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Palladium-Catalyzed Oxidative Coupling of the Allenic C−H Bond with α-Diazo Esters: Synthesis of [3]Dendralenes

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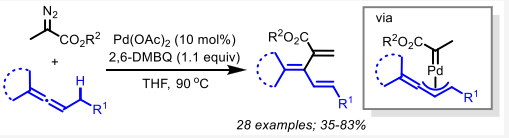
ABSTRACT: A palladium-catalyzed highly regio- and stereoselective allenic C−H oxidative coupling with α-diazo esters is developed. The reaction pathway involves allylic palladium carbene as the key intermediate, which is followed by a carbene migratory insertion process. The reaction proceeds efficiently under mild conditions without external base, providing substituted [3]dendralenes bearing various functional groups.



Dendralenes are a type of unique acyclic cross-conjugated polyenes,[1] among which [3]dendralenes were the simplest dendralenes first reported in 1955.[2] Recently, dendralenes have become an attractive type of molecule in polymer chemistry,[3] theoretical chemistry,[4] and synthetic chemistry.[5] In particular, [3]dendralenes have attracted attention because of their occurrence as motifs in an increasing number of natural products[6] and also their engagement in the diene-transmissive Diels−Alder reaction (DTDA),[7] which can be employed for rapidly constructing complex multicyclic frameworks.

The development of synthetic methods toward these cross-conjugated polyenes has been crucial in this arena. In 1991, Cadogan and co-workers prepared [3]dendralene in six steps from 3-sulfolene.[8] Subsequently, Sherburn and co-workers disclosed the first general method toward [*n*]dendralene synthesis in small scale.[9] However, these methods, including those reported in 1955, all proceeded at high temperature. A breakthrough was made by Sherburn and co-workers in 2009, who successfully synthesized dendralenes on a multigram scale through a combination of Ni(0)-catalyzed Kumada−Tamao−Corriu coupling and Pd(0)-catalyzed Negishi coupling (Scheme 1a).[10] After that, many other methods using different transition metal catalysts were reported (Scheme 1b,c).[11] While significant progress has been made, there are some limitations to these methods. For example, the building blocks used in the dendralene synthesis usually contain alkenyl metal groups, preinstalled directing groups, leaving groups, and so on, which adds extra steps for the synthesis.

On the other hand, transition-metal-catalyzed C−H functionalization has become a powerful tool for constructing carbon−carbon and carbon−heteroatom bonds, dramatically simplifying the synthesis of complex molecules.[12] In the palladium-catalyzed allylic C−H oxidation reaction, early studies on cyclic or acyclic alkenes by the group of Åkermark,[13] Bäckvall,[14] White,[15] and Shi[16] showed that the reactions proceed via π-allylpalladium(II) intermediates generated through allylic C−H bond cleavage. However, reports on the dendralene synthesis involving C−H bond cleavage are scarce.[17] In particular, we were inspired by Bäckvall and co-workers who reported a straightforward synthesis of [3]-dendralene derivatives through palladium-catalyzed allenic C−H bond oxidation (Scheme 1d).[17b] In connection to our

Scheme 1. Transition-Metal-Catalyzed Synthesis of Dendralene

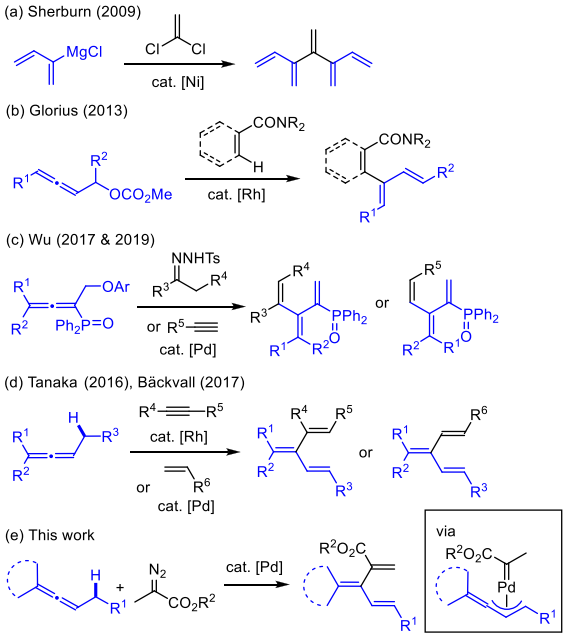


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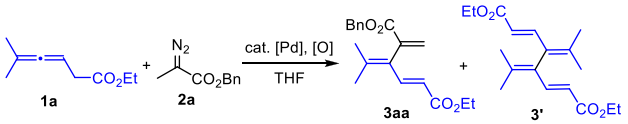
Table 1. Optimization of the Reaction Conditions[a]



entry	[Pd] (5 mol %)	[O] (equiv)	solvent	T (°C)	yield[b] (%) 3aa, 3′	rec. 1a[b] (%)
1	$PdCl_2$	BQ (1.5)	THF	80	36, 5	27
2	$Pd(OAc)_2$/L[c]	BQ (1.5)	THF	80	35, 4	26
3	$Pd(OAc)_2$	BQ (1.5)	THF	80	42, 6	20
4[d]	$Pd(OAc)_2$	BQ (1.5)	THF	80	39, 14	
5[e]	$Pd(OAc)_2$	BQ (1.5)	THF	80	43, 15	
6	$Pd(OAc)_2$	BQ (1.1)	THF	80	42, 4	20
7	$Pd(OAc)_2$	BQ (2.0)	THF	80	37, 3	38
8	$Pd(OAc)_2$	BQ (2.5)	THF	80	33, 3	50
9	$Pd(OAc)_2$	BQ (1.1)	dioxane	80	32, –	6
10	$Pd(OAc)_2$	BQ (1.1)	DME	80	39, –	37
11[f]	$Pd(OAc)_2$	BQ (1.1)	THF	80	48, 8	7
12[f]	$Pd(OAc)_2$	BQ (1.1)	THF	90	59, 3	6
13[f]	$Pd(OAc)_2$	2,6-DMBQ (1.1)	THF	90	73,[g] 6	

[a]The reaction was conducted in the indicated solvent (1 mL) at 80 °C using **1a** (0.1 mmol), **2a** (0.2 mmol), and palladium catalyst (5 mol %) under an atmosphere of N_2 for 10 h. [b]The yields were determined by ^{1}H NMR (400 MHz) using $MeNO_2$ as the internal standard. [c]The complex of $Pd(OAc)_2$ with 1,2-bis(phenylmethanesulfinyl)ethane (white catalyst). [d]DMSO (1 equiv) was added as an additive. [e](Salen)CrCl (1 equiv) was added as an additive. [f]10 mol % $Pd(OAc)_2$ was used. [g]Isolated yield.

interest in cross-coupling reactions with carbene precursors,[18] we envisioned that the π-allylpalladium(II) intermediate generated through selective allenic C−H bond cleavage may also participate in coupling with α-diazo esters via carbene migratory insertion,[19] affording [3]dendralene derivatives. Herein, we report a synthesis of [3]dendralenes based on such a strategy (Scheme 1e).

The study began with the $PdCl_2$-catalyzed reaction of the easily accessible ethyl 5-methylhexa-3,4-dienoate **1a** with benzyl 2-diazopropanoate **2a** using BQ (p-benzoquinone) as the oxidant in THF at 80 °C (Table 1). Upon reaction for 10 h, the desired [3]dendralene **3aa** could be obtained in 36% yield, along with the formation of dimer **3′** in 5% yield (entry 1). Next, the $Pd(OAc)_2$/bis-sulfoxide complex, which was effective for allylic C−H bond activation,[15,16] was examined as the catalyst. However, the reaction could not be improved (entry 2). We observed that $Pd(OAc)_2$ could afford a slightly improved yield (entry 3), and thus, we focused on this palladium catalyst for further optimization. Some additives, such as DMSO[15a] and (salen)CrCl,[19] have been demonstrated to promote allylic C−H activation. However, these additives were found to not be effective in our reaction (entries 4 and 5). Then, the loading of BQ was examined. We found that 1.1 equiv of BQ was suitable for the reaction (entries 6−8). We also examined other solvents such as dioxane and DME (1,2-dimethoxyethane), but the yield of **3aa** was not improved (entries 9 and 10). The yield of **3aa** could be slightly increased by increasing the loading of $Pd(OAc)_2$ from 5 to 10 mol % (entry 11). When the temperature was elevated to 90 °C, a 59% yield of **3aa** was produced (entry 12). When 2,6-DMBQ (2,6-dimethylbenzoquinone) was used as the oxidant instead of BQ, the product could be obtained in 73% isolated yield.

With the optimized reaction conditions in hand, we proceeded to explore the scope of various substituted allenes **1** with α-diazo esters **2** (Scheme 2). With respect to α-diazo esters, when benzyl 2-diazopropanoate **2a** was applied to the reaction on a 0.3 mmol scale, it afforded **3aa** in 76% yield. Both electron-donating groups, such as p-Ph and p-OMe, and electron-withdrawing groups, such as p-Cl and p-CF_3, could give the corresponding products in good yields (**3ab**−**3ae**). The α-diazo esters bearing the groups of benzhydryl, naphthalen-2-ylmethyl, and furan-2-ylmethyl afforded the corresponding [3]dendralene products **3af**, **3ag**, and **3ah** in good yields. In addition, the reaction with the 2-diazopropanoates bearing adamantyl and 2-methoxyethyl groups also afforded the corresponding products (**3ak**, **3al**).

Subsequently, the scope of allenes for this coupling reaction was investigated. In addition to the two methyl substituents on the allene moiety, cyclopentylidene (**1b**), cyclohexylidene (**1c**), cycloheptylidene (**1d**), and tetrahydro-4*H*-pyran-4-ylidene (**1e**) allenes also afforded the corresponding [3]-dendralenes (**3ba**−**3ea**) in 60−85% yields. However, when the ester group on allene was changed to phenyl, the yield of product (**3fa**) diminished to 35%. Allene substrates bearing an amide functionality proceeded well and gave the corresponding [3]dendralenes (**3ga**−**3ii**, **3ik**−**3im**) in good yields. Monomethyl-substituted allene **1j** also underwent allenic C−H oxidation and afforded the product **3ja** in 80% yield with an E/Z value of 2:1. However, no product was obtained when monosubstituted allene **1k** was used as a result of a lack of stabilization of the substitutent.[1c,5b] However, when ethyl 2-diazobutanoate (**2n**) was used, **3in** was isolated in only 36% yield, which might be attributed to the steric effect in the β-H elimination process.

To demonstrate the synthetic usefulness of this reaction, a scale-up experiment was conducted. Thus, 3 mmol of ethyl 5-methylhexa-3,4-dienoate **1a** was reacted with **2a** under standard conditions, and the corresponding [3]dendralene product **3aa** was isolated in 79% yield (0.748 g) (eq 1). Considering the potential of regioselective functionalization of dendralenes,[11c] we have also carried out a site-selective epoxidation experiment of product **3aa** by treatment with *m*-

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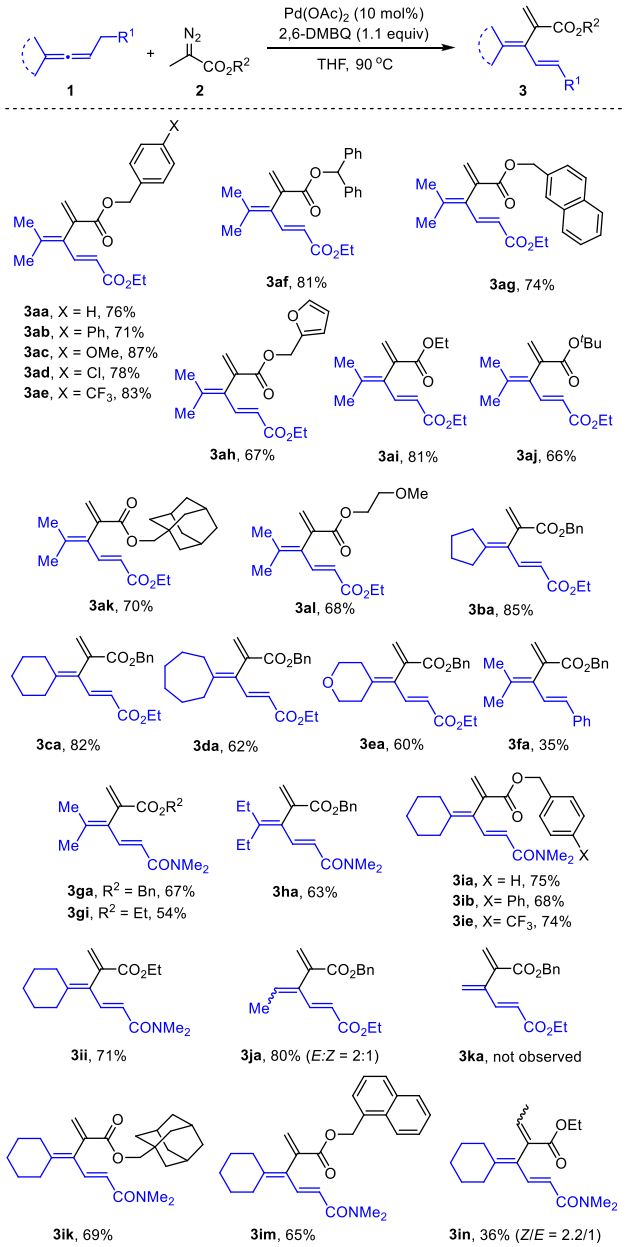
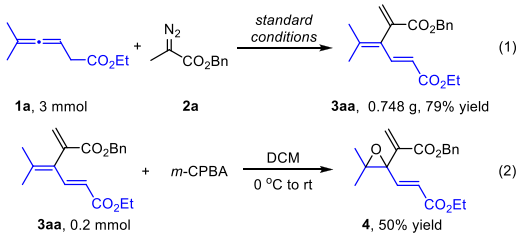
Scheme 2. Substrate Scope for the Reaction of Allenes and α-Diazo Esters[a]

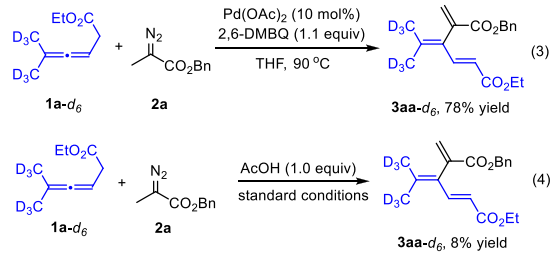


[a]Reaction conditions: allene **1** (0.3 mmol), α-diazo ester **2** (0.6 mmol), $Pd(OAc)_2$ (10 mol %), 2,6-dimethylbenzoquinone (1.1 equiv), THF (3 mL), 90 °C, 10 h. All of the yields refer to the isolated products.



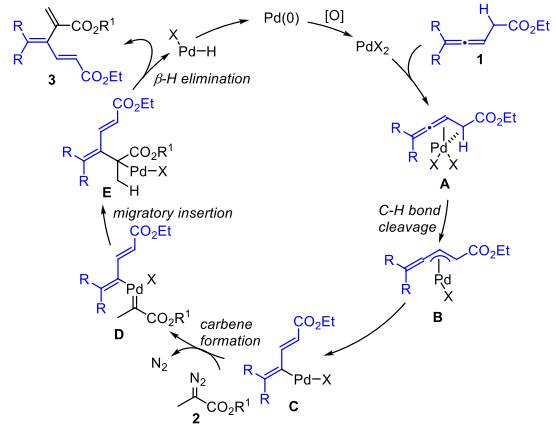
CPBA. The epoxidation product **4** could be obtained in 50% yield (eq 2).[11c]

In order to gain insights into the reaction mechanism, we carried out the reaction with the deuterium-labeled substrate **1a**-d_6. The corresponding [3]dendralene product **3aa**-d_6 was obtained in 78% yield without scrambling of the deuterium content (eq 3). Moreover, when the reaction was carried out in



the presence of 1.0 equiv of acetic acid as additive under the otherwise identical reaction conditions, the yield was decreased to 8% (eq 4). Since there is no deuterium loss in the CD_3 group in this reaction, it rules out the pathway involving allenic C−H bond cleavage in the methyl group to form a vinyl-Pd carbene followed by migratory insertion, β-H elimination, and rearrangement to give the product **3aa** (see the Supporting Information for the details). A possible reaction mechanism was proposed for the palladium-catalyzed oxidative coupling of the allenic C−H bond with α-diazo esters (Scheme 3).

Scheme 3. Proposed Reaction Mechanism



$Pd(OAc)_2$ reacts with allene **1** to give intermediate **A**. Next, selective allenic C−H bond cleavage generates the π-allylpalladium(II) intermediate **B**, which may transfer to the vinylpalladium intermediate **C**. Then, α-diazo ester **2** reacts with **C** to give palladium carbene intermediate **D**. Subsequently, migratory insertion occurs to form intermediate **E**, which undergoes β-H elimination to release [3]dendralene product **3**. Palladium(II) species is regenerated through oxidation by 2,6-DMBQ to the next catalytic cycle.

In conclusion, we have developed an allenic C−H oxidation with α-diazo esters to afford [3]dendralenes. Simple allenoate-based allenes are used as the substrates, without preinstalled directing groups or leaving groups. The reaction proceeds under mild conditions and tolerates various functional groups, giving highly stereoselective products. The reaction could be carried out without the use of the external base, and it can be run in gram scale. The reaction may find applications in the synthesis of this unique type of unsaturated compounds.

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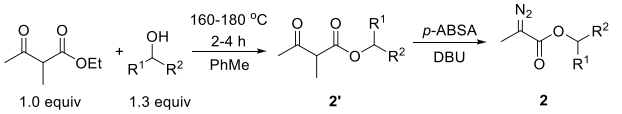
EXPERIMENTAL SECTION

General Methods. All of the palladium-catalyzed reactions were performed under a nitrogen atmosphere in a flame-dried reaction tube. An oil bath was used for heating reactions. All of the solvents were distilled under a nitrogen atmosphere prior to use. Toluene, dioxane, and THF were dried over Na with benzophenone-ketyl intermediate as indicator. MeCN and MeOH were dried over CaH_2. For chromatography, 200−300 mesh silica gel (Qingdao, China) was employed. ^{1}H NMR spectra were recorded on a Bruker ARX 400 instrument (400 MHz); ^{13}C NMR spectra were recorded on a Bruker ARX 400 instrument (100 MHz). The data for NMR spectra were reported as follows: chemical shifts (δ) were reported in ppm using tetramethylsilane as internal standard when using $CDCl_3$ as solvent, and coupling constants (J) were in Hertz (Hz). IR spectra were recorded on a Nicolet 5MX-S infrared spectrometer and were reported in terms of frequency of absorption (cm^{-1}). High-resolution mass spectra (HRMS) were obtained on a Bruker APEX IV FTMS instrument and a Bruker Solarix XR FTMS instrument by ESI. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. PE, petroleum ether; EA, ethyl acetate.

Preparation of the Allenes. Allenes **1a**−**1e**, **1f**, **1j**, and **1k** were synthesized according to the literature.[17b,20] General procedure for the preparation of allenes **1g**−**1i**:[21]



Under a N_2 atmosphere, a solution of substituted propargyl alcohol (8 mmol, 1 equiv) and 1,1-dimethoxy-*N*,*N*-dimethylethan-1-amine (40 mmol, 5 equiv) was dissolved in 20 mL of dry toluene, and the solution was stirred at 110 °C in an oil bath for 5 h. After the reaction, the solution was cooled to room temperature and ethyl acetate (10 mL) was added. Then, 20 mL of 4 M HCl solution was added. The resulting mixture was extracted with ethyl acetate (2 × 20 mL). The combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography with petroleum ether−ethyl acetate (PE:EA = 2:1) as the eluent to afford the products.

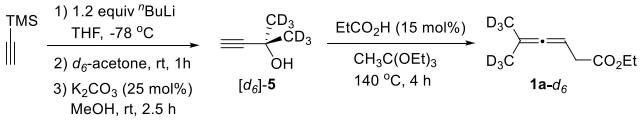
*Ethyl 4-(Tetrahydro-4H-pyran-4-ylidene)but-3-enoate (**1e**).* Yield: 227 mg (12%, 10 mmol scale); colorless oil; R_f = 0.3 (PE:EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.24−5.18 (m, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.73 (t, J = 5.4 Hz, 4H), 3.02 (d, J = 7.1 Hz, 2H), 2.26−2.22 (m, 4H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 199.9, 171.7, 99.0, 83.4, 68.5, 60.7, 35.4, 31.3, 14.2; HRMS (ESI, m/z): calcd for $C_{11}H_{17}O_3$ $[M + H]^+$ 197.1178, found 197.1172; IR (film): 1100, 1166, 1236, 1739, 2847, 2954, 2973 cm^{-1}.

*N,N,5-Trimethylhexa-3,4-dienamide (**1g**).* Yield: 129 mg (11%, 8 mmol scale); colorless oil; R_f = 0.3 (PE:EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.16−5.09 (m, 1H), 3.04 (d, J = 7.0 Hz, 2H), 3.03 (s, 3H), 2.95 (s, 3H), 1.69 (s, 3H), 1.68 (s, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 202.6, 171.2, 96.2, 83.0, 37.4, 35.4, 35.3, 20.4; HRMS (ESI, m/z): calcd for $C_9H_{16}NO$ $[M + H]^+$ 154.1232, found 154.1226; IR (film): 1132, 1393, 1450, 1496, 1652, 2921 cm^{-1}.

*5-Ethyl-N,N-dimethylhepta-3,4-dienamide (**1h**).* Yield 111 mg (9%, 7 mmol scale); colorless oil; R_f = 0.5 (PE:EA = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37−5.30 (m, 1H), 3.07 (d, J = 6.8 Hz, 2H), 3.03 (s, 3H), 2.95 (s, 3H), 1.97 (qd, J = 7.4, 3.1 Hz, 4H), 1.00 (t, J = 7.4 Hz, 6H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 201.1, 171.4, 109.3, 86.8, 37.6, 35.4, 35.3, 25.6, 12.4; HRMS (ESI, m/z): calcd for $C_{11}H_{20}NO$ $[M + H]^+$ 182.1545, found 182.1539; IR (film): 1134, 1395, 1461, 1655, 2931, 2972 cm^{-1}.

*4-Cyclohexylidene-N,N-dimethylbut-3-enamide (**1i**).* Yield 241 mg (16%, 8 mmol scale); colorless oil; R_f = 0.4 (PE:EA = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.15−5.10 (m, 1H), 3.05 (d, J = 6.7 Hz, 2H), 3.03 (s, 3H), 2.95 (s, 3H), 2.12−2.09 (m, 4H), 1.63−1.53 (m, 6H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 199.2, 171.3, 103.6, 82.9, 37.5, 35.7, 35.5, 31.4, 27.4, 26.1; HRMS (ESI, m/z): calcd for $C_{12}H_{20}NO$ $[M + H]^+$ 194.1545, found 194.1539; IR (film): 1132, 1397, 1448, 1652, 2852, 2930 cm^{-1}.

*Synthesis of Allene **1a**-d_6.*

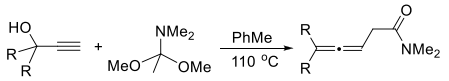


[d_6]-**5** was synthesized according to the procedure described in the literature[22] starting with 20 mmol of ethynyltrimethylsilane, which was used for the next step without further purification. [d_6]-**5** was reacted with triethyl orthoacetate under the catalysis of 15 mol % $EtCO_2H$ and heated at 140 °C with an oil bath for 4 h while stirring.[17b] **1a**-d_6 was afforded in 31% yield in three steps.

*Ethyl 5-(Methyl-d_3)hexa-3,4-dienoate-6,6,6-d_3 (**1a**-d_6).* Yield: 986 mg (31%) in three steps; colorless oil; R_f = 0.5 (PE:EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.08 (t, J = 7.1 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 2.97 (d, J = 7.1 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 203.0, 172.0, 96.0, 81.9, 60.6, 35.3, 19.5, 14.2; HRMS (ESI, m/z): calcd for $C_9H_9D_6O_2$ $[M + H]^+$ 161.1449, found 161.1442; IR (film): 1163, 1258, 1321, 1460, 1735, 2930 cm^{-1}.

Preparation of the α-Diazo Esters. α-Diazo esters **2a**, **2j**, **2l**, and **2n** were prepared following the procedure described in the literature from corresponding esters.[23a] α-Diazo esters **2f**, **2h**, and **2k** were prepared following the procedure in the literature starting from the reaction of 2,2,5,6-tetramethyl-4*H*-1,3-dioxin-4-one with the corresponding alcohol, while **2i** was prepared by reaction of ethyl 2-methyl-3-oxobutanoate with *p*-ABSA in CH_3CN.[23b]

*Procedure for the Preparation of α-Diazo Esters **2b**, **2c**, **2d**, **2e**, **2g**, and **2m**.*



Ethyl 2-methyl-3-oxobutanoate (10 mmol, 1.0 equiv), alcohol (13 mmol, 1.3 equiv), and toluene (3 mL) were added to a 25 mL round-bottom flask. Distillation devices were set up, and the reaction mixture was heated at 160−180 °C with an oil bath. The azeotrope of toluene and ethanol was distilled. The reaction mixture was allowed to cool to room temperature after 2−4 h when no azeotrope was distilled off. The mixture was filtered through flash column chromatography on silica gel (1:1 EtOAc/petroleum ether). Then, the solvent was evaporated *in vacuo* and the crude product was purified by SiO_2 gel column chromatography (1:10 EtOAc:petroleum ether) which afforded **2′** as liquid oil.

Under a N_2 atmosphere, DBU (1.5 equiv) was slowly added to a mixture of **2′** (1.0 equiv), *p*-ABSA (1.5 equiv), and acetonitrile (0.3 M) at 0 °C in a 50 mL Schlenk flask. The reaction mixture was allowed to warm to room temperature and was stirred overnight. Twenty mL of saturated NH_4Cl solution was added to quench the reaction. The crude reaction mixture was extracted with dichloromethane (3 × 20 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting residue was purified by SiO_2 gel column chromatography (1:20 EtOAc:petroleum ether), which afforded α-diazo esters **2**.

*[1,1′-Biphenyl]-4-ylmethyl 2-Methyl-3-oxobutanoate (**2b′**).* Yield: 707 mg (25%); colorless oil; R_f = 0.5 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61−7.58 (m, 4H), 7.47−7.41 (m, 4H), 7.38 (tt, J = 7.4, 1.2 Hz, 1H), 5.22 (s, 2H), 3.57 (q, J = 7.2 Hz, 1H), 2.22 (s, 3H), 1.38 (d, J = 7.2 Hz, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 203.5, 170.4, 141.5, 140.6, 134.3, 128.8, 128.8, 127.5, 127.4, 127.1, 66.9, 53.7, 28.5, 12.8; HRMS (ESI, m/z): calcd for $C_{18}H_{19}O_3$ $[M + H]^+$ 283.1334, found 283.1327; IR (film): 1155, 1195, 1235, 1488, 1719, 1746 cm^{-1}.

*[1,1′-Biphenyl]-4-ylmethyl 2-Diazopropanoate (**2b**).* Yield: 601 mg (44%); yellow solid; R_f = 0.8 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59−7.57 (m, 4H), 7.45−7.41 (m, 4H), 7.34 (tt, J = 7.4, 1.2 Hz, 1H), 5.24 (s, 2H), 1.98 (s, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 167.8, 141.2, 140.7, 135.2, 128.8, 128.6, 127.5, 127.3, 127.2,

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66.2, 8.5; HRMS (ESI, m/z): calcd for $C_{16}H_{14}N_2NaO_2$ $[M + Na]^+$ 289.0953, found 289.0946; IR (film): 1135, 1308, 1319, 1487, 1695, 2084 cm^{-1}.

*4-Methoxybenzyl 2-Diazopropanoate (**2c**).* Yield: 350 mg (35%); yellow oil; R_f = 0.5 (PE:EA = 10:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.32−7.27 (m, 2H), 6.90−6.86 (m, 2H), 5.14 (s, 2H), 3.80 (s, 3H), 1.96 (s, 3H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.6, 130.0, 128.3, 113.9, 66.2, 55.3, 8.5; HRMS (ESI, m/z): calcd for $C_{11}H_{12}N_2NaO_3$ $[M + Na]^+$ 243.0746, found 243.0734; IR (film): 1128, 1250, 1305, 1516, 1694, 2085 cm^{-1}. **2c′** was obtained in 46% yield as a colorless oil. The data of **2c′** were in accordance with the literature.[24]

*4-Chlorobenzyl 2-Methyl-3-oxobutanoate (**2d′**).* Yield: 2.144 g (36%, 25 mmol scale); colorless oil; R_f = 0.4 (PE:EA = 10:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.35−7.32 (m, 2H), 7.29−7.27 (m, 2H), 5.14 (d, J = 2.4 Hz, 2H), 3.55 (q, J = 7.2 Hz, 1H), 2.20 (s, 3H), 1.36 (d, J = 7.2 Hz, 3H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 203.4, 170.2, 134.4, 133.9, 129.7, 128.9, 66.2, 53.6, 28.5, 12.8; HRMS (ESI, m/z): calcd for $C_{12}H_{14}ClO_3$ $[M + H]^+$ 241.0631, found 241.0626; IR (film): 1094, 1153, 1195, 1240, 1717, 1744 cm^{-1}.

*4-Chlorobenzyl 2-Diazopropanoate (**2d**).* Yield: 786 mg (39%); yellow oil; R_f = 0.5 (PE:EA = 10:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34−7.27 (m, 4H), 5.16 (s, 2H), 1.97 (s, 3H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 134.7, 134.1, 129.5, 128.8, 65.6, 8.5; HRMS (ESI, m/z): calcd for $C_{10}H_9ClN_2NaO_2$ $[M + Na]^+$ 247.0250, found 247.0251; IR (film): 1139, 1319, 1383, 1494, 1696, 2083 cm^{-1}.

*4-(Trifluoromethyl)benzyl 2-Methyl-3-oxobutanoate (**2e′**).* Yield: 2.826 g (69%, 15 mmol scale); colorless oil; R_f = 0.5 (PE:EA = 5:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 8.1 Hz, 2H), 5.23 (d, J = 3.1 Hz, 2H), 3.59 (q, J = 7.2 Hz, 1H), 2.22 (s, 3H), 1.39 (d, J = 7.2 Hz, 3H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 203.4, 170.2, 139.3, 130.6 (q, J = 32.5 Hz), 128.2, 125.6 (q, J = 3.8 Hz), 124.0 (q, J = 271.9 Hz), 66.1, 53.5, 28.5, 12.8; HRMS (ESI, m/z): calcd for $C_{13}H_{14}F_3O_3$ $[M + H]^+$ 275.0895, found 275.0888; IR (film): 1067, 1126, 1165, 1326, 1718, 1747 cm^{-1}.

*4-(Trifluoromethyl)benzyl 2-Diazopropanoate (**2e**).* Yield: 500 mg (19%); yellow oil; R_f = 0.5 (PE:EA = 10:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.64−7.60 (m, 2H), 7.48−7.44 (m, 2H), 5.26 (s, 2H), 1.99 (s, 3H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.7, 140.2, 130.4 (q, J = 32.4 Hz), 128.0, 125.6 (q, J = 3.8 Hz), 124.0 (q, J = 272.3 Hz), 65.4, 8.4; HRMS (ESI, m/z): calcd for $C_{11}H_{10}F_3N_2O_2$ $[M + H]^+$ 259.0694, found 259.0685; IR (film): 1068, 1132, 1169, 1329, 1697, 2088 cm^{-1}.

*Naphthalen-2-ylmethyl 2-Diazopropanoate (**2g**).* **2g′** was prepared according to the literature procedure.[25] **2g** was isolated as yellow oil in 40% yield (592 mg). R_f = 0.5 (PE:EA = 10:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.85−7.82 (m, 4H), 7.50−7.45 (m, 3H), 5.37 (s, 2H), 1.99 (s, 3H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.6, 133.6, 133.2, 133.1, 128.4, 128.0, 127.7, 127.3, 126.3, 126.3, 125.8, 66.6, 8.5; HRMS (ESI, m/z): calcd for $C_{14}H_{12}N_2NaO_2$ $[M + Na]^+$ 263.0796, found 263.0791; IR (film): 1125, 1308, 1351, 1691, 2085 cm^{-1}.

*Furan-2-ylmethyl 2-Diazopropanoate (**2h**).* Yield: 246 mg (17%); yellow oil; R_f = 0.7 (PE:EA = 5:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.43−7.41 (m, 1H), 6.42−6.41 (m, 1H), 6.37−6.35 (m, 1H), 5.15 (s, 2H), 1.96 (s, 3H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 149.7, 143.2, 110.7, 110.6, 58.2, 8.5; HRMS (ESI, m/z): calcd for $C_8H_8N_2NaO_3$ $[M + Na]^+$ 203.0433, found 203.0421; IR (film): 1126, 1154, 1324, 1375, 1697, 2088 cm^{-1}.

*((3r,5r,7r)-Adamantan-1-yl)methyl 2-Diazopropanoate (**2k**).* Yield: 932 mg (47%); yellow solid; R_f = 0.8 (PE:EA = 5:1); ^1H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 2H), 1.99−1.97 (m, 6H), 1.74−1.63 (m, 6H), 1.53−1.52 (m, 6H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.4, 168.1, 74.2, 39.2, 37.0, 33.4, 28.0, 8.4; HRMS (ESI, m/z): calcd for $C_{14}H_{20}N_2NaO_2$ $[M + Na]^+$ 271.1422, found 271.1411; IR (film): 1138, 1306, 1329, 1697, 2081, 2851, 2907 cm^{-1}.

*Naphthalen-1-ylmethyl 2-Diazopropanoate (**2m**).* **2m′** was prepared according to the literature procedure.[25] **2m** was isolated as yellow oil in 43% yield (730 mg). R_f = 0.7 (PE:EA = 5:1); ^1H NMR (400 MHz, $CDCl_3$) δ 8.03−8.01 (m, 1H), 7.88−7.82 (m, 2H), 7.57−7.49 (m, 3H), 7.46−7.42 (m, 1H), 5.66 (s, 2H), 1.95 (s, 3H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 133.7, 131.7, 131.6, 129.3, 128.7, 127.3, 126.6, 126.0, 125.3, 123.6, 64.8, 8.5; HRMS (ESI, m/z): calcd for $C_{14}H_{12}N_2NaO_2$ $[M + Na]^+$ 263.0796, found 263.0792; IR (film): 1132, 1320, 1351, 1376, 1693, 2085 cm^{-1}.

General Procedure for the Palladium-Catalyzed Oxidative Coupling of the Allenic C−H Bond with α-Diazo Esters. $Pd(OAc)_2$ (6.7 mg, 0.03 mmol) and 2,6-dimethylbenzoquinone (44.9 mg, 0.33 mmol, 1.1 equiv) were weighed in a 10 mL oven-dried reaction flask. The flask was degassed in a vacuum and backfilled with N_2 three times, followed by the addition of dry degassed THF (3 mL). Then, allene **1** (0.3 mmol, 1.0 equiv) and α-diazo ester **2** (2.0 equiv) were added using a microsyringe successively. The reaction mixture was stirred at 90 °C with an oil bath under N_2 for 10 h. After the reaction, the mixture was allowed to warm to room temperature and filtered through flash column chromatography on silica gel (EA:PE = 1:1). Then, the solvent was evaporated *in vacuo* and the crude product was purified by silica gel column chromatography (EA-PE), which afforded product **3** as a liquid oil.

Procedure for the Scale-up Experiment. $Pd(OAc)_2$ (67.4 mg, 0.3 mmol) and 2,6-dimethylbenzoquinone (449.3 mg, 3.3 mmol, 1.1 equiv) were weighed in a 100 mL oven-dried reaction flask. The flask was degassed in a vacuum and backfilled with N_2 three times, followed by the addition of dry degassed THF (20 mL). Then, under N_2, a solution of allene **1a** (3.0 mmol, 1.0 equiv) and α-diazo ester **2a** (2.0 equiv) in 10 mL of THF was added using a syringe. The reaction mixture was stirred at 90 °C with an oil bath under N_2 for 10 h. After the reaction, the mixture was allowed to warm to room temperature and was filtered through flash column chromatography on silica gel (EA:PE = 1:1). Then, the solvent was evaporated *in vacuo* and the crude product was purified by silica gel column chromatography (EA:PE = 1:20), which afforded product **3aa** (0.748 g, 79% yield) as a colorless oil.

*6-Benzyl 1-Ethyl (E)-5-methylene-4-(propan-2-ylidene)hex-2-enedioate (**3aa**).* Yield: 71.7 mg (76%); colorless oil; R_f = 0.2 (PE:EA = 20:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 15.5 Hz, 1H), 7.35−7.30 (m, 5H), 6.59 (d, J = 1.6 Hz, 1H), 5.59 (d, J = 15.6 Hz, 1H), 5.56 (d, J = 1.6 Hz, 1H), 5.18 (s, 2H), 4.18 (q, J = 7.1 Hz, 2H), 2.03 (s, 3H), 1.76 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.6, 165.9, 144.5, 141.7, 138.3, 136.0, 130.5, 129.5, 128.5, 128.1, 127.8, 118.0, 66.6, 60.2, 23.6, 20.5, 14.3; HRMS (ESI, m/z): calcd for $C_{19}H_{23}O_4$ $[M + H]^+$315.1596, found 315.1591; IR (film): 1186, 1256, 1293, 1370, 1615, 1718 cm^{-1}.

*6-([1,1′-Biphenyl]-4-ylmethyl) 1-Ethyl (E)-5-methylene-4-(propan-2-ylidene)hex-2-enedioate (**3ab**).* Yield: 82.8 mg (71%); colorless oil; R_f = 0.2 (PE:EA = 20:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 15.5 Hz, 1H), 7.60−7.56 (m, 4H), 7.44−7.36 (m, 5H), 6.61 (d, J = 1.6 Hz, 1H), 5.61 (d, J = 15.5 Hz, 1H), 5.57 (d, J = 1.6 Hz, 1H), 5.22 (s, 2H), 4.17 (q, J = 7.1 Hz, 2H), 2.04 (s, 3H), 1.78 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.6, 166.0, 144.5, 141.7, 141.1, 140.7, 138.3, 135.0, 130.6, 129.6, 128.8, 128.4, 127.5, 127.3, 127.1, 118.1, 66.4, 60.2, 23.7, 20.5, 14.3; HRMS (ESI, m/z): calcd for $C_{25}H_{27}O_4$ $[M + H]^+$ 391.1909, found 391.1904; IR (film): 1253, 1292, 1371, 1488, 1615, 1713 cm^{-1}.

*1-Ethyl 6-(4-Methoxybenzyl) (E)-5-Methylene-4-(propan-2-ylidene)hex-2-enedioate (**3ac**).* Yield: 89.7 mg (87%); colorless oil; R_f = 0.2 (PE:EA = 20:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 15.5 Hz, 1H), 7.31−7.27 (m, 2H), 6.88−6.85 (m, 2H), 6.56 (d, J = 1.7 Hz, 1H), 5.57 (d, J = 15.5 Hz, 1H), 5.53 (d, J = 1.8 Hz, 1H), 5.11 (s, 2H), 4.18 (q, J = 7.1 Hz, 2H), 3.79 (s, 3H), 2.02 (s, 3H), 1.75 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.6, 166.0, 159.5, 144.5, 141.7, 138.4, 130.4, 129.8, 129.6, 128.1, 118.0, 113.9, 66.5, 60.2, 55.3, 23.6, 20.5, 14.3; HRMS (ESI, m/z): calcd for $C_{20}H_{25}O_5$ $[M + H]^+$ 345.1702, found 345.1696; IR (film): 1175, 1248, 1294, 1717, 2848, 2921 cm^{-1}.

*6-(4-Chlorobenzyl) 1-Ethyl (E)-5-methylene-4-(propan-2-ylidene)hex-2-enedioate (**3ad**).* Yield: 89.7 mg (87%); colorless oil; R_f = 0.2 (PE:EA = 20:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 15.5 Hz, 1H), 7.34−7.28 (m, 4H), 6.60 (d, J = 1.4 Hz, 1H), 5.59−5.55 (m, 2H), 5.16 (s, 2H), 4.20 (q, J = 7.1 Hz, 2H), 2.05 (s, 3H),

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1.78 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 167.5, 165.8, 144.5, 141.6, 138.1, 134.4, 134.0, 130.7, 129.4, 129.4, 128.7, 118.1, 65.8, 60.3, 23.6, 20.5, 14.3; HRMS (ESI, m/z): calcd for $C_{19}H_{22}ClO_4$ $[M + H]^+$ 349.1207, found 349.1203; IR (film): 1186, 1249, 1293, 1369, 1494, 1615, 1715 cm^{-1}.

*1-Ethyl 6-(4-(Trifluoromethyl)benzyl) (E)-5-Methylene-4-(propan-2-ylidene)hex-2-enedioate (**3ae**).* Yield: 94.9 mg (83%); colorless oil; R_f = 0.2 (PE:EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 15.5 Hz, 1H), 7.63−7.61 (m, 2H), 7.45−7.43 (m, 2H), 6.64 (d, J = 1.5 Hz, 1H), 5.61 (d, J = 1.5 Hz, 1H), 5.59 (d, J = 15.5 Hz, 1H), 5.25 (s, 2H), 4.20 (q, J = 7.1 Hz, 2H), 2.06 (s, 3H), 1.80 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 167.5, 165.7, 144.6, 141.6, 139.9, 138.0, 131.0, 130.3 (q, J = 32.5 Hz), 129.4, 127.8, 125.5 (q, J = 3.8 Hz), 124.0 (q, J = 272.7 Hz), 118.1, 65.7, 60.3, 23.6, 20.5, 14.3; HRMS (ESI, m/z): calcd for $C_{20}H_{22}F_3O_4$ $[M + H]^+$ 383.1470, found 383.1468; IR (film): 1128, 1165, 1293, 1326, 1617, 1717 cm^{-1}.

*6-Benzhydryl 1-Ethyl (E)-5-methylene-4-(propan-2-ylidene)hex-2-enedioate (**3af**).* Yield: 95.2 mg (81%); colorless oil; R_f = 0.2 (PE:EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 15.5 Hz, 1H), 7.31−7.27 (m, 10H), 6.88 (s, 1H), 6.64 (d, J = 1.5 Hz, 1H), 5.58 (d, J = 15.5 Hz, 1H), 5.57 (d, J = 1.5 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 2.05 (s, 3H), 1.72 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 167.6, 165.1, 144.4, 141.6, 140.2, 138.5, 130.5, 129.6, 128.5, 127.9, 126.9, 118.3, 77.4, 60.2, 23.6, 20.5, 14.4; HRMS (ESI, m/z): calcd for $C_{25}H_{27}O_4$ $[M + H]^+$ 391.1909, found 391.1905; IR (film): 1185, 1246, 1293, 1615, 1712, 2983 cm^{-1}.

*1-Ethyl 6-(Naphthalen-2-ylmethyl) (E)-5-Methylene-4-(propan-2-ylidene)hex-2-enedioate (**3ag**).* Yield: 80.4 mg (74%); colorless oil; R_f = 0.2 (PE:EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 15.5 Hz, 1H), 7.84−7.77 (m, 4H), 7.49−7.47 (m, 2H), 7.41 (dd, J = 8.5, 1.6 Hz, 1H), 6.62 (d, J = 1.7 Hz, 1H), 5.61 (d, J = 15.5 Hz, 1H), 5.57 (d, J = 1.7 Hz, 1H), 5.34 (s, 2H), 4.16 (q, J = 7.1 Hz, 2H), 2.04 (s, 3H), 1.78 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 167.6, 166.0, 144.5, 141.7, 138.3, 133.4, 133.2, 133.1, 130.6, 129.6, 128.3, 128.0, 127.7, 127.0, 126.3, 126.2, 125.6, 118.1, 66.8, 60.2, 23.7, 20.5, 14.3; HRMS (ESI, m/z): calcd for $C_{23}H_{25}O_4$ $[M + H]^+$ 365.1753, found 365.1748; IR (film): 1134, 1185, 1248, 1293, 1615, 1713 cm^{-1}.

*1-Ethyl 6-(Furan-2-ylmethyl) (E)-5-Methylene-4-(propan-2-ylidene)hex-2-enedioate (**3ah**).* Yield: 61.0 mg (67%); colorless oil; R_f = 0.2 (PE:EA = 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 15.5 Hz, 1H), 7.41−7.40 (m, 1H), 6.57 (d, J = 1.6 Hz, 1H), 6.40−6.39 (m, 1H), 6.36−6.34 (m, 1H), 5.56 (d, J = 15.4 Hz, 1H), 5.56 (d, J = 1.7 Hz, 1H), 5.13 (s, 2H), 4.18 (q, J = 7.1 Hz, 2H), 2.02 (s, 3H), 1.74 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 167.6, 165.7, 149.4, 144.6, 143.2, 141.6, 138.0, 130.7, 129.4, 117.9, 110.6, 110.5, 60.2, 58.6, 23.5, 20.5, 14.3; HRMS (ESI, m/z): calcd for $C_{17}H_{21}O_5$ $[M + H]^+$ 305.1389, found 305.1386; IR (film): 1186, 1258, 1294, 1369, 1616, 1720 cm^{-1}.

*Diethyl (E)-5-Methylene-4-(propan-2-ylidene)hex-2-enedioate (**3ai**).* Yield: 61.5 mg (81%); pale yellow oil; R_f = 0.1 (PE:EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 15.5 Hz, 1H), 6.55 (d, J = 1.8 Hz, 1H), 5.59 (d, J = 15.5 Hz, 1H), 5.53 (d, J = 1.8 Hz, 1H), 4.22−4.16 (m, 4H), 2.04 (s, 3H), 1.79 (s, 3H), 1.30−1.24 (m, 6H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 167.7, 166.1, 144.3, 141.8, 138.6, 129.9, 129.6, 117.9, 61.0, 60.2, 23.6, 20.5, 14.3, 14.2; HRMS (ESI, m/z): calcd for $C_{14}H_{21}O_4$ $[M + H]^+$ 253.1440, found 253.1427; IR (film): 1189, 1293, 1368, 1615, 1717, 2916, 2979 cm^{-1}.

*6-(tert-Butyl) 1-Ethyl (E)-5-methylene-4-(propan-2-ylidene)hex-2-enedioate (**3aj**).* Yield: 55.8 mg (66%); pale yellow oil; R_f = 0.3 (PE:EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 15.4 Hz, 1H), 6.43 (d, J = 1.9 Hz, 1H), 5.60 (d, J = 15.4 Hz, 1H), 5.44 (d, J = 1.9 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 2.02 (s, 3H), 1.79 (s, 3H), 1.45 (s, 9H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 167.8, 165.3, 143.8, 141.9, 140.0, 130.0, 128.7, 117.7, 80.9, 60.2, 28.0, 23.6, 20.4, 14.3; HRMS (ESI, m/z): calcd for $C_{16}H_{25}O_4$ $[M + H]^+$ 281.1753, found 281.1750; IR (film): 1264, 1293, 1369, 1616, 1714, 2985 cm^{-1}

*6-(((3r,5r,7r)-Adamantan-1-yl)methyl) 1-Ethyl (E)-5-methylene-4-(propan-2-ylidene)hex-2-enedioate (**3ak**).* Yield: 78.4 mg (70%); pale yellow oil; R_f = 0.2 (PE:EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 15.5 Hz, 1H), 6.56 (d, J = 1.8 Hz, 1H), 5.61 (d, J = 15.5 Hz, 1H), 5.51 (d, J = 1.8 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.72 (s, 2H), 2.04 (s, 3H), 1.97−1.95 (m, 3H), 1.80 (s, 3H), 1.73−1.63 (m, 6H), 1.49 (d, J = 2.2 Hz, 6H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 167.7, 166.3, 144.0, 141.8, 138.7, 129.8, 129.8, 118.1, 74.4, 60.2, 39.3, 37.0, 33.5, 28.0, 23.7, 20.4, 14.3; HRMS (ESI, m/z): calcd for $C_{23}H_{33}O_4$ $[M + H]^+$ 373.2379, found 373.2376; IR (film): 1250, 1291, 1451, 1615, 1717, 2849, 2903 cm^{-1}.

*1-Ethyl 6-(2-Methoxyethyl) (E)-5-Methylene-4-(propan-2-ylidene)hex-2-enedioate (**3al**).* Yield: 57.7 mg (68%); colorless oil; R_f = 0.1 (PE:EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 15.5 Hz, 1H), 6.59 (d, J = 1.6 Hz, 1H), 5.59 (d, J = 15.5 Hz, 1H), 5.57 (d, J = 1.6 Hz, 1H), 4.31−4.28 (m, 2H), 4.18 (q, J = 7.1 Hz, 2H), 3.61−3.59 (m, 2H), 3.37 (s, 3H), 2.04 (s, 3H), 1.79 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 167.7, 166.0, 144.5, 141.7, 138.2, 130.5, 129.5, 117.9, 70.4, 64.1, 60.2, 59.0, 23.6, 20.5, 14.3; HRMS (ESI, m/z): calcd for $C_{15}H_{23}O_5$ $[M + H]^+$ 283.1545, found 283.1541; IR (film): 1187, 1252, 1294, 1372, 1614, 1721 cm^{-1}.

*6-Benzyl 1-Ethyl (E)-4-cyclopentylidene-5-methylenehex-2-enedioate (**3ba**).* Yield: 86.6 mg (85%); colorless oil; R_f = 0.4 (PE:EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 15.6 Hz, 1H), 7.34−7.31 (m, 5H), 6.54 (d, J = 1.5 Hz, 1H), 5.60 (d, J = 1.5 Hz, 1H), 5.56 (d, J = 15.6 Hz, 1H), 5.19 (s, 2H), 4.18 (q, J = 7.1 Hz, 2H), 2.62 (t, J = 7.1 Hz, 2H), 2.22 (t, J = 7.1 Hz, 2H), 1.77−1.73 (m, 2H), 1.67−1.63 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 167.6, 165.8, 157.8, 143.0, 138.4, 136.0, 130.2, 128.5, 128.1, 127.9, 126.5, 116.7, 66.6, 60.2, 33.5, 31.2, 26.3, 26.0, 14.4; HRMS (ESI, m/z): calcd for $C_{21}H_{25}O_4$ $[M + H]^+$ 341.1753, found 341.1748; IR (film): 1173, 1248, 1282, 1614, 1716, 2956 cm^{-1}.

*6-Benzyl 1-Ethyl (E)-4-cyclohexylidene-5-methylenehex-2-enedioate (**3ca**).* Yield: 87.6 mg (82%); colorless oil; R_f = 0.2 (PE:EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 15.5 Hz, 1H), 7.36−7.31 (m, 5H), 6.57 (d, J = 1.7 Hz, 1H), 5.63 (d, J = 15.5 Hz, 1H), 5.54 (d, J = 1.7 Hz, 1H), 5.18 (s, 2H), 4.18 (q, J = 7.1 Hz, 2H), 2.53−2.50 (m, 2H), 2.18−2.15 (m, 2H), 1.65−1.55 (m, 4H), 1.52−1.47 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 167.7, 166.1, 152.5, 141.1, 138.2, 136.0, 130.1, 128.5, 128.1, 127.9, 126.4, 118.5, 66.6, 60.2, 33.9, 30.7, 28.4, 28.1, 26.5, 14.4; HRMS (ESI, m/z): calcd for $C_{22}H_{27}O_4$ $[M + H]^+$ 355.1909, found 355.1901; IR (film): 1163, 1292, 1613, 1712, 2856, 2934 cm^{-1}.

*6-Benzyl 1-Ethyl (E)-4-cycloheptylidene-5-methylenehex-2-enedioate (**3da**).* Yield: 68.3 mg (62%); pale yellow oil; R_f = 0.1 (PE:EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 15.5 Hz, 1H), 7.39−7.34 (m, 5H), 6.60 (d, J = 1.6 Hz, 1H), 5.62 (d, J = 15.5 Hz, 1H), 5.56 (d, J = 1.6 Hz, 1H), 5.20 (s, 2H), 4.21 (q, J = 7.1 Hz, 2H), 2.66−2.63 (m, 2H), 2.31−2.28 (m, 2H), 1.70−1.67 (m, 2H), 1.56−1.51 (m, 4H), 1.47−1.43 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 167.7, 166.1, 153.5, 141.5, 138.3, 135.9, 130.2, 129.3, 128.5, 128.1, 127.9, 118.1, 66.6, 60.2, 34.8, 31.5, 29.1, 28.1, 27.5, 26.9, 14.4; HRMS (ESI, m/z): calcd for $C_{23}H_{29}O_4$ $[M + H]^+$ 369.2066, found 369.2060; IR (film): 1172, 1293, 1455, 1612, 1713, 2856, 2929 cm^{-1}.

*6-Benzyl 1-Ethyl (E)-5-methylene-4-(tetrahydro-4H-pyran-4-ylidene)hex-2-enedioate (**3ea**).* Yield: 64.5 mg (60%); pale yellow oil; R_f = 0.3 (PE:EA = 7:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 15.5 Hz, 1H), 7.35−7.31 (m, 5H), 6.61 (d, J = 1.6 Hz, 1H), 5.69 (d, J = 15.5 Hz, 1H), 5.58 (d, J = 1.6 Hz, 1H), 5.18 (s, 2H), 4.19 (q, J = 7.1 Hz, 2H), 3.74 (t, J = 5.4 Hz, 2H), 3.59 (t, J = 5.4 Hz, 2H), 2.64 (t, J = 5.4 Hz, 2H), 2.28 (t, J = 5.4 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 167.4, 165.7, 146.0, 140.1, 137.6, 135.8, 130.7, 128.6, 128.3, 128.0, 127.9, 119.6, 68.5, 68.4, 66.8, 60.4, 34.2, 31.3, 14.3; HRMS (ESI, m/z): calcd for $C_{21}H_{25}O_5$ $[M + H]^+$ 357.1702, found 357.1698; IR (film): 1174, 1298, 1615, 1713, 2847, 2914, 2964 cm^{-1}.

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*Benzyl (E)-4-Methyl-2-methylene-3-styrylpent-3-enoate (**3fa**).* Yield: 33.3 mg (35%); pale yellow oil; R_f = 0.2 (PE:EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.26 (m, 10H), 7.20−7.16 (m, 1H), 6.61 (d, J = 1.9 Hz, 1H), 6.22 (d, J = 16.0 Hz, 1H), 5.59 (d, J = 1.9 Hz, 1H), 5.20 (s, 2H), 2.00 (s, 3H), 1.76 (s, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 166.7, 139.4, 138.0, 136.3, 135.5, 130.6, 129.9, 128.8, 128.5, 128.5, 128.0, 127.8, 127.1, 126.8, 126.4, 66.4, 23.3, 20.2; HRMS (ESI, m/z): calcd for $C_{22}H_{23}O_2$ $[M + H]^+$ 319.1698, found 319.1692; IR (film): 1173, 1256, 1307, 1720, 2916, 3029 cm^{-1}.

*Benzyl (E)-6-(Dimethylamino)-2-methylene-6-oxo-3-(propan-2-ylidene)hex-4-enoate (**3ga**).* Yield: 62.8 mg (67%); colorless oil; R_f = 0.5 (PE:EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 15.0 Hz, 1H), 7.35−7.29 (m, 5H), 6.56 (d, J = 1.8 Hz, 1H), 5.92 (d, J = 15.0 Hz, 1H), 5.54 (d, J = 1.8 Hz, 1H), 5.18 (s, 2H), 2.97 (s, 3H), 2.84 (s, 3H), 2.03 (s, 3H), 1.77 (s, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 167.3, 166.4, 142.5, 139.5, 139.1, 136.1, 130.0, 129.7, 128.5, 128.1, 128.0, 117.3, 66.5, 37.1, 35.7, 23.5, 20.4; HRMS (ESI, m/z): calcd for $C_{19}H_{24}NO_3$ $[M + H]^+$ 314.1756, found 314.1751; IR (film): 1126, 1179, 1255, 1392, 1597, 1647, 1720 cm^{-1}.

*Ethyl (E)-6-(Dimethylamino)-2-methylene-6-oxo-3-(propan-2-ylidene)hex-4-enoate (**3gi**).* Yield: 67.1 mg (54%); pale yellow oil; R_f = 0.2 (PE:EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 15.0 Hz, 1H), 6.53 (d, J = 1.8 Hz, 1H), 5.99 (d, J = 15.0 Hz, 1H), 5.52 (d, J = 1.8 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.00 (s, 6H), 2.03 (s, 3H), 1.78 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 167.4, 166.6, 142.3, 139.6, 139.3, 129.8, 129.4, 117.1, 60.9, 37.2, 35.8, 23.5, 20.4, 14.2; HRMS (ESI, m/z): calcd for $C_{14}H_{22}NO_3$ $[M + H]^+$ 252.1600, found 252.1593; IR (film): 1189, 1255, 1393, 1596, 1647, 1718, 2923 cm^{-1}.

*Benzyl (E)-3-(3-(Dimethylamino)-3-oxoprop-1-en-1-yl)-4-ethyl-2-methylenehex-3-enoate (**3ha**).* Yield: 64.6 mg (63%); pale yellow oil; R_f = 0.5 (PE:EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 15.0 Hz, 1H), 7.32−7.28 (m, 5H), 6.55 (d, J = 1.8 Hz, 1H), 5.95 (d, J = 15.0 Hz, 1H), 5.55 (d, J = 1.8 Hz, 1H), 5.17 (s, 2H), 2.97 (s, 3H), 2.85 (s, 3H), 2.41 (q, J = 7.5 Hz, 2H), 2.09 (q, J = 7.5 Hz, 2H), 1.07 (t, J = 7.5 Hz, 3H), 0.93 (t, J = 7.5 Hz, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 167.3, 166.6, 153.6, 139.4, 138.8, 136.0, 129.7, 128.9, 128.5, 128.1, 127.9, 117.8, 66.5, 37.1, 35.7, 27.5, 24.0, 14.0, 12.8; HRMS (ESI, m/z): calcd for $C_{21}H_{28}NO_3$ $[M + H]^+$ 342.2069, found 342.2064; IR (film): 1175, 1392, 1599, 1646, 1719, 2922, 2968 cm^{-1}.

*Benzyl (E)-3-Cyclohexylidene-6-(dimethylamino)-2-methylene-6-oxohex-4-enoate (**3ia**).* Yield: 79.9 mg (75%); yellow oil; R_f = 0.3 (PE:EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 15.0 Hz, 1H), 7.33−7.30 (m, 5H), 6.54 (d, J = 1.8 Hz, 1H), 5.96 (d, J = 15.0 Hz, 1H), 5.53 (d, J = 1.8 Hz, 1H), 5.18 (s, 2H), 2.97 (s, 3H), 2.85 (s, 3H), 2.54−2.51 (m, 2H), 2.19−2.16 (m, 2H), 1.62−1.55 (m, 4H), 1.51−1.47 (m, 2H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 167.4, 166.6, 150.7, 139.0, 138.3, 136.0, 129.6, 128.5, 128.1, 128.0, 126.6, 117.8, 66.5, 37.1, 35.8, 33.8, 30.7, 28.3, 28.2, 26.6; HRMS (ESI, m/z): calcd for $C_{22}H_{28}NO_3$ $[M + H]^+$ 354.2069, found 354.2064; IR (film): 1136, 1393, 1597, 1646, 1720, 2851, 2928 cm^{-1}.

*[1,1′-Biphenyl]-4-ylmethyl (E)-3-Cyclohexylidene-6-(dimethylamino)-2-methylene-6-oxohex-4-enoate (**3ib**).* Yield: 87.2 mg (68%); pale yellow oil; R_f = 0.5 (PE:EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 15.0 Hz, 1H), 7.58−7.54 (m, 4H), 7.46−7.35 (m, 5H), 6.56 (d, J = 1.7 Hz, 1H), 5.96 (d, J = 15.0 Hz, 1H), 5.54 (d, J = 1.7 Hz, 1H), 5.22 (s, 2H), 2.93 (s, 3H), 2.82 (s, 3H), 2.55−2.52 (m, 2H), 2.20−2.17 (m, 2H), 1.65−1.50 (m, 6H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 167.4, 166.6, 150.7, 141.0, 140.6, 139.0, 138.9, 135.0, 129.7, 128.9, 128.6, 127.5, 127.2, 127.1, 126.6, 117.8, 66.3, 37.1, 35.7, 33.9, 30.7, 28.4, 28.2, 26.6; HRMS (ESI, m/z): calcd for $C_{28}H_{32}NO_3$ $[M + H]^+$ 430.2382, found 430.2376; IR (film): 1139, 1187, 1646, 1719, 2852, 2898, 2929 cm^{-1}.

*4-(Trifluoromethyl)benzyl (E)-3-Cyclohexylidene-6-(dimethylamino)-2-methylene-6-oxohex-4-enoate (**3ie**).* Yield: 93.3 mg (74%); pale yellow oil; R_f = 0.4 (PE:EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 15.0 Hz, 1H), 7.61−7.56 (m, 2H), 7.46−7.41 (m, 2H), 6.57 (d, J = 1.7 Hz, 1H), 5.94 (d, J = 15.0 Hz, 1H), 5.57 (d, J = 1.7 Hz, 1H), 5.23 (s, 2H), 2.98 (s, 3H), 2.83 (s, 3H), 2.59−2.49 (m, 2H), 2.29−2.14 (m, 2H), 1.56 (m, 6H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 167.2, 166.4, 150.8, 140.0, 138.9, 138.6, 130.4, 130.1, 128.1, 126.4, 125.4 (q, J = 3.8 Hz), 117.7, 65.5, 37.0, 35.7, 33.8, 30.7, 28.4, 28.3, 26.5; HRMS (ESI, m/z): calcd for $C_{23}H_{27}F_3NO_3$ $[M + H]^+$ 422.1943, found 422.1927; IR (film): 1131, 1327, 1394, 1647, 1724, 2934 cm^{-1}.

*Ethyl (E)-3-cyclohexylidene-6-(dimethylamino)-2-methylene-6-oxohex-4-enoate (**3ii**).* Yield: 103.8 mg (71%); pale yellow oil; R_f = 0.3 (PE:EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 15.0 Hz, 1H), 6.50 (d, J = 1.5 Hz, 1H), 6.03 (d, J = 15.0 Hz, 1H), 5.50 (d, J = 1.6 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.00 (s, 6H), 2.54−2.52 (m, 2H), 2.20−2.17 (m, 2H), 1.66−1.55 (m, 6H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 167.5, 166.8, 150.4, 139.2, 139.1, 129.0, 126.7, 117.6, 60.9, 37.2, 35.8, 33.8, 30.6, 28.3, 28.2, 26.6, 14.2; HRMS (ESI, m/z): calcd for $C_{17}H_{26}NO_3$ $[M + H]^+$ 292.1913, found 292.1906; IR (film): 1194, 1249, 1393, 1596, 1646, 1718, 2850, 2932 cm^{-1}.

*6-Benzyl 1-Ethyl (2E,4E)-4-ethylidene-5-methylenehex-2-enedioate (**3ja**).* Yield: 71.9 mg (80%), colorless oil, R_f = 0.3 (PE:EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 15.8 Hz, 1H), 7.35−7.32 (m, 8H), 6.63 (d, J = 1.6 Hz, 0.42H), 6.36 (d, J = 1.7 Hz, 1H), 6.18 (q, J = 7.2 Hz, 0.46H), 5.94 (q, J = 7.3 Hz, 1H), 5.68 (d, J = 15.8 Hz, 1H), 5.67 (d, J = 1.7 Hz, 1H), 5.60 (d, J = 15.9 Hz, 0.56H), 5.19 (s, 1H), 5.18 (s, 2H), 4.21−4.15 (m, 3H), 1.95 (d, J = 7.2 Hz, 3H), 1.72 (d, J = 7.1 Hz, 1.39H), 1.30−1.25 (m, 4.7H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 167.2, 167.1, 166.1, 165.4, 146.9, 144.6, 140.9, 139.1, 138.4, 136.4, 136.3, 135.9, 135.8, 135.1, 131.0, 129.1, 128.6, 128.5, 128.2, 128.1, 127.9, 120.3, 117.8, 114.3, 66.8, 66.7, 60.4, 60.3, 20.7, 20.4, 14.3, 14.3; HRMS (ESI, m/z): calcd for $C_{18}H_{21}O_4$ $[M + H]^+$ 301.1440, found 301.1434; IR (film): 760, 1176, 1272, 1714, 2959 cm^{-1}.

*6-(((3r,5r,7r)-Adamantan-1-yl)methyl) 1-Ethyl (E)-4-cyclohexylidene-5-methylenehex-2-enedioate (**3ik**).* Yield: 84.5 mg (69%); yellow oil; R_f = 0.4 (PE:EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 15.0 Hz, 1H), 6.51 (d, J = 2.0 Hz, 1H), 6.03 (d, J = 15.0 Hz, 1H), 5.49 (d, J = 2.0 Hz, 1H), 3.71 (s, 2H), 2.99 (s, 6H), 2.55−2.53 (m, 2H), 2.22−2.19 (m, 2H), 1.95−1.91 (m, 3H), 1.72−1.54 (m, 12H), 1.48 (d, J = 2.1 Hz, 6H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 167.4, 167.0, 150.2, 139.2, 139.1, 129.0, 126.9, 117.7, 74.4, 39.2, 37.2, 36.9, 35.8, 33.9, 33.4, 30.6, 28.4, 28.2, 28.0, 26.6; HRMS (ESI, m/z): calcd for $C_{26}H_{38}NO_3$ $[M + H]^+$ 412.2852, found 412.2851; IR (film): 1248, 1393, 1597, 1648, 1718, 2850, 2908 cm^{-1}.

*Naphthalen-1-ylmethyl (E)-3-Cyclohexylidene-6-(dimethylamino)-2-methylene-6-oxohex-4-enoate (**3im**).* Yield: 79.1 mg (65%); pale yellow oil; R_f = 0.4 (PE:EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99−7.96 (m, 1H), 7.87−7.81 (m, 3H), 7.54−7.49 (m, 3H), 7.42 (dd, J = 8.2, 7.1 Hz, 1H), 6.51 (d, J = 1.8 Hz, 1H), 5.90 (d, J = 15.0 Hz, 1H), 5.63 (s, 2H), 5.50 (d, J = 1.8 Hz, 1H), 2.93 (s, 3H), 2.67 (s, 3H), 2.50−2.47 (m, 2H), 2.11−2.09 (m, 2H), 1.57−1.48 (m, 4H), 1.41−1.36 (m, 2H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 167.3, 166.6, 150.6, 139.0, 138.9, 133.7, 131.5, 131.5, 129.6, 129.2, 128.6, 127.4, 126.6, 126.5, 125.9, 125.2, 123.7, 117.7, 65.0, 36.9, 35.7, 33.8, 30.6, 28.2, 28.1, 26.6; HRMS (ESI, m/z): calcd for $C_{26}H_{30}NO_3$ $[M + H]^+$ 404.2226, found 404.2218; IR (film): 1188, 1392, 1598, 1645, 1719, 2855, 2926 cm^{-1}.

*Ethyl (4E)-3-cyclohexylidene-6-(dimethylamino)-2-ethylidene-6-oxohex-4-enoate (**3in**).* Yield: 33.3 mg (36%); pale yellow oil; R_f = 0.4 (PE:EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 14.9 Hz, 0.46H), 7.82 (d, J = 14.9 Hz, 1H), 7.12 (q, J = 7.0 Hz, 0.46H), 6.11 (d, J = 14.9 Hz, 1H), 5.97 (d, J = 14.9 Hz, 0.46H), 5.89 (q, J = 7.2 Hz, 1H), 4.17−4.11 (m, 2.9H), 3.02−2.99 (m, 8.8 H), 2.94−2.92 (m, 0.9H), 2.60−2.55 (m, 0.9H), 2.51−2.48 (m, 2H), 2.24−2.21 (m, 2H), 2.10 (d, J = 7.2 Hz, 3H), 1.64 (d, J = 7.0 Hz, 1.4H), 1.61−1.56 (m, 8.8H), 1.22 (td, J = 7.2, 1.5 Hz, 4.4H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 167.7, 167.7, 167.4, 167.1, 150.8, 150.3, 140.6, 140.3, 139.6, 138.2, 132.2, 131.6, 128.6, 124.1, 117.7, 116.8, 60.5, 60.2, 37.4, 37.3, 35.8, 35.7, 33.7, 33.6, 30.7, 30.5, 28.4, 28.3, 28.0, 26.7, 15.6, 15.1, 14.3, 14.2; HRMS (ESI, m/z): calcd for $C_{18}H_{28}NO_3$ $[M + H]^+$ 306.2069, found 306.2068; IR (film): 1192, 1391, 1595, 1645, 1713, 2853, 2933 cm^{-1}.

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*Diethyl (2E,6E)-4,5-di(propan-2-ylidene)octa-2,6-dienedioate (**3′**).* Pale yellow oil; R_f = 0.3 (PE:EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 15.3 Hz, 2H), 5.45 (d, J = 15.3 Hz, 2H), 4.18 (q, J = 7.1 Hz, 4H), 2.06 (s, 6H), 1.64 (s, 6H), 1.29 (t, J = 7.1 Hz, 6H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 168.0, 144.2, 140.6, 130.5, 117.6, 60.2, 22.9, 20.1, 14.3; HRMS (ESI, m/z): calcd for $C_{18}H_{27}O_4$ $[M + H]^+$ 307.1909, found 307.1903; IR (film): 1162, 1261, 1289, 1367, 1612, 1710 cm^{-1}.

Transformation of [3]Dendralene 3aa with *m*-CPBA. Following the procedure reported in the literature,[26] to a 10 mL oven-dried reaction flask was added [3]dendralene **3aa** (0.2 mmol, 62.8 mg, 1.0 equiv) in 2 mL of dry DCM. Then, the solution was cooled to 0 °C with stirring. Once at 0 °C, *m*-CPBA (85% pure, 1.8 equiv) was added in one portion. The reaction mixture was stirred at 0 °C for 20 min. Then, the reaction was allowed to warm to rt overnight. After the reaction, the reaction mixture was diluted with DCM and saturated $NaHSO_3$/$Na_2S_2O_5$. Subsequent transfer to a separatory funnel and extraction with DCM (5 mL × 3) followed by a washing of the collected organic extracts with D.I. water, drying of the resulting organic layers over anhydrous Na_2SO_4, salt filtration, and rotary evaporation afforded the crude product. Purification by silica gel column chromatography eluting with EA:PE = 1:10 afforded the compound **4** as a colorless oil, 32.9 mg, 50% yield.

*Benzyl (E)-2-(2-(3-Ethoxy-3-oxoprop-1-en-1-yl)-3,3-dimethyloxiran-2-yl)acrylate (**4**).* R_f = 0.4 (PE:EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.35 (m, 5H), 7.13 (d, J = 15.6 Hz, 1H), 6.48 (d, J = 1.1 Hz, 1H), 6.01 (d, J = 15.6 Hz, 1H), 5.93 (d, J = 1.1 Hz, 1H), 5.26 (q, J = 12.4 Hz, 2H), 4.19 (q, J = 6.9 Hz, 2H), 1.32 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H), 1.19 (s, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 166.0, 164.6, 143.5, 138.0, 135.5, 129.3, 128.7, 128.4, 128.2, 123.8, 67.2, 66.9, 66.6, 60.6, 20.4, 19.6, 14.2; HRMS (ESI, m/z): calcd for $C_{19}H_{23}O_5$ $[M + H]^+$ 331.1545, found 331.1541; IR (film): 1147, 1177, 1273, 1308, 1377, 1719 cm^{-1}.

Deuterium-Labeling Experiment. $Pd(OAc)_2$ (4.4 mg, 0.02 mmol) and 2,6-dimethylbenzoquinone (30.0 mg, 0.22 mmol, 1.1 equiv) were weighed in a 10 mL oven-dried reaction flask. The flask was degassed in a vacuum and backfilled with N_2 three times, followed by the addition of dry degassed THF (2 mL). Then, **1a**-d_6 (0.3 mmol, 1.0 equiv) and α-diazo ester **2a** were added using a microsyringe successively. AcOH (12.0 mg, 1.0 equiv) was added to the mixture. The reaction mixture was stirred at 90 °C with an oil bath under N_2 for 10 h. After the reaction, the mixture was allowed to warm to room temperature and filtered through flash column chromatography on silica gel (1:1 EtOAc/petroleum ether). Then, the solvent was evaporated *in vacuo* and the crude product was purified by silica gel column chromatography (EtOAc/petroleum ether), which afforded product **3aa**-d_6 as a colorless oil without any scrambling of the deuterium content. This experiment can rule out the reaction mechanism that involves allenic C−H bond cleavage of the methyl group, followed by rearrangement to form [3]dendralene **3aa**.

*6-Benzyl 1-Ethyl (E)-5-methylene-4-(propan-2-ylidene-d_6)hex-2-enedioate (**3aa**-d_6).* Yield: 50.0 mg (78%) without HOAc; 4.9 mg (8%) with AcOH; R_f = 0.2 (PE:EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 15.5 Hz, 1H), 7.35−7.30 (m, 5H), 6.59 (d, J = 1.6 Hz, 1H), 5.59 (d, J = 15.5 Hz, 1H), 5.56 (d, J = 1.6 Hz, 1H), 5.18 (s, 2H), 4.18 (q, J = 7.2 Hz, 2H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 167.6, 165.9, 141.7, 138.3, 136.0, 130.5, 129.6, 128.6, 128.5, 128.1, 127.9, 118.0, 66.6, 60.2, 14.3; HRMS (ESI, m/z): calcd for $C_{19}H_{17}D_6O_4$ $[M + H]^+$ 321.1973, found 321.1970; IR (film): 1166, 1190, 1269, 1292, 1615, 1716 cm^{-1}.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c03033.

Discussion on an alternative reaction pathway and ^{1}H and ^{13}C spectra for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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