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Supporting Information

Higher Acenes by On-Surface Dehydrogenation: From Heptacene to Undecacene

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Supporting Information

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1. General information

1.1. Synthesis of acene precursors

Reactions under argon atmosphere were carried out in solvents dried by passing through an activated alumina column on a PureSolv^{TM} solvent purification system (Innovative Technologies, Inc., MA). Analytical thin layer chromatography was carried out using TLC-aluminum sheets with 0.2 mm of silica gel (Merck GF_{234}) using UV light as the visualizing agent and an acidic solution of vanillin in ethanol as the developing agent. Chromatographic purifications were carried out using flash grade silica gel (SDS Chromatogel 60 ACC, 40-63 μm). Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. All reagents were used as purchased and used with no further purification, unless otherwise stated.

NMR spectra were recorded at 25 ºC on a Bruker Avance 300, 400 Ultrashield and Bruker Avance 500 Ultrashield apparatus, or at 125 ºC on a Bruker Avance 500 Ultrashield apparatus. The signals are given as δ (ppm) downfield from tetramethylsilane, with calibration on the residual protio-solvent used (δH = 7.26 ppm and δC = 77.00 ppm for $CDCl_3$, δH = 6.00 ppm and δC = 73.78 ppm for $C_2D_2Cl_4$). Mass spectra were recorded on a Waters LCT Premier Spectrometer (ESI and APCI) or on an Autoflex Bruker Daltonics (MALDI and LDI). Melting points were determined using a Büchi melting point apparatus.

1.2. On-surface studies: sample preparation, nc-AFM and STM measurements

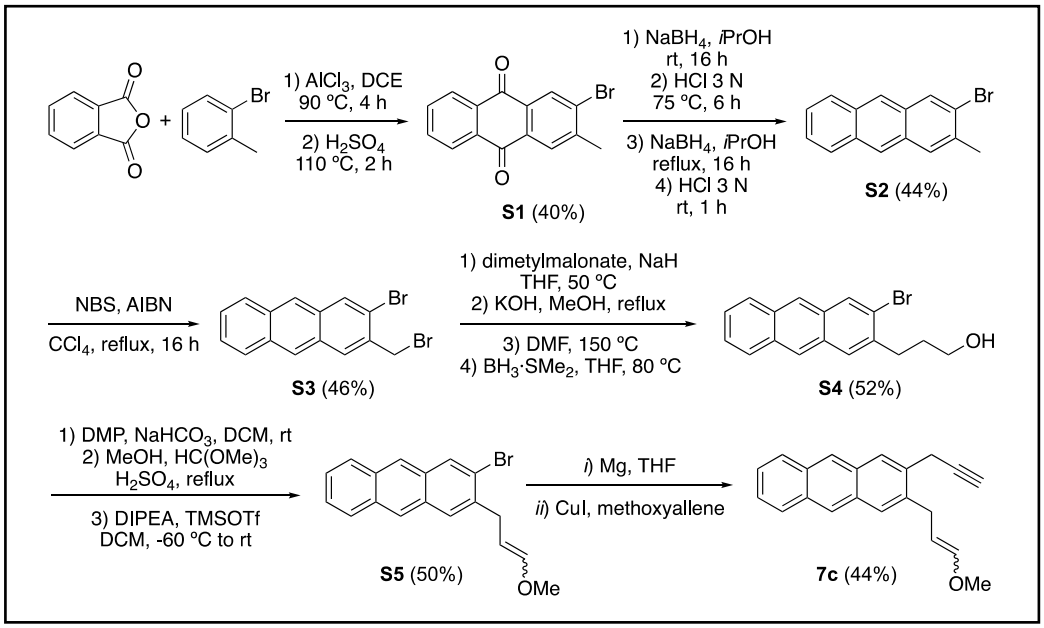
All experiments were performed in an ultra-high-vacuum (UHV) multi-chamber system equipped with a low-temperature scanning probe microscope (Omicron GmbH) that could be operated in a scanning tunneling and non-contact atomic force microscopy (STM, nc-AFM) modes. Au(111) samples were prepared in a standard procedure including Ar^+ ion bombardment and subsequent thermal annealing at 720 K. All molecules were evaporated thermally on a sample kept at room temperature from a water-cooled Knudsen cell equipped with 3 crucibles (Kentax GmbH). The sublimation temperatures of precursor molecules established with the application of a quartz microbalance were the following: terahydroheptacene 468 K, terahydrooctacene 473 K, terahydrononacene 533 K, terahydrodecacene 543 K and terahydroundecacene 557 K. nc-AFM measurements were performed using a qPlus sensor [1] operated in the constant height frequency modulation mode with the bias voltage V set to 0 V, the Q-factor 16 780, and the resonance frequency 24 580 Hz. To obtain ultimate spatial resolution in nc-AFM measurements, CO molecules were picked up by the tungsten nc-AFM tip using a procedure described previously.[2] All STM/STS/nc-AFM measurements were performed at liquid helium (~4.5 K) temperature. For all STM and STS experiments electrochemically etched Pt−Ir tips were applied as probes. All STS data were collected using a lock-in amplifier (Zurich Instruments MFLI) with a central frequency of 680 Hz and amplitude of 20 mV (rms). Thermally induced dehydrogenation of

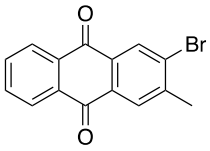
precursor molecules was performed in a preparation chamber using a resistive heater. The samples were heated for 10 min at temperatures ranging from 480 K up to 520 K with temperature monitored by a thermocouple located at a sample stage.

2. Synthesis of acene precursors

Terminal alkynes **7a,b** and hydroacene **1a** were prepared according to our previously reported procedures.[3]

*2.1. Synthesis of **7c***

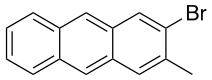




2-Bromo-3-methylanthracene-9,10-dione (S1). To a mixture of phthalic anhydride (23.6 g, 160 mmol), 1-bromo-2-methylbenzene (17.1 g, 100 mmol) and anhydrous DCE (200 mL), $AlCl_3$ (33.2 g, 250 mmol) was added in small portions at 0 ºC. Then the resulting mixture was warmed up to 90 ºC and stirred at that temperature for 4 h. The reaction mixture was diluted with DCE (500 mL), cooled down to 0 ºC, and then cold water (100 mL) was slowly added at that temperature causing the formation of a white precipitate. Then 6 N aqueous HCl was added until all the solid disappeared (*ca.* 500 mL). The resulting mixture was extracted with CH_2Cl_2 (3x300 mL), and the combined organic phases were then washed with water (500 mL) and a saturated $NaHCO_3$ aqueous solution (3x400 mL). The aqueous extracts were acidified to pH = 2 by addition of aqueous HCl (37%) and then extracted with CH_2Cl_2 (500 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated to give a light brown solid that was directly suspended in H_2SO_4 (400 mL) at 0 ºC. The resulting dark mixture was allowed to reach rt and then gradually heated to 110 ºC and maintained at that temperature for 2 h. After cooling down to rt the reaction was poured into ice-water (600 mL) and once the resulting mixture reached rt the product was extracted with CH_2Cl_2 (3x500 mL). The combined organic layers were dried over $MgSO_4$, filtered, and the volatiles removed under reduced pressure. Purification by column

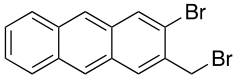
chromatography (cyclohexane:CH_2Cl_2 95:5 to 1:1) gave an orange solid that was further purified by precipitation from CH_2Cl_2:MeOH mixtures to afford the product as a yellow solid (12.03 g, 39.95 mmol, yield over 2 steps = 40%).

Melting point = 134-136 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.33 – 8.28 (m, 2H), 8.14 (s, 1H), 7.85 – 7.80 (m, 2H), 2.59 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.7, 181.9, 145.1, 134.3, 134.2, 133.4, 133.3, 132.3, 132.2, 132.1, 131.2, 129.2, 127.3, 127.3, 23.5. HRMS (ESI+) *m/z* calc. for $C_{15}H_9BrNaO_2$ $[M+Na]^+$: 322.9678. Found: 322.9686.



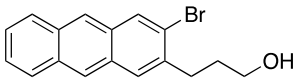
2-Bromo-3-methylanthracene (S2). $NaBH_4$ (2.72 g, 71.90 mmol) was added to a suspension of **S1** (5.00 g, 16.60 mmol) in *i*PrOH (160 mL), the resulting mixture was stirred at rt for 16 h and then poured into ice-water (400 mL). The green solid was filtered, washed with water, and treated with HCl 3 N (250 mL) at 80 ºC for 6 h. After cooling down to rt the suspended greenish solid was filtered-off, washed with water and dried under reduced and subsequently suspended in *i*PrOH (160 mL) and treated with $NaBH_4$ (3.78 g, 99.60 mmol). The mixture was refluxed for 16 h and then cooled down to 0 ºC, quenched by the slow addition of HCl 1 N until bubbling ceased and then stirred at rt for 1 h. The suspended solid was filtered-off, washed with water and dried under reduced pressure. Purification by sequential precipitations from CH_2Cl_2:pentane mixtures afforded the product as a yellow solid with limited solubility in standard organic solvents (1.98 g, 7.30 mmol, yield = 44%).

Melting point = 269-271 ºC. ^{1}H NMR (500 MHz, $CDCl_3$, 328K) δ 8.32 (s, 1H), 8.31 (s, 1H), 8.27 (s, 1H), 8.01 – 7.97 (m, 2H), 7.86 (s, 1H), 7.51 – 7.44 (m, 2H), 2.63 (d, *J* = 1.1 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$, 328K) δ 134.6, 132.0, 131.7, 131.4, 130.7, 130.7, 128.3, 128.1, 128.1, 125.5, 125.5, 125.4, 124.9, 123.8, 23.3. HRMS (APCI+) *m/z* calc. for $C_{15}H_{12}Br$ $[M+H]^+$: 271.0117. Found: 271.0116.



2-Bromo-3-(bromomethyl)anthracene (S3). **S2** (1.90 g, 7.00 mmol) was suspended in CCl_4 (300 mL) and then NBS (1.38 g, 7.75 mmol) and AIBN (230.0 mg, 1.40 mmol) were sequentially added. The resulting mixture was refluxed for 16 h, then cooled down to rt and the volatiles removed under reduced pressure. Purification by column chromatography (cyclohexane:CH_2Cl_2 95:5 to 1:1) afforded a brown solid that was further purified by precipitation from CH_2Cl_2:pentane mixtures to give the product as a yellow solid with limited solubility in standard organic solvents (1.12 g, 3.20 mmol, yield = 46%).

Melting point = 187-189 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.33 (s, 1H), 8.29 (s, 1H), 8.13 (s, 1H), 8.01 (dd, *J* = 6.6, 3.3 Hz, 2H), 7.56 – 7.49 (m, 2H), 4.84 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.5, 132. 6, 132.2, 132.1, 131.8, 130.8, 130.1, 128.3, 128.2, 126.8, 126.4, 126.1, 125.2, 120.9, 34.4. HRMS (APCI+) *m/z* calc. for $C_{15}H_{11}Br_2$ $[M+H]^+$: 348.9222. Found: 348.9229.



3-(3-Bromoanthracen-2-yl)propan-1-ol (S4). Sodium hydride (132.8 mg, 3.32 mmol, 60% in mineral oil) was suspended in THF (60 mL) and cooled to 0 ºC. Dimethyl malonate (0.36 mL, 3.18 mmol) was added dropwise over a 30-minute period and the reaction was stirred for an additional 30 min at 0 ºC. **S3** (1.06 g, 3.02 mmol) was then added in a single portion causing the immediate formation of a white precipitate and the mixture was heated at 50 ºC for 3 h. After cooling down to room temperature, the suspension was diluted with EtOAc (300 mL) and washed with H_2O (60 mL). The aqueous layer was extracted with EtOAc (60 mL) and the combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure.

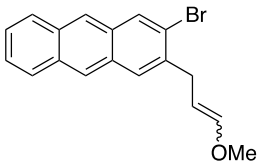
The crude diester was suspended in MeOH (60 mL) and solid KOH (1.68 g, 30.2 mmol) was added at room temperature. The resulting mixture was refluxed for 16 h, then cooled down to room temperature and the volatiles removed under reduced pressure. The solid was suspended in H_2O (100 mL) and the aqueous mixture was washed with Et_2O (80 mL) and then acidified by the slow addition of concentrated HCl to pH < 1. The product was extracted with EtOAc (3x80 0 mL) and the combined organic layers were then dried over $MgSO_4$, filtered and concentrated under reduced pressure to obtain crude diacid as a yellow solid.

The diacid was directly dissolved in DMF (12 mL) and heated at 150 ºC for 1 h. After cooling down to rt the mixture was diluted with H_2O (60 mL) and the pH was adjusted to pH < 1 by the slow addition of concentrated HCl. The product was extracted with EtOAc (3x50 mL) and the combined organic layers were washed with a 12 M HCl aqueous solution (100 mL), then dried over $MgSO_4$, filtered and concentrated under reduced pressure to obtain the crude carboxylic acid as yellow solid, which was taken to the next step without further purification.

$BH_3{\cdot}SMe_2$ (0.44 mL, 4.54 mmol) was added dropwise to a solution of the crude carboxylic acid in anhydrous THF (30 mL) at 0 ºC. Once the addition was completed the ice bath was removed, the resulting mixture was allowed to warm to room temperature and then heated gradually to 80 ºC. After stirring at that temperature for 2 h without any condenser, the mixture was cooled to 0 ºC and quenched by slow addition of 1 M solution of HCl (50 mL). The product was extracted with EtOAc (3x60 mL) and the combined organic layers washed with brine (120 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by column chromatography (cyclohexane:EtOAc 7:3) afforded the product as a white solid with limited

solubility in standard organic solvents that was further washed with pentane to give pure alcohol (492.3 mg, 1.56 mmol, yield over 4 steps = 52 %).

Melting point = 167-169 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 – 8.35 (m, 1H), 8.32 (d, *J* = 1.1 Hz, 1H), 8.28 (s, 1H), 8.03 – 7.98 (m, 2H), 7.88 (d, *J* = 1.0 Hz, 1H), 7.52 – 7.46 (m, 2H), 3.82 (t, *J* = 6.3 Hz, 2H), 3.09 – 3.02 (m, 2H), 2.12 – 2.03 (m, 2H), 1.40 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.7, 132.0, 131.8, 131.4, 131.3, 130.6, 128.2, 125.7, 124.9, 123.1, 62.2, 32.9, 32.6 (4 peaks missing due to overlapping). HRMS (APCI+) *m/z* calc. for $C_{17}H_{16}BrO$ $[M+H]^+$: 315.0379. Found: 315.0368.



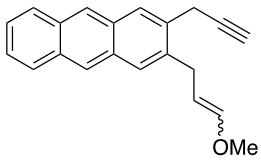
2-Bromo-3-(3-methoxyallyl)anthracene (S5). **S4** (480.0 mg, 1.52 mmol) was suspended in CH_2Cl_2 (150 mL) and then DMP (775.2 mg, 1.84 mmol) and $NaHCO_3$ (255.2 mg, 3.04 mmol) were sequentially added. The resulting mixture was stirred at rt for 1 h, then a saturated solution of $NaHCO_3$ (100 mL) was added, the organic layer was separated, the aqueous one extracted with CH_2Cl_2 (100 mL) and the combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure.

The resulting crude aldehyde was directly suspended in MeOH (800 mL) and $HC(OMe)_3$ (0.32 mL, 3.04 mmol) was subsequently added followed by 2 drops of H_2SO_4. The reaction was refluxed for 1.5 h and then cooled down to rt. Na_2CO_3 (644.4 mg, 6.08 mmol) was added and the mixture stirred at rt for 20 min, then filtered and concentrated under reduced pressure. Filtration through a short pad of silica (cyclohexane:CH_2Cl_2:Et_3N 80:20:1 to 50:50:1) afforded the crude acetal as an orange solid, which was directly taken to the next step without further purification.

To a solution of acetal in anhydrous CH_2Cl_2 (80 mL) under Ar atmosphere was added DIPEA (0.53 mL, 3.04 mmol) followed by TMSOTf (0.41 mL, 2.28 mmol) at -60 ºC and the resulting mixture was allowed to warm to 0 ºC and stirred for 16 h. The reaction was quenched by the addition of saturated solution of $NaHCO_3$ (50 mL) and the aqueous layer was extracted with CH_2Cl_2 (50 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by column chromatography (cyclohexane:CH_2Cl_2:Et_3N 90:10:1 to 80:10:1) afforded the product as a yellow solid (*Z*:*E* = 2:1, 248.7 mg, 0.76 mmol, yield over 3 steps = 50%).

Melting point = 113-115 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 0.5H, *E*), 8.36 (s, 1H, *Z*), 8.32 (s, 0.5H, *E*), 8.31 (s, 1H, *Z*), 8.28 (s, 0.5H, *E*), 8.27 (s, 1H, *Z*), 8.04 – 7.96 (m, 3H, *E*+*Z*), 7.90 (s, 1H, *Z*), 7.87 (s, 0.5H, *E*), 7.51 – 7.44 (m, 3H, *E*+*Z*), 6.53 (d, *J* = 12.6 Hz, 0.5H, *E*), 6.17 (dt, *J* =

6.1, 1.4 Hz, 1H, *Z*), 5.06 (dt, *J* = 12.6, 7.3 Hz, 0.5H, *E*), 4.75 (td, *J* = 7.4, 6.1 Hz, 1H, *Z*), 3.72 (dt, *J* = 7.5, 1.3 Hz, 2H, *Z*), 3.70 (s, 3H, *Z*), 3.64 (s, 1.5H, *E*), 3.58 (d, *J* = 7.3 Hz, 1H, *E*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 147.7, 137.7, 137.4, 131.9, 131.9, 131.8, 131.7, 131.3, 131.2, 131.0, 130.7, 130.6, 128.2, 128.2, 128.1, 127.8, 127.6, 125.8, 125.8, 125.6, 125.6, 125.5, 124.9, 124.8, 123.4, 123.2, 103.5, 100.1, 59.8, 56.2, 34.4, 30.9 (3 aromatic C missing due to overlapping). HRMS (APCI+) *m/z* calc. for $C_{17}H_{12}Br$ [M-OMe]$^+$: 295.0117. Found: 295.0105.

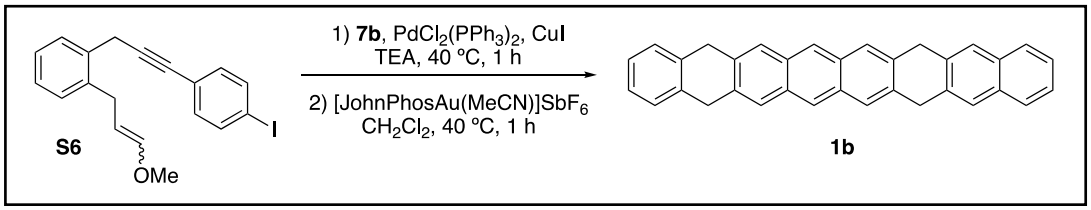


2-(3-Methoxyallyl)-3-(prop-2-yn-1-yl)anthracene (7c). A flask containing Mg turnings (81.7 mg, 3.36 mmol) was flame dried under an Ar stream, cooled, and charged with 0.4 mL of anhydrous THF followed by 5 μL of 1,2-dibromoethane. After 2 min stirring at room temperature, a solution of **S5** (220.0 mg, 0.67 mmol) in anhydrous THF (0.2 mL) was added. After heating at 50 ºC for 1 h, the reaction was cooled down to room temperature and added over a mixture of CuI (6.4 mg, 0.03 mmol) and methoxyallene (0.11 mL, 1.34 mmol) in anhydrous THF (0.1 mL). The resulting mixture was heated at 60 ºC for 16 h and then cooled down to room temperature, diluted with EtOAc (10 mL) and quenched by the addition of a saturated solution of $NaHCO_3$ (10 mL). The organic layer was separated and the aqueous phase was extracted with EtOAc (10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by column chromatography (pentane/CH_2Cl_2/Et_3N 98:2:1 to 95:5:1) gave the title compound as a pale yellow solid (*Z*:*E* = 2:1, 84.4 mg, 0.29 mmol, yield = 44%).

Melting point = 96-98 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1.5H, *E*+*Z*), 8.37 (s, 0.5H, *E*), 8.36 (s, 1H, *Z*), 8.18 (s, 1H, *Z*), 8.14 (s, 0.5H, *E*), 8.04 – 7.98 (m, 3H, *E*+*Z*), 7.84 (s, 1.5H, *E*+*Z*), 7.50 – 7.43 (m, 3H, *E*+*Z*), 6.44 (dd, *J* = 12.6, 1.4 Hz, 0.5H, *E*), 6.12 (dt, *J* = 6.1, 1.5 Hz, 1H, *Z*), 5.02 (dt, *J* = 12.7, 6.9 Hz, 0.5H, *E*), 4.61 (td, *J* = 7.3, 6.1 Hz, 1H, *Z*), 3.84 (dd, *J* = 2.7, 1.2 Hz, 2H, *Z*), 3.82 (dd, *J* = 3.1, 1.0 Hz, 1H, *E*), 3.72 (s, 3H, *Z*), 3.64 (dt, *J* = 7.4, 1.3 Hz, 2H, *Z*), 3.61 (s, 1.5H, *E*), 3.52 (dt, *J* = 7.0, 0.9 Hz, 1H, *E*), 2.37 (t, *J* = 2.6 Hz, 1H, *Z*), 2.36 (t, *J* = 2.7 Hz, 0.5H, *E*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 147.1, 137.1, 137.1, 132.9, 132.7, 131.8, 131.7, 131.6, 131.5, 131.3, 131.2, 130.8, 130.8, 128.2, 128.2, 128.1, 128.1, 127.2, 127.1, 126.8, 126.8, 125.6, 125.6, 125.3, 125.2, 125.2, 125.1, 125.1, 125.0, 104.2, 100.7, 81.9, 81.6, 71.6, 71.6, 59.8, 56.1, 31.2, 27.9, 23.0, 22.7. HRMS (ESI+) *m/z* calc. for $C_{21}H_{19}O$ [M+H]$^+$: 287.1430. Found: 287.1425.

2.2. *Synthesis of hydroacenes **1***

2.2.1. *Synthesis of **1b***

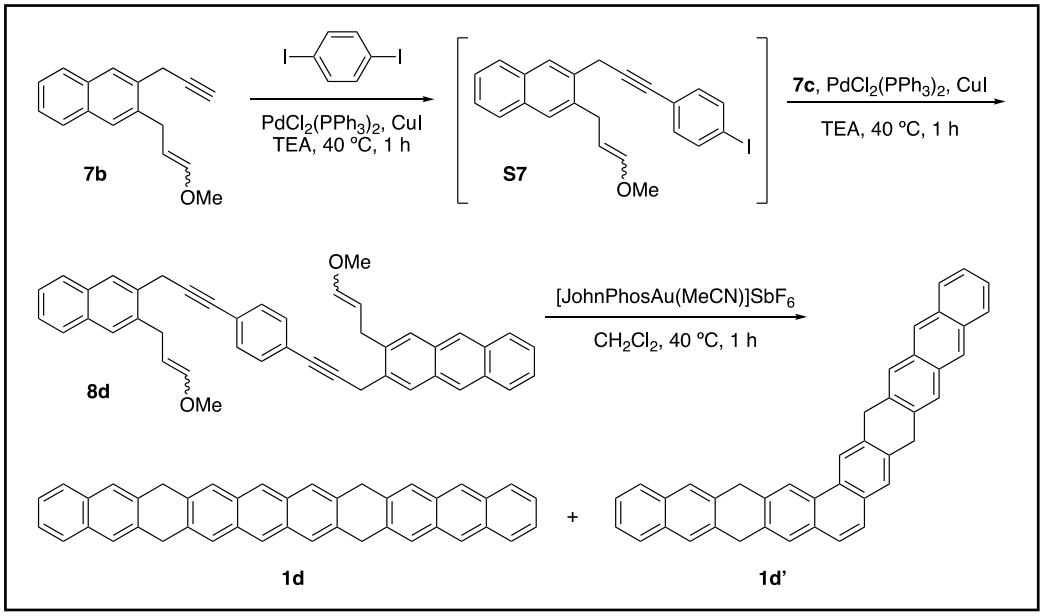


5,9,16,20-Tetrahydrooctacene (1b). $PdCl_2(PPh_3)_2$ (8.8 mg, 0.0125 mmol) and CuI (4.8 mg, 0.025 mmol) were suspended in NEt_3 (1.5 mL) and the mixture was bubbled with Ar for 10 min. A solution of **S6**[3] (97.1 mg, 0.25 mmol) and **7b** (64.3 mg, 0.27 mmol) in degassed NEt_3 (1 mL) were subsequently added and the reaction was stirred at 40 ºC for 1 h. Then the mixture was diluted with EtOAc (1 mL), filtered through a short pad of silica gel compacted with EtOAc/NEt_3 99:1, and concentrated under reduced pressure. Purification by column chromatography (cyclohexane:EtOAc: NEt_3 95:5:1) afforded the mixture of dienynes **8b** as an unstable pale yellow oil, which was directly submitted to the next reaction.

The mixture of dienynes (49.7 mg, 0.10 mmol) was dissolved in CH_2Cl_2 (1 mL) and cationic gold catalyst [JohnPhosAu(MeCN)]SbF_6 (**A**, 1.9 mg, 2.5 mol%) was subsequently added. The reaction was heated to 40 ºC for 1 h and then cooled to room temperature and quenched by the addition of one drop of NEt_3. After removing the volatiles the crude was washed and centrifuged with a 1:3 mixture of CH_2Cl_2:MeOH (3x6 mL) and the remaining solid was dried under reduced pressure to afford the product as an insoluble white solid (13.6 mg, 0.031 mmol, yield over 2 steps = 15%).

Melting point > 300 ºC. HRMS (LDI-) *m/z* calc. for $C_{34}H_{23}$ $[M-H]^-$: 431.1805. Found: 431.1812.

2.2.2. *Synthesis of **1d/1d'***

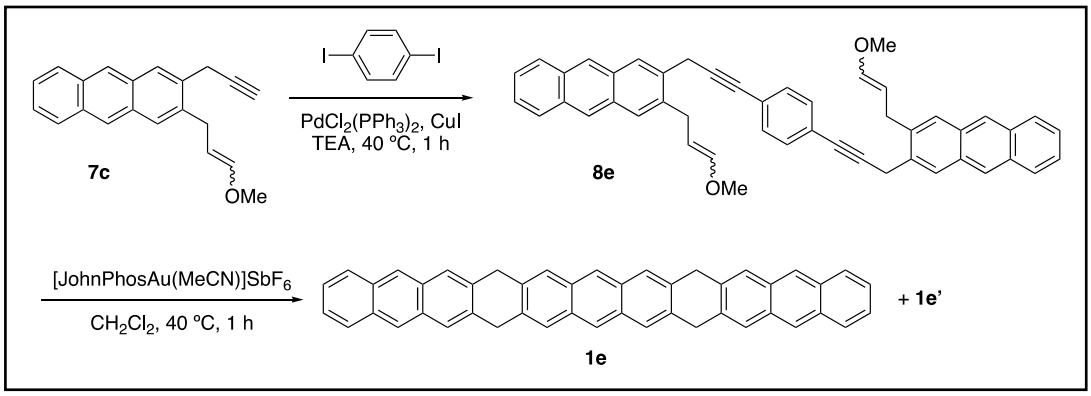


6,10,19,23-Tetrahydrodecacene (1d). $PdCl_2(PPh_3)_2$ (11.9 mg, 0.017 mmol) and CuI (6.5 mg, 0.034 mmol) were suspended in NEt_3 (2 mL) and the mixture was bubbled with Ar for 10 min. 1,4-Diiodobenzene (130.0 mg, 0.41 mmol) and a solution of **7b** (80.1 mg, 0.34 mmol) in degassed NEt_3 (1 mL) were subsequently added and the reaction was stirred at 40 ºC for 1 h. Then the mixture was diluted with EtOAc (1 mL), filtered through a short pad of silica gel compacted with EtOAc/NEt_3 99:1, and concentrated under reduced pressure. The crude enyne was dissolved in degassed NEt_3 (1 mL) and added to a mixture of $PdCl_2(PPh_3)_2$ (8.8 mg, 0.0125 mmol), CuI (4.8 mg, 0.025 mmol), and **7c** (85.9 mg, 0.30 mmol) in degassed NEt_3 (1.5 mL) and the mixture was stirred at 40 ºC for 1 h. Then the mixture was diluted with EtOAc (1 mL), filtered through a short pad of silica gel compacted with EtOAc/NEt_3 99:1, and concentrated under reduced pressure. Purification by column chromatography (cyclohexane:EtOAc: NEt_3 95:5:1) afforded the mixture of dienynes **8d** as an unstable yellow solid, which was directly submitted to the next reaction.

Inside a glovebox filled with Ar, the mixture of dienynes **8d** (59.7 mg, 0.10 mmol) was dissolved in anhydrous and degassed CH_2Cl_2 (1 mL) and cationic gold catalyst [JohnPhosAu(MeCN)]SbF_6 (**A**, 1.9 mg, 2.5 mol%) was subsequently added. The reaction was heated to 40 ºC for 1 h and then cooled to room temperature and quenched by the addition of one drop of degassed NEt_3. After removing the volatiles the crude was washed and centrifuged with a 1:3 mixture of degassed CH_2Cl_2:MeOH (3x6 mL) and the remaining solid was dried under reduced pressure to afford an inseparable mixture of **1d** and **1d'** as an insoluble yellow solid, which was kept under Ar all the time due to its instability in the presence of oxygen (18.1 mg, 0.034 mmol, yield over 2 steps = 11%).

Melting point > 300 ºC. HRMS (MALDI+) *m/z* calc. for $C_{42}H_{28}$ $[M]^+$: 532.2191. Found: 532.2184.

2.2.3. *Synthesis of **1e/1e'***



7,11,20,24-Tetrahydroundecacene (1e). $PdCl_2(PPh_3)_2$ (3.5 mg, 0.005 mmol) and CuI (1.9 mg, 0.01 mmol) were suspended in NEt_3 (2 mL) and the mixture was bubbled with Ar for 10 min. 1,4-Diiodobenzene (16.5 mg, 0.05 mmol) and a solution of **7c** (30.1 mg, 0.105 mmol) in degassed NEt_3 (1 mL) were subsequently added and the reaction was stirred at 40 ºC for 2 h. Then the

mixture was allowed to cool to rt and the precipitate was filtered, washed with NEt_3 (2 mL), and dried under reduced pressure. The crude dienynes **8e** were directly taken inside a glovebox filled with Ar and dissolved in anhydrous and degassed CH_2Cl_2 (2 mL). Then cationic gold catalyst [JohnPhosAu(MeCN)]SbF_6 (**A**, 1.9 mg, 5 mol%) was added and the reaction was heated to 40 ºC for 1 h and then cooled to room temperature and quenched by the addition of one drop of degassed NEt_3. After removing the volatiles the crude was washed with degassed pentane (2x4 mL) and the remaining solid was passed through a short pad of SiO_2 eluting with degassed CH_2Cl_2. After removal of the volatiles under reduced pressure a mixture of **1e** and **1e'** was obtained as an orange solid, which was kept under Ar all the time due to its instability in the presence of oxygen (2.3 mg, 0.004 mmol, yield over 2 steps = 8%).

HRMS (LDI+) *m/z* calc. for $C_{46}H_{30}$ $[M]^+$: 582.2348. Found: 582.2325.

3. Additional STM and STS data

3.1. Tip-induced molecule manipulation leading to undecacene

Figure S1 shows sequential tip-induced dehydrogenation of the tetrahydroundecacene precursor leading to dihydroundecacene intermediate and the target undecacene.

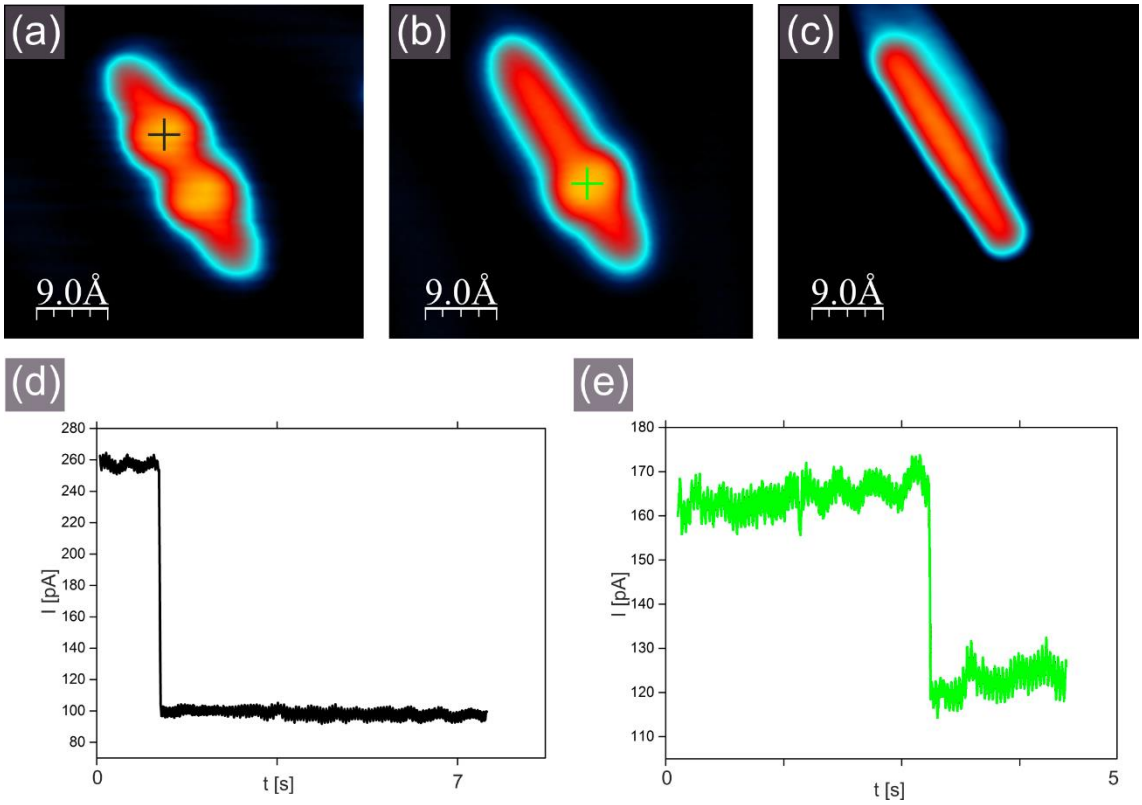


Figure S1. Tip-induced sequential dehydrogenation leading to parent undecacene, (a) tetrahydroundecacene, (b) dihydroundecacene, (c) undecacene. The atom manipulation was performed following the procedure described previously [4] with the bias voltage raised up to 3.0 V with the tip positioned above the pair of methylene moieties assigned for dehydrogenation as indicated by black and green crosses in (a) and (b); (d) and (e) show current versus time traces recorded during atom manipulation leading to the transformation of the tetrahydroundecacene into dihydroundecacene (d) and subsequently dihydroundecacene into undecacene (e); bias voltage + 2.0 V, tunnelling current 30 pA, slight asymmetry in panel (c) results from attachment of hydrogen at the tip apex during manipulation process.

3.2. Scanning tunneling spectroscopy

Figure S2 shows STS curves recorded over on-surface generated acenes. In Figure S3 the STS data for kinked acene isomers are shown.

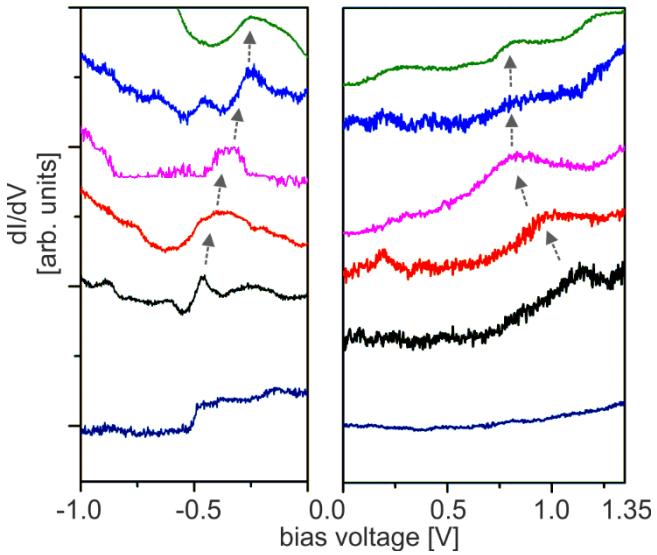


Figure S2. Filled (left) and empty (right) state dI/dV curves acquired for the acene series with resonance shifts indicated by grey arrows, green – undecacene, blue – decacene, pink – nonacene, red – octacene, black – heptacene, dark blue spectrum displayed in the bottom shows reference STS data recorded over Au(111) with clearly discernible surface state onset at -0.5 V.

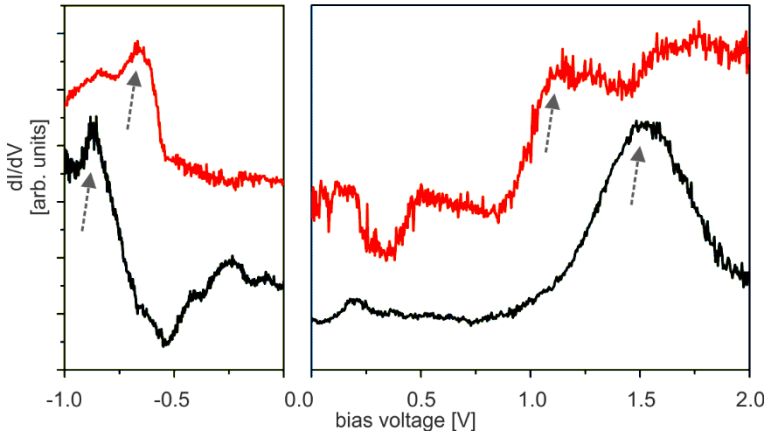


Figure S3. Filled (left) and empty (right) state dI/dV curves acquired for kinked decacene and undecacene isomers with resonance shifts indicated by grey arrows, red – kinked undecacene isomer, black – kinked decacene isomer.

Table S1 shows STS recorded energies of filled and empty state resonances and transport gaps for acenes on Au(111). The measurements clearly show the decrease of the gap value when the number of annulated rings grows. However, for the longest acenes – as visualized in Figure 3 (main text) – we observe the indication for the saturation of further band gap lowering in higher acenes. Finally, the sound of the Clar's sextet rule is apparently demonstrated by comparison of the transport gap for the longest linear and kinked acenes. The measurements clearly show that the kinked acenes, which contain two migrating Clar's sextets are characterized by a much larger gap value and expected increased stability.

Table S1. STS recorded filled- and empty state resonances for the acene series (values for pentacene and hexacene are taken from literature).

Molecule	Filled state [V]	Empty state [V]	STS transport gap [eV]
pentacene[1]	-0.90	1.30	2.20
hexacene[2]	-0.65	1.20	1.85
heptacene	-0.45	1.16	1.61
octacene	-0.40	1.01	1.41
nonacene	-0.35	0.88	1.23
decacene	-0.25	0.87	1.12
kinked decacene isomer	-0.87	1.50	2.37
undecacene	-0.24	0.85	1.09
kinked undecacene isomer	-0.67	1.15	1.82

3.3. Tip-induced lateral manipulation

Figure S4 shows unintentional manipulation of heptacene, octacene, and decacene molecules leading to partially uncovered Au(111) area and clearly gathered molecular species. The manipulation points to the small molecule-surface interaction potential variation resulting from weak van der Waals type of interaction.

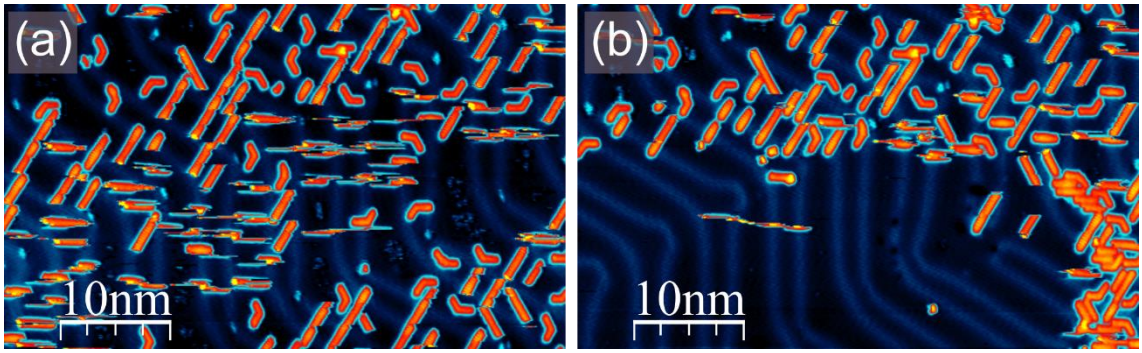


Figure S4. STM filled state images indicating mobility of generated heptacene, octacene and decacene molecules, both panels show the same area; in (a) the molecules clearly exhibit mobility, which leads to their lateral displacement and the clearly recorded partially uncovered area in (b); tunnelling current: (a) 200 pA, (b) 30 pA, bias voltage -1.0 V.

3.4. Additional STM images

Figure S5a shows typical STM appearance of Au(111) sample after deposition of undecacene precursors. It is clear that apart from tetrahydroundecacenes smaller fragments marked with white circles are also recorded. After thermal treatment both undecacene and its kinked isomer are generated as shown in Figure S5b.

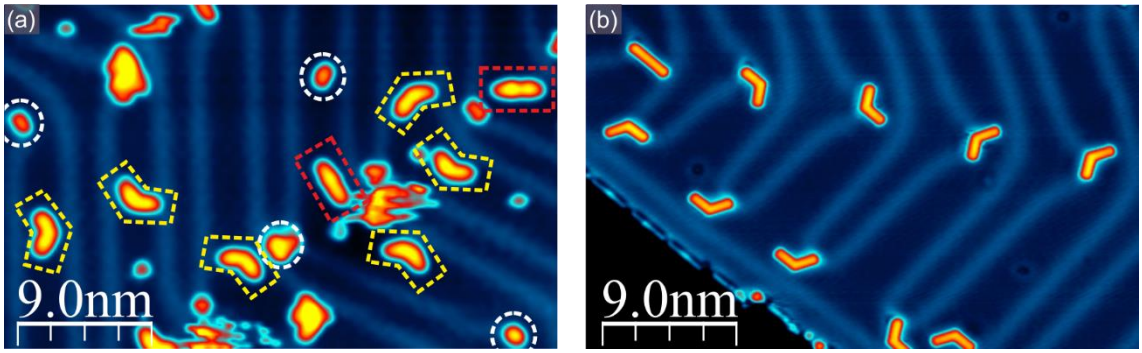


Figure S5. Empty state overview STM images before (a) and after (b) undecacene generation, yellow contours indicate kinked tetrahydroundecacene isomers, whereas red ones show undecacene precursors; white dashed circles mark smaller fragment found after molecule deposition, after annealing at 520 K for 10 minutes both undecacene and its kinked isomer are clearly visible. Please note the presence of undecacene molecules located at the surface step, at lower terrace and aligned along the step in panel (b); tunnelling current: (a) 50 pA, (b) 30 pA, bias voltage +2.0 V.

Figure S6 shows additional larger scale STM images of the mixture of heptacene, octacene and decacene precursors (S6a) and parent heptacenes, octacenes and decacenes (S6b) obtained after thermal annealing of the sample at 520 K.

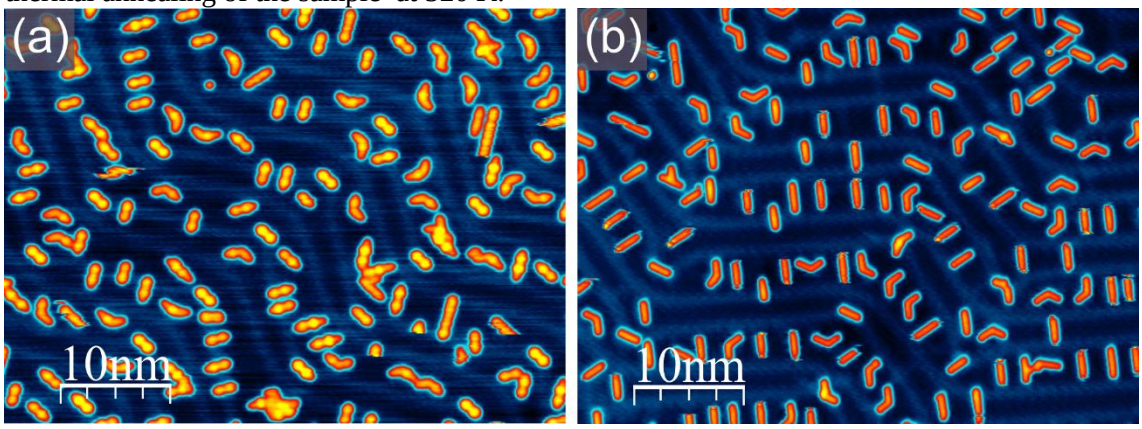


*Figure S6. On-surface generation of higher acenes; (a-b) empty state STM images of the Au(111) surface partially covered with (a) hydrogen protected precursors **1a**, **1b**, **1d**, and **1d'**, and (b) heptacene (**2**), octacene (**3**), decacene (**5**) and its kinked isomer (**5'**). Precursor molecules are easily discernible by the presence of two pronounced lobes corresponding to two non-aromatic rings each containing two methylene groups. Tunneling current 30 pA, bias voltage + 2.0 V.*

In Figure S7 an example of the hydrogen migration along the precursor molecule edges[4] is visualized. Panels (a) and (b) show the kinked tetrahydroundecacene isomer **1e'** imaged after deposition on the Au(111) surface with clearly visible different localization of the methylene moieties imaged as bright lobes.

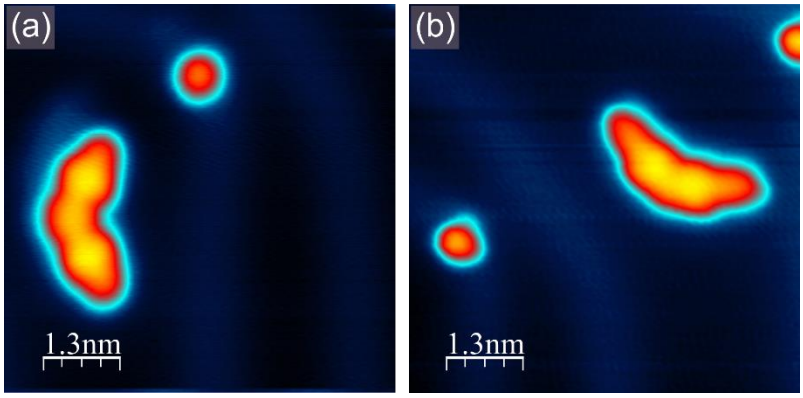
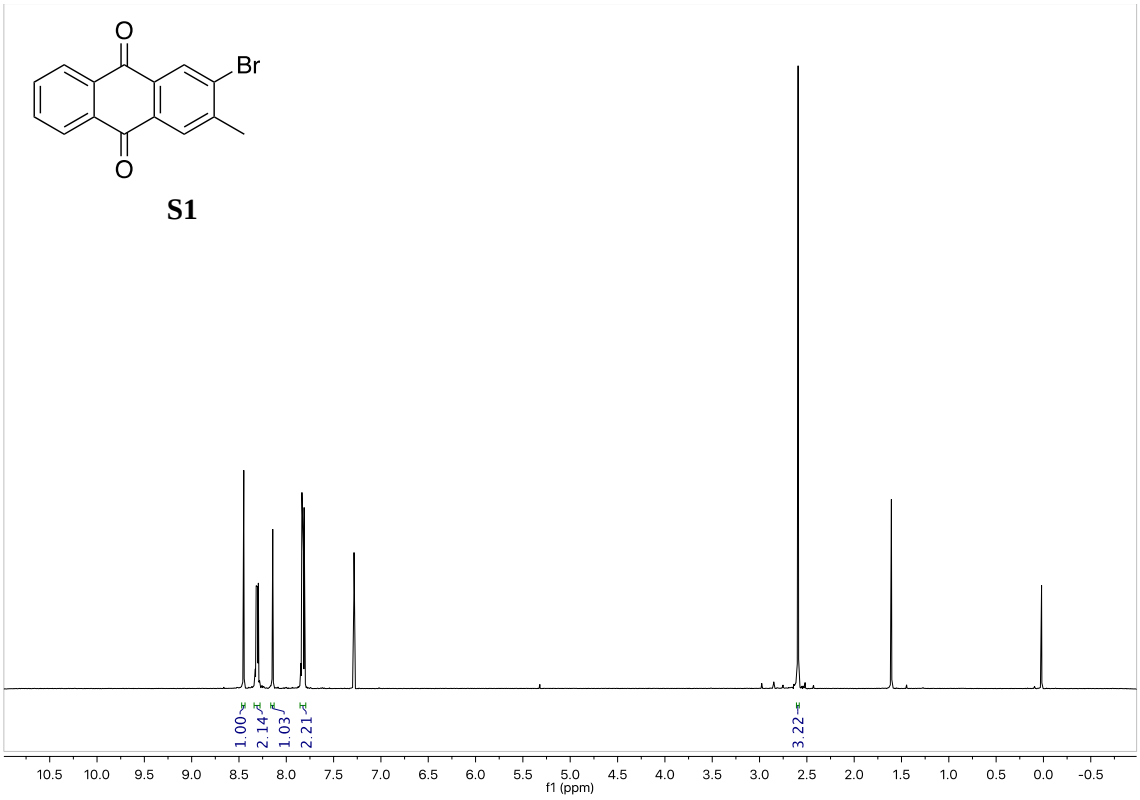
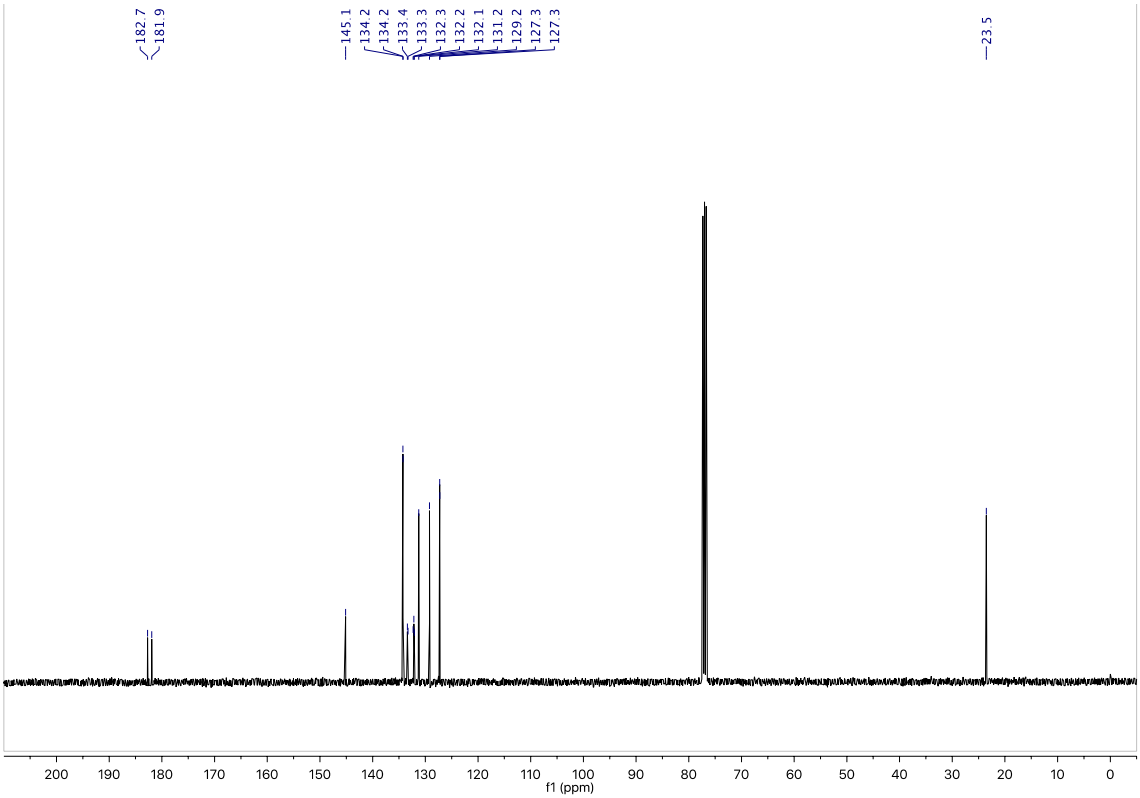


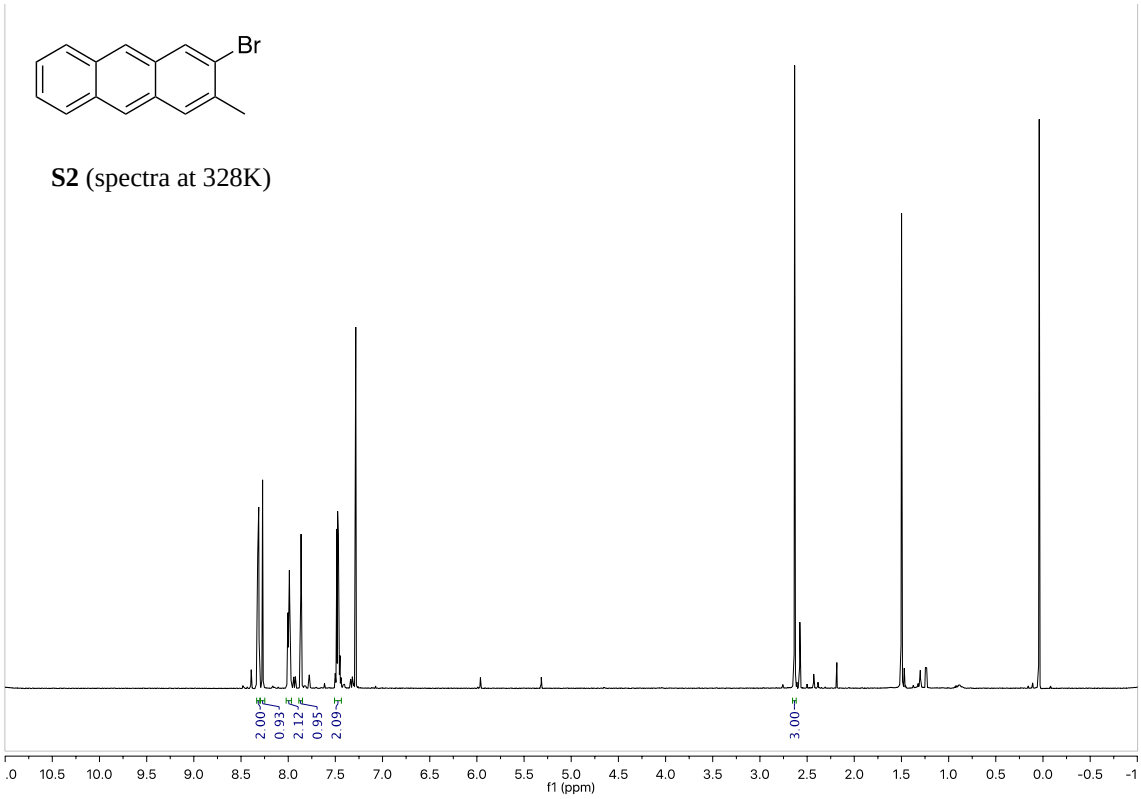
*Figure S7. Empty state STM images of the kinked isomer of undecacene precursor (**1e'**) after deposition on the Au(111) surface with clearly discernible differences in the positions of methylene moieties for molecules shown in (a) and (b). Tunneling current: 30 pA, bias voltage: +2.0 V.*

4. ^{1}H and ^{13}C NMR spectra

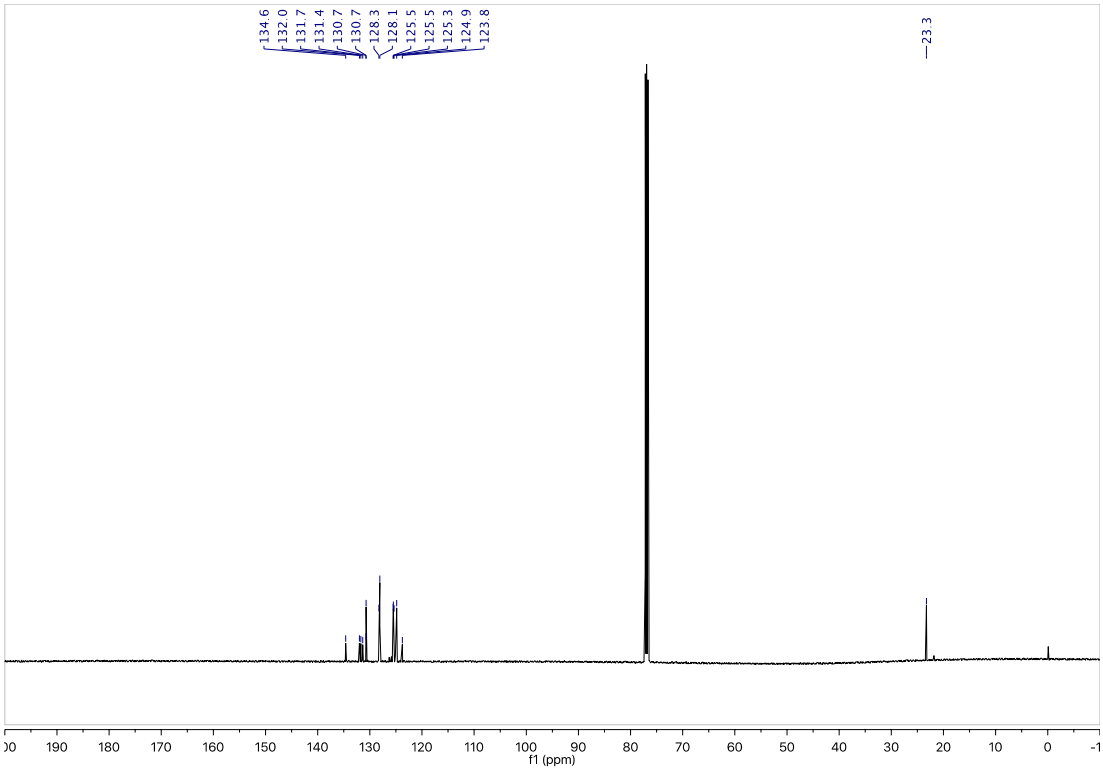


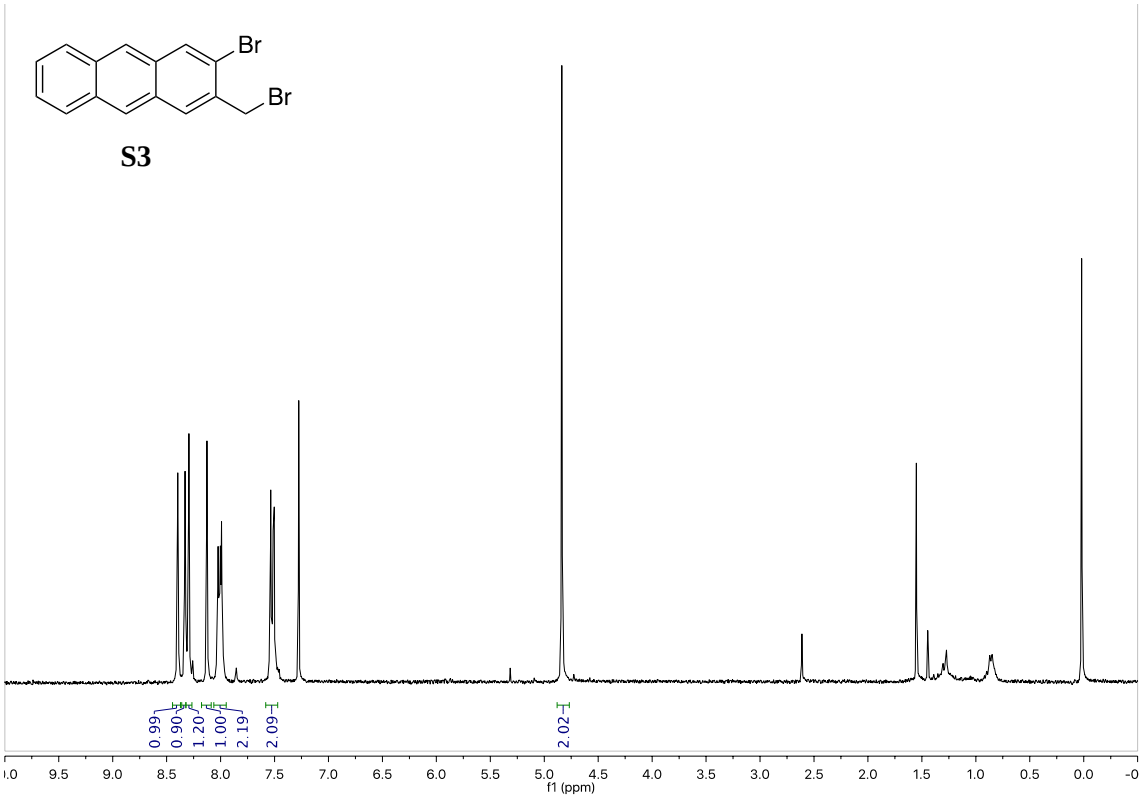
S1

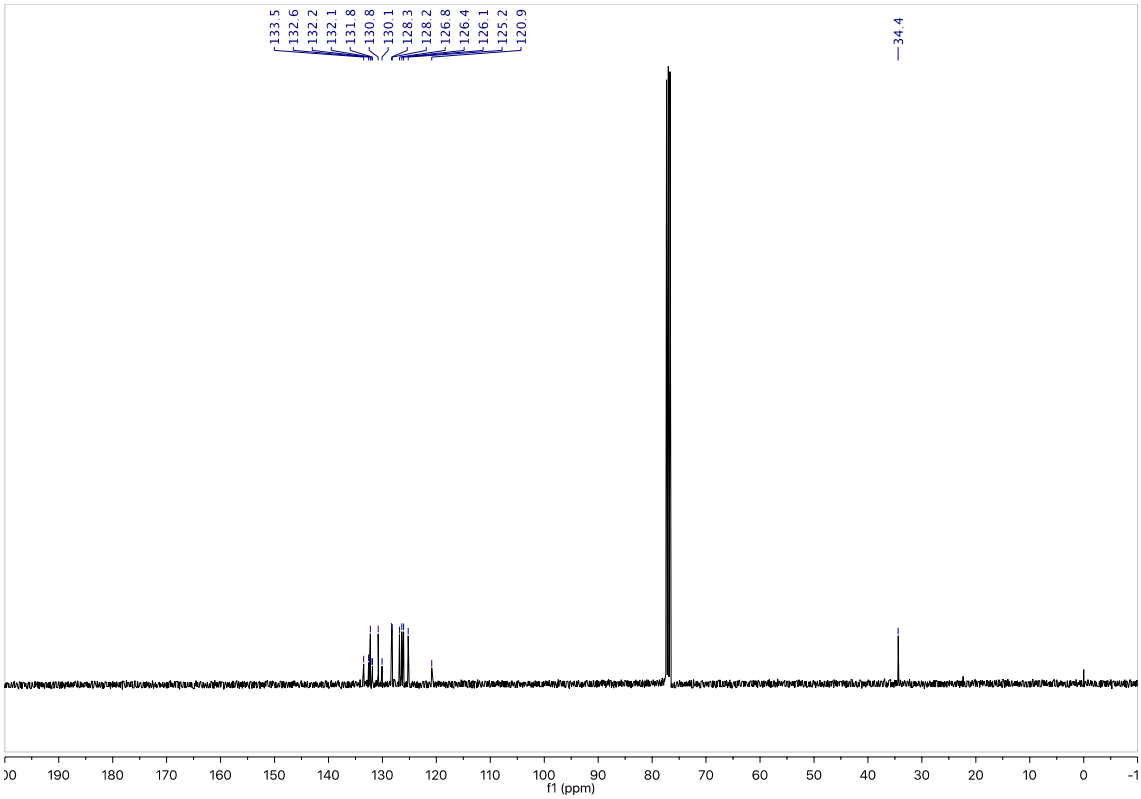


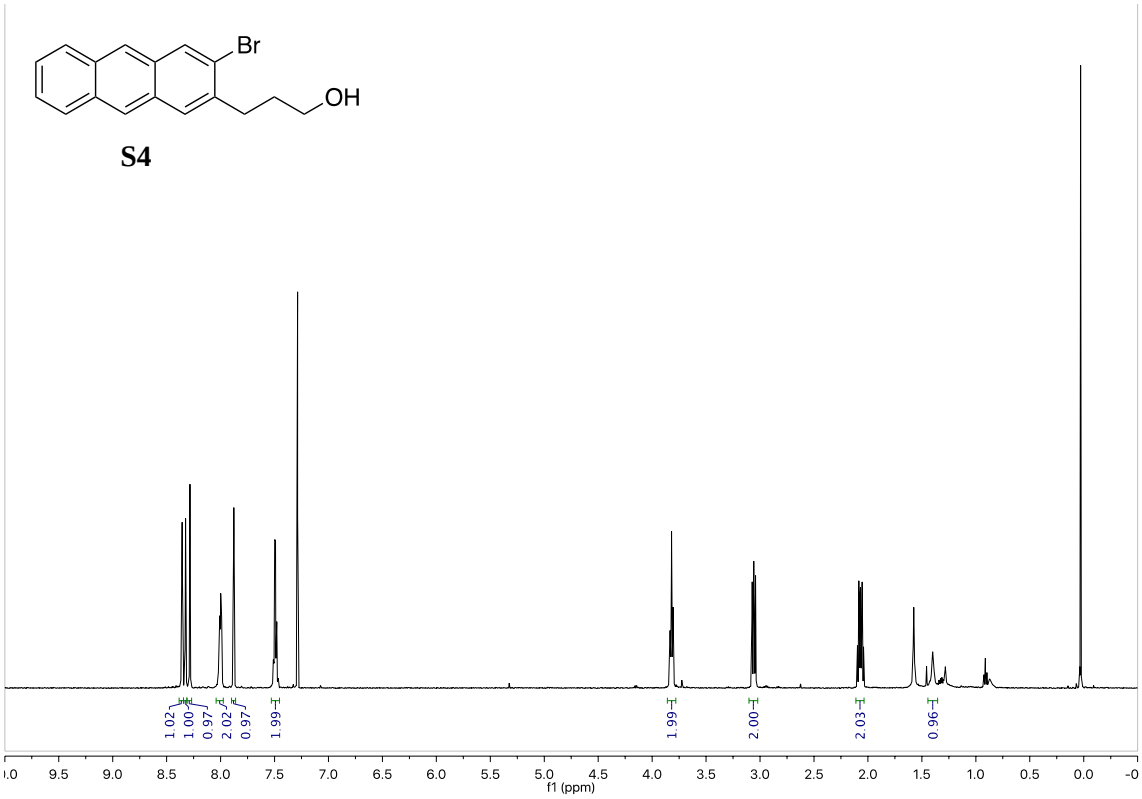


S2 (spectra at 328K)




Br
Br
S3
0.99
0.90
1.20
1.00
2.19
2.09
2.02
f1 (ppm)


133.5
132.6
132.2
132.1
131.8
130.8
130.1
128.3
128.2
126.8
126.4
126.1
125.2
120.9
34.4
f1 (ppm)


Br
OH
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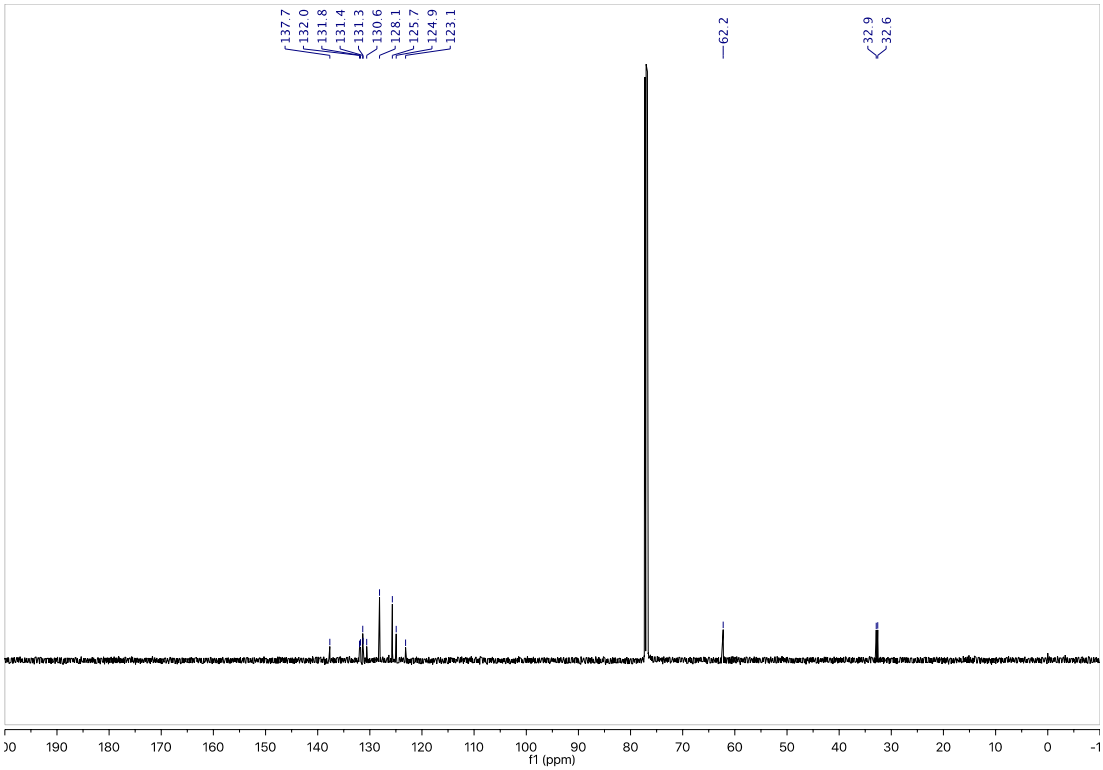
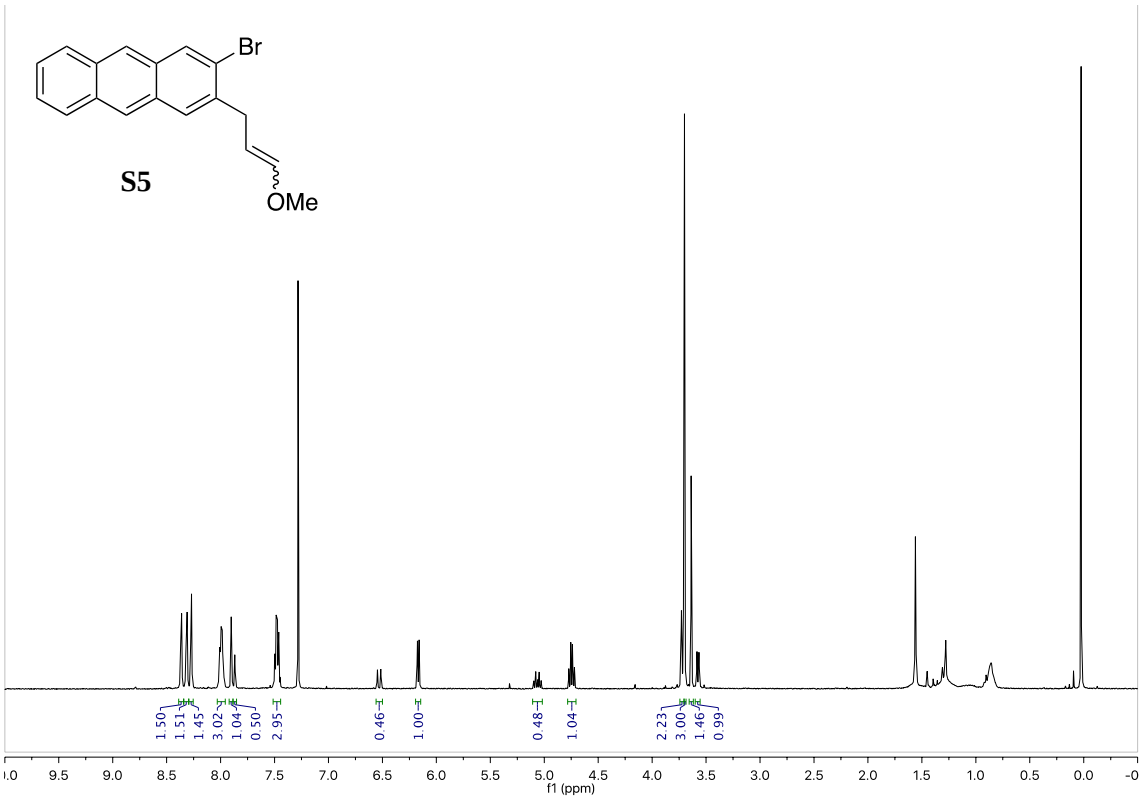
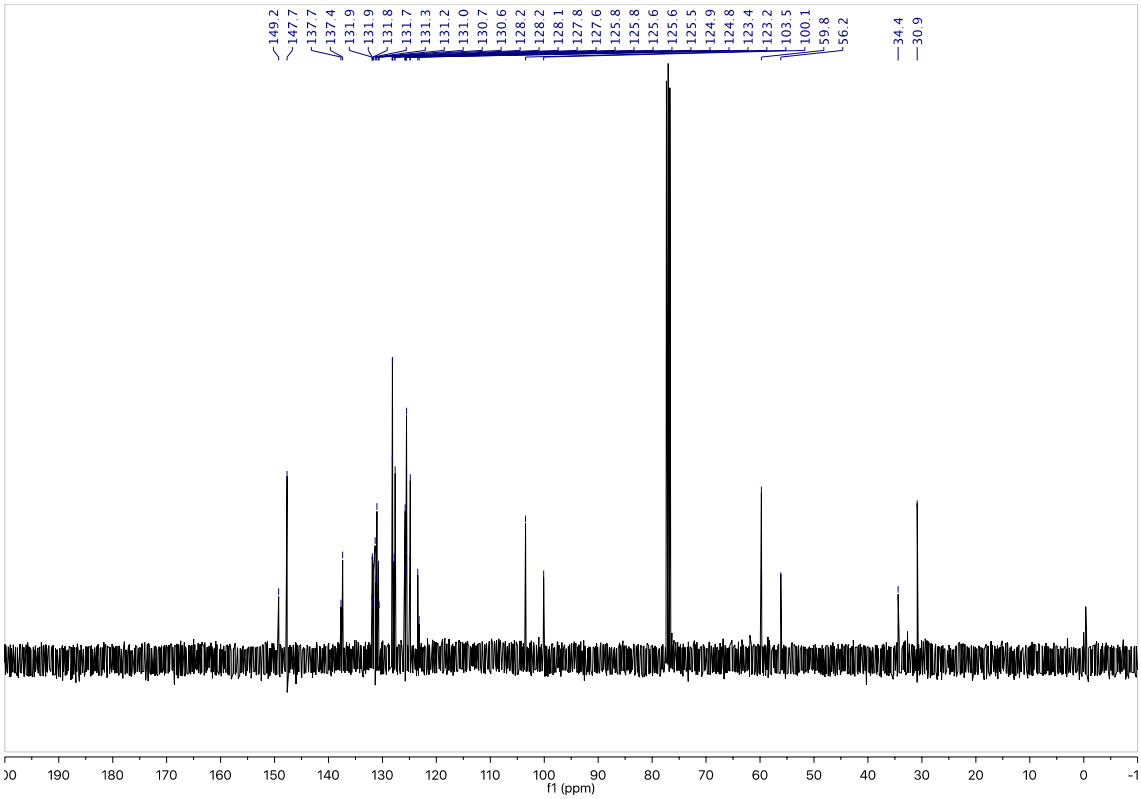
1.00
0.97
2.02
0.97
1.99
1.99
2.00
2.03
0.96
f1 (ppm)

S4


137.7
132.0
131.8
131.4
131.3
130.6
128.1
125.7
124.9
123.1
62.2
32.9
32.6
f1 (ppm)


Br
S5
OMe
1.50
1.51
1.45
3.02
1.04
0.50
2.95
0.46
1.00
0.48
1.04
2.23
3.00
1.46
0.99
f1 (ppm)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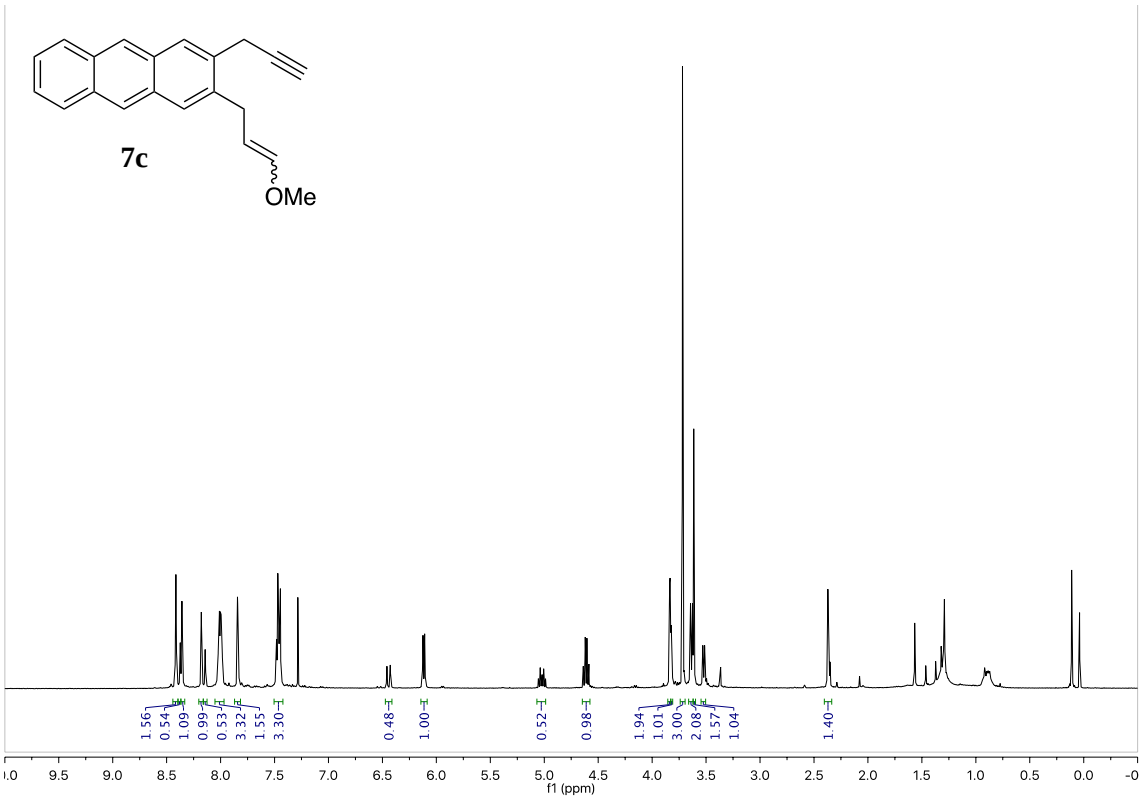
147.7
137.7
137.4
131.9
131.9
131.8
131.7
131.3
131.2
131.0
130.7
130.6
128.2
128.2
128.1
127.8
127.6
125.8
125.8
125.6
125.6
125.5
124.9
124.8
123.4
123.2
103.5
100.1
59.8
56.2
34.4
30.9
f1 (ppm)


7c
OMe
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0.54
1.09
0.99
0.53
3.32
1.55
3.30
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1.00
0.52
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1.01
3.00
2.08
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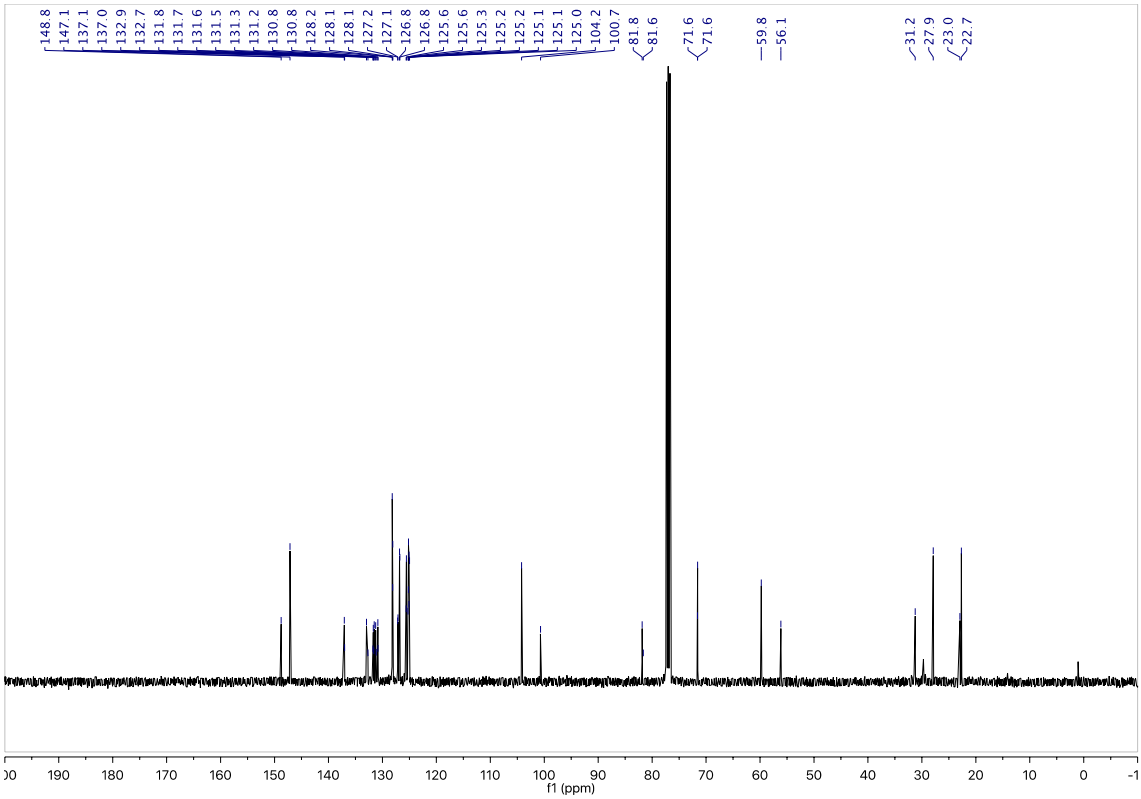
1.40
f1 (ppm)


148.8
147.1
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132.9
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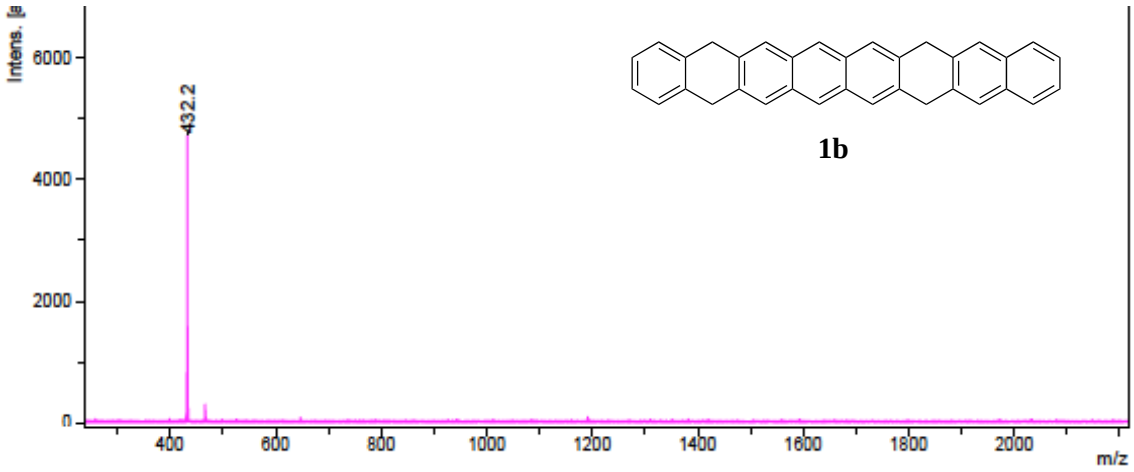
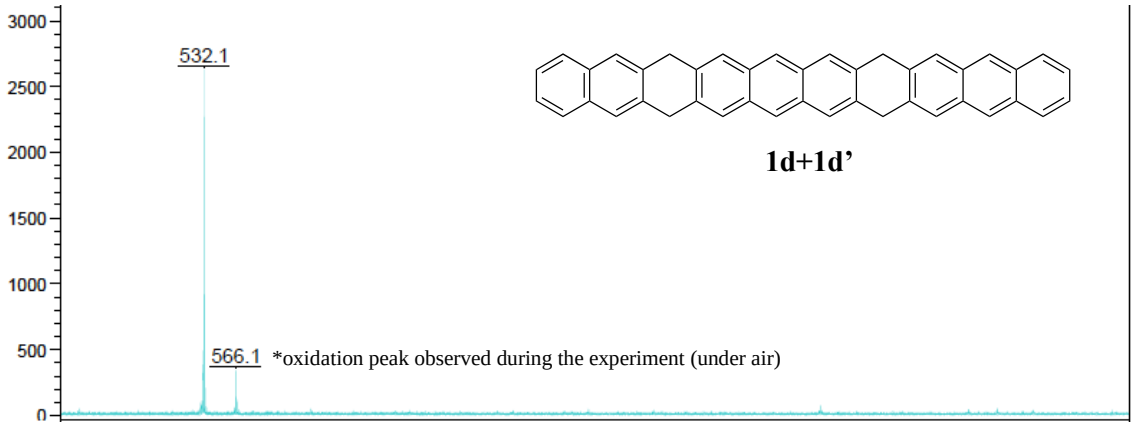
126.8
126.8
125.6
125.6
125.3
125.2
125.2
125.1
125.1
125.0
104.2
100.7
81.8
81.6
71.6
71.6
59.8
56.1
31.2
27.9
23.0
22.7
f1 (ppm)

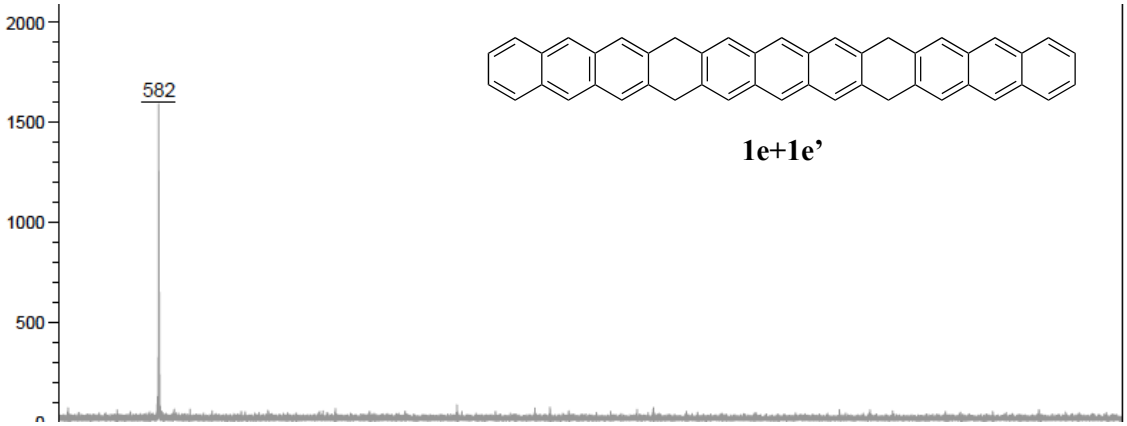
5. MALDI-MS spectra of hydroacenes 1



1b



1d+1d'



1e+1e'

6. References

1 F. J. Giessibl, *Appl. Phys. Lett.* **2000**, *76*, 1470.
2 L. Gross, F. Mohn, N. Moll, P. Liljeroth, G. Meyer, *Science* **2009**, *325*, 1110−1114.
3 R. Dorel, P. R. McGonigal, A. M. Echavarren, *Angew. Chem. Int. Ed.* **2016**, *55*, 11120-11123.
4 R. Zuzak, R. Dorel, M. Krawiec, B. Such, M. Kolmer, M. Szymonski, A. M. Echavarren, S. Godlewski, *ACS Nano* **2017**, *11*, 9321-9329.