = 8.5, 6.4 Hz, 4H), 1.54 – 1.48 (m, 4H), 1.28 (s, 48H), 0.90 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C): δ [ppm] = 153.04, 128.52, 125.06, 122.03, 115.58, 69.66, 56.22, 31.94, 29.71, 29.68, 29.63, 29.61, 29.43, 29.38, 26.15, 22.71, 14.15. ESI-HRMS: *m/z* calcd for $[M\text{-}OH]^+$ $C_{44}H_{75}O_3$, 651.5716; found 651.5698 (error = -2.0 ppm).



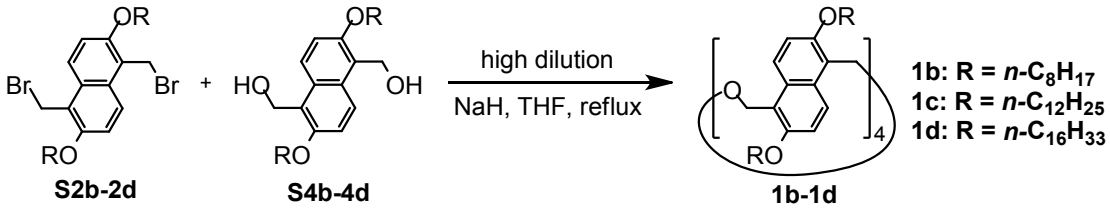
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 °C) of diol **S4d**



^{13}C NMR spectrum (126 MHz, $CDCl_3$, 25 °C) of diol **S4d**

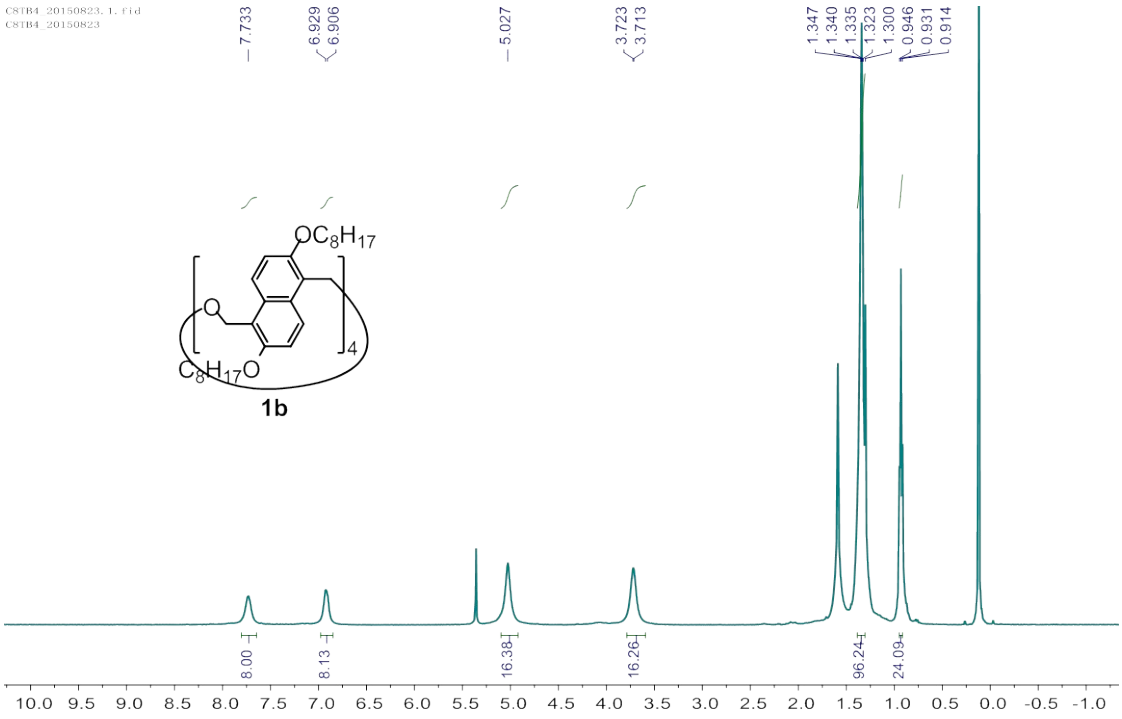


ESI mass spectrum of diol **S4d**

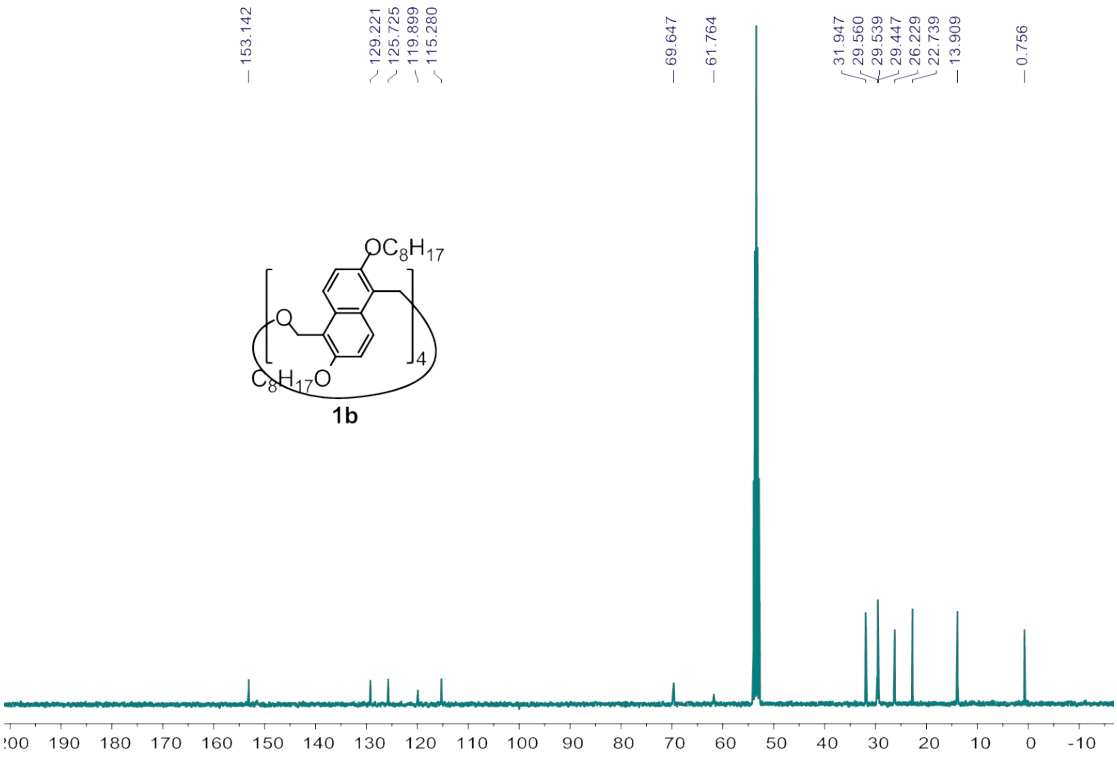


General procedure for 1b-d: To the mixture of NaH (2.0 g, 50 mmol) and Cs_2CO_3 (4.9 g, 15 mmol) in dry THF (500 mL) at reflux was added the solution of dibromide **S2** (5.0 mmol) and diol **S4** (5.0 mmol) in dry warm THF (60 mL) dropwise through a syringe pump. The resulting mixture was stirred at reflux for another 30h. The solvent was removed under reduced pressure. The residue was suspended in H_2O (100 mL), and then extracted with CH_2Cl_2 (100 mL × 3). The combined organic phase was washed with saturated NaCl and dried over anhydrous Na_2SO_4. Then, the solvent was removed with rotary evaporator to give the crude product which was purified by column chromatography (SiO_2, petroleum ether: ethylacetate = 100:1 ~ 10:1) to give pure **TA4** as white solid.

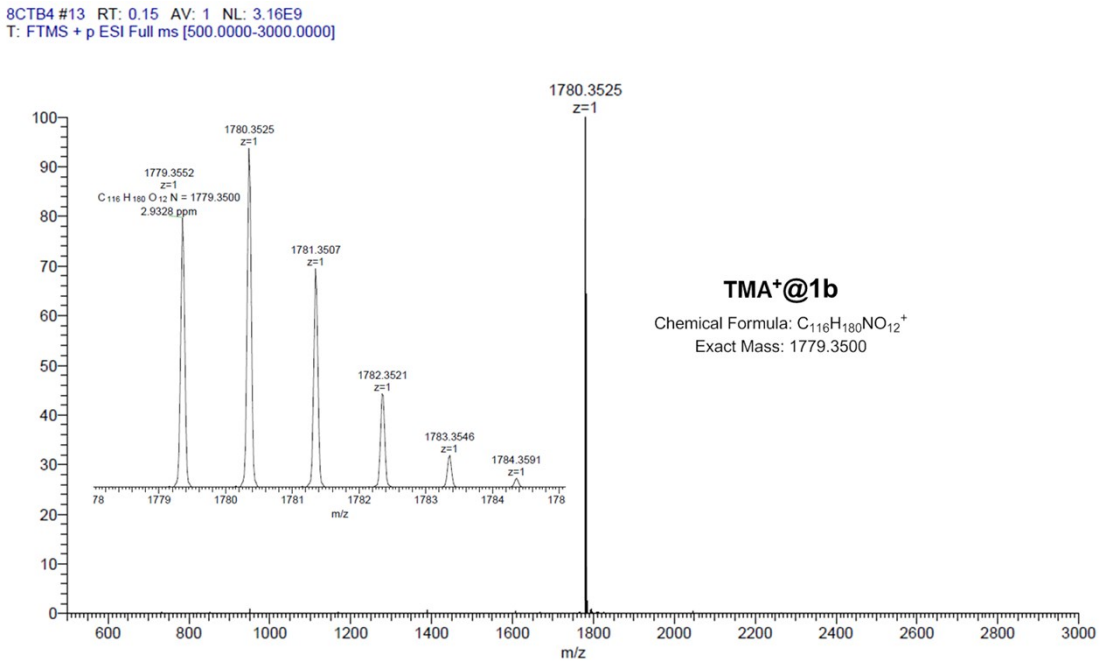
1b was obtained in 13% yield as a white solid. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ [ppm] = 7.73 (s, 8H), 6.92 (d, *J* = 9.2 Hz, 8H), 5.03 (s, 16H), 3.79 – 3.59 (m, 16H), 1.38 – 1.30 (m, 96H), 0.93 (t, *J* = 6.4 Hz, 24H). ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): δ [ppm] = 153.14, 129.22, 125.72, 119.90, 115.28, 69.65, 31.95, 29.56, 29.54, 29.45, 26.23, 22.74, 13.91. ESI-HRMS: *m/z* calcd for $[M+TMA]^+$ $C_{116}H_{180}NO_{12}^+$, 1779.3500; found 1779.3552 (error = 2.9 ppm). Tetramethylammonium (TMA) Hexafluorophosphate was added to facilitate the ionization of **1b**.



^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 25 °C) of **1b**.

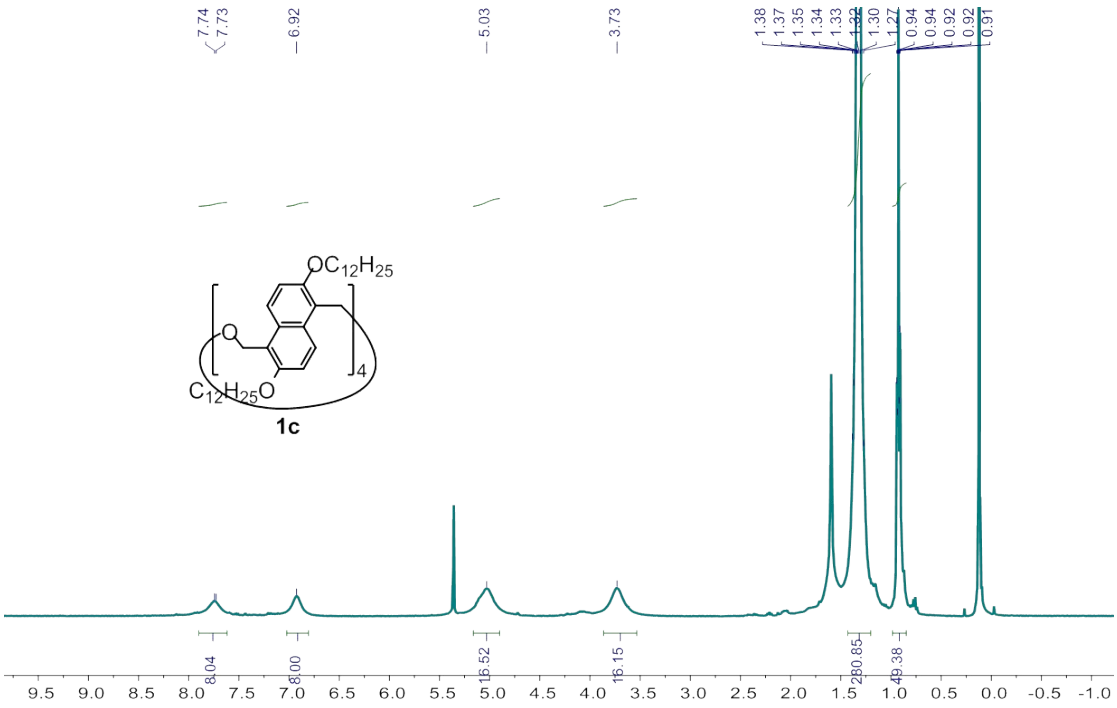


^{13}C NMR spectrum (101 MHz, CD_2Cl_2, 25 °C) of **1b**

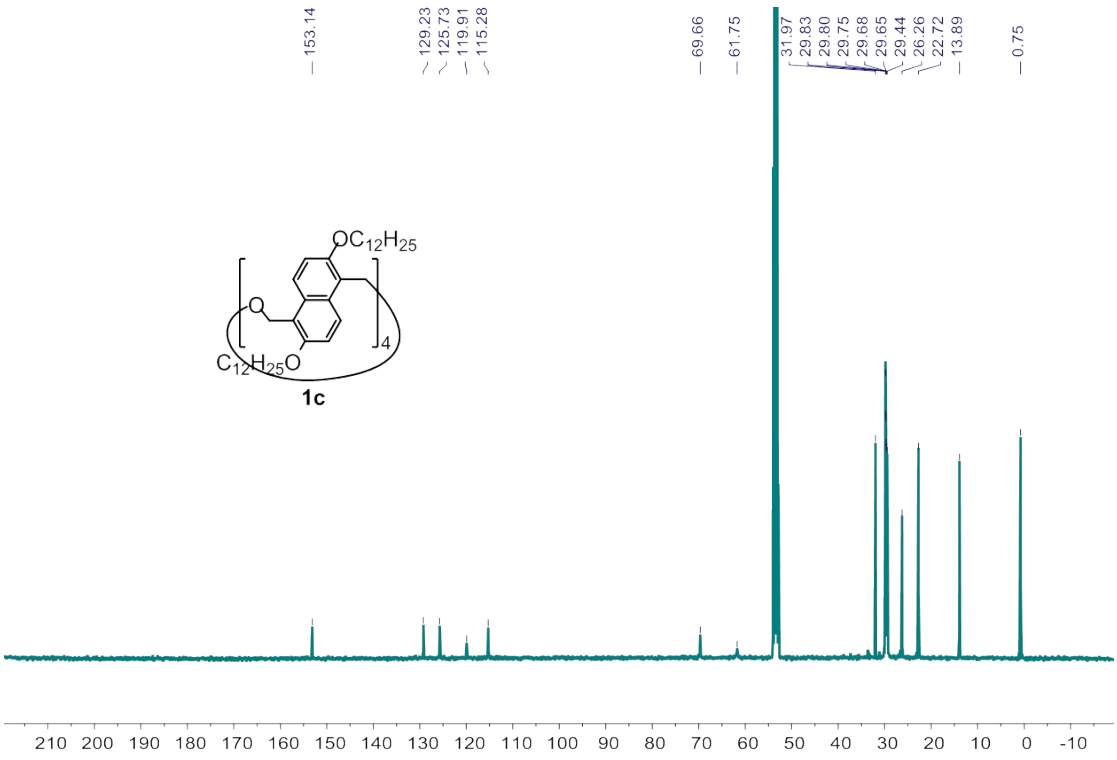


ESI-TOF mass spectrum of **TMA$^+$@1b**

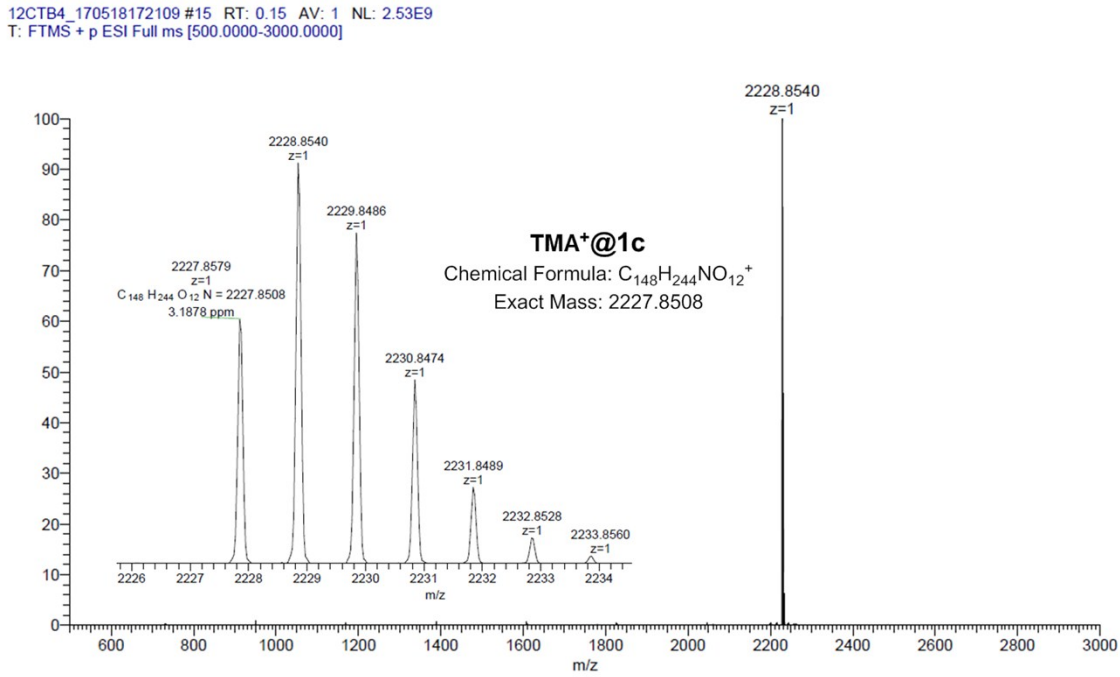
1c was obtained in 14% yield as a white solid. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ [ppm] = 7.73 (s, 8H), 6.92 (d, *J* = 9.2 Hz, 8H), 5.03 (s, 16H), 3.79 – 3.59 (m, 16H), 1.38 – 1.30 (m, 96H), 0.93 (t, *J* = 6.4 Hz, 24H). ^{13}C NMR (101 MHz, CD_2Cl_2, 25 °C): δ [ppm] = 153.14, 129.22, 125.72, 119.90, 115.28, 69.65, 31.95, 29.56, 29.54, 29.45, 26.23, 22.74, 13.91. ESI-HRMS: *m/z* calcd for $[M+TMA]^+$ $C_{148}H_{244}NO_{12}^+$, 2227.8508; found 2227.8579 (error = 3.2 ppm). Tetramethylammonium (TMA) Hexafluorophosphate was added to facilitate the ionization of **1c**.



^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 25 °C) of **1c**

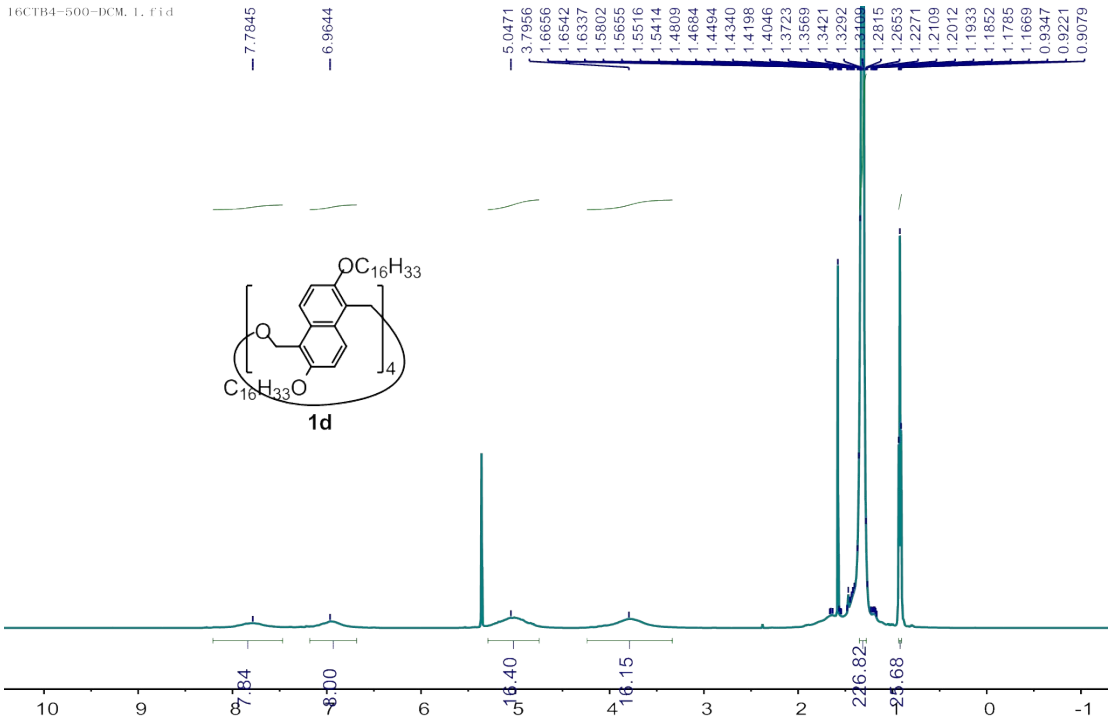


^{13}C NMR spectrum (101 MHz, CD_2Cl_2, 25 °C) of **1c**

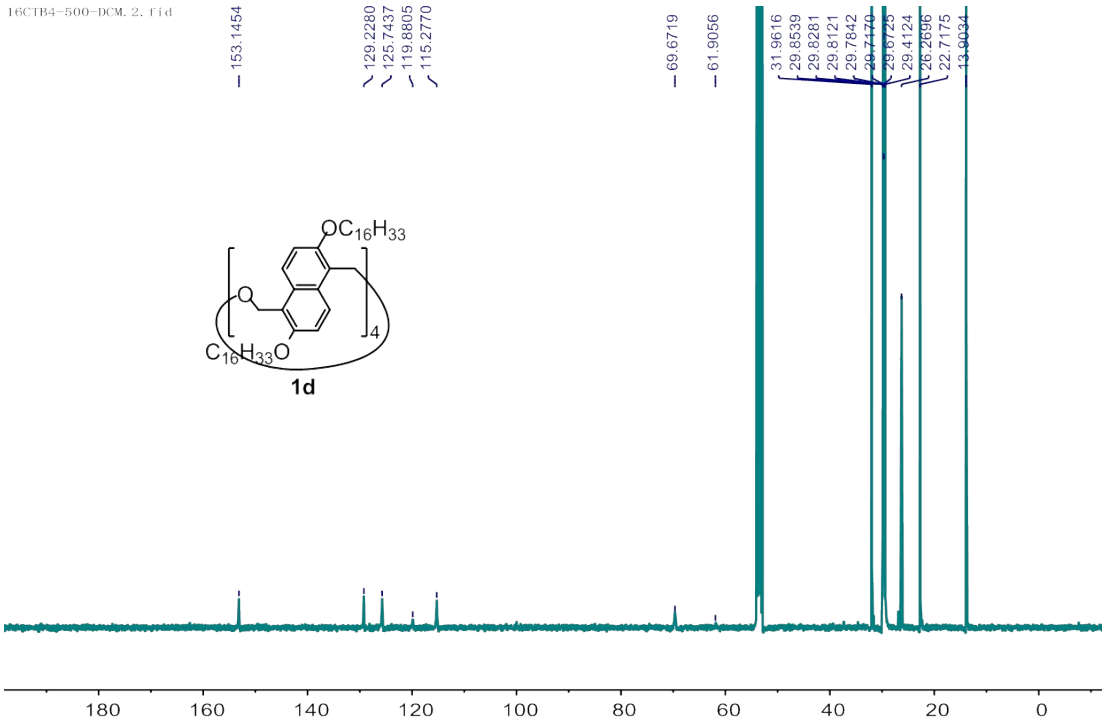


ESI-TOF mass spectrum of **TMA$^+$@1c**

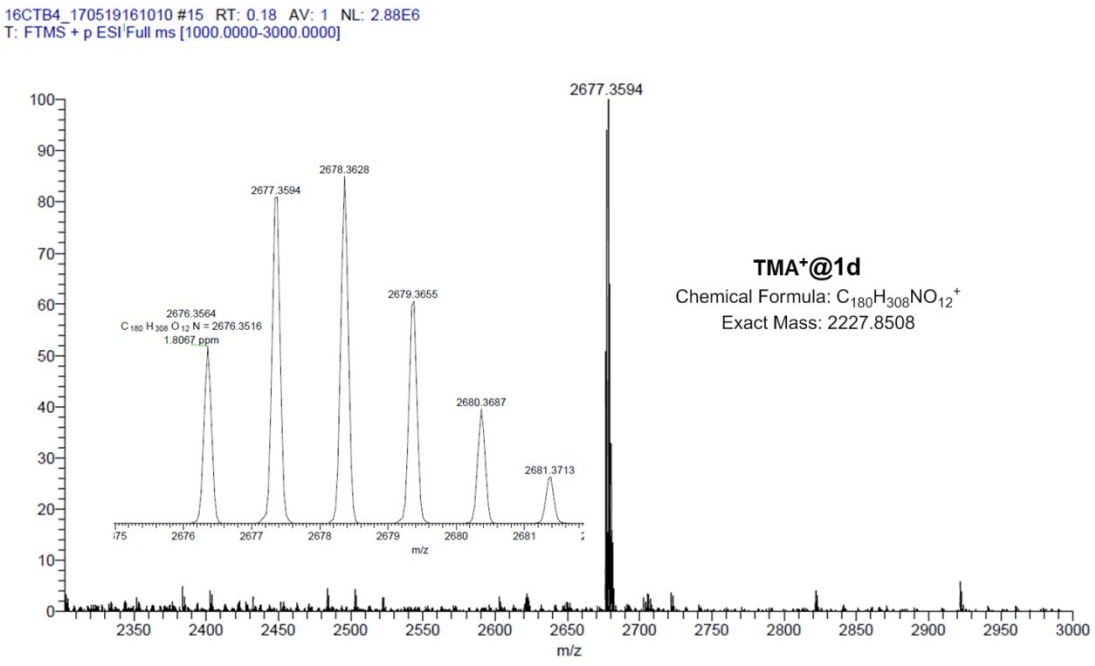
1d was obtained in 11% yield as a white solid. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 ^{o}C): δ [ppm] = 7.78 (s, 8H), 6.96 (s, 8H), 5.05 (s, 16H), 3.80 (s, 16H), 1.32 (m, 224H), 0.91 (m, 24H). ^{13}C NMR (126 MHz, CD_2Cl_2, 25 ^{o}C): δ [ppm] = 153.15, 129.23, 125.74, 115.28, 69.67, 61.91, 31.96, 29.85, 29.83, 29.81, 29.78, 29.72, 29.67, 29.41, 26.27, 22.72, 13.90; ESI-HRMS: *m/z* calcd for $[M+TMA]^+$ $C_{180}H_{308}NO_{12}^+$, 2676.3516; found 2676.3509 (error = 2.1 ppm). Tetramethylammonium (TMA) Hexafluorophosphate was added to facilitate the ionization of **1d**.



^{1}H NMR spectrum (500 MHz, CD_2Cl_2, 25 ^{o}C) of **1d**



^{13}C NMR spectrum (126 MHz, CD_2Cl_2, 25 °C) of **1d**



ESI-TOF mass spectrum of **TMA$^+$@1d**

2. Properties of the Oxatub[4]arenes

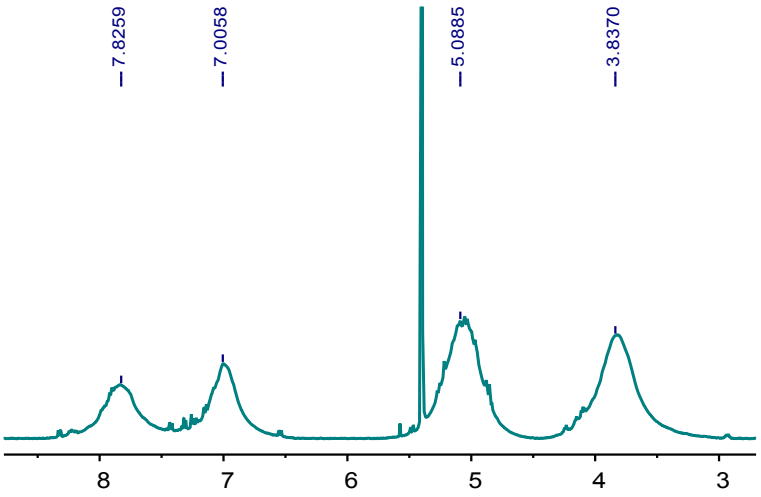


Figure S1 Partial ^{1}H NMR spectrum (500 MHz, CD_2Cl_2, 1.0 mM, 25 ^{o}C) of **1d**.

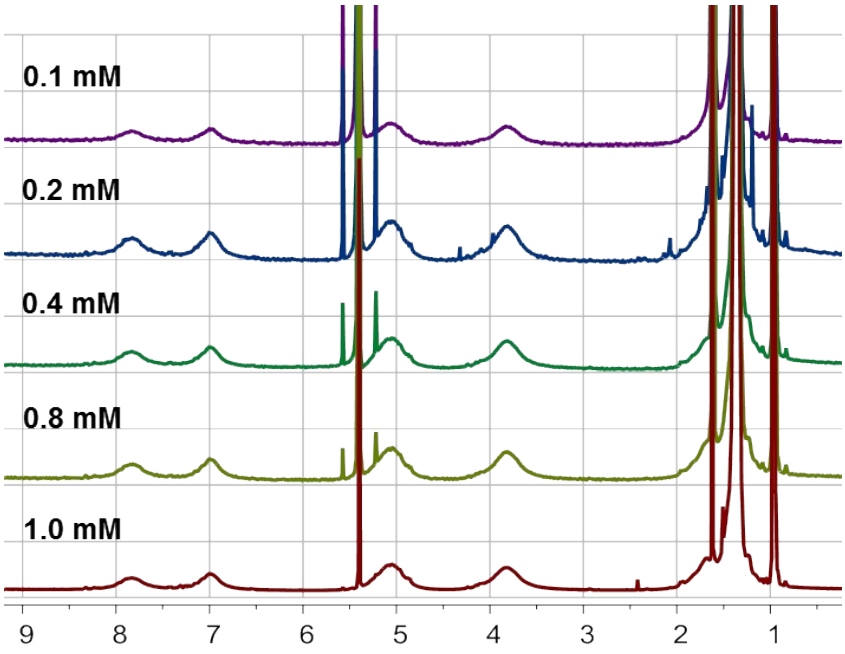


Fig. S2. ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 25 ^{o}C) of **1d** at various concentrations. Numbers of scan: 512 (0.1 mM), 512 (0.2 mM), 256 (0.4 mM), 64 (0.8 mM), 32 (1.0 mM). The peak shapes are exactly the same, suggesting the peak broadening of **1d** is not due to aggregation in solution but because of slower conformational interconversion.

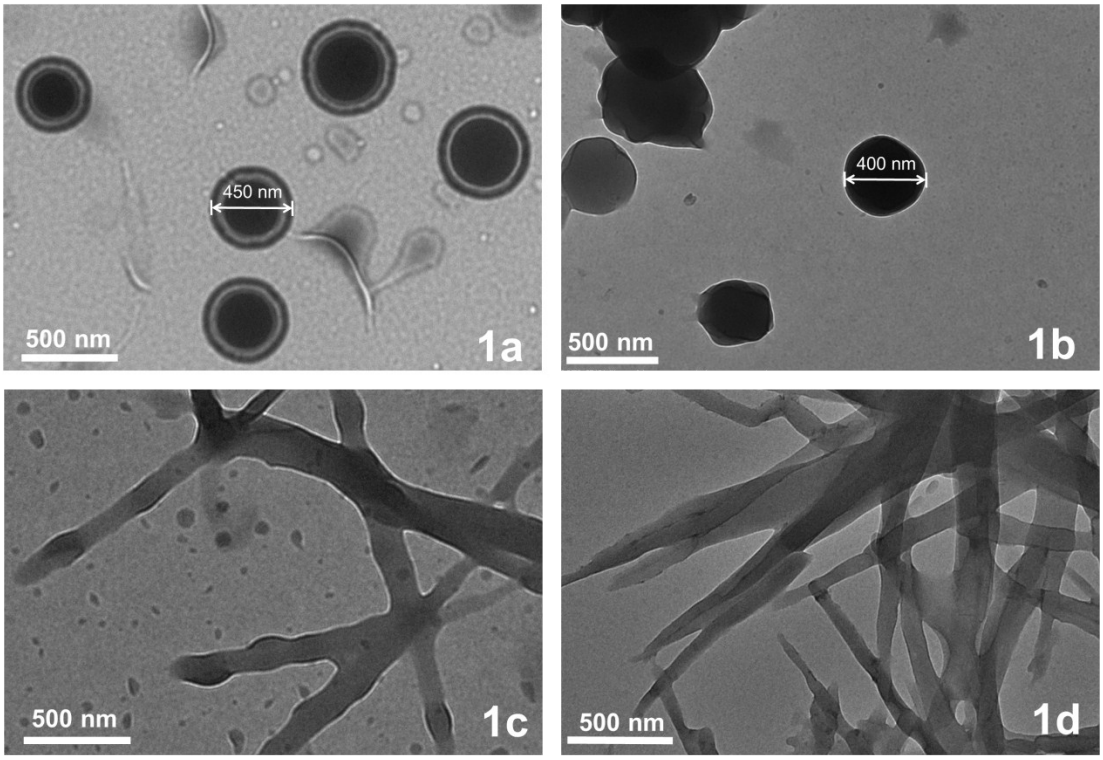


Figure *S3*. TEM images of **1a**, **1b**, **1c** and **1d**. At the nanoscale, the structures of **1a** and **1b** appear to be spherical nanodisks with diameters of about 400 nm. **1c** and **1d** self-assemble into ribbon-like structures with smaller size and less regular shapes. These indicate that the self-assembly of **1a** and **1b** are more organized than **1c** and **1d**. The sample for TEM experiments for **1a**-**1d** was prepared by as follows: 0.1 mL dichloromethane solution of the corresponding compound (20 mM) was dispersed into 1.0 mL acetone and sonicated for 1 min. Then a drop of above dispersion was put on carbon-supported film and dried.

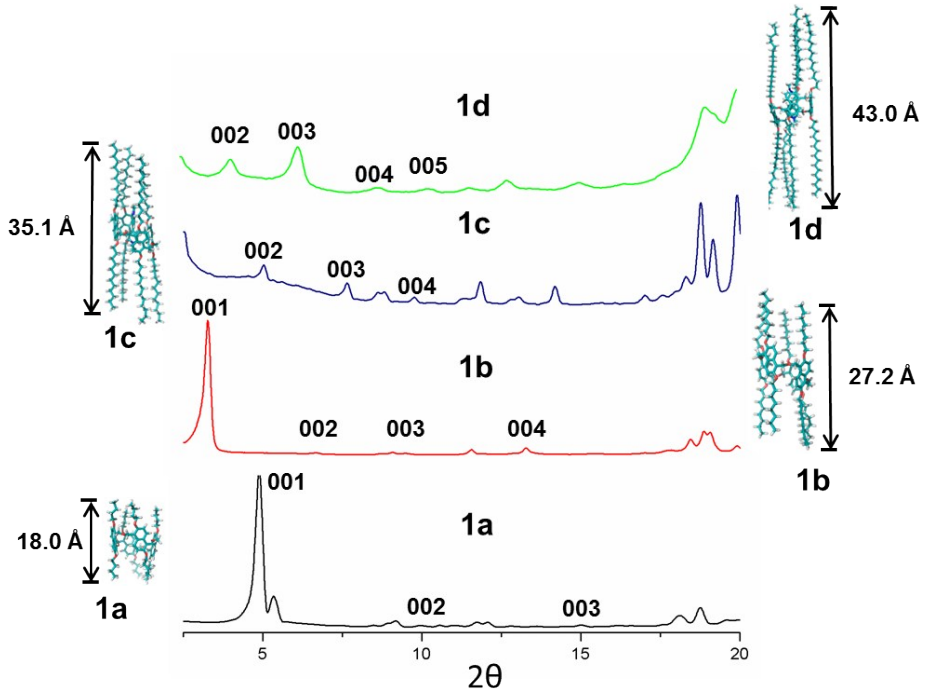


Figure S4. Powder XRD diffraction patterns and energy-minimized structures of **1a**-**1d**. The diffraction signals of **1a** and **1b** are stronger than those of **1c** and **1d**, suggesting the higher ordering and closer packing of **1a** and **1b** in the solid state.

3. NMR Spectra of Host-Guest Complexes

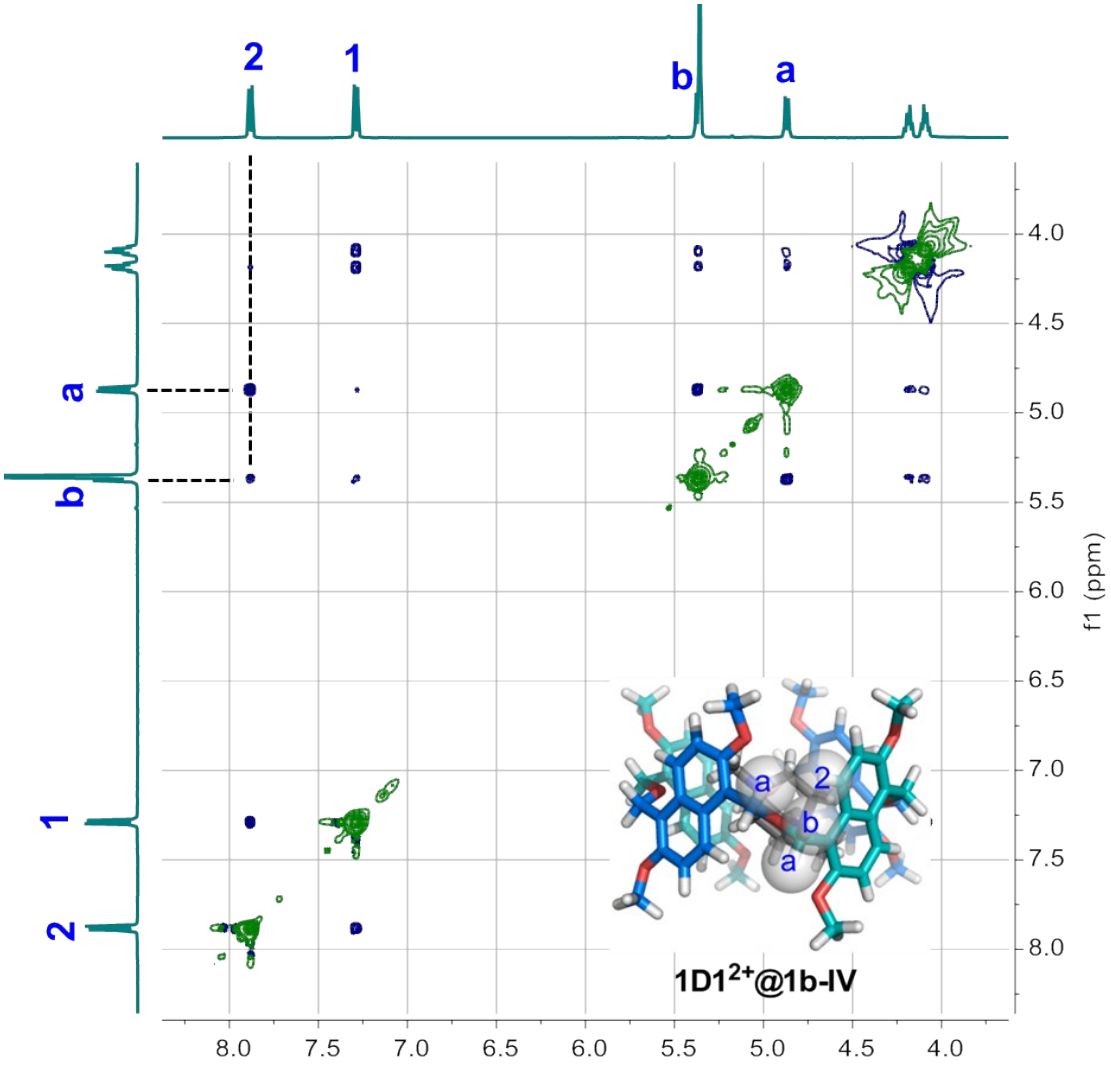


Fig. S5 Partial ^{1}H, ^{1}H-ROESY NMR spectra (500 MHz, CD_2Cl_2:CD_3CN =5:1, 2.0 mM, 25 °C) of **1D1^{2+}@1b** and Energy-minimized structures.

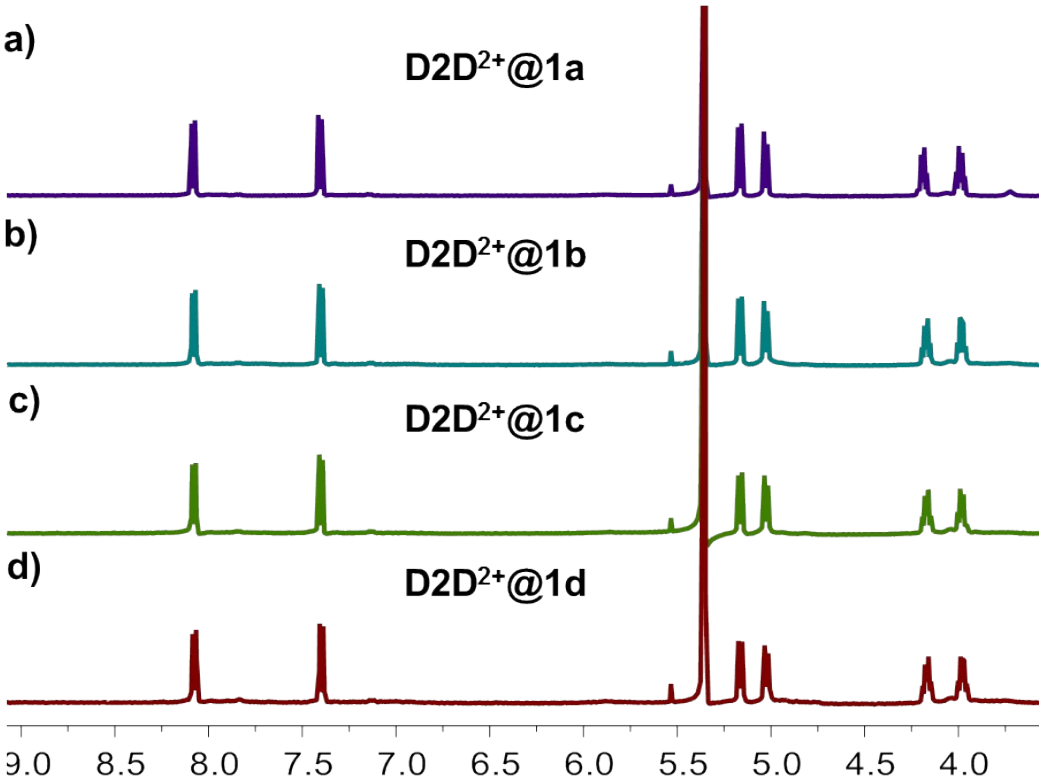


Fig. S6 Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2:CD_3CN =5:2, 1.0 mM, 25 °C) of a) **D2D^{2+}@1a**, b) **D2D^{2+}@1b**, c) **D2D^{2+}@1c**, d) **D2D^{2+}@1d**.

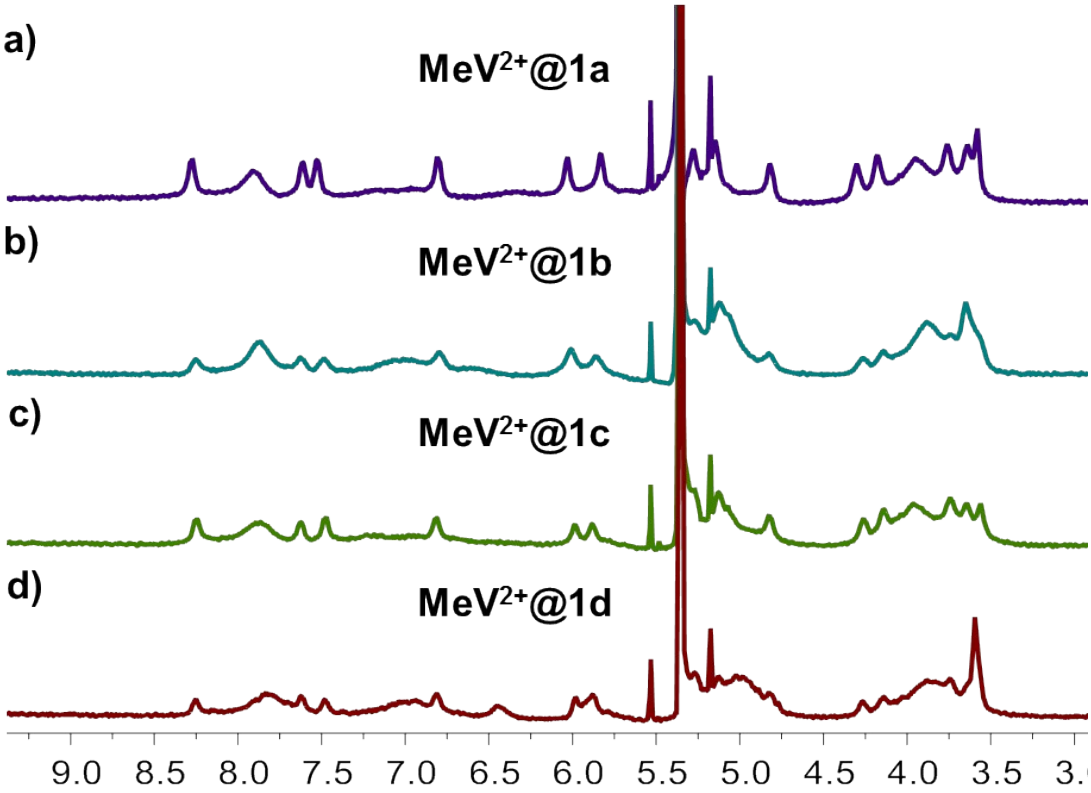


Fig. S7 Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2:CD_3CN =5:2, 1.0 mM, 25 ^{o}C) of a) **MeV^{2+}@1a**, b) **MeV^{2+}@1b**, c) **MeV^{2+}@1c**, d) **MeV^{2+}@1d**.

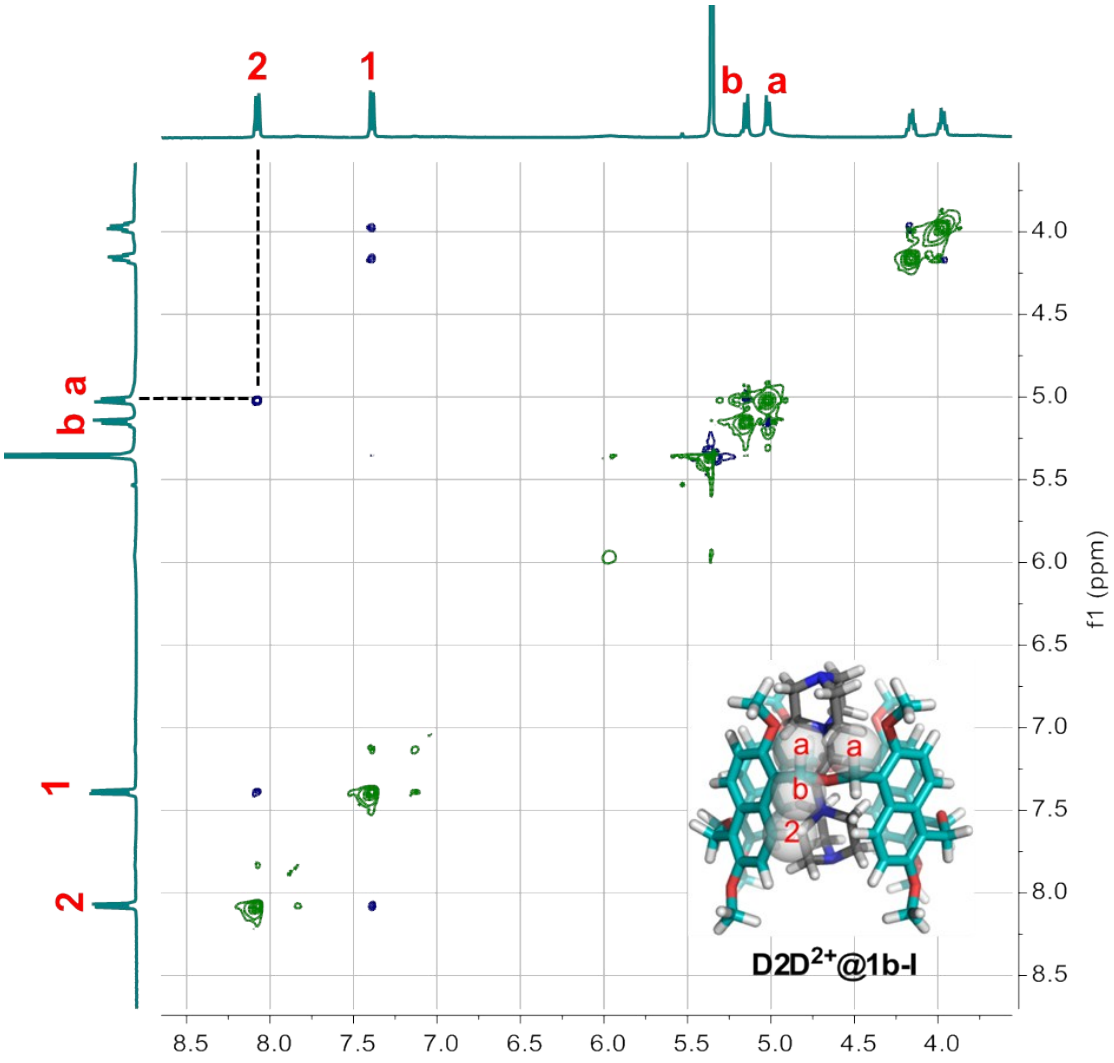


Fig. S8 Partial ^{1}H, ^{1}H-ROESY NMR spectra (500 MHz, CD_2Cl_2:CD_3CN =5:2, 2.0 mM, 25 ^{o}C) of **D2D $^{2+}$@1b** and Energy-minimized structures.

4. Binding Constants Determined by ITC

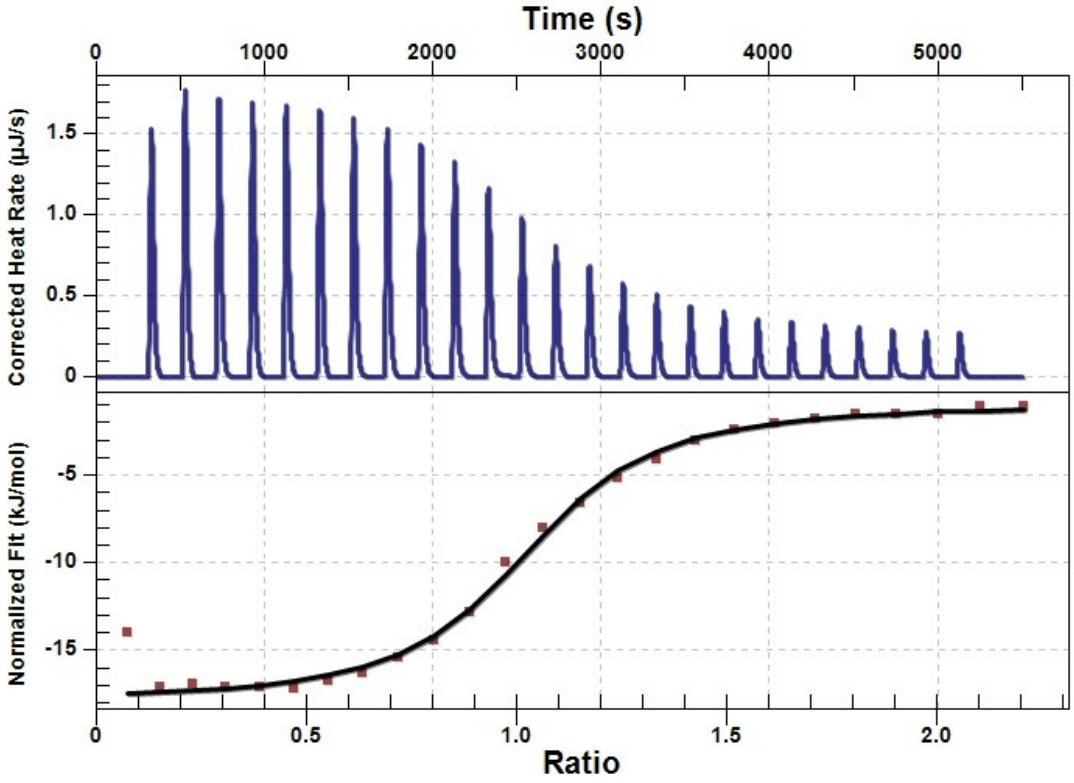


Fig. S9 Titration plots (heat rate versus time and heat versus guest/host ratio) obtained from ITC experiments of **1a** (0.15 mM) with **D2D**-$2PF_6$ (1.00 mM) in the 3:2 mixture of 1,2-dichloroethane and CH_3CN.

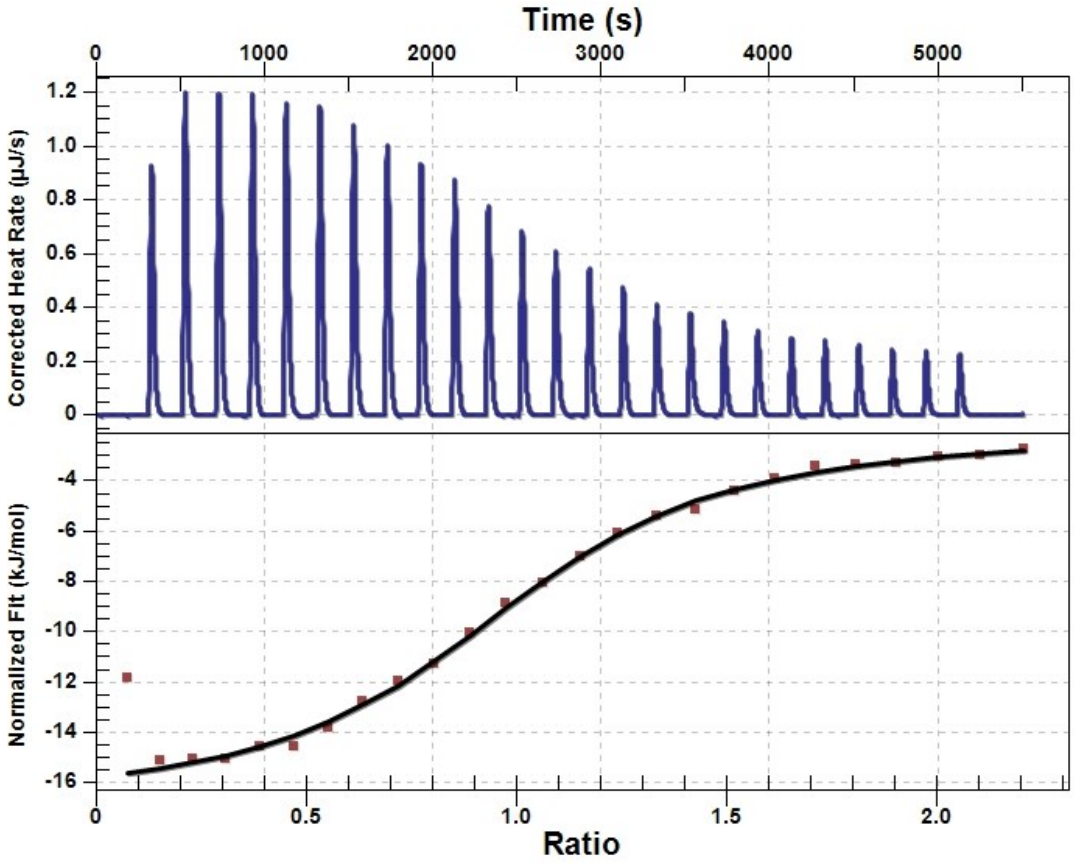


Fig. S10 Titration plots (heat rate versus time and heat versus guest/host ratio) obtained from ITC experiments of **1b** (0.15 mM) with **D2D**-$2PF_6$ (1.00 mM) in the 3:2 mixture of 1,2-dichloroethane and CH_3CN.

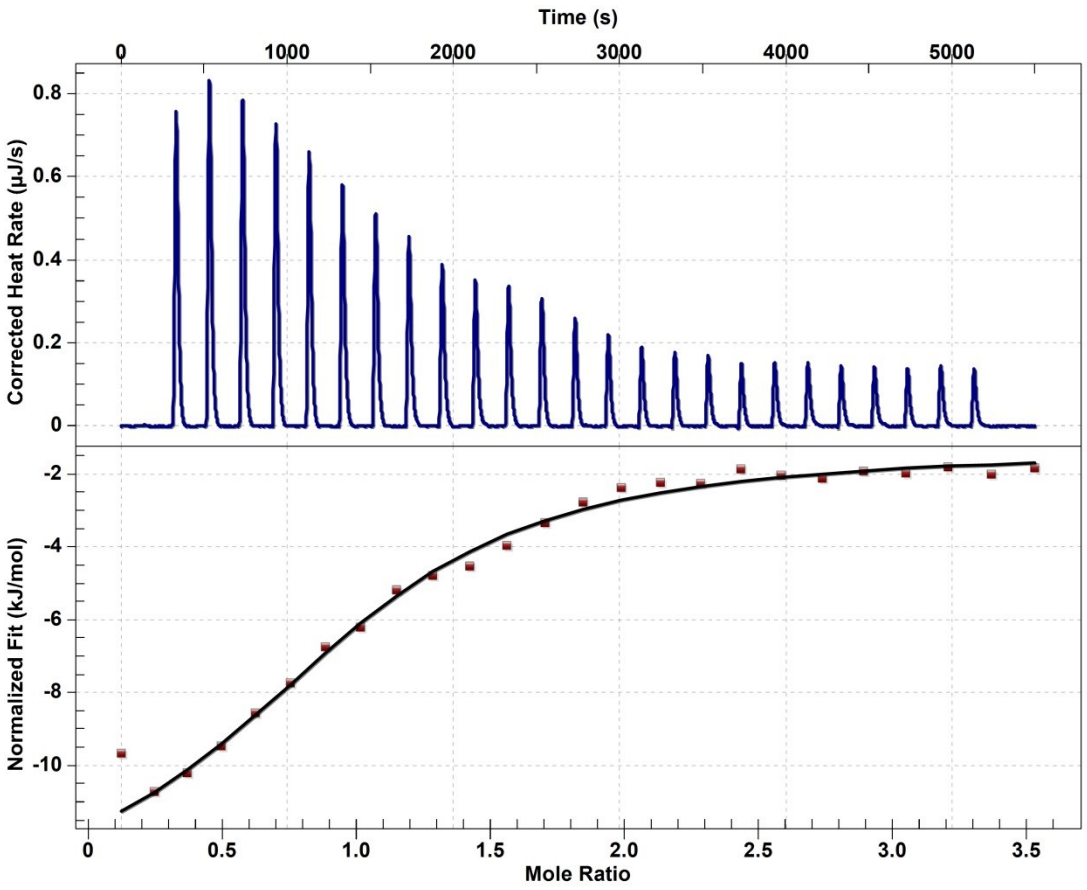


Fig. S11 Titration plots (heat rate versus time and heat versus guest/host ratio) obtained from ITC experiments of **1c** (0.10 mM) with **D2D**-2PF_6 (1.00 mM) in the 3:2 mixture of 1,2-dichloroethane and CH_3CN.

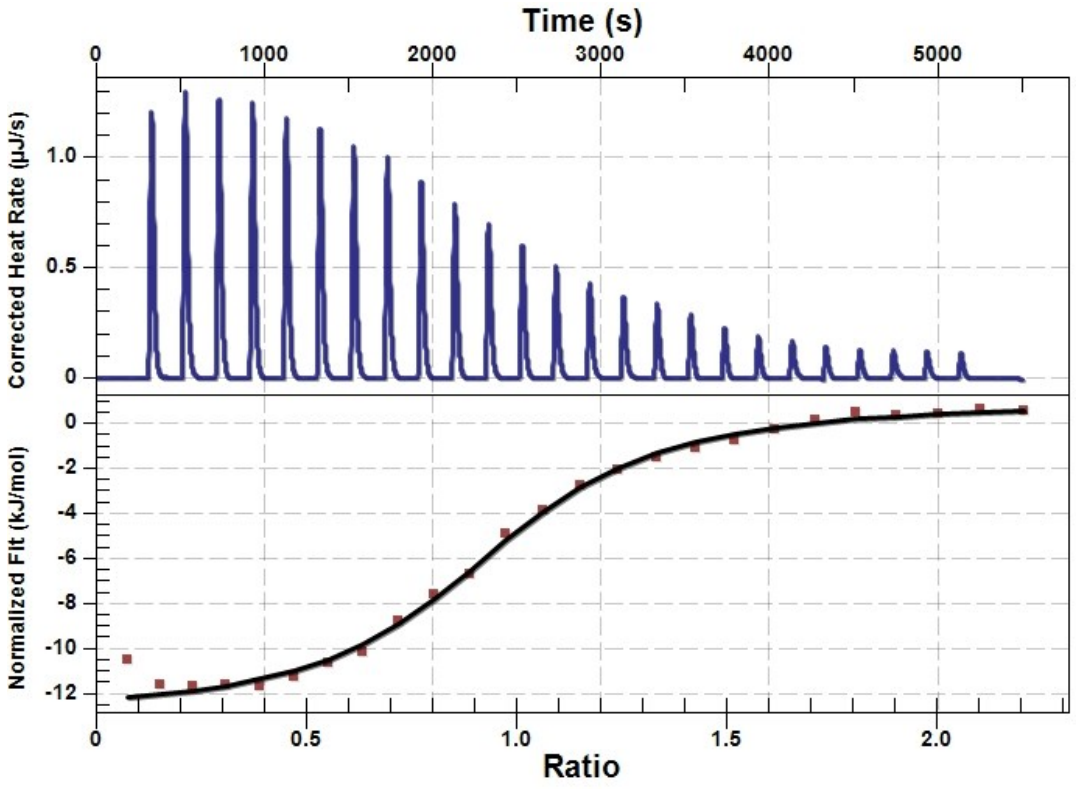


Fig. S12 Titration plots (heat rate versus time and heat versus guest/host ratio) obtained from ITC experiments of **1a** (0.15 mM) with **MeV-2PF$_6$** (1.00 mM) in the 3:2 mixture of 1,2-dichloroethane and CH_3CN.

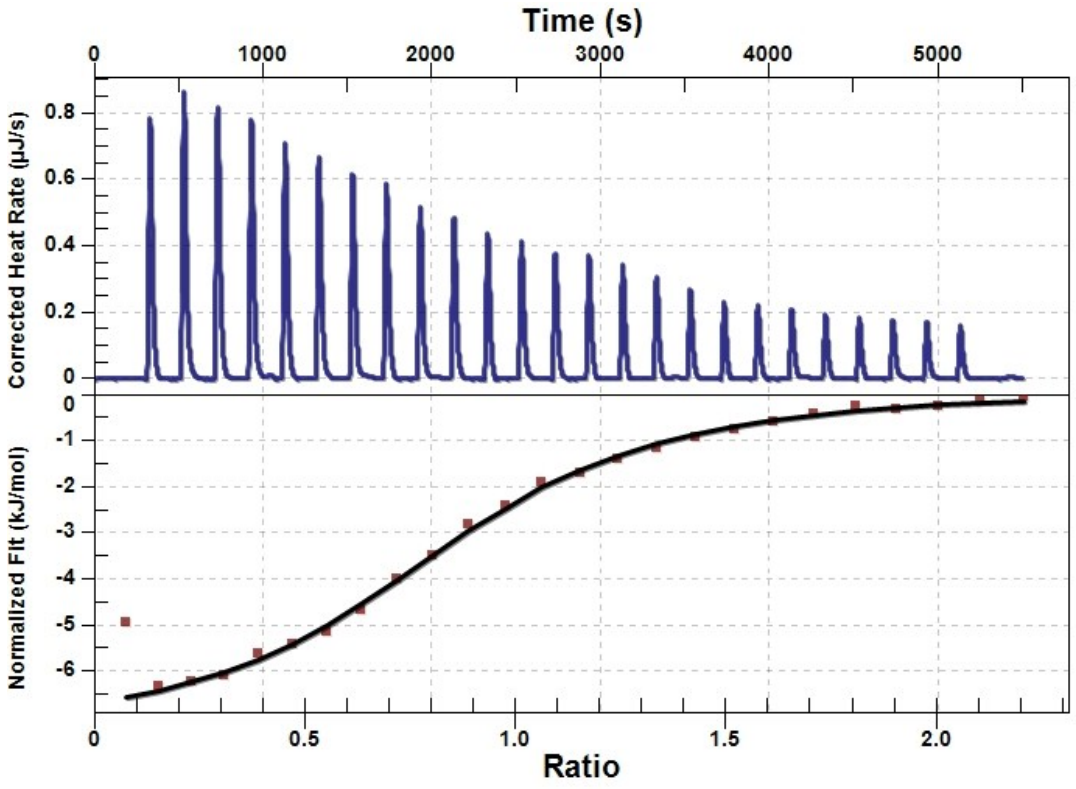


Fig. S13 Titration plots (heat rate versus time and heat versus guest/host ratio) obtained from ITC experiments of **1b** (0.15 mM) with **MeV-2PF$_6$** (1.00 mM) in the 3:2 mixture of 1,2-dichloroethane and CH_3CN.

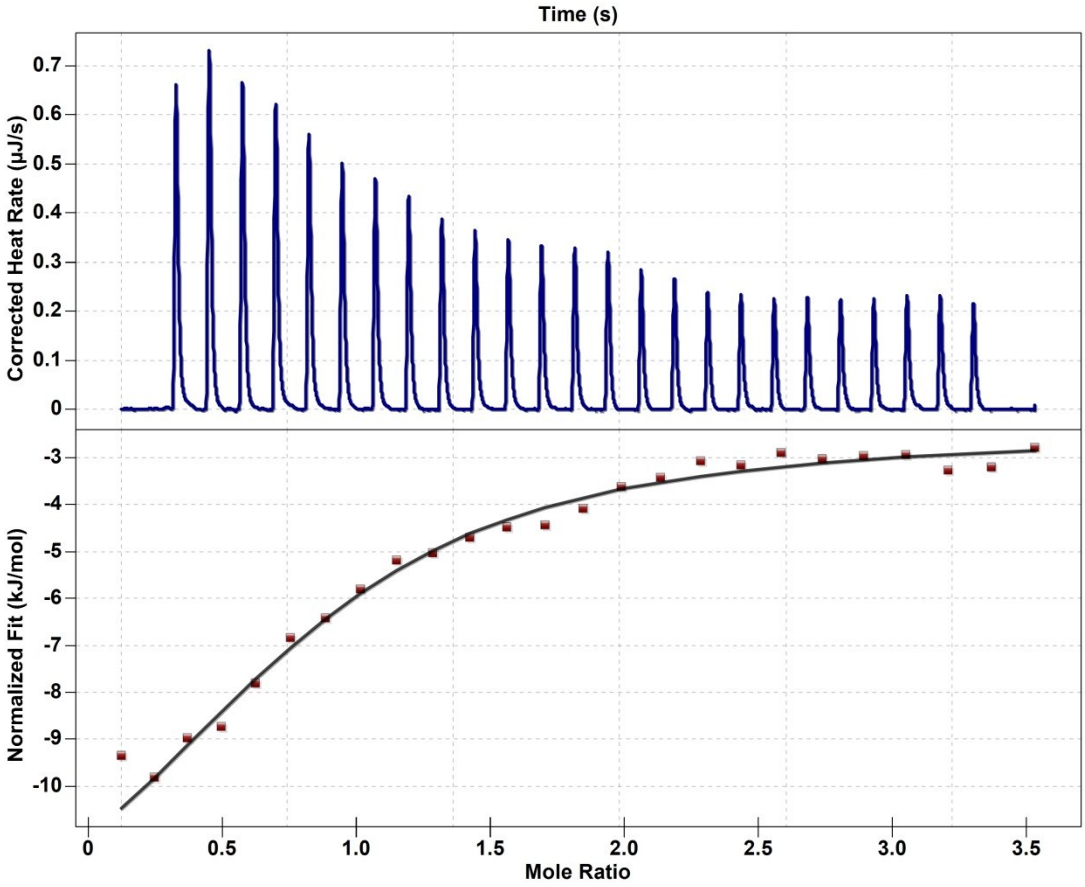


Fig. S14 Titration plots (heat rate versus time and heat versus guest/host ratio) obtained from ITC experiments of **1c** (0.10 mM) with **MeV-2PF$_6$** (1.00 mM) in the 3:2 mixture of 1,2-dichloroethane and CH_3CN.

5. TEM and Powder XRD Experiments

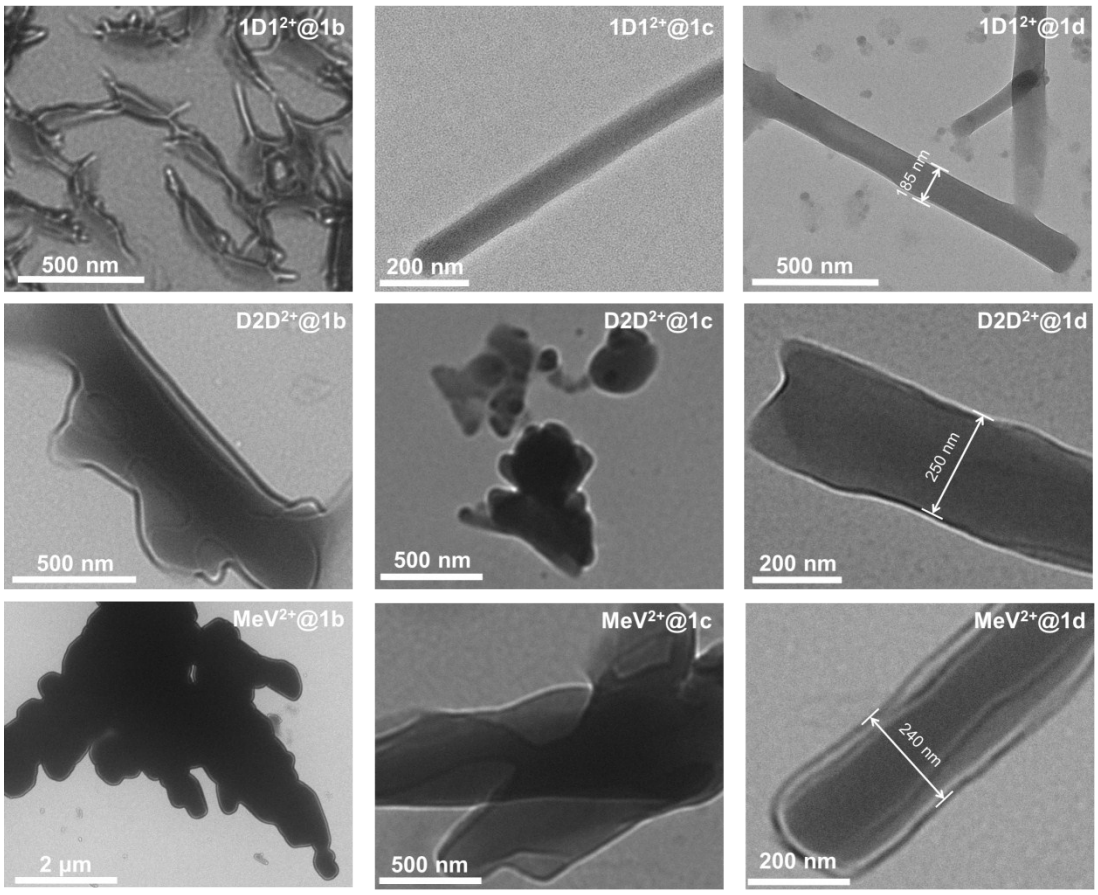


Figure *S15*. TEM images of the host-guest complexes of **1b-1d** with $\mathbf{1D1^{2+}}$, $\mathbf{D2D^{2+}}$ or $\mathbf{MeV^{2+}}$**.** At the nanoscale, the complexes of **1d** existed as nano-rod or nanosheets with a width of ca. 200 nm. The complexes of **1c** appear to be nano-rod or membrane-like assemblies. The structures of the complexes of **1b** appear to be irregular. Generally, the addition of guests induced drastic structural changes of the oxatub[4]arenes. But different guests and the same oxatub[4]arene show rather similar structure.

The samples of the complexes for TEM experiments were prepared using the following steps: the corresponding host-guest complexes (5.0 mg) was dispersed to 1.0 mL ether and sonicated for 1 minute. Then a drop of the above suspension was put on carbon-supported film and dried.

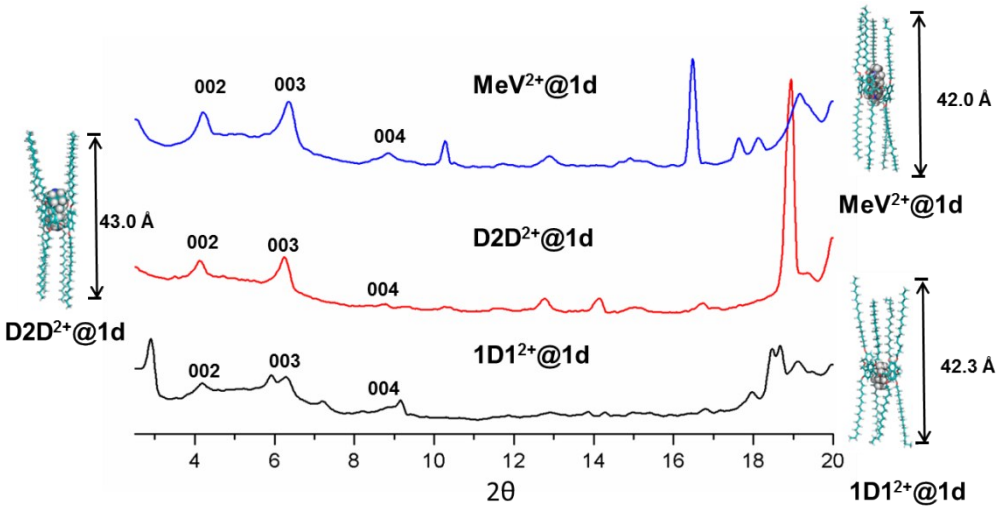


Figure S16. Powder XRD diffraction patterns and energy-minimized structures of the complexes of **1d** with three guests. The similar diffraction peaks (002, 003 and 004) indicate similar molecular packing for the three complexes in solid state. This result support the conclusion that different guests and thus the induced different conformation of oxatub[4]arene result in rather similar structures in the solid state.

6. X-Ray Single Crystal Structure of 1a

Crystal of **1a** was obtained by slow evaporation of 1:1 CH_2Cl_2-MeCN solution. The reflections were collected at 120 K with an Agilent Super-Nova dual wavelength diffractometer with a micro-focus X-ray source and multilayer optics monochromatized Mo-*K*α (λ=0.71073 Å) radiation for **1a**. *CrysAlisPro*[2] was used for both data collection and processing. The intensities were corrected for absorption using analytical face index absorption correction method.[3] The structures were solved by Direct method with *SHELXT*[4] and refined by full-matrix least-squares methods using the *OLEX2*,[5] which utilizes the *SHELXL-2015* module[6]. All non-hydrogen atoms in the structures were refined with anisotropic thermal parameters.

Crystal data for **1a:** $C_{80}H_{104}O_{12}$, M = 1257.63, monoclinic, a = 18.8502(5) Å b = 9.25277(17) Å c = 20.4322(5) Å, α = 90.00°, β = 106.169(3)°, γ = 90.00°, V = 3422.75(15) Å^3, T = 120.15(10) K, space group $P2_1/n$, Z = 2, 20660 reflections measured, 7487 independent reflections (R_{int} = 0.0317). The final R_1 value was 0.0470 ($I > 2\sigma(I)$). The final $wR(F^2)$ value was 0.0998 ($I > 2\sigma(I)$). The final R_1 value was 0.0756 (all data). The final $wR(F^2)$ value was 0.1123 (all data). The goodness of fit on F^2 was 1.025. CCDC-1577176 contains the supplementary data for this structure. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

7. References

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