Oxidative Generation of *N*-Acyliminium Ions from *N*-1-(Tributylstannyl)alkyl Carboxamides and Carbamates and Their Reactions with Carbon Nucleophiles

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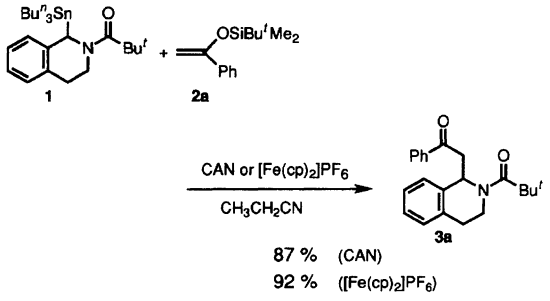
Oxidation of *N*-1-(tributylstannyl)alkyl carboxamides and carbamates with ammonium hexanitratocerate-(IV) or ferrocenium hexafluorophosphate generates their *N*-acyliminium ions by the elimination of tributylstannyl radical under mild reaction conditions. The iminium ions thus formed react with various carbon nucleophiles to give the corresponding addition products.

Although a variety of cation radicals can be generated from organosulfur and nitrogen compounds, these species have been hardly utilized for carbon–carbon bond forming reactions.[1] Recently we reported a method for the transformation of cation radicals of sulfides into carbocations by the use of stannyl sulfides.[2] That is, cation radicals of 2-tributylstannyl-1,3-dithianes generated by the oxidation with metallic oxidants readily cleave into the α-carbocations of sulfides by eliminating tributylstannyl radical, which react with various carbon nucleophiles such as silyl enol ethers.[3]

Application of this method was further examined to generate iminium ions from cation radicals of *N*-1-stannylalkylamino derivatives. It was supposed that the oxidation of *N*-1-(tributylstannyl)alkyl carboxamides and carbamates would give their cation radicals, from which the stannyl radical would be eliminated to generate *N*-acyliminium ions, useful synthetic intermediates for the preparation of various organonitrogen compounds.[4] In this paper are disclosed a full accounts on the generation of *N*-acyliminium ions from various *N*-1-(tributylstannyl)alkyl carboxamides and carbamates and on the utilization of these intermediates for carbon–carbon bond formation.[5]

Results and Discussion

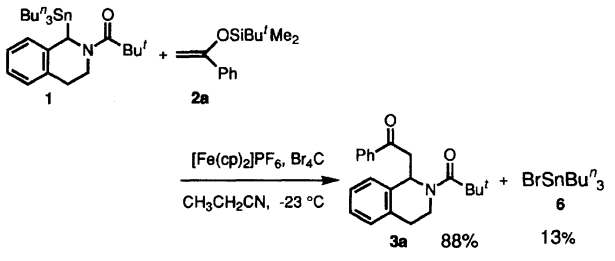
Reactions of 2-Pivaloyl-1-tributylstannyl-1,2,3,4-tetrahydroisoquinoline with Carbon Nucleophiles. 2-Pivaloyl-1-tributylstannyl-1,2,3,4-tetrahydroisoquinoline (**1**) was chosen as a model substrate and was prepared by the stannylation of the anion of 2-pivaloyl-1,2,3,4-tetrahydroisoquinoline generated by the Seebach's method.[6] The reaction of **1** and α-(*t*-butyldimethylsiloxy)styrene (**2a**) was tried in the presence of 2 molar amounts of various metallic oxidants such as Mn^{III}, Ag^{II}, Fe^{III}, and Ce^{IV} compounds. When ammonium hexanitratocerate(IV) (CAN) or ferrocenium hexafluorophosphate[7] ($[Fe(cp)_2]PF_6$) was used as an oxidant, the addition product **3a** was obtained in 87% or 92% yield respectively by the treatment of a mixture of **1** and 2 molar amounts of **2a** in propiononitrile with CAN at −23 °C or with $[Fe(cp)_2]PF_6$ at 0 °C (Eq. 1).



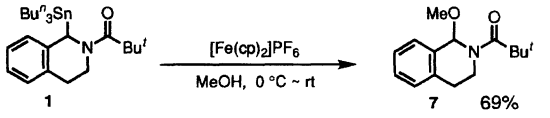
(1)

The cation radical **4** was considered to fragment into the *N*-acyliminium ion **5** and tributylstannyl radical in the same manner as the cleavage of the cation radicals of the 2-tributylstannyl-1,3-dithianes,[3] and the resulting *N*-acyliminium ion **5** reacts electrophilically with the silyl enol ether **2a** (Scheme 1).

To confirm the formation of tributylstannyl radical, **1** was treated with **2a** and CAN in the presence of carbon tetrabromide as a radical trapping reagent.[8] Actually, bromotributylstannane (**6**) was obtained along with the addition product **3a** (Eq. 2). The formation of the *N*-acyliminium ion was also supported by the reaction with methanol: When **1** was treated with $[Fe(cp)_2]PF_6$ in methanol, 1-methoxy-2-pivaloyl-1,2,3,4-tetrahydroisoquinoline (**7**) was obtained (Eq. 3).



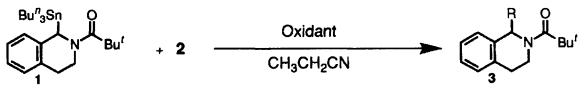
(2)

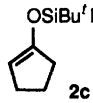


(3)

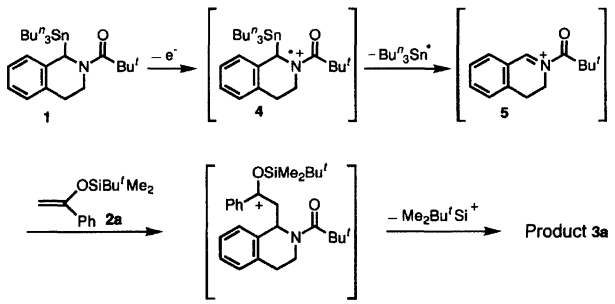
As the cation radical **4** apparently fragments to form the *N*-acyliminium ion **5**, the reactions of the 1-stannylisoquinoline **1** and various carbon nucleophiles **2** were

Table 1. The Reactions of **1** with Carbon Nucleophiles **2**



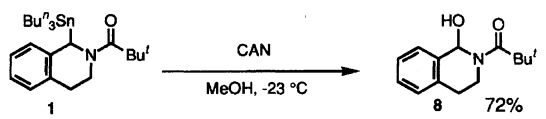
C-Nucleophile	Oxidant	Temp/°C	Product (R)	Yield/%
 **2a**	CAN	−23	$PhCOCH_2-$	87
	$[Fe(cp)_2]PF_6$	0	**3a**	92
 **2b**	$[Fe(cp)_2]PF_6$	−23	Pr^iCOCH_2- **3b**	72
 **2c**	$[Fe(cp)_2]PF_6$	−23	 **3c**	74[a]
 **2d**	CAN	−23	EtO_2CCH_2-	62
	$[Fe(cp)_2]PF_6$	0	**3d**	73
 **2e**	$[Fe(cp)_2]PF_6$	−23	$CH_2=CHCOCH_2-$ **3e**	43
 **2f**	$[Fe(cp)_2]PF_6$	−23	**3a**	90
 **2g**	$[Fe(cp)_2]PF_6$	−23	CH_3COCH_2- **3g**	76
 **2h**	$[Fe(cp)_2]PF_6$	−23—r.t.	 **3h**	32
 **2i**	CAN	−23	$CH_2=CHCH_2-$	17
	$[Fe(cp)_2]PF_6$	r.t.	**3i**	61
 **2j**	CAN	−23	**3i**	48
	$[Fe(cp)_2]PF_6$	r.t.		62
Me_3SiCN **2k**	$[Fe(cp)_2]PF_6$	r.t.	NC- **3k**	53

a) Diastereomer ratio 1 : 1.



Scheme 1.

examined in the presence of CAN or $[Fe(cp)_2]PF_6$. As shown in Table 1, **1** reacted with various electron-rich olefins such as aromatic and aliphatic silyl enol ethers **2a**—**c**, a ketene silyl acetal **2d**, vinyl ethers **2f** and **2g**, giving the addition products in good yield. Furthermore, the addition reaction proceeded with such weak nucleophiles as furan (**2h**), allyltrimethylsilane (**2i**), allyltriphenylstannane (**2j**), and cyanotrimethylsilane (**2k**), and the corresponding addition products were obtained in reasonable yield. In these reactions, $[Fe(cp)_2]PF_6$ was found to be a more suitable oxidant as compared with CAN in respect to the product yield, particularly in the reactions with less reactive nucleophiles such as furan (**2h**) and allyltrimethylsilane (**2i**). That is, the reaction of **1** and the allylsilane **2i** with CAN gave 2-privaloyl-1,2,3,4-tetrahydro-1-isoquinolinol (**8**) as a main product in 53% yield and the desired product **3i** was isolated only in 13% yield. Treatment of **1** with CAN in methanol also introduced a hydroxyl group to give the isoquinolinol **8** without yielding the 1-methoxyisoquinoline **7** (Eq. 4). The formation of the isoquinolinol **8** suggests that the iminium intermediate **5** is attacked preferentially by nitrate rather than by the nucleophiles such as the allylsilane **2i** and methanol.



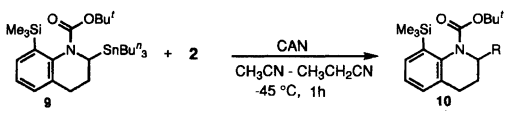
(4)

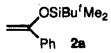
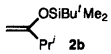
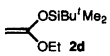
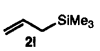
Reactions of *N*-1-Stannylalkyl Carbamates and Carbon Nucleophiles. As mentioned above, a benzylic iminium ion, the *N*-acylisoquinolinium ion **5**, is generated under the mild reaction conditons by the introduction of a stannyl group to the amide. To examine the generality of this method to generate non-benzylic iminium ions, various *N*-1-stannylalkyl carbamates were prepared and submitted for the oxidation with metallic oxidants.

A carbamate of 2-stannylquinoline, 1-*t*-butoxycarbonyl-2-tributylstannyl-8-trimethylsilyl-1,2,3,4-tetrahydroquinoline (**9**) was treated with the silyl enol ether **2a** in the presence of $[Fe(cp)_2]PF_6$, but the stannylquinoline **9** was recovered. In contrast with the stannylisoquinoline **1**, the oxidation potential of the quinoline **9** is higher than that of **1** and the quinoline **9** was hard to be oxidized with $[Fe(cp)_2]PF_6$. But the oxidation with CAN proceeded smoothly and **9** reacted with various carbon nucleophiles. Table 2 shows the results of these experiments. Similar to the reactions of the isoquinoline **1**, the stannylquinoline **9** reacted with the electron-rich olefins **2a**, **2b**, and **2d**, and cyanotrimethylsilane (**2k**), giving the addition products **10** in good yield. But the reaction of **9** and the allylsilane **2i** didn't give the desired product and afforded a complex mixture. Taking account of the result observed in the allylation of the isoquinoline **1**, the attack of nitrate to the iminium intermediate generated from the quinoline **9** seems to proceed preferentially over the attack of a weak nucleophile such as the allylsilane **2i**.

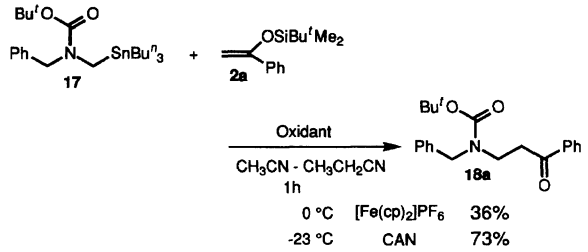
In addition to the stannyl isoquinoline and quinoline, iminium ions were also generated from stannyl carbamates prepared from cyclic amines. According to the Beak and Lee's method,[9] tributylstannyl group was introduced to various carbamate derivatives of monocyclic amines such as pyrrolidine, piperidine, and perhydroazepine. These cyclic carbamates **11**, **12**, and **13** were also hard to be oxidized with $[Fe(cp)_2]PF_6$, and CAN was employed as the oxidant. As shown in Table 3, the present method was well applied for the introduction of side chain into the 2-position of pyrrolidine, piperidine, and perhydroazepine derivatives, and the key intermediates for the synthesis of pyrrolidine and piperidine alkaloids[10] were prepared in good yield. Only the stannylpiperidine **12** exceptionally failed to react with allyltrimethylsilane (**2i**).

Table 2. The Reactions of **9** with Carbon Nucleophiles **2**

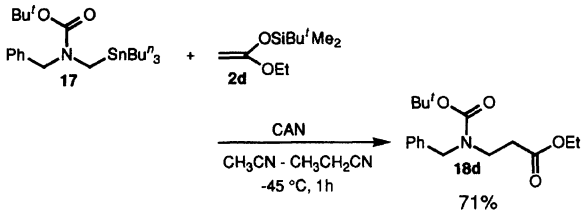


C-Nucleophile	Product (R)	Yield/%
	$PhCOCH_2$– **10a**	87
	Pr^iCOCH_2– **10b**	79
	EtO_2CCH_2– **10d**	76
Me_3SiCN **2k**	NC– **10k**	75
	—	0

From a carbamate of an acyclic stannyl amine, *t*-butyl (*N*-benzyl-*N*-tributylstannylmethyl)carbamate (**17**), the iminium ion was also generated by the oxidation with CAN and reacted with **2a** and a ketene silyl acetal **2d** to afford the adducts **18** (Eqs. 5 and 6).



(5)

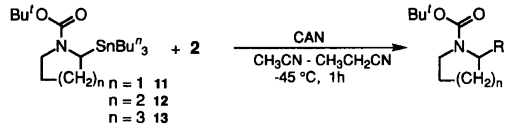


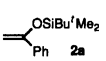
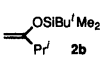
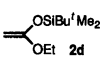
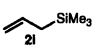
(6)

Although these nitrogen compounds containing a stannyl group were readily oxidized with CAN, their parent compounds having no stannyl group were not oxidized with CAN or $[Fe(cp)_2]PF_6$ under the same reaction conditions. The oxidation potentials (E_{ox}) of the stannyl nitrogen compounds were measured by cyclic voltammogram and compared with those of the parent compounds. For example, E_{ox} value of the stannyl amide **1** was 1.28 V lower than that of the parent compound and E_{ox} value of the stannylquinoline **9** was 0.52 V lower than that of the non-substituted compound (vs. Ag/Ag^+, CH_3CN, irreversible). Thus, the introduction of a stannyl group lowers the oxidation potentials of amides and carbamates. The same effect of stannyl, silyl or germyl group on lowering the oxidation potentials of ethers and sulfides has been also reported in detail.[11]

Generally *N*-1-stannylalkyl carboxamides and carbamates are utilized as precursors of α-amino carbanions.[12] In contrast, the present method enables the generation of the cationic species, *N*-acyliminium ions. By the electrooxidation of amines, an alkoxyl or a hydroxyl group is introduced on the α-carbon of amines,[13] and it is known that α-alkoxyl amino compounds can be transformed to iminium ions under acidic conditions, particularly with Lewis acids.[14] The oxidation of *N*-1-stannylalkyl nitrogen compounds realizes an

Table 3. The Reactions of **11**—**13** with Carbon Nucleophiles **2**



C-Nucleophile	Product (R)	n		Yield/%
	PhCOCH$_2$–	1	**14a**	92
		2	**15a**	87
		3	**16a**	85
	Pr^{i}COCH$_2$–	1	**14b**	94
		2	**15b**	76
		3	**16b**	90
	EtO$_2$CCH$_2$–	1	**14d**	85
		2	**15d**	79
		3	**16d**	82
	NC–	1	**14k**	89
		2	**15k**	80
		3	**16k**	83
	CH_2=$CHCH_2$–	1	**14i**	89
		2	—	0
		3	**16i**	83

alternative method for the generation of the iminium ions under almost neutral conditions.

Experimental

General. IR spectra were measured with a Horiba FT 300-S spectrometer. ^{1}H NMR spectra (500 MHz) were recorded on a Bruker AM 500 spectrometer with $CHCl_3$ (δ=7.24) as an internal standard. ^{13}C NMR spectra (125 MHz) were recorded on a Bruker AM 500 spectrometer with $CDCl_3$ (δ=77.00) as an internal standard. In the ^{13}C NMR spectra, the rotameric resonance is placed in parentheses after the first resonance. High-resolution mass spectra were recorded on JEOL JMS-SX102A mass spectrometer operating at 70 eV. All melting points are uncorrected.

Cyclic voltammetry was measured with a Hokuto Denko HA-151 potentiostat/galvanostat connected to a Hokuto Denko HA-111 function generator with Riken Denshi F-35 X-Y recorder. We used an undevided cell equipped with platinum disk anode and a platinum wire cathode in 0.1 M Et_4NClO_4/CH_3CN (1 M=1 mol dm^{-3}). Ag/AgI (saturated NaI solution in CH_3CN) electrode was used as the reference. The sweep rate was 100 mV s^{-1}.

Acetonitrile and propiononitrile were distilled from P_2O_5, then CaH_2, and dried over Molecular Sieves 4A (MS 4A). CAN (Kanto Chemical Co., Inc., guaranteed grade) was dried under vacuum at 80 °C before use. $[Fe(cp)_2]PF_6$, was prepared by the known method.[7] Silyl enol ethers (**2a**—**2e**),[15] vinyl ethers (**2f** and **2g**),[16] allyltrimethylsilane (**2i**),[17] allyltriphenylstannane (**2j**),[18] and cyanotrimethylsilane (**2k**)[19] were synthesized according to the literature procedures.

Reactions were monitored by thin-layer chromatography (TLC) using pre-coated silica-gel plates (Merck Kieselgel 60 F-254 Art.5715). Silica-gel column chromatography was carried out with Merch Kieselgel 60 Art.7734. Preparative TLC was performed on a silica-gel (Wakogel B-5F).

All the reactions were carried out under an argon atmosphere.

Preparation of *N*-1-(Tributylstannyl)alkyl Carboxamides and Carbamates. 2-Pivaloyl-1-tributylstannyl-1,2,3,4-tetrahydroisoquinoline (**1**) was prepared according to a literature.[6] 1-*t*-Butoxycarbonyl-2-tributylstannylpyrrolidine (**11**), 1-*t*-butoxycarbonyl-2-tributylstannylpiperidine (**12**), and 1-*t*-butoxycarbonyl-2-tributylstannylperhydroazepine (**13**) were prepared by the method of Beak and Lee.[9] 1-*t*-Butoxycarbonyl-2-tributylstannyl-8-trimethylsilyl-1,2,3,4-tetrahydroquinoline (**9**) was prepared from 1-*t*-butoxycarbonyl-8-trimethylsilyl-1,2,3,4-tetrahydroquinoline[9] in the same manner of the Beak's method[9] and purified by silica-gel column chromatography. *t*-Butyl (*N*-benzyl-*N*-tributylstannylmethyl)carbamate (**17**) was prepared from tributylstannylmethyliodide and *t*-butyl *N*-benzylcarbamate in the same manner of a literature[12] and purified by silica-gel column chromatography. Spectral data and physical properties of the new compounds are as follows.

1-*t*-Butoxycarbonyl-2-tributylstannyl-8-trimethylsilyl-1,2,3,4-tetrahydroquinoline (9). Colorless oil; IR (neat) 2954, 2924, 2866, 1680, 1377, 1248, and 1169 cm^{-1}; ^{1}H NMR δ=0.24 (9H, s), 0.81—0.90 (15H, m), 1.26 (9H, s), 1.28—1.32 (6H, m), 1.45—1.48 (6H, m), 1.81—1.85 (1H, m), 2.30—2.40 (2H, m), 2.50—2.53 (1H, m), 2.64—2.69 (1H, m), 7.01 (1H, br), 7.11—7.12 (1H, m), and 7.29—7.30 (1H, m); ^{13}C NMR δ=0.05, 11.37, 13.75, 26.60, 27.66, 28.00, 28.50, 29.31, 45.23, 79.85, 125.51, 128.88, 132.49, 134.78, 135.41, 150.35, and 157.66. HRMS Found: *m/z* 595.2853. Calcd for $C_{29}H_{53}NO_2SiSn$: M, 595.2873.

***t*-Butyl (*N*-Benzyl-*N*-tributylstannylmethyl)carbamate (17).** Colorless oil; IR (neat) 2954, 2920, 1680, 1456, 1400, 1242, 1161, 879, and 702 cm^{-1}; ^{1}H NMR δ= 0.78—0.87 (15H, m), 1.24—1.28 (6H, m), 1.35—1.50 (6H, m), 1.43, 1.44 (9H, 2s), 2.77, 2.96 (2H, 2t, *J*=12.9 Hz), 4.38 (2H, s), 7.20—7.26 (3H, m), and 7.29—7.32 (2H, m). HRMS Found: *m/z* 511.2469. Calcd for $C_{25}H_{45}NO_2SSn$: M, 511.2477.

General Procedure for the Reaction of 2-Pivaloyl-1-tributylstannyl-1,2,3,4-tetrahydroisoquinoline (1) with Carbon Nucleophiles. To a propiononitrile (15 ml) solution of $[Fe(cp)_2]PF_6$ (0.70 g, 2.1 mmol) was added a propiononitrile (5.0 ml) solution of 2-pivaloyl-1-tributylstannyl-1,2,3,4-tetrahydroisoquinoline (**1**) (0.51 g, 1.0 mmol) and the carbon nucleophile **2** (2.0 mmol) at −45 °C—r.t. After stirring for 1 h, saturated aqueous solution of sodium hydrogencarbonate was added to the reaction mixture, and the mixture was filtered through Celite. Organic materials were extracted with dichloromethane, and the combined extracts were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by column chromatography (hexane : ethyl acetate=1 : 3, v/v) or preparative TLC (hexane : ethyl acetate=1 : 4) to afford the desired product **3**.

Spectral data and physical properties of the products are as follows.

1-Phenacyl-2-pivaloyl-1,2,3,4-tetrahydroisoquinoline (3a). Colorless crystals; mp 130 °C (hexane-ethyl acetate); IR (KBr) 3527, 1668, 1618, 1277, and 746 cm^{-1};

^{1}H NMR δ=1.25 (9H, s), 2.81 (1H, dt, J=16.2 and 3.3 Hz), 2.96—3.03 (1H, m), 3.33 (1H, dd, J=15.0 and 5.8 Hz), 3.53 (2H, br), 4.32 (1H, m), 6.15 (1H, t, J=5.8 Hz), 7.10—7.18 (4H, m), 7.43—7.46 (2H, m), 7.52—7.55 (1H, m), and 7.97—7.99 (2H, m); ^{13}C NMR δ=28.13, 28.63, 38.79, 40.18, 45.92, 51.33, 126.32, 126.83, 127.01, 128.24, 128.57, 128.77, 133.04, 133.35, 136.94, 137.05, 176.52, and 197.45. Found: C, 78.60; H, 7.55; N, 4.45%. Calcd for $C_{22}H_{25}NO_2$: C, 78.77; H, 7.51; N, 4.18%.

2-Pivaloyl-1-(3-methyl-2-oxobutyl)-1,2,3,4-tetrahydroisoquinoline (3b). Colorless crystals; mp 94—95 °C (hexane-ethyl acetate); IR (KBr) 3388, 2970, 1703, 1616, 1479, and 1173 cm^{-1}; ^{1}H NMR δ=1.02 (3H, d, J=6.8 Hz), 1.09 (3H, d, J=7.0 Hz), 1.26 (9H, s), 2.68—2.78 (3H, m), 2.93—3.00 (1H, m), 3.07 (1H, br), 3.42 (1H, br), 4.31 (1H, br), 5.97 (1H, t, J=6.6 Hz), 7.08—7.13 (4H, m); ^{13}C NMR δ=17.63, 18.43, 28.14, 28.79, 38.76, 39.76, 40.76, 47.59, 50.67, 126.33, 126.76, 128.86, 133.28, 137.21, 176.46, and 211.58. Found: C, 75.50; H, 8.89; N, 4.76%. Calcd for $C_{19}N_{27}NO_2$: C, 75.71; H, 9.03: N, 4.65%.

1-(2-Oxocyclopentyl)-2-pivaloyl-1,2,3,4-tetrahydroisoquinoline (3c). Less polar isomer: Colorless oil; IR (neat) 2966, 2879, 1736, 1626, 1414, 1157, and 756 cm^{-1}; ^{1}H NMR δ=1.29 (9H, s), 1.62—1.76 (2H, m), 2.02—2.28 (4H, m), 2.42 (1H, br), 2.75—2.83 (1H, m), 2.92—2.99 (1H, m), 3.60 (1H, br), 4.27 (1H, br), 5.74 (1H, br), 7.01 (1H, br), and 7.06—7.17 (3H, m). HRMS Found: m/z 299.1884. Calcd for $C_{19}H_{25}NO_2$: M, 299.1887.

More polar isomer: Colorless oil; IR (neat) 2970, 1726, 1612, 1419, 1180, and 748 cm^{-1}; ^{1}H NMR δ=1.29 (9H, s), 1.61—1.77 (2H, m), 2.00—2.04 (1H, m), 2.11 (1H, br), 2.24—2.27 (2H, m), 2.42 (1H, br), 2.75—2.78 (1H, m), 2.94—3.00 (1H, m), 3.37 (1H, br), 4.29 (1H, br), 5.59 (1H, d, J=4.3 Hz), 7.06—7.07 (1H, m), 7.11—7.14 (1H, m), 7.16—7.19 (1H, m), and 7.44—7.45 (1H, m). HRMS Found: m/z 299.1881. Calcd for $C_{19}H_{25}NO_2$: M, 299.1887.

1-Ethoxycarbonylmethyl-2-pivaloyl-1,2,3,4-tetrahydroisoquinoline (3d). Colorless crystals; mp 86—87 °C (hexane–ethyl acetate); IR (KBr) 3303, 2974, 1732, 1624, 1292, and 754 cm^{-1}; ^{1}H NMR δ=1.24 (3H, t, J=7.2 Hz), 1.29 (9H, s), 2.71—2.79 (3H, m), 2.94—3.01 (1H, m), 3.43 (1H, br), 4.10 (2H, q, J=7.2 Hz), 4.32 (1H, br), 5.98 (1H, br), 7.08—7.10 (1H, m), and 7.14—7.18 (3H, m); ^{13}C NMR δ=14.11, 28.27, 28.91, 38.85, 39.81, 41.67, 51.25, 60.71, 126.37, 126.90, 127.01, 128.84, 133.42, 136.57, 170.74, and 176.47. Found: C, 71.18; H, 8.33; N, 4.77%. Calcd for $C_{18}H_{25}NO_3$: C, 71.26; H, 8.31; N, 4.62%.

1-(2-Oxo-3-butenyl)-2-pivaloyl-1,2,3,4-tetrahydroisoquinoline (3e). Colorless oil; IR (neat) 3425, 3386, 2960, 1664, 1616, 1419, and 762 cm^{-1}; ^{1}H NMR δ=1.28 (9H, s), 2.78 (1H, dt, J=14.0 and 3.1 Hz), 2.92 (1H, dd, J=14.3 and 6.9 Hz), 2.95—3.01 (1H, m), 3.14 (1H, br), 3.49 (1H, br), 4.30 (1H, br), 5.86 (1H, d, J=10.8 Hz), 6.02 (1H, t, J=6.7 Hz), 6.29 (1H, d, J=17.6 Hz), 6.45 (1H, dd, J=17.6 and 10.6 Hz), 7.09—7.11 (1H, m), and 7.13—7.16 (3H, m). HRMS Found: m/z 216.1399. Calcd for $C_{14}H_{18}NO$: M−C_4H_5O, 216.1389.

1-Acetonyl-2-pivaloyl-1,2,3,4-tetrahydroisoquinoline (3g). Colorless oil; IR (neat) 2970, 1711, 1626, 1415, 1167, and 756 cm^{-1}; ^{1}H NMR δ=1.27 (9H, s), 2.25 (3H, s), 2.71—2.77 (2H, m), 2.94—3.01 (1H, m), 3.11—3.16 (1H, m), 3.44 (1H, br), 4.29 (1H, br), 6.01—6.04 (1H, m), 7.08—7.10 (1H, m), and 7.14—7.16 (3H, m). HRMS Found: m/z 273.1721. Calcd for $C_{17}H_{23}NO_2$: M, 273.1730.

1-(2-Furyl)-2-pivaloyl-1,2,3,4-tetrahydroisoquinoline (3h). Colorless oil; IR (neat) 2976, 1631, 1412, 1176, and 742 cm^{-1}; ^{1}H NMR δ=1.32 (9H, s), 2.75—2.78 (1H, m), 3.00—3.07 (1H, m), 3.42 (1H, br), 4.29 (1H, br), 5.95 (1H, br), 6.23 (1H, dd, J=3.0 and 1.9 Hz), 6.76 (1H, br), 7.14—7.20 (4H, m), and 7.31 (1H, s). HRMS Found: m/z 283.1559. Calcd for $C_{18}H_{21}NO_2$: M, 283.1573

1-Allyl-2-pivaloyl-1,2,3,4-tetrahydroisoquinoline (3i). Colorless oil; IR (neat) 2976, 1628, 1417, 1171, 914, and 754 cm^{-1}; ^{1}H NMR δ=1.28 (9H, s), 2.52—2.63 (2H, m), 2.72—2.76 (1H, m), 2.92—2.99 (1H, m), 3.47 (1H, br), 4.25 (1H, br), 4.97—5.00 (2H, m), 5.73 (1H, br), 5.79—5.88 (1H, m), 7.07—7.09 (1H, m), and 7.11—7.14 (3H, m). HRMS Found: m/z 257.1776. Calcd for $C_{17}H_{23}NO$: M, 257.1781

1-Cyano-2-pivaloyl-1,2,3,4-tetrahydroisoquinoline (3k). Colorless crystals; mp 131 °C (hexane–ethyl acetate); IR (KBr) 2978, 2943, 2231, 1630, 1408, 1169, and 750 cm^{-1}; ^{1}H NMR δ=1.34 (9H, s), 2.83—2.88 (1H, m), 2.99—3.06 (1H, m), 3.57—3.63 (1H, m), 4.39—4.44 (1H, m), 6.38 (1H, s), 7.17—7.18 (1H, m), and 7.27—7.29 (2H, m), and 7.32—7.34 (1H, m); ^{13}C NMR δ=27.93, 28.41, 38.92, 42.12, 45.68, 118.19, 127.31, 127.39, 128.54, 128.70, 129.21, 133.51, and 177.06. Found: C, 74.26; H, 7.55; N, 11.45%. Calcd for $C_{15}H_{18}N_2O$: C, 74.35; H, 7.49; N, 11.56%.

1-Methoxy-2-pivaloyl-1,2,3,4-tetrahydroisoquinoline (7). Reaction was carried out in methanol as a nucleophile and solvent. Colorless oil; IR (neat) 3340, 2960, 1724, 1628, 1257, 1086, and 756 cm^{-1}; ^{1}H NMR δ=1.06 (9H, s), 3.11 (2H, t, J=6.7 Hz), 3.50—3.54 (2H, m), 3.88 (3H, s), 6.34 (1H, br), 7.23—7.27 (2H, m), 7.41—7.44 (1H, m), and 7.83—7.85 (1H, m). HRMS Found: m/z 247.1578. Calcd for $C_{15}H_{21}NO_2$: M, 247.1573.

2-Pivaloyl-1,2,3,4-tetrahydro-1-isoquinolinol (8). Colorless crystals; mp 71—72 °C (hexane–ethyl acetate); IR (KBr) 3336, 2970, 1695, 1637, 1537, 1217, 762, and 661 cm^{-1}; ^{1}H NMR δ=1.09 (9H, s), 3.22 (2H, t, J=6.9 Hz), 3.48 (2H, dd, J=12.8 and 6.8 Hz), 5.97 (1H, bs), 7.28—7.29 (1H, m), and 7.39—7.42 (1H, m), 7.49—7.52 (1H, m), 7.76—7.78 (1H, m), and 10.15 (1H, s). Found: C, 71.80; H, 8.07; N, 5.96%. Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00%.

General Procedure for the Reaction of 1-*t*-Butoxycarbonyl-2-tributylstannyl-8-trimethylsilyl-1,2,3,4-tetrahydroquinoline (9) with Carbon Nucleophiles. To a propiononitrile (10 ml) and acetonitrile (10 ml) solution of CAN (1.25 g, 2.28 mmol) was added a propiononitrile (5.0 ml) solution of 1-*t*-butoxycarbonyl-2-tributylstannyl-8-trimethylsilyl-1,2,3,4-tetrahydroquinoline (**9**) (0.68 g, 1.1 mmol) and the carbon nucleophile **2** (2.3 mmol) at −45 °C. After stirring for 2 h, saturated aqueous solution of sodium hydrogencarbonate was added to the reaction mixture, and the mixture was filtered through Celite. Organic materials were extracted with dichloromethane, and the combined extracts were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by column chromatography (hexane : ethyl acetate=1 : 6, v/v) to afford the desired product **10**.

Spectral data and physical properties of the products are as follows.

1-*t*-Butoxycarbonyl-2-phenacyl-8-trimethylsilyl-1,

2,3,4-tetrahydroquinoline (10a). Colorless oil; IR (KBr) 3057, 2970, 2954, 2902, 1697, 1687, 1587, 1369, 758, and 690 cm^{-1}; ^1H NMR δ=0.33 (9H, s), 1.37 (2H, br), 1.55 (9H, br s), 2.46—2.59 (2H, m), 2.90 (1H, br), 3.52—3.55 (1H, m), 5.03 (1H, br), 7.10—7.15 (2H, m), 7.43—7.46 (3H, m), 7.54—7.57 (1H, m), and 7.92—7.94 (2H, m); ^{13}C NMR δ=0.27, 26.82, 28.22, 31.43, 44.90, 52.06, 80.51, 124.90, 127.81, 128.42, 133.00, 133.22, 135.83, 136.48, 138.02, 141.25, 155.82, and 197.59. HRMS Found: *m/z* 423.231. Calcd for $C_{25}H_{33}NO_3Si$: M, 423.2231.

1-*t*-Butoxycarbonyl-2-(3-methyl-2-oxobutyl)-8-trimethylsilyl-1,2,3,4-tetrahydroquinoline (10b). Colorless oil; IR (KBr) 2970, 2875, 1705, 1427, 1369, 1248, 1169, and 773 cm^{-1}; ^1H NMR δ=0.26 (9H, s), 1.03, 1.05 (6H, 2d, *J*=6.9 Hz), 1.48—1.53 (2H, m), 1.78 (9H, br s), 2.43—2.59 (4H, m), 2.90—2.93 (1H, m), 4.81 (1H, br), 7.06—7.11 (2H, m), and 7.38—7.39 (1H, m); ^{13}C NMR δ=17.83, 17.89, 26.72, 28.13, 31.30, 40.78, 46.10, 51.32, 81.28, 124.73, 127.71, 133.10, 135.38, 137.92, 141.30, 154.81, and 211.89. HRMS Found: *m/z* 389.2383. Calcd for $C_{22}H_{35}NO_3Si$: M, 389.2388.

1-*t*-Butoxycarbonyl-2-ethoxycarbonylmethyl-8-trimethylsilyl-1,2,3,4-tetrahydroquinoline (10d). Colorless oil; IR (KBr) 2976, 2900, 1736, 1703, 1427, 1369, 1319, 1169, 843, and 764 cm^{-1}; ^1H NMR δ=0.25 (9H, s), 1.22 (2H, t, *J*=7.1 Hz), 1.33—1.58 (2H, m), 1.49 (9H, br s), 2.22—2.53 (3H, m), 2.77 (1H, br), 4.08—4.12 (2H, m), 4.43 (0.1H, br), 4.79 (0.9H, br), 7.07—7.09 (2H, m), and 7.66—7.67 (1H, m); ^{13}C NMR δ=0.31, 14.11, 26.77, 28.33, 31.07, 40.43, 52.20, 60.37, 80.66, 125.04, 127.92, 133.38, 135.44, 138.38, 141.25, 155.06, and 171.03. HRMS Found: *m/z* 391.2158. Calcd for $C_{21}H_{33}NO_4Si$: M, 391.2180.

1-*t*-Butoxycarbonyl-2-cyano-8-trimethylsilyl-1,2,3,4-tetrahydroquinoline (10k). Colorless crystals; mp 111—112 °C (hexane); IR (KBr) 2976, 2900, 2247, 1702, 1429, 1369, 1315, 1250, 1167, 845, and 777 cm^{-1}; ^1H NMR δ=0.30 (9H, s), 1.52 (9H, s), 1.93 (1H, br), 2.29—2.69 (3H, br), 5.25 (0.6H, br), 5.68 (0.4H, br), 7.13—7.18 (2H, m), and 7.43 (1H, br); ^{13}C NMR δ=0.20, (0.29), 25.98, 28.19, 30..61, 43.70, (45.23), 82.20, (82.54), 118.38, 126.08, 128.12, 134.07, 139.10, 139.84, and 153.10. Found: C, 65.20; H, 7.81; N, 8.58%. Calcd for $C_{18}H_{26}N_2O_2Si$: C, 65.42; H, 7.93; N, 8.48%.

General Procedure for the Reaction of Stannyl Cyclic Carbamates 11, 12, and 13 with Carbon Nucleophiles. To a propiononitrile (10 ml) and acetonitrile (10 ml) solution of CAN (1.64 g, 2.1 mmol) was added a propiononitrile (5.0 ml) solution of stannyl cyclic carbamates (1.0 mmol) and the carbon nucleophile **2** (2.0 mmol) at −45 °C. After stirring for 2 h, saturated aqueous solution of sodium hydrogencarbonate was added to the reaction mixture, and the mixture was filtered through Celite. Organic materials were extracted with dichloromethane, and the combined extracts were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by column chromatography (hexane : ethyl acetate=1 : 4, v/v) to afford the desired product.

Spectral data and physical properties of the products are as follows.

1-t-Butoxycarbonyl-2-phenacylpyrrolidine (14a).[10] Colorless crystals; mp 59—60 °C (hexane); IR (KBr) 3425, 2981, 1680, 1599, 1400, 1169, and 758 cm^{-1}; ^1H NMR δ=1.44 (9H, s), 1.74 (1H, br), 1.82—1.86 (2H, m), 2.04 (1H, br), 2.82 (1H, br), 3.32 (1H, br), 3.39 (1H, br), 3.47—3.52 (0.5H, m), 3.74—3.79 (0.5H, m), 4.28—4.34 (1H, m), 7.43—7.46 (2H, m), 7.54 (1H, br), and 7.97—8.00 (2H, m); ^{13}C NMR δ=22.69, (23.47), 28.44, 30.26, (31.26), 42.95, (43.69), 46.13, (46.54), 54.09, (54.28), 79.06, (79.58), 128.08, 128.22, 128.50, 132.91, 133.13, 136.77, 154.17, (154.30), 198.53, and (198.99). Found: C, 70.73; H, 8.01; N, 4.79%. Calcd for $C_{17}H_{23}NO_3$: C, 70.56; H, 8.01; N, 4.84%.

1-*t*-Butoxycarbonyl-2-(3-methyl-2-oxobutyl)pyrrolidine (14b). Colorless oil; IR (KBr) 2970, 2875, 1695, 1460, 1171, and 711 cm^{-1}; ^1H NMR δ=1.06 (6H, d, *J*=6.9 Hz), 1.43 (9H, s), 1.52—1.62 (1H, m), 1.78 (2H, br), 2.01—2.08 (1H, m), 2.40 (1H, dd, *J*=16.6 and 10.0 Hz), 2.56 (1H, br), 2.95—2.98 (0.5H, m), 3.10—3.14 (0.5H, m), 3.29 (2H, br), and 4.10 (1H, br); ^{13}C NMR δ=17.99, (18.14), 22.71, (23.49), 28.41, 30.83, (31.49), 40.92, 44.35, (44.99), 45.99, (46.45), 53.25, (53.46), 78.95, (79.27), 154.15, 213.01, and (213.20). Found: C, 65.68; H, 9.80; N, 5.61%. Calcd for $C_{14}H_{25}NO_3$: C, 65.85; H, 9.87; N, 5.49%.

1-*t*-Butoxycarbonyl-2-ethoxycarbonylmethylpyrrolidine (14d).[20] Colorless oil; IR (KBr) 2976, 2933, 1734, 1695, 1394, 1169, 1032, and 771 cm^{-1}; ^1H NMR δ=1.22 (3H, br s), 1.43 (9H, s), 1.68—1.82 (3H, m), 1.99—2.09 (1H, m), 2.24—2.29 (1H, m), 2.75—2.78 (0.5H, m), 2.91—2.95 (0.5H, m), 3.30 (2H, br), and 4.10 (3H, br); ^{13}C NMR δ=14.03, 22.63, (23.36), 28.31, 30.34, (31.08), 38.36, (39.20), 46.01, (46.40), 53.90, 60.10, 79.00, (79.32), 154.08, and 171.33. Found: C, 60.58; H, 9.03; N, 5.52%. Calcd for $C_{13}H_{23}NO_4$: C, 60.68; H, 9.01; N, 5.44%.

1-*t*-Butoxycarbonyl-2-cyanopyrrolidine (14k).[21] Colorless crystals; mp 58 °C (hexane); IR (KBr) 2976, 2937, 2243, 1695, 1460, 1163, 1122, and 762 cm^{-1}; ^1H NMR δ=1.46, 1.49 (9H, 2s), 2.00—2.23 (4H, m), 3.10—3.51 (1H, m), 3.31—3.36 (1H, m), 3.47—3.51 (1H, m), 4.43, 4.53 (1H, 2br s); ^{13}C NMR δ=23.63, (24.47), 28.12, 30.63, (31.48), 45.54, (45.85), 46.86, (47.01), 80.72, (81.17), 118.99, 152.84, and (153.49). Found: C, 60.95; H, 7.98; N, 14.22%. Calcd for $C_{10}H_{16}N_2O_2$: C, 61.20; H, 8.22; N, 14.27%.

2-Allyl-1-*t*-butoxycarbonylpyrrolidine (14i). Colorless oil; IR (KBr) 3076, 2974, 2877, 1695, 1643, 1369, 1109, and 773 cm^{-1}; ^1H NMR δ=1.44 (9H, s), 1.69—1.92 (4H, m), 2.07—2.13 (1H, m) 2.41—2.53 (1H, br), 3.30—3.38 (2H, m), 3.75—3.87 (1H, m), 5.01 (1H, d, *J*=8.3 Hz), 5.03 (1H, d, *J*=15.6 Hz), and 5.72 (1H, br); ^{13}C NMR δ=22.84, (23.51), 28.44, 29.12, (30.03), 38.10, (38.96), 46.20, (46.59), 56.65, 78.91, 116.85, 135.16, and 154.40. HRMS Found: *m/z* 211.1565. Calcd for $C_{12}H_{21}NO_2$: M, 211.1573.

1-*t*-Butoxycarbonyl-2-phenacylpiperidine (15a). Colorless crystals; mp 79—80 °C (hexane); IR (KBr) 3442, 2974, 2860, 1689, 1599, 1410, 1269, and 694 cm^{-1}; ^1H NMR δ=1.35 (9H, s), 1.54—1.65 (6H, m), 2.84—2.89 (1H, m), 3.13 (1H, dd, *J*=14.4 and 6.1 Hz), 3.20 (1H, dd, *J*=14.4 and 8.6 Hz), 4.01 (1H, br s), 4.81 (1H, br s), 7.44—7.47 (2H, m), 7.53—7.56 (1H, m), and 7.96—7.98 (2H, m); ^{13}C NMR δ=18.81, 25.22, 28.31, 39,10, 48.11, 79.46, 128.22, 128.58, 133.05, 136.76, 154.63, and 198.33. Found: C, 71.14; H, 8.13; N, 4.44%. Calcd for $C_{18}H_{25}NO_3$: C, 71.26; H, 8.31; N, 4.62%.

1-*t*-Butoxycarbonyl-2-(3-methyl-2-oxobutyl)piperidine (15b). Colorless oil; IR (KBr) 2970, 2933, 1693,

1462, 1410, 1367, 1265, and 1163 cm^{-1}; ^1H NMR δ=1.02 (6H, d, J=7.0 Hz), 1.38 (9H, s), 1.42—1.56 (6H, m), 2.53 (1H, dd, J=15.1 and 6.0 Hz), 2.61 (1H, br), 2.69 (1H, dd, J=15.1 and 8.5 Hz), 2.73 (1H, br), 3.90 (1H, br), and 4.64 (1H, br); ^{13}C NMR δ=17.85, 18.01, 18.77, 25.16, 28.08, 28.23, 39.34, 40.57, 47.07, 79.27, 154.56, and 212.31. HRMS Found: m/z 269.2011. Calcd for $C_{15}H_{27}NO_3$: M, 269.3642.

1-*t*-Butoxycarbonyl-2-ethoxycarbonylmethylpiperidine (15d).[21] Colorless oil; IR (KBr) 2976, 2937, 2866, 1736, 1693, 1367, 1267, and 1165 cm^{-1}; ^1H NMR δ=1.18 (3H, t, J=7.1 Hz), 1.38 (9H, s), 1.43—1.61 (6H, m), 2.43—2.52 (2H, m), 2.69—2.74 (1H, m), 3.92 (1H, br), 4.04 (2H, q, J=7.1 Hz), and 4.63 (1H, br); ^{13}C NMR δ=14.05, 18.75, 25.19, 28.08, 28.27, 35.20, 39.08, 47.80, 60.32, 79.35, 154.59, and 171.27. Found: C, 61.68; H, 9.10; N, 51.8%. Calcd for $C_{14}H_{25}NO_4$: C, 61.97; H, 9.29; N, 5.16%.

1-*t*-Butoxycarbonyl-2-cyanopiperidine (15k). Colorless crystals; mp 56 °C (hexane); IR (KBr) 2976, 2860, 2233, 1705, 1398, 1161, 866, and 771 cm^{-1}; ^1H NMR δ=1.46 (9H, s), 1.54—1.92 (6H, m), 2.93 (1H, br), 4.03 (1H, br), and 5.22 (1H, br); ^{13}C NMR δ=20.20, 24.41, 28.12, 28.33, 41.98, 43.76, 81.26, 117.62 and 153.80. Found: C, 62.76; H, 8.65; N, 13.05%. Calcd for $C_{11}H_{18}N_2O_2$: C, 62.83; H, 8.63; N, 13.32%.

1-*t*-Butoxycarbonyl-2-phenacylperhydroazepine (16a). Colorless crystals; mp 72 °C (hexane); IR (KBr) 3437, 2972, 2927, 1680, 1672, 1406, 1180, 987, and 760 cm^{-1}; ^1H NMR δ=1.22—1.27 (2H, m), 1.35, 1.42 (9H, 2s), 1.31—1.54 (2H, m), 1.63—1.78 (3H, m), 1.97—2.07 (1H, m), 2.77—2.93 (2H, m), 3.16 (0.5H, dd, J=14.1 and 5.6 Hz), 3.26 (0.5H, dd, J=14.1 and 5.2 Hz), 3.54—3.57 (0.5H, m), 3.75—3.78 (0.5H, m), 4.38—4.50 (1H, m), 7.42—7.45 (2H, m), 7.50—7.56 (1H, m), 7.93—7.95 (1H, m), and 7.98—8.00 (1H, m); ^{13}C NMR δ=25.32, (25.35), 28.36, (28.46), 28.89, (29.19), 29.50, (29.55), 33.28 (34.40), 41.99, (42.82), 44.02, (44.48), 53.54, (53.75), 79.15, (79.68), 128.32, (128.46), 128.56, (128.63), 132.98, (133.16), 136.87, (137.02), 155.16, (155.57), 198.33, and (198.92). Found: C, 72.07; H, 8.65; N, 4.39%. Calcd for $C_{19}H_{27}NO_3$: C, 71.89; H, 8.57; N, 4.41%.

1-*t*-Butoxycarbonyl-(3-methyl-2-oxobutyl)perhydroazepine (16b). Colorless oil; IR (KBr) 2970, 2925, 1689, 1410, 1365, and 1163 cm^{-1}; ^1H NMR δ=1.02—1.05 (6H, m), 1.18—1.50 (4H, m), 1.41, 1.42 (9H, 2s), 1.61—1.73 (3H, m), 1.99—2.04 (1H, m), 2.42—2.69 (3H, m), 2.73—2.83 (1H, m), 3.51—3.54 (0.5H, m), 3.68—3.71 (0.5H, m), 4.22 (0.5H, br), and 4.30—4.36 (0.5H, m); ^{13}C NMR δ=17.77, (17.84), 17.88, (18.00), 25.10 (25.33), 28.27, (28.31), 28.84, (28.98), 29.13, (29.20), 33.58, (33.94), 40.50, (41.09), 42.14, (42.71), 45.40, (45.67), 52.38, (52.75), 78.87, (79.25), 155.07 (155.32), 212.37, and (212.70). Found: C, 67.59; H, 10.40; N, 5.09%. Calcd for $C_{16}H_{29}NO_3$: C, 67.81; H, 10.31; N, 4.94%.

1-*t*-Butoxycarbonyl-2-ethoxycarbonylmethylperhydroazepine (16d). Colorless oil; IR (KBr) 2974, 2927, 2856, 1736, 1689, 1410, and 1167 cm^{-1}; ^1H NMR δ=1.21—1.25 (3H, m), 1.26—1.53 (4H, m), 1.44, 1.45 (9H, 2s), 1.64—1.78 (3H, m), 2.00—2.10 (1H, m), 2.28—2.34 (1H, m), 2.45—2.51 (1H, m), 2.71—2.78 (1H, m), 3.59—3.62 (0.5H, m), 3.71—3.74 (0.5H, m), 4.06—4.12 (2H, m), 4.19—4.26 (0.5H, m), and 4.36—4.42 (0.5H, m); ^{13}C NMR δ=14.03, (14.07), 25.00, (25.30), 28.30, (28.36), 28.85, 29.25, (29.31), 33.45, (33.74), 39.56, (40.05), 41.92, (42.14), 52.43 (53.38), 60.14, 78.93, (79.27), 155.08, (155.36), and 171.13. Found: C, 62.94; H, 9.26; N, 5.01%. Calcd for $C_{15}N_{27}NO_4$: C, 63.13; H, 9.54; N, 4.91%.

1-*t*-Butoxycarbonyl-2-cyanoperhydroazepine (16k). Colorless oil; IR (KBr) 2976, 2939, 2239, 1699, 1471, 1402, and 1163 cm^{-1}, ^1H NMR δ=1.31—1.58 (3H, m), 1.45, 1.48 (9H, 2s), 1.71—1.72 (2H, m), 1.78—1.84 (2H, m), 2.20—2.29 (1H, m), 2.96—3.04 (1H, m), 3.75—3.78 (0.6H, m), 3.85—3.88 (0.4H, m), 4.74 (0.4H, dd, J=9.6 and 6.8 Hz), and 5.10 (0.6H, dd, J=9.6 and 6.8 Hz); ^{13}C NMR δ=24.08, (24.81), 28.00, 28.16, (28.22), 28.27, (28.49), 32.29, (32.59), 42.96, (43.51), 45.67, (47.09), 80.65, (81.09), 118.96, (119.09), 153.71, and (154.66). Found: C, 64.14; H, 8.86; N, 12.23%. Calcd for $C_{12}H_{20}N_2O_2$: C, 64.26; H, 8.99; N, 12.49%.

2-Allyl-1-*t*-butoxycarbonylperhydroazepine (16i). Colorless oil; IR (KBr) 2972, 2925, 1691, 1412, 1365, 1165, and 984 cm^{-1}; ^1H NMR δ=1.16—1.51 (4H, m), 1.43, 1.44 (9H, 2s), 1.60—1.77 (3H, m), 1.94—2.04 (1H, m), 2.08—2.20 (2H, m), 2.66 (1H, t, J=12.7 Hz), 3.58—3.61 (0.5H, m), 3.74—3.77 (0.5H, m), 3.86—3.91 (0.5H, m), 4.07—4.12 (0.5H, m), 4.94—5.00 (2H, m), and 5.69—5.80 (1H, m); ^{13}C NMR δ=24.98, (25.31), 28.48, 28.89, (29.22), 29.74, 33.74, (34.00), 39.44, (39.78), 41.44, (41.86), 54.29, (55.58), 78.72, (78.96), 116.30, (116.50), 135.41, 155.56, and (155.80). HRMS Found: m/z 239.1877. Calcd for $C_{14}H_{25}NO_2$: M, 239.1886.

General Procedure for the Reaction of *t*-Butyl (*N*-benzyl-*N*-tributylstannylmethyl)carbamate (17) with Carbon Nucleophiles. To a propiononitrile (2 ml) and acetonitrile (2 ml) solution of CAN (0.22 g, 0.41 mmol) was added a propiononitrile (5.0 ml) solution of *t*-butyl (*N*-benzyl-*N*-tributylstannylmethyl)carbamate (**17**) (0.10 g, 0.2 mmol) and the carbon nucleophile **2** (0.4 mmol) at −23 °C. After stirring for 2 h, saturated aqueous solution of sodium hydrogencarbonate was added to the reaction mixture, and the mixture was filtered through Celite. Organic materials were extracted with dichloromethane, and the combined extracts were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by preparative TLC (hexane : ethyl acetate=1 : 6, v/v) to afford the desired product **18**.

Spectral data and physical properties of the products are as follows.

3-(*N*-Benzyl-*N*-*t*-butoxycarbonyl)amino-1-phenyl-1-propanone (18a). Colorless crystals; mp 61 °C (hexane); IR (KBr) 3429, 2978, 2933, 1681, 1595, 1365, 1171, and 696 cm^{-1}; ^1H NMR δ=1.43, 1.45 (9H, 2s), 3.11 (1H, br s), 3.24 (1H, br s), 3.56, 3.61 (2H, 2br s), 4.47 (2H, s), 7.23—7.31 (5H, m), 7.41—7.44 (2H, m), 7.52—7.54 (1H, m), and 7.88—7.91 (2H, m). Found: C, 73.59; H, 7.32; N, 4.26%. Calcd for $C_{21}H_{25}NO_3 \cdot 1/5H_2O$: C, 73.53; H, 7.46; N, 4.08%.

Ethyl 3-(*N*-Benzyl-*N*-*t*-butoxycarbonyl)aminopropanoate (18 d). Colorless oil; IR (KBr) 2978, 2935, 1736, 1695, 1468, 1165, and 700 cm^{-1}; ^1H NMR δ=1.21 (3H, t, J=7.1 Hz), 1.42, 1.43, 1.45, 1.47 (9H, 4s), 2.47 (1H, br), 2.53 (1H, br), 3.40 (1H, br), 3.48 (1H, br), 4.07 (2H, q, J=7.1 Hz), 4.43 (2H, br s), 7.21—7.23 (3H, m), and 7.27—7.30 (2H, m). HRMS Found: m/z 307.1779. Calcd for $C_{17}H_{25}NO_4$: M, 307.1785.

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