Electronic Supplementary Material (ESI) for Chemical Communications.
This journal is © The Royal Society of Chemistry 2015

Electronic Supporting Information for

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

Dominik Wendinger,[a] Johanna A. Januszewski,[a] Frank Hampel,[a] and Rik R. Tykwinski*[a]

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

General Experimental

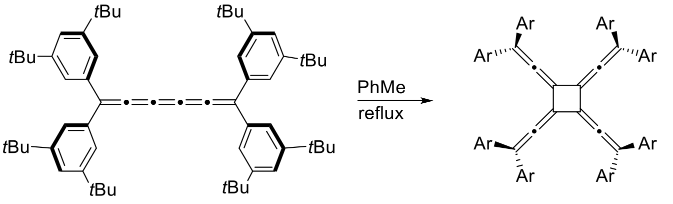
a. Chemicals

All chemicals were purchased from commercial suppliers and used as received. THF and Et_2O were distilled from sodium/benzophenone, and CH_2Cl_2 was distilled from CaH_2. Na_2SO_4 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 (^{1}H NMR) and 75 MHz (^{13}C NMR), or a Bruker Avance 400 operating at 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR), at rt, if not otherwise specified. Signals were referenced to residual solvent peaks (δ in parts per million (ppm) ^{1}H: $CDCl_3$, 7.24 ppm, CD_2Cl_2: 5.32 ppm; ^{13}C: $CDCl_3$, 77.0 ppm, CD_2Cl_2: 53.8 ppm) and recorded at ambient probe temperature. Coupling constants were assigned as observed. $CDCl_3$ (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



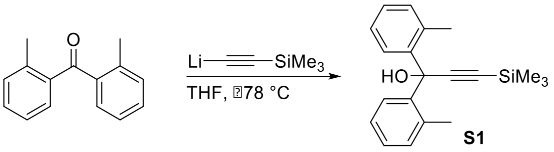
[5]*t*BuPh

4a Ar = 3,5-$(tBu)_2C_6H_3$

1,2,3,4-Tetrakis(2,2-bis(3,5-di-*t*-butylphenyl)vinylidene)cyclobutane (4a)

[5]*t*BuPh[1] (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_2Cl_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_2Cl_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) Å, b = 19.3824(4) Å, c = 14.8604(7) Å, V = 5582.8(3) Å^3, Z = 2, ρ_{calcd} = 0.987 mg mm^{-3}; μ(CuKα) = 0.403 mm^{-1}; λ = 1.5418 Å; 172.9(3) K; 2θ max = 102.76°; total data collected = 5632; R_1 = 0.0759 [2509 observed reflections with $F \geq \varepsilon\ 2\sigma(F)$]; wR_2 = 0.2091 for 294 variables, 2972 data, and 46 restraints; residual electron density = 0.41 and –0.32 e 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.



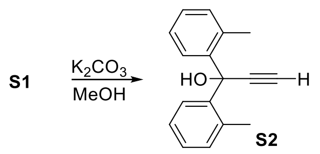
1,1-Di-*o*-tolyl-3-(trimethylsilyl)prop-2-yn-1-ol (S1)

To a solution of trimethylsilylacetylene (0.687 g, 1.00 mL, 7.00 mmol) in THF (15 mL) at −78 °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_4Cl (40 mL), and Et_2O

---

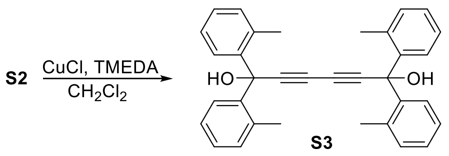
[1] For the synthesis of **[5]*t*BuPh** see: J. A. Januszewski, D. Wendinger, C. D. Methfessel, F. Hampel and R. R. Tykwinski, *Angew. Chem., Int. Ed.*, 2013, **52**, 1817; *Angew. Chem.*, 2013, **125**, 1862.

(60 mL) was added. The layers were separated, the organic phase was washed with saturated aq NaCl (60 mL), dried (Na_2SO_4), and filtered. Solvent removal afforded **S1** (1.88 g, 100%) as a colorless solid. Mp 71 °C. R_f = 0.49 (hexanes/CH_2Cl_2 1:2). IR (ATR) 3581 (m), 2957 (m), 2160 (w), 1455 (m), 1247 (m), 1162 (m), 1039 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 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); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.7, 136.5, 132.2, 127.9, 127.2, 125.4, 106.8, 92.3, 74.8, 21.2, –0.2. EI MS *m/z* 308 (M^+, 10), 217 ($[M - o\text{-Tol}]^+$, 100); EI HRMS *m/z* calcd. for $C_{20}H_{24}OSi$ (M^+) 308.1591, found 308.1574.



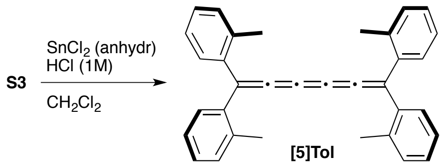
1,1-Di-*o*-tolylprop-2-yn-1-ol (S2)

To a solution of **S1** (1.82 g, 5.89 mmol) in MeOH (50 mL) was added K_2CO_3 (0.81 g, 5.9 mmol). After stirring for 1 h, the reaction mixture was quenched via the addition of saturated aq NH_4Cl (30 mL), and CH_2Cl_2 (50 mL) was added. The layers were separated, the organic phase was washed with saturated aq NH_4Cl (40 mL) and saturated aq NaCl (40 mL), dried (Na_2SO_4), and filtered. Solvent removal afforded **S2** (1.19 g, 85%) as a colorless oil. R_f = 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, $CDCl_3$) 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); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.5, 136.2, 132.2, 128.1, 127.2, 125.5, 85.4, 76.0, 74.7, 21.1. EI MS *m/z* 236 (M^+, 21), 195 (M^+, 100); EI HRMS *m/z* calcd. for $C_{17}H_{16}O$ (M^+) 236.1196, found 236.1188.



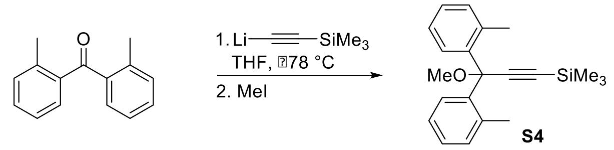
1,1,6,6-Tetra-*o*-tolylhexa-2,4-diyne-1,6-diol (S3)

To a solution of **S2** (1.12 g, 4.74 mmol) in CH_2Cl_2 (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 CH_2Cl_2 (20 mL)]. The reaction mixture was stirred for 3 h, saturated aq NH_4Cl (50 mL) was added, and the mixture was extracted with CH_2Cl_2 (50 mL). The organic phase was washed with saturated aq NH_4Cl (100 mL) and saturated aq NaCl (100 mL), dried (Na_2SO_4), and filtered. Solvent removal and purification via column chromatography (silica, hexanes/CH_2Cl_2 1:2) afforded **S3** (557 mg, 50%) as a colorless solid. Mp 150 °C. R_f = 0.09 (hexanes/CH_2Cl_2 1:2). IR (ATR) 3515 (m), 3407 (br), 2961 (w), 2208 (w), 1456 (m), 1356 (w), 1028 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 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); ^{13}C NMR (75 MHz, $CDCl_3$) 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 $C_{34}H_{30}O_2$ (M^+) 470.2240 , found $C_{34}H_{30}O_2$ 470.2244.



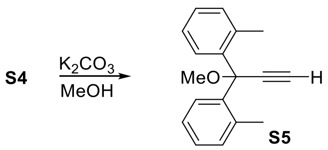
1,1,6,6-Tetra-*o*-tolylhexa-1,2,3,4,5-pentaene ([5]Tol)

To a solution of **S3** (1.80 g, 3.83 mmol) in CH_2Cl_2 (100 mL) was added $SnCl_2$ (1.45 g, 7.65 mmol) and HCl (1 M in Et_2O, 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 CH_2Cl_2, affording **[5]Tol** (1.54 g, 92%) as an orange solid. Mp 165 °C (decomp). R_f = 0.51 (hexanes/EtOAc 20:1). UV-Vis (CH_2Cl_2) λ_{max} 267 (42200), 361 (12000), 460 (47100) nm; IR (ATR) 3054 (vw), 3007 (vw), 2957 (m), 2161 (m), 1990 (m), 1451 (s) cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2) δ 7.24–7.22 (m, 8 H), 7.17–7.15 (m, 8 H), 2.31 (s, 12 H); ^{13}C NMR (100 MHz, CD_2Cl_2) 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 $C_{34}H_{29}$ (M^+) 437.2264, found 437.2267.



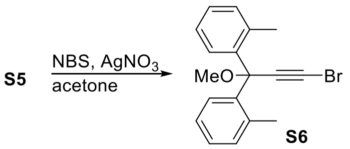
(3-Methoxy-3,3-di-*o*-tolylprop-1-yn-1-yl)trimethylsilane (S4)

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 N_2 atmosphere via a syringe. The reaction mixture was stirred for 60 min and a solution of di-*o*-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 NH_4Cl (80 mL), and Et_2O (60 mL) was added. The layers were separated, the organic phase was washed with saturated aq NaCl (60 mL), dried (Na_2SO_4), and filtered. Solvent removal and purification via column chromatography (silica, hexanes/CH_2Cl_2 1:2) afforded **S4** (3.53 g, 92%) as a colorless oil. R_f = 0.70 (hexanes/CH_2Cl_2 1:2). IR (ATR) 2957 (m), 2822 (w), 2155 (w), 1458 (m), 1249 (m), 1070 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 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); ^{13}C NMR (75 MHz, $CDCl_3$) 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 $C_{21}H_{26}OSi$ (M^+) 322.1743, found 322.1743.



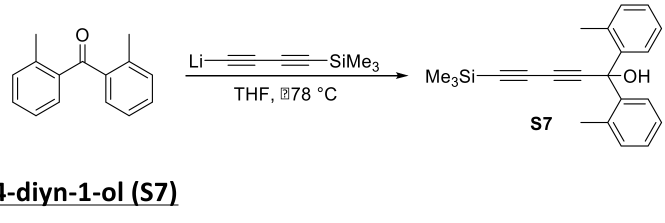
2,2'-(1-Methoxyprop-2-yne-1,1-diyl)bis(methylbenzene) (S5)

To a solution of **S4** (4.39 g, 13.6 mmol) in MeOH (80 mL) was added K_2CO_3 (1.88 g, 13.6 mmol). After stirring for 30 min, the reaction mixture was quenched via the addition of saturated aq NH_4Cl (30 mL), and CH_2Cl_2 (50 mL) was added. The layers were separated, the organic phase was washed with saturated aq NH_4Cl (40 mL) and saturated aq NaCl (40 mL), dried (Na_2SO_4), and filtered. Solvent removal afforded **S5** (2.98 g, 88%) as a colorless solid. Mp 48 °C. R_f = 0.34 (hexanes). IR (ATR) 3266 (s), 3060 (vw), 2932 (m), 1457 (s), 1069 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 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); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.8, 136.7, 132.1, 128.6, 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); EI HRMS *m/z* calcd. for $C_{18}H_{18}O$ (M$^+$) 250.1358, found 250.1349.



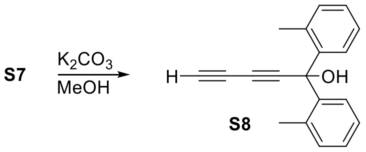
2,2'-(3-Bromo-1-methoxyprop-2-yne-1,1-diyl)bis(methylbenzene) (S6)

To a solution of **S5** (1.67 g, 6.67 mmol) in acetone (20 mL) were added $AgNO_3$ (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 Et_2O (20 mL) was added. The organic phase was separated, dried (Na_2SO_4), and filtered. Solvent removal afforded **S6** as a pale yellow solid (2.17 g, 99%). Mp 74 °C. R_f = 0.55 (hexanes/EtOAc 20:1). IR (ATR) 3060 (w) 2925 (m), 2198 (w), 1932 (m), 1454 (s), 1161 (s), 1068 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 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); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 136.8, 132.2, 128.6, 128.0, 125.2, 82.1, 79.1, 51.6, 48.9, 21.1. ESI HRMS calcd. for $C_{18}H_{17}{}^{79}BrNaO$ (M$^+$) 351.0355, found 351.0354.



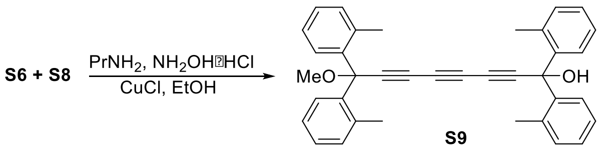
1,1-Bi-*o*-tolylpenta-2,4-diyn-1-ol (S7)

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 Et_2O, 10.4 mL, 15.6 mmol) under a N_2 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*-tolylmethanone (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 NH_4Cl (70 mL), and Et_2O (50 mL) was added. The layers were separated, the organic phase was dried (Na_2SO_4), 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. R_f = 0.17 (hexanes/EtOAc 20:1). IR (ATR) 3522 (s), 2958 (m), 2095 (m), 1249 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 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); ^{13}C NMR (75 MHz, $CDCl_3$) 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. EI MS *m/z* 332 (M^+, 42), 73 ($SiMe_3$, 100), EI HRMS *m/z* calcd. for $C_{22}H_{24}OSi$ (M^+) 332.1596, found 332.1586.



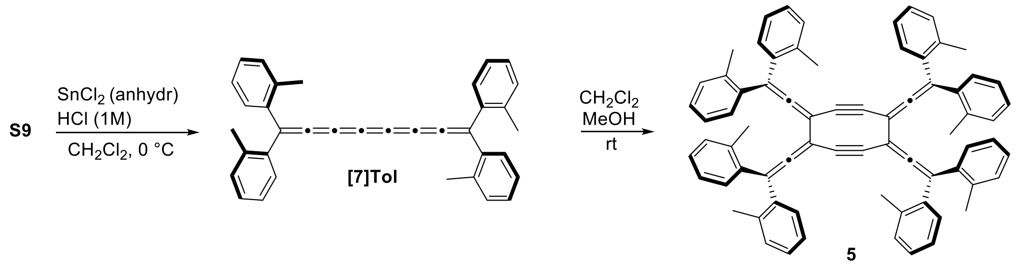
1,1-Di-*o*-tolylpenta-2,4-diyn-1-ol (S8)

To a solution of **S7** (1.0 g, 3.0 mmol) in MeOH (40 mL) was added K_2CO_3 (0.42 g, 3.0 mmol). The reaction mixture was stirred for 30 min and quenched via the addition of saturated aq NH_4Cl (40 mL). The layers were separated, and the aqueous phase was extracted with CH_2Cl_2 (2 x 20 mL). The organic phases were combined and washed with saturated aq NH_4Cl (30 mL) and saturated aq NaCl (30 mL), dried (Na_2SO_4), and filtered. Solvent removal and recrystallization from hexanes afforded **S8** (442 mg, 56%) as a colorless solid. Mp 68 °C. R_f = 0.42 (hexanes/CH_2Cl_2 1:2). IR (ATR) 3517 (m), 3388 (br), 3284 (m), 3056 (vw), 2928 (vw), 1967 (w), 1457 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{19}H_{16}NaO$ ($[M + Na]^+$) 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 $NH_2(OH)\bullet HCl$ (0.708 g, 10.2 mmol) and *n*$PrNH_2$ (1.21 g, 1.67 mL, 20.4 mmol), and the solution was then purged with N_2 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 N_2 for 10 min and stirred for 1 h at rt. The reaction was quenched via addition of water (50 mL), and Et_2O (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_2SO_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), 2042 (m), 1458 (m), 1064 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.83–7.72 (m, 4 H), 7.27–7.18 (m, 8 H), 7.13–7.08 (m, 4 H), 3.25 (s, 3 H), 2.71 (s, 1 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, 128.6, 128.4, 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)

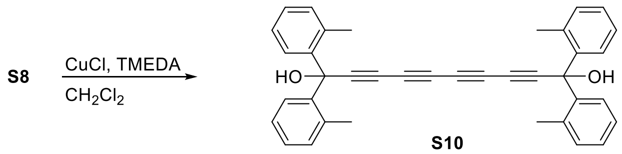
To a solution of **S9** (0.200 g, 0.393 mmol) in CH_2Cl_2 (15 mL) was added anhydrous $SnCl_2$ (224 mg, 1.18 mmol) and HCl (1 M in Et_2O, 1.6 mL, 1.6 mmol) at 0 °C under a N_2 atmosphere. After 30 min, the solution was filtered through a plug of basic alumina oxide and eluted with CH_2Cl_2 affording 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_2Cl_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_2Cl_2) λ_{max} 297, 319, 444, 516 nm. IR (ATR) 3059 (m), 2966 (m), 2848 (m), 2059 (s), 1606 (s), 1442 (s) cm^{-1}; ^1H 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*-tolylvinylidene)cycloocta-1,5-diyne (5)

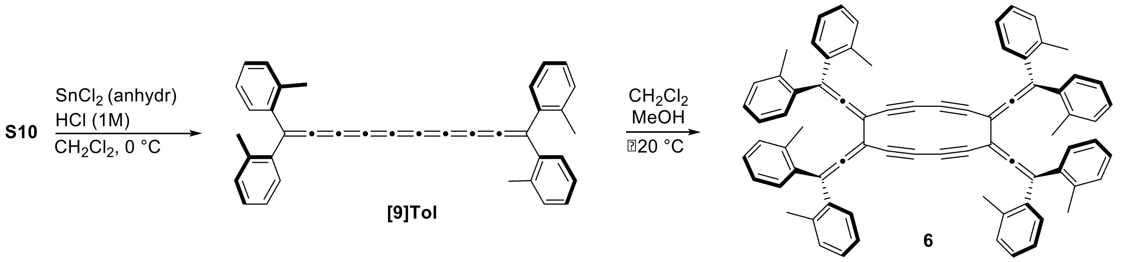
Mp 190 °C (decolorization). R_f = 0.34 (hexanes/EtOAc 20:1). UV-Vis (CH_2Cl_2) λ_{max} 228, 275 nm. IR 3062 (w), 3014 (w), 2947 (w), 2914 (w), 2177 (w), 1594 (m), 1483 (s), 1444 (s), 1265 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.17–7.10 (m, 16 H), 6.97–6.92 (m, 8 H), 6.84–6.82 (m, 8 H). ^{13}C NMR (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**: $C_{72}H_{56}\bullet 2CH_2Cl_2$, M = 1091.02; triclinic crystal system; space group P-1, a = 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) Å^3, Z = 1, ρ_{calcd} = 1.249 mg mm^{-3}; μ(CuKα) = 2.181 mm^{-1}; λ = 1.5418 Å; 173 K; 2θ max = 123.92°; total data collected = 6450; R_1 = 0.0529 [3828 observed reflections with $F \geq \varepsilon\ 2\sigma(F)$]; wR_2 = 0.1474 for 356 variables, 4350 data, and 0 restraints; residual electron density = 0.43 and –0.54 e Å^{-3}. 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_2Cl_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_2Cl_2 (20 mL)]. The reaction mixture was stirred for 3 h, saturated aq NH_4Cl (50 mL) was added, and the mixture was extracted with CH_2Cl_2 (50 mL). The organic phase was washed with saturated aq NH_4Cl (100 mL) and saturated aq NaCl (100 mL), dried (Na_2SO_4), and filtered. Solvent removal and purification via column chromatography (silica, hexanes/CH_2Cl_2 1:2) afforded **S10** (285 mg, 65%) as an off-white solid. Mp 150 °C. R_f = 0.17 (hexanes/CH_2Cl_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, $CDCl_3$) δ 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, $CDCl_3$) δ 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_2Cl_2 (15 mL) was added anhydrous $SnCl_2$ (209 mg, 1.10 mmol) and HCl (1 M in Et_2O, 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_2Cl_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_2Cl_2 (10 mL), filtered through a short plug of silica, and recrystallized from

CH_2Cl_2/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. R_f = 0.78 (hexanes/CH_2Cl_2 1:2). UV-Vis (CH_2Cl_2) λ_{max} 339, 368, 514, 555, 661 nm.

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

R_f = 0.29 (hexanes/EtOAc 20:1) UV-Vis (CH_2Cl_2) λ_{max} 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, $CDCl_3$) 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). ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{76}H_{56}$ (M^+) 968.4377, found 968.4373.

Crystal data for **6**: $C_{76}H_{56}$, M = 969.21; monoclinic crystal system; space group $P2_1/c$, a = 16.2177(3) Å, b = 9.01016(14) Å, c = 21.3998(4) Å, β = 98.2323(18)°, V = 3094.81(10) $Å^3$, Z = 2, ρ_{calcd} = 1.040 mg mm^{-3}; μ(Cu$K\alpha$) = 0.444 mm^{-1}; λ = 1.5418 Å; 172.9(3) K; $2\theta_{max}$ = 117.84°; total data collected = 7901; R_1 = 0.0617 [3761 observed reflections with $F \geq \varepsilon\ 2\sigma(F)$]; wR_2 = 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

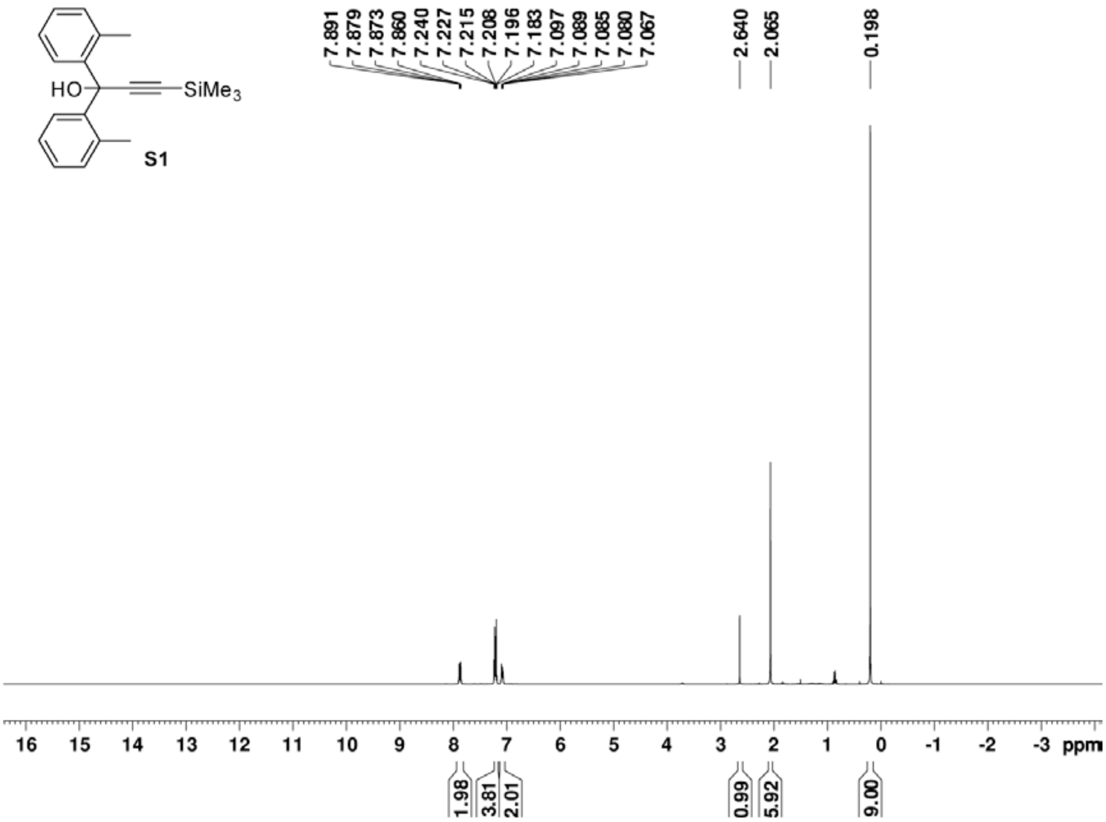


Figure S1: ^{1}H NMR spectrum of **S1** in $CDCl_3$, 300 MHz.

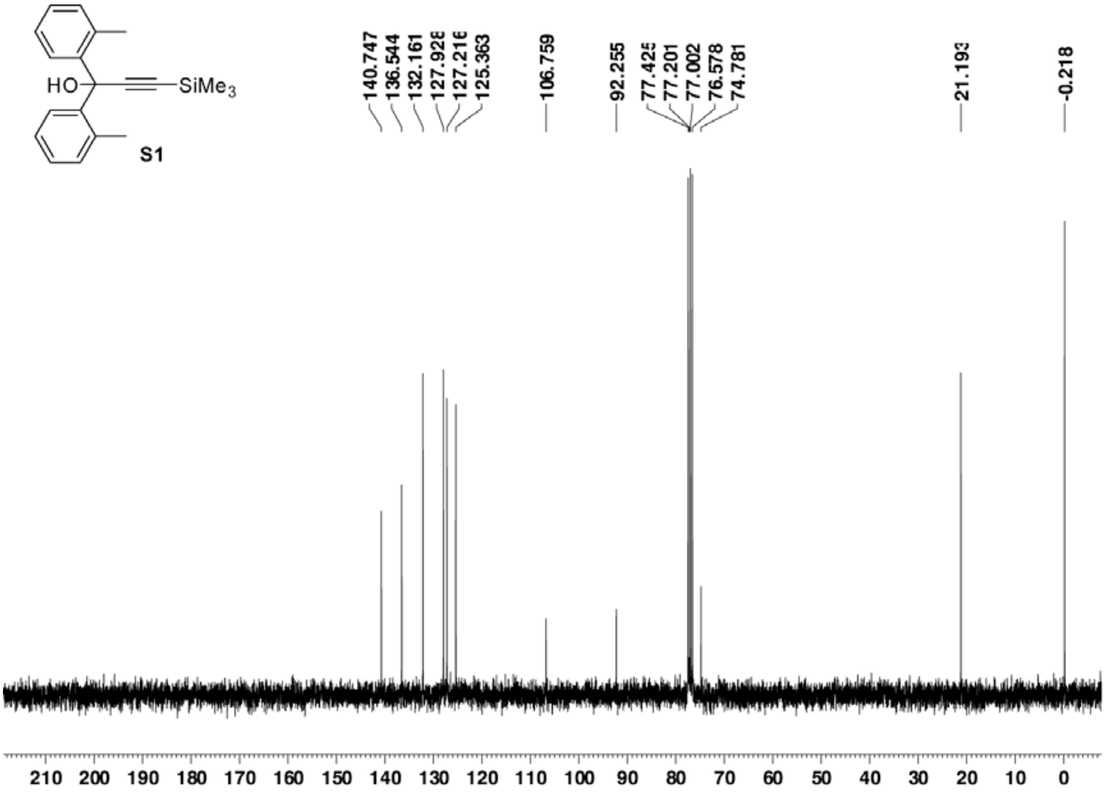


Figure S2: ^{13}C NMR spectrum of **S1** in $CDCl_3$, 75 MHz.

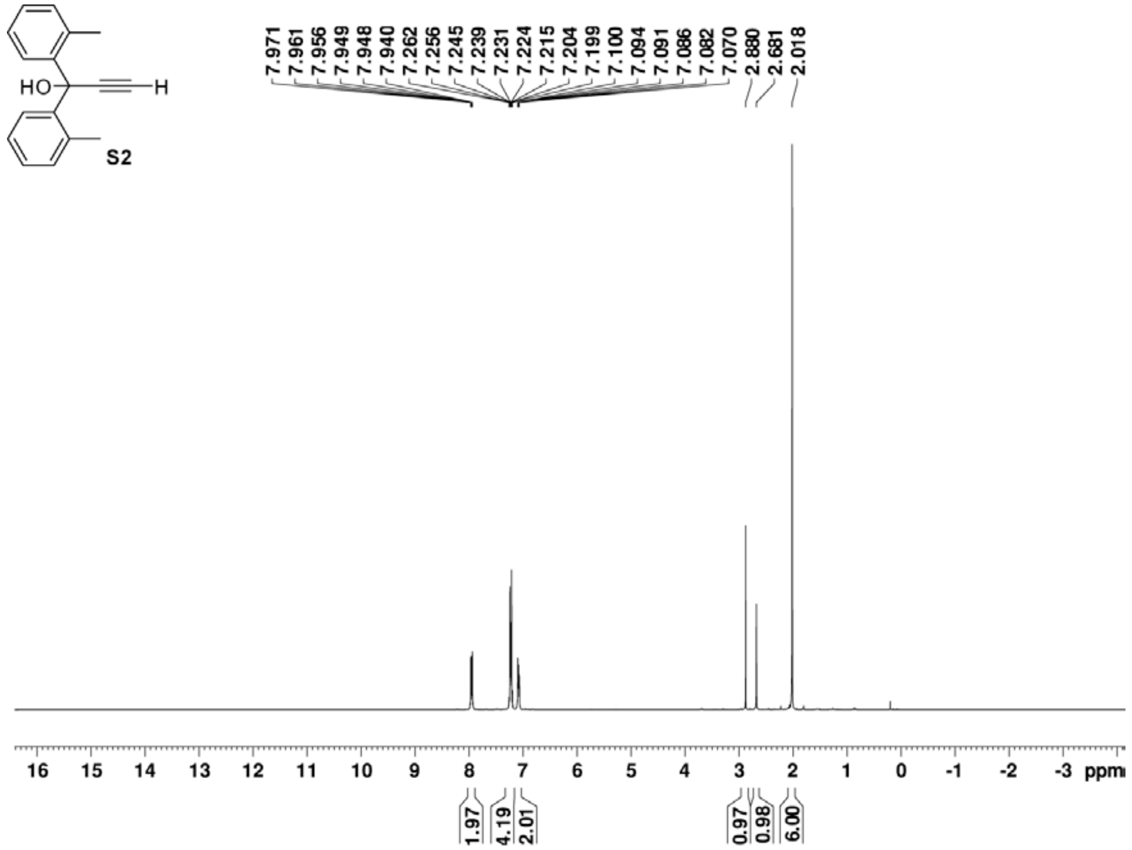


Figure S3: ^{1}H NMR spectrum of **S2** in CDCl$_3$, 300 MHz.

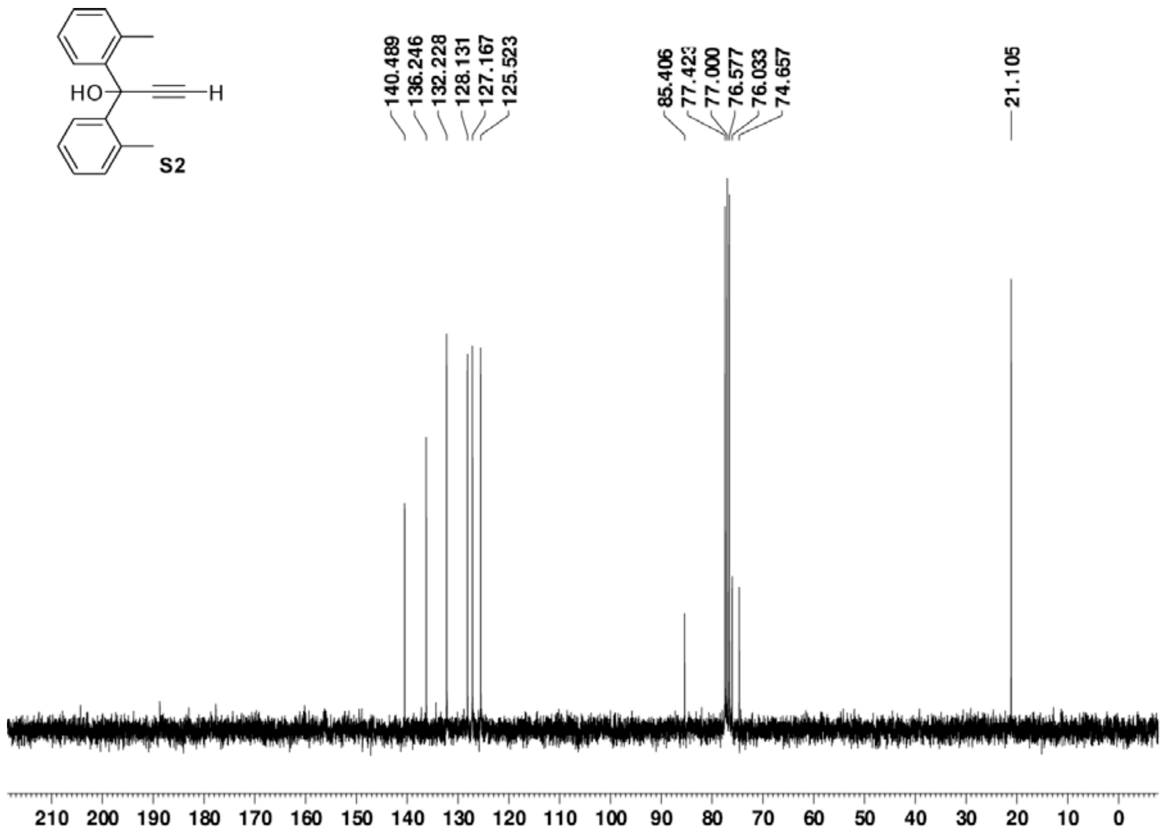


Figure S4: ^{13}C NMR spectrum of **S2** in CDCl$_3$, 75 MHz.

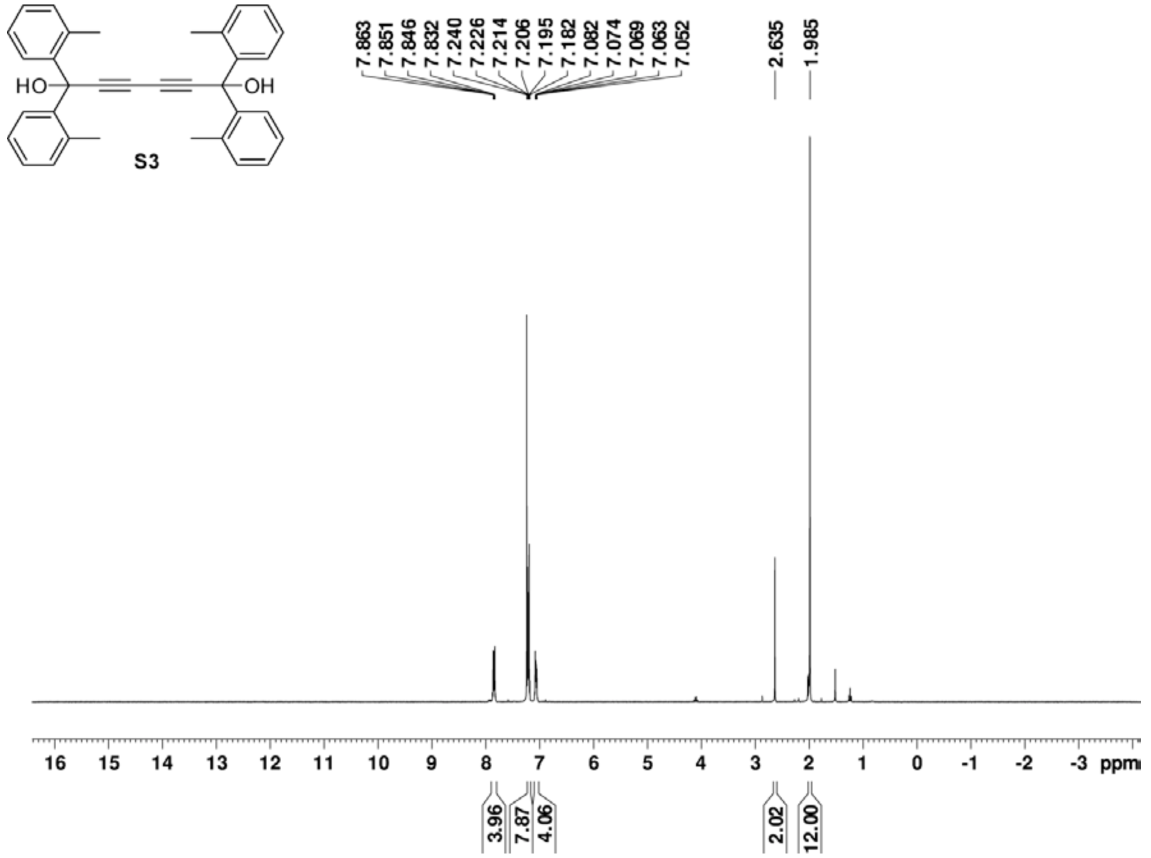


Figure S5: ^{1}H NMR spectrum of **S3** in $CDCl_3$, 300 MHz.

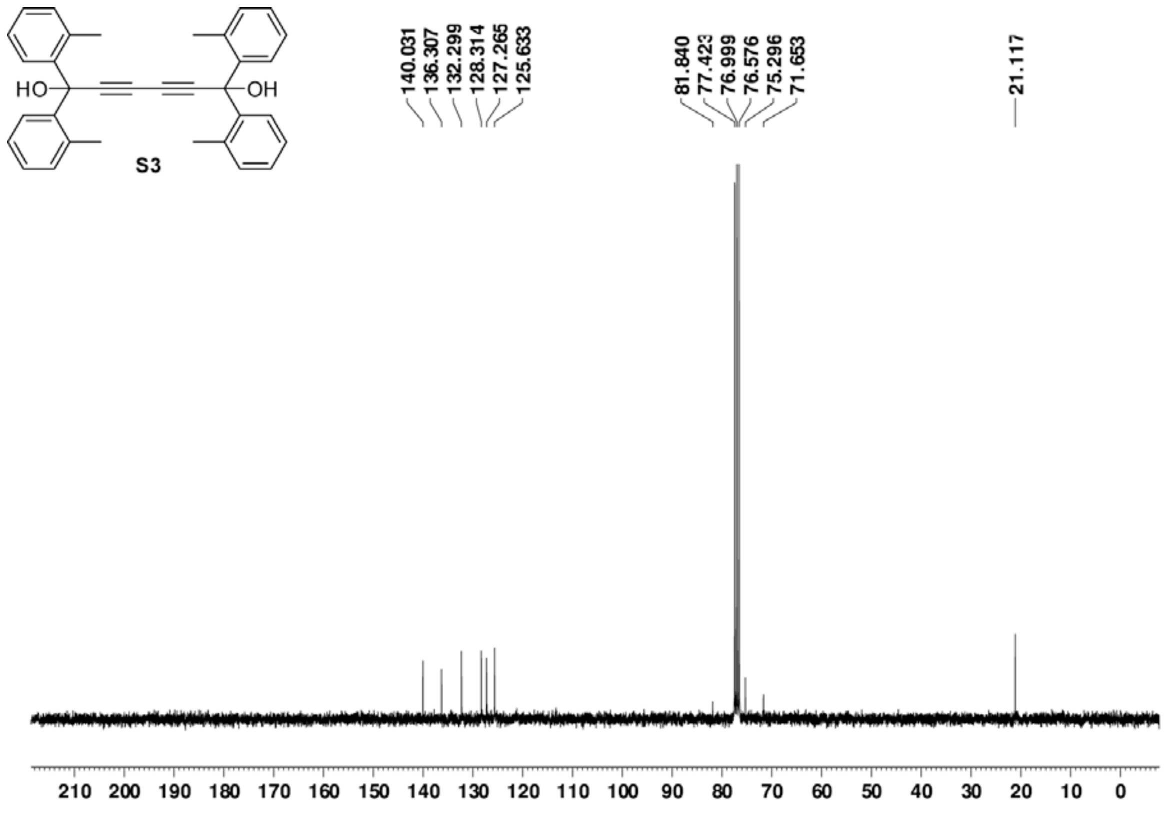


Figure S6: ^{13}C NMR spectrum of **S3** in $CDCl_3$, 75 MHz.

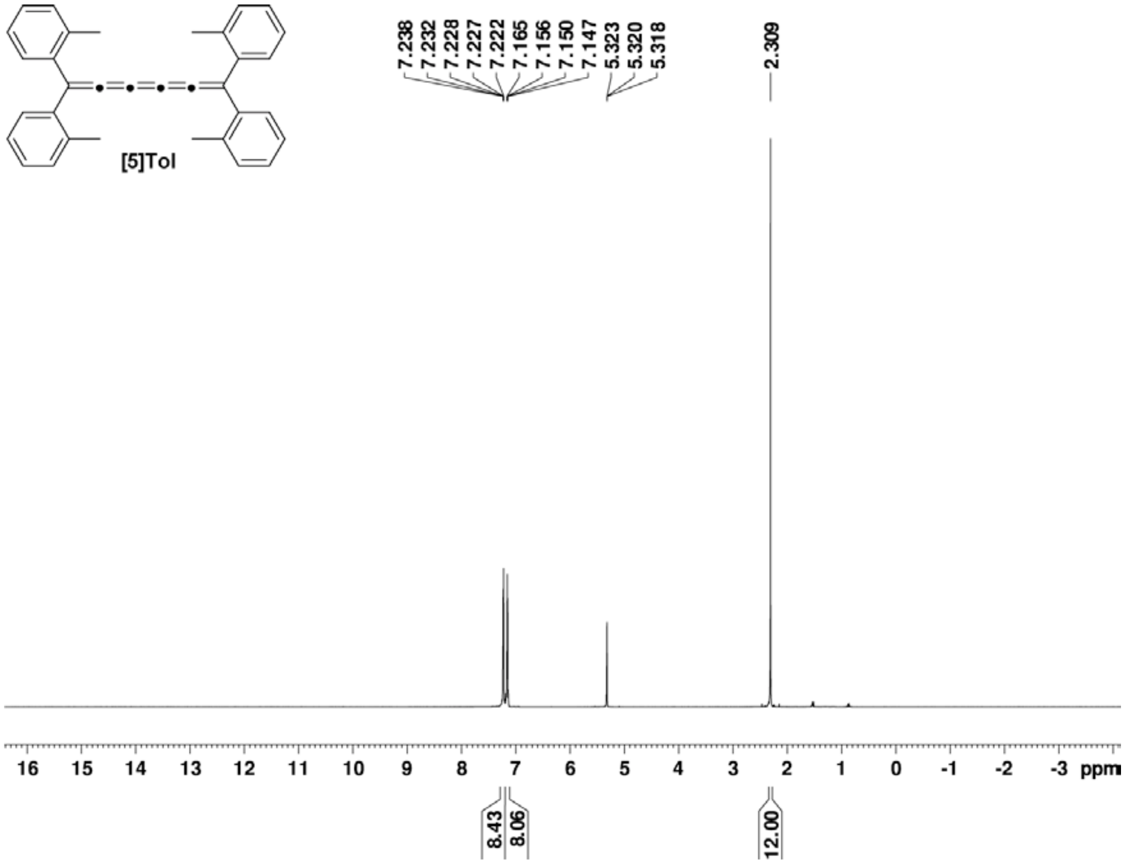


Figure S7: ^{1}H NMR spectrum of **[5]Tol** in CD_2Cl_2, 400 MHz.

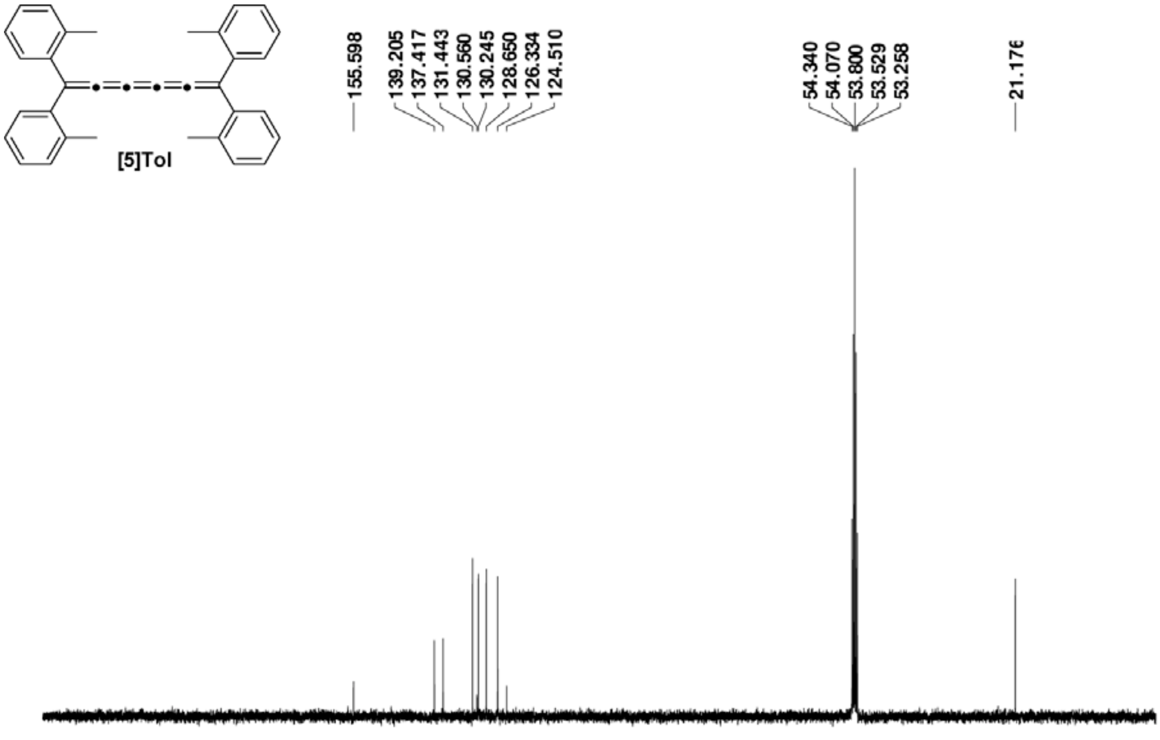


Figure S8: ^{13}C NMR spectrum of **[5]Tol** in CD_2Cl_2, 100 MHz.

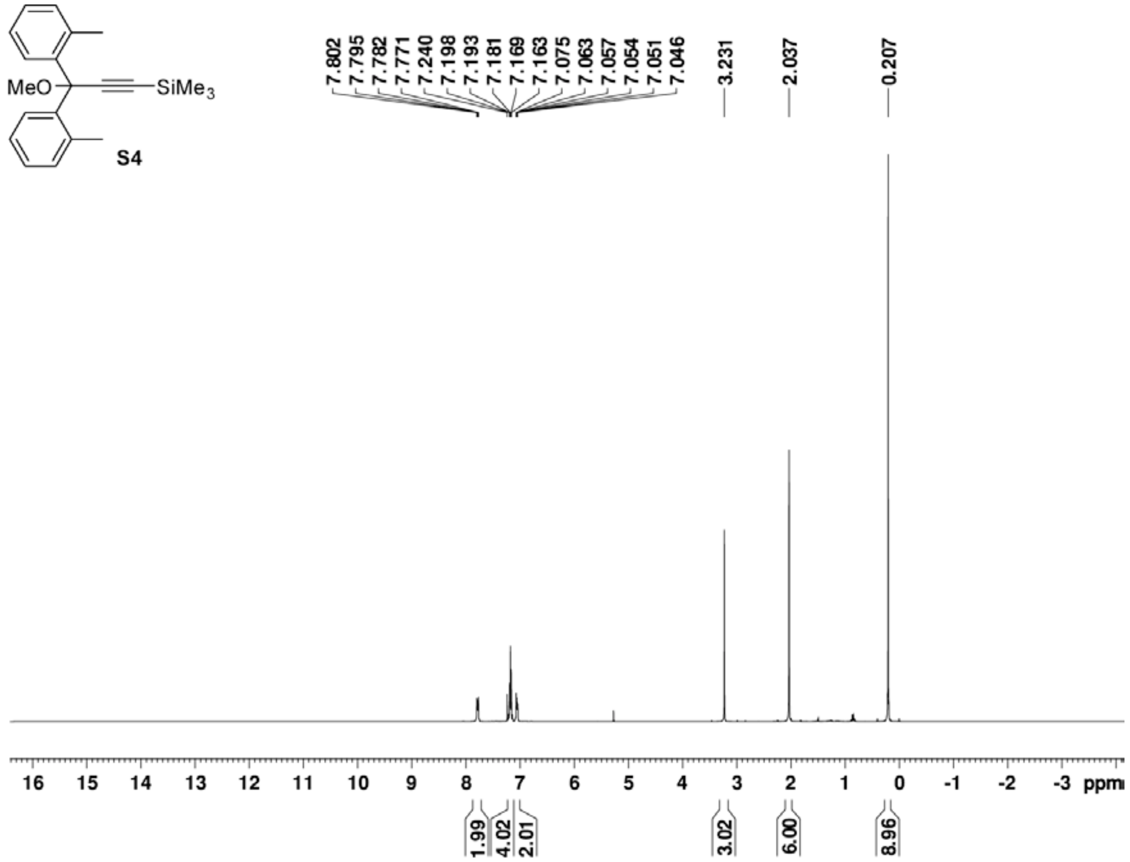


Figure S9: ^{1}H NMR spectrum of **S4** in $CDCl_3$, 300 MHz.

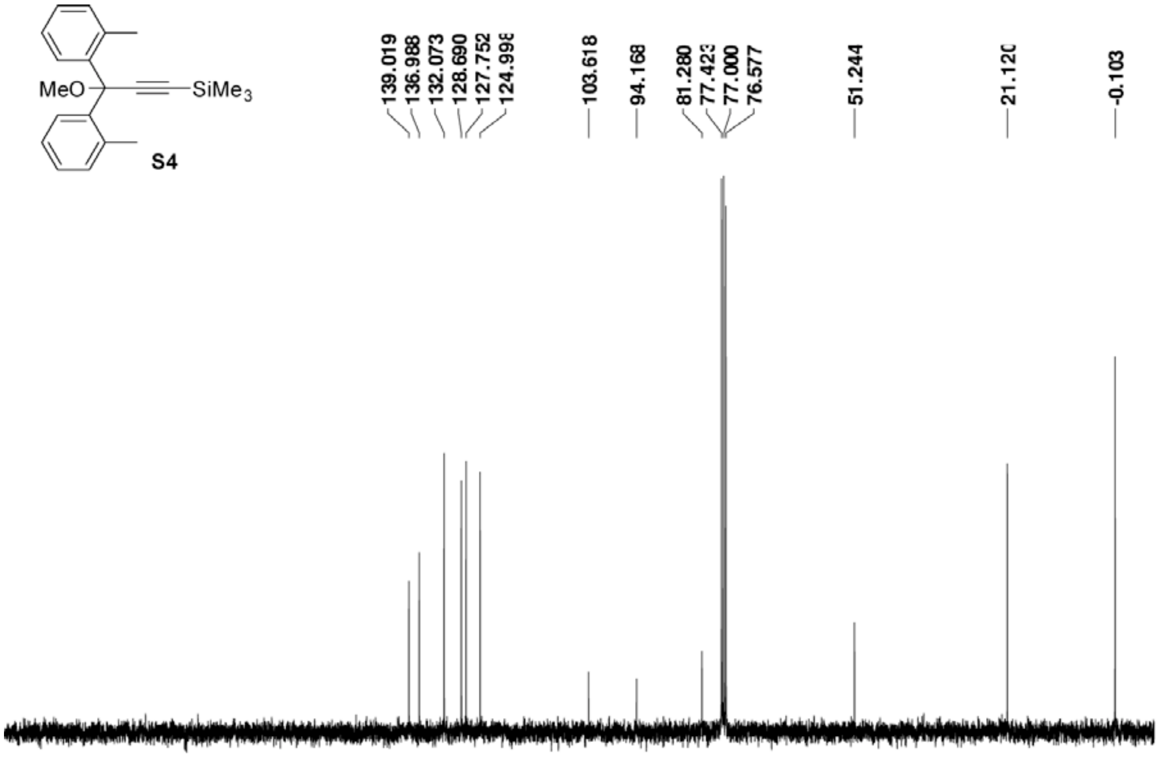


Figure S10: ^{13}C NMR spectrum of **S4** in $CDCl_3$, 75 MHz.

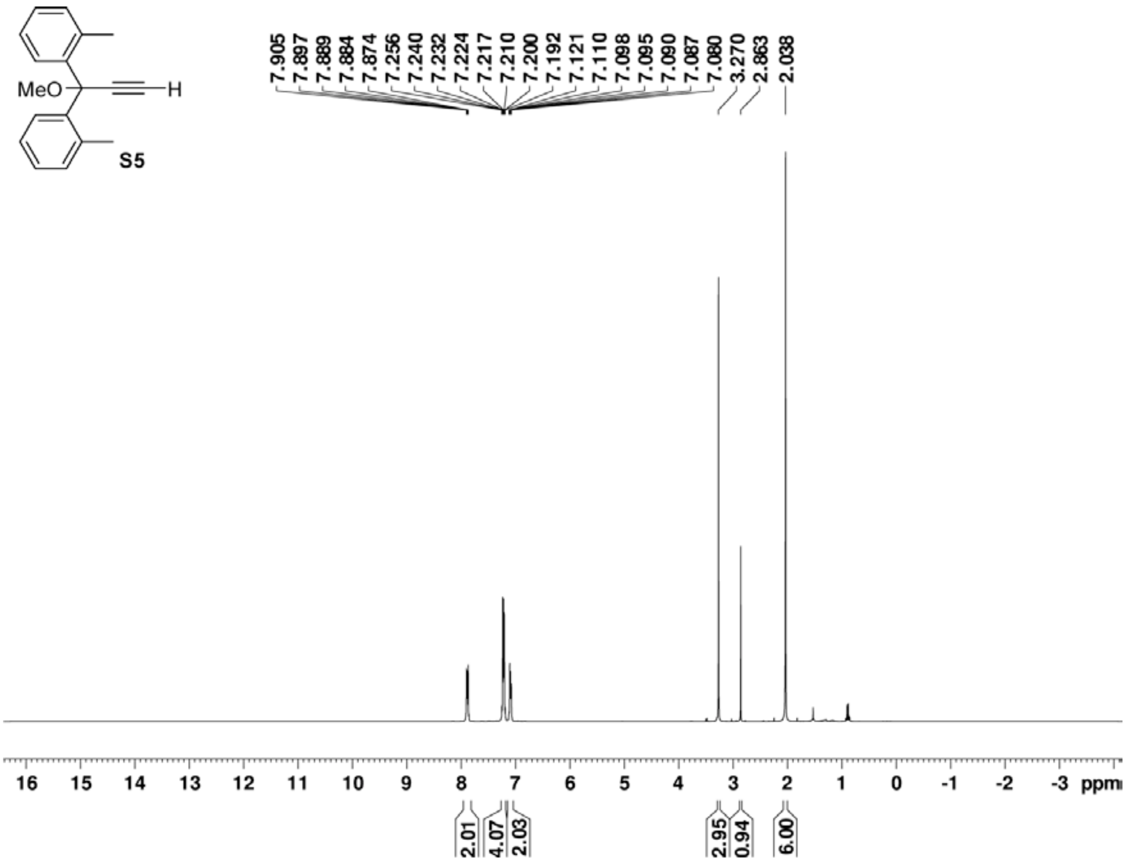


Figure S11: ^{1}H NMR spectrum of **S5** in CDCl$_3$, 300 MHz.

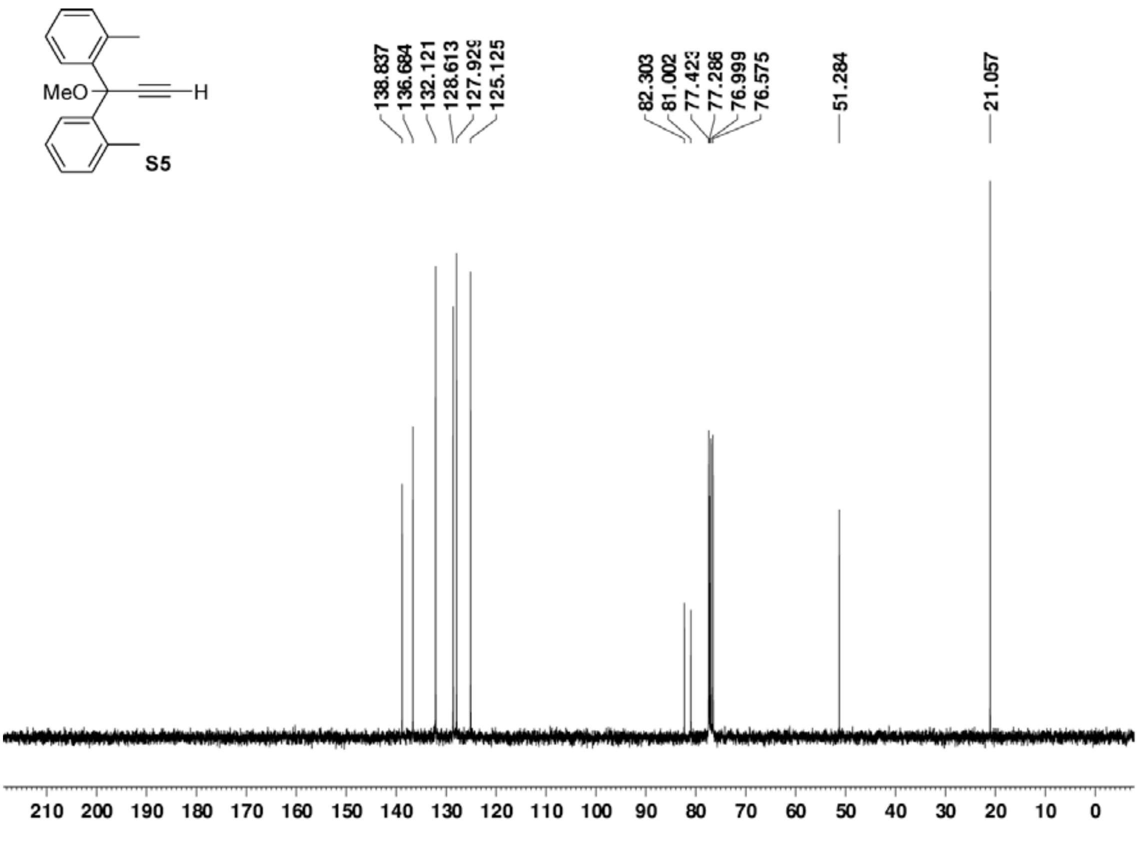


Figure S12: ^{13}C NMR spectrum of **S5** in CDCl$_3$, 75 MHz.

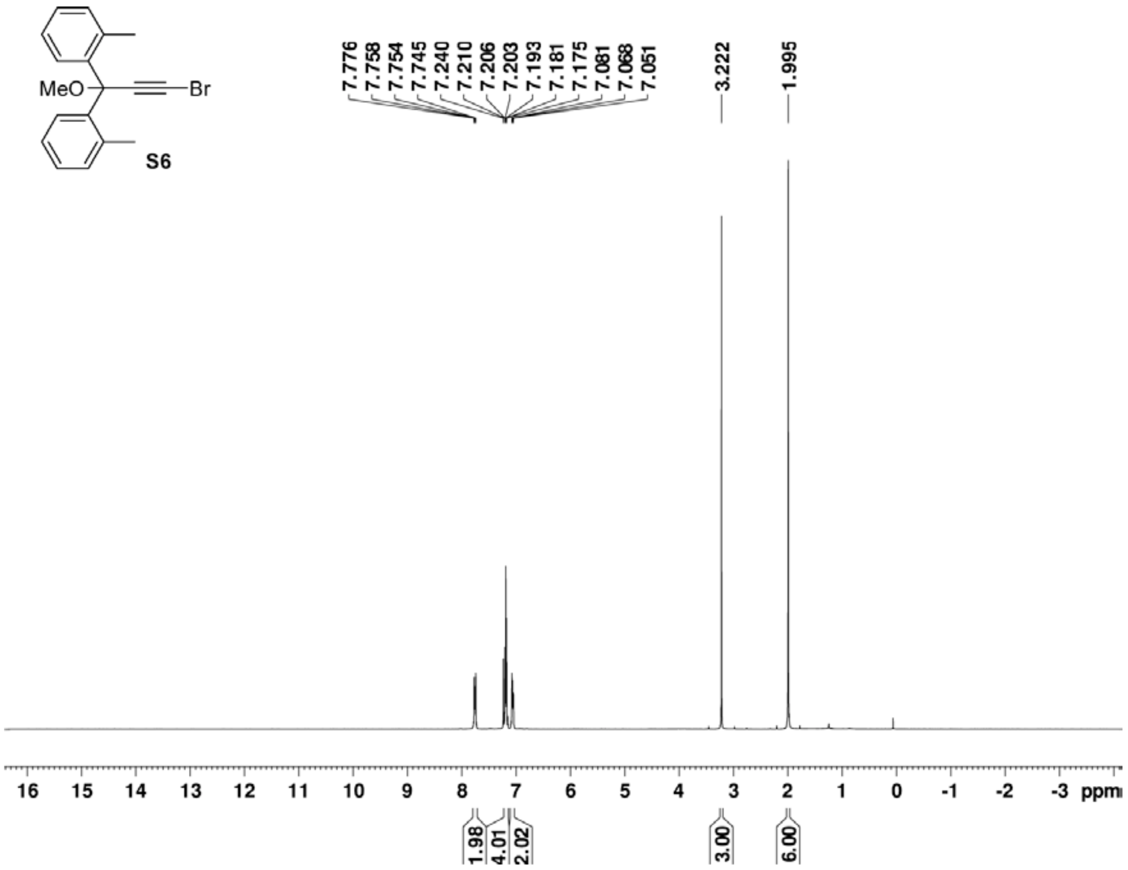


Figure S13: ^{1}H NMR spectrum of **S6** in CDCl$_3$, 300 MHz.

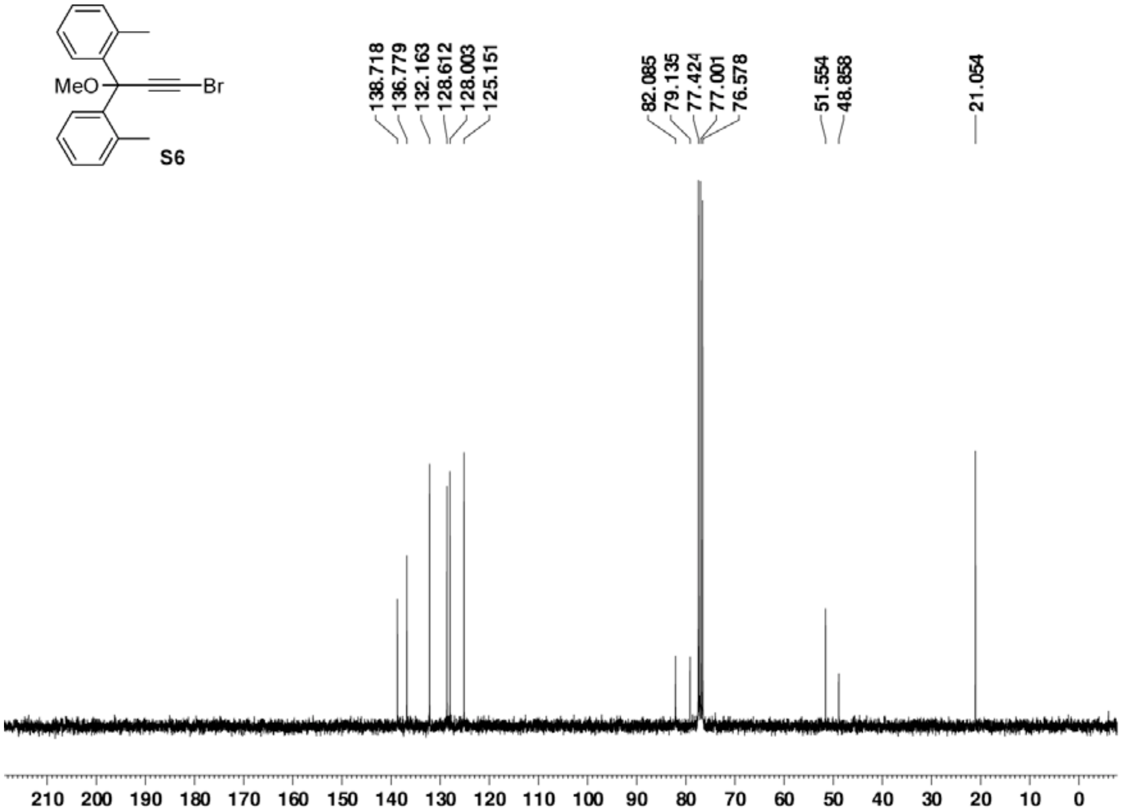


Figure S14: ^{13}C NMR spectrum of **S6** in CDCl$_3$, 75 MHz.

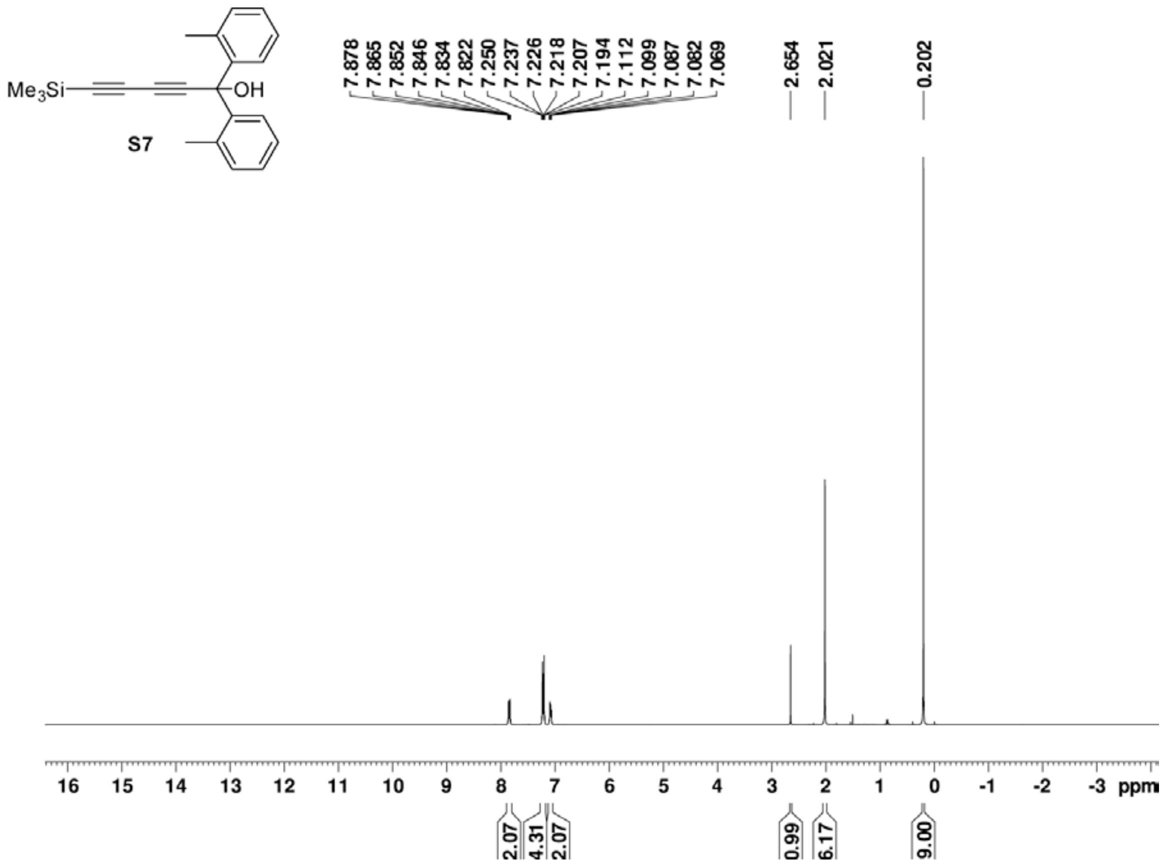


Figure S15: ^{1}H NMR spectrum of **S7** in CDCl$_3$, 300 MHz.

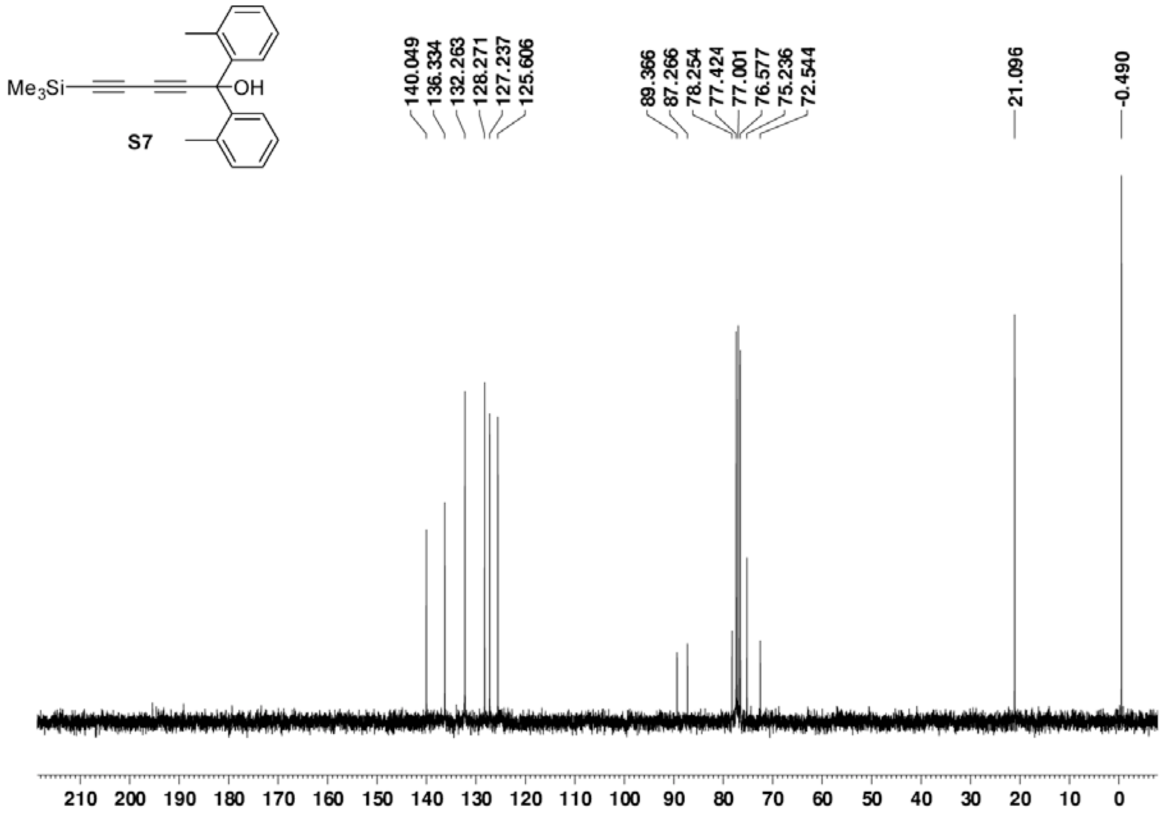


Figure S16: ^{13}C NMR spectrum of **S7** in CDCl$_3$, 75 MHz.

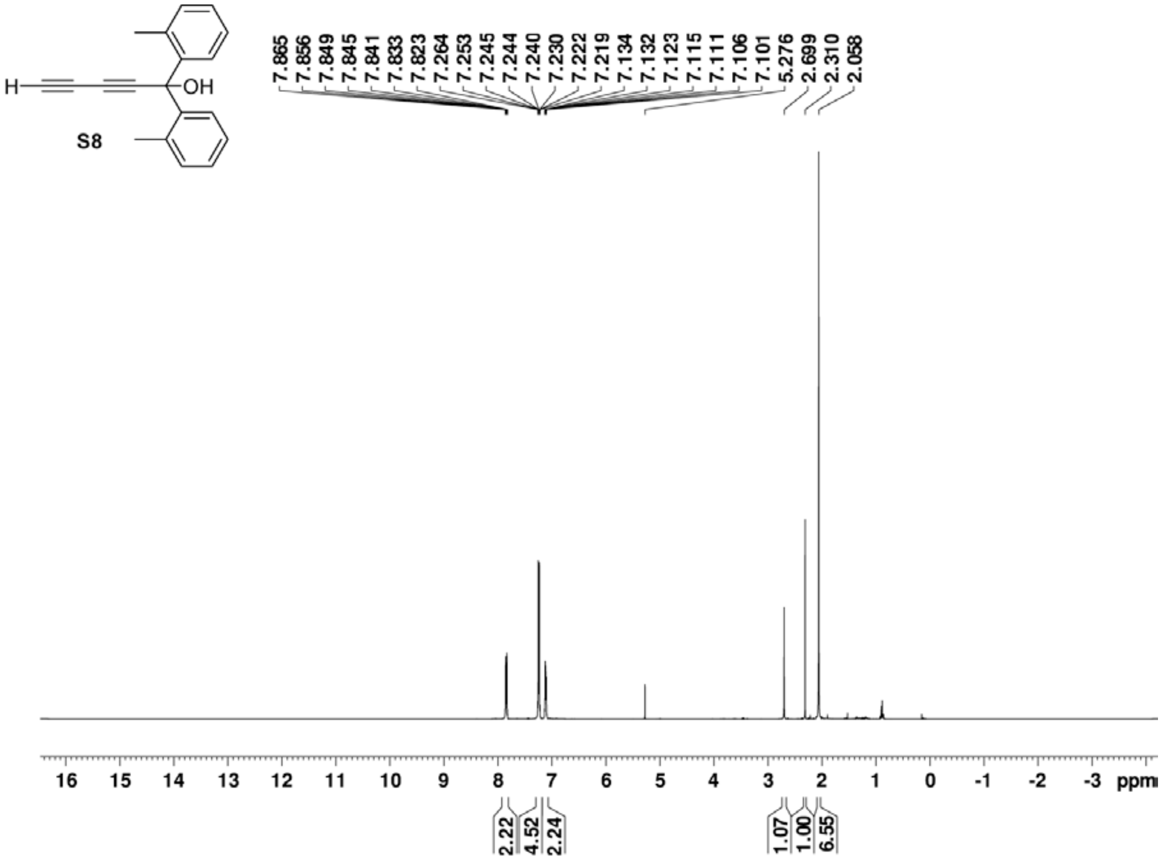


Figure S17: ^1H NMR spectrum of **S8** in $CDCl_3$, 400 MHz.

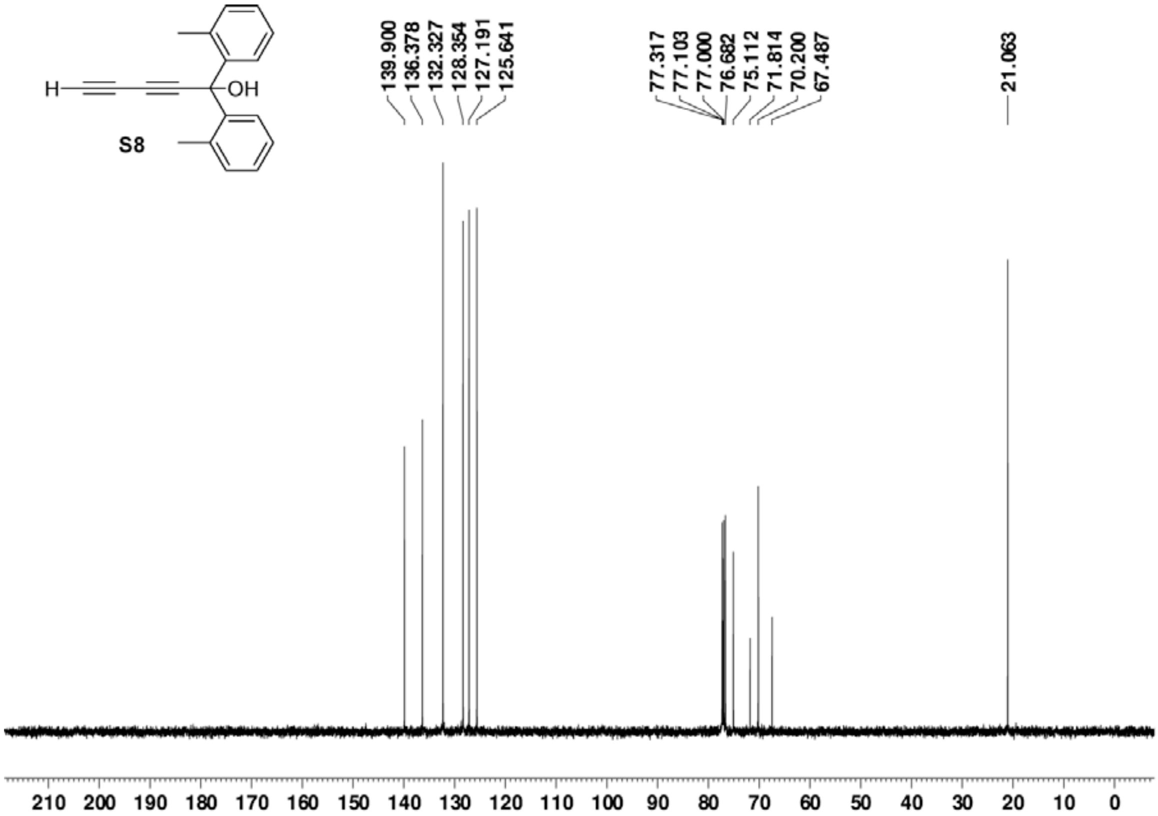


Figure S18: ^{13}C NMR spectrum of **S8** in $CDCl_3$, 100 MHz.

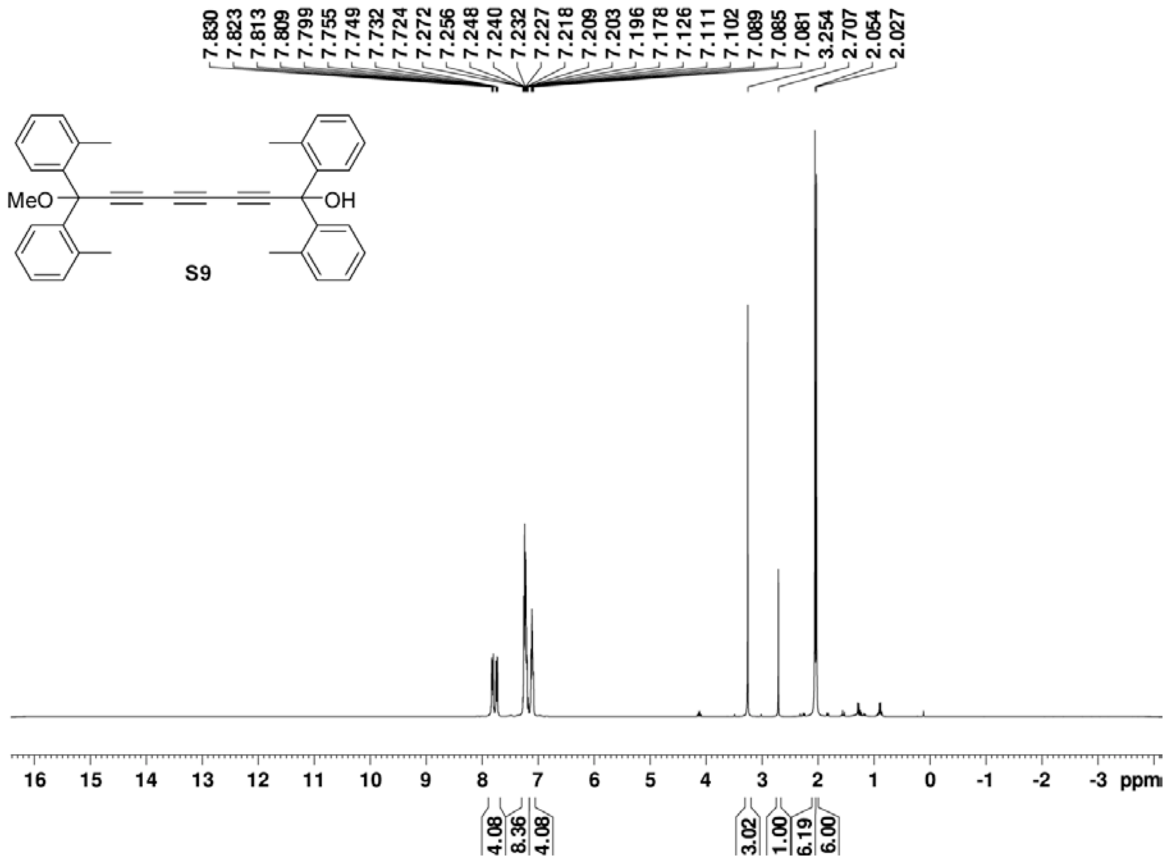


Figure S19: ^{1}H NMR spectrum of **S9** in $CDCl_3$, 300 MHz.

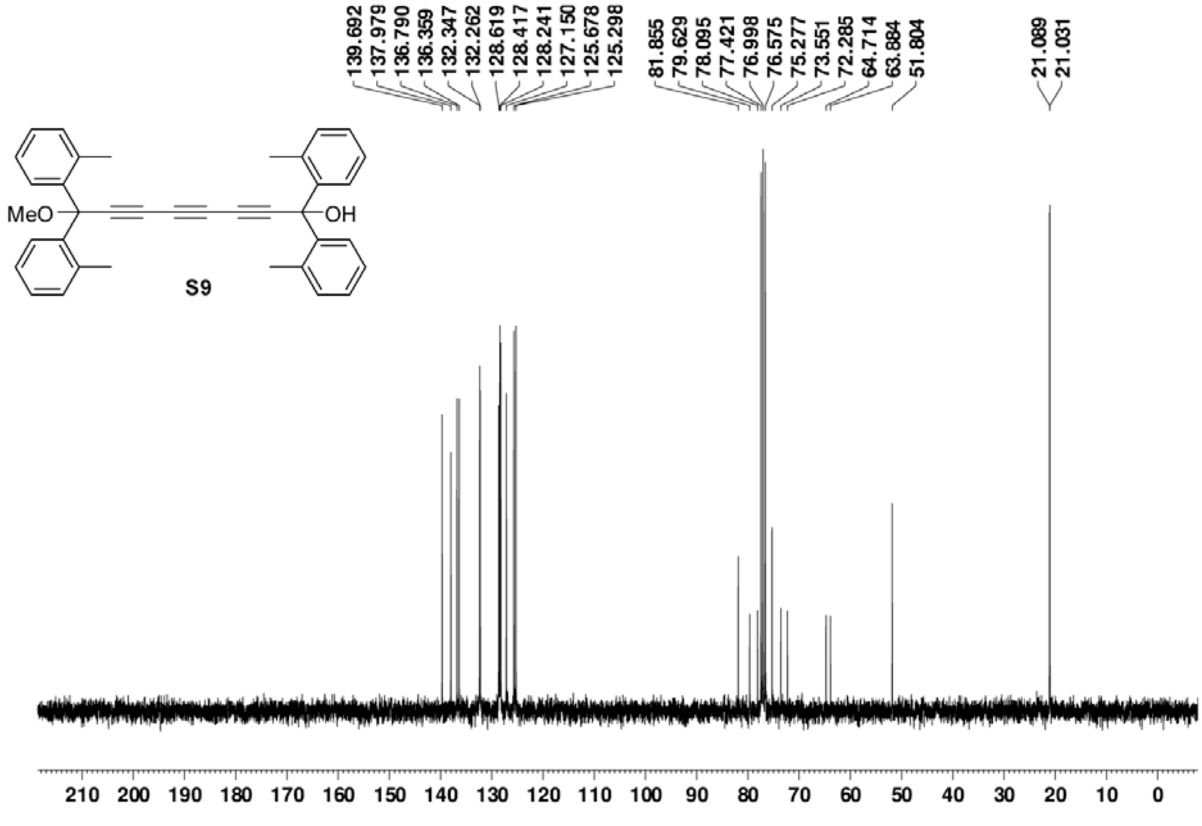


Figure S20: ^{1}H NMR spectrum of **S9** in $CDCl_3$, 300 MHz.

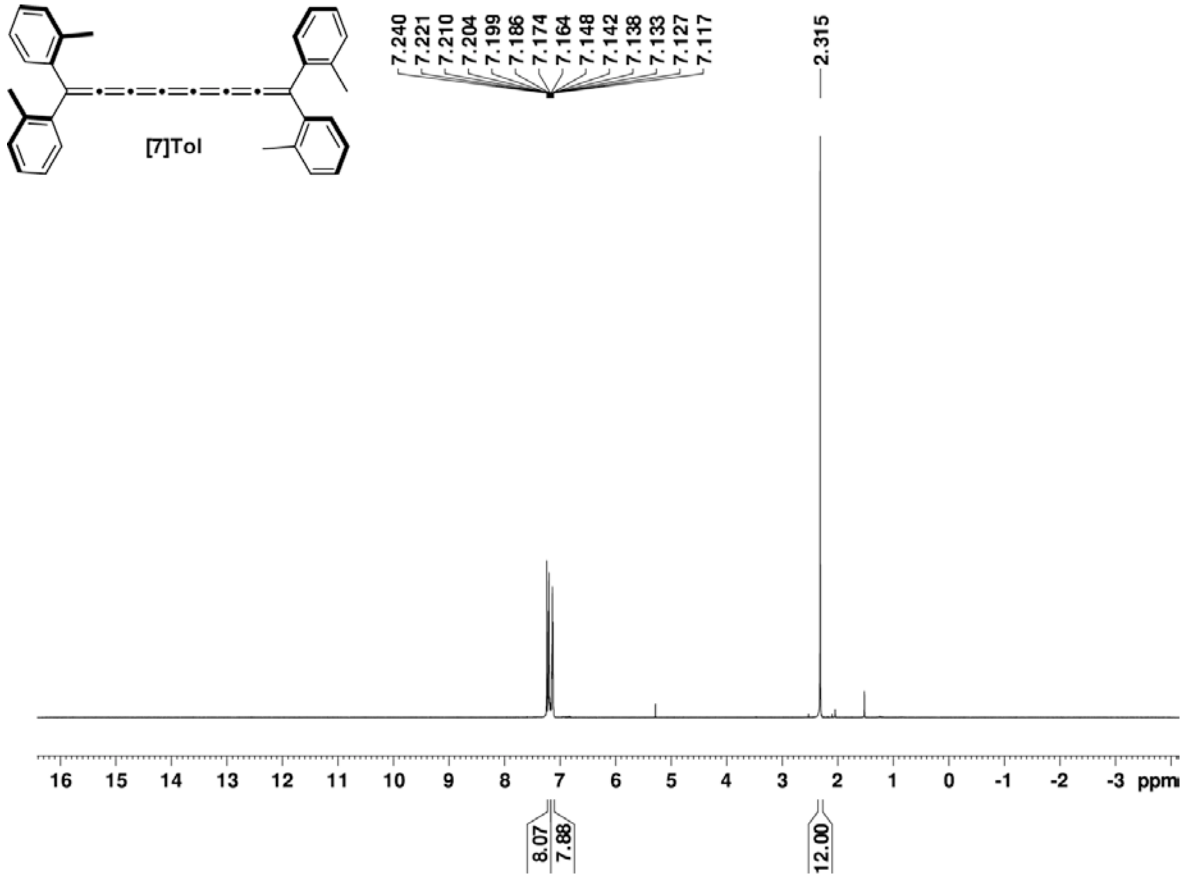


Figure S21: ^{1}H NMR spectrum of **[7]Tol** in $CDCl_3$, 300 MHz.

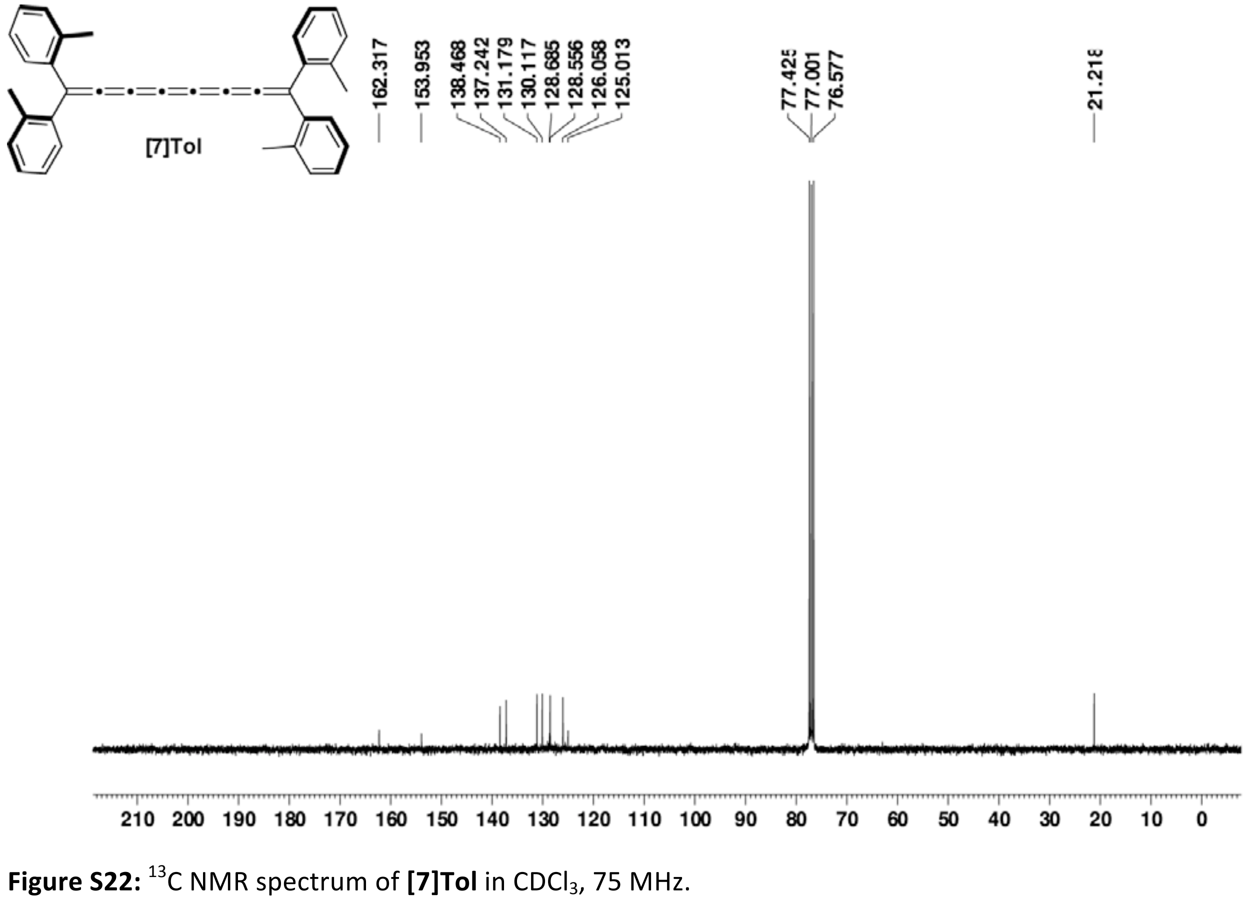


Figure S22: ^{13}C NMR spectrum of **[7]Tol** in $CDCl_3$, 75 MHz.

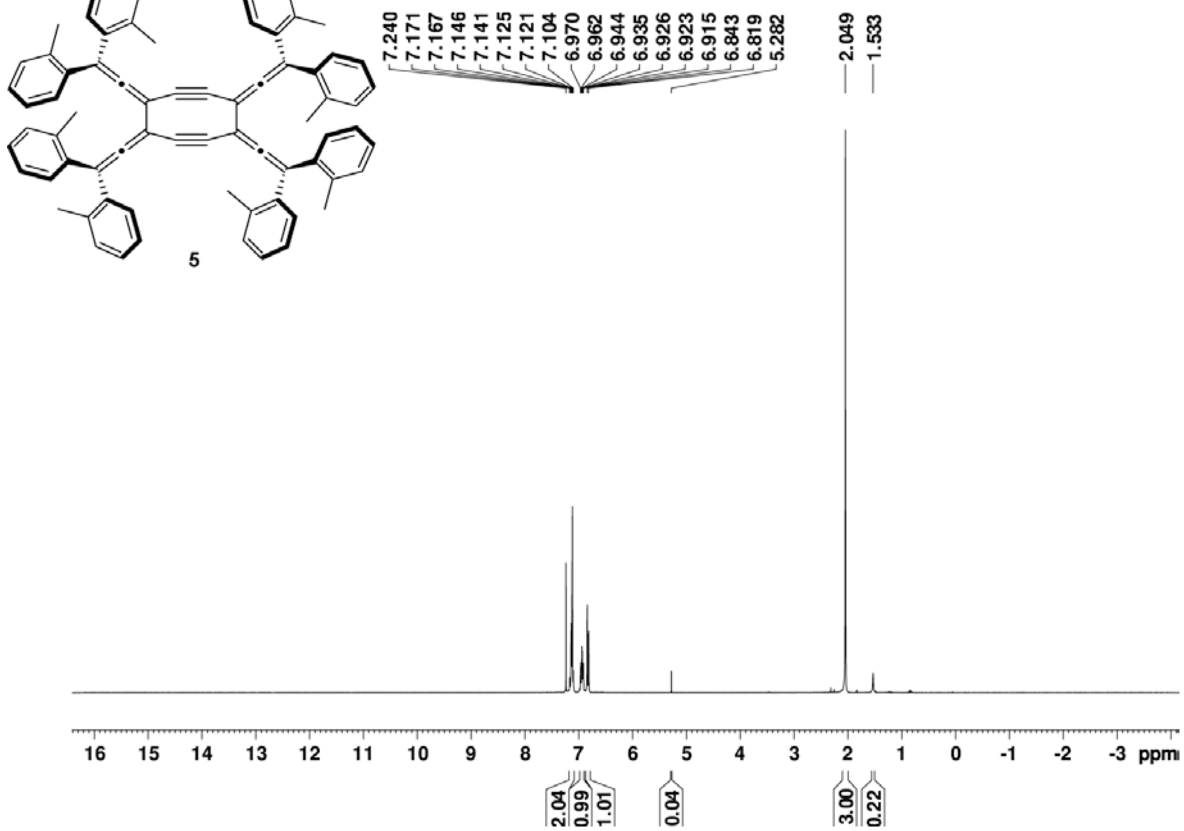


Figure S23: ^{1}H NMR spectrum of **5** in $CDCl_3$, 300 MHz.

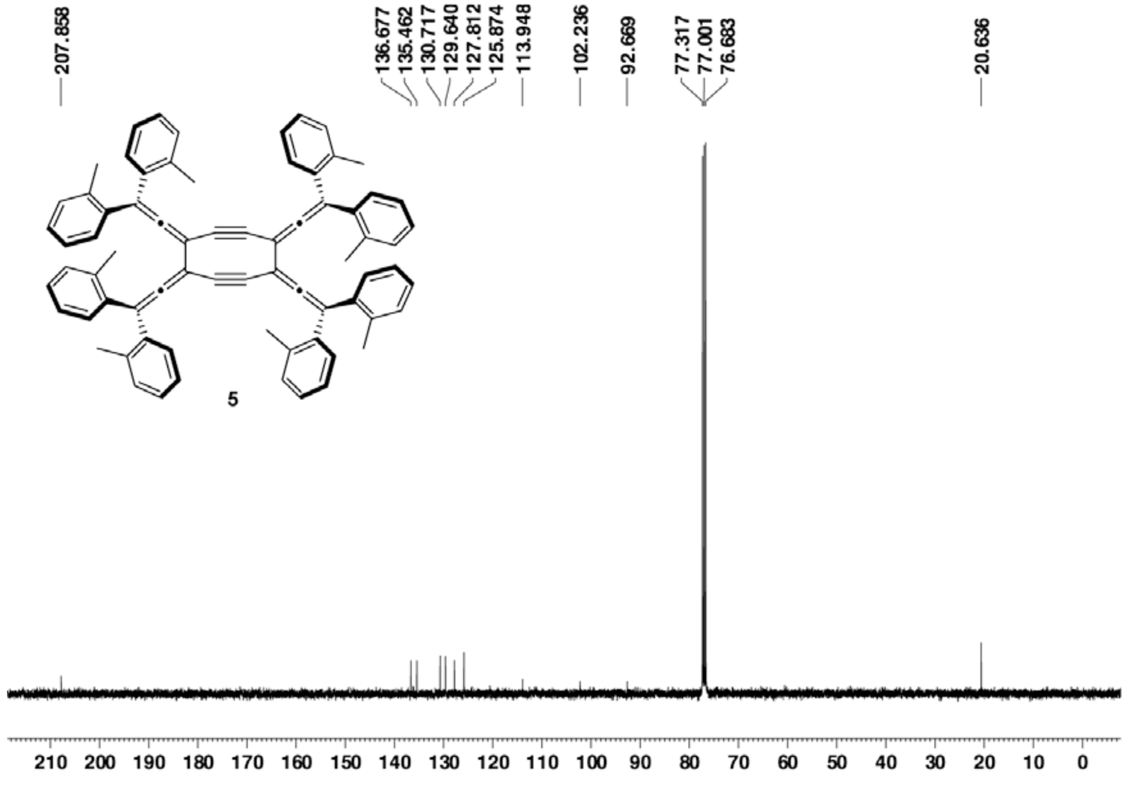


Figure S24: ^{13}C NMR spectrum of **5** in $CDCl_3$, 75 MHz.

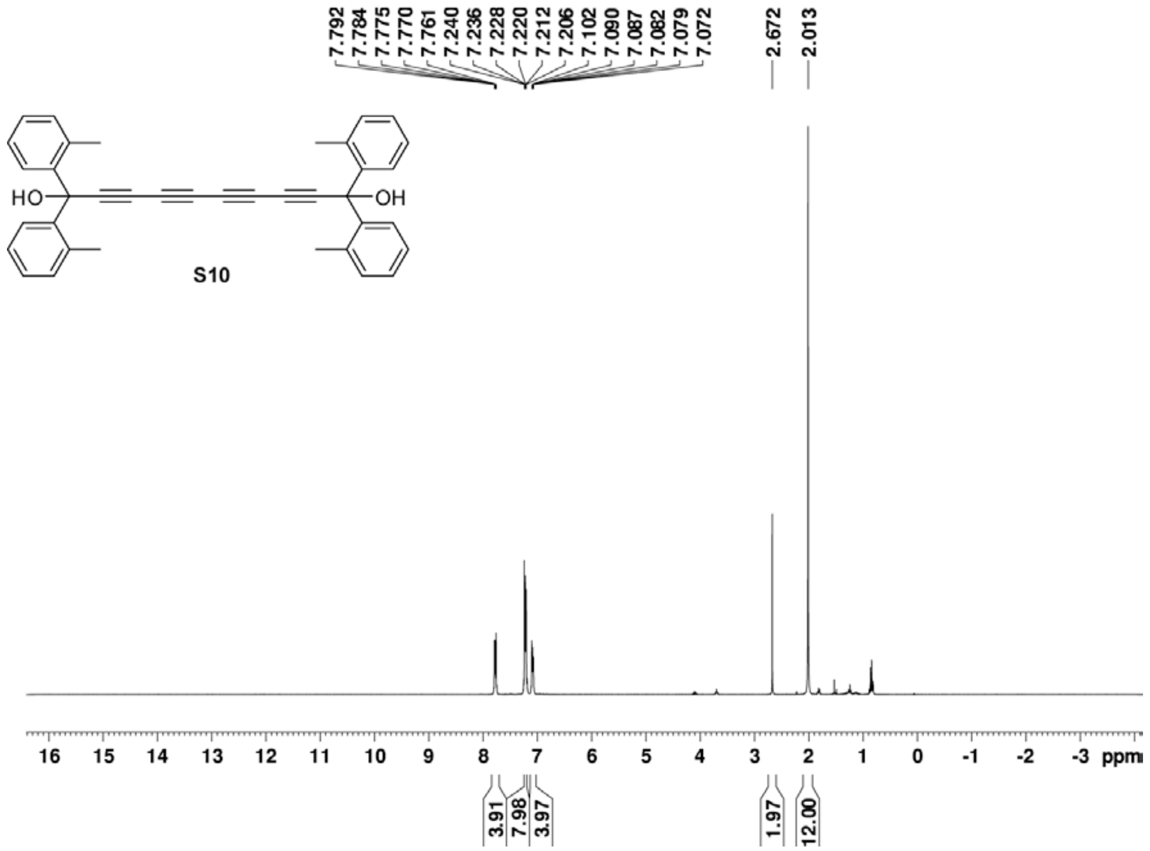


Figure S25: ^{1}H NMR spectrum of **S10** in CDCl$_3$, 300 MHz.

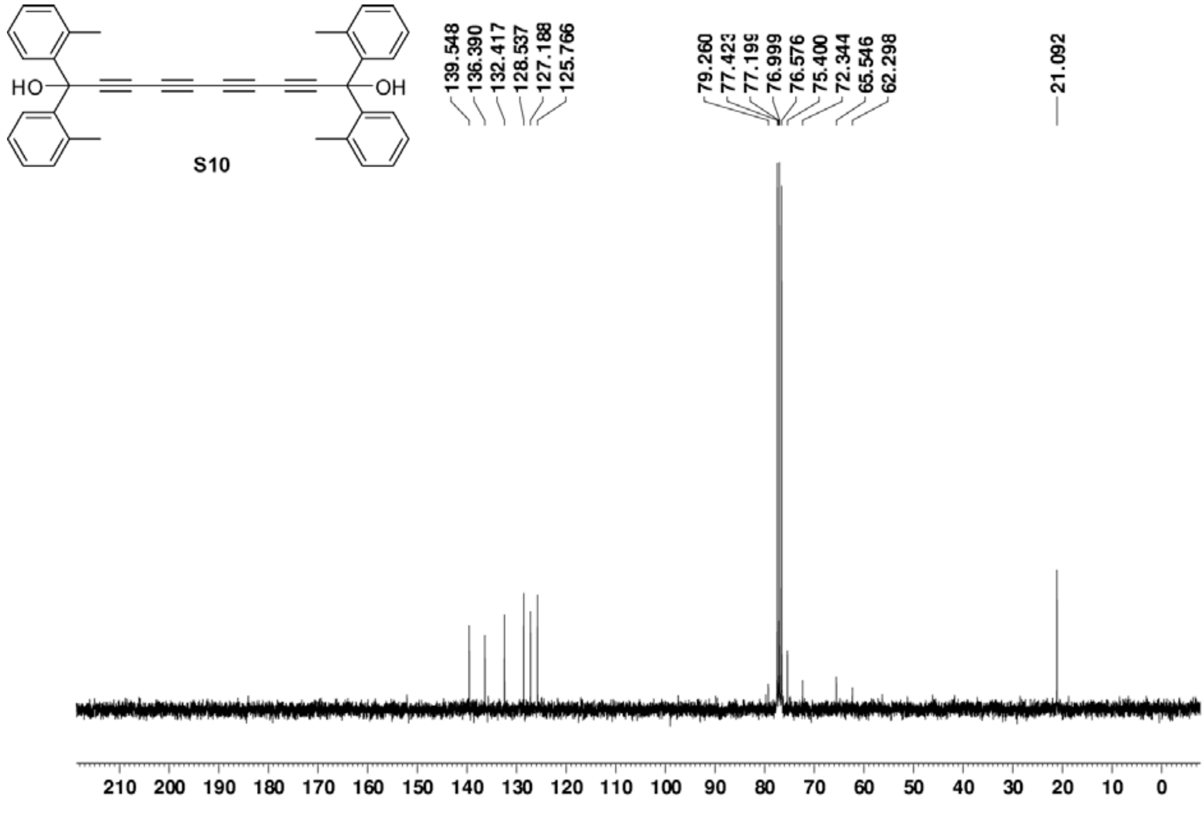


Figure S26: ^{13}C NMR spectrum of **S10** in CDCl$_3$, 75 MHz.

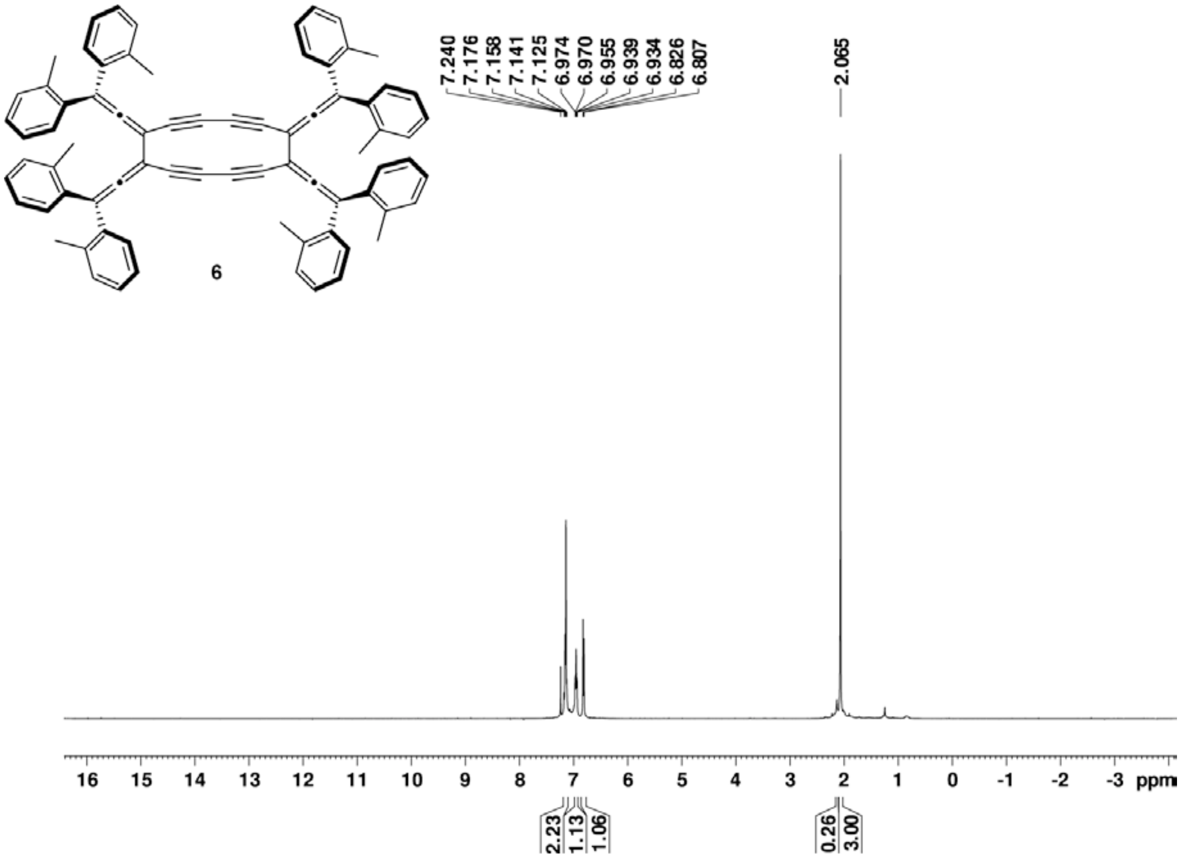


Figure S27: ^{1}H NMR spectrum of **6** in $CDCl_3$, 400 MHz.

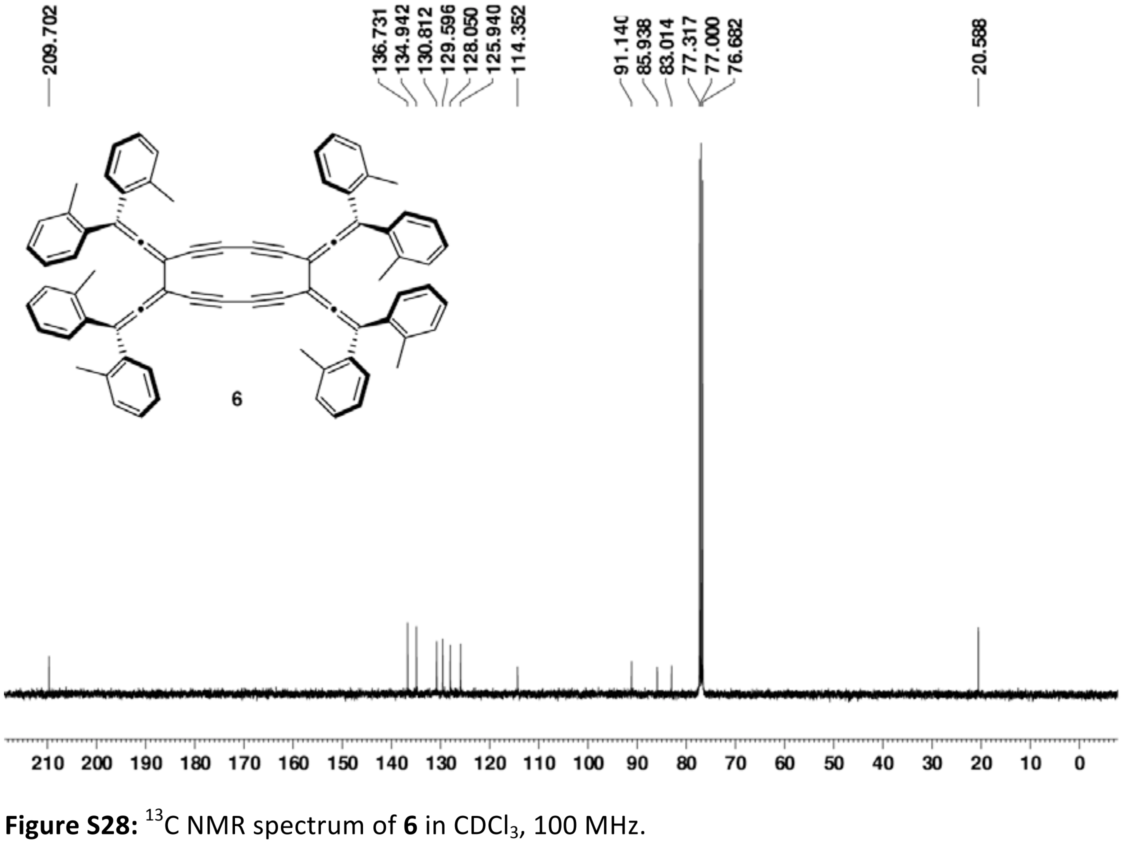


Figure S28: ^{13}C NMR spectrum of **6** in $CDCl_3$, 100 MHz.

UV/Vis absorption spectra

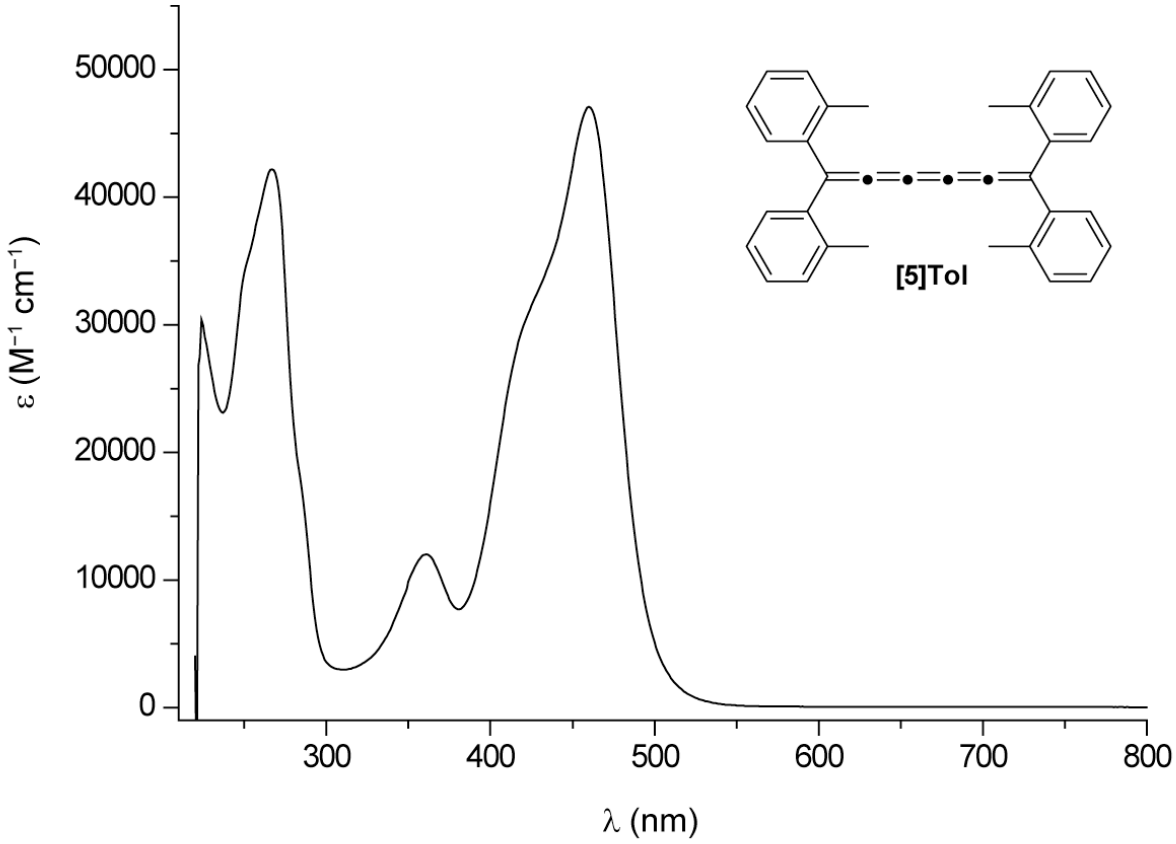


Figure S29: Quantitative UV/Vis spectrum of **[5]Tol** in CH_2Cl_2.

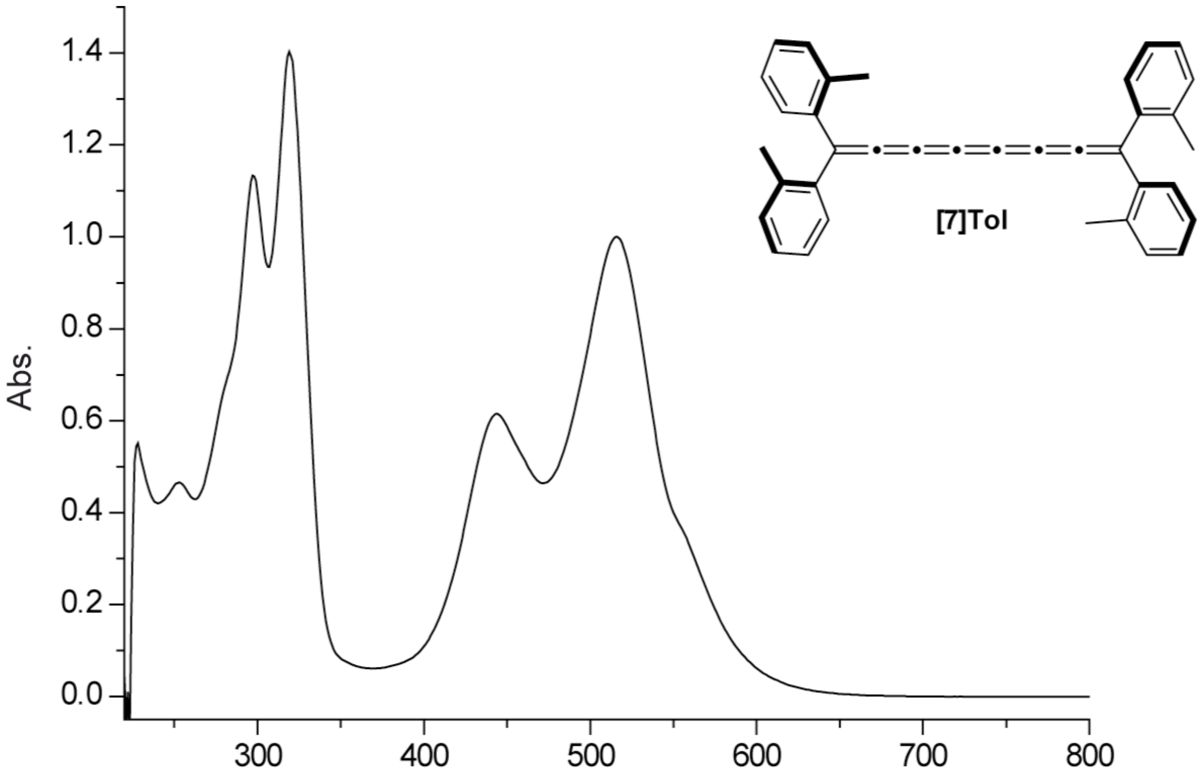


Figure S30: Qualitative UV/Vis spectrum of **[7]Tol** in CH_2Cl_2.

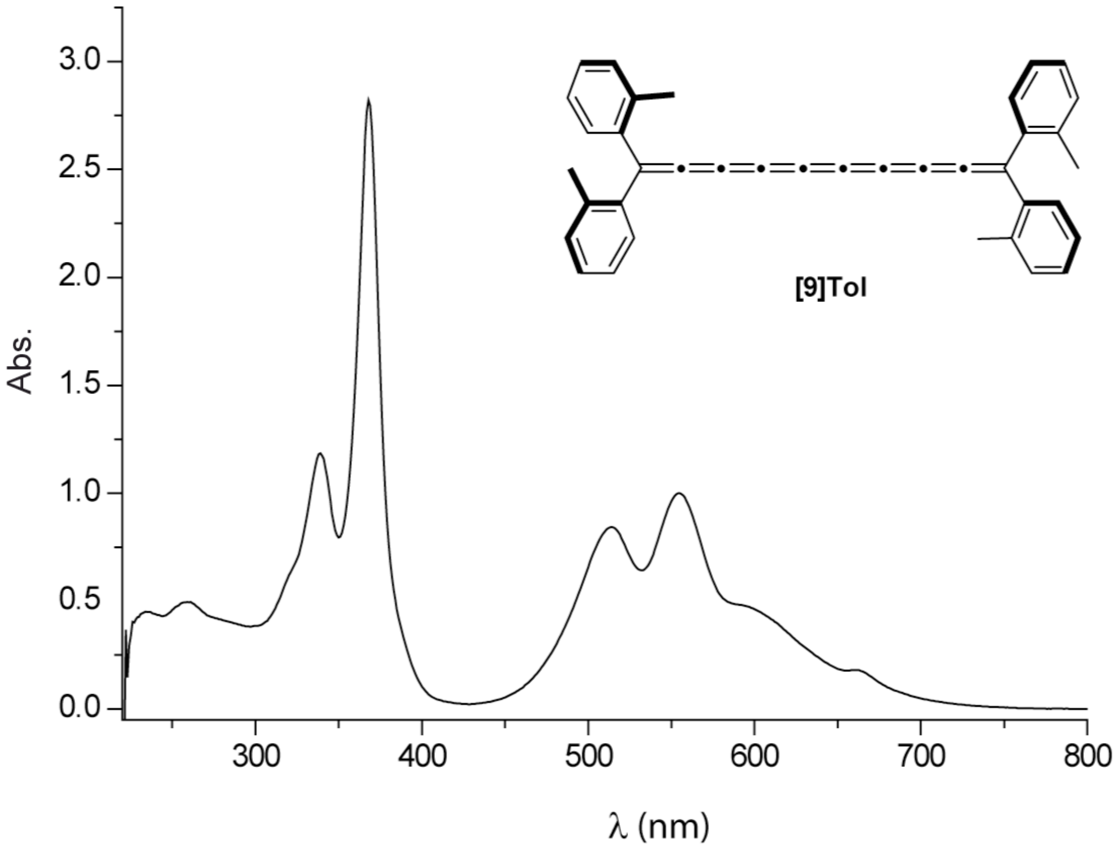


Figure S31: Qualitative UV/Vis spectrum of **[9]Tol** in CH_2Cl_2.

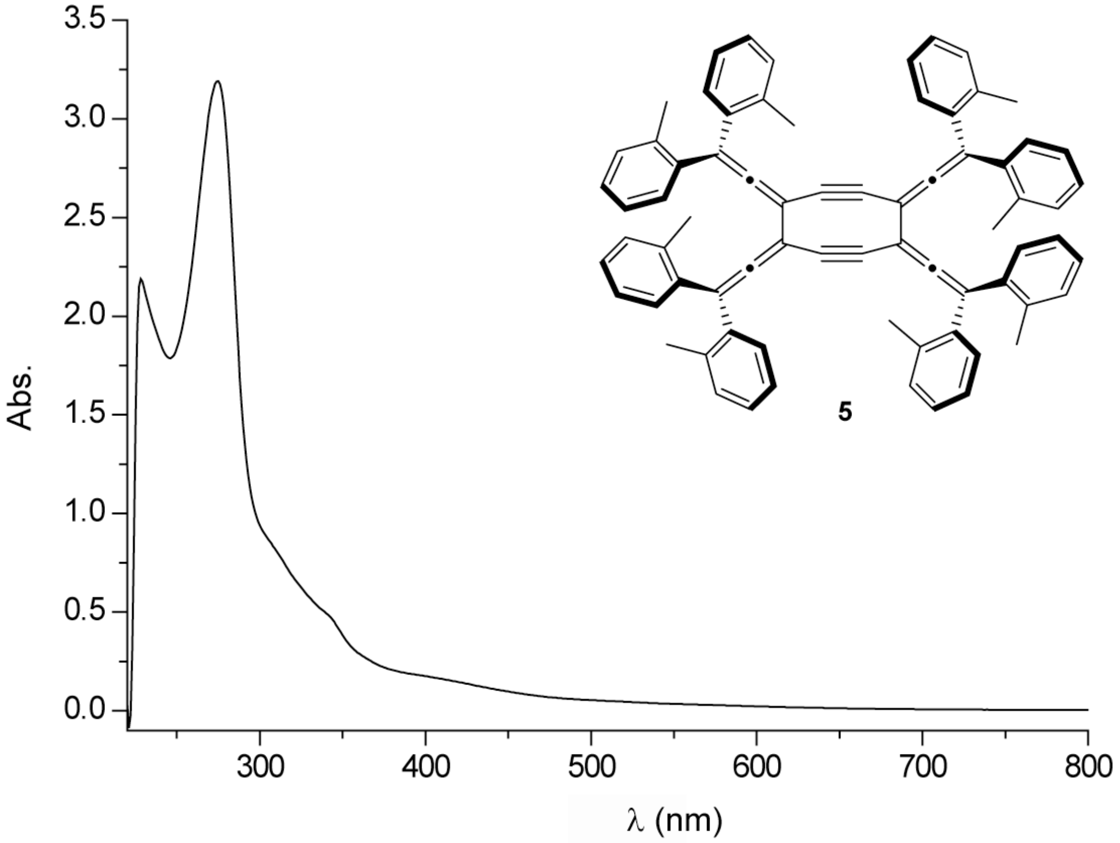


Figure S32: Qualitative UV/Vis spectrum of **5** in CH_2Cl_2.

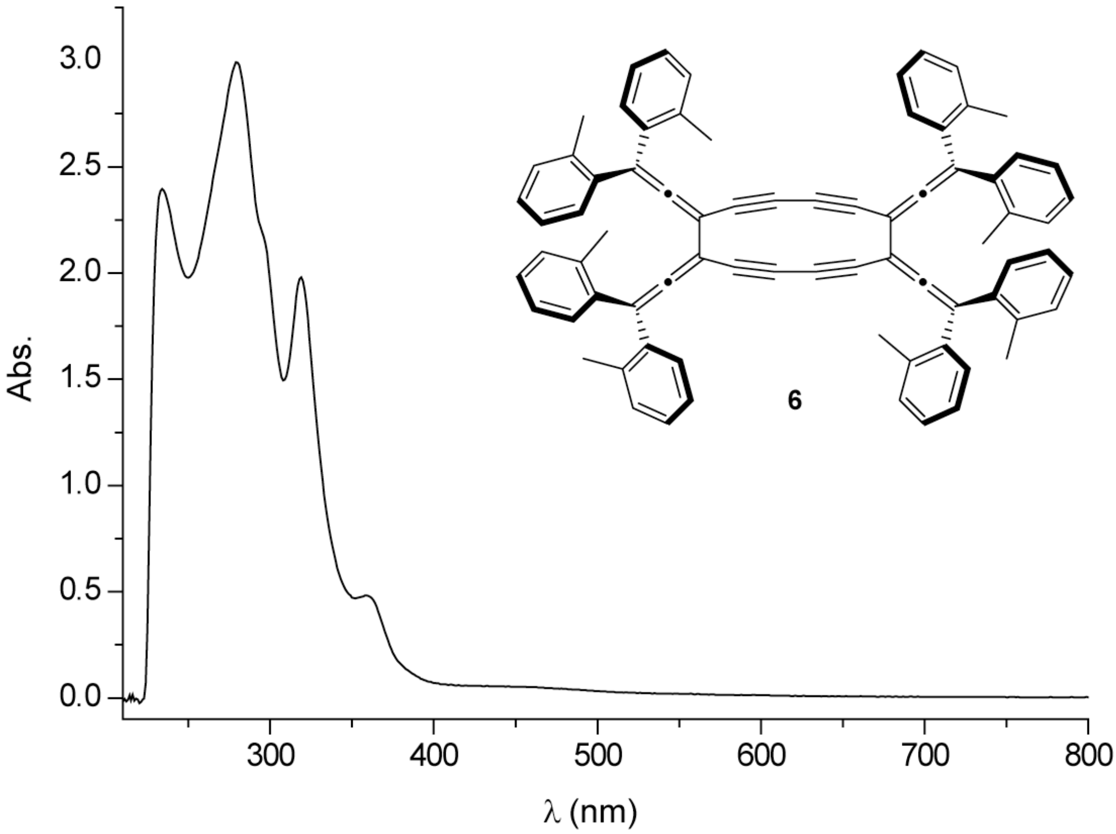


Figure S33: Qualitative UV/Vis spectrum of **6** in CH_2Cl_2.