Lewis Acid Promoted Reactions of 1,1-Diarylallenes and Ketone Derivatives: Synthesis of Indenes by an Addition/Cyclization Reaction

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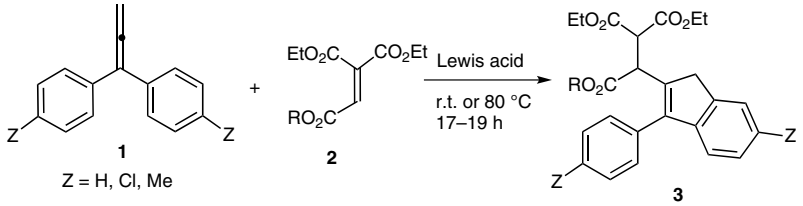
Abstract: The Lewis acid promoted reaction of 1,1-diarylallenes with ketone derivatives was examined. The tin(IV) chloride promoted reaction of diarylallenes with vinyl ketones gave indene derivatives through a conjugate addition/cyclization reaction. The reaction of diphenylallene with diethyl oxomalonate in the presence of one equivalent of tin(IV) chloride at –40 °C gave diethyl hydroxy(3-phenyl-1*H*-inden-2-yl)malonate as the major product through a carbonyl addition/cyclization reaction, whereas the same reactants in the presence of 0.2 equivalents of tin(IV) chloride at 80 °C gave diethyl (3-phenyl-1*H*-inden-2-yl)malonate. Diethyl hydroxy(3-phenyl-1*H*-inden-2-yl)malonate was also converted into the latter product on heating at 80 °C in the presence of 0.2 equivalents of tin(IV) chloride.

Key words: allenes, Lewis acids, ketones, cyclizations, Michael additions, addition reactions

Because of their structural feature comprising two adjacent carbon–carbon double bonds, allene derivatives play an important role in organic synthesis[1] and the transition-metal-catalyzed reactions of allenes to give a variety of products have been studied extensively.[2] Although Lewis acids are important catalysts in organic synthesis,[3] few examples of Lewis acid promoted reactions of allenes have been reported.[4] We recently showed that the reaction of arylallenes **1** with ethylene-1,1,2-tricarboxylate triesters **2** in the presence of tin(IV) chloride gives the corresponding indene derivatives **3** efficiently through a conjugate addition/cyclization reaction (Scheme 1).[5] In this reaction, the phenylallene moiety reacts with tin(IV) chloride coordinated ethylene-1,1,2-tricarboxylates **2** to form a phenyl allylic cation intermediate that undergoes cyclization.

The examination of other electrophiles that can be activated by Lewis acids to form indenes is of synthetic and mechanistic interest.[6,7] We examined the Lewis acid promoted reactions of 1,1-diarylallenes with ketone derivatives, such as vinyl ketones **4** (for 1,4-addition) and diethyl oxomalonate (**6**) (for 1,2-addition). For comparison, we also examined the Lewis acid catalyzed reactions of diethyl oxomalonate (**6**) with 1,1-dialkylallenes.

As previously described,[5] the tin(IV) chloride promoted reaction of 1,1-diphenylallene (**1a**) with diethyl benzylidenemalonate as a Michael acceptor failed to proceed through a conjugate addition/cyclization. Highly reactive electrophiles may be required. We therefore examined the reactions of simple reactive vinyl ketones. Because tin(IV) chloride has been shown to be an effective catalyst for indene formation through the reaction of ethylene-1,1,2-tricarboxylates **2** with arylallenes,[5] we first examined the tin(IV) chloride promoted reaction. The reaction of 1,1-diarylallenes **1a**–**b** with vinyl ketones **4** in the presence of tin(IV) chloride in dichloromethane or chloroform at room temperature gave the corresponding indene derivatives **5** (Scheme 2). Both reactants **1** and **4** are unstable in the presence of the Lewis acid. Optimum yields of indenes **5** were obtained under the reaction conditions shown in Table 1.[8] For example, the reaction of allene **1a** in the presence of two equivalents of vinyl ketone **4a** and one equivalent of tin(IV) chloride in chloroform for five minutes gave the indene derivative **5a** in 54% yield (Table 1, entry 1). The reaction of allene **1a** with ketone **4a** in the presence of zinc(II) iodide or aluminum(III) chloride resulted in decomposition of the substrates and did not give the indene product. Tin(IV) chloride may have suitable Lewis acidity for this indene formation, as in the case of ethylene-1,1,2-tricarboxylates.[5]



Scheme 1

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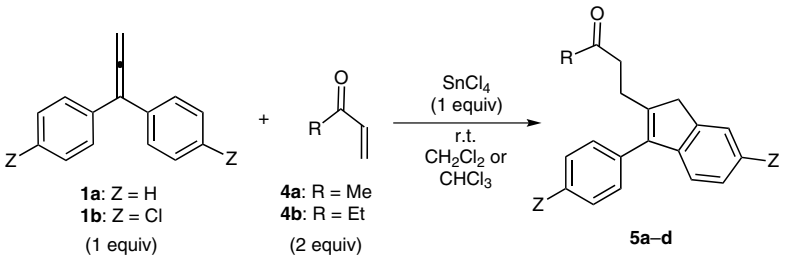


Scheme 2

Table 1 Reactions of 1,1-Diarylallenes **1a–b** with Vinyl Ketones **4a–b**

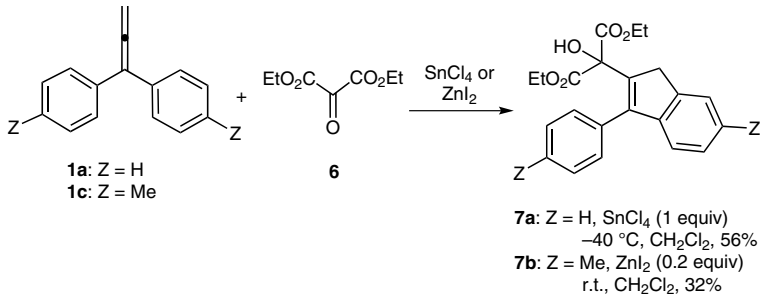
Entry[a]	Allene	Ketone	Solvent	Time	Product	Yield (%)[c]
1	**1a**	**4a**	$CHCl_3$	5 min[b]	**5a**	54
2	**1a**	**4b**	$CHCl_3$	5 min[b]	**5b**	58
3	**1b**	**4a**	CH_2Cl_2	overnight	**5c**	58
4	**1b**	**4b**	$CHCl_3$	1 h[b]	**5d**	50

[a] Reactions were carried out with **1** (1.0 mmol), **4** (2.0 mmol), and $SnCl_4$ (1.0 mmol) in the appropriate solvent (4–8 mL).
[b] To monitor the progress of the reaction, parallel experiments were carried out in an NMR tube (0.1-mmol scale).
[c] Isolated yield.

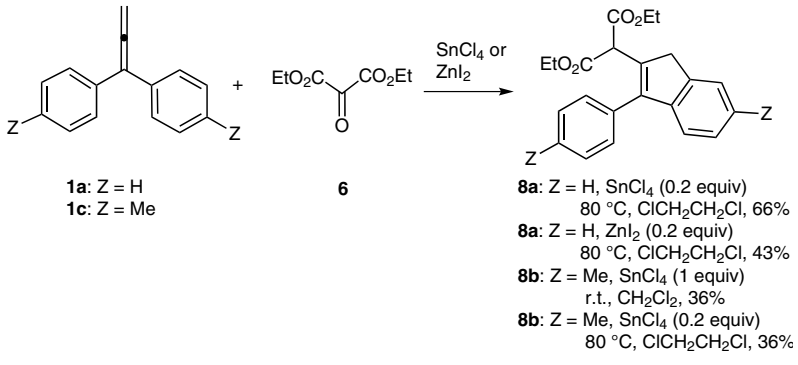
Under similar conditions, other α,β-conjugated carbonyl compounds, such as trimethyl phosphonoacrylate, dimethyl (dicyanomethylene)malonate,[9] methyl acrylate, or cyclohex-2-en-1-one, gave complex mixtures or unreacted starting materials.

Next, we examined the 1,2-addition reactions of activated carbonyl compounds with diarylallenes. The reaction of 1,1-diphenylallene (**1a**) and diethyl oxomalonate (**6**) in the presence of one equivalent of tin(IV) chloride in dichloromethane at –40 °C gave the hydroxy(indenyl)malonate **7a** in 56% yield (Scheme 3). The reaction of 1,1-bis(4-chlorophenyl)allene (**1b**) and oxomalonate **6** at various temperatures gave complex mixtures, possibly including indene derivatives. The products could not be isolated or purified.

When the reaction of **1a** with **6** was carried out in the presence of 0.2 equivalents of tin(IV) chloride at 80 °C in 1,2-dichloroethane, the indenylmalonate **8a** was obtained as the major product in 66% yield (Scheme 4). At room temperature, this reaction gave a complex mixture of products including hydroxy(indenyl)malonate **7a** and indenylmalonate **8a**. Zinc(II) iodide was also an effective catalyst for indene formation.



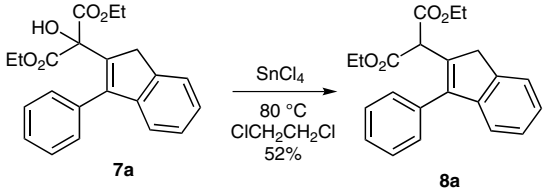
Scheme 3



Scheme 4

The reaction of 1,1-di(4-tolyl)allene (**1c**) and oxomalonate **6** in the presence of 1.0 or 0.2 equivalents of tin(IV) chloride at room temperature gave indenylmalonate **8b** as the major product (Scheme 4). The reaction of allene **1c** and oxomalonate **6** in the presence of 0.2 equivalents of zinc(II) iodide at room temperature gave hydroxy(indenyl)malonate **7b** as the major product in 32% yield (Scheme 3).

On heating at 80 °C in the presence of tin(IV) chloride, **7a** was transformed into **8a** in 52% yield (Scheme 5). The mechanism for the reduction of **7a** to **8a** is unclear. It might involve a Lewis acid catalyzed process, possibly related to reported results for disproportionation of allylic alcohols,[10] although **8a** was the only isolated and identified product. The stable enolate of the malonate generated in situ may also facilitate the reaction.



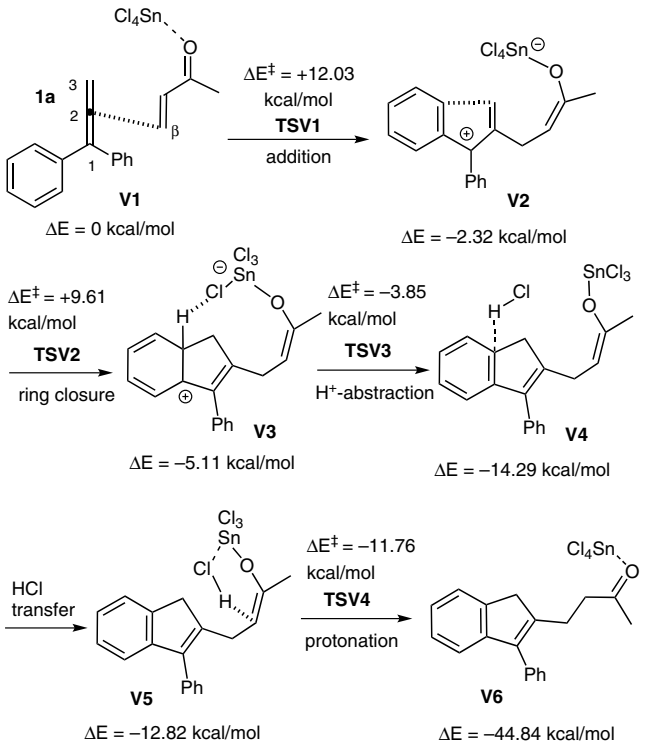
Scheme 5

The reaction of **1a** with other carbonyl compounds such as ethyl glyoxylate, benzaldehyde, acetyl chloride, or acetic anhydride under similar conditions gave complex mixtures or unreacted starting materials.

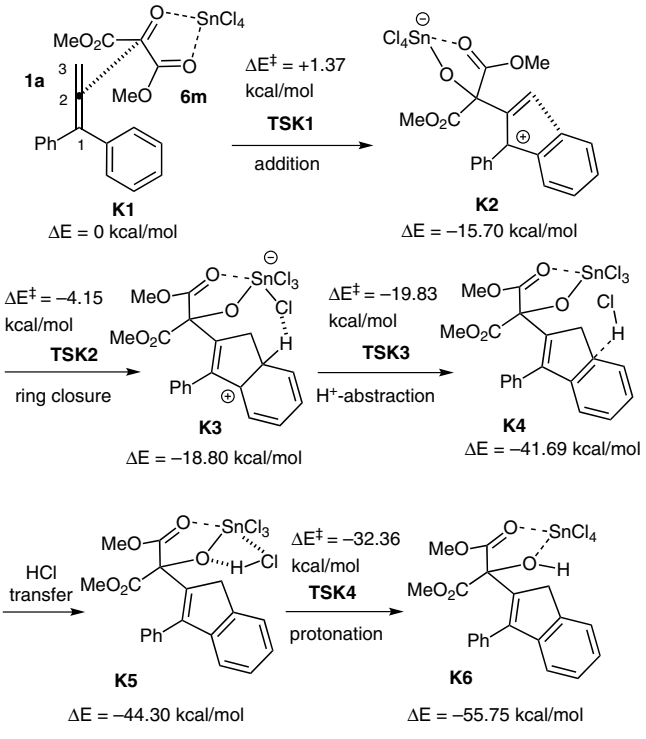
The mechanism for indene formation from a vinyl ketone (Scheme 2) may be similar to the reaction with ethylene-1,1,2-tricarboxylates (Scheme 1).[5] To clarify the mechanisms for indene formation, we carried out density functional theory calculations for the addition–cyclization reactions of the model compounds trimethyl ethylene-1,1,2-tricarboxylate (**2m**) (Scheme S1 in the Supporting Information), but-3-en-2-one (**4a**) (Scheme 6), and dimethyl oxomalonate (**6m**) (Scheme 7). The structure of each intermediate and transition state (TS) was optimized by B3LYP/LANL2DZ calculations (see Supporting Information).

Initially, tin(IV) chloride might coordinate to the carbonyl group of but-3-en-2-one (**4a**) (Scheme 6). The reaction starts from the reactant complex **V1**. Transition state **TSV1**, formed by conjugate addition of the allene at the C2 position to the tin(IV) chloride coordinated **4a**, leads to intermediate **V2**. The cyclization transition state **TSV2**, formed from intermediate **V2** then leads to the indene skeleton **V3**. The proton abstraction transition state **TSV3** leads to intermediate **V4**, and subsequent transfer of hydrogen chloride gives intermediate **V5**. Protonation through **TSV4** gives the product complex **V6**.

The proposed mechanism for indene formation with an oxomalonate is shown in Scheme 7. The reactant complex **K1** consists of allene **1a** and tin(IV) chloride coordinated to oxomalonate **6m** through the ketone group and one es-



Scheme 6 Proposed mechanism and B3LYP/LANL2DZ calculated energies for the reaction of 1,1-diphenylallene (**1a**) with but-3-en-2-one (**4a**) in the presence of tin(IV) chloride (see Scheme 2); ΔE = sum of electronic and zero-point energies (kcal/mol)

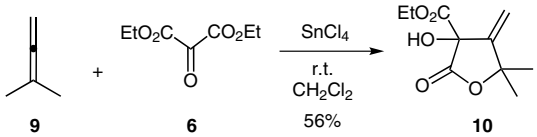


Scheme 7 Proposed mechanism and B3LYP/LANL2DZ calculated energies for the reaction of 1,1-diphenylallene (**1a**) with dimethyl oxomalonate (**6m**) in the presence of tin(IV) chloride (for Scheme 3)

ter group.[11] The coordination increases the electrophilicity of the ketone carbonyl carbon of oxomalonate **6m**. Carbonyl addition at the C2 position of allene **1a** from the tin(IV) chloride coordinated **6m** gives a phenyl allylic cation intermediate **K2** via **TSK1**. Cyclization (**TSK2**) gives the indene skeleton **K3**. Proton abstraction (**TSK3**) then gives intermediate **K3** and subsequent transfer of hydrogen chloride gives the intermediate **K5**. Protonation (**TSK4**) leads to the product complex **K6**.

The cyclization of the phenyl allylic cation intermediates may be considered as a 4π-electrocyclization.[10b,12] Vibrational analysis of the transition states for the cyclization steps (**TSV2** and **TSK2**) and for **TST2** (for the cyclization step in Scheme 1; Scheme S1) shows that a conrotatory motion, consistent with 4π-electrocyclization, occurs (Figure 1 and Figure S1 in the Supporting Information). For all three reactions, the addition step is rate determining; the activation energy (**TSK1**, $\Delta E^{\ddagger} = +1.37$ kcal/mol) for the addition step of oxomalonate **6m** is the smallest among these. The activation energy of the subsequent cyclization step (**TSK2**, $\Delta E^{\ddagger} = -4.15$ kcal/mol) is slightly higher than that for ethylene-1,1,2-tricarboxylate **2m** (**TST2**, $\Delta E^{\ddagger} = -6.63$ kcal/mol). Side reactions[4a] may result in lower yields of the products **7**.

For comparison, we also examined the Lewis acid-catalyzed reactions of diethyl oxomalonate (**6**) with 1,1-dialkylallenes. The reaction of 1,1-dimethylallene (**9**) with oxomalonate **6** in the presence of one equivalent of tin(IV) chloride at room temperature gave the hydroxy γ-lactone **10** in 56% yield (Scheme 8). In the presence of titanium(IV) chloride, this reaction gave a small amount of **10**, which could not be isolated, along with a complex mixture. Aluminum(III) chloride did not give **10**, and a complex mixture was obtained. Reduction of the hydroxy group in product **10** was not observed.



Scheme 8

The formation of the γ-lactone **10** from **6** and **9** may proceed through the allylic cationic intermediate **A** (Scheme 9). Similar hydroxy γ-lactone products have been reported for the Lewis acid-catalyzed reactions of **6** with phenylallene[4a] or with monoaryl-substituted methylenecyclopropanes.[13]

In summary, Lewis Acid-catalyzed reactions of 1,1-diarylallenes with ketone derivatives were examined. The tin(IV) chloride-promoted reaction of diarylallenes with vinyl ketones **4** gave indene derivatives **5** through a conjugate addition/cyclization reaction. The cyclization may be considered as a 4π-electrocyclization. The reaction of 1,1-diphenylallene (**1a**) with diethyl oxomalonate (**6**) in the presence of one equivalent of tin(IV) chloride at –40

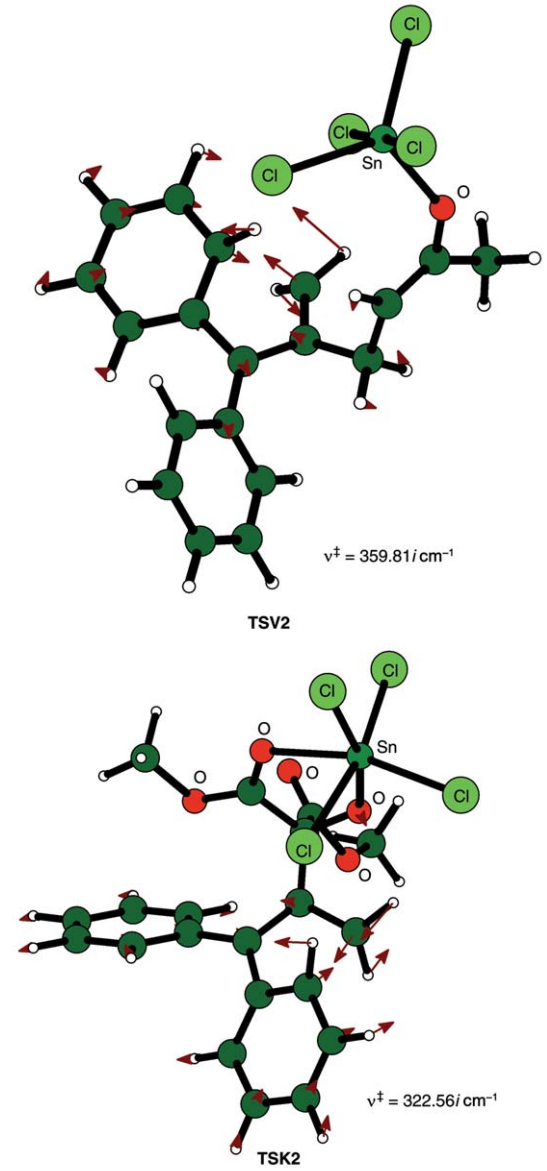
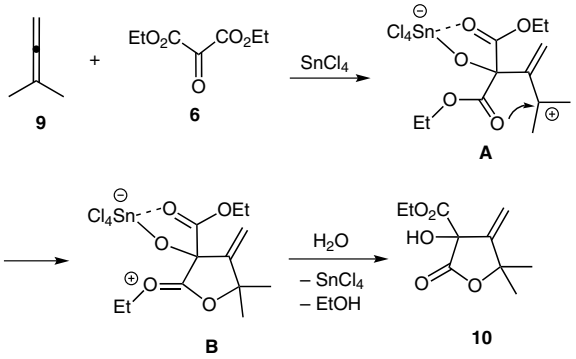


Figure 1 B3LYP/LANL2DZ-optimized structures of **TSV2** and **TSK2** and their reaction-coordinate vectors corresponding to the sole imaginary frequency



Scheme 9

°C gave hydroxy(indenyl)malonate **7a** as the major product through a carbonyl addition/cyclization reaction. The reaction of **1a** with **6** in the presence of tin(IV) chloride at 80 °C gave indenylmalonate **8a**. Lewis acid-catalyzed reactions of diethyl oxomalonate (**6**) and 1,1-dimethylallene gave the γ-lactone **10**. Further investigation of the scope of the cyclization reactions is under way.

Melting points are uncorrected. IR spectra were recorded in the FT-mode on a JASCO FT/IR-460 Plus spectrophotometer. ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were recorded at 100.6 MHz on a Varian INOVA-400 spectrometer. ^{1}H chemical shifts are reported in ppm relative to Me_4Si and ^{13}C chemical shifts are reported in ppm relative to $CDCl_3$ (77.1 ppm). ^{13}C multiplicities were determined by DEPT and HSQC experiments. Mass spectra were recorded by EI or FAB techniques on a JEOL JMS-700 mass spectrometer. All reactions were carried out under N_2.

Allenes **1a–c** were prepared according to the literature.[5,14]

4-(3-Phenyl-1*H*-inden-2-yl)butan-2-one (5a): Typical Procedure

$SnCl_4$ (261 mg, 120 μL, 1 mmol) was added to a soln of vinyl ketone **4a** (140 mg, 162 μL, 2 mmol) and allene **1a** (192 mg, 1 mmol) in $CHCl_3$ (4 mL), and the mixture was stirred at r.t. for 5 min. The reaction was quenched by successive addition of H_2O (4 mL) and sat. aq. $NaHCO_3$ (40 mL). The mixture was extracted with CH_2Cl_2 (3 × 60 mL) and the organic phase was dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography (silica gel, CH_2Cl_2) to give a pale-yellow oil; yield: 142 mg (54%); R_f = 0.7 (CH_2Cl_2).

IR (neat): 2924, 1713, 1659, 1447, 1270, 910, 733 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.10 (s, 3 H), 2.65 (t-like, *J* = 7.6 Hz, 2 H), 2.80 (t-like, *J* = 7.6 Hz, 2 H), 3.45 (s, 2 H), 7.15–7.25 (m, 3 H), 7.35–7.38 (m, 3 H), 7.44–7.48 (m, 3 H). Selected NOEs were observed between δ = 3.45 [indene C(1)H_2] and δ = 2.65 (CH_2CO), 2.80 (CH_2CH$_2$CO).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 23.15 (t), 29.88 (q), 40.67 (t), 43.71 (t), 119.72 (d), 123.59 (d), 124.43 (d), 126.37 (d), 127.36 (d), 128.64 (d), 129.12 (d), 135.23 (s), 139.83 (s), 142.30 (s), 142.83 (s), 146.20 (s), 207.93 (s). Selected HMBC correlations were observed between δ = 2.80 (CH_2CH$_2$CO) and δ = 142.83 [indene *C*(2)], 139.83 [indene *C*(3)], 40.67 [indene *C*(1)H$_2$]; between δ = 2.65 (CH_2CO) and δ = 142.83 [indene *C*(2)]; and between δ = 3.45 [indene C(1)H_2] and δ = 142.83 [indene *C*(2)], 139.83 [indene *C*(3)].

MS (EI): *m/z* (%) =262 (44) [M$^+$], 204 (100).

HRMS (EI): *m/z* [M$^+$] calcd for $C_{19}H_{18}O$: 262.1358; found: 262.1358.

Compounds **5b–d** were similarly prepared.

1-(3-Phenyl-1*H*-inden-2-yl)pentan-3-one (5b)

Pale-yellow oil; yield: 161 mg (58%); R_f = 0.7 (CH_2Cl_2).

IR (neat): 2975, 2936, 1713, 1659, 1460, 1446, 1270, 1112 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (t, *J* = 7.3 Hz, 3 H), 2.39 (q, *J* = 7.3 Hz, 2 H), 2.61–2.65 (m, 2 H), 2.79–2.83 (m, 2 H), 3.44 (s, 2 H), 7.15–7.25 (m, 3 H), 7.34–7.38 (m, 3 H), 7.43–7.48 (m, 3 H). Selected NOEs were observed between δ = 3.44 [indene C(1)H_2] and δ = 2.61–2.65 (CH_2CO), 2.79–2.83 (CH_2CH$_2$CO).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 7.86 (q), 23.21 (t), 35.91 (t), 40.71 (t), 42.37 (t), 119.70 (d), 123.59 (d), 124.40 (d), 126.36 (d), 127.34 (d), 128.63 (d), 129.12 (d), 135.26 (s), 139.73 (s), 142.33 (s), 143.08 (s), 146.23 (s), 210.60 (s). Selected HMBC correlations were observed between δ = 2.79–2.83 (CH_2CH$_2$CO) and δ = 143.08 [indene *C*(2)], 139.73 [indene *C*(3)], 40.71 [indene *C*(1)H$_2$]; between δ = 2.61–2.65 (CH_2CO) and δ = 143.08 [indene *C*(2)]; and between δ = 3.44 [indene C(1)H_2] and δ = 143.08 [indene *C*(2)], 139.73 [indene *C*(3)].

MS (EI): *m/z* (%) =276 (79) [M$^+$], 204 (100).

HRMS (EI): *m/z* [M$^+$] calcd for $C_{20}H_{20}O$: 276.1514; found: 276.1512.

4-[6-Chloro-3-(4-chlorophenyl)-1*H*-inden-2-yl]butan-2-one (5c)

Pale-yellow oil; yield: 193 mg (58%); R_f = 0.6 (CH_2Cl_2).

IR (neat): 2921, 1716, 1591, 1573, 1489, 1361, 1158, 1093, 1015 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.11 (s, 3 H), 2.62–2.66 (m, 2 H), 2.73–2.77 (m, 2 H), 3.41 (s, 2 H), 7.02 (d, *J* = 8.1 Hz, 1 H), 7.19 (dd, *J* = 8.1, 1.9 Hz, 1 H), 7.27 (d-like, *J* = 8.5 Hz, 2 H), 7.39 (br d, *J* = 1.5 Hz, 1 H), 7.43 (d-like, *J* = 8.5 Hz, 2 H). Selected NOEs were observed between δ = 3.41 [indene C(1)H_2] and δ = 2.62–2.66 (CH_2CO), 2.73–2.77 (CH_2CH$_2$CO), 7.39 [indene C(7)*H*].

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.98 (t), 29.89 (q), 40.49 (t), 43.28 (t), 120.19 (d), 124.04 (d), 126.59 (d), 129.01 (d), 130.36 (d), 130.57 (s), 133.18 (s), 133.44 (s), 138.11 (s), 143.82 (s), 143.82 (s), 144.32 (s), 207.41 (s). Selected HMBC correlations were observed between δ = 2.73–2.77 (CH_2CH$_2$CO) and δ = 143.82 [indene *C*(2)], 138.11 [indene *C*(3)], 40.49 [indene *C*(1)H$_2$]; between δ = 2.62–2.66 (CH_2CO) and δ = 143.82 [indene *C*(2)], and between δ = 3.41 [indene C(1)H_2] and δ = 143.82 [indene *C*(2)], 133.18 [indene *C*(3)].

MS (EI): *m/z* (%) = 332 (40) [M$^+$], 331 (13) [M$^+$], 330 (64) [M$^+$], 274 (41), 272 (58), 237 (89), 86 (83), 84 (100).

HRMS (EI): *m/z* [M$^+$] calcd for $C_{19}H_{16}Cl_2O$: 330.0578, 331.0612, 332.0549; found: 330.0577, 331.0605, 332.0563.

1-[6-Chloro-3-(4-chlorophenyl)-1*H*-inden-2-yl]pentan-3-one (5d)

Colorless crystals; yield: 174 mg (50%); mp 69–71 °C (EtOAc–hexane); R_f = 0.6 (CH_2Cl_2).

IR (KBr): 2971, 2937, 2903, 2878, 1710, 1491, 1458, 1376, 1094, 1015, 819 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (t, *J* = 7.3 Hz, 3 H), 2.39 (q, *J* = 7.3 Hz, 2 H), 2.62 (t-like, *J* = 7.3 Hz, 2 H), 2.76 (t-like, *J* = 7.3 Hz, 2 H), 3.42 (s, 2 H), 7.02 (d, *J* = 8.1 Hz, 1 H), 7.20 (dd, *J* = 8.1, 2.0 Hz, 1 H), 7.28 (d-like, *J* = 8.5 Hz, 2 H), 7.40 (br d, *J* = 1.3 Hz, 1 H), 7.44 (d-like, *J* = 8.5 Hz, 2 H). Selected NOEs were observed between δ = 3.42 [indene C(1)H_2] and δ = 2.62 (CH_2CO), 2.76 (CH_2CH$_2$CO), 7.40 [indene C(7)*H*].

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 7.86 (q), 23.08 (t), 35.97 (t), 40.56 (t), 41.98 (t), 120.21 (d), 124.07 (d), 126.62 (d), 129.03 (d), 130.39 (d), 130.59 (s), 133.25 (s), 133.45 (s), 138.08 (s), 143.85 (s), 144.06 (s), 144.38 (s), 210.17 (s). Selected HMBC correlations were observed between δ = 2.76 (CH_2CH$_2$CO) and δ = 138.08 [indene *C*(3)], 40.56 [indene *C*(1)H$_2$]; and between δ = 3.42 [indene C(1)H_2] and δ = 133.18 [indene *C*(3)].

MS (FAB): *m/z* = 346, 345 [M + 1]$^+$.

HRMS (FAB): *m/z* [M + Na]$^+$ calcd for $C_{20}H_{18}Cl_2NaO$: 367.0632; found: 367.0631.

Anal. Calcd for $C_{20}H_{18}Cl_2O$: C, 69.57; H, 5.25. Found: C, 69.29; H, 5.11.

Diethyl Hydroxy(3-phenyl-1*H*-inden-2-yl)malonate (7a)

$SnCl_4$ (261 mg, 120 μL, 1 mmol) was added to a soln of diethyl oxomalonate (**6**) (174 mg, 152 μL, 1 mmol) and allene **1a** (192 mg, 1 mmol) in CH_2Cl_2 (2 mL) at –40 °C and the mixture was stirred at –40 °C overnight. The reaction was quenched successively with H_2O (4 mL) and sat. aq $NaHCO_3$ (40 mL). The mixture was extracted with CH_2Cl_2 (3 × 60 mL) and the organic phase was dried

(Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane–Et_2O) to give a pale-yellow oil; yield: 205 mg (56%); R_f = 0.3 (hexane–Et_2O, 2:1).

IR (neat): 3475, 2981, 1738, 1462, 1444, 1392, 1368, 1264, 1206, 1159, 1094, 1037 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.19 (t, *J* = 7.1 Hz, 6 H), 3.71 (s, 2 H), 3.88 (dq, *J* = 10.8, 7.1 Hz, 2 H), 4.04 (dq, *J* = 10.8, 7.1 Hz, 2 H), 4.14 (br s, 1 H), 7.06–7.08 (m, 1 H), 7.22–7.26 (m, 2 H), 7.33–7.45 (m, 5 H), 7.47–7.49 (m, 1 H). Selected NOEs were observed between δ = 3.71 [indene C(1)H_2] and δ = 7.47–7.49 [indene C(7)*H*].

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.91 (q), 39.67 (t), 62.86 (t), 78.92 (s), 121.07 (d), 123.60 (d), 125.81 (d), 126.48 (d), 127.83 (d), 128.13 (d), 129.44 (d), 134.56 (s), 137.02 (s), 142.12 (s), 143.70 (s), 146.19 (s), 169.77 (s). Selected HMBC correlations were observed between δ = 3.71 [indene C(1)H_2] and δ = 78.92 [*C*$(CO_2Et)_2$OH], 123.60 [indene *C*(7)].

MS (EI): *m/z* (%) =366 (5) [M^+], 348 (100).

HRMS (EI): *m/z* [M^+] calcd for $C_{22}H_{22}O_5$: 366.1467; found: 366.1461.

Diethyl Hydroxy[6-methyl-3-(4-methylphenyl)-1*H*-inden-2-yl]malonate (7b)

ZnI_2 (32 mg, 0.1 mmol) was added to a soln of diethyl oxomalonate (**6**) (87 mg, 76 μL, 0.5 mmol) and allene **1c** (110 mg, 0.5 mmol) in CH_2Cl_2 (2 mL), and the mixture was stirred at r.t. overnight. The reaction was quenched by successive addition of H_2O (2 mL) and sat. aq $NaHCO_3$ (20 mL). The mixture was extracted with CH_2Cl_2 (3 × 30 mL) and the organic phase was dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane–Et_2O) to give a pale-yellow oil: yield: 63 mg (32%); R_f = 0.2 (hexane–Et_2O, 2:1).

IR (neat): 3478, 2981, 2923, 1788, 1742, 1509, 1445, 1368, 1268, 1173, 1096, 1037 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.18 (t, *J* = 7.1 Hz, 6 H), 2.38 (s, 3 H), 2.39 (s, 3 H), 3.65 (s, 2 H), 3.88 (dq, *J* = 10.6, 7.1 Hz, 2 H), 4.04 (dq, *J* = 10.6, 7.1 Hz, 2 H), 4.13 (br s, 1 H), 6.97 (d, *J* = 7.7 Hz, 1 H), 7.05 (br d, *J* = 7.7 Hz, 1 H), 7.22 (d, *J* = 7.9 Hz, 2 H), 7.28 (d, *J* = 7.9 Hz, 2 H), 7.29 (br s, 1 H). Selected NOEs were observed between δ = 3.65 [indene C(1)H_2] and δ = 7.29 [indene C(7)*H*].

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.89 (q), 21.37 (q), 21.53 (q), 39.36 (t), 62.79 (t), 78.95 (s), 120.73 (d), 124.44 (d), 127.15 (d), 128.75 (d), 129.25 (d), 131.64 (s), 135.58 (s), 135.69 (s), 137.36 (s), 142.38 (s), 143.57 (s), 143.71 (s), 169.89 (s). Selected HMBC correlations were observed between δ = 3.65 [indene C(1)H_2] and δ = 78.95 [*C*$(CO_2Et)_2$OH], 124.44 [indene *C*(7)].

MS (EI): *m/z* (%) =394 (9.4) [M^+], 376 (65), 321 (90), 303 (47), 247 (100).

HRMS (EI): *m/z* [M^+] calcd for $C_{24}H_{26}O_5$: 394.1780; found: 394.1779.

Diethyl (3-Phenyl-1*H*-inden-2-yl)malonate (8a); Typical Procedure

$SnCl_4$ (5.2 mg, 2.4 μL, 0.02 mmol) was added to a soln of diethyl oxomalonate (**6**) (17.4 mg, 0.1 mmol) and allene **1a** (19.2 mg, 0.1 mmol) in $ClCH_2CH_2Cl$ (0.4 mL), and the mixture was heated at 80 °C overnight. The reaction mixture was cooled to r.t. and quenched by addition of sat. aq $NaHCO_3$ (5 mL). The mixture was extracted with CH_2Cl_2 (3 × 10 mL) and the organic phase was dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane–Et_2O) to give a pale-yellow oil; yield: 23.1 mg (66%); R_f = 0.6 (hexane–Et_2O, 2:1).

IR (neat): 2980, 2929, 1732, 1461, 1444, 1367, 1304, 1148, 1031 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.27 (t, *J* = 7.1 Hz, 6 H), 3.80 (s, 2 H), 4.15–4.27 (m, 4 H), 4.76 (s, 1 H), 7.22–7.27 (m, 3 H), 7.39–7.43 (m, 3 H), 7.47–7.52 (m, 3 H). Selected NOEs were observed between δ = 3.80 [indene C(1)H_2] and δ = 4.76 [C*H*$(CO_2Et)_2$], 7.47–7.52 [indene C(7)*H*].

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.14 (q), 39.20 (t), 52.31 (d), 61.84 (t), 120.65 (d), 123.85 (d), 125.47 (d), 126.31 (d), 127.99 (d), 128.80 (d), 129.23 (d), 134.03 (s), 134.09 (s), 143.35 (s), 144.53 (s), 144.94 (s), 168.16 (s). Selected HMBC correlations were observed between δ = 3.80 [indene C(1)H_2] and δ = 52.31 [*C*H$(CO_2Et)_2$], 123.85 [indene *C*(7)]; and between δ = 4.76 [C*H*$(CO_2Et)_2$] and δ = 39.20 [indene *C*(1)H_2].

MS (EI): *m/z* = 350 [M^+].

HRMS (EI): *m/z* [M^+] calcd for $C_{22}H_{22}O_4$: 350.1518; found: 350.1518.

Diethyl [6-Methyl-3-(4-tolyl)-1*H*-inden-2-yl]malonate (8b)

$SnCl_4$ (130 mg, 60 μL, 0.5 mmol) was added to a soln of diethyl oxomalonate (**6**) (87 mg, 76 μL, 0.5 mmol) and allene **1c** (110 mg, 0.5 mmol) in CH_2Cl_2 (2 mL), and the mixture was stirred at r.t. overnight. The reaction was quenched by successive addition of H_2O (2 mL) and sat. aq $NaHCO_3$ (20 mL). The mixture was extracted with CH_2Cl_2 (3 × 30 mL) and the organic phase was dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane–Et_2O) to give a pale-yellow oil; yield: 69 mg (36%); R_f = 0.5 (hexane–Et_2O, 2:1).

IR (KBr): 2981, 1729, 1307, 1225, 1159, 1030 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.26 (t, *J* = 7.1 Hz, 6 H), 2.40 (s, 3 H), 2.42 (s, 3 H), 3.74 (s, 2 H), 4.14–4.26 (m, 4 H), 4.75 (s, 1 H), 7.10 (br d, *J* = 7.8 Hz, 1 H), 7.13 (d, *J* = 7.8 Hz, 1 H), 7.29 (br s, 4 H), 7.32 (br s, 1 H). Selected NOEs were observed between δ = 3.74 [indene C(1)H_2] and δ = 7.10 [indene C(7)*H*].

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.14 (q), 21.41 (q), 21.53 (q), 38.89 (t), 52.31 (d), 61.75 (t), 120.32 (d), 124.73 (d), 126.96 (d), 129.07 (d), 129.47 (d), 131.20 (s), 132.68 (s), 135.22 (s), 137.62 (s), 142.48 (s), 143.65 (s), 144.27 (s), 168.30 (s). Selected HMBC correlations were observed between δ = 3.74 [indene C(1)H_2] and δ = 124.73 [indene *C*(7)]; and between δ = 4.75 [C*H*$(CO_2Et)_2$] and δ = 38.89 [indene *C*(1)H_2].

MS (EI): *m/z* (%) =378 (84) [M^+], 305 (55), 259 (31), 231 (100).

HRMS (EI): *m/z* [M^+] calcd for $C_{24}H_{26}O_4$: 378.1831; found: 378.1833.

Ethyl 3-Hydroxy-5,5-dimethyl-4-methylene-2-oxotetrahydrofuran-3-carboxylate (10)

$SnCl_4$ (130 mg, 60 μL, 0.5 mmol) was added to a soln of diethyl oxomalonate (**6**) (87 mg, 76 μL, 0.5 mmol) and allene **9** (34 mg, 50 μL, 0.5 mmol) in CH_2Cl_2 (2 mL), and the mixture was stirred at r.t. overnight. The reaction was quenched by successive addition of H_2O (2 mL) and sat. aq $NaHCO_3$ (20 mL). The mixture was extracted with CH_2Cl_2 (3 × 30 mL) and the organic phase was dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane–Et_2O) to give a colorless oil; yield: 61 mg (56%); R_f = 0.6 (hexane–Et_2O, 1:1).

IR (neat): 3449, 2985, 1781, 1747, 1370, 1291, 1231, 1180, 1114, 1031 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$: δ = 1.30 (t, *J* = 7.1 Hz, 3 H), 1.61 (s, 3 H), 1.66 (s, 3 H), 4.26–4.38 (m, 3 H), 5.36 (d, *J* = 1.5 Hz, 1 H), 5.43 (d, *J* = 1.5 Hz, 1 H). Selected NOEs were observed between δ = 5.36 (=C*H*H) and δ = 1.61, 1.66 [C(CH_3)$_2$].

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.85 (q), 28.17 (q), 29.69 (q), 63.91 (t), 76.71 (s), 86.80 (s), 112.35 (t), 150.98 (s), 169.19 (s), 171.29 (s). Selected HMBC correlations were observed between δ = 5.36, 5.43 (=CH_2) and δ = 150.98 (*C*=CH_2), 86.80 [*C*(CH_3)$_2$], 76.71

[*C*(CO_2Et)OH]; and between δ = 1.61, 1.66 [C(CH_3)$_2$] and δ = 150.98 (*C*=CH_2).

MS (EI): *m/z* = 214 [M^+].

HRMS (EI): *m/z* [M^+] calcd for $C_{10}H_{14}O_5$: 214.0841; found: 214.0841.

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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