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Samarium triflate-catalyzed dimerization of vinylarenes

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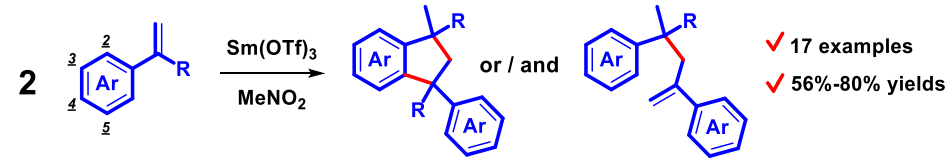
Abstract

We report the preparation of substituted indanes and their dimeric isomers via the samarium triflate-mediated [$Sm(OTf)_3$, 10 mol%] self-dimerization of vinylarenes in $MeNO_2$ at 25 °C for 10 h. The diverse products were obtained in moderate to high yields. The synthesis involves a (3+2) annulation via the formation of carbon-carbon bonds. Plausible mechanisms are proposed and discussed. The investigation of various rare metal triflates catalyst loadings, reaction conditions, and substrate scope led to an operationally easy one-pot Friedel-Crafts reaction protocol.

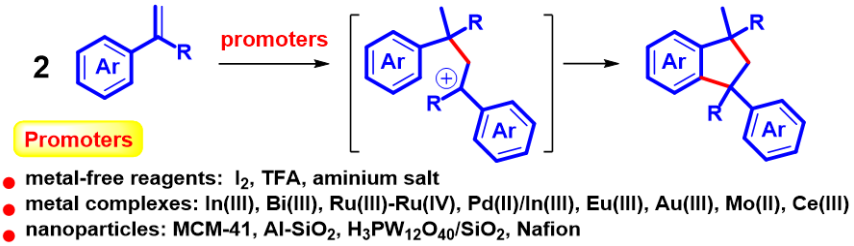


R = Me,
Ar = Ph, 4-$CF_3C_6H_4$, 4-MeC_6H_4, 3-$MeOC_6H_4$, 4-ClC_6H_4, 4-FC_6H_4, 3-FC_6H_4, 3,4-$(MeO)_2C_6H_3$
3,4-$CH_2O_2C_6H_3$, 3,4,5-$(MeO)_3C_6H_2$, 2,4-$(MeO)_2C_6H_3$, 2-thienyl, 4-PhC_6H_4, 2-naphthyl, 4-$NO_2C_6H_4$
3,4-$Cl_2C_6H_3$
R = Ar = Ph

Keywords: Samarium triflate, vinylarenes, indane, dimerization

Introduction

The catalytic self-dimerization reaction of vinyl arenes (e.g. α-methylstyrenes) to derive functionalized indanes is one of the most straightforward and useful transformations used to construct carbon-carbon (C-C) bonds. After pioneer work by Bergmann and co-workers,[1] various promoter-mediated synthetic routes have been documented via the intermolecular hydroarylation of vinyl arenes followed by spontaneous intramolecular ring-closure of the resulting dimeric isomers (Scheme 1). They include different metal-free reagents (I_2, TFA, aminium salt),[2-5] transition-metal complexes (In^{3+}, Bi^{3+}, Ru^{3+}-Ru^{+4}, Pd^{2+}/In^{3+}, Eu^{3+}, Au^{3+}, Mo^{2+}, Ce^{3+}),[6-13] nanoparticles (MCM-41, Al-SiO_2, $H_3PW_{12}O_{40}/SiO_2$, Nafion)[14-17] or other methods.[18-21] On the basis of observations, attempts to develop new and efficient catalyst systems for the self-dimerization of vinyl arenes are still in demand. In an ongoing effort to emphasize the synthetic applications of metal triflates,[22-28] we present, herein, a Ln(OTf)$_3$ (lanthanide triflate)-mediated synthesis of substituted indanes.[29-30] To the best of our knowledge, no examples have been reported for Ln(OTf)$_3$-mediated self-dimerizations of this type.



Scheme 1. Self-dimerization of vinyl arenes.

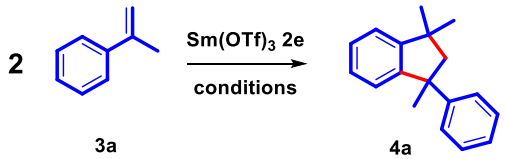
Results and Discussion

After perusing literature on the synthesis of substituted indanes and reviewing our previous studies on metal triflate (**1**)-promoted reactions, 10 commercially available Ln(OTf)$_3$ **2a**-**2j** (10 mol%) promoted dimerizations of starting α-methylstyrene (**3a**) were examined in $MeNO_2$ (5 mL) at 25 °C for 5 h. However, no obvious yield changes occurred with the isolation of **4a** using 5 mol% of La(OTf)$_3$ (**2a**), Ce(OTf)$_3$ (**2b**), Pr(OTf)$_3$ (**2c**), Nd(OTf)$_3$ (**2d**), Sm(OTf)$_3$ (**2e**), Eu(OTf)$_3$ (**2f**), Gd(OTf)$_3$ (**2g**), Dy(OTf)$_3$ (**2h**), Er(OTf)$_3$ (**2i**) or Yb(OTf)$_3$ (**2j**). Only Sm(OTf)$_3$ (**2e**) and Gd(OTf)$_3$ (**2g**) provided **4a** in better (66% and 47%) yields, respectively. Other catalysts produced **4a** in low yields (trace amounts to 20%). On the basis of the results, Sm(OTf)$_3$ (**2e**) was controlled as a catalyst to screen the optimal conditions (Table 1, entry 1). For comparing the advantages of the shown synthetic procedure with others previously described in the literature (e.g. $InBr_3$,[6] $BiCl_3$,[7] or TFA[18]), we found that Sm(OTf)$_3$ was the first lanthanide catalyst to promote the formation of substituted indanes via self-dimerization of α-methylstyrene. Nevertheless, Sm(OTf)$_3$ is relatively expensive because samarium is a rare metal resource.

Further variations in the reaction parameters, such as catalyst loading, the solvent system, temperature and reaction time, were carried out as follows. In entry 2, decreasing the catalytic equivalent of Sm(OTf)$_3$ (10 → 5 mol%) diminished the yield of **4a** (66 → 39%). Entry 3 showed that excess amounts (20 mol%) of Sm(OTf)$_3$ did not increase the catalytic ability to provide a better yield, and a similar yield (64%) was observed. After elevating the temperature (25 → 75 °C), **4a** was isolated in only a 41% yield (entry 4). Under a refluxing $MeNO_2$ (101 °C) condition, **4a** was isolated in a low yield (35%), and a very complex mixture was detected, as shown in entry 5. With longer reaction times (5 → 10, 20 h), **4a** was formed in higher yield (83%, 80%) (entries

6-7). Furthermore, controlling the reaction conditions for the combination of $Sm(OTf)_3$ (10 mol%), 25 °C and 10 h, different solvents were examined. After changing the reaction solvent from $MeNO_2$ to PhMe and CH_2Cl_2, **4a** was produced in lower yields (28%, 60%) than $MeNO_2$ (entries 8 & 9). In particular, entry 10 showed that the use of DMF did not give the desired product **4a**. On the basis of TLC monitoring, only the starting material **3a** was detected. However, treatment of **3a** with diluted $MeNO_2$ afforded **4a** in a similar yield (80%) (entry 11). This meant that the reaction concentration was not a main factor affecting the **4a** yield.

Table 1. Optimal conditions[a-b]



entry	$Sm(OTf)_3$ (mol%)	solvent (mL)	temp (°C)	time (h)	yield[b] (%)
1	10	$MeNO_2$	25	5	66
2	5	$MeNO_2$	25	5	39
3	20	$MeNO_2$	25	5	64
4	10	$MeNO_2$	75	5	41
5	10	$MeNO_2$	101	5	35
6	10	$MeNO_2$	25	10	83
7	10	$MeNO_2$	25	20	80
8	10	PhMe	25	10	28[c]
9	10	CH_2Cl_2	25	10	60
10	10	DMF	25	10	ND[d]
11	10	$MeNO_2$[e]	25	10	80

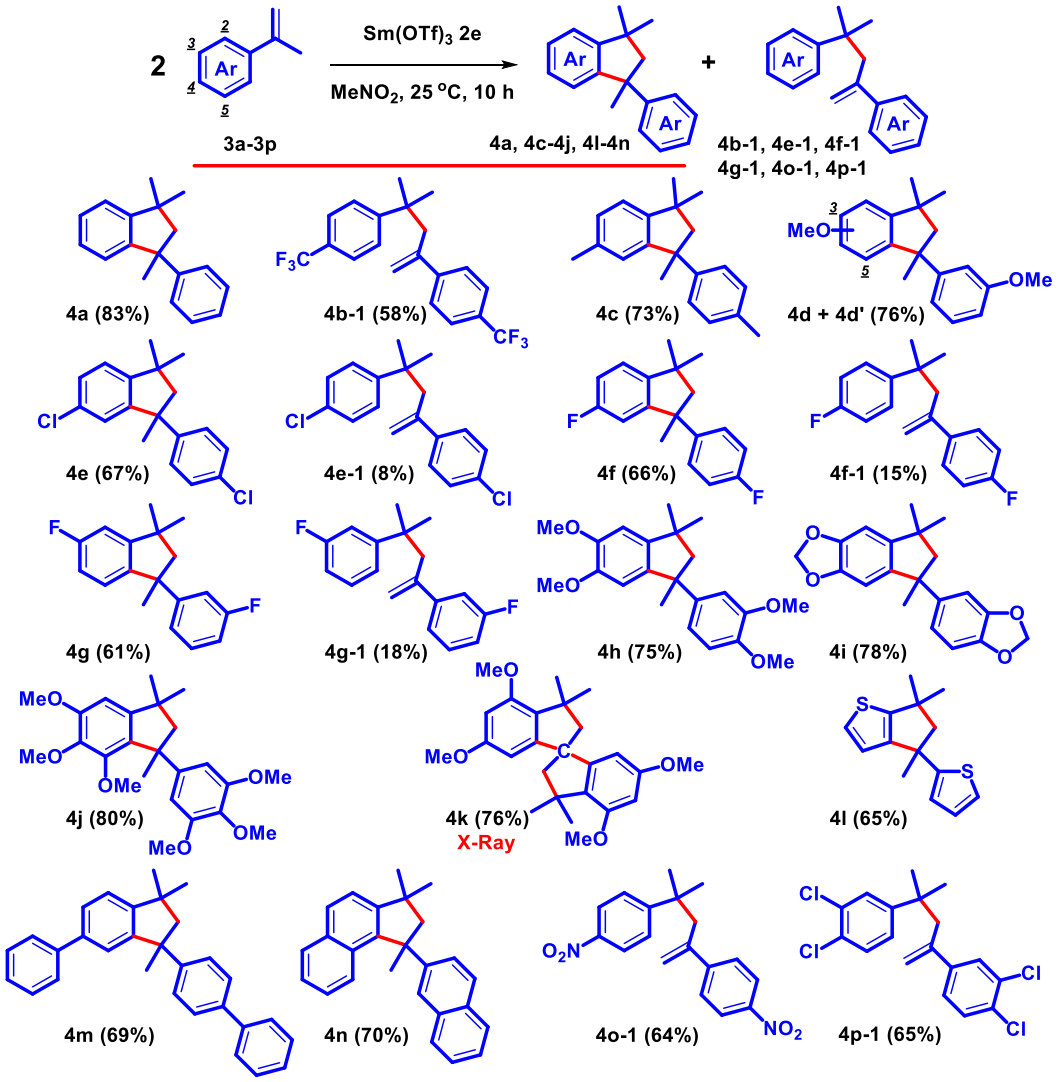
[a] Reaction was run on **3a** (1.0 mmol), solvent (5 mL). [b] Isolated yields. [c] Complex reaction mixture (TLC). [d] No reaction. [e] Solvent (10 mL).

On the basis of the highest observed yield (entry 6, 83%), the combination of 10 mol% $Sm(OTf)_3$/$MeNO_2$ (5 mL)/25 °C/10 h was selected as the optimal reaction conditions for the formation of dimer **4a**. On the other hand, $Sm(OTf)_3$ has been reported as a catalyst for different reaction types, including Ferrier rearrangement,[31] Friedel-Crafts alkylation,[32] aza-Diels–Alder cycloaddition,[33] conjugated addition[34] and cross-coupling.[35] Remarkably, there are few examples of samarium salt-catalyzed reactions having been performed in comparison with other commercially available samarium complexes.[36-40] With the optimal reaction conditions in hand (Table 1, Entry 6), we then explored the scope of the conversion with other substrates (Table 2).

For the aryl substituent of α-methylvinyl arenes **3a**-**p**, the Ar ring with diversified electron-neutral, electron-donating or electron-withdrawing groups was examined next, including **a** Ph, **b** 4-$CF_3C_6H_4$, **c** 4-MeC_6H_4, **d** 3-$MeOC_6H_4$, **e** 4-ClC_6H_4, **f** 4-FC_6H_4, **g** 3-FC_6H_4, **h** 3,4-$(MeO)_2C_6H_3$, **i** 3,4-$CH_2O_2C_6H_3$, **j** 3,4,5-$(MeO)_3C_6H_2$, **k** 2,4-$(MeO)_2C_6H_3$, **l** 2-thienyl, **m** 4-PhC_6H_4, **n** 2-naphthyl, **o** 4-$NO_2C_6H_4$ and **p** 3,4-$Cl_2C_6H_3$. By the $Sm(OTf)_3$-mediated self-dimerization of **3a**-**p**, two kinds of dimers, cyclized indanes (**4a**, **4c**-**n**) and acyclic isomers (**4b**-**1**, **4e**-**1**, **4f**-**1**, **4g**-**1**, **4o**-**1**, **4p**-**1**), were provided in a range of 56-83% and 8%-65% yields, respectively. In all examples, the four electron-neutral aryl groups (for **3a**, **3c**, **3m**-**n**), five electron-donating oxygenated aryl groups (for **3d**, **3h**-**k**) and one heterocyclic group (for **3l**) could trigger the ring-closure to produce a benzo-fused indane skeleton.

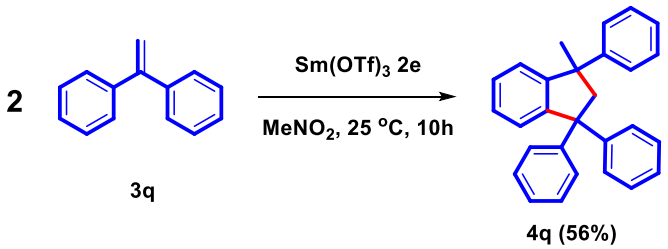
However, six electron-withdrawing aryl groups (for **3b**, **3e**-**f**, **3g**, **3o**-**p**) afforded an acyclic dimer or a mixture of a cyclic indane and acyclic dimer. One reason for this is the electron-deficient aryl group does not have enough electron density to promote spontaneous annulation such that sole acyclic dimers would form, especially for 4-trifluoromethylphenyl, 4-nitrophenyl and 3,4-dichlorophenyl groups. However, another three weaker electron-withdrawing aryl groups (fluoro-, chloro-) obtained a mixture of a cyclic indane and acyclic dimer. Among these products **4**, only **3d** (Ar = 3-MeOC_6H_4) provided the unseparated mixture of products **4d** (for 3-MeO) and **4d'** (for 5-MeO) with a ratio of 80:20. During the ring-closure procedure, the methoxy group at the C-5 position exhibited a bulkier steric hindrance such that the isolated yield of **4d'** was lower. Under the kinetically controlled conditions (for 25 °C), the terminal methylene group of acyclic isomers **4b**-**1**, **4e**-**1**, **4f**-**1**, **4g**-**1**, **4o**-**1** and **4p**-**1** could demonstrate that *exo*-chemoselectivity. The similar phenomenon had described by Peppe and Nishibayashi groups, respectively.[6,8]

Table 2. $Sm(OTf)_3$-catalyzed self-dimerization of **3**[a-b]



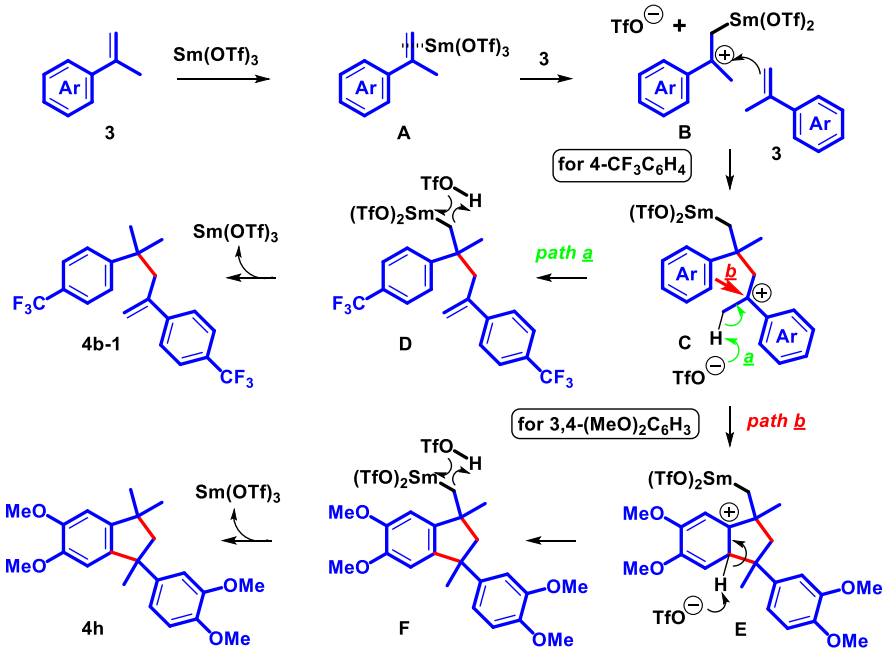
[a] The synthesis was run on 1.0 mmol scale with **3a**-**p**, $Sm(OTf)_3$ (60 mg, 10 mol%), $MeNO_2$ (5 mL), 10 h, 25 °C. [b] Isolated yield.

α-Phenylstyrene (**3q**) was also studied (Table 2). On the basis of the styrene skeleton, changing the α-methyl group to α-phenyl was tested. Under the above-mentioned conditions, treatment of **3q** with $Sm(OTf)_3$ afforded **4q** in a 56% yield along with a 25% yield of unknown and unanalyzed products mixture (Scheme 2).



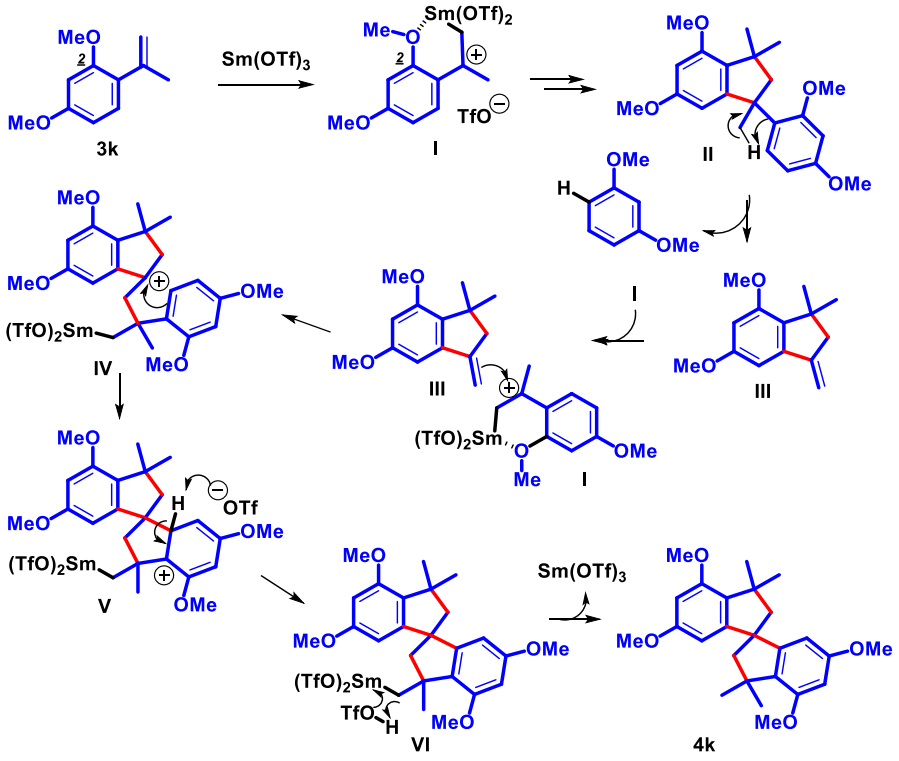
Scheme 2. Synthesis of indane **4q**.

Based on experimental results, a possible reaction mechanism with both electron-withdrawing 4-trifluoromethylphenyl group and electron-donating 3,4-dimethoxyphenyl groups is shown in Scheme 3. How were two dimers **4b**-**1** and **4h** produced? The event is initiated to form **A** by complexation of an olefinic moiety of **3** with $Sm(OTf)_3$. After releasing a triflate anion, **B**, with a methylene samarium arm, is generated. Then, participation of another **3** converts the resulting **B** into **C** having a tertiary carbocation. On the basis of the structure on **C**, *path a* (green) shows that the 4-CF_3 group decreases the electron density of Ar such that the triflate anion could trap the proton to stabilize carbocation. Following *in-situ* formed triflic acid-promoted protodemetalation of **D**, the removal of $Sm(OTf)_3$ afforded **4b-1**. For *path b* (red), owing to Ar = 3,4-$(MeO)_2$, the electron-rich arene could attack the carbocation to give **E** via the five-membered ring closure procedure. Following the triflate anion-mediated dehydrogenative aromatization of **E**, and then, triflic acid-promoted protodemetalation of **F**, tetramethoxyindane **4h** is obtained along with the recovery of $Sm(OTf)_3$. From the plausible mechanisms, we understand that electron-density on arene is a key factor in affecting the reaction pathway and product distribution.



Scheme 3. Plausible mechanism.

In particular, when Ar with a 2,4-dimethoxy group was treated with the above reaction conditions, only **4k** was generated in a 76% yield. The spiro structure of bis-indane **4k** was determined by single-crystal X-ray crystallography.[41] We postulated that three equivalents of **3k** were involved to generate **4k** (Scheme 4). According to a series of reaction steps in Scheme 3, *path b*, **II** is produced from **I** with an oxygen-chelated samarium complex conformation. By removal of 1,3-dimethoxybenzene, **III** should be formed. This is a very important step for the formation of a bis-indane skeleton because the formed 3-carbon fragment could construct a spiro ring. Furthermore, intermolecular Friedel-Crafts type coupling of the corresponding **III** with another **I** produces **IV**. Next, electron-rich arene attacks the carbocation to give **V** via intramolecular benzannulation. Following the above-mentioned steps (triflate anion-mediated dehydrogenative aromatization of **V** followed by triflic acid-promoted protodemetalation of **VI**), tetramethoxy spiro-indane **4k** is obtained along with the recovery of $Sm(OTf)_3$. Compared with the formation of oxygenated indanes **4h**-**k**, only **4k** was produced as a spiro system under similar reaction conditions. The detailed reasons are still unclear, however, we believe that the 2-MeO group of **3k** plays a role in triggering the removal of 1,3-dimethoxybenzene more easily than other oxygenated vinylarenes **3h**-**j** during the conversion process from **II** to **III**.



Scheme 4. Plausible Mechanism of **4k**.

Conclusions

We have developed a mild synthesis of substituted indanes and dimeric isomers in moderate yields via a 10 mol% $Sm(OTf)_3$-mediated self-dimerization reaction of substituted vinylarenes in $MeNO_2$ at 25 ^{o}C for 10 h. The control of reaction parameters such as the lanthanide triflates catalyst loading, the reaction temperature, the solvent and the time, had to be finely tuned to explore optimal conditions. Furthermore, the proposed

mechanisms for the formation of **4b-1**, **4h** and **4k** are discussed. Further investigation regarding synthetic applications of lanthanide triflates will be conducted and published in due course.

Experimental Section

General. All reagents and solvents were obtained from commercial sources and used without further purification. Reactions were routinely carried out under an atmosphere of air with magnetic stirring. Products in organic solvents were dried with anhydrous magnesium sulfate before concentration in vacuo. All reactions were monitored by TLC on silica gel 60 F_{254} (Merck) with detection by UV light. Column chromatography was performed using silica gel (200-300 mesh). Melting points were determined with a SMP3 melting apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 spectrometer operating at 400 and 100 MHz, respectively. Chemical shifts (δ) are reported in parts per million (ppm) and the coupling constants (J) are given in Hertz (Hz). High resolution mass spectra (HRMS) were measured with a mass spectrometer Finnigan/Thermo Quest MAT 95XL. X-ray crystal structures were obtained with an Enraf-Nonius FR-590 diffractometer (CAD4, Kappa CCD).

General procedure for the preparation of compounds 4a, **4c-n, 4q, 4b-1**, **4e-1**, **4f-1**, **4g-1**, **4o-1 and 4p-1.** $Sm(OTf)_3$ (60 mg, 0.1 mmol) was added to a solution of **3** (1.0 mmol) in $MeNO_2$ (5 mL) at 25 ^oC. The reaction mixture was stirred at 25 ^oC for 10 h. The solvent of reaction mixture was concentrated and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine (2 × 10 mL), dried ($MgSO_4$), filtered and evaporated to afford crude product mixture under reduced pressure. The remaining mixture was separated by flash column chromatography (silica gel, eluent: hexanes/EtOAc 100:1 → 20:1) affording compounds **4a**, **4c-n, 4q, 4b-1**, **4e-1**, **4f-1**, **4g-1**, **4o-1 and 4p-1**.

1,1,3-Trimethyl-3-phenylindan (4a).[7] Colorless oil (98 mg, 83%); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{18}H_{21}$ 237.1643, found 237.1644; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.25 (m, 9H), 2.58 (d, *J* 13.2, 1H), 2.35 (d, *J* 13.2, 1H), 1.84 (s, 3H), 1.50 (s, 3H), 1.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1, 151.0, 148.7, 128.0 (2×), 127.2, 126.64 (2×), 126.61, 125.5, 125.0, 122.5, 59.2, 50.8, 42.8, 30.9, 30.7, 30.4.

4-Methyl-2,4-di(4-trifluoromethylphenyl)-1-pentene (4b-1). Colorless oil (108 mg, 58%); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{20}H_{19}F_6$ 373.1391, found 373.1396; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.34 (m, 4H), 7.27 (d, *J* 8.4, 2H), 7.16 (d, *J* 8.4, 2H), 5.18 (d, *J* 1.2, 1H), 4.95 (s, 1H), 2.86 (s, 2H), 1.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 146.3, 145.5, 128.9 (d, *J* 32.6), 127.9 (d, *J* 31.9), 126.8 (2×), 126.4 (2×), 124.2 (q, *J* 269.8), 124.1 (d, *J* 269.9), 124.8 (q, *J* 3.8, 2×), 124.6 (d, *J* 3.8, 2×), 118.8, 50.0, 38.7, 28.6 (2×).

1,1,3,5-Tetramethyl-3-*p*-tolylindan (4c).[16] Colorless oil (96 mg, 73%); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{20}H_{25}$ 265.1956, found 265.1953; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20-7.17 (m, 6H), 7.02 (s, 1H), 2.49 (d, *J* 13.2, 1H), 2.46 (s, 3H), 2.40 (s, 3H), 2.28 (d, *J* 13.2, 1H), 1.78 (s, 3H), 1.44 (s, 3H), 1.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 149.1, 148.1, 136.1, 134.8, 128.6 (2×), 128.0, 126.6 (2×), 125.4, 122.2, 59.5, 50.3, 42.5, 30.8 (2×), 30.5, 21.4, 20.9.

5-Methoxy-1-(3-methoxyphenyl)-1,3,3-trimethylindan (4d) and 4-methoxy-3-(3-methoxyphenyl)-1,1,3-trimethylindan (4d').[18] Unseparated binary mixture; ratio **4d**/**4d'** 80:20; Colorless oil (112 mg, 76%); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{20}H_{25}O_2$ 297.1855, found 297.1856; for major product **4d**, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (t, *J* 8.0, 1H), 7.08 (d, *J* 8.0, 1H), 6.86-6.70 (m, 5H), 3.87 (s, 3H), 3.78 (s, 3H), 2.46 (d, *J* 12.8, 1H), 2.22 (d, *J* 13.2, 1H), 1.69 (s, 3H), 1.36 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 159.2, 153.7,

153.1, 140.6, 128.8, 125.6, 119.3, 113.3, 112.5, 109.9, 107.7, 59.4, 55.3, 55.0, 50.1, 42.8, 31.1, 30.4, 30.2; GC-MS: *m*/*z* (%) 297 (65) [M + H^+], 282 (45), 267 (12), 236 (10), 158 (24), 144 (23), 91 (10).

5-Chloro-3-(4-chlorophenyl)-1,1,3-trimethylindan (4e).[7] Colorless solid (102 mg, 67%); mp 81-82 °C (from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{18}H_{19}Cl_2$ 305.0864, found 305.0866; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.27-7.20 (m, 3H), 7.13-7.07 (m, 3H), 7.04 (d, *J* 2.0, 1H), 2.37 (d, *J* 12.8, 1H), 2.20 (d, *J* 12.8, 1H), 1.65 (s, 3H), 1.32 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 150.6, 150.3, 148.7, 132.4, 131.5, 128.2 (2×), 128.0 (2×), 127.7, 124.9, 123.9, 59.2, 50.5, 42.6, 30.59, 30.57, 30.3.

2,4-Di(4-chlorophenyl)-4-methyl-1-pentene (4e-1).[42] Colorless oil (12 mg, 8%); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{18}H_{19}Cl_2$ 305.0864, found 305.0868; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.19-7.15 (m, 6H), 7.12-7.08 (m, 2H), 5.12 (d, *J* 1.6, 1H), 4.08 (d, *J* 0.4, 1H), 2.77 (s, 2H), 1.22 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 147.3, 145.4, 141.5, 132.7, 131.3, 128.1 (2×), 127.79 (2×), 127.76 (2×), 127.4 (2×), 117.5, 49.7, 38.4, 28.8 (2×).

5-Fluoro-3-(4-fluorophenyl)-1,1,3-trimethylindan (4f).[18] Colorless oil (90 mg, 66%); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{18}H_{19}F_2$ 273.1455, found 273.1456; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.15-7.11 (m, 3H), 7.00-6.91 (m, 3H), 6.76 (dd, *J* 2.4, 9.2, 1H), 2.39 (d, *J* 12.8, 1H), 2.22 (d, *J* 13.2, 1H), 1.66 (s, 3H), 1.33 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 162.3 (d, *J* 242.6), 161.0 (d, *J* 243.3), 150.7 (d, *J* 6.8), 147.5 (d, *J* 2.3), 146.1 (d, *J* 3.0), 128.0 (d, *J* 7.6, 2×), 123.7 (d, *J* 8.3), 114.7 (d, *J* 20.4, 2×), 114.4 (d, *J* 22.7), 111.4 (d, *J* 21.2), 59.6, 50.2, 42.4, 30.8, 30.7, 30.4.

2,4-Di(4-fluorophenyl)-4-methyl-1-pentene (4f-1).[42] Colorless oil (20 mg, 15%); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{18}H_{19}F_2$ 273.1455, found 273.1458; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 6.85-6.76 (m, 4H), 6.56-6.49 (m, 4H), 4.74 (d, *J* 1.6, 1H), 4.44 (d, *J* 0.8, 1H), 2.43 (s, 2H), 0.88 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 161.9 (d, *J* 244.1), 160.8 (d, *J* 242.6), 145.6, 144.5, 139.1, 128.0 (d, *J* 7.6, 2×), 127.4 (d, *J* 7.6, 2×), 116.9, 114.7 (d, *J* 21.2, 2×), 114.3 (d, *J* 20.5, 2×), 50.1, 38.5, 29.0 (2×).

5-Fluoro-1-(3-fluorophenyl)-1,3,3-trimethylindan (4g). Colorless oil (83 mg, 61%); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{18}H_{19}F_2$ 273.1455, found 273.1457; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.23-7.17 (m, 1H), 7.05 (d, *J* 8.4, 1H), 7.04 (d, *J* 8.4, 1H), 6.97-6.91 (m, 2H), 6.88-6.82 (m, 2H), 2.41 (d, *J* 13.2, 1H), 2.22 (d, *J* 13.2, 1H), 1.65 (s, 3H), 1.33 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 164.0 (d, *J* 242.6), 162.7 (d, *J* 243.3), 154.5 (d, *J* 6.8), 153.6 (d, *J* 5.3), 143.4 (d, *J* 3.0), 129.4 (d, *J* 8.3), 125.9 (d, *J* 8.4), 122.2 (d, *J* 3.0), 113.9 (d, *J* 19.7), 113.7 (d, *J* 19.0), 112.4 (d, *J* 20.5), 109.5 (d, *J* 21.2), 59.3, 50.3, 42.9, 30.9, 30.4, 30.1.

2,4-Di(3-fluorophenyl)-4-methyl-1-pentene (4g-1). Colorless oil (24 mg, 18%); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{18}H_{19}F_2$ 273.1455, found 273.1455; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.18-7.12 (m, 2H), 7.03-7.01 (m, 1H), 6.98-6.96 (m, 1H), 6.94-6.90 (m, 1H), 6.88-6.83 (m, 2H), 6.80-6.75 (m, 1H), 5.16 (d, *J* 1.6, 1H), 4.84 (s, 1H), 2.78 (s, 2H), 1.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 162.6 (d, *J* 242.6), 162.5 (d, *J* 242.6), 151.7 (d, *J* 8.8), 145.4 (d, *J* 2.3), 138.9 (d, *J* 8.2), 129.4 (d, *J* 8.3), 129.1 (d, *J* 8.3), 122.1 (d, *J* 2.3), 121.6 (d, *J* 2.3), 117.9, 113.6 (d, *J* 20.5), 113.3 (d, *J* 22.0), 113.2 (d, *J* 21.2), 112.3 (d, *J* 21.2), 49.6, 38.7, 28.6 (2×).

1-(3,4-Dimethoxyphenyl)-5,6-dimethoxy-1,3,3-trimethylindan (4h).[19] Colorless oil (134 mg, 75%); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{22}H_{29}O_4$ 357.2066, found 357.2067; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 6.74-6.69 (m 4H), 6.60 (s, 1H), 3.92 (s, 3H), 3.84 (s, 3H), 3.83 (s, 3H), 3.78 (s, 3H), 2.34 (d, *J* 13.2, 1H), 2.17 (d, *J* 13.2, 1H), 1.66 (s, 3H), 1.32 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 148.7, 148.3, 148.2, 146.7, 143.9, 143.8, 140.1, 118.5, 110.38, 110.36, 107.4, 105.1, 59.7, 56.0, 55.9, 55.7 (2×), 50.3, 42.7, 30.8, 30.7, 30.4.

5-Benzo[1,3]dioxol-5-yl-5,7,7-trimethyl-6,7-dihydro-5*H*-indeno[5,6-*d*][1,3]dioxole (4i).[20] Colorless oil (126 mg, 78%); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{20}H_{21}O_4$ 325.1440, found 325.1438; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 6.71-6.62 (m, 4H), 6.53 (s, 1H), 5.96 (d, *J* 1.6, 1H), 5.95 (d, *J* 1.2, 1H), 5.91 (d, *J* 2.0, 1H), 5.91 (d, *J* 1.6, 1H), 2.34 (d, *J* 13.2, 1H), 2.16 (d, *J* 12.8, 1H), 1.61 (s, 3H), 1.29 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ*

147.4, 147.2, 146.7, 145.3, 145.2 (2×), 141.5, 119.4, 107.6, 107.4, 104.9, 102.8, 101.0, 100.8, 59.7, 50.3, 42.6, 30.93, 30.87, 30.4.

4,5,6-Trimethoxy-1,1,3-trimethyl-3-(3,4,5-trimethoxyphenyl)indan (4j).[20] Colorless oil (166 mg, 80%); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{24}H_{33}O_6$ 417.2277, found 417.2273; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 6.46 (s, 1H), 6.40 (s, 2H), 3.89 (s, 3H), 3.82 (s, 3H), 3.80 (s, 3H), 3.75 (s, 6H), 3.60 (s, 3H), 2.32 (d, *J* 13.2, 1H), 2.12 (d, *J* 12.8, 1H), 1.76 (s, 3H), 1.30 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 153.8, 152.4 (2×), 150.2, 147.7, 146.9, 141.0, 135.7, 132.8, 103.9 (2×), 100.8, 60.8, 60.5, 60.1, 60.0, 56.0, 55.9 (2×), 51.0, 43.4, 31.0, 30.5, 29.1.

4,5',6,7'-Tetramethoxy-3,3,3',3'-tetramethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] (4k). Colorless solid (150 mg, 76%); mp 154-155 °C (from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{25}H_{33}O_4$ 397.2379, found 397.2381; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 6.33 (d, *J* 2.0, 1H), 6.27 (d, *J* 2.0, 1H), 6.26 (d, *J* 2.0, 1H), 5.91 (d, *J* 2.0, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 3.67 (s, 3H), 3.51 (s, 3H), 2.53 (d, *J* 12.8, 1H), 2.28 (d, *J* 13.2, 1H), 2.14 (d, *J* 13.2, 1H), 2.07 (d, *J* 12.8, 1H), 1.45 (s, 3H), 1.40 (s, 3H), 1.36 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 160.9, 160.2, 156.9, 156.6, 155.2, 154.1, 130.0, 128.0, 98.9, 97.9, 97.6, 96.8, 60.5, 57.1, 56.7, 55.43, 55.37, 55.1, 54.9, 44.1, 43.5, 31.9, 30.0, 29.0, 28.9. Single-crystal X-Ray diagram: crystal of compound **4k** was grown by slow diffusion of EtOAc into a solution of compound **4k** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the triclinic crystal system, space group P -1, *a* = 9.4024(3) Å, *b* = 15.5199(5) Å, *c* = 16.4035(6) Å, *V* = 2163.91(13) Å^3, *Z* = 2, d_{calcd} = 1.217 g/cm^3, *F*(000) = 856, 2*ϑ* range 1.328~26.411°, R indices (all data) R1 = 0.0976, wR2 = 0.2137.

4,6,6-Trimethyl-4-thien-2-yl-5,6-dihydro-4*H*-cyclopenta[*b*]thiophene (4l). Colorless oil (81 mg, 65%); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{14}H_{17}S_2$ 249.0772, found 249.0773; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.21 (d, *J* 4.8, 1H), 7.12 (dd, *J* 0.8, 4.8, 1H), 6.87 (dd, *J* 3.6, 4.8, 1H), 6.78 (d, *J* 4.8, 1H), 6.69 (dd, *J* 0.8, 3.6, 1H), 2.72 (d, *J* 12.8, 1H), 2.54 (d, *J* 13.2, 1H), 1.72 (s, 3H), 1.40 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 152.3, 149.6, 127.9, 126.4, 123.0, 122.5, 121.3, 121.2, 64.0, 46.8, 42.3, 31.8, 31.6, 31.3.

4-(1,3,3-Trimethyl-6-phenylindan-1-yl)biphenyl (4m).[8] Colorless solid (134 mg, 69%); mp 102-103 °C (from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{30}H_{29}$ 389.2269, found 389.2271; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.66-7.32 (m, 17H), 2.54 (d, *J* 13.2, 1H), 2.32 (d, *J* 12.8, 1H), 1.82 (s, 3H), 1.44 (s, 3H), 1.16 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 151.5, 150.0, 149.4, 141.6, 140.9, 140.0, 138.3, 128.7 (4x), 127.2 (2×), 127.1 (2×), 127.0 (2×), 126.9 (2×), 126.7 (2×), 126.5, 123.7, 122.9, 59.4, 50.7, 42.7, 30.9, 30.7, 30.5.

1,3,3-Trimethyl-1-naphthalen-2-yl-2,3-dihydro-1H-cyclopenta[*a*]naphthalene (4n).[21] Colorless solid (118 mg, 70%); mp 117-118 °C (from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{26}H_{25}$ 337.1956, found 337.1952; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.97-7.84 (m, 5H), 7.74 (d, *J* 8.8, 1H), 7.56-7.49 (m, 4H), 7.38 (dt, *J* 1.2, 8.0, 1H), 7.33 (dd, *J* 2.0, 8.8, 1H), 7.19 (dt, *J* 1.2, 8.4, 1H), 2.58 (d, *J* 13.6, 1H), 2.46 (d, *J* 13.2, 1H), 2.19 (s, 3H), 1.56 (s, 3H), 1.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 149.4, 148.6, 142.7, 133.9, 133.3, 131.7, 129.8, 128.8, 128.7, 128.1, 128.0, 127.4, 126.3, 125.8, 125.6, 125.3, 125.0, 124.5, 123.5, 121.3, 61.4, 52.1, 43.3, 31.4, 31.3, 28.1.

4-Methyl-2,4-di(4-nitrophenyl)-1-pentene (4o-1). Colorless solid (104 mg, 64%); mp 124-125 °C (from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{18}H_{19}N_2O_4$ 327.1345 found 327.1345; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.08-8.02 (m, 4H), 7.39 (d, *J* 8.8, 2H), 7.31 (d, *J* 8.8, 2H), 5.26 (d, *J* 1.2, 1H), 4.96 (d, *J* 0.8, 1H), 2.90 (s, 2H), 1.29 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 156.0, 149.4, 146.8, 146.0, 144.3, 127.2 (2×), 127.0 (2×), 123.4 (2×), 123.1 (2×), 120.7, 49.4, 39.4, 28.7 (2×).

4-Methyl-2,4-di(3,4-dichlorophenyl)-1-pentene (4p-1).[43] Colorless oil (121 mg, 65%); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{18}H_{17}Cl_4$ 373.0084, found 373.0086; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.23 (d, *J* 8.4, 1H), 7.21 (d, *J* 8.4, 1H), 7.18 (d, *J* 2.4, 1H), 7.09 (d, *J* 2.4, 1H), 7.01 (dd, *J* 2.6, 8.4, 1H), 6.92 (dd, *J* 2.0, 8.4, 1H), 5.15 (d, *J* 1.2,

1H), 4.91 (d, *J* 1.2, 1H), 2.72 (s, 2H), 1.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 148.5, 144.3, 142.6, 132.0, 131.8, 130.8, 129.7, 129.6, 129.5, 128.5, 128.3, 125.8, 125.6, 118.5, 49.9, 38.3, 28.5 (2×).

1-Methyl-1,3,3-triphenylindan (4q).[18] Colorless oil (101 mg, 56%); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{28}H_{25}$ 361.1956, found 361.1958; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.31-7.01 (m, 19H), 3.40 (d, *J* 13.6, 1H), 3.10 (d, *J* 13.2, 1H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 150.5, 149.3, 148.8, 148.5, 147.5, 128.8 (2×), 128.7 (2×), 127.9 (2×), 127.8 (2×), 127.6 (2×), 127.4, 127.3, 126.9 (2×), 126.8, 126.0, 125.64, 125.57, 125.0, 61.3, 60.9, 51.2, 31.9.

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Supplementary Material

Scanned photocopies of NMR ($CDCl_3$) spectral data were supported.

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