

A Shape-Persistent Arylene Ethynylene Macrocycle with Multiple Acetamides Modified Cavity: Synthesis and Gelation

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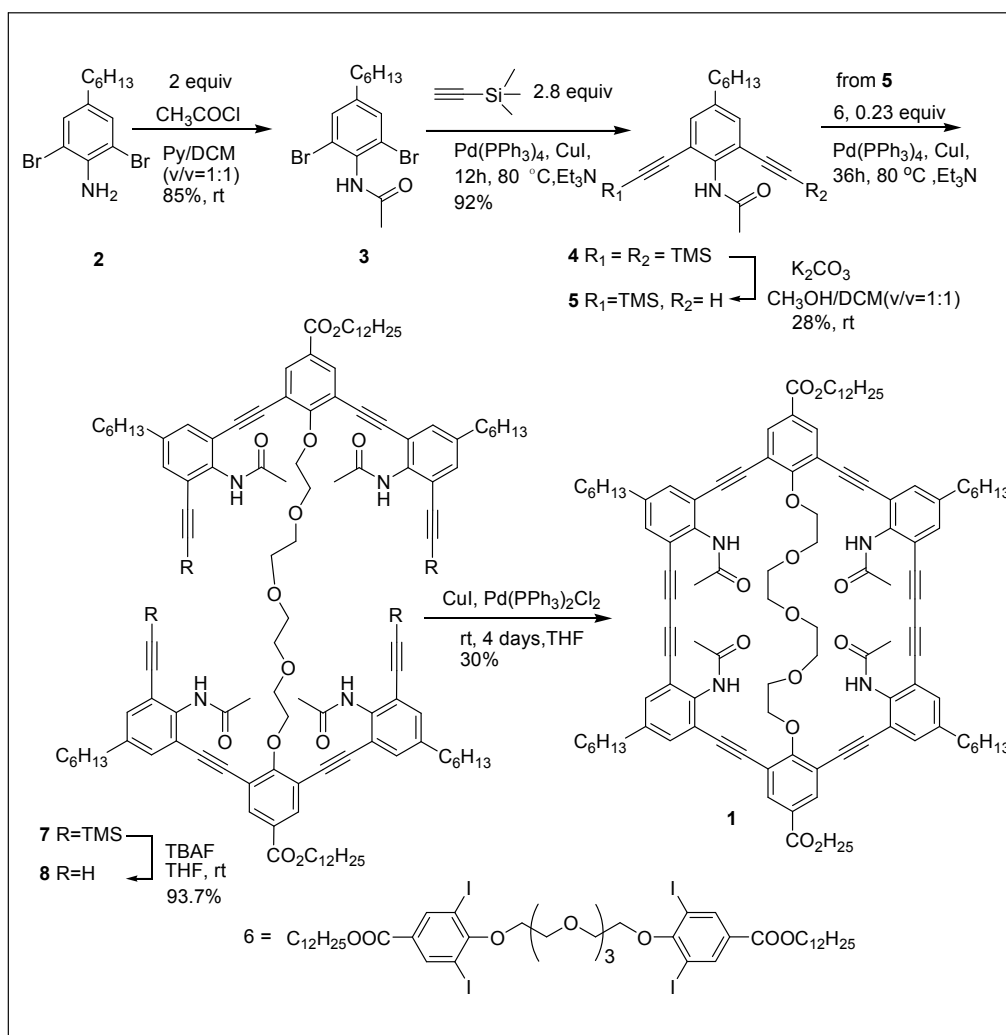
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1. General remarks

All reagents and starting compounds were purchased from commercial sources and used without further purification. The solvents were dried using standard methods. All reactions were carried out under nitrogen atmosphere unless otherwise noted. ¹H and ¹³C NMR were recorded on Bruker AV-400 spectrometer with residual solvent peaks (CDCl₃: ¹H: δ = 7.26, ¹³C: δ = 77.23). Maldi-Tof MS were recorded on a PerSeptive Biosystem Voyager-DE STR and IonSpec 4.7 Tesla FTMS for HR Maldi-Tof. Dynamic laser scattering (DLS) was performed on Brookhaven BI-200SM. The fluorescence photograph was obtained with ZEISS Axiocam HRc photometer with excitation wavelength of 359 nm. The fluorescence emission was recorded on HITACHI F-2700.

2. Synthetic details



Scheme S1: Synthesis of target macrocycle 1

Compound **2**^{S1} and **6**^{S2} were prepared according to literature methods.

Compound 3:

To a mixture of **2** (2.0 g, 5.97 mmol), pyridine (20 ml), dichloride methane (20 ml) in 100 mL three necked flask was added dropwise chloride acetate (0.938 g, 11.94 mmol) under nitrogen atmosphere in 30 min. at rt.. After continuous stirring for 4 hours, the precipitates were filtered. The resulted reaction mixture was absorbed on silica gel and purified by column chromatography (CC) (hexane as eluent) to yield **3** (1.92 g, 5.09 mmol) as a white solid in 85% yield. ¹H NMR (400 MHz, CDCl₃, 323 K) δ(ppm) 7.41 (br, 2H), 6.97 (br, 1H), 2.53 (t, 2H), 2.21 (s, 3H), 1.57 (m, 2H), 1.29 (m, 6H), 0.88 (t, 3H). ¹³C NMR (101 MHz, CDCl₃, 323 K) δ(ppm) 169.44, 144.83,

132.63, 131.90, 123.73, 34.93, 31.57, 30.84, 28.85, 22.91, 22.54, 14.10. MS(GC-MS): m/z: calcd for C₁₄H₁₉Br₂NO :376.98; found: 377.0. Anal. Calcd for C₁₄H₁₉Br₂NO: C, 44.59; H, 5.08; N, 3.71. Found: C, 44.67; H, 5.08; N, 3.57.

Compound 4:

To a degassed mixture of **3** (1.5 g, 3.98 mmol), Pd(PPh₃)₄ (0.138 g, 0.1194 mmol) and CuI (0.038 g, 0.1991 mmol) in triethylamine (30 ml), ethynyltrimethylsilane (1.1 g, 11.15 mmol) was added. The reaction mixture was stirred under nitrogen at 80 °C for 12 h. The resulted reaction mixture was absorbed on silica gel and purified by column chromatography (CC) (silica gel, hexane/ethyl acetate (5:1/v:v)) to yield **4** (1.51 g, 3.67 mmol) as a yellow oil in 80% yield. ¹H NMR (400 MHz, CDCl₃) δ(ppm) 7.25 (br, 2H), 7.15 (s, 1H), 2.49 (t, 2H), 2.15 (br, 3H), 1.55 (m, 2H), 1.27 (m, 6H), 0.86 (t, 3H), 0.22 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ(ppm) 167.68, 140.18, 138.19, 132.49, 120.94, 101.62, 98.59, 34.89, 31.54, 30.85, 28.72, 22.89, 22.41, 13.99, -0.17. MS(GC-MS): m/z: calcd for C₂₄H₃₇NOSi₂ : 411.24; found: 411.3. Anal. Calcd for C₂₄H₃₇NOSi₂: C, 70.01; H, 9.06; N, 3.40. Found: C, 69.43; H, 9.11; N, 3.34.

Compound 5:

To a stirred solution of **4** (1.5 g, 3.643 mmol) in THF (20 ml) was added dropwise a solution of K₂CO₃ (0.05 g, 0.019 mmol) in a mixed solvent of CH₃OH:CH₂Cl₂ (1:1/v:v) (2.5 ml) in 30 minutes. Subsequent CC (silica gel, hexane/THF (5:1/v:v)) furnished **5** (0.35 g, 1.031 mmol) in 28% yield as an orange solid. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.30 (s, 2H), 7.20 (s, 1H), 3.25 (s, 1H), 2.52 (t, 2H), 2.18 (br, 3H), 1.56 (m, 2H), 1.28 (m, 6H), 0.87 (t, 3H), 0.23 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 168.33, 140.64, 138.22, 133.16, 132.90, 121.16, 120.25, 101.43, 99.27, 81.90, 80.27, 34.90, 31.55, 30.84, 28.75, 23.10, 22.45, 13.99, - 0.19. MS(GC-MS): m/z: Calcd for C₂₁H₂₉NOSi : 339.2; found: 339.2. Anal. Calcd for C₂₁H₂₉NOSi: C, 74.28; H, 8.61; N, 4.13. Found: C, 74.62; H, 8.58; N, 3.98.

Compound 7:

To a degassed solution of **6** (1.34 g, 1.051 mmol) in triethylamine (30 ml), was added Pd(PPh₃)₄ (0.0365 g, 0.0316 mmol), CuI (0.010 g, 0.0526 mmol), **5** (1.5 g, 4.42 mmol). The reaction mixture was stirred under nitrogen at rt. for 36 h. The

resulted reaction mixture was absorbed on silica gel and purified by column chromatography (CC) (hexane/ethyl acetate (10:3/v:v)) as eluent) to yield **7** (1.7 g, 0.802 mmol) as a yellow oil in 76% yield. ¹H NMR (400 MHz, CDCl₃) δ(ppm) 8.04 (s, 4H), 7.88 (s, 4H), 7.29 (s, 4H), 4.50 (t, 4H), 4.30 (t, 4H), 3.81 (t, 4H), 3.48 (t, 4H), 3.33 (t, 4H), 2.53 (t, 8H), 2.18 (s, 12H), 1.76 (m, 4H), 1.58 (m, 8H), 1.25 (m, 60H), 0.88 (t, 18H), 0.22 (s, 36H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 168.40, 164.69, 163.39, 140.69, 138.04, 134.85, 133.04, 132.13, 125.69, 121.62, 120.58, 117.44, 101.65, 99.12, 91.47, 89.02, 73.52, 70.57, 70.30, 65.43, 35.04, 31.86, 31.63, 30.96, 29.60, 29.51, 29.30, 28.93, 28.67, 25.94, 23.16, 22.63, 22.53, 14.06, -0.11. MS(MALDI-TOF): m/z: calcd for C₁₃₀H₁₈₂N₄O₁₃Si₄ : 2120.281; found: 2120.062. Anal. Calcd for C₁₃₀H₁₈₂N₄O₁₃Si₄: C, 73.61; H, 8.65; N, 2.64. Found: C, 73.23; H, 8.71; N, 2.46.

Compound 8:

To a stirred solution of **7** (1.0 g, 0.471 mmol) in THF (30 ml) was added dropwise a solution of TBAF (0.30 g, 0.95 mmol) in THF for 30 minutes. After the reaction mixture was stirred in the air at rt. for 2 h., subsequent CC (silica gel, hexane/THF (4:5/v:v)) yield **8** (0.81 g, 0.442 mmol) in 93.7% yield as a white solid. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.08 (s, 6H), 7.33 (s, 6H), 6.97 (s, 4H), 4.52 (t, 4H), 4.31 (t, 4H), 3.83 (t, 4H), 3.53 (t, 4H), 3.39 (t, 4H), 3.25 (s, 4H), 2.55 (t, 8H), 2.21 (s, 12H), 1.75 (m, 4H), 1.60 (m, 8H), 1.26 (m, 60H), 0.89 (t, 18H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 168.97, 164.83, 163.55, 141.39, 137.92, 135.03, 133.83, 132.74, 128.24, 126.21, 125.52, 120.76, 91.44, 89.04, 82.01, 80.35, 73.66, 70.52, 70.11, 65.67, 35.08, 31.92, 31.66, 31.02, 30.32, 29.64, 29.36, 28.94, 28.71, 25.99, 23.46, 22.70, 22.59, 14.12. HRMS(MALDI/DHB): m/z calcd. for C₁₁₈H₁₅₀N₄O₁₃Na⁺: 1855.1131, found: 1854.1073

Macrocycle 1:

To a degassed solution of **8** (0.3 g, 0.1637 mmol) in dry THF (500 ml) was added Pd(PPh₃)₂Cl₂ (11 mg, 0.016 mmol), diisopropylethylamine (0.6 g, 4.646 mmol) and CuI (5.0 mg, 0.026 mmol). The reaction mixture was stirred under air at rt. for 4 days. After removal of the solvent, the resulted reaction mixture was absorbed on silica gel

and purified by column chromatography (CC) (hexane/ethyl acetate (100:1/v:v)) as eluent) to remove the catalysts. Further purification with SEC (bio-bead®, Toluene) yielded **1** (0.09 g, 0.049 mmol) as a yellow oil in 30% yield. ¹H NMR (400 MHz, CDCl₃) δ(ppm) 8.49 (s, 4H), 8.09 (s, 4H), 7.31 (s, 4H), 4.36 (t, 6H), 3.87 (t, 4H), 3.66 (t, 6H), 2.93 (s, 4H), 2.53 (t, 8H), 2.30 (s, 12H), 1.80 (m, 4H), 1.59 (m, 8H), 1.30 (m, 60H), 0.89 (t, 18H). ¹³C NMR (101 MHz, CDCl₃) δ(ppm) 170.03, 164.76, 164.30, 141.65, 139.31, 134.62, 133.65, 132.55, 126.40, 121.01, 116.98, 90.94, 89.51, 79.53, 78.04, 73.86, 71.53, 70.25, 65.68, 35.07, 31.91, 31.63, 30.91, 29.63, 29.56, 29.34, 28.92, 28.76, 26.00, 23.47, 22.57, 14.09. HRMS(MALDI/DHB): *m/z* calcd. for C₁₁₈H₁₄₆N₄O₁₃: 1828.0920, found: *m/z* = 1828.0921.

Reference:

- S1. L. Shu and M. Mayor, *Chem. Commun.* **2006**, 4134.
S2. H. W. Gibson, H. Wang, K. Bonrad, J. W. Jones, C. Slebodnick, L. N. Zackharov, A. L. Rheingold, B. Habenicht, P. Lobue, A. Ratliff, *Org. Biomol. Chem.*, **2005**, *3*, 2114–2121.

Fig S1. ^1H NMR of compound **3** at 298K (top) and 325 K (bottom) in CDCl_3

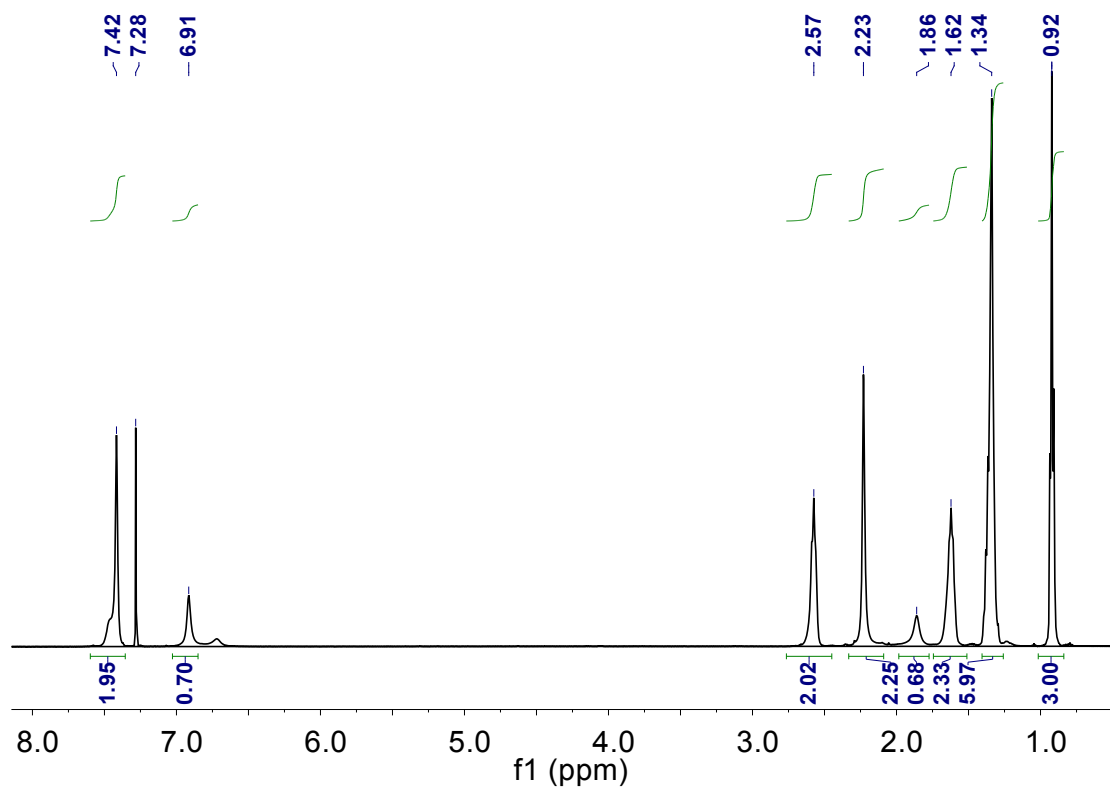
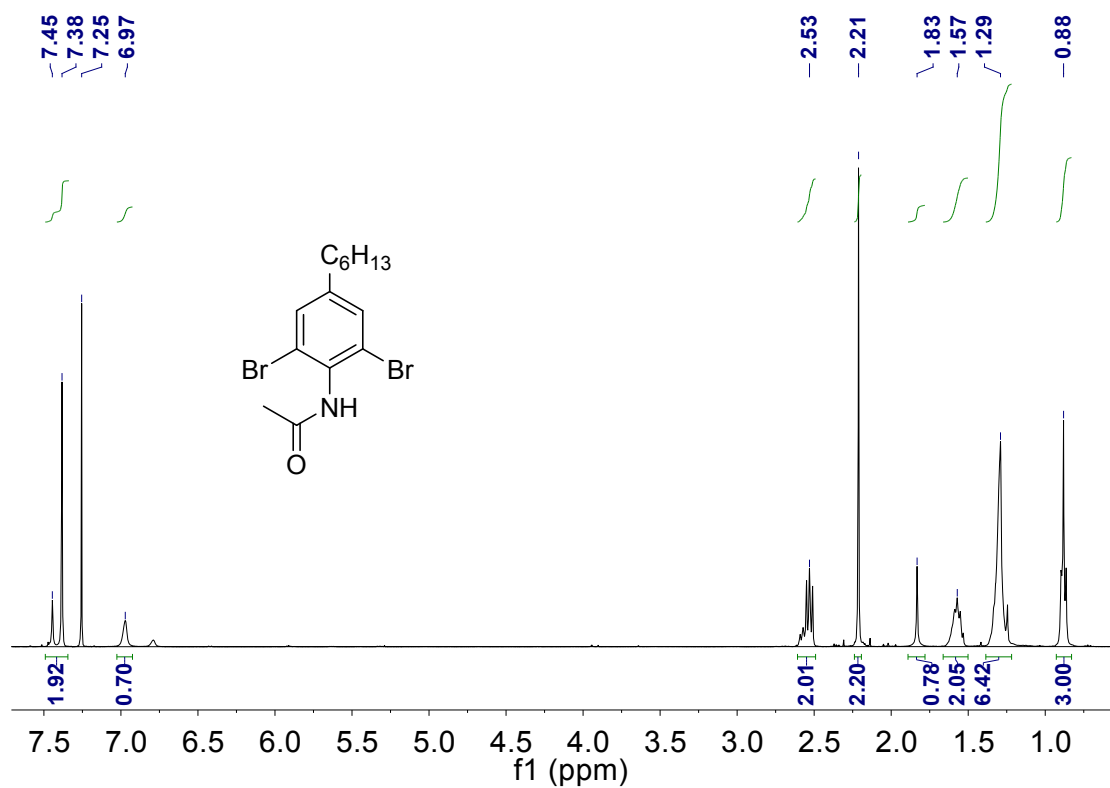


Fig. S2. ^{13}C NMR of compound **3** at 298K (top) and 325 K (bottom) in CDCl_3

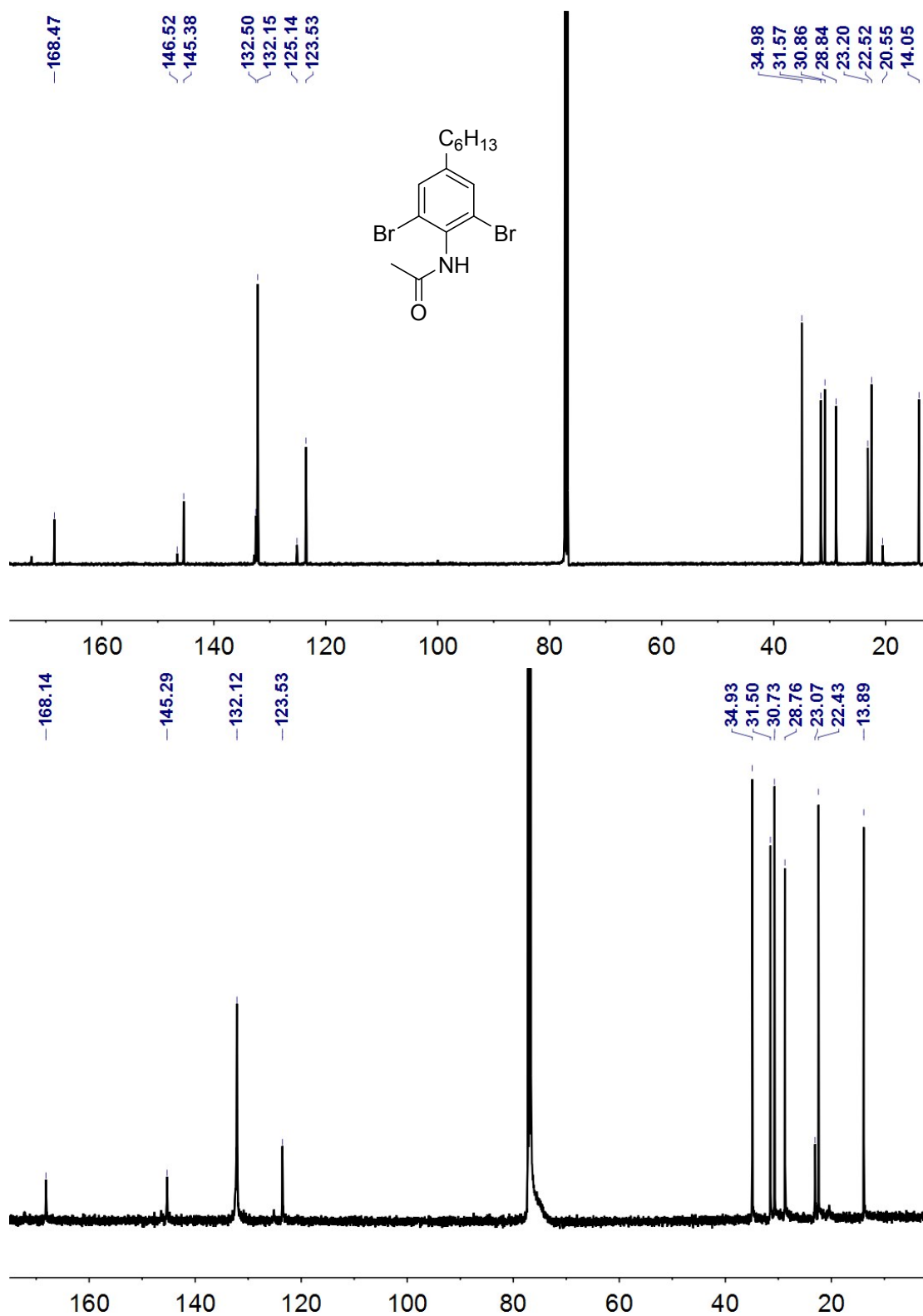


Fig S3. ^1H NMR and ^{13}C NMR of compound 4

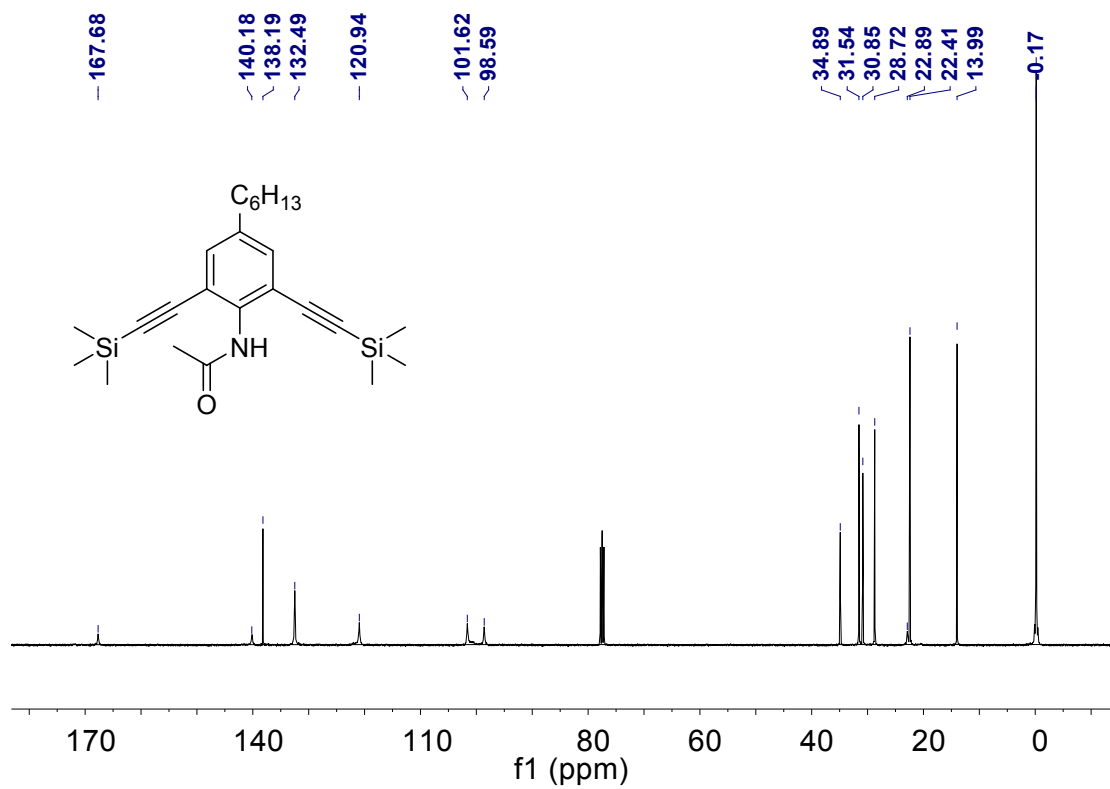
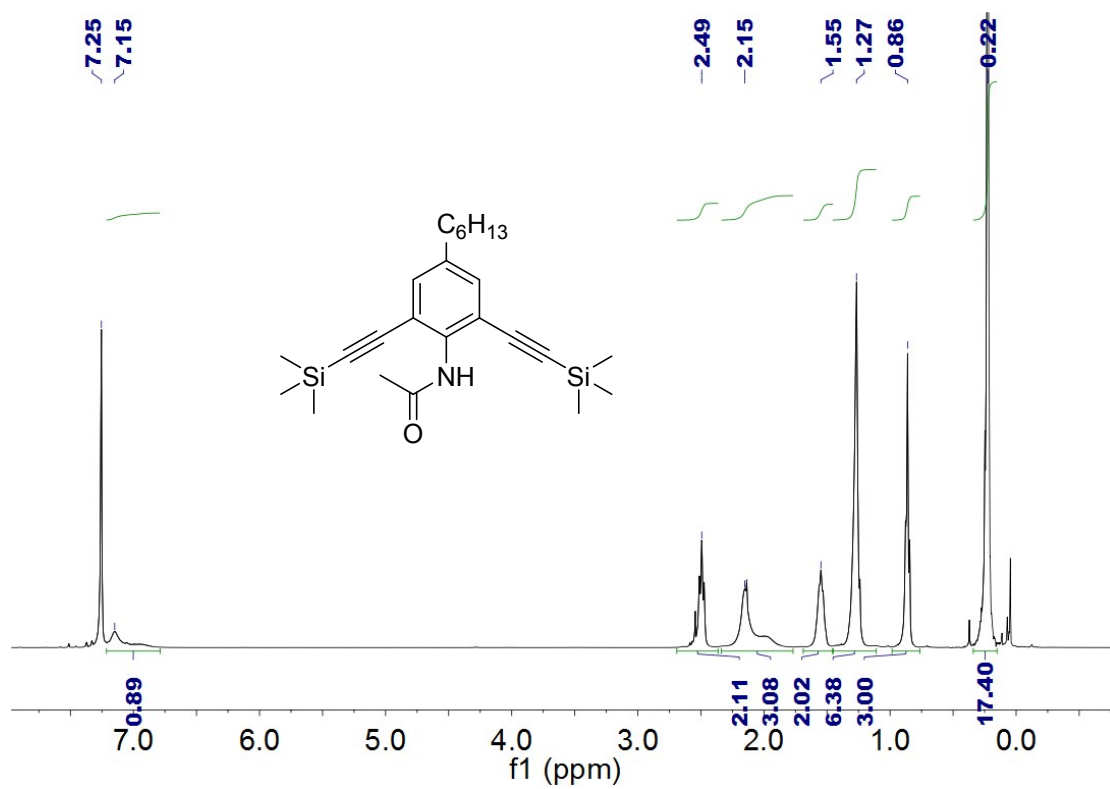


Fig S4. ^1H NMR and ^{13}C NMR spectrum of compound **5**.

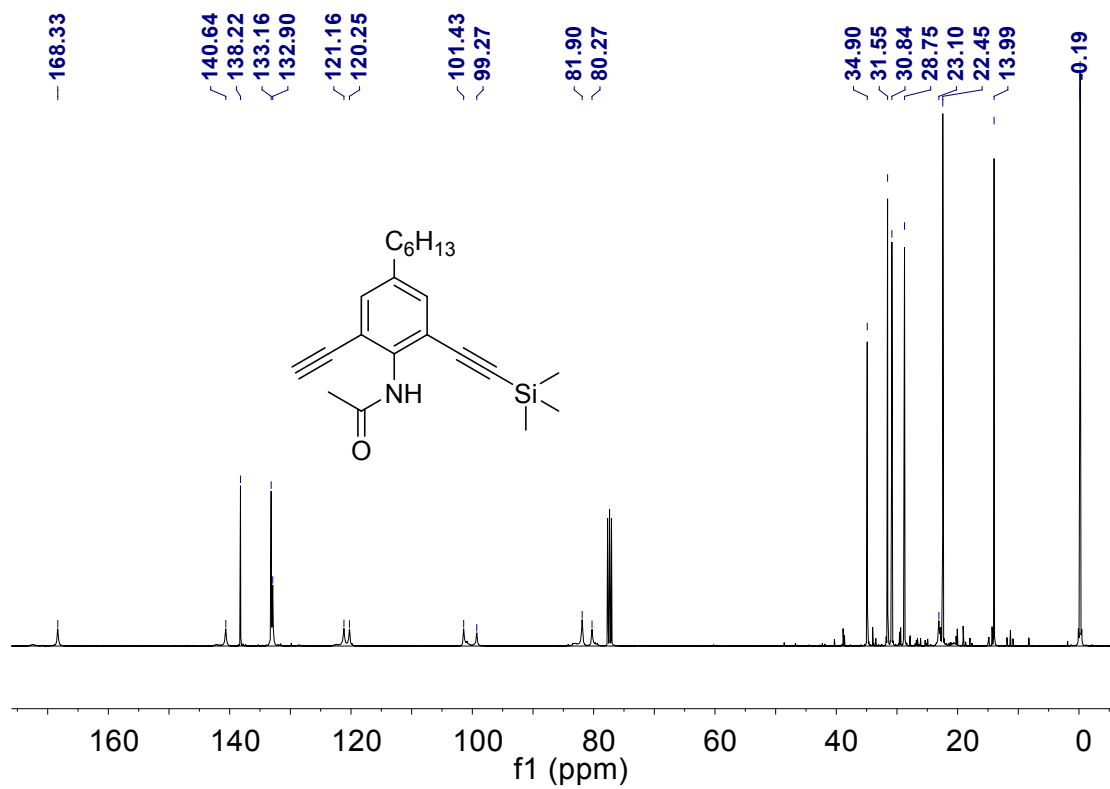
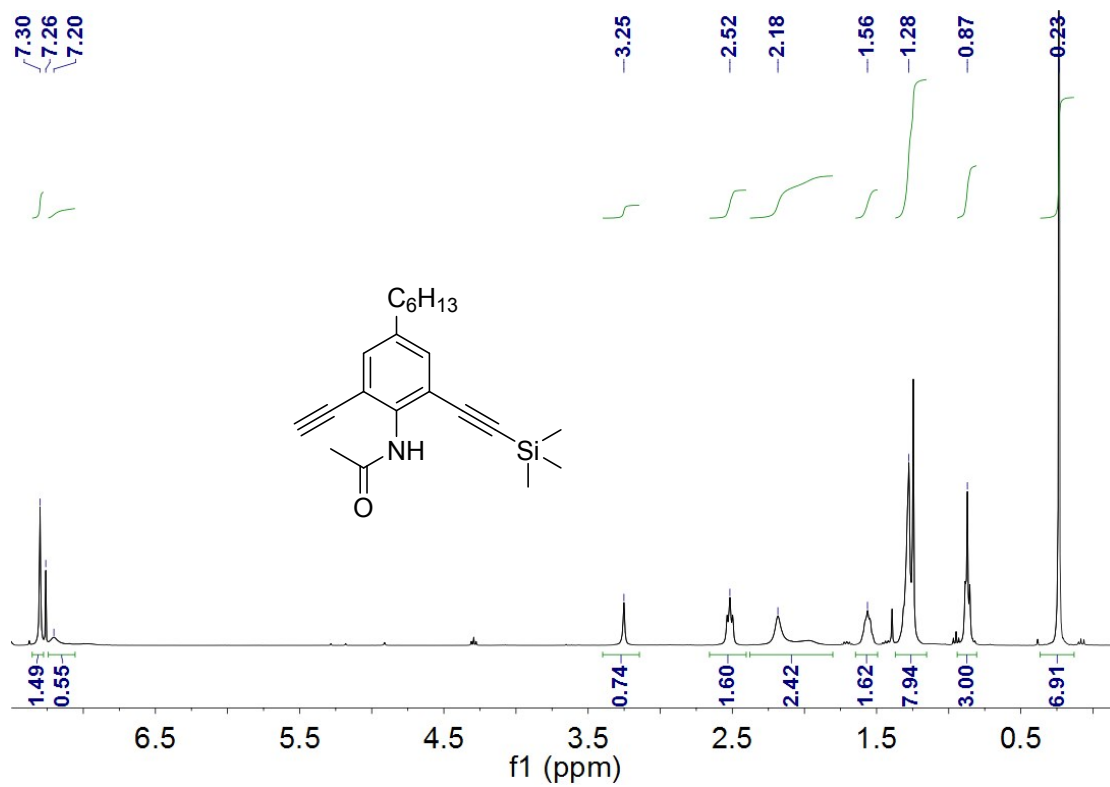


Fig S5. ^1H NMR and ^{13}C NMR spectrum of compound 7.

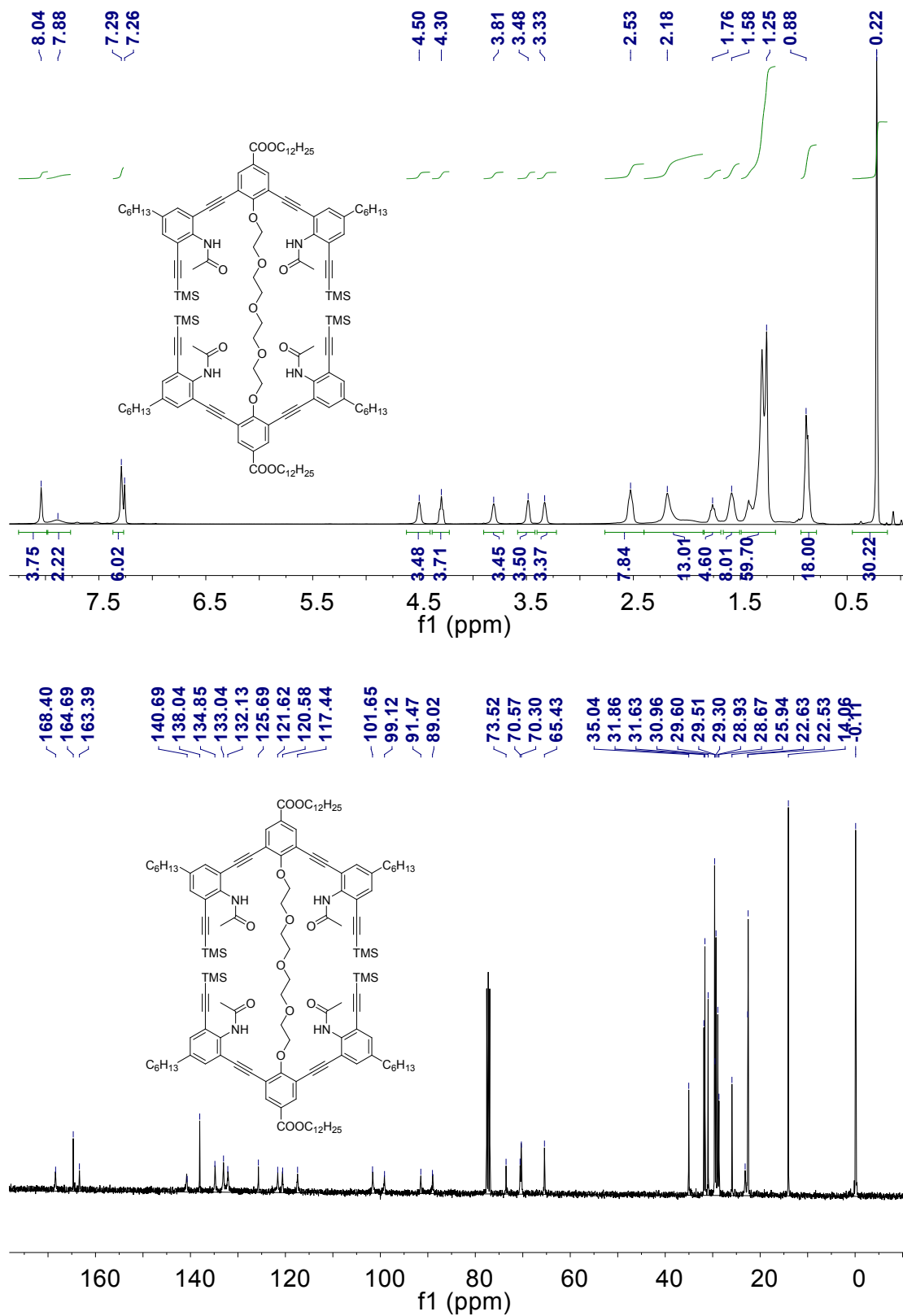


Fig S6. ^1H NMR and ^{13}C NMR spectrum of compound **8**.

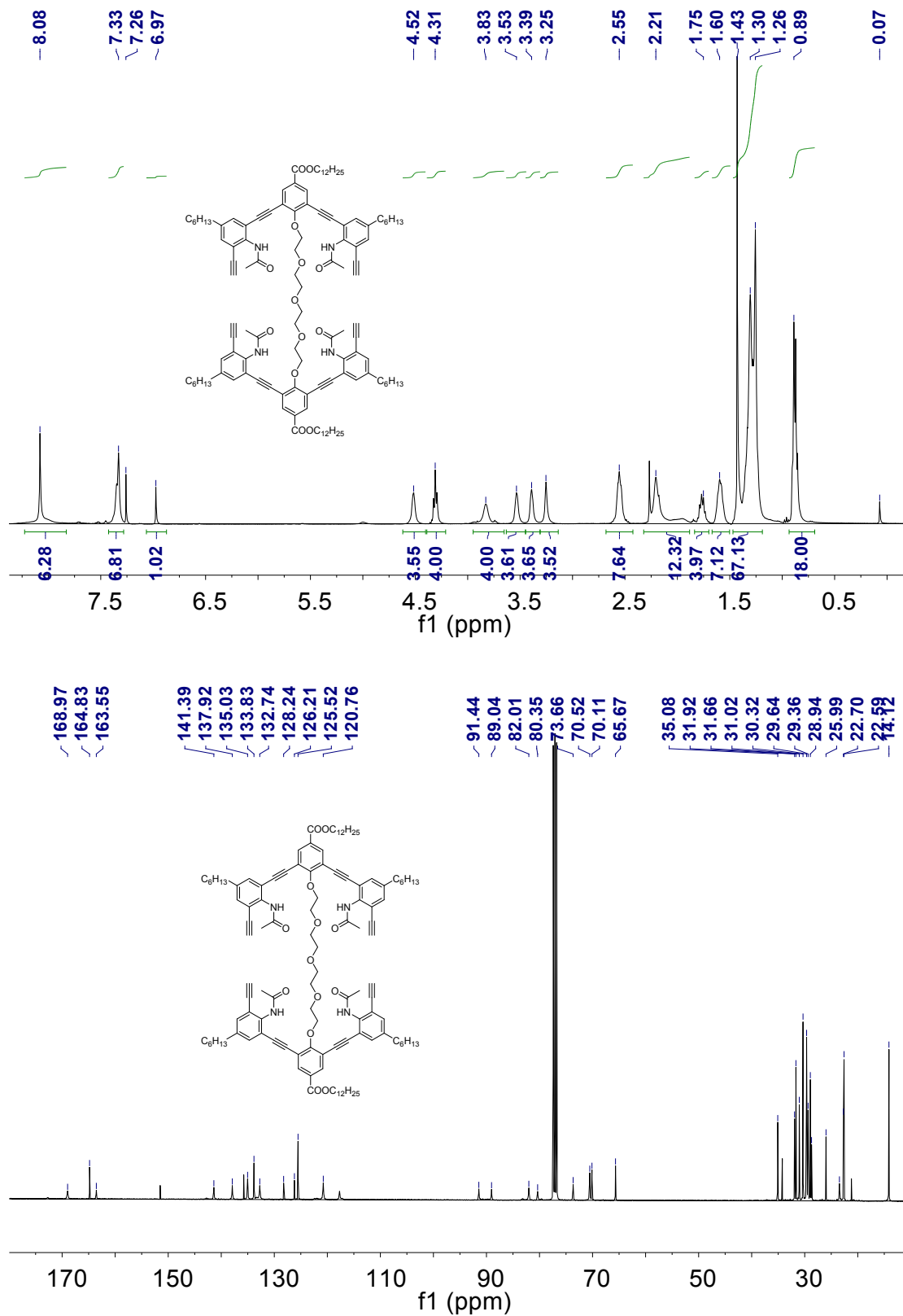
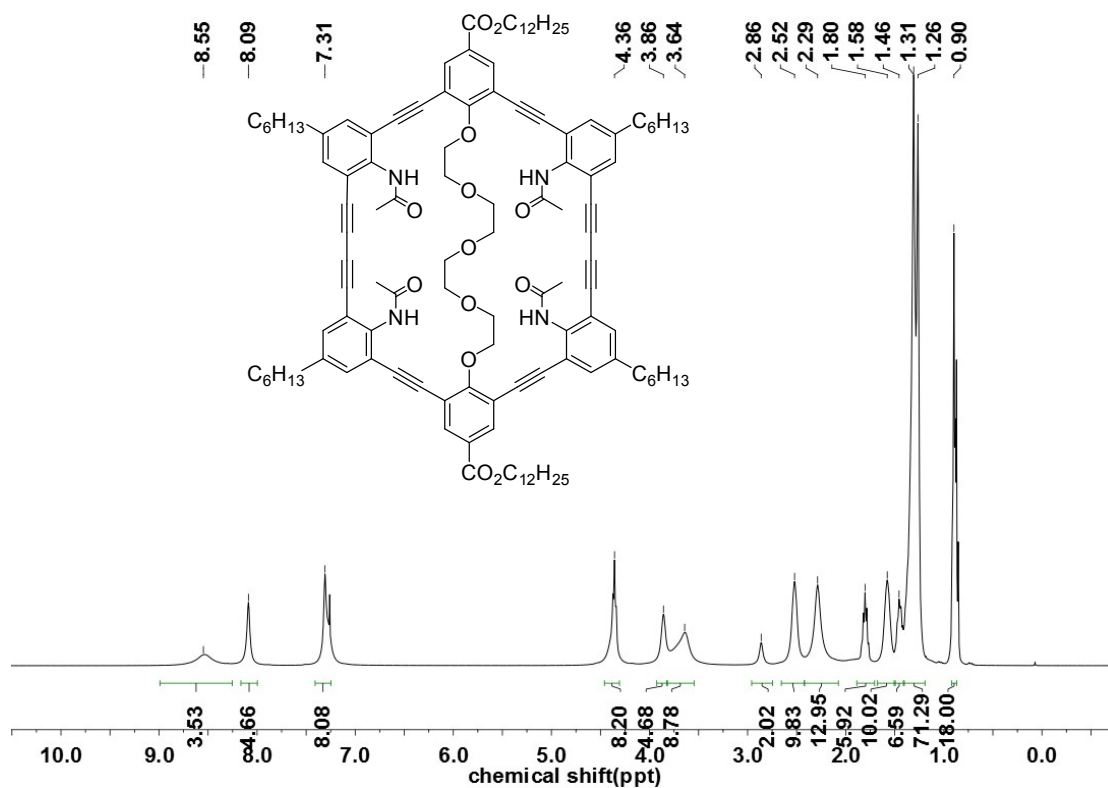


Fig S7. ^1H NMR and ^{13}C NMR spectrum of Macrocycle **1**



^{13}C NMR spectrum of macrocycle **1**

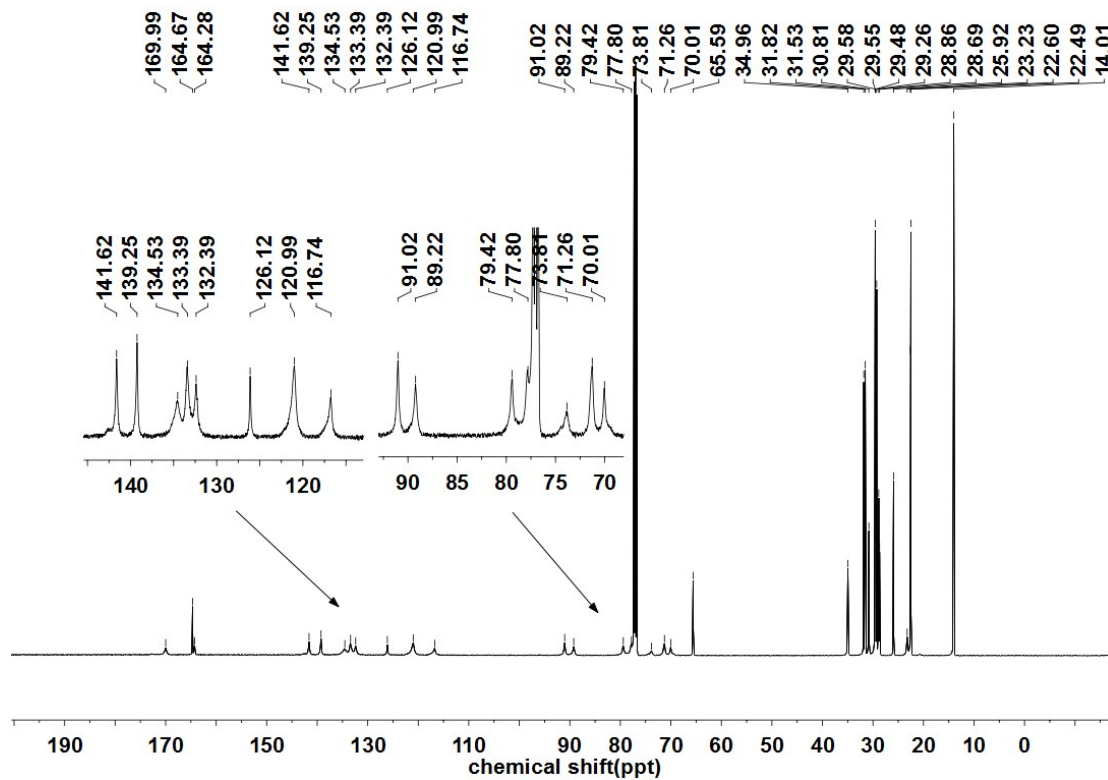


Fig. S8. X-ray crystal structure of compound **3** (left) and their three-dimensional packing (right, viewed along the b axis). Crystal data of compound **3**: C₁₄H₁₈Br₂NO, M = 376.09, Centric, Monoclinic P21/c, a = 12.0433 Å, b = 9.2013 Å, c = 14.9449 Å, α = 90.000 (deg), β = 101.240 (deg), γ = 90.000 (deg), V = 1624.3(4) Å³, Z = 4, μ(MoKa) = 4.980 mm⁻¹, wR2 = 0.1901, GooF = 1.001.

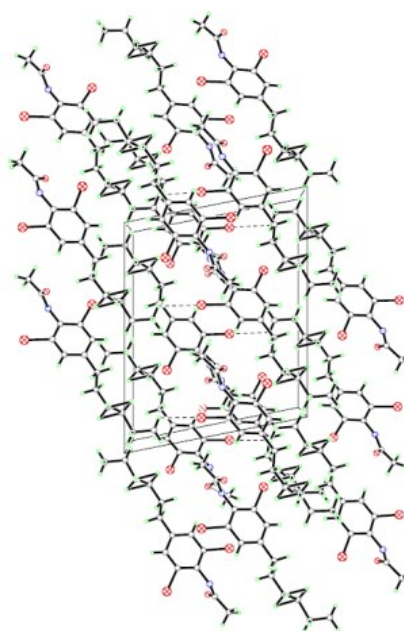
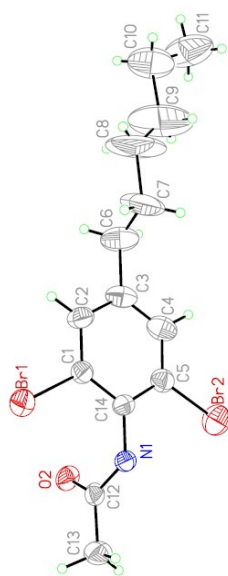


Fig.S9. (a) Concentration-dependent emission spectra and (b) the relationship between the intensity of emission peaks and concentrations.

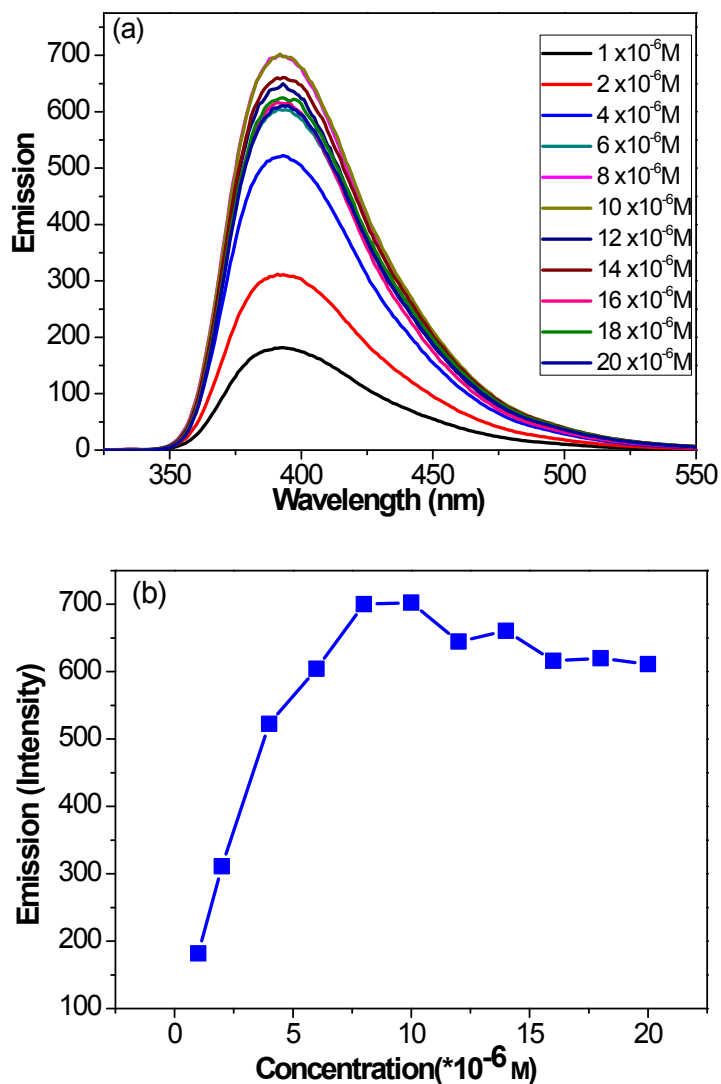


Fig. S10. FT-IR spectra of gel

