

A Solvent-Driven Molecular Spring

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1. Materials and methods

Phthalimide potassium, hydrazine hydrate, and 3,5-bis(trifluoromethyl)phenyl isocyanate were reagent grade and used as received. The 1-(10-bromodecyloxy)-4-methoxybenzene^{S1} and copillar[5]arene **1**^{S2} were synthesized according to literature procedures. Solvents were either employed as purchased or dried according to procedures described in the literature. ¹H NMR spectra were collected on a Varian Unity INOVA-400 spectrometer with internal standard TMS. ¹³C NMR spectra were recorded on a Varian Unity INOVA-400 spectrometry at 100 MHz. ESI mass spectrometry were performed on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. HRMS were obtained on a Bruker 7-Tesla FT-ICRMS equipped with an electrospray source (Billerica, MA, USA) or on a WATERS GCT Premier (USA). MALDI-TOF spectrometry was performed on a 4700 MALDI-TOF-TOF (Applied Biosystems, U.S.A). The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus.

2. Proton assignments of 2, 3, 4 and 5

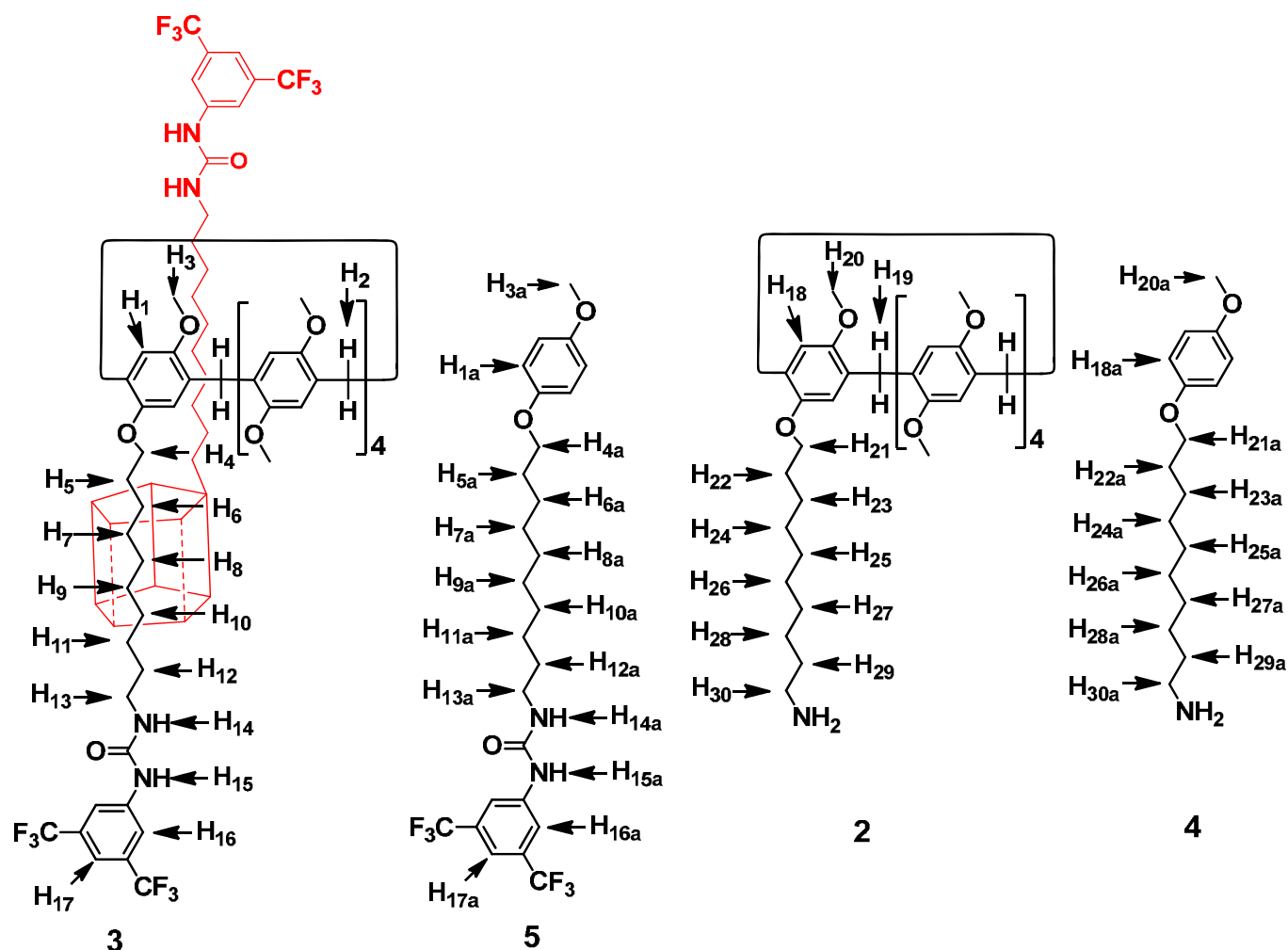
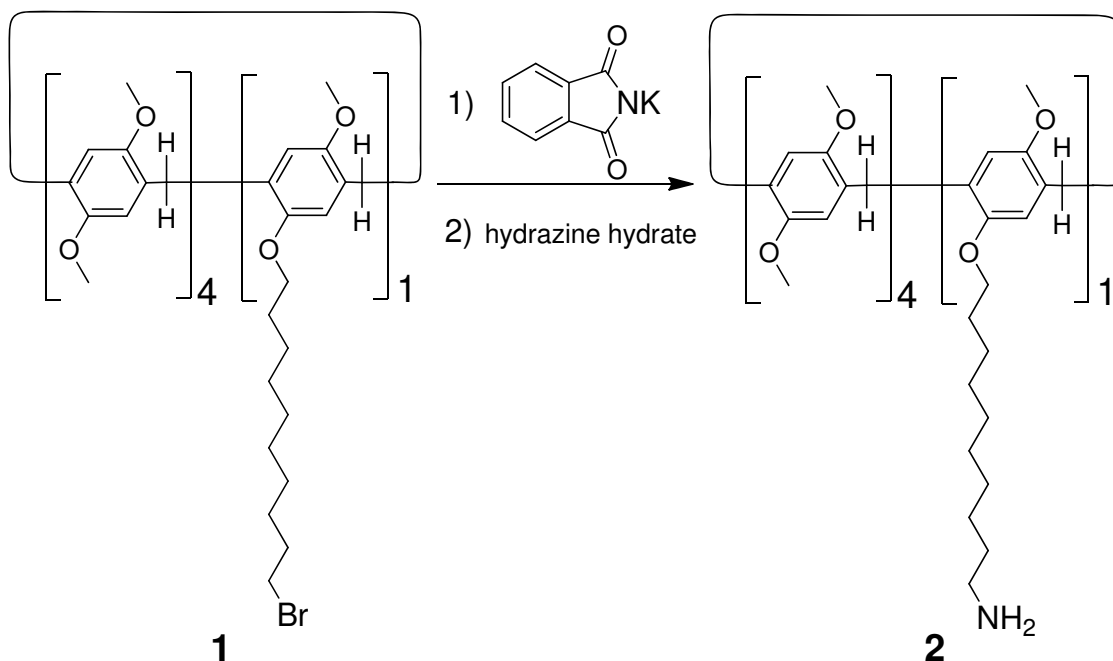


Fig. S1. Proton assignments of 2, 3, 4 and 5.

3. Synthesis of **2**



A mixture of copillar[5]arene **1**^{S2} (0.95 g, 1.0 mmol) and phthalimide potassium (0.21 g, 1.1 mmol) in 50 mL of DMF was stirred at 90 °C for 24 h under nitrogen atmosphere. Then DMF was removed by rotary evaporation. The resulting oil was dissolved in THF (30 mL), methanol (3 mL) and hydrazine hydrate (3 mL). After stirred at 50 °C for 24 h, the reaction mixture was concentrated by rotary evaporation. The resulting residue was dissolved in CH₂Cl₂ (150 mL) and washed with H₂O (2 × 100 mL). The organic layer was dried over anhydrous Na₂SO₄ and evaporated to afford the crude product, which was isolated by flash column chromatography using dichloromethane/methanol (20:1). The fractions containing the product were combined and concentrated under vacuum to give copillar[5]arene **2** (0.62 g, 69%) as a white solid. Mp 140.4–140.9 °C. The proton NMR spectrum of **2** is shown in Fig. S2. ¹H NMR (400 MHz, chloroform-*d*, 25 °C) δ (ppm): 6.96–6.79 (m, 10H), 3.91 (t, *J* = 6.4 Hz, 2H), 3.85–3.63 (m, 37H), 1.91–1.81 (m, 2H), 1.60–1.49 (m, 2H), 1.42–1.32 (m, 2H), 1.31–1.15 (m, 4H), 0.97–0.81 (m, 2H), 0.58–0.39 (m, 2H), –0.43 (s, 2H), –0.57 (s, 2H). The ¹³C NMR spectrum of **2** is shown in Fig. S3. The ¹³C NMR (100 MHz, chloroform-*d*, 25 °C) δ (ppm): 150.52, 150.38, 150.30, 149.82, 128.39, 128.25, 128.23, 128.18, 128.10, 128.04, 114.48, 113.90, 113.49, 113.40, 113.35, 76.98, 67.85, 55.67, 55.58, 55.49, 55.43, 55.41, 55.31, 41.54, 29.61, 29.48, 29.34, 29.17, 28.83, 25.67, 25.15. LRESIMS is shown in Fig. S4: *m/z* 892.7 [M + H]⁺ (100%). HRESIMS: *m/z* calcd for [M]⁺ C₅₄H₆₉NO₁₀, 891.4924, found 891.4921, error 0.3 ppm.

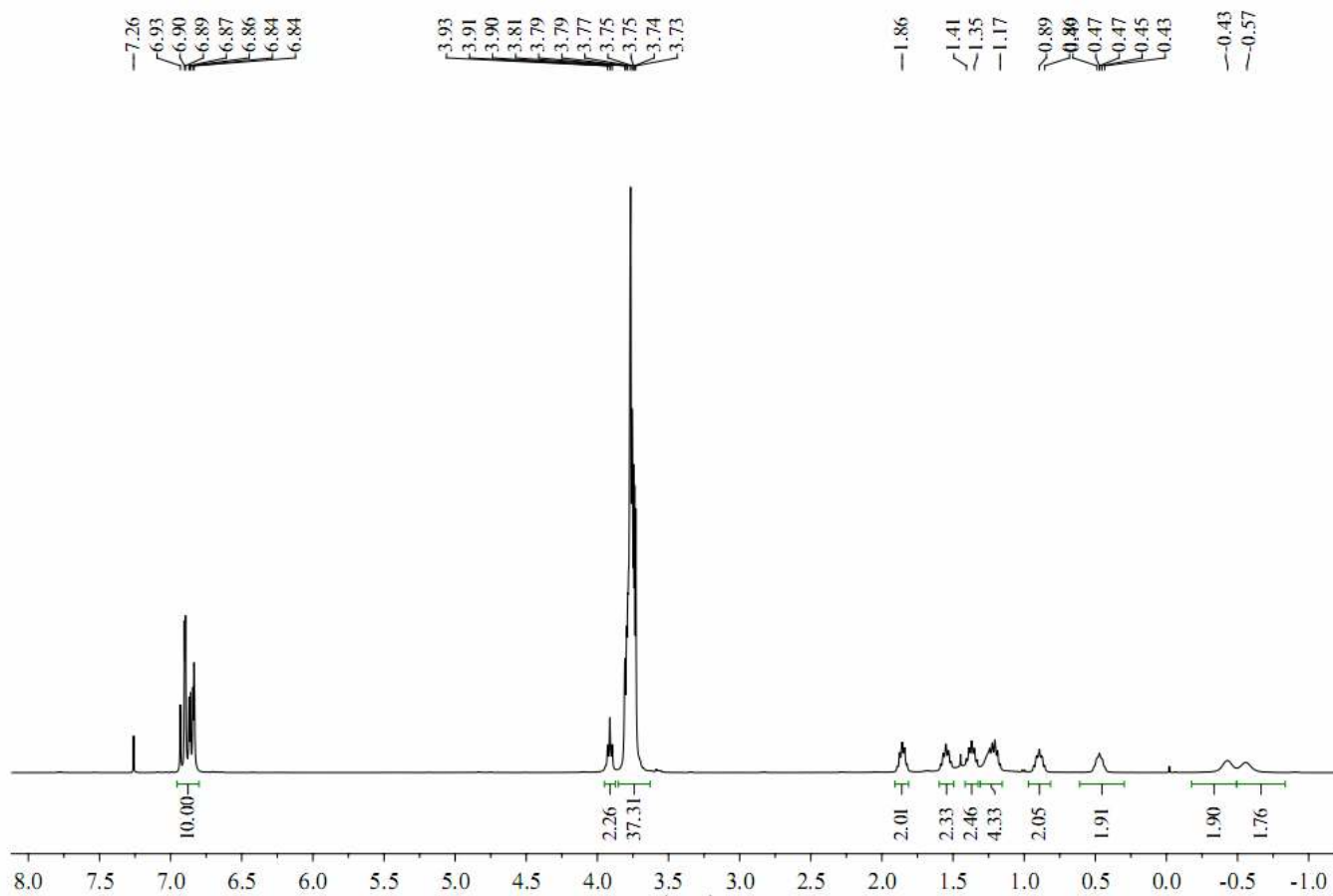


Fig. S2 ^1H NMR spectrum (400 MHz, chloroform-*d*, 25 °C) of **2** at 88 mM.

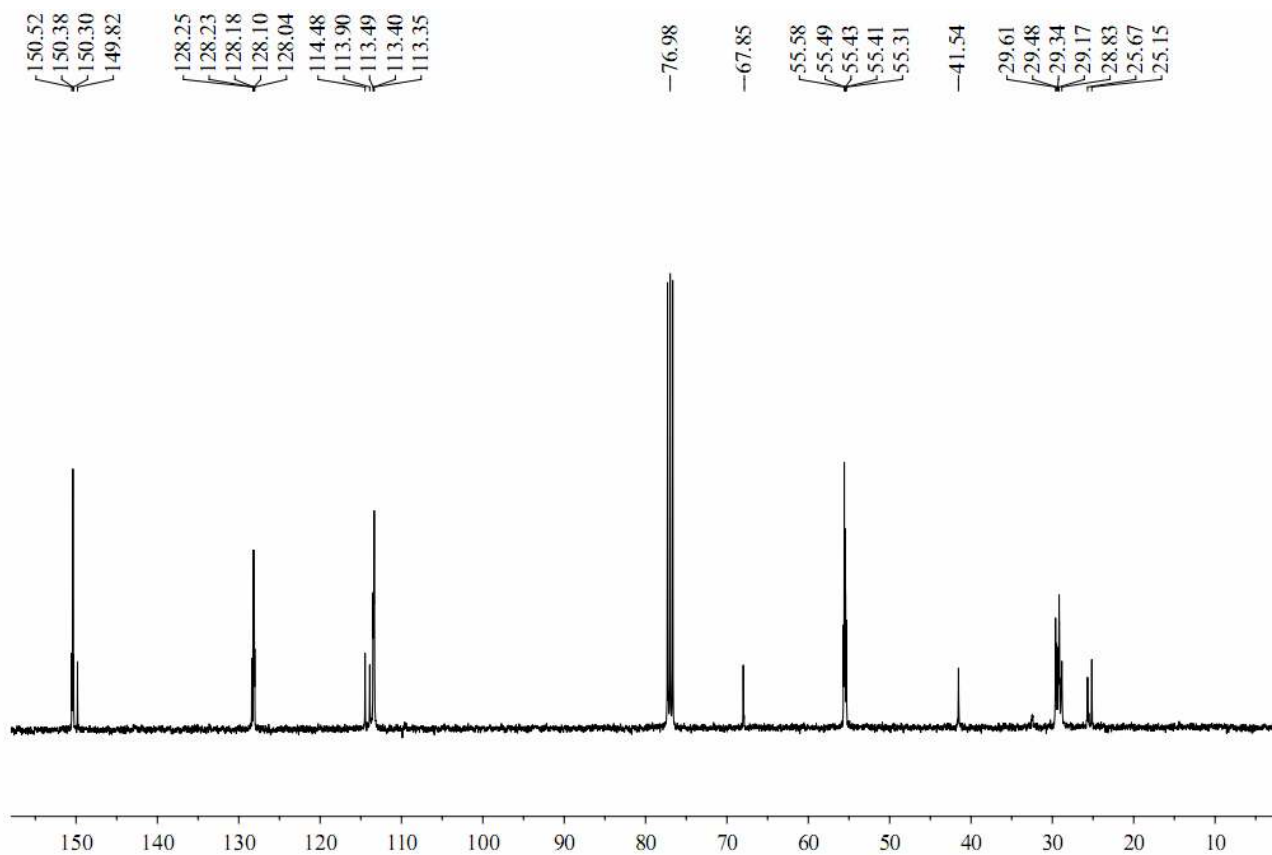


Fig. S3. ^{13}C NMR spectrum (100 MHz, chloroform-*d*, 25 °C) of **2** at 88 mM.

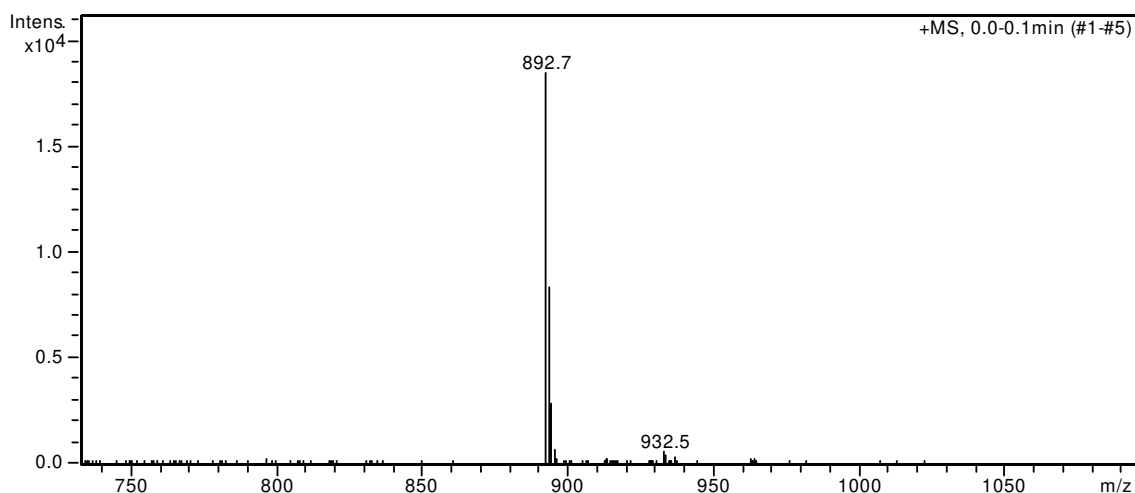
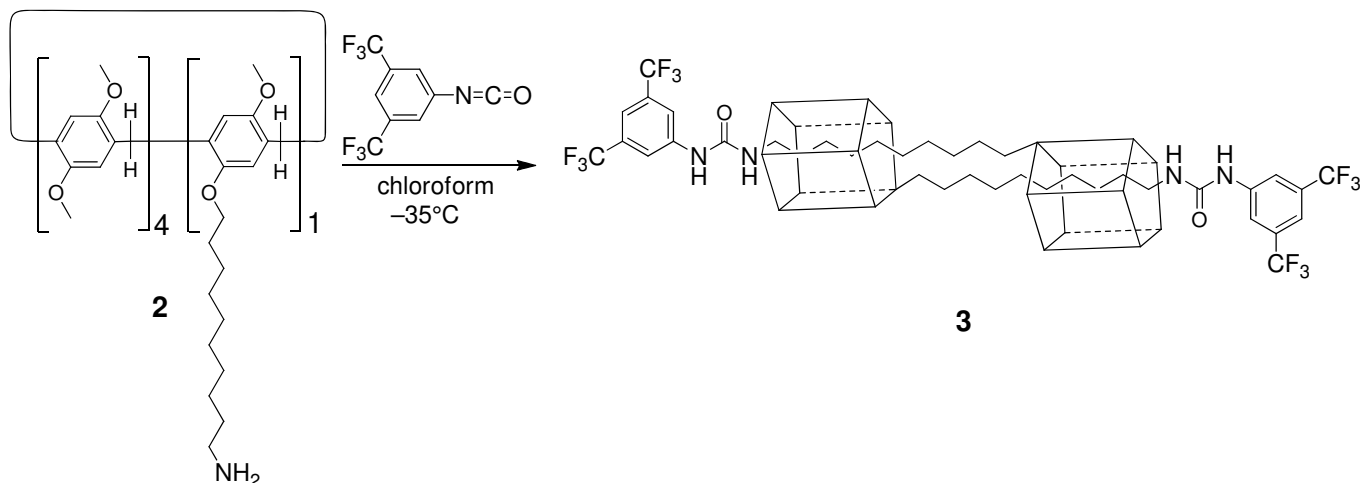


Fig. S4. Electrospray ionization mass spectrum of **2** in a mixture of chloroform and methanol. Assignment of the main peak: m/z 892.7 $[M + H]^+$ (100%).

4. Synthesis of **3**



To a solution of **2** (0.60 g, 0.67 mmol) in chloroform (10 mL), 3,5-bis(trifluoromethyl)phenyl isocyanate (0.71 g, 2.8 mmol) was added under nitrogen atmosphere. After stirring at -35 °C for 72 h, the reaction mixture was concentrated by rotary evaporation. The resulting residue was dissolved in CH_2Cl_2 (50 mL) and washed with H_2O (2×100 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to afford the crude product which was isolated by flash column chromatography using dichloromethane/petroleum ether (3:1). The fractions containing the product were combined and concentrated under vacuum to give **3** (0.23 g, 30%,) as a white solid. Mp 250.4 – 251.3 °C. The proton NMR spectrum of **3** is shown in Fig. S5. ^1H NMR (400 MHz, chloroform- d , 25 °C) δ (ppm): 8.02 (s, 2H), 7.48 (s, 1H), 7.05–6.94 (m, 5H), 6.93–6.83 (m, 5H), 4.00–3.65 (m, 39H), 2.31 (b, 1H), 2.04–1.87 (m, 2H), 1.58 (s, 2H), 1.48–1.36 (m, 2H), 1.25–1.14 (m, 2H), 0.82–0.70 (m, 2H), 0.50 (b, 2H), 0.15–0.00 (m, 2H), 1.32–1.54 (m, 2H), -2.00 (s, 2H). The ^{13}C NMR spectrum of copillar[5]arene **2** is shown in Fig. S6. The ^{13}C NMR (100 MHz, chloroform- d , 25 °C) δ (ppm): 152.54, 150.86, 149.77, 142.17, 132.15, 132.02, 131.82, 129.31, 129.03, 128.66, 128.47, 124.75, 122.04, 117.56, 114.93, 114.56, 114.42, 113.49, 113.23, 113.01, 68.69, 56.74, 56.48, 56.23, 55.34, 38.97, 31.25, 30.71, 30.49, 30.08, 28.84, 26.85, 26.17, 24.92. MALDI-TOF MS is

shown in Fig. S7: m/z 2315.9 $[M + Na]^+$ (100%). HRESIMS: m/z calcd for $[M + 2Na]^{2+}$ $C_{126}H_{144}F_{12}N_4O_{22}Na_2$, 1169.9946, found 1169.9835, error 9.5 ppm.

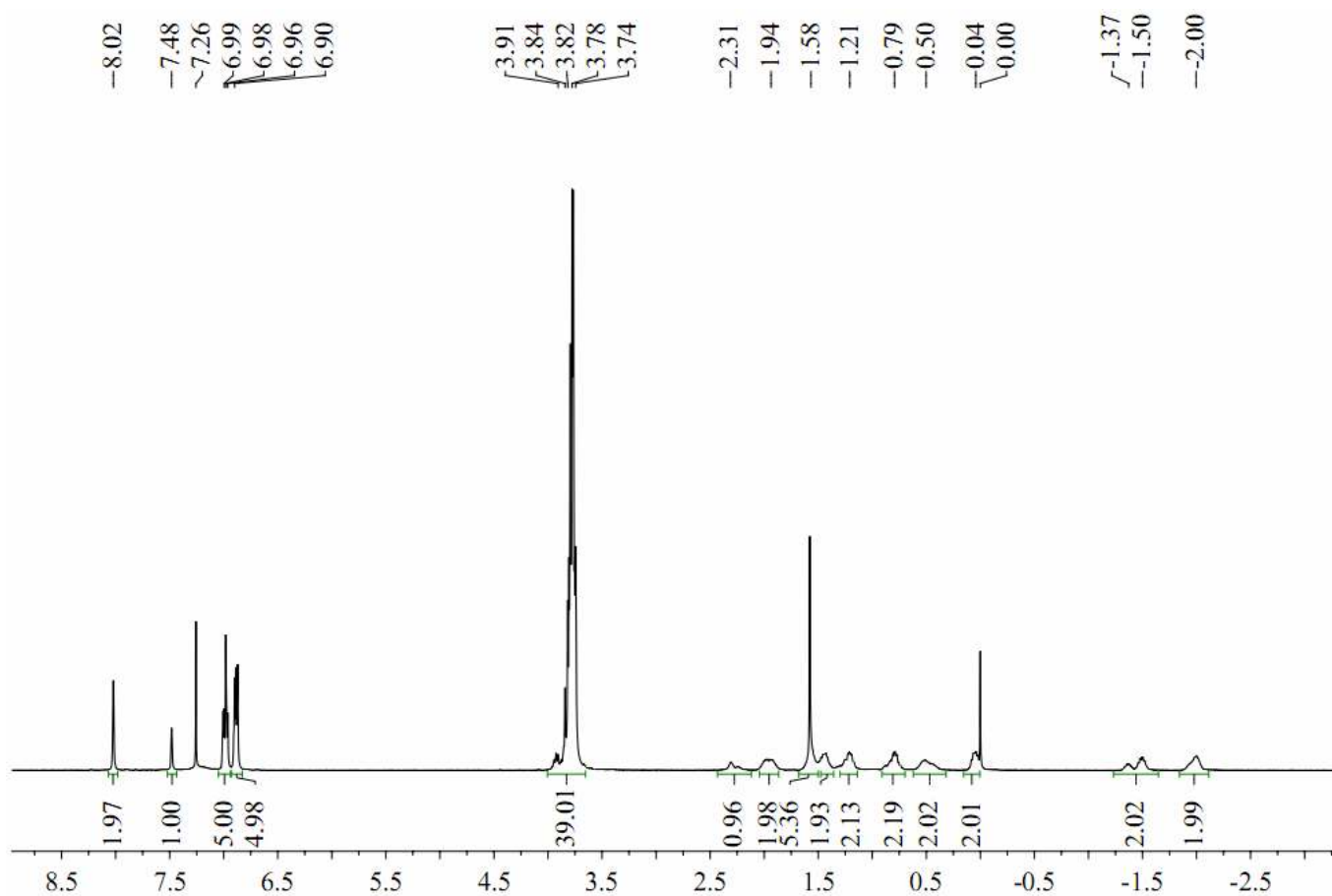


Fig. S5 1H NMR spectrum (400 MHz, chloroform-*d*, 25 °C) of **3**.

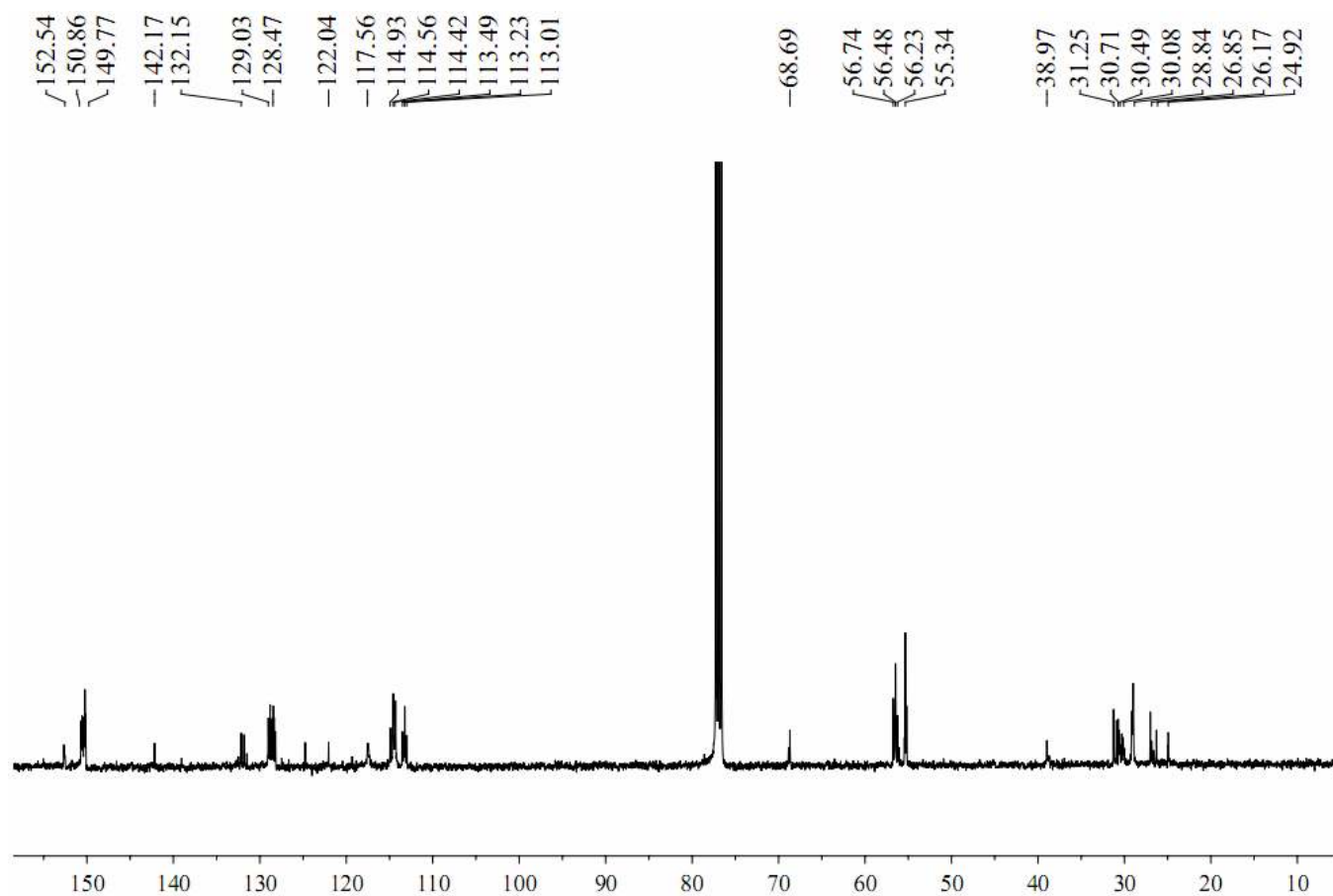


Fig. S6. ^{13}C NMR spectrum (100 MHz, chloroform-*d*, 25 °C) of **3**.

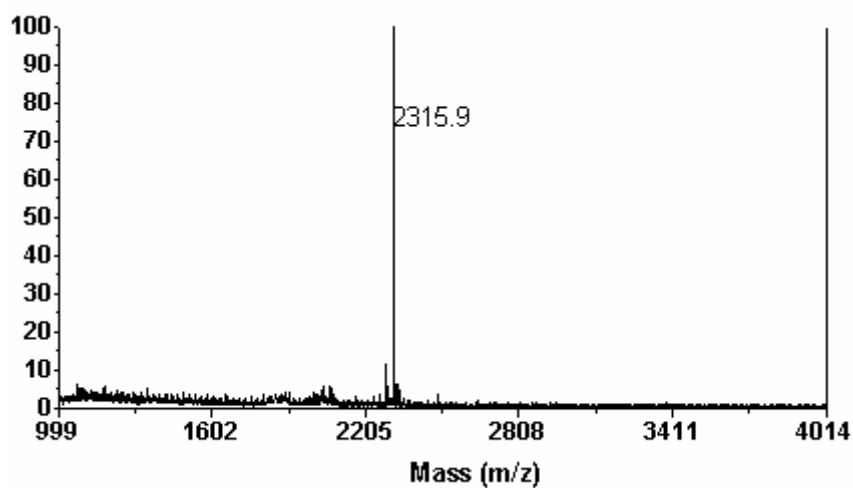
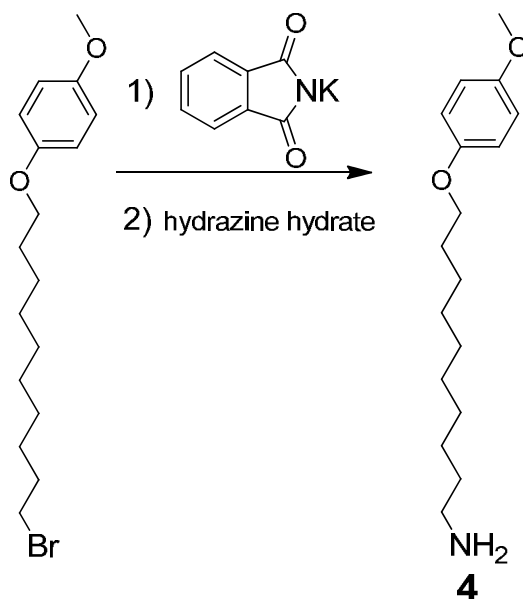


Fig. S7. MALDI-TOF mass spectrum of **3**. Assignment of the main peak: m/z 2315.9 $[\text{M} + \text{Na}]^+$ (100%).

5. Synthesis of **4**



A mixture of 1-(10-bromodecyloxy)-4-methoxybenzene **1**^{S1} (3.4 g, 10 mmol) and phthalimide potassium (2.0 g, 11 mmol) in 50 mL of DMF was stirred at 90 °C for 24 h under nitrogen atmosphere. Then DMF was removed by rotary evaporation. The resulting oil was dissolved in THF (40 mL), methanol (4 mL) and hydrazine hydrate (4 mL). After stirring at 50 °C for 24 h, the reaction mixture was concentrated by rotary evaporation. The resulting residue was dissolved in CH₂Cl₂ (200 mL) and washed with H₂O (2 × 100 mL). The organic layer was dried over anhydrous Na₂SO₄ and evaporated to afford the crude product, which was isolated by flash column chromatography using dichloromethane/methanol (10:1). The fractions containing the product were combined and concentrated under vacuum to give **4** (1.3 g, 46%) as a white solid. Mp 84.6–85.2 °C The proton NMR spectrum of **4** is shown in Fig. S8. ¹H NMR (400 MHz, chloroform-*d*, 25 °C) δ (ppm): 6.82 (s, 4H), 3.89 (t, *J* = 6.6 Hz, 2H), 3.75 (s, 3H), 2.67 (t, *J* = 6.9 Hz, 2H), 1.82–1.68 (m, 2H), 1.58 (s, 2H), 1.48–1.38 (m, *J* = 7.0 Hz, 4H), 1.30 (s, 10H). The ¹³C NMR spectrum of **4** is shown in Fig. S9. The ¹³C NMR (100 MHz, chloroform-*d*, 25 °C) δ (ppm): ¹³C NMR (101 MHz, CDCl₃) δ 153.54, 153.19, 115.30, 114.49, 68.52, 55.59, 42.07, 33.59, 29.44, 29.41, 29.37, 29.29, 26.78, 25.94. LRESIMS is shown in Fig. S10: *m/z* 280.2 [M + H]⁺ (100%). HRESIMS: *m/z* calcd for [M]⁺ C₁₇H₂₉NO₂, 279.2198, found 271.2198, error 0 ppm.

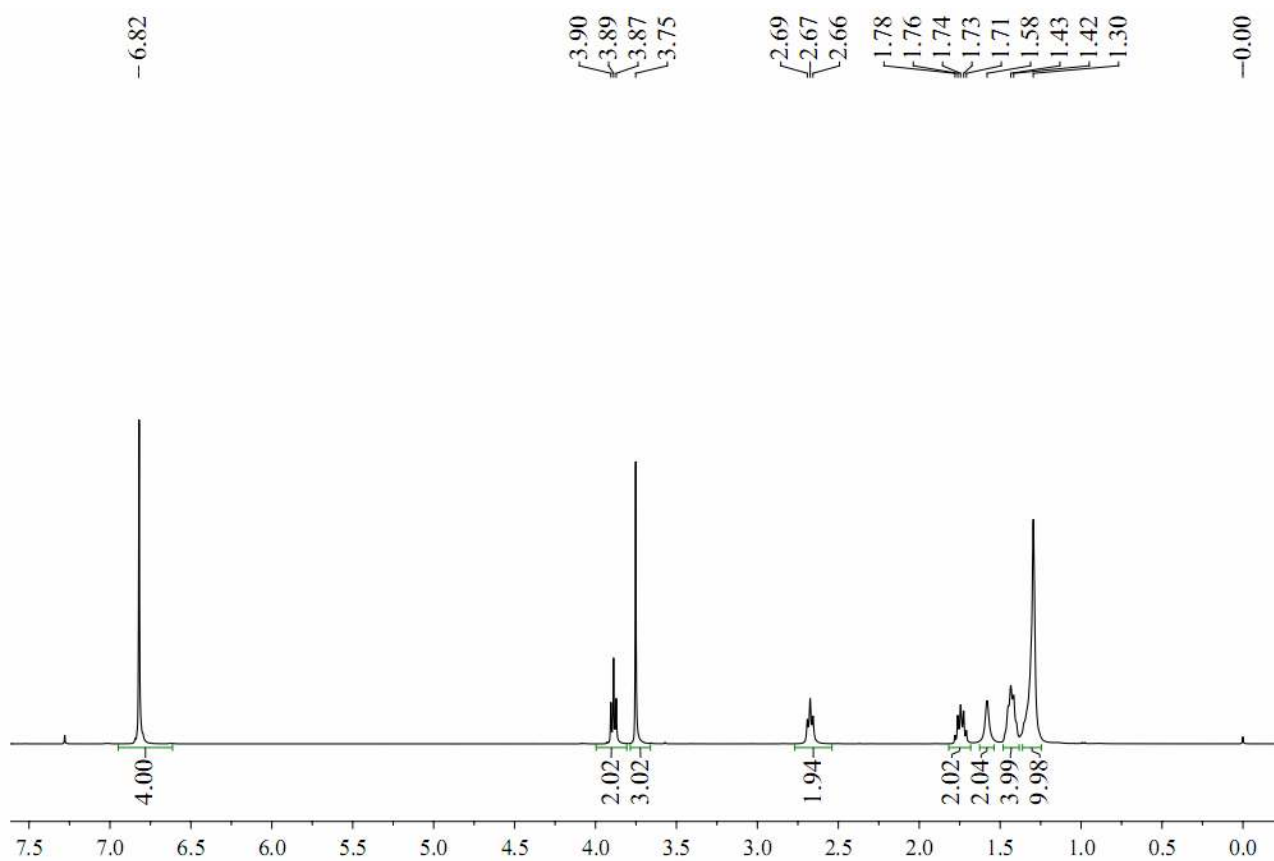


Fig. S8 ^1H NMR spectrum (400 MHz, chloroform-*d*, 25 °C) of **4**.

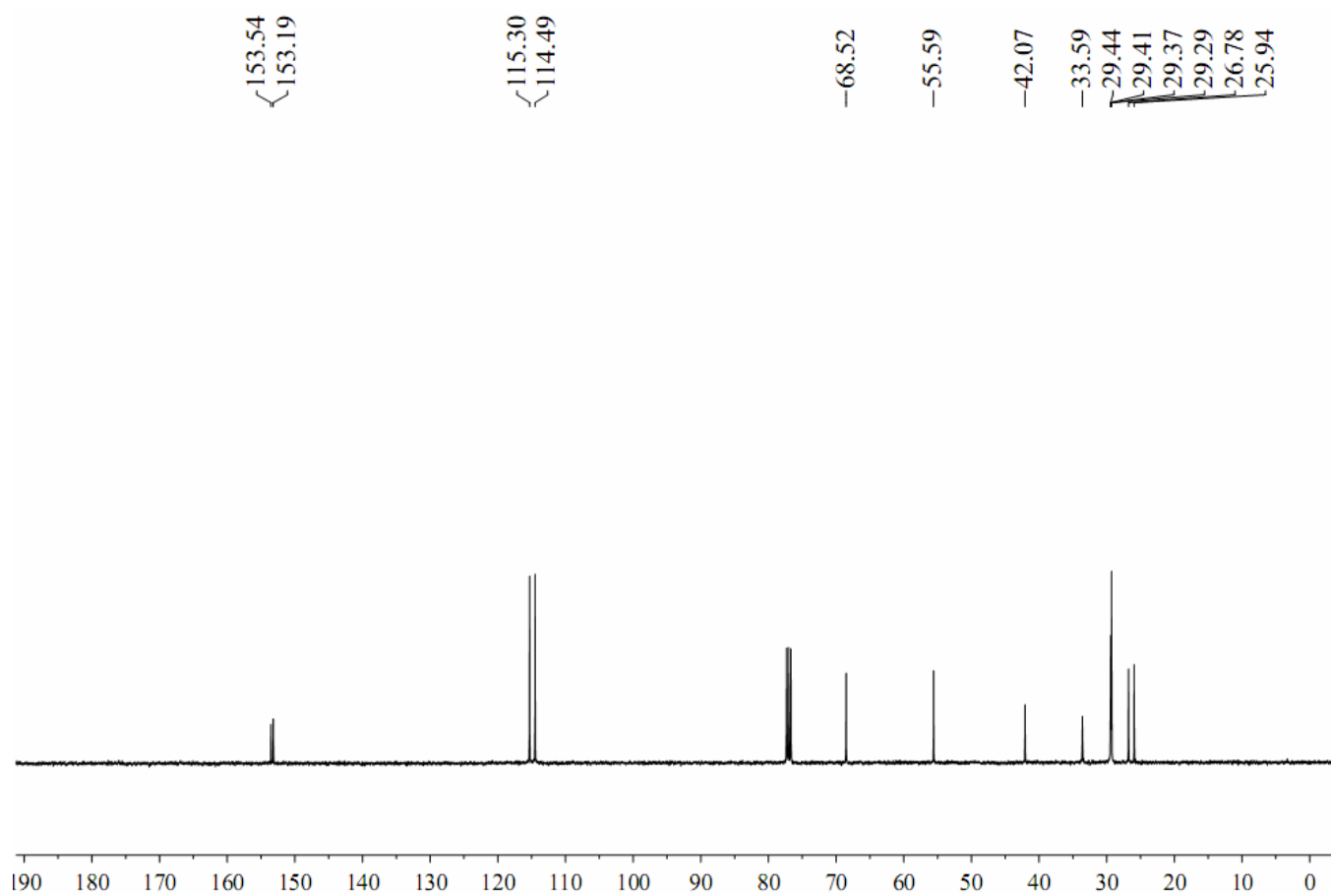


Fig. S9. ^{13}C NMR spectrum (100 MHz, chloroform-*d*, 25 °C) of **4**.

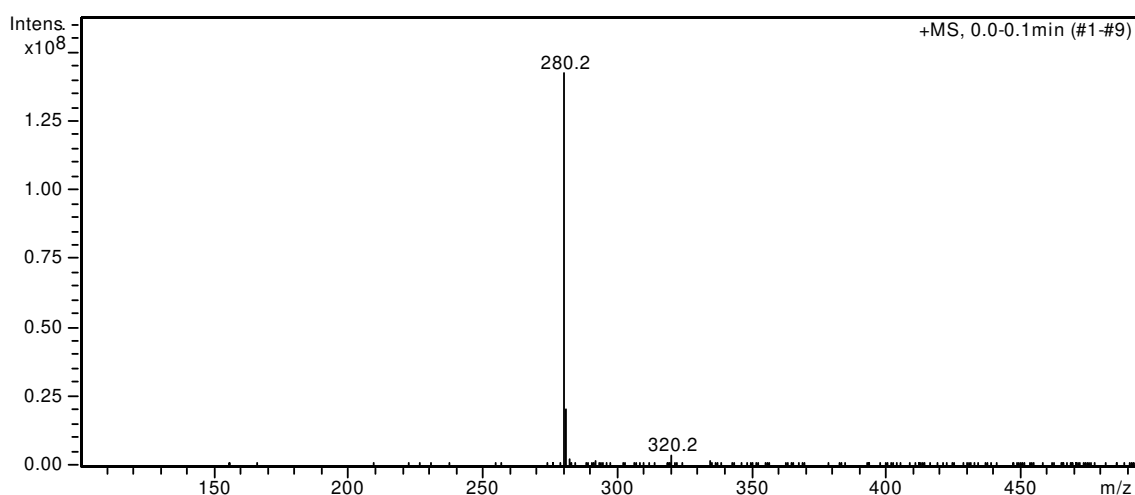
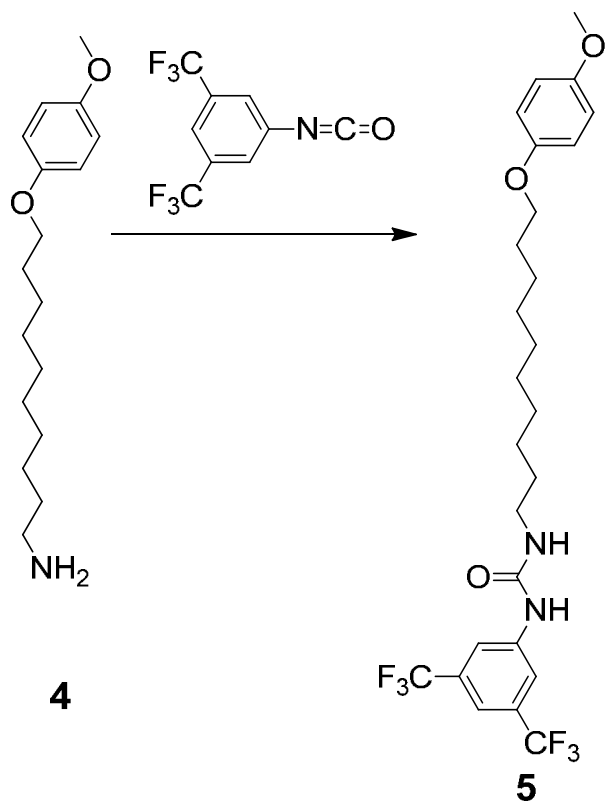


Fig. S10. Electrospray ionization mass spectrum of **4** in a mixture of chloroform and methanol. Assignment of the main peak: m/z 280.2 $[M + H]^+$ (100%).

6. Synthesis of **5**



To a solution of **4** (0.79 g, 2.83 mmol) in chloroform (100 mL), 3,5-bis(trifluoromethyl)phenyl isocyanate (0.87 g, 3.4 mmol) was added under nitrogen atmosphere. After stirring at room temperature for 48 h, the reaction mixture was concentrated by rotary evaporation. The resulting residue was dissolved in CH_2Cl_2 (50 mL) and washed with H_2O (2×100 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to afford the crude product which was isolated by flash column chromatography using dichloromethane/petroleum ether (2:1). The fractions containing the product were combined and concentrated under vacuum to give **5** (0.95 g, 63%) as a white solid. Mp 80.5–81.4 °C. The proton NMR spectrum of **5** is shown in Fig. S11. ^1H NMR (400 MHz,

chloroform-*d*, 25 °C) δ (ppm): 7.84 (s, 2H), 7.47 (s, 1H), 6.88 (s, 1H), 6.83 (s, 4H), 4.85 (t, $J = 6.4$ Hz, 1H), 3.91 (t, $J = 6.5$ Hz, 2H), 3.77 (s, 3H), 3.31–3.20 (m, 2H), 1.80–1.69 (m, 2H), 1.55–1.48 (m, 2H), 1.46–1.39 (m, 6.7 Hz, 2H), 1.38–1.22 (m, 10H). The ^{13}C NMR spectrum of **5** is shown in Fig. S12. The ^{13}C NMR (100 MHz, chloroform-*d*, room temperature) δ (ppm): 155.58, 153.63, 153.15, 140.51, 132.25, 131.92, 124.36, 121.65, 118.35, 115.44, 114.62, 68.69, 55.67, 40.27, 29.76, 29.29, 29.25, 29.19, 29.11, 26.73, 25.89. LRESIMS is shown in Fig. S13: m/z 535.2 $[\text{M} + \text{H}]^+$ (100%). HRESIMS: m/z calcd for $[\text{M}]^+ \text{C}_{26}\text{H}_{32}\text{F}_2\text{N}_3\text{O}_6$, 534.2318, found 534.2317, error 0.1 ppm.

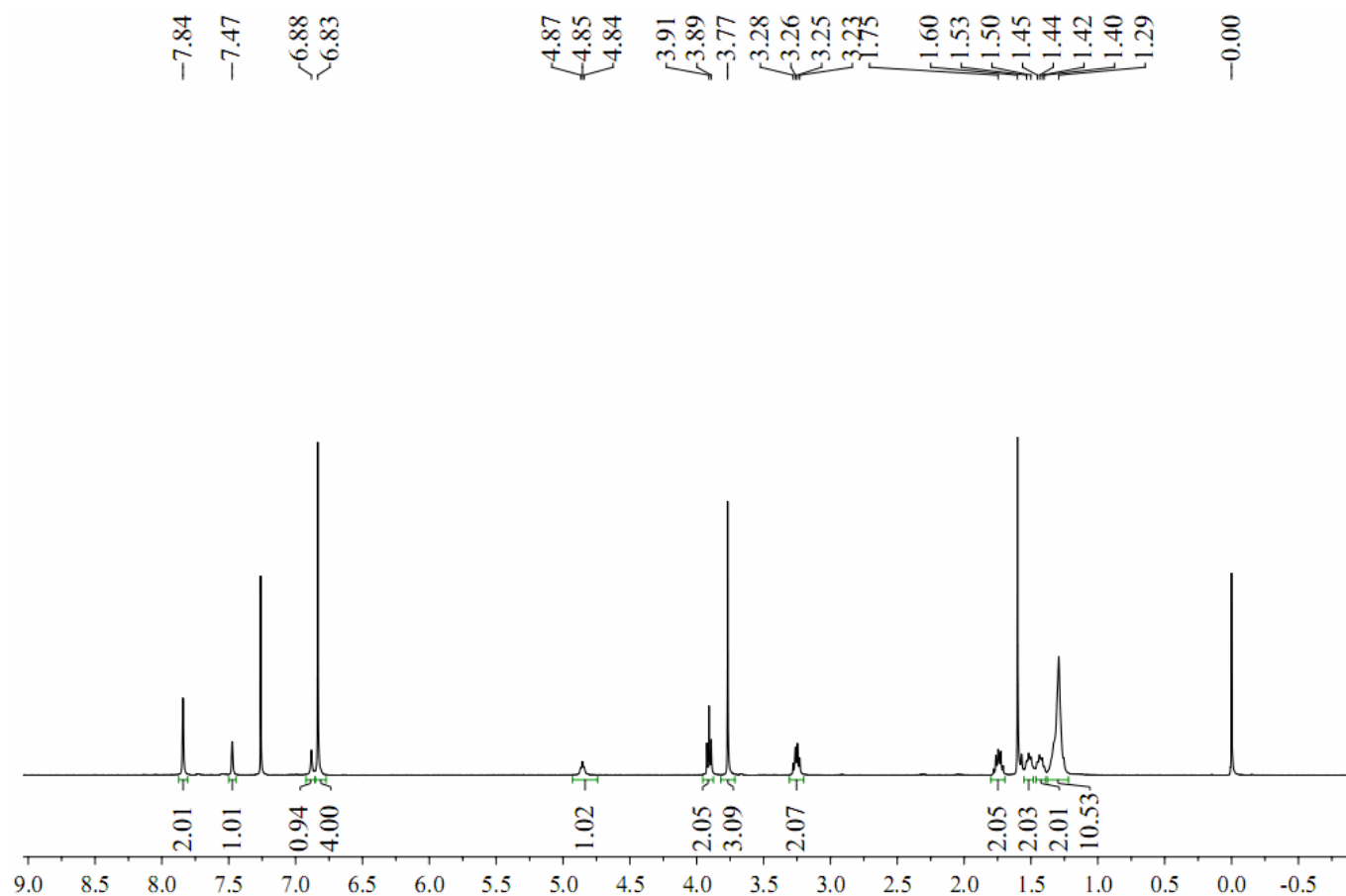


Fig. S11 ^1H NMR spectrum (400 MHz, chloroform-*d*, 25 °C) of **5**.

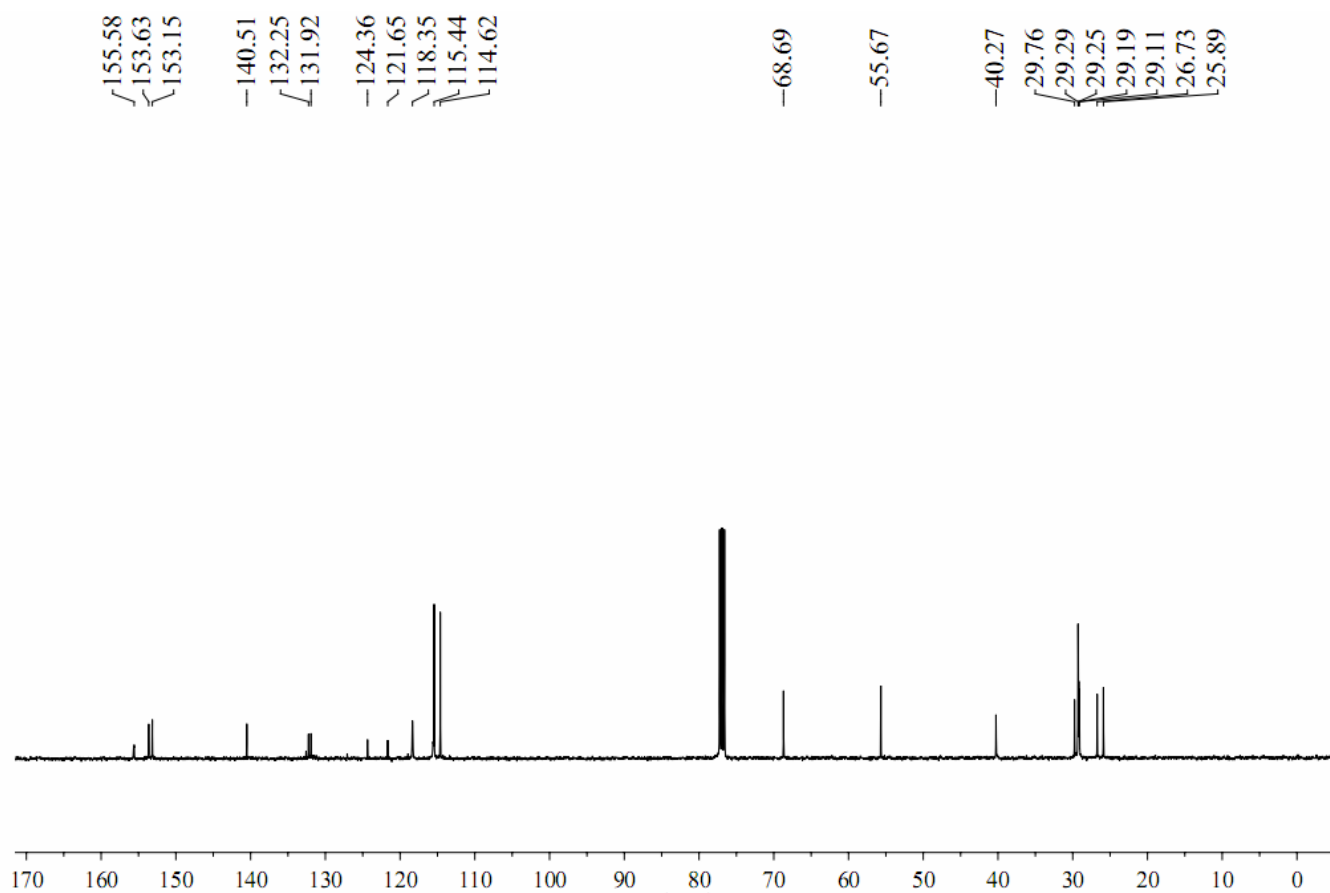


Fig. S12. ^{13}C NMR spectrum (100 MHz, chloroform-*d*, 25 °C) of **5**.

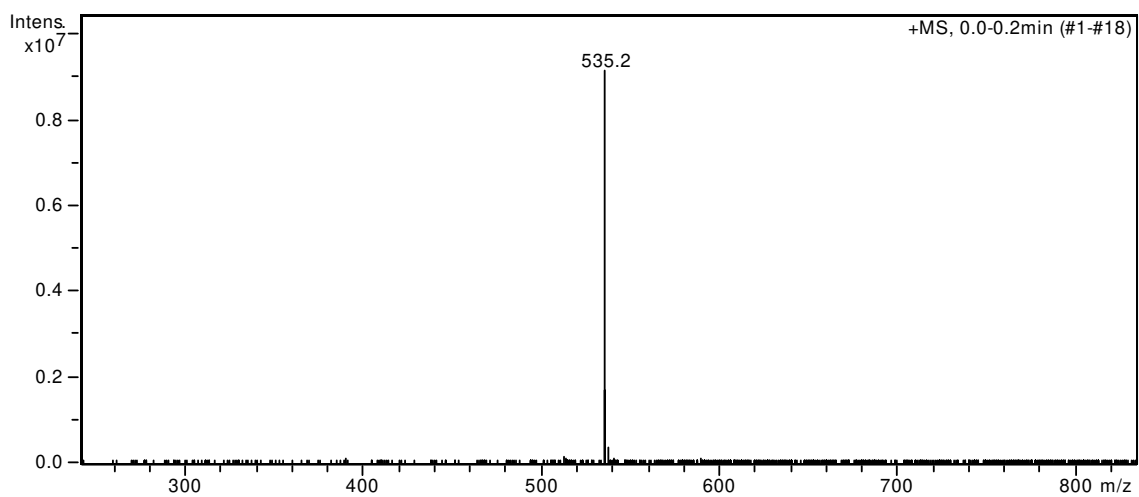


Fig. S13. Electrospray ionization mass spectrum of **5** in a mixture of chloroform and methanol. Assignment of the main peak: m/z 535.2 $[\text{M} + \text{H}]^+$ (100%).

7. Partial COSY spectrum of **2** in chloroform-*d*

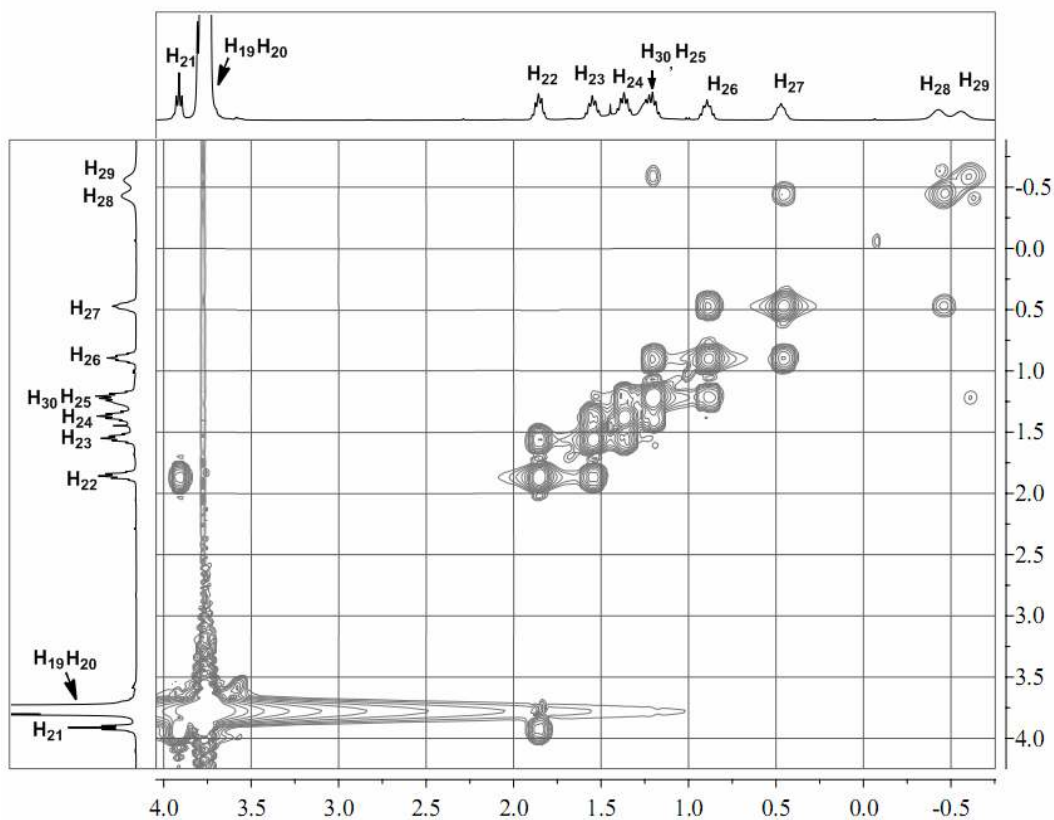


Fig. S14. Partial COSY spectrum (400 MHz, chloroform-*d*, 25 °C) of **2**.

8. ^1H NMR spectra of **2** and **4** in chloroform-*d*

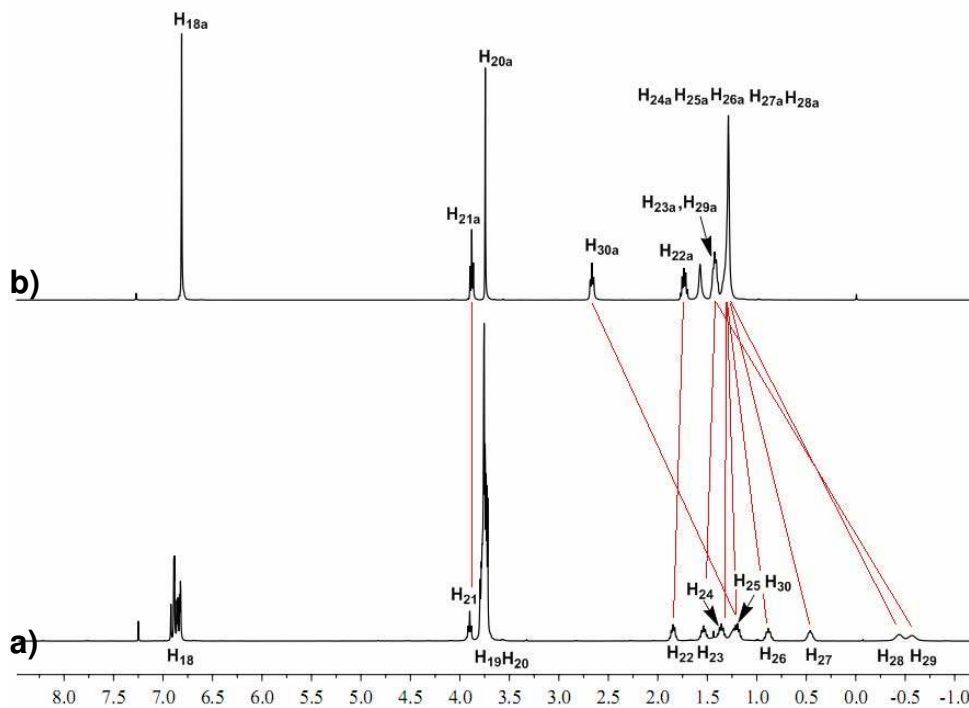


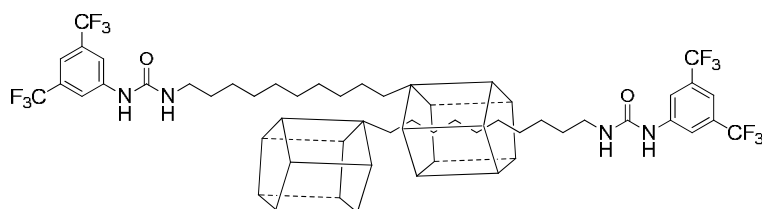
Fig. S15. ^1H NMR spectra (400 MHz, chloroform-*d*, 25 °C) of **2** (a) and **4** (b).

9. $\Delta\delta$ of decyl protons on **2** compared with **4** in chloroform-*d*

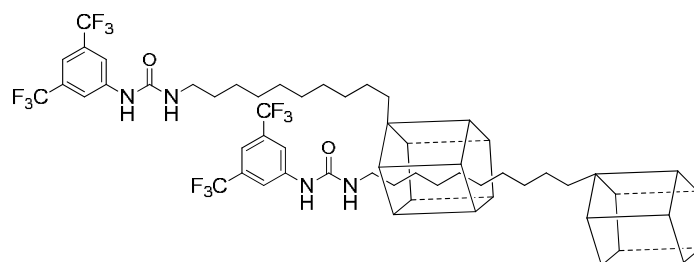
protons of 4	H _{21a}	H _{22a}	H _{23a}	H _{24a}	H _{25a}	H _{26a}	H _{27a}	H _{28a}	H _{29a}	H _{30a}
δ	3.89	1.76	1.43	1.30	1.30	1.30	1.30	1.30	1.43	2.67
protons of 2	H ₂₁	H ₂₂	H ₂₃	H ₂₄	H ₂₅	H ₂₆	H ₂₇	H ₂₈	H ₂₉	H ₃₀
δ	3.91	1.86	1.55	1.37	1.21	0.89	0.47	-0.43	-0.55	1.21
$\Delta\delta$	0.02	0.10	0.12	0.07	-0.09	-0.41	-0.83	-1.73	-1.98	-1.46

Table S1. Chemical shift changes of decyl protons on **2** compared with **4** in chloroform-*d*.

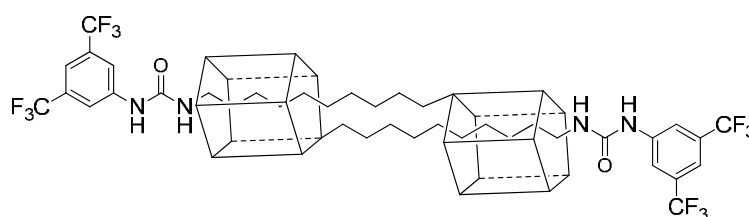
10. The three possible structure of **3** from MALDI-TOF mass spectrometry



a singly threaded rotaxane



a singly threaded rotaxane



a doubly threaded rotaxane dimer

Fig. S16. The three possible structures of **3** from MALDI-TOF mass spectrometry.

11. COSY spectrum of 5 in chloroform-d

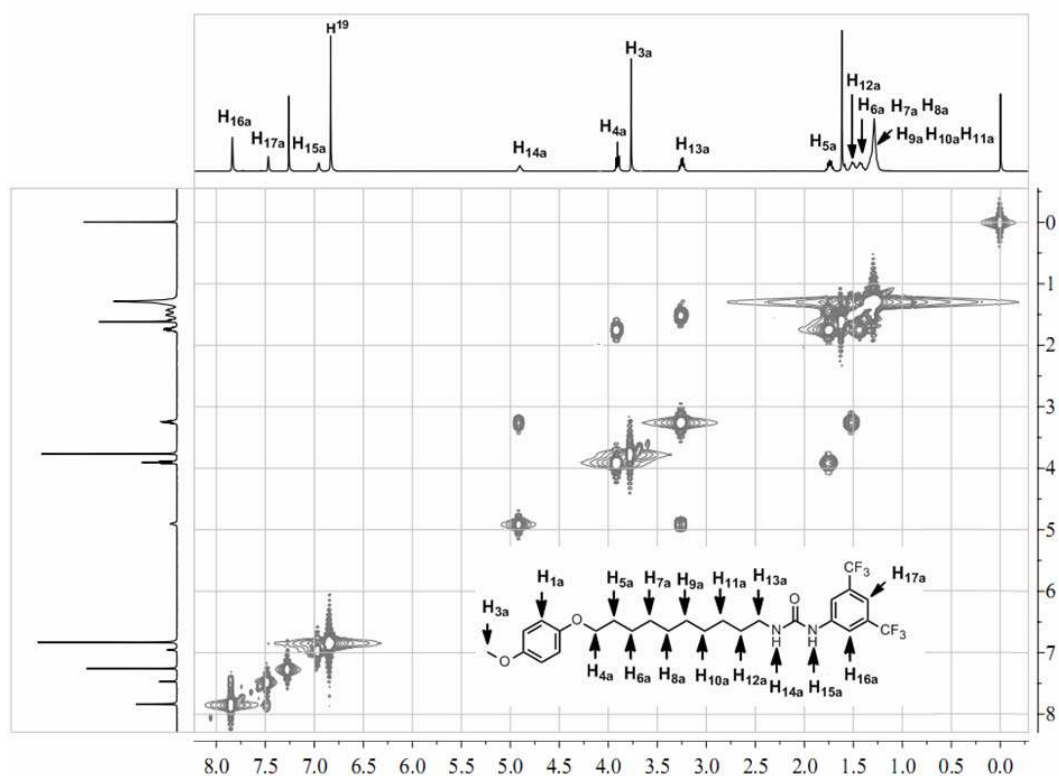


Fig. S17. COSY spectrum (400 MHz, chloroform-d, 25 °C) of 5.

12. NOESY spectrum of 3 in chloroform-d

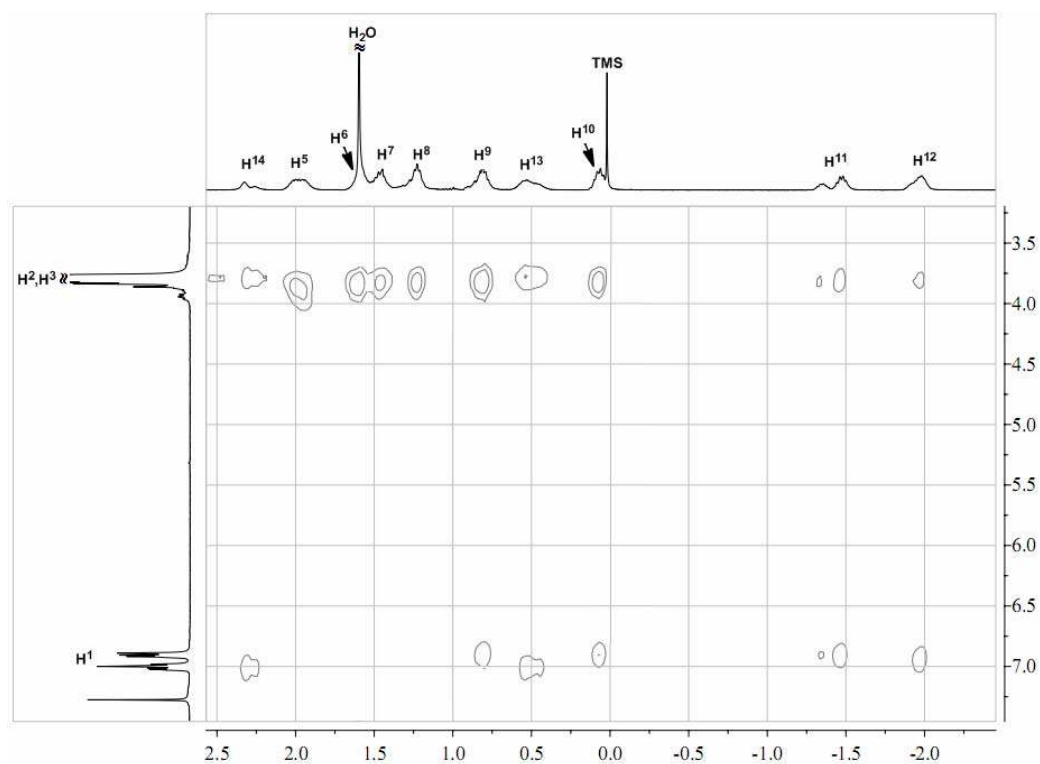


Fig. S18. NOESY spectrum (400 MHz, chloroform-d, 25 °C) of 3.

13. COSY spectrum of 3

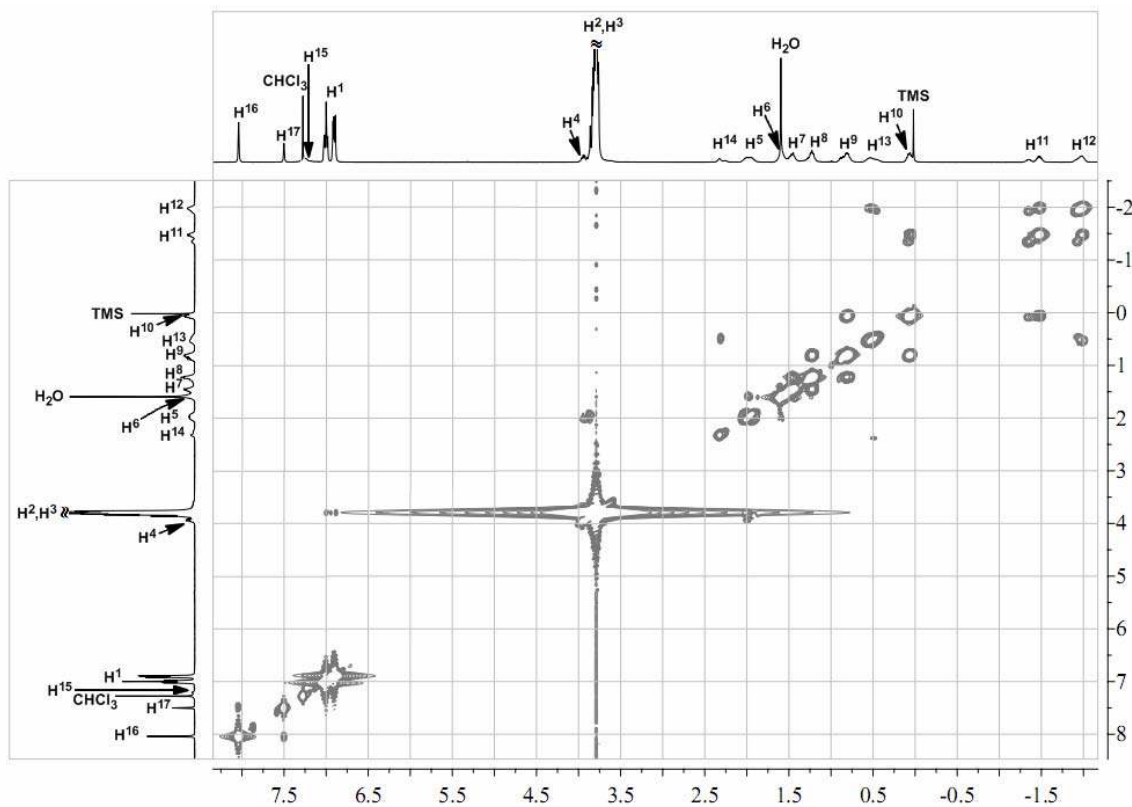


Fig. S19. COSY spectrum (400 MHz, chloroform-*d*, 25 °C) of 3.

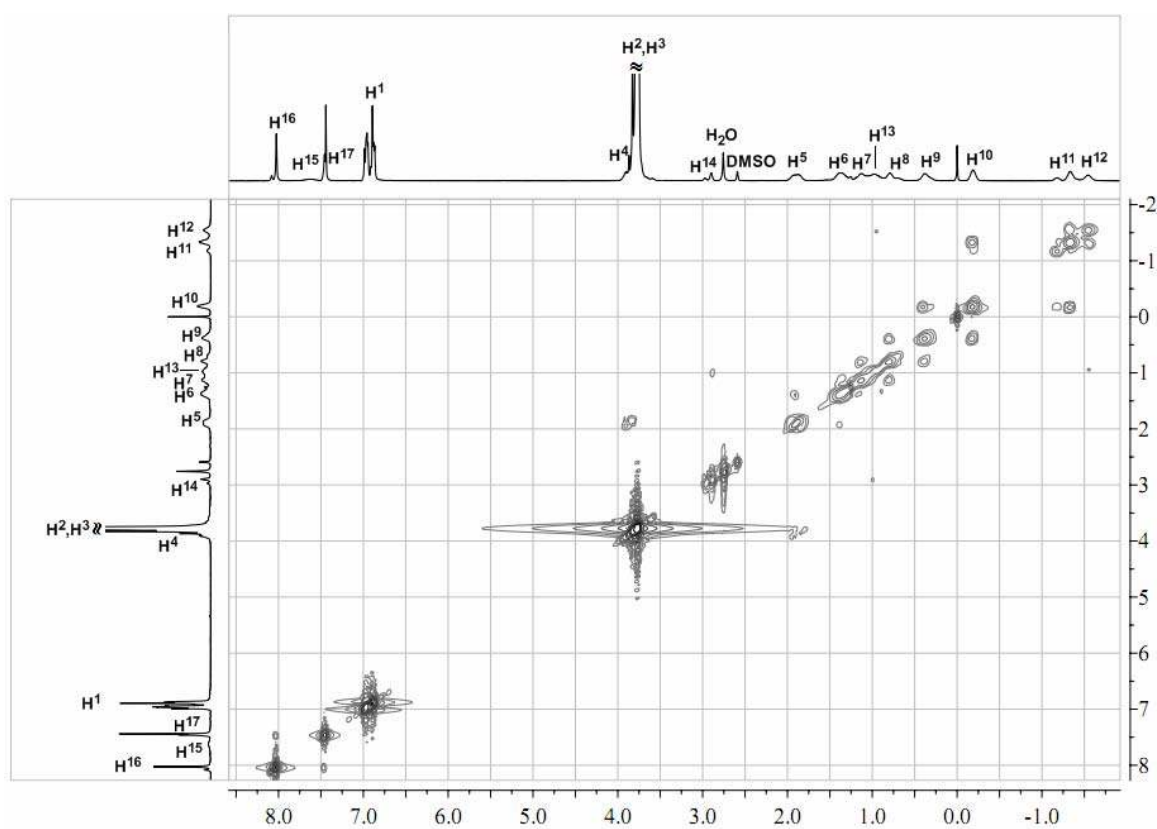


Fig. S20. COSY spectrum (400 MHz, chloroform-*d*/DMSO-*d*₆=10/1, 25 °C) of 3.

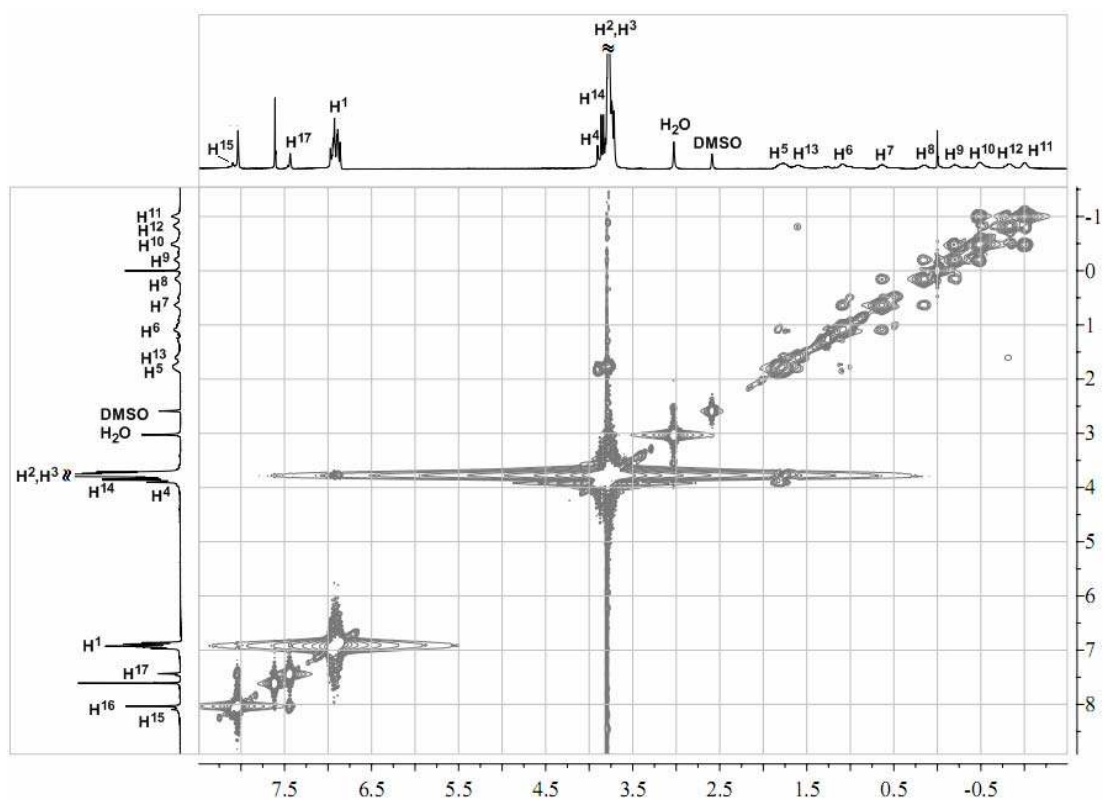


Fig. S21. COSY spectrum (400 MHz, chloroform-*d*/DMSO-*d*₆=5/1, 25 °C) of **3**.

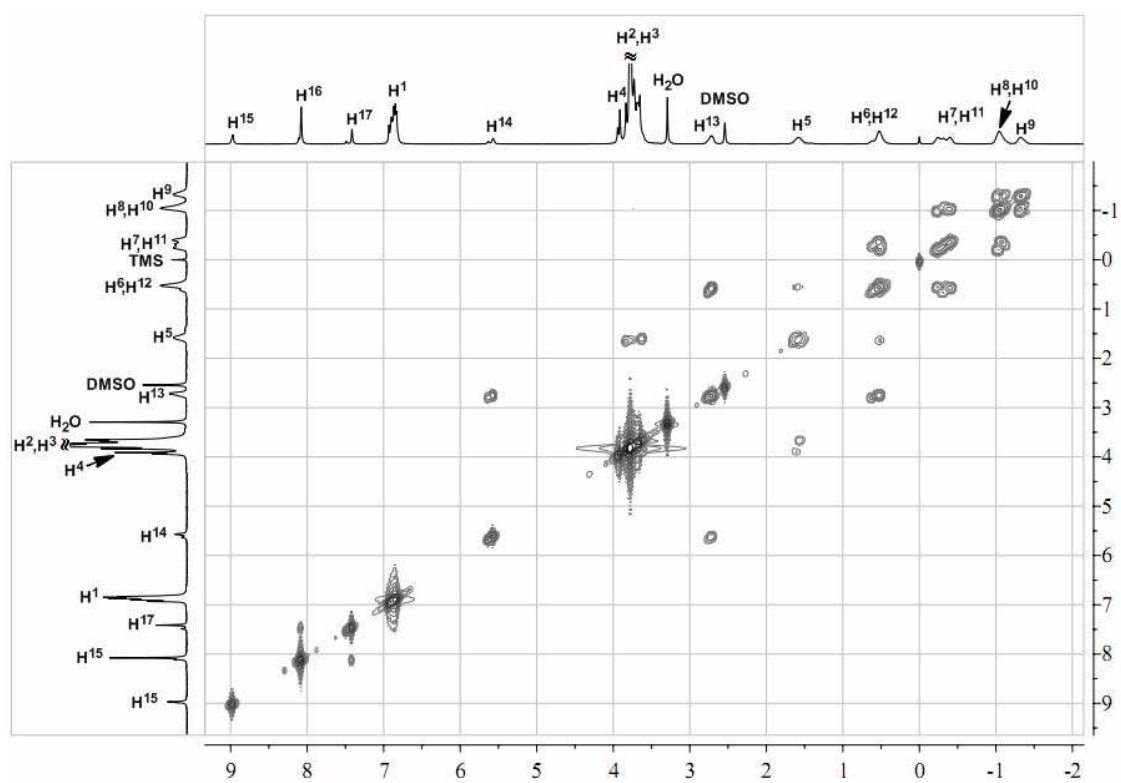


Fig. S22. COSY spectrum (400 MHz, chloroform-*d*/DMSO-*d*₆=1/1, 25 °C) of **3**.

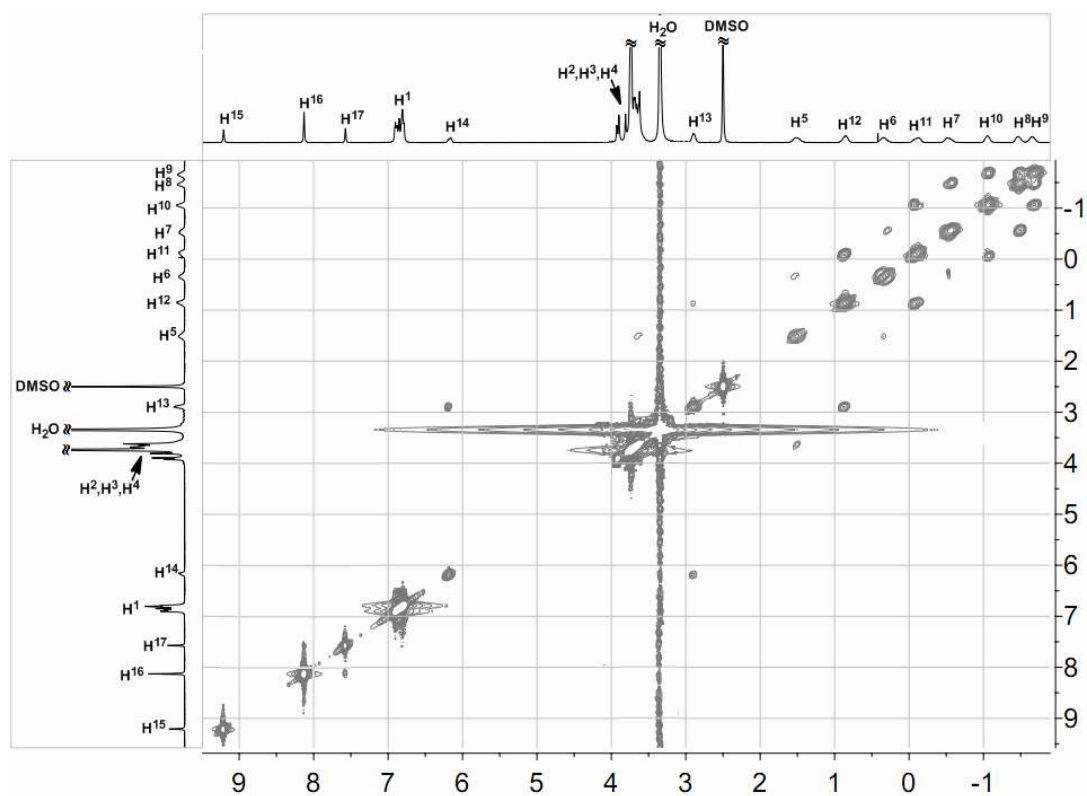


Fig. S23. COSY spectrum (400 MHz, DMSO- d_6 , 25 °C) of **3**

14. ^1H NMR spectra of **3** with and without trifluoroacetate anion in chloroform- d

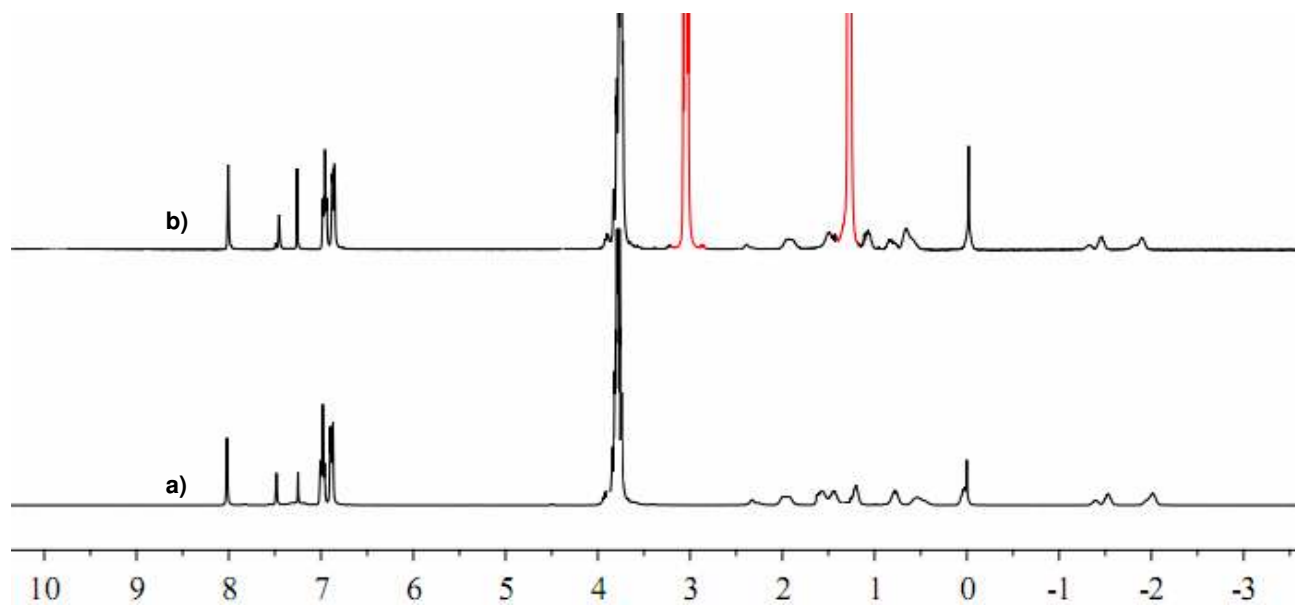


Fig. S24. ^1H NMR spectrum (400 MHz, chloroform- d , 25 °C) of **3** (a) and **3** with 4 equiv of triethylammonium trifluoroacetate (b). The red peaks are signals from triethylammonium trifluoroacetate.

15. Partial ^1H NMR spectra of **5** in different solvent mixtures

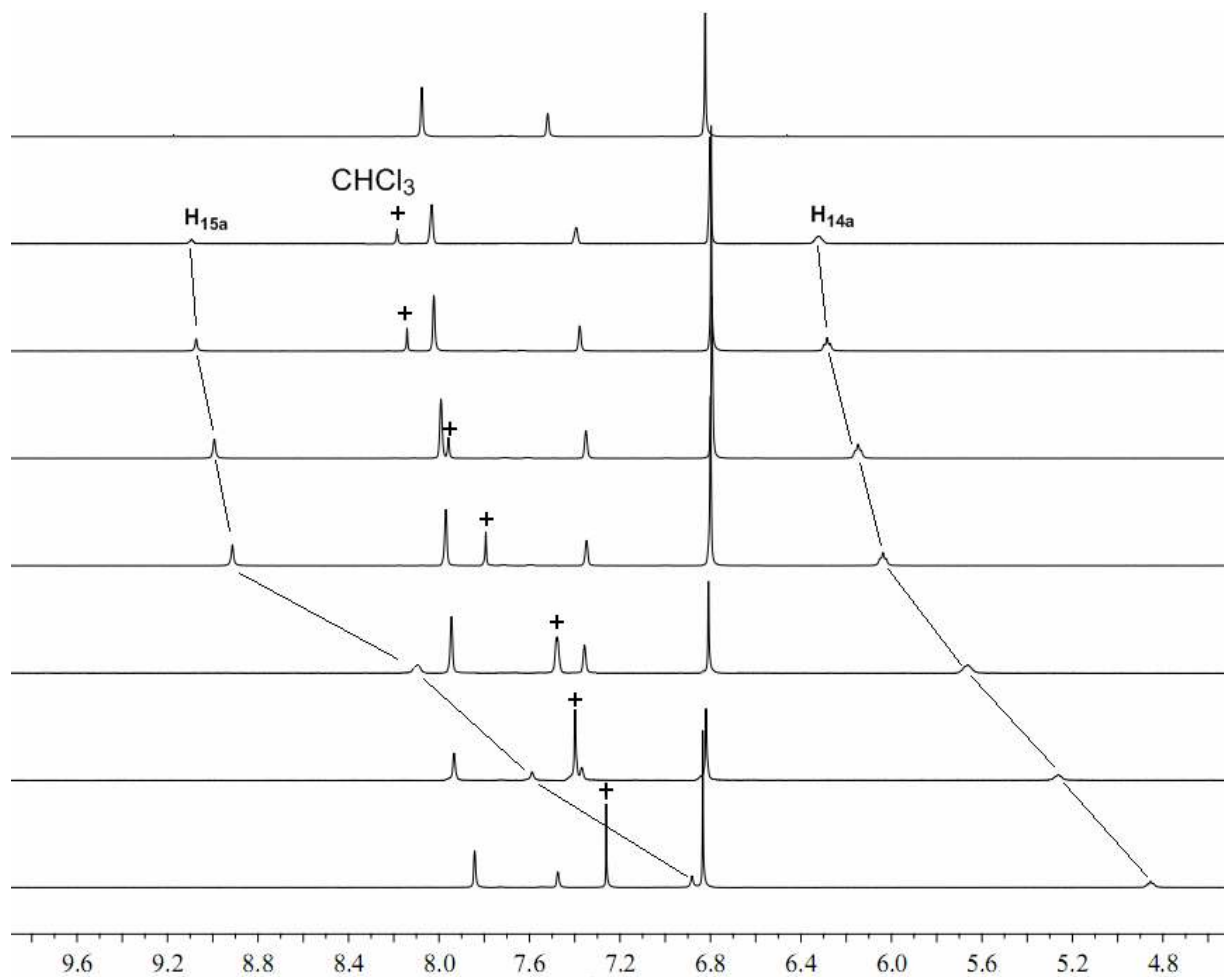


Fig. S25. Partial ^1H NMR spectra (400 MHz, 25 °C) of (a) **5** in chloroform-*d*; (b) **5** in 10:1 (v/v) chloroform-*d*/DMSO-*d*₆; (c) **5** in 5:1 chloroform-*d*/DMSO-*d*₆; (d) **5** in 2:1 chloroform-*d*/DMSO-*d*₆; (e) **5** in 1:1 chloroform-*d*/DMSO-*d*₆; (f) **5** in 1:2 chloroform-*d*/DMSO-*d*₆; (g) **5** in 1:4 chloroform-*d*/DMSO-*d*₆; (h) **5** in DMSO-*d*₆. The numbers correspond to the proton assignments indicated in Scheme 1.

16. Chemical shifts of protons on **5** in different solvent mixtures

Number	a	b	c	d	e	f	g	h
H _{4a}	3.91	3.90	3.89	3.89	3.88	3.88	3.87	3.86
H _{5a}	1.75	1.74	1.74	1.72	1.71	1.69	1.68	1.66
H _{6a}	1.43	1.43	1.42	1.41	1.40	1.40	1.39	1.38
H _{7a}	1.29	1.29	1.29	1.29	1.29	1.28	1.28	1.28
H _{8a}	1.29	1.29	1.29	1.29	1.29	1.28	1.28	1.28
H _{9a}	1.29	1.29	1.29	1.29	1.29	1.28	1.28	1.28
H _{10a}	1.29	1.29	1.29	1.29	1.29	1.28	1.28	1.28
H _{11a}	1.29	1.29	1.29	1.29	1.29	1.28	1.28	1.28
H _{12a}	1.52	1.51	1.51	1.50	1.48	1.47	1.47	1.44
H _{13a}	3.26	3.23	3.21	3.20	3.15	3.14	3.12	3.09
H _{14a}	4.85	5.28	5.68	6.04	6.15	6.28	6.32	
H _{15a}	6.88	7.56	8.08	8.91	8.99	9.07	9.10	

Table S2. Chemical shifts of the decyl protons of **5** in different solvent mixtures. (a) chloroform-*d*; (b) 10:1 chloroform-*d*/DMSO-*d*₆ v/v; (c) 5:1 chloroform-*d*/DMSO-*d*₆ v/v; (d) 2:1 chloroform-*d*/DMSO-*d*₆ v/v; (e) 1:1 chloroform-*d*/DMSO-*d*₆ v/v; (f) 1:2 chloroform-*d*/DMSO-*d*₆ v/v; (g) 1:4 chloroform-*d*/DMSO-*d*₆ v/v; (h) DMSO-*d*₆. As the polarity of the solvent increased, the peak areas of H_{14a} and H_{15a} decreased. When in DMSO-*d*₆, the peaks from H_{14a} and H_{15a} can't be found.

17. $\Delta\delta$ of protons on **3** compared with **5** in different solvent mixtures

Number	a	b	c	d	e	f	g	h
H ₄	0	0.01	0	0.02	-0.02	0	0.02	0.03
H ₅	0.19	0.15	0.08	-0.11	-0.13	-0.15	-0.15	-0.16
H ₆	0.15	-0.05	-0.34	-0.85	-0.89	-0.98	-1	-1.03
H ₇	0.16	-0.16	-0.65	-1.44	-1.55	-1.64	-1.7	-1.81
H ₈	-0.08	-0.5	-1.14	-2.32	-2.4	-2.59	-2.63	-2.74
H ₉	-0.5	-0.91	-1.49	-2.5	-2.67	-2.84	-2.92	-2.94
H ₁₀	-1.25	-1.48	-1.78	-2.18	-2.4	-2.46	-2.42	-2.34
H ₁₁	-2.74	-2.61	-2.29	-1.77	-1.69	-1.56	-1.54	-1.41
H ₁₂	-3.52	-3.06	-2.34	-1.65	-0.96	-0.77	-0.69	-0.59
H ₁₃	-2.76	-2.25	-1.6	-0.57	-0.43	-0.37	-0.28	-0.09
H ₁₄	-2.55	-2.38	-1.9	-0.67	-0.47	-0.42	-0.28	
H ₁₅	0.38	0.06	0.01	-0.01	0.06	0.03	0.08	

Table S3. $\Delta\delta$ of protons on **3** compared with **5** in different solvents mixtures. (a) chloroform-*d*; (b) 10:1 chloroform-*d*/DMSO-*d*₆ v/v; (c) 5:1 chloroform-*d*/DMSO-*d*₆ v/v; (d) 2:1 chloroform-*d*/DMSO-*d*₆ v/v; (e) 1:1 chloroform-*d*/DMSO-*d*₆ v/v; (f) 1:2 chloroform-*d*/DMSO-*d*₆ v/v; (g) 1:4 chloroform-*d*/DMSO-*d*₆ v/v; (h) DMSO-*d*₆.

18. Upfield $\Delta\delta$ of decyl protons on **3** compared with **5** in different solvent mixtures

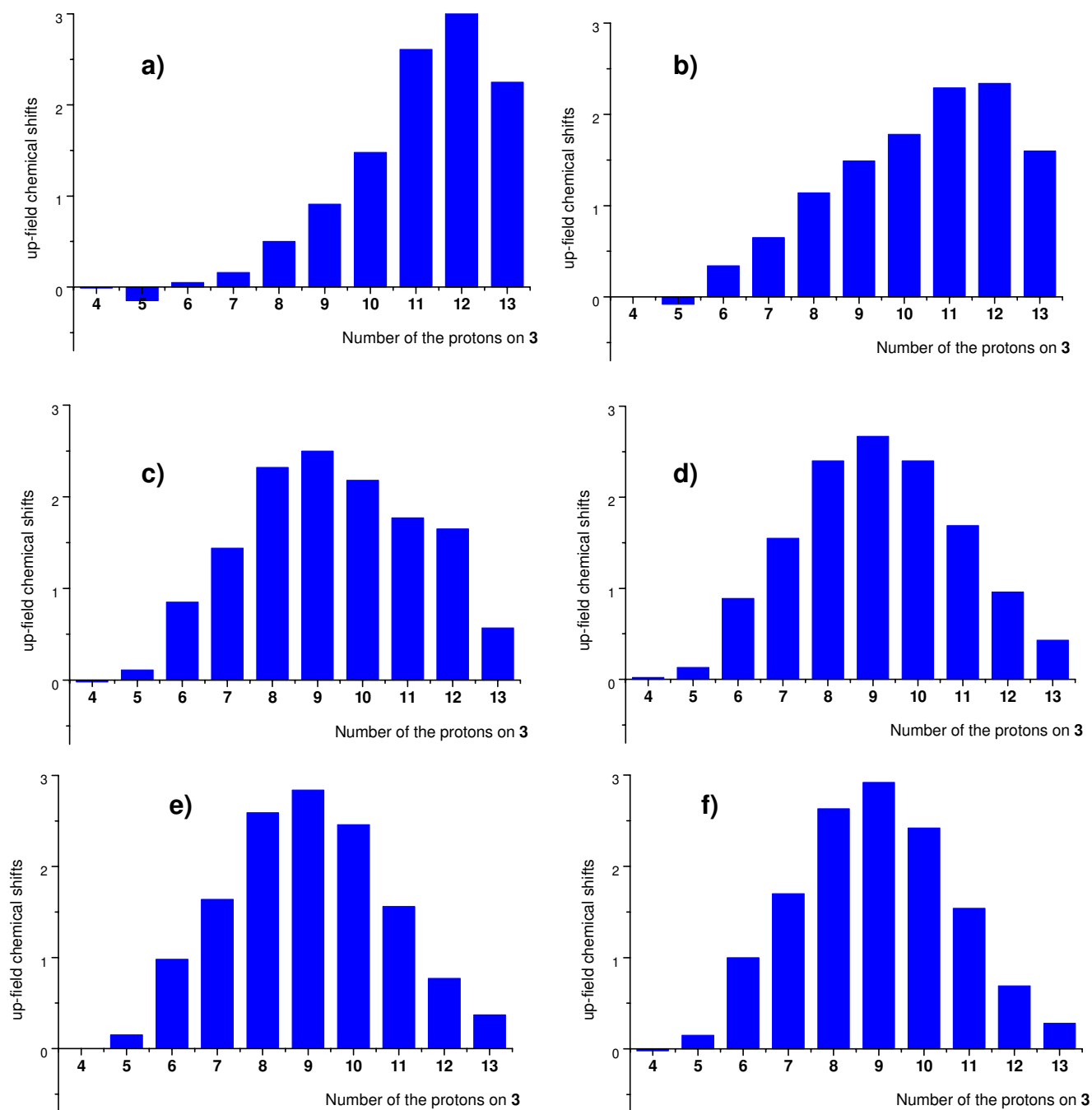


Fig. S26. Up-field shifts ($\Delta\delta$) between decyl protons on **3** and **5** in different mixed solvents. (a) 10:1 chloroform-*d*/DMSO-*d*₆ v/v; (b) 5:1 chloroform-*d*/DMSO-*d*₆ v/v; (c) 2:1 chloroform-*d*/DMSO-*d*₆ v/v; (d) 1:1 chloroform-*d*/DMSO-*d*₆ v/v; (e) 1:2 chloroform-*d*/DMSO-*d*₆ v/v; (f) 1:4 chloroform-*d*/DMSO-*d*₆ v/v.

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