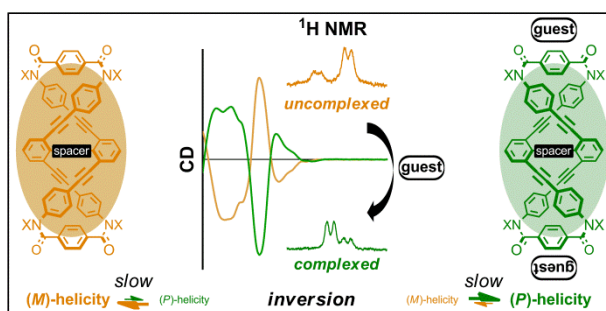


Supplementary Information

Controllability of dynamic double helices: quantitative analysis of the inversion of a screw-sense preference upon complexation

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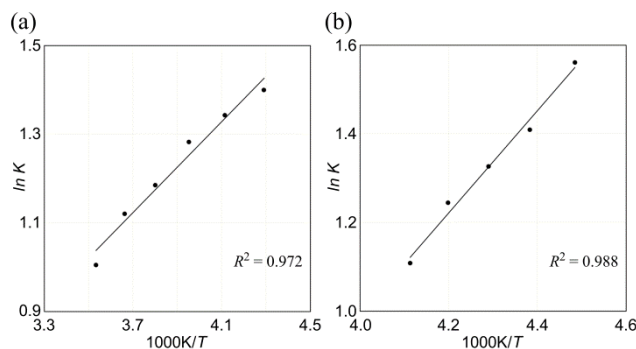


Figure S2. Plots of $\ln K$ versus $1/T$ for the dynamic interconversion between two forms with (*M*)- or (*P*)-helicity in a solution of (a) (R,R,R,R) -**1b** and (b) (R,R,R,R) -**2b**, based on values of integral for protons H^{Da} and H^{Db} , measured in $CDCl_3$ at (a) 233-283 K and (b) 223-243 K.

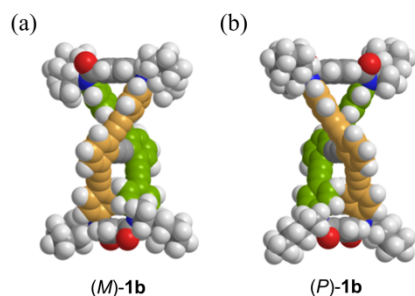


Figure S3A. Energy-minimized structures for (R,R,R,R) -**1b**, (a) (M) -**1b** (rel. 0 kJ mol^{-1} , most stable) and (b) (P) -**1b** (+2.65 kJ mol^{-1}), obtained by a conformational search using MacroModel software (v9.9 OPLS_2005, Monte Carlo Multiple Minimum method, non-solvated, 50 000 steps).

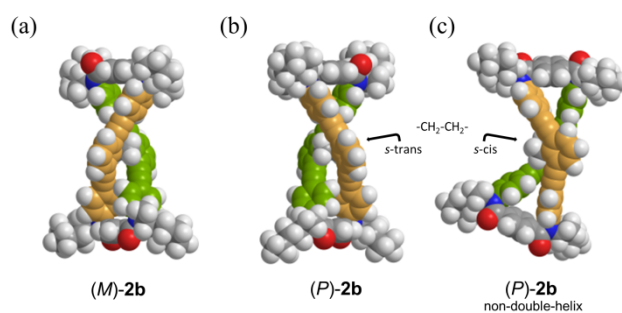


Figure S3B. Energy-minimized structures for (R,R,R,R) -**2b**, (a) (M) -**2b** (rel. 0 kJ mol^{-1}), (b) (P) -**2b** (+2.93 kJ mol^{-1}) and non-double-helical form (-1.57 kJ mol^{-1} , most stable), obtained by a conformational search using MacroModel software (v9.9 OPLS_2005, Monte Carlo Multiple Minimum method, non-solvated, 50 000 steps).

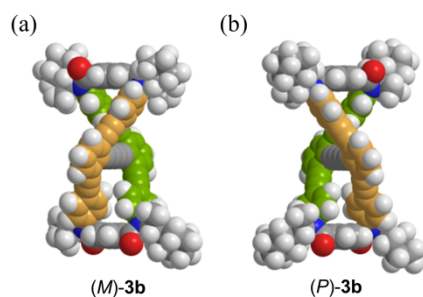


Figure S3C. Energy-minimized structures for (R,R,R,R) -**3b**, (a) (M) -**3b** (rel. 0 kJ mol⁻¹, most stable) and (b) (P) -**3b** (+1.48 kJ mol⁻¹), obtained by a conformational search using MacroModel software (v9.9 OPLS_2005, Monte Carlo Multiple Minimum method, non-solvated, 50 000 steps).

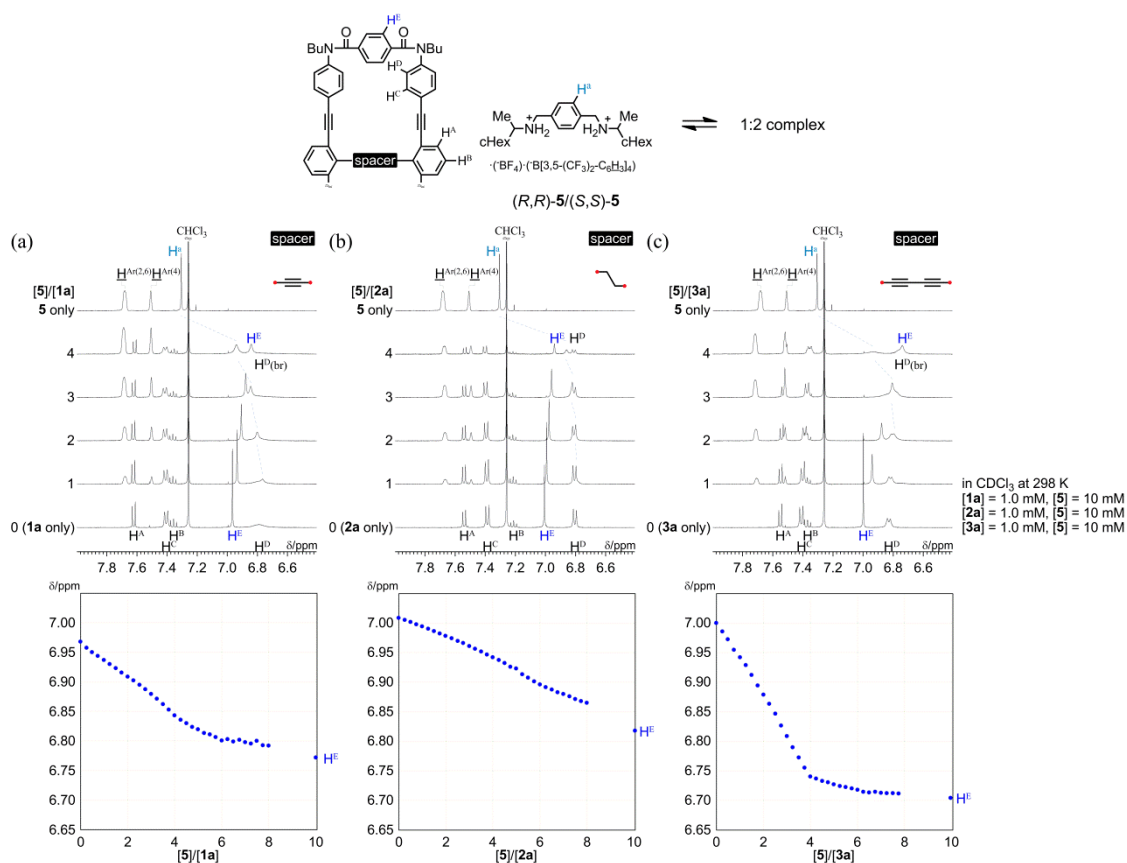


Figure S4. Partial ¹H NMR spectra (400 MHz) of (a) **1a**, (b) **2a**, and (c) **3a** in the presence of (R,R) -**5**/ (S,S) -**5** (0–4 equiv.) (top), and plots of the chemical shift (δ /ppm) for the phenylene protons H^E versus equivalents of **5** ($[5]/[1a]$, $[5]/[2a]$, or $[5]/[3a]$) added (bottom).

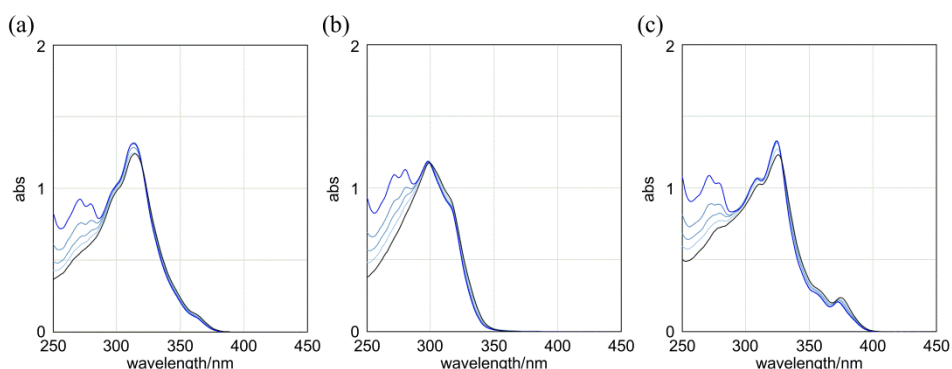


Figure S5. UV spectra of (a) **1a** (9.5×10^{-5} M), (b) **2a** (1.0×10^{-4} M), and (c) **3a** (1.0×10^{-4} M) in the presence of (*R,R*)-**5** (blue lines) [0 (**1a**, **2a**, or **3a** only, black line), 1, 2, 4, and 8 equiv.], measured in CH_2Cl_2 at room temperature.

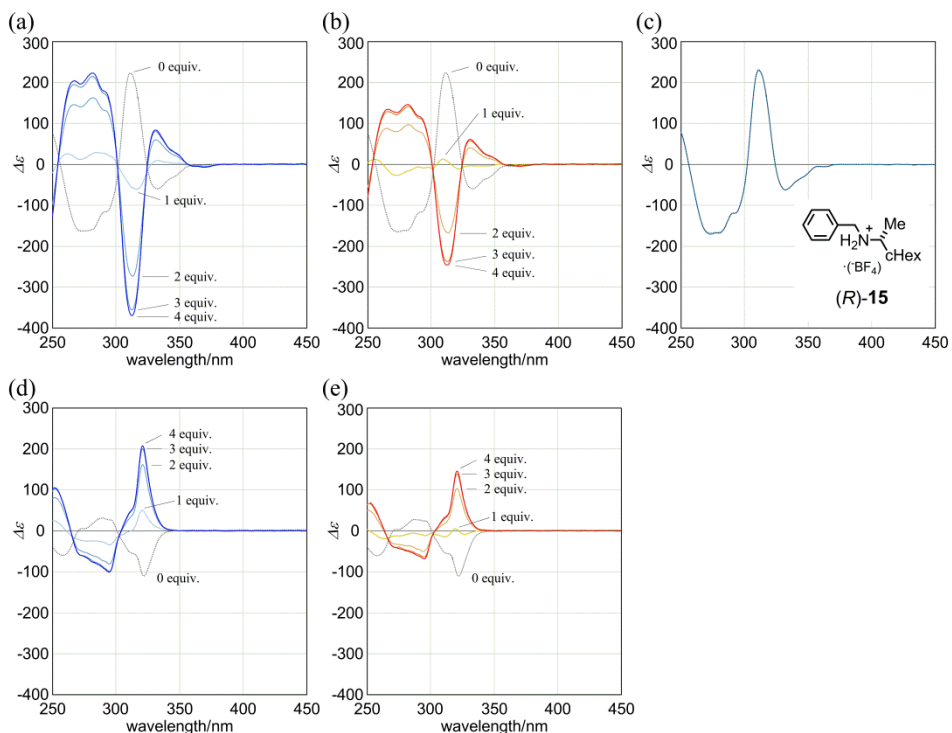


Figure S6. CD spectra of (a) (*R,R,R,R*)-**1b** (9.9×10^{-5} M) in the presence of (*R,R*)-**5** [0 (**1b** only, black dashed line), and 1-4 equiv. (blue lines)], (b) (*R,R,R,R*)-**1b** (1.0×10^{-4} M) in the presence of (*S,S*)-**5** [0 (**1b** only), and 1-4 equiv. (red lines)], (c) (*R,R,R,R*)-**1b** (9.2×10^{-5} M) in the presence of (*R*)-**15** [0 (**1b** only), and 8 equiv. (light blue line)], (d) (*R,R,R,R*)-**2b** (1.1×10^{-4} M) in the presence of (*R,R*)-**5** [0 (**2b** only, black dashed line), and 1-4 equiv. (blue lines)], and (e) (*R,R,R,R*)-**2b** (1.1×10^{-4} M) in the presence of (*S,S*)-**5** [0 (**2b** only), and 1-4 equiv. (red lines)]. All spectra were measured in CH_2Cl_2 at 293 K.

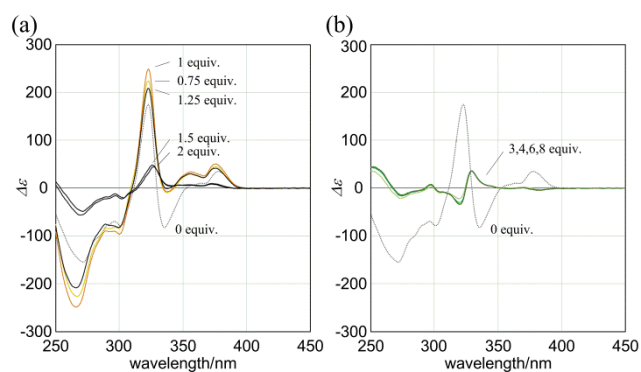


Figure S7. CD spectra of (R,R,R,R) -**3b** (1.1×10^{-4} M) in the presence of **4** (a) [0 (**3b** only), 0.75 and 1 equiv. (orange lines), and 1.25-2 equiv. (black solid lines)], and (b) [0 (**3b** only), and 3-8 equiv. (green lines)]. All spectra were measured in CH_2Cl_2 at 293 K.

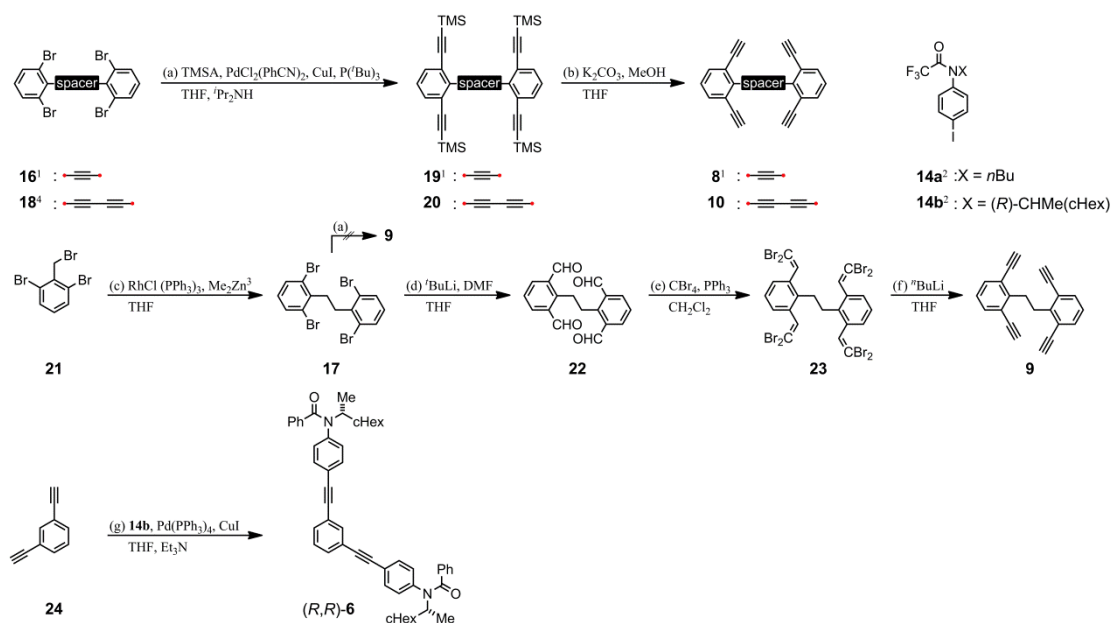
Table S1. Binding constants,^a obtained by a curve fitting method, based on CD titration experiments.

		<i>(R,R)</i> - 5 or <i>(S,S)</i> - 5 ^b			
[1a] = 1.16×10 ⁻⁴ /M		281 nm	312 nm	332 nm	
	<i>K</i> /M ⁻¹	2.44×10 ⁴	2.33×10 ⁴	1.97×10 ⁴	
	$\Delta\epsilon_{\max}$	-5.65×10 ¹	9.31×10 ¹	-1.75×10 ¹	
	χ^2	5.02×10 ⁰	2.62×10 ¹	6.48×10 ⁻¹	
	<i>R</i> ²	9.98×10 ⁻¹	9.95×10 ⁻¹	9.96×10 ⁻¹	
[2a] = 1.00×10 ⁻⁴ /M		254 nm	292 nm	322 nm	
	<i>K</i> /M ⁻¹	2.05×10 ⁴	6.91×10 ⁴	1.70×10 ⁴	
	$\Delta\epsilon_{\max}$	1.81×10 ¹	-1.53×10 ¹	3.02×10 ¹	
	χ^2	9.67×10 ⁻¹	1.40×10 ⁰	4.54×10 ⁻¹	
	<i>R</i> ²	9.92×10 ⁻¹	9.72×10 ⁻¹	9.98×10 ⁻¹	
[3a] = 1.03×10 ⁻⁴ /M		262 nm	322 nm	335 nm	376 nm
	<i>K</i> /M ⁻¹	1.64×10 ⁴	2.03×10 ⁴	1.35×10 ⁵	2.33×10 ⁴
	$\Delta\epsilon_{\max}$	-8.38×10 ¹	8.06×10 ¹	-1.55×10 ¹	1.52×10 ¹
	χ^2	1.67×10 ¹	9.79×10 ⁰	1.52×10 ⁰	5.68×10 ⁻¹
	<i>R</i> ²	9.94×10 ⁻¹	9.97×10 ⁻¹	9.71×10 ⁻¹	9.90×10 ⁻¹

^aAssume 1:2 complexation (*K*₁ = *K*₂). Doubled concentration (= [terephthalamide unit]) was used.^b[*(R,R)*-**5**] or [*(S,S)*-**5**] = 0-8 equiv.**Table S2.** Binding constants,^a obtained by a curve fitting method, based on CD titration experiments.

		<i>(R,R)</i> - 5 ^b			<i>(S,S)</i> - 5 ^b		
[(R,R,R,R)-3b] = 1.03×10 ⁻⁴ /M ⁻¹		323 nm	335 nm	378 nm	323 nm	335 nm	378 nm
	<i>K</i> /M ⁻¹	2.62×10 ⁴	5.23×10 ⁴	3.31×10 ⁴	2.11×10 ⁴	3.28×10 ⁴	2.11×10 ⁴
	$\Delta\Delta\epsilon_{\max}$	-3.05×10 ²	1.30×10 ²	-5.88×10 ¹	-1.71×10 ²	9.60×10 ¹	-3.42×10 ¹
	χ^2	1.51×10 ²	1.82×10 ¹	4.45×10 ⁰	2.67×10 ²	9.48×10 ⁰	1.22×10 ¹
	<i>R</i> ²	9.98×10 ⁻¹	9.98×10 ⁻¹	9.98×10 ⁻¹	9.87×10 ⁻¹	9.98×10 ⁻¹	9.85×10 ⁻¹

^aAssume 1:2 complexation (*K*₁ = *K*₂). Doubled concentration (= [terephthalamide unit]) was used.^b[*(R,R)*-**5**] or [*(S,S)*-**5**] = 0-6 equiv.



Scheme S1. Preparation of tetraynes **8-10** and single-stranded model (*R,R*)-**6**. Yields: (a) 77% for **19**, 88% for **20**; (b) 97% for **10**; (c) 66%; (d) 35%; (e) 90%; (f) 73%; (g) 95%.

Experimental

Preparation of **19¹**

To a solution of **16¹** (799 mg, 1.62 mmol), P(*t*Bu)₃ (1.5 mL of 5.0 mmol/10 mL toluene solution), PdCl₂(PhCN)₂ (146 mg, 0.381 mmol), and CuI (73 mg, 0.38 mmol) in THF (12 mL) and *i*Pr₂NH (5 mL) was added TMSA (2.3 mL, 16 mmol) at room temperature under an argon atmosphere, and the mixture was stirred for 2 hours. To the reaction mixture were added aq. HCl and chloroform, and the organic layer was separated, concentrated, and purified by column chromatography on SiO₂ (hexane) to give **19** (700 mg) as a brownish-white solid in 77% yield. The TMS groups were removed with K₂CO₃ in MeOH and THF to give **8**, according to the literature.

Preparation of **11a¹** (TFA-protected) [X = *n*Bu]

To a solution of **8¹** (206 mg, 0.751 mmol) and **14a²** (1.34 g, 3.61 mmol) in Et₂NH (26 mL) and CH₃CN (130 mL) were added Pd(PPh₃)₄ (60 mg, 0.052 mmol) and CuI (18 mg, 0.095 mmol) at 80 °C under an argon atmosphere, and the mixture was stirred at that temperature for 2 hours. The reaction mixture was diluted with ethyl acetate, and the organic layer was washed with water, concentrated, and then purified by column chromatography on SiO₂ (dichloromethane) to give **11a¹** (701 mg) as a yellowish-white amorphous solid in 75% yield. An analytical sample was obtained as a yellowish-white solid through purification by GPC (chloroform, RI detected). **11a¹**: mp 79-81 °C; elemental analyses Found: C, 66.78; H, 4.78; N, 4.48%. Calc. for C₇₀H₅₈N₄O₄F₁₂·(EtOH): C, 66.87;

H, 4.99; N, 4.33%; IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 3061, 2960, 2934, 2874, 2212, 1698, 1510, 1209, 1149; ^1H NMR δ_{H} (400 MHz; CDCl_3 ; Me_4Si)/ppm 7.63 (4H, d, $J = 7.6$ Hz), 7.44-7.40 (8+2H, m), 7.02 (8H, d, $J = 8.0$ Hz), 3.66 (8H, t, $J = 7.2$ Hz), 1.47 (8H, quin, $J = 7.2$ Hz), 1.30 (8H, sext, $J = 7.2$ Hz), 0.89 (12H, t, $J = 7.2$ Hz); ^{13}C NMR δ_{C} (100 MHz; CDCl_3)/ppm 156.4 ($\text{C}(\text{=O})\text{CF}_3$), 138.8, 132.8, 131.8, 128.3, 128.0, 128.0, 126.0, 123.7, 116.3 (C_2F_5), 94.9, 93.0, 89.3, 51.5, 28.8, 19.8, 13.6; FD-LRMS m/z 1246.40 (M^+ , 100%), 1247.41 ($[\text{M}+1]^+$, 79), 1248.41 ($[\text{M}+2]^+$, 33), 1249.41 ($[\text{M}+3]^+$, 10); FD-HRMS Found: 1246.42712. Calc. for $\text{C}_{70}\text{H}_{58}\text{N}_4\text{O}_4\text{F}_{12}$: 1246.42664.

Preparation of **1a** [X = *n*Bu]

To an ice-cooled solution of **11a'** (394 mg, 0.316 mmol) in THF (13 mL) were added 60% NaH in oil (628 mg, 15.7 mmol) and MeOH (13 mL), and the mixture was stirred at room temperature for 1 hour, and then diluted with dichloromethane. The organic layer was washed with water, concentrated, and then purified by column chromatography on Al_2O_3 (1:1 dichloromethane/hexane) to give tetraaniline **1a** (147 mg) as a yellow solid in 54% yield, which was immediately subjected to the next reaction.

To a solution of **1a** (147 mg, 0.170 mmol) in toluene (33 mL) and THF (33 mL) containing Et_3N (0.47 mL, 3.4 mmol) was added at 80 °C terephthaloyl chloride in two portions (77 mg, 0.38 mmol and 39 mg, 0.19 mmol) over a period of 4 hours. The reaction mixture was diluted with chloroform and water. The organic layer was separated, concentrated, and purified by column chromatography on SiO_2 (chloroform), followed by GPC (chloroform, RI detected) to give **1a** (157 mg) as a white solid in 82% yield. An analytical sample was suspended in refluxed EtOH, and collected as a white solid through filtration. A single crystal was obtained as colorless needles by recrystallization from chloroform with a diffused vapor of benzene. **1a**: mp >300 °C; elemental analyses Found: C, 82.86; H, 5.95; N, 4.89%. Calc. for $\text{C}_{78}\text{H}_{66}\text{N}_4\text{O}_4 \cdot (\text{H}_2\text{O})_{0.5}$: C, 82.73; H, 5.96; N, 4.95%; UV $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 362sh (log ϵ 4.13), 315 (5.12) and 300sh (5.02); IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 3058, 2956, 2930, 2870, 2208, 1658, 1510; ^1H NMR δ_{H} (400 MHz; CDCl_3 ; Me_4Si)/ppm 7.62 (4H, d, $J = 8.0$ Hz), 7.41 (8H, d, $J = 8.4$ Hz), 7.36 (2H, t, $J = 8.0$ Hz), 6.97 (8H, s), 6.79 (8H, br s), 4.10-4.00 (4H, m), 3.61-3.54 (4H, m), 1.54-1.45 (8H, m), 1.37-1.27 (8H, m), 0.87 (12H, t, $J = 7.2$ Hz); ^{13}C NMR δ_{C} (100 MHz; CDCl_3)/ppm 170.0, 142.9, 137.4, 132.7, 132.6, 128.4, 128.1, 127.3, 126.6, 126.2, 121.4, 94.2, 92.9, 89.3, 49.1, 29.7, 20.1, 13.8; FD-LRMS m/z 1122.64 (M^+ , 100%), 1123.64 ($[\text{M}+1]^+$, 86), 1124.65 ($[\text{M}+2]^+$, 39), 1125.65 ($[\text{M}+3]^+$, 13); FD-HRMS Found: 1122.50852. Calc. for $\text{C}_{78}\text{H}_{66}\text{N}_4\text{O}_4$: 1122.50840.

Preparation of **11b'** (TFA-protected) [X = (*R*)-CHMe(cHex)]

To a solution of **8** (199 mg, 0.725 mmol) and (*R*)-**14b**² (1.50 g, 3.53 mmol) in Et_2NH (26 mL) and CH_3CN (126 mL) were added $\text{Pd}(\text{PPh}_3)_4$ (57 mg, 0.049 mmol) and CuI (17 mg, 0.089

mmol) at 80 °C under an argon atmosphere, and the mixture was stirred at that temperature for 17 hours. The reaction mixture was diluted with ethyl acetate, and the organic layer was washed with water, concentrated, and then purified by column chromatography on SiO₂ (5:1 chloroform/hexane) to give **11b'** (804 mg) as a yellowish-white solid in 76% yield. An analytical sample was obtained as a yellowish-brown solid through purification by GPC (chloroform, RI detected). **11b'**: mp 110.0-112.0 °C; $[\alpha]_D^{26} -59.0$ (*c* 1.00 in CHCl₃); elemental analyses Found: C, 69.83; H, 5.64; N, 3.70%. Calc. for C₈₆H₈₂N₄O₄F₁₂·(EtOH): C, 70.01; H, 5.88; N, 3.71%; IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 3061, 2932, 2853, 2213, 1696, 1508, 1208, 1188, 1149; ¹H NMR δ_{H} (400 MHz; CDCl₃; Me₄Si)/ppm 7.63 (4H, d, *J* = 7.6 Hz), 7.42 (2H, t, *J* = 7.6 Hz), 7.41 (8H, d, *J* = 8.0 Hz), 6.99 (8H, d, *J* = 8.0 Hz), 4.34 (4H, dq, *J* = 6.8, 10 Hz), 1.92 (4H, d, *J* = 12 Hz), 1.80-1.60 (16H, m), 1.41-0.84 (24H, m), 1.03 (12H, d, *J* = 6.8 Hz); ¹³C NMR δ_{C} (100 MHz; CDCl₃)/ppm 156.7 (C(=O)CF₃), 135.9, 132.3, 132.1, 131.8, 130.3, 129.0, 128.3, 128.1, 126.0, 123.8, 116.4 (CF₃), 95.0, 93.1, 89.4, 59.8, 40.2, 30.6, 29.7, 26.1, 25.9, 25.7, 16.2; FD-LRMS *m/z* 1462.78 (M⁺, 100%), 1463.78 ([M+1]⁺, 98), 1464.79 ([M+2]⁺, 51), 1465.79 ([M+3]⁺, 18); FD-HRMS Found: 1462.61329. Calc. for C₈₆H₈₂N₄O₄F₁₂: 1462.61444.

Preparation of (*R,R,R,R*)-**1b** [X = (*R*)-CHMe(cHex)]

To an ice-cooled solution of **11b'** (402 mg, 0.275 mmol) in THF (11 mL) were added 60% NaH in oil (925 mg, 23.1 mmol) and MeOH (11 mL), and the mixture was stirred at room temperature for 1 hour, and then diluted with dichloromethane. The organic layer was washed with water, concentrated, and then purified by column chromatography on Al₂O₃ (1:1 dichloromethane/hexane) to give tetraaniline **11b** (239 mg) as a yellowish-white solid in 81% yield, which was immediately subjected to the next reaction.

To a solution of **11b** (239 mg, 0.221 mmol) in toluene (43 mL) and THF (43 mL) containing Et₃N (0.62 mL, 4.5 mmol) was added at 80 °C terephthaloyl chloride in four portions (100 mg, 0.493 mmol, 101 mg, 0.498 mmol, 295 mg, 1.45 mmol and 297 mg, 1.46 mmol) over a period of 7 hours. The reaction mixture was diluted with chloroform and water. The organic layer was separated, concentrated, and purified by column chromatography on SiO₂ (chloroform), followed by GPC (chloroform, RI detected) to give (*R,R,R,R*)-**1b** (52 mg) as a white solid in 18% yield. An analytical sample was suspended in refluxed EtOH, and collected as a white solid through filtration. (*R,R,R,R*)-**1b**: mp 228-272 °C (dec); $[\alpha]_D^{24} -280$ (*c* 1.00 in CHCl₃); elemental analyses Found: C, 82.85; H, 6.75; N, 4.11%. Calc. for C₉₄H₉₀N₄O₄·(H₂O): C, 83.15; H, 6.83; N, 4.13%; UV $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 363sh (log ϵ 4.12), 314 (5.13) and 300sh (5.03); CD $\lambda(\text{CH}_2\text{Cl}_2)/\text{nm}$ 363 ($\Delta\epsilon$ -5.6), 358 (-4.8), 332 (-60.8), 311 (+224.9), 293 (-118.7), 291 (-117.6), 282sh (-161.6) and 273 (-168.2); IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 3059, 2927, 2851, 2209, 1658, 1509; ¹H NMR δ_{H} (400 MHz; CDCl₃; Me₄Si)/ppm (303K) [two sets] [7.65, 7.63] (4H, [d, *J* = 7.6 Hz]×2), 7.45 (4H, br d), [7.37, 7.36] (2H, [t, *J* = 7.6 Hz]×2), 7.36 (4H, br d), 7.11 (4H, br d), [6.93, 6.92] (8H, s×2), [6.48, 6.39] (4H, br d×2),

[4.57, 4.36] (4H, [dq, $J = 6.8, 10$ Hz] $\times 2$), [2.16, 1.99] (4H, [br d] $\times 2$), 1.84-1.48 (16H, m), 1.33-0.88 (24H, m), [1.24, 0.99] (12H, [d, $J = 6.8$ Hz] $\times 2$); ^{13}C NMR δ_{C} (100 MHz; CDCl_3)/ppm (296 K) [two sets] [170.6, 170.3], [141.2, 140.8], [138.0, 137.9], 132.6, 132.3, 131.6, 130.4, 129.7, 128.4, 128.0, 127.1, [126.8, 126.7], [126.2, 126.2], 121.6, [94.2, 94.1], [92.9, 92.9], 89.4, [58.8, 56.9], [42.0, 40.0], [31.2, 30.6], [30.2, 30.0], 26.2, [26.0, 26.0], 25.9, [17.1, 16.5]; FD-LRMS m/z 1118.63 ($[\text{M}-2\times\text{CHMe}(\text{cHex})+2]^+$, 7%), 1119.62 ($[\text{M}-2\times\text{CHMe}(\text{cHex})+3]^+$, 6), 1228.74 ($[\text{M}-\text{CHMe}(\text{cHex})+1]^+$, 47), 1229.75 ($[\text{M}-\text{CHMe}(\text{cHex})+2]^+$, 43), 1230.75 ($[\text{M}-\text{CHMe}(\text{cHex})+3]^+$, 22), 1338.87 (M^+ , 93), 1339.87 ($[\text{M}+1]^+$, 100), 1340.87 ($[\text{M}+2]^+$, 56), 1341.88 ($[\text{M}+3]^+$, 22), 1342.89 ($[\text{M}+4]^+$, 6); FD-HRMS Found: 1338.69741. Calc. for $\text{C}_{94}\text{H}_{90}\text{N}_4\text{O}_4$: 1338.69620.

Preparation of **17**

To a solution of **21** (10.9 g, 33.2 mmol) and $\text{RhCl}(\text{PPh}_3)_3$ (624 mg, 0.674 mmol) in THF (166 mL) was added a 1M solution of Me_2Zn in heptane (34 mL) at room temperature under an argon atmosphere,³ the mixture was refluxed for 17 h. The reaction was quenched with aq. HCl, and extracted with ethyl acetate. The organic layer was separated, concentrated, and purified by column chromatography on SiO_2 (dichloromethane), followed by GPC (chloroform, RI detected) to give **17** (5.47 g) as a white solid in 66% yield. **17**: mp 159.0-160.0 °C; elemental analyses Found: C, 33.63; H, 2.20%. Calc. for $\text{C}_{14}\text{H}_{10}\text{Br}_4$: C, 33.78; H, 2.02%; IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ 2946, 1551, 1447, 1426, 1153, 1107, 764, 720, 707; ^1H NMR δ_{H} (400 MHz; CDCl_3 ; Me_4Si)/ppm 7.47 (4H, d, $J = 8.0$ Hz), 6.91 (2H, t, $J = 8.0$ Hz), 3.37 (4H, s); ^{13}C NMR δ_{C} (100 MHz; CDCl_3)/ppm 139.2, 132.3, 128.7, 126.0, 34.9; FD-LRMS m/z 493.79 (M^+ , 18%), 495.79 ($[\text{M}+2]^+$, 70), 496.79 ($[\text{M}+3]^+$, 11), 497.78 ($[\text{M}+4]^+$, 100), 498.79 ($[\text{M}+5]^+$, 16), 499.78 ($[\text{M}+6]^+$, 65), 500.79 ($[\text{M}+7]^+$, 10), 501.78 ($[\text{M}+8]^+$, 17).

Preparation of **22**

To an acetone-dry ice-cooled solution of **17** (200 mg, 0.402 mmol) in THF (13 mL) was added a 1.6M solution of $t\text{BuLi}$ in pentane (4 mL), and the mixture was stirred at that temperature for 1 hour. To the mixture was added DMF (0.5 mL, 6 mmol), and the mixture was stirred at that temperature for 5 hours, followed by stirring at room temperature for 16 hours. The reaction mixture was quenched with aq. NH_4Cl , and extracted with dichloromethane. The organic layer was separated, concentrated, and purified by column chromatography on SiO_2 (dichloromethane) to give **22** (41 mg) as a white solid in 35% yield. An analytical sample was suspended in dichloromethane and hexane, and collected as a white solid through filtration. **22**: mp 206.5-208.0 °C; IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ 3086, 2914, 2872, 2812, 2777, 1686, 1577; ^1H NMR δ_{H} (400 MHz; CDCl_3 ; Me_4Si)/ppm 10.25 (4H, s), 8.06 (4H, d, $J = 7.6$ Hz), 7.61 (2H, t, $J = 7.6$ Hz), 3.89 (4H, s); ^{13}C NMR δ_{C} (100 MHz; CDCl_3)/ppm 191.5, 144.4, 137.2, 135.5, 127.6, 27.6; FD-LRMS m/z 276.05 ($[\text{M}-(\text{H}_2\text{O})]^+$, 100%), 294.06 (M^+ , 83); FD-HRMS Found: 294.09089. Calc. for $\text{C}_{18}\text{H}_{14}\text{O}_4$: 294.08921.

Preparation of **12a'** (TFA-protected) [X = *n*Bu]

To an ice-cooled solution of **22** (261 mg, 0.887 mmol) and CBr₄ (3.52 g, 10.6 mmol) in CH₂Cl₂ (110 mL) was added PPh₃ (5.57 g, 21.3 mmol), the mixture was stirred at room temperature for 15 min. After removal of a solid by filtration, the filtrate was concentrated and purified by column chromatography on SiO₂ (dichloromethane) to give **23** (736 mg) as a white amorphous solid in 90% yield, which was immediately subjected to the next reaction.

To an acetone-dry ice-cooled solution of **23** (1.65 g, 1.80 mmol) in THF (405 mL) was added a 1.6M solution of ^{*n*}BuLi in hexane (9 mL), and the mixture was stirred at that temperature for 10 min. The reaction mixture was quenched with aq. NH₄Cl, and extracted with ethyl acetate. The organic layer was separated, washed with brine, concentrated, and purified by column chromatography on SiO₂ (1:4 dichloromethane/hexane) to give **9** (365 mg) as a white solid in 73% yield, which was subjected to the next reactions without further purification.

To a solution of **9** (158 mg, 0.568 mmol) and **14a** (1.02 g, 2.74 mmol) in Et₃N (23 mL) and THF (23 mL) were added Pd(PPh₃)₄ (182 mg, 0.158 mmol) and CuI (59 mg, 0.31 mmol) at 60 °C under an argon atmosphere, and the mixture was stirred at that temperature for 14 hours. The reaction mixture was diluted with ethyl acetate, and the organic layer was washed with water, concentrated, and then purified by column chromatography on SiO₂ (1:1 dichloromethane/hexane) to give **12a'** (274 mg) as a yellowish-white solid in 39% yield. An analytical sample was obtained as a yellowish-white solid through purification by GPC (chloroform, RI detected). **12a'**: mp 169.0-171.0 °C; elemental analyses Found: C, 66.98; H, 4.97; N, 4.48%. Calc. for C₇₀H₆₂N₄O₄F₁₂: C, 67.19; H, 4.99; N, 4.48%; IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 3064, 2961, 2934, 2874, 2210, 1698, 1510, 1210, 1150; ¹H NMR δ_{H} (400 MHz; CDCl₃; Me₄Si)/ppm 7.53 (8H, d, *J* = 8.4 Hz), 7.21 (4H, d, *J* = 8.0 Hz), 7.19 (8H, d, *J* = 8.4 Hz), 7.00 (2H, t, *J* = 8.0 Hz), 3.76 (8H, t, *J* = 7.6 Hz), 3.74 (4H, s), 1.57 (8H, quin, *J* = 7.6 Hz), 1.36 (8H, sext, *J* = 7.6 Hz), 0.93 (12H, t, *J* = 7.6 Hz); ¹³C NMR δ_{C} (100 MHz; CDCl₃)/ppm 156.4 (C(=O)CF₃), 144.9, 138.7, 132.6, 132.4, 128.3, 126.0, 124.3, 123.5, 116.4 (CF₃), 91.5, 89.6, 51.6, 32.7, 28.9, 19.8, 13.7; FD-LRMS *m/z* 1250.53 (M⁺, 100%), 1251.53 ([M+1]⁺, 79), 1252.53 ([M+2]⁺, 33), 1253.54 ([M+3]⁺, 9).

Preparation of **2a** [X = *n*Bu]

To an ice-cooled solution of **12a'** (178 mg, 0.142 mmol) in THF (5.6 mL) were added 60% NaH in oil (248 mg, 6.20 mmol) and MeOH (5.6 mL), and the mixture was stirred at room temperature for 20 min, and then diluted with dichloromethane. The organic layer was washed with water, concentrated, and then purified by column chromatography on Al₂O₃ (hexane-dichloromethane) to give tetraaniline **12a** (118 mg) as a yellow solid in 96% yield, which was immediately subjected to the next reaction.

To a solution of **12a** (118 mg, 0.136 mmol) in toluene (26 mL) and THF (26 mL) containing Et₃N (0.38 mL, 2.7 mmol) was added at 80 °C terephthaloyl chloride (62 mg, 0.31 mmol), and the mixture was stirred at that temperature for 75 min. The reaction mixture was diluted with chloroform and water. The organic layer was separated, concentrated, and purified by column chromatography on SiO₂ (1:1 ethyl acetate/chloroform), followed by GPC (chloroform, RI detected) to give **2a** (96 mg) as a white solid in 63% yield. An analytical sample was suspended in refluxed EtOH, and collected as a white solid through filtration. **2a**: mp >300 °C; elemental analyses Found: C, 82.93; H, 6.26; N, 4.95%. Calc. for C₇₈H₇₀N₄O₄: C, 83.10; H, 6.26; N, 4.97%; UV λ_{max}(CH₂Cl₂)/nm 315sh (log ε 4.98) and 299 (5.08); IR (KBr) ν_{max}/cm⁻¹ 3061, 2957, 2930, 2870, 2208, 1656, 1509; ¹H NMR δ_H(400 MHz; CDCl₃; Me₄Si)/ppm 7.55 (4H, d, *J* = 7.6 Hz), 7.39 (8H, d, *J* = 8.0 Hz), 7.22 (2H, t, *J* = 7.6 Hz), 7.01 (8H, s), 6.81 (8H, d, *J* = 8.0 Hz), 3.85 (8H, br t), 3.78 (4H, br s), 1.53 (8H, quin, *J* = 7.6 Hz), 1.33 (8H, sext, *J* = 7.6 Hz), 0.88 (12H, t, *J* = 7.6 Hz); ¹³C NMR δ_C(100 MHz; CDCl₃)/ppm 169.8, 144.3, 142.8, 137.3, 133.5, 132.2, 128.2, 127.4, 126.2, 123.6, 121.6, 92.5, 89.6, 49.3, 32.4, 29.7, 20.1, 13.8; FD-LRMS *m/z* 1126.58 (M⁺, 100%), 1127.59 ([M+1]⁺, 91), 1128.59 ([M+2]⁺, 42), 1129.60 ([M+3]⁺, 14).

Preparation of **12b'** (TFA-protected) [X = (*R*)-CHMe(cHex)]

To a solution of **9** (365 mg, 1.31 mmol) and (*R*)-**14b** (2.68 g, 6.30 mmol) in Et₃N (52 mL) and THF (52 mL) were added Pd(PPh₃)₄ (422 mg, 0.365 mmol) and CuI (138 mg, 0.724 mmol) at 60 °C under an argon atmosphere, and the mixture was stirred at that temperature for 9 hours. The reaction mixture was diluted with ethyl acetate, and the organic layer was washed with water, concentrated, and then purified by column chromatography on SiO₂ (1:1 dichloromethane/hexane-dichloromethane) to give **12b'** (1.57 g) as a yellowish-white amorphous solid in 82% yield. An analytical sample was obtained as a yellowish-white solid through purification by GPC (chloroform, RI detected). **12b'**: mp 112.0-114.0 °C; [α]_D²⁶ -37.4 (*c* 1.00 in CHCl₃); elemental analyses Found: C, 69.40; H, 5.82; N, 3.66%. Calc. for C₈₆H₈₆N₄O₄F₁₂·(H₂O): C, 69.53; H, 5.97; N, 3.77%; IR (KBr) ν_{max}/cm⁻¹ 3063, 2931, 2853, 2209, 1695, 1508, 1208, 1188, 1148; ¹H NMR δ_H(400 MHz; CDCl₃; Me₄Si)/ppm 7.52 (8H, d, *J* = 7.2 Hz), 7.21 (4H, d, *J* = 7.6 Hz), 7.16 (8H, br d), 7.01 (2H, t, *J* = 7.6 Hz), 4.44 (4H, dq, *J* = 6.8, 10 Hz), 3.76 (4H, s), 1.99 (4H, br d), 1.87-1.57 (16H, m), 1.52-1.36 (4H, m), 1.32-0.91 (20H, m), 1.13 (12H, d, *J* = 6.8 Hz); ¹³C NMR δ_C(100 MHz; CDCl₃)/ppm 156.8 (C(=O)CF₃), 144.9, 135.8, 132.6, 131.9, 131.7, 130.6, 129.3, 126.0, 124.4, 123.5, 116.5 (CF₃), 91.5, 89.7, 59.8, 40.3, 32.7, 30.7, 29.7, 26.1, 25.9, 25.8, 16.4; FD-LRMS *m/z* 1466.84 (M⁺, 100%), 1467.85 ([M+1]⁺, 97), 1468.84 ([M+2]⁺, 53), 1469.85 ([M+3]⁺, 19); FD-HRMS Found: 1466.64672. Calc. for C₈₆H₈₆N₄O₄F₁₂: 1466.64574.

Preparation of (*R,R,R,R*)-**2b** [X = (*R*)-CHMe(cHex)]

To an ice-cooled solution of **12b'** (401 mg, 0.273 mmol) in THF (11 mL) were added 60% NaH in oil (440 mg, 11.0 mmol) and MeOH (11 mL), and the mixture was stirred at room temperature for 40 min, and then diluted with dichloromethane. The organic layer was washed with water, concentrated, and then purified by column chromatography on Al₂O₃ (hexane-1:5 ethyl acetate/hexane) to give tetraaniline **12b** (209 mg) as a white amorphous solid in 71% yield, which was immediately subjected to the next reaction.

To a solution of **12b** (209 mg, 0.193 mmol) in toluene (37 mL) and THF (37 mL) containing Et₃N (0.55 mL, 4.0 mmol) was added at 80 °C terephthaloyl chloride (418 mg, 2.06 mmol), and the mixture was stirred at that temperature for 3.5 hours. The reaction mixture was diluted with chloroform and water. The organic layer was separated, concentrated, and purified by column chromatography on Al₂O₃ (1:5 ethyl acetate/hexane-ethyl acetate), followed by GPC (chloroform, RI detected) to give (*R,R,R,R*)-**2b** (102 mg) as a white solid in 39% yield. An analytical sample was suspended in refluxed EtOH, and collected as a white solid through filtration. (*R,R,R,R*)-**2b**: mp >300 °C; [α]_D²⁶ -393 (*c* 1.00 in CHCl₃); elemental analyses Found: C, 82.83; H, 6.84; N, 4.10%. Calc. for C₉₄H₉₄N₄O₄·(H₂O): C, 82.91; H, 7.11; N, 4.11%; UV λ_{\max} (CH₂Cl₂)/nm 317sh (log ϵ 5.02) and 299 (5.11); CD λ (CH₂Cl₂)/nm 321 ($\Delta\epsilon$ -111.9), 314 (-58.4), 312 (-57.6), 295 (+25.5), 294 (+25.2), 289 (+29.7), 275 (+4.1), 274 (+4.2) and 258 (-61.9); IR (KBr) ν_{\max} /cm⁻¹ 3063, 2927, 2851, 2203, 1656, 1508; ¹H NMR δ_{H} (400 MHz; CDCl₃; Me₄Si)/ppm (303 K) 7.56 (4H, d, *J* = 8.0 Hz), 7.39 (8H, d, *J* = 8.8 Hz), 7.24 (2H, t, *J* = 8.0 Hz), 6.95 (8H, s), 6.77 (8H, br s), 4.55-4.46 (4H, m), 2.10 (4H, br d), 1.84-1.48 (20H, br m), 1.31-0.91 (32H, br m); ¹³C NMR δ_{C} (100 MHz; CDCl₃)/ppm 170.5, 144.6, 140.8, 138.0, 133.7, 131.9, 129.9, 127.1, 126.2, 123.5, 121.7, 92.8, 89.9, 57.6, 41.4, 32.6, 30.8, 30.2, 26.2, 26.0, 26.0, 16.8; FD-LRMS *m/z* 1342.90 (M⁺, 91%), 1343.90 ([M+1]⁺, 100), 1344.91 ([M+2]⁺, 58), 1345.91 ([M+3]⁺, 22), 1346.91 ([M+4]⁺, 7); FD-HRMS Found: 1342.72602. Calc. for C₉₄H₉₄N₄O₄: 1342.72750.

Preparation of **20**

To a solution of **18**⁴ (790 mg, 1.53 mmol), P(*t*Bu)₃ (1 mL of 5.0 mmol/10 mL toluene solution), PdCl₂(PhCN)₂ (138 mg, 0.360 mmol), and CuI (69 mg, 0.36 mmol) in THF (12 mL) and *i*Pr₂NH (4 mL) was added TMSA (3.3 mL, 23 mmol) at room temperature under an argon atmosphere, and the mixture was stirred for 3 hours, followed by addition of TMSA (1.1 mL, 7.8 mmol) and stirring for additional 1 hour. To the reaction mixture were added aq. HCl and chloroform, and the organic layer was separated, concentrated, and purified by column chromatography on SiO₂ (hexane-dichloromethane) to give **20** (787 mg) as a brownish-white solid in 88% yield. An analytical sample was obtained as a white solid through purification by GPC (chloroform, RI detected). **20**: mp 148.0-149.0 °C; elemental analyses Found: C, 73.57; H, 7.17%. Calc. for C₃₆H₄₂Si₄: C, 73.65; H, 7.21%; IR (KBr) ν_{\max} /cm⁻¹ 3065, 2959, 2898, 2155, 1556, 1455,

1250, 979, 841; $^1\text{H NMR}$ δ_{H} (400 MHz; CDCl_3 ; Me_4Si)/ppm 7.40 (4H, d, $J = 8.0$ Hz), 7.20 (2H, t, $J = 8.0$ Hz), 0.28 (36H, s); $^{13}\text{C NMR}$ δ_{C} (100 MHz; CDCl_3)/ppm 131.6, 128.0, 128.0, 127.1, 102.5, 100.1, 81.9, 80.6, 0.0; FD-LRMS m/z 586.24 (M^+ , 100%), 587.24 ($[\text{M}+1]^+$, 59), 588.24 ($[\text{M}+2]^+$, 30), 589.24 ($[\text{M}+3]^+$, 10).

Preparation of **13a'** (TFA-protected) [$\text{X} = n\text{Bu}$]

A mixture of **20** (837 mg, 1.43 mmol), K_2CO_3 (789 mg, 5.71 mmol), MeOH (29 mL), and THF (29 mL) was stirred at room temperature for 1.5 hour, and diluted with ethyl acetate and water. The organic layer was separated, concentrated, and purified by column chromatography on Al_2O_3 (hexane-1:1 dichloromethane/hexane) to give **10** (412 mg) as a brownish-white solid in 97%, which was subjected to the next reactions without further purification.

To a solution of **10** (220 mg, 0.738 mmol) and **14a** (1.24 g, 3.34 mmol) in Et_2NH (25 mL) and CH_3CN (120 mL) were added $\text{Pd}(\text{PPh}_3)_4$ (54 mg, 0.047 mmol) and CuI (16 mg, 0.084 mmol) at 80°C under an argon atmosphere, and the mixture was stirred at that temperature for 8 hours. The reaction mixture was diluted with ethyl acetate, and the organic layer was washed with water, concentrated, and then purified by column chromatography on SiO_2 (1:1 dichloromethane/hexane-dichloromethane) to give **13a'** (714 mg) as an orange amorphous solid in 75% yield. An analytical sample was obtained as an orange solid through purification by GPC (chloroform, RI detected). **13a'**: mp $69\text{--}71^\circ\text{C}$; elemental analyses Found: C, 67.40; H, 4.68; N, 4.32%. Calc. for $\text{C}_{72}\text{H}_{58}\text{N}_4\text{O}_4\text{F}_{12}\cdot(\text{EtOH})$: C, 67.47; H, 4.90; N, 4.25%; IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ 3059, 2961, 2936, 2874, 2214, 1698, 1510, 1209, 1150; $^1\text{H NMR}$ δ_{H} (400 MHz; CDCl_3 ; Me_4Si)/ppm 7.62 (8H, d, $J = 8.4$ Hz), 7.58 (4H, d, $J = 7.6$ Hz), 7.42 (2H, t, $J = 7.6$ Hz), 7.10 (8H, d, $J = 8.4$ Hz), 3.63 (8H, t, $J = 7.2$ Hz), 1.46 (8H, quin, $J = 7.2$ Hz), 1.27 (8H, sext, $J = 7.2$ Hz), 0.87 (12H, t, $J = 7.2$ Hz); $^{13}\text{C NMR}$ δ_{C} (100 MHz; CDCl_3)/ppm 156.4 ($\text{C}(\text{=O})\text{CF}_3$), 139.2, 132.8, 131.4, 129.0, 128.3, 127.3, 127.1, 123.4, 116.2 (CF_3), 93.6, 88.9, 82.0, 81.9, 51.5, 28.8, 19.7, 13.6; FD-LRMS m/z 1270.56 (M^+ , 100%), 1271.56 ($[\text{M}+1]^+$, 85), 1272.56 ($[\text{M}+2]^+$, 39), 1273.56 ($[\text{M}+3]^+$, 12); FD-HRMS Found: 1270.42487. Calc. for $\text{C}_{72}\text{H}_{58}\text{N}_4\text{O}_4\text{F}_{12}$: 1270.42664.

Preparation of **3a** [$\text{X} = n\text{Bu}$]

To an ice-cooled solution of **13a'** (355 mg, 0.276 mmol) in THF (11 mL) were added 60% NaH in oil (883 mg, 22.1 mmol) and MeOH (11 mL), and the mixture was stirred at room temperature for 35 min, and then diluted with dichloromethane. The organic layer was washed with water, concentrated, and then purified by column chromatography on Al_2O_3 (1:1 dichloromethane/hexane) to give tetraaniline **13a** (239 mg) as a yellowish-white amorphous solid in 98% yield, which was immediately subjected to the next reaction.

To a solution of **13a** (239 mg, 0.269 mmol) in toluene (52 mL) and THF (52 mL)

containing Et₃N (0.75 mL, 5.4 mmol) was added at 80 °C terephthaloyl chloride in two portions (120 mg, 0.591 mmol and 62 mg, 0.31 mmol) over a period of 2.5 hours. The reaction mixture was diluted with chloroform and water. The organic layer was separated, concentrated, and purified by column chromatography on SiO₂ (chloroform-1:1 ethyl acetate chloroform), followed by GPC (chloroform, RI detected) to give **3a** (78 mg) as a white solid in 25% yield. An analytical sample was suspended in refluxed EtOH, and collected as a white solid through filtration. **3a**: mp >300 °C; elemental analyses Found: C, 82.51; H, 5.88; N, 4.76%. Calc. for C₈₀H₆₆N₄O₄·(EtOH): C, 82.52; H, 6.08; N, 4.69%; UV λ_{max}(CH₂Cl₂)/nm 375 (log ε 4.37), 357sh (4.46), 325 (5.08), 310sh (5.00) and 280sh (4.85); IR (KBr) ν_{max}/cm⁻¹ 3055, 2956, 2930, 2870, 2211, 1657, 1510; ¹H NMR δ_H(400 MHz; CDCl₃; Me₄Si)/ppm 7.55 (4H, d, *J* = 8.0 Hz), 7.41 (8H, d, *J* = 8.8 Hz), 7.37 (2H, t, *J* = 8.0 Hz), 7.00 (8H, s), 6.83 (8H, br d), 4.16 (4H, br s), 3.57 (4H, br s), 1.51 (8H, br s), 1.31 (8H, sext, *J* = 7.6 Hz), 0.86 (12H, t, *J* = 7.6 Hz); ¹³C NMR δ_C(100 MHz; CDCl₃)/ppm 169.4, 143.5, 137.2, 132.4, 131.6, 128.7, 128.2, 127.7, 127.2, 125.9, 121.1, 93.6, 88.2, 81.1, 80.7, 49.4, 29.7, 20.1, 13.8; FD-LRMS *m/z* 1146.65 (M⁺, 100%), 1147.65 ([M+1]⁺, 91), 1148.65 ([M+2]⁺, 42), 1149.66 ([M+3]⁺, 14); FD-HRMS Found: 1146.50630. Calc. for C₈₀H₆₆N₄O₄: 1146.50840.

Preparation of **13b'** (TFA-protected) [X = (*R*)-CHMe(cHex)]

To a solution of **10** (192 mg, 0.644 mmol) and (*R*)-**14b** (1.41 g, 3.32 mmol) in Et₂NH (25 mL) and CH₃CN (120 mL) were added Pd(PPh₃)₄ (54 mg, 0.047 mmol) and CuI (16 mg, 0.084 mmol) at 80 °C under an argon atmosphere, and the mixture was stirred at that temperature for 8 hours. The reaction mixture was diluted with ethyl acetate, and the organic layer was washed with water, concentrated, and then purified by column chromatography on SiO₂ (1:1 dichloromethane/hexane-dichloromethane) to give **13b'** (834 mg) as a brownish-white solid in 87% yield. An analytical sample was obtained as a white solid through purification by GPC (chloroform, RI detected). **13b'**: mp 113.0-115.0 °C; [α]_D²⁵ -145 (*c* 1.00 in CHCl₃); elemental analyses Found: C, 70.37; H, 5.54; N, 3.69%. Calc. for C₈₈H₈₂N₄O₄F₁₂·(H₂O): C, 70.20; H, 5.62; N, 3.72%; IR (KBr) ν_{max}/cm⁻¹ 3061, 2931, 2853, 2211, 1698, 1509, 1208, 1188, 1150; ¹H NMR δ_H(400 MHz; CDCl₃; Me₄Si)/ppm 7.64 (4H, br d), 7.56 (4H, br d), 7.56 (4H, d, *J* = 7.6 Hz), 7.42 (2H, t, *J* = 7.6 Hz), 7.07 (8H, br d), 4.33 (4H, dq, *J* = 6.8, 10 Hz), 1.90 (4H, br d), 1.82-1.51 (16H, br m), 1.42-0.88 (24H, m), 0.98 (12H, d, *J* = 6.8 Hz); ¹³C NMR δ_C(100 MHz; CDCl₃)/ppm 156.7 (C(=O)CF₃), 136.3, 132.5, 132.0, 131.3, 130.8, 129.3, 129.0, 127.4, 127.1, 123.6, 116.3 (CF₃), 93.7, 89.1, 82.1, 82.0, 59.8, 40.2, 30.5, 29.7, 26.1, 25.9, 25.7, 16.2; FD-LRMS *m/z* 1486.75 (M⁺, 100%), 1487.75 ([M+1]⁺, 99), 1488.75 ([M+2]⁺, 51), 1489.76 ([M+3]⁺, 19), 1490.76 ([M+4]⁺, 6); FD-HRMS Found: 1486.61481. Calc. for C₈₈H₈₂N₄O₄F₁₂: 1486.61444.

Preparation of (*R,R,R,R*)-**3b** [X = (*R*)-CHMe(cHex)]

To an ice-cooled solution of **13b'** (428 mg, 0.288 mmol) in THF (12 mL) were added 60% NaH in oil (923 mg, 23.1 mmol) and MeOH (12 mL), and the mixture was stirred at room temperature for 40 min, and then diluted with dichloromethane. The organic layer was washed with water, concentrated, and then purified by column chromatography on Al₂O₃ (hexane-2:3 dichloromethane/hexane-dichloromethane) to give tetraaniline **13b** (293 mg) as a yellowish-white solid in 92% yield, which was immediately subjected to the next reaction.

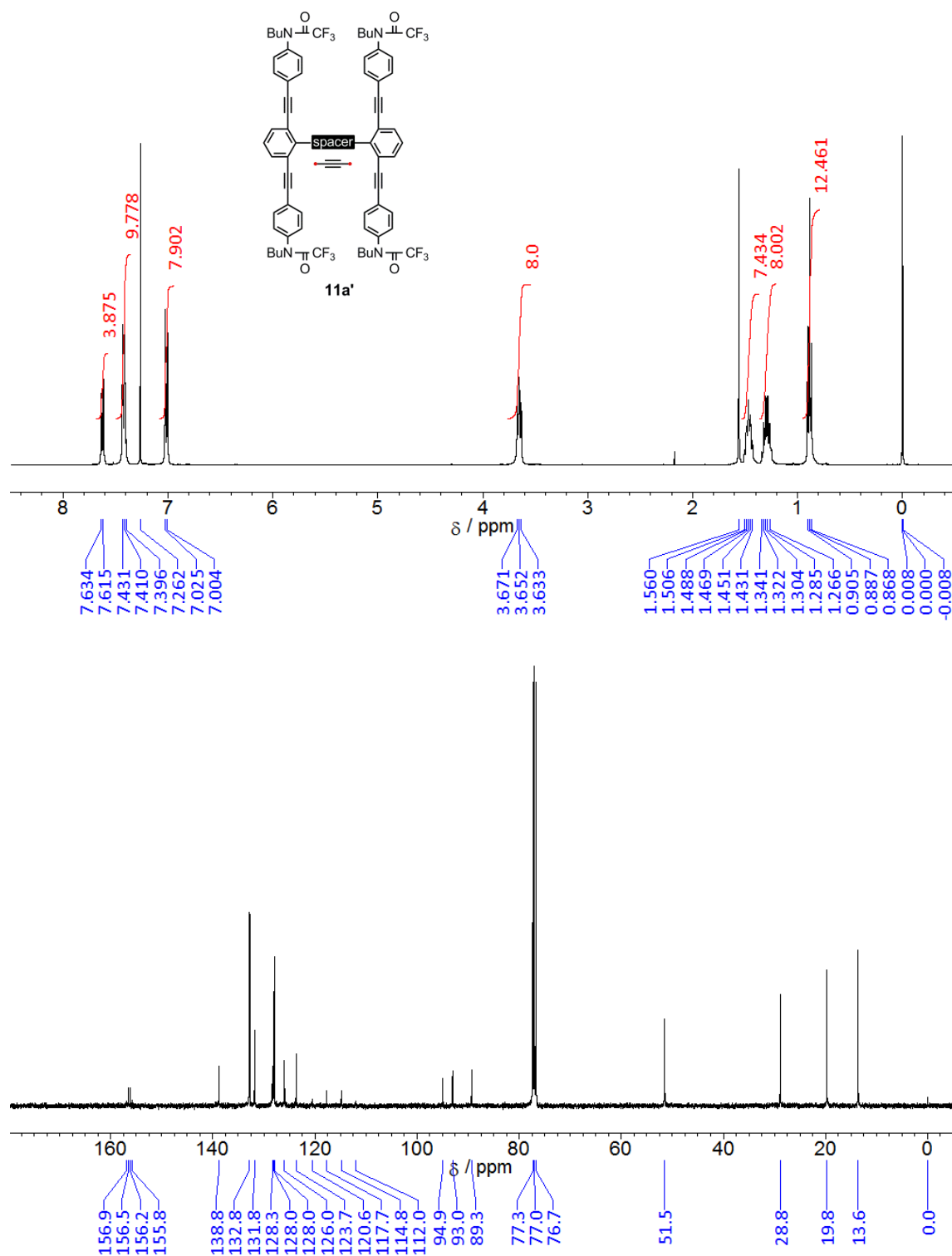
To a solution of **13b** (293 mg, 0.265 mmol) in toluene (51 mL) and THF (51 mL) containing Et₃N (0.74 mL, 5.3 mmol) was added at 80 °C terephthaloyl chloride in three portions (119 mg, 0.586 mmol, 118 mg, 0.581 mmol and 121 mg, 0.596 mmol) over a period of 4 hours, followed by stirring at that temperature for additional 9 hours. The reaction mixture was diluted with chloroform and water. The organic layer was separated, concentrated, and purified by column chromatography on SiO₂ (1:9 ethyl acetate/dichloromethane), followed by GPC (chloroform, RI detected) to give (*R,R,R,R*)-**3b** (136 mg) as a white solid in 38% yield. An analytical sample was suspended in refluxed EtOH, and collected as a white solid through filtration. (*R,R,R,R*)-**3b**: mp >300 °C; [α]_D²⁵ -434 (*c* 1.00 in CHCl₃); elemental analyses Found: C, 83.14; H, 6.57; N, 4.02%. Calc. for C₉₆H₉₀N₄O₄·(H₂O): C, 83.44; H, 6.71; N, 4.05%; UV λ_{\max} (CH₂Cl₂)/nm 375 (log ϵ 4.36), 357sh (4.45), 326 (5.08), 310 (5.00) and 280sh (4.86); CD λ (CH₂Cl₂)/nm 378 ($\Delta\epsilon$ +35.5), 335 (-80.1), 323 (+170.3), 301 (-77.9), 296 (-67.1), 284sh (-99.7) and 271 (-153.8); IR (KBr) ν_{\max} /cm⁻¹ 3051, 2928, 2852, 2209, 1656, 1509; ¹H NMR δ_{H} (400 MHz; CDCl₃)/ppm (323 K) 7.55 (4H, d, *J* = 8.0 Hz), 7.40 (8H, br d), 7.37 (2H, t, *J* = 8.0 Hz), 6.97 (8H, s), 6.80 (8H, br s), 4.52 (4H, br s), 2.10 (4H, br d), 1.84-1.62 (16H, br m), 1.32-0.93 (36H, br m); ¹³C NMR δ_{C} (100 MHz; CDCl₃)/ppm (296 K) [two sets] [169.7, 169.6], 141.8, 137.6, 132.0, 131.5, 128.7, 127.5, 127.2, 126.1, 121.2, 93.6, 88.2, 81.1, 80.9, 57.5, 42.5, 30.4, 26.2, 26.0, 26.0, 16.6; FD-LRMS *m/z* 1252.74 ([M-CHMe(cHex)+1]⁺, 27%), 1253.75 ([M-CHMe(cHex)+2]⁺, 26), 1362.87 (M⁺, 90), 1363.87 ([M+1]⁺, 100), 1364.87 ([M+2]⁺, 55), 1365.87 ([M+3]⁺, 23), 1366.88 ([M+4]⁺, 8); FD-HRMS Found: 1362.69500. Calc. for C₉₆H₉₀N₄O₄: 1362.69620.

Preparation of (*R,R*)-**6**

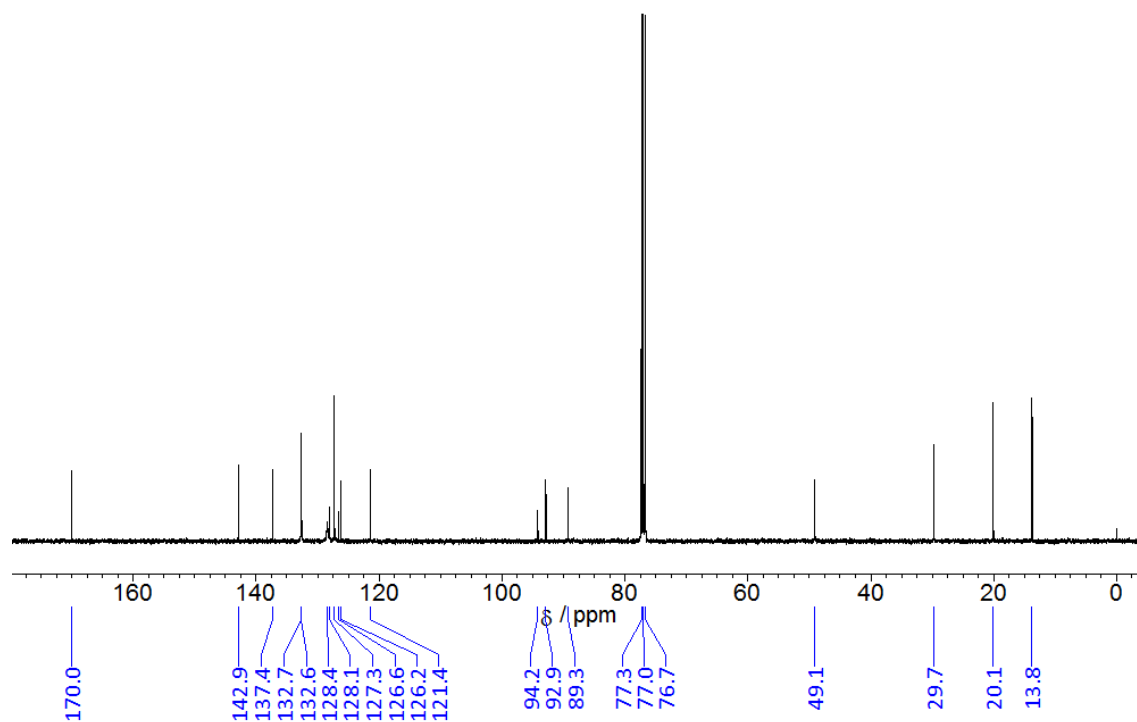
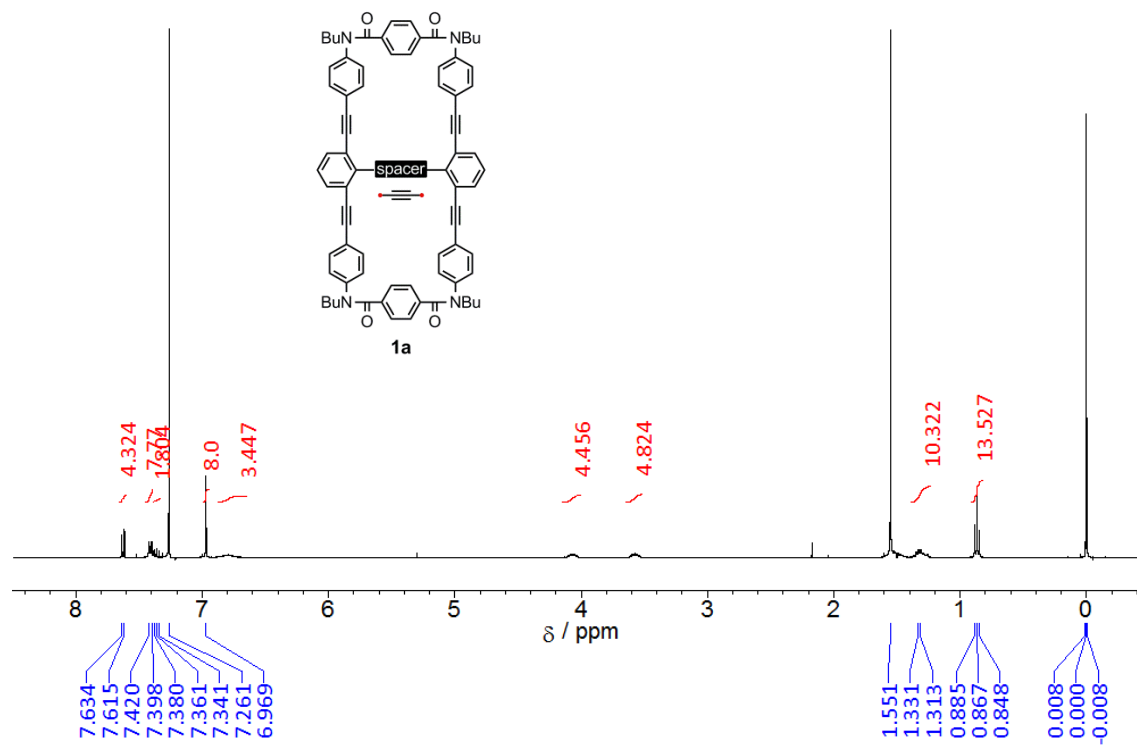
To a solution of **24** (0.32 mL, 2.4 mmol) and (*R*)-**14b** (2.50 g, 5.78 mmol) in Et₃N (48 mL) and THF (48 mL) were added Pd(PPh₃)₄ (387 mg, 0.335 mmol) and CuI (128 mg, 0.672 mmol) at 62 °C under an argon atmosphere, and the mixture was stirred at that temperature for 1.5 hours. The reaction mixture was diluted with ethyl acetate, and the organic layer was washed with water, concentrated, and then purified by column chromatography on SiO₂ (1:2 dichloromethane/hexane) to give (*R,R*)-**6** (1.69 g) as a brownish-white amorphous solid in 95% yield. An analytical sample was obtained as a white amorphous solid through purification by GPC (chloroform, RI detected). (*R,R*)-**6**: mp 107.0-109.5 °C; [α]_D²⁶ -123 (*c* 1.00 in CHCl₃); elemental analyses Found: C, 84.40; H, 7.28;

N, 3.69%. Calc. for C₅₂H₅₂N₂O₂: C, 84.75; H, 7.11; N, 3.80%; UV $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 309 (log ϵ 4.75) and 298 (4.75); CD $\lambda(\text{CH}_2\text{Cl}_2)/\text{nm}$ 310 ($\Delta\epsilon$ -6.4), 308 (-6.1), 294 (-8.1), 278 (-5.9), 276 (-6.3) and 252 (+1.3); IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 3058, 2928, 2850, 2211, 1648, 1509; ¹H NMR $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})/\text{ppm}$ 7.61 (1H, br t), 7.45-7.42 (2H, m), 7.35 (4H, d, $J = 8.4 \text{ Hz}$), 7.30 (1H, dd, $J = 7.6, 8.4 \text{ Hz}$), 7.30-7.23 (4H, m), 7.22-7.10 (6H, m), 6.99 (4H, d, $J = 8.4 \text{ Hz}$), 4.48 (2H, br s), 2.16 (2H, br d), 1.88-1.58 (10H, br m), 1.36-0.93 (10H, br m), 1.21 (6H, d, $J = 6.8 \text{ Hz}$); ¹³C NMR $\delta_{\text{C}}(100 \text{ MHz}; \text{CDCl}_3)/\text{ppm}$ 170.8, 142.1, 137.1, 134.4, 132.0, 131.4, 129.4, 129.2, 128.5, 128.3, 127.7, 123.3, 121.3, 89.3, 89.1, 59.3, 41.5, 30.8, 30.4, 26.3, 26.1, 26.0, 16.8; FD-LRMS m/z 736.50 (M^+ , 100%), 737.51 ($[\text{M}+1]^+$, 63), 738.51 ($[\text{M}+2]^+$, 19); FD-HRMS Found: 736.40464. Calc. for C₅₂H₅₂N₂O₂: 736.40288.

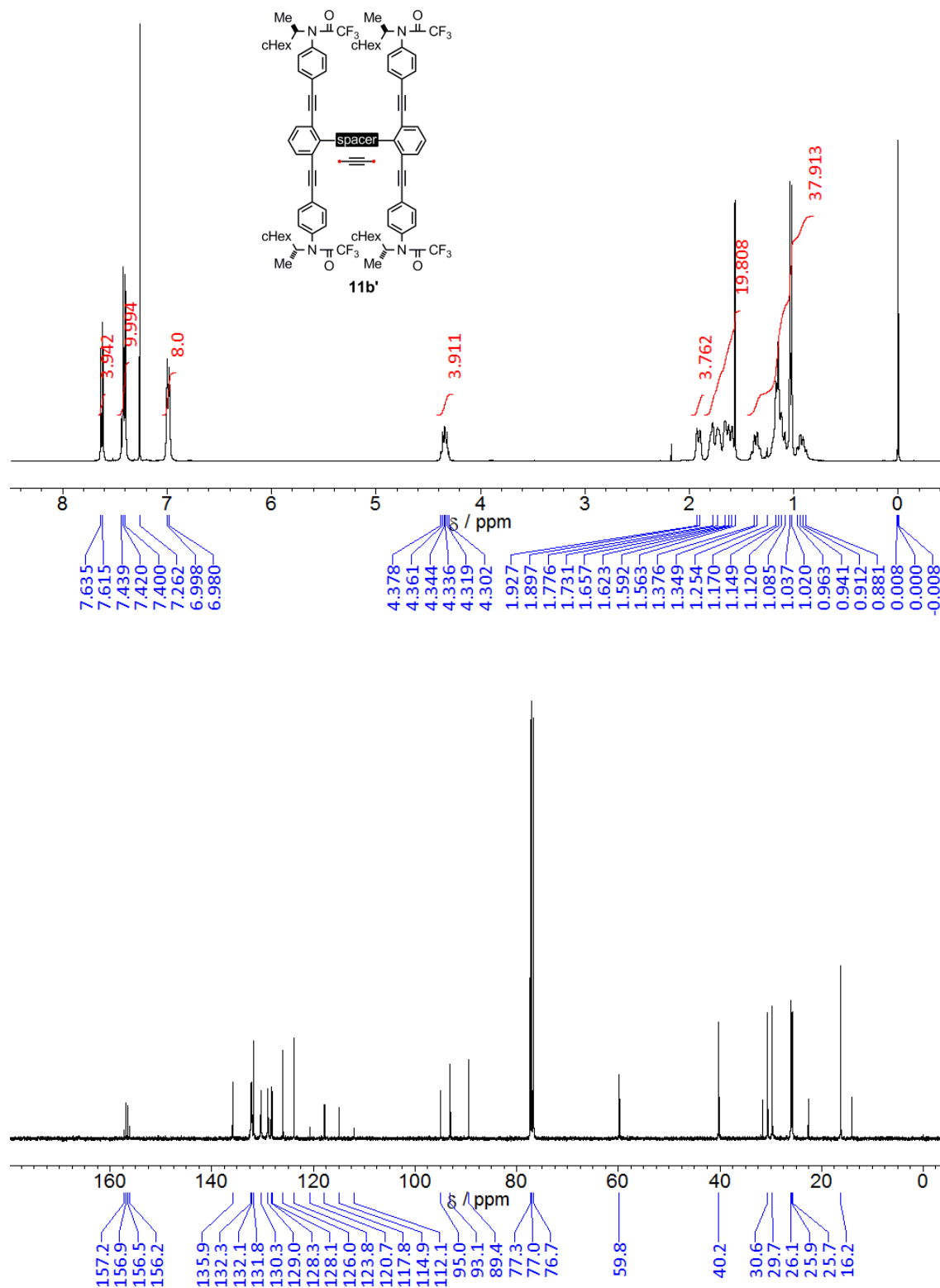
^1H and ^{13}C NMR spectra of new compounds



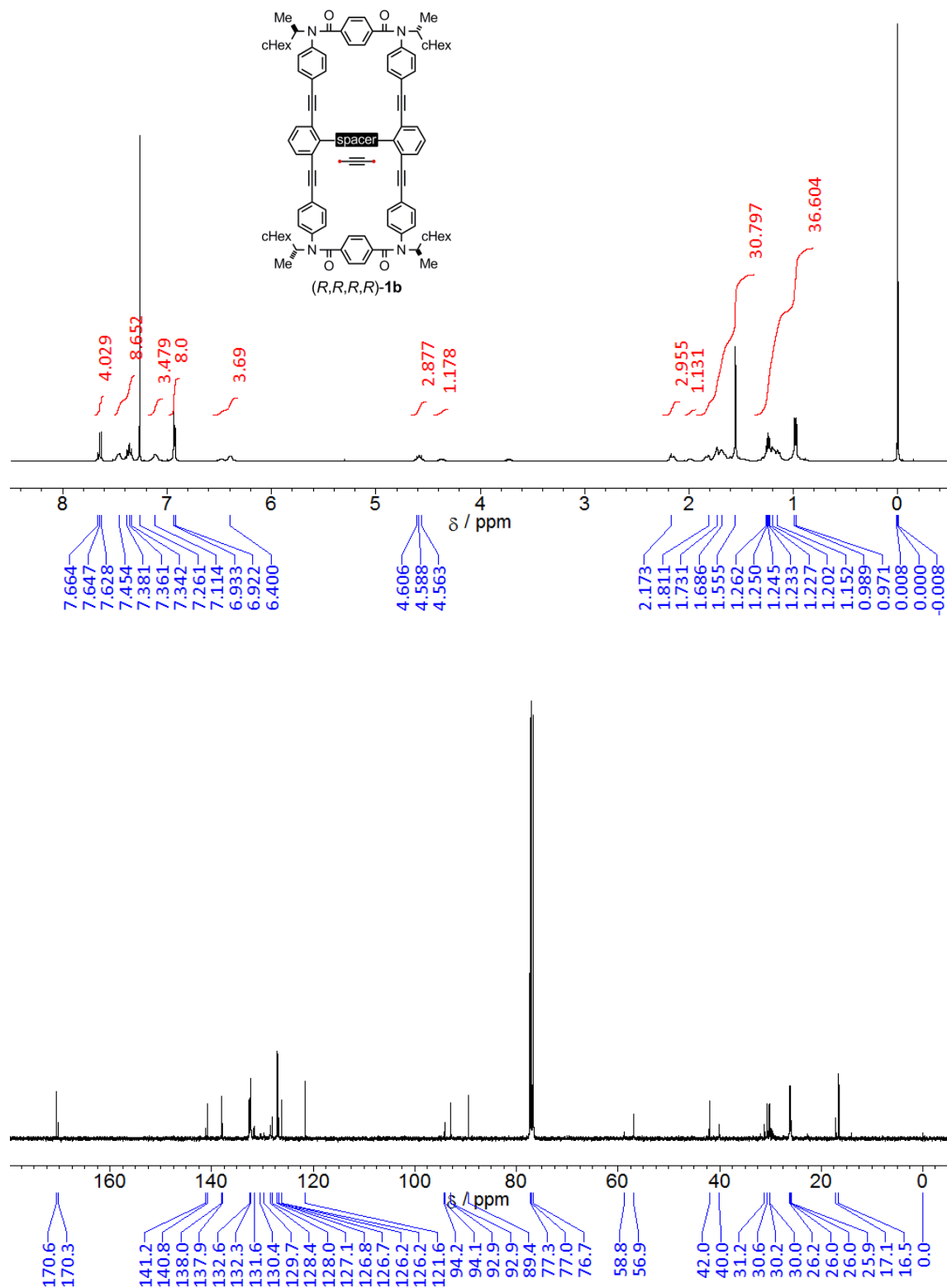
^1H (400 MHz, upper) and ^{13}C (100 MHz, lower) NMR spectra of **11a'**, measured in CDCl_3 at room temperature.



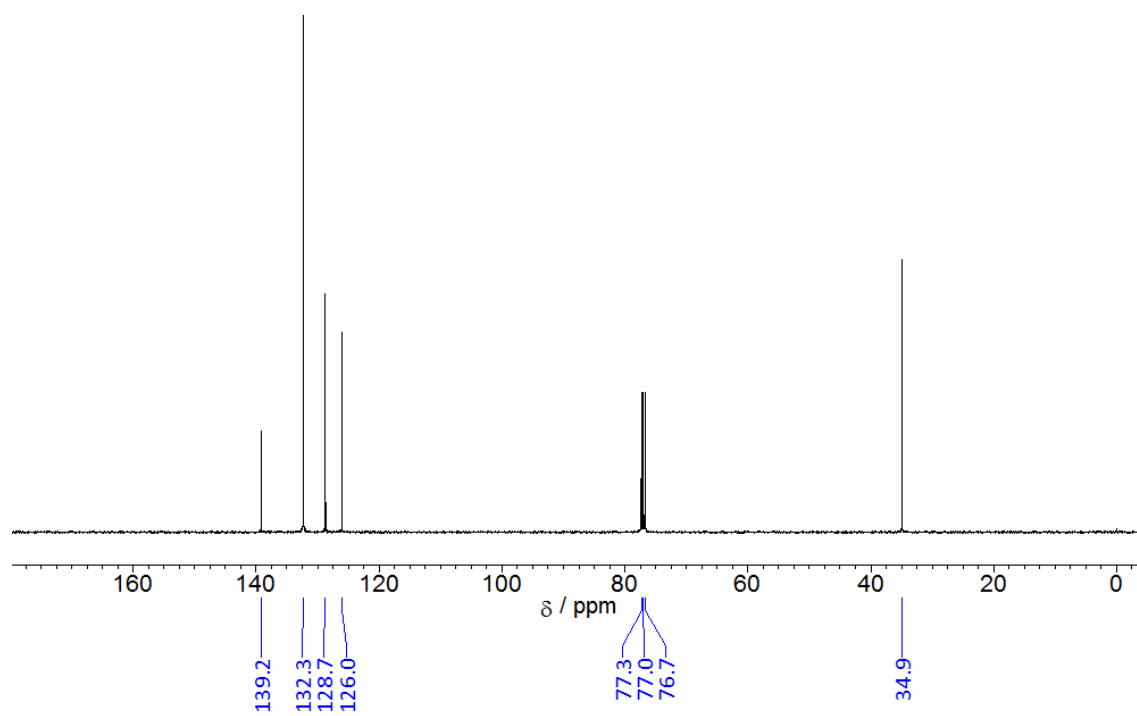
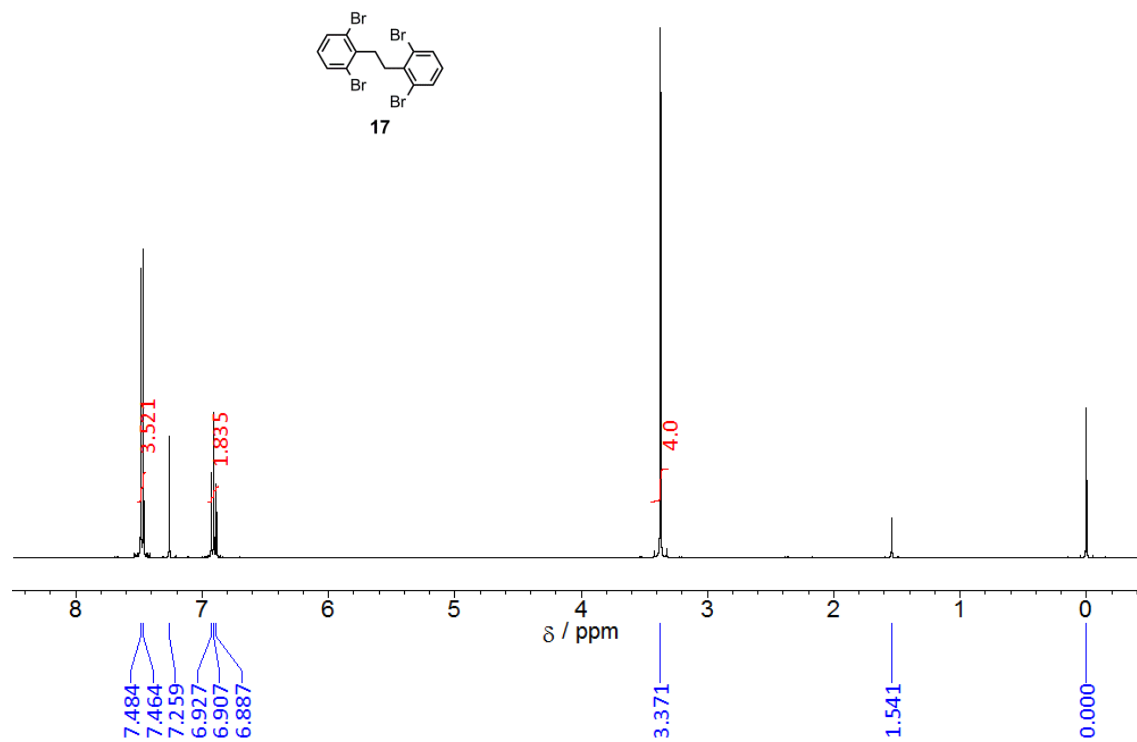
¹H (400 MHz, upper) and ¹³C (100 MHz, lower) NMR spectra of **1a**, measured in CDCl₃ at room temperature.



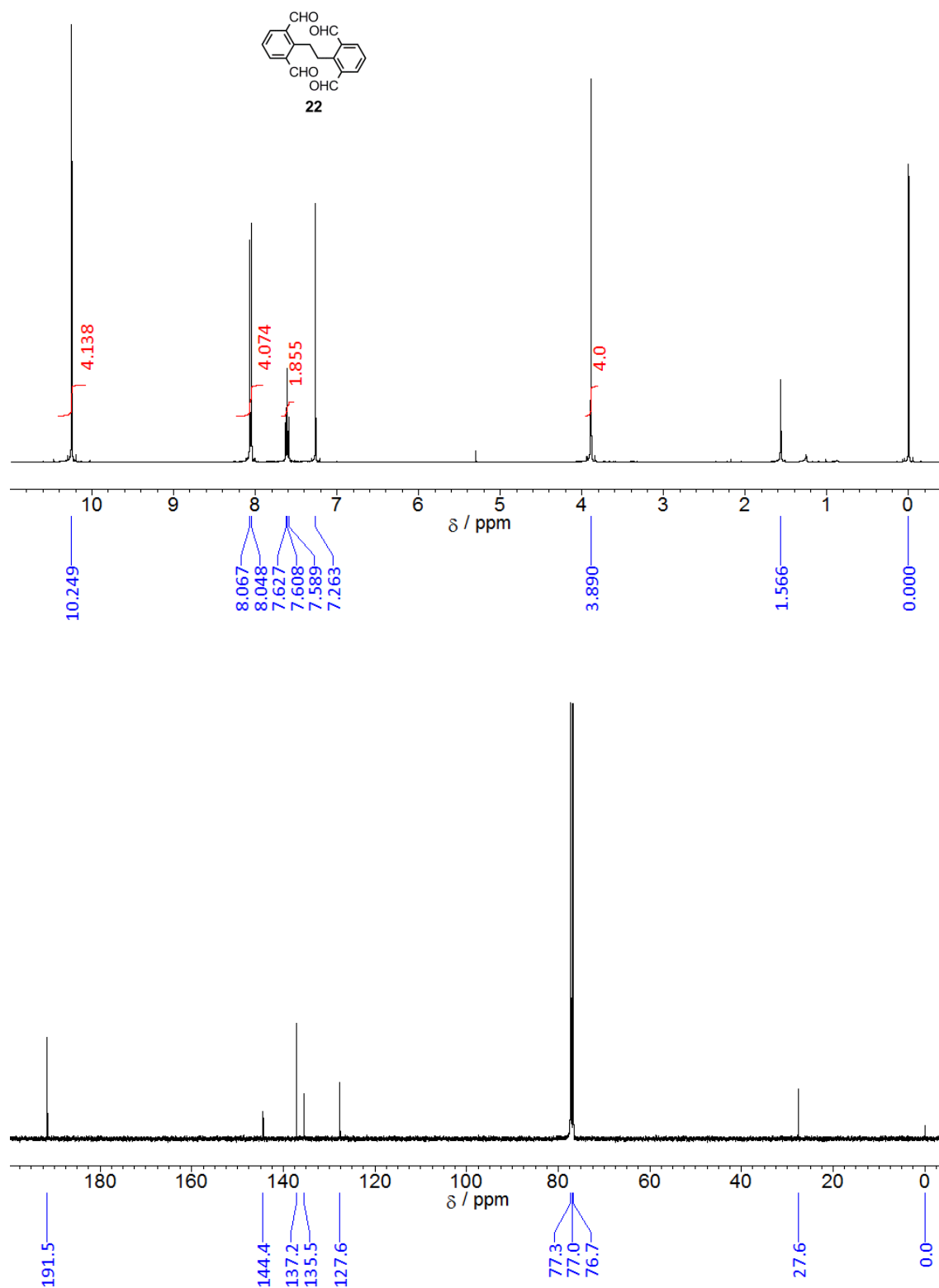
¹H (400 MHz, upper) and ¹³C (100 MHz, lower) NMR spectra of **11b'**, measured in CDCl₃ at room temperature, cont. residual hexane in the latter spectrum.



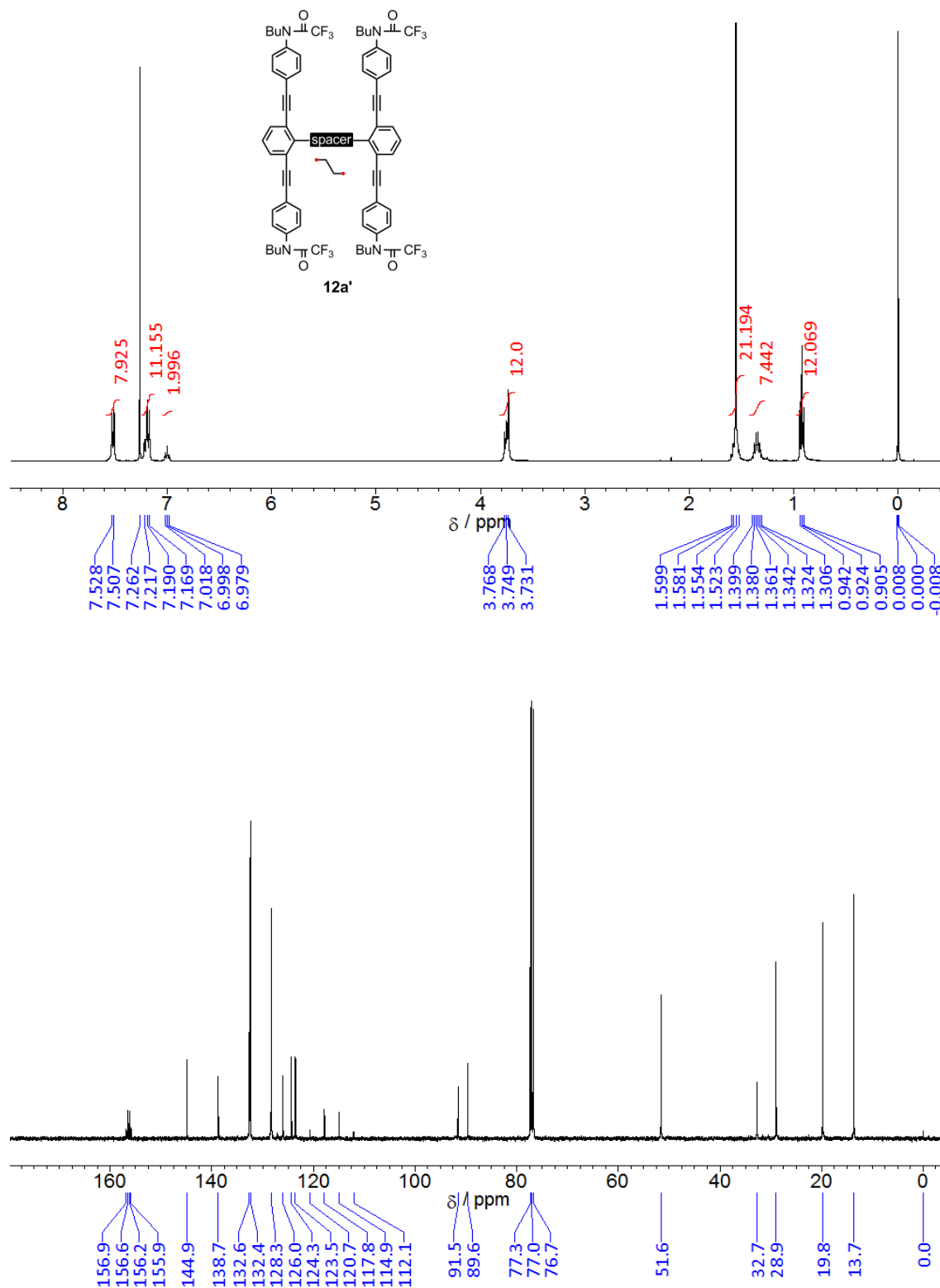
^1H (400 MHz, upper) and ^{13}C (100 MHz, lower) NMR spectra of (R,R,R,R) -**1b**, measured in CDCl_3 at room temperature, cont. residual hexane in the latter spectrum.



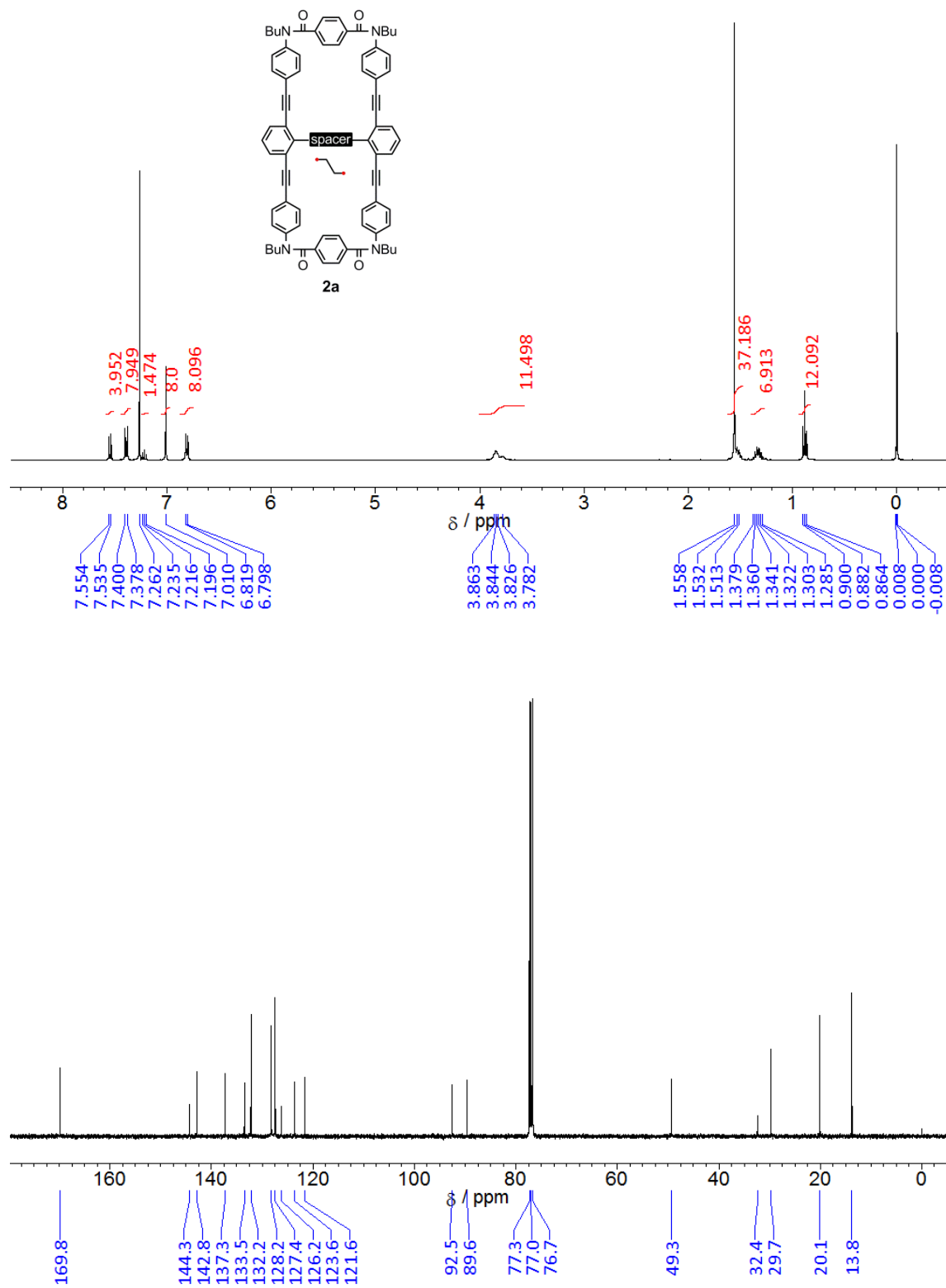
^1H (400 MHz, upper) and ^{13}C (100 MHz, lower) NMR spectra of **17**, measured in CDCl_3 at room temperature.



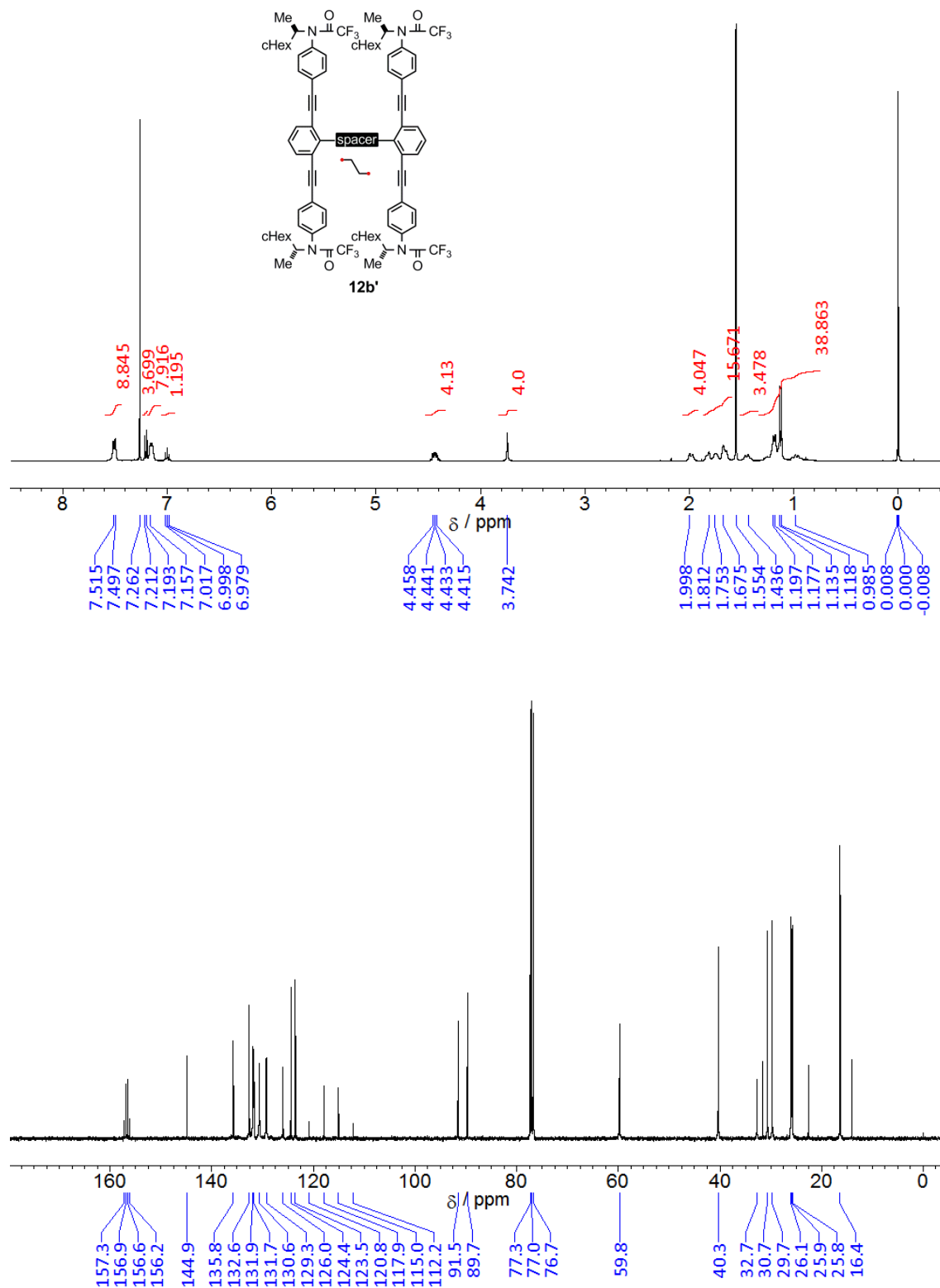
¹H (400 MHz, upper) and ¹³C (100 MHz, lower) NMR spectra of **22**, measured in CDCl₃ at room temperature.



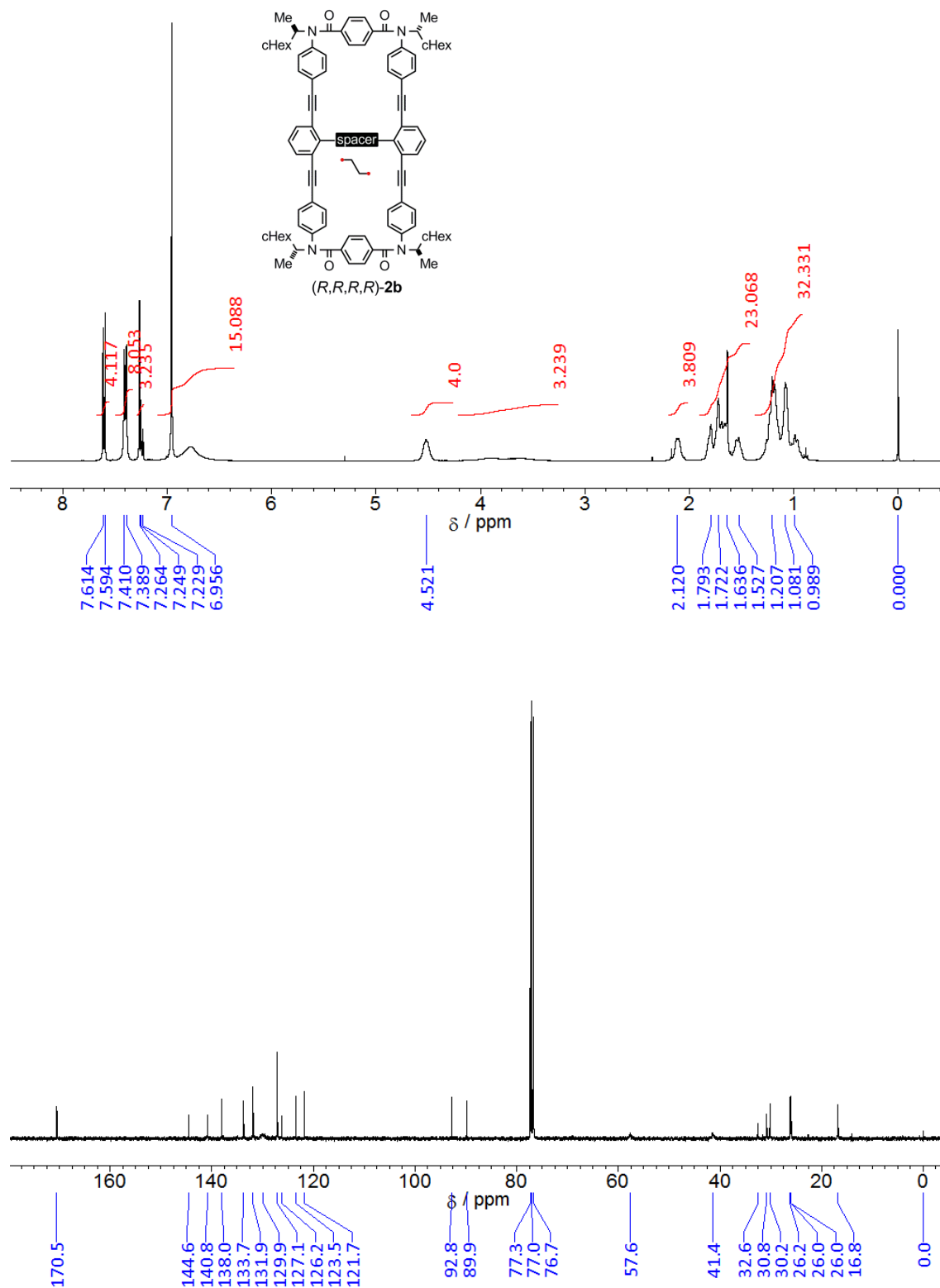
¹H (400 MHz, upper) and ¹³C (100 MHz, lower) NMR spectra of **12a'**, measured in CDCl₃ at room temperature.

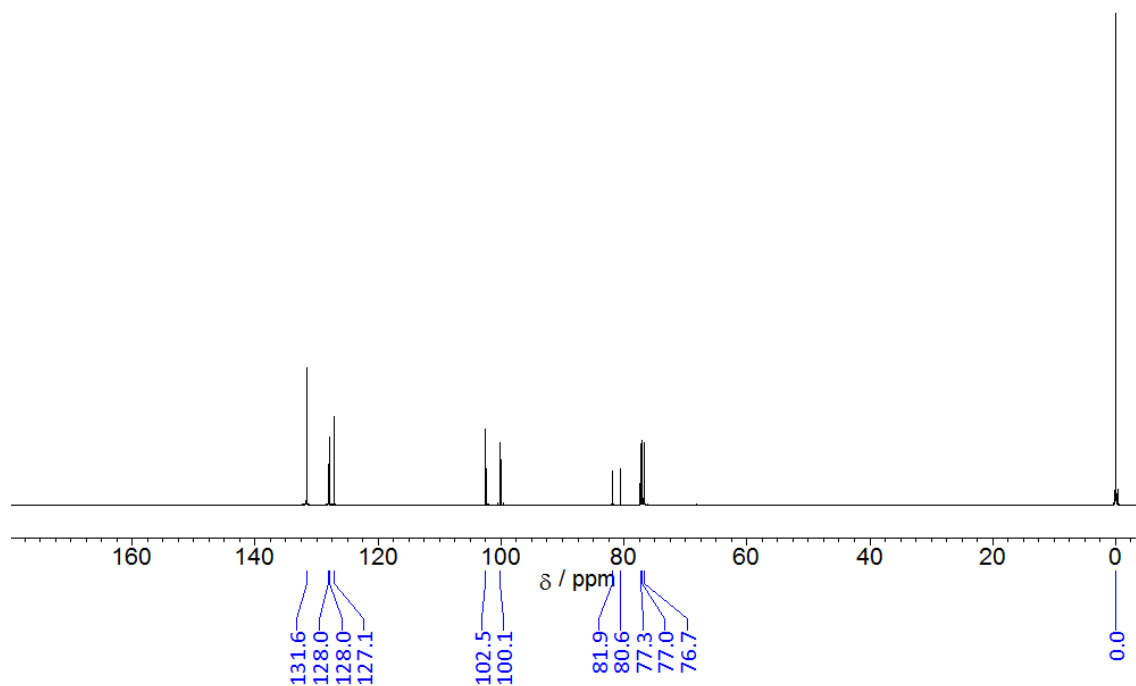
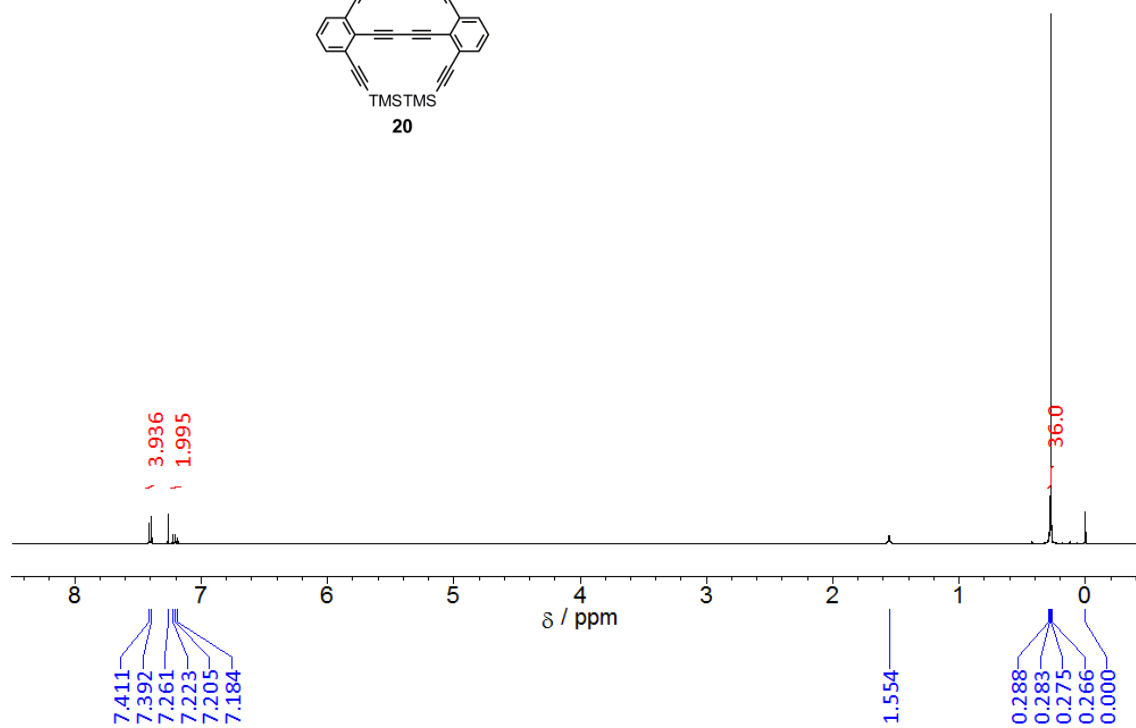
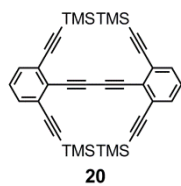


¹H (400 MHz, upper) and ¹³C (100 MHz, lower) NMR spectra of **2a**, measured in CDCl₃ at room temperature.

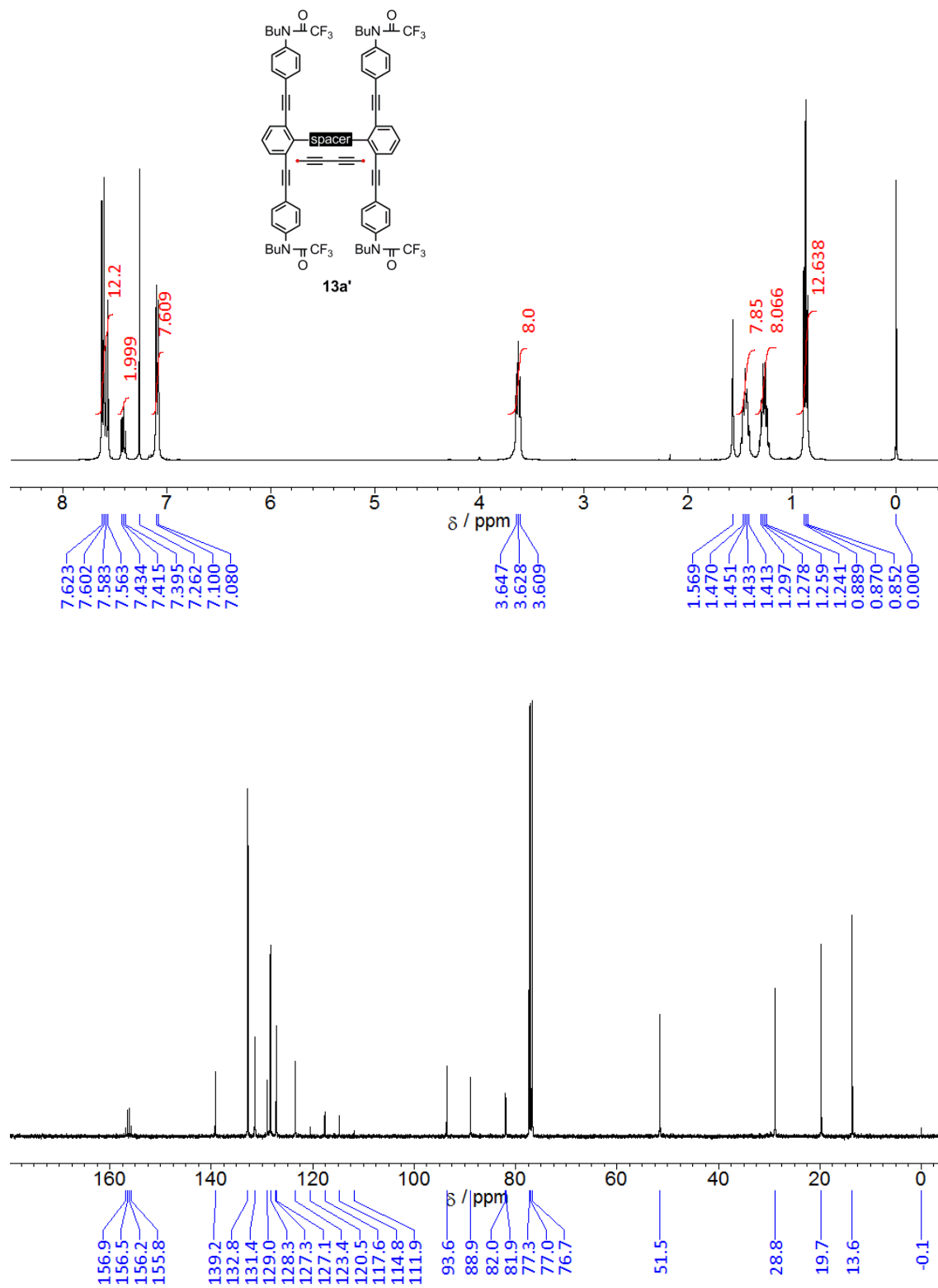


¹H (400 MHz, upper) and ¹³C (100 MHz, lower) NMR spectra of **12b'**, measured in CDCl₃ at room temperature, cont. residual hexane in the latter spectrum.

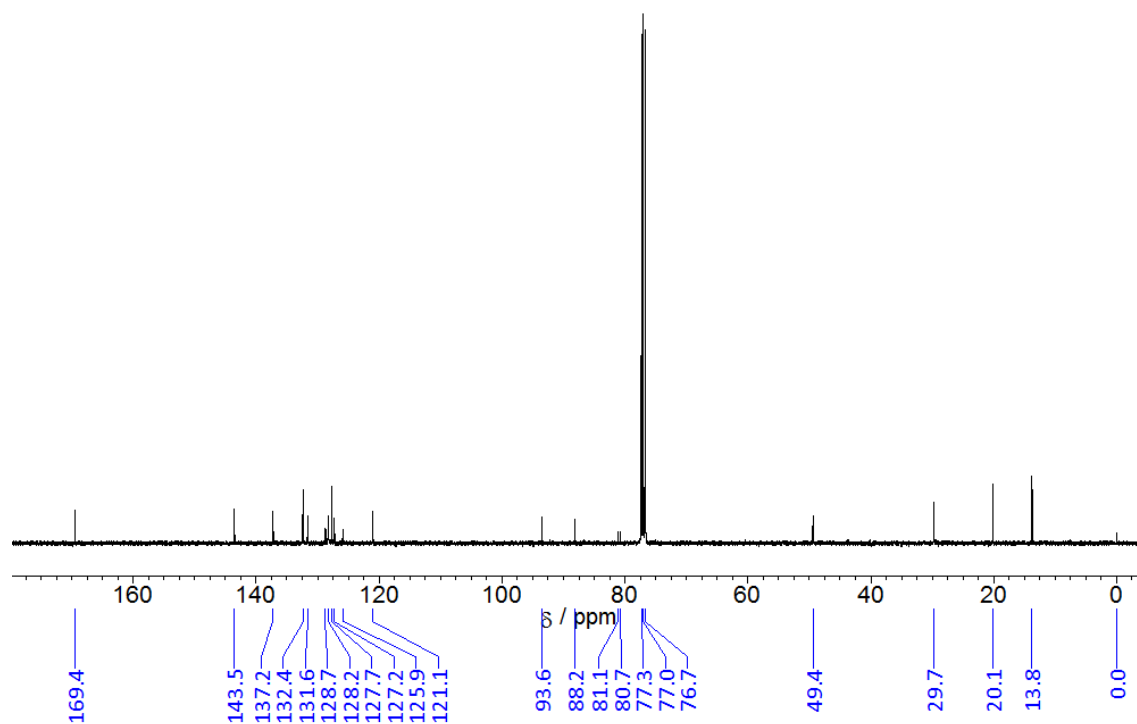
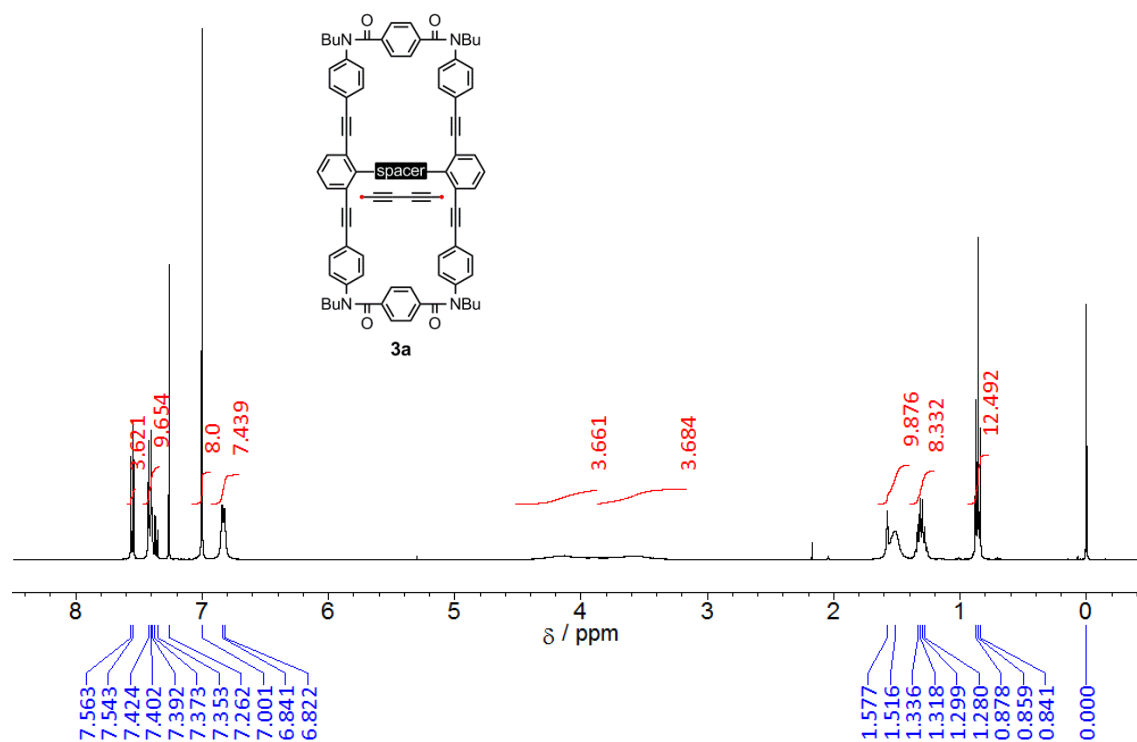




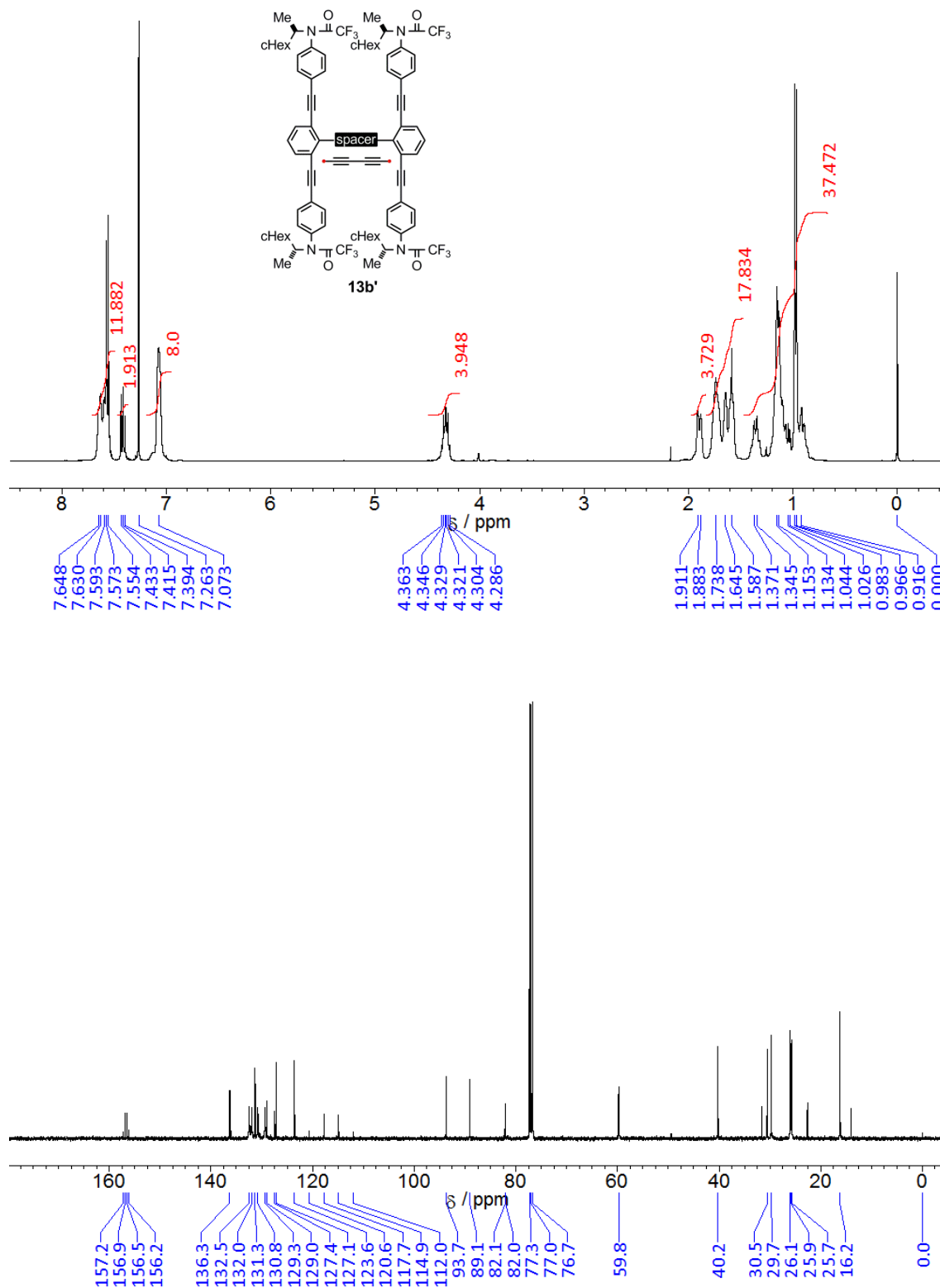
^1H (400 MHz, upper) and ^{13}C (100 MHz, lower) NMR spectra of **20**, measured in CDCl_3 at room temperature.



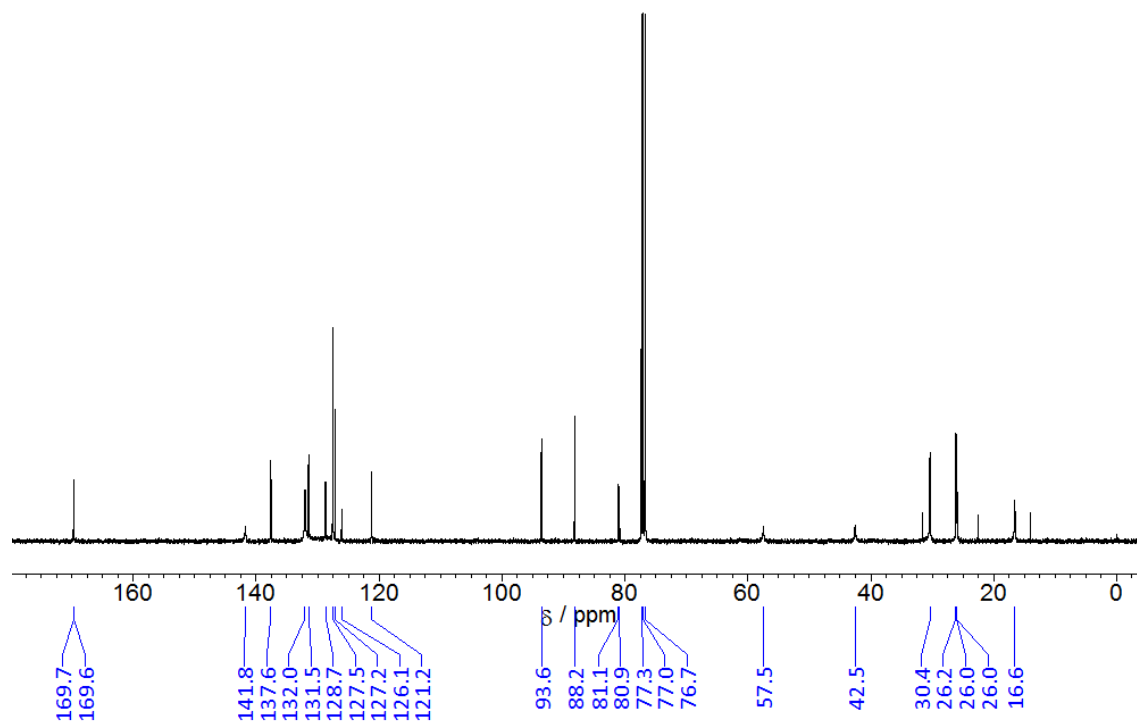
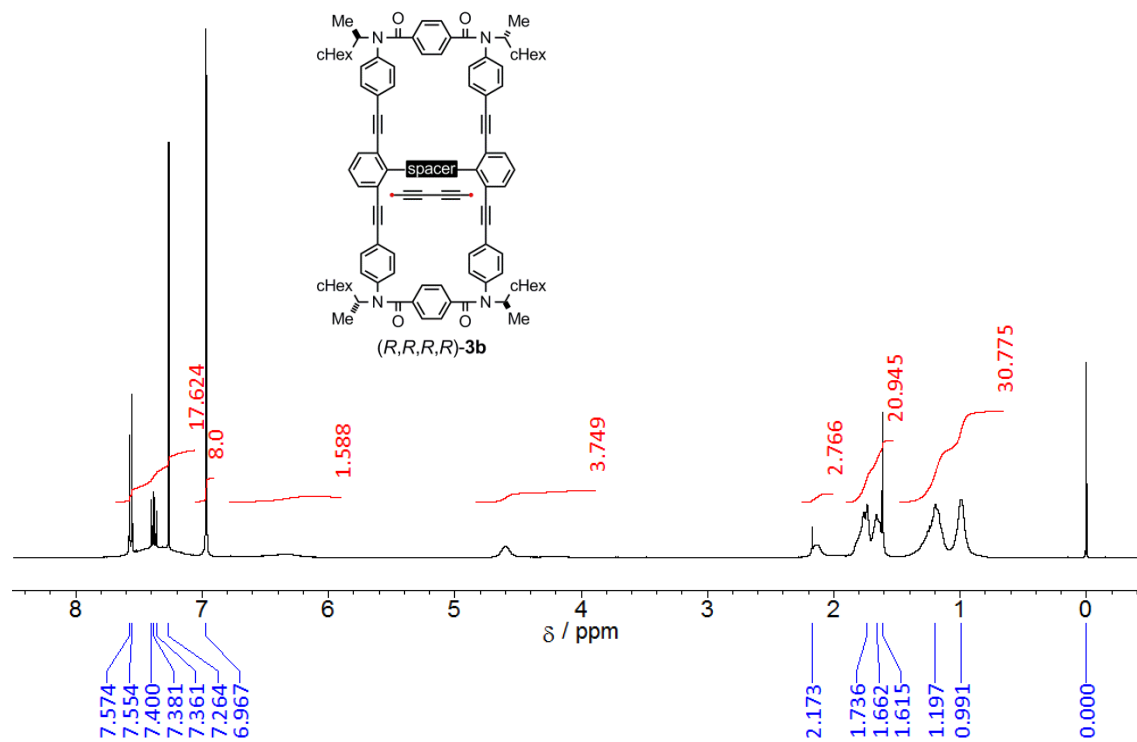
¹H (400 MHz, upper) and ¹³C (100 MHz, lower) NMR spectra of **13a'**, measured in CDCl₃ at room temperature.



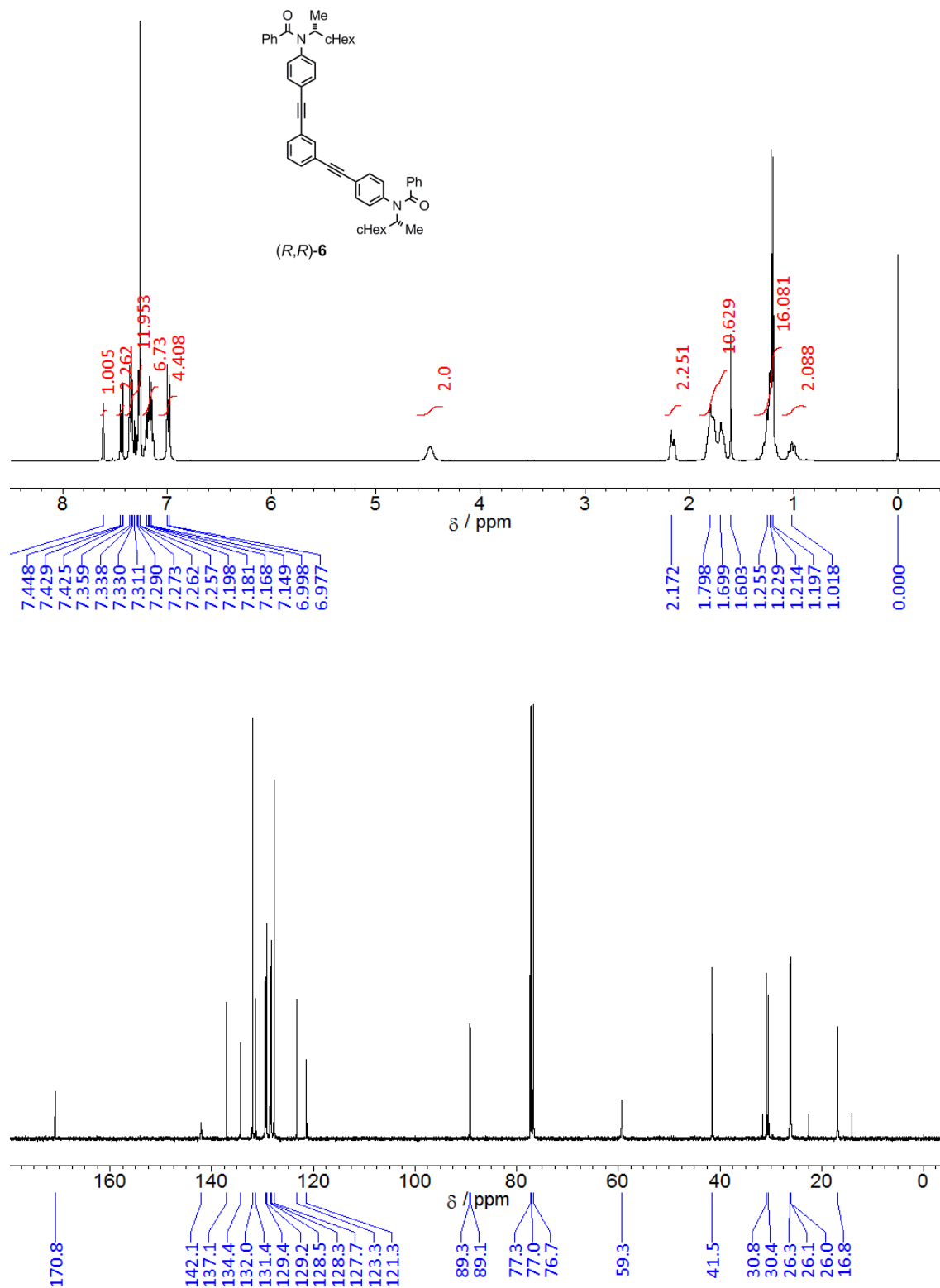
¹H (400 MHz, upper) and ¹³C (100 MHz, lower) NMR spectra of **3a**, measured in CDCl₃ at room temperature.



¹H (400 MHz, upper) and ¹³C (100 MHz, lower) NMR spectra of **13b'**, measured in CDCl₃ at room temperature, cont. residual hexane in the latter spectrum.



^1H (400 MHz, upper) and ^{13}C (100 MHz, lower) NMR spectra of (R,R,R,R) -**3b**, measured in CDCl_3 at room temperature, cont. residual hexane in the latter spectrum.



^1H (400 MHz, upper) and ^{13}C (100 MHz, lower) NMR spectra of (R,R) -6, measured in CDCl_3 at room temperature, cont. residual hexane in the latter spectrum.

References

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- 3 K. Sato, Y. Inoue, T. Mori, A. Sakaue, A. Tarui, M. Omote, I. Kumadaki and A. Ando, *Org. Lett.*, 2014, **16**, 3756–3759.
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