Rearrangement of *cis*- and *trans*-2-Methyl-1-(substituted phenyl)isoindolinium 2-Methylides

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Fluoride ion induced desilylation of *cis*-2-methyl-1-(substituted phenyl)-2-[(trimethylsilyl)methyl]-isoindolinium iodides *cis*-**5** gave mixtures of the Sommelet–Hauser rearrangement products **7** and the Stevens products **8** in a ratio about 8.5:1.5. Similar treatments of the *trans*-isomers (*trans*-**5**) afforded exclusively **8**. The pathways of the ylide rearrangement are discussed.

Introduction

Sommelet–Hauser rearrangement of ammonium ylides is an attractive method in ring enlargement reactions of cyclic amines because the rearrangement occurs regioselectively under mild conditions.[1] We have previously reported the syntheses of seven- to 10-membered cyclic amines by fluoride ion induced desilylation of *N*-[(trimethylsilyl)methyl]-α-phenyl cyclic ammonium salts.[2] The ammonium salts used in these reactions were mixtures of the cis- and trans-isomers between the *N*-[(trimethylsilyl)-methyl] groups and the α-phenyl because of the difficulty in isolating pure isomers. However, the isomers may exhibit different chemical behavior. In this paper, we describe the reaction of *cis*- and *trans*-2-methyl-1-phenyl-2-[(trimethylsilyl)methyl]isoindolinium iodides (*cis*-**5** and *trans*-**5**) with cesium fluoride.

Results and Discussion

Quaternization of 1-(substituted phenyl)-2-[(trimethylsilyl)methyl]isoindolines (**4**) with iodomethane, which was prepared starting from *N*-[(trimethylsilyl)methyl]-phthalimide (**1**) via the alcohols **2**, gave *cis*-2-methyl-1-(substituted phenyl)-2-[(trimethylsilyl)methyl]isoindolinium iodides (*cis*-**5**) as the main products (Scheme 1, Table 1). The reaction of 2-methyl-1-(substituted phenyl)-isoindolines (**3**) with (trimethylsilyl)methyl triflate afforded mainly the trans-isomers (*trans*-**5**). The major geometrical isomer of **5d** prepared from **4d** was assigned to have the cis configuration based on an X-ray crystallographic analysis.[19] Those of **5a–c** obtained from **4a–c** were also assigned as cis by comparison of the chemical shifts of the trimethylsilyl groups (cis < trans) in ^{1}H NMR spectroscopy (Table 2).[3] Isolation of each isomer (above 90% purity) was achieved by repeated recrystallization, but the isolated yields were below 7%. Therefore, mixtures of the two isomers of which ratios were determined by the integrated values of ^{1}H NMR were treated with cesium fluoride in HMPA at room temperature. The reaction products consisted of 1,3-disubstituted 6-methyl-5,6,7,12-tetrahydrodibenzo[*c*,*f*]azocines (**7**, Sommelet–Hauser rearrangement product) and 4-(substituted phenyl)-2-methyl-1,2,3,4-tetrahydroisoquinolines **8** (Stevens product) accompanied by a small amount of 1-(substituted phenyl)-2-methylisoindolines **9**. The results are summarized in Table 3.

Scheme 1

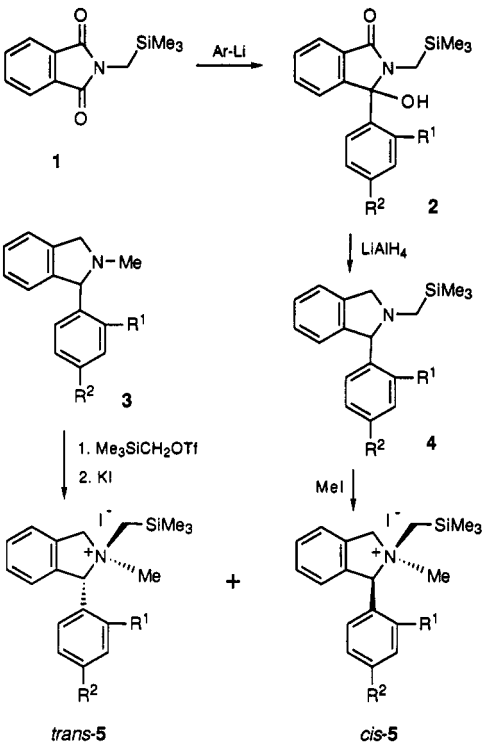

Table 1. ***cis*- and *trans*-2-Methyl-1-(substituted phenyl)-2-[(trimethylsilyl)methyl]isoindolinium Iodides (*cis*-5 and *trans*-5)**

entry	R^1	R^2	starting amines	yield of 5 (%)	ratio[a] of *cis*:*trans*
1	H	H	**4a**	68	67:33
2	H	H	**3a**	70	13:87
3	H	OMe	**4b**	76	70:30
4	H	OMe	**3b**	37	15:85
5	H	CF_3	**4c**	52	80:20
6	H	CF_3	**3c**	50	3:97
7	Me	H	**4d**	68	72:28

[a] Determined from the proton ratios of ^{1}H NMR.

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(2) (a) Shirai, N.; Sumiya, F.; Sato, Y.; Hori, M. *J. Org. Chem.* **1989**, *54*, 836. (b) Sumiya, F.; Shirai, N.; Sato, Y. *Chem. Pharm. Bull.* **1991**, *39*, 36. (c) Kitano, T.; Shirai, N.; Sato, Y. *Synthesis* **1991**, 996. (d) Kitano, T.; Shirai, N.; Sato, Y. *Chem. Pharm. Bull.* **1992**, *40*, 768. (e) Sato, Y.; Shirai, N.; Machida, Y.; Ito, E.; Yasui, T.; Kurono, Y.; Hatano, K. *J. Org. Chem.* **1992**, *57*, 6711. (f) Kitano, T.; Shirai, N.; Motoi, M.; Sato, Y. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2851.

(3) A similar relationship in ^{1}H NMR spectroscopy was observed by Sato et al.[2e] in the study of *cis*- and *trans*-2-methyl-1-phenyl-2-[(trimethylsilyl)methyl]-1,2,3,4-tetrahydroisoquinolinium iodides.

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Table 2. Chemical Shifts of the Me_3Si Groups of Ammonium Salts 5 in ^1H NMR

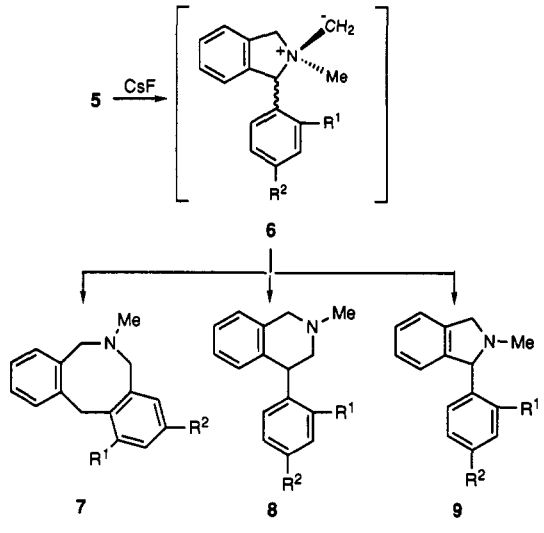
	^1H NMR ($CDCl_3$), δ (Me_3Si)			
	5a	**5b**	**5c**	**5d**
cis	0.26	0.26	0.29	0.27
trans	0.36	0.36	0.36	0.33

Table 3. Reaction of 2-Methyl-2-(trimethylsilyl)methyl-1-(substituted phenyl)isoindolinium Iodides (*cis*-5 and *trans*-5) with CsF[a]

	ammonium salts 5		products 7–9	
entry		ratio[b] of *cis*:*trans*	total yield (%)	ratio[c] of 7:8:9
1[d]	**5a**	92:8	89	82:18:0
2	**5a**	70:30	92	63:37:0
3	**5a**	37:63	91	35:65:0
4	**5a**	25:75	85	20:75:5[b]
5	**5a**	13:87	84	7:84:9[b]
6	**5b**	15:85	83	13:85:2[b]
7	**5b**	45:55	80	40:59:1[b]
8	**5b**	70:30	83	66:34:0
9	**5b**	90:10	89	82:18:0
10	**5c**	3:97	80	3:94:3[b]
11	**5c**	51:49	86	45:53:2[b]
12	**5c**	80:20	85	66:34:0
13	**5c**	97:3	93	81:19:0
14	**5d**	55:45	82	48:52:0
15	**5d**	75:25	94	56:44:0
16	**5d**	95:5	93	68:32:0

[a] The reaction was carried out in HMPA at room temperature for 24 h. [b] Determined from the proton ratios of ^1H NMR. [c] Determined from the integrated values of GLC analysis (5% SE-30). [d] Reaction time, 3 h.

Scheme 2



The ratios of **7a** and **8a** to the total amines are plotted against the ratio of the two isomers [*cis*-**5a**/(*cis*-**5a** + *trans*-**5a**)] in Figure 1. The plots show a linear relationship, and the line of **7a** crosses near the zero point. Similar relationships are observed between **5b–d** and their reaction products **7b–c** and **8b–d** (Figure 2A,B). Figure 2 suggests that *trans*-ylides **6** give exclusively the Stevens product **8** but *cis*-ylides **6** produce mixtures of the Sommelet–Hauser **7** and the Stevens product **8**.

We reported previously that, in the studies of ammonium ylides in nonbasic media, Stevens rearrangement products **16a** from benzylammonium *N*-alkylides **12a**[4a] were not

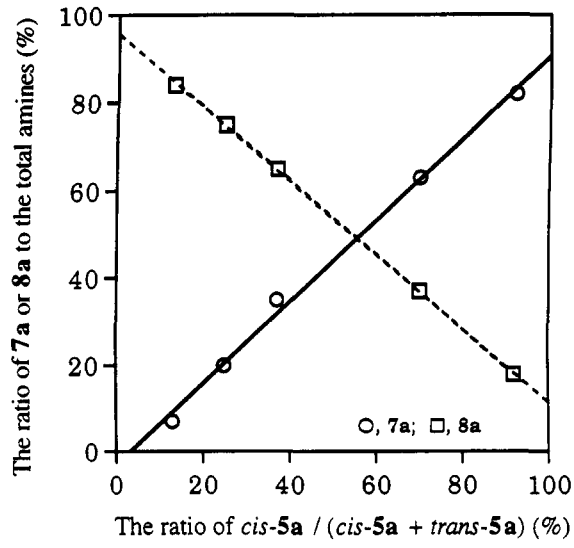


Figure 1. Relationship between the ratio *cis*-**5a**/(*cis*-**5a** + *trans*-**5a**) and the ratio **7a** or **8a** to the total amines. The lines through the data were obtained from regression fit.

formed by a [1,2] radical migration pathway as has been suggested previously[5] but produced via a [2,3] sigmatropic migration giving isotoluene intermediates **13a** followed by a radical-forming and -recombination process (Scheme 4).[4] α-Phenylcycloammonium *N*-methylides[2a,b] **12b** changed to isotoluene derivatives **13b**, but further conversion to Sommelet–Hauser products **14b** or Stevens products **16b** was not observed at room temperature. Aromatization of **13b** to **14b** occurred with the aid of a strong base via a deprotonation–recombination process.

[2,3] Sigmatropic migration in *cis*-**6** easily occurs to give 6-methyl-4a,5,6,7-tetrahydrodibenzo[*c*,*f*]azocine (**10**), and its main portion is subsequently aromatized to **7** (Scheme 3). However, the [2,3] sigmatropic migration may be difficult in *trans*-**6** because the ylide carbanions are located far from the phenyl groups, requiring a strained, high-energy transition state. Homolysis of the carbon–nitrogen bond occurs to give a diradical intermediate **11** which is changed to **8** by a radical-recombination process. Two paths are possible in the conversion from *cis*-**6** to **8**: a [2,3] sigmatropic rearrangement followed by a [1,3] radical migration via **10** and **11** or direct [1,2] shift via **11**. It is still unclear why a symmetry-forbidden [1,3] hydrogen shift to get from **10** to **7** occurred quickly in this case, contrary to our previous observation.[2]

The product ratios **7a–c**/**8a–c** were roughly between 8:2 and 9:1 except for **5d** (7:3) (see Figure 2A). When the ylide reactions giving Stevens products (e.g., **16** in Scheme 4) as the main products were carried out in the presence of DBU, the main products changed to the Sommelet–Hauser rearrangement products (e.g., **14**).[4b] The reaction of **5a–d** with cesium fluoride was repeated in the presence of DBU. The results are summarized in Table 4. No change was observed in the ratios of the products from **5a–c** (entries 1–6), but the ratio of **7d** to **8d** was changed to a value similar to those from **5a–c** (compare entries 7 and 8). The [1,2] radical migration pathway from *cis*-**6** may contribute to the formation of **8**. Change of the ratio of **7d** to **8d** (68:32 to 83:17) by the DBU addition might

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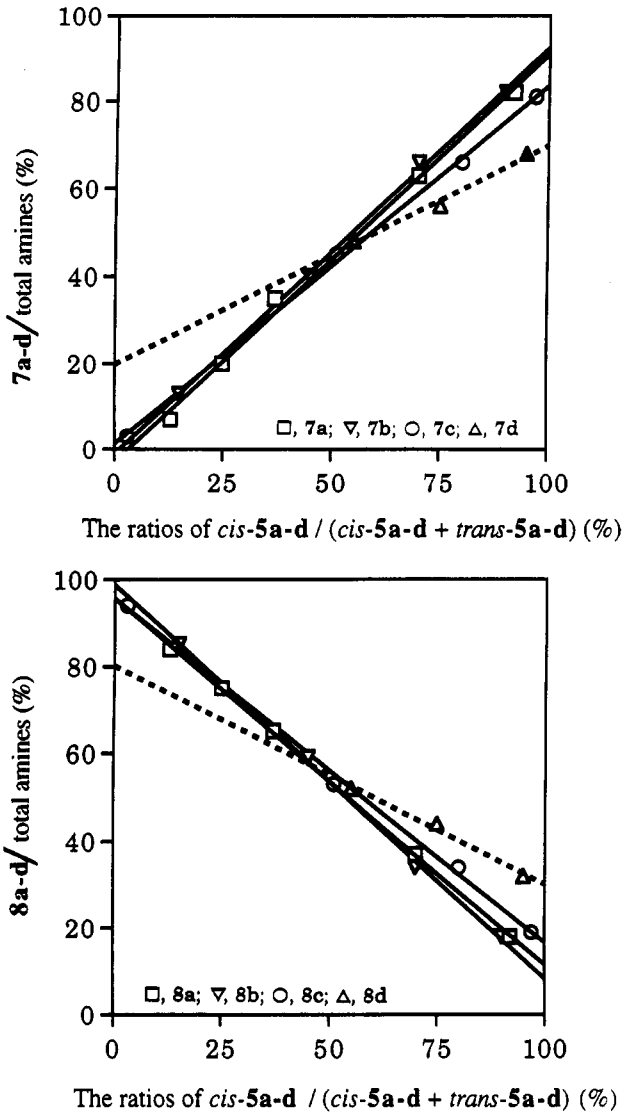


Figure 2. Relationship between the ratios of *cis*-**5a–d**/(*cis*-**5a–d** + *trans*-**5a–d**) and the ratios of **7a–d** (top, A) or **8a–d** (bottom, B) to the total amines. The lines through the data were obtained from regression fit.

indicate that about 15% of **8d** was formed via **10d** under the nonbasic conditions.[4b]

Thus, for *cis*-**6**, a [2,3] sigmatropic rearrangement giving **10** competed with a [1,2] radical migration pathway giving **8** in a ratio of about 8.5:1.5, but for *trans*-**6**, the [1,2] radical rearrangement occurred exclusively to give **8**. Fluoride ion induced desilylation of 2-methyl-2-[(trimethylsilyl)-methyl]isoindolinium iodide (**17**) did not form the expected 2-methyl-1,2,3,4-tetrahydroisoquinoline (Stevens rearrangement product) but gave only 2,2-dimethylisoindolinium salts.[6] This suggests that the radical-forming pathway from **6** requires the presence of the 1-phenyl groups. The radicals in **11** may be stabilized by the adjacent amino and two phenyl groups, respectively.

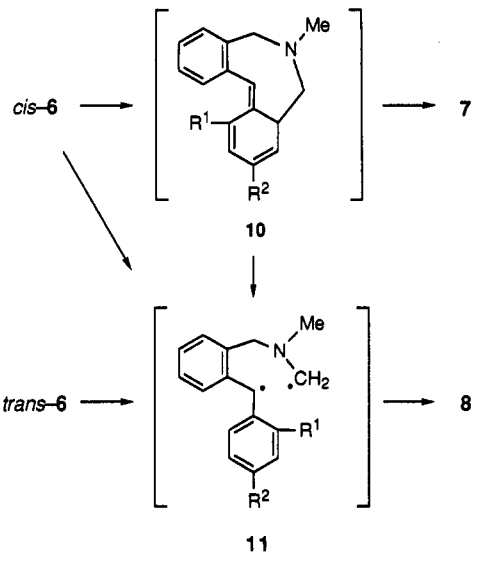
Experimental Section

All reactions were carried out in N_2 or Ar. HMPA was dried by distillation under reduced pressure from sodium. Ether and THF were distilled from Na benzophenone ketyl. CsF was dried over P_2O_5 at 190 °C under reduced pressure. ^1H NMR spectra were recorded at 270 or 400 MHz. Mass spectra were obtained using EI ionization. Distillation was carried out using a Büchi Kugelrohr distillation apparatus. All melting and boiling points are uncorrected.

1-Phenyl-2-[(trimethylsilyl)methyl]isoindole (4a). A solution of phenyllithium, prepared from bromobenzene (24.9 g, 162 mmol) and Li (2.3 g, 331 mmol) in Et_2O (80 mL), was slowly added to a refluxing solution of *N*-[(trimethylsilyl)methyl]-phthalimide[7] (**1**, 27.5 g, 10 mmol) in Et_2O (30 mL) and stirred for 1 h. The reaction was quenched with water (50 mL), and the

(6) The mechanism of this reaction is still unclear.

Scheme 3



Scheme 4

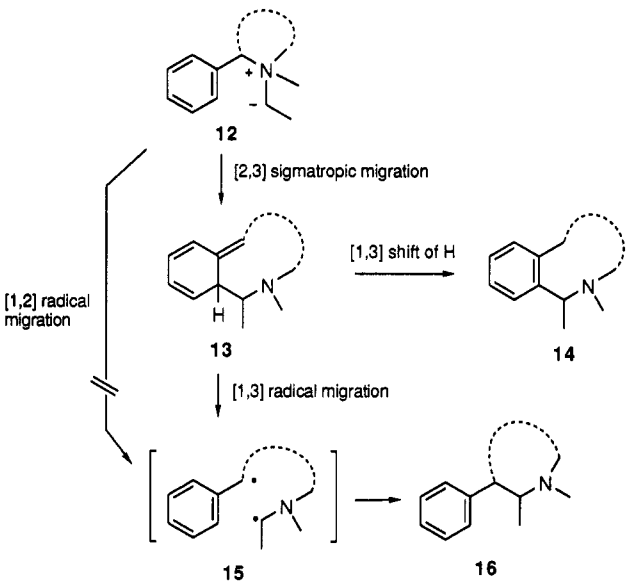
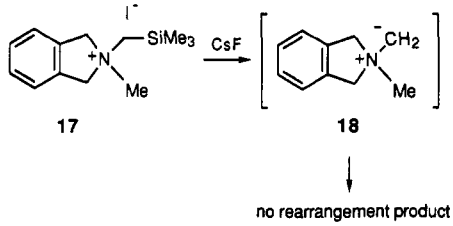


Table 4. Effect of DBU Addition to the Reaction Products

entry	ammonium salts	*cis*:*trans*	condns: additive	condns: temp (°C)/time (h)	products: total yield (%)	products: ratio[b] of 7:8
1	**5a**	92:8		rt/3	89	85:15
2	**5a**	92:8	DBU	10/3	93	83:17
3	**5b**	90:10		rt/24	89	82:18
4	**5b**	90:10	DBU	10/3	94	85:15
5	**5c**	97:3		rt/24	93	81:19
6	**5c**	97:3	DBU	10/24	91	78:22
7	**5d**	95:5		rt/24	93	68:32
8	**5d**	95:5	DBU	10/24	95	83:17

[a] Determined from the proton ratios of ^1H NMR. [b] Determined from the integrated values of GLC analysis (5% SE-30).

Scheme 5



mixture was extracted with Et_2O (3 × 30 mL). The extract was washed with saturated NaCl, dried ($MgSO_4$), and concentrated under reduced pressure. Recrystallization of the residue from a mixture of $CHCl_3$ and hexane gave 1-hydroxy-1-phenyl-2-[(trimethylsilyl)methyl]isoindolinone (**2a**, 27.0 g, 83%): mp 168–169 °C; IR (Nujol) 3220, 1664, 1610, 1250, 863 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.06 (s, 9 H), 2.39 (d, 1 H, J = 15.4 Hz), 2.78 (d, 1 H, J = 15.4 Hz), 2.80 (s, 1 H), 7.25–7.30 (m, 1 H), 7.31–7.38 (m, 5 H), 7.44–7.48 (m, 2 H), 7.77–7.81 (m, 1 H). Anal. Calcd for $C_{18}H_{21}NO_2Si$: C, 69.42; H, 6.80; N, 4.50. Found: C, 69.53; H, 6.77; N, 4.44.

2a (9.0 g, 29 mmol) was slowly added to a mixture of $LiAlH_4$ (4.4 g, 117 mmol) in Et_2O (160 mL), and the mixture was stirred for 2 h at reflux. The reaction was quenched with saturated sodium potassium tartrate and extracted with Et_2O (3 × 50 mL). The extract was washed with saturated NaCl, dried ($MgSO_4$), concentrated, and distilled to give **4a** (6.4 g, 78%): bp 130 °C (0.08 mmHg); IR (Nujol) 1600, 1245, 1060, 880, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.06 (s, 9 H), 2.01 and 2.30 (AB-q, 2 H, J = 14.2 Hz), 3.89 and 4.24 (AB-q, 2 H, J = 11.4 Hz), 4.75 (bs, 1 H), 6.73 (d, 1 H, J = 7.4 Hz), 7.09 (t, 1 H, J = 7.3 Hz), 7.18 (t, 1 H, J = 7.3 Hz), 7.24 (d, 1 H, J = 7.6 Hz), 7.28–7.42 (m, 5 H); mass spectrum m/e 281 (22, M^+), 280 (23), 209 (18), 208 (100), 204 (18), 179 (24), 178 (15), 91 (14); exact mass[8] calcd for $C_{18}H_{23}NSi$ 281.1599, found 281.1640.

1-(4-Methoxyphenyl)-2-[(trimethylsilyl)methyl]isoindoline (4b). A solution of (4-methoxyphenyl)lithium[9] in THF (40 mL) was added to a solution of **1** (11.6 g, 50 mmol) in THF (120 mL) under ice cooling and was stirred for 1 h. The reaction was quenched and treated in a manner similar to that described for **2b**. Recrystallization of the residue from EtOAc gave 1-hydroxy-1-(4-methoxyphenyl)-2-[(trimethylsilyl)methyl]isoindolinone (**2b**, 10.4 g, 61%): mp 193–194 °C; IR (KBr) 3450, 1663, 1250, 1175, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.08 (s, 9 H), 2.46 and 2.72 (AB-q, 2 H, J = 5.3 Hz), 2.60 (s, 1 H), 3.80 (s, 3 H), 6.86 (d, 2 H, J = 9.2 Hz), 7.25–7.29 (m, 3 H), 7.43–7.48 (m, 2 H), 7.77–7.81 (m, 1 H). Anal. Calcd for $C_{19}H_{23}NO_3Si$: C, 66.83; H, 6.79; N, 4.10. Found: C, 66.79; H, 6.90; N, 4.07.

In a manner similar to that described for **4a**, **2b** (9.7 g, 28 mmol) was added to a mixture of $LiAlH_4$ (3.2 g, 85 mmol) in Et_2O (150 mL) and treated to give **4b** (6.6 g, 75%): bp 160–165 °C (0.45–0.55 mmHg); IR (film) 2953, 1510, 1462, 1287, 1246, 1038, 851, 741 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.05 (s, 9 H), 1.97 and 2.29 (AB-q, 2 H, J = 14.1 Hz), 3.67 (d, 1 H, J = 11.7 Hz), 3.82 (s, 3 H), 4.38 (d, 1 H, J = 11.7 Hz), 4.49 (bs, 1 H), 6.72 (d, 1 H, J = 7.5 Hz), 6.89 (d, 2 H, J = 8.8 Hz), 7.09 (t, 1 H, J = 7.3 Hz), 7.17 (t, 1 H, J = 7.3 Hz), 7.23 (d, 1 H, J = 7.3 Hz), 7.31 (d, 2 H, J = 8.6 Hz); mass spectrum m/e 311 (15, M^+), 239 (19), 238 (100), 209 (18), 204 (14), 203 (18), 121 (25), 59 (12); exact mass[8] calcd for $C_{19}H_{25}NOSi$ 311.1699, found 311.1706.

1-[4-(Trifluoromethyl)phenyl]-2-[(trimethylsilyl)methyl]isoindoline (4c). A solution of **1** (13.3 g, 57 mmol) in Et_2O (80 mL) was added at 0 °C to a solution of [4-(trifluoromethyl)-phenyl]lithium, which was prepared from 4-bromobenzotrifluoride (13.0 g, 58 mmol) and n-BuLi (1.45 M in hexane, 40 mL, 58 mmol) in Et_2O (120 mL).[10] The reaction was similarly quenched with H_2O and treated. The residue was recrystallized from MeOH to give 1-hydroxy-1-[4-(trifluoromethyl)phenyl]-2-[(trimethylsilyl)methyl]isoindolinone (**2c**, 16.5 g, 76%): mp 159–160 °C; IR (KBr) 3285, 1674, 1327, 1246, 1173, 1128, 1069, 851 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.04 (s, 9 H), 2.30 and 2.62 (AB-q, 2 H, J = 15.4 Hz), 4.24 (s, 1 H), 7.21–7.26 (m, 1 H), 7.38–7.50 (m, 3 H), 7.58–7.66 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ −1.0 (3 C), 30.0, 91.1, 122.6, 123.2, 124.0 (q, J_{CF} = 271.0 Hz), 125.6 (d, 2 C, J_{CF} = 3.6 Hz), 126.9 (2 C), 129.8, 130.7, 131.0 (q, J_{CF} = 32.9 Hz), 132.4, 142.8, 148.3, 167.4; mass spectrum m/e 379 (2, M^+), 364 (29), 351 (23), 350 (88), 258 (14), 75 (22), 74 (10), 73 (100). Anal. Calcd for $C_{19}H_{20}F_3NO_2Si$: C, 60.14; H, 5.31; N, 3.69. Found: C, 60.01; H, 5.44; N, 3.85.

In a similar manner to that described for **4a**, **2c** (2.3 g, 6 mmol) and $LiAlH_4$ (0.9 g, 24 mmol) were treated in Et_2O (30 mL) and worked up. The crude product was distilled at reduced pressure to give **4c** (1.4 g, 68%): bp 145 °C (0.62 mmHg); IR (film) 2760, 1325, 1250, 1163, 1125, 1067, 855, 743 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.07 (s, 9 H), 2.04 and 2.23 (AB-q, 2 H, J = 13.8 Hz), 3.73 (bd, 1 H, J = 11.5 Hz), 4.42 (d, 1 H, J = 12.2 Hz), 4.63 (bs, 1 H), 6.68 (d, 1 H, J = 7.3 Hz), 7.10 (t, 1 H, J = 7.3 Hz), 7.17–7.27 (m, 2 H), 7.54 (d, 2 H, J = 8.1 Hz), 7.62 (d, 2 H, J = 8.1 Hz); mass spectrum m/e 349 (19, M^+), 348 (25), 277 (19), 276 (100), 209 (14), 179 (15), 178 (14), 73 (16); exact mass[8] calcd for $C_{19}H_{22}F_3NSi$ 349.1468, found 349.1489.

1-(2-Methylphenyl)-2-[(trimethylsilyl)methyl]isoindoline (4d). A solution of (4-methylphenyl)lithium, prepared from 4-methylbromobenzene (13.1 g, 77 mmol) and Li (1.2 g, 173 mmol) in Et_2O (50 mL), was added to a refluxing solution of *N*-[(trimethylsilyl)methyl]phthalimide (15.1 g, 65 mmol) in Et_2O (100 mL) and worked up in a similar manner as described for **2a**. The crude product was recrystallized from EtOAc to give 1-hydroxy-1-(2-methylphenyl)-2-[(trimethylsilyl)methyl]isoindolinone (**2d**, 17.0 g, 80%): mp 135–136 °C; IR (Nujol) 3184, 1671, 1433, 1246, 1040, 866, 845, 765 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.09 (s, 9 H), 1.56 (s, 3 H), 2.27 (d, 1 H, J = 15.3 Hz), 2.43 (s, 1 H), 2.79 (d, 1 H, J = 15.3 Hz), 7.04 (d, 1 H, J = 7.5 Hz), 7.19 (d, 1 H, J = 6.4 Hz), 7.28 (t, 1 H, J = 7.4 Hz), 7.36 (t, 1 H, J = 7.8 Hz), 7.45–7.51 (m, 2 H), 7.80–7.83 (m, 1 H), 8.17 (d, 1 H, J = 7.9 Hz). Anal. Calcd for $C_{19}H_{23}NO_2Si$: C, 70.11; H, 7.12; N, 4.30. Found: C, 70.08; H, 7.14; N, 4.32.

In a manner similar to that described for **4a**, **2d** (11.1 g, 24 mmol) and $LiAlH_4$ (3.9 g, 102 mmol) were treated in Et_2O (150 mL) and worked up. The crude product was distilled to give **4d** (7.5 g, 75%): bp 150–170 °C (0.62–0.68 mmHg); IR (film) 2953, 2889, 2753, 1462, 1248, 887, 856 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.07 (s, 9 H), 1.98 and 2.28 (AB-q, 2 H, J = 14.2 Hz), 2.38 (s, 3 H), 3.70 (d, 1 H, J = 12.1 Hz), 4.42 (d, 1 H, J = 12.1 Hz), 4.82 (bs, 1 H), 6.70 (d, 1 H, J = 7.4 Hz), 7.04–7.51 (m, 7 H); mass spectrum m/e 295 (15, M^+), 223 (18), 222 (100), 204 (27), 179 (18), 178 (17), 105 (27), 73 (15); exact mass[8] calcd for $C_{19}H_{25}NSi$ 295.1750, found 295.1690.

1-(4-Methoxyphenyl)-2-methylisoindoline (3b). In the same way as described for **2b**, a solution of (4-methoxyphenyl)-lithium[9] (53 mmol) in THF (30 mL) was added to a solution of *N*-methylphthalimide (5.8 g, 36 mmol) in THF (100 mL) and treated to give 1-hydroxy-1-(4-methoxyphenyl)-2-methylisoindolinone (4.2 g, 43%): mp 182–183 °C; IR (KBr) 3200, 1684, 1597, 1512, 1314, 1256, 1173, 1034 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.64 (s, 3 H), 3.79 (s, 3 H), 4.24 (s, 1 H), 6.85 (d, 2 H, J = 8.9 Hz), 7.24–7.68 (m, 6 H).

1-Hydroxy-1-(4-methoxyphenyl)-2-methylisoindolinone (5.6 g, 21 mmol) and $LiAlH_4$ (3.1 g, 83 mmol) was treated in Et_2O (120 mL) and worked up to give **3b** (4.0 g, 81%): bp 140–160 °C (0.9–1.6 mmHg); IR (film) 2938, 2836, 2772, 1613, 1512, 1462, 1246, 1036 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.46 (s, 3 H), 3.74 (dd, 1 H, J = 12.6, 3.0 Hz), 3.82 (s, 3 H), 4.36 (d, 1 H, J = 12.6 Hz), 4.49 (bs, 1 H), 6.77 (d, 1 H, J = 7.5 Hz), 6.90 (d, 2 H, J = 8.7 Hz), 7.13 (t, 1 H, J = 7.3 Hz), 7.20 (t, 1 H, J = 7.3 Hz), 7.24–7.28 (m, 3 H); mass spectrum m/e 239 (31, M^+), 238 (55), 237 (7), 148 (4), 133 (11), 132 (100), 131 (10), 117 (15). Anal. Calcd for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.15; H, 7.20; N, 5.63.

2-Methyl-1-[4-(trifluoromethyl)phenyl]isoindoline (3c). In the same way, a solution of *N*-methylphthalimide (5.6 g, 35 mmol) in Et_2O (70 mL) was treated with [4-(trifluoromethyl)-phenyl]lithium[10] (34 mmol) in Et_2O (130 mL) and worked up to give 1-hydroxy-2-methyl-1-[4-(trifluoromethyl)phenyl]isoindo-

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linone (9.1 g, 88%): mp 228–229 °C; IR (KBr) 3272, 1678, 1429, 1329, 1167, 1125, 1069, 766 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.62 (s, 3 H), 4.45 (s, 1 H), 7.28 (d, 1 H, J = 8.3 Hz), 7.39 (dt, 1 H, J = 7.6, 1.0 Hz), 7.47–7.65 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 23.9, 90.6, 122.8, 123.3, 123.9 (q, J_{CF} = 272.2 Hz), 125.7 (q, 2 C, J_{CF} = 3.6 Hz), 126.6 (2 C), 129.8, 130.0, 130.8 (q, J_{CF} = 32.9 Hz), 132.8, 142.1, 148.3, 167.9. Anal. Calcd for $C_{16}H_{12}F_3NO_2$: C, 62.54; H, 3.94; N, 4.56. Found: C, 62.48; H, 4.23; N, 4.64.

1-Hydroxy-2-methyl-1-[4-(trifluoromethyl)phenyl]isoindolinone (6.3 g, 20 mmol) was treated with $LiAlH_4$ (3.1 g, 81 mmol) in Et_2O (120 mL) and worked up to give **3c** (4.3 g, 76%): mp 85–86 °C; bp 100–120 °C (0.8–0.9 mmHg); IR (KBr) 2793, 1464, 1327, 1287, 1167, 1117, 1067, 1019, 743 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.48 (s, 3 H), 3.83 (dd, 1 H, J = 2.6, 13.0 Hz), 4.42 (d, 1 H, J = 13.0 Hz), 4.66 (bs, 1 H), 6.74 (d, 1 H, J = 7.5 Hz), 7.14 (t, 1 H, J = 7.5 Hz), 7.21–7.28 (m, 2 H), 7.51 (d, 2 H, J = 8.0 Hz), 7.63 (d, 2 H, J = 8.0 Hz). Anal. Calcd for $C_{16}H_{14}F_3N$: C, 69.31; H, 5.09; N, 5.05. Found: C, 69.17; H, 5.33; N, 4.80.

2-Methyl-1-phenyl-2-[(trimethylsilyl)methyl]isoindolinium Iodide (5a). **(A)** A solution of **4a** (6.4 g, 23 mmol) and iodomethane (15.6 g, 110 mmol) in MeCN (50 mL) was heated at 60 °C overnight. The solvent was evaporated under reduced pressure. The gummy residue was dissolved in 70% MeOH (200 mL) and decolorized by Norit (neutralized), and the solvent was evaporated under reduced pressure. Recrystallization of the residue from MeOH–Et_2O gave a mixture of *cis*-**5a** and *trans*-**5a** (67:33, 6.5 g, 68%). Repetition of the recrystallization afforded pure *cis*-**5a**: mp 185–187 °C; IR (Nujol) 1257, 860, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.26 (s, 9 H), 2.26 (d, 1 H, J = 15.0 Hz), 2.98 (d, 1 H, J = 15.0 Hz), 3.80 (s, 3 H), 4.60 (d, 1 H, J = 13.8 Hz), 5.20 (d, 1 H, J = 13.8 Hz), 6.90 (s, 1 H), 7.24 (d, 1 H, J = 7.5 Hz), 7.44–7.53 (m, 8 H). Anal. Calcd for $C_{19}H_{26}INSi$: C, 53.90; H, 6.19; N, 3.31. Found: C, 53.93; H, 6.13; N, 2.98.

(B) A solution of 2-methyl-1-phenylisoindoline[11] (**3a**) (2.2 g, 11 mmol) and (trimethylsilyl)methyl triflate (4.4 g, 19 mmol) in CH_2Cl_2 (15 mL) was heated at reflux overnight. The solvent was evaporated under reduced pressure, and the residue was dissolved in a mixture of $CHCl_3$ (50 mL) and saturated KI solution (85 mL).[12] After the mixture was stirred at room temperature overnight, the $CHCl_3$ layer was separated and the aqueous layer was extracted with $CHCl_3$ (2 × 30 mL). The combined extract was dried ($MgSO_4$) and concentrated, and the residue was recrystallized from MeOH–Et_2O to give a mixture of *cis*-**5a** and *trans*-**5a** (13:87, 3.1 g, 70%). Repetition of recrystallization from MeOH–Et_2O gave 92% purity of *trans*-**5a**: ^1H NMR ($CDCl_3$) δ 0.36 (s, 9 H), 2.78 (s, 3 H), 3.21 (d, 1 H, J = 13.7 Hz), 4.61 (d, 1 H, J = 13.7 Hz), 4.92 (d, 1 H, J = 13.7 Hz), 5.58 (d, 1 H, J = 13.7 Hz), 6.80 (s, 1 H), 7.12 (d, 1 H, J = 7.9 Hz), 7.41–7.55 (m, 8 H).

1-(4-Methoxyphenyl)-2-methyl-2-[(trimethylsilylmethyl]isoindolinium Iodide (5b). **(A)** A solution of **4b** (6.6 g, 21 mmol) and iodomethane (11 g, 80 mmol) in MeCN (50 mL) was heated for 5 h, and the solvent was evaporated under reduced pressure. The residue was treated in a similar manner as described for **5a** (A). Recrystallization of the crude product from EtOAc gave a mixture of *cis*-**5b** and *trans*-**5b** (70:30, 7.3 g, 76%). Repeated recrystallization from MeOH–Et_2O gave pure *cis*-**5b**: mp 153–157 °C; IR (KBr) 2953, 1610, 1512, 1462, 1256, 1179, 1032, 860, 847 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.26 (s, 9 H), 2.31 and 2.88 (AB-q, 2 H, J = 14.5 Hz), 3.74 (s, 3 H), 3.85 (s, 3 H), 4.57 and 5.17 (AB-q, 2 H, J = 14.1 Hz), 6.80 (s, 1 H), 6.98–7.11 (br, 2 H), 7.24 (d, 1 H, J = 7.1 Hz), 7.42–7.50 (m, 3 H), 7.50–8.45 (br, 2 H). Anal. Calcd for $C_{20}H_{28}INOSi$: C, 52.98; H, 6.22; N, 3.09. Found: C, 52.72; H, 6.10; N, 2.98.

(B) A solution of **3b** (4.0 g, 17 mmol) and (trimethylsilyl)-methyl triflate (10.7 g, 45 mmol) in CH_2Cl_2 (70 mL) was heated at reflux for 10 h. The mixture was worked up, and the counterion was changed to iodide in a manner similar to that described for **5a** (B). Recrystallization of the residue from MeOH–Et_2O gave a mixture of *cis*-**5b** and *trans*-**5b** (15:85, 7.3 g, 37%). Further purification gave 90% purity of *trans*-**5b**: ^1H NMR ($CDCl_3$) δ 0.36 (s, 9 H), 2.74 (s, 3 H), 3.14 and 4.52 (AB-q, 2 H, J = 14.7 Hz), 3.88 (s, 3 H), 4.94 and 5.49 (AB-q, 2 H, J = 13.7 Hz), 6.73 (s, 1 H), 6.86–7.05 (br, 2 H), 7.09 (d, 1 H, J = 7.5 Hz), 7.38–7.85 (m, 3 H), 7.85–8.05 (br, 2 H).

2-Methyl-1-[4-(trifluoromethyl)phenyl]-2-[(trimethylsilyl)methyl]isoindolinium Iodide (5c). **(A)** In the same way as described above, a solution of **4c** (1.4 g, 4 mmol) and iodomethane (3.4 g, 24 mmol) in MeCN (20 mL) was heated and worked up to give a mixture of *cis*-**5c** and *trans*-**5c** (80:20, 1.1 g, 52%). Recrystallization from MeOH–Et_2O was repeated to give pure *cis*-**5c**: mp 192–193 °C; IR (KBr) 2957, 1327, 1258, 1167, 1123, 1069, 856, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.29 (s, 9 H), 2.24 and 3.23 (AB-q, 2 H, J = 14.5 Hz), 3.84 (s, 3 H), 4.66 and 5.13 (AB-q, 2 H, J = 14.0 Hz), 7.09 (s, 1 H), 7.24 (d, 1 H, J = 7.3 Hz), 7.43–7.66 (m, 3 H), 7.73 (br-d, 2 H, J = 7.3 Hz), 7.75–9.30 (br, 2 H). Anal. Calcd for $C_{20}H_{25}F_3INSi$: C, 48.88; H, 5.13; N, 2.86. Found: C, 48.64; H, 5.20; N, 2.86.

(B) A solution of **3c** (4.3 g, 15 mmol) and (trimethylsilyl)-methyl triflate (14.2 g, 60 mmol) was heated in CH_2Cl_2 (70 mL) and worked up in a manner similar to that described for **5a** to give a mixture of *cis*-**5c** and *trans*-**5c** (3:97, 3.8 g, 50%). Recrystallization of the mixture gave 98% purity of *trans*-**5c**: IR (KBr) 1462, 1327, 1256, 1171, 1128, 1069, 855, 752 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.36 (s, 9 H), 2.83 (s, 3 H), 3.24 and 4.74 (AB-q, 2 H, J = 14.5 Hz), 4.93 and 5.55 (AB-q, 2 H, J = 13.6 Hz), 7.10 (s, 1 H), 7.12 (d, 1 H, J = 7.0 Hz), 7.43–7.56 (m, 3 H), 7.80 (br-d, 2 H, J = 7.6 Hz), 7.82–8.80 (br, 2 H).

2-Methyl-1-(2-methylphenyl)-2-[(trimethylsilyl)methyl]-isoindolinium Iodide (5d). **(A)** In the same way, a solution of **4d** (7.5 g, 26 mmol) and iodomethane (14 g, 102 mmol) in MeCN (50 mL) was heated and treated to give a mixture of *cis*-**5d** and *trans*-**5d** (72:28, 7.6 g, 68%). Recrystallization from MeOH–Et_2O gave pure *cis*-**5d**: mp 178–179 °C; IR (KBr) 2957, 1460, 1252, 856, 748 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.27 (s, 9 H), 2.44 and 2.47 (AB-q, 2 H, J = 14.7 Hz), 2.79 (s, 3 H), 3.75 (s, 3 H), 4.66 (d, 1 H, J = 13.7 Hz), 5.86 (d, 1 H, J = 13.7 Hz), 6.85 (s, 1 H), 6.89 (d, 1 H, J = 7.9 Hz), 7.11 (d, 1 H, J = 7.5 Hz), 7.25 (m, 1 H), 7.39–7.49 (m, 4 H), 7.56 (d, 1 H, J = 7.5 Hz). Anal. Calcd for $C_{20}H_{28}INSi$: C, 54.92; H, 6.45; N, 3.20. Found: C, 54.72; H, 6.38; N, 2.97.

trans-**5d** (not isolated): ^1H NMR ($CDCl_3$) δ 0.33 (s, 9 H), 2.76 (s, 3 H), 2.82 (s, 3 H), 3.06 (d, 1 H, J = 14.2 Hz), 4.59 (d, 1 H, J = 14.2 Hz), 4.89 (d, 1 H, J = 13.8 Hz), 6.01 (d, 1 H, J = 13.8 Hz), 6.90 (s, 1 H), 6.98 (d, 1 H, J = 7.0 Hz), 7.00 (d, 1 H, J = 7.5 Hz), 7.29 (m, 1 H), 7.39–7.49 (m, 4 H), 7.53 (d, 1 H, J = 7.7 Hz).

Reaction of 5a–d with CsF. General Procedure. Ammonium salt **5** (1 mmol) was placed in a 20-mL flask equipped with a magnetic stirrer, septum, and a test tube which was connected to the flask by a short piece of rubber tubing. CsF (0.76 g, 5 mmol) was placed in the test tube. The apparatus was dried under reduced pressure and was flushed with N_2. HMPA (5 mL) [and DBU (0.76 g, 5 mmol)] was added to the flask by syringe. CsF was added from the test tube. The mixture was stirred at room temperature (at 10 °C when DBU was added) for 24 h. The reaction mixture was poured into 1.5% $NaHCO_3$ (100 mL) and extracted with Et_2O (4 × 50 mL). The ethereal extract was dried ($MgSO_4$) and concentrated under reduced pressure. The residue was distilled to give a mixture of 1- or 3-substituted 6-methyl-5,6,7,12-tetrahydrodibenzo[*c,f*]azocine (**7**), 4-(2- or 4-substituted phenyl)-2-methyl-1,2,3,4-tetrahydroisoquinoline (**8**), and 1-(2- or 4-substituted phenyl)-2-methylisoindoline (**9**). The product ratio was calculated from the integrated values of the GLC analysis (2 m, 5% silicone SE-30) or determined from the proton ratios of ^1H NMR. The ratio and yields are shown in Table 2. The products were isolated on silica gel columns (EtOAc–hexane).

6-Methyl-5,6,7,12-tetrahydrodibenzo[*c,f*]azocine (7a): mp 93–95 °C (lit.[15] mp 92 °C).

3-Methoxy-6-methyl-5,6,7,12-tetrahydrodibenzo[*c,f*]azocine (7b): mp 100–101 °C (lit.[16] mp 101.5–102.5 °C).

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6-Methyl-3-(trifluoromethyl)-5,6,7,12-tetrahydrodibenzo[*c,f*]azocine (7c): mp 124–125 °C (MeOH); IR (KBr) 2882, 1321, 1279, 1177, 1115, 1078, 758, 721 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.93 (s, 3 H), 3.72 and 4.46 (AB-q, 2 H, J = 12.8 Hz), 3.93 (d, 1 H, J = 14.9 Hz), 3.96 (d, 1 H, J = 14.9 Hz), 4.66 (d, 1 H, J = 14.8 Hz), 4.68 (d, 1 H, J = 14.8 Hz), 7.05–7.11 (m, 2 H), 7.18 (td, 1 H, J = 7.2, 1.7 Hz), 7.30–7.32 (m, 2 H), 7.42 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 37.2, 39.4, 61.5, 61.7, 124.2 (q, J_{CF} = 272.2 Hz), 124.9 (q, J_{CF} = 3.7 Hz), 126.4, 127.9 (q, J_{CF} = 2.9 Hz), 128.2 (q, J_{CF} = 32.3 Hz), 128.3, 128.9, 129.3, 131.6, 136.4, 137.5, 141.6, 146.7. Anal. Calcd for $C_{17}H_{16}F_3N$: C, 70.09; H, 5.54; N, 4.8. Found: C, 70.24; H, 5.84; N, 4.85.

1,6-Dimethyl-5,6,7,12-tetrahydrodibenzo[*c,f*]azocine (7d): mp 85–87 °C (EtOAc–hexane); IR (KBr) 2920, 1460, 1040, 776 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.98 (s, 3 H), 2.62 (s, 3 H), 3.92 and 4.32 (AB-q, 2 H, J = 13.5 Hz), 3.92 (d, 1 H, J = 14.8 Hz), 3.96 (d, 1 H, J = 14.0 Hz), 4.65 (bd, 2 H, J = 15.0 Hz), 6.90–7.52 (m, 7 H); mass spectrum m/z 238 (18, M^+), 237 (100), 236 (48), 222 (35), 206 (26), 178 (25), 146 (66), 132 (72). Anal. Calcd for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.90. Found: C, 85.85; H, 8.18; N, 5.80.

2-Methyl-4-phenyl-1,2,3,4-tetrahydroisoquinoline[16] (8a): a viscous oil.

2-Methyl-4-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (8b): mp 117–118 °C (Et_2O) [lit.[17] mp 121–122 °C (Me_2CO–Et_2O)].

2-Methyl-4-[4-(trifluoromethyl)phenyl]-1,2,3,4-tetrahydroisoquinoline (8c): mp 90–91 °C; bp 100–130 °C (0.7 mmHg); IR (KBr) 2789, 1325, 1161, 1123, 1065, 749 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.42 (s, 3 H), 2.61 (dd, 1 H, J = 11.5, 7.5 Hz), 2.99 (dd, 1 H, J = 11.5, 5.5 Hz), 3.70 (s, 2 H), 4.32 (apparent t, 1 H), 6.83 (d, 1 H, J = 7.7 Hz), 7.06–7.11 (m, 2 H), 7.14–7.18 (m, 1 H), 7.31 (d, 2 H, J = 8.1 Hz), 7.53 (d, 2 H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 45.7, 46.0, 58.3, 61.3, 124.3 (q, J_{CF} = 272.2 Hz), 125.2 (q, 2 C, J_{CF} = 3.7 Hz), 126.3, 126.4, 126.5, 128.7 (q, J_{CF} = 32.3 Hz), 129.4 (2 C), 129.5, 135.2, 136.0, 149.1. Anal. Calcd for $C_{17}H_{16}F_3N$: C, 70.09; H, 5.54; N, 4.81. Found: C, 70.23; H, 5.72; N, 4.86.

2-Methyl-4-(2-methylphenyl)-1,2,3,4-tetrahydroisoquinoline (8d): bp 150–160 °C (1.0 mmHg); IR (film) 2938, 2778, 1491, 1460, 1377, 1103 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.40 (bs, 3 H), 2.44 (s, 3 H), 2.50 (q, 1 H, J = 11.5, 9.0 Hz), 3.03 (ddd, 1 H, J = 11.5, 5.9, 1.5 Hz), 3.60 and 3.81 (AB-q, 2 H, J = 14.7 Hz), 4.59 (dd, 1 H, J = 9.0, 5.9 Hz), 6.78 (d, 1 H, J = 7.9 Hz), 6.93 (d, 1 H, J = 7.3 Hz), 7.03–7.20 (m, 6 H). Anal. Calcd for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.90. Found: C, 85.85; H, 8.00; N, 5.83.

2-Methyl-2-[(trimethylsilyl)methyl]isoindolinium Iodide (17). In a manner similar to that described for **4a**, 1 (1.2 g, 5 mmol) and $LiAlH_4$ (0.8 g, 20 mmol) were treated in Et_2O (15 mL) and worked up to give 2-[(trimethylsilyl)methyl]isoindoline (0.7 g, 67%): bp 70–85 °C (0.42–0.50 mmHg); IR (film) 2955, 2757, 1248, 860, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.14 (s, 9 H), 2.32 (s, 2 H), 3.92 (s, 4 H), 7.18 (s, 4 H); mass spectrum m/z 205 (21, M^+), 204 (54), 190 (18), 133 (11), 132 (100), 131 (11), 105 (31), 73 (18). Anal. Calcd for $C_{12}H_{19}NSi$: C, 70.18; H, 9.32; N, 6.82. Found: C, 69.99; H, 9.20; N, 6.96.

A solution of 2-[(trimethylsilyl)methyl]isoindoline (0.7 g, 3 mmol) and iodomethane (1.8 g, 13 mmol) in MeCN (10 mL) was stirred for 3 h at −20 °C. The solvent was evaporated under reduced pressure, and the residue was recrystallized from MeCN to give 17 (0.8 g, 73%): mp 239–240 °C; IR (KBr) 2949, 2934, 2892, 1460, 1437, 1258, 855, 758 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.33 (s, 9 H), 3.60 (s, 3 H), 3.87 (s, 2 H), 5.07 and 5.15 (AB-q, 4 H, J = 14.0 Hz), 7.37–7.45 (m, 4 H). Anal. Calcd for $C_{13}H_{22}INSi$: C, 44.96; H, 6.38; N, 4.03. Found: C, 44.73; H, 6.31; N, 3.72.

Reaction of 17 with CsF. In a manner similar to that described for **5**, 17 (347 mg, 1 mmol) and CsF (0.76 g, 5 mmol) were treated in HMPA (5 mL). The reaction mixture was poured into water (100 mL) and extracted with Et_2O (4 × 50 mL). The aqueous layer was condensed under reduced pressure to dryness and extracted with $CHCl_3$ (100 mL). Evaporation of the solvent gave 2,2-dimethylisoindolinium iodide (223 mg, 81%): mp 256–257 °C (lit.[18] mp 253–255 °C). No product was obtained from the ethereal extract.

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