Electronic Supplementary Information for:

Ortho-methylated tribenzotriquinacenes – paving the way to curved carbon networks

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Contents:

1. General Experimental Procedure

All chemicals were used as received without further purification unless otherwise stated. Reactions requiring anhydrous conditions were performed in dried glassware under an atmosphere of dry argon or nitrogen. Water free solvents were dried and distilled prior to use according to standard protocols.

Reaction progress was monitored by thin-layer chromatography (TLC) on Merck pre-coated plates (TLC silica gel 60 F_{254}, 0.20 mm) with indicated solvents (v/v). Flash column chromatography was performed on silica gel (particle size: 0.04-0.063 mm) purchased from Merck with indicated solvents (v/v) using columns with aligned length and diameter.

High performance liquid chromatography (HPLC) was performed using a Jasco MD-2010 plus multiwavelength detector, Jasco DG-2080-53 3-Line degasser, Jasco LC-Net II/ ADC and Jasco PU-2080 plus intelligent HPLC pump. For analytical and semi-preparative purposes were used a Reprosil C18-PQ-Jasco (5µ, 250 x 4 mm) column and a Reprosil C18-PQ-Jasco (5µ, 250 x 10 mm) column, respectively. Medium pressure liquid chromatography (MPLC) was performed as follows: pressure, 16 bar; column, 50 × 2.5 cm; RP-18 silica gel, YMC ODS-A, 15 µm; detector, Knauer Variable Wavelength Monitor.

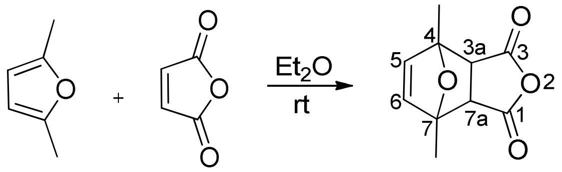
^{1}H- and ^{13}C-NMR were recorded on Bruker DMX 600 FT-NMR- (600 MHz), Bruker AVANCE 400 FT-NMR- (400 MHz) and Bruker 250 FT-NMR- (250 MHz) spectrometer. Chemical shifts are referenced relative to internal chloroform ($CDCl_3$: ^{1}H, δ=7.26; ^{13}C, δ=77.16) and dimethyl sulfoxide (DMSO: ^{1}H, δ=2.50; ^{13}C, δ=39.52) in ppm, respectively. Coupling patterns are assigned as s (singlet), d (doublet), t (triplet), q (quartet) or m (multiplet) (or combinations) and coupling constants are reported in Hz.

Melting points (mp) were determined by using a Reichert Austria Kofler instrument and are uncorrected. Infrared (IR) spectra were recorded on a Jasco FT-IR-410 and Jasco FT-IR-430 spectrometer, respectively, using an ATR unit in both cases. Absorptions are reported in cm^{-1}.

Electrospray ionization (ESI) mass spectrometry and Atmospheric pressure chemical ionization (APCI) mass spectrometry were performed on a Bruker Daltonik micrOTOF Focus. Electron impact (EI) mass spectrometry was performed on a Finnigan MAT 90 or Varian MS 320. UV/VIS spectra were recorded on a Kontron Instruments Uvikon 943. Elemental analysis (EA) was performed on an Elementar Vario Micro.

2. Experimental Procedure and Characterization

Synthesis of 4,7-Dimethyl-3a,4,7,7a-tetrahydro-4,7-epoxyisobenzofuran-1,3-dione (6)[1]

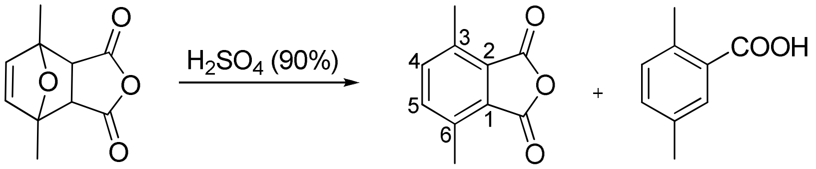


4 **5** **6** (76%)

To a suspension of maleic anhydride (**5**) (30.6 g, 312 mmol) in anhydrous Et_2O (39 mL) was added slowly 2,5-dimethylfuran (**4**) (30.0 g, 312 mmol) under vigorous stirring and a flow of Ar. The reaction mixture was stirred for 66 h at rt meanwhile the anhydride dissolved and the product precipitated. The mixture was cooled to 0 °C, filtered and washed well with cold Et_2O to afford the Diels-Alder adduct **6** (46.0 g, 76%) as light yellow crystals.

mp. 63-64 °C
^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.35 (2H, s, 5/6-H), 3.16 (2H, s, 3a/7a-H), 1.76 (6H, s, C*H*$_3$) ppm.

Synthesis of 3,6-Dimethylphthalic anhydride (7)[1]



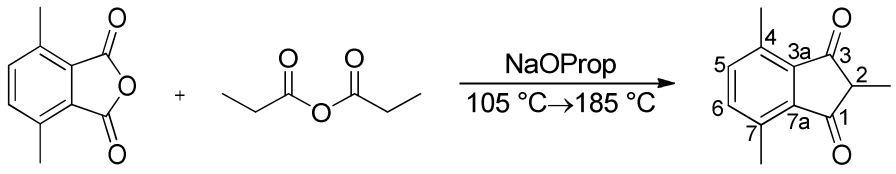
6 **7** (52%)

The powdered Diels-Alder adduct **6** (42.0 g, 216 mmol) was slowly added to 90% sulfuric acid (410 mL) under vigorous stirring at -10 to -6 °C. After stirring for 2.5 h at 0 °C **6** was completely dissolved and the temperature of the reaction mixture was allowed to rise to 10 °C. After pouring on a sufficient amount of ice the light brown precipitate was filtered, washed with cold water and dissolved in 5% aqueous NaOH. By adding glacial acetic acid (75 mL) the by-product 2,5-dimethylbenzoic acid (1.86 g, 12.4 mmol, 6%) was obtained after filtration as a colorless solid. The filtrate was strongly acidified with conc. HCl to precipitate the phthalic anhydride **7**, which was collected by filtration and recrystallized from Et_2O to obtain **7** as colourless crystals (19.8 g, 52%).

mp. 143-145 °C (from Et_2O)
R_f 0.45 (CyH/EtOAc 2:1)

FT-IR (ATR): $\tilde{\nu}$ = 3070 (w, ν(C-H$_{arom}$)), 2975 (w, ν(C-H)), 2929 (w, ν(C-H)), 1831 (s, ν(C=O)), 1751 (s, ν(C=O)), 1563 (w), 1497 (m, ν(C=C$_{arom}$)), 1443 (w), 1378 (m), 1356 (m), 1240 (s, ν(C-O-C)), 1194 (s, ν(C-O-C)), 1159 (m), 1035 (m), 882 (s), 847 (s), 747 (s), 674 (m), 630 (m) cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (2H, s, 4/5-H), 2.68 (6H, s, C*H*$_3$) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.4 (C$_q$, *C*=O), 138.0 (C$_q$), 137.9 (C$_t$, C-4/5), 128.7 (C$_q$), 17.5 (C$_p$, *C*H$_3$) ppm.
MS (EI, 70 eV): m/z = 176 (M$^+$, 100%), 148 (M$^+$-CO, 62), 132 (M$^+$-CO$_2$, 67), 120 (14), 104 (86), 91.1 (16), 77 (30), 63 (21), 51 (32).

Synthesis of 2,4,7-Trimethyl-1*H*-indene-1,3(2*H*)-dione (8)

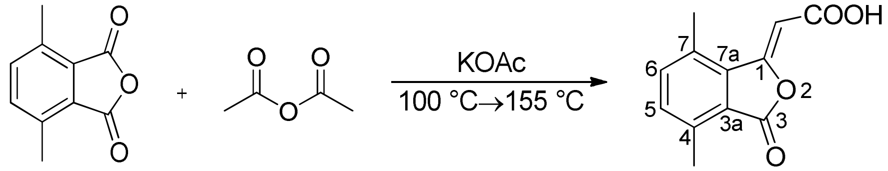


7 **8** (29%)

A mixture of 3,6-dimethylphthalic anhydride (**7**) (3.51 g, 19.9 mmol), freshly fused sodium propionate (3.07 g, 32.0 mmol) and propanoic anhydride (15 mL) was heated at 105 °C for 1 h and further 19.5 h at 185 °C whereas the reaction mixture turned orange-brown and a solid formed. After cooling to rt water (35 mL) and conc. HCl (8 mL) were added. The solid dissolved and two phases separated. After separation of the layers, the aqueous phase was extracted with CH_2Cl_2 (3x25 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated. Column chromatography of the oily residue over silica gel (pentane/EtOAc 100:1-40:1-35:1-30:1) afforded the dione **8** as a colourless solid (1.08 g, 29%).

mp. 88-91 °C
R$_f$ 0.37 (pentane/EtOAc 20:1)
FT-IR (ATR): $\tilde{\nu}$ = 3030 (w, ν(C-H$_{arom}$)), 2979 (w, ν(C-H)), 2936 (w, ν(C-H)), 2876 (w, ν(C-H)), 1729 (m, ν(C=O)), 1689 (vs, ν(C=O)), 1564 (m), 1492 (w, ν(C=C$_{arom}$)), 1451 (w), 1373 (m), 1340 (m), 1283 (m), 1229 (s), 1185 (m), 1077 (m), 1033 (w), 948 (m), 881 (w), 831 (m), 803 (w), 773 (w), 710 (w) cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (2H, s, 5/6-H), 2.99 (1H, q, $^3J_{2,Me}$ = 7.6 Hz, 2-H), 2.69 (6H, s, C*H*$_3$), 1.38 (3H, d, $^3J_{Me,2}$ = 7.6 Hz, CHC*H*$_3$) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.7 (C$_q$, *C*=O), 139.6 (C$_q$), 137.4 (C$_t$, C-5/6), 136.2 (C$_q$), 49.6 (C$_t$, C-2), 18.6 (C$_p$, *C*H$_3$), 10.7 (C$_p$, CH*C*H$_3$) ppm.
MS (EI, 70 eV): m/z = 188 (M$^+$, 100%), 173 (M$^+$-Me, 7), 159 (67), 145 (M$^+$-Me-CO, 51), 132 (36), 117 (17), 104 (17), 91 (9), 77 (13), 63 (7), 51 (11).

Synthesis of 4,7-Dimethylindan-1,3-dione (9)[2]



7 36%

A mixture of 3,6-dimethylphthalic anhydride (10.3 g, 58.5 mmol), freshly fused KOAc (9.15 g, 93.2 mmol) and Ac_2O (20mL) was heated at 100 °C for 1 h and after addition of further Ac_2O (13 ml) for 7 h at 155 °C whereas a dark brown solid formed. After cooling to rt water (50 mL) was added. The brown solid was filtered and washed well with water. The solid residue was extracted with 5% aqueous $NaHCO_3$ (1.3 L). Acidification of the extract with conc. HCl afforded 3,6-dimethylphthalidylideneacetic acid as a yellow solid which was filtered and dried over P_4O_{10} (4.62 g, 36%).

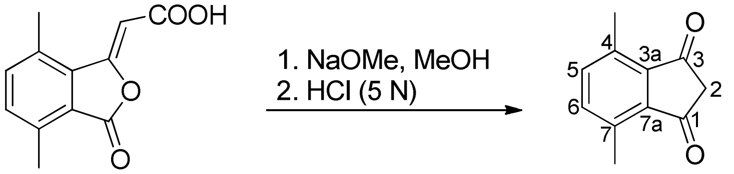
mp. 262-264 °C

FT-IR (ATR): $\tilde{\nu}$ = 3060 (w, ν(C-H_{arom})), 3032 (w, ν(C-H_{arom})), 2927 (w, ν(C-H)), 2731 (w), 2629 (w), 2588 (w), 2530 (w), 1788 (s, ν(C=O)), 1701 (s, ν(C=O)), 1670 (w), 1639 (vs, ν(C=C)), 1504 (m, ν(C=C_{arom})), 1423 (m), 1381 (m), 1348 (w), 1321 (m), 1269 (m), 1223 (s), 1176 (s), 1144 (m), 1039 (w), 985 (vs), 957 (s), 908 (s), 831 (s), 793 (m), 715 (m), 673 (m) cm^{-1}.

^{1}H NMR (400 MHz, DMSO): δ = 12.6 (1H, br.s, COO*H*), 7.61 (1H, d, $^3J_{6,5}$ = 7.7 Hz, 6-H or 5-H), 7.48 (1H, d, $^3J_{5,6}$ = 7.8 Hz, 5-H or 6-H), 5.88 (1H, s, C*H*COOH), 2.59 (3H, s, CH_3), 2.53 (3H, s, CH_3) ppm.

^{13}C NMR (100 MHz, DMSO): δ = 165.8 (C_q), 164.5 (C_q), 153.5 (C_q), 137.4 (C_t, C-6), 137.0 (C_q, C-4), 135.8 (C_q, C-7a), 133.8 (C_t, C-5), 132.6 (C_q, C-7), 122.1 (C_q, C-3a), 99.9 (C_t, *C*HCOOH), 19.5 (C_p, C(7)CH_3), 16.5 (C_p, C(4)CH_3) ppm.

MS (EI, 70 eV): m/z = 219 (M^+, 16%), 200 (M^+-H_3O^+, 100), 172 (41), 144 (13), 115 (20), 103 (8), 91 (8).

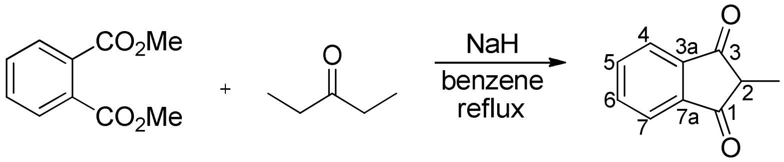


9 (73%)

NaOMe (8.22 g Na in 100 mL MeOH) was added to a solution of 3,6-dimethylphthalidylideneacetic acid (7.83 g, 35.9 mmol) in MeOH (240 mL) under vigorous stirring. The reaction mixture was agitated for 2 h at rt and further 5 h at 102 °C. After cooling to rt the red suspension was filtered. Decarboxylation was accomplished by adding the obtained yellow solid to hot (80 °C) 5 N HCl (125 mL). After 30 min the resulting solid was filtered and dried over P_4O_{10} to obtain the dion **9** (4.52 g, 73%).

mp. 186-187 °C
R$_f$ 0.45 (CyH/EtOAc 4:1)
FT-IR (ATR): $\tilde{\nu}$ = 2995 (w, ν(C-H)), 2956 (w, ν(C-H)), 2924 (w, ν(C-H)), 1726 (m, ν(C=O)), 1691 (s, ν(C=O)), 1604 (w), 1574 (w), 1560 (w), 1495 (w), 1435 (w), 1377 (m), 1336 (m), 1238 (m), 1190 (m), 1159 (m), 1130 (w), 1038 (w), 924 (w), 841 (m), 644 (w), 613 (m) cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (2H, s, 5/6-H), 3.19 (2H, s, 2-H), 2.69 (6H, s, C*H*$_3$) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.1 (C_q, *C*=O), 141.0 (C_q, C-3a/7a), 137.3 (C_t, C-5/6), 136.2 (C_q, C-4/7), 46.2 (C_s, C-2), 18.6 (C_p, *C*H$_3$) ppm.
MS (EI, 70 eV): m/z = 174 (M^+, 100%), 146 (M^+-CO, 62), 131 (M^+-CO-CH_3 16), 117 (49), 103 (23), 91 (13), 77 (17).

Synthesis of 2-Methyl-1*H*-indene-1,3(2*H*)-dione (10)[3]



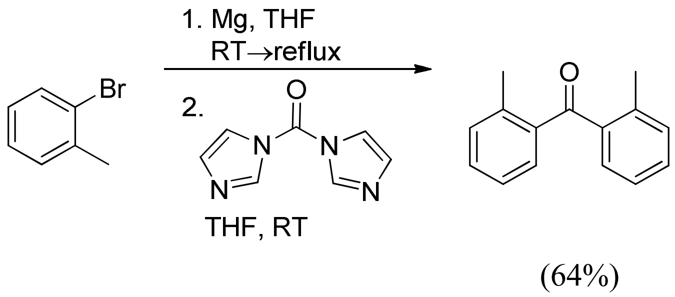
10 (50%)

Under a flow of Ar NaH (5.00 g, 60% suspension in mineral oil, 125 mmol) was suspended in anhydrous benzene. 3-Pentanone (8.87 g, 103 mmol) and diethyl phthalate (20.0 g, 103 mmol) were added dropwise. The reaction mixture was stirred for 1 h at rt and refluxed for 3 d. After cooling the solid was filtered, washed with benzene and dried in vacuo. The solid was dissolved in water (500 mL) and the solution was acidified with conc. HCl to obtain a yellow oil from which **10** crystallized as a yellow solid. The solid was filtered and dried in vacuo (8.23 g, 50%).

mp. 79-81 °C
R$_f$ 0.26 (CyH/Et_2O 4:1)
FT-IR (ATR): $\tilde{\nu}$ = 3070 (w, ν(C-H$_{arom}$)), 2975 (w, ν(C-H)), 2931 (w, ν(C-H)), 2875 (w, ν(C-H)), 1740 (s, ν(C=O)), 1698 (vs, ν(C=O)), 1589 (s, ν(C=C$_{arom}$)), 1449 (m), 1369 (m), 1350 (m), 1326 (m), 1286 (s), 1230 (s), 1174 (m), 1154 (m), 1124 (m), 1083 (m), 1041 (w), 1008 (w), 975 (w), 931 (s), 799 (m), 739 (vs), 687 (m), 609 (w) cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98-7.96 (2H, m, 4/7-H), 7.87-7.82 (2H, m, 5/6-H), 3.04 (1H, q, $^3J_{2,Me}$ = 7.7 Hz, 2-H), 1.41 (3H, d, $^3J_{Me,2}$ = 7.7 Hz, C*H*$_3$) ppm.

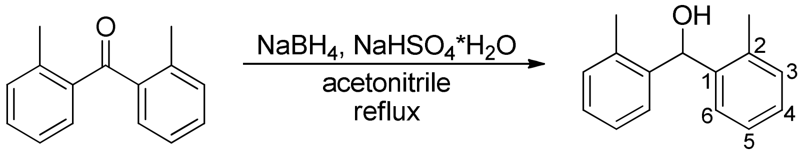
^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.2 (C_q, *C*=O), 142.1 (C_q, C-3a/7a), 135.8 (C_t, C-5/6), 123.4 (C_t, C-4/7), 48.9 (C_t, C-2), 10.6 (C_p, *C*H_3) ppm.
MS (EI, 70 eV): m/z = 160 (M^+, 100%), 131 (22), 104 (78), 76 (34), 50 (17).

Synthesis of Bis(2-methylphenyl)methanol (12)[4]



The Grignard reagent, freshly prepared from *o*-bromotoluene (51.5 g, 301 mmol) and Mg (7.32 g, 301 mmol) in THF (110 mL), was added dropwise under a flow of Ar to a suspension of 1,1′-carbonyldiimidazole (18.2 g, 112 mmol) in THF (500 mL). After stirring for 3.5 h at rt the resulting mixture was quenched with aq NH_4Cl. After addition of water (100 mL) and EtOAc (300 mL) and separation of the layers the aqueous phase was extracted with EtOAc. The combined organic extracts were washed with water (150 mL) and dried over Na_2SO_4. Evaporation of the solvent and column chromatography of the oily residue over silica gel (P/Et_2O 20:1 and P/Et_2O 40:1) afforded bis(2-methylphenyl)methanone as a colourless solid (15.1 g, 64%).

mp. 69-70 °C
R_f 0.45 (pentane/Et_2O 40:1)
FT-IR (ATR) **:** $\tilde{\nu}$ = 3065 (w, ν(C-H_{arom})), 3019 (w, ν(C-H)), 2961 (m, ν(C-H)), 2924 (w, ν(C-H)), 2854 (w, ν(C-H)), 1695 (w), 1652 (s, ν(C=O)), 1621 (w), 1597 (w), 1570 (m), 1484 (m, ν(C=C_{arom})), 1449 (m, δ(CH_3)), 1428 (m, δ(CH_3)), 1378 (w), 1300 (m), 1285 (m), 1254 (vs), 1200 (m), 1159 (w), 1124 (w), 1100 (w), 1033 (m), 991 (w), 956 (w), 923 (vs), 876 (m), 808 (m), 770 (s), 736 (vs), 692 (m), 636 (s) cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41-7.37 (2H, m, C*H*), 7.32-7.27 (4H, m, C*H*), 7.22-7.18 (2H, m, C*H*), 2.44 (6H, s, C*H*$_3$) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.9 (C_q, *C*=O), 139.2 (C_q), 138.3 (C_q), 131.6 (C_t, *C*H), 131.2 (C_t, *C*H), 130.4 (C_t, *C*H), 125.6 (C_t, *C*H), 20.8 (C_p, *C*H_3).

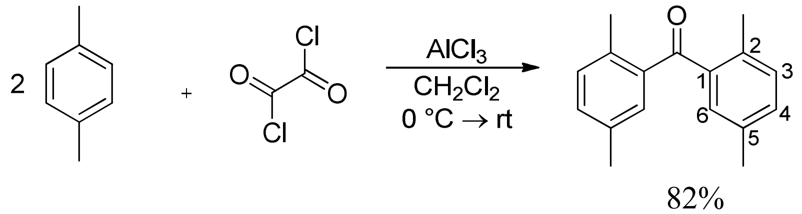


11 (96%)

To a solution of bis(2-methylphenyl)methanone (15.0 g, 71.3 mmol) in acetonitrile (200 mL) $NaHSO_4*H_2O$ (6.89 g, 49.9 mmol) and $NaBH_4$ (8.10 g, 214 mmol) were added. The reaction mixture was heated to reflux for 26 h. After addition of water (350 mL) and CH_2Cl_2 (500 mL) the layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2x200 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated. The solid residue was recrystallized from CH_2Cl_2 to obtain **11** as colourless crystals (14.5 g, 96%).

mp. 119-121 °C (from CH_2Cl_2)
R$_f$ 0.32 (CyH/Et_2O 4:1)
FT-IR (ATR): $\tilde{\nu}$ = 3168 (m, ν(O-H)), 3063 (w, ν(C-H$_{arom}$)), 3016 (w, ν(C-H$_{arom}$)), 2967 (w, ν(C-H)), 2939 (w, ν(C-H)), 2904 (w, ν(C-H)), 2854 (w, ν(C-H)), 1603 (w), 1483 (w, ν(C=C)), 1457 (m, δ(CH_3)), 1378 (w), 1343 (w), 1299 (w), 1281 (w), 1257 (m), 1221 (w), 1205 (w), 1174 (m), 1153 (w), 1112 (w), 1101 (m), 1033 (s), 1019 (s), 970 (w), 949 (w), 873 (m), 829 (w), 800 (m), 748 (vs), 724 (vs), 645 (m), 629 (m), 612 (s) cm^{-1}.
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.31-7.27 (2H, m, 6-H), 7.23-7.16 (6H, m, 3/4/5-H), 6.16 (1H, s, C*H*OH), 2.29 (6H, s, C*H*$_3$), 1.91 (1H, br.s, O*H*) ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 141.1 (C$_q$), 138.2 (C$_q$), 132.8 (C$_t$, *C*H), 130.0 (C$_t$, *C*H), 128.8 (C$_t$, C-6), 128.4 (C$_t$, *C*H), 72.6 (C$_t$, *C*HOH), 21.4 (C$_p$, *C*H$_3$) ppm.
MS (EI, 70 eV): m/z = 212 (M^+, 16%), 194 (M^+-H_2O, 19), 179 (M^+-Me-H_2O, 40), 165 (10), 149 (12), 119 ($C_6H_4(CH_3)C(H)O^+$, 100), 105 (42), 91 (55), 77 (17), 65 (20).

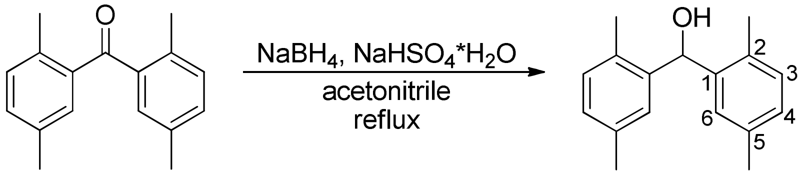
Synthesis of Bis(2,5-dimethylphenyl)methanol (12)[5]



82%

Under a flow of Ar oxalyl chloride (15.6 g, 125 mmol) was added dropwise to a solution of freshly distilled anhydrous *p*-xylene (10.6 g, 99.8 mmol) in CH_2Cl_2 (500 mL) at 0 °C. After portionwise addition of $AlCl_3$ (13.3 g, 100 mmol) the reaction mixture was warmed to rt and agitated for 1 h, during which time dissolution of the solid and gas evolution were observed. A second equivalent of *p*-xylene (10.6 g, 99.8 mmol) was added and the reaction mixture was stirred for further 42 h. After cooling to 0 °C water (290 mL) was added carefully and the resulting two phases were separated. The aqueous phase was extracted with CH_2Cl_2 (3x70 mL) and the combined organic layers were dried over Na_2SO_4. Evaporation of the solvent and column chromatography of the residue over silica gel (petroleum ether/EtOAc 20:1) afforded bis(2,5-dimethylphenyl)methanol as a colourless oil (19.5 g, 82%).

R_f 0.45 (petroleum ether/EtOAc 20:1)
FT-IR (ATR) **:** $\tilde{\nu}$ = 3017 (w, ν(C-H_{arom})), 2967 (w, ν(C-H)), 2923 (m, ν(C-H)), 2867 (w, ν(C-H)), 1839 (w), 1735 (w), 1661 (vs, ν(C=O)), 1608 (w), 1567 (w), 1495 (m, ν(C=C_{arom})), 1447 (m, δ(CH_3)), 1383 (w), 1301 (s), 1261 (s), 1203 (w), 1175 (m), 1097 (w), 1037 (w), 1003 (w), 957 (m), 892 (w), 814 (vs, δ(=C-H)), 792 (s), 748 (w), 659 (m) cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21-7.14 (4H, m, 3-H/4-H), 7.11 (2H, s, 6-H), 2.37 (6H, s, C*H*$_3$), 2.29 (6H, s, C*H*$_3$) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.3 (C_q, *C*=O), 139.2 (C_q), 135.1 (C_q), 135.0 (C_q), 131.9 (C_t, *C*H), 131.4 (C_t, *C*H), 130.7 (C_t, C-6), 20.9 (C_p, *C*H$_3$), 20.2 (C_p, *C*H$_3$) ppm.
MS (EI, 70 eV): m/z = 238 (M^+, 14%), 223 (M^+-Me, 100), 208 (M^+-2Me, 21), 178 (M^+-4Me, 5), 165 (5), 133 (19), 105 (20), 77 (17).



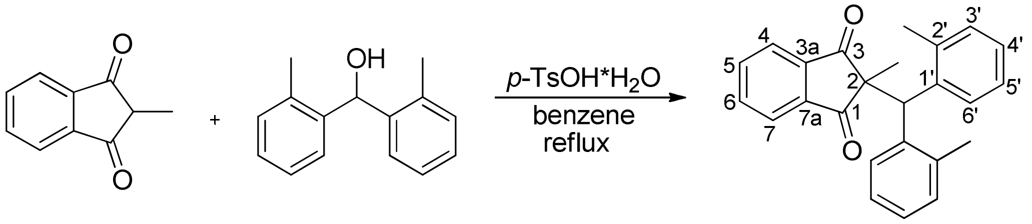
12 (95%)

To a solution of bis(2,5-dimethylphenyl)methanol (18.1 g, 75.8 mmol) in acetonitrile (230 mL) $NaHSO_4*H_2O$ (7.33 g, 53.1 mmol) and $NaBH_4$ (8.61 g, 228 mmol) were added. The reaction mixture was heated to reflux for 20 h. After addition of water (230 mL) and CH_2Cl_2 (200 mL) the layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3x50 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated. The solid residue was recrystallized from CH_2Cl_2 to obtain **12** as colourless crystals (17.3 g, 95%).

mp. 147-148 °C (from CH_2Cl_2)
R_f 0.30 (CyH/Et_2O 3:1)
FT-IR (ATR): $\tilde{\nu}$ = 3295 (m, ν(O-H)), 3017 (w, ν(C-H_{arom})), 2919 (m, ν(C-H)), 2862 (w, ν(C-H)), 2729 (w), 1613 (w), 1497 (m, ν(C=C)), 1444 (m, δ(CH_3)), 1336 (w), 1294 (m), 1242 (m), 1201 (w), 1151 (m), 1112 (m), 1013 (s), 942 (w), 893 (m), 798 (s, δ(=C-H)), 742 (w), 658 (w), 627 (m) cm^{-1}.
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.11 (2H, s, 6-H), 7.06-7.00 (4H, m, 3-H/4-H), 6.09 (1H, s, C*H*OH), 2.29 (6H, s, C(5)C*H*$_3$), 2.24 (6H, s, C(2)*C*H$_3$), 1.86 (1H, br.s, O*H*) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 140.8 (C_q, C-2), 135.6 (C_q, C-5), 132.7 (C_q, C-1), 130.5 (C_t, C-3), 128.3 (C_t, C-4), 127.2 (C_t, C-6), 70.4 (C_t, *C*HOH), 21.3 (C_p, C(5)*C*H_3), 18.8 (C_p, C(2)*C*H_3) ppm.
MS (EI, 70 eV): m/z = 240.2 (M^+, 32%), 225.1 (M^+-Me, 18), 207.1 (M^+-Me-H_2O, 66), 192.1 (16), 178.1 (6), 133.1 ($C_6H_3(CH_3)_2C(H)O^+$, 100), 119.1 (31), 106.1 (45), 91.1 (44), 77.1 (16), 65.1 (6).

Synthesis of 2-(Bis(2-methylphenyl)methyl)-2-methyl-1*H*-indene-1,3(2*H*)-dione (13a)



10 **11** **13a** (90%)

A solution of dione **10** (6.50 g, 40.6 mmol), alcohol **11** (10.3 g, 48.5 mmol) and *p*-toluenesulfonic acid monohydrate (926 mg, 4.86 mmol) in anhydrous benzene (140 mL) was heated under reflux (bath temperature: 110 °C) for 17 h while the water which formed during the reaction was removed through a water separator. The solvent was removed by distillation and the residue was dissolved in $CHCl_3$ (100 mL). The solution was extracted with 5% aqueous Na_2CO_3 (2x50 mL) and the organic layer was dried over Na_2SO_4. Evaporation of the solvent and recrystallation of the residue from EtOH/H_2O afforded the dione **13a** as colourless needles (12.9 g, 90%).

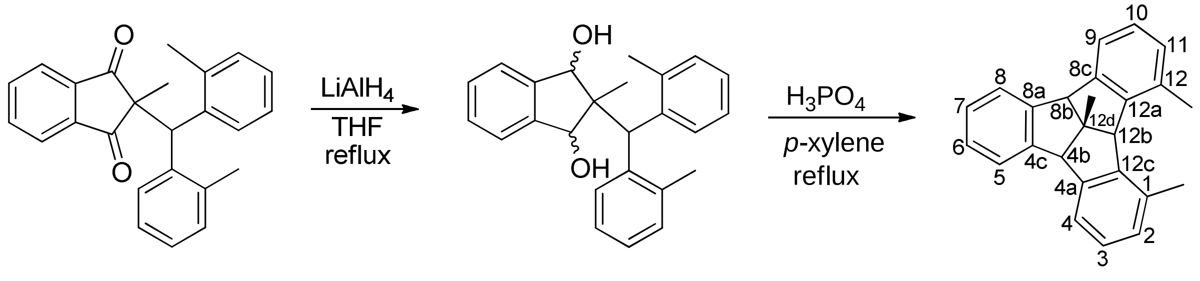
mp. 141-142 °C (from EtOH/H_2O)
R_f 0.38 (CyH/EtOAc 8:1)
EA: Found: C, 84.6; H, 6.3. Calc. for $C_{25}H_{22}O_2$: C, 84.7; H, 6.3%.
UV/Vis: λ_{max} (acetonitrile, lgε) = 303 (2.76), 249 (4.09) (sh), 225 (4.74), 196 (4.71) nm.
FT-IR (ATR): $\tilde{\nu}$ = 3063 (w, ν(C-H_{arom})), 3020 (w, ν(C-H_{arom})), 3000 (w, ν(C-H)), 2966 (w, ν(C-H)), 2932 (w, ν(C-H)), 2871 (w, ν(C-H)), 1735 (m, ν(C=O)), 1698 (s, ν(C=O)), 1596 (m, ν(C=C_{arom})), 1487 (m, ν(C=C_{arom})), 1450 (m, δ(CH_3)), 1376 (m), 1349 (w), 1330 (w), 1267 (m), 1243 (m), 1203 (w), 1179 (w), 1159 (w), 1144 (w), 1096 (w), 1051 (w), 1035 (w), 1014 (w), 979 (m), 954 (w), 904 (w), 871 (w), 815 (w), 788 (w), 761 (s), 748 (s), 719 (s), 700 (m), 682 (w), 668 (w), 657 (w), 644 (w), 619 (w), 607 (w) cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84-7.79 (2H, m, C*H*), 7.71-7.67 (2H, m, C*H*), 7.65 (2H, d, ^3J = 7.7 Hz, 6'-H), 7.04-6.94 (6H, m, 3'/4'/5'-H), 5.14 (1H, s, C*H*(PhMe)$_2$), 2.39 (6H, s, C(2')C*H*$_3$), 1.35 (3H, s, C(2)C*H*$_3$) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.4 (C_q, *C*=O), 141.7 (C_q, C-3a/7a), 138.2 (C_q), 136.4 (C_q), 135.5 (C_t, *C*H), 130.9 (C_t, *C*H'), 130.3 (C_t, C-6'), 126.7 (C_t, *C*H'), 125.9 (C_t, *C*H'), 123.1 (C_t, *C*H), 58.4 (C_q, C-2), 47.8 (C_t, *C*H(PhMe)$_2$), 20.6 (C_p, C(2')*C*H$_3$), 19.7 (C_p, C(2)*C*H$_3$) ppm.

Accurate mass (ESI,+): Found: 377.15099. Calc. for $C_{25}H_{22}O_2$+Na^+: 377.15120.

MS (EI, 70 eV): m/z = 354 (M^+, 1%), 339 (M^+-Me, 1), 195 ($CH(C_6H_4CH_3)_2^+$, 100), 180 ($CH(C_6H_4CH_3)_2^+$-Me, 23), 165 ($CH(C_6H_4CH_3)_2^+$-2Me, 32) 152 (5), 141 (2), 128 (5), 115 (12), 104 (14), 91 (15), 77 (25), 65 (14), 51 (6).

Synthesis of 4b,8b,12b,12d-Tetrahydro-1,12,12d-trimethyldibenzo[2,3:4,5]pentaleno-[1,6-ab]indene (15a)



13a **14a** (93%) **15a** (16%)

Under a flow of Ar a solution of dione **13a** (12.6 g, 35.5 mmol) in anhydrous THF (100 mL) was added dropwise to a suspension of $LiAlH_4$ (4.72 g, 124 mmol) in anhydrous THF (150 mL). The reaction mixture was heated under reflux for 4 h The solvent was evaporated and the solid residue was taken up in Et_2O (400 mL). The mixture was carefully hydrolyzed with small pieces of ice and the organic layer was decanted from the resulting aluminium salts. The decantation process was repeated several times (700 mL). The organic layers were combined and the solvent was evaporated. Column chromatography of the solid residue over silica gel (CyH/EtOAc 8:1-1:1) afforded the diol **14a** as a colourless solid (11.8 g, 93%) which is a mixture of *all-cis*-**14a** and *cis,trans*-**14a** (^{1}H-NMR: 6:94) and could be used without further separation of the isomers.

The mixture of diol **14a** (11.7 g, 32.6 mmol), orthophosphoric acid (2 mL, 85%) and *p*-xylene (150 mL) was heated under reflux for 22 h while the water which formed during the reaction was removed through a water separator. The hot solution was filtered through a layer (2 cm) of K_2CO_3. Evaporation of the solvent and column chromatography of the residue over silica gel (pentane/CH_2Cl_2 50:1-40:1-10:1) was used to reduce impurities to a possible minimum. The orange solid was recrystallized from acetonitrile to obtain Me_3-TBTQ **15a** as slightly yellow crystals (1.23 g, 12%). The mother liquor was concentrated and the residue was further purified by MPLC (acetonitrile/H_2O 85:15) to afford a second part of **15a** (432 mg, 4%).

mp. 163-165 °C (from acetonitrile)

R$_f$ 0.35 (pentane/CH_2Cl_2 30:1)

EA: Found: C, 92.7; H, 7.9. Calc. for $C_{25}H_{22}$: C, 93.1; H, 6.9.

UV/Vis: λ_{max} (acetonitrile, lgε) = 275 (2.79), 268 (2.82), 227 (4.05) (sh), 200 (4.67) nm.

FT-IR (ATR): $\tilde{\nu}$ = 3064 (w, ν(C-H$_{arom}$)), 3024 (w, ν(C-H$_{arom}$)), 2973 (w, ν(C-H)), 2942 (w, ν(C-H)), 2915 (w, ν(C-H)), 2890 (w, ν(C-H)), 2859 (w, ν(C-H)), 2850 (w, ν(C-H)), 1583 (w), 1465 (m, ν(C=C$_{arom}$)), 1373 (w), 1321 (w), 1289 (w), 1257 (w), 1244 (w), 1226 (w), 1208 (w), 1179 (w), 1168 (w), 1150 (w), 1139 (w), 1081 (w), 1039 (w), 1028 (w), 979 (w), 960 (w), 945 (w), 901 (w), 876 (w), 855 (w), 835 (w), 809 (w), 793 (m), 765 (s), 748 (s), 734 (vs), 720 (s), 707 (m), 666 (w), 642 (w), 623 (w), 612 (w), 601 (w) cm^{-1}.

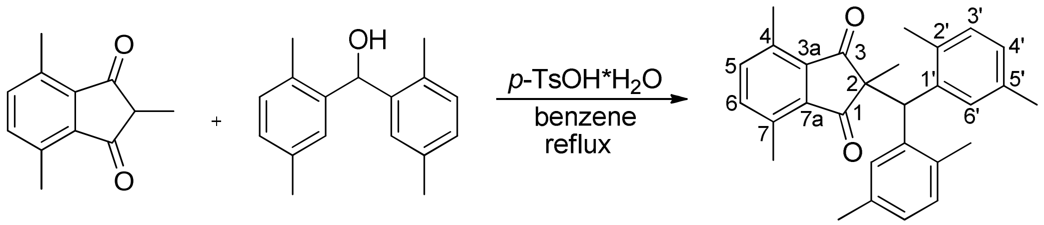
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50-7.46 (2H, m, C*H*), 7.28 (2H, d, ^3J = 7.3 Hz, 4/9-H), 7.22-7.19 (2H, m, C*H*), 7.11 (2H, dd, ^3J = 7.4 Hz, ^3J = 7.4 Hz, 3/10-H), 6.95 (2H, d, ^3J = 7.4 Hz, 2/11-H), 4.58 (1H, s, 12b-H), 4.33 (2H, s, 4b/8b-H), 2.48 (6H, s, CH_3), 1.62 (3H, s, C(12d)CH_3) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.9 (C_q, C-4a/8c), 145.6 (C_q, C-4c/8a), 143.2 (C_q, C-12a/12c), 135.2 (C_q, C-1/12), 129.2 (C_t, C-2/11), 127.9 (C_t, C-3/10), 127.5 (C_t, *C*H), 124.4 (C_t, *C*H), 122.2 (C_t, C-4/9), 63.2 (C_t, C-4b/8b), 62.8 (C_t, C-12b), 60.3 (C_q, C-12d), 27.7 (C_p, C(12d)*C*H_3), 22.2 (C_p, *C*H_3) ppm.

Accurate mass (ESI, +): Found: 323.17954. Calc. for $C_{25}H_{22}+H^+$: 323.17943.

MS (EI, 70 eV): m/z = 322 (M^+, 100%), 307 (M^+-Me, 44), 292 (M^+-2Me, 100), 276 (5), 265 (5), 245 (5), 231 (12), 215 (11), 206 (7), 192 (14), 178 (9), 146 (6), 138 (5), 129 (4), 105 (4), 91 (4).

Synthesis of 2-(Bis(2,5-dimethylphenyl)methyl)-2,4,7-trimethyl-1*H*-indene-1,3(2*H*)-dione (13b)

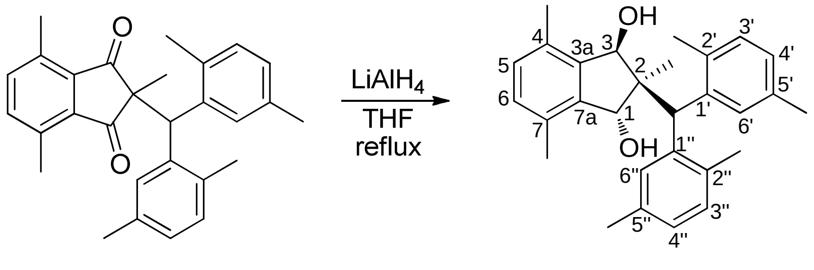


8 **12** **13b** (86%)

A solution of dione **8** (1.00 g, 5.31 mmol), alcohol **12** (1.92 g, 7.99 mmol) and *p*-toluenesulfonic acid monohydrate (161 mg, 846 μmol) in anhydrous benzene (50 mL) was heated under reflux (bath temperature: 110 °C) for 17 h in a soxhlet apparatus filled with molecular sieve (4 Å). The solvent was removed by distillation The resulting yellow solid was dissolved in $CHCl_3$ (35 mL) and the solution was extracted with 5% aqueous Na_2CO_3 (2x80 mL). The organic layer was dried over Na_2SO_4. Evaporation of the solvent and column chromatography of the residue over silica gel (CyH/Et_2O 30:1) afforded the dione **13b** as a colourless solid (1.87 g, 86%).

mp. 169-171 °C
R$_f$ 0.40 (CyH/Et_2O 10:1)
EA: Found: C, 84.8; H, 7.5. Calc. for $C_{29}H_{30}O_2$: C, 84.8; H, 7.4%
UV/Vis: λ_{max} (acetonitrile, lgε) = 323 (3.36), 278 (3.43) (sh), 257 (3.92) (sh), 231 (4.56), 204 (4.59) (sh), 194 (4.67) nm.
FT-IR (ATR): $\tilde{\nu}$ = 2964 (w, ν(C-H)), 2924 (w, ν(C-H)), 2867 (w, ν(C-H)), 2737 (w), 1725 (m, ν(C=O)), 1687 (s, ν(C=O)), 1612 (w), 1568 (w), 1498 (m, ν(C=C_{arom})), 1446 (m, δ(CH_3)), 1376 (m), 1337 (m), 1259 (m), 1193 (w), 1157 (w), 1080 (m), 1034 (m), 968 (m), 893 (w), 798 (s, δ(=C-H)), 726 (w) cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (2H, s, 6'-H), 7.21 (2H, s, 5/6-H), 6.82 (2H, d, $^3J_{3',4'}$ = 7.7 Hz, 3'-H), 6.73 (2H, d, $^3J_{4',3'}$ = 7.7 Hz, 4'-H), 4.97 (1H, s, C*H*(PhMe$_2$)$_2$), 2.60 (6H, s, C(4/7)C*H*$_3$), 2.28 (6H, s, C(2')C*H*$_3$), 2.24 (6H, s, C(5')C*H*$_3$), 1.32 (3H, s, C(2)C*H*$_3$) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.0 (C_q, *C*=O), 139.7 (C_q, C-3a/7a), 138.2 (C_q, C-1'), 136.6 (C_t, C-5/6), 135.3 (C_q, C-4/7), 135.1 (C_q, C-5'), 133.2 (C_q, C-2'), 130.8 (C_t, C-6'), 130.6 (C_t, C-3'), 127.2 (C_t, C-4'), 58.9 (C_q, C-2), 48.5 (C_t, *C*H(PhMe$_2$)$_2$), 21.4 (C_p, C(5')*C*H$_3$), 20.0 (C_p, C(2')*C*H$_3$), 18.8 (C_p, C(2)*C*H$_3$), 18.6 (C_p, C(4/7)*C*H$_3$) ppm.
Accurate mass (ESI,+): Found: 433.21383. Calc. for $C_{29}H_{30}O_2$+Na^+: 433.21380.
MS (EI, 70 eV): m/z = 410 (M^+, 1%), 395 (M^+-Me, 1), 223 ($CH(C_6H_3(CH_3)_2)_2^+$, 100), 208 ($CH(C_6H_3(CH_3)_2)_2^+$-Me, 7), 193 ($CH(C_6H_3(CH_3)_2)_2^+$-2Me, 15), 178 (5), 152 (4), 115 (4), 91 (3), 77 (3).

Synthesis of 2-(Bis(2,5-dimethylphenyl)methyl)-2,4,7-trimethyl-2,3-dihydro-1*H*-indene-1,3-diol (14b)

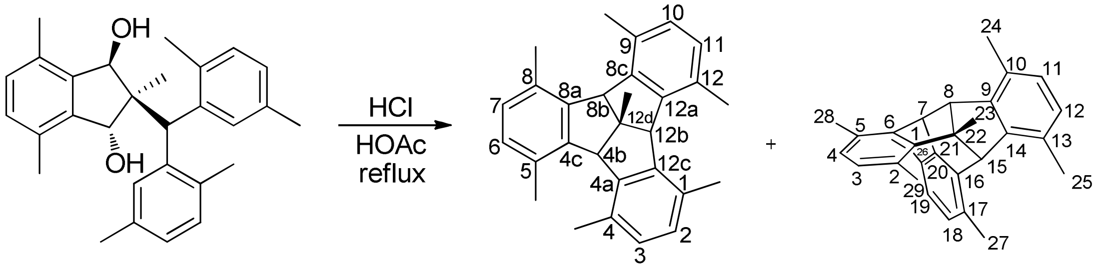


13b *rac*-**14b** (98%)

Under a flow of Ar a solution of dione **13b** (1.78 g, 4.33 mmol) in anhydrous THF (8 mL) was added dropwise to a suspension of $LiAlH_4$ (175 mg, 4.61 mmol) in anhydrous THF (5 mL). The reaction mixture was heated under reflux for 2.5 h The solvent was evaporated almost to dryness and the solid residue was taken up in Et_2O (20 mL). The mixture was carefully hydrolyzed with small pieces of ice and the organic layer was decanted from the resulting aluminium salts. The decantation process was repeated several times (5x20 mL). The organic layers were combined and the solvent was evaporated to obtain the diol **14b** as a colourless solid (1.74 g, 98 %), which may be used without further purification.

mp. 164-166 °C
R$_f$ 0.65 (CyH/EtOAc 2:1)
EA: Found: C, 83.8; H, 8.4. Calc. for $C_{29}H_{34}O_2$: C, 84.0; H, 8.3%
UV/Vis: λ_{max} (acetonitrile, lgε) = 278 (2.54), 270 (2.55), 223 (3.73) (sh), 203 (4.22) nm.
FT-IR (ATR): $\tilde{\nu}$ = 3551 (m, ν(O-H)), 3023 (w, ν(C-H$_{arom}$)), 2946 (w, ν(C-H)), 2921 (w, ν(C-H)), 2893 (w, ν(C-H)), 2862 (w, ν(C-H)), 1610 (w, ν(C=C)), 1495 (m, ν(C=C)), 1455 (m, δ(CH_3)), 1415 (w), 1382 (m), 1286 (w), 1261 (m), 1223 (m), 1189 (m), 1163 (m), 1132 (m), 1099 (m), 1086 (m), 1070 (m), 1047 (s), 1033 (s), 957 (w), 941 (w), 893 (w), 820 (s, δ(=C-H)), 806 (s, δ(=C-H)), 740 (m), 672 (m), 649 (m), 629 (m) cm^{-1}.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.86 (1H, s, 6’’-H), 7.16 (1H, s, 6’-H), 7.13 (1H, d, $^3J_{3',4'}$ = 7.8 Hz, 3’-H), 7.04 (1H, d, $^3J_{3'',4''}$ = 7.7 Hz, 3’’-H), 7.01-6.97 (3H, m, 4’’/5/6-H), 6.94 (1H, d, $^3J_{4',3'}$ = 7.7 Hz, 4’-H), 5.80 (1H, d, $^3J_{1,OH}$ = 4.0 Hz, 1-H), 5.16 (1H, s, C*H*(PhMe$_2$)$_2$), 5.06 (1H, s, 3-H), 2.69 (3H, s, C(2’)C*H*$_3$), 2,46 (3H, s, C(5’’)C*H*$_3$), 2.34 (3H, s, C(7)C*H*$_3$), 2.29 (3H, s, C(4)C*H*$_3$), 2.27 (3H, s, C(2’’)C*H*$_3$), 2.25 (3H, s, C(5’)C*H*$_3$), 1.58 (1H, d, $^3J_{OH,3}$ = 2.9 Hz, C(3)O*H*), 1.26 (3H, s, C(2)C*H*$_3$), 0.95 (1H, d, $^3J_{OH,1}$ = 4.3 Hz, C(1)O*H*) ppm.
^{13}C NMR (150 MHz, $CDCl_3$): δ = 142.1 (C$_q$, C-1’’), 141.2 (C$_q$, C-7a), 139.3 (C$_q$, C-3a), 138.7 (C$_q$, C-1’), 135.5 (C$_q$, C-5’’), 135.3 (C$_q$, C-5’), 134.3 (C$_q$, C-2’’), 133.7 (C$_q$, C-7), 133.0 (C$_t$, C-6’), 132.5 (C$_q$, C-4), 132.2 (C$_q$, C-2’), 131.5 (C$_t$, C-3’’), 131.5 (C$_t$, C-6), 131.4 (C$_t$, C-3’), 129.4 (C$_t$, C-5), 128.5 (C$_t$, C-6’’), 127.6 (C$_t$, C-4’), 127.4 (C$_t$, C-4’’), 84.4 (C$_t$, C-1), 79.9 (C$_t$, C-3), 55.6 (C$_q$, C-2), 45.8 (C$_t$, *C*H(PhMe$_2$)$_2$), 21.9 (C$_p$, C(5’’)*C*H$_3$), 21.5 (C$_p$, C(5’)*C*H$_3$), 20.7 (C$_p$, C(2’’)*C*H$_3$), 20.3 (C$_p$, C(2’)*C*H$_3$), 18.3 (C$_p$, C(7)*C*H$_3$), 17.7 (C$_p$, C(2)*C*H$_3$), 17.5 (C$_p$, C(4)*C*H$_3$) ppm.
Accurate Mass (ESI, +): Found: 437.24510. Calc. for $C_{29}H_{34}O_2+Na^+$: 437.24510.
MS (EI, 70 eV): m/z = 396 (M^+-H_2O, <1%), 378 (M^+-2H_2O, 1), 363 (M^+-2H_2O-Me, 1), 290 (4), 223 ($CH(C_6H_3(CH_3)_2)_2^+$, 100), 209 ($CH(C_6H_3(CH_3)_2)_2^+$-Me, 10), 193 ($CH(C_6H_3(CH_3)_2)_2^+$-2Me, 13), 173 (7), 118 (8), 91 (5), 77 (3).

Synthesis of 4b,8b,12b,12d-Tetrahydro-1,4,5,8,9,12,12d-heptamethyldibenzo[2,3:4,5]-pentaleno[1,6-ab]indene (15b)



***rac*-14b** **15b** (1%) **16** (36%)

To boiling acetic acid (195 mL) was added diol **14b** (2.80 g, 6.75 mmol) and conc. HCl (7 mL). After agitating for 5.5 h the reaction mixture was quenched with water (250 mL) to precipitate a light brown solid which was filtered. The solid was taken up in CH_2Cl_2 (100 mL), the organic layer was extracted with water (2x25 mL) and the combined aqueous layers were extracted with CH_2Cl_2 (25 mL). The CH_2Cl_2 phases were combined and the solvent was evaporated. Column chromatography of the residue over silica gel (pentane/CH_2Cl_2 10:1) afforded a mixture of Me_7-TBTQ **15b**, the rearrangement product **16** and traces of impurities which were separated by semi-preparative HPLC (MeOH R_t(**16**)=7.5 min, R_t(**15b**)=10.0 min; acetonitrile/H_2O 90:10 R_t(**15b**)=21.1 min) to obtain both Me_7-TBTQ **15b** (27.0 mg, 1%) and the rearrangement product **16** (915 mg, 36%) as colourless crystals.

Experimental data for 15b:
mp. 168-169 °C
R_f 0.31 (pentane/CH_2Cl_2 10:1)
EA:Found: C, 92.1; H, 7.8. Calc. for $C_{29}H_{30}$: C, 92.0; H, 8.0%
UV/Vis: λ_{max} (acetonitrile, lgε) = 274 (2.28), 226 (4.39) (sh), 205 (4.74) nm.
FT-IR (ATR): $\tilde{\nu}$ = 3033 (w, ν(C-H_{arom})), 3001 (w, ν(C-H)), 2937 (m, ν(C-H)), 2914 (m, ν(C-H)), 2893 (m, ν(C-H)), 2862 (m, ν(C-H)), 2829 (w, ν(C-H)), 2729 (w, ν(C-H)), 1728 (w), 1601 (w), 1487 (m, ν(C=C_{arom})), 1444 (s, δ(CH_2/CH_3)), 1375 (m, δ(CH_3)), 1277 (w), 1215 (w), 1171 (w), 1111 (w), 1059 (m), 1034 (m), 968 (w), 941 (w), 914 (w), 868 (w), 800 (s, δ(=C-H)$_{1,4\ subst.}$), 714 (w), 692 (w) cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.86 (6H, s, C*H*), 4.27 (3H, s, 4b/8b/12b-H), 2.38 (18H, s, C*H*$_3$), 1.44 (3H, s, C(12d)C*H*$_3$) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.6 (C_q), 131.8 (C_q, *C*C), 129.3 (C_t, *C*H), 61.1 (C_t, C-4b/8b/12b), 60.3 (C_q, C-12d), 26.1 (C_p, C(12d)*C*H$_3$), 20.8 (C_p, *C*H$_3$) ppm.
Accurate Mass (APCI,+): Found: 379.24150. Calc. for $C_{29}H_{30}$+H^+: 379.24203.
MS (EI, 70 eV): m/z = 378 (M^+, 38%), 363 (M^+-Me, 53), 348 (M^+-2Me, 6), 333 (M^+-3Me, 6), 318 (M^+-4Me, 4), 234 (40), 174 (3), 159 (4), 18 (100).

Experimental data for 16:

mp. 220-221 °C

R$_f$ 0.33 (pentane/CH_2Cl_2 10:1)

EA: Found: C, 91.9; H, 7.9. Calc. for $C_{29}H_{30}$: C, 92.0; H, 8.0%

UV/Vis (acetonitrile, lgε): λ_{max} = 276 (3.14) (sh), 251 (4.00) (sh), 208 (4.98) nm.

FT-IR (ATR): $\tilde{\nu}$ = 3030 (w, ν(C-H$_{arom}$)), 3006 (w, ν(C-H$_{arom}$)), 2956 (m, ν(C-H)), 2918 (m, ν(C-H)), 2864 (w, ν(C-H)), 1491 (m, ν(C=C$_{arom}$)), 1448 (m, δ(CH_2/CH_3)), 1375 (m, δ(CH_3)), 1282 (w), 1217 (w), 1163 (w), 1097 (w), 1028 (w), 939 (w), 897 (w), 860 (w), 798 (s, δ(=C-H)$_{1,4\ subst.}$), 760 (w), 737 (w), 675 (w) cm^{-1}.

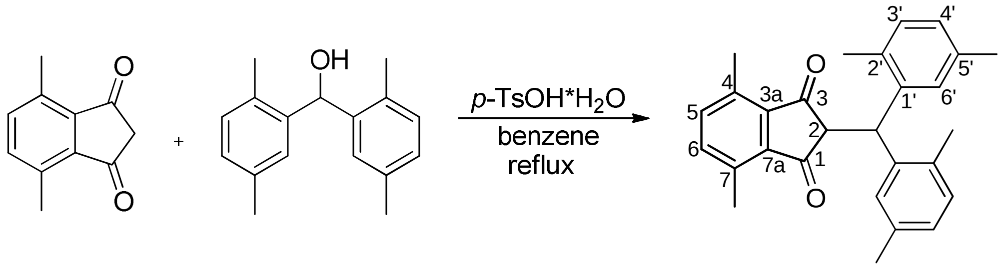
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.76 (1H, d, $^3J_{11,12}$ = 7.9 Hz, 11-H), 6.72 (3H, d, ^3J = 8.0 Hz, 3/4/12-H), 6.62 (1H, d, $^3J_{18,19}$ = 8.1 Hz, 18-H), 6.60 (1H, d, $^3J_{19,18}$ = 8.0 Hz, 19-H), 4.49 (1H, d, $^3J_{7,8}$ = 5.1 Hz, 7-H), 4.23 (1H, d, $^4J_{15,8}$ = 1.1 Hz, 15-H), 3.84 (1H, dd, $^3J_{8,7}$ = 5.2 Hz, $^4J_{8,15}$ = 1.1 Hz, 8-H), 2.35 (3H, s, 29-H), 2.33 (3H, s, 28-H), 2.31 (3H, s, 27-H), 2.29 (6H, s, 24/26-H), 2.28 (3H, s, 25-H), 1.49 (3H, s, 23-H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.4 (C$_q$, C-6/14), 141.9 (C$_q$, C-1), 140.0 (C$_q$, C-16), 138.1 (C$_q$, C-9/21), 132.2 (C$_q$, C-10), 131.9 (C$_q$, C-2), 130.9 (C$_q$, C-20), 130.3 (C$_q$, C-17), 129.2 (C$_t$, C-3), 129.0 (C$_q$, C-13), 128.3 (C$_t$, C-4 or C-12), 128.3 (C$_t$, C-4 or C-12), 128.0 (C$_q$, C-5), 127.9 (C$_t$, C-19), 127.8 (C$_t$, C-18), 127.2 (C$_t$, C-11), 64.3 (C$_t$, C-8), 62.7 (C$_q$, C-22), 50.2 (C$_t$, C-15), 44.0 (C$_t$, C-7), 22.6 (C$_p$, C-23), 20.1 (C-29), 20.0 (C$_p$, C-25), 20.0 (C$_p$, C-28), 19.4 (C$_p$, C-26), 19.3 (C$_p$, C-27), 18.6 (C$_p$, C-24) ppm.

Accurate Mass (APCI,+): Found: 379.24200. Calc. for $C_{29}H_{30}+H^+$: 379.24203.

MS (EI, 70 eV): m/z = 378 (M^+, 43%), 363 (M^+-Me, 100), 348 (M^+-2Me, 31), 333 (M^+-3Me, 22), 318 (M^+-4Me, 15), 303 (M^+-5Me 8), 257 (6), 234 (56), 219 (15), 206 (8), 191 (6), 159 (5), 141 (8), 128 (10), 119 (6).

Synthesis of 2-(Bis(2,5-dimethylphenyl)methyl)-4,7-dimethyl-1*H*-indene-1,3(2*H*)-dione (13c)

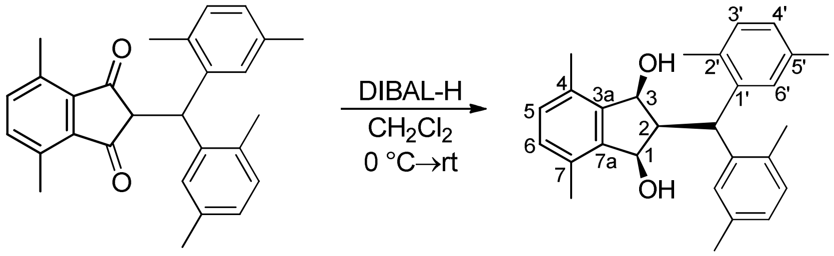


9 **12** **13c** (94%)

A solution of dione **9** (450 mg, 2.58 mmol), alcohol **12** (745 mg, 3.10 mmol) and *p*-toluenesulfonic acid monohydrate (66.0 mg, 347 µmol) in anhydrous benzene (60 mL) was heated under reflux (bath temperature: 110 °C) for 5 d in a soxhlet apparatus filled with molecular sieve (4 Å). After the first and second day, respectively, an additional amount of alcohol (124 mg, 0.516 mmol and 62.0 mg, 0.258 mmol) and *p*-toluenesulfonic acid monohydrate (16.0 mg, 84.1 µmol and 9.00 mg, 47.3 µmol) was added. The solvent was removed by distillation The resulting orange solid was dissolved in $CHCl_3$ (30 mL) and the solution was extracted with 5% aqueous Na_2CO_3 (2x40 mL) and water (40 mL). The organic layer was dried over Na_2SO_4. Evaporation of the solvent and column chromatography of the residue over silica gel (CyH/EtOAc 20:1 and CyH/EtOAc 45:1) afforded the dione **13c** as a light yellow solid (963 mg, 94%).

mp. 159-160 °C
R_f 0.25 (CyH/EtOAc 45:1)
EA: Found: C, 84.6; H, 7.1. Calc. for $C_{28}H_{28}O_2$: C, 84.8; H, 7.1%
UV/Vis: λ_{max} (acetonitrile, lgε) = 321 (3.50), 255 (4.03) (sh), 231 (4.74), 197 (4.80) nm.
FT-IR (ATR): $\tilde{\nu}$ = 3017 (w, ν(C-H_{arom})), 2963 (w, ν(C-H)), 2924 (m, ν(C-H)), 2863 (w, ν(C-H)), 2729 (w ν(CH_3)), 1727 (m, ν(C=O)), 1695 (s, ν(C=O)), 1611 (w), 1564 (w), 1498 (m, ν(C=C_{arom})), 1450 (m), 1379 (m), 1339 (m), 1248 (s), 1198 (m), 1162 (w), 1141 (m), 1034 (w), 997 (w), 958 (w), 883 (w), 827 (m), 810 (s, δ(=C-H)$_{1,4\ subst.}$), 731 (m), 627 (m) cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (2H, s, 5/6-H), 7.27 (2H, s, 6'-H), 6.87 (2H, d, $^3J_{3',4'}$ = 7.7 Hz, 3'-H), 6.83 (2H, dd, $^3J_{4',3'}$ = 7.8 Hz, $^4J_{4',6'}$ = 1.4 Hz, 4'-H), 5.17 (1H, d, $^3J_{CH,2}$ = 2.9 Hz, C*H*($PhMe_2$)$_2$), 3.75 (1H, d, $^3J_{2,CH}$ = 2.8 Hz, 2-H), 2.58 (6H, s, C(4/7)CH_3), 2.25 (6H, s, C(5')CH_3), 2.12 (6H, s, C(2')CH_3) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.6 (C_q, *C*=O), 140.5 (C_q, C-3a/7a), 139.2 (C_q, C-1'), 137.0 (C_t, C-5/6), 135.6 (C_q, C-4/7), 135.1 (C_q, C-5'), 132.8 (C_q, C-2'), 130.5 (C_t, C-6'), 130.3 (C_t, C-3'), 127.3 (C_t, C-4'), 58.3 (C_t, C-2), 44.4 (C_t, *C*H($PhMe_2$)$_2$), 21.3 (C_p, C(5')*C*H_3), 19.4 (C_p, C(2')*C*H_3), 18.5 (C_p, C(4/7)*C*H_3) ppm.
Accurate mass (APCI,-): Found: 395.20151. Calc. for $C_{28}H_{28}O_2$-H^+: 395.20165.
MS (EI, 70 eV): m/z = 396 (M^+, 40%), 378 (M^+-H_2O, 12), 363 (M^+-H_2O-Me, 14), 223 ($CH(C_6H_3(CH_3)_2)_2^+$, 100), 207 (40), 193 ($CH(C_6H_3(CH_3)_2)_2^+$-2Me, 25), 178 (10), 165 (6), 115 (11), 77 (9).

Synthesis of 2-(Bis(2,5-dimethylphenyl)methyl)-4,7-dimethyl-2,3-dihydro-1*H*-indene-1,3-diol (14c)



13c **14c** (59%)

Under a flow of Ar a solution of dione **13c** (7.50 g, 18.9 mmol) in anhydrous CH_2Cl_2 (190 mL) was cooled to 0 °C. A solution of diisobutylaluminium hydride (52.3 mL, 52.3 mmol; 1.0 M in CH_2Cl_2) was added dropwise to the reaction mixture which was stirred at rt for 3 d. After addition of water (150 mL) the mixture was extracted with CH_2Cl_2 and the combined organic extracts were washed with water and dried over Na_2SO_4. After evaporation of the solvent a yellow solid was obtained, which was identified (NMR) as a 1:1.2 mixture of the desired diol and the single reduction product.

The solid was again dissolved in anhydrous CH_2Cl_2 and cooled to 0°C. Diisobutylaluminium hydride (30.7 mL, 30.7 mmol; 1.0 M in CH_2Cl_2) was added dropwise and the reaction mixture was stirred at rt for 7 d. After addition of water the layers were separated. The aqueous phase was extracted with CH_2Cl_2 and the combined organic extracts were washed with water and dried over Na_2SO_4. Evaporation of the solvent yielded a yellow solid which was recrystallized from EtOH/H_2O to obtain the colourless product **14c** (3.75 g, 50%). The filtrate was concentrated in vacuum and the residue was chromatographed over silica gel (CyH/Et_2O 5:1) to afford a second part of the diol **14c** (673 mg, 9%).

mp. 255-257 C (from EtOH/H_2O)

R_f 0.14 (CyH/Et_2O 5:1)

EA: Found: C, 84.05; H, 8.2. Calc. for $C_{28}H_{32}O_2$: C, 84.0; H, 8.05%

UV/Vis: λ_{max} (acetonitrile, lgε) = 278 (3.03), 270 (2.99), 222 (4.29) (sh), 200 (4.86) nm.

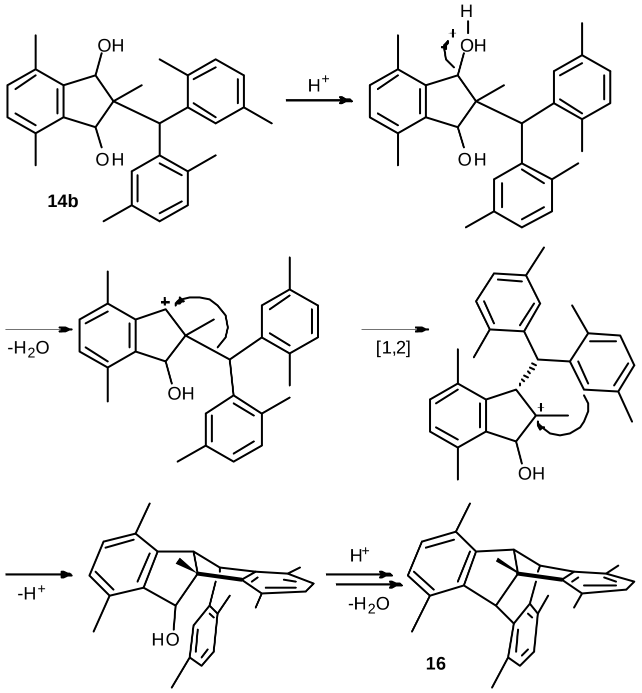
FT-IR (ATR): $\tilde{\nu}$ = 3426 (m, ν(O-H)), 3013 (m, ν(C-H_{arom})), 2922 (m, ν(C-H)), 2858 (m, ν(C-H)), 2725 (w), 1608 (w, ν(C=C_{arom})), 1499 (s, ν(C=C_{arom})), 1449 (m), 1380 (m), 1311 (w), 1281 (w), 1244 (w), 1204 (m), 1158 (m), 1097 (w), 1039 (m), 1002 (s), 927 (w), 890 (w), 812 (s, $\delta(=C\text{-}H)_{1,4\ subst.}$)), 735 s), 698 (m), 634 (m) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (2H, s, 6'-H), 7.06 (2H, d, $^3J_{3',4'}$ = 7.8 Hz, 3'-H), 7.04 (2H, s, 5/6-H), 6.93 (2H, dd, $^3J_{4',3'}$ = 7.8 Hz, $^3J_{4',6'}$ = 1.3 Hz, 4'-H), 5.00 (1H, d, $^3J_{CH,2}$ = 11.8 Hz, *C*H($PhMe_2)_2$), 4.80 (2H, dd, $^3J_{1/3,OH}$ = 7.2 Hz, $^3J_{1/3,2}$ = 4.4 Hz, 1/3-H), 3.02 (1H, dt, $^3J_{2,CH}$ = 11.8 Hz, $^3J_{2,1/3}$ = 4.4 Hz, 2-H), 2.56 (6H, s, C(2')C*H*$_3$), 2.32 (6H, s, C(5')C*H*$_3$), 2.29 (6H, s, C(4/7)C*H*$_3$), 1.77 (2H, d, $^3J_{OH,1/3}$ = 7.2 Hz, O*H*) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.7 (C_q, C-3a/4a), 140.9 (C_q, C-1'), 135.3 (C_q, C-5'), 133.6 (C_q, C-2'), 132.3 (C_q, C-4/7), 131.0 (C_t, C-3'), 130.4 (C_t, C-5/6), 129.0 (C_t, C-6'), 127.0 (C_t, C-4'), 74.3 (C_t, C-1/3), 55.9 (C_t, C-2), 37.3 (C_t, *C*H($PhMe_2)_2$), 21.5 (C_p, C(5')*C*H_3), 20.4 (C_p, C(2')*C*H_3), 17.9 (C_p, C(4/7)*C*H_3) ppm.

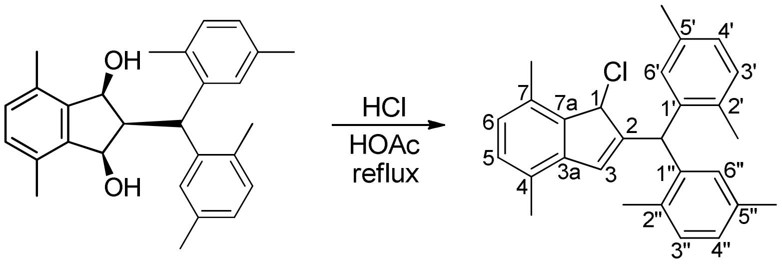
Accurate mass (ESI,+): Found: 423.22932. Calc. for $C_{28}H_{32}O_2+Na^+$: 423.22945.

MS (EI, 70 eV): m/z = 382 (M^+-H_2O, 1%), 364 (M^+-$2H_2O$, 100), 349 (M^+-$2H_2O$-Me, 75), 334 (M^+-$2H_2O$-2Me, 5), 259 (52), 223 ($CH(C_6H_3(CH_3)_2)_2^+$, 62), 207 (51), 193 ($CH(C_6H_3(CH_3)_2)_2^+$-2Me, 23), 159 (39), 146 (9), 119 (11), 105 (7), 91 (10).



Scheme S 1: Wagner-Meerwein rearrangement and double cyclodehydration of **14b** to **16**
Although the tertiary carbocation is less stabilized compared to the secondary benzylic cation the formation of a less strained product in the subsequent cyclization furthers the reaction via the tertiary cation.

Synthesis of 2-(Bis(2,5-dimethylphenyl)methyl)-1-chloro-4,7-dimethyl-1*H*-indene (17)



14c **17** (75%)

To boiling acetic acid (6 mL) was added diol **14c** (103 mg, 257 µmol) and conc. HCl (0.6 mL). After agitating for 4 h the reaction mixture was quenched with water (30 mL) to precipitate a white solid which was filtered. The solid was taken up in CH_2Cl_2 and the organic layer was extracted with water (2x30 mL). The CH_2Cl_2 phases were combined and the solvent was evaporated. Column chromatography of the residue over silica gel (pentane/CH_2Cl_2 25:1-3:1) afforded the chlorinated elimination product **17** as a colourless solid (77.0 mg, 75%).

mp. 195-197 °C
R$_f$ 0.45 (pentane/CH_2Cl_2 25:1)
EA: Found: C; 83.9; H, 7.4. Calc. for $C_{28}H_{29}Cl$: C, 83.9; H, 7.3%

UV/Vis (acetonitrile, lgε): λ_{max} = 317 (2.95), 277 (3.17), 271 (3.13), 240 (3.93) (sh), 233 (3.99), 198 (4.30) nm.

FT-IR (ATR): $\tilde{\nu}$ = 3017 (w, ν(C-H_{arom})), 2920 (w, ν(C-H)), 2863 (w, ν(C-H)), 2733 (w), 1610 (w), 1496 (s, ν(C=C_{arom})), 1453 (m, δ(CH_2/CH_3)), 1378 (w, δ(CH_3)); 1290 (w), 1256 (w), 1227 (w), 1183 (w), 1157 (w), 1097 (w), 1034 (w), 997 (w), 876 (m), 802 (vs, ν(C-Cl)), 768 (w), 745 (m), 727 (m), 628 (w) cm^{-1}.

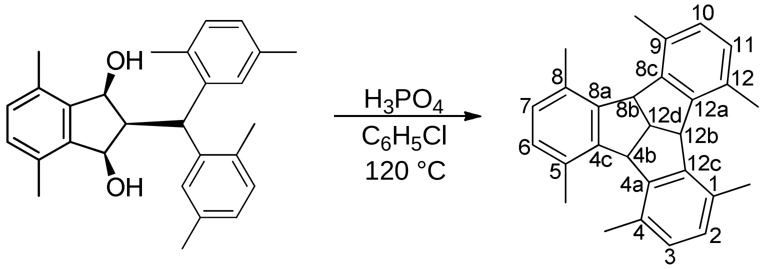
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.10 (1H, d, $^3J_{3',4'}$ = 7.3 Hz, 3'-H), 7.08 (1H, d, $^3J_{3'',4''}$ = 7.3 Hz, 3''-H), 7.01 (2H, d, ^3J = 7.7 Hz, 5/4''-H), 6.97 (1H, dd, $^3J_{4',3'}$ = 7.6 Hz, $^4J_{4',6'}$ = 1.2 Hz, 4'-H), 6.89 (1H, d, $^3J_{6,5}$ = 7.8 Hz, 6-H), 6.87 (1H, s, 6''-H), 6.56 (1H, s, 6'-H), 6.07 (1H, s, 3-H), 5.58 (1H, s, C*H*($PhMe_2$)$_2$), 5.12 (1H, s, 1-H), 2.39 (3H, s, C(5')CH_3), 2.38 (3H, s, C(7)CH_3), 2.30 (3H, s, C(5'')CH_3), 2.23 (3H, s, C(4)CH_3), 2.20 (3H, s, C(2')CH_3), 2.15 (3H, s, C(2'')CH_3) ppm.

^{13}C NMR (150 MHz, $CDCl_3$): δ = 151.2 (C_q, C-2), 141.8 (C_q, C-7a), 141.0 (C_q, C-3a), 140.2 (C_q, C-1''), 139.3 (C_q, C-1'), 135.4 (C_q, C-5''), 135.2 (C_q, C-5'), 134.0 (C_q, C-2''), 133.9 (C_q, C-2'), 132.4 (C-7), 130.8 (C_t, C-3''), 130.8 (C_t, C-5), 130.3 (C_t, C-3'), 129.9 (C_t, C-3), 129.7 (C_t, C-6''), 129.2 (C_t, C-2'), 128.2 (C_q, C-4), 127.8 (C_t, C-6), 127.6 (C_t, C-4''), 127.3 (C_t, C-4'), 60.9 (C_t, C-1), 43.3 (C_t, *C*H($PhMe_2$)$_2$), 21.4 (C_p, C(5'')*C*H_3), 21.4 (C_p, C(2')*C*H_3), 19.2 (C_p, C(5')*C*H_3), 19.1 (C_p, C(2'')*C*H_3), 18.2 (C_p, C(7)*C*H_3), 18.1 (C_p, C(4)*C*H_3) ppm.

Accurate mass (EI): Found: 400.19526. Calc. for $C_{28}H_{29}Cl^+$: 400.19523.

MS (EI, 70 eV): m/z = 400 (M^+, 25%), 365 (M^+-Cl, 54), 349 (10), 259 (16), 244 (17), 223 ($CH(C_6H_3(CH_3)_2)_2^+$, 100), 207 (10), 192 (8), 119 (14), 91 (6).

Synthesis of 4b,8b,12b,12d-Tetrahydro-1,4,5,8,9,12-hexamethyldibenzo[2,3:4,5]-pentaleno[1,6-ab]indene (15c)



14c **15c**

A mixture of diol **14c** (100 mg, 250 µmol), orthophosphoric acid (0.2 mL, 85%) and chlorobenzene (5 mL) was heated at 120 °C for 4 d. Evaporation of the solvent, column chromatography of the residue over silica gel (pentane/CH_2Cl_2 10:1) and semi-preparative HPLC (acetonitrile/H_2O 95:5 R_t(**15c**)=12.4 min; acetonitrile/H_2O 90:10 R_t(**15c**)=20.1 min) afforded **15c** as colourless crystals (5.0 mg, 6%).

mp. 202-203 °C (from EtOH/H_2O)

R_f 0.27 (pentane/CH_2Cl_2 10:1)

EA: Found: C; 92.0; H, 7.7. Calc. for $C_{28}H_{28}$: C, 92.3; H, 7.7%

UV/Vis (acetonitrile, lgε): λ_{max} = 339 (2.42), 271 (2.62), 225 (4.37) (sh), 206 (4.63) nm.

FT-IR (ATR): $\tilde{\nu}$ = 3034 (w, ν(C-H_{arom})), 3007 (w, ν(C-H)), 2953 (m, ν(C-H)), 2911 (m, ν(C-H)), 2864 (m, ν(C-H)), 2732 (w), 1602 (w), 1575 (w), 1487 (m, ν(C=C_{arom})), 1446 (m, δ(CH_2/CH_3)), 1377 (m, δ(CH_3)), 1327 (w), 1283 (w), 1252 (w), 1201 (w), 1163 (w), 1059 (w),1031 (m), 940 (w), 897 (w), 870 (w), 800 (s, δ(=C-H)$_{1,4\ subst.}$), 773 (w), 725 (w), 687 (w), 658 (w), 643 (w), 618 (w) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.85 (6H, s, C*H*), 4.73 (3H, d, ^3J = 9.0 Hz, 4b/8b/12b-H), 4.29 (1H, q, ^3J = 9.0 Hz, 12d-H), 2.39 (18H, s, CH_3) ppm.

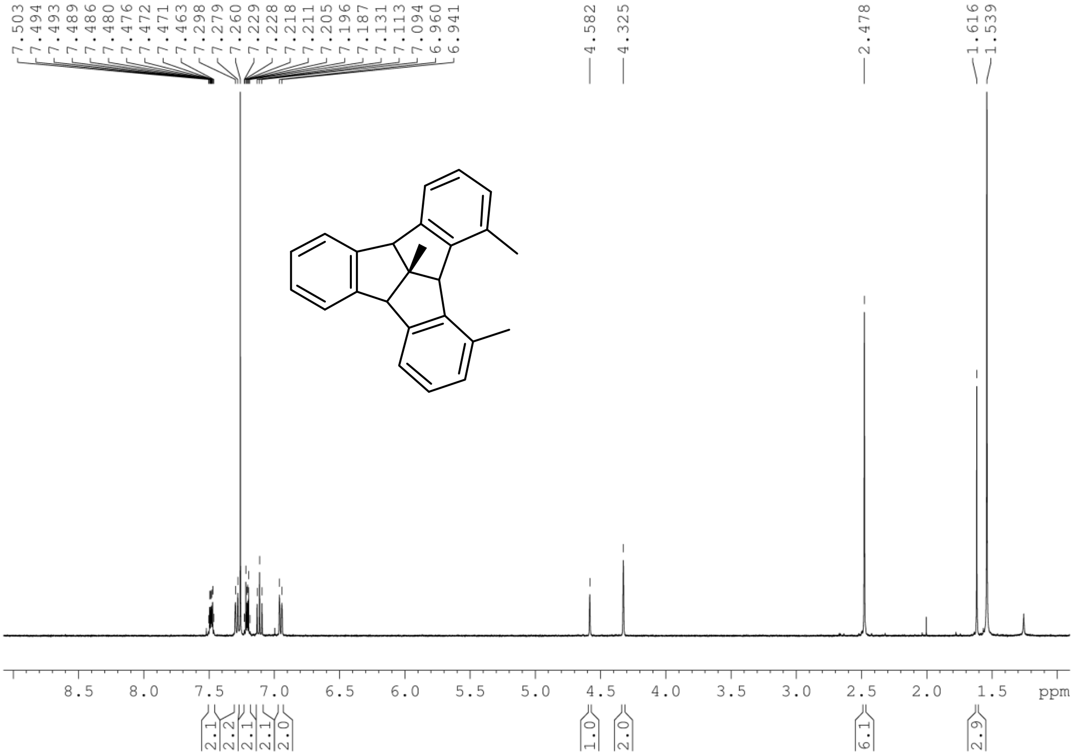
^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.0 (C_q), 131.7 (C_q, *C*CH_3), 129.3 (C_t, *C*H), 53.7 (C_t, C-4b/8b/12b), 52.8 (C_t, C-12d), 20.9 (C_p, *C*H_3) ppm.

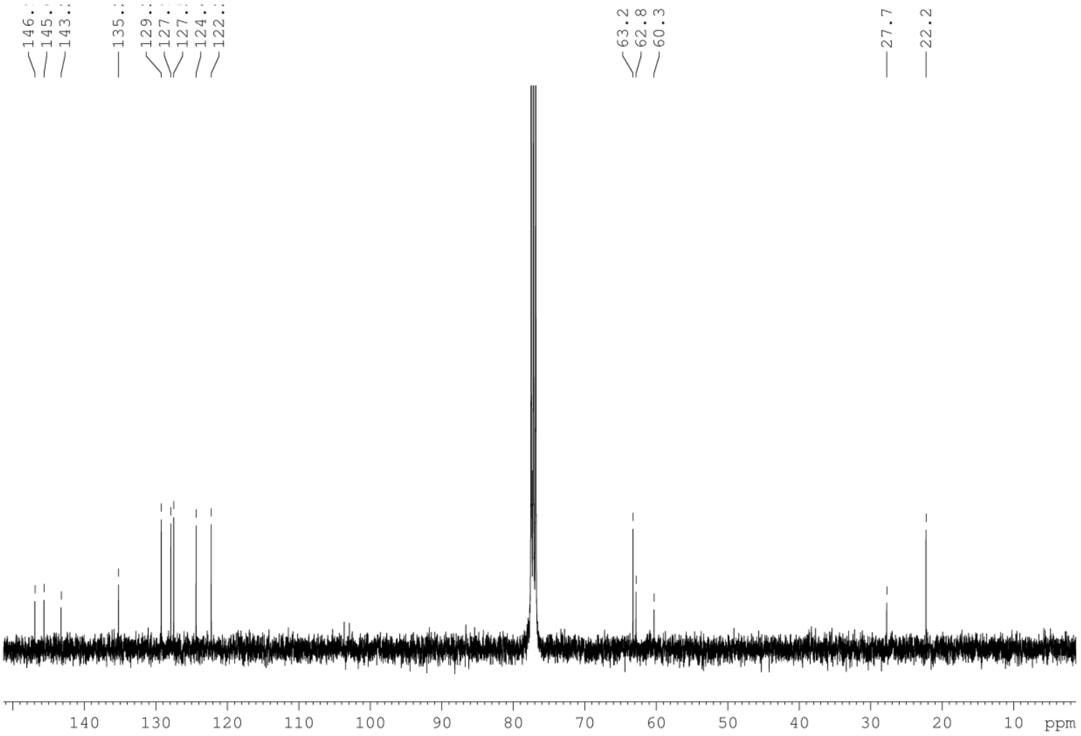
Accurate mass (ESI,+): Found: 365.22602. Calc. for $C_{28}H_{28}+H^+$: 365.22638.

MS (EI, 70 eV): m/z = 364 (M^+, 86%), 349 (M^+-Me, 100), 334 (M^+-2Me, 10), 319 (M^+-3Me, 12), 304 (M^+-4Me, 9), 289 (M^+-5Me, 5), 243 (12), 234 (26), 221 (62), 206 (15), 191 (10), 171 (6), 157 (13), 143 (53), 129 (20).

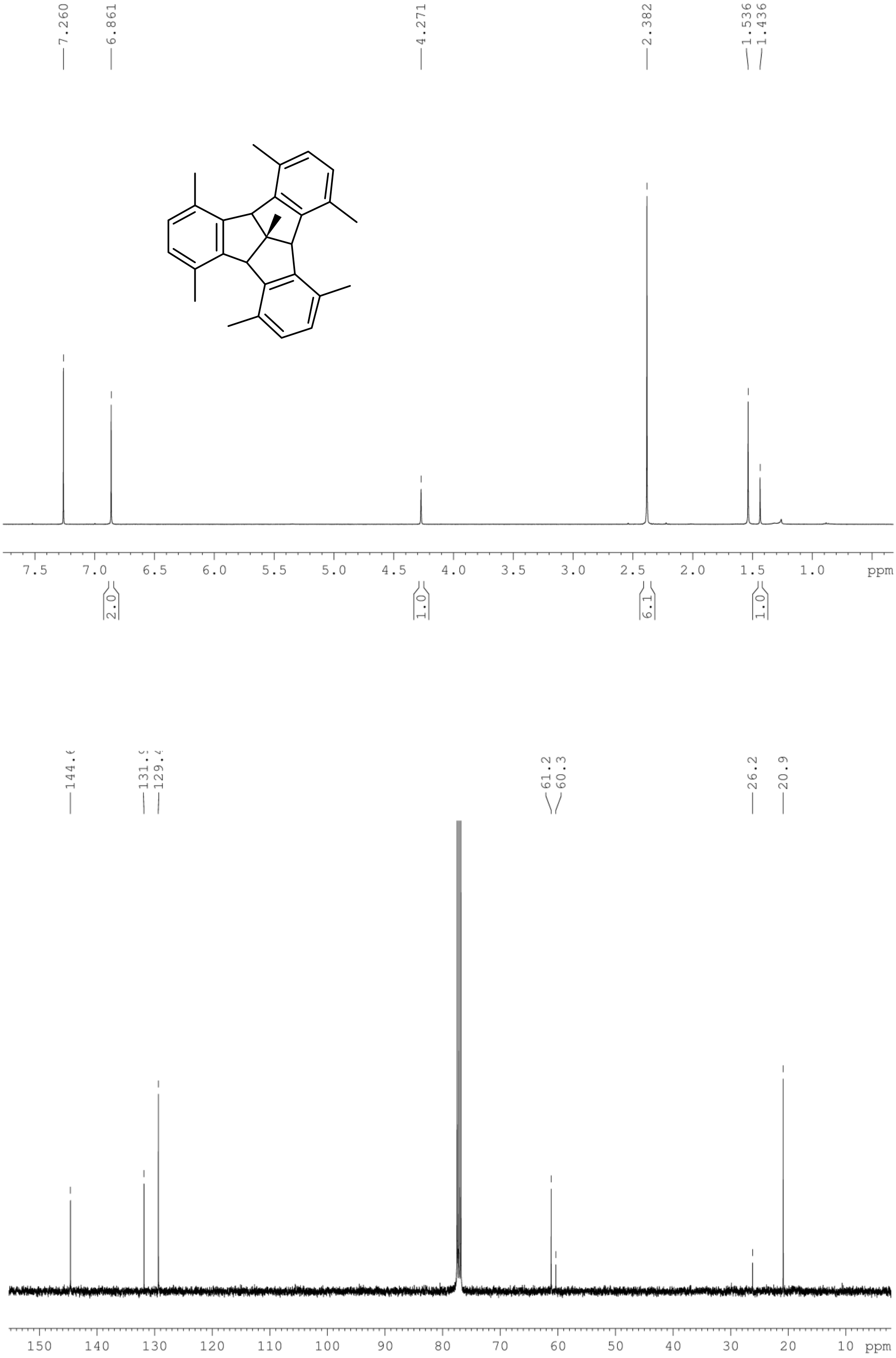
3. NMR spectra

^{1}H-/^{13}C-NMR spectra of Me$_3$-TBTQ **15a**:

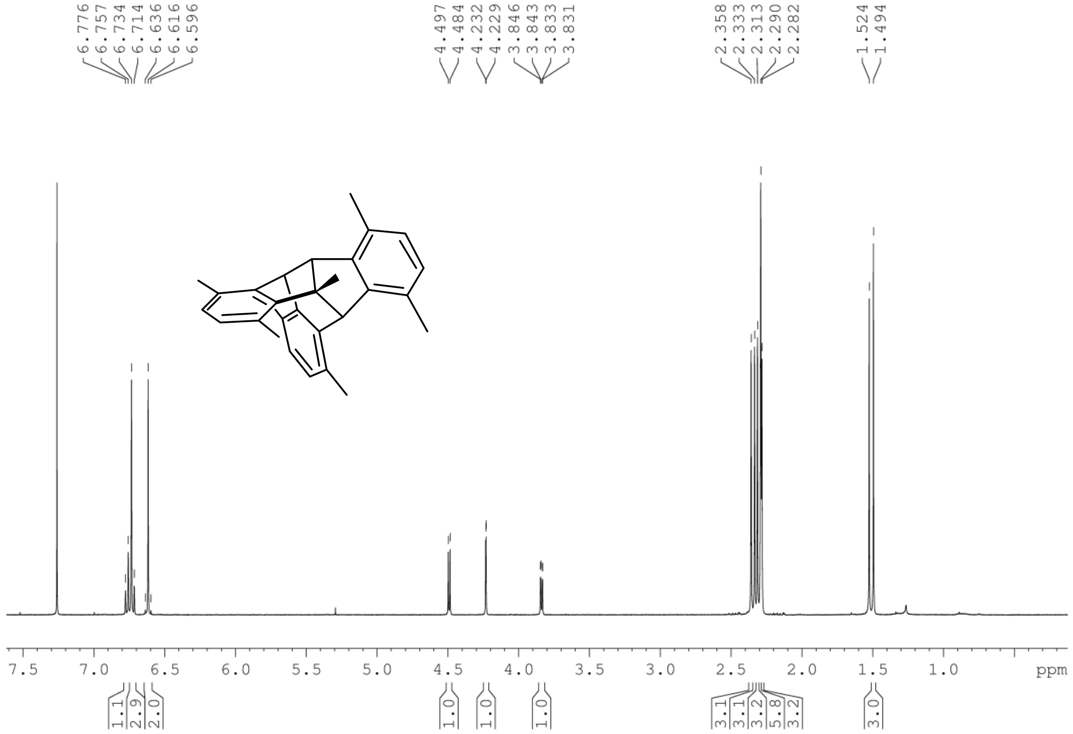


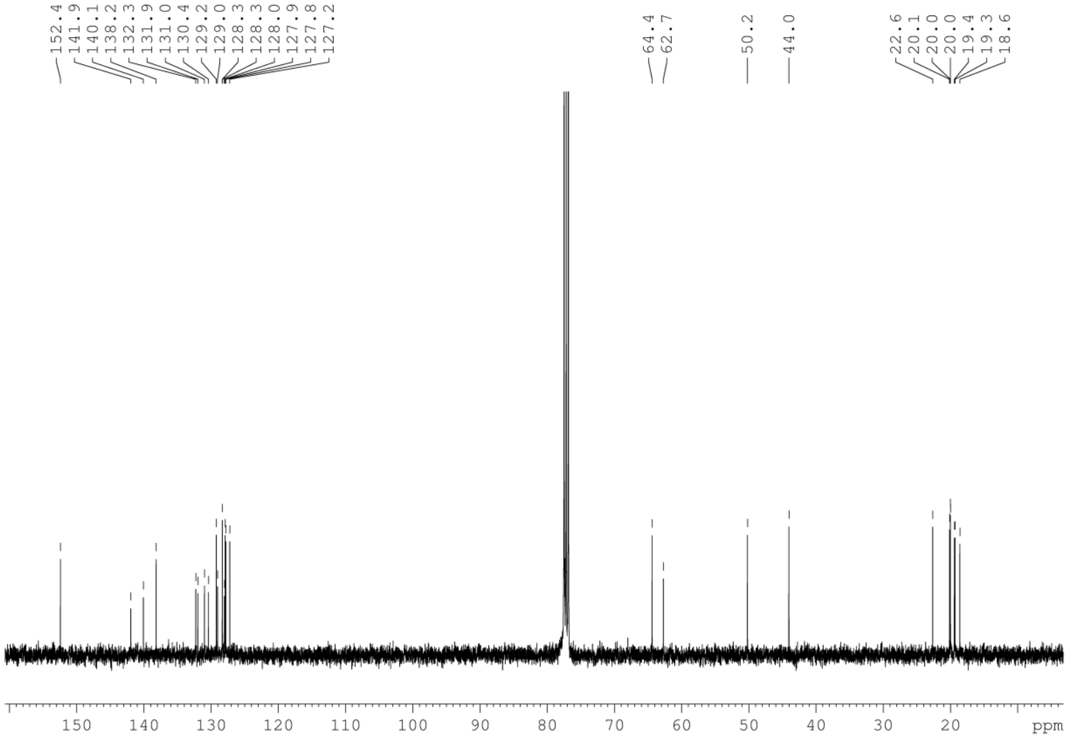


^{1}H-/^{13}C-NMR spectra of Me$_7$-TBTQ **15b**:

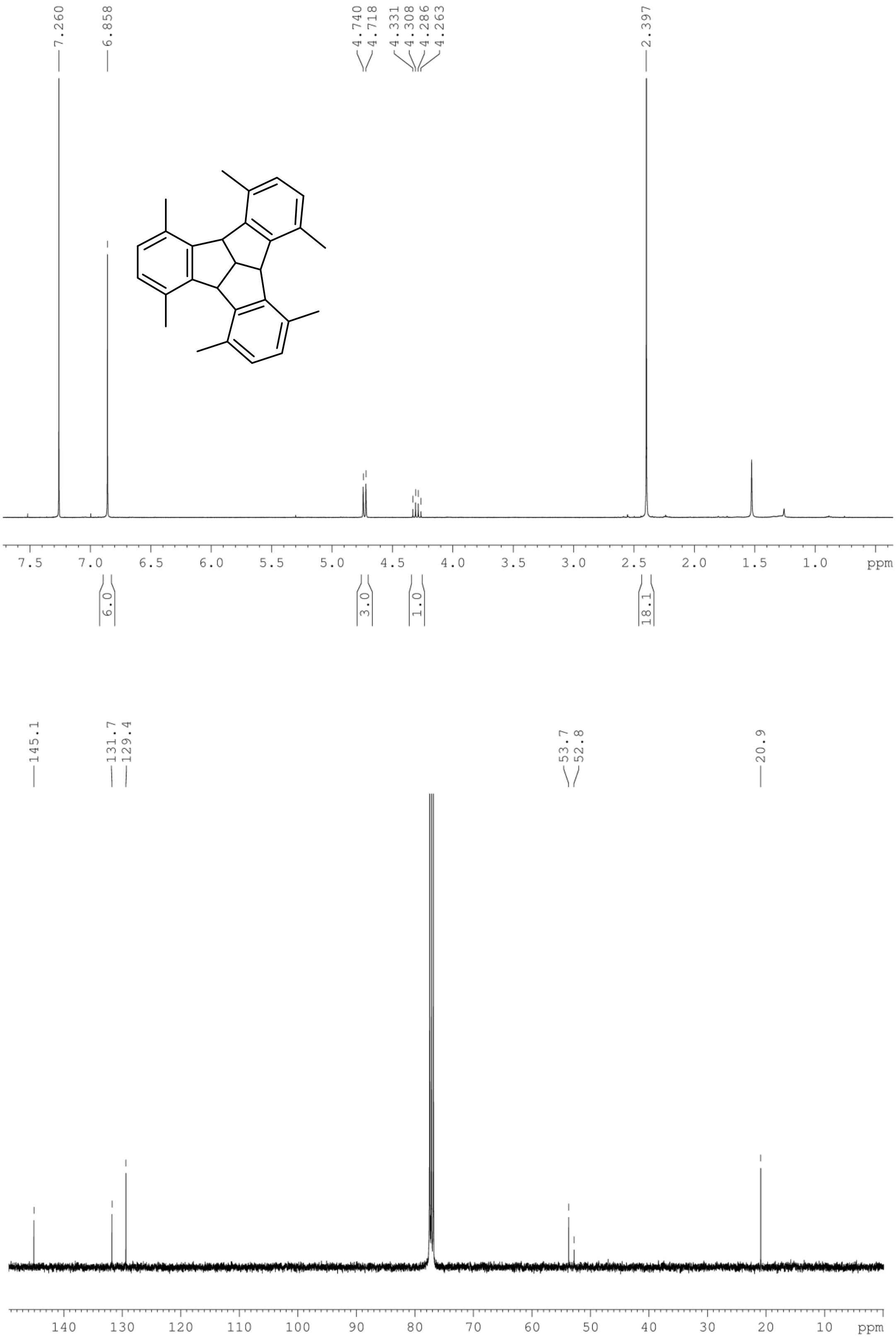


^{1}H-/^{13}C-NMR spectra of rearrangement product **16**:





^{1}H-/^{13}C-NMR spectra of Me$_6$-TBTQ **15c**:



4. X-Ray Christallography

The crystal data of **15a**, **15b**, **15c** and **16** were collected on a Bruker X8APEX diffractometer with a CCD area detector and multi-layer mirror monochromated $\text{Mo}_{\text{K}\alpha}$ radiation. The structure was solved using direct methods, refined with the Shelx software package (G. Sheldrick, *Acta Cryst.*, **2008**, *A64*, 112–122) and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factors calculations. All hydrogen atoms were assigned to idealised geometric positions.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-837041 (**15a**), CCDC-837042 (**15b**), CCDC-837043 (**16**), and CCDC-837044 (**15c**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

Table S 1: Crystal data for of Me_3-TBTQ **15a**

CCDC	837041
Empirical formula	$C_{25}H_{22}$
Formula weight ($g \cdot mol^{-1}$)	322.43
Temperature (K)	100(2)
Radiation, λ (Å)	$Mo_{K\alpha}$ 0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	9.6681(9)
b (Å)	23.199(2)
c (Å)	15.9130(14)
α (°)	90.00
β (°)	104.037(4)
γ (°)	90.00
Volume ($Å^3$)	3462.5(5)
Z	8
Calculated density ($Mg \cdot m^{-3}$)	1.237
Absorption coefficient (mm^{-1})	0.070
$F(000)$	1376
Theta range for collection	1.58 to 26.16°
Reflections collected	265328
Independent reflections	6834
Minimum/maximum transmission	0.6174/0.6849
Refinement method	Full-matrix least-squares on F^2
Data / parameters / restrains	6834 / 457 / 0
Goodness-of-fit on F^2	1.147
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0512$, $wR^2 = 0.1145$
R indices (all data)	$R_1 = 0.0653$, $wR^2 = 0.1227$
R_{int}	0.0591
Maximum/minimum residual electron density ($e \cdot Å^{-3}$)	0.298 / –0.257

Table S 2: Crystal data for Me$_7$-TBTQ **15b**

CCDC	837042
Empirical formula	$C_{29}H_{30}$
Formula weight (g·mol^{-1})	378.53
Temperature (K)	100(2)
Radiation, λ (Å)	Mo$_{K\alpha}$ 0.71073
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions	
a (Å)	12.2086(9)
b (Å)	13.1797(10)
c (Å)	14.0845(10)
α (°)	70.585(3)
β (°)	76.790(3)
γ (°)	87.887(3)
Volume (Å^3)	2079.0(3)
Z	4
Calculated density (Mg·m^{-3})	1.209
Absorption coefficient (mm^{-1})	0.068
F(000)	816
Theta range for collection	1.58 to 25.94°
Reflections collected	85497
Independent reflections	8025
Minimum/maximum transmission	0.6308/0.7453
Refinement method	Full-matrix least-squares on F^2
Data / parameters / restrains	8025 / 537 / 0
Goodness-of-fit on F^2	1.071
Final R indices [I>2σ(I)]	$R_1 = 0.0385$, $wR^2 = 0.1030$
R indices (all data)	$R_1 = 0.0434$, $wR^2 = 0.1121$
R$_{int}$	0.0359
Maximum/minimum residual electron density (e·Å^{-3})	0.340 / –0.292

Table S 3: Crystal data for rearrangement product **16**

CCDC	837043
Empirical formula	$C_{29}H_{30}$
Formula weight (g·mol^{-1})	378.53
Temperature (K)	100(2)
Radiation, λ (Å)	$Mo_{K\alpha}$ 0.71073
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions	
a (Å)	9.7227(9)
b (Å)	9.7586(9)
c (Å)	23.813(2)
α (°)	98.641(4)
β (°)	95.323(4)
γ (°)	106.968(4)
Volume (Å^3)	2114.1(3)
Z	4
Calculated density (Mg·m^{-3})	1.189
Absorption coefficient (mm^{-1})	0.067
F(000)	816
Theta range for collection	1.75 to 26.56°
Reflections collected	60649
Independent reflections	8664
Minimum/maximum transmission	0.9764/0.9920
Refinement method	Full-matrix least-squares on F^2
Data / parameters / restrains	8664 / 537 / 0
Goodness-of-fit on F^2	1.175
Final R indices [I>2σ(I)]	$R_1 = 0.0655$, $wR^2 = 0.1565$
R indices (all data)	$R_1 = 0.0681$, $wR^2 = 0.1578$
R_{int}	0.0571
Maximum/minimum residual electron density (e·Å^{-3})	0.882 / –0.396

Table S 4: Crystal data for Me$_6$-TBTQ **15c**

CCDC	837044
Empirical formula	$C_{28}H_{28}$
Formula weight (g·mol^{-1})	364.50
Temperature (K)	103(2)
Radiation, λ (Å)	Mo$_{K\alpha}$ 0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	11.5014(4)
b (Å)	13.1875(5)
c (Å)	13.0975(6)
α (°)	90.00
β (°)	102.852(2)
γ (°)	90.00
Volume (Å^3)	1936.79(13)
Z	4
Calculated density (Mg·m^{-3})	1.250
Absorption coefficient (mm^{-1})	0.070
F(000)	784
Theta range for collection	2.13 to 26.76°
Reflections collected	4131
Independent reflections	4131
Minimum/maximum transmission	group 2//m for scaling
Refinement method	Full-matrix least-squares on F^2
Data / parameters / restrains	4131 / 259 / 0
Goodness-of-fit on F^2	1.095
Final R indices [I>2σ(I)]	$R_1 = 0.0447$, $wR^2 = 0.1170$
R indices (all data)	$R_1 = 0.0481$, $wR^2 = 0.1199$
R_{int}	0.066
Maximum/minimum residual electron density (e·Å^{-3})	0.367 / –0.357

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