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Reaction of *N*,*N*-Dialkyl-*N*-(trimethylsilyl)methyl-γ-substituted Allylammonium Salts with Cesium Fluoride

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The reaction of *N*,*N*-dialkyl-*N*-(trimethylsilyl)methyl-γ-(methoxycarbonyl or cyano)allylammonium salts (1e, g, h) with cesium fluoride in *N*,*N*-dimethylformamide (DMF) did not form the expected allyl rearrangement products 3 of *N*-methylides 2, and instead gave *N*,*N*-dialkyl-3-(methoxycarbonyl or cyano)-2-(fluoromethyl)propylamines (9e, g, h) as the main product. The reaction mechanism is discussed.

Key words ammonium ylide; fluoro compound; sigmatropic rearrangement; Stevens rearrangement; Sommelet–Hauser rearrangement

[2,3] Sigmatropic rearrangement of benzylammonium or allylammonium *N*-alkylides[1] is useful for the synthesis of 2-methylbenzylamines or but-3-enylamines because the reaction proceeds with high regio- and stereoselectivity.[2] Fluoride ion-induced desilylation of [(trimethylsilyl)-methyl]ammonium salts is superior to other methods for the generation of *N*-methylides,[3,4] especially those with a functional group.[5] In this paper, we report the reaction of γ-substituted allylammonium *N*-methylides.

The treatment of *N*,*N*-dimethyl-*N*-[(trimethylsilyl)-methyl]cinnamylammonium (**1a**), -hexa-2,4-dienylammonium (**1b**), -5-phenylpenta-2,4-dienylammonium (**1c**) or -4-(benzoyloxy)- but-2-enylammonium halide (**1d**) with cesium fluoride in dimethylformamide (DMF) (method A) gave the corresponding allyl rearrangement products **3a**—**d** of the ylides **2a**—**d** in good yields (Table 1, entries 1—4), and the reaction of *N*-benzyl-*N*-methyl-*N*-[(trimethylsilyl)methyl]cinnamylammonium bromide (**1f**) yielded a mixture of the allyl and Sommelet–Hauser rearrangement products **3f** and **6f** (entry 7).[6]

However, the reaction of (*E*)-*N*-benzyl-*N*-methyl-3-methoxycarbonyl-*N*-trimethylsilylmethyl-2-propenylammonium hexafluorophosphate (**1g**) gave a mixture of methyl 2-(*N*-benzyl-*N*-methylamino)methyl-2-butenoate (**4g**), methyl 5-(*N*-benzyl-*N*-methylamino)-2-pentenoate (**5g**), methyl 2-benzyl-3-formylpropionate (**7g**) and methyl 4-[*N*-methyl-*N*-(trimethylsilyl)methylamino]-5-phenyl-2-pentenoate (**8g**) (entry 8), and the product from (*E*)-*N*,*N*-dimethyl-3-methoxycarbonyl-*N*-trimethylsilylmethyl-2-propenylammonium bromide (**1e**) was a complex mixture (entry 5). Thus, the reactions of 3-(methoxycarbonyl)prop-2-enylammonium salts **1e, g** were different from those of **1a**—**d, f**.

Compound **4g** may be formed by isomerization of **3g**, and **5g** is a [1,2] rearrangement product of **2g** (Chart 2). Compound **8g** should be a [1,2] rearrangement product of the ylide **10g**, and **7g** may be a hydrolysis product of the enamine **13g**, which was formed from **10g** *via* consecutive [2,3] and [3,3] sigmatropic migrations. We initially considered that **10g** was generated by intermolecular proton transfer from **1g** to **2g** (path b), since we had previously inferred that, in the *N*-methylide formation by desilylation of *N*-(ethoxycarbonyl)methyl-*N*-methyl-*N*-[(trimethylsilyl)methyl]benzylammonium bromide, an intermolecular proton transfer from the starting salt to the ylide might occur competitively with isomerization of the ylide at room temperature, but was decreased at 60 °C.[5]

However, when **1g** was allowed to react with cesium fluoride at 60 °C, methyl 4-(*N*-benzyl-*N*-methylamino)-3-fluoromethylbutyrate (**9g**) was newly formed as the main product (entry 9). The addition of a solution of **1g** in DMF to a suspension of cesium fluoride in DMF (method B) resulted in a considerable increase in the amount of **9g** at 60 °C, but not at room temperature (compare entries 8—11). The fluorine atom in **9g** should originate from the excess of cesium fluoride rather than from the hexafluorophosphate anion, since the formation of **9g** was not affected by exchange of the counter ion to perchlorate (entry 11).

The ylide anion of **2g** may attack the β-carbon that is charged relatively positively by conjugation with a methoxycarbonyl group to give an azetidinium intermediate **14**, the ring of which is subsequently opened by a nucleophilic attack of fluoride ion to give **15** (Chart 3). The reaction of **1e** with cesium fluoride in method B gave a mixture of methyl 2-(dimethylaminomethyl)but-2-

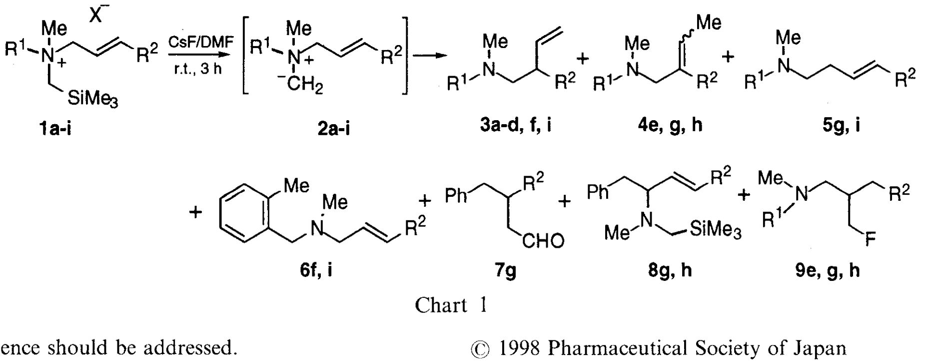

Chart 1

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Table 1. Reaction of (Trimethylsilylmethyl)ammonium Salts **1** with CsF in DMF

Entry		R^1	R^2	X	Method[a]	Reaction Temp. (°C)	Total yield (%)	Isolated yield of (%)						
								3	**4**	**5**	**6**	**7**	**8**	**9**
1	**1a**	Me	Ph	Br	A	RT	88	88	0	0	—	—	—	0
2	**1b**	Me	CH=CH–Me	I	A	RT	66[b]	66	0	0	—	—	—	0
3	**1c**	Me	CH=CH–Ph	I	A	RT	81	81	0	0	—	—	—	0
4	**1d**	Me	CH_2OCOPh	I	A	RT	81	81	0	0	—	—	—	0
5	**1e**	Me	CO_2Me	Br	A	RT	—				Complex mixture			
6	**1e**	Me	CO_2Me	Br	B	60	18	0	6	0	—	—	—	12
7	**1f**	Bn	Ph	Br	A	RT	58	38	0	0	20	0	0	0
8	**1g**	Bn	CO_2Me	PF_6	A	RT	32	0	3	3	0	5	21	0
9	**1g**	Bn	CO_2Me	PF_6	A	60	76	0	0	5	0	8	27	36
10	**1g**	Bn	CO_2Me	PF_6	B	RT	70	0	9	11	0	8	42	0
11	**1g**	Bn	CO_2Me	PF_6 or ClO_4	B	60	84	0	0	11	0	4	13	56
12	**1h**	Bn	CN	PF_6	B	60	90	0	7	0	0	0	9	74
13	**1i**	Bn	Cl	PF_6	B	60	94	42[c]	0	5	47	0	0	0

[a] Method A: CsF was added to a solution of **1** at room temperature; Method B: A solution of **1** in DMF was slowly added to a suspension of CsF in DMF. [b] **1b** was not isolated. Yield was calculated from (*E*,*E*)-*N*-methyl-*N*-[(trimethylsilyl)methyl]hexa-2,4-dienylamine. [c] A mixture of **3i** (R^2=Cl) and **3i′** (R^2=F) (2:8).

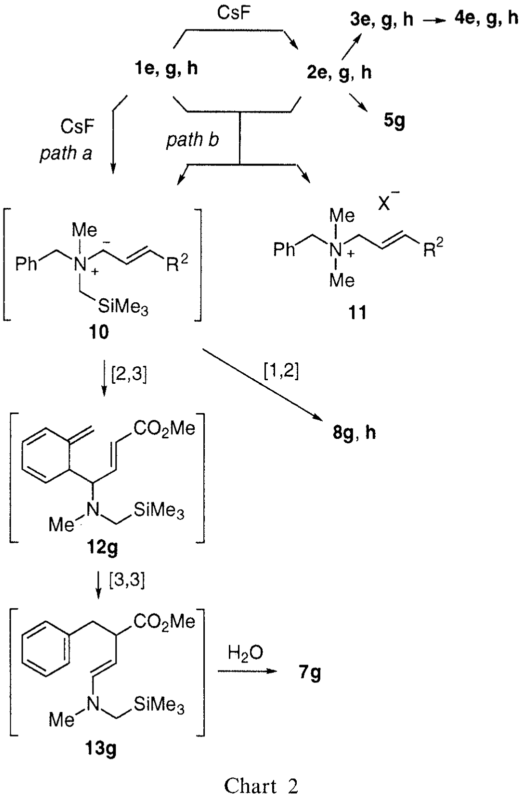

Chart 2

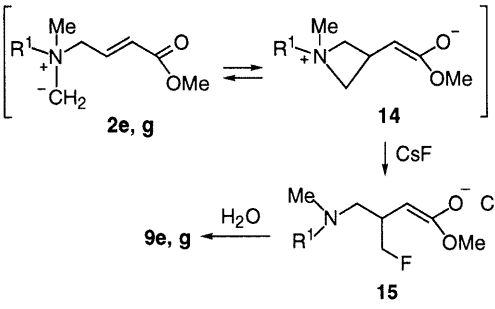

Chart 3

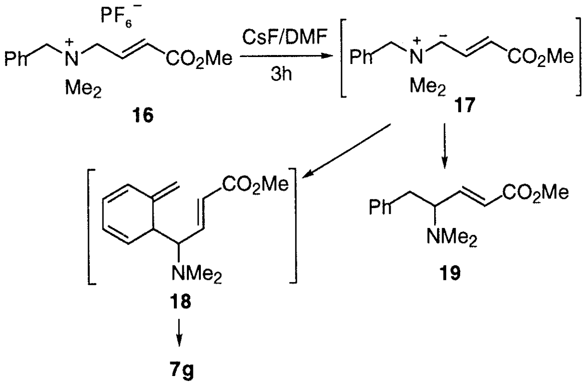

Chart 4

enoate (**4e**) and methyl 4-dimethylamino-3-(fluoromethyl)-butyrate (**9e**) (entry 6). A similar formation of the fluoro compound **9h** was observed in the reaction of (*E*)-*N*-benzyl-3-cyano-*N*-methyl-*N*-trimethylsilylmethyl-2-propenylammonium hexafluorophosphate (**1h**), but not in that of the *N*-(3-chloroprop-2-enyl) analogue **1i** (entry 13). Thus, the presence of a strong γ-electron-withdrawing group (R^2) seems to cause a characteristic reaction.

It is well known that cesium fluoride reacts as a base with active methylene compounds.[7] Treatment of *N*-benzyl-*N*,*N*-dimethyl-3-(methoxycarbonyl)prop-2-enylammonium hexafluorophosphate (**16**) with cesium fluoride in DMF at 60 °C gave a mixture of methyl 4-dimethylamino-5-phenylpenta-2-enoate (**19**) (41%) and **7g** (10%) (Chart 4). The ylide **17** was apparently generated by the reaction of **16** with cesium fluoride. It is likely that **10** was directly produced from **1** by cesium fluoride (path a), and not by proton transfer from **1** to **2** (path b), as we had initially supposed (Chart 2).

Experimental

All reactions were carried out under N_2. DMF was dried by distillation from BaO under reduced pressure. CsF was dried over P_2O_5 at 190 °C under reduced pressure. Distillation was carried out using a Kugelrohr distillation apparatus. All melting and boiling points are uncorrected.

(*E*,*E*)-*N*,*N*-Dimethyl-*N*-[(trimethylsilyl)methyl]hexa-2,4-dienylammonium Iodide (1b) A mixture of $SOCl_2$ (18 ml, 240 mmol) and sorbic acid (4.51 g, 40 mmol) was heated at 65 °C for 3 h and the excess $SOCl_2$ was removed under reduced pressure. A benzene (40 ml) solution of the residue was added dropwise to a stirred mixture of methyl[(trimethylsilyl)methyl]amine (4.69 g, 40 mmol), benzene (40 ml) and 10% aqueous

NaOH (40ml), and the reaction mixture were stirred at 40 °C for 2h. The organic layer was separated and the aqueous layer was extracted with $\mathrm{Et_2O}$. The combined organic layers were washed with water and saturated brine, dried ($\mathrm{MgSO_4}$) and concentrated under reduced pressure. The residue was distilled to give (*E,E*)-*N*-methyl-*N*-[(trimethylsilyl)methyl]hexa-2,4-dienamide (7.36g, 87%) as a colorless oil. IR (film) $\mathrm{cm^{-1}}$: 1653, 855. The nonequivalence of the protons in the ^{1}H-NMR spectrum is considered to be due to hindered rotation of the amide group (isomer-1/isomer-2, 2:1); ^{1}H-NMR (270MHz; $\mathrm{CDCl_3}$) isomer-1, δ: 0.08 (9H, s), 1.83 (3H, d, $J=6.2$Hz), 3.02 (2H, s), 3.07 (3H, s), 6.02—6.07 (3H, m), 7.22 (1H, dd, $J=14.9$, 10.8Hz); isomer-2, δ: 0.09 (9H, s), 1.87 (3H, d, $J=6.2$Hz), 2.95 (2H, s), 3.01 (3H, s), 5.80—6.36 (3H, m), 7.55—7.65 (1H, m). *Anal.* Calcd for $\mathrm{C_{11}H_{21}NOSi}$: C, 62.50; H, 10.01; N, 6.63. Found: C, 62.18; H, 10.08; N, 6.62.

A solution of *N*-methyl-*N*-[(trimethylsilyl)methyl]hexa-2,4-dienamide (4.23g, 20mmol) in $\mathrm{Et_2O}$ (50ml) was added dropwise to a suspension of $\mathrm{LiAlH_4}$ (0.94g, 24mmol) in $\mathrm{Et_2O}$ (100ml) at room temperature. The reaction was quenched with water (2ml) after 3h and the mixture was filtered. The filtrate was extracted with 1 M aqueous HCl. The acid extract was washed with $\mathrm{Et_2O}$, made alkaline with 10% aqueous NaOH, and then extracted with $\mathrm{Et_2O}$. The ethereal extract was washed with water, dried ($\mathrm{MgSO_4}$) and evaporated under reduced pressure. The residue was distilled to give (*E,E*)-*N*-methyl-*N*-[(trimethylsilyl)methyl]hexa-2,4-dienylamine (3.32g, 84%) as a colorless oil. IR (film) $\mathrm{cm^{-1}}$: 855. ^{1}H-NMR (270MHz; $\mathrm{CDCl_3}$) δ: 0.06 (9H, s), 1.74 (3H, d, $J=6.6$Hz), 1.87 (2H, s), 2.20 (3H, s), 2.94 (2H, d, $J=6.6$Hz), 5.54—6.74 (4H, m). *Anal.* Calcd for $\mathrm{C_{11}H_{23}NSi}$: C, 66.93; H, 11.74; N, 7.10. Found: C, 66.61; H, 11.84, N, 6.98.

N-Methyl-*N*-[(trimethylsilyl)methyl]hexa-2,4-dienylamine was quaternized with iodomethane. However, the ammonium iodide **1b** was not crystallized. The reaction with CsF was carried out in one pot starting from the hexa-2,4-dienylamine, without isolation of **1b** (see reaction of **1b** with CsF).

(*E,E*)-*N,N*-Dimethyl-*N*-(trimethylsilyl)methyl-5-phenylpenta-2,4-dienylammonium Iodide (1c) In a manner similar to that described above, (*E,E*)-5-phenylpenta-2,4-dienoic acid (5.23g, 30mmol) was treated with $\mathrm{SOCl_2}$ (18ml, 240mmol) and then with methyl[(trimethylsilyl)methyl]amine (3.52g, 30 mmol) to give (*E,E*)-*N*-methyl-*N*-(trimethylsilyl)methyl-5-phenylpenta-2,4-dienamide (6.56g, 80%), mp 67—69 °C (from hexane). The nonequivalence of the protons in the ^{1}H-NMR spectrum is considered to be due to hindered rotation of the amide group (isomer-1/isomer-2, 3:1); ^{1}H-NMR (270MHz; $\mathrm{CDCl_3}$) δ: 6.83—7.27 (3H, m), 7.27—7.46 (5H, m); isomer-1 δ: 0.10 (9H, s), 3.04 (2H, s), 3.12 (3H, s), 6.48 (1H, d, $J=14.7$Hz); isomer-2 δ: 0.13 (9H, s), 2.99 (2H, s), 3.03 (3H, s), 6.42 (1H, s). *Anal.* Calcd for $\mathrm{C_{16}H_{23}NOSi}$: C, 70.28; H, 8.48; N, 5.12. Found: C, 70.25; H, 8.54; N, 5.33.

N-Methyl-*N*-(trimethylsilyl)methyl-5-phenylpenta-2,4-dienamide (1.73g, 6.3mmol) and $\mathrm{LiAlH_4}$ (0.29g, 7.6mmol) were treated in $\mathrm{Et_2O}$ (20ml) for 3h, in a manner similar to that described for **1b**, and worked up to give (*E,E*)-*N*-methyl-*N*-(trimethylsilyl)methyl-5-phenylpenta-2,4-dienylamine (4.93g, 95%) as a colorless oil. ^{1}H-NMR (270MHz; $\mathrm{CDCl_3}$) δ: 0.22 (9H, s), 2.06 (2H, s), 2.39 (3H, s), 3.19 (2H, d, $J=8.6$Hz), 6.00 (1H, dt, $J=15.2$, 8.6Hz), 6.45 (1H, dd, $J=15.2$, 10.6Hz), 6.65 (1H, d, $J=16.2$Hz), 6.93 (1H, dd, $J=16.2$, 10.6Hz), 7.32—7.58 (5H, m). *Anal.* Calcd for $\mathrm{C_{16}H_{25}N}$: C, 74.07; H, 9.71; N, 5.04. Found: C, 73.77; H, 9.82; N, 5.21.

A solution of *N*-methyl-*N*-(trimethylsilyl)methyl-5-phenylhexa-2,4-dienylamine (3.89g, 15mmol) and iodomethane (5.60g, 40mmol) in MeCN (15ml) was allowed to react to give **1c** (5.48g, 91%), mp 172—174 °C (from acetone–$\mathrm{Et_2O}$). ^{1}H-NMR (500MHz; $\mathrm{CDCl_3}$) δ: 0.34 (9H, s), 3.32 (2H, s), 3.36 (6H, s), 4.55 (2H, d, $J=7.6$Hz), 5.90 (1H, dt, $J=15.2$, 7.6Hz), 6.79 (1H, d, $J=15.9$Hz), 6.84 (1H, dd, $J=15.9$, 9.2Hz), 6.98 (1H, dd, $J=15.2$, 9.2Hz), 7.06—7.42 (5H, m). *Anal.* Calcd for $\mathrm{C_{17}H_{28}INSi}$: C, 50.87; H, 7.03; N, 3.49. Found: C, 51.12; H, 6.89; N, 3.53.

(*E*)-4-Benzoyloxy-*N,N*-dimethyl-*N*-trimethylsilylmethyl-2-butenylammonium Iodide (1d) A mixture of methyl(trimethylsilylmethyl)amine (1.52g, 13mmol), 4-chloro-2-butenyl benzoate (2.06g, 9.8mmol) and $\mathrm{K_2CO_3}$ (1.66g, 12mmol) in MeCN (10ml) was heated at reflux overnight and quenched with water (50ml). The mixture was extracted with $\mathrm{Et_2O}$, and the extract was dried ($\mathrm{MgSO_4}$), concentrated and distilled to give (*E*)-4-[methyl(trimethylsilylmethyl)amino]but-2-enyl benzoate (1.86g, 65%) as a colorless oil. IR (film) $\mathrm{cm^{-1}}$: 1723, 855. ^{1}H-NMR (400MHz; $\mathrm{CDCl_3}$) δ: 0.06 (9H, s), 1.89 (2H, s), 2.22 (3H, s), 2.97 (2H, d, $J=5.5$Hz), 4.81 (2H, dd, $J=5.5$, 0.9Hz), 5.53—5.79 (2H, m), 7.41—7.58 (5H, m). *Anal.* Calcd for $\mathrm{C_{16}H_{25}NO_2Si}$: C, 65.93; H, 8.65; N, 4.81. Found: C, 65.84; H, 8.56; N, 5.11.

A solution of 4-[methyl(trimethylsilylmethyl)amino]but-2-enyl benzoate (0.73g, 2.5mmol) and iodomethane (1.42g, 10mmol) in acetone (10ml) was stirred at room temperature for 3h and the solvent was removed under reduced pressure. The residue was recrystallized to give **1d** (0.93g, 86%), mp 164—165 °C (from EtOH). IR (KBr) $\mathrm{cm^{-1}}$: 1711, 851. ^{1}H-NMR (270MHz; $\mathrm{CDCl_3}$) δ: 0.30 (9H, s), 3.31 (2H, s), 3.36 (6H, s), 4.53 (2H, d, $J=7.6$Hz), 4.94 (2H, d, $J=5.0$Hz), 5.99 (1H, dt, $J=15.5$, 7.6Hz), 6.59 (1H, dt, $J=15.5$, 5.0Hz), 7.43—8.06 (5H, m). *Anal.* Calcd for $\mathrm{C_{17}H_{28}INO_2Si}$: C, 47.11; H, 6.51; N, 3.23. Found: C, 46.99; H, 6.52; N, 3.51.

(*E*)-*N,N*-Dimethyl-3-methoxycarbonyl-*N*-trimethylsilylmethyl-2-propenylammonium Bromide (1e) Methyl 4-bromocrotonate (3.26g, 15.5 mmol) was added dropwise to a solution of dimethyl(trimethylsilylmethyl)amine (2.0g, 15.5mmol) in acetone (20ml) at room temperature. The precipitated crystals were collected by filtration after 3h and recrystallized to give **1e** (3.27g, 70%), mp 123—124 °C (from acetone). ^{1}H-NMR (270MHz; $\mathrm{CDCl_3}$) δ: 0.34 (9H, s), 3.25 (2H, s), 3.42 (6H, s), 3.81 (3H, s), 4.85 (2H, d, $J=7.1$Hz), 6.62 (1H, d, $J=17.2$Hz), 6.92 (1H, dt, $J=17.2$, 7.1Hz). *Anal.* Calcd for $\mathrm{C_{11}H_{24}BrNO_2Si}$: C, 42.58; H, 7.80; N, 4.51. Found: C, 42.28; H, 7.55; N, 4.39.

(*E*)-*N*-Benzyl-*N*-methyl-3-methoxycarbonyl-*N*-trimethylsilylmethyl-2-propenylammonium Hexafluorophosphate (1g) A solution of *N*-methyl-*N*-[(trimethylsilyl)methyl]benzylamine (5.0g, 24mmol) and methyl 4-bromocrotonate (4.31g, 24mmol) in acetone (30ml) was stirred overnight and the solvent was removed under reduced pressure. The residue was dissolved in water (50ml) and the resultant solution was mixed with a solution of $\mathrm{NH_4PF_6}$ (2.25g, 12mmol) in water (10ml). The precipitated crystals were collected by filtration after 1h and recrystallized to give **1g** (3.67g, 68%), mp 130—131 °C (from EtOH–water). IR (KBr) $\mathrm{cm^{-1}}$: 1721, 841. ^{1}H-NMR (500MHz; $\mathrm{CDCl_3}$) δ: 0.31 (9H, s), 2.97, 3.05 (2H, ABq, $J=15.3$Hz), 3.02 (3H, s), 3.78 (3H, s), 4.04 (1H, dd, $J=14.0$, 7.3Hz), 4.11 (1H, dd, $J=14.0$, 7.3Hz), 4.41, 4.48 (2H, ABq, $J=15.3$Hz), 6.39 (1H, d, $J=15.6$Hz), 6.90 (1H, dt, $J=15.6$, 7.3Hz), 7.44—7.54 (5H, m). *Anal.* Calcd for $\mathrm{C_{17}H_{28}F_6NO_2PSi}$: C, 45.23; H, 6.25; N, 3.10. Found: C, 45.07; H, 6.24; N, 3.12.

When an aqueous solution of the residue was mixed with a solution of $\mathrm{NaClO_4}$ (1.47g, 12mmol) in water (10ml), crystals of the perchlorate **1g** were obtained, mp 160—161 °C (from EtOH–water).

(*E*)-*N*-Benzyl-3-cyano-*N*-methyl-*N*-trimethylsilylmethyl-2-propenylammonium Hexafluorophosphate (1h) In a manner similar to that described for **1g**, benzyl bromide (1.47g, 8.3mmol) and 4-[methyl(trimethylsilylmethyl)amino]crotononitrile (1.44g, 7.9mmol) were kept overnight in MeCN (10ml). An aqueous solution of the residue was mixed with a solution of $\mathrm{NH_4PF_6}$ (1.29g, 8.3mmol) in water (5ml). The precipitated crystals were collected by filtration and recrystallized to give **1h** (2.80g, 85%), mp 144—145 °C (from EtOH–water). ^{1}H-NMR (500MHz, $\mathrm{CD_3OD}$) δ: 0.33 (9H, s), 3.04, 3.15 (2H, ABq, $J=14.7$Hz), 3.08 (3H, s), 4.04—4.15 (2H, m), 4.48, 4.54 (2H, ABq, $J=12.8$Hz), 6.13 (1H, d, $J=15.9$Hz), 7.09 (1H, dt, $J=15.9$, 7.3Hz), 7.5—7.6 (5H, m). *Anal.* Calcd for $\mathrm{C_{16}H_{25}F_6N_2PSi}$: C, 45.93; H, 6.02; N, 6.69. Found: C, 45.73; H, 6.04; N, 6.78.

(*E*)-*N*-Benzyl-3-chloro-*N*-methyl-*N*-trimethylsilylmethyl-2-propenyl ammonium Hexafluorophosphate (1i) In a manner similar to that described for **1g**, *N*-methyl-*N*-(trimethylsilylmethyl)benzylamine (6.22g, 30mmol) and (*E*)-1,3-dichloropropene (3.66g, 33mmol) were kept in acetone (30ml). The residue was dissolved in water (40ml) and the resultant solution was mixed with a solution of $\mathrm{NH_4PF_6}$ (4.89g, 30mmol) in water (15ml). The precipitated crystals were collected by filtration and recrystallized to give **1i** (9.63g, 75%), mp 162—163.5 °C (from EtOH–water). ^{1}H-NMR (400MHz; $\mathrm{CDCl_3}$) δ: 0.34 (9H, s), 3.12, 3.20 (2H, ABq, $J=15.0$Hz), 3.16 (3H, s), 4.50 (1H, dd, $J=13.2$, 7.7Hz), 4.76, 5.09 (2H, ABq, $J=12.8$Hz), 4.79 (1H, dd, $J=13.2$, 7.7Hz), 6.09 (1H, dt, $J=13.2$, 7.7Hz), 7.12 (1H, d, $J=13.2$Hz), 7.45—7.53 (3H, m), 7.63—7.65 (2H, m). *Anal.* Calcd for $\mathrm{C_{15}H_{25}F_6NPSi}$: C, 42.1; H, 5.9; N, 3.3. Found: C, 42.0; H, 5.9; N, 3.4.

(*E*)-*N*-Benzyl-*N,N*-dimethyl-3-(methoxycarbonyl)prop-2-enylammonium Hexafluorophosphate (16) In a manner similar to that described for **1g**, *N,N*-dimethylbenzylamine (2.85g, 20mmol) and methyl 4-bromocrotonate (3.59g, 20mmol) were kept in MeCN (20ml). The residue was dissolved in water (30ml) and the resultant solution was mixed with a solution of $\mathrm{NH_4PF_6}$ (3.26g, 20mmol) in water (20ml). The precipitated crystals were collected by filtration and recrystallized to give **16** (6.90 g, 91%), mp 125—126 °C (from water). ^{1}H-NMR (500 MHz, CD_3OD) δ: 3.05 (6H, s), 3.80 (3H, s), 4.16 (2H, d, $J=6.7$ Hz), 4.55 (2H, s), 6.41 (1H, d, $J=15.2$ Hz), 7.08 (1H, dt, $J=15.2$, 6.7 Hz), 7.52—7.59 (5H, m). *Anal.* Calcd for $C_{14}H_{20}F_6NO_2P$: C, 44.33; H, 5.31; N, 3.69. Found: C, 44.15; H, 5.27; N, 3.84.

Reaction of 1b with CsF A solution of *N*-methyl-*N*-[(trimethylsilyl)methyl]hexa-2,4-dienylamine (0.79 g, 4.0 mmol) and iodomethane (5.6 g, 40 mmol) in DMF (20 ml) was heated at 60 °C for 3 h. The excess iodomethane and about 10 ml of DMF were removed by distillation under reduced pressure and CsF (1.82 g, 12 mmol) was added under N_2. The mixture was stirred for 20 h at room temperature, quenched with 1% aqueous $NaHCO_3$ (100 ml) and extracted with Et_2O. The extract was washed with water, dried ($MgSO_4$) and concentrated under reduced pressure. The residue was distilled at 65 °C (20 mmHg) and the distillate was chromatographed on a silica gel column with hexane–Et_2O (1.5 : 1) as the eluent to give (*E*)-*N*,*N*-dimethyl-2-vinyl-3-pentenylamine **3b** (370 mg, 66%) as a colorless oil. ^{1}H-NMR (270 MHz; $CDCl_3$) δ: 1.68 (3H, dd, $J=5.0$, 1.0 Hz), 2.22 (6H, s), 2.24 (1H, dd, $J=7.9$, 5.9 Hz), 2.28 (1H, dd, $J=7.9$, 5.9 Hz), 2.84—2.95 (1H, m), 5.03 (1H, d, $J=12.5$ Hz), 5.04 (1H, d, $J=15.8$ Hz), 5.25—5.75 (2H, m), 5.74 (1H, ddd, $J=15.8$, 10.0, 9.9 Hz). *Anal.* Calcd for $C_9H_{17}N$: C, 77.64; H, 12.31; N, 10.06. Found: C, 77.57; H, 12.31; N, 10.09.

Reaction of 1c with CsF The ammonium salt **1c** (0.80 g, 2.0 mmol) was placed in a 20-ml flask equipped with a septum and a test tube was connected to the flask by a short piece of rubber tubing. CsF (0.912 g, 6.0 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 *via* a syringe and CsF was added from the test tube. The mixture was stirred for 20 h at room temperature, poured into 1% aqueous $NaHCO_3$ (100 ml) and extracted with Et_2O (4 × 50 ml). The extract was washed with water, dried ($MgSO_4$) and concentrated under reduced pressure. The residue was distilled at 85—88 °C (0.5 mmHg) and the distillate was chromatographed on a silica gel column with hexane–Et_2O (1.5 : 1) to give (*E*)-*N*,*N*-dimethyl-4-phenyl-2-vinyl-3-butenylamine **3c** (332 mg, 81%) as a colorless oil. ^{1}H-NMR (270 MHz; $CDCl_3$) δ: 2.26 (6H, s), 2.34 (1H, dd, $J=11.9$, 7.3 Hz), 2.43 (1H, dd, $J=11.9$, 8.2 Hz), 3.10—3.15 (1H, m), 5.12 (1H, dd, $J=10.5$, 1.3 Hz), 5.13 (1H, dd, $J=17.5$, 1.3 Hz), 5.84 (1H, ddd, $J=17.5$, 10.5, 9.9 Hz), 6.15 (1H, dd, $J=15.8$, 7.3 Hz), 6.42 (1H, d, $J=15.8$ Hz), 7.16—7.38 (5H, m). *Anal.* Calcd for $C_{14}H_{19}N$: C, 83.53; H, 9.51; N, 6.96. Found: C, 83.34; H, 9.72; N, 6.91.

Reaction of 1d with CsF In a manner similar to that described for **1c**, the ammonium salt **1d** (0.87 g, 2.0 mmol) was treated with CsF (0.912 g, 6.0 mmol) in DMF (10 ml) and worked up. The residue was distilled at 118—120 °C (0.7 mmHg) and the distillate was chromatographed on a silica gel column with hexane–Et_2O (1.5 : 1) to give 2-[(dimethylamino)methyl]but-3-enyl benzoate **3d** (380 mg, 81%) as a colorless oil. ^{1}H-NMR (400 MHz; $CDCl_3$) δ: 2.25 (6H, s), 2.39 (2H, d, $J=8.1$ Hz), 2.75 (1H, br s), 4.27 (1H, dd, $J=10.8$, 5.3 Hz), 4.40 (1H, dd, $J=10.8$, 6.9 Hz), 5.16 (1H, dd, $J=10.8$, 1.6 Hz), 5.20 (1H, dd, $J=17.2$, 1.6 Hz), 5.79 (1H, ddd, $J=17.2$, 10.3, 8.1 Hz), 7.29—7.93 (5H, m). *Anal.* Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00. Found: C, 71.87; H, 8.29; N, 5.84.

Reaction of 1e with CsF (Method A) In a manner similar to that described for the reaction of **1c** with CsF, **1e** (3.10 g, 10 mmol) were treated with CsF (4.56 g, 30 mmol) in DMF (30 ml). The color of the reaction mixture changed to black and a complex mixture formed that was difficult to separate. (Method B): CsF (4.56 g, 30 mmol) was placed in a 100-ml flask equipped with a magnetic stirrer, a septum and a 30 ml dropping funnel which contained **1e** (3.10 g, 10 mmol). The apparatus was dried under reduced pressure and flushed with N_2. DMF (2 × 20 ml) was added *via* a syringe to the flask and dropping funnel, respectively. The solution of **1e** in DMF was then added dropwise to the suspension of CsF in DMF at 60 °C and the mixture was stirred for 3 h. The mixture was quenched with 1% aqueous $NaHCO_3$ (200 ml) and extracted with Et_2O. The extract was washed with water, dried ($MgSO_4$) and concentrated under reduced pressure. The residue was distilled at 75—110 °C (0.6 mmHg) and the distillate (310 mg) was chromatographed on a silica gel column with $CHCl_3$–MeOH (10 : 1) as the eluent to give methyl 2-(dimethylaminomethyl)but-2-enoate **4e** (94 mg, 6%) and methyl 4-dimethylamino-3-(fluoromethyl)butyrate **9e** (213 mg, 12%).

4e: A colorless oil. ^{1}H-NMR (500 MHz; $CDCl_3$) δ: 1.88 (3H, d, $J=7.2$ Hz), 2.23 (6H, s), 3.16 (2H, s), 3.75 (3H, s), 7.04 (1H, t, $J=7.2$ Hz). ^{13}C-NMR (125 MHz; $CDCl_3$) δ: 14.6, 45.4 (2C), 51.8, 53.8, 130.4, 141.1, 168.2. *Anal.* Calcd for $C_8H_{15}NO_2$: C, 61.12; H, 9.62; N, 8.91. Found: C, 61.32; H, 9.55; N, 8.88.

9e: A colorless oil. ^{1}H-NMR (500 MHz; $CDCl_3$) δ: 2.26 (6H, s), 2.36—2.38 (3H, m), 2.45 (2H, $J=5.5$ Hz), 3.69 (3H, s), 4.44, 4.54 (2H, ABq, $J_{F-H}=47.0$ Hz, $J=3.7$ Hz). ^{13}C-NMR (125 MHz; $CDCl_3$) δ: 33.6 (d, $J_{F-C}=6.2$ Hz), 34.7 (d, $J_{F-C}=18.6$ Hz), 45.7 (2C), 51.6, 59.9 (d, $J_{F-C}=5.2$ Hz), 84.5 (d, $J_{F-C}=168.6$ Hz), 173.0. MS *m*/*z* (rel. int. %): 177 (M^+, 13), 146 (28), 58 (100). HR-MS Calcd for $C_8H_{16}FNO_2$: 177.1165. Found: 177.1190.

Reaction of 1g with CsF (Method A) In a manner similar to that described for **1c**, the ammonium salt **1g** (0.91 g, 2.0 mmol) was treated with CsF (0.912 g, 6.0 mmol) in DMF (10 ml) at room temperature for 3 h. The residue of the ethereal extract was distilled at 75—125 °C (0.6 mmHg) and the distillate (193 mg) was chromatographed on a silica gel column with hexane–Et_2O (1.5 : 1) as the eluent to give methyl 2-(*N*-benzyl-*N*-methylamino)methyl-2-butenoate (**4g**) (14 mg, 3%), methyl 5-(*N*-benzyl-*N*-methylamino)-2-pentenoate (**5g**) (14 mg, 3%), methyl 2-benzyl-3-formylpropionate **7g** (21 mg, 5%) and methyl 4-[*N*-methyl-*N*-(trimethylsilyl)methylamino]-5-phenyl-2-pentenoate (**8g**) (129 mg, 27%) (Table 1, entry 8).

4g: A colorless oil. IR (film) cm^{-1}: 1717. ^{1}H-NMR (500 MHz; $CDCl_3$) δ: 1.79 (3H, d, $J=7.3$ Hz), 2.07 (3H, s), 3.19 (2H, s), 3.42 (2H, s), 3.66 (3H, s), 6.93 (1H, q, $J=7.3$ Hz), 7.16—7.27 (5H, m). ^{13}C-NMR (126 MHz; $CDCl_3$) δ: 14.6, 41.8, 51.7, 52.1, 62.4, 126.9, 128.1 (2C), 129.1 (2C), 130.8, 139.2, 141.3. 168.5. *Anal.* Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00. Found: C, 71.84; H, 8.29; N, 5.96.

5g: A colorless oil. IR (film) cm^{-1}: 1725. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 2.24 (3H, s), 2.43 (2H, dd, $J=7.3$, 6.7 Hz), 2.55 (2H, dd, $J=7.3$, 6.7 Hz), 3.54 (2H, s), 3.73 (3H, s), 5.86 (1H, dt, $J=15.9$, 1.8 Hz), 6.96 (1H, dt, $J=15.9$, 6.7 Hz), 7.24—7.33 (5H, m). *Anal.* Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00. Found: C, 71.95; H, 8.35; N, 5.92.

7g: A colorless oil. IR (film) cm^{-1}: 1732. ^{1}H-NMR (500 MHz; $CDCl_3$) δ: 2.52 (1H, dd, $J=18.3$, 4.9 Hz), 2.76 (1H, dd, $J=13.4$, 8.5 Hz), 2.83 (1H, dd, $J=18.3$, 8.5 Hz), 3.08 (1H, dd, $J=13.4$, 6.7 Hz), 3.16—3.22 (1H, m), 3.67 (3H, s), 7.15 (2H, d, $J=6.7$ Hz), 7.21—7.31 (3H, m), 9.69 (1H, s). ^{13}C-NMR (100 MHz; $CDCl_3$) δ: 37.6, 40.8, 44.4, 52.0, 126.8, 128.6 (2C), 128.9 (2C), 138.1, 174.5, 199.9. *Anal.* Calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84. Found: C, 69.66; H, 6.90.

8g: A colorless oil. IR (film) cm^{-1}: 1726, 855. ^{1}H-NMR (270 MHz; $CDCl_3$) δ: 0.03 (9H, s), 1.93, 2.09 (2H, ABq, $J=14.2$ Hz), 2.03 (3H, s), 2.67 (1H, dd, $J=13.5$, 8.9 Hz), 3.03 (1H, ddd, $J=$ 13.5, 8.9, 4.6 Hz), 3.27 (1H, m), 3.71 (3H, s), 5.71 (1H, d, $J=15.8$ Hz), 6.92 (1H, dd, $J=15.8$, 7.9 Hz), 7.13—7.28 (5H, m). *Anal.* Calcd for $C_{17}H_{27}NO_2Si$: C, 66.84; H, 8.91; N, 4.58. Found: C, 66.81; H, 8.98; N, 4.66.

When the same reaction was carried out at 60 °C, **5g** (23 mg, 3%), **7g** (33 mg, 5%), **8g** (165 mg, 27%) and methyl 4-(*N*-benzyl-*N*-methylamino)-3-fluoromethylbutyrate (**9g**) (183 mg, 36%) were obtained (entry 9).

9g: A colorless oil. IR (film) cm^{-1}: 1738. ^{1}H-NMR (500 MHz; $CDCl_3$) δ: 2.18 (3H, s), 2.29—2.35 (1H, m), 2.37—2.49 (4H, m), 3.48, 3.50 (2H, ABq, $J=13.0$ Hz), 3.68 (3H, s), 4.48 (2H, ddd, $J_{F-H}=47.6$, $J=9.2$, 4.0 Hz), 7.15—7.34 (5H, m). ^{13}C-NMR (125 MHz; $CDCl_3$) δ: 33.6 (d, $J_{F-C}=4.0$ Hz), 34.9 (d, $J_{F-C}=17.6$ Hz), 42.3, 51.4, 57.8 (d, $J_{F-C}=5.0$ Hz), 62.8, 84.6 (d, $J_{F-C}=168.6$ Hz), 126.9, 128.2 (2C), 128.8 (2C), 139.1, 173.1. *Anal.* Calcd for $C_{14}H_{20}FNO_2$: C, 66.38; H, 7.96; N, 5.53. Found: C, 66.35; H, 8.06; N, 5.49.

(Method B) In a manner similar to that described for **1e** (method B), a solution of **1g** (0.91 g, 2.0 mmol) in DMF (5 ml) was added to a suspension of CsF (0.912 g, 6.0 mmol) in DMF (5 ml) at room temperature. The reaction mixture was worked up and the distillate at 75—125 °C (0.6 mmHg) (415 mg) was chromatographed on a silica gel column with hexane–Et_2O (1.5 : 1) to give **4g** (42 mg, 9%), **5g** (51 mg, 11%), **7g** (33 mg, 8%) and **8g** (257 mg, 42%) (entry 10).

When the same reaction was carried out at 60 °C, **5g** (51 mg, 11%), **7g** (16 mg, 4%), **8g** (79 mg, 13%) and **9g** (284 mg, 56%) were obtained (entry 11).

Reaction of 1h with CsF In a manner similar to that described for **1e** (method B), **1h** (0.42 g, 1.0 mmol) and CsF (0.46 g, 3.0 mmol) were reacted in DMF (10 ml) at 60 °C. The distillate (207 mg) was chromatographed on a silica gel column with hexane–Et_2O (2 : 1) to give 2-[(*N*-benzyl-*N*-methylamino)methyl]-2-butenonitrile **4h** (15 mg, 7%), 4-[(*N*-methyl-*N*-(trimethylsilyl)methylamino]-5-phenyl-2-pentenonitrile **8h** (24 mg, 9%) and 4-(*N*-benzyl-*N*-methylamino)-3-fluoromethylbutyronitrile **9h** (163 mg, 74%).

4h: A colorless oil. ^{1}H-NMR (400 MHz; $CDCl_3$) δ: 2.03 (3H, d, $J=7.0$ Hz), 2.25 (3H, s), 3.16 (2H, s), 3.58 (2H, s), 6.44 (1H, br s), 7.25—7.38 (5H, m). *Anal.* Calcd for $C_{13}H_{16}N_2$: C, 77.96; H, 8.05; N, 13.99. Found: C, 77.96; H, 8.21; N, 14.11.

8h: A colorless oil. IR (film) cm^{-1}: 2222, 856. ^1H-NMR (400 MHz; $CDCl_3$) δ: 0.04 (9H, s), 1.93, 2.04 (2H, ABq, J=14.8 Hz), 2.29 (3H, s), 2.59 (1H, dd, J=13.6, 9.6 Hz), 3.04 (1H, dd, J=9.6, 4.8 Hz), 3.21—3.26 (1H, m), 5.27 (1H, dd, J=16.5, 1.5 Hz), 6.62 (1H, dd, J=16.5, 7.3 Hz), 7.10—7.29 (5H, m). ^{13}C-NMR (100 MHz; $CDCl_3$) δ: −1.5 (3C), 36.2, 41.3, 45.1, 70.2, 101.5, 117.3, 126.5, 128.6 (2C), 129.3 (2C), 154.0. *Anal.* Calcd for $C_{16}H_{24}N_2Si$: C, 70.53; H, 8.88; N, 10.28. Found: C, 70.34; H, 8.75; N, 10.38.

9h: A colorless oil. IR (film) cm^{-1}: 2247. ^1H-NMR (500 MHz; $CDCl_3$) δ: 2.21 (3H, s), 2.23—2.34 (1H, m), 2.40—2.44 (2H, m), 2.45—2.49 (2H, m), 3.51 (2H, dd, J=12.8 Hz), 4.55 (1H, ddd, J_{F-H}= 47.0 Hz, J=9.2, 5.5 Hz), 4.57 (1H, ddd, J_{F-H}=47.0 Hz, J=9.2, 3.7 Hz), 7.24—7.33 (5H, m). ^{13}C-NMR (125 MHz; $CDCl_3$) δ: 17.0 (d, J_{F-C}=5.2 Hz), 35.4 (d, J_{F-C}=18.6 Hz), 42.5, 56.6 (d, J_{F-C}=6.2 Hz), 62.9, 86.3 (d, J_{F-C}=169.7 Hz), 118.2, 127.3, 128.4 (2C), 128.8 (2C), 138.6. *Anal.* Calcd for $C_{13}H_{17}FN_2$: C, 70.88; H, 7.78; N, 12.72. Found: C, 70.73; H, 7.79; N, 12.66.

Reaction of 1i with CsF In a manner similar to that described for **1g** (method B), **1i** (0.86 g, 2 mmol) and CsF (0.92 g, 6 mmol) were allowed to react in DMF (10 ml) at 60 °C. The distillate (460 mg) at 85—115 °C (0.5 mmHg) was chromatographed on a silica gel column with hexane–Et_2O (2 : 1) to give *N*-benzyl-2-chloro-*N*-methyl-3-butenylamine **3i** (33 mg, 8%), *N*-benzyl-4-fluoro-*N*-methyl-3-butenylamine **3i′** (135 mg, 34%, a halogen-exchanged product of **3i**), *N*-benzyl-4-chloro-*N*-methyl-3-butenylamine **5i** (21 mg, 5%) and 3-chloro-*N*-methyl-*N*-(2-methylbenzyl)-2-propenylamine **6i** (197 mg, 47%).

3i: A colorless oil. ^1H-NMR (400 MHz; $CDCl_3$) δ: 2.28 (3H, s), 2.43 (1H, dd, J=12.5, 3.6 Hz), 2.52 (1H, dd, J=12.5, 10.6 Hz), 3.55, 3.72 (2H, ABq, J=12.8 Hz), 4.20—4.24 (1H, m), 5.15 (1H, dt, J=10.6, 1.5 Hz), 5.33 (1H, dt, J=17.2, 1.5 Hz), 5.77 (1H, ddd, J=17.2, 12.6, 5.9 Hz), 7.29—7.36 (5H, m). ^{13}C-NMR (100 MHz; $CDCl_3$) δ: 41.7, 62.3, 62.9, 68.3, 116.0, 127.5, 128.5 (2C), 129.4 (2C), 137.7, 138.2. *Anal.* Calcd for $C_{12}H_{16}ClN$: C, 68.73; H, 7.69; N, 6.68. Found: C, 68.50; H, 7.63; N, 6.50.

3i′: A colorless oil. ^1H-NMR (400 MHz; $CDCl_3$) δ: 2.32 (3H, s), 2.60, 2.75 (2H, ddd, J_{F-H}=21.6 Hz, J=13.9, 7.7 Hz), 3.61 (2H, s), 5.00—5.19 (1H, m), 5.24 (1H, d, J=11.0 Hz), 5.36 (1H, dt, J=17.2, 1.5 Hz), 5.82—5.94 (1H, m), 7.23—7.32 (5H, m). ^{13}C-NMR (100 MHz; $CDCl_3$) δ: 42.9, 60.9 (d, J_{F-C}=22.0 Hz), 62.6, 91.5 (d, J_{F-C}=170.2 Hz), 117.3 (d, J_{F-C}=11.7 Hz), 127.1, 128.3 (2C), 129.0 (2C), 135.1 (d, J_{F-C}=19.8 Hz), 138.6. *Anal.* Calcd for $C_{12}H_{16}FN$: C, 74.58; H, 8.34; N, 7.25. Found: C, 74.45; H, 8.35; N, 7.18.

5i: A colorless oil. ^1H-NMR (270 MHz; $CDCl_3$) δ: 2.20 (3H, s), 2.26 (2H, td, J=7.3, 6.6 Hz), 2.45 (2H, t, J=7.3 Hz), 3.49 (2H, s), 5.92 (1H, dt, J=13.2, 6.6 Hz), 6.00 (1H, d, J=13.2 Hz), 7.22—7.35 (5H, m). *Anal.* Calcd for $C_{12}H_{16}ClN$: C, 68.73; H, 7.69; N, 6.68. Found: C, 68.57; H, 7.69; N, 6.68.

6i: A colorless oil. ^1H-NMR (270 MHz; $CDCl_3$) δ: 2.18 (3H, s), 2.34 (3H, s), 3.02 (2H, d, J=6.6 Hz), 3.44 (2H, s), 5.99 (1H, dt, J=13.2, 6.6 Hz), 6.13 (1H, d, J=13.2 Hz), 7.09—7.33 (4H, m). *Anal.* Calcd for $C_{12}H_{16}ClN$: C, 68.73; H, 7.69; N, 6.68. Found: C, 68.66; H, 7.70; N, 6.59.

Reaction of 16 with CsF The salt **16** (0.76 g, 2.0 mmol) and CsF (0.92 g, 6.0 mmol) were allowed to react in DMF (10 ml) at 60 °C in a manner similar to that described for **1g** (method B). The reaction was quenched with 1% aqueous $NaHCO_3$ (100 ml) and extracted with Et_2O. The organic layer was extracted with 1 M HCl (2 × 20 ml), dried ($MgSO_4$) and evaporated under reduced pressure to give **7g** (41 mg, 10%). The acid extract was made alkaline with 2 M aqueous NaOH and extracted with Et_2O. The ethereal extract was washed with water, dried ($MgSO_4$), concentrated and distilled to give methyl 4-dimethylamino-5-phenylpent-2-enoate **19** (182 mg, 39%) as a colorless oil. ^1H-NMR (400 MHz; $CDCl_3$) δ: 2.35 (6H, s), 2.69—2.73 (1H, m), 3.07—3.16 (1H, br s), 3.23—3.30 (1H, br s), 3.70 (3H, s), 5.78 (1H, d, J=15.9 Hz), 6.86 (1H, dd, J=15.9, 8.5 Hz), 7.13—7.27 (5H, m). ^{13}C-NMR (125 MHz; $CDCl_3$) δ: 38.1, 41.5, 41.6, 51.5, 67.9, 123.7, 126.3, 128.4 (2C), 129.2 (2C), 138.4, 146.0, 166.2. *Anal.* Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00. Found: C, 71.81; H, 8.24; N, 5.99.

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