Novel Isomerization Reaction of *N*,*N*-Dimethyl-α-(methoxycarbonyl)-4-substituted-benzylammonium *N*-Methylides

Chen Zhang, Hiroto Ito, Yasuhiro Maeda, Naohiro Shirai, Shin-ichi Ikeda, and Yoshiro Sato*

Faculty of Pharmaceutical Sciences, Nagoya City University, Tanabe-dori, Mizuho-ku, Nagoya 467-8603, Japan

Received August 24, 1998

Fluoride ion-induced desilylation of *N*,*N*-dimethyl-*N*-[(trimethylsilyl)methyl]-α-(methoxycarbonyl)-4-substituted benzylammonium salts (**7**) gave two Stevens rearrangement products: methyl 3-(dimethylamino)-2-(4-substituted phenyl)propionates (**13**) from *N*-methylides **8**, and methyl 3-(dimethylamino)-3-(4-substituted phenyl)propionates (**15**) from *N*-benzylides **10**. Additional Stevens rearrangement products, methyl 2-(dimethylamino)-3-(4-substituted phenyl)propionates (**16**), were competitively formed from ylides **12** when the cesium fluoride used was not predried. The mechanism of the isomerization from methylides **8**, which was initially generated, to **10** and **12** is discussed.

Introduction

Fluoride ion-induced desilylation of α-(trimethylsilyl)-alkylammonium salts provides a useful method for the selective formation of *N*-alkylides.[1] Since this reaction proceeds quantitatively in nonbasic media, we previously examined the possibility of *N*-methylide formation in molecules with acidic hydrogen(s) which can be deprotonated under basic conditions.[2,3] On the basis of the results of the reaction of *N*-[(trimethylsilyl)methyl]benzylammonium salts (**1**, R = CO_2Me or CN) with cesium fluoride (Scheme 1), we presumed that *N*-methylides **2** are initially formed. However, two isomerization routes subsequently occur to give ylides **3** by intramolecular [1,3] proton transfer (path *a*) and ylides **4** by intermolecular proton transfer with **1** (path c).[2] Later, we noticed that the direct deprotonation of **1** with cesium fluoride (path b) is more important for the formation of **4** than path c.[3] Thus, *N*-methylide formation by desilylation is not simple in molecules with electron-withdrawing groups. In this paper, we report the reaction of *N*,*N*-dimethyl-*N*-[(trimethylsilyl)methyl]-α-(methoxycarbonyl)-4-substituted benzylammonium salts (**7**) with cesium fluoride.

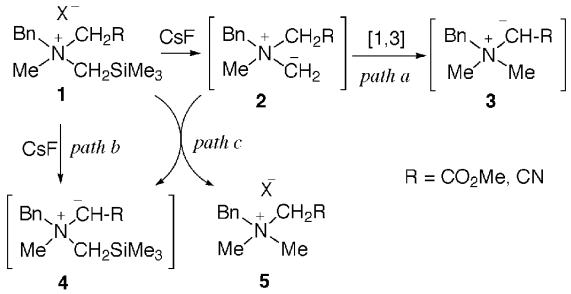
Results and Discussion

N,*N*-Dimethyl-*N*-[(trimethylsilyl)methyl]-α-(methoxycarbonyl)-4-substituted benzylammonium salts (**7a**−**e**) were prepared by reacting α-(4-substituted phenyl)-glycine methyl esters (**6**) with (chloromethyl)trimethylsilane followed by quaternization with iodomethane (Scheme 2, Table 1).

The reaction of *N*,*N*-dimethyl-*N*-[(trimethylsilyl)-methyl]-α-(methoxycarbonyl)benzylammonium iodide (**7a**) with cesium fluoride in DMF at room temperature gave a mixture of compounds **13a** and **15a**, and a third compound **16a** was also obtained when the cesium fluoride used was not predried over phosphorus pentoxide at 180 °C under reduced pressure (Table 1, entries 1, 2). All of these products are constructed of methoxycarbonyl, dimethylamino, and phenyl groups. Compound **16a** was easily separated by column chromatography and determined to be methyl 2-(dimethylamino)-3-phenylpropionate. However, separation of **13a** and **15a** was difficult, and some of **13a** was deaminated to methyl 2-phenylpropenoate (**14a**) during handling. When the methoxycarbonyl groups of **13a** and **15a** (7:3 mixture) were reduced with lithium aluminum hydride to the corresponding alcohols **17** and **18**, the alcohols could be separated by column chromatography (Scheme 3). The structure of alcohol **17** was determined to be 3-(dimethylamino)-2-phenylpropanol while **18** was 3-(dimethylamino)-3-phenylpropanol. Thus, the original products **13a** and **15a** were assigned to be methyl 3-(dimethylamino)-2-phenylpropionate and methyl 3-(dimethylamino)-3-phenylpropionate, respectively.

Three isomers **13a**, **15a**, and **16a** are the Stevens rearrangement products formed from *N*-ylides **8a**, **10a**, and **12a**, respectively. Ylide **8a** should be initially formed by the desilylation of **7a**, and ylide **10a** may be formed from **8a** via an azetidinium ring intermediate **9** which is formed by nucleophilic attack of the carbonyl carbon by the ylide-anion of **8a** (Scheme 2).

Scheme 1



* Corresponding author. Phone: 81-52-836-3459. Fax: 81-52-836-3459. E-mail: ysato@phar.nagoya-cu.ac.jp.

(1) (a) Vedejs, E.; West, F. G. *Chem. Rev.* **1986**, *86*, 941. (b) Sato, Y. *J. Synth. Org. Chem. Jpn.* **1992**, *50*, 977. (c) Sato, Y.; Shirai, N. *Yakugaku Zasshi* **1994**, *114*, 880.

(2) Zhang, C.; Maeda, Y.; Shirai, N.; Sato, Y. *J. Chem. Soc. Perkin Trans. 1* **1997**, 25.

(3) Zhang, C.; Maeda, Y.; Sato, Y. *Chem. Pharm. Bull.* **1998**, *46*, 572.

10.1021/jo981729h CCC: $18.00
Published on Web 12/29/1998

Scheme 2

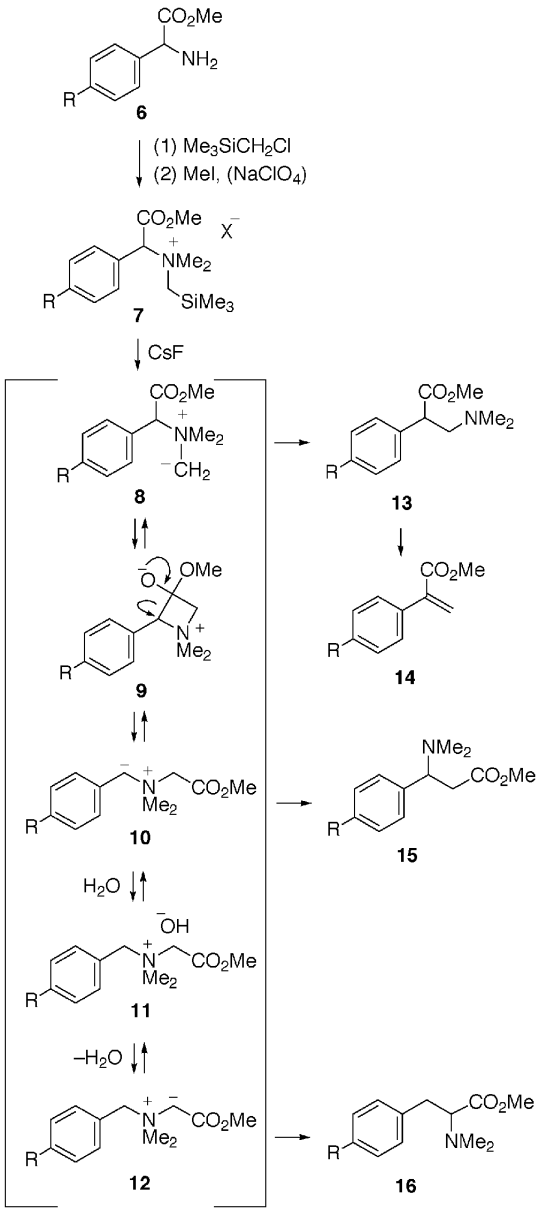


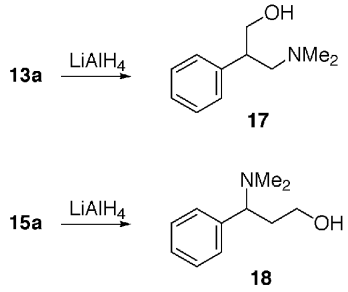
Table 1. Reaction of *N*,*N*-Dimethyl-*N*-[(trimethylsilyl)methyl]-α-(methoxycarbonyl)-4-substituted-benzylammonium Salts (7) with CsF in DMF at Room Temperature

					product proportions[a]		
entry	salt	R	X	total yield (%)	**13**	**15**	**16**
1	**7a**	H	I	81	70	30	0
2	**7a**	H	I	27[b]	65	16	19
3	**7b**	Me	ClO_4	89	80	20	0
4	**7c**	OMe	I	50	100	0	0
5	**7d**	F	ClO_4	86	80	20	0
6	**7d**	F	ClO_4	33[b]	69	19	12
7	**7e**	Cl	ClO_4	95[c]	77	23	0

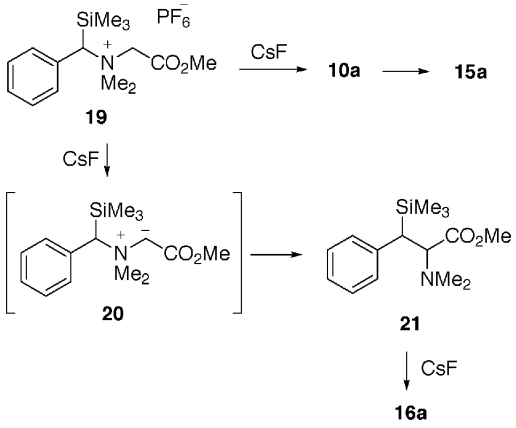
[a] Proportions of the products were determined by integration of the ^1H signals in 400- or 500-MHz NMR. [b] CsF was not predried. [c] Includes methyl 2-(4-chlorophenyl)propenoate (**14e**, 9%).

To examine the generality of this novel chemical behavior of ylide **8a**, 4-methylbenzylammonium (**7b**), 4-methoxybenzylammonium (**7c**), 4-fluorobenzylammonium (**7d**), and 4-chlorobenzylammonium salts (**7e**) were similarly treated with cesium fluoride. The results are listed in Table 1. Two types of Stevens rearrangement products **13b**,**d**,**e** and **15b**,**d**,**e** were formed from **7b**,**d**,**e** using predried cesium fluoride (entries 3, 5, and 7). Contamination by a third Stevens product **16d** was observed when **7d** was treated with cesium fluoride which was not predried (entry 6). However, a 4-methoxybenzyl analogue **7c** gave only a normal rearrangement product **13c** (entry 4). The strong electron-releasing ability of the methoxy group may inhibit the conversion of **9c** to **10c**.

Scheme 3



Scheme 4

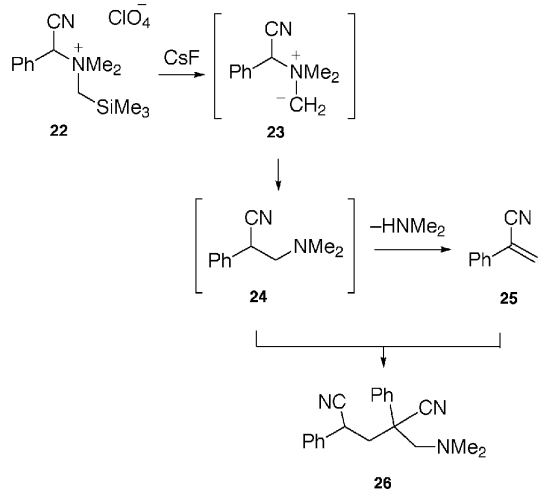


The formation of **16** in the presence of a trace amount of water may result from the isomerization of **10** to **12** via ammonium hydroxides **11**. Recently, Jon'czyk and Zdrojewski[4] reported that equilibration of ylides $PhCH^--N^+CH_2CN$ and $PhCH_2N^+-CH^-CN$ is facilitated in the presence of water. We tried to generate **10a** by reacting *N*,*N*-dimethyl-*N*-(methoxycarbonyl)methyl-α-(trimethylsilyl)benzylammonium hexafluorophosphate (**19**) with cesium fluoride (Scheme 4). When 3 mol equiv of cesium fluoride were used, the main product was not **15a** (20%) but rather **16a** (53%), despite the absence of water. The use of an equimolar amount of cesium fluoride gave **16a** (30%) and methyl 2-(dimethylamino)-3-phenyl-3-(trimethylsilyl)propionate (**21**, 8%), which is a Stevens rearrangement product of ylide **20**. When isolated **21** was stirred in a suspension of cesium fluoride in DMF at room temperature, it was desilylated to **16a** in 85% yield.[5] These results suggest that fluoride ion acts on **19** as an α-deprotonation reagent rather than a desilylation reagent, and the isomerization of ylide **10a** to **12a** does not occur in the absence of water.

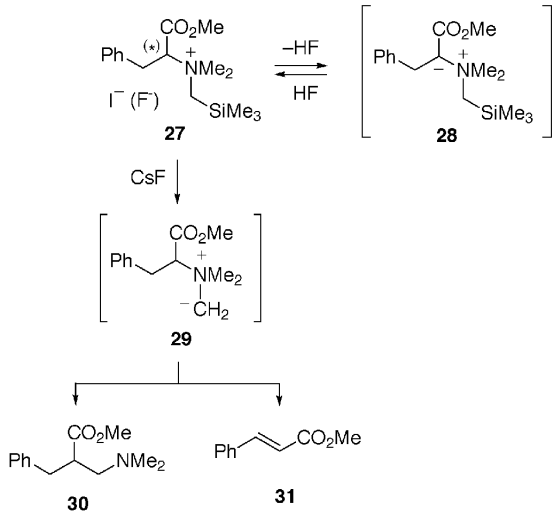
The novel isomerization of ylides **8** to ylides **10** resulted from the intramolecular nucleophilic attack of the car-

(4) Zdrojewski, T.; Jon'czyk, A. *J. Org. Chem.* **1998**, *63*, 452.
(5) Fluoride ion-induced desilylation of benzyltrimethylsilane has been reported previously: Ricci, A.; Fioreza, M.; Grifagni, M. A.; Batolini, G. *Tetrahedron Lett.* **1982**, *48*, 5079.

Scheme 5



Scheme 6



bonyl-carbons by the ylide-anions. When *N*,*N*-dimethyl-*N*-[(trimethylsilyl)methyl]-α-cyanobenzylammonium perchlorate (**22**) was prepared as an α-cyano-analogue of **7a** from *N*,*N*-dimethyl-α-cyanobenzylamine and treated with cesium fluoride, a mixture of 2-phenylacrylonitrile (**25**, 25%) and *N*,*N*-dimethyl-2,4-dicyano-2,4-diphenylbutylamine (**26**, 30%) was formed (Scheme 5). The former may be produced from Stevens rearrangement product **24** of ylide **23** by deamination, while the latter is a Michael-type condensation product of **24** with **25**. Isomerization of **23** to other ylides did not occur in this reaction.

(*S*)-(+)-*N*,*N*-Dimethyl-*N*-[(trimethylsilyl)methyl]-1-(methoxycarbonyl)-2-phenylethylammonium iodide (**27**), which is a homologue of **7a**, was prepared from *l*-phenylalanine methyl ester and treated with cesium fluoride (Scheme 6). *dl*-Methyl 2-benzyl-3-(dimethylamino)propionate (**30**, 61%, Stevens rearrangement product of ylide **29**) and methyl cinnamate (**31**, 13%, Hofmann elimination product of **29**) were obtained; however, isomeric products of **30**, which should be formed via isomerization of ylide **29**, were not obtained. It is well-known that the configuration of the migrating group is retained in a Stevens rearrangement.[6] However, the chirality of **27** was not retained in **30**. Quick racemization of **27** may occur by the fluoride ion-induced α-deprotonation of **27** to ylide **28** and vice versa.

(6) Markó, I. E. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 3, p 913.

Experimental Section

DMF was dried by distillation from BaO under reduced pressure. CsF was dried over P_2O_5 at 180 °C under reduced pressure. Aluminum oxide (Merck Aluminum oxide 90, 70−230 mesh) or silica gel (BW-200, Fuji-Silysia) was used for column chromatography. Distillation was performed on a Büchi Kugelrohr distillation apparatus. All melting points and boiling points are uncorrected.

***N*,*N*-Dimethyl-*N*-[(trimethylsilyl)methyl]-α-(methoxycarbonyl)-4-substituted-benzylammonium Salts (7a−e). General Procedure.** A suspension of *dl*-α-phenylglycine methyl ester hydrochloride (**6a**) or an analogue; 4-methylphenyl- (**6b**), 4-methoxyphenyl- (**6c**), 4-fluorophenyl- (**6d**), or 4-chlorophenyl- (**6e**) (50 mmol), (chloromethyl)trimethylsilane (9.2 g, 75 mmol), KI (12.5 g, 75 mmol), and K_2CO_3 (10.4 g, 75 mmol) in DMF (200 mL) was stirred at 100 °C for 1 h. The mixture was poured into water (500 mL) and extracted with EtOAc (4 × 100 mL). The extract was washed with water (3 × 100 mL) and saturated aqueous NaCl (2 × 50 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was chromatographed on a silica gel column (EtOAc/hexane, 1:10) and distilled to give the following esters.

Methyl 2-[(trimethylsilyl)methyl]amino-2-phenylacetate: yield 6.82 g (54%); bp 100 °C (4 mmHg); IR (film) 1740, 1251, 854 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.05 (s, 9 H), 1.74 (s, 1 H), 1.92 and 1.98 (AB-q, J = 13.4 Hz, 2 H), 3.67 (s, 3 H), 4.29 (s, 1 H), 7.27−7.38 (m, 5 H). Anal. Calcd for $C_{13}H_{21}NO_2Si$: C, 62.11; H, 8.42; N, 5.57. Found: C, 61.98; H, 8.53; N, 5.55.

Methyl 2-[(trimethylsilyl)methyl]amino-2-(4-methylphenyl)acetate: yield 6.60 g (50%); bp 90 °C (0.5 mmHg); IR (film) 1730, 1240, 850 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 9 H), 1.72 (br s, 1 H), 1.92 and 1.97 (AB-q, J = 13.1 Hz, 2 H), 2.34 (s, 3 H), 3.68 (s, 3 H), 4.26 (s, 1 H), 7.15 (d, J = 7.9 Hz, 2 H), 7.25 (d, J = 7.9 Hz, 2 H). Anal. Calcd for $C_{14}H_{23}NO_2Si$: C, 63.35; H, 8.73; N, 5.28. Found: C, 63.34; H, 8.69; N, 5.28.

Methyl 2-[(trimethylsilyl)methyl]amino-2-(4-methoxyphenyl)acetate: yield 6.11 g (45%); bp 90 °C (0.5 mmHg); IR (film) 1740, 1251, 855 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.04 (s, 9 H), 1.73 (br s, 1 H), 1.92 and 1.96 (AB-q, J = 13.1 Hz, 2 H), 3.68 (s, 3 H), 3.79 (s, 3 H), 4.24 (s, 1 H), 6.87 (d, J = 8.5 Hz, 2 H), 7.28 (d, J = 8.5 Hz, 2 H). Anal. Calcd for $C_{14}H_{23}NO_3Si$: C, 59.75; H, 8.24; N, 4.98. Found: C, 59.59; H, 8.12; N, 4.68.

Methyl 2-[(trimethylsilyl)methyl]amino-2-(4-fluorophenyl)acetate: yield 6.86 g (51%); bp 100−110 °C (1 mmHg); IR (film) 1746, 1248, 844 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 9 H), 1.67 (br s, 1 H), 1.89 and 1.98 (AB-q, J = 13.2 Hz, 2 H), 3.69 (s, 3 H), 4.26 (s, 1 H), 7.03 (t, J_{F-H} = 8.8, J = 8.8 Hz, 2 H), 7.34 (dd, J_{F-H} = 5.4, J = 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 2.7 (3 C), 37.8, 52.1, 68.4, 115.4 (d, J_{F-C} = 21.7 Hz, 2 C), 129.2 (d, J_{F-C} = 8.3 Hz, 2 C), 134.1 (d, J_{F-C} = 3.2 Hz), 162.0 (d, J_{F-C} = 246.2 Hz), 173.5. Anal. Calcd for $C_{13}H_{20}FNO_2Si$: C, 57.96; H, 7.48; N, 5.20. Found: C, 57.96; H, 7.45; N, 5.21.

Methyl 2-[(trimethylsilyl)methyl]amino-2-(4-chlorophenyl)acetate: yield 7.28 g (51%); bp 100−110 °C (1 mmHg); IR (film) 1745, 1250, 855 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.00 (s, 9 H), 1.64 (s, 1 H), 1.90 and 1.84 (AB-q, J = 13.4 Hz, 2 H), 3.63 (s, 3 H), 4.20 (s, 1 H), 7.26 (s, 4 H). Anal. Calcd for $C_{13}H_{20}ClNO_2Si$: C, 54.62; H, 7.05; N, 4.90. Found: C, 54.43; H, 7.15; N, 4.86.

A mixture of methyl 2-[(trimethylsilyl)methyl]amino-2-(4-substituted phenyl)acetate (20 mmol) described above, iodomethane (28.4 g, 100 mmol), and K_2CO_3 (2.8 g, 20 mmol) in MeCN (100 mL) was stirred for 12 h and filtered. The filtrate was concentrated under reduced pressure to give the following ammonium salts.

***N,N*-Dimethyl-*N*-[(trimethylsilyl)methyl]-α-(methoxycarbonyl)benzylammonium iodide (7a):** yield 4.90 g (60%); mp 165−167 °C (recrystallized from acetone−Et_2O); IR (Nujol) 1750, 1210, 860 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.32 (s, 9 H), 3.36 and 3.82 (AB-q, J = 13.4 Hz, 2 H), 3.40 (s, 3 H), 3.47 (s, 3 H), 3.75 (s, 3 H), 6.84 (s, 1 H), 7.47−7.59 (m, 3 H), 7.77−7.79 (m, 2 H). Anal. Calcd for $C_{15}H_{26}INO_2Si$: C, 44.23; H, 6.43; N, 3.44. Found: C, 44.12; H, 6.29; N, 3.39.

***N,N*-Dimethyl-*N*-[(trimethylsilyl)methyl]-α-(methoxycarbonyl)-4-methylbenzylammonium Perchlorate (7b).** The residue was not crystallized, and the counteranion was changed to perchlorate as follows: a solution of the residue in $CHCl_3$ (20 mL) was stirred with a saturated aqueous solution of $NaClO_4$ (30 mL) for 3 h. The $CHCl_3$ layer was separated, and the aqueous layer was extracted with $CHCl_3$ (4 × 50 mL). The combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure to give **7b** (3.94 g, 50%); mp 124−126 °C (recrystallized from acetone−Et_2O); IR (Nujol) 1740, 1260, 850 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.31 (s, 9 H), 2.41 (s, 3 H), 3.32 and 3.50 (AB-q, J = 14.6 Hz, 2 H), 3.27 (s, 3 H), 3.30 (s, 3 H), 3.77 (s, 3 H), 5.57 (s, 1 H), 7.31 (d, J = 8.1 Hz, 2 H), 7.47 (d, J = 8.1 Hz, 2 H). Anal. Calcd for $C_{16}H_{28}ClNO_6Si$: C, 48.78; H, 7.16; N, 3.56. Found: C, 48.59; H, 7.26; N, 3.59.

***N,N*-Dimethyl-*N*-[(trimethylsilyl)methyl]-α-(methoxycarbonyl)-4-methoxybenzylammonium iodide (7c):** yield 4.87 g (56%); a viscous oil. This salt was not crystallized and was used for the next reaction without further purification. IR (Nujol) 1750, 1240, 840 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.29 (s, 9 H), 3.28 and 3.33 (AB-q, J = 14.5 Hz, 2 H), 3.35 (s, 3 H), 3.39 (s, 3 H), 3.65 (s, 3 H), 3.81 (s, 3 H), 6.53 (s, 1 H), 6.95 (d, J = 8.6 Hz, 2 H), 7.64 (d, J = 8.6 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.19 (3 C), 51.0, 52.1 (2 C), 53.4, 55.5, 56.1, 76.5, 114.9 (2 C), 118.2 (2 C), 161.9, 167.6.

***N,N*-Dimethyl-*N*-[(trimethylsilyl)methyl]-α-(methoxycarbonyl)-4-fluorobenzylammonium Perchlorate (7d).** The iodide salt was not crystallized, and the counteranion was changed to perchlorate in a manner similar to that described for **7b**: yield 7.55 g (95%); mp 168−170 °C (recrystallized from water); IR (KBr) 1740, 1210, 849 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 0.32 (s, 9 H), 3.18 and 3.40 (AB-q, J = 14.4 Hz, 2 H), 3.24 (s, 3 H), 3.29 (s, 3 H), 3.83 (s, 3 H), 5.52 (s, 1 H), 7.35 (t, J_{F-H} = 8.8, J = 8.8 Hz, 2 H), 7.71 (dd, J_{F-H} = 5.1, J = 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, CD_3OD) δ −0.7 (3 C), 52.5, 53.3, 54.3, 58.4, 79.2, 117.9 (d, J_{F-H} = 21.7 Hz, 2 C), 124.3, 135.8 (d, J_{F-C} = 8.3 Hz, 2 C), 166.2, 168.2 (d, J_{F-C} = 252.4 Hz). Anal. Calcd for $C_{15}H_{25}ClFNO_6Si$: C, 45.28; H, 6.33; N, 3.52. Found: C, 45.19; H, 6.09; N, 3.55.

***N,N*-Dimethyl-*N*-[(trimethylsilyl)methyl]-α-(methoxycarbonyl)-4-chlorobenzylammonium Perchlorate (7e).** In the same way, the counteranion was changed to perchlorate: yield 4.22 g (51%); mp 159−163 °C (recrystallized from EtOH−Et_2O); IR (Nujol) 1750, 1240, 1210, 850 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.27 (s, 9 H), 3.35 and 3.60 (AB-q, J = 14.3 Hz, 2 H), 3.35 (s, 3 H), 3.38 (s, 3 H), 3.69 (s, 3 H), 6.65 (s, 1 H), 7.50 (d, J = 8.8 Hz, 2 H), 7.60 (d, J = 8.8 Hz, 2 H). Anal. Calcd for $C_{15}H_{25}Cl_2NO_6Si$: C, 43.48; H, 6.08; N, 3.38. Found: C, 43.19; H, 5.96; N, 3.54.

Reaction of 7a with CsF. A. Salt **7a** (0.81 g, 2 mmol) was placed in a 20-mL flask equipped with a magnetic stirrer, a septum, and a test tube which was connected to the flask with a short bent glass tubing. CsF (0.96 g, 6 mmol) was placed in the test tube. The apparatus was dried under reduced pressure and flushed with N_2. DMF (10 mL) was added to the flask with a syringe, and CsF was added from the test tube. The mixture was stirred for 12 h at room temperature, poured into water (100 mL), and extracted with Et_2O (4 × 50 mL). The extract was washed with water (3 × 100 mL) and saturated aqueous NaCl (50 mL), dried ($MgSO_4$), and concentrated under reduced pressure to give a mixture of methyl 3-(dimethylamino)-2-phenylpropionate (**13a**) and methyl 3-(dimethylamino)-3-phenylpropionate (**15a**), yield 335 mg (81%); ratio 70:30 (determined by the integrated values of ^1H NMR of the mixture); a colorless oil; bp 100 °C (1 mmHg); ^1H NMR (500 MHz, $CDCl_3$) **13a**: δ 2.27 (s, 6 H), 2.44 (dd, J = 12.4, 5.1 Hz, 1 H), 3.15 (dd, J = 12.4, 10.1 Hz, 1 H), 3.68 (s, 3 H), 3.81 (dd, J = 10.1, 5.1 Hz, 1 H), 7.18−7.34 (m, 5 H); **15a**: δ 2.17 (s, 6 H), 2.70 (dd, J = 15.0, 7.6 Hz, 1 H), 2.97 (dd, J = 15.0, 7.3 Hz, 1 H), 3.58 (s, 3 H), 3.88 (dd, J = 7.6, 7.3 Hz, 1 H), 7.18−7.34 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) **13a**: δ 45.8 (2 C), 51.1, 52.6, 63.8; **15a**: δ 39.0, 42.6, 52.1 (2 C), 67.8; others: 128.7, 128.9, 129.0 (2 C), 129.2 (2 C), 129.5 (2 C), 129.9 (2 C), 138.7, 139.2, 173.6, 175.1. Anal. Calcd for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.46; H, 8.44; N, 6.51.

An aliquot of **13a** was changed to methyl 2-phenylpropenoate[7] (**14a**) during handling. Compound **14a** was separated on a silica gel column (EtOAc/hexane, 1:10): bp 72−75 °C (0.6 mmHg) [lit.[7] 73 °C (0.6 mmHg)].

B. The reaction described above was carried out with CsF (Aldrich reagent was used without further drying) and worked up to give a mixture of **13a**, **15a**, and methyl 2-(dimethylamino)-3-phenylpropionate[8] (**16a**) (ratio 65:16:19, determined from the proton ratios in ^1H NMR), yield 112 mg (27%). Compound **16a** was separated from the mixture on an aluminum oxide column (EtOAc/hexane, 1:10): a colorless oil; bp 82−85 °C (0.7 mmHg) (lit.[8] 256−258 °C).

$LiAlH_4$ Reduction of 13a and 15a. A mixture of **13a** and **15a** (238 mg, 1.15 mmol, ratio 7:3) was dissolved in Et_2O (5 mL) and added dropwise to a suspension of $LiAlH_4$ (46 mg, 1.2 mmol) in Et_2O (5 mL). The mixture was stirred for 2 h at room temperature, poured into saturated potassium sodium tartrate, and extracted with Et_2O (3 × 10 mL). The extract was washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was chromatographed on an aluminum oxide column (EtOAc/hexane, 3:10) to give 3-(dimethylamino)-2-phenylpropanol (**17**) (140 mg, 68%) and 3-(dimethylamino)-3-phenylpropanol (**18**) (30 mg, 15%).

17: bp 100 °C (1.5 mmHg); IR (film) 3300 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 6 H), 2.55 (ddd, J = 12.2, 3.1, 2.6 Hz, 1 H), 2.99 (t, J = 12.2 Hz, 1 H), 3.15−3.22 (m, 1 H), 3.84 (ddd, J = 10.5, 4.0, 2.6 Hz, 1 H), 3.96 (t, J = 10.5 Hz, 1 H), 5.40−6.20 (br s, 1 H), 7.15−7.31 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.4, 45.8 (2 C), 66.6, 70.5, 126.8, 127.4 (2 C), 128.5 (2 C), 140.4. Anal. Calcd for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.42; H, 9.83; N, 7.52.

18: bp 100 °C (1.5 mmHg) [lit.[9] 100 °C (1.5 mmHg)].

Reaction of 7b with CsF. In a manner similar to that described for **7a** (**A**), salt **7b** (0.76 g, 2 mmol) was allowed to react with CsF (0.96 g, 6 mmol) in DMF (10 mL) and worked up to give a mixture of methyl 3-(dimethylamino)-2-(4-methylphenyl)propionate (**13b**) and methyl 3-(dimethylamino)-3-(4-methylphenyl)propionate (**15b**), yield 394 mg (89%), ratio 80:20 (determined by the integrated values in ^1H NMR of the mixture); bp 85−90 °C (0.5 mmHg); ^1H NMR (500 MHz, $CDCl_3$) **13b**: δ 2.26 (s, 6 H), 2.31 (s, 3 H), 2.42 (dd, J = 12.2, 5.2 Hz, 1 H), 3.12 (dd, J = 12.2, 10.1 Hz, 1 H), 3.66 (s, 3 H), 3.77 (dd, J = 10.1, 5.2 Hz, 1 H), 7.11 (d, J = 7.2 Hz, 2 H), 7.20 (d, J = 7.2 Hz, 2 H); **15b**: δ 2.16 (s, 6 H), 2.32 (s, 3 H), 2.67 (dd, J = 15.0, 7.9 Hz, 1 H), 2.95 (dd, J = 15.0, 7.3 Hz, 1 H), 3.57 (s, 3 H), 3.87 (dd, J = 7.9, 7.3 Hz, 1 H), 7.11 (d, J = 7.4 Hz, 2 H), 7.40 (d, J = 7.4 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) **13b**: δ 20.9, 45.6 (2 C), 49.8, 51.9, 62.9; **15b**: δ 21.0, 38.2 (2 C), 42.0, 51.4, 65.7; the others: 127.7 (2 C), 128.1 (2 C), 128.7 (2 C), 129.3 (2 C), 134.4, 135.3, 136.9, 137.0, 172.2, 173.7. Anal. Calcd for $C_{13}H_{19}NO_2$: C, 70.56; H, 8.65; N, 6.33. Found: C, 70.34; H, 8.67; N, 6.09.

Reaction of 7c with CsF. A solution of **7c** (0.88 g, 2 mmol) in DMF (30 mL) was placed in a 50-mL three-neck flask, and an aliquot of DMF was distilled off at 80 °C (25 mmHg) to remove any remaining water. To the remaining solution (ca. 15 mL) was added CsF (0.96 g, 6 mmol), and the mixture was stirred for 12 h, poured into water (100 mL), and extracted with EtOAc (4 × 50 mL). The extract was washed with water, dried ($MgSO_4$), concentrated under reduced pressure, and distilled to give methyl 3-(dimethylamino)-2-(4-methoxyphenyl)propionate (**13c**), yield 118 mg (50%); bp 120−130 °C

(7) Heck, R., F.; Winstein, S. *J. Org. Chem.* **1972**, *37*, 820.
(8) Corey, E. J.; McCaully, R. J.; Sachdev, H. S. *J. Am. Chem. Soc.* **1970**, *92*, 2476.
(9) Stelmeah, H.; Connors, K. A. *J. Am. Chem. Soc.* **1970**, *92*, 863.

(0.75 mmHg); IR (film) 1740, 1040 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.27 (s, 6 H), 2.43 (dd, J = 12.3, 5.3 Hz, 1 H), 3.11 (dd, J = 12.3, 10.0 Hz, 1 H), 3.67 (s, 3 H), 3.77 (dd, J = 10.0, 5.3 Hz, 1 H), 3.78 (s, 3 H), 6.85 (d, J = 6.6 Hz, 2 H), 7.24 (d, J = 6.6 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 45.7 (2 C), 49.4, 52.0, 55.2, 62.9, 114.1 (2 C), 128.9 (2 C), 129.5, 159.0, 173.9. Anal. Calcd for $C_{13}H_{19}NO_3$: C, 65.80; H, 8.07; N, 5.90. Found: C, 65.96; H, 8.29; N, 5.64.

Reaction of 7d with CsF. A. In a manner similar to that described for **7a** (**A**), salt **7d** (0.89 g, 2 mmol) was allowed to react with CsF (0.96 g, 6 mmol) in DMF (10 mL) and worked up to give a mixture of methyl 3-(dimethylamino)-2-(4-fluorophenyl)propionate (**13d**) and methyl 2-(dimethylamino)-3-(4-fluorophenyl)propionate (**15d**), yield 386 mg (86%), bp 85−90 °C (0.6 mmHg), ratio 80:20 (determined by the integrated values in ^1H NMR of the mixture); ^1H NMR (500 MHz, $CDCl_3$) **13d**: δ 2.26 (s, 6 H), 2.44 (dd, J = 12.5, 5.5 Hz, 1 H), 3.08 (dd, J = 12.5, 10.0 Hz, 1 H), 3.68 (s, 3 H), 3.79 (dd, J = 10.0, 5.5 Hz, 1 H), 7.01 (dd, J_{F-H} = 11.9, J = 5.5 Hz, 2 H), 7.30 (dd, J_{F-H} = 8.9, J = 5.5 Hz, 2 H); **15d**: δ 2.16 (s, 6 H), 2.66 (dd, J = 14.9, 8.2 Hz, 1 H), 2.95 (dd, J = 14.9, 6.7 Hz, 1 H), 3.57 (s, 3 H), 3.85 (dd, J = 8.2, 6.7 Hz, 1 H), 6.99−7.03 (m, 2 H), 7.22 (dd, J_{F-H} = 8.8, 5.5 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) **13d**: δ 45.7 (2 C), 49.5, 52.1, 62.9; **15d**: δ 38.4, 42.2 (2 C), 51.6, 65.6; the others: 115.0 (d, J_{F-C} = 20.7 Hz, 2 C), 115.6 (d, J_{F-C} = 21.7 Hz, 2 C), 129.5 (d, J_{F-C} = 7.2 Hz, 2 C), 129.8 (d, J_{F-C} = 8.3 Hz, 2 C), 133.2 (d, J_{F-C} = 3.1 Hz), 134.6, 162.1 (d, J_{F-C} = 245.2 Hz), 162.2 (d, J_{F-C} = 246.2 Hz), 172.1, 173.6. Anal. Calcd for $C_{12}H_{16}FNO_2$: C, 63.98; H, 7.16; N, 6.22. Found: C, 63.87; H, 7.21; N, 6.05.

B. In a manner similar to that described for **7a** (**B**), salt **7d** (0.80 g, 2 mmol) was allowed to react with CsF (0.96 g, 6 mmol, not predried) in DMF and worked up to give a mixture of **13d**, **15d**, and methyl 2-(dimethylamino)-3-(4-fluorophenyl)propionate (**16d**), yield 140 mg (33%), ratio 69:19:12. Compound **16d** was separated on an aluminum oxide column (EtOAc/hexane, 1:10): a colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 2.38 (s, 6 H), 2.89 (dd, J = 13.4, 5.8 Hz, 1 H), 3.02 (dd, J = 13.4, 9.4 Hz, 1 H), 3.37 (dd, J = 9.4, 5.8 Hz, 1 H), 3.61 (s, 3 H), 6.96 (dd, J_{F-H} = 8.8, J = 8.5 Hz, 2 H), 7.15 (dd, J_{F-H} = 5.5, J = 8.5 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 35.0, 41.9 (2 C), 51.1, 69.6, 115.1 (d, J_{F-C} = 21.7 Hz, 2 C), 130.5 (d, J_{F-C} = 8.3 Hz, 2 C), 133.8, 161.6 (d, J_{F-C} = 234.1 Hz), 171.7. Anal. Calcd for $C_{12}H_{16}FNO_2$: C, 63.98; H, 7.16; N, 6.22. Found: C, 63.90; H, 7.25; N, 6.11.

Reaction of 7e with CsF. In a manner similar to that described for **7a** (**A**), salt **7e** (0.89 g, 2 mmol) was allowed to react with CsF (0.96 g, 6 mmol) in DMF (10 mL) and worked up. The ethereal extract was concentrated, and the residue was chromatographed on an aluminum oxide column (EtOAc/hexane, 1:10) to give methyl 3-(dimethylamino)-2-(4-chlorophenyl)propionate (**13e**) (311 mg, 66%), methyl 2-(4-chlorophenyl)propenoate[10] (**14e**) (44 mg, 9%), and methyl 2-(dimethylamino)-3-(4-chlorophenyl)propionate (**15e**) (93 mg, 20%).

13e: a colorless oil; IR (film) 1740, 1490, 1200 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.27 (s, 6 H), 2.46 (dd, J = 12.3, 5.5 Hz, 1 H), 3.08 (dd, J = 12.3, 9.5 Hz, 1 H), 3.68 (s, 3 H), 3.78 (dd, J = 9.5, 5.5 Hz, 1 H), 7.26 (d, J = 8.8 Hz, 2 H), 7.28 (d, J = 8.8 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 45.6 (2 C), 49.6, 52.1, 62.7, 128.8 (2 C), 129.3 (2 C), 133.3, 135.9, 173.2. Anal. Calcd for $C_{12}H_{16}ClNO_2$: C, 59.63; H, 6.67; N, 5.79. Found: C, 59.51; H, 6.82; N, 5.59.

14e: a colorless oil (lit.[10]); IR (film) 1720, 1500, 1200, 1095 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 3 H), 5.89 (s, 1 H), 6.38 (s, 1 H), 7.31−7.54 (m, 4 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 55.3, 130.3, 131.3 (2 C), 132.7 (2 C), 137.2, 138.1, 143.2, 169.8.

15e: a colorless oil; IR (film) 1740, 1470, 1180 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.37 (s, 6 H), 2.89 (dd, J = 13.6, 6.2 Hz, 1 H), 3.01 (dd, J = 13.6, 9.2 Hz, 1 H), 3.38 (dd, J = 9.2, 6.2 Hz, 1 H), 3.61 (s, 3 H), 7.12 (d, J = 8.2 Hz, 2 H), 7.23 (d, J = 8.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.1, 41.8 (2 C), 51.1, 69.4, 128.5 (2 C), 130.5 (2 C), 132.3, 136.7, 171.7. Anal. Calcd for $C_{12}H_{16}ClNO_2$: C, 59.63; H, 6.67; N, 5.79. Found: C, 59.55; H, 6.90; N, 5.66.

***N,N*-Dimethyl-*N*-[(methoxycarbonyl)methyl]-α-(trimethylsilyl)benzylammonium Hexafluorophosphate (19).** Methyl bromoacetate (3.20 g, 20.8 mmol) was added dropwise to a solution of *N,N*-dimethyl-α-(trimethylsilyl)benzylamine[11] (2.85 g, 13.8 mmol) in MeCN (30 mL) at room temperature, and the mixture was stirred for 24 h. The solvent was evaporated under reduced pressure. The residue was dissolved in $CHCl_3$ (30 mL) and stirred with saturated aqueous NH_4PF_6 (10 mL) for 30 min. The $CHCl_3$ layer was separated, and the aqueous layer was extracted with $CHCl_3$ (3 × 20 mL). The combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure to give **19** (1.94 g, 33%): mp 121 °C (recrystallized from EtOH−Et_2O); IR (Nujol) 1759, 1462, 833 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.26 (s, 9 H), 3.31 (s, 3 H), 3.51 (s, 3 H), 3.79 (s, 3 H), 3.93 and 4.07 (AB-q, J = 17.1 Hz, 2 H), 4.75 (s, 1 H), 7.21−7.54 (m, 5 H). Anal. Calcd for $C_{15}H_{26}F_6NO_2PSi$: C, 42.35; H, 6.16; N, 3.29. Found: C, 42.17; H, 6.21; N, 3.34.

Reaction of 19 with CsF. A. In a manner similar to that described for **7a** (**A**), **19** (0.46 g, 1 mmol) was allowed to react with 3 mol equiv of CsF (0.46 g, 3 mmol) in DMF (10 mL) and worked up to give a mixture of **15a** and **16a** (151 mg, 73%, ratio 28:72). The product ratio was determined by the integrated values in ^1H NMR of the mixture.

B. In the same way, **19** (0.34 g, 0.8 mmol) was treated with an equimolar amount of CsF (0.13 g, 0.8 mmol) in DMF (10 mL) and worked up. The residue from the ethereal extract was chromatographed on an aluminum oxide column (Et_2O/hexane, 1:3) to give **16a** (57 mg, 30%) and methyl 2-(dimethylamino)-3-phenyl-3-(trimethylsilyl)propionate **21** (18 mg, 8%), a colorless oil; IR (film) 1749, 849 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ −0.06 (s, 9 H), 2.33 (s, 6 H), 2.72 (d, J = 13.2 Hz, 1 H), 3.43 (s, 3 H), 3.71 (d, J = 13.2 Hz, 1 H), 7.01−7.09 (m, 3 H), 7.16−7.22 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −1.6 (3 C), 37.1, 42.1 (2 C), 50.4, 69.8, 125.0 (2 C), 128.1, 128.2 (2 C), 141.2, 170.1. Anal. Calcd for $C_{15}H_{25}NO_2Si$: C, 64.47; H, 9.02; N, 5.01. Found: C, 64.23; H, 9.03; N, 4.99.

Reaction of 21 with CsF. A mixture of **21** (13 mg, 0.05 mmol) and CsF (23 mg, 0.15 mmol) in DMF (2 mL) was stirred at room temperature for 24 h and worked up in a manner similar to that described above to give **16a** (9 mg, 85%).

***N,N*-Dimethyl-*N*-[(trimethylsilyl)methyl]-α-cyanobenzylammonium Perchlorate (22).** (Trimethylsilyl)methyl triflate (4.72 g, 20 mmol) was added to a solution of *N,N*-dimethyl-α-cyanobenzylamine[12] (3.2 g, 20 mmol) in CH_2Cl_2 (100 mL), and the mixture was stirred at room temperature for 24 h. The mixture was concentrated under reduced pressure. The residue was dissolved in $CHCl_3$ (20 mL) and stirred with saturated aqueous $NaClO_4$ (30 mL) for 3 h. The $CHCl_3$ layer was separated, and the aqueous layer was extracted with $CHCl_3$ (3 × 20 mL). The combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure to give **22** (2.42 g, 35%): mp 152−153 °C (recrystallized from MeOH−Et_2O); IR (KBr) 2250, 1470, 850 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.35 (s, 9 H), 3.23 (s, 2 H), 3.27 (s, 3 H), 3.35 (s, 3 H), 6.23 (s, 1 H), 7.58−7.80 (m, 5 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ −0.6 (3 C), 51.4, 52.1, 56.9, 71.6, 113.2, 124.1, 130.2 (2 C), 132.3 (2 C), 133.2. Anal. Calcd for $C_{14}H_{23}ClN_2O_4Si$: C, 48.48; H, 6.68; N, 8.06. Found: C, 48.17; H, 6.86; N, 8.03.

Reaction of 22 with CsF. In a manner similar to that described for **7a**, **22** (0.56 g, 1.6 mmol) was allowed to react with CsF (0.96 g, 6 mmol) and worked up. The residue of the ethereal extract was chromatographed on a silica gel column (EtOAc/hexane, 1:10) to give 2-phenylacrylonitrile[13] (**25**) (52 mg, 25%) and *N,N*-dimethyl-2,4-dicyano-2,4-diphenylbutylamine (**26**) (80 mg, 30%, a 1:1 mixture of diastereoisomers), a colorless oil; bp 170 °C (0.55 mmHg); IR (film) 2250, 1450,

(10) Takaoka, T.; Tanaka, K.; Kato, K. *Jpn. Kokai Tokkyo Koho*. JP-05125115, 1993. (*Chem. Abstr.* **1993**, *119*, 272538s).

(11) Maeda, Y.; Sato, Y. *J. Chem. Soc. Perkin Trans. 1* **1997**, 1491.

(12) Taylor, H. M.; Hauser, C. R. *Organic Syntheses*; Wiley: New York, 1973; Coll. Vol. 5, p 437.

(13) Steward, J. M.; Chang, C. H. *J. Org. Chem.* **1956**, *21*, 635.

1040, 700 cm^{-1}. The diastereomers were separated by preparative TLC (Al_2O_3, EtOAc−hexane, 1:4).

26 (isomer-1): ^1H NMR (500 MHz, $CDCl_3$) δ 2.28 (s, 6 H), 2.64 (dd, J = 14.0, 8.6 Hz, 1 H), 2.65 (dd, J = 14.0, 5.5 Hz, 1 H), 2.79 and 2.82 (AB-q, J = 14.0 Hz, 2 H), 3.82 (dd, J = 8.6, 5.5 Hz, 1 H), 7.23−7.54 (m, 10 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 34.0, 42.9, 47.6, 48.9, 69.3, 119.5, 121.0, 126.3, 126.7, 127.4, 127.6, 128.7, 129.0 (2 C), 129.1, 129.2, 129.3, 129.3, 134.9, 135.3. Anal. Calcd for $C_{20}H_{21}N_3$: C, 79.17; H, 6.98; N, 13.85. Found: C, 79.25; H, 7.04; N, 13.70.

26 (isomer-2): ^1H NMR (500 MHz, $CDCl_3$) δ 2.29 (s, 6 H), 2.35 (dd, J = 14.7, 4.9 Hz, 1 H), 2.87 (dd, J = 14.7, 14.0 Hz, 2 H), 2.94 (dd, J = 14.0, 8.5 Hz, 1 H), 3.77 (dd, J = 8.5, 4.9 Hz, 1 H), 7.13−7.39 (m, 10 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 34.0, 42.6, 47.5, 48.6, 69.1, 120.0, 120.9, 126.3, 127.4 (2 C), 127.6, 128.3, 128.4 (2 C), 129.1, 129.2 (2 C), 129.3, 135.5, 135.8. Anal. Calcd for $C_{20}H_{21}N_3$: C, 79.17; H, 6.98; N, 13.85. Found: C, 79.25; H, 7.04; N, 13.70.

(*S*)-(+)-*N*,*N*-Dimethyl-*N*-[(trimethylsilyl)methyl]-1-(methoxycarbonyl)-2-phenylethylammonium Iodide (27). In a manner similar to that described for **7**, a mixture of *l*-phenylalanine methyl ester hydrochloride (2.0 g, 9.6 mmol), (chloromethyl)trimethylsilane (2.5 g, 20 mmol), KI (3.4 g, 20 mmol), and K_2CO_3 (2.1 g, 15 mmol) in DMF (30 mL) was stirred for 1 h and worked up to give (*S*)-(+)-methyl 2-[(trimethylsilyl)methyl]amino-3-phenylpropionate (2.0 g, 37%): bp 100 °C (2 mmHg); $[\alpha]^{22}_D$ +33.1° (*c* 0.22, MeOH); ^1H NMR (270 MHz, $CDCl_3$) δ 0.08 (s, 9 H), 1.41 (br s, 1 H), 1.98 and 2.11 (AB-q, J = 13.2 Hz, 2 H), 2.99 (dd, J = 13.2, 7.1 Hz, 1 H), 3.02 (dd, J = 13.2, 7.1 Hz, 1 H), 3.50 (t, J = 7.1 Hz, 1 H), 3.70 (s, 3 H), 7.24−7.37 (m, 5 H). Anal. Calcd for $C_{14}H_{23}NO_2Si$: C, 63.35; H, 8.73; N, 5.28. Found: C, 63.12; H, 8.68; N, 5.22.

Iodomethane (7.1 g, 50 mmol) was added to a mixture of (*S*)-(+)-methyl 2-[(trimethylsilyl)methyl]amino-3-phenylpropionate (1.3 g, 5 mmol) and K_2CO_3 (0.7 g, 5 mmol) in MeCN (15 mL). The mixture was stirred for 12 h and filtered, and the filtrate was concentrated to give **27** (1.1 g, 40%): mp 132−133.5 °C (recrystallized from acetone−Et_2O); $[\alpha]^{22}_D$ +2.7° (*c* 0.1, MeOH); ^1H NMR (500 MHz, $CDCl_3$) δ 0.38 (s, 9 H), 3.17 (t, J = 12.2 Hz, 1 H), 3.50 (s, 3 H), 3.51 and 3.71 (AB-q, J = 14.6 Hz, 2 H), 3.58 (s, 3 H), 3.62 (s, 3 H), 3.70 (dd, J = 12.2, 4.6 Hz, 1 H), 5.0 (dd, J = 12.2, 4.6 Hz, 1 H), 7.30−7.36 (m, 5 H). Anal. Calcd for $C_{16}H_{28}INO_2Si$: C, 45.60; H, 6.70; N, 3.32. Found: C, 45.34; H, 6.66; N, 3.23.

Reaction of 27 with CsF. In a manner similar to that described for **7a**, **27** (0.42 g, 1 mmol) was allowed to react with CsF (0.46 g, 3 mmol) in DMF (5 mL) and worked up. The residue was chromatographed on a silica gel column (Et_2O/hexane, 1:10) to give methyl 2-[(dimethylamino)methyl]-3-phenylpropionate (**30**) (142 mg, 64%) and methyl cinnamate (**31**) (16 mg, 10%).

30: bp 120−130 °C (0.75 mmHg); $[\alpha]^{22}_D$ 0.00° (*c* 0.1, MeOH); IR (film) 1750, 1150 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.22 (s, 6 H), 2.28 (dd, J = 12.2, 4.4 Hz, 1 H), 2.68 (dd, J = 12.2, 7.8 Hz, 1 H), 2.80−2.89 (m, 3 H), 3.59 (s, 3 H), 7.15−7.21 (m, 3 H), 7.25−7.29 (m, 2 H). Anal. Calcd for $C_{13}H_{19}NO_2$: C, 70.56; H, 8.65; N, 6.33. Found: C, 70.62; H, 8.66; N, 6.23.

JO981729H