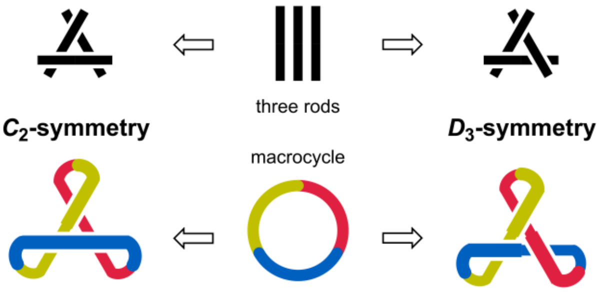
Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Dual dynamic chirality generated in the assembly of three achiral rods through the three-fold twisting of a macrocycle

Ryo Katoono,* Kazuki Sakamoto and Takanori Suzuki

Department of Chemistry, Faculty of Science, Hokkaido University



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Supplementary Figures

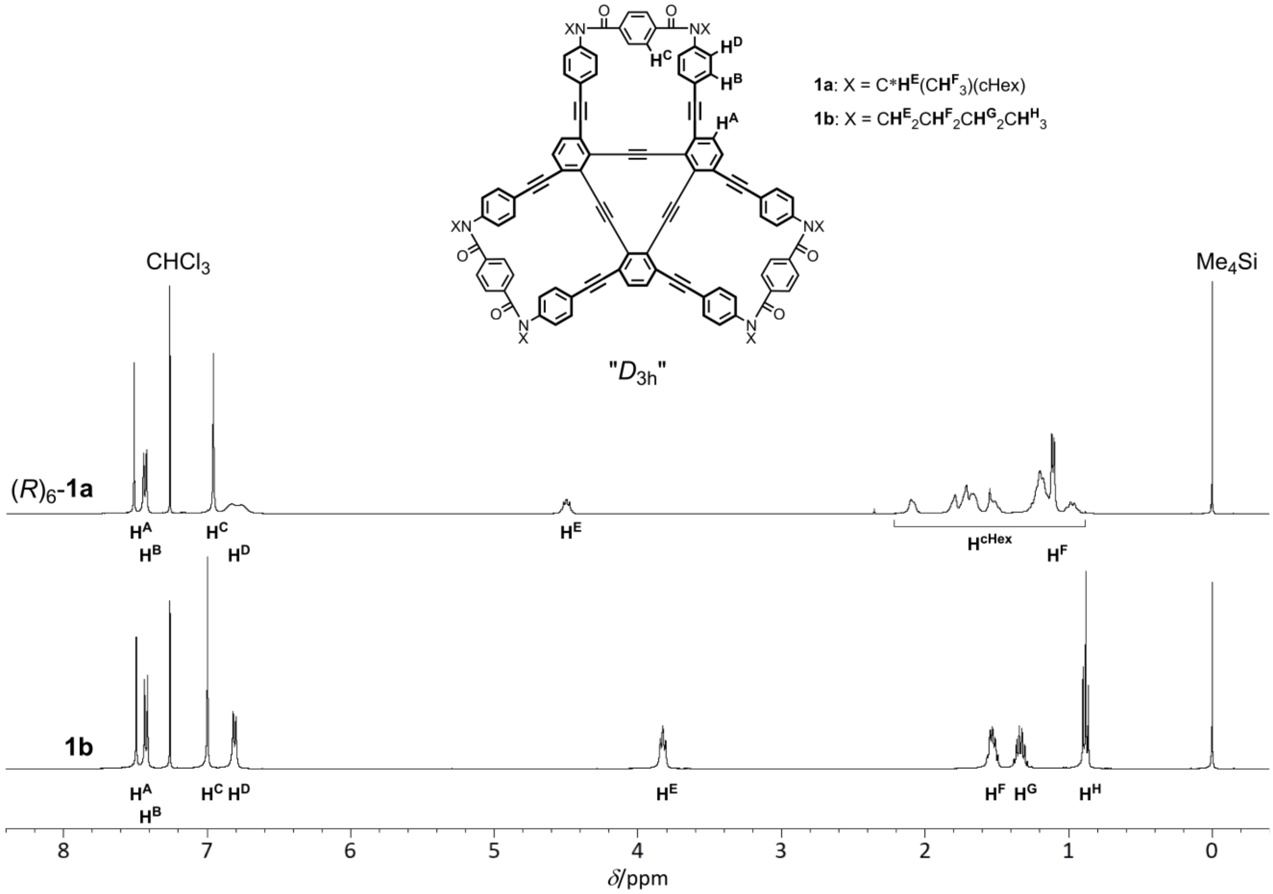


Fig.S1A ^{1}H NMR spectra (400 MHz) of (*R*)$_6$-**1a** and **1b**, measured in chloroform-*d* at room temperature.

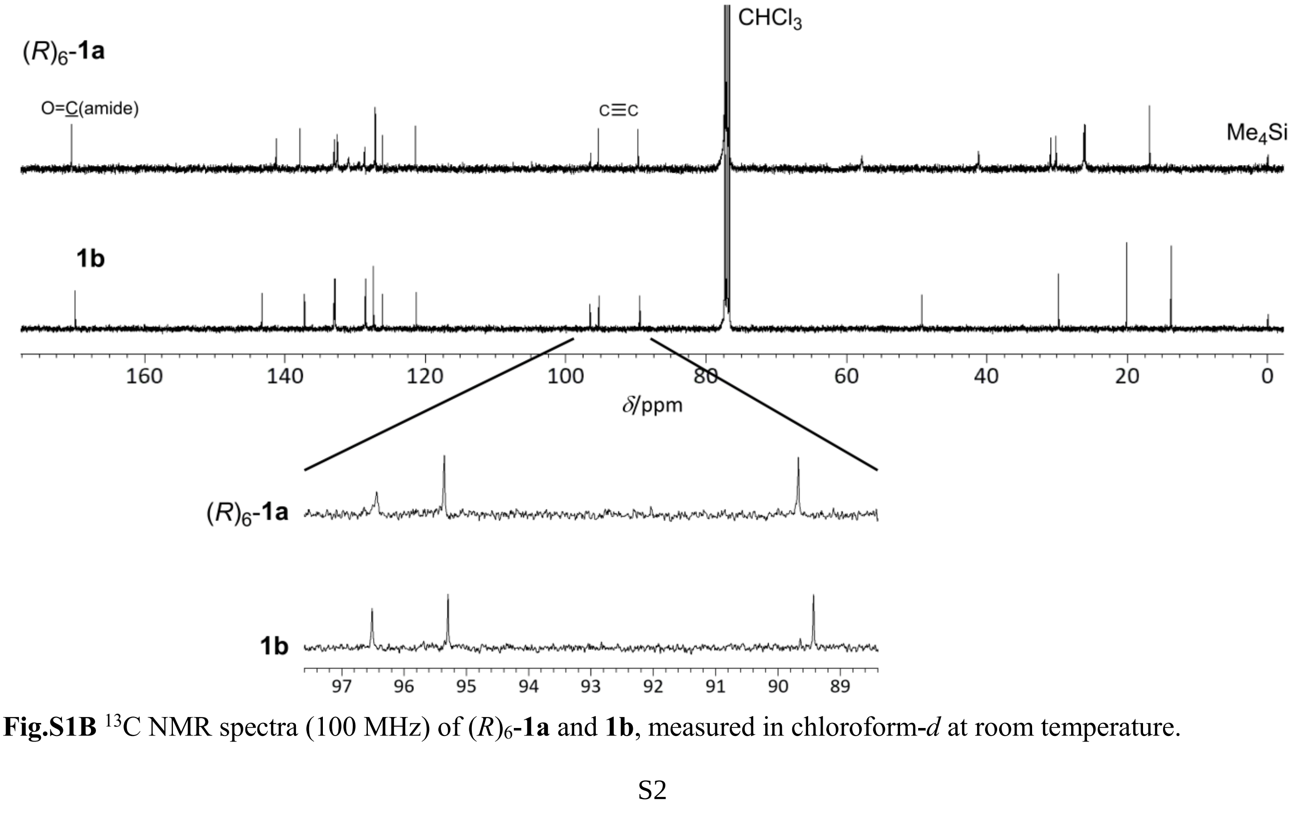


Fig.S1B ^{13}C NMR spectra (100 MHz) of (*R*)$_6$-**1a** and **1b**, measured in chloroform-*d* at room temperature.

(a) $(R)_6$-**1a**

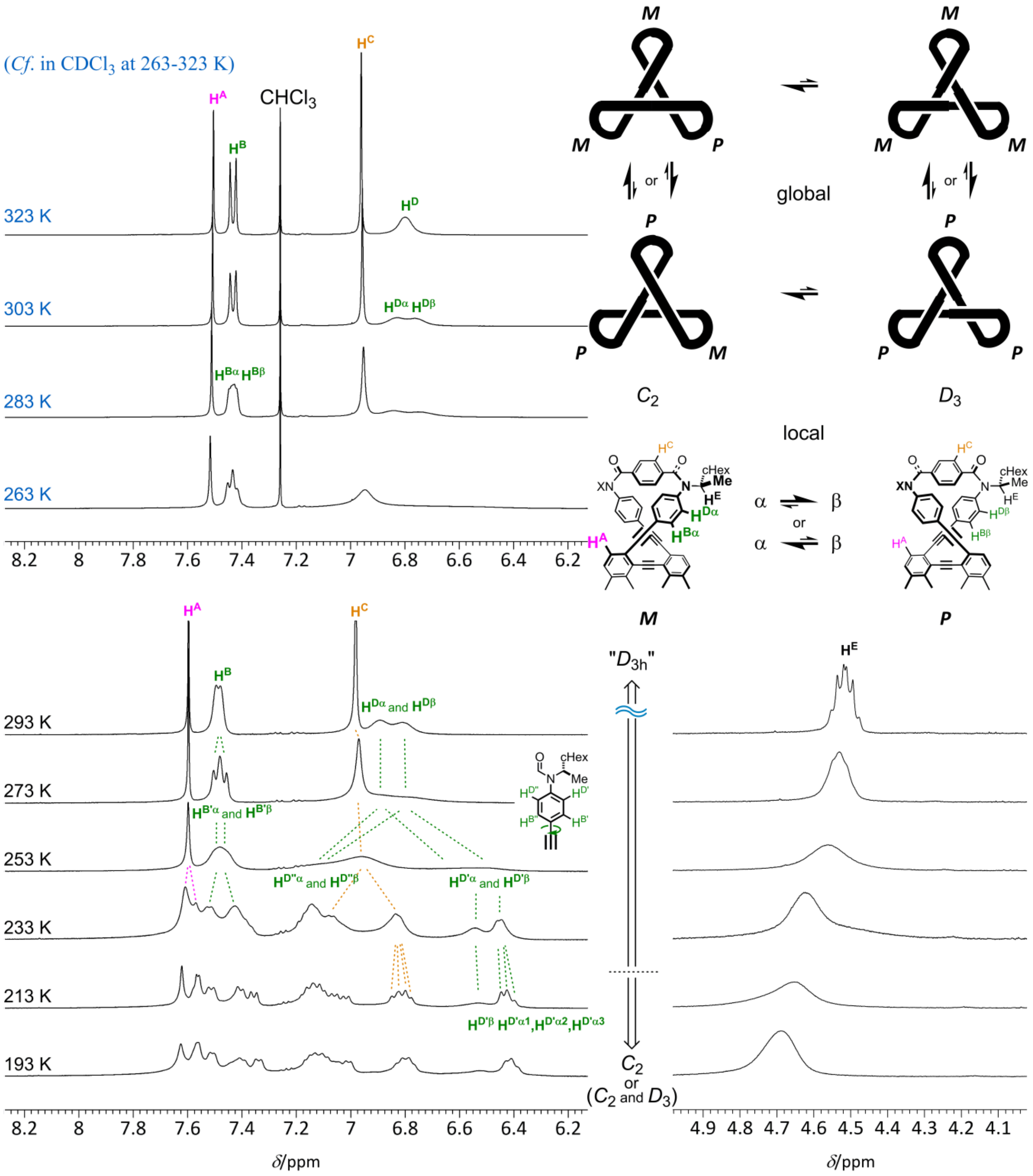


Fig.S2a Partial VT-^{1}H NMR spectra (400 MHz; left: aromatic protons, and right: methylene protons) of $(R)_6$-**1a**, measured in dichloromethane-d_2 at 193-293 K.

(b) **1b**

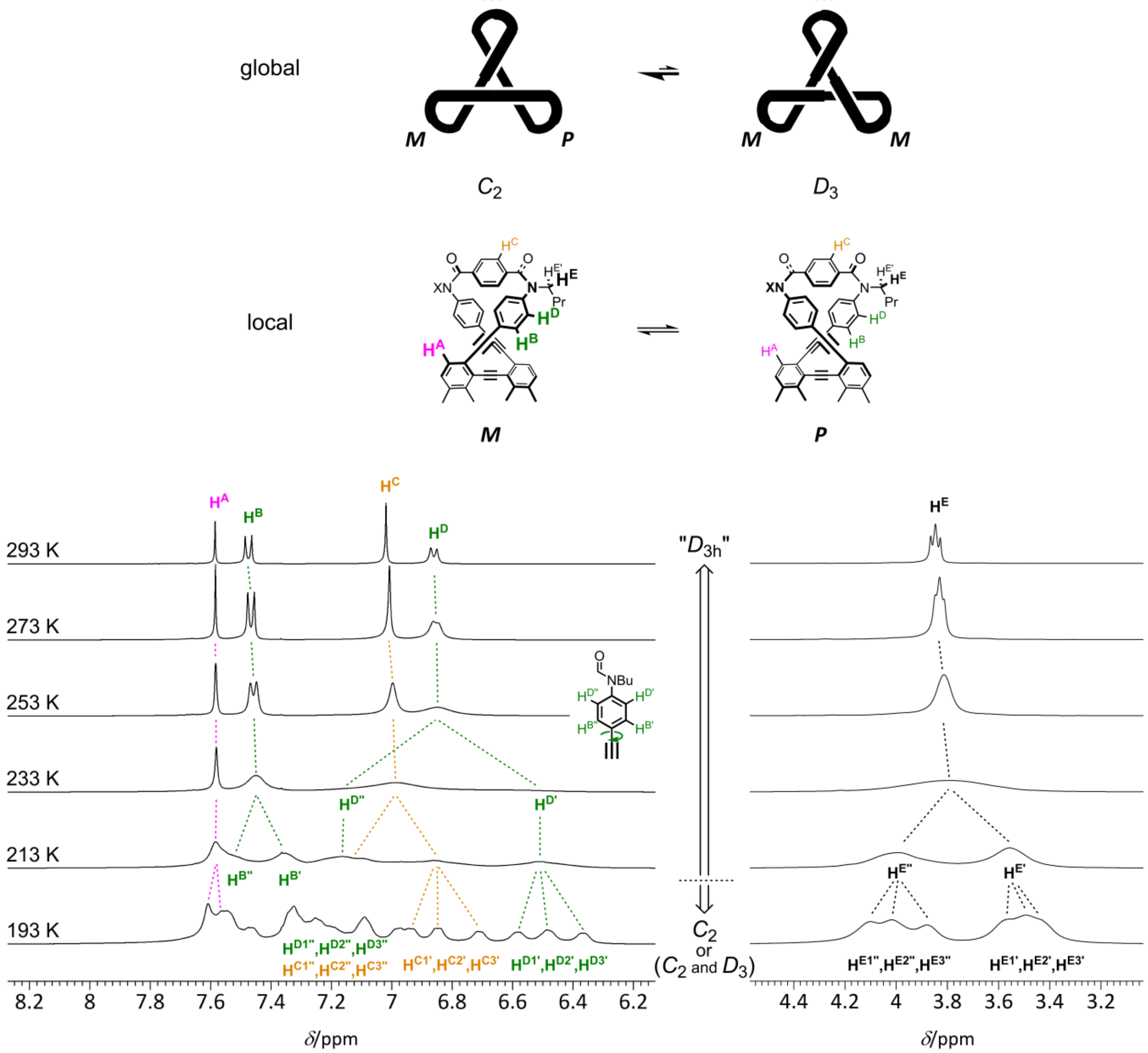


Fig.S2b Partial VT-^{1}H NMR spectra (400 MHz; left: aromatic protons, and right: methylene protons) of **1b**, measured in dichloromethane-d_2 at 193-293 K.

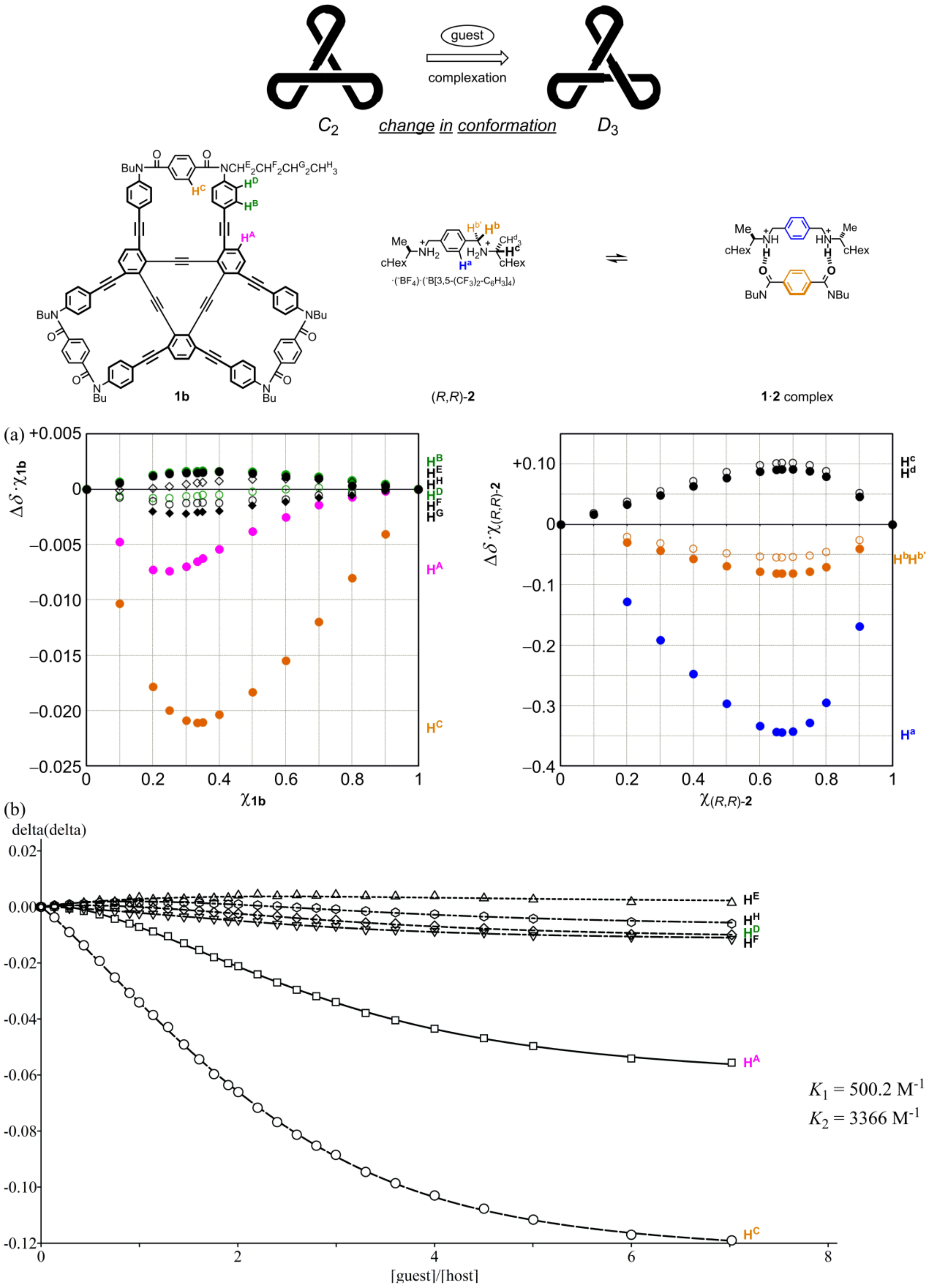


Fig.S3A Complexation of **1b** with a chiral guest (*R*,*R*)-**2**: (a) Job plots based on changes in the chemical shifts ($\Delta\delta = \delta_{\mathbf{1b}\cdot\mathbf{2}} - \delta_{\mathbf{1b}}$) of **1b** (left) and (*R*,*R*)-**2** (right), measured in 1.7vol% acetonitrile-d_3/chloroform-*d* at 303 K. [**1b**]+[**2**] = 2 mM. $\chi_{\mathbf{1b}}$ = [**1b**]/[**1b**]+[**2**], and (b) fitted with a 1:2 model.[1] [**1b**] = 0.667 mM, [**2**] = 0-7 mM.

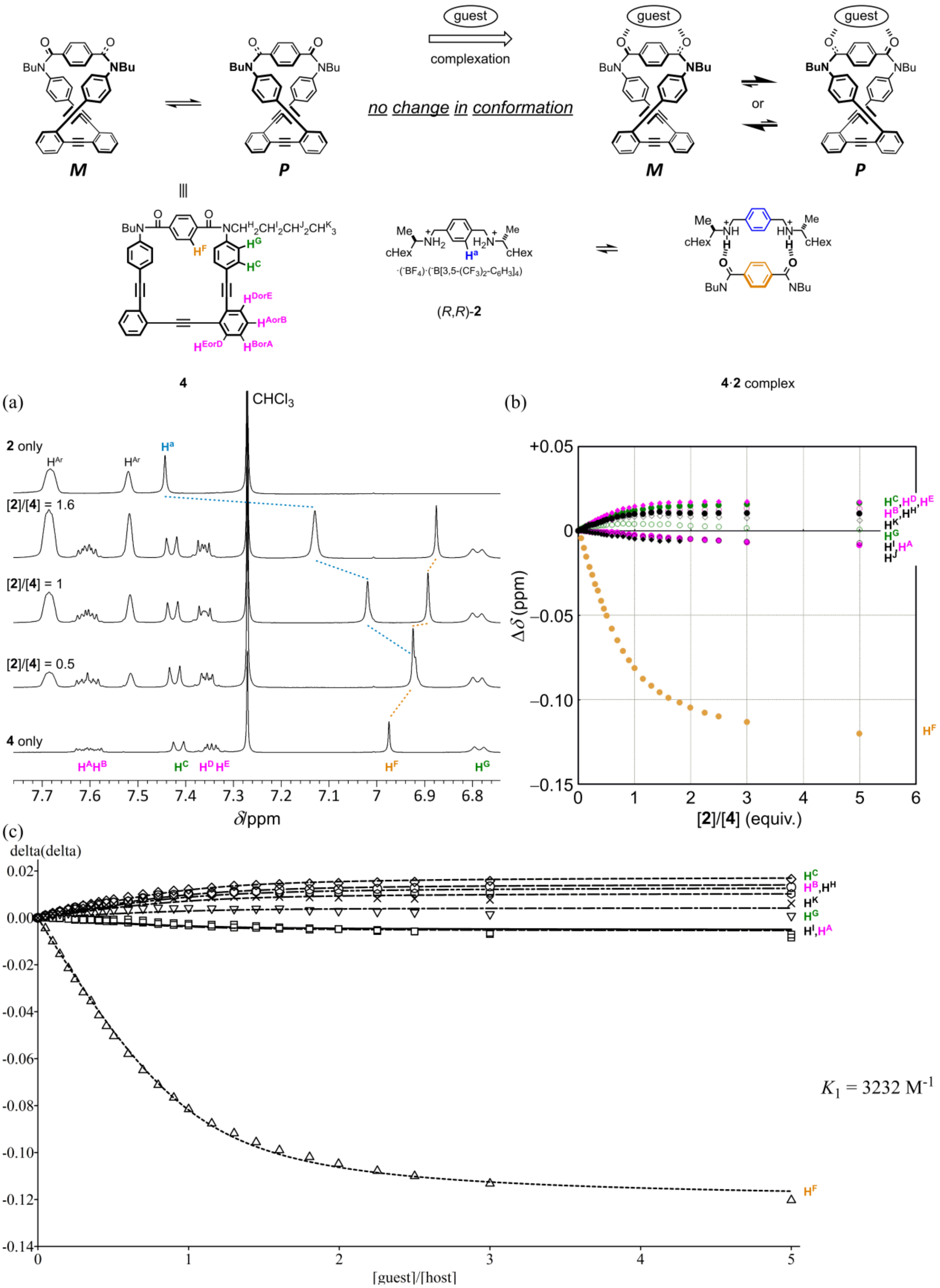
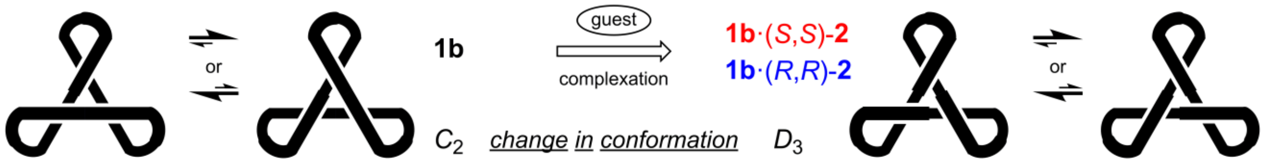


Fig.S3B (a) Partial ^{1}H NMR spectra (aromatic region) of **4**^{2} (2 mM) in the presence of (*R*,*R*)-**2** [0 (**4** only), 0.5, 1 and 1.6 equiv.), and (*R*,*R*)-**2**. All spectra were measured in 1.7vol% acetonitrile-*d*$_3$/chloroform-*d* at 303 K; (b) titration curves based on changes in the chemical shifts ($\Delta\delta = \delta_{4\cdot 2} - \delta_4$) for protons H^A-H^K of **4**; (c) fitted with a 1:1 model.[1] [**4**] = 2 mM, [**2**] = 0-10 mM.



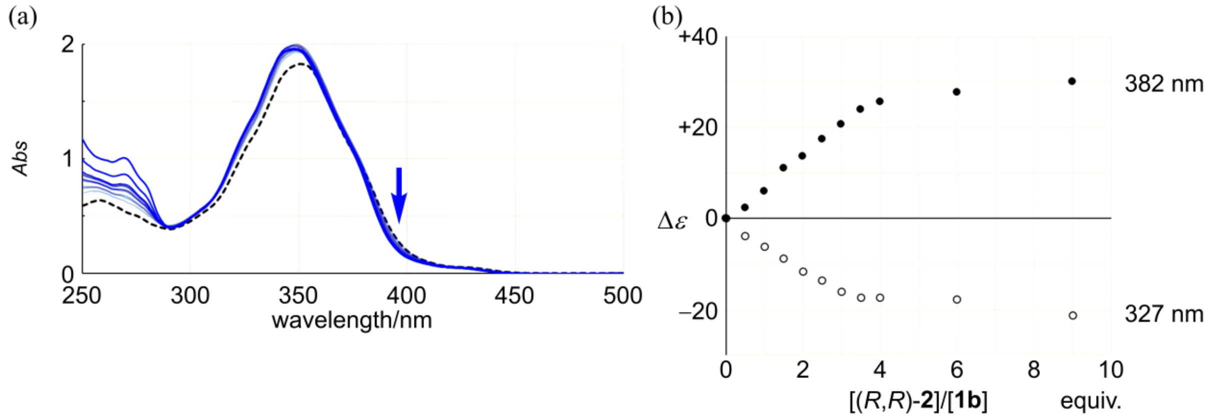


Fig.S4 (a) UV spectra of **1b** (8.7×10^{-5} M) in the presence of (*R*,*R*)**-2** [0 (black broken line), 3, 4, 6 and 9 equiv. (blue solid lines)]; (b) plots of induced molar CD at 382 nm or 327 nm versus equivalents of the guest added. All spectra were measured in dichloromethane at room temperature.

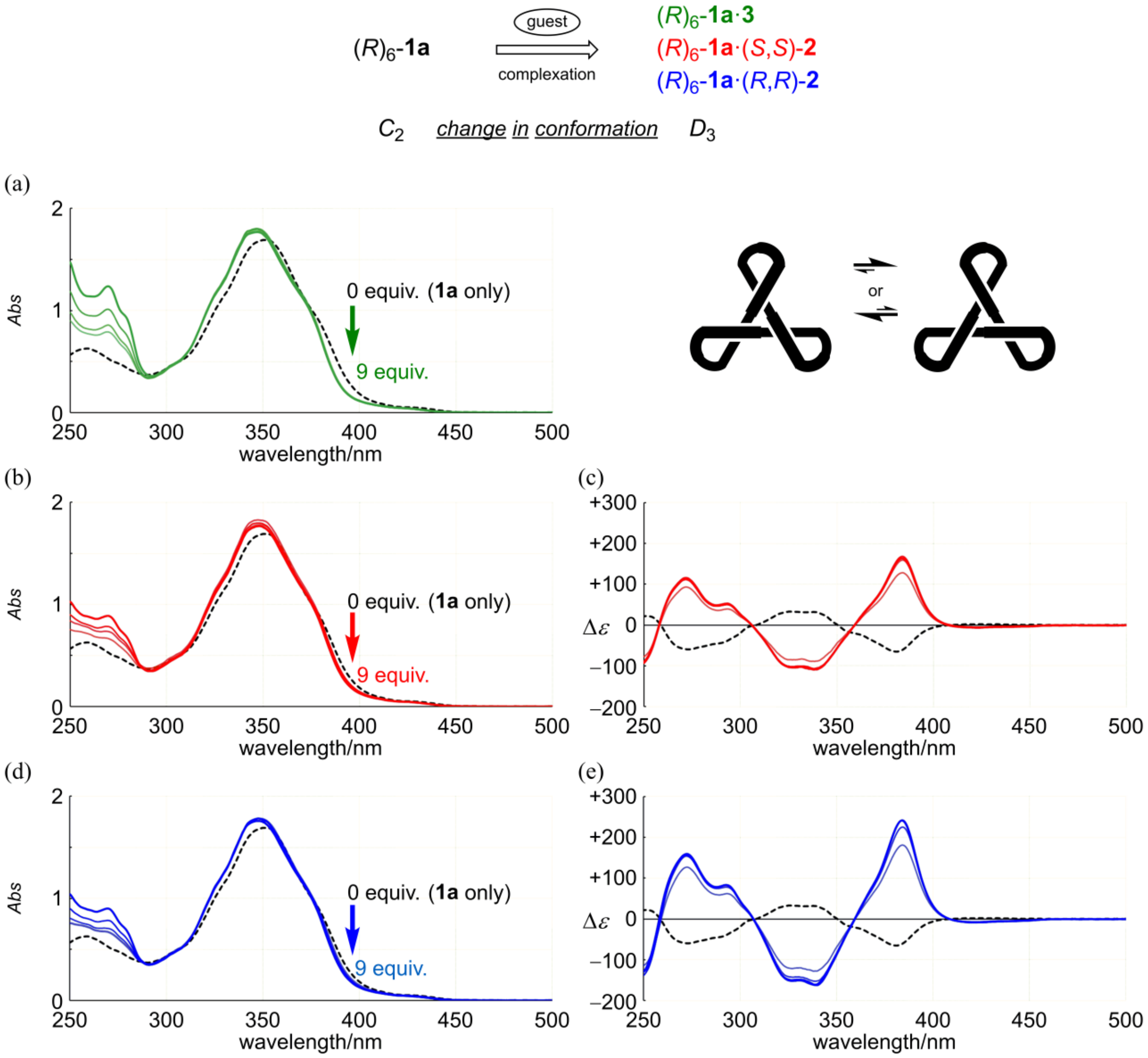


Fig.S5A UV (left) and CD (right) spectra of $(R)_6$-**1a** (7.8×10^{-5} M) in the presence of a ditopic guest [0 (**1a** only, black broken line), 3, 4, 6 and 9 equiv. (colored solid lines): (a) **3**, (b)(c) (*S*,*S*)-**2**, or (d)(e) (*R*,*R*)-**2**, measured in dichloromethane at 293 K. Cell length = 0.1 cm.

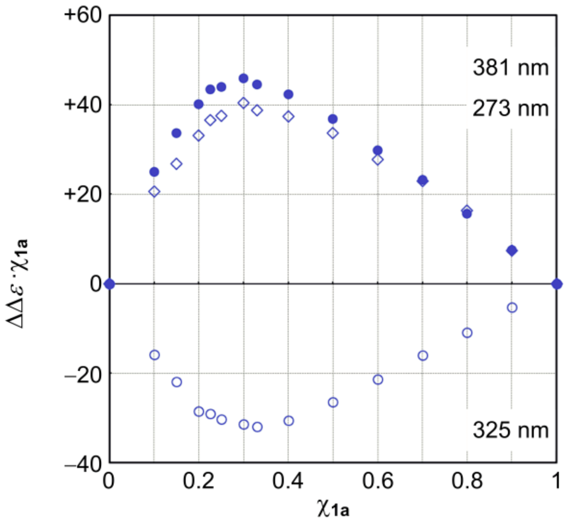


Fig.S5B A Job plot based on changes in molar CDs ($\Delta\Delta\varepsilon = \Delta\varepsilon_{\mathbf{1a}\cdot\mathbf{2}} - \Delta\varepsilon_{\mathbf{1a}}$) upon complexation of ($R$)$_6$-**1a** with ($R$,$R$)-**2**, measured in dichloromethane at 293 K. [**1a**]+[**2**] = 8 × 10^{-5} M. $\chi_{\mathbf{1a}}$ = [**1a**]/[**1a**]+[**2**].

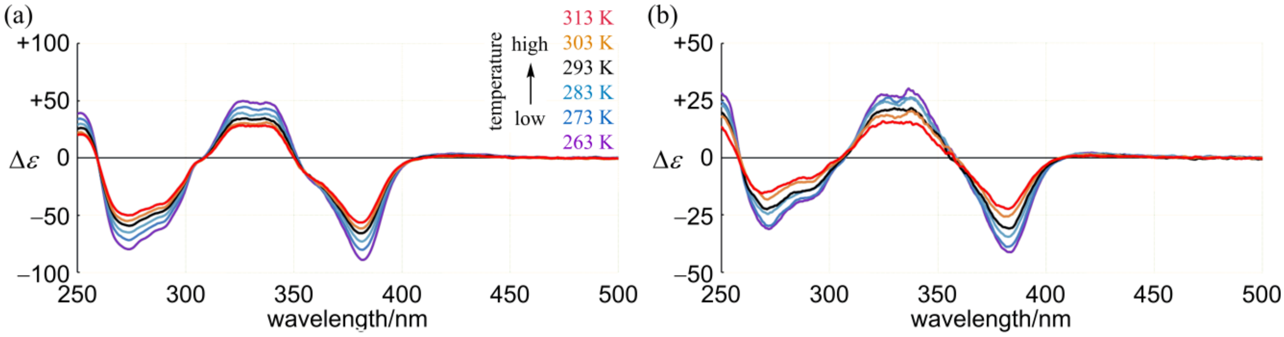
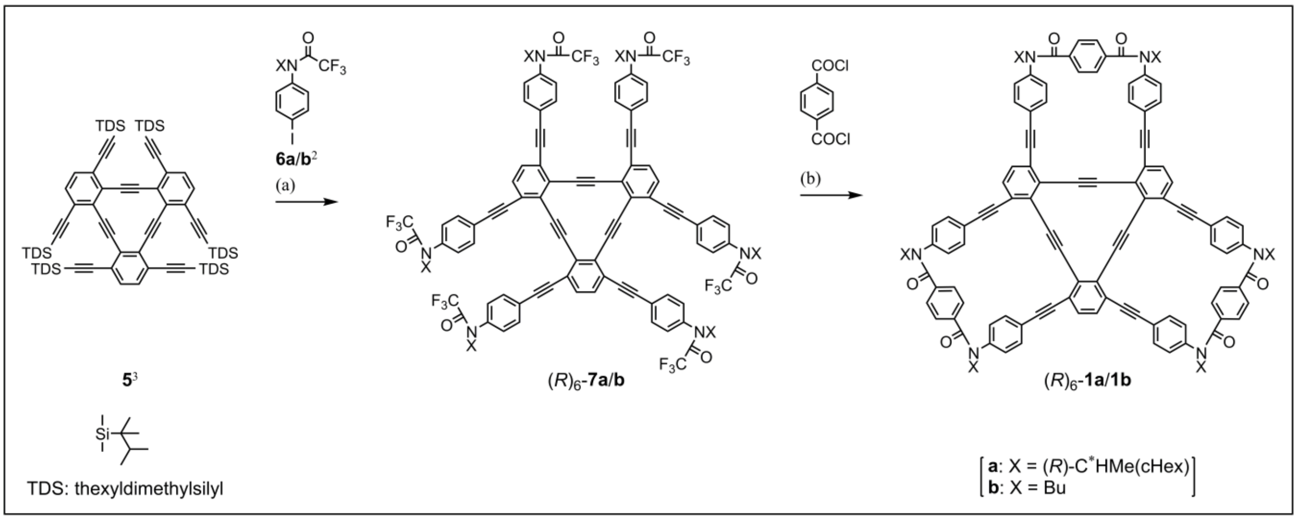


Fig.S6 VT-CD spectra of (a) (R)$_6$-**1a**, and (b) **1b** (8.7 × 10^{-5} M) in the presence of (S,S)-**2** (9 equiv.), measured in dichloromethane at 263-313 K.

Experimental



Scheme S1. Synthesis of **1**. Reagents and yields: (a) **6a**/**b**, $Pd(PPh_3)_4$, CuI, ″tetrabutylammonium fluoride (TBAF), THF, Et_3N (**7a**: 72%, **7b**: 72%); (b) i) NaH, MeOH, THF (**7a'**: 87%, **7b'**: 96%); ii) terephthaloyl chloride, Et_3N, toluene (**1a**: 57%, **1b**: 76%).

Preparation of (*R*)$_6$-**7a** [X = (*R*)-C*HMe(cHex)]

To a solution of **5**^{3} (779 mg, 0.600 mmol), (*R*)-**6a**^{2} (2.30 g, 5.41 mmol), $Pd(PPh_3)_4$ (210 mg, 0.182 mmol) and CuI (35 mg, 0.18 mmol) in THF (27 mL) and Et_3N (53 mL) was added a diluted solution of TBAF (3.8 mL, 3.8 mmol) in THF (5 mL) at 50 °C via a syringe pump over 80 min under an argon atmosphere, and the mixture was further stirred for 10 min. After removal of a solid by filtration through a Celite pad, the filtrate was concentrated. The residue was dissolved in ethyl acetate, and which was washed with 1M aq. HCl and brine, dried over magnesium sulfate, and then concentrated. The resulting solid was dissolved in dichloromethane (5 mL) containing Et_3N (0.75 mL), which was treated with trifluoroacetic anhydride (TFAA, 0.65 mL), followed by satd. aq. $NaHCO_3$. The organic layer was separated, washed with brine, dried over magnesium sulfate, and then concentrated. The crude product was purified by column chromatography on SiO_2 (ethyl acetate/dichloromethane) to give (*R*)$_6$-**7a** (967 mg) as a yellow solid in 72% yield. An analytic sample was obtained as a yellow solid by further purification through GPC (chloroform; JAIGEL-2H & 2.5H, Japan Analytical Industry Co., Ltd., Japan), HPLC with a standard normal-phase column (methanol/dichloromethane; YMC-Pack SIL, SIL-06, YMC Co., Ltd., Japan), followed by washing in refluxed ethanol. (*R*)$_6$-**7a**: mp 164-180 °C (dec); $[\alpha]_D^{25} = -3.2$ (c = 0.0898 gdL^{-1} in chloroform); IR (KBr) ν_{max}/cm^{-1} 3047, 2979, 2931, 2853, 2202, 1698, 1509, 1208, 1148; ^1H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.50 (6H, s), 7.35 (br.d), 7.33 (br.d), 7.00 (12H, 6r.m), 4.34 (br.dq), 1.93 (6H, br.d), 1.79-0.93 (60H, br.m), 1.06 (18H, d, J = 6.8 Hz); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 156.7 ($\underline{C}(=O)CF_3$), 136.2, 132.8, 132.4, 132.0, 130.1, 129.5, 128.8, 125.9, 123.6, 116.5 ($\underline{C}F_3$), 96.6, 95.4, 89.4, 60.2, 40.2, 30.7, 29.8, 26.1, 26.0, 25.7, 16.3; FD-LRMS m/z 2227.0 (M^+, 72%), 2228.0 ($[M+1]^+$, 100), 2229.0 ($[M+2]^+$, 81), 2230.0 ($[M+3]^+$, 44), 2231.0 ($[M+4]^+$, 18), 2232.0 ($[M+5]^+$, 6); FD-HRMS Found: 2226.89788, Calc. for $C_{132}H_{120}F_{18}N_6O_6$: 2226.89819.

Preparation of $(R)_6$-**1a** [X = (R)-C*HMe(cHex)]

To an ice-cooled solution of $(R)_6$-**7a** (600 mg, 0.269 mmol) in THF (32 mL) were added 60% NaH in oil (1.29 g, 32.3 mmol) and MeOH (2.1 mL), and the mixture was stirred at room temperature for 20 min, diluted with dichloromethane, and then quenched with water in an ice water bath. The organic layer was separated, washed with brine, dried over magnesium sulfate, and then concentrated. The resulting solid was purified by column chromatography on SiO_2 (dichloromethane) to give $(R)_6$-**7a'** (388 mg) as a yellow solid in 87% yield. $(R)_6$-**7a'**: ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.33 (6H, s), 7.07 (12H, d, $J = 8.8$ Hz), 6.24 (12H, d, $J = 8.8$ Hz), 3.54 (6H, br.s), 3.28-3.25 (6H, m), 1.80-1.00 (66H, br.m), 1.09 (18H, d, $J = 6.4$ Hz).

To a refluxed solution of $(R)_6$-**7a'** (388 mg, 0.234 mmol) in toluene (94 mL) containing Et_3N (0.25 mL) were added several portions of terephthaloyl chloride (158+155+160+154 mg, total 3.09 mmol) at an interval of 20 min. The mixture was diluted with dichloromethane, which was washed with 1M aq. NaOH. The organic layer was separated, dried over magnesium sulfate, and then passed through an Al_2O_3/Celite pad. The filtrate was concentrated and purified by column chromatography on Al_2O_3/SiO_2 (tetrahydrofuran/dichloromethane) to give $(R)_6$-**1a** (273 mg) as a yellow solid in 57% yield. An analytic sample was obtained as a yellow solid by further purification through GPC (chloroform), HPLC with a standard normal-phase column (methanol/dichloromethane), followed by washing in refluxed ethanol. $(R)_6$-**1a**: mp >300 °C; $[\alpha]_D^{25} = -318$ ($c = 0.209$ gdL^{-1} in chloroform); IR (KBr) ν_{max}/cm^{-1} 3065, 3040, 2970, 2925, 2850, 2196, 1657, 1598, 1509; ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.51 (6H, s), 7.44 (12H, d, $J = 8.0$ Hz), 6.96 (12H, s), 6.84 (br.s), 6.75 (br.s), 4.51 (6H, br.dq), 2.09 (6H, br.d), 1.79-1.49 (30H, br.m), 1.25-0.93 (30H, br.m), 1.10 (18H, br.d); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 170.4, 141.3, 137.8, 133.0, 132.5, 130.9 (br.), 128.7, 127.1, 126.1, 121.4, 96.4, 95.4, 89.7, 57.8, 41.2, 30.9, 30.1, 26.2, 26.0, 26.0, 16.8; FD-LRMS *m/z* 1821.8 ($[(M+2)–CHMe(cHex)×2]^+$, 7%), 1931.9 ($[(M+2)–CHMe(cHex)]^+$, 37), 2041.1 (M^+, 26), 2042.0 ($[M+1]^+$, 74), 2043.0 ($[M+2]^+$, 100), 2044.0 ($[M+3]^+$, 73), 2045.0 ($[M+4]^+$, 64); FD-HRMS Found: 2041.02076, Calc. for $C_{144}H_{132}N_6O_6$: 2041.02083; UV λ_{max}(CH_2Cl_2)/nm (log ε) 380 (sh. 4.98), 351 (5.29), 330 (sh. 5.12); CD λ(CH_2Cl_2)/nm ($\Delta\varepsilon$) 427 (+3), 381 (–65), 336 (+35), 328 (+35), 274 (–59), 252 (+26).

Preparation of **7b** [X = ^{n}Bu]

To a solution of **5** (806 mg, 0.620 mmol), **6b**[2] (2.10 g, 5.66 mmol), $Pd(PPh_3)_4$ (217 mg, 0.187 mmol) and CuI (37 mg, 0.19 mmol) in THF (27 mL) and Et_3N (55 mL) was added a diluted solution of TBAF (3.9 mL, 3.9 mmol) in THF (5 mL) at 50 °C via a syringe pump over 80 min under an argon atmosphere, and the mixture was further stirred for 10 min. After removal of a solid by filtration through a Celite pad, the filtrate was concentrated. The residue was dissolved in ethyl acetate, and which was washed with 1M aq. HCl, dried over magnesium sulfate, and then concentrated. The resulting solid was dissolved in dichloromethane (8 mL) containing Et_3N (0.75 mL), which was treated with trifluoroacetic anhydride (TFAA, 0.7 mL), followed by satd. aq. $NaHCO_3$. The organic layer was separated, washed with brine, dried over magnesium sulfate, and then concentrated. The crude product was purified by column chromatography on SiO_2 (ethyl acetate/dichloromethane) to give **7b** (853 mg) as a yellow solid in 72% yield. An analytic sample was obtained as a yellow solid by further purification through GPC (chloroform), HPLC with a standard normal-phase column (methanol/dichloromethane), followed by washing in refluxed ethanol.

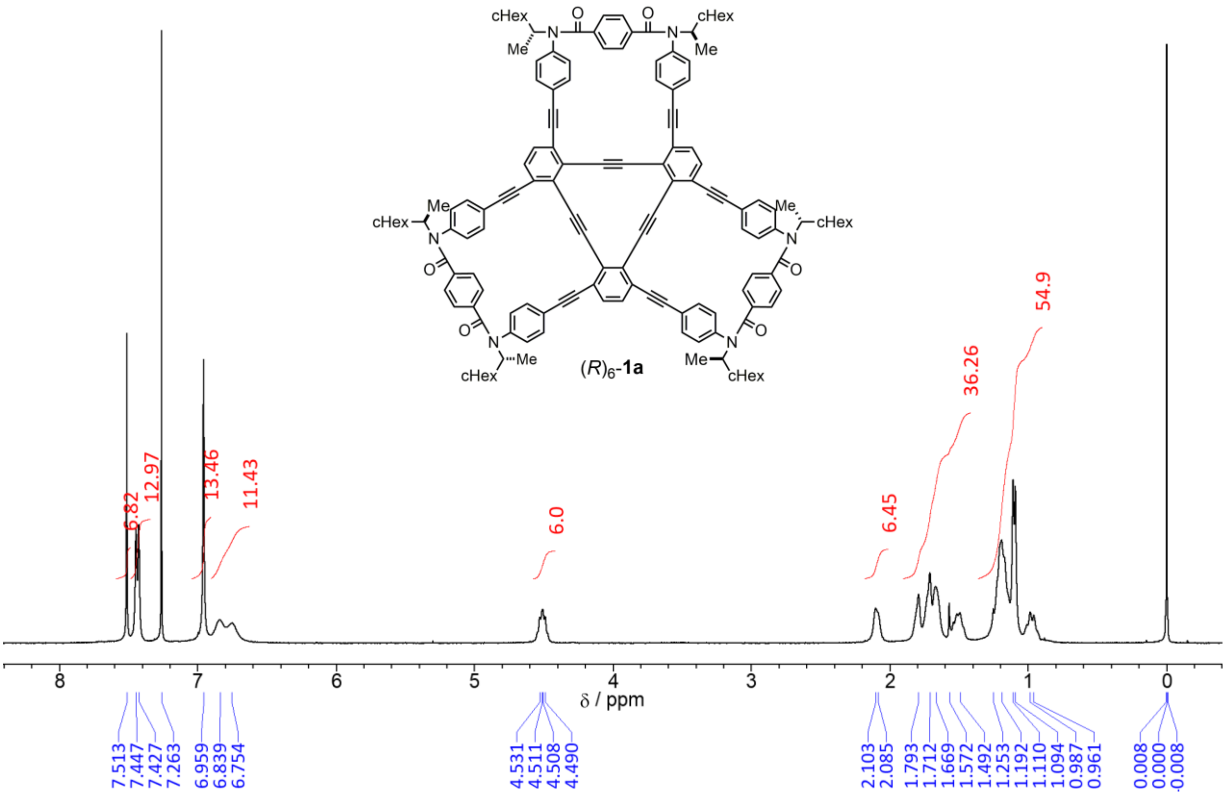
7b: mp 255-258 °C (dec); IR (KBr) ν_{max}/cm^{-1} 3069, 3046, 2960, 2935, 2874, 2201, 1698, 1510, 1208, 1147; ^{1}H NMR δ_H(400 MHz; CDCl$_3$; Me$_4$Si)/ppm 7.50 (6H, s), 7.34 (12H, d, *J* = 8.4 Hz), 7.00 (12H, d, *J* = 8.4 Hz), 3.67 (12H, t, *J* = 7.2 Hz), 1.53-1.46 (12H, m), 1.37-1.28 (12H, m), 0.92 (18H, t, *J* = 7.2 Hz); ^{13}C NMR δ_C(100 MHz; CDCl$_3$)/ppm 156.3 ($\underline{C}$(=O)CF$_3$), 138.9, 133.1, 132.0, 129.4, 127.8, 125.9, 123.5, 116.4 ($\underline{C}$F$_3$), 96.6, 95.3, 89.3, 51.7, 28.9, 19.8, 13.7; FD-LRMS *m*/*z* 1902.6 (M$^+$, 83%), 1903.6 ([M+1]$^+$, 100), 1904.6 ([M+2]$^+$, 64), 1905.6 ([M+3]$^+$, 29), 1906.6 ([M+4]$^+$, 13); FD-HRMS Found: 1902.61527, Calc. for $C_{108}H_{84}F_{18}N_6O_6$: 1902.61649.

Preparation of **1b** [X = ^{n}Bu]

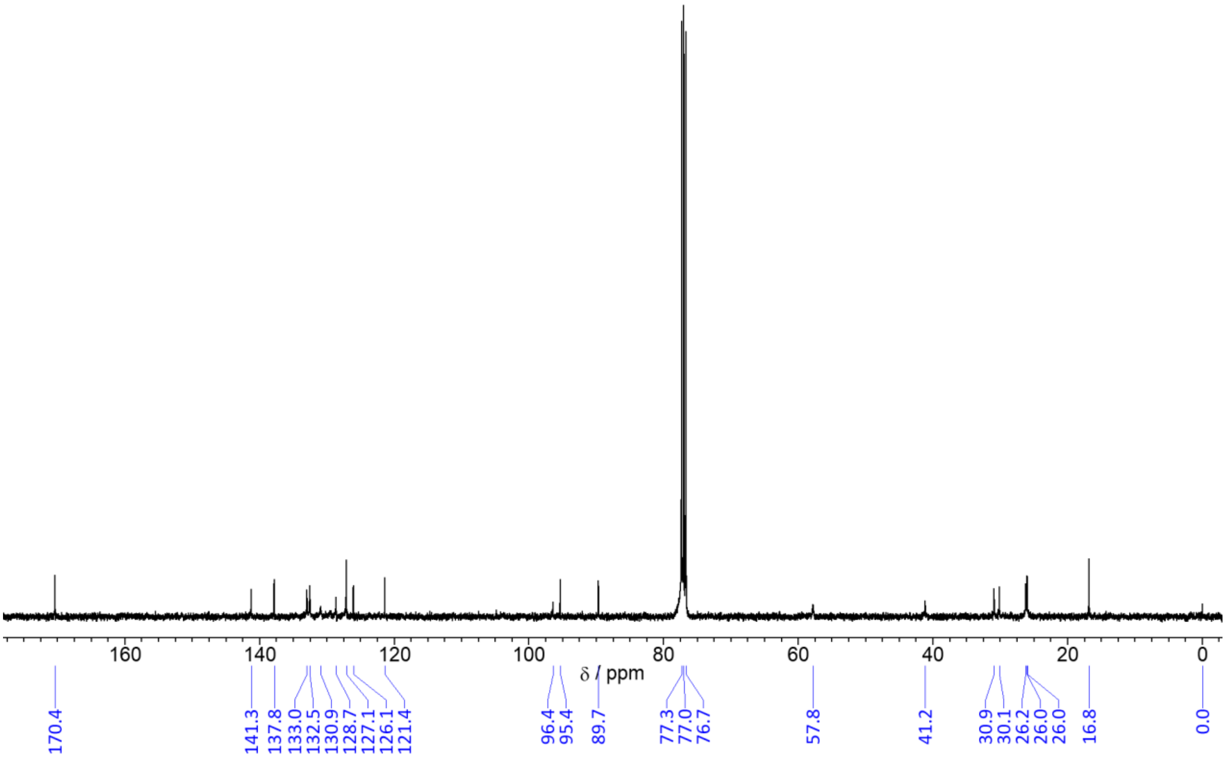
To an ice-cooled solution of **7b** (502 mg, 0.263 mmol) in THF (32 mL) were added 60% NaH in oil (168 mg, 4.20 mmol) and MeOH (2.1 mL), and the mixture was stirred at room temperature for 15 min, diluted with dichloromethane, and then quenched with water in an ice water bath. The organic layer was separated, washed with brine, dried over magnesium sulfate, and then concentrated. The resulting solid was purified by column chromatography on SiO$_2$ (dichloromethane) to give **7b'** (336 mg) as a yellow solid in 96% yield. **7b'**: ^{1}H NMR δ_H(400 MHz; CDCl$_3$; Me$_4$Si)/ppm 7.34 (6H, s), 7.11 (12H, d, *J* = 8.8 Hz), 6.28 (12H, d, *J* = 8.8 Hz), 3.66 (6H, br.s), 3.07 (12H, t, *J* = 7.2 Hz), 1.62-1.55 (12H, m), 1.47-1.38 (12H, m), 0.97 (18H, t, *J* = 7.2 Hz).

To a solution of **7b'** (386 mg, 0.253 mmol) in toluene (101 mL) containing Et$_3$N (0.25 mL) was added terephthaloyl chloride (168 mg, 0.827 mmol) at 100 °C. The mixture was further stirred at that temperature for 18 min, diluted with dichloromethane, which was washed with 1M aq. NaOH. The organic layer was separated, dried over magnesium sulfate, and then passed through an Al$_2$O$_3$/Celite pad. The filtrate was concentrated and purified by column chromatography on Al$_2$O$_3$/SiO$_2$ (tetrahydrofuran/dichloromethane) to give **1b** (328 mg) as a yellow solid in 76% yield. An analytic sample was obtained as a yellow solid by further purification through GPC (chloroform), HPLC with a standard normal-phase column (methanol/dichloromethane), followed by washing in refluxed ethanol. **1b**: mp >300 °C; IR (KBr) ν_{max}/cm^{-1} 3064, 3037, 2955, 2927, 2860, 2196, 1652, 1598, 1510; ^{1}H NMR δ_H(400 MHz; CDCl$_3$; Me$_4$Si)/ppm 7.50 (6H, s), 7.43 (12H, d, *J* = 8.8 Hz), 7.00 (12H, s), 6.81 (12H, br.d), 3.83 (12H, t, *J* = 7.2 Hz), 1.56-1.49 (12H, m), 1.38-1.29 (12H, m), 0.88 (18H, t, *J* = 7.2 Hz); ^{13}C NMR δ_C(100 MHz; CDCl$_3$)/ppm 169.9, 143.3, 137.2, 133.0, 132.9, 128.6, 128.5, 127.4, 126.1, 121.3, 96.5, 95.3, 89.4, 49.2, 29.8, 20.1, 13.8; FD-LRMS *m*/*z* 1716.9 (M$^+$, 60%), 1717.9 ([M+1]$^+$, 100), 1718.9 ([M+2]$^+$, 82), 1719.9 ([M+3]$^+$, 44), 1720.9 ([M+4]$^+$, 19), 1721.9 ([M+5]$^+$, 6); FD-HRMS Found: 1716.73879, Calc. for $C_{120}H_{96}N_6O_6$: 1716.73913; UV λ_{max}(CH$_2$Cl$_2$)/nm (log ε) 380 (sh. 5.00), 351 (5.32), 330 (sh. 5.16).

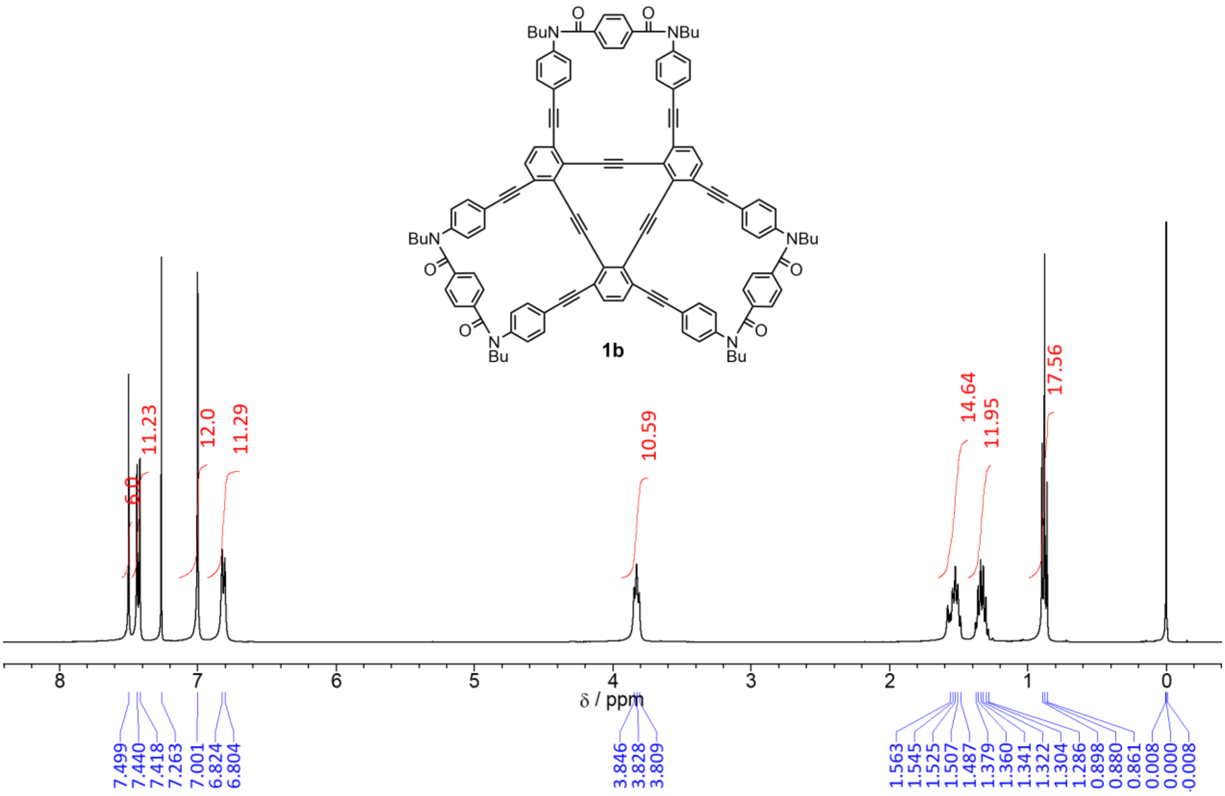
^{1}H and ^{13}C NMR spectra of new compounds



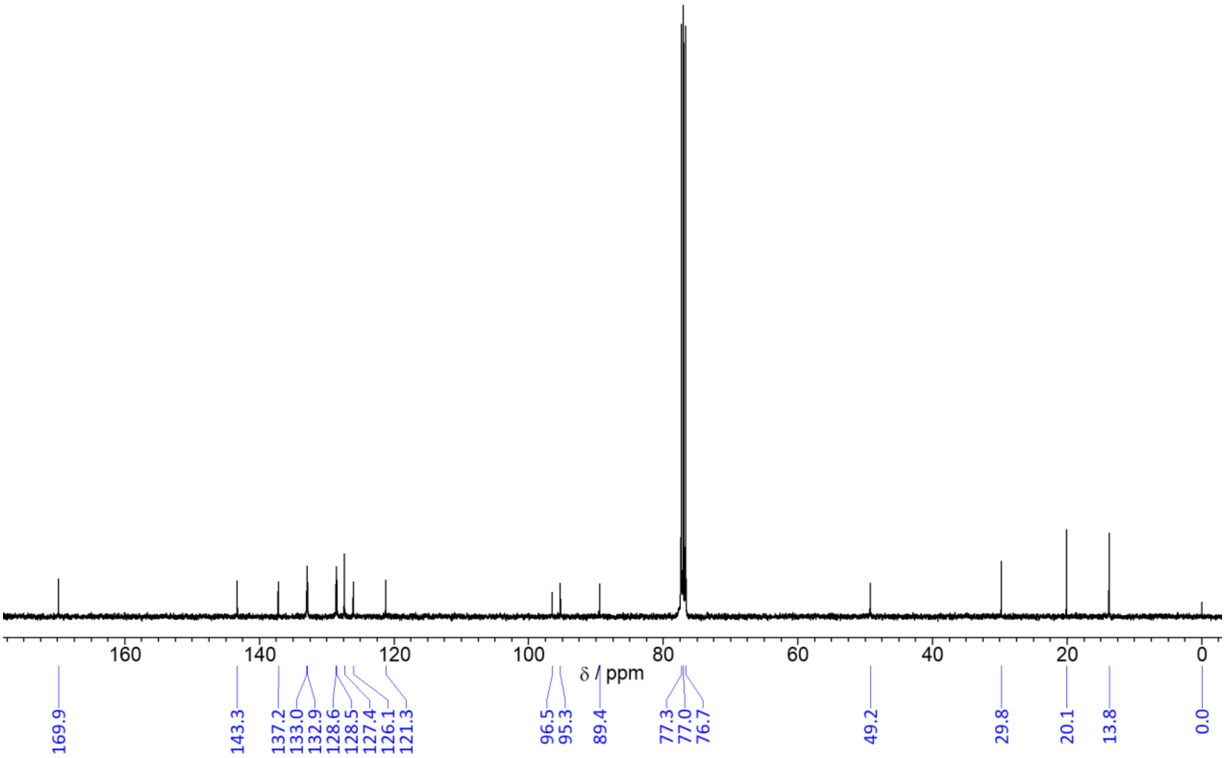
^{1}H NMR spectrum (400 MHz) of (*R*)$_6$-**1a**, measured in chloroform-*d* at room temperature.



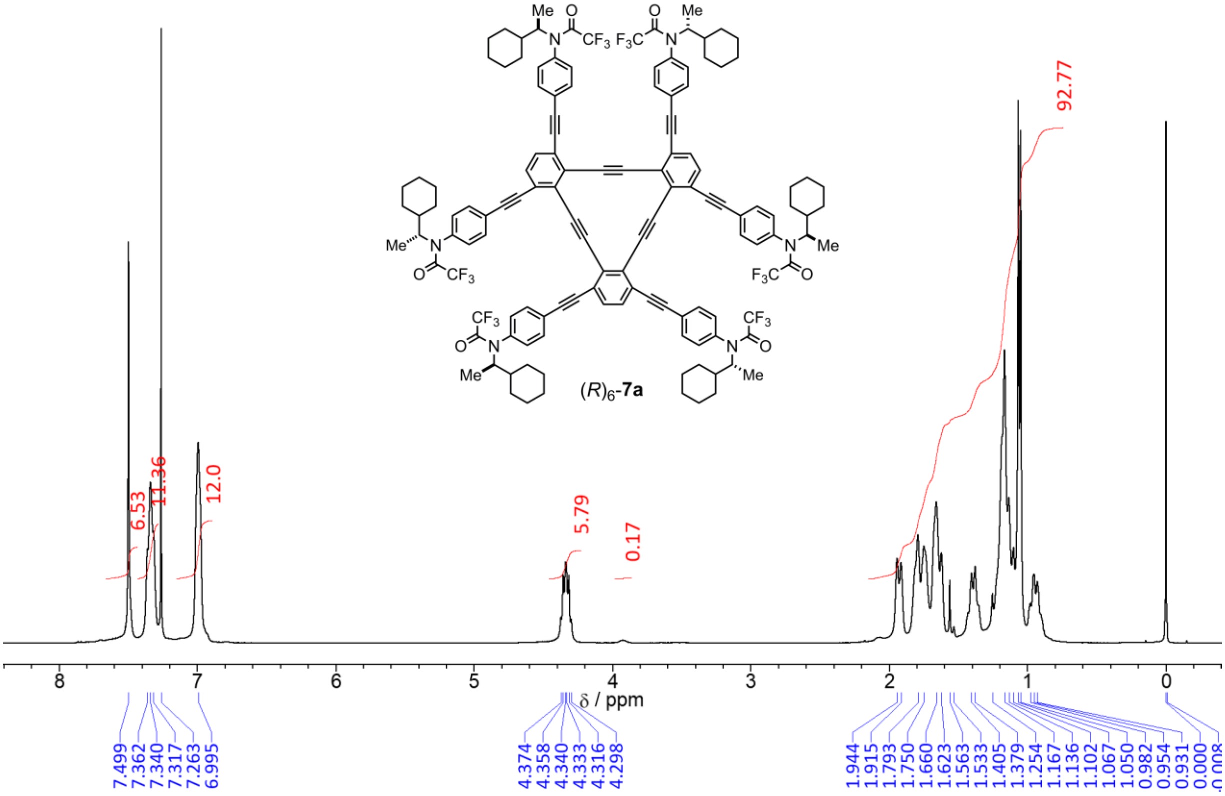
^{13}C NMR spectrum (100 MHz) of (*R*)$_6$-**1a**, measured in chloroform-*d* at room temperature.



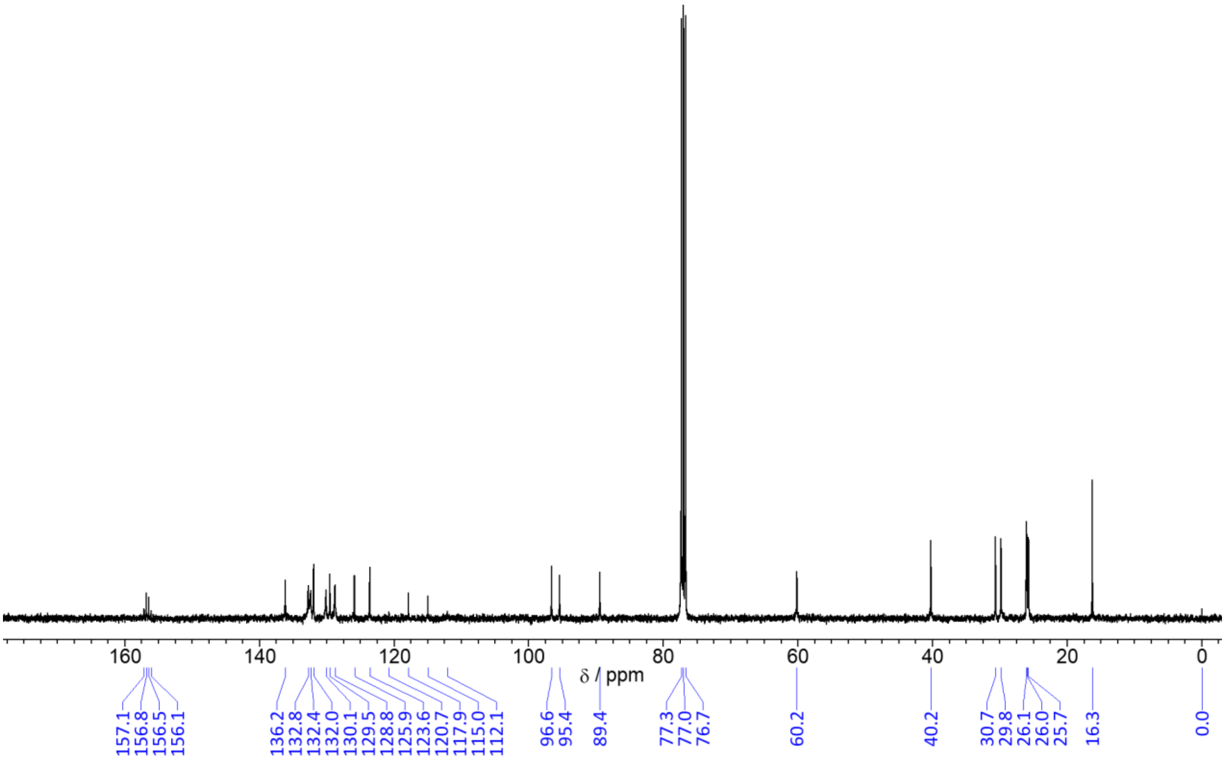
^{1}H NMR spectrum (400 MHz) of **1b**, measured in chloroform-*d* at room temperature.



^{13}C NMR spectrum (100 MHz) of **1b**, measured in chloroform-*d* at room temperature.



^{1}H NMR spectrum (400 MHz) of (R)$_6$-**7a**, measured in chloroform-*d* at room temperature.



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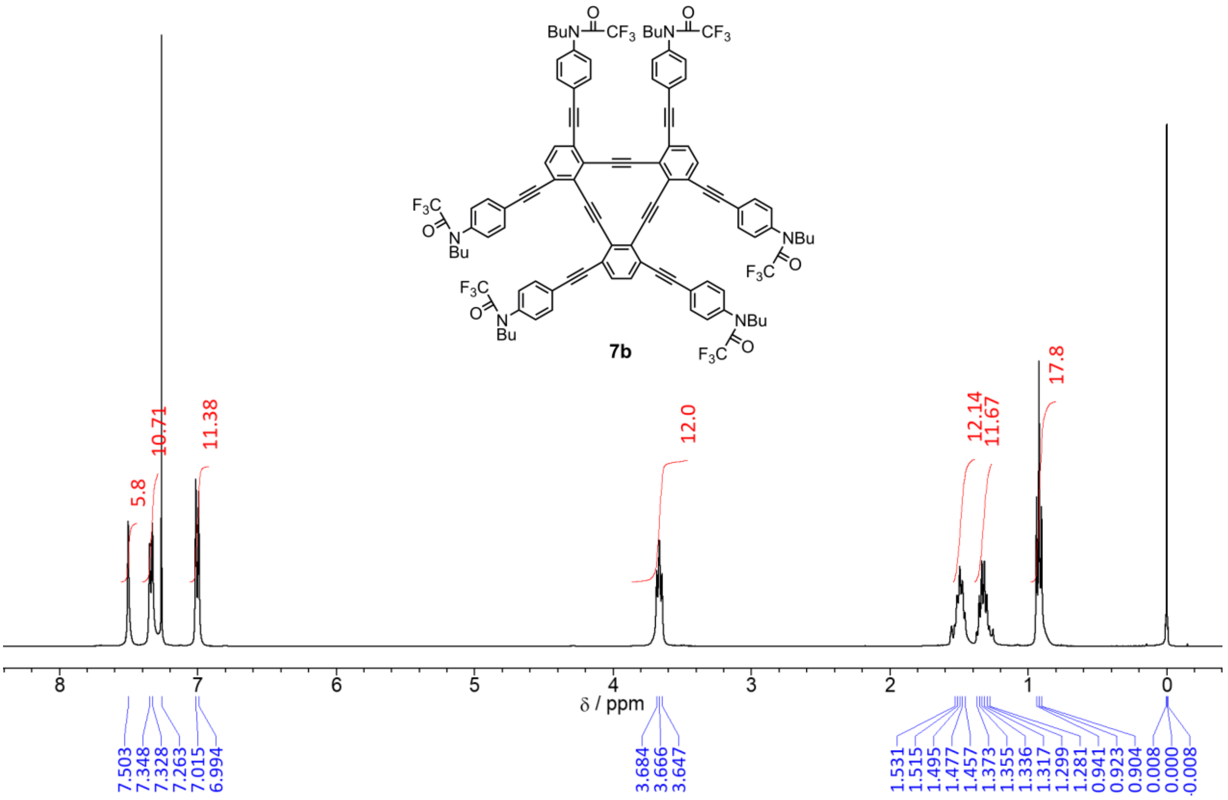

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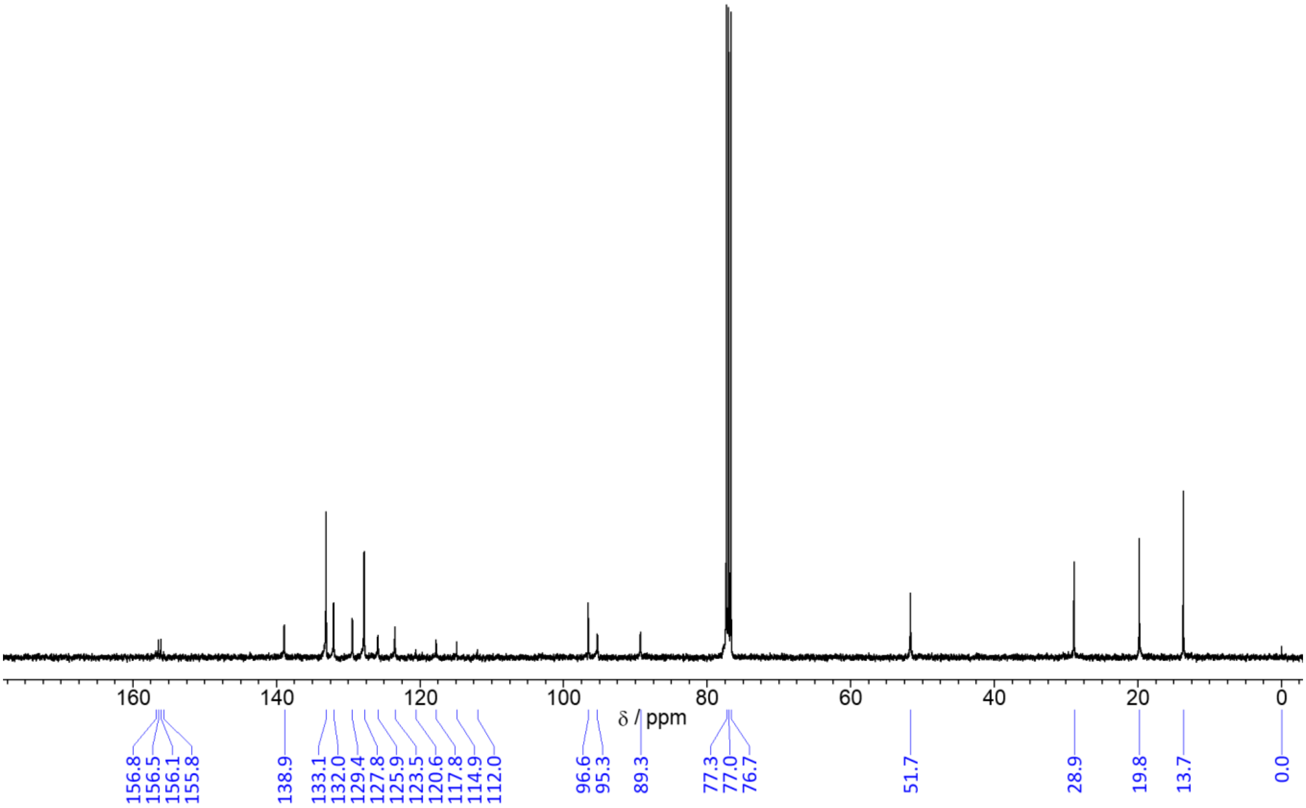
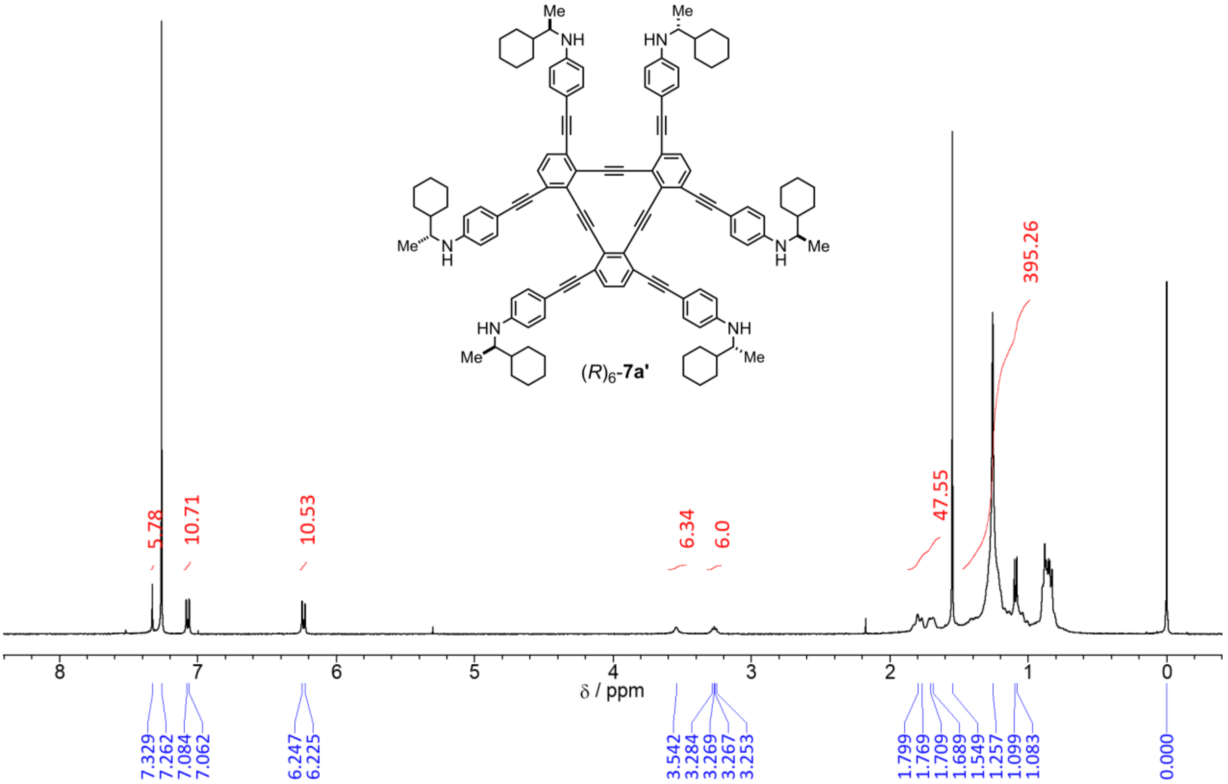
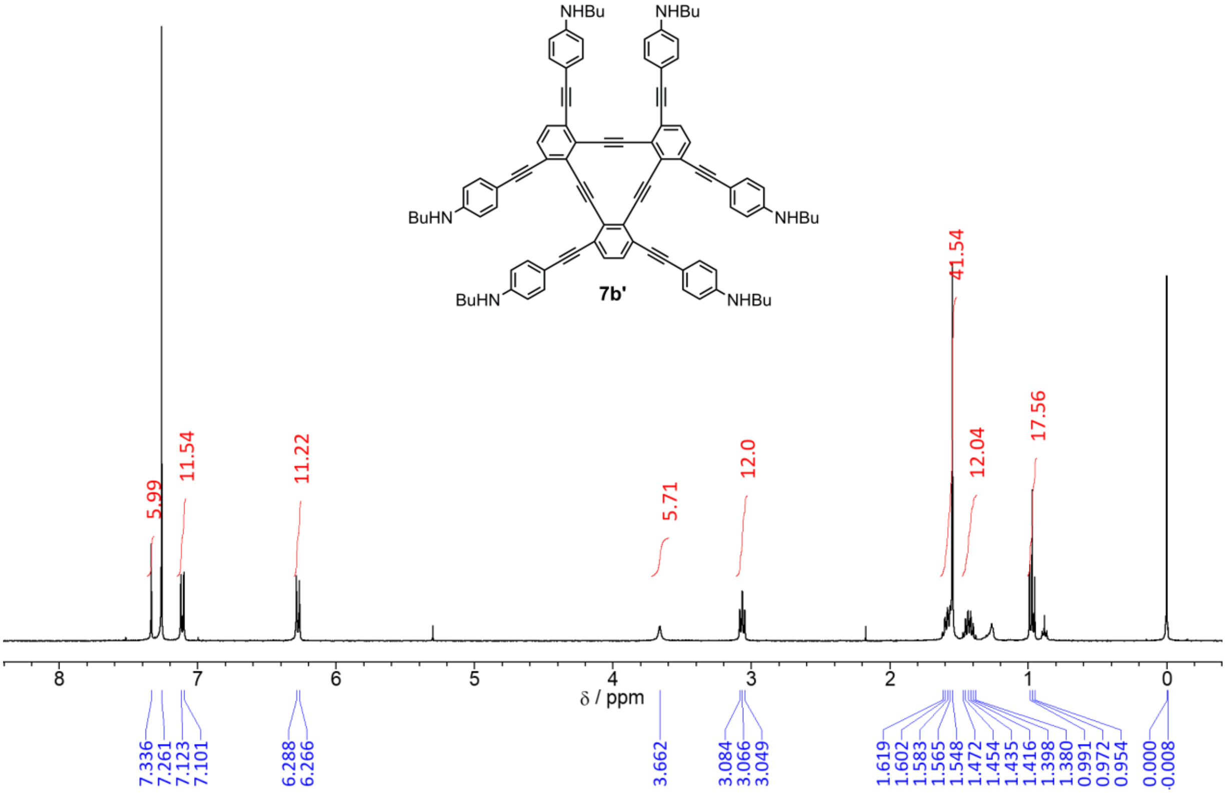


^{13}C NMR spectrum (100 MHz) of **7b**, measured in chloroform-*d* at room temperature.



^{1}H NMR spectrum (400 MHz) of (R)$_6$-**7a'**, cont. residual solvents (dichloromethane, acetone and hexane), measured in chloroform-*d* at room temperature.



^{1}H NMR spectrum (400 MHz) of **7b'**, cont. residual solvents (dichloromethane, acetone and hexane), measured in chloroform-*d* at room temperature.

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