Indane dimerization products obtained by treatment of *N*-acylindan-1-amines with ethyl polyphosphate (EPP)

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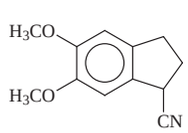
This report describes the diverse dimeric products obtained by treatment of *N*-acylindan-1-amines with ethyl polyphosphate in chloroform–diethyl ether solution at 80 °C for 8 h. Possible mechanisms for such reactions are discussed.

Given the difficulties previously encountered on attempting to synthesize 5,6-dimethoxyindane-1-carbonitrile **1**[1] and bearing in mind that several diarylacetonitriles were successfully prepared from *N*-formyl(diaryl)methylamines **2** and ethyl polyphosphate (EPP),[2] the same reagent and identical conditions were employed with *N*-formyl-5,6-dimethoxyindan-1-amine **3a**,



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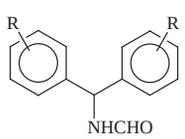
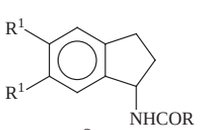


2

which was prepared from 5,6-dimethoxyindan-1-one. The reaction product isolated on treating the amide **3a** with EPP for 8 h at 80 °C had a molecular weight (MW) of 354 and its spectroscopic features showed that the indane structure had apparently undergone dimerization (Scheme 1). The structure of the



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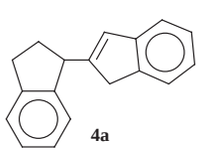
3a $R^1 = OCH_3$, R = H ⟶ MW = 354
3b $R^1 = OCH_3$, R = Ph ⟶ MW = 354 and benzonitrile
3c R^1 = H, R = Ph ⟶ MW = 232 and benzonitrile

Scheme 1

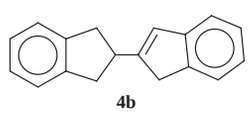
product of MW 354 was tentatively assigned to 5,5′,6,6′-tetramethoxy-2,2′,3,3′-tetrahydro-1,2′-bi-1*H*-indenyl **7b**.

This result prompted us to determine how the nitrogen group had been eliminated. For this purpose amide **3b** was prepared and treated with EPP under identical conditions to render, in addition to the 354 MW compound, benzonitrile. In an attempt to explain whether the observed behaviour of amides **3** depended on the presence of methoxy groups in the aromatic ring, the EPP reaction was tested on amide **3c**, obtained by direct benzoylation of indan-1-amine. When **3c** was treated with EPP according to the general method, a 232 MW oil and benzonitrile were obtained. The product of MW 232 was tentatively assigned structure **4a** by comparison with data found in the literature[3] of similar compounds, as well as by its NMR spectroscopy data. The ^{1}H NMR spectrum showed a single vinylic proton, methine triplet and six methylene protons. The presence of benzonitrile would support the conclusion that the production of **4a** and **7b** dimers would take place *via* a "nitrilium" ion. Such ions are the most commonly invoked intermediate in the Bischler–Napieralski synthesis and retro-Ritter amide degradation reaction.[4]

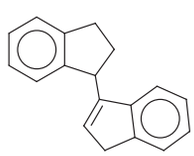
MW = 232



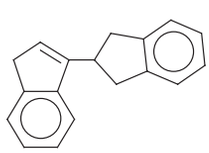
4a



4b

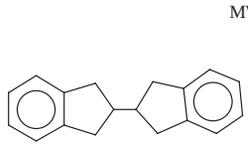


4c



4d

MW = 234



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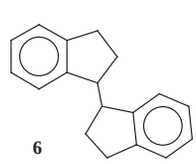

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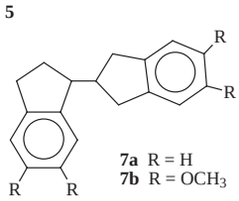


7a R = H
7b R = OCH_3

The above dimers could be structurally similar to the estrogenic, artificial hormones hexestrol and diethylstilbestrol,[5] hence the importance of knowing with certainty the structures of these dimers. Such dimers have been known for several years and in the literature there are numerous relevant articles;[6] however, there are serious discrepancies when attempting to correlate their structures with ^{1}H NMR spectroscopic data;[7] furthermore, there are practically no ^{13}C NMR data available.

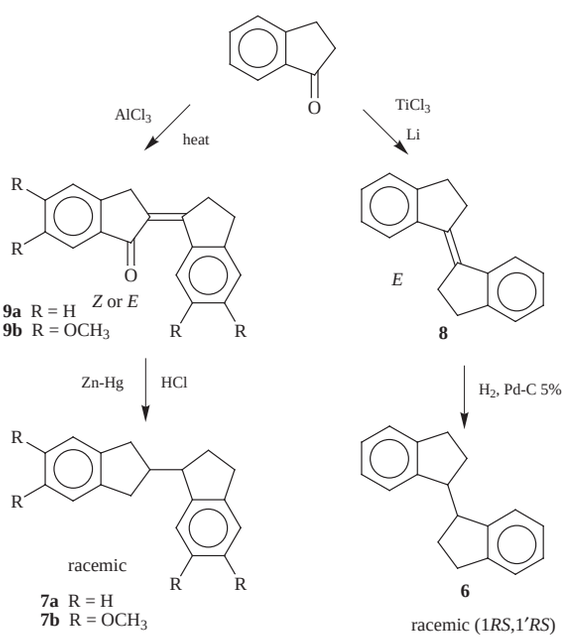
For the 232 MW compound, with a single olefinic hydrogen there are four possible isomers (**4a**, **b**, **c** and **d**). On hydrogenation of the double bond the number decreases to three (**5**, **6** as *meso* and/or *racemic* forms, and **7a**). Through which carbon atoms indane units are linked and what position is occupied by the double bond are problems which must be solved to determine the structure of these dimers. Our first efforts were directed to determine which carbon atoms were involved in the linkage of the indane units. For this purpose, the 232 MW compound was catalytically hydrogenated, to render the 234 MW compound. The ^{13}C NMR spectrum showed six aliphatic carbons, which allowed the possibility of the C-2–C-2′ isomer **5**

Table 1 ^{13}C NMR Chemical shifts for compounds **4a**, **6**, **7a**, **7b** and **10**

	C-1	C-2	C-3	C-1′ or C-3′	C-2′	C-3′ or C-1′	OCH_3	Aromatic carbons
6	47.5	26.6	31.5					123.8 124.3 125.8 126.2 144.5 145.7
7a	49.4	29.6	31.2	36.8	43.7	37.8	—	124.2 124.4 125.8 126.0 126.3 143.1 143.4 144.3 146.3
7b	49.4	29.8	31.1	36.6	44.2	37.7	55.9	107.7 134.7 134.9 136.0 138.0 147.7 147.8 148.0

	C-1	C-1′	C-2′	C-3′	OCH_3	Aromatic and alkenic carbons
4a	38.5	47.2	31.6	33.6		120.0 123.4 123.8 124.4 124.5 126.2 126.5 127.1 143.2 143.7 145.0 145.6 152.2
10	38.3	47.1	31.4	34.1	55.8 56.1	104.0 107.5 107.6 108.2 126.4 135.2 135.4 137.3 137.7 146.4 147.9 148.1 151.4

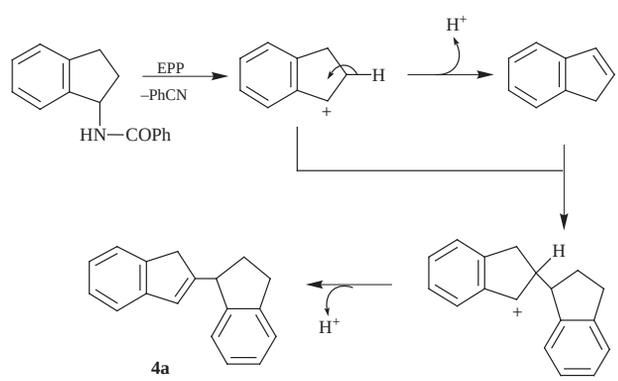
to be ruled out at once. Therefore, the syntheses of the other two possible dimerization products, namely 2,2′,3,3′-tetrahydro-1,1′-bi-1*H*-indenyl **6** and 2,2′,3,3′-tetrahydro-1,2′-bi-1*H*-indenyl **7a**, were carried out according to Scheme 2.



Scheme 2

The *racemic* (1*RS*,1′*RS*) dimer **6** was successfully prepared by treating indan-1-one with Li–$TiCl_3$[8] to obtain **8** as the *E* isomer;[6] catalytic reduction of **8** rendered **6** in 85% yield as a racemic mixture. The ^{13}C NMR spectrum of **6** failed to coincide with that of the 234 MW compound. It was then decided not to synthesize the *meso* (1*R*,1′*S*) isomer but to start by synthesizing compound **7a**. This compound was prepared by treatment of indan-1-one with $AlCl_3$ to afford **9a**.[9,10] Clemmensen reduction of **9a** rendered **7a** in 40% yield. The ^1H and ^{13}C NMR spectra (Table 1) of compound **7a** allowed the 1,2′-biindanyl structure to be assigned to the product of MW 234.

To assign the position of the double bond, both mechanistic considerations and spectroscopic observations were taken into account. As already mentioned, "nitrilium" ions seem to be invariable intermediates in these reactions.[4c] The loss of a nitrile

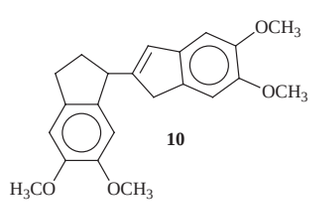


Scheme 3

molecule would generate an indanyl carbocation (Scheme 3), which would then lose a proton to yield the indene.[3] In turn, this indene would attack through C-2 position another molecule of carbocation to yield the more stabilized carbocation intermediate. According to the proposed mechanism and taking into account the stability of the probable carbocation, the production of compound **4a** is reasonable. As a further confirmation of the structure, the methylene hydrogen atoms of the indene unit in isomer **4a** are diastereotopic. The fact that these hydrogen atoms are present in ^1H NMR as two doublets with *J* 19 Hz and the presence of four aliphatic atoms in the ^{13}C NMR seems to confirm the structure of **4a**.

The demonstration of the structure of the dimer **7b** was made through the synthesis of this compound (Scheme 2). Clemmensen reduction of **9b** yielded two products, one of 354 MW and another of 352 MW. By spectroscopic comparison of the latter with **4a**, it was assigned structure **10**. In addition on catalytic hydrogenation of **10**, compound **7b** was obtained. Finally the spectroscopic data of **7b** are coincident with those of the compound obtained by treatment of **3a** and **3b** with EPP.

The mechanism outlined in Scheme 3 strongly supports the presence of compound **4a,** and eventually **10**, but fails to



explain how the structure **7b** was obtained, because production of this compound would involve a reductive process.

The reduction potentials of dimers **10** and **4a** were analysed by cyclic voltammetry (potentials from 0 to −2000 mV) to find, as expected, that it proved easier to reduce the non-methoxylated than the methoxylated compound.[11] Similar results were recorded in the cyclic voltammetry of *N*-benzoyl-5,6-dimethoxyindan-1-amine **3b** and *N*-benzoylindan-1-amine **3c**. It could thus be concluded that if dimerization of *N*-formyl-**3a** or *N*-benzoyl-5,6-dimethoxyindan-1-amine **3b** takes place by a mechanism similar to that of *N*-benzoylindan-1-amine **3c**, then subsequent reduction should not occur as a redox reaction.

A search of the literature showed that one non-catalytic method for the reduction of alkenes, carbonyls, imines, alcohols and halogen derivatives to alkanes is the so-called "ionic hydrogenation" method.[12] Such hydrogenation involves the formation of a carbocation by protonation of a double bond or by heterolysis of a C–X bond that reacts with a hydride donor to form the hydrogenated product. Reagent pairs of trifluoroacetic acid and an organosilane have proven to be the best though not the only ones available. Thus, "ionic hydrogenation" may also be carried out with phosphoric acid, polyphosphoric acid and alkyl- and aryl-sulfonic acids, as well as other acids, as proton donors, while cycloheptatriene, xanthene, adamantene, aliphatic and aromatic hydrocarbons, alcohols and other compounds have been employed as hydride donors. Considering the controversial structure of EPP and taking into account the fact that in these cases the reagent is generated *in situ* starting from phosphorus pentoxide and diethyl ether–chloroform as solvent, it could be that the more stable carbocation (MW 353, Scheme 2) favours the action of some of these components as hydride donors, which could explain the observed result. It is not possible to eliminate the same substrate–product system as hydride donor. Experimentally, it has been observed that the "ionic hydrogenation" acts selectively on the double bond of several 2-benzylidene-1,3-dioxoindanes.[11] However, even though we have demonstrated that *N*-acyl-5,6-dimethoxyindan-1-amines **3a** and **b** are deamidated, the formation of indene and the corresponding carbocation fails to explain why the reduced compound **7b** is obtained. In other words, the formation mechanism of this compound of MW 354 remains unclear.

Experimental

General

Infrared spectra were recorded on a Jasco A200 spectrometer as mulls or neat. The ^{1}H NMR spectra were recorded on a Bruker AC 200 or Bruker MSL 300 spectrometer using deuteriochloroform. Chemical shifts are reported in ppm units, and coupling constants (J) are in Hz. The mass spectra were obtained on VG-ZAB spectrometer. Melting points (uncorrected) were obtained on a Thomas Hoover apparatus. The cyclovoltammetry experiments were performed on a TEQ-V1.00 apparatus using glassy carbon and platinum wire as working electrodes, and calomel as reference electrode; support electrolyte: lithium perchlorate 0.1 M; solvent: acetonitrile. Merck silica gel 60 PF_{254} was used for preparative thin-layer chromatography (PTLC). Ethyl polyphosphate (EPP) was prepared by the method of Pollman and Schramm.[13] Solvents and reagents were purified using standard procedures.

1-Aminoindanes

A solution of the appropriate indan-1-one (5.2 mmol), and hydroxylamine hydrochloride (1 g, 14.5 mmol) in 30% aqueous sodium hydroxide (10 ml), and ethanol (20 ml) was boiled under reflux for 20 min, cooled, and diluted with water (10 ml). Raney nickel (1.5 g) was added in ethanol (20 ml) and aqueous sodium hydroxide (20 ml; 2 M). The mixture was magnetically stirred for 1 h. The resulting amine was extracted with chloroform. Evaporation of the solvent afforded the crude amine which was converted into the appropriate *N*-acyl-derivative without purification.

N-Formyl-5,6-dimethoxyindan-1-amine (3a)

To a cold solution of acetic formic anhydride (obtained from acetic anhydride (20 ml) and formic acid (10 ml) heated for 2 h) was added, dropwise and with stirring, 5,6-dimethoxyindan-1-amine (900 mg, 4.66 mmol) at such a rate that the temperature never rose above 40 °C. After stirring for 30 min, ether was added and the solution was stirred at room temperature overnight. The reaction mixture was diluted with ether, washed with water, saturated aqueous $NaCO_3H$, aqueous HCl (5%), and finally with water. The organic layer was dried ($MgSO_4$), filtered, and concentrated *in vacuo* to give **3a** (630 mg, 2.85 mmol, 55% from 5,6-dimethoxyindan-1-one) as a solid. Mp: 106–108 °C (from ethanol–water) (Found: C, 65.28; H, 6.67; N, 6.30. $C_{12}H_{15}NO_3$ requires C, 65.14; H, 6.83; N, 6.33%); ν_{max} (neat)/cm^{-1}: 3285 (NH), 2900 and 2820 (formyl group), 1640 (CO); δ_H: 1.60–1.90 (1H, m), 2.30–2.50 (1H, m), 2.60–2.90 (2H, m), 3.80 (6H, s, OCH_3), 5.40 (1H, m), 6.25 (1H, br s, NH), 6.70 (2H, s, Ar), 8.20 (1H, br s, CHO).

N-Benzoyl-5,6-dimethoxyindan-1-amine (3b)

The corresponding amine (900 mg, 4.66 mmol) was treated with benzoyl chloride (0.9 ml, 7.7 mmol) in dry benzene (1.5 ml) and pyridine (2.5 ml) to give **3b** (926 mg, 3.12 mmol, 60% from 5,6-dimethoxyindan-1-one) as a solid. Mp: 142–143 °C (from ethanol) (Found: C, 72.46; H, 6.62; N, 4.73. $C_{19}H_{20}NO_3$ requires C, 72.71; H, 6.44; N, 4.71%); ν_{max} (neat)/cm^{-1}: 3285 (NH), 1620 (CO); δ_H: 1.70–2.10 (1H, m), 2.30–2.80 (3H, m), 3.70 (3H, s, OCH_3), 3.80 (3H, s, OCH_3), 5.50 (1H, m), 6.45 (1H, br s, NH), 6.60 (1H, s, ArH), 6.80 (1H, s, ArH), 7.20–7.40 (3H, m, ArH), 7.60–7.80 (2H, m, ArH).

N-Benzoylindan-1-amine (3c)

Indan-1-amine (620 mg, 4.66 mmol) was treated following the above mentioned procedure for **3b** to render the *N*-benzoyl derivative **3c** (860 mg, 3.66 mmol, 70% from indan-1-one) as a solid. Mp: 135–136 °C (ethanol) (lit.,[14] 140–141 °C); ν_{max} (neat)/cm^{-1}: 3250 (NH), 1620 (CO); δ_H: 1.80–2.10 (1H, m), 2.50–3.10 (3H, m), 5.60 (1H, m), 6.20 (1H, br s, NH), 7.10–7.50 (3H, m, ArH), 7.60–7.80 (2H, m, ArH).

Treatment of amides (3a, b and c) with EPP

The amide (1 mmol) was heated with a solution of EPP in $CHCl_3$–ether (2.64 g EPP, concentration: 0.547 g ml^{-1}) at 80 °C for 8 h. The solvent was evaporated and the residue was treated with ice–water and then extracted with CH_2Cl_2 (3 × 30 ml), the extract was washed with 5% aqueous $NaCO_3H$ (2 × 40 ml) and water, dried over $MgSO_4$, filtered, concentrated *in vacuo* and separated by PTLC.

5,5′,6,6′-Tetramethoxy-2,2′,3,3′-tetrahydro-1,2′-bi-1*H*-indenyl (7b). The title compound was obtained from **3a** with EPP, and was separated by PTLC (eluted with benzene). The upper band afforded **7b** (35 mg, 20%) as an oil. In the case of **3b**, the residue was chromatographed on a column of silica gel 60 (35–70 mesh, ASTM), elution with benzene gave the benzonitrile, and elution with CH_2CI_2 gave **7b** (50 mg, 30%) as an oil (Found: C, 74.36; H, 7.29. $C_{22}H_{26}O_4$ requires C, 74.55; H, 7.39%); δ_H: 1.85 (1H, m, H-2), 2.25 (1H, m, H-2), 2.60–3.00 (6H, m, Ar-CH_2), 3.10 (1H, m, H-2′), 3.30 (1H, m, H-1), 3.85, 3.90, 3.95 (12H, s, OCH_3), 6.70, 6.75, 6.77, 6.80 (4H, s, ArH); δ_C: see Table 1; *m/z* 354 (M^+, 25.3%), 178 (17.9), 177 (100.0), 176 (6.9).

Compound **7b** was obtained in a yield of 80% by catalytic

reduction of **10** (100 mg) with Pd–C 10% (250 mg) at 55 psi, for 24 h. This compound was also obtained by the Clemmensen reduction (see below).

2-(2′,3′-Dihydro-1′*H*-inden-1′-yl)-1*H*-indene (4a). The title compound was obtained from **3c** and EPP, and was separated by PTLC and eluted with hexane to give **4a**[3] (87 mg, 75%) as an oil; δ_H: 2.10 (1H, m, H-2′), 2.50 (1H, m, H-2′), 3.05 (2H, m, H-3′), 3.28 (1H, d, *J* 19, H-1); 3.38 (1H, d, *J* 19, H-1), 4.34 (1H, t, *J* 7.89, H-1′), 6.70 (1H, br s, H-3), 7.10–7.40 (8H, m, ArH); δ_C: see Table 1; *m*/*z* 232 (M^+, 34.2%), 217 (13.0), 215 (14.2), 118 (11.2), 117 (100.0), 116 (11.8).

(*E*)-2,2′,3,3′-Tetrahydro-1,1′-bi-1*H*-indenylidene (8)[6]

Lithium wire (0.5 g, 72.46 mmol) and $TiCl_3$ (3.7 g, 24 mmol) were slurried in 40 ml of dry 1,2-dimethoxyethane (DME) under a nitrogen atmosphere, then the mixture was refluxed for 1 h and after cooling, a solution of indan-1-one (0.7 g, 5.3 mmol) in DME (3 ml) was added. After an additional 16 h at reflux, the reaction mixture was cooled to room temperature, diluted with petroleum ether, and filtered through a small pad of Florisil on a sintered glass filter. The filtrate was concentrated *in vacuo* to yield the crude product **8** (406 mg, 66%) as a solid. Mp: 138–139 °C (methanol) (lit.,[6] 140–141 °C); δ_H: 3.20 (8H, s), 7.10–7.40 (6H, m, ArH), 7.50–7.70 (2H, m, ArH).

***rac*-2,2′,3,3′-Tetrahydro-1,1′-bi-1*H*-indenyl (6)**

A mixture of **8** (140 mg, 0.6 mmol), heptane (40 ml), and Pd–C 5% (220 mg) was stirred with hydrogen under 57 psi at room temperature for 24 h. The filtered solution was evaporated *in vacuo* to yield **6** (120 mg, 85%) as an oil.[6] δ_H: 1.60–2.20 (4H, m, H-2), 3.00 (4H, br t, *J* 8, H-3), 3.80–4.10 (2H, m, H-1), 7.20 (8H, br s, ArH); δ_C: see Table 1, *m*/*z* 234 (M^+, 3.1%), 149 (27.1), 133 (36.6), 132 (39.4), 118 (20.3), 117 (100.0), 116 (46.4), 115 (49.3).

General procedure for condensation of indan-1-ones

A few crystals of $AlCl_3$ were added to melted indan-1-one or 5,6-dimethoxyindan-1-one (500 mg), and the mixture was heated for 15 min at a temperature 30 °C above the melting temperature of the indanone. Then the residue was triturated with cold water (20 ml) and the emulsion extracted with CH_2C1_2. The organic extract was washed with water and dried over Na_2SO_4, and evaporated *in vacuo* to give **9a**[10] from indan-1-one and **9b**[15] from 5,6-dimethoxyindan-1-one.

Compound **9a** (290 mg, 65%) was obtained as yellow crystals. Mp: 142–143 °C (from ethanol–ethyl acetate) (lit.,[10] 142–143 °C); δ_H: 3.00–3.20 (2H, m), 3.50–3.70 (2H, m), 4.1 (2H, s), 7.30–7.60 (6H, m, ArH), 7.85 (2H, m, ArH).

Compound **9b** (300 mg, 65%) was obtained as orange crystals. Mp: 142–143 °C (from benzene) (lit.,[15] 142–143 °C); δ_H: 3.00 (2H, m), 3.50 (2H, m), 3.75 (2H, m), 3.80, 3.90, 4.00 (12H, s, OCH_3), 6.60, 6.70, 7.20, 7.30 (4H, s, ArH).

Clemmensen reduction of 9a and 9b

A mixture of zinc (8.3 g), $HgCl_2$ (1.4 g), concentrated HCl (0.6 ml), and water (14 ml) was stirred for 15 min at room temperature. The aqueous solution was decanted, and the amalgamated zinc was covered with ethanol (8.7 ml; 95%), and concentrated HC1 (3.5 ml). The compound **9a** or **9b** (1.5 mmol) was added, and the mixture was heated under reflux for 3 h, and then water (15 ml) was added. The liquid phase was extracted with $CHCl_3$ (2 × 20 ml) and the combined organic extracts were washed with water, dried over Na_2SO_4, filtered and concentrated *in vacuo* to give a residue which was chromatographed by PTLC, and eluted with hexane–benzene (95 : 5).

2,2′,3,3′-Tetrahydro-1,2′-bi-1*H*-indenyl (7a)

The title compound was obtained by the Clemmensen reduction of **9a** and was isolated from the upper band of the PTLC as a colourless oil (140 mg, 40%) (Found: C, 92.40; H, 7.80. $C_{18}H_{18}$ requires C, 92.26; H, 7.74%); δ_H: 1.90 (1H, m, H-2), 2.20 (1H, m, H-2), 2.70–3.10 (6H, m, Ar-CH_2), 3.15 (1H, m, H-2′), 3.35 (1H, m, H-1), 7.10–7.40 (8H, m, ArH); δ_C: see Table 1; *m*/*z* 234 (M^+, 21.7%), 118 (34. 4), 117 (100.0), 116 (36.1).

Compound **7a** was also obtained by catalytic reduction of **4a** using Pd/C (10%), during 24 h at 55 psi (80% yield).

5,5′,6,6′-Tetramethoxy-2,2′,3,3′-tetrahydro-1,2′-bi-1*H*-indenyl (7b). The title compound was obtained by the Clemmensen reduction of **9b** and was isolated from the upper band of the PLTC as an oil (210 mg, 40%) and compound **10** was isolated from the lower band as crystals (100 mg, 18%). Data for compound **10**: mp: 113–114 °C (ethanol) (lit.,[16] 113–114 °C); δ_H 2.05 (1H, m, H-2′), 2.80–3.05 (1H, m, H-2′), 2.90 (2H, m, H-3′), 3.20 (1H, d, *J* 19, H-1), 3.30 (1H, d, *J* 19, H-1), 4.25 (1H, t, *J* 7.9, H-1′), 3.75, 3.80, 3.90, 3.95 (12H, s, OCH_3), 6.53 (1H, br s), 6.65 (1H, s), 6.80 (1H, s), 6.90 (1H, s), 7.00 (1H, s); δ_C: see Table 1, *m*/*z* 352 (M^+, 100%), 321 (22.7), 178 (14.1), 177 (96.7), 176 (16.2).

The catalytic reduction of **10** using Pd/C (10%), for 24 h at 55 psi gave **7b** (90% yield).

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