Pd-catalyzed allylation of CH acids under phase-transfer conditions

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The composition of the products obtained by Pd-catalyzed allylation of diethyl (alkyl)-malonates and ethyl cyanoacetate with allylic acetates under phase-transfer conditions using potassium carbonate or phosphate as bases depended strongly on the nature of the reactants and the ligands used. The highest yields and the fraction of the "linear" regioisomers were achieved in the reactions of prenyl or 3-methylbut-1-en-3-yl acetates in the presence of phosphordiamidite ligands.

Key words: allylation, CH acids, Pd complexes, cross-coupling, phosphordiamidites, ligands, phase-transfer conditions, Tsuji—Trost reaction.

The Pd-catalyzed reaction of stabilized anions of CH acids with allylic carboxylates (the Tsuji—Trost reaction) is a good alternative for the application of allylic halides and was employed in the synthesis of practically useful substances.[1] The need of preliminary conversion of the starting CH acid into the carbanion using strong bases such as NaH, LDA, or a system *N*,*O*-bis(trimethylsilyl)acetamide—potassium acetate is the main disadvantage of this method, which places serious restrictions to its wide application. In the mid-1980s, Russian researchers showed that the extension of the phase-transfer concept on the Tsuji—Trost reaction allowed allylation of several CH and NH acids to proceed using such inexpensive safe bases as alkali metal carbonates and hydroxides.[2] Since then, only scarce examples of the use of alkali carbonates for the deprotonation of CH acids aimed at asymmetric addition to 3-acetoxy-1,3-diphenylprop-1-ene have been documented.[3] An interesting recent development is allylation in the presence of R_2NLi generated *in situ* from lithium metal and a secondary amine with α-methylstyrene as a hydrogen acceptor.[4,5]

Recently[6] we have published preliminary results of successful Pd-catalyzed prenylation of diethyl malonate with prenyl and 3-methylbut-1-en-3-yl acetates (C_5-synthons) under phase-transfer conditions in the presence of potassium carbonate with a good regioselectivity provided by a phosphordiamidite ligand. It should be noted that the Tsuji—Trost reaction[1] is routinely studied with C_5-synthons as the linear terpenoind analogs, for example, neryl acetate (*Z*-3,7-dimethylocta-2,6-dienyl acetate). Under conditions of phase-transfer catalysis, no target products were obtained from the latter.[2a] In the present work, the results of allylation of malonates and cyanoacetates with allylic acetates using potassium carbonate or phosphate as the bases are summarized.

Allylation of diethyl malonate (**1**) with very reactive allyl acetate (**2a**) (Scheme 1, Table 1, *cf.* Ref. 2a) in the presence of a $Pd(dba)_2$—PPh_3 catalytic system (dba is dibenzylideneacetone) and K_2CO_3 in toluene proceeded even without a phase-transfer catalyst (PTC) (see Table 1, entry *1*) giving the monoallylation product **3a** in high yield. With potassium phosphate, which is better soluble in toluene, the formation of diallylation product **4a** was also observed (see Table 1, entry *2*). Mixtures of both products were obtained with K_2CO_3 and quaternary ammonium salts as PTC (see Table 1, entries *3*—*5*). It is of note that diallylation product **4a** formed exclusively in the presence of a K_2CO_3—Bu_4NBr system in CH_2Cl_2 (see Table 1, entry *6*). No PTC is required for the reactions carried out in aprotic polar solvents, for example, DMF and DMSO (see Table 1, entries *7* and *8*). This allowed us to somewhat simplify the synthetic procedure.

Nearly quantitative yields of the diallylation products were obtained with tributylphosphine as a ligand (see Table 1, entry *9*). Surprisingly, the electron-rich sterically hindered phosphines (tricyclohexylphosphine PCy_3 and S-PHOS) were less applicable for our goal (see Table 1, entries *10* and *11*), which is probably due to the strong shielding of the palladium atom in the activated complex. Finally, the catalytic systems on the base of recently synthesized phosphite (**L1**) and phosphoramidite (**L2**) ligands[7] were found ineffective (see Table 1, entries

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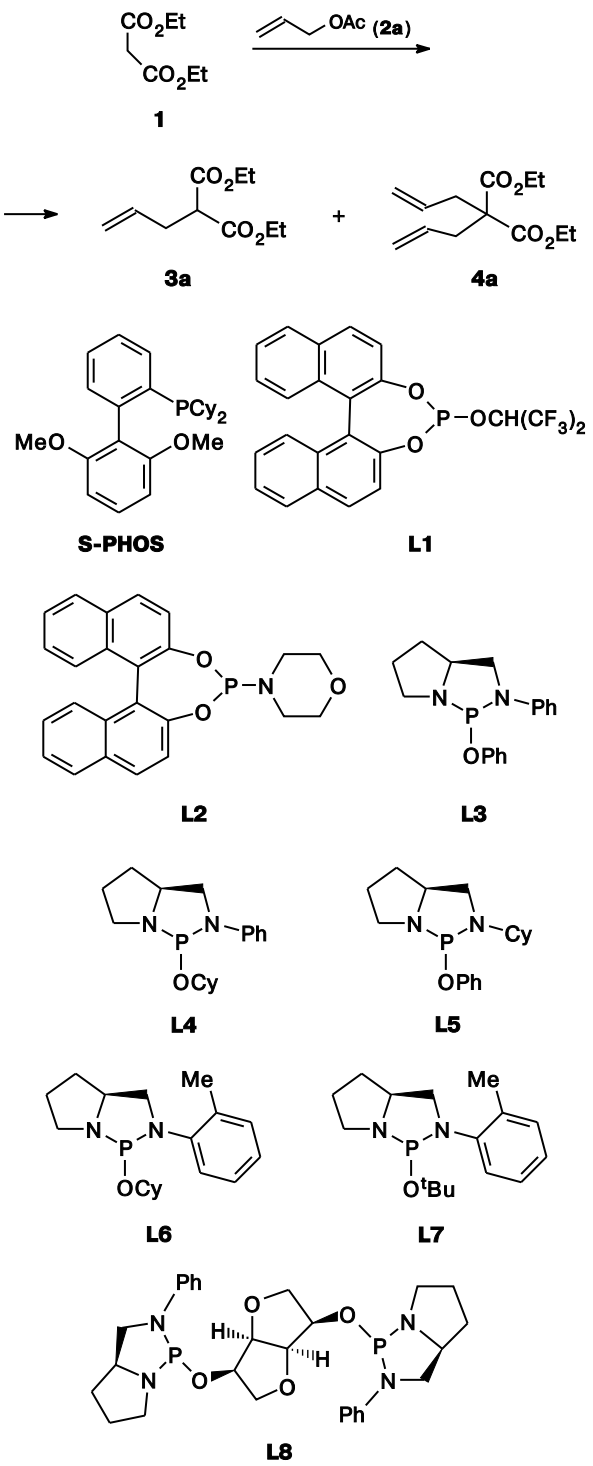
12 and *13*), while phosphordiamidite (**L3**) provided the quantitative yield of diallylation product **4a** (see Table 1, entry *14*).

Scheme 1



Reagents and condition: 2a, $Pd(dba)_2$, ligand, base, solvent, PTC, 20 °C, 18 h (see Table 1).

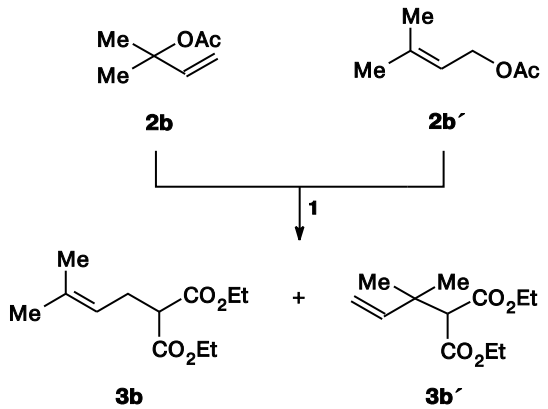
Table 1. Reaction of diethyl malonate (**1**) with allyl acetate (**2a**)[a]

Entry	Solvent	PTC	Ligand	GS data	
				Conversion of **1** (%)	**3a** : **4a**
1	Toluene	—	PPh_3	98	100 : 0
2	Toluene[b]	—	PPh_3	100	49 : 51
3	Toluene	$BnEt_3NCl$	PPh_3	100	45 : 55
4	Toluene	Bu_4NBF_4	PPh_3	100	73 : 27
5	Toluene	Bu_4NBr	PPh_3	100	11 : 89
6	CH_2Cl_2	Bu_4NBr	PPh_3	100	0 : 100
7	DMF	—	PPh_3	100	23 : 77
8	DMSO	—	PPh_3	100	0 : 100
9	DMF	—	PBu_3	100	1 : 99
10	DMF	—	PCy_3	—	—
11	DMF	—	S-PHOS	85	93 : 7
12	DMF	—	**L1**	—	—
13	DMF	—	**L2**	6	100 : 0
14	DMF	—	**L3**	100	0 : 100

[a] Conditions: 2.4 equiv. AllOAc, 3 equiv. K_2CO_3, 2 mol.% $Pd(dba)_2$, 8 mol.% phosphine or 4 mol.% phosphordiamidite, 10 mol.% PTC, 20 °C, 18 h.
[b] K_3PO_4 was used as a base.

Based on these data, we studied prenylation of diethyl malonate (**1**) with 3-methylbut-1-en-3-yl acetate (**2b**) and its isomer, prenyl acetate, (**2b´**). The isomers **2b** and **2b´** usually produce a similar set of the products because they generate the same π-allyl complex in the catalytic cycle (Scheme 2, *cf.* Ref. 8). In the case of tertiary acetate **2b**, no variations in the phosphine ligands provides the high fraction of "linear" isomer **3b** (Table 2, entries *1—6*) (*cf.* Ref. 9).

Scheme 2



The fraction of isomer **3b** reached 77% with the use of phosphordiamidite ligands **L3—L6** (see Table 2, entries *7—12*) with nearly complete conversion of the starting CH acid **1**. In the case of sterically more hindered ligand **L7** and bidentate ligand **L8**, the fraction of the "linear" isomer (see Table 2, entries *13* and *14*) decreased noticeably.

Table 2. Reaction of diethyl malonate (**1**) with allylic acetates **2b** and **2b´**[a]

Entry	Allylic acetate	Solvent	PTC	Ligand	GC data	
					Conversion of **1** (%)	**3b** : **3b´**
1	**2b**	DMF	—	PPh_3	100	16 : 84
2	**2b**	CH_2Cl_2	Bu_4NBr	PPh_3	53	6 : 94
3	**2b**	DMF	—	PBu_3	76	44 : 56
4	**2b**	CH_2Cl_2	Bu_4NBr	PBu_3	81	17 : 83
5	**2b**	DMF	—	PCy_3	—	—
6	**2b**	DMF	—	S-PHOS	44	48 : 52
7	**2b**	DMF	—	**L3**	100	77 : 23
8	**2b**	DMSO[b]	—	**L3**	100	68 : 32
9	**2b**	DMF	—	**L4**	100	77 : 23
10	**2b**	DMF	—	**L5**	98	77 : 23
11	**2b**	CH_2Cl_2	Bu_4NBr	**L5**	98	69 : 31
12	**2b**	DMF	—	**L6**	97	67 : 33
13	**2b**	DMF	—	**L7**	84	26 : 74
14	**2b**	DMF	—	**L8**	83	40 : 60
15	**2b´**	DMF	—	PPh_3	—	—
16	**2b´**	DMF	—	PBu_3	57	40 : 60
17	**2b´**	DMSO	—	PBu_3	98	43 : 57
18	**2b´**	DMF	—	PCy_3	—	—
19	**2b´**	DMF	—	S-PHOS	—	—
20	**2b´**	DMF	—	**L3**	18	77 : 23
21	**2b´**	DMF	—	**L4**	94	71 : 29

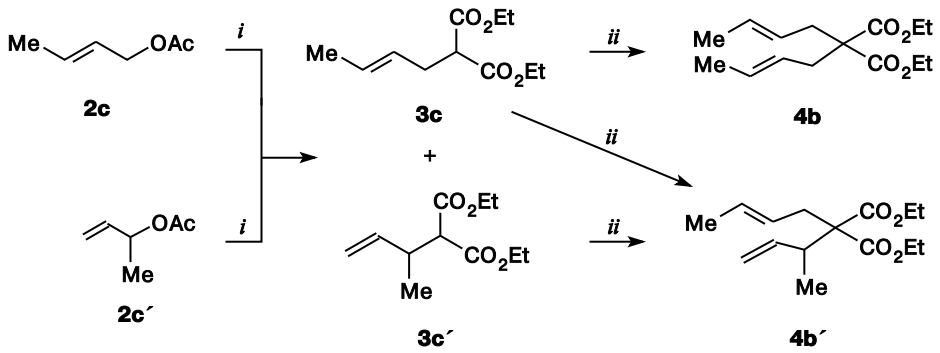
[a] Conditions: 1.5 equiv. **2b** or **2b´**, 2 eqiuv. K_2CO_3, 2 mol.% $Pd(dba)_2$, 8 mol.% phosphine or 4 mol.% phosphordiamidite, 10 mol.% PTC, 20 °C, 18 h.

[b] Yields in *N*,*N*-dimethylacetamide and *N*-methylpyrrolidone are ~90%, in *N*,*N´*-dimethylpropyleneurea (DMPU) is 64% (**3b** : **3b´** ≈ 70 : 30), in HMPA no reaction was observed.

The use of prenyl acetate **2b´** led to a decrease in the product yields (see Table 2, entries *15—21*). This fact could be explained by slower coordination of palladium with the sterically less accessible trisubstituted double bond of **2b´** as compared with **2b**. The close ratios of "linear" and "branched" isomers **3b**/**3b´** obtained under similar reaction conditions deserve attention (*cf.* entries *3* and *16*, *7* and *20*, *9* and *21*). This fact indicated that the "allylic carboxylate memory effect", which is common for the fully deprotonated CH acids,[8] is not observed. Probably, K_2CO_3 provided low concentration of the carbanion which in turn decreases the rate of the reaction of the carbanion with the second reaction species. Probably, this species, which also has low quasi-steady-state concentration, is the resulting π-allyl organopalladium complex (identical for both allylic acetates **2b** and **2b´**) rather than its precursors (different for **2b** and **2b´**), which can also react with carbanions.

Reaction of crotyl acetate **2c** and its isomer **2c´** with an excess of diethyl malonate (**1**) afforded a mixture of iso-

Scheme 3

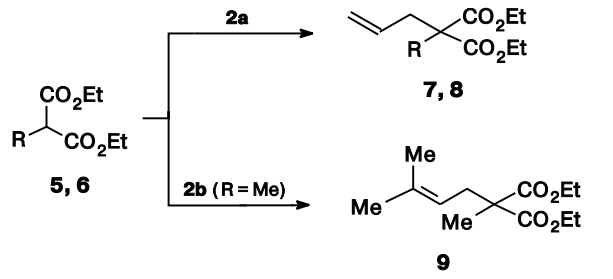


Reagents and conditions: *i.* **1** (1.5 equiv.), $Pd(dba)_2$, ligand, K_2CO_3, DMF, 20 °C; *ii.* the same with starting ratio **1** : **2c** (or **2c´**) = 1 : 4.

meric monosubstitution products **3c** and **3c´** (Scheme 3). The isomer ratio depended on the nature of the ligand. Ligands PPh_3, **L3**, and **L8** afforded isomers **3c** and **3c´** in ~2 : 3, ~3 : 2, and 2 : 1 ratios, respectively. With the excess of substrates **2c** or **2c´**, the subsequent allylation proceeded readily to give compounds **4b** and **4b´**.

The data for allylation of the *C*-substituted malonates **5** and **6** are summarized in Scheme 4 and in Table 3. The reaction of methyl-substituted derivative **5** with allyl acetate (**2a**) proceeded smoothly, while in the case of 3-methylbut-1-en-3-yl acetate (**2b**) the high yield of product **9** was achieved only in the presence of phosphordiamidite ligand **L4** (see Table 3, entry *6*). It is of note that no formation of a "branched" isomer, homolog of compound **3b´**, was observed under these conditions. The reactions of sterically more hindered diethyl cyclohexylmalonate (**6**) with unsubstituted allyl acetate (**2a**) furnished compound **8** in yields from low to moderate (entries *7—10*). Therefore, attempts to prenylate malonate **6** with either **2b** or **2b´** failed.

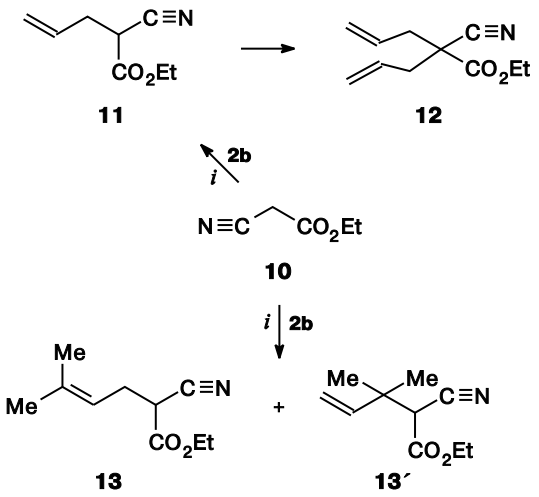
Scheme 4



R = Me (**5**, **7**), Cy (**6**, **8**)

Allylation of ethyl cyanoacetate (**10**), which is a stronger CH acid (pK_a ~13) than diethyl malonate (**1**) (pK_a ~15)[10] and hence is less nucleophilic, was also studied. With the excess of reactive allyl acetate (**2a**), the initially formed allylation product **11** underwent readily additional allylation (Scheme 5, Table 4, entries *1* and *2*). Prenylation of compound **10** with **2b** in the presence of phosphines yielded exclusively "branched" product **13´** (see Table 4, entries *3* and *4*), while phosphordiamidite **L3** provided some "linear" isomer **13** (see Table 4, entry *5*). It is of note that in this experiment the excess of ethyl cyanoacetate (**10**) has to be used otherwise product **13** underwent readily additional prenylation.

Scheme 5



i. $Pd(dba)_2$, ligand, K_2CO_3, DMF 20 °C.

In summary, we have demonstrated that Pd-catalyzed allylation and, in particular, prenylation, of the CH acids could successfully be carried out using K_2CO_3 as a base. Phosphordiamidite ligands favored the formation of "linear" isomers. The obtained results opened the prospects for the development of convenient methods toward functionalized unsaturated compounds, for example, terpenoids of practical value.[1,11]

Table 3. Allylation of malonates **5** and **6**

Entry	R	CH acid	Allylic acetate[a]	Ligand	Solvent	Product	Yield[b] (%)
1	Me	**5**	**2a**	PPh_3	DMF	**7**	100
2	Me	**5**	**2b**	PPh_3	DMF	**9**	0
3	Me	**5**	**2b**	PBu_3	DMF	**9**	0
4	Me	**5**	**2b**	PBu_3	DMSO	**9**	36
5	Me	**5**	**2b**	**L3**	DMSO	**9**	23
6	Me	**5**	**2b**	**L4**	DMSO	**9**	94
7	Cy	**6**	**2a**	PPh_3	DMF	**8**	51
8	Cy	**6**	**2a**	PBu_3	DMF	**8**	27
9	Cy	**6**	**2a**	**L3**	DMF	**8**	5
10	Cy	**6**	**2a**	**L3**	DMSO	**8**	19

[a] 1.5 equiv. **2a** or **2b** was used.
[b] The yield is taken to be equal to the conversion of the starting CH acids determined by GC.

Table 4. Allylation of ethyl cyanoacetate (**10**)

Entry	Allylic acetate	Ligand	Product	Yield[a] (%)
1	**2a** (0.5 equiv.)	PPh_3	**11**	100[b]
2	**2a** (2.5 equiv.)	PPh_3	**12**	100
3	**2b** (2.5 equiv.)	PPh_3	**13´**	37
4	**2b** (2.5 equiv.)	PBu_3	**13´**	100
5	**2b** (0.5 equiv.)	**L3**	**13**+**13´**	31+69[b]

[a] The yield is taken to be equal to the conversion of compound **10** determined by GC.
[b] The same, with account of the excess of compound **10**.

Experimental

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer in $CDCl_3$ at 300.13 and 75.47 MHz, respectively. Chemical shifts are given in the δ scale relative to a signal of the residual protons (^1H) or a signal of a deuterated solvent (^{13}C). The chromatomass spectrometry was performed on an Agilent Technologies 85973 Network (EI, 70 eV) mass spectrometer coupled with an Agilent Technologies 6890 chromatograph, which was equipped with a capillary column (HP-5MS 30000×0.25 mm), the temperature of injector and flame ionization detector was 280 °C, the thermostat temperature was programmed as follows: 60 (5 min), then 60→300 °C 10 deg min^{-1}, flow rate of the carrier gas (helium) was 2 mL min^{-1}. During the analysis, the total ion current and the signal of the flame ionization detector were registered in parallel. The GC analysis was carried out on a Chrom-5 chromatograph (the injector and detector temperature was 270 °C) on a column (2×2500 mm) with SE-30 on Chromaton N-AW-DMCS (the thermostat temperature of 150—180 °C depending on the nature of the sample) or a capillary column (0.2×25000 mm) with SE-30 (the thermostat temperature was programmed as follows: 120→230 °C, 10—15 deg min^{-1}). The composition of the mixtures was calculated using a normalization method.

Commercially available CH acids **1**, **5**, and **10**; allylic acetates **2a** and **2b´**; quaternary ammonium salts and phosphines (PPh_3 and PBu_3) (Aldrich) were used. Diethyl cyclohexylmalonate (**6**), which was synthesized by the known procedure,[12] was a kind gift from G. M. Zhdankina and G. V. Kryshtal. Allylic acetates **2c** and **2c´** were synthesized by acylation of the corresponding alcohols with acetic anhydride in the presence of DMAP by the standard procedure. 3-Methylbut-1-en-3-yl acetate (**2b**) was obtained by acylation of 3-methylbut-1-en-3-ol with acetic anhydride in CH_2Cl_2 in the presence of NEt_3 and DMAP as described.[13] Potassium carbonate (Reakhim, USSR) was calcined in air, kept in a closed vessel, and ground in a mortar prior to use. Potassium phosphate (granulated, Aldrich) was ground in a mortar prior to use. Bis(dibenzylideneacetone)-palladium ($Pd(dba)_2$)[14] and S-PHOS[15] were synthesized by the known methods. Ligands **L1—L8** were obtained by the known procedures,[16,17] their physicochemical properties were described previously.[6,7a,b,d] The solvents were distilled prior to use.

Allylation of CH acids (general procedure). A CH acid (0.5 mmol), a solvent (1 mL), and PTC (0.05 mmol, if required) were placed in a Schlenk tube equipped with magnetic stirring bar and a rubber septum. The mixture was deaerated three times by evacuation and refilling with argon (in the case of CH_2Cl_2, evacuation was carried out with care, boiling of the solvent being controlled). The catalyst, $Pd(dba)_2$ (6 mg, 0.01 mmol), and a ligand (0.04 mmol) were added, and the mixture was stirred until the color changed from dark-red to yellow. To a stirred mixture, an allylic acetate (1.25 mmol in the case of CH acids **1** and **10** and 0.75 mmol in the case of CH acids **5** and **6**) was added. After 10 min, potassium carbonate (2 mmol in the case of CH acids **1** and **10** and 1 mmol in the case of CH acids **5** and **6**) was added. Each opening of the Schlenk tube was followed by evacuation and refilling with argon. The mixture was stirred for 18 h at ~20 °C (GC monitoring; in most cases, the reaction completed in 5—6 h). For the GC analysis, an aliquot was treated with water and extracted with diethyl ether. The products were isolated analogously; the extract was dried with Na_2SO_4 and concentrated *in vacuo*, followed by column chromatography of the residue (SiO_2, eluent — gradient of EtOAc in petroleum ether, 0→5%). No separation of the resulting "linear" and "branched" isomers by column chromatography occurred. However, mono- and diallylation products and the starting CH acids exhibited different R_f on TLC. Diethyl allyl(cyclohexyl)malonate (**8**)[18] was identified by GC/MS (*m/z*: 282 $[M]^+$).

Diethyl allylmalonate (3a). ^1H NMR, δ: 1.24 (t, 6 H, *J* = 7.0 Hz); 2.61 (t, 2 H, *J* = 7.0 Hz); 3.39 (t, 1 H, *J* = 7.4 Hz); 4.17 (q, 4 H, *J* = 7.0 Hz); 5.03 (d, 1 H, *J* = 11.3 Hz); 5.09 (d, 1 H, *J* = 17.7 Hz); 5.76 (m, 1 H). The product is identical to the authentic sample.

Diethyl diallylmalonate (4a), colorless oil. ^1H NMR, δ: 1.23 (t, 6 H, *J* = 7.3 Hz); 2.62 (d, 4 H, *J* = 7.3 Hz); 4.17 (q, 4 H, *J* = 7.3 Hz); 5.08 (d, 1 H, *J* = 11.2 Hz); 5.09 (d, 1 H, *J* = 16.1 Hz); 5.65 (m, 1 H). The spectral data of **4a** are in good agreement with the published data.[19]

Diethyl (3-methylbut-2-en-1-yl)malonate (3b) and diethyl (3-methylbut-1-en-3-yl)malonate (3b´), colorless oil.

Compound **3b**. ^1H NMR, δ: 1.24 (t, 6 H, *J* = 7.0 Hz); 1.62 (s, 3 H); 1.67 (s, 3 H); 2.57 (t, 2 H, *J* = 7.4 Hz); 3.30 (t, 1 H, *J* = 7.7 Hz); 4.17 (q, 4 H, *J* = 6.6 Hz); 5.06 (br.t, 1 H, *J* = 7.4 Hz). The spectral data of **3b** are in good agreement with the published data.[8b,18,19] MS (*m/z*): 228 $[M]^+$.

Compound **3b´**. ^1H NMR, δ: 1.23 (s, 6 H); 1.24 (t, 6 H, *J* = 7.0 Hz); 3.31 (s, 1 H); 4.15 (q, 4 H, *J* = 6.6 Hz); 4.98 (d, 1 H, *J* = 10.3 Hz); 5.01 (d, 1 H, *J* = 17.7 Hz); 6.05 (dd, 1 H, *J* = 17.7 Hz, *J* = 10.3 Hz). The spectral data of **3b´** are in good agreement with the published data.[8b,20] MS (*m/z*): 228 $[M]^+$.

Diethyl (but-2-en-1-yl)malonate (3c) and diethyl (but-1-en-3-yl)malonate (3c´). Unseparable mixture in the ratio of **3c** : **3c´** = 2 : 1 were obtained by the reaction of diethyl malonate (**1**) (0.75 mmol) and crotyl acetate (0.5 mmol) (**2c**) (ligand **L8**), colorless oil.

Compound **3c** (*E*/*Z* = 9 : 1). ^1H NMR, δ: 1.21 (t, 6 H, *J* = 6.9 Hz); 1.58 (d, 3 H, *J* = 6.2 Hz); 2.51 (t, 1.8 H, *J* = 7.7 Hz, $=CCH_2$ *E*-isomer); 2.59 (t, 0.2 H, *J* = 7.7 Hz, $=CCH_2$, *Z*-isomer); 3.31 (t, 1 H, *J* = 7.3 Hz); 4.15 (q, 4 H, *J* = 6.2 Hz); 5.33 (m, 1 H); 5.48 (m, 1 H). The spectral data of **3c** are in good agreement with the published data.[8b,18,19] MS (*m/z*): 214 $[M]^+$.

Compound **3c´**. ^1H NMR, δ: 1.05 (d, 3 H, *J* = 6.7 Hz); 1.19 (t, 3 H, *J* = 6.9 Hz); 1.22 (t, 3 H, *J* = 6.9 Hz); 2.89 (m, 1 H); 3.22 (d, 1 H, *J* = 8.8 Hz); 4.08—4.17 (m, 4 H); 4.96 (d, 1 H, *J* = 10.3 Hz); 5.04 (d, 1 H, *J* = 17.2 Hz); 5.73 (m, 1 H). The spectral data of **3c´** are in good agreement with the published data.[8b,20] MS (*m/z*): 214 $[M]^+$.

A mixture of diethyl di(byt-2-en-1-yl)malonate (4b), diethyl (but-2-en-1-yl)(but-1-en-3-yl)malonate (4b´) and compound (3c´) (59 : 14 : 27) was obtained by the reaction of diethyl malonate (**1**) (0.5 mmol) with crotyl acetate (**2c**) (2 mmol) in the presence of ligand **L8**. Column chromatography afforded the mixture of compounds **4b** and **4b´** in the ratio of 7 : 3, colorless oil.

Compound **4b**. ^1H NMR, δ: 1.22 (t, 6 H, *J* = 7.1 Hz); 1.62 (d, 6 H, *J* = 6.4 Hz); 2.53 (d, 4 H, *J* = 7.3 Hz); 4.16 (q, 4 H, *J* = 7.1 Hz); 5.26 (m, 2 H); 5.47 (m, 2 H). The spectral data of **4b** are in good agreement with the published data.[21] MS (*m/z*): 268 $[M]^+$.

Compound **4b´**. ^1H NMR, δ (characteristic signals): 1.09 (d, 3 H, *J* = 7.3 Hz); 2.60 (d, 3H, *J* = 7.7 Hz); 2.84 (quint, 1 H, *J* = 7.8 Hz); 5.02 (d, 1 H, *J* = 10.3 Hz); 5.03 (d, 1 H, *J* = 17.6 Hz); 5.78 (m, 1 H); other signals overlap with the signals of compound **4b**. The spectral data of **4b´** are in good agreement with the published data.[22] MS (*m/z*): 268 $[M]^+$.

Diethyl allyl(methyl)malonate (7). ^{1}H NMR, δ: 1.23 (t, 6 H, J = 6.8 Hz); 1.37 (s, 3 H); 2.59 (d, 2 H, J = 6.4 Hz); 4.16 (q, 4 H, J = 6.8 Hz); 5.07 (d, 1 H, J = 10.7 Hz); 5.08 (d, 1 H, J = 16.1 Hz); 5.66 (m, 1 H). The spectral data of **7** are in good agreement with the published data.[23]

Diethyl methyl(3-methylbut-2-en-1-yl)malonate (9). ^{1}H NMR, δ: 1.24 (t, 6 H, J = 6.8 Hz); 1.37 (s, 3 H); 1.62 (s, 3 H); 1.69 (s, 3 H); 2.58 (d, 2 H, J = 7.3 Hz); 4.17 (q, 4 H, J = 6.8 Hz); 5.01 (m, 1 H). ^{13}C NMR, δ: 13.9 (Me); 17.8 (Me); 19.5 (Me); 25.9 (Me); 33.9 (CH_2); 53.8 (C); 61.0 (OCH_2); 118.0 (=CH); 135.4 (=C); 172.2 (C=O). The spectral data of **9** are in good agreement with the published data.[24]

Ethyl 2-cyanopent-4-enoate (11). ^{1}H NMR, δ: 1.32 (t, 3 H, J = 7.0 Hz); 2.61—2.69 (m, 2 H); 3.56 (t, 1 H, J = 6.8 Hz); 4.48—4.59 (m, 2 H); 5.17—5.30 (m, 2 H); 5.80 (m, 1 H). The spectral data of **11** are in good agreement with the published data.[19]

Ethyl 2-allyl-2-cyanopent-4-enoate (12). ^{1}H NMR, δ: 1.30 (t, 3 H, J = 7.0 Hz); 2.48—2.63 (m, 4 H); 4.25 (q, 2 H, J = 7.0 Hz); 5.20—5.28 (m, 4 H); 5.80 (m, 2 H). The spectral data of **12** are in good agreement with the published data.[19]

Ethyl 3,3-dimethyl-2-cyanopent-4-enoate (13´). ^{1}H NMR, δ: 1.28 (s, 6 H); 1.30 (t, 3 H, J = 7.3 Hz); 3.36 (s, 1 H); 4.24 (q, 2 H, J = 6.8 Hz); 5.14 (d, 1 H, J = 17.1 Hz); 5.15 (d, 1 H, J = 10.7 Hz); 5.91 (dd, 1 H, J = 17.6 Hz, J = 10.8 Hz). ^{13}C NMR, δ: 14.0 (Me); 24.5 (Me); 25.2 (Me); 40.0 (C); 48.7 (CH); 62.4 (OCH_2); 114.3 ($=CH_2$); 115.6 (CN); 142.2 (=CH); 164.8 (C=O). The spectral data of **13´** are in good agreement with the published data.[8a]

Ethyl 5-methyl-2-cyanohex-4-enoate (13) was obtained as a mixture with isomer **13´** (31 : 69). ^{1}H NMR, δ: 1.31 (d, 3 H, J = 7.3 Hz); 1.67 (br.s, 3 H); 1.74 (br.s, 3 H); 2.65 (t, 2 H, J = 6.6 Hz); 3.47 (t, 1 H, J = 6.6 Hz); 4.26 (q, 2 H, J = 6.8 Hz); 5.18 (br.s, 1 H). The spectral data of **13** are in good agreement with the published data.[8a]

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