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Lewis Acid Promoted Reactions of Ethenetricarboxylates with Allenes: Synthesis of Indenes and γ-Lactones via Conjugate Addition/Cyclization Reaction

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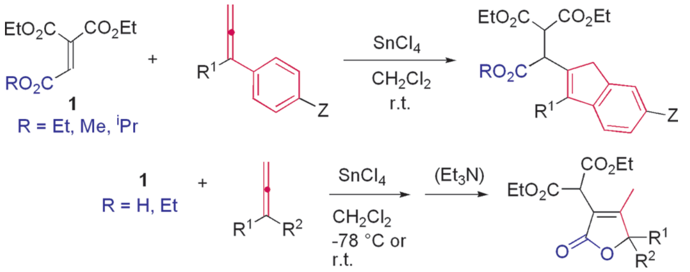

Indenes are important core structures in organic chemistry. Few simple arylallenes have been used to construct indene skeletons by Friedel−Crafts reaction. Lewis acid catalyzed reaction of ethenetricarboxylates **1** and arylallenes has been examined in this study. The reaction of arylallenes and ethenetricarboxylate triesters with $SnCl_4$ gave indene derivatives efficiently, via a conjugate addition/Friedel−Crafts cyclization reaction. On the other hand, the reactions of 1,1-diethyl 2-hydrogen ethenetricarboxylate and arylallenes or alkylallenes with $SnCl_4$ at −78 °C or room temperature and subsequent treatment with Et_3N gave γ-lactones. The reactions of triethyl ethenetricarboxylate and 1,1-dialkylallenes with $SnCl_4$ at room temperature also gave γ-lactones.

Introduction

Indenes are important core structures in organic chemistry. They serve as building blocks for bioactive pharmaceutical compounds[1] and functional materials.[2] They are also used as ligands in metallocene-based olefin polymerization catalysts.[3] There have been a number of reports on the development of synthetic methods to construct indene ring systems.[4] Among the methods developed, Lewis acid catalyzed intramolecular and intermolecular Friedel−Crafts reactions of arynes leading to indene derivatives have been effectively utilized.[5] Allene derivatives play an important

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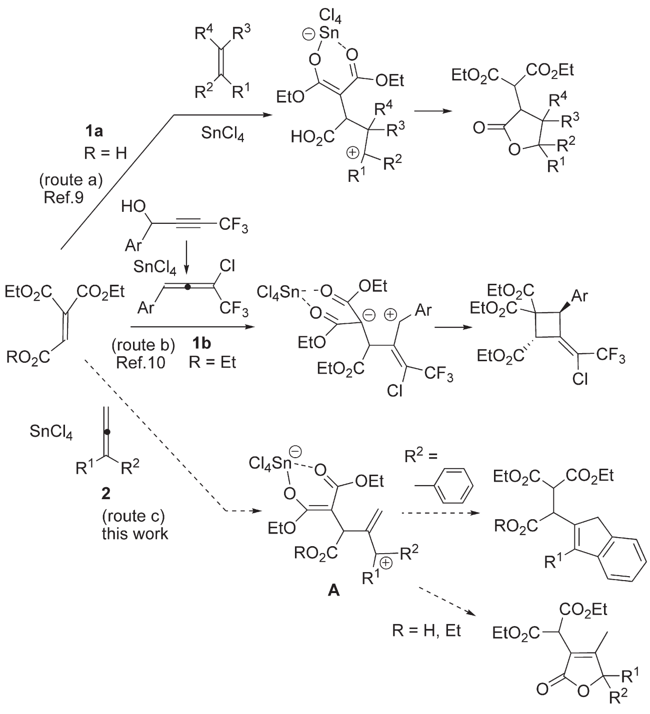
SCHEME 1



role in organic synthesis because of their structural features.[6] However, few simple arylallenes have been used to construct indene skeletons by Friedel−Crafts reaction.[7,8] Herein, we report a new indene formation via Lewis acid promoted conjugate addition/Friedel−Crafts reactions of arylallenes.

We have recently studied various Lewis acid promoted reactions of ethenetricarboxylate derivatives **1** and reported that they function as highly electrophilic Michael acceptors. For example, the reaction of 1,1-diethyl 2-hydrogen ethenetricarboxylate (**1a**) and various alkenes in the presence of a Lewis acid gave cycloadduct γ-lactones (route a in Scheme 1).[9] We have also reported that the reaction of ethenetricarboxylate triester with chloroallenes, which are generated in situ by the reaction of γ-trifluoromethyl-α-aryl propargyl alcohols and SnCl$_4$, gave cyclobutane derivatives (route b).[10] Simple arylallenes are expected to add to ethenetricarboxylates in the presence of Lewis acid and undergo further bond formation reaction on benzene ring via the common zwitterionic intermediate **A** (route c). In this study, Lewis acid catalyzed reactions of ethenetricarboxylates and arylallenes and also alkylallenes for comparison have been examined.

TABLE 1. Reaction of 1b−e and Arylallenes 2a−c,e[a]

entry	1	2	Lewis Acid (equiv)	temp[b]	3	X	Z^1	Z^2	yield (%)[c]
1	**1b**	**2a**	SnCl$_4$ (0.2)	rt	**3a**	CO$_2$Et	H	H	99
2	**1b**	**2a**	SnCl$_4$ (1.0)	rt	**3a**	CO$_2$Et	H	H	86
3	**1b**	**2a**	AlCl$_3$ (0.2)	80 °C	**3a**	CO$_2$Et	H	H	69
4	**1b**	**2a**	ZnI$_2$ (0.2)	80 °C	**3a**	CO$_2$Et	H	H	71
5	**1c**	**2a**	SnCl$_4$ (0.2)	rt	**3b**	CO$_2$Me	H	H	81
6	**1c**	**2a**	SnCl$_4$ (1.0)	rt	**3b**	CO$_2$Me	H	H	71
7	**1d**	**2a**	SnCl$_4$ (1.0)	rt	**3c**	CO$_2$^{i}Pr	H	H	93
8	**1e**	**2a**	SnCl$_4$ (1.0)	rt	**3d**	CN	H	H	64
9	**1b**	**2b**	SnCl$_4$ (1.0)	rt	**3e**	CO$_2$Et	Cl	Cl	81
10	**1b**	**2b**	SnCl$_4$ (0.2)	80 °C	**3e**	CO$_2$Et	Cl	Cl	92
11	**1b**	**2c**	SnCl$_4$ (0.2)	rt	**3f**	CO$_2$Et	Me	Me	79
12	**1b**	**2c**	SnCl$_4$ (1.0)	rt	**3f**	CO$_2$Et	Me	Me	99
13	**1b**	**2c**	SnCl$_4$ (0.2)	80 °C	**3f**	CO$_2$Et	Me	Me	86
14	**1b**	**2e**	SnCl$_4$ (0.2)	rt	**3g**	CO$_2$Et	OMe	H	0[d]
15	**1b**	**2e**	ZnI$_2$ (0.2)	rt	**3g**	CO$_2$Et	OMe	H	30[e]
16	**1b**	**2e**	AlCl$_3$ (0.2)	rt	**3g**	CO$_2$Et	OMe	H	44[e]

[a] Reactions were carried out with 0.5−1.0 mmol of **1**, 1 equiv of **2**, and Lewis acid in 1−2 mL of solvent for 17−19 h. [b] CH$_2$Cl$_2$ was used as a solvent at rt, and ClCH$_2$CH$_2$Cl was used at 80 °C. [c] Isolated yield. [d] A complex mixture. [e] Small amounts of impurity could not be removed. A trace amount of the possible indene regioisomer could be formed as a minor product; however, it was not confirmed because of the difficulty in removal of other impurities.

Results and Discussion

A Lewis acid catalyzed reaction of ethenetricarboxylates and arylallenes has been examined. The arylallenes were prepared from 1,1-dibromocyclopropanes.[6a,11] Since SnCl$_4$ has been shown to be an effective catalyst for reactions of ethenetricarboxylates **1** with alkenes and allenes (Scheme 1),[9,10] the SnCl$_4$-catalyzed reaction was initially examined. The reaction of 1,1-diarylallenes **2a,b,c** and ethenetricarboxylate triesters **1b−d** and the analogue **1e** with SnCl$_4$ at room temperature overnight gave indene derivatives **3a−f** in 64−99% yield, via conjugate addition/Friedel−Crafts cyclization reaction (eq 1, Table 1, entries 1−13). The indene structure of the product **3b** was determined by X-ray analysis (Figure S1 in Supporting Information).

The catalytic use (0.2 equiv) of other Lewis acids such as AlCl$_3$ and ZnI$_2$ was also effective for the indene formation for the reaction of **1b** and **2a**. The reaction temperature was raised to 80 °C in 1,2-dichloroethane when the reaction did not go to completion at room temperature (entries 3, 4, 10). The reaction of **1b** and **2a** with 0.2 equiv of $ZnBr_2$ at room temperature or 80 °C also produced indene **3a**; however the reaction did not go to completion, and the product **3a** could not be isolated from the starting material **1b** by column chromatography. Use of 0.2 equiv of FeCl$_3$, TiCl$_4$, InBr$_3$, Zn(OTf)$_2$, Sc(OTf)$_3$, and BF$_4$·Et$_2$O at room temperature or 80 °C gave starting materials or complex mixtures. The appropriate selection of Lewis acids among numerous Lewis acids is still a difficult task.[12,5a] The alkene **1** needs to be activated with Lewis acid for 1,1-diphenylallene **2a**, which has relatively low nucleophilicity and is unstable.[6] SnCl$_4$ may have suitable Lewis acidity for this reaction.

The reaction of **2a** and 1,1-diethyl 2-ethyl, methyl, and isopropyl ethenetricarboxylates **1b−d** gave indene derivatives smoothly,; however, 1,1-diethyl 2-*tert*-butyl ethenetricarboxylate

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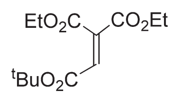
TABLE 2. Reaction of 1b–e and 1-Aryl-1-methylallenes 2f–h

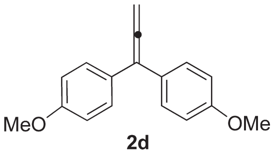
entry	1	2	$SnCl_4$ (equiv)	3	R	Z	yield (%)
1	**1b**	**2f**	1.0	**3h**	Et	H	53
2	**1c**	**2f**	1.0	**3i**	Me	H	48
3	**1b**	**2g**	1.0	**3j**	Et	Cl	52
4	**1b**	**2h**	0.2	**3k**	Et	Me	65[a]

[a] Use of 1 equiv of $SnCl_4$ gave **3k** in lower yield (ca. 19%) as a mixture with diethyl malonate.

(**1f**, X = $CO_2{}^tBu$) gave a mixture containing a dimethyl-γ-lactone derivative by the Lewis acid catalyzed formal isomerization reaction of **1f**.[9]

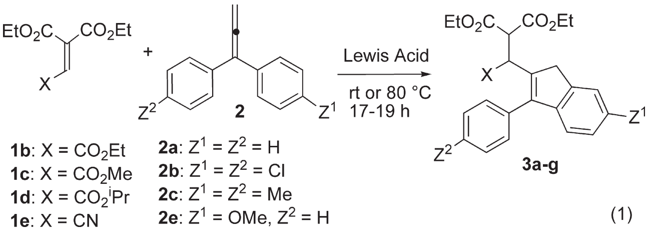


1f



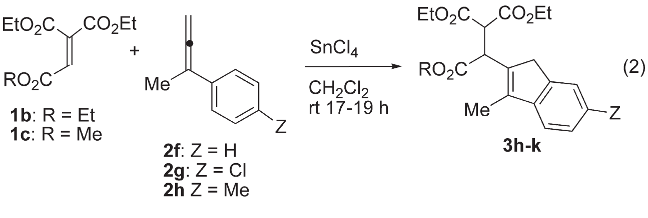
2d

The reaction of **1b** and 1,1-di(4-methoxyphenyl)allene (**2d**, $Z^1 = Z^2 =$ OMe) with $SnCl_4$ or ZnI_2 (0.2 equiv) at room temperature gave a complex mixture along with an unreacted starting material **1b**. The reaction of unsymmetrically substituted 1,1-diarylallene **2e** with $SnCl_4$ (0.2 equiv) also gave a complex mixture. The reaction with ZnI_2 or $AlCl_3$ (0.2 equiv) gave an indene derivative **3g** as a major product but in lower yield (30–44% yield) (Table 1, entries 15 and 16).



(1)

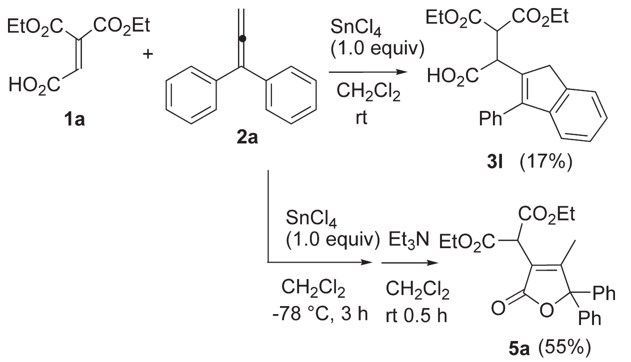
The reaction of 1-aryl-1-methylallenes **2f,g,h** and ethenetricarboxylate triesters **1b,c** with $SnCl_4$ gave indene derivatives **3h–k** with somewhat lower yields than the corresponding 1,1-diarylallenes (48–65% yield, eq 2, Table 2). This may be due to the lower stability of the intermediate **A** (Scheme 1) for R^1 = Me, compared to R^1 = aryl. For 1-aryl-1-methylallenes, use of 1 equiv of $SnCl_4$ gave better yields than the catalytic use of $SnCl_4$ or other Lewis acids except for entry 4.



(2)

The reaction of phenylallene **2i** (PhCH=C=CH_2) and **1b** in the presence of $SnCl_4$ gave a complex mixture. The reaction of diethyl benzylidenemalonate (PhCH=C(CO_2Et)$_2$) with allene **2a** in the presence of $SnCl_4$ was also examined. The reaction gave the starting material, diethyl benzylidenemalonate, and a complex mixture, and the possible indene product could not be isolated. Thus, the high reactivity of ethenetricarboxylate triesters **1** compared to benzylidenemalonate was shown by this efficient indene formation.

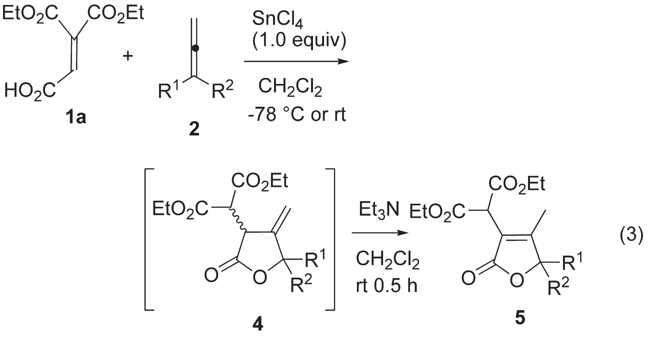
SCHEME 2



The reactions of 1,1-diethyl 2-hydrogen ethenetricarboxylate (**1a**) and allene **2a** in the presence of $SnCl_4$ (1 equiv) at room temperature gave indene derivative **3l** in 17% yield along with a complex mixture (Scheme 2). Interestingly, the reactions of **1a** and **2a** at −78 °C and subsequent treatment with Et_3N gave γ-lactone **5a** in 55% yield.

A Lewis acid catalyzed cycloaddition reaction of 1,1-diethyl 2-hydrogen ethenetricarboxylate (**1a**) and various aryl and alkyl allenes has also been examined (eq 3, Table 3). The reactions of **1a** and 1-aryl-1-methylallenes **2f,g** and phenylallene **2i** in the presence of $SnCl_4$ (1 equiv) at −78 °C and subsequent treatment with Et_3N gave α,β-unsaturated-γ-lactones **5f,g** as the only isolable products. The reaction of 1-aryl-1-methylallenes **2f,g** at room temperature decreased the yields of the lactone **5f,g**, but the formation of the corresponding indene derivatives was not observed (entries 1–4). The reactions of **1a** and alkyl allenes **2j,k,l** in the presence of $SnCl_4$ at −78 °C or room temperature and treatment with Et_3N gave α,β-unsaturated-γ-lactones **5j,k,l** in 17–49% yield.

The reactions of 1,1-diethyl 2-hydrogen ethenetricarboxylate (**1a**) and allenes **2** in the presence of $SnCl_4$ gave exomethylene γ-lactones **4** and/or the conjugated isomers, α,β-unsaturated-γ-lactones **5** after usual workup. The exomethylene γ-lactones **4** are unstable to distillation or column chromatography and difficult to be purified. Treatment of γ-lactones **4** or the mixture of **4** and **5** with Et_3N gave γ-lactones **5**. For dialkyl substituted allenes, **2j,k,l** and phenylallene **2i**, the product yields increased slightly at room temperature (entries 5–11).



(3)

Next, the $SnCl_4$-catalyzed reaction of triethyl ethenetricarboxylate (**1b**) and alkylallenes **2j,k,l** was examined. The reaction of 1,1-dialkylallenes at room temperature also gave γ-lactones with better yields than the reaction of **1a** and **2a–c**, in 49–82% yield (eq 4).[13] One ethyl group is lost in the reaction.[14]

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[13] Use of 0.2 equiv of $SnCl_4$ led to incomplete reaction.

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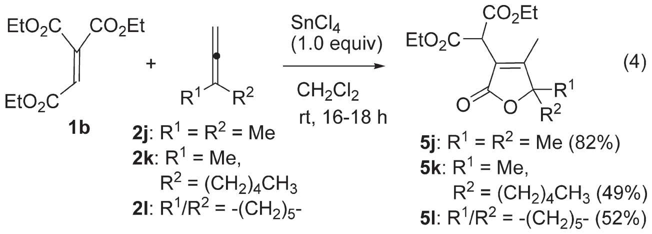
TABLE 3. Reaction of 1a and Aryl and Alkylallenes 2[a]

entry	2	R^1	R^2	temp/time	5	yield (%)
1	**2f**	Me	Ph	−78 °C/3 h	**5f**	49
2	**2f**	Me	Ph	rt/17 h	**5f**	25
3	**2g**	Me	4-Cl-C_6H_4	−78 °C/3 h	**5g**	45
4	**2g**	Me	4-Cl-C_6H_4	rt/17 h	**5g**	38
5	**2i**	H	Ph	−78 °C/3 h	**5i**	43
6	**2i**	H	Ph	rt/17 h	**5i**	63
7	**2j**	Me	Me	−78 °C/3 h	**5j**	39 (49[b])
8	**2j**	Me	Me	rt/17 h	**5j**	46
9	**2k**	Me	$(CH_2)_4CH_3$	−78 °C/3 h	**5k**	14
10	**2k**	Me	$(CH_2)_4CH_3$	rt/17 h	**5k**	17
11	**2l**		-$(CH_2)_5$-	rt/17 h	**5l**	31[c]

[a] Reactions were carried out with 0.5 mmol of **2**, 1 equiv (0.5 mmol) of **1a**, and 1 equiv (0.5 mmol) of $SnCl_4$ in CH_2Cl_2 (2 mL) unless otherwise stated. [b] 2 equiv of **1a** was used. [c] At −78 °C, a trace amount of **5l** formed.

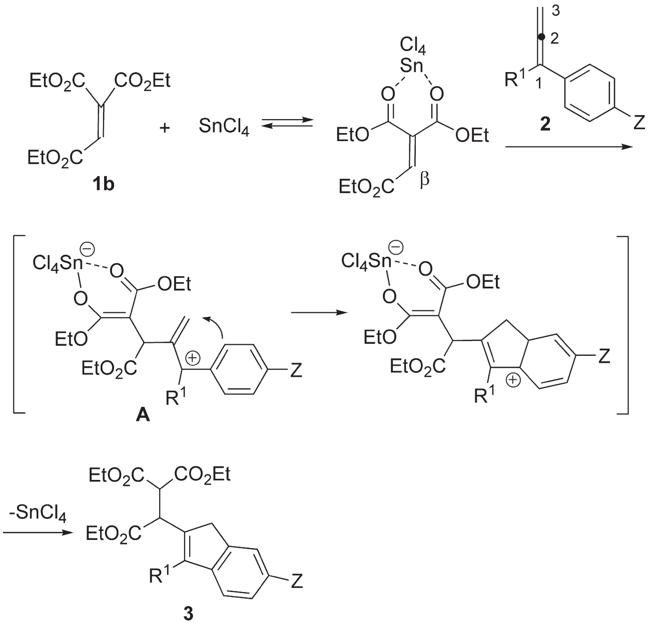
In the reaction of **1b** and **2j**, other Lewis acids, $AlCl_3$, $FeCl_3$, $TiCl_4$, and $ZnBr_2$, gave a small amount of **5j**, which could not be isolated, along with the starting material **1b** and complex mixtures. Efficiency of $SnCl_4$ may arise from its suitable Lewis acidity for the reaction of **1b** and **2j**, similar to the reaction of **1b** and **2a**. Stronger Lewis acids such as $AlCl_3$ and $FeCl_3$, may lead to decomposition of starting materials or products. Further study on the choice of Lewis acids is under investigation.



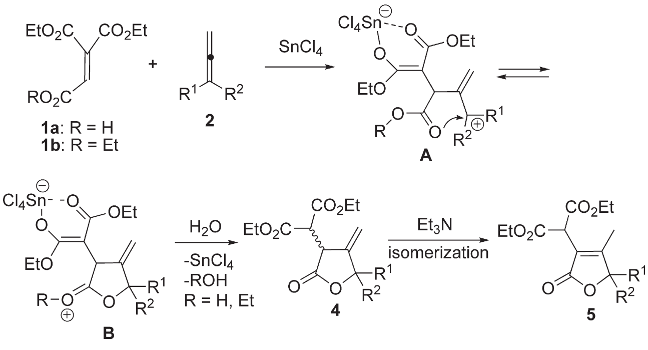
The probable mechanism for indene formation is shown in Scheme 3. Initially, $SnCl_4$ may coordinate to **1** in the diester moiety as shown. The coordination increases the electrophilicity of C_β of **1**. Conjugate addition of allene at C_2 to $SnCl_4$-coordinated **1** gives a stabilized allylic and benzylic cation intermediate **A**.[15] Friedel−Crafts cyclization from the intermediate **A** leads to the indene skeleton. The transformation might also be considered as 4π-electrocycization of a dienyl cation.[16] Further study on the effect of Lewis acids to conjugate addition and cyclization is under investigation.

Formation of γ-lactones from **1a** and **1b** may also proceed through the common allylic cation intermediate **A** (Scheme 4). Formation of intermediate **B** may be reversible. The reaction of **1a** and arylarenes at lower temperature leads to γ-lactones **4** and **5**. At higher temperature the equilibrium moves to the stable C−C bond formation through a Friedel−Crafts reaction in the case of arylallenes. Using these simple aryl and alkylallenes, cyclobutanes have not been formed under the reaction conditions.

SCHEME 3



SCHEME 4



In summary, a new reaction of ethenetricarboxylates and arylallenes in the presence of $SnCl_4$ to give indene derivatives **3** was found. The tandem conjugate addition/Friedel−Crafts cyclization of arylallenes may become a useful method to synthesize functionalized indene derivatives. Investigation of the detailed reaction mechanism, further study on the use of the other electrophiles in indene fomation, and transformation of the products to potentially useful compounds are under investigation.

Experimental Section

Typical Experimental Procedure (eq 1, Table 1, entry 1). To a solution of **1** (122 mg, 0.5 mmol) in CH_2Cl_2 (1 mL) were added allene (**2a**) (96 mg, 0.5 mmol) and $SnCl_4$ (26 mg, 12 μL, 0.1 mmol). The mixture was stirred at room temperature for 17 h. The reaction mixture was quenched by water and then saturated aqueous $NaHCO_3$. The mixture was extracted with dichloromethane, and the organic phase was dried (Na_2SO_4) and evaporated *in vacuo*. The residue was purified by column chromatography over silica gel with hexane−ether as eluent to give **3a** (218 mg, 99%).

3a. R_f = 0.4 (hexane−ether = 2:1); colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.913 (t, J = 7.1 Hz, 3H), 1.21 (t, J = 7.1 Hz, 3H), 1.25 (t, J = 7.1 Hz, 3H), 3.42 (d, J = 23.0 Hz, 1H), 3.67 (d, J = 23.0 Hz, 1H), 3.79 (dq, J = 10.6, 7.1 Hz, 1H), 4.01 (dq, J = 10.8, 7.1 Hz, 1H), 4.09−4.24 (m, 5H), 4.50 (d, J = 11.7 Hz, 1H), 7.18−7.26 (m, 3H), 7.38−7.51 (m, 6H). Selected NOEs are between δ 4.50 (C*H*) and δ 4.09−4.24 (C*H*($CO_2Et)_2$), 7.38−7.51 (Ph) and between δ 3.67 (indene C(1)H*H*) and δ

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[15] 1,1-Diphenylallene **2a** has larger HOMO at C_2 (HOMO coefficients: C_2, +0.44; C_1, +0.36; C_3, −0.07). These calculations were performed at the RHF/STO-3G//B3LYP/6-31G* level.

[16] (a) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, 1970. (b) Habermas, K. L.; Denmark, S. E.; Jones, T. K. *Org. React.* **1994**, *45*, 1. (c) Pellissier, H. *Tetrahedron* **2005**, *61*, 6479. (d) Frontier, A. J.; Collison, C. *Tetrahedron* **2005**, *61*, 7577. (e) Suzuki, T.; Ohwada, T.; Shudo, K. *J. Am. Chem. Soc.* **1997**, *119*, 6774.

4.09−4.24 (C*H*(CO$_2$Et)$_2$); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ (ppm) 13.7 (q), 14.0 (q), 14.1 (q), 37.9 (t), 44.8 (d), 54.1 (d), 61.59 (t), 61.62 (t), 61.9 (t), 120.7 (d), 123.8 (d), 125.4 (d), 126.4 (d), 127.9 (d), 128.7 (d), 129.2 (d), 134.0 (s), 135.2 (s), 142.7 (s), 144.5 (s), 145.2 (s), 167.2 (s), 167.8 (s), 171.6 (s). Selected HMBC correlations are between δ 4.50 (C*H*) and δ 135.2 (indene *C*(2)), 144.5 (indene *C*(3)), 37.9 (indene *C*(1)H$_2$), between δ 4.09−4.24 (C*H*(CO$_2$Et)$_2$) and δ 135.2 (indene *C*(2)), and between δ 3.42, 3.67 (indene C(1)*H$_2$*) and δ 135.2 (indene *C*(2)), 144.5 (indene *C*(3)); IR (neat) 2982, 1733, 1462, 1444, 1369, 1300, 1230, 1159, 1029 cm^{-1}; MS (EI) *m*/*z* 436 (M$^+$, 19), 390 (48), 380 (46), 337 (100%); HRMS M$^+$ 436.1885 (calcd for $C_{26}H_{28}O_6$ 436.1886).

3b. R_f = 0.3 (hexane−ether = 2:1); colorless crystals, mp 102−104 °C (hexane−EtOAc); ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 0.906 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H), 3.41 (d, *J* = 23.0 Hz, 1H), 3.67 (d, *J* = 23.0 Hz, 1H), 3.72 (s, 3H), 3.79 (dq, *J* = 10.7, 7.1 Hz, 1H), 4.01 (dq, *J* = 10.7, 7.1 Hz, 1H), 4.11−4.24 (m, 2H), 4.19 (d, *J* = 11.7 Hz, 1H) 4.53 (d, *J* = 11.7 Hz, 1H), 7.18−7.26 (m, 3H), 7.38−7.43 (m, 1H), 7.44−7.51 (m, 5H). Selected NOEs are between δ 4.53 (C*H*) and δ 4.19 (C*H*(CO$_2$Et)$_2$), 7.44−7.51 (Ph) and between δ 3.67 (indene C(1)H*H*) and δ 4.19 (C*H*(CO$_2$Et)$_2$); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ (ppm) 13.6 (q), 14.0 (q), 38.0 (t), 44.6 (d), 52.7 (q), 54.1 (d), 61.6 (t), 61.9 (t), 120.7 (d), 123.8 (d), 125.5 (d), 126.4 (d), 127.9 (d), 128.7 (d), 129.1 (d), 133.9 (s), 135.0 (s), 142.7 (s), 144.5 (s), 145.1 (s), 167.1 (s), 167.8 (s), 172.2 (s). Selected HMBC correlations are between δ 4.53 (C*H*) and δ 135.0 (indene *C*(2)), 144.5 (indene *C*(3)), 38.0 (indene *C*(1)H$_2$), between δ 4.19 (C*H*(CO$_2$Et)$_2$) and δ 135.0 (indene *C*(2)), and between δ 3.41, 3.67 (indene C(1)*H$_2$*) and δ 135.0 (indene *C*(2)), 144.5 (indene *C*(3)); IR (KBr) 2992, 1750, 1734, 1371, 1311, 1286, 1266, 1146 cm^{-1}; MS (EI) *m*/*z* 422 (M$^+$, 34), 390 (92), 298 (55), 288 (51), 203 (100%); HRMS M$^+$ 422.1730 (calcd for $C_{25}H_{26}O_6$ 422.1729). Anal. Calcd for $C_{25}H_{26}O_6$: C, 71.07; H, 6.20. Found: C, 71.02; H, 6.21.

3c. R_f = 0.5 (hexane−ether = 2:1); colorless crystals, mp 82−83 °C (hexane); ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 0.912 (t, *J* = 7.1 Hz, 3H), 1.18 (d, *J* = 6.2 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.28 (d, *J* = 6.2 Hz, 3H), 3.43 (d, *J* = 22.9 Hz, 1H), 3.67 (d, *J* = 22.9 Hz, 1H), 3.79 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.01 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.09−4.23 (m, 2H), 4.18 (d, *J* = 11.7 Hz, 1H) 4.46 (d, *J* = 11.7 Hz, 1H), 5.00 (septet, *J* = 6.2 Hz, 1H), 7.18−7.26 (m, 3H), 7.38−7.42 (m, 1H), 7.46−7.51 (m, 5H). Selected NOEs are between δ 4.46 (C*H*) and δ 4.18 (C*H*(CO$_2$Et)$_2$), 7.46−7.51 (Ph) and between δ 3.67 (indene C(1)H*H*) and δ 4.18 (C*H*(CO$_2$Et)$_2$); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ (ppm) 13.7 (q), 14.0 (q), 21.6 (q), 21.7 (q), 37.8 (t), 45.1 (d), 54.1 (d), 61.6 (t), 61.8 (t), 69.1 (d), 120.6 (d), 123.8 (d), 125.3 (d), 126.4 (d), 127.8 (d), 128.7 (d), 129.2 (d), 134.0 (s), 135.4 (s), 142.7 (s), 144.5 (s), 145.2 (s), 167.2 (s), 167.8 (s), 170.9 (s). Selected HMBC correlations are between δ 4.46 (C*H*) and δ 135.4 (indene *C*(2)), 144.5 (indene *C*(3)), 37.8 (indene *C*(1)H$_2$), between δ 4.18 (C*H*(CO$_2$Et)$_2$) and δ 135.4 (indene *C*(2)), and between δ 3.43, 3.67 (indene C(1)*H$_2$*) and δ 135.4 (indene *C*(2)), 144.5 (indene *C*(3)); IR (KBr) 2986, 1736, 1726, 1461, 1369, 1311, 1230, 1104, 1038 cm^{-1}; MS (EI) *m*/*z* 450 (M$^+$, 67), 390 (99), 362 (86), 288 (88), 244 (75), 216 (100%); HRMS M$^+$ 450.2046 (calcd for $C_{27}H_{30}O_6$ 450.2042). Anal. Calcd for $C_{27}H_{30}O_6$: C, 71.98; H, 6.71. Found: C, 71.87; H, 6.68.

3d. R_f = 0.3 (hexane−ether = 2:1); pale yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 1.02 (t, *J* = 7.1 Hz, 3H), 1.28 (d, *J* = 7.1 Hz, 3H), 3.64 (d, *J* = 22.7 Hz, 1H), 3.72 (d, *J* = 22.7 Hz, 1H), 3.91 (d, *J* = 10.6 Hz, 1H), 3.96 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.08 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.21−4.33 (m, 2H), 4.63 (d, *J* = 10.6 Hz, 1H), 7.18−7.23 (m, 1H), 7.25−7.31 (m, 2H), 7.37−7.40 (m, 2H), 7.43−7.48 (m, 1H), 7.51−7.55 (m, 3H). Selected NOEs are between δ 4.63 (C*H*) and δ 3.91 (C*H*(CO$_2$Et)$_2$), 7.37−7.40 (Ph) and between δ 3.64, 3.72 (indene C(1)*H$_2$*) and δ 3.91 (C*H*(CO$_2$Et)$_2$), 7.51−7.55 (Ar); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ (ppm) 13.8 (q), 14.0 (q), 30.6 (d), 38.2 (t), 54.2 (d), 62.4 (t), 62.7 (t), 118.2 (s), 121.1 (d), 124.0 (d), 126.2 (d), 126.8 (d), 128.5 (d), 128.8 (d), 129.2 (d), 131.5 (s), 133.1 (s), 142.2 (s), 144.4 (s), 145.7 (s), 165.3 (s), 165.9 (s). Selected HMBC correlations are between δ 4.63 (C*H*) and δ 131.5 (indene *C*(2)), 145.7 (indene *C*(3)), 38.2 (indene *C*(1)H$_2$), between δ 3.91 (C*H*(CO$_2$Et)$_2$) and δ 131.5 (indene *C*(2)), and between δ 3.64, 3.72 (indene C(1)*H$_2$*) and δ 131.5 (indene *C*(2)), 145.7 (indene *C*(3)); IR (neat) 2983, 2244, 1758−1732, 1491, 1463, 1444, 1391, 1370, 1300, 1258, 1192, 1096, 1030 cm^{-1}; MS (EI) *m*/*z* 389 (M$^+$, 100), 343 (13), 315 (24), 286 (29), 270 (43%); HRMS M$^+$ 389.1624 (calcd for $C_{24}H_{23}NO_4$ 389.1627).

3e. R_f = 0.6 (hexane−ether = 2:1); colorless crystals, mp 88−89 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 0.953 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 3.41 (d, *J* = 23.2 Hz, 1H), 3.64 (d, *J* = 23.2 Hz, 1H), 3.84 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.03 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.10−4.25 (m, 4H), 4.16 (d, *J* = 11.7 Hz, 1H), 4.40 (d, *J* = 11.7 Hz, 1H), 7.05 (dd, *J* = 8.1, 0.4 Hz, 1H), 7.23 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.39 (bd, *J* = 8.1 Hz, 2H), 7.44 (dd, *J* = 1.9, 0.4 Hz, 1H), 7.48 (d-like, *J* = 8.1 Hz, 2H). Selected NOEs are between δ 4.40 (C*H*) and δ 4.16 (C*H*(CO$_2$Et)$_2$), 7.39 (Ar) and between δ 3.64 (indene C(1)H*H*) and δ 4.16 (C*H*(CO$_2$Et)$_2$); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ (ppm) 13.8 (q), 14.0 (q), 14.1 (q), 37.9 (t), 44.9 (d), 53.8 (d), 61.7 (t), 61.8 (t), 62.0 (t), 121.2 (d), 124.3 (d), 126.8 (d), 129.2 (d), 130.5 (d), 131.8 (s), 132.0 (s), 134.1 (s), 136.2 (s), 142.8 (s), 143.3 (s), 144.2 (s), 167.1 (s), 167.6 (s), 171.1 (s). Selected HMBC correlations are between δ 4.40 (C*H*) and δ 136.2 (indene *C*(2)), 142.8 (indene *C*(3)), 37.9 (indene *C*(1)H$_2$), between δ 4.16 (C*H*(CO$_2$Et)$_2$) and δ 136.2 (indene *C*(2)), and between δ 3.41, 3.64 (indene C(1)*H$_2$*) and δ 136.2 (indene *C*(2)), 142.8 (indene *C*(3)); IR (KBr) 2984, 1737, 1728, 1307, 1252, 1229, 1162, 1039 cm^{-1}; MS (EI) *m*/*z* 506 (M$^+$, 6.3), 504 (M$^+$, 8.8), 460 (15), 458 (22), 430 (23), 384 (26), 356 (35), 271 (81), 249 (100%); HRMS M$^+$ 504.1113, 506.1095 (calcd for $C_{26}H_{26}Cl_2O_6$ 504.1106, 506.1077). Anal. Calcd for $C_{26}H_{26}Cl_2O_6$: C, 61.79; H, 5.19. Found: C, 61.91; H, 5.21.

3f. R_f = 0.6 (hexane−ether = 2:1); colorless crystals, mp 87−88 °C (hexane); ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 0.918 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 2.39 (s, 3H), 2.42 (s, 3H), 3.36 (d, *J* = 22.9 Hz, 1H), 3.61 (d, *J* = 22.9 Hz, 1H), 3.79 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.00 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.08−4.23 (m, 4H), 4.17 (d, *J* = 11.7 Hz, 1H), 4.48 (d, *J* = 11.7 Hz, 1H), 7.05 (dd, *J* = 7.7, 0.6 Hz, 1H), 7.08 (d, *J* = 7.7 Hz, 1H), 7.28 (d, *J* = 7.7 Hz, 2H), 7.28−7.29 (m, 1H), 7.36 (d, *J* = 7.7 Hz, 2H). Selected NOEs are between δ 4.48 (C*H*) and δ 4.17 (C*H*(CO$_2$Et)$_2$), 7.36 (Ar) and between δ 3.61 (indene C(1)H*H*) and δ 4.17 (C*H*(CO$_2$Et)$_2$); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ (ppm) 13.7 (q), 14.0 (q), 14.1 (q), 21.4 (q), 21.5 (q), 37.6 (t), 44.8 (d), 54.0 (d), 61.5 (t), 61.6 (t), 61.8 (t), 120.3 (d), 124.7 (d), 127.1 (d), 129.0 (d), 129.4 (d), 131.2 (s), 133.8 (s), 135.2 (s), 137.4 (s), 142.7 (s), 143.0 (s), 144.3 (s), 167.2 (s), 167.9 (s), 171.7 (s). Selected HMBC correlations are between δ 4.48 (C*H*) and δ 133.8 (indene *C*(2)), 144.3 (indene *C*(3)), 37.6 (indene *C*(1)H$_2$), between δ 4.17 (C*H*(CO$_2$Et)$_2$) and δ 133.8 (indene *C*(2)), and between δ 3.36, 3.61 (indene C(1)*H$_2$*) and δ 133.8 (indene *C*(2)), 144.3 (indene *C*(3)); IR (KBr) 2981, 1758, 1736, 1646, 1508, 1464, 1370, 1263, 1160, 1022 cm^{-1}; MS (EI) *m*/*z* 464 (M$^+$, 22), 418 (21), 326 (42), 231 (100%); HRMS M$^+$ 464.2197 (calcd for $C_{28}H_{32}O_6$ 464.2199). Anal. Calcd for $C_{28}H_{32}O_6$: C, 72.39; H, 6.94. Found: C, 72.66; H, 7.07.

3g (including a small amount of impurity). R_f = 0.4 (hexane−ether = 2:1); pale yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 0.913 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 3.38 (d, *J* = 22.7 Hz, 1H), 3.63 (d, *J* = 22.7 Hz, 1H), 3.79 (dq, *J* = 10.6, 7.1 Hz, 1H), 3.82 (s, 3H), 4.01 (dq, *J* = 10.6, 7.1 Hz, 1H), 4.10−4.24 (m, 4H), 4.17 (d, *J* = 11.7 Hz, 1H), 4.46 (d, *J* = 11.7 Hz, 1H), 6.79 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.06 (d, *J* = 2.0 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 7.37−7.42 (m, 1H), 7.47−7.50 (m, 4H). Selected NOEs are between δ 4.46 (C*H*) and δ 4.17 (C*H*(CO$_2$Et)$_2$), 7.47−7.50 (Ar) and between δ 3.63 (indene C(1)H*H*) and δ 4.17 (C*H*(CO$_2$Et)$_2$); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ (ppm) 13.7 (q), 14.0 (q), 14.1 (q), 37.9 (t), 44.8 (d), 54.0 (d), 55.6 (q), 61.5 (t), 61.6 (t), 61.8 (t), 110.2 (d), 112.1 (d), 121.0 (d), 127.8 (d), 128.7 (d), 129.1 (d), 132.7 (s), 134.2 (s), 138.3 (s), 144.0 (s), 144.5 (s), 158.4 (s), 167.2 (s), 167.8 (s), 171.7 (s). Selected HMBC correlations are between δ 4.46 (C*H*) and δ 132.7 (indene *C*(2)), 144.0 (indene *C*(3)), 37.9 (indene *C*(1)H$_2$), between δ 4.17 (C*H*(CO$_2$Et)$_2$) and δ 132.7 (indene *C*(2)), and between δ 3.38, 3.63 (indene C(1)*H*$_2$) and δ 132.7 (indene *C*(2)), 144.0 (indene *C*(3)); IR (neat) 2982, 1732, 1609, 1480, 1466, 1445, 1369, 1287, 1269, 1248, 1176, 1032 cm^{-1}; MS (EI) *m*/*z* 466 (M$^+$, 76), 420 (66), 318 (76), 233 (100%); HRMS M$^+$ 466.1990 (calcd for $C_{27}H_{30}O_7$ 466.1992).

3h. R_f = 0.4 (hexane−ether = 2:1); colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 0.972 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 2.16 (t, *J* = 2.0 Hz, 3H), 3.22 (dq, *J* = 22.2, 2.0 Hz, 1H), 3.44 (d, *J* = 22.2, 2.0 Hz, 1H), 3.91−4.30 (m, 6H), 4.19 (d, *J* = 11.8 Hz, 1H), 4.50 (d, *J* = 11.8 Hz, 1H), 7.16−7.22 (m, 1H), 7.26−7.31 (m, 2H), 7.40 (d, *J* = 7.3 Hz, 1H). Selected NOEs are between δ 4.50 (C*H*) and δ 4.19 (C*H*(CO$_2$Et)$_2$), 2.16 (C*H*$_3$), between δ 3.44 (indene C(1)H*H*) and δ 4.19 (C*H*(CO$_2$Et)$_2$), and between δ 2.16 (C*H*$_3$) and δ 7.26−7.31 (indene H(4)); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ (ppm) 10.6 (q), 13.8 (q), 14.05 (q), 14.12 (q), 37.7 (t), 44.8 (d), 53.8 (d), 61.4 (t), 61.6 (t), 61.9 (t), 119.2 (d), 123.5 (d), 125.1 (d), 126.3 (d), 133.4 (s), 138.8 (s), 142.6 (s), 145.9 (s), 167.4 (s), 168.0 (s), 171.6 (s). Selected HMBC correlations are between δ 4.50 (C*H*) and δ 133.4 (indene *C*(2)), 138.8 (indene *C*(3)), 37.7 (indene *C*(1)H$_2$), between δ 4.19 (C*H*(CO$_2$Et)$_2$) and δ 133.4 (indene *C*(2)), and between δ 3.22, 3.44 (indene C(1)*H*$_2$) and δ 133.4 (indene *C*(2)), 138.8 (indene *C*(3)); IR (neat) 2982, 1733, 1467, 1369, 1300, 1158, 1030 cm^{-1}; MS (EI) *m*/*z* 374 (M$^+$, 56), 328 (83), 300 (100%); HRMS M$^+$ 374.1726 (calcd for $C_{21}H_{26}O_6$ 374.1729). Anal. Calcd for $C_{21}H_{26}O_6$: C, 67.36; H, 7.00. Found: C, 67.18; H, 6.97.

3i. R_f = 0.4 (hexane−ether = 2:1); colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 0.973 (t, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 2.15 (t, *J* = 2.2 Hz, 3H), 3.22 (dq, *J* = 22.5, 2.2 Hz, 1H), 3.44 (d, *J* = 22.5, 2.2 Hz, 1H), 3.67 (s, 3H), 3.91−4.05 (m, 2H), 4.17−4.30 (m, 2H), 4.19 (d, *J* = 11.8 Hz, 1H), 4.52 (d, *J* = 11.8 Hz, 1H), 7.16−7.22 (m, 1H), 7.26−7.31 (m, 2H), 7.39 (d-like, *J* = 7.3 Hz, 1H). Selected NOEs are between δ 4.52 (C*H*) and δ 4.19 (C*H*(CO$_2$Et)$_2$), 2.15 (C*H*$_3$), between δ 3.44 (indene C(1)H*H*) and δ 4.19 (C*H*(CO$_2$Et)$_2$), and between δ 2.15 (C*H*$_3$) and δ 7.26−7.31 (indene H(4)); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ (ppm) 10.6 (q), 13.8 (q), 14.1 (q), 37.7 (t), 44.6 (d), 52.5 (q), 53.8 (d), 61.6 (t), 62.0 (t), 119.2 (d), 123.5 (d), 125.2 (d), 126.3 (d), 133.2 (s), 138.9 (s), 142.6 (s), 145.8 (s), 167.4 (s), 168.0 (s), 172.2 (s). Selected HMBC correlations are between δ 4.52 (C*H*) and δ 133.2 (indene *C*(2)), 138.9 (indene *C*(3)), 37.7 (indene *C*(1)H$_2$), between δ 4.19 (C*H*(CO$_2$Et)$_2$) and δ 133.2 (indene *C*(2)), and between δ 3.22, 3.44 (indene C(1)*H*$_2$) and δ 133.2 (indene *C*(2)), 138.9 (indene *C*(3)); IR (neat) 2982, 1758−1733, 1468, 1436, 1369, 1299, 1161, 1032 cm^{-1}; MS (EI) *m*/*z* 360 (M$^+$, 45), 328 (92), 300 (100%); HRMS M$^+$ 360.1573 (calcd for $C_{20}H_{24}O_6$ 360.1573).

3j. R_f = 0.5 (hexane−ether = 1:1); colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 0.976 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 2.13 (t, *J* = 2.2 Hz, 3H), 3.21 (dq, *J* = 22.7, 1.6 Hz, 1H), 3.43 (d, *J* = 22.7, 1.6 Hz, 1H), 3.91−4.30 (m, 6H), 4.16 (d, *J* = 11.7 Hz, 1H), 4.47 (d, *J* = 11.7 Hz, 1H), 7.19 (dd, *J* = 8.0, 0.5 Hz, 1H), 7.26 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.36 (dd, *J* = 2.0, 0.5 Hz, 1H). Selected NOEs are between δ 4.47 (C*H*) and δ 4.16 (C*H*(CO$_2$Et)$_2$), 2.13 (C*H*$_3$), between δ 3.43 (indene C(1)H*H*) and δ 4.16 (C*H*(CO$_2$Et)$_2$), and between δ 2.13 (C*H*$_3$) and δ 7.19 (indene H(4)); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ (ppm) 10.6 (q), 13.8 (q), 14.05 (q), 14.13 (q), 37.6 (t), 44.8 (d), 53.7 (d), 61.5 (t), 61.6 (t), 62.0 (t), 120.0 (d), 123.9 (d), 126.5 (d), 128.3 (s), 129.6 (s), 131.1 (s), 133.9 (s), 138.2 (s), 144.2 (s), 144.4 (s), 167.4 (s), 167.9 (s), 171.4 (s). Selected HMBC correlations are between δ 4.47 (C*H*) and δ 133.9 (indene *C*(2)), 138.2 (indene *C*(3)), 37.6 (indene *C*(1)H$_2$), between δ 4.16 (C*H*(CO$_2$Et)$_2$) and δ 133.9 (indene *C*(2)), and between δ 3.21, 3.43 (indene C(1)*H*$_2$) and δ 133.9 (indene *C*(2)), 138.2 (indene *C*(3)); IR (neat) 2982, 1733, 1467, 1391, 1369, 1300, 1227, 1160, 1096, 1029 cm^{-1}; MS (EI) *m*/*z* 410 (M$^+$, 23), 408 (M$^+$, 60), 364 (22), 362 (59), 334 (74), 153 (100%); HRMS M$^+$ 408.1334, 410.1319 (calcd for $C_{21}H_{25}ClO_6$ 408.1340, 410.1310).

3k. R_f = 0.4 (hexane−ether = 2:1); pale yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 0.983 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 2.13 (t, *J* = 2.2 Hz, 3H), 2.38 (s, 3H), 3.17 (dq, *J* = 22.6, 1.8 Hz, 1H), 3.40 (d, *J* = 22.6, 2.0 Hz, 1H), 3.91−4.29 (m, 6H), 4.18 (d, *J* = 11.8 Hz, 1H), 4.47 (d, *J* = 11.8 Hz, 1H), 7.09 (d-like, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.22 (bs, 1H). Selected NOEs are between δ 4.47 (C*H*) and δ 4.18 (C*H*(CO$_2$Et)$_2$), 2.13 (C*H*$_3$), between δ 3.40 (indene C(1)H*H*) and δ 4.18 (C*H*(CO$_2$Et)$_2$), and between δ 2.13 (C*H*$_3$) and δ 7.17 (indene H(4)); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ (ppm) 10.6 (q), 13.8 (q), 14.05 (q), 14.13 (q), 21.5 (q), 37.5 (t), 44.8 (d), 53.7 (d), 61.4 (t), 61.6 (t), 61.9 (t), 118.8 (d), 124.4 (d), 126.9 (d), 132.3 (s), 134.8 (s), 138.6 (s), 142.9 (s), 143.4 (s), 167.5 (s), 168.0 (s), 171.7 (s). Selected HMBC correlations are between δ 4.47 (C*H*) and δ 132.3 (indene *C*(2)), 138.6 (indene *C*(3)), 37.5 (indene *C*(1)H$_2$), between δ 4.18 (C*H*(CO$_2$Et)$_2$) and δ 132.3 (indene *C*(2)), and between δ 3.17, 3.40 (indene C(1)*H*$_2$) and δ 132.3 (indene *C*(2)), 138.6 (indene *C*(3)); IR (neat) 2982, 1752, 1734, 1369, 1299, 1159, 1030 cm^{-1}; MS (EI) *m*/*z* 388 (M$^+$, 93), 342 (100), 314 (92), 268 (88%); HRMS M$^+$ 388.1886 (calcd for $C_{22}H_{28}O_6$ 388.1886). Anal. Calcd for $C_{22}H_{28}O_6$: C, 68.02; H, 7.27. Found: C, 67.73; H, 7.00.

3l. R_f = 0.3 (hexane−ether = 1:2); colorless crystals, mp 156−159 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 0.917 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H), 3.48 (d, *J* = 22.9 Hz, 1H), 3.66 (d, *J* = 22.9 Hz, 1H), 3.80 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.03 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.09−4.24 (m, 2H), 4.14 (d, *J* = 11.6 Hz, 1H) 4.54 (d, *J* = 11.6 Hz, 1H), 7.18−7.24 (m, 3H), 7.39−7.50 (m, 6H). Selected NOEs are between δ 4.54 (C*H*) and δ 4.14 (C*H*(CO$_2$Et)$_2$), 7.39−7.50 (Ph) and between δ 3.66 (indene C(1)H*H*) and δ 4.14 (C*H*(CO$_2$Et)$_2$); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ (ppm) 13.7 (q), 14.0 (q), 37.9 (t), 44.5 (d), 53.9 (d), 61.8 (t), 62.1 (t), 120.8 (d), 123.9 (d), 125.6 (d), 126.5 (d), 128.0 (d), 128.8 (d), 129.2 (d), 133.8 (s), 134.2 (s), 142.7 (s), 145.0 (s), 145.3 (s), 166.9 (s), 167.6 (s), 176.5 (s). Selected HMBC correlations are between δ 4.54 (C*H*) and δ 134.2 (indene *C*(2)), 145.3 (indene *C*(3)), 37.9 (indene *C*(1)H$_2$), between δ 4.14 (C*H*(CO$_2$Et)$_2$) and δ 134.2 (indene *C*(2)), and between δ 3.48, 3.66 (indene C(1)*H*$_2$) and δ 134.2 (indene *C*(2)), 145.3 (indene *C*(3)); IR (KBr) 3050−2590, 2981, 1746, 1705, 1463, 1296, 1267, 1189, 1149, 1031 cm^{-1}; MS (EI) *m*/*z* 408 (M$^+$, 6.8), 390 (21), 364 (32), 298 (37), 244 (59), 215 (75), 204 (100%); HRMS M$^+$ 408.1574 (calcd for $C_{24}H_{24}O_6$ 408.1573).

Typical Procedure for Preparation of γ-Lactones. To a solution of 1,1-diethyl 2-hydrogen ethenetricarboxylate (**1a**) (108 mg, 0.5 mmol) (prepared from 1,1-diethyl 2-*tert*-butyl ethenetricarboxylate (**1f**) upon treatment with CF$_3$CO$_2$H)[9] in dichloromethane (1 mL) was added 3-methyl-1,2-butadiene (**2j**) (34 mg, 50 μL, 0.5 mmol), followed by SnCl$_4$ (130 mg, 60 μL, 0.5 mmol) at −78 °C. The mixture was stirred for 3 h. The reaction mixture was quenched by water. The mixture was extracted with dichloromethane, and the organic phase was washed with saturated aqueous NaHCO$_3$, dried (Na$_2$SO$_4$), and evaporated *in vacuo* to give crude γ-lactone **4** (R^1 = R^2 = Me).

4 (R^1 = R^2 = Me). Colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 1.29 (t, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.52 (s, 3H), 1.56 (s, 3H), 3.97 (ddd, *J* = 3.8, 3.3, 2.8 Hz, 1H), 4.01 (d, *J* = 3.8 Hz, 1H), 4.18−4.32 (m, 4H), 5.09 (dd, *J* = 2.8, 1.3 Hz, 1H), 5.12 (dd, *J* = 3.3, 1.3 Hz, 1H). Selected NOEs are between δ 5.12 (=CH*H*) and δ 1.52, 1.56 ((C*H*$_3$)$_2$), between δ 5.09 (=C*H*H) and δ 3.97 (C*H*), 4.01 (C*H*(CO$_2$Et)$_2$), between δ 3.97 (C*H*) and δ 1.52

(CH_3), and between δ 4.01 (CH(CO$_2$Et)$_2$) and δ 1.56 (CH_3); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ (ppm) 13.95 (q), 14.00 (q), 26.9 (q), 29.4 (q), 43.4 (d), 51.9 (d), 62.0 (t), 62.2 (t), 86.4 (s), 107.3 (t), 149.7 (s), 167.0 (s), 167.2 (s), 173.5 (s). Selected HMBC correlations are between δ 5.09, 5.12 (=CH_2), 1.52, 1.56 ((CH_3)$_2$) and δ 149.7 (C=CH$_2$), between δ 5.09, 5.12 (=CH_2), 1.52, 1.56 ((CH_3)$_2$) and δ 86.4 (OC(CH$_3$)$_2$), and between δ 5.09, 5.12 (=CH_2) and δ 43.4 (CH); IR (neat) 2980, 1771, 1750, 1466, 1371, 1283, 1247, 1178, 1119, 1033 cm^{-1}.

To a solution of the crude **4** (R^1 = R^2 = Me) in dichloromethane (1 mL) was added triethylamine (51 mg, 69 μL, 0.5 mmol) at room temperature. The mixture was stirred for 1 h. The reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography over silica gel eluting with hexane−ether (1:1) to give to give **5j** (110 mg, 39%).

5j. R_f = 0.4 (hexane−ether = 1:1); colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 1.28 (t, J = 7.1 Hz, 6H), 1.47 (s, 6H), 2.05 (s, 3H), 4.23 (q, J = 7.1 Hz, 2H), 4.24 (q, J = 7.1 Hz, 2H), 4.61 (s, 1H). Selected NOEs are between δ 1.47 ((CH_3)$_2$) and δ 2.05 (CH_3); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ (ppm) 12.2 (q), 14.1 (q), 24.5 (q), 47.7 (d), 62.2 (t), 86.6 (s), 119.0 (s), 166.8 (s), 170.1 (s), 171.6 (s). Selected HMBC correlations are between δ 1.47 ((CH_3)$_2$) and δ 170.1 (C=CCH$_3$), 86.6 (OC(CH$_3$)$_2$) and between δ 2.05 (CH_3) and δ 170.1 (C=CCH$_3$), 86.6 (OC(CH$_3$)$_2$), 119.0 (C=CCH$_3$); IR (neat) 2982, 1755, 1681, 1465, 1368, 1293, 1264, 1156, 1032 cm^{-1}; MS (EI) m/z 284 (M$^+$, 100), 269 (29%); HRMS M$^+$ 284.1263 (calcd for $C_{14}H_{20}O_6$ 284.1260).

5a. R_f = 0.2 (CH$_2$Cl$_2$); colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 1.26 (t, J = 7.1 Hz, 6H), 2.06 (s, 3H), 4.24 (q, J = 7.1 Hz, 4H), 4.74 (s, 1H), 7.29−7.32 (m, 4H), 7.36−7.40 (m, 6H). Selected NOEs are between δ 2.06 (CH_3) and δ 4.74 (CH(CO$_2$Et)$_2$), 7.29−7.32 (Ph); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ (ppm) 14.1 (q), 14.4 (q), 48.0 (d), 62.3 (t), 93.6 (s), 121.0 (s), 128.0 (d), 128.6 (d), 129.0 (d), 138.2 (s), 166.6 (s), 168.1 (s), 171.9 (s). Selected HMBC correlations are between δ 2.06 (CH_3) and δ 168.1 (C=CCH$_3$), 93.6 (OCPh$_2$), 121.0 (C=CCH$_3$) and between δ 4.74 (CH(CO$_2$Et)$_2$) and δ 168.1 (C=CCH$_3$), 121.0 (C=CCH$_3$), 166.6 (CO$_2$Et), 171.9 (OC=O); IR (neat) 2983, 1755, 1677, 1447, 1305, 1177, 1157, 1034 cm^{-1}; MS (EI) m/z 408 (M$^+$, 24), 303 (82), 229 (63), 202 (58), 105 (100%); HRMS M$^+$ 408.1574 (calcd for $C_{24}H_{24}O_6$ 408.1573).

5f. R_f = 0.4 (hexane−ether = 1:1); colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 1.25 (t, J = 7.1 Hz, 3H), 1.30 (t, J = 7.1 Hz, 3H), 1.88 (s, 3H), 1.89 (s, 3H), 4.228 (q, J = 7.1 Hz, 2H), 4.233−4.29 (m, 2H), 4.68 (s, 1H), 7.31−7.40 (m, 5H). Selected NOEs are between δ 1.88 (CH_3), 1.89 (CH_3) and δ 7.31−7.40 (Ph); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ (ppm) 12.5 (q), 14.05 (q), 14.06 (q), 22.3 (q), 47.8 (d), 62.3 (t), 88.8 (s), 119.3 (s), 125.7 (d), 128.85 (d), 128.85 (d), 137.5 (s), 166.6 (s), 166.7 (s), 169.6 (s), 172.2 (s). Selected HMBC correlations are between δ 1.88 (CH_3), 1.89 (CH_3) and δ 169.6 (C=CCH$_3$), 88.8 (OCMePh) and between δ 4.68 (CH(CO$_2$Et)$_2$) and δ 169.6 (C=CCH$_3$), 119.3 (C=CCH$_3$), 166.6 (CO$_2$Et), 166.7 (CO$_2$Et), 172.2 (OC=O); IR (neat) 2984, 1754, 1678, 1447, 1369, 1306, 1250, 1155, 1029 cm^{-1}; MS (EI) m/z 346 (M$^+$, 22), 303 (100), 229 (69%); HRMS M$^+$ 346.1422 (calcd for $C_{19}H_{22}O_6$ 346.1416).

5g. R_f = 0.4 (hexane−ether = 1:1); colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 1.26 (t, J = 7.1 Hz, 3H), 1.31 (t, J = 7.1 Hz, 3H), 1.87 (s, 3H), 1.88 (s, 3H), 4.24 (q, J = 7.1 Hz, 2H), 4.23−4.29 (m, 2H), 4.67 (s, 1H), 7.26 (d-like, J = 8.8 Hz, 2H), 7.35 (d-like, J = 8.8 Hz, 2H). Selected NOEs are between δ 1.87 (CH_3), 1.88 (CH_3) and δ 7.26 (Ar); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ (ppm) 12.4 (q), 14.0 (q), 22.2 (q), 47.7 (d), 62.3 (t), 88.1 (s), 119.6 (s), 127.2 (d), 129.0 (d), 134.9 (s), 136.1 (s), 166.49 (s), 166.54 (s), 169.2 (s), 171.9 (s). Selected HMBC correlations are between δ 1.87 (CH_3), 1.88 (CH_3) and δ 169.2 (C=CCH$_3$), 88.1 (OCMeAr) and between δ 4.67 (CH(CO$_2$Et)$_2$) and δ 169.2 (C=CCH$_3$), 119.6 (C=CCH$_3$), 166.49 (CO$_2$Et), 166.54 (CO$_2$Et), 171.9 (OC=O); IR (neat) 2984, 1753, 1678, 1494, 1306, 1250, 1155, 1097, 1034, 1013 cm^{-1}; MS (EI) m/z 382 (M$^+$, 10), 380 (M$^+$, 27), 339 (49), 337 (100), 291 (65), 263 (86), 139 (91%); HRMS M$^+$ 380.1025, 382.1004 (calcd for $C_{19}H_{21}ClO_6$ 380.1027, 328.0997). Anal. Calcd for $C_{19}H_{21}ClO_6$: C, 59.92; H, 5.56. Found: C, 59.63; H, 5.55.

5i. R_f = 0.3 (hexane−ether = 1:1); colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 1.28 (t, J = 7.1 Hz, 3H), 1.31 (t, J = 7.1 Hz, 3H), 1.91 (s, 3H), 4.21−4.33 (m, 4H), 4.71 (s, 1H), 5.70 (s, 1H), 7.23−7.25 (m, 2H), 7.38−7.41 (m, 3H). Selected NOEs are between δ 5.70 (OCHPh) and δ 1.91 (CH_3), 7.23−7.25 (Ph); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ (ppm) 13.4 (q), 14.1 (q), 47.9 (d), 62.3 (t), 62.4 (t), 85.8 (d), 120.4 (s), 127.4 (d), 129.2 (d), 129.7 (d), 134.2 (s), 165.1 (s), 166.58 (s), 166.64 (s), 172.8 (s). Selected HMBC correlations are between δ 5.70 (OCHPh) and δ 172.8 (CO−O), 165.1 (C=CCH$_3$), 134.2 (Ph) and between δ 1.91 (CH_3) and δ 165.1 (C=CCH$_3$), 85.8 (OCHPh), 120.4 (C=CCH$_3$); IR (neat) 2984, 1752, 1679, 1456, 1369, 1307, 1261, 1156, 1030 cm^{-1}; MS (EI) m/z 332 (M$^+$, 85), 258 (50), 213 (67), 169 (99), 105 (100%); HRMS M$^+$ 332.1261 (calcd for $C_{18}H_{20}O_6$ 332.1260).

5k. R_f = 0.4 (hexane−ether = 1:1); colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 0.859 (t, J = 7.0 Hz, 3H), 0.98−1.08 (m, 1H), 1.19−1.32 (m, 5H), 1.275 (t, J = 7.1 Hz, 3H), 1.277 (t, J = 7.1 Hz, 3H), 1.44 (s, 3H), 1.61−1.68 (m, 1H), 1.83−1.90 (m, 1H), 2.00 (s, 3H), 4.20−4.26 (m, 4H), 4.62 (s, 1H). Selected NOEs are between δ 1.44 (CH_3) and δ 2.00 (CH_3); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ (ppm) 12.4 (q), 14.02 (q), 14.08 (q), 14.11 (q), 22.46 (t), 22.48 (t), 23.8 (q), 31.7 (t), 37.0 (t), 47.8 (d), 62.2 (t), 88.9 (s), 120.0 (s), 166.80 (s), 166.82 (s), 169.1 (s), 172.0 (s). Selected HMBC correlations are between δ 1.44 (CH_3) and δ 169.1 (C=CCH$_3$), 88.9 (OCCH$_3$) and between δ 2.00 (CH_3) and δ 169.1 (C=CCH$_3$), 88.9 (OCCH$_3$), 120.0 (C=CCH$_3$); IR (neat) 2938, 2865, 1752, 1464, 1369, 1305, 1256, 1154, 1036 cm^{-1}; MS (EI) m/z 341 ((M+1)$^+$, 35), 340 (M$^+$, 3.4), 297 (100%); HRMS M$^+$ 340.1890 (calcd for $C_{18}H_{28}O_6$ 340.1886).

5l. R_f = 0.6 (hexane−ether = 1:1); colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 1.20−1.28 (m, 1H), 1.28 (t, J = 7.1 Hz, 6H), 1.52 (bd, J = 10.3 Hz, 2H), 1.66−1.84 (m, 7H), 2.03 (s, 3H), 4.226 (q, J = 7.1 Hz, 2H), 4.227 (q, J = 7.1 Hz, 2H), 4.61 (s, 1H). Selected NOEs are between δ 2.03 (CH_3) and δ 4.61 (CH(CO$_2$Et)$_2$); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ (ppm) 12.4 (q), 14.0 (q), 21.9 (t), 24.6 (t), 33.2 (t), 47.7 (d), 62.1 (t), 88.3 (s), 119.1 (s), 166.8 (s), 170.3 (s), 171.9 (s). Selected HMBC correlations are between δ 2.03 (CH_3) and δ 170.3 (C=CCH$_3$), 88.3 (OC(CH$_2$)$_5$-), 119.1 (C=CCH$_3$) and between δ 4.61 (CH(CO$_2$Et)$_2$) and δ 170.3 (C=CCH$_3$), 119.1 (C=CCH$_3$), 166.8 (CO$_2$Et), 171.9 (OC=O); IR (neat) 2983, 2939, 2864, 1750, 1676, 1449, 1368, 1307, 1265, 1227, 1155, 1033 cm^{-1}; MS (EI) m/z 324 (M$^+$, 100), 279 (51), 232 (78), 223 (71), 133 (69%); HRMS M$^+$ 324.1574 (calcd for $C_{17}H_{24}O_6$ 324.1573). Anal. Calcd for $C_{17}H_{24}O_6$: C, 62.95; H, 7.46. Found: C, 62.49; H, 7.38.

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Supporting Information Available: Additional experimental procedures, spectral data, and crystallographic data including CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.