Palladium-Catalyzed Highly Regio- and Stereoselective Addition of Organoboronic Acids to Allenes in the Presence of AcOH

Shengming Ma,*[a, b] Ning Jiao,[a] and Longwu Ye[b]

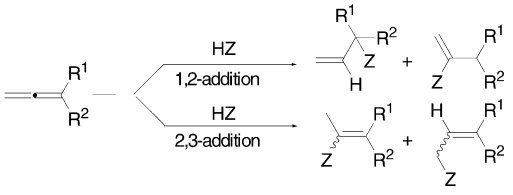
Abstract: The Pd^0-catalyzed regio- and stereoselective addition of organoboronic acids to allenes leads to stereodefined tri- or tetrasubstituted alkenes. Furthermore, this method shows high substitutent-loading capability and tolerance of various substitutents. A hydropalladation–Suzuki coupling mechanism, which may account for the regio- and stereoselectivity, is proposed.

Keywords: alkenes · allenes organoboronic acids · palladium

Introduction

Organoboronic acids enjoy high prestige as reagents in metal-catalyzed C–C bond-formation reactions. The most notable progress is in rhodium- and nickel-catalyzed conjugate additions to unsaturated C–C bonds[1–3] aldehydes,[4] and *N*-sulfonylimines[5] reported by Miyaura, Hayashi, and Shirakawa. Although organoboronic acids are widely used in palladium-catalyzed Suzuki cross-coupling reactions,[6] transition-metal-catalyzed addition reactions of organoboronic acids to electron-rich unsaturated compounds are rare.[7]

However, palladium-catalyzed reactions of allenes,[8] especially addition reactions with different nucleophiles to form a carbon–carbon or carbon–heteroatom bond,[9–11] have become an important area of study in synthetic organic chemistry.[9,10] In principle six different products[12] can be obtained by addition of allenes to HZ (Scheme 1), owing to regio- and stereoselectivity; this problem must be addressed in order to make this addition synthetically attractive. Here, we report the first highly regio- and stereoselective palladium-catalyzed hydroarylation or hydroalkenylation of allenes forming tri- or tetrasubstituted alkenes.



Scheme 1. Regioselectivity in addition of allenes.

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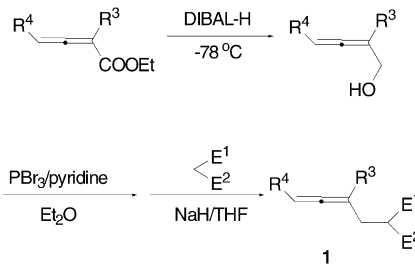
Results and Discussion

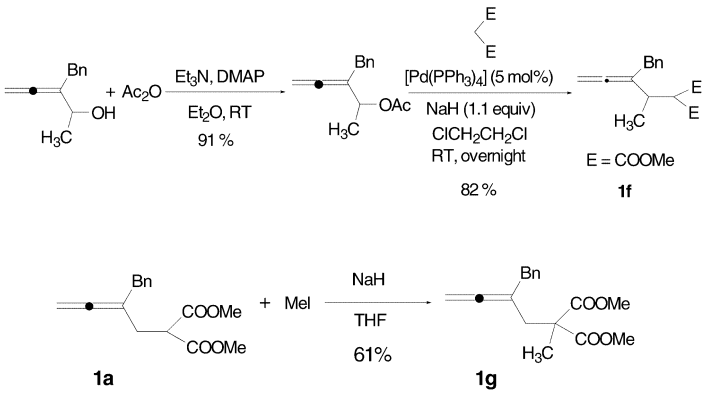
Synthesis of 2-(2′,3′-dienyl)malonates 1: Compounds **1a–1e** were prepared from the alkylation of malonates with the corresponding 2,3-dienyl bromides in THF with NaH as the base.[13,14] 2,3-Dienyl bromides were prepared from 2,3-dien-1-ols[15] and PBr_3 (Scheme 2).[13,16] Allenic compound **1f** was prepared by Pd^0-catalyzed 2,3-allenylation of malonate, and **1g** was synthesized by methylation of **1a** (Scheme 3).2,3-Allenoates **2a–f** were synthesized according to the Wittig-type reactions shown in Scheme 4.[13,17,18]



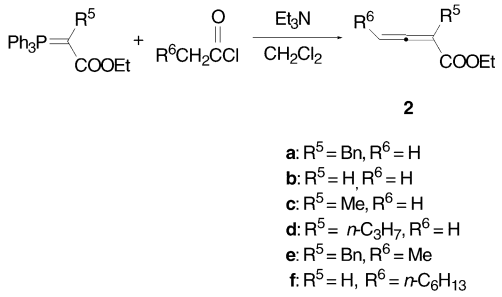
1a: R^3 = Bn, R^4 = H, E^1 = E^2 = COOMe
1b: R^3 = H, R^4 = H, E^1 = E^2 = COOMe
1c: R^3 = Bn, R^4 = H, E^1 = E^2 = CN
1d: R^3 = H, R^4 = H, E^1 = COOEt, E^2 = CN
1e: R^3 = H, R^4 = *n*-C_6H_{13}, E^1 = E^2 = COOMe

Scheme 2. Synthesis of 2-(2′,3′-dienyl)malonates.

 DOI: 10.1002/chem.200305301 © 2003 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Scheme 3. Synthesis of **1f** and **1g**.

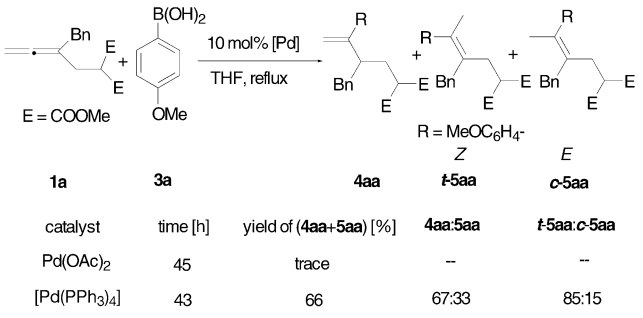


Scheme 4. Synthesis of 2,3-allenoates.

The palladium-catalyzed addition reaction of organoboronic acid with allenes: During our recent research on the chemistry of 2,3-allenylmalonates,[13,19] we observed that the $Pd(OAc)_2$-catalyzed reaction of dimethyl 2-(2′-benzyl-2′,3′-butadienyl)malonate (**1a**) with 4-methoxyphenylboronic acid (**3a**) did not give addition products in decent yields (Scheme 5). Fortunately, after some screening, we found that the reaction of **1a** with **3a** afforded an unexpected 67:33 mixture of hydroarylation products **4aa** and **5aa** in a 66% combined yield in the presence of 10 mol% $[Pd(PPh_3)_4]$ (Scheme 5). Interestingly, we found that the reaction occurred in the presence of AcOH (40 mol%), demonstrating a high regioselectivity, giving tetrasubstituted **5aa** as the major product in 75% yield (**5aa**/**4aa** = 95:5, *t*-**5aa**/*c*-**5aa** (*Z*/*E*) = 87:13) (entry 1, Table 1). The effects of different acids and temperature on the reaction are summarized in Table 1.

Based on these results, conditions A (10 mol% $[Pd(PPh_3)_4]$, 20% AcOH, RT) were applied for the highly regio- and stereo-selective formation of tri- or tetrasubstituted alkenes **5**. The results of the reaction of different 2,3-allenylmalonates with arylboronic acid under conditions A are summarized in Table 2. The configurations of the C=C bond in **5** were determined by the ^1H–^1H NOESY spectra. In order to expand the scope of the Pd^0-catalyzed hydroarylation, we also studied the reaction of 2,3-allenoates with organoboronic acid. The $[Pd(PPh_3)_4]$-catalyzed reaction of ethyl 2-benzylbuta-2,3-dienoate (**2a**) with 4-methoxyphenylboronic acid (**3a**) afforded a mixture of **6aa** and **7aa** (**7aa**/**6aa** = 96:4, (*E*)-**7aa**/(*Z*)-**7aa** = 96:4) in 69% yield in the presence of 20 mol% AcOH (entry 1, Table 3). After some screening, we found that both the regio- and stereoselectivity were improved when 100 mol% AcOH was used in the reaction (entry 2, Table 3). By using the standard conditions B (10 mol% $[Pd(PPh_3)_4]$, 100% AcOH, RT), the hydroarylation with arylboronic acid of various 2,3-allenoates bearing different substituents was studied; the results are summarized in Table 3.

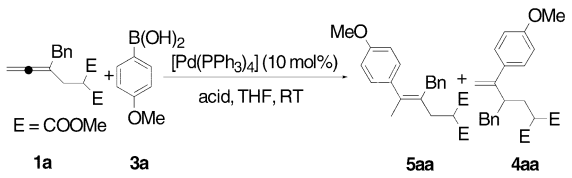
To establish the stereochemistry of this reaction further, the structure of the (*E*)-**7ac** was determined by X-ray diffraction[20] (Figure 1).The reactions of ethyl 2-benzylbuta-2,3-dienoate (**2a**) with different arylboronic acids are summarized in Table 4. The corresponding reaction with 1-alke-



catalyst	time [h]	yield of (**4aa**+**5aa**) [%]	**4aa**:**5aa**	*t*-**5aa**:*c*-**5aa**
$Pd(OAc)_2$	45	trace	--	--
$[Pd(PPh_3)_4]$	43	66	67:33	85:15

Scheme 5. The Pd-catalyzed addition reaction of **1a** with **3a** with the different catalysts.

Table 1. Pd^0-catalyzed addition of 2-benzyl-2,3-propadienyl malonate (**1a**) with 4-methoxyphenylboronic acid (**2a**) in the presence of different acids.[a]



	Acid (%)	Time [h]	Yield of (**4aa**+**5aa**) [%]	**5aa**/**4aa**	*t*-**5aa**/*c*-**5aa**
1[b]	AcOH (40)	5	75	95:5	87:13
2	AcOH (40)	16	74	>97:3	91:9
3	AcOH (20)	22	81	>97:3	91:9
4	AcOH (10)	22	82	>96:4	90:10
5[b]	AcOH (20)	5	79	>96:4	87:13
6[b]	HCO_2H (20)	32	65	83:17	88:12
7[b]	$EtCO_2H$ (20)	4	71	>96:4	88:12
8[b]	AcOH (10)	8.5	70	95:5	87:13
9[c]	AcOH (10)	4	67	95:5	85:15

[a] Reaction with **1a** and **2a** (2.0 equiv) in 3 mL solvent in the presence of 10 mol% $[Pd(PPh_3)_4]$ and acid. [b] Reaction under reflux in THF. [c] Reaction in a sealed tube at 85°C.

Abstract in Chinese: 通过各种官能团化的联烯在钯催化下与有机硼酸的加成反应， 本文描述了一种方便有效、高区域、高立体选择性地合成三取代或四取代烯烃化合物的方法。同时，该方法还具有很强的取代基装载能力和官能团容忍度。并提出了可能的反应机理：钯氢化－Suzuki 偶联并解释了反应的区域和立体选择性。

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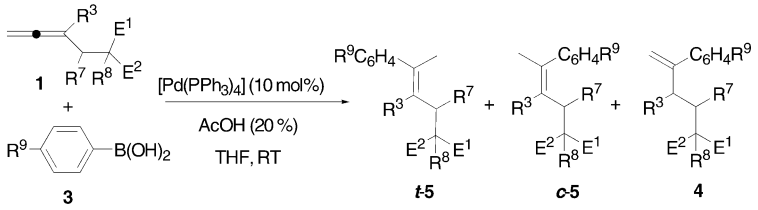
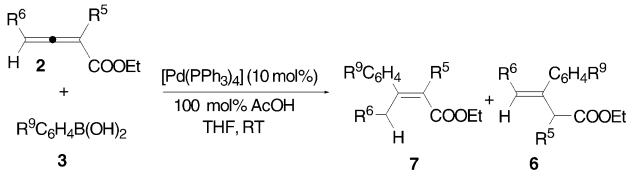
Table 2. Pd^0-catalyzed addition reaction of 2-(2′,3′-allenyl)malonates with different organoboronic acids under conditions A.[a]



	1 R^3/R^7/R^8/**1**	E^1/E^2	R^9 (**3**)	Time [h]	Yield of **5** [%]	**5**/**4** (*t*-**5**:*c*-**5**)
1	Bn/H/H/**1a**	COOMe/COOMe	OMe (**3a**)	22	79 (**5aa**)	>97:3 (91:9)
2	Bn/H/H/**1a**	COOMe/COOMe	H (**3b**)	40	73 (**5ab**)	97:3 (90:10)
3	H/H/H/**1b**	COOMe/COOMe	OMe (**3a**)	14	62 (**5ba**)	>99:1 (>99:1)
4[b]	H/H/H/**1b**	COOMe/COOMe	OMe (**3a**)	7	66 (**5ba**)	>98:2 (>98:2)
5	H/H/H/**1b**	COOMe/COOMe	H (**3b**)	16	49 (**5bb**)	>97:3 (>98:2)
6	Bn/H/H/**1c**	CN/CN	OMe (**3a**)	72	30 (**5ca**)	100:0 (92:8)
7	H/H/H/**1d**	CN/COOEt	OMe (**3a**)	22	73 (**5da**)	100:0 (100:0)
8	Bn/Me/H/**1f**	COOMe/COOMe	OMe (**3a**)	72	84 (**5fa**)	100:0 (90:10)
9	Bn/H/Me/**1g**	COOMe/COOMe	OMe (**3a**)	40	91 (**5ga**)	>99:1 (95:5)

[a] Reaction with **1** and **3** (2.0 equiv) in the presence of 10 mol% $[Pd(PPh_3)_4]$ and 20% AcOH in THF. [b] Reaction under reflux in THF.

Table 3. Pd^0-catalyzed addition of 2,3-allenoates with different organoboronic acids under conditions B.[a]



Entry	R^5/R^6 (**2**)	R^9 (**3**)	Time [h]	Yield of **7** [%]	**7**/**6**	**7** (*E*/*Z*)
1[b]	Bn/H (**2a**)	MeO (**3a**)	17	66 (**7aa**)	96:4	96:4
2	Bn/H (**2a**)	MeO (**3a**)	12	66 (**7aa**)	>98:2	>98:2
3	H/H (**2b**)	MeO (**3a**)	30	62 (**7ba**)	>99:1	>98:2
4	H/H (**2b**)	H (**3b**)	14	70 (**7bb**)	>99:1	>99:1
5	H/H (**2b**)	Me (**3c**)	10	75 (**7bc**)	>99:1	>99:1
6	Me/H (**2c**)	MeO (**3a**)	22	73 (**7ca**)	>99:1	>99:1
7	*n*-C_3H_7/H (**2d**)	MeO (**3a**)	10	86 (**7da**)	>98:2	97:3
8	*n*-C_3H_7/H (**2d**)	H (**3b**)	34	31 (**7db**)	>98:2	>99:1
9	Bn/Me (**2e**)	MeO (**3a**)	32	18 (**7ea**)	>98:2	>98:2
10	H/*n*-C_6H_{13} (**2f**)	MeO (**3a**)	36	46 (**7fa**)	>98:2	>98:2

[a] Reaction with **2** and **3** (2.0 equiv) in the presence of 10 mol% $[Pd(PPh_3)_4]$ and 100% AcOH in THF. [b] 20% AcOH was used.

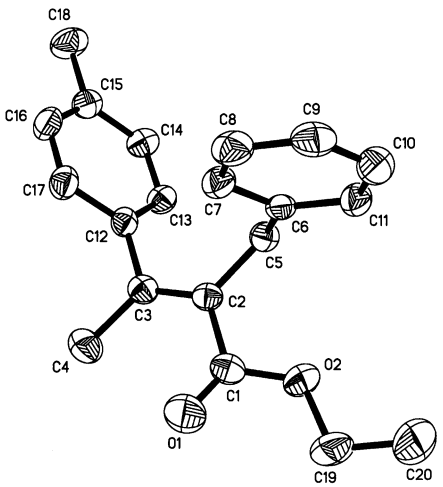
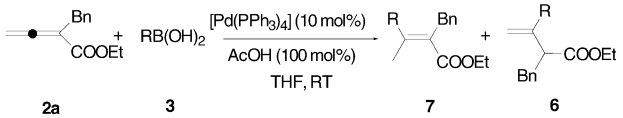


Figure 1. ORTEP representation of (*E*)-**7ac**.

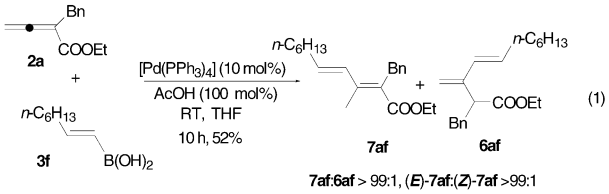
Table 4. Pd^0-catalyzed addition of 2-benzylbuta-2,3-dienoic acid ethyl ester **2a** with different organoboronic acids under conditions B.[a]



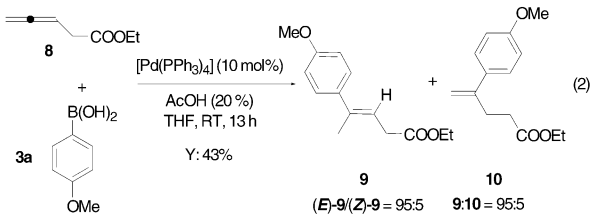
	R	**3**	Time [h]	Yield of **7**+**6** [%]	**7**/**6**	**7** (*E*/*Z*)
1	4-$MeOC_6H_4$	**3a**	12	66 (**7aa**, **6aa**)	>98:2	>98:2
2	Ph	**3b**	24	60 (**7ab**, **6ab**)	96:4	96:4
3	4-MeC_6H_4	**3c**	9	61 (**7ac**, **6ac**)	97:3	98:2
4	3-$NO_2C_6H_4$	**3d**	21	63 (**7ad**, **6ad**)	96:4	92:8
5	4-PhC_6H_4	**3e**	36	63 (**7ae**, **6ae**)	95:5	94:6

[a] Reaction with **2a** and **3** (2.0 equiv) in the presence of 10 mol% $[Pd(PPh_3)_4]$ and 100% AcOH in THF.

nylboronic acid **3f** also afforded conjugated diene *E*-**7af** highly regio- and stereoselectively [Eq. (1)].



The reaction of ethyl 3,4-pentadienoate **8** with **3a** behaved similarly [Eq. (2)].



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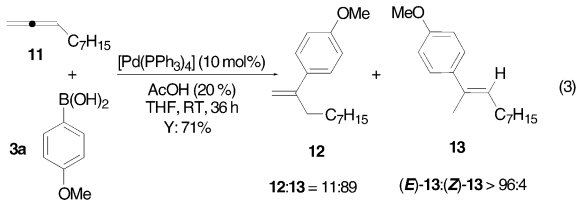
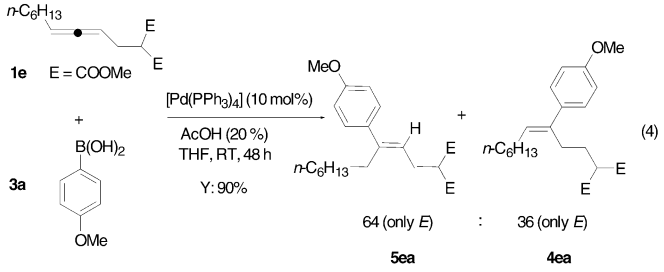
Furthermore, the reaction of a simple allene , e.g., 1,2-decadiene (**11**), with 4-methoxyphenylboronic acid (**3a**) under the standard conditions afforded a mixture **12** and **13** (**13**/**12** = 89:11, *E*-**13**/*Z*-**13** > 96:4) in 71 % yield [Eq. (3)].

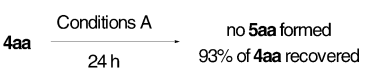


Mechanism: From these results it should be noted that:

1) The regioselectivity is controlled by the relative steric hindrance of the two C=C bonds of the allenes, with the hydroarylation or hydroalkenylation occurring highly regioselectively with the terminal C=C bond.
2) The stereoselectivity may be determined by the relative steric hindrance of R^1 and R^2 (Scheme 1) (compare entries 1, 2, 6, and 8 with entries 3–5, 7, and 9, Table 2.) These results were further supported by the reaction of **1e**. It was due to introduction of the *n*-hexyl group to the terminal position that the regioselectivity dropped dramatically while the stereoselectivity was still excellent [Eq. (4)].

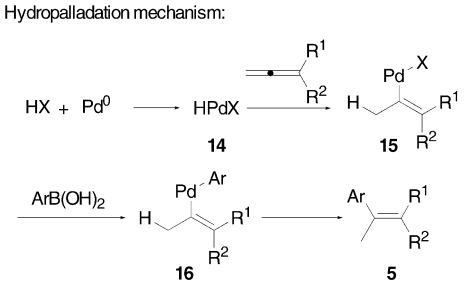


3) A Pd^0 complex is required, since none of the expected products was formed in the reaction with 10 mol % $Pd(OAc)_2$ as the catalyst (Scheme 5).
4) The interconversion between **4aa** and **5aa** under conditions A was not observed, indicating that the regioselectivity is not controlled thermodynamically (Scheme 6).



Scheme 6. The possibility of interconversion between **4aa** and **5aa** under the standard conditions A.

Based on these results we have proposed a rationale for the reaction of allenes with organoboronic acids under the standard conditions A or B. Firstly, a highly regioselective oxidative addition reaction occurs between the HX and Pd^0 to afford palladium hydride species **14**, which may undergo hydropalladation with the less sterically hindered terminal C=C bond in the allene moiety to afford an alkenylpalladium intermediate **15**.[21] Suzuki coupling of **15** with aryl 1-alkenylboronic acid affords the tri- or tetrasubstituted alkene **5** (Scheme 7).[22]



Scheme 7. Rationale for the regioselectivity control.

Conclusion

We have demonstrated the highly selective palladium-catalyzed addition of organoboronic acids to allenes in the presence of AcOH. The advantages of this method are easy availability and diversity of the starting compounds, and high regio- and stereoselectivity leading to stereodefined tri- or tetrasubstituted alkenes. Although the mechanism needs further attention, the current reaction may open a new area for the control of regio- and stereoselectivity in the transition metal-catalyzed addition of allenes. Further studies on details of the mechanism, the scope, and the synthetic applications of this reaction are being carried out in our laboratory.

Experimental Section

The starting 2-(2′,3′-dienyl)malonates **1a**,[13] **1b**,[13] and **1e**[13] were prepared according to literature procedures.

Typical preparation of 1c–1d

Methyl 2-(2′-benzyl-2′,3′-butadienyl)malononitrile ***(1c)***: The reaction of 3-bromomethyl-4-phenyl-1,2-butadiene acetate (2.65 g, 12 mmol),[13] malononitrile (1.1 g, 16.8 mmol), and NaH (60 % dispersion in mineral oil, 0.528 g, 13.2 mmol) afforded **1c** (1.50 g, 60 %) by means of the reported procedures.[23] Liquid; IR(neat):$\tilde{\nu}$ = 2912, 2258, 1961, 1602, 1496, 1455, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.18–7.37 (m, 5H), 5.03–5.12 (m, 2H), 3.72 (t, J = 7.30 Hz, 1H), 3.38–3.43 (m, 2H), 2.49–2.60 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 205.41, 137.39, 128.67, 128.66, 126.97, 112.42, 97.52, 80.45, 39.16, 31.56, 21.15 ppm; MS: m/z (%): 208 (8.72) $[M]^+$, 91 (100); HRMS: m/z (EI): calcd for $C_{14}H_{12}N_2$: 208.10005; found: 208.09895.

Ethyl 2-cyanohexa-4,5-dienoate ***(1d)***: The reaction of 4-bromo-1,2-butadiene[13] (1.06 g, 8 mmol), ethyl cyanoacetate (1.27 g, 11.2 mmol), and NaH (60 % dispersion in mineral oil, 0.352 g, 8.8 mmol) afforded **1d** (0.35 g, 26 %) by means of the reported procedures.[13,14] Liquid; IR(neat): $\tilde{\nu}$ = 2989, 2252, 1958, 1745, 1260 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 5.14–5.23 (m, 1H), 4.81–4.92 (m, 2H), 4.27 (q, J = 7.09 Hz, 2H), 3.60 (dd, J = 7.65, 6.05 Hz, 1H), 2.56–2.68 (m, 2H), 1.32 ppm (t, J = 7.09 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 208.93, 165.38, 116.05, 84.84, 77.26, 62.81, 37.07, 28.43, 13.87 ppm; MS: m/z (%): 165 (0.72) $[M]^+$, 53 (100); HRMS: m/z (EI): calcd for $C_9H_{11}NO_2$: 165.07898; found: 165.07414.

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Preparation of 2-methyl-2-(2′-benzyl-2′,3′-butadienyl)malonate (1f)

Synthesis of 3-benzylpenta-3,4-dien-2-yl acetate:[23] 3-Benzylpenta-3,4-dien-2-ol[23,24] (3.48 g, 18.4 mmol) and Et_3N (3.8 mL) was added to a mixture of Ac_2O (2.86 g, 28 mmol) and DMAP (242.5 mg, 2.0 mmol) in Et_2O (70 mL). The resulting mixture was stirred at RT for 1 h, while being monitored by TLC. After evaporation to dryness, the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/diethyl ether, 20:1) to afford of 3-benzylpenta-3,4-dien-2-yl acetate (3.62 g, 91 %).[23]

*Synthesis of 2-methyl-2-(2′-benzyl-2′,3′-butadienyl)malonate (**1f**)*: Dimethyl malonate (4.68 mL, 39.0 mmol) was added dropwise to a mixture of [Pd(PPh$_3$)$_4$] (0.754 g, 0.65 mmol, 5 mol %) and NaH (60 % dispersion in mineral oil, 0.572 g, 14.3 mmol) in dry 1,2-dichloroethane (104 mL); this was followed by the addition of 3-benzylpenta-3,4-dien-2-yl acetate[23] (2.63 g, 13 mmol) under nitrogen. The resulting mixture was stirred at RT for 18 h, while being monitored by TLC. The solution was quenched with an aqueous saturated solution of NaCl (10 mL) and extracted with diethyl ether (200 mL). The organic layer was dried over anhydrous sodium sulfate. After evaporation to dryness, the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 20:1) to afford **1f** (3.07 g, 82 %). Viscous liquid; IR (neat): $\tilde{\nu}$ = 2955, 1956, 1758, 1737, 1602, 1496, 1435, 1282 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.18 (m, 5H), 4.73–4.68 (m, 2H), 3.71 (s, 3H), 3.66 (s, 3H), 3.48 (d, J = 10.26 Hz, 1H), 3.37–3.35 (m, 2H), 2.80–2.68 (m, 1H), 1.02 ppm (d, J = 6.75 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 204.50, 167.76, 167.50, 137.80, 128.02, 127.05, 125.18, 105.21, 77.20, 55.04, 51.29, 51.24, 37.42, 34.36, 16.74 ppm; MS: m/z (%): 288 (4.01) $[M]^+$, 156 (100); elemental analysis calcd (%) for $C_{17}H_{20}O_4$: C 70.83, H 6.94; found: C 70.90, H 7.00.

Typical preparation of 1-methyl-2-(2′-benzyl-2′,3′-butadienyl)malonate (1g): Compound **1a** (272 mg, 1.0 mmol) was added dropwise to a mixture of NaH (60 % dispersion in mineral oil, 48 mg, 1.2 mmol) in THF (3 mL); then MeI (213 mg, 1.5 mmol) was added dropwise under nitrogen. The resulting mixture was stirred at RT for 5 h, while being monitored by TLC. The solution was quenched with an aqueous saturated solution of NaCl (2 mL) and extracted with diethyl ether (20 mL). The organic layer was dried over anhydrous sodium sulfate. After evoporation to dryness, the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 10:1) to afford **1g** (171 mg, 61 %). Viscous liquid; IR (neat): $\tilde{\nu}$ = 2952, 1957, 1735, 1604, 1495, 1259 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.08–7.31 (m, 5H), 4.54–4.63 (m, 2H), 3.62 (s, 6H), 3.20 (t, J = 2.63 Hz, 2H), 2.49 (t, J = 2.63 Hz, 2H), 1.41 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 207.50, 172.26, 138.85, 128.88, 128.19, 126.29, 97.84, 76.29, 53.47, 52.36, 40.61, 36.25, 19.82 ppm; MS: m/z (%): 288 (6.37) $[M]^+$, 142 (100); HRMS: m/z (EI): calcd for $C_{17}H_{20}O_4$: 288.13616; found: 288.13924.

Synthesis of 2,3-allenoates 2: These were prepared according to literature procedures.[13,17,18]

The palladium-catalyzed addition reaction

Typical procedure under conditions A: Compound **1a** (68 mg, 0.25 mmol) and AcOH (2.9 μL, 20 mol %) were added under nitrogen to a mixture of [Pd(PPh$_3$)$_4$] (29 mg, 0.025 mmol, 10 mol %) and **3a** (76 mg, 0.50 mmol) in THF (3 mL). The resulting mixture was stirred at RT for 22 h, while being monitored by TLC. After evaporation to dryness, the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/diethyl ethyl acetate, 20:1) to afford **4aa** and **5aa** (77 mg, 81 %, **5aa**/**4aa** > 97:3, *t*-**5aa**/*c*-**5aa** = 91:9).

Typical procedure under conditions B: Compound **2a** (51 mg, 0.25 mmol) and AcOH (15 μL, 100 mol %) were added under nitrogen to a mixture of [Pd(PPh$_3$)$_4$] (29 mg, 0.025 mmol, 10 mol %) and 4-methoxyphenylboronic acid **3a** (76 mg, 0.50 mmol) in THF (3 mL). The resulting mixture was stirred at RT for 12 h, while being monitored by TLC. After evaporation to dryness, the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 40:1) to afford **6aa** and **7aa** (51 mg, 66 %, **7aa**/**6aa** > 98:2, *E*-**7aa**/*Z*-**7aa** > 98:2).

*Methyl 2-(2′-benzyl-3′-(4″-methoxyphenyl)but-2′-enyl)malonate (**5aa**)*: The reaction of **1a** (68 mg, 0.25 mmol) and 4-methoxyphenylboronic acid **3a** (76 mg, 0.50 mmol) afforded **4aa** and **5aa** (77 mg, 81 %, **5aa**/**4aa** > 97:3, *t*-**5aa**/*c*-**5aa** = 91:9) under conditions A. Compound *t*-**5aa**: viscous liquid; IR (neat): $\tilde{\nu}$ = 2953, 1737, 1608, 1510, 1436, 1244 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.03–7.21 (m, 3H), 6.99 (d, J = 8.85 Hz, 4H), 6.78 (d, J = 8.85 Hz, 2H), 3.71 (s, 3H), 3.67 (s, 6H), 3.56 (t, J = 7.90 Hz, 1H), 3.23 (s, 2H), 2.65 (d, J = 7.90 Hz, 2H), 1.96 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 169.54, 158.02, 140.04, 136.73, 136.49, 129.44, 128.90, 128.48, 128.30, 125.90, 113.66, 55.15, 52.44, 50.21, 37.88, 29.43, 21.50 ppm; MS: m/z (%): 382 (94.50) $[M]^+$, 91 (100); elemental analysis calcd (%) for $C_{23}H_{26}O_5$: C 72.23, H 6.85; found: C 72.37, H 7.19.

Compound *c*-**5aa**: viscous liquid; IR (neat): $\tilde{\nu}$ = 2952, 1736, 1608, 1510, 1494, 1244 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12–7.31 (m, 5H), 6.86 (d, J = 8.80 Hz, 2H), 6.81 (d, J = 8.80 Hz, 2H), 3.75 (s, 3H), 3.53 (s, 6H), 3.50 (s, 2H), 3.33 (t, J = 7.70 Hz, 1H), 2.51 (d, J = 7.70 Hz, 2H), 1.97 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 169.45, 158.06, 139.56, 136.67, 136.37, 129.41, 129.09, 128.53, 128.31, 126.09, 113.70, 55.20, 52.32, 50.37, 36.77, 31.43, 22.27 ppm; MS: m/z (%): 382 (28.16) $[M]^+$, 91 (100); HRMS: m/z (EI): calcd for $C_{23}H_{26}O_5$: 382.17803; found: 382.17515.

*Methyl 2-(2′-benzyl-3′-(4″-methoxyphenyl)but-3′-enyl)malonate (**4aa**)*: Viscous liquid; IR(neat): $\tilde{\nu}$ = 2953, 1751, 1735, 1607, 1511, 1436, 1248 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.07–7.30 (m, 7H), 6.82 (d, J = 9.00 Hz, 2H), 5.29 (s, 1H), 5.00 (s, 1H), 3.80 (s, 3H), 3.68 (s, 3H), 3.58 (s, 3H), 3.52 (dd, J = 10.3, 4.80 Hz, 1H), 2.82–2.97 (m, 2H), 2.58–2.71 (m, 1H), 2.15–2.37 (m, 1H), 2.02–2.13 ppm (m, 1H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 169.98, 169.68, 158.99, 149.91, 139.64, 134.81, 129.12, 128.14, 127.73, 126.04, 113.55, 112.43, 55.21, 52.48, 52.26, 49.53, 43.47, 41.80, 32.81 ppm; MS: m/z (%): 382 (34.60) $[M]^+$, 159 (100); elemental analysis calcd (%) for $C_{23}H_{26}O_5$: C 72.23, H 6.85; found: C 72.27, H 7.13.

*Methyl 2-(2′-benzyl-3′-phenylbut-2′-enyl)malonate (**5ab**)*: The reaction of **1a** (136 mg, 0.50 mmol) and **3b** (122 mg, 1.00 mmol) afforded **4ab** and **5ab** (131 mg, 75 %, **5ab**/**4ab** = 97:3, *t*-**5ab**/*c*-**5ab** = 90:10) under conditions A. Compound *t*-**5ab**: viscous liquid; IR (neat): $\tilde{\nu}$ = 2953, 1736, 1601, 1453, 1436, 1242 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.10–7.38 (m, 8H), 7.07 (d, J = 8.80 Hz, 2H), 3.75 (s, 6H), 3.64 (t, J = 7.80 Hz, 1H), 3.29 (s, 2H), 2.74 (d, J = 7.80 Hz, 2H), 2.05 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 169.52, 144.42, 139.91, 136.98, 129.45, 128.50, 128.32, 128.30, 127.84, 126.35, 125.95, 52.49, 50.15, 37.86, 29.30, 21.42 ppm; MS: m/z (%): 352 (13.05) $[M]^+$, 91 (100); elemental analysis calcd (%) for $C_{22}H_{24}O_4$: C 74.98, H 6.86; found: C 74.95, H 6.96.

Compound *c*-**5ab**: viscous liquid; IR (neat): $\tilde{\nu}$ = 2953, 1736, 1601, 1436, 1244 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.19–7.40 (m, 8H), 7.14 (d, J = 8.70 Hz, 2H), 3.58 (s, 8H), 3.39 (t, J = 7.65 Hz, 1H), 2.56 (d, J = 7.65 Hz, 2H), 2.06 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 169.43, 144.00, 139.45, 137.16, 129.42, 128.57, 128.32, 128.03, 126.45, 126.16, 52.39, 50.38, 36.65, 31.37, 22.20 ppm; MS: m/z (%): 352 8.20) $[M]^+$, 91 (100); elemental analysis calcd (%) for $C_{22}H_{24}O_4$: C 74.98, H 6.86; found: C 74.98, H 6.83.

*Methyl 2-(3′-(4″-methoxyphenyl)but-2′-enyl)malonate (**5ba**)*: The reaction of **1b** (46 mg, 0.25 mmol) and 4-methoxyphenylboronic acid (**3a**) (76 mg, 0.50 mmol) afforded **4ba** and **5ba** (46 mg, 63 %, **5ba**/**4ba** > 99:1, *t*-**5ba**/*c*-**5ba** > 99:1) under conditions A. Compound *t*-**5ba**: viscous liquid; IR (neat): $\tilde{\nu}$ = 2954, 1736, 1608, 1513, 1247 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, J = 8.90 Hz, 2H), 6.84 (d, J = 8.90 Hz, 2H), 5.59 (t, J = 7.42 Hz, 1H), 3.80 (s, 3H), 3.74 (s, 6H), 3.50 (t, J = 7.42 Hz, 1H), 2.80 (t, J = 7.42 Hz, 2H), 2.03 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 169.48, 158.69, 137.30, 135.85, 126.75, 121.33, 113.48, 55.23, 52.52, 51.67, 28.18, 15.93 ppm; MS: m/z (%): 292 (78.91) $[M]^+$, 161 (100); elemental analysis calcd (%) for $C_{16}H_{20}O_5$: C 65.74, H 6.90; found: C 65.71, H 6.77.

*Methyl 2-(3′-phenylbut-2′-enyl)malonate (**5bb**)*: The reaction of **1b** (46 mg, 0.25 mmol) and **3b** (61 mg, 0.50 mmol) afforded **4bb** and **5bb** (32 mg, 51 %, **5bb**/**4bb** > 97:3, *t*-**5bb**/*c*-**5bb** > 98:2) under conditions A. Compound *t*-**5bb**: viscous liquid; IR (neat): $\tilde{\nu}$ = 2954, 1737, 1598, 1494, 1436, 1232 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12–7.31 (m, 5H), 5.59 (t, J = 7.55 Hz, 1H), 3.67 (s, 6H), 3.43 (t, J = 7.55 Hz, 1H), 2.74 (t, J = 7.55 Hz, 2H), 1.98 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 169.41, 143.32, 138.00, 128.14, 126.92, 125.71, 122.86, 52.57, 51.56, 28.18, 15.93 ppm; MS: m/z (%): 262 (28.98) $[M]^+$, 143 (100); elemental analysis calcd (%) for $C_{15}H_{18}O_4$: C 68.69, H 6.92; found: C 68.73, H 7.01.

*2-(2′-Benzyl-3′-(4″-methoxyphenyl)but-2′-enyl)malononitrile (**5ca**)*: The reaction of **1c** (50 mg, 0.24 mmol) and 4-methoxyphenylboronic acid (**3a**) (73 mg, 0.48 mmol) afforded **5ca** (23 mg, 30 %, *t*-**5ca**/*c*-**5ca** = 92:8) under conditions A. Compound *t*-**5ca**: viscous liquid; IR (neat): $\tilde{\nu}$ =

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2919, 2256, 1608, 1510, 1245 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.19–7.36 (m, 3H), 7.15 (d, J = 8.75 Hz, 2H), 7.10 (d, J = 7.45 Hz, 2H), 6.89 (d, J = 8.75 Hz, 2H), 3.80 (s, 3H), 3.45 (t, J = 8.18 Hz, 1H), 3.41 (s, 2H), 2.86 (d, J = 8.18 Hz, 2H), 2.16 ppm (s, 3H); MS: m/z (%): 316 (20.04) $[M]^+$, 91 (100); elemental analysis calcd (%) for $C_{21}H_{20}N_2O$: C 79.72, H 6.37, N 8.85; found: C 79.49, H 6.21, N 8.48.

*2-Cyano-5-(4′-methoxyphenyl)hex-4-enoic acid ethyl ester (**5da**)*: The reaction of **1d** (38 mg, 0.23 mmol) and **3a** (70 mg, 0.46 mmol) afforded **5da** (46 mg, 73%, *t*-**5da**/*c*-**5da** = 100:0) under conditions A. Compound *t*-**5da**: viscous liquid; IR (neat): $\tilde{\nu}$ = 2983, 2251, 1744, 1608, 1512, 1248 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.33 (d, J = 8.65 Hz, 2H), 6.87 (d, J = 8.65 Hz, 2H), 5.69 (dt, J = 7.21, 1.37 Hz, 1H), 4.28 (q, J = 7.18 Hz, 2H), 3.82 (s, 3H), 3.61 (t, J = 7.21 Hz, 1H), 2.87 (t, J = 7.21 Hz, 2H), 2.08 (s, 3H), 1.33 ppm (t, J = 7.18 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 165.77, 158.98, 139.45, 135.24, 126.90, 118.74, 116.42, 113.57, 62.89, 55.28, 37.72, 29.18, 16.26, 14.01 ppm; MS: m/z (%): 273 (14.42) $[M]^+$, 161 (100); elemental analysis calcd (%) for $C_{16}H_{19}NO_3$: C 70.31, H 7.01, N 5.12; found: C 70.00, H 7.18, N 5.06.

*Methyl 2-(1′-methyl-2′-benzyl-3′-(4″-methoxyphenyl)but-2′-enyl)malonate (**5fa**)*: The reaction of **1f** (72 mg, 0.25 mmol) and **3a** (76 mg, 0.50 mmol) afforded **5fa** (83 mg, 84%, *t*-**5ca**/*c*-**5ca** = 90:10) under conditions A. Compound *t*-**5fa**: viscous liquid; IR (neat): $\tilde{\nu}$ = 2951, 1756, 1740, 1608, 1506, 1250 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.04–7.12 (m, 5H), 7.03 (d, J = 8.85 Hz, 2H), 6.79 (d, J = 8.85 Hz, 2H), 3.75 (s, 3H), 3.73 (s, 3H), 3.68 (s, 3H), 3.63–3.71 (m, 1H), 3.56 (d, J = 11.60 Hz, 1H), 3.43 (AB, A part of AB, J = 15.75 Hz, $\Delta\nu$ = 41.35 Hz, 1H), 3.30 (AB, B part of AB, J = 15.75 Hz, $\Delta\nu$ = 41.35 Hz, 1H), 2.13 (s, 3H), 0.92 ppm (t, J = 7.20 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 169.13, 168.59, 157.78, 140.72, 137.45, 136.74, 133.40, 128.92, 128.39, 127.95, 125.55, 113.62, 56.66, 55.13, 52.48, 52.28, 36.77, 22.08, 18.01 ppm; MS: m/z (%): 396 (30.33) $[M]^+$, 91 (100); elemental analysis calcd (%) for $C_{24}H_{28}O_5$: C 72.71, H 7.12; found: C 72.72, H 7.15.

Compound *c*-**5fa**: viscous liquid; IR (neat): $\tilde{\nu}$ = 2954, 1759, 1736, 1609, 1511, 1244 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.20–7.35 (m, 5H), 7.19 (d, J = 8.75 Hz, 2H), 6.93 (d, J = 8.75 Hz, 2H), 3.84 (s, 3H), 3.61 (s, 3H), 3.57 (s, 2H), 3.51 (s, 3H), 3.34–3.44 (m, 2H), 1.91 (s, 3H), 0.90 ppm (d, J = 6.20 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 168.97, 168.37, 158.04, 139.77, 137.10, 136.43, 132.51, 128.89, 128.36, 128.07, 125.80, 113.68, 56.22, 55.18, 52.31, 52.14, 37.49, 33.41, 22.94, 18.16 ppm; MS: m/z (%): 396 (31.79) $[M]^+$, 91 (100); elemental analysis calcd (%) for $C_{24}H_{28}O_5$: C 72.71, H 7.12; found: C 72.66, H 7.33.

*Methyl 2-methyl-2-(2′-benzyl-3′-(4″-methoxyphenyl)but-2′-enyl)malonate (**5ga**)*: The reaction of **1g** (72 mg, 0.25 mmol) and **3a** (76 mg, 0.50 mmol) afforded **4ga** and **5ga** (87 mg, 92%, **5ga**/**4ga** > 99:1, *t*-**5ga**/*c*-**5ga** = 95:5) under conditions A. Compound *t*-**5ga**: viscous liquid; IR (neat): $\tilde{\nu}$ = 2952, 1733, 1608, 1575, 1510, 1244 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.98–7.26 (m, 7H), 6.84 (d, J = 8.50 Hz, 2H), 3.79 (s, 3H), 3.71 (s, 6H), 3.20 (s, 2H), 2.89 (s, 2H), 2.05 (s, 3H), 1.54 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 173.01, 157.98, 140.26, 138.63, 136.84, 128.89, 128.33, 128.09, 125.67, 113.62, 55.09, 53.76, 52.47, 38.34, 34.23, 22.48, 20.01 ppm; MS: m/z (%): 396 (22.88) $[M]^+$, 91 (100); elemental analysis calcd (%) for $C_{24}H_{28}O_5$ (%): C 72.71, H 7.12; found: C 73.15, H 7.24.

*Ethyl 2-benzyl-3-(4′-methoxyphenyl)but-2-enoate (**7aa**)*: The reaction of **2a** (51 mg, 0.25 mmol) and **3a** (76 mg, 0.50 mmol) afforded **6aa** and **7aa** (51 mg, 66%, **7aa**/**6aa** > 98:2, (*E*)-**7aa**/(*Z*)-**7aa** > 98:2) under conditions B. Compound (*E*)-**7aa**: viscous liquid; IR (neat): $\tilde{\nu}$ = 2979, 1713, 1608, 1511, 1495, 1248 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.04–7.31 (m, 7H), 6.88 (d, J = 8.80 Hz, 2H), 4.12 (q, J = 7.40 Hz, 2H), 3.80 (s, 3H), 3.60 (s, 2H), 2.30 (s, 3H), 1.13 ppm (t, J = 7.40 Hz, 3H); MS: m/z (%): 310 (71.48) $[M]^+$, 236 (100); elemental analysis calcd (%) for $C_{20}H_{22}O_3$: C 77.39, H 7.14; found: C 77.60, H 7.38. The following ^{1}H NMR data were discernible for **6aa**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31 (d, J = 8.70 Hz, 2H), 5.37 (s, 1H), 5.27 (s, 1H), 3.81 (s, 3H), 3.23 (dd, J = 13.78, 9.30 Hz, 1H), 2.96 (dd, J = 13.78, 5.65 Hz, 1H).

Compound (*Z*)-**7aa**: viscous liquid; IR (neat): $\tilde{\nu}$ = 2962, 1704, 1607, 1510, 1255, 1032 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.16–7.23 (m, 5H), 7.08 (d, J = 9.00 Hz, 2H), 6.78 (d, J = 9.00 Hz, 2H), 3.76 (s, 2H), 3.75 (q, J = 7.10 Hz, 2H), 3.74 (s, 3H), 2.07 (s, 3H), 0.75 ppm (t, J = 7.10 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 170.39, 158.80, 143.90, 139.12, 136.19, 129.32, 128.41, 128.26, 128.23, 126.07, 113.38, 60.16, 55.26, 36.34, 21.79, 13.61 ppm; MS: m/z (%): 310 (38.84) $[M]^+$, 236 (100); HRMS: m/z (EI): calcd for $C_{20}H_{22}O_3$: 310.15690; found 310.15213.

*Ethyl 3-(4′-methoxyphenyl)but-2-enoate (**7ba**)*: The reaction of **2b** (56 mg, 0.50 mmol) and **3a** (152 mg, 1.0 mmol) afforded **6ba** and **7ba** (68 mg, 62%, **7ba**/**6ba** > 99:1, (*E*)-**7ba**/(*Z*)-**7ba** > 98:2) under conditions B. Compound (*E*)-**7ba**: viscous liquid; IR(neat): $\tilde{\nu}$ = 1710, 1626, 1604, 1513, 1162 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44 (d, J = 9.0 Hz, 2H), 6.88 (d, J = 9.0 Hz, 2H), 6.11 (q, J = 1.1 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.81 (s, 3H), 2.56 (d, J = 1.1 Hz, 3H), 1.31 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 166.98, 160.30, 154.79, 134.15, 127.56, 115.16, 113.70, 59.62, 55.21, 17.54, 14.29 ppm; MS: m/z (%): 220 (100) $[M]^+$, 175 (61.79), 148 (21.44); elemental analysis calcd (%) for $C_{13}H_{16}O_3$: C 70.89, H 7.32; found: C 70.77, H 7.40.

*Ethyl 3-phenylbut-2-enoate (**7bb**)*: The reaction of **2b** (28 mg, 0.25 mmol) and **3b** (61 mg, 0.50 mmol) afforded **7bb** (33 mg, 70%, **7bb**/**6bb** > 99:1, (*E*)-**7bb**/(*Z*)-**7bb** > 99:1) under conditions B. Compound (*E*)-**7bb**: viscous liquid; IR(neat): $\tilde{\nu}$ = 1714, 1629, 1167 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.51 (m, 2H), 7.33–7.39 (m, 3H), 6.14 (q, J = 1.2 Hz, 1H), 4.22 (q, J = 7.2 Hz, 2H), 2.58 (d, J = 1.2 Hz, 3H), 1.32 ppm (t, J = 7.2 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 166.86, 155.51, 142.14, 128.94, 128.44, 126.25, 117.09, 59.81, 17.89, 14.29 ppm; MS: m/z (%): 190 (61.27) $[M]^+$, 115 (100); HRMS: m/z (EI): calcd for $C_{12}H_{14}O_2$: 190.09937; found: 190.10266.

*Ethyl 3-(4′-methylphenyl)but-2-enoate (**7bc**)*: The reaction of **2b** (28 mg, 0.25 mmol) and **3c** (68 mg, 0.50 mmol) afforded **7bc** (38 mg, 75%, **7bc**/**6bc** > 99:1, (*E*)-**7bc**/(*Z*)-**7bc** > 99:1) under conditions B. Compound (*E*)-**7bc**: viscous liquid; IR(neat): $\tilde{\nu}$ = 2963, 1716, 1629, 1262 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 8.2 Hz, 2H), 6.14 (q, J = 1.2 Hz, 1H), 4.21 (q, J = 7.0 Hz, 2H), 2.57 (d, J = 1.2 Hz, 3H), 2.37 (s, 3H), 1.32 ppm (t, J = 7.0 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 166.97, 155.39, 139.16, 139.09, 129.14, 126.16, 116.20, 59.74, 21.16, 17.77, 14.33 ppm; MS: m/z (%): 204 (100) $[M]^+$; elemental analysis calcd (%) for $C_{13}H_{16}O_2$: C 76.44, H 7.90; found: C 76.12, H 8.05.

*Ethyl 2-methyl-3-(4′-methoxyphenyl)but-2-enoate (**7ca**)*: The reaction of **2c** (63 mg, 0.50 mmol) and **3a** (152 mg, 1.0 mmol) afforded **7ca** (85 mg, 73%, **7ca**/**6ca** > 99:1, (*E*)-**7ca**/(*Z*)-**7ca** > 99:1) under conditions B. Compound (*E*)-**7ca**: viscous liquid; IR(neat): $\tilde{\nu}$ = 2934, 1712, 1608, 1511, 1247 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.08 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 4.25 (q, J = 7.1 Hz, 2H), 3.80 (s, 3H), 2.23 (q, J = 1.5 Hz, 3H), 1.78 (q, J = 1.5 Hz, 3H), 1.33 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 170.10, 158.46, 144.88, 135.54, 128.55, 124.59, 113.53, 60.24, 55.14, 23.15, 17.41, 14.25 ppm; MS: m/z (%): 234 (97.05) $[M]^+$, 160 (100); HRMS: m/z (EI): calcd for $C_{14}H_{18}O_3$: 234.12559; found: 234.12689.

*Ethyl 2-propyl-3-(4′-methoxyphenyl)but-2-enoate (**7da**)*: The reaction of **2d** (39 mg, 0.25 mmol) and **3a** (76 mg, 0.50 mmol) afforded **6da** and **7da** (56 mg, 86%, **7da**/**6da** > 98:2, *E*-**7da**/*Z*-**7da** = 97:3) under conditions B. Compound (*E*)-**7da**: viscous liquid; IR (neat): $\tilde{\nu}$ = 2961, 1714, 1609, 1511, 1246, 1137 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.00 (d, J = 8.7 Hz, 2H), 6.81 (d, J = 8.7 Hz, 2H), 4.20 (q, J = 7.3 Hz, 2H), 3.75 (s, 3H), 2.08 (s, 3H), 2.03–2.14 (m, 2H), 1.21–1.37 (m, 5H), 0.71 ppm (t, J = 7.5 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 170.33, 158.41, 142.52, 135.28, 130.67, 128.40, 113.53, 60.24, 55.16, 33.03, 23.35, 22.27, 14.29, 13.87 ppm; MS: m/z (%): 262 (98.94) $[M]^+$, 159 (100); elemental analysis calcd (%) for $C_{16}H_{22}O_3$: C 73.25, H 8.45; found: C 72.96, H 8.60.

Compound (*Z*)-**7da**: viscous liquid; IR (neat): $\tilde{\nu}$ = 2960, 1708, 1608, 1511, 1248, 1104 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.03 (d, J = 8.7 Hz, 2H), 6.76 (d, J = 8.7 Hz, 2H), 3.78 (q, J = 7.4 Hz, 2H), 3.72 (s, 3H), 2.34 (t, J = 7.8 Hz, 2H), 2.02 (s, 3H), 1.35–1.49 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H), 0.82 ppm (t, J = 7.5 Hz, 3H); MS: m/z (%): 262 (100) $[M]^+$; HRMS: m/z (EI): calcd for $C_{16}H_{22}O_3$: 262.15690; found: 262.15502.

*Ethyl 2-propyl-3-phenylbut-2-enoate (**7db**)*: The reaction of **2d** (39 mg, 0.25 mmol) and **3b** (61 mg, 0.50 mmol) afforded **6db** and **7db** (18 mg, 32%, **7db**/**6db** > 98:2, (*E*)-**7db**/(*Z*)-**7db** > 99:1) under conditions B. Compound (*E*)-**7db**: viscous liquid; IR(neat): $\tilde{\nu}$ = 2961, 1716, 1626, 1599, 1220, 1137 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.22–7.39 (m, 3H), 7.10–7.17 (m, 2H), 4.28 (q, J = 7.2 Hz, 2H), 2.16 (s, 3H), 2.10 (t, J = 7.8 Hz, 2H), 1.30–1.38 (m, 5H), 0.76 ppm (t, J = 7.2 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 170.22, 143.09, 143.00, 130.74, 128.25, 127.17, 126.88, 60.32, 32.99, 23.29, 22.25, 14.32, 13.85 ppm; MS: m/z (%): 232

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(86.35) $[M]^+$, 129 (100); HRMS: *m/z* (EI): calcd for $C_{15}H_{20}O_2$: 232.14633; found: 232.14620.

*Ethyl 2-benzyl-3-(4′-methoxyphenyl)pent-2-enoate (**7ea**)*: The reaction of **2e** (108 mg, 0.50 mmol) and 4-methoxyphenylboronic acid (**3a**) (152 mg, 1.0 mmol) afforded **6ea** and **7ea** (28 mg, 18%, **7ea**/**6ea** > 98:2, (*E*)-**7ea**/(*Z*)-**7ea** > 98:2) under conditions B. Compound *E*-**7ea**: viscous liquid; IR(neat): $\tilde{\nu}$ = 2975, 1713, 1607, 1510, 1248 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.07–7.28 (m, 7H), 6.88 (d, J = 8.7 Hz, 2H), 4.11 (q, J = 7.1 Hz, 2H), 3.80 (s, 3H), 3.53 (s, 2H), 2.63 (q, J = 7.4 Hz, 2H), 1.14 (t, J = 7.1 Hz, 3H), 1.00 ppm (t, J = 7.4 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 169.40, 158.67, 151.06, 139.89, 133.24, 128.92, 128.21, 128.18, 128.16, 125.83, 113.61, 60.22, 55.18, 36.96, 29.88, 14.03, 12.92 ppm; MS: *m/z* (%): 324 (87.21) $[M]^+$, 249 (100); elemental analysis calcd for $C_{21}H_{24}O_3$ (%): C 77.75, H 7.46; found: C 77.78, H 7.58.

*Ethyl 3-(4′-methoxyphenyl)dec-2-enoate (**7fa**)*: The reaction of **2f** (98 mg, 0.50 mmol) and **3a** (152 mg, 1.0 mmol) afforded **6fa** and **7fa** (72 mg, 47%, **7fa**/**6fa** > 98:2, (*E*)-**7fa**/(*Z*)-**7fa** > 98:2) under conditions B. Compound (*E*)-**7fa**: viscous liquid; IR(neat): $\tilde{\nu}$ = 2928, 1712, 1604, 1512, 1252, 1159 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41 (d, J = 9.0 Hz, 2H), 6.89 (d, J = 9.0 Hz, 2H), 5.99 (s, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.82 (s, 3H), 3.07 (t, J = 7.7 Hz, 2H), 1.18–1.48 (m, 13H), 0.85 ppm (t, J = 6.8 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 166.67, 160.29, 160.23, 133.42, 127.95, 115.40, 113.80, 59.65, 55.27, 31.78, 30.71, 29.74, 29.25, 29.07, 22.59, 14.32, 14.07 ppm; MS: *m/z* (%): 304 (36.25) $[M]^+$, 220 (100); elemental analysis calcd (%) for $C_{19}H_{28}O_3$: C 74.96, H 9.27; found: C 74.93, H 9.05.

*Ethyl 2-benzyl-3-phenylbut-2-enoate (**7ab**)*: The reaction of **2a** (51 mg, 0.25 mmol) and **3b** (61 mg, 0.50 mmol) afforded **6ab** and **7ab** (42 mg, 60%, **7ab**/**6ab** = 96:4, (*E*)-**7ab**/(*Z*)-**7ab** = 96:4) under conditions B. Compound (*E*)-**7ab**: viscous liquid; IR(neat): $\tilde{\nu}$ = 2980, 1716, 1631, 1600, 1494, 1051 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.08–7.41 (m, 10H), 4.14 (q, J = 7.2 Hz, 2H), 3.58 (s, 2H), 2.33 (s, 3H), 1.15 ppm (t, J = 7.2 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 169.09, 145.98, 142.90, 139.79, 128.76, 128.40, 128.21, 128.14, 127.18, 127.02, 125.86, 60.26, 36.83, 23.42, 14.02 ppm; MS: *m/z* (%): 280 (7.50) $[M]^+$, 206 (100); HRMS: *m/z* (EI): calcd for $C_{19}H_{20}O_2$: 280.14633; found: 280.14576.

*Ethyl 2-benzyl-3-(4′-methylphenyl)but-2-enoate (**7ac**)*: The reaction of **2a** (51 mg, 0.25 mmol) and **3c** (68 mg, 0.50 mmol) afforded **6ac** and **7ac** (45 mg, 61%, **7ac**/**6ac** = 97:3, (*E*)-**7ac**/(*E*)-**7ac** = 98:2) under conditions B. Compound (*E*)-**7ac**: white solid, m.p. 58–61 °C (*n*-hexane/ethyl acetate); IR(KBr): $\tilde{\nu}$ = 2985, 1711, 1628, 1251, 1182 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.06–7.28 (m, 9H), 4.11 (q, J = 7.1 Hz, 2H), 3.57 (s, 2H), 2.34 (s, 3H), 2.30 (s, 3H), 1.13 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 169.20, 146.06, 139.93, 139.91, 136.89, 129.04, 128.54, 128.20, 128.13, 126.97, 125.82, 60.22, 36.86, 23.47, 21.13, 14.02 ppm; MS: *m/z* (%): 294 (70.92) $[M]^+$, 220 (100); elemental analysis calcd (%) for $C_{20}H_{22}O_2$: C 81.60, H 7.53; found: C 81.88, H 7.63.

*Ethyl 2-benzyl-3-(3′-nitrophenyl)but-2-enoate (**7ad**)*: The reaction of **2a** (51 mg, 0.25 mmol) and **3d** (84 mg, 0.50 mmol) afforded **6ad** and **7ad** (51 mg, 63%, **7ad**/**6ad** = 96:4, (*E*)-**7ad**/(*Z*)-**7ad** = 92:8) under conditions B. Compound (*E*)-**7ad**: viscous liquid; IR(neat): $\tilde{\nu}$ = 2981, 1715, 1531, 1350, 1051 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04–8.19 (m, 2H), 7.48–7.57 (m, 2H), 7.08–7.28 (m, 3H), 7.01–7.04 (m, 2H), 4.15(q, J = 7.2 Hz, 2H), 3.52 (s, 2H), 2.31 (s, 3H), 1.16 ppm (t, J = 7.2 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$):δ = 168.49, 148.21, 144.27, 142.77, 138.79, 133.36, 130.64, 129.57, 128.34, 128.08, 126.22, 122.31, 122.28, 60.63, 36.79, 23.10, 13.98 ppm; MS: *m/z* (%): 325 (28.28) $[M]^+$, 234 (100); elemental analysis calcd (%) for $C_{19}H_{19}NO_4$: C 70.14, H 5.89, N 4.31; found: C 70.08, H 6.03, N 4.32.

*Ethyl 2-benzyl-3-(4′-phenylphenyl)but-2-enoate (**7ae**)*: The reaction of **2a** (51 mg, 0.25 mmol) and **3e** (99 mg, 0.50 mmol) afforded **6ae** and **7ae** (56 mg, 63%, **7ae**/**6ae** = 95:5, (*E*)-**7ae**/(*Z*)-**7ae** = 94:6) under conditions B. Compound (*E*)-**7ae**: white solid, m.p. 68–70 °C (*n*-hexane/ethyl acetate); IR(KBr): $\tilde{\nu}$ = 2991, 1710, 1636, 1602, 1313, 1201 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.08–7.62 (m, 14H), 4.13(q, J = 7.1 Hz, 2H), 3.62 (s, 2H), 2.35 (s, 3H), 1.14 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 169.11, 145.64, 141.82, 140.54, 140.09, 139.82, 128.92, 128.76, 128.23, 128.20, 127.58, 127.34, 127.10, 126.98, 125.91, 60.30, 36.94, 23.36, 14.03 ppm; MS: *m/z* (%): 356 (60.95) $[M]^+$, , 282 (100); elemental analysis calcd for $C_{25}H_{24}O_2$ (%): C 84.24, H 6.79; found: C 84.09, H, 6.89.

*Ethyl 2-benzyl-3-methylundeca-2,4-dienoate (**7af**)*: The reaction of **2a** (32 mg, 0.16 mmol) and **3f** (50 mg, 0.32 mmol) afforded **7af** (26 mg, 52%, **7af**/**6af** > 99:1, 2(*E*),4(*E*)-**7af**:2(*Z*),4(*E*)-**7af** > 99:1) under conditions B. Compound 2(*E*),4(*E*)-7**af**: viscous liquid; IR(neat): $\tilde{\nu}$ = 2927, 1711, 1633, 1603, 1228 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.22–7.28 (m, 2H), 7.12–7.21 (m, 3H), 6.53 (d, J = 14.9 Hz, 1H), 6.06 (dt, J = 14.9, 7.3 Hz, 1 H), 4.11(q, J = 7.1 Hz, 2H), 3.82 (s, 2H), 2.11–2.19 (m, 5H), 1.22–1.44 (m, 8H), 1.17 (t, J = 7.1 Hz, 3H), 0.88 ppm (t, J = 6.6 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 169.85, 140.49, 139.85, 136.99, 128.69, 128.26, 127.47, 125.92, 60.22, 34.83, 33.51, 31.66, 29.14, 28.81, 22.58, 16.86, 14.11, 14.07 ppm; MS: *m/z* (%): 314 (5.96) $[M]^+$, 84 (100); HRMS: *m/z* (EI): calcd for $C_{21}H_{30}O_2$: 314.22458; found: 314.22340.

*Ethyl 4-(4′-methoxyphenyl)pent-3-enoate (**9**)*: The reaction of **8** (32 mg, 0.25 mmol) and **3a** (76 mg, 0.50 mmol) afforded **9** and **10** (25 mg, 43%, **9**/**10** = 95:5, (*E*)-**9**/(*Z*)-**9** = 95:5) under conditions A. Compound (*E*)-**9**: viscous liquid; IR (neat): $\tilde{\nu}$ = 2958, 1736, 1608, 1513, 1249, 1179 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34 (d, J = 9.0 Hz, 2H), 6.85 (d, J = 9.0 Hz, 2H), 5.87 (dq, J = 7.1, 0.9 Hz, 1H), 4.17 (q, J = 7.2 Hz, 2H), 3.81 (s, 3H), 3.23 (d, J = 7.1 Hz, 2H), 2.03 (d, J = 0.9 Hz, 3H), 1.28 ppm (t, J = 7.2 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 172.05, 158.73, 137.25, 135.58, 126.78, 117.70, 113.50, 60.65, 55.24, 34.51, 16.21, 14.22; MS: *m/z* (%): 234 (33.03) $[M]^+$, 161 (100); HRMS: *m/z* (EI): calcd for $C_{14}H_{18}O_3$: 234.12559; found: 234.12960.

*2-(4′-Methoxyphenyl)dec-1-ene (**12**)[25] and 2-(4′-methoxyphenyl)dec-2-ene (**13**)*: The reaction of **11** (69 mg, 0.50 mmol) and **3a** (152 mg, 1.00 mmol) afforded **12** and **13** (88 mg, 71%, **13**/**12** = 89:11, *E*-**13**/*Z*-**13** > 96:4) under conditions A. Compound **12**:[25] liquid; IR (neat): $\tilde{\nu}$ = 2926, 1608, 1512, 1464, 1247 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37 (d, J = 8.90 Hz, 2H), 7.21 (d, J = 8.90 Hz, 2H), 5.21 (d, J = 1.40 Hz, 1H), 4.98 (d, J = 1.40 Hz, 1H), 3.83 (s, 3H), 2.48 (t, J = 7.35 Hz, 2H), 1.39–1.52 (m, 2H), 1.20–1.38 (m, 10H), 0.89 ppm (t, J = 6.65 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 158.87, 147.98, 133.79, 127.12, 113.51, 110.44, 55.22, 35.37, 31.85, 29.41, 29.36, 29.27, 28.30, 22.66, 14.11 ppm; MS: *m/z* (%): 246 (12.61) $[M]^+$, 148 (100).

Compound (*E*)-**13**: viscous liquid; IR (neat): $\tilde{\nu}$ = 1686, 1607, 1509, 1494, 1247, 1177 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 (d, J = 9.00 Hz, 2H), 6.88 (d, J = 9.00 Hz, 2H), 5.74 (t, J = 8.00 Hz, 1H), 3.83 (s, 3H), 2.21 (q, J = 7.07 Hz, 2H), 2.03 (s, 3H), 1.21–1.58 (m, 10H), 0.93 ppm (t, J = 6.75 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 158.30, 136.63, 133.70, 127.24, 126.52, 113.45, 55.23, 31.89, 29.74, 29.38, 29.27, 28.75, 22.68, 15.77, 14.11 ppm; MS: *m/z* (%): 246 (38.60) $[M]^+$, , 161 (100); HRMS: *m/z* (EI): calcd for $C_{17}H_{26}O$: 246.19837; found: 246.20135.

*Methyl 2-(3′-(4′′-methoxyphenyl)dec-2′-enyl)malonate (**5ea**) and methyl 2-(3′-(4′′-methoxyphenyl)dec-3′-enyl)malonate (**4ea**)*: The reaction of **1e** (65 mg, 0.24 mmol) and **3a** (73 mg, 0.48 mmol) afforded *E*-**4ea** and *E*-**5ea** (82 mg, 90%, (*E*)-**5ea**/(*E*)-**4ea** = 64:36) under conditions A. Compound (*E*)-**5ea**: viscous liquid; IR (neat): $\tilde{\nu}$ = 2927, 1754, 1737, 1608, 1511, 1247 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.24 (d, J = 8.85 Hz, 2H), 6.84 (d, J = 8.85 Hz, 2H), 5.46 (t, J = 7.53 Hz, 1H), 3.82 (s, 3H), 3.75 (s, 6H), 3.49 (t, J = 7.53 Hz, 1H), 2.80 (t, J = 7.53 Hz, 2H), 2.43–2.51 (m, 2H), 1.17–1.38 (m, 10H), 0.87 ppm (t, J = 6.75 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 169.50, 158.60, 142.85, 135.15, 127.40, 121.75, 113.48, 55.21, 52.55, 51.92, 31.78, 29.85, 29.54, 29.12, 28.63, 27.98, 22.60, 14.07 ppm; MS: *m/z* (%): 376 (46.92) $[M]^+$, 217 (100); HRMS: *m/z* (EI): calcd for $C_{22}H_{32}O_5$: 376.22497; found: 376.22749.

Compound (*E*)-**4ea**: viscous liquid; IR (neat): $\tilde{\nu}$ = 2926, 1739, 1608, 1512, 1246 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27 (d, J = 8.75 Hz, 2H), 6.85 (d, J = 8.75 Hz, 2H), 5.64 (t, J = 7.20 Hz, 1H), 3.81 (s, 3H), 3.72 (s, 6H), 3.37 (t, J = 7.60 Hz, 1H), 2.52 (t, J = 7.95 Hz, 2H), 2.13 (q, J = 7.10 Hz, 2H), 1.94 (q, J = 7.67 Hz, 2H), 1.17–1.42 (m, 8H), 0.86 ppm (t, J = 7.15 Hz, 3H); MS: *m/z* (%): 376 (M^+, 16.47), 91 (100); elemental analysis: calcd for $C_{22}H_{32}O_5$ (%): C 70.19, H 8.57; found: C 69.81, H 8.96.

Acknowledgment

Financial support from the Major State Basic Research Development Program (Grant No. G2000077500) and the National Natural Science Foundation of China is greatly appreciated.

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[20] Crystal data: $C_{20}H_{22}O_2$, $M = 294.38$, colorless, triclinic, space group $P\bar{1}$, $Mo_{K\alpha}$, final R indices $[I>2\sigma(I)]$, $R1 = 0.0596$, $wR2 = 0.1563$, $a = 8.3551(12)$, $b = 10.5105(16)$, $c = 11.1855(16)$ Å, $\alpha = 114.865(2)°$, $\beta = 96.820(3)°$, $\gamma = 102.076(3)°$, $V = 847.5(2)$ Å^3, $T = 293(2)$ K, $Z = 2$, collected/unique reflections: 5172/3731 ($R_{int} = 0.0979$), no observation $[I>2\sigma(I)]$ 2121, parameters 288. CCDC 213522 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

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Received: July 4, 2003 [F5301]

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