Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Dynamic or undynamic chirality generated by helical arrangement of a shape-persistent ring and rod doubly bridged in a molecule

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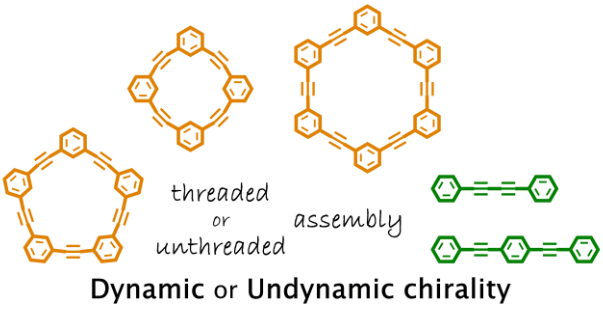

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Supplementary Figures

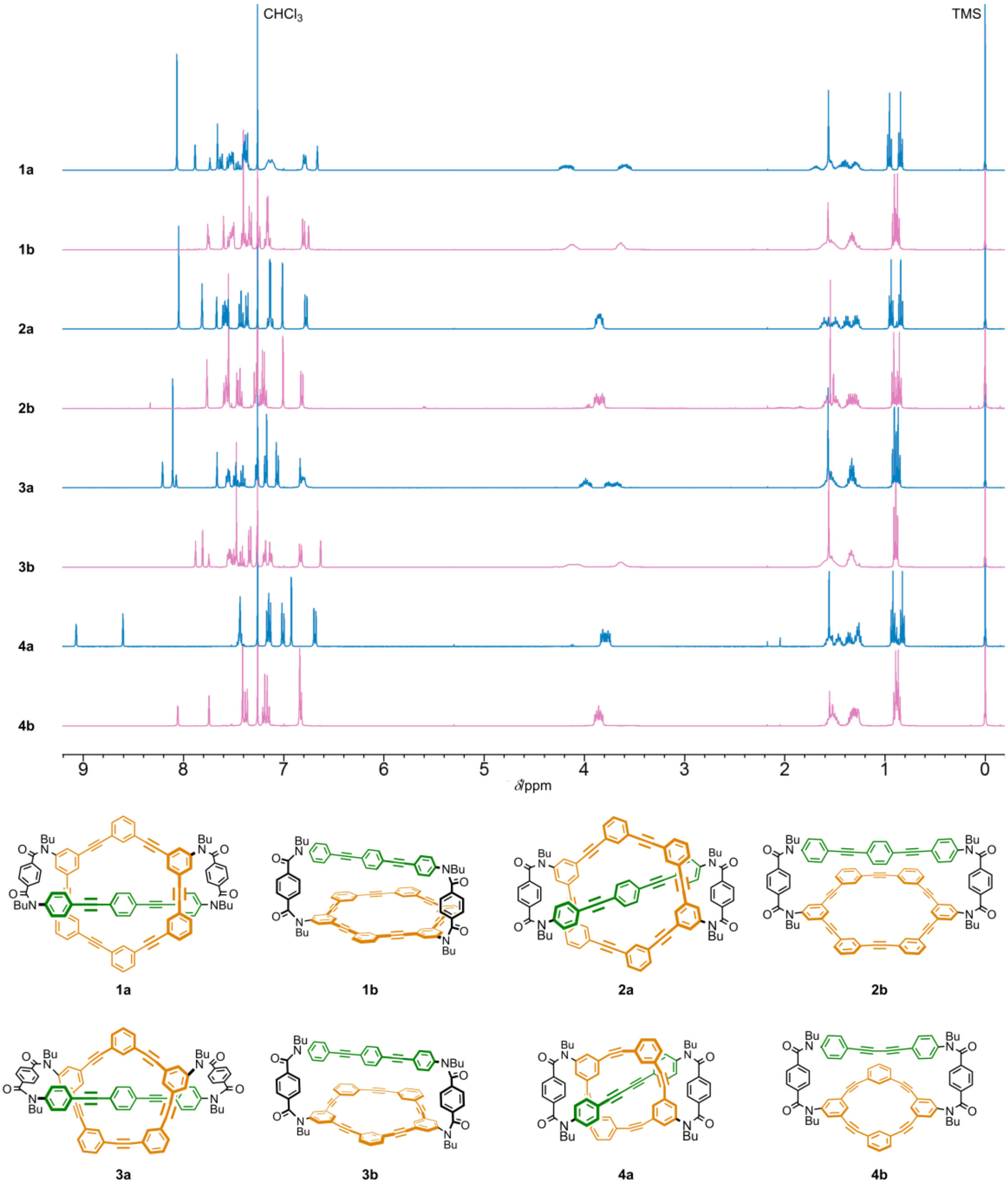


Fig. S1a ^{1}H NMR spectra (400 MHz) of **1a**/**b**, **2a**/**b**, **3a**/**b** and **4a**/**b**, measured in chloroform-*d* at room temperature.

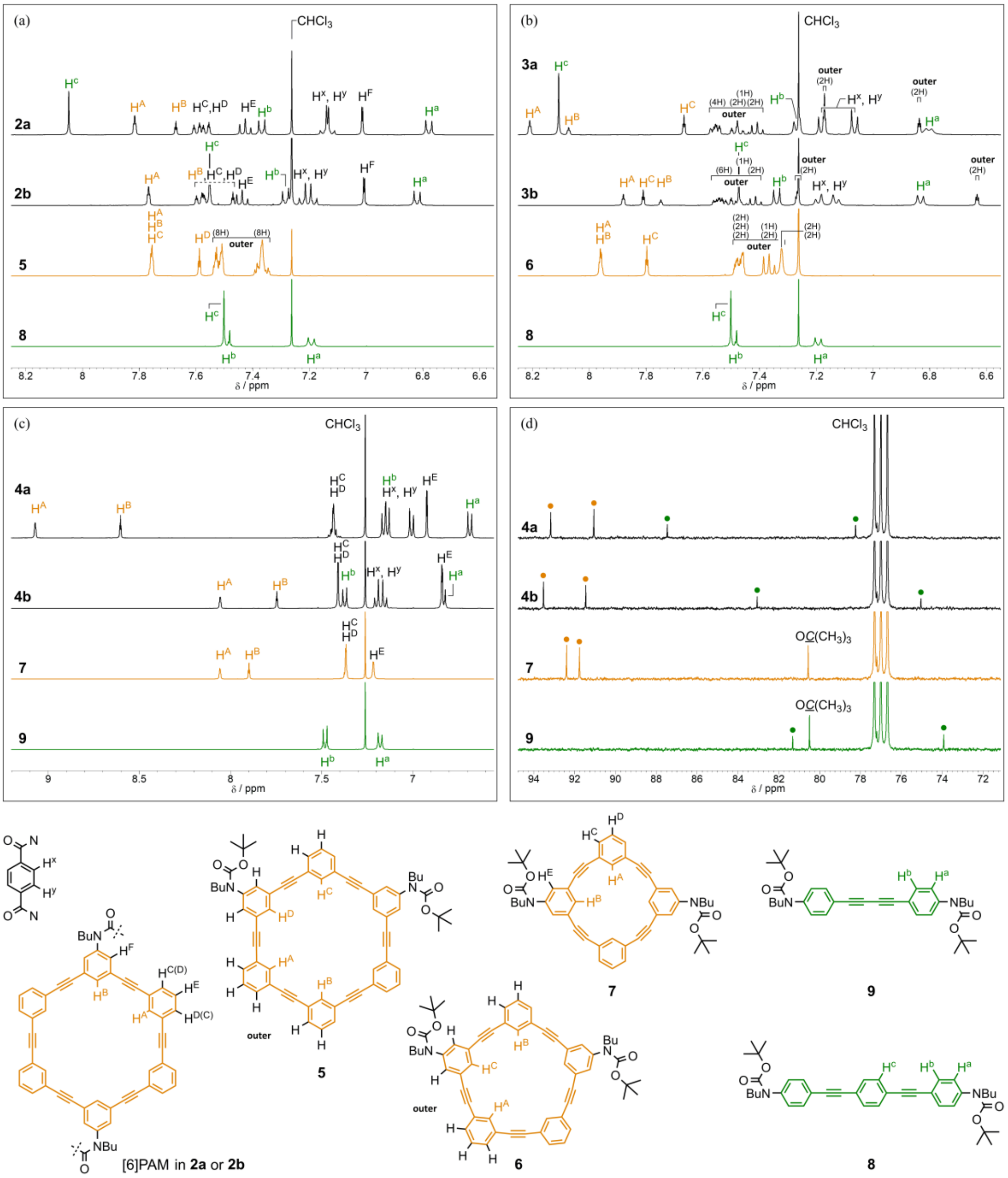


Fig. S1b (a)-(c) Partial ^{1}H NMR spectra (400 MHz) of (a) **2a**, **2b**, **5** and **8**, (b) **3a**, **3b**, **6** and **8**, and (c) **4a**, **4b**, **7** and **9**. (d) Partial ^{13}C NMR spectra (100 MHz) of **4a**, **4b**, **7** and **9**. All spectra were measured in chloroform-*d* at room temperature.

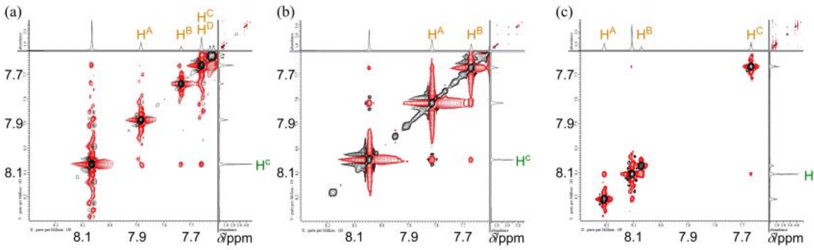


Fig. S2 Partial 2D ROESY spectra (600 MHz) of (a) **1a**, (b) **2a** and (c) **3a**. All spectra were measured in chloroform-*d* at room temperature.

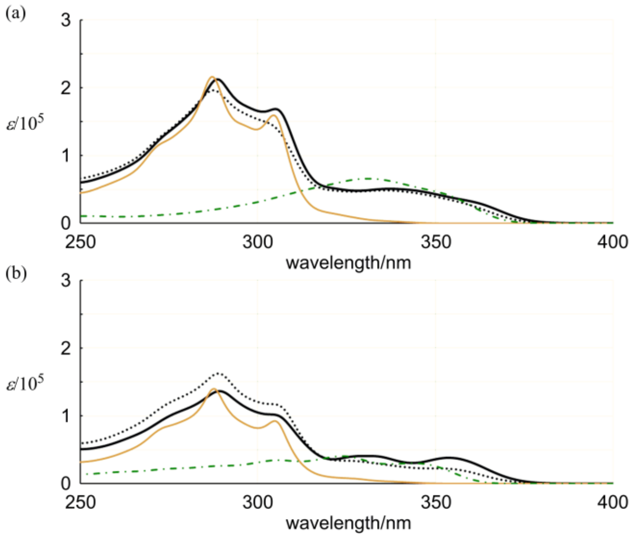


Fig. S3 UV spectra of (a) **3a**, **3b**, **6** and **8**, and (b) **4a**, **4b**, **7** and **9**. Black solid line: threaded form **a**, black dashed line: unthreaded form **b**, orange solid line: ring, and green dashed line: rod. All spectra were measured in dichloromethane at room temperature.

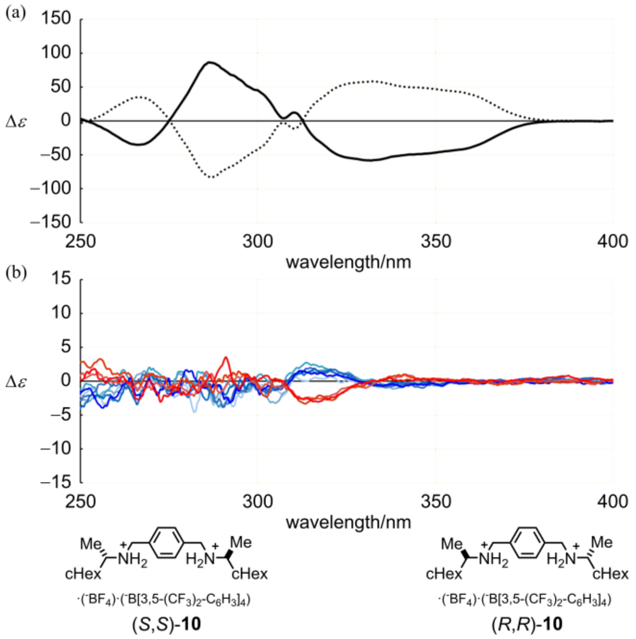


Fig. S4 CD spectra of (a) (–)-**3a** (solid line, first fraction) and (+)-**3b** (dashed line, second fraction), measured at 293 K; (b) CD spectra of **4b** ([**4b**] = 1.17 × 10^{-4} M) in the presence of (*R*,*R*)-**10** (1, 2, 4, 6, 8, and 10 equiv. blue lines) or (*S*,*S*)-**10** (2, 4, and 8 equiv. red lines), measured at 263 K. All spectra were measured in dichloromethane. Chemical structures of chiral ditopic guests (*S*,*S*)-**10** and (*R*,*R*)-**10**.

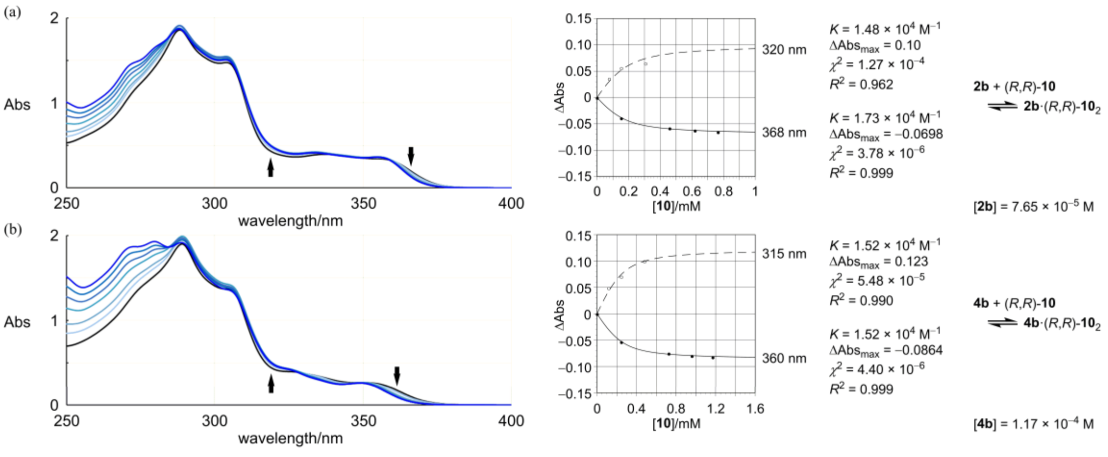


Fig. S5 UV spectra of (a) **2b** and (b) **4b** in the presence of (*R*,*R*)-**10** [0 (**2b** or **4b** only, black line)-10 equiv. (blue lines)], measured in dichloromethane at room temperature, titration curves and binding constants,[a] obtained by a curve-fitting method, based on a change in absorbance (ΔAbs = $\mathrm{Abs_{complex}}$ – $\mathrm{Abs_0}$) upon complexation.

[a] Assume 1:2 complexation ($K_1 = K_2$). Doubled concentration (= [terephthalamide unit]) was used for calculation.

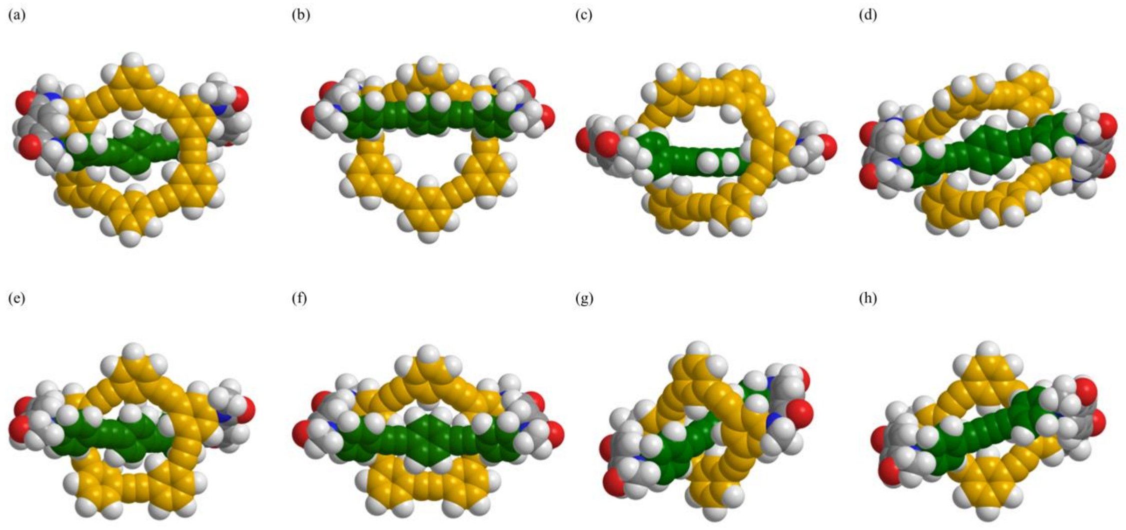


Fig. S6 The most energy-minimized structures for models **1'-4'** (NMe): (a) **1a'** (rel. 0 kJ mol^{-1}), (b) **1b'** (+4.40 kJ mol^{-1}), (c) **2a'** (rel. 0 kJ mol^{-1}), (d) **2b'** (+11.3 kJ mol^{-1}), (e) **3a'** (+9.40 kJ mol^{-1}), (f) **3b'** (rel. 0 kJ mol^{-1}), (g) **4a'** (+14.3 kJ mol^{-1}) and (h) **4b'** (rel. 0 kJ mol^{-1}), obtained by conformational searches using MacroModel software (v9.9 OPLS_2005, Monte Carlo Multiple Minimum method, non-solvated, 50 000 steps). No conformation with any local helical form (*m*- or *p*-helicity) in the terephthalamide unit was found for **1'** (101 conformers found within 30 kJ mol^{-1}), **2'** (47) or **4'** (14). However, for **3'** (50) a local helical form in the terephthalamide unit was found at a higher energy level (+23.8 kJ mol^{-1} relative to the most energy-minimized conformer (f)).

Cf.

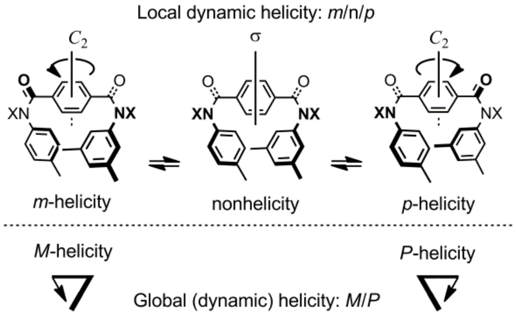
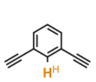
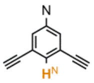


Table S1 Chemical shifts (δ/ppm) for central phenylene protons (H^c) of rod and interior protons (H^H) of PAMs, measured in chloroform-*d* at room temperature.

	central phenylene protons	interior protons H^H	interior protons H^N
[6]PAM in **1a**	8.07 (4H)	7.88 (2H) 7.74 (1H) 7.66 (1H)	7.66 (2H)
[6]PAM in **2a**	8.05 (4H)	7.82 (2H+2H)	7.67 (2H)
[5]PAM in **3a**	8.11 (4H)	8.21 (2H) 8.07 (1H)	7.67 (2H)
[4]PAM in **4a**	–	9.07 (2H)	8.60 (2H)
[6]PAM (**5**)		7.75 (2H+1H+1H)	7.58 (2H)
[5]PAM (**6**)		7.96 (2H+1H)	7.80 (2H)
[4]PAM (**7**)		8.06 (2H)	7.90 (2H)
rod (**8**)	7.50 (4H)		
[6]PAM		7.5-7.6[a]	
[5]PAM		7.97[b]	
[4]PAM		8.07[c]	



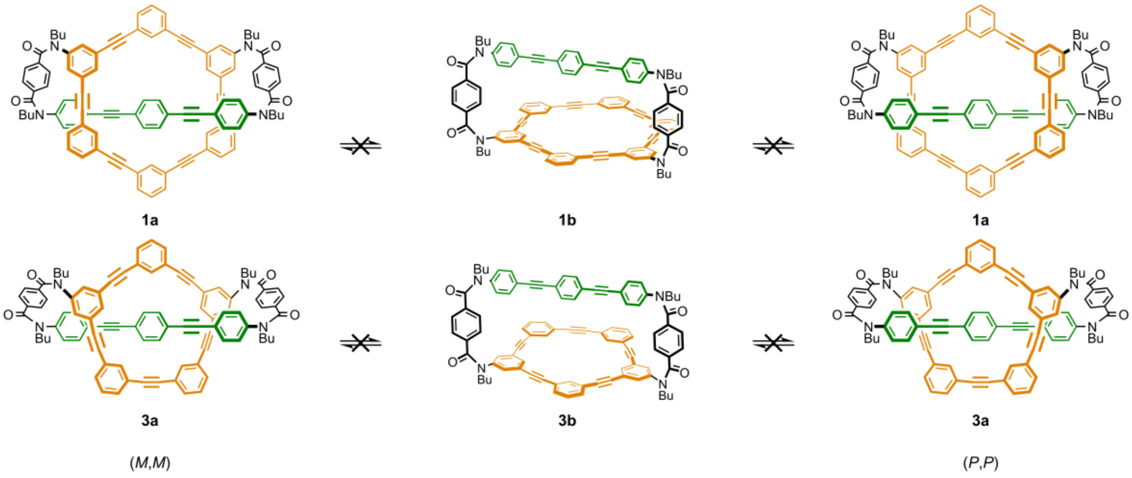


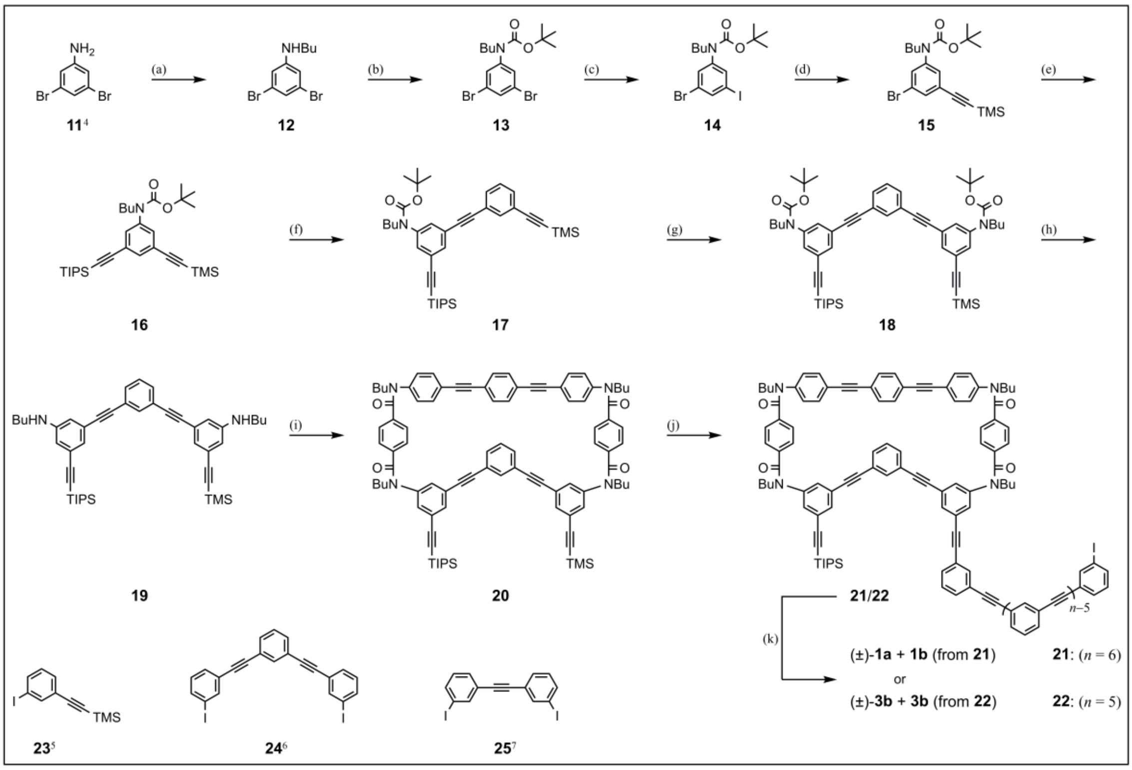
[a] alkylated analogs, from ref 1.

[b] parent hydrocarbon ($C_{40}H_{20}$), from ref 2.

[c] parent hydrocarbon ($C_{32}H_{16}$), from ref 3.

Experimental





Scheme S1. Synthesis of (±)-**1a**/**1b** and (±)-**3a**/**3b**. Reagents and yields: (a) 1-bromobutane, NaH, THF (78%); (b) di-^{t}butyl dicarbonate (Boc$_2$O), 4-dimetylaminopyridine (DMAP), Et$_3$N, THF (99%); (c) ^{n}BuLi, 1,2-diiodoethane, diethyl ether (96%); (d) trimethylsilylacetylene (TMSA), PdCl$_2$(PPh$_3$)$_2$, CuI, Et$_3$N, THF (96%); (e) triisopropylsilylacetylene (TIPSA), Pd(PPh$_3$)$_4$, CuI, ^{i}Pr$_2$NH, THF (97%); (f) i) K$_2$CO$_3$, MeOH, THF (94% for **16'**); ii) **23**[5], Pd(PPh$_3$)$_4$, CuI, ^{i}Pr$_2$NH, THF (95%); (g) i) K$_2$CO$_3$, MeOH, THF (93% for **17'**); ii) **15**, Pd(PPh$_3$)$_4$, CuI, ^{i}Pr$_2$NH, THF (80%); (h) trifluoroacetic acid (TFA), CH$_2$Cl$_2$ (97%); (i) i) TFA, CH$_2$Cl$_2$ (88% for **8'**), ii) terephthaloyl chloride, **8'**, Et$_3$N, toluene, THF (43%); (j) i) K$_2$CO$_3$, MeOH, THF (96% for **20'**); ii) **24**[6]/**25**[7], Pd(PPh$_3$)$_4$, CuI, Et$_3$N, THF (66% for **21**, 72% for **22**); (k) i) tetra-^{n}butylammonium fluoride (TBAF), THF (95% for **21'**, 97% for **22'**); ii) Pd(PPh$_3$)$_4$, CuI, Et$_3$N, THF (45% for (±)-**1a**/**1b**, 78% for (±)-**3a**/**3b**).

Preparation of **13**

To an ice-cooled solution of **11** (27.3 g, 109 mmol) in THF (120 mL) were added NaH (60% dispersion in oil, 8.70 g, 218 mmol) and 1-bromobutane (11.7 mL, 109 mmol), the mixture was stirred at room temperature for 5 h. After addition of water, the mixture was diluted with ethyl acetate, and which was separated. The organic layer was washed with brine, dried over magnesium sulfate, and then purified by column chromatography on SiO_2 (dichloromethane/hexane) to give **12** (25.9 g) as a reddish yellow oil in 78% yield. **12**: ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 6.92 (1H, t, J = 1.6 Hz), 6.63 (2H, d, J = 1.6 Hz), 3.74 (1H, br.t), 3.07 (1H, dd, J = 5.6, 6.8 Hz), 3.05 (1H, dd, J = 5.6, 6.8 Hz), 1.62-1.55 (2H, m), 1.46-1.37 (2H, m), 0.96 (3H, t, J = 7.2 Hz).

To a refluxed solution of **12** (9.21 g, 30.0 mmol), DMAP (76 mg, 0.35mmol) and Et_3N (8.4 mL, 60 mmol) in THF (100 mL) was added Boc_2O (13.8 mL, 60 mmol), and the mixture was further refluxed for 20 h. After removal of the solvent by evaporation, the residue was purified by column chromatography on SiO_2 (dichloromethane/hexane) to give **13** (12.1 g) as a white solid in 99% yield. An analytical sample was obtained as colorless crystals by recrystallization from methanol. **13**: mp 54.0-54.5 °C; elemental analyses Found: C, 44.14; H, 5.15; N, 3.48%. Calc. for $C_{15}H_{21}Br_2NO_2$: C, 44.25; H, 5.20; N, 3.44%; IR (KBr) ν_{max}/cm^{-1} 3111, 3074, 3010, 2979, 2959, 2931, 2899, 2876, 2858, 1711, 1584, 1552; ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.48 (1H, t, J = 2.0 Hz), 7.31 (2H, d, J = 2.0 Hz), 3.59 (2H, t, J = 7.6 Hz), 1.56-1.46 (2H, m), 1.45 (9H, s), 1.35-1.26 (2H, m), 0.91 (3H, t, J = 7.6 Hz); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 153.9, 144.9, 131.2, 128.7, 122.2, 81.0, 49.6, 30.5, 28.2, 19.8, 13.7; FD-LRMS m/z 405.0 (M^+, 54%), 406.0 ($[M+1]^+$, 10), 407.0 ($[M+2]^+$, 100), 408.0 ($[M+3]^+$, 18), 409.0 ($[M+4]^+$, 52), 410.0 ($[M+5]^+$, 9).

Preparation of **14**

To a solution of **13** (15.0 g, 37.0 mmol) in diethyl ether (370 mL) was added ^{n}BuLi (1.6 M in hexane, 23.7 mL, 38.8 mmol) at −87 °C under an argon atmosphere, and the mixture was stirred at that temperature for 3 min. To the mixture was added a solution of 1,2-diiodoethane (12.5 g, 44.3 mmol) in diethyl ether (60 mL), and the mixture was further stirred for 20 min. After addition of water, the organic layer was separated, dried over magnesium sulfate, and then purified by column chromatography on SiO_2 (dichloromethane/hexane) to give **14** (16.1 g) as a white solid in 96% yield. An analytical sample was obtained as colorless crystals by recrystallization from methanol. **14**: mp 71.0-72.0 °C; elemental analyses Found: C, 39.57; H, 4.68; N, 3.11%. Calc. for $C_{15}H_{21}BrINO_2$: C, 39.67; H, 4.66; N, 3.08%; IR (KBr) ν_{max}/cm^{-1} 3096, 3068, 3010, 2977, 2957, 2929, 2897, 2875, 2857, 1711, 1578, 1545; ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.67 (1H, t, J = 1.6 Hz), 7.50 (1H, t, J = 1.6 Hz), 7.34 (1H, t, J = 1.6 Hz), 3.58 (2H, t, J = 7.6 Hz), 1.55-1.45 (2H, m), 1.45 (9H, s), 1.35-1.25 (2H, m), 0.91 (3H, t, J = 7.6 Hz); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 153.8, 144.7, 136.8, 134.5, 129.4, 122.2, 93.3, 80.9, 49.6, 30.5, 28.2, 19.8, 13.7; FD-LRMS m/z 452.9 (M^+, 100%), 453.9 ($[M+1]^+$, 17), 454.9 ($[M+2]^+$, 98), 455.9 ($[M+3]^+$, 16).

Preparation of **15**

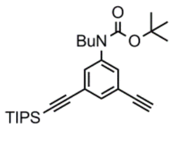
To a solution of **14** (5.85 g, 12.9 mmol), $PdCl_2(PPh_3)_2$ (96 mg, 0.14 mmol) and CuI (25 mg, 0.13 mmol) in THF (65 mL) and Et_3N (65 mL) was added TMSA (2.0 mL, 14 mmol) at room temperature under an argon atmosphere, and the mixture was stirred at that temperature for 7 h. After removal of a solid by filtration through a Celite pad, the filtrate was concentrated and purified by column chromatography on SiO_2 (dichloromethane/hexane) to give **15** (5.26 g) as a pale yellow oil in 96% yield. An analytical sample was obtained as a colorless oil by further purification through GPC (chloroform). **15**: elemental analyses Found: C, 56.41; H, 7.16; N, 3.29%. Calc. for $C_{20}H_{30}BrNO_2Si$: C, 56.59; H, 7.12; N, 3.30%; IR (KBr) ν_{max}/cm^{-1} 3070, 2961, 2932, 2873, 2160, 1707, 1591, 1559; ^1H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.44 (1H, br.dd), 7.31 (1H, br.t), 7.22 (1H, br.t), 3.59 (2H, t, J = 7.6 Hz), 1.53-1.46 (2H, m), 1.44 (9H, s), 1.34-1.25 (2H, m), 0.90 (3H, t, J = 7.6 Hz), 0.24 (9H, s); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 154.1, 143.7, 132.0, 130.6, 128.8, 125.1, 121.5, 102.8, 96.1, 80.6, 49.6, 30.5, 28.3, 19.8, 13.7, –0.2; FD-LRMS m/z 423.1 (M^+, 96%), 424.1 ($[M+1]^+$, 28), 425.1 ($[M+2]^+$, 100), 426.1 ($[M+3]^+$, 27), 427.1 ($[M+4]^+$, 7).

Preparation of **16**

To a solution of **15** (676 mg, 1.59 mmol) and TIPSA (0.72 mL, 3.2 mmol) in THF (8 mL) and $^iPr_2NH$ (8 mL) were added $Pd(PPh_3)_4$ (55 mg, 0.048 mmol) and CuI (18 mg, 0.095 mmol) at room temperature under an argon atmosphere, and the mixture was stirred at 78-79 °C for 40 min. After removal of a solid by filtration through a Celite pad, the filtrate was concentrated and purified by column chromatography on SiO_2 (dichloromethane/hexane), followed by GPC (chloroform) to give **16** (813 mg) as a pale yellow oil in 97% yield. An analytical sample was obtained as a colorless oil by further purification through GPC (chloroform). **16**: elemental analyses Found: C, 70.56; H, 9.98; N, 2.59%. Calc. for $C_{31}H_{51}NO_2Si_2$: C, 70.80; H, 9.77; N, 2.66%; IR (KBr) ν_{max}/cm^{-1} 3066, 2960, 2943, 2894, 2865, 2153, 1707, 1582; ^1H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.40 (1H, t, J = 1.6 Hz), 7.25-7.20 (2H, br.m), 3.59 (2H, t, J = 7.6 Hz), 1.54-1.46 (2H, m), 1.43 (9H, s), 1.34-1.25 (2H, m), 1.12 (21H, s), 0.90 (3H, t, J = 7.6 Hz), 0.24 (9H, s); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 154.2, 142.6, 132.9, 130.7, 130.4, 124.2, 123.8, 105.6, 103.6, 95.1, 91.6, 80.4, 49.5, 30.5, 28.3, 19.9, 18.6, 13.7, 11.2, –0.2; FD-LRMS m/z 525.3 (M^+, 100%), 526.3 ($[M+1]^+$, 45), 527.3 ($[M+2]^+$, 16), 528.3 ($[M+3]^+$, 4).

Preparation of **17**

To a solution of **16** (10.5 g, 20.0 mmol) in THF (100 mL) and MeOH (100 mL) was added K_2CO_3 (2.76 g, 20.0 mmol) at room temperature, and the mixture was stirred at that temperature for 15 min. After removal of a solid by filtration, the filtrate was concentrated and purified by column chromatography on SiO_2 (dichloromethane/hexane) to give **16'** (8.51 g) as a white solid in 94% yield. **16'**: ^1H



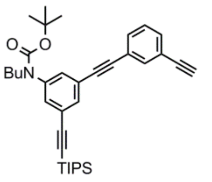
16'

NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.43 (1H, t, *J* = 1.6 Hz), 7.30-7.22 (2H, br.m), 3.60 (2H, t, *J* = 7.6 Hz), 3.08 (1H, s), 1.54-1.47 (2H, m), 1.44 (9H, s), 1.35-1.25 (2H, m), 1.13 (21H, br.m), 0.90 (3H, t, *J* = 7.2 Hz).

To a solution of **23** (8.73 g, contained 1-bromo-3-(2-trimethylsilyl)ethynylbenzene in a ratio of 5:1), $Pd(PPh_3)_4$ (563 mg, 0.487 mmol) and CuI (187 mg, 0.982 mmol) in THF (65 mL) and $^i Pr_2NH$ (80 mL) was added a solution of **16'** (7.33 g, 16.2 mmol) in THF (15 mL) via a syringe pump over 2 h at 43-45 °C under an argon atmosphere, and the mixture was stirred at that temperature for 20 min. After removal of a solid by filtration through a Celite pad, the filtrate was concentrated and purified by column chromatography on SiO_2 (dichloromethane/hexane) to give **17** (9.59 g) as a colorless oil in 95% yield. An analytical sample was obtained as a colorless oil by further purification through GPC (chloroform). **17**: elemental analyses Found: C, 74.77; H, 9.06; N, 2.21%. Calc. for $C_{39}H_{55}NO_2Si_2$: C, 74.82; H, 8.86; N, 2.24%; IR (KBr) ν_{max}/cm^{-1} 3063, 2959, 2943, 2894, 2865, 2157, 1706, 1595, 1582; ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.65-7.64 (1H, br.m), 7.46 (1H, t, *J* = 1.6 Hz), 7.46 (1H, dt, *J* = 1.6, 8.0 Hz), 7.43 (1H, dt, *J* = 1.6, 8.0 Hz), 7.31-7.24 (3H, br.m), 3.62 (2H, t, *J* = 7.6 Hz), 1.57-1.49 (2H, m), 1.45 (9H, s), 1.36-1.27 (2H, m), 1.14 (21H, s), 0.91 (3H, t, *J* = 7.2 Hz), 0.25 (9H, s); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 154.3, 142.7, 135.1, 132.6, 131.8, 131.5, 130.5, 130.2, 128.4, 124.4, 123.6, 123.5, 123.1, 105.6, 104.0, 95.1, 91.8, 89.1, 88.6, 80.5, 49.6, 30.5, 28.3, 19.9, 18.6, 13.8, 11.3, –0.1; FD-LRMS *m/z* 625.4 (M$^+$, 100%), 626.4 ([M+1]$^+$, 54), 627.4 ([M+2]$^+$, 22), 628.4 ([M+3]$^+$, 6).

Preparation of **18**

To a solution of **17** (3.19 g, 5.10 mmol) in THF (27 mL) and MeOH (27 mL) was added K_2CO_3 (687 mg, 4.98 mmol) at room temperature, and the mixture was stirred at that temperature for 25 min. After removal of the solvents by evaporation, the residue was purified by column chromatography on SiO_2 (dichloromethane/hexane) to give **17'** (2.62 g) as a white solid in 93% yield. **17'**: ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.66 (1H, t, *J* = 1.6 Hz), 7.49 (1H, dt, *J* = 1.6, 8.0 Hz), 7.48 (1H, t, *J* = 1.6 Hz), 7.45 (1H, dt, *J* = 1.6, 8.0 Hz), 7.33-7.26 (3H, m), 3.62 (2H, t, *J* = 7.6 Hz), 3.10 (1H, s), 1.57-1.49 (2H, m), 1.45 (9H, s), 1.37-1.27 (2H, m), 1.14 (21H, s), 0.90 (3H, t, *J* = 7.2 Hz).



17'

To a solution of **15** (739 mg, 1.74 mmol), $Pd(PPh_3)_4$ (40 mg, 0.035 mmol) and CuI (13 mg, 0.068 mmol) in $^i Pr_2NH$ (6 mL) and THF (4.5 mL) was added a solution of **17'** (633 mg, 1.14 mmol) in THF (1.8 mL) via a syringe pump over 1 h at 80 °C under an argon atmosphere, and the mixture was further stirred at that temperature for 1.5 h. After removal of a solid by filtration through a Celite pad, the filtrate was concentrated and purified by column chromatography on SiO_2 (dichloromethane/hexane), followed by GPC (chloroform) to give **18** (817 mg) as a pale yellow amorphous solid in 80% yield. An analytical sample was obtained as a white amorphous solid by further purification through GPC (chloroform). **18**: mp 65.0-66.0 °C; elemental analyses Found: C, 74.89; H, 8.61; N, 3.01%. Calc. for $C_{56}H_{76}N_2O_4Si_2$: C, 74.95; H, 8.54; N, 3.12%; IR (KBr) ν_{max}/cm^{-1}

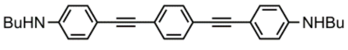
3064, 2960, 2941, 2864, 2158, 1705, 1596, 1582; ^{1}H NMR δ_H(400 MHz; CDCl$_3$; Me$_4$Si)/ppm 7.69 (1H, br.t), 7.51-7.47 (4H, m), 7.36-7.33 (1H, m), 7.31 (2H, br.t), 7.29-7.25 (2H, br.m), 3.63 (2H, t, J = 7.6 Hz), 3.61 (2H, t, J = 7.6 Hz), 1.55-1.48 (4H, m), 1.45 (9H, s), 1.45 (9H, s), 1.36-1.28 (4H, m), 1.14 (21H, s), 0.92 (3H, t, J = 7.6 Hz), 0.91 (3H, t, J = 7.6 Hz), 0.26 (9H, s); ^{13}C NMR δ_C(100 MHz; CDCl$_3$)/ppm 154.3, 142.8, 134.7, 132.6, 131.5, 130.5 (br.m), 130.2, 128.6, 124.4, 124.0, 123.7, 123.6, 123.3, 105.6, 103.5, 95.4, 91.8, 89.1, 89.1, 88.8, 88.7, 80.5, 80.5, 49.6, 49.6, 30.6, 28.3, 19.9, 18.6, 13.8, 11.3, –0.1; FD-LRMS *m/z* 796.5 ([M−(BOC)]$^+$, 22%), 797.5 ([M+1−(BOC)]$^+$, 15), 798.5 ([M+2−(BOC)], 7), 896.6 (M$^+$, 100), 897.6 ([M+1]$^+$, 72), 898.6 ([M+2]$^+$, 34), 899.6 ([M+3]$^+$, 12), 900.6 ([M+4]$^+$, 3).

Preparation of **19**

To a solution of **18** (3.16 g, 3.52 mmol) in CH$_2$Cl$_2$ (230 mL) was added TFA (23 mL) at room temperature. The mixture was stirred at room temperature for 1 h, neutralized with satd. aq. NaHCO$_3$, and separated. The organic layer was dried over magnesium sulfate, concentrated, and purified by column chromatography on SiO$_2$ (dichloromethane/hexane) to give **19** (2.39 g) as a white amorphous solid in 97% yield. **19**: ^{1}H NMR δ_H(400 MHz; CDCl$_3$; Me$_4$Si)/ppm 7.67 (1H, br.dd), 7.47-7.43 (2H, m), 7.31 (1H, t, J = 7.6 Hz), 7.00-6.99 (2H, m), 6.72-6.68 (2H, br.m), 6.68-6.66 (2H, m), 3.65 (2H, br.s), 3.11 (2H, t, J = 7.2 Hz), 3.10 (2H, t, J = 7.2 Hz), 1.64-1.56 (4H, m), 1.48-1.38 (4H, m), 1.13 (21H, s), 0.97 (3H, t, J = 7.2 Hz), 0.96 (3H, t, J = 7.2 Hz).

Preparation of **20**

To a solution of **8** (554 mg, 0.892 mmol) in CH$_2$Cl$_2$ (60 mL) was added TFA (5.9 mL) at room temperature. The mixture was stirred at room temperature for 1 h, diluted with dichloromethane, neutralized with aq. 1M NaOH, and separated. The organic layer was dried over magnesium sulfate, passed through a Celite/SiO$_2$ pad, and then concentrated. The residue was suspended in dichloromethane/hexane, and then collected by filtration to give **8'** (331 mg) as a pale yellow solid in 88% yield. **8'**: ^{1}H NMR δ_H(400 MHz; CDCl$_3$; Me$_4$Si)/ppm 7.43 (4H, s), 7.34 (4H, d, J = 8.8 Hz), 6.54 (4H, d, J = 8.8 Hz), 3.82 (2H, br.s), 3.14 (4H, t, J = 7.2 Hz), 1.65-1.58 (4H, m), 1.48-1.39 (4H, m), 0.97 (6H, t, J = 7.6 Hz).



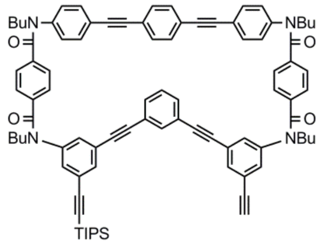
8'

To a solution of terephthaloyl chloride (507 mg, 2.50 mmol) in toluene (70 mL) was added a solution of **19** (858 mg, 1.23 mmol) in toluene (7 mL) containing Et$_3$N (0.4 mL) at 56 °C over a period of 1.5 h. The reaction mixture was further stirred for 30 min at that temperature, and then passed through a Celite pad to remove a solid. The filtrate was immediately subjected to the following reaction [acid chloride preparation].

Each solution of **8'** (482 mg, 1.15 mmol) in THF (70 mL) and as-prepared acid chloride in toluene (70 mL) was simultaneously added via addition funnels over 20 min to refluxed THF (210 mL) containing Et_3N (0.4 mL), and the mixture was further stirred for 2 h at that temperature. After removal of the solvents by evaporation, the residue was dissolved in dichloromethane, which was washed with satd. aq. $NaHCO_3$, dried over magnesium sulfate, and then passed through a Celite/Al_2O_3 pad. The filtrate was concentrated, and then purified by column chromatography on Al_2O_3/SiO_2 (ethyl acetate/dichloromethane), followed by GPC (chloroform) to give **20** (680 mg) as a white solid in 43% yield. An analytical sample was obtained as a white solid by HPLC with a standard normal-phase column (ethyl acetate/dichloromethane; YMC-Pack SIL, SIL-06, YMC Co., Ltd.). **20**: mp 181.5-182.0 °C; elemental analyses Found: C, 79.34; H, 7.15; N, 3.93%. Calc. for $C_{92}H_{96}N_4O_4Si_2\cdot(EtOH)$: C, 79.28; H, 7.22; N, 3.93%; IR (KBr) ν_{max}/cm^{-1} 3062, 3041, 2956, 2931, 2862, 2215, 2152, 1655, 1650, 1596, 1579, 1518; ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm[11] 7.56 (3H, br.s), 7.49 (2H, br.d), 7.42 (4H, br.d), 7.34 (1H, t, J = 7.6 Hz), 7.25-7.20 (2H, br.m), 7.10 (8H, br.s), 6.82 (2H, br.d), 6.80 (2H, br.d), 6.71-6.62 (2H, m), 4.41-3.39 (8H, br.m), 1.70-1.46 (8H, br.m), 1.43-1.26 (8H, m), 1.16-1.12 (21H, m), 0.95-0.88 (12H, m), 0.28 (9H, s); ^{13}C NMR δ_C(100 MHz; $CDCl_3$; 313 K)/ppm 169.8, 169.6, 168.6, 143.5, 143.5, 143.3, 137.6, 137.3, 136.7 (br.m), 133.3, 133.1 (br.m), 132.7, 132.4, 132.3, 131.5, 128.8 (br.), 128.7, 128.7, 128.5, 127.7, 127.5, 127.1, 127.1, 124.4, 124.4, 124.3, 124.0, 123.2 (br.m), 123.1, 123.0, 121.2, 121.1, 105.2, 103.3, 96.6, 93.4, 90.8 (br.m), 89.9, 89.7, 88.3, 88.3, 49.8, 49.7, 49.6, 29.8, 29.7, 29.7, 20.1, 20.1, 20.1, 18.6, 13.7, 11.3, –0.2; FD-LRMS m/z 1376.6 (M$^+$, 88%), 1377.7 ([M+1]$^+$, 100), 1378.7 ([M+2]$^+$, 65), 1379.7 ([M+3]$^+$, 31), 1380.7 ([M+4]$^+$, 11), 1381.7 ([M+5]$^+$, 4).

Preparation of **21** (n = 6)

To a solution of **20** (525 mg, 0.381 mmol) in THF (7 mL) and MeOH (7 mL) was added K_2CO_3 (104 mg, 0.754 mmol) at room temperature, and the mixture was stirred at that temperature for 15 min. After removal of a solid by filtration, the filtrate was concentrated and purified by column chromatography on SiO_2 (ethyl acetate/dichloromethane) to give **20'** (479 mg) as a white solid in 96% yield. **20'**: ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm[11] 7.60 (3H, br.m), 7.50 (2H, dd, J = 1.2, 7.6 Hz), 7.42 (2H, d, J = 8.4 Hz), 7.39 (2H, d, J = 8.8 Hz), 7.34 (1H, br.t), 7.29-7.26 (2H, br.m), 7.12 (2H, d, J = 8.4 Hz), 7.10 (4H, s), 7.09 (2H, d, J = 8.8 Hz), 6.83 (2H, d, J = 8.4 Hz), 6.80 (2H, d, J = 8.0 Hz), 6.70 (1H, t, J = 1.6 Hz), 6.66 (1H, br.s), 4.40-3.34 (8H, br.m), 3.21 (1H, s), 1.70-1.45 (8H, br.m), 1.41-1.28 (8H, m), 1.16-1.11 (21H, m), 0.95-0.88 (12H, m).



20'

To a solution of **24** (486 mg, 0.917 mmol), $Pd(PPh_3)_4$ (9 mg, 0.008 mmol) and CuI (3 mg, 0.02 mmol) in Et_3N (22 mL) was added a solution of **20'** (287 mg, 0.220 mmol) in THF (3 mL) via a syringe pump over 3 h at 60 °C under an argon atmosphere, and the mixture was further stirred at that temperature for 30 min. After dilution with ethyl acetate, the organic layer was washed with 0.5 M aq. HCl and brine, dried over magnesium sulfate, concentrated, and then purified by column chromatography on SiO_2 (dichloromethane/hexane), followed by GPC (chloroform) to give **21** (249 mg) as a pale yellow solid in 66% yield. An analytical sample was obtained as a white solid by further purification with HPLC (ethyl acetate/dichloromethane). **21**: mp 164-165 °C; elemental analyses Found: C, 77.51; H, 5.97; N, 3.19%. Calc. for $C_{111}H_{99}IN_4O_4Si\cdot(EtOH)$: C, 77.38; H, 6.03; N, 3.19%; IR (KBr) ν_{max}/cm^{-1} 3059, 3039, 2955, 2929, 2861, 2214, 2150, 1655, 1650, 1596, 1579, 1517; ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si; 313 K)/ppm[11] 7.89 (1H, t, J = 1.6 Hz), 7.73 (1H, br.t), 7.69 (1H, br.dt), 7.67 (1H, br.ddd), 7.64 (1H, br.t), 7.55-7.46 (8H, m), 7.40 (2H, d, J = 8.4 Hz), 7.39 (2H, d, J = 8.4 Hz), 7.41-7.25 (6H, m), 7.12 (4H, s), 7.09 (4H, s), 7.07 (1H, t, J = 8.0 Hz), 6.83 (2H, d, J = 8.4 Hz), 6.79 (2H, d, J = 8.4 Hz), 6.76 (1H, dd, J = 1.6, 2.0 Hz), 6.67 (1H, br.t), 4.68-3.21 (8H, br.m), 1.68-1.47 (8H, br.m), 1.41-1.28 (8H, m), 1.14-1.10 (21H, m), 0.94 (3H, t, J = 7.2 Hz), 0.93 (3H, t, J = 7.2 Hz), 0.90 (3H, t, J = 7.2 Hz), 0.88 (3H, t, J = 7.2 Hz); ^{13}C NMR δ_C(100 MHz; $CDCl_3$; 313 K)/ppm 169.8, 169.7, 168.7, 168.6, 143.7, 143.6, 143.3, 143.3, 140.2, 137.6 (br.), 137.5, 137.3 (br.m), 136.6 (br.m), 134.7, 134.6, 133.0 (br.m), 132.7, 132.4, 132.4, 132.1, 132.1, 131.6, 131.5, 130.7, 129.8, 128.9 (br.), 128.8, 128.7, 128.6, 128.5, 127.7, 127.5, 127.3, 127.1, 125.1, 124.6, 124.4, 124.3, 123.9, 123.8, 123.3, 123.3, 123.1, 123.0, 122.8, 121.2, 121.1, 105.2, 93.6, 93.4, 90.8 (br.m), 90.2, 90.1, 89.9, 89.9, 89.7, 89.5, 88.9, 88.4, 88.4, 88.3, 49.9, 49.9, 49.7, 49.7, 29.8, 29.8, 20.1, 20.1, 20.1, 18.6, 13.8, 13.7, 13.7, 11.3; FD-LRMS *m/z* 1706.7 (M$^+$, 77%), 1707.7 ([M+1]$^+$, 100), 1708.7 ([M+2]$^+$, 69), 1709.7 ([M+3]$^+$, 33), 1710.7 ([M+4]$^+$, 13), 1711.7 ([M+5]$^+$, 5).

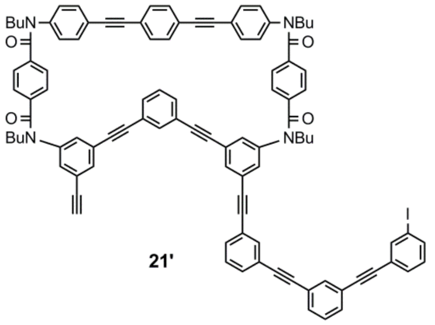
Preparation of **22** (n = 5)

To a solution of **25** (1.10 g, 2.56 mmol), $Pd(PPh_3)_4$ (24 mg, 0.021 mmol) and CuI (11 mg, 0.058 mmol) in Et_3N (61 mL) was added a solution of **20'** (840 mg, 0.643 mmol) in THF (7 mL) via a syringe pump over 3 h at 50 °C under an argon atmosphere, and the mixture was further stirred at that temperature for 30 min. After dilution with ethyl acetate, the organic layer was washed with 0.5 M aq. HCl and brine, dried over magnesium sulfate, concentrated, and then purified by column chromatography on SiO_2 (dichloromethane/hexane), followed by GPC (chloroform) to give **22** (743 mg) as a pale yellow amorphous solid in 72% yield. An analytical sample was obtained as a white solid by further purification with HPLC (ethyl acetate/dichloromethane). **22**: mp 169-170 °C; elemental analyses Found: C, 75.98; H, 6.07; N, 3.39%. Calc. for $C_{103}H_{95}IN_4O_4Si\cdot(EtOH)$: C, 76.25; H, 6.16; N, 3.39%; IR (KBr) ν_{max}/cm^{-1} 3059, 3041, 2955, 2930, 2862, 2214, 2150, 1651, 1595, 1580, 1517; ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si; 313 K)/ppm[11] 7.89 (1H, t, J = 1.6 Hz), 7.72 (1H, br.t), 7.67 (1H, ddd, J = 1.2, 2.0, 8.0 Hz), 7.64 (1H, br.t), 7.55-7.47 (6H, m), 7.40 (2H, d, J = 8.4 Hz), 7.40 (2H, d, J = 8.4 Hz), 7.40-7.25 (5H, m), 7.12 (4H, s), 7.10 (4H, s), 7.07 (1H, t, J = 8.0 Hz), 6.82 (2H, d, J = 8.4 Hz), 6.79 (2H, d, J = 8.4 Hz), 6.76 (1H, dd, J = 1.6, 2.0 Hz), 6.67 (1H, br.s), 4.42-3.34 (8H, br.m), 1.67-1.49 (8H, br.m), 1.41-1.28 (8H, m), 1.15-1.11 (21H, m), 0.94 (3H, t, J = 7.2 Hz), 0.93 (3H, t, J = 7.2 Hz), 0.90 (3H, t, J = 7.2 Hz), 0.88 (3H, t, J = 7.6 Hz); ^{13}C NMR δ_C(100 MHz; $CDCl_3$; 323 K)/ppm 169.8, 169.6, 168.7, 168.6, 143.8, 143.6, 143.4, 143.4, 140.3, 137.6, 137.6, 137.4, 136.9 (br.m), 136.7 (br.m), 134.6, 133.0 (br.m), 132.7, 132.4, 132.4, 132.1, 132.0, 131.6 (br.m), 130.7, 129.8, 129.0, 128.8, 128.7, 128.5, 127.7, 127.5, 127.3, 127.1, 125.0, 124.6, 124.5, 124.4, 123.9, 123.6, 123.3, 123.2, 123.1, 122.9, 121.3, 121.2, 105.3, 93.6, 93.4, 90.9 (br.), 90.9 (br.), 90.2, 90.1, 89.9, 89.9, 89.8, 89.5, 88.7, 88.4, 88.4 (br.), 88.3, 49.9, 49.9, 49.7, 49.7, 29.8, 29.8 (br.), 20.1, 20.1, 20.1, 18.6, 13.7, 13.7 (br.m), 11.4; FD-LRMS *m*/*z* 1606.7 (M^+, 82%), 1607.7 ($[M+1]^+$, 100), 1608.7 ($[M+2]^+$, 67), 1609.7 ($[M+3]^+$, 31), 1610.7 ($[M+4]^+$, 12), 1611.7 ($[M+5]^+$, 4).

Preparation of (±)-**1a** and **1b**

To a solution of **21** (205 mg, 0.120 mmol) in THF (4 mL) was added TBAF (1 M in THF, 0.13 mL, 0.13 mmol) at room temperature, and the mixture was stirred at that temperature for 30 min. After removal of the solvent, the residue was dissolved in ethyl acetate, and which was washed with 0.5 M aq. HCl and brine, dried over magnesium sulfate, concentrated, and then purified by column chromatography on SiO_2 (dichloromethane/hexane) to give **21'** (176 mg) as a white solid in 95% yield.

21': ^{1}H NMR ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm[11] 7.89 (1H, t, *J* = 1.6 Hz), 7.75 (1H, br.t), 7.70 (1H, br.dt), 7.68-7.66 (2H, m), 7.61 (1H, br.t), 7.56-7.47 (7H, m), 7.43-7.28 (10H, m), 7.13 (4H, s), 7.10 (4H, br.d), 7.08 (1H, t, *J* = 7.6 Hz), 6.83 (4H, br.d), 6.76 (1H, t, *J* = 1.2 Hz), 6.70 (1H, br.t), 4.43-3.37 (8H, br.m), 3.20 (1H, s), 1.58 (8H, br.s), 1.42-1.26 (8H, m), 0.94 (3H, t, *J* = 7.2 Hz), 0.92 (3H, t, *J* = 7.6 Hz), 0.88 (3H, t, *J* = 7.2 Hz), 0.88 (3H, t, *J* = 7.2 Hz).



21'

To a solution of $Pd(PPh_3)_4$ (65 mg, 0.056 mmol) and CuI (11 mg, 0.058 mmol) in Et_3N (14 mL) was added a solution of **21'** (145 mg, 0.0934 mmol) in THF (7 mL) via a syringe pump over 9 h at 75 °C under an argon atmosphere. After removal of the solvents by evaporation, the residue was dissolved in dichloromethane, and which was washed with 0.5 M aq. HCl and brine, dried over magnesium sulfate, and then purified by column chromatography on SiO_2 (ethyl acetate/dichloromethane), followed by GPC (chloroform) to give a purified mixture of (±)-**1a** and **1b** (60 mg, (±)-**1a**:**1b** = 1:1.2) as a white solid in 45% yield. (–)-**1a**, **1b** and (+)-**1a** were isolated in this order by HPLC separation with a chiral stationary column (5:95 ethanol/chloroform; CHIRALPAK IF, DAICEL Co.). Each analytical sample was obtained as a white solid by reprecipitation with ethyl acetate/hexane.

(+)-**1a**: mp 264-265 °C (dec); $[\alpha]_D^{28}$ = +411 (*c* = 0.445 gdL^{-1} in chloroform); IR (KBr) ν_{max}/cm^{-1} 3060, 3039, 2955, 2929, 2870, 2861, 2214, 1656, 1650, 1595, 1579, 1518; ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 8.07 (4H, s), 7.88 (2H, br.dt), 7.74 (1H, br.dt), 7.66 (3H, br.t), 7.62 (2H, dd, *J* = 1.6, 8.0 Hz), 7.55 (2H, dt, *J* = 1.6, 8.0 Hz), 7.55-7.50 (4H, m), 7.46 (1H, br.dd), 7.41-7.35 (9H, m), 7.16 (4H, br.d), 7.11 (4H, br.d), 6.79 (4H, d, *J* = 8.0 Hz), 6.66 (2H, dd, *J* = 1.2, 2.0 Hz), 4.25-4.11 (4H, m), 3.66-3.54 (4H, m), 1.75-1.62 (2H, m), 1.61-1.48 (6H, m), 1.49-1.22 (8H, m), 0.96 (6H, t, *J* = 7.2 Hz), 0.85

(6H, t, *J* = 7.2 Hz); ^{13}C NMR δ_C(100 MHz; CDCl$_3$)/ppm 169.3, 169.2, 143.8, 143.1, 137.4, 136.6, 135.1, 134.6, 134.4, 133.3, 132.4, 132.1, 131.9, 131.9, 131.7, 131.5, 131.3, 129.0, 128.8, 128.7, 128.4, 128.2, 127.4, 124.4, 123.9, 123.7, 123.6, 123.3, 123.1, 122.8, 120.9, 91.5, 90.3, 89.9, 89.4, 89.2, 89.1, 88.9, 88.7, 50.2, 49.5, 29.7, 29.7, 20.2, 20.1, 13.8, 13.7; FD-LRMS *m*/*z* 1422.5 (M$^+$, 89%), 1423.5 ([M+1]$^+$, 100), 1424.5 ([M+2]$^+$, 66), 1425.5 ([M+3]$^+$, 29), 1426.5 ([M+4]$^+$, 10), 1427.5 ([M+5]$^+$, 3); FD-HRMS Found: 1422.60403, Calc. for $C_{102}H_{78}N_4O_4$: 1422.60230; UV λ_{max}(CH$_2$Cl$_2$)/nm (log ε) 333 (sh. 4.72), 305 (5.36), 289 (5.45); CD λ(CH$_2$Cl$_2$)/nm ($\Delta\varepsilon$) 348 (+24.5), 340 (+20.7), 321 (+100.3), 312 (+10.3), 306 (+97.2), 283 (–34.6), 271 (–0.1).

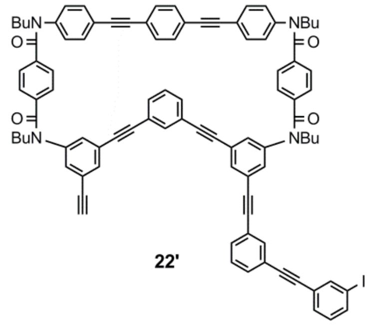
(–)-**1a**: mp 264-265 °C (dec); $[\alpha]_D^{29} = -400$ (c = 0.217 gdL^{-1} in chloroform); FD-LRMS *m*/*z* 1422.6 (M$^+$, 87%), 1423.6 ([M+1]$^+$, 100), 1424.6 ([M+2]$^+$, 62), 1425.6 ([M+3]$^+$, 27), 1426.6 ([M+4]$^+$, 10), 1427.6 ([M+5]$^+$, 4); FD-HRMS Found: 1422.60220, Calc. for $C_{102}H_{78}N_4O_4$: 1422.60230; CD λ(CH$_2$Cl$_2$)/nm ($\Delta\varepsilon$) 348 (–24.2), 340 (–20.2), 321 (–97.3), 312 (–8.9), 306 (–93.7), 283 (+39.2), 271 (+2.2).

1b: mp 239.0-239.5 °C (dec); IR (KBr) ν_{max}/cm^{-1} 3060, 3039, 2955, 2929, 2870, 2860, 2213, 1656, 1650, 1595, 1580, 1518; ^{1}H NMR δ_H(400 MHz; CDCl$_3$; Me$_4$Si)/ppm 7.76 (2H, br.dt), 7.74 (1H, br.dt), 7.60 (2H, t, *J* = 1.6 Hz), 7.57-7.48 (8H, m), 7.42-7.31 (5H, m), 7.40 (4H, s), 7.33 (4H, d, *J* = 8.4 Hz), 7.24 (2H, dd, *J* = 1.6, 2.0 Hz), 7.18 (4H, d, *J* = 8.4 Hz), 7.15 (4H, d, *J* = 8.4 Hz), 6.80 (4H, d, *J* = 8.4 Hz), 6.75 (2H, dd, *J* = 1.6, 2.0 Hz), 4.18-4.07 (4H, br.m), 3.75-3.52 (4H, br.m), 1.70-1.39 (8H, br.m), 1.41-1.25 (8H, m), 0.91 (6H, t, *J* = 7.2 Hz), 0.88 (6H, t, *J* = 7.2 Hz); ^{13}C NMR δ_C(100 MHz; CDCl$_3$)/ppm 169.8, 168.5, 143.6, 143.2, 137.5, 136.4, 136.2, 135.3, 135.3, 133.3, 132.4, 131.9, 131.7, 131.5, 131.3, 130.8, 128.9, 128.8, 128.7, 128.6, 128.4, 127.5, 127.2, 124.6, 123.8, 123.6, 123.3, 123.0, 123.0, 122.7, 121.3, 90.3, 90.1, 89.9, 89.8, 89.5, 89.0, 88.4, 87.9, 49.9, 49.8, 29.7, 29.7, 20.1, 13.8, 13.7; FD-LRMS *m*/*z* 1422.5 (M$^+$, 87%), 1423.5 ([M+1]$^+$, 100), 1424.5 ([M+2]$^+$, 60), 1425.5 ([M+3]$^+$, 24), 1426.5 ([M+4]$^+$, 9), 1427.5 ([M+5]$^+$, 3); FD-HRMS Found: 1422.60199, Calc. for $C_{102}H_{78}N_4O_4$: 1422.60230; UV λ_{max}(CH$_2$Cl$_2$)/nm (log ε) 362 (sh. 4.56), 337 (sh. 4.66), 303 (sh. 5.25), 287 (5.36).

Preparation of (±)-**3a** and **3b**

To a solution of **22** (413 mg, 0.257 mmol) in THF (9 mL) was added TBAF (1 M in THF, 0.28 mL, 0.28 mmol) at room temperature, and the mixture was stirred at that temperature for 30 min. After removal of the solvent, the residue was dissolved in ethyl acetate, and which was washed with 0.5 M aq. HCl and brine, dried over magnesium sulfate, concentrated, and then purified by column chromatography on SiO$_2$ (ethyl acetate/dichloromethane) to give **22'** (363 mg) as a white solid in 97% yield. **22'**: ^{1}H NMR δ_H(400 MHz; CDCl$_3$; Me$_4$Si)/ppm[11] 7.89 (1H, t, *J* = 1.6 Hz), 7.73 (1H, br.t), 7.68 (1H, ddd, *J* = 1.2, 2.0, 8.0 Hz), 7.66 (1H, br.t), 7.61 (1H, br.t), 7.56-7.47 (5H, m), 7.41 (2H, d, *J* = 8.4 Hz), 7.40 (2H, d, *J* = 8.4 Hz), 7.40-7.28 (5H, m), 7.13 (4H, s), 7.11 (4H, br.d), 7.08 (1H, t, *J* = 8.0 Hz), 6.83 (4H, br.d), 6.75 (1H, br.t), 6.70 (1H, br.t), 4.37-3.46 (8H, br.m), 3.21 (1H, s), 1.58 (8H, br.s), 1.42-1.28 (8H, m), 0.94 (3H, t, *J* = 7.2 Hz), 0.92 (3H, t, *J* = 7.6 Hz), 0.90 (3H, t, *J* = 7.2 Hz), 0.88 (3H, t, *J*

= 7.2 Hz).



22'

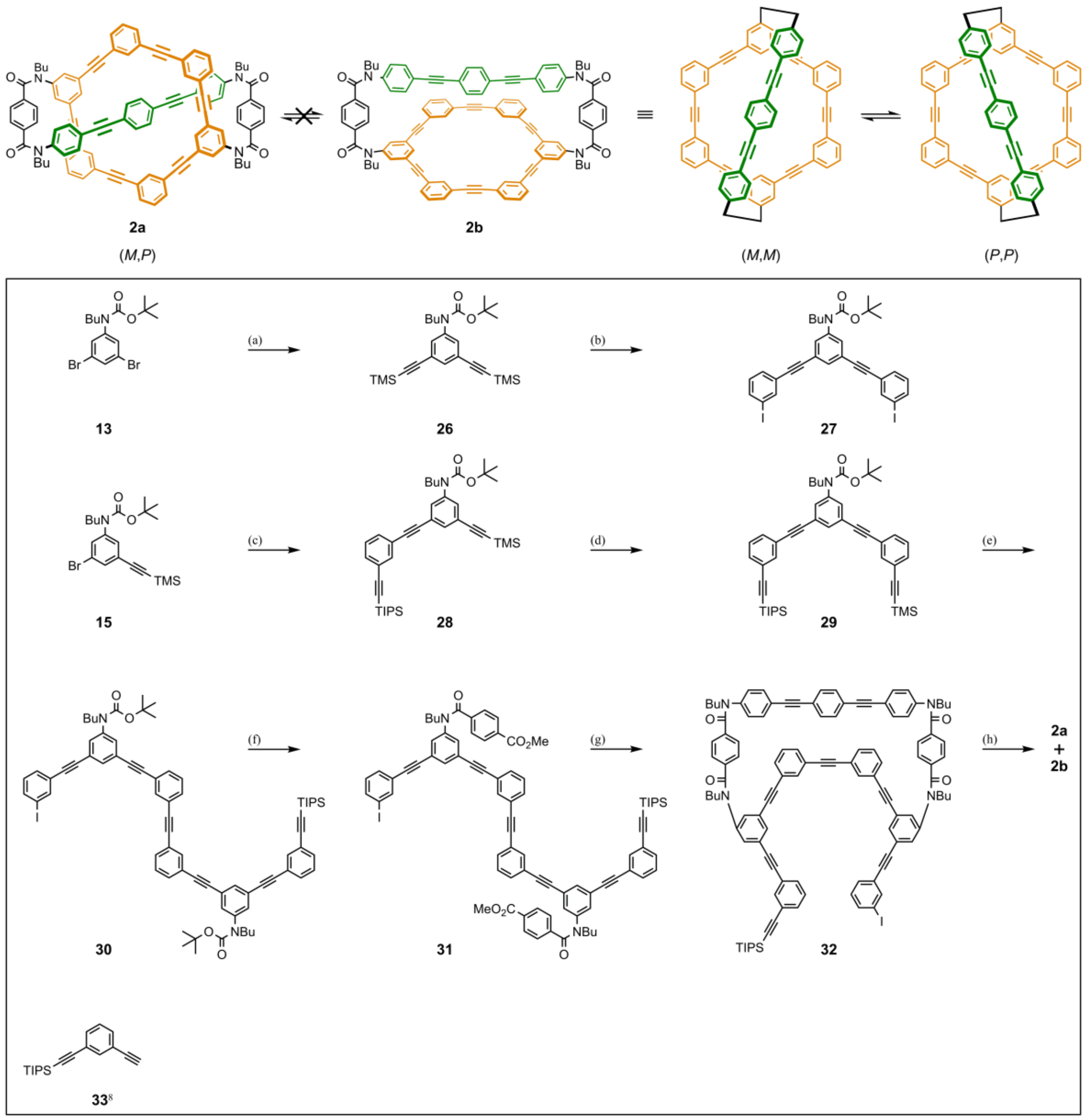
To a solution of $Pd(PPh_3)_4$ (240 mg, 0.208 mmol) and CuI (42 mg, 0.22 mmol) in Et_3N (52 mL) was added a solution of **22'** (504 mg, 0.347 mmol) in THF (27 mL) via a syringe pump over 35 h at 75 °C under an argon atmosphere. After removal of the solvents by evaporation, the residue was dissolved in dichloromethane, and which was washed with 0.5 M aq. HCl and brine, dried over magnesium sulfate, and then purified by column chromatography on SiO_2 (ethyl acetate/dichloromethane), followed by GPC (chloroform) to give a purified mixture of (±)-**3a** and **3b** (358 mg, (±)-**3a**:**3b** = 1:5.5) as a yellow solid in 78% yield. (–)-**3a** was first isolated by HPLC with a chiral stationary column (5:95 ethanol/chloroform; CHIRALPAK IF, DAICEL Co.), and **3b** and (+)-**3a** were eluted in this order and collected as a mixture. Next, **3b** and (+)-**3a** were partly separated by repeated HPLC with a standard normal-phase column (8:92 tetrahydrofuran/dichloromethane). Each analytical sample was obtained as a white solid by reprecipitation with ethyl acetate/hexane.

(–)-**3a**: mp 263-266 °C (dec); $[\alpha]_D^{29} = -315$ (c = 0.221 gdL^{-1} in chloroform); IR (KBr) ν_{max}/cm^{-1} 3060, 3040, 2954, 2929, 2869, 2860, 2208, 1655, 1650, 1591, 1578, 1518; ^1H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 8.21 (2H, t, J = 1.6 Hz), 8.11 (4H, s), 8.07 (1H, t, J = 1.6 Hz), 7.67 (2H, t, J = 1.6 Hz), 7.57-7.43 (7H, m), 7.41 (2H, t, J = 8.0 Hz), 7.27 (4H, d, J = 8.4 Hz), 7.18 (4H, d, J = 8.4 Hz), 7.17 (2H, t, J = 1.6 Hz), 7.06 (4H, d, J = 8.4 Hz), 6.84 (2H, t, J = 1.6 Hz), 6.80 (4H, br.d), 4.04-3.93 (4H, m), 3.79-3.64 (4H, m), 1.63-1.45 (8H, m), 1.39-1.27 (8H, m), 0.91 (6H, t, J = 7.2 Hz), 0.87 (6H, t, J = 7.2 Hz); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 169.4, 169.3, 143.8, 143.1, 137.7, 137.1, 136.6, 136.3, 132.2, 132.0, 131.0, 130.9, 130.2, 130.2, 129.2, 129.0, 128.7, 128.3, 127.6, 124.2, 124.2, 123.6, 123.4, 123.3, 123.2, 120.9, 93.9, 90.8, 90.3, 90.2, 89.9, 89.3, 89.3, 50.6, 49.2, 29.8, 29.5, 20.1, 20.1, 13.8, 13.7; FD-LRMS m/z 1322.6 (M^+, 95%), 1323.6 ($[M+1]^+$, 100), 1324.6 ($[M+2]^+$, 58), 1325.6 ($[M+3]^+$, 23), 1326.6 ($[M+4]^+$, 8); FD-HRMS Found: 1322.57117, Calc. for $C_{94}H_{74}N_4O_4$: 1322.57100; UV $\lambda_{max}(CH_2Cl_2)$/nm (log ε) 356 (sh. 4.56), 337 (4.71), 305 (5.23), 289 (5.33); CD $\lambda(CH_2Cl_2)$/nm ($\Delta\varepsilon$) 358 (–41.5), 332 (–58.1), 310 (+12.4), 307 (+4.2), 286 (+86.2), 266 (–35.1).

(+)-**3a**: $[\alpha]_D^{20} = +316$ (c = 0.0217 gdL^{-1} in chloroform); FD-LRMS m/z 1322.5 (M^+, 95%), 1323.5 ($[M+1]^+$, 100), 1324.5 ($[M+2]^+$, 56), 1325.5 ($[M+3]^+$, 21), 1326.5 ($[M+4]^+$, 7), 1327.5 ($[M+5]^+$, 2); FD-HRMS Found: 1322.56948, Calc. for $C_{94}H_{74}N_4O_4$: 1322.57100; CD $\lambda(CH_2Cl_2)$/nm ($\Delta\varepsilon$) 358 (+41.8), 332 (+58.3), 310 (–11.1), 307 (–2.6), 286 (–81.2), 266 (+34.9).

3b: mp 246.5-247.0 °C (dec); IR (KBr) ν_{max}/cm^{-1} 3062, 3040, 2957, 2929, 2870, 2861, 2213, 1655, 1649, 1592, 1580, 1518; ^1H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.88 (2H, br.dt), 7.81 (2H, t, J = 1.6 Hz), 7.75 (1H, br.dt), 7.57-7.51 (5H, m), 7.51-7.39 (4H, m), 7.47 (4H, s), 7.34 (4H, d, J = 8.4 Hz), 7.27 (2H, dd, J = 1.6, 2.0 Hz), 7.19 (4H, d, J = 8.0 Hz), 7.13 (4H, d, J = 8.0 Hz), 6.83 (4H, d, J = 8.4 Hz), 6.63 (2H, dd, J = 1.6, 2.0 Hz), 4.14 (2H, br.s), 4.07 (2H, br.s), 3.63 (4H, br.s), 1.70-1.41 (8H, br.m), 1.39-1.28 (8H, m), 0.89 (6H, t, J = 7.2 Hz), 0.89 (6H, t, J = 7.2 Hz); ^{13}C NMR δ_C(100 MHz;

$CDCl_3$)/ppm 169.3, 169.3, 144.0, 142.9, 137.9, 137.6, 136.5, 132.3, 131.8, 130.7, 130.2, 130.0, 129.7, 129.0, 129.0, 128.4, 128.2, 127.6, 127.0, 124.4, 123.9, 123.6, 123.3, 123.2, 123.1, 121.3, 91.3, 91.0, 90.5, 89.8, 89.7, 89.4, 89.1, 50.5, 49.3, 29.8, 29.7, 20.1, 13.8; FD-LRMS *m*/*z* 1322.6 (M^+, 95%), 1323.6 ($[M+1]^+$, 100), 1324.6 ($[M+2]^+$, 56), 1325.6 ($[M+3]^+$, 21), 1326.6 ($[M+4]^+$, 7); FD-HRMS Found: 1322.57095, Calc. for $C_{94}H_{74}N_4O_4$: 1322.57100; UV λ_{max}(CH_2Cl_2)/nm (log ε) 355 (sh. 4.53), 336 (4.69), 304 (sh. 5.16), 287 (5.29).



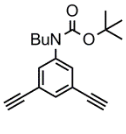
Scheme S2. Synthesis of **2a**/**2b**. Reagents and yields: (a) TMSA, $Pd(PPh_3)_4$, CuI, Et_3N (100%); (b) i) K_2CO_3, MeOH, THF (93% for **26'**); ii) 1,3-diiodobenzene, $Pd(PPh_3)_4$, CuI, Et_3N (63%); (c) **33**[8], $Pd(PPh_3)_4$, CuI, $^i Pr_2NH$, THF (98%); (d) i) K_2CO_3, MeOH, THF (96% for **28'**); ii) **23**, $Pd(PPh_3)_4$, CuI, $^i Pr_2NH$, THF (89%); (e) i) K_2CO_3, MeOH, THF (93% for **29'**); ii) **27**, $Pd(PPh_3)_4$, CuI, $^i Pr_2NH$, THF (69%); (f) i) TFA, CH_2Cl_2 (91% for **30'**); ii) methyl 4-(chloroformyl)benzoate, Et_3N, toluene (92%); (g) i) LiOH, H_2O, MeOH, THF (97% for **31'**); ii) $SOCl_2$, $BnEt_3NCl$, CH_2Cl_2; iii) **8'**, Et_3N, THF, toluene (51%); (h) i) TBAF, THF (94% for **32'**); ii) $Pd(PPh_3)_4$, CuI, Et_3N, THF (30%).

Preparation of **26**

To a solution of **13** (2.06 g, 5.06 mmol), $Pd(PPh_3)_4$ (176 mg, 0.152 mmol) and CuI (60 mg, 0.32 mmol) in Et_3N (50 mL) was added TMSA (2.86 mL, 20.2 mmol) at room temperature under an argon atmosphere, and the mixture was stirred at 52 °C for 8 h. After removal of a solid by filtration through a Celite pad, the filtrate was concentrated and purified by column chromatography on SiO_2 (dichloromethane/hexane) to give **26** (2.22 g) as a light-brown oil in 100% yield. An analytical sample was obtained as a colorless oil by further purification through GPC (chloroform). **26**: elemental analyses Found: C, 67.89; H, 8.96; N, 3.17%. Calc. for $C_{25}H_{39}NO_2Si_2$: C, 67.97; H, 8.90; N, 3.17%; IR (neat) $\nu_{\max}$/cm^{-1} 3067, 2961, 2932, 2900, 2874, 2863, 2155, 1707, 1581; ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.42 (1H, t, *J* = 1.2 Hz), 7.23 (2H, br.d), 3.58 (2H, t, *J* = 7.6 Hz), 1.52-1.44 (2H, m), 1.43 (9H, s), 1.33-1.24 (2H, m), 0.89 (3H, t, *J* = 7.2 Hz), 0.24 (18H, s); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 154.2, 142.6, 133.0, 130.6, 123.8, 103.5, 95.1, 80.4, 49.5, 30.5, 28.3, 19.9, 13.7, –0.2; FD-LRMS *m*/*z* 441.3 (M$^+$, 100%), 442.3 ([M+1]$^+$, 41), 443.3 ([M+2]$^+$, 16), 444.3 ([M+3]$^+$, 4).

Preparation of **27**

To a solution of **26** (2.01 g, 4.55 mmol) in THF (23 mL) and MeOH (23 mL) was added K_2CO_3 (1.26 g, 9.09 mmol) at room temperature, and the mixture was stirred at that temperature for 30 min. After removal of a solid by filtration, the filtrate was concentrated and purified by column chromatography on SiO_2 (dichloromethane/hexane) to give **26'** (1.25 g) as a white solid in 93% yield. **26'**: ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.44 (1H, t, *J* = 1.2 Hz), 7.31 (2H, br,d), 3.60 (2H, d, *J* = 7.6 Hz), 3.09 (2H, s), 1.55-1.45 (2H, m), 1.44 (9H, s), 1.34-1.25 (2H, m), 0.90 (3H, t, *J* = 7.6 Hz).



26'

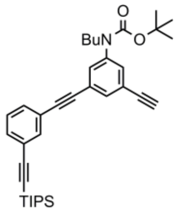
To a solution of **26'** (1.25 g, 4.21 mmol) and 1,3-diiodobenzene (5.56 g, 16.8 mmol) in Et_3N (90 mL) were added $Pd(PPh_3)_4$ (486 mg, 0.421 mmol) and CuI (162 mg, 0.851 mmol) at room temperature under an argon atmosphere, and the mixture was stirred at 50 °C for 18 h. After removal of a solid by filtration through a Celite pad, the filtrate was concentrated and purified by column chromatography on SiO_2 (dichloromethane/hexane) to give **27** (1.85 g) as a yellow oil in 63% yield. An analytical sample was obtained as a white amorphous solid by further purification through GPC (chloroform). **27**: mp 74-75 °C; elemental analyses Found: C, 53.11; H, 4.07; N, 2.01%. Calc. for $C_{31}H_{29}I_2NO_2$: C, 53.09; H, 4.17; N, 2.00%; IR (KBr) $\nu_{\max}$/cm^{-1} 3052, 2955, 2927, 2870, 2860, 2211, 1702, 1586, 1546; ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.90 (2H, t, *J* = 1.2 Hz), 7.69 (2H, ddd, *J* = 1.2, 2.0, 8.0 Hz), 7.51 (1H, t, *J* = 1.6 Hz), 7.49 (2H, br.ddd), 7.34 (2H, br.d), 7.09 (2H, t, *J* = 8.0 Hz), 3.64 (2H, t, *J* = 7.6 Hz), 1.58-1.50 (2H, m), 1.46 (9H, s), 1.37-1.28 (2H, m), 0.92 (3H, t, *J* = 7.6 Hz); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 154.2, 142.9, 140.1, 137.5, 132.0, 130.7, 130.2, 129.8, 124.8, 123.6, 93.7, 89.2, 88.4, 80.5, 49.5, 30.5, 28.3, 19.8, 13.8; FD-LRMS *m*/*z* 701.0 (M$^+$, 100%), 702.0 ([M+1]$^+$, 36), 703.0 ([M+2]$^+$, 7).

Preparation of **28**

To a solution of **15** (3.00 g, 7.08 mmol) and **33** (5.19 g, 18.4 mmol) in THF (35 mL) and $^i Pr_2NH$ (35 mL) were added $Pd(PPh_3)_4$ (245 mg, 0.212 mmol) and CuI (84 mg, 0.44 mmol) at room temperature under an argon atmosphere, and the mixture was stirred at 80 °C for 16 h. After removal of a solid by filtration through a Celite pad, the filtrate was concentrated and purified by column chromatography on SiO_2 (dichloromethane/hexane) to give **28** (4.32 g) as a pale yellow oil in 98% yield. An analytical sample was obtained as a colorless oil by further purification through GPC (chloroform). **28**: elemental analyses Found: C, 74.79; H, 9.11; N, 2.19%. Calc. for $C_{39}H_{55}NO_2Si_2$: C, 74.82; H, 8.86; N, 2.24%; IR (KBr)* ν_{max}/cm^{-1} 3063, 2959, 2942, 2892, 2864, 2157, 1706, 1595, 1582 (*too highly viscous to be applied to a plate of NaCl); ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.63 (1H, br.dt), 7.48 (1H, t, *J* = 1.6 Hz), 7.45 (1H, br.dd), 7.43 (1H, d, *J* = 1.6 Hz), 7.31-7.26 (3H, br.m), 3.61 (2H, t, *J* = 7.6 Hz), 1.55-1.47 (2H, m), 1.44 (9H, s), 1.35-1.26 (2H, m), 1.14 (21H, s), 0.91 (3H, t, *J* = 7.6 Hz), 0.25 (9H, s); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 154.3, 142.8, 135.1, 132.6, 131.9, 131.3, 130.4, 130.4, 128.3, 124.0, 123.9, 123.7, 123.0, 106.0, 103.6, 95.3, 91.5, 89.2, 88.6, 80.4, 49.5, 30.5, 28.3, 19.9, 18.6, 13.8, 11.3, –0.1; FD-LRMS *m*/*z* 625.4 (M^+, 100%), 626.4 ($[M+1]^+$, 56), 627.4 ($[M+2]^+$, 23), 628.4 ($[M+3]^+$, 6).

Preparation of **29**

To a solution of **28** (4.02 g, 6.43 mmol) in THF (16 mL) and MeOH (16 mL) was added K_2CO_3 (890 mg, 6.45 mmol) at room temperature, and the mixture was stirred at that temperature for 20 min. After removal of a solid by filtration, the filtrate was concentrated and purified by column chromatography on SiO_2 (dichloromethane/hexane) to give **28'** (3.43 g) as a pale yellow oil in 96% yield. **28'**: ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.64 (1H, br.dt), 7.48 (1H, t, *J* = 1.6 Hz), 7.47-7.43 (2H, m), 7.35 (1H, br.m), 7.31-7.27 (2H, m), 3.62 (2H, t, *J* = 7.6 Hz), 3.10 (1H, s), 1.56-1.48 (2H, m), 1.47 (9H, s), 1.36-1.27 (2H, m), 1.14 (21H, s), 0.91 (3H, t, *J* = 7.6 Hz).

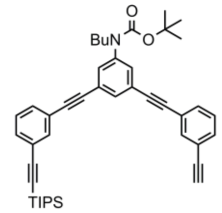


28'

To a solution of **23** (3.35 g, contained 1-bromo-3-(2-trimethylsilyl)ethynylbenzene in a ratio of 5:1), $Pd(PPh_3)_4$ (215 mg, 0.186 mmol) and CuI (71 mg, 0.37 mmol) in ^{i}Pr$_2$NH (31 mL) and THF (25 mL) was added a solution of **28'** (3.43 g, 6.20 mmol) in THF (6 mL) via a syringe pump over 1.5 h at 50 °C under an argon atmosphere, and the mixture was further stirred at that temperature for 30 min. After removal of a solid by filtration through a Celite pad, the filtrate was concentrated and purified by column chromatography on SiO_2 (dichloromethane/hexane) to give **29** (3.99 g) as a pale yellow amorphous solid in 89% yield. An analytical sample was obtained as a pale yellow oil due to residual hexane, which was indicated by a result of the elemental analyses, by further purification through HPLC. **29**: elemental analyses Found: C, 77.79; H, 8.55; N, 1.81%. Calc. for $C_{47}H_{59}NO_2Si_2$: C, 77.74; H, 8.19; N, 1.93%; IR (KBr) ν_{max}/cm^{-1} 3062, 2959, 2941, 2891, 2864, 2158, 1704, 1595, 1582; ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.65 (2H, br.dt), 7.52 (1H, t, *J* = 1.6 Hz), 7.48-7.42 (4H, m), 7.34-7.27 (4H, m), 3.64 (2H, t, *J* = 7.6 Hz), 1.58-1.50 (2H, m), 1.46 (9H, s), 1.37-1.28 (2H, m), 1.14 (21H, s), 0.92 (3H, t, *J* = 7.2 Hz), 0.26 (9H, s); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 154.3, 142.9, 135.1, 135.1, 132.1, 132.0, 131.8, 131.5, 131.3, 130.2, 128.4, 123.9, 123.9, 123.5, 123.1, 123.0, 106.0, 104.0, 95.1, 91.5, 89.3, 89.3, 88.6, 88.6, 80.5, 49.6, 30.6, 28.3, 19.9, 18.6, 13.8, 11.3, –0.1; FD-LRMS *m*/*z* 725.4 (M^+, 100%), 726.4 ($[M+1]^+$, 64), 727.4 ($[M+2]^+$, 28), 728.4 ($[M+3]^+$, 9), 729.4 ($[M+4]^+$, 2).

Preparation of **30**

To a solution of **29** (2.36 g, 3.25 mmol) in THF (12 mL) and MeOH (8 mL) was added K_2CO_3 (448 mg, 3.25 mmol) at room temperature, and the mixture was stirred at that temperature for 10 min. After removal of a solid by filtration, the filtrate was concentrated and purified by column chromatography on SiO_2 (dichloromethane/hexane) to give **29'** (1.97 g) as a pale yellow oil in 93% yield. **29'**: ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.67-7.66 (2H, br.m), 7.54 (1H, t, J = 1.2 Hz), 7.50 (1H, dt, J = 1.2, 7.6 Hz), 7.48-7.44 (3H, m), 7.37-7.28 (4H, br.m), 3.64 (2H, t, J = 7.6 Hz), 3.10 (1H, s), 1.58-1.51 (2H, m), 1.46 (9H, s), 1.38-1.28 (2H, m), 1.14 (21H, s), 0.92 (3H, t, J = 7.6 Hz).

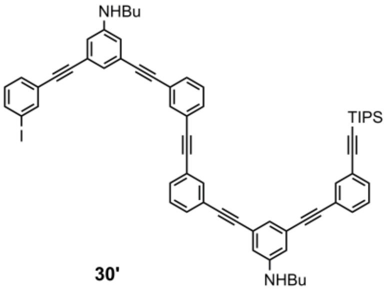


29'

To a solution of **27** (6.92 g, 9.86 mmol), $Pd(PPh_3)_4$ (348 mg, 0.301 mmol) and CuI (116 mg, 0.609 mmol) in $^i Pr_2NH$ (30 mL) and THF (24 mL) was added a solution of **29'** (1.97 g, 3.01 mmol) in THF (6 mL) via a syringe pump over 1.5 h at 50 °C under an argon atmosphere, and the mixture was further stirred at that temperature for 30 min. After removal of a solid by filtration through a Celite pad, the filtrate was concentrated and purified by column chromatography on SiO_2 (dichloromethane/hexane) to give **30** (2.59 g) as a white amorphous solid in 69% yield. An analytical sample was obtained as a white solid by further purification with HPLC (dichloromethane/hexane), followed by GPC (chloroform). **30**: mp 74-75 °C; elemental analyses Found: C, 73.36; H, 6.46; N, 2.26%. Calc. for $C_{75}H_{79}IN_2O_4Si$: C, 73.39; H, 6.49; N, 2.28%; IR (KBr) ν_{max}/cm^{-1} 3061, 2957, 2939, 2929, 2862, 2215, 2156, 1702, 1596; ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.90 (1H, t, J = 1.6 Hz), 7.72 (2H, br.t), 7.68 (1H, ddd, J = 1.2, 2.0, 8.0 Hz), 7.66 (1H, br.dt), 7.55-7.44 (9H, m), 7.38-7.32 (6H, m), 7.30 (1H, br.t), 7.09 (1H, t, J = 7.6 Hz), 3.65 (2H, t, J = 7.2 Hz), 3.65 (2H, t, J = 7.6 Hz), 1.59-1.51 (4H, m), 1.46 (18H, br.s), 1.38-1.29 (4H, m), 1.14 (21H, s), 0.93 (6H, t, J = 7.2 Hz); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 154.3, 154.3, 143.0, 142.9, 140.2, 137.5, 135.1, 134.6, 132.1, 132.1, 132.0, 131.6, 131.6, 131.5 (br), 131.3, 130.7, 130.3, 130.2 (br.), 129.9, 128.6, 128.4, 124.9, 123.9, 123.9, 123.8, 123.7, 123.4, 123.4, 123.3, 123.2, 123.0, 106.0, 93.7, 91.5, 89.4, 89.3, 89.2, 89.1, 89.1, 88.7, 88.7, 88.6, 88.4, 80.6, 80.5, 49.6, 30.6, 28.3, 19.9, 18.6, 13.8, 11.3; FD-LRMS m/z 1026.4 ($[M-(BOC)_2]^+$, 55%), 1027.4 ($[M+1-(BOC)_2]^+$, 42), 1028.4 ($[M+2-(BOC)_2]^+$, 19), 1029.4 ($[M+3-(BOC)_2]^+$, 6), 1030.4 ($[M+4-(BOC)_2]^+$, 2), 1070.3 ($[M-(TIPS)]^+$, 3), 1071.3 ($[M+1-(TIPS)]^+$, 15), 1072.3 ($[M+2-(TIPS)]^+$, 11), 1073.3 ($[M+3-(TIPS)]^+$, 5), 1074.3 ($[M+4-(TIPS)]^+$, 2), 1126.4 ($[M-(BOC)]^+$, 96), 1127.4 ($[M+1-(BOC)]^+$, 100), 1128.4 ($[M+2-(BOC)]^+$, 54), 1129.4 ($[M+3-(BOC)]^+$, 20), 1130.4 ($[M+4]^+$, 6), 1226.5 (M^+, 30), 1227.5 ($[M+1]^+$, 26), 1228.5 ($[M+2]^+$, 13), 1229.5 ($[M+3]^+$, 5), 1230.5 ($[M+4]^+$, 1).

Preparation of **31**

To a solution of **30** (1.54 g, 1.25 mmol) in CH_2Cl_2 (82 mL) was added TFA (8.2 mL) at room temperature. The mixture was stirred at room temperature for 30 min, neutralized with 1M aq. NaOH, and separated. The organic layer was dried over magnesium sulfate, passed through a Celite/SiO_2 pad,

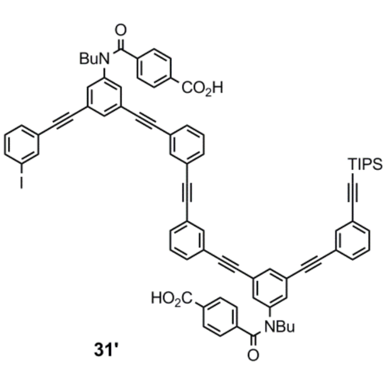


30'

and then concentrated. The residue was purified by column chromatography on SiO_2 (dichloromethane/hexane) to give **30'** (1.17 g) as a white amorphous solid in 91% yield. **30'**: ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.89 (1H, t, J = 1.6 Hz), 7.71 (2H, t, J = 1.6 Hz), 7.68-7.64 (2H, m), 7.50-7.42 (7H, m), 7.37-7.26 (3H, m), 7.08 (1H, t, J = 7.6 Hz), 7.06 (1H, t, J = 1.2 Hz), 7.05 (1H, t, J = 1.2 Hz), 6.75-6.71 (4H, m), 3.72 (2H, br.s), 3.15 (2H, br.t), 3.14 (2H, br.t), 1.67-1.59 (4H, m), 1.50-1.40 (4H, m), 1.13 (21H, s), 0.98 (6H, t, J = 7.6 Hz).

To a solution of **30'** (1.17 g, 1.14 mmol) in toluene (20 mL) containing Et_3N (0.8 mL) were added two portions of methyl 4-(chloroformyl)benzoate (477+238 mg, 2.40+1.20 mmol) at room temperature, and the reaction mixture was stirred at 80 °C for each 1.5 h. The mixture was diluted with dichloromethane, and which was washed with satd. aq. $NaHCO_3$, dried over magnesium sulfate, and then passed through a Celite/Al_2O_3 pad. The filtrate was concentrated and purified by column chromatography on Al_2O_3/SiO_2 (ethyl acetate/dichloromethane) to give **31** (1.42 g) as a white amorphous solid in 92% yield. An analytical sample was obtained as a white solid by further purification through GPC (chloroform). **31**: mp 104-105 °C; elemental analyses Found: C, 73.69; H, 5.52; N, 2.07%. Calc. for $C_{83}H_{75}IN_2O_6Si$: C, 73.76; H, 5.59; N, 2.07%; IR (KBr) ν_{max}/cm^{-1} 3059, 2940, 2861, 2214, 2154, 1725, 1652, 1595, 1580; ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.91 (4H, d, J = 8.4 Hz), 7.87 (1H, t, J = 1.6 Hz), 7.71-7.67 (3H, m), 7.63 (1H, br.dt), 7.53-7.35 (15H, m), 7.30 (1H, br.dt), 7.16 (4H, br.d), 7.09 (1H, br.t), 3.93 (4H, t, J = 7.6 Hz), 3.88 (3H, s), 3.87 (3H, s), 1.68-1.60 (4H, m), 1.44-1.35 (4H, m), 1.13 (21H, s), 0.95 (6H, t, J = 7.6 Hz); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 169.2, 166.3, 143.4, 140.2, 140.0, 140.0, 137.8, 135.0, 134.6, 133.2, 132.2, 131.9, 131.8, 131.5 (br.m), 131.3, 131.0 (br.m), 130.7, 130.7, 130.6, 130.6, 129.9, 129.3, 128.6, 128.5, 128.4, 124.7, 124.6, 124.5, 124.4, 124.0, 123.4, 123.4, 122.8, 122.8, 122.5, 105.8, 93.7, 91.7, 90.3, 90.2, 90.1, 89.3, 89.1, 89.1, 88.5, 87.9, 87.9, 87.7, 52.2, 50.2, 29.7, 20.1, 18.6, 13.8, 11.2; FD-LRMS m/z 1307.4 ([M–(^{i}Pr)]$^+$, 63%), 1308.4 ([M+1–(^{i}Pr)]$^+$, 58), 1309.4 ([M+2–(^{i}Pr)]$^+$, 30), 1310.4 ([M+3–(^{i}Pr)]$^+$, 12), 1311.4 ([M+4–(^{i}Pr)]$^+$, 4), 1350.4 (M$^+$, 99), 1351.4 ([M+1]$^+$, 100), 1352.4 ([M+2]$^+$, 56), 1353.4 ([M+3]$^+$, 22), 1354.4 ([M+4]$^+$, 7).

Preparation of **32**



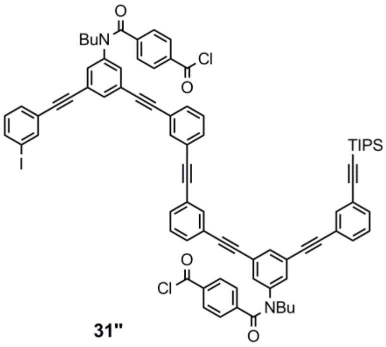
31'

To a solution of **31** (1.42 g, 1.05 mmol) in THF (22 mL) and MeOH (7 mL) was added a solution of $LiOH \cdot H_2O$ (224 mg, 5.25 mmol) in water (7 mL) at room temperature, and the resulting suspension was stirred at 40-50 °C for 2 h and turned transparent. The reaction mixture was acidified with 1M aq. HCl, and extracted with ethyl acetate. The organic layer was dried over magnesium sulfate, and concentrated to give carboxylic acid **31'**

(1.35 g) as an off-white amorphous solid in 97% yield.

To a refluxed solution of **31'** (627 mg, 0.474 mmol) in CH_2Cl_2 (15 mL) containing a catalytic amount of benzyltriethylammonium chloride was added $SOCl_2$ (0.20 mL, 2.8 mmol), and the mixture was refluxed for 1.5 h, and concentrated to give acid chloride **31''**, which was dissolved in THF, and immediately subjected to the following reaction.

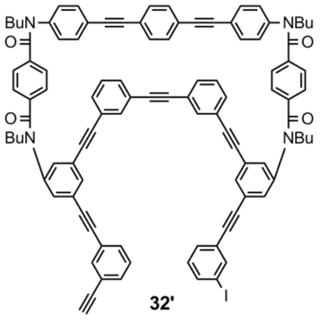
To a solution of **8'** (191 mg, 0.454 mmol) and Et_3N (0.64 mL, 4.6 mmol) in toluene (56 mL) and THF (30 mL) was added a solution of **31''** in THF (30 mL) at 92 °C, and the mixture was stirred at 95 °C for 1 h. After removal of the solvents by evaporation, the residue was dissolved in dichloromethane, and which was washed with 1M aq. NaOH, dried over magnesium sulfate, passed through a Celite/Al_2O_3 pad, and then concentrated. The crude product was purified by column chromatography on SiO_2/Al_2O_3 (ethyl acetate/dichloromethane), followed by GPC (chloroform) to give **32** (398 mg) as a white solid in 51% yield. An analytical sample was obtained as a white solid by further purification with HPLC (ethyl acetate/dichloromethane). **32**: mp 165-166 °C; elemental analyses Found: C, 77.62; H, 5.73; N, 3.28%. Calc. for $C_{111}H_{99}IN_4O_4Si\cdot(EtOH)_{1/2}$: C, 77.71; H, 5.94; N, 3.24%; IR (KBr) ν_{max}/cm^{-1} 3059, 2955, 2929, 2861, 2213, 2154, 1651, 1595, 1581, 1517; ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.91 (1H, t, J = 1.6 Hz), 7.71-7.59 (10H, br.m), 7.54-7.47 (7H, m), 7.40-7.28 (7H, m), 7.13 (8H, br.s), 7.11-7.05 (3H, m), 6.98 (2H, br.m), 6.82 (2H, d, J = 8.4 Hz), 6.82 (2H, d, J = 8.4 Hz), 3.87 (8H, t, J = 7.6 Hz), 1.64-1.50 (8H, m), 1.41-1.27 (8H, m), 1.13 (21H, s), 0.93 (6H, t, J = 7.2 Hz), 0.87 (6H, t, J = 7.2 Hz); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 169.1, 169.0, 169.0, 143.6, 143.6, 143.2, 140.1, 137.8, 136.9, 136.6, 135.0, 134.7, 134.7, 133.4, 133.4, 132.3, 131.9, 131.7, 131.7, 131.5, 131.4, 131.3, 130.8, 130.7 (br.m), 130.5, 130.4, 130.0, 128.8, 128.7, 128.5, 128.4, 128.1, 127.3, 124.5, 124.3, 124.2, 124.1, 123.5, 123.4, 123.2, 123.1, 122.9, 122.9, 122.6, 121.0, 105.8, 93.8, 92.0, 91.1, 91.0, 90.2, 90.1, 90.0, 89.8, 89.3, 89.2, 89.1, 88.8, 88.4, 88.4, 88.1, 50.0, 49.8, 29.6, 20.1, 20.1, 18.6, 13.8, 13.7, 11.2; FD-LRMS *m/z* 1706.6 (M$^+$, 80%), 1707.6 ([M+1]$^+$, 100), 1708.6 ([M+2]$^+$, 71), 1709.6 ([M+3]$^+$, 35), 1710.6 ([M+4]$^+$, 14), 1711.6 ([M+5]$^+$, 5).



31''

Preparation of **2a** and **2b**

To a solution of **32** (341 mg, 0.200 mmol) in THF (8 mL) was added TBAF (1 M in THF, 0.22 mL, 0.22 mmol) at room temperature, and the mixture was stirred at that temperature for 30 min. After removal of the solvent by evaporation, the residue was dissolved in ethyl acetate, and which was washed with 0.5 M aq. HCl, dried over magnesium sulfate, concentrated, and then purified by column chromatography on SiO_2 (ethyl acetate/dichloromethane), followed by GPC (chloroform) to give **32'** (291 mg) as a white solid in 94% yield. **32'**: ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.93 (1H, t, J = 1.6 Hz), 7.72-7.59 (10H, br.m), 7.55-7.49 (7H, m), 7.41-7.32 (7H, m), 7.14 (8H, br.s), 7.09 (3H, br.t), 7.00 (2H, br.t), 6.84 (4H, d, J = 8.8 Hz), 3.88 (8H, br.t), 3.11 (1H, s), 1.64-1.50 (8H, m), 1.42-1.27 (8H, m), 0.93 (6H, t, J = 7.2 Hz), 0.88 (6H, t, J = 7.6 Hz).

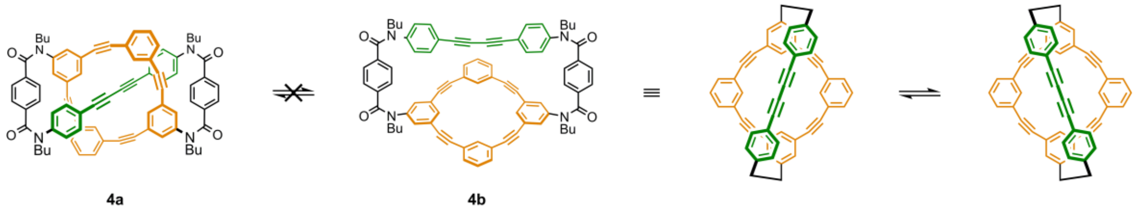


32'

To a solution of $Pd(PPh_3)_4$ (130 mg, 0.113 mmol) and CuI (22 mg, 0.12 mmol) in Et_3N (28 mL) was added a solution of **32'** (291 mg, 0.188 mmol) in THF (13 mL) via a syringe pump over 20 h at 73-75 °C under an argon atmosphere. After removal of the solvents by evaporation, the residue was purified by column chromatography on SiO_2 (ethyl acetate/dichloromethane), followed by GPC (chloroform) to give a mixture containing **2a** and **2b** (81 mg, **2a**:**2b** = 1.8:1) as a pale yellow solid in 30% yield. **2b** and **2a** were isolated in this order by HPLC separation (1:9 tetrahydrofuran/chloroform). Each analytical sample was obtained as a white solid by reprecipitation with ethyl acetate/hexane.

2a: mp >300 °C; IR (KBr) $\nu_{\mathrm{max}}/\mathrm{cm}^{-1}$ 3057, 2955, 2928, 2870, 2862, 2216, 1647, 1595, 1580, 1518; ^{1}H NMR δ_{H}(400 MHz; $CDCl_3$; Me_4Si)/ppm 8.05 (4H, s), 7.82 (4H, br.dt), 7.67 (2H, t, J = 1.2 Hz), 7.60 (4H, dt, J = 1.6, 7.6 Hz), 7.56 (4H, dt, J = 1.6, 7.6 Hz), 7.43 (4H, br.t), 7.37 (4H, d, J = 8.8 Hz), 7.15 (4H, d, J = 8.8 Hz), 7.12 (4H, d, J = 8.8 Hz), 7.01 (4H, d, J = 1.2 Hz), 6.78 (4H, d, J = 8.8 Hz), 3.87 (4H, t, J = 7.6 Hz), 3.84 (4H, t, J = 7.6 Hz), 1.65-1.46 (8H, m), 1.43-1.24 (8H, m), 0.94 (6H, t, J = 7.2 Hz), 0.84 (6H, t, J = 7.2 Hz); ^{13}C NMR δ_{C}(100 MHz; $CDCl_3$)/ppm 169.5, 169.4, 143.6, 143.2, 137.3, 136.7, 134.8, 133.7, 132.4, 132.0, 131.9, 131.5, 130.6, 128.9, 128.3, 128.1, 127.4, 124.1, 123.7, 123.5, 123.0, 120.9, 91.7, 90.1, 89.5, 89.3, 88.6, 49.9, 49.6, 29.7, 20.2, 20.1, 13.8, 13.7; FD-LRMS m/z 1422.6 (M$^+$, 89%), 1423.6 ([M+1]$^+$, 100), 1424.6 ([M+2]$^+$, 61), 1425.6 ([M+3]$^+$, 25), 1426.6 ([M+4]$^+$, 9), 1427.6 ([M+5]$^+$, 3); FD-HRMS Found: 1422.60434, Calc. for $C_{102}H_{78}N_4O_4$: 1422.60230; UV λ_{max}(CH_2Cl_2)/nm (log ε) 359 (sh. 4.62), 334 (4.72), 306 (5.34), 289 (5.43).

2b: mp >253 °C (dec); IR (KBr) $\nu_{\mathrm{max}}/\mathrm{cm}^{-1}$ 3061, 3039, 2955, 2928, 2870, 2860, 2212, 1655, 1650, 1595, 1574, 1516; ^{1}H NMR δ_{H}(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.77 (4H, br.dt), 7.60-7.53 (8H, m), 7.55 (4H, s), 7.47 (2H, t, J = 1.6 Hz), 7.44 (4H, br.dt), 7.28 (4H, d, J = 8.4 Hz), 7.22 (4H, d, J = 8.4 Hz), 7.18 (4H, d, J = 8.4 Hz), 7.01 (4H, d, J = 1.2 Hz), 6.82 (4H, d, J = 8.4 Hz), 3.88 (4H, t, J = 7.6 Hz), 3.82 (4H, t, J = 7.6 Hz), 1.62-1.45 (8H, m), 1.40-1.25 (8H, m), 0.91 (6H, t, J = 7.2 Hz), 0.86 (6H, t, J = 7.2 Hz); ^{13}C NMR δ_{C}(100 MHz; $CDCl_3$)/ppm 169.4, 169.2, 143.6, 143.2, 137.3, 136.7, 135.6, 133.0, 132.5, 131.9, 131.5, 131.2, 130.4, 128.9, 128.4, 128.3, 127.2, 124.2, 123.5, 123.3, 123.1, 121.2, 90.9, 90.0, 89.9, 89.4, 88.4, 50.1, 49.8, 29.6, 20.1, 20.1, 13.8, 13.8; FD-LRMS m/z 1422.6 (M$^+$, 90%), 1423.6 ([M+1]$^+$, 100), 1424.6 ([M+2]$^+$, 64), 1425.6 ([M+3]$^+$, 27), 1426.6 ([M+4]$^+$, 9), 1427.6 ([M+5]$^+$, 3); FD-HRMS Found: 1422.60445, Calc. for $C_{102}H_{78}N_4O_4$: 1422.60230; UV λ_{max}(CH_2Cl_2)/nm (log ε) 359 (sh. 4.64), 337 (4.72), 304 (5.29), 288 (5.39).

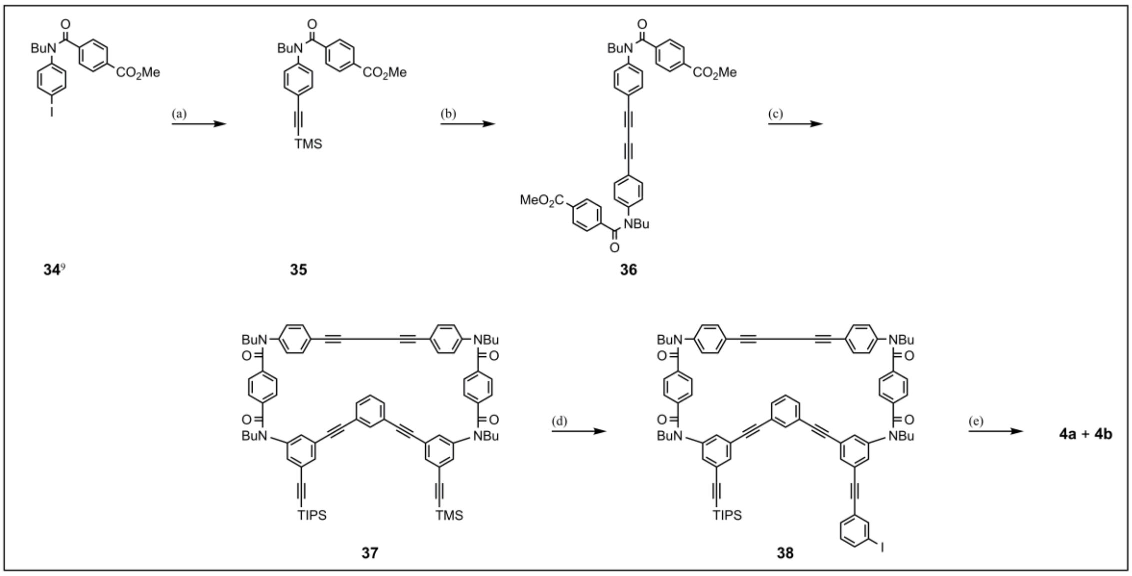


4a
(*M*,*P*)

4b

(*M*,*M*)

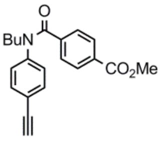
(*P*,*P*)



Scheme S3. Synthesis of **4a**/**4b**. Reagents and yields: (a) TMSA, $PdCl_2(PPh_3)_2$, CuI, Et_3N (99%); (b) i) K_2CO_3, MeOH, THF (93% for **35'**); ii) CuCl, *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA), acetone (71%); (c) i) LiOH, H_2O, MeOH, THF (65% for **36'**); ii) $SOCl_2$, $BnEt_3NCl$, CH_2Cl_2; iii) **19**, Et_3N, THF, toluene (67%); (d) i) K_2CO_3, MeOH, THF (97% for **37'**); ii) 1,3-diiodobenzene, $Pd(PPh_3)_4$, CuI, Et_3N, THF (82%); (e) i) TBAF, THF (91% for **38'**); ii) $Pd(PPh_3)_4$, CuI, Et_3N, THF (5%).

Preparation of **35**

To a suspended solution of **34** (3.19 g, 7.29 mmol), $PdCl_2(PPh_3)_2$ (76 mg, 0.11 mmol) and CuI (34 mg, 0.18 mmol) in Et_3N (60 mL) was added TMSA (1.1 mL, 7.8 mmol) at room temperature under an argon atmosphere, and the reaction mixture was stirred at the temperature for 21 h. After removal of a solid by filtration through a Celite pad, the filtrate was concentrated and purified by column chromatography on SiO_2 (ethyl acetate/dichloromethane) to give **35** (2.94 g) as a pale yellow oil in 99% yield.



35'

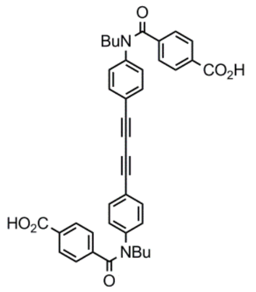
To a solution of **35** (2.94 g, 7.23 mmol) in THF (35 mL) and MeOH (35 mL) was added K_2CO_3 (974 mg, 7.06 mmol), and the mixture was stirred at room temperature for 25 min, and then diluted with ethyl acetate. The diluted solution was washed with water and brine, dried over magnesium sulfate, and then purified by column chromatography on SiO_2 (ethyl acetate/dichloromethane) to give **35'** (2.26 g) as a white solid in 93% yield. An analytical sample was obtained as a white solid by precipitation in ethyl acetate. **35'**: mp 123-124 °C; elemental analyses Found: C, 75.19; H, 6.17; N, 4.19%. Calc. for $C_{21}H_{21}NO_3$: C, 75.20; H, 6.31; N, 4.18%; IR (KBr) ν_{max}/cm^{-1} 3285, 3060, 2951, 2872, 2106, 1721, 1637, 1598, 1504; ^{1}H NMR δ_{H}(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.85 (2H, d, J = 8.4 Hz), 7.33 (2H, d, J = 8.4 Hz), 7.32 (2H, d, J = 8.4 Hz), 6.96 (2H, d, J = 8.4 Hz), 3.92 (2H, t, J = 7.6 Hz), 3.88 (3H, s), 3.07 (1H, s), 1.63-1.56 (2H, m), 1.41-1.32 (2H, m), 0.92 (3H, t, J = 7.2 Hz); ^{13}C NMR δ_{C}(100 MHz; $CDCl_3$)/ppm 169.2, 166.3, 143.3, 140.4, 133.0, 130.9, 129.1, 128.5, 127.6, 120.7, 82.5, 78.2, 52.2, 50.0, 29.8, 20.1, 13.8; FD-LRMS m/z 335.2 (M^+, 100%), 336.2 ($[M+1]^+$, 23), 337.2 ($[M+2]^+$, 3).

Preparation of **36**

To an ice-cooled solution of CuCl (242 mg, 2.44 mmol) and TMEDA (1.22 mL, 8.15 mmol) in acetone (87 mL) was added a solution of **35'** (3.58 g, 10.7 mmol) in acetone (44 mL) under an oxygen atmosphere, and the mixture was stirred at room temperature for 10 days. After removal of the solvent by evaporation, the residue was dissolved in dichloromethane, and which was washed with 0.5 M aq. HCl, dried over magnesium sulfate, and concentrated. The resulting solid was separated by column chromatography on SiO_2 (ethyl acetate/dichloromethane) to give **36** as a white solid and unreacted **35'** (895 mg, recov. 25%), which underwent a repeated procedure similar to the above (CuCl, TMEDA, acetone, dichloromethane). Combined solids were washed with methanol to give **36** (2.54 g) as a white solid in 71% yield. An analytical sample was obtained as a white solid by further purification through GPC (chloroform). **36**: mp 151-152 °C; elemental analyses Found: C, 75.01; H, 5.95; N, 4.14%. Calc. for $C_{42}H_{40}N_2O_6\cdot(EtOH)_{1/4}$: C, 75.03; H, 6.15; N, 4.12%; IR (KBr) ν_{max}/cm^{-1} 3059, 2951, 2934, 2873, 2857, 2152, 1725, 1640, 1594, 1504; ^{1}H NMR δ_{H}(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.85 (4H, d, J = 8.4 Hz), 7.35 (4H, d, J = 8.4 Hz), 7.33 (4H, d, J = 8.4 Hz), 6.97 (4H, d, J = 8.4 Hz), 3.92 (4H, t, J = 7.6 Hz), 3.88 (6H, s), 1.63-1.56 (4H, m), 1.41-1.32 (4H, m), 0.92 (6H, t, J = 7.2 Hz); ^{13}C NMR δ_{C}(100 MHz; $CDCl_3$)/ppm 169.2, 166.2, 143.8, 140.2, 133.4, 131.0, 129.2, 128.5, 127.6, 120.0, 80.9, 74.6, 52.2, 50.1, 29.8, 20.1, 13.8; FD-LRMS m/z 668.3 (M^+, 100%), 669.3 ($[M+1]^+$, 47), 670.3 ($[M+2]^+$, 13), 671.3 ($[M+3]^+$, 3).

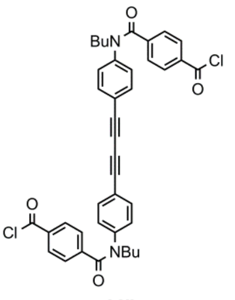
Preparation of **37**

To a suspension of **36** (2.04 g, 3.06 mmol) in THF (64 mL) and MeOH (20 mL) was added a solution of $LiOH\cdot H_2O$ (643 mg, 15.3 mmol) in water (20 mL) at room temperature, and the mixture was stirred at 45-48 °C for 3 h and turned transparent. The reaction mixture was acidified with 1M aq. HCl, and extracted with ethyl acetate. The organic layer was dried over magnesium sulfate, and concentrated. The resulting solid was washed in refluxed methanol, and collected by filtration to give carboxylic acid **36'** (1.27 g) as a reddish-white solid in 65% yield.



36'

To a refluxed solution of **36'** (1.16 g, 1.81 mmol) in CH_2Cl_2 (0.12 L) containing a catalytic amount of benzyltriethylammonium chloride was added $SOCl_2$ (1.1 mL, 15 mmol), and the mixture was refluxed for 2 h, and concentrated to give acid chloride **36''** as a yellow solid, which was dissolved in THF, and immediately subjected to the following reaction.

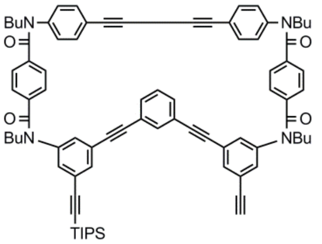


36''

To a solution of **19** (1.20 g, 1.73 mmol) and Et$_3$N (2.5 mL, 18 mmol) in toluene (190 mL) and THF (100 mL) was added a solution of **36''** in THF (100 mL) at 99-100 °C, and the mixture was stirred at 99-100 °C for 1 h. After removal of the solvents by evaporation, the residue was dissolved in dichloromethane, and which was washed with satd. aq. NaHCO$_3$, dried over magnesium sulfate, passed through a Celite/Al$_2$O$_3$ pad, and then concentrated. The crude product was purified by column chromatography on SiO$_2$/Al$_2$O$_3$ (ethyl acetate/dichloromethane) to give **37** (1.50 g) as a pale-yellowish-white solid in 67% yield. An analytical sample was obtained as a white solid by further purification with HPLC (ethyl acetate/dichloromethane). **37**: mp 161-162 °C; elemental analyses Found: C, 78.59; H, 7.09; N, 4.24%. Calc. for C$_{86}$H$_{92}$N$_4$O$_4$Si$_2$·(EtOH): C, 78.41; H, 7.33; N, 4.16%; IR (KBr) ν_{max}/cm^{-1} 3062, 2956, 2932, 2863, 2213, 2152, 1654, 1596, 1580; ^{1}H NMR δ_{H}(400 MHz; CDCl$_3$; Me$_4$Si)/ppm 8.05 (1H, br.s), 7.61 (1H, t, *J* = 1.6 Hz), 7.55 (1H, t, *J* = 1.6 Hz), 7.53-7.49 (2H, br.m), 7.43-7.36 (5H, m), 7.12-7.07 (1H, br.m), 7.10 (4H, br.s), 7.10 (4H, br.s), 7.02 (1H, t, *J* = 1.6 Hz), 6.91 (1H, t, *J* = 1.6 Hz), 6.85 (1H, t, *J* = 1.6 Hz), 6.79 (2H, d, *J* = 8.4 Hz), 6.78 (2H, d, *J* = 8.4 Hz), 3.86 (8H, br.s), 1.64-1.48 (8H, m), 1.42-1.26 (8H, m), 1.18-1.15 (21H, m), 0.94 (3H, t, *J* = 7.2 Hz), 0.93 (3H, *J* = 7.6 Hz), 0.87 (6H, t, *J* = 7.2 Hz), 0.30 (9H, s); ^{13}C NMR δ_{C}(100 MHz; CDCl$_3$)/ppm 169.3, 169.0, 168.9, 144.0, 144.0, 143.4, 143.4, 137.0, 136.8 (br.), 136.7, 136.6, 134.5, 134.2, 133.2, 131.4 (br.m), 130.9, 130.6, 130.5, 130.2, 128.7, 128.3, 128.1, 127.9, 127.1, 127.1, 124.6, 124.5, 123.9, 123.9, 123.1, 123.0, 119.5, 119.4, 104.9, 102.9, 96.6, 93.2, 90.2, 88.6, 88.6, 81.4, 74.8, 74.6, 49.8, 49.7 (br.), 49.6, 29.6 (br.), 29.5, 29.5, 20.0, 20.0, 20.0, 18.6, 13.7, 13.7, 11.2, –0.3; FD-LRMS *m*/*z* 1300.7 (M$^+$, 94%), 1301.7 ([M+1]$^+$, 100), 1302.7 ([M+2]$^+$, 62), 1303.7 ([M+3]$^+$, 28), 1304.7 ([M+4]$^+$, 10), 1305.7 ([M+5]$^+$, 3).

Preparation of **38**

To a solution of **37** (616 mg, 0.473 mmol) in THF (4.4 mL) and MeOH (4.4 mL) was added K$_2$CO$_3$ (148 mg, 1.07 mmol) at room temperature, and the mixture was stirred at that temperature for 16 min. After removal of a solid by filtration, the filtrate was concentrated and purified by column chromatography on SiO$_2$ (ethyl acetate/dichloromethane) to give **37'** (562 mg) as a white solid in 97% yield. **37'**: ^{1}H NMR δ_{H}(400 MHz; CDCl$_3$; Me$_4$Si)/ppm 8.07 (1H, br.s), 7.59 (1H, t, *J* = 1.6 Hz), 7.56 (1H, br.t), 7.53-7.50 (2H, m), 7.43-7.36 (5H, m), 7.12-7.02 (10H, br.m), 6.92 (1H, br.t), 6.89 (1H, br.t), 6.80 (2H, d, *J* = 8.4 Hz), 6.78 (2H, d, *J* = 8.4 Hz), 3.96-3.75 (8H, br.m), 3.20 (1H, s), 1.64-1.46 (8H, m), 1.43-1.26 (8H, m), 1.19-1.15 (21H, m), 0.94 (3H, t, *J* = 7.2 Hz), 0.94 (3H, t, *J* = 7.6 Hz), 0.87 (6H, t, *J* = 7.2 Hz).

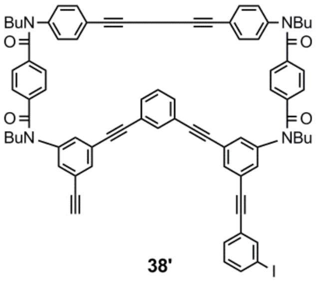


37'

To a solution of 1,3-diiodobenzene (2.23 g, 6.75 mmol), $Pd(PPh_3)_4$ (292 mg, 0.253 mmol) and CuI (96 mg, 0.50 mmol) in Et_3N (44 mL) was added a solution of **37'** (2.08 g, 1.69 mmol) in THF (7.4 mL) via a syringe pump over 2 h at 60 °C under an argon atmosphere, and the mixture was further stirred at that temperature for 30 min. After removal of a solid by filtration through a Celite/SiO_2 pad, the filtrate was concentrated, and then purified by column chromatography on SiO_2 (ethyl acetate/dichloromethane), followed by GPC (chloroform) to give **38** (1.99 g) as a pale-yellowish white amorphous solid in 82% yield. An analytical sample was obtained as a white solid by further purification with HPLC (ethyl acetate/dichloromethane). **38**: mp 169-170 °C; elemental analyses Found: C, 74.23; H, 6.05; N, 3.86%. Calc. for $C_{89}H_{87}IN_4O_4Si{\cdot}(EtOH)$: C, 73.96; H, 6.34; N, 3.79%; IR (KBr) ν_{max}/cm^{-1} 3056, 2955, 2928, 2861, 2212, 2148, 1652, 1595, 1576; ^1H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 8.08 (1H, br.s), 7.95 (1H, t, J = 1.6 Hz), 7.73 (1H, ddd, J = 1.2, 1.6, 8.0 Hz), 7.60 (2H, br.t), 7.56-7.51 (3H, m), 7.43 (2H, d, J = 8.4 Hz), 7.40 (2H, d, J = 8.8 Hz), 7.39 (1H, br.t), 7.18 (1H, br.s), 7.15-7.10 (9H, m), 7.02 (1H, br.t), 6.92 (1H, t, J = 1.6 Hz), 6.88 (1H, t, J = 1.6 Hz), 6.80 (2H, d, J = 8.4 Hz), 6.79 (2H, d, J = 8.8 Hz), 4.13-3.60 (8H, br.m), 1.65-1.48 (8H, m), 1.43-1.24 (8H, m), 1.19-1.15 (21H, m), 0.95 (3H, t, J = 7.6 Hz), 0.94 (3H, t, J = 7.6 Hz), 0.87 (3H, t, J = 7.2 Hz), 0.86 (3H, t, J = 7.6 Hz); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 169.3, 169.0, 169.0, 144.1, 144.0, 143.6, 143.4, 140.2, 137.8, 137.0, 136.8, 136.7, 136.6, 134.4, 133.6, 133.2, 133.2, 131.5 (br.m), 131.0, 130.7, 130.3, 130.2, 129.9, 128.7, 128.3, 128.1, 127.9, 127.1, 127.1, 124.7, 124.4, 124.2, 124.1, 123.9, 123.1, 123.0, 119.5, 119.4, 104.9, 93.7, 93.3, 90.3, 90.1, 89.3, 88.7, 88.6, 88.6, 81.5, 81.4, 74.7, 49.9, 49.7, 49.7, 29.6, 29.6, 20.1, 20.1, 20.0, 20.0, 18.6, 13.8, 13.7, 13.7, 13.7, 11.2; FD-LRMS m/z 1430.5 (M^+, 94%), 1431.5 ($[M+1]^+$, 100), 1432.5 ($[M+2]^+$, 57), 1433.5 ($[M+3]^+$, 23), 1434.5 ($[M+4]^+$, 8), 1435.5 ($[M+5]^+$, 2).

Preparation of **4a** and **4b**

To a solution of **38** (1.84 g, 1.28 mmol) in THF (34 mL) was added TBAF (1 M in THF, 1.40 mL, 1.40 mmol) at room temperature, and the mixture was stirred at that temperature for 20 min. After removal of the solvent by evaporation, the residue was dissolved in ethyl acetate, and which was washed with 0.5 M aq. HCl, dried over magnesium sulfate, concentrated, and then purified by column chromatography on SiO_2 (ethyl acetate/dichloromethane), followed by GPC (chloroform) to give **38'** (1.49 g) as a white solid in 91% yield. **38'**: ^1H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 8.12 (1H, br.s), 7.95 (1H, t, J = 1.6 Hz), 7.73 (1H, ddd, J = 1.2, 2.0, 8.0 Hz), 7.62 (1H, t, J = 1.2 Hz), 7.59 (1H, t, J = 1.2 Hz), 7.56-7.53 (3H, br.m), 7.45-7.38 (5H, m), 7.19 (1H, br.t), 7.15-7.08 (10H, m), 6.97 (1H, t, J = 1.6 Hz), 6.92 (1H, t, J = 1.6 Hz), 6.82 (2H, d, J = 8.8 Hz), 6.82 (2H, d, J = 8.8 Hz), 3.93-3.84 (8H, br.m), 3.25 (1H, s), 1.66-1.47 (8H, m), 1.43-1.26 (8H, m), 0.95 (3H, t, J = 7.6 Hz), 0.94 (3H, t, J = 7.2 Hz), 0.87 (3H, t, J = 7.2 Hz), 0.86 (3H, t, J = 7.6 Hz).

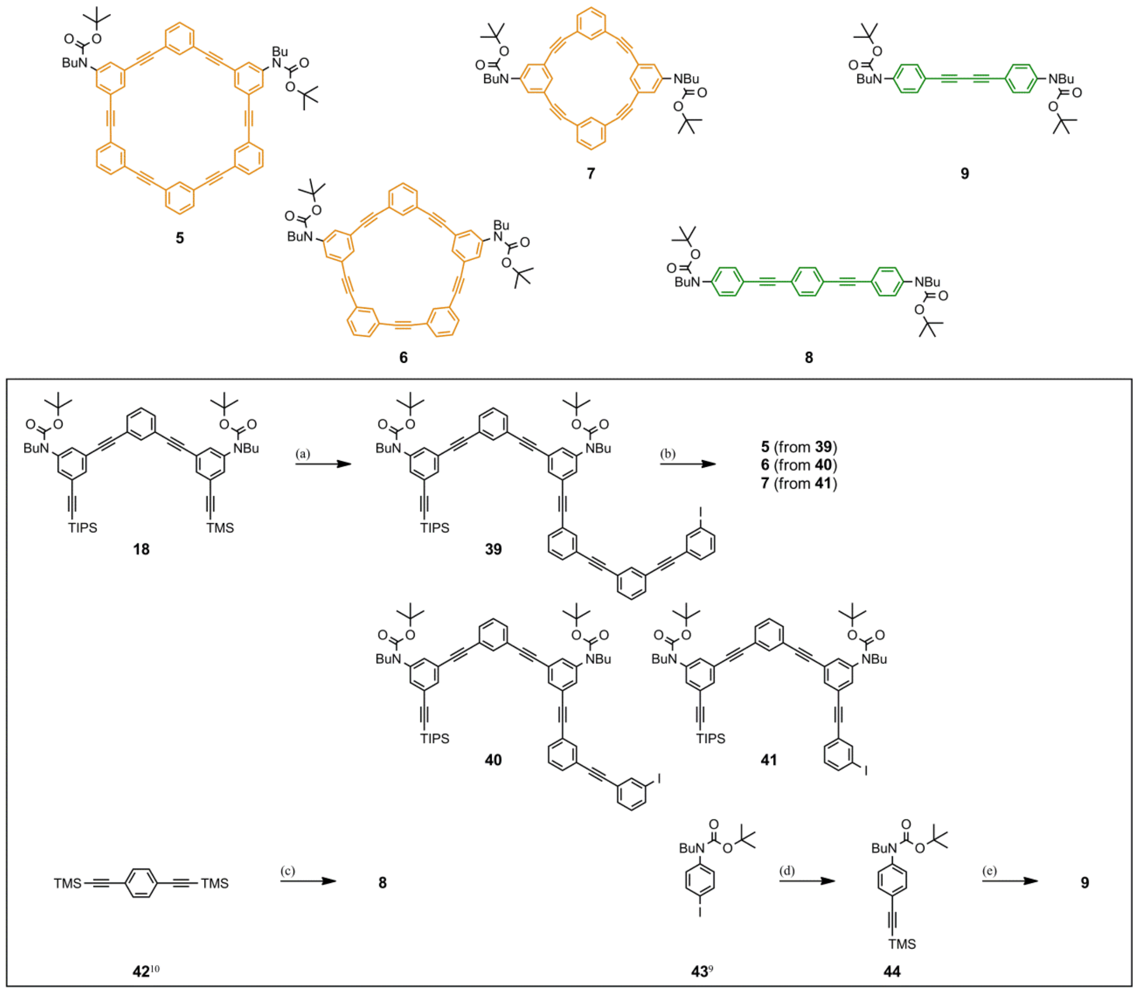


38'

To a solution of $Pd(PPh_3)_4$ (275 mg, 0.238 mmol) and CuI (48 mg, 0.25 mmol) in Et_3N (60 mL) was added a solution of **38'** (506 mg, 0.397 mmol) in THF (30 mL) via a syringe pump over 43 h at 80 °C under an argon atmosphere. After removal of the solvents by evaporation, the residue was purified by column chromatography on SiO_2 (ethyl acetate/dichloromethane), followed by GPC (chloroform) to give a mixture of **4a** and **4b** (25 mg, **4a**:**4b** = 1.6:1) as a white solid in 5% yield. **4b** and **4a** were isolated in this order by HPLC separation (1:9 tetrahydrofuran/chloroform). Each analytical sample was obtained as a white solid by reprecipitation with ethyl acetate/hexane.

4a: mp 242-243 °C; IR (KBr) ν_{max}/cm^{-1} 3064, 2952, 2930, 2868, 2860, 2194, 2147, 1649, 1599, 1587; ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 9.07 (2H, br.m), 8.60 (2H, t, J = 1.6 Hz), 7.46-7.40 (6H, m), 7.16 (4H, d, J = 8.4 Hz), 7.14 (4H, d, J = 8.4 Hz), 7.01 (4H, d, J = 8.4 Hz), 6.92 (4H, d, J = 1.6 Hz), 6.69 (4H, d, J = 8.4 Hz), 3.82 (4H, t, J = 7.6 Hz), 3.76 (4H, t, J = 7.6 Hz), 1.60-1.43 (8H, m), 1.41-1.22 (8H, m), 0.92 (6H, t, J = 7.2 Hz), 0.83 (6H, t, J = 7.2 Hz); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 169.7, 169.7, 144.4, 143.5, 142.2, 140.9, 137.4, 137.0, 132.8, 129.1, 128.8, 128.8, 128.0, 128.0, 127.9, 124.4, 123.6, 118.9, 93.2, 91.1, 87.5, 78.2, 50.1, 49.0, 29.8, 29.6, 20.1, 20.1, 13.8, 13.7; FD-LRMS m/z 1146.5 (M^+, 100%), 1147.5 ($[M+1]^+$, 90), 1148.5 ($[M+2]^+$, 43), 1149.5 ($[M+3]^+$, 14), 1150.5 ($[M+4]^+$, 4); FD-HRMS Found: 1146.50948, Calc. for $C_{80}H_{66}N_4O_4$: 1146.50840; UV λ_{max}(CH_2Cl_2)/nm (log ε) 354 (4.58), 331 (4.61), 305 (sh. 5.01), 289 (5.14).

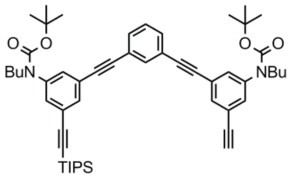
4b: mp 218-219 °C (dec); IR (KBr) ν_{max}/cm^{-1} 3061, 3040, 2955, 2930, 2870, 2861, 2205, 1656, 1650, 1590, 1567, 1502; ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 8.06 (2H, br.dd), 7.75 (2H, t, J = 1.6 Hz), 7.41 (6H, d, J = 1.2 Hz), 7.37 (4H, d, J = 8.8 Hz), 7.20 (4H, d, J = 8.4 Hz), 7.15 (4H, d, J = 8.4 Hz), 6.84 (4H, d, J = 1.6 Hz), 6.83 (4H, d, J = 8.8 Hz), 3.88 (4H, t, J = 7.2 Hz), 3.84 (4H, t, J = 7.6 Hz), 1.59-1.46 (8H, m), 1.38-1.27 (8H, m), 0.89 (6H, t, J = 7.2 Hz), 0.87 (6H, t, J = 7.2 Hz); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 169.2, 169.2, 144.3, 144.1, 142.1, 138.8, 137.1, 136.9, 133.3, 129.2, 128.5, 128.4, 128.3, 127.3, 127.2, 124.5, 123.5, 119.8, 93.5, 91.5, 83.1, 75.0, 50.1, 49.9, 29.7, 20.1, 20.1, 13.8, 13.7; FD-LRMS m/z 1146.5 (M^+, 100%), 1147.5 ($[M+1]^+$, 91), 1148.5 ($[M+2]^+$, 42), 1149.5 ($[M+3]^+$, 14), 1150.5 ($[M+4]^+$, 4); FD-HRMS Found: 1146.50891, Calc. for $C_{80}H_{66}N_4O_4$: 1146.50840; UV λ_{max}(CH_2Cl_2)/nm (log ε) 353 (sh. 4.35), 331 (sh. 4.50), 306 (sh. 5.06), 289 (5.21).



Scheme S4. Synthesis of PAMs **5-7** and rods **8-9**. Reagents and yields: (a) i) K_2CO_3, MeOH, THF (100% for **18'**); ii) **24**/**25**/1,3-diiodobenzene, $Pd(PPh_3)_4$, CuI, Et_3N, THF (79% for **39**, 69% for **40**, 78% for **41**); (b) i) TBAF, THF (98% for **39'**, 96% for **40'**, 91% for **41'**); ii) $Pd(PPh_3)_4$, CuI, Et_3N, THF (66% for **5**, 55% for **6**, 5% for **7**); (c) **43**[9], $Pd(PPh_3)_4$, CuI, TBAF, Et_3N, THF (98%); (d) TMSA, $PdCl_2(PPh_3)_2$, CuI, Et_3N (99%); (e) i) K_2CO_3, MeOH, THF (93% for **44'**); ii) CuCl, TMEDA, acetone (39%).

Preparation of **39**

To a solution of **18** (2.82 g, 3.14 mmol) in THF (17 mL) and MeOH (17 mL) was added K_2CO_3 (442 mg, 3.20 mmol) at room temperature, and the mixture was stirred at that temperature for 16 min. After removal of the solvents by evaporation, the residue was purified by column chromatography on SiO_2 (dichloromethane/hexane) to give **18'** (2.59 g) as a white amorphous solid in 100% yield. **18'**: ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.70-7.69 (1H, m), 7.51-7.48 (4H, m), 7.37-7.33 (2H, m), 7.32-7.29 (2H, br.m), 7.27 (1H, br.t), 3.62 (4H, t, J = 7.6 Hz), 3.11 (1H, s), 1.57-1.49 (4H, m), 1.45 (18H, s), 1.37-1.27 (4H, m), 1.14 (21H, s), 0.92 (3H, t, J = 7.2 Hz), 0.91 (3H, t, J = 7.2 Hz).



18'

To a solution of **24** (904 mg, 1.71 mmol), $Pd(PPh_3)_4$ (18 mg, 0.016 mmol) and CuI (6 mg, 0.03 mmol) in Et_3N (40 mL) was added a solution of **18'** (356 mg, 0.431 mmol) in THF (4 mL) via a syringe pump over 3 h at 60 °C under an argon atmosphere, and the mixture was further stirred at that temperature for 30 min. After removal of a solid by filtration through a Celite/SiO_2 pad, the filtrate was concentrated and purified by column chromatography on SiO_2 (dichloromethane/hexane), followed by GPC (chloroform) to give **39** (417 mg) as a white amorphous solid in 79% yield. An analytical sample was obtained as a white amorphous solid by further purification through GPC (chloroform). **39**: mp 74-76 °C; elemental analyses Found: C, 73.27; H, 6.56; N, 2.24%. Calc. for $C_{75}H_{79}IN_2O_4Si$: C, 73.39; H, 6.49; N, 2.28%; IR (KBr) ν_{max}/cm^{-1} 3061, 2958, 2939, 2929, 2862, 2215, 2152, 1702, 1699, 1596, 1582; ^1H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.90 (1H, t, J = 1.6 Hz), 7.74-7.70 (3H, m), 7.68 (1H, ddd, J = 1.2, 2.0, 8.0 Hz), 7.55 (1H, t, J = 1.6 Hz), 7.52-7.48 (8H, m), 7.38-7.26 (7H, m), 7.09 (1H, t, J = 8.0 Hz), 3.65 (2H, t, J = 7.6 Hz), 3.62 (2H, t, J = 7.6 Hz), 1.61-1.50 (4H, m), 1.47 (9H, s), 1.45 (9H, s), 1.39-1.27 (4H, m), 1.14 (21H, br.s), 0.93 (3H, t, J = 7.2 Hz), 0.92 (3H, t, J = 7.2 Hz); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 154.3, 154.3, 143.0, 142.8, 140.2, 137.4, 134.7, 134.7 (br.m), 132.6, 132.1, 131.6, 131.6 (br.), 131.5, 131.5, 130.7, 130.5, 130.3, 130.2, 129.9, 128.6, 125.0, 124.4, 123.9, 123.6, 123.4, 123.3, 123.3, 123.2, 105.6, 93.7, 91.9, 89.7, 89.3, 89.3, 89.1, 89.1, 88.8, 88.7, 88.3, 80.5, 80.5, 49.6, 30.6, 30.6, 28.3, 28.3, 19.9, 19.9, 18.6, 13.8, 13.8, 11.3; FD-LRMS m/z 1026.5 ($[M-(BOC)_2]^+$, 4%), 1027.5 ($[M+1-(BOC)_2]^+$, 4), 1070.4 ($[M-(TIPS)]^+$, 5), 1071.4 ($[M+1-(TIPS)]^+$, 5), 1126.5 ($[M-(BOC)]^+$, 26), 1127.5 ($[M+1-(BOC)]^+$, 22), 1128.5 ($[M+2-(BOC)]^+$, 11), 1129.5 ($[M+3-(BOC)]^+$, 3), 1226.5 (M^+, 100), 1227.5 ($[M+1]^+$, 89), 1228.5 ($[M+2]^+$, 44), 1229.5 ($[M+3]^+$, 15), 1230.5 ($[M+4]^+$, 4).

Preparation of **40**

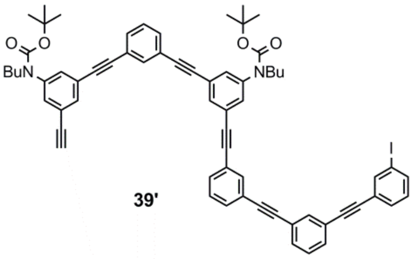
To a solution of **25** (726 mg, 1.69 mmol), $Pd(PPh_3)_4$ (17 mg, 0.015 mmol) and CuI (6 mg, 0.03 mmol) in Et_3N (40 mL) was added a solution of **18'** (348 mg, 0.422 mmol) in THF (4 mL) via a syringe pump over 3 h at 50-53 °C under an argon atmosphere, and the mixture was further stirred at that temperature for 30 min. After removal of a solid by filtration through a Celite/SiO_2 pad, the filtrate was concentrated and purified by column chromatography on SiO_2 (dichloromethane/hexane), followed by GPC (chloroform) to give **40** (328 mg) as a white amorphous solid in 69% yield. An analytical sample was obtained as a white amorphous solid by further purification through GPC (chloroform). **40**: mp 67-68 °C; elemental analyses Found: C, 71.37; H, 6.84; N, 2.44%. Calc. for $C_{67}H_{75}IN_2O_4Si$: C, 71.38; H, 6.71; N, 2.48%; IR (KBr) ν_{max}/cm^{-1} 3061, 2958, 2939, 2930, 2862, 2216, 2151, 1702, 1699, 1596, 1582; ^1H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.90 (1H, t, J = 1.6 Hz), 7.74-7.69 (2H, m), 7.68 (1H, ddd, J = 1.2, 1.6, 8.0 Hz), 7.55 (1H, t, J = 1.6 Hz), 7.52-7.48 (6H, m), 7.38-7.26 (6H, m), 7.09 (1H, t, J = 8.0 Hz), 3.65 (2H, t, J = 7.6 Hz), 3.63 (2H, t, J = 7.6 Hz), 1.61-1.50 (4H, m), 1.47 (9H, s), 1.45 (9H, s), 1.38-1.28 (4H, m), 1.14 (21H, br.s), 0.93 (3H, t, J = 7.2 Hz), 0.92 (3H, t, J = 7.2 Hz); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 154.2, 154.2, 142.9, 142.8, 140.1, 137.4, 134.7, 134.6, 132.5, 132.1, 131.6, 131.5, 130.7, 130.5, 130.2, 130.1, 129.8, 128.5, 125.0, 124.4, 123.8, 123.8, 123.6, 123.3, 123.2, 123.2, 123.2, 105.5, 93.7, 91.8, 89.7, 89.3, 89.2, 89.1, 88.8, 88.7, 88.7, 88.3, 80.5, 80.4, 49.5, 30.6, 30.5, 28.3, 28.3, 19.9, 19.9, 18.6, 13.7, 13.7, 11.2; FD-LRMS *m*/*z* 1026.4 ([M−(BOC)]$^+$, 37%), 1027.4 ([M+1−(BOC)]$^+$, 28), 1028.4 ([M+2−(BOC)]$^+$, 12), 1029.4 ([M+3−(BOC)]$^+$, 4), 1126.5 (M$^+$, 100), 1127.5 ([M+1]$^+$, 82), 1128.5 ([M+2]$^+$, 38), 1129.5 ([M+3]$^+$, 13), 1130.5 ([M+4]$^+$, 3).

Preparation of **41**

To a solution of 1,3-diiodobenzene (768 mg, 2.33 mmol), Pd(PPh$_3$)$_4$ (67 mg, 0.058 mmol) and CuI (22 mg, 0.12 mmol) in Et$_3$N (54 mL) was added a solution of **18'** (469 mg, 0.568 mmol) in THF (5.5 mL) via a syringe pump over 3.5 h at 60 °C under an argon atmosphere, and the mixture was further stirred at that temperature for 30 min. After removal of a solid by filtration through a Celite/SiO$_2$ pad, the filtrate was concentrated and purified by column chromatography on SiO$_2$ (dichloromethane/hexane) to give **41** (458 mg) as a white amorphous solid in 78% yield. An analytical sample was obtained as a white amorphous solid by further purification through GPC (chloroform). **41**: mp 52-54 °C; elemental analyses Found: C, 69.01; H, 6.95; N, 2.71%. Calc. for $C_{59}H_{71}IN_2O_4Si$: C, 68.99; H, 6.97; N, 2.73%; IR (KBr) ν_{max}/cm^{-1} 3061, 2958, 2940, 2930, 2863, 2215, 2153, 1703, 1582; ^{1}H NMR δ_H(400 MHz; CDCl$_3$; Me$_4$Si)/ppm 7.90 (1H, t, *J* = 1.6 Hz), 7.71-7.70 (1H, br.m), 7.69 (1H, ddd, *J* = 1.2, 1.6, 8.0 Hz), 7.53 (1H, t, *J* = 1.6 Hz), 7.51-7.48 (4H, m), 7.38-7.26 (5H, m), 7.10 (1H, t, *J* = 8.0 Hz), 3.65 (2H, t, *J* = 8.0 Hz), 3.63 (2H, t, *J* = 7.6 Hz), 1.59-1.50 (4H, m), 1.47 (9H, s), 1.45 (9H, s), 1.38-1.28 (4H, m), 1.14 (21H, br.s), 0.93 (3H, t, *J* = 7.2 Hz), 0.92 (3H, t, *J* = 7.2 Hz); ^{13}C NMR δ_C(100 MHz; CDCl$_3$)/ppm 154.3, 143.0, 142.8, 140.2, 137.5, 134.7, 132.6, 132.1, 131.6, 131.6, 130.7, 130.5, 130.4, 130.2, 130.2, 129.9, 128.6, 124.9, 124.4, 123.9, 123.7, 123.6, 123.3, 123.2, 105.6, 93.7, 91.9, 89.3, 89.3, 89.1, 88.8, 88.7, 88.4, 80.6, 80.5, 49.6, 30.6, 30.6, 28.3, 28.3, 19.9, 19.9, 18.6, 13.8, 11.3; FD-LRMS *m*/*z* 926.3 ([M−(BOC)]$^+$, 29%), 927.3 ([M+1−(BOC)]$^+$, 20), 928.3 ([M+2−(BOC)]$^+$, 8), 929.3 ([M+3−(BOC)]$^+$, 2), 1026.4 (M$^+$, 100), 1027.4 ([M+1]$^+$, 72), 1028.4 ([M+2]$^+$, 30), 1029.4 ([M+3]$^+$, 10), 1030.4 ([M+4]$^+$, 3).

Preparation of **5** ([6]PAM)

To a solution of **39** (425 mg, 0.346 mmol) in THF (10 mL) was added TBAF (1 M in THF, 0.37 mL, 0.37 mmol) at room temperature, and the mixture was stirred at that temperature for 20 min. After removal of the solvent, the residue was dissolved in ethyl acetate, and which was washed with 0.1 M aq. HCl and brine, dried over magnesium sulfate, concentrated, and then purified by column chromatography on SiO$_2$ (dichloromethane/hexane), followed by GPC (chloroform) to give **39'** (364 mg) as a white amorphous solid in 98% yield. **39'**: ^{1}H NMR δ_H(400 MHz; CDCl$_3$; Me$_4$Si)/ppm 7.89 (1H, t, *J* = 1.6 Hz), 7.73-7.70 (3H, m), 7.66 (1H, ddd, *J* = 1.2, 2.0, 8.0 Hz), 7.56 (1H, t, *J* = 1.6 Hz), 7.53-7.45 (8H, m), 7.41-7.29 (7H, m), 7.07 (1H, t, *J* = 8.0



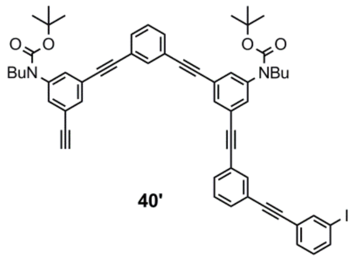
39'

Hz), 3.65 (2H, t, *J* = 7.6 Hz), 3.62 (2H, t, *J* = 7.6 Hz), 3.11 (1H, s), 1.61-1.49 (4H, m), 1.47 (9H, s), 1.45 (9H, s), 1.39-1.27 (4H, m), 0.93 (3H, t, *J* = 7.6 Hz), 0.91 (3H, t, *J* = 7.6 Hz).

To a solution of $Pd(PPh_3)_4$ (175 mg, 0.152 mmol) and CuI (25 mg, 0.13 mmol) in Et_3N (40 mL) was added a solution of **39'** (280 mg, 0.261 mmol) in THF (20 mL) via a syringe pump over 26 h at 75 °C under an argon atmosphere. After removal of a solid by filtration, the filtrate was concentrated and then purified by column chromatography on SiO_2 (dichloromethane/hexane), followed by GPC (chloroform) to give **5** (164 mg) as a pale yellowish-white solid in 66% yield. An analytical sample was obtained as a white solid by repeating column chromatography on SiO_2 (dichloromethane/hexane), followed by suspension in methanol. **5**: mp 209-210 °C (dec); elemental analyses Found: C, 83.79; H, 6.30; N, 2.90%. Calc. for $C_{66}H_{58}N_2O_4$: C, 84.05; H, 6.20; N, 2.97%; IR (KBr) ν_{max}/cm^{-1} 3060, 2959, 2928, 2871, 2861, 2215, 1702, 1596, 1581; ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.77-7.73 (4H, m), 7.58 (2H, t, *J* = 1.2 Hz), 7.54-7.49 (8H, m), 7.40-7.33 (8H, m), 3.66 (4H, t, *J* = 7.6 Hz), 1.60-1.52 (4H, m), 1.47 (18H, s), 1.34-1.30 (4H, m), 0.93 (6H, t, *J* = 7.6 Hz); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 154.3, 142.9, 135.2, 135.1, 135.1, 132.6, 131.3, 131.3, 131.2, 131.2, 129.9, 128.6, 128.5, 123.9, 123.8, 123.4, 123.3, 123.3, 123.2, 89.4, 89.3, 89.2, 89.1, 88.8, 88.8, 80.5, 49.6, 30.6, 28.3, 19.9, 13.8; FD-LRMS *m*/*z* 842.4 ([M−(BOC)]$^+$, 13%), 843.4 ([M+1−(BOC)]$^+$, 10), 844.4 ([M+2−(BOC)]$^+$, 3), 942.5 (M$^+$, 100), 943.5 ([M+1]$^+$, 73), 944.5 ([M+2]$^+$, 28), 945.5 ([M+3]$^+$, 7); UV λ_{max}(CH_2Cl_2)/nm (log ε) 305 (5.27), 287 (5.39), 272 (sh. 5.15).

Preparation of **6** ([5]PAM)

To a solution of **40** (236 mg, 0.209 mmol) in THF (6 mL) was added TBAF (1 M in THF, 0.20 mL, 0.20 mmol) at room temperature, and the mixture was stirred at that temperature for 20 min. After removal of the solvent, the residue was dissolved in ethyl acetate, and which was washed with 0.1 M aq. HCl and brine, dried over magnesium sulfate, concentrated, and then purified by column chromatography on SiO_2 (dichloromethane/hexane), followed by GPC (chloroform) to give **40'** (195 mg) as a white amorphous solid in 96% yield. **40'**: ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.90 (1H, t, *J* = 1.6 Hz), 7.72-7.70 (2H, m), 7.68 (1H, ddd, *J* = 1.2, 1.6, 8.0 Hz), 7.55 (1H, t, *J* = 1.6 Hz), 7.53-7.48 (6H, m), 7.38-7.33 (5H, m), 7.31 (1H, br.t), 7.09 (1H, t, *J* = 8.0 Hz), 3.65 (2H, t, *J* = 7.6 Hz), 3.63 (2H, t, *J* = 7.6 Hz), 3.11 (1H, s), 1.63-1.45 (4H, m), 1.47 (9H, s), 1.45 (9H, s), 1.39-1.27 (4H, m), 0.93 (3H, t, *J* = 7.2 Hz), 0.91 (3H, t, *J* = 7.2 Hz).

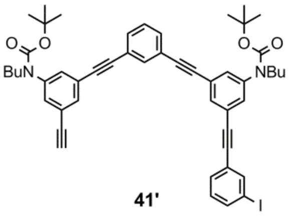


40'

To a solution of $Pd(PPh_3)_4$ (144 mg, 0.125 mmol) and CuI (26 mg, 0.14 mmol) in Et_3N (31 mL) was added a solution of **40'** (213 mg, 0.219 mmol) in THF (18 mL) via a syringe pump over 22 h at 75 °C under an argon atmosphere. After removal of a solid by filtration, the filtrate was concentrated and then purified by column chromatography on SiO_2 (dichloromethane/hexane), followed by GPC (chloroform) to give **6** (102 mg) as a white solid in 55% yield. An analytical sample was obtained as a white solid by further purification through GPC (chloroform), followed by suspension in methanol. **6**: mp 221.0-221.5 °C (dec); elemental analyses Found: C, 82.61; H, 6.53; N, 3.25%. Calc. for $C_{58}H_{54}N_2O_4$: C, 82.63; H, 6.46; N, 3.32%; IR (KBr) ν_{max}/cm^{-1} 3060, 2966, 2929, 2872, 2864, 2214, 1708, 1592, 1582; ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.97-7.95 (3H, m), 7.80 (2H, t, J = 1.6 Hz), 7.49-7.45 (6H, m), 7.39-7.32 (7H, m), 3.66 (4H, t, J = 7.6 Hz), 1.59-1.52 (4H, m), 1.47 (18H, s), 1.38-1.29 (4H, m), 0.93 (6H, t, J = 7.6 Hz); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 154.3, 143.1, 137.8, 137.8, 135.2, 130.1, 130.1, 130.0, 128.8, 128.7, 128.7, 123.9, 123.9, 123.5, 123.4, 123.3, 90.0, 89.9, 89.8, 89.4, 89.3, 80.6, 49.6, 30.6, 28.3, 19.9, 13.8; FD-LRMS *m*/*z* 742.4 ([M−(BOC)]$^+$, 14%), 743.4 ([M+1−(BOC)]$^+$, 8), 744.4 ([M+2−(BOC)]$^+$, 3), 842.5 (M$^+$, 100), 843.5 ([M+1]$^+$, 68), 844.5 ([M+2]$^+$, 24), 845.5 ([M+3]$^+$, 5); UV λ_{max}(CH_2Cl_2)/nm (log ε) 304 (5.20), 287 (5.33), 272 (sh. 5.06).

Preparation of **7** ([4]PAM)

To a solution of **41** (412 mg, 0.401 mmol) in THF (11 mL) was added TBAF (1 M in THF, 0.43 mL, 0.43 mmol) at room temperature, and the mixture was stirred at that temperature for 20 min. After removal of the solvent, the residue was dissolved in ethyl acetate, and which was washed with 0.1 M aq. HCl, dried over magnesium sulfate, concentrated, and then purified by column chromatography on SiO_2 (dichloromethane/hexane), followed by GPC (chloroform) to give **41'** (316 mg) as a white amorphous solid in 91% yield. **41'**: ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.90 (1H, t, J = 1.6 Hz), 7.72 (1H, br.t), 7.67 (1H, ddd, J = 1.2, 1.6, 8.0 Hz), 7.54-7.47 (5H, m), 7.37-7.31 (5H, m), 7.08 (1H, t, J = 8.0 Hz), 3.67-3.61 (4H, m), 3.12 (1H, s), 1.59-1.49 (4H, m), 1.47 (9H,s), 1.46 (9H, s), 1.38-1.27 (4H, m), 0.93 (3H, t, J = 7.2 Hz), 0.92 (3H, t, J = 7.2 Hz).



41'

To a solution of $Pd(PPh_3)_4$ (252 mg, 0.218 mmol) and CuI (42 mg, 0.22 mmol) in Et_3N (54 mL) was added a solution of **41'** (316 mg, 0.363 mmol) in THF (27 mL) via a syringe pump over 36 h at 75-80 °C under an argon atmosphere. After removal of a solid by filtration, the filtrate was concentrated and then purified by column chromatography on SiO_2 (dichloromethane/hexane), followed by GPC (chloroform) to give **7** (14 mg) as a white solid in 5% yield. An analytical sample was obtained as a white solid by further purification with HPLC (dichloromethane), followed by suspension in ethyl acetate/methanol. **7**: mp 210-211 °C (dec); elemental analyses Found: C, 78.02; H, 6.99; N, 3.39%. Calc. for $C_{50}H_{50}N_2O_4 \cdot C_4H_8O_2$: C, 78.04; H, 7.03; N, 3.37%; IR (KBr) ν_{max}/cm^{-1} 3056, 2962, 2929, 2872, 2203, 1708, 1590; ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 8.06-8.05 (2H, m), 7.90 (2H, t, J = 1.6 Hz), 7.38-7.36 (6H, m), 7.22 (4H, br.d), 3.64 (4H, t, J = 7.6 Hz), 1.58-1.51 (4H, m), 1.46 (18H, s), 1.38-1.28 (4H, m), 0.92 (6H, t, J = 7.6 Hz); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 154.3, 143.4, 141.9, 139.2, 129.0, 128.2, 127.1, 124.0, 123.6, 92.4, 91.8, 80.6, 49.7, 30.6, 28.3, 19.9, 13.8; FD-LRMS *m*/*z* 742.3 (M$^+$, 100), 743.4 ([M+1]$^+$, 60), 744.4 ([M+2]$^+$, 18), 745.4 ([M+3]$^+$, 4); UV

λ_{max}(CH_2Cl_2)/nm (log ε) 305 (4.97), 288 (5.15), 273 (sh. 4.91).

Preparation of **8**

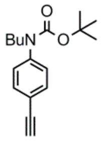
To a solution of **42** (472 mg, 1.74 mmol), **43** (1.45 g, 3.86 mmol), $Pd(PPh_3)_4$ (58 mg, 0.050 mmol) and CuI (21 mg, 0.11 mmol) in Et_3N (52 mL) and THF (10 mL) was added TBAF (1 M in THF, 0.60 mL, 0.60 mmol) at 43 °C, and the mixture was stirred at that temperature for 2 h. After removal of a solid by filtration through a Celite/SiO_2 pad, the filtrate was concentrated, and then purified by column chromatography on SiO_2 (dichloromethane/hexane) to give **8** (1.06 g) as a yellow solid in 98% yield. An analytical sample was obtained as colorless crystals by further purification through GPC (chloroform), followed by recrystallization from methanol. **8**: mp 101.5-102.0 °C; elemental analyses Found: C, 77.23; H, 7.84; N, 4.44%. Calc. for $C_{40}H_{48}N_2O_4$: C, 77.39; H, 7.79; N, 4.51%; IR (KBr) ν_{max}/cm^{-1} 3041, 3008, 2975, 2964, 2955, 2928, 2873, 2864, 2209, 1694, 1600, 1518; ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.49 (4H, d, J = 8.4 Hz), 7.50 (4H, s), 7.19 (4H, d, J = 8.4 Hz), 3.64 (4H, t, J = 7.6 Hz), 1.56-1.49 (4H, m), 1.44 (18H, s), 1.36-1.26 (4H, m), 0.90 (6H, t, J = 7.2 Hz); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 154.3, 142.7, 131.9, 131.4, 126.6, 123.0, 120.1, 90.9, 89.0, 80.2, 49.5, 30.5, 28.2, 19.8, 13.7; FD-LRMS *m/z* 620.4 (M^+, 100%), 621.4 ($[M+1]^+$, 45), 622.4 ($[M+2]^+$, 12); UV λ_{max}(CH_2Cl_2)/nm (log ε) 350 (sh. 4.67), 331 (4.82).

Preparation of **44**

To a solution of **43** (5.16 g, 13.8 mmol), $PdCl_2(PPh_3)_2$ (136 mg, 0.194 mmol) and CuI (65 mg, 0.34 mmol) in Et_3N (100 mL) was added TMSA (2.0 mL, 14 mmol) at room temperature under an argon atmosphere, and the reaction mixture was stirred at the temperature for 22 h. After removal of a solid by filtration through a Celite pad, the filtrate was concentrated and purified by column chromatography on SiO_2 (dichloromethane/hexane) to give **44** (4.69 g) as a white solid in 99% yield.

To a solution of **44** (4.69 g, 13.6 mmol) in THF (66 mL) and MeOH (66 mL) was added K_2CO_3 (1.87 g, 13.6 mmol), and the mixture was stirred at room temperature for 40 min, and then diluted with ethyl acetate. The diluted solution was washed with water and brine, dried over magnesium sulfate, and then purified by column chromatography on SiO_2 (dichloromethane/hexane) to give **44'** (3.44 g) as a white solid in 93% yield. An analytical sample of **44'** was obtained as colorless crystals by recrystallization from dichloromethane/hexane. **44'**: mp 71-72 °C; elemental analyses Found: C, 74.66; H, 8.66; N, 4.97%. Calc. for $C_{17}H_{23}NO_2$: C, 74.69; H, 8.48; N, 5.12%; IR (KBr) ν_{max}/cm^{-1} 3241, 2954, 2929, 2872, 2103, 1915, 1683, 1602, 1506; ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.45 (2H, d, J = 8.4 Hz), 7.15 (2H, d, J = 8.4 Hz), 3.62 (2H, t, J = 7.6 Hz), 3.06 (1H, s), 1.54-1.47 (2H, m), 1.43 (9H, s), 1.34-1.25 (2H, m), 0.89 (3H, t, J = 7.2 Hz); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 154.3, 143.1, 132.5, 126.7, 119.3, 83.3, 80.3, 77.1, 49.5, 30.6, 28.3, 19.9, 13.7; FD-LRMS *m/z* 273.2 (M^+, 100%), 274.2 ($[M+1]^+$, 20).

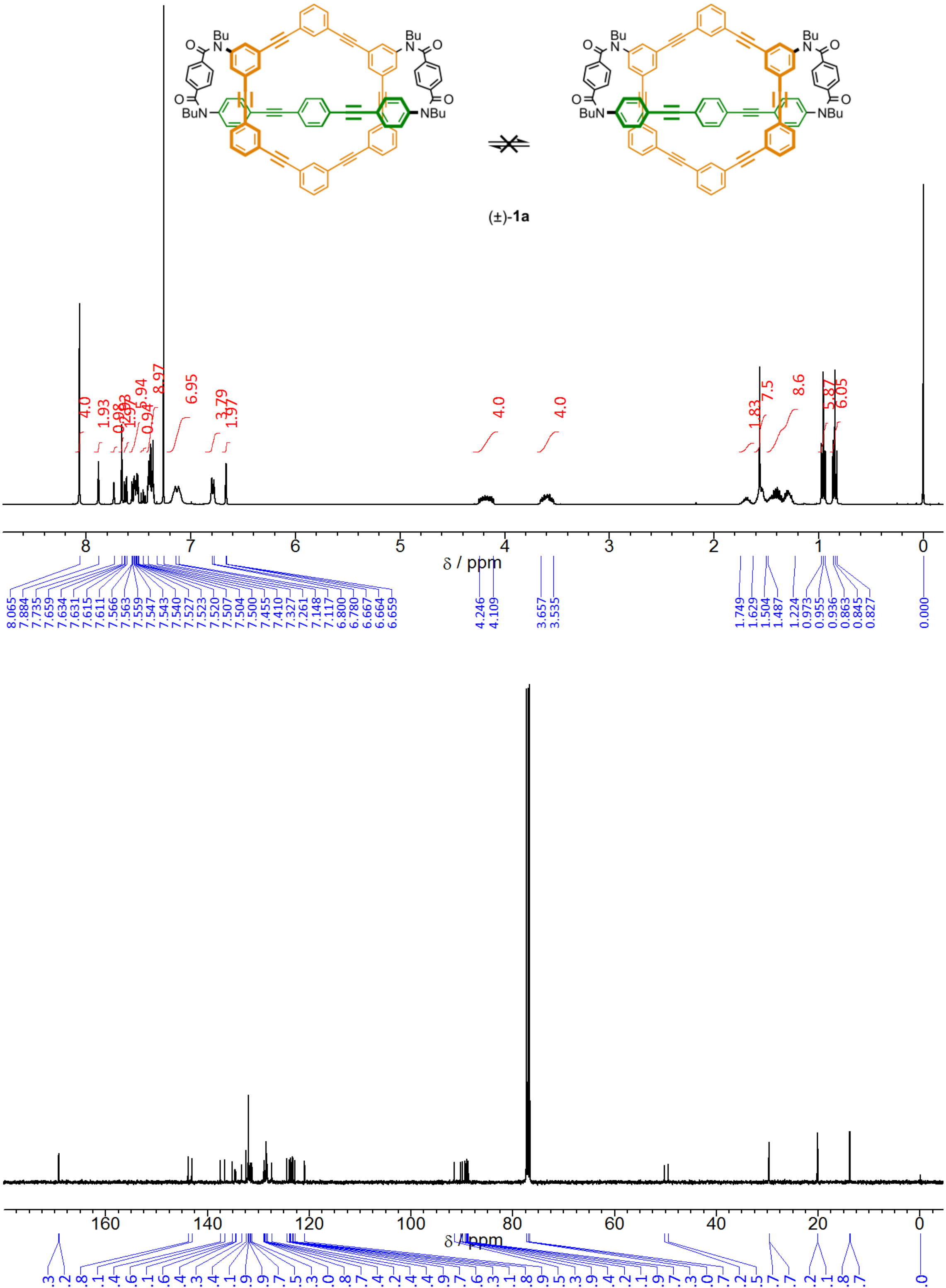
Preparation of **9**



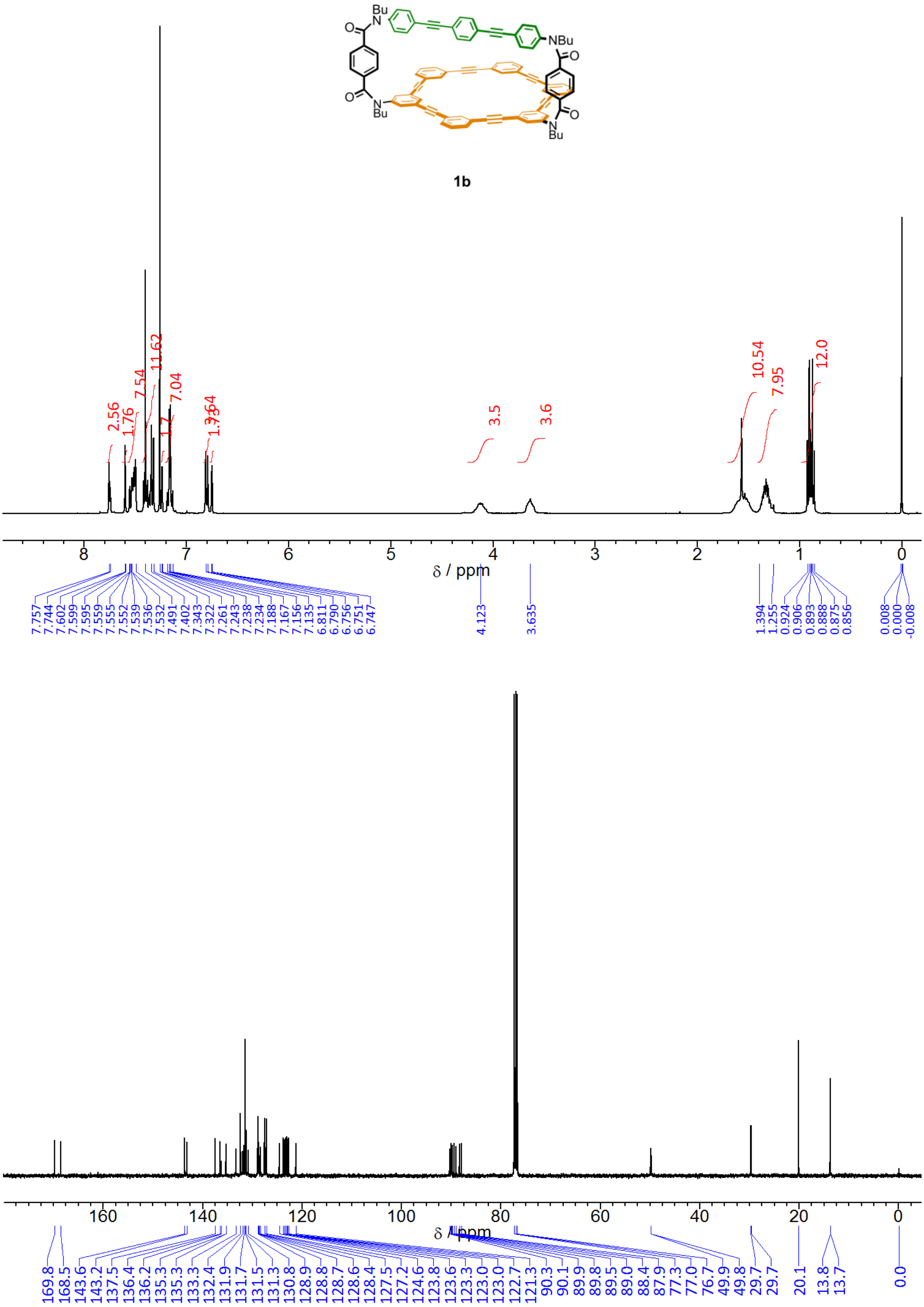
44'

To an ice-cooled solution of CuCl (46 mg, 0.46 mmol) and TMEDA (0.22 mL, 1.5 mmol) in acetone (15 mL) was added a solution of **44'** (487 mg, 1.78 mmol) in acetone (8 mL) under an oxygen atmosphere, and the mixture was stirred at room temperature for 8 days. After removal of the solvent by evaporation, the residue was dissolved in dichloromethane, and which was washed with diluted aq. HCl, dried over magnesium sulfate, and concentrated. The resulting solid was separated by column chromatography on SiO_2 (dichloromethane/hexane) to give **9** (236 mg) as a white solid in 49% yield and **44'** (194 mg, recov. 40%). An analytical sample was obtained as coloress crystals by recrystallization from methanol. **9**: mp 97.5-98.0 °C; elemental analyses Found: C, 75.05; H, 8.15; N, 5.13%. Calc. for $C_{34}H_{44}N_2O_4$: C, 74.97; H, 8.14; N, 5.14%; IR (KBr) ν_{max}/cm^{-1} 3070, 3042, 2963, 2929, 2871, 2148, 1698, 1597, 1504; ^{1}H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si)/ppm 7.48 (4H, d, J = 8.4 Hz), 7.18 (4H, d, J = 8.4 Hz), 3.63 (4H, t, J = 7.6 Hz), 1.56-1.48 (4H, m), 1.44 (18H, s), 1.35-1.26 (4H, m), 0.90 (6H, t, J = 7.6 Hz); ^{13}C NMR δ_C(100 MHz; $CDCl_3$)/ppm 154.2, 143.5, 132.9, 126.6, 118.8, 81.3, 80.5, 73.9, 49.5, 30.6, 28.3, 19.9, 13.8; FD-LRMS m/z 544.3 (M^+, 100%), 545.4 ($[M+1]^+$, 39), 546.4 ($[M+2]^+$, 8); UV λ_{max}(CH_2Cl_2)/nm (log ε) 344 (4.48), 324 (4.61), 306 (4.54), 288 (sh. 4.42), 275 (sh. 4.35), 261 (sh. 4.24).

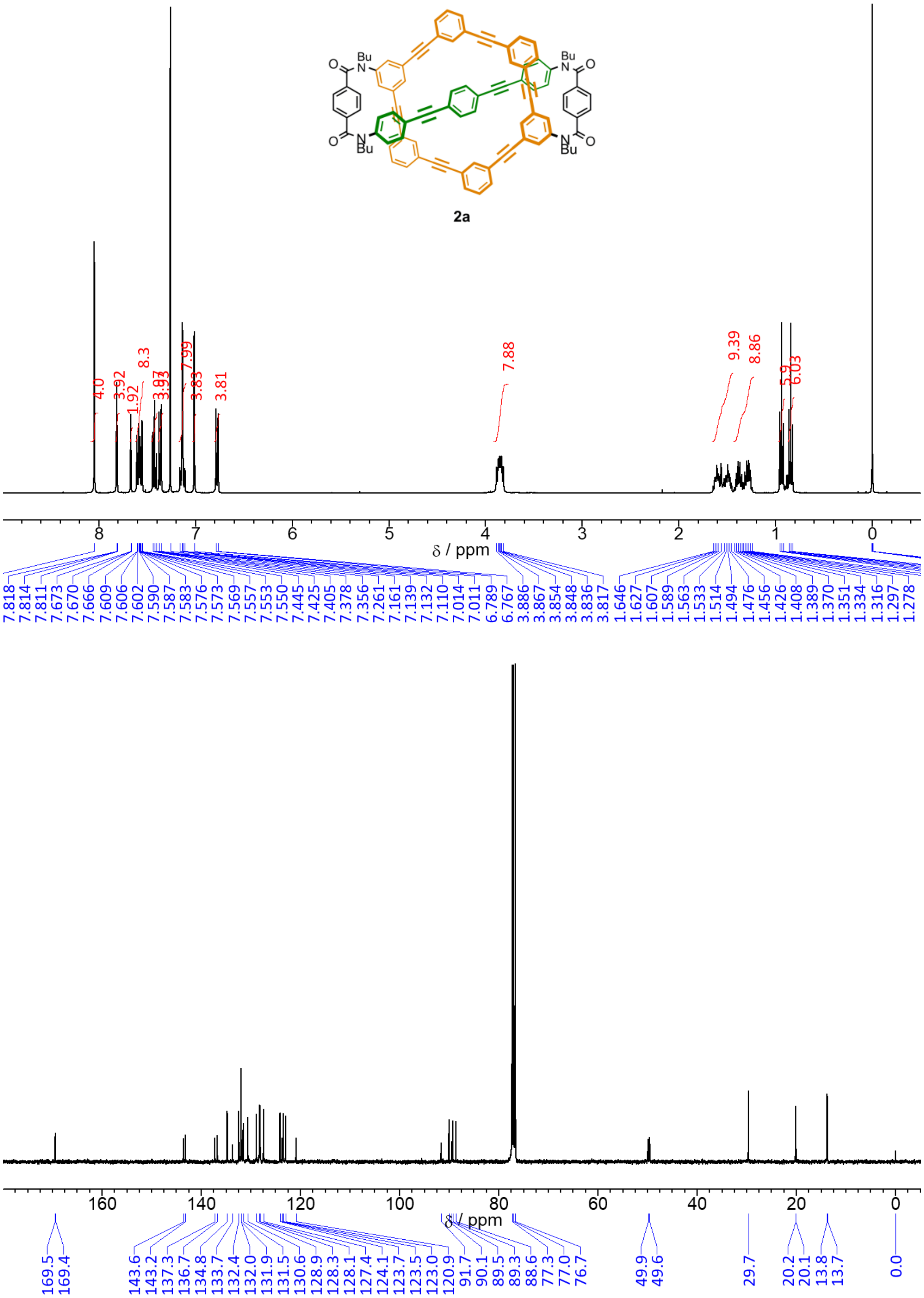
^{1}H and ^{13}C NMR spectra of new compounds



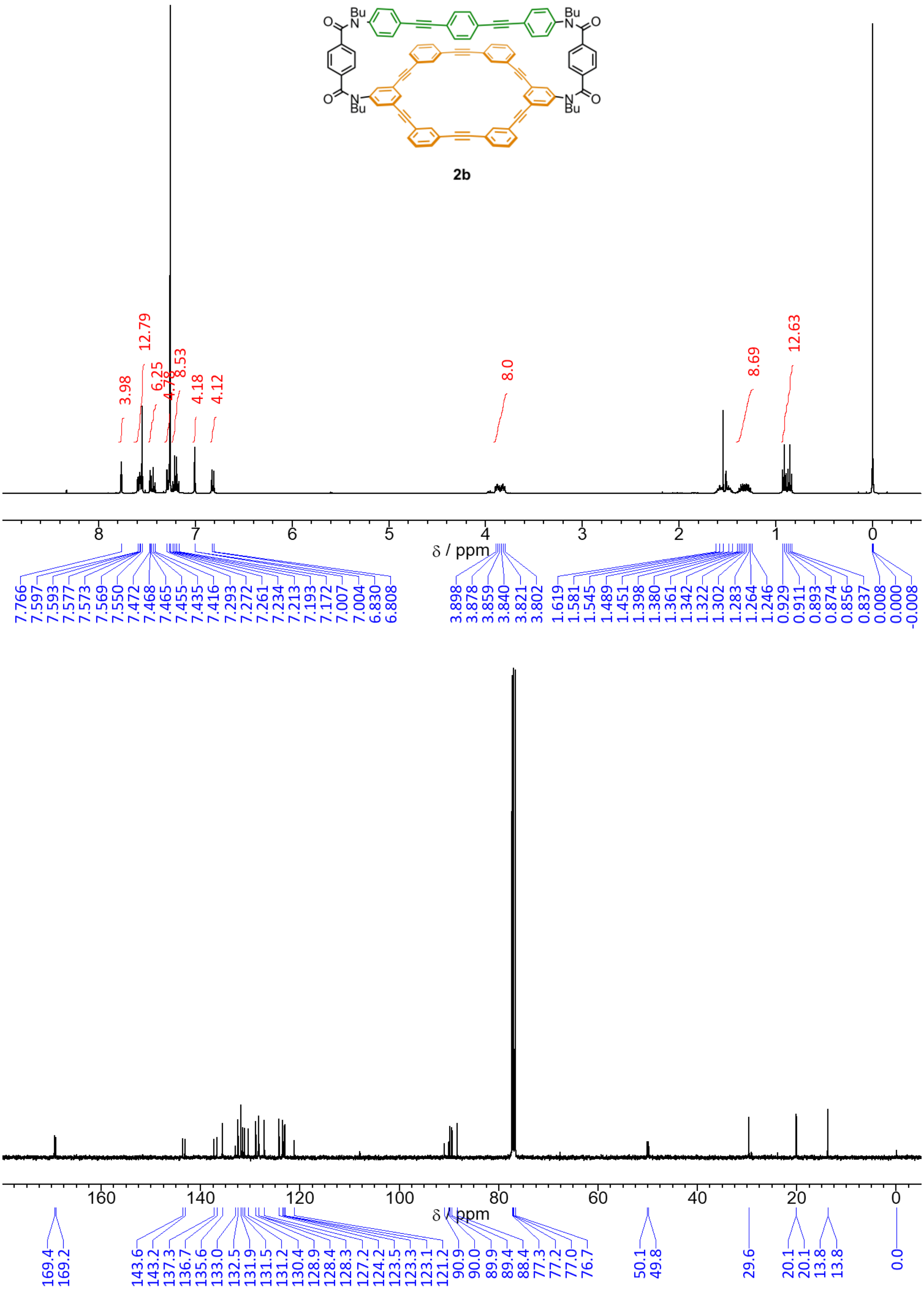
^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **1a** (second fraction), measured in chloroform-*d* at room temperature.



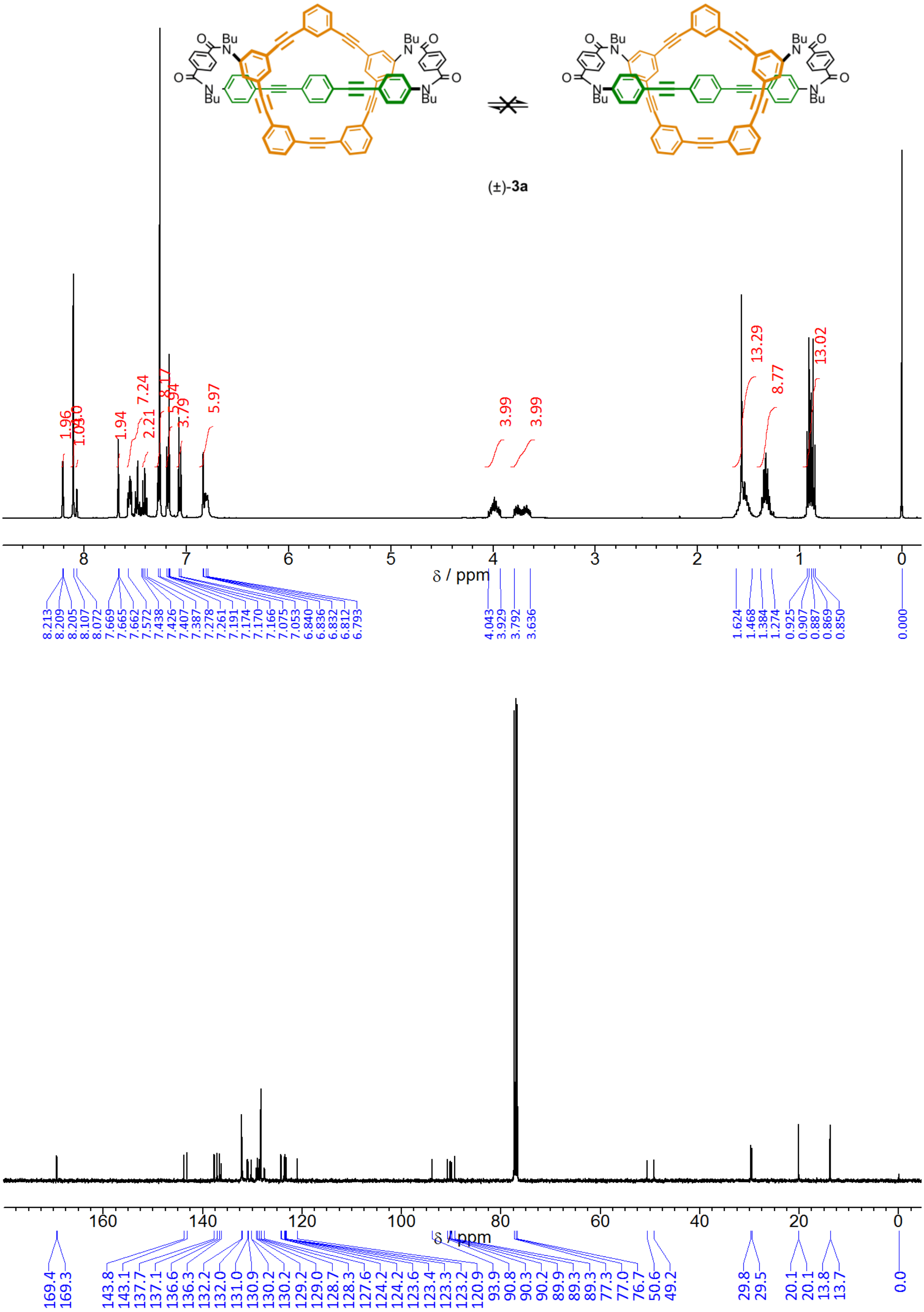
^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **1b**, measured in chloroform-*d* at room temperature.



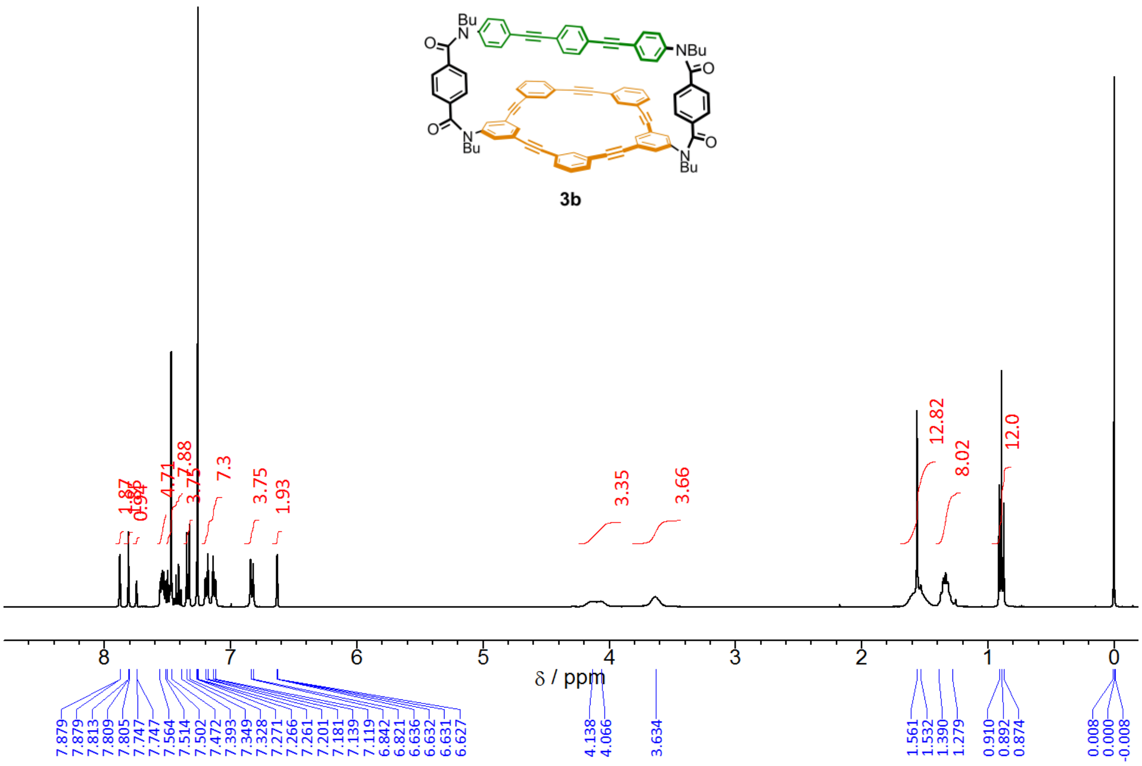
^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **2a**, measured in chloroform-*d* at room temperature.

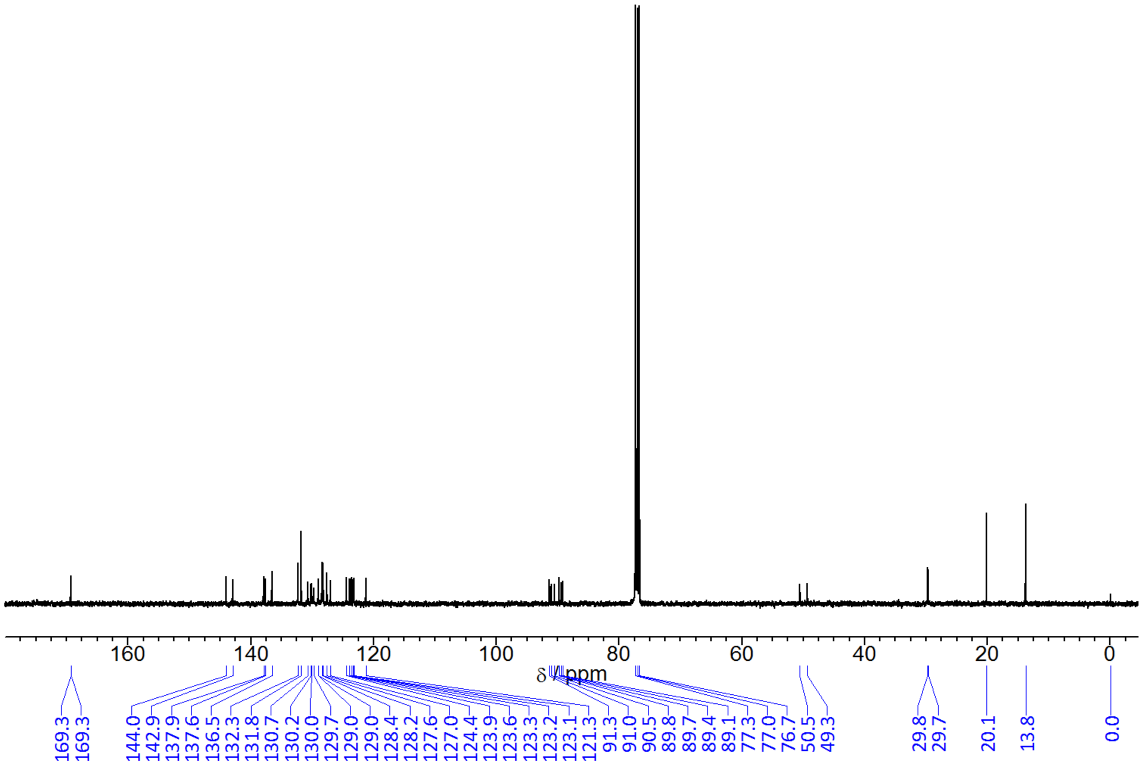


^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **2b**, containing residual solvents, measured in chloroform-*d* at room temperature.

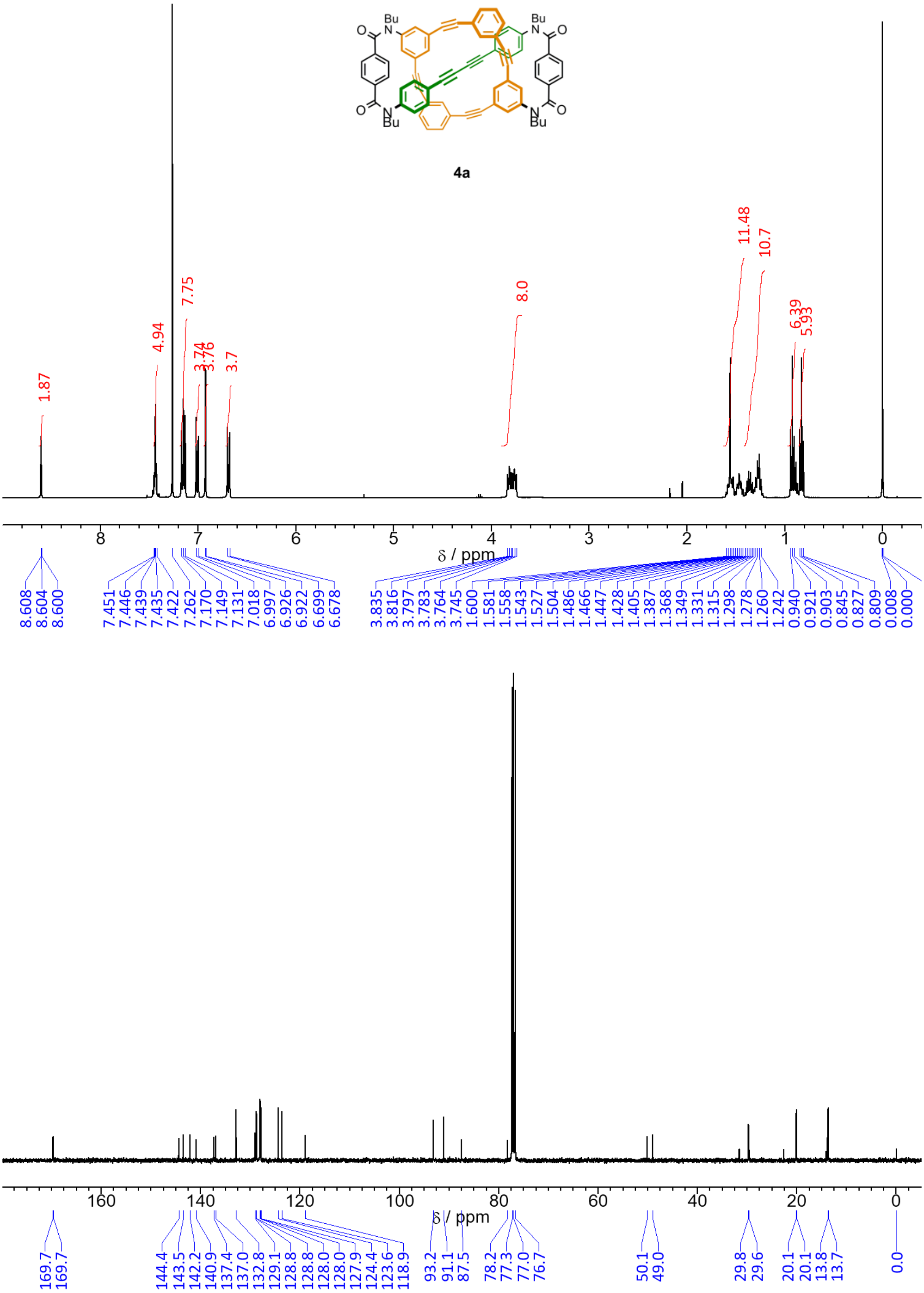


^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **3a** (first fraction), measured in chloroform-*d* at room temperature.



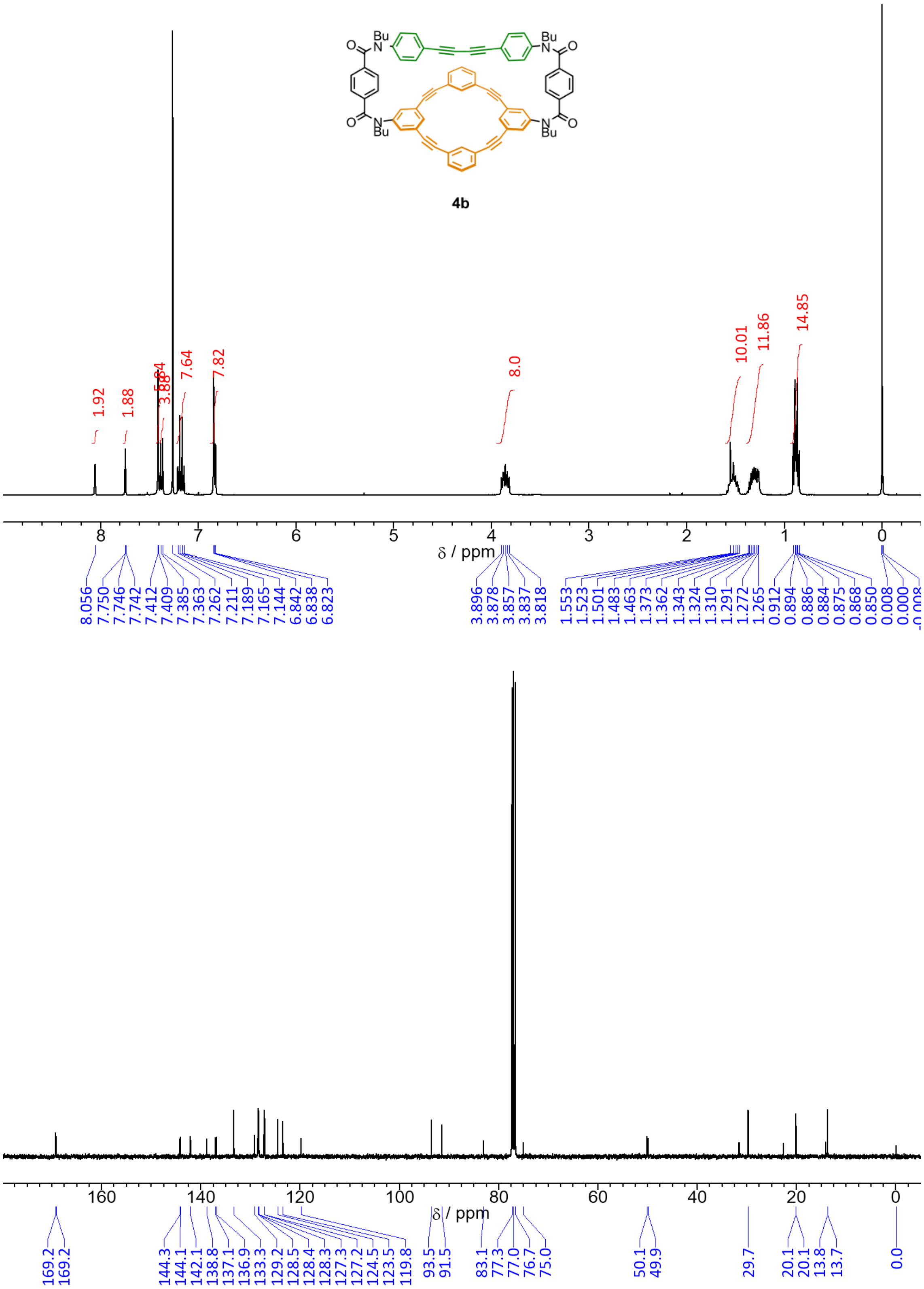


^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **3b**, measured in chloroform-*d* at room temperature.



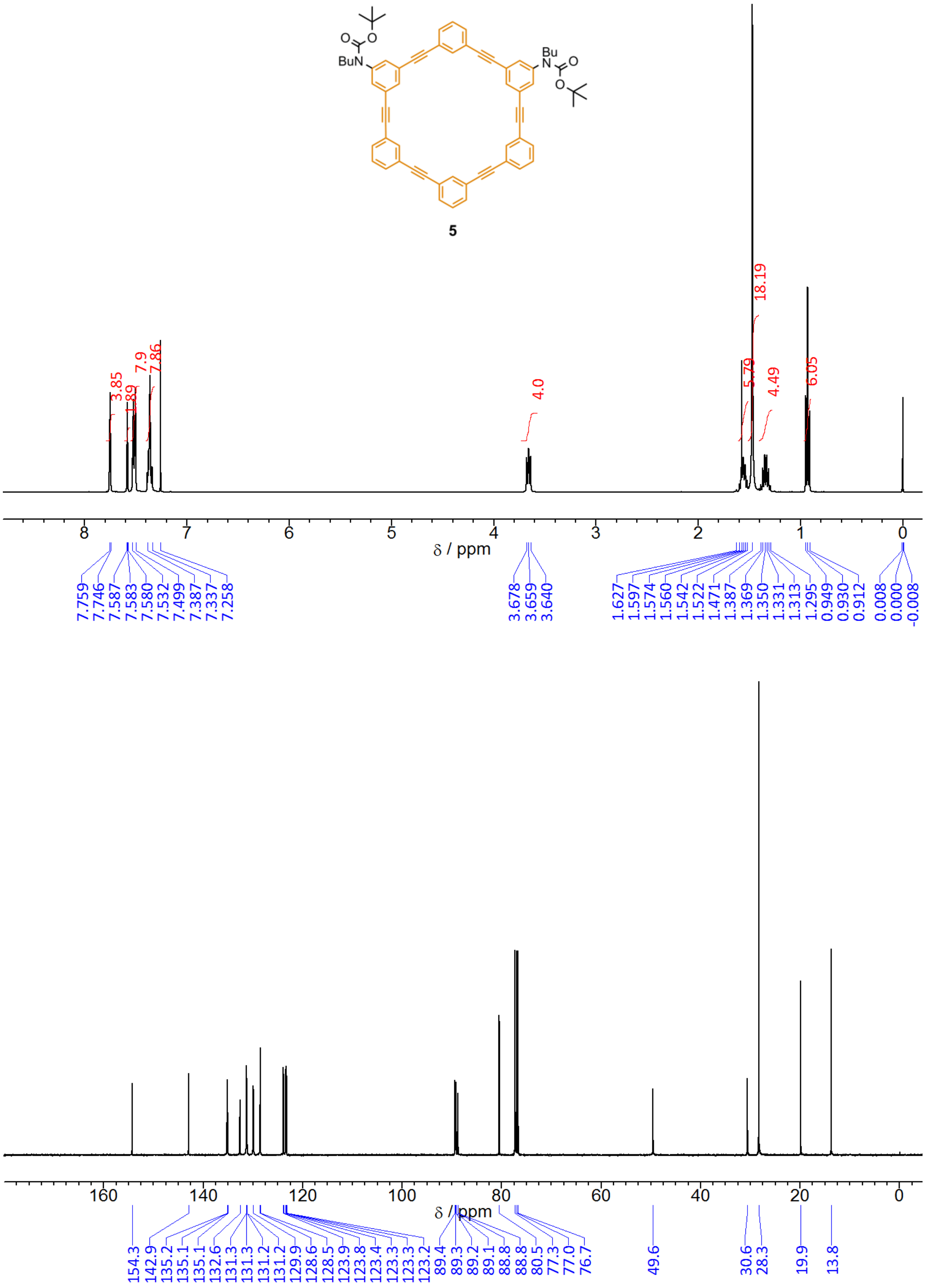
4a

^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **4a**, containing residual solvents, measured in chloroform-*d* at room temperature.

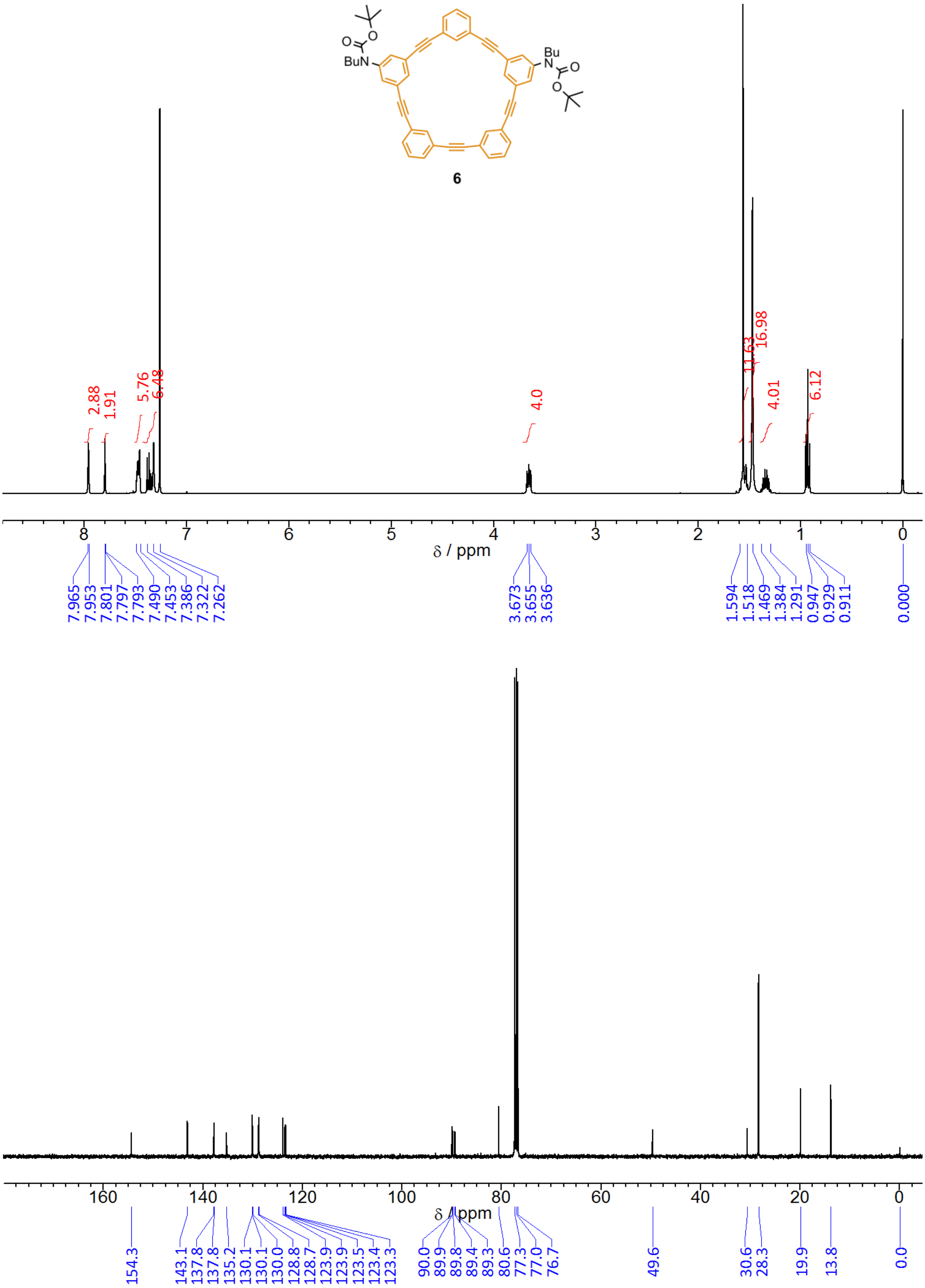


4b

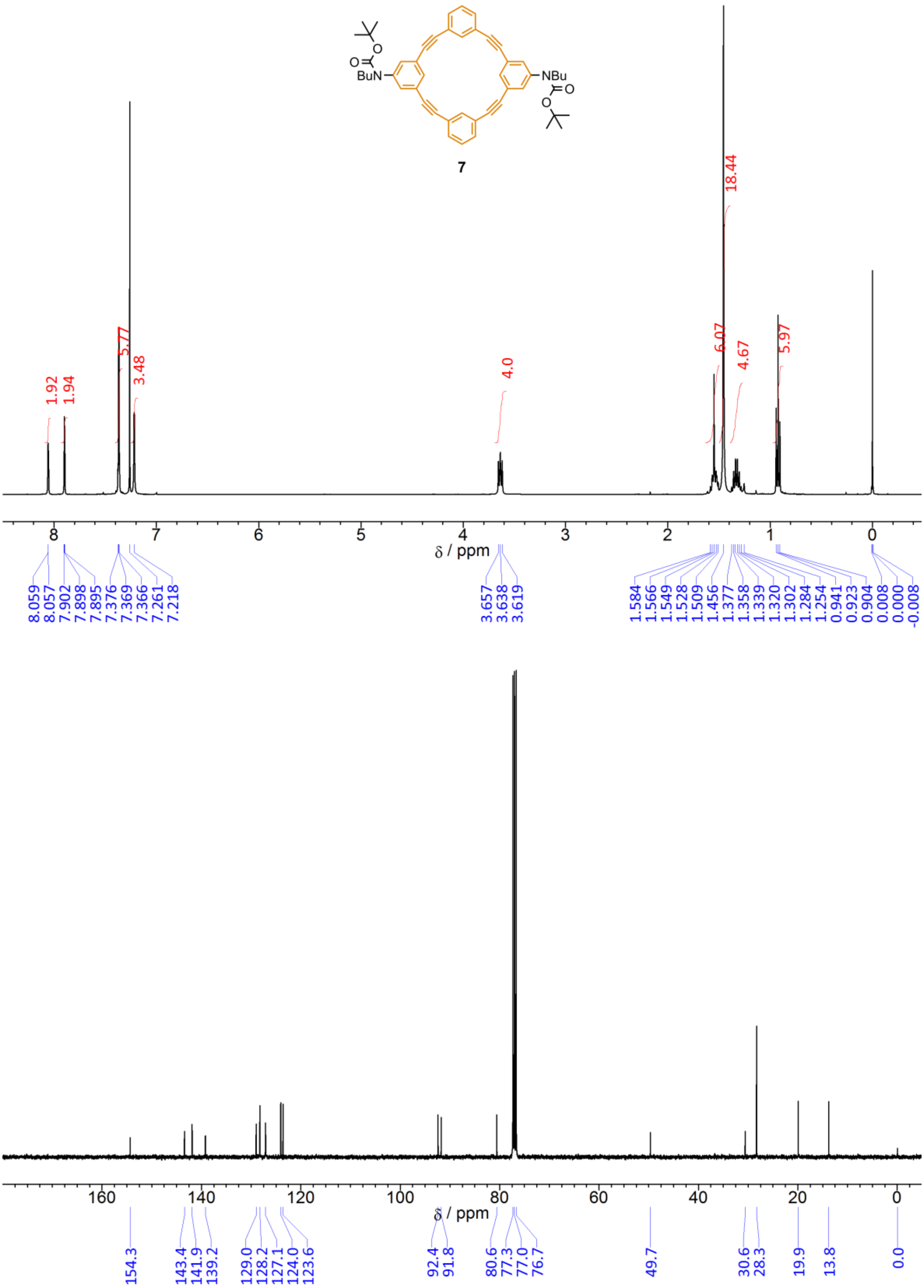
^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **4b**, containing residual solvents, measured in chloroform-*d* at room temperature.



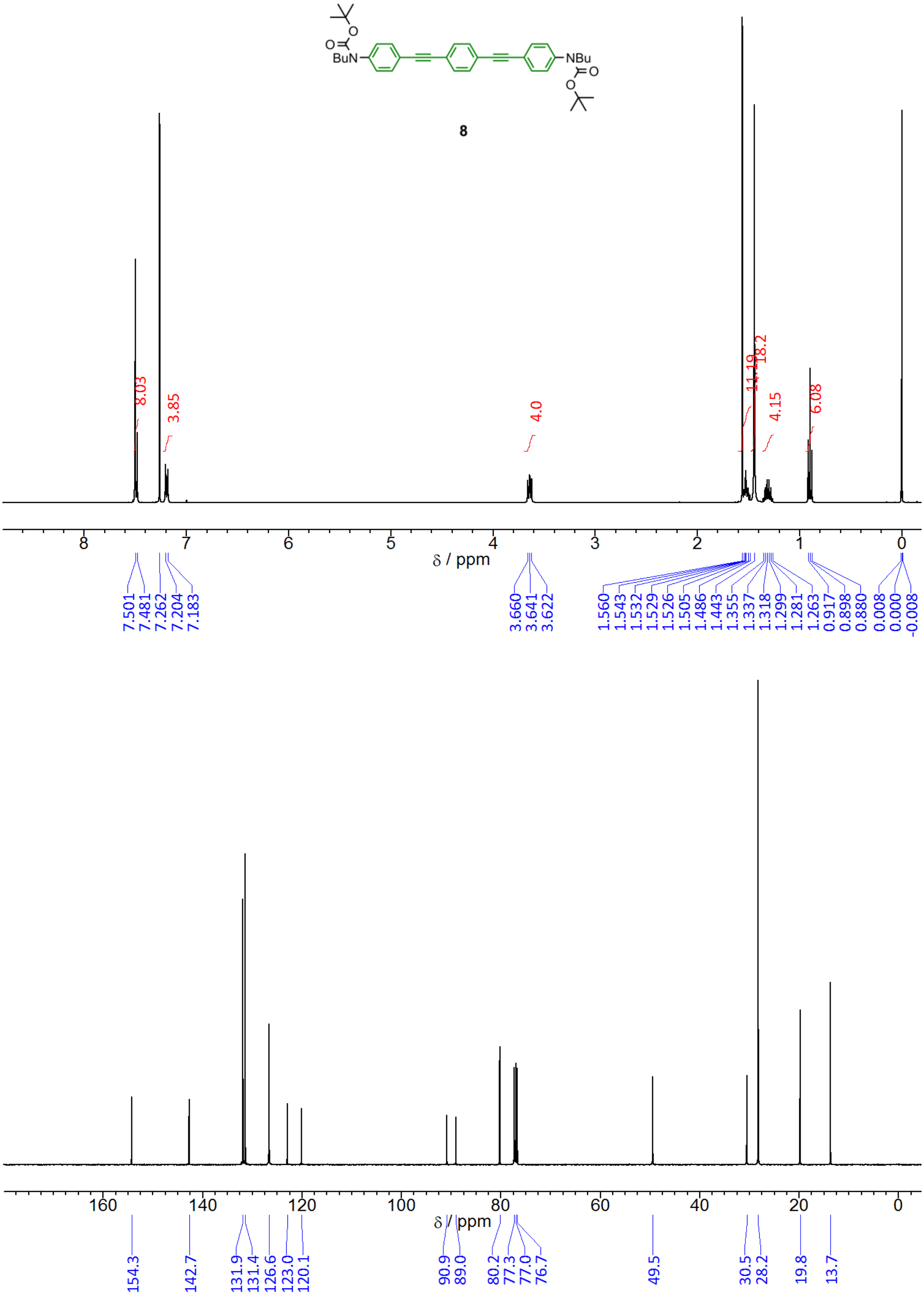
^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **5**, measured in chloroform-*d* at room temperature.



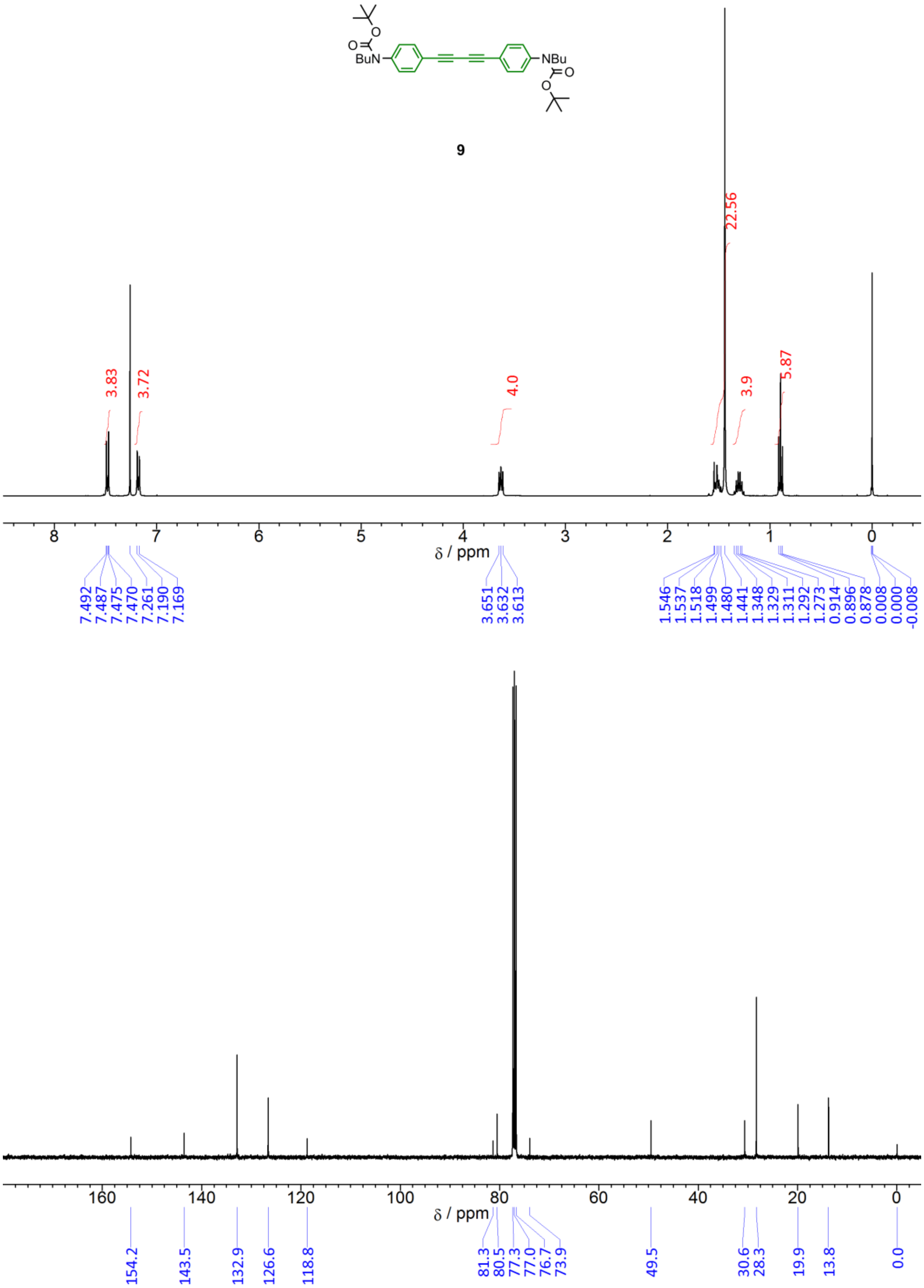
^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **6**, measured in chloroform-*d* at room temperature.



^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **7**, measured in chloroform-*d* at room temperature.

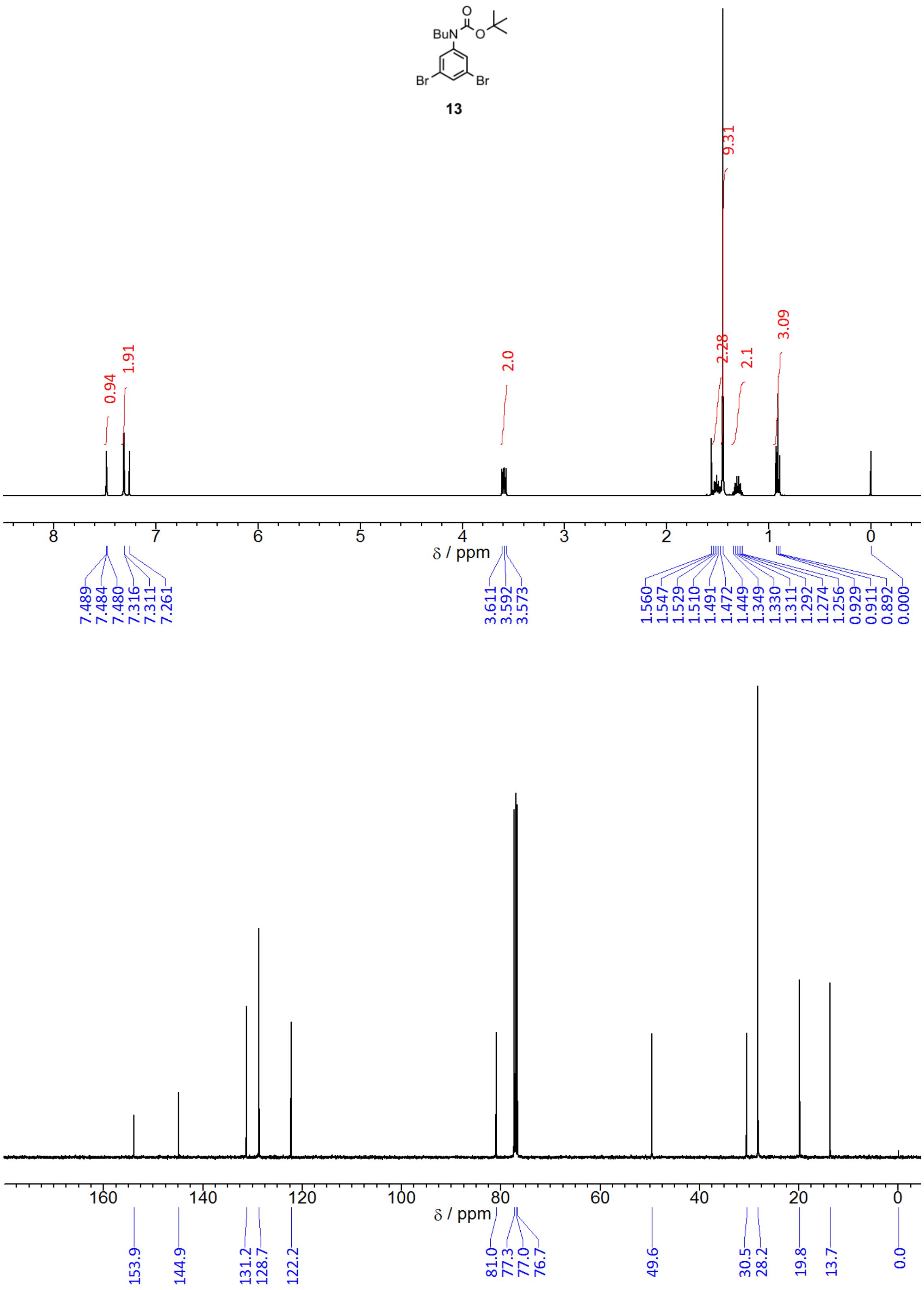


^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **8**, measured in chloroform-*d* at room temperature.

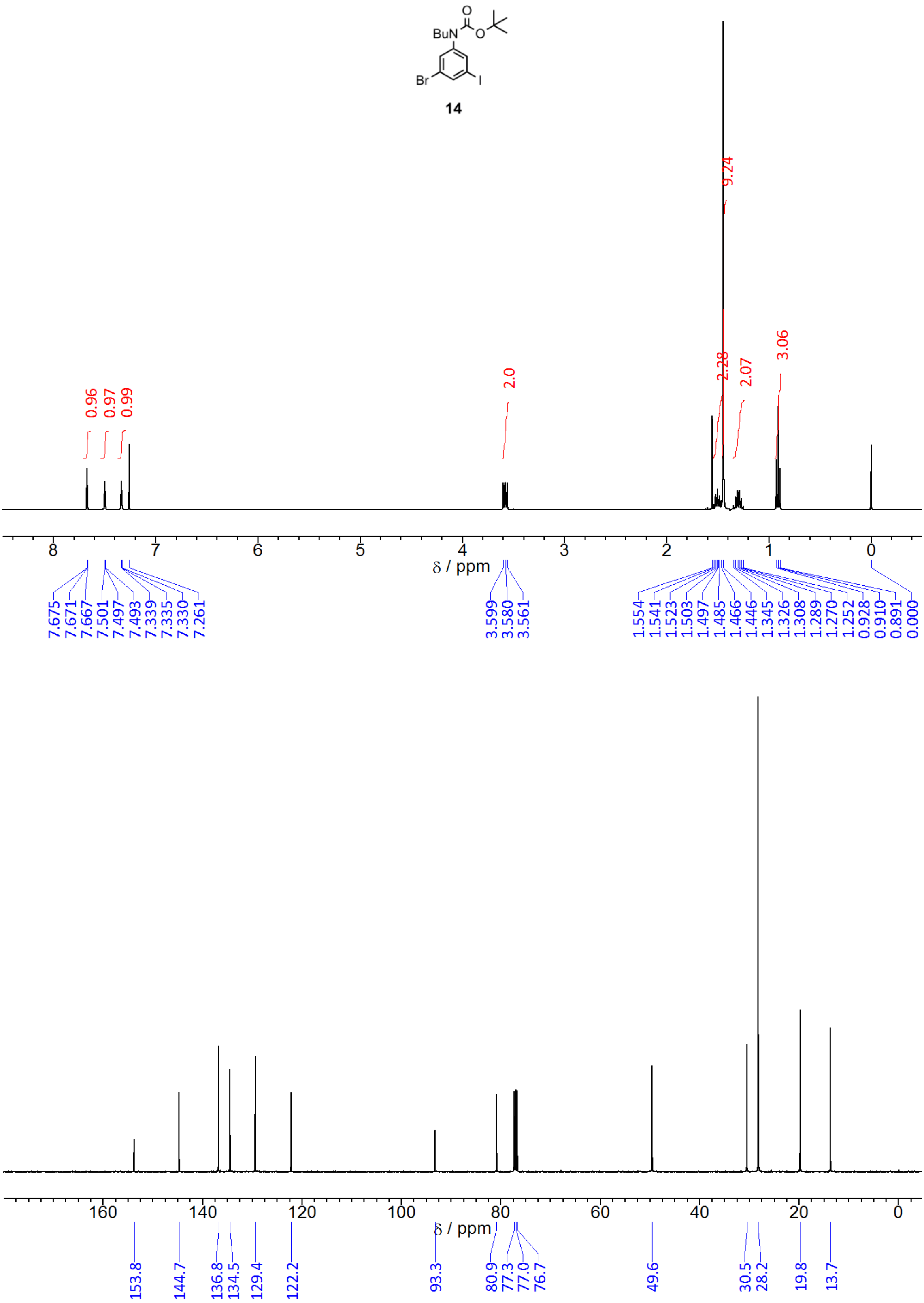


9

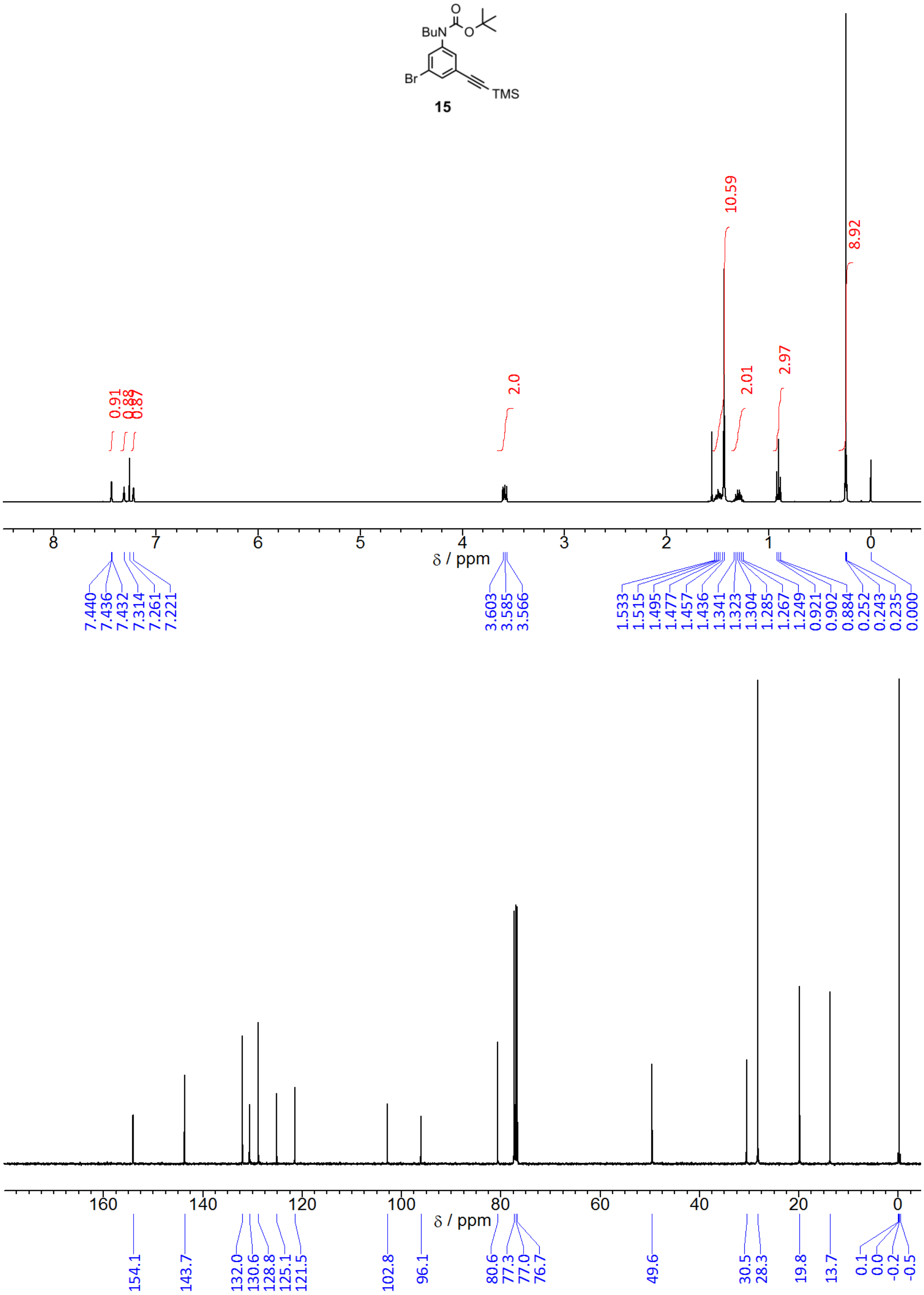
^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **9**, measured in chloroform-*d* at room temperature.



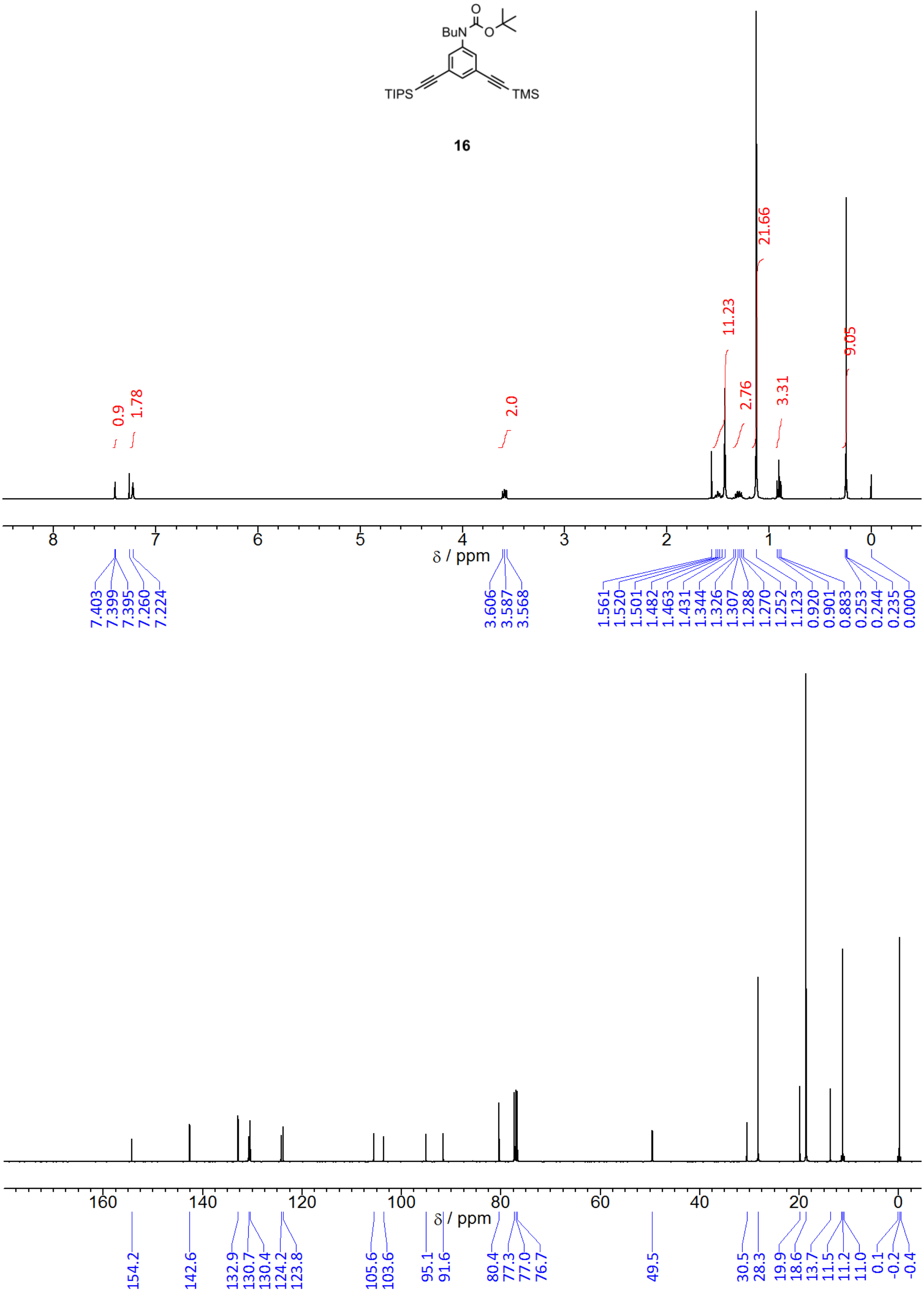
^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **13**, measured in chloroform-*d* at room temperature.



^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **14**, measured in chloroform-*d* at room temperature.

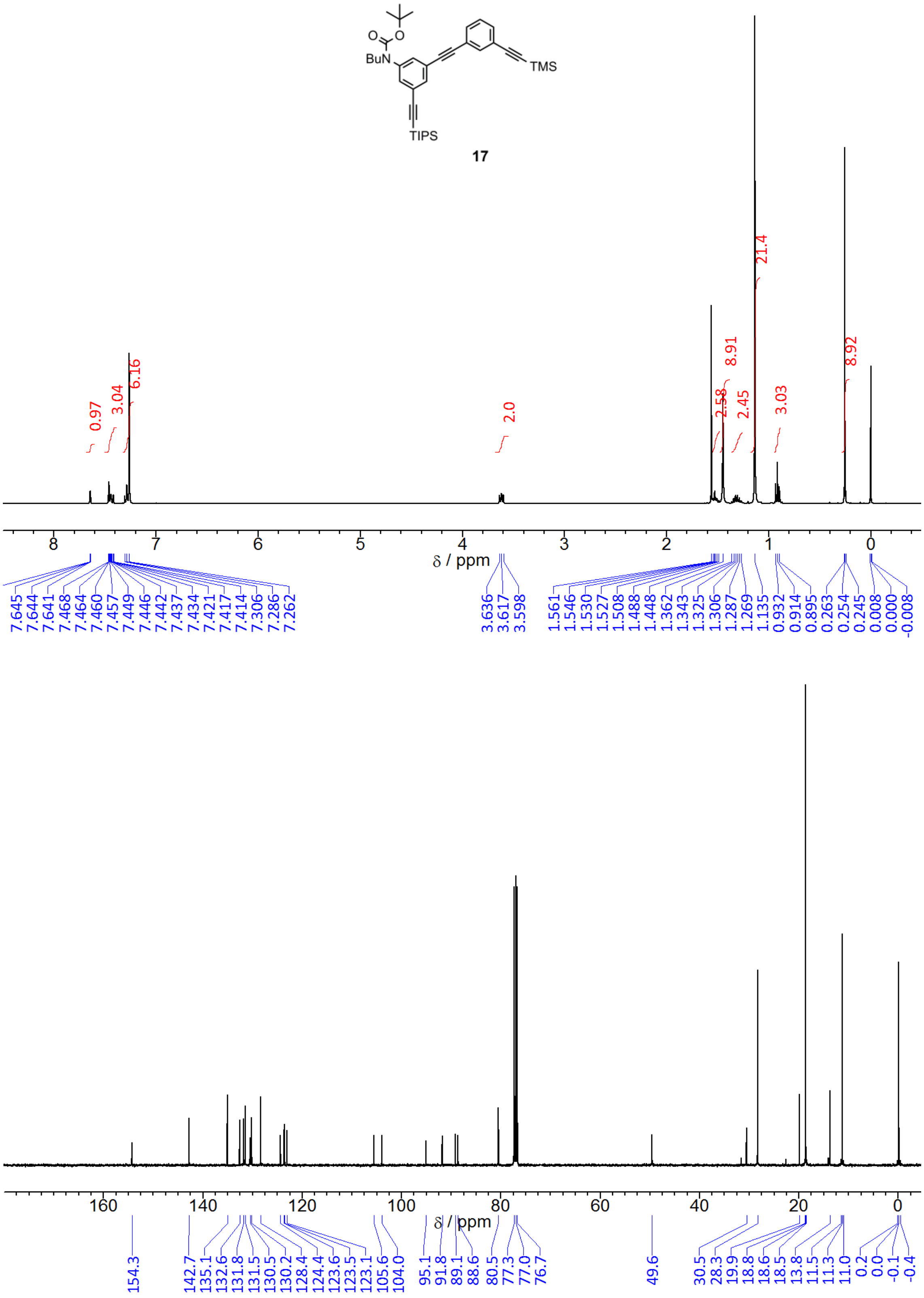


^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **15**, measured in chloroform-*d* at room temperature.

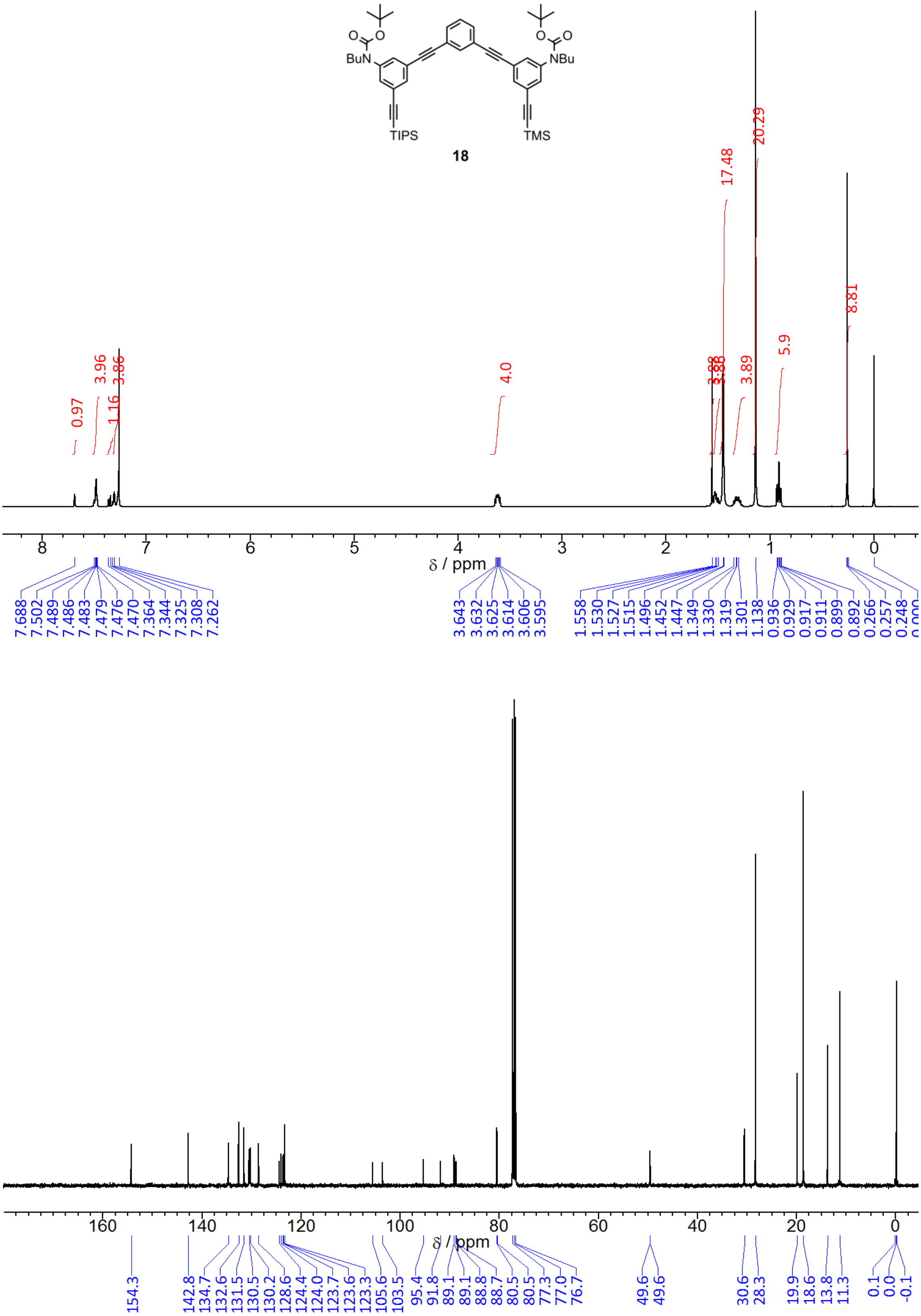


16

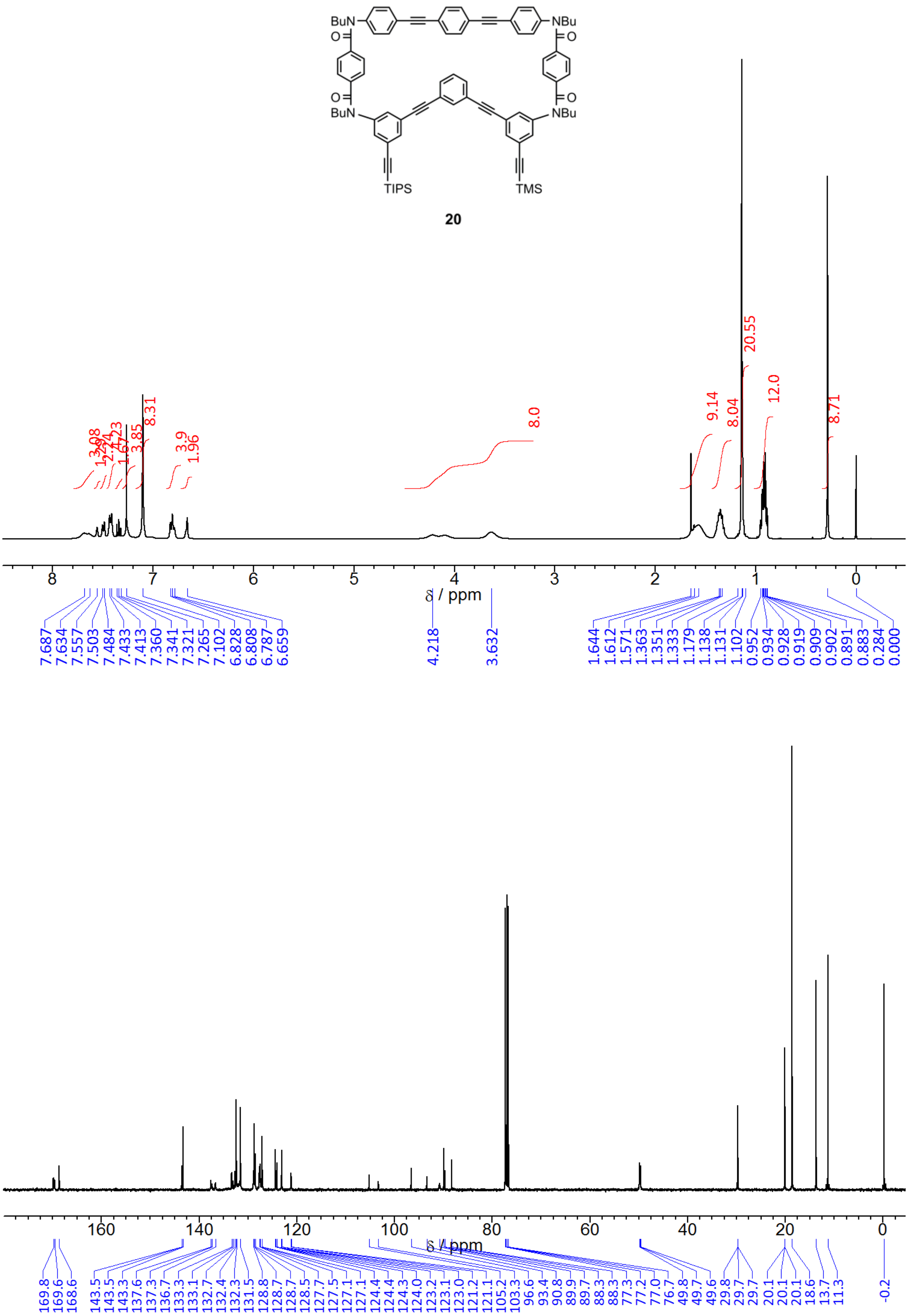
^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **16**, measured in chloroform-*d* at room temperature.



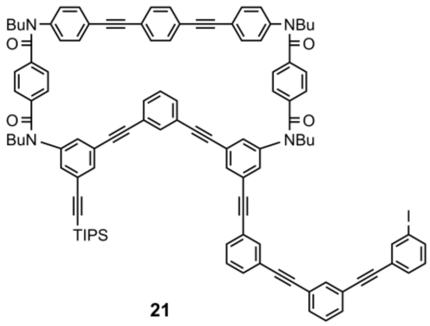
^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **17**, measured in chloroform-*d* at room temperature.



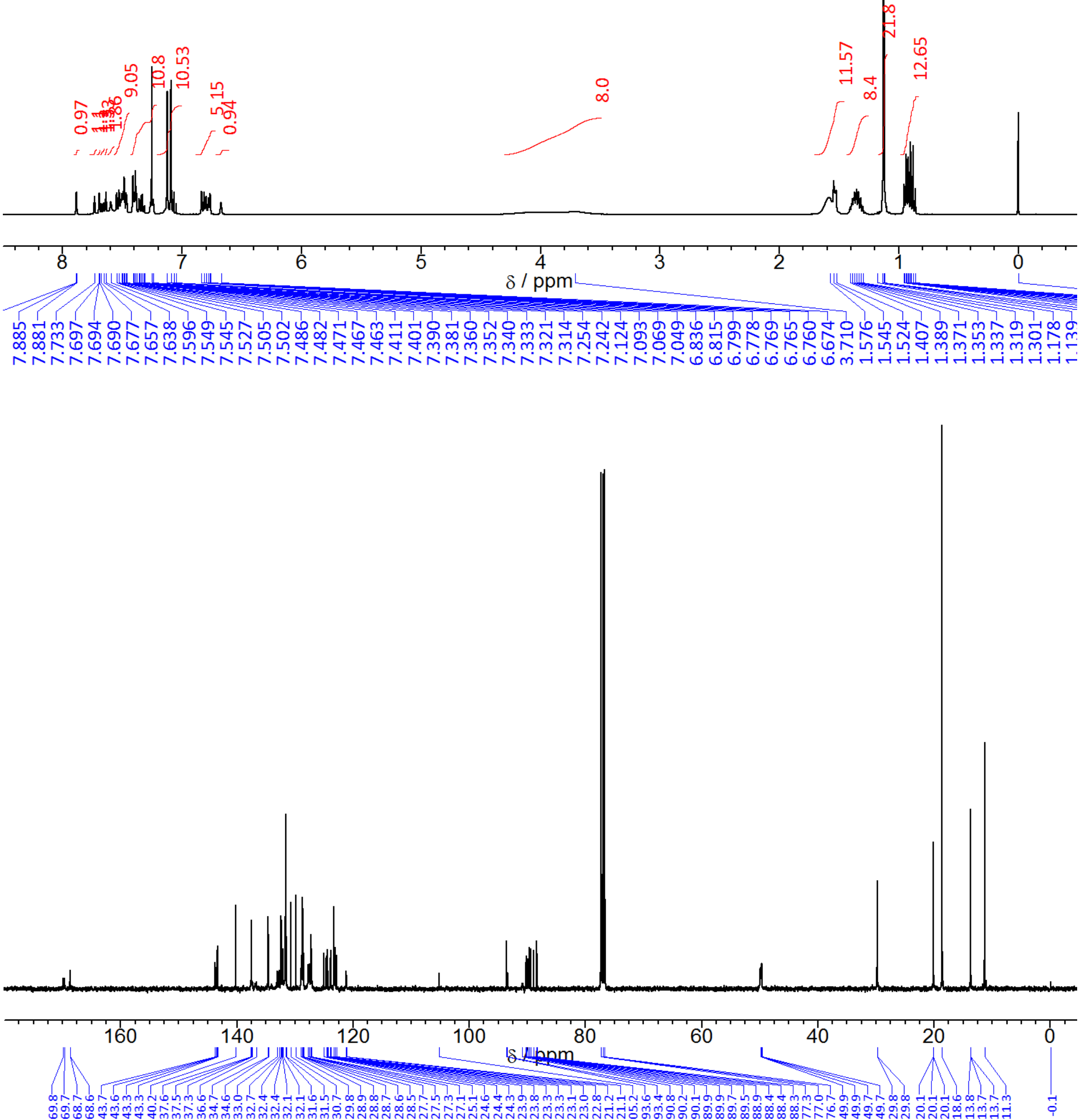
^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **18**, measured in chloroform-*d* at room temperature.



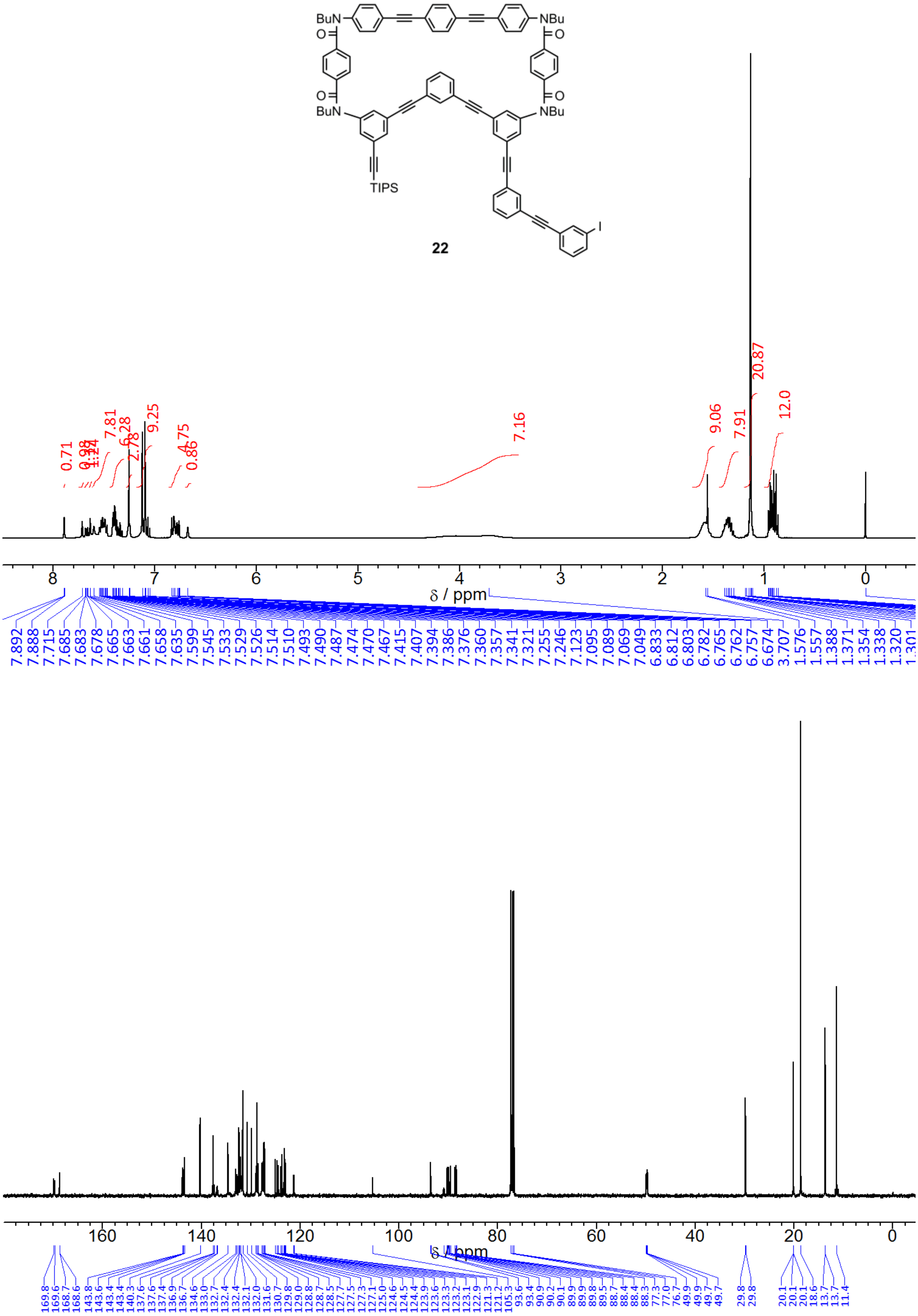
^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **20**, measured in chloroform-*d* at room temperature.



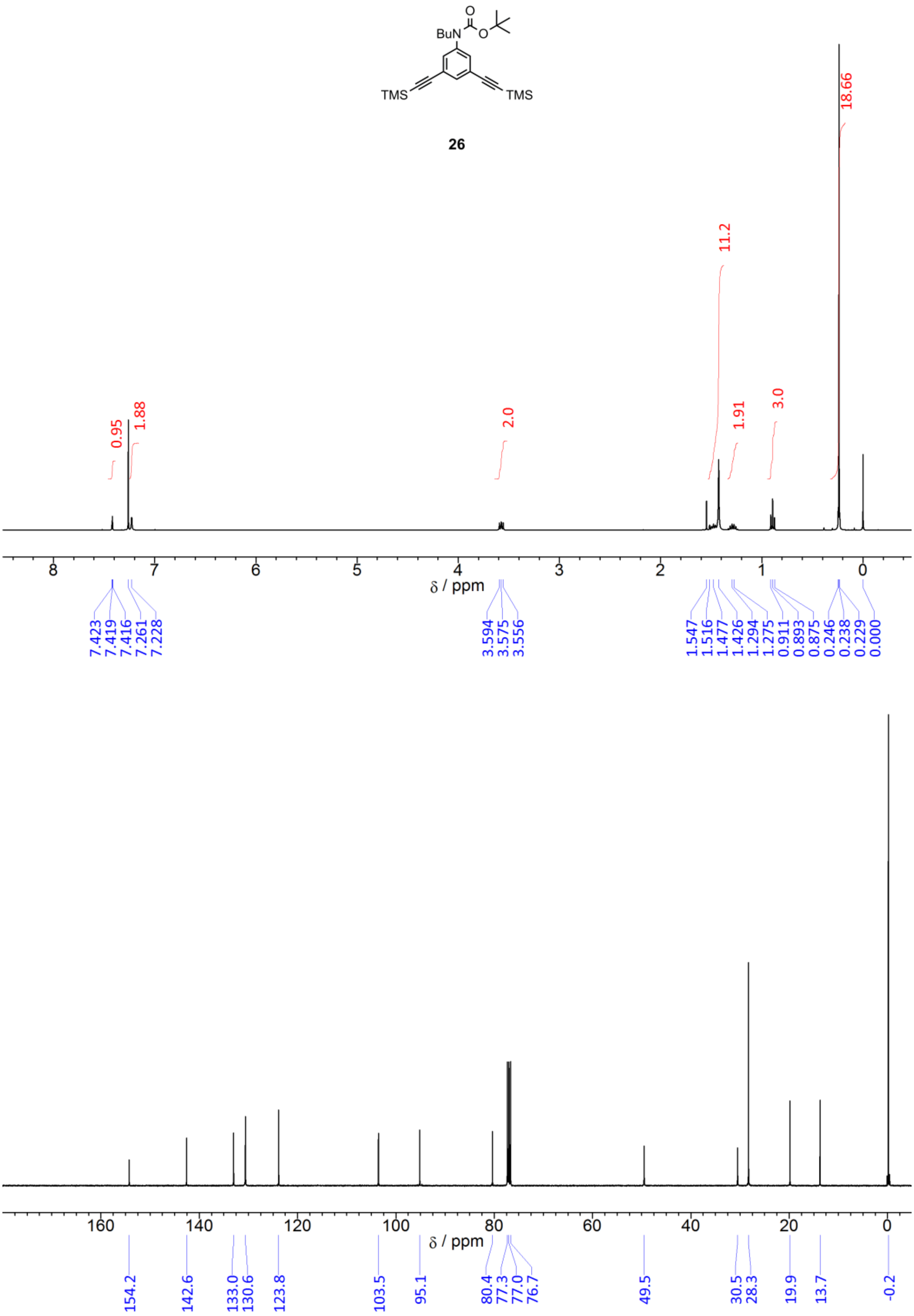
21



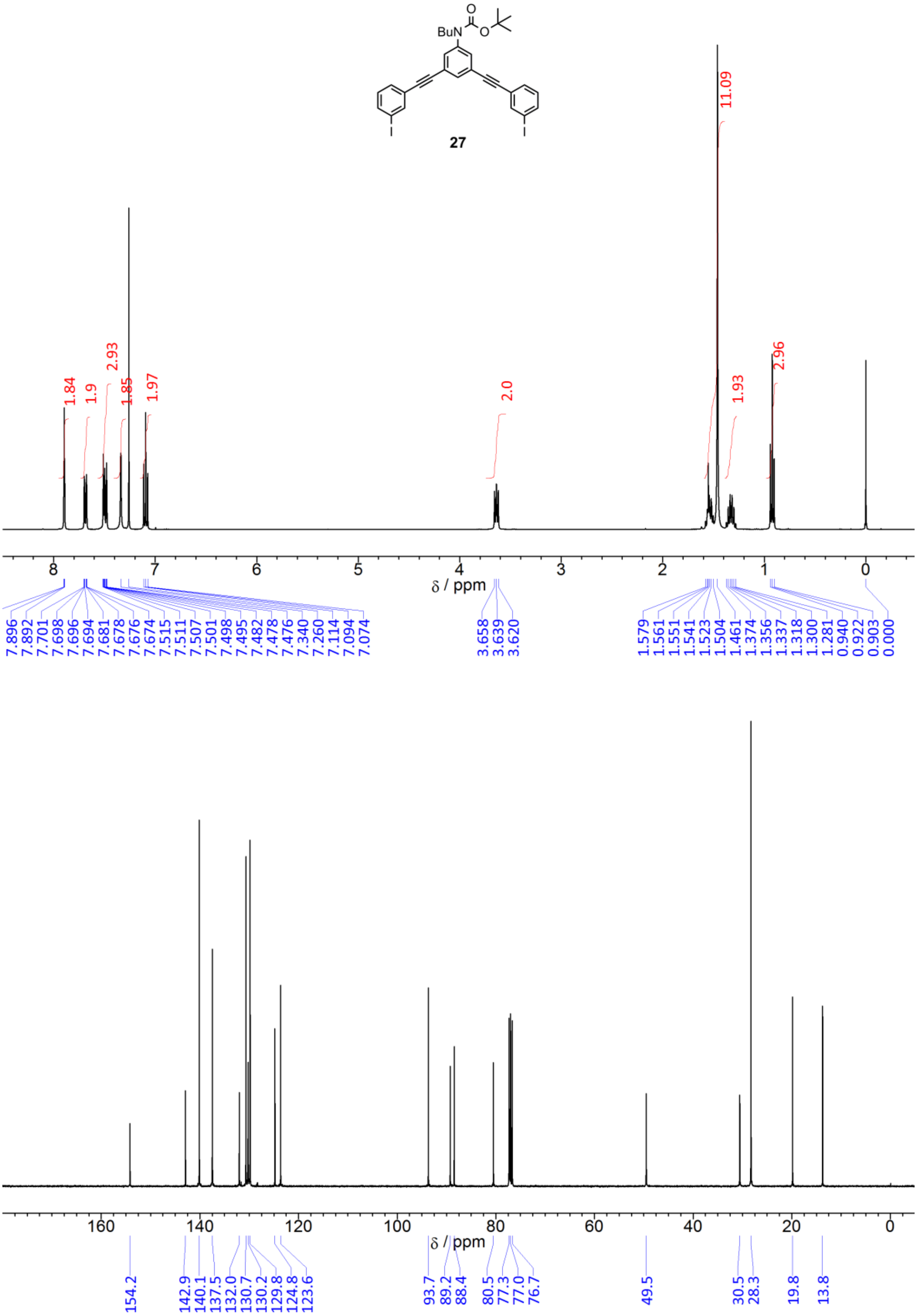
^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **21**, measured in chloroform-*d* at room temperature.



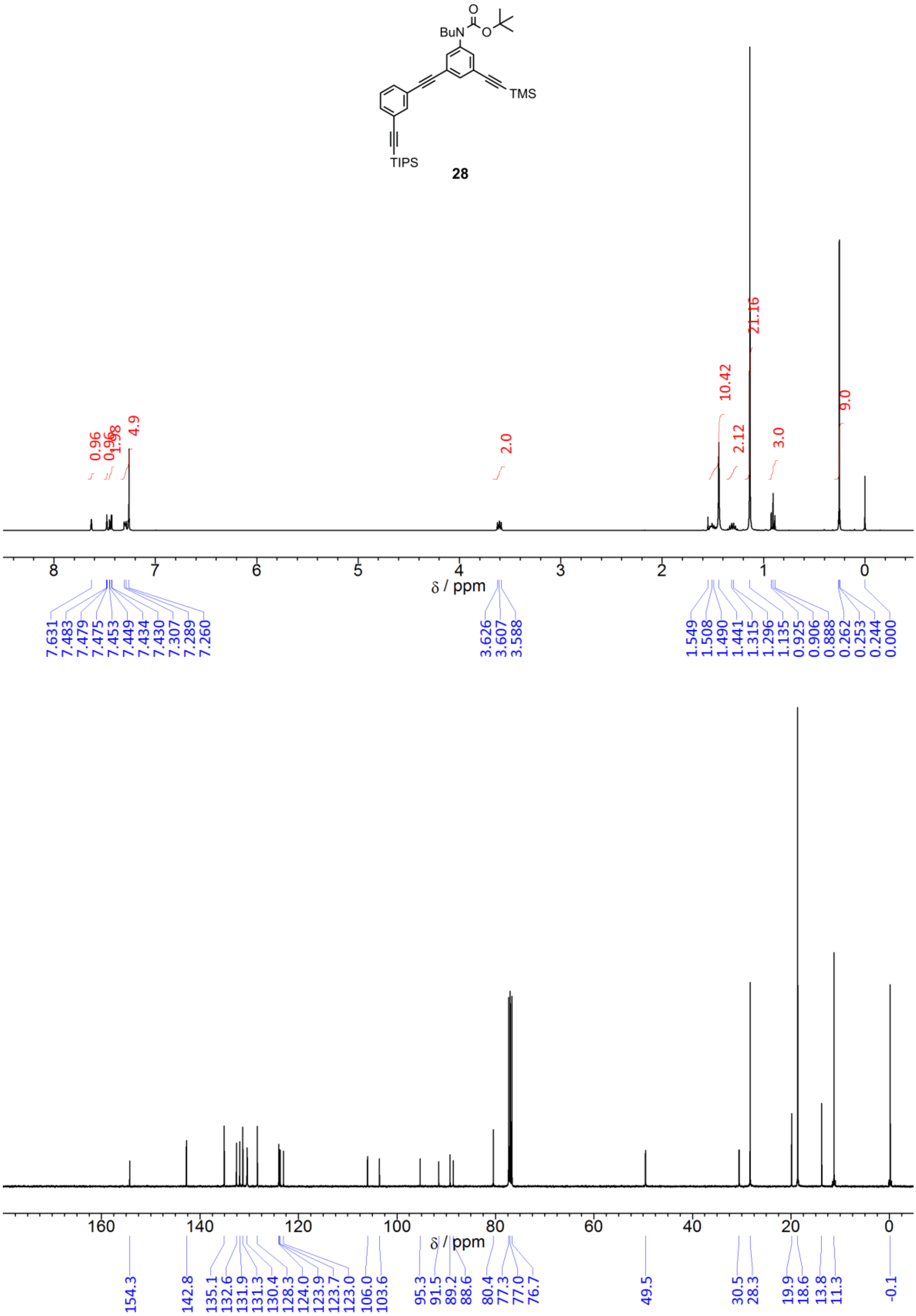
^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **22**, measured in chloroform-*d* at room temperature.



^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **26**, measured in chloroform-*d* at room temperature.

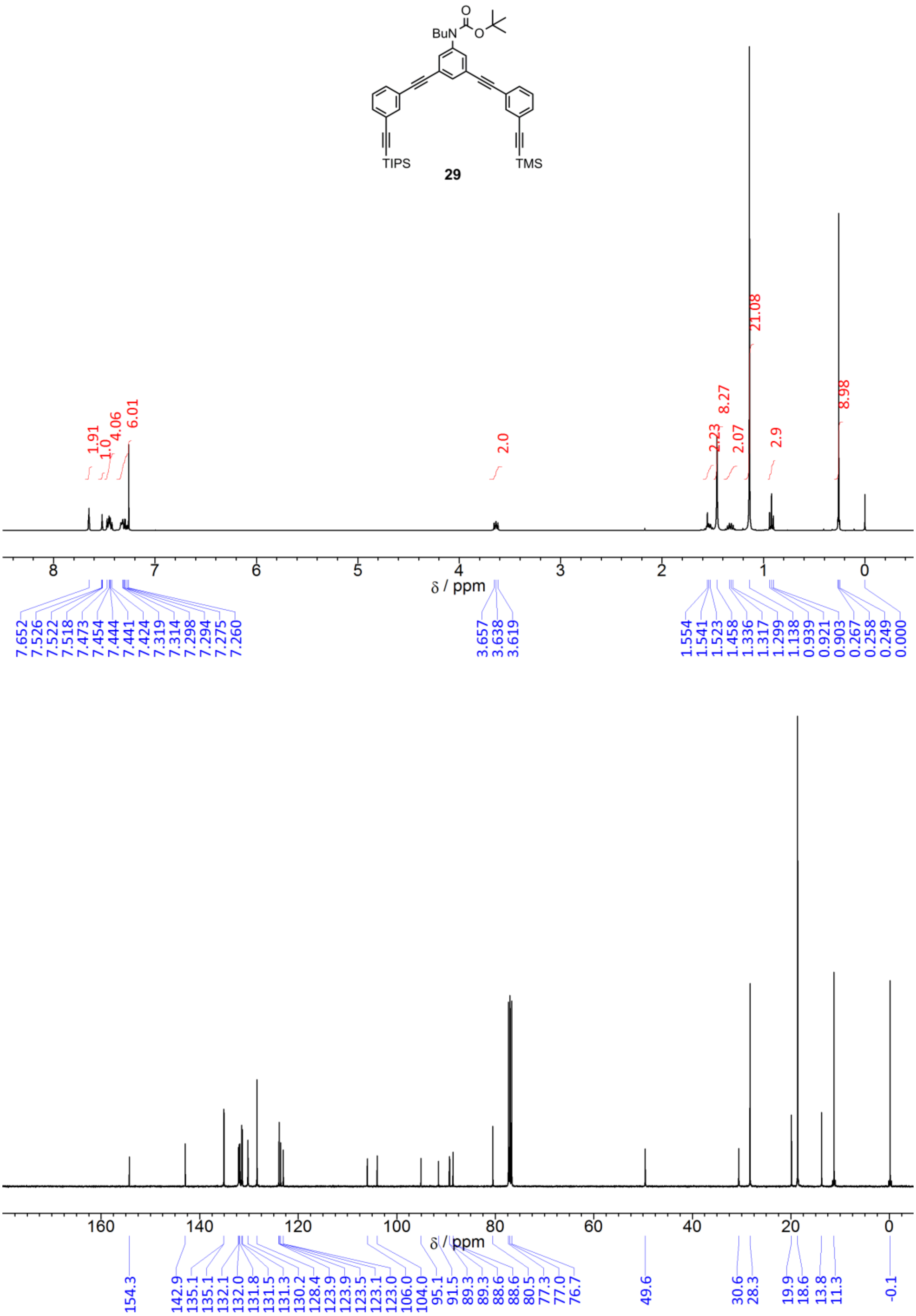


^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **27**, measured in chloroform-*d* at room temperature.

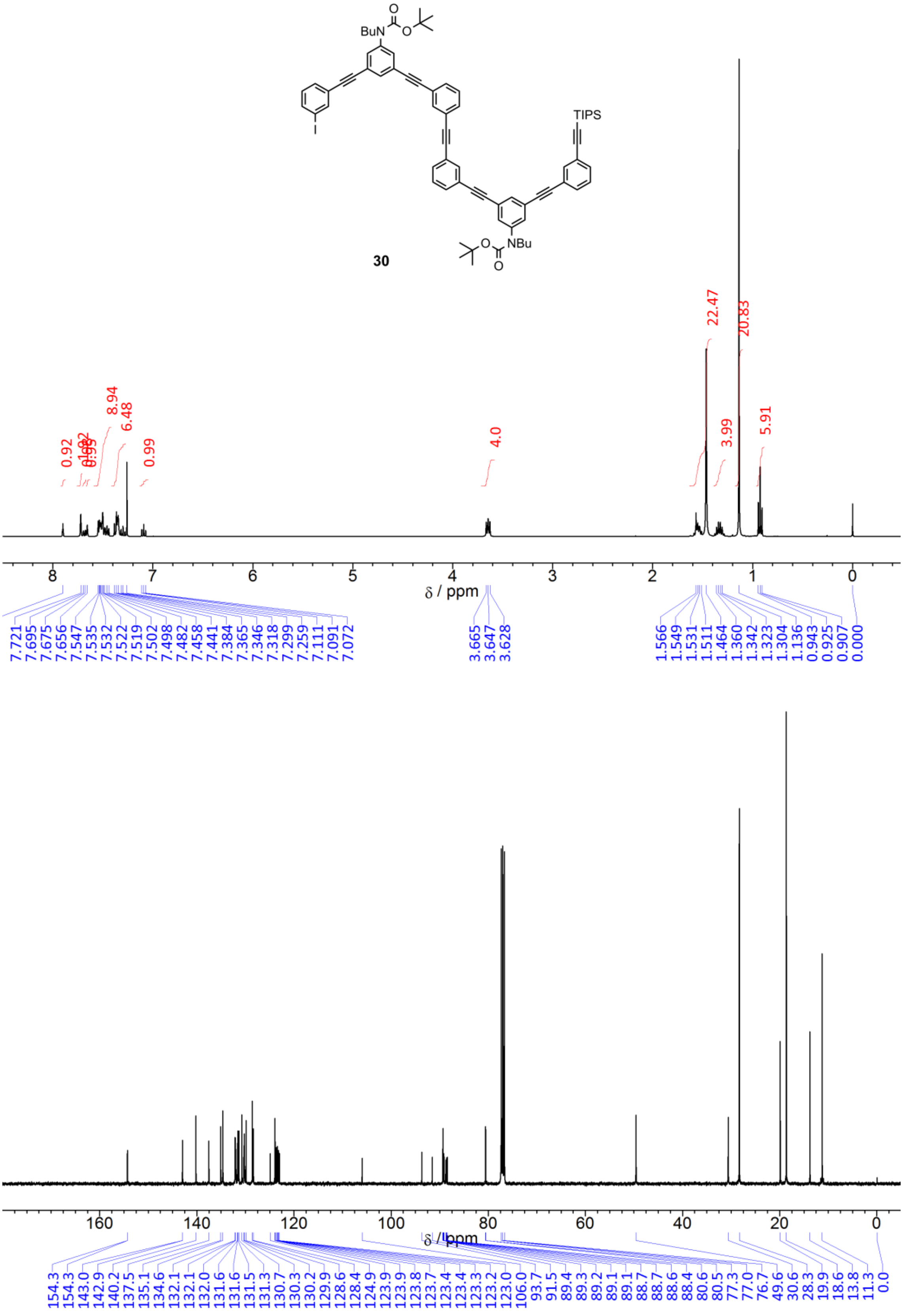


28

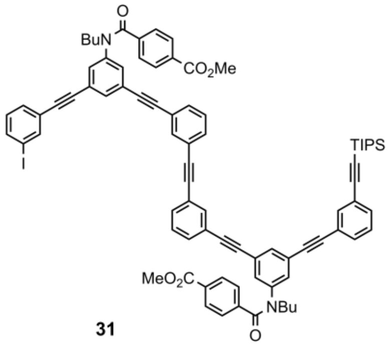
^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **28**, measured in chloroform-*d* at room temperature.



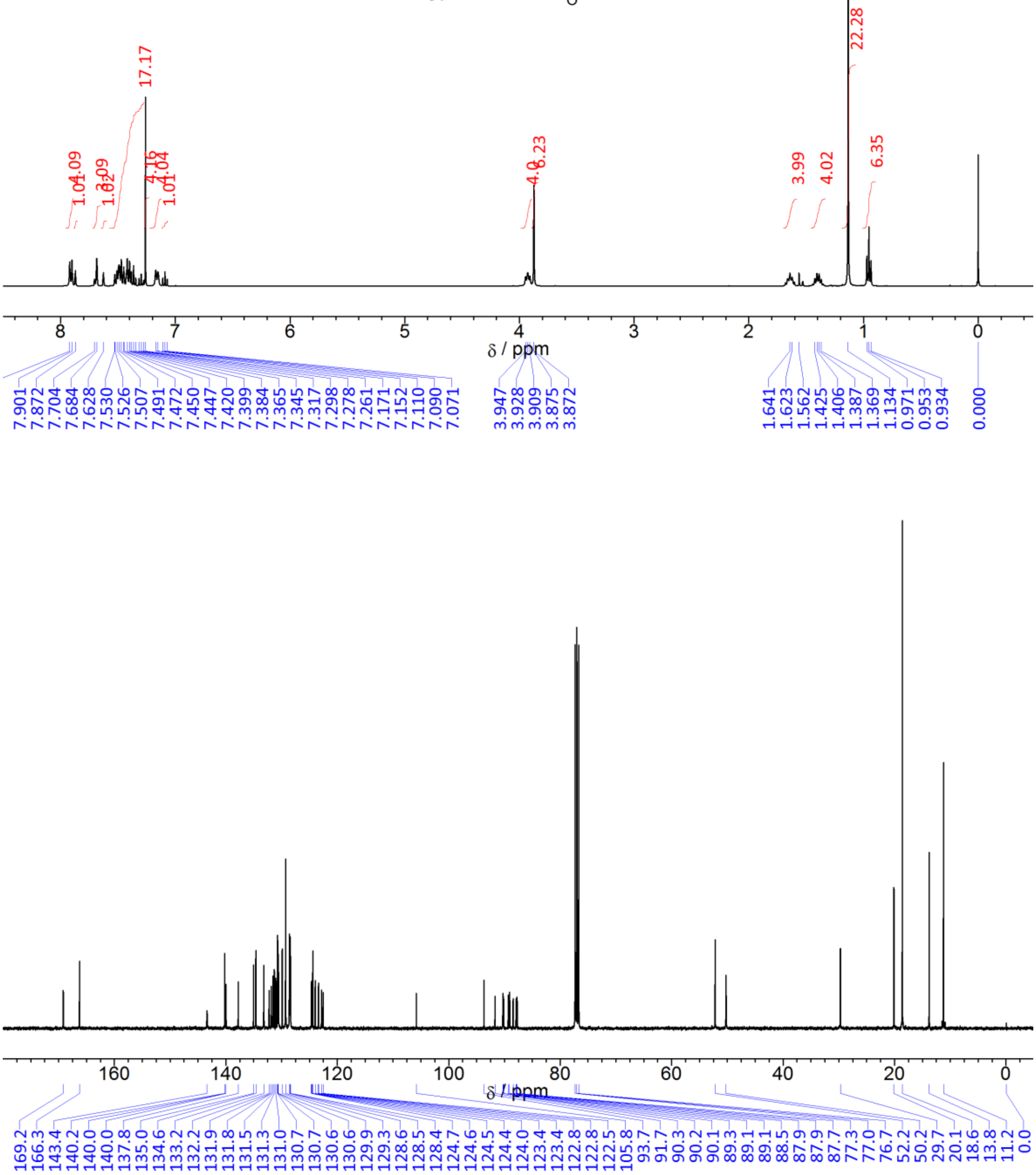
^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **29**, measured in chloroform-*d* at room temperature.


30

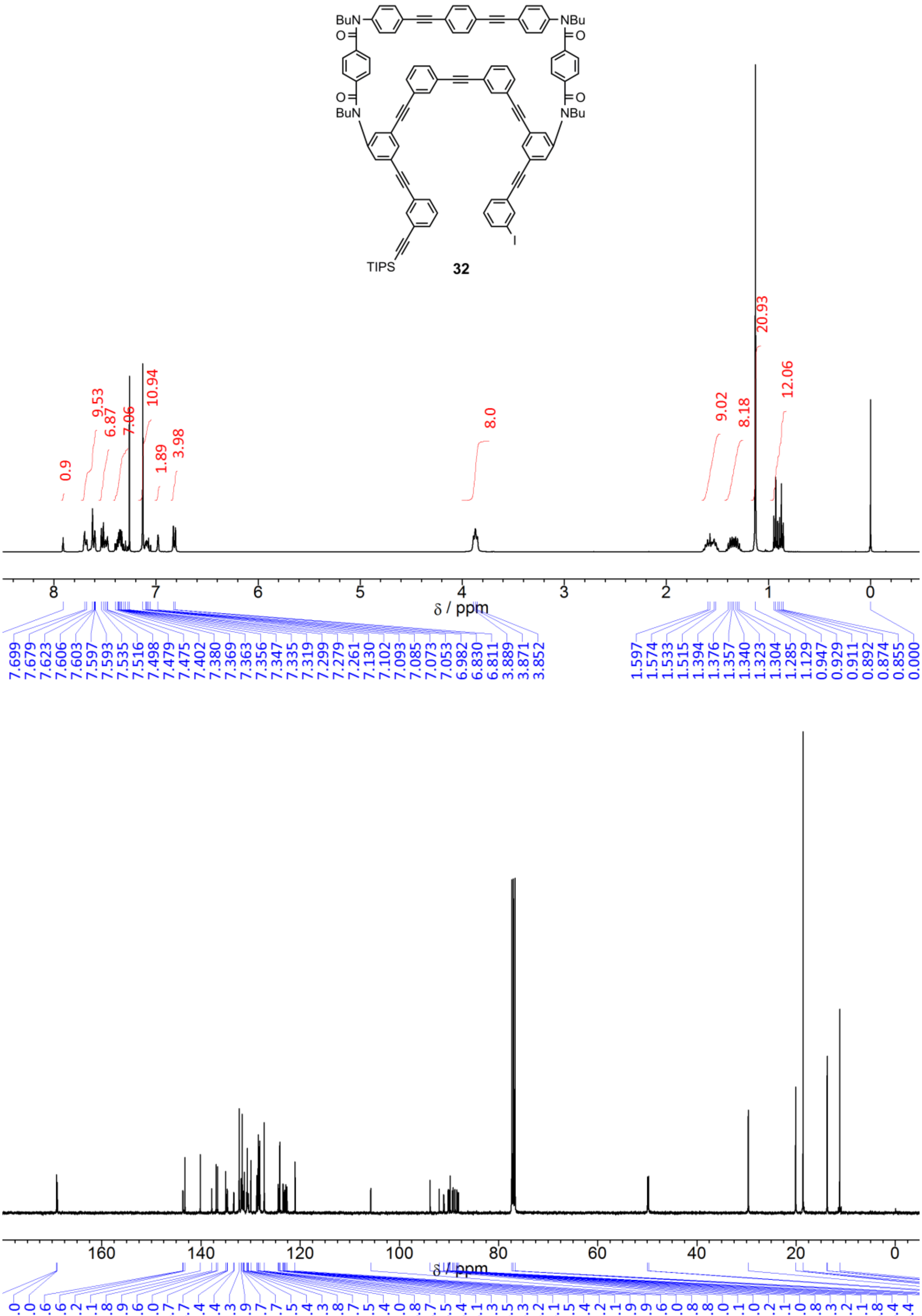
^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **30**, measured in chloroform-*d* at room temperature.



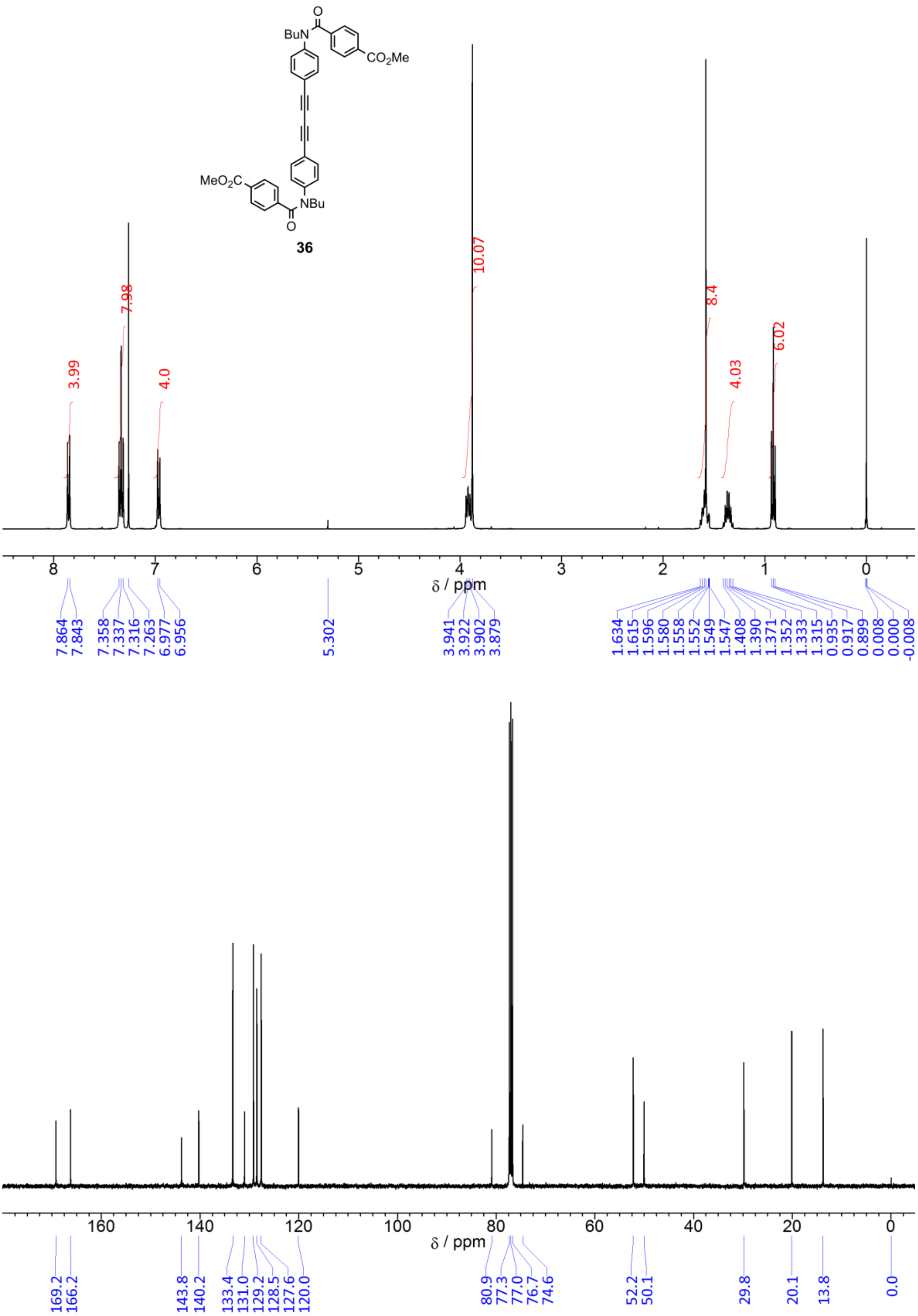
31



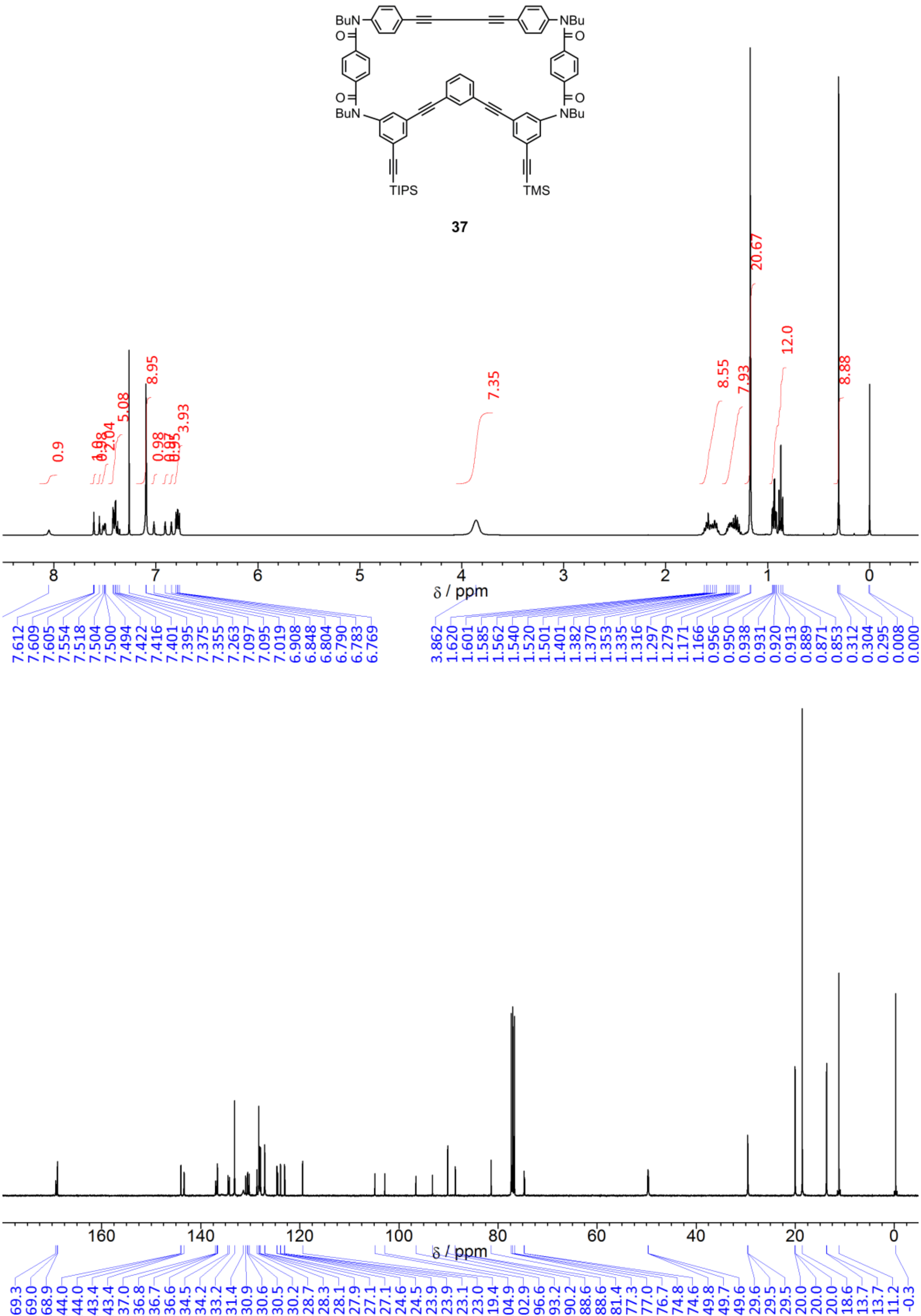
^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **31**, measured in chloroform-*d* at room temperature.



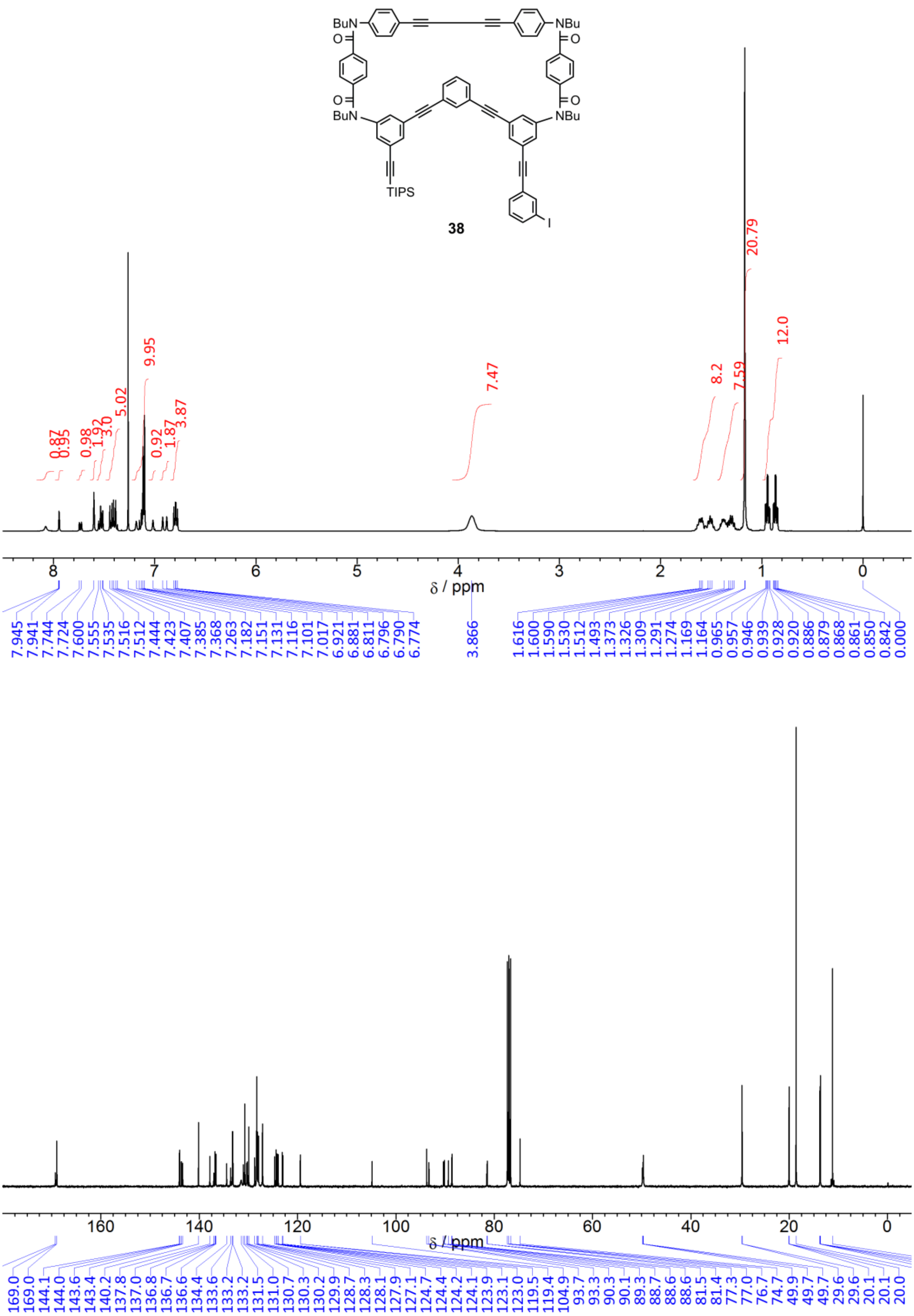
^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **32**, measured in chloroform-*d* at room temperature.



^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **36**, measured in chloroform-*d* at room temperature.

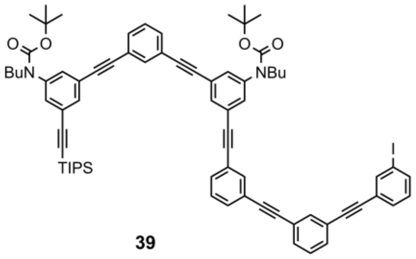


^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **37**, measured in chloroform-*d* at room temperature.

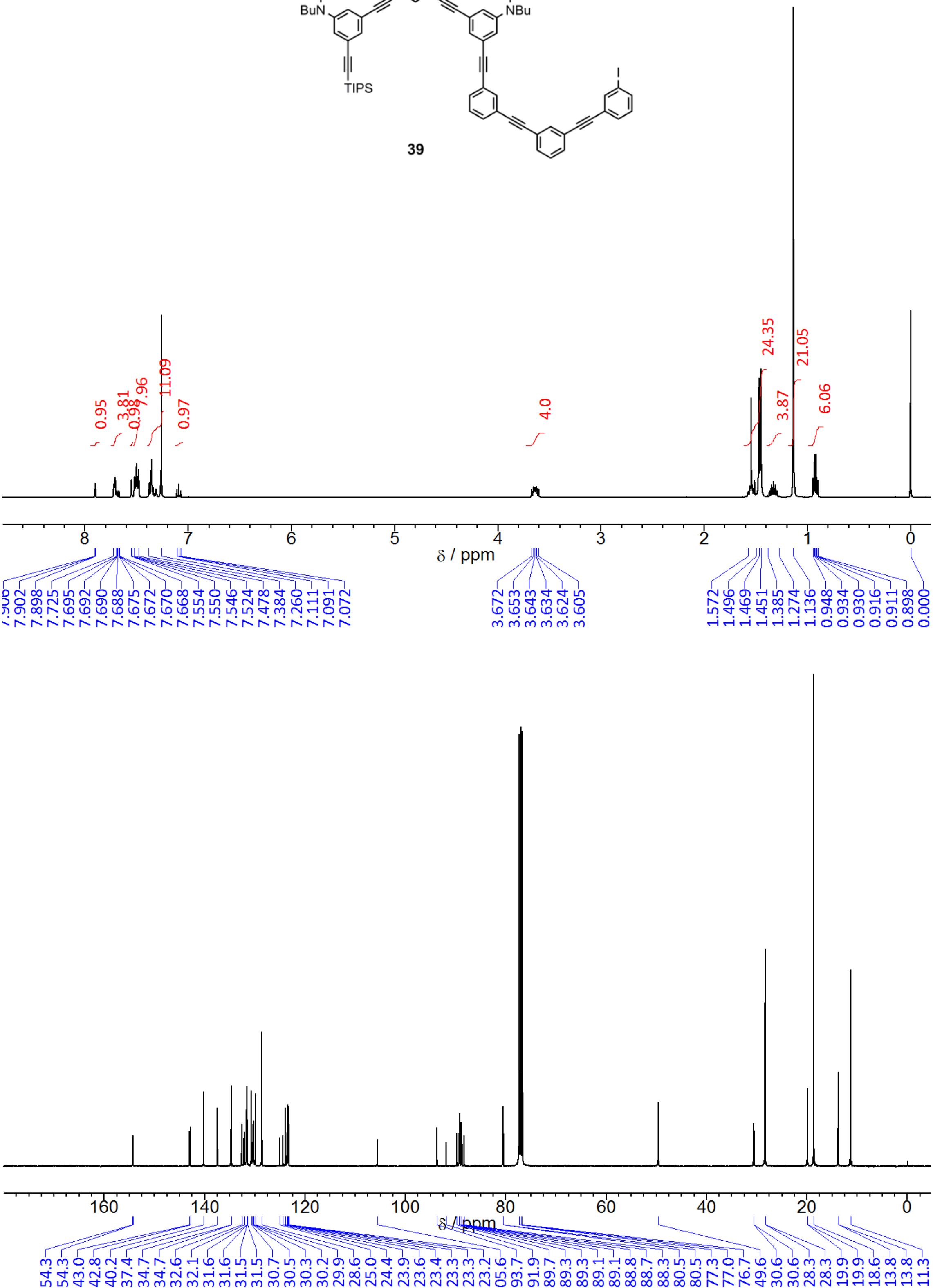


38

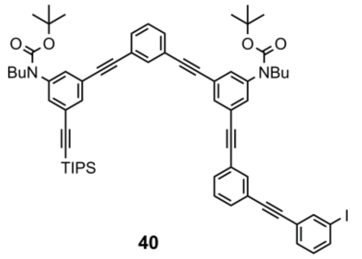
^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **38**, measured in chloroform-*d* at room temperature.



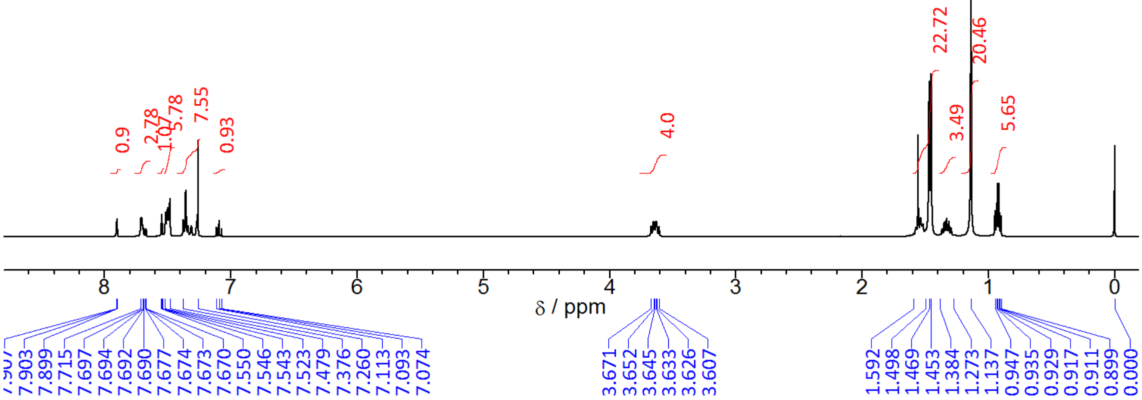
39

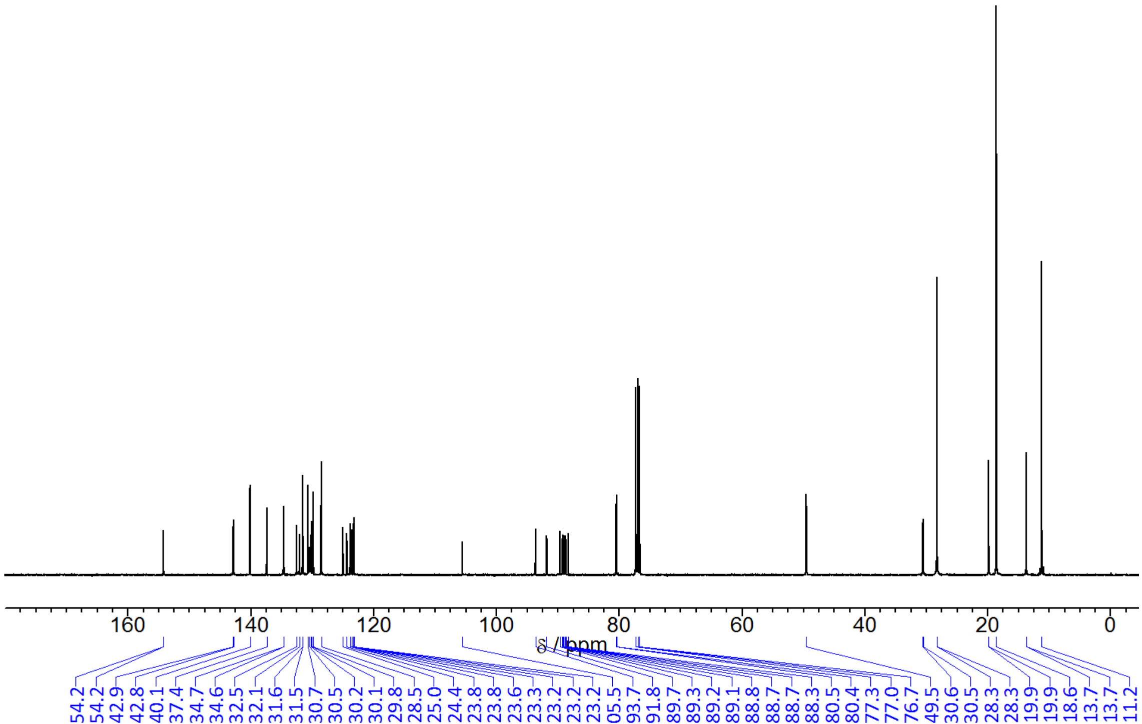


^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **39**, measured in chloroform-*d* at room temperature.



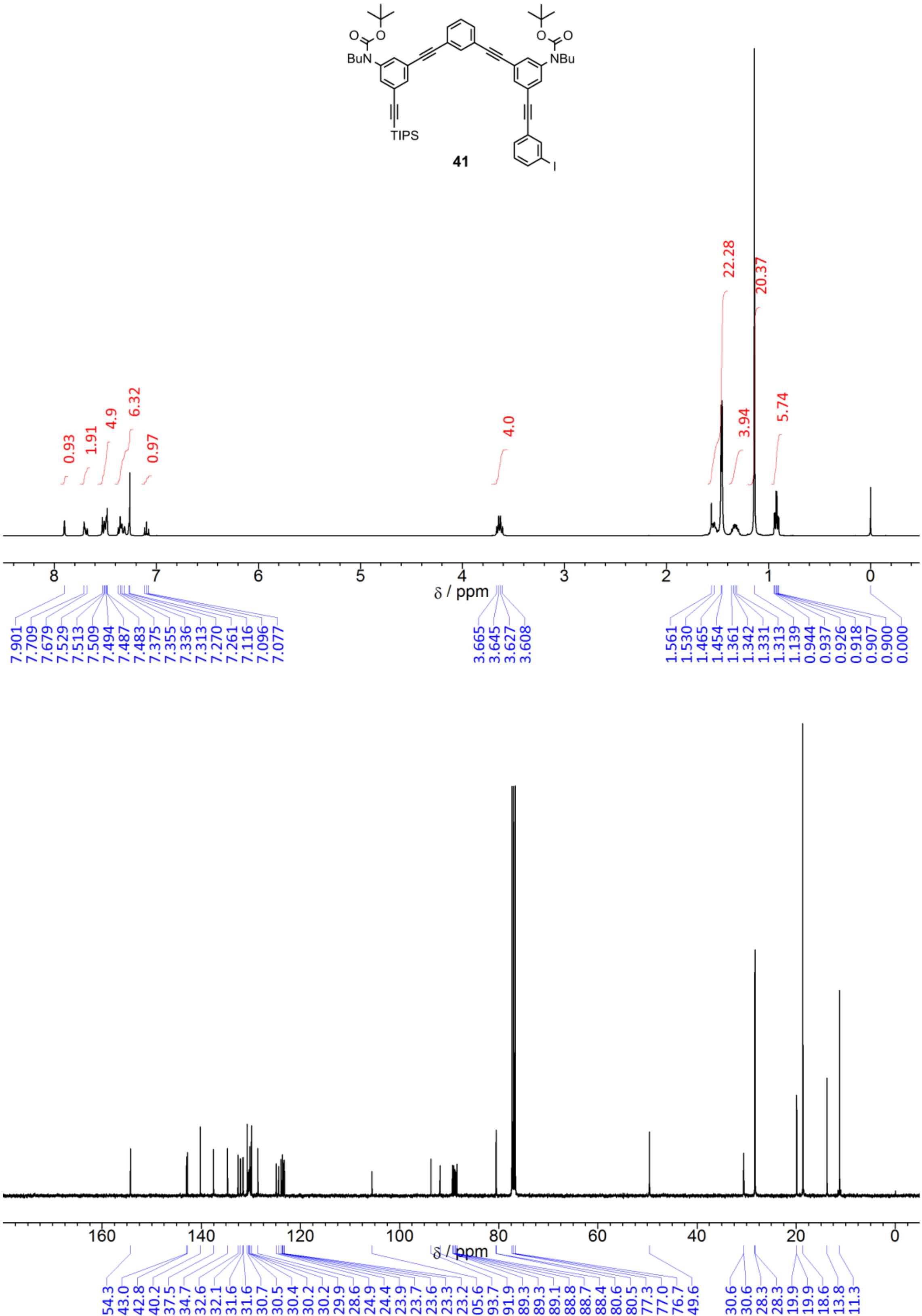
40





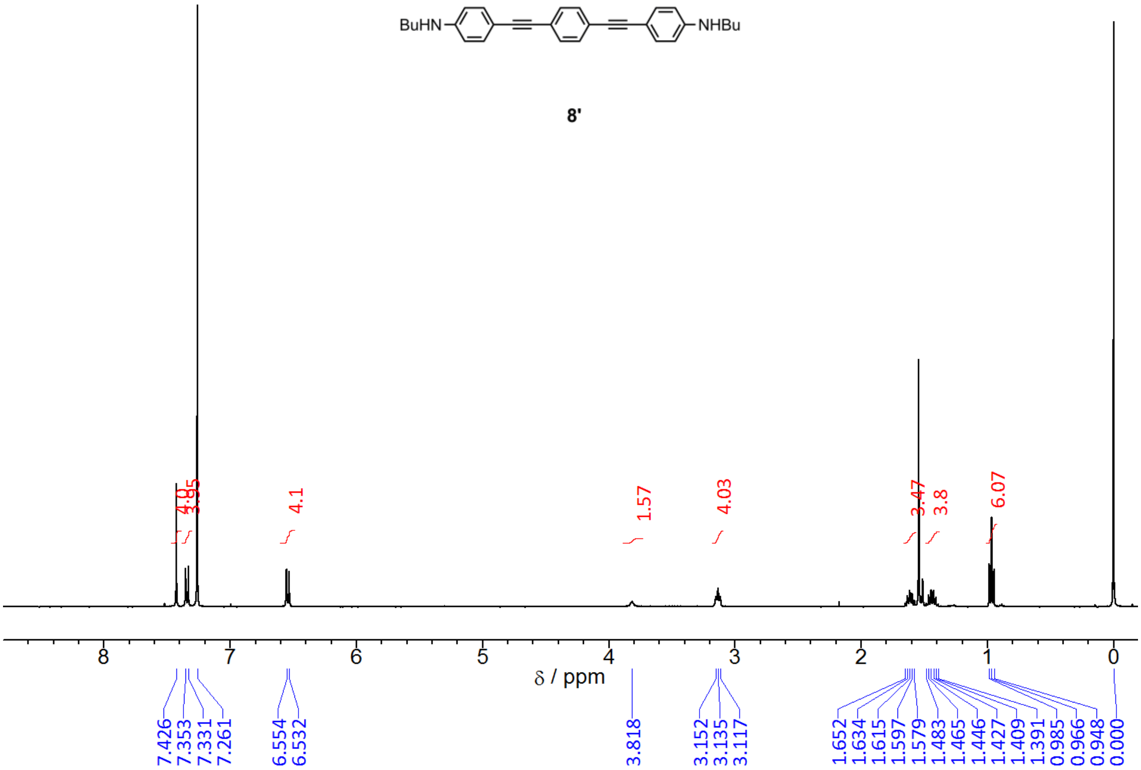
^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **40**, measured in chloroform-*d* at room temperature.

41

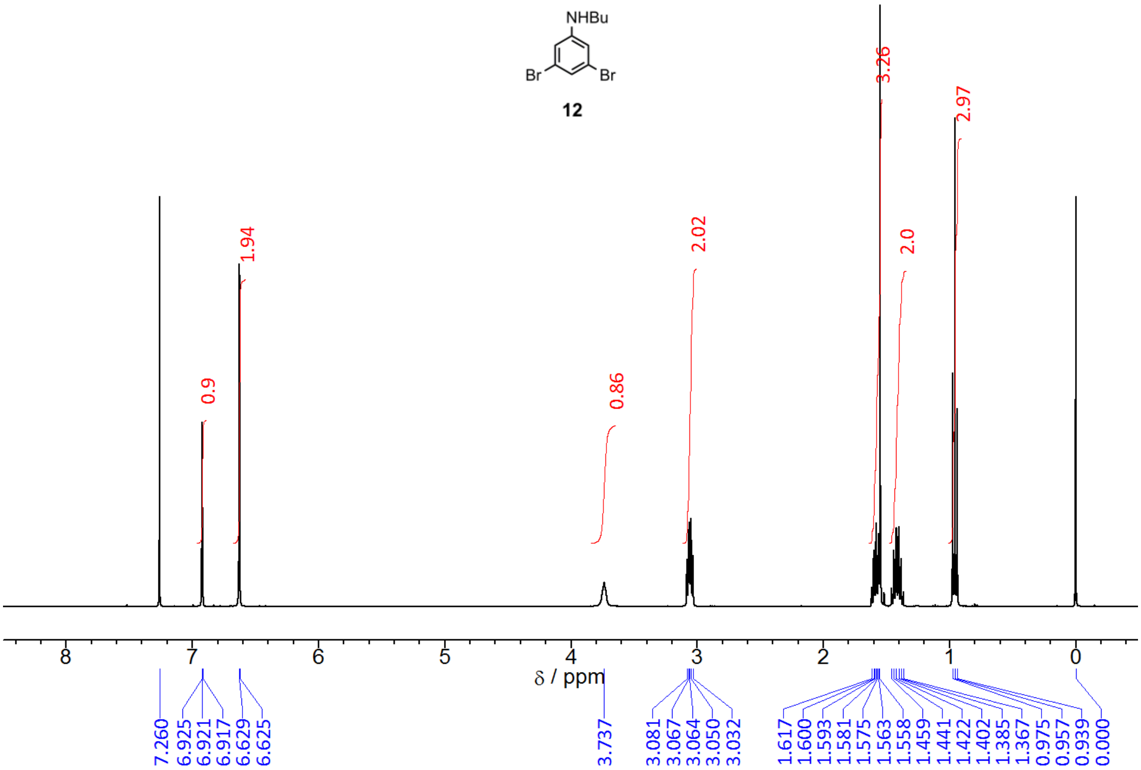


^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **41**, measured in chloroform-*d* at room temperature.

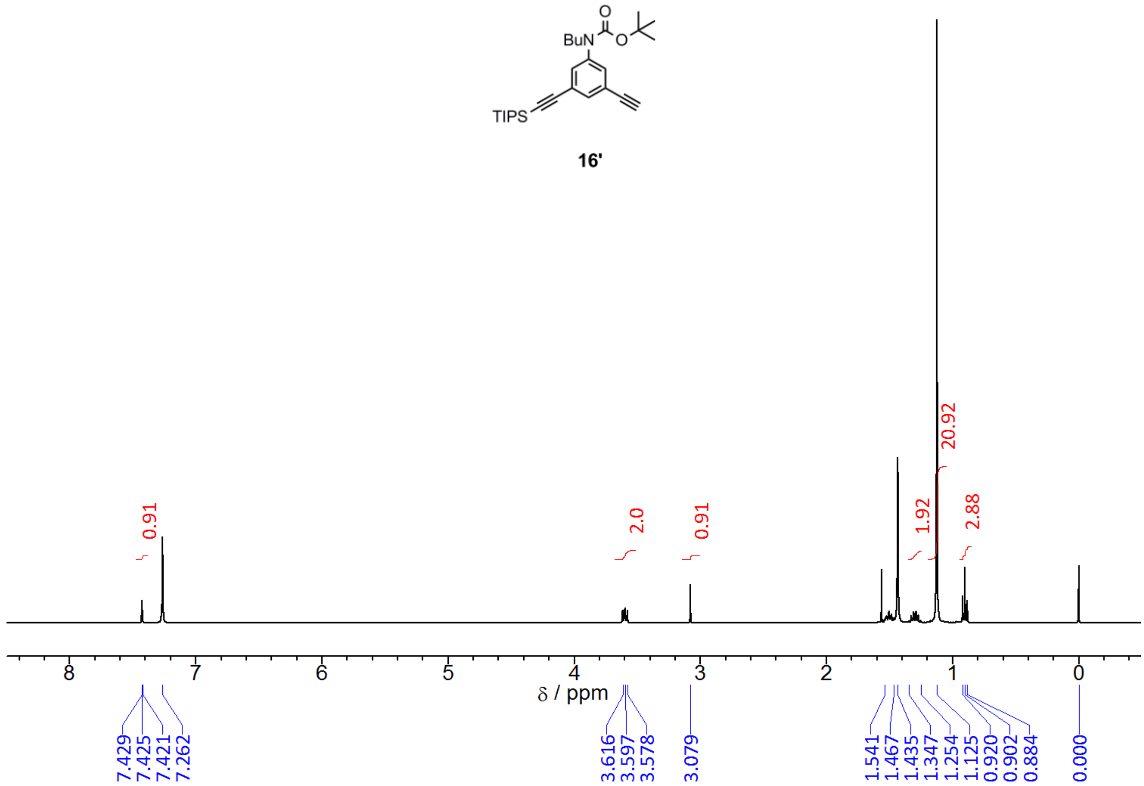
^{1}H NMR spectra of new compounds (unprotected)



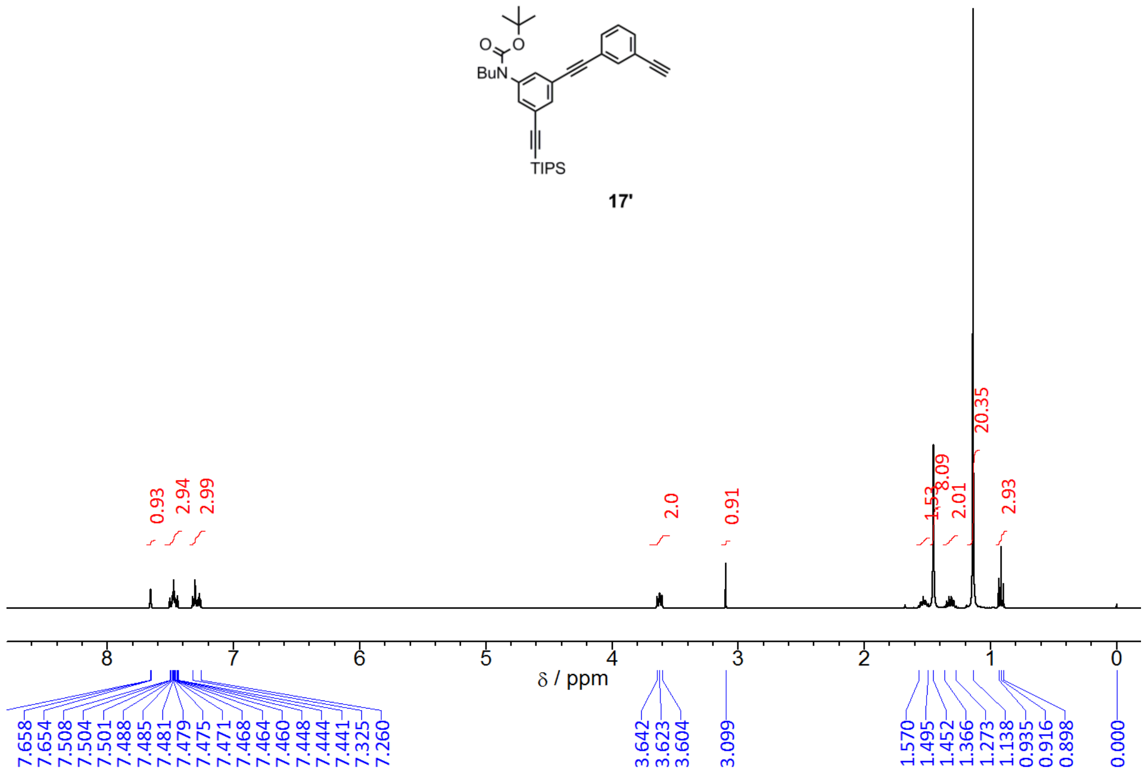
^{1}H NMR spectrum (400 MHz) of **8'**, measured in chloroform-*d* at room temperature.



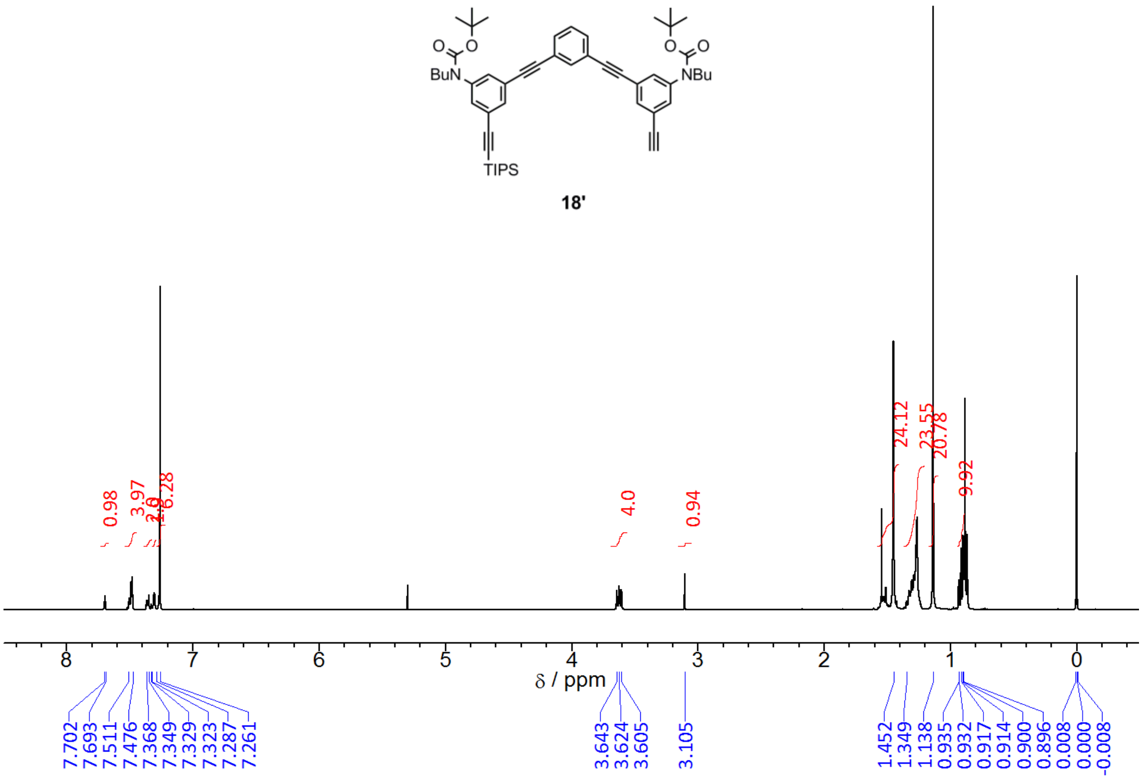
^{1}H NMR spectrum (400 MHz) of **12**, measured in chloroform-*d* at room temperature.



^{1}H NMR spectrum (400 MHz) of **16'**, measured in chloroform-*d* at room temperature.

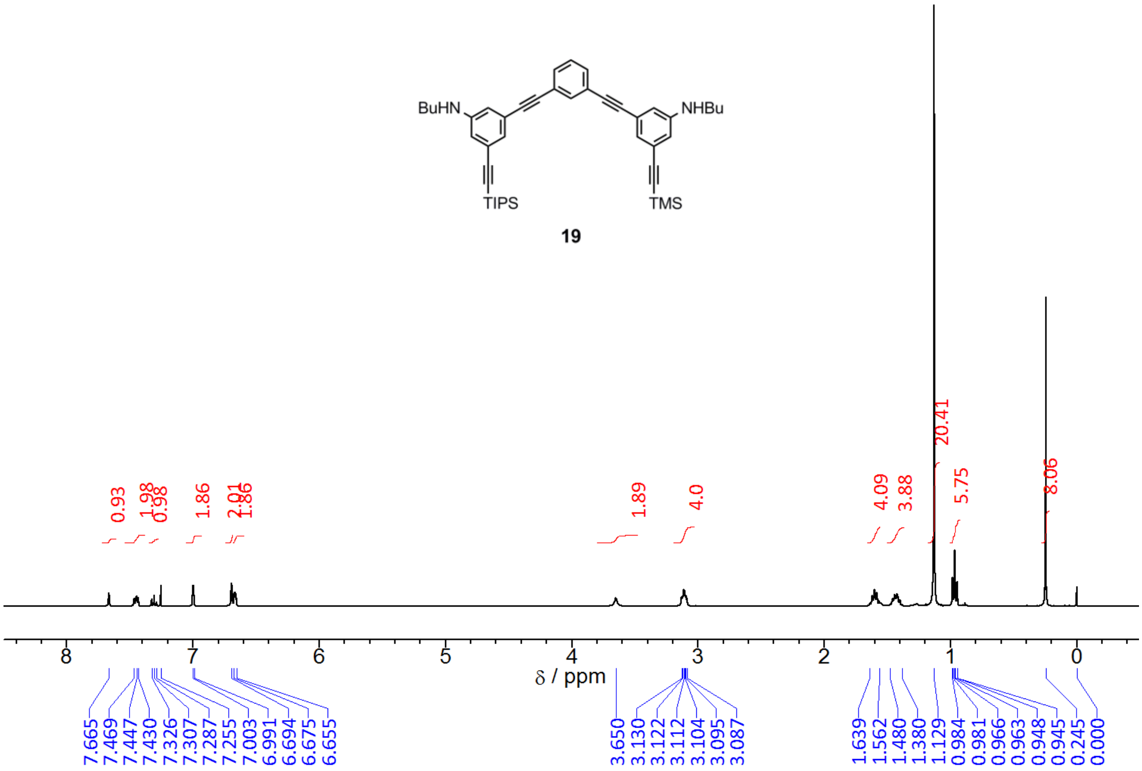


^{1}H NMR spectrum (400 MHz) of **17'**, measured in chloroform-*d* at room temperature.



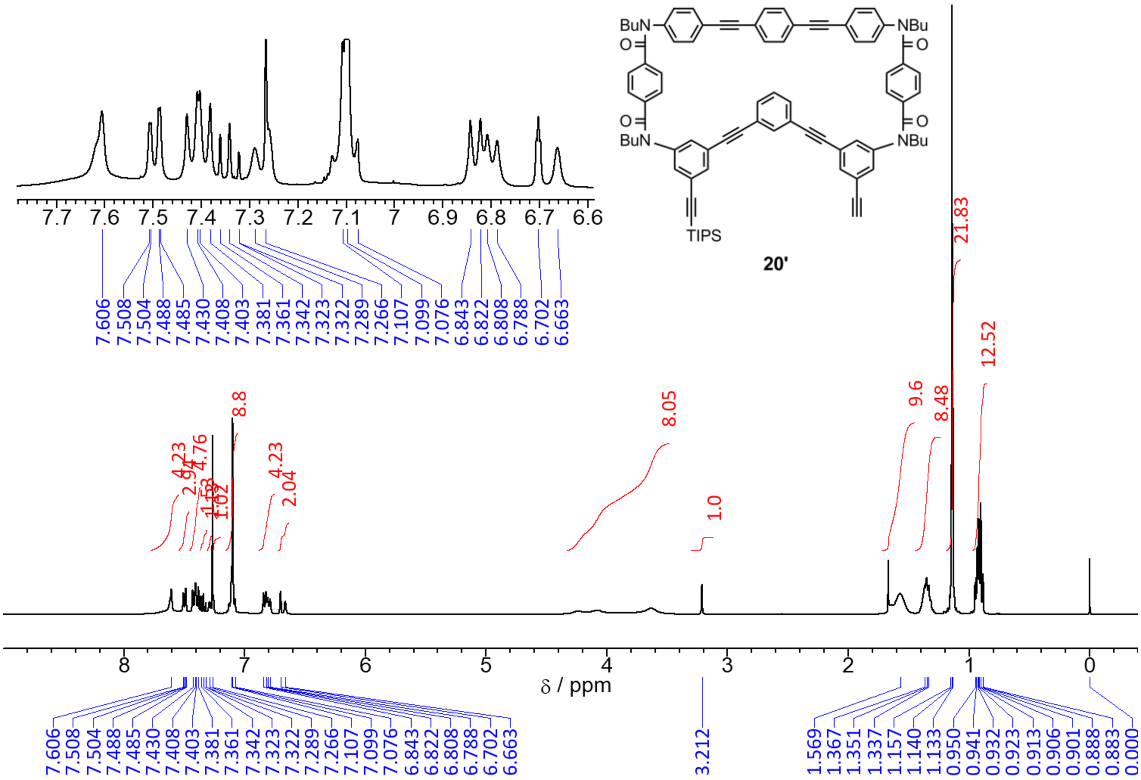
18'

^{1}H NMR spectrum (400 MHz) of **18'**, measured in chloroform-*d* at room temperature.

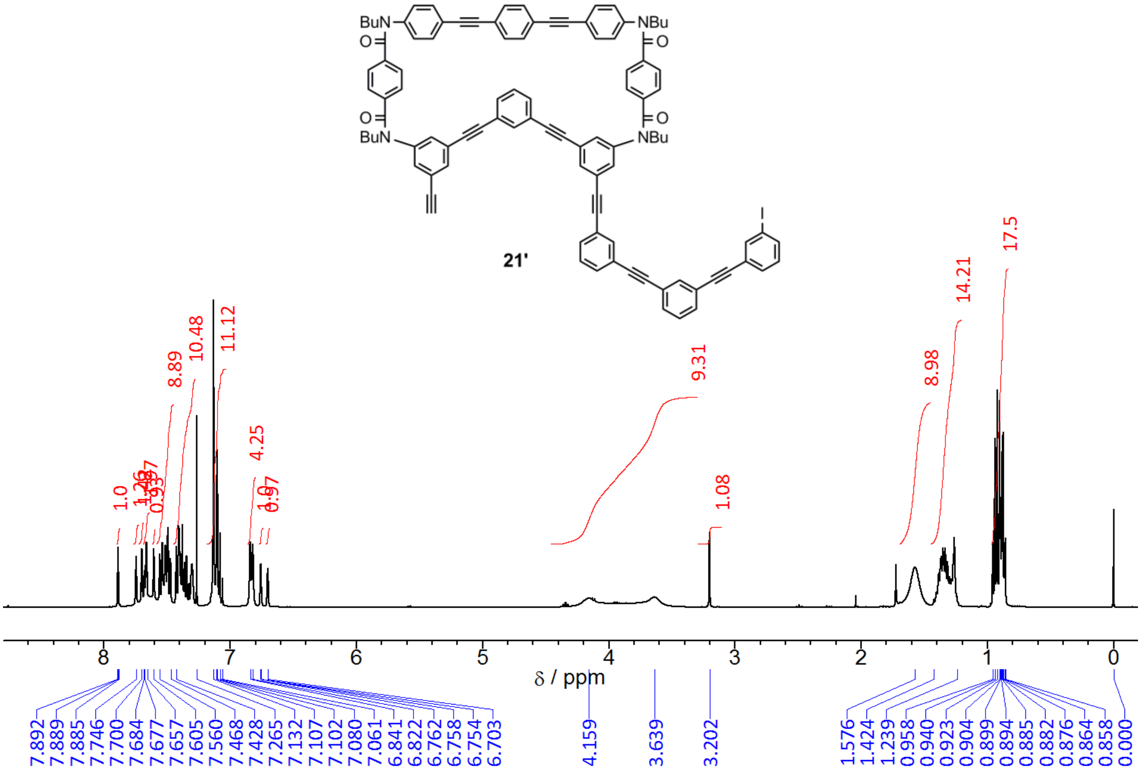


19

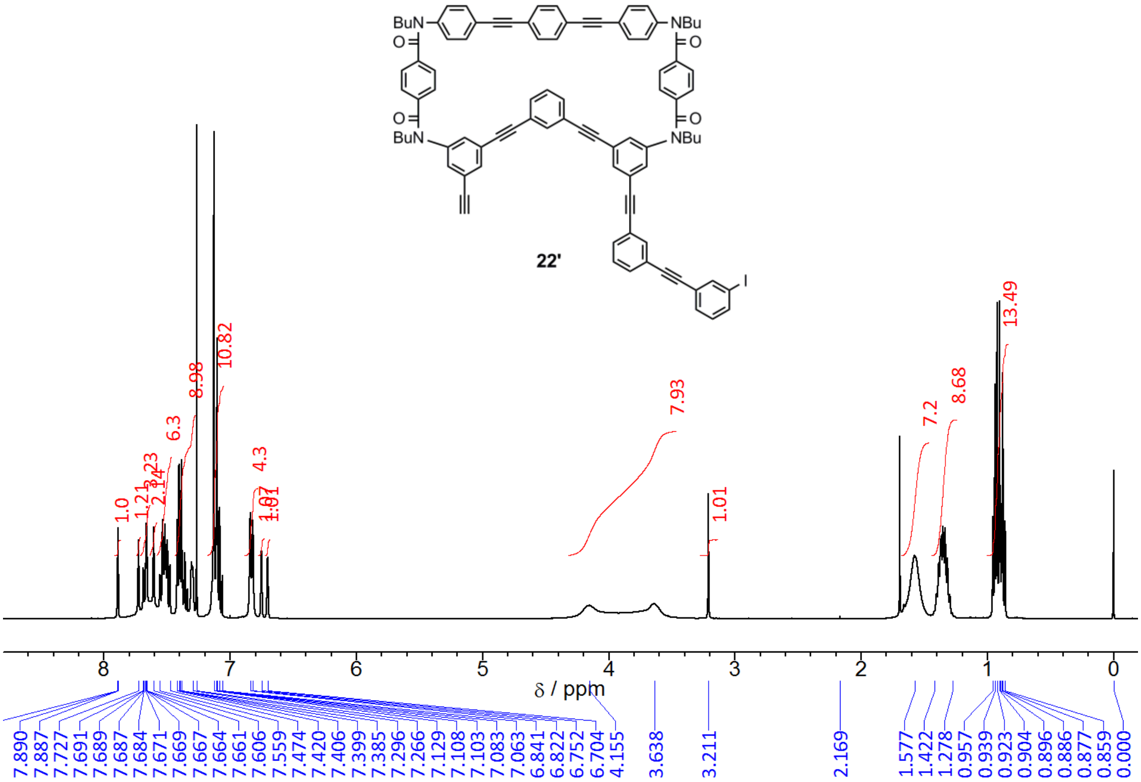
^{1}H NMR spectrum (400 MHz) of **19**, measured in chloroform-*d* at room temperature.



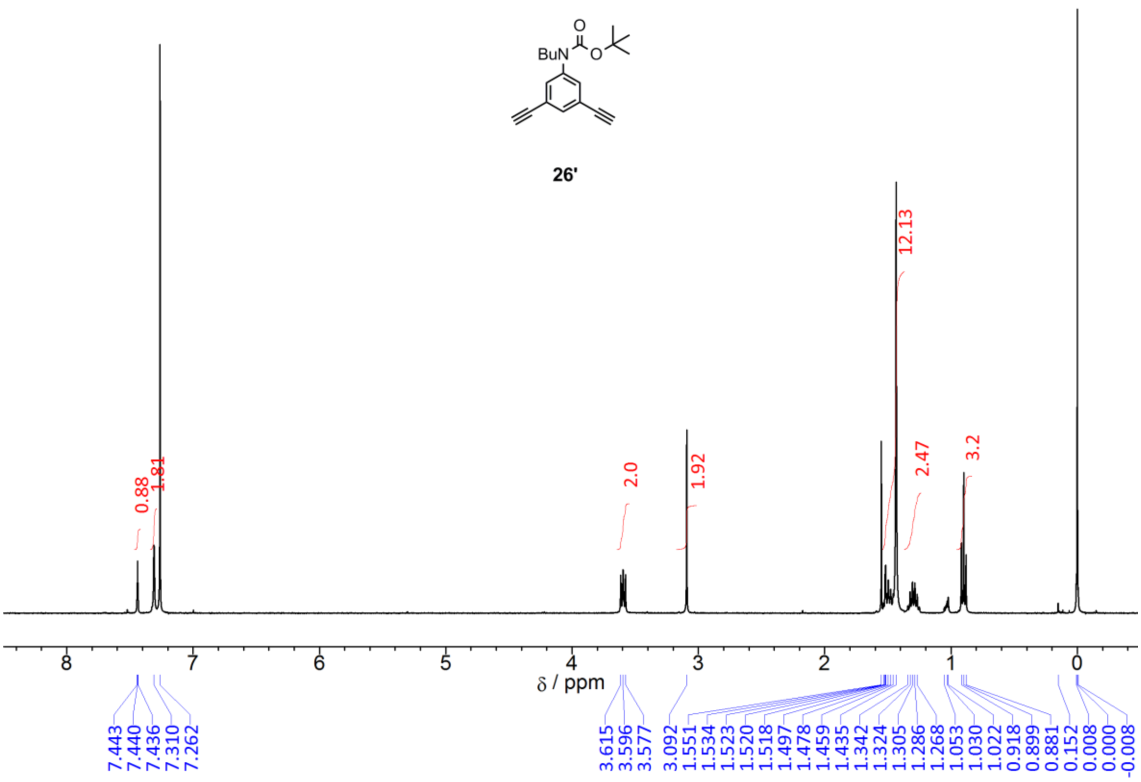
^{1}H NMR spectrum (400 MHz) of **20'**, measured in chloroform-*d* at room temperature.



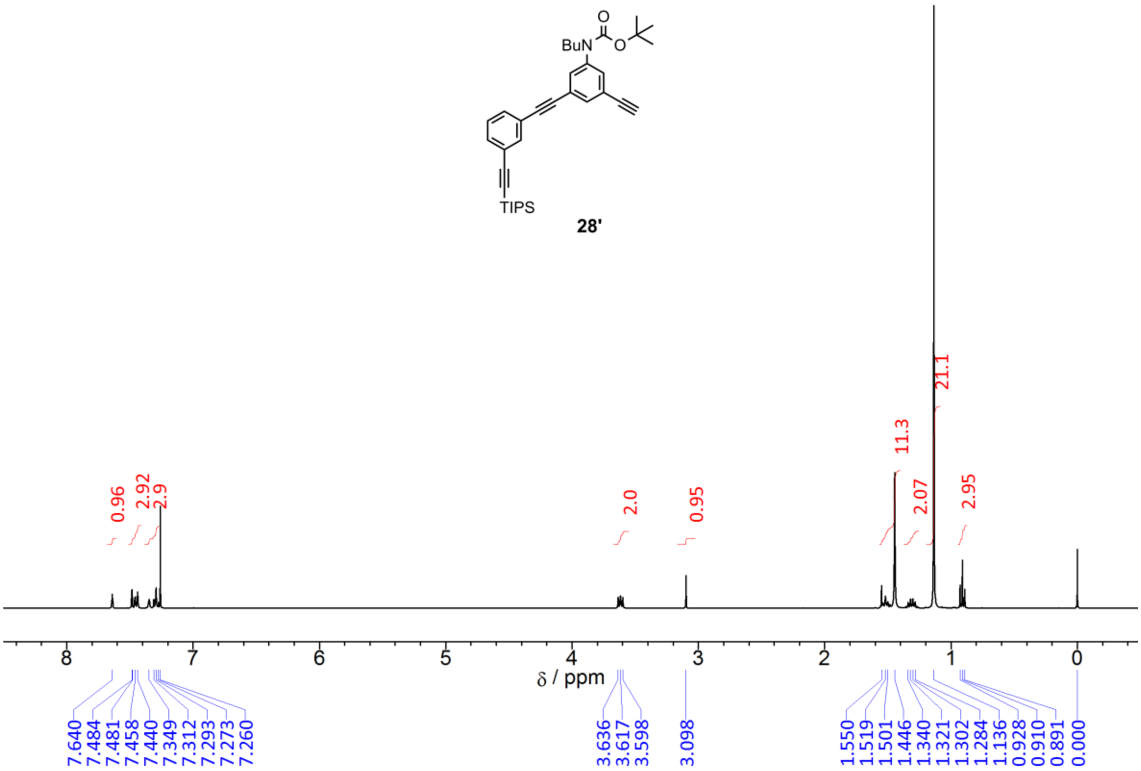
^{1}H NMR spectrum (400 MHz) of **21'**, containing residual solvents, measured in chloroform-*d* at room temperature.



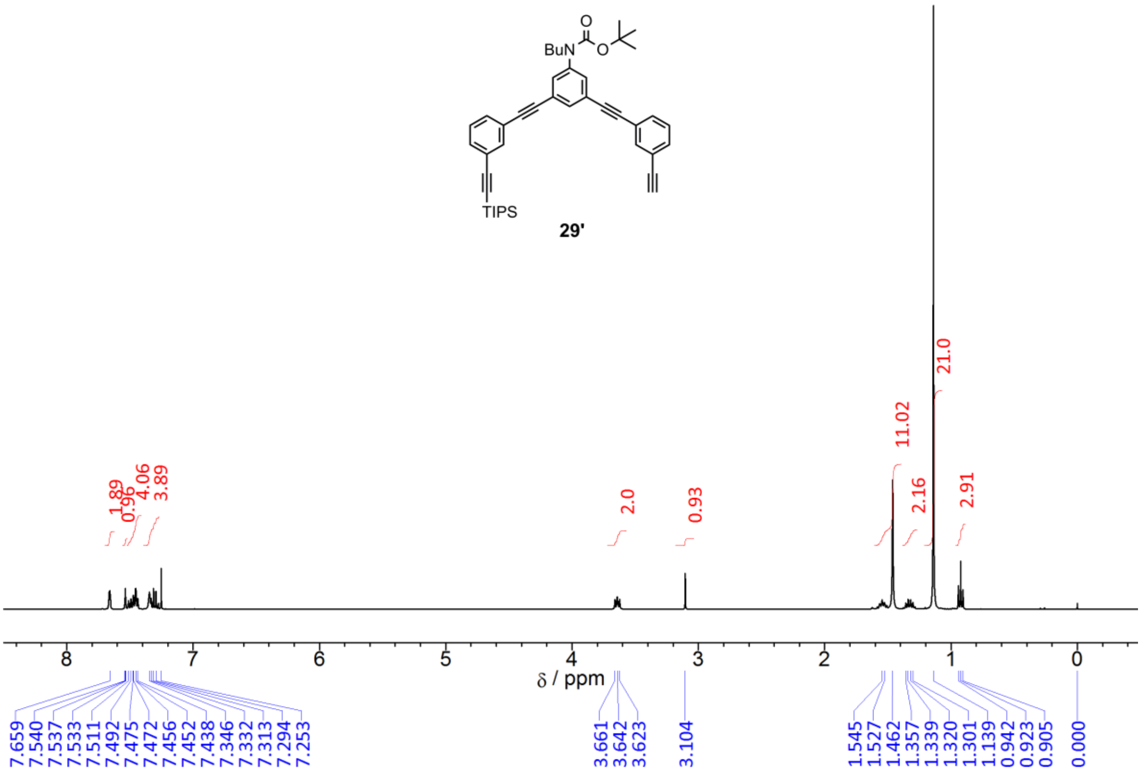
^{1}H NMR spectrum (400 MHz) of **22'**, measured in chloroform-*d* at room temperature.



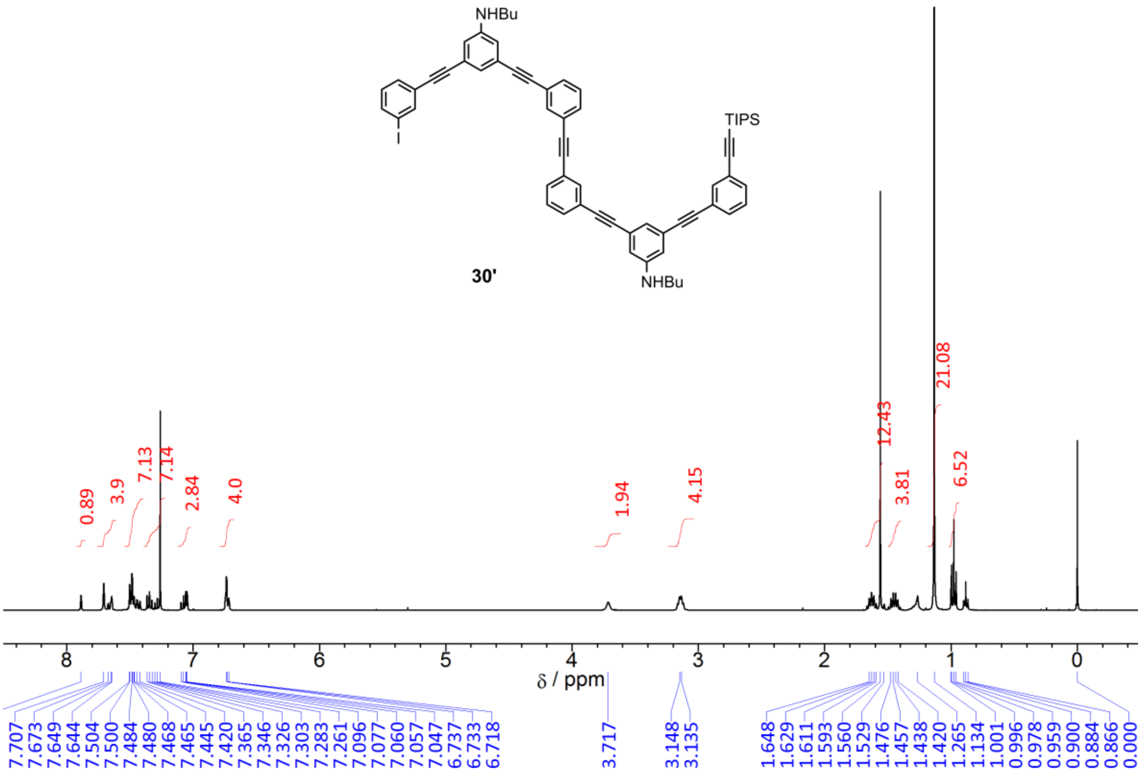
^{1}H NMR spectrum (400 MHz) of **26'**, measured in chloroform-*d* at room temperature.



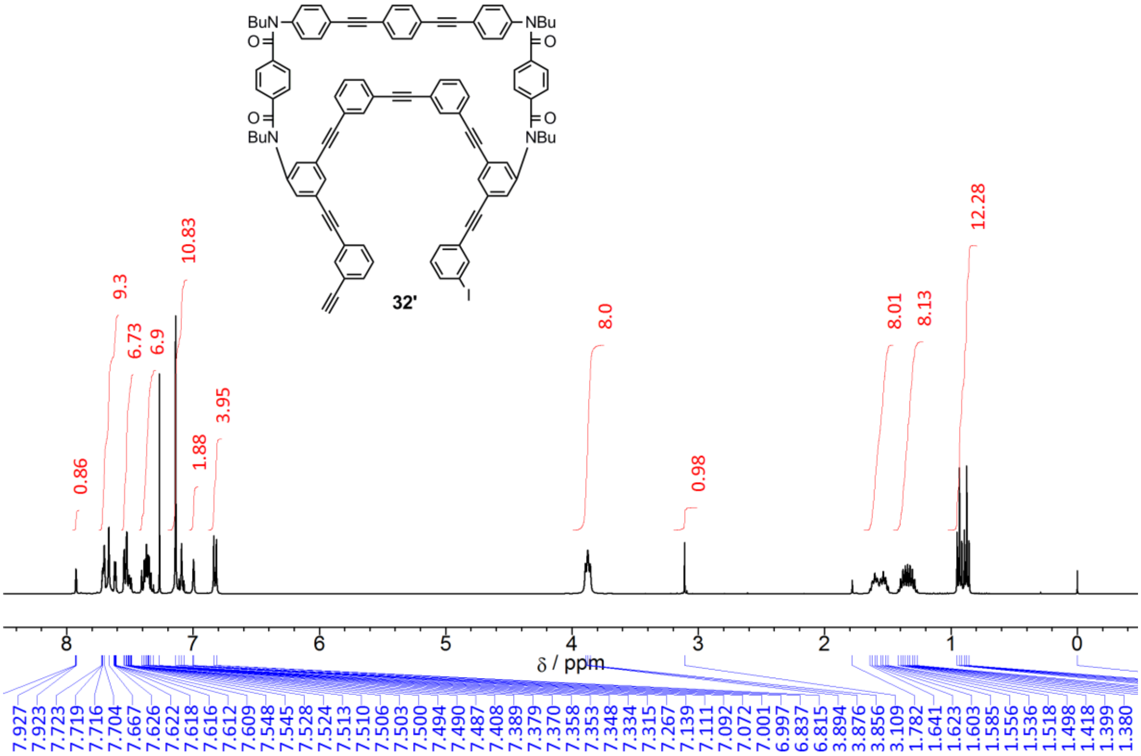
^{1}H NMR spectrum (400 MHz) of **28'**, measured in chloroform-*d* at room temperature.



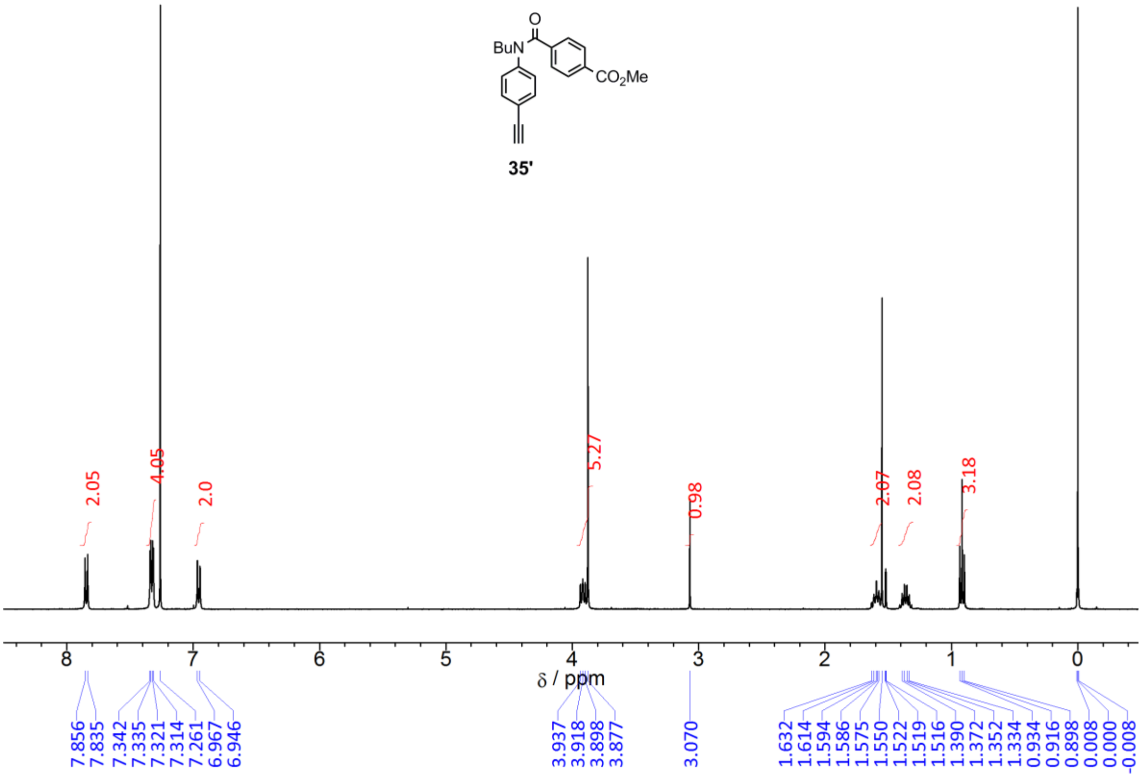
^{1}H NMR spectrum (400 MHz) of **29'**, measured in chloroform-*d* at room temperature.



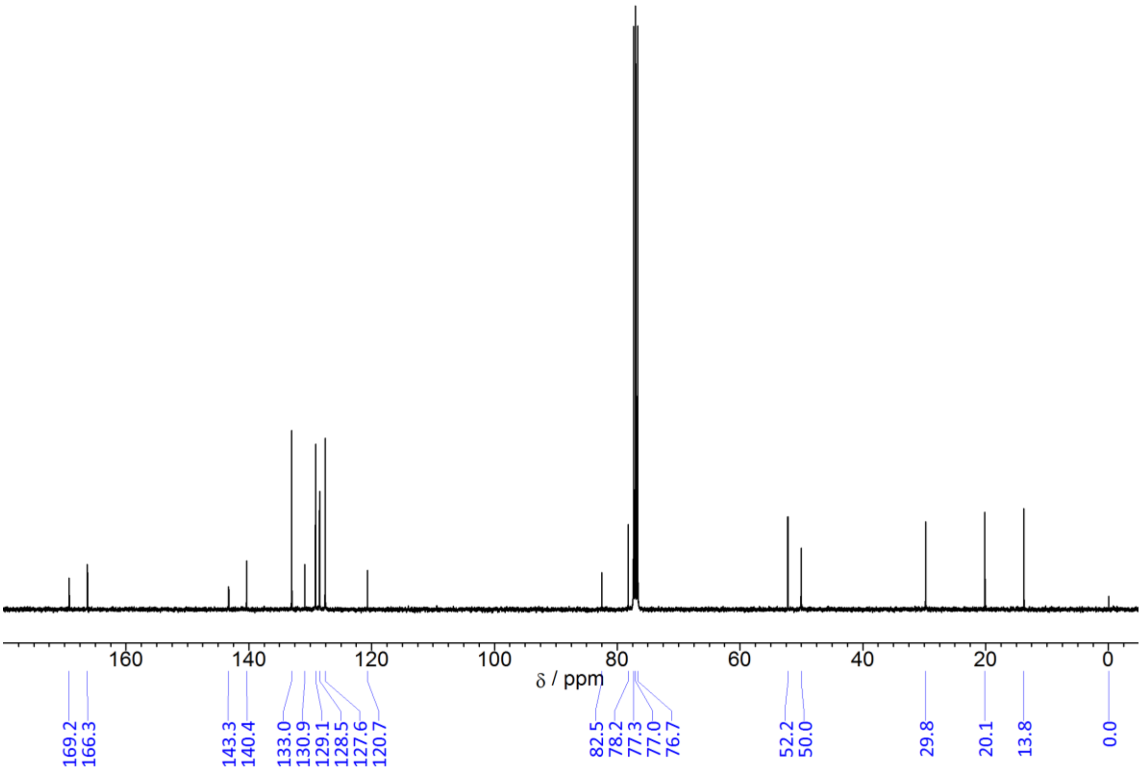
^{1}H NMR spectrum (400 MHz) of **30'**, measured in chloroform-*d* at room temperature.



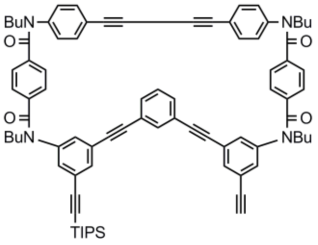
^{1}H NMR spectrum (400 MHz) of **32'**, measured in chloroform-*d* at room temperature.



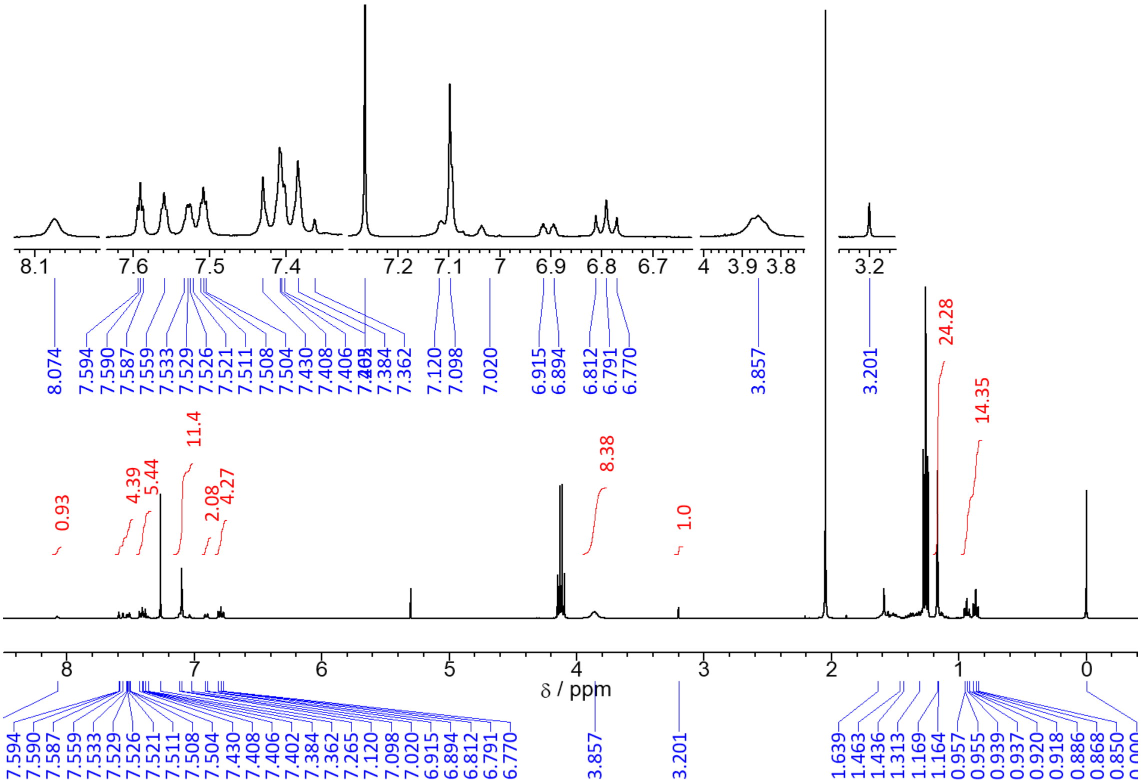
^{1}H NMR spectrum (400 MHz) of **35'**, measured in chloroform-*d* at room temperature.



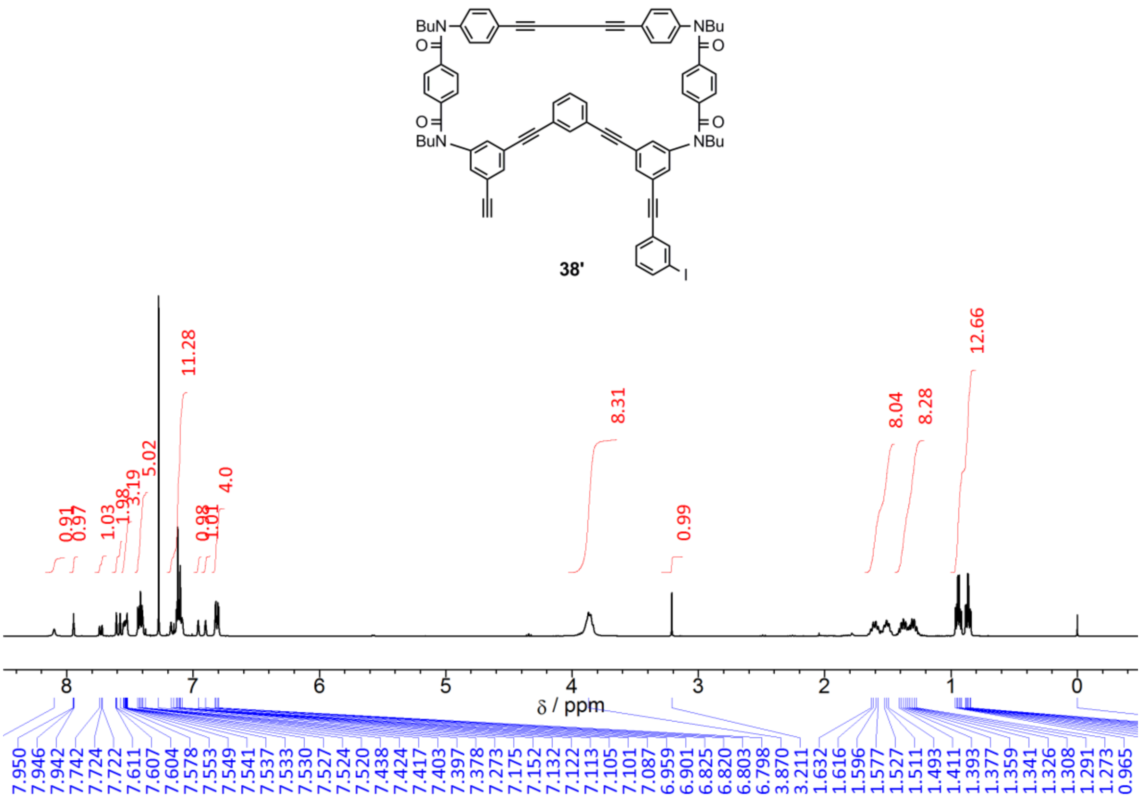
^{13}C NMR spectrum (100 MHz) of **35'**, measured in chloroform-*d* at room temperature.



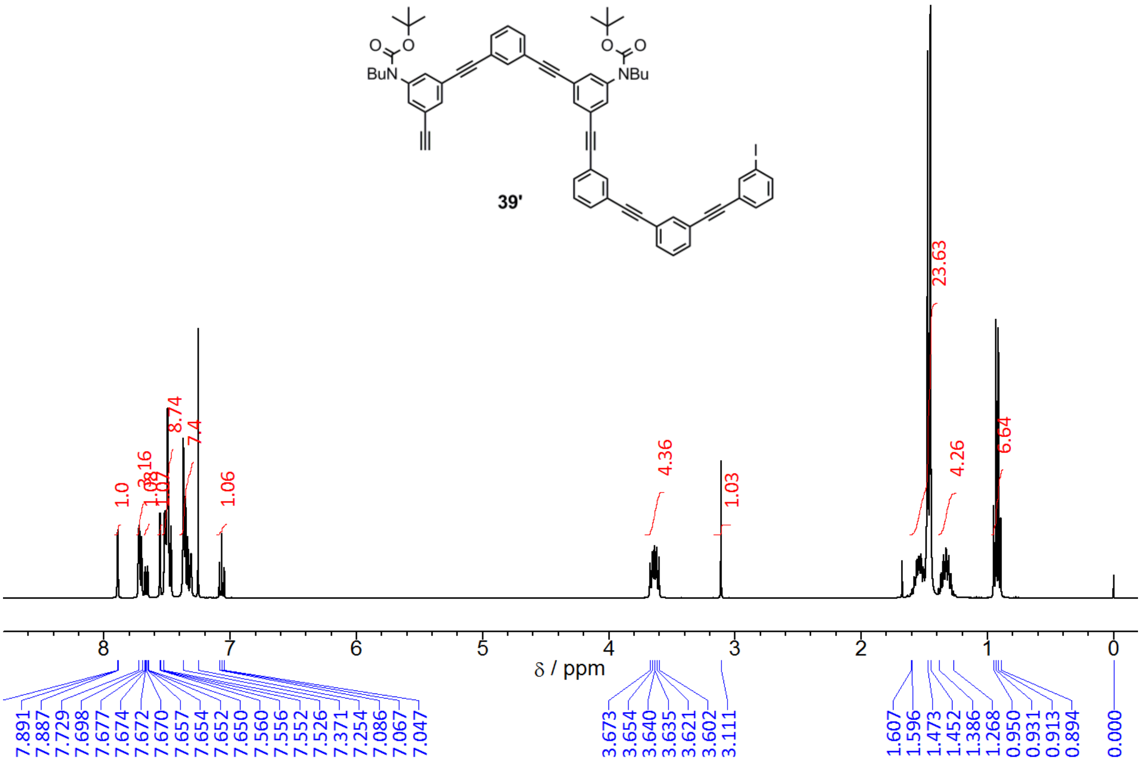
37'



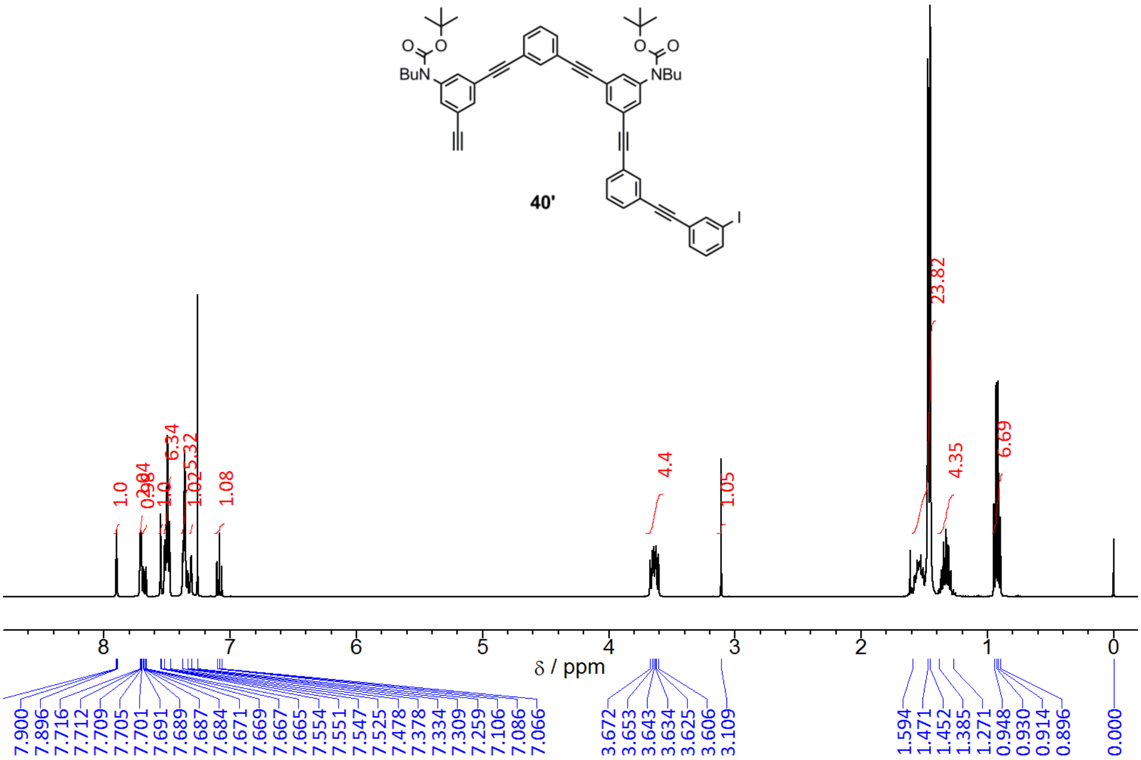
^{1}H NMR spectrum (400 MHz) of **37'**, containing residual solvents, measured in chloroform-*d* at room temperature.



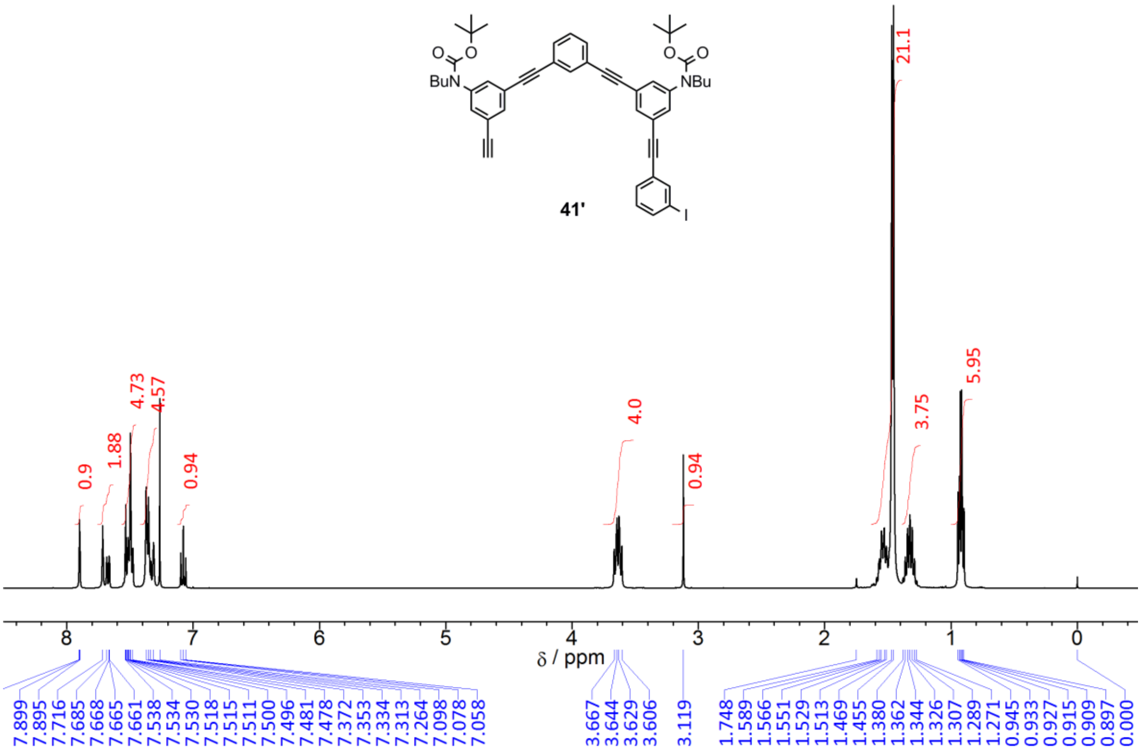
^{1}H NMR spectrum (400 MHz) of **38'**, measured in chloroform-*d* at room temperature.



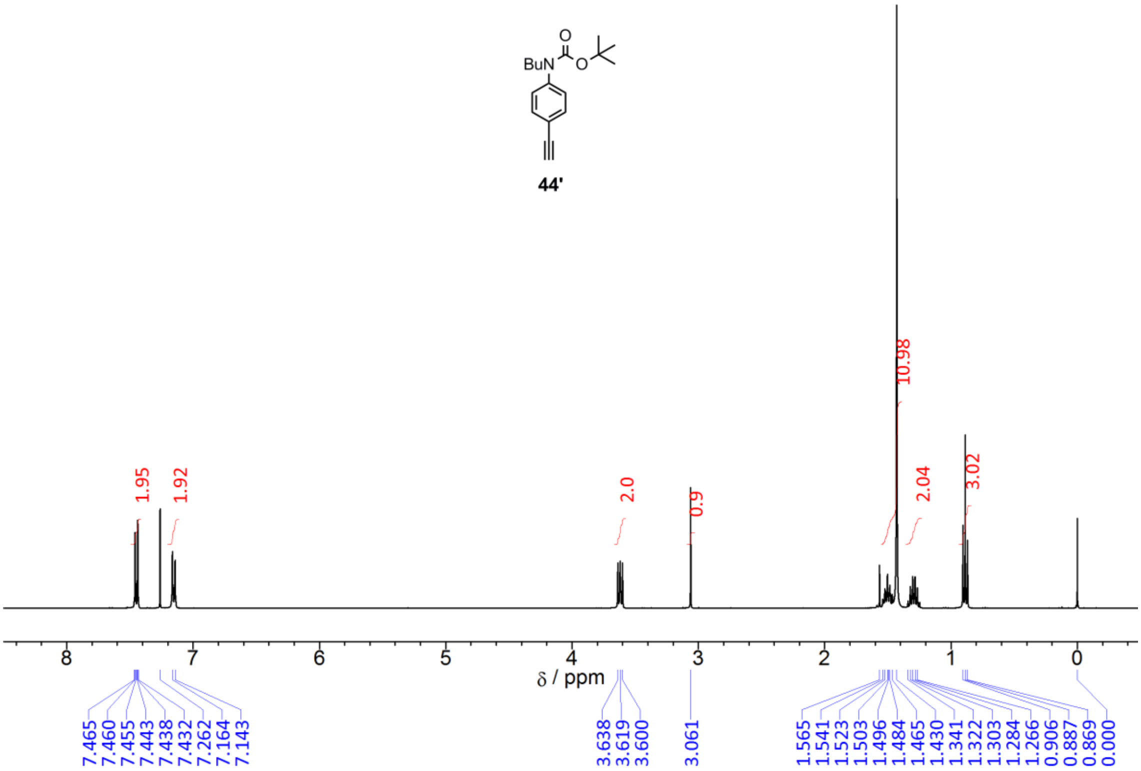
^{1}H NMR spectrum (400 MHz) of **39'**, measured in chloroform-*d* at room temperature.



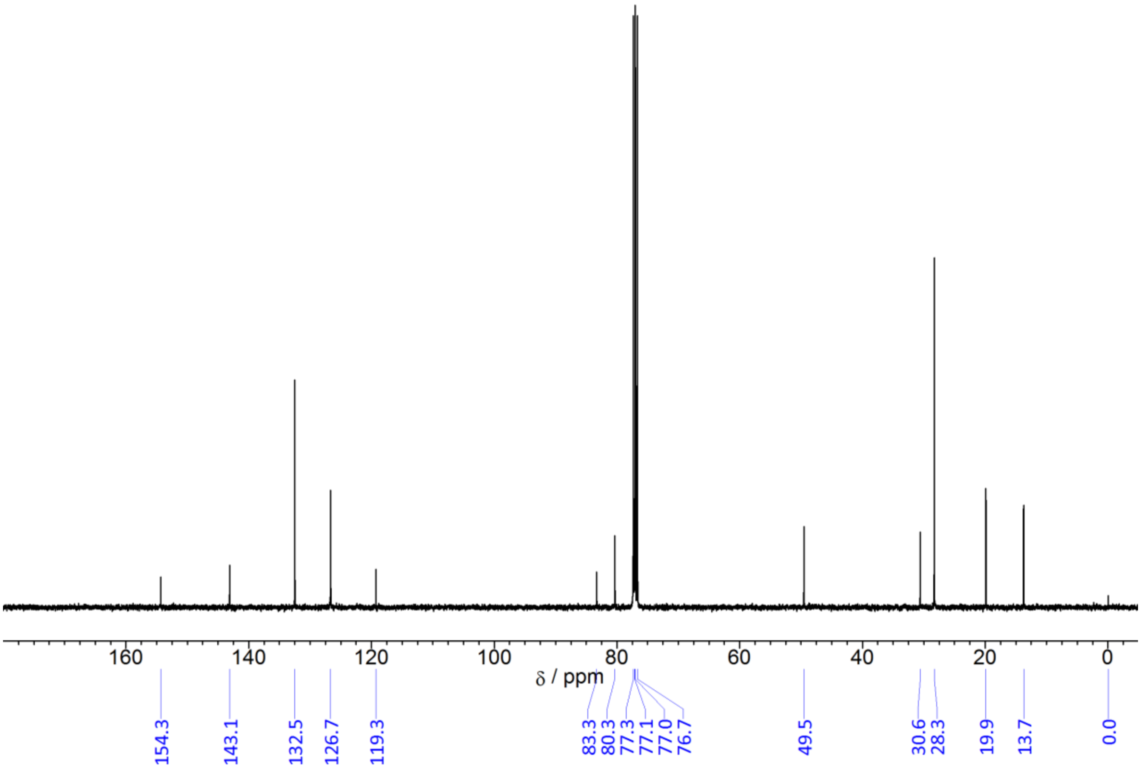
^{1}H NMR spectrum (400 MHz) of **40'**, measured in chloroform-*d* at room temperature.



^{1}H NMR spectrum (400 MHz) of **41'**, measured in chloroform-*d* at room temperature.



^{1}H NMR spectrum (400 MHz) of **44'**, measured in chloroform-*d* at room temperature.



^{13}C NMR spectrum (100 MHz) of **44'**, measured in chloroform-*d* at room temperature.

References and note

1 P.-H. Ge, W. Fu, W. A. Herrmann, E. Herdtweck, C. Campana, R. D. Adams and U. H. F. Bunz, *Angew. Chem. Int. Ed.*, 2000, **39**, 3607–3610.

2 J. Yamakawa, M. Ohkoshi, F. Takahashi, T. Nishiuchi, Y. Kuwatani, T. Nishinaga, M. Yoshida and M. Iyoda, *Chem. Lett.*, 2008, **37**, 784–785.

3 T. Kawase, N. Ueda, H. R. Darabi and M. Oda, *Angew. Chem. Int. Ed. Engl.*, 1996, **35**, 1556–1558.

4 S. H. Chanteau and J. M. Tour, *J. Org. Chem.*, 2003, **68**, 8750–8766.

5 A. Orita, D. L. An, T. Nakano, J. Yaruva, N. Ma and J. Otera, *Chem. Eur. J.*, 2002, **8**, 2005–2010.

6 H.-B. Yang, K. Ghosh, N. Das and P. J. Stang, *Org. Lett.*, 2006, **8**, 3991–3994.

7 A. Orita, K. Miyamoto, M. Nakashima, F. Ye and J. Otera, *Adv. Synth. Catal.*, 2004, **346**, 767–776.

8 S. Y.-L. Leung, A. Y.-Y. Tam, C.-H. Tao, H. S. Chow and V. W.-W. Yam, *J. Am. Chem. Soc.*, 2012, **134**, 1047–1056.

9 R. Katoono, H. Kawai, M. Ohkita, K. Fujiwara and T. Suzuki, *Chem. Commun.*, 2013, **49**, 10352–10354.

10 A. M. Sanders, T. J. Dawidczyk, H. E. Katz and J. D. Tovar, *ACS Macro Lett.*, 2012, **1**, 1326–1329.

11 The central phenylene protons (4H) of 1,4-bis(phenylethynyl)benzene in **20**/**20'**, **21**/**21'** and **22**/**22'** were not assigned due to broadening.