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

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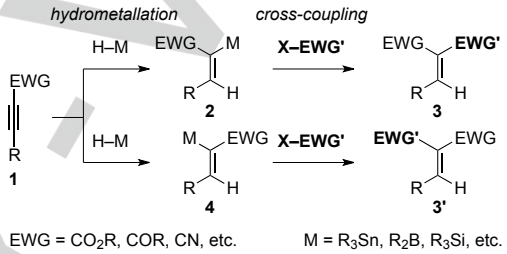
Abstract: A method for stereoselective syntheses of alkylidenemalonates and related α,β-unsaturated esters via a hydrostannylation–cross-coupling process has been developed. Pd-catalyzed and radical hydrostannylation of propiolate derivatives stereoselectively provided α-alkoxycarbonyl (*E*)- and (*Z*)-vinylstannanes, 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 construct 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; 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 using hydrometallation followed by cross-coupling.

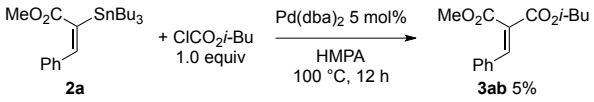
Our strategy is shown in Scheme 1. Regio- and stereoselective hydrometallation of alkyne **1**, bearing an electron-withdrawing group, gives the metallated alkene **2** or **4**. The subsequent transition metal-catalyzed cross-coupling reaction selectively produces the *E*/*Z*-isomers of doubly activated olefins **3** and **3'**. Since 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 using sequential hydrostannylation–cross-coupling.



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

Results and Discussion

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



Scheme 2. The reaction of **2a** with $ClCO_2$*i*-Bu under the condition 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 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 the

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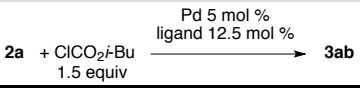
ligand. The isomerization of the olefinic geometry was suppressed when the reaction was conducted at 80 °C, giving **3ab** selectively in 48% yield after 24 h (Table 1, entry 1). The retention of the configuration was confirmed by NOESY correlations between the methoxy and the aromatic protons, and the methyl protons of the isobutoxy group and the vinylic proton of **3ab**.

Table 1. Optimization of reaction conditions.[a]



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

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

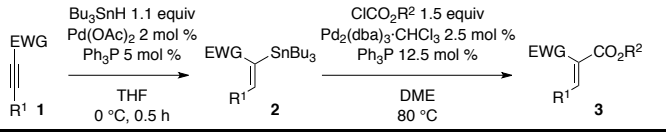
Significant solvent effects were observed; the reaction in DMF gave a complex mixture containing no detectable amount of **3ab** (entry 2). Although no reaction proceeded in acetonitrile (entry 3), the reaction in DCE gave **3ab** in 62% yield (entry 4). Among the tested solvents, the reaction proceeded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

The choice of 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 allylpalladium chloride dimer accelerated the reaction to give **3ab** in 80% yield after 7 h (entry 9). Tris(dibenzylideneacetone) dipalladium chloroform adduct ($Pd_2(dba)_3{\cdot}CHCl_3$) was found to be an excellent catalyst for this reaction to produce **3ab** in 83% yield after 4 h (entry 10). With bis(triphenylphosphine)palladium dichloride or benzylbis(triphenylphosphine)palladium chloride, no reaction proceeded, and **2a** was recovered quantitatively (entries 6 and 7). Ligands other than triphenylphosphine, such as triphenylarsine[9] and bis(diphenylphosphino)ethane, turned out to be less effective (entries 11 and 12). Commonly used additives were tested under the conditions of entry 10; however, no reaction proceeded in the presence of lithium chloride,[10] and the addition of cesium fluoride[11] resulted in decomposition of **2a** (not shown in the table).

To our delight, the efficient reaction rate was maintained with 2 mol % palladium catalyst to give **3ab** in 83% yield after 6 h (entry 15). Further decrease of 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] giving (*E*)-vinylstannanes **2** in 64–83% yield (Table 2).[7b,12,13] The conditions for the cross-coupling were compatible with various functional groups, such as esters (entries 1–3), an amide (entry 4), and a cyanide (entry 5), to give the products **3** in 67–89% yield. Substrates bearing either an electron-rich or electron-deficient aromatic ring (entries 6–8) as well as an alkyl group (entries 9 and 10) gave the products in good yields. It is noteworthy that phenethylidenemalonate **3ib**, unavailable from the Knoevenagel condensation, was prepared without migration of the C=C bond (entry 9). Moreover, a Cbz group (entry 11) and a sterically crowded menthyloxy- or 8-phenylmenthyloxycarbonyl group (entries 12 and 13) could also be introduced to **2a** to give the corresponding benzylidenemalonates **3ac**, **3ak**, and **3al**, respectively, in good yields.

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



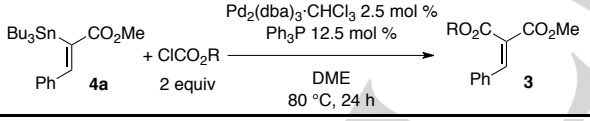
entry	1	R^1	EWG	2	yield	R^2	3	time h	yield[a]
1[b]	**1a**	Ph	CO_2Me	**2a**	69%	*i*-Bu	**3ab**	6	83%
2	**1b**	Ph	CO_2*i*-Bu	**2b**	67%	Me	**3ba**	12	72%
3	**1c**	Ph	CO_2Bn	**2c**	72%	Me	**3ca**	12	67%
4	**1d**	Ph	$CONMe_2$	**2d**	73%	*i*-Bu	**3db**	12	74%
5	**1e**	Ph	CN	**2e**	64%	*i*-Bu	**3eb**	12	89%
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 yield. [b] $Pd_2(dba)_3{\cdot}CHCl_3$ (1 mol %), Ph_3P (5 mol %). [c] Including 9% impurity. Yield was estimated with ^1H NMR (see Experimental Section). [d] Based on two-step yield and the estimated yield of **2i**. [e] Men = menthyl, ϕMen = 8-phenylmenthyl. [f] $ClCO_2R^2$ (2.0 equiv).

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 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, propiolate **1j**, bearing an alkyl group, propiolamide **1d**, and propiolonitrile **1e** were inapplicable because the radical hydrostannylation step resulted in a complex mixture (**1j** and **1e**) or recovery of the starting material (**1d**).

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

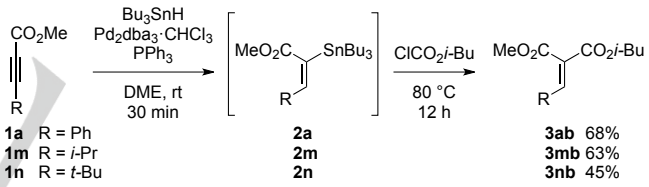


entry	R	3	yield[a]
1	*i*-Bu	**3ba**	48%
2	Men[b]	**3ka**	48%
3	ϕMen[b]	**3la**	45%
4	Bn	**3ca**	trace

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

The retention of the configuration was confirmed by NOESY experiments of **3ba**, showing 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, since isomerization of (*Z*)-vinylstannane to the (*E*)-isomers under cross-coupling conditions was previously 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 thermal instability of the chloroformate. The observed lower reactivity of (*Z*)-stannane **4a** is likely attributed 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).

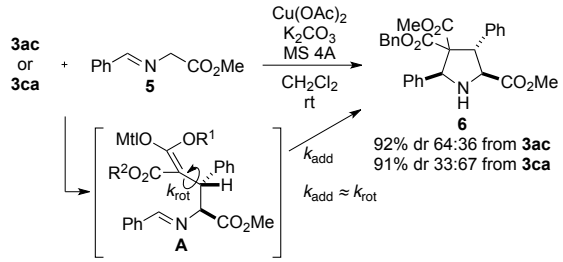
The developed hydrostannylation–cross-coupling sequence was performable in one-pot (Scheme 3). A solution of **1a** and tributylstannane (1.1 equiv) was stirred at 0 °C in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ and triphenylphosphine (2.5 and 12.5 mol %, respectively). When complete consumption of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



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

Finally, (*E*)- and (*Z*)-alkylidenemalonates **3ac** and **3ca**, bearing two different ester moieties, were subjected to the reported copper-catalyzed [3+2] cycloaddition (Scheme 4).[15] A solution of **3ac** and glycine derivative **5** was stirred at rt in the presence of copper diacetate (10 mol %), potassium carbonate (2 equiv), and MS 4Å. After 12 h, pyrrolidine **6** was obtained in 92% yield as a 64:36 mixture of the diastereomers at the stereogenic center on the quaternary carbon. This result indicates that this cycloaddition proceeded mainly via stepwise bond formation and not via a concerted mechanism proposed in the literature. In turn, the reaction of **3ca** gave **6** with 33:67 diastereomeric ratio (dr). Therefore, the diastereoselectivity of the cycloaddition partially reflected the stereochemistry of the malonates utilized. The irreversibility of the cycloaddition reaction was confirmed by the following experiments. When **6** with dr 64:36 and 33:67 were each treated with the above reaction conditions for 12 h, no epimerization of **6** occurred, recovering **6** with unchanged dr. Accordingly, in this step-wise

cycloaddition, the rate constant of 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 of **3ac** and **3ca**, shedding light on the mechanism.

Conclusions

We developed a stereo- and regioselective synthesis of doubly activated olefins, using 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 various 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. The extension of this methodology utilizing other cross-coupling reactions is underway in this laboratory.

Experimental Section

General. All the reactions were performed under argon atmosphere. 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 (500 MHz for ^{1}H and 125 MHz for ^{13}C) was measured in $CDCl_3$. Chemical shifts and coupling constants (*J*) are presented in ppm δ relative to tetramethylsilane and Hz, respectively. Abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. ^{13}C peak multiplicity assignments were made based on DEPT data. ^{13}C–^{117}Sn and ^{13}C–^{119}Sn coupling constants of satellite peaks in ^{13}C NMR are not reported for clarity. For confirmation of *E*/*Z*-geometry 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. The wave numbers of maximum absorption peaks of IR spectroscopy are presented in cm^{-1}. A quadrupole mass spectrometer was used for EIMS, while ESIMS was measured with TOF.

Preparation of Starting Materials. Chloroformates were purified by distillation before use. Alkynes **1c**,[18] **1d**,[19] **1e**,[20] **1f**,[21] **1g**,[22] **1h**,[23] and **1i**;[24] 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-bottom flask. To the stirred solution cooled at –78 °C, a 1.6 M hexane solution of BuLi (6.4 mL, 10 mmol) and $ClCO_2Me$ (1.5 mL, 20 mmol) were dropwise added at 30 min interval. After 10 min, the cooling bath was removed, and the mixture was stirred for additional 30 min. After addition of sat. aq $NaHCO_3$, the whole was extracted twice with AcOEt, and the combined organic layers were washed with brine, dried over 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: 7.55–7.65 (m, 2H), 7.45 (m, 1H), 7.35–7.40 (m, 2H), 4.03 (d, *J* = 7.0, 2H), 2.05 (m, 1H), 0.99 (d, *J* = 6.5, 6H). ^{13}C NMR: 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). IR (neat): 2967, 2936, 2878, 2222, 1709, 1281, 1188, 1169. EIMS *m*/*z*: 202 (M^+), 146 (M – isobutene), 129 (M – *i*-BuO). ^{1}H NMR, ^{13}C NMR, IR and EIMS data were in good agreement with published data.[25]

Methyl 4-methylpent-2-ynoate (1m): 3-methyl-1-butyne (2.0 mL, 20 mmol) was dissolved in THF (20 mL) in a dry 50-mL round-bottom flask. To the stirred solution cooled at –78 °C, a 1.6 M hexane solution of BuLi (14 mL, 22 mmol) and $ClCO_2Me$ (1.8 mL, 24 mmol) were dropwise added at 30 min interval. After 10 min, the cooling bath was removed, and the mixture was stirred for additional 30 min. After addition of sat. aq $NaHCO_3$, the whole was extracted twice with Et_2O, and the combined organic layers were washed with brine, dried over 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: 3.75 (s, 3H), 2.70 (septet, *J* = 7.0, 1H), 1.24 (d, *J* = 7.0, 6H). ^{13}C NMR: 154.3 (C), 94.3 (C), 72.0 (C), 52.4 (CH_3), 21.6 (CH_3), 20.4 (CH). ^{1}H and ^{13}C NMR spectra were in good agreement with published data.[26]

Methyl 4,4-dimethylpent-2-ynoate (1n): The same procedure as that for **1m** using 3,3-dimethyl-1-butyne (2.5 mL, 20 mmol) in place of 3-methyl-1-butyne afforded the title compound (95%) as a pale yellow oil, which was used for the next step without further purification. ^{1}H NMR: 3.76 (s, 3H), 1.29 (s, 9H). ^{13}C NMR: 154.4 (C), 96.9 (C), 71.4 (C), 52.5 (CH_3), 31.6 (C), 29.9 (CH_3). ^{1}H and ^{13}C NMR spectra were in good agreement with published data.[27]

General Procedure for Pd-Catalyzed Hydrostannylation (Table 2, entries 1 and 11–13). (*E*)-Methyl 3-Phenyl-2-(tributylstannyl)acrylate (2a): to avoid the use of $Pd(PPh_3)_4$,[7a] $Pd(OAc)_2$ was utilized, instead: **1a** (1.5 mL, 10 mmol), $Pd(OAc)_2$ (45 mg, 0.20 mmol), and Ph_3P (130 mg, 0.500 mmol) were dissolved in THF (20 mL) in a dry 100-mL round-bottom flask. To the solution cooled in an ice–water bath, was added Bu_3SnH (3.3 mL, 12 mmol). The mixture was stirred for 30 min, and the cooling bath was removed. The mixture was concentrated *in vacuo*, and the residue was 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: 7.29–7.33 (m, 4H), 7.25 (m, 1H), 6.71 (s, 1H), 3.69 (s, 3H), 1.45–1.65 (m, 6H), 1.34 (sextet, *J* = 7.5, 6H), 1.06 (t, *J* = 8.0, 6H), 0.91 (t, *J* = 7.5, 9H). ^{13}C NMR: 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). IR (neat): 2955, 2922, 1703, 1207. EIMS *m*/*z*: 451 (M^+), 395 (M – Bu). Anal. Calcd for $C_{22}H_{36}O_2Sn$: 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 (6.71 ppm, $^3J_{H–Sn}$ = 59 Hz).[13]

(*E*)-Isobutyl 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: 7.20–7.35 (m, 3H), 6.71 (s, 1H), 3.87 (d, *J* = 6.5, 2H), 1.88

(nonet, *J* = 6.5, 1H), 1.47–1.65 (m, 6H), 1.34 (sextet, *J* = 7.5, 6H), 1.07 (t, *J* = 8.5, 6H), 0.91 (t, *J* = 7.5, 9H), 0.84 (d, *J* = 6.5, 6H). ^{13}C NMR: 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). IR (neat): 2959, 2924, 2874, 2855, 1701, 1173. EIMS *m*/*z*: 437 (M – Bu). HRMS–ESI (*m*/*z*): $[M + Na]^+$ calcd for $C_{25}H_{42}O_2SnNa$, 517.2099; found, 517.2098. The *E*-geometry was confirmed by the H–Sn coupling constant of the satellite peaks of the β-H (6.71 ppm, $^3J_{H–Sn}$ = 58 Hz).[13]

(*E*)-Benzyl 3-Phenyl-2-(tributylstannyl)acrylate (2c): Purified by column chromatography (hexane to hexane/Et_2O 50:1). From 0.8-mmol **1c**, the title compound (301 mg, 72%) was obtained as a pale yellow oil: ^{1}H NMR: 7.34–7.21 (m, 10H), 6.71 (s, 1H), 5.14 (s, 2H), 1.63–1.42 (m, 6H), 1.38–1.21 (m, 6H), 1.10–0.96 (m, 6H), 0.88 (t, *J* = 7.0, 9H). ^{13}C NMR: 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). IR (KBr): 2955, 2924, 2870, 2853, 1701, 1375, 1206, 1167. ESIMS *m*/*z*: 551 (M + Na). HRMS–ESI (*m*/*z*): $[M + Na]^+$ calcd for $C_{28}H_{40}O_2SnNa$, 551.1948; found, 551.1947. The *E*-geometry was confirmed by the H–Sn coupling constant of the satellite peaks of the β-H (6.71 ppm, $^3J_{H–Sn}$ = 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: 7.27–7.31 (m, 4H), 7.22 (m, 1H), 6.57 (s, 1H), 2.95 (s, 3H), 2.71 (s, 3H), 1.46–1.65 (m, 6H), 1.35 (sextet, *J* = 7.0, 6H), 1.07 (t, *J* = 7.0, 6H), 0.91 (t, *J* = 7.0, 9H). ^{13}C NMR: 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). IR (neat): 2955, 2924, 2855, 1717, 1605, 1462, 1254, 1076. EIMS *m*/*z*: 465 (M^+), 408 (M – Bu). HRMS–ESI (*m*/*z*): $[M + H]^+$ calcd for $C_{23}H_{40}OSn$, 466.2126; found, 466.2125. The *E*-geometry was confirmed by the H–Sn coupling constant of the satellite peaks of the β-H (6.58 ppm, $^3J_{H–Sn}$ = 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: 7.83 (d, *J* = 7.0, 2H), 7.35–7.45 (m, 3H), 7.06 (s, 1H), 1.64 (m, 6H), 1.37 (sextet, *J* = 7.5, 6H), 1.07 (m, 6H), 0.92 (t, *J* = 7.5, 9H). ^{13}C NMR: 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). IR (neat): 2955, 2924, 2855, 2176, 1713, 1585, 1562, 1076, 1049. EIMS *m*/*z*: 362 (M – Bu), 306 (M – 2Bu). HRMS–ESI (*m*/*z*): $[M + Na]^+$ calcd for $C_{21}H_{33}NSnNa$, 442.1527; found, 442.1529. Anal. Calcd for $C_{21}H_{33}NSn$: 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 (7.06 ppm, $^3J_{H–Sn}$ = 47 Hz).[13]

(*E*)-Methyl 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: 7.23–7.31 (m, 3H), 6.99 (tt, *J* = 9.0, 2.0, 2H), 6.66 (s, 1H), 3.69 (s, 3H), 1.47–1.62 (m, 6H), 1.34 (sextet, *J* = 7.5, 6H), 1.06 (t, J = 8.0, 6H), 0.91 (t, *J* = 7.5, 9H). ^{13}C NMR: 173.5 (C), 162.4 (d, J_{F-C} = 246, C), 141.0 (CH), 139.2 (C), 133.2 (C), 129.6 (CH), 115.3 (d, J_{F-C} = 22, CH), 51.4 (CH_3), 28.7 (CH_2), 27.2 (CH_2), 13.7 (CH_3), 10.6 (CH_2). IR (neat): 2959, 2920, 2847, 2816, 1701, 1601, 1508, 1234, 1157. EIMS *m*/*z*: 470 (M^+), 413 (M – Bu). HRMS–ESI (*m*/*z*): $[M + Na]^+$ calcd for $C_{22}H_{35}FO_2SnNa$, 493.1535; found, 493.1534. The *E*-geometry was confirmed by the H–Sn coupling constant of the satellite peaks of the β-H (6.66 ppm, $^3J_{H–Sn}$ = 58 Hz).[13]

(*E*)-Methyl 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: 7.26 (dt, *J* = 8.5, 3.0, 2H), 6.83 (dt, *J* = 8.5, 3.0, 2H), 6.64 (s, 1H), 3.80 (s, 3H), 3.70 (s, 3H), 1.47–1.64 (m, 6H), 1.34 (sextet, *J* = 7.5, 6H), 1.05 (t, *J* = 8.0, 6H), 0.90 (t, *J* = 7.5, 9H). ^{13}C NMR: 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). IR (neat): 2997, 2955, 2924, 2851, 1701, 1508, 1250, 1164, 1034. EIMS *m*/*z*: 425 (M – Bu). HRMS–ESI (*m*/*z*): $[M + Na]^+$ calcd for $C_{23}H_{38}O_3SnNa$, 505.1735; found, 505.1736. The *E*-geometry was confirmed by the H–Sn coupling constant of the satellite peaks of the β-H (6.64 ppm, $^3J_{H–Sn}$ = 60 Hz).[13]

(*E*)-Methyl 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: 7.21 (d, *J* = 7.5, 1H), 7.08–7.17 (m, 3H), 6.91 (s, 1H), 3.58 (s, 3H), 2.32 (s, 3H), 1.47–1.64 (m, 6H), 1.34 (sextet, *J* = 7.5, 6H), 1.06 (t, *J* = 8.0, 6H), 0.91 (t, *J* = 7.5, 9H). ^{13}C NMR: 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). IR (neat): 2955, 2928, 1701, 1196. EIMS *m*/*z*: 465 (M^+), 409 (M – Bu). Anal. Calcd for $C_{23}H_{38}O_2Sn$: 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 (6.91 ppm, $^3J_{H–Sn}$ = 55 Hz).[13]

(*E*)-Methyl 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: 7.30 (td, *J* = 8.0, 2.0, 2H), 7.22 (dd, *J* = 8.0, 2.0, 2H), 7.17 (t, *J* = 8.0, 1H), 7.14–7.33 (m, 0.54H impurity), 6.16 (t, *J* = 7.0, 1H), 4.29 (s, 0.18H impurity), 3.76 (d, *J* = 7.0, 2H), 3.74 (s, 3H), 3.70 (s, 0.27H impurity), 1.38–1.57 (m, 6H), 1.24–1.32 (m, 6H + 0.54H impurity), 1.16–1.24 (m, 0.54H impurity) 0.82–1.16 (m, 15H + 0.81H impurity), 0.61–0.80 (m, 0.54H impurity). ^{13}C NMR: 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). IR (neat): 2955, 2924, 2851, 1709, 1597, 1192. EIMS *m*/*z*: 409 (M – Bu). HRMS–ESI (*m*/*z*): $[M + Na]^+$ calcd for $C_{23}H_{38}O_2SnNa$, 489.1786; found, 489.1786. The *E*-geometry was confirmed by the H–Sn coupling constant of the satellite peaks of the β-H (6.16 ppm, $^3J_{H–Sn}$ = 56 Hz).[13] The impurity was assigned as regioisomer, (*E*)-methyl 4-phenyl-3-(tributylstannyl)but-2-enoate by analogy with the previous report.[8a] The yield was determined by the integration area of ^{1}H NMR signals at 4.29 and 6.16 ppm. The mixture was used in the next reaction without further purification.

(*E*)-Methyl 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: 6.04 (t, *J* = 7.0, 1H), 3.69 (s, 3H), 2.40 (q, *J* = 7.0, 2H), 1.37–1.53 (m, 8H), 1.25–1.35 (m, 12H), 0.85–1.04 (m, 18H). ^{13}C NMR: 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). IR (neat): 2955, 2924, 2855, 1709, 1601, 1462, 1177. EIMS *m*/*z*: 403 (M – Bu). The *E*-geometry was confirmed by the H–Sn coupling constant of the satellite peaks of the β-H (6.04 ppm, $^3J_{H–Sn}$ = 60 Hz).[13] ^{1}H NMR, ^{13}C NMR, IR, and MS were in good agreement with the published data.[28]

General Procedure for Cross-Coupling Reaction (Table 2, entry 11). (*E*)-Benzyl Methyl Benzylidenemalonate (3ac): **2a** (225 mg, 0.500 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (13 mg, 2.5 mol %), Ph_3P (16 mg, 12.5 mol %),

and $ClCO_2i$-Bu (0.10 mL, 0.75 mmol) were dissolved in DME (5 mL) in a dry 30-mL round-bottom flask. The solution was stirred at 80 °C for 12 h. After addition of H_2O, the mixture was cooled to rt and extracted with AcOEt twice. The combined organic layers were washed with brine, dried over 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: 7.79 (s, 1H), 7.44–7.31 (m, 10H), 5.30 (s, 2H), 3.83 (s, 3H). ^{13}C NMR: 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). IR (neat): 2978, 2947, 2886, 1732, 1620, 1504, 1458, 1373, 1258, 122, 1053. ESIMS *m*/*z*: 319 (M + Na). HRMS–ESI (*m*/*z*): [M + Na]$^+$ calcd for $C_{18}H_{16}O_4Na$, 319.0941; found, 319.0945. ^{1}H and ^{13}C NMR are in good agreement with those reported.[4b]

(*E*)-Isobutyl Methyl 2-Benzylidenemalonate (3ab). Step-wise Procedure (Table 2, entry 1): according to the General Procedure using 1.00-mmol **2a** with $Pd_2(dba)_3{\cdot}CHCl_3$ (10 mg, 1.0 mol %), Ph_3P (13 mg, 5.0 mol %), $ClCO_2i$-Bu (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)**: **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-bottom flask under argon atmosphere. To the stirred solution cooled in an ice–water bath, was added Bu_3SnH (0.30 mL, 1.1 mmol). After 30 min, the solution was warmed up 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 rt. The whole was extracted twice with AcOEt, and the combined organic layers were washed with brine, dried over 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: 7.75 (s, 1H), 7.30–7.50 (m, 5H), 4.04 (d, *J* = 7.0, 2H), 3.85 (s, 3H), 2.01 (nonet, *J* = 7.0, 1H), 0.97 (d, *J* = 7.0, 6H). ^{13}C NMR: 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). IR (neat): 2961, 1724, 1630, 1260, 1219, 1200, 1082, 1061. EIMS *m*/*z*: 262 (M$^+$), 206 (M – *i*-Bu), 189 (M – *i*-BuO). HRMS–ESI (*m*/*z*): [M + H]$^+$ calcd for $C_{15}H_{19}O_4$, 263.1278; found, 263.1276. The (*E*)-geometry was confirmed by NOESY correlations between the methoxy and the aromatic protons (3.85 and 7.30–7.50 ppm, respectively), and the methyl protons of the isobutoxy group (0.97 ppm) and the vinylic proton (7.75 ppm).

(*E*)-((1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl) Methyl 2-Benzylidenemalonate (3ak): Purified by column chromatography (hexane/Et_2O 50:1 to 10:1). From 0.5-mmol **2a**, the title compound (171 mg, 89%) was obtained as a pale yellow oil: ^{1}H NMR: 7.72 (s, 1H), 7.42–7.46 (m, 2H), 7.34–7.40 (m, 3H), 4.82 (td, *J* = 11.0, 4.5, 1H), 3.83 (s, 3H), 2.10 (ddt, *J* = 1,0, 12.0, 4.0, 1H), 1.92 (d septet, *J* = 3.0, 7.0, 1H), 1.70 (ddd, *J* = 15.0, 5.0, 2.0, 2H), 1.52 (m, 1H), 1.44 (ddt, *J* = 12.0, 11.0, 3.0, 1H), 1.03–1.14 (m, 2H), 0.92 (d, *J* = 6.5, 3H), 0.91 (d, *J* = 7.0, 3H), 0.87 (m, 1H), 0.79 (d, *J* = 7.0, 3H). ^{13}C NMR: 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). IR (neat): 2955, 2928, 2870, 1713, 1628, 1258, 1200, 1157. EIMS *m*/*z*: 344 (M$^+$), 313 (M – OMe). HRMS–ESI (*m*/*z*): [M + Na]$^+$ calcd for $C_{20}H_{28}O_4Na$, 367.1880; found, 367.1880. $[\alpha]^{25}_D$ –26.2 (*c* 1.00, $CHCl_3$). The (*E*)-geometry was assigned by analogy.

(*E*)-Methyl ((1*R*,2*S*,5*R*)-(2-Phenylpropan-2-yl)-5-methylcyclohexyl) 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: ^{1}H NMR: 7.38–7.36 (m, 3H), 7.34–7.26 (m, 4H), 7.24 (dt, *J* = 8.0, 1.5, 2 H), 7.06 (s, 1H), 6.99 (tt, *J* = 7.0, 1.5, 1H), 4.99 (td, *J* = 10.5, 4.5, 1H), 3.82 (s, 3H), 2.07 (ddd, *J* = 12.5, 10.5, 3.0, 1H), 1.99 (dtd, *J* = 10.5, 4.0, 1.5, 1H), 1.67–1.59 (m, 2H), 1.50 (m, 1H), 1.34 (s, 3H), 1.25 (s, 3H), 1.16–1.02 (m, 2H), 0.88 (d, *J* = 7.5, 3H). ^{13}C NMR: 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). IR (neat): 2982, 2951, 2909, 1740, 1697, 1636, 1620, 1258, 1219, 1057, 1026. ESIMS *m*/*z*: 443 (M + Na). HRMS–ESI (*m*/*z*): [M + Na]$^+$ calcd for $C_{27}H_{32}O_4Na$, 443.2193; found, 443.2197. $[\alpha]^{25}_D$ –7.5 (*c* 1.00, $CHCl_3$). The (*E*)-geometry was assigned by analogy.

(*Z*)-Isobutyl Methyl 2-Benzylidenemalonate (3ba). **Table 2, entry 2**: from 0.5-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 3, entry 1**: 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): ^{1}H NMR: 7.77 (s. 1H), 7.30–7.50 (m, 5H), 4.04 (d, *J* = 7.0, 2H), 3.85 (s, 3H), 1.95 (nonet, *J* = 7.0, 1H), 0.87 (d, *J* = 7.0, 6H). ^{13}C NMR: 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). IR (neat): 2957, 1730, 1630, 1261, 1211, 1202, 1087, 1063. EIMS *m*/*z*: 262 (M$^+$), 206 (M – isobutene), 189 (M – O*i*-Bu). HRMS–ESI (*m*/*z*): [M + Na]$^+$ calcd for $C_{15}H_{18}O_4Na$, 285.1097; found, 285.1094. The (*Z*)-geometry was confirmed by NOESY correlation between the methyl protons of the isobutoxy group (0.87 ppm) and the aromatic protons (7.30–7.50 ppm).

(*Z*)-Benzyl Methyl 2-Benzylidenemalonate (3ca): Purified by column chromatography (hexane to hexane/AcOEt 10/1). From 0.5-mmol **2c**, the title compound (106 mg, 67%) was obtained as a pale yellow oil: ^{1}H NMR: 7.79 (s, 1H), 7.46–7.31 (m, 10H), 5.30 (s, 2H), 3.83 (s, 3H). ^{13}C NMR: 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). IR (KBr): 3021, 1701, 1670, 1261, 1215, 770, 756, 696, 669. ESIMS *m*/*z*: 319 (M+Na). HRMS–ESI (*m*/*z*): [M + Na]$^+$ calcd for $C_{18}H_{16}O_4Na$, 319.0941; found, 319.0945. ^{1}H and ^{13}C NMR are in good agreement with those reported.[4b]

(*E*)-Isobutyl 2-(Dimethylcarbamoyl)-3-phenylacrylate (3db): Purified by column chromatography (hexane/AcOEt 20:1 to 1:2). From 0.5-mmol **2d**, the title compound (101 mg, 74%) was obtained as a pale yellow oil: ^{1}H NMR: 7.68 (s, 1H), 7.50 (dd, *J* = 1.5, 5.0, 2H), 7.34–7.42 (m, 3H), 3.96–4.10 (br m, 2H), 3.09 (s, 3H), 2.85 (s, 3H), 2.02 (nonet, *J* = 6.5, 1H), 0.95 (d, *J* = 6.6, 6H). ^{13}C NMR: 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). IR (neat): 2963, 1713, 1639, 1246, 1196, 1153. EIMS *m*/*z*: 219 (M – isobutene). HRMS–ESI (*m*/*z*): [M + H]$^+$ calcd for $C_{16}H_{22}NO_3$, 276.1600; found, 276.1595. Anal. Calcd for $C_{16}H_{21}NO_3$: 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.

(*E*)-Isobutyl 2-Cyano-3-phenylacrylate (3eb): Purified by column chromatography (hexane/AcOEt 50:1 to 20:1). From 0.5-mmol **2e**, the title compound (111 mg, 89%) was obtained as a white solid of mp 38–39 °C: ^{1}H NMR: 8.26 (s, 1H), 8.00 (d, *J* = 7.0, 2H), 7.57 (t, *J* = 7.0, 1H), 7.51 (t, *J* = 7.0, 2H), 4.11 (d, *J* = 6.5, 2H), 2.09 (nonet, *J* = 6.5, 1H), 1.03 (d, *J* = 6.5, 6H). ^{13}C NMR: 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). IR (neat): 2967, 2222, 1724, 1609, 1265, 1188. EIMS *m*/*z*: 229 (M$^+$), 173 (M – isobutene). HRMS–ESI (*m*/*z*): [M + H]$^+$ calcd for

$C_{14}H_{16}NO_2$, 252.0995; found, 252.0990. The (*E*)-geometry was assigned by analogy.

(*E*)-Isobutyl Methyl 2-(4-Fluorobenzylidene)malonate (3fb): Purified by column chromatography (hexane/AcOEt 20:1 to 5:1). From 0.5-mmol **2f**, the title compound (133 mg, 90%) was obtained as a pale yellow oil: ^{1}H NMR: 7.70 (s, 1H), 7.44 (ddt, *J* = 8.5, 5.0, 2.5, 2H), 7.09 (tt, *J* = 8.5, 2.5, 2H), 4.03 (d, *J* = 6.5, 2H), 3.86 (s, 3H), 2.01 (nonet, *J* = 6.5, 1H), 0.97 (d, *J* = 6.5, 6H). ^{13}C NMR: 166.0 (d, J_{C-F} = 271, C), 163.9 (C), 162.9 (C), 141.1 (CH), 131.5 (d, J_{C-F} = 9, CH), 129.0 (C), 125.7 (C), 116.1 (d, J_{C-F} = 22, CH), 71.6 (CH_2), 52.6 (CH_3), 27.7 (CH), 19.0 (CH_3). IR (neat): 3005, 2970, 1736, 1369, 1219. EIMS *m*/*z*: 280 (M^+), 224 (M – isobutene). HRMS–ESI (*m*/*z*): [M + Na]$^+$ calcd for $C_{15}H_{17}FO_4Na$, 303.1003; found, 303.1002. The (*E*)-geometry was assigned by analogy.

(*E*)-Isobutyl Methyl 2-(4-Methoxybenzylidene)malonate (3gb): Purified by column chromatography (hexane/AcOEt 20:1 to 5:1). From 0.5-mmol **2g**, the title compound (112 mg, 76%) was obtained as a pale yellow oil: ^{1}H NMR: 7.69 (s, 1H), 7.40 (dt, *J* = 9.0, 3.0, 2H), 6.90 (dt, *J* = 9.0, 3.0, 2H), 4.02 (d, *J* = 6.5, 2H), 3.87 (s, 3H), 3.84 (s, 3H), 2.00 (m, 1H), 0.96 (d, *J* = 7.0, 6H). ^{13}C NMR: 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). IR (neat) 2963, 2901, 2847, 1717, 1601, 1512, 1258, 1173. EIMS *m*/*z*: 292 (M^+), 219 (M – O*i*-Bu). HRMS–ESI (*m*/*z*): [M + Na]$^+$ calcd for $C_{16}H_{20}O_5Na$, 315.1203; found, 315.1202. The (*E*)-geometry was assigned by analogy.

(*E*)-Isobutyl Methyl 2-(2-Methylbenzylidene)malonate (3hb): Purified by column chromatography (hexane/Et_2O 50:1 to 5:1). From 0.5-mmol **2h**, the title compound (93.6 mg, 70%) was obtained as a pale yellow oil: ^{1}H NMR: 7.99 (s, 1H), 7.32 (d, *J* = 7.5, 1H), 7.28 (t, *J* = 7.5, 1H), 7.21 (d, *J* = 7.5, 1H), 7.17 (t, *J* = 7.5, 1H), 4.04 (d, *J* = 6.5, 2H), 3.74 (s, 3H), 2.38 (s, 3H), 2.02 (nonet, *J* = 6.5, 1H), 0.97, (d, *J* = 6.5, 6H). ^{13}C NMR: 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). IR (neat): 3021, 2963, 2874, 1724, 1254, 1215, 1069. EIMS *m*/*z*: 277 (M – Me), 261 (M – OMe). HRMS–ESI (*m*/*z*): [M + H]$^+$ calcd for $C_{16}H_{21}O_4$, 277.1434; found, 277.1436. The (*E*)-geometry was assigned by analogy.

(*E*)-Isobutyl Methyl 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: 7.32 (t, *J* = 7.0, 2H), 7.25 (m, 1H), 7.22 (t, *J* = 7.0, 2H), 7.11 (t, *J* = 8.0, 1H), 3.96 (d, *J* = 6.5, 2H), 3.86 (s, 3H), 3.64 (d, *J* = 8.0, 2H), 1.96 (nonet, *J* = 6.5, 1H), 0.93 (d, *J* = 6.5, 6H). ^{13}C NMR: 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). IR (neat): 2990, 2955, 29905, 1724, 1643, 1601, 1366, 1250, 1231, 1200, 1065. EIMS *m*/*z*: 276 (M^+), 203 (M – O*i*-Bu). Anal. Calcd for $C_{16}H_{20}O_4$: 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.

(*E*)-Isobutyl Methyl 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: 7.02 (t, *J* = 7.5, 1H), 3.96 (d, *J* = 6.5, 2 H), 3.82, (s, 3H), 2.30 (q, *J* = 7.5, 2H), 1.97 (nonet, *J* = 6.5, 1H), 1.44–1.50 (m, 2H), 1.23–1.40 (m, 6H), 0.94 (d, *J* = 6.5, 6H), 0.88 (t, *J* = 6.9, 3H). ^{13}C NMR: 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). IR (neat): 2955, 2928, 1724, 1643, 1605, 1246, 1227, 1065. EIMS *m*/*z*: 271 (M + H), 239 (M – OMe). HRMS–ESI (*m*/*z*): [M + H]$^+$ calcd for $C_{15}H_{27}O_4$, 271.1904; found, 271.1906. The (*E*)-geometry was assigned by analogy.

(*Z*)-((1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl) Methyl 2-Benzylidenemalonate (3ka): Purified by column chromatography (hexane to hexane/AcOEt 20/1). From 2.22-mmol **4a**, the title compound (370 mg, 48%) was obtained as a white solid of mp 92–94 °C: ^{1}H NMR: 7.72 (s, 1H), 7.52–7.47 (m, 2H), 7.43–7.34 (m, 3H), 4.88 (dt, *J* = 4.5, 11.0, 1H), 3.83 (s, 3H), 2.16 (m, 1H), 1.85 (d sextet, 1H, *J* = 2.5, 7.0, 1H), 1.72–1.65 (m, 2H), 1.52 (m, 1H), 1.39 (ddt, *J* = 12.5, 11.0, 1.0, 1H), 1.13–0.95 (m, 2H), 0.93 (d, *J* = 6.5, 3H), 0.88 (m, 1H), 0.82 (d, *J* = 7.0, 3H), 0.77 (d, *J* = 3.0, 3H). ^{13}C NMR: 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). $[\alpha]^{25}_D$ –40.2 (*c* 1.00, $CHCl_3$). IR (neat): 2951, 2920, 1728, 1628, 1454, 1258, 1200, 1065, 764. ESIMS *m*/*z*: 367 (M + Na). HRMS–ESI (*m*/*z*): [M + Na]$^+$ calcd for $C_{21}H_{28}O_4Na$, 367.1880; found, 367.1882. The (*Z*)-geometry was assigned by analogy.

(*Z*)-1-((1*R*,2*S*,5*R*)-(2-Phenylpropan-2-yl)-5-methylcyclohexyl) 3-Methyl 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. ^{1}H NMR: 7.71 (s, 1H), 7.49 (dd, *J* = 7.5, 2.0, 2H), 7.41–7.17 (m, 7H), 7.10 (dt, *J* = 7.0, 2.0, 1H), 4.92 (dt, *J* = 4.0, 10.5, 1H), 3.84 (s, 3H), 2.21 (ddd, *J* = 3.0, 5.5, 11.5, 1H), 1.85 (ddd, *J* = 3.5, 9.0, 12.0, 1H), 1.53–1.43 (m, 2H), 1.28 (m, 1H), 1.20 (s, 3H), 1.17 (s, 3H), 0.98–0.66 (m, 3H), 0.86 (d, *J* = 6.5, 3H). ^{13}C NMR: 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). IR (neat): 2947, 1721, 1697, 1261, 1207, 1053. ESIMS *m*/*z*: 443 (M + Na). HRMS–ESI (*m*/*z*): [M + Na]$^+$ calcd for $C_{27}H_{32}O_4Na$, 443.2193; found, 443.2192. $[\alpha]^{25}_D$ –31.3 (*c* 1.00, $CHCl_3$). The (*Z*)-geometry was assigned by analogy.

(*E*)-Isobutyl Methyl 2-(2-Methylpropylidene)malonate (3mb): according to the one-pot procedure for **3ab** 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: 6.68 (d, *J* = 10.0, 1H), 3.96 (d, *J* = 6.5, 2H), 3.82 (s, 3H), 2.67 (m, 1H), 1.97 (nonet, *J* = 6.5, 1H), 1.07 (d, *J* = 6.5, 6H), 0.94 (d, *J* = 6.5, 6H). ^{13}C NMR: 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). IR (KBr): 2963, 2932, 2874, 1732, 1647, 1248, 1223, 1150, 1055, 999. EIMS *m*/*z*: 172 (M – isobutene), 155 (M – O*i*-Bu), 131, 122, 103, 91. HRMS–ESI (*m*/*z*): [M + Na]$^+$ calcd for $C_{12}H_{20}O_4Na$, 251.1254; found 251.1251, The (*E*)-geometry was assigned by analogy.

(*E*)-Isobutyl Methyl 2-(2,2-Dimethylpropylidene)malonate (3nb): according to the one-pot procedure for **3ab** 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: 6.91 (s, 1H), 3.95 (d, *J* = 6.5, 2H), 3.81 (s, 3H), 1.94 (m, 1H), 1.13 (s, 9H), 0.93 (d, *J* = 6.5, 6H). ^{13}C NMR: 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). IR (KBr): 2961, 2934, 2874, 1732, 1643, 1246, 1196, 1070, 1001. EIMS *m*/*z*: 186 (M – isobutene), 171, 136, 105, 91. HRMS–ESI (*m*/*z*): [M + Na]$^+$ calcd for $C_{13}H_{22}O_4Na$, 265.1410; found 265.1406, The (*E*)-geometry was assigned by analogy.

(*Z*)-Methyl 3-Phenyl-2-(tributylstannyl)acrylate (4a): **1a** (1.5 mL, 10 mmol) was placed in a dry 100-mL round-bottom flask. To the flask were added THF (10 mL), Bu_3SnH (3.0 mL, 11 mmol), and AIBN (25 mg, 0.15 mmol). 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: 8.37 (s, 1H), 7.2–7.4 (m, 5H), 3.78 (s, 3H), 1.10–1.51 (m, 12H), 0.7–0.9 (m, 15H). ^{13}C NMR: 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). IR (neat): 2955, 2922, 2870, 2853, 1710, 1695, 1230, 1194, 1074. EIMS *m*/*z*: 451 (M^+), 395 (M – Bu). The *Z*-geometry was confirmed by the H–Sn coupling constant of the β-H (8.37 ppm, $^3J_{H–Sn}$ = 100 Hz).[13] ^{1}H NMR and ^{13}C NMR were in good agreement with the published data.[29]

(2*SR*,3*SR*,4*SR*,5*SR*)- and (2*SR*,3*SR*,4*RS*,5*SR*)-4-Benzyl 2,4-Dimethyl 3,5-Diphenylpyrrolidine-2,4,4-tricarboxylate (6): Conducted according to the reported procedure[15] 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: 7.49 (dt, *J* = 2.0, 8.5, 2H), 7.37–7.18 (m, 11H), 6.94 (dd, *J* = 2.0, 7.0, 0.72H), 6.84 (dd, *J* = 2.0, 7.0, 1.28H), 5.37 (s, 0.36H), 5.35 (s, 0.64H), 4.91 (d, *J* = 7.5, 0.64H), 4.88 (d, *J* = 7.5, 0.36H), 4.45 (d, *J* = 6.5, 0.64H), 4.43 (d, *J* = 6.5, 0.36H), 4.24–4.21 (m, 1.36H), 4.12 (d, *J* = 12.5, 0.64H), 3.77 (s, 3H), 3.12 (s, 2.16H), 3.10 (s, 1.08H). ^{13}C NMR: 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). IR (KBr): 3435, 2954, 2927, 1719, 1630, 1437, 1383, 1265, 1213, 905, 733, 702, 650. ESIMS *m*/*z*: 474 (M + H). HRMS–ESI (*m*/*z*): $[M + H]^+$ calcd for $C_{28}H_{28}NO_6$, 474.1911; found, 474.1914. The diastereomeric ratio (64:36) was determined by the integration area of ^{1}H NMR signals at 6.94 ppm and 6.84 ppm. The relative configuration was determined after conversion into the known trimethyl ester with the established stereochemistry as follows. 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 rt under H_2 atmosphere. The mixture was filtered through celite, which was successively washed with THF. To the combined filtrate, was added 1 M THF solution of $TMSCHN_2$ (1.2 mmol, 20 equiv). After 15 min, the mixture was concentrated *in vacuo* to give the title compound (24.0 mg, 92%) as a yellow oil: ^{1}H NMR: 7.47 (d, *J* = 7.5, 2H), 7.36–7.14 (m, 8H), 5.33, (s, 1H), 4.42 (d, *J* = 7.0, 1H), 4.24 (d, *J* = 7.0, 1H), 3.77 (s, 3H), 3.17 (s, 3H), 3.13 (s, 3H). ^{1}H NMR is in good agreement with that reported.[30]

Acknowledgements

We thank JSPS [Grant-in-Aid for Young Scientist (B), Grant-in-Aid for Scientific Research (C), and Postdoctral Fellowship for RC] and MEXT (Platform for Drug Design, Discovery and Development) for financial support.

Keywords: cross-coupling reaction • alcoxycarbonylation • one-pot reaction • Michael acceptor • dienophile

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Entry for the Table of Contents

FULL PAPER

Pd-catalyzed and radical hydrostannylation of propiolate derivatives stereoselectively provided α-alkoxycarbonyl (*E*)- and (*Z*)-vinylstannanes, respectively, which were then converted into alkyli-denemalonates by the Stille coupling reaction. A one-pot process was also realizable for the Pd-catalyzed reactions.

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