Electronic Supporting Information for

Thermal dimerization of [n]cumulenes (n = 5, 7, 9)

Dominik Wendinger,¹ Johanna A. Januszewski,¹ Frank Hampel,¹ and Rik R. Tykwinski*¹

Department of Chemistry and Pharmacy & Interdisciplinary Center for Molecular Materials (ICMM), Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Henkestrasse 42, 91054 Erlangen (Germany)

E-mail: rik.tykwinski@fau.de
Homepage: http://www.chemie.uni-erlangen.de/tykwinski
Table of Contents for the Electronic Supporting Information:

Contents
1. General Experimental........................................................................................................... 3
2. Synthetic Procedures and Spectral Characterization of Compounds
3. $^1$H and $^{13}$C NMR spectra for new compounds ............................................................ 12
4. UV/Vis absorption spectra.................................................................................................... 26
General Experimental

a. Chemicals

All chemicals were purchased from commercial suppliers and used as received. THF and Et₂O were distilled from sodium/benzophenone, and CH₂Cl₂ was distilled from CaH₂. Na₂SO₄ was used as the drying reagent after aqueous work-up. Analytical TLC was performed on Al plates coated with silica gel (0.20 mm) and containing a fluorescent indicator (Macherey-Nagel, ALUGRAM® SIL G/UV254). Column chromatography was carried out on silica gel (Macherey-Nagel, M-N Silica Gel 60A, 230–400 mesh).

b. Instrumentation

NMR spectra were recorded on a Bruker Avance 300 operating at 300 MHz (¹H NMR) and 75 MHz (¹³C NMR), or a Bruker Avance 400 operating at 400 MHz (¹H NMR) and 100 MHz (¹³C NMR), at rt, if not otherwise specified. Signals were referenced to residual solvent peaks (δ in parts per million (ppm)) ¹H: CDCl₃, 7.24 ppm, CD₂Cl₂: 5.32 ppm; ¹³C: CDCl₃, 77.0 ppm, CD₂Cl₂: 53.8 ppm) and recorded at ambient probe temperature. Coupling constants were assigned as observed. CDCl₃ (99.8%, Deutero GmbH) was stored over 4 Å molecular sieves. IR spectra were recorded on a Varian 660-IR (ATR mode) spectrometer. Characteristic IR bands were recorded in cm⁻¹ and classified as strong (s), medium (m), weak (w), very weak (vw), and broad (br). Mass spectra were recorded from Micromass Zabspec (EI), Bruker micro TOF II (ESI), and Bruker maxis 4G (APPI) instruments. IR spectra were recorded on a Varian 660-IR spectrometer. UV-Vis spectra were recorded on a Varian Cary 5000 UV-Vis-NIR spectrophotometer (λ in nm;). Melting points were measured with an Electrothermal 9100 instrument.
Synthetic Procedures and Spectral Characterization of Compounds

1,2,3,4-Tetrakis(2,2-bis(3,5-di-\text{-}t\text{-}butylphenyl)vinyldene)cyclobutane (4a)

[\text{5\text{-}tBuPh}] (0.030 g, 0.036 mmol) was dissolved in toluene (5 mL) and heated to reflux for 4 d under air. Evaporation of the solvent afforded a red solid that contained more than one compound according to TLC analysis. The solid was dissolved in CH$_2$Cl$_2$, and this solution was overlayed with hexanes. This crystallization gave colorless square crystals, which were characterized by X-ray crystallographic analysis showing that the sample was compound 4a. Unfortunately, the formation of 4a was not reproducible and no further, meaningful characterization could be achieved.

A crystal suitable for X-ray crystallographic analysis has been grown from a CH$_2$Cl$_2$ solution layered with hexanes. Crystal data for 4a: C$_{124}$H$_{168}$, $M = 1658.58$; tetragonal crystal system; space group P4/n, $a = 19.3824(4) \, \text{Å}$, $b = 19.3824(4) \, \text{Å}$, $c = 14.8604(7) \, \text{Å}$, $V = 5582.8(3) \, \text{Å}^3$, $Z = 2$, $\rho_{\text{calc}} = 0.987 \, \text{mg mm}^{-3}$; $\mu_{\text{CuK}} = 0.403 \, \text{mm}^{-1}$; $\lambda = 1.5418 \, \text{Å}$; $2\theta_{\text{max}} = 102.76^\circ$; total data collected = 5632; $R_1 = 0.0759$ [2509 observed reflections with $F \geq 2\sigma(F)$]; $wR_2 = 0.2091$ for 294 variables, 2972 data, and 46 restraints; residual electron density = 0.41 and $-0.32 \, \text{e} \, \text{Å}^{-3}$. Three t-butyl groups show disorder, which have been resolved and refined to the following occupation factors: C18 – C20:C18a – C20a = 75:25%, C22 – C24:C22a – C24a = 75:25%, C38 – C40:C38a – C40a = 75:25%. The crystal diffraction was very low, even under Cu radiation, and a maximum resolution limit of only 1.0 Angstrom could be reached. Nevertheless, structural solution and refinement was successful. CCDC 1402907.

1,1-Di-o-tolyl-3-(trimethylsilyl)prop-2-yn-1-ol (S1)

To a solution of trimethylsilylacetylene (0.687 g, 1.00 mL, 7.00 mmol) in THF (15 mL) at $-78 \, ^\circ\text{C}$ was added n-BuLi (2.5 M in hexanes, 2.44 mL, 6.10 mmol) under a N$_2$ atmosphere via a syringe. The reaction mixture was stirred for 1 h and a solution of di-o-tolylmethanone (1.28 g, 6.08 mmol) in THF (10 mL) was added. The cooling bath was removed, the reaction was allowed to warm to rt, and stirred for 3 h. The reaction was quenched via the addition of saturated aq NH$_4$Cl (40 mL), and Et$_2$O

(60 mL) was added. The layers were separated, the organic phase was washed with saturated aq NaCl (60 mL), dried (Na₂SO₄), and filtered. Solvent removal afforded S1 (1.88 g, 100%) as a colorless solid. Mp 71 °C. Rₜ = 0.49 (hexanes/CH₂Cl₂ 1:2). IR (ATR) 3581 (m), 2957 (m), 2160 (w), 1455 (m), 1247 (m), 1162 (m), 1039 (s) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.89–7.86 (m, 2 H), 7.23–7.18 (m, 4 H), 7.10–7.07 (m, 2 H), 2.64 (s, 1 H), 2.07 (s, 6 H), 0.20 (s, 9 H); ¹³C NMR (75 MHz, CDCl₃) δ 140.7, 136.5, 132.2, 127.9, 127.2, 125.4, 92.3, 74.8, 21.2, –0.2. El MS m/z 308 (M⁺, 10), 217 ([M – o-Tol]⁺, 100); El HRMS m/z calcd. for C₂₀H₂₄O₅Si (M⁺) 308.1591, found 308.1574.

1,1-Di-o-tolyprop-2-yn-1-ol (S2)

To a solution of S1 (1.82 g, 5.89 mmol) in MeOH (50 mL) was added K₂CO₃ (0.81 g, 5.9 mmol). After stirring for 1 h, the reaction mixture was quenched via the addition of saturated aq NH₄Cl (30 mL), and CH₂Cl₂ (50 mL) was added. The layers were separated, the organic phase was washed with saturated aq NH₄Cl (40 mL) and saturated aq NaCl (40 mL), dried (Na₂SO₄), and filtered. Solvent removal afforded S2 (1.19 g, 85%) as a colorless oil. Rₜ = 0.12 (hexanes/EtOAc 20:1). IR (ATR) 3532 (br), 3281 (m), 3050 (w), 3017 (w), 2960 (w), 2925 (w), 1599 (w), 1455 (s), 1318 (m), 1286 (m) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.97–7.94 (m, 2 H), 7.26–7.20 (m, 4 H), 7.10–7.07 (m, 2 H), 2.88 (s, 1 H), 2.68 (s, 1 H), 2.02 (s, 6 H); ¹³C NMR (75 MHz, CDCl₃) δ 140.5, 136.2, 132.2, 128.1, 127.2, 125.5, 85.4, 76.0, 74.7, 21.1. El MS m/z 236 (M⁺, 21), 195 (M⁺, 100); El HRMS m/z calcd. for C₁₇H₁₆O (M⁺) 236.1196, found 236.1188.

1,1,6,6-Tetra-o-tolylhexa-2,4-diyn-1,6-diol (S3)

To a solution of S2 (1.12 g, 4.74 mmol) in CH₂Cl₂ (30 mL) was added a solution of Hay catalyst [CuCl (0.470 g, 4.74 mmol) and TMEDA (1.10 g, 1.43 mL, 9.49 mmol) in CH₂Cl₂ (20 mL)]. The reaction mixture was stirred for 3 h, saturated aq NH₄Cl (50 mL) was added, and the mixture was extracted with CH₂Cl₂ (50 mL). The organic phase was washed with saturated aq NH₄Cl (100 mL) and saturated aq NaCl (100 mL), dried (Na₂SO₄), and filtered. Solvent removal and purification via column chromatography (silica, hexanes/CH₂Cl₂ 1:2) afforded S3 (557 mg, 50%) as a colorless solid. Mp 150 °C. Rₜ = 0.09 (hexanes/CH₂Cl₂ 1:2). IR (ATR) 3515 (m), 3407 (br), 2961 (w), 2208 (w), 1456 (m), 1356 (w), 1028 (s) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.86–7.83 (m, 4 H), 7.23–7.18 (m, 8 H), 7.08–7.05 (m, 4 H), 2.63 (s, 2 H), 1.99 (s, 12 H); ¹³C NMR (75 MHz, CDCl₃) δ 140.0, 136.3, 132.3, 128.3,
127.3, 125.6, 81.8, 75.3, 71.7, 21.1. APPI HRMS m/z calcd. for C₃₄H₃₀O₂ (M⁺) 470.2240 , found C₃₄H₃₀O₂ 470.2244.

SnCl₂ (anhyd) HCl (1M) CH₂Cl₂

To a solution of S₃ (1.80 g, 3.83 mmol) in CH₂Cl₂ (100 mL) was added SnCl₂ (1.45 g, 7.65 mmol) and HCl (1 M in Et₂O, 11.5 mL). After the reaction was judged complete by TLC analysis (ca. 1 h), the solution was filtered through a plug of basic alumina oxide and eluted with CH₂Cl₂, affording [5]Tol (1.54 g, 92%) as an orange solid. Mp 165 °C (decomp.). Rᵥ = 0.51 (hexanes/EtOAc 20:1). UV-Vis (CH₂Cl₂) λmax 267 (42200), 361 (47100) nm; IR (ATR) 3054 (vw), 3007 (vw), 2957 (m), 2161 (m), 1990 (m), 1451 (s) cm⁻¹; ¹H NMR (400 MHz, CD₂Cl₂) δ 7.24–7.22 (m, 8 H), 7.17–7.15 (m, 8 H), 2.31 (s, 12 H); ¹³C NMR (100 MHz, CD₂Cl₂) δ 155.6, 139.2, 137.4, 131.4, 130.6, 130.2, 128.7, 126.3, 124.5, 21.2. APPI HRMS m/z calcd. for C₃₄H₂₉ (M⁺) 437.2264, found 437.2267.

1,1,6,6-Tetra-ο-tolylhexa-1,2,3,4,5-pentaene ([5]Tol)

(3-Methoxy-3-di-ο-tolylprop-1-yn-1-yl)trimethylsilane ([S₄])

To a solution of trimethylsilylacetylene (1.18 g, 1.71 mL, 12.0 mmol) in THF (20 mL) at −78 °C was added n-BuLi (2.5 M in hexanes, 4.7 mL, 12 mmol) under a N₂ atmosphere via a syringe. The reaction mixture was stirred for 60 min and a solution of di-ο-tolylmethanone (2.5 g, 12 mmol) in THF (20 mL) was added. The cooling bath was removed, the reaction was stirred for 3 h at rt, and MeI (20 g, 9.0 mL, 0.14 mol) was added. The reaction mixture was stirred overnight. The reaction was quenched via the addition of saturated aq NH₄Cl (80 mL), and Et₂O (60 mL) was added. The layers were separated, the organic phase was washed with saturated aq NaCl (60 mL), dried (Na₂SO₄), and filtered. Solvent removal and purification via column chromatography (silica, hexanes/CH₂Cl₂ 1:2) afforded S₄ (3.53 g, 92%) as a colorless oil. Rᵥ = 0.70 (hexanes/CH₂Cl₂ 1:2). IR (ATR) 2957 (m), 2822 (w), 2155 (w), 1458 (m), 1249 (m), 1070 (s) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.80–7.77 (m, 2 H), 7.20–7.16 (m, 4 H), 7.08–7.05 (m, 2 H), 3.23 (s, 3 H), 2.04 (s, 6 H), 0.21 (s, 9 H); ¹³C NMR (75 MHz, CDCl₃) δ 139.0, 137.0, 132.1, 128.7, 127.8, 125.0, 103.6, 94.2, 81.3, 51.2, 21.1, –0.1. APPI HRMS m/z calcd. for C₂₁H₂₉OSi (M⁺) 322.1743, found 322.1743.
2,2’-(1-Methoxyprop-2-yne-1,1-diyl)bis(methylbenzene) (S5)

To a solution of S4 (4.39 g, 13.6 mmol) in MeOH (80 mL) was added K₂CO₃ (1.88 g, 13.6 mmol). After stirring for 30 min, the reaction mixture was quenched via the addition of saturated aq NH₄Cl (30 mL), and CH₂Cl₂ (50 mL) was added. The layers were separated, the organic phase was washed with saturated aq NH₄Cl (40 mL) and saturated aq NaCl (40 mL), dried (Na₂SO₄), and filtered. Solvent removal afforded S5 (2.98 g, 88%) as a colorless solid. Mp 48 °C. Rᶠ = 0.34 (hexanes). IR (ATR) 3266 (s), 3060 (vw), 2932 (m), 1457 (s), 1069 (s) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.91–7.87 (m, 2 H), 7.26–7.19 (m, 4 H), 7.12–7.08 (m, 2 H), 3.27 (s, 3 H), 2.86 (s, 1 H), 2.04 (s, 6 H); ¹³C NMR (75 MHz, CDCl₃) δ 138.8, 136.7, 132.1, 128.9, 127.9, 125.1, 82.3, 81.0, 77.3, 51.3, 21.1. EI MS m/z 250 (M⁺, 10), 235 ([M – Me]⁺, 100), 159 ([M – o-Tol]⁺, 80); ESI HRMS calcd. for C₁₈H₁₈O (M⁺) 250.1358, found 250.1349.

2,2’-(3-Bromo-1-methoxyprop-2-yne-1,1-diyl)bis(methylbenzene) (S6)

To a solution of S5 (1.67 g, 6.67 mmol) in acetone (20 mL) were added AgNO₃ (206 mg, 1.21 mmol) and NBS (1.78 g, 10.0 mmol). After stirring for 5 min at rt, the solution was cooled to 0 °C, and water (20 mL) was added. The solution was stirred for 10 min at 0 °C, and Et₂O (20 mL) was added. The organic phase was separated, dried (Na₂SO₄), and filtered. Solvent removal afforded S6 as a pale yellow solid (2.17 g, 99%). Mp 74 °C. Rᶠ = 0.55 (hexanes/EtOAc 20:1). IR (ATR) 3060 (w), 2925 (m), 2198 (w), 1932 (m), 1454 (s), 1161 (s), 1068 (s) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.78–7.75 (m, 2 H), 7.21–7.17 (m, 4 H), 7.08–7.05 (m, 2 H), 3.22 (s, 3 H), 2.00 (s, 6 H); ¹³C NMR (75 MHz, CDCl₃) δ 138.7, 136.8, 132.2, 128.6, 128.0, 125.8, 82.1, 79.1, 51.6, 48.9, 21.1. ESI HRMS calcd. for C₁₈H₁₇BrNaO (M⁺) 351.0355, found 351.0354.

1,1-Bi-o-tolylpenta-2,4-diyn-1-ol (S7)

To a solution of 1,4-bis(trimethylsilyl)buta-1,3-diyne (3.00 g, 15.4 mmol) in THF (25 mL) at 0 °C was added MeLi•LiBr complex (1.5 M in Et₂O, 10.4 mL, 15.6 mmol) under a N₂ atmosphere via a syringe. The cooling bath was removed, and the red-brown mixture was stirred for 0.5 h before it was cooled
again to 0 °C. A solution of di-o-tolylmethane (3.24 g, 15.4 mmol) in THF (25 mL) was added. The cooling bath was removed, and the reaction was stirred overnight. The solution was quenched via the addition of saturated aq NH₄Cl (70 mL), and Et₂O (50 mL) was added. The layers were separated, the organic phase was dried (Na₂SO₄), and filtered. Solvent removal, column chromatography (silica gel, hexanes/EtOAc 20:1), and recrystallization from hexanes afforded S7 (4.6 g, 90%) as an off-white solid. Mp 96 °C. Rᵥ = 0.17 (hexanes/EtOAc 20:1). IR (ATR) 3522 (s), 2958 (m), 2095 (m), 1249 (m) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.88–7.82 (m, 2 H), 7.25–7.19 (m, 4 H), 7.11–7.07 (m, 2 H), 2.65 (s, 1 H), 2.02 (s, 6 H), 0.20 (s, 9 H); ¹³C NMR (75 MHz, CDCl₃) δ 140.0, 136.3, 132.3, 128.3, 127.3, 125.6, 89.4, 87.3, 78.3, 75.2, 72.5, 21.1, −0.5. El MS m/z 332 (M⁺, 42), 73 (SiMe₃, 100), El HRMS m/z calcd. for C₂₂H₂₄OSi (M⁺) 332.1596, found 332.1586.

1,1-Di-o-tolylpenta-2,4-diyn-1-ol (S8)
To a solution of S7 (1.0 g, 3.0 mmol) in MeOH (40 mL) was added K₂CO₃ (0.42 g, 3.0 mmol). The reaction mixture was stirred for 30 min and quenched via the addition of saturated aq NH₄Cl (40 mL). The layers were separated, and the aqueous phase was extracted with CH₂Cl₂ (2 x 20 mL). The organic phases were combined and washed with saturated aq NH₄Cl (30 mL) and saturated aq NaCl (30 mL), dried (Na₂SO₄), and filtered. Solvent removal and recrystallization from hexanes afforded S8 (442 mg, 56%) as a colorless solid. Mp 68 °C. Rᵥ = 0.42 (hexanes/CH₂Cl₂ 1:2). IR (ATR) 3517 (m), 3388 (br), 3284 (vw), 2928 (vw), 1967 (w), 1457 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.86–7.82 (m, 2 H), 7.26–7.22 (m, 4 H), 7.13–7.10 (m, 2 H), 2.70 (s, 1 H), 2.31 (s, 1 H), 2.06 (s, 6 H); ¹³C NMR (100 MHz, CDCl₃) δ 139.9, 136.4, 132.3, 128.4, 127.2, 125.6, 77.1, 75.1, 71.8, 70.2, 67.5, 21.1. ESI HRMS m/z calcd. for C₁₉H₁₆NaO ([M + Na⁺]⁺) 283.1093, found 283.1101.

8-Methoxy-1,1,8,8-tetra-o-tolylocta-2,4,6-triyn-1-ol (S9)
To a solution of compound S6 (4.194 g, 12.74 mmol) in EtOH (50 mL) were added NH₂(OH)•HCl (0.708 g, 10.2 mmol) and nPrNH₂ (1.21 g, 1.67 mL, 20.4 mmol), and the solution was then purged with N₂ for 5 min. CuCl (0.857 g, 8.66 mmol) and diyne S8 (1.326 g, 5.094 mmol) were added. The solution was again purged with N₂ for 10 min and stirred for 1 h at rt. The reaction was quenched via addition of water (50 mL), and Et₂O (50 mL) was added. The organic phase was separated, washed
with water (2 x 30 mL) and saturated aq NaCl (2 x 30 mL), dried (Na$_2$SO$_4$), and filtered. Solvent removal and purification via column chromatography (hexanes/EtOAc 20:1) afforded S9 as a colorless solid (2.21 g, 85% based on S8). Mp 159 °C. $R_f = 0.15$ (hexanes/EtOAc 20:1). IR (ATR) 3568 (w), 2950 (w), 1645 (m), 1536 (s), 1454 (m), 1264 (m), 1160 (m), 1064 (m), 923 (s), 823 (s), 748 (s), 708 (s), 688 (w), 608 (w).$^1$H NMR (300 MHz, CDCl$_3$) δ 7.83–7.72 (m, 4 H), 7.27–7.18 (m, 4 H), 7.13–7.08 (m, 4 H), 3.05 (s, 3 H), 2.71 (s, 3 H), 2.05 (s, 6 H), 2.03 (s, 6 H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 139.7, 138.0, 136.8, 136.4, 132.35, 132.26, 128.4, 128.6, 128.2, 127.2, 125.7, 125.3, 81.9, 79.6, 78.1, 75.3, 73.6, 72.3, 64.7, 63.9, 51.8, 21.1, 21.0. ESI HRMS calcd. for C$_{37}$H$_{32}$NaO$_2$ ([M + Na]$^+$) 531.2295 found 531.2291.

1,1,8,8-Tetra-o-tolylocta-1,2,3,4,5,6,7-heptaene ([7]Tol)

To a solution of S9 (0.200 g, 0.393 mmol) in CH$_2$Cl$_2$ (15 mL) was added anhydrous SnCl$_2$ (224 mg, 1.18 mmol) and HCl (1 M in Et$_2$O, 1.6 mL, 1.6 mmol) at 0 °C under a N$_2$ atmosphere. After 30 min, the solution was filtered through a plug of basic alumina oxide and eluted with CH$_2$Cl$_2$ affording mainly [7]Tol and small amounts of 5 as judged by TLC analysis. The solution was concentrated to 10 mL and layered with MeOH. After 24 h at rt red crystalline 5 (43 mg, 24%) was filtered off and washed with cold MeOH. When the CH$_2$Cl$_2$ solution of [7]Tol was stored at −20 °C crystalline [7]Tol (or mixtures of [7]Tol and 5) could be obtained by removing the solvent via a pipette (ca. 18 mg, ca. 10%).

[7]Tol: Mp 155 °C (decolorization). $R_f = 0.43$ (hexanes/EtOAc 20:1). UV-Vis (CH$_2$Cl$_2$) $\lambda_{max}$ 297, 319, 444, 516 nm. IR (ATR) 3059 (m), 2966 (m), 2914 (s), 2848 (m), 2059 (s), 1666 (s), 1442 (s) cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.22–7.12 (m, 16 H), 2.32 (s, 12 H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 162.3, 154.0, 138.5, 137.2, 131.2, 130.1, 128.7, 128.6, 126.1, 125.0, 21.2. APPI HRMS m/z calcd. for C$_{36}$H$_{28}$ (M$^+$) 460.2186, found 460.2179.

3,4,7,8-Tetrakis(2,2-di-o-tolyvinylidene)cycloocta-1,5-diyne (5)

Mp 190 °C (decolorization). $R_f = 0.34$ (hexanes/EtOAc 20:1). UV-Vis (CH$_2$Cl$_2$) $\lambda_{max}$ 228, 275 nm. IR 3062 (w), 3014 (w), 2947 (w), 2914 (w), 2177 (w), 1594 (m), 1483 (s), 1444 (s), 1265 (s) cm$^{-1}$. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.17–7.10 (m, 16 H), 6.97–6.92 (m, 8 H), 6.84–6.82 (m, 8 H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 207.9, 136.7, 135.5, 130.7, 129.6, 127.8, 125.9, 113.9, 102.2, 92.7, 20.6. APPI HRMS m/z calcd. for C$_{72}$H$_{56}$ (M$^+$) 920.4377, found 920.4362.
Crystal data for 5: C_{72}H_{56}\cdot 2\text{CH}_2\text{Cl}_2, M = 1091.02; triclinic crystal system; space group P-1, α = 9.7822(5) Å, b = 12.5174(6) Å, c = 12.6361(8) Å, α = 104.011(5)°, β = 90.739(4)°, γ = 104.207(4)°, V = 1451.00(14) Å³, Z = 1, \( \rho_{\text{calcd}} = 1.249 \text{ mg mm}^{-3}; \mu(\text{CuKα}) = 2.181 \text{ mm}^{-1}; \lambda = 1.5418 \text{ Å}; 2θ max = 123.92°; \text{total data collected} = 6450; R_1 = 0.0529 \text{ for} 3828 \text{ observed reflections with} F \geq 2σ(F); wR_2 = 0.1474 \text{ for} 356 \text{ variables,} 4350 \text{ data, and} 0 \text{ restraints; residual electron density = 0.43 and} -0.54 \text{ e Å}^{-3}. \text{CCDC 1402909.}

1,1,10,10-Tetra-o-tolyldeca-2,4,6,8-tetrayne-1,10-diol (S10)

To a solution of S8 (0.44 g, 1.7 mmol) in CH\(_2\)Cl\(_2\) (30 mL) was added a solution of Hay catalyst [CuCl (0.168 g, 1.70 mmol) and TMEDA (0.40 g, 0.51 mL, 3.4 mmol) in CH\(_2\)Cl\(_2\) (20 mL)]. The reaction mixture was stirred for 3 h, saturated aq NH\(_4\)Cl (50 mL) was added, and the mixture was extracted with CH\(_2\)Cl\(_2\) (50 mL). The organic phase was washed with saturated aq NH\(_4\)Cl (100 mL) and saturated aq NaCl (100 mL), dried (Na\(_2\)SO\(_4\)), and filtered. Solvent removal and purification via column chromatography (silica, hexanes/CH\(_2\)Cl\(_2\) 1:2) afforded S10 (285 mg, 65%) as an off-white solid. Mp 150 °C. \( R_1 = 0.17 \) (hexanes/CH\(_2\)Cl\(_2\) 1:2). IR (ATR) 3524 (w), 3058 (w), 3017 (w), 2957 (w), 2927 (w), 2210 (w), 1456 (m), 1066 (m) cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.79–7.76 (m, 4 H), 7.24–7.21 (m, 8 H), 7.10–7.07 (m, 4 H), 2.67 (s, 2 H), 2.01 (s, 12 H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 139.5, 136.4, 132.4, 128.5, 127.2, 125.8, 79.3, 75.4, 72.3, 65.5, 62.3, 21.1. ESI HRMS m/z calcd. for C\(_{38}\)H\(_{30}\)NaO\(_2\) ([M + Na]') 541.2138, found 541.2144.

1,1,10,10-Tetra-o-tolyldeca-1,2,3,4,5,6,7,8,9-nonaene ([9]Tol)

To a solution of S10 (0.191 g, 0.368 mmol) in CH\(_2\)Cl\(_2\) (15 mL) was added anhydrous SnCl\(_2\) (209 mg, 1.10 mmol) and HCl (1 M in Et\(_2\)O, 1.5 mL, 1.5 mmol) at 0 °C under a N\(_2\) atmosphere. After 2 h, the solution was filtered through a plug of basic alumina oxide and eluted with CH\(_2\)Cl\(_2\) affording [9]Tol (violet) together with 6 (yellow) as judged by TLC analysis. The solution was concentrated to 10 mL and layered with MeOH. After 24 h at –20 °C the formed grey needles were filtered off, washed with cold MeOH, dissolved in CH\(_2\)Cl\(_2\) (10 mL), filtered through a short plug of silica, and recrystallized from
CH₂Cl₂/MeOH. After additional 24–48 h crystalline 6 could be obtained (ca. 10–20 mg, 5-10%). [9]Tol: Could not be isolated due to instability of the product. Rᵣ = 0.78 (hexanes/CH₂Cl₂ 1:2). UV-Vis (CH₂Cl₂) λₘₐₓ 339, 368, 514, 555, 661 nm.

5,6,11,12-Tetakis(2,2-di-o-tolylvinylidene)cyclododeca-1,3,7,9-tetrayne (6)

Rᵣ = 0.29 (hexanes/EtOAc 20:1) UV-Vis (CH₂Cl₂) λₘₐₓ 226, 280, 319, 358 nm. IR (ATR) 3061 (w), 3014 (w), 2962 (w), 2922 (w), 1484 (s), 1454 (s) cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.18–7.13 (m, 16 H), 6.97–6.93 (m, 8 H), 6.83–6.81 (m, 8 H), 2.07 (s, 24 H). ¹³C NMR (100 MHz, CDCl₃) δ 209.7, 136.7, 134.9, 130.8, 129.6, 128.0, 125.9, 114.4, 91.1, 85.9, 83.0, 20.6. APPI HRMS m/z calcd. for C₇₆H₅₆ (M⁺) 968.4377, found 968.4373.

Crystal data for 6: C₇₆H₅₆, M = 969.21; monoclinic crystal system; space group P2₁/c, a = 16.2177(3) Å, b = 9.01016(14) Å, c = 21.3998(4) Å, β = 98.2323(18)°, V = 3094.81(10) Å³, Z = 2, ρcalc = 1.040 mg mm⁻³; μ(CuKα) = 0.444 mm⁻¹; λ = 1.5418 Å; 172.9(3) K; 2θmax = 117.84°; total data collected = 7901; R₁ = 0.0617 [3761 observed reflections with F ≥ 2σ(F)]; wR₂ = 0.1947 for 352 variables, 4392 data, and 1 restraint; residual electron density = 0.44 and –0.28 e Å⁻³. One carbon atom showed disorder, which has been resolved and refined to the following occupation factor C37:C37a = 70:30. CCDC 1402908.
$^1$H and $^{13}$C NMR spectra for new compounds

**Figure S1:** $^1$H NMR spectrum of **S1** in CDCl$_3$, 300 MHz.

**Figure S2:** $^{13}$C NMR spectrum of **S1** in CDCl$_3$, 75 MHz.
Figure S3: $^1$H NMR spectrum of S2 in CDCl$_3$, 300 MHz.

Figure S4: $^{13}$C NMR spectrum of S2 in CDCl$_3$, 75 MHz.
Figure S5: $^1$H NMR spectrum of S3 in CDCl$_3$, 300 MHz.

Figure S6: $^{13}$C NMR spectrum of S3 in CDCl$_3$, 75 MHz.
Figure S7: $^1$H NMR spectrum of [5]Tol in CD$_2$Cl$_2$, 400 MHz.

Figure S8: $^{13}$C NMR spectrum of [5]Tol in CD$_2$Cl$_2$, 100 MHz.
Figure S9: $^1$H NMR spectrum of S4 in CDCl$_3$, 300 MHz.

Figure S10: $^{13}$C NMR spectrum of S4 in CDCl$_3$, 75 MHz.
Figure S11: $^1$H NMR spectrum of S5 in CDCl$_3$, 300 MHz.

Figure S12: $^{13}$C NMR spectrum of S5 in CDCl$_3$, 75 MHz.
Figure S13: $^1$H NMR spectrum of S6 in CDCl$_3$, 300 MHz.

Figure S14: $^{13}$C NMR spectrum of S6 in CDCl$_3$, 75 MHz.
Figure S15: $^1$H NMR spectrum of S7 in CDCl$_3$, 300 MHz.

Figure S16: $^{13}$C NMR spectrum of S7 in CDCl$_3$, 75 MHz.
Figure S17: $^1$H NMR spectrum of S8 in CDCl$_3$, 400 MHz.

Figure S18: $^{13}$C NMR spectrum of S8 in CDCl$_3$, 100 MHz.
Figure S19: $^1$H NMR spectrum of S9 in CDCl$_3$, 300 MHz.

Figure S20: $^1$H NMR spectrum of S9 in CDCl$_3$, 300 MHz.
Figure S21: $^1$H NMR spectrum of [7]Tol in CDCl$_3$, 300 MHz.

Figure S22: $^{13}$C NMR spectrum of [7]Tol in CDCl$_3$, 75 MHz.
Figure S23: $^1$H NMR spectrum of 5 in CDCl$_3$, 300 MHz.

Figure S24: $^{13}$C NMR spectrum of 5 in CDCl$_3$, 75 MHz.
Figure S25: $^1$H NMR spectrum of S10 in CDCl$_3$, 300 MHz.

Figure S26: $^{13}$C NMR spectrum of S10 in CDCl$_3$, 75 MHz.
Figure S27: $^1$H NMR spectrum of 6 in CDCl$_3$, 400 MHz.

Figure S28: $^{13}$C NMR spectrum of 6 in CDCl$_3$, 100 MHz.
UV/Vis absorption spectra

Figure S29: Quantitative UV/Vis spectrum of [5]Tol in CH$_2$Cl$_2$.

Figure S30: Qualitative UV/Vis spectrum of [7]Tol in CH$_2$Cl$_2$. 
Figure S31: Qualitative UV/Vis spectrum of [9]Tol in CH₂Cl₂.

Figure S32: Qualitative UV/Vis spectrum of 5 in CH₂Cl₂.
Figure S33: Qualitative UV/Vis spectrum of 6 in CH$_2$Cl$_2$. 