Control of Regioselectivity in Pd(0)-Catalyzed Coupling−Cyclization Reaction of 2-(2′,3′-Allenyl)malonates with Organic Halides

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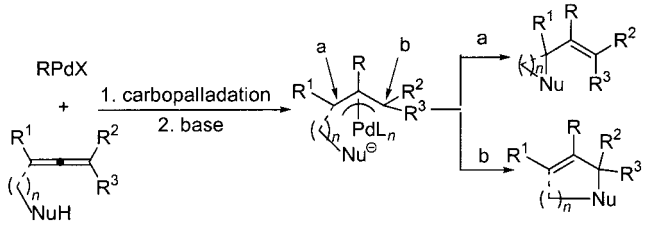
The regioselectivity in the Pd(0)-catalyzed coupling−cyclization of 2-(2′,3′-allenyl)malonates with organic halides is determined by the steric and electronic effects of both substrates. By deliberate control of the reaction conditions, the regioselectivity of this reaction can be tuned. With conditions A and B, the reaction afforded vinylic cyclopropane derivatives, while with conditions C and D, the reaction afforded cyclopentene derivatives in a highly selective manner. Under similar conditions, 1-alkenyl halides tend to form more three-membered cyclic products. The increased steric hindrance at the 2′-positon of the allene moiety and aryl halides favors the formation of five-membered cyclic products. The regioselectivity of the reaction may be explained by the comparison of the relative stabilities of syn- and anti-type π-allyl palladium intermediates.

The carbopalladation reaction of allenes[1] was reported to afford a π-allyl palladium intermediate,[2] which can be further trapped by either a β-H elimination reaction or a nucleophilic substitution reaction (Scheme 1).[3]

Here a major concern is the control of the regioselectivity of the nucleophilic substitution process.[4] Recently, during the course of our study of coupling−cyclization reaction of functionalized allenes,[5] we have developed a set of reaction conditions under which the coupling−cyclization reactions afforded the pathyway a-type products (n = 1), i.e., cyclopropane derivatives, in a highly selective manner starting from dimethyl 2-(2′,3′-allenyl)-malonate and organic halides.[6] These results are quite contrary to those reported by Cazes et al.[7] In this paper, we wish to report the details of this reaction. Interestingly, the regioselectivity can be tuned by the deliberate selection of solvents, bases, catalysts, and substrates.

Scheme 1



Highly Regioselective Formation of Vinylic Cyclopropane Derivatives. The Pd(PPh$_3$)$_4$-catalyzed coupling−cyclization reaction of dimethyl 2-(2′,3′-butadienyl)-malonate (**1a**) and PhI was studied in different solvents (Scheme 1 and Table 1). The reactions in DMF and DMSO afforded a mixture of cyclopropane derivative **2a** and cyclopentene derivative **3a** in good combined yields (entries 1 and 2, Table 1). However, it is interesting to observe that the corresponding reaction in toluene, benzene, and CH_3CN afforded **2a** with an excellent selectivity, albeit in low yields (entries 3−5, Table 1). To our surprise, with the addition of *a catalytic amount (10 mol %) of n-Bu$_4$NBr*, the reaction in CH_3CN afforded **2a** as the sole product in 80% yield (entry 6, Table 1)! Furthermore, the reaction in THF afforded **2a** in 85% yield even in the absence of *n*-Bu$_4$NBr (entry 7, Table 1). Two sets of reaction conditions (A and B) were defined in Scheme 2.

The results of the Pd(PPh$_3$)$_4$-catalyzed coupling−cyclization reactions of **1a** with different organic halides obtained by applying both conditions A and B to afford cyclopropane derivatives as the sole products are summarized in Table 2.

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(4) (a) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395. (b) Trost, B. M. *J. Organomet. Chem.* **1986**, *300*, 263.

(5) For some of our most recent results, see: Ma, S.; Shi, Z. *J. Org. Chem.* **1998**, *63*, 6387. Ma, S.; Duan, D.; Shi, Z. *Org. Lett.* **2000**, *2*, 1419. Ma, S.; Shi, Z.; Wu, S. *Tetrahedron: Astmmetry* **2001**, *12*, 193. Ma, S.; Wu, S. *J. Org. Chem.* **1999**, *64*, 9314; Ma, S.; WU, S. *Chem. Commun.* **2001**, 441. Ma, S.; Zhang, J. *Chem. Commun.* **2000**, 117. Ma, S.; Li, L. *Org. Lett.* **2000**, *2*, 941. Ma, S.; Xie, H. *Org. Lett.* **2000**, *2*, 3801. Ma, S.; Zhao, S. *J. Am. Chem. Soc.* **1999**, *121*, 7943.

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(7) (a) Ahmar, M.; Cazes, B.; Gore, J. *Tetrahedron Lett.* **1985**, *26*, 3795. (b) Ahmar, M.; Cazes, B.; Gore, J. *Tetrahedron* **1987**, *43*, 3453. (c) Cazes, B. *Pure Appl. Chem.* **1990**, *62*, 1867. (d) Besson, L.; Bazin, J.; Gore, J.; Cazes, B. *Tetrahedron Lett.* **1994**, *35*, 2881. (e) Gamez, P.; Ariente, C.; Gore, J.; Cazes, B. *Tetrahedron* **1998**, *54*, 14835.

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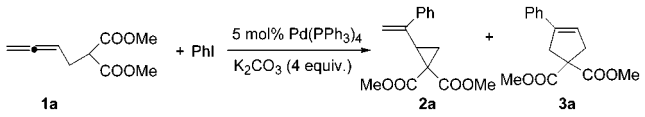
Table 1. $Pd(PPh_3)_4$-Catalyzed Coupling−Cyclization of 1a with PhI under Different Reaction Conditions[a]

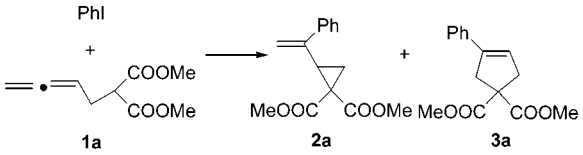


1a 2a 3a

entry	solvent	additive	*T* (°C)	time (h)	**2a** (%)	**3a** (%)
1	DMF	−	60	25	65	8
2	DMSO	−	62	22	49	21
3	toluene	−	82	15.5	30	0
4	benzene	−	80	15	40	0
5	CH_3CN	−	reflux	19.5	32	0
6	**CH_3CN**	***n*-Bu_4NBr**	**reflux**	**15**	**80**	**0**
7	**THF**	−	**reflux**	**15.5**	**85**	**0**

[a] PhI (1.2 equiv) was used.

Scheme 2

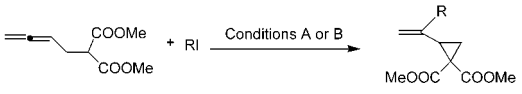


1a 2a 3a

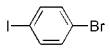
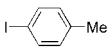
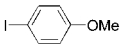
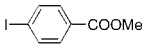
Conditions A = 5 mol % $Pd(PPh_3)_4$, K_2CO_3 (4 equiv.), 10 mol % of *n*-Bu_4NBr, CH_3CN, reflux

Conditions B = 5 mol % $Pd(PPh_3)_4$, K_2CO_3 (4 equiv.), THF, reflux

Table 2. $Pd(PPh_3)_4$-Catalyzed Coupling−Cyclization of Dimethyl 2-(2′,3′-Propadienyl)malonate with Organic Halides under Conditions A and B[a]



1a 2

entry	RI	Conditions A[b]		Conditions B[b]	
		time (h)	**2** (%)	time (h)	**2** (%)
1	PhI	15	80 (**2a**)	15.5	85 (**2a**)
2		17	83 (**2b**)	25.3	76 (**2b**)
3		24	82 (**2c**)	23	57 (**2c**)
4		17	69 (**2d**)	24.5	59 (**2d**)
5		16	46 (**2e**)	25.3	45 (**2e**)
6		23	86 (**2f**)	23	91 (**2f**)
7		24	58 (**2g**)	24.67	73 (**2g**)
8		16	67 (**2h**)	23.83	61 (**2h**)

[a] 1.2 equiv of RI was used for Conditions A, and 1.3 equiv of RI was used for Conditions B. [b] See text.

Furthermore, it is interesting to observe that the Pd-$(PPh_3)_4$-catalyzed reaction of dimethyl 2-(2′-benzyl-2′,3′-butadienyl)malonate (**1b**) (a benzyl group was introduced at the 2-position of the allenyl moiety) with PhI afforded the three-membered cyclic product **2i** in 80% yield under conditions A, while under conditions B, the corresponding reaction did not afford either cyclopropane derivative **2i** or five-membered cyclic product **3i** in decent yields (Scheme 3), implying that conditions A afforded the cyclopropane derivative **2i** even with the increased steric hindrance at the 2-position of the allene moiety.

Scheme 3

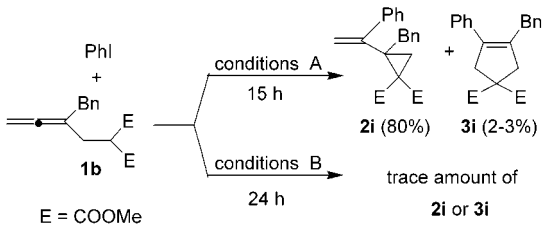
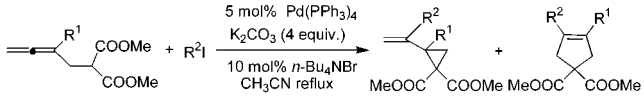
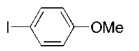
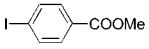
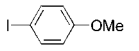
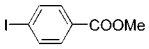


Table 3. Pd(0)-Catalyzed Coupling−Cyclization Reaction of 2′-Substituted 2-(2′,3′-Allenyl)malonates with Differently Structured Organic Halides under Conditions A[a]



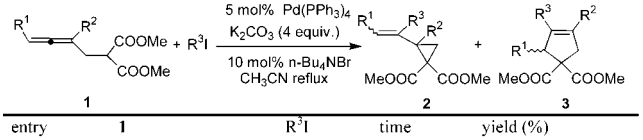
1 2 3

entry	1		R^2I	time	yield of **2**	yield of
	R^1	substrate		(h)	(%)	**3** (%)
1	Bn	**1b**	PhI	15	80 (**2i**)	2-3
2	Bn	**1b**		29	63 (**2j**)	0
3	Bn	**1b**		24	82 (**2k**)	16 (**3k**)
4	Bn	**1b**		24	84 (**2l**)	0
5	Bn	**1b**		15	67 (**2m**)	0
6	Bn	**1b**		12	45 (**2n**)	0
7	Bn	**1b**		14	97 (**2o**)	0
8	*n*-Pr	**1c**	PhI	44	77 (**2p**)	0
9	*n*-Pr	**1c**		26	45 (**2q**)	0
10	*n*-Pr	**1c**		26	71 (**2r**)	0
11	*n*-Pr	**1c**		15	71 (**2s**)	0
12	*n*-Pr	**1c**		15	70 (**2t**)	0
13	*n*-Pr	**1c**		12	57 (**2u**)	0
14	*n*-Pr	**1c**		14	79 (**2v**)	0

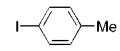
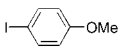
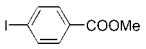
[a] RI (1.2 equiv) was used.

The results of the Pd(0)-catalyzed reaction of differently 2′-substituted 2-(2′,3′-allenyl)malonates with organic halides are summarized in Table 3. From Table 3, it should be noted that (1) the regioselectivity for the formation of the three-membered cyclic products is high and (2) the configuration of the C═C bond in 1-alkenyl

Table 4. Pd(0)-Catalyzed Coupling−Cyclization Reaction of 4′-Substituted 2-(2′,3′-Allenyl)malonates with Organic Halides under Conditions A[a]



1 2 3

entry	1			R^3I	time	yield (%)	
	R^1	R^2			(h)	**2** (*E*/*Z*)[b]	**3**
1	*n*-C_6H_{13}	H	**1d**	PhI	12	72 (25:75) (**2w**)	6 (**3w**)
2	*n*-C_6H_{13}	H	**1d**		12	88 (44:56) (**2x**)	4 (**3x**)
3	*n*-C_6H_{13}	H	**1d**		17	57 (42:58) (**2y**)	9 (**3y**)
4	*n*-C_6H_{13}	H	**1d**		7 d	71 (48:52) (**2z**)	8 (**3z**)
5	*n*-C_6H_{13}	H	**1d**		19	88 (19:81) (**2α**)	0
6	*n*-Pr	Me	**1e**	PhI	16	42 (0:100) (**2β**)	21 (**3β**)

[a] R^3I (1.2 equiv) was used. [b] Determined by 300 MHz ^1H NMR spectra.

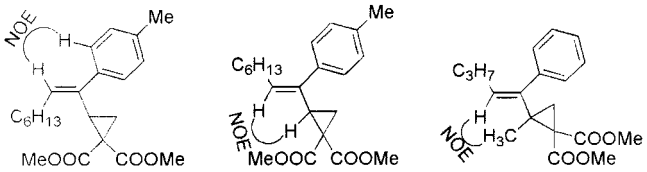


Figure 1.

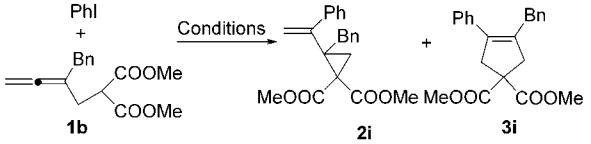
iodide remained unchanged during the reaction (entries 4−6 and 11−13, Table 3).

Further introduction of a substitutent at the 4-position of the allene moiety gave high ratios of cyclopropane/cyclopentene derivatives, although the formation of five-membered cyclic products were also observed (Table 4). The configurations of the C=C bond in **2** were determined by the $^1H-^1H$ NOESY spectra (Figure 1).

Highly Regioselective Synthesis of Cyclopentene Derivatives. To investigate the possibility of developing a set of general reaction conditions for the exclusive formation of cyclopentene derivatives, an enormous number of reaction conditions were screened and the results are shown in Tables 1 and 2 in Supporting Information. In both CH_3CN and THF, the effect of a base on the regioselectivity is obvious: with LiOH, NaOH, KOH, LDA, *n*-BuLi, or NaH, the reaction afforded five-membered cyclic product **3i** with an excellent regioselectivity. With the observation that the reaction using NaH as the readily available base afforded **3i** in 53% yield (see Table 2 in Supporting Information), we developed a set of reaction conditions, i.e., 5 mol % $Pd(PPh_3)_4$, NaH (1.1 equiv), DMSO, 85 °C (Conditions C), for the highly regioselective and high-yielding preparation of cyclopentene derivative **3i** (Scheme 4). Here the solvent (DMSO) and the catalyst ($Pd(PPh_3)_4$) are the keys for a good yield of **3i**. The corresponding results are summarized in Table 5. The conversion of **2i** to **3i** under Conditions C was not observed (Scheme 5).

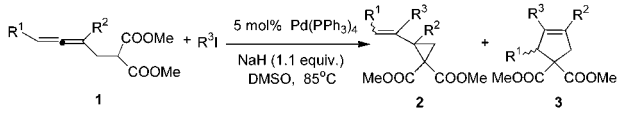
In most cases involving aryl iodides except entries 6, 7, 10, and 11 (Table 5), the cyclopentene derivatives **3** are the only products formed. However, even under Conditions C, the corresponding reactions with 1-alkenyl iodide afforded a mixture of both cyclopropane and cyclopentene derivatives with low selectivities, favoring

Scheme 4

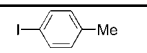
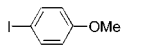
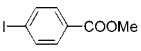
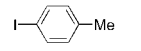
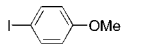
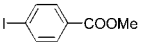
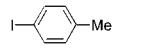
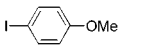
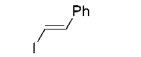
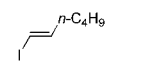
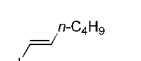
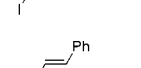


Conditions	2i	3i
2 mol % $Pd_2(dba)_3{\cdot}CHCl_3$, 4 mol % dppe, K_2CO_3 (4.0 equiv.), 10 mol % of *n*-Bu_4NBr, and DMSO, 85 °C, 24 h	49%	13%
2 mol % $Pd_2(dba)_3{\cdot}CHCl_3$, 4 mol % dppe, NaH (1.1 equiv.), DMSO, 85 °C 12.5 h	14%	58%
5 mol % $Pd(PPh_3)_4$, NaH (1.1 equiv.), DMSO, 85 °C (**Conditions C**)	0	88%

Table 5. Pd(0)-Catalyzed Coupling−Cyclization Reaction of 1 with Organic Halides under Conditions C[a]



1 2 3

entry	1			R^3I	time	yield (%)	
	R^1	R^2			(h)	**2**	**3**
1	H	Bn	**1b**		11	0 (**2χ**)	79 (**3χ**)
2	H	Bn	**1b**		11	0 (**2j**)	98 (**3j**)
3	H	Bn	**1b**		14	0 (**2k**)	77 (**3k**)
4	H	*n*-Pr	**1c**	PhI	12	0 (**2p**)	65 (**3p**)
5	H	*n*-Pr	**1c**		10	0 (**2δ**)	54 (**3δ**)
6	H	*n*-Pr	**1c**		15	7 (**2q**)	47 (**3q**)
7	H	*n*-Pr	**1c**		15	8 (**2r**)	54 (**3r**)
8	*n*-C_6H_{13}	H	**1d**	PhI	9	0 (**2w**)	81 (**3w**)
9[b]	*n*-C_6H_{13}	H	**1d**	PhI	9	0 (**2w**)	95 (**3w**)
10	*n*-C_6H_{13}	H	**1d**		9	5 (53:47)[c] (**2x**)	82 (**3x**)
11	*n*-C_6H_{13}	H	**1d**		9.5	20(56:44)[c] (**2y**)	78 (**3y**)
12	H	Bn	**1b**		37	39 (**2l**)	32 (**3l**)
13	H	Bn	**1b**		11	40 (**2m**)	24 (**3m**)
14	H	*n*-Pr	**1c**		11	32 (**2t**)	18 (**3t**)
15	H	H	**1a**		12	45 (**2e**)	0 (**3e**)

[a] R^3I (1.2 equiv) was used. [b] THF was used as the solvent. [c] *E*-**2**/*Z*-**2** ratio determined by 300 MHz ^1H NMR spectra.

Scheme 5

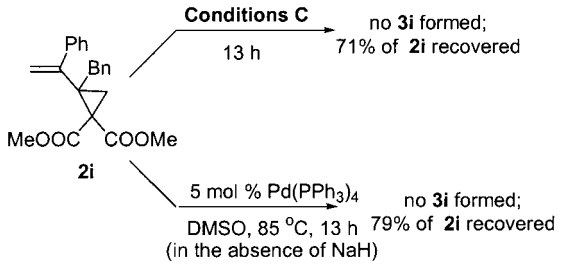
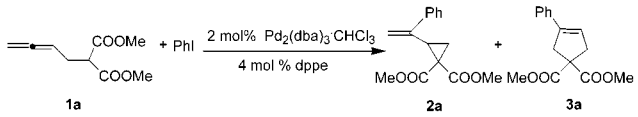


Table 6. Pd(0)-Catalyzed Reaction of 1a with PhI in Different Solvents Using NaH as the Base[a]



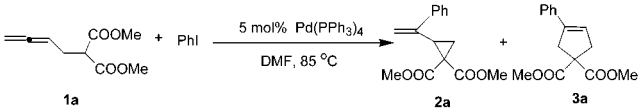
entry	solvent	base[b]	*T* (°C)	time (h)	yield of **2a** (%)	yield of **3a** (%)
1[c]	DMSO	NaH (1.1)	85	12	8	42
2	DMSO	NaH (1.1)	85	12	22	51
3	DMF	NaH (1.1)	85	12	5	60
4[c]	DMF	NaH (1.1)	85	10	5	67
5	DMF	KOH (2.0)	85	10	4	51
6	toluene	NaH (1.1)	85	12	0	trace
7	CH_3CN	NaH (1.1)	reflux	12	9	22
8	THF	NaH (1.1)	reflux	7	0	26
9	THF	LiOH (2.0)	reflux	12	0	3
10	THF	NaOH (2.0)	reflux	12	0	20
11	THF	LDA (1.1)	reflux	12	trace	trace
12	THF	*n*-BuLi (1.1)	reflux	12	trace	trace

[a] PhI (1.2 equiv) was used. [b] Numbers in parentheses are the equivalents of the base used in the reaction. [c] $Pd(PPh_3)_4$ (5 mol %) was used instead of $Pd_2(dba)_3$·$CHCl_3$ and dppe as the catalyst.

the formation of cyclopropane derivatives (entries 12−14, Table 5). The reaction of **1a** with *E*-(1-phenyl ethenyl) iodide afforded the three-membered cyclic product **2e** in a highly selective manner in 45% yield, probably due to the steric effect at the 2′-position (entry 15, Table 5).

With the decreased steric hindrance at the 2-position of the allene moiety, the regioselectivity control for the formation of five-membered cyclic products would be a new challenge. The similar reaction of dimethyl 2-(2′,3′-butadienyl)malonate **1a** with PhI under Conditions C afforded a mixture of **2a** and **3a** in 8 and 42% yields, respectively (entry 1, Table 6). When the reaction using NaH as the base was carried out in other solvents, the selectivity was still not good enough (entries 2−4, Table 6). Thus, the effects of different bases for this reaction in THF were studied (entries 8−12, Table 6). In most cases, excellent selectivities with low yields were achieved (entries 8−10, Table 6). Better yields were achieved with KOH as the base and DMF as the solvent (entry 5, Table 6). With these results in hand, we were able to develop a set of optimized reaction conditions for the cyclopentene-formation reaction, i.e., Conditions D (Conditions D = 5 mol % $Pd(PPh_3)_4$, NaOH (2.0 equiv), DMF, 85 °C) (entry 5, Table 7). The amount of NaOH used is important for both the regioselectivity and yield of **3a** (compare entries 3−5, Table 7). Some typical results are summarized in Table 8. It is obvious that the reactions of **1c** with *p*-methylphenyl iodide and *p*-methoxylphenyl iodide under Conditions D afforded the five-membered rings **3** exclusively (compare entries 3 and 5 in Table 8 with entries 6 and 7 in Table 5).

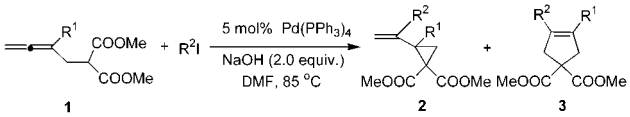
Table 7. Effect of Base on the Pd(0)-Catalyzed Reaction of 1a with PhI in DMF[a]



entry	base[b]	time (h)	yield of (**2a** + **3a**) (%)	**2a**:**3a**[c]
1	*n*-BuLi (1.1)	10.5	46	0:100
2	KOH (2.0)	10.5	31	0:100
3	NaOH (1.2)	12	75	13:87
4	NaOH (1.5)	12	40	0:100
5	**NaOH (2.0)**	**10.5**	**66**	**0:100**

[a] PhI (1.2 equiv) was used. [b] Numbers in parentheses are the equivalents of the base used in the reaction. [c] Determined by 300 MHz ^1H NMR spectra.

Table 8. Pd(0)-Catalyzed Coupling−Cyclization Reaction of 2′-Substituted 2-(2′,3′-Allenyl)malonates with Differently Structured Organic Halides under Conditions D[a]



entry	**1** R[1]	**1** substrate	R^2I	time (h)	yield of **2** (%)	yield of **3** (%)
1	H	**1a**	I-C6H4-Me	11	0 (**2c**)	63 (**3c**)
2	H	**1a**	I-C6H4-OMe	11	0 (**2d**)	57 (**3d**)
3	*n*-Pr	**1c**	I-C6H4-OMe	10.5	0 (**2q**)	51 (**3q**)
4[b]	*n*-Pr	**1c**	I-C6H4-OMe	11	0 (**2q**)	70 (**3q**)
5	*n*-Pr	**1c**	I-C6H4-COOMe	10.5	0 (**2r**)	52 (**3r**)
6[b]	*n*-Pr	**1c**	I-C6H4-COOMe	11	13 (**2r**)	59 (**3r**)

[a] RI (1.2 equiv) was used. [b] NaH (1.1 equiv) was used instead of NaOH as the base.

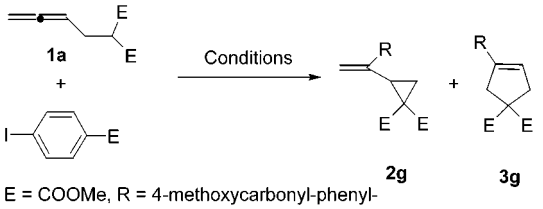
Here, the electronic effect of the substituent in aryl iodide again has a major effect on the regioselectivity. Using *p*-methoxycarbonylphenyl iodide, the reaction afforded **2g** and **3g** in 55% combined yield with a ratio of 34:66 (**2g**/**3g**). Similar reaction under Cazes' conditions[7,8] afforded **2g** and **3g** in very low yields with 37% of **1a** recovered (Scheme 6).

On the basis of these results, it is obvious that the steric hindrance of the allene moiety is one of the major factors controlling the regioselectivity of this coupling−cyclization reaction. A similar phenomenon was observed with aryl iodide. The corresponding reaction of **1b** with *o*-methylphenyl iodide under Conditions A afforded the cyclopentene derivative **3i-*o*-Me** in 80% yield as the sole product (compare Scheme 7 with the results in Table 3).

When a mixture of an equimolar ratio of **1b**, PhI, and *o*-methylphenyl iodide was submitted to Conditions A,

(8) Cazes' conditions: compound **1a** and 1.06 equiv of NaH in THF were stirred at rt for 1∼2 h first, and then the above solution was added to another flask that was charged with 2 mol % $Pd_2(dba)_3$·$CHCl_3$ and 4 mol % dppe in THF. The solution was then treated with PhI and stirred under reflux. See: Ahmar, M.; Cazes, B.; Gore, J. *Tetrahedron* **1987**, *43*, 3453.

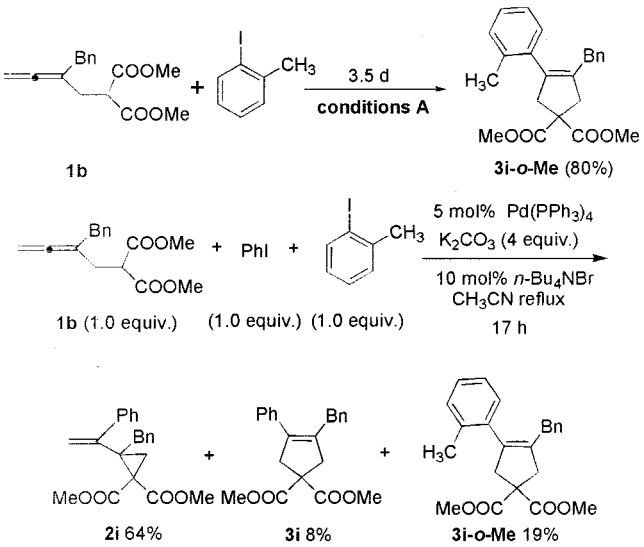
Scheme 6



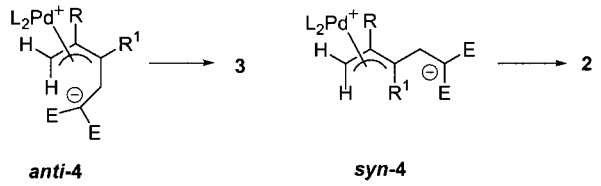
Conditions D:	11 h, yield 55%	34[a] :	66[a]
Cazes' Conditions:[7,8]	48 h	trace	trace[b]

[a] Determined by 300 MHz ^{1}H NMR spectra. [b] Compound **1a** (37%) was recovered.

Scheme 7



Scheme 8

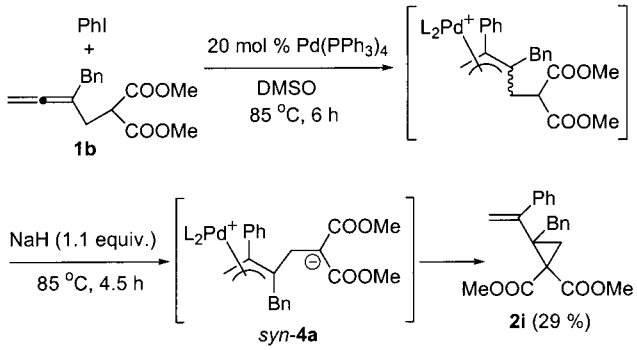


the reaction afforded **2i** in 64% yield, **3i** in 8% yield, and **3i-*o*-Me** in 19% yield, respectively (Scheme 7), implying a strong steric effect on the regioselectivity of this reaction.

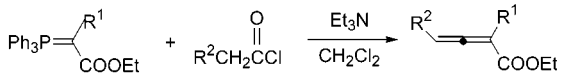
Mechanistic Consideration. For the regioselectivity of this coupling−cyclization reaction, two types of π-allyl palladium intermediates, i.e., anti- and syn-**4**, may be considered (Scheme 8). It is commonly believed that anti-**4** will lead to the favorable formation of five-membered cyclic products **3**, while syn-**4** will form three-membered cyclic products **2**.[7c] Thus, compared with alkenyl halide, due to the larger steric hindrance, aryl halides tend to favor the formation of five-membered cyclic products **3**. With the introduction of non-hydrogen R^1, the reaction also tends to form five-membered ring **3** via anti-**4**.

The carbopalladation reaction may occur before or after deprotonation of the malonate moiety. When **1b** and PhI were treated with 20 mol % $Pd(PPh_3)_4$ in DMSO for 6 h first followed by the addition of NaH, the reaction afforded **2i** in 29% yield exclusively (compare this result

Scheme 9



Scheme 10



b: R^1 = Bn	b: R^2 = H	b: R^1 = Bn, R^2 = H
c: R^1 = n-C_3H_7	c: R^2 = H	c: R^1 = n-C_3H_7, R^2 = H
d: R^1 = H	d: R^2 = n-C_6H_{13}	d: R^1 = H, R^2 = n-C_6H_{13}
e: R^1 = CH_3	e: R^2 = n-C_3H_7	e: R^1 = CH_3, R^2 = n-C_3H_7

with those in Scheme 4), implying that three-membered cyclic products may be formed via intermediate syn-**4a** (Scheme 9), which may be formed exclusively in a thermodynamically controlled manner due to the absence of a base.

Thus, it is reasonable that under relatively weaker basic conditions, the reaction favors the formation of three-membered cyclic products via intermediate syn-**4**.

Conclusion

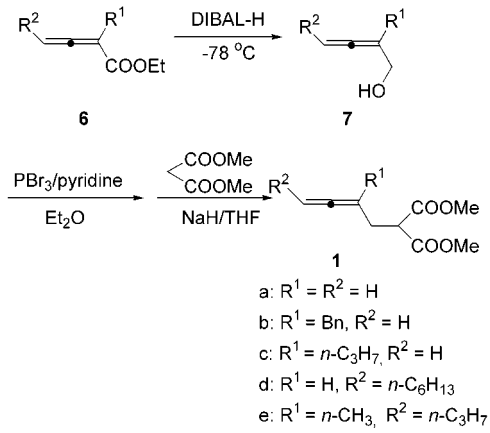
(1) The regioselectivity of this reaction can be tuned: with Conditions A and B, the reaction tends to afford three-membered cyclic products **2**, while with Conditions C and D, the reaction favors the formation of five-membered cyclic products **3**. (2) The regioselectivity depends largely on the structures of both organic halides and 2-(2′,3′-allenyl)malonates. The reaction with 1-alkenyl halides favors the formation of three-membered cyclic products **2**. (3) The electronic effects of the substituent in aryl halides have an influence on the regioselectivity. (4) With increased steric effects at the 2′-position of the allene moiety and organic halides, the reaction tends to form five-membered cyclic products.

Experimental Section

Starting Materials: Synthesis of 2,3-Allenoic Acid Esters 6b−e.[9,10] These compounds were synthesized according to the Wittig-type reactions shown in Scheme 10.

1. 2-Benzylbuta-2,3-dienoic Acid Ethyl Ester (6b). To a solution of **4b** (87.6 g, 0.2 mol) in dichloromethane (300 mL) was added a solution of Et_3N (36.2 mL, 0.26 mol) in 30 mL of dichloromethane dropwise within 45 min. After the solution was stirred for 5 min at rt, acetyl chloride **5b** (18.5 mL, 0.26 mol) in 20 mL of CH_2Cl_2 was added dropwise, and the solution was stirred overnight at rt. Then, the solvent was removed in vacuo. The residue was treated with 150 mL of ether and then filtered. The organic phase was combined and dried over anhydrous sodium sulfate. After evaporation, the residue was purified by flash chromatography on silica gel (eluent, 40:1 petroleum ether/ethyl acetate) to afford 19.4 g (56%) of

Scheme 11



2-benzylbuta-2,3-dienoic acid ethyl ester (**6b**): IR (neat) 2585, 1967, 1712, 1602, 1496, 1258 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.13−7.34 (m, 5 H), 5.08−5.14 (m, 2 H), 4.20 (q, J = 7.12 Hz, 2 H), 3.53−3.62 (m, 2 H), 1.26 (t, J = 7.02 Hz, 3 H).

2. 2-Methylhepta-2,3-dienoic Acid Ethyl Ester (6e). Starting from **4e** (19 g, 52.5 mmol) and **5e** (6.4 g, 53.1 mmol) afforded 7.6 g (86%) of **6e**: IR (neat) 2962, 1961, 1712, 1459, 1368, 1272 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.38−5.54 (m, 1 H), 4.08−4.26 (m, 2 H), 2.02−2.18 (m, 2 H), 1.83−1.91 (m, 3 H), 1.41−1.58 (m, 2 H), 1.27 (t, J = 7.33 Hz, 3 H), 0.98 (t, J = 7.33 Hz, 3 H); MS m/z (%) 168 (M^+, 12.23), 139 (100).

3. Compounds **6c** and **6d** are known compounds prepared as reported.[9,10]

Synthesis 2,3-Allen-1-ols 7b−e. Syntheses of 2,3-allenols **7** were performed by the reduction reaction of 2,3-allenoates **6** with DIBAL-H (Scheme 11).

1. Synthesis of 2-Benzylbuta-2,3-dien-1-ol (7b): Typical Procedure. A dry three-necked flask equipped with a magnetic stirring bar, and a dropping funnel was charged with **6b** (10.1 g, 50 mmol) in dry toluene (130 mL). The solution was rapidly stirred, and DIBAL-H (1.0 M solution in toluene, 105 mL, 2.1 equiv) was added dropwise at −78 °C under nitrogen. When the addition was complete, the mixture was stirred at −78 °C for 4 h. After the starting material **6b** disappeared completely as monitored by TLC, 50 mL of methanol was added to quench the reaction at 0 °C. Then, 150 mL of brine was added, and the mixture was stirred for 5 min, filtered, and separated; the aqueous layer was extracted with ether (3 × 50 mL). The combined ether layer was dried over anhydrous sodium sulfate. Evaporation and purification with flash chromatography on silica gel (eluent, 10:1 petroleum ether/ethyl acetate) afforded 5.3 g (67%) of **7b**:[11] liquid; IR (neat) 3347, 2912, 1951, 1599, 1491 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.05−7.50 (m, 5 H), 4.65−5.05 (m, 2 H), 4.03 (t, J = 2.59 Hz, 2 H), 3.39 (t, J = 2.59 Hz, 2 H), 1.50−1.89 (br s, 1 H); MS m/z (%) 160 (M^+, 59.43), 115 (100).

2. 2-Propylbuta-2,3-dien-1-ol (7c). Starting from **6c** (7.7 g, 50 mmol) afforded 2.94 g (53%) of **7c**:[12] liquid; IR (neat) 3387, 2962, 1958, 1723, 1459, 1179 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.71−4.98 (m, 2 H), 4.03 (t, J = 2.97 Hz, 2 H), 1.82−2.09 (m, 2 H), 1.57 (s, 1 H), 1.32−1.55 (m, 2 H), 0.98 (t, J = 7.34 Hz, 3 H); MS m/z (%) 112 (M^+, 3.68), 95 (100).

3. Deca-2,3-dien-1-ol (7d). Starting from **6d** (15.7 g, 80 mmol) afforded 1.64 g (13%) of **7d**. The yield was improved to 42% using the corresponding methyl ester: liquid; IR (neat) 3346, 2926, 1963, 1466, 1378, 1180, 1015 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.20−5.39 (m, 2 H), 4.00−4.20 (m, 2 H), 1.92−2.10 (m, 2 H), 1.55 (brs, 1 H), 1.10−1.40 (m, 8 H), 0.87 (t, J = 6.66 Hz, 3 H); MS m/z (%) 137 ($M^+ - CH_3$, 1.74), 84 (100).

4. 2-Methylhepta-2,3-dien-1-ol (7e). Starting from **6e** (2.6 g, 16.8 mmol) afforded 1.34 g (63%) of **7e**:[13] liquid; IR (neat) 3317, 2959, 1967, 1458, 1377 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.19−5.31 (m, 1 H), 3.98 (s, 2 H), 1.98 (dt, J = 7.08, 7.08 Hz, 2 H), 1.70 (d, J = 2.92 Hz, 3 H), 1.31−1.54 (m, 2 H), 0.92 (t, J = 7.34 Hz, 3 H); MS m/z (%) 126 (M^+, 6.86), 84 (100).

Synthesis of 2-(2′,3′-Dienyl)malonates 1. Compounds **1a−e** were prepared from the alkylation reaction of malonates with the corresponding bromide and NaH in THF as reported.[14] 2,3-Dienyl bromides were prepared from 2,3-dien-1-ols[15] and PBr_3 as reported.[16]

1. Methyl 2-(2′,3′-Butadienyl)malonate (1a).[17] Starting from 4-bromo-1,2-butadiene[16] (5.3 g, 40 mmol) afforded 5.15 g (70%) of **1a**: liquid; IR (neat) 2956, 1957, 1737, 1437, 1271 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.02−5.13 (m, 1 H), 4.61−4.72 (m, 2 H), 3.68 (s, 6 H), 3.45 (t, J = 7.34 Hz, 1 H), 2.48−2.59 (m, 2 H); MS m/z (%) 184 (M^+, 6.64), 93 (100).

2. Methyl 2-(2′-Benzyl-2′,3′-butadienyl)malonate (1b). Starting from 3-bromomethyl-4-phenyl-1,2-butadiene (4.2 g, 19 mmol) afforded 4.27 g (82%) of **1b**: liquid; IR (neat) 3029, 2955, 1960, 1737, 1602, 1493 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.15−7.36 (m, 5 H), 4.66 (br s, 2 H), 3.63 (s, 6 H), 3.50 (t, J = 7.59 Hz, 1 H), 3.26 (s, 2 H), 2.38−2.49 (m, 2 H); MS m/z (%) 274 (M^+, 0.49), 142 (100); HRMS m/z (EI) calcd for $C_{16}H_{18}O_4$ 274.12051, found 274.11866.

3. Methyl 2-(2′-Propyl-2′,3′-butadienyl)malonate (1c). Starting from 3-bromomethyl-1,2-hexadiene (3.15 g, 18 mmol) afforded 3.7 g (91%) of **1c**: liquid; IR (neat) 2957, 1958, 1755, 1739, 1436 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.65−4.76 (m, 2 H), 3.70 (s, 6 H), 3.57 (t, J = 7.56 Hz, 1 H), 2.47−2.56 (m, 2 H), 1.88−2.02 (m, 2 H), 1.33−1.50 (m, 2 H), 0.87 (t, J = 7.31 Hz, 3 H); MS m/z (%) 226 (M^+, 13.42), 79 (100); HRMS m/z (EI) calcd for $C_{12}H_{18}O_4$ 226.12051, found 226.12083.

4. Methyl 2-(Deca-2′,3′-dienyl)malonate (1d). Starting from 1-bromo-2,3-decadiene (1.09 g, 5.0 mmol) afforded 0.80 g (60%) of **1d**: liquid; IR (neat) 2955, 2929, 1960, 1756, 1739, 1436 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.98−5.18 (m, 2 H), 3.67 (s, 6 H), 3.44 (t, J = 7.52 Hz, 1 H), 2.43−2.55 (m, 2 H), 1.78−1.92 (m, 2 H), 1.13−1.38 (m, 8 H), 0.81 (t, J = 6.75 Hz, 3 H); MS m/z (%) 268 (M^+, 1.03), 138 (100); HRMS m/z (EI) calcd for $C_{15}H_{24}O_4$ 268.16746, found 268.16992.

5. Methyl 2-(2′-Methylhepta-2′,3′-dienyl)malonate (1e). Starting from 1-bromo-2-methyl-2,3-heptadiene (0.47 g, 2.46 mmol) afforded 0.31 g (53%) of **1e**: liquid; IR (neat) 2957, 1960, 1756, 1738, 1436 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.00−5.11 (m, 1 H), 3.72 (s, 6 H), 3.56 (dt, J = 7.40 and 1.34 Hz, 1 H), 2.56 (dd, J = 7.40, 3.05 Hz, 2 H), 1.88 (dt, J = 7.19, 7.19 Hz, 2 H), 1.69 (d, J = 2.57 Hz, 3 H), 1.26−1.42 (m, 2 H), 0.90 (t, J = 7.33 Hz, 3 H); MS m/z (%) 240 (M^+, 24.4), 93 (100); HRMS m/z (EI) calcd for $C_{13}H_{20}O_4$ 240.13616, found 240.13347.

Pd(0)-Catalyzed Coupling−Cyclization Reaction of 2-(2′,3′-Butadienyl)malonates with Organic Halides. Conditions A: Preparation of 1,1-Bis(methoxycarbonyl)-2-(1′-phenylethenyl)cyclopropane (2a). Typical Procedure. To a mixture of potassium carbonate (352 mg, 2.55 mmol), TBAB (20 mg, 0.064 mmol, 10 mol %), and $Pd(PPh_3)_4$ (37 mg, 0.032 mmol, 5 mol %) in CH_3CN (3 mL) were added dimethyl 2-(2′,3′-butadienyl)malonate **1a** (117 mg, 0.64 mmol) and iodobenzene (156 mg, 0.76 mmol, 1.2 equiv) subsequently under nitrogen. The resulting mixture was refluxed for 15 h as monitored by TLC. After filtration, washing with ether, and evaporation, the residue was purified by flash chromatography

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on silica gel (eluent, 20:1 petroleum ether/ethyl acetate) to afford 132 mg (80%) of **2a**.

Conditions B: Preparation of 1,1-Bis(methoxycarbonyl)-2-(1′-phenylethenyl)cyclopropane (2a). Typical Procedure. To a mixture of potassium carbonate (201 mg, 1.5 mmol, 4.0 equiv) and $Pd(PPh_3)_4$ (21 mg, 5 mol %) in THF (3 mL) were added subsequently dimethyl 2-(2′,3′-butadienyl)-malonate **1a** (67 mg, 0.36 mmol) and iodobenzene (96 mg, 0.47 mmol, 1.3 equiv) under nitrogen. Then, the resulting mixture was refluxed for 15.5 h as monitored by TLC. After filtration, washing with ether, and evaporation, the residue was purified by flash chromatography on silica gel (eluent, 20:1 petroleum ether/ethyl acetate) to afford 81 mg (85%) of **2a**.

Conditions C: Preparation of 1-Phenyl-2-benzyl-4,4-bis(methoxycarbonyl)cyclopentene (3i). Typical Procedure. To a mixture of NaH (60% dispersion in mineral oil, 7 mg, 1.1 equiv) and $Pd(PPh_3)_4$ (8.7 mg, 5 mol %) in dry DMSO (1.5 mL) were added subsequently dimethyl 2-(2′-benzyl-2′,3′-butadienyl)malonate **1b** (41 mg, 0.15 mmol) dropwise and iodobenzene (37 mg, 1.2 equiv) under nitrogen. The resulting mixture was heated at 85 °C for 12 h as monitored by TLC. Then, the reaction was quenched with an aqueous solution of saturated NaCl (2 mL) and the mixture extracted with ether (20 mL). The organic layer was washed with brine (3 × 8 mL) and dried over anhydrous sodium sulfate. After evaporation, the residue was purified by flash chromatography on silica gel (eluent, 10:1 petroleum ether/ethyl acetate) to afford 46 mg (88%) of **3i**.

Conditions D: Preparation of 1-Phenyl-4,4-bis(methoxycarbonyl)cyclopentene (3a). Typical Procedure. To a mixture of anhydrous sodium hydroxide (20 mg, 0.5 mmol, 2.0 equiv) and $Pd(PPh_3)_4$ (14.5 mg, 5 mol %) in anhydrous DMF (2.0 mL) were added subsequently dimethyl 2-(2′,3′-butadienyl)malonate **1a** (46 mg, 0.25 mmol) dropwise and iodobenzene (61 mg, 1.2 equiv) under nitrogen. The resulting mixture was heated at 85 °C for 10.5 h as monitored by TLC. Then, 30 mL of ether was added, and the solution was washed with brine (3 × 8 mL), dried over anhydrous sodium sulfate, and filtered. The solvent was removed in vacuo, and the residue was purified via flash chromatography on silica gel (eluent, 20:1 petroleum ether/ethyl acetate) to afford 43 mg (66%) of **3a**.

1. 1,1-Bis(methoxycarbonyl)-2-(1′-phenylethenyl)cyclopropane (2a). Starting from **1a** (117 mg, 0.64 mmol) and PhI (157 mg, 0.77 mmol) afforded 132 mg (80%) of **2a** using Conditions A; starting from **1a** (67 mg, 0.36 mmol) and PhI (96 mg, 0.47 mmol) afforded 81 mg (85%) of **2a** using Conditions B: liquid; IR (neat) 1624, 1728 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, J = 8.17 Hz, 2 H), 7.20−7.40 (m, 3 H), 5.51 (s, 1 H), 5.05 (s, 1 H), 3.78 (s, 3 H), 3.44 (s, 3 H), 2.99 (t, J = 8.05 Hz, 1 H), 2.04 (dd, J = 8.05 and 5.15 Hz, 1 H), 1.60 (dd, J = 8.05 and 5.15 Hz, 1 H); MS m/z (%) 260 (M^+, 2.91), 200 (100); HRMS m/z (EI) calcd for $C_{15}H_{16}O_4$ 260.1049, found 260.1053.

2. 1,1-Bis(methoxycarbonyl)-2-(1′-(4″-bromophenyl)-ethenyl)cyclopropane (2b). Starting from **1a** (100 mg, 0.543 mmol) and 4-bromophenyl iodide (183 mg, 0.65 mmol) afforded 184 mg (purity 87%, yield 87%) of **2b** using Conditions A; starting from **1a** (79 mg, 0.429 mmol) and 4-bromophenyl iodide (158 mg, 0.556 mmol) afforded 111 mg (76%) of **2b** using Conditions B: liquid; IR (neat) 1585, 1622, 1716 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, J = 8.62 Hz, 2 H), 7.33 (d, J = 8.62 Hz, 2 H), 5.50 (s, 1 H), 5.07 (s, 1 H), 3.78 (s, 3 H), 3.47 (s, 3 H), 2.92 (t, J = 8.54 Hz, 1 H), 2.02 (dd, J = 8.54 and 5.34 Hz, 1 H), 1.59 (dd, J = 8.54 and 5.34 Hz, 1 H); MS m/z (%) 340 ($M(^{81}Br)^+$, 4.50), 338 ($M(^{79}Br)^+$, 4.65), 278(100); HRMS m/z (EI) calcd for $C_{15}H_{15}BrO_4$ 338.0154, found 338.0148.

3. 1,1-Bis(methoxycarbonyl)-2-(1′-(4″-methylphenyl)-ethenyl)cyclopropane (2c). Starting from **1a** (140 mg, 0.76 mmol) and 4-iodotoluene (199 mg, 0.91 mmol) afforded 170 mg (82%) of **2c** using Conditions A; starting from **1a** (92 mg, 0.50 mmol) and 4-iodotoluene(131 mg, 0.65 mmol) afforded 78 mg (57%) of **2c** using Conditions B: liquid; IR (neat) 1606, 1732 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, J = 7.95 Hz, 2 H), 7.12 (d, J = 7.95 Hz, 2 H), 5.47 (s, 1 H), 5.00 (s, 1 H), 3.78 (s, 3 H), 3.46 (s, 3 H), 2.98 (t, J = 8.52 Hz, 1 H), 2.32 (s, 3 H), 2.05 (dd, J = 8.52, 5.02 Hz, 1 H), 1.63 (dd, J = 8.52, 5.02 Hz, 1 H); MS m/z (%) 274 (M^+, 6.36), 155 (100); HRMS m/z (EI) calcd for $C_{16}H_{18}O_4$ 274.1205, found 274.1205.

4. 1,1-Bis(methoxycarbonyl)-2-(1′-(4″-methoxyphenyl)-ethenyl)cyclopropane (2d). Starting from **1a** (118 mg, 0.641 mmol) and 4-iodoanisole (180 mg, 0.769 mmol) afforded 128 mg (69%) of **2d** using Conditions A; starting from **1a** (105 mg, 0.571 mmol) and 4-iodoanisole (174 mg, 0.742 mmol) afforded 98 mg (59%) of **2d** using Conditions B: liquid; IR (neat) 1606, 1724 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, J = 7.06 Hz, 2 H), 6.86 (d, J = 7.06 Hz, 2 H), 5.43 (s, 1 H), 4.97 (s, 1 H), 3.82 (s, 3 H), 3.80 (s, 3 H), 3.47 (s, 3 H), 2.97 (t, J = 8.00 Hz, 1 H), 2.06 (dd, J = 8.00, 5.04 Hz, 1 H), 1.59 (dd, J = 8.00, 5.04 Hz, 1 H); MS m/z (%) 290 (M^+, 9.31), 230 (100); HRMS m/z (EI) calcd for $C_{16}H_{18}O_5$ 290.1154, found 290.1145.

5. (*E*)-1,1-Bis(methoxycarbonyl)-2-(1′-methylene-3′-phenyl-2′-propenyl)cyclopropane (2e). Starting from **1a** (94 mg, 0.511 mmol) and (*E*)-1-iodo-2-phenylethylene[18] (141 mg, 0.613 mmol) afforded 67 mg (46%) of **2e** using Conditions A; starting from **1a** (101 mg, 0.549 mmol) and (*E*)-1-iodo-2-phenylethylene (164 mg, 0.714 mmol) afforded 71 mg (45%) of **2e** using Conditions B: liquid; IR (neat) 1603, 1730 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.10−7.38 (m, 5 H), 6.71 (s, 2 H), 5.21 (s, 1 H), 5.02 (s, 1 H), 3.75 (s, 3 H), 3.49 (s, 3 H), 2.81 (t, J = 8.40 Hz, 1 H), 1.95 (dd, J = 8.40, 4.97 Hz, 1 H), 1.48 (dd, J = 8.40, 4.97 Hz, 1 H); MS m/z (%) 286 (M^+, 9.77), 167 (100); HRMS m/z (EI) calcd for $C_{17}H_{18}O_4$ 286.1205, found 286.1198.

6. 1,1-Bis(methoxycarbonyl)-2-(1′-naphthylethenyl)cyclopropane (2f). Starting from **1a** (97 mg, 0.527 mmol) and 1-iodonaphthalene[19] (162 mg, 0.632 mmol) afforded 166 mg (purity 93%, yield 95%) of **2f** using Conditions A; starting from **1a** (80 mg, 0.435 mmol) and 1-iodonaphthalene (133 mg, 0.566 mmol) afforded 122 mg (91%) of **2f** using Conditions B: liquid; IR (neat) 1580, 1625, 1723 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.10−8.15 (m, 7 H), 5.44 (s, 1 H), 5.32 (s, 1 H), 3.69 (s, 3 H), 3.61 (s, 3 H), 3.07 (t, J = 8.53 Hz, 1 H), 1.95 (dd, J = 8.53, 5.06 Hz, 1 H), 1.64 (dd, J = 8.53, 5.06 Hz, 1 H); MS m/z (%) 310 (M^+, 5.39), 191 (100); HRMS m/z (EI) calcd for $C_{19}H_{18}O_4$ 310.1205, found 310.1244.

7. 1,1-Bis(methoxycarbonyl)-2-(1′-(4″-methoxycarbonylphenyl)ethenyl)cyclopropane (2g). Starting from **1a** (120 mg, 0.652 mmol) and 4-iodobenzoic acid methyl ester[20] (199 mg, 0.76 mmol) afforded 120 mg (58%) of **2g** using Conditions A; starting from **1a** (82 mg, 0.446 mmol) and 4-iodobenzoic acid methyl ester (152 mg, 0.58 mmol) afforded 103 mg (73%) of **2g** using Conditions B: liquid; IR (neat) 1608, 1727 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, J = 8.44 Hz, 2 H), 7.52 (d, J = 8.44 Hz, 2 H), 5.62 (s, 1 H), 5.17 (s, 1 H), 3.90 (s, 3 H), 3.79 (s, 3 H), 3.43 (s, 3 H), 2.98 (t, J = 8.52 Hz, 1 H), 2.03 (dd, J = 8.52, 5.15 Hz, 1 H), 1.63 (dd, J = 8.52, 5.15 Hz, 1 H); MS m/z (%) 318 (M^+, 1.08), 258 (100); HRMS m/z (EI) calcd for $C_{17}H_{18}O_6$ 318.1103, found 318.1098.

8. (*E*)-1,1-Bis(methoxycarbonyl)-2-(1′-methylene-2′-heptenyl)cyclopropane (2h). Starting from **1a** (94 mg, 0.511 mmol) and (*E*)-1-iodo-1-hexene[21] (129 mg, 0.613 mmol) afforded 91 mg (67%) of **2h** using Conditions A; starting from **1a** (95 mg, 0.516 mmol) and (*E*)-1-iodo-1-hexene (141 mg, 0.67 mmol) afforded **2h** (84 mg, yield 61%) using Conditions B: liquid; IR (neat) 1607, 1647, 1730 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.00 (d, J = 16.36 Hz, 1 H), 5.80 (dt, J = 16.36, 6.82 Hz, 1 H), 4.95 (s, 1 H), 4.79 (s, 1 H), 3.71 (s, 3 H), 3.53 (s, 3 H), 2.69 (t, J = 8.18 Hz, 1 H), 2.01 (q, J = 6.74 Hz, 2 H), 1.88 (dd, J = 8.18, 4.88 Hz, 1 H), 1.41 (dd, J = 8.18, 4.88 Hz, 1 H), 1.10−1.35 (m, 4 H), 0.87 (t, J = 7.02 Hz, 3 H); MS m/z (%) 91 (100),

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265 ($M^+ - 1$, 0.52); HRMS *m/z* (EI) calcd for $C_{15}H_{22}O_4$ 266.1518, found 266.1516.

9. 1,1-Bis(methoxycarbonyl)-2-benzyl-2-(1′-phenylethenyl)cyclopropane (2i). Starting from **1b** (41 mg, 0.15 mmol) and PhI (37 mg, 0.18 mmol) afforded 41 mg (80%) of **2i** using Conditions A: liquid; IR (neat) 3030, 2954, 1735, 1601, 1493, 1432, 1370 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.41−7.55 (m, 2 H), 7.10−7.38 (m, 6 H), 6.87−6.98 (m, 2 H), 5.52 (s, 1 H), 4.98 (s, 1 H), 3.90 (s, 3 H), 3.50 (s, 3 H), 3.26 (AB, A part of AB, J = 13.72 Hz, $\Delta\nu$ = 290.15 Hz, 1 H), 2.30 (AB, B part of AB, J = 13.72 Hz, $\Delta\nu$ = 290.15 Hz, 1 H), 2.00 (AB, A part of AB, J = 5.46 Hz, $\Delta\nu$ = 29.57 Hz, 1 H), 1.91 (AB, B part of AB, J = 5.46 Hz, $\Delta\nu$ = 29.57 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 168.1, 143.8, 138.5, 138.4, 129.7, 128.5, 128.2, 127.8, 127.0, 126.8, 118.2, 53.1, 52.7, 42.4, 41.4, 40.7, 23.9; MS *m/z* (%) 350 (M^+, 1.29), 231 (100); HRMS *m/z* (EI) calcd for $C_{22}H_{22}O_4$ 350.15181, found 350.14733.

10. 1,1-Bis(methoxycarbonyl)-2-benzyl-2-(1′-(4″-methoxyphenyl)ethenyl)cyclopropane (2j). Starting from **1b** (41 mg, 0.15 mmol) and 4-iodoanisole (42 mg, 0.18 mmol) afforded 36 mg (63%) of **2j** using Conditions A: viscous liquid; IR (neat) 3029, 2952, 1725, 1607, 1513, 1435 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, J = 8.75 Hz, 2 H), 7.05−7.16 (m, 3 H), 6.73−6.88 (m, 4 H), 5.34 (s, 1 H), 4.70 (s, 1 H), 3.82 (s, 3 H), 3.74 (s, 3 H), 3.43 (s, 3 H), 3.17 (AB, A part of AB, J = 13.68 Hz, $\Delta\nu$ = 294.18 Hz, 1 H), 2.19 (AB, B part of AB, J = 13.68 Hz, $\Delta\nu$ = 294.18 Hz, 1 H), 1.92 (AB, A part of AB, J = 5.45 Hz, $\Delta\nu$ = 31.40 Hz, 1 H), 1.82 (AB, B part of AB, J = 5.45 Hz, $\Delta\nu$ = 31.40 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.9, 168.1, 159.4, 143.1, 138.5, 131.0, 129.6, 128.2, 126.7, 116.3, 113.9, 55.5, 53.1, 52.7, 42.6, 41.3, 40.6, 23.8; MS *m/z* (%) 380 (M^+, 21.34), 229 (100); HRMS *m/z* (EI) calcd for $C_{23}H_{24}O_5$ 380.16238, found 380.16477.

11. 1,1-Bis(methoxycarbonyl)-2-benzyl-2-(1′-(4″-methoxycarbonyl)phenyl-ethenyl)cyclopropane (2k). Starting from **1b** (41 mg, 0.15 mmol) and 4-iodobenzoic acid methyl ester (47 mg, 0.18 mmol) afforded 50 mg (82%) of **2k**, and 10 mg (16%) of **3k** using Conditions A. **2k**: viscous liquid; IR (neat) 2952, 1724, 1608, 1435, 1281 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, J = 8.42 Hz, 2 H), 7.46 (d, J = 8.42 Hz, 2 H), 7.03−7.17 (m, 3 H), 6.77−6.90 (m, 2 H), 5.56 (s, 1 H), 4.94 (s, 1 H), 3.85 (s, 3 H), 3.84 (s, 3 H), 3.44 (s, 3 H), 3.17 (AB, A part of AB, J = 13.80 Hz, $\Delta\nu$ = 279.00 Hz, 1 H), 2.24 (AB, B part of AB, J = 13.80 Hz, $\Delta\nu$ = 279.00 Hz, 1 H), 1.91 (AB, J = 5.38 Hz, $\Delta\nu$ = 13.85 Hz, 2 H); MS *m/z* (%) 408 (M^+, 6.69), 348 (100); HRMS *m/z* (EI) calcd for $C_{24}H_{24}O_6$ 408.15729, found 408.15967.

12. (*E*)-1,1-Bis(methoxycarbonyl)-2-benzyl-2-(1′-methylene-3′-phenyl-2′-propenyl)cyclopropane (2l). Starting from **1b** (68 mg, 0.25 mmol) and (*E*)-1-iodo-2-phenylethylene (69 mg, 0.3 mmol) afforded 79 mg (84%) of **2l** using Conditions A: viscous liquid; IR (neat) 3027, 2951, 1734, 1603, 1495, 1435 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, J = 7.22 Hz, 2 H), 7.23−7.31 (m, 2 H), 7.07−7.22 (m, 5 H), 6.96−7.07 (m, 2 H), 6.60 (d, J = 16.64 Hz, 1 H), 5.11 (s, 1 H), 4.63 (s, 1 H), 3.87 (s, 3 H), 3.45 (s, 3 H), 3.31 (AB, A part of AB, J = 13.61 Hz, $\Delta\nu$ = 342.50 Hz, 1 H), 2.17 (AB, B part of AB, J = 13.61 Hz, $\Delta\nu$ = 342.50 Hz, 1 H), 1.81 (AB, J = 3.60 Hz, $\Delta\nu$ = 12.00 Hz, 2 H); MS *m/z* (%) 376 (M^+, 7.07), 165 (100); HRMS *m/z* (EI) calcd for $C_{24}H_{24}O_4$ 376.16746, found 376.16917.

13. (*E*)-1,1-Bis(methoxycarbonyl)-2-benzyl-2-(1′-methylene-2′-heptenyl)cyclopropane (2m). Starting from **1b** (71 mg, 0.26 mmol) and (*E*)-1-iodo-1-hexene (66 mg, 0.31 mmol) afforded 60 mg (67%) of **2m** using Conditions A: viscous liquid; IR (neat) 2954, 1736, 1434, 1240 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.08−7.20 (m, 3 H), 6.91−7.01 (m, 2 H), 6.12 (dt, J = 15.98, 7.00 Hz, 1 H), 5.86 (d, J = 15.98 Hz, 1 H), 4.87 (s, 1 H), 4.44 (s, 1 H), 3.80 (s, 3 H), 3.54 (s, 3 H), 3.24 (d, J = 13.50 Hz, 1 H), 1.98−2.30 (m, 3 H), 1.73 (AB, J = 5.15 Hz, $\Delta\nu$ = 18.35 Hz, 2 H), 1.15−1.41 (m, 4 H), 0.77−0.92 (m, 3 H); MS *m/z* (%) 356 (M^+, 9.84), 91 (100); HRMS *m/z* (EI) calcd for $C_{22}H_{28}O_4$ 356.19876, found 356.19623.

14. (*Z*)-1,1-Bis(methoxycarbonyl)-2-benzyl-2-(1′-methylene-2′-heptenyl)cyclopropane (2n). Starting from **1b** (41 mg, 0.15 mmol) and (*Z*)-1-iodo-1-hexene[22] (38 mg, 0.18 mmol) afforded 23 mg (45%) of **2n** using Conditions A: viscous liquid; IR (neat) 2954, 1736, 1435, 1264 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.98−7.23 (m, 5 H), 5.68 (d, J = 11.78 Hz, 1 H), 5.51 (dt, J = 11.78, 6.98 Hz, 1 H), 4.89 (s, 1 H), 4.79 (s, 1 H), 3.75 (s, 3 H), 3.58 (s, 3 H), 3.07 (AB, A part of AB, J = 13.98 Hz, $\Delta\nu$ = 187.67 Hz, 1 H), 2.45 (AB, B part of AB, J = 13.98 Hz, $\Delta\nu$ = 187.67 Hz, 1 H), 1.86−1.97 (m, 3 H), 1.76 (d, J = 5.44 Hz, 1 H), 1.12−1.29 (m, 4 H), 0.74−0.86 (m, 3 H); MS *m/z* (%) 356 (M^+, 1.47), 91 (100); HRMS *m/z* (EI) calcd for $C_{22}H_{28}O_4$ 356.19876, found 356.19738.

15. 1,1-Bis(methoxycarbonyl)-2-benzyl-2-(1′-(2″-thienyl)-ethenyl)cyclopropane (2o). Starting from **1b** (68 mg, 0.25 mmol) and 2-iodothiophene[23] (63 mg, 0.3 mmol) afforded 86 mg (97%) of **2o** using Conditions A: viscous liquid; IR (neat) 3028, 2952, 1735, 1602, 1495, 1435 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.75−7.32 (m, 8 H), 5.37 (s, 1 H), 4.56 (s, 1 H), 3.84 (s, 3 H), 3.42 (s, 3 H), 3.32 (AB, A part of AB, J = 13.49 Hz, $\Delta\nu$ = 345.48 Hz, 1 H), 2.17 (AB, B part of AB, J = 13.49 Hz, $\Delta\nu$ = 345.48 Hz, 1 H), 1.87 (AB, J = 5.23 Hz, $\Delta\nu$ = 20.31 Hz, 2 H); MS *m/z* (%) 356 (M^+, 10.66), 354 (100); HRMS *m/z* (EI) calcd for $C_{20}H_{20}O_4S$ 356.10823, found 356.10914.

16. 1,1-Bis(methoxycarbonyl)-2-propyl-2-(1′-phenylethenyl)cyclopropane (2p). Starting from **1c** (56.5 mg, 0.25 mmol) and PhI (61 mg, 0.3 mmol) afforded 58 mg (77%) of **2p** using Conditions A: viscous liquid; IR (neat) 2941, 1740, 1433 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, J = 8.69 Hz, 2 H), 7.15−7.32 (m, 3 H), 5.62 (s, 1 H), 5.14 (s, 1 H), 3.78 (s, 3 H), 3.43 (s, 3 H), 1.82−2.00 (m, 2 H), 1.44−1.47 (m, 2 H), 1.12−1.35 (m, 2 H), 0.66−0.81 (m, 3 H); MS *m/z* (%) 302 (M^+, 30.80), 242 (100); HRMS *m/z* (EI) calcd for $C_{18}H_{22}O_4$ 302.15181, found 302.15451.

17. 1,1-Bis(methoxycarbonyl)-2-propyl-2-(1′-(4″-methoxyphenyl)ethenyl)cyclopropane (2q). Starting from **1c** (56.5 mg, 0.25 mmol) and 4-iodoanisole (70 mg, 0.3 mmol) afforded 37 mg (45%) of **2q** using Conditions A: IR (neat) 2956, 1737, 1608, 1514, 1435 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.49 (d, J = 6.77 Hz, 2 H), 6.80 (d, J = 6.77 Hz, 2 H), 5.51 (s, 1 H), 5.04 (s, 1 H), 3.77 (s, 3 H), 3.75 (s, 3 H), 3.42 (s, 3 H), 1.80−2.00 (m, 2 H), 1.48−1.55 (m, 2 H), 1.08−1.28 (m, 2 H), 0.71 (t, J = 7.33 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.9, 168.2, 159.3, 143.3, 130.8, 128.0, 115.0, 113.8, 55.4, 52.9, 52.6, 41.7, 41.0, 36.8, 24.1, 20.6, 14.0; MS *m/z* (%) 332 (M^+, 78.78), 272 (100); HRMS *m/z* (EI) calcd for $C_{19}H_{24}O_5$ 332.16238, found 332.16497.

18. 1,1-Bis(methoxycarbonyl)-2-propyl-2-(1′-(4″-methoxycarbonylphenyl) ethenyl)cyclopropane (2r). Starting from **1c** (56.5 mg, 0.25 mmol) and 4-iodobenzoic acid methyl ester (79 mg, 0.3 mmol) afforded 64 mg (71%) of **2r** using Conditions A: viscous liquid; IR (neat) 2955, 1725, 1608, 1435, 1279 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, J = 8.49 Hz, 2 H), 7.68 (d, J = 8.49 Hz, 2 H), 5.78 (s, 1 H), 5.31 (s, 1 H), 3.88 (s, 3 H), 3.84 (s, 3 H), 3.48 (s, 3 H), 1.80−2.12 (m, 2 H), 1.48−1.72 (m, 2 H), 1.12−1.38S (m, 2 H), 0.76 (t, J = 7.30 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.6, 168.1, 167.1, 143.3, 142.9, 129.8, 129.3, 126.7, 118.9, 53.0, 52.7, 52.3, 41.2, 41.1, 36.7, 24.1, 20.6, 14.0; MS *m/z* (%) 360 (M^+, 21.45), 300 (100); HRMS *m/z* (EI) calcd for $C_{20}H_{24}O_6$ 360.15729, found 360.15819.

19. (*E*)-1,1-Bis(methoxycarbonyl)-2-propyl-2-(1′-methylene-3′-phenyl-2-propenyl)cyclopropane (2s). Starting from **1c** (56.5 mg, 0.25 mmol) and (*E*)-1-iodo-2-phenylethylene (69 mg, 0.3 mmol) afforded 62 mg (71%) of **2s** using Conditions A: viscous liquid; IR (neat) 2956, 1736, 1608, 1435, 1222 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.11−7.44 (m, 5 H), 7.02 (d, J = 16.57 Hz, 1 H), 6.61 (d, J = 16.57 Hz, 1 H), 5.31 (s, 1 H), 5.12 (s, 1 H), 3.81 (s, 3 H), 3.43 (s, 3 H), 1.98−2.10 (m, 1 H), 1.83 (AB, A part of AB, J = 4.62 Hz, $\Delta\nu$ = 109.83 Hz, 1 H), 1.47 (AB, B part of AB, J = 4.62 Hz, $\Delta\nu$ = 109.83 Hz, 1 H), 1.10−1.41 (m, 2 H), 0.78 (t, J = 7.34 Hz, 3 H), 0.58−0.72 (m, 1 H);

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MS *m*/*z* (%) 328 (M^+, 10.75), 268 (100); HRMS *m*/*z* (EI) calcd for $C_{20}H_{24}O_4$ 328.16746, found 328.17123.

20. (*E*)-1,1-Bis(methoxycarbonyl)-2-propyl-2-(1′-methylene-2′-heptenyl)cyclopropane(2t). Starting from **1c** (56.5 mg, 0.25 mmol) and (*E*)-1-iodo-1-hexene (63 mg, 0.3 mmol) afforded 54 mg (70%) of **2t** using Conditions A: viscous liquid; IR (neat) 2957, 1738, 1435, 1222 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.13 (dt, J = 15.92, 7.08 Hz, 1 H), 5.92 (d, J = 15.92 Hz, 1 H), 5.11 (s, 1 H), 4.96 (s, 1 H), 3.79 (s, 3 H), 3.57 (s, 3 H), 1.92−2.14 (m, 4 H), 1.81 (AB, A part of AB, J = 4.89 Hz, $\Delta\nu$ = 109.51 Hz, 1 H), 1.45 (AB, B part of AB, J = 4.89 Hz, $\Delta\nu$ = 109.51 Hz, 1 H), 1.11−1.41 (m, 5 H), 0.89 (t, J = 7.06 Hz, 3 H), 0.82 (t, J = 7.34 Hz, 3 H), 0.58−0.72 (m, 1 H); MS *m*/*z* (%) 308 (M^+, 7.96), 41 (100); HRMS *m*/*z* (EI) calcd for $C_{18}H_{28}O_4$ 308.19876, found 308.19912.

21. (*Z*)-1,1-Bis(methoxycarbonyl)-2-propyl-2-(1′-methylene-2′-heptenyl)cyclopropane (2u). Starting from **1c** (56.5 mg, 0.25 mmol) and (*Z*)-1-iodo-1-hexene (63 mg, 0.3 mmol) afforded 44 mg (57%) of **2u** using Conditions A: viscous liquid; IR (neat) 2957, 1738, 1435, 1223, 1120 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.67 (d, J = 11.78 Hz, 1 H), 5.51 (dt, J = 11.78, 7.05 Hz, 1 H), 5.06 (s, 1 H), 5.05 (s, 1 H), 3.70 (s, 3 H), 3.56 (s, 3 H), 2.03−2.26 (m, 2 H), 1.86 (AB, A part of AB, dd, J = 5.19, 1.58 Hz, $\Delta\nu$ = 132.63 Hz, 1 H), 1.42 (AB, B part of AB, J = 5.19 Hz, $\Delta\nu$ = 132.63 Hz, 1 H), 1.71−1.82 (m, 1 H), 1.10−1.37 (m, 6 H), 0.71−0.95 (m, 7 H); MS *m*/*z* (%) 308 (M^+, 6.28), 248 (100); HRMS *m*/*z* (EI) calcd for $C_{18}H_{28}O_4$ 308.19876, found 308.19952.

22. 1,1-Bis(methoxycarbonyl)-2-propyl-2-(1′-(2″-thienyl)ethenyl)cyclopropane (2v). Starting from **1c** (56.5 mg, 0.25 mmol) and 2-iodothiophene (63 mg, 0.3 mmol) afforded 61 mg (79%) of **2v** using Conditions A: viscous liquid; IR (neat) 2956, 1737, 1620, 1435, 1223 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, J = 2.94 Hz, 1 H), 7.13 (dd, J = 2.94, 0.86 Hz, 1 H), 6.93−7.00 (m, 1 H), 5.63 (s, 1 H), 5.08 (s, 1 H), 3.80 (s, 3 H), 3.46 (s, 3 H), 2.02−2.17 (m, 1 H), 1.92 (AB, A part of AB, dd, J = 5.10, 1.7 Hz, $\Delta\nu$ = 119.95 Hz, 1 H), 1.52 (AB, B part of AB, J = 5.10 Hz, $\Delta\nu$ = 119.95 Hz, 1 H), 1.13−1.41 (m, 2 H), 0.81 (t, J = 7.35 Hz, 3 H), 0.63−0.77 (m, 1 H); MS *m*/*z* (%) 308 (M^+, 8.49), 219 (100); HRMS *m*/*z* (EI) calcd for $C_{16}H_{20}O_4S$ 308.10823, found 308.10760.

23. 1,1-Bis(methoxycarbonyl)-2-((1′-phenyl)oct-1′-enyl)-cyclopropane (2w). Starting from **1d** (40.2 mg, 0.15 mmol) and PhI (37 mg, 0.18 mmol) afforded 37 mg (72%) of **2w** and 3 mg (6%) of **3w** using Conditions A. **2w**: viscous liquid; IR (neat) 2926, 1730, 1437, 1281, 1130 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) ***E*-isomer** δ 6.99−7.28 (m, 5 H), 5.79 (dt, J = 7.28, 1.84 Hz, 1 H), 3.72 (s, 3 H), 3.31 (s, 3 H), 2.95 (t, J = 8.88 Hz, 1 H), 2.10−2.31 (m, 2 H), 1.72 (AB, A part of AB, dd, J = 8.88, 4.74 Hz, $\Delta\nu$ = 23.48 Hz, 1 H), 1.64 (AB, B part of AB, dd, J = 8.88, 4.74 Hz, $\Delta\nu$ = 23.48 Hz, 1 H), 1.00−1.39 (m, 8 H), 0.83 (t, J = 6.42 Hz, 3 H); ***Z*-isomer** δ 6.99−7.28 (m, 5 H), 5.45 (t, J = 7.46, Hz, 1 H), 3.65 (s, 3 H), 3.53 (s, 3 H), 2.82 (t, J = 8.72 Hz, 1 H), 1.83−1.97 (m, 3 H), 1.40−1.51 (m, 1 H), 1.00−1.39 (m, 8 H), 0.78 (t, J = 6.86 Hz, 3 H); MS *m*/*z* (%) 344 (M^+, 6.34), 141 (100); HRMS *m*/*z* (EI) calcd for $C_{21}H_{28}O_4$ 344.19876, found 344.20307.

24. 1,1-Bis(methoxycarbonyl)-2-(1′-(4″-methylphenyl)-oct-1′-enyl)cyclopropane (2x). Starting from **1d** (40.2 mg, 0.15 mmol) and 4-iodotoluene (43 mg, 0.19 mmol) afforded 47 mg (88%) of **2x** and 2 mg (4%) of **3x** using Conditions A. **2x**: viscous liquid; IR (neat) 2924, 1731, 1513, 1437, 1281 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) ***E*-isomer** δ 6.94−7.26 (m, 4 H), 5.75 (dt, J = 7.27, 1.95 Hz, 1 H), 3.71 (s, 3 H), 3.33 (s, 3 H), 2.93 (t, J = 8.70 Hz, 1 H), 2.24 (s, 3 H), 2.05−2.21 (m, 2 H), 1.71 (AB, A part of AB, dd, J = 8.70, 4.73 Hz, $\Delta\nu$ = 26.24 Hz, 1 H), 1.63 (AB, B part of AB, dd, J = 8.70, 4.73 Hz, $\Delta\nu$ = 26.24 Hz, 1 H), 1.05−1.45 (m, 8 H), 0.80 (t, J = 6.70 Hz, 3 H); ***Z*-isomer** δ 6.94−7.26 (m, 4 H), 5.39 (dt, J = 7.44, 1.16 Hz, 1 H), 3.65 (s, 3 H), 3.51 (s, 3 H), 2.79 (dt, J = 8.99, 1.05 Hz, 1 H), 2.25 (s, 3 H), 1.84−1.96 (m, 3 H), 1.43 (AB, B part of AB, dd, J = 8.99, 5.04 Hz, 1 H), 1.05−1.45 (m, 8 H), 0.76 (t, J = 6.86 Hz, 3 H); MS *m*/*z* (%) 358 (M^+, 11.97), 298 (100); HRMS *m*/*z* (EI) calcd for $C_{22}H_{30}O_4$ 358.21441, found 358.21098.

25. 1,1-Bis(methoxycarbonyl)-2-(1′-(4″-methoxyphenyl)-oct-1′-enyl)cyclopropane (2y). Starting from **1d** (40.2 mg, 0.15 mmol) and 4-iodoanisole (42 mg, 0.18 mmol) afforded 32 mg (57%) of **2y** and 5 mg (9%) of **3y** using Conditions A. **2y**: viscous liquid; IR (neat) 2953, 1730, 1608, 1512, 1437, 1283 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) ***E*-isomer** δ 7.08 (d, J = 8.81 Hz, 2 H), 6.74 (d, J = 8.81 Hz, 2 H), 5.71 (dt, J = 7.24, 1.98 Hz, 1 H), 3.72 (s, 3 H), 3.71 (s, 3 H), 3.34 (s, 3 H), 2.92 (t, J = 8.94 Hz, 1 H), 2.07−2.30 (m, 2 H), 1.72 (AB, A part of AB, dd, J = 8.94, 4.72 Hz, $\Delta\nu$ = 27.67 Hz, 1 H), 1.63 (AB, B part of AB, dd, J = 8.94, 4.72 Hz, $\Delta\nu$ = 27.67 Hz, 1 H), 1.04−1.35 (m, 8 H), 0.82 (t, J = 6.54 Hz, 3 H); ***Z*-isomer** δ 7.04 (d, J = 8.52 Hz, 2 H), 6.79 (d, J = 8.52 Hz, 2 H), 5.39 (dt, J = 7.37, 1.07 Hz, 1 H), 3.73 (s, 3 H), 3.64 (s, 3 H), 3.52 (s, 3 H), 2.79 (dt, J = 8.92, 1.07 Hz, 1 H), 1.80−1.98 (m, 3 H), 1.45 (AB, B part of AB, dd, J = 8.92, 5.04 Hz, 1 H), 1.04−1.35 (m, 8 H), 0.77 (t, J = 6.78 Hz, 3 H); MS *m*/*z* (%) 374 (M^+, 19.55), 44 (100); HRMS *m*/*z* (EI) calcd for $C_{22}H_{30}O_5$ 374.20932, found 374.21264.

26. 1,1-Bis(methoxycarbonyl)-2-(1′-(4″-methoxycarbonylphenyl)oct-1′-enyl)cyclopropane (2z). Starting from **1d** (40.2 mg, 0.15 mmol) and 4-iodobenzoic acid methyl ester (48 mg, 0.18 mmol) afforded 43 mg (71%) of **2z** and 5 mg (8%) of **3z** using Conditions A. **2z**: viscous liquid; IR (neat) 2953, 1726, 1607, 1437, 1278 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) ***E*-isomer:** δ 7.93 (d, J = 8.20 Hz, 2 H), 7.18 (d, J = 8.20 Hz, 2 H), 5.90 (dt, J = 7.25 and 1.99 Hz, 1 H), 3.83 (s, 3 H), 3.72 (s, 3 H), 3.00 (s, 3 H), 2.95 (t, J = 9.14 Hz, 1 H), 2.11−2.35 (m, 2 H), 1.61−1.73 (m, 2 H), 0.94−1.37 (m, 8 H), 0.82 (t, J = 6.84 Hz, 3 H); ***Z*-isomer:** δ 7.88 (d, J = 8.52 Hz, 2 H), 7.24 (d, J = 8.52 Hz, 2 H), 5.51 (t, J = 7.62 Hz, 1 H), 3.85 (s, 3 H), 3.65 (s, 3 H), 3.52 (s, 3 H), 2.81 (t, J = 8.56 Hz, 1 H), 1.80−1.97 (m, 3 H), 1.38−1.53 (m, 1 H), 0.94−1.37 (m, 8 H), 0.77 (t, J = 6.93 Hz, 3 H); MS *m*/*z* (%) 402 (M^+, 3.79), 342 (100); HRMS *m*/*z* (EI) calcd for $C_{23}H_{30}O_6$ 402.20424, found 402.20062. **1-(4′-Methoxycarbonylphenyl)-4,4-bis(methoxycarbonyl)-5-(*n*-hexyl)cyclopentene (3z)**: viscous liquid; IR (neat) 2953, 1735, 1607, 1435, 1280 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, J = 7.85 Hz, 2 H), 7.43 (d, J = 7.85 Hz, 2 H), 5.93 (s, 1 H), 3.88−4.01 (m, 1 H), 3.84 (s, 3 H), 3.70 (s, 3 H), 3.66 (s, 3 H), 3.37 (AB, A part of AB, J = 18.42 Hz, $\Delta\nu$ = 143.78 Hz 1 H), 2.89 (AB, B part of AB, J = 18.42 Hz, $\Delta\nu$ = 148.78 Hz 1 H), 1.23−1.46 (m, 2 H), 0.88−1.20 (m, 8 H), 0.73 (t, J = 6.75 Hz, 3 H); MS *m*/*z* (%) 402 (M^+, 31.66), 254 (100); HRMS *m*/*z* (EI) calcd for $C_{23}H_{30}O_6$ 402.20424, found 402.20502.

27. 1,1-Bis(methoxycarbonyl)-2-(1′-((*E*)-2″-phenylethenyl)oct-1′-enyl)cyclopropane (2α). Starting from **1d** (40.2 mg, 0.15 mmol) and (*E*)-1-iodo-2-phenylethylene (41.4 mg, 0.18 mmol) afforded 49 mg (88%) of **2**α using Conditions A: viscous liquid; IR (neat) 2927, 1730, 1590, 1436, 1285 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) ***E*-isomer** δ 6.46−7.48 (m, 7 H), 5.74 (t, J = 7.47 Hz, 1 H), 3.74 (s, 3 H), 3.45 (s, 3 H), 2.61 (t, J = 8.45 Hz, 1 H), 2.04−2.27 (m, 2 H), 1.61−1.75 (m, 2 H), 0.94−1.40 (m, 8 H), 0.56−0.93 (m, 3 H); ***Z*-isomer** δ 6.46−7.48 (m, 7 H), 5.44 (t, J = 7.51 Hz, 1 H), 3.73 (s, 3 H), 3.43 (s, 3 H), 2.81 (t, J = 8.28 Hz, 1 H), 2.04−2.27 (m, 2 H), 1.77−2.00 (m, 1 H), 1.41−1.59 (m, 1 H), 0.94−1.40 (m, 8 H), 0.56−0.93 (m, 3 H); MS *m*/*z* (%) 370 (M^+, 9.22), 310 (100); HRMS *m*/*z* (EI) calcd for $C_{23}H_{30}O_4$ 370.21441, found 370.21503.

28. 1,1-Bis(methoxycarbonyl)-2-methyl-2-((1′-phenyl)-pent-1′-enyl)cyclopropane (2*β*). Starting from **1e** (36 mg, 0.15 mmol) and PhI (37 mg, 0.18 mmol) afforded 20 mg (42%) of **2***β* and 10 mg (21%) of **3***β* using Conditions A. ***Z*-2***β*: viscous liquid; IR (neat) 2957, 1737, 1600, 1436, 1235 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.04−7.29 (m, 5 H), 5.61 (t, J = 7.44 Hz, 1 H), 3.70 (s, 3 H), 3.58 (s, 3 H), 1.77−1.92 (m, 3 H), 1.37 (AB, B part of AB, J = 5.31 Hz, 1 H), 1.30 (s, 3 H), 1.13−1.26 (m, 2 H), 0.76 (t, J = 7.35 Hz, 3 H); MS *m*/*z* (%) 316 (M^+, 9.90), 256 (100); HRMS *m*/*z* (EI) calcd for $C_{19}H_{24}O_4$ 316.16746, found 316.16741. **1-Phenyl-2-methyl-4,4-bis(methoxycarbonyl)-5-propyl-cyclopentene (3*β*)**: viscous liquid; IR (neat) 2956, 1736, 1434, 1253, 1159 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.16−7.40 (m, 5 H), 3.88−3.97 (m, 1 H), 3.76 (s, 3 H), 3.74 (s, 3 H), 3.50 (AB, A part of AB, J = 16.02 Hz, $\Delta\nu$ = 227.76 Hz 1 H), 2.74 (AB, B part of AB, J = 16.02 Hz, $\Delta\nu$ = 227.76 Hz 1 H), 1.73 (s, 3 H), 1.18−1.41 (m, 2 H), 0.92−1.13 (m, 2 H), 0.68

(t, J = 7.18 Hz, 3 H); MS m/z (%) 316 (M^+, 21.72), 256 (100); HRMS m/z (EI) calcd for $C_{19}H_{24}O_4$ 316.16746, found 316.16896.

29. 1-Phenyl-2-benzyl-4,4-bis(methoxycarbonyl)cyclopentene (3i). Starting from **1b** (41 mg, 0.15 mmol) and PhI (37 mg, 0.18 mmol) afforded 46 mg (88%) of **3i** using Conditions C: viscous liquid; IR (neat) 1736, 1494, 1434, 1263 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.02−7.31 (m, 10 H), 3.65 (s, 6 H), 3.51 (s, 2 H), 3.40 (s, 2 H), 2.97 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 139.2, 136.8, 134.9, 134.0, 128.8, 128.7, 128.6, 127.8, 127.4, 126.4, 57.6, 53.1, 45.1, 44.5, 35.1; MS m/z (%) 350 (M^+, 38.30), 290 (100); HRMS m/z (EI) calcd for $C_{22}H_{22}O_4$ 350.15181, found 350.14790.

30. 1-(4′-Methylphenyl)-2-benzyl-4,4-bis(methoxycarbonyl)cyclopentene (3χ). Starting from **1b** (41 mg, 0.15 mmol) and 4-iodotoluene (40 mg, 0.18 mmol) afforded 43 mg (79%) of **3χ** using Conditions C: viscous liquid; IR (neat) 3026, 2952, 1736, 1514, 1495, 1434, 1262 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.08−7.32 (m, 9 H), 3.72 (s, 6 H), 3.57 (s, 2 H), 3.44 (s, 2 H), 3.03 (s, 2 H), 2.34(s, 3 H); MS m/z (%) 364 (M^+, 61.81), 304 (100); HRMS m/z (EI) calcd for $C_{23}H_{24}O_4$ 364.16746, found 364.16657.

31. 1-(4′-Methoxyphenyl)-2-benzyl-4,4-bis(methoxycarbonyl)cyclopentene (3j). Starting from **1b** (41 mg, 0.15 mmol) and 4-iodoanisole (42 mg, 0.18 mmol) afforded 56 mg (98%) of **3j** using Conditions C: viscous liquid; IR (neat) 2953, 1735, 1609, 1512, 1495, 1435 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.00−7.26 (m, 7 H), 6.80 (d, J = 8.80 Hz, 2 H), 3.73 (s, 3 H), 3.65 (s, 6 H), 3.50 (s, 2 H), 3.40 (s, 2 H), 2.96(s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.8, 158.9, 139.3, 134.3, 132.7, 129.2, 128.9, 128.8, 128.7, 128.6, 126.3, 114.0, 57.5, 55.5, 53.1, 45.1, 44.5, 35.1; MS m/z (%) 380 (M^+, 94.31), 229 (100); HRMS m/z (EI) calcd for $C_{23}H_{24}O_5$ 380.16238, found 380.16258.

32. 1-(4′-Methoxycarbonylphenyl)-2-benzyl-4,4-bis(methoxycarbonyl)cyclopentene (3k). Starting from **1b** (41 mg, 0.15 mmol) and 4-iodobenzoic acid methyl ester (47 mg, 0.18 mmol) afforded 47 mg (77%) of **3k** using Conditions C: viscous liquid; IR (neat) 2953, 1735, 1607, 1435, 1277 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, J = 8.29 Hz, 2 H), 7.31 (d, J = 8.29 Hz, 2 H), 7.02−7.26 (m, 5 H), 3.84 (s, 3 H), 3.65 (s, 6 H), 3.51 (s, 2 H), 3.40 (s, 2 H), 3.00 (s, 2 H); MS m/z (%) 408 (M^+, 28.21), 348 (100); HRMS m/z (EI) calcd for $C_{24}H_{24}O_6$ 408.15729, found 408.15473.

33. 1-Phenyl-2-propyl-4,4-bis(methoxycarbonyl)cyclopentene (3p). Starting from **1c** (56.5 mg, 0.25 mmol) and PhI (61 mg, 0.3 mmol) afforded 49 mg (65%) of **3p** using Conditions C: viscous liquid; IR (neat) 2956, 1737, 1434, 1262 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.12−7.38 (m, 5 H), 3.74 (s, 6 H), 3.37 (s, 2 H), 3.14 (s, 2 H), 2.18 (t, J = 7.44 Hz, 2 H), 1.49−1.54 (m, 2 H), 0.86 (t, J = 7.34 Hz, 3 H); MS m/z (%) 302 (M^+, 38.29), 242 (100); HRMS m/z (EI) calcd for $C_{18}H_{22}O_4$ 302.15181, found 302.15330.

34. 1-(4′-Methylphenyl)-2-propyl-4,4-bis(methoxycarbonyl)cyclopentene (3δ). Starting from **1c** (56.5 mg, 0.25 mmol) and 4-iodotoluene (65.4 mg, 0.3 mmol) afforded 43 mg (54%) of **3δ** using Conditions C: viscous liquid; IR (neat) 2958, 1756, 1732, 1432, 1271 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.05 (s, 4 H), 3.66 (s, 6 H), 3.28 (s, 2 H), 3.05 (s, 2 H), 2.25 (s, 3 H), 2.10 (t, J = 7.70 Hz, 2 H), 1.32−1.47 (m, 2 H), 0.79 (t, J = 7.34 Hz, 3 H); MS m/z (%) 316 (M^+, 47.23), 256 (100); HRMS m/z (EI) calcd for $C_{19}H_{24}O_4$ 316.16746, found 316.17144.

35. 1-(4′-Methoxyphenyl)-2-propyl-4,4-bis(methoxycarbonyl)cyclopentene (3q). Starting from **1c** (56.5 mg, 0.25 mmol) and 4-iodoanisole (70.2 mg, 0.3 mmol) afforded 39 mg (47%) of **3q** and 6 mg (7%) of **2q** using Conditions C. **3q**: viscous liquid; IR (neat) 2956, 1736, 1620, 1512, 1250 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, J = 8.44 Hz, 2 H), 6.88 (d, J = 8.44 Hz, 2 H), 3.82 (s, 3 H), 3.76 (s, 6 H), 3.36 (s, 2 H), 3.14 (s, 2 H), 2.19 (t, J = 7.54 Hz, 2 H), 1.36−1.62 (m, 2 H), 0.89 (t, J = 7.30 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 158.3, 134.9, 131.8, 129.5, 128.8, 113.5, 57.3, 55.2, 52.8, 44.9, 44.1, 30.8, 21.2, 14.0; MS m/z (%) 332 (M^+, 4.12), 317 (100); HRMS m/z (EI) calcd for $C_{19}H_{24}O_5$ 332.16238, found 332.15920.

36. 1-(4′-Methoxycarbonylphenyl)-2-propyl-4,4-bis(methoxycarbonyl)cyclopentene (3r). Starting from **1c** (56.5 mg, 0.25 mmol) and 4-iodobenzoic acid methyl ester (79 mg, 0.3 mmol) afforded 49 mg (54%) of **3r** and 7 mg (8%) of **2r** using Conditions C. **3r**: viscous liquid; IR (neat) 2956, 1731, 1608, 1432, 1276 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, J = 8.28 Hz, 2 H), 7.31 (d, J = 8.28 Hz, 2 H), 3.92 (s, 3 H), 3.77 (s, 6 H), 3.41 (s, 2 H), 3.18 (s, 2 H), 2.21 (t, J = 7.62 Hz, 2 H), 1.40−1.55 (m, 2 H), 0.89 (t, J = 7.34 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.4, 166.9, 141.8, 138.5, 131.7, 129.5, 128.3, 127.7, 127.6, 57.3, 52.9, 52.0, 44.6, 44.3, 30.9, 21.1, 14.0; MS m/z (%) 360 (M^+, 20.32), 300 (100); HRMS m/z (EI) calcd for $C_{20}H_{24}O_6$ 360.15729, found 360.15892.

37. 1-Phenyl-4,4-bis(methoxycarbonyl)-5-(*n*-hexyl)cyclopentene (3w). Starting from **1d** (40.2 mg, 0.15 mmol) and PhI (37 mg, 0.18 mmol) afforded 42 mg (81%) of **3w** using Conditions C: viscous liquid; IR (neat) 2953, 1736, 1434, 1252 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.20−7.49 (m, 5 H), 5.86 (s, 1 H), 3.93−4.05 (m, 1 H), 3.76 (s, 3 H), 3.72 (s, 3 H), 3.40 (AB, A part of AB, J = 17.53 Hz, $\Delta\nu$ = 140.67 Hz 1 H), 2.93 (AB, B part of AB, dd, J = 17.53, 3.16 Hz, $\Delta\nu$ = 140.67 Hz 1 H), 1.31−1.50 (m, 2 H), 0.98−1.30 (m, 8 H), 0.80 (t, J = 6.86 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.1, 170.9, 146.3, 135.9, 128.6, 127.7, 126.5, 122.0, 64.8, 53.1, 52.7, 50.1, 39.4, 31.8, 29.8, 29.7, 27.1, 22.8, 14.3; MS m/z (%) 344 (M^+, 47.52), 196 (100); HRMS m/z (EI) calcd for $C_{21}H_{28}O_4$ 344.19876, found 344.19945.

38. 1-(4′-Methylphenyl)-4,4-bis(methoxycarbonyl)-5-(*n*-hexyl)cyclopentene (3x). Starting from **1d** (40.2 mg, 0.15 mmol) and 4-iodotoluene (40 mg, 0.18 mmol) afforded 44 mg (82%) of **3x** and 3 mg (5%) of **2x** using Conditions C. **3x**: viscous liquid; IR (neat) 2952, 1737, 1434, 1251 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, J = 8.00 Hz, 2 H), 7.06 (d, J = 8.00 Hz, 2 H), 5.74 (t, J = 2.40 Hz, 1 H), 3.91 (t, J = 4.97 Hz, 1 H), 3.69 (s, 3 H), 3.65 (s, 3 H), 3.32 (AB, A part of AB, J = 17.44 Hz, $\Delta\nu$ = 138.45 Hz 1 H), 2.86 (AB, B part of AB, dd, J = 17.44, 3.20 Hz, $\Delta\nu$ = 138.45 Hz 1 H), 2.27 (s, 3 H), 1.25−1.40 (m, 2 H), 0.86−1.16 (m, 8 H), 0.74 (t, J = 6.89 Hz, 3 H); MS m/z (%) 358 (M^+, 57.67), 299 (100); HRMS m/z (EI) calcd for $C_{22}H_{30}O_4$ 358.21441, found 358.20982.

39. 1-(4′-Methoxyphenyl)-4,4-bis(methoxycarbonyl)-5-(*n*-hexyl)cyclopentene (3y). Starting from **1d** (40.2 mg, 0.15 mmol) and 4-iodoanisole (42 mg, 0.18 mmol) afforded 44 mg (78%) of **3y** and 11 mg (20%) of **2y** using Conditions C. **3y**: viscous liquid; IR (neat) 2953, 1736, 1607, 1512, 1458, 1258 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.18 (d, J = 8.59 Hz, 2 H), 6.66 (d, J = 8.59 Hz, 2 H), 5.56 (s, 1 H), 3.74 (t, J = 5.46 Hz, 1 H), 3.62 (s, 3 H), 3.57 (s, 3 H), 3.53 (s, 3 H), 3.19 (AB, A part of AB, J = 17.22 Hz, $\Delta\nu$ = 139.01 Hz 1 H), 2.73 (AB, B part of AB, dd, J = 17.22, 3.01 Hz, $\Delta\nu$ = 139.01 Hz 1 H), 1.12−1.33 (m, 2 H), 0.78−1.10 (m, 8 H), 0.62 (t, J = 6.76 Hz, 3 H); MS m/z (%) 374 (M^+, 5.25), 73 (100); HRMS m/z (EI) calcd for $C_{22}H_{30}O_5$ 374.20933, found 374.21299.

40. (*E*)-1-(2′-Phenylethenyl)-2-benzyl-4,4-bis(methoxycarbonyl)cyclopentene (3l). Starting from **1b** (41 mg, 0.15 mmol) and 1-iodo-2-phenylethylene (41.4 mg, 0.18 mmol) afforded 18 mg (32%) of **3l** and 22 mg (39%) of **2l** using Conditions C. **3l**: viscous liquid; IR (neat) 1735, 1494, 1432, 1254 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.98−7.32 (m, 11 H), 6.46 (d, J = 16.04 Hz, 1 H), 3.63 (s, 6 H), 3.56 (s, 2 H), 3.28 (s, 2 H), 2.95 (s, 2 H); MS m/z (%) 376 (M^+, 77.96), 316 (100); HRMS m/z (EI) calcd for $C_{24}H_{24}O_4$ 376.16746, found 376.16831.

41. (*E*)-1-Benzyl-2-(hex-1′-enyl)-4,4-bis(methoxycarbonyl)cyclopentene (3m). Starting from **1b** (68 mg, 0.25 mmol) and (*E*)-1-iodo-1-hexene (63 mg, 0.3 mmol) afforded 21 mg (24%) of **3m** and 36 mg (40%) of **2m** using Conditions C. **3m**: viscous liquid; IR (neat) 2955, 1737, 1434, 1259 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.04−7.30 (m, 5 H), 6.37 (d, J = 15.60 Hz, 1 H), 5.65 (dt, J = 15.60, 6.97 Hz, 1 H), 3.68 (s, 6 H), 3.50 (s, 2 H), 3.18 (s, 2 H), 2.92 (s, 2 H), 2.08−2.10 (m, 2 H), 1.20−1.46 (m, 4 H), 0.90 (t, J = 7.12 Hz, 3 H); MS m/z (%) 356 (M^+, 21.92), 91 (100); HRMS m/z (EI) calcd for $C_{22}H_{28}O_4$ 356.19876, found 356.19571.

42. (*E*)-1-(Hex-1′-enyl)-2-propyl-4,4-bis(methoxycarbonyl)cyclopentene (3t). Starting from **1c** (56.5 mg, 0.25 mmol) and (*E*)-1-iodo-1-hexene (63 mg, 0.3 mmol) afforded 14 mg (18%) of **3t** and 25 mg (32%) of **2t** using Conditions C. **3t**: viscous liquid; IR (neat) 2957, 1738, 1434, 1258, 1164 cm^{-1};

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.16 (d, J = 15.63 Hz, 1 H), 5.47 (dt, J = 15.63, 6.94 Hz, 1 H), 3.66 (s, 6 H), 3.06 (s, 2 H), 2.97 (s, 2 H), 1.96−2.11 (m, 4 H), 1.09−1.43 (m, 6 H), 0.73−0.87 (m, 6 H); MS *m*/*z* (%) 308 (M^+, 28.22), 248 (100); HRMS *m*/*z* (EI) calcd for $C_{18}H_{28}O_4$ 308.19876, found 308.19851.

43. (*E*)-1,1-Bis(methoxycarbonyl)-2-(1′-methylene-3′-phenyl-2-propenyl)cyclopropane (2e). Starting from **1a** (46 mg, 0.25 mmol) and (*E*)-1-iodo-2-phenylethylene (69 mg, 0.3 mmol) afforded 32 mg (45%) of **2e** using Conditions C.

44. 1-Benzyl-2-(2′-methylphenyl)-4,4-bis(methoxycarbonyl)cyclopentene (3i-*o*-Me). Starting from **1b** (41 mg, 0.15 mmol) and *o*-iodotoluene (40 mg, 0.18 mmol) afforded 44 mg (80%) of **3i-*o*-Me** using Conditions A. viscous liquid; IR (neat) 2952, 1736, 1492, 1435, 1262 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.89−7.13 (m, 9 H), 3.66 (s, 6 H), 3.20 (s, 2 H), 3.17 (s, 2 H), 2.95 (s, 2 H), 2.19 (s, 3 H); MS *m*/*z* (%) 364 (M^+, 42.17), 304 (100); HRMS *m*/*z* (EI) calcd for $C_{23}H_{24}O_4$ 364.16746, found 364.17161.

45. 1-Phenyl-4,4-bis(methoxycarbonyl)cyclopentene (3a).[17] Starting from **1a** (46 mg, 0.25 mmol) and PhI (61 mg, 0.3 mmol) afforded 43 mg (66%) of **3a** using Conditions D: IR (neat) 1600, 1734 cm^{-1}; ^{1}H NMR δ 7.15−7.55 (m, 5 H), 6.03 (s, 1 H), 3.77 (s, 6 H), 3.43 (s, 2 H), 3.22 (s, 2 H); MS (*m*/*e*) 260 (M^+, 19.96), 200 (100).

46. 1-(4′-Methylphenyl)-4,4-bis(methoxycarbonyl)cyclopentene (3c). Starting from **1a** (46 mg, 0.25 mmol) and 4-iodotoluene (65 mg, 0.3 mmol) afforded 43 mg (63%) of **3c** using Conditions D: white solid; mp 53−54 °C (*n*-hexane/ethyl acetate); IR (KBr) 1733, 1608, 1514, 1435, 1263 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, J = 8.05 Hz, 2 H), 7.14 (d, J = 8.05 Hz, 2 H), 5.93−5.98 (m, 1 H), 3.78 (s, 6 H), 3.27−3.44 (m, 2 H), 3.17−3.25 (m, 2 H), 2.35 (s, 3 H); MS *m*/*z* (%) 274 (M^+, 19.11), 214 (100); HRMS *m*/*z* (EI) calcd for $C_{16}H_{18}O_4$ 274.12051, found 274.11918.

47. 1-(4′-Methoxyphenyl)-4,4-bis(methoxycarbonyl)cyclopentene (3d). Starting from **1a** (46 mg, 0.25 mmol) and 4-iodoanisole (71 mg, 0.3 mmol) afforded 41 mg (57%) of **3d** using Conditions D: viscous liquid; IR (neat) 2956, 1735, 1607, 1576, 1436, 1259 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, J = 8.81 Hz, 2 H), 6.85 (d, J = 8.81 Hz, 2 H), 5.87−5.91 (m, 1 H), 3.81 (s, 3 H), 3.68 (s, 6 H), 3.37−3.41 (m, 2 H), 3.18−3.11 (m, 2 H); MS *m*/*z* (%) 290 (M^+, 31.98), 230 (100); HRMS *m*/*z* (EI) calcd for $C_{16}H_{18}O_5$ 290.11543, found 290.11997.

48. 1-(4′-Methoxycarbonylphenyl)-4,4-bis(methoxycarbonyl)cyclopentene (3g). Starting from **1a** (46 mg, 0.25 mmol) and 4-iodobenzoic acid methyl ester (79 mg, 0.3 mmol) afforded 44 mg (55%) of **3g** and **2g** (molar ratio of **3g**/**2g** = 66:34 as determined by 300 MHz ^{1}H NMR spectra) using Conditions D. **3g**: white solid; mp 99−101 °C (*n*-hexane); IR (KBr) 2953, 1734, 1630, 1608, 1436, 1277 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, J = 8.55 Hz, 2 H), 7.47 (d, J = 8.55 Hz, 2 H), 6.17−6.21 (m, 1 H), 3.92 (s, 3 H), 3.78 (s, 6 H), 3.42−3.48 (m, 2 H), 3.21−3.28 (m, 2 H); MS *m*/*z* (%) 318 (M^+, 9.39), 258 (100); HRMS *m*/*z* (EI) calcd for $C_{17}H_{18}O_6$ 318.11034, found 318.11030.

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Supporting Information Available: Tables 1 and 2, NMR spectra for all the new products, and ^{1}H−^{1}H NOESY spectra of ***E*-2x**, ***Z*-2x**, and ***Z*-2β**. This material is available free of charge via the Internet at http://pubs.acs.org.

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