Supporting Information

Synthesis of a higher fullerene precursor - an “unrolled” C_{84} fullerene.

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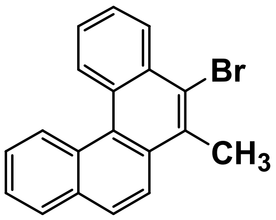
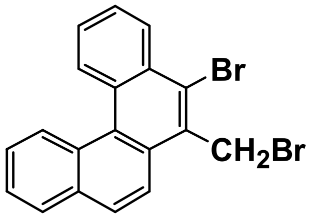
Contents

Experimental Section.



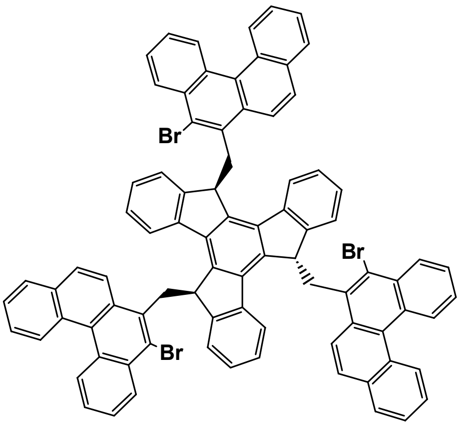
5-Bromo-6-methylbenzo[*c*]phenanthrene (2).

N-bromosuccinimide (NBS) (5.3 g, 30 mmol) was added to a solution of **1** (7.26 g, 30 mmol) in 250 mL of acetonotrile. The resulting mixture was stirred for 4 hours at room temperature and diluted with 300 mL of water. The aqueous phase was extracted three times with 100 mL of dichloromethane (DCM). The organic phases were combined, dried over Na_2SO_4 and evaporated. The crude product was purified by silica gel chromatography using 10:1 mixture of PE/DCM. Colorless oil (5.3 g, 54%). The ^{1}H and ^{13}C NMR spectra were identical to that reported previously [13].



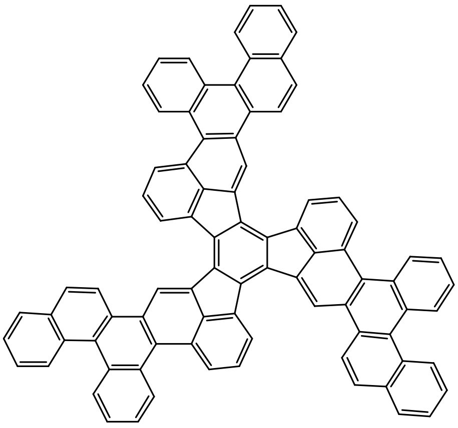
5-Bromo-6-(bromomethyl) benzo[*c*]phenanthrene (3).

3.2 g (10 mmol) of compound **2** were dissolved in 50 mL of CCl_4. 2.0 g (11 mmol) of NBS and catalytic amounts of benzoyl peroxide (BPO) were added. The resulting mixture was refluxed for 3h, cooled, filtered through silica gel and evaporated. The crude product was dissolved in small ammount of DCM and presipitated through addition of PE. The white solid was filtrated and recrystallized from ethanol yielding 2.7 g (68%) of crystalline solid. $R_f = 0.63$ (CCl_4); ^1H NMR ($CDCl_3$, 300 HMz) δ = 8.90-8.97 (m, 2H), 8.57-8.60 (m, 1H), 8.14 (d, *J* = 9Hz 1H), 8.00-8.04 (m, 2H), 7.62-7.71 (m, 4H), 5.35 (s, 2H); ^{13}C NMR ($CDCl_3$, 75.4 HMz) δ =133.23 (C), 131.40 (C), 131.38 (C), 131.17 (C), 129.75 (C), 128.81 (C) ,128.69 (CH), 128.58 (2×CH), 128.41 (CH), 128.25 (CH), 128.15 (C), 127.35 (CH), 127.25(CH) ,126.63 (CH), 126.48 (CH), 126.01 (C), 121.95 (CH), 32.40 (CH_2); Mp: 142 °C; MALDI-MS (DCTB) *m/z* = 397.89 $[M]^+$.



Compound 5.

THF was refluxed over KOH and distilled over metallic sodium. THF was degazed using ”freeze-thaw-pump” technique and additionally distilled under reduced pressue before use. All follow-up manipulations were carried out under argon atmosphere using Schlenk technique. 345 mg (1 mmol) of truxene were suspended in 20 ml of THF using ultrasonic bath. 2.0 ml of 1.6M nBuLi in hexane (3.2 mmol) were slowly added to the mixture at -78 ^{o}C. After stirring for about 40 min, the mixture was slowly warmed to 0 ^{o}C. After 1 h the solution of **3** 1.32 g (3.3 mmol) in THF (15 ml) was drop-wise added to the red solution of truxene trianion. The resulting mixture was stirred for 2 h and diluted with EtOAc, washed with saturated aqueous NaCl solution, dried over Na_2SO_4 and evaporated. The crude product was purified by silica gel chromatography using CCl_4 as a solvent. The fractions containing the product were concentrated and the product was precipitated through addition of hexane, filtered and dried. White powder (490 mg, 38%) $R_f = 0.23$ (CCl_4); ^1H NMR ($CDCl_3$, 300 HMz) $\delta = 9.0\text{-}8.4$ (m, 9H), 8.4-6.0 (m, 33H), 6.0-3.0 (m, 9H); ^{13}C NMR ($CDCl_3$, 75.4 HMz) $\delta = 147.08$, 146.51, 146.21, 145.25, 142.20, 141.35, 140.39, 140.09, 139.71, 139.06, 137.41, 137.12, 136.81, 134.72, 134.53, 134.42, 132.74, 132.53, 131.34, 131.26, 131.18, 130.89, 130.36, 130.22, 130.20, 129.69, 129.46, 128.85, 128.72, 128.52, 128.31, 128.22, 127.89, 127.69, 127.52, 127.26, 127.04, 126.72, 126.71, 126.40, 126.24, 126.22, 126.06, 126.02, 125.89, 125.86, 125.76, 125.43, 125.25, 125.02, 124.80, 122.78, 122.63, 122.33, 121.94, 45.01 (CH), 44.98 (2×CH), 39.26 (CH_2), 37.85 (CH_2) , 37.06 (CH_2), (24 signals were not observed due to overlapping); Mp: 176 °C; MALDI-MS (DCTB) $m/z = 1296.25$ $[M]^+$ (Exact Mass: 1296.15). Anal. Calcd. for $C_{84}H_{51}Br_3$: C, 77.61; H, 3.96; Found: C, 75.82; H, 3.03.



Compound 6

A mixture of **5** (390 mg, 0.3 mmol), $Pd(OAc)_2$ (70 mg, 0.3 mmol), trimethylbenzylammoniumbromide (140 mg, 0.3 mmol) and Cs_2CO_3 (500 mg, 1.5 mmol) in dimethylacetamide (20 ml) was stirred at 150°C for 48 h. The mixture was cooled and solid was filtered off, washed with DCM, acetone and water. The solid obtained was suspended in aqueous NaCN and stirred for 3 h, filtered off and washed with water, acetone and DCM to give **6** as orange powder. The product was purified from trace ammounts of bisfunctionalazed truxene (see Fig. S-7) by gradient sublimation. Orange powder (114 mg, 36%). The product was too insoluble for NMR characterization. Mp > 350°C; *m/z* = 1050.33 (Exact Mass: 1050.33) $[M]^+$; HRMS Calcd. for $C_{84}H_{42}$ 1050.3287; Found 1050.3313; Anal. Calcd. for $C_{84}H_{42}$: C, 95.97; H, 4.03; Found: C, 95.91; H, 3.97

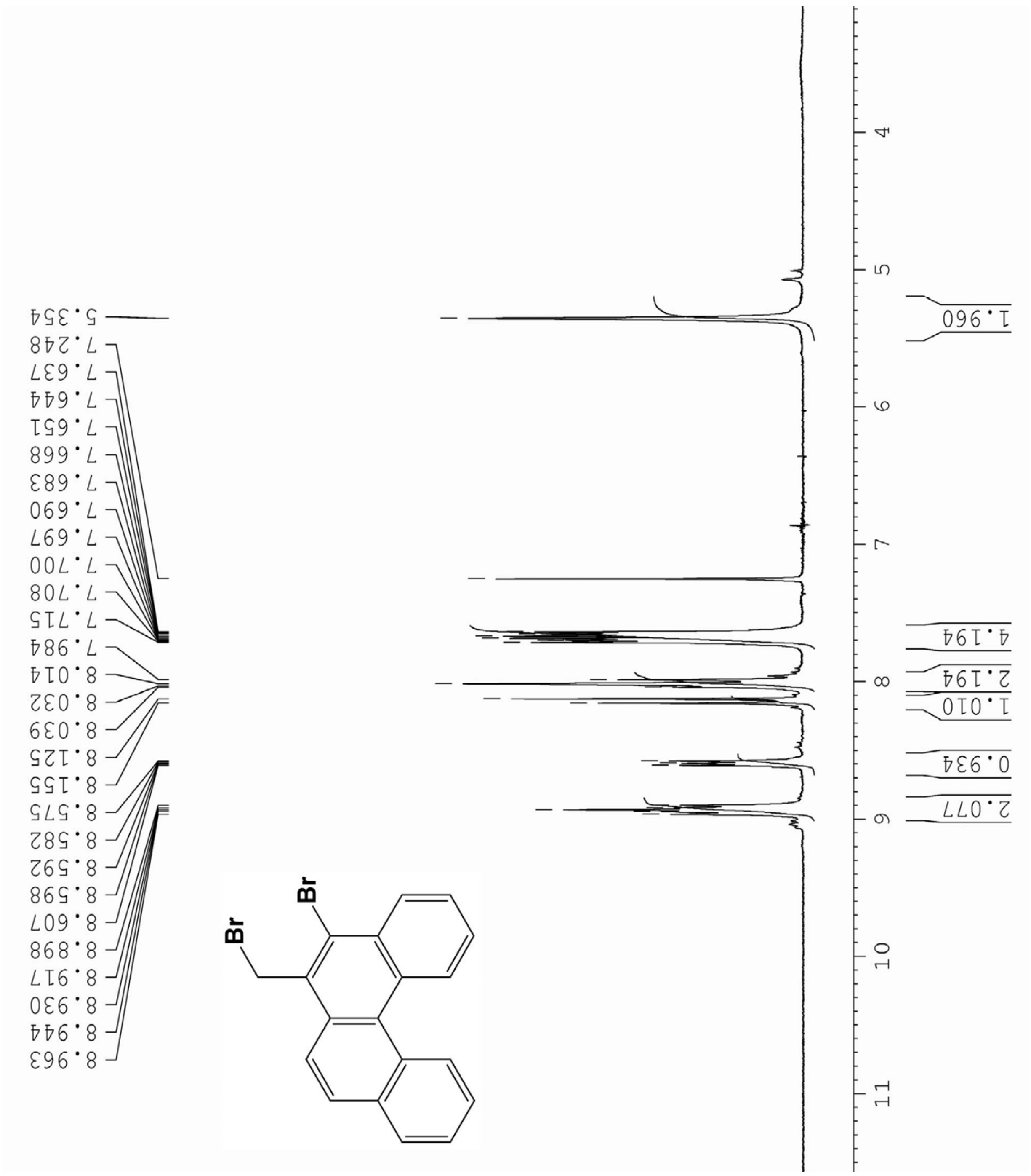


Fig S1. ^{1}H NMR spectrum of **3** **(**$CDCl_3$, 300MHz**)**.

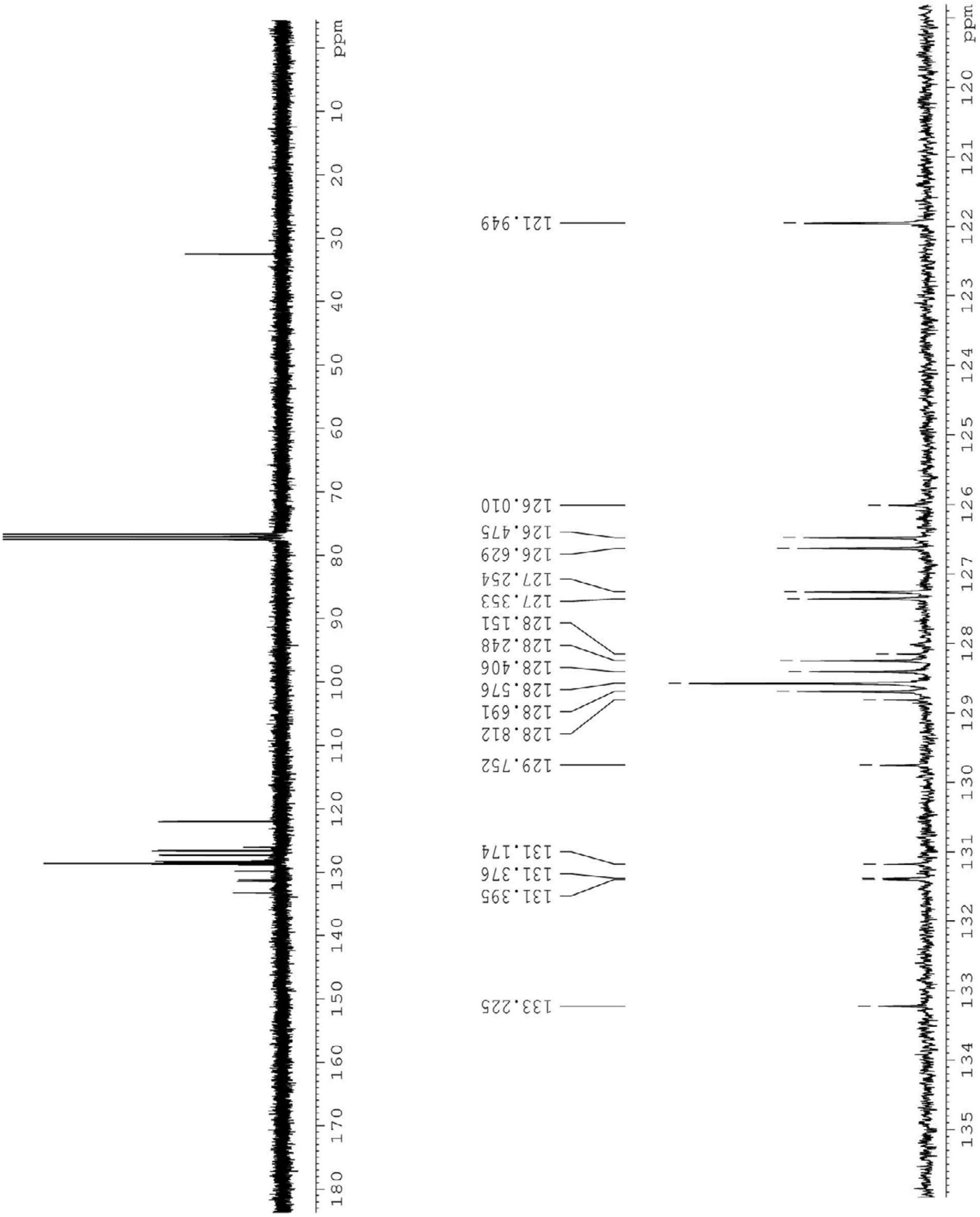


Fig S2. ^{13}C NMR spectrum of **3** (CDCl$_3$, 74.5 MHz).

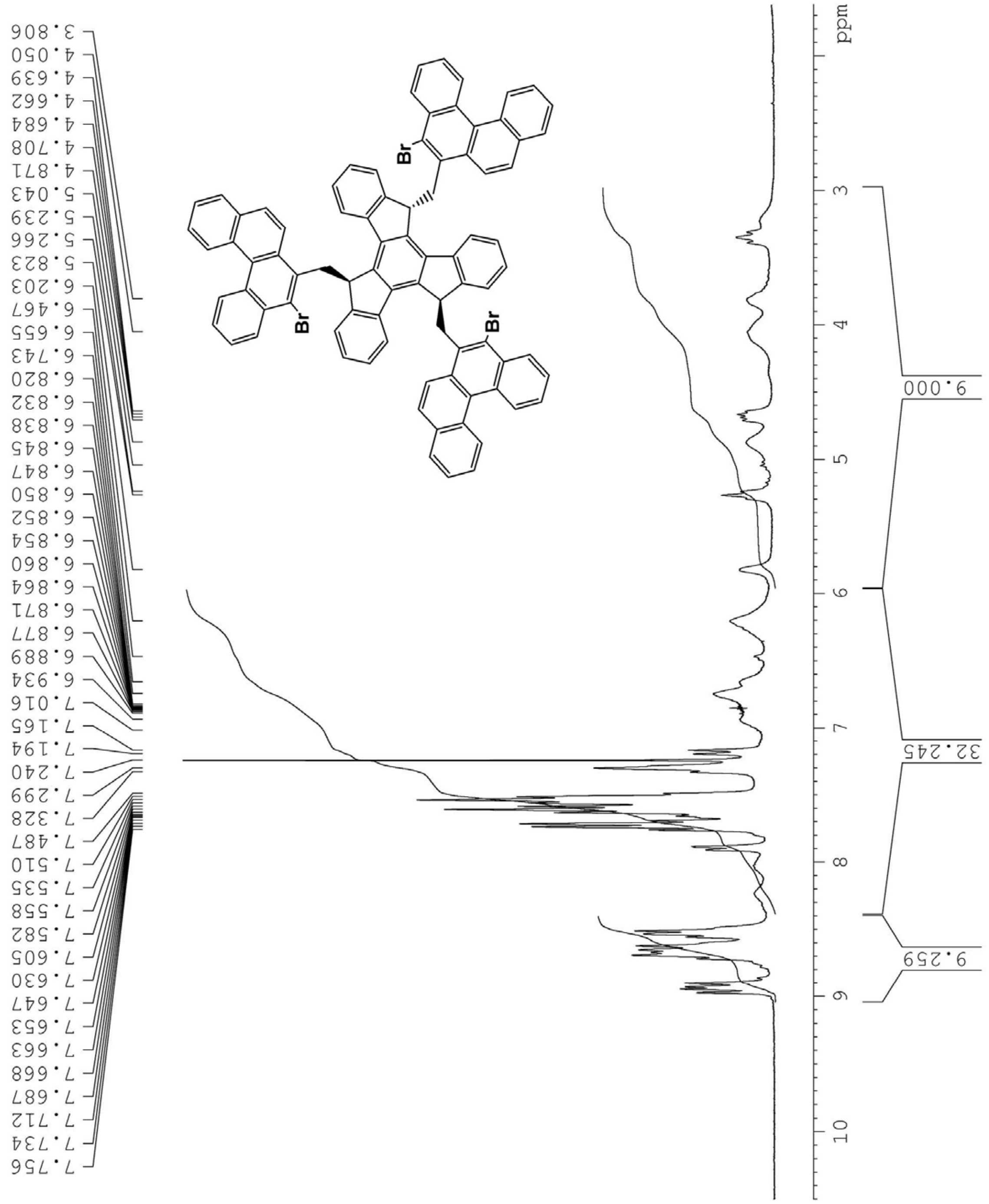


Fig S3. ^{1}H NMR spectrum of **5** **(**CDCl$_3$, 300MHz**)**.

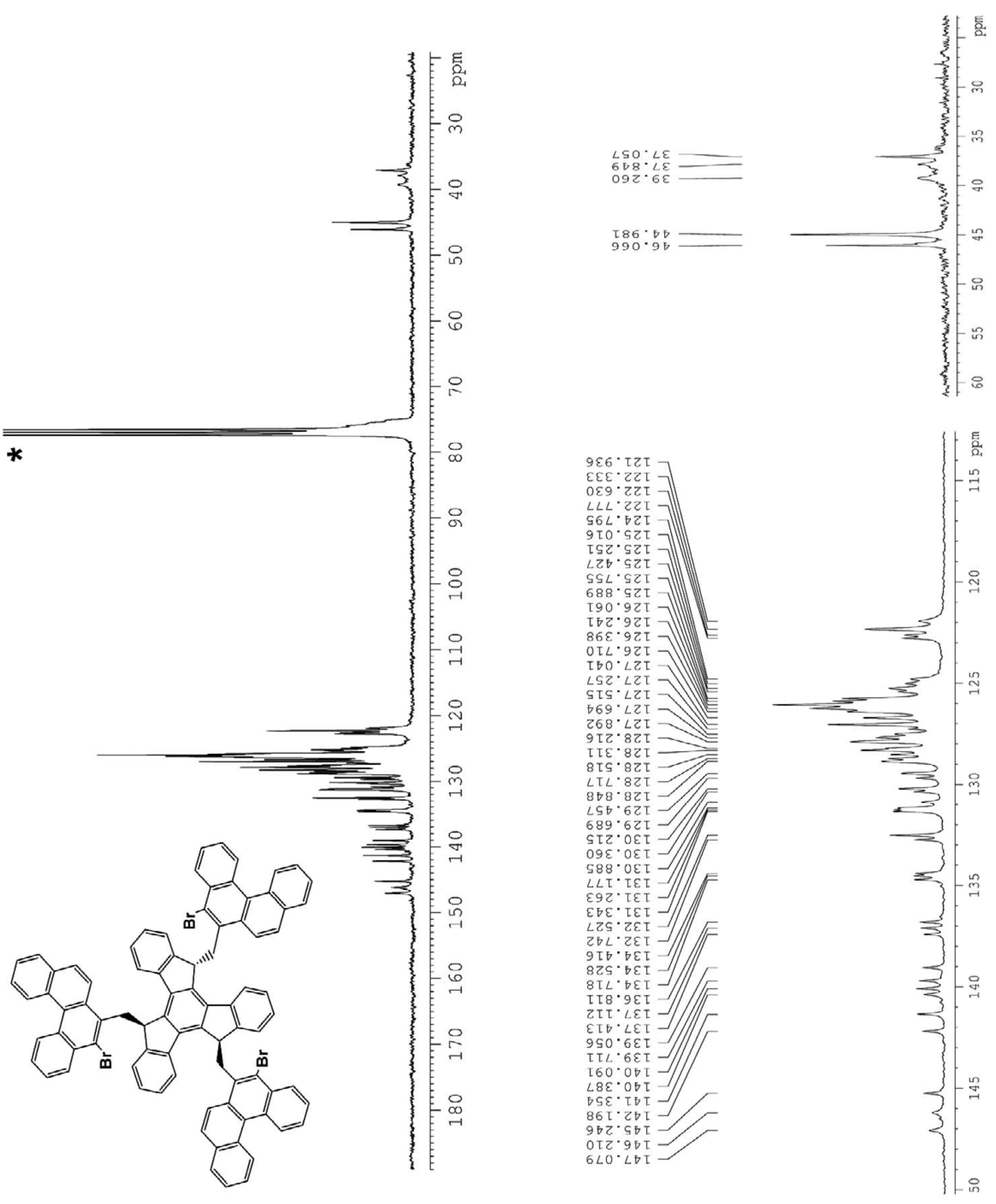


Fig S4. ^{13}C NMR spectrum of **5** (CDCl$_3$, 74.5 MHz).

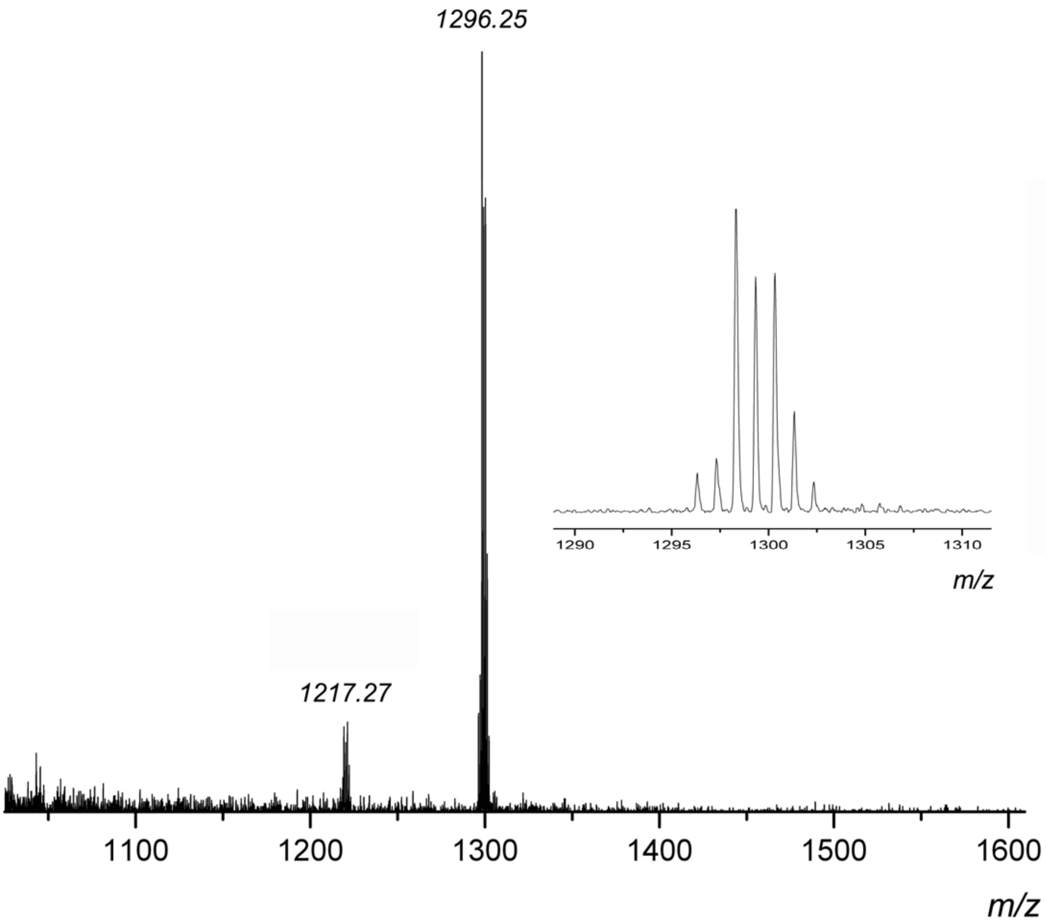


Fig S5. MALDI-MS of **5**. DCTB (trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenyl idene] malononitrile) was used as a matrix. The main signal at 1296.25 m/z corresponds to a molecular ion, the small one at 1217.21 m/z corresponds to $[M-Br]^+$.

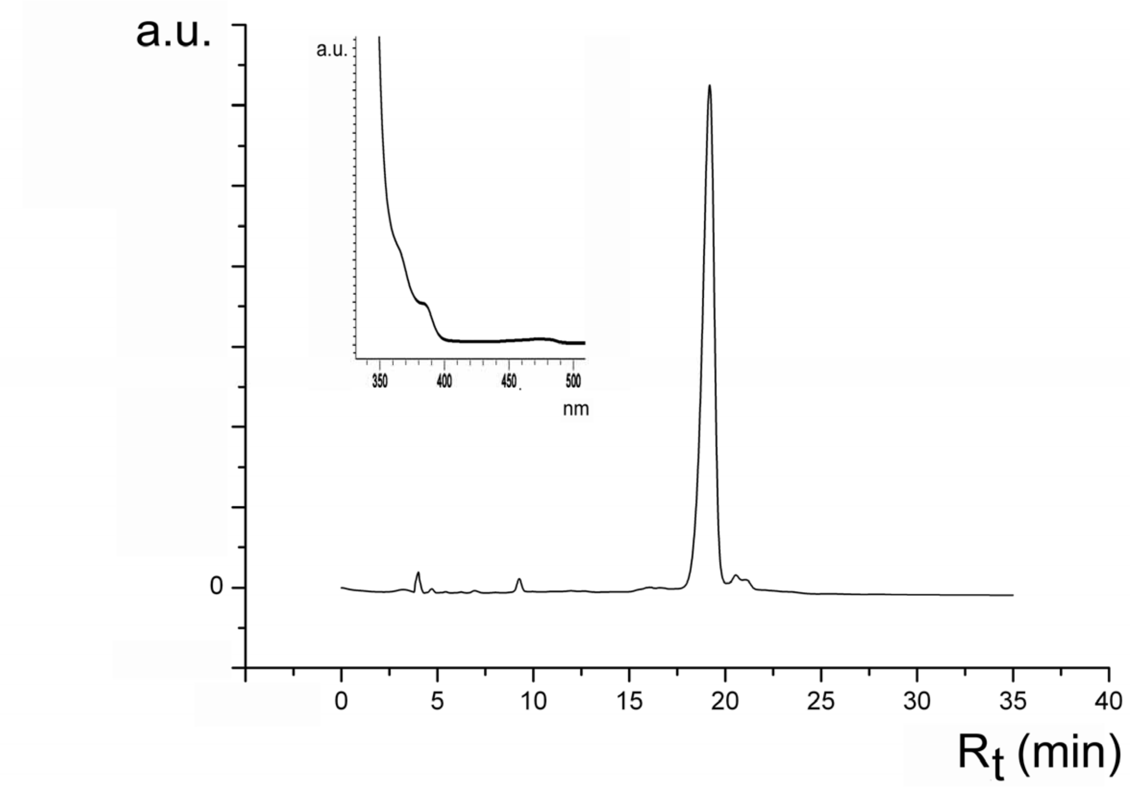


Fig S6. HPLC profile of **5 (***anti* isomer**)**. Buckyprep column (4.6 mm × 250 mm), monitored at 300 nm with toluene:MeOH 1:1 as eluent. UV/VIS absorption spectra (left top).

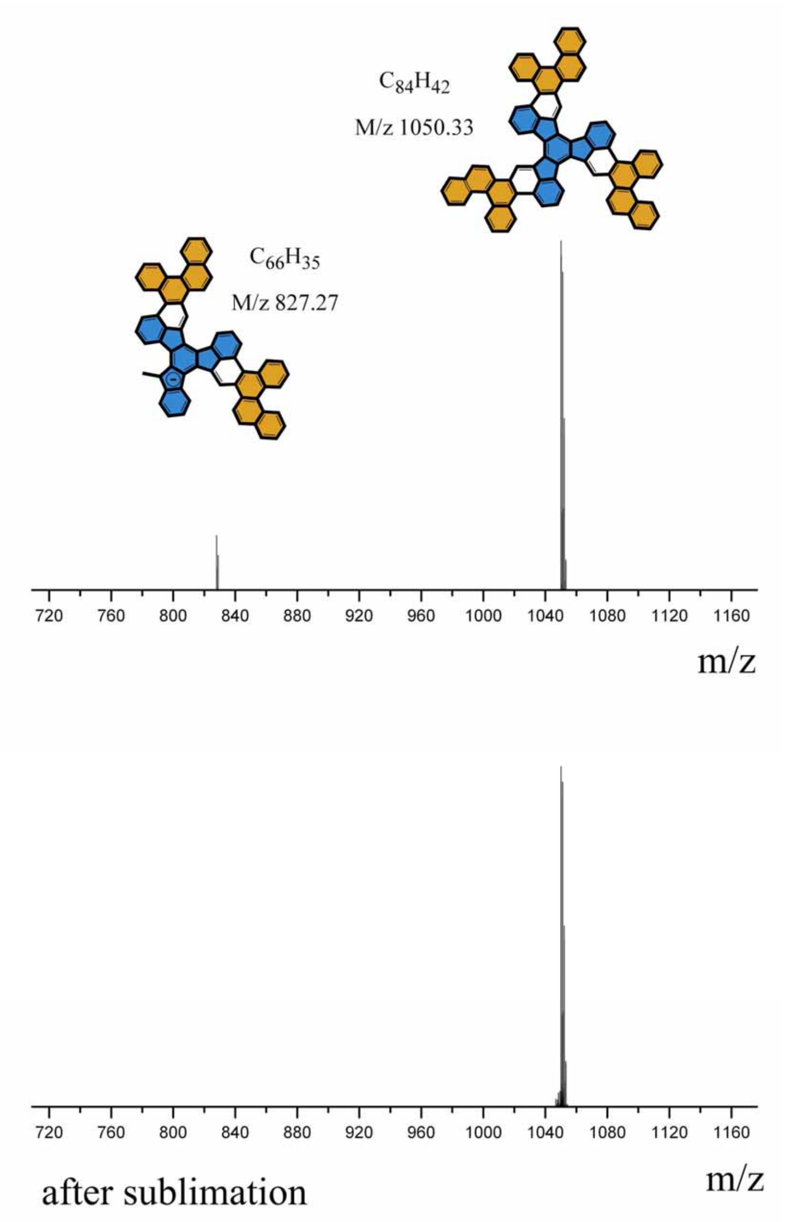


Fig S7. LDI-MS of **6** before (top) and after gradient sublimation (bottom). Formation of byproduct $C_{66}H_{55}$ is a results of C-C cleavage of benzophenanthrene fragment during palladium-catalyzed arylation.