Tris(pentafluorophenyl)boron as an Efficient, Air Stable, and Water Tolerant Lewis Acid Catalyst

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Tris(pentafluorophenyl)boron is an efficient, air stable, and water tolerant Lewis acid catalyst for the aldol-type and Michael reactions of silyl enol ethers with carbonyl compounds or other electrophiles (trimethyl orthoformate, dimethyl acetal, and chloromethyl methyl ether), the allylation reaction of allylsilanes with aldehydes, and the Diels–Alder reaction of dienes with α,β-unsaturated aldehydes. A solution of formaldehyde in water is applicable as an electrophile. Also, the aldol-type reaction of ketene silyl acetals with aromatic or aliphatic imines is successfully carried out using the same catalyst.

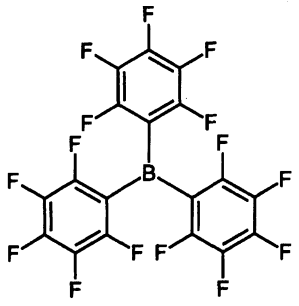
The Lewis acid promoted condensation of trimethylsilyl enol ethers with carbonyl compounds has become a popular tool in organic synthesis, since it is carried out relatively easily from readily available starting materials.[1] This reaction is quite distinguishable from conventional aldol reactions carried out under basic conditions; it proceeds in a highly regioselective manner to afford cross aldols in high yields. However, the method requires a stoichiometric amount of Lewis acid, such as titanium tetrachloride, which can be troublesome with acid labile substrates. In addition, the acidic conditions sometimes lead to dehydration products. Several modifications of the original procedure were designed to overcome these difficulties: the catalytic use of mild Lewis acids, such as trityl salts,[2] fluoride anion,[3] dimethylaluminum chloride,[4] clay montmorillonite,[5] lithium perchlorate,[6] a combined system of diphenyltin sulfide or Lawesson's reagent and silver perchlorate,[7] cationic iron complexes,[8] bismuth(III) chloride–methallic iodide systems,[9] and samarium(II) iodide.[10] These reactions are usually carried out under strictly non-aqueous conditions. The presence of even a small amount of water causes lower yields, probably due to a rapid decomposition or deactivation of the promoters and the hydrolysis of the silyl enol ethers. Kobayashi and his colleagues showed that lanthanide triflates[11] and scandium triflate[12] were useful catalysts for the aldol-type reaction of silyl enol ethers with aldehydes in an aqueous media.

The aldol-type reaction of ketene silyl acetal derivatives with imines in place of aldehydes in the presence of Lewis acids is of great interest owing to its application to β-lactam synthesis.[13] Condensation using a stoichiometric amount of Lewis acid, such as $TiCl_4$, was first reported by Ojima and his colleagues.[14] Recently, the catalysts trimethylsilyl triflate,[15] diphosphonium salts,[16] iron(II) iodide,[17] trityl hexafluoroantimonate,[17] and clay montmorillonite,[18] were successfully applied to the same system. Except for clay montmorillonite, however, use has so far been limited to non-enolizable imines.

To obviate some of these inherent problems associated with classical Lewis acids, we investigated the possibility of developing new classes of catalysts derived from traditional metal complexes. We describe here that tris(pentafluorophenyl)boron (**1**) is an efficient catalyst in the aldol-type reactions of silyl enol ethers or ketene silyl acetals with aldehydes or imines and some other useful carbon–carbon bond formation reactions (Fig. 1).[19]

Results and Discussion

Aldol-Type Reactions of Silyl Enol Ethers with Aldehydes or Other Electrophiles. We chose organoboron reagent **1** as an air stable, water tolerant Lewis acid catalyst, which is readily prepared as a white solid from boron trichloride by a reaction with pentafluorophenyllithium.[20] This reagent does not re-



1

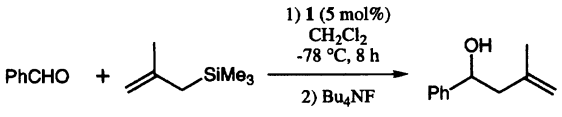
Fig. 1.

act with pure oxygen,[20] and can be readily handled in air. It is also very thermally stable, even at 270 °C, and soluble in many organic solvents.[20] We first determined the effect of the solvents in the model reaction of 1-phenyl-1-trimethylsiloxy-1-propene with benzaldehyde in the presence of 2 mol% of **1**, and found that dichloromethane was the most effective solvent; 1,2-dichloroethane, chloroform, ether, and toluene were relatively less effective; propionitrile and THF gave no desired product, even at room temperature.

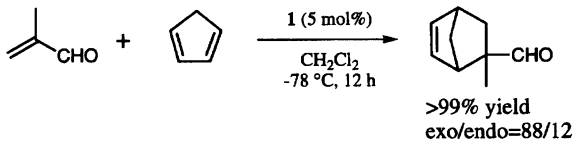
The reactions of various silyl enol ethers or ketene silyl acetals with aldehydes or other electrophiles were explored in order to learn about the generality and scope of the above-mentioned catalytic aldol-type reaction. The results of catalysis are collected in Table 1. Unless otherwise noted, **1** was handled in air (not anhydrous grade). Catalysis was carried out using 2 mol% catalyst loading and a 0.5 M concentration (1 M=1 mol dm^{-3}) in each substrate in a dichloromethane solution. The following characteristic features of these reactions are noted: (1) in every case, the reactions proceeded smoothly under extremely mild conditions to give the corresponding aldol-type adducts in high yields after a treatment with aqueous HCl or TBAF; (2) the products could be isolated as β-trimethylsilyloxy ketones when crude adducts were worked up without acid; (3) aromatic aldehydes were relatively more reactive than aliphatic aldehydes; (4) the present reaction could be carried out in aqueous media so that the reaction of the silyl enol ether derived from propiophenone with a commercial aqueous solution of formaldehyde took place without incident (Entry 10);[11a,11e,12] (5) the rate of an aldol-type reaction was remarkably increased by using an anhydrous solution of **1** in toluene under an argon atmosphere (Entries 2 and 3); (6) silyl enol ether **3** could be reacted with chloromethyl methyl ether (MOMCl) (Entry 11) or trimethylorthoformate (Entry 12); using the above reactions (Entries 10, 11, and 12) we could introduce hydroxymethyl, methoxymethyl, or dimethoxymethyl C1 groups at the α-position of the carbonyl group; (7) the aldol-type reaction of silyl enol ether **3** with benzaldehyde dimethyl acetal also proceeded smoothly to give the corresponding β-methoxy ketone in high yield (Entry 13);[21] (8) **1** was an efficient catalyst for the reaction of ketene silyl acetals with aldehydes; in both aromatic and aliphatic aldehydes the reactions advanced and gave the corresponding adducts in high yields (Entries 14 and 15).[8] In order to clarify the efficiency of the pentafluorophenyl group, it was confirmed that the reaction did not proceed when triphenylboron was used in place of **1** under the same condition with Entry 1.

Michael Reaction of Silyl Enol Ethers with α,β-Unsaturated Ketones. We were interested in determining whether **1** would enable a conjugate addition to α,β-unsaturated ketones which could be realized under catalytic conditions.[6,8,9,22] A complete and regioselective conversion to the desired adduct was, in fact, achieved within a few hours at −78 °C. Several examples are listed in Table 2. In no case was a 1,2-addition product obtained. The product could be isolated as a synthetically valuable silyl enol ether when the crude product was worked up without acid.

Allylation and Diels–Alder Reactions with Aldehydes. Further, **1** was applied as a Lewis acid catalyst for other carbon-carbon bond formation reactions: the allylation reaction[11d,23] of benzaldehyde with 2-methallyltrimethylsilane proceeded smoothly in the presence of a catalytic amount of **1** (not anhydrous grade) to obtain 3-methyl-1-phenyl-3-buten-1-ol (Eq. 1); the Diels–Alder reaction[24] of cyclopentadiene with 2-methyl-2-propanal also proceeded smoothly in the presence of a catalytic amount of **1** (not anhydrous grade) (Eq. 2).

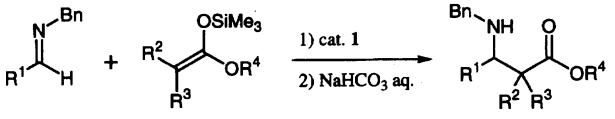


(1)



(2)

Aldol-Type Reaction of Ketene Silyl Acetals with Aromatic or Aliphatic *N*-Benzylimines. In a continuing study, **1** was investigated as a catalyst for the aldol-type reaction between ketene silyl acetals and imines based on the belief that **1** would possibly work as a highly active catalyst because of its stability and comparatively low value of bond energy and affinity toward nitrogen-containing compounds (Eq. 3).[20,25]

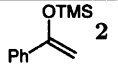
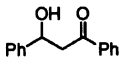
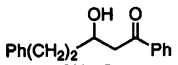
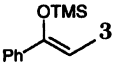
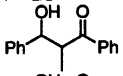
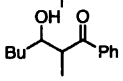
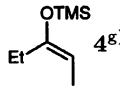
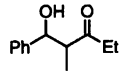
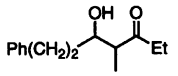
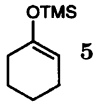
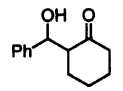
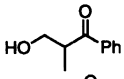
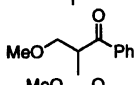
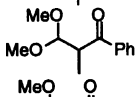
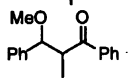
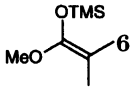
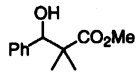
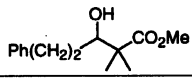


(3)

Although **1** as a white solid can be readily handled in air because of its water tolerance, we used an anhydrous solution of **1** in toluene as a catalyst in the aldol-type reaction of ketene silyl acetals with imines, because imines are very moisture-sensitive compounds under acidic conditions. *N*-Benzylimines derived from various aldehydes and benzylamine were chosen because it is known that β-benzylamino acid esters produced by the present aldol-type reaction are readily debenzylated by hydrogenolysis over palladium on carbon.[26]

The conditions and results of this reaction of ketene silyl acetals with *N*-benzylimines are summarized in Table 3. Catalysis was carried out using 0.2—10 mol% catalyst loading and 0.1 M concentration in each imine

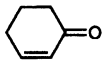
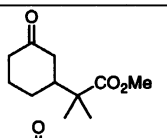
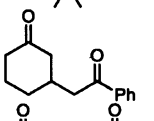
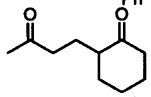
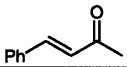
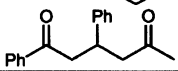
Table 1. Tris(pentafluorophenyl)boron Catalyzed Aldol-Type Reactions[a)]

Entry	Electrophile	Silyl enol ether	Temp °C	Time h	Product	Yield[b)] %
1	PhCHO	 **2**	−78	12		84
2[c)]			−78	6.5		99
3[d)]			−78	6.5		96
4	$Ph(CH_2)_2CHO$		−78	5.5		78
5	PhCHO	 **3**	−78	8		86[e)]
6	BuCHO		0	7		66[f)]
7	PhCHO	 **4**[g)]	−78	6		94[h)]
8	$Ph(CH_2)_2CHO$		−40	2.5		90[i)]
9	PhCHO	 **5**	−40	2.5		85[j)]
10	HCHO[k)]	**3**	0	7		65
11	CH_3OCH_2Cl		25	24		72
12	$CH(OMe)_3$		25	48		65
13	$PhCH(OMe)_2$		0	3.5		95[l)]
14	PhCHO	 **6**	−78	5		96
15	$Ph(CH_2)_2CHO$		0	13.5		84

a) The reaction of silyl enol ether (1.2 molar amount) with electrophile (1.0 molar amount) in the presence of **1** (not anhydrous grade, 2 mol%) was carried out in CH_2Cl_2. b) Yield of isolated, purified product. c) 2 mol% of anhydrous **1** was used. d) 1 mol% of anhydrous **1** was used. e) *syn*/*anti*=55:45 by ^{1}H NMR assay. f) *syn*/*anti*=75:25 by ^{1}H NMR assay. g) *E*/*Z*=84:16. h) *syn*/*anti*=36:64 by ^{1}H NMR assay. i) *syn*/*anti*=38:62 by ^{1}H NMR assay. j) *syn*/*anti*=28:72 by ^{1}H NMR assay. k) To a solution of 37% aqueous HCHO (1 mL) and **1** (0.04 mmol, 10 mol%) in 5:1 mixed solvent (1 mL) of THF–CH_2Cl_2 was added dropwise a solution of silyl enol ether (0.4 mmol) in 5:1 mixed solvent (2 mL) of THF–CH_2Cl_2 at 0 °C for 4.5 h. l) *syn*/*anti*=62:38 by ^{1}H NMR assay.

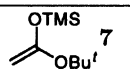
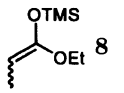
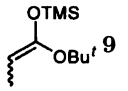
in a toluene solution. The following characteristic features of these reactions are noted: (1) in every case, the reactions proceeded smoothly under extremely mild conditions to give the corresponding β-amino acid esters in high yield after a treatment with aqueous sodium hydrogencarbonate; (2) the aldol-type condensation proceeded smoothly, even with aliphatic enolizable imines derived from primary and secondary aliphatic aldehydes; (3) chemical yields of the β-amino acid esters given in the reaction of aromatic imines were relatively better than aliphatic imines; (4) the reactivities of ketene silyl acetals to *N*-benzylidenebenzylamine were in the order: (*E*)-**9** (R^2=H, R^3=Me)>**7** (R^2=H, R^3=H)>**6** (R^2=Me, R^3=Me)≅(*Z*)-**9** (R^2=Me, R^3=H); (5) reactivities of ketene silyl acetals to *N*-butylidenebenzylamine and *N*-(2-methylbutylidene)benzylamine were in the order: **7**>(*E*)-**8**; and (6) the *syn*–*anti* stereoselectivity in these condensations of *N*-benzylidenebenzylamine was dependent on the geometry of the ketene silyl acetal double bond: (*E*)- and (*Z*)-ketene silyl acetals gave *anti* and *syn* products as major diastereomers, respectively. The different reactivities of ketene silyl acetals with imines, (4) and (5), can be understood in terms of nucleophilicity of ketene silyl acetals and a

Table 2. Tris(pentafluorophenyl)boron Catalyzed Michael Reactions[a)]

Entry	Electrophile	Silyl enol ether	Temp °C	Time h	Product	Yield[b)] %
1		**6**	−78	2.7		85
2		**2**	−78	2		84
3		**5**	−78	4		89
4		**2**	−78	2		93

a) The reaction of silyl enol ether (1.2 molar amount) with electrophile (1.0 molar amount) in the presence of **1** (2 mol%) was carried out in CH_2Cl_2. b) Yield of isolated, purified product.

Table 3. Tris(pentafluorophenyl)boron Catalyzed Aldol-Type Reaction of Imines[a)]

Entry	Imine	Ketene silyl acetal[b)]	*E* : *Z*	Condition °C, h	$B(C_6F_5)_3$ mol%	Yield[c)] %	*anti* : *syn*[d)]
1	PhCH=NBn	 **7**		−78, 13 to 25, 8.5	5	99	
2				−78, 13 to 25, 22.5	2	89	
3		 **8**	85 : 15	−78, 13.5 to 25, 2	1	>99	75 : 25[e)]
4[f)]			85 : 15	−78, 13.5 to 25, 2	1	>99	75 : 25[e)]
5[g)]			85 : 15	−78, 13.5 to 25, 6	0.2	>99	81 : 19[e)]
6		 **9**	>99 : 1	−78, 13 to 25, 4	2	99	80 : 20[e)]
7			>99 : 1	−78, 13 to 25, 8	1	85	75 : 25[e)]
8			<1 : 99	−78, 13 to 25, 4	2	48	26 : 74[e)]
9		**6**		−78, 17 to 25, 4	10	97	
10				−78, 11 to 60, 24	2	68	
11	PrCH=NBn	**7**		−78, 20 to 25, 4	2	>99	
12		**8**	85 : 15	−78, 20 to 25, 4	2	84	[62 : 38][h)]
13	*s*-BuCH=NBn	**7**		−78, 24 to 25, 2	2	>99	
14		**8**	85 : 15	−78, 24 to 25, 2	2	59	N.D.[i)]

a) See typical procedure. b) 2 molar amounts of ketene silyl acetal per imine was used. c) Isolated yield. d) The ratio was determined by ^{1}H NMR analysis. e) The stereochemistry of the products was established on the basis of vicinal coupling constant $J_{2,3}$ ($J_{anti} > J_{syn}$).[14,27)] f) Dichloromethane was used as solvent. g) A 0.25 M solution of imine in toluene. h) The stereochemistry of the products was not determined. i) N. D.=not determined.

steric hindrance between ketene silyl acetals and imines.

The powerful efficiency of **1** as a catalyst in the aldol-type reaction of imines was demonstrated in comparison with other Lewis acid catalysts,[15—18)] as shown in Table 4.

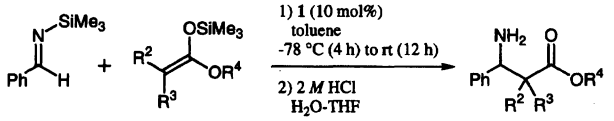
Aldol-Type Reaction of Ketene Silyl Acetals with *N*-Trimethylsilylimines and Synthesis of β-Lactams. The aldol-type reaction of ketene silyl acetals with *N*-trialkylsilylimines in the presence of a stoichiometric amount of zinc iodide or trimethylsilyl triflate was previously reported by Colvin and his colleagues.[28)] The use of *N*-trialkylsilylimine can be advantageous, since *N*-substituent can be easily deprotected from *N*-trialkylsilyl β-amino acid esters produced by the reaction.

We found that **1** was an effective Lewis acid catalyst for the above reaction of *N*-trimethylsilylimines. Although the reaction of non-substituted ketene silyl acetal **7** with *N*-trimethylsilylbenzaldimine in the presence of 10 mol% of **1** almost did not proceed, the reaction of mono- or di-substituted ketene silyl acetal with *N*-trimethylsilylbenzylideneamine proceeded smoothly to give the corresponding β-amino acid ester in good yield (Eq. 4).

Table 4. Lewis Acid Catalyzed Aldol-Type Reaction of Ketene Silyl Acetals with *N*-Benzylidenebenzylamine (PhCH=NBn)

Ketene silyl acetal	Catalyst	mol%	Yield %	Reference
8	**1**	0.2	>99	Table 3
8	Fe-Mont	—[a)]	97	Ref. 18
8	TMSOTf	10	95	Ref. 15, 18
	FeI_2	10	77	Ref. 17
	$TrSbCl_6$	10	71	Ref. 17
6	**1**	10	97	Table 3
6	$(Bu_3P^+)_2O(OTf^-)_2$	7	54	Ref. 16

a) 500 mg of Fe-Mont per 1 mmol of the imine was used.



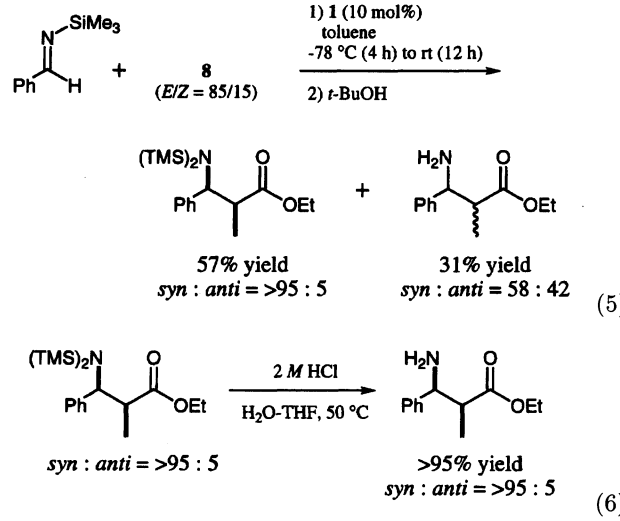
7 <14% yield

8 (*E*/*Z* = 85/15) 82% yield (*syn* : *anti* = 84 : 16)

6 83% yield

(4)

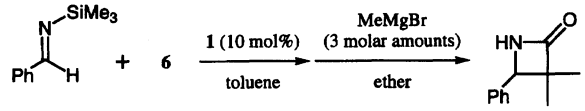
In cases in which the above reaction of **8** with *N*-trimethylsilylbenzylideneamine was quenched with *t*-butyl alcohol before an acidic treatment, ethyl 3-bis(trimethylsilyl)amino-2-methyl-3-phenylpropanoate was isolated in 57% yield and with >95% *syn* selectivity (Eq. 5). Interestingly, this compound is tolerant of a weak acid, such as silica gel and saturated aqueous NH_4Cl. Therefore, the removal of trimethylsilyl groups was performed by an acidic treatment (2 M HCl, 50 °C) to give ethyl 3-amino-2-methyl-3-phenylpropanoate in a quantitative yield (Eq. 6).



(5)

(6)

N-Unsubstituted *β*-lactams have become very attractive synthetic targets. Most existing methods often require elaborate procedures to deblock the nitrogen atom. 3,3-Dimethyl-4-phenylazetidin-2-one was synthesized in moderate yield by an in situ treatment of the intermediate *N*,*N*-bis(trimethylsilyl) *β*-amino acid esters with MeMgBr (Eq. 7).[28)]



(7)

In summary, **1** has been found to be an efficient catalyst not only in the aldol-type or Michael reaction of silyl enol ethers with carbonyl compounds, but also in the aldol-type reaction of ketene silyl acetals with imines. Although **1** acts better as a catalyst for these reactions under an anhydrous condition, **1** exposed to air is also available. This new catalyst is believed to have potential as an air stable and mild Lewis acid catalyst applicable to solving environmental problems in industrial processes.

Experimental

General. Infrared (IR) spectra were recorded on a Shimadzu FTIR-8100 spectrometer. ^{1}H NMR spectra were measured on Varian Gemini 300 (300 MHz) and VXR 500 (500 MHz) spectrometers. The chemical shifts of ^{1}H NMR are expressed in parts per million downfield relative to the internal tetramethylsilane (δ=0 ppm) or chloroform (δ=7.26 ppm). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; br, broad peak. The high-resolution fast atom bombardment mass spectrum (HRFABMS) was conducted at Daikin Industries, Ltd., Japan. The molecular ion is indicated by M^+. For thin-layer chromatographic (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used. The products were purified by preparative column chromatography on silica gel 60 E. Merck Art 9385. Microanalyses were accomplished at School of Agriculture, Nagoya University.

Materials. Tris(pentafluorophenyl)boron as a white solid and its anhydrous solution in toluene were kindly donated by Toso-Akuzo Chemical Co., Ltd., Japan. Reactions involving air- or moisture sensitive compounds were conducted in appropriate round-bottomed flasks with mag-

netic stirring bars under an atmosphere of dry argon. In experiments requiring dry solvents, dichloromethane and toluene were distilled from calcium hydride. Unless otherwise noted, materials were obtained from commercial suppliers, and were used without further purification.

Preparation of Silyl Enol Ethers and Ketene Silyl Acetals. Silyl enol ethers and ketene silyl acetals were prepared in good yields from chlorotrimethylsilane and lithium enolates, which were generated in situ by the addition of the corresponding carbonyl compounds into lithium diisopropylamide (LDA).[29]

1-Phenyl-1-(trimethylsilyloxy)ethylene (2): Obtained from Chisso Co., Ltd., Japan.

(*Z*)-1-Phenyl-1-(trimethylsilyloxy)propene (3):[30] (90% yield, $E/Z = <2/98$); ^{1}H NMR ($CDCl_3$) δ=0.13 (9H, s, $(CH_3)_3Si$), 1.72 (3H, d, J=7 Hz, CH_3), 5.32 (1H, q, J=7 Hz, CH), 7.17—7.48 (5H, m, Ph).

(*E*)-3-Trimethylsilyloxy-2-pentene (4):[30] Lithium 2,2,6,6-tetramethylpiperidine (LTMP) was used instead of LDA (33% yield, E/Z=84/16); ^{1}H NMR ($CDCl_3$) δ=0.14 (9H, s, $(CH_3)_3Si$), 0.97 (3H, t, J=7 Hz, CH_3CH_2), 1.47 (3H, d, J=7 Hz, CH_3CH), 2.00 (2H, q, J=7 Hz, CH_2), 4.57 (1H, q, J=7 Hz, CH).

1-Trimethylsilyloxy-1-cyclohexene (5): Obtained from Aldrich Chemical Company, Inc.

1-Methoxy-2-methyl-1-trimethylsilyloxy-1-propene (6): Obtained from Aldrich Chemical Company, Inc.

1-(*t*-Butoxy)-1-(trimethylsilyloxy)ethylene (7):[31] ^{1}H NMR ($CDCl_3$) δ=0.23 (9H, s, $(CH_3)_3Si$), 1.35 (9H, s, *t*-Bu), 3.42 (1H, d, J=1.8 Hz, C*H*H), 3.44 (1H, d, J=1.8 Hz, CH*H*).

1-Ethoxy-1-(trimethylsilyloxy)propene (8):[32] (E/Z=85/15); ^{1}H NMR ($CDCl_3$) δ=0.23 (9H, s, $(CH_3)_3Si$), 1.23 (3H, t, J=7 Hz, CH_3CH_2), 1.52 (3H, d, J=7 Hz, CH_3CH), 3.47 (0.15H, q, J=7 Hz, (*Z*)-CH), 3.74 (0.85H, q, J=7 Hz, (*E*)-CH), 3.69 (0.30H, q, J=7 Hz, (*Z*)-CH_2), 3.83 (1.70H, q, J=7 Hz, (*E*)-CH_2).

1-(*t*-Butoxy)-1-(trimethylsilyloxy)propene (9):[29b,30] ^{1}H NMR ($CDCl_3$) for **(*E*)-isomer** δ=0.20 (9H, s, $(CH_3)_3Si$), 1.32 (9H, s, *t*-Bu), 1.49 (3H, d, J=6.6 Hz, CH_3CH), 3.90 (1H, q, J=6.6 Hz, CH_3CH); ^{1}H NMR ($CDCl_3$) for **(*Z*)-isomer** δ=0.21 (9H, s, $(CH_3)_3Si$), 1.28 (9H, s, *t*-Bu), 1.48 (3H, d, J=6.8 Hz, CH_3CH), 4.01 (1H, q, J=6.8 Hz, CH_3CH).

Typical Procedure for the Carbon–Carbon Bond Formation Reactions of Silyl Enol Ethers with Aldehydes or Other Electrophiles. To a solution of **1** (10.6 mg, 0.02 mmol) in dichloromethane (2 mL) was added benzaldehyde (102 μL, 1.0 mmol) and **4** (E/Z=84 : 16; 189.9 mg, 1.2 mmol) at −78°C. After the reaction mixture was stirred at the same temperature for 6 h, it was treated with 1 M HCl, extracted with ether, dried over anhydrous magnesium sulfate, and concentrated in vacuum. The residue was chromatographed on silica gel, eluting with hexane/ethyl acetate (10 : 1—5 : 1) to afford 1-hydroxy-2-methyl-1-phenyl-3-pentanone[33] as a colorless oil (181.2 mg, 94% yield) (Entry 7 in Table 1). *Syn*/*anti* ratio of the above products was 36 : 64 by ^{1}H NMR assay. ^{1}H NMR ($CDCl_3$) δ=0.95 (3H, t, J=7.2 Hz, CH_3CH_2), 1.02 (3H, d, J=7.0 Hz, CH_3CH), 2.20—2.70 (2H, m, CH_2CO), 2.80—3.02 (1H, m, CH_3CH), 3.12—3.18 (1H, br, OH), 4.77 (0.64H, dd, J=4.4, 8.0 Hz, C*H*OH (*anti* isomer)), 5.07 (0.36H, dd, J=3.6, 3.8 Hz, C*H*OH (*syn* isomer)), 7.20—7.40 (5H, m, Ph).

1-Hydroxy-1,3-diphenyl-3-propanone (Entries 1—3 in Table 1):[34] ^{1}H NMR ($CDCl_3$) δ=3.37 (2H, d, J=6.0 Hz, CH_2), 3.63 (1H, d, J=2.6 Hz, OH), 5.35 (1H, dt, J=2.6, 6.0 Hz, C*H*OH), 7.20—7.65 (8H, m, ArH), 7.85—8.02 (2H, m, ArH).

3-Hydroxy-1,5-diphenyl-1-pentanone (Entry 4 in Table 1):[11c] ^{1}H NMR ($CDCl_3$) δ=1.70—2.07 (2H, m, $PhCH_2CH_2$), 2.65—3.00 (3H, m, $PhCH_2$ and O*H*), 3.13 (1H, d, J=4.2 Hz, C*H*HCO), 3.40 (1H, d, J=3.0 Hz, CH*H*CO), 4.15—4.33 (1H, m, C*H*OH), 7.10—7.65 (8H, m, ArH), 7.94 (2H, d, J=7.2 Hz, ArH).

3-Hydroxy-2-methyl-1,3-diphenyl-1-propanone (Entry 5 in Table 1):[30] ^{1}H NMR ($CDCl_3$) δ=1.05 (1.35H, d, J=7.2 Hz, CH_3 (*anti* isomer)), 1.19 (1.65H, d, J=7.2 Hz, CH_3 (*syn* isomer)), 2.90—3.23 (1H, br, OH), 3.60—3.80 (1H, m, $CHCH_3$), 4.98 (0.45H, d, J=8.0 Hz, C*H*OH (*anti* isomer)), 5.22 (0.55H, d, J=3.0 Hz, C*H*OH (*syn* isomer)), 7.20—7.60 (8H, m, ArH), 7.92—8.02 (2H, m, ArH).

3-Hydroxy-2-methyl-1-phenyl-1-heptanone (Entry 6 in Table 1):[35] ^{1}H NMR ($CDCl_3$) δ=0.92 (3H, t, J=7.0 Hz, CH_3CH_2), 1.26 (3H, d, J=7.2 Hz, CH_3CH), 1.20—1.70 (6H, m, $Me(CH_2)_3$), 2.92—3.00 (0.25H, br, OH (*anti* isomer)), 3.12—3.20 (0.75H, br, OH (*syn* isomer)), 3.40—3.63 (1H, m, MeC*H*), 3.78—3.93 (0.25H, m, C*H*OH (*anti* isomer)), 3.97—4.15 (0.75H, m, C*H*OH (*syn* isomer)), 7.40—7.65 (3H, m, ArH), 7.96 (2H, d, J=8.0 Hz, ArH).

5-Hydroxy-4-methyl-7-phenyl-3-heptanone (Entry 8 in Table 1):[11e] ^{1}H NMR ($CDCl_3$) δ=1.04 (3H, t, J=7.2 Hz, CH_3CH_2), 1.10—1.18 (3H, m, CH_3CH), 1.50—1.95 (3H, m, CH_2CHOH and O*H*), 2.30—3.00 (4H, m, $PhCH_2$ and CH_2CO), 3.62—3.78 (0.62H, m, C*H*OH (*anti* isomer)), 3.87—4.00 (0.38H, m, C*H*OH (*syn* isomer)), 7.10—7.40 (5H, m, ArH).

2-(α-Hydroxybenzyl)cyclohexanone (Entry 9 in Table 1):[28] ^{1}H NMR ($CDCl_3$) δ=1.20—2.70 (9H, m, *c*-C_6H_9), 3.09 (0.28H, d, J=3.2 Hz, OH (*syn* isomer)), 3.99 (0.72H, d, J=2.6 Hz, OH (*anti* isomer)), 4.79 (0.72H, dd, J=2.6, 8.8 Hz, C*H*OH (*anti* isomer)), 5.36—5.42 (0.28H, br, C*H*OH (*syn* isomer)), 7.20—7.42 (5H, m, Ph).

1-Hydroxy-2-methyl-3-phenyl-3-propanone (Entry 10 in Table 1):[11e] ^{1}H NMR ($CDCl_3$) δ=1.23 (3H, d, J=7.2 Hz, CH_3CH), 2.20—2.65 (1H, br, OH), 3.55—4.00 (3H, m, $MeCHCH_2$), 7.40—7.65 (3H, m, ArH), 7.90—8.02 (2H, m, ArH).

1-Methoxy-2-methyl-3-phenyl-3-propanone (Entry 11 in Table 1):[36] ^{1}H NMR ($CDCl_3$) δ=1.21 (3H, d, J=5.6 Hz, CH_3CH), 3.33 (3H, s, CH_3O), 3.42—3.54 (1H, m, MeC*H*), 3.64—3.90 (2H, m, CH_2OMe), 7.40—7.65 (3H, m, ArH), 7.99 (2H, d, J=8.2 Hz, ArH).

1,1-Dimethoxy-2-methyl-3-phenyl-3-propanone (Entry 12 in Table 1):[37] ^{1}H NMR ($CDCl_3$) δ=1.21 (3H, d, J=7.0 Hz, CH_3CH), 3.33 (3H, s, CH_3O), 3.44 (3H, s, CH_3O), 3.83 (1H, dq, J=7.0, 8.0 Hz, MeC*H*), 4.65 (1H, d, J=8.0 Hz, $CH(OMe)_2$), 7.40—7.62 (3H, m, ArH), 7.97 (2H, dd, J=1.6, 6.8 Hz, ArH).

3-Methoxy-2-methyl-1,3-diphenyl-1-propanone (Entry 13 in Table 1):[38] ^{1}H NMR ($CDCl_3$) δ=0.86 (1.14H, d, J=7.2 Hz, CH_3CH (*anti* isomer)), 1.36 (1.86H, d, J=6.8 Hz, CH_3CH (*syn* isomer)), 3.09 (1.14H, s, CH_3O (*anti* isomer)), 3.21 (1.86H, s, CH_3O (*syn* isomer)), 3.71—3.91 (1H, m, MeC*H*), 4.47 (0.62H, d, J=8.0 Hz, PhC*H* (*syn* isomer)),

4.48 (0.38H, d, J=9.6 Hz, PhC*H* (*anti* isomer)), 7.10—8.10 (10H, m, 2Ph).

Methyl 3-Hydroxy-2,2-dimethyl-3-phenylpropanoate (Entry 14 in Table 1):[11c] ^{1}H NMR ($CDCl_3$) δ=1.10 (3H, s, CH_3), 1.14 (3H, s, CH_3), 3.00—3.30 (1H, br, OH), 3.71 (3H, s, CH_3O), 4.89 (1H, s, PhC*H*), 7.20—7.40 (5H, m, Ph).

Methyl 3-Hydroxy-2,2-dimethyl-5-phenylpentanoate (Entry 15 in Table 1):[11c] ^{1}H NMR ($CDCl_3$) δ= 1.16 (3H, s, CH_3), 1.18 (3H, s, CH_3), 1.50—1.88 (2H, m, CH_2CHOH), 2.40 (1H, t, J=7.4 Hz, OH), 2.54—2.74 (2H, m, PhCH_2), 2.86—3.04 (1H, m, C*H*OH), 7.10—7.40 (5H, m, Ph).

Methyl 2-Methyl-2-(3-oxocyclohexyl)propanoate (Entry 1 in Table 2):[39] ^{1}H NMR ($CDCl_3$) δ=1.16 (3H, s, CH_3), 1.18 (3H, s, CH_3), 1.07—2.45 (9H, m, *c*-C_6H_9), 3.69 (3H, s, CH_3O).

3-Phenacylcyclohexanone (Entry 2 in Table 2):[40] ^{1}H NMR ($CDCl_3$) δ=1.20—2.65 (9H, m, *c*-C_6H_9), 2.85—3.10 (2H, m, PhCOCH_2), 7.40—7.65 (3H, m, ArH), 7.94 (2H, dd, J=1.7, 6.8 Hz, ArH).

2-(3-Oxobutyl)cyclohexanone (Entry 3 in Table 2):[41] ^{1}H NMR ($CDCl_3$) δ=1.00—2.60 (13H, m, *c*-C_6H_9 and $(CH_2)_2CO$), 2.13 (3H, s, CH_3CO).

1,3-Diphenyl-1,5-hexanedione (Entry 4 in Table 2):[40] ^{1}H NMR ($CDCl_3$) δ=2.09 (3H, s, CH_3CO), 2.89 (2H, dd, J=7.0, 7.0 Hz, MeCOCH_2), 3.32 (2H, dd, J=3.6, 7.0 Hz, PhCOCH_2). 3.89 (1H, quintet, J=7.0 Hz, PhC*H*), 7.15—7.60 (8H, m, ArH), 7.92 (2H, d, J=10 Hz, ArH).

The Allylation Reaction of 1-(Trimethylsilyl)-2-methyl-2-propene with Benzaldehyde. To a mixed solution of benzaldehyde (102 μL, 1.0 mmol) and 1-(trimethylsilyl)-2-methyl-2-propene[42] (154 mg, 1.2 mmol) in dichloromethane (2 mL) was added **1** (25.6 mg, 0.05 mmol) at −78°C. After the reaction mixture was stirred at the same temperature for 8 h, it was treated with 1 M HCl and a solution of TBAF (1 mL, 1 M in THF), extracted with ether, dried over anhydrous magnesium sulfate, and concentrated in vacuum. The residue was chromatographed on silica gel, eluting with hexane/ethyl acetate (10:1—5:1) to afford 3-methyl-1-phenyl-3-buten-1-ol[43] as a colorless oil (151 mg, 93 % yield). ^{1}H NMR ($CDCl_3$) δ=1.80 (3H, s, CH_3), 2.15—2.20 (1H, br, OH), 2.42 (2H, d, J=7.2 Hz, CH_2CHOH), 4.81 (1H, t, J=7.2 Hz, C*H*OH), 4.86 (1H, s, C*H*H=C), 4.93 (1H, s, CH*H*=C), 7.20—7.45 (5H, m, Ph).

The Diels–Alder Reaction of Cyclopentadiene with 2-Methyl-2-propanal. To a mixed solution of 2-methyl-2-propanal (82.8 μL, 1.0 mmol) and **1** (25.6 mg, 0.05 mmol) in dichloromethane (2 mL) was added dropwise freshly cyclopentadiene (260 mg, 4.0 mmol) at −78 °C. After the reaction mixture was stirred at the same temperature for 12 h, it was treated with aqueous sodium hydrogencarbonate, extracted with ether, dried over anhydrous magnesium sulfate, and concentrated in vacuum. The residue was chromatographed on silica gel, eluting with hexane/ethyl acetate (20:1) to afford 2-methylbicyclo[2.2.1]-hept-5-ene-2-carbaldehyde[44] as a colorless oil (136 mg, >99 % yield). *exo*/*endo* Ratio of the above products was 88:12 by ^{1}H NMR analysis. ^{1}H NMR ($CDCl_3$) δ=0.73 (1H, s, C*H*H), 0.79 (1H, s, CH*H*), 1.01 (3H, s, CH_3), 2.22 (1H, d, J=3.8 Hz, MeCC*H*H), 2.28 (1H, d, J=3.8 Hz, MeCCH*H*), 2.82 (1H, br, C*H*CH=CHCH), 2.92 (1H, br, CHCH=CHC*H*), 6.11 (1H, dd, J=3.1, 5.6 Hz, C*H*=CH), 6.30 (1H, dd, J=3.1, 5.6 Hz, CH=C*H*), 9.41 (0.12H, s, C*H*O (*endo* isomer)), 9.70 (0.88H, s, C*H*O (*exo* isomer)).

Preparation of *N*-Benzylimines. A mixture of benzylamine (10 mmol), aldehyde (10 mmol), and $MgSO_4$ (3 g) in benzene (10 mL) was stirred at room temperature for several hours. The reaction mixture was filtered, and the filtrate was concentrated. The residue was distilled under reduced pressure.

***N*-Benzylidenebenzylamine:**[45] ^{1}H NMR ($CDCl_3$) δ=4.83 (2H, d, J=1.3 Hz, NCH_2), 7.30—7.45 (8H, m, ArH), 7.79 (2H, dd, J=2.3, 6.0 Hz, ArH), 8.40 (1H, s, N=CH).

***N*-Butylidenebenzylamine:**[46] ^{1}H NMR ($CDCl_3$) δ= 0.97 (3H, t, J=7.4 Hz, CH_3), 1.52—1.68 (2H, m, C$H_2$$CH_3$), 2.24—2.35 (2H, m, CHC$H_2$), 4.57 (2H, s, PhC$H_2$), 7.20—7.36 (5H, m, Ph), 7.78 (1H, t, J=6.0 Hz, CHN).

***N*-(2-Methylbutylidene)benzylamine:**[47] ^{1}H NMR ($CDCl_3$) δ=0.92 (3H, t, J=7.4 Hz, CH_3CH_2), 1.09 (3H, d, J=6.8 Hz, CHCH_3), 1.34—1.68 (2H, m, C$H_2$$CH_3$), 2.25—2.38 (1H, m, C*H*CH_3), 4.56 (2H, s, PhCH_2), 7.20—7.36 (m, 5H, Ph), 7.61 (1H, d, J=7.5 Hz, CHN).

Typical Procedure for the Aldol-Type Reactions of Ketene Silyl Acetals with *N*-Benzylimines. To a solution of *N*-benzylidenebenzylamine (116.8 mg, 0.6 mmol) and **8** (208.9 mg, 1.2 mmol, E/Z=85:15) in dry toluene (6 mL) was added an anhydrous solution of **1** in toluene (24 μL, 0.006 mmol, 0.247 M) dropwise at −78 °C. After being stirred for 13.5 h at −78 °C, the reaction mixture was warmed to 25 °C and stirred for a further 2 h. After aqueous sodium hydrogencarbonate (0.1 mL) was poured into the resultant solution, the mixture was dried over $MgSO_4$, filtered, and concentrated in vacuum to give the crude oil, which was purified by column chromatography on silica gel (eluant: hexane–EtOAc, 15:1) to afford ethyl 3-benzylamino-2-methyl-3-phenylpropanoate[18] (178 mg, >99% yield) as a colorless oil (Entry 3 in Table 3). ^{1}H NMR ($CDCl_3$) for *anti* isomer δ=0.90 (3H, d, J=7.5 Hz, CH_3CH), 1.26 (3H, t, J=7.0 Hz, CH_3CH_2), 1.60—1.90 (1H, br, NH), 2.62—2.78 (1H, m, CH_3C*H*), 3.45 (1H, d, J=13.0 Hz, PhC*H*H), 3.59 (1H, d, J=13.0 Hz, PhCH*H*), 3.74 (1H, d, J=9.5 Hz, PhC*H*N), 4.12—4.24 (2H, m, CH_3CH_2), 7.18—7.38 (10H, m, ArH); ^{1}H NMR ($CDCl_3$) for *syn* isomer δ=1.05 (3H, t, J=7.5 Hz, CH_3CH_2), 1.19 (3H, d, J=7.0 Hz, CH_3CH), 3.49 (1H, d, J=13.5 Hz, PhC*H*H), 3.69 (1H, d, J=13.5 Hz, PhCH*H*), 3.92 (1H, d, J=6.0 Hz, PhC*H*N), 3.96 (2H, dq, J=1.5, 7.5 Hz, CH_3CH_2), other resonances could not be discerned for *syn* isomer.

***t*-Butyl 3-(Benzylamino)-3-phenylpropanoate** (Entries 1 and 2 in Table 3): IR (film) 3340, 3029, 2979, 1725, 1455, 1368, 1152, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ= 1.37 (9H, s, *t*-Bu), 1.85—1.95 (1H, br, NH), 2.53 (1H, dd, J=5.4, 15.3 Hz, C*H*HCO_2), 2.64 (1H, dd, J=8.7, 15.3 Hz, CH*H*CO_2), 3.54 (1H, d, J=13.2 Hz, PhC*H*HN), 3.64 (1H, d, J=13.2 Hz, PhCH*H*N), 4.07 (1H, dd, J=5.4, 8.7 Hz, PhC*H*N), 7.20—7.38 (10H, m, 2Ph). Found: C, 77.09; H, 8.10; N, 4.44%. Calcd for $C_{20}H_{25}NO_2$: C, 77.14; H, 8.09; N, 4.50%.

***t*-Butyl 3-(Benzylamino)-2-methyl-3-phenylpropanoate** (Entries 6—8 in Table 3): IR (film) 3340, 3029, 2979, 1728, 1455, 1368, 1150, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) for *anti* isomer δ=0.86 (3H, d, J=7.5 Hz, CH_3CH), 1.46 (9H, s, *t*-Bu), 1.60—1.80 (1H, br, NH), 2.50—2.66 (1H,

m, CH_3CH), 3.45 (1H, d, J=13.5 Hz, PhC*H*H), 3.58 (1H, d, J=13.5 Hz, PhCH*H*), 3.71 (1H, d, J=9.5 Hz, PhC*H*N), 7.20—7.36 (10H, m, 2Ph); ^{1}H NMR ($CDCl_3$) for *syn* isomer δ=1.22 (3H, d, J=7.5 Hz, CH_3CH), 1.24 (9H, s, *t*-Bu), 3.47 (1H, d, J=13.5 Hz, PhC*H*H), 3.66 (1H, d, J=13.5 Hz, PhCH*H*), 3.84 (1H, d, J=7.0 Hz, PhC*H*N), other resonances could not be discerned for *syn* isomer. Found: C, 77.46; H, 8.48; N, 4.43%. Calcd for $C_{21}H_{27}NO_2$: C, 77.50; H, 8.36; N, 4.30%.

Methyl 3-(Benzylamino)-2,2-dimethyl-3-phenylpropanoate (Entries 9 and 10 in Table 3):[14] ^{1}H NMR ($CDCl_3$) δ=1.03 (3H, s, CH_3CCH_3), 1.18 (3H, s, CH_3CCH_3), 1.80—2.00 (1H, br, NH), 3.40 (1H, d, J=13.5 Hz, PhC*H*H), 3.62—3.68 (4H, complex of s and d, CO_2CH_3 and PhC*H*H), 3.89 (1H, s, PhC*H*N), 7.18—7.38 (10H, m, 2Ph).

***t*-Butyl 3-(Benzylamino)hexanoate** (Entry 11 in Table 3): IR (film) 3330, 2959, 1727, 1368, 1157, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.91 (3H, t, J=7.1 Hz, CH_2CH_3), 1.20—1.58 (5H, m, $(CH_2)_2CH_3$ and N*H*), 1.45 (9H, s, *t*-Bu), 2.37 (2H, d, J=3.1 Hz, CH_2CO_2), 3.00 (1H, quintet, J=6.2 Hz, CH), 3.76 (1H, d, J=12.0 Hz, PhC*H*HN), 3.80 (1H, d, J=12.0 Hz, PhCH*H*N), 7.20—7.38 (5H, m, Ph). Found: C, 73.46; H, 9.96; N, 5.33%. Calcd for $C_{17}H_{27}NO_2$: C, 73.61; H, 9.81; N, 5.05%.

Ethyl 3-(Benzylamino)-2-methylhexanoate (Entry 12 in Table 3):[18] ^{1}H NMR ($CDCl_3$) δ=0.83—0.95 (3H, m, $CH_2CH_2CH_3$), 1.12 (1.86H, d, J=7.0 Hz, CH_3CH (*anti* isomer)), 1.14 (1.14H, d, J=7.0 Hz, CH_3CH (*syn* isomer)), 1.18—1.52 (8H, m, CH_3CH_2O, $CH_3(CH_2)_2$, and N*H*), 2.62—2.75 (1H, m, C*H*CH_3), 2.83 (0.38H, q, J=5.5 Hz, C*H*NH (*syn* isomer)), 2.89 (0.62H, dt, J=3.5, 6.8 Hz, C*H*NH (*anti* isomer)), 3.74 (1H, d, J=13.5 Hz, PhC*H*HN), 3.79 (1H, d, J=13.5 Hz, PhCH*H*N), 4.06—4.20 (2H, m, $COCH_2$), 7.20—7.38 (5H, m, Ph).

***t*-Butyl 3-(Benzylamino)-4-methylhexanoate** (Entry 13 in Table 3): IR (film) 3340, 2965, 1728, 1368, 1154, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.86 (3H, d, J=6.5 Hz, $CHCH_3$), 0.90 (3H, t, J=7.5 Hz, CH_2CH_3), 1.05—1.72 (4H, m, $CH_2CHCHNH$), 1.44 (9H, s, *t*-Bu), 2.20 (1H, dd, J=9.0, 15.0 Hz, C*H*HCO_2), 2.33 (1H, dd, J=4.0, 15.0 Hz, CH*H*CO_2), 2.94—3.00 (1H, m, PhC*H*N), 3.75 (1H, d, J=12.0 Hz, PhC*H*HN), 3.85 (1H, d, J=12.0 Hz, PhCH*H*), 7.20—7.35 (5H, m, Ph). Found: C, 74.38; H, 10.09; N, 4.77%. Calcd for $C_{18}H_{29}NO_2$: C, 74.18; H, 10.03; N, 4.81%.

Ethyl 3-(Benzylamino)-2,4-dimethylhexanoate (Entry 14 in Table 3): IR (film) 3350, 2965, 1732, 1455, 1188, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.82—0.96 (6H, m, $2CH_3$), 1.10—1.30 (8H, m, 2Me and CH_2), 1.40—1.70 (2H, NH and CH), 2.60—2.73 (1H, m, $CHCO_2$), 2.78—2.86 (1H, m, CHN), 3.74—3.84 (2H, m, PhCH_2), 4.07—4.20 (2H, m, CO_2CH_2), 7.20—7.38 (5H, m, Ph). Found: C, 73.46; H, 10.00; N, 5.25%. Calcd for $C_{17}H_{27}NO_2$: C, 73.61; H, 9.81; N, 5.05%.

Typical Procedure for the Aldol-Type Reactions of Ketene Silyl Acetals with *N*-Trimethylsilylimines: To a solution of *N*-trimethylsilylbenzylideneamine[28] (106.4 mg, 0.6 mmol) and **6** (243.8 μL, 1.2 mmol) in dry toluene (5 mL) was added an anhydrous solution of **1** in toluene (243 μL, 0.06 mmol, 0.247 M) dropwise at −78 °C. After being stirred for 4 h at −78 °C, the reaction mixture was warmed to room temperature and stirred for a further 12 h. After aqueous sodium hydrogencarbonate (0.1 mL) was poured into the resultant solution, the mixture was dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuum. To the residue was added THF (5 mL) and 2 M HCl (5 mL). After being stirred at 50 °C for 6 h, the mixture was cooled to room temperature and 2 M NaOH (7 mL) was poured. The mixture was extracted with ethyl acetate, dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuum. The residue was chromatographed on silica gel, eluting with hexane/ethyl acetate (1 : 1) to afford methyl 3-amino-2,2-dimethyl-3-phenylpropanoate[48] (103.3 mg, 83% yield) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ=1.09 (3H, s, CH_3CCH_3), 1.15 (3H, s, CH_3CCH_3), 1.80—1.95 (2H, br, NH_2), 3.70 (3H, s, CO_2CH_3), 4.23 (1H, s, PhC*H*N), 7.24—7.35 (5H, m, Ph).

***t*-Butyl 3-Amino-3-phenylpropanoate:**[49] ^{1}H NMR ($CDCl_3$) δ=1.42 (9H, s, *t*-Bu), 1.67—1.75 (2H, br, NH_2), 2.58 (2H, d, J=6.8 Hz, CH_2), 4.37 (1H, t, J=6.8 Hz, CH), 7.21—7.40 (5H, m, Ph).

Ethyl 3-Amino-2-methyl-3-phenylpropanoate:[50] (*syn* : *anti* = 84 : 16); ^{1}H NMR ($CDCl_3$) for *syn* isomer δ= 1.11 (3H, t, J=7.1 Hz, CH_2CH_3), 1.18 (3H, d, J=7.0 Hz, $CHCH_3$), 2.32—2.55 (2H, br, NH_2), 2.64—2.82 (1H, m, C*H*CH_3), 4.02 (2H, q, J=7.1 Hz, CH_2CH_3), 4.26 (1H, d, J=6.1 Hz, PhC*H*N), 7.18—7.38 (5H, m, Ph); ^{1}H NMR ($CDCl_3$) for *anti* isomer δ=0.88 (3H, d, J=7.1 Hz, $CHCH_3$), 1.28 (3H, t, J=7.1 Hz, CH_2CH_3), 4.19 (2H, q, J=7.1 Hz, CH_2CH_3), other resonances could not be discerned for *anti* isomer.

Ethyl 3-Bis(trimethylsilyl)amino-2-methyl-3-phenylpropanoate: This compound was isolated by column chromatography on silica gel and subsequent distillation after work-up with *t*-butyl alcohol in place of 2 M HCl. IR (film) 1734, 1250, 1044, 941, 837 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=−0.65—0.55 (18H, br, $N(Si(CH_3)_3)_2$), 1.11 (3H, t, J=7.1 Hz, CH_2CH_3), 1.34 (3H, d, J=7.1 Hz, $CHCH_3$), 3.19 (1H, dq, J=7.1, 11.3 Hz, C*H*CH_3), 4.02 (2H, dq, J=2.7, 7.1 Hz, CH_2CH_3), 4.63 (1H, d, J=11.3 Hz, PhCH), 7.13—7.37 (5H, m, Ph). HRFABMS, Found: m/z 352.2120. Calcd for $C_{18}H_{33}NO_2Si_2$: MH^+, 352.2128.

3,3-Dimethyl-4-phenylazetidin-2-one:[28] To a solution of *N*-trimethylsilylbenzylideneamine[28] (106.4 mg, 0.6 mmol) and **6** (243.8 μL, 1.2 mmol) in dry toluene (5 mL) was added an anhydrous solution of **1** in toluene (243 μL, 0.06 mmol, 0.247 M) dropwise at −78 °C. After being stirred for 4 h at −78 °C, the reaction mixture was warmed to room temperature and stirred for a further 12 h. To the solution was added ether (1 mL) and methylmagnesium bromide (2.0 mL, 1.8 mmol, 0.89 M in ether); the mixture was then stirred at room temperature for 1 d. After the reaction was quenched with saturated aqueous ammonium chloride, the mixture was extracted with ether, dried over anhydrous magnesium sulfate, filtrated, and concentrated in vacuum. The residue was chromatographed on silica gel, eluting with hexane/ethyl acetate (5 : 1) to afford 3,3-dimethyl-4-phenylazetidin-2-one (43.1 mg, 41% yield) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ=0.78 (3H, s, CH_3CCH_3), 1.48 (3H, s, CH_3CCH_3), 4.52 (1H, s, CH), 5.86—6.00 (1H, br, NH), 7.22—7.45 (5H, m, Ph).

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