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TRANSITION METAL-CATALYZED SUBSTITUTION REACTION OF ALLYLIC PHOSPHATES WITH GRIGNARD REAGENTS

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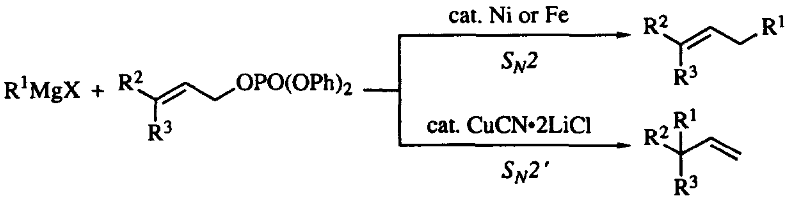
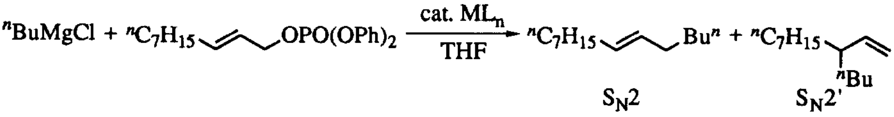
Abstract: *S_N2-selective Grignard coupling with primary allylic diphenylphosphates was successfully achieved using Ni or Fe catalyst. In sharp contrast, a catalytic amount of CuCN•2LiCl promoted a S_N2'-selective coupling reaction. In the presence of the copper catalyst, stereochemically homogeneous γ-disubstituted allyl Grignard reagents reacted at the less substituted allylic terminus (α-position) with an allylic diphenylphosphate selectively without losing the double bond geometry.*

Cross-coupling reaction of allylic alcohol derivatives or allylic halides with organometallics is a recognized method for synthesis of olefinic compounds. Numerous important works on the reaction have been reported, however, control of the regio- and stereochemistry remains an unsolved problem.[1] We recently reported that phosphate esters were the most effective leaving groups for a γ-selective cross-coupling reaction of alcohol derivatives with allylic Grignard reagents[2] and for a S_N2'-, (*E*)-, and antiselective reaction between organocuprates and allylic alcohol derivatives.[3] Here, we disclose transition metal-catalyzed regioselective substitution reactions of allylic diphenylphosphates with Grignard reagents: S_N2-selective coupling reaction using Ni or Fe catalyst and S_N2'-selective coupling reaction using a catalytic amount of CuCN•2LiCl.[4] We further found that stereochemically homogeneous γ-disubstituted allyl Grignard reagents reacted at the less substituted allylic terminus (α-position) with an allylic diphenylphosphate selectively without losing the double bond geometry in the presence of the copper catalyst.



Transition metal-catalyzed substitution reaction of alkyl halides with Grignard reagents is generally described as the Kharasch reaction.[5] In the cross-coupling reaction of allylic substrates, the regioselectivity has been actively studied with a variety of the leaving groups[1c] but to a lesser extent with phosphate leaving groups.[6] We examined the transition metal catalysts most suitable for the regioselective coupling of allylic phosphates with Grignard reagents. Treatment of (*E*)-2-decenyl 1-diphenylphosphate with 2 equiv of *n*-butylmagnesium chloride in the presence of various transition metal catalysts (5–10 mol%) in THF furnished a mixture of S_N2 and S_N2' coupling products. The results are summarized in Table 1.

Table 1. Cross-Coupling Reaction of (*E*)-2-Decenyl 1-diphenylphosphate with ^{n}BuMgCl in the Presence of Various Metal Catalysts[a]



Entry	ML$_n$	Conditions	Yield, %[b]	S_N2:S_N2'[c]
1	——	0 °C, 6 h	32	91:9
2	Ti(O^{i}Pr)$_4$	-23 °C, 5 h	10	89:11
3	CrCl$_2$	-23 °C, 6 h	48	81:19
4	MnCl$_2$	-30 °C, 5 h	20	93:7
5	Fe(acac)$_3$[d]	-76 °C, 1 h	94	$\boxed{99:1}$
6	Fe(dbm)$_3$[e]	-74 °C, 1 h	63	$\boxed{99:1}$
7	CoCl$_2$	-73 °C, 1 h	64	81:19
8	(^{n}BuC≡C)$_2$Co	-23 °C, 4 h	59	48:52
9	NiBr$_2$	-73 °C, 2 h	93	$\boxed{>99:1}$
10	Ni(acac)$_2$[d]	-73 °C, 1 h	83	$\boxed{>99:1}$
11	Ni(CN)$_2$	-23 °C, 3 h	79	52:48
12	Ni(CN)$_2$/ether	-40 °C, 7 h	94	11:89
13	CuCN•2LiCl	-76 °C, 1 h	98	$\boxed{1:99}$
14	^{n}BuC≡CCu	-75 °C, 1 h	95	14:86
15	CuI•2LiCl	-73 °C, 1 h	95	20:80
16	CuBr$_2$	-78 °C, 1 h	88	20:80
17	Li$_2$CuCl$_4$	-78 °C, 1 h	74	51:49
18	CuBr•Me$_2$S	-78 °C, 1 h	65	66:34
19	CuOTf	-75 °C, 1 h	62	81:19
20	CuSCN	-43 °C, 1 h	94	91:9
21	AgNO$_3$	-23 °C, 5 h	55	96:4
22	CeCl$_3$	-20 °C, 3 h	7	97:3

[a] The reaction was carried out using butylmagnesium chloride (2 equiv), (*E*)-2-decenyl 1-diphenylphosphate (1 equiv), and metal catalyst (0.05-0.1 equiv) in THF. [b] Isolated yield. [c] Determined by GC analysis. [d] acac = acetylacetonato. [e] dbm = dibenzoylmethanato.

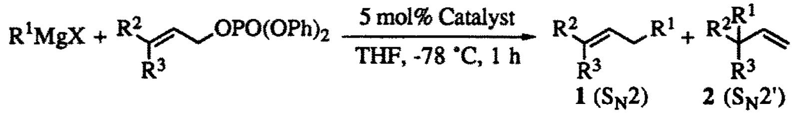
As a consequence, iron, nickel, and copper compounds showed remarkable catalytic activities and the coupling products were obtained in high yields at low temperature (entries 5, 6, and 9–20). In addition, nearly exclusive S_N2-selectivities were obtained using Fe[7] and Ni catalysts[8] (entries 5, 6, 9, and 10), while the regioselectivities of the reaction by Cu catalysts varied from 1/99 to 91/9 depending on the ligands (entries 13-20).[9] The highest S_N2'-regioselectivity (S_N2/S_N2'=1/99) was observed for CuCN•2LiCl which was shown to be effective for the stoichiometric S_N2'-selective cross-coupling reaction between Grignard reagents and allylic phosphates.[3,10] In the absence of the catalysts, the reaction proceeded slowly above 0 °C with S_N2/S_N2' ratio of 91/9 (entry 1).

We then studied the cross-coupling reaction between various Grignard reagents and primary allylic diphenylphosphates using nickel, iron, and copper catalysts (Table 2). In the reaction using $Ni(acac)_2$ catalyst, the S_N2 coupling products **1a**–**1j** were selectively obtained in moderate yields.[11] Use of methyl and *iso*-propyl Grignard reagents resulted in low yields because of a competitive homo-coupling reaction or reduction (entries 1 and 7). $(^nBuC{\equiv}C)_2Ni$ was effective to obtain a higher yield in the reaction with geranyl diphenylphosphate (entries 23 and 24). The *E*/*Z* ratio of the S_N2 coupling product **1h**, derived from (*Z*)-2-decenyl 1-diphenylphosphate, was 81/19 because of a rapid isomerization of the π-allylnickel intermediate (entry 20).[5c] These difficulties were overcome by $Fe(acac)_3$ catalyst. For example, reaction of methyl Grignard reagent selectively afforded the S_N2 coupling product **1a** in high yield without contamination of homo-coupling products (entry 2). In the butylation of (*Z*)-2-decenyl 1-diphenylphosphate, most of the double bond geometry of the product **1h** was retained (entry 21).[12]

In contrast, all the reactions using CuCN•2LiCl catalyst proceeded smoothly to afford the S_N2' coupling products **2a**–**2j** in high yields. Nearly exclusive S_N2'-selectivities were obtained in the reaction of alkyl Grignard reagents with (*E*)-2-decenyl 1-diphenylphosphate (entries 3, 6, 8, and 10). Noteworthy is the fact that even *tert*-butylmagnesium chloride showed a high S_N2'-selectivity in spite of the steric hindrance (entry 10). Higher reaction temperature (0 °C) and less polar solvent (4:1 toluene-ether) were requisite to obtain high regioselectivities for *tert*-butyl, benzyl, vinyl, and phenyl Grignard reagents (entries 9, 10, 12, 13, 15, 16, 18, and 19). (*Z*)-2-decenyl 1-diphenylphosphate afforded similar results (S_N2/S_N2'<1/99) to the corresponding *E*-isomer in the reaction with *n*-butyl Grignard reagent (entries 6 and 22). Existence of two alkyl substituents or a conjugated phenyl group at the C-3 position of the allylic diphenylphosphate had no effect on the reaction course (entries 25, 27, and 28).

This method was further successfully applied to the regio-controlled allyl-allyl coupling which was important for selective 1,5-diene synthesis.[14] Some results of the reaction between (*E*)-2-decenyl or (*E*)-2-hexenyl 1-diphenylphosphate and γ-substituted allyl Grignard reagents are listed in Table 3 and have the following characteristic features: (1) In the presence of the copper catalyst, allylic magnesium reagents reacted at the less substituted allylic terminus (α-position) with the allylic phosphate selectively.[15] The α-S_N2' selectivity in the reaction of cinnamylmagnesium chloride was improved using less polar solvent (3:2 toluene-ether, entries 3 and 4). (2) Use of γ-disubstituted allyl Grignard reagents resulted in higher α- and S_N2'-selectivities (entries 5 and 6). Especially, geranylmagnesium chloride afforded the α-S_N2' coupling product **4e** almost exclusively (entry 6). In contrast, an alkyl substituent at the β-position reduced both α- and S_N2'-selectivities (entry 7). (3) No remarkable *E*, *Z*-stereoselectivities were observed for the α-S_N2' coupling products **4** other than cinnamylmagnesium chloride due to a rapid isomerization of the γ-substituted allyl Grignard reagents.[16]

Table 2. Transition Metal-Catalyzed Cross-Coupling Reaction Between Alkyl Grignard Reagents and Primary Allylic Diphenylphosphates[a]



Entry	R^1MgX	R^2	R^3	Catalyst[b]	Products	Yield, %[c]	$S_N2:S_N2'$[d]
1	MeMgI	$^nC_7H_{15}$	H	Ni	1a + 2a	26[e]	94:6
2				Fe		87	97:3
3				Cu		87	2:98
4	^nBuMgCl	$^nC_7H_{15}$	H	Ni	1b + 2b	73	> 99:1
5				Fe		94	99:1
6				Cu		98	1:99
7	^iPrMgBr	$^nC_7H_{15}$	H	Ni	1c + 2c	53[f]	> 99:1
8				Cu		83	2:98
9	^tBuMgCl	$^nC_7H_{15}$	H	Cu	1d + 2d	88	30:70
10				Cu[g,h]		80	2:98
11	$PhCH_2MgBr$	$^nC_7H_{15}$	H	Ni[i]	1e + 2e	75	> 99:1
12				Cu		96	18:82
13				Cu[h]		98	8:92
14	$H_2C{=}CHMgBr$	$^nC_7H_{15}$	H	Ni	1f + 2f	78	> 99:1
15				Cu		86	95:5
16				Cu[h]		81	33:67
17	PhMgBr	$^nC_7H_{15}$	H	Ni	1g + 2g	65	92:8
18				Cu		97	88:12
19				Cu[g,h]		99	12:88
20	^nBuMgCl	H	$^nC_7H_{15}$	Ni[i]	1h + 2h	81[j]	99:1
21				Fe		93[k]	98:2
22				Cu		91	< 1:99
23	^nBuMgCl	$Me_2C{=}CH(CH_2)_2$	Me	Ni[l]	1i + 2i	26	97:3
24				$(^nBuC{\equiv}C)_2Ni$[i]		38	99:1
25				Cu		97	3:97
26	^nBuMgCl	Ph	H	Ni	1j + 2j	84	> 99:1
27				Cu		77	11:89
28				Cu[g,h]		79	6:94

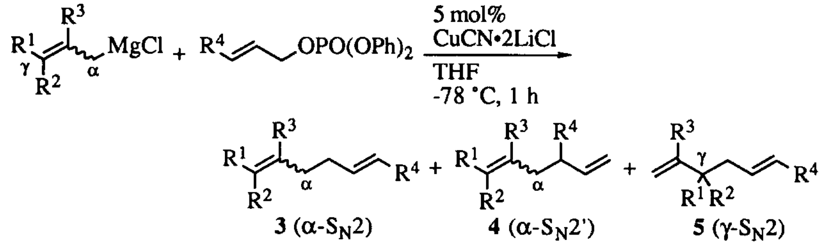
[a] Unless otherwise noted, the reaction was carried out using Grignard reagent (2 equiv), allylic diphenylphosphate (1 equiv), and Ni or Cu catalyst (0.05 equiv) in THF at -78 °C for 1 h. [b] Ni = $Ni(acac)_2$; Cu = $CuCN{\cdot}2LiCl$; Fe = $Fe(acac)_3$. [c] Isolated yield. [d] Determined by GC analysis. [e] Homo-coupling products of (*E*)-2-decenyl 1-diphenylphosphate was mostly obtained (64% yield). [f] Reduced products of the allylic phosphate were formed as a minor product (28% yield). [g] A 4:1 mixture of toluene and ether was used as solvent. [h] The reaction was performed at 0 °C for 1 h. [i] The reaction was performed at -45 °C for 2 h. [j] The *E*/*Z* ratio of the S_N2 coupling product **1h** was 81/19. [k] The *E*/*Z* ratio of **1h** was 6/94. [l] The reaction was performed at -20 °C for 2 h.

Control of the stereochemistry of carbon-carbon bond forming reaction by allylic organometallics is a challenging problem in organic synthesis.[17] We recently found that stereochemically homogeneous allylic metals were successfully generated from the corresponding allylic chlorides and reactive metals at low temperature.[18] Thus, we used this method to investigate the stereodivergent α-S_N2' coupling reaction.

Treatment of geranylmagnesium chloride (**7**), prepared from geranyl chloride (**6**) and Rieke magnesium[19] in THF below -100 °C, with (*E*)-2-hexenyl 1-diphenylphosphate in the presence of 5 mol% of CuCN•2LiCl gave the *trans*-isomer of the α-S_N2' coupling product (*E*)-**4e** preferentially (α/γ>99/1, S_N2/S_N2'=6/94, *E*/*Z*=95/5, 30% yield, eq. 1). Similarly, the *cis*-isomer (*Z*)-**4e** was selectively obtained from neryl chloride (**8**, eq. 2). This is the first example of the generation of stereoretained allylic copper reagents.

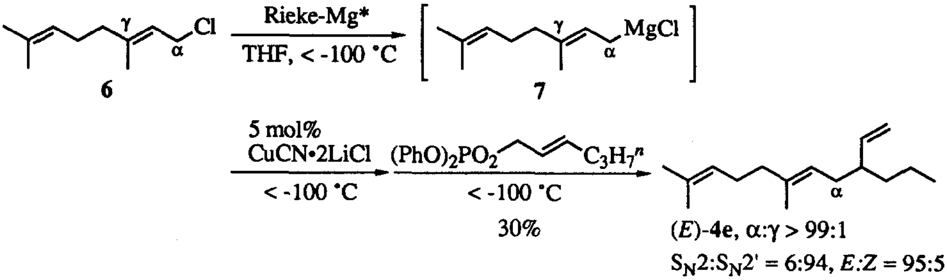
In conclusion, the present method appears to assure an excellent carbon-carbon bond forming reaction for the following reasons: (1) various Grignard reagents and allylic phosphates can be used; (2) both S_N2 and S_N2' coupling products are readily obtainable simply by changing the catalyst of the reaction; (3) in the presence of copper catalyst, allylic magnesium reagents react selectively at the less substituted allylic terminus; and (4) stereoretentive α-S_N2' coupling can be achieved using stereochemically homogeneous γ-disubstituted allyl Grignard reagent and copper catalyst at low temperature.

Table 3. Cross-Coupling of (*E*)-2-Decenyl or (*E*)-2-Hexenyl 1-Diphenylphosphate with γ-Substituted Allyl Grignard Reagents[a]

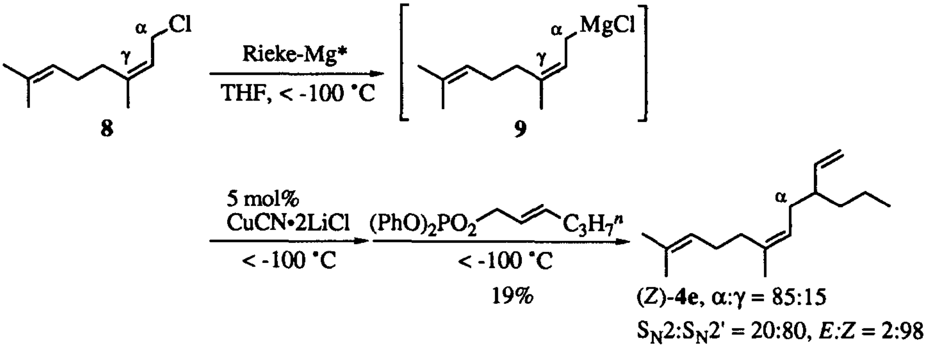


Entry	R^1	R^2	R^3	R^4	Products	Yield, %[b]	α:γ[c]	S_N2:S_N2'[c]	3:4:5[c,d]
1	Me	H	H	$^nC_7H_{15}$	**3a+4a+5a**	90[e]	79:21	27:73	6:73:21
2	$^nC_3H_7$	H	H	$^nC_7H_{15}$	**3b+4b+5b**	96[f]	76:24	29:71	5:71:24
3	Ph	H	H	$^nC_7H_{15}$	**3c+4c+5c**	97[g]	30:70	76:24	6:24:70
4	Ph	H	H	$^nC_7H_{15}$	**3c+4c+5c**	89[g,h]	86:14	19:81	5:81:14
5	Me	Me	H	$^nC_7H_{15}$	**3d+4d+5d**	95	96:4	6:94	2:94:4
6	$Me_2C{=}CH(CH_2)_2$	Me	H	$^nC_3H_7$	**3e+4e+5e**	90[i]	>99:1	2:98	2:98:0
7	C_2H_5	H	Me	$^nC_7H_{15}$	**3f+4f+5f**	99[j]	66:34	40:60	6:60:34

[a] Unless otherwise specified, the reaction was carried out using allylic Grignard reagent (1.2 equiv), (*E*)-2-decenyl 1-diphenylphosphate (1 equiv), and CuCN•2LiCl (0.05 equiv) in THF at -78 °C for 1 h. [b] Isolated yield. [c] Determined by GC analysis. [d] The corresponding γ-S_N2' product was not obtained in all experiments. [e] The *E*/*Z* ratio of α-S_N2' coupling product **4a** was 55/45. [f] The *E*/*Z* ratio of **4b** was 63/37. [g] The *E*/*Z* ratio of **4c** was >99/1. [h] The reaction was performed in a 3:2 mixture of toluene and ether at 0 °C for 1 h. [i] The *E*/*Z* ratio of **4e** was 73/27. [j] The *E*-isomer of **4f** was produced as the major product.



(1)



(2)

Experimental Section

General Methods.

Analytical TLC was done on E. Merck precoated (0.25 mm) silica gel 60 F_{254} plates. Column chromatography was conducted by using silica gel 60 (E. Merck 9385, 230–400 mesh). Infrared (IR) spectra were recorded on a Shimadzu FTIR-8100 spectrometer. ^{1}H NMR spectra were measured on a Varian Gemini-200 (200 MHz) spectrometer. Chemical shifts of ^{1}H NMR spectra were reported relative to tetramethylsilane (δ 0). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Mass spectra were recorded with a JEOR JMS-AX505HA mass spectrometer. Analytical gas-liquid phase chromatography (GLC) was performed on a Shimadzu GC-8A instrument equipped with a flame ionization detector and a capillary column of PEG-HT (0.25x25000 mm) using nitrogen as carrier gas. Microanalyses were accomplished at the Faculty of Agriculture, Nagoya University. All experiments were carried out under an atmosphere of dry argon. Dry THF was used as purchased from Aldrich (anhydrous, 99.9%). Allylic diphenylphosphates were synthesized from the corresponding allylic alcohols by phosphorylation with diphenyl phosphorochloridate and triethylamine in the presence of a catalytic amount of 4-(dimethylamino)pyridine in CH_2Cl_2. Allylic chlorides were prepared by treatment of the corresponding allylic alcohols with a mixture of *N*-chlorosuccinimide and dimethyl sulfide in CH_2Cl_2.[20] Other chemicals were purchased and used as such.

General Procedure for Transition Metal-Catalyzed Cross-Coupling Reaction Between Alkyl Grignard Reagents and Primary Allylic Diphenylphosphates (Table 2). A mixture of transition metal catalyst (0.025 mmol) and allylic diphenylphosphate (0.50 mmol) was dissolved in dry THF (4 mL) under argon atmosphere. The solution was cooled to -78 °C and a solution of alkyl Grignard reagent (1.0 mmol) in THF was added dropwise. The resulting mixture was stirred for 1 h at this temperature. The reaction mixture was poured into a saturated aqueous NH_4Cl solution and extracted with ether. The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (hexane) to afford a mixture of coupling products: the S_N2/S_N2' ratio was determined by GC analysis.

(3*E*)-3-Undecene (1a): TLC R_f 0.72 (hexane); IR (neat) 2961, 2926, 2874, 2855, 1462, 1379, 965, 723 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 3 H, *J* = 6.5 Hz, CH_3), 0.96 (t, 3 H, *J* = 7.4 Hz, CH_3), 1.17–1.46 (m, 10 H, 5 CH_2), 1.87–2.08 (m, 4 H, 2 CH_2), 5.31–5.52 (m, 2 H, 2 vinyls); MS (EI, 70 ev) *m/z* (rel) 154 (100, M^+), 126 (20.94), 111 (35.53). Anal. Calcd for $C_{11}H_{22}$: C, 85.63; H, 14.37. Found: C, 85.31; H, 14.88.

3-Methyl-1-decene (2a): TLC R_f 0.72 (hexane); IR (neat) 3079, 2959, 2926, 2857, 1640, 1418, 1375, 994, 911, 723, 681 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 3 H, *J* = 6.4 Hz, CH_3), 0.97 (d, 3 H, *J* = 6.8 Hz, CH_3), 1.15–1.40 (m, 12 H, 6 CH_2), 2.10 (m, 1 H, CH), 4.86–4.99 (m, 2 H, 2 vinyls), 5.70 (ddd, 1 H, *J* = 7.6, 10.2, 17.5 Hz, vinyl). Anal. Calcd for $C_{11}H_{22}$: C, 85.63; H, 14.37. Found: C, 85.61; H, 14.44.

(6*E*)-6-Tetradecene (1b): TLC R_f 0.72 (hexane); IR (neat) 2959, 2926, 2874, 2855, 1466, 1379, 967, 723 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 6 H, *J* = 6.3 Hz, 2 CH_3), 1.15–1.47 (m, 16 H, 8 CH_2), 1.85–2.13 (m, 4 H, 2 CH_2), 5.36–5.42 (m, 2 H, 2 vinyls). Anal. Calcd for $C_{14}H_{28}$: C, 85.63; H, 14.37. Found: C, 85.43; H, 14.59.

5-Vinyldodecane (2b):[21] TLC R_f 0.72 (hexane); IR (neat) 3077, 2959, 2926, 2857, 1825, 1640, 1466, 1420, 1379, 995, 911, 762, 725, 683 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 6 H, *J* = 6.5 Hz, 2 CH_3), 1.07–1.47 (m, 18 H, 9 CH_2), 1.82–2.04 (br, 1 H, CH), 4.92 (dd, 1 H, *J* = 2.2, 16.4 Hz, vinyl), 4.94 (dd, 1 H, *J* = 2.2, 11.0 Hz, vinyl), 5.53 (ddd, 1 H, *J* = 8.8, 11.0, 16.4 Hz, vinyl); MS (EI, 70 ev) *m/z* (rel) 196 (58.88, M^+), 168 (39.37), 154 (55.26), 140 (100), 125 (97.31), 112 (95.56), 111 (92.52). Anal. Calcd for $C_{14}H_{28}$: C, 85.63; H, 14.37. Found: C, 85.40; H, 14.71.

(4*E*)-2-Methyl-4-dodecene (1c): TLC R_f 0.67 (hexane); IR (neat) 2957, 2926, 2855, 1466, 1383, 1368, 1167, 967, 911, 723 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.87 (d, 6 H, *J* = 6.4 Hz, 2 CH_3), 0.88 (t, 3 H, *J* = 6.5 Hz, CH_3), 1.14–1.45 (m, 10 H, 5 CH_2), 1.47–1.67 (m, 1 H, CH), 1.82–1.91 (m, 2 H, CH_2), 1.91–2.08 (m, 2 H, CH_2), 5.33–5.42 (m, 2 H, 2 vinyls). Anal. Calcd for $C_{13}H_{26}$: C, 85.63; H, 14.37. Found: C, 85.58; H, 14.50.

3-Isopropyl-1-decene (2c): TLC R_f 0.67 (hexane); IR (neat) 3077, 2959, 2924, 2857, 1638, 1466, 1420, 1385, 1368, 997, 911, 723, 681 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.82 (d, 3 H, *J* = 6.8 Hz, CH_3), 0.87 (d, 3 H, *J* = 6.6 Hz, CH_3), 0.88 (t, 3 H, *J* = 6.5 Hz, CH_3), 1.05–1.46 (m, 12 H, 6 CH_2), 1.48–1.66 (m, 1 H, CH), 1.66–1.82 (m, 1 H, CH), 4.91 (dd, 1 H, *J* = 2.2, 17.0 Hz, vinyl), 4.99 (dd, 1 H, *J* = 2.2, 10.4 Hz, vinyl), 5.55 (ddd, 1 H, *J* = 9.2, 10.4, 17.0 Hz, vinyl). Anal. Calcd for $C_{13}H_{26}$: C, 85.63; H, 14.37. Found: C, 85.40; H, 14.54.

3-*tert*-Butyl-1-decene (2d): TLC R_f 0.65 (hexane); IR (neat) 3075, 2959, 2859, 1638, 1468, 1418, 1395, 1366, 999, 911, 656 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.85 (s, 9 H, 3 CH_3), 0.88 (t, 3 H, *J* = 6.2 Hz, CH_3), 1.12–1.40 (m, 12 H, 6 CH_2), 1.50–1.67 (m, 1 H, CH), 4.90 (dd, 1 H, *J* = 2.6, 17.0 Hz, vinyl), 5.01 (dd, 1 H, *J* = 2.6, 10.4 Hz, vinyl), 5.54 (dt, 1 H, *J* = 17.0, 10.4 Hz, vinyl); MS (EI, 70 ev) *m/z* (rel) 196 (9.63, M^+), 168 (10.90), 154 (7.60), 140 (100), 138 (29.78), 111 (42.21). Anal. Calcd for $C_{14}H_{28}$: C, 85.63; H, 14.37. Found: C, 85.40; H, 14.70.

(3*E*)-1-Phenyl-3-undecene (1e):[22] TLC R_f 0.56 (hexane); IR (neat) 3029, 2957, 2926, 2855, 1497, 1455, 968, 745, 698 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 3 H, *J* = 6.5 Hz, CH_3), 1.16–1.42 (m, 10 H, 5 CH_2), 1.89–2.02 (m, 2 H, CH_2), 2.23–2.36 (m, 2 H, CH_2), 2.60–2.72 (m, 2 H, CH_2), 5.33–5.54 (m, 2 H, 2 vinyls), 7.12–7.34 (m, 5 H, aromatic); MS (EI, 70 ev) *m/z* (rel) 230 (86.90, M$^+$), 131 (41.69), 117 (28.59), 104 (100). Anal. Calcd for $C_{17}H_{26}$: C, 88.63; H, 11.37. Found: C, 88.38; H, 11.94.

3-Benzyl-1-decene (2e): TLC R_f 0.49 (hexane); IR (neat) 3029, 2957, 2926, 2855, 1640, 1605, 1497, 1455, 994, 912, 745, 698 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (t, 3 H, *J* = 6.4 Hz, CH_3), 1.10–1.50 (m, 12 H, 6 CH_2), 2.16–2.38 (m, 1 H, CH), 2.52–2.72 (m, 2 H, CH_2), 4.86 (dd, 1 H, *J* = 2.2, 17.0 Hz, vinyl), 4.93 (dd, 1 H, *J* = 2.2, 10.4 Hz, vinyl), 5.60 (ddd, 1 H, *J* = 8.6, 10.4, 17.0 Hz, vinyl), 7.10–7.32 (m, 5 H, aromatic). Anal. Calcd for $C_{17}H_{26}$: C, 88.63; H, 11.37. Found: C, 88.50; H, 11.67.

(4*E*)-1,4-dodecadiene (1f):[23] TLC R_f 0.69 (hexane); IR (neat) 3081, 2959, 2926, 2855, 1640, 1433, 1379, 992, 968, 912 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 3 H, *J* = 6.4 Hz, CH_3), 1.13–1.44 (m, 10 H, 5 CH_2), 1.90–2.12 (m, 2 H, CH_2), 2.68–2.84 (m, 2 H, CH_2), 4.94–5.09 (m, 2 H, 2 vinyls), 5.32–5.55 (m, 2 H, 2 vinyls), 5.83 (ddd, 1 H, *J* = 6.4, 10.0, 12.6 Hz, vinyl). Anal. Calcd for $C_{12}H_{22}$: C, 86.66; H, 13.33. Found: C, 86.39; H, 13.42.

(2*E*)-1-Phenyl-2-decene (1g):[24] TLC R_f 0.56 (hexane); IR (neat) 3063, 3029, 2957, 2926, 2855, 1605, 1495, 1455, 1075, 1030, 968, 745, 698 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 3 H, *J* = 6.5 Hz, CH_3), 1.15–1.47 (m, 10 H, 5 CH_2), 1.90–2.12 (m, 2 H, CH_2), 3.33 (d, 2 H, *J* = 4.8 Hz, CH_2), 5.42–5.66 (m, 2 H, 2 vinyls), 7.13–7.35 (m, 5 H, aromatic); MS (EI, 70 ev) *m/z* (rel) 216 (99.76, M$^+$), 143 (20.19), 129 (85.58), 117 (99.76), 115 (99.88), 104 (100). Anal. Calcd for $C_{16}H_{24}$: C, 88.82; H, 11.18. Found: C, 88.72; H, 11.59.

3-Phenyl-1-decene (2g): TLC R_f 0.56 (hexane); IR (neat) 3029, 2957, 2928, 2857, 1638, 1493, 1455, 992, 912, 756, 698 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.86 (t, 3 H, *J* = 6.6 Hz, CH_3), 1.10–1.44 (m, 10 H, 5 CH_2), 1.69 (dt, 2 H, *J* = 7.0, 7.4 Hz, CH_2), 3.23 (q, 1 H, *J* = 7.6 Hz, CH), 4.94–5.08 (m, 2 H, 2 vinyls), 5.95 (ddd, 1 H, *J* = 7.6, 9.8, 17.4 Hz, vinyl), 7.13–7.36 (m, 5 H, aromatic); MS (EI, 70 ev) *m/z* (rel) 216 (71.46, M$^+$), 132 (37.45), 117 (100), 115 (54.51), 104 (40.24). Anal. Calcd for $C_{16}H_{24}$: C, 88.82; H, 11.18. Found: C, 88.73; H, 11.74.

(6*Z*)-6-Tetradecene (1h): TLC R_f 0.72 (hexane); IR (neat) 3006, 2959, 2926, 2857, 1466, 1379, 967, 723 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 6 H, *J* = 6.0 Hz, 2 CH_3), 1.13–1.44 (m, 16 H, 8 CH_2), 1.91–2.14 (m, 4 H, 2 CH_2), 5.36 (m, 2 H, 2 vinyls); MS (EI, 70 ev) *m/z* (rel) 196 (100, M$^+$), 168 (36.91), 154 (17.17), 140 (21.03), 125 (43.56), 111 (99.79). Anal. Calcd for $C_{14}H_{28}$: C, 85.63; H, 14.37. Found: C, 85.40; H, 15.01.

2,6-Dimethyl-6-vinyl-2-decene (2i):[25] TLC R_f 0.84 (hexane); IR (neat) 3083, 2963, 2930, 2861, 1638, 1414, 1377, 1003, 911, 835 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 3 H, *J* = 6.7 Hz, CH_3), 0.95 (s, 3 H, CH_3), 1.10–1.37 (m, 8 H, 4 CH_2), 1.58 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3), 1.78–1.95 (m, 2 H, CH_2), 4.88 (dd, 1 H, *J* = 1.6, 17.6 Hz, vinyl), 4.97 (dd, 1 H, *J* = 1.6, 10.8 Hz, vinyl), 5.09 (tt, 1 H, *J* = 1.4, 7.1 Hz, vinyl), 5.70 (dd, 1 H, *J* = 10.8, 17.6 Hz, vinyl). Anal. Calcd for $C_{14}H_{26}$: C, 86.52; H, 13.48. Found: C, 86.37; H, 14.18.

(1*E*)-1-Phenyl-1-heptene (1j):[26] TLC R_f 0.58 (hexane); IR (neat) 3027, 2957, 2926, 2857, 1599, 1495, 963, 743, 693 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.90 (t, 3 H, *J* = 6.5 Hz, CH_3), 1.19–1.58 (m, 6 H, 3 CH_2), 2.20 (q, 2 H, *J* = 6.9 Hz, CH_2), 6.22 (dt, 1 H, *J* = 16.0, 6.4 Hz, vinyl), 6.38 (d, 1 H, *J* = 16.0 Hz, vinyl), 7.13–7.38 (m, 5 H, aromatic); MS (EI, 70 ev) *m/z* (rel) 174 (99.76, M$^+$), 145 (11.10), 131 (28.93), 117 (99.88), 115 (99.94), 104 (100). Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.33; H, 10.91.

3-Phenyl-1-heptene (2j):[27] TLC R_f 0.58 (hexane); IR (neat) 3029, 2959, 2930, 2859, 1638, 1601, 1493, 1453, 994, 912, 754, 700 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (t, 3 H, *J* = 7.0 Hz, CH_3), 1.08–1.39 (m, 4 H, 2 CH_2), 1.70 (q, 2 H, *J* = 7.4 Hz, CH_2), 3.23 (q, 1 H, *J* = 7.5 Hz, CH), 4.95–5.07 (m, 2 H, 2 vinyls), 5.95 (ddd, 1 H, *J* = 7.6, 9.6, 17.4 Hz, vinyl), 7.13–7.35 (m, 5 H, aromatic). Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.51; H, 10.71.

General Procedure for Preparation of Allylic Grignard Reagent.[28] Magnesium turnings (1.0 g, 41 mmol) were placed in a 60-mL Schlenk tube under argon atmosphere and vigorously stirred for 3-5 days at room temperature. The resulting activated Mg turnings were covered with dry THF (5 mL), cooled to -15 °C, and a solution of allylic chloride (10 mmol) in THF (15 mL) was added dropwise for 1-2 h at this temperature. The mixture was stirred for 2-3 h at 0 °C. The resulting clear solution (0.40-0.45 M) was ready to use.

General Procedure for Copper-Catalyzed Cross-Coupling Reaction of (*E*)-2-Decenyl 1-Diphenylphosphate with γ-Substituted Allyl Grignard Reagents (Table 3). A mixture of CuCN (2.2 mg, 0.025 mmol) and LiCl (2.1 mg, 0.050 mmol)[29] was dissolved in dry THF (4 mL) under argon atmosphere, and then (*E*)-2-decenyl 1-diphenylphosphate (194 mg, 0.50 mmol) was added. To the resulting solution was added dropwise a solution of allylic magnesium chloride (0.40-0.45 M, 0.60 mmol) in THF at -78 °C under argon atmosphere. The reaction mixture was stirred for 1 h at this temperature. A saturated NH_4Cl aqueous solution (10 mL) was added to the mixture at -78 °C, and the aqueous layer was extracted with ether. The combined organic extracts were dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (hexane) to afford a mixture of coupling products: the γ/α and S_N2/S_N2' ratios were determined by GC analysis.

5-Vinyl-2-dodecene (4a): TLC R_f 0.67 (hexane); IR (neat) 3079, 2959, 2926, 2855, 1640, 1377, 994, 967, 911 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 3 H, *J* = 6.4 Hz, CH_3), 1.10–1.45 (m, 12 H, 6 CH_2), 1.60 (d, 1.65 H, *J* = 5.8 Hz, 0.55 CH_3), 1.64 (d, 1.35 H, *J* = 3.6 Hz, 0.45 CH_3), 1.85–2.22 (m, 3 H, CH_2 and CH), 4.87–5.01 (m, 2 H, 2 vinyls), 5.40 (m, 2 H, 2 vinyls), 5.45–5.85 (m, 1 H, vinyl); MS (EI, 70 ev) *m/z* (rel) 194 (17.17, M$^+$), 179 (99.79), 165 (57.94), 151 (29.83), 138 (87.45), 123 (99.89), 109 (100), 105 (21.67). Anal. Calcd for $C_{14}H_{26}$: C, 86.52; H, 13.48. Found: C, 86.32; H, 13.97.

7-Vinyl-4-tetradecene (4b): TLC R_f 0.65 (hexane); IR (neat) 3077, 2959, 2926, 2857, 1638, 1541, 1509, 1420, 1379, 994, 967, 911 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 6 H, *J* = 7.2 Hz, 2 CH_3), 1.12–1.47 (m, 14 H, 7 CH_2), 1.90–2.12 (m, 5 H, 2 CH_2 and CH), 4.87–5.00 (m, 2 H, 2 vinyls), 5.33–5.43 (m, 2 H, 2 vinyls), 5.47–5.69 (m, 1 H, vinyl); MS (EI, 70 ev) *m/z* (rel) 222 (22.42, M$^+$), 216 (43.78), 208 (15.34), 179 (40.24), 166 (9.01), 154 (13.95), 145 (13.84), 132 (36.48), 117 (100), 115 (54.18), 104 (22.32). Anal. Calcd for $C_{16}H_{30}$: C, 86.40; H, 13.60. Found: C, 86.48; H, 13.97.

(1*E*)-1-Phenyl-4-vinyl-1-undecene (4c): TLC R_f 0.46 (hexane); IR (neat) 3081, 3027, 2957, 2926, 2855, 1640, 1599, 1495, 1466, 1418, 1377, 994, 965, 912, 743, 693 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 3 H, *J* = 6.4 Hz, CH_3), 1.12–1.48 (m, 12 H, 6 CH_2), 2.02–2.30 (m, 3 H, CH_2 and CH), 4.93–5.05 (m, 2 H, 2 vinyls), 5.54–5.74 (m, 1 H, vinyl), 6.18 (dt, 1 H, *J* = 15.8, 6.8 Hz, vinyl), 6.38 (d, 1 H, *J* = 15.8 Hz, vinyl), 7.13–7.40 (m, 5 H, aromatic). Anal. Calcd for $C_{19}H_{28}$: C, 88.99; H, 11.01. Found: C, 88.89; H, 11.27.

2-Methyl-5-vinyl-2-dodecene (4d): TLC R_f 0.65 (hexane); IR (neat) 3077, 2959, 2926, 2855, 1640, 1456, 1377, 994, 911 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 3 H, *J* = 6.5 Hz, CH_3), 1.12–1.45 (m, 12 H, 6 CH_2), 1.59 (s, 3 H, CH_3), 1.69 (s, 3 H, CH_3), 1.88–2.22 (m, 3 H, CH_2 and CH), 4.88–5.00 (m, 2 H, 2 vinyls), 5.05–5.16 (m, 1 H, vinyl), 5.50–5.69 (m, 1 H, vinyl). Anal. Calcd for $C_{15}H_{28}$: C, 86.46; H, 13.54. Found: C, 86.30; H, 13.81.

4-Methyl-6-vinyl-3-tridecene (4f): TLC R_f 0.74 (hexane); IR (neat) 3075, 2961, 2926, 2855, 1646, 1509, 1458, 1377, 994, 967, 911, 889 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 3 H, *J* = 6.4 Hz, CH_3), 0.92 (t, 3 H, *J* = 7.4 Hz, CH_3), 1.12–1.50 (m, 12 H, 6 CH_2), 1.65 (s, 3 H, CH_3), 1.87–2.20 (m, 5 H, 2 CH_2 and CH), 4.86–4.99 (m, 2 H, 2 vinyls), 5.16 (m, 1 H, vinyl), 5.42–5.65 (m, 1 H, vinyl); MS (EI, 70 ev) *m/z* (rel) 222 (27.68, M$^+$), 208 (13.63), 193 (68.13), 180 (8.58), 152 (15.24), 138 (33.80), 123 (99.79), 109 (100). Anal. Calcd for $C_{16}H_{30}$: C, 86.41; H, 13.60. Found: C, 86.30; H, 14.02.

(6*E*)-2,6-Dimethyl-9-vinyl-2,6-dodecadiene ((*E*)-4e). A mixture of freshly cut lithium (32 mg, 4.61 mmol), anhydrous magnesium chloride (224 mg, 2.35 mmol), and naphthalene (641 mg, 5.00 mmol) in 7 mL of dry THF was stirred at room temperature for 14 h under argon atmosphere. To the resulting black suspension of magnesium powder in THF was slowly added a solution of geranyl chloride (119 mg, 0.69 mmol) in THF (1.5 mL) below -100 °C. After being stirred for 20 min, a solution of CuCN (3.0 mg, 0.033 mmol) and LiCl (5.7 mg, 0.13 mmol) in THF (2 mL) was slowly added and the mixture was stirred for another 10 min at this temperature. Then, a solution of (*E*)-2-hexenyl 1-diphenylphosphate (161 mg, 0.48 mmol) in THF (2 mL) was added below -100 °C and the reaction mixture was stirred for 1 h. To the mixture was added a saturated aqueous NH_4Cl solution and extracted with ether. The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (hexane) to afford (*E*)-4e (32 mg, 30% yield, α/γ>99/1, S_N2/S_N2'=6/94, *E*/*Z*=95/5) as a colorless oil: TLC R_f 0.61 (hexane); IR (neat) 3077, 2961, 2928, 2872, 1640, 1456, 1377, 1107, 994, 911, 741 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 3 H, *J* = 5.9 Hz, CH_3), 1.10–1.45 (m, 4 H, 2 CH_2), 1.58 (s, 3 H, CH_3), 1.60 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3), 1.88–2.15 (m, 7 H, 3 CH_2 and CH), 4.87–5.00 (m, 2 H, 2 vinyls), 5.10 (m, 1 H, vinyl), 5.12 (m, 1 H, vinyl), 5.49–5.69 (m, 1 H, vinyl). Anal. Calcd for $C_{16}H_{28}$: C, 87.19; H, 12.80. Found: C, 87.09; H, 13.09.

The *cis*-isomer (Z)-4e (19% yield, α/γ>85/15, S_N2/S_N2'=20/80, *E*/*Z*=2/98) was synthesized from neryl chloride (**8**) under the similar reaction condition.

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References and Notes

1. Reviews: (a) Magid, R. M. *Tetrahedron* **1980**, *36*, 1901. (b) Carruthers, W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 7, p 705, 721. (c) Klunder, J. M.; Posner, G. H. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Pattenden, G., Eds.; Pergamon Press: Oxford, 1991; Vol. 3, p 220. (d) Frost, C. G.; Howarth, J.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1992**, *3*, 1089.
2. Yanagisawa, A.; Hibino, H.; Nomura, N.; Yamamoto, H. *J. Am. Chem. Soc.* **1993**, *115*, 5879.

3. (a) Yanagisawa, A.; Noritake, Y.; Nomura, N.; Yamamoto, H. *Synlett* **1991**, 251. (b) Yanagisawa, A.; Nomura, N.; Noritake, Y.; Yamamoto, H. *Synthesis* **1991**, 1130. Dr. T. Tanaka, Teijin Company, Ltd., has reported similar reactions in cyclic cases: (c) Tanaka, T.; Bannai, K.; Hazato, A.; Koga, M.; Kurozumi, S.; Kato, Y. *Tetrahedron* **1991**, *47*, 1861.
4. A preliminary communication of the catalytic S_N2'-selective coupling reaction: Yanagisawa, A.; Nomura, N.; Yamamoto, H. *Synlett* in press.
5. (a) Kharasch, M. S.; Reinmuth, O. *Grignard Reactions of Nonmetallic Substances*; Prentice-Hall, Englewood Cliffs: New Jersey, 1954; p 122. (b) Elsom, L. F.; Hunt, J. D.; Mckillop, A. *Organomet. Chem. Rev. (A)* **1972**, *8*, 135. (c) Felkin, H.; Swierczewski, G. *Tetrahedron* **1975**, *31*, 2735. (d) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978; p 372.
6. Reaction of primary allylic diethylphosphates with Grignard reagents in the presence of copper catalyst was reported to selectively provide the S_N2-coupling products, see: (a) Bourgain-Commerçon, M.; Normant, J.-F.; Villieras, J. *J. Chem. Res. (S)* **1977**, 183; *(M)*, 2101. (b) Araki, S.; Butsugan, Y. *Chem. Lett.* **1982**, 177. (c) Araki, S.; Butsugan, Y. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1446. See also: (d) Araki, S.; Sato, T.; Butsugan, Y. *J. Chem. Soc., Chem. Commun.* **1982**, 285. (e) Araki, S.; Butsugan, Y. *J. Chem. Soc., Perkin Trans 1* **1984**, 969.
7. A preliminary communication of the iron-catalyzed S_N2-selective Grignard coupling reaction has appeared: Yanagisawa, A.; Nomura, N.; Yamamoto, H. *Synlett* **1991**, 513.
8. Nickel-catalyzed S_N2-selective coupling of allylic chlorides with organozinc reagents has been reported: (a) Sekiya, K.; Nakamura, E. *Tetrahedron Lett.* **1988**, *29*, 5155. (b) Nakamura, E.; Aoki, S.; Sekiya, K.; Oshino, H.; Kuwajima, I. *J. Am. Chem. Soc.* **1987**, *109*, 8056.
9. An excellent study on the regiochemistry of copper-catalyzed reactions between Grignard reagents and allylic substrates: Bäckvall, J.-E.; Sellén, M.; Grant, B. *J. Am. Chem. Soc.* **1990**, *112*, 6615.
10. Copper-catalyzed S_N2'-selective coupling reaction of organotitanium reagents with primary allylic diethylphosphates has recently been reported: (a) Arai, M.; Nakamura, E.; Lipshutz, B. H. *J. Org. Chem.* **1991**, *56*, 5489. (b) Arai, M.; Lipshutz, B. H.; Nakamura, E. *Tetrahedron* **1992**, *48*, 5709. See also: (c) Venanzi, L. M.; Lehmann, R.; Keil, R.; Lipshutz, B. H. *Tetrahedron Lett.* **1992**, *33*, 5857.
11. The S_N2 coupling product **1d** was not obtained at all because of the rapid reduction by ^{t}BuMgCl.
12. In the iron-catalyzed Kharasch type reaction, Fe(I) or Fe(0) species is suggested to be an active catalyst.[5d,13]
13. Lehr, G. F.; Lawler, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 4048.
14. A recent review: Billington, D. C. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Pattenden, G., Eds.; Pergamon Press: Oxford, 1991; Vol. 3, p 413.
15. In the absence of the copper catalyst, a highly γ-S_N2 selective coupling occurred.[2]
16. Hutchinson, D. A.; Beck, K. R.; Benkeser, R. A.; Gruntzner, J. B. *J. Am. Chem. Soc.* **1973**, *95*, 7075.
17. (a) Schlosser, M. *Pure Appl. Chem.* **1988**, *60*, 1627. (b) Guo, B.-S.; Doubleday, W.; Cohen, T. *J. Am. Chem. Soc.* **1987**, *109*, 4710. (c) Yanagisawa, A.; Habaue, S.; Yamamoto, H. *J. Am. Chem. Soc.* **1991**, *113*, 8955. A review: (d) Wardell, J. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 1, p 97.

18. Yanagisawa, A.; Habaue, S.; Yamamoto, H. *J. Am. Chem. Soc.* **1991**, *113*, 5893.
19. Burns, T. P.; Rieke, R. D. *J. Org. Chem.* **1987**, *52*, 3674.
20. Davisson, V. J.; Woodside, A. B.; Neal, T. R.; Stremler, K. E.; Muehlbacher, M.; Poulter, C. D. *J. Org. Chem.* **1986**, *51*, 4768.
21. Normant, J. F.; Commercon, A.; Gendreau, Y.; Bourgain, M.; Villieras, J. *Bull. Soc. Chim. Fr. II* **1979**, 309.
22. Barton, D. H. R.; Tachdjian, C. *Tetrahedron* **1992**, *48*, 7109.
23. Alexakis, A.; Cahiez, G.; Normant, J. F. *Synthesis* **1979**, 826.
24. Takasago, M.; Takaoka, K.; Seno, M. *J. Jpn. Oil Chem. Soc.* **1971**, *20*, 415.
25. Calò, V.; Lopez, L.; Pesce, G.; Calianno, A. *J. Org. Chem.* **1982**, *47*, 4482.
26. Negishi, E.; Takahashi, T.; Baba, S.; Van Horn, D. E. ; Okukado, N. *J. Am. Chem. Soc.* **1987**, *109*, 2393.
27. Gendreau, Y.; Normant, J. F.; Villieras, J. *J. Organomet. Chem.* **1977**, *142*, 1.
28. Baker, K. V.; Brown, J. M.; Hughes, N.; Skarnulis, A. J.; Sexton, A. *J. Org. Chem.* **1991**, *56*, 698.
29. A mixture of CuCN and LiCl was appropriately dried with a dryer beforehand under reduced pressure (<10 Torr).

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