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Construction of functionalized indans by thallium(III) promoted ring contraction of 3-alkenols

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Abstract—An efficient four step protocol for the construction of functionalized indans was developed. 1-Tetralones were transformed into unsaturated esters by Reformatsky reaction with bromo-esters (ethyl 2-bromopropionate, ethyl bromoacetate or ethyl 2-bromobutyrate), followed by dehydration of the β-hydroxy-ester formed. Reduction of the ester moiety led to homoallylic alcohols bearing an endocyclic double bond. The oxidative rearrangement of these 3-alkenols was performed by thallium trinitrate (TTN) in a 2:1 mixture of AcOH/H_2O, leading to the ring contraction products in moderate to very good yield. Fourteen examples of this sequence were studied. The oxidation of 3-alkenols prepared from 2-tetralones with TTN was also investigated. With these substrates the ring contraction reaction was not observed.

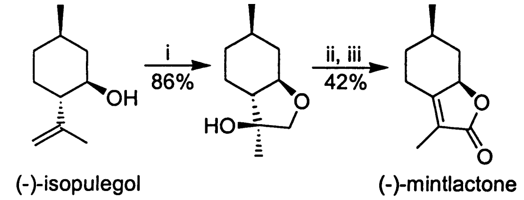
1. Introduction

The reaction of alkenols with thallium(III) salts has been reported in several papers.[1] The most studied substrates were 4-alkenols, which led to cyclic ethers (tetrahydrofurans and/or tetrahydropyrans) by electrophilic cyclization when treated with thallium(III).[2–11]

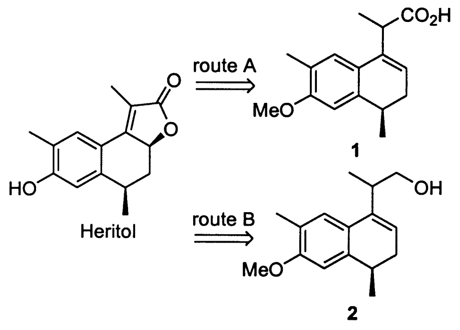
The reaction of 3-alkenols with thallium(III) salts has also been described in some papers. The cyclization of a number of homoallylic alcohols with thallium(III) salts led to tetrahydrofurans.[3,11–14] This reaction has been performed under several different conditions. A short total synthesis of (−)-mintlactone was recently achieved by thallium(III) induced cyclization of (−)-isopulegol, a monoterpenic 3-alkenol, as the key step[15] (Scheme 1). However, electrophilic cyclization is not the only possible reaction between 3-alkenols and thallium(III) salts. Kocovský et al.[5,6,16] showed that a successful fragmentation reaction can also take place treating some 3-alkenols bearing an endocyclic double bond with TTN.

Unsaturated carboxylic acids can also undergo thallium(III) mediated cyclization, leading to the corresponding lactones.[17]

Recently, we planned the total synthesis of heritol,[18] using a thallium(III) promoted cyclization to construct the lactone moiety. In our synthetic plan, it was considered that the heritol could be synthesized through two possible routes, where **1** and **2** would be the key intermediates, as depicted in Scheme 2. To check the feasibility of the route A, the behavior of β,γ-unsaturated carboxylic acids analogous to **1** was investigated.[19] Unfortunately, in this study only decarboxylation products were obtained, after treatment with TTA. Therefore, we decided to investigate the route B, which is similar to that employed for the synthesis of mintlactone (cf. Scheme 1). In our preliminary communication of this work,[20] we report our studies concerning the



Scheme 1. *Reagents and conditions*: (i) TTA, AcOH/H_2O (1:1), 40 min, rt; (ii) $SOCl_2$, Et_2O, 24 h, rt; (iii) $CrO_3·2py$, CH_2Cl_2.



Scheme 2.

Keywords: thallium trinitrate; ring contraction; indans; alkenols; homoallylic alcohols.

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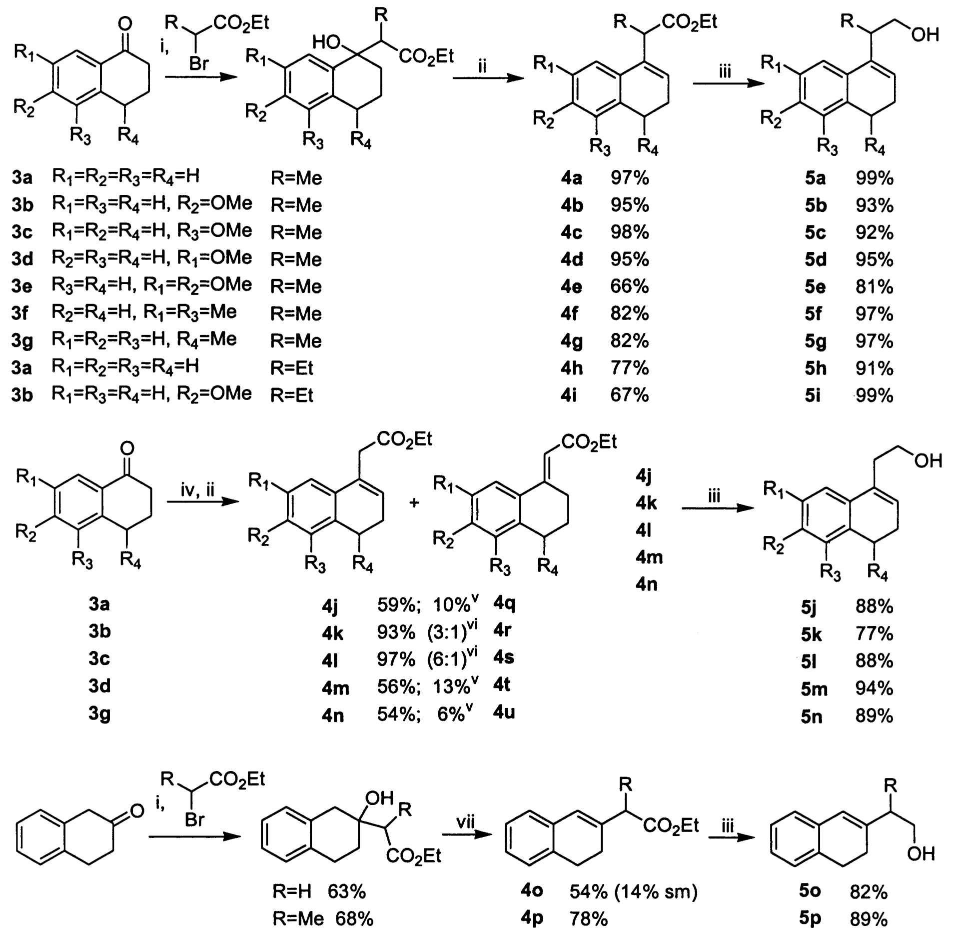


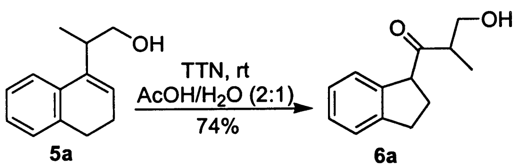
Scheme 3. *Reagents and conditions*: (i) Zn, benzene, I_2 (cat), reflux; (ii) 6 M HCl, THF, rt; (iii) $LiAlH_4$, THF, 0°C; (iv) $BrCH_2CO_2Et$, Zn, benzene, I_2 (cat), reflux; (v) isolated yield for each ester; (vi) crude yield and ratio of the isomeric esters; (vii) *p*-TsOH, benzene, reflux.

reaction of two alkenols such as **2** with thallium(III) salts. These reactions do not furnish any cyclization product, leading exclusively to the corresponding ring contraction products in very good yields. If at the first sight this result was disappointed and useless, we quickly realized that this reaction could overcome the drawback of our methodology for the construction of indans from 1,2-dihydronaphthalenes by thallium(III) promoted ring contraction.[21] In such a study, it was observed that ring contraction products can only be obtained with substrates that do not bear an alkyl group at double bond.

In the present paper, we describe a systematic study exploring the scope and limitations of the mentioned thallium(III) promoted rearrangement of 3-alkenols, as a tool for synthesizing functionalized indans,[22] which are an important moiety on several compounds of remarkable biological activities, such as Crixivan®[23] and Aricept®.[24] These compounds are used in the treatment of AIDS and Alzheimer, respectively.

2. Results and discussion

The preparation of the 3-alkenols **5a–p** was performed in three steps from commercially available tetralones, as shown in Scheme 3. Thus, Reformatsky reaction of the tetralones **3a–g** with ethyl 2-bromopropionate or ethyl 2-bromobutyrate led to the corresponding β-hydroxy-esters, which were dehydrated without purification with 6 M HCl in THF, giving the products **4a–i**. Reduction of these esters with lithium aluminum hydride gave the desired substrates **5a–i**, in excellent yield. This sequence was also performed with the tetralones **3a–d** and **3g** and ethyl bromoacetate, allowing the preparation of the 3-alkenols **5j–n**. However, in these reactions the desired β,γ-unsaturated esters **4j–n** were obtained together with significant amounts of the α,β-unsaturated isomers **4q–u**. The isomeric esters were easily separated by flash chromatography. The preparation of the alkenols **5o** and **5p** was similar to the alkenols **5a–n**, except that the dehydration of the corresponding hydroxy-esters was performed by *p*-TsOH in refluxing benzene. Using HCl in THF, as for the alkenols **5a–n**, the starting material was recovered.



Scheme 4.

Table 1. TTN-mediated rearrangement of **5b–i**

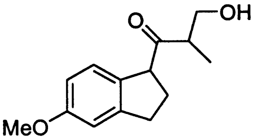
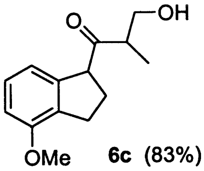
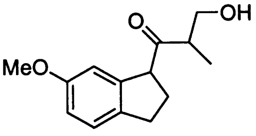
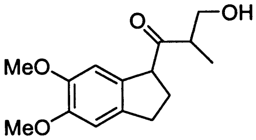
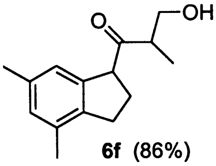
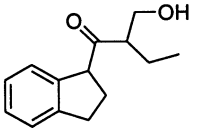
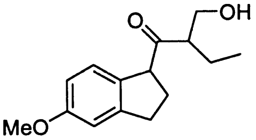
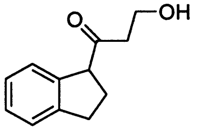
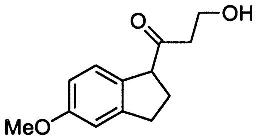
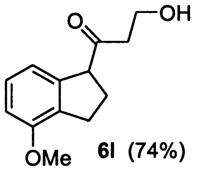
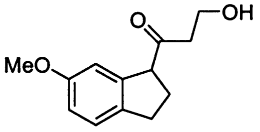
Entry	Substrate	Product (yield)
1	**5b**	 **6b** (79%)
2	**5c**	 **6c** (83%)
3	**5d**	 **6d** (82%)
4	**5e**	 **6e** (89%)
5	**5f**	 **6f** (86%)
6	**5h**	 **6h** (65%)
7	**5i**	 **6i** (68%)

Table 2. TTN-mediated rearrangement of **5j–m**

Entry	Substrate	Product (yield)
1	**5j**	 **6j** (73%)
2	**5k**	 **6k** (72%)
3	**5l**	 **6l** (74%)
4	**5m**	 **6m** (70%)

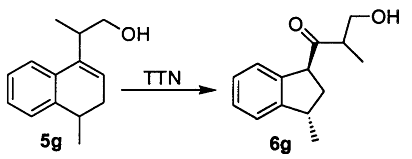
Having an efficient way to prepare 3-alkenols, we turned our attention to their reaction with thallium(III) salts. Firstly, the behavior of the alkenol **5a** was investigated. Several conditions were tested and better results were obtained by performing the reaction with TTN in a 2:1 mixture of AcOH/H_2O at room temperature.[25] In such a condition, after 15 min, an oxidative rearrangement took place smoothly, leading to the indan **6a** as the only isolated product (Scheme 4). Under all the conditions studied, we could not find any evidence in the ^1H NMR spectra for the formation of cyclization products.

To check the generality of the above mentioned rearrangement, the reaction of the 3-alkenols **5b–f** and **5h–m** with TTN, under similar conditions, was then investigated, as shown in Tables 1 and 2. Alkenols derived from ethyl 2-bromopropionate (**5b–f**, entries 1–5, Table 1) always gave better yields than those prepared from ethyl 2-bromobutyrate (**5h** and **5i**, entries 6 and 7, Table 1) and ethyl bromoacetate (**5j–m**, entries 1–4, Table 2). Somewhat surprisingly, it was not observed any difference in reactivity between substrates bearing methoxy groups at the *para* position of the migrating carbon (entry 1, Table 1 and entry 2, Table 2) and at the *meta* position (entries 2 and 3, Table 1 and entries 3 and 4, Table 2). Dimethoxy- and dimethyl-substituted substrates (entries 4 and 5, respectively, Table 1) also furnished ring contraction products in very good yields.

It is worth noting that the ring contraction products **6a–f** and **6h** and **6i** possess two chiral centers and, therefore, it could be expected that these products would be obtained as a mixture of diastereomers. However, a single set of signals was observed in the ^1H and ^{13}C NMR spectra, thus meaning that probably a single diastereomer has been formed in each case. A possible explanation could be the formation of a chelate between the hydroxyl group and the thallium(III), similarly to that observed in the oxymercuration of 3- and 4-alkenols, which occurs with high degree of diastereoselectivity.[26]

The reaction of the alkenols **5g** and **5n**, which bear a methyl group at the non-aromatic ring, was also studied. Treatment of **5g** with TTN, under the same conditions used for the other alkenols, furnished the ring contraction product **6g** in 53% yield, together with 34% of the starting material (entry 1, Table 3). Similar results were obtained utilizing longer reaction times (entries 2 and 3), excess of TTN (entry 4) and different ratio of AcOH/H_2O (entry 5). Although a significant amount of starting material was recovered, this reaction appears to be synthetically useful, because only the *trans*-1,3-disubstituted indan was obtained. The *trans*

Table 3. Reaction of **5g** with TTN

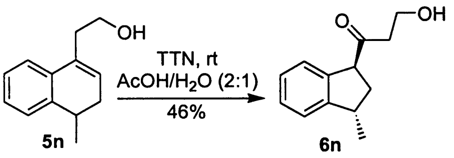


Entry	Conditions	**6g**[a] (%)	**5g**[b] (%)
1	1.1 TTN, AcOH/H_2O (2:1), 25 min	53	34
2	1.1 TTN, AcOH/H_2O (2:1), 40 min	34	30
3	1.1 TTN, AcOH/H_2O (2:1), 1 h	37	33
4	2 TTN, AcOH/H_2O (2:1), 1 h	43	17
5	1.2 TTN, AcOH/H_2O (1:1), 1 h	37	33

[a] Isolated yield; based on the total amount of s.m. utilized.

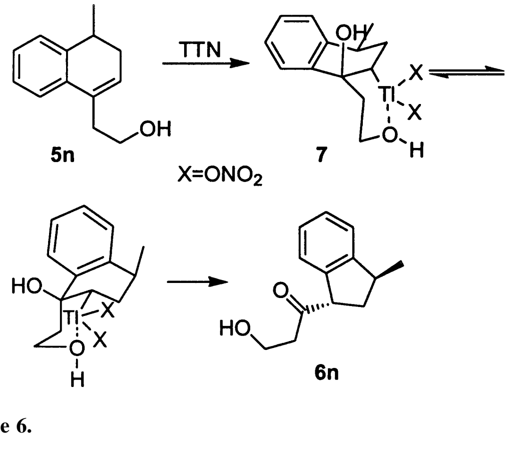
[b] Starting material recovered after flash chromatography.

relationship in **6g** was determined by comparison of its NMR data with those of other indans previously prepared.[27] The alkenol **5n** reacts with TTN similarly to **5g**, giving only the diastereomer **6n**, in 46% yield (Scheme 5).

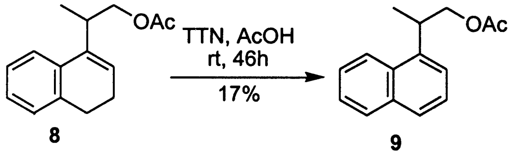


Scheme 5.

The formation of the *trans*-1,3-indans can be explained by the mechanism shown in Scheme 6, exemplified for **5n**. Thus, the *trans* diaxial addition of the thallium(III) led to the oxythallated adduct **7**. After ring inversion, to reach the required anti-periplanar conformation of the migrating carbon and the thallium-carbon bond, the rearrangement takes place, leading to the *trans* isomer. To check the role of the hydroxy group in the course of the reaction, the acetate **8**, derived from the alkenol **5a**, was prepared and submitted to treatment with TTN. To oxidize the acetate **8** it was necessary 46 h, being obtained a black oil from which it was possible to isolate only the naphthalene **9**,[28] in 17% yield, as depicted in Scheme 7. Therefore, it seems that the hydroxy group of the side chain plays an important role in the reaction. From our point of view, this group allows good solubilization of the substrate, as well as chelation with the thallium(III), which would facilitate the electrophilic addition.

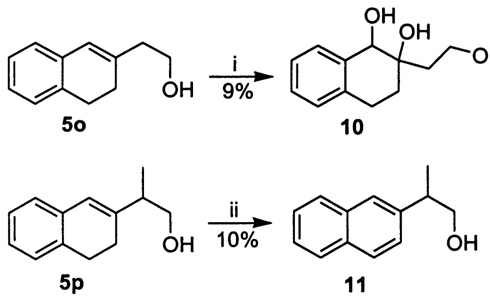


Scheme 6.



Scheme 7.

Our next goal was the study of the thallium(III) promoted oxidation of the alkenols **5o** and **5p**, which were prepared from 2-tetralone. Although we anticipated that the ring contraction reaction could be troublesome with such substrates,[29] we hoped the cyclization reaction would occur instead. Eventually, it was found that the oxidation of **5o** and **5p** with TTN under different conditions led always to a mixture of several compounds. We were able to isolate and characterize only the triol **10** and the naphthalene **11**,[28] both in poor yield, as shown in Scheme 8.



Scheme 8. *Reagents and conditions*: (i) TTN, AcOH/H_2O (2:1), rt; (ii) TTN, AcOH, rt.

In conclusion, a four step protocol was developed to transform commercially available 1-tetralones into highly functionalized indans in very good overall yield. The key step in this sequence is a thallium(III) mediated ring contraction of 3-alkenols. Moreover, in addition to cyclization and fragmentation reactions previously described in the literature, this paper shows that a third reaction pathway, an oxidative rearrangement, can be observed by the treatment of a 3-alkenol bearing an endocyclic double bond with thallium(III) salts.

3. Experimental

Warning! thallium salts are toxic and must be handled with care.

3.1. General

1-Tetralone (**3a**), 2-tetralone, ethyl bromoacetate and ethyl 2-bromopropionate were purchased from Aldrich and distilled prior to use. Zinc powder was activated by washing several times with 10% aqueous HCl, water, saturated aqueous $HgCl_2$, water and acetone. The zinc obtained was then dried in an oven (ca. 120°C) and storaged in a desiccator. Benzene was distilled from sodium wire and storaged in a bottle also containing sodium wire. THF was freshly distilled from sodium/benzophenone for the reduction reactions and used as received for the dehydration reactions. Other reagents were used as received from Aldrich and/or Acros. Column chromatography was performed using silica gel Acros 200–400 Mesh. TLC analyses were performed with silica gel plates Merck, using vanilline or *p*-anisaldehyde solution for visualization. ^{1}H and ^{13}C NMR spectra were recorded on Bruker spectrometers. IR spectra were measured on a Perkin–Elmer 1750-FT. Gas chromatography analyses were performed in a HP-6890 series II. Melting points are uncorrected. High resolution mass spectra on a VG Autospec/Fission Instrument.

3.1.1. 2-(3,4-Dihydro-naphthalen-1-yl)-propionic acid ethyl ester (4a). General procedure for the preparation of the esters 4a–n. To a stirred suspension of Zn (1.57 g, 24.0 mmol), benzene (40 mL), 1-tetralone (2.92 g, 20.0 mmol) and iodine (one crystal) was added ethyl 2-bromopropionate (2.9 mL, 22 mmol). The mixture was refluxed (CAUTION! a vigorous reflux is observed in the beginning) for 2.5 h and 10% aqueous H$_2$SO$_4$ was added at 0°C. The aqueous phase was extracted two times with AcOEt, washed two times with brine and dried over anhydrous MgSO$_4$. The solvent was removed under reduced pressure to give a residue (4.81 g), which was submitted to the dehydration reaction without purification.

To a stirred solution of the crude hydroxy-ester in THF (20 mL) was added an aqueous solution of HCl (6 M, 20 mL). The mixture was stirred for 2 h at room temperature. The aqueous phase was extracted two times with ethyl acetate, washed with saturated aqueous NaHCO$_3$, water and brine, and dried over anhydrous MgSO$_4$. The solvent was removed under reduced pressure to give **4a** (4.33 g, 18.8 mmol, 94%). An analytical sample was prepared by distillation (115°C/0.35 mmHg): colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.19 (t, J=7.1 Hz, 3H), 1.42 (d, J=7.1 Hz, 3H), 2.26–2.30 (m, 2H), 2.71–2.75 (m, 2H), 3.72 (q, J=7.1 Hz, 1H), 4.12 (q, J=7.1 Hz, 2H), 6.02 (t, J=4.7 Hz, 1H), 7.12–7.28 (m, 4H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 14.1, 17.0, 23.1, 28.2, 41.5, 60.6, 122.4, 125.8, 126.4, 126.8, 127.7, 134.2, 136.2, 136.8, 175.1.

3.1.2. 2-(6-Methoxy-3,4-dihydro-naphthalen-1-yl)-propionic acid ethyl ester (4b). Colorless oil; bp: 145°C/0.15 mmHg; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.19 (t, J=7.1 Hz, 3H), 1.41 (d, J=7.1 Hz, 3H), 2.23–2.30 (m, 2H), 2.69–2.74 (m, 2H); 3.69 (q, J=7.1 Hz, 1H), 3.79 (s, 3H), 4.12 (q, J=7.1 Hz, 2H), 5.89 (t, J=4.0 Hz, 1H), 6.69–6.73 (m, 2H), 7.19–7.22 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.1, 16.9, 23.0, 28.7, 41.7, 55.2, 60.6, 110.9, 114.0, 123.3, 123.6, 127.3, 135.7, 138.6, 158.4, 175.2.

3.1.3. 2-(5-Methoxy-3,4-dihydro-naphthalen-1-yl)-propionic acid ethyl ester (4c). Pale yellow oil; bp: 135°C/0.25 mmHg; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.18 (t, J=7.1 Hz, 3H), 1.41 (d, J=7.1 Hz, 3H), 2.21–2.78 (m, 2H), 2.71–2.77 (m, 2H), 3.71 (q, J=7.1 Hz, 1H), 3.81 (s, 3H), 4.11 (q, J=7.1 Hz, 2H), 6.02 (t, J=4.7 Hz, 1H), 6.77 (d, J=8.2 Hz, 1H), 6.93 (d, J=7.8 Hz, 1H), 7.14 (t, J=8.1 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.1, 17.1, 19.7, 22.5, 41.8, 55.5, 60.6, 109.7, 115.4, 124.7, 126.0, 126.4, 135.3, 136.0, 156.2, 175.2.

3.1.4. 2-(7-Methoxy-3,4-dihydro-naphthalen-1-yl)-propionic acid ethyl ester (4d). Pale yellow oil; bp: 131°C/0.20 mmHg; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.19 (t, J=7.1 Hz, 3H), 1.42 (d, J=7.1 Hz, 3H), 2.22–2.29 (m, 2H), 2.62–2.68 (m, 2H), 3.69 (q, J=7.1 Hz, 1H), 3.76 (s, 3H), 4.12 (q, J=7.1 Hz, 2H), 6.04 (t, J=4.3 Hz, 1H), 6.67 (dd, J=2.5 and 8.2 Hz, 1H), 6.89 (d, J=2.5 Hz), 7.03 (d, J=8.2 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.1, 17.0, 23.5, 27.2, 41.6, 55.2, 60.6, 109.2, 111.4, 126.5, 128.3, 128.8, 135.2, 136.1, 158.4, 175.0.

3.1.5. 2-(6,7-Dimethoxy-3,4-dihydro-naphthalen-1-yl)-propionic acid ethyl ester (4e). Colorless oil; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.20 (t, J=6.8 Hz, 3H), 1.44 (d, J=6.8 Hz, 3H), 2.23–2.30 (m, 2H), 2.64–2.72 (m, 2H), 3.68 (q, J=6.8 Hz, 1H), 3.87 (s, 3H), 3.88 (s, 3H), 4.13 (q, J=6.8 Hz, 2H), 5.94 (t, J=4.5 Hz, 1H), 6.70 (s, 1H), 6.92 (s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.2, 16.8, 23.3, 27.9, 42.0, 56.0, 56.2, 60.7, 107.5, 111.7, 123.8, 127.1, 129.6, 135.7, 147.3, 147.7, 175.2.

3.1.6. 2-(5,7-Dimethyl-3,4-dihydro-naphthalen-1-yl)-propionic acid ethyl ester (4f). Pale yellow oil; ^{1}H NMR (200 MHz, CDCl$_3$) δ 1.20 (t, J=7.2 Hz, 3H), 1.41 (d, J=7.2 Hz, 3H), 2.20–2.30 (m, 2H), 2.25 (s, 3H), 2.28 (s, 3H), 2.60–2.68 (m, 2H), 3.72 (q, J=7.2 Hz, 1H), 4.13 (q, J=7.2 Hz, 2H), 6.00 (t, J=4.4 Hz, 1H), 6.87 (s, 1H), 6.98 (s, 1H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 14.1, 17.2, 19.7, 21.2, 22.9, 23.4, 41.6, 60.5, 121.2, 125.2, 125.3, 129.7, 131.9, 134.0, 134.8, 136.3, 175.3.

3.1.7. 2-(4-Methyl-3,4-dihydro-naphthalen-1-yl)-propionic acid ethyl ester (4g). Colorless oil; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.13–1.23 (m, 6H), 1.42–1.45 (m, 3H), 2.05–2.18 (m, 1H), 2.40–2.51 (m, 1H), 2.81–2.93 (m, 1H), 3.70–3.78 (m, 1H), 4.11 (quintet, J=7.1 Hz, 2H), 5.91–5.95 (m, 1H), 7.16–7.21 (m, 3H), 7.26–7.31 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.1, 16.7, 17.1, 19.8, 20.0, 30.8, 31.0, 32.1, 32.1, 41.4, 41.5, 60.58, 60.61, 122.5, 122.6, 124.0, 124.3, 126.25, 126.29, 126.5, 127.2, 133.3, 135.4, 135.7, 141.7, 141.8, 175.1.

3.1.8. 2-(3,4-Dihydro-naphthalen-1-yl)-butyric acid ethyl ester (4h). Pale yellow oil; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.95 (t, J=7.4 Hz, 3H), 1.20 (t, J=7.1 Hz, 3H), 1.69–1.83 (m, 1H), 1.91–2.06 (m, 1H), 2.24–2.30 (m, 1H), 2.72 (t, J=7.8 Hz, 2H), 3.49 (dd, J=6.4 and 8.4 Hz, 1H), 4.14 (q, J=7.1 Hz, 1H), 6.06 (t, J=4.6 Hz, 1H), 7.11–7.21 (m, 3H), 7.33 (d, J=7.4 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 12.4, 14.2, 23.1, 25.2, 28.3, 49.0, 60.5, 122.5, 126.4, 126.8, 127.7, 134.5, 134.9, 136.8, 174.4.

3.1.9. 2-(6-Methoxy-3,4-dihydro-naphthalen-1-yl)-butyric acid ethyl ester (4i). Yellow oil; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.95 (t, J=7.4 Hz, 3H), 1.20 (t, J=7.1 Hz, 3H), 1.66–1.80 (m, 1H), 1.93–2.02 (m, 1H), 2.22–2.29 (m, 2H), 2.70 (t, J=7.8 Hz, 2H), 3.44 (dd, J=6.6 and 8.2 Hz, 1H), 3.79 (s, 3H), 4.13 (q, J=7.1 Hz, 2H), 5.93 (t, J=4.6 Hz, 1H), 6.70–6.74 (m, 2H), 7.24–7.27 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 12.4, 14.2, 23.1, 25.1, 28.8, 49.3, 55.2, 60.5, 110.9, 114.0, 123.8, 123.9, 127.6, 134.5, 138.7, 158.5, 174.5.

3.1.10. 2-(3,4-Dihydro-naphthalen-1-yl)-acetic acid ethyl ester (4j). Colorless oil; ^{1}H NMR (200 MHz, CDCl$_3$) δ 1.23 (t, J=7.2 Hz, 3H), 2.26–2.36 (m, 2H), 2.75–2.83 (m, 3H), 3.42 (s, 1H), 3.43 (s, 1H), 4.14 (q, J=7.2 Hz, 3H), 5.99 (t, J=4.5 Hz, 1H), 7.11–7.19 (m, 4H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 14.2, 23.2, 28.0, 39.2, 60.7, 122.6, 126.4, 127.0, 127.6, 129.1, 130.2, 134.3, 136.3, 171.9.

4q: colorless oil; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.32 (t, J=7.2 Hz, 3H), 1.85 (quintet, J=6.2 Hz, 2H), 2.79 (t, J=6.2 Hz, 2H), 3.15–3.23 (m, 2H), 4.20 (q, J=7.2 Hz, 2H), 6.33 (t, J=2 Hz, 1H), 7.12–7.31 (m, 3H), 7.63–7.67 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.4, 22.8, 28.1, 30.2, 59.7, 112.6, 124.8, 126.4, 129.2, 129.5, 134.3, 140.3, 154.7, 167.1.

3.1.11. 2-(6-Methoxy-3,4-dihydro-naphthalen-1-yl)-acetic acid ethyl ester (4k). Pale yellow oil; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.23 (t, J=7.1 Hz, 3H), 2.26–2.33 (m, 2H), 2.76 (t, J=8.2 Hz, 2H), 3.39 (s, 1H), 3.40 (s, 1H), 3.79 (s, 3H), 4.14 (q, J=7.1 Hz, 2H), 5.86 (t, J=4.5 Hz, 1H), 6.68–6.72 (m, 2H), 7.10–7.13 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.2, 23.2, 28.6, 39.3, 55.2, 60.7, 110.9, 114.0, 123.9, 126.5, 127.5, 129.9, 138.2, 158.6, 172.0.

4r: pale yellow oil; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.31 (t, J=7.1 Hz, 3H), 1.83 (quintet, J=6.4 Hz, 2H), 2.76 (t, J=6.2 Hz, 1H), 3.15–3.20 (m, 2H), 3.80 (s, 3H), 4.19 (q, J=7.1 Hz, 2H), 6.23 (t, J=1.8 Hz, 1H), 6.64 (d, J=2.7 Hz, 1H), 6.74 (dd, J=2.7 and 8.8 Hz, 1H), 7.61 (d, J=8.8 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.4, 22.7, 28.2, 30.7, 55.3, 59.5, 110.3, 112.9, 113.3, 126.5, 126.9, 142.2, 154.6, 160.7, 167.3.

3.1.12. 2-(5-Methoxy-3,4-dihydro-naphthalen-1-yl)-acetic acid ethyl ester (4l). Pale yellow oil; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.21 (t, J=7.1 Hz, 3H), 2.24–2.31 (m, 2H), 2.79 (t, J=8.1 Hz, 2H), 3.40 (s, 1H), 3.41 (s, 1H), 3.81 (s, 3H), 4.13 (q, J=7.1 Hz, 2H), 5.99 (t, J=4.6 Hz, 1H), 6.77 (d, J=8.2 Hz, 1H), 6.84 (d, J=7.6 Hz, 1H), 7.13 (t, J=8.0 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.2, 19.7, 22.7, 39.6, 55.6, 60.7, 109.9, 115.7, 124.2, 126.5, 129.3, 130.1, 135.3, 156.2, 171.9.

4s: white solid; mp: 44°C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.31 (t, J=7.1 Hz, 3H), 1.85 (quintet, J=1.85 Hz, 2H), 2.74 (t, J=6.3 Hz, 2H), 3.13–3.17 (m, 2H), 3.82 (s, 3H), 4.20 (q, J=7.1 Hz, 2H), 6.32 (t, J=1.5 Hz, 1H), 6.81–6.84 (m, 1H), 7.15 (t, J=8.0 Hz, 1H), 7.24–7.27 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.4, 22.4, 23.1, 27.3, 55.5, 59.7, 110.6, 112.7, 117.0, 126.3, 129.0, 135.5, 155.3, 157.1, 167.1.

3.1.13. 2-(7-Methoxy-3,4-dihydro-naphthalen-1-yl)-acetic acid ethyl ester (4m). Pale yellow oil; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.23 (t, J=7.1 Hz, 3H), 2.25–2.32 (m, 1H), 2.71 (t, J=8.0 Hz, 2H), 3.40 (s, 1H), 3.41 (s, 1H), 3.77 (s, 3H), 4.14 (q, J=7.1 Hz, 2H), 6.01 (t, J=4.6 Hz, 1H), 6.68 (dd, J=2.6 and 8.2 Hz, 1H), 6.79 (d, J=2.6 Hz, 1H), 7.03 (d, J=8.2 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.1, 23.5, 27.0, 39.2, 55.2, 60.6, 109.3, 111.5, 128.1, 128.4, 129.6, 130.1, 135.2, 158.3, 171.7.

4t: pale yellow oil; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.32 (t, J=7.1 Hz, 3H), 1.83 (quintet, J=6.2 Hz, 2H), 2.73 (t, J=6.2 Hz, 2H), 3.14–3.19 (m, 2H), 3.81 (s, 3H) 4.21 (q, J=7.1 Hz, 2H), 6.30 (t, J=1.9 Hz, 1H), 6.86 (dd, J=2.6 and 8.4 Hz, 1H), 7.05 (d, J=8.4 Hz, 1H), 7.14 (d, J= 2.6 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.3, 22.9, 28.0, 29.3, 55.4, 59.7, 109.0, 112.5, 116.4, 130.0, 132.8, 135.0, 154.7, 158.0, 167.0.

3.1.14. 2-(4-Methyl-3,4-dihydro-naphthalen-1-yl)-acetic acid ethyl ester (4n). Colorless oil; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.18 (d, J=7.1 Hz, 3H), 1.24 (d, J=7.1 Hz, 3H), 2.08–2.18 (m, 1H), 2.44–2.53 (m, 1H), 2.91 (sx, J=6.9 Hz, 1H), 3.36–3.50 (m, 2H), 4.11 (q, J=7.1 Hz, 3H), 5.89–5.92 (m, 1H), 7.15–7.31 (m, 4H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.2, 20.1, 31.1, 32.2, 39.2, 60.7, 122.8, 126.28, 126.30, 127.4, 127.6, 129.7, 133.4, 141.3, 171.9.

4u: colorless oil; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.27–1.33 (m, 6H), 1.56–1.67 (m, 1H), 1.89–2.00 (m, 1H), 2.87–2.93 (m, 1H), 3.13–3.28 (m, 2H), 4.20 (q, J=7.1 Hz, 2H), 6.30 (t, J=2.0 Hz, 1H), 7.15–7.32 (m, 3H), 7.59–7.62 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.3, 20.7, 25.3, 29.8, 33.0, 59.5, 112.5, 124.9, 126.2, 127.4, 129.6, 133.8, 144.9, 154.9, 166.9.

3.1.15. 2-(3,4-Dihydro-naphthalen-2-yl)-acetic acid ethyl ester (4o). General procedure for the preparation of the esters 4o–p. The Reformatsky reaction was performed as above, using 2-tetralone (5.85 g, 40.0 mmol), benzene (80 mL), Zn (3.14 g, 48 mmol), ethyl bromoacetate (4.9 mL, 44 mmol), iodine (one crystal) and 3.5 h under reflux. The residue was distilled (135°C, 0.3 mmHg), giving the corresponding hydroxy-ester (5.89 g, 25.1 mmol, 63%) as yellow oil.

To a stirred solution of the hydroxy-ester (4.69 g, 20.0 mmol) in anhydrous benzene (20 mL), was added *p*-toluenesulfonic acid monohydrate (40 mg). The mixture was refluxed for 48 h using Dean–Stark apparatus and, then, poured into water. The aqueous phase was extracted twice with ethyl acetate. The combined organic phases were washed with brine and dried over anhydrous MgSO$_4$. The solvent was removed under reduced pressure. The residue was purified by flash chromatography (gradient elution, 5–20% ethyl acetate in hexane) giving the starting material (0.643 g, 2.74 mmol, 14%) and ester **4o** (2.34 g, 2.74 mmol, 54%): colorless oil; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.26 (t, J=7.1 Hz, 3H), 2.35 (t, J=8.1 Hz, 2H), 2.84 (t, J=8.1 Hz, 2H), 3.20 (s, 2H), 4.16 (q, J=7.1 Hz, 2H), 6.34 (s, 1H), 6.98–7.02 (m, 1H), 7.08–7.16 (m, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.2, 27.2, 28.0, 43.0, 60.6, 125.9, 126.1, 126.4, 126.8, 127.2, 134.0, 134.2, 134.5, 171.2.

3.1.16. 2-(3,4-Dihydro-2-naphthalen-1-yl)-propionic acid ethyl ester (4p). Colorless oil; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.24 (t, J=7.1 Hz, 1H), 1.35 (t, J=7.1 Hz, 1H), 2.27–2.36 (m, 2H), 2.80 (t, J=8.0 Hz, 2H), 3.21–3.34 (m, 1H), 4.14 (q,

J=7.1 Hz, 2H), 6.34 (d, J=0.9 Hz, 1H), 6.99–7.16 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 15.6, 25.3, 28.2, 46.7, 60.6, 124.1, 126.0, 126.5, 126.8, 127.2, 128.3, 134.3, 134.8, 174.1.

3.1.17. 2-(3,4-Dihydro-1-naphthalen-1-yl)-propan-1-ol (5a). General procedure for the preparation of the 3-alkenols 5a–p. To a stirred suspension of $LiAlH_4$ (3.24 g, 85.0 mmol) in anhydrous THF (85 mL) was added dropwise, over a period of 30 min and at 0°C, a solution of the ester **4a** (19.7 g, 85.4 mmol) in anhydrous THF (85 mL). The mixture was stirred at room temperature for 2 h and water was carefully added dropwise, followed by 10% aqueous H_2SO_4. The aqueous phase was extracted two times with ethyl acetate, washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure giving the alkenol **5a** (15.9 g, 84.4 mmol, 99%): viscous colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.22 (d, J=6.9 Hz, 3H), 2.22–2.33 (m, 2H), 2.68–2.76 (m, 2H), 3.09 (sx, J=6.5 Hz, 1H), 3.55–3.64 (m, 1H), 3.71–3.79 (m, 1H), 5.94 (m, 1H), 7.14–7.34 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 16.9, 23.0, 28.4, 36.3, 66.7, 122.2, 124.2, 126.4, 126.8, 127.8, 134.6, 137.0, 138.0.

3.1.18. 2-(6-Methoxy-3,4-dihydro-1-naphthalen-1-yl)-propan-1-ol (5b). White solid; mp: 67°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19 (d, J=6.9 Hz, 3H), 2.19–2.29 (m, 2H), 2.68 (t, J=6.8 Hz, 2H), 3.01 (sx, J=6.5 Hz, 1H), 3.51–3.57 (m, 1H), 3.69–3.74 (m, 1H), 3.78 (s, 3H), 5.78–5.81 (m, 1H), 6.66–6.73 (m, 2H), 7.22–7.25 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.9, 23.0, 28.9, 36.5, 55.2, 66.8, 110.9, 114.0, 121.6, 123.5, 127.7, 137.7, 138.8, 158.5.

3.1.19. 2-(5-Methoxy-3,4-dihydro-1-naphthalen-1-yl)-propan-1-ol (5c). Pale yellow solid; mp: 65°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18 (d, J=6.9 Hz, 3H), 2.16–2.28 (m, 2H), 2.57–2.68 (m, 1H), 2.76–2.86 (m, 1H), 3.02 (sx, J=6.5 Hz, 1H), 3.53–3.58 (m, 1H), 3.70–3.75 (m, 1H), 3.83 (s, 3H), 5.93–5.96 (m, 1H), 6.78 (d, J=8.2 Hz, 1H), 6.98 (d, J=7.8 Hz, 1H), 7.15 (t, J=8.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.0, 19.9, 22.5, 36.7, 55.6, 66.9, 109.7, 115.3, 124.4, 125.0, 126.4, 135.8, 137.9, 156.2.

3.1.20. 2-(7-Methoxy-3,4-dihydro-1-naphthalen-1-yl)-propan-1-ol (5d). Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.21 (d, J=6.9 Hz, 3H), 2.21–2.28 (m, 2H), 2.65 (t, J=7.9 Hz, 2H), 3.03 (sx, J=6.6 Hz, 1H), 3.56–3.62 (m, 1H), 3.71–3.77 (m, 1H), 3.80 (s, 3H), 5.95–5.98 (m, 1H), 6.70 (dd, J=2.6 and 8.2 Hz, 1H), 6.90 (d, J=2.6 Hz, 1H), 7.07 (d, J=8.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.0, 23.4, 27.5, 36.5, 55.3, 68.4, 109.4, 110.9, 124.8, 128.3, 129.2, 135.7, 138.0, 158.4.

3.1.21. 2-(6,7-Dimethoxy-3,4-dihydro-1-naphthalen-1-yl)-propan-1-ol (5e). Viscous pale yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.20 (d, J=6.9 Hz, 3H), 2.18–2.29 (m, 2H), 2.60–2.68 (m, 2H), 3.02 (sx, J=6.5 Hz, 1H), 3.55–3.63 (m, 1H), 3.70–3.78 (m, 1H), 3.87 (s, 3H), 3.88 (s, 3H), 5.84 (t, J=4.5 Hz, 1H), 6.71 (s, 1H), 6.90 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 17.0, 23.2, 28.1, 36.6, 56.0, 56.3, 66.8, 107.1, 111.6, 122.0, 127.4, 129.9, 137.7, 147.3, 147.7.

3.1.22. 2-(5,7-Dimethyl-3,4-dihydro-1-naphthalen-1-yl)-propan-1-ol (5f). Viscous pale yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.20 (d, J=6.9 Hz, 3H), 2.18–2.23 (m, 2H), 2.26 (s, 3H), 2.30 (s, 3H), 2.48–2.76 (m, 2H), 3.08 (sx, J=6.5 Hz, 1H), 3.53–3.61 (m, 1H), 3.69–3.77 (m, 1H), 5.93 (t, J=4.4 Hz, 1H), 6.88 (s, 1H), 7.03 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 17.1, 19.8, 21.2, 22.8, 23.6, 36.4, 66.9, 121.0, 123.8, 129.7, 132.2, 134.4, 134.8, 134.9, 138.2.

3.1.23. 2-(4-Methyl-3,4-dihydro-1-naphthalen-1-yl)-propan-1-ol (5g). Viscous colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.17–1.25 (m, 6H), 1.99–2.19 (m, 1H), 2.35–2.53 (m, 1H), 2.78–2.91 (m, 1H), 3.09 (sx, J=6.5 Hz, 1H), 3.53–3.63 (m, 1H), 3.71–3.80 (m, 1H), 5.81–5.89 (m, 1H), 7.18–7.24 (m, 3H), 7.32–7.37 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 16.8, 17.0, 19.5, 20.0, 30.7, 30.9, 32.1, 36.3, 66.7, 66.8, 122.2, 122.3, 122.4, 122.6, 126.1, 126.19, 126.25, 126.6, 127.1, 133.6, 133.8, 137.2, 137.5, 141.7, 141.9.

3.1.24. 2-(3,4-Dihydro-1-naphthalen-1-yl)-butan-1-ol (5h). Viscous colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, J=7.4 Hz, 3H), 1.51–1.74 (m, 3H), 2.25–2.31 (m, 2H), 2.72 (m, 2H), 2.88 (quintet, J=6.3 Hz, 1H), 3.63–3.77 (m, 2H), 5.93 (t, J=4.7 Hz, 1H), 7.13–7.24 (m, 3H), 7.33 (d, J=7.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.8, 23.1, 24.1, 28.6, 43.9, 65.2, 122.4, 124.8, 126.4, 126.8, 127.8, 135.2, 136.8.

3.1.25. 2-(6-Methoxy-3,4-dihydro-1-naphthalen-1-yl)-butan-1-ol (5i). Viscous pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, J=7.4 Hz, 3H), 1.49–1.74 (m, 2H), 1.8 (br s, 1H), 2.22–2.29 (m, 2H), 2.70 (t, J=7.9 Hz, 2H), 2.83 (quintet, J=6.4 Hz, 1H), 3.61–3.78 (m, 2H), 3.79 (s, 3H), 5.80 (t, J=4.5 Hz, 1H), 6.70–6.74 (m, 2H), 7.23–7.26 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.8, 23.0, 24.0, 29.1, 44.0, 55.2, 65.1, 110.9, 114.0, 122.3, 123.6, 128.3, 136.4, 138.9, 158.4.

3.1.26. 2-(6-Methoxy-3,4-dihydro-1-naphthalen-1-yl)-ethan-1-ol (5k). Viscous pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.99 (br s, 1H), 2.20–2.27 (m, 2H), 2.66–2.74 (m, 4H), 3.74 (t, J=6.6 Hz, 2H), 3.78 (s, 3H), 5.80 (t, J=4.5 Hz, 1H), 6.68–6.71 (m, 2H), 7.14–7.17 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.1, 28.9, 36.1, 55.2, 61.2, 110.9, 114.0, 123.8, 124.8, 127.4, 132.4, 138.6, 158.5.

3.1.27. 2-(5-Methoxy-3,4-dihydro-1-naphthalen-1-yl)-ethan-1-ol (5l). Viscous colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.21–2.28 (m, 2H), 2.70–2.78 (m, 4H), 3.76 (t, J=6.4 Hz, 2H), 3.83 (s, 3H), 5.96 (t, J=4.5 Hz, 1H), 6.80 (d, J=8.2 Hz, 1H), 6.91 (d, J=7.7 Hz, 1H), 7.13–7.19 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.0, 22.5, 36.4, 55.6, 61.3, 109.8, 115.6, 124.7, 126.5, 127.8, 132.6, 135.3, 156.3.

3.1.28. 2-(7-Methoxy-3,4-dihydro-1-naphthalen-1-yl)-ethan-1-ol (5m). Viscous pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.84 (br s, 1H), 2.12–2.18 (m, 2H), 2.55–2.63 (m, 4H), 3.66–3.70 (m, 2H), 3.69 (s, 3H), 5.86 (t, J=4.5 Hz, 1H), 6.59 (dd, J=2.6 and 8.2 Hz, 1H), 6.74 (d, J=2.6, 1H), 6.96 (d, J=8.2 Hz, 1H); ^{13}C NMR (75 MHz,

$CDCl_3$) δ 23.4, 27.3, 35.9, 55.2, 61.0, 109.5, 111.0, 127.9, 128.2, 128.8, 132.6, 135.3, 158.3.

3.1.29. 2-(4-Methyl-3,4-dihydro-1-naphthalen-1-yl)-ethan-1-ol (5n). Viscous colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.22 (d, J=7.0 Hz, 3H), 2.04–2.13 (m, 1H), 2.39–2.48 (m, 1H), 2.70–2.75 (m, 2H), 2.87 (sx, J=7.0 Hz, 1H), 3.78 (t, J=6.5 Hz, 2H), 5.86 (t, J=4.5 Hz, 1H), 7.16–7.21 (m, 3H); 7.23–7.27 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.0, 31.1, 32.2, 36.0, 61.3, 122.8, 125.9, 126.27, 126.34, 127.3, 132.2, 133.4, 141.6.

3.1.30. 2-(3,4-Dihydro-2-naphthalen-1-yl)-ethan-1-ol (5o). Viscous colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.89 (br s, 1H), 2.24 (t, J=8.0 Hz, 2H), 2.43 (dt, J=0.7 and 6.4 Hz, 2H), 2.80 (t, J=8.1 Hz, 2H), 3.75 (t, J=6.4 Hz, 2H), 6.28 (t, J=1.2 Hz, 1H), 6.96–6.98 (m, 1H), 7.06–7.13 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.2, 28.1, 40.6, 60.5, 124.7, 125.6, 126.0, 126.5 (×2), 127.2, 134.4, 138.0.

3.1.31. 2-(3,4-Dihydro-2-naphthalen-1-yl)-propan-1-ol (5p). Viscous colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10 (d, J=6.9 Hz, 3H), 2.13 (br s, 1H), 2.19–2.25 (m, 1H), 2.51 (sx, J=6.6 Hz, 1H), 2.78 (t, J=8.1 Hz, 2H), 3.51–3.63 (m, 2H), 6.30 (d, J=0.8 Hz, 1H), 6.98–7.01 (m, 1H), 7.07–7.15 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.3, 24.8, 28.2, 43.5, 65.6, 123.7, 125.2, 126.50, 126.54, 127.2, 134.3, 134.8.

3.1.32. 1-(2,3-Dihydro-1*H*-inden-1-yl)-3-hydroxy-2-methyl-propan-1-one (6a). General procedure for the thallium(III) mediated oxidation of the alkenols 5a–p. To a stirred solution of **5a** (0.128 g, 0.677 mmol) in acetic acid/H_2O (2:1, 3.6 mL) was added TTN·3H_2O (0.33 g, 0.75 mmol), which promptly dissolved. The mixture was stirred for 15 min and an abundant precipitation was observed. $NaHCO_3$ was carefully added dropwise. After slowly addition of water and ethyl acetate, the aqueous phase was extracted two times with ethyl acetate. The organic phase was then washed with brine and dried over anhydrous $MgSO_4$. The residue was purified by flash chromatography (gradient elution, 30–40% ethyl acetate in hexane) immediately after concentration of the solvent under reduced pressure, giving the indan **6a** (0.102 g, 0.500 mmol, 74%): viscous colorless oil; IR (film): 3478, 1706 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.14 (d, J=7.2 Hz, 3H), 2.0 (br s, 1H), 2.19–2.48 (m, 2H), 2.86–3.20 (m, 3H), 3.59–3.82 (m, 2H), 4.28 (dd, J=5.6 and 8.3 Hz, 1H), 7.11–7.28 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.7, 28.6, 32.0, 46.8, 57.0, 64.5, 124.7, 124.9, 126.4, 127.5, 140.9, 144.7, 215.1; MS *m/z* (%) 204 (M^+, 12), 117 (100), 91 (7), 87 (13). HRMS calcd for $C_{13}H_{16}O_2$ 204.1150, found 204.1147.

3.1.33. 1-(5-Methoxy-2,3-dihydro-1*H*-inden-1-yl)-3-hydroxy-2-methyl-propan-1-one (6b). The reaction was performed following the general procedure, using **5b** (0.100 g, 0.458 mmol), acetic acid/H_2O (2:1, 2.5 mL), TTN·3H_2O (0.23 g, 0.51 mmol) and reaction time of 20 min. The residue was purified by flash chromatography (gradient elution, 30–40% ethyl acetate in hexane) giving the indan **6b** (0.085 g, 0.36 mmol, 79%): viscous colorless oil; IR (film): 3496, 2938, 1706 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.09 (d, J=7.2 Hz, 3H), 2.22–2.42 (m, 2H), 2.68 (br s, 1H), 2.83–2.93 (m, 1H), 3.00–3.11 (m, 2H), 3.55–3.60 (m, 1H), 3.71–3.77 (m, 1H), 3.75 (s, 3H), 4.18 (dd, J=5.3 and 8.3 Hz, 1H), 6.70 (dd, 2.5 and 8.3 Hz, 1H), 6.79 (d, J=2.5 Hz, 1H), 7.13 (d, J=8.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 28.9, 32.2, 46.5, 55.4, 56.2, 64.5, 110.2, 112.5, 125.3, 133.0, 146.4, 160.0, 215.3; MS *m/z* (%) 234 (M^+, 3), 147 (100), 115 (5), 91 (7). HRMS calcd for $C_{14}H_{18}O_3$ 234.1256, found 234.1258.

3.1.34. 1-(4-Methoxy-2,3-dihydro-1*H*-inden-1-yl)-3-hydroxy-2-methyl-propan-1-one (6c). The reaction was performed following the general procedure, using **5c** (0.226 g, 1.04 mmol), acetic acid/H_2O (2:1, 4.8 mL), TTN·3H_2O (0.47 g, 1.1 mmol) and reaction time of 15 min. The residue was purified by flash chromatography (gradient elution, 30–50% ethyl acetate in hexane) giving the indan **6c** (0.188 g, 0.860 mmol, 83%): viscous colorless oil; IR (film): 3455, 2939, 1704 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08 (d, J=7.2 Hz, 3H), 2.23–2.42 (m, 2H), 2.83–2.93 (m, 1H), 2.97–3.08 (m, 2H), 3.55–3.62 (m, 1H), 3.71–3.77 (m, 1H), 3.80 (s, 3H), 4.26 (dd, J=5.4 and 8.5 Hz, 1H), 6.71 (d, J=8.1 Hz, 1H), 6.85 (d, J=7.6 Hz, 1H), 7.14 (t, J=7.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 28.3, 28.8, 46.7, 55.2, 57.5, 64.4, 109.1, 117.0, 128.1, 132.5, 142.7, 156.3, 215.1; MS *m/z* (%) 234 (M^+, 11), 147 (100), 115 (9), 91 (12). HRMS calcd for $C_{14}H_{18}O_3$ 234.1256, found 234.1254.

3.1.35. 1-(6-Methoxy-2,3-dihydro-1*H*-inden-1-yl)-3-hydroxy-2-methyl-propan-1-one (6d). The reaction was performed following the general procedure, using **5d** (0.115 g, 0.527 mmol), acetic acid/H_2O (2:1, 3 mL), TTN·3H_2O (0.26 g, 0.58 mmol) and reaction time of 20 min. The residue was purified by flash chromatography (gradient elution, 30–40% ethyl acetate in hexane) giving the indan **6d** (0.101 g, 0.431 mmol, 82%): viscous pale yellow oil; IR (film): 3478, 2938, 1706, 1493 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11 (d, J=7.2 Hz, 3H), 2.24–2.43 (m, 3H), 2.81–2.91 (m, 1H), 2.97–3.09 (m, 2H), 3.60–3.65 (m, 1H), 3.74–3.80 (m, 1H), 3.76 (s, 3H), 4.23 (dd, J=5.8 and 8.2 Hz, 1H), 6.76 (dd, J=2.3 and 8.2 Hz, 1H), 6.80 (d, J=2.3 Hz, 1H), 7.14 (d, J=8.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 29.2, 31.2, 46.8, 55.5, 57.3, 64.6, 110.3, 113.6, 125.3, 136.6, 142.3, 158.7, 215.1; MS *m/z* (%) 234 (M^+, 11), 147 (100), 115 (7). HRMS calcd for $C_{14}H_{18}O_3$ 234.1256, found 234.1256.

3.1.36. 1-(5,7-Dimethoxy-2,3-dihydro-1*H*-inden-1-yl)-3-hydroxy-2-methyl-propan-1-one (6e). The reaction was performed following the general procedure, using **5e** (0.140 g, 0.557 mmol), acetic acid/H_2O (2:1, 3 mL), TTN·3H_2O (0.27 g, 0.61 mmol) and reaction time of 20 min. The residue was purified by flash chromatography (gradient elution, 40–60% ethyl acetate in hexane) giving the indan **6e** (0.130 g, 0.493 mmol, 89%): white solid; mp: 72°C; IR (film): 3550, 3324, 1705 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.99 (d, 7.2 Hz, 3H), 2.21–2.34 (m, 3H), 2.53 (br s, 1H), 2.73–3.04 (m, 3H), 3.48–3.56 (m, 1H), 3.65–3.71 (m, 1H), 3.74 (s, 3H), 3.76 (s, 3H), 4.11 (t, J=6.9 Hz, 1H), 6.69 (s, 1H), 6.71 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.7, 28.8, 31.8, 46.4, 55.8, 56.0, 57.2, 64.5, 107.7, 107.8, 132.2, 136.5, 147.9, 148.9, 215.5; MS *m/z*

(%) 264 (M^+, 5), 177 (100), 146 (25), 131 (9), 91 (8). HRMS calcd for $C_{15}H_{20}O_4$ 264.1362, found 264.1358.

3.1.37. 1-(4,6-Dimethyl-2,3-dihydro-1*H*-inden-1-yl)-3-hydroxy-2-methyl-propan-1-one (6f). The reaction was performed following the general procedure, using **5f** (0.172 g, 0.794 mmol), acetic acid/H_2O (2:1, 4 mL), TTN·$3H_2O$ (0.39 g, 0.87 mmol) and reaction time of 15 min. The residue was purified by flash chromatography (gradient elution, 20–40% ethyl acetate in hexane) giving the indan **6f** (0.158 g, 0.679 mmol, 86%): viscous colorless oil; IR (film): 3444, 2935, 1703 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.11 (d, J=7.2 Hz, 3H), 2.21 (s, 3H), 2.27 (s, 3H), 2.29–2.44 (m, 2H), 2.72–3.08 (m, 4H), 3.56–3.63 (m, 1H), 3.70–3.79 (m, 1H), 4.24 (dd, J=5.5 and 8.2 Hz, 1H), 6.84 (s, 1H), 6.88 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.6, 19.0, 21.0, 28.1, 30.2, 46.5, 56.9, 64.3, 122.4, 129.2, 133.9, 136.2, 140.4, 140.6, 215.4; MS *m*/*z* (%) 232 (M^+, 8), 145 (100), 129 (11), 115 (9), 105 (4). HRMS calcd for $C_{15}H_{20}O_2$ 232.1463, found 232.1342.

3.1.38. 1-(*trans*-3-Methyl-2,3-dihydro-1*H*-inden-1-yl)-3-hydroxy-2-methyl-propan-1-one (6g). The reaction was performed following the general procedure, using **5g** (0.233 g, 1.15 mmol), acetic acid/H_2O (2:1, 6 mL), TTN·$3H_2O$ (0.56 g, 1.3 mmol) and reaction time of 25 min. The residue was purified by flash chromatography (gradient elution, 20–30% ethyl acetate in hexane) giving the starting material (0.0799 g, 0.395 mmol, 34%) and the indan **6g** (0.133 g, 0.608 mmol, 53%): viscous colorless oil; IR (film): 3467, 2958, 2929, 2871, 1707, 757 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.12 (d, J=7.2 Hz, 3H), 1.28 (d, J=6.8 Hz, 3H), 1.75–1.90 (m, 1H), 2.5 (br s, 1H), 2.54–2.66 (m, 1H), 2.97–3.13 (m, 1H), 3.42 (sx, J=7.2 Hz, 1H), 3.51–3.59 (m, 1H), 3.66–3.75 (m, 1H), 4.26 (dd, J=3.1 and 8.6 Hz, 1H), 7.12–7.27 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.7, 20.1, 37.6, 38.4, 46.2, 55.6, 64.3, 123.8, 124.6, 126.5, 127.7, 140.2, 149.2, 214.7; MS *m*/*z* (%) 218 (M+, 11), 200 (17), 169 (7), 131 (100), 115 (32). HRMS calcd for $C_{14}H_{18}O_2$ 218.1307, found 218.1313.

3.1.39. 1-(2,3-Dihydro-1*H*-inden-1-yl)-3-hydroxy-2-ethyl-propan-1-one (6h). The reaction was performed following the general procedure, using **5h** (0.179 g, 0.884 mmol), acetic acid/H_2O (2:1, 4.5 mL), TTN·$3H_2O$ (0.43 g, 0.97 mmol) and reaction time of 20 min. The residue was purified by flash chromatography (gradient elution, 30–40% ethyl acetate in hexane) giving the starting material (0.015 g, 0.075 mmol, 8%) and the indan **6h** (0.125 g, 0.573 mmol, 65%): viscous colorless oil; IR (film): 3456, 2964, 1704 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, J=7.5 Hz, 3H), 1.48–1.77 (m, 2H), 2.20–2.41 (m, 3H), 2.86–2.99 (m, 2H), 3.04–3.14 (m, 1H), 3.64–3.82 (m, 2H), 4.26 (dd, J=5.3 and 8.3 Hz, 1H), 7.11–7.27 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.8, 21.5, 28.7, 32.0, 54.1, 57.5, 62.5, 124.8, 125.0, 126.4, 127.5, 140.9, 144.7, 214.7; HRMS calcd for $C_{14}H_{18}O_2$ 218.1307, found 218.1302.

3.1.40. 1-(5-Methoxy-2,3-dihydro-1*H*-inden-1-yl)-3-hydroxy-2-ethyl-propan-1-one (6i). The reaction was performed following the general procedure, using **5i** (0.100 g, 0.431 mmol), acetic acid/H_2O (2:1, 2.5 mL), TTN·$3H_2O$ (0.21 g, 0.474 mmol) and reaction time of 15 min. The residue was purified by flash chromatography (gradient elution, 20–40% ethyl acetate in hexane) giving the indan **6i** (0.0722 g, 0.291 mmol, 68%): viscous pale yellow oil; IR (film): 3484, 2938, 1702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, J=7.5 Hz, 3H), 1.48–1.74 (m, 2 H), 2.21–2.48 (m, 3H), 2.83–2.97 (m, 2H), 3.01–3.12 (m, 1H), 3.64–3.82 (m, 2H), 3.77 (s, 3H), 4.18 (dd, J=5.0 and 8.3 Hz, 1H), 6.70 (dd, J=2.5 and 8.3 Hz, 1H), 6.79 (d, J=2.4 Hz, 1H), 7.16 (d, J=8.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.9, 21.5, 29.0, 32.2, 53.8, 55.4, 56.7, 62.6, 110.4, 112.5, 125.3, 132.9, 146.4, 159.7; HRMS calcd for $C_{15}H_{20}O_3$ 248.1412, found 248.1448.

3.1.41. 1-(2,3-Dihydro-1*H*-inden-1-yl)-3-hydroxy-propan-1-one (6j). The reaction was performed following the general procedure, using **5j** (0.489 g, 2.79 mmol), acetic acid/H_2O (2:1, 15 mL), TTN.$3H_2O$ (1.36 g, 3.07 mmol) and reaction time of 20 min. The residue was purified by flash chromatography (gradient elution, 30–40% ethyl acetate in hexane) giving the indan **6j** (0.388 g, 2.04 mmol, 73%): viscous colorless oil; IR (film): 3410, 1706 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.28–2.39 (m, 2H), 2.62–2.89 (m, 3H), 2.90–3.17 (m, 2H), 3.82 (t, J= 5.8 Hz, 2H), 4.10 (t, J=7.0 Hz, 1H), 7.15–7.29 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 28.6, 31.9, 42.2, 57.9, 58.5, 124.8, 125.0, 126.6, 127.7, 140.5, 144.6, 211.8; MS *m*/*z* (%) 190 (M^+, 11), 172 (1), 117 (100), 91 (13), 73 (7). HRMS calcd for $C_{12}H_{14}O_2$ 190.0994, found 190.1080.

3.1.42. 1-(5-Methoxy-2,3-dihydro-1*H*-inden-1-yl)-3-hydroxy-propan-1-one (6k). The reaction was performed following the general procedure, using **5k** (0.146 g, 0.715 mmol), acetic acid/H_2O (2:1, 3.5 mL), TTN·$3H_2O$ (0.35 g, 0.79 mmol) and reaction time of 20 min. The residue was purified by flash chromatography (gradient elution, 30–40% ethyl acetate in hexane) giving the indan **6k** (0.113 g, 0.513 mmol, 72%): viscous pale yellow oil; IR (film): 3497, 2942, 1708 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.33 (q, J=7.1 Hz, 2H), 2.64–2.82 (m, 2H), 2.85–2.95 (m, 1H), 3.00–3.10 (m, 1H), 3.77 (s, 3H), 3.78–3.83 (m, 2H), 4.03 (t, J=6.9 Hz, 1H), 6.73 (dd, J=2.5 and 8.3 Hz, 1H), 6.80 (d, J=2.5 Hz, 1H), 7.15 (d, J=8.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.9, 32.1, 42.0, 55.4, 57.7, 57.9, 110.3, 112.7, 125.4, 132.5, 146.3, 159.7, 212.0; MS *m*/*z* (%) 220 (M^+, 4), 147 (100), 115 (7). HRMS calcd for $C_{13}H_{16}O_3$ 220.1100, found 220.1097.

3.1.43. 1-(4-Methoxy-2,3-dihydro-1*H*-inden-1-yl)-3-hydroxy-propan-1-one (6l). The reaction was performed following the general procedure, using **5l** (0.132 g, 0.646 mmol), acetic acid/H_2O (2:1, 3 mL), TTN·$3H_2O$ (0.32 g, 0.71 mmol) and reaction time of 20 min. The residue was purified by flash chromatography (gradient elution, 30–40% ethyl acetate in hexane) giving the indan **6l** (0.097 g, 0.48 mmol, 74%): viscous pale yellow oil; IR (film): 3448, 1706, 1594 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.29–2.36 (m, 2H), 2.6 (br s, 1H), 2.63–2.83 (m, 2H), 2.85–3.06 (m, 2H), 3.79–3.83 (m, 2H), 3.82 (s, 3H), 4.08–4.13 (m, 1H), 6.73 (d, J=8.1 Hz, 1H), 6.86 (d, J=7.6 Hz, 1H), 7.17 (dd, J=7.6 and 8.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.3, 28.6, 42.1, 55.2, 57.9, 59.0, 109.2, 117.0, 128.2, 132.4, 142.3, 156.4, 211.6; MS *m*/*z* (%) 220 (M^+, 10), 147 (100), 131 (10), 115 (15), 91 (21). HRMS calcd for $C_{13}H_{16}O_3$ 220.1100, found 220.1096.

3.1.44. 1-(6-Methoxy-2,3-dihydro-1*H*-inden-1-yl)-3-hydroxy-propan-1-one (6m). The reaction was performed following the general procedure, using **5m** (0.233 g, 1.14 mmol), acetic acid/H_2O (2:1, 6 mL), TTN·3H_2O (0.56 g, 1.3 mmol) and reaction time of 20 min. The residue was purified by flash chromatography (gradient elution, 20–40% ethyl acetate in hexane) giving the indan **6m** (0.175 g, 0.795 mmol, 70%): viscous pale yellow oil; IR (film): 3414. 2944, 1706, 1491 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.22–2.30 (m, 2H), 2.56–2.98 (m, 4H), 3.69 (s, 3H), 3.73–3.77 (m, 2H), 3.98 (t, J=7.0 Hz, 1H), 6.68 (d, J=2.5 Hz, 1H), 6.71 (d, J=2.6 Hz, 1H), 7.06–7.08 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.0, 30.9, 42.0, 55.4, 57.8, 58.7, 110.2, 113.6, 125.3, 136.4, 141.8, 158.8, 211.5; MS m/z (%) 220 (M^+, 17), 147 (100), 131 (5), 115 (9). HRMS calcd for $C_{13}H_{16}O_3$ 220.1100, found 220.1116.

3.1.45. 1-(*trans*-3-Methyl-2,3-dihydro-1*H*-inden-1-yl)-3-hydroxy-propan-1-one (6n). The reaction was performed following the general procedure, using **5n** (0.189 g, 0.927 mmol), acetic acid/H_2O (2:1, 4.5 mL), TTN·3H_2O (0.45 g, 1.0 mmol) and reaction time of 35 min. The residue was purified by flash chromatography (gradient elution, 30–40% ethyl acetate in hexane) giving the indan **6n** (0.0847 g, 0.424 mmol, 46%): viscous colorless oil; IR (film): 3454, 2957, 1705 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.29 (d, J=6.9 Hz, 1H), 1.82–1.92 (m, 1H), 2.5 (br s, 1H), 2.53–2.63 (m, 1H), 2.66–2.86 (m, 2H), 3.39 (sx, J=7.2 Hz, 1H), 3.81 (t, J=5.4 Hz, 2H), 4.09 (dd, J=3.2 and 8.7 Hz, 1H), 7.16–7.29 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.2, 37.7, 38.5, 42.2, 57.4, 57.9, 124.0, 124.8, 126.7, 127.9, 140.1, 149.2, 211.4; MS m/z (%) 204 (M^+, 4), 186 (11), 131 (100), 91 (18). HRMS calcd for $C_{13}H_{15}O_2$ 204.1150, found 204.1191.

3.1.46. Oxidation of the alkenol 5o by TTN. The reaction was performed following the general procedure, using **5o** (0.110 g, 0.628 mmol), acetic acid/H_2O (2:1, 3 mL), TTN·3H_2O (0.31 g, 0.691 mmol) and reaction time of 10 min. The residue was purified by flash chromatography (gradient elution, 10–30% ethyl acetate in hexane) giving the triol **10** (0.0114 g, 0.0547 mmol, 9%): pale yellow oil; IR (film): 2931, 2871, 1634 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.17–2.26 (m, 1H), 2.38–2.66 (m, 3H), 2.78–2.92 (m, 2H), 4.00–4.05 (m, 2H), 4.77 (s, 1H), 7.14–7.19 (m, 1H), 7.23–7.29 (m, 2H), 7.37–7.45 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.9, 29.9, 37.2, 66.0, 80.3, 95.1, 126.9, 128.0, 128.4, 129.6, 133.0, 136.5.

3.1.47. Oxidation of the alkenol 5p by TTN. The reaction was performed following the general procedure, using **5p** (0.144 g, 0.763 mmol), acetic acid (3.5 mL), TTN·3H_2O (0.37 g, 0.84 mmol) and reaction time of 5 min. The residue was purified by flash chromatography (gradient elution, 5–40% ethyl acetate in hexane) giving a yellow oil (0.0382 g). This oil was further purified by flash chromatography (gradient elution, 5–30% ethyl acetate in hexane) giving the naphthalene **11** (0.014 mg, 0.076 mmol, 10%): pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.37 (d, J=7.0 Hz, 3H), 3.12 (sx, J=6.9 Hz, 1H), 3.78 (s, 1H), 3.80 (d, J=0.9 Hz. 1H), 7.38 (dd, J=1.8 and 8.5 Hz, 1H), 7.43–7.47 (m, 2H), 7.680–7.683 (m, 1H), 7.79–7.83 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.6, 42.6, 68.6, 125.5, 125.8, 126.07, 126.10, 126.5, 127.6 (×2), 128.4, 132.5, 133.6, 141.1; MS m/z (%) 186 (M^+, 28), 168 (1.5), 155 (100), 128 (17), 115 (13).

3.1.48. Oxidation of the acetate 8 by TTN. The reaction was performed following the general procedure, using **8** (0.0867 g, 0.376 mmol), acetic acid (2 mL), TTN·3H_2O (0.18 g, 0.41 mmol) and reaction time of 46 h. The residue was purified by flash chromatography (gradient elution, 10–30% ethyl acetate in hexane) giving the naphthalene **9** (0.0146 g, 0.0640 mmol, 17%): pale yellow oil; IR (film): 2971, 1739, 1233, 778 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45 (d, J=6.9 Hz, 3H), 2.01 (s, 3H), 3.95–4.06 (m, 1H), 4.21 (dd, J=8.0 and 10.8 Hz, 1H), 4.42 (dd, J=6.0 and 10.8 Hz), 7.39–7.57 (m, 4H), 7.75 (d, J=7.8 Hz, 1H), 7.86 (dd, J=1.6 and 7.8 Hz, 1H), 8.16 (d, J=8.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.1, 20.9, 33.2, 69.3, 123.0, 123.1, 125.5, 126.1, 127.2, 129.0, 131.8, 134.0, 139.1, 171.2.

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25. In the preliminary communication,[20] the thallium(III) mediated ring contractions were performed using a 1:1 mixture of AcOH/H_2O. However, on reexamination of the reaction conditions, we observed that a 2:1 ratio of AcOH/H_2O allows a faster solubilization of the substrate.
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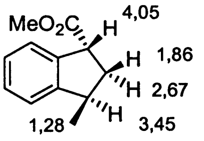
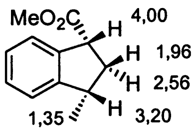
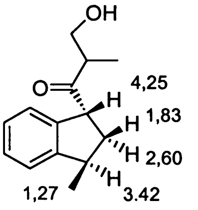
27. As depicted below, comparison of the ^1H NMR data of the previously described 1,3-disubstituted indans *cis*-**12** and *trans*-**12** (Beckwith, A. L. J.; Gerba, S. *Aust. J. Chem.* **1992**, *45*, 289) with the indans **6g** and **6n** allows to assign their relative configuration unambiguously.



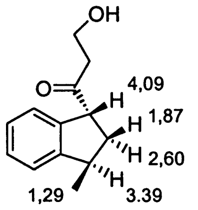
***trans*-12**



***cis*-12**

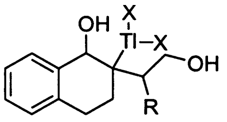


***trans*-6g**



***trans*-6n**

28. The aromatization of 1,2-dihydronaphthalenes by TTN has been observed and discussed in other studies.[21]
29. The addition of TTN to **5o** or **5p** would lead to the intermediate **13**, shown below. Previous results from our group demonstrated that the ring contraction is not favored in this kind of oxythallated adduct. (Ferraz, H. M. C.; Silva, Jr., L. F. *Tetrahedron Lett.* **1997**, *38*, 1899. Ferraz, H. M. C.; Silva, Jr., L. F. *J. Org. Chem.* **1998**, *63*, 1716).



R=H or Me
X=ONO_2

13