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Efficient synthesis and conformational investigations of *cis*-pentacenediols

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Abstract

Diisobutylaluminum hydride is utilized to reduce pentacene-6,13-diones to the corresponding diols, useful precursors to functionalized pentacenes. This pathway is mild and efficient, and produces the *cis*-diols as major products. Further, we found the *cis*-diols adopt *endo* conformation, which cannot flip to the *exo* conformation under ambient conditions. Due to the *cis* and *endo* orientation, the *cis*-diols can be potential bidentates in catalysis, molecular propellers, and optoelectronic devices.

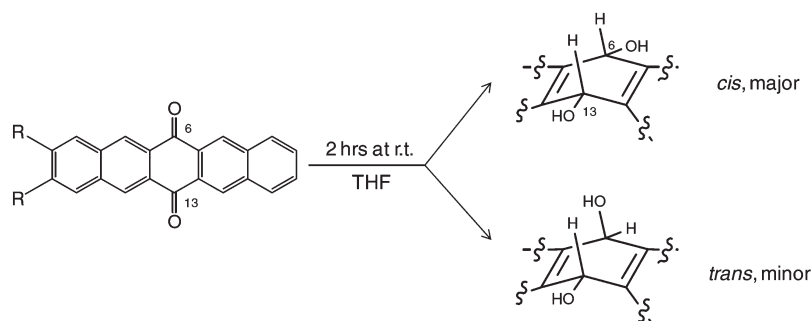
Keywords: Pentacene, Pentacenediol, Reduction of pentacenedione, Diisobutylaluminum hydride, Low-temperature NMR

Pentacene, the work horse in the field of organic field-effect transistors, is prepared from pentacene-6,13-dione via two pathways, either a one-step reaction with Al–Hg amalgam,^{1,2} or by a stepwise conversion involving metal hydride reduction to 6,13-dihydropentacene-6,13-diol, followed by aromatization with tin chloride.^{3,4} Because of the health and environmental risks involved in the use of mercury, the former methodology has almost been phased out in industry, and is only occasionally executed in research labs. Compared with the former, the latter proceeds in a reproducible and clean fashion, and hence is dominant in the literatures. Metal hydrides, such as, KBH_4 , NaBH_4 , and LiAlH_4 , are able to deliver good results with pentacene-6,13-dione;^{3–5} however, they fail to reduce 2,3-dibromopentacene-6,13-dione, a useful intermediate in the synthesis of functionalized pentacenes.^{2,6} Herein we report diisobutylaluminum hydride (DIBAH) as a useful reagent for reduction of pentacenediones. Easily handled DIBAH is mild, and very useful in reducing carbonyl functionality,^{7–10} but its application with pentacene-6,13-dione has not been investigated so far. As discussed later, this methodology delivers the *cis*-diol as the major product, and therefore the *cis*-diol can be separated as a pure isomer (Scheme 1). In view of the two hydroxyls' specific orientation and the two flanking naphthyl moieties, we envision the *cis*-diols as useful bidentates to coordinate with suitable centers, and thus to have potential applications in catalysis, molecular propellers, and/or optoelectronic devices.

Our efforts to reduce 2,3-dibromopentacene-6,13-dione with metal hydride revealed that neither NaBH_4 nor LiAlH_4 was effective, even at elevated temperatures, but DIBAH readily realized this.^{11,12} We attribute this to the excellent solubil-

ity of DIBAH. In contrast, it has been reported that a successful reduction of the unsaturated pentacene-6,13-dione needs a stepwise addition of KBH_4 over a period of 10-days.³ Very likely, the metal hydrides suffered because of their poor solubility in the system.

In order to better understand the reactivity of DIBAH within this system, we further investigated the reduction of the unsubstituted pentacene-6,13-dione as a model substrate. Compared with literatures,^[3–5] our procedure with DIBAH offers conveniences in handling and stoichiometric addition. Furthermore, it is mild and efficient—in less than 2 h, and at rt, the reaction is complete, producing an approximately 2:1 mixture of the *cis* and *trans* isomers of 6,13-dihydropentacene-6,13-diol with good yield (the major product was assigned based on a previous report).³ When NaBH_4 or LiAlH_4 was applied, the *trans* isomer was reported as the major product.^{4,5} A density functional theory (DFT) analysis of the energy states during the reduction, summarized in Figure 1, provides a rationale for the observed selectivity.^{13–16} The reduction of the first carbonyl group proceeds via a hydride-ion transfer from the reducing agent DIBAH to the diketone A. First the intermediate B is formed from an acid-base reaction between the unshared electron pair on oxygen of A with the aluminum atom of DIBAH, and then the intermediate D forms after transfer of a hydride-ion from DIBAH to the carbon atom of the carbonyl group. Our theoretical calculation suggests that the first reaction from A to B is a downhill one with no transition state, whereas in the second reaction from B to D, a transition state C exists. Similarly the second carbonyl group is reduced following the same pathway. The product selectivity occurs at the second transition state F, but its ori-



Scheme 1. Conversion of pentacene-6,13-dione to 6,13-dihydropentacene-6,13-diol with diisobutylaluminum hydride. R = H or Br.

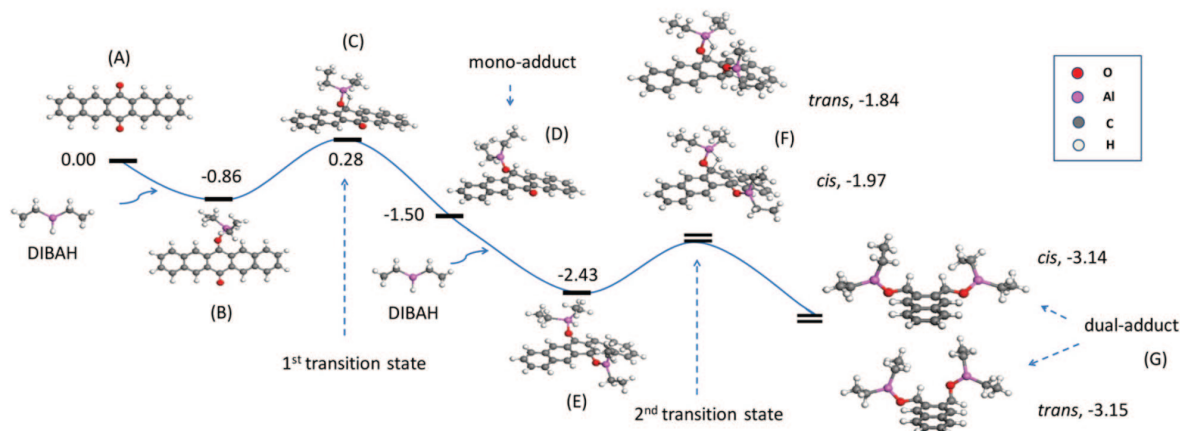


Figure 1. Calculated energy states (energy is in eV) from pentacene-6,13-dione to the dual-adducts before hydrolysis. It suggests that in the second transition state, the activation energy for the *cis* isomer is 0.13 eV lower than that for the *trans* one. Such a difference results in the *cis* isomer being a dominant product. (A) the substrate; (B) the complex between the substrate and a single DIBAH; (C) the 1st transition state; (D) the mono-adduct; (E) the complex between the mono-adduct and another DIBAH; (F) the 2nd transition states for the *trans* and *cis* isomers, respectively; and (G) the two dual-adducts before hydrolysis.

gin can date back to the mono-adduct D, which adopts a puckered conformation along its 6 and 13 carbons with a dihedral angle being 160°. As a result of this conformation, the second hydride is delivered from the *exo* face to furnish the *endo* alcohol. In fact, our calculation suggests an energy difference of 0.13 eV between the second transition states. Hence the *cis* isomer is a dominant product.

Our careful assignment of the ¹H NMR spectra of 6,13-dihydropentacene-6,13-diol leads to another finding that differs from a previous report.⁴ The *cis*-diol is expected to have five peaks in the ¹H NMR spectrum: three signals for aromatic hydrogens, one for the carbinol CH, and another one for the hydroxyl groups. And the expected relative integration ratio should be 4:4:4:2:2. In various deuterated solvents such as THF-*d*₈, CDCl₃, acetone-*d*₆, and DMSO-*d*₆, we found that the three aromatic hydrogen peaks are in good agreement with the literature, but a difference arose in the assignments for the carbinol CH and the OH groups. For example in acetone-*d*₆, these two very peaks for *cis* isomer are at 5.91 and 5.67 ppm, respectively. As shown in Figure 2a, they are coupled with ³J_H = ~7.0 Hz. A ¹H-¹³C HSQC experiment demonstrated that the hydrogen at 5.91 ppm is directly bonded to a carbon, whereas the peak at 5.67 ppm is missing from the HSQC due to its lack of attachment to carbon. Upon deuterium exchange in acetone-*d*₆, the peak at 5.67 ppm disappeared completely, and at the same time, the peak at 5.91 ppm collapsed to a singlet, indicating that the hydrogen at 5.67 ppm is active and labile to deuterium exchange, and is therefore assigned as the hydroxylic hydrogen. The 2D NMR plus the deuterium exchange

experiment unambiguously led us to assign the peak at 5.91 ppm to the 6,13-CH hydrogen, and the peak at 5.67 ppm to the hydroxylic hydrogen. A previous report for *cis*-pentacenediol has described the H6 and H13 as displaying discrete peaks in ¹H NMR, separated by at least 0.1 ppm.⁴

As shown in Figure 1, the *cis* isomer is predicted to adopt the *endo* conformation. The disparity between our observations and that reported led us to investigate whether the pentacenediol could exist as both *endo*- and *exo*-conformers and how easily these could interconvert. To answer these questions, we performed a series of NMR experiments on the *cis* isomer at varying temperatures at 600 MHz. In ¹H NMR, all peaks kept their chemical shift with varying temperatures, except one, the hydroxylic hydrogen, which migrated dramatically from 5.67 ppm at 298 K to 6.44 ppm at 205 K (Figure 3). However, no change was observed in the ¹³C spectra over the same temperature range, suggesting the ¹H signal change for the OH is not associated with major conformational changes in the dihydropentacene skeleton. We suspect the change is probably due to the temperature-dependent geometry of hydrogen-bonding.¹⁷ As we did not observe the CH peak resolving into two peaks at a low temperature of 205 K, it could be either that at 205 K, the isomeric flip is too fast for the NMR window to detect or that only *endocis* isomer exists and no flipping occurs at all. Our verdict favors the latter one. As shown in Scheme 1, the *endocis* isomer can be viewed as a boat conformation of cyclohexane with 4 sp² carbons on sides. Consequently, flipping between *exo* and *endo* conformations, if any, probably involves extreme energy. Collectively, our results suggest that the

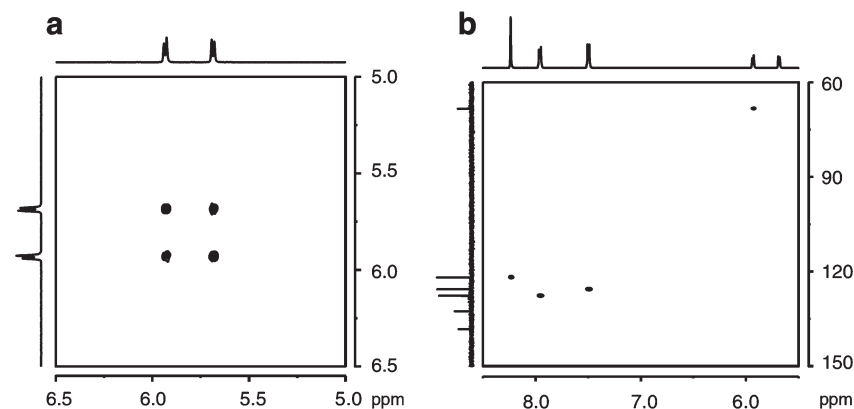


Figure 2. 2D NMR spectra of *cis*-6,13-dihydropentacene-6,13-diol in acetone-*d*₆. (a) ¹H-¹H COSY in the region of 5.0–6.5 ppm, indicating that the peaks at 5.67 and 5.91 ppm couple to each other with ³J_H = ~7.0 Hz. (b) ¹H-¹³C HSQC indicates that the proton at 5.91 ppm is directly bonded to a carbon, whereas the one at 5.67 ppm is not. Plus the fact that the proton at 5.67 ppm is labile to deuterium exchange, the peak at 5.67 ppm is assigned to the hydroxylic proton. For clarity, ¹H NMR at x-axis is shown from 5.5 to 8.5 ppm and ¹³C NMR at y-axis, from 60 to 150 ppm.

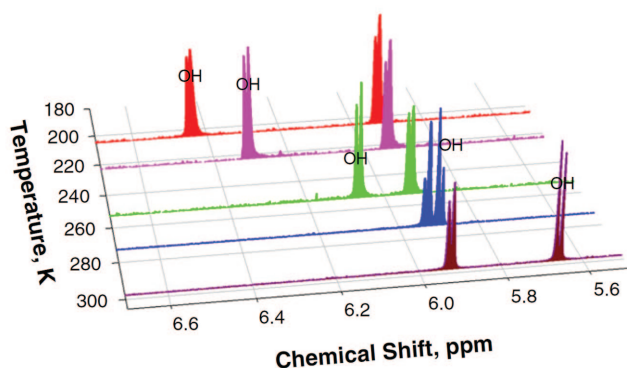


Figure 3. NMR spectra of *cis*-6,13-dihydropentacene-6,13-diol in acetone-*d*₆ between 205 and 293 K (for clarity, only 5.5–6.7 ppm is displayed). In contrast to the immobile peak at 5.91 ppm, the hydroxylic hydrogen peak migrated dramatically from 5.67 ppm at 298 K to 6.44 ppm at 205 K. The symbol OH highlights the peaks of hydroxylic hydrogen, and the normal direction stands for the normalized intensity.

DIBAH reduction of pentacenediones selectively furnishes the *cis*-6,13-diol as a single major conformer displaying only one carbinol CH peak in ¹H NMR.

In summary, DIBAH is effective at converting pentacene-6,13-diones into 6,13-dihydropentacene-6,13-diols. This transformation proceeds with good selectivity for production of the *cis* isomer, which can be isolated in pure form. Considering the specific orientation of hydroxyl functionality and the two rigid conjugated flanks, we foresee that the *cis*-diol isomer will possibly find applications in catalysis, molecular propellers, and optoelectronic devices. This pathway is likely to be applicable as a means of reducing other functionalized pentacenediones, and we are now actively pursuing in that direction.

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- Synthesis of 6,13-dihydropentacene-6,13-diol*: To a suspension of pentacene-6,13-dione (308.3 mg, 1 mmol) in anhydrous THF (30 mL) was added dropwise DIBAH in toluene (1.5 M, 2 mL). The reaction mixture was then stirred at rt for 2 h, followed by addition of saturated aqueous Rochelle's salt solution (25 mL). The resulting mixture was stirred at rt for another 2 h. Filtration and copious washing with distilled water and CH₂Cl₂ gave an orange solid (250 mg, 80%). NMR confirmed this orange solid is a mixture of *cis*-6,13-dihydropentacene-6,13-diol and *trans*-6,13-dihydropentacene-6,13-diol (*cis/trans*, 2:1). HRFAB: calcd for C₂₂H₁₆O₂, 312.1151; found 312.1140.
Careful purification of this mixture one time with column chromatography (eluent: Hex/EtOAc, 4:1) resulted in pure *cis*-6,13-dihydropentacene-6,13-diol (75 mg, 24%). Mp, 230 °C (decomp.). ¹H NMR (400 MHz, acetone-*d*₆): 8.22 (4H, s), 7.94 (4H, m), 7.48 (4H, m), 5.91 (2H, d, J = 6.8 Hz), 5.64 (2H, d, J = 7.0 Hz); ¹³C NMR (100 MHz, acetone-*d*₆): 139.2, 133.6, 128.7, 126.6, 122.9, 68.4; ¹H NMR (400 MHz,

THF- d_8): 8.17 (4H, s), 7.87 (4H, m), 7.40 (4H, m), 5.77 (2H, d, $J = 7.5$ Hz), 5.59 (2H, d, $J = 7.8$ Hz); ^{13}C NMR (100 MHz, THF- d_8): 139.4, 133.7, 128.5, 126.2, 122.4, 69.2. ^1H NMR (400 MHz, CDCl_3): 8.08 (4H, s), 7.90 (4H, m), 7.53 (4H, m), 5.90 (2H, d, $J = 7.1$ Hz), 3.30 (2H, d, $J = 7.1$ Hz); HRFAB: calcd for $\text{C}_{22}\text{H}_{16}\text{O}_2$, 312.1151; found 312.1165.

Trans-6,13-dihydropentacene-6,13-diol: NMR spectra were obtained via spectrum subtraction. ^1H NMR (400 MHz, acetone- d_6): 8.10 (4H, s), 7.89 (4H, m), 7.45 (4H, m), 6.15 (2H, m), 5.08 (2H, m); ^{13}C NMR (100 MHz, acetone- d_6): 139.3, 133.8, 128.5, 126.7, 125.2, 70.5; ^1H NMR (400 MHz, CDCl_3): 8.14 (4H, s), 7.91 (4H, m), 7.52 (4H, m), 6.22 (2H, d, $J = 5.8$ Hz), 2.28 (2H, d, $J = 5.8$ Hz).

12. *Synthesis of 2,3-dibromo-6,13-dihydropentacene-6,13-diol*: 2,3-dibromopentacene-6,13-dione (116 mg, 0.25 mmol) was used to prepare the target molecule, following a similar procedure as described in Note 11. Filtration and copious washing with distilled water and CH_2Cl_2 gave an orange solid. The solid was stirred with THF (20 mL) and the resulting suspension was filtered. Addition of CH_2Cl_2 (20 mL) to this THF filtrate resulted in an orange solid (*cis*, 30 mg, 25%). Further chromatographic purification on the residue failed to separate the *trans*-isomer due to its very limited

solubility. ^1H NMR (400 MHz, THF- d_8): 8.31 (2H, s), 8.17 (s, 2H), 8.15 (s, 2H), 7.88 (m, 2H), 7.41 (m, 2H), 5.77–5.72 (m, 4H); ^{13}C NMR (100 MHz, THF- d_8): 141.6, 138.9, 133.8, 133.5, 133.2, 128.6, 126.4, 122.5, 121.9, 121.5, 69.1, HRFAB: calcd for $\text{C}_{22}\text{H}_{14}\text{Br}_2\text{O}_2$, 467.9361; found 467.8355.

13. *Experimental details in theoretical calculation*: The reaction pathway is investigated using the density functional theory (DFT) method. The B3LYP exchange-correlation functional is used. The C, H, Al, and O atoms are treated with the 6-31g (d,p) basis set. All minima and transition states are confirmed via harmonic vibrational frequency calculations. All calculations are performed using the GAUSSIAN 03 software package.
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Supplementary data follows.

Supporting Information for:

Efficient synthesis and conformational investigations of cis-pentacenediols

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Figure S1: ^1H NMR of *cis*-6,13-dihydropentacene-6,13-diol (400 MHz, acetone- d_6). The insert is the NMR after D_2O exchange, where the hydroxylic hydrogen peak is absent.

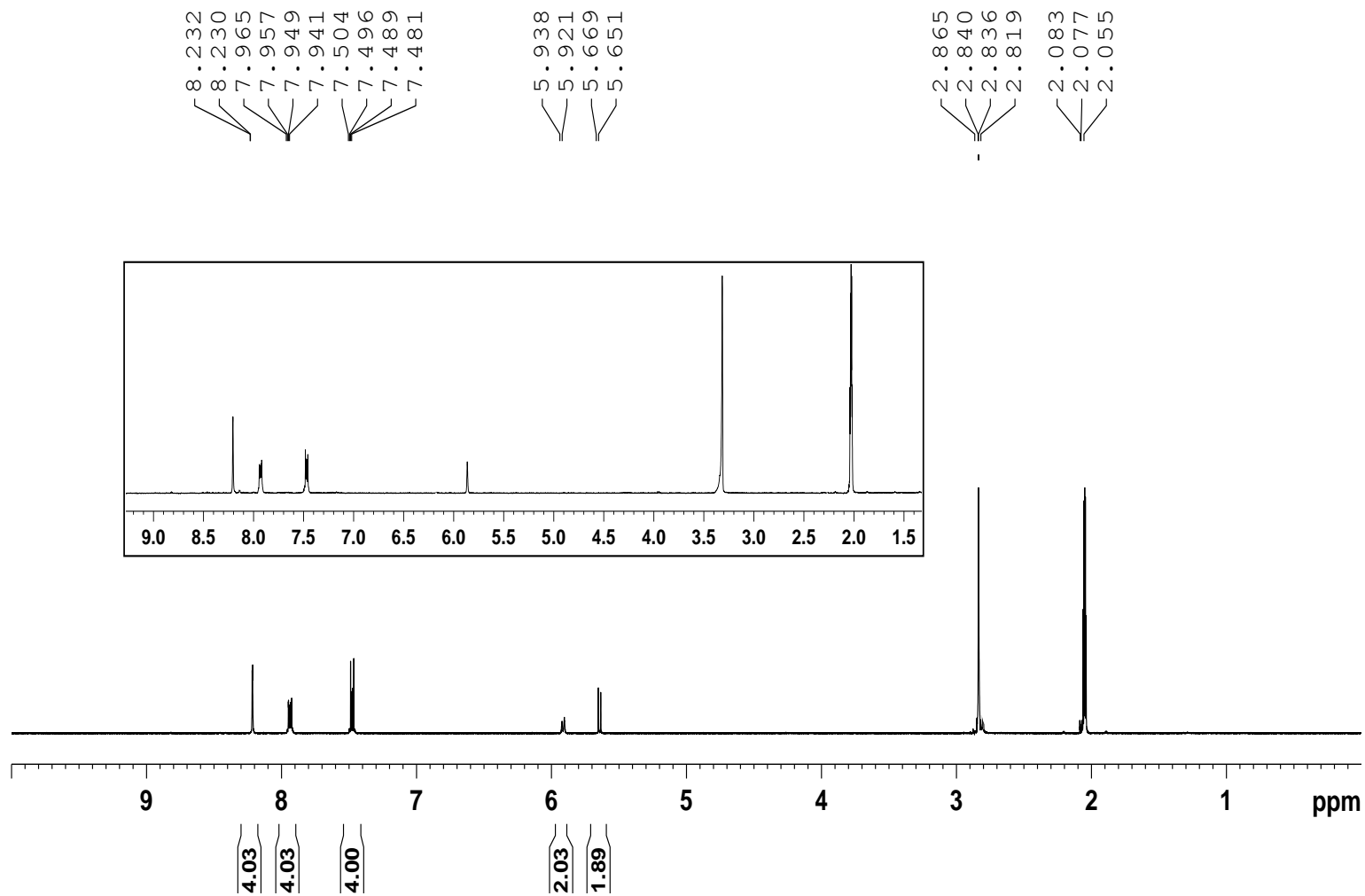


Figure S2: ^{13}C NMR of *cis*-6,13-dihydropentacene-6,13-diol (100 MHz, acetone- d_6)

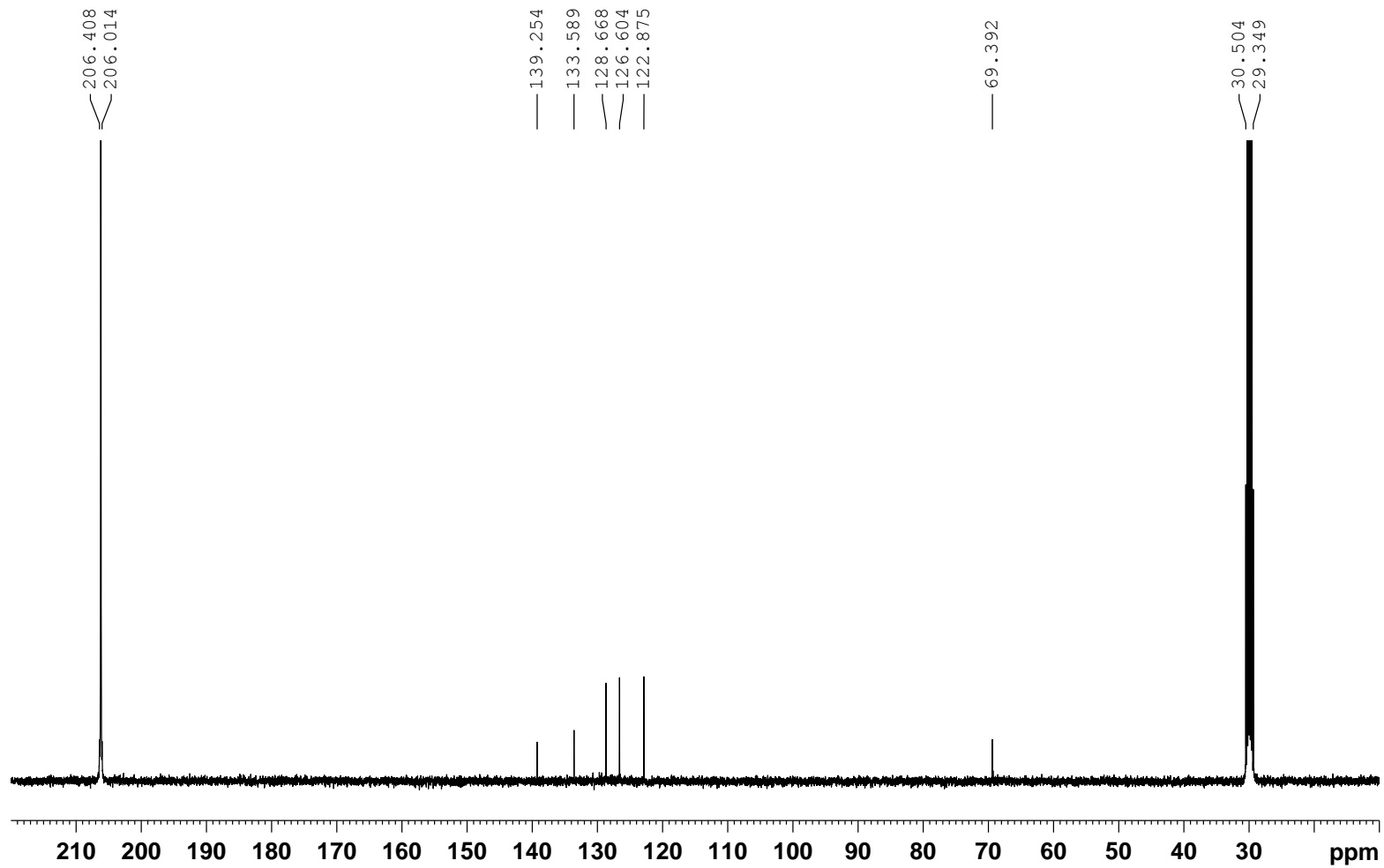


Figure S3: ^1H NMR of mixture of *trans* and *cis*-6,13-dihydropentacene-6,13-diol (400 MHz, acetone- d_6) after D_2O exchange, where OH peak does not show up

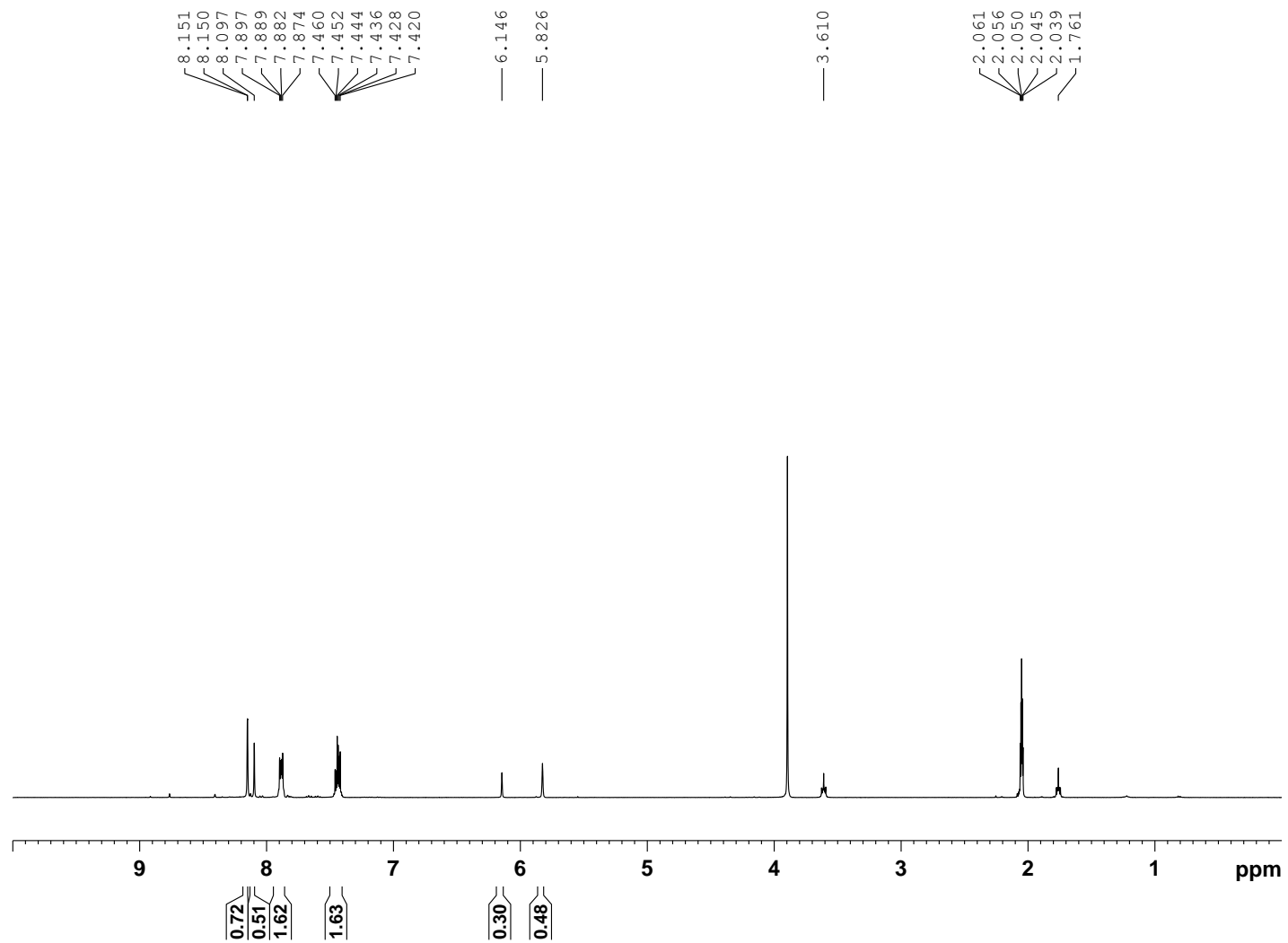


Figure S4: ^{13}C NMR of mixture of *trans* and *cis*-6,13-dihydropentacene-6,13-diol (100 MHz, acetone- d_6)

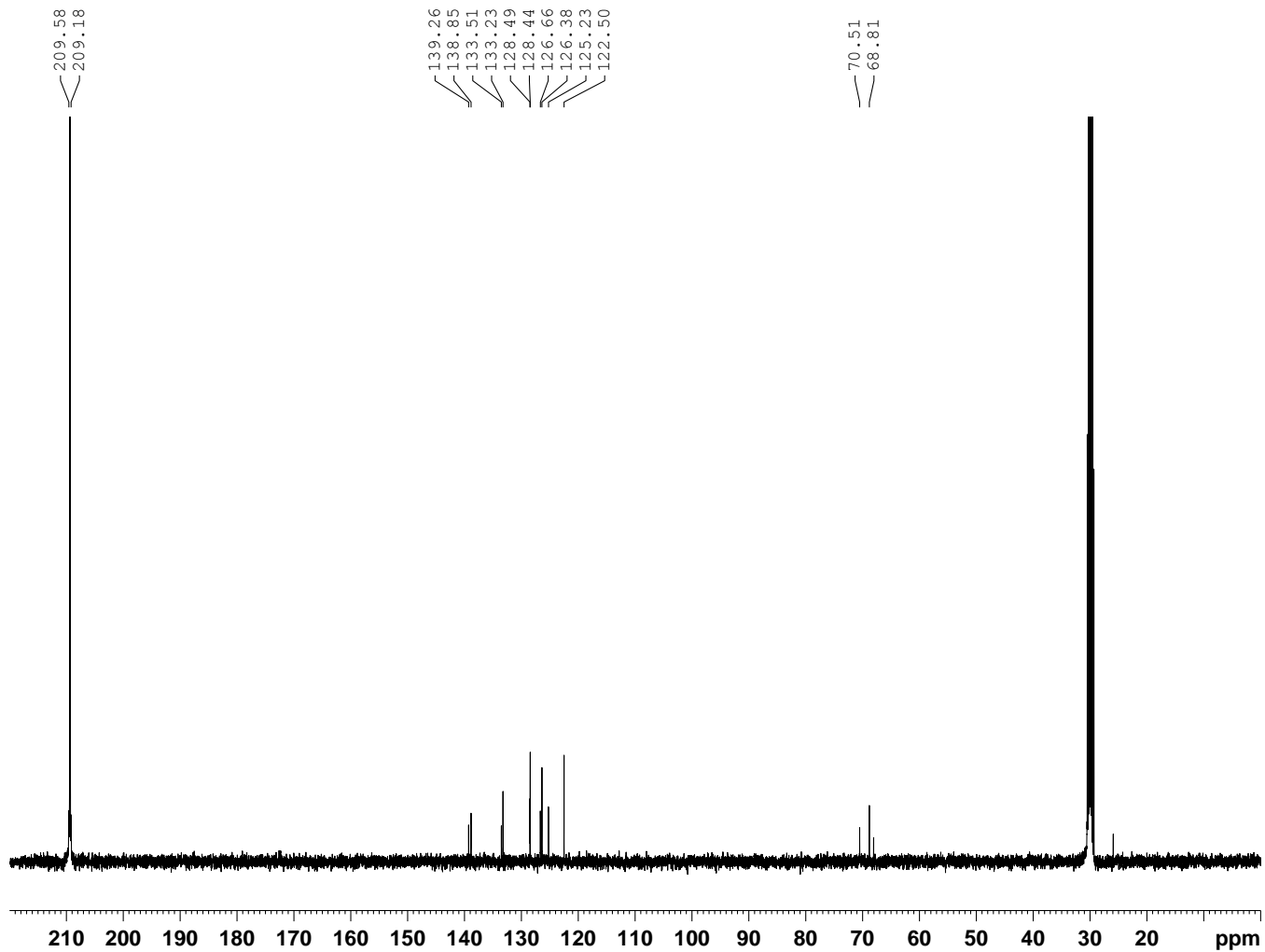


Figure S5: ^1H NMR of cis-2,3-dibromo-6,13-dihydropentacene-6,13-diol (400 MHz, $\text{THF-}d_8$). The insert is the NMR after D_2O exchange, where the hydroxylic hydrogen peak is absent.

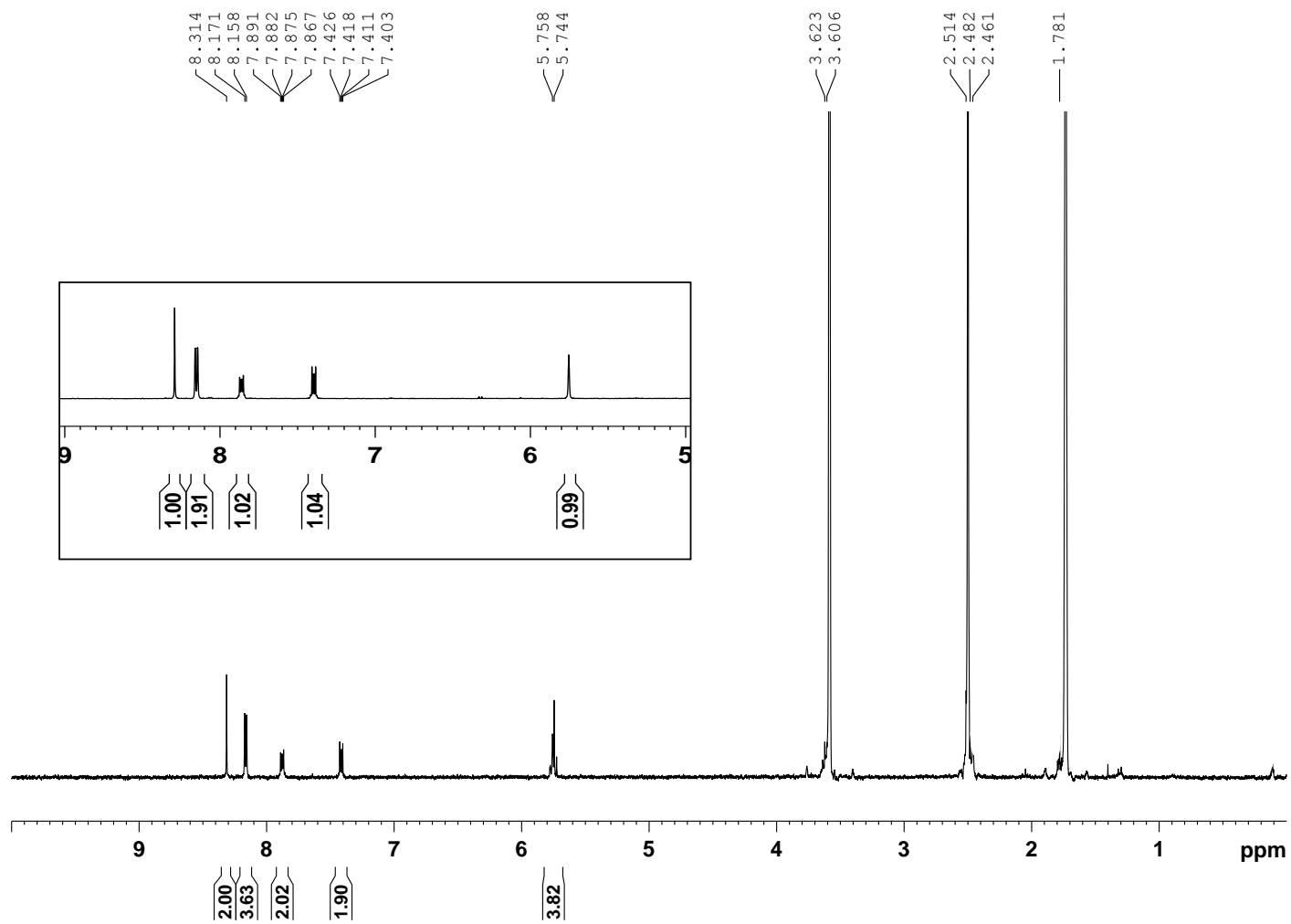


Figure S6: ^{13}C NMR of *cis*-2,3-dibromo-6,13-dihydropentacene-6,13-diol (100 MHz, $\text{THF-}d_8$)

