A practical general method for the preparation of long acenes
Andrej Jancarik, Gaspard Levet, André Gourdon

To cite this version:
Andrej Jancarik, Gaspard Levet, André Gourdon. A practical general method for the preparation of long acenes. Chemistry - A European Journal, Wiley-VCH Verlag, inPress, 10.1002/chem.201805975 . hal-01961616
A practical general method for the preparation of long acenes

Andrej Jancarik, * Gaspard Levet and André Gourdon*

Abstract: The field of long acenes, the narrowest of the zig-zag graphene nanoribbons, has been an area of significant interest in the past decade due to potential applications in organic electronics, spintronics and plasmonics. However their low solubility and high reactivity has so far hindered their preparation on large scales. We report here a concise strategy for the synthesis of higher acenes through Diels-Alder condensation of arynes with a protected tetraene ketone. After deprotection by cleavage of the ketal, the obtained monoketone precursors cleanly yield the corresponding acenes through quantitative cheletropic thermal decarbonylation in the solid state, at moderate temperatures of 155 to 205 °C. This approach allows the preparation of heptacene, benz[a]hexacene, cis- and trans-dibenzoheptacene and offers a valuable new method for the synthesis of even larger acenes.

Acenes are polyaromatic hydrocarbons consisting of linearly fused benzene units and can be considered as the narrowest zig-zag graphene nanoribbons. This topology, with only one Clar aromatic sextet[1] spread over the entire molecule, leads to a decrease of the HOMO-LUMO gap and an increase in the chemical reactivity with increasing number of benzene rings. The nature of electronic structure of long acenes is still actively discussed, in particular the partial contribution of the open-shell singlet state to the electronic ground-state configuration beyond decacene.[2–5] On the other hand, these compounds are predicted to show attractive electronic and magnetic properties.[6] They have been suggested for use as molecular wires in single molecule electronics, for solar-cells applications,[7] for spintronics[6] and plasmonics,[9] as semi-conducting materials[10,11] in organic-field effect transistors[12] and in organic light emitting diodes.[13]

To overcome the inherent fragility of long acenes and to improve their solubility and processability, it is possible to attach electron deficient or bulky substituents[14–20] or to introduce heteroatoms into the acene framework like sulfur or nitrogen atoms.[15,14–17,21,22] However, the electronic properties of such materials cannot be compared with their parent acenes.

Since these later are poorly soluble, prone to (photo)oxidation and dimerize in solution, their synthesis remains “a formidable challenge” to quote R. Dorel and A.M. Echavarren.[16] The only way to study them is to prepare more stable, and if possible soluble, precursors that can be converted in a final step in the solid state through a unimolecular process to the target acenes. This approach has been employed for the synthesis of acenes[23] up to undecacene[24] in low concentration in argon cold matrices, or in PMMA[25] by photochemical bis-decarbonylation using the Strating-Zwanenburg reaction,[26] and to explore their photophysical properties.[16,27,28] More recently, long acenes have been isolated by on-surface synthesis at low-temperature metallic surfaces under ultra-high vacuum, through deoxygenation of epoxides.[29–31] dehydrogenation of partially saturated precursors[32,33] and bis-decarbonylation of α-diketones.[34,35] These strategies allowed the investigation through scanning tunnelling spectroscopy of the electronic properties[36] of polyacenes up to undecacene and to follow the decrease in energy gap as the number of six-membered rings increases.

In contrast, the preparation in bulk of acenes beyond pentacene has been described only recently. Hexacene has been prepared in 2012 by T.J. Chow et al.[37] by cheletropic thermal decarbonylation of the carbonyl-bridged precursor and heptacene by H.F. Bettinger et al. in 2017[38] by thermal cleavage of diheptacene in the solid state, more than 70 years after the first attempted synthesis. Both studies showed that these two long acenes are stable at room temperature, resolving an old controversy and opening new avenues to the preparation of even longer acenes.

We present here a strategy, summarized in the Scheme 1, general enough to prepare a large variety of long acenes beyond pentacene. The starting compound is (1s,4s)-7,7-dimethoxy-2,3,5,6-tetramethylenecyclo[2.2.1]heptane 1.[39] This tetraene can undergo Diels-Alder cycloaddition with arynes, to give, after aromatization, stable, non-planar and not fully aromatized protected acenes, which after cleavage of the ketals yields the CO bridged precursors.

![Scheme 1](image)

Supporting information for this article is given via a link at the end of the document

---

A. Jancarik
CEMES-CNRS
29 Rue J. Marvig, 31055 Toulouse, France
and
Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences, 166 10 Prague 6, Czech Republic
E-mail : Andrej.jancarik@cemes.fr

G. Levet, A. Gourdon
CEMES-CNRS
29 Rue J. Marvig, 31055 Toulouse, France
E-mail : Andre.gourdon@cemes.fr

*Corresponding author.

Supporting information for this article is given via a link at the end of the document.
Quantitative formation of the target acene is then carried out by heating in the solid state at ca 200°C with carbon monoxide as the sole by-product. This has allowed preparation of heptacene, dibenzopentacene isomers, and benzoheptacene as representative examples of this method (Figure 1).

![Figure 1](image)

Figure 1 Seven-membered ring acenes: 2, heptacene; 3, dibenzo[a,l]pentacene; 4, dibenzo[a,n]pentacene; 5, benzo[a]hexacene.

1s,4s)-7,7-dimethoxy-2,3,5,6-tetramethylenebicyclo[2.2.1]heptane 1. Compound 1 can be obtained from dimethyl fulvene in seven steps as described in ref[39] and we have recently reinvestigated and simplified this synthesis at larger scale, ca tens of grams[41] to obtain 1 without any need of purification by chromatography.

Heptacene 2. Heptacene has recently been prepared in bulk, by thermal cleavage of diheptacene by H.F. Bettinger et al.[38] more than seventy years after the first attempted synthesis by Clar.[42] Before this breakthrough, heptacene in stabilizing matrix had been observed by D.C. Neckers et al.[25] through photogeneration from a bridged α-diketone using a polymer matrix, and under UHV by on-surface dehydrogenation of the corresponding hydroacene,[32] or using surface-assisted decarboxylation of an α-diketone precursor on a Ag(111).[34] Using our strategy, we have also obtained heptacene in bulk, which remains so far the longest acene made as pure solid. Diels-Alder addition of 1 with two 2,3-naphthyn molecules, prepared in situ by reaction of CsF with 3-(trimethylsilyl)naphthalene-2-yl trifluoromethanesulfonate in acetonitrile (route A) or n-butyllithium with 2,3-dibromonaphthalene in toluene (route B), followed by oxidation with DDQ in toluene, gives 6 in ca 60% yields. The moderately soluble colourless carbonyl adduct 7 is then obtained by cleavage of the ketal by trimethylsilyl iodide in DCM in 99% yield.

![Scheme 2](image)

Scheme 2. Synthesis of heptacene 2: (a) A, n-BuLi, toluene. (b) DDQ, toluene 63%. or (a) B, CsF/acetonitrile. (b) DDQ, toluene 60%. (c) TMSI, DCM, 99%. (d) neat, 220°C, quant.

![Figure 2](image)

Figure 2. Formation of heptacene 2 by thermal decarboxylation of 7: (a) Thermal Gravimetric Analysis of 7 showing the decarboxylation at 205 °C to yield 2. (b) FTIR spectra (KBr pellets) of 2 and 7 showing the disappearance of the CO peak at 1782 cm⁻¹. (c) Carbon CPMAS spectra of 7 (bottom, blue), 2 (middle, red) just after decarboxylation, and 2 after six weeks at room temperature under argon (top, green).
The conversion of 7 to heptacene (Figure 2) was followed by thermal gravimetric analysis (Figure 2a). A weight loss of 7.9% (calcd. 6.9%) accompanied by a color change from white to dark blue, occurred at 205 °C, corresponding to the formation of heptacene by chelotropic CO extrusion. Under these conditions, heptacene is thermally stable up to 420 °C. The CO extrusion can also be followed by FTIR with the disappearance of the carbonyl peak of 7 observed at 1782 cm⁻¹ (Figure 2b). This transformation has been also shown by solid state cross-polarization magic angle spinning (CP-MAS) NMR spectroscopy (Figure 2c). The spectrum of the precursor 7 showed three signals, one at 56.3 ppm (bridgehead sp3 carbons), a broad peak at 119-137 ppm (aromatic carbons) and the carbonyl carbon at 195.1 ppm. After heating for 15 minutes at 220 °C in a glove box, the peaks corresponding to bridgehead and carbonyl carbons disappear leaving only a narrower doublet at 125.6 and 129.0 ppm (aromatic carbons). Keeping 2 in a glove-box for six weeks did not lead to any significant change in the spectrum. This is in contrast with results reported for thermally prepared heptacene which progressively dimerizes to diheptacene. It is proposed that the packing of our precursor 7 does not favor the dimerization of heptacene 2 in the solid state.

Dibenzopentacenes 3 and 4. Dibenzopentacenes (DBPen) have been extensively studied both theoretically and experimentally (in the case of trans-DBPen) for their potential uses in organic electronics. This interest has been renewed by the discovery of superconductivity of trans-DBPen doped with alkali metals with a high critical temperature of 33.1 K. However these results have never been reproduced and are still controversial. One explanation could be that the known synthesis of 3 (4 has not yet been described) leads to raw products, requiring multiple train-sublimation purifications so that the exact superconductive phase from raw trans-DBPen remains unknown.

Following the route described in Scheme 2 with 1,2-naphthylene in place of 2,3-naphthylene, we have obtained dibenzo[a,l]pentacene 3 (trans-DBPen) and dibenzo[a,l]pentacene 4 (cis-DBPen) as shown in Scheme 3. Diels-Alder addition of 1 with 1,2-naphthylene, prepared in situ by reaction of 1-(trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate with CsF in acetonitrile, followed by aromatization using DDQ in refluxing toluene gave a 1:1 mixture of isomers 8a and 8b in 77% yield. These two regioisomers can be separated by chiral HPLC giving 8b and a mixture of the trans-DBPen 8a diastereoisomers which has not been resolved (see Sup. Mat.). The proton NMR of 8a shows a sp3 singlet at 4.91 ppm, integrating for two hydrogens, whereas that of 8b shows two singlets at 4.85 and 4.96 ppm each integrating for one hydrogen, further indicating their different aromatic conjugation.

Cleavage of the ketal 8a/8b by trimethylsilyl iodide in dichloromethane yielded the stable and soluble DBPen precursors 9a/9b respectively in nearly quantitative yields.

The TGA profiles of these precursors (Sup. Mat) exhibit CO expulsion at 185 °C for 9a and 155 °C for 9b, with corresponding weight losses of 6.4% and 7.6% (calcd. 6.9%) together with a color change from white to deep red. Differential thermal analysis (DTA) showed a phase transition at 465 °C for 3 and at 350 °C for 4. Vaporization started for both compounds at ca 320-350 °C. As in the case of heptacene, the CO extrusion has been followed by carbon CP-MAS NMR and FTIR in the solid state (see Sup. Mat.). Similarly, the spectra of cis-DBPen 9b showed a C sp3 peak at 55.0 ppm, a multiplet between 110 and 140 ppm (C arom.) and a very weak singlet at 191.1 ppm for the CO carbon. For the trans-DBPen isomer 9a, peaks are seen at 55.7 ppm (C sp3) and 110-140 ppm (C arom.) with the peak for the carbonyl not apparent. Heating the solid samples for 15 min in a glove-box at 170 °C for 9a or 200 °C for 9b gave the corresponding acenes 3 and 4. After CO extrusion, the solid state 13C NMR spectra shows only one peak at 125.5 ppm for 3 and 125.9 ppm for 4 attributed to the aromatic carbon atoms. Comparison of the infra-red spectra of the carbonyl precursors 9a and 9b, before and after decarbonylation shows the loss of carbonyl bands at 1785 cm⁻¹ (9a) and 1787 cm⁻¹ (9b) respectively. As DBPen isomers are less prone to dimerization in solution at room temperature, it is possible to carry out this decarbonylation in a high boiling point solvent like 1,1,2,2-tetrachloroethane under moderate pressure. The UV-Vis spectra of DBPen isomers were obtained by dissolving the precursors 9a/9b and heating at 190 °C for 15 min to obtain the compounds.

![Scheme 3. Preparation of trans 3 and cis-dibenzopentacene 4: (a) CsF, acetonitrile, 77%. (b) after separation of isomers: TMSi, DCM, 99%. (c) neat. 200°C, quant.](Image 341x455 to 528x758)
The spectra were measured at room temperature (Figure 3 and Sup Mat).

The p band regions of 3 and 4 shows a pattern very similar to that of pentacene with four bands at 427, 459, 490 and 527 nm for 3 (426, 455, 489, 526 nm for 4), with an hypsochromic shift of 45-65 nm with respect to pentacene in solution due to the addition of a second aromatic sextet.\(^{[47]}\)

**Benz[a]hexacene 5.** In order to extend the potential of this approach, we have focused on the preparation of asymmetric acenes through reaction of only one diene of the tetraene 1 (Scheme 4).

Diels-Alder addition of 1 with 1.3 equivalents of 2,3-naphthylene, prepared in situ by reaction of CsF with 3-(trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate, AcOEt, acetone-d$_3$, 46%. (b) 1-(trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate, CsF, acetone-d$_3$; DDQ, toluene, 80%. (c) TMSI, DCM, 96% (d) neat, 200°C, quant.

Absorption spectra of thin films. Solid state absorption spectra of thin films of compounds 9a, 9b and 12 were obtained by spin-casting on a quartz plate (transparency $>93\%$ at a wavelength 380 nm) from a solution of these compounds in DCM and drying in air. They were then converted to the corresponding acenes 2-4 by heating at 200°C under an argon atmosphere for one minute and the spectra recorded under argon. Due to the low solubility of 7 it was not possible to spincast thin layers of this compound. However, optical absorption spectra of thin films of heptacene 2 were obtained recently by H.F. Bettinger by sublimation on sapphire at low temperature (16 K).\(^{[39]}\) It was shown that annealing the films to higher temperatures resulted in a decrease of the poorly resolved p bands. Figure 4 shows the optical absorption spectra of benz[a]hexacene 5 and its carbonylated precursor 12.

The spectrum of 12 shows three main bands at 401, 379 and 351 nm attributed to the anthracene parts present in the structure. These features disappear after decarbonylation, with the spectrum of 5 comprising four bands at 609, 665, 717, 770 nm with a pattern similar to those of DBPen 3 and 4 with a bathochromic shift of ca 190 nm (see Sup. Mat). The thin layer spectra of the DBPen isomers 3 and 4 also show a four bands pattern similar to those observed in solution with a bathochromic shift of 55-60 nm as expected for thin films versus solution spectra.

To sum up, we describe here a general method allowing for the preparation of pure oligoacenes larger than pentacene,
Conflicts of interest

The authors declare no conflict of interest.
Symmetrical and non-symmetrical chemically fragile and poorly soluble acenes beyond pentacene can be obtained from a protected bicyclic tetraene. The method involves Diels-Alder addition with arynes, oxidation and cleavage of the ketal to give a soluble and stable polyaromatic ketone. Solid state cheletropic decarbonylation gives the targeted oligoacene in quantitative yield.
S1. Experimental procedures

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 F254). 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 (CD2Cl2 at δH = 5.33 ppm, δC = 53.84 ppm; CDCl3 at δH = 7.26 ppm, δC = 77.16 ppm; tetrachloroethane-d2 at δH = 6.00 ppm, δC = 73.78 ppm). Chemical shifts are reported in parts per million (ppm) on the δ 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 ZrO2 rotors. 13C-CP/MAS were recorded with a recycle delay of 1.5 s and a contact time of 3 ms. All chemical shifts for 13C 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.

Absorption spectra of thin films and in solution
Solid state absorption spectra of compounds 9a/9b, 12 were obtained by spin-coating on a quartz plate (1 mm thickness, transparency > 93 % at a wavelength 380 nm). A solution with maximum concentration (1 mg/mL for 9a, 0.25 mg/mL for 9b, 0.6 mg/mL for 12) of each compound in dichloromethane was spincasted at 500 rpm for 30 s. The glass plates were installed diagonally inside a 1x1 cm quartz cuvette. All these compounds were converted to the corresponding acenes 3-5 by heating at 200 °C for 1 min under an argon atmosphere and recorded under argon by keeping the glass plate inside a 1x1 cm quartz cuvette. The UV – Vis spectra for 7 and 2 were not measured due to high insolubility. The absorption spectra in solution were made by dissolving compound 9a (1.63 mg) and 9b (1.14 mg) in 1,1,2,2-tetrachloroethane (200 mL) and measured in 1x1 cm quartz cuvette. These solutions of 9a and 9b were precisely degassed in an Young tube and then heated at 190 °C for 15 min to produce 3 and 4. The formed solutions of 3 and 4 were cooled to room temperature and in a glovebox transferred to a 1x1 cm quartz cuvettes.

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.
S2 Peak attribution in NMR spectra

19,19-dimethoxy-7,16-dihydro-7,16-methanoheptacene (6)

\[
\text{\includegraphics[width=0.5\textwidth]{s2_diagram1.png}}
\]

\(^1\)H NMR (300 MHz, CDCl\(_3\)): 3.30 (6H, s, H10), 4.47 (2H, s, H1), 7.39 - 7.42 (4H, m, H8), 7.87 (4H, s, H3), 7.91 - 7.94 (4H, m, H7), 8.27 (4H, s, H5).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)):
51.44 (C10), 54.74 (C1), 120.28 (C3), 123.39 (C9), 125.17 (C8), 126.07 (C5), 128.08 (C7), 131.37 (C4), 131.67 (C6), 142.19 (C2).

7,16-dihydro-7,16-methanoheptacen-19-one (7)

\[
\text{\includegraphics[width=0.5\textwidth]{s2_diagram2.png}}
\]

\(^1\)H NMR (500 MHz, tetrachloroethane-d\(_2\), 80°C): 5.01 (2H, s), 7.49 (4H, dd, \(J = 6.5, 3.1\)), 8.01 (4H, dd, \(J = 6.5, 3.3\)), 8.10 (4H, s), 8.42 (4H, s).

\(^{13}\)C NMR (126 MHz, tetrachloroethane-d\(_2\)): Not recorded due to the low solubility.

19,19-dimethoxy-8,17-dihydro-8,17-methanodibenzo[a,l]pentacene (8a)

\[
\text{\includegraphics[width=0.5\textwidth]{s2_diagram3.png}}
\]

\(^1\)H NMR (500 MHz, CD\(_2\)Cl\(_2\)): 3.28 (6H, s, H17), 4.91 (2H, s, H1), 7.56 (2H, ddd, \(J = 8.0, 6.9, 1.2, H14\)), 7.64 (2H, ddd, \(J = 8.4, 6.9, 1.4, H13\)), 7.67 - 7.72 (4H, Abq, \(J_{AB} = 9.4, H10, H11\)), 7.86 (2H, dd, \(J = 7.8, 1.4, H15\)), 7.86 (2H, s, H7), 8.66 (2H, d, \(J = 8.0, H12\)), 8.67 (2H, s, H4).

\(^{13}\)C NMR (126 MHz, CD\(_2\)Cl\(_2\)):
51.67 (C17), 56.03 (C1), 116.53 (C4), 122.21 (C7), 123.09 (C12), 126.64 (C14), 126.87 (C11), 126.88 (C16), 126.89 (C13), 127.44 (C10), 129.00 (C15), 129.24 (C5), 130.86 (C8), 131.23 (C6), 132.59 (C9), 145.10 (C3), 145.24 (C2).

19,19-dimethoxy-8,17-dihydro-8,17-methanodibenzo[a,n]pentacene (8b)

\[
\text{\includegraphics[width=0.5\textwidth]{s2_diagram4.png}}
\]
$^1$H NMR (500 MHz, CD$_2$Cl$_2$): 3.27 (6H, s, H18), 4.85 (1H, d, J = 1.5, H1), 4.96 (1H, d, J = 1.5, H4), 7.55 (2H, ddd, J = 8.1, 7.0, 1.2, H14), 7.64 (2H, ddd, J = 8.4, 6.9, 1.4, H15), 7.69 (2H, d, J = 8.95, H9), 7.71 (2H, d, J = 8.95, H10) 7.84 (2H, s, H5), 7.86 (2H, ddd, J = 7.9, 1.4, H13), 8.67 (2H, dd, J = 8.5, 1.1, H16), 8.68 (2H, s, H8).

$^{13}$C NMR (126 MHz, CD$_2$Cl$_2$): 51.67 (C18), 55.59 (C1), 56.47 (C4), 116.55 (C8), 122.19 (C5), 123.08 (C16), 126.64 (C14), 126.86 (C10), 126.87 (C17), 126.89 (C15), 127.43 (C9), 128.99 (C13), 130.85 (C12), 131.22 (C6), 132.59 (C11), 145.01 (C2), 145.33 (C3).

8,17-dihydro-8,17-methanodibenzo[a,l]pentacen-19-one (9a)

8,17-dihydro-8,17-methanodibenzo[a,n]pentacen-19-one (9b)

(1S)-13,13-dimethoxy-2,3-dimethylene-1,2,3,4,5,12-hexahydro-1,4-methanotetracene (10)

(8R)-19,19-dimethoxy-8,17-dihydro-8,17-methanobenz[a]hexacene (11)
H23.24, 7.85 (1H, s, H19), 7.86 (1H, dd, J = 8.7, 0.9, H27), 7.87 (1H, s, H11), 7.89 (1H, s, H14), 7.94 – 7.97 (2H, m, H3, H6), 8.29 (2H, s, H7, H10), 8.67 (1H, d, J = 8.0, H30), 8.67 (1H, s, H22).

$^{13}$C NMR (126 MHz, CD$_2$Cl$_2$): 50.94 (C34), 51.13 (C33), 54.71 (C15), 55.15 (C18), 115.91 (C22), 119.99 (C11), 120.01 (C14), 121.56 (C19), 122.49 (C30), 124.73 (C31), 125.04 (C1, C2), 125.73 (C7, C10), 126.08 (C26), 126.28 (C29), 126.30 (C24), 126.83 (C23), 127.81 (C3, C6), 128.40 (C27), 128.84 (C21), 130.25 (C26), 130.80 (C20), 131.01 (C12, C13), 131.51 (C4, C5), 131.96 (C25), 142.69 (C12), 142.77 (C13), 143.84 (C16), 144.06 (C8).

(8R)-8,17-dihydro-8,17-methanobenz[a]hexacen-19-one (12)

$^1$H NMR (500 MHz, tetrachloroethane-d$_2$): 5.08 (1H, s), 5.14 (1H, s), 7.48 (2H, dd, J = 6.7, 3.2), 7.62 (1H, ddd, J = 7.9, 6.7, 0.9), 7.69 (1H, ddd, J = 8.2, 6.9, 1.0), 7.74 (1H, d, J = 9.3), 7.77 (1H, d, J = 9.3), 7.89 (1H, d, J = 7.8), 8.00 (2H, dd, J = 6.6, 3.3), 8.04 (1H, s), 8.10 (1H, s), 8.12 (1H, s), 8.40 (2H, s), 8.71 (1H, d, J = 8.5), 8.85 (1H, s).

$^{13}$C NMR (126 MHz, tetrachloroethane-d$_2$): 56.86, 57.29, 116.03, 120.54, 120.55, 121.71, 122.56, 125.49 (2C), 126.21 (2C), 126.66, 126.70 (2C), 127.18, 127.91 (2C), 128.55 (2C), 129.40, 129.86, 130.74 (2C), 131.16, 131.49 (2C), 131.81, 136.40, 136.49, 137.79, 137.97, 193.08 (C=O).
AJ154_500MHz.58.fid
AJ154 cdcl3 13C{1H}
AJ176_500MHz.80.fid
AJ176 cd2cl2 13C{1H}

11
AJ178 TCE-D2 13C{1H} Jmod

12
Overnight Keto.4.fid
Sample: AG164
Probe: 3.2 Vr=12kHz
13C CP MAS

C arom

CO

C sp3

7
Sample: AG164-200C
Probe: 3.2 Vr=15kHz
13C CP MAS
Sample: AJ173
Probe: 2.5 Vr=14kHz
13C CP MAS

C arom

C sp3

CO?

9a
Sample: AJ173 - heated
Probe: 2.5 Vr=14kHz
13C CP MAS

![NMR Spectrum](image)

[Chemical Structure Image]
Sample: AJ172
Probe: 2.5 Vr=14kHz
13C CP MAS

C arom

C sp3

CO

9b
Sample: AJ172 - heated
Probe: 2.5 Vr=14kHz
13C CP MAS
Sample: AJ174
Probe: 2.5 Vr=14kHz
13C CP MAS

CO
C sp3
C arom

12
Sample: AJ174 - heated
Probe: 2.5 Vr=14kHz
13C CP MAS

C arom

5
Infrared spectra of acenes and precursors (KBr pellets)

Infrared spectra of heptacene 2 and its precursor 7.

Infrared spectra of trans-DBPen 3 and its precursor 9a.
Infrared spectra of cis-DBPen 4 and its precursor 9b.

Infrared spectra of benzohexacene 5 and its precursor 12.
Thermal Gravimetric Analysis of compounds 9b/3, 9a/4, and 12/5 showing the decarbonylation temperatures.

- 185 °C Compound 9a-> compound 4
- 175 °C Compound 12 -> compound 5
- 155 °C Compound 9b-> compound 3