Electronic Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION

Merging tribenzotriquinacene with hexa-*peri*-hexabenzocoronene: A cycloheptatriene unit generated by Scholl reaction

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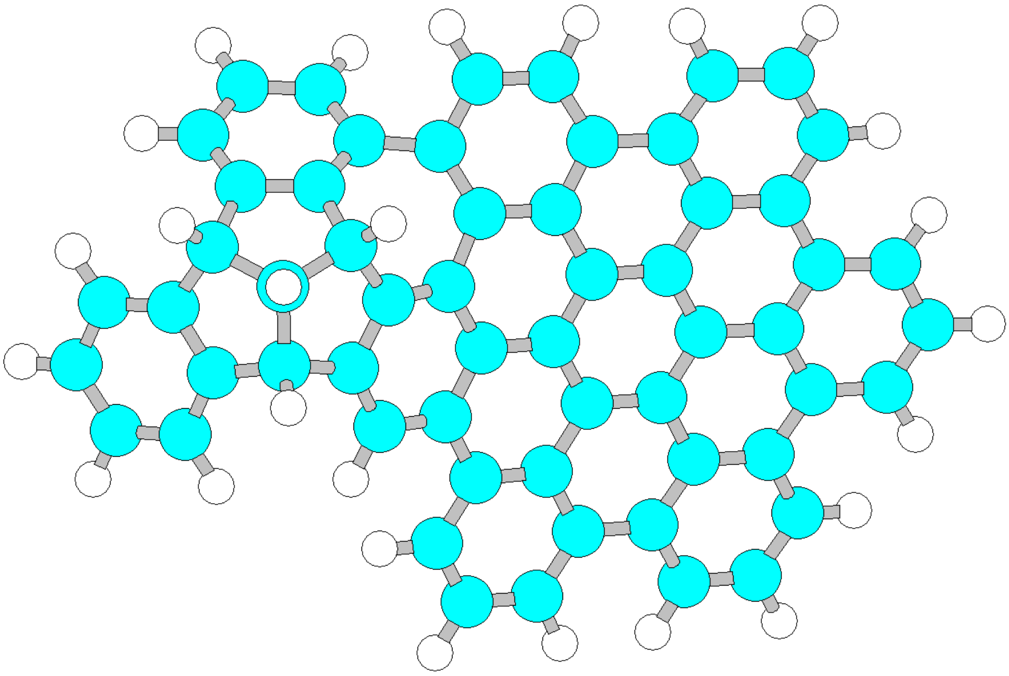
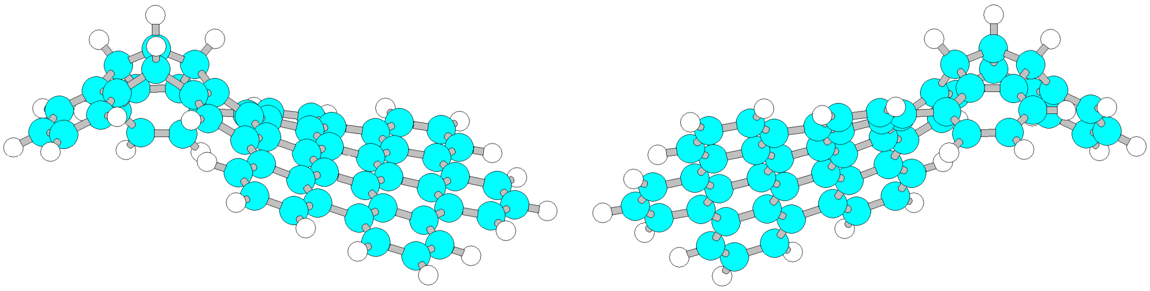
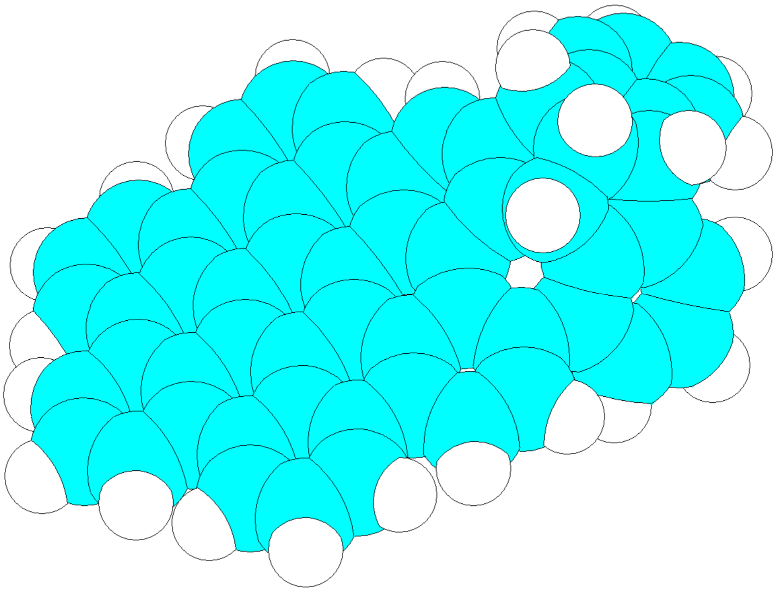


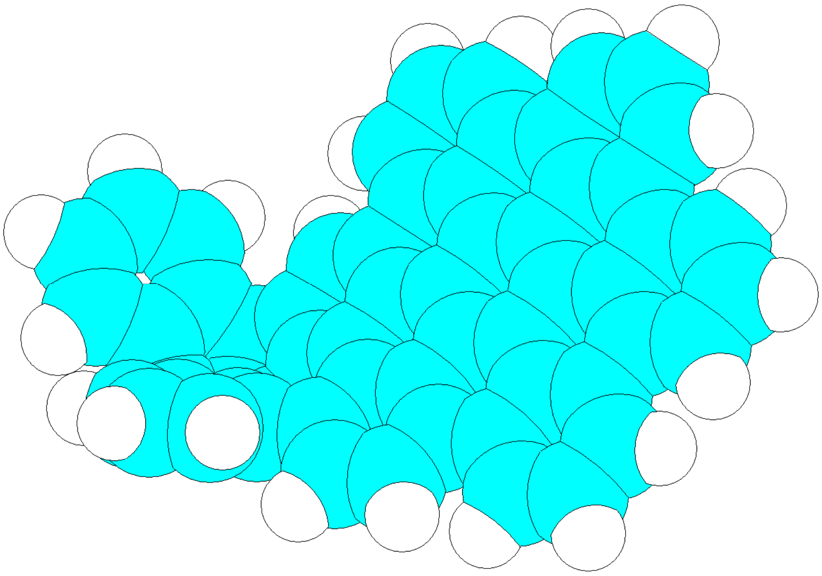
The merged scaffolds of the parent tribenzotriquinacene and hexa-*peri*-hexabenzocoronene.

All structures have been generated by semi-empirical calculation (AM1, HyperChem®).

Below: Two ball-and-stick representations as side views; next page: two space-filling representations in tilted views from the convex and the concave side of the TBTQ core, respectively.





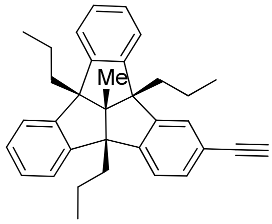


Contents

Experimental Section

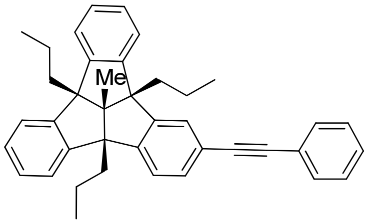
General. Melting points (uncorrected) were measured with an Electrothermal melting point apparatus. IR spectra were recorded with an FT-IR spectrometer, model Nicolet-380. NMR spectra were measured with a Bruker DRX 500 instrument (^{1}H, 500 MHz, ^{13}C, 125.7 MHz). Mass spectra were recorded with a Fisons VG Autospec X double-focusing mass spectrometer. MALDI measurements were performed with a Voyager-DE MALDI-TOF by use of 2-[(2-*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malonitrile (DCTB) as a matrix. Accurate mass measurements were carried out with the Fisons VG sector-field instrument (EI) and a FT-ICR mass spectrometer, Bruker APEX III (7.0 T) (MALDI). Absorption spectra were recorded with Perkin-Elmer Lambda 40 spectrophotometer and fluorescence spectra with Perkin-Elmer LS50B spectrophotometer. Dichloromethane, petroleum ether (60–80 °C), ethyl acetate, diethyl ether and cyclohexane were distilled before use. All other chemicals were purchased from Alfa Aesar or Sigma-Aldrich and used as delivered. For column chromatography Merck silica gel (0.063-0.200 mm) was used. Reactions requiring anhydrous conditions were carried out in oven-dried glassware under argon. Dibromomethyltriphosphonium bromide was synthesized according to the literature.[1,2]

2-(Ethynyl)-12d-methyl-4b,8b,12b-tri-*n*-propyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (5)



A suspension of TBTQ aldehyde **4**[3] (2.50 g, 5.56 mmol), dibromomethyltriphosphonium bromide (7.72 g, 13.90 mmol) and 18-crown-6 (0.293 g, 1.11 mmol) in dichloromethane (90 mL) was vigorously stirred under a gentle flow of argon while freshly ground potassium hydroxide (1.56 g, 27.80 mmol) was added. Stirring was continued at ambient temperature for 2 h under argon. The suspension was filtered through a pad of silica gel and the solvent was removed under reduced pressure. Column chromatography of the solid residue through silica gel (cyclohexane/EtOAc 95:5) furnished a yellow sticky solid (2.81 g, 4.67 mmol). This material was dissolved in anhydrous THF (85 mL) and the solution was stirred at –78 °C while *n*-butyllithium (7.30 mL, 11.68 mmol) (1.6 M solution in hexanes) was added dropwise. After stirring at this temperature for a further 2 h, the mixture was allowed to warm up and stirring was continued for 1 h at ambient temperature. The reaction was quenched by careful addition of water (10–15 mL) and a few drops of diluted aqueous hydrochloric acid were added. The resulting mixture was extracted with diethyl ether (3 × 25 mL). The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified by column chromatography through silica gel (cyclohexane/CH_2Cl_2 8:1) to furnish the TBTQ acetylene **5** (1.625 g, 66%) as an off-white solid, mp 179–181 °C. IR (neat): $\tilde{\nu}$ = 3280, 2956, 2868, 2361, 1477, 1281, 1032, 745, 508 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.45 (s, 1H, Ar-H), 7.32–7.34 (m, 3H, Ar-H), 7.26–7.30 (m, 3H, Ar-H), 7.14–7.19 (m, 4H, Ar-H), 3.03 (s, 1H, CCH), 2.13–2.21 (m, 6H, $CH_2CH_2CH_3$), 1.65 (s, 3H, CH_3), 1.17–1.26 (m, 6H, $CH_2CH_2CH_3$), 0.98–0.95 (m, 9H, $CH_2CH_2CH_3$); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 149.2 (C), 148.3 (C), 148.05 (C), 148.00 (C), 147.6 (C), 131.2 (C), 127.37 (CH), 127.33 (CH), 127.28 (CH), 123.44 (CH), 123.39 (CH), 123.37 (CH), 123.30 (CH), 123.2 (CH), 120.7 (C), 84.3 (C), 76.3 (CH), 71.9 (C), 67.34 (C), 67.28 (C), 67.08 (C), 40.9 (CH_2), 40.8 (CH_2), 40.6 (CH_2), 27.0 (12d-CH_3), 20.50 (CH_2), 20.47 (CH_2), 20.45 (CH_2), 15.1 (CH_3), several $C^{ar}H$ resonances were not resolved; MS (EI, 70 eV): *m/z* (%), 444 (4, $[M]^{+\bullet}$), 401 (100, $[M - C_3H_7]^+$), 377 (11), 359 (6), 329 (7), 315 (7), 313 (12); accurate mass (EI-MS) of $[M]^{+\bullet}$: calcd. for $C_{34}H_{36}$ 444.2817; found 444.2826.

12d-Methyl-2-phenylethynyl-4b,8b,12b-tri-*n*-propyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (6)



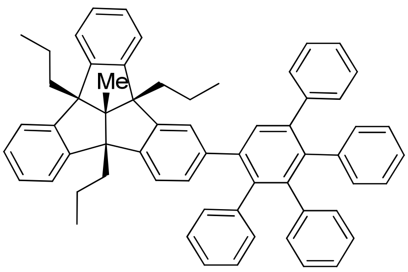
The solution of hydrocarbon **5** (501 mg, 1.13 mmol), iodobenzene (0.140 mL, 1.24 mmol) and triethylamine (0.630 mL, 4.50 mmol) in extra pure and anhydrous *N*,*N*-dimethylformamide (12 mL) was degassed through 4–5 freeze-pump-thaw-cycles. The solution was still below room temperature when a mixture of $Pd(PPh_3)_2Cl_2$ (40 mg, 0.056 mmol) and copper(I) iodide (21 mg, 0.113 mmol) was added. The reaction mixture was stirred at room temperature for 20 h. After the completion of reaction, a little amount of water was added and the solvent was removed under reduced pressure. The resulting residue was diluted with water (50 mL) and extracted with dichloromethane (3 × 20 mL). The combined organic layers were washed with brine and then with water, dried over sodium sulfate, filtered and concentrated under reduced pressure. Column chromatography of the residue through silica gel (petroleum ether/CH_2Cl_2 10:1) afforded the TBTQ-tolane **6** (586 mg, 74 %) as a colorless amorphous solid, mp 244–245 °C. IR (neat): $\tilde{\nu}$ = 3022, 2955, 2868, 2362, 1477, 1452, 1152, 754, 691 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): 7.55–7.57 (m, 2H, Ar-H), 7.49

(s, 1H, Ar-H), 7.29–7.39 (m, 9H, Ar-H), 7.16–7.21 (m, 4H, Ar-H), 2.17–2.23 (m, 6H, $C\mathit{H}_2CH_2CH_3$), 1.67 (s, 3H, CH_3), 1.22–1.28 (m, 6H, $CH_2C\mathit{H}_2CH_3$), 0.95–0.99 (m, 9H, $CH_2CH_2C\mathit{H}_3$); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 148.7 (C), 148.4 (C), 148.08 (C), 148.03 (C), 147.7 (C), 131.6 (CH), 130.8 (CH), 128.3 (C), 128.1 (C), 127.34 (CH), 127.32 (CH), 127.28 (CH), 126.6 (CH), 123.5 (CH), 123.44 (CH), 123.41 (CH), 123.39 (CH), 123.36 (CH), 123.27 (CH), 121.9 (C), 90.1 (C), 88.5 (C), 71.9 (C), 67.35 (C), 67.30 (C), 67.14 (C), 40.9 (CH_2), 40.8 (CH_2), 40.7 (CH_2), 27.0 (12d-CH_3), 20.51 (CH_2), 20.47 (CH_2), 15.1 (CH_3), two $C^{ar}H$ and one CH_2 resonances were not resolved; MS (EI, 70 eV): *m/z* (%), 520 (14, $[M]^{+\bullet}$), 477 (100, $[M - C_3H_7]^+$), 435 (7), 405 (7), 391 (7), 389 (10), 238.6 (8, $[M - C_3H_7]^{2+\bullet}$); accurate mass (EI-MS) of $[M]^{+\bullet}$: calcd. for $C_{40}H_{40}$ 520.3130; found 520.3161.

General procedure for the synthesis of compounds 7 and 9

The respective TBTQ acetylene **5** (301 mg, 0.680 mmol) or **6** (350 mg, 0.673 mmol) was mixed with tetraphenylcyclopentadienone (1.1 equiv) in diphenyl ether (5 mL) and the given mixture was heated to 250 °C (metal bath temperature) in Schlenk tube under argon for 20 h. During this time the colour of the reaction mixture turned dark-orange. After completion of reaction (as monitored by TLC), the mixture was allowed to cool to room temperature and the solvent was removed by Kugelrohr distillation (100 °C, 10^{-2} mbar). Column chromatography of the solid residue through silica gel furnished the corresponding oligophenylphenyl derivatives **7** and **9**.

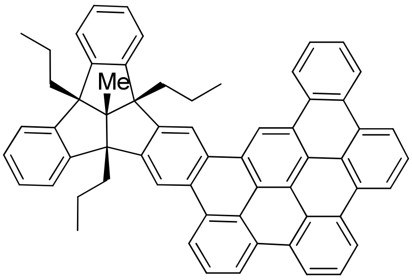
12d-Methyl-2-(2,3,4,5-tetraphenyl)phenyl-4b,8b,12b-tri-*n*-propyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (7)



Purification by column chromatography (petroleum ether/CH_2Cl_2, gradient 9:1 to 5:1); off-white solid; yield 456 mg (84%); mp 169–172 °C. IR (neat): $\tilde{\nu}$ = 3021, 2922, 2848, 1599, 1477, 1441, 1027, 753, 696, 507 cm^{-1}; ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.47 (s, 1H, Ar-H), 7.31–7.36 (m, 3H, Ar-H), 7.25 (d, *J* = 7.9 Hz, 1H, Ar-H), 7.14–7.19 (m, 9H, Ar-H), 7.11 (t, *J* = 7.5 Hz 1H, Ar-H), 7.02–7.04 (m, 5H, Ar-H), 6.98–7.00 (m, 4H, Ar-H), 6.90–6.98 (m, 7H, Ar-H), 6.84–6.87 (m, 1H, Ar-H), 2.15–2.19 (m, 4H, $C\mathit{H}_2CH_2CH_3$), 1.85 (m, 1H, $C\mathit{H}_2CH_2CH_3$)

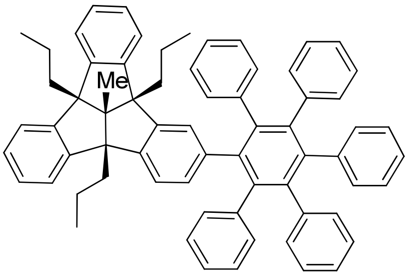
1.77 (m, 1H, C$H_2CH_2CH_3$), 1.60 (s, 3H, CH_3), 1.14–1.21 (m, 4H, CH_2CH_2CH_3), 0.90–1.02 (m, 7H, CH_2CH_2CH_3 and CH_2CH_2CH_3), 0.85–0.90 (m, 4H, Ar-H); ^{13}C NMR (125.7 MHz, CD_2Cl_2): δ 148.1 (C), 148.01 (C), 147.97 (C), 147.5 (C), 146.3 (C), 141.8 (C), 141.7 (C), 140.9 (C), 140.62 (C), 140.60 (C), 140.55 (C), 140.25 (C), 140.22 (C), 139.2 (C), 139.1 (C), 131.7 (CH), 131.6 (CH), 131.51 (CH), 131.48 (CH), 131.43 (CH), 131.40 (CH), 131.3 (CH), 129.9 (2 CH), 128.9 (CH), 127.5 (2 CH), 127.20 (CH), 127.16 (CH), 127.15 (CH), 127.05 (CH), 127.03 (CH), 126.97 (CH), 126.8 (2 CH), 126.53 (CH), 126.51 (CH), 126.2 (CH), 125.8 (CH), 125.5 (CH), 125.4 (CH), 125.2 (CH), 123.38 (CH), 123.31 (CH), 123.30 (CH), 123.26 (CH), 122.8 (CH), 71.8 (C), 67.2 (C), 66.9 (2C), 40.8 (CH_2), 40.5 (CH_2), 40.4 (CH_2), 26.9 (12d-CH_3), 20.4 (CH_2), 20.3 (CH_2), 20.2 (CH_2), 14.90 (CH_3), 14.85 (CH_3), 14.83 (CH_3), one C and some C^{ar}H resonances were not resolved; MS (EI, 70 eV): *m/z* (%), 800 (25, $[M]^{+\bullet}$), 757 (100, $[M - C_3H_7]^+$), 715 (5), 378.7 (11, $[M - C_3H_7]^{2+\bullet}$); accurate mass (EI-MS) of $[M]^{+\cdot}$: calcd. for $C_{62}H_{56}$ 800.4382; found 800.4391.

Dibenzo{dibenzo[*fg*,*ij*]phenanthro[9,10,1,2,3-*pqrst*]pentapheno}triquinacene 8



Copper(II) trifluoromethanesulfonate (1.41 g, 3.90 mmol) was completely dried under vaccum and heating. After cooling aluminium(III) chloride (540 mg, 4.05 mmol) and dry and degassed carbon disulfide (165 mL) were added under argon atmosphere. The suspension was vigorously stirred for 10 min, warmed to 45 °C (oil bath temperature) then the oligophenylene-TBTQ **7** (125 mg, 0.156 mmol) dissolved in the same solvent (5 mL) was injected through a septum. After being stirred for 24 h to 30 h (checked by TLC), the reaction was quenched by adding methanol (10 mL). The solvents were removed under vacuum and the residue was diluted with water (30 mL) and extracted with dichloromethane (4 x 25 mL). The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, passed through a pad of silica gel and concentrated under reduced pressure. Column chromatography of the residue through silica gel (petroleum ether/CH_2Cl_2 gradient 6:1 to 2:1) afforded the compound **8** (70 mg, 56%) as a yellow-orange colored solid, mp >250 °C (decomp.). IR (neat): $\tilde{\nu}$ = 3053, 2953, 2920, 2867, 1504, 1453, 1409, 1055, 786, 742, 621, 506 cm^{-1}; UV/vis (CH_2Cl_2): λ_{max} = 310, 323, 335, 365, 376 nm ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C): δ 9.91 (s, 1H, Ar-H), 8.94 (d, *J* = 8.0 Hz, 1H, Ar-H), 8.90 (s, 1H, Ar-H), 8.79 (d, *J* = 8.0 Hz, 1H, Ar-H), 8.74 (s, 1H, Ar-H), 8.69 (d, *J* = 8.0 Hz, 1H, Ar-H), 8.62–8.66 [m, 3H, Ar-H, overlapping signals at δ 8.653 (d, $J \approx 8.0$ Hz, 1H, Ar-H), δ 8.648 (d, $J \approx 8.0$ Hz, 1H, Ar-H) and δ 8.632 (d, $J \approx 8.0$ Hz, 1H, Ar-H)], 8.57 [apparent t, 2H, overlapping signals at δ 8.582 (d, $J \approx 8.0$ Hz, 1H, Ar-H) and δ 8.564 (d, $J \approx 8.0$ Hz, 1H, Ar-H)], 7.96 (d, $J = 8.0$ Hz, 1H, Ar-H), 7.85–7.88 [m, 2H, overlapping signals at δ 7.87 (t, $J = 7{,}5$ Hz, 1H, Ar-H) and δ 7.86 (d, $J = 7.5$ Hz, 1H, Ar-H), 7.82 (t, $J = 8.0$ Hz, 1H, Ar-H), 7.75 (t, $J = 8.0$ Hz, 2H, Ar-H), 7.68 (t, $J = 8.0$ Hz, 1H, Ar-H), 7.60–7.63 [m, 2H, overlapping signals at δ 7.615 (t, $J \approx 7.5$ Hz, 1H, Ar-H) and δ 7.616 (d, $J \approx 7.5$ Hz, 1H, Ar-H), 7.58 (d, $J = 7.5$ Hz, 1H, Ar-H), 7.51 (td, $J = 7.5$ Hz, $J = 1.1$ Hz, 1H, Ar-H), 7.44 (td, $J = 7.5$ Hz, $J = 1.0$ Hz, 1H, Ar-H), 7.38 (td, $J = 7.5$ Hz, $J = 1.1$ Hz, 1H, Ar-H), 2.62–2.68 (m, 4H, $C\mathit{H}_2CH_2CH_3$), 2.43–2.47 (m, 2H, $C\mathit{H}_2CH_2CH_3$), 1.94 (s, 3H, 12d-CH_3), 1.55–1.60 (m, 4H, $CH_2C\mathit{H}_2CH_3$), 1.46–1.51 (m, 1H, $CH_2C\mathit{H}_2CH_3$, partially hidden under H_2O signal), 1.20 (t, $J = 7.5$ Hz, 6H, $CH_2CH_2C\mathit{H}_3$), 1.15 (t, $J = 7.5$ Hz, 3H, $CH_2CH_2C\mathit{H}_3$), 0.98–1.02 (m, 1H, $CH_2C\mathit{H}_2CH_3$); ^{13}C NMR (125.7 MHz, $C_2D_2Cl_4$, 23 °C): δ 148.83 (C), 148.76 (C), 148.74 (C), 148.49 (C), 148.39 (C), 148.24 (C), 129.82 (C), 129.80 (C), 129.62 (2 C), 129.56 (C), 129.03 (C), 128.98 (C), 128.94 (C), 128.8 (C), 128.6 (C), 127.9 (CH), 127.7 (CH), 127.53 (CH), 127.47 (CH), 127.1 (2 CH), 125.74 (CH), 125.61 (CH), 125.58 (CH), 125.2 (C), 124.0 (CH), 123.86 (CH), 123.82 (CH), 123.79 (CH), 123.3 (CH), 123.0 (CH), 121.8 (C), 120.93 (CH), 120.90 (CH), 120.88 (CH), 120.74 (CH), 120.64 (CH), 120.55 (CH), 120.52 (C), 120.4 (C), 119.0 (C), 117.7 (CH), 117.6 (CH), 113.3 (CH), 72.7 (C), 67.8 (C), 67.7 (C), 67.6 (C), 41.8 (CH_2), 41.6 (CH_2), 41.1 (CH_2), 20.8 (2 CH_2), 20.6 (CH_2), 15.60 (CH_3), 15.51 (CH_3), 15.45 (CH_3), 15.38 (CH_3), three arene C resonances were not resolved; MS [(+)-MALDI, CH_2Cl_2/DCTB]: *m/z* 792 (100, $[M]^{+\bullet}$), 793 (74, $^{13}C_1$-$[M]^{+\bullet}$), 794 (29, $^{13}C_2$-$[M]^{+\bullet}$), 795 (10, $^{13}C_3$-$[M]^{+\bullet}$); 1584.80 (4, $[2\ M]^{+\bullet}$); accurate mass (MALDI-MS, CH_2Cl_2/DHB) of $[M]^{+\bullet}$: calcd. for $C_{62}H_{48}$ 792.3756; found 792.3758.

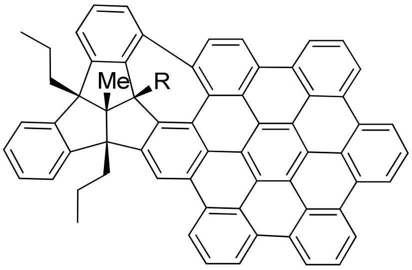
12d-Methyl-2-pentaphenylphenyl-4b,8b,12b-tri-*n*-propyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (9)



Purification by column chromatography (petroleum ether/CH_2Cl_2, gradient 9:1 to 4:1); colorless amorphous solid; yield 460 mg (78%); mp 164–167 °C. IR (neat): $\tilde{\nu}$ = 3054, 2953, 2867, 1599, 1477, 1440, 1071, 1027, 737, 695, 557 cm^{-1}; ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.34 (d, $J = 7.5$ Hz, 1H, Ar-H), 7.14–7.23 (m, 4H, Ar-H), 7.07–7.10 (m, 2H, Ar-H), 6.82–6.95

(broad m, 22H, Ar-H), 6.74–6.79 (m, 3H, Ar-H), 6.65 (d, *J* = 7.5 Hz, 1H, Ar-H), 6.62 (t, *J* = 7.4 Hz, 1H, Ar-H), 6.56 (t, *J* = 7.4 Hz, 1H, Ar-H), 6.49 (t, *J* = 7.5 Hz, 1H, Ar-H), 2.05–2.18 (m, 2H, $CH_2CH_2CH_3$), 1.94–1.97 (m, 3H, $CH_2CH_2CH_3$), 1.88–1.91 (m, 1H, $CH_2CH_2CH_3$), 1.52 (s, 3H, CH_3), 1.12–1.19 (m, 1H, $CH_2CH_2CH_3$) partially overlapping with 1.01–1.12 (m, 3H, $CH_2CH_2CH_3$), 0.96 (t, *J* = 7.5 Hz, 3H, $CH_2CH_2CH_3$), 0.93 (t, *J* = 7.5 Hz, 3H, $CH_2CH_2CH_3$), almost completely hidden at ca. 0.85–0.90 (m, 1H, $CH_2CH_2CH_3$), 0.85 (t, *J* = 7.5 Hz, 3H, $CH_2CH_2CH_3$), 0.64–0.70 (m, 1H, $CH_2CH_2CH_3$); ^{13}C NMR (125.7 MHz, CD_2Cl_2): δ 148.9 (C), 148.24 (C), 148.16 (C), 147.1 (C), 147.0 (C), 144.2 (C), 140.83 (C), 140.79 (C), 140.75 (C), 140.68 (C), 140.18 (C), 140.16 (C), 140.07 (C), 140.04 (C), 139.3 (C), 131.83 (CH), 131.81 (CH), 131.79 (CH), 131.74 (2 CH), 131.70 (CH), 131.63 (CH), 131.2 (CH), 130.6 (CH), 127.48 (CH), 127.46 (CH), 127.11 (CH), 127.04 (CH), 126.90 (2 CH), 126.88 (2 CH), 126.83 (CH), 126.69 (CH), 126.63 (CH), 125.61 (CH), 125.54 (CH), 125.52 (CH), 125.46 (CH), 125.39 (CH), 123.66 (2 CH), 123.55 (CH), 123.4 (CH), 122.3 (CH), 71.5 (C), 67.2 (C), 66.6 (C), 66.5 (C), 41.3 (CH_2), 40.4 (CH_2), 39.8 (CH_2), 20.4 (CH_2), 20.2 (CH_2), 20.0 (CH_2), 15.1 (CH_3), 14.80 (CH_3), 14.73 (CH_3), 14.65 (CH_3), several arene C and CH resonances were not resolved; MS (EI, 70 eV): *m/z* 876 (30, $[M]^{+\bullet}$), 833 (100, $[M - C_3H_7]^+$), 791 (12), 416.7 (25, $[M - C_3H_7]^{2+\bullet}$); MS [(+)-ESI, CH_2Cl_2/MeOH/$AgBF_4$]: *m/z* 983 (72, $[M + {}^{107}Ag]^+$), 984 (45), 985 (100), 986 (62), 987 (20), 988 (8); accurate mass [(+)-ESI, CH_2Cl_2/$AgBF_4$] of $[M + {}^{107}Ag]^+$: calcd for $C_{68}H_{60}{}^{107}Ag$ 983.3741, found 983.3746.

Dibenzo(hexa-*peri*-hexabenzocoroneno)triquinacene 10



(R = *n*-propyl)

Copper(II) trifluoromethanesulfonate (2.24 g, 6.22 mmol) was completely dried under vaccum and heating. After cooling aluminium(III) chloride (847 mg, 6.37 mmol) and dry and degassed carbon disulfide (200 mL) were added under argon atmosphere. The suspension was vigorously stirred for 10 min, warmed to 45 °C (oil bath temperature) then the oligophenylene-TBTQ **9** (130 mg, 0.148 mmol) dissolved in the same solvent (5 mL) was injected through a septum. After being stirred for 3 d, the reaction was quenched by adding methanol (15 mL). The solvents were removed under vacuum and the residue was diluted with water (40 mL) and extracted with dichloromethane (4 x 30 mL). The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, passed through a thick pad of silica gel and concentrated under reduced pressure. Column chromatography of the residue through silica gel (petroleum ether/CH_2Cl_2 gradient 5:1 to CH_2Cl_2 only) afforded the compound **10** (76 mg, 59%) as a yellow-orange solid; mp >250 °C (decomp.). IR (neat): $\tilde{\nu}$ = 3072, 2955, 2924, 2867, 1516, 1454, 1377, 1030, 759, 743, 655, 514 cm^{-1}; UV/vis (CH_2Cl_2): λ_{max} = 364, 398, 415 nm; ^1H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C): δ 9.41 (d, *J* = 8.5 Hz, 1H, Ar-H), 9.32 (d, *J* = 8.0 Hz, 1H, Ar-H), 9.25 (s, 1H, Ar-H), 9.10 (d, *J* = 8.0 Hz, 1H, Ar-H), 9.05 (d, *J* = 8.5 Hz, 1H, Ar-H), 8.97 (d, *J* = 8.0 Hz, 1H, Ar-H), 8.77 (d, *J* = 8.0 Hz, 1H, Ar-H), 8.72 (d, *J* = 8.5 Hz, 2H, Ar-H), 8.66 [apparent t, 2H, overlapping signals at δ 8.670 (d, *J* ≈ 8.5 Hz, 1H, Ar-H) and δ 8.650 (d, *J* ≈ 8.5 Hz, 1H, Ar-H)], 8.24 (t, *J* = 8.0 Hz, 1H, Ar-H), 8.01 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.93 [apparent q, 2H, overlapping signals at δ 7.934 (t, *J* = 7.0 Hz, 1H, Ar-H) and δ 7.920 (t, *J* = 7.0 Hz, 1H, Ar-H), 7.75 (d, *J* = 7.5 Hz, 1H, Ar-H), 7.68–7.71 [m, 2H, overlapping signals at δ 7.698 (t, *J* ≈ 7.5 Hz, 1H, Ar-H) and δ 7.690 (d, *J* = 7.5 Hz, 1H, Ar-H)], 7.66 (d, *J* = 7.5 Hz, 1H, Ar-H), 7.59 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.52 (t, *J* = 8.0 Hz, 1H, Ar-H), 7.46 (t, *J* = 7.5 Hz, 1H, Ar-H), 2.62–2.71 (m, 4H, $CH_2CH_2CH_3$), 1.94–1.97 (m, 5H, $CH_2CH_2CH_3$ and 12d-CH_3), 1.66–1.72 (m, 3H, $CH_2CH_2CH_3$), 1.24 (t, *J* = 7.5 Hz, 3H, $CH_2CH_2CH_3$), 1.02–1.17 (m, 1H, $CH_2CH_2CH_3$) overlapping with 1.11 (t, *J* = 7.5 Hz, 3H, $CH_2CH_2CH_3$), 0.97–1.06 (m, 1H, $CH_2CH_2CH_3$), 0.85–0.93 (m, 1H, $CH_2CH_2CH_3$), 0.55 (t, *J* = 7.5 Hz, 3H, $CH_2CH_2CH_3$); ^{13}C NMR (125.7 MHz, $C_2D_2Cl_4$, 50 °C): δ 149.23 (C), 149.20 (C), 148.4 (C), 146.1 (C), 145.2 (C), 144.3 (C), 136.5 (C), 135.3 (C), 129.7 (CH), 129.6 (C), 129.4 (C), 129.0 (C), 128.8 (C), 128.7 (C), 128.40 (C), 128.38 (C), 128.26 (C), 128.0 (CH), 127.9 (C), 127.7 (CH), 127.50 (CH), 127.47 (CH), 126.7 (C), 126.2 (CH), 125.7 (C), 125.4 (2 CH), 125.1 (CH), 124.9 (C), 123.96 (C), 123.93 (2 CH), 123.6 (C), 123.4 (C), 123.1 (C), 122.87 (C), 122.6 (CH), 121.6 (CH), 121.3 (CH), 120.9 (CH), 120.6 (2 CH), 120.4 (CH), 120.2 (2 CH), 120.0 (C), 120.0 (CH), 119.66 (C), 119.58 (C), 119.50 (C), 119.0 (C), 117.2 (CH), 71.7 (C), 69.2 (C), 68.3 (C), 66.6 (C), 41.5 (CH_2), 41.1 (CH_2), 32.9 (CH_2), 21.2 (CH_2), 20.88 (CH_2), 20.85 (CH_2), 15.5 (CH_3), 15.38 (CH_3), 15.35 (CH_3), 14.7 (CH_3), two arene C were not resolved; MS [(+)-MALDI, CH_2Cl_2/DCTB]: *m/z* 862 (100, $[M]^{+\bullet}$), 863 (79, $^{13}C_1$-$[M]^{+\bullet}$), 864 (34, $^{13}C_2$-$[M]^{+\bullet}$), 865 (12, $^{13}C_3$-$[M]^{+\bullet}$); 1724.8 (4, $[2\ M]^{+\bullet}$); accurate mass [(+)-MALDI, CH_2Cl_2/DHB] of $[M]^{+\bullet}$ calcd for $C_{68}H_{46}$ 862.3599, found 862.3598.

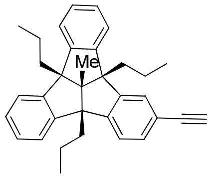
References

1 P. Wolkoff, *Can. J. Chem.,* 1975, **53**, 1333.

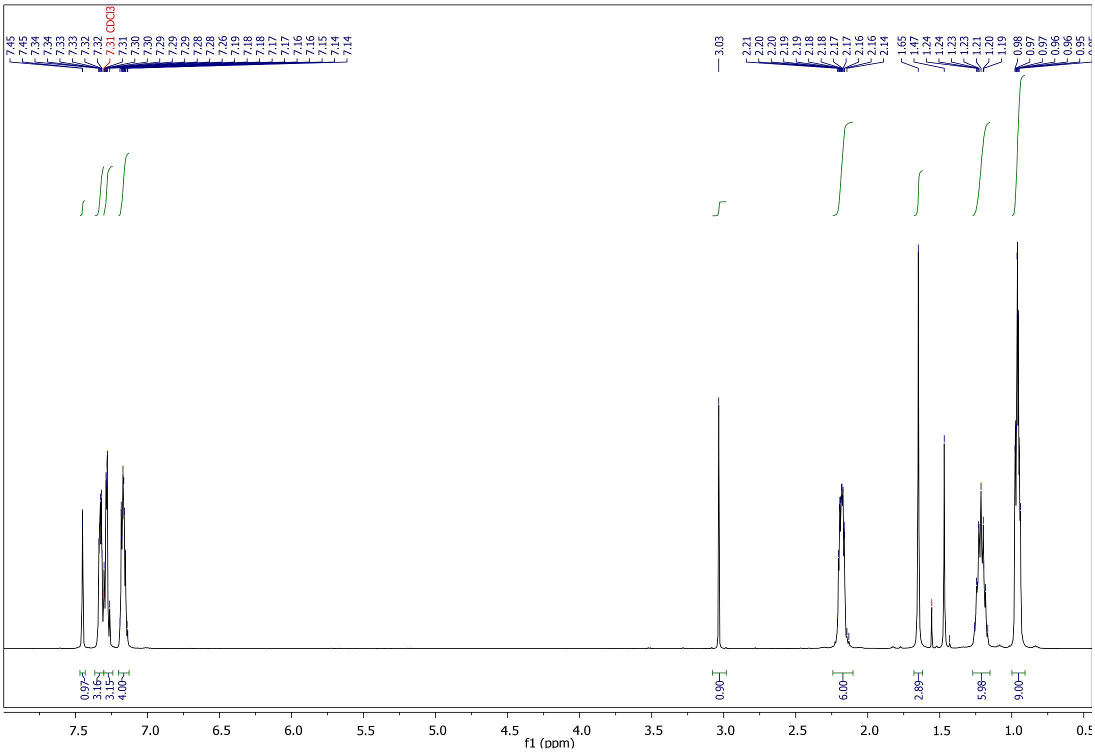
2 O. Tosic, J. Mattay, *Eur. J. Org. Chem.*, 2011, 371.

3 W. X. Niu, T. Wang, Q. Q. Hou, Z. Y. Li, X. P. Cao, *D. Kuck, J. Org. Chem.* 2010, **75**, 6704.

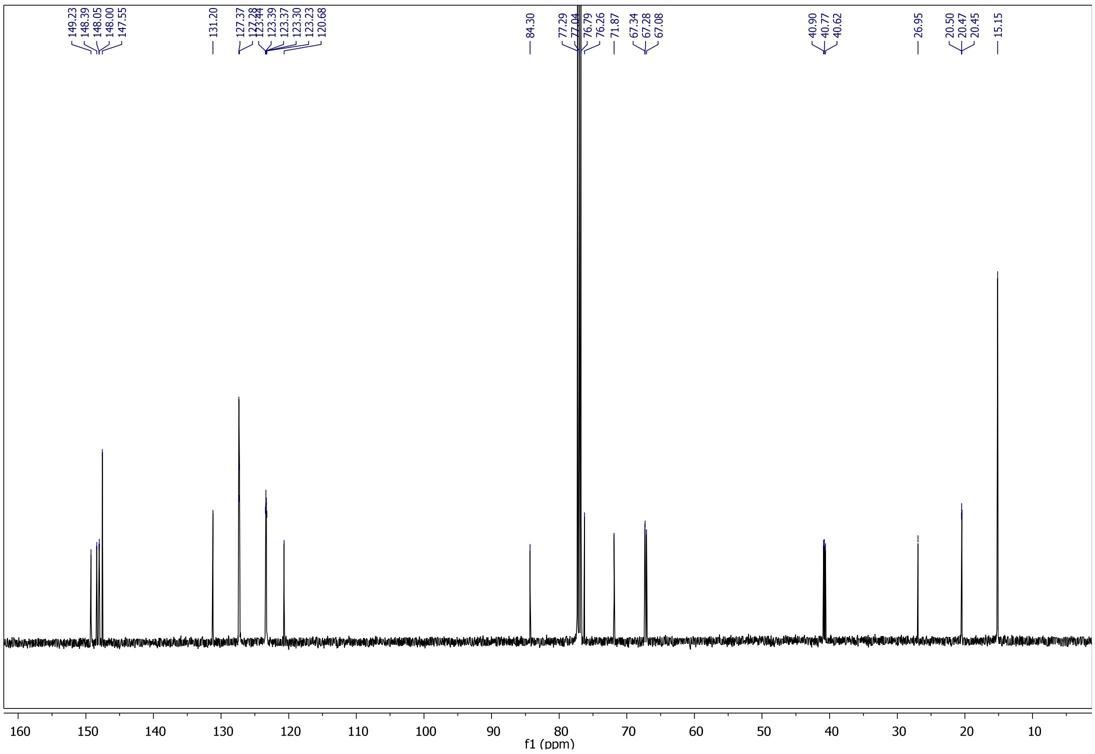
2-(Ethynyl)-12d-methyl-4b,8b,12b-tri-*n*-propyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (5)



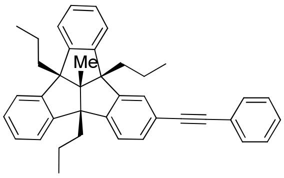
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



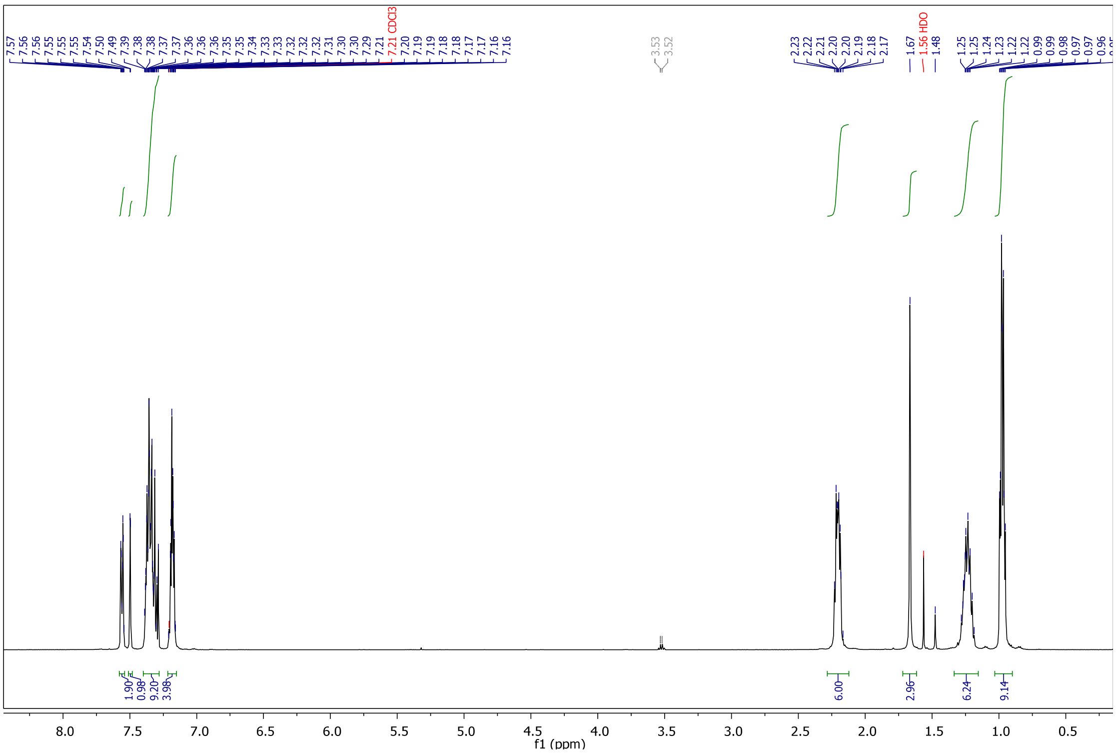
^{13}C NMR spectrum (126 MHz, $CDCl_3$)



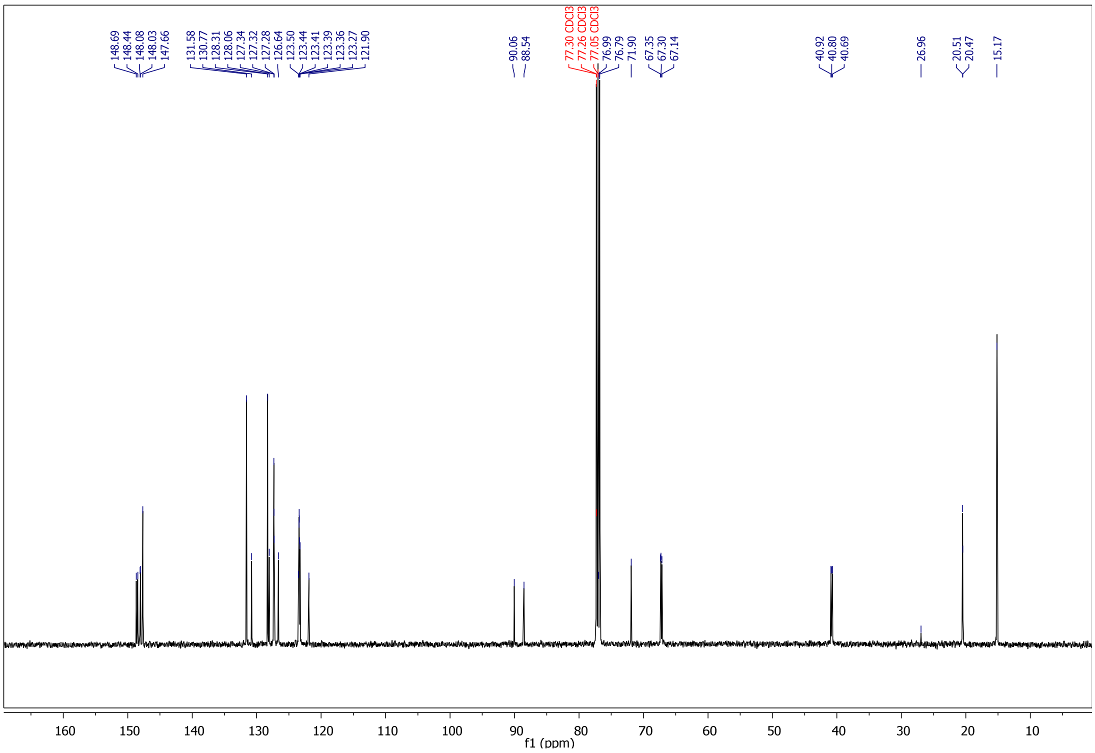
12d-Methyl-2-phenylethynyl-4b,8b,12b-tri-*n*-propyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (6)



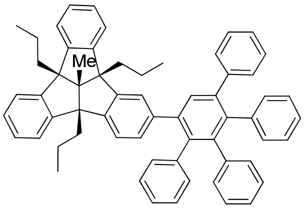
^{1}H NMR spectrum (500 MHz, CDCl$_3$)



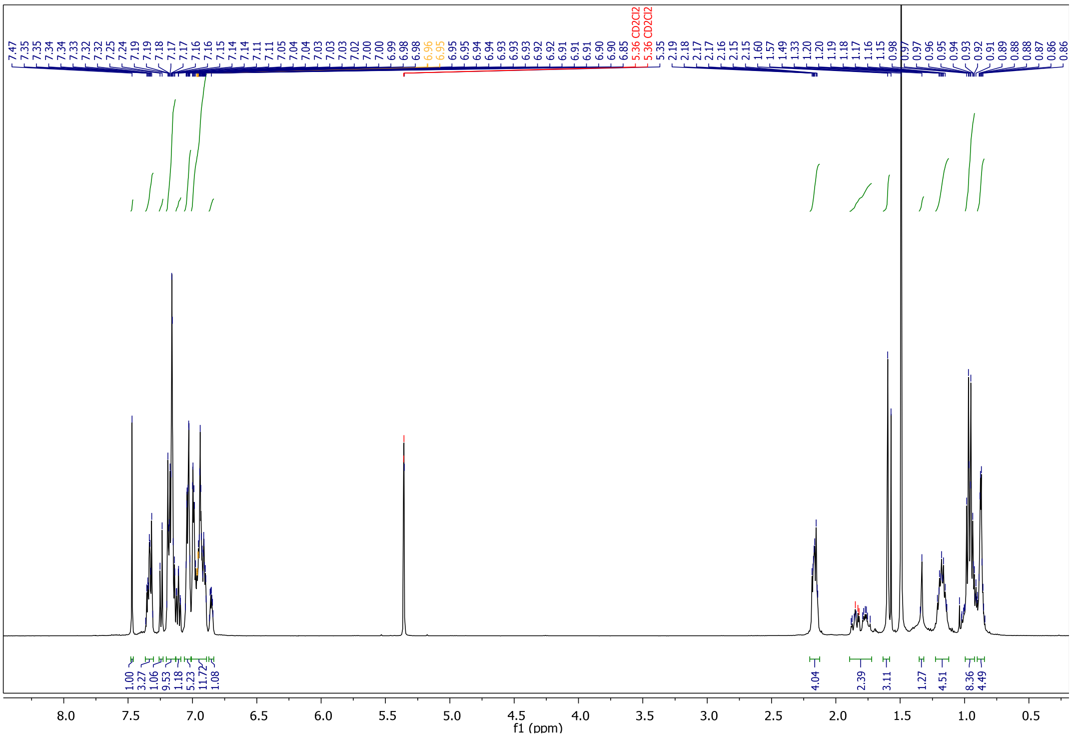
^{13}C NMR spectrum (126 MHz, CDCl$_3$)



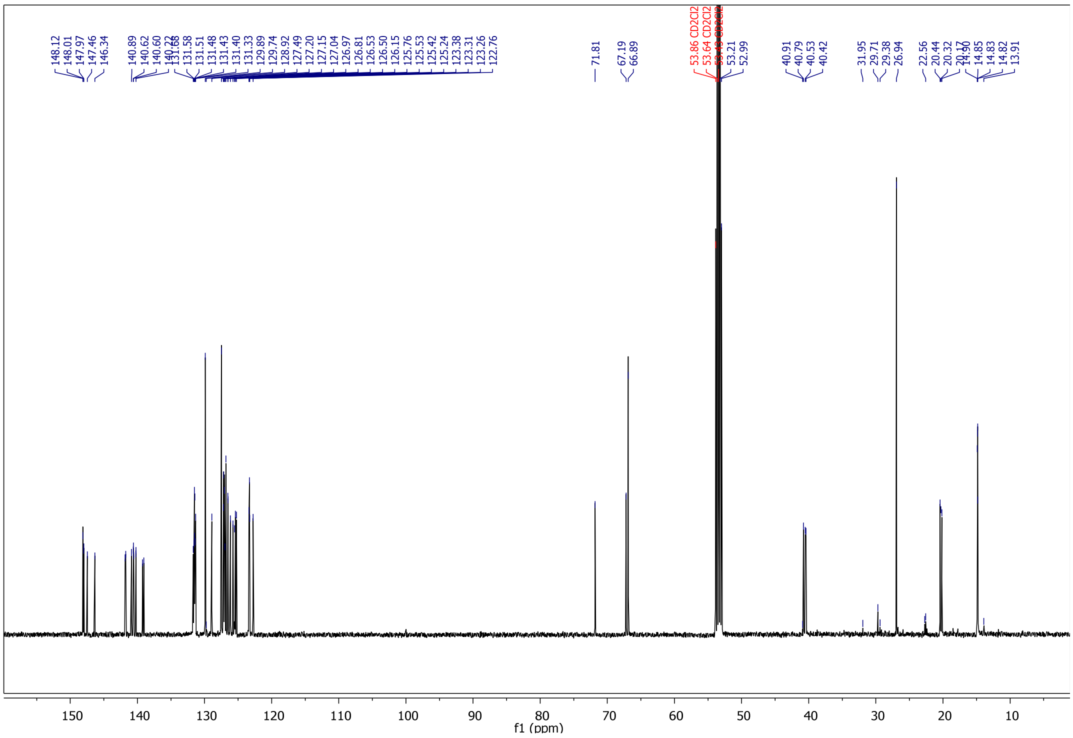
12d-Methyl-2-(2,3,4,5-tetraphenyl)phenyl-4b,8b,12b-tri-*n*-propyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (7)



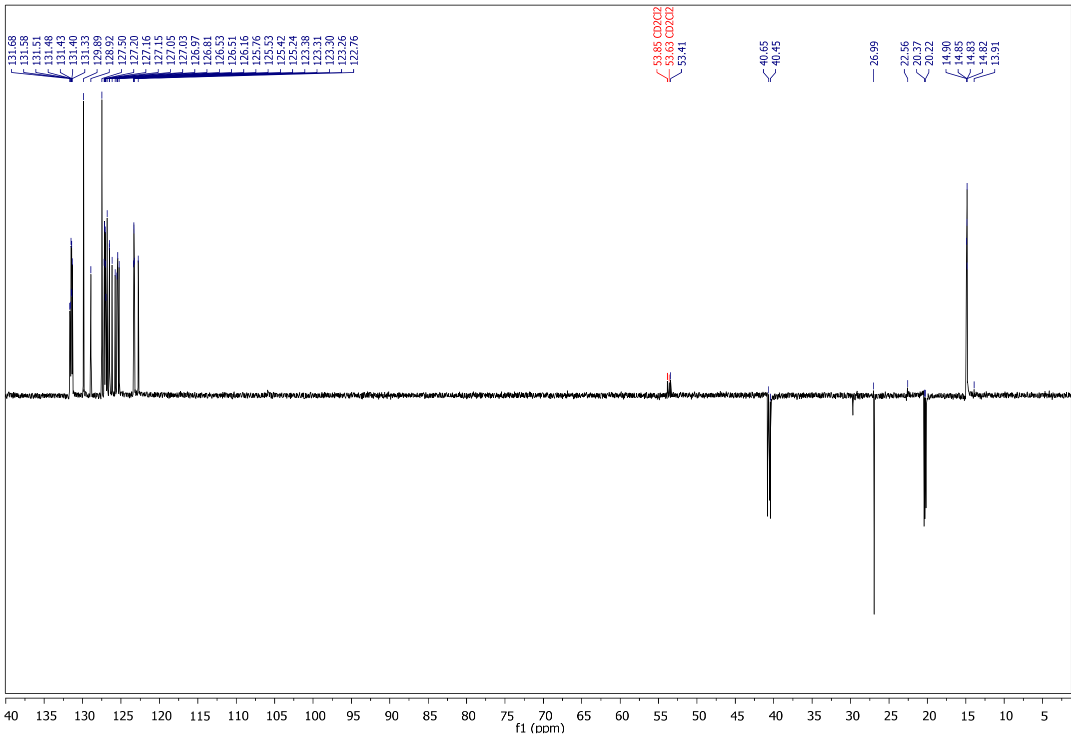
^{1}H NMR spectrum (500 MHz, CD_2Cl_2)



^{13}C NMR spectrum (126 MHz, CD_2Cl_2)



DEPT NMR spectrum (126 MHz, CD_2Cl_2)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131.58
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131.48
131.43
131.40
131.33
129.89
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127.50
127.20
127.16
127.15
127.05
127.03
126.97
126.81
126.53
126.51
126.16
125.76
125.53
125.42
125.24
123.38
123.31
123.30
123.26
122.76
53.85 CD2Cl2
53.63 CD2Cl2
53.41
40.65
40.45
26.99
22.56
20.37
20.22
14.90
14.85
14.83
14.82
13.91
40
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
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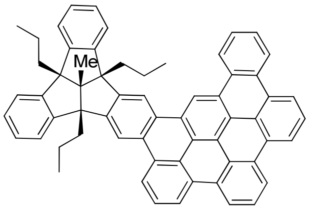
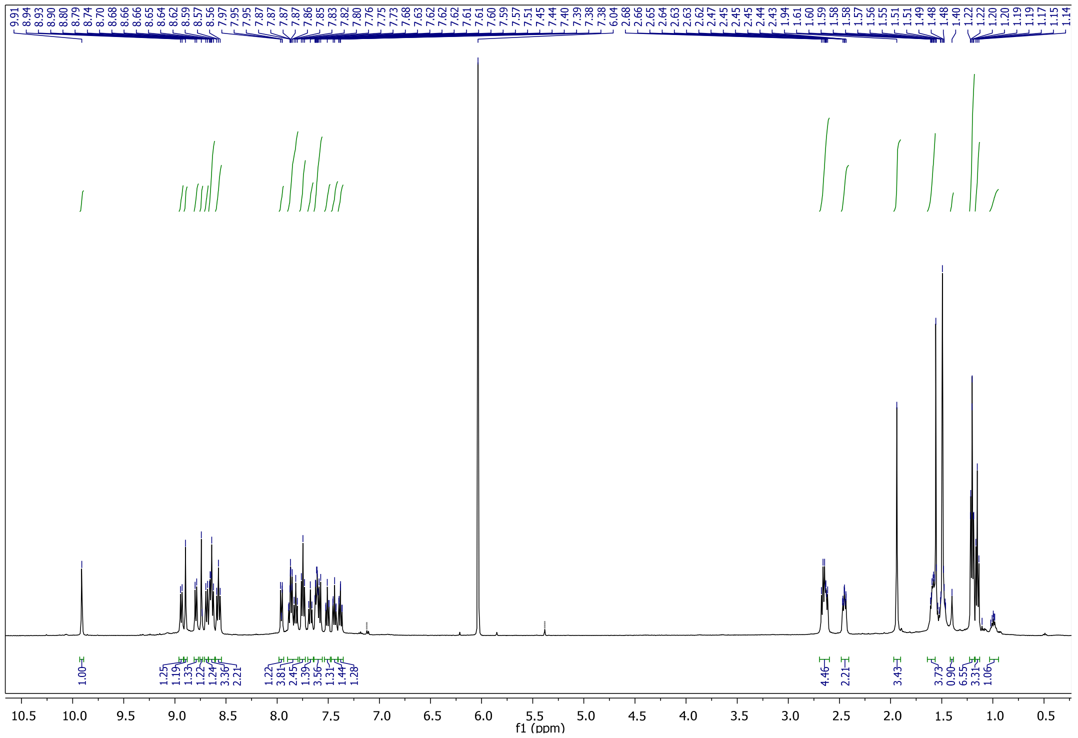
35
30
25
20
15
10
5
f1 (ppm)

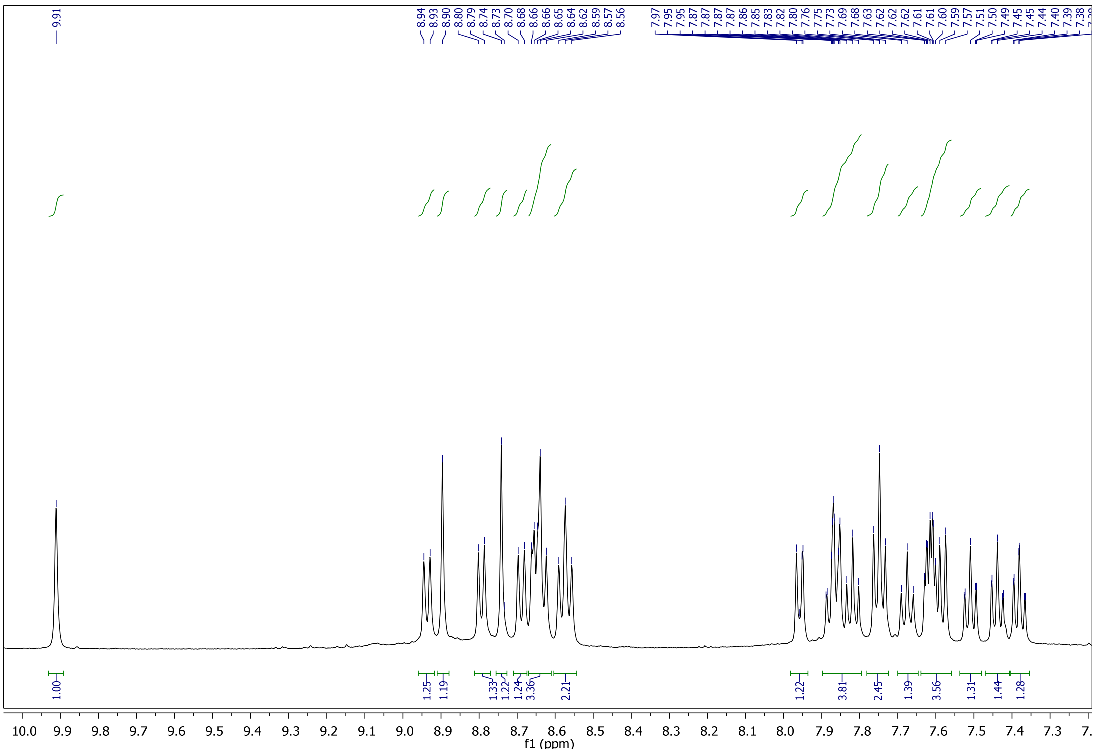
Dibenzo{dibenzo[*fg*,*ij*]phenanthro[9,10,1,2,3-*pqrst*]pentapheno}triquinacene 8



^{1}H NMR spectrum (500 MHz, $C_2D_2Cl_4$, 110 °C)

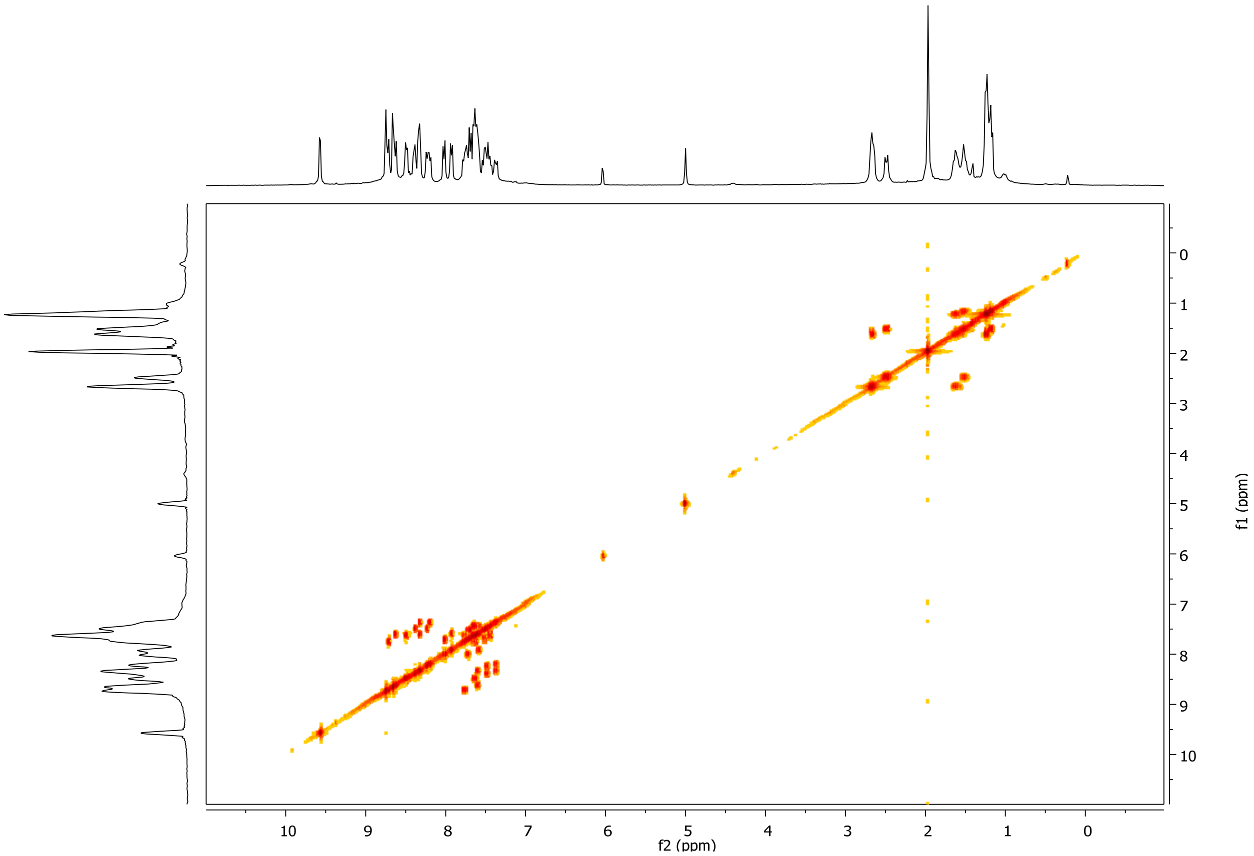


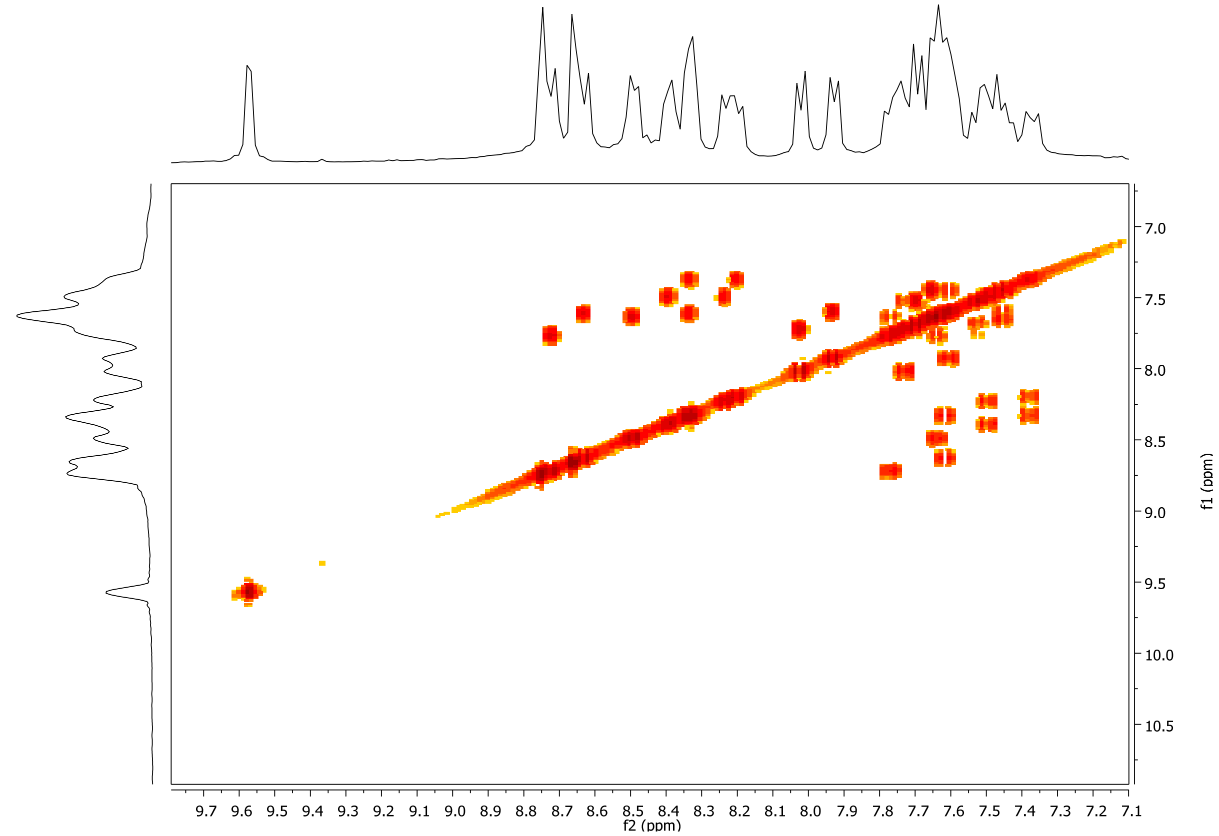
^{1}H NMR spectrum (500 MHz, $C_2D_2Cl_4$, 110 °C, magnified aromatic region)



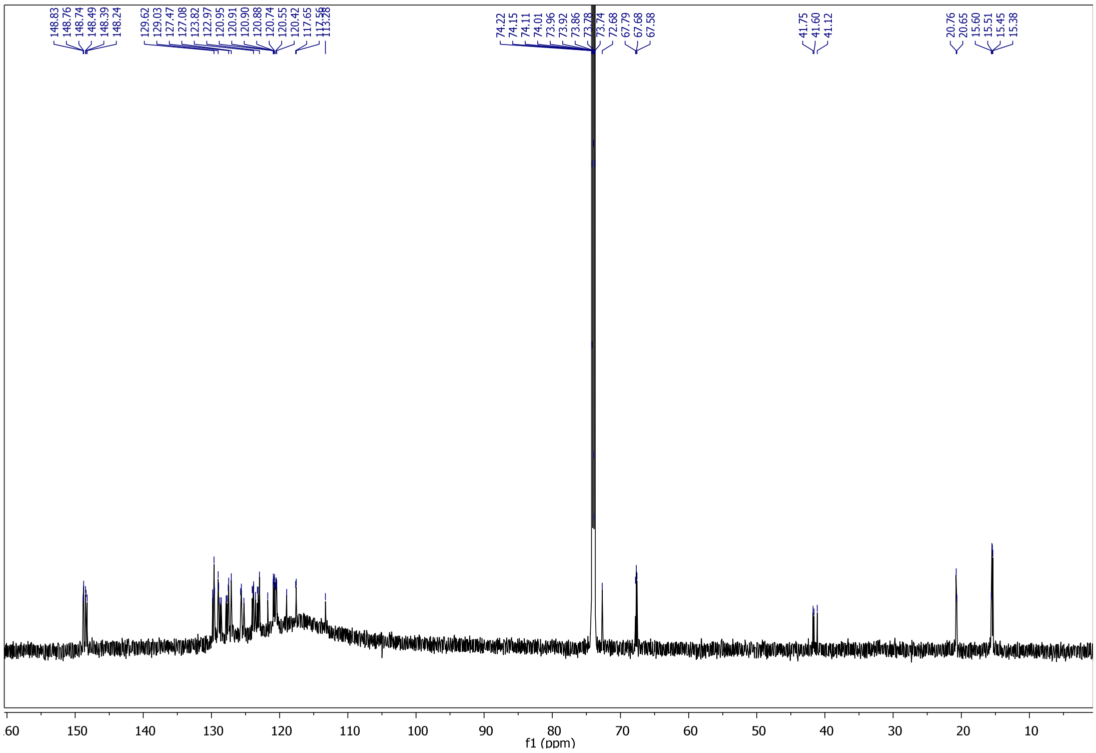
$^{1}H,^{1}H$ COSY spectrum (500 MHz, $C_2D_2Cl_4$, 100 °C).

Note: For technical reasons, this COSY spectrum was measured at 100 °C only. This gave rise to deviating chemical shifts as compared to the data obtained at 110 °C (see text and ESI data given above).

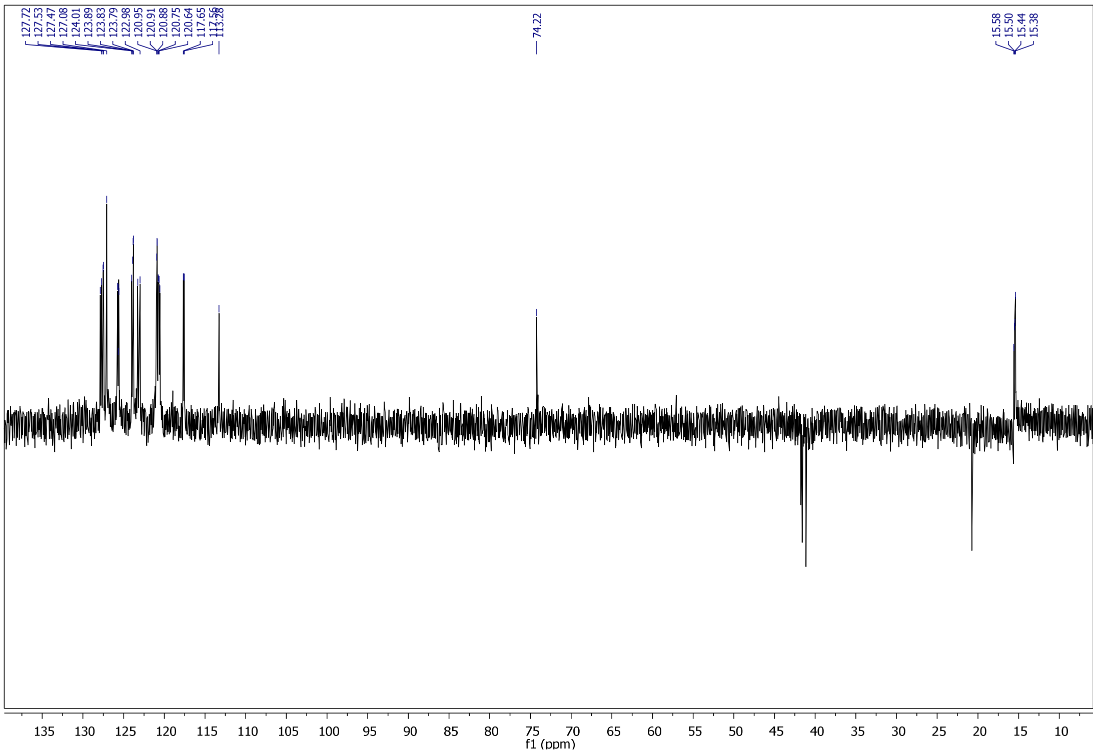




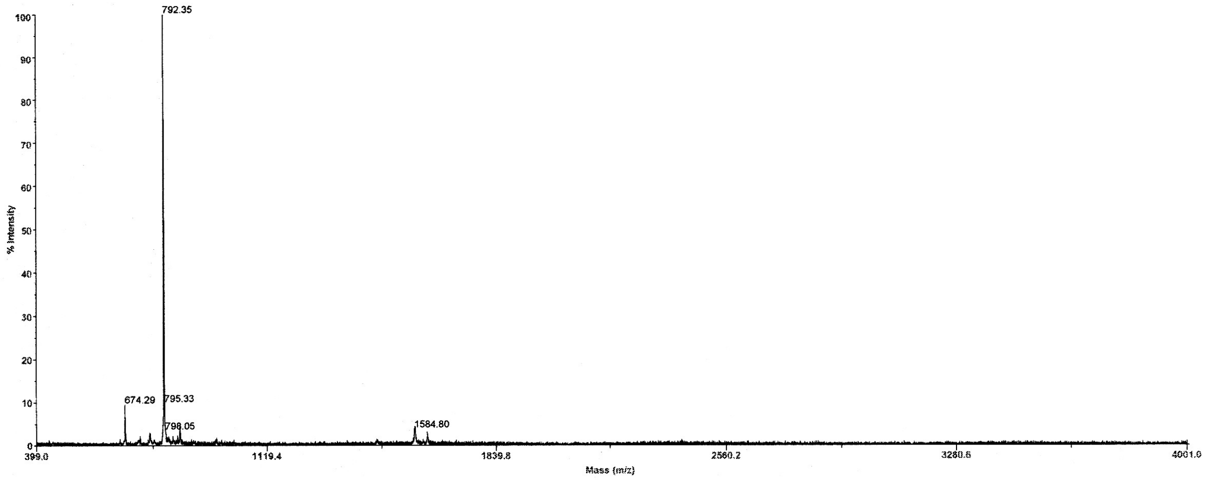
^{13}C NMR spectrum (126 MHz, $C_2D_2Cl_4$, 23 °C)

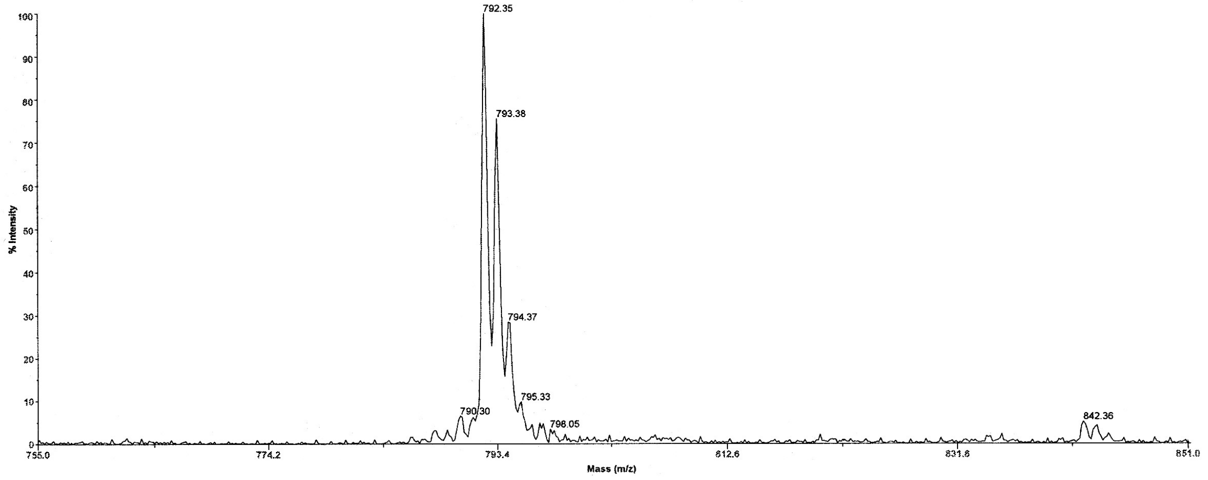


DEPT NMR spectrum (126 MHz, $C_2D_2Cl_4$, 23 °C)

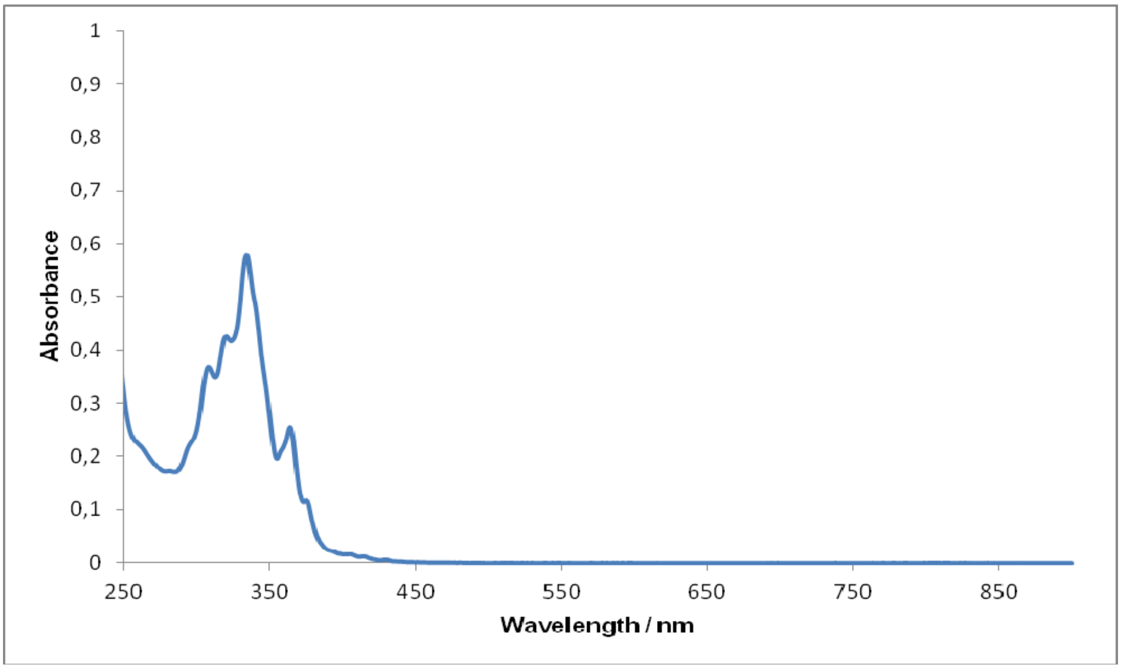


(+)-MALDI-ToF mass spectrum (CH_2Cl_2/DCTB) of compound **8** ($M^{\bullet+}$ *m*/*z* 792)

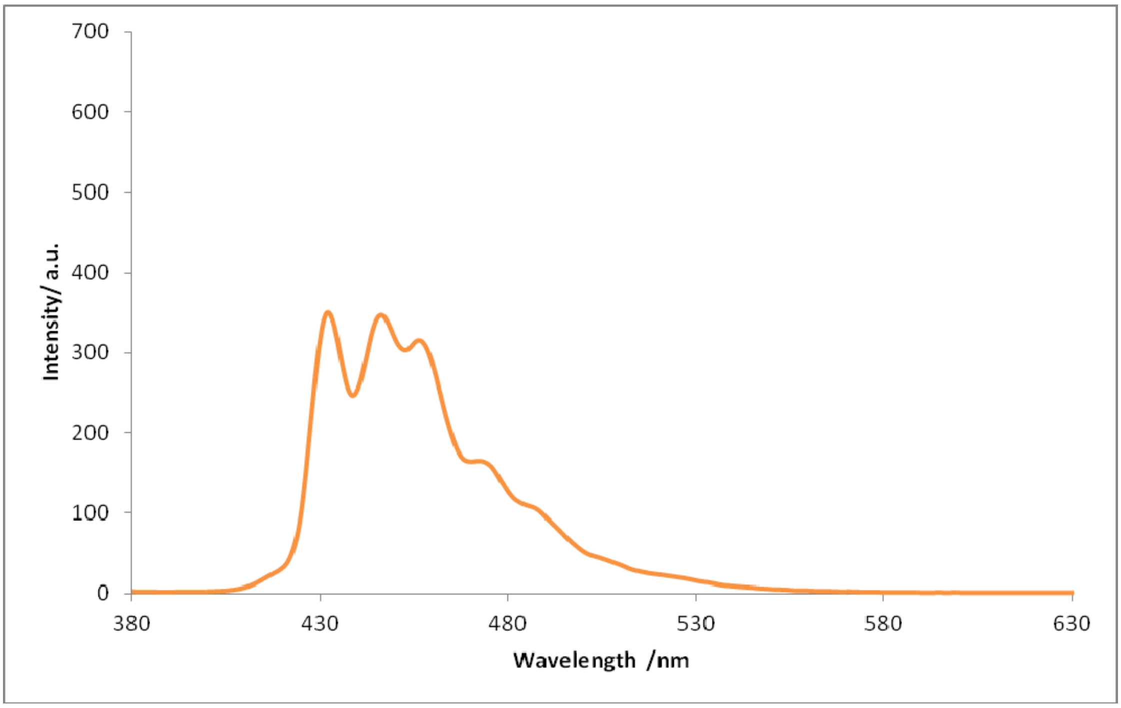




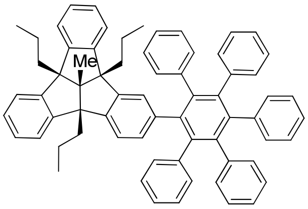
UV/Vis spectrum (solvent: CH_2Cl_2, concentration unknown)



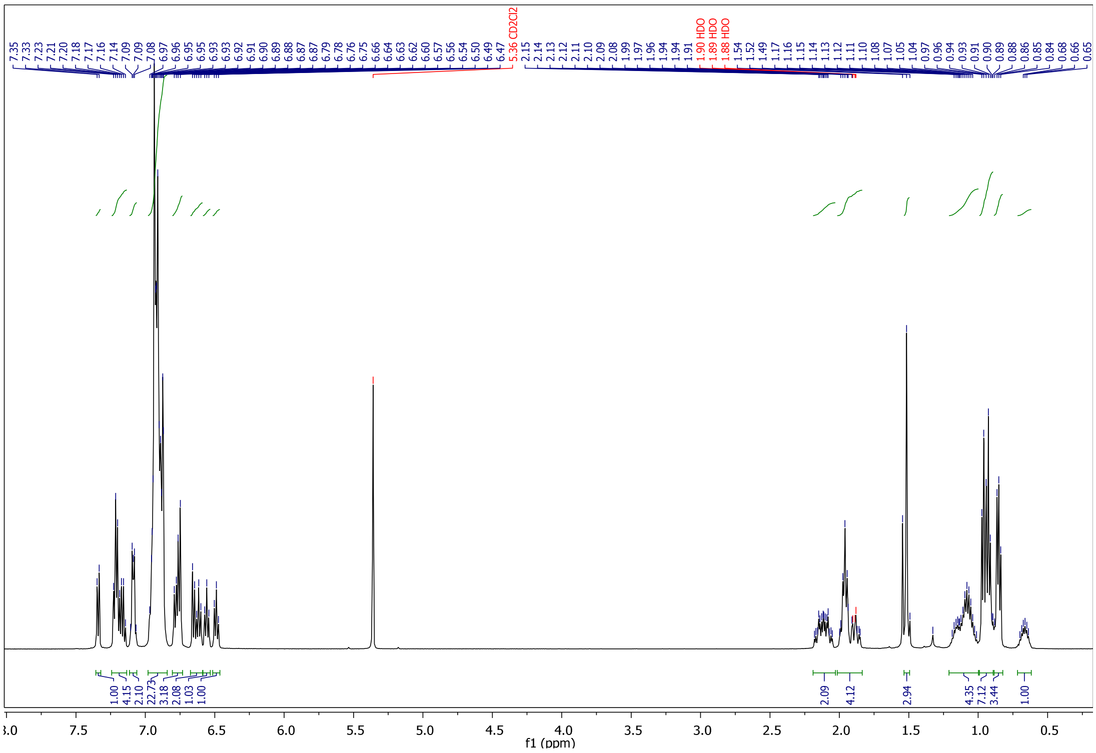
Luminsicence spectrum (solvent: CH_2Cl_2, concentration unknown)



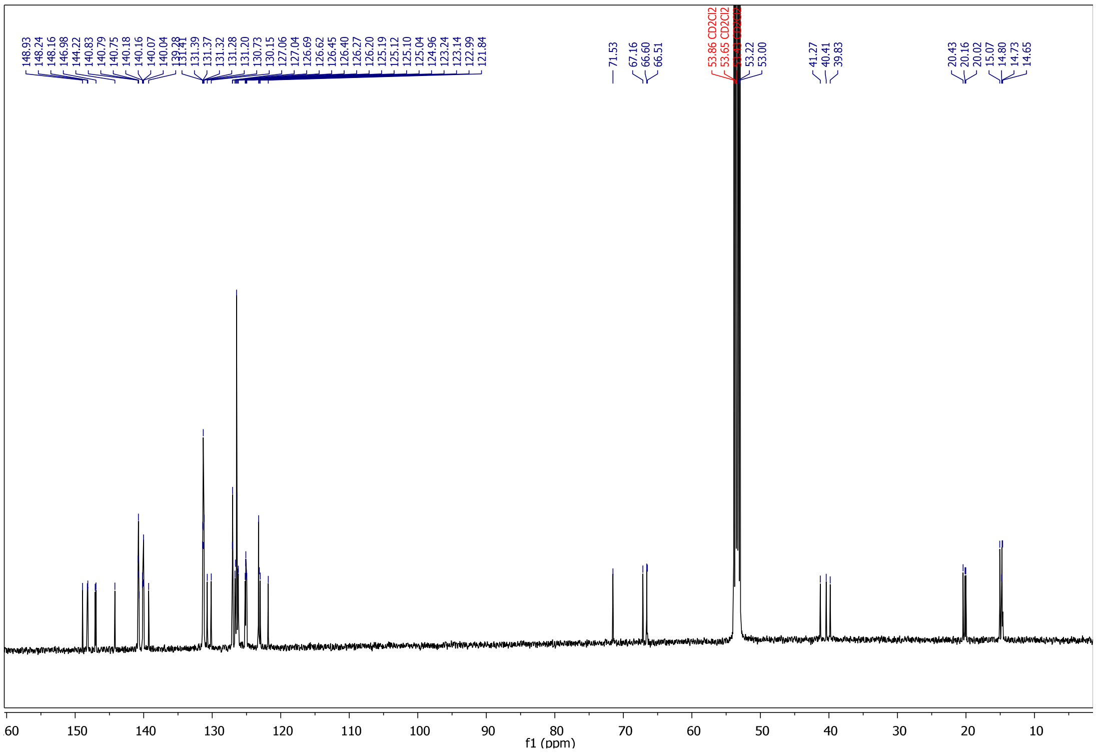
12d-Methyl-2-pentaphenylphenyl-4b,8b,12b-tri-*n*-propyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (9)



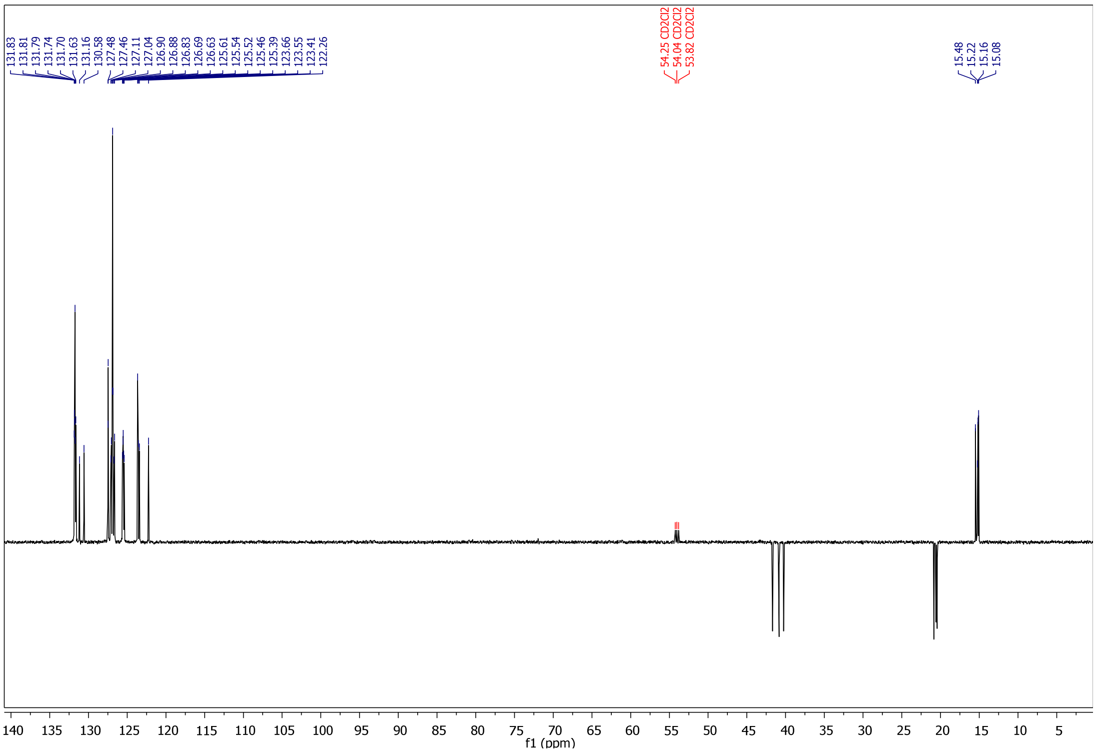
^{1}H NMR spectrum (500 MHz, CD_2Cl_2)



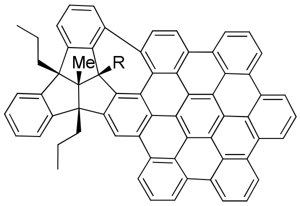
^{13}C NMR spectrum (126 MHz, CD_2Cl_2)



DEPT NMR spectrum (126 MHz, CD_2Cl_2)

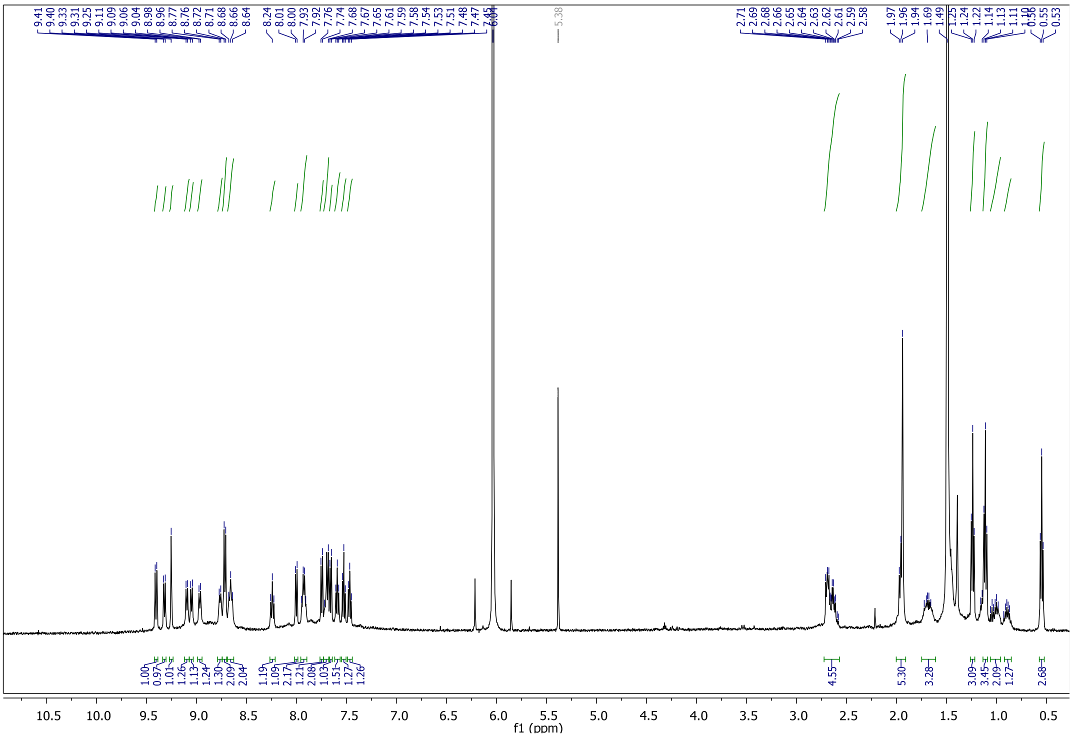


Dibenzo(hexa-*peri*-hexabenzocoroneno)triquinacene 10

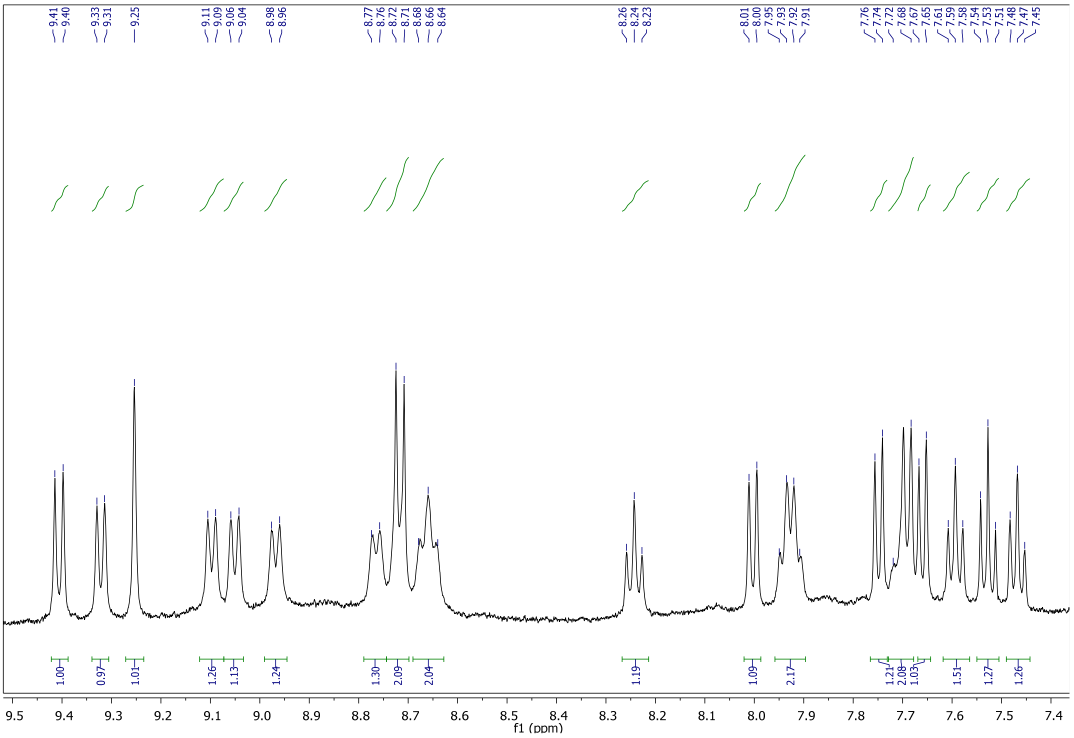


(R = *n*-propyl)

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C)

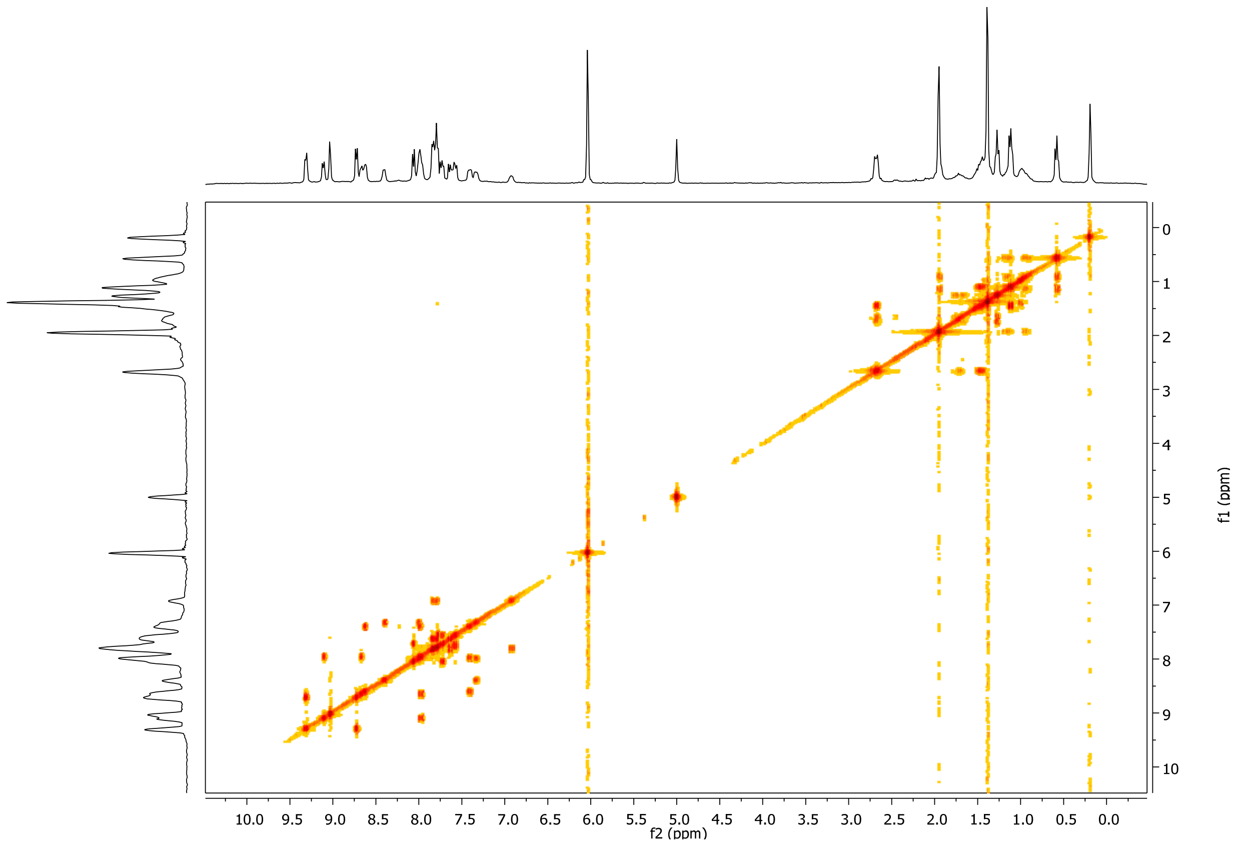


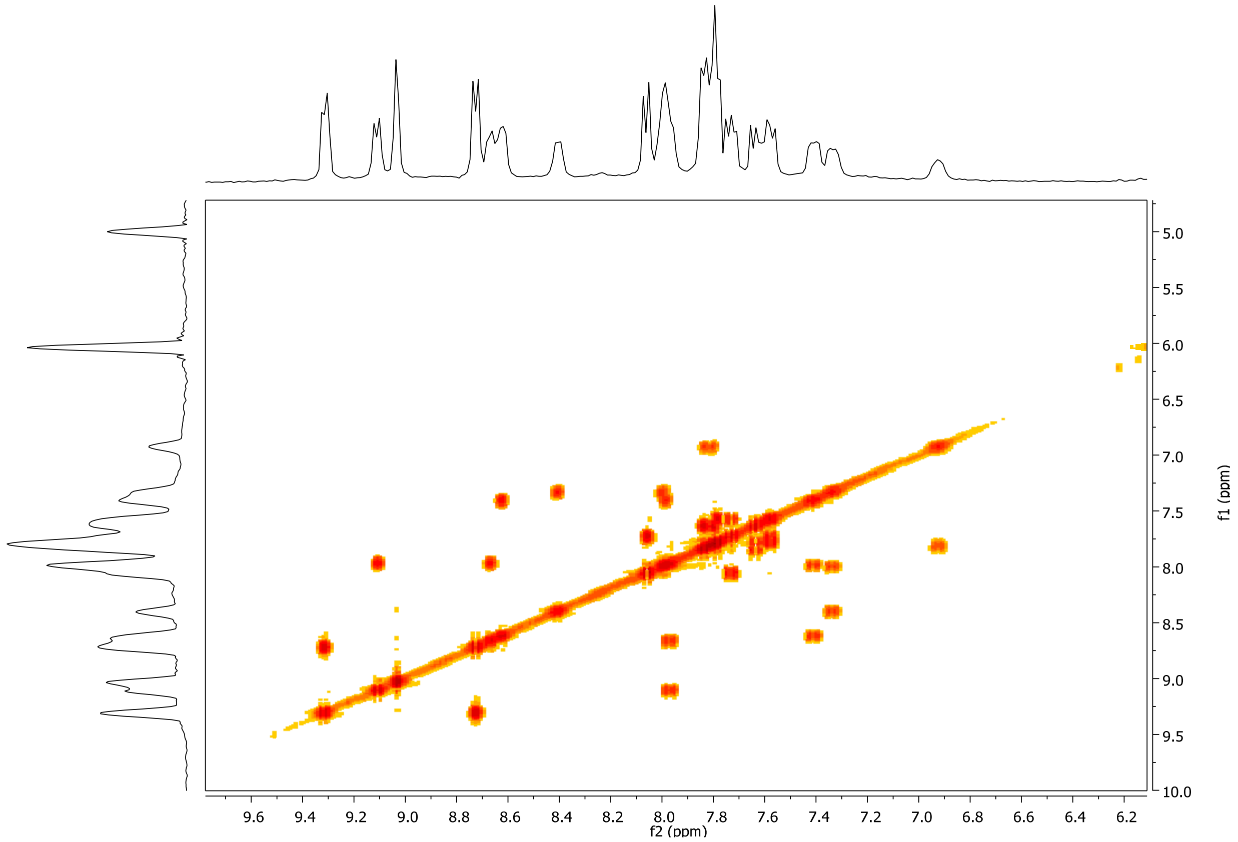
^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C, magnified aromatic region)



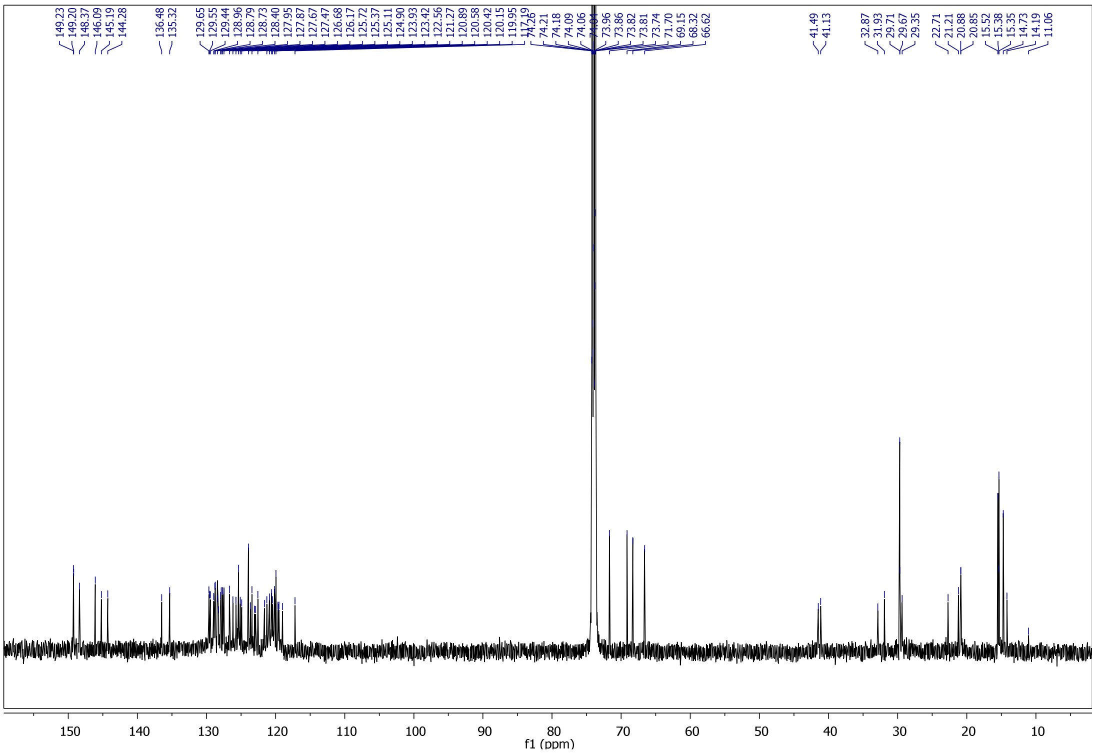
^{1}H,^{1}H COSY spectrum (500 MHz, $C_2D_2Cl_4$, 100 °C).

Note: For technical reasons, this COSY spectrum was measured at 100 °C only. This gave rise to deviating chemical shifts as compared to the data obtained at 110 °C (see text and ESI data given above).

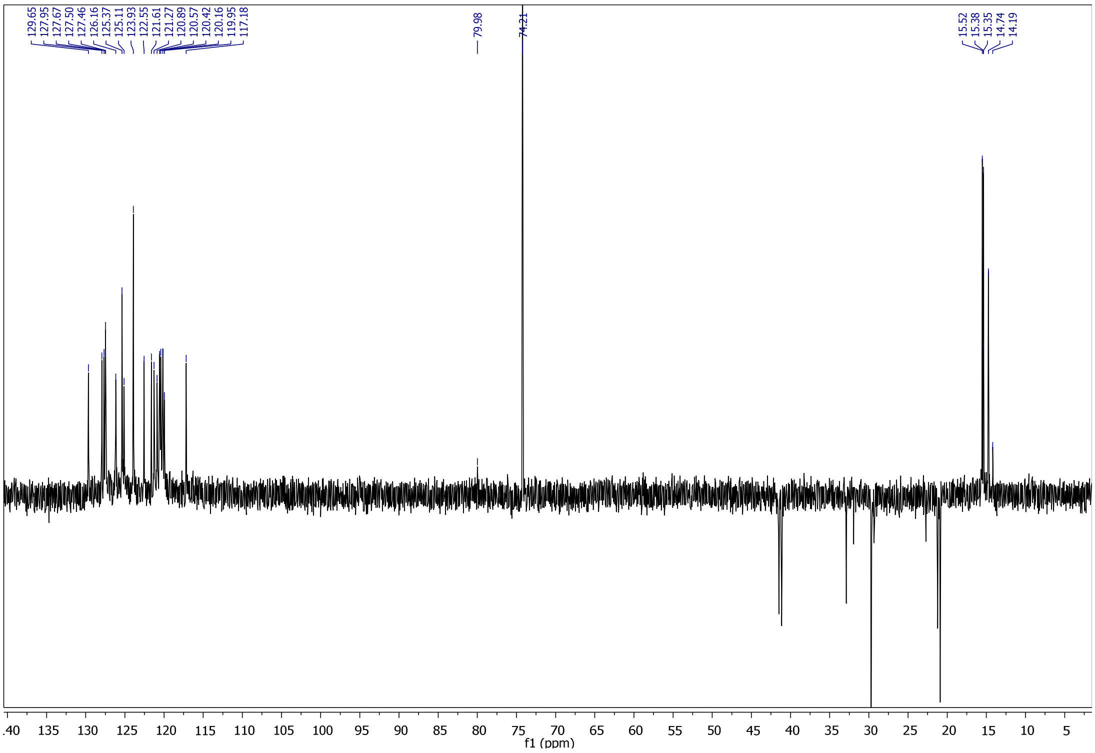




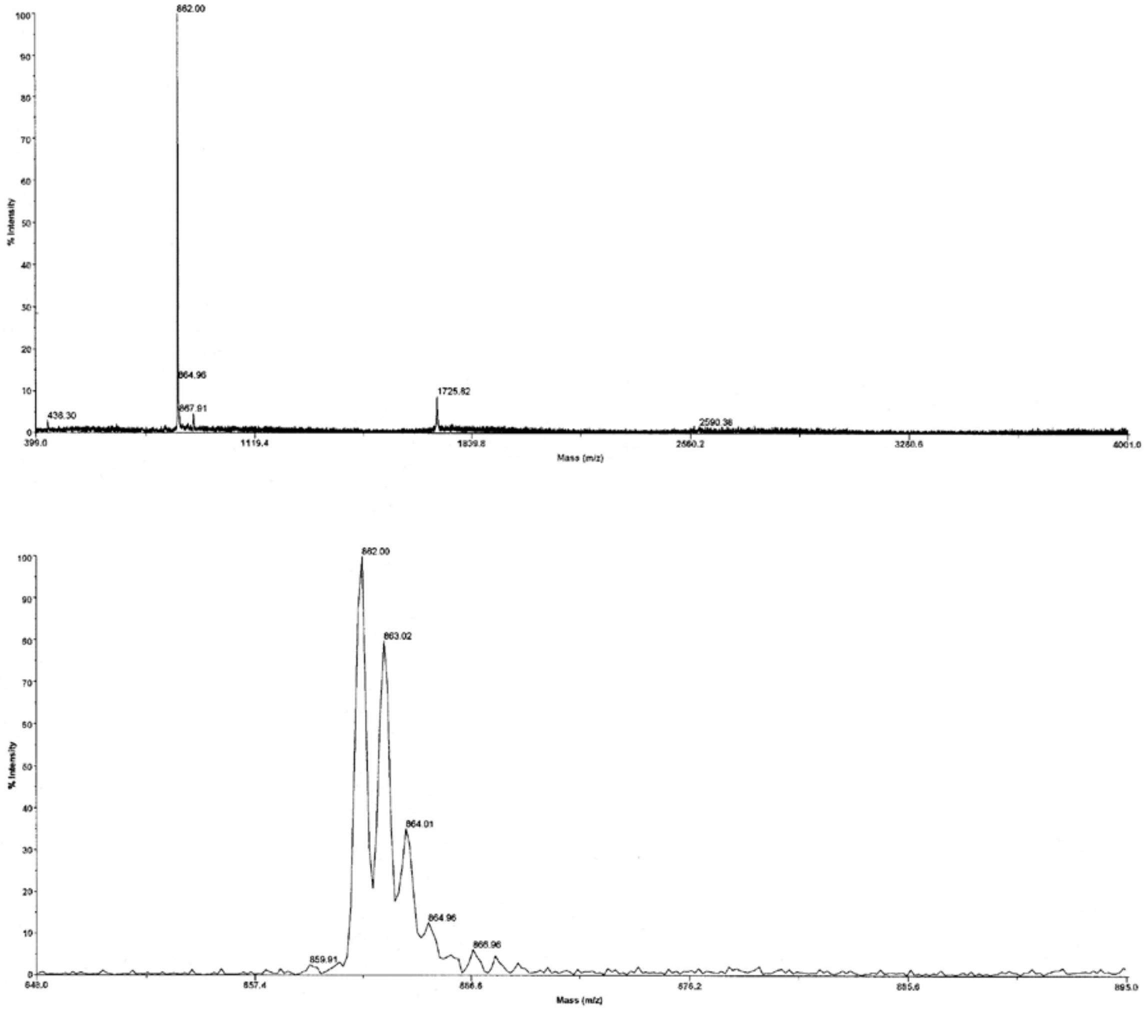
^{13}C NMR spectrum (126 MHz, $C_2D_2Cl_4$, 50 °C)



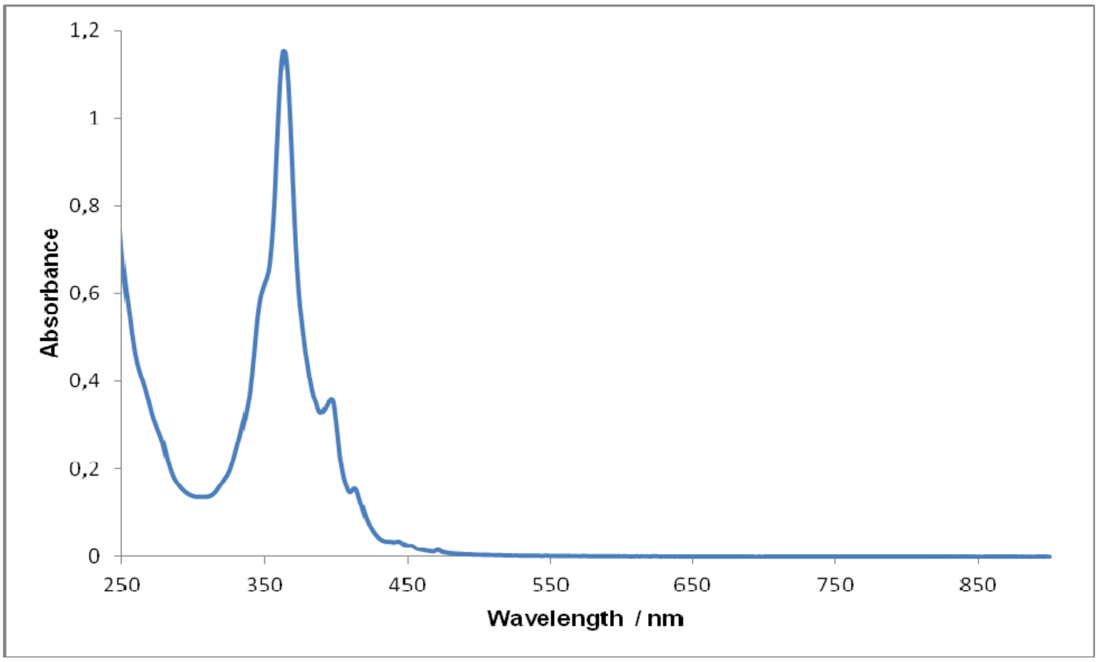
DEPT NMR spectrum (126 MHz, $C_2D_2Cl_4$, 50 °C)



(+)-MALDI-ToF mass spectrum (CH_2Cl_2/DCTB) of compound **10** ($M^{\bullet+}$ *m*/*z* 862)



UV/Vis spectrum (solvent: CH_2Cl_2, concentration unknown)



Luminescence spectrum (solvent: CH_2Cl_2, concentration unknown)