During the last years we have witnessed progressive evolution of preparation of acenes with length up to dodecacene by on-surface synthesis in UHV or generation of acenes up to decacene in solid matrices at low temperatures. While these protocols with very specific conditions produce the acenes in amount of few molecules, the strategies leading to the acenes in large quantities dawdle behind. Only recently and after 70 years of synthetic attempts, heptacene has been prepared in bulk phase. However, the preparative scale synthesis of higher homologues still remains a formidable challenge. Here we report the preparation and characterisation of nonacene and show its excellent thermal and in-time stability.
Preparative-scale synthesis of nonacene

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Abstract:

Over the last decade, particular attention has been brought to long unsubstituted acenes (longer than pentacene) from both experimental and theoretical points of view.1 The nature of their electronic structure such as gap stabilization2–4 and open shell singlet ground state for longer acenes is still actively discussed.5–9 Furthermore, longer acenes can be seen as the narrowest zig-zag graphene nanoribbons (ZGNR) and could display spin-polarized edge-states of interest for carbon-based spin electronics.10,11

However, acenes longer than pentacene are challenging to prepare and to handle. First, intermolecular \(\pi-\pi\) stacking between these planar and rigid molecules rapidly limits their solubility as their sizes increase. Second, acenes possess only one Clar aromatic sextet spread over the whole skeleton, leading to a decrease of the HOMO-LUMO gap with an increasing number of benzene rings, and therefore to an increase of the chemical reactivity. Although photooxidation with molecular oxygen can be avoided by working under argon, rapid dimerization in solution even at low concentration might become a problematic limitation.

Several strategies have been pursued to prepare long acenes, all relying on the same concept: masked stable and soluble precursors are prepared and purified by standard in-solution chemistry techniques and, in a final step, the masking groups are removed in the solid state or at low temperature in very dilute conditions on surfaces or in matrices. In particular Neckers, Bettinger and coworkers have explored the photogeneration, in stabilizing matrices, of hexacene,12 heptacene13–16, octacene, nonacene17, and undecacene18 by photodecarbonylation of precursors comprising two bridging \(\alpha\)-diketone groups, following Yamada’s concept19 using the Strating-Zwanenburg20 reaction. Long acenes can also be prepared by on-surface synthesis in Ultra High Vacuum (UHV) and observed at liquid helium temperature and their electronic structures mapped by Scanning Tunneling Spectroscopy (STS). Higher acenes up to undecacene have been obtained by deoxygenation of epoxides4,21,22 dehydrogenation of
partially saturated precursors,\textsuperscript{23,24} or thermal or photo decarbonylation of diketone adducts.\textsuperscript{25–27}

However, both types of generation, in stabilizing matrices or on surfaces in UHV only give minute amounts of materials and cannot be used for macroscopic amounts of materials needed for applications. Indeed, the preparation of acenes longer than pentacene in a pure state is very recent despite 70 years of claims,\textsuperscript{28} and so far limited to hexacene and heptacene. In 2012, Chow and coworkers isolated hexacene by decarbonylation of a monoketone precursor in the solid state and its structure was determined by X-ray diffraction.\textsuperscript{29} They demonstrated that a field-effect transistor made with a single crystal of hexacene showed a hole mobility significantly higher than pentacene. In 2017, Bettinger \textit{et al.} have reported the formation of heptacene in the solid state by thermal cycloreversion from a mixture of diheptacenes obtained in solution.\textsuperscript{30} More recently, we have also obtained heptacene and benzohexacene by cheletropic decarbonylation at moderate temperature, confirming the thermal stability of these higher acenes.\textsuperscript{31} The preparation of even longer acenes in bulk form has been indeed an attracting challenge since Clar’s prediction in 196\textsuperscript{32} claiming that the synthesis of octacene (and beyond) was a remote target. And in a recent review, C. Tönshoff and H. F. Bettinger conclude that “It is not even clear if acenes larger than that of heptacene can exist outside the special environment provided by matrix isolation or on-surface synthesis”.\textsuperscript{33}

To answer this question, we present here the synthesis of nonacene 1 and demonstrate its surprising stability.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{nonacene.png}
\caption{Molecular structure of nonacene 1.}
\end{figure}

**Results and discussion**

As nonacene was expected to be highly insoluble and reactive, our strategy is based on pure soluble and chemically stable masked nonacene, that could be deprotected quantitatively by heating at medium temperatures in the solid state. In previous contributions, we have shown that 7,7-dimethoxy-2,3,5,6-tetramethylenebicyclo[2.2.1]-heptane (further in the text as tetraene) (scheme 1), which can be prepared at the tens of grams scale,\textsuperscript{35} can undergo successive Diels-Alder reaction with arynes to provide non-planar, soluble, and not fully delocalized acene precursors. In these compounds, one of the benzene rings is bridged by a dimethyl ketal group.

\begin{equation}
\begin{array}{c}
\text{Scheme 1. Schematic strategy of the preparation of various acenes starting from 7,7-dimethoxy-2,3,5,6-tetramethylenebicyclo[2.2.1]-heptane. Diels-Alder addition (a) with arynes, followed by aromatization gives a non-planar bridging dimethylketal, which can be deprotected (b) to yield a polyaromatic precursor bridged by a carbonyl group. (c) Solid state thermal or photochemical decarbonylation gives the acene with only carbon monoxide as by-product.}
\end{array}
\end{equation}

Cleavage of this ketal yields the corresponding polyaromatic acene precursors comprising norbornadiene-7-one moieties, mentioned simply as ketone precursors in this report. These compounds are at least partially soluble, chemically stable and can be purified by standard insolution techniques such as chromatography or recrystallization. They are stable enough to be stored in the dark for long period of time. The final step is a thermal or photochemical cheletropic decarbonylation in the solid state yielding the corresponding acenes in quantitative yields without any non-volatile by-products. It has been shown that this method of
decarbonylation was very effective to prepare sensitive high quality materials, such as pentacene and hexacene,\textsuperscript{36} for opto-electronic devices.

Our exploration of nonacene 1 commenced with the synthesis of such a carbonylated precursor 7a/7b which can be easily transformed in the solid-state form to the nonacene by simple heating.

The synthesis of the precursors 7a/7b leading to nonacene 1 follows the route shown in scheme 2 with four synthetic steps starting from the diene 2, which can be prepared in two steps from the tetraene shown in scheme 1 above.\textsuperscript{34}

![Scheme 2](image)

\textbf{Scheme 2.} Synthesis of nonacene 1: a) CsF, acetonitrile/THF (4:1), room temperature, 16 h., 62 % (anti : syn 1:2); b) CsF, acetonitrile/THF (5:1), room temperature, 16 h., 98 % (anti : syn 1:2); c) DDQ, toluene, room temperature, 4 h., 94 %; d) TMSI, room temperature, 24 h., 94% for 7a and 48 h., 95% for 7b; e) neat 350 °C, 20 min., quant.

The key reaction of the synthetic sequence is the double Diels-Alder reaction of the diene 2 and the \textit{in situ} generated bis(aryne) obtained by fluoride-induced decomposition of 2,5-bis(trimethylsilyl)-1,4-phenylene bis(trifluoromethanesulfonate) 3.\textsuperscript{37,38,39} Alternatively, the Diels-Alder reaction can be carried out from the aryne precursor 4 (synthesized from the same tetraene in three steps in 33% yield), with the diene 2. The formed mixture of these two isomers \textit{syn} and \textit{anti} 5a/5b can be easily separated on silica gel. As expected the NMR spectra of the two isomers are almost identical and owing to their symmetry and to the distance between the ketal groups, it is not possible to assign their structures by proton and carbon NMR spectroscopy. Fortunately, slow evaporation of a solution of the isomer 5b in a mixture of solvents (hexane/EtOAc) provided suitable crystals for X-ray analysis (Fig. 1).
It shows that the two naphthalene ends of the *anti*-isomer 5b are perfectly parallel to each other and the angle between naphthalene and anthracene units is 105.5°.

Surprisingly, these products 5a and 5b were formed in the ratio 1:2 in favour of syn-isomer 5a. Indeed, considering the distance between the reactive sites, a statistical ratio 1:1 was initially expected. In order to investigate the stereoselectivity of the Diels-Alder reactions between the diene 2 and the benzyne compounds in acetonitrile, their transition states (TS) were determined by using density functional theory (DFT). By using Gaussian 16, Revision C.01, the geometries of TS were optimized with QST3 method at the B3LYP/6-31+G(d,p) level of theory with the polarizable continuum model (PCM) to include solvent effects (acetonitrile). Subsequently, single point energy calculations of TS were calculated at the M06-2X/6-31+G(d,p) level of theory with PCM (acetonitrile). Based on the activation energy determined by the calculations, anti/syn ratio was estimated to 1/1.64, which is consistent with the observed stereoselectivity in the experiment (anti/syn = 1/2) (See supporting information for details).

The isomers 5a and 5b underwent smooth aromatization by DDQ at room temperature in almost quantitative yield. Then, the two dimethylketal groups of 6a/6b were cleaved by trimethylsilyl iodide, which afforded the corresponding carbonyl isomers 7a and 7b in 94% and 95% yield, respectively. The anti-isomer 7b is less soluble in many organic solvents than its counterpart 7a, likely due to the ability to pack in quasi one-dimensional chains with efficient π-π stacking, which is not the case for U-shape isomer 7a. Both isomers are colourless chemically stable compounds.

Decarbonylation of 7a/7b in the solid state can be followed by thermal gravimetric analysis (TGA) as shown in Fig. 2.

![Fig. 2. TGA thermograms of 7a/7b showing the weight loss of two CO groups (ca 12 and 13%; calc. 10.5 %).](image-url)
A weight loss of 11.9% for syn-isomer and 13.0% for anti-isomer (calcd 10.5%) correspond to the loss of two carbonyl groups per molecule. The full decarbonylation occurred below 190°C in a one step process for both isomers. However, in the case of syn-isomer 7a, the TGA thermogram consists of a gradual weight loss starting at about 60°C. This can be explained by a lower thermal stability compared to the anti-isomer (starting around 180°C). The decarbonylation is accompanied by a colour change from white to anthracite and the formation of nonacene. Under these conditions, nonacene is surprisingly thermally stable up to almost 500°C. The formation of nonacene 1 by loss of two carbonyl groups is also evident during the high-resolution ESI MS measurement of 7a/7b in which only a peak at m/z 478.1731 from 7a or 478.1727 from 7b corresponding to the formula C_{38}H_{22} (calcd m/z: 478.1722) was recorded.

The decarbonylation process was also followed by FTIR experiments (Fig. 3), where the stretching vibration of carbonyl peak at 1780 cm\(^{-1}\) disappear after heating the carbonyl precursor in KBr pellet.

![FTIR spectra](image)

**Fig. 3.** FTIR spectra (KBr pellets) of the carbonylated precursors 7b (in blue) with a strong CO peak at 1781 cm\(^{-1}\) and of the resulting nonacene 1 (in red) after 1 min. heating at 350°C in glovebox.

This transformation has been also followed by solid state cross-polarization magic angle spinning (CP-MAS) NMR spectroscopy. The spectrum of the precursor 7a shows (Fig. 4) three groups of signals, one at 57 ppm (bridgehead sp\(^3\) carbons), a complex peak at 120-137 ppm (aromatic carbons) and the carbonyl carbons at 193 and 198 ppm. Despite the symmetry of the molecule, the different environments in the solid state of the two carbonyl groups is a cause of these two signals. After heating the sample for 20 minutes at 200°C under inert atmosphere, the carbonyl signals disappear and aromatic region get narrower (Fig. 4). However, a smaller and broader sp\(^3\) signal at 54 ppm remains. We attribute this peak to partial dimerization/polymerization by of the decarbonylated compound. Upon heating at higher temperatures, this peak decreases whereas the peak attributed to the aromatic carbons gets narrower with a decrease of the shoulder at 137 ppm. The evolution of the CPMAS spectrum of the isomer 7b is very similar (see SI).
Fig. 4: Evolution of the CPMAS $^{13}$C NMR spectra of 7a (left) in function of the temperature.

This behaviour is very reminiscent to that of heptacene.$^{30}$ The latter molecule dimerizes in solution during its preparation, but cycloreversion to heptacene of the two dimers has been observed by heating for 12 min at 300°C in the solid state. However, after several weeks, some of the heptacene reacted back to the dimers.

Based on the TGA experiment, the formed nonacene is surprisingly stable almost up to 500°C, which allows to realize the extrusion of carbonyl groups at much higher temperature. In a new experiment we carried out the decarbonylation of the precursors $7a/7b$ at 350°C for 20 min (Fig. 6). Gratifyingly, the decarbonylation process was much cleaner with only a sharp doublet in aromatic region without any signs of dimerization. Keeping these samples in the NMR rotor at room temperature in a glove box for 2 months did not lead to any degradation or dimerization of nonacene 1 suggesting that the nonacene prepared under these conditions is stable.

Fig. 6. Evolution of the CPMAS spectra of $7a/7b$ by decarbonylation at 350°C for 20 min to form the nonacene 1.
Alternatively, nonacene 1 can also be obtained by decarbonylation in a solvent at high temperature. For instance, the soluble precursor 7a was dissolved in chlorobenzene and the solution was thoroughly degassed. This solution was heated at 200°C for 10 minutes and the formation of a dark violet precipitate was observed. This suspension was drop-casted on an indium-tin oxide (ITO) glass slide without any matrix and dried. In a parallel experiment, the suspension was mixed with 2,5-dihydroxy benzoic acid as a matrix and then drop-casted on an ITO glass slide and dried. These ITO glass slides were introduced in a MALDI chamber, and the high-resolution mass spectra (HRMS) were recorded. Both spectra showed only the parent peak corresponding to the nonacene 1, and no trace of a dimer as was observed for heptacene.\(^{30}\) These results suggest that, in contrast with heptacene, nonacene 1 is so highly insoluble that just after decarbonylation, immediate precipitation of the monomer prevents the dimerization in solution.

**Summary and outlook**

In summary, pure nonacene can be prepared by thermal bis-decarbonylation of precursors either in the solid state, or in high boiling point solvents. This long acene is surprisingly thermally stable up to 450°C and does not decompose at room temperature under dry argon. Our preparation procedure could as well be applied for the construction of substituted nonacenes and to even longer acenes, opening the way to OFETs and molecular spintronics applications.

**Methods**

**Direct synthesis of 6a/6b.** A well-dried Schlenk flask was charged with diene 2 (200 mg, 0.72 mmol) and CsF (480 mg, 3.16 mmol, 4.0 equiv.) under argon and then anhydrous acetonitrile (16 mL) was added. The heterogeneous mixture was cooled to 0°C and then solution of aryne precursor bis(trimethylsilyl)-1,4-phenylene bis(trifluoromethanesulfonate) (298 mg, 0.58 mmol, 0.8 equiv.) in anhydrous THF (4 mL) was added dropwise. The reaction was allowed to warm to room temperature overnight. Progress of the reaction was controlled by TLC, eluent (hexane - EtOAc 3:2). Reaction time depending on a scale of the reaction (1-3 days). After the evaporation of the solvent, the residue was chromatographed on silica gel (hexane : acetone 3:1) to get the desired product as a mixture of two regioisomers as a colourless solid. This mixture (146 mg, 0.23 mmol) was dissolved in anhydrous toluene (15 mL) under argon. The solution was cooled to 0°C and then DDQ (53 mg, 0.231 mmol, 2 equiv.) was added in one portion. The reaction mixture was stirred at 0°C for 10 min. and then 6 hours at room temperature. The volume of the reaction mixture was reduced to a half and the mixture was filtered over a frit S4. The solid was washed with toluene and finally with methanol to get the first isomer 6b (40 mg) as a white solid. The mother liquor was evaporated and the residue was purified by chromatography on silica gel (hexane : acetone 3:1) to get the second isomer 6a (82 mg) as a white solid. The ratio of isomers is 1:2 and combined yield is 54 % after two synthetic steps.

**Synthesis of 7a: In a well dried Schlenk flask,** 6a (160 mg, 0.255 mmol) was dissolved in anhydrous dichloromethane (10 mL) under argon. Then trimethylsilyl iodide (109 μL, 0.766 mmol, 3 equiv.) was added dropwise and the homogeneous reaction mixture was stirred overnight at room temperature. Next day the heterogeneous reaction mixture was stirred on air at room temperature for 6 hours to complete the hydrolysis of formed iodo-methoxy intermediate. The product was collected by filtration over a glass frit filter S4, washed with mixture of solvents (hexane : dichloromethane, 4:1) to afford first portion of pure compound 7a as a white.
solid. The mother liquor was evaporated and the residue was purified by chromatography on silica gel (hexane : acetone 3:1) to get the second portion of the product as a white solid. The combined yield was (130 mg, 95%).

$^1$H NMR (500 MHz, CD$_2$Cl$_2$): 4.99 (4H, s), 7.41 - 7.44 (4H, m), 7.78 – 7.81 (4H, m), 7.93 (4H, s), 8.04 (4H, s), 8.36 (2H, s).

$^{13}$C NMR (126 MHz, CD$_2$Cl$_2$): 57.55, 120.88, 121.22, 126.57, 126.76, 128.34, 131.61, 133.31, 137.61, 137.93, 194.46 ppm.

CP MAS: 56.99 (bridgehead), 120.20-137.12 (aromatic), 193.26 and 197.73 (C=O) ppm.

DCI MS: 478 ([M – 2 x CO] + ).

HR DCI MS: calcd for C$_{38}$H$_{22}$478.1722 (M – 2xCO); found 478.1727.

Synthesis of 7b: In a well dried Schlenk flask, 6b (25 mg, 39.89 μmol) was suspended in anhydrous dichloromethane (4 mL) under argon. Then trimethylsilyl iodide (23 μL, 159.6 μmol, 4 equiv.) was added dropwise and the heterogeneous reaction mixture was stirred overnight at room temperature. Next day the heterogeneous reaction mixture was stirred on air at room temperature for 6 hours to complete the hydrolysis of formed iodo-methoxy intermediate. The product was collected by filtration over a glass frit filter S4, washed with mixture of solvents (dichloromethane: acetone, 4:1) to afford pure compound 7b (20 mg, 94 %) as a white solid.

CP MAS: 55.83 (bridgehead), 119.23-136.01 (aromatic), 195.55 (C=O) ppm.

DCI MS: 478 ([M – 2 x CO] + ).

HR DCI MS: calcd for C$_{38}$H$_{22}$478.1722 (M – 2xCO); found 478.1731.

Preparation of Nonacene 1
Nonacene was obtained by heating 7a or 7b in the solid state at 350°C under vacuum for 15 min or as a suspension by heating a purged solution of 7a in chlorobenzene 10 min. at 200°C

CP MAS: 125.5 - 128.8 ppm

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Author contributions
A.J. and J.H. performed the syntheses and characterization of all products. M.S realized all the MALDI experiments. Y.N. did the simulations and calculations. A.J. and A.G designed and supervised the project.

Competing interests
The authors declare no competing interests.
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SUPPLEMENTARY INFORMATION

Preparative-scale synthesis of nonacene
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General procedures and methods

General information

Starting compounds, catalysts and solvents were purchased from Sigma-Aldrich and TCI. Flash column chromatography was performed by using silica gel (60 Å pore size, 40-63 μm Merck). The reactions were monitored by thin layer chromatography (TLC) on silica gel-coated plates (Merck 60 F$_{254}$). The NMR spectroscopic data in solution were recorded with Bruker Avance 300 MHz and 500 MHz instruments and were calibrated by using the residual undeuterated solvent as an internal reference (CD$_2$Cl$_2$ at $\delta$H = 5.33 ppm, $\delta$C = 53.84 ppm; CDCl$_3$ at $\delta$H = 7.26 ppm, $\delta$C = 77.16 ppm; tetrachloroethane-d$_2$ at $\delta$H = 6.00 ppm, $\delta$C = 73.78 ppm). Chemical shifts are reported in parts per million (ppm) on the $\delta$ scale and coupling constants (J) are in Hertz (Hz). The abbreviations used to describe the multiplicities are s = singlet, dd = doublet of doublets ddd = doublet of doublet of doublet. Mass spectra were recorded at the Service Commun de Spectrometrie de Masse of University Paul Sabatier (Toulouse 3), Toulouse (France) and CP MAS NMR were recorded at the Laboratoire de Chimie de Coordination on a Bruker Avance IIIHD 400 spectrometer equipped with a 2.5 mm probe. Samples were spun at 14 kHz at the magic angle using ZrO$_2$ rotors. $^{13}$C-CP/MAS were recorded with a recycle delay of 1.5 s and a contact time of 3 ms. All chemical shifts for $^{13}$C are relative to TMS. Thermal analyses (TG/DSC) were carried out on a Setaram Labsys instrument under flowing helium (45 mL min$^{-1}$) with the heating rate of 10 °C min$^{-1}$ from 30 °C to 550 °C. The samples (5 mg) were contained in 100 μL aluminum crucibles. IR spectra were measured on a PerkinElmer Spectrum 100 FT-IR spectrometer with samples as KBr pellets. UV - Vis spectra were recorded on a Varian Cary 5000 spectrophotometer.

Thermal Gravimetric Analysis

Ca 3-5 mg of samples were precisely weighed in a 100 μl alumina crucible and placed into a Setaram Labsys device. Before analysis, sample and analysis chamber were purged first in vacuo and then by flowing helium (45 ml/min) during 8 hours. The absence of oxygen was checked with a lambda analyzer (Setnag JC15V) coupled with the Labsys device. Dual thermogravimetry (TG) and differential thermal analysis (DTA) of samples were made simultaneously using a ramp rate of 10 °C/min, from 30 °C to 550 °C and with a helium flow of 45 ml/min.
MS MALDI measurements:
Saturated solution of the carbonyl precursor 7a or 7b in dichloromethane was drop-casted on an indium-tin oxide (ITO) glass slide without any matrix to avoid possible side reactions of the later generated reactive starphene molecules. After evaporation of the solvent, the coated ITO glass slide was heated in a glovebox at 200°C for 1 min. and then subjected to the MALDI chamber for the measurement. In the second experiment, the soluble precursor 7a was dissolved in chlorobenzene and the solution was thoroughly degassed. This solution was heated at 200°C for 10 min. during a dark violet precipitate was formed. This heterogenous solution was drop-casted on an indium-tin oxide (ITO) glass slide without any matrix and dried. After evaporation of the solvent, the coated ITO glass slide was subjected to the MALDI chamber for the measurement. In a parallel experiment was the heterogenous solution mixed with 2,5-dihydroxy benzoic acid as a matrix and then drop-casted on an indium-tin oxide (ITO) glass slide and dried. After evaporation of the solvent, the coated ITO glass slide was subjected to the MALDI chamber for the measurement. ITO glass slides and cover slips were obtained from Bruker (Bremen, Germany). The laser spot was set at the small focus with a laser intensity 41% and calibrated on red phosphorus clusters.

FTIR spectra in KBr pellet
KBr pellets were prepared from 1 mg of 7a, 7b, respectively and 100 mg of anhydrous KBr. Compounds 7a/b were converted to nonacene 1 by heating the pellets on a heating plate at 200 or 350°C for 30 s under inert atmosphere and then immediately measured under ambient conditions. Alternatively, 1 mg of 7a/7b were heated at 200°C/350°C to give 1 and the pellets were prepared from 1. Another solution was to use 1 obtained by precipitation from chlorobenzene as for Maldi MS (see above). In this case, it was not possible to remove traces of chlorobenzene from dried 1.

Theoretical calculation:
Diels-Alder selectivity: To gain insight into the selectivity of the Diels-Alder reaction between diene and aryne, we conducted density functional theory (DFT) calculations of transition states (TS) to form 5a/5b using GRRM 17i with Gaussian 16 Rev. C.01. The geometries of the TS were optimized with QST3 method at the B3LYP/6-31+G(d,p) level of theory, and the energies of TS were calculated by single point calculations at the M06-2X/6-31+G(d,p) level of theory with according to a previous paper dealing with the Diels-Alder reaction. The polarizable continuum model (PCM) was used for the geometry optimization and the single point
calculations to take into consideration the effect of the reaction solvent (acetonitrile). As shown in SI (page S28), 8 structures were determined as TS. Based on the calculated energies of TS, syn/anti ratio of 1 was estimated to 1.64/1, which is consistent with the observed stereoselectivity in the experiment (syn/anti = 2/1).

The synthesis of nonacene 1

(1R, 4S)-11,11-dimethoxy-2,3-dimethylene-1,2,3,4-tetrahydro-1,4-methanoanthracene (2)

The diene 2 was prepared according to our previously published method and the $^1$H NMR and $^{13}$C NMR spectra were in agreement with our previous data.$^3$

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): 3.11 (3H, s), 3.33 (3H, s), 4.09 (2H, s), 5.12 (2H, s), 5.29 (2H, s), 7.39 – 7.49 (2H, m), 7.63 (2H, s), 7.74 – 7.80 (2H, m).

(13S)-15,15-dimethoxy-3-(trimethylsilyl)-5,6,13,14-tetrahydro-6,13-methanopentacen-2-yl trifluoromethanesulfonate (4)

The aryne precursor 4 was prepared according to our previously published method and the $^1$H NMR and $^{13}$C NMR spectra were in agreement with our previous data.$^4$
$^1$H NMR (300 MHz, CD$_2$Cl$_2$): 0.30 (9H, s), 3.08 (3H, s), 3.28 (3H, s), 3.32 – 3.45 (2H, m), 3.65 – 3.77 (2H, m), 4.00 (2H, s), 7.06 (1H, s), 7.26 (1H, s), 7.35 – 7.41 (2H, m), 7.59 (2H, s), 7.68 – 7.74 (2H, m).

(6S, 10R, 17S, 21R)-23,23,24,24-tetramethoxy-6,7,9,10,17,18,20,21-octahydro-6,21:10,17-dimethanononacene (5b) and (6S, 10S, 17R, 21R)-23,23,24,24-tetramethoxy-6,7,9,10,17,18,20,21-octahydro-6,21:10,17-dimethanononacene (5a)

A well dried flask was charged with compound 4 (200 mg, 0.348 mmol, 1.0 equiv.), diene 2 (97 mg, 0.348 mmol, 1.0 equiv.) and CsF (106 mg, 0.699 mmol, 2 equiv.) under argon and then anhydrous CH$_3$CN (16 mL) and THF (3.2 mL) were added. The reaction mixture was stirred at room temperature overnight. After the evaporation of the solvent, the residue was purified by column chromatography on silica gel (gradient from chloroform to chloroform : aceton 20:1) was resolved first isomer 5b (75 mg) from second isomer 5a (140 mg) both as a white amorphous solid (combined yield 215 mg, 98 %). Both compounds were used directly in the next step without full characterization.

Isomer 5a:

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): 3.06 (6H, s), 3.24 (6H, s), 3.26 – 3.32 (4H, m), 3.52 – 3.61 (4H, m), 3.95 (4H, s), 6.84 (2H, s), 7.35 – 7.40 (4H, m), 7.58 (4H, s), 7.68 – 7.73 (4H, m).

$^{13}$C NMR (126 MHz, CD$_2$Cl$_2$): not measured

Isomer 5b:

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): 3.07 (6H, s), 3.19 – 3.27 (4H, m), 3.29 (6H, s), 3.55 – 3.64 (4H, m), 3.96 (4H, s), 6.84 (2H, s), 7.31 – 7.36 (4H, m), 7.55 (4H, s), 7.64 – 7.69 (4H, m).

$^{13}$C NMR (126 MHz, CD$_2$Cl$_2$): not measured

(6S, 10R, 17S, 21R)-23,23,24,24-tetramethoxy-6,10,17,21-tetrahydro-6,21:10,17-dimethanononacene and (6a) and (6S, 10S, 17R, 21R)-23,23,24,24-tetramethoxy-6,10,17,21-tetrahydro-6,21:10,17-dimethanononacene (6b)
Direct synthesis from 2 without isolation of 5a/b: A well-dried Schlenk flask was charged with diene 2 (200 mg, 0.72 mmol) and CsF (480 mg, 3.16 mmol, 4.0 equiv.) under argon and then anhydrous acetonitrile (16 mL) was added. The heterogenous mixture was cooled to 0°C and then solution of aryne precursor bis(trimethylsilyl)-1,4-phenylene bis(trifluoromethanesulfonate) (298 mg, 0.58 mmol, 0.8 equiv.) in anhydrous THF (4 mL) was added dropwise. The reaction was allowed to warm to room temperature overnight. Progress of the reaction was controlled by TLC, eluent (hexane - EtOAc 3:2). Reaction time depending on a scale of the reaction (1-3 days). After the evaporation of the solvent, the residue was chromatographed on silica gel (hexane : acetone 3:1) to get the desired product as a mixture of two regioisomers as a colorless solid. This mixture (146 mg, 0.23 mmol) was dissolved in anhydrous toluene (15 mL) under argon. The solution was cooled to 0°C and then DDQ (53 mg, 0.231 mmol, 2 equiv.) was added in one portion. The reaction mixture was stirred at 0°C for 10 min. and then 6 hours at room temperature. The volume of the reaction mixture was reduced to a half and the mixture was filtered over a frita S4. The solid was washed with toluene and finally with methanol to get the first isomer 6b (40 mg) as a white solid. The mother liquor was evaporated and the residue was purified by chromatography on silica gel (hexane : acetone 3:1) to get the second isomer 6a (82 mg) as a white solid. The ratio of isomers is 1:2 and combined yield is 54 % after two synthetic steps.

Synthesis by oxidation of 5a/b: The compound 5a or 5b (140 mg, 0.22 mmol) was dissolved in anhydrous toluene (17 mL) under argon. The solution was cooled to 0°C and then DDQ (111 mg, 0.488 mmol, 2.2 equiv.) was added in one portion. The reaction mixture was stirred at 0°C for 10 min. and then 6 hours at room temperature. The isomer 6b was isolated by filtration the heterogenous reaction mixture over a frita S4. The collected solid was washed with toluene and then with methanol and finally dried to get the product 6b as a white solid (130 mg, 94%). Evaporation of the reaction mixture of the isomer 6a followed by chromatography on silica gel (hexane : acetone 3:1) afforded the product as a white solid (129 mg, 94%).
$^1$H NMR (500 MHz, CD$_2$Cl$_2$): 3.23 (6H, s, $H12$), 3.26 (6H, s, $H12$), 4.71 (4H, s, $H2$), 7.33 - 7.36 (4H, m, $H7$), 7.68 – 7.71 (4H, m, $H6$), 7.70 (4H, s, $H4$), 7.77 (4H, s, $H9$), 8.12 (2H, s, $H11$).

$^{13}$C NMR (126 MHz, CD$_2$Cl$_2$): 51.54 (C12), 51.58 (C12), 55.20 (C2), 120.43 (C9), 120.87 (C4), 124.77 (C1), 125.96 (C7), 126.04 (C11), 128.14 (C6), 131.39 (C10), 133.08 (C5), 142.94 (C8), 143.61 (C3).

DCI MS: 627 ([M + H]$^+$).

HR DCI MS: calcd for C$_{44}$H$_{35}$O$_4$ 627.2530; found 627.2511.

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): 3.21 (6H, s), 3.22 (6H, s), 4.71 (4H, s), 7.37 – 7.40 (4H, m), 7.72 – 7.77 (4H, m), 7.73 (4H, s), 7.77 (4H, s), 8.12 (2H, s).

$^{13}$C NMR (126 MHz, CD$_2$Cl$_2$): not measured due to the low solubility

DCI MS: 627 ([M + H]$^+$).

HR DCI MS: calcd for C$_{44}$H$_{35}$O$_4$ 627.2530; found 627.2523.
In a well dried Schlenk flask, 6a (160 mg, 0.255 mmol) was dissolved in anhydrous dichloromethane (10 mL) under argon. Then trimethylsilyl iodide (109 μL, 0.766 mmol, 3 equiv.) was added dropwise and the homogeneous reaction mixture was stirred overnight at room temperature. Next day the heterogeneous reaction mixture was stirred on air at room temperature for 6 hours to complete the hydrolysis of formed iodo-methoxy intermediate. The product was collected by filtration over a glass frit filter S4, washed with mixture of solvents (hexane : dichloromethane, 4:1) to afford first portion of pure compound 7a as a white solid. The mother liquor was evaporated and the residue was purified by chromatography on silica gel (hexane : acetone 3:1) to get the second portion of the product as a white solid. The combined yield was (130 mg, 95%).

$^1$H NMR (500 MHz, CD$_2$Cl$_2$): 4.99 (4H, s, H2), 7.41 - 7.44 (4H, m, H7), 7.78 – 7.81 (4H, m, H6), 7.93 (4H, s, H4), 8.04 (4H, s, H9), 8.36 (2H, s, H11).

$^{13}$C NMR (126 MHz, CD$_2$Cl$_2$): 57.55 (C2), 120.88 (C9), 121.22 (C4), 126.57 (C7), 126.76 (C11), 128.34 (C6), 131.61 (C10), 133.31 (C5), 137.61 (C8), 137.93 (C3), 194.46 (C=O).

CP MAS: 56.99 (bridgehead), 120.20-137.12 (aromatic), 193.26 and 197.73 (C=O).

IR (KBr pellet): 3056 m, 3012 m, 2954 m, 2922 m, 2853 m, 1793 s (C=O), 1610 w, 1582 w, 1499 m, 1441 w, 1420 m, 1401 w, 1339 w, 1283 w, 1265 w, 1207 w, 1175 wm, 1152 wm, 1135 m, 1094 w, 1019 w, 979 wm, 949 w, 916 ms, 880 ms, 820 w, 799 w, 782 w, 748 ms, 686 m, 590 w, 558 w, 524 wm, 492 wm, 474 m cm$^{-1}$.

DCI MS: 478 ([M – 2 x CO]$^+$).

HR DCI MS: calcd for C$_{38}$H$_{22}$ 478.1722 (M – 2xCO); found 478.1727.
(6S, 10S, 17R, 21R)-6,10,17,21-tetrahydro-6,21:10,17-dimethanononacene-23,24-dione (7b)

In a well dried Schlenk flask, 6b (25 mg, 39.89 μmol) was suspended in anhydrous dichloromethane (4 mL) under argon. Then trimethylsilyl iodide (23 μL, 159.6 μmol, 4 equiv.) was added dropwise and the heterogenous reaction mixture was stirred overnight at room temperature. Next day the heterogeneous reaction mixture was stirred on air at room temperature for 6 hours to complete the hydrolysis of formed iodo-methoxy intermediate. The product was collected by filtration over a glass frit filter S4, washed with mixture of solvents (dichloromethane : acetone, 4:1) to afford pure compound 7b (20 mg, 94 %) as a white solid.

**CP MAS:** 55.83 (bridgehead), 119.23-136.01 (aromatic), 195.55 (C=O).

**IR** (KBr pellet) cm⁻¹: 3052 wm, 3012 wm, 1781 s (C=O), 1649 w, 1609 w, 1581 w, 1500 wm, 1440 w, 1420 m, 1397 wm, 1341 w, 1284 w, 1265 w, 1213 w, 1208 w, 1184 wm, 1144 wm, 1136 m, 1020 w, 979 wm, 938 w, 929 m, 911 m, 891 m, 881 m, 818 w, 800 w, 753 m, 709 w, 666 wm, 656 w, 607 w, 558 w, 529 w, 477 m.

**DCI MS:** 478 ([M – 2 x CO]⁺).

**HR DCI MS:** calcd for C₃₈H₂₂ 478.1722 (M – 2xCO); found 478.1731.

Nonacene (1)
Nonacene was obtained by heating 7a or 7b in the solid state at 200°C or 350°C under vacuum for 15 min.

**IR (KBr pellet) cm\(^{-1}\):** 3045 m, 3018 m, 2925 w, 1924 wb, 1790 wb, 1624 w, 1507 w, 1500 w, 1450 w, 1445 w, 1418 w, 1362 w, 1296 w, 1269 w, 1162 w, 1123 w, 1104 w, 997 w, 952 w, 904 s, 735 ms, 621 w, 538 w, 466 m.

**CP MAS:** 125.5 - 128.8

**MALDI MS:** calcd for C\(_{38}\)H\(_{22}\) 478.1722; found 478.179 - 478.335 (for details see page 23-26).
$^1$H and $^{13}$C NMR spectra of 5a/b – 7a/b
jancarik_a_300b.18.fid
AJ189

S16
13C CPMAS spectra of transformations 7a/b → 1

(top, black) = just after decarbonylation
(bottom, blue) = after two months at room temperature under argon
At 200 °C, the reaction yields product 1 from precursor 7b.

At 350 °C, the reaction yields product 1 from precursor 7b.

(top, black) = just after decarbonylation
(bottom, blue) = after two months at room temperature under argon
IR spectra of transformations $7a/b \rightarrow 1$
Thermal Gravimetric Analysis of 7a/b

7a

- 2 x C=O = - 10.5% (teor.)

1

- 2 x C=O = - 10.5% (teor.)

7b

Temperature °C

Weight loss in %

-10 -5 0 10

60 160 260 360 460 560

160 °C

190 °C

syn-isomer

Temperature °C

Weight loss in %

-10 -5 0 10

60 160 260 360 460 560

195 °C

200 °C

anti-isomer
MALDI MS Analysis of 1 generated in different conditions

MS MALDI spectrum of 1, generated from 7a in solid state form on ITO glass slide.
MS MALDI spectrum of 1, generated from 7b in solid state form on ITO glass slide.
MS MALDI spectrum of 1, generated from 7a in chlorobenzene, measured without matrix.
MS MALDI spectrum of 1, generated from 7a in chlorobenzene, measured with DHB as a matrix.
Theoretical calculation of Diels Alder reaction

anti1 (+0.35 kcal/mol)

anti2 (+1.35 kcal/mol)

syn1 (0 kcal/mol)

syn2 (+1.60 kcal/mol)

anti/syn = 1 : 1.64
(observed: anti/syn = 1 : 2)

Gaussian 16, Revision A.03
M06-2X/6-31+G(d,p)/def2-SVP/6-31+G(d,p)
Acetonitrile (PCM method), 298.15 K
Single crystals of 5b grown by slow evaporation of a mixture of hexane: EtOAc were selected in mother liquor from a flask and covered with perfluorated polyether oil on a microscope slide. An appropriate crystal was selected using a polarizing microscope, fixed on the tip of a MiTeGen® MicroMount, transferred to a goniometer head, and shock cooled by the crystalcooling device. Crystallographic data were collected at 193(2) K on a Bruker-AXS Kappa APEX II Quazar diffractometer equipped with a 30W air-cooled microfocus source using Mo Kα radiation (λ=0.71073 Å). Phi- and omega-scans were used. Space group was determined on the basis of systematic absences and intensity statistics. Semi-empirical absorption correction was employed. The structure was solved using an intrinsic phasing method (SHELXT), and refined using the least-squares method on $F^2$. All non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were refined isotropically at calculated positions using a riding model with their isotropic displacement parameters constrained to be equal to 1.5 times the equivalent isotropic displacement parameters of their pivot atoms for terminal sp³ carbon and 1.2 times for all other carbon atoms.

The solvent molecule (ethyl acetate on a special position) was disordered over two positions, for which occupancies were refined. Several restraints (SAME, SIMU, DELU) were applied to refine the molecule and to avoid the collapse of the structure during the least-squares refinement by the large anisotropic displacement parameters. A bond length was restrained with DFIX to suitable target values.
CCDC-2071402 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/.

**Selected data for 5b:** C_{44}H_{38}O_{4}, C_{4}H_{8}O_{2} M = 718.85, Monoclinic, space group P2_1/n, \( a = 16.0184(9) \) Å, \( b = 7.0568(5) \) Å, \( c = 16.9607(11) \) Å, \( \beta = 99.492(2)^{\circ} \), \( V = 1891.0(2) \) Å\(^3\), \( Z = 2 \), crystal size 0.24 x 0.22 x 0.15 mm\(^3\), 49831 reflections collected (4682 independent, \( R_{int} = 0.0659 \)), 328 parameters, 193 restraints, \( R1 [I>2\sigma(I)] = 0.0499 \), \( wR2 [all data] = 0.1425 \), largest diff. peak and hole: 0.268 and \(-0.193\) eÅ\(^{-3}\).

**Figure**: Molecular structure of 5b. Thermal ellipsoids represent 50% probability level. Hydrogen atoms and solvent molecule were omitted for clarity.

**Table 1.** Crystal data and structure refinement for 5b.

| Identification code | A1189_a |
|---------------------|---------|
| Empirical formula   | C_{48}H_{46}O_{6} |
| Formula weight      | 718.85 |
| Temperature         | 193(2) K |
| Wavelength          | 0.71073 Å |
| Crystal system      | Monoclinic |
| Space group         | P2_1/n |

S30
| Property                                      | Value                                      |
|----------------------------------------------|--------------------------------------------|
| **Unit cell dimensions**                     |                                            |
| a                                            | 16.0184(9) Å                               |
| b                                            | 7.0568(5) Å                                |
| c                                            | 16.9607(11) Å                              |
| **Volume**                                   | 1891.0(2) Å³                              |
| **Z**                                        | 2                                          |
| **Density (calculated)**                     | 1.262 Mg/m³                                |
| **Absorption coefficient**                   | 0.082 mm⁻¹                                 |
| **F(000)**                                   | 764                                        |
| **Crystal size**                             | 0.24 x 0.22 x 0.15 mm³                     |
| **Theta range for data collection**          | 3.162 to 28.278°                           |
| **Index ranges**                             | -21<h<21, -9<k<9, -22<l<22                 |
| **Reflections collected**                    | 49831                                      |
| **Independent reflections**                  | 4682 [R(int) = 0.0659]                     |
| **Completeness to theta = 25.242°**          | 99.6 %                                     |
| **Absorption correction**                    | Semi-empirical from equivalents           |
| **Max. and min. transmission**               | 0.7457 and 0.6994                         |
| **Refinement method**                        | Full-matrix least-squares on F²           |
| **Data / restraints / parameters**           | 4682 / 193 / 328                           |
| **Goodness-of-fit on F²**                    | 1.022                                      |
| **Final R indices [I>2sigma(I)]**            | R1 = 0.0499, wR2 = 0.1236                  |
| **R indices (all data)**                     | R1 = 0.0834, wR2 = 0.1425                  |
| **Extinction coefficient**                   | n/a                                        |
| **Largest diff. peak and hole**              | 0.268 and -0.193 e.Å⁻³                    |
Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for 5b. U(eq) is defined as one third of the trace of the orthogonalized U^ij tensor.

|     | x        | y        | z        | U(eq) |
|-----|----------|----------|----------|-------|
| O(1) | 3955(1)  | 9047(2)  | 4269(1)  | 42(1) |
| O(2) | 2558(1)  | 9149(2)  | 3651(1)  | 42(1) |
| C(1) | 186(1)   | 3395(2)  | 4614(1)  | 29(1) |
| C(2) | 792(1)   | 4818(2)  | 4749(1)  | 29(1) |
| C(3) | 604(1)   | 6461(2)  | 5146(1)  | 28(1) |
| C(4) | 1216(1)  | 8102(2)  | 5317(1)  | 33(1) |
| C(5) | 2014(1)  | 7758(2)  | 5007(1)  | 31(1) |
| C(6) | 2206(1)  | 6158(2)  | 4652(1)  | 31(1) |
| C(7) | 1638(1)  | 4524(3)  | 4475(1)  | 37(1) |
| C(8) | 3199(1)  | 6335(3)  | 4504(1)  | 33(1) |
| C(9) | 3665(1)  | 6383(2)  | 5332(1)  | 33(1) |
| C(10)| 4243(1)  | 5169(3)  | 5725(1)  | 35(1) |
| C(11)| 4636(1)  | 5601(3)  | 6522(1)  | 38(1) |
| C(12)| 5225(1)  | 4359(3)  | 6966(1)  | 46(1) |
| C(13)| 5609(1)  | 4809(4)  | 7724(1)  | 58(1) |
| C(14)| 5429(1)  | 6521(4)  | 8071(1)  | 63(1) |
| C(15)| 4860(1)  | 7757(4)  | 7663(1)  | 53(1) |
| C(16)| 4441(1)  | 7334(3)  | 6883(1)  | 40(1) |
| C(17)| 3843(1)  | 8598(3)  | 6443(1)  | 38(1) |
| C(18)| 3458(1)  | 8109(2)  | 5698(1)  | 33(1) |
| C(19)| 2784(1)  | 9071(2)  | 5096(1)  | 33(1) |
| C(20)| 3122(1)  | 8499(3)  | 4315(1)  | 36(1) |
| C(21)| 4074(1)  | 11042(3)| 4253(2)  | 64(1) |
| C(22)| 2713(2)  | 8396(4)  | 2908(1)  | 63(1) |
| C(23)| 2671(12)| 3550(30)| 7124(13)| 94(4) |
| C(24)| 2206(11)| 1910(20)| 6874(10)| 70(3) |
| O(3) | 2609(12)| 990(20) | 7575(11)| 73(2) |
| C(25)| 2322(16)| -630(30)| 7805(11)| 64(3) |
| O(4) | 1801(5) | -1423(12)| 7279(5) | 81(3) |
| C(26)| 2751(14)| -1700(20)| 8488(10)| 58(3) |
| C(23')| 2741(14)| -1150(20)| 8368(11)| 57(3) |
| C(24')| 2289(15)| -590(30)| 7596(10)| 65(3) |
| O(3')| 2544(12)| 1400(20)| 7548(11)| 68(2) |
|       |       |       |       |       |
|-------|-------|-------|-------|-------|
| C(25') | 2374(10) | 2490(20) | 6931(10) | 68(2) |
| O(4')  | 1957(5)  | 1619(12) | 6338(5)  | 82(3) |
| C(26') | 2322(14) | 4610(20) | 6822(12) | 94(4) |
Table 3. Bond lengths [Å] and angles [°] for 5b.

| Bond                  | Distance   |
|-----------------------|------------|
| O(1)-C(20)            | 1.4039(18) |
| O(1)-C(21)            | 1.422(2)   |
| O(2)-C(20)            | 1.400(2)   |
| O(2)-C(22)            | 1.425(2)   |
| C(1)-C(2)             | 1.389(2)   |
| C(1)-C(3)#1           | 1.395(2)   |
| C(1)-H(1)             | 0.9500     |
| C(2)-C(3)             | 1.398(2)   |
| C(2)-C(7)             | 1.519(2)   |
| C(3)-C(4)             | 1.513(2)   |
| C(4)-C(5)             | 1.481(2)   |
| C(4)-H(4A)            | 0.9900     |
| C(4)-H(4B)            | 0.9900     |
| C(5)-C(6)             | 1.339(2)   |
| C(5)-C(19)            | 1.531(2)   |
| C(6)-C(7)             | 1.469(2)   |
| C(6)-C(8)             | 1.530(2)   |
| C(7)-H(7A)            | 0.9900     |
| C(7)-H(7B)            | 0.9900     |
| C(8)-C(9)             | 1.529(2)   |
| C(8)-C(20)            | 1.560(3)   |
| C(8)-H(8)             | 1.0000     |
| C(9)-C(10)            | 1.353(2)   |
| C(9)-C(18)            | 1.430(2)   |
| C(10)-C(11)           | 1.427(2)   |
| C(10)-H(10)           | 0.9500     |
| C(11)-C(12)           | 1.412(3)   |
| C(11)-C(16)           | 1.425(3)   |
| C(12)-C(13)           | 1.367(3)   |
| C(12)-H(12)           | 0.9500     |
| C(13)-C(14)           | 1.395(3)   |
| C(13)-H(13)           | 0.9500     |
| C(14)-C(15)           | 1.365(3)   |
| C(14)-H(14)           | 0.9500     |
| C(15)-C(16)           | 1.414(2)   |
| C(15)-H(15)           | 0.9500     |
C(16)-C(17) 1.427(3)
C(17)-C(18) 1.357(2)
C(17)-H(17) 0.9500
C(18)-C(19) 1.518(2)
C(19)-C(20) 1.563(2)
C(19)-H(19) 1.0000
C(21)-H(21A) 0.9800
C(21)-H(21B) 0.9800
C(21)-H(21C) 0.9800
C(22)-H(22A) 0.9800
C(22)-H(22B) 0.9800
C(22)-H(22C) 0.9800
C(23)-C(24) 1.41(2)
C(23)-H(23A) 0.9800
C(23)-H(23B) 0.9800
C(23)-H(23C) 0.9800
C(24)-O(3) 1.414(9)
C(24)-H(24A) 0.9900
C(24)-H(24B) 0.9900
O(3)-C(25) 1.313(19)
C(25)-O(4) 1.250(19)
C(25)-C(26) 1.456(18)
C(26)-H(26A) 0.9800
C(26)-H(26B) 0.9800
C(26)-H(26C) 0.9800
C(23')-C(24') 1.44(2)
C(23')-H(23D) 0.9800
C(23')-H(23E) 0.9800
C(23')-H(23F) 0.9800
C(24')-O(3') 1.466(16)
C(24')-H(24C) 0.9900
C(24')-H(24D) 0.9900
O(3')-C(25') 1.293(18)
C(25')-O(4') 1.273(18)
C(25')-C(26') 1.506(18)
C(26')-H(26D) 0.9800
C(26')-H(26E) 0.9800
C(26')-H(26F) 0.9800
C(20)-O(1)-C(21)  113.94(15)
C(20)-O(2)-C(22)  113.97(15)
C(2)-C(1)-C(3)#1  122.83(15)
C(2)-C(1)-H(1)    118.6
C(3)#1-C(1)-H(1)  118.6
C(1)-C(2)-C(3)    118.63(13)
C(1)-C(2)-C(7)    119.05(14)
C(3)-C(2)-C(7)    122.32(13)
C(1)#1-C(3)-C(2)  118.55(14)
C(1)#1-C(3)-C(4)  118.55(14)
C(2)-C(3)-C(4)    122.90(13)
C(5)-C(4)-C(3)    112.11(13)
C(5)-C(4)-H(4A)   109.2
C(3)-C(4)-H(4A)   109.2
C(5)-C(4)-H(4B)   109.2
C(3)-C(4)-H(4B)   109.2
H(4A)-C(4)-H(4B)  107.9
C(6)-C(5)-C(4)    124.99(14)
C(6)-C(5)-C(19)   108.29(13)
C(4)-C(5)-C(19)   126.54(14)
C(5)-C(6)-C(7)    125.01(14)
C(5)-C(6)-C(8)    107.55(14)
C(7)-C(6)-C(8)    127.39(14)
C(6)-C(7)-C(2)    112.58(14)
C(6)-C(7)-H(7A)   109.1
C(2)-C(7)-H(7A)   109.1
C(6)-C(7)-H(7B)   109.1
C(2)-C(7)-H(7B)   109.1
H(7A)-C(7)-H(7B)  107.8
C(9)-C(8)-C(6)    105.59(12)
C(9)-C(8)-C(20)   98.39(13)
C(6)-C(8)-C(20)   98.54(13)
C(9)-C(8)-H(8)    117.1
C(6)-C(8)-H(8)    117.1
C(20)-C(8)-H(8)   117.1
C(10)-C(9)-C(18)  121.03(15)
C(10)-C(9)-C(8)   132.80(16)
C(18)-C(9)-C(8) 106.16(14)
C(9)-C(10)-C(11) 119.31(17)
C(9)-C(10)-H(10) 120.3
C(11)-C(10)-H(10) 120.3
C(12)-C(11)-C(16) 118.57(16)
C(12)-C(11)-C(10) 121.64(18)
C(16)-C(11)-C(10) 119.78(16)
C(13)-C(12)-C(11) 121.0(2)
C(13)-C(12)-H(12) 119.5
C(11)-C(12)-H(12) 119.5
C(12)-C(13)-C(14) 120.4(2)
C(12)-C(13)-H(13) 119.8
C(14)-C(13)-H(13) 119.8
C(15)-C(14)-C(13) 120.48(19)
C(15)-C(14)-H(14) 119.8
C(13)-C(14)-H(14) 119.8
C(14)-C(15)-C(16) 120.9(2)
C(14)-C(15)-H(15) 119.6
C(16)-C(15)-H(15) 119.6
C(15)-C(16)-C(11) 118.68(18)
C(15)-C(16)-C(17) 122.08(18)
C(11)-C(16)-C(17) 119.23(15)
C(18)-C(17)-C(16) 119.38(17)
C(18)-C(17)-H(17) 120.3
C(16)-C(17)-H(17) 120.3
C(17)-C(18)-C(9) 121.19(16)
C(17)-C(18)-C(19) 132.55(17)
C(9)-C(18)-C(19) 106.26(14)
C(18)-C(19)-C(5) 105.46(13)
C(18)-C(19)-C(20) 98.48(13)
C(5)-C(19)-C(20) 98.40(13)
C(18)-C(19)-H(19) 117.1
C(5)-C(19)-H(19) 117.1
C(20)-C(19)-H(19) 117.1
O(2)-C(20)-O(1) 110.92(13)
O(2)-C(20)-C(8) 117.55(14)
O(1)-C(20)-C(8) 108.41(14)
O(2)-C(20)-C(19) 109.28(13)
O(1)-C(20)-C(19)     116.16(13)
C(8)-C(20)-C(19)     93.81(13)
O(1)-C(21)-H(21A)    109.5
O(1)-C(21)-H(21B)    109.5
H(21A)-C(21)-H(21B)  109.5
O(1)-C(21)-H(21C)    109.5
H(21A)-C(21)-H(21C)  109.5
H(21B)-C(21)-H(21C)  109.5
O(2)-C(22)-H(22A)    109.5
O(2)-C(22)-H(22B)    109.5
H(22A)-C(22)-H(22B)  109.5
O(2)-C(22)-H(22C)    109.5
H(22A)-C(22)-H(22C)  109.5
H(22B)-C(22)-H(22C)  109.5
C(24)-C(23)-H(23A)   109.5
C(24)-C(23)-H(23B)   109.5
H(23A)-C(23)-H(23B)  109.5
C(24)-C(23)-H(23C)   109.5
H(23A)-C(23)-H(23C)  109.5
H(23B)-C(23)-H(23C)  109.5
C(23)-C(24)-O(3)     88.9(12)
C(23)-C(24)-H(24A)   113.8
O(3)-C(24)-H(24A)    113.8
C(23)-C(24)-H(24B)   113.8
O(3)-C(24)-H(24B)    113.8
H(24A)-C(24)-H(24B)  111.1
C(25)-O(3)-C(24)     121.1(15)
O(4)-C(25)-O(3)      113.8(15)
O(4)-C(25)-C(26)     120.5(17)
O(3)-C(25)-C(26)     123.0(17)
C(25)-C(26)-H(26A)   109.5
C(25)-C(26)-H(26B)   109.5
H(26A)-C(26)-H(26B)  109.5
C(25)-C(26)-H(26C)   109.5
H(26A)-C(26)-H(26C)  109.5
C(25)-C(26)-H(26D)   109.5
H(26B)-C(26)-H(26D)  109.5
C(24')-C(23')-H(23D) 109.5
C(24')-C(23')-H(23E) 109.5
H(23D)-C(23')-H(23E) 109.5
C(24')-C(23')-H(23F) 109.5
H(23D)-C(23')-H(23F) 109.5
H(23E)-C(23')-H(23F) 109.5
C(23')-C(24')-O(3') 102.0(13)
C(23')-C(24')-H(24C) 111.4
O(3')-C(24')-H(24C) 111.4
C(23')-C(24')-H(24D) 111.4
O(3')-C(24')-H(24D) 111.4
H(24C)-C(24')-H(24D) 109.2
C(25')-O(3')-C(24') 126.4(12)
O(4')-C(25')-O(3') 111.2(13)
O(4')-C(25')-C(26') 111.9(16)
O(3')-C(25')-C(26') 133.9(17)
C(25')-C(26')-H(26D) 109.5
C(25')-C(26')-H(26E) 109.5
H(26D)-C(26')-H(26E) 109.5
C(25')-C(26')-H(26F) 109.5
H(26D)-C(26')-H(26F) 109.5
H(26E)-C(26')-H(26F) 109.5

Symmetry transformations used to generate equivalent atoms:
#1  -x,-y+1,-z+1
Table 4. Anisotropic displacement parameters (Å² x 10³) for 5b. The anisotropic displacement factor exponent takes the form: -2π² [ h²a*²U₁₁ + ... + 2hkab*U₁₂ ]

|      | U¹¹ | U²² | U³³ | U¹² | U¹³ | U¹² |
|------|-----|-----|-----|-----|-----|-----|
| O(1) | 26(1)| 55(1)| 47(1)| 6(1)| 8(1)| -11(1)|
| O(2) | 33(1)| 57(1)| 34(1)| 6(1)| 1(1)| -2(1)|
| C(1) | 25(1)| 30(1)| 33(1)| -4(1)| 5(1)| -2(1)|
| C(2) | 22(1)| 33(1)| 32(1)| -2(1)| 5(1)| -2(1)|
| C(3) | 24(1)| 31(1)| 30(1)| 0(1)| 4(1)| -4(1)|
| C(4) | 26(1)| 34(1)| 40(1)| -4(1)| 6(1)| -6(1)|
| C(5) | 22(1)| 38(1)| 31(1)| -1(1)| 2(1)| -5(1)|
| C(6) | 21(1)| 42(1)| 31(1)| -3(1)| 3(1)| -4(1)|
| C(7) | 26(1)| 41(1)| 45(1)| -12(1)| 10(1)| -5(1)|
| C(8) | 22(1)| 46(1)| 31(1)| -3(1)| 4(1)| -4(1)|
| C(9) | 21(1)| 46(1)| 31(1)| -3(1)| 4(1)| -7(1)|
| C(10)| 23(1)| 48(1)| 35(1)| -2(1)| 7(1)| -4(1)|
| C(11)| 22(1)| 59(1)| 34(1)| 3(1)| 6(1)| -5(1)|
| C(12)| 32(1)| 68(1)| 40(1)| 7(1)| 6(1)| 4(1)|
| C(13)| 40(1)| 91(2)| 40(1)| 8(1)| 0(1)| 9(1)|
| C(14)| 45(1)| 106(2)| 34(1)| -6(1)| -5(1)| 4(1)|
| C(15)| 40(1)| 83(2)| 36(1)| -12(1)| 1(1)| -2(1)|
| C(16)| 26(1)| 62(1)| 32(1)| -3(1)| 4(1)| -6(1)|
| C(17)| 29(1)| 49(1)| 37(1)| -7(1)| 5(1)| -9(1)|
| C(18)| 23(1)| 42(1)| 36(1)| -1(1)| 5(1)| -9(1)|
| C(19)| 24(1)| 38(1)| 38(1)| -3(1)| 2(1)| -7(1)|
| C(20)| 23(1)| 50(1)| 35(1)| 2(1)| 3(1)| -7(1)|
| C(21)| 43(1)| 60(1)| 89(2)| 5(1)| 17(1)| -20(1)|
| C(22)| 67(1)| 86(2)| 35(1)| 2(1)| 2(1)| 15(1)|
| C(23)| 97(8)| 79(8)| 110(8)| -21(6)| 27(7)| -2(7)|
| C(24)| 81(5)| 66(6)| 75(4)| -12(5)| 42(4)| 2(4)|
| O(3) | 80(4)| 57(5)| 92(4)| -11(4)| 44(3)| -4(4)|
| C(25)| 74(4)| 37(4)| 86(5)| -13(4)| 31(5)| -3(4)|
| O(4) | 78(5)| 83(5)| 76(5)| -19(4)| -6(4)| 3(4)|
| C(26)| 91(6)| 30(8)| 57(6)| -9(5)| 26(5)| -22(7)|
| C(27)| 91(7)| 17(7)| 77(7)| 2(5)| 48(5)| -10(7)|
| C(28)| 75(4)| 47(4)| 82(5)| -7(5)| 41(5)| -2(4)|
| O(3')| 77(4)| 52(5)| 81(3)| -6(4)| 34(3)| -4(4)|
|     |    |    |    |    |    |    |    |
|-----|----|----|----|----|----|----|----|
| C(25') | 75(5) | 62(6) | 80(4) | -9(5) | 48(4) | -9(5) |
| O(4')  | 85(5) | 96(5) | 64(4) | -16(4) | 14(4) | -14(4) |
| C(26') | 119(9) | 90(7) | 76(8) | 21(6) | 25(8) | -38(8) |
Table 5. Hydrogen coordinates ($x \times 10^4$) and isotropic displacement parameters ($\AA^2 \times 10^3$) for 5b.

|     | x    | y    | z    | U(eq) |
|-----|------|------|------|-------|
| H(1) | 314  | 2277 | 4347 | 35    |
| H(4A)| 945  | 9266 | 5069 | 40    |
| H(4B)| 1346 | 8310 | 5902 | 40    |
| H(7A)| 1916 | 3387 | 4742 | 45    |
| H(7B)| 1540 | 4288 | 3892 | 45    |
| H(8) | 3300 | 5458 | 4101 | 40    |
| H(10)| 4386 | 4041 | 5472 | 42    |
| H(12)| 5357 | 3192 | 6736 | 56    |
| H(13)| 6001 | 3952 | 8015 | 69    |
| H(14)| 5705 | 6829 | 8595 | 76    |
| H(15)| 4743 | 8917 | 7908 | 64    |
| H(17)| 3715 | 9772 | 6670 | 46    |
| H(19)| 2683 | 10450| 5177 | 40    |
| H(21A)| 3813 | 11540| 3730 | 95    |
| H(21B)| 4681 | 11327| 4343 | 95    |
| H(21C)| 3810 | 11635| 4673 | 95    |
| H(22A)| 3255 | 8876 | 2794 | 95    |
| H(22B)| 2257 | 8784 | 2480 | 95    |
| H(22C)| 2733 | 7010 | 2940 | 95    |
| H(23A)| 2477 | 4075 | 7598 | 141   |
| H(23B)| 2586 | 4496 | 6693 | 141   |
| H(23C)| 3274 | 3238 | 7255 | 141   |
| H(24A)| 2343 | 1355 | 6374 | 85    |
| H(24B)| 1587 | 2057 | 6844 | 85    |
| H(26A)| 2456 | -2901| 8527 | 87    |
| H(26B)| 2750 | -962 | 8978 | 87    |
| H(26C)| 3337 | -1947| 8419 | 87    |
| H(23D)| 3349 | -1191| 8349 | 86    |
| H(23E)| 2547 | -2401| 8507 | 86    |
| H(23F)| 2633 | -223 | 8771 | 86    |
| H(24C)| 1669 | -705 | 7572 | 78    |
| H(24D)| 2464 | -1354| 7162 | 78    |
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