Metal-Free Synthesis of Indanes by Iodine(III)-Mediated Ring Contraction of 1,2-Dihydronaphthalenes

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Um protocolo livre de metais foi desenvolvido para sintetizar indanos através da contração de anel de 1,2-di-hidronaphtalenos promovida por PhI(OH)OTs (HTIB ou reagente de Koser). Este rearranjo oxidativo pode ser realizado em diversos solventes (MeOH, CH₃CN, 2,2,2-trifluoroetanol (TFE), 1,1,1,3,3,3-hexafluoropropanol (HFIP), e uma mistura 1:4 de TFE:CH₂Cl₂) em condições brandas. A contração de anel fornece indanos trans-1,3-dissubstituídos diastereoseletivamente, os quais são difíceis de obter em química orgânica sintética.

A metal-free protocol was developed to synthesize indanes by ring contraction of 1,2-dihydronaphthalenes promoted by PhI(OH)OTs (HTIB or Koser’s reagent). This oxidative rearrangement can be performed in several solvents (MeOH, CH₃CN, 2,2,2-trifluoroethanol (TFE), 1,1,1,3,3,3-hexafluoropropanol (HFIP), and a 1:4 mixture of TFE:CH₂Cl₂) under mild conditions. The ring contraction diastereoselectively gives functionalized trans-1,3-disubstituted indanes, which are difficult to obtain in synthetic organic chemistry.

Keywords: indanes, hypervalent iodine, ring contraction, 1,2-dihydronaphthalenes, rearrangements

Introduction

The indane ring system is present in several natural products and in non-natural compounds with remarkable biological activity.1 Consequently, efforts have continuously been made to develop new routes to obtain molecules with this unit.2 A typical strategy to synthesize a functionalized indane is by selecting an appropriate indanone, which is then elaborated into the target molecule.3,4 As tetralones are usually cheaper than indanones, the preparation of indanes starting from a tetralone (or a derivative) through a ring contraction rearrangement could be advantageous.4

In the last years, hypervalent iodine reagents have become an essential tool in synthetic organic chemistry due to the plethora of reactions that can be performed with them in excellent yield and selectivities.5 Moreover, hypervalent iodine compounds represent in many cases an alternative to toxic heavy metals.6 Although the oxidative rearrangement of alkenes mediated by iodine(III) has been described in some papers,6 the ring contraction of 1,2-dihydronaphthalenes was reported for a few substrates using only p-Me-C₆H₄-IF₂,6 which led to fluorinated indanes.

Herein, we describe an efficient metal-free protocol for the synthesis of indanes under mild conditions. In a preliminary communication, we report the ring contraction of 1,2-dihydronaphthalenes (which are obtained from 1-tetralones) mediated by PhI(OH)OTs (HTIB or Koser’s reagent) for a few substrates.7 In this article, the oxidation of several additional substrates is presented, better defining the reaction scope. Additionally, other reaction conditions were

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‡Dedicated with deep respect to Prof. Miuako K. Kuya
discovered using fluoroalcohols as solvent, which highly improved isolated yields. The best condition employed a 4:1 mixture of CH$_2$Cl$_2$-TFE that led to indanes in very good yield and with high diastereoselectivity.

**Results and Discussion**

**Ring contractions in methanol**

The required 1,2-dihydronaphthalenes are readily available substrates that can be prepared from 1-tetralones by reduction or Grignard reaction followed by dehydration (see Supplementary Information, SI, for details). This work was initiated studying the oxidation of 1a with the readily available iodine(III) reagents HTIB, PhI(OAc)$_2$, and PhI(OCOCF$_3$)$_2$ in methanol. Mixtures of several compounds and/or starting material were obtained using PhI(OAc)$_2$ or PhI(OCOCF$_3$)$_2$. Albeit the addition product 3a was isolated as the major component, the desired indane 2a was isolated using HTIB (Table 1, entry 1). Thus, HTIB was selected for further tests. When the reaction was performed at −10 °C, the overall isolated yield was lower (2a: 24%, trans-3a: 20%, cis-3a: 15%) than at room temperature. The use of trimethylorthoformate (TMOF) as solvent, instead of MeOH, also decreased the global yield (2a: 14%, trans-3a: 12%, cis-3a: 2%). These two trends are opposite to that observed in analogous thallium(III) promoted oxidation of 1,2-dihydronaphthalenes. Although indane 2a was obtained in only 36%, we decided to study the behavior of the methyl-substituted 1,2-dihydronaphthalene 1b, hoping to obtain a higher yield of the ring contraction product. Indeed, when 1b was treated with HTIB, the desired trans-indane 2b was obtained in 55% yield, together with the addition products 3b (entry 2). The ring contraction of 1,2-dihydronaphthalene 1c was performed with 3.6 equiv. of HTIB, which delivered indane 2c in 62% yield, as a single diastereomer, together with the addition product 3c in 35% yield (entry 3). With a lower amount of HTIB, the yield of 2c is smaller. A similar pattern was also observed in Tl(III) reactions, where an excess of the oxidant increased the yield of the indane. It is important to note that the diastereoselective synthesis of trans-1,3-disubstituted indanes is a difficult task in synthetic organic chemistry. Compound 2c is a synthetic intermediate in the synthesis of (±)-indatraline, which displays several interesting biological activities. The presence of donating groups at the aromatic ring may facilitate the rearrangement of 1,2-dihydronaphthalenes by increasing the migratory aptitude of the migrating carbon. Indeed, the oxidation of alkene 1d, that bears an amide group para to the migrating carbon, with HTIB gave the desired acetal 2d in much higher yield than the corresponding non-substituted substrate 1a (entry 4). However, the treatment of alkene 1e with HTIB gave indane 2e in comparable yield to that obtained for the substrate 1a (cf. entries 1 and 5). When HTIB was added to a methanol solution of substrates 1f-g, which bear a methoxy group at the aromatic ring, the mixture immediately became black, leading to indanes 2f-2g in low yield (entries 6 and 7). Low yields in iodine(III)-mediated oxidation of methoxy-substituted substrates has also been observed by others. Considering our experience in the oxidations of alkenes mediated by Tl(III), we expected that the trisubstituted 1,2-dihydronaphthalene 1h would have a different behavior.

<table>
<thead>
<tr>
<th>entry</th>
<th>Substrate</th>
<th>Product (yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="1a.png" alt="Image" /></td>
<td><img src="2a.png" alt="Image" /> (36%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td><img src="3a.png" alt="Image" /> (trans 28%) (cis: 14%)</td>
</tr>
<tr>
<td>2</td>
<td><img src="1b.png" alt="Image" /></td>
<td><img src="2b.png" alt="Image" /> (55%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td><img src="3b.png" alt="Image" /> (12%) (cis:trans = 3:4)</td>
</tr>
<tr>
<td>3</td>
<td><img src="1c.png" alt="Image" /></td>
<td><img src="2c.png" alt="Image" /> (62%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td><img src="3c.png" alt="Image" /> (35%) (cis:trans = 1:4)</td>
</tr>
<tr>
<td>4</td>
<td><img src="1d.png" alt="Image" /></td>
<td><img src="2d.png" alt="Image" /> (62%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td><img src="3d.png" alt="Image" /> (trans 19%) (cis 7%)</td>
</tr>
<tr>
<td>5</td>
<td><img src="1e.png" alt="Image" /></td>
<td><img src="2e.png" alt="Image" /> (23%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td><img src="3e.png" alt="Image" /> (trans 27%) (cis 17%)</td>
</tr>
<tr>
<td>6</td>
<td><img src="1f.png" alt="Image" /></td>
<td><img src="2f.png" alt="Image" /> (2%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td><img src="3f.png" alt="Image" /> (trans 25%) (cis 17%)</td>
</tr>
<tr>
<td>7</td>
<td><img src="1g.png" alt="Image" /></td>
<td><img src="2g.png" alt="Image" /> (12%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td><img src="3g.png" alt="Image" /> (trans 6%) (cis 3%)</td>
</tr>
<tr>
<td>8</td>
<td><img src="1h.png" alt="Image" /></td>
<td><img src="2h.png" alt="Image" /> (trans 60%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td><img src="3h.png" alt="Image" /> (trans 21%)</td>
</tr>
</tbody>
</table>
toward HTIB from that of the disubstituted alkene 1a. Indeed, when 1h was treated with HTIB in MeOH only the addition product 3h was isolated (entry 8). It is important to note that the acetal moiety in indanes like 2a-o can be easily transformed without epimerization into the corresponding aldehyde.2

**Ring contractions in acetonitrile**

The conditions used by Kirschning and co-workers6 in the oxidation of carbohydrates were also applied in the oxidation of 1,2-dihydronaphthalenes. Naphthalene (4a) was isolated in 30% yield when 1a was treated with HTIB in CH₃CN (Table 2, entry 1). NMR analysis of the crude product indicates the presence of indane 5a as a minor component, which decomposed during the purification step.15 Similarly, 4a was obtained in 48% yield when the reaction was performed in CH₂Cl₂, as solvent. However, when 1h was treated with HTIB in CH₃CN indane 5h was isolated in 51% yield (entry 2), which should be compared to exclusive formation of addition products in MeOH reactions (Table 1, entry 8). Ring contractions of epoxides can also be performed by treatment with Brønsted or Lewis acids.4 However, compound 5h can not be prepared in this manner, as no ring contraction product was obtained from the epoxide prepared from 1h.14-17 The oxidative rearrangement of other 4-alkyl-1,2-dihydronaphthalenes was also investigated. The reaction of alkenes 1i and 1g, which bear a methoxy group in the aromatic ring, with HTIB in CH₃CN furnished indanes 5i and 5g, respectively, in low yield (Table 2, entries 3 and 4), similarly to the disubstituted alkenes (Table 1, entries 6-7). Trisubstituted alkenes 1k-m were transformed into indanes 5k-m11 in good yield (entries 5-7). Thus, the ring contraction is not precluded by the presence of bulky alkyl groups. The behavior of alkene 1n is slightly different to that observed for other substrates. The reaction of 1n with HTIB in CH₃CN led mainly to indane 5n and ketone 6n18 in 26 and 23% yield, respectively. The tetralone 6n is formed by migration of the phenyl group.6 The reaction of 1n with HTIB led to a nearly 1:1 mixture of the rearrangement products 5n and 6n, because the aromatic rings have similar migratory aptitude. In theory, if the migratory aptitude of the aromatic rings was different, the ratio of the rearrangement products could be modified. Indeed, when 1o, which has two Cl atoms in one of the rings, was treated with HTIB, trans-indane 5o was isolated and the product of migration of the C₆H₃Cl₂ group was not formed, because of the low migratory aptitude of C₆H₃Cl₂. However, a small amount of the tetralone 7o, which is formed by migration of hydride,15,16 was isolated (entry 9). Finally, we investigated the ring contraction in a seven-membered ring substrate. When alkene 1p was treated with HTIB in CH₃CN, the substituted tetralin 5p was obtained in good yield (entry 10). The ring contractions in CH₃CN were performed under inert atmosphere and in the presence of molecular sieves. When these conditions were

Table 2. Oxidation of 1,2-dihydronaphthalenes with HTIB in CH₃CN

<table>
<thead>
<tr>
<th>entry</th>
<th>Substrate</th>
<th>Product (yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="1a" /></td>
<td><img src="image2" alt="4a" /> (30%) <img src="image3" alt="5a" /></td>
</tr>
<tr>
<td>2</td>
<td><img src="image4" alt="1h" /></td>
<td><img src="image5" alt="5h" /> (51%)</td>
</tr>
<tr>
<td>3</td>
<td><img src="image6" alt="1k" /></td>
<td><img src="image7" alt="5k" /> (52%)</td>
</tr>
<tr>
<td>4</td>
<td><img src="image8" alt="1l" /></td>
<td><img src="image9" alt="4l" /> (2%)</td>
</tr>
<tr>
<td>5</td>
<td><img src="image10" alt="1m" /></td>
<td><img src="image11" alt="4m" /> (13%)</td>
</tr>
<tr>
<td>6</td>
<td><img src="image12" alt="1n" /></td>
<td><img src="image13" alt="4n" /> (6%)</td>
</tr>
<tr>
<td>7</td>
<td><img src="image14" alt="1p" /></td>
<td><img src="image15" alt="5p" /> (52%)</td>
</tr>
<tr>
<td>8</td>
<td><img src="image16" alt="1q" /></td>
<td><img src="image17" alt="4q" /> (6%)</td>
</tr>
<tr>
<td>9</td>
<td><img src="image18" alt="1r" /></td>
<td><img src="image19" alt="5r" /> (5%)</td>
</tr>
<tr>
<td>10</td>
<td><img src="image20" alt="1s" /></td>
<td><img src="image21" alt="4s" /> (28%)</td>
</tr>
</tbody>
</table>

*Yield not determined; * together with 1i, ca. 20%.
not followed, lower yields were observed. The preparation of indanes analogues to 5 from 1,2-dihydronaphthalenes has been reported in a two-step protocol using NBS/water followed by reaction with Et₂Zn, which requires anhydrous conditions.¹⁷

**Ring contractions in fluorinated solvents**

After investigating the oxidation of 1,2-dihydronaphthalenes with HTIB in methanol and in acetonitrile, we focused on the more polar solvents 2,2,2-trifluoroethanol (TFE) and 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) because we envisioned that the formation of by-products could be decreased performing the reaction in these high polar low nucleophilic solvents. Since the first report by Kita et al.,¹⁹ the fluoroalcohols TFE²⁰ and HFIP²¹ have been used as solvent in several reactions with hypervalent iodine compounds. However, TFE and HFIP have never been used in the oxidative rearrangement of alkenes.° ¹⁶

For the alkene 1a, the yield of the desired product jumped from 36% (cf. entry 1, Table 1) to more than double (73%, Table 3, entry 1). The reaction of 1b with HTIB in TFE led to indane 8b in higher yield than in MeOH (55% vs. 70%), although the diastereoselectivity is lower (entry 2 of Tables 1 and 3, respectively). The ring contraction of 1q in TFE led to 8q in 65% yield, as a 10:1 mixture of trans:cis diastereomers, respectively. Considering our previous work on the synthesis of 3-phenyl-1-indanamines,⁷ the indane 8q could be used as an intermediate in the synthesis of (±)-irindalone.²² Moreover, this new method to obtain fluorinated acetals, which have different applications,²³ is more efficient than the previous described.²⁴-²⁶ The oxidation of trisubstituted alkenes 1h and 1p with HTIB in TFE gave indanes 5h and 5p, respectively, in higher yield than using acetonitrile (cf. Table 2, entries 2 and 10 with entries 4 and 7 of Table 3). On the other hand, 1k led to 5k in lower yield and diastereoselectivity than in acetonitrile (entry 5 of Tables 2 and 3).

Although the HTIB-mediated oxidation of 1,2-dihydronaphthalenes in TFE led to the rearrangement products in higher yields than in other solvents, the diastereoselectivity is lower. Thus, several conditions were tested trying to optimize the diastereoselectivity, without decreasing the isolated yields. Eventually, this goal was achieved by performing the reaction in a 4:1 mixture of CH₂Cl₂:TFE as solvent. Although CH₂Cl₂ is the major component of the mixture, TFE must have a crucial role because the reaction of 1a with HTIB in pure CH₂Cl₂ gave naphthalene (cf. entry 1, Table 2). The indane 8a was obtained from 1a in a yield comparable to the reaction in only TFE (73% vs. 67% yield, entry 1, Table 3). The alkene 1q gave the indane 8q in 69% yield, as a trans:cis

### Table 3. Reaction of 1,2-dihydronaphthalenes with HTIB in fluoroalcohols

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product (isolated yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a</td>
<td>F₃CH₂CO – OCH₂CF₃ 8a (A: 73% (B: 67%)</td>
</tr>
<tr>
<td>2</td>
<td>1b</td>
<td>F₃CH₂CO – OCH₂CF₃ 8b (A: 70%, trans:cis = 5:1)</td>
</tr>
<tr>
<td>3</td>
<td>1q</td>
<td>F₃CH₂CO – OCH₂CF₃ 8q (A: 65%, trans:cis = 10:1)</td>
</tr>
<tr>
<td>4</td>
<td>1h</td>
<td>O 5h (A: 72%)</td>
</tr>
<tr>
<td>5</td>
<td>1k</td>
<td>O 5k (A: 53%, trans:cis = 2:1)</td>
</tr>
<tr>
<td>6</td>
<td>1m</td>
<td>i-Pr 5m (B: 62%, trans:cis = 9:1)</td>
</tr>
<tr>
<td>7</td>
<td>1p</td>
<td>i-Pr 5p (B: 62%)</td>
</tr>
<tr>
<td>8</td>
<td>1a</td>
<td>OH 9a (D: 34%)</td>
</tr>
<tr>
<td>9</td>
<td>1a</td>
<td>OH 9a (E: 48%)</td>
</tr>
<tr>
<td>10</td>
<td>1a</td>
<td>OH 9a (E: 17%)</td>
</tr>
<tr>
<td>11</td>
<td>1a</td>
<td>OH 9a (E: 74%)</td>
</tr>
</tbody>
</table>

`¹⁶ Table 3. Reaction of 1,2-dihydronaphthalenes with HTIB in fluoroalcohols`
Mechanism discussion

The exclusive formation of trans-1,3-disubstituted indanes in the ring contractions in methanol can be explained by the mechanism detailed below. The electrophilic anti-addition of HTIB to the double bond would lead to 12a, through the cyclic organoiodine intermediate 11. The approach of the electrophile occurs opposite to the remote methyl group,27-29 explaining the stereoselectivity of this ring contraction, as well as of the other reactions discussed below. The adduct 12a would equilibrate to its more stable conformational isomer 12b, on which the required anti-periplanarity for the rearrangement is achieved. Migration of the aryl group (carbon 8a) on 13 would displace PhI giving the oxonium 14, which would furnish the trans-indane 2b after addition of MeOH (Scheme 1). The diastereoselective formation of the trans products in ring contractions in TFE or in CH₂Cl₂/TFE can be explained by similar mechanisms. However, considering the anhydrous conditions of the ring contraction in CH₃CN, the mechanism is probably different, as shown in Scheme 2 for 1n. The stereoselective electrophilic addition of HTIB to the alkene 1n would give the bis-benzylic carbocation 15. The hydroxyl group would attack the C1 position of 15, giving the four-membered ring intermediate 16,6 which would ring open to form 17. The ring contraction would take place on its conformer (18) giving trans-5n (path a, Scheme 2). The solvent may have some influence in the stereoselectivity of the electrophilic addition of the iodine(III), explaining the formation of 17.

Scheme 1. Mechanism for the ring contraction of 1b in MeOH.

Scheme 2. Rearrangements of 1n in CH₃CN.
cis-1,3-disubstituted indanes. Alternatively, the cis indanes can be formed by epimerization of the ketone moiety of the corresponding trans isomers. Starting from trisubstituted double bonds, the ring contraction lead to ketones which are always obtained as a free carboxyl. Aldehydes are formed from disubstituted alkenes. In the presence of a nucleophilic solvent, such as MeOH or TFE, acetals were isolated. On the other hand, free aldehydes were obtained in CH₃CN or in HFIP.

The formation of the cis-2,4-disubstituted-1-tetralone 6n can be explained by the mechanism shown in path b of Scheme 2. The Ph group would migrate on intermediate 17, with the exit of PhI, leading to cis-6n. trans-6n can be formed either by isomerization of cis-isomer or the addition of I(III) to 1n could take place by the other face. In acetonitrile oxidations, small amounts of naphthalenes were isolated in some reactions, which are formed by addition followed by elimination.

A plausible mechanism to explain the formation of the products of addition of MeOH is shown in Scheme 3, using substrate 1a as example.6,8 The methoxy group of 19 would intramolecularly displace PhI, giving the oxonium 20. Methanol would attack the C1 benzylic position of 20, furnishing trans-3a (path a). Alternatively, the intermolecular displacement of PhI by MeOH in the intermediate 19 would lead to cis-3a (path b). The preferential formation of the trans isomers (Table 1) indicates that the intramolecular process is favored. The formation of cis- and trans-isomers has also been observed in the reaction of indene with iodosobenzene derivatives in methanol.19 However, the oxidation of cyclohexenes with iodine(III) led to rearrangement products6 cis-isomers6,31-33 or trans-isomers31,34 depending mainly on the reaction conditions.

![Scheme 3. Mechanism for the formation of addition products 3a.](image)

As described above, the solvent has a crucial role in the oxidation of 1,2-dihydronaphthalenes with HTIB. In methanol, ring contraction is favored toward the addition of solvent for disubstituted double bonds. However, for trisubstituted substrates, the nucleophilic attack of MeOH is faster, probably because the required conformations for the rearrangements are disfavored with an additional methyl group (12b and 13 with Me instead H⁺ in Scheme 1). In anhydrous acetonitrile, there is no good nucleophile and ring contraction of trisubstituted alkenes occurs through the formation of a tertiary benzylic carbocation (like 15). For disubstituted double bonds, the ring contraction would occur through a less favored secondary benzylic carbocation and, thus, the formation of naphthalenes predominates. In TFE or in CH₂Cl₂/TFE, ring contraction was observed for either di- or trisubstituted 1,2-dihydronaphthalenes. The mechanism described for MeOH is the major pathway, as acetals are isolated for dissubstituted alkenes. Ring contraction also takes place with trisubstituted substrates, because a less nucleophilic species is present, making the formation of addition products more difficult.

**Conclusions**

A one-step, fast, mild and metal-free protocol was developed for the synthesis of indanes through ring contraction of readily available 1,2-dihydronaphthalenes mediated by HTIB. This oxidative rearrangement is diasteroselective giving 1,3-trans-disubstituted indanes preferentially or exclusively. The developed methodology facilitates the access to this structural motif, which is difficult to construct. Moreover, indanes bearing different functional groups can be easily obtained by changing the reaction conditions. In summary, the protocol herein presented will be useful in synthetic organic chemistry and in medicinal chemistry to access functionalized indanes in an expeditious manner. The protocol represents a green alternative to the analogous reaction using toxic thallium(III) salts,8,9,13,35,36

**Experimental**

**General procedure**

*Synthesis of 4-(4-fluorophenyl)-3,4-dihydronaphthalene-1(2H)-one*

To a dry round bottom flask under nitrogen atmosphere, AlCl₃ (7.8 g, 59 mmol) was added followed by the addition of fluorobenzene (10.8 mL, 11.1 g, 115 mmol). After cooling the flask to 0 °C, 1-naftol (3.0 g, 20.8 mmol) was added portion-wise under strong stirring (cake forms). After the addition, the flask was charged with a condenser and stirred at 75 °C for 1.5 h. The reaction was again cooled to 0 °C and quenched by adding ice through the condenser (strongly exothermic), until no gas evolution could be observed. The reaction mixture was extracted with CH₂Cl₂ (3 × 25 mL), the organics washed with 1 mol L⁻¹ NaOH...
(2 x 20 mL) and brine, dried with Na₂SO₄, filtered and concentrated to give a thick brown oil (5.48 g). The crude oil was purified by column chromatography (10% Et₂O in hexane), where the o-isomer elutes first followed by the m- and p-isomers. As the m- and p-isomers have the same Rₜ value, the mixed fractions were checked by GC to collect fractions with pure p-product 4-(4-fluorophenyl)-3,4-dihydronaphthalen-1(2H)-one (1g) (1.14 g, 4.75 mmol, 23%).

**Synthesis of 1-(4-fluorophenyl)-1,2-dihydronaphthalene (1c)**

4-(4-fluorophenyl)-3,4-dihydronaphthalen-1(2H)-one (806 µL, 3.36 mmol) was added to a round bottom flask, diluted with MeOH (25 mL) followed by cooling to 0 °C and addition of NaBH₄ (140 mg, 3.68 mmol). The reaction was quenched with H₂O after 1 h and adjusted to pH 5 with 10% HCl. After evaporation of the MeOH, the aqueous phase was extracted with EtOAc (3 x 15 mL), followed by the washing of the organics with brine, dried with Na₂SO₄, filtered and concentrated to give a crude yellow oil of 4-(4-fluorophenyl)-1,2,3,4-tetrahydronaphthalen-1-ol (928 mg), which was used in the next step without any further purification. The crude tetralol (928 mg) was added to a dry round bottom flask, followed by dry toluene (20 mL) and a few crystals of p-TsOH (cat.). The flask was equipped with a dean-stark trap and refluxed until no alcohol remained according to TLC (ca. 1.5 h). The reaction was quenched with a saturated NaHCO₃ solution and diluted with EtOAc. The organic phase was washed with saturated NaHCO₃ (2 x 15 mL), brine (2 x 15 mL), dried with Na₂SO₄, filtered and concentrated to give a crude brown oil (761 mg). It was purified by column chromatography (hexane) to afford 1c as colorless oil (728 mg, 3.25 mmol, 97% over 2 steps); 1H NMR (400 MHz, CDCl₃) δ 2.56 (dd, 1H, J 13.8, 9.7, 4.2 and 2.0 Hz), 2.67 (dd, 1H, J 12.1, 7.4, 4.6 and 1.8 Hz), 4.12 (dd, 1H, J 9.3 and 7.7 Hz), 5.99 (dt, 1H, J 9.6 and 4.4 Hz), 6.55 (dt, 1H, J 9.6 and 1.5 Hz), 6.81 (d, 1H, J 7.7 Hz), 7.03-6.95 (m, 2H), 7.14-7.07 (m, 2H), 7.22-7.14 (m, 3H); 13C NMR (75 MHz, CDCl₃) δ 32.2, 43.2, 115.3 (d, J 21 Hz), 126.4, 127.1, 127.1, 127.5, 127.9, 128.2, 129.9 (d, J 8 Hz), 134.2, 137.8, 140.3 (d, J 3 Hz), 161.7 (d, J 245 Hz); HRMS (m/z) calcd. for C₁₅H₁₅F₂ 275.1254, found 275.1252.

**Reaction of 1,2-dihydro-6-methoxynaphthalene (1f) with HTIB in MeOH**

To a solution of 1f (0.328 g, 2.05 mmol) in MeOH (8 mL) was added HTIB (0.941 g, 2.40 mmol) at 0 °C. Immediately after addition of HTIB the reaction became dark. The mixture was stirred at room temperature for 1 h. The reaction was extracted with EtOAc, washed with H₂O, with brine, and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure. The crude product was purified by column (0-25% EtOAc in hexane), affording 2f (0.0137 g, 0.0616 mmol, 3%), as colorless oil, trans-3f (0.117 g, 0.526 mmol, 26%) and cis-3f (0.0779 g, 0.350 mmol, 17%), both as yellow oils. cis-1,2,3,4-Tetrahydro-1,2,7-trimethoxynaphthalene (3f); colorless oil; IR νmax/cm⁻¹ (film) 1101, 1249, 1499, 2834, 2933; 1H NMR (500 MHz, CDCl₃) δ 1.91-1.94 (m, 1H), 2.16-2.23 (m, 1H), 2.67-2.74 (m, 1H), 2.92-2.96 (m, 1H), 3.47 (s, 3H), 3.50 (m, 3H), 3.61-3.69 (m, 1H), 3.79 (s, 3H), 4.30 (d, 1H, J 3.1 Hz), 6.80 (dd, 1H, J 8.3, 2.6 Hz), 6.86 (d, 1H, J 2.6 Hz), 7.04 (d, 1H, J 8.3 Hz); 13C NMR (75 MHz, CDCl₃) δ 22.7, 26.1, 55.3, 56.5, 57.4, 77.9, 78.2, 114.3, 114.4, 128.5, 129.7, 135.7, 157.5; LRMS (m/z, %) 222 (M⁺, 17), 191 (7), 190 (52); 189 (9), 164 (100); HRMS (m/z) calcd. for C₁₃H₁₅O₃ [M + Na]+ 245.1148, found 245.1141.

**Reaction of 1,2-dihydro-6,7-dimethoxynaphthalene (1g) with HTIB in MeOH**

As 1f, but using 1g (0.0744 g, 0.391 mmol), HTIB (0.153 g, 0.391 mmol), and MeOH (2.0 mL). The reaction was stirred for 1 h at 0 °C. The crude product was purified by column (0-30% EtOAc in hexane), affording 2g (0.0116 g, 0.0460 mmol, 12%) and trans-3g (0.0080 g, 0.032 mmol, 8%), both as a colorless oil. trans-1,2,3,4-Tetrahydro-1,2,6,7-tetramethoxynaphthalene (3g); colorless oil; IR νmax/cm⁻¹ (film) 1121, 1258, 1515, 2830, 2934; 1H NMR (300 MHz, CDCl₃) δ 1.88-1.97 (m, 1H), 2.05-2.15 (m, 1H), 2.62-2.82 (m, 2H), 3.44 (s, 3H), 3.51 (s, 3H), 3.71 (ddd, 1H, J 7.2, 4.8, 2.7 Hz), 3.84 (s, 3H), 3.87 (3H, s), 4.21 (d, 1H, J 4.8 Hz), 6.58 (1H), 6.83 (s, 1H); 13C NMR (75 MHz, CDCl₃) δ 23.4, 25.1, 55.9, 56.0, 56.7, 57.2, 77.2, 79.5, 111.1, 112.4, 126.5, 129.3, 147.5, 148.7; HRMS (m/z) calcd. for C₁₄H₁₄O₄ [M + Na]+ 275.1254, found 275.1252.

**Synthesis of 1-(dimethoxymethyl)-5-acetamido-indane (2d)**

To a stirred mixture of 1d (0.254 g, 1.36 mmol) and MeOH (27 mL), was added HTIB (0.590 g, 1.50 mmol) at once at 0 °C. After 35 min the reaction was quenched with saturated solution of NaHCO₃. The aqueous phase was extracted with EtOAc (3 x 10 mL), washed with brine (2 x 10 mL) and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure. The crude product was purified by column (hexane:EtOAc, 3:7) giving 2d (72%, 0.244 g, 0.98 mmol) as a yellow solid, trans-3d (10%, 0.035 g, 0.14 mmol) as a solid and cis-3d (7%, 0.025 g, 0.10 mmol) as a solid. 1-(Dimethoxymethyl)-5-acetamido-indane (2d): mp 68.4-69.3 °C; IR νmax/cm⁻¹ (film) 828, 1058, 1124, 1372, 1426, 1492, 1546, 1602,
Metal-Free Synthesis of Indanes by Iodine(III)-Mediated Ring Contraction


1667; \(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta\) 1.85-2.28 (m, 3H), 2.13 (s, 3H), 2.70-2.90 (m, 2H), 3.37 (s, 3H), 3.41 (s, 3H), 4.27 (d, 1H, J 7.4 Hz), 7.16 (dd, 1H, J 1.4, 8.2 Hz), 7.32 (d, 1H, J 8.0 Hz), 7.46 (s, 1H), 7.84 (s, 1H); \(^1^\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 24.3, 27.5, 31.4, 47.0, 52.9, 54.2, 107.2, 116.4, 118.2, 125.6, 136.8, 138.7, 145.5, 168.6; LRMS (m/z, %) 249 (M\(^+\), 2.4%), 218 (6), 186 (3), 174 (14), 144 (6), 132 (13), 115 (5), 103 (3), 75 (100); HRMS (m/z) calcd. for \(\text{C}_{22}\text{H}_{23}\text{NO}\) [M + H\(^+\)] 320.1438, found 320.1440.

To a solution of trans-\(\text{C}_{22}\text{H}_{23}\text{NO}\) [M + H\(^+\)] 320.1438, found 320.1440.

\(N\)-trans-5,6-dimethoxy-5,6,7,8-tetrahydropyridinenaphthalene-2-yl)acetamide (trans-3d): mp 108.7-110.5 \(^\circ\)C; IR \(\nu\)\(_{max}\)/cm\(^{-1}\) (film) 830, 915, 1091, 1331, 1372, 1439, 1505, 1544, 1598, 1614, 1671, 2934, 3302, 3507; \(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta\) 1.81-2.18 (m, 2H), 2.13 (s, 3H), 2.58-2.90 (m, 2H), 3.44 (s, 3H), 3.48 (s, 3H), 3.67-3.74 (m, 1H) 4.21 (d, 1H, J 4.8 Hz), 7.21-7.27 (m, 2H), 7.34 (s, 1H), 7.56 (s, 1H). \(^1^\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 23.3, 24.5, 25.5, 56.5, 57.3, 77.8, 79.2, 117.5, 119.4, 130.5, 130.6, 133.7, 137.9, 168.3; LRMS (m/z, %) 249 (M\(^+\), 23%), 217 (27), 191 (100); HRMS (m/z) calcd. for \(\text{C}_{18}\text{H}_{19}\text{NO}\) [M + Na\(^+\)] 272.1257, found 272.1262.

Syntheses of cis and trans-1-(2,3)-dihydro-1-methyl-1H-inden-3-ylpentan-1-one (SI)

To a solution of 11 (0.129 g, 0.647 mmol) and molecular sieves (3 Å, 0.065 g) in anhydrous CH\(_2\)CN (6.5 mL) under N\(_2\) was added HTIB (0.489 g, 1.25 mmol) at 0 \(^\circ\)C. The reaction was stirred for 15 min at 0 \(^\circ\)C. A saturated solution of NaHCO\(_3\) was added until pH 7. The organic phase was washed with H\(_2\)O, with brine and dried over anhydrous MgSO\(_4\). The solvent was removed under reduced pressure. The crude product was purified by column (0-10% EtOAc in hexane), affording 5l (0.0681 g, 0.315 mmol, 49%) as a trans-cis (10:1) mixture. Naphthalene 4l (0.0031 g, 0.016 mmol, 2%) was also isolated as a colorless oil. cis and trans-5l: yellow oil; IR \(\nu\)\(_{max}\)/cm\(^{-1}\) (film) 755, 1460, 1711, 2870, 2931, 2959; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (trans isomer) 0.87 (t, 3H, J 7.3 Hz), 1.21-1.25 (m, 1H), 1.28 (d, 3H, J 6.9 Hz), 1.51-1.56 (m, 2H), 2.41-2.62 (m, 3H), 3.40 (sext, 1H, J 6.8 Hz), 4.08 (dd, 1H, J 8.7, 3.4 Hz), 7.14-7.28 (m, 4H), (cis isomer) 0.91 (t, 3H, J 7.5 Hz), 1.35 (d, 3H, J 6.9 Hz), 1.81-1.85 (m, 2H), 3.21 (sext, 1H, J 7.2 Hz) (other signals overlap with the trans form); \(^1^\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (trans isomer) 13.8, 20.2, 22.3, 25.8, 37.8, 38.5, 40.1, 57.0, 123.8, 124.7, 126.6, 127.6, 140.7, 149.3, 210.8 (cis isomer) 13.9, 19.7, 22.4, 25.9, 38.3, 40.8, 123.5, 124.6, 127.4, 141.0, 148.8, 211.3 (other signals overlap with the trans form); LRMS (m/z, %) 216 (M\(^+\), 5), 131 (100); HRMS (m/z) calcd. for \(\text{C}_{19}\text{H}_{20}\text{O}\) [M + H\(^+\)] 217.1587, found 217.1586.

Reaction of 4-isopropyl-1-methyl-1,2-dihydronaphthalene (1m) with HTIB in CH\(_2\)CN

The typical procedure for reactions in CH\(_2\)CN was followed, but using 5m (0.187 g, 1.00 mmol). The crude product was purified by flash column chromatography (gradient elution, 0-20% EtOAc in hexanes), affording indane 4m (0.0981 g, 0.485 mmol, 48%)\(^{12}\) as a trans-cis (5:1 by \(^1\)H NMR after purification) mixture, as yellow oil. Naphthalene 4m (0.0244 g, 0.132 mmol, 13%)\(^{12}\) was also isolated as colorless oil.

Reaction of 1,2-dihyrold-7-methoxy-4-methylnaphthalene (1i) with HTIB in CH\(_2\)CN

To a solution of 1i (0.178 g, 1.02 mmol) and molecular sieves (3 Å, 0.100 g) in CH\(_2\)CN (10 mL) under N\(_2\) was added HTIB (0.442 g, 1.13 mmol) at 0 \(^\circ\)C. The ice bath was removed. The mixture was stirred for 15 min at room temperature. A saturated solution of NaHCO\(_3\) was added until pH 7. The organic phase was washed with H\(_2\)O, with brine and dried over anhydrous MgSO\(_4\). The solvent was removed under reduced pressure. The crude product was purified by column (0-40% EtOAc in hexane), affording 5i (0.0231 g, 0.121 mmol, 12%), as a yellow oil and a mixture 1:1 of 4i and starting material (0.0361 g), as a colorless oil.

Reaction of 1,2-dihydrol-6-methoxy-4,7-dimethynaphthalene (1j) with HTIB in CH\(_2\)CN

As for 1i, but using 1j (0.197 g, 1.05 mmol), molecular sieves (3 Å, 0.100 g), HTIB (0.489 g, 1.25 mmol), CH\(_2\)CN (10 mL). The mixture was stirred for 30 min at room temperature. The crude product was purified by column (0-40% EtOAc in hexane) affording 5j (0.0420 g, 0.204 mmol, 20%) and impure 4j (0.0594 g). Impure 4j was purified by column (10% EtOAc in hexane), affording 4j (0.0381 g, 0.205 mmol, 20%).

Reaction of 1,2-dihydrol-1-methyl-4-phenylnaphthalene (1n) with HTIB in CH\(_2\)CN

As for 1i, but using 1n (0.165 g, 0.750 mmol), molecular sieves (3 Å, 0.0750 g), HTIB (0.353 g, 0.901 mmol), and
CH$_2$CN (7.5 mL). The mixture was stirred for 20 min at room temperature. The product crude was purified by column (0-10% EtOAc in hexane) affording 5n (0.0452 g, 0.191 mmol, 26%), and 6n (0.0414 g, 0.175 mmol, 23%), as a yellow oil and as a cis:trans mixture (6:1). 4n (7.00 mg, 0.0321 mmol, 4%) was isolated, as a colorless oil.

**Reaction of 4-(3,4-dichlorophenyl)-1-methyl-2-dihydro-naphthalene (1o) with HTIB in CH$_2$CN**

As for 1i, but using 1o (0.118 g, 0.408 mmol), molecular sieves (3 Å, 0.0413 g), HTIB (0.194 g, 0.495 mmol), and CH$_2$CN (4.0 mL). The mixture was stirred for 20 min at room temperature. The product was purified by column (0-30% EtOAc in hexane) affording 5o (0.0430 g, 0.141 mmol, 35%) and 7o (0.0070 g, 0.023 mmol, 6%), both as a yellow oil. trans-(3,4-Dichlorophenyl)-2,3-dihydro-1-methyl-1H-inden-3-yl)methanone (5o): IR $\nu_{\text{max}}$/cm$^{-1}$ (film) 755, 1030, 1206, 1687, 2867, 2925, 2958; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.34 (d, 3H, J 6.9 Hz), 2.02 (ddd, 1H, J 12.8, 7.6, 8.7 Hz), 2.68 (ddd, 1H, J 12.5, 7.8, 4.0 Hz), 3.49 (sext, 1H, J 7.2 Hz), 4.95 (dd, 1H, J 8.8, 3.9 Hz), 7.04 (d, 1H, J 7.5 Hz), 7.11-7.14 (m, 1H), 7.24-7.25 (m, 2H), 7.59 (d, 1H, J 8.4 Hz), 7.86 (ddd, 1H, J 8.3, 2.0 Hz), 8.11 (d, 1H, J 2.0 Hz); $^1$C NMR (75 MHz, CDCl$_3$) $\delta$ 20.4, 38.4, 38.5, 51.3, 124.0, 124.0, 126.6, 127.9, 127.9, 130.8, 130.8, 133.5, 136.4, 137.7, 140.0, 149.4, 198.2; LRMS (m/z, %) 305 (M$^+$, 1%), 131 (100); HRMS (m/z) calcd. for C$_{13}$H$_{10}$ClF$_2$O [$M + Na]^+$ 351.0790, found 351.0801.

**Synthesis of 1-[bis(trifluoromethoxy)methyl]-2,3-dihydro-1H-indene (8a)**

To a stirred mixture of 1a (0.102 g, 0.78 mmol) and TFE (6 mL), was added HTIB (0.34 g, 0.86 mmol) at once at 0°C. After 30 min the reaction was quenched with saturated solution of NaHCO$_3$ until pH 7. The aqueous phase was extracted with EtOAc (3 × 10 mL), washed with brine (2 × 10 mL) and dried over anhydrous MgSO$_4$. The solvent was removed under reduced pressure. The crude product was purified by column (hexane:EtOAc, 9:1) giving 8a (73%, 0.19 g, 0.57 mmol) as a light yellow oil; IR $\nu_{\text{max}}$/cm$^{-1}$ (film) 2949, 2855, 1406, 1281, 1164, 1078; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.96-2.08 (m, 1H), 2.18-2.30 (m, 1H), 2.82-3.03 (m, 2H), 3.47 (q, 1H, J 7.9 Hz), 3.86-4.07 (m, 4H), 4.70 (d, 1H, J 7.9 Hz), 7.15-7.24 (m, 3H), 7.38-7.41 (m, 1H); $^1$C NMR (75 MHz, CDCl$_3$) $\delta$ 27.1, 31.2, 47.2, 61.9 (q, J 34.9 Hz), 63.4 (q, J 34.9 Hz), 105.4, 123.7 (q, J 276 Hz), 123.8 (q, J 276 Hz), 124.6, 125.5, 125.6, 127.6, 140.8, 144.6; LRMS (m/z, %) 328 (M$^+$, 1.3%), 211 (70), 129 (21), 117 (100); HRMS (m/z) calcd. for C$_{13}$H$_{11}$F$_3$O$_2$ [M + Na]$^+$ 351.0790, found 351.0801.

**Synthesis of 1-[bis(trifluoromethoxy)methyl]-2,3-dihydro-3-methyl-1H-indene (8b)**

As for 1a, but using 1b (0.146 g, 1.01 mmol). HTIB was added at once. The reaction was quenched after 7 min. Compound 8b was obtained as a yellow oil (70%, 0.243 g, 0.710 mmol) as a 5:1 trans:cis mixture; IR $\nu_{\text{max}}$/cm$^{-1}$ (film) 2961, 2932, 2872, 1458, 1281, 1174, 1078, 758; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ (trans isomer) 1.27 (d, 3H, J 6.9 Hz), 1.81 (ddd, 1H, J 13.2, 8.5, 7.3 Hz), 2.32 (ddd, 1H, J 13.2, 7.8, 4.2 Hz), 3.22-3.34 (m, 1H), 3.43-3.50 (m, 1H), 3.82-4.06 (m, 4H), 4.64 (d, 1H, J 8.1 Hz), 7.18-7.36 (m, 4H), (cis isomer) 1.33 (d, 3H, J 6.9 Hz), 2.40-2.55 (m, 1H), 4.75 (d, 1H, J 8.4 Hz), 7.08-7.13 (m, 1H), 7.41-7.44 (m, 1H), 7.68-7.72 (m, 1H) (other signals overlap with the trans form); $^1$C NMR (75 MHz, CDCl$_3$) $\delta$ (trans isomer) 20.5, 35.9, 37.6, 46.0, 61.6, 63.8 (q, J 34.7 Hz), 105.1, 123.5, 123.6 (q, J 276 Hz), 123.8 (q, J 276 Hz), 125.8, 126.6, 127.8, 140.3, 149.2, (cis isomer) 19.7, 36.9, 37.7, 45.6, 105.7, 123.3, 124.8, 126.7, 127.6, 130.2, 137.5 (other signals overlap with the trans form); LRMS (m/z, %) (major distereomer) 242 (M$^+$ - CF$_3$CH$_2$OH, 17%), 211 (69), 131 (100), (minor distereomer) 342 (M$^+$, 3%), 242 (9), 211 (75), 131 (100); HRMS (m/z) calcd. for C$_{13}$H$_{11}$F$_3$O$_2$ [M + Na]$^+$ 365.0947, found 365.0960.

**Synthesis of 1-(2,3-dihydro-1H-inden-3-yl)ethanone (5h)**

As for 1a, but using 1h (0.158 g, 1.10 mmol). The reaction was quenched after 30 min. The crude product was...
purified by column (5-10% EtOAc in hexane) affording 5h’ (72%, 0.127 g, 0.791 mmol), as a light yellow oil.

**Synthesis of 1-(1,2,3,4-tetrahydroxynaphthalene-4-yl) ethanone (5p)**

As for 1a, but using 1p (0.158 g, 1.00 mmol). The reaction was quenched after 20 min. The crude product was purified using column (hexane:EtOAc, 9:1) giving 5p’ (62%, 0.107 g, 0.62 mmol), as a light yellow oil.

**Synthesis of 1-(trans-2,3-dihydro-1-methyl-1H-inden-3-yl)-3-(4-fluorophenyl)-2,3-dihydro-1H-indene (5q)**

A dry round bottom flask was charged with 1q (240 mg, 1.07 mmol), CHCl3/TFE (4:1 v/v) followed by HTIB (550 mg, 1.40 mmol) at room temperature. The reaction color changed towards yellow within a minute. After 10 min at room temperature, the reaction was quenched with H2O, washed with H2O (2 × 20 mL), with 50% NaHCO3 solution (2 × 20 mL), with H2O (20 mL), with brine (2 × 20 mL), dried over anhydrous Na2SO4, and filtered. The solvent was removed under reduced pressure to give a brownish oil. The crude product was purified by column (0-25% EtOAc in hexane) giving 8q (312 mg, 0.739 mmol, 69%), as a trans: cis (17:1) mixture as colorless oil; 1H NMR (300 MHz, CDCl3) δ (trans isomer) 2.18 (ddd, 1H, J 13.5, 8.5, 7.7 Hz), 2.60 (ddd, 1H, J 13.5, 8.2, 4.2 Hz), 4.11-3.80 (m, 4H), 4.43 (t, J 8.2, 4.2 Hz), 4.74 (d, 1H, J 7.7 Hz), 7.03-6.93 (m, 3H), 7.29-7.20 (m, 2H), 7.47-7.39 (m, 1H); 13C NMR (125 MHz, CDCl3) δ (trans isomer) 38.0, 46.5, 21.7, 21.7, 25.3, 31.3, 50.2, 100.6, 124.7, 125.2, 126.0, 127.4, 128.3, 129.5 (d, J 8, 140.8 Hz), 140.8, 141.2, 147.2, 161.8 (d, J 245 Hz); HRMS (m/z) calcld. for C23H17F4O2 [M + Na]+ 445.1009, found 445.1017.

**Synthesis of 1-(trans-2,3-dihydro-1-methyl-1H-inden-3-yl)-2,3-dihydro-1H-indene (8a)**

As for 1q, but using 1a (0.130 g, 1.00 mmol). HTIB (0.510 g, 1.30 mmol) was added at 0 ºC. The reaction was stirred for 10 min at room temperature. The crude product was purified by column (1-20% EtOAc in hexane) affording 8a (67%, 0.221 g, 0.673 mmol), as a yellow oil.

**Synthesis of 1-(2,3-dihydro-1-methyl-1H-inden-3-yl)-2-methylpropan-1-one (5m)**

As for 1q, but using 1m (0.108 g, 0.580 mmol). HTIB (1.3 equiv.) was added at 0 ºC. The reaction was quenched after 2 min at 0 ºC. The crude product was purified by column (2-30% EtOAc in hexane) affording 5m’ (62%, 0.073 g, 0.359 mmol), as a light yellow oil.

**Synthesis of 2,3-dihydro-1H-indene-1-carbaldehyde (5a)**

To a stirred solution of 1a (0.122 g, 0.937 mmol) in HFIP (4.0 mL) was added HTIB (0.404 g, 1.04 mmol) at 0 ºC. After 1 min the reaction was quenched with saturated solution of Na2S4O6 (5.0 mL). The resulting mixture was extracted with EtOAc (3 × 10 mL). The organic layer was washed with brine and dried over anhydrous MgSO4. The solvent was removed under reduce pressure and the crude product was purified by column (5-10% EtOAc in hexane) giving 5a’ (58%, 0.080 g, 0.55 mmol) as a light yellow oil.

**Reaction of 1,2-dihydroxynaphthalene (1a) with HTIB in HFIP/CH2Cl2 followed by in situ reduction with NaBH4**

To a stirred solution of 1a (0.050 g, 0.38 mmol) in HFIP (0.8 mL) and CH2Cl2 (3.2 mL) was added at 0 ºC HTIB (0.19 g, 0.49 mmol). The mixture was stirred for 15 min. Then, NaBH4 (0.72 g, 1.9 mmol) was added and the reaction was allowed to reach room temperature while stirring for 20 min. Alcohol 9a was obtained as a mixture with ditosilate 10a as a yellow oil after column chromatography (AcOEt in hexanes, 1:10). A second column chromatography (20% AcOEt in hexanes) allowed complete separation of the products giving 9a’ (48%, 0.027 g, 0.18 mmol) as a yellow oil and 10a (17%, 0.031 g, 0.066 mmol) as a white solid. (2,3-dihydro-1H-inden-1-yl)methylene bis(4-methylbenzenesulfonate) (10a): IR νmax/cm−1 (film) 1376, 1193, 1178, 750 cm−1; 1H RMN (200 MHz, CDCl3) δ 2.10-2.21 (m, 2H), 2.41 (s, 3H), 2.75-2.87 (m, 2H), 3.55-3.64 (m, 1H), 6.50 (d, J 3.8 Hz, 1H), 6.99-7.20 (m, 6H), 7.28-7.32 (m, 2H), 7.44-7.50 (m, 2H), 7.71-7.77 (m, 2H); 13C RMN (75 MHz, CDCl3) δ 21.7, 21.7, 25.3, 31.3, 50.2, 100.6, 124.7, 125.2, 126.3, 127.8, 128.1, 129.6, 133.2, 135.3, 138.5, 145.0, 145.1, 145.2; HRMS (m/z) calcld. for C25H25O2S2 [M + Na]+ 495.0907, found 495.0910.

**Synthesis of (2,3-dihydro-1H-inden-1-yl)methanol (9a)**

To a stirred mixture of 1a (0.13 g, 1.0 mmol) and H2O (0.40 mL, 22 mmol) was added CH2Cl2/HFIP (16 mL/4 mL) at 0 ºC. HTIB (0.51 g, 1.3 mmol) was added dropwise. The mixture was stirred for 5 min at the same temperature. NaBH4 was added (0.19 g, 5.0 mmol) at room temperature. The mixture was stirred for 70 min and H2O was added. The
resulting mixture was extracted with EtOAc. The organic layer was washed with brine and dried over anhydrous MgSO₄. The solvent was removed under reduce pressure and the crude product was purified by column (0-20% EtOAc in hexane) giving 9a (0.109 g, 0.736 mmol, 74%) as a light yellow oil.

Supplementary Information

Supplementary information concerning spectroscopic data, experimental procedures and NMR copies are available free of charge at http://jbcs.sbq.org.br as PDF file.

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References


10. For an example, see discussion at Silva Jr., L. F.; Craveiro, M. V.; Org. Lett. 2008, 10, 5417.


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Supplementary Information

Metal-Free Synthesis of Indanes by Iodine(III)-Mediated Ring Contraction of 1,2-Dihydronaphthalenes

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Experimental

General information

HTIB was used as received. Methanol and acetonitrile were distilled from magnesium turnings and CaH₂, respectively. These solvents were stored in a bottle containing 4 Å molecular sieves. THF and Et₂O were freshly distilled from sodium/benzophenone. Column chromatography was performed using silica gel 200-400 mesh. TLC analyses were performed using silica gel plates, using solutions of phosphomolybdic acid and p-anisaldehyde for visualization. NMR spectra were recorded using CDCl₃ as solvent and TMS as internal pattern. The substrates 1a, 1b, 1c, 1e, 1g, 1h, 1j and 1k were prepared as previously described.1-3 See the previous communication for experimental procedures of the HTIB oxidations in MeOH with 1a, 1b, 1c, 1d and 1g, and in MeCN with 1a, 1g and 1l.4

Preparation of 1,2-dihydronaphthalenes

7-Acetamido-1,2-dihydronaphthalene (1d)

In a solution of 6-amino-1-tetralone (1.00 g, 6.21 mmol) and DMAP (0.020 g) in Et₃N (25 mL) was added Ac₂O (2.0 mL). The mixture was stirred for 1 h at room temperature. The reaction was quenched with MeOH (10 mL) and H₂O (15 mL), extracted with EtOAc (3 × 15 mL), washed with brine (2 × 10 mL) and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography (silica gel 200-400 mesh, 60% EtOAc in hexanes) giving 6-acetamido-1-tetralone5 (92%, 1.16 g, 5.72 mmol) as a light-yellow solid; mp 124.5-126.7 ºC (124.5-125 ºC); ¹H NMR (200 MHz, CDCl₃) δ 2.02-2.17 (m, 2H), 2.22 (s, 3H), 2.62 (t, 2H, J 6.5 Hz), 2.92 (t, 2H, J 6.0 Hz), 7.27 (dd, 1H, J 2.4 and 8.6 Hz), 7.72 (s, 1H), 7.96 (d, 1H, J 8.4 Hz), 8.31 (1H, s); ¹³C NMR (75 MHz, CDCl₃) δ 23.2, 24.7, 29.9, 38.9, 117.5, 118.5, 128.4, 142.7, 146.3, 169.0, 197.7.

To a stirred solution of 6-acetamido-1-tetralone (1.12 g, 5.50 mmol) in anhydrous MeOH (70 mL) was added NaBH₄ (0.25 g, 6.61 mmol) in portions at 0 ºC. The mixture was stirred for 1 h at room temperature. The reaction was quenched with H₂O (20 mL) and a 10% aqueous solution of HCl was added dropwise until pH ca. 7. The resulting solution was extracted with EtOAc (3 × 15 mL), washed with brine (20 mL) and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure giving 6-acetamido-1-tetralol (78%, 0.882 mg, 4.30 mmol) as a pale-yellow solid. The 1-tetralol (0.841 g, 4.10 mmol) was used without purification in a dehydration reaction using toluene (45 mL), a few crystals of p-TsOH and reaction time of 3 h at 130 ºC, using a Dean-Stark apparatus. The resulting residue was purified by flash chromatography (silica gel 200-400 mesh, 80% EtOAc in hexanes) affording 1d (95%, 0.728 g, 3.89 mmol) as a pale-yellow solid. Experimental data has not been previously reported: mp: 89.3-90.6 ºC; IR v max/cm⁻¹ (film) 497, 566, 684, 834, 883, 1018, 1266, 1328, 1370, 1421, 1536, 1594, 1666, 2829, 2883, 2933, 3032,
Metal-Free Synthesis of Indanes by Iodine(III)-Mediated


3297: ¹H NMR (200 MHz, CDCl₃) δ 2.14 (s, 3H), 2.20-2.31 (m, 2H), 2.72 (t, 2H, J 8.1 Hz), 5.90-5.99 (m, 1H), 6.40 (d, 1H, J 9.6 Hz), 6.92 (d, 1H, J 8.0 Hz), 7.23 (dd, 1H, J 2.2 and 8.0 Hz), 7.31 (s, 1H), 7.89 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 22.9, 24.4, 27.6, 117.8, 119.4, 126.1, 127.0, 127.6, 130.4, 136.3, 136.5, 168.6; LRMS m/z (%) 187 (M⁺, 72%), 146 (9), 144 (100), 143 (100), 130 (29), 115 (24), 91 (8), 77 (6), 51 (5), 43 (23); HRMS (m/z) calcd. for C₁₂H₁₃NO [M + H]⁺ 188.1070, found 188.1067.

1,2-Dihydro-6-methoxynaphthalene (1f)

NaBH₄ (0.455 g, 12.0 mmol) was added dropwise to a solution of 7-methoxy-1-tetralone (1.52 g, 8.63 mmol) in MeOH (50 mL) at 0 ºC. The mixture was stirred at room temperature. After 2 h, the reaction was quenched with H₂O and a 10% aqueous solution of HCl was added dropwise until pH ca. 5. The MeOH was removed under reduced pressure and the residue was extracted with EtOAc, washed with brine, and dried over anhydrous MgSO₄. The crude product was transferred to an Erlenmeyer and diluted with Et₂O. A sat. solution of NaHCO₃ was added until ca. pH 7. The solution was extracted with Et₂O, washed with sat. solution of NaCl and dried over anhydrous MgSO₄. The residue was purified by flash column chromatography (gradient elution, 0-30% of EtOAc in hexanes), affording 5j (1.08 g, 6.20 mmol, 62%), as a colorless oil.

1,2-Dihydro-7-methoxy-4-methylnaphthalene (1i)

A solution of 6-methoxy-1-tetralone (1.76 g, 10.0 mmol) in Et₂O (7.0 mL) was added to a solution of MeMgI [prepared from MeI (1.7 mL, 27.0 mmol), Mg (0.673 g, 27.7 mmol) and I₂ (some crystals) in anhydrous Et₂O (7.0 mL)]. The mixture was refluxed for 4.5 h. After that, a solution of HCl 6 mol L⁻¹ (6 mL) was added dropwise at 0 ºC. The solution was stirred for 15 min at room temperature. The organic layer was washed with brine and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (gradient elution, 0-30% of EtOAc in hexanes), affording 5j (1.08 g, 6.20 mmol, 62%), as a colorless oil.

4-n-Butyl-1,2-dihydro-1-methylnaphthalene (II)

The reaction was performed as indicated for 1i. A mixture of 4-methyl-1-tetralone (1.42 g, 8.86 mmol) in Et₂O (12.0 mL) was added to a solution of n-BuMgI [prepared from 1-bromobutane (1.46 g, 10.6 mmol), Mg (0.245 g, 10.1 mmol), I₂ (some crystals) and anhydrous Et₂O (12.0 mL)]. The mixture was refluxed for 3 h. The crude product was purified by flash column chromatography (gradient elution, 0-5% of EtOAc in hexanes), affording the olefin 1l (0.805 g, 4.02 mmol, 45%), as a colorless oil. Starting material was recovered (0.214 g, 1.34 mmol, 15%).

1,2-Dihydro-4-isopropyl-1-methylnaphthalene (1m)

The reaction was performed as indicated for 1i. A mixture of 4-methyl-1-tetralone (0.961 g, 6.00 mmol) in Et₂O (4.0 mL), i-PrMgI [prepared from 2-bromopropane (1.93 g, 15.7 mmol), Mg (0.321 g, 13.2 mmol), I₂ (some crystals) in anhydrous Et₂O (6.0 mL)] was stirred for 5.5 h. The crude product was purified by flash column chromatography (gradient elution, 0-20% of EtOAc in hexanes), affording 1m (0.387 g, 2.08 mmol, 35%) as a colorless oil.

1,2-Dihydro-1-methyl-4-phenylnaphthalene (1n)

The reaction was performed as indicated for 1i. A mixture of 4-methyl-1-tetralone (0.641 g, 4.00 mmol) in Et₂O (0.5 mL) and PhMgBr [prepared from bromobenzene...
(0.792 g, 5.04 mmol), Mg (0.117 g, 4.81 mmol), I₂ (some crystals) in anhydrous Et₂O (1.0 mL) was refluxed for 1.5 h. The crude product was purified by flash column chromatography (gradient elution, 10-15% of EtOAc in hexanes), affording the 1,2-dihydronaphthalene 1n (0.682 g, 3.10 mmol, 78%), as a colorless oil.

4-(3,4-Dichlorophenyl)1,2-dihydro-1-methylnaphthalene (1o)

The reaction was performed as indicated for 1i. A mixture of 4-methyl-1-tetralone (0.645 g, 4.03 mmol) in Et₂O (0.5 mL) and 1,2-ClPhMgBr [prepared from 4-bromo-1,2-dichlorobenzene (1.15 g, 5.09 mmol), Mg (0.117 g, 4.81 mmol), I₂ (some crystals) in anhydrous Et₂O (1.0 mL)] was refluxed for 2 h. The crude product was purified by flash column chromatography (gradient elution, 10-30% of EtOAc in hexanes), affording the 1-(3,4-dichlorophenyl)-1,2,3,4-tetrahydro-4-methylnaphthalen-1-ol (0.870 g, 2.83 mmol, 70%), as a colorless oil. The isolated alcohol was dissolved in anhydrous toluene (3.5 mL). Some crystals of p-toluenesulfonic acid were added to that solution. The reaction was refluxed for 6 h. The reaction was extracted with EtOAc. The organic phase was washed with H₂O, saturated solution of NaHCO₃, saturated solution of NaCl and dried over anhydrous MgSO₄. The crude product was purified by flash column chromatography (isocratic elution with hexanes), furnishing the desired alkene 1o (0.385 g, 1.33 mmol, 56%), as a colorless oil; IR ν₃000/cm⁻¹ (film) 1121, 1258, 1515, 2830, 2934; ¹H NMR (300 MHz, CDCl₃) δ 19.8, 31.4, 32.1, 125.3, 126.2, 126.2, 127.4, 127.7, 128.1, 130.2, 130.5, 131.0, 132.3, 133.4, 137.5, 140.9, 141.5; HRMS (m/z) calcd. for C₁₄H₂₀O₄ [M + Na]⁺ 275.1254, found 275.1252.

6,7-Dihydro-9-methyl-5H-benzo[7]annulene (1p)

The reaction was performed as indicated for 1i. A mixture of 1-benzosuberone (0.481 g, 3.00 mmol) in anhydrous Et₂O (2.0 mL), MeMgI [prepared from MeI (0.5 mL, 8.10 mmol), Mg (0.202 g, 8.31 mmol) and I₂ (some crystals) in anhydrous Et₂O (2.0 mL)] was stirred for 4 h under reflux. The crude product was purified by flash column chromatography (gradient elution, 0-10% of EtOAc in hexanes), affording 1p (0.403 g, 2.55 mmol, 85%), as a colorless oil.

References

1. Ferraz, H. M. C.; Carneiro, V. M. T.; Silva Jr., L. F.; Synthesis 2009, 385 (see ref. 13 in the article).
Figure S1. $^1$H NMR spectrum of 2d (CDCl$_3$, TMS, 200 MHz, $\delta$).

Figure S2. $^{13}$C NMR spectrum of 2d (CDCl$_3$, TMS, 50 MHz, $\delta$).
Figure S3. $^1$H NMR spectrum of trans-3d (CDCl$_3$, TMS, 200 MHz, δ).

Figure S4. $^1$H NMR spectrum of cis-3d (CDCl$_3$, TMS, 200 MHz, δ).
Figure S5. $^{13}$C NMR spectrum of $cis$-3d (CDCl$_3$, TMS, 75 MHz, $\delta$).

Figure S6. $^1$H NMR spectrum of $cis$-3f (CDCl$_3$, TMS, 500 MHz, $\delta$).
Figure S7. $^{13}$C NMR spectrum of cis-3f (CDCl$_3$, TMS, 75 MHz, $\delta$).

Figure S8. $^1$H NMR spectrum of 2g (CDCl$_3$, TMS, 300 MHz, $\delta$).
Figure S9. $^{13}$C NMR spectrum of 2g (CDCl$_3$, TMS, 75 MHz, δ).

Figure S10. $^{1}$H NMR spectrum of trans-3g (CDCl$_3$, TMS, 300 MHz, δ).
Figure S11. $^{13}$C NMR spectrum of trans-3g (CDCl$_3$, TMS, 75 MHz, $\delta$).

Figure S12. $^1$H NMR spectrum of 1o (CDCl$_3$, TMS, 300 MHz, $\delta$).
Figure S13. $^1$H NMR spectrum of 1o (CDCl$_3$, TMS, 300 MHz, $\delta$) - expansion.

Figure S14. $^{13}$C NMR spectrum of 1o (CDCl$_3$, TMS, 75 MHz, $\delta$).
Figure S15. $^{13}$C NMR spectrum of 1o (CDCl$_3$, TMS, 75 MHz, $\delta$) - expansion.

Figure S16. DEPT 135 spectrum of 1o (CDCl$_3$, TMS, 75 MHz, $\delta$).
Figure S17. $^1$H NMR spectrum of $1q$ (CDCl$_3$, TMS, 400 MHz, δ).

Figure S18. $^{13}$C NMR spectrum of $1q$ (CDCl$_3$, TMS, 75 MHz, δ).
Figure S19. $^1$H NMR spectrum of $5I$ (CDCl$_3$, TMS, 300 MHz, $\delta$).

Figure S20. $^{13}$C NMR spectrum of $5I$ (CDCl$_3$, TMS, 75 MHz, $\delta$).
Figure S21. $^1$H NMR spectrum of 5m (CDCl$_3$, TMS, 300 MHz, $\delta$).

Figure S22. $^{13}$C NMR spectrum of 5m (CDCl$_3$, TMS, 75 MHz, $\delta$).
Figure S23. $^1$H NMR spectrum of 5n (CDCl$_3$, TMS, 500 MHz, $\delta$).

Figure S24. $^{13}$C NMR spectrum of 5n (CDCl$_3$, TMS, 75 MHz, $\delta$).
Figure S25. DEPT 135 spectrum of 5n (CDCl₃, TMS, 75 MHz, δ).

Figure S26. ¹H NMR spectrum of 6n (CDCl₃, TMS, 300 MHz, δ).
Figure S27. $^{13}$C NMR spectrum of 6n (CDCl$_3$, TMS, 75 MHz, $\delta$).

Figure S28. $^1$H NMR spectrum of 5o (CDCl$_3$, TMS, 500 MHz, $\delta$).
Figure S29. $^1$H NMR spectrum of 5o (CDCl$_3$, TMS, 500 MHz, $\delta$) - expansion.

Figure S30. $^{13}$C NMR spectrum of 5o (CDCl$_3$, TMS, 125 MHz, $\delta$).
Figure S31. $^{13}$C NMR spectrum of 5o (CDCl$_3$, TMS, 125 MHz, $\delta$) - expansion.

Figure S32. DEPT 135 spectrum of 5o (CDCl$_3$, TMS, 125 MHz, $\delta$).
Figure S33. $^1$H NMR spectrum of $8a$ (CDCl$_3$, TMS, 300 MHz, $\delta$).

Figure S34. $^{13}$C NMR spectrum of $8a$ (CDCl$_3$, TMS, 75 MHz, $\delta$).
Figure S35. $^1$H NMR spectrum of $8b$ (CDCl$_3$, TMS, 300 MHz, $\delta$).

Figure S36. $^{13}$C NMR spectrum of $8b$ (CDCl$_3$, TMS, 75 MHz, $\delta$).
Figure S37. $^1$H NMR spectrum of $8q$ (CDCl$_3$, TMS, 300 MHz, $\delta$).

Figure S38. $^{13}$C NMR spectrum of $8q$ (CDCl$_3$, TMS, 125 MHz, $\delta$).
Figure S39. $^{13}$C NMR spectrum of 8q (CDCl$_3$, TMS, 125 MHz, $\delta$) – expansions.

Figure S40. $^1$H NMR spectrum of 10a (CDCl$_3$, TMS, 200 MHz, $\delta$).
Figure S41. $^{13}$C NMR spectrum of 10a (CDCl$_3$, TMS, 50 MHz, $\delta$).

Figure S42. $^1$H NMR spectrum of 9a (CDCl$_3$, TMS, 200 MHz, $\delta$).
Figure S43. $^{13}$C NMR spectrum of 9a (CDCl$_3$, TMS, 50 MHz, δ).