Preparation of a Key Tetraene Precursor for the Synthesis of Long Acenes

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Gaspard Levet,[a] Nguyen Khanh Hung,[a] Michal Šámal,[b] Jiří Rybáček,[b] Ivana Cisařová,[b] Andrej Jancarik*[a,b] and André Gourdon*[a]

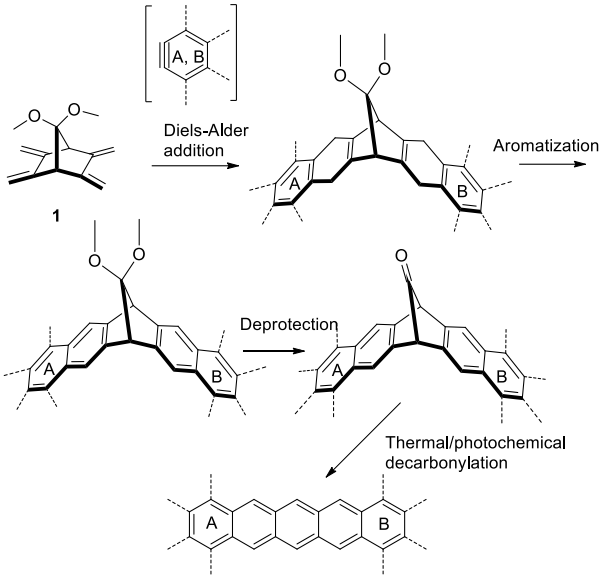
Abstract: *The tetraene 7,7-dimethoxy-2,3,5,6-tetramethylenebicyclo[2.2.1]heptane is a key compound for the preparation of a large variety of acenes protected by a carbonyl bridge. We report here a medium scale preparation in seven steps of this valuable starting material. Diels-Alder addition between 6,6-dimethyl fulvene and maleic anhydride, followed by carboxylation, ozonolysis of the double bond, reduction of the four ester group, then chlorination of the alcohol groups and dehydrochlorination give the target compound in 17% overall yield.*

Introduction

Acenes, molecules comprising linearly fused benzene rings, have attracted a lot of interest for a long time and have also experienced a renewed interest[1,2] in the past decade for potential applications in molecular electronics,[3,4] spintronics[5] and plasmonics.[6]

However, the preparation of acenes longer than pentacene faces two main difficulties. First, the extension of the planar aromatic cores increases the intermolecular π–π interactions, leading to less and less soluble compounds. Second, the reduction of the HOMO-LUMO gap increases the chemical reactivity towards oxidation and favours dimerization reaction even at very low concentration. To avoid these difficulties, long acenes have been studied under very high dilution conditions, on surfaces in UHV at liquid helium temperature or in cold matrices. In both types of experiments, stable and soluble precursors (epoxides, diketone or partially hydrogenated acenes) are prepared in solution and then, respectively, sublimated in UHV or dissolved in solvents which are then frozen to minimize the diffusion. The last reaction step yielding the acenes is done in situ thermally,[6-13] by tip-induced reactions,[7] or optically at low temperature.[15–21] Indeed these experiments are limited to minute amounts of compounds so that the preparation of long acenes as a material for organic thin-film transistors for instance is still a challenge. So far, the only long unsubstituted acenes prepared on macroscopic scale have been hexacene, benzohexacene and heptacene by thermal cheletropic decarbonylation of a monoketone precursor,[22,23] and heptacene by thermal cleavage of diheptacenes in the solid state at 300°C.[24]

In order to overcome this limitation and to find a general practical route to many long acenes, we have recently investigated the use of the tetraene (7,7-dimethoxy-2,3,5,6-tetramethylenebicyclo[2.2.1]heptane) **1** (scheme 1) as a key and valuable compound to access symmetrical or asymmetrical acenes.[23] The concept is the following one:



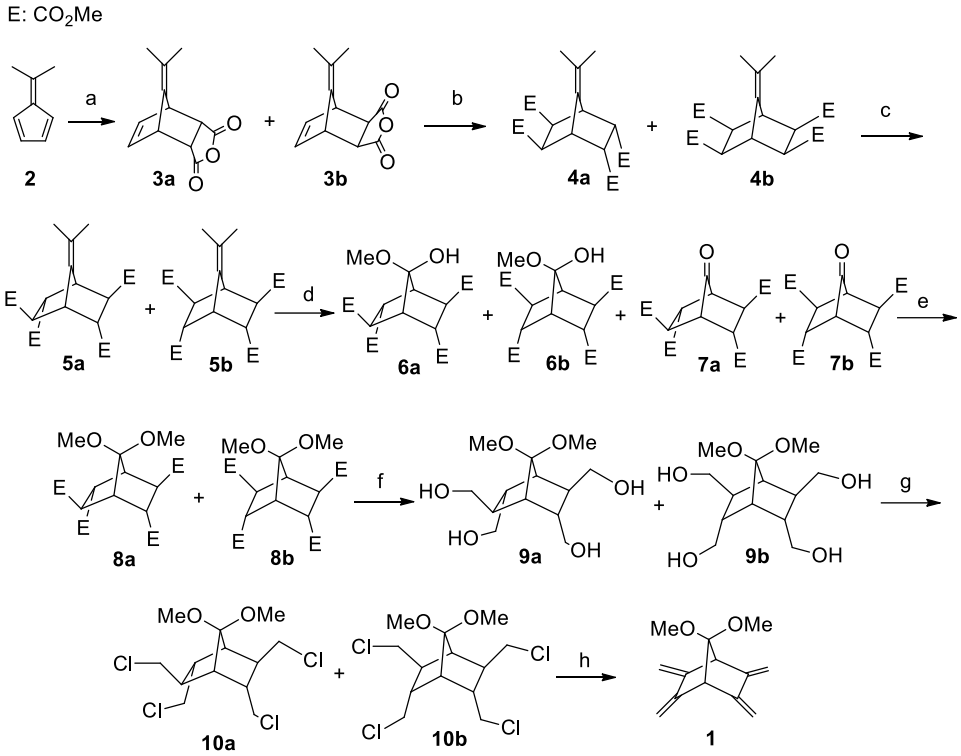
Scheme 1. *Preparation of symmetrical (A=B) and non-symmetrical (A≠B) acenes by cheletropic decarbonylation of CO bridged precursors.*

Diels-Alder reaction of aryne(s) with the diene parts of the tetraene **1** gives, after aromatization by DDQ, a non-planar acene bridged by a dimethyl ketal. The non-planarity of the molecule reduces π–π intermolecular stacking and provides some solubility whereas the bridge breaks the electronic delocalisation which reduces the chemical reactivity. Deprotection of the ketal gives a stable non-planar carbonyl bridged compound. The final step is a cheletropic thermal or photochemical decarbonylation, not in solution but in the solid or vapour phase. Photodecarbonylation can also be done in solid matrices at low temperature. Such final step is quantitative, without any non-gaseous by-product and can be used to prepare high-quality acenes for opto-electronic devices.[4] Our route allows the preparation of symmetrical or non-symmetrical acenes and could give an access to very long acenes by multiple Diels-Alder reactions.

In order to explore the synthetic potential of this promising starting material for the preparation of long acenes, we have reinvestigated and completed the synthesis of **1**, previously described in parts in small scale and only for endo-endo isomers by Roth in 1991,[25] but here at larger scales (tens of grams). Therefore, we present here procedures minimizing separations by chromatography and relying on recrystallizations or simple washings on short plugs of silica gel, eventually at the expense of preparative yields.

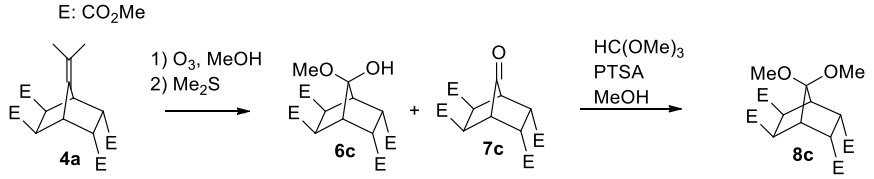
Results and Discussion

The general synthetic route (scheme 2) follows in large parts the one described by Roth[25], but at larger scale with some experimental differences that will be explained below.



Scheme 2*. Synthesis of* ***1****. a) maleic anhydride, DCM; 86% b) Pd/C, $CuCl_2$, CO, MeOH; 74% c) K_2CO_3, MeOH; 88% d) O_3, Me_2S, DCM-MeOH; e) $HC(OMe)_3$, APTS, MeOH; 82% for two steps f) $LiAlH_4$, THF; 94% g) Cl2, PPh3, imidazole, DCM-ACN-pyridine; 68% g) t-BuOK, DMF; 61%.*

Diels-Alder addition between 6,6-dimethylfulvene **2** [26] and maleic anhydride gives a ca 1:1 mixture of endo- and exo-isomers **3a** and **3b** in around 90% yield.[27–30] The next step is a palladium catalysed carboxylation according to Stille.[31] In contrast with Roth[23] who only explored the addition on the endo-isomer **3a**, we obtained the mixture of isomers **4a** and **4b** (yield 71-74%) by carboxylation of the mixture of isomers **3a** and **3b** with a higher palladium loading (2%) and a longer reaction time (48 h). The following step is the ozonolysis of the double bond to form the carbonyl bridge. For the isomer **4a**, which is less sterically crowded, the ozonolysis gives a mixture of hemiacetal **6c** and ketone **7c** (scheme 3). Then the mixture is protected as the ketal **8c** in 89% overall yield.



Scheme 3. *Ozonolysis of* ***4a*** *followed by protection of the bridging ketone.*

As this reaction does not proceed well with the compound **4b** due to steric hindrance,[32] with, in particular, the formation of epoxides, we prepare **5a**/**b** by isomerisation in basic medium in 88% yield. Then ozonolysis in a 1:1 mixture of dichloromethane and methanol at -70°C, followed by quenching by dimethylsulfide gave a mixture of hemiacetal **6a**/**b** and carbonyl-bridged **7a**/**b** in the ratio 4:1. At larger scale, this ozonolysis can be performed at

high concentration (218 mmol.L-1). The mixture of **6a**/**b** and **7a**/**b** is then treated with trimethylorthoformate and a catalytic amount of PTSA in methanol to obtain the ketal **8a**/**b** in 82-89% yield for the two steps. Then reduction of the four ester groups by $LiAlH_4$ in THF gives the mixture of tetraol isomers **9a**/**b** at 94% yield. The poorly soluble tetraols are then chlorinated by gaseous chlorine in a solution of triphenylphosphine in dichloromethane/acetonitrile/pyridine to give the mixture of isomers **10a**/**b** in 68% yield. Attempts to carry out this step by other procedures to avoid gaseous chlorine ($SOCl_2$, CCl_4-PPh_3, mesylation, tosylation) led to intractable complex mixtures. The reported quadruple dehydrochlorination of **10a** was carried out in scale of few hundred milligrams, in very harsh reaction conditions (heating with CsF at 210°C in HMPA)[25] and moderate yield (78%). In our hands, this protocol led only to a complex mixture of inseparable products. As it can be hardly envisaged to apply this method for large scale preparation in carcinogenic HMPA, we developed a new alternative protocol using mild reaction conditions which can be easily conducted in large scale. After several attempts we found to be most effective base potassium tert-butoxide in anhydrous DMF at 50°C which provide the target product **1** in 61% yields as a stable colourless crystalline compound.

X-ray structure

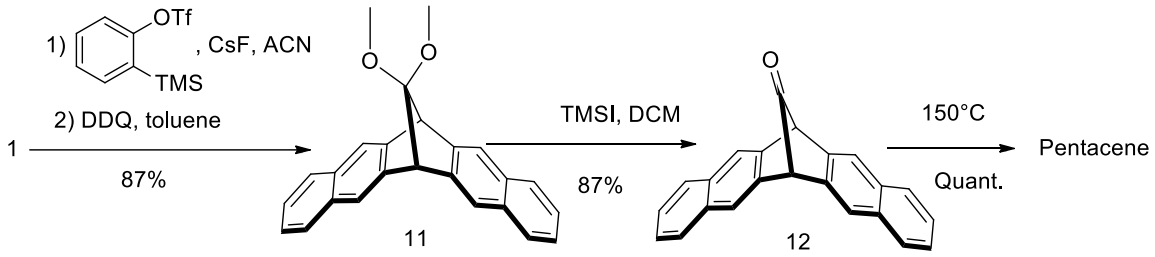
The molecular structure of **1** was confirmed by a single-crystal X-ray crystallographic analysis (CCDC 1911789, Figure 1).

Figure 1. *ORTEP plot of **1** (probability ellipsoid: 50%)*

The molecule crystallizes in the monoclinic space group P21 with 2 molecules per unit cell. The dihedral angle between the planes C8-C3-C4-C9 and C11-C7-C6-C10 containing the dienes is 112°.

Application to the preparation of pentacene

As an example of the use of **1** in the straightforward preparation of long acenes, 6,13-dihydro-6,13-methanopentacen-15-one (**12**) can be prepared in 2 steps starting from **1** (scheme 4), following the route described in scheme 1. Compound 12 has been described as a new type of soluble pentacene precursor for organic thin-film transistors.[4, 33] Pentacene films were obtained by spin-coating of stable and soluble **12**, evaporation of the solvent and decarbonylation. This CO extrusion at 150°C gave films of pentacene of high quality stable up to 350°C.



Scheme 4**. Preparation of pentacene from **1

Diels-Alder addition of **1** and benzyne, generated in situ by the action of CsF on 2-(trimethylsilyl)phenyl trifluoromethanesulfonate in acetonitrile, gives, after oxidation by DDQ, 15,15-dimethoxy-6,13-dihydro-6,13-methanopentacene (**11**) in 87% yield. Then the ketone is deprotected by trimethylsilyl iodide to give 6,13-dihydro-6,13-methanopentacen-15-one (**12**) in 87% yield.

Conclusions

To sum-up, we present here the synthesis of the tetraene 7,7-dimethoxy-2,3,5,6-tetramethylenebicyclo[2.2.1]heptane (**1**) from 6,6-dimethylfulvene **2** in 8 steps, with a total yield of ca 17%, at the tens of grams scale. 1 allows the preparation of stable and soluble protected acenes by Diels-Alder [4+2] addition. As an example, in the case of pentacene, the deprotection of the bridging carbonyl group, followed by a thermal or photochemical decarbonylation in the solid state gives an access to pure pentacene in 76% yield from **1**.

Experimental section

All reagents and solvents were obtained from commercial sources and used as received. Methanol was dried over molecular sieves (3Å). Other anhydrous solvents were purchased in anhydrous quality and used as received. Ozone was generated from a C-Lasky series Ozone Generator C-L010-DT / C-L010-DS (AirTree Ozone Technology Co.). TLC was performed on silica gel 60 F254-coated aluminium sheets (Merck) and spots were detected by the solution of $Ce(SO_4)_2$. $4H_2O$ (1%) and $H_3P(Mo_3O_{10})_4$ (2%) in sulfuric acid (10%). Flash chromatography was performed on silica gel 60 (0.040-0.063 mm, Fluka). 1H NMR spectra were measured on a Bruker AC 300 at 300 MHz at 25°C, in $CDCl_3$, DMSO-d6 and tetrachloroethane-d2 as indicated in 5 mm PFG probe. For standardisation of 1H NMR

spectra the internal signal of TMS (δ 0.0, $CDCl_3$) or residual signals of solvents (δ 7.26 for CDCl3, δ 2.5 for DMSO-d6, 6.0 for TCE-d2) were used. In the case of 13C spectra the residual signals of solvents (δ 77.00 for CDCl3, 73.78 for DMSO-d6) were used. The chemical shifts are given in δ-scale, the coupling constants J are given in Hz. All shifts were reported in ppm and processed with MestreNova (Mestrelabs). The ESI mass spectra were recorded using ZQ micromass mass spectrometer (Waters) equipped with an ESCi multimode ion source and controlled by MassLynx software. Alternatively, the low resolution ESI mass spectra were recorded using a quadrupole orthogonal acceleration time-of-flight tandem mass spectrometer (Q-Tof micro, Waters) and high resolution ESI mass spectra using a hybrid FT mass spectrometer combining a linear ion trap MS and the Orbitrap mass analyzer (LTQ Orbitrap XL, Thermo Fisher Scientific). The conditions were optimised for suitable ionisation in the ESI Orbitrap source (sheath gas flow rate 35 a.u., aux gas flow rate 10 a.u. of nitrogen, source voltage 4.3 kV, capillary voltage 40 V, capillary temperature 275 °C, tube lens voltage 155 V). The samples were dissolved in methanol and applied by direct injection. As a mobile phase 80% methanol was used (flow rate 100 μl/min). Crystallographic data were collected on Bruker D8 VENTURE Kappa Duo PHOTON100 by IμS micro-focus sealed tube MoKα radiation (λ = 0.71073 Å) at a temperature of 120(2) K. The structures were solved by direct methods (XP[34]) and refined by full matrix least squares based on F2 (SHELXL20182).[35] The hydrogen atoms on carbon were fixed into idealized positions (riding model) and assigned temperature factors either Hiso(H) = 1.2 Ueq (pivot atom). Supplementary crystallographic data for this paper can be obtained free of charge from The Cambridge Crystallographic Centre via www.ccdc.cam.ac.uk/data_request/cif) under the reference: CCDC 1911789.

2 Syntheses

5-(propan-2-ylidene)cyclopenta-1,3-diene (2)

Cyclopentadiene was prepared from its dimer by heating at 220 °C under argon in a distillation apparatus. Cyclopentadiene was collected in a round-bottom flask which was cooled to -20°C using dry ice/ ethanol cooling bath. The freshly distilled cyclopentadiene (96.3 g, 1.46 mol) was dissolved under argon in a solution of acetone (97.1 mL, 1.31 mol, 0.9 equiv.) in methanol (800 mL) keeping the temperature of reaction mixture below -10°C. Then pyrrolidine (144 mL, 1.75 mol, 1.2 equiv.) was added dropwise and the yellow reaction mixture was warmed to room temperature over 1h. Then acetic acid (117 mL, 2.04 mol, 1.4 equiv.) was slowly added. After 10 min. the reaction mixture was poured in cold water (2 L) and extracted twice with diethyl ether. Combined organic layers were dried over anhydrous magnesium sulfate and all volatiles were removed in vacuum. The product 1 (139 g, quant.) was obtained as a yellow oil and used in next step without any further purification. 1H NMR and 13C NMR were in agreement with the published data for **2** prepared at the 5 mmol scale.[36,37]

(1S,2R,6S,7R) (3a) and (1S,2S,6R,7R)-10-iso-Propylidene-4-oxatricyclo[5.2.1.02.6]dec-8-ene-3,5-dione (3b)

5-(Propan-2-ylidene)cyclopenta-1,3-diene **2** (139 g, 1.31 mol) was dissolved in dichloromethane (600 mL) under argon and then maleic anhydride (135 g, 1.38 mol, 1.05 equiv.) was added as a solid. The deep yellow reaction mixture was stirred at room temperature for 16 h. Then the reaction mixture was concentrated in vacuum and the semisolid residue was treated with diethylether to get white crystalline compound as a single exo-isomer **3b** (80 g). The mother liquor was evaporated and the residue was filtered through a short plug of silica gel (eluent dichloromethane) to get a mixture of endo **3a** and exo **3b** isomers contaminated with maleic anhydride. This mixture was recrystallized from diethyl ether / hexane to get a portion of mixture of both isomers (123 g, enriched with endo **3a**). The mother liquor was evaporated and the solid was finally purified by column chromatography on silica gel (hexane/diethyl ether 3:1) to remove the remaining maleic anhydride and get the final portion (27 g) of mixture of both isomers **3a** and **3b**. Total yield of both isomers is 86 % (230 g). 1H and 13C NMR of **3a/b** were in agreement with the published data (synthesis at the 100 mmol scale).[30]

TLC (hexane/diethyl ether 3:1): for **3a** Rf = 0.4, for **3b** Rf = 0.3

1H NMR (300 MHz, $CDCl_3$), isomer **3a**: 6.44 (t, J = 2.0 Hz, 2H), 3.95–3.90 (m, 2H), 3.52 (dd, J = 3.0, 1.7 Hz, 2H), 1.58 (s, 6H).

1H NMR (300 MHz, $CDCl_3$), isomer **3b**: 6.46–6.42 (m, 3H), 3.92 (ddt, J = 3.6, 3.0, 1.9 Hz, 1H), 3.89–3.85 (m, 2H), 3.52 (dd, J = 3.1, 1.7 Hz, 1H), 3.04 (s, 2H), 1.59 (s, 6H), 1.58 (s, 2H).

(1R,2S,3R,4S,5R,6S)-tetramethyl 7-(propan-2-ylidene)bicyclo[2.2.1]heptane-2,3,5,6-tetracarboxylate (4a) and (1r,2R,3S,4r,5R,6S)-tetramethyl 7-(propan-2-ylidene)bicyclo[2.2.1]heptane-2,3,5,6-tetracarboxylate (4b)

A mixture of isomer **3a** and **3b** (50.5 g, 0.247 mol), anhydrous $CuCl_2$ (116 g, 0.87 mol., 3.5 equiv.) and 10% Pd/C (6.42 g, 4.94 mmol, 2 mol. %) were placed in an autoclave under argon. Then anhydrous methanol (500 mL) was added and the reaction mixture was bubbled with argon for 10 min. Then the reaction mixture was pressurized with carbon monoxide (2-5 atm.) and stirred at room temperature for 48 h. The solvent was removed in vacuum and the residue was diluted with dichloromethane and neutralized with saturated sodium hydrogen carbonate solution. This mixed organic-water phase was filtered over a Celite to remove all insoluble inorganics. The filtered solids were washed thoroughly with methanol and dichloromethane. The organic phase was separated and the water phase was extracted with dichloromethane. All combined organic portions were dried over anhydrous magnesium sulfate and evaporated in vacuum. The residue was adsorbed on short plug of silica gel and washed with hexane/EtOAc 20:1 to remove all impurities. Finally, the product was eluted with mixture of dichloromethane/ EtOAc 1:1. Rotoevaporation gave an oily mixture of two isomers **4a** and **4b** (67.4 g, 74 %). 1H NMR of **4a/4b** and 13C NMR of **4b** were in agreement with the published data obtained in the 15 g scale.[38,39] For the analytical purposes,

compound **4a** and **4b** were resolved by column chromatography on silice gel (eluent hexane/EtOAc 2:1).

TLC (hexane/EtOAc 2:1): for **4a** Rf = 0.4, for **4b** Rf = 0.3.

1H NMR (300 MHz, $CDCl_3$), isomer **4a**: 3.66 (s, 6H), 3.59 (s, 6H), 3.42 (s, 2H), 3.26 (dd, J = 2.6, 1.8 Hz, 2H), 3.05 (dd, J = 2.6, 1.8 Hz, 2H), 1.70 (s, 6H).

13C NMR (75 MHz, $CDCl_3$), isomer **4a**: 20.79, 42.79, 44.50, 45.43, 51.76, 51.90, 121.86, 135.18, 172.15, 172.89.

ESI MS, isomer **4a**: 391 ([M+Na]+).

HR ESI MS, isomer **4a**: calcd for $C_{18}H_{24}O_8Na$ 391.13634; found 391.13600.

1H NMR (300 MHz, $CDCl_3$), isomer **4b**: δ 3.7 (s, 12H), 3.4 (s, 2H), 2.8 (s, 4H), 1.7 (s, 6H).

13C NMR (75 MHz, $CDCl_3$), isomer **4b**: 20.93, 42.82, 49.29, 51.95, 124.89, 133.19, 172.03.

ESI MS, isomer 4b: 391 ([M+Na]+).

HR ESI MS, isomer **4b**: calcd for $C_{18}H_{24}O_8Na$ 391.13634; found 391.13581.

Tetramethyl (1r,2R,3R,4r,5S,6S)-7.7-dimethoxybicyclo[2.2.1]heptane-2,3,5,6-tetracarboxylate (8c)

In a round-bottom flask was prepared solution of **4a** (511 mg, 1.4 mmol, 1 eq.) in a mixture of dichloromethane (14 mL) and methanol (14 mL) was cooled to -70 °C and bubbled with ozone (2L/min) until the colour of the reaction mixture became light blue (3 h). The reaction mixture was bubbled with air for 10 min. to remove excess ozone. Dimethyl sulfide (0.15 mL, 2 mmol, 1.4 eq.) was added at -70 °C and the mixture was left to warm to room temperature overnight (ca 17h). All volatiles were removed in vacuo to afford a mixture of hemiacetal **6c** and ketone **7c** in the ratio 4:1 in a form of sticky oil. The well-dried mixture of **6c** and **7c** was dissolved in a mixture of absolute methanol (20 mL) and triethyl orthoformate (15 mL). To this p-toluenesulfonic acid (50 mg, 0.2 mmol) was added and the solution heated at 64 °C for 3-5 days. The conversion of reaction was monitored by NMR. When the reaction was completed, all volatiles were evaporated. The residue was diluted with dichloromethane then overlaid with saturated sodium hydrogen carbonate (aq solution) and extracted with dichloromethane. The organic layers were gathered and dried over anhydrous magnesium sulfate. After evaporation the white solid was poured into diethylether and sonicated for 5 min. The product **8c** (480 mg, 1.23 mmol, 89%) was filtered as a white solid.

1H NMR (300 MHz, $CDCl_3$): 3.68 (s, 6H), 3.67 (s, 6H), 3.43 (s, 2H), 3.36 (dd, J = 2.6, 1.7 Hz, 2H), 3.31 (s, 3H), 3.28 (s, 3H), 2.92 (dd, J = 2.5, 1.7 Hz, 2H).

13C NMR (75 MHz, $CDCl_3$): 43.13, 43.79, 44.58, 51.10, 51.57, 51.76, 51.97, 112.09, 172.23, 172.40.

CI MS: 388 ([M]+).

HR CI MS: calcd for $C_{13}H_{24}O_{10}$ 388.1369; found 388.1357

(1S,2R,3R,4S,5R,6R)-tetramethyl 7-(propan-2-ylidene)bicyclo[2.2.1]heptane-2,3,5,6-tetracarboxylate (5a) and (1r,2R,3R,4s,5S,6S)-tetramethyl 7-(propan-2-ylidene)bicyclo[2.2.1]heptane-2,3,5,6-tetracarboxylate (5b)

To a solution of **4a** and **4b** (67.4 g, 0.183 mol) in absolute methanol (500 mL) was added in one portion anhydrous potassium carbonate (22.8 g, 0.165 mol, 0.9 equiv.) under argon. Then the heterogeneous reaction mixture was stirred at room temperature for 16 h. The reaction mixture was concentrated on a rotoevaporator, then diluted with aqueous solution of ammonium chloride and extracted with dichloromethane. All combined organic portions were dried over anhydrous magnesium sulfate and evaporated in vacuum. The residue was filtered through a short plug of silica gel (eluent dichloromethane/EtOAc 1:1) to get a mixture of **5a** and **5b** isomers (in ratio 5:1) as white solid (59.1 g, 88 %). 1H NMR and 13C NMR of **5a** were in agreement with the published data obtained at the 15g scale.[38,39]

1H NMR (300 MHz, $CDCl_3$), isomer **5a**: 3.8 (s, 6H), 3.7 (s, 6H), 3.4 (d, J = 4.8 Hz, 2H), 3.2 (t, J = 5.0 Hz, 2H), 3 (d, J = 5.6 Hz, 2H), 1.6 (s, 6H).

1H NMR (300 MHz, $CDCl_3$), isomer **5b**: 1.55 (s, 3H), 1.66 (s, 3H), 3.04 (bs, 1H), 3.06 (bs, 1H), 3.16 (d, J = 4.2 Hz, 1H), 3.18 (d, J = 4.3 Hz, 1H), 3.40 (bs, 1H), 3.49 (td, J = 4.1, 1.5 Hz, 1H), 3.63 (s, 6H), 3.67 (s, 6H).

13C NMR (75 MHz, $CDCl_3$), isomer **5b**: 20.18, 20.62, 42.87, 44.71, 46.51, 48.22, 52.06, 52.34, 120.97, 136.07, 172.49, 173.49.

ESI MS, isomer **5b**: 391 ([M+Na]+).

HR ESI MS, isomer **5b**: calcd for $C_{18}H_{24}O_8Na$ 391.13634; found 391.13602.

(1S,2R,3R,4S,5R,6R)-tetramethyl 7,7-dimethoxybicyclo[2.2.1]heptane-2,3,5,6-tetracarboxylate (8a) and (1r,2R,3R,4s,5S,6S)-tetramethyl 7,7-dimethoxybicyclo[2.2.1]heptane-2,3,5,6-tetracarboxylate (8b)

A solution of **5a/5b** (48.4 g, 0.131 mol) in an anhydrous mixture of dichloromethane (300 mL) and methanol (300 mL) was cooled to -70°C and bubbled with ozone (2L/min) until the colour of the reaction mixture became light blue (3 h). The reaction mixture was bubbled with nitrogen for 10 min. to remove excess of ozone. Dimethyl sulfide (13.5 mL, 0.183 mol, 1.4 equiv.) was added at -70 °C and the mixture was left to warm to room temperature overnight. All volatiles were removed in vacuum to afford a mixture of hemiacetal **6a/6b** and ketone **6a/b** in the ratio 4:1 in a form of sticky oil. The well-dried mixture of **6a/b** and **7c/d** was dissolved in a mixture of anhydrous methanol (100 mL) and trimethyl orthoformate (100 mL). To this solution was added p-toluenesulfonic acid (2.49 g, 13.1 mmol, 0.1 equiv.) and the reaction mixture was heated at 60°C for 24h under argon. All volatiles were removed in vacuum and the residue was diluted with dichloromethane then overlaid with saturated

sodium hydrogen carbonate (aq. solution) and extracted with dichloromethane. All combined organic portions were dried over anhydrous magnesium sulfate. After evaporation the semisolid residue was crystallised from a mixture of hexane/diethyl ether 1:2 to get first portion of product (31.5 g) as a crystalline solid. The mother liquor was evaporated and the residue was adsorbed on short plug of silica gel and washed with hexane/EtOAc 20:1 to remove all impurities. Finally, the product was eluted with mixture of dichloromethane/ EtOAc 1:1. After evaporation, a second portion of **8a/b** (10.1g) was obtained as a crystalline solid. The total yield was 41.6 g (82%). 1H NMR of **8a** are in agreement with published data.

1H NMR (300 MHz, $CDCl_3$): 3.75 (s, 6H), 3.70 (s, 6H), 3.55 – 3.49 (m, 2H), 3.17 (s, 6H), 3.08 (d, J = 4.8 Hz, 2H), 2.88 (d, J = 5.7 Hz, 2H).

13C NMR (75 MHz, $CDCl_3$): 43.40, 45.31, 45.40, 50.68, 52.37, 52.46, 112.76, 172.75, 173.11.

ESI MS: 411 ([M+Na]+).

HR ESI MS: calcd for $C_{17}H_{24}O_{10}Na$ 411.12617; found 411.12627.

((1R,2S,3S,4R,5S,6S)-7,7-dimethoxybicyclo[2.2.1]heptane-2,3,5,6-tetrayl)tetramethanol (9a) and ((1r,2R,3R,4s,5S,6S)-7,7-dimethoxybicyclo[2.2.1]heptane-2,3,5,6-tetrayl)tetramethanol (9b)

A well-dried round bottom flask equipped with reflux condenser was loaded with lithium aluminum hydride (15.4 g, 0.405 mol, 5 equiv.) and purged with argon. Freshly distilled anhydrous tetrahydrofuran (500 mL) was added and the mixture was cooled to -70 °C. To this very viscous heterogeneous solution was added dropwise by cannula a solution of **8a/b** (31.5 g, 81.1 mmol) in dry tetrahydrofuran (200 mL). The reaction mixture was allowed to warm up to room temperature over a period of 5 h. The reaction mixture was then heated at 70 °C for 16 h. Then the reaction mixture was cooled back to room temperature and quenched with minimum amount of saturated aqueous solution of magnesium sulfate. The whole reaction mixture was adsorbed on silica gel and the product was extracted by continuous extraction using THF as an eluent. After evaporation of the solvent, the product **9a/b** (21 g, 94 %) was obtained as white crystalline compound. 1H NMR of **9a** is in agreement with the published data.[25]

1H NMR (300 MHz, DMSO): 1.44 (dd, J = 7.2, 7.2 Hz, 2H), 1.75-1.74(m, 2H), 1.96 (d, J = 3.3 Hz, 2H), 3.10 (s, 6H), 3.34 – 3.49 (m, 8H), 4.40 – 4.46 (m, 4H).

13C NMR (75 MHz, DMSO): 40.59, 41.83, 44.45, 48.99, 61.12, 64.38, 113.54.

ESI MS: 299 ([M+Na]+).

HR ESI MS: calcd for $C_{13}H_{24}O_6Na$ 299.14651; found 299.14630

(1S,2R,3R,4S,5R,6R)-2,3,5,6-tetrakis(chloromethyl)-7,7-dimethoxybicyclo[2.2.1]heptane (10a) and (1r,2R,3R,4s,5S,6S)-2,3,5,6-tetrakis(chloromethyl)-7,7-dimethoxybicyclo[2.2.1]heptane (10b)

Into a cooled (0°C) solution of triphenylphosphine (91.1 g, 0.347 mol, 8 equiv.) in dichloromethane (400 mL) was bubbled gaseous chlorine. When triphenylphosphine was consumed (the colour of the reaction turned to yellow), argon was bubbled in the reaction mixture to remove excess of chlorine. Then this solution of chlorophosphonium salt was added dropwise (by cannula) to a solution of imidazole (47.3 g, 0.694 mol, 16 equiv.) in a mixture of solvents acetonitrile – pyridine (200 mL : 200 mL) at 0°C. Then tetraol **9a/b** (12 g, 43.4 mmol) was added portion-wise and the reaction mixture was warmed to room temperature and stirred for 30 min. Then the reaction mixture was heated at 55°C for 24 h under argon. The reaction mixture was diluted with chloroform and extracted several times with 2 M HCl and finally a saturated aqueous solution of NaHCO3. The organic phase was dried with $MgSO_4$ and evaporated. To the solid residue was added diethyl ether and precipitated triphenylphosphinoxide was filtered over a frit. The filtrate was evaporated and the residue was chromatographed on silica gel (hexane:EtOAc 6:1) to get the desired tetrachloro product **10a/b** (10.4 g, 68 %) as a white crystalline compound. 1H NMR of **10a** is in agreement with the published data.[25]

1H NMR (300 MHz, $CDCl_3$): 1.72 (td, J = 7.8, 6.5 Hz, 2H), 2.21 – 2.30 (m, 2H), 2.32 – 2.34 (m, 2H), 3.24 (s, 6H), 3.45 (t, J = 10.8 Hz, 2H), 3.62 – 6.38 (m, 2H), 3.74 3.86 (m, 4H).

13C NMR (75 MHz, $CDCl_3$): 42.53, 44.46, 45.47, 45.96, 48.13, 50.12, 112.82.

CI MS: 348 ([M]+).

HR CI MS: calcd for $C_{13}H_{20}O_2Cl_4$ 348.0217; found 348.0215

7,7-dimethoxy-2,3,5,6-tetramethylenebicyclo[2.2.1]heptane (1)

In a well dried Schlenk flask, a solution of potassium tert-butoxide (16.7g, 0.149 mol, 5 equiv.) in anhydrous DMF (100 mL) was cooled to 0°C. To this solution was added dropwise a solution of the tetrachloride **10a/b** (10.4 g, 29.7 mmol) in anhydrous DMF (20 mL). After the complete addition, the reaction mixture was warmed to room temperature and finally heated at 50°C overnight under argon. The reaction mixture was diluted with water and extracted with EtOAc. The combined organic portions were dried over anhydrous $MgSO_4$. The solvents were removed in vacuum and the residue was chromatographed on silica gel (gradient from hexane/dichloromethane 6:1 to 2:1) to get the desired product **1** (3.7g, 61 %) as a white crystalline compound. 1H NMR is in agreement with the published data.[25]

1H NMR (300 MHz, $CDCl_3$): 3.27 (s, 6H), 3.47 (s, 2H), 5.01 (s, 4H), 5.30 (s, 4H).

13C NMR (75 MHz, $CDCl_3$): 50.90, 58.52, 103.47, 110.85, 146.65.

CI MS: 205 ([M+H]+).

HR CI MS: calcd for $C_{13}H_{17}O_2$ 205.1229; found 205.1230

15,15-dimethoxy-6,13-dihydro-6,13-methanopentacene (11)

A well dried Schlenk flask was charged with tetraene **1** (500 mg, 2.45 mmol, 1 equiv.) and dry CsF (1.49 g, 9.79 mmol, 4 equiv.) under argon and then anhydrous acetonitrile was added (50 mL). The reaction mixture was cooled to 0°C and then 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1.3 mL, 5.39 mmol, 2.2 equiv.) was added dropwise. The mixture was stirred at room temperature overnight. After evaporation of the solvent, the residue was filtered over short plug of silica gel and flushed with hexane/THF 20:1. Rotoevaporation of the organic solvents gave the crude product which was well dried under vacuum and then dissolved in anhydrous toluene (40 mL) under argon. This solution was cooled to 0°C and DDQ (1.11 g, 4.9 mmol, 2 equiv.) was added in one portion. The reaction mixture was warmed to room temperature and stirred for 3 h. After filtration to remove reduce DDQ, evaporation of solvents gave a residue which was chromatographed on silica gel (hexane/dichloromethane 2:3) to get the product **11** (751 mg, 87%) as a white crystalline compound.

1H NMR (300 MHz, $CDCl_3$): 3.22 (s, 6H), 7.35 – 7.41 (m, 4H), 4.69 – 7.75 (m, 8H).

13C NMR (75 MHz, $CDCl_3$): 51.54, 55.32, 120.88, 125.49, 125.99, 128.17, 133.04, 143.91.

DCI MS: 353 ([M + H]+).

HR DCI MS: calcd for $C_{25}H_{21}O_2$ 353.1536; found 353.1529.

6,13-dihydro-6,13-methanopentacen-15-one (12)

In a well-dried Schlenk flask, **11** was dissolved (140 mg, 0.4 mmol) in anhydrous dichloromethane (15 mL) under argon. Then trimethylsilyl iodide (68 μL, 0.48 mmol, 1.2 equiv) was added dropwise and reaction mixture was stirred overnight at room temperature. The reaction mixture was then heated at 40°C for 1 h, then cooled to room temperature and rotoevaporated. Sonication of the residue in a mixture of solvents (hexane/diethyl ether 4:1) yielded pure product **12** (106 mg, 87 %) as a white powder. 1H NMR is in agreement with published data.[33]

1H NMR (300 MHz, [D2]tetrachloroethane): 5.00 (s, 2H), 7.45 – 7.51 (m, 4H), 7.80 – 7.85 (m, 4H), 7.95 (s, 4H).

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