

Electronic Supplementary Information

Efficient control of movements in non-photoresponsive molecular machines by photo-induced proton-transfer strategy

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1. Materials and methods

P- and *M*-**HA** was prepared according to literature procedure.^{S1} Unless otherwise indicated, all reagents were obtained from commercial sources. Melting points were determined using WRR melting point apparatus, and were not corrected. ¹H NMR spectra were recorded on the Bruker DMX300 NMR and Bruker® Avance III 500 MHz NMR spectrometer. Electrospray ionization mass spectra (ESI-MS) were recorded on the Thermo Fisher® Exactive high-resolution LC-MS spectrometer. All solvents used, except THF and H₂O, were dried through 4A molecular sieve.

2. ¹H NMR study of the association of HA with G1

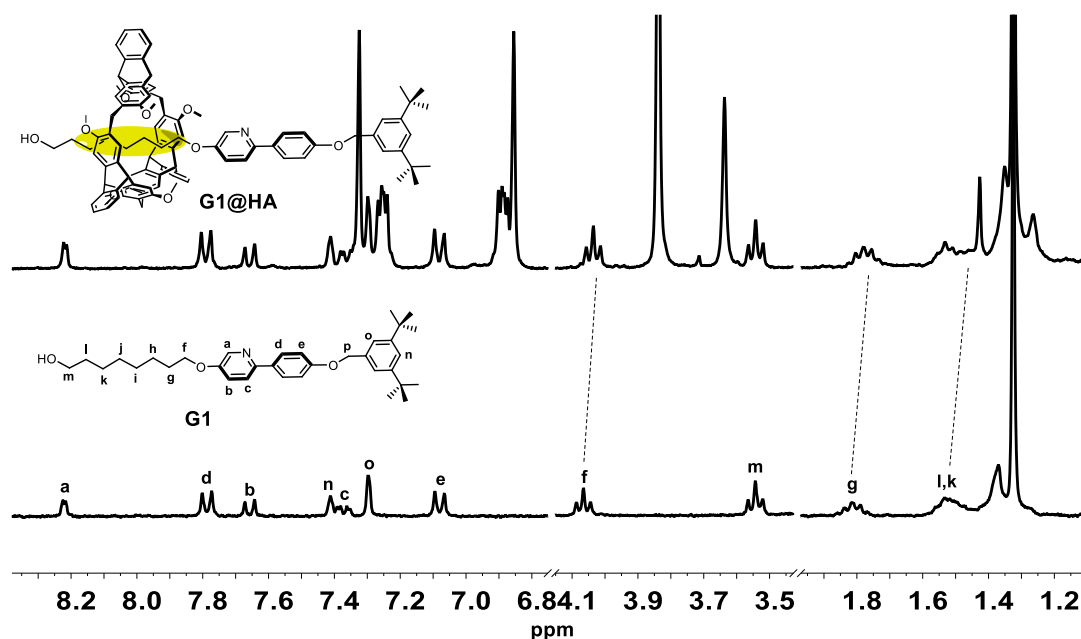


Fig. S1. Association of **HA** with **G1** (300 MHz, CD₃OD/CD₂Cl₂ = 11:5 v/v, 298 K). Compared with the ¹H NMR spectrum of **G1**, the aromatic protons and H^m of **G1@HA** have no chemical shifts while the proton H^f-H^l slightly upshifted, indicating **HA** inclined to located at the position of H^f to H^l.

3. ^1H NMR study of photo-induced motion of HA on G1

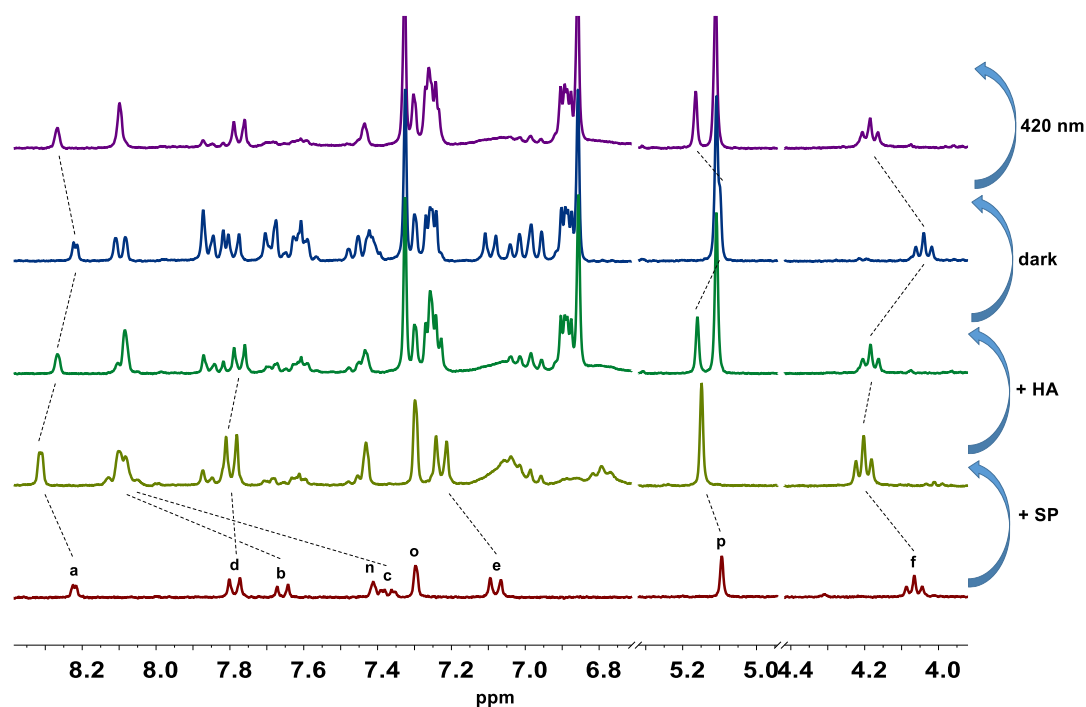
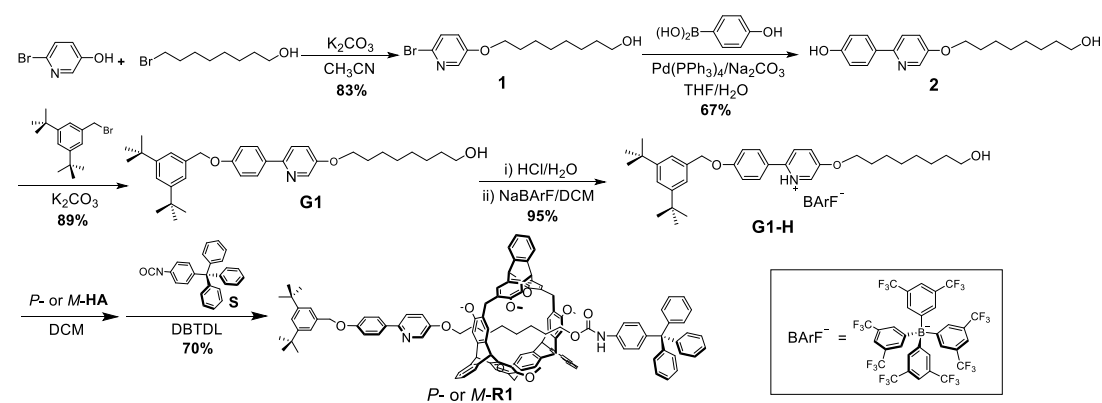


Fig. S2. Photo acid induced association and disassociation of **HA** with the pyridine part of **G1** (300 MHz, $\text{CD}_3\text{OD}/\text{CD}_2\text{Cl}_2 = 11:5$ v/v, 298 K).

4. Synthesis of new compounds



Scheme S1. Synthetic route of [2]rotaxane *P-* or *M-R1*.

Synthesis of 1. A mixture of 6-bromopyridin-3-ol (1.0 g, 5.7 mmol), 8-bromo-1-octanol (1.4 g, 6.9 mmol) and anhydrous potassium carbonate (1.5 g) were refluxed in

dried acetonitrile for 8 h. Then the solution was cooled to room temperature and remove the insoluble matter by filtration. After the solvent was removed under reduced pressure, the yellow oily liquid was further purified by silica gel chromatography with petroleum ether/ethyl acetate = 1:1 (v/v) to give a colorless oily liquid product **1** (1.4 g, 83%). ¹H NMR (500 MHz, CD₃CN, 298 K) δ (ppm): 8.03 (d, *J* = 5 Hz, 1H), 7.42 (d, *J* = 10 Hz, 1H), 7.23-7.20 (m, 1H), 4.01 (t, *J* = 5 Hz, 2H), 3.47 (t, *J* = 5 Hz, 2H), 1.78-1.72 (m, 2H), 1.48-1.30 (m, 10H). ¹³C NMR (125 MHz, CD₃CN, 298 K) δ (ppm): 156.3, 138.7, 132.1, 129.1, 125.9, 69.8, 62.5, 33.5, 30.0, 29.9, 29.7, 26.5, 26.4. HRMS (ESI): *m/z* calcd for [M+H]⁺ (C₁₃H₂₁BrO₂N⁺), 301.0672; found *m/z* 301.0671.

Synthesis of 2. Compound **1** (1.0 g, 3.3 mmol) and 4-hydroxyphenylboronic acid (0.45 g, 3.3 mmol) were dissolved in THF (100 ml) and H₂O (60 ml). Then anhydrous Na₂CO₃ (13 g, 2M) was added. After argon was injected into the solution for 0.5 h, tetrakis (triphenylphosphine) palladium (200 mg, 0.17 mmol) was added. The mixture was heated to 70 °C overnight and then cooled to room temperature. The mixture was washed with DCM. Then the organic layer was collected and dried with anhydrous MgSO₄. After solvent was evaporated in vacuum, the crude product was further purified by chromatography with petroleum ether/ethyl acetate = 1:2 (v/v) to give a yellow solid **2** (0.7 g, 67%). M. p.: 129.3-130.3 °C. ¹H NMR (500 MHz, CD₃CN, 298 K) δ (ppm): 8.27 (d, *J* = 5 Hz, 1H), 7.84-7.82 (m, 2H), 7.66 (d, *J* = 10 Hz, 1H), 7.32-7.30 (m, 1H), 7.03 (s, 1H), 6.88-6.86 (m, 2H), 4.06 (t, *J* = 5 Hz, 2H), 3.50-3.46 (m, 2H), 1.82-1.75 (m, 2H), 1.48-1.33 (m, 10 H). ¹³C NMR (125 MHz, CD₃CN, 298 K) δ (ppm): 158.2, 155.0, 150.2, 138.2, 132.0, 128.4, 122.8, 120.7, 116.3, 69.4, 62.5, 33.6,

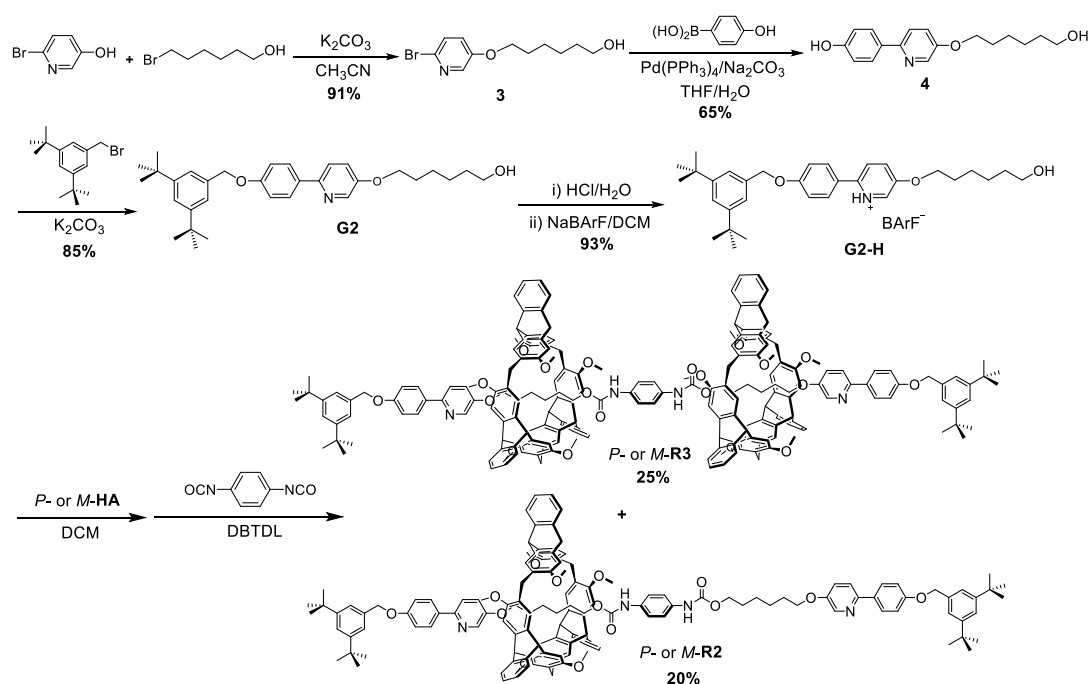
30.1, 30.0, 29.8, 26.5, 26.5. HRMS (ESI): m/z calcd for $[M+H]^+$ ($C_{19}H_{25}O_3N^+$), 315.1837; found m/z 315.1830.

Synthesis of G1. Compound **2** (0.5 g, 1.6 mmol) and 3, 5-di-tert-butylbenzyl bromide (0.5 g, 1.9 mmol) was dissolved in acetonitrile. After anhydrous K_2CO_3 (1.0 g) was added, the mixture was reflux for 6 h. And then purified by chromatography with DCM to give a yellow-brown powder **G1** (0.73 g, 89%). M. p.: 80.7-82.2 °C. 1H NMR (500 MHz, $DMSO-d_6$, 298 K) δ (ppm): 8.30 (d, $J = 5$ Hz, 1H), 7.96-7.94 (m, 2H), 7.82-7.80 (m, 1H), 7.43-7.40 (m, 1H), 7.36 (s, 1H), 7.30 (s, 2H), 7.10-7.08 (m, 2H), 5.10 (s, 2H), 4.05 (t, $J = 5$ Hz, 2H), 3.38 (t, $J = 5$ Hz, 2H), 1.74-1.72 (m, 2H), 1.43-1.29 (m, 28H). ^{13}C NMR (125 MHz, $DMSO-d_6$, 298 K) δ (ppm): 158.7, 153.6, 150.4, 148.3, 137.2, 136.0, 131.2, 127.1, 122.1, 122.0, 121.4, 119.8, 114.9, 70.1, 68.0, 60.7, 34.5, 32.5, 31.3, 28.9, 28.8, 28.6, 25.5, 25.4. HRMS (ESI): m/z calcd for $[M+H]^+$ ($C_{34}H_{48}O_3N^+$), 518.3556; found m/z 518.3551.

Synthesis of G1-H. Excess HCl (0.16 mL) was added to compound **G1** (0.1 g, 0.19 mmol) in water (2 mL). After stirred at room temperature for 30 min, a solution of NaBARF (0.17 g, 0.2 mmol) in DCM (2 mL) was added. Then, the mixture was stirred overnight and the organic layer was separated, washed with water three times and dried with anhydrous $MgSO_4$. The DCM was removed in vacuum to afford **G1-H** as a yellow solid (0.25 g, 95%). M. p.: 51.2-52.5 °C. 1H NMR (500 MHz, CD_3CN , 298 K) δ (ppm): 8.21 (d, $J = 5$ Hz, 1H), 8.12-8.14 (m, 2H), 7.79-7.77 (m, 2H), 7.72-7.70 (m, 8H), 7.68 (s, 4H), 7.48 (t, $J = 5$ Hz, 1H), 7.36 (s, 2H), 7.28-7.26 (m, 2H), 5.19 (s, 2H), 4.21 (t, $J = 5$ Hz, 2H), 3.50 (t, $J = 5$ Hz, 2H), 1.86-1.82 (m, 2H), 1.51-1.46 (m, 4H), 1.42-1.31

(m, 24H). ^{13}C NMR (125 MHz, CD_3CN , 298 K) δ (ppm): 162.9, 162.6 (q, $^1J_{\text{CB}} = 50$ Hz), 157.2, 152.2, 146.1, 136.6, 135.6, 135.0, 130.2, 130.0 (m), 127.9, 127.2, 125.4 (q, $^1J_{\text{CF}} = 275$ Hz), 123.5, 123.4, 123.4, 117.1, 71.8, 71.5, 62.5, 35.5, 33.5, 31.6, 30.0, 29.8, 29.3, 26.5, 26.3. HRMS (ESI): m/z calcd for $[\text{M-BArF}]^+$ ($\text{C}_{34}\text{H}_{48}\text{O}_3\text{N}^+$), 518.3629; found m/z 518.3631.

Synthesis of *P*- or *M*-R1. Compound **G1-H** (0.35 g, 0.26 mmol) and *P*- or *M*-**HA** (50 mg, 0.05 mmol) was dissolved in DCM (0.5 ml) and the solution was stirred for 2 h. After **S** (0.12 g, 0.33 mmol) and 2 drops of DBTDL (Dibutyltin dilaurate) was added, the mixture was stirred for another 2 h. And then purified through chromatography with DCM to afford *P*- or *M*-**HA** as a white solid (66 mg, 70%). M. p.: 156.9-157.1 °C. ^1H NMR (500 MHz, $\text{CD}_3\text{OD}/\text{CD}_2\text{Cl}_2 = 11:5$ v/v, 298 K) δ (ppm): 8.03 (s, 1H), 8.03-8.02 (m, 2H), 7.92 (d, $J = 10$ Hz, 1H), 7.53 (d, $J = 5$ Hz, 2H), 7.45 (t, $J = 5$ Hz, 1H), 7.41 (s, 3H), 7.36-7.35 (m, 6H), 7.28-7.17 (m, 25H), 6.89-6.84 (m, 9H), 6.70 (s, 3H), 5.17 (s, 2H), 5.12-5.11 (m, 6H), 3.94-3.88 (m, 2H), 3.82 (s, 8H), 3.68-3.67 (m, 16H), 2.77-2.67 (br, 2H), 1.44-0.88 (m, 18H), 0.90-0.88 (br, 2H), -0.07 (s, 4H), -1.00 (s, 2H), -1.14 (s, 2H), -1.16 (s, 2H). ^{13}C NMR (125 MHz, $\text{CD}_3\text{OD}/\text{CD}_2\text{Cl}_2 = 11:5$ v/v, 298 K) δ (ppm): 160.5, 155.4, 155.0, 154.9, 152.0, 150.5, 148.0, 147.6, 147.6, 145.6, 145.5, 142.6, 138.3, 138.2, 138.0, 137.9, 137.2, 132.9, 132.6, 131.9, 128.7, 128.3, 127.5, 127.5, 126.8, 126.3, 126.2, 125.4, 125.4, 123.7, 123.0, 122.9, 122.0, 118.8, 116.1, 108.2, 108.0, 71.8, 69.1, 65.5, 56.4, 56.3, 35.5, 31.8, 29.0, 28.1, 27.7, 27.5, 25.2, 24.3. HRMS (ESI): m/z calcd for $[\text{M}+\text{H}]^+$ ($\text{C}_{129}\text{H}_{124}\text{O}_{10}\text{N}_2^+$), 1860.9211; found m/z 1860.9209.



Scheme S2. Synthetic route of *P*- or *M*-R2 and *P*- or *M*-R3.

Synthesis of 3. The method to synthesize compound **3** is the same with **1**. Compound **3** was given as a colorless liquid (1.43 g, 91%). ¹H NMR (500 MHz, CD₃CN, 298 K) δ (ppm): 8.06 (d, *J* = 5 Hz, 1H), 7.45 (d, *J* = 10 Hz, 1H), 7.26-7.23 (m, 1H), 4.04 (t, *J* = 5 Hz, 2H), 3.51 (q, *J* = 5 Hz, 2H), 1.83-1.76 (m, 2H), 1.58-1.35 (m, 6H). ¹³C NMR (125 MHz, CD₃CN, 298 K) δ (ppm): 156.2, 138.7, 132.2, 129.1, 125.9, 69.7, 62.4, 33.4, 29.7, 26.3, 26.3. HRMS (ESI): *m/z* calcd for [M+H]⁺ (C₁₁H₁₇BrNO₂⁺), 273.0364; found *m/z* 273.0360.

Synthesis of 4. The method to synthesize compound **4** is the same with **2**. Compound **4** was given as a yellow solid (0.68 g, 65%). M. p.: 148.8-150.1 °C. ¹H NMR (500 MHz, CD₃CN, 298 K) δ (ppm): 8.30 (s, 1H), 7.87-7.85 (m, 2H), 7.70 (d, *J* = 10 Hz, 1H), 7.35-7.33 (m, 1H), 7.06 (s, 1H), 6.91-6.89 (m, 2H), 4.09 (t, *J* = 5 Hz, 2H), 3.52 (q, *J* = 5 Hz, 2H), 1.83-1.79 (m, 2H), 1.56-1.41 (m, 6H). ¹³C NMR (125 MHz, CD₃CN,

298 K) δ (ppm): 158.2, 155.0, 150.2, 138.2, 132.0, 128.4, 122.8, 120.6, 116.3, 69.3, 62.5, 33.5, 29.9, 26.4, 26.3. HRMS (ESI): m/z calcd for $[M+H]^+$ ($C_{17}H_{22}NO_3^+$), 288.1522; found m/z 288.1520.

Synthesis of G2. The method to synthesize **G2** is the same with **G1**. **G2** was given as colorless liquid (0.72 g, 85%). 1H NMR (500 MHz, CD_3CN , 298 K) δ (ppm): 8.28 (s, 1H), 7.93-7.91 (m, 2H), 7.69 (d, $J = 10$ Hz, 1H), 7.46 (s, 1H), 7.34 (s, 2H), 7.32-7.28 (m, 1H), 7.08-7.06 (m, 2H), 5.10 (s, 2H), 4.06 (t, $J = 5$ Hz, 2H), 3.50 (t, $J = 5$ Hz, 2H), 1.81-1.77 (m, 2H), 1.53-1.43 (m, 6H), 1.32 (s, 18H). ^{13}C NMR (125 MHz, CD_3CN , 298 K) δ (ppm): 160.1, 155.1, 152.0, 149.9, 138.3, 137.4, 132.8, 128.3, 123.4, 123.0, 122.7, 120.8, 115.9. HRMS (ESI): m/z calcd for $[M+H]^+$ ($C_{32}H_{44}NO_3^+$), 490.3243; found m/z 490.3240.

Synthesis of G2-H. The method to synthesize **G2-H** is the same with **G2-H**. **G2-H** was given as a yellow solid (0.2 g, 93%). M. p.: 53.3-55.6 °C. 1H NMR (500 MHz, CD_3CN , 298 K) δ (ppm): 8.23 (s, 1H), 8.16-8.12 (m, 2H), 7.80-7.78 (m, 2H), 7.74-7.70 (m, 8H), 7.69 (s, 4H), 7.50 (s, 1H), 7.38 (s, 2H), 7.29-7.28 (m, 2H), 5.21 (s, 2H), 4.24 (t, $J = 5$ Hz, 2H), 3.54 (t, $J = 5$ Hz, 2H), 1.91-1.85 (m, 2H), 1.57-1.43 (m, 6H), 1.35 (s, 18H). ^{13}C NMR (125 MHz, CD_3CN , 298 K) δ (ppm): 162.9, 162.6 (q, $^1J_{CB} = 200$ Hz), 157.2, 152.2, 146.1, 136.6, 135.6, 135.0, 130.3, 130.2, 129.9 (m), 128.7, 127.9, 127.2, 126.5, 124.8, 124.3, 124.2, 123.5, 123.4, 123.4, 122.2, 117.1, 71.8, 71.5, 62.4, 35.5, 33.4, 31.6, 31.6, 29.4, 26.2, 26.2. HRMS (ESI): m/z calcd for $[M-BArF]^+$ ($C_{32}H_{44}NO_3^+$), 490.3312; found m/z 490.3324.

Synthesis of *P*- or *M*-R2** and *P*- or *M*-**R3**.** *P*- or *M*-**HA** (50 mg, 0.05 mmol) and **G2-H** (70 mg, 0.05 mmol) were dissolved in dried CH₂Cl₂ (0.5 ml). After stirred 2 h, 1, 4-phenylene diisocyanate (10 mg, 0.07 mmol) and 2 drops of DBTDL was added and continued to stir for two hours. Then the mixture was purified by silica gel chromatography with DCM as eluent to afford *P*- or *M*-**R2** (22 mg, 20%, M. p.: 134.2-135.1 °C) and *P*- or *M*-**R3** (40 mg, 25%, M. p.: 197.0-203.1 °C) simultaneously as white solid. ¹H NMR (500 MHz, CD₃OD/CD₂Cl₂ = 11:5 v/v, 298 K) for **R2** δ (ppm): 8.19 (d, *J* = 5 Hz, 2H), 7.94 (d, *J* = 10 Hz, 4H), 7.78 (d, *J* = 5 Hz, 2H), 7.58 (s, 4H), 7.45 (s, 2H), 7.42 (s, 6H), 7.34 (s, 4H), 7.26-7.26 (m, 6H), 7.24-7.21 (m, 2H), 7.17 (d, *J* = 10 Hz, 4H), 6.91-6.89 (m, 6H), 6.79 (s, 6H), 5.17 (s, 4H), 5.14 (s, 4H), 3.74 (m, 24H), 2.29 (m, 6H), 2.04 (m, 6H), 1.61 (m, 12H), 1.35-1.29 (m, 36H). ¹³C NMR (125 MHz, CD₃OD/CD₂Cl₂ = 11:5 v/v, 298 K) for **R2** δ (ppm): 159.4, 153.9, 151.0, 146.5, 142.9, 142.0, 140.1, 138.2, 137.3, 136.8, 134.5, 133.6, 129.6, 129.5, 127.6, 126.4, 125.2, 124.4, 122.7, 121.9, 121.8, 120.9, 115.0, 107.0, 70.7, 67.9, 55.2, 34.5, 31.7, 29.5, 29.4, 29.4, 29.3, 29.1, 29.0, 28.0, 26.9, 24.9, 22.4, 13.3. MS (MALDI-TOF): *m/z* calcd for [M+H]⁺ (C₁₄₁H₁₄₇N₄O₁₄⁺), 2121.09; found *m/z* 2121.07.

¹H NMR (300 MHz, CD₂Cl₂, 298 K) for **R3** δ (ppm): 8.27 (d, *J* = 3 Hz, 2H), 8.18 (d, *J* = 9 Hz, 4H), 7.93-7.90 (m, 6H), 7.50 (s, 6H), 7.45 (s, 6H), 7.43 (s, 2H), 7.40 (s, 4H), 7.32-7.18 (m, 18H), 6.95-6.92 (m, 18H), 6.72 (s, 6H), 5.21 (s, 6H), 5.18 (s, 4H), 5.12 (s, 6H), 3.94 (s, 18H), 3.75 (s, 12H), 3.68 (s, 18H), 3.11 (m, 4H), 2.53 (m, 4H), 1.41-1.31 (m, 36H), -0.21 (s, 4H), -0.44 (s, 4H), -1.55 (s, 8H). ¹³C NMR (125 MHz, CD₃OD/CD₂Cl₂ = 11:5 v/v, 298 K) for **R3** δ (ppm): 154.9, 154.8, 152.0, 147.5, 147.4,

145.6, 145.5, 138.2, 138.0, 135.5, 128.6, 127.5, 127.4, 126.2, 126.1, 125.4, 123.7, 122.9, 122.9, 121.7, 116.0, 108.2, 107.9, 107.9, 71.7, 68.5, 56.4, 56.2, 35.5, 31.8, 29.0, 27.3, 23.2, 23.0. MS (MALDI-TOF): m/z calcd for $[M+H]^+$ ($C_{211}H_{209}N_4O_{20}^+$), 3120.54; found m/z 3120.59.

5. Characterization of new compounds

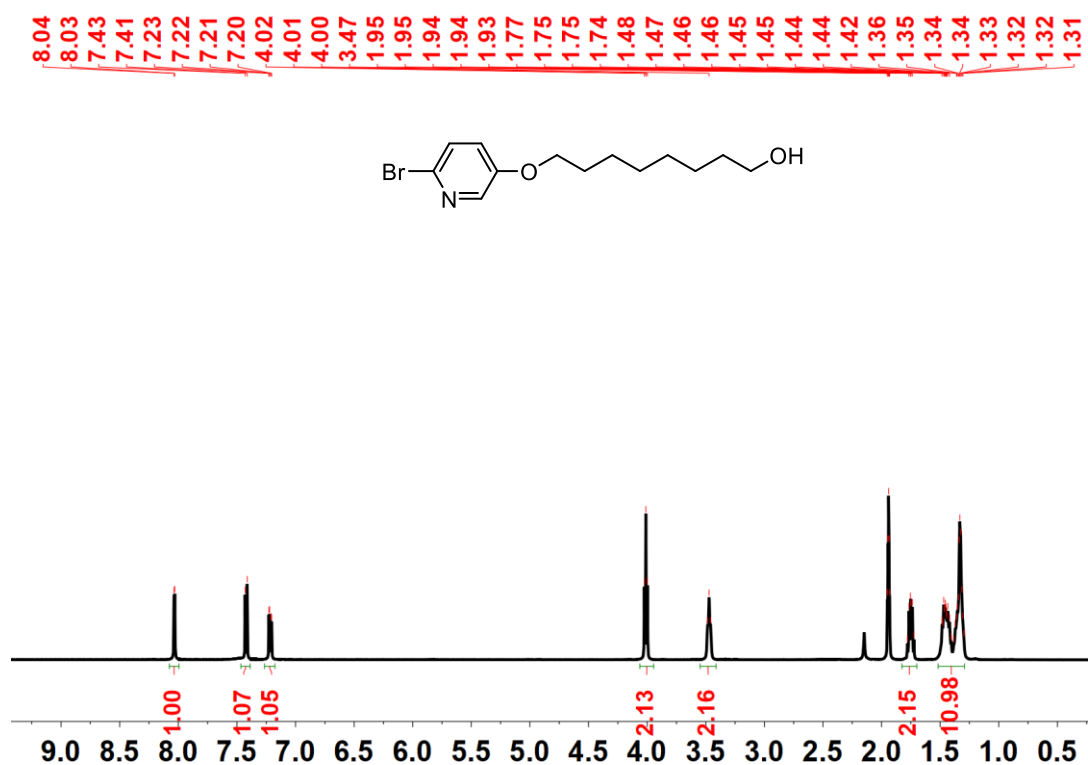


Fig. S3. 1H NMR spectrum (500 MHz, CD_3CN , 298 K) of compound 1.

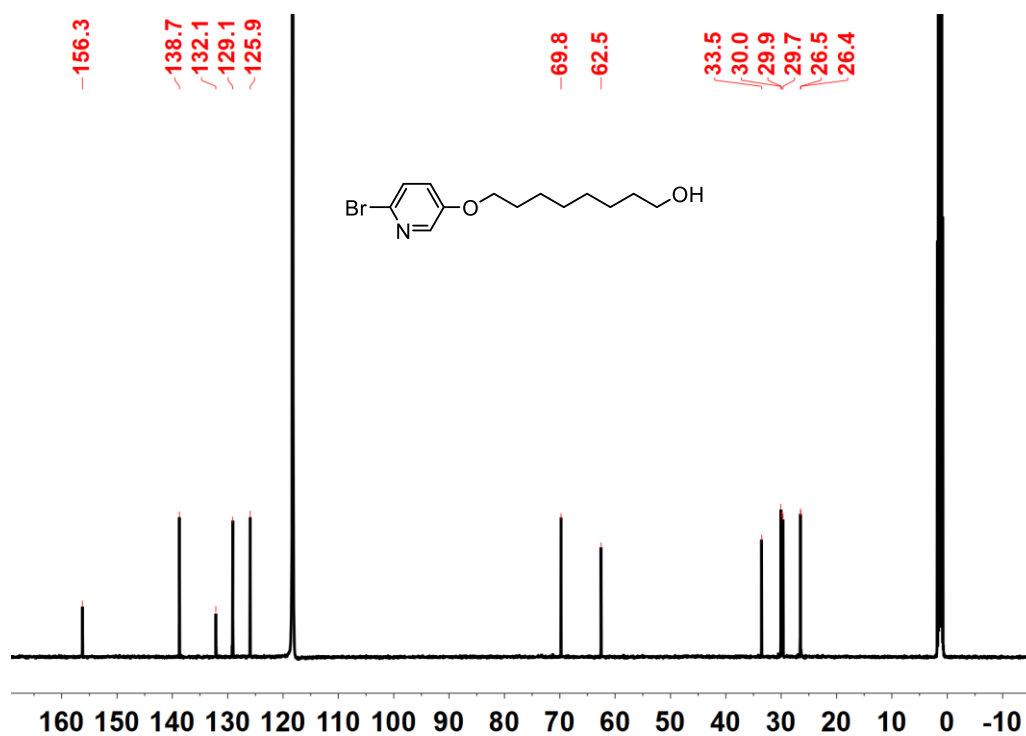


Fig. S4. ¹³C NMR spectrum (125 MHz, CD₃CN, 298 K) of compound 1.

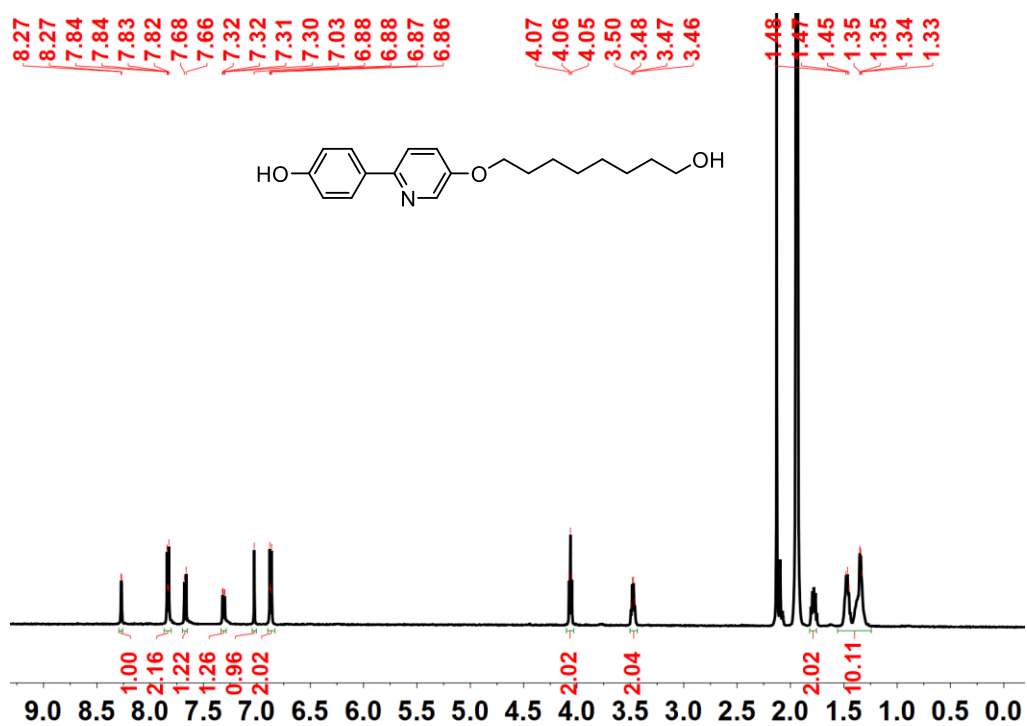


Fig. S5. ¹H NMR spectrum (500 MHz, CD₃CN, 298 K) of compound 2.

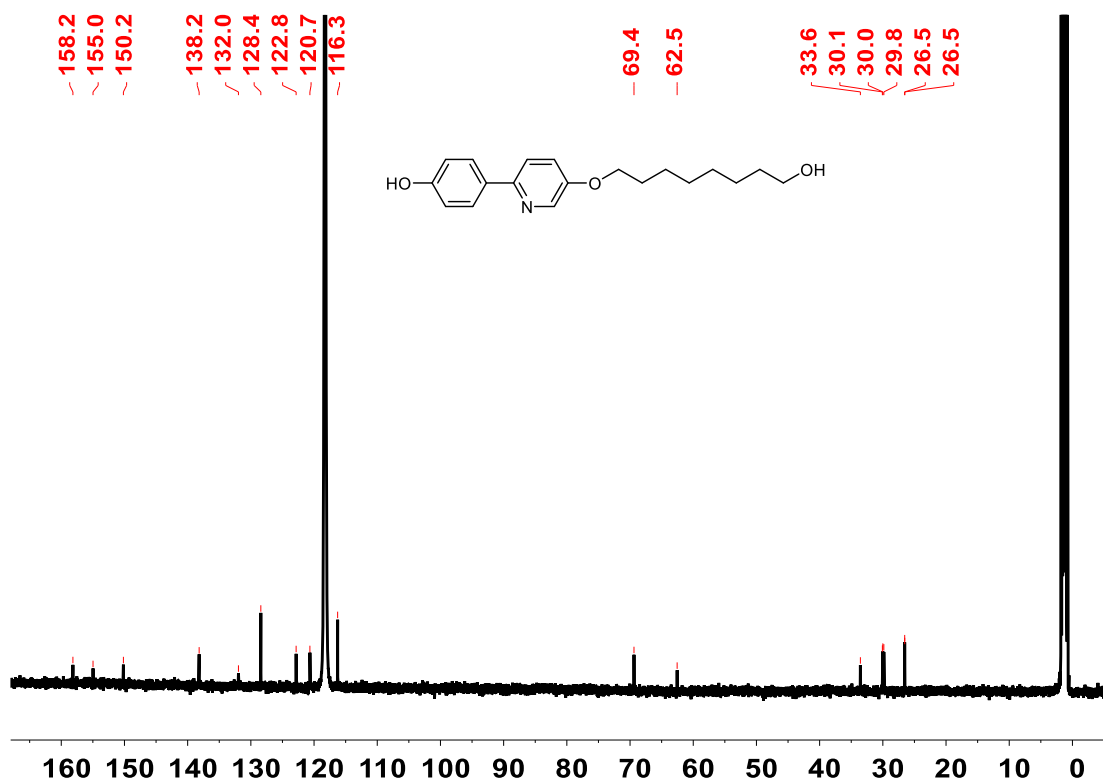


Fig. S6. ^{13}C NMR spectrum (125 MHz, CD_3CN , 298 K) of compound 2.

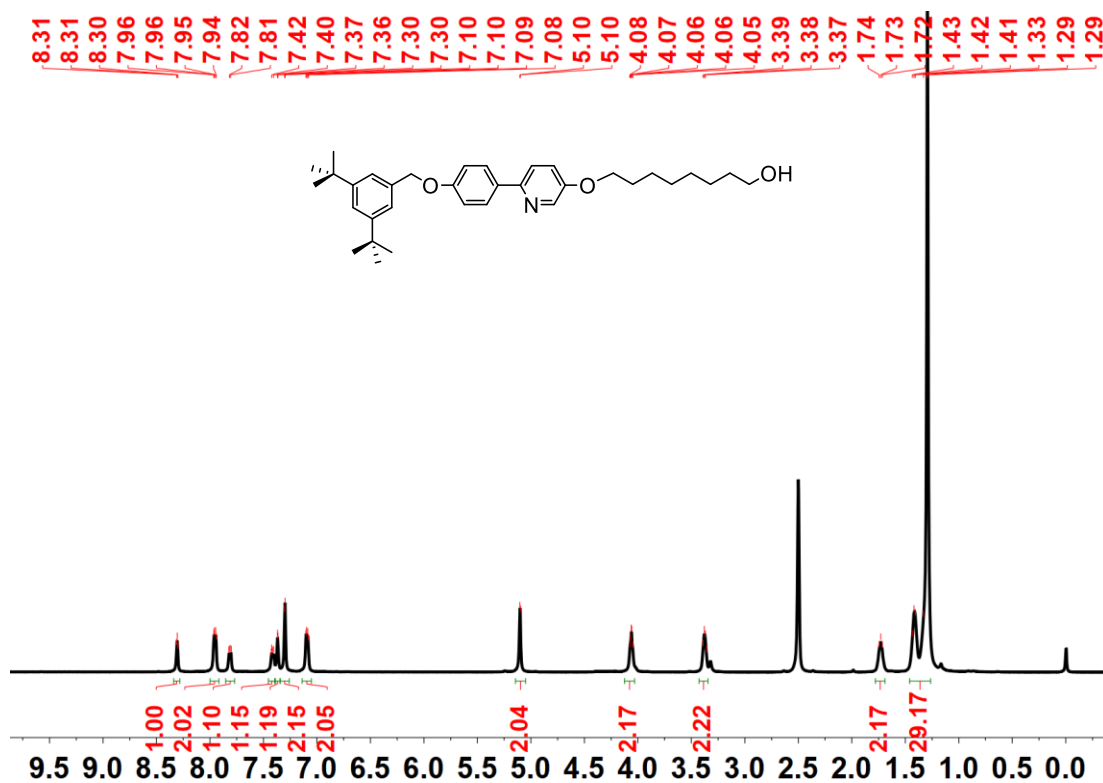


Fig. S7. ^1H NMR spectrum (500 MHz, CD_3CN , 298 K) of compound G1.

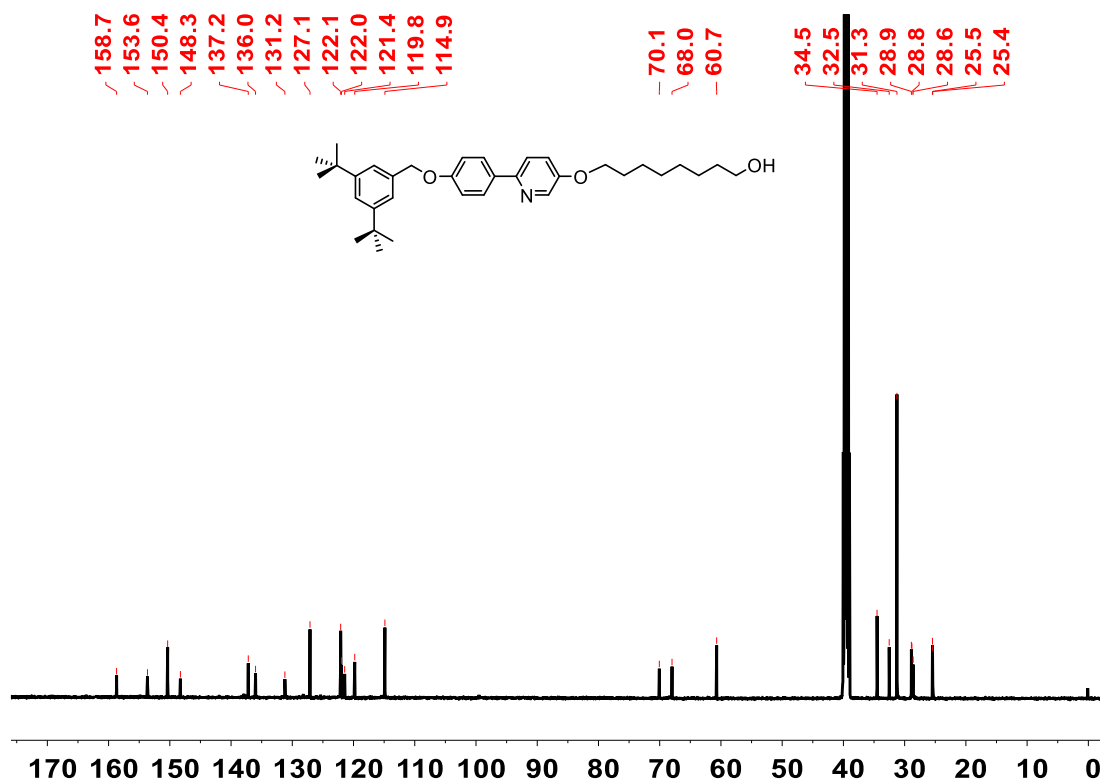


Fig. S8. ¹³C NMR spectrum (125 MHz, CD₃CN, 298 K) of compound G1.

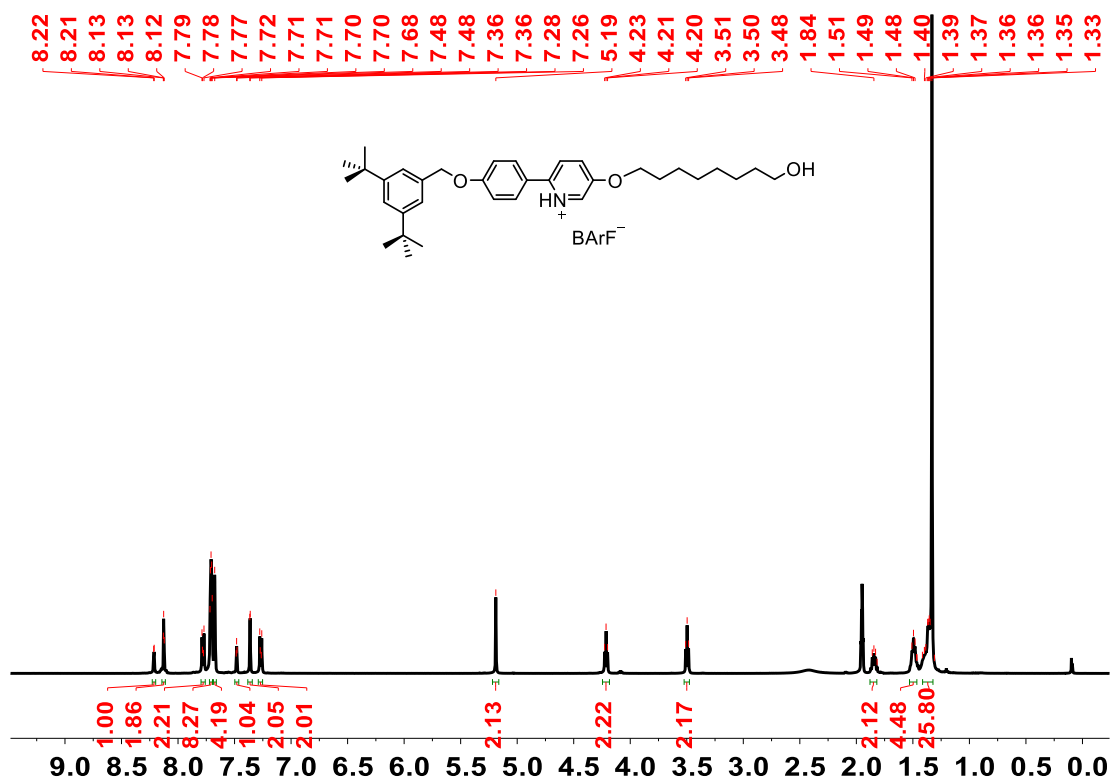


Fig. S9. ¹H NMR spectrum (500 MHz, CD₃CN, 298 K) of compound G1-H.

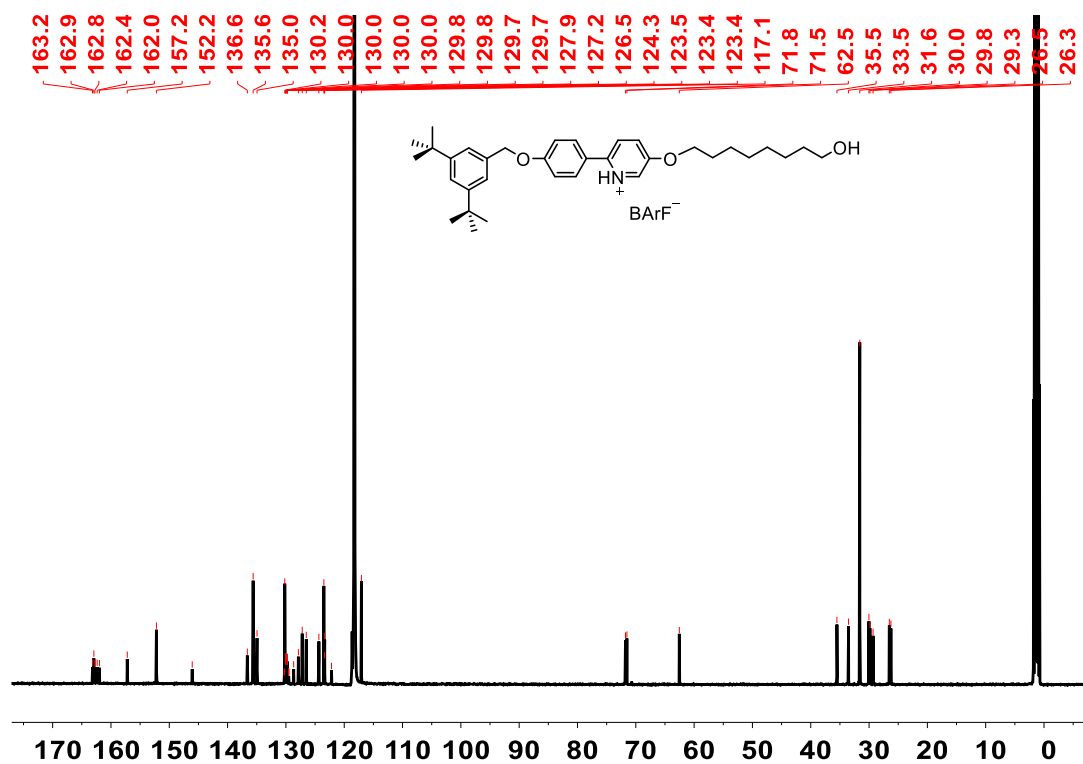


Fig. S10. ¹³C NMR spectrum (125 MHz, CD₃CN, 298 K) of compound **G1-H**.

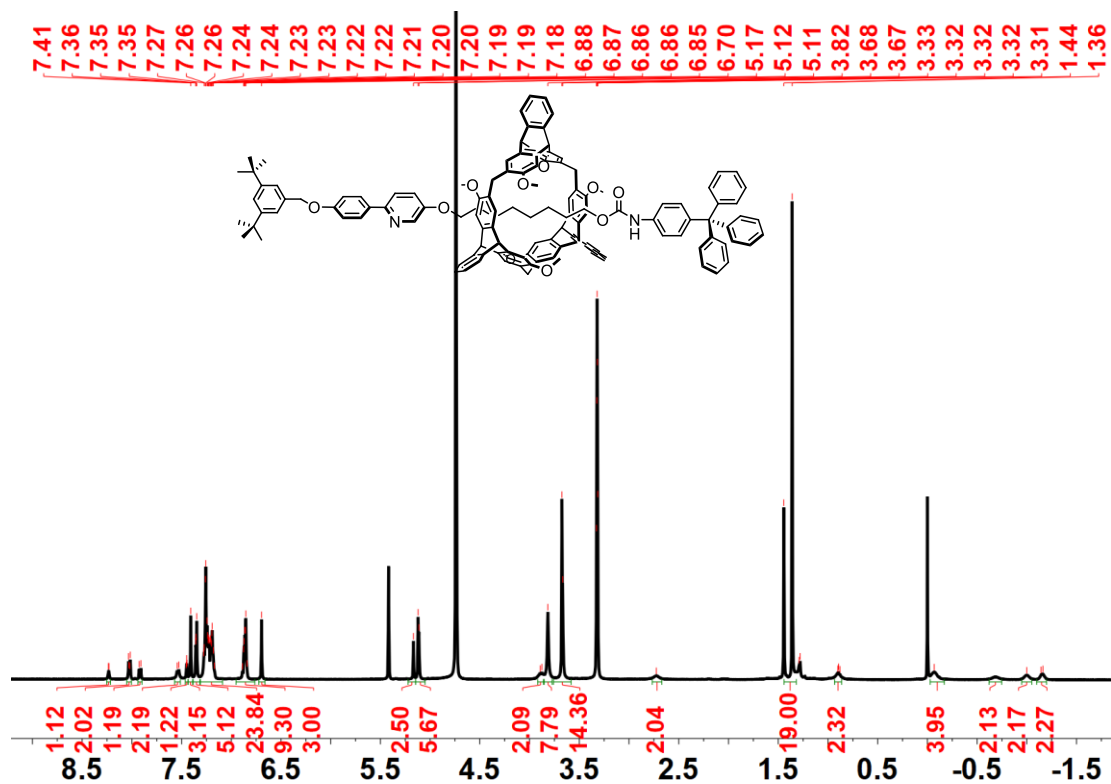


Fig. S11. ¹H NMR spectrum (500 MHz, CD₃OD/CD₂Cl₂ = 11:5 v/v, 298 K) of compound **R1**.

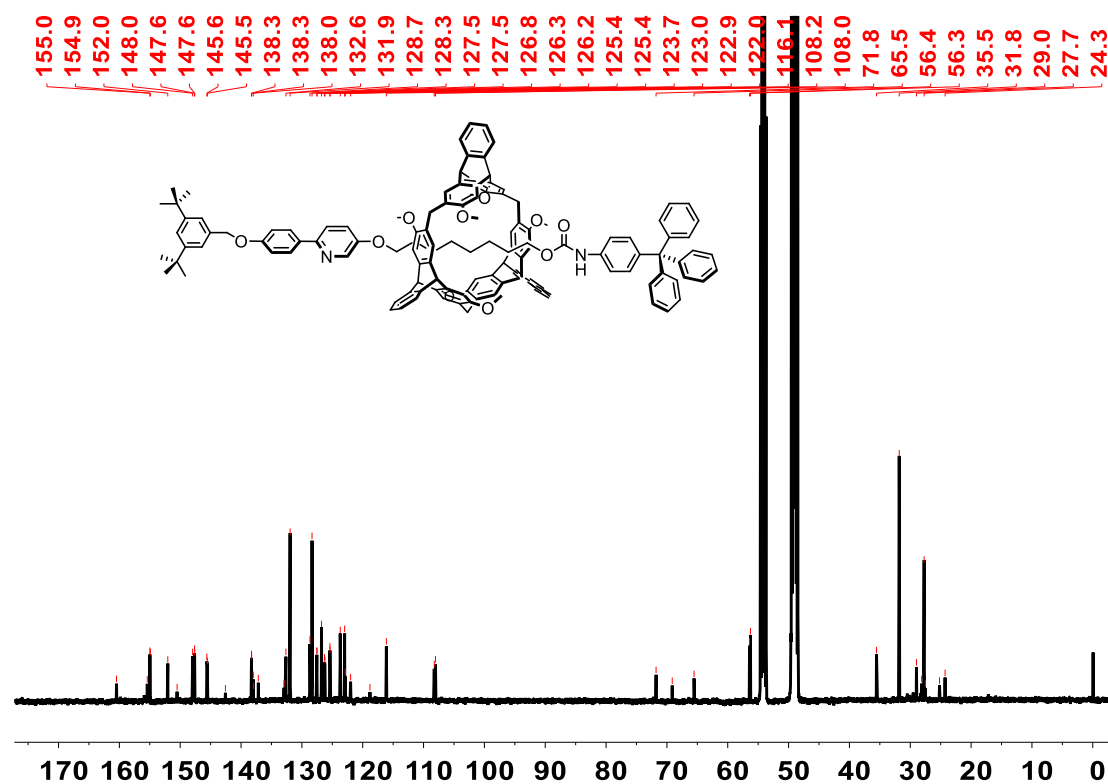


Fig. S12. ¹³C NMR spectrum (125 MHz, CD₃OD/CD₂Cl₂ = 11:5 v/v, 298 K) of compound R1.

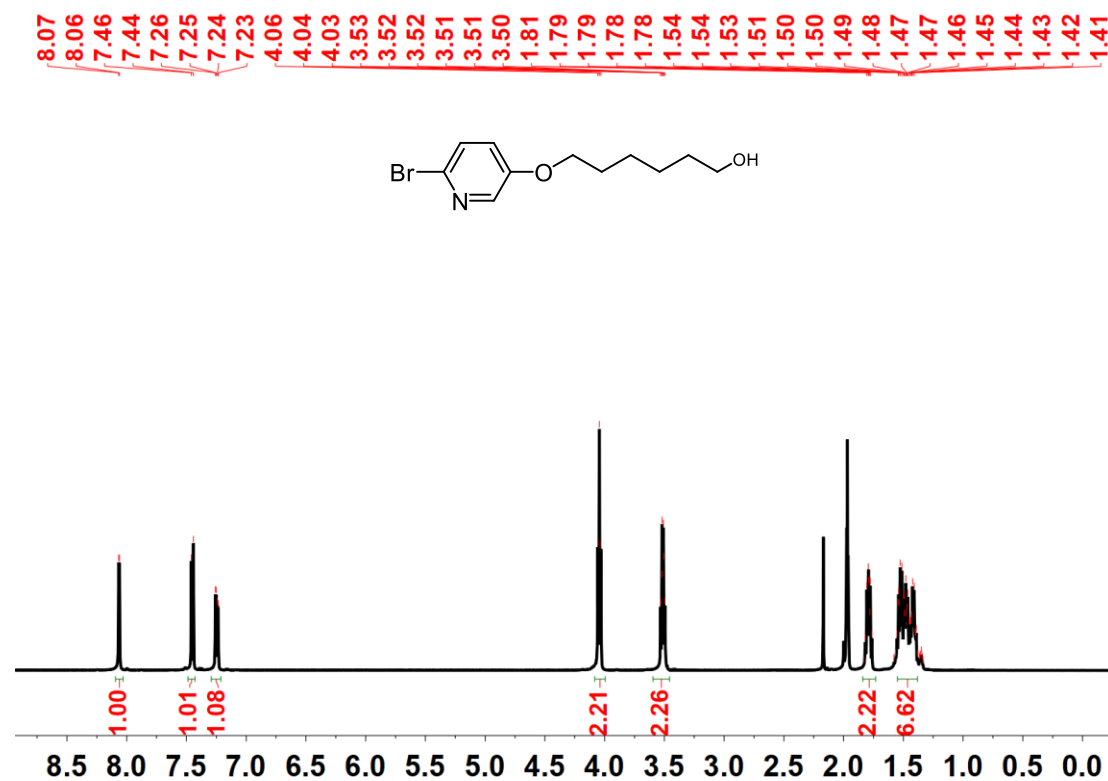


Fig. S13. ¹H NMR spectrum (500 MHz, CD₃CN, 298 K) of compound 3.

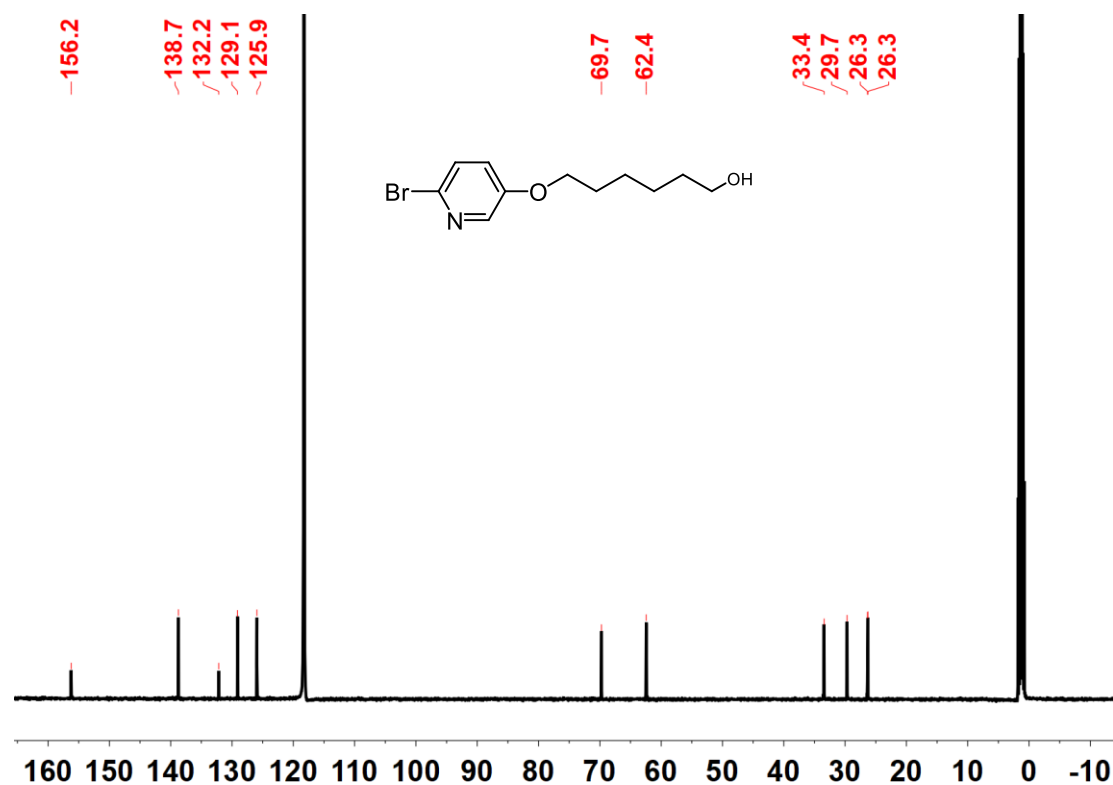


Fig. S14. ¹³C NMR spectrum (125 MHz, CD₃CN, 298 K) of compound 3.

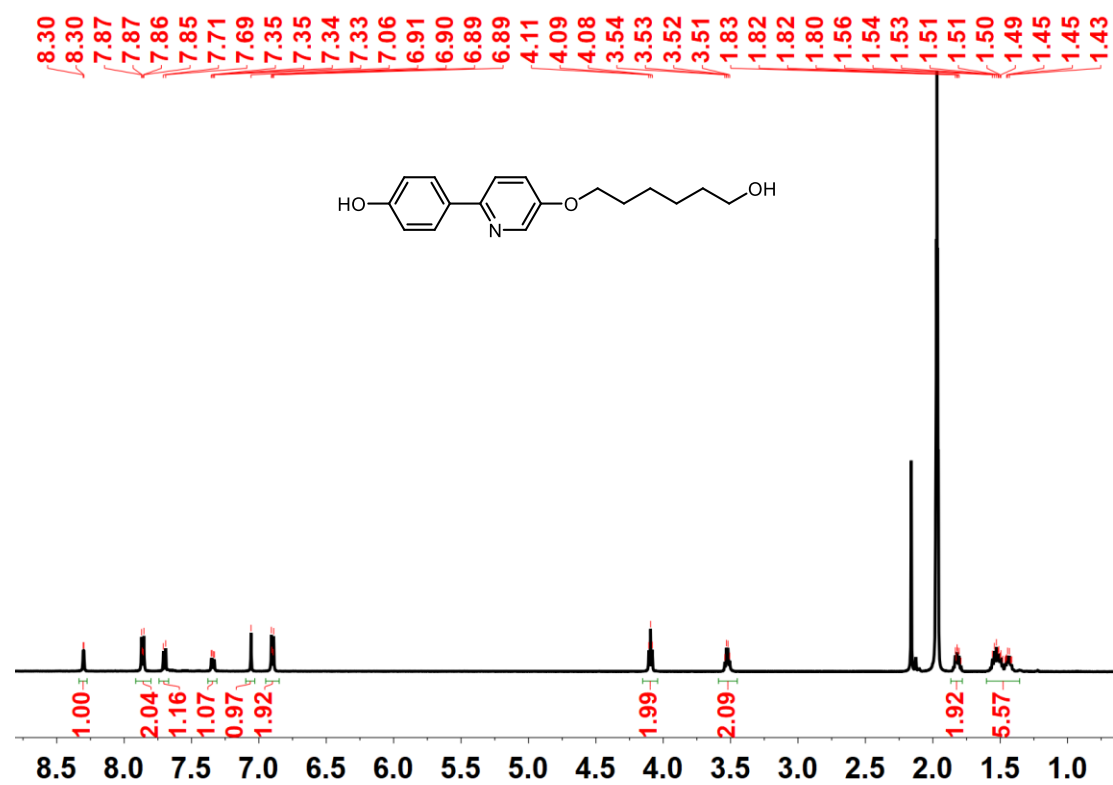


Fig. S15. ¹H NMR spectrum (500 MHz, CD₃CN, 298 K) of compound 4.

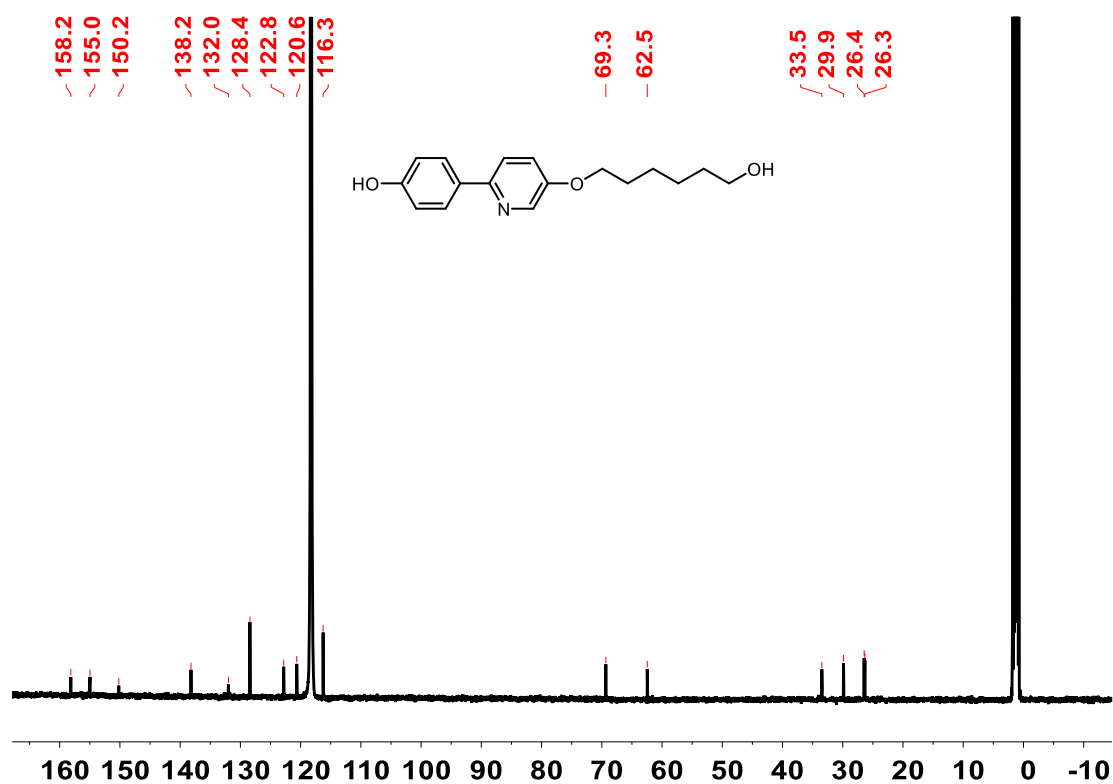


Fig. S16. ¹³C NMR spectrum (125 MHz, CD₃CN, 298 K) of compound 4.

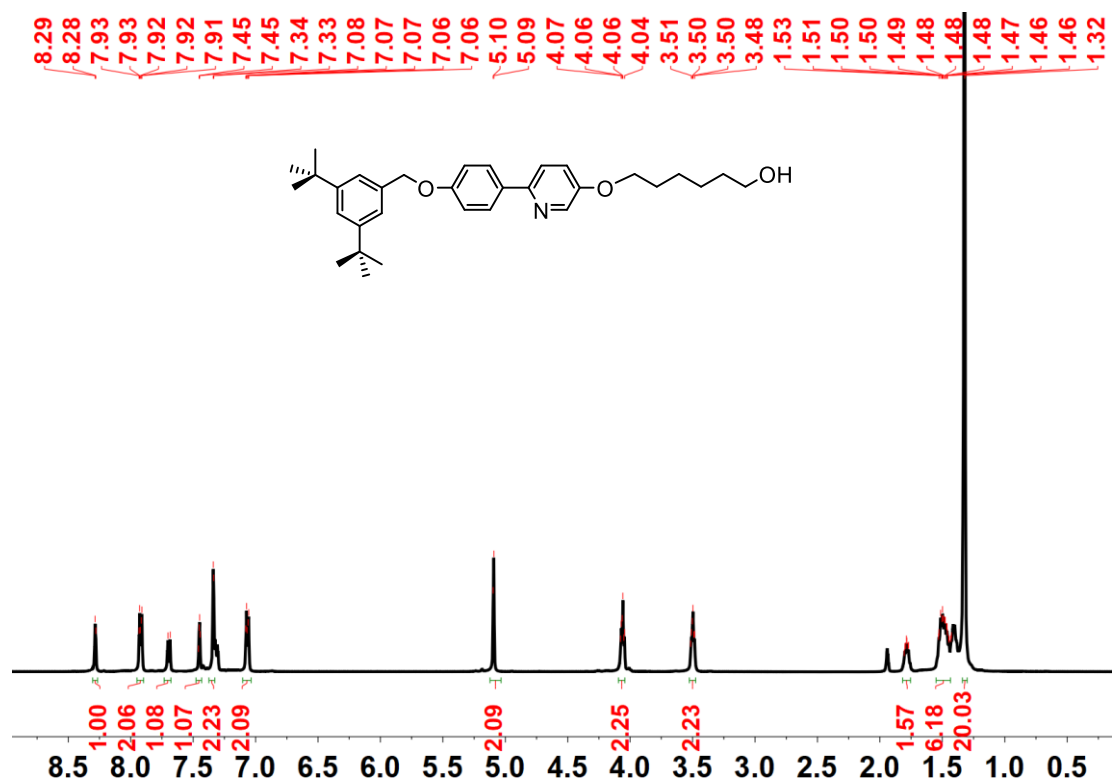


Fig. S17. ¹H NMR spectrum (500 MHz, CD₃CN, 298 K) of compound G2.

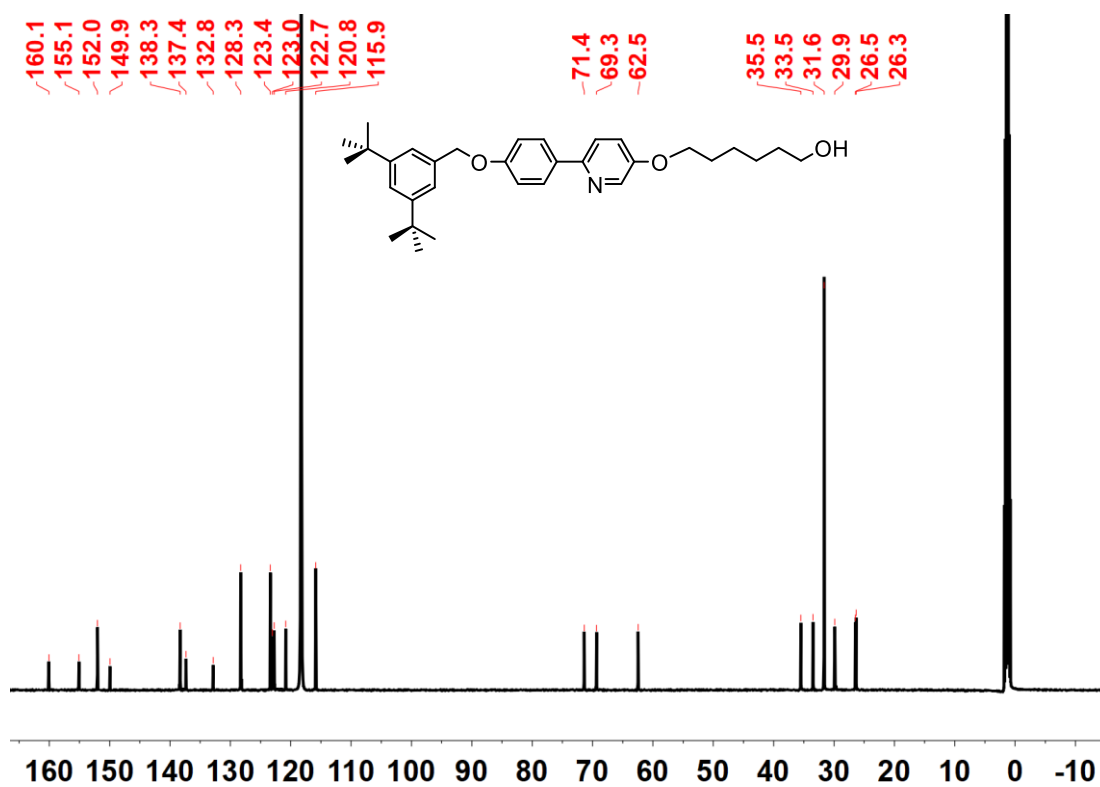


Fig. S18. ¹³C NMR spectrum (125 MHz, CD₃CN, 298 K) of compound G2.

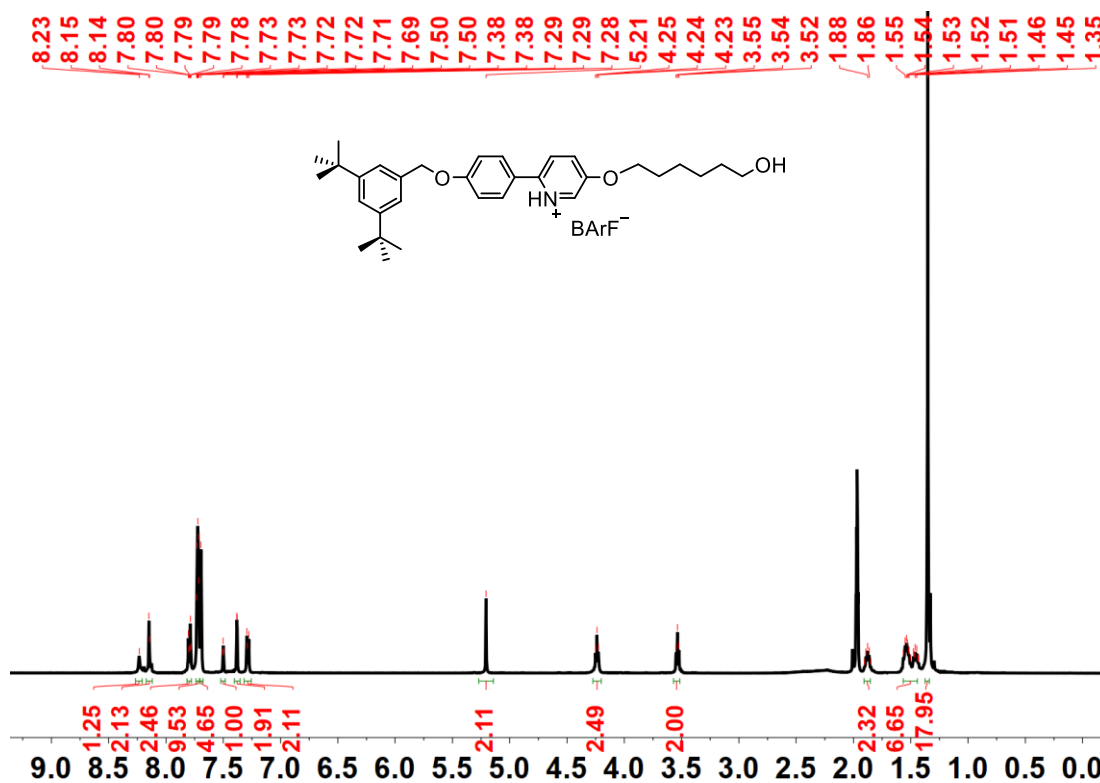


Fig. S19. ¹H NMR spectrum (500 MHz, CD₃CN, 298 K) of compound G2-H.

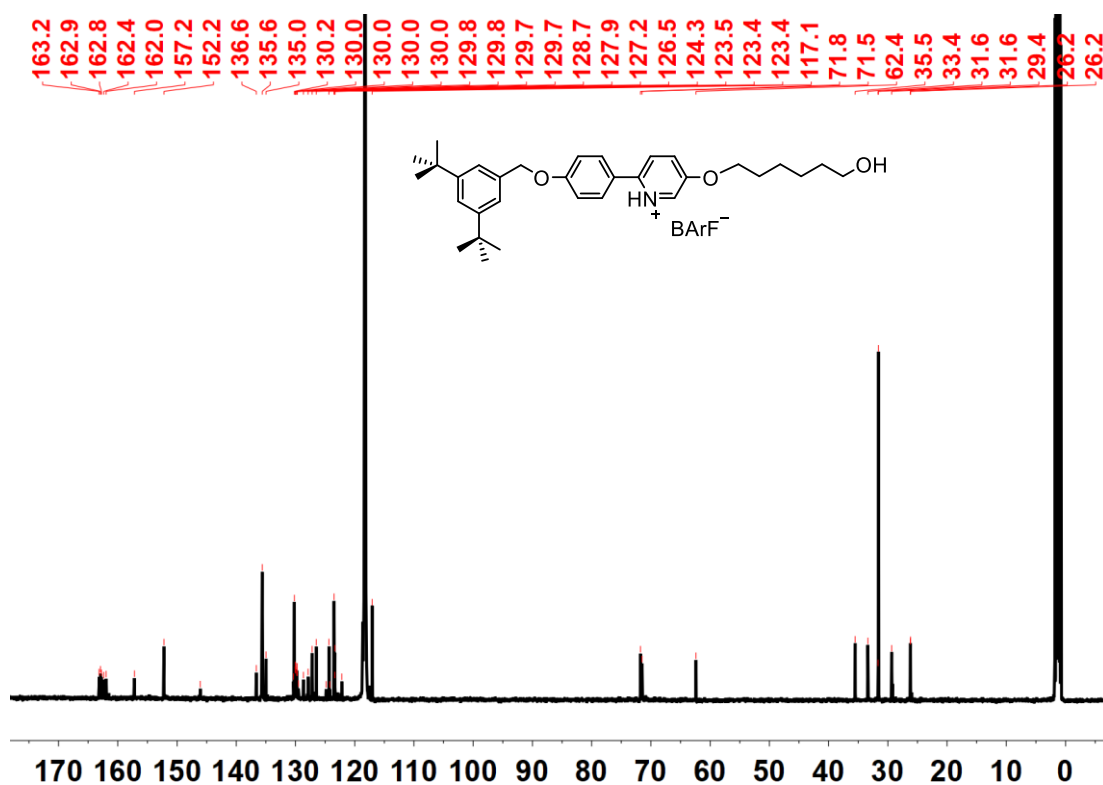


Fig. S20. ¹³C NMR spectrum (125 MHz, CD₃CN, 298 K) of compound **G2-H**.

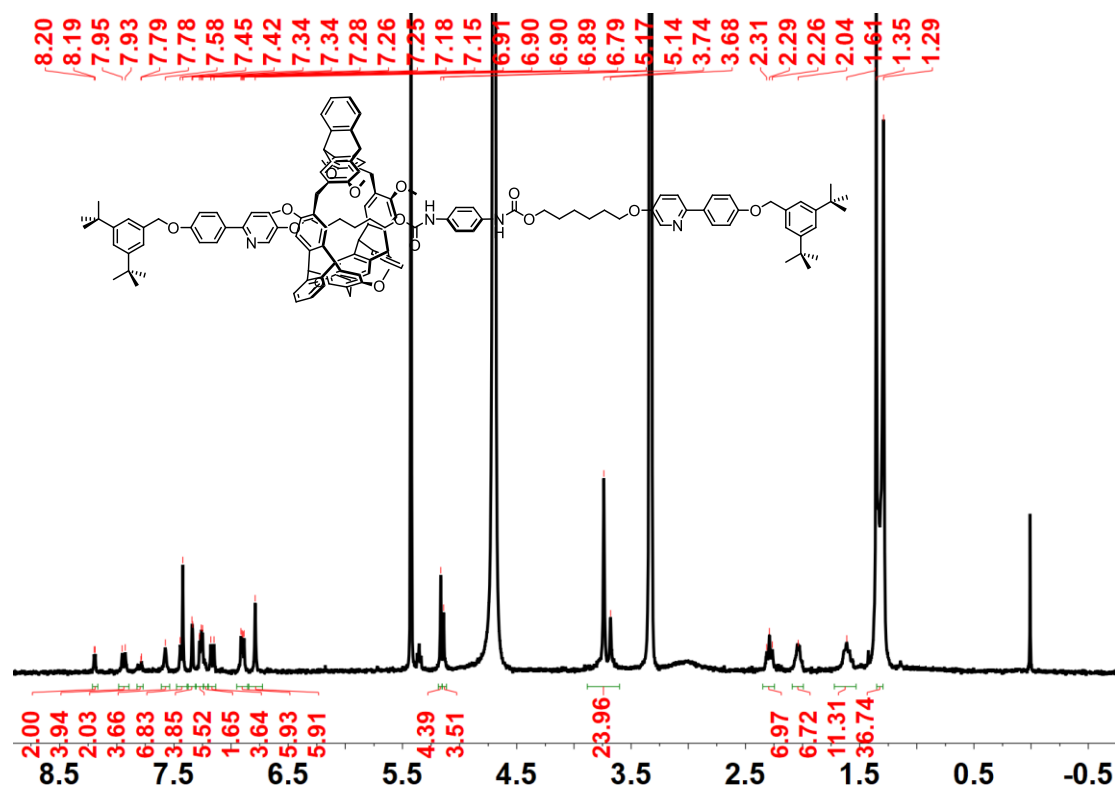


Fig. S21. ¹H NMR spectrum (500 MHz, CD₃OD/CD₂Cl₂ = 11:5 v/v, 298 K) of compound **R2**.

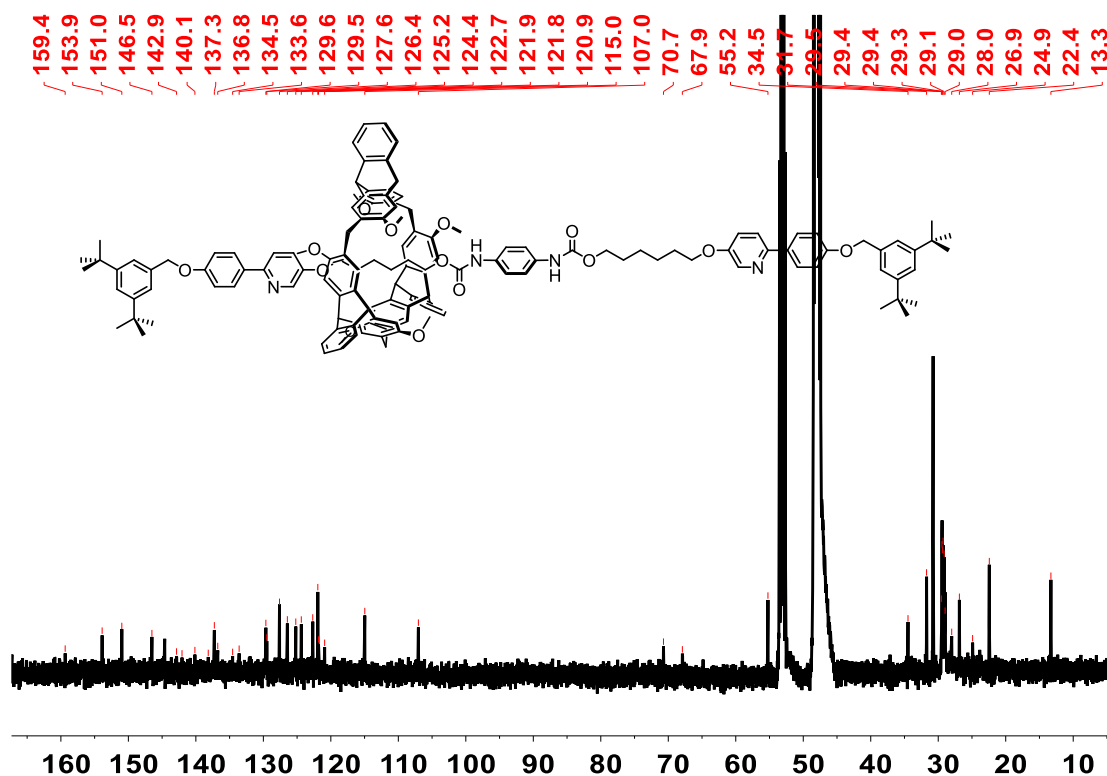


Fig. S22. ^{13}C NMR spectrum (125 MHz, $\text{CD}_3\text{OD}/\text{CD}_2\text{Cl}_2 = 11:5$ v/v, 298 K) of compound **R2**.

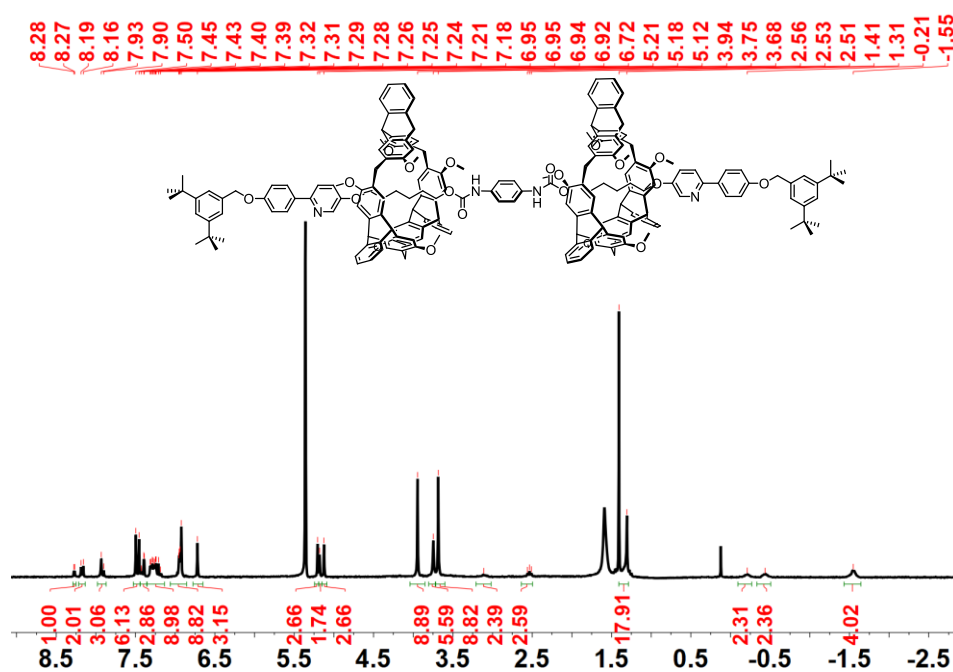


Fig. S23. ^1H NMR spectrum (300 MHz, CD_2Cl_2 , 298 K) of compound **R3**.

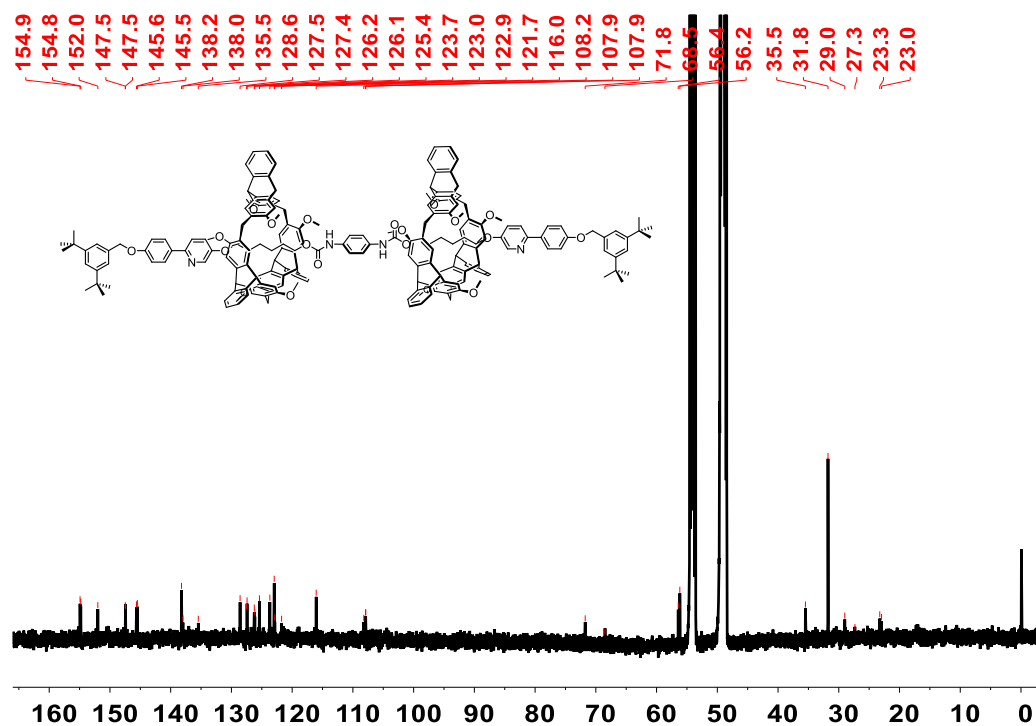


Fig. S24. ^{13}C NMR spectrum (125 MHz, $\text{CD}_3\text{OD}/\text{CD}_2\text{Cl}_2 = 11:5$ v/v, 298 K) of compound **R3**.

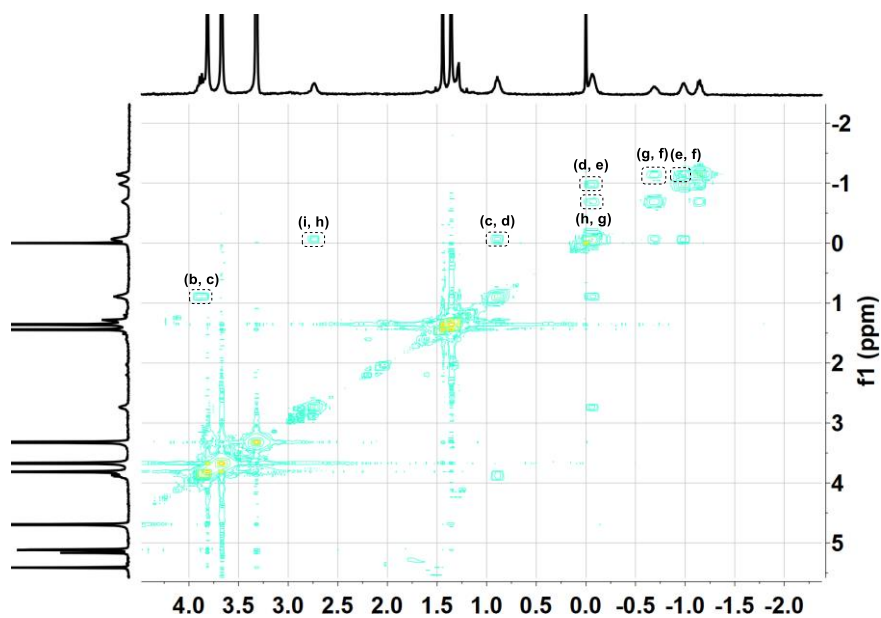


Fig. S25. 2D COSY spectrum (500 MHz, $\text{CD}_3\text{OD}/\text{CD}_2\text{Cl}_2 = 11:5$ v/v, 298 K) of **R1**.

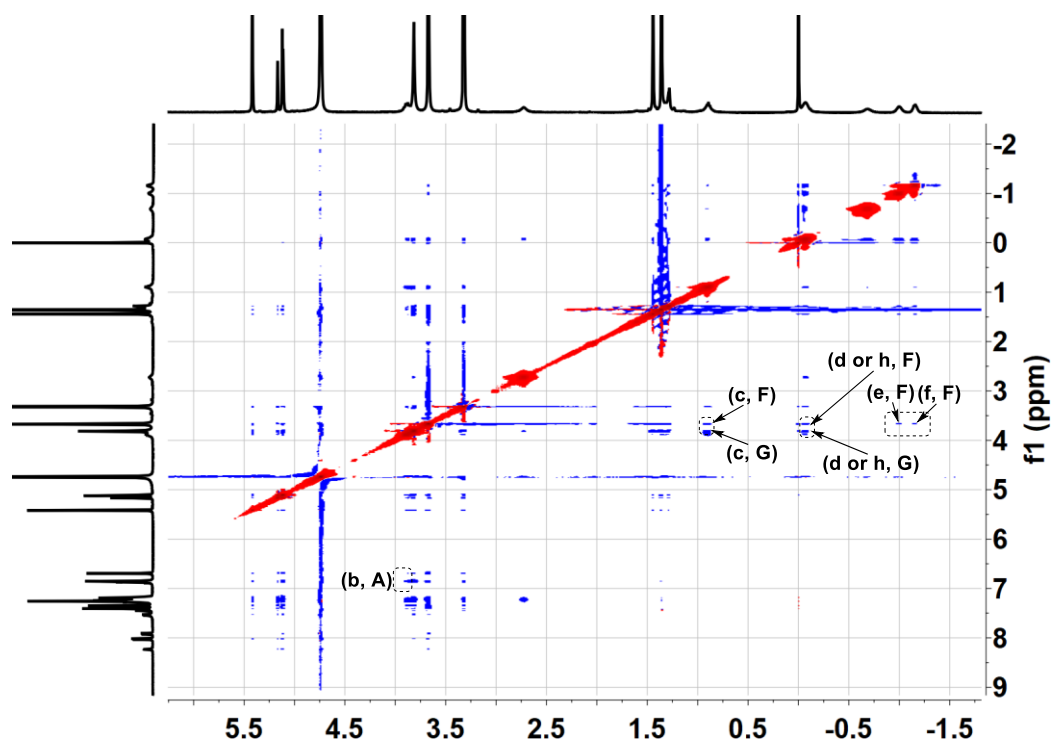


Fig. S26. 2D ROESY spectrum (500 MHz, $\text{CD}_3\text{OD}/\text{CD}_2\text{Cl}_2 = 11:5$ v/v, 298 K) of **R1**.

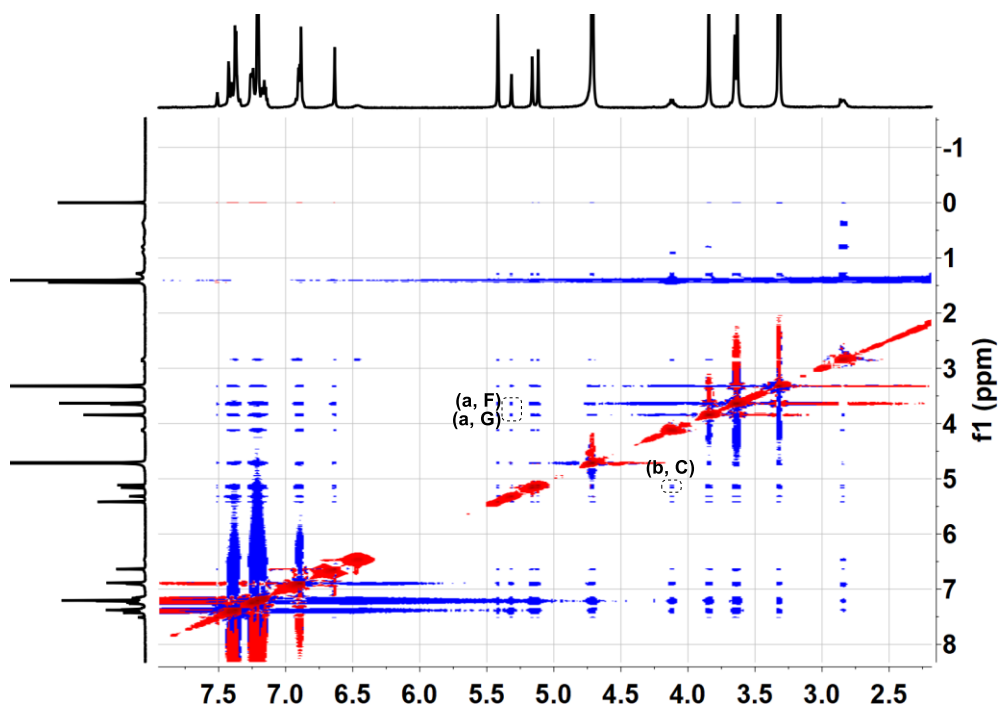


Fig. S27. 2D NOESY spectrum (500 MHz, $\text{CD}_3\text{OD}/\text{CD}_2\text{Cl}_2 = 11:5$ v/v, 298 K) of **R1-**

H.

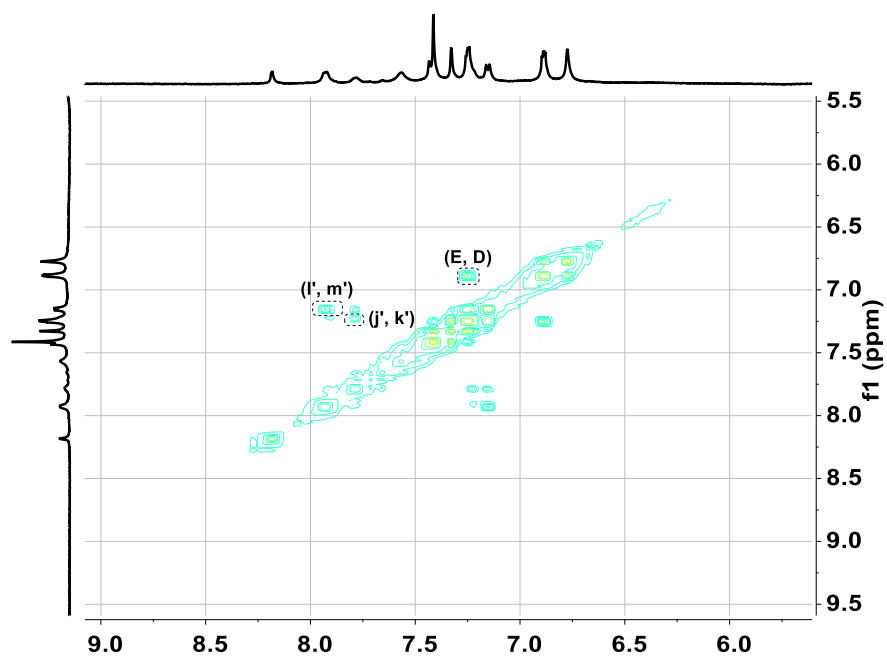


Fig. S28. 2D COSY spectrum (500 MHz, $\text{CD}_3\text{OD}/\text{CD}_2\text{Cl}_2 = 11:5$ v/v, 298 K) of **R2**.

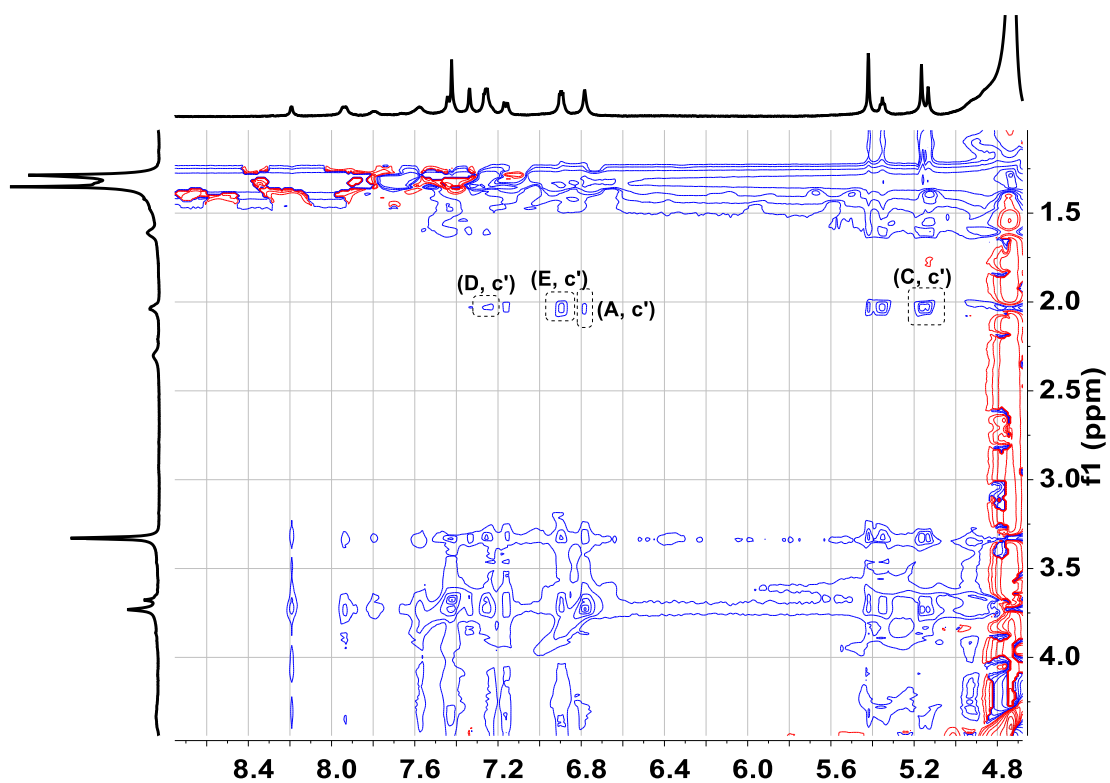


Fig. S29. 2D ROESY spectrum (500 MHz, $\text{CD}_3\text{OD}/\text{CD}_2\text{Cl}_2 = 11:5$ v/v, 298 K) of **R2**.

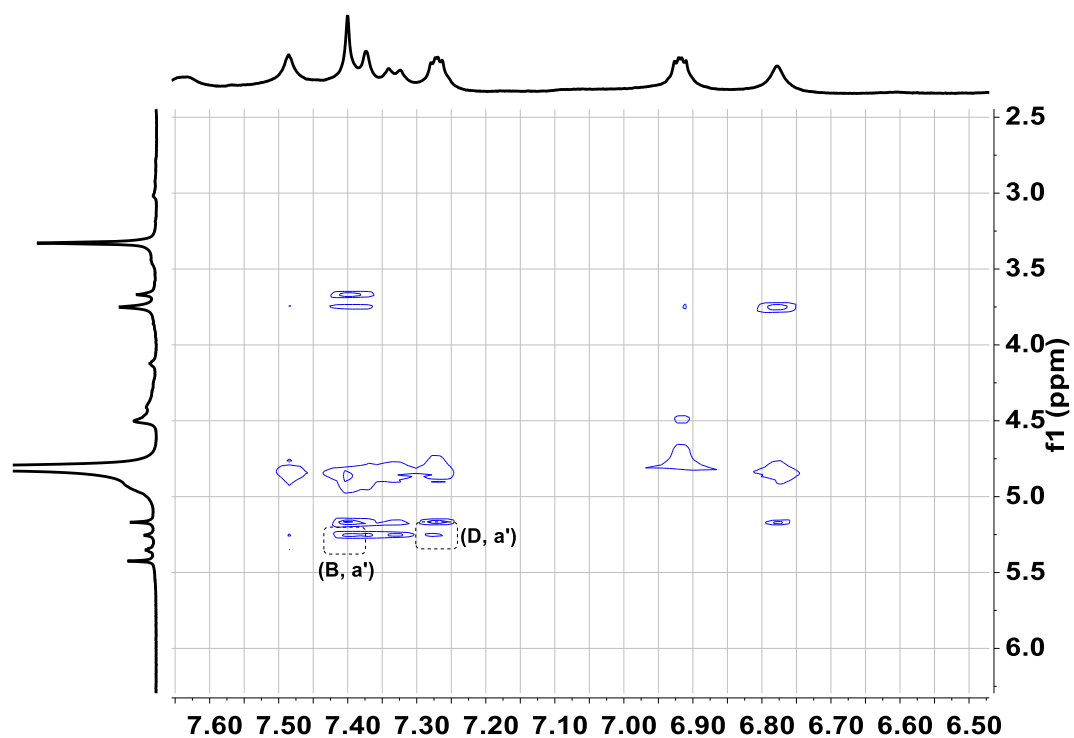


Fig. S30. 2D NOESY spectrum (500 MHz, $\text{CD}_3\text{OD}/\text{CD}_2\text{Cl}_2 = 11:5$ v/v, 298 K) of **R2-H**.

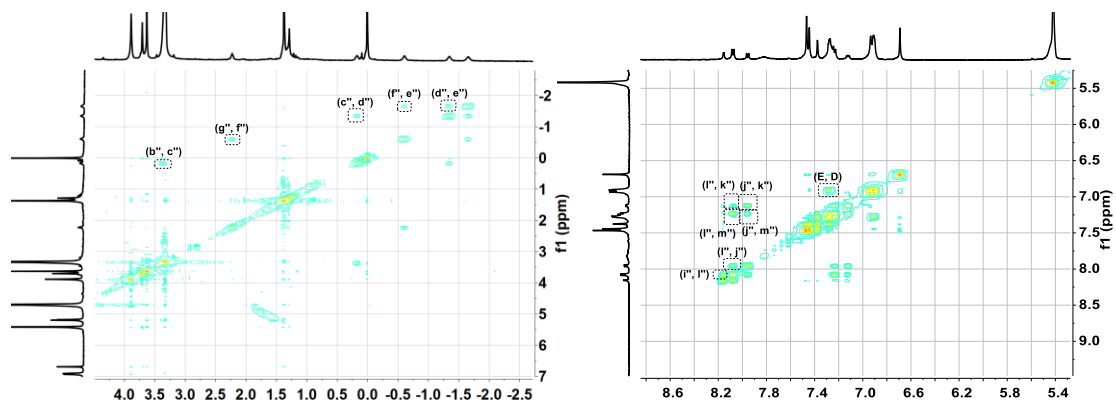


Fig. S31. 2D COSY spectrum (500 MHz, $\text{CD}_3\text{OD}/\text{CD}_2\text{Cl}_2 = 11:5$ v/v, 298 K) of **R3**.

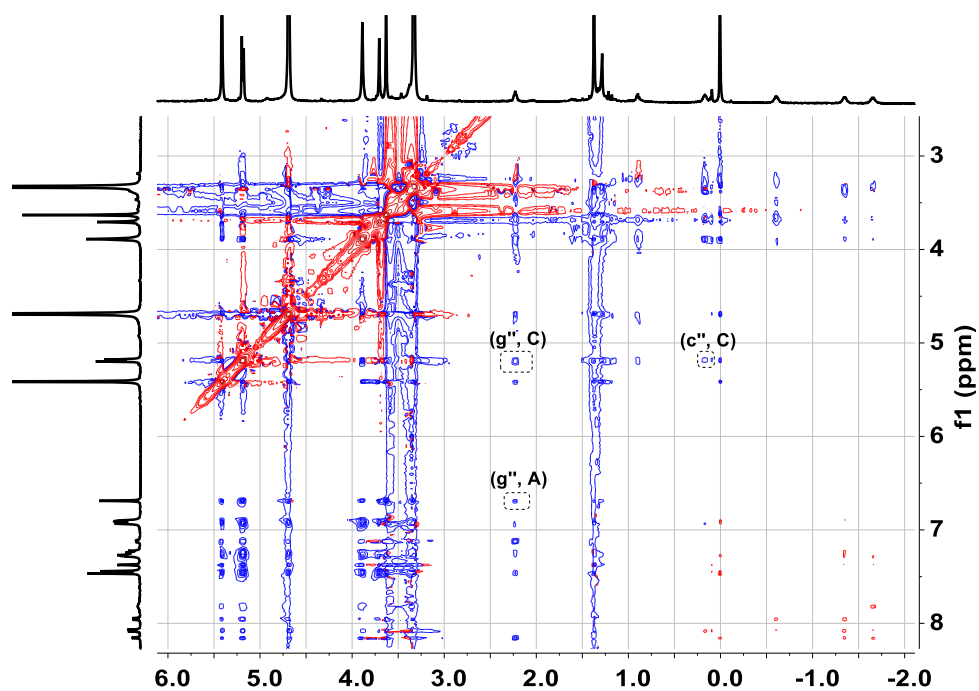


Fig. S32. 2D ROESY spectrum (500 MHz, $\text{CD}_3\text{OD}/\text{CD}_2\text{Cl}_2 = 11:5$ v/v, 298 K) of **R3**.

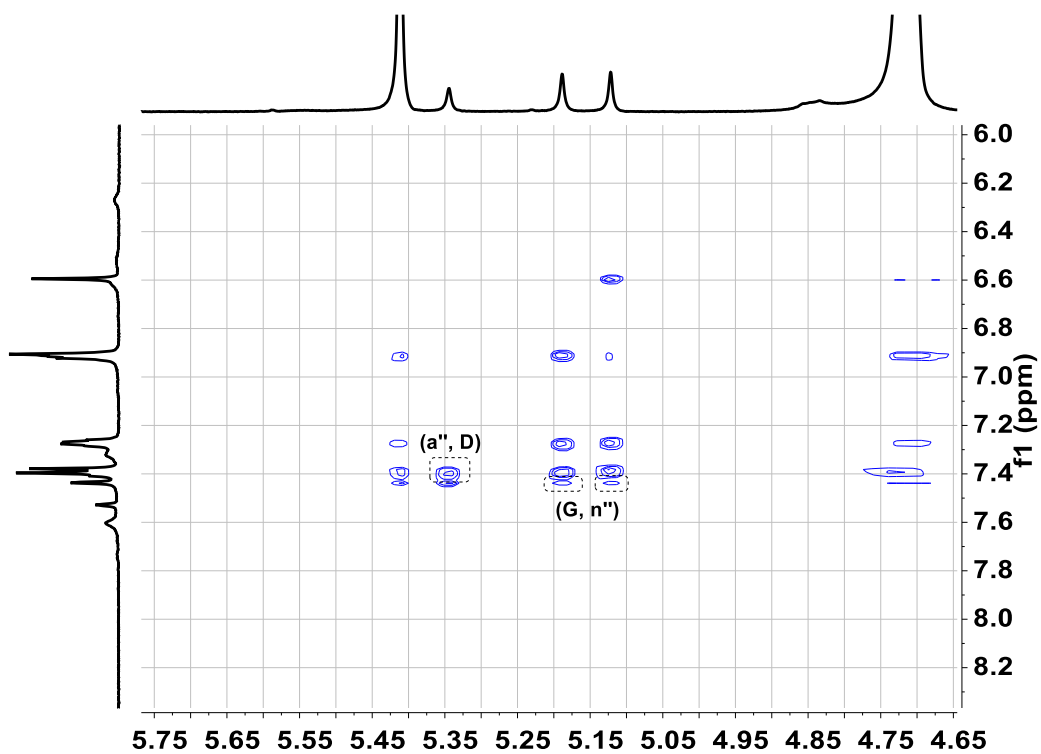


Fig. S33. 2D ROESY spectrum (500 MHz, $\text{CD}_3\text{OD}/\text{CD}_2\text{Cl}_2 = 11:5$ v/v, 298 K) of **R3-H**.

6. Variable-temperature ^1H NMR experiments

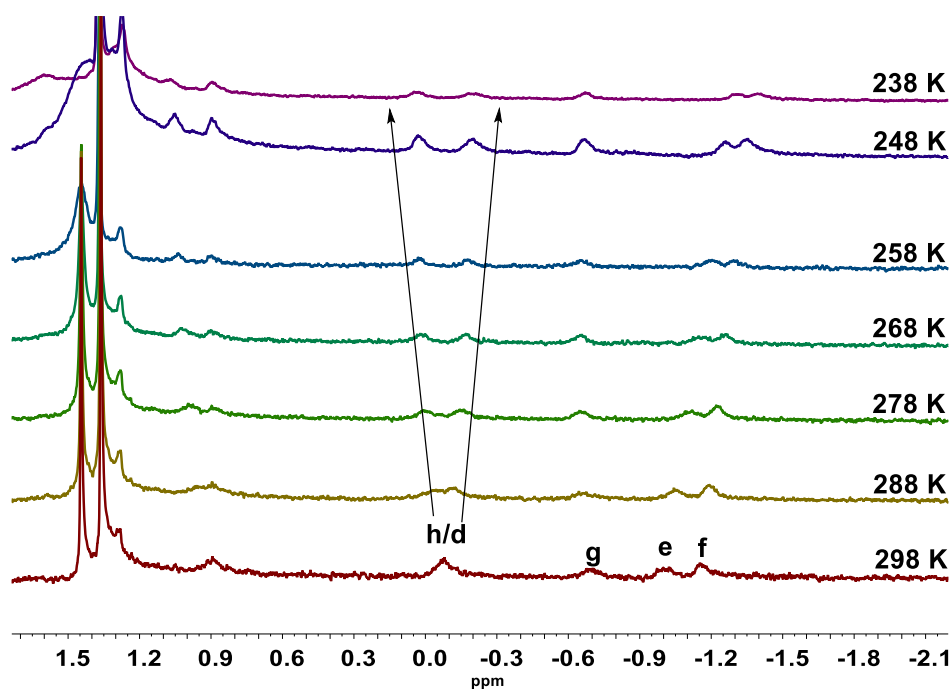


Fig. S34. Variable-temperature ^1H NMR experiments of **R1** (500 MHz, $\text{CD}_3\text{OD}/\text{CD}_2\text{Cl}_2$ = 11:5 v/v).

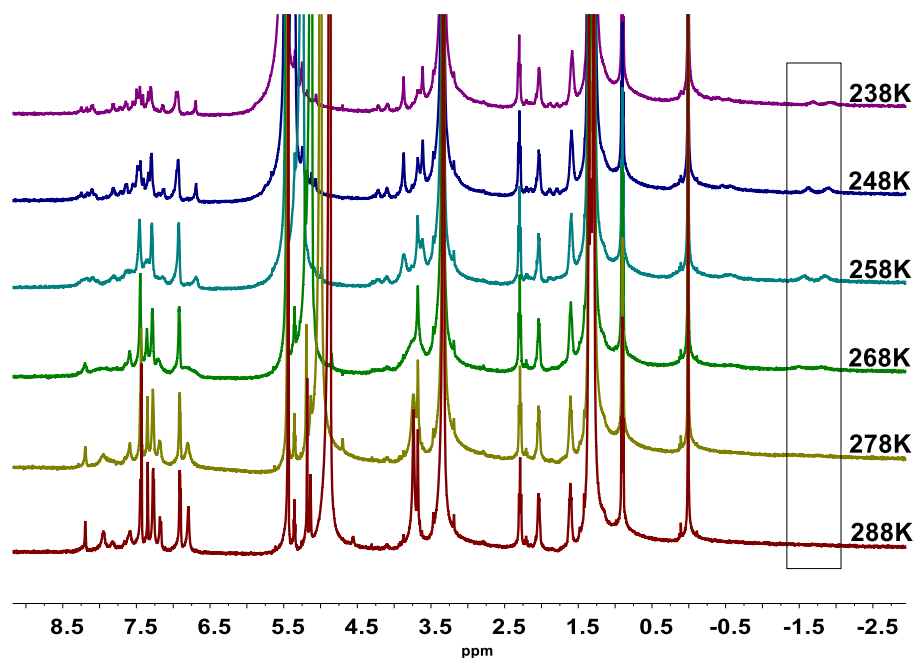


Fig. S35. Variable-temperature ^1H NMR experiments of **R2** (500 MHz, $\text{CD}_3\text{OD}/\text{CD}_2\text{Cl}_2$ = 11:5 v/v).

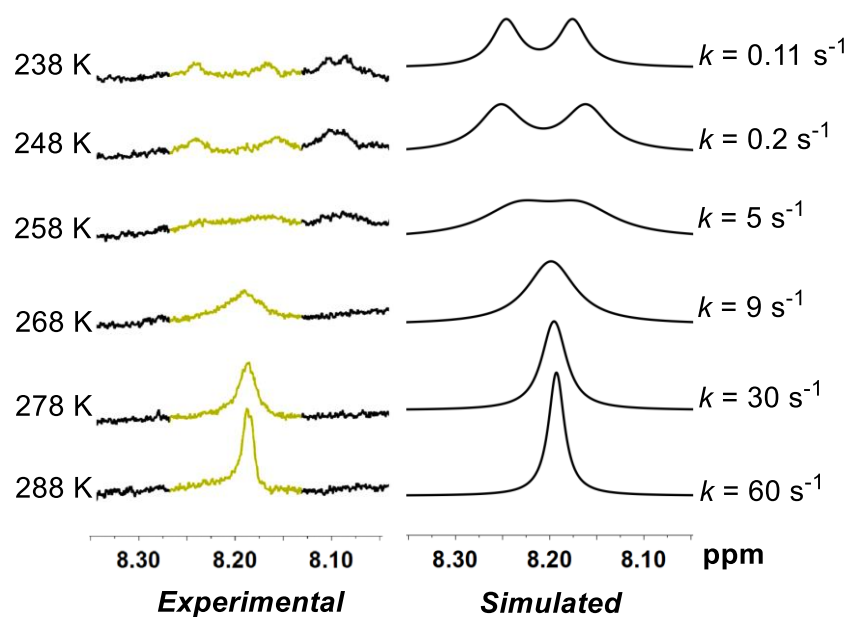


Fig. S36. Experimentally measured (left) and simulated (right) variable-temperature ^1H NMR (500 MHz, $\text{CD}_3\text{OD}/\text{CD}_2\text{Cl}_2 = 11:5$ v/v) spectra of H^{i} of **R2**.

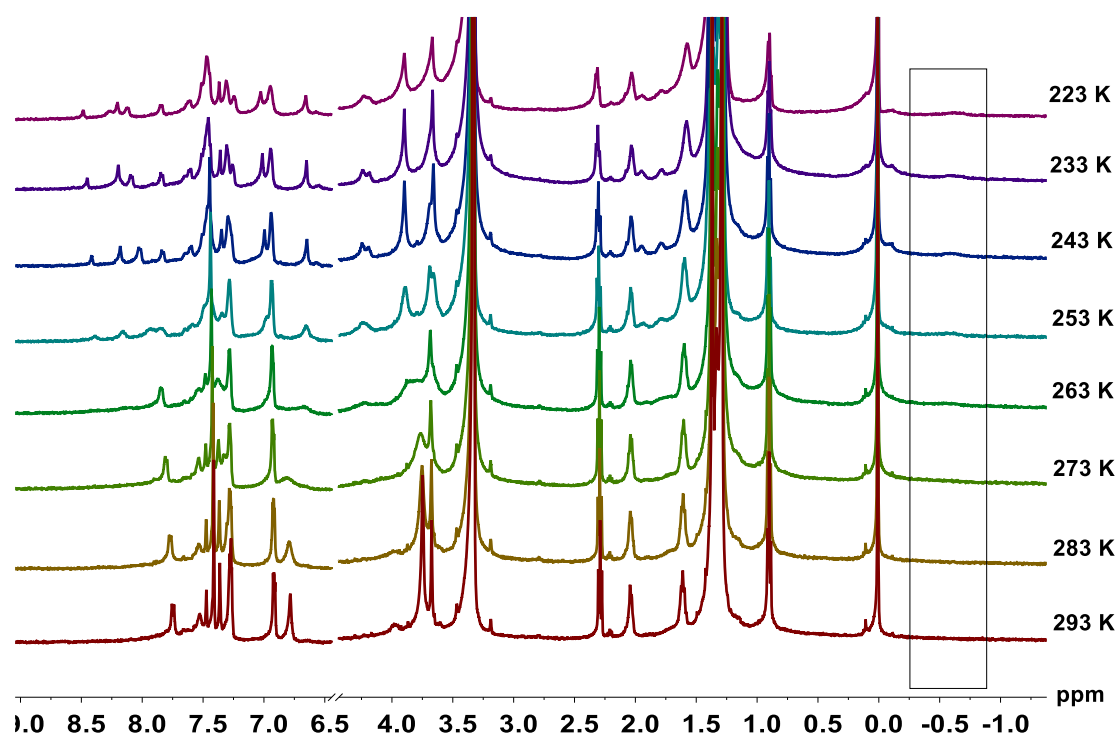


Fig. S37. Variable-temperature ^1H NMR experiments of **R2-H** (500 MHz, $\text{CD}_3\text{OD}/\text{CD}_2\text{Cl}_2 = 11:5$ v/v).

7. CD spectra of chiral rotaxanes

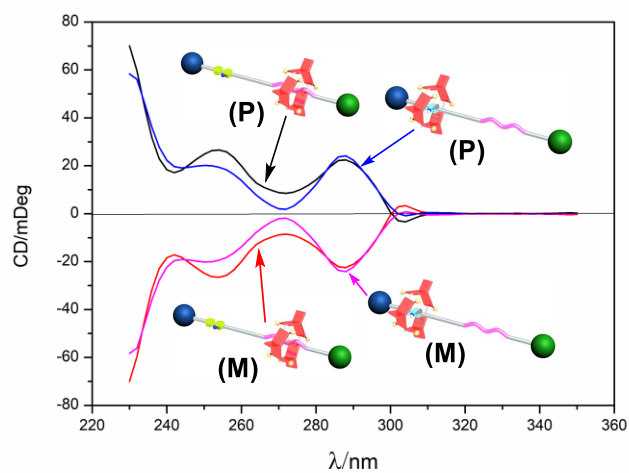


Fig. S38. Comparison of CD spectra of *P*- or *M*-R1 and *P*- or *M*-R1-H.

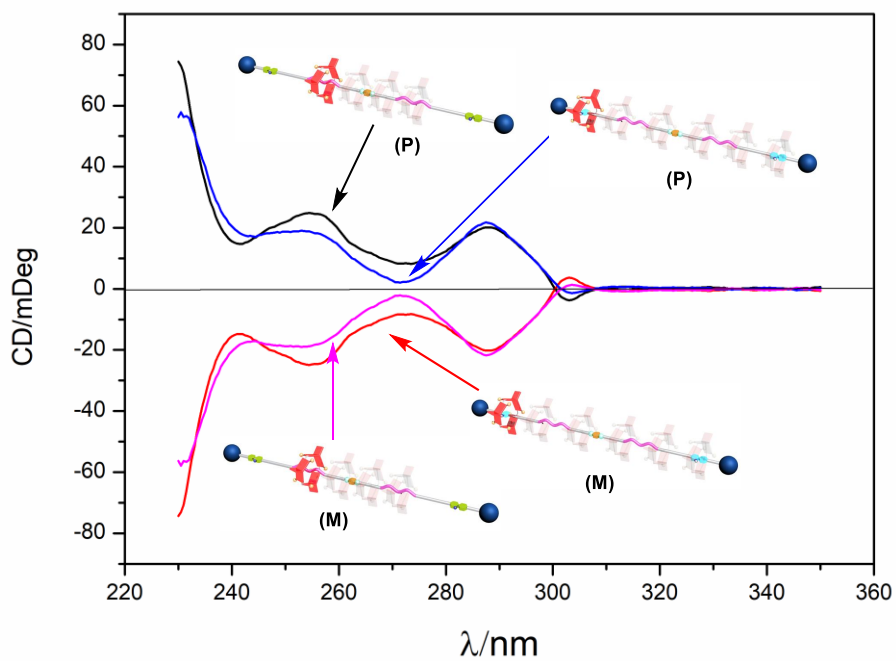


Fig. S39. Comparison of CD spectra of *P*- or *M*-R2 and *P*- or *M*-R2-H.

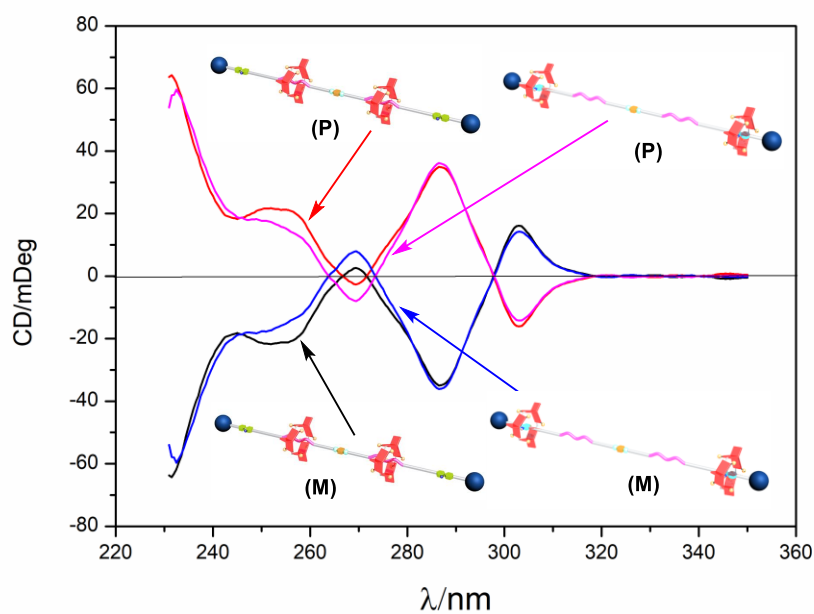


Fig. S40. Comparison of CD spectra of *P*- or *M*-**R3** and *P*- or *M*-**R3-H**.

8. Acid-base controlled motion

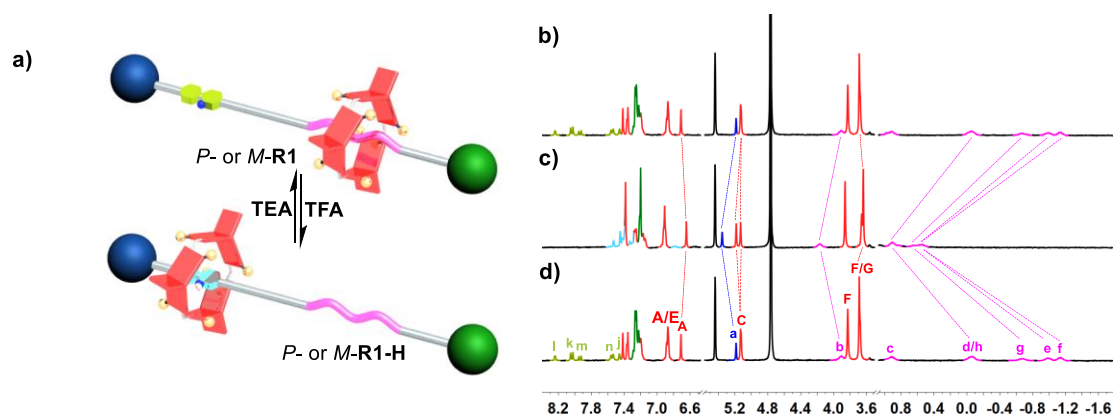


Fig. S41 Acid-base driven motion of (a) *P*- or *M*-**R1** and partial ^1H NMR spectra ($\text{CD}_3\text{OD}/\text{CD}_2\text{Cl}_2 = 11:5$ v/v, 298 K, 300 MHz) of d) *P*- or *M*-**R1**, c) *P*- or *M*-**R1** + 1.2 equiv TFA, b) *P*- or *M*-**R1** + 1.2 equiv TFA + 1.5 equiv TEA.

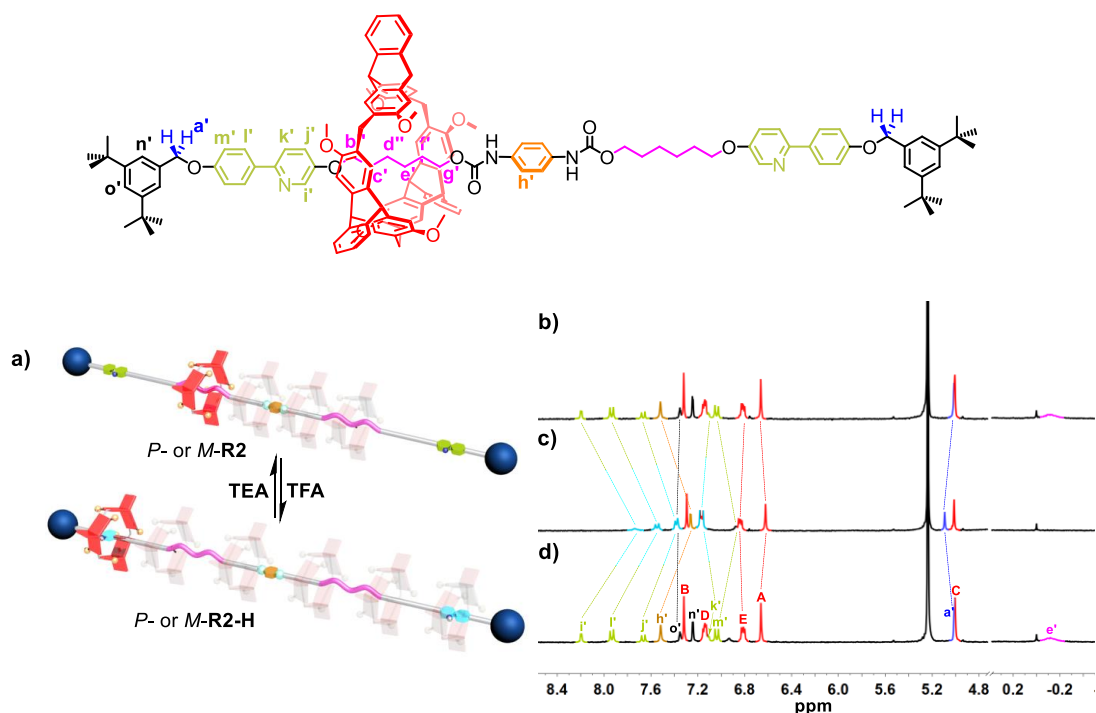


Fig. S42 Acid-base driven motion of (a) *P*- or *M*-R2 and partial ¹H NMR spectra (CD₃OD/CD₂Cl₂ = 11:5 v/v, 298 K, 300 MHz) of d) *P*- or *M*-R2, c) *P*- or *M*-R2 + 5.0 equiv TFA, b) *P*- or *M*-R2 + 5.0 equiv TFA + 5.5 equiv TEA.

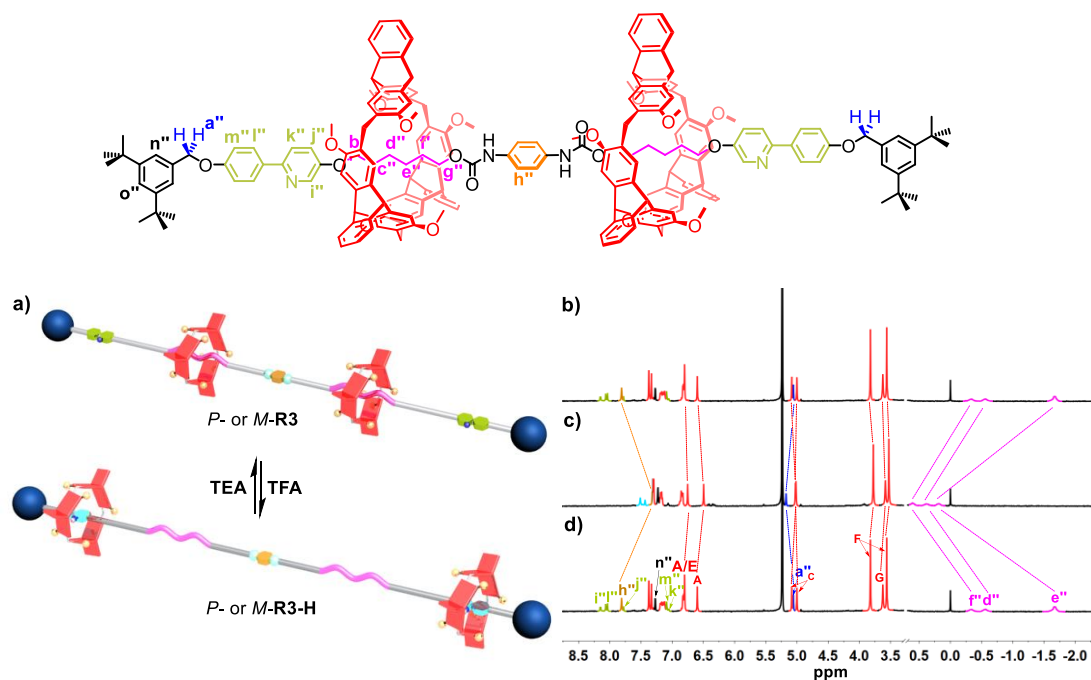


Fig. S43 Acid-base driven motion of (a) *P*- or *M*-R3 and partial ¹H NMR spectra (CD₃OD/CD₂Cl₂ = 11:5 v/v, 298 K, 300 MHz) of d) *P*- or *M*-R3, c) *P*- or *M*-R3 + 5.0 equiv TFA, b) *P*- or *M*-R3 + 5.0 equiv TFA + 5.5 equiv TEA.

9. NMR study of photo controlled motion of R2 and R3

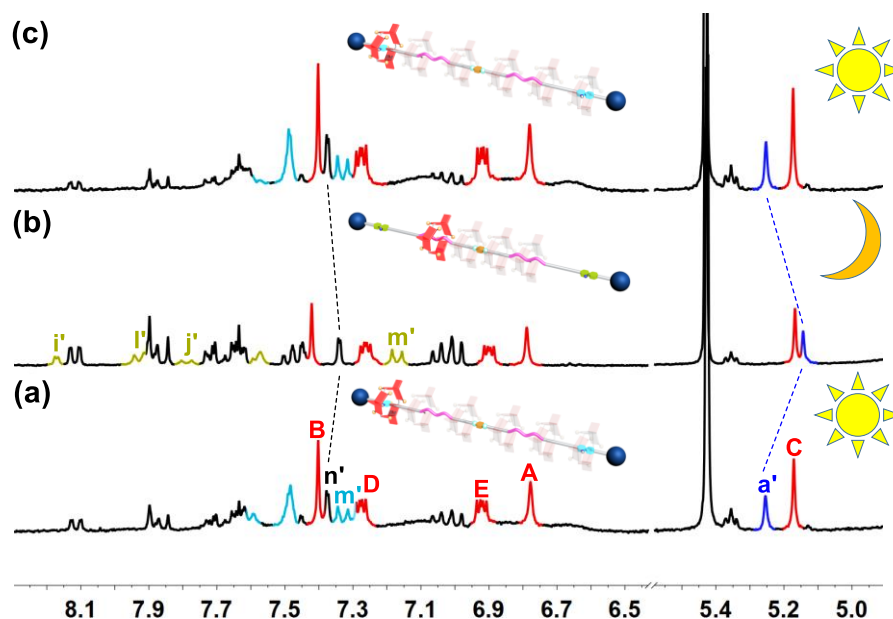


Fig. S44 Partial ^1H NMR spectra (CD₃OD/CD₂Cl₂ = 11:5 v/v, 298 K, 300 MHz) of (a) **R2** + 2.3 equiv **1-SP**, (b) **R2** + 2.3 equiv **1-SP** in the dark for 3.5 h, (c) b was irradiated by 420 nm or sunlight for 5 min.

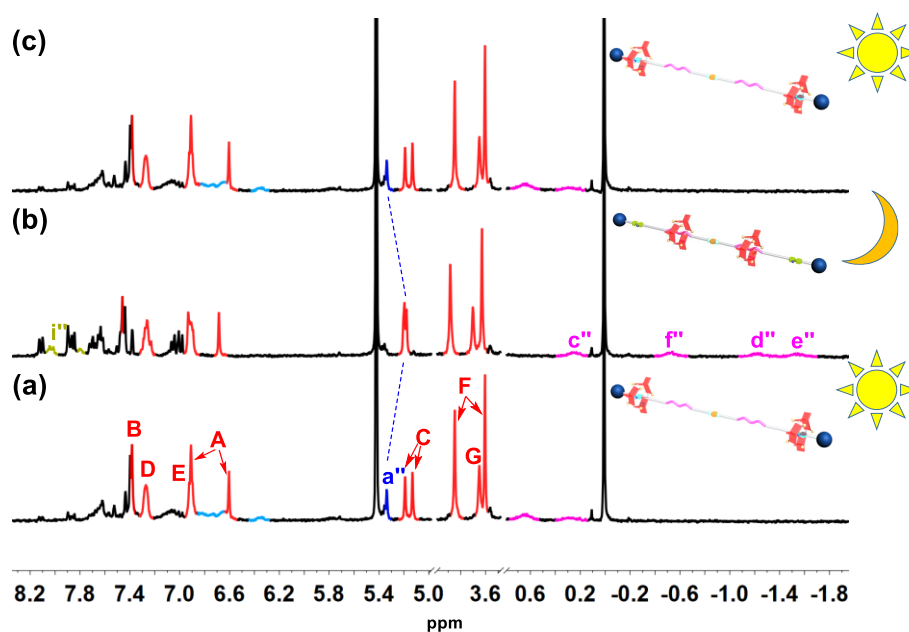


Fig. S45 Partial ^1H NMR spectra (CD₃OD/CD₂Cl₂ = 11:5 v/v, 298 K, 300 MHz) of (a) **R3** + 2.3 equiv **1-SP**, (b) **R3** + 2.3 equiv **1-SP** in the dark for 3.5 h, (c) b was irradiated by 420 nm or sunlight for 5 min.

10. Time-dependent ^1H NMR study of photo-driven motion

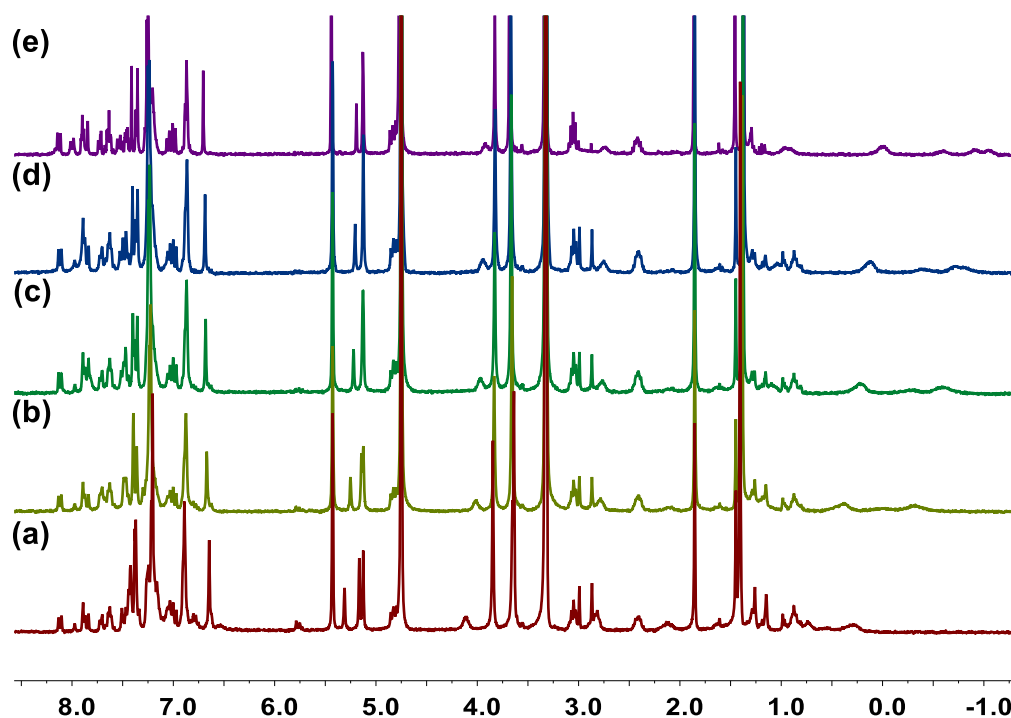


Fig. S46. ^1H NMR spectra (300 MHz, 298 K, $\text{CD}_3\text{OD}/\text{CD}_2\text{Cl}_2 = 11/5$ v/v) of **R1-H** and **1-SP** treated in the dark for (a) 20 min, (b) 40 min, (c) 60 min, (d) 80 min and (e) 150 min.

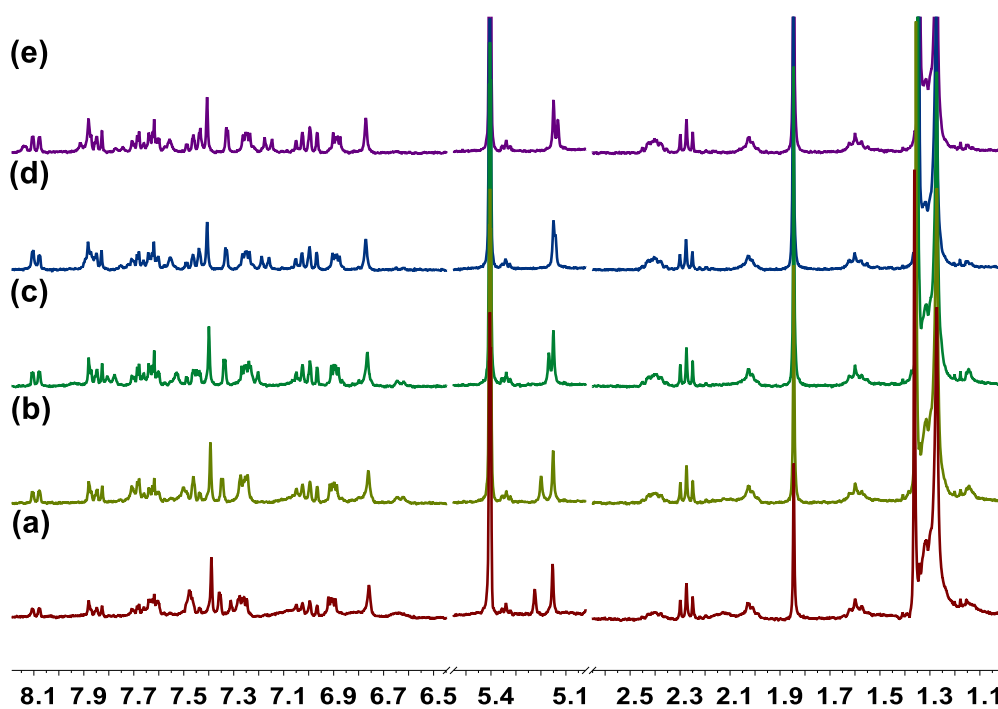


Fig. S47. ^1H NMR spectra (300 MHz, 298 K, $\text{CD}_3\text{OD}/\text{CD}_2\text{Cl}_2 = 11/5$ v/v) of **R2-H** and **1-SP** treated in the dark for (a) 10 min, (b) 20 min, (c) 30 min, (d) 55 min and (e) 85 min.

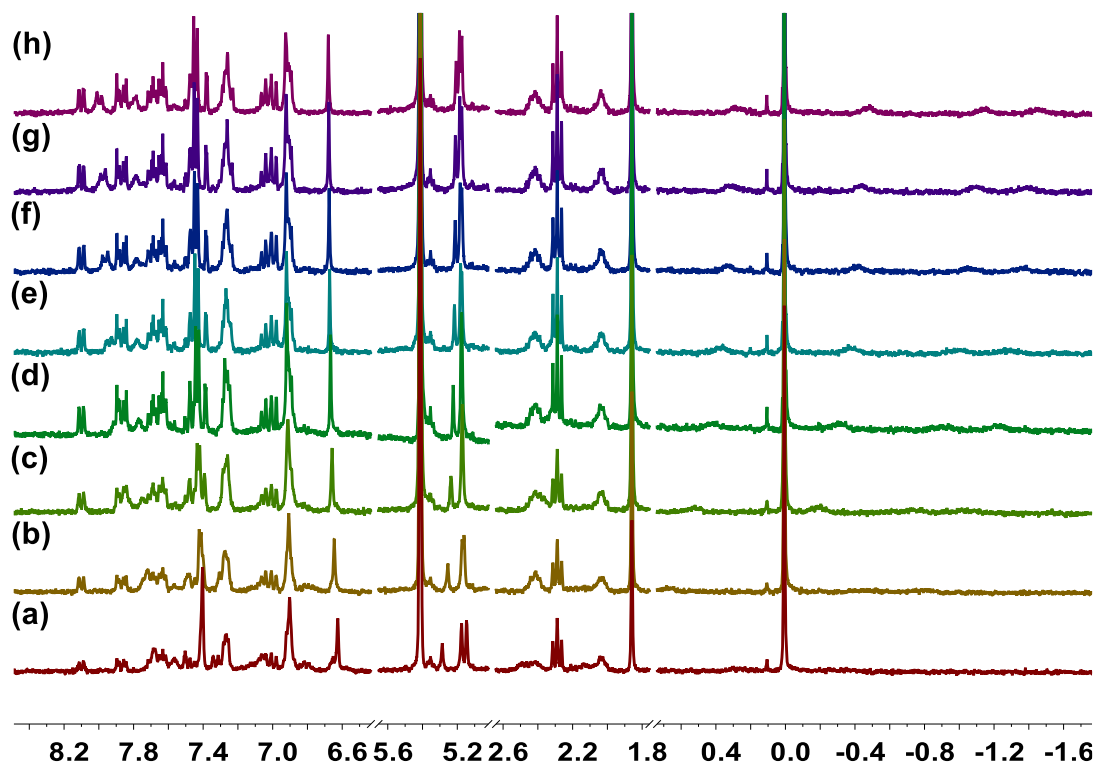


Fig. S48. ^1H NMR spectra (300 MHz, 298 K, $\text{CD}_3\text{OD}/\text{CD}_2\text{Cl}_2 = 11/5$ v/v) of **R3-H** and **1-SP** treated in the dark for (a) 10 min, (b) 20 min, (c) 30 min, (d) 40 min (e) 50 min, (f) 60 min, (g) 70 min, (h) 130 min.

11. Sustainability of acid-base controlled and photo controlled motion patterns

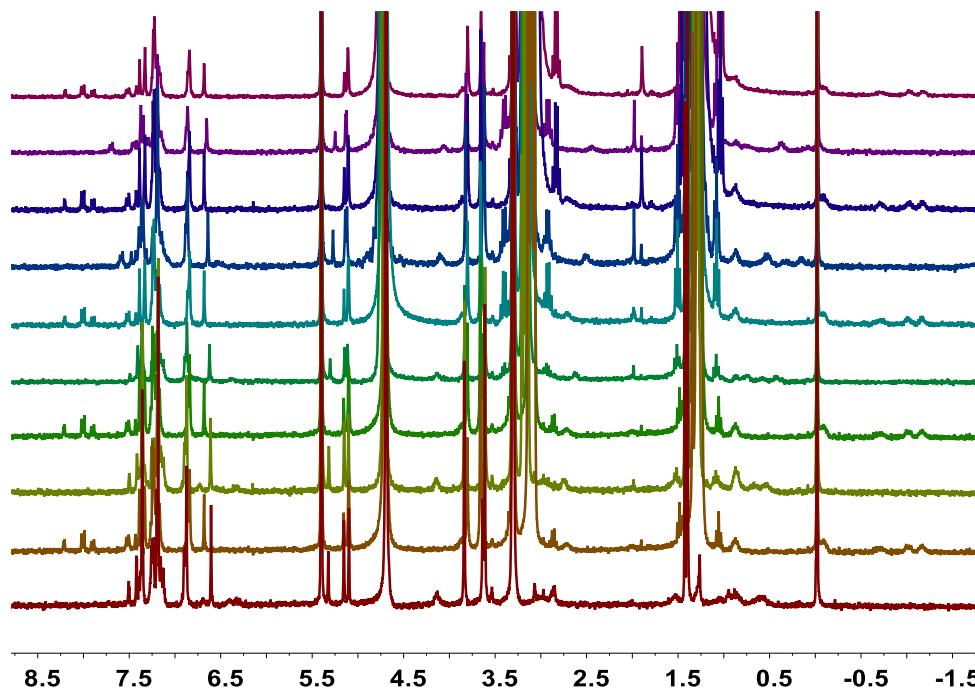


Fig. S49. Five motion cycles of **R1** induced through alternating TEA and TFA.

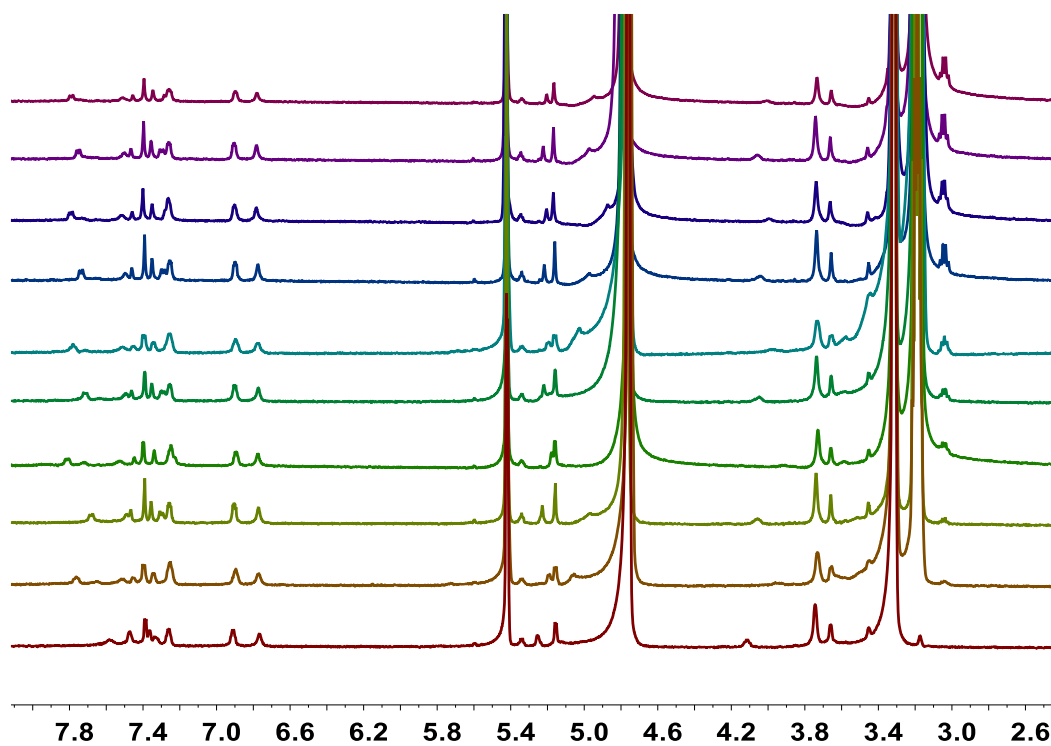


Fig. S50. Five motion cycles of **R2** induced through alternating TEA and TFA.

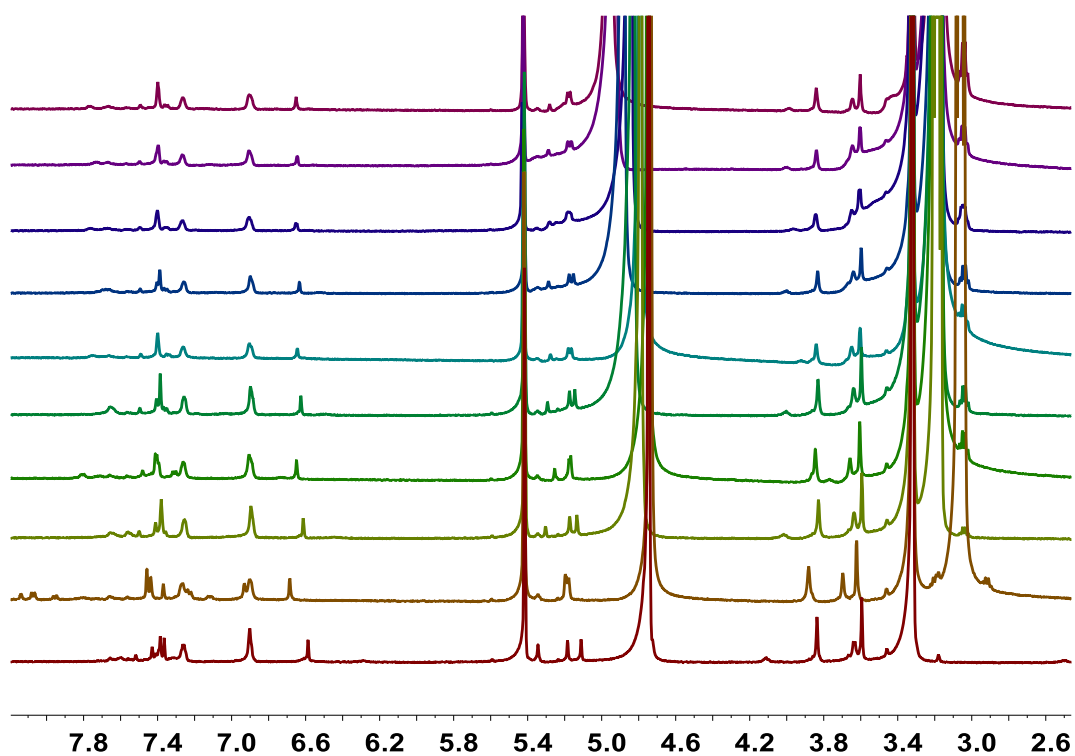


Fig. S51. Five motion cycles of **R3** induced through alternating TEA and TFA.

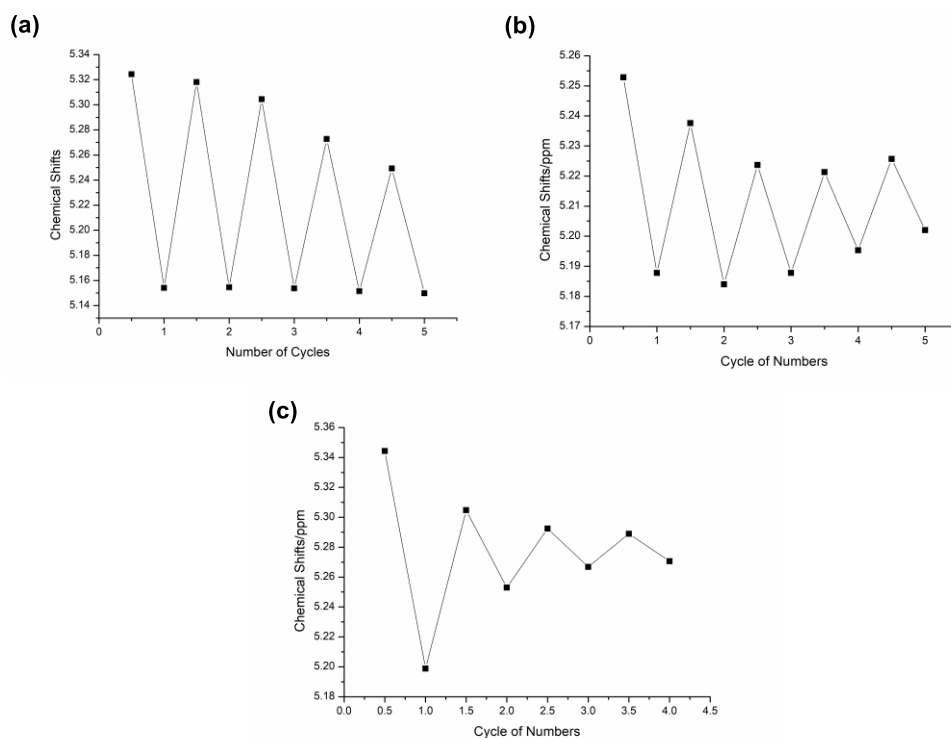


Fig. S52. Sustainability of acid-base controlled motion of (a) **R1**, (b) **R2** and (c) **R3**. Recorded H^a for **R1**, $H^{a'}$ for **R2** and $H^{a''}$ for **R3**.

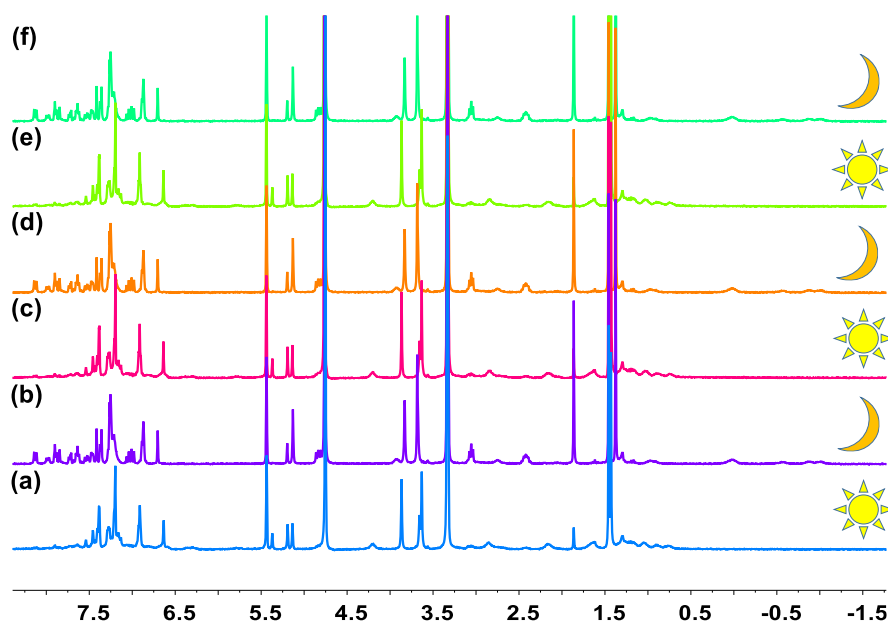


Fig. S53. Motion cycles of **R1** induced by photo in the presence of photoacid (300 MHz, 298 K, $CD_3OD/CD_2Cl_2 = 11/5$ v/v). (a) and (b) is the first cycle, (c) and (d) is the cycle 2, and (e) and (f) is the cycle 50.

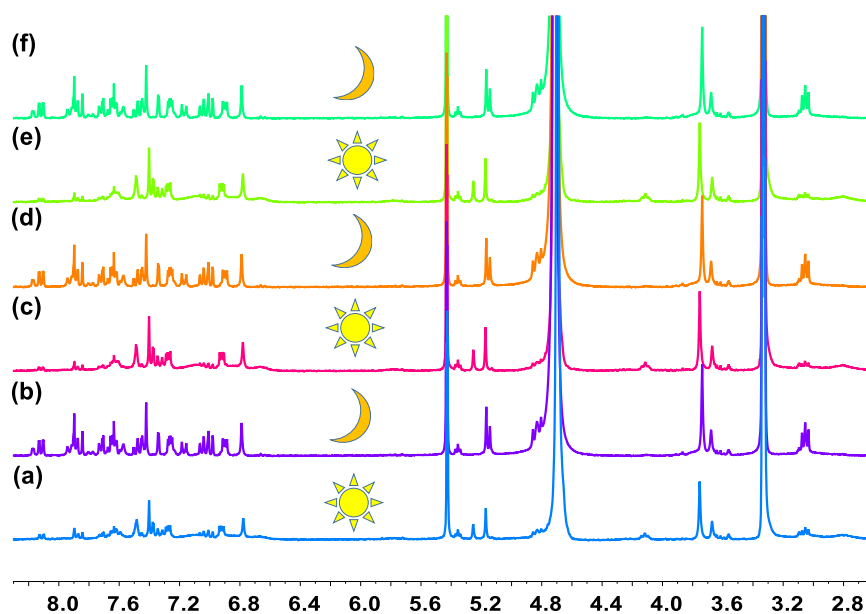


Fig. S54. Motion cycles of **R2** induced by photo in the present of photoacid (300 MHz, 298 K, $\text{CD}_3\text{OD}/\text{CD}_2\text{Cl}_2 = 11/5$ v/v). (a) and (b) is the first cycle, (c) and (d) is the cycle 2, and (e) and (f) is the cycle 50.

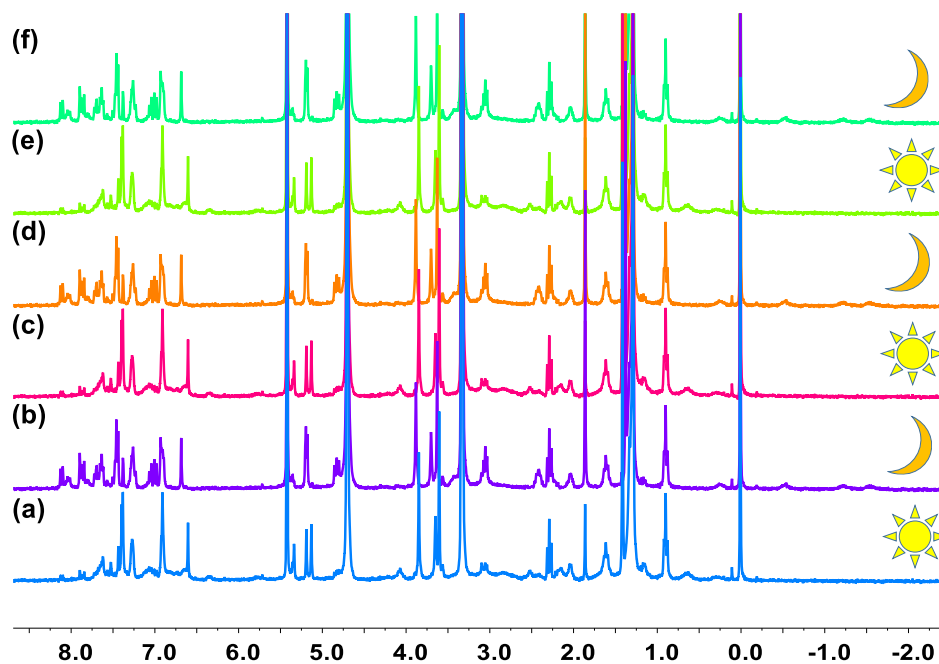


Fig. S55. Motion cycles of **R3** induced by photo in the present of photoacid (300 MHz, 298 K, $\text{CD}_3\text{OD}/\text{CD}_2\text{Cl}_2 = 11/5$ v/v). (a) and (b) is the first cycle, (c) and (d) is the cycle 2, and (e) and (f) is the cycle 50.

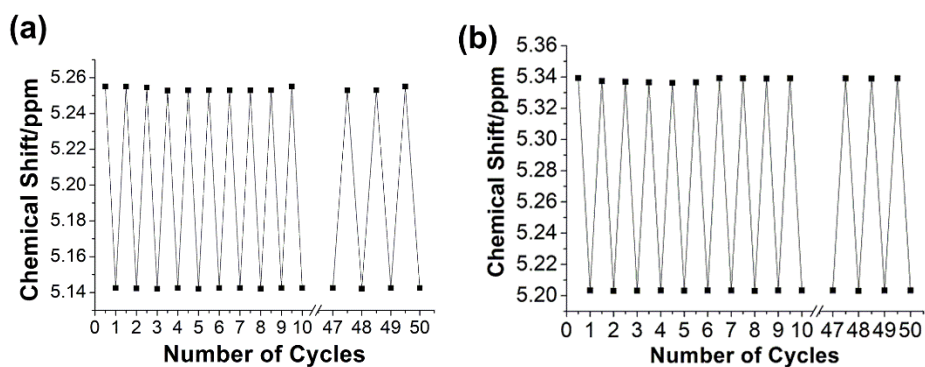


Fig. S56. Sustainability of photo controlled motion of (a) **R2** and (b) **R3**. Recorded H^a for **R2** and $H^{a''}$ for **R3**.

Reference

S1. G. W. Zhang, P.-F. Li, Z. Meng, H.-X. Wang, Y. Han and C.-F. Chen, *Angew. Chem., Int. Ed.*, 2016, **55**, 5304-5394.