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Hydrostannylation–Cross-Coupling Strategy for the Stereoselective Synthesis of Alkylidenemalonates and Related α,β-Unsaturated Esters

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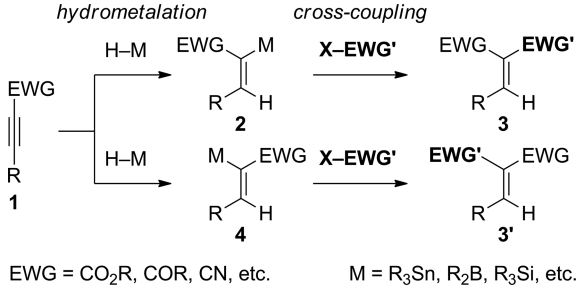
A method for the stereoselective synthesis of alkylidenemalonates and related α,β-unsaturated esters by a hydrostannylation–cross-coupling process has been developed. Pd-catalyzed and radical hydrostannylation of propiolate derivatives stereoselectively provided α-alkoxycarbonyl (*E*)- and (*Z*)-vinylstannanes, respectively, which were then converted into alkylidenemalonates by the Stille coupling reaction. A one-pot process was also realizable for the Pd-catalyzed reactions.

Introduction

Doubly activated olefins, such as alkylidenemalonates and α-alkylidene β-keto esters, are useful compounds and are often utilized as powerful Michael acceptors[1] or highly reactive dienophiles[2] in cycloaddition reactions. The Knoevenagel condensation, which is the addition of an active methylene compound to an aldehyde followed by dehydration, is the most widely used method for the preparation of this class of compounds.[3] However, this reaction is generally inapplicable to *E*/*Z*-selective syntheses of olefins bearing two different electron-withdrawing groups, giving a mixture of the isomers depending on their thermodynamic stability.[4] To achieve the desired stereochemistry in a stereospecific cycloaddition reaction,[2] it is important to prepare substrates *E*/*Z*-selectively. Furthermore, the Knoevenagel condensation is commonly conducted in the presence of acid and base catalysts at high temperatures, and therefore the reactions with easily enolizable aldehydes, such as 2-arylalkanals, are often problematic.[5,6] These limitations led us to develop a stereoselective synthesis of doubly activated olefins from alkynes by hydrometalation followed by cross-coupling.

Our strategy is shown in Scheme 1. The regio- and stereoselective hydrometalation of alkyne **1**, bearing an electron-withdrawing group, gives the metalated alkene **2** or **4**. The subsequent transition-metal-catalyzed cross-coupling reaction selectively produces the *E*/*Z* isomers of doubly activated olefins **3** and **3′**. Because both stereoselective hydrostannylation[7] and acylation of α-stannyl α,β-unsaturated carbonyl compounds by cross-coupling[8] have been reported separately, we chose tin as the metal component to prove the validity of the concept. Herein we report a method for the stereoselective synthesis of both isomers of alkylidenemalonates and related α,β-unsaturated esters under mild conditions through sequential hydrostannylation–cross-coupling reactions.



Scheme 1. Hydrometalation–cross-coupling strategy to selectively obtain (*E*)- and (*Z*)-alkylidenemalonates.

Results and Discussion

We first tested the reported conditions for the acylation of α-stannyl α,β-unsaturated carbonyl compounds in the reaction of (*E*)-vinylstannane **2a**, prepared by Pd-catalyzed hydrostannylation of methyl phenylpropiolate (see below), with isobutyl chloroformate. A solution of **2a** and isobutyl chloroformate in hexamethylphosphoramide (HMPA) was stirred in the presence of $[Pd(dba)_2]$ (5 mol-%) at 100 °C.[8a] Although **2a** disappeared after 12 h (TLC monitoring), the expected (*E*)-benzylidenemalonate **3ab** was obtained in only 5% yield along with unidentified byproducts (Scheme 2). Thus, we decided to explore new conditions.

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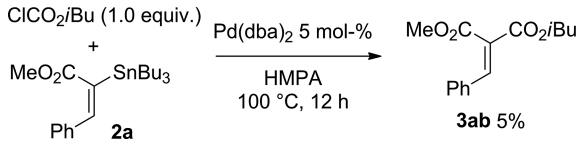
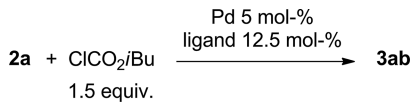


Scheme 2. Reaction of **2a** with $ClCO_2$*i*Bu under the conditions of ref.[8a]

A mixture of **2a** and isobutyl chloroformate (1.5 equiv.) in toluene was stirred at 100 °C in the presence of palladium diacetate (5 mol-%) and triphenylphosphine (12.5 mol-%). After 9 h, the expected (*E*)-benzylidenemalonate **3ab** was obtained in 58% yield; however, a trace amount (<1%) of the stereoisomer **3ba** was observed by ^{1}H NMR analysis of the crude product. It was confirmed that the isomerization of **3ab** takes place at 100 °C in toluene, even in the absence of the palladium catalyst and ligand. The isomerization of the olefinic geometry was suppressed when the reaction was conducted at 80 °C, giving **3ab** selectively in 48% yield after 24 h (Table 1, entry 1). The retention of the configuration was confirmed by NOESY correlations between the methoxy and aromatic protons, and the methyl protons of the isobutoxy group and the vinylic proton of **3ab**.

Table 1. Optimization of the acylation reaction conditions.[a]



Entry	Pd source	Ligand	Solvent	*T* [°C]	Time [h]	Yield[b] [%]
1	$Pd(OAc)_2$	Ph_3P	toluene	80	24	48
2	$Pd(OAc)_2$	Ph_3P	DMF	80	24	0
3	$Pd(OAc)_2$	Ph_3P	MeCN	80	24	0
4	$Pd(OAc)_2$	Ph_3P	DCE	80	24	62
5	$Pd(OAc)_2$	Ph_3P	DME	80	15	75
6	$[PdCl_2(PPh_3)_2]$	Ph_3P	DME	80	7	0
7	$[PdBn(PPh_3)_2Cl]$	Ph_3P	DME	80	7	0
8	$[Pd(PPh_3)_4]$	none	DME	80	24	60
9	$[Pd_2(allyl)_2Cl_2]$	Ph_3P	DME	80	7	80
10	$[Pd_2(dba)_3]\cdot CHCl_3$	Ph_3P	DME	80	4	83
11	$[Pd_2(dba)_3]\cdot CHCl_3$	Ph_3As	DME	80	4	51
12	$[Pd_2(dba)_3]\cdot CHCl_3$	dppe	DME	80	4	0
13	$[Pd_2(dba)_3]\cdot CHCl_3$	Ph_3P	DME	40	24	0
14	$[Pd_2(dba)_3]\cdot CHCl_3$	Ph_3P	DME	60	24	70
15[c]	$[Pd_2(dba)_3]\cdot CHCl_3$	Ph_3P	DME	80	6	83
16[d]	$[Pd_2(dba)_3]\cdot CHCl_3$	Ph_3P	DME	80	8	66

[a] Conducted with 0.15 mmol **2a** and 1.5 mL solvent; DCE = 1,2-dichloroethane, DME = 1,2-dimethoxyethane. [b] Determined by ^{1}H NMR analysis of the crude mixture with Ph_3CH as internal standard. [c] $[Pd_2(dba)_3]\cdot CHCl_3$ (1.0 mol-%) and Ph_3P (5.0 mol-%). [d] $[Pd_2(dba)_3]\cdot CHCl_3$ (0.5 mol-%) and Ph_3P (2.5 mol-%).

Significant solvent effects were observed; the reaction in DMF gave a complex mixture containing no detectable amount of **3ab** (entry 2). Although no reaction occurred in acetonitrile (entry 3), the reaction in DCE gave **3ab** in 62% yield (entry 4). Of the tested solvents, the reaction proceeded most smoothly in DME, with **3ab** produced in 75% yield after 15 h (entry 5).

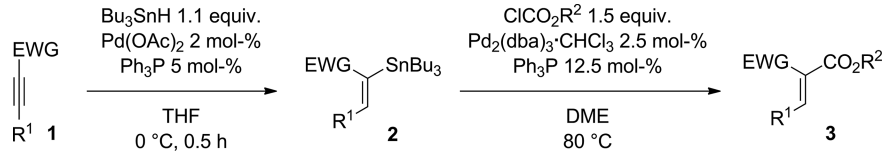
The palladium source was also important. Although the reaction with tetrakis(triphenylphosphine)palladium was slower (60% yield after 24 h, entry 8), the use of the allylpalladium chloride dimer accelerated the reaction to give **3ab** in 80% yield after 7 h (entry 9). The tris(dibenzylideneacetone)dipalladium chloroform adduct $[Pd_2(dba)_3\cdot CHCl_3]$ was found to be an excellent catalyst for this reaction, producing **3ab** in 83% yield after 4 h (entry 10). With bis(triphenylphosphine)palladium dichloride or benzylbis(triphenylphosphine)palladium chloride, no reaction occurred, and **2a** was recovered quantitatively (entries 6 and 7). Ligands other than triphenylphosphine, such as triphenylarsine[9] and bis(diphenylphosphanyl)ethane (dppe), turned out to be less effective (entries 11 and 12). Commonly used additives were tested under the conditions of entry 10; however, no reaction occurred in the presence of lithium chloride[10] and the addition of cesium fluoride[11] resulted in the decomposition of **2a** (not shown in the Table 1).

The efficient reaction rate was maintained with 2 mol-% palladium catalyst, giving **3ab** in 83% yield after 6 h (entry 15). A further decrease in the catalyst loading (1 mol-%) or lower reaction temperatures (40 or 60 °C), however, resulted in significant deceleration of the reaction (entries 16, 13, and 14).

With the best conditions for the cross-coupling reaction in hand (Table 1, entry 10), the substrate scope was investigated. Not only with propiolate derivatives, but also with propiolamide and propiolonitrile derivatives, the Pd-catalyzed regio- and stereoselective hydrostannylation proceeded under modified conditions[7a] to give (*E*)-vinylstannanes **2** in yields of 64–83% (Table 2).[7b,12,13] The conditions for cross-coupling were compatible with various functional groups, such as esters (entries 1–3), an amide (entry 4), and a cyanide (entry 5), giving the products **3** in yields of 67–89%. Substrates bearing either an electron-rich or -deficient aromatic ring (entries 6–8) or an alkyl group (entries 9 and 10) gave the products in good yields. It is noteworthy that phenethylidenemalonate **3ib**, unavailable by the Knoevenagel condensation, was prepared without migration of the C=C bond (entry 9). Moreover, a Cbz group (entry 11) and the sterically crowded menthyloxy- and 8-phenylmenthyloxycarbonyl groups (entries 12 and 13) could also be introduced into **2a** to give the corresponding benzylidenemalonates **3ac**, **3ak**, and **3al**, respectively, in good yields.

The reaction of (*Z*)-vinylstannane was also investigated. Following a report on radical hydrostannylation,[7c] (*Z*)-vinylstannane **4a** was prepared stereo- and regioselectively in 69% yield by using AIBN and tributylstannane.[12] The geometry of the vinylstannane clearly affected the reaction time and yield; the reaction of **4a** with isobutyl, menthyl, and 8-phenylmenthyl chloroformate under the optimized conditions for **2a** required a longer reaction time (24 h) and gave lower yields (45–48%; Table 3, entries 1–3) than the reactions of **2a** (75–89%; Table 2, entries 1, 12, and 13). Comparable results are likely to be obtained from the same reaction sequence with propiolates **1f**–**h**, which bear substituted benzene rings.[7c] Unfortunately, this strategy could

Table 2. Scope of the Pd-catalyzed hydrostannylation–cross-coupling process.

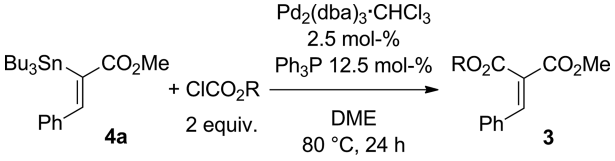


Entry	1	R^1	EWG	2	Yield [%]	R^2	3	Time [h]	Yield[a] [%]
1[b]	**1a**	Ph	CO_2Me	**2a**	69	*i*Bu	**3ab**	6	83
2	**1b**	Ph	CO_2*i*Bu	**2b**	67	Me	**3ba**	12	72
3	**1c**	Ph	CO_2Bn	**2c**	72	Me	**3ca**	12	67
4	**1d**	Ph	$CONMe_2$	**2d**	73	*i*Bu	**3db**	12	74
5	**1e**	Ph	CN	**2e**	64	*i*Bu	**3eb**	12	89
6	**1f**	4-FC_6H_4	CO_2Me	**2f**	77	*i*Bu	**3fb**	12	90
7	**1g**	4-$MeOC_6H_4$	CO_2Me	**2g**	73	*i*Bu	**3gb**	12	76
8	**1h**	2-MeC_6H_4	CO_2Me	**2h**	68	*i*Bu	**3hb**	12	70
9	**1i**	Bn	CO_2Me	**2i**	69[c]	*i*Bu	**3ib**	12	57[d]
10	**1j**	hexyl	CO_2Me	**2j**	83	*i*Bu	**3jb**	12	79
11	**1a**	Ph	CO_2Me	**2a**	69	Bn	**3ac**	12	61
12	**1a**	Ph	CO_2Me	**2a**	69	Men[e]	**3ak**	12	89
13[f]	**1a**	Ph	CO_2Me	**2a**	69	ϕMen[e]	**3al**	24	75

[a] Isolated yields. [b] $[Pd_2(dba)_3]$·$CHCl_3$ (1 mol-%) and Ph_3P (5 mol-%). [c] Included 9% impurity, yield was estimated by ^1H NMR analysis (see the Exp. Sect.). [d] Based on a two-step yield and the estimated yield of **2i**. [e] Men = menthyl, ϕMen = 8-phenylmenthyl. [f] $ClCO_2R^2$ (2.0 equiv.).

not be applied to propiolate **1j**, bearing an alkyl group, propiolamide **1d**, and propiolonitrile **1e** because the radical hydrostannylation step resulted in a complex mixture (**1j**, **1e**) or recovery of the starting material (**1d**).

Table 3. Cross-coupling reactions of (*Z*)-vinylstannane **4a**.



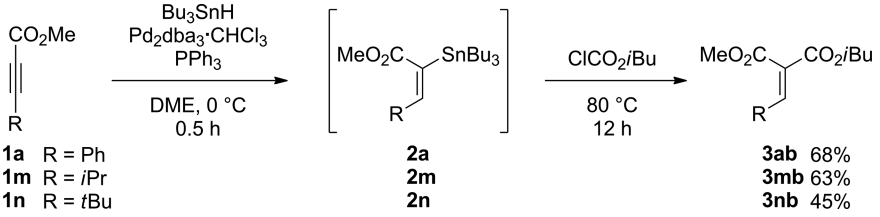
Entry	R	3	Yield[a] [%]
1	*i*Bu	**3ba**	48
2	Men[b]	**3ka**	48
3	ϕMen[b]	**3la**	45
4	Bn	**3ca**	Trace

[a] Isolated yield. [b] Men = menthyl, ϕMen = 8-phenylmenthyl.

The retention of the configuration was confirmed by NOESY experiments on **3ba**, which showed correlation between the methyl protons of the isobutoxy group and the aromatic protons. Nevertheless, it is noteworthy that the desired malonates were obtained in geometrically pure form because the isomerization of (*Z*)-vinylstannane to the *E* isomer under the cross-coupling conditions has previously been reported.[8a,14] The reaction with benzyl chloroformate only gave a trace amount of the desired **3ca** (Table 3, entry 4), probably due to low reactivity of **4a** as well as the thermal instability of the chloroformate. The observed lower reactivity of (*Z*)-vinylstannane **4a** is likely due to the steric hindrance of the adjacent phenyl group. Alternatively, the same products can be obtained in better yields from (*E*)-vinylstannane by exchanging the electron-withdrawing groups of the two reaction partners (**2** and chloroformate, e.g., Table 2, entries 1 and 2, and 3 and 11).

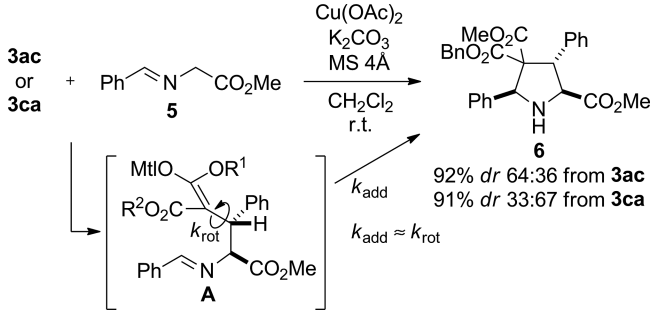
This hydrostannylation–cross-coupling sequence could be performed in one pot (Scheme 3). A solution of **1a** and tributylstannane (1.1 equiv.) was stirred at 0 °C in the presence of $[Pd_2(dba)_3]$·$CHCl_3$ and triphenylphosphine (2.5 and 12.5 mol-%, respectively). When the complete consumption of **1a** was confirmed by TLC monitoring after 0.5 h, the solution was warmed to 80 °C and isobutyl chloroformate (1.5 equiv.) was added to the solution. After 12 h, the yield of **3ab** (68%) was better than the overall yield of the sequential reactions (Table 2, entry 1). To realize an efficient one-pot reaction, the amount of stannane was important; when an excess of stannane (1.5 equiv.) was used in the hydrostannylation step, the coupling reaction was retarded, and around 30% of **2a** remained after 12 h. Propiolates **1m** and **1n**, which bear secondary and tertiary alkyl groups, respectively, could also be used, and the corresponding (*E*)-alkylidenemalonates **3mb** and **3nb** were obtained in good overall yields (63 and 45%, respectively) despite the steric hindrance.

Finally, (*E*)- and (*Z*)-alkylidenemalonates **3ac** and **3ca**, bearing two different ester moieties, were subjected to the previously reported copper-catalyzed [3+2] cycloaddition reaction (Scheme 4).[15] A solution of **3ac** and glycine derivative **5** was stirred at room temperature in the presence of copper diacetate (10 mol-%), potassium carbonate (2 equiv.), and molecular sieves (4 Å). After 12 h, pyrrolidine **6** was obtained in 92% yield as a 64:36 mixture of diastereomers at the stereogenic quaternary carbon. This



Scheme 3. One-pot Pd-catalyzed hydrostannylation–cross-coupling reactions.

result indicates that this cycloaddition reaction proceeded mainly by stepwise bond formation and not by a concerted mechanism as proposed in the literature. In turn, the reaction of **3ca** gave **6** with a 33:67 diastereomeric ratio (*dr*). Therefore the diastereoselectivity of the cycloaddition partially reflects the stereochemistry of the malonates utilized. The irreversibility of the cycloaddition reaction was confirmed by the following experiments. When diastereomeric mixtures of **6** with *dr* values of 64:36 and 33:67 were each treated under the above reaction conditions for 12 h, **6** did not undergo epimerization, but was recovered with an unchanged *dr*. Accordingly, in this stepwise cycloaddition, the rate constant for the cyclization of intermediate **A** (k_{add}) should be competitive with that of the indicated C–C bond rotation (k_{rot}).[16] This clearly exemplifies the utility of stereoselectively prepared malonates as probes to examine reaction mechanisms.[4b,17]



Scheme 4. Copper-catalyzed [3+2] cycloaddition reactions of **3ac** and **3ca**, shedding light on the mechanism.

Conclusions

We have developed a stereo- and regioselective synthesis of doubly activated olefins by hydrostannylation of alkynes bearing an electron-withdrawing group and a subsequent cross-coupling reaction. Alkylidenemalonates, as well as α-carbamoyl- and α-cyano-α,β-unsaturated esters, were stereoselectively prepared by this method. The mild and neutral reaction conditions allowed us to prepare such esters bearing a variety of functional groups, and were shown to be desirable especially for olefins that easily undergo isomerization, such as phenethylidenemalonate. This new methodology is a favorable option even for substrates that are unsuitable for the conventional Knoevenagel condensation reactions. This methodology is now being extended to include other cross-coupling reactions.

Experimental Section

General: All the reactions were performed under argon. Anhydrous solvents were purchased and used as reaction solvents. Starting materials, reagents, and solvents were purchased and used as supplied unless otherwise noted. Silica gel was used for column chromatography unless otherwise noted. NMR spectra (500 MHz for ^{1}H and 125 MHz for ^{13}C) were recorded in $CDCl_3$ with tetramethylsilane as internal standard. Abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; sext, sextet; sept, septet; m, multiplet; br., broad. ^{13}C NMR peak multiplicity assignments were made based on DEPT data. The ^{13}C–^{117}Sn and ^{13}C–^{119}Sn coupling constants of the satellite peaks in the ^{13}C NMR spectra are not reported for clarity. For confirmation of the *E*/*Z* geometries of **2** and **4**, average of ^{1}H–^{117}Sn and ^{1}H–^{119}Sn coupling constants, usually differing by 1–3 Hz,[13] were reported as H–Sn coupling constants due to insufficient resolution. A quadrupole mass spectrometer was used to record EI-MS, whereas ESI-MS were recorded by TOF.

Preparation of the Starting Materials: The chloroformates were purified by distillation before use. Alkynes **1c**,[18] **1d**,[19]**1e**,[20] **1f**,[21] **1g**,[22] **1h**,[23] **1i**,[24] 8-phenylmenthyl chloroformate,[25] and imine **5**[15] were prepared according to the literature.

Isobutyl 3-Phenylpropiolate (1b): Phenylacetylene (1.1 mL, 10 mmol) was dissolved in THF (10 mL) in a dry 50-mL round-bottomed flask. A 1.6 M hexane solution of BuLi (6.4 mL, 10 mmol) and $ClCO_2$*i*Bu (2.6 mL, 20 mmol) were added dropwise 30 min apart to the stirred solution cooled to –78 °C. After 10 min, the cooling bath was removed and the mixture was stirred for an additional 30 min. After addition of satd. aq. $NaHCO_3$, the whole was extracted twice with AcOEt and the combined organic layers were washed with brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (hexane to hexane/AcOEt, 10:1) to afford the title compound (2.05 g, 98%) as a pale-yellow oil. ^{1}H NMR: δ = 7.65–7.55 (m, 2 H), 7.45 (m, 1 H), 7.40–7.35 (m, 2 H), 4.03 (d, J = 7.0 Hz, 2 H), 2.05 (m, 1 H), 0.99 (d, J = 6.5 Hz, 6 H) ppm. ^{13}C NMR: δ = 154.1 (C), 132.9 (CH), 130.5 (CH), 128.5 (CH), 119.6 (C), 86.0 (C), 80.6 (C), 71.9 (CH_2), 27.6 (CH), 18.9 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2967, 2936, 2878, 2222, 1709, 1281, 1188, 1169 cm^{-1}. MS (EI): *m*/*z* = 202 [M]$^+$, 146 [M – isobutene]$^+$, 129 [M – *i*BuO]$^+$. The ^{1}H and ^{13}C NMR, IR, and EIMS data are in good agreement with published data.[26]

Methyl 4-Methylpent-2-ynoate (1m): 3-Methylbut-1-yne (2.0 mL, 20 mmol) was dissolved in THF (20 mL) in a dry 50-mL round-bottomed flask. A 1.6 M hexane solution of BuLi (14 mL, 22 mmol) and $ClCO_2Me$ (1.8 mL, 24 mmol) were added dropwise 30 min apart to the stirred solution cooled to –78 °C. After 10 min, the cooling bath was removed and the mixture was stirred for an additional 30 min. After addition of satd. aq. $NaHCO_3$, the whole was extracted twice with Et_2O and the combined organic layers were washed with brine, dried with Na_2SO_4, and concentrated in vacuo to afford the title compound (95%) as a pale-yellow oil, which was used for the next step without further purification. ^{1}H

NMR: δ = 3.75 (s, 3 H), 2.70 (sept, J = 7.0 Hz, 1 H), 1.24 (d, J = 7.0 Hz, 6 H) ppm. ^{13}C NMR: δ = 154.3 (C), 94.3 (C), 72.0 (C), 52.4 (CH_3), 21.6 (CH_3), 20.4 (CH) ppm. The ^{1}H and ^{13}C NMR spectra are in good agreement with published data.[27]

Methyl 4,4-Dimethylpent-2-ynoate (1n): The same procedure as that used for **1m** with 3,3-dimethylbut-1-yne (2.5 mL, 20 mmol) in place of 3-methylbut-1-yne afforded the title compound (95%) as a pale-yellow oil, which was used for the next step without further purification. ^{1}H NMR: δ = 3.76 (s, 3 H), 1.29 (s, 9 H) ppm. ^{13}C NMR: δ = 154.4 (C), 96.9 (C), 71.4 (C), 52.5 (CH_3), 31.6 (C), 29.9 (CH_3) ppm. The ^{1}H and ^{13}C NMR spectra are in good agreement with published data.[28]

General Procedure for Pd-Catalyzed Hydrostannylation − Methyl (*E*)-3-Phenyl-2-(tributylstannyl)acrylate (2a): To avoid the use of $[Pd(PPh_3)_4]$,[7a] $Pd(OAc)_2$ was utilized instead. Propiolate **1a** (1.5 mL, 10 mmol), $Pd(OAc)_2$ (45 mg, 0.20 mmol), and Ph_3P (130 mg, 0.50 mmol) were dissolved in THF (20 mL) in a dry 100-mL round-bottomed flask. Bu_3SnH (3.3 mL, 12 mmol) was added to the solution cooled in an ice-water bath. The mixture was stirred for 30 min, and then the cooling bath was removed. The mixture was concentrated in vacuo and the residue purified by column chromatography (hexane to hexane/Et_2O, 20:1) to afford the title compound (3.21 g, 69%) as a pale-yellow oil. ^{1}H NMR: δ = 7.33–7.29 (m, 4 H), 7.25 (m, 1 H), 6.71 (s, 1 H), 3.69 (s, 3 H), 1.65–1.45 (m, 6 H), 1.34 (sext, J = 7.5 Hz, 6 H), 1.06 (t, J = 8.0 Hz, 6 H), 0.91 (t, J = 7.5 Hz, 9 H) ppm. ^{13}C NMR: δ = 173.7 (C), 142.2 (CH), 139.4 (C), 137.0 (C), 128.4 (CH), 128.1 (CH), 127.9 (CH), 51.4 (CH_3), 28.8 (CH_2), 27.2 (CH_2), 13.7 (CH_3), 10.6 (CH_2) ppm. IR (neat): $\tilde{\nu}$ = 2955, 2922, 1703, 1207 cm^{-1}. MS (EI): m/z = 451 $[M]^+$, 395 $[M - Bu]^+$. $C_{22}H_{36}O_2Sn$ (451.22): calcd. C 58.56, H 8.04; found C 58.53, H 8.21. The *E* geometry was confirmed by the H–Sn coupling constant of the satellite peaks of the β-H (δ = 6.71 ppm, $^3J_{H\text{-}Sn}$ = 59 Hz).[13]

Isobutyl (*E*)-3-Phenyl-2-(tributylstannyl)acrylate (2b): Purified by column chromatography (hexane to hexane/Et_2O, 50:1). From 10 mmol **1b**, the title compound (3.31 g, 67%) was obtained as a pale-yellow oil. ^{1}H NMR: δ = 7.35–7.20 (m, 3 H), 6.71 (s, 1 H), 3.87 (d, J = 6.5 Hz, 2 H), 1.88 (nonet, J = 6.5 Hz, 1 H), 1.65–1.47 (m, 6 H), 1.34 (sext, J = 7.5 Hz, 6 H), 1.07 (t, J = 8.5 Hz, 6 H), 0.91 (t, J = 7.5 Hz, 9 H), 0.84 (d, J = 6.5 Hz, 6 H) ppm. ^{13}C NMR: δ = 173.5 (C), 142.0 (CH), 139.8 (C), 137.1 (CH), 128.3 (CH), 127.9 (CH), 124.5 (C), 70.7 (CH_2), 28.8 (CH_2), 27.6 (CH), 27.3 (CH_2), 19.2 (CH_3), 13.7 (CH_3), 10.6 (CH_2) ppm. IR (neat): $\tilde{\nu}$ = 2959, 2924, 2874, 2855, 1701, 1173 cm^{-1}. MS (EI): m/z = 437 $[M - Bu]^+$. HRMS (ESI): calcd. for $C_{25}H_{42}O_2SnNa$ 517.2099 $[M + Na]^+$; found 517.2098. The *E* geometry was confirmed by the H–Sn coupling constant of the satellite peaks of the β-H (δ = 6.71 ppm, $^3J_{H\text{-}Sn}$ = 58 Hz).[13]

Benzyl (*E*)-3-Phenyl-2-(tributylstannyl)acrylate (2c): Purified by column chromatography (hexane to hexane/Et_2O, 50:1). From 0.80 mmol **1c**, the title compound (301 mg, 72%) was obtained as a pale-yellow oil. ^{1}H NMR: δ = 7.34–7.21 (m, 10 H), 6.71 (s, 1 H), 5.14 (s, 2 H), 1.63–1.42 (m, 6 H), 1.38–1.21 (m, 6 H), 1.10–0.96 (m, 6 H), 0.88 (t, J = 7.0 Hz, 9 H) ppm. ^{13}C NMR: δ = 173.0 (C), 142.4 (CH), 139.3 (C), 136.9 (C), 135.8 (C), 128.8 (CH), 128.4 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 66.3 (CH_2), 28.7 (CH_2), 27.2 (CH_2), 13.7 (CH_3), 10.6 (CH_2) ppm. IR (KBr): $\tilde{\nu}$ = 2955, 2924, 2870, 2853, 1701, 1375, 1206, 1167 cm^{-1}. MS (ESI): m/z = 551 [M + Na]. HRMS (ESI): calcd. for $C_{28}H_{40}O_2SnNa$ 551.1948 $[M + Na]^+$; found 551.1947. The *E* geometry was confirmed by the H–Sn coupling constant of the satellite peaks of the β-H (δ = 6.71 ppm, $^3J_{H\text{-}Sn}$ = 58 Hz).[13]

(*E*)-*N*,*N*-Dimethyl-3-phenyl-2-(tributylstannyl)acrylamide (2d): Purified by column chromatography (hexane to hexane/Et_2O, 50:1). From 2.5 mmol **1d**, the title compound (851 mg, 73%) was obtained as a pale-yellow oil. ^{1}H NMR: δ = 7.31–7.27 (m, 4 H), 7.22 (m, 1 H), 6.57 (s, 1 H), 2.95 (s, 3 H), 2.71 (s, 3 H), 1.65–1.46 (m, 6 H), 1.35 (sext, J = 7.0 Hz, 6 H), 1.07 (t, J = 7.0 Hz, 6 H), 0.91 (t, J = 7.0 Hz, 9 H) ppm. ^{13}C NMR: δ = 174.1 (C), 143.2 (CH), 138.0 (C), 137.5 (C), 128.5 (CH), 127.7 (CH), 127.6 (CH), 37.1 (CH_3), 34.2 (CH_3), 28.9 (CH_2), 27.3 (CH_2), 13.7 (CH_3), 10.5 (CH_2) ppm. IR (neat): $\tilde{\nu}$ = 2955, 2924, 2855, 1717, 1605, 1462, 1254, 1076 cm^{-1}. MS (EI): m/z = 465 $[M]^+$, 408 $[M - Bu]^+$. HRMS (ESI): calcd. for $C_{23}H_{40}OSn$ 466.2126 $[M + H]^+$; found 466.2125. The *E* geometry was confirmed by the H–Sn coupling constant of the satellite peaks of the β-H (δ = 6.57 ppm, $^3J_{H\text{–}Sn}$ = 62 Hz).[13]

(*E*)-3-Phenyl-2-(tributylstannyl)acrylonitrile (2e): Purified by column chromatography (hexane to hexane/Et_2O, 50:1). From 1.0 mmol **1e**, the title compound (269 mg, 64%) was obtained as a pale-yellow oil. ^{1}H NMR: δ = 7.83 (d, J = 7.0 Hz, 2 H), 7.45–7.35 (m, 3 H), 7.06 (s, 1 H), 1.64 (m, 6 H), 1.37 (sext, J = 7.5 Hz, 6 H), 1.07 (m, 6 H), 0.92 (t, J = 7.5 Hz, 9 H) ppm. ^{13}C NMR: δ = 156.0 (CH), 136.2 (C), 130.1 (CH), 128.8 (CH), 128.6 (CH), 121.2 (C), 111.2 (C), 28.6 (CH_2), 27.2 (CH_2), 13.6 (CH_3), 10.9 (CH_2) ppm. IR (neat): $\tilde{\nu}$ = 2955, 2924, 2855, 2176, 1713, 1585, 1562, 1076, 1049 cm^{-1}. MS (EI): m/z = 362 $[M - Bu]^+$, 306 $[M - 2Bu]^+$. HRMS (ESI): calcd. for $C_{21}H_{33}NSnNa$ 442.1527 $[M + Na]^+$; found 442.1529. $C_{21}H_{33}NSn$ (418.19): calcd. C 60.31, H 7.95, N 3.35; found C 60.56, H 8.10, N 3.36. The *E* geometry was confirmed by the H–Sn coupling constant of the satellite peaks of the β-H (δ = 7.06 ppm. $^3J_{H\text{-}Sn}$ = 47 Hz).[13]

Methyl (*E*)-3-(4-Fluorophenyl)-2-(tributylstannyl)acrylate (2f): Purified by column chromatography (hexane to hexane/Et_2O, 50:1). From 1.0 mmol **1f**, the title compound (363 mg, 77%) was obtained as a pale-yellow oil. ^{1}H NMR: δ = 7.31–7.23 (m, 2 H), 6.99 (tt, J = 9.0, 2.0 Hz, 2 H), 6.66 (s, 1 H), 3.69 (s, 3 H), 1.62–1.47 (m, 6 H), 1.34 (sext, J = 7.5 Hz, 6 H), 1.06 (t, J = 8.0 Hz, 6 H), 0.91 (t, J = 7.5 Hz, 9 H) ppm. ^{13}C NMR: δ = 173.5 (C), 162.4 (d, $J_{F\text{-}C}$ = 246 Hz, C), 141.0 (CH), 139.2 (C), 133.2 (C), 129.6 (CH), 115.3 (d, $J_{F\text{-}C}$ = 22 Hz, CH), 51.4 (CH_3), 28.7 (CH_2), 27.2 (CH_2), 13.7 (CH_3), 10.6 (CH_2) ppm. IR (neat): $\tilde{\nu}$ = 2959, 2920, 2847, 2816, 1701, 1601, 1508, 1234, 1157 cm^{-1}. MS (EI): m/z = 470 $[M]^+$, 413 $[M - Bu]^+$. HRMS (ESI): calcd. for $C_{22}H_{35}FO_2SnNa$ 493.1535 $[M + Na]^+$; found 493.1534. The *E* geometry was confirmed by the H–Sn coupling constant of the satellite peaks of the β-H (δ = 6.66 ppm, $^3J_{H\text{-}Sn}$ = 58 Hz).[13]

Methyl (*E*)-3-(4-Methoxyphenyl)-2-(tributylstannyl)acrylate (2g): Purified by column chromatography (hexane to hexane/Et_2O, 50:1). From 1.0 mmol **1g**, the title compound (352 mg, 73%) was obtained as a pale-yellow oil. ^{1}H NMR: δ = 7.26 (dt, J = 8.5, 3.0 Hz, 2 H), 6.83 (dt, J = 8.5, 3.0 Hz, 2 H), 6.64 (s, 1 H), 3.80 (s, 3 H), 3.70 (s, 3 H), 1.64–1.47 (m, 6 H), 1.34 (sext, J = 7.5 Hz, 6 H), 1.05 (t, J = 8.0 Hz, 6 H), 0.90 (t, J = 7.5 Hz, 9 H) ppm. ^{13}C NMR: δ = 173.9 (C), 159.5 (C), 142.0 (CH), 136.4 (C), 129.7 (C), 129.5 (CH), 113.7 (CH), 55.2 (CH_3), 51.3 (CH_3), 28.7 (CH_2), 27.2 (CH_2), 13.7 (CH_3), 10.6 (CH_2) ppm. IR (neat): $\tilde{\nu}$ = 2997, 2955, 2924, 2851, 1701, 1508, 1250, 1164, 1034 cm^{-1}. MS (EI): m/z = 425 $[M - Bu]^+$. HRMS (ESI): calcd. for $C_{23}H_{38}O_3SnNa$ 505.1735 $[M + Na]^+$; found 505.1736. The *E* geometry was confirmed by the H–Sn coupling constant of the satellite peaks of the β-H (δ = 6.64 ppm, $^3J_{H\text{-}Sn}$ = 60 Hz).[13]

Methyl (*E*)-3-(*o*-Tolyl)-2-(tributylstannyl)acrylate (2h): Purified by column chromatography (hexane to hexane/Et_2O, 50:1). From 2.5 mmol **1h**, the title compound (685 mg, 68%) was obtained as a

yellow oil. ^{1}H NMR: δ = 7.21 (d, J = 7.5 Hz, 1 H), 7.17–7.08 (m, 3 H), 6.91 (s, 1 H), 3.58 (s, 3 H), 2.32 (s, 3 H), 1.64–1.47 (m, 6 H), 1.34 (sext, J = 7.5 Hz, 6 H), 1.06 (t, J = 8.0 Hz, 6 H), 0.91 (t, J = 7.5 Hz, 9 H) ppm. ^{13}C NMR: δ = 173.2 (C), 143.1 (CH), 139.8 (C), 137.0 (C), 135.4 (C), 129.9 (CH), 127.9 (CH), 127.6 (CH), 125.7 (CH), 51.2 (CH_3), 28.8 (CH_2), 27.2 (CH_2), 19.8 (CH_3), 13.7 (CH_3), 10.6 (337, CH_2) ppm. IR (neat): $\tilde{\nu}$ = 2955, 2928, 1701, 1196 cm^{-1}. MS (EI): m/z = 465 [M]$^+$, 409 [M – Bu]$^+$. $C_{23}H_{38}O_2Sn$ (465.24): calcd. C 59.37, H 8.23; found C 59.55, H 8.31. The E geometry was confirmed by the H–Sn coupling constant of the satellite peaks of the β-H (δ = 6.91 ppm, $^3J_{H\text{-}Sn}$ = 55 Hz).[13]

Methyl (*E*)-4-Phenyl-2-(tributylstannyl)but-2-enoate (2i): Purified by column chromatography (hexane to hexane/Et_2O, 50:1). From 2.5 mmol **1i**, a mixture of the title compound (69%) and an impurity (6%) was obtained as a pale-yellow oil (878 mg). ^{1}H NMR: δ = 7.30 (td, J = 8.0, 2.0 Hz, 2 H), 7.22 (dd, J = 8.0, 2.0 Hz, 2 H), 7.17 (t, J = 8.0 Hz, 1 H), 7.33–7.14 (m, 0.54 H impurity), 6.16 (t, J = 7.0 Hz, 1 H), 4.29 (s, 0.18 H impurity), 3.76 (d, J = 7.0 Hz, 2 H), 3.74 (s, 3 H), 3.70 (s, 0.27 H impurity), 1.57–1.38 (m, 6 H), 1.32–1.24 (m, 6 H, 0.54 H impurity), 1.24–1.16 (m, 0.54 H impurity) 1.16–0.82 (m, 15 H, 0.81 H impurity), 0.80–0.61 (m, 0.54 H impurity) ppm. ^{13}C NMR: δ = 171.7 (C), 150.3 (CH), 139.8 (C), 136.4 (C), 128.8 (CH), 128.5 (CH), 126.1 (CH), 51.3 (CH_3), 38.5 (CH_2), 28.9 (CH_2), 27.2 (CH_2), 13.7 (CH_3), 10.3 (CH_2) ppm. IR (neat): $\tilde{\nu}$ = 2955, 2924, 2851, 1709, 1597, 1192 cm^{-1}. MS (EI): m/z = 409 [M – Bu]$^+$. HRMS (ESI): calcd. for $C_{23}H_{38}O_2SnNa$ 489.1786 [M + Na]$^+$; found 489.1786. The E geometry was confirmed by the H–Sn coupling constant of the satellite peaks of the β-H (δ = 6.16 ppm, $^3J_{H\text{-}Sn}$ = 56 Hz).[13] The impurity was assigned as the regioisomer, methyl (*E*)-4-phenyl-3-(tributylstannyl)but-2-enoate by analogy with a previous report.[8a] The yield was determined by the integration area of the ^{1}H NMR signals at δ = 4.29 and 6.16 ppm. The mixture was used in the next reaction without further purification.

Methyl (*E*)-2-(Tributylstannyl)non-2-enoate (2j): Purified by column chromatography (hexane to hexane/Et_2O, 50:1). From 2.5 mmol **1j**, the title compound (955 mg, 83%) was obtained as a pale-yellow oil. ^{1}H NMR: δ = 6.04 (t, J = 7.0 Hz, 1 H), 3.69 (s, 3 H), 2.40 (q, J = 7.0 Hz, 2 H), 1.53–1.37 (m, 8 H), 1.35–1.25 (m, 12 H), 0.85–1.04 (m, 18 H) ppm. ^{13}C NMR: δ = 171.8 (C), 153.7 (CH), 135.2 (C), 51.1 (CH_3), 32.2 (CH_2), 31.6 (CH_2), 29.2 (CH_2), 28.86 (CH_2), 28.85 (CH_2), 27.2 (CH_2), 22.6 (CH_2), 14.1 (CH_2), 13.7 (CH_3), 10.2 (CH_2) ppm. IR (neat): $\tilde{\nu}$ = 2955, 2924, 2855, 1709, 1601, 1462, 1177 cm^{-1}. MS (EI): m/z = 403 [M – Bu]$^+$. The E geometry was confirmed by the H–Sn coupling constant of the satellite peaks of the β-H (δ = 6.04 ppm, $^3J_{H\text{-}Sn}$ = 60 Hz).[13] The ^{1}H and ^{13}C NMR, IR, and MS data are in good agreement with the published data.[7b]

General Procedure for the Cross-Coupling Reaction – Benzyl Methyl (*E*)-Benzylidenemalonate (3ac): Compound **2a** (225 mg, 0.50 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (13 mg, 2.5 mol-%), Ph_3P (16 mg, 12.5 mol-%), and $ClCO_2Bn$ (0.10 mL, 0.75 mmol) were dissolved in DME (5 mL) in a dry 30-mL round-bottomed flask. The solution was stirred at 80 °C for 12 h. After the addition of H_2O, the mixture was cooled to room temp. and extracted with AcOEt twice. The combined organic layers were washed with brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (hexane/Et_2O, 50:1 to 10:1) to give the title compound (90 mg, 61%) as a pale-yellow oil. ^{1}H NMR: δ = 7.79 (s, 1 H), 7.44–7.31 (m, 10 H), 5.30 (s, 2 H), 3.83 (s, 3 H) ppm. ^{13}C NMR: δ = 167.0 (C), 163.9 (C), 143.1 (CH), 135.5 (C), 132.7 (C), 130.7 (CH), 129.4 (CH), 128.9 (CH), 128.6 (CH), 128.3 (CH), 127.9 (CH), 125.6 (C), 67.2 (CH_2), 52.7 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2978, 2947, 2886, 1732, 1620, 1504, 1458, 1373, 1258, 122, 1053 cm^{-1}. MS (ESI): m/z = 319 [M + Na]$^+$. HRMS (ESI): calcd. for $C_{18}H_{16}O_4Na$ 319.0941 [M + Na]$^+$; found 319.0945. The ^{1}H and ^{13}C NMR data are in good agreement with those reported.[4b]

Isobutyl Methyl (*E*)-2-Benzylidenemalonate (3ab): Step-wise procedure (Table 2, entry 1): Prepared according to the General Procedure by using 1.0 mmol **2a** with $[Pd_2(dba)_3]\cdot CHCl_3$ (10 mg, 1.0 mol-%), Ph_3P (13 mg, 5.0 mol-%), $ClCO_2iBu$ (0.20 mL, 1.5 mmol), and DME (10 mL) for 6 h, the title compound (226 mg, 83%) was obtained as a pale-yellow oil after purification by column chromatography (hexane to hexane/AcOEt, 10:1). One-pot procedure (Scheme 3): Propiolate **1a** (0.15 mL, 1.0 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (26 mg, 2.5 mol-%), and Ph_3P (32 mg, 12.5 mol-%) were dissolved in DME (2 mL) in a dry 30-mL round-bottomed flask under argon. Bu_3SnH (0.30 mL, 1.1 mmol) was added to the stirred solution cooled in an ice-water bath. After 30 min, the solution was warmed to 80 °C, and isobutyl chloroformate (0.20 mL, 1.5 mmol) was added to the solution. After 12 h, H_2O was added and the mixture was cooled to room temp. The whole was extracted twice with AcOEt and the combined organic layers were washed with brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (hexane/Et_2O, 50:1 to 10:1) to give the title compound (182 mg, 68%) as a pale-yellow oil. ^{1}H NMR: δ = 7.75 (s, 1 H), 7.50–7.30 (m, 5 H), 4.04 (d, J = 7.0 Hz, 2 H), 3.85 (s, 3 H), 2.01 (nonet, J = 7.0 Hz, 1 H), 0.97 (d, J = 7.0 Hz, 6 H) ppm. ^{13}C NMR: δ = 167.2 (C), 164.0 (C), 142.4 (CH), 132.8 (C), 130.6 (CH), 129.4 (CH), 128.9 (CH), 125.9 (C), 71.5 (CH_2), 52.6 (CH_3), 27.7 (CH), 18.9 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2961, 1724, 1630, 1260, 1219, 1200, 1082, 1061 cm^{-1}. MS (EI): m/z = 262 [M]$^+$, 206 [M – iBu]$^+$, 189 [M – iBuO]$^+$. HRMS (ESI): calcd. for $C_{15}H_{19}O_4$ 263.1278 [M + H]$^+$; found 263.1276. The E geometry was confirmed by NOESY correlations between the methoxy and the aromatic protons (δ = 3.85 and 7.30–7.50 ppm, respectively), and the methyl protons of the isobutoxy group (δ = 0.97 ppm) and the vinylic proton (δ = 7.75 ppm).

[(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl] Methyl (*E*)-2-Benzylidenemalonate (3ak): Purified by column chromatography (hexane/Et_2O, 50:1 to 10:1). From 0.50 mmol **2a**, the title compound (171 mg, 89%) was obtained as a pale-yellow oil. $[\alpha]_D^{25}$ = –26.2 (c = 1.00, $CHCl_3$). ^{1}H NMR: δ = 7.72 (s, 1 H), 7.46–7.42 (m, 2 H), 7.40–7.34 (m, 3 H), 4.82 (td, J = 11.0, 4.5 Hz, 1 H), 3.83 (s, 3 H), 2.10 (dtd, J = 12.0, 4.0, 1.0 Hz, 1 H), 1.92 (septd, J = 7.0, 3.0 Hz, 1 H), 1.70 (ddd, J = 15.0, 5.0, 2.0 Hz, 2 H), 1.52 (m, 1 H), 1.44 (ddt, J = 12.0, 11.0, 3.0 Hz, 1 H), 1.14–1.03 (m, 2 H), 0.92 (d, J = 6.5 Hz, 3 H), 0.91 (d, J = 7.0 Hz, 3 H), 0.87 (m, 1 H), 0.79 (d, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR: δ = 167.2 (C), 163.6 (C), 142.1 (CH), 132.9 (C), 130.5 (CH), 129.3 (CH), 128.8 (CH), 126.3 (C), 75.8 (CH), 52.4 (CH_3), 47.1 (CH), 40.6 (CH_2), 34.1 (CH_2), 31.4 (CH), 26.2 (CH), 23.4 (CH_3), 22.0 (CH_3), 20.8 (CH_3), 16.3 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2955, 2928, 2870, 1713, 1628, 1258, 1200, 1157 cm^{-1}. MS (EI): m/z = 344 [M]$^+$, 313 [M – OMe]$^+$. HRMS (ESI): calcd. for $C_{20}H_{28}O_4Na$ 367.1880 [M + Na]$^+$; found 367.1880. The E geometry was assigned by analogy.

Methyl [(1*R*,2*S*,5*R*)-(2-Phenylpropan-2-yl)-5-methylcyclohexyl] (*E*)-2-Benzylidenemalonate (3al): Purified by column chromatography (hexane/Et_2O, 50:1 to 10:1). From 2.2 mmol **2a**, the title compound (698 mg, 75%) was obtained as a pale-yellow oil. $[\alpha]_D^{25}$ = –7.5 (c = 1.00, $CHCl_3$). ^{1}H NMR: δ = 7.38–7.36 (m, 3 H), 7.34–7.26 (m, 4 H), 7.24 (dt, J = 8.0, 1.5 Hz, 2 H), 7.06 (s, 1 H), 6.99 (tt, J = 7.0, 1.5 Hz, 1 H), 4.99 (td, J = 10.5, 4.5 Hz, 1 H), 3.82 (s, 3 H), 2.07 (ddd, J = 12.5, 10.5, 3.0 Hz, 1 H), 1.99 (dtd, J = 10.5, 4.0, 1.5 Hz, 1 H), 1.67–1.59 (m, 2 H), 1.50 (m, 1 H), 1.34 (s, 3 H), 1.25 (s, 3

H), 1.16–1.02 (m, 2 H), 0.88 (d, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR: δ = 167.0 (C), 163.1 (C), 151.1 (C), 141.7 (CH), 132.9 (C), 130.3 (CH), 129.3 (CH), 128.7 (CH), 128.0 (CH), 126.0 (C), 125.4 (CH), 125.1 (CH), 76.0 (CH), 52.4 (CH_3), 50.6 (CH), 41.6 (CH_2), 39.8 (C), 34.4 (CH_2), 31.3 (CH), 26.82 (CH), 26.77 (CH_2), 26.3 (CH_3), 21.7 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2982, 2951, 2909, 1740, 1697, 1636, 1620, 1258, 1219, 1057, 1026 cm^{-1}. MS (ESI): m/z = 443 [M + Na]$^+$. HRMS (ESI): calcd. for $C_{27}H_{32}O_4Na$ 443.2193 [M + Na]$^+$; found 443.2197. The E geometry was assigned by analogy.

Isobutyl Methyl (*Z*)-2-Benzylidenemalonate (3ba): From 0.50 mmol **2b**, the title compound (93.1 mg, 72%) was obtained as a pale-yellow oil after purification by column chromatography (hexane to hexane/Et_2O, 50:1; Table 2, entry 2). From 0.5 mmol **4a**, the title compound (65.8 mg, 48%) was obtained as a pale-yellow oil after purification by column chromatography (hexane to hexane/Et_2O, 50:1; Table 3, entry 1). ^{1}H NMR: δ = 7.77 (s. 1 H), 7.50–7.30 (m, 5 H), 4.04 (d, J = 7.0 Hz, 2 H), 3.85 (s, 3 H), 1.95 (nonet, J = 7.0 Hz, 1 H), 0.87 (d, J = 7.0 Hz, 6 H) ppm. ^{13}C NMR: δ = 166.8 (C), 164.6 (C), 142.6 (CH), 132.9 (C), 130.5 (CH), 129.3 (CH), 128.8 (CH), 126.0 (C), 71.9 (CH_2), 52.6 (CH_3), 27.4 (CH), 18.9 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2957, 1730, 1630, 1261, 1211, 1202, 1087, 1063 cm^{-1}. MS (EI): m/z = 262 [M]$^+$, 206 [M – isobutene]$^+$, 189 [M – O*i*Bu]$^+$. HRMS (ESI): calcd. for $C_{15}H_{18}O_4Na$ 285.1097 [M + Na]$^+$; found 285.1094. The Z geometry was confirmed by NOESY correlation between the methyl protons of the isobutoxy group (δ = 0.87 ppm) and the aromatic protons (δ = 7.30–7.50 ppm).

Benzyl Methyl (*Z*)-2-Benzylidenemalonate (3ca): Purified by column chromatography (hexane to hexane/AcOEt, 10:1). From 0.50 mmol **2c**, the title compound (106 mg, 67%) was obtained as a pale-yellow oil. ^{1}H NMR: δ = 7.79 (s, 1 H), 7.46–7.31 (m, 10 H), 5.30 (s, 2 H), 3.83 (s, 3 H) ppm. ^{13}C NMR: δ = 166.4 (C), 164.4 (C), 143.0 (CH), 134.8 (C), 132.6 (C), 130.5 (CH), 129.4 (CH), 128.8 (CH), 128.7 (CH), 128.5 (CH), 127.9 (CH), 125.5 (C), 67.5 (CH_2), 52.6 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3021, 1701, 1670, 1261, 1215, 770, 756, 696, 669 cm^{-1}. MS (ESI): m/z = 319 [M + Na]$^+$. HRMS (ESI): calcd. for $C_{18}H_{16}O_4Na$ 319.0941 [M + Na]$^+$; found 319.0945. The ^{1}H and ^{13}C NMR data are in good agreement with those reported.[4b]

Isobutyl (*E*)-2-(Dimethylcarbamoyl)-3-phenylacrylate (3db): Purified by column chromatography (hexane/AcOEt, 20:1 to 1:2). From 0.50 mmol **2d**, the title compound (101 mg, 74%) was obtained as a pale-yellow oil. ^{1}H NMR: δ = 7.68 (s, 1 H), 7.50 (dd, J = 5.0, 1.5 Hz, 2 H), 7.42–7.34 (m, 3 H), 4.10–3.96 (br. m, 2 H), 3.09 (s, 3 H), 2.85 (s, 3 H), 2.02 (nonet, J = 6.5 Hz, 1 H), 0.95 (d, J = 6.6 Hz, 6 H) ppm. ^{13}C NMR: δ = 167.2 (C), 164.7 (C), 140.4 (CH), 133.1 (C), 130.4 (CH), 129.6 (CH), 128.9 (CH), 127.8 (C), 71.4 (CH_2), 37.5 (CH_3), 34.6 (CH_3), 27.7 (CH), 19.0 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2963, 1713, 1639, 1246, 1196, 1153 cm^{-1}. MS (EI): m/z = 219 [M – isobutene]$^+$. HRMS (ESI): calcd. for $C_{16}H_{22}NO_3$ 276.1600 [M + H]$^+$; found 276.1595. $C_{16}H_{21}NO_3$ (275.35): calcd. C 69.79, H 7.69, N 5.09; found C 69.69, H 7.68, N 4.83. The E geometry was assigned by analogy.

Isobutyl (*E*)-2-Cyano-3-phenylacrylate (3eb): Purified by column chromatography (hexane/AcOEt, 50:1 to 20:1). From 0.50 mmol **2e**, the title compound (111 mg, 89%) was obtained as a white solid, m.p. 38–39 °C. ^{1}H NMR: δ = 8.26 (s, 1 H), 8.00 (d, J = 7.0 Hz, 2 H), 7.57 (t, J = 7.0 Hz, 1 H), 7.51 (t, J = 7.0 Hz, 2 H), 4.11 (d, J = 6.5 Hz, 2 H), 2.09 (nonet, J = 6.5 Hz, 1 H), 1.03 (d, J = 6.5 Hz, 6 H) ppm. ^{13}C NMR: δ = 162.4 (C), 154.9 (CH), 133.2 (CH), 131.4 (C), 131.0 (CH), 129.2 (CH), 115.3 (C), 102.9 (C), 72.4 (CH_2), 27.7 (CH), 18.9 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2967, 2222, 1724, 1609, 1265, 1188 cm^{-1}. MS (EI): m/z = 229 [M]$^+$, 173 [M – isobutene]$^+$. HRMS (ESI): calcd. for $C_{14}H_{16}NO_2Na$, 252.0995 [M + Na]$^+$; found 252.0990. The E geometry was assigned by analogy.

Isobutyl Methyl (*E*)-2-(4-Fluorobenzylidene)malonate (3fb): Purified by column chromatography (hexane/AcOEt, 20:1 to 5:1). From 0.50 mmol **2f**, the title compound (133 mg, 90%) was obtained as a pale-yellow oil. ^{1}H NMR: δ = 7.70 (s, 1 H), 7.44 (ddt, J = 8.5, 5.0, 2.5 Hz, 2 H), 7.09 (tt, J = 8.5, 2.5 Hz, 2 H), 4.03 (d, J = 6.5 Hz, 2 H), 3.86 (s, 3 H), 2.01 (nonet, J = 6.5 Hz, 1 H), 0.97 (d, J = 6.5 Hz, 6 H) ppm. ^{13}C NMR: δ = 166.0 (d, $J_{C\text{-}F}$ = 271 Hz, 1 C), 163.9 (C), 162.9 (C), 141.1 (CH), 131.5 (d, $J_{C\text{-}F}$ = 9 Hz, CH), 129.0 (C), 125.7 (C), 116.1 (d, $J_{C\text{-}F}$ = 22 Hz, CH), 71.6 (CH_2), 52.6 (CH_3), 27.7 (CH), 19.0 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 3005, 2970, 1736, 1369, 1219 cm^{-1}. MS (EI): m/z = 280 [M]$^+$, 224 [M – isobutene]$^+$. HRMS (ESI): calcd. for $C_{15}H_{17}FO_4Na$ 303.1003 [M + Na]$^+$; found 303.1002. The E geometry was assigned by analogy.

Isobutyl Methyl (*E*)-2-(4-Methoxybenzylidene)malonate (3gb): Purified by column chromatography (hexane/AcOEt, 20:1 to 5:1). From 0.50 mmol **2g**, the title compound (112 mg, 76%) was obtained as a pale-yellow oil. ^{1}H NMR: δ = 7.69 (s, 1 H), 7.40 (dt, J = 9.0, 3.0 Hz, 2 H), 6.90 (dt, J = 9.0, 3.0 Hz, 2 H), 4.02 (d, J = 6.5 Hz, 2 H), 3.87 (s, 3 H), 3.84 (s, 3 H), 2.00 (m, 1 H), 0.96 (d, J = 7.0 Hz, 6 H) ppm. ^{13}C NMR: δ = 167.7 (C), 164.4 (C), 161.6 (C), 142.1 (CH), 131.5 (CH), 125.3 (C), 123.2 (C), 114.4 (CH), 71.4 (CH_2), 55.4 (CH_3), 52.5 (CH_3), 27.8 (CH), 19.0 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2963, 2901, 2847, 1717, 1601, 1512, 1258, 1173 cm^{-1}. MS (EI): m/z = 292 [M]$^+$, 219 [M – O*i*Bu]$^+$. HRMS (ESI): calcd. for $C_{16}H_{20}O_5Na$ 315.1203 [M + Na]$^+$; found 315.1202. The E geometry was assigned by analogy.

Isobutyl Methyl (*E*)-2-(2-Methylbenzylidene)malonate (3hb): Purified by column chromatography (hexane/Et_2O, 50:1 to 5:1). From 0.50 mmol **2h**, the title compound (93.6 mg, 70%) was obtained as a pale-yellow oil. ^{1}H NMR: δ = 7.99 (s, 1 H), 7.32 (d, J = 7.5 Hz, 1 H), 7.28 (t, J = 7.5 Hz, 1 H), 7.21 (d, J = 7.5 Hz, 1 H), 7.17 (t, J = 7.5 Hz, 1 H), 4.04 (d, J = 6.5 Hz, 2 H), 3.74 (s, 3 H), 2.38 (s, 3 H), 2.02 (nonet, J = 6.5 Hz, 1 H), 0.97, (d, J = 6.5 Hz, 6 H) ppm. ^{13}C NMR: δ = 166.9 (C), 163.9 (C), 141.8 (CH), 137.7 (C), 132.5 (C), 130.5 (CH), 130.1 (CH), 127.6 (CH), 127.2 (C), 126.1 (CH), 71.5 (CH_2), 52.3 (CH_3), 27.7 (CH), 19.9 (CH_3), 19.0 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 3021, 2963, 2874, 1724, 1254, 1215, 1069 cm^{-1}. MS (EI): m/z = 277 [M – Me]$^+$, 261 [M – OMe]$^+$. HRMS (ESI): calcd. for $C_{16}H_{21}O_4$, 277.1434 [M + H]$^+$; found 277.1436. The E geometry was assigned by analogy.

Isobutyl Methyl (*E*)-2-(2-Phenylethylidene)malonate (3ib): Purified by column chromatography (silica gel DIOL, hexane to hexane/AcOEt, 5:1). From the mixture including 0.68 mmol **2i** (347 mg), the title compound (107 mg, 57%) was obtained as a pale-yellow oil. ^{1}H NMR: δ = 7.32 (t, J = 7.0 Hz, 2 H), 7.25 (m, 1 H), 7.22 (t, J = 7.0 Hz, 2 H), 7.11 (t, J = 8.0 Hz, 1 H), 3.96 (d, J = 6.5 Hz, 2 H), 3.86 (s, 3 H), 3.64 (d, J = 8.0 Hz, 2 H), 1.96 (nonet, J = 6.5 Hz, 1 H), 0.93 (d, J = 6.5 Hz, 6 H) ppm. ^{13}C NMR: δ = 165.8 (C), 163.8 (C), 147.2 (CH), 137.0 (C), 128.75 (CH), 128.70 (CH), 128.5 (C), 126.8 (CH), 71.3 (CH_2), 52.2 (CH_3), 35.9 (CH_2), 27.6 (CH), 18.9 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2990, 2955, 2905, 1724, 1643, 1601, 1366, 1250, 1231, 1200, 1065 cm^{-1}. MS (EI): m/z = 276 [M]$^+$, 203 [M – O*i*Bu]$^+$. $C_{16}H_{20}O_4$ (276.33): calcd. C 69.54, H 7.30; found C 69.46, H 7.37. The yield was calculated on the basis of the two-step yield (39%) and the estimated yield of **2i** (69%). The E geometry was assigned by analogy.

Isobutyl Methyl (*E*)-2-Heptylidenemalonate (3jb): Purified by column chromatography (hexane to hexane/AcOEt, 50:1). From 0.5 mmol **2j**, the title compound (107 mg, 79%) was obtained as a

pale-yellow oil. ^{1}H NMR: δ = 7.02 (t, J = 7.5 Hz, 1 H), 3.96 (d, J = 6.5 Hz, 2 H), 3.82, (s, 3 H), 2.30 (q, J = 7.5 Hz, 2 H), 1.97 (nonet, J = 6.5 Hz, 1 H), 1.50–1.44 (m, 2 H), 1.40–1.23 (m, 6 H), 0.94 (d, J = 6.5 Hz, 6 H), 0.88 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR: δ = 166.1 (C), 164.0 (C), 150.1 (CH), 128.2 (C), 71.2 (CH_2), 52.1 (CH_3), 31.5 (CH_2), 29.8 (CH_2), 28.9 (CH_2), 28.2 (CH_2), 27.7 (CH), 22.5 (CH_2), 19.0 (CH_3), 14.0 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2955, 2928, 1724, 1643, 1605, 1246, 1227, 1065 cm^{-1}. MS (EI): m/z = 271 [M + H]$^+$, 239 [M – OMe]$^+$. HRMS (ESI): calcd. for $C_{15}H_{27}O_4$ 271.1904 [M + H]$^+$; found 271.1906. The *E* geometry was assigned by analogy.

[(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl] Methyl (*Z*)-2-Benzylidenemalonate (3ka): Purified by column chromatography (hexane to hexane/AcOEt, 20:1). From 2.2 mmol **4a**, the title compound (370 mg, 48%) was obtained as a white solid, m.p. 92–94 °C. $[\alpha]_D^{25}$ = –40.2 (c = 1.00, $CHCl_3$). ^{1}H NMR: δ = 7.72 (s, 1 H), 7.52–7.47 (m, 2 H), 7.43–7.34 (m, 3 H), 4.88 (td, J = 11.0, 4.5 Hz, 1 H), 3.83 (s, 3 H), 2.16 (m, 1 H), 1.85 (sextd, J = 7.0, 2.5 Hz, 1 H), 1.72–1.65 (m, 2 H), 1.52 (m, 1 H), 1.39 (ddt, J = 12.5, 11.0, 1.0 Hz, 1 H), 1.13–0.95 (m, 2 H), 0.93 (d, J = 6.5 Hz, 3 H), 0.88 (m, 1 H), 0.82 (d, J = 7.0 Hz, 3 H), 0.77 (d, J = 3.0 Hz, 3 H) ppm. ^{13}C NMR: δ = 166.4 (C), 164.7 (C), 141.8 (CH), 132.8 (C), 130.5 (CH), 129.5 (CH), 128.7 (CH), 126.5 (C), 76.1 (CH), 52.4 (CH_3), 46.8 (CH_3), 40.0 (CH_2), 34.1 (CH_2), 31.4 (CH), 25.5 (CH), 23.0 (CH_2), 22.0 (CH), 20.7 (CH_3), 15.8 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2951, 2920, 1728, 1628, 1454, 1258, 1200, 1065, 764 cm^{-1}. MS (ESI): m/z = 367 [M + Na]$^+$. HRMS (ESI): calcd. for $C_{21}H_{28}O_4Na$ 367.1880 [M + Na]$^+$; found 367.1882. The *Z* geometry was assigned by analogy.

[(1*R*,2*S*,5*R*)-(2-Phenylpropan-2-yl)-5-methylcyclohexyl] Methyl (*Z*)-2-Benzylidenemalonate (3la): Purified by column chromatography (hexane to hexane/AcOEt, 10:1). From 2.2 mmol **4a**, the title compound (430 mg, 45%) was obtained as a colorless oil. $[\alpha]_D^{25}$ = –31.3 (c = 1.00, $CHCl_3$). ^{1}H NMR: δ = 7.71 (s, 1 H), 7.49 (dd, J = 7.5, 2.0 Hz, 2 H), 7.41–7.17 (m, 7 H), 7.10 (dt, J = 7.0, 2.0 Hz, 1 H), 4.92 (td, J = 10.5, 4.0 Hz, 1 H), 3.84 (s, 3 H), 2.21 (ddd, J = 11.5, 5.5, 3.0 Hz, 1 H), 1.85 (ddd, J = 12.0, 9.0, 3.5 Hz, 1 H), 1.53–1.43 (m, 2 H), 1.28 (m, 1 H), 1.20 (s, 3 H), 1.17 (s, 3 H), 0.98–0.66 (m, 3 H), 0.86 (d, J = 6.5 Hz, 3 H) ppm. ^{13}C NMR: δ = 165.8 (C), 164.4 (C), 150.7 (C), 142.1 (CH), 132.9 (C), 130.3 (CH), 129.5 (CH), 128.5 (CH), 127.8 (CH), 126.6 (C), 125.4 (CH), 125.1 (CH), 76.7 (CH), 52.3 (CH_3), 50.4 (CH), 40.4 (CH_2), 40.0 (CH_2), 34.3 (CH_3), 31.2 (CH), 28.8 (CH), 27.2 (CH_2), 23.4 (CH_3), 21.7 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2947, 1721, 1697, 1261, 1207, 1053 cm^{-1}. MS (ESI): m/z = 443 [M + Na]$^+$. HRMS (ESI): calcd. for $C_{27}H_{32}O_4Na$ 443.2193 [M + Na]$^+$; found 443.2192. The *Z* geometry was assigned by analogy.

Isobutyl Methyl (*E*)-2-(2-Methylpropylidene)malonate (3mb): According to the one-pot procedure used for the synthesis of **3ab** but by using 0.75 mmol **1m** in place of **1a**, the title compound (109 mg, 63%) was obtained as a pale-yellow oil. ^{1}H NMR: δ = 6.68 (d, J = 10.0 Hz, 1 H), 3.96 (d, J = 6.5 Hz, 2 H), 3.82 (s, 3 H), 2.67 (m, 1 H), 1.97 (nonet, J = 6.5 Hz, 1 H), 1.07 (d, J = 6.5 Hz, 6 H), 0.94 (d, J = 6.5 Hz, 6 H) ppm. ^{13}C NMR: δ = 166.2 (C), 164.1 (C), 155.4 (CH), 126.2 (C), 71.2 (CH_2), 52.1 (CH_3), 29.5 (CH), 27.7 (CH), 21.8 (CH_3), 19.0 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 2963, 2932, 2874, 1732, 1647, 1248, 1223, 1150, 1055, 999 cm^{-1}. MS (EI): m/z = 172 [M – isobutene]$^+$, 155 [M – O*i*Bu]$^+$, 131, 122, 103, 91. HRMS (ESI): calcd. for $C_{12}H_{20}O_4Na$ 251.1254 [M + Na]$^+$; found 251.1251. The *E* geometry was assigned by analogy.

Isobutyl Methyl (*E*)-2-(2,2-Dimethylpropylidene)malonate (3nb): According to the one-pot procedure used for the synthesis of **3ab** but by using 1.5 mmol **1n** in place of **1a**, the title compound (163 mg, 45%) was obtained as a pale-yellow oil. ^{1}H NMR: δ = 6.91 (s, 1 H), 3.95 (d, J = 6.5 Hz, 2 H), 3.81 (s, 3 H), 1.94 (m, 1 H), 1.13 (s, 9 H), 0.93 (d, J = 6.5 Hz, 6 H) ppm. ^{13}C NMR: δ = 167.5 (C), 164.4 (C), 155.4 (CH), 128.3 (C), 71.3 (CH_2), 52.1 (CH_3), 34.2 (CH), 28.8 (CH_3), 27.7 (C), 18.9 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 2961, 2934, 2874, 1732, 1643, 1246, 1196, 1070, 1001 cm^{-1}. MS (EI): m/z = 186 [M – isobutene]$^+$, 171, 136, 105, 91. HRMS (ESI): calcd. for $C_{13}H_{22}O_4Na$ 265.1410 [M + Na]$^+$; found 265.1406. The *E* geometry was assigned by analogy.

Methyl (*Z*)-3-Phenyl-2-(tributylstannyl)acrylate (4a): Compound **1a** (1.5 mL, 10 mmol) was placed in a dry 100-mL round-bottomed flask. THF (10 mL), Bu_3SnH (3.0 mL, 11 mmol), and AIBN (25 mg, 0.15 mmol) were added to the flask. The mixture was stirred for 3 h and then concentrated in vacuo. The residue was purified by column chromatography (hexane to hexane/AcOEt, 50:1) to afford the title compound (3.13 g, 69%) as a colorless oil. ^{1}H NMR: δ = 8.37 (s, 1 H), 7.40–7.20 (m, 5 H), 3.78 (s, 3 H), 1.10–1.51 (m, 12 H), 0.90–0.70 (m, 15 H) ppm. ^{13}C NMR: δ = 172.3 (C), 153.8 (CH), 139.2 (C), 138.7 (C), 128.5 (CH), 128.1 (CH), 127.9 (CH), 51.7 (CH_3), 28.8 (CH_2), 27.1 (CH_2), 13.6 (CH_3), 11.7 (CH_2) ppm. IR (neat): $\tilde{\nu}$ = 2955, 2922, 2870, 2853, 1710, 1695, 1230, 1194, 1074 cm^{-1}. MS (EI): m/z = 451 [M]$^+$, 395 [M – Bu]$^+$. The *Z* geometry was confirmed by the H–Sn coupling constant of the β-H (δ = 8.37 ppm, $^3J_{H\text{-}Sn}$ = 100 Hz).[13] The ^{1}H and ^{13}C NMR data are in good agreement with the published data.[29]

4-Benzyl 2,4-Dimethyl (2*SR*,3*SR*,4*SR*,5*SR*)- and (2*SR*,3*SR*,4*RS*,5*SR*)-3,5-Diphenylpyrrolidine-2,4,4-tricarboxylate (6): Conducted according to the reported procedure[15] by using **3ac** (0.20 mmol). Purification of the crude material by column chromatography (hexane/AcOEt, 10:1 to 1:1) gave the title compound (87 mg, 92%) as a pale-yellow oil. ^{1}H NMR: δ = 7.49 (td, J = 8.5, 2.0 Hz, 2 H), 7.37–7.18 (m, 11 H), 6.94 (dd, J = 7.0, 2.0 Hz, 0.72 H), 6.84 (dd, J = 7.0, 2.0 Hz, 1.28 H), 5.37 (s, 0.36 H), 5.35 (s, 0.64 H), 4.91 (d, J = 7.5 Hz, 0.64 H), 4.88 (d, J = 7.5 Hz, 0.36 H), 4.45 (d, J = 6.5 Hz, 0.64 H), 4.43 (d, J = 6.5 Hz, 0.36 H), 4.24–4.21 (m, 1.36 H), 4.12 (d, J = 12.5 Hz, 0.64 H), 3.77 (s, 3 H), 3.12 (s, 2.16 H), 3.10 (s, 1.08 H) ppm. ^{13}C NMR: δ = 174.2 (minor C), 173.1 (major C), 169.8 (minor C), 169.34 (minor C), 169.25 (major C), 169.1 (major C), 138.6 (minor C), 138.5 (major C), 138.2 (minor C), 138.1 (major C), 134.9 (minor C), 134.7 (major C), 128.9 (CH), 128.8 (CH), 128.7 (CH), 128.45 (CH), 128.36 (CH), 128.30 (CH), 128.25 (CH), 128.17 (CH), 128.15 (CH), 128.04 (CH), 127.98 (CH), 127.8 (CH), 127.68 (CH), 127.65 (CH), 127.6 (CH), 127.53 (CH), 127.46 (CH), 79.72 (major CH_2), 79.66 (minor CH_2), 71.3 (major C), 71.2 (minor C), 68.23 (minor CH), 68.17 (major CH), 67.1 (major CH), 67.0 (minor CH), 66.3 (minor CH), 66.1 (major CH), 56.3 (major CH_3), 56.2 (minor CH_3), 52.5 (major CH_3), 51.7 (minor CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3435, 2954, 2927, 1719, 1630, 1437, 1383, 1265, 1213, 905, 733, 702, 650 cm^{-1}. MS (ESI): m/z = 474 [M + H]$^+$. HRMS (ESI): calcd. for $C_{28}H_{28}NO_6$ 474.1911 [M + H]$^+$; found 474.1914. The diastereomeric ratio (64:36) was determined by the integration area of the ^{1}H NMR signals at δ = 6.94 and 6.84 ppm. The relative configuration was determined after the conversion of **6** into the known trimethyl ester with the established stereochemistry (see below). The stereochemistry of the quaternary carbon was not determined.

Determination of the Relative Configuration of 6 − Trimethyl (2*SR*,3*SR*,5*SR*)-3,5-Diphenylpyrrolidine-2,4,4-tricarboxylate: A mixture of **6** (30.0 mg, 0.063 mmol) and 10% Pd/C (6 mg, 0.1 equiv.) in a 5:1 mixture of THF/MeOH (2 mL) was stirred for 4 h at room temp. under H_2. The mixture was filtered through Celite, which was successively washed with THF. A 1 M THF solution

of $TMSCHN_2$ (1.2 mmol, 20 equiv.) was added to the combined filtrate. After 15 min, the mixture was concentrated in vacuo to give the title compound (24.0 mg, 92%) as a yellow oil. ^1H NMR: δ = 7.47 (d, J = 7.5 Hz, 2 H), 7.36–7.14 (m, 8 H), 5.33, (s, 1 H), 4.42 (d, J = 7.0 Hz, 1 H), 4.24 (d, J = 7.0 Hz, 1 H), 3.77 (s, 3 H), 3.17 (s, 3 H), 3.13 (s, 3 H) ppm. The ^1H NMR data are in good agreement with those reported.[30]

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