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Metal-Free Domino One-Pot Decarboxylative Cyclization of Cinnamic Acid Esters: Synthesis of Functionalized Indanes

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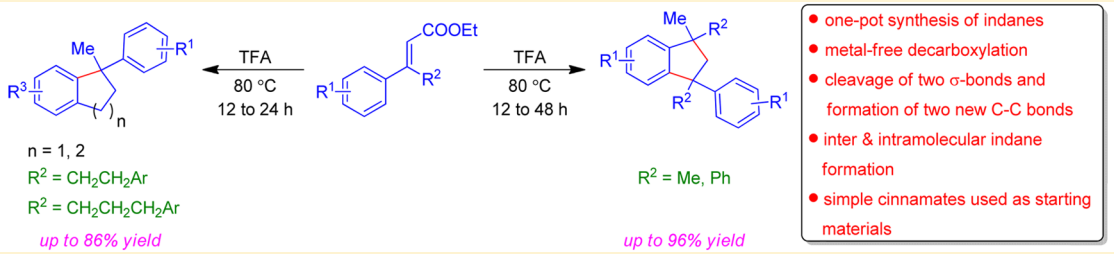
Supporting Information



ABSTRACT: Trifluoroacetic acid promoted unprecedented domino reaction for the synthesis of diverse indanes starting from simple cinnamic acid esters is described. Their formation can be explained via acid triggered decarboxylation of cinnamic acid esters and subsequent inter/intramolecular cyclization. Overall process involves in the intramolecular cleavage of two σ-bonds (C−O and C−C) and inter/intramolecular construction of two/one C−C σ-bond(s). Significantly, this protocol was successful without the aid of any metal salts.

INTRODUCTION

Decarboxylation reaction has emerged as a powerful tool in recent years for the synthesis of various acyclic/polycyclic, natural/un-natural and biologically active molecules.[1] The carboxylic acids and their derivatives serve as potential synthetic precursors for this purpose.[2] Among them, the benzoic acids have been applied for the synthesis of structurally diverse arenes.[3] Olefinic carboxylic acids and their esters have been used for the synthesis of olefins via decarboxylation.[4] The well-known Krapcho decarboxylation reaction comprises the loss of an alkoxycarbonyl group from α-carbon, but successful only when there is another electron-withdrawing group connected to the same α-carbon (i.e., β-keto or β-ester etc.).[5] While, the functionalized benzoic acids have been used for the synthesis of biaryls, biaryl acetylenes and cyclic systems via the decarboxylation followed by coupling with suitable partners, in the presence of a transition-metal catalyst.[6] The derivatives of malonic acids under decarboxylation furnishes amino acids, ketals, ketones, naphthalene and quinolone derivatives.[7] Most of these decarboxylation reactions are assisted by expensive metal catalysts and reagents, while, the reports on metal-free decarboxylations are limited.[8] Very recently the research group of Kundu et al. established a metal-free decarboxylative cyclization followed by ring expansion, for the construction of heterocycles.[9] The cinnamic acid ester derivatives, besides being biologically active, are also useful synthetic precursors for various cyclic systems present in natural products and biologically active compounds.[10]

Indane is an ubiquitous core in natural and un-natural compounds of biological importance.[11] For example, the indanes **A** and **B** are composites in ignition resistant thermoplastics.[11a] While, 1-methyl-1-phenyl-indane **C** exhibits retinoic acid receptor (RAR) agonistic activity[11b] and the methyl-phenyl-indane is found to be a part structure in anticancer natural product haouamine-A **D**[11c,d] (Figure 1).

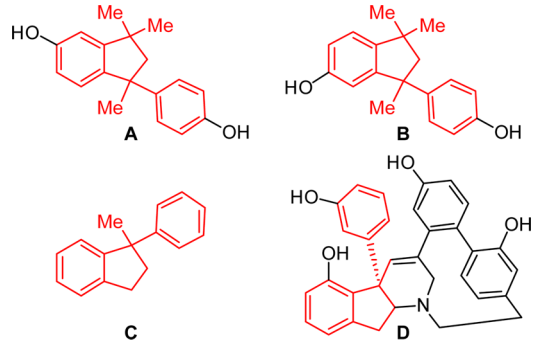


Figure 1. Important compounds with indane skeleton.

In continuation to our research interests in the development of one-pot synthetic protocols for the efficient synthesis of various cyclic systems,[12] herein we report an unprecedented trifluoroacetic acid promoted one-pot[13] decarboxylation followed by intermolecular domino carbo-cyclization for the synthesis of indanes starting from readily available ethyl-3-phenylbut-2-enoates. Significantly, indane products with a quaternary carbon atom were accomplished using this strategy. Notably, the present protocol was found successful without the

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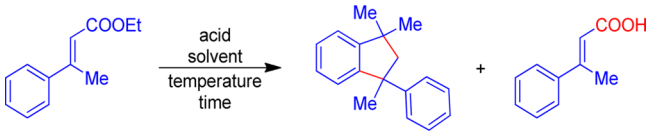
aid of any metal-catalysts. Moreover, this strategy was also found amenable to carbon tethered cinnamic acid esters and enabled the synthesis of novel indane products with a quaternary carbon atom. Unlike the Krapcho decarboxylation reaction, the present method was successful without the support of a second electron-withdrawing group at the α-carbon. It is worth noting that in our previous reports,[12] for the synthesis of indanones or lactones, it was observed that the reaction between cinnamic acid esters and arenes or phenols exclusively proceeds through an intermolecular Friedel–Crafts alkylation and intramolecular condensation as key steps, in the presence of strong protic acid (TfOH)[12g] or Lewis acid ($FeCl_3$),[12e] respectively. In addition, exclusive reaction of cinnamic acid esters without external arenes with TfOH, gave indenones via intramolecular condensation.[12d] Surprisingly, in the present study, the same esters upon treatment with trifluoroacetic acid (i.e., CF_3CO_2H as reagent and also as medium), totally changed the chemoselectivity as well as the reaction path and afforded the indanes.

RESULTS AND DISCUSSION

The synthetic study was initiated by choosing cinnamic acid ester **1a** as model substrate. Thus, the ester **1a** was reacted with trifluoroacetic acid [(TFA), as a reagent as well as medium] at 120 °C for 12 h. To our delight, the indane **2a** was obtained as the sole product in an unprecedented manner (Table 1, entry 1).

Table 1. Optimization Studies for One-Pot Decarboxylative Cyclodimerization to Give Indane 2a[a]



1a **2a** **3a**

entry	acid (equiv)	solvent (mL)	temp (°C)	time (h)	yield **2a** (%)[b]	yield **3a** (%)[b]
1	–[c]	TFA (3.0)	120	12	62	–
2	–[c]	AcOH (3.0)	120	24	–	–[d]
3	TFA (5 equiv)	DCE (1.0)	80	24	–	38
4	TFA (5 equiv)	$CHCl_3$ (1.0)	80	24	–	32
5	TFA (5 equiv)	DCM (1.0)	40	48	–	20
6	TFA (5 equiv)	THF (1.0)	70	24	–	–[d]
7	TFA (5 equiv)	DMF (1.0)	80	40	–	–[d]
8	$AlCl_3$ (3 equiv)	DCE (1.0)	80	24	–	–[e]
9	–[c]	TfOH (1.0)	80	24	–	–[e]
10	*p*-TSA (1 equiv)	DCE (0.5)	80	24	–	–[d]
11	$AuCl_3$ (5 mol %)	DCE (1.0)	80	24	–	–[d]
12	–[c]	TFA (3)	80	24	86	–

[a]Unless otherwise mentioned, all reactions were carried out by using 100 mg (0.53 mmol) of cinnamic acid ester **1a**. [b]Isolated yields of chromatographically pure products. [c]Acid was used as the solvent. [d]No progress of the reaction; only the starting material was recovered. [e]Reaction is not clean; no significant spot on TLC is seen.

The chemical structure of the product **2a** was confirmed from its spectroscopic data. We believed that this reaction might proceed via the formation of the corresponding carboxylic acid (i.e., β-methylcinnamic acid). This carboxylic acid further would undergo acid mediated decarboxylation and generate the styrene intermediate, which in turn could undergo cyclodimerization to afford indane **2a**. It is worth noting that the possible formation of indenone through intramolecular Friedel–Crafts acylation was not observed. To further improve the yield of **2a**, the ester **1a** was screened under different conditions (Table 1). Therefore, **1a** was subjected with the acetic acid, however, led to the recovery of starting material **1a** (Table 1, entry 2). On the other hand, the reaction with 5 equiv of TFA in DCE or $CHCl_3$ or DCM, gave the hydrolyzed cinnamic acid **2a**, albeit in poor yields (Table 1, entries 3 to 5). Other solvents such as THF and DMF were also found ineffective (Table 1, entries 6 and 7). While, the reaction was inconclusive with strong acids, such as, $AlCl_3$ and trifluoromethanesulfonic acid (TfOH), [i.e., neither the product **2a** nor the starting material **1a** was obtained (Table 1, entries 8 and 9)]. Also, the reaction with *p*-TSA and $AuCl_3$ showed no progress (Table 1, entries 10 and 11). Since the reaction was smooth in TFA, we presumed that the reduction of temperature with prolonged reaction time might improve the yield. To our delight, the reaction at 80 °C for 24 h, furnished the indane **2a**, in very good yield (Table 1, entry 12). Among all explored reaction conditions, the conditions with trifluoroacetic acid as solvent at 80 °C for 24 h were best and gave the indane **2a**, in very good yield (Table 1, entry 12).

In order to check the scope and generality of the method, the optimized conditions (Table 1, entry 12) were applied on other cinnamic acid esters **1a–l**. Gratifyingly, the protocol was amenable to those esters **1a–l** with various functional groups on the aromatic ring and furnished the indanes **2a–l** (Table 2). Significantly, the reaction was also compatible with electron donating *meta*-methoxy group on the aromatic ring of the cinnamic acid ester **1g** and furnished the indane **2g** along with minor regioisomer (Table 2). The formation of minor regioisomer can be justified due to the cyclization at the *ortho*-carbon to the methoxy group (Table 2). Moreover, the reaction was also performed at low temperatures, however, it showed no significant improvement of para selectivity toward the cyclization to give exclusively **2g**. On the other hand, to our delight, the reaction with *para*-methoxy cinnamic acid ester **1i**, as anticipated, furnished the indane **2h** as sole product (Table 2), the dimethyl ether of composite in ignition resistant thermoplastics (see compound **B**, Figure 1). It is worth mentioning that the electron withdrawing groups on the aromatic ring retarded the reaction. Hence, no product **2i** was formed with *para*-nitro cinnamic acid ester **2i**, which is usual in Friedel–Crafts alkylations (Table 2). Notably, the reaction was also quite successful with benzophenone derived cinnamic acid ester **1l** as well and gave the triphenyl indane **2l**, in excellent yield (Table 2).

Since the indanes **2** contain no double bond, we presumed that the geometry of the double bond of the synthetic precursors (i.e., cinnamic acid esters) **1** is insignificant. Thus, the *Z*-isomer **1′** must also produce the same indane product **2**. Therefore, the *Z*-isomer **1a′** was subjected, under standard conditions. As anticipated, the indane **2a** (Scheme 1) was formed as the sole product in comparable yield to that obtained from **1a** (i.e., the formation of **2a** from **1a**; Table 2). It is worth mentioning that the possibility for the formation of indenone

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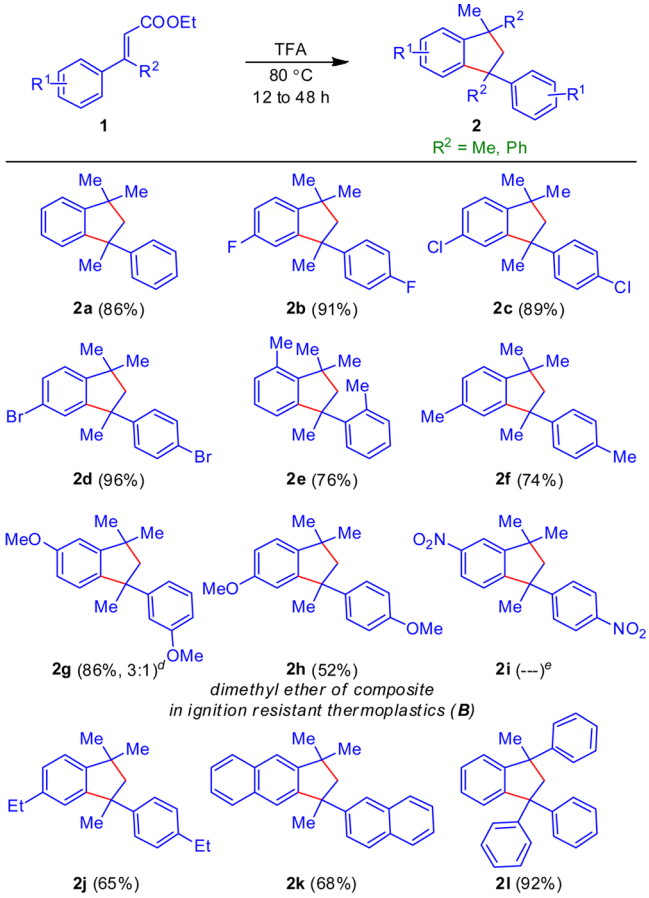
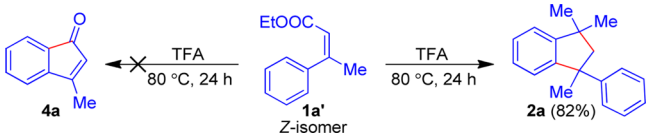
Table 2. Scope of Domino Decarboxylation and Dimerization for Indanes 2[a,b,c]



[a]Reaction conditions: cinnamic acid esters **1a–l** (0.53 mmol) in trifluoroacetic acid (3.0 mL) at 80 °C for 12 to 48 h. [b]Yields in the parentheses are isolated yields of chromatographically pure products **2a–l**. [c]All the reactions have been carried out on *E*-isomer of **1**. [d]Only the major product of the regioisomeric mixture is shown, ratio in the parentheses indicates the ratio of two regioisomers. [e]No progress of the reaction.

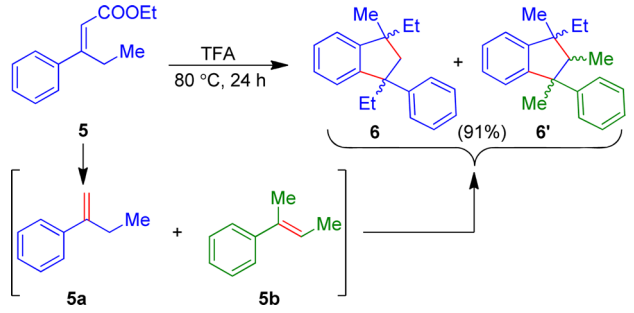
Scheme 1. Selective Formation of Indane 2a from the *Z*-Isomer 1a′



4a, was not observed, in spite of favorable *Z*-geometry of the double bond of **1a′** for intramolecular condensation[12d] (i.e., Friedel–Crafts acylation) (Scheme 1).

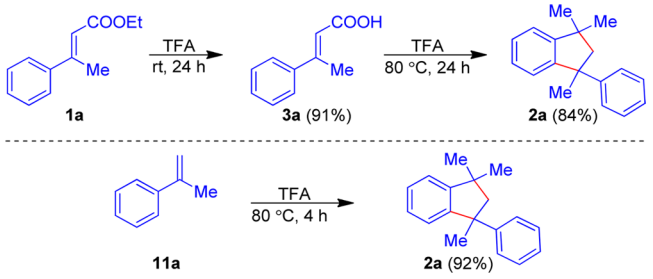
When the reaction was carried out with 3-aryl-3-ethyl prop-2-enoate **5**, as expected, resulted a complex mixture of indanes **6** and **6′**. This can be explained via the formation of styrenes **5a** and **5b** with terminal and internal double bonds and subsequent homo and hetero cyclodimerization (Scheme 2). On the similar grounds, it was presumed that tetrasubstituted acrylate, for example, ethyl α,β-dimethyl-beta-phenyl acrylate, would also proceed through the formation of same mixture of alkene intermediates (**5a** and **5b**) that are feasible from the acrylate **5**. Hence, it would lead to the same complex mixture of indanes (**6** and **6′**) that were obtained from **5**.

Scheme 2. Formation of Mixture of Indanes 6 and 6′ from 5



Since, the cinnamic acid **3a** was formed as the byproduct during the course of optimization; we speculated that the acid **3a** may be one of the feasible intermediates. Therefore, the cinnamic acid **3a** was also reacted with TFA, under standard conditions. Gratifyingly, as expected, afforded the indane **2a**, in very good yield (Scheme 3). Thus, it reveals that the acid **3** would be one of the reaction intermediates of this process. Since, the products **2** have no carbonyl group; we presumed that certainly decarboxylation could have taken place from the acid **3a** to give styrene as the subsequent intermediate. To further confirm this, the reaction was performed with α-methylstyrene **11a**, under established condition. To our delight, as anticipated, it furnished the indane **2a**, in excellent yield (Scheme 3). With these control experiments, it is confirmed that the acid **3a** and styrene **11a** are consecutive intermediates of this strategy.

Scheme 3. Control Experiments That Proves the Intermediacy of the Acid 3a and the Styrene 11a to Give Indane 2a



Moreover the reaction of ethyl (2*E*)-3,4-dihydronaphthalen-1(2*H*)-ylideneacetate **7**, under established conditions, gave the α-methyl naphthalene **8** (Scheme 4). With this outcome, we can ascertain sequential steps for the conversion of **7** to **8**, such as (i) formation of acid **7a**; (ii) decarboxylation to give olefin **7b** and (iii) aromatization to give **8**. In addition, in this case, the intramolecular aromatization would be the driving force that could override the intermolecular cyclodimerization.

After the effective construction of indanes **2a–i**, to further demonstrate the applicability of the method, we envisioned that cinnamic acid ester **9** with an appropriate carbon tether would furnish the indane **10** (Scheme 5).

The requisite carbon tethered cinnamic acid esters **9** were prepared from simple benzaldehydes **13** by using stepwise Grignard/Barbier reaction, Jeffery–Heck and Wittig–Horner–Wadsworth–Emmons protocol. Notably, each step of the sequence progressed smoothly and afforded the desired cinnamates **9**, as depicted in Table 3.

Finally, these cinnamic acid esters **9a–j** were treated with TFA, under established conditions. Gratifyingly, this intramolecular

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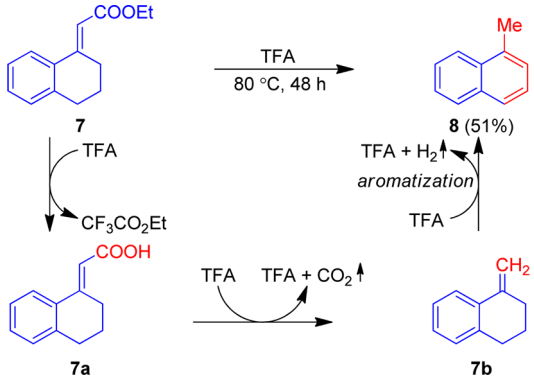
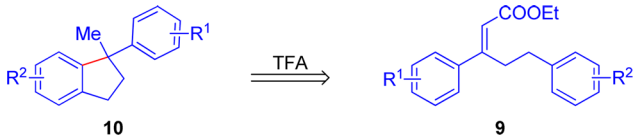
Scheme 4. Formation of α-Methyl Naphthalene 8 from the Ester 7



Scheme 5. Possibility for the Intramolecular Cyclization to 10



carbocyclization variant was also found amenable and furnished the novel analogous indanes **10a–j** with a quaternary carbon atom (Table 4). Significantly, the reaction showed good substrate scope. Also, compatible with alkyl, bromo and chloro substituents on the carbon tethered aromatic ring. Notably, the reaction was also amenable with electron releasing methoxy groups on the tethered aromatic moiety (entries **1oi** and **10j**). In a similar context, as noticed above (Table 2, for compound **2i**), electron withdrawing nitro group retarded the reaction (Table 4, for compound **10k**). Gratifyingly, the reaction was also amenable with the homologated ester **9l** and furnished the tetralin derivative **10l** (Table 4). It is worth mentioning that the product **10l** accompanied the minor indane as an inseparable mixture. This may be due to the isomerization of the terminal double bond into internal one and subsequent internal cyclization. However, after careful column chromatography and by collecting of first few fractions, relatively pure NMR spectra were obtained for **10l**. Gratifyingly, the product **C/10a** is a RAR transactivator. Also, interestingly, the compound **10l** is a methyl analogue of another RAR agonist 1-phenyl tetralin.

It is important to note that the β,β-disubstitution (alkyl/aryl or aryl/aryl) pattern on the cinnamic acid esters is vital to drive the reaction to give indanes, because when simple ethyl cinnamate **1l** (eq 1), α-aryl methyl acrylate **16** (eq 2) and a 1:1 mixture of α-benzyl methyl acrylate **17** and α-methyl-β-aryl methyl acrylate **17′** (eq 3) were subjected, under the established conditions, it showed no progress and led to the recovery of the starting materials (Scheme 6). This can be justified based on the fact that these systems (eq 1–3) are devoid of second β-alkyl/aryl groups, hence, may not be easy to facilitate formation of β-carbocation/double bond isomerization and subsequent decarboxylation step.

On the basis of the above control experiments, the overall reaction mechanism for this domino process is shown in Scheme 7. Initially, the ester **1a** would transform into the acid **3a** through acid mediated hydrolysis of ester **1a**. Acid promoted decarboxylation of **3a** generates the styrene **11a**. Finally, the styrene **11a** undergoes cyclodimerization via activation of olefin by the acid and affords the indane **2a** (Scheme 7). A similar sort of mechanism would be proposed for the formation of indane **10a** starting from **9a** via the formation of styrene derivative **12a** that undergoes subsequent intramolecular carbocyclization (Scheme 7).

In summary, we have developed a domino inter and intramolecular carbocyclizations, for the synthesis of functionalized indanes. Notably, this decarboxylation was promoted by acid without the aid of metal-catalysts. Significantly, the overall domino protocol involves the cleavage of two σ-bonds (C–O and C–C) and construction of one or two new C–C σ-bond(s) via carbocylization or cyclodimerization, respectively.

EXPERIMENTAL SECTION

General Considerations. IR spectra were recorded on FTIR spectrophotometer. ^{1}H NMR spectra were recorded on 400 MHz spectrometer at 295 K in $CDCl_3$; chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) (δ_H = 0.00 ppm) or $CHCl_3$ (δ_H = 7.25 ppm). ^{13}C NMR spectra were recorded at RT in $CDCl_3$; chemical shifts (δ ppm) are reported relative to $CHCl_3$ [δ_C = 77.00 ppm (central line of triplet)]. In the ^{13}C NMR, the nature of carbons (C, CH, CH_2 and CH_3) was determined by recording the DEPT-135 spectra, and is given in parentheses and noted as s = singlet (for C), d = doublet (for CH), t = triplet (for CH_2) and q = quartet (for CH_3). In the ^{1}H NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, sept = septet, dd = doublet of doublet, m = multiplet and br. s = broad singlet. The assignment of signals was confirmed by ^{1}H, ^{13}C CPD and DEPT spectra. High-resolution mass spectra (HRMS) were recorded on a Q-TOF electron spray ionization (ESI) mode and atmospheric pressure chemical ionization (APCI) modes. All small scale dry reactions were carried out using Schlenk tubes under inert atmosphere. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents. Reactions were generally run under argon or a nitrogen atmosphere. Solvents were distilled prior to use; petroleum ether with a boiling range of 60 to 80 °C was used. Trifluoroacetic acid with the purity of 98% was purchased from local sources and used as received. Acme's silica gel (60–120 mesh) was used for column chromatography (approximately 20 g per one gram of crude material).

GP-1 (General Procedure for the Synthesis of Esters 9). To the oil suspension of 60% NaH (192.4 mg, 4.8 mmol) in THF (8 mL) at 0 °C under nitrogen atmosphere, was added triethylphosphanoacetate (1.3 g, 5.8 mmol) in dropwise and allowed the reaction mixture to stir at the same temperature for 0.25 h for the generation of ylide. To this resultant reaction mixture was added ketone **13** (500–728 mg, 2.40 mmol) in dry THF (1.5 mL) and allowed the reaction mixture to stir at 65 °C for 12 h. Progress of the ester **9** formation was monitored by TLC until the reaction is completed. Then, the mixture was quenched by the addition of aqueous NH_4Cl solution and then extracted with ethyl acetate (3 × 20 mL). The organic layer was washed with saturated NaCl solution, dried (Na_2SO_4), and filtered. Evaporation of the solvent under reduced pressure and purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the esters **9** (36–44%) and **9′** (46–58%) as viscous liquid.

GP-2 (General Procedure for the Synthesis of Indanes 2 and 10). In an oven-dried Schlenk tube, were added ester **1/9** (87.7–113.5 mg, 0.43 mmol) and trifluoroacetic acid (3.0 mL) at room temperature under nitrogen atmosphere and allowed the reaction mixture to stir at 80 °C for 12 to 48 h. Progress of the indane **2/10** formation was monitored by TLC until the reaction is completed. Then, the mixture was quenched by the addition of aqueous $NaHCO_3$ solution and then extracted with ethyl acetate (3 × 20 mL). The organic layer was washed with saturated NaCl solution, dried (Na_2SO_4), and filtered. Evaporation of the solvent under reduced pressure and purification of the crude material by silica gel column chromatography

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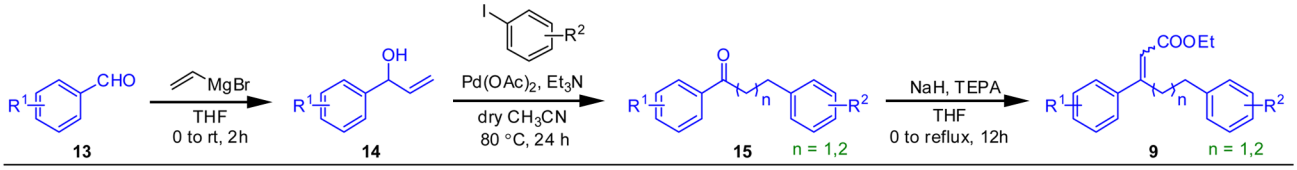
Table 3. Schematic Results Towards the Synthesis of Cinnamates 9 Starting from Simple Benzaldehydes 13[b]



13a	14a (86%)	15a (84%)	9a (88%)
13b	14b (83%)	15b (79%)	9b (87%)
13c	14c (88%)	15c (69%)	9c (90%)
13d	14d (91%)	15d (86%)	9d (87%)
13a	14a (86%)	15e (82%)	9e (88%)
13b	14b (83%)	15f (80%)	9f (86%)
13c	14c (88%)	15g (66%)	9g (91%)
13d	14d (91%)	15h (83%)	9h (88%)
13a	14a (86%)	15i (86%)	9i (88%)
13a	14a (86%)	15j (82%)	9j (80%)
13a	14a (86%)	15k (81%)	9k (42%)
13a	14e (78%)[a]	15l (64%)	9l (80%)

[a]The homo allylic alcohol **14e** was prepared by using zinc mediated Barbier reaction.[14] [b]The yields in the parentheses are isolated yields of chromatographically pure products.

(petroleum ether/ethyl acetate) furnished the indane **2**/**10** (65−94%) as viscous oil/solid and 1-methyl-1-phenyl-tetralin **10i** as viscous oil (52%).

*1,1,3-Trimethyl-3-phenylindane (**2a**).* **GP-2** was carried out with ester **1a** (95 mg, 0.50 mmol) and trifluoroacetic acid (3 mL) for indane formation at 80 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1) furnished the indane **2a** (50.7 mg, 86%) as colorless viscous oil. [TLC control (petroleum ether/ethyl acetate 99:1), R_f (**1a**) = 0.30, R_f

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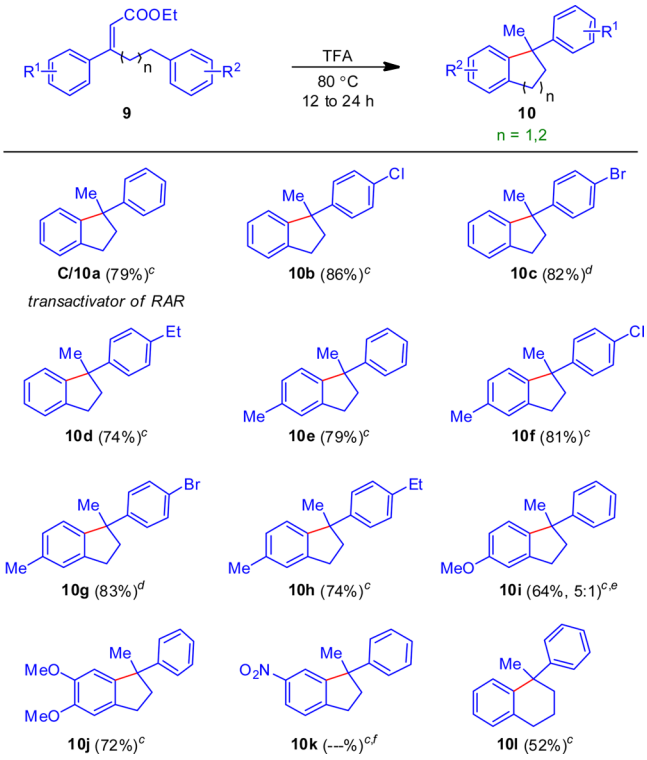
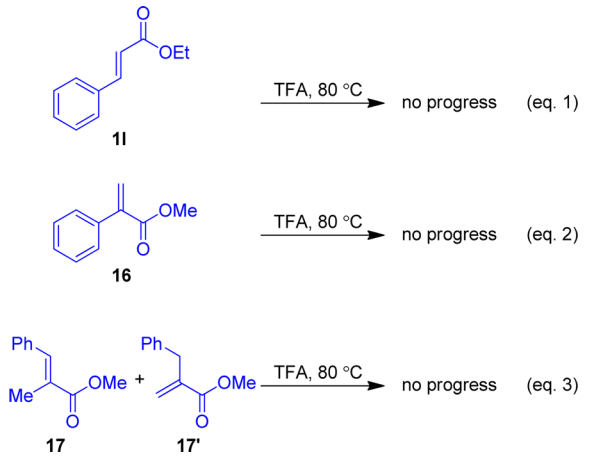
Table 4. Scope of Intramolecular Domino Decarboxylation and Cyclization to Cyclic Products 10[a,b]

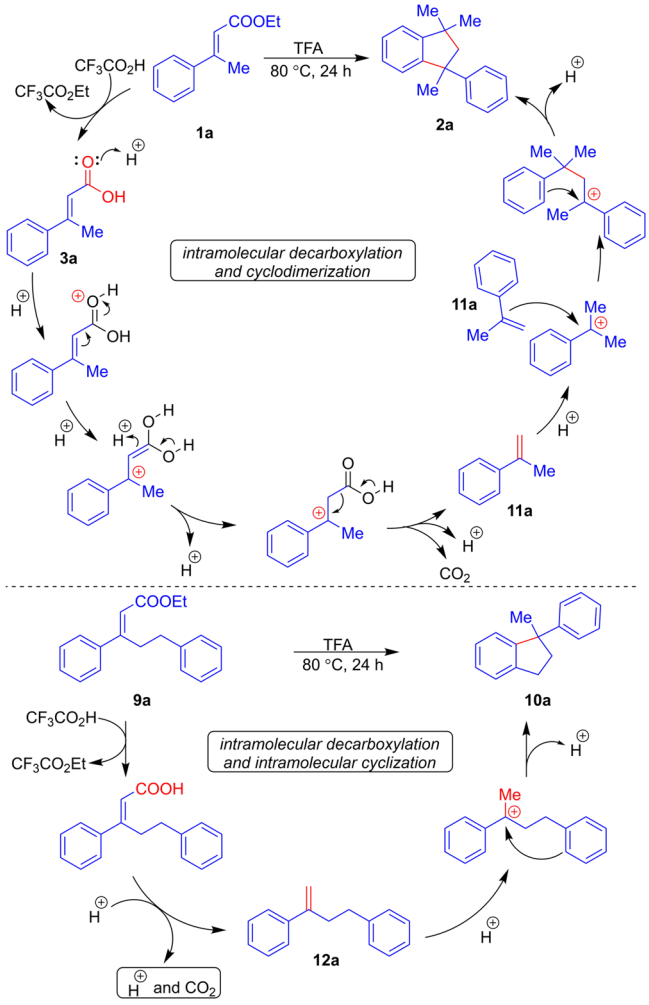


[a]Reaction conditions: cinnamic acid esters **9a–k** (0.53 mmol) in trifluoroacetic acid (3.0 mL) at 80 °C for 12 to 48 h. [b]Yields in the parentheses are isolated yields of chromatographically pure products **10a–k**. [c]Reaction was carried out on *E*-isomer. [d]Reaction was conducted on *Z*-isomer. [e]Only the major product **10i** of the regioisomeric mixture is shown, ratio in the parentheses indicates the ratio of two regioisomers. [f]No progress of the reaction.

Scheme 6. Scope of the Reaction with Cinnamates 1l, 16 and 17



Scheme 7. Possible Mechanism for the Formation of Indanes 2 and 10



(**2a**) = 0.90, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.30–7.08 (m, 9H), 2.39 (d, 1H, J = 13.2 Hz), 2.20 (d, 1H, J = 13.2 Hz), 1.67 (s, 3H), 1.33 (s, 3H), 1.02 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 152.2 (C_q), 151.0 (C_q), 148.7 (C_q), 128.0 (2 × CH), 127.2 (CH), 126.7 (2 × CH), 126.6 (CH), 125.4 (CH), 125.0 (CH), 122.5 (CH), 59.2 (CH_2), 50.8 (C_q), 42.8 (C_q), 30.9 (CH_3), 30.6 (CH_3), 30.4 (CH_3) ppm. IR (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 2959, 1486, 1401, 1094, 1012, 820 cm^{-1}.

*5-Fluoro-3-(4-fluorophenyl)-1,1,3-trimethylindane (**2b**).* **GP-2** was carried out with ester **1b** (104 mg, 0.50 mmol) and trifluoroacetic acid (3 mL) for indane formation at 80 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1) furnished the indane **2b** (61.9 mg, 91%) as colorless viscous oil. [TLC control (petroleum ether/ethyl acetate 99:1), R_f (**1b**) = 0.30, R_f (**2b**) = 0.90, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.16–7.08 (m, 3H), 7.01–6.89 (m, 3H), 6.77 (dd, 1H, J = 9.3 and 2.5 Hz), 2.37 (d, 1H, J = 12.7 Hz), 2.23 (s, 1H, J = 12.7 Hz), 1.66 (s, 3H), 1.33 (s, 3H), 1.03 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 163.5 (d, J = 243.6 Hz, C_q), 162.2 (d, J = 244.3 Hz, C_q), 150.8 (d, J = 7.3 Hz, C_q), 147.5 (C_q), 146.0 (d, J = 2.9 Hz, C_q), 128.1 (d, 2C, J = 7.3 Hz, 2 × CH), 123.8 (d, J = 8.8 Hz, CH), 114.8 (d, 2C, J = 21.3 Hz, 2 × CH), 114.4 (d, J = 22.0 Hz, CH), 111.4 (d, J = 22.0 Hz, CH), 59.5 (t, CH_2), 50.2 (d, J = 1.5 Hz, C_q), 42.4 (C_q), 30.8 (CH_3), 30.7 (CH_3), 30.4 (CH_3) ppm. IR (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 2959, 1605, 1507, 1422, 1227, 1163, 1015, 821 cm^{-1}.

*5-Chloro-3-(4-chlorophenyl)-1,1,3-trimethylindane (**2c**).* **GP-2** was carried out with ester **1c** (112.4 mg, 0.50 mmol) and trifluoroacetic acid (3 mL) for indane formation at 80 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1) furnished the indane **2c** (68.1 mg, 89%) as colorless viscous oil. [TLC control (petroleum ether/ethyl acetate 99:1), R_f (**1c**) = 0.30, R_f (**2c**) = 0.90, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.28–7.16 (m, 3H), 7.15–7.06 (m, 3H), 7.03 (d, 1H, J = 1.9 Hz), 2.34 (d, 1H, J = 12.7 Hz), 2.20 (d, 1H, J = 13.2 Hz), 1.64 (s, 3H), 1.31 (s, 3H), 1.02 (s, 3H) ppm.

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^{13}C NMR ($CDCl_3$, 100 MHz) δ = 150.6 (C_q), 150.3 (C_q), 148.7 (C_q), 132.4 (C_q), 131.5 (C_q), 128.2 (2 × CH), 128.0 (2 × CH), 127.7 (CH), 124.9 (CH), 123.9 (CH), 59.1 (CH_2), 50.4 (C_q), 42.6 (C_q), 30.6 (2 × CH_3), 30.3 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2958, 1486, 1401, 1095, 1013, 820, 723 cm^{-1}.

5-Bromo-3-(4-bromophenyl)-1,1,3-trimethylindane (2d). **GP-2** was carried out with ester **1d** (134.5 mg, 0.50 mmol) and trifluoroacetic acid (3 mL) for indane formation at 80 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1) furnished the indane **2d** (94.6 mg, 96%) as color semisolid. [TLC control (petroleum ether/ethyl acetate 99:1), R_f (**1d**) = 0.30, R_f (**2d**) = 0.90, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.41 (dd, 1H, J = 7.8 and 2.0 Hz), 7.37 (dd, 2H, J = 8.3 and 2.0 Hz), 7.19 (d, 1H, J = 2.0 Hz), 7.08 (d, 1H, J = 7.8 Hz), 7.04 (dd, 2H, J = 8.3 and 2.0 Hz), 2.36 (d, 1H, J = 13.2 Hz), 2.36 (d, 1H, J = 13.2 Hz), 1.64 (s, 3H), 1.32 (s, 3H), 1.03 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 151.2 (C_q), 150.7 (C_q), 149.3 (C_q), 131.2 (2 × CH), 130.6 (CH), 128.5 (2 × CH), 127.9 (CH), 124.5 (CH), 120.5 (C_q), 119.7 (C_q), 59.1 (CH_2), 50.6 (C_q), 42.7 (C_q), 30.6 (2 × CH_3), 30.3 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2961, 2927, 1485, 1464, 1397, 1368, 1073, 1008, 826 cm^{-1}.

1,3,3,4-Tetramethyl-1-(2-methylphenyl)indane (2e). **GP-2** was carried out with ester **1e** (102 mg, 0.50 mmol) and trifluoroacetic acid (3 mL) for indane formation at 80 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1) furnished the indane **2e** (50.2 mg, 76%) as colorless viscous oil. [TLC control (petroleum ether/ethyl acetate 99:1), R_f (**1e**) = 0.30, R_f (**2e**) = 0.90, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.20−7.00 (m, 6H, ArH), 6.88 (d, 1H, J = 7.5 Hz), 2.58 (d, 1H, J = 13.2 Hz), 2.48 (s, 3H), 2.22 (s, 3H, CH_3), 2.15 (d, 1H, J = 13.2 Hz), 1.79 (s, 3H), 1.53 (s, 3H), 1.27 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 151.4 (C_q), 147.6 (C_q), 147.4 (C_q), 136.1 (C_q), 133.9 (C_q), 132.5 (CH), 129.6 (CH), 127.5 (CH), 126.9 (CH), 126.0 (CH), 125.2 (CH), 122.6 (CH), 57.9 (CH_2), 50.2 (C_q), 44.2 (s, C_q), 30.9 (CH_3), 29.5 (CH_3), 28.1 (CH_3), 22.4 (CH_3), 19.3 (CH_3) ppm. IR (neat; MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2958, 1568, 1524, 1455, 1361, 1313, 1192, 1018, 810, 724 cm^{-1}.

1,1,3,5-Tetramethyl-3-(4-methylphenyl)indane (2f). **GP-2** was carried out with ester **1f** (102 mg, 0.50 mmol) and trifluoroacetic acid (3 mL) for indane formation at 80 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1) furnished the indane **2f** (48.8 mg, 74%) as colorless viscous oil. [TLC control (petroleum ether/ethyl acetate 99:1), R_f (**1f**) = 0.30, R_f (**2f**) = 0.90, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.20−7.05 (m, 6H), 6.95 (s, 1H), 2.41 (d, 1H, J = 13.2 Hz), 2.40 (s, 3H), 2.34 (s, 3H), 2.23 (d, 1H, J = 13.2 Hz), 1.71 (s, 3H), 1.37 (s, 3H), 1.09 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 149.3 (C_q), 149.1 (C_q), 148.1 (C_q), 136.1 (C_q), 134.8 (C_q), 128.6 (2 × CH), 128.0 (CH), 126.6 (2 × CH), 125.4 (CH), 122.2 (CH), 59.5 (CH_2), 50.3 (C_q), 42.5 (C_q), 30.8 (2 × CH_3), 30.5 (CH_3), 21.4 (CH_3), 20.9 (CH_3) ppm. IR (neat; MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2956, 1510, 1454, 1360, 1312, 1188, 1018, 816, 725 cm^{-1}.

5-Methoxy-1-(3-methoxyphenyl)-1,3,3-trimethylindane (2g) and 4-Methoxy-3-(3-methoxyphenyl)-1,1,3-trimethylindane (2g′). **GP-2** was carried out with ester **1g** (110.1 mg, 0.50 mmol) and trifluoroacetic acid (3 mL) for indane formation at 80 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3) furnished 3:1 regioisomeric mixture indanes **2g** and **2g′** (63.7 mg, 86%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:5), R_f (**1g**) = 0.30, R_f (**2g** and **2g′**) = 0.80, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz; peaks due to the major isomer **2g**) δ = 7.19 (dd, 1H, J = 7.8 and 7.8 Hz), 7.07 (d, 1H, J = 8.3 Hz), 6.90−6.65 (m, 5H), 3.86 (s, 3H), 3.77 (s, 3H), 2.46 (d, 1H, J = 12.7 Hz), 2.21 (d, 1H, J = 12.7 Hz), 1.68 (s, 3H), 1.35 (s, 3H), 1.05 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz; peaks due to the major isomer **2g**) δ = 159.3 (C_q), 159.2 (C_q), 153.7 (C_q), 153.1 (C_q), 140.6 (C_q), 128.8 (CH), 125.5 (CH), 119.3 (CH), 113.3 (CH), 112.5 (CH), 109.8 (CH), 107.7 (CH), 59.4 (CH_2), 55.3 (CH_3), 55.0 (CH_3), 50.1 (C_q), 42.8 (C_q), 31.1 (CH_3), 30.4 (CH_3), 30.2 (CH_3), 20.9 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2958, 1591, 1507, 1313, 1251, 1183, 1060, 1036, 826 cm^{-1}.

5-Methoxy-3-(4-methoxyphenyl)-1,1,3-trimethylindane (2h). **GP-2** was carried out with ester **1h** (110.1 mg, 0.50 mmol) and trifluoroacetic acid (3 mL) for indane formation at 80 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1) furnished the indane **2h** (38.5 mg, 52%) as pale yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:5), R_f (**1h**) = 0.30, R_f (**2h**) = 0.80, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.15−7.05 (m, 3H), 6.90−6.75 (m, 3H), 6.63 (s, 1H), 3.78 (s, 3H), 3.77 (s, 3H), 2.34 (d, 1H, J = 13.2 Hz), 2.19 (d, 1H, J = 13.2 Hz), 1.66 (s, 3H), 1.31 (s, 3H), 1.03 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 158.9 (C_q), 157.3 (C_q), 150.5 (C_q), 144.5 (C_q), 143.0 (C_q), 127.6 (2 × CH), 123.1 (CH), 113.2 (2 × CH), 113.1 (CH), 109.9 (CH), 59.7 (CH_2), 55.4 (CH_3), 55.2 (CH_3), 50.1 (C_q), 42.1 (C_q), 30.9 (2 × CH_3), 30.8 (CH_3), 30.5 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2954, 1597, 1511, 1311, 1249, 1180, 1035, 825 cm^{-1}.

5-Ethyl-3-(4-ethylphenyl)-1,1,3-trimethylindane (2j). **GP-2** was carried out with ester **1j** (109 mg, 0.50 mmol) and trifluoroacetic acid (3 mL) for indane formation at 80 °C for 48 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1) furnished the indane **2j** (47.4 mg, 65%) as colorless viscous oil. [TLC control (petroleum ether/ethyl acetate 99:1), R_f (**1j**) = 0.30, R_f (**2j**) = 0.90, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2961, 1510, 1455, 1369, 1311, 1017, 828 cm^{-1}. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.20−7.05 (m, 6H), 6.94 (s, 1H), 2.75−2.55 (m, 4H), 2.36 (d, 1H, J = 12.7 Hz), 2.18 (d, 1H, J = 12.7 Hz), 1.67 (s, 3H), 1.33 (s, 3H), 1.30−1.15 (m, 6H), 1.03 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 149.5 (C_q), 149.0 (C_q), 148.3 (C_q), 142.6 (C_q), 141.1 (C_q), 127.3 (2 × CH), 126.8 (CH), 126.6 (2 × CH), 124.3 (CH), 122.2 (CH), 59.5 (CH_2), 50.4 (C_q), 42.5 (C_q), 30.9 (CH_3), 30.7 (CH_3), 30.5 (CH_3), 28.8 (CH_2), 28.2 (CH_2), 15.8 (CH_3), 15.4 (CH_3) ppm.

1,1,3-Trimethyl-3-(2-naphthyl)-2,3-dihydro-1H-cyclopenta[b]-naphthalene (2k). **GP-2** was carried out with ester **1k** (120.2 mg, 0.50 mmol) and trifluoroacetic acid (3 mL) for indane formation at 80 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1) furnished the indane **2k** (57.2 mg, 68%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate 99:1), R_f (**1k**) = 0.30, R_f (**2k**) = 0.90, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.90−7.70 (m, 5H), 7.63 (d, 1H, J = 8.3 Hz), 7.50−7.20 (m, 4H), 7.27 (dd, 1H, J = 8.3 and 6.8 Hz), 7.20 (d, 1H, J = 6.8 Hz), 7.08 (dd, 1H, J = 8.3 and 6.8 Hz), 2.44 (d, 1H, J = 13.7 Hz), 2.36 (d, 1H, J = 13.7 Hz), 2.06 (s, 3H), 1.43 (s, 3H), 1.39 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 149.4 (C_q), 148.6 (C_q), 142.7 (C_q), 133.9 (C_q), 133.3 (C_q), 131.7 (C_q), 129.7 (C_q), 128.8 (CH), 128.7 (CH), 128.1 (CH), 128.0 (CH), 127.4 (CH), 126.3 (CH), 125.8 (CH), 125.6 (CH), 125.3 (CH), 125.0 (CH), 124.5 (CH), 123.5 (CH), 121.3 (CH), 61.3 (CH_2), 52.1 (C_q), 43.3 (C_q), 31.4 (CH_3), 31.3 (CH_3), 28.1 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2960, 1560, 1456, 1377, 1277, 1138, 820, 746 cm^{-1}.

1-Methyl-1,3,3-triphenylindane (2l). **GP-2** was carried out with ester **1l** (126 mg, 0.50 mmol) and trifluoroacetic acid (3 mL) for indane formation at 80 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1) furnished the indane **2l** (83 mg, 92%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate 99:1), R_f (**1l**) = 0.30, R_f (**2l**) = 0.90, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.35−6.95 (m, 19H), 3.39 (d, 1H, J = 13.2 Hz), 3.09 (d, 1H, J = 13.2 Hz), 1.54 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 150.5 (C_q), 149.3 (C_q), 148.8 (C_q), 148.5 (C_q), 147.4 (C_q), 128.7 (2 × CH), 128.6 (2 × CH), 127.9 (2 × CH), 127.8 (2 × CH), 127.6 (2 × CH), 127.4 (CH), 127.3 (CH), 126.9 (2 × CH), 126.8 (CH), 126.0 (CH), 125.6 (CH), 125.5 (CH), 125.0 (CH), 61.3 (CH_2), 60.9 (C_q), 51.1 (C_q), 28.8 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2959, 1594, 1453, 1374, 1277, 1132, 818, 748 cm^{-1}.

Ethyl-trimethyl-phenylindanes (6 and 6′). **GP-2** was carried out with ester **5** (102 mg, 0.50 mmol) and trifluoroacetic acid (3 mL) for

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indane formation at 80 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1) furnished the mixture of indanes **6** and **6′** (60.1 mg, 91%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate 99:1), R_f (**5**) = 0.30, R_f (**6** and **6′**) = 0.90, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.35−7.00 (m, 8H), 6.84 (d, 1H, J = 7.3 Hz), 2.20−1.95 (m, 1H), 1.49 (s, 3H, CH_3), 1.17 (s, 3H, CH_3) 0.91 (d, 3H, J = 7.3 Hz), 0.79 (q, 2H, J = 7.3 Hz), 0.65 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 151.8 (C_q), 150.8 (C_q), 150.2 (C_q), 127.8 (2 × CH), 127.2 (2 × CH), 127.0 (ArCH), 126.9 (ArCH), 126.7 (ArCH), 125.6 (ArCH), 124.8 (ArCH), 123.2 (ArCH), 55.1 (CH), 52.0 (C_q), 46.2 (C_q), 35.5 (CH_3), 33.4 (CH_3), 23.1 (CH_2), 9.1 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2960, 1594, 1457, 1378, 1266, 1136, 820, 724 cm^{-1}. HRMS (APCI$^+$) m/z calculated for $[C_{20}H_{25}]^+$ = $[M + H]^+$: 265.1951, found 265.1959.

*1-Methylnaphthalene (**8**).* **GP-2** was carried out with ester **7** (108 mg, 0.50 mmol) and trifluoroacetic acid (3 mL) for indane formation at 80 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1) furnished the 1-methylnaphthalene **8** (38 mg, 53%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate 99:1), R_f (**7**) = 0.28, R_f (**8**) = 0.90, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 8.14 (d, 1H, J = 7.9 Hz), 8.00 (d, 1H, J = 7.4 Hz), 7.86 (d, 1H, J = 7.9 Hz), 7.75−7.40 (m, 4H, ArH), 2.84 (s, 3H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 134.2 (C_q), 133.5 (C_q), 132.6 (C_q), 128.5 (CH), 126.5 (CH), 126.3 (CH), 125.6 (CH), 125.5 (CH), 125.4 (CH), 124.1 (CH), 19.3 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2959, 1590, 1462, 1378, 1276, 1134, 820, 738 cm^{-1}.

*Ethyl-3-phenyl-5-phenylpent-2-enoate (**9a** and **9a′**).* **GP-1** was carried out with NaH (192.4 mg, 4.8 mmol), triethylphosphanoacetate (1.3 g, 5.8 mmol), ketone **13a** (500.0 mg, 2.40 mmol) and dry THF (9 mL) for esters formation **9a** and **9a′** at 65 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished the esters **9a** (291.2 mg, 44%) and **9a′** (295.9 mg, 44%) as colorless viscous liquids. [TLC control (petroleum ether/ethyl acetate 95:5), R_f (**13a**) = 0.35, R_f (**9a**) = 0.65, R_f (**9a′**) = 0.60, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz, peaks due to *E*-isomer **9a**) δ = 7.52−7.32 (m, 5H), 7.32−7.19 (m, 4H), 7.17 (t, 1H, J = 7.3 Hz), 6.07 (s, 1H), 4.20 (q, 2H, J = 7.3 Hz), 3.50−3.30 (m, 2H), 2.80−2.65 (m, 2H), 1.30 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 166.3 (C_q), 159.3 (C_q), 141.5 (C_q), 141.0 (C_q), 129.0 (CH), 128.6 (2 × CH), 128.4 (2 × CH), 128.2 (2 × CH), 126.7 (2 × CH), 125.9 (CH), 117.8 (CH), 59.9 (CH_2), 35.1 (CH_2), 33.1 (CH_2), 14.3 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2980, 2929, 1709, 1623, 1494, 1453, 1349, 1161, 1036, 745, 697 cm^{-1}. HRMS (ESI$^+$) m/z calculated for $[C_{19}H_{21}O_2]^+$ = $[M + H]^+$: 281.1536, found 281.1546.

*Ethyl-3-(4-chlorophenyl)-5-phenylpent-2-enoate (**9b** and **9b′**).* **GP-1** was carried out with NaH (192.4 mg, 4.8 mmol), triethylphosphanoacetate (1.3 g, 5.8 mmol), ketone **13b** (587.3 mg, 2.40 mmol) and dry THF (9 mL) for esters formation **9b** and **9b′** at 65 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished the esters **9b** (317.5 mg, 42%) and **9b′** (340.3 mg, 45%) as colorless viscous liquids. [TLC control (petroleum ether/ethyl acetate 95:5), R_f (**13b**) = 0.35, R_f (**9b**) = 0.65, R_f (**9b′**) = 0.60, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz, peaks due to *E*-isomer **9b**) δ = 7.29 (d, 2H, J = 8.8 Hz), 7.26 (d, 2H, J = 8.8 Hz), 7.22−7.05 (m, 5H), 5.95 (s, 1H), 4.11 (q, 2H, J = 7.3 Hz), 3.35−3.25 (m, 2H), 2.70−2.55 (m, 2H), 1.22 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 166.1 (C_q), 157.9 (C_q), 141.2 (C_q), 139.4 (C_q), 134.9 (C_q), 128.8 (2 × CH), 128.4 (2 × CH), 128.3 (2 × CH), 128.0 (2 × CH), 126.0 (CH), 118.2 (CH), 60.0 (CH_2), 35.0 (CH_2), 32.9 (CH_2), 14.3 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2979, 2928, 1708, 1622, 1492, 1454, 1368, 1261, 1159, 1093, 1011, 824, 746, 697 cm^{-1}. HRMS (ESI$^+$) m/z calculated for $[C_{19}H_{20}ClO_2]^+$ = $[M + H]^+$: 315.1146, found 315.1143.

*Ethyl-3-(4-bromophenyl)-5-phenylpent-2-enoate (**9c** and **9c′**).* **GP-1** was carried out with NaH (192.4 mg, 4.8 mmol), triethylphosphanoacetate (1.3 g, 5.8 mmol), ketone **13c** (694.1 mg, 2.40 mmol) and dry THF (9 mL) for esters formation **9c** and **9c′** at 65 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished the esters **9c** (319.1 mg, 37%) and **9c′** (457.2 mg, 53%) as colorless viscous liquids. [TLC control (petroleum ether/ethyl acetate 95:5), R_f (**13c**) = 0.37, R_f (**9c**) = 0.66, R_f (**9c′**) = 0.62, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz, peaks due to *Z*-isomer **9c′**) δ = 7.49 (d, 2H, J = 8.3 Hz), 7.27 (dd, 2H, J = 7.8 and 7.3 Hz), 7.19 (t, 1H, J = 7.3 Hz), 7.11 (d, 2H, J = 7.8 Hz), 7.06 (d, 2H, J = 8.3 Hz), 5.90 (s, 1H), 4.00 (q, 2H, J = 7.3 Hz), 2.82−2.60 (m, 4H), 1.10 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 165.6 (C_q), 157.3 (C_q), 140.5 (C_q), 138.6 (C_q), 131.1 (2 × CH), 129.0 (2 × CH), 128.5 (2 × CH), 128.2 (2 × CH), 126.2 (CH), 121.8 (C_q), 118.2 (CH), 60.0 (CH_2), 41.8 (CH_2), 33.7 (CH_2), 14.0 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2979, 2924, 1722, 1641, 1487, 1454, 1278, 1225, 1160, 1038, 1010, 824, 699 cm^{-1}. HRMS (ESI$^+$) m/z calculated for $[C_{19}H_{20}BrO_2]^+$ = $[M + H]^+$: 359.0641, found 359.0647.

*Ethyl-3-(4-ethylphenyl)-5-phenylpent-2-enoate (**9d** and **9d′**).* **GP-1** was carried out with NaH (192.4 mg, 4.8 mmol), triethylphosphanoacetate (1.3 g, 5.8 mmol), ketone **13d** (587.3 mg, 2.40 mmol) and dry THF (9 mL) for esters formation **9d** and **9d′** at 65 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished the esters **9d** (296.2 mg, 40%) and **9d′** (348.1 mg, 47%) as colorless viscous liquids. [TLC control (petroleum ether/ethyl acetate 95:5), R_f (**13d**) = 0.35, R_f (**9d**) = 0.65, R_f (**9d′**) = 0.60, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz, peaks due to *E*-isomer **9d**) δ = 7.41 (d, 2H, J = 7.8 Hz), 7.32−7.10 (m, 7H), 6.08 (s, 1H), 4.20 (q, 2H, J = 7.3 Hz), 3.50−3.30 (m, 2H), 2.80−2.66 (m, 2H), 2.68 (q, 2H, J = 7.8 Hz), 1.30 (t, 3H, J = 7.3 Hz), 1.26 (t, 3H, J = 7.8 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 166.5 (C_q), 159.3 (C_q), 145.4 (C_q), 141.7 (C_q), 138.2 (C_q), 128.5 (2 × CH), 128.3 (2 × CH), 128.1 (2 × CH), 126.7 (2 × CH), 125.9 (CH), 116.9 (CH), 59.8 (CH_2), 35.3 (CH_2), 33.0 (CH_2), 28.5 (CH_2), 15.4 (CH_3), 14.3 (q, CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2980, 2927, 1709, 1621, 1455, 1366, 1263, 1155, 1091, 1013, 825, 750, 699 cm^{-1}. HRMS (ESI$^+$) m/z calculated for $[C_{21}H_{25}O_2]^+$ = $[M + H]^+$: 309.1849, found 309.1846.

*Ethyl (2E)-5-(4-methylphenyl)-3-phenylpent-2-enoate (**9e** and **9e′**).* **GP-1** was carried out with NaH (192.4 mg, 4.8 mmol), triethylphosphanoacetate (1.3 g, 5.8 mmol), ketone **13e** (538.3 mg, 2.40 mmol) and dry THF (9 mL) for esters formation **9e** and **9e′** at 65 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished the esters **9e** (303.8 mg, 43%) and **9e′** (332.1 mg, 47%) as colorless viscous liquids. [TLC control (petroleum ether/ethyl acetate 95:5), R_f (**13e**) = 0.35, R_f (**9e**) = 0.65, R_f (**9e′**) = 0.60, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz, peaks due to *E*-isomer **9e**) δ = 7.52−7.31 (m, 5H), 7.12 (d, 2H, J = 7.3 Hz), 7.08 (d, 2H, J = 7.3 Hz), 6.06 (s, 1H), 4.20 (q, 2H, J = 7.3 Hz), 3.45−3.25 (m, 2H), 2.75−2.62 (m, 2H), 2.31 (s, 3H), 1.31 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 166.3 (C_q), 159.4 (C_q), 141.1 (C_q), 138.5 (C_q), 135.3 (C_q), 128.9 (3 × CH), 128.6 (2 × CH), 128.3 (2 × CH), 126.7 (2 × CH), 117.7 (CH), 59.9 (CH_2), 34.7 (CH_2), 33.3 (CH_2), 21.0 (CH_3), 14.3 (q, CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2979, 2925, 1708, 1621, 1514, 1446, 1368, 1263, 1153, 1038, 1026, 874, 808, 770, 695 cm^{-1}. HRMS (ESI$^+$) m/z calculated for $[C_{20}H_{23}O_2]^+$ = $[M + H]^+$: 295.1693, found 295.1691.

*Ethyl-3-(4-chlorophenyl)-5-(4-methylphenyl)pent-2-enoate (**9f** and **9f′**).* **GP-1** was carried out with NaH (192.4 mg, 4.8 mmol), triethylphosphanoacetate (1.3 g, 5.8 mmol), ketone **13f** (620.9 mg, 2.40 mmol) and dry THF (9 mL) for esters formation **9f** and **9f′** at 65 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished the esters **9f** (315.6 mg, 40%) and **9f′** (363.1 mg, 46%) as colorless viscous liquids. [TLC control (petroleum ether/ethyl acetate 95:5), R_f (**13f**) = 0.35, R_f (**9f**) = 0.65, R_f (**9f′**) = 0.60, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz, peaks due to *E*-isomer **9f**) δ = 7.38 (d, 2H, J = 8.8 Hz), 7.35 (d, 2H, J = 8.8 Hz), 7.10 (d, 2H, J = 8.3 Hz), 7.07 (d, 2H, J = 8.3 Hz), 6.03 (s, 1H), 4.21 (q, 2H, J = 7.3 Hz), 3.40−3.25 (m, 2H), 2.75−2.60 (m, 2H), 2.31 (s, 3H), 1.31 (t, 3H,

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J = 7.3 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 166.1 (C_q), 158.0 (C_q), 139.5 (C_q), 138.2 (C_q), 135.4 (C_q), 134.9 (C_q), 129.0 (2 × CH), 128.8 (2 × CH), 128.3 (2 × CH), 128.0 (2 × CH), 118.1 (CH), 60.0 (CH_2), 34.6 (CH_2), 33.1 (CH_2), 21.0 (CH_3), 14.3 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2980, 2926, 1713, 1624, 1491, 1368, 1172, 1094, 1012, 829 cm^{-1}. HRMS (ESI$^+$) m/z calculated for $[C_{20}H_{22}ClO_2]^+$ = $[M + H]^+$: 329.1303, found 329.1302.

*Ethyl-3-(4-bromophenyl)-5-(4-methylphenyl)pent-2-enoate (**9g** and **9g′**).* **GP-1** was carried out with NaH (192.4 mg, 4.8 mmol), triethylphosphanoaetate (1.3 g, 5.8 mmol), ketone **13g** (727.7 mg, 2.40 mmol) and dry THF (9 mL) for esters formation **9g** and **9g′** at 65 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished the esters **9g** (322.7 mg, 36%) and **9g′** (492.4 mg, 55%) as pale yellow viscous liquids. [TLC control (petroleum ether/ethyl acetate 95:5), R_f (**13g**) = 0.37, R_f (**9g**) = 0.66, R_f (**9g′**) = 0.62, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz, peaks due to *Z*-isomer **9g′**) δ = 7.48 (d, 2H, J = 8.3 Hz), 7.15−7.02 (m, 4H), 7.00 (d, 2H, J = 8.3 Hz), 5.89 (s, 1H), 3.99 (q, 2H, J = 7.3 Hz), 2.75−2.58 (m, 4H), 2.31 (s, 3H), 1.10 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 165.7 (C_q), 157.4 (C_q), 138.7 (C_q), 137.4 (C_q), 135.7 (C_q), 131.1 (2 × CH), 129.1 (2 × CH), 129.0 (2 × CH), 128.1 (2 × CH), 121.8 (C_q), 118.1 (CH), 59.9 (CH_2), 42.0 (CH_2), 33.3 (CH_2), 21.0 (CH_3), 14.0 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2980, 2924, 1721, 1640, 1514, 1490, 1377, 1223, 1158, 1091, 1039, 1014, 830, 809 cm^{-1}. HRMS (ESI$^+$) m/z calculated for $[C_{20}H_{22}BrO_2]^+$ = $[M + H]^+$: 373.0798, found 373.0795.

*Ethyl-3-(4-ethylphenyl)-5-(4-methylphenyl)pent-2-enoate (**9h** and **9h′**).* **GP-1** was carried out with NaH (192.4 mg, 4.8 mmol), triethylphosphanoaetate (1.3 g, 5.8 mmol), ketone **13h** (605.5 mg, 2.40 mmol) and dry THF (9 mL) for esters formation **9h** and **9h′** at 65 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished the esters **9h** (309.6 mg, 40%) and **9h′** (371.5 mg, 48%) as colorless viscous liquids. [TLC control (petroleum ether/ethyl acetate 95:5), R_f (**13h**) = 0.35, R_f (**9h**) = 0.65, R_f (**9h′**) = 0.60, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz, peaks due to *E*-isomer **9h**) δ = 7.42 (d, 2H, J = 8.3 Hz), 7.23 (d, 2H, J = 8.3 Hz), 7.15 (d, 2H, J = 7.8 Hz), 7.09 (d, 2H, J = 7.8 Hz), 6.08 (s, 1H), 4.21 (q, 2H, J = 7.3 Hz), 3.45−3.30 (m, 2H), 2.75−2.62 (m, 2H), 2.68 (q, 2H, J = 7.8 Hz), 2.32 (s, 3H), 1.31 (t, 3H, J = 7.3 Hz), 1.27 (t, 3H, J = 7.8 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 166.5 (C_q), 159.3 (C_q), 145.4 (C_q), 138.6 (C_q), 138.2 (C_q), 135.3 (C_q), 128.9 (2 × CH), 128.3 (2 × CH), 128.1 (2 × CH), 126.7 (2 × CH), 116.8 (CH), 59.8 (CH_2), 34.9 (CH_2), 33.2 (CH_2), 28.5 (CH_2), 21.0 (CH_3), 15.4 (CH_3), 14.3 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2965, 2932, 1707, 1620, 1607, 1453, 1368, 1263, 1155, 1031, 829, 747, 697 cm^{-1}. HRMS (ESI$^+$) m/z calculated for $[C_{22}H_{30}NO_2]^+$ = $[M + NH_4]^+$: 340.2271, found 340.2272.

*Ethyl-5-(3-methoxyphenyl)-3-phenylpent-2-enoate (**9i** and **9i′**).* **GP-1** was carried out with NaH (192.4 mg, 4.8 mmol), triethylphosphanoaetate (1.3 g, 5.8 mmol), ketone **13i** (576.0 mg, 2.40 mmol) and dry THF (9 mL) for esters formation **9i** and **9i′** at 65 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 96:4) furnished the esters **9i** (305.2 mg, 41%) and **9i′** (357.3 mg, 48%) as colorless viscous liquids. [TLC control (petroleum ether/ethyl acetate 95:5), R_f (**13i**) = 0.25, R_f (**9i**) = 0.50, R_f (**9i′**) = 0.40, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz, peaks due to *E*-isomer **9i**) δ = 7.52−7.32 (m, 5H), 7.18 (dd, 1H, J = 7.8 and 7.8 Hz), 6.82 (d, 1H, J = 7.8 Hz), 6.77 (s, 1H), 6.73 (d, 1H, J = 7.8 Hz), 6.07 (s, 1H), 4.21 (q, 2H, J = 7.3 Hz), 3.79 (s, 3H), 3.41 (dd, 2H, J = 8.3 and 7.8 Hz), 2.72 (dd, 2H, J = 8.3 and 7.8 Hz), 1.31 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 166.3 (C_q), 159.5 (C_q), 159.2 (C_q), 143.1 (C_q), 141.0 (C_q), 129.2 (CH), 129.0 (CH), 128.6 (2 × CH), 126.7 (2 × CH), 120.9 (CH), 117.9 (CH), 114.1 (CH), 111.3 (CH), 59.9 (CH_2), 55.1 (CH_3), 35.1 (CH_2), 32.9 (CH_2), 14.3 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2966, 2931, 1706, 1621, 1607, 1454, 1369, 1264, 1155, 1032, 748, 697 cm^{-1}. HRMS (ESI$^+$) m/z calculated for $[C_{20}H_{22}NaO_3]^+$ = $[M + Na]^+$: 333.1461, found 333.1467.

*Ethyl-5-(3,4-dimethoxyphenyl)-3-phenylpent-2-enoate (**9j** and **9j′**).* **GP-1** was carried out with NaH (192.4 mg, 4.8 mmol), triethylphosphanoaetate (1.3 g, 5.8 mmol), ketone **13j** (648.2 mg, 2.40 mmol) and dry THF (9 mL) for esters formation **9j** and **9j′** at 65 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished the esters **9j** (293.9 mg, 36%) and **9j′** (359.2 mg, 44%) as colorless viscous liquids. [TLC control (petroleum ether/ethyl acetate 85:15), R_f (**13j**) = 0.35, R_f (**9j**) = 0.55, R_f (**9j′**) = 0.50, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz, peaks due to *E*-isomer **9j**) δ = 7.52−7.30 (m, 5H), 6.80−6.60 (m, 3H), 6.04 (s, 1H), 4.19 (q, 2H, J = 7.3 Hz), 3.85 (s, 3H), 3.84 (s, 3H), 3.40 (dd, 2H, J = 8.3 and 7.8 Hz), 2.68 (dd, 2H, J = 8.3 and 7.8 Hz), 1.30 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 166.3 (C_q), 159.4 (C_q), 148.7 (C_q), 147.2 (C_q), 141.1 (C_q), 134.1 (C_q), 128.9 (CH), 128.5 (2 × CH), 126.7 (2 × CH), 120.3 (CH), 117.9 (CH), 111.8 (CH), 111.1 (CH), 59.8 (CH_2), 55.9 (CH_3), 55.8 (CH_3), 34.6 (CH_2), 32.9 (CH_2), 14.3 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2965, 2930, 1707, 1620, 1606, 1453, 1368, 1264, 1154, 1110, 1031, 747, 696 cm^{-1}. HRMS (ESI$^+$) m/z calculated for $[C_{21}H_{24}NaO_4]^+$ = $[M + Na]^+$: 363.1567, found 363.1571.

*Ethyl-5-(4-nitrophenyl)-3-phenylpent-2-enoate (**9k**).* **GP-1** was carried out with NaH (192.4 mg, 4.8 mmol), triethylphosphanoaetate (1.3 g, 5.8 mmol), ketone **13k** (612.2 mg, 2.40 mmol) and dry THF (9 mL) for ester formation **9k** at 65 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished the ester **9k** (327.8 mg, 42%) as pale yellow semisolid. [TLC control (petroleum ether/ethyl acetate 85:15), R_f (**13k**) = 0.35, R_f (**9k**) = 0.55, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.09 (d, 2H, J = 8.8 Hz), 7.45−7.36 (m, 5H), 7.35 (d, 2H, J = 8.8 Hz), 6.07 (s, 1H), 4.18 (q, 2H, J = 7.3 Hz), 3.43 (dd, 2H, J = 7.8 and 7.8 Hz), 2.83 (dd, 2H, J = 7.8 and 7.8 Hz), 1.29 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 166.2 (C_q), 158.4 (C_q), 149.2 (C_q), 146.4 (C_q), 140.5 (C_q), 129.3 (2 × CH), 129.2 (CH), 128.7 (2 × CH), 126.6 (2 × CH), 123.5 (2 × CH), 118.4 (CH), 60.0 (CH_2), 34.8 (CH_2), 32.2 (CH_2), 14.3 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2970, 2932, 1708, 1619, 1602, 1550, 1453, 1264, 1158, 1050, 1032, 746 cm^{-1}. HRMS (ESI$^+$) m/z calculated for $[C_{19}H_{20}NO_4]^+$ = $[M + H]^+$: 326.1387, found 326.1379.

*Ethyl-3,6-diphenylhex-2-enoate (**9l** and **9l′**).* **GP-1** was carried out with NaH (192.4 mg, 4.8 mmol), triethylphosphanoaetate (1.3 g, 5.8 mmol), ketone **13l** (538.3 mg, 2.40 mmol) and dry THF (9 mL) for esters formation **9l** and **9l′** at 65 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished the esters **9l** (261.4 mg, 37%) and **9l′** (303.8 mg, 43%) as colorless viscous liquids. [TLC control (petroleum ether/ethyl acetate 95:5), R_f (**13l**) = 0.35, R_f (**9l**) = 0.65, R_f (**9l′**) = 0.60, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz, peaks due to *E*-isomer **9l**) δ = 7.40−7.30 (m, 5H), 7.23 (dd, 2H, J = 7.8 and 7.3 Hz), 7.20−7.08 (m, 3H), 6.04 (s, 1H), 4.20 (q, 2H, J = 7.3 Hz), 3.20−3.10 (m, 2H), 2.70−2.60 (m, 2H), 1.82−1.65 (m, 2H), 1.30 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 166.5 (C_q), 160.3 (C_q), 142.2 (C_q), 141.2 (C_q), 128.9 (CH), 128.5 (2 × CH), 128.4 (2 × CH), 128.2 (2 × CH), 126.7 (2 × CH), 125.7 (CH), 117.7 (CH), 59.9 (t, CH_2), 35.9 (CH_2), 30.7 (CH_2), 30.6 (CH_2), 14.3 (q, CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2979, 2931, 1709, 1623, 1494, 1451, 1368, 1157, 1042, 875, 749, 697 cm^{-1}. HRMS (ESI$^+$) m/z calculated for $[C_{20}H_{23}O_2]^+$ = $[M + H]^+$: 295.1693, found 295.1694.

*1-Methyl-1-phenylindane (**10a**).* **GP-2** was carried out with ester **9a** (140 mg, 0.50 mmol) and trifluoroacetic acid (3 mL) for indane formation at 80 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1) furnished the indane **10a** (82.2 mg, 79%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate 99:1), R_f (**9a**) = 0.30, R_f (**10a**) = 0.90, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.30−7.00 (m, 9H), 3.00−2.75 (m, 2H), 2.45−2.32 (m, 1H), 2.25−2.10 (m, 1H), 1.66 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 150.9 (C_q), 149.0 (C_q), 143.6 (C_q), 128.0 (2 × CH), 126.6 (2 × CH), 126.5 (CH), 126.4 (CH), 125.7 (CH), 124.5 (CH), 124.2 (CH), 52.0 (C_q), 44.1 (CH_2), 30.4 (CH_2), 27.4 (CH_3) ppm. IR (MIR-ATR,

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4000−600 cm^{-1}) ν_{max} = 2961, 1492, 1479, 1454, 1372, 1096, 1012, 821, 763, 724 cm^{-1}.

*1-(4-Chlorophenyl)-1-methylindane (**10b**).* **GP-2** was carried out with ester **9b** (157.4 mg, 0.50 mmol) and trifluoroacetic acid (3 mL) for indane formation at 80 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1) furnished the indane **10b** (104.5 mg, 86%) as colorless viscous oil. [TLC control (petroleum ether/ethyl acetate 99:1), R_f (**9b**) = 0.30, R_f (**10b**) = 0.90, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.30−7.15 (m, 5H), 7.10 (d, 2H, J = 8.3 Hz), 7.05−6.95 (m, 1H), 3.00−2.75 (m, 2H), 2.40−2.28 (m, 1H), 2.23−2.12 (m, 1H), 1.64 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 150.4 (C_q), 147.6 (C_q), 143.5 (C_q), 131.5 (C_q), 128.1 (2 × CH), 128.0 (2 × CH), 126.8 (CH), 126.6 (CH), 124.6 (CH), 124.0 (CH), 51.7 (C_q), 44.1 (CH_2), 30.3 (CH_2), 27.3 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2961, 2850, 1490, 1477, 1455, 1372, 1095, 1012, 821, 759, 724 cm^{-1}. HRMS (ESI$^+$) m/z calculated for $[C_{16}H_{14}Cl]^+$ = $[(M - H_2) + H]^+$: 241.0779, found 241.0785.

*1-(4-Bromophenyl)-1-methylindane (**10c**).* **GP-2** was carried out with ester **9c′** (179.6 mg, 0.50 mmol) and trifluoroacetic acid (3 mL) for indane formation at 80 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1) furnished the indane **10c′** (117.7 mg, 82%) as colorless viscous oil. [TLC control (petroleum ether/ethyl acetate 99:1), R_f (**9c′**) = 0.25, R_f (**10c**) = 0.90, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.36 (d, 2H, J = 8.8 Hz), 7.32−7.15 (m, 3H), 7.05 (d, 2H, J = 8.8 Hz), 7.02 (dd, 1H, J = 8.3 and 2.9 Hz), 3.00−2.75 (m, 2H), 2.40−2.28 (m, 1H), 2.23−2.12 (m, 1H), 1.64 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 150.4 (C_q), 148.2 (C_q), 143.5 (C_q), 131.0 (2 × CH), 128.5 (2 × CH), 126.8 (CH), 126.6 (CH), 124.6 (CH), 124.0 (CH), 119.6 (C_q), 51.8 (C_q), 44.1 (CH_2), 30.3 (CH_2), 27.3 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2960, 2926, 2850, 1486, 1455, 1394, 1078, 1008, 818, 759, 714 cm^{-1}. HRMS (ESI$^+$) m/z calculated for $[C_{16}H_{14}{}^{79}Br]^+$ = $[(M - H_2) + H]^+$: 285.0273, found 285.0271.

*1-(4-Ethylphenyl)-1-methylindane (**10d**).* **GP-2** was carried out with ester **9d** (154.2 mg, 0.50 mmol) and trifluoroacetic acid (3 mL) for indane formation at 80 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1) furnished the indane **10d** (87.5 mg, 74%) as colorless viscous oil. [TLC control (petroleum ether/ethyl acetate 99:1), R_f (**9d**) = 0.32, R_f (**10d**) = 0.90, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.30−7.22 (m, 2H), 7.22−7.15 (m, 2H), 7.14−7.00 (m, 4H), 2.95−2.85 (m, 2H), 2.60 (q, 2H, J = 7.8 Hz), 2.42−2.32 (m, 1H), 2.23−2.12 (m, 1H), 1.65 (s, 3H), 1.21 (t, 3H, J = 7.8 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 151.1 (C_q), 146.3 (C_q), 143.6 (C_q), 141.5 (C_q), 127.4 (2 × CH), 126.5 (2 × CH), 126.5 (CH), 126.4 (CH), 124.5 (CH), 124.2 (CH), 51.7 (C_q), 44.1 (CH_2), 30.4 (CH_2), 28.2 (t, CH_2), 27.5 (CH_3), 15.4 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2961, 2929, 2868, 1510, 1477, 1455, 1372, 1061, 1019, 825, 758, 725, 699 cm^{-1}. HRMS (ESI$^+$) m/z calculated for $[C_{18}H_{21}]^+$ = $[M + H]^+$: 237.1638, found 237.1637.

*1,5-Dimethyl-1-phenylindane (**10e**).* **GP-2** was carried out with ester **9e** (147.2 mg, 0.50 mmol) and trifluoroacetic acid (3 mL) for indane formation at 80 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1) furnished the indane **10e** (87.8 mg, 79%) as colorless viscous oil. [TLC control (petroleum ether/ethyl acetate 99:1), R_f (**9e**) = 0.32, R_f (**10e**) = 0.90, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.35−7.11 (m, 6H), 7.01 (d, 1H, J = 7.3 Hz), 6.86 (s, 1H), 2.95−2.75 (m, 2H), 2.44−2.31 (m, 1H), 2.30 (s, 3H), 2.23−2.10 (m, 1H), 1.65 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 151.1 (C_q), 149.1 (C_q), 140.6 (C_q), 136.0 (C_q), 127.9 (2 × CH), 127.4 (CH), 126.6 (2 × CH), 125.6 (CH), 124.8 (CH), 124.2 (CH), 51.9 (C_q), 44.4 (CH_2), 30.0 (CH_2), 27.4 (CH_3), 21.4 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2959, 2862, 1599, 1493, 1454, 1443, 1372, 1029, 811, 763, 755, 699 cm^{-1}. HRMS (ESI$^+$) m/z calculated for $[C_{17}H_{17}]^+$ = $[(M - H_2) + H]^+$: 221.1325, found 221.1323.

*1-(4-Chlorophenyl)-1,5-dimethylindane (**10f**).* **GP-2** was carried out with ester **9f** (164.4 mg, 0.50 mmol) and trifluoroacetic acid (3 mL) for indane formation at 80 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1) furnished the indane **10f** (104.2 mg, 81%) as colorless viscous oil. [TLC control (petroleum ether/ethyl acetate 99:1), R_f (**9f**) = 0.30, R_f (**10f**) = 0.90, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.23 (d, 2H, J = 8.3 Hz), 7.17 (d, 1H, J = 7.8 Hz), 7.13 (d, 2H, J = 8.3 Hz), 7.05 (d, 1H, J = 7.8 Hz), 6.84 (s, 1H), 2.97−2.77 (m, 2H), 2.44−2.30 (m, 1H), 2.34 (s, 3H), 2.24−2.10 (m, 1H), 1.65 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 150.6 (C_q), 147.7 (C_q), 140.5 (C_q), 136.2 (C_q), 131.4 (C_q), 128.1 (2 × CH), 128.0 (2 × CH), 127.6 (CH), 124.6 (CH), 124.3 (CH), 51.6 (C_q), 44.4 (CH_2), 29.9 (CH_2), 27.2 (CH_3), 21.4 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2959, 2926, 2852, 1491, 1454, 1398, 1095, 1012, 826, 810, 719, 709 cm^{-1}. HRMS (ESI$^+$) m/z calculated for $[C_{17}H_{16}Cl]^+$ = $[(M - H_2) + H]^+$: 255.0935, found 255.0931.

*1-(4-Bromophenyl)-1,5-dimethylindane (**10g**).* **GP-2** was carried out with ester **9g′** (186.6 mg, 0.50 mmol) and trifluoroacetic acid (3 mL) for indane formation at 80 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1) furnished the indane **10g** (125.1 mg, 83%) as colorless viscous oil. [TLC control (petroleum ether/ethyl acetate 99:1), R_f (**9g′**) = 0.25, R_f (**10g**) = 0.90, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.37 (d, 2H, J = 8.8 Hz), 7.15 (d, 1H, J = 7.8 Hz), 7.06 (d, 2H, J = 8.8 Hz), 7.03 (d, 1H, J = 7.8 Hz), 6.82 (s, 1H), 2.95−2.75 (m, 2H), 2.41−2.26 (m, 1H), 2.32 (s, 3H), 2.25−2.10 (m, 1H), 1.63 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 150.6 (C_q), 148.3 (C_q), 140.5 (C_q), 136.2 (C_q), 131.0 (2 × CH), 128.5 (2 × CH), 127.7 (CH), 124.6 (CH), 124.3 (CH), 119.6 (C_q), 51.7 (C_q), 44.3 (CH_2), 29.9 (CH_2), 27.2 (CH_3), 21.4 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2959, 2925, 2853, 1488, 1455, 1394, 1077, 1008, 823, 811, 703 cm^{-1}. HRMS (ESI$^+$) m/z calculated for $[C_{17}H_{16}{}^{79}Br]^+$ = $[(M - H_2) + H]^+$: 299.0430, found 299.0426.

*1-(4-Ethylphenyl)-1,5-dimethylindane (**10h**).* **GP-2** was carried out with ester **9h** (161.2 mg, 0.50 mmol) and trifluoroacetic acid (3 mL) for indane formation at 80 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1) furnished the indane **10h** (92.6 mg, 74%) as colorless viscous oil. [TLC control (petroleum ether/ethyl acetate 99:1), R_f (**9h**) = 0.32, R_f (**10h**) = 0.90, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.20−6.98 (m, 6H), 6.87 (s, 1H), 2.91−2.80 (m, 2H), 2.62 (q, 2H, J = 7.8 Hz), 2.42−2.30 (m, 1H), 2.32 (s, 3H), 2.23−2.15 (m, 1H), 1.65 (s, 3H), 1.23 (t, 3H, J = 7.8 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 151.3 (C_q), 146.4 (C_q), 141.4 (C_q), 140.6 (C_q), 135.9 (C_q), 127.4 (2 × CH), 127.3 (CH), 126.5 (2 × CH), 124.8 (CH), 124.1 (CH), 51.6 (C_q), 44.4 (CH_2), 30.0 (CH_2), 28.3 (CH_2), 27.4 (CH_3), 21.4 (CH_3), 15.4 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2960, 2926, 2868, 1512, 1492, 1454, 1372, 1019, 829, 810 cm^{-1}. HRMS (ESI$^+$) m/z calculated for $[C_{19}H_{21}]^+$ = $[(M - H_2) + H]^+$: 249.1638, found 249.1634.

*5-Methoxy-1-methyl-1-phenylindane (**10i** and **10i′**).* **GP-2** was carried out with ester **9i** (155.1 mg, 0.50 mmol) and trifluoroacetic acid (3 mL) for indane formation at 80 °C for 48 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3) furnished the miture of indanes **10i** and **10i′** (76.2 mg, 64%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate 97:3), R_f (**9i**) = 0.25, R_f (**10i** and **10i′**) = 0.65, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz; peaks due to major isomer) δ = 7.30−7.10 (m, 5H), 6.96 (d, 1H, J = 8.3 Hz), 6.82 (s, 1H), 6.76 (d, 1H, J = 8.3 Hz), 3.81 (s, 3H), 2.95−2.75 (m, 2H), 2.45−2.32 (m, 1H), 2.27−2.10 (m, 1H), 1.65 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz; peaks due to major isomer) δ = 158.9 (C_q), 149.3 (C_q), 145.2 (C_q), 143.1 (C_q), 127.9 (2 × CH), 126.5 (2 × CH), 125.6 (CH), 124.8 (CH), 112.4 (CH), 109.7 (CH), 55.4 (CH_3), 51.4 (C_q), 44.5 (CH_2), 30.5 (CH_2), 27.7 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2960, 2926, 2854, 1489, 1454, 1393, 1076, 1065, 1010, 824, 813, 710 cm^{-1}. HRMS (ESI$^+$) m/z calculated for $[C_{17}H_{19}O]^+$ = $[M + H]^+$: 239.1430, found 239.1425.

*5,6-Dimethoxy-1-methyl-1-phenylindane (**10j**).* **GP-2** was carried out with ester **9j** (170.1 mg, 0.50 mmol) and trifluoroacetic acid (3 mL) for indane formation at 80 °C for 24 h. Purification of the crude material

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by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1) furnished the indane **10j** (96.5 mg, 72%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10), R_f (**9j**) = 0.25, R_f (**10j**) = 0.60, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.35−7.10 (m, 5H), 6.81 (s, 1H), 6.57 (s, 1H), 3.89 (s, 3H), 3.80 (s, 3H), 2.90−2.75 (m, 2H), 2.42−2.28 (m, 1H), 2.25−2.15 (m, 1H), 1.67 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 149.3 (C_q), 148.2 (C_q), 148.1 (C_q), 142.5 (C_q), 135.2 (C_q), 128.0 (2 × CH), 126.5 (2 × CH), 125.7 (CH), 107.4 (CH), 107.2 (CH), 56.0 (CH_3), 55.9 (CH_3), 52.2 (C_q), 44.8 (CH_2), 30.3 (CH_2), 27.4 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2959, 2926, 2853, 1488, 1455, 1394, 1077, 1060, 1011, 823, 814, 711 cm^{-1}. HRMS (ESI$^+$) m/z calculated for $[C_{18}H_{20}NaO_2]^+$ = $[M + Na]^+$: 291.1356, found 291.1353.

*1-Methyl-1-phenyl-1,2,3,4-tetrahydronaphthalene (**10l**).* **GP-2** was carried out with ester **9l** (147 mg, 0.50 mmol) and trifluoroacetic acid (3 mL) for indane formation at 80 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1) furnished the indane **10l** (58 mg, 52%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate 99:1), R_f (**9l**) = 0.30, R_f (**10l**) = 0.90, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.35−6.95 (m, 9H), 2.84 (dd, 2H, J = 6.4 and 6.3 Hz), 2.10−2.00 (m, 1H), 1.95−1.84 (m, 1H), 1.83−1.63 (m, 4H), 1.30 (dd, 1H, J = 7.3 and 6.4 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 151.6 (C_q), 144.4 (C_q), 137.0 (C_q), 129.2 (CH), 129.0 (CH), 128.9 (CH), 127.7 (2 × CH), 127.4 (2 × CH), 125.7 (CH), 125.4 (CH), 42.9 (C_q), 41.4 (CH_2), 30.2 (CH_2), 30.0 (CH_2), 19.5 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2959, 1492, 1480, 1454, 1376, 1086, 1010, 763 cm^{-1}.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02015.

Copies of ^{1}H NMR and ^{13}C NMR spectra of all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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