slowly. The mixture was stirred overnight, and the precipitate that formed was collected by filtration and recrystallized from methanol to yield the pyrene linked azide **3** as fluffy needles: ^{1}H NMR (DMSO-d_6) δ 10.25 (s, 1 H), 8.5 (t, 1 H), 8.35–8 (mult, 9 H), 7.9–7.15 (2 d, 4 H), 2.58 (t, 2 H), 1.9–1.4 (m, 8 H). Elemental anal. Calcd for $C_{29}H_{25}N_5O_2$: C, 73.24; H, 5.30; N, 14.73. Found: C, 72.88; H, 5.33; N, 14.52.

2-Methoxy-5-[(dimethylamino)carbonyl]-3*H*-azepine. An acetonitrile/methanol (4:1 v/v, 10 mL) solution of DAA (10 mg) was purged with N_2 and irradiated at 254 nm (Rayonet) for 7 min. The solvent was removed under vacuum, and the crude reaction mixture was analyzed by NMR spectroscopy. The results are reported in Table I. The 3*H*-azepine was isolated by chromatography on silica gel (31% based upon the amount of DAA consumed): ^{1}H NMR (DMSO-d_6) δ 6.9 (d, 1 H), 6.00 (d, 1 H), 5.38 (t, 1 H), 3.65 (s, 3 H); high-resolution mass spectrum calcd for $C_{10}H_{14}N_2O_2$ 194.1055, found 194.1042.

2-Ethoxy-5-[(dimethylamino)carbonyl]-3*H*-azepine was prepared similarly by photolysis of DAA in acetonitrile containing ethanol: ^{1}H NMR ($CDCl_3$) δ 7.02 (d, 1 H), 6.1 (d, 1 H), 5.42 (t, 1 H), 4.15 (q, 2 H), 2.95–2.8 (d, 6 H), 2.7 (d, 1 H), 1.28 (t, 3 H); high-resolution mass spectrum calcd for $C_{11}H_{16}N_2O_2$ 202.1202, found 202.1212.

Photolysis of Linked Azide 3. Photolysis and quantitative analysis were performed analogously to the method outlined above. Because of their insolubility and the necessity to keep the photolysis to low conversion, the structural assignments for the photoproducts from **3** were based on comparison of ^{1}H NMR spectra with those of the analogous, fully characterized products from photolysis of DAA. The spectra are displayed in Figure 3. There is a clear correspondence of the proton resonances between the authentic product Figures 3E and 3F and that from irradiation of **3**, Figure 3D. Irradiation in a methanol/CH_3CN (1:4 v/v) solution gives linked aniline derivative (13%) on the basis of the NMR spectrum [(DMSO-d_6, 200 MHz) δ 6.5 (q, 2 H), 5.55 (s, 1 H)] and linked methoxyazepine derivative (60%) on the basis of the NMR spectrum [δ 7.0 (d, 1 H), 6.4 (d, 1 H), 6.0 (t, 1 H), 3.6 (s, 3 H)]. Irradiation in ethanol/CH_3CN (1:4 v/v) gives linked aniline derivative (19%) and ethoxy-substituted azepine derivative (58%) on the basis of the NMR spectrum [(DMSO-d_6) δ 7.0 (d, 1 H), 6.4 (d, 1 H), 5.95 (t, 1 H), 4.05 (q, 2 H)].

Acridine Linked Azide (4). The ethyl chloroformate mixed anhydride from 6-[(4-azidobenzoyl)amino]hexanoic acid (0.50 g, 1.8 mmol) was prepared as for **3**. 9-Aminoacridine (0.40 g, 2.01 mmol) in *N*,*N*-dimethylformamide (10 mL) and methylene chloride (10 mL) was added slowly at 0 °C to the mixed anhydride solution. The mixture was stirred for 12 h, and the precipitate was collected by filtration and washed with water. Recrystallization from methanol yielded 100 mg (12%) of azide **4** as yellow needles: ^{1}H NMR (200 MHz) δ 10.6 (s, 1 H), 8.5 (s, 1 H), 8.2–7.5 (m, 10 H), 7.15 (d, 2 H), 2.7 (t, 2 H), 1.9–1.4 (m, 8 H). Elemental anal. Calcd for $C_{26}H_{24}N_6O_2 \cdot {}^1/_2H_2O$: C, 67.66; H, 5.46; N, 18.21. Found: C, 67.61; H, 5.20; N, 18.09.

Photolysis of Azide 4. This compound was irradiated and analyzed in the same was as described above for pyrene linked azide **3**; the relevant ^{1}H NMR spectrum is shown in Figure 3C. The products formed by irradiation in methanol/acetonitrile (1:5 v/v) solution were the corresponding aniline (61% yield), on the basis of integration of the characteristic peaks in the NMR spectrum [δ 6.5 (q, 2 H), 5.5 (s, 2 H)], and the corresponding methoxyazepine (50% yield), on the basis of the integration of its characteristic peaks in the NMR spectrum [δ 6.95 (d, 2 H), 6.3 (d, 1 H), 5.9 (t, 1 H), 3.6 (s, 3 H)]. Similarly, the products from photolysis in ethanol/acetonitrile (1:5 v/v) solution were identified as the aniline (73%) and the corresponding ethoxyazepine (26%) on the basis of integration of the characteristic peaks in its ^{1}H NMR spectrum [δ 7.1 (d, 1 H), 6.3 (d, 1 H), 5.95 (d, 1 H), 4.1 (q, 2 H)].

Acknowledgment. The work at the University of Illinois was supported by grants from the National Science Foundation and the National Institute of Health. The work at the University of Copenhagen was supported by the NOVO Foundation (a Hallas-Moller scholarship for P.E.N.).

Reaction of Allylic Tin Reagents with Nitrogen Heteroaromatics Activated by Alkyl Chloroformates: Regioselective Synthesis of α-Allylated 1,2-Dihydropyridines and Change of the Regioselectivity Depending on Methyl Substituents at the Allylic Moiety

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Allyltin reagents readily react with pyridine and some substituted pyridines activated by alkyl chloroformates to give α-allylated 1,2-dihydropyridines regioselectively. Functional substituents such as halogeno, acetoxy, and formyl groups can be tolerated, demonstrating high chemoselectivity of the reactions. The regiochemistry of the attack on pyridine nuclei changes from α-addition to α- and γ-addition (nonregioselective) to γ-addition, depending on methyl substituents at the allylic moiety (from allyl to methallyl and crotyl to prenyl groups). It is also found that the reactions occur at the γ-position of allylic tin reagents, indicating the S_N2' character of the reactions. The present effective allylation method can be extended to isoquinoline and quinoline systems.

Regioselective addition of organometallic reagents to *N*-acylpyridinium salts has been increasingly important in the preparation of 2- and 4-substituted 1,2- and 1,4-dihydropyridines, which have proven to be valuable as synthetic intermediates for a variety of alkaloids as well as NADH models.[1-5] We have recently reported that a variety of alkynyl and alkenyl Grignard reagents add to *N*-(methoxycarbonyl)pyridinium chlorides (**1a**) in a highly

(1) For reviews on dihydropyridine chemistry, see: (a) Eisner, U.; Kuthan, J. *Chem. Rev.* **1972**, *72*. 1. (b) Stout, D. M.; Meyers, A. I. *Ibid.* **1982**, *82*, 223.

(2) (a) Yamaguchi, R.; Nakazono, Y.; Matsuki, T.; Hata, E.; Kawanisi, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 215 and references cited therein. (b) Yamaguchi, R.; Hata, E.; Matsuki, T.; Kawanisi, M. *J. Org. Chem.* **1987**, *52*, 2094.

(3) (a) Akiba, K.; Iseki, Y.; Wada, M. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1994. (b) Akiba, K.; Ohtani, A.; Yamamoto, Y. *J. Org. Chem.* **1986**, *51*, 5328 and references cited therein.

(4) (a) Comins, D. L.; Abdullah, A. H. *J. Org. Chem.* **1982**, *47*, 4315. (b) Comins, D. L.; Brown, J. D. *Tetrahedron Lett.* **1984**, *25*, 3297.

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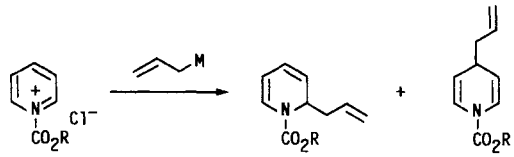
Table I. Reactions of Allylmetal Reagents with *N*-(Alkoxycarbonyl)pyridinium Chlorides

entry	M	R	product	yield,[a] %	α regioselectivity,[b] %
1	MgBr	Me	**2a**	56	79
2	$SnBu_3$	Me	**2a**	89	94
3	$SiMe_3$	Me	**2a**	0	
4	$SnBu_3$	Et	**2b**	84	93
5	$SnBu_3$	CH_2CCl_3	**2c**	84	95
6	$SnBu_3$	$CH_2CH{=}CH_2$	**2d**	64	91

[a] Combined, isolated yield. [b] Determined VPC.

Scheme I



1 2 3

regioselective 1,2-addition manner to afford 2-substituted 1,2-dihydropyridines exclusively.[2] In view of the recent interest in the allyl group as a versatile functional carbon substituent and allylation of *N*-heterocycles,[6,7] we wish to report here an effective method for regio- and chemoselective α-allylation of *N*-(alkoxycarbonyl)pyridinium salts by means of allyltin reagents and that the regioselectivity is highly dependent on methyl substituents at the allylic moiety.[8,9] We also describe the effective α-allylation of isoquinolinium and quinolinium salts.

Results and Discussion

At first we observed that the reaction of allylmagnesium bromide with *N*-(methoxycarbonyl)pyridinium chloride (**1a**) resulted in rather low α-regioselectivity (79%) and chemical yield (57%) (Table I, entry 1) (Scheme I).[10] We have found, however, that allyltributyltin readily reacts with **1a** produced in situ to afford 2-allyl-1-(methoxycarbonyl)-1,2-dihydropyridine (**2a**) with 94% regioselectivity in 87% chemical yield (Table I, entry 2). However, allyltrimethylsilane, which has been widely used as an allylating reagent,[6a-g] did not react with **1a** at all (Table I, entry 3), indicating that an allylstannane is sufficiently nucleophilic to react with 1-acylpyridinium salt.[11]

Similar high α-regioselectivity was observed in the reactions of a few other *N*-(alkoxycarbonyl)pyridinium salts with allyltributyltin. The results are summarized in Table I. In addition to the higher regioselectivity and chemical yield, a practical advantage of the allyltin reagent over the allyl Grignard reagent is that the former does not react with chloroformate esters or pyridine. Hence, pyridinium salts need not be prepared in advance and the reactions can be accomplished by simply adding chloroformate esters to a solution of pyridine and allyltributyltin in dichloromethane. Furthermore, the resulting tributyltin chloride can be recovered almost quantitatively and recycled to prepare allyltributyltin.

We next examined the extension of this highly effective allylation method to substituted pyridines (Scheme II). As shown in Table II, high α-regioselectivity was observed in most of the cases and functionalized groups such as hal-

Scheme II

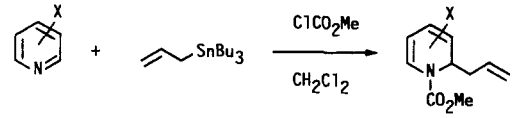
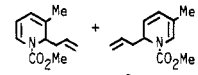
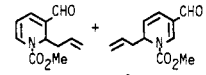
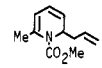


Table II. Allylation of Substituted Pyridines by Means of Allyltin Reagents

entry	reactant	temp(°C)	product	yield(%)[a]	α-selectivity(%)[b]
1		0	 **4a** (75:25)[c] **4b**	74	89
2		−78	 **5**	87	93
3		−78	 **6**	87	94
4		−78	 **7**	94	91
5		−78	 **8a** (76:24)[c] **8b**	88	86
6		r.t.[d]	 **9**	65,[e] 28	95
7		r.t.[d]	 **10**	66,[e] 38	99

[a] Combined, isolated yield. [b] Determined by VPC and/or ^1H NMR. [c] Determined by ^1H NMR. [d] rt = room temperature. [e] Allyltrimethyltin was used.

(5) For synthesis of some piperidine alkaloids starting from 2-substituted 1,2-dihydropyridines, see Ogawa, M.; Kuriya, N.; Natsume, M. *Tetrahedron Lett.* **1984**, *25*, 969 and references cited therein.

(6) (a) Hart, D. J.; Tsai, Y. *Tetrahedron Lett.* **1981**, *22*, 1567. (b) Kraus, G. A.; Neuenschwander, K. *J. Chem. Soc., Chem. Commun.* **1982**, 134. (c) Aratani, M.; Sawada, K.; Hashimoto, M. *Tetrahedron Lett.* **1982**, *23*, 3921. (d) Kozikowski, A. P.; Park, P. *J. Org. Chem.* **1984**, *49*, 1674. (e) Shono, T.; Matsumura, Y.; Onomura, O.; Kanazawa, T.; Habuka, M. *Chem. Lett.* **1984**, 1101. (f) Ohga, K.; Yoon, U. C.; Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 213. (g) Mitsui, H.; Zenki, S.; Shiota, T.; Murahashi, S. *J. Chem. Soc., Chem. Commun.* **1984**, 874.

(7) For reactions of allylic tin reagents with *preformed stable* iminium salts, see: (a) Photochemical addition to 1-methyl-2-phenyl-1-pyrrolium perchlorate in MeOH: Borg, R. M.; Mariano, P. S. *Tetrahedron Lett.* **1986**, *27*, 2821. (b) Addition to the trifluoroacetate salt of dihydro-β-carboline: Grieco, P. A.; Bahsas, A. *J. Org. Chem.* **1987**, *52*, 1378. See also Lewis acid promoted reactions of allylic tin reagents with aldimines and 4-functionalized azetidinones: (c) Keck, G. E.; Enholm, E. J. *J. Org. Chem.* **1985**, *50*, 147. (d) Yamamoto, Y.; Komatsu, T.; Maruyama, K. *Ibid.* **1985**, *50*, 3115. (e) Martel, A.; Daris, J.; Bachand, C.; Menard, M.; Durst, T.; Belleau, B. *Can. J. Chem.* **1983**, *61*, 1899. (f) Fujimoto, K.; Iwano, Y.; Hirai, K. *Tetrahedron Lett.* **1985**, *26*, 88. (g) Fliri, H.; Mak, C. *J. Org. Chem.* **1985**, *50*, 3438.

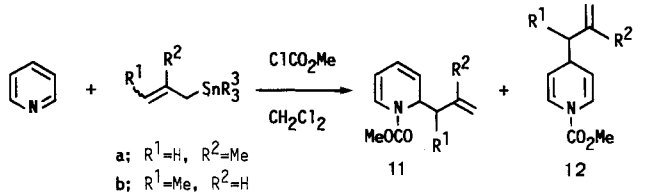
(8) A part of this paper has appeared in a preliminary form: Yamaguchi, R.; Moriyasu, M.; Yoshioka, M.; Kawanisi, M. *J. Org. Chem.* **1985**, *50*, 287.

(9) For other work on reactions of organotin reagents with N-acylated N-heteroaromatics and imines, see: (a) Yamaguchi, R.; Moriyasu, M.; Kawanisi, M. *Tetrahedron Lett.* **1986**, *27*, 211. (b) Yamaguchi, R.; Moriyasu, M.; Takase, I.; Kawanisi, M.; Kozima, S. *Chem. Lett.* **1987**, 1519. (c) Yamaguchi, R.; Otsuji, A.; Utimoto, K. *J. Am. Chem. Soc.* **1988**, *110*, 2186. (d) Yamaguchi, R.; Hata, E.; Utimoto, K. *Tetrahedron Lett.* **1988**, *29*, 1785. (e) Yamaguchi, R.; Hamasaki, T.; Utimoto, K. *Chem. Lett.*, in press.

(10) In the reaction with allyl Grignard reagent, the pyridinium salt must be prepared in advance and the reaction should be conducted at −78 °C.

(11) It has been suggested that allylstannanes are more nucleophilic than allylsilanes: Hosomi, A.; Iguchi, H.; Endo, M.; Sakurai, H. *Chem. Lett.* **1979**, 977.

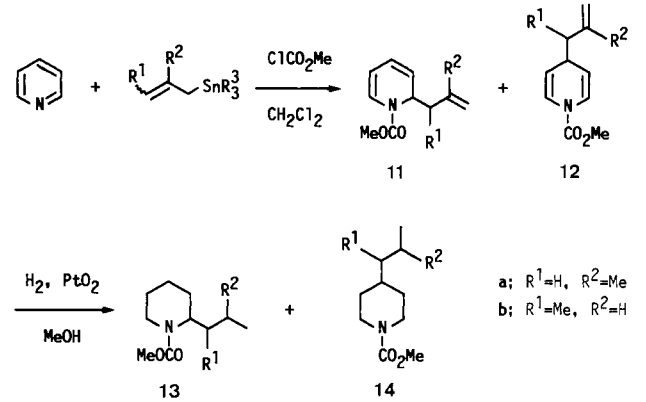
Table III. Reactions of Methallyl- and Crotyltin Reagents with Pyridine Activated by Methyl Chloroformate



entry	R^1	R^2	R^3	temp, °C	product	yield,[a] %	ratio,[b] 11/12
1	H	Me	Bu	0	**11a,12a**	87	36/64
2	H	Me	Bu	−40	**11a,12a**	59	30/70
3	H	Me	Me	0	**11a,12a**	68	42/58
4	Me	H	Bu	0	**11b,12b**	54	48/52
5	Me	H	Bu	−10	**11b,12b**	59	45/55

[a] Combined, isolated yield. [b] Determined by VPC.

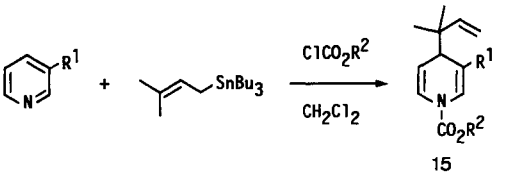
Scheme III



ogeno, acetoxy, and formyl can be tolerated. The reactions of pyridinium salts derived from 2- and 4-methylpyridines gave rather low yields of products probably because of the reduced electrophilicity, though the yields could be improved by making use of allyltrimethyltin (entries 6 and 7).

In the cases of 3-substituted pyridines, out of the two kinds of α-addition products (i.e., 1,2- and 1,6-adducts), the 1,2-addition products were predominantly formed irrespective of the nature of the 3-substituents (entries 1–5). Especially, 3-halo- and 3-acetoxypyridines give the 1,2-adducts with high regioselectivity (entries 2–4). Recently it has been reported in studies on hydride reduction of 3-substituted *N*-(alkoxycarbonyl)pyridinium salts that electron-donating groups as well as halogens at the 3-position cause selective addition of hydride to the 2-position ("ortho-directing effect"), whereas electron-withdrawing groups exhibit poor regioselectivity.[12] It is noteworthy in the present reactions that with an electron-withdrawing group such as formyl, 1,2-addition predominates (entry 5).[13] It should also be noted that the reaction of 3-bromopyridinium salt with allyl Grignard reagent gave only a trace of the allylated product but a large amount of triallylcarbinol (81%) via the attack on the carbonyl carbon, demonstrating the superiority of the allyltin reagent.

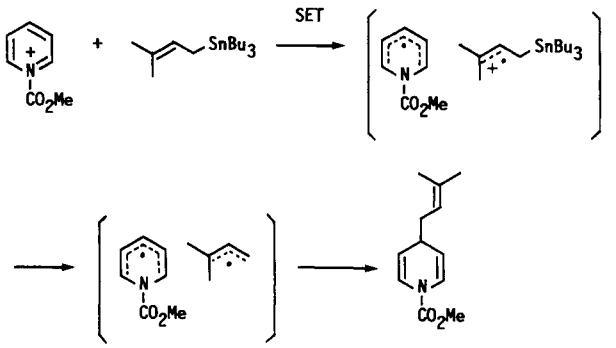
Table IV. Reactions of Prenyltributyltin with Pyridines Activated by Alkyl Chloroformate



entry	R^1	R^2	product	yield,[a,b] %
1	H	CH_2CCl_3	**15a**	66
2	CO_2Me	Me	**15b**	99
3	CHO	Me	**15c**	98
4	CN	Me	**15d**	94

[a] Isolated yield. [b] The selectivity was >95% by ^1H NMR.

Scheme IV



We next examined the reaction of methyl-substituted allylic tin reagents with pyridinium salt to see how the regioselectivity is changed. The results of the reactions of methallyl- and crotyltin reagents are summarized in Table III (Scheme III). Since the adducts, **11** and **12**, were relatively unstable, **11** and **12** were perhydrogenated over PtO_2 in MeOH and further characterized.[14] As shown in Table III, the 1,2- and 1,4-addition products were formed in comparable ratios and essentially no regioselectivity was observed in any case. It should be mentioned that the crotyltin reagent reacts at the γ-position of the allylic moiety exclusively, indicating the S_N2' character of the reactions.

Furthermore, we have interestingly found that prenyltributyltin attacks on the γ-position of pyridinium salts exclusively,[15] while the S_N2' character of the reactions is preserved. The results are summarized in Table IV. Whereas the reaction of prenyltributyltin with pyridine activated by methyl chloroformate was sluggish probably due to steric hindrance, the use of β-trichloroethyl chloroformate gave the 1,4-adduct in moderate yield (entry 1). On the other hand, the reactions with 3-substituted pyridines with electron-withdrawing groups proceeded smoothly to give the 1,4-addition products in high yields (entries 2–4).

The above results have shown the following two features: First, the regioselectivity of the attack on pyridinium salt is deeply influenced by methyl substituents on allylic tin reagents. Second, allylic tin reagents react at the γ-positions of allylic groups exclusively, indicating an S_N2' character similar to that of the Lewis acid promoted re-

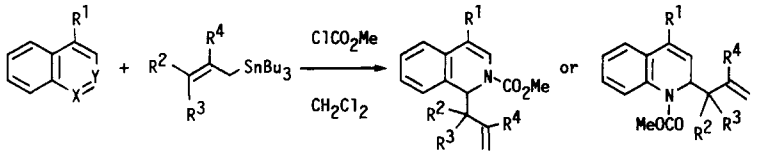
(12) Sundberg, R. J.; Hamilton, G.; Trindle, C. *J. Org. Chem.* **1986**, *51*, 3672.

(13) We have recently observed that alkynyltin reagents exhibit much higher selectivity of the 1,2-addition in reactions with 3-acylpyridinium salts, probably due to some intramolecular interaction between trialkyltin and 3-acyl groups in the reaction intermediates.[9d] A similar effect might induce the preferential 1,2-addition in the present case. For another example of intramolecular interaction between trialkyltin and acyl groups, see: Jousseaume, B.; Villeneuve, P. *J. Chem. Soc., Chem. Commun.* **1987**, 513.

(14) The diastereochemistry (threo and erythro) of **11b**, **12b**, **13b**, and **14b** has not been determined.

(15) We have observed that benzyltin reagents also show exclusive γ-selectivity.[9a]

Table V. Reactions of Allylic Tin Reagents with Isoquinolines and Quinoline Activated by Methyl Chloroformate



16 17

entry	X	Y	R^1	R^2	R^3	R^4	product	yield,[a,b] %
1	CH	N	H	H	H	H	**16a**	93
2	CH	N	H	H	H	Me	**16b**	92
3	CH	N	H	H, Me[c]		H	**16c**[d]	89
4	CH	N	H	Me	Me	H	**16d**	95
5	CH	N	CHO	H	H	H	**16e**	94
6	CH	N	Br	H	H	H	**16f**	97
7	N	CH	H	H	H	H	**17a**	92
8	N	CH	H	H	H	Me	**17b**	80[e]

[a] Isolated yield. [b] The selectivity was >95% by ^{1}H NMR. [c] A mixture of trans,cis isomers. [d] A mixture of diastereoisomers. [e] A small amount of a regioisomer (ca. 8%) was detected by ^{1}H NMR.

actions of allylic tin reagents with carbonyl compounds[16] and aldimines.[7c,d] The S_N2' character of the present reaction excludes a mechanism via a π-allylic radical intermediate, which might be formed by the single-electron transfer from the allylic tin reagent to the pyridinium salt, because it is expected that the allylic radical strongly prefers reacting at the less substituted allyl carbon terminus (Scheme IV).[17,18]

On the other hand, the diverse change of the regioselectivity of the attack on pyridinium salt by methyl-substituted allylic tin reagents is quite interesting. We recently reported that reactions of *N*-(methoxycarbonyl)-pyridinium salt with alkynyl and alkenyl Grignard reagents proceed in a highly regioselective 1,2-addition manner, while alkyl Grignard reagents show a lack of regioselectivity.[2a] These results have been rationalized by the HSAB principle;[19] harder alkynyl and alkenyl groups prefer the 1,2-addition, while less hard alkyl groups do not show an appreciable preference of the regiochemistry. Furthermore, it has been reported that very soft organocopper reagents prefer the 1,4-addition.[3a,4a] The present remarkable change of the regiochemistry from the 1,2- to the 1,4-addition, depending on the allylic groups of organotin reagents, may be explained in the same context as above; the relative hardness of allylic groups is supposed to be allyl > methallyl = crotyl > prenyl (primary > secondary > tertiary),[20] and this order is in good agreement with the regiochemistry shown above. Another explanation is that the steric bulkiness of allylic groups may alter the regiochemistry, as it has been reported that bulky N-substituents induce a preferential 1,4-addition.[3a,4a] Thus, it should be highly probable that the former effect works in accordance with the latter.

Since the present method for allylation of pyridinium salts by means of organotin reagents has been found to be very effective, we next examined reactions of isoquinolinium and quinolinium salts with allylic tin reagents. As shown in Table V, allylic groups can be effectively introduced to the α-positions of isoquinoline and quinoline systems. Formyl and bromo groups on heteroaromatic rings are intact, indicating the high chemoselectivity of the reactions.

Experimental Section

All temperatures are uncorrected. IR spectra were obtained on a Hitachi 215 or JASCO IR-810 spectrometer. The mass spectra were taken by using a Hitachi RMS-4 mass spectrometer. The ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were obtained on Varian EM-390, Varian CFT-20, and JEOL FX-90Q spectrometers, Me_4Si being chosen as the internal standard. Analytical VPC were carried out on a Shimadzu GC-4C gas chromatograph with 10% SE-30 and 10% HVSG on Chromsorb W columns. Preparative VPC were performed on a Varian 920 gas chromatograph with a 10% SE-30 on Chromsorb W column. Microanalyses were performed by the Kyoto University Elemental Analysis Center. All reactions were carried out under an Ar atmosphere, unless otherwise noted. CH_2Cl_2 was distilled over P_2O_5 before use.

General Procedure for the Reactions of Allyltin Reagents with Pyridine and Substituted Pyridines Activated by Alkyl Chloroformates. To a solution of pyridine (2.2 mmol) and allyltin reagent (2.0 mmol) in dry dichloromethane (5 mL) was added the alkyl chloroformate (2.2–3.0 mmol) dropwise for 5–10 min under ice cooling or at the temperature indicated. The mixture was stirred until the reaction finished (usually 2–5 h) (the reaction was monitored by TLC). After the solvent was evaporated, the residue was rapidly chromatographed on silica gel. Elution by hexane gave tributyltin chloride, and subsequent elution with CH_2Cl_2 afforded the product(s).

2-Allyl-1-(methoxycarbonyl)-1,2-dihydropyridine (2a): MS *m/z* (relative intensity) 179 (M^+, 1), 138 (M^+ – 41, 100), 94 (57); IR (neat) 1715 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.49–6.84 (br, 1 H), 5.39–6.08 (m, 3 H), 4.57–5.33 (m, 4 H), 3.73 (s, 3 H), 1.99–2.53 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 154.3 (s), 133.5 (s), 125.2 d), 122.3 (d), 121.7 (d), 117.7 (t), 105.9 (d), 53.0 (q), 52.0 (d), 38.6 (t). Anal. Calcd for $C_{10}H_{13}NO_2$: C, 66.72; H, 7.31. Found: C, 66.98; H, 7.33.

2-Allyl-1-(ethoxycarbonyl)-1,2-dihydropyridine (2b): MS *m/z* (relative intensity) 152 (M^+ – 41, 40), 80 (100); IR (neat) 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.50–6.80 (br, 1 H), 5.40–5.97 (m, 2 H), 4.60–5.33 (m, 5 H), 4.15 (q, 2 H, J = 7 Hz), 2.10–2.35 (m, 2 H), 1.27 (t, 3 H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 153.4 (s), 133.9 (d), 125.6 (d), 122.2 (d), 121.6 (d), 117.7 (t), 105.5 (d), 62.0 (t), 51.8 (d), 38.5 (t), 14.5 (q).

2-Allyl-1-((2,2,2-trichloroethoxy)carbonyl)-1,2-dihydropyridine (2c): MS *m/z* (relative intensity) 258, 256, 254 (M^+ – 41, 7, 22, 24), 80 (100); IR (neat) 1715 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.70 (d, 1 H, J = 7 Hz), 5.45–6.05 (m, 2 H), 4.67–5.40 (m, 7 H), 2.13–2.45 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 151.5 152.1 (s), 133.1 132.8 (d), 123.9 125.0 (d), 121.3 121.7 (d), 118.0 118.3 (d), 106.9 107.1 (d), 95.3 95.0 (s), 75.2 (t), 52.1 52.4 (d), 38.1 39.0 (t).

(16) For example: Naruta, Y.; Ushida, S.; Maruyama, K. *Chem. Lett.* **1979**, 919. See also ref 11.

(17) For photoinduced additions of allylsilanes and allylstannane to iminium salts via radical intermediates, see ref 6f and 7a.

(18) One of the referees suggested that the reaction of the pyridinyl and the tin substituted cation radical might give **15**. However, this possibility seems unlikely, because it has been strongly proposed that β-silyl and β-stannyl cation radicals rapidly undergo demetalation to produce allyl radicals before the cation radical–radical couplings: see ref 6f and 7a.

(19) Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 581, 643.

(20) Ho, T. *Hard and Soft Acids and Bases Principle in Organic Chemistry*; Academic: New York, 1977.

(21) Hill, R. K.; Yuri, T. *Tetrahedron* **1977**, *33*, 1569.

2-Allyl-1-((allyloxy)carbonyl)-1,2-dihydropyridine (2d): MS *m/z* (relative intensity) 164 (M^+ - 41, 87), 120 (100); IR (neat) 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.57–6.80 (br, 1 H), 4.40–6.15 (m, 12 H), 2.07–2.40 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 153.3 (s), 133.5 (d), 132.4 (d), 124.8 (d), 122.4 (d), 121.9 (d), 117.9 (t), 117.8 (t), 105.8 (d), 66.6 (t), 51.8 (d), 38.4 (t).

2-Allyl-1-(methoxycarbonyl)-3-methyl- and 2-Allyl-1-(methoxycarbonyl)-5-methyl-1,2-dihydropyridines (4a and 4b). Since **4a** and **4b** could not be separated by VPC or column chromatography, the following spectral data were elucidated from those of the mixture. **4a**: MS *m/z* (relative intensity) 152 (M^+ - 41, 100), 108 (84); IR (neat) 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ (80 °C) 6.56 (d, 1 H, J = 7 Hz), 5.83–5.97 (m, 2 H), 4.58–5.33 (m, 4 H), 3.75 (s, 3 H), 2.28 (t, 2 H, J = 6 Hz), 1.78 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 154.1 (s), 134.5 (d), 131.6 (s), 122.8 (d), 122.1 (d), 117.4 (t), 106.8 (d), 55.8 (d), 53.0 (q), 36.1 (t), 21.1 (q). **4b**: ^1H NMR ($CDCl_3$) δ (80 °C) 6.44 (s, 1 H), 5.83–5.97 (m, 2 H), 4.85–5.33 (m, 4 H), 3.75 (s, 3 H), 2.28 (t, 2 H, J = 6 Hz), 1.72 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 154.1 (s), 134.0 (d), 130.9 (s), 125.4 (d), 120.0 (d), 117.5 (t), 106.8 (d), 56.2 (d), 51.4 (q), 38.3 (t), 17.8 (q). An elemental analysis of the mixture was made. Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82. Found: C, 68.19; H, 7.93.

2-Allyl-3-chloro-1-(methoxycarbonyl)-1,2-dihydropyridine (5): MS *m/z* (relative intensity) 215, 213 (M^+, 1, 4), 174, 172 (M^+ - 41, 36, 100), 154, 152 (22, 52); IR (neat) 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ (80 °C) 6.69 (d, 1 H, J = 7 Hz), 6.06 (d, 1 H, J = 6 Hz), 5.58–5.94 (m, 1 H), 4.83–5.31 (m, 4 H), 3.78 (s, 3 H), 2.42 (t, 2 H, J = 6 Hz); ^{13}C NMR ($CDCl_3$) δ 154.0 (s), 133.1 (d), 123.6 (d), 120.4 (s), 120.0 (d), 118.2 (t), 105.1 (d), 57.4 (d), 53.4 (q), 35.9 (t). Anal. Calcd for $C_{10}H_{12}ClNO_2$: C, 56.22; H, 5.66. Found: C, 56.09; H, 5.80.

2-Allyl-3-bromo-1-(methoxycarbonyl)-1,2-dihydropyridine (6): MS *m/z* (relative intensity) 259, 257 (M^+, 3, 3), 218, 216 (M^+ - 41, 98, 100), 174, 172 (46, 48); IR (neat) 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ (80 °C) 6.69 (d, 1 H, J = 7 Hz), 6.19 (d, 1 H, J = 6 Hz), 5.47–6.06 (m, 1 H), 4.83–5.25 (m, 4 H), 3.73 (s, 3 H), 2.36 (t, 2 H, J = 6 Hz); ^{13}C NMR ($CDCl_3$) δ 153.5 (s), 133.0 (d), 124.5 (d), 124.1 (d), 118.2 (t), 114.4 (s), 105.7 (d), 58.6 (d), 53.3 (q), 35.8 (t). Anal. Calcd for $C_{10}H_{12}BrNO_2$: C, 46.17; H, 5.42. Found: C, 45.88; H, 5.32.

3-Acetoxy-2-allyl-1-(methoxycarbonyl)-1,2-dihydropyridine (7): MS *m/z* (relative intensity) 237 (M^+, 2), 196 (M^+ - 41, 45), 154 (100); IR (neat) 1755, 1710 cm^{-1}; ^1H NMR δ (80 °C) 6.39 (d, 1 H, J = 7 Hz), 5.81 (d, 1 H, J = 6 Hz), 5.44–6.08 (m, 1 H), 4.69–9.25 (m, 4 H), 3.72 (s, 3 H), 2.28 (t, 2 H, J = 6 Hz); ^{13}C NMR ($CDCl_3$) δ 168.0 (s), 154.0 (s), 143.2 (s), 133.4 (d), 123.0 (d), 117.7 (t), 109.2 (d), 104.1 (d), 54.3 (d), 53.1 (q), 36.8 (t), 21.0 (q). Anal. Calcd for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37. Found: C, 60.46; H, 6.34.

2-Allyl-3-formyl-1-(methoxycarbonyl)-1,2-dihydropyridine (8a): MS *m/z* (relative intensity) 207 (M^+, 1), 166 (M^+ - 41, 53), 122 (100); IR (neat) 1720, 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.33 (s, 1 H), 7.15 (d, 1 H, J = 7 Hz), 6.80 (d, 1 H, J = 6 Hz), 5.30–5.93 (m, 3 H), 4.73–5.10 (m, 2 H), 3.75 (s, 3 H), 2.18 (t, 2 H, J = 6 Hz); ^{13}C NMR ($CDCl_3$) δ 189.3 (d), 153.7 (s), 141.8 (d), 134.4 (d), 133.5 (s), 121.9 (d), 118.0 (t), 104.6 (d), 53.6 (q), 49.5 (d), 37.6 (t). Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32. Found: C, 63.46; H, 6.33.

2-Allyl-5-formyl-1-(methoxycarbonyl)-1,2-dihydropyridine (8b): MS *m/z* (relative intensity) 207 (M^+, 2), 166 (M^+ - 41, 100), 122 (72); IR (neat) 1720, 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.18 (s, 1 H), 7.55 (s, 1 H), 6.45 (d, 1 H, J = 9 Hz), 5.50–5.97 (m, 2 H), 4.77–5.15 (m, 3 H), 3.87 (s, 3 H), 2.30 (t, 2 H, J = 6 Hz); ^{13}C NMR ($CDCl_3$) δ 187.5 (d), 153.3 (s), 143.3 (d), 132.0 (d), 122.6 (d), 119.5 (s), 117.2 (d), 54.4 (d), 54.2 (d), 40.0 (t). Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32. Found: C, 63.33; H, 6.40.

2-Allyl-1-(methoxycarbonyl)-6-methyl-1,2-dihydropyridine (9): MS *m/z* (relative intensity) 193 (M^+, 1), 152 (100), 108 (73); IR (neat) 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.20–6.00 (m, 4 H), 4.67–5.13 (m, 3 H), 3.68 (s, 3 H), 2.15 (t, 2 H, J = 7 Hz), 2.07 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 155.1 (s), 134.0 (s), 133.9 (d), 123.6 (d), 122.3 (d), 117.2 (t), 112.0 (d), 52.6 (q), 52.3 (d), 36.7 (t), 21.6 (q). Since **9** was relatively labile, **9** was perhydrogenated over PtO_2 in MeOH to give 1-(methoxycarbonyl)-2-methyl-6-propylpiperidine (dihydropinidine):[21] MS *m/z* (relative intensity) 199 (M^+, 3), 156 (M^+ - 43, 100); IR (neat) 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.95–4.47 (m, 2 H), 3.63 (s, 3 H), 1.00–1.70 (m, 10 H), 1.13 (d, 3 H, J = 7 Hz), 0.87 (dist t, 3 H); ^{13}C NMR ($CDCl_3$) δ 156.6 (s), 52.2 (q), 50.4 (d), 46.1 (d), 37.4 (t), 30.4 (t), 27.7 (t), 20.6 (t), 20.5 (q), 14.2 (t), 14.1 (q).

2-Allyl-1-(methoxycarbonyl)-4-methyl-1,2-dihydropyridine (10): MS *m/z* (relative intensity) 152 (M^+ - 41, 100); IR (neat) 1710, 1650 cm^{-1}; ^1H NMR $CDCl_3$ δ 6.50–6.80 (br, 1 H), 5.50–6.00 (m, 1 H), 4.50–5.33 (m, 5 H), 3.67 (s, 3 H), 2.08–2.13 (m, 2 H), 1.70 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 153.9 (s), 133.8 (d), 129.6 (s), 124.9 (d), 124.3 (d), 117.5 (t), 109.3 (d), 53.0 (q), 52.2 (d), 38.7 (t), 20.4 (q). Since **10** was relatively labile, **10** was perhydrogenated over PtO_2 in MeOH to give 1-(methoxycarbonyl)-4-methyl-2-propylpiperidine: MS *m/z* (relative intensity) 156 (M^+ - 43, 100); IR (neat) 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.90–4.70 (br, 2 H), 3.93 (s, 3 H), 2.97–3.50 (m, 1 H), 0.80–2.23 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 156.7 (s), 53.4 50.8 (d), 52.2 52.3 (q), 37.6 39.0 (t), 36.7 37.2 (t), 35.7 34.2 (t), 31.3 32.6 (t), 26.3 25.3 (q), 21.5 22.3 (d), 19.4 19.6 (t), 14.1 14.0 (q). Anal. Calcd for $C_{11}H_{21}NO_2$: C, 66.29; H, 10.62. Found: C, 66.49; H, 10.84.

Reactions of (2-Methyl-2-propenyl)tributyltin and (2-Butenyl)tributyltin Reagents with 1-(Methoxycarbonyl)-pyridinium Chloride. The procedures were essentially the same as those above. (2-Butenyl)tributyltin was a mixture of stereoisomers (trans:cis = 59:41 by ^{119}Sn NMR). Each of the 1,2- and 1,4-adducts was isolated by preparative VPC.

1-(Methoxycarbonyl)-2-(2-methyl-2-propenyl)-1,2-dihydropyridine (11a): MS *m/z* (relative intensity) 138 (M^+ - 55, 100), 94 (66); IR (neat) 1715, 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.53–6.90 (br, 1 H), 5.93 (dd, 1 H, J = 5 and 9 Hz), 5.16–5.73 (m, 2 H), 4.60–5.10 (m, 3 H), 3.77 (s, 3 H), 2.23 (d, 2 H, J = 7 Hz), 1.80 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 149.8 (s), 141.1 140.6 (s), 125.1 124.4 (d), 122.9 122.5 (d), 121.7 121.1 (d), 113.6 (t), 106.1 (d), 53.0 52.7 (q), 50.3 (d), 41.5 (t), 22.3 (q).

1-(Methoxycarbonyl)-4-(2-methyl-2-propenyl)-1,4-dihydropyridine (12a): MS *m/z* (relative intensity) 138 (M^+ - 55, 100), 94 (73); IR (neat) 1730, 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.60–6.93 (br, 2 H), 3.63–4.97 (m, 4 H), 4.80 (s, 3 H), 2.97–3.33 (m, 1 H), 2.13 (d, 2 H, J = 7 Hz), 1.70 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 151.9 (s), 124.3 (s), 122.4 (d), 112.5 (t), 109.9 (d), 53.3 (q), 47.3 (t), 30.6 (d), 22.4 (q).

1-(Methoxycarbonyl)-2-(1-methyl-2-propenyl)-1,4-dihydropyridine (11b): MS *m/z* (relative intensity) 138 (M^+ - 55, 100), 94 (71); IR (neat) 1720, 1645 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.71–7.90 (br, 1 H), 4.50–6.11 (m, 7 H), 3.78 (s, 3 H), 2.25–2.79 (m, 1 H), 1.04 0.96 (d, 3 H, J = 6 Hz); ^{13}C NMR ($CDCl_3$) δ 154.6 (s), 140.2 (d), 125.5 (d), 122.2 (d), 120.8 (d), 115.0 (t), 106.2 (d), 56.0 (d), 53.0 (q), 42.6 (d), 14.2 (q).

1-(Methoxycarbonyl)-4-(1-methyl-2-propenyl)-1,2-dihydropyridine (12b): MS *m/z* (relative intensity) 138 (M^+ - 55, 100), 94 (65); IR (neat) 1730, 1695, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.10–7.27 (m, 1 H), 6.71–7.00 (br, 1 H), 6.52–6.19 (m, 1 H), 4.68–5.26 (m, 4 H), 3.82 (s, 3 H), 2.90–3.11 (br, 1 H), 1.95–2.31 (m, 1 H), 1.35 0.98 (d, 3 H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 154.4 (s), 149.7 141.5 (d), 123.5 122.7 (d), 114.6 114.3 (t), 108.7 107.7 (d), 53.3 (q), 43.4 52.6 (d), 37.9 (d), 20.0 15.3 (q).

Reduction of 11 and 12. A mixture of **11a** and **12a** (**11b** and **12b**) was perhydrogenated over PtO_2 in MeOH and each of the products, **13a** and **14a** (**13b** and **14b**), was isolated by preparative VPC.

1-(Methoxycarbonyl)-2-(2-methylpropyl)piperidine (13a): MS *m/z* (relative intensity) 199 (M^+, 3), 142 (M^+ - 57, 100); IR (neat) 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.77–4.50 (m, 2 H), 3.63 (s, 3 H), 2.57–3.00 (m, 1 H), 1.04–2.05 (m, 9 H), 0.90 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 156.1 (s), 52.3 (q), 48.9 (d), 39.0 (t), 38.8 (d), 28.8 (t), 25.7 (t), 24.9 (t), 23.0 (q), 22.6 (q), 19.0 (t). Anal. Calcd for $C_{11}H_{21}NO_2$: C, 66.29; H, 10.62. Found: C, 66.31; H, 10.90.

1-(Methoxycarbonyl)-4-(2-methylpropyl)piperidine (14a): MS *m/z* (relative intensity) 199 (M^+, 30), 184 (M^+ - 15, 100); IR (neat) 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.07 (br d, 2 H, J = 13 Hz), 3.63 (s, 3 H), 2.71 (dt, 2 H, J = 13 and 2 Hz), 0.90–1.80 (m, 8 H), 0.85 (d, 6 H, J = 6 Hz); ^{13}C NMR ($CDCl_3$) δ 155.9 (s), 52.4 (q), 46.0 (t), 44.2 (t), 33.5 (d), 32.4 (t), 24.5 (d), 22.8 (q). Anal. Calcd for $C_{11}H_{21}NO_2$: C, 66.29; H, 10.62. Found: C, 66.48; H, 10.89.

1-(Methoxycarbonyl)-2-(1-methylpropyl)piperidine (13b): MS *m/z* (relative intensity) 142 (M^+ - 57, 100); IR (neat) 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.77–4.30 (m, 2 H), 3.70 (s, 3 H), 2.53–3.97 (m, 1 H), 1.03–2.10 (br, 9 H), 0.73–1.00 (m, 6 H); ^{13}C NMR ($CDCl_3$)

δ 156.5 (s), 55.9, 55.4 (d), 52.3 (q), 39.5 (t), 32.0 (d), 26.3 26.1 (t), 25.6 (t), 26.0 25.0 (t), 19.2 19.0 (t), 15.9 14.8 (q), 11.1 11.0 (q). Anal. Calcd for $C_{11}H_{21}NO_2$: C, 66.29; H, 10.62. Found: C, 66.32; H, 10.76.

1-(Methoxycarbonyl)-4-(1-methylpropyl)piperidine (14b): MS m/z (relative intensity) 199 (M^+, 23), 184 ($M^+ - 15$, 100); IR (neat) 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.23 (br d, 2 H, J = 13 Hz), 3.77 (s, 3 H), 2.70 (br t, 2 H, J = 13 Hz), 0.73–2.87 (m, 14 H); ^{13}C NMR ($CDCl_3$) δ 52.4 (q), 44.6 (t), 44.6 (t), 40.8 (d), 39.1 (d), 29.7 (t), 28.1 (t), 26.4 (t), 15.6 (q), 11.7 (q). Anal. Calcd for $C_{11}H_{21}NO_2$: C, 66.29; H, 10.62. Found: C, 66.55; H, 10.86.

Reactions of (3-Methyl-2-butenyl)tributyltin with Pyridines Activated by Alkyl Chloroformates. The procedures were essentially the same as those above.

4-(1,1-Dimethyl-2-propenyl)-1-((2,2,2-trichloroethoxy)carbonyl)-1,4-dihydropyridine (15a): IR (neat) 1730, 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.83 (d, 2 H, J = 9 Hz), 5.73 (dd, 1 H, J = 10 and 16 Hz), 4.70–5.10 (m, 6 H), 2.70–2.87 (m, 1 H), 0.97 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 149.5 (s), 146.2 (d), 123.7 123.1 (d), 112.1 (t), 109.0 108.5 (d), 94.9 (s), 75.4 (t), 42.4 (d), 41.4 (s), 23.3 (q). Anal. Calcd for $C_{13}H_{16}Cl_3NO_2$: C, 48.10; H, 4.97. Found: C, 48.20; H, 5.06.

1,3-Bis(methoxycarbonyl)-4-(1,1-dimethyl-2-propenyl)-1,4-dihydropyridine (15b): IR (neat) 1745, 1710, 1680, 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.89 (s, 1 H), 6.87 (d, 1 H, J = 8 Hz), 5.57–5.93 (m, 2 H), 5.10 (dd, 1 H, J = 6 and 8 Hz), 4.67–4.97 (m, 2 H), 3.85 (s, 3 H), 3.70 (s, 3 H), 3.31 (d, 1 H, J = 6 Hz), 0.91 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 168.5 (s), 151.7 (s), 145.7 (d), 133.3 (d), 123.3 (d), 111.7 (t), 110.7 (s), 109.5 (d), 54.0 (q), 51.4 (q), 43.5 (s), 41.4 (d), 23.1 (q), 22.3 (q). Anal. Calcd for $C_{14}H_{19}NO_4$: C, 63.38; H, 7.22. Found: C, 63.57; H, 7.33.

4-(1,1-Dimethyl-2-propenyl)-3-formyl-1-(methoxycarbonyl)-1,4-dihydropyridine (15c): IR (neat) 1749, 1670, 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.40 (s, 1 H), 7.68 (s, 1 H), 6.87 (d, 1 H, J = 8 Hz), 5.53–5.93 (m, 1 H), 5.17 (dd, 1 H, J = 6 and 8 Hz), 3.87 (s, 3 H), 3.30 (d, 1 H, J = 6 Hz), 0.87 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 190.6 (d), 151.4 (s), 145.4 (d), 142.2 (d), 123.3 (d), 121.7 (s), 112.0 (t), 110.8 (d), 54.3 (q), 43.3 (s), 39.3 (d), 23.4 (q), 22.9 (q). Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28. Found: C, 66.49; H, 7.44.

3-Cyano-4-(1,1-dimethyl-2-propenyl)-1-(methoxycarbonyl)-1,4-dihydropyridine (15d): IR (neat) 2210, 1745, 1680, 1615 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.57 (s, 1 H), 6.83 (d, 1 H, J = 8 Hz), 5.67–6.03 (m, 1 H), 4.83–5.27 (m, 3 H), 3.87 (s, 3 H), 2.90 (d, 1 H, J = 6 Hz), 1.07 (s, 3 H), 1.03 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 150.7 (s), 144.4 (d), 137.5 (d), 123.0 (d), 120.0 (s), 113.6 (t), 108.1 (d), 91.3 (s), 54.4 (q), 43.9 (d), 43.4 (s), 23.5 (q), 22.9 (q). Anal. Calcd for $C_{13}H_{16}N_2O_2$: C, 67.22; H, 6.94. Found: C, 67.25; H, 7.03.

Reactions of Allylic Tin Reagents with Isoquinolines and Quinoline Activated by Methyl Chloroformate. The procedures were essentially the same as those above.

1-Allyl-2-(methoxycarbonyl)-1,2-dihydroisoquinoline (16a): MS m/z (relative intensity) 229 (M^+, 2), 188 ($M^+ - 41$, 100); IR (neat) 1715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.13–7.25 (m, 5 H), 5.10–6.00 (m, 3 H), 4.73–5.10 (m, 2 H), 3.78 (s, 3 H), 2.37 (t, 2 H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 153.6 (s), 133.9 (d), 132.3 (s), 130.4 (s), 129.2 (d), 127.7 (d), 126.7 (d), 124.7 (d), 117.8 (t), 108.7 (d), 55.7 (d), 53.0 (q), 40.1 (t). Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59. Found: C, 73.25; H, 6.67.

2-(Methoxycarbonyl)-1-(2-methyl-2-propenyl)-1,2-dihydroisoquinoline (16b): mp 61 °C; MS m/z (relative intensity) 243 (M^+, 5), 188 ($M^+ - 55$, 100); IR (CCl_4) 1710 cm^{-1}; ^1H NMR δ 6.63–3.72 (m, 5 H), 5.83 (t, 1 H, J = 7 Hz), 5.10–5.57 (m, 1 H), 4.73 (br s, 1 H), 4.50 (br s, 1 H), 3.71 (s, 3 H), 1.62–2.62 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 153.5 154.2 (s), 141.4 140.9 (s), 132.7 (s), 130.0 130.3 (s), 127.5 (d), 126.7 (d), 126.3 126.0 (d), 124.8 124.9 (d), 124.6 124.2 (d), 114.2 114.4 (t), 54.1 54.6 (d), 53.1 52.7 (q), 43.2 43.5 (t), 22.4 22.2 (q). Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04. Found: C, 73.86; H, 7.34.

2-(Methoxycarbonyl)-1-(1-methyl-2-propenyl)-1,2-dihydroisoquinoline (16c): MS m/z (relative intensity) 188 ($M^+ - 55$, 100); IR (neat) 1715, 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.00–7.60 (m, 5 H), 5.30–5.97 (m, 2 H), 4.57–5.27 (m, 3 H), 3.77 3.73 (s, 3 H), 2.30–2.73 (m, 1 H), 0.73–1.07 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 154.1 153.7 153.6 (s), 140.9 140.4 139.8 139.6 (d), 130.9 130.6 130.5 130.4 (s), 127.7 127.6 127.5 (d), 126.2 126.1 (d), 126.0 125.8 (s), 125.0 124.9 (d), 124.6 124.4 (d), 115.3 115.0 (t), 109.9 109.7 109.5 109.3 (d), 60.2 60.1 59.5 (d), 53.0 52.9 52.6 (q), 43.0 42.5 42.0 (d), 16.5 16.4 16.2 (q). Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04. Found: C, 74.22; H, 7.04.

1-(1,1-Dimethyl-2-propenyl)-2-(methoxycarbonyl)-1,2-dihydroisoquinoline (16d): MS m/z (relative intensity) 188 ($M^+ - 69$, 100); IR (neat) 1720, 1635 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.63–7.17 (m, 5 H), 5.57–6.00 (m, 2 H), 5.33–4.97 (m, 1 H), 4.60–4.90 (m, 2 H), 3.70 (s, 3 H), 0.97 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 154.3 (s), 144.7 (d), 131.7 (s), 128.5 (d), 127.5 (d), 127.2 (s), 126.2 (d), 126.0 (d), 124.2 (d), 111.9 (t), 110.8 (d), 62.2 (d), 53.1 (q), 45.1 (s), 23.8 (q), 23.2 (q). Anal. Calcd for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44. Found: C, 74.40; H, 7.57.

1-Allyl-4-formyl-2-(methoxycarbonyl)-1,2-dihydroisoquinoline (16e): MS m/z (relative intensity) 216 ($M^+ - 41$, 100); IR (neat) 1730, 1670, 1615 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.47 (s, 1 H), 8.30–8.47 (m, 1 H), 7.63 (s, 1 H), 6.93–7.30 (m, 3 H), 5.20–5.90 (m, 2 H), 4.73–5.03 (m, 2 H), 3.87 (s, 3 H), 2.37 (t, 2 H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 189.1 (d), 152.8 (s), 145.2 (d), 132.6 (d), 131.2 (s), 128.0 (d), 126.4 (s), 126.2 (d), 124.8 (d), 118.9 (t), 118.7 (s), 56.8 (d), 54.3 (q), 41.3 (t). Anal. Calcd for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88. Found: C, 69.62; H, 5.58.

1-Allyl-4-bromo-2-(methoxycarbonyl)-1,2-dihydroisoquinoline (16f): MS m/z (relative intensity) 266, 268 ($M^+ - 41$, 100); IR (neat) 1720, 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.90–7.80 (m, 5 H), 5.13–6.00 (m, 2 H), 4.80–5.10 (m, 2 H), 3.80 (s, 3 H), 2.37 (t, 2 H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 152.6 153.2 (s), 133.3 133.0 (d), 132.3 (s), 129.2 (s), 128.0 (d), 126.1 (d), 125.3 (d), 124.7 (d), 118.2 (t), 103.8 (s), 55.5 56.2 (d), 53.4 (q), 39.9 40.1 (t). Anal. Calcd for $C_{14}H_{14}BrNO_2$: C, 54.56; H, 4.58. Found: C, 54.71; H, 4.50.

2-Allyl-1-(methoxycarbonyl)-1,2-dihydroquinoline (17a): MS m/z (relative intensity) 229 (M^+, 1), 118 ($M^+ - 41$, 100), 144 (71); IR (neat) 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.51 (d, 1 H, J = 9 Hz), 5.97 (dd, 1 H, J = 6 and 9 Hz), 5.47–5.90 (m, 1 H), 4.76–5.22 (m, 3 H), 3.74 (s, 3 H), 2.13 (t, 2 H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 154.8 (s), 134.7 (s), 133.6 (d), 129.2 (d), 127.5 (d), 127.3 (s), 126.2 (d), 125.1 (d), 124.7 (d), 124.2 (d), 117.5 (t), 52.7 (d), 52.4 (q), 37.7 (t). Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59. Found: C, 73.28; H, 6.65.

1-(Methoxycarbonyl)-2-(2-methyl-2-propenyl)-1,2-dihydroquinoline (17b): MS m/z (relative intensity) 243 (M^+, 2), 188 ($M^+ - 55$, 100), 144 (59); ^1H NMR ($CDCl_3$) δ 7.54 (d, 1 H, J = 7 Hz), 6.82–7.29 (m, 3 H), 6.40 (d, 1 H, J = 9 Hz), 5.95 (dd, 1 H, J = 6 and 9 Hz), 4.97–5.35 (m, 1 H), 4.74 (br s, 1 H), 4.52 (br s, 1 H), 3.68 (s, 3 H), 1.93–2.22 (m, 2 H), 1.28 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 154.8 (s), 141.1 (s), 134.2 (s), 129.7 (d), 127.4 (d), 127.3 (s), 126.2 (d), 125.1 (d), 124.9 (d), 124.2 (d), 113.6 (t), 52.7 (q), 50.8 (d), 41.0 (t), 22.2 (q). Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04. Found: C, 73.80; H, 6.99.

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