JOC Article

Electroreductive Intramolecular Coupling of Aromatic β- and γ-Imino Esters: A New Synthetic Method for *N*-Alkoxycarbonyl-2-aryl-3-ones and *cis*-2-Aryl-3-ols of Pyrrolidines and Piperidines

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The electroreduction of aromatic β- and γ-imino esters prepared from β-alanine and GABA in the presence of chlorotrimethylsilane and subsequent *N*-alkoxycarbonylation of the resulting five- and six-membered cyclized amines gave mixed ketals of *N*-alkoxycarbonyl-2-arylpyrrolidin-3-ones and 2-arylpiperidin-3-ones, respectively. The best result of the electroreductive intramolecular coupling was achieved using Bu_4NClO_4 as a supporting electrolyte and a Pb cathode in THF. Acid hydrolysis of the mixed ketals afforded *N*-alkoxycarbonyl-2-arylpyrrolidin-3-ones and 2-arylpiperidin-3-ones in good yields. The reduction of these ketones with $NaBH_4$ in methanol afforded the corresponding *N*-alkoxycarbonyl-*cis*-2-arylpyrrolidin-3-ols and *cis*-2-arylpiperidin-3-ols diastereospecifically.

Introduction

Pyrrolidine and piperidine skeletons are widely found in many natural products and biologically active compounds. Therefore, a number of methods for the synthesis of these compounds have been developed.[1] On the other hand, reductive coupling of imines with carbonyl compounds has been known to be useful for the synthesis of nitrogen-containing compounds such as β-amino alcohols.[2] In our preliminary report, we disclosed that electroreduction is also an efficient tool for the reductive coupling of aromatic imines with carbonyl compounds.[3] In addition, we have recently reported that the reductive intramolecular coupling of aromatic α-imino esters prepared from chiral α-amino acids was achieved by electroreduction in the presence of chlorotrimethylsilane (CTMS) to give mixed ketals of *cis*-2,4-disubstituted azetidin-3-ones stereoselectively (Scheme 1).[4] At present, electroreduction is only one method for the reductive intramolecular coupling of imino esters. To extend the synthetic potential of the intramolecular coupling of imino esters, in this paper, we report the electroreduction of aromatic β- and γ-imino acid methyl esters in the presence of CTMS produced mixed ketals of 2-arylpyrrolidin-3-ones and 2-arylpiperidin-3-ones. This reaction provides a new synthetic route to *N*-alkoxycarbonyl-2-arylpyrrolidin-3-ones and 2-arylpiperidin-3-ones from β-alanine and γ-aminobutyric acid (GABA), respectively (Scheme 2). In recent years, *N*-BOC-2-phenylpiperidin-3-one attracts much interest as a useful synthon for the synthesis of neurokinin receptor antagonists.[5] Among them, it has been reported that *N*-BOC-2-phenylpiperidin-3-one was reduced with L-Selectride in THF to *cis*-*N*-BOC-2-phenylpiperidin-3-ol, a precursor of neurokinin NK1 receptor antagonist L-733,060 (Scheme 3).[5a] We also found that the reduction of *N*-alkoxycarbonyl-2-arylpyrrolidin-3-ones and 2-arylpiperidin-3-ones with $NaBH_4$ in methanol gave the corresponding *cis*-2-arylpyrrolidin-3-

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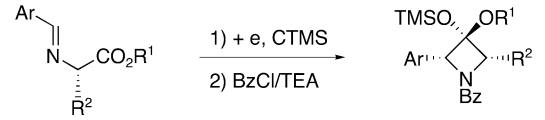

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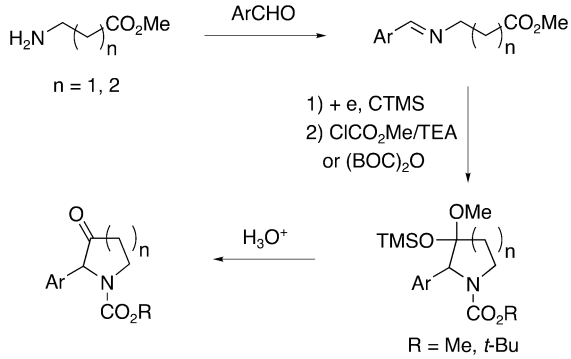

(1) For recent reviews, see: (a) Bailey, P. D.; Millwood, P. A.; Smith, P. D. *Chem. Commun.* **1998**, 633. (b) Laschat, S.; Dickner, T. *Synthesis* **2000**, 1781. (c) Mitchinson, A.; Nadin, A. *J. Chem. Chem., Perkin Trans. 1* **2000**, 2862. (d) Bates, R. W.; Sa-Ei, K. *Tetrahedron* **2002**, *58*, 5957. (e) Weintraub, P. M.; Sabol, J. S.; Kane, J. M.; Borcherding, D. R. *Tetrahedron* **2003**, *59*, 2953.

(2) (a) Roskamp, E. J.; Pedersen, S. F. *J. Am. Chem. Soc.* **1987**, *109*, 6551. (b) Machrouhi, F.; Namy, J.-L. *Tetrahedron Lett.* **1999**, *40*, 1315. (c) Tanaka, Y.; Taniguchi, N.; Uemura, M. *Org. Lett.* **2002**, *4*, 835.

(3) Preliminary communication: Shono, T.; Kise, N.; Kunimi, N.; Nomura, R. *Chem. Lett.* **1991**, 2191.

(4) Kise, N.; Ozaki, H.; Moriyama, N.; Kitagishi, Y.; Ueda, N. *J. Am. Chem. Soc.* **2003**, *125*, 11591.

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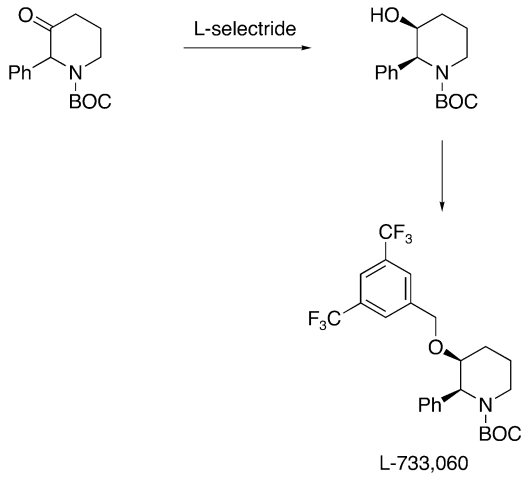
SCHEME 3



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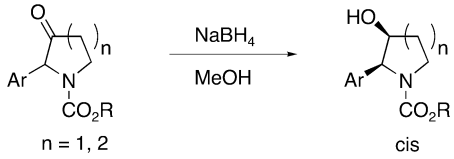
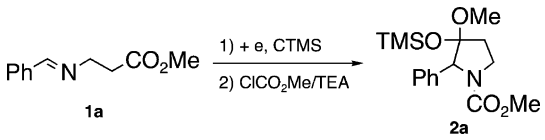


ols and *cis*-2-arylpiperidin-3-ols diastereospecifically in good yields (Scheme 4).

Results and Discussion

According to our study,[4] we surveyed conditions for the electroreductive intramolecular coupling of β-imino esters using *N*-benzyliden-β-alanine methyl ester (**1a**) as a substrate and THF as a solvent in the presence of 5 equiv of chlorotrimethylsilane (CTMS) and triethylamine (TEA). The results are summarized in Table 1. The reductive coupling product, mixed ketal of 2-phenypyrrolidin-3-one, was isolated as methyl carbamate **2a**, since free pyrrolidine was air-sensitive. The product **2a** was obtained as a mixture of two diastereomers **2a′** and **2a″**. The stereochemistry of each isomer could not be determined. The best result (70% combined yield of **2a′** and **2a″**) was obtained when the electroreduction was carried out with Bu_4NClO_4 as a supporting electrolyte and a Pb cathode (Table 1, run 1). The presence of CTMS was essential for the reductive coupling (run 2); a complex mixture was obtained in the absence of CTMS. Although the addition of TEA was not crucial, the absence of TEA somewhat decreased the yield of **2a** (run 3). Some other tetrabutylammonium salts also afforded comparable results to run 1 (runs 4−7), whereas the use of $LiClO_4$ produced a complex mixture (run 8). The yields obtained with several other cathodes were slightly less than or nearly equal to that in run 1 (runs 9−15).

TABLE 1. Electroreductive Coupling of 1a to 2a



run	solvent[a]	additive[b]	cathode	yield (%) of **2a**[c]	**2a′**/**2a″**[d]
1	Bu_4NClO_4/THF	CTMS/TEA	Pb	70	42:58
2	Bu_4NClO_4/THF	none	Pb	0	
3	Bu_4NClO_4/THF	CTMS	Pb	56	42:58
4	Bu_4NBF_4/THF	CTMS/TEA	Pb	70	41:59
5	Bu_4NPF_6/THF	CTMS/TEA	Pb	63	43:57
6	Bu_4NBr/THF	CTMS/TEA	Pb	69	47:53
7	Bu_4NCl/THF	CTMS/TEA	Pb	60	52:48
8	$LiClO_4$/THF	CTMS/TEA	Pb	0	
9	Bu_4NClO_4/THF	CTMS/TEA	Pt	64	34:66
10	Bu_4NClO_4/THF	CTMS/TEA	Au	66	43:57
11	Bu_4NClO_4/THF	CTMS/TEA	Ag	65	41:59
12	Bu_4NClO_4/THF	CTMS/TEA	Cu	67	40:60
13	Bu_4NClO_4/THF	CTMS/TEA	Zn	68	30:70
14	Bu_4NClO_4/THF	CTMS/TEA	Sn	60	34:66
15	Bu_4NClO_4/THF	CTMS/TEA	Al	52	26:74

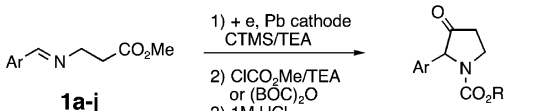
[a] 0.3 M electrolyte in solvent. [b] 5 equiv to **1a**. [c] Isolated yields. [d] Diastereomeric ratios determined by ^1H NMR spectra. **2a′** was less polar than **2a″** in TLC analysis on silica gel (hexanes−ethyl acetate).

The diastereomeric mixture of the mixed ketal **2a** was easily and quickly hydrolyzed to the corresponding ketone **3a** in quantitative yield by treatment with 1 M HCl/dioxane at room temperature. Therefore, ketone **3a** could be more conveniently prepared without isolation of **2a**. A variety of *N*-arylmethylidene-β-alanine methyl esters **1a**−**j** were electrochemically reduced under the same conditions as run 1 in Table 1, the resulted pyrrolidines were protected with a MOC (methoxycarbonyl) or BOC group, and then the crude mixed ketals were hydrolyzed with 1 M HCl to ketones **3** or **4**. The results were summarized in Table 2. All substrates except for **1h** gave the corresponding *N*-protected 2-arylpyrrolidin-3-ones **3** and **4** in moderate to good yields. These results show that the reductive coupling was less affected by substitution of both electron-donating and electron-withdrawing groups. In the case of **1h** (Ar = 1-naphthyl), the yield of **3h** decreased probably due to steric hindrance. In the case of acid-sensitive substrate **1j** (Ar = 2-furyl), the acid hydrolysis was carried out at 0 °C.

The electroreductive method was also effective for the construction of piperidines. The electroreduction of *N*-benzylidene-GABA methyl esters (**5a**) occurred under the same conditions as run 1 in Table 1. The resulting mixed ketal of 2-phenylpiperidin-3-one was isolated as methyl carbamate **6a** in a 72% yield (Scheme 5). The mixed ketal **6a** was also obtained as a mixture of two diastereomers (**6a′**/**6a″** = 33:67), and the diastereomeric mixture was easily hydrolyzed to ketone **7a** with 1 M HCl/dioxane at room temperature. Next, a variety of *N*-arylmethylidene-GABA methyl esters **5a**−**j** were electrochemically reduced, protected with a MOC or BOC group, and successively hydrolyzed to give the corresponding ketones **7** or **8** (Table 3). Similarly to the pyrrolidine formation described above, aryl substitution minimally influenced the piperidine formation except for the case of the 1-naphthyl group (**5h**).

(5) (a) Calvez, O.; Langlois, N. *Tetrahedron Lett.* **1999**, *40*, 7099. (b) Kulagowski, J. J.; Curtis, N. R.; Swain, C. J.; Williams, B. J. *Org. Lett.* **2001**, *3*, 667. (c) Lee, J.; Hoang, T.; Lewis, S.; Weissman, S. A.; Askin, D.; Volante, R. P.; Reider, P. J. *Tetrahedron Lett.* **2001**, *42*, 6223. (d) Maligres, P. E.; Waters, M. M.; Lee, J.; Reamer, R. A.; Askin, D.; Ashwood, M. S.; Cameron, M. *J. Org. Chem.* **2002**, *67*, 1093. (e) Yamazaki, N.; Atobe, M.; Kibayashi, C. *Tetrahedron Lett.* **2002**, *43*, 7979. (f) Huang, P.-Q.; Liu, L.-X.; Wei, B.-G.; Ruan, Y.-P. *Org. Lett.* **2003**, *5*, 1927. (g) Bhaskar, G.; Rao, B. V. *Tetrahedron Lett.* **2003**, *44*, 915.

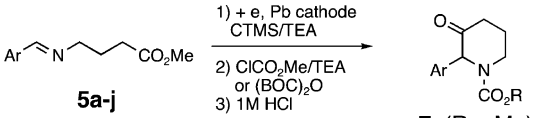
TABLE 2. Electroreductive Coupling of β-Imino Esters[a]



imine	Ar	product	yield[b] (%)
1a	C_6H_5	**3a**	68
		4a	70
1b	*p*-$MeOC_6H_4$	**3b**	64
		4b	65
1c	*m*-$MeOC_6H_4$	**3c**	64
		4c	60
1d	*o*-$MeOC_6H_4$	**3d**	65
		4d	64
1e	3,4-$(MeO)_2C_6H_3$	**3e**	63
		4e	62
1f	*p*-FC_6H_4	**3f**	58
		4f	56
1g	*p*-NCC_6H_4	**3g**	55
		4g	62
1h	1-naphthyl	**3h**	35
1i	2-naphthyl	**3i**	60
		4i	56
1j	2-furyl	**3j**	56

[a] The electroreduction was carried out in 0.3 M Bu_4NClO_4/THF. [b] Isolated yields.

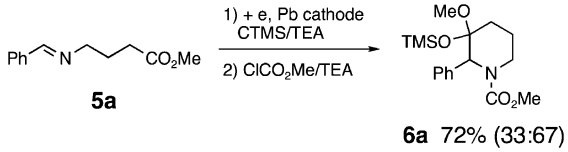
TABLE 3. Electroreductive Coupling of γ-Imino Esters[a]



imine	Ar	product	yield[b] (%)
5a	Ph	**7a**	70
		8a	69
5b	*p*-$MeOC_6H_4$	**7b**	72
		8b	65
5c	*m*-$MeOC_6H_4$	**7c**	69
		8c	65
5d	*o*-$MeOC_6H_4$	**7d**	72
		8d	66
5e	3,4-$(MeO)_2C_6H_3$	**7e**	69
		8e	70
5f	*p*-FC_6H_4	**7f**	67
		8f	67
5g	*p*-NCC_6H_4	**7g**	59
		8g	52
5h	1-naphthyl	**7h**	25
5i	2-naphthyl	**7i**	63
		8i	57
5j	2-furyl	**7j**	51

[a] The electroreduction was carried out in 0.3 M Bu_4NClO_4/THF. [b] Isolated yields.

SCHEME 5

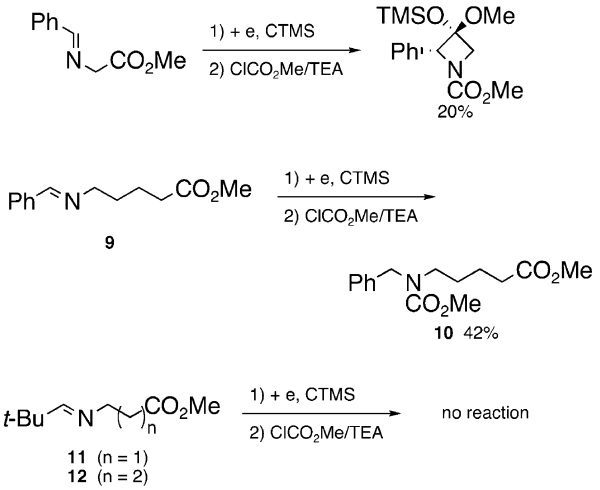


As previously reported,[4] a mixed ketal of 2-phenylazetidin-3-one was formed in poor yield (20%) by the electroreduction of *N*-benzylidene glycine methyl ester (Scheme 6). The seven-membered cyclized product could not be obtained from aromatic δ-imino ester **9** by this methodology; simply reduced amine **10** was the only one isolatable product. In addition, aliphatic imines **11** and **12** were not reduced under the conditions.

The speculated mechanism of the electroreductive coupling can be illustrated in Scheme 7, similarly to the previous report.[4] The equilibrium of the formation of an imine **1a**·CTMS complex was also observed in the ^1H NMR analysis of **1a** in the presence of CTMS (Table 4). One-electron transfer to **1a**·CTMS complex followed by *N*-silylation and further one-electron transfer to the resulting radical **A** generates the anion **B**. Intramolecular attack of the carbanion to the ester group in **B** forms *O*-anion **C**, which is subsequently *O*-silylated to **D**. The pyrrolidine **E** is obtained by *N*-desilylation of **D** during workup.

Reduction of *N*-Alkoxycarbonyl-2-aryl-3-ones of Pyrrolidines and Piperidines. It has already been known that the reduction of *N*-BOC-2-phenylpiperidin-3-one (**7a**) with L-Selectride at −78 °C afforded *N*-BOC-*cis*-2-phenylpiperidin-3-ol stereospecifically (Scheme 3).[5a] We surveyed the reduction of **7a** with several hydride reagents as depicted in Table 5. It was found that all hydride reagents employed gave only the *cis*-isomer of the alcohol **16a**. Therefore, other *N*-alkoxycarbonyl-2-aryl-3-ones of pyrrolidines (**3** and **4**) and piperidines (**7** and **8**) were reduced with $NaBH_4$ in methanol (Table 6), since it is the most economical and convenient method. Of the alcohols **13**−**16** obtained as single stereoisomers, *N*-BOC-*cis*-2-phenyl-3-ols **14a** and **16a** were confirmed by comparison of their spectroscopic data with reported ones.[6] The stereostructures of several *N*-MOC-2-aryl-3-ols, **13a**, **13f**, **13g**, **15a**, and **15d**, were established to be 2,3-cis by X-ray crystallographic analysis. These results imply that the other alcohols **13**−**16** also possess 2,3-cis configuration.

SCHEME 6



Conclusion

This paper describes the electroreductive intramolecular coupling of aromatic β- and γ-imino esters in the

(6) Tomooka, K.; Nakazaki, A.; Nakai, T. *J. Am. Chem. Soc.* **2000**, *122*, 408.

SCHEME 7

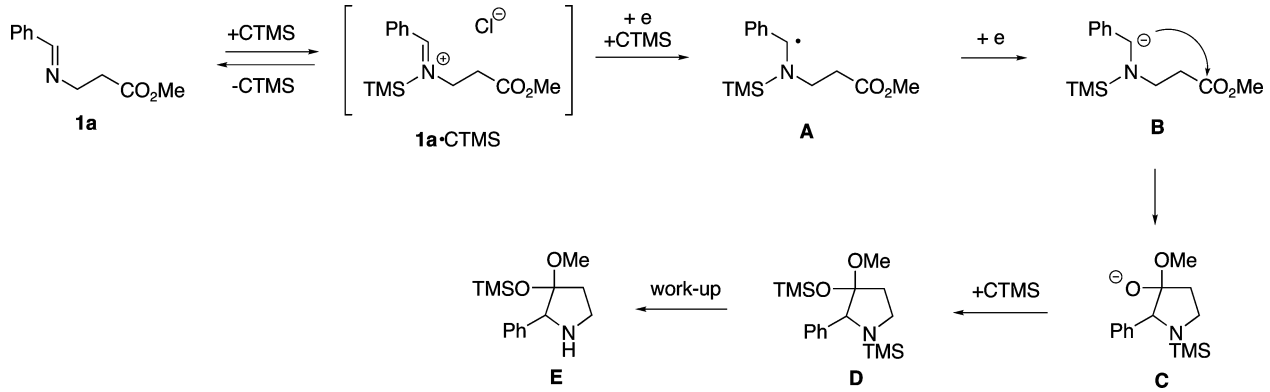
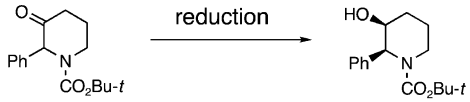


TABLE 4. ^{1}H NMR Chemical Shifts of 1a in the Presence of CTMS

CTMS (equiv)	CH=N (δ)	NCH_2 (δ)
0	8.33	3.89
0.5	8.53	4.06
1.0	8.69	4.16
2.0	8.71	4.17
3.0	8.73	4.18
3.0[a]	8.33	3.88

[a] 3 equiv of TEA was added.

TABLE 5. Reduction of 7a to 16a



7a *cis*-**16a**

reagent	solvent	*T* (°C)	yield[a] (%)
L-Selectride	THF	−78	82
$NaBH_4$	CH_3OH	5	93
$LiBH_4$	THF	5	80
Bu_4NBH_4	CH_2Cl_2	5	51

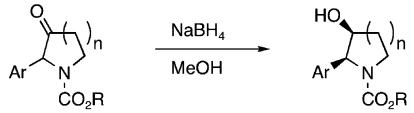
[a] Isolated yields.

presence of CTMS and TEA followed by *N*-alkoxycarbonylation to produce *N*-alkoxycalbonyl mixed ketals of 2-arylpyrrolidin-3-ones and 2-arylpiperidin-3-ones. The addition of CTMS to the catholyte is essential to promote the electroreductive coupling. Because the *N*-alkoxycalbonyl mixed ketals were easily hydrolyzed to ketones by treatment with 1 M HCl, this electroreduction provides a new method for the synthesis of *N*-protected 2-arylpyrrolidin-3-ones and 2-arylpiperidin-3-ones from β-alanine and GABA, respectively. In addition, these *N*-alkoxycalbonyl-2-aryl-3-ones of pyrrolidines and piperidines were stereospecifically transformed to the corresponding *N*-alkoxycalbonyl-*cis*-2-aryl-3-ols by reduction with $NaBH_4$ in methanol.

Experimental Section

General Procedures. Column chromatography was performed on silica gel 60. THF was distilled from sodium benzophenone ketyl radical. CTMS and TEA were distilled from CaH_2. Aromatic β- or γ-imino esters were prepared by treatment of β-alanine or GABA methyl ester with aromatic aldehydes in dichloromethane in the presence of magnesium sulfate at room temperature and isolated by distillation in vacuo or by recrystallization from hexanes−ethyl acetate (**1g**,**i** and **5g**,**i**).

TABLE 6. Reduction of 2-Aryl-3-ones of Pyrrolidines and Piperidines[a]



3 (n = 1, R = Me)
4 (n = 1, R = *t*-Bu)
7 (n = 2, R = Me)
8 (n = 2, R = *t*-Bu)

cis-**13**
cis-**14**
cis-**15**
cis-**16**

ketone	Ar	*n*	alcohol	yield[b] (%)
3a	C_6H_5	1	**13a**	84
4a			**14a**	88
3b	*p*-$MeOC_6H_4$	1	**13b**	71
4b			**14b**	85
3c	*m*-$MeOC_6H_4$	1	**13c**	71
4c			**14c**	83
3d	*o*-$MeOC_6H_4$	1	**13d**	74
4d			**14d**	82
3e	3,4-$(MeO)_2C_6H_3$	1	**13e**	75
4e			**14e**	80
3f	*p*-FC_6H_4	1	**13f**	62
4f			**14f**	79
3g	*p*-NCC_6H_4	1	**13g**	64
4g			**14g**	68
3i	2-naphthyl	1	**13i**	74
4i			**14i**	84
7a	C_6H_5	2	**15a**	86
8a			**16a**	93
7b	*p*-$MeOC_6H_4$	2	**15b**	90
8b			**16b**	83
7c	*m*-$MeOC_6H_4$	2	**15c**	79
8c			**16c**	86
7d	*o*-$MeOC_6H_4$	2	**15d**	66
8d			**16d**	76
7e	3,4-$(MeO)_2C_6H_3$	2	**15e**	78
8e			**16e**	87
7f	*p*-FC_6H_4	2	**15f**	74
8f			**16f**	77
7g	*p*-NCC_6H_4	2	**15g**	52
8g			**16g**	58
7i	2-naphthyl	2	**15i**	84
8i			**16i**	76

[a] The reduction was carried out with $NaBH_4$ in methanol at 5 °C. [b] Isolated yields.

Typical Procedure for Electroreduction of Imino Esters 1 and 5. A 0.3 M solution of Bu_4NClO_4 in THF (15 mL) was placed in the cathodic chamber of a divided cell (40-mL beaker, 3-cm diameter, 6-cm height) equipped with a lead cathode (5 × 5 cm^2), a platinum anode (2 × 1 cm^2), and a ceramic cylindrical diaphragm (1.5-cm diameter). A 0.3 M solution of Bu_4NClO_4 in DMF (4 mL) was placed in the anodic chamber (inside the diaphragm). Imino ester (**1a**) (191 mg, 1 mmol), CTMS (0.64 mL, 5 mmol), and triethylamine (0.70 mL,

5 mmol) were added to the cathodic chamber. After 300 C of electricity was passed at a constant current of 100 mA at room temperature, the catholyte was evaporated in vacuo. The residue was diluted with Et_2O (30 mL) and 1 M $NaHCO_3$ (30 mL). To the mixture was added $ClCO_2Me$ (0.39 mL, 5 mmol) dropwise, and then the suspended mixture was stirred at room temperature for 1 h. Insoluble Bu_4NClO_4 was filtered off, and the filtrate was extracted with Et_2O three times. The crude mixture was purified by column chromatography on silica gel (hexanes−ethyl acetate, 50:1) to give **2a** in a 70% yield as a mixture of two diastereomers (**2a′**:**2a″** = 42:58). These isomers **2a′** and **2a″** could be separated by further column chromatography on silica gel (hexanes−ethyl acetate, 100:1).

Hydrolysis of Mixed Ketal 2a to Ketone 3a. To a solution of **2a** (0.5 mmol) in dioxane (2.5 mL) was added 1 M HCl (2.5 mL). The mixture was stirred at room temperature for 1 h, diluted with H_2O (10 mL), and then extracted with Et_2O three times. The produced **3a** was isolated by column chromatography on silica gel in a 96% yield.

Typical Procedure for Synthesis of Ketones 3, 4, 7, and 8 from Imino Esters 1 and 5 by Successive Electrolysis and Hydrolysis. After electroreduction of **1a** (1 mmol) was carried out as described above, the catholyte was evaporated in vacuo. The residue was diluted with Et_2O (30 mL) and 1 M $NaHCO_3$ (30 mL). To the mixture was added $(BOC)_2O$ (0.44 g, 2 mmol), and then the suspended mixture was stirred at room temperature for 1 h. Insoluble Bu_4NClO_4 was filtered off, and the filtrate was extracted with Et_2O three times. After the solvent was removed, to the residue were added dioxane (2.5 mL) and 1 M HCl (2.5 mL). The mixture was stirred at room temperature for 1 h, diluted with H_2O (10 mL), and extracted with Et_2O three times. The crude mixture was purified by column chromatography on silica gel to give **4a** in a 70% yield.

1-MOC-2-phenylpyrrolidin-3-one (3a): colorless paste; R_f 0.24 (hexanes−ethyl acetate, 2:1); IR (neat) 1759, 1699, 1601, 1545, 1493, 916, 773, 741, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.48−2.80 (m, 2 H), 3.67 (brs, 3 H), 3.85−3.98 (m, 1 H), 4.05−4.25 (m, 1 H), 4.96 (s, 1 H), 7.23−7.41 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 35.1 (t), 42.1 (t), 52.6 (q), 65.3 (d), 125.4 (d), 127.6 (d), 128.5 (d), 136.1 (s), 155.3 (s), 208.6 (s). Anal. Calcd for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.68; H, 6.04; N, 6.31.

1-BOC-2-phenylpyrrolidin-3-one (4a): white solid; R_f 0.17 (hexanes−ethyl acetate, 5:1); mp 103−105 °C; IR (KBr) 1753, 1674, 1495, 1475, 741, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (brs, 9 H), 2.63−2.76 (m, 2 H), 3.87−3.94 (m, 1 H), 4.01−4.09 (m, 1 H), 4.85 (brs, 1 H), 7.22−7.37 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 27.9 (q), 35.1 (t), 41.6 (t), 67.6 (d), 80.2 (s), 125.6 (d), 127.5 (d), 128.4 (d), 137.4 (s), 154.2 (s), 209.5 (s). Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 68.90; H, 7.33; N, 5.41.

1-MOC-2-(4-methoxyphenyl)pyrrolidin-3-one (3b): colorless paste; R_f 0.21 (hexanes−ethyl acetate, 2:1); IR (neat) 1761, 1701, 1609, 1512, 773, 733 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.58−2.79 (m, 2 H), 3.68 (brs, 3 H), 3.79 (s, 3 H), 3.83−3.95 (m, 1 H), 4.04−4.22 (m, 1 H), 6.85−6.91 (m, 2 H), 7.14−7.21 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 35.1 (t), 42.1 (t), 52.6 (q), 55.1 (q), 64.7 (d), 114.0 (d), 126.6 (d), 128.3 (s), 155.3 (s), 159.0 (s), 209.1 (s). Anal. Calcd for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.07; N, 5.62. Found: C, 62.50; H, 6.06; N, 5.43.

1-BOC-2-(4-methoxyphenyl)pyrrolidin-3-one (4b): white solid; R_f 0.50 (hexanes−ethyl acetate, 1:1); mp 69−71 °C; IR (KBr) 1757, 1674, 1607, 1585, 1512, 1475, 862, 822 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28 (brs, 9 H), 2.62−2.74 (m, 2 H), 3.79 (s, 3 H), 3.84−3.92 (m, 1 H), 3.99−4.08 (m, 1 H), 4.81 (brs, 1 H), 6.86−6.90 (m, 2 H), 7.13−7.19 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 27.9 (q), 35.0 (t), 41.5 (t), 54.9 (q), 65.1 (d), 80.0 (s), 113.8 (d), 126.7 (d), 129.5 (s), 154.1 (s), 158.9 (s), 209.8 (s). Anal. Calcd for $C_{16}H_{21}NO_4$: C, 65.96; H, 7.27; N, 4.81. Found: C, 65.88; H, 7.25; N, 4.74.

1-MOC-2-(3-methoxyphenyl)pyrrolidin-3-one (3c): colorless paste; R_f 0.22 (hexanes−ethyl acetate, 2:1); IR (neat) 1761, 1705, 1601, 1585, 1491, 773, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.58−2.79 (m, 2 H), 3.68 (brs, 3 H), 3.80 (s, 3 H), 3.84−3.96 (m, 1 H), 4.04−4.23 (m, 1 H), 4.92 (s, 1 H), 6.80−6.87 (m, 3 H), 7.23−7.31 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 35.1 (t), 42.2 (t), 52.7 (q), 55.1 (q), 65.3 (d), 111.5 (d), 113.0 (d), 117.6 (d), 129.6 (d), 137.7 (s), 155.4 (s), 159.7 (s), 208.4 (s). Anal. Calcd for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.07; N, 5.62. Found: C, 62.74; H, 6.12; N, 5.43.

1-BOC-2-(3-methoxyphenyl)pyrrolidin-3-one (4c): colorless paste; R_f 0.42 (hexanes−ethyl acetate, 2:1); IR (neat) 1761, 1699, 1601, 1585, 1491, 777, 737, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27 (brs, 9 H), 2.62−2.74 (m, 2 H), 3.80 (s, 3 H), 3.85−3.92 (m, 1 H), 4.00−4.07 (m, 1 H), 4.83 (brs, 1 H), 6.76−6.87 (m, 3 H), 7.24−7.28 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 27.9 (q), 35.1 (t), 41.6 (t), 55.0 (q), 65.7 (d), 80.2 (s), 111.4 (d), 112.9 (d), 117.8 (d), 129.5 (d), 138.9 (s), 154.2 (s), 159.7 (s), 209.2 (s). Anal. Calcd for $C_{16}H_{21}NO_4$: C, 65.96; H, 7.27; N, 4.81. Found: C, 66.12; H, 7.38; N, 4.69.

1-MOC-2-(2-methoxyphenyl)pyrrolidin-3-one (3d): white solid; R_f 0.39 (hexanes−ethyl acetate, 1:1); mp 124−125 °C; IR (KBr) 1757, 1705, 1688, 1599, 1589, 1497, 772, 762 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.63−2.81 (m, 2 H), 3.63 (brs, 3 H), 3.77 (s, 3 H), 3.84 (dt, 1 H, J = 8.6, 10.8 Hz), 3.98−4.18 (m, 1 H), 4.86 (brs, 1 H), 6.85 (d, 1 H, J = 8.4 Hz), 6.94 (d, 1 H, J = 7.3 Hz), 7.18−7.45 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 36.3 (t), 42.9 (t), 52.2 (q), 55.0 (q), 63.6 (d), 110.8 (d), 120.3 (d), 126.4 (s), 129.5 (d), 132.1 (d), 154.8 (s), 155.7 (s), 210.7 (s). Anal. Calcd for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.07; N, 5.62. Found: C, 62.58; H, 6.10; N, 5.55.

1-BOC-2-(2-methoxyphenyl)pyrrolidin-3-one (4d): white solid; R_f 0.43 (hexanes−ethyl acetate, 5:1); mp 128−129 °C; IR (KBr) 1755, 1674, 1601, 1589, 1495, 1483, 783, 758 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (brs, 9 H), 2.66−2.77 (m, 2 H), 3.77 (s, 3 H), 3.78−3.85 (m, 1 H), 3.98−4.07 (m, 1 H), 4.81 (brs, 1 H), 6.85 (d, 1 H, J = 8.0 Hz), 6.93 (t, 1 H, J = 7.5 Hz), 7.17−7.31 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 28.0 (q), 36.1 (t), 42.4 (t), 55.0 (q), 63.7 (d), 79.8 (s), 110.7 (d), 119.9 (d), 127.0 (s), 129.4 (d), 132.3 (d), 154.3 (s), 155.9 (s), 211.7 (s). Anal. Calcd for $C_{16}H_{21}NO_4$: C, 65.96; H, 7.27; N, 4.81. Found: C, 65.86; H, 7.22; N, 4.70.

1-MOC-2-(3,4-dimethoxyphenyl)pyrrolidin-3-one (3e): colorless paste; R_f 0.24 (hexanes−ethyl acetate, 1:1); IR (neat) 1759, 1699, 1593, 1514, 916, 806, 772, 731 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.65−2.73 (m, 2 H), 3.70 (brs, 3 H), 3.86 (s, 3 H), 3.89 (s, 3 H), 3.83−3.97 (m, 1 H), 4.07−4.21 (m, 1 H), 4.90 (s, 1 H), 6.74−6.79 (m, 1 H), 6.80−6.86 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 35.1 (t), 42.1 (t), 52.7 (q), 55.8 (q), 55.8 (q), 64.9 (d), 109.1 (d), 110.1 (d), 117.2 (d), 128.6 (s), 148.6 (s), 149.1 (s), 155.4 (s), 208.8 (s). Anal. Calcd for $C_{14}H_{17}NO_5$: C, 60.21; H, 6.14; N, 5.02. Found: C, 60.04; H, 6.12; N, 4.88.

1-BOC-2-(3,4-dimethoxyphenyl)pyrrolidin-3-one (4e): colorless paste; R_f 0.41 (hexanes−ethyl acetate, 1:1); IR (neat) 1759, 1699, 1595, 1516, 862, 810, 768, 731 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.31 (brs, 9 H), 2.63−2.75 (m, 2 H), 3.85−3.91 (m, 1 H), 3.87 (s, 3 H), 3.88 (s, 3 H), 4.00−4.08 (m, 1 H), 4.81 (brs, 1 H), 6.75−6.80 (m, 2 H), 6.84 (d, 1 H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 28.0 (q), 35.1 (t), 41.6 (t), 55.7 (q), 65.3 (d), 80.3 (s), 108.9 (d), 111.1 (d), 117.6 (d), 129.9 (s), 148.5 (s), 149.0 (s), 154.3 (s), 209.7 (s). Anal. Calcd for $C_{17}H_{23}NO_5$: C, 63.54; H, 7.21; N, 4.36. Found: C, 63.75; H, 7.34; N, 4.19.

1-MOC-2-(4-fluorophenyl)pyrrolidin-3-one (3f): colorless paste; R_f 0.23 (hexanes−ethyl acetate, 2:1); IR (neat) 1763, 1705, 1605, 1508, 862, 822, 773 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.59−2.82 (m, 2 H), 3.69 (brs, 3 H), 3.83−3.95 (m, 1 H), 4.06−4.22 (m, 1 H), 4.93 (s, 1 H), 7.00−7.09 (m, 2 H), 7.20−7.28 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 35.2 (t), 42.2 (t), 52.8 (q), 64.7 (d), 115.5 (d, J_{CCF} = 21.7 Hz), 127.2 (d, J_{CCCF} = 7.8 Hz), 132.0 (s), 155.4 (s), 162.2 (s, J_{CF} = 244.4 Hz), 208.6 (s). Anal. Calcd for $C_{12}H_{12}FNO_3$: C, 60.76; H, 5.10; N, 5.90. Found: C, 60.85; H, 5.17; N, 5.69.

1-BOC-2-(4-fluorophenyl)pyrrolidin-3-one (4f): colorless paste; R_f 0.47 (hexanes−ethyl acetate, 2:1); IR (neat) 1755, 1674, 1603, 1510, 860, 826, 791, 756 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12−1.60 (m, 9 H), 2.62−2.77 (m, 2 H), 3.85−3.92 (m, 1 H),

4.01−4.08 (m, 1 H), 4.84 (brs, 1 H), 7.02−7.07 (m, 2 H), 7.19−7.26 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 27.8 (q), 35.1 (t), 41.5 (t), 65.0 (d), 80.2 (s), 115.3 (d, J_{CCF} = 21.0 Hz), 127.2 (d, J_{CCCF} = 7.6 Hz), 133.3 (s), 154.0 (s), 162.0 (d, J_{CF} = 244.2 Hz), 209.3 (s). Anal. Calcd for $C_{15}H_{18}FNO_3$: C, 64.50; H, 6.50; N, 5.01. Found: C, 64.57; H, 6.45; N, 4.90.

1-MOC-2-(4-cyanophenyl)pyrrolidin-3-one (3g): colorless paste; R_f 0.53 (hexanes−ethyl acetate, 1:2); IR (neat) 2230, 1763, 1705, 1607, 1502, 773, 733 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.59−2.86 (m, 2 H), 3.69 (brs, 3 H), 3.85−3.97 (m, 1 H), 4.06−4.26 (m, 1 H), 5.00 (s, 1 H), 3.37−3.43 (m, 2 H), 7.63−7.69 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 35.4 (t), 42.2 (t), 52.9 (q), 65.1 (d), 111.6 (s), 118.2 (s), 126.2 (d), 132.3 (d), 141.2 (s), 155.2 (s), 207.3 (s). Anal. Calcd for $C_{13}H_{12}N_2O_3$: C, 63.93; H, 4.95; N, 11.47. Found: C, 63.75; H, 4.91; N, 11.29.

1-BOC-2-(4-cyanophenyl)pyrrolidin-3-one (4g): white solid; R_f 0.48 (hexanes−ethyl acetate, 1:1); mp 133−134 °C; IR (KBr) 2232, 1757, 1676, 1609, 1504, 1475, 860, 826, 791, 754 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.26 (brs, 6 H), 1.46 (brs, 3 H), 2.63−2.71 (m, 1 H), 2.73−2.81 (m, 1 H), 3.86−3.93 (m, 1 H), 4.03−4.11 (m, 1 H), 4.91 (brs, 1 H), 7.39 (d, 2 H, J = 8.3 Hz), 7.66 (d, 2 H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 27.8 (q), 35.3 (t), 41.6 (t), 65.4 (d), 80.7 (s), 111.3 (s), 118.3 (s), 126.3 (d), 132.2 (d), 142.5 (s), 153.9 (s), 208.0 (s). Anal. Calcd for $C_{16}H_{18}N_2O_3$: C, 67.12; H, 6.34; N, 9.78. Found: C, 67.15; H, 6.37; N, 9.70.

1-MOC-2-(1-naphthyl)pyrrolidin-3-one (3h): colorless paste; R_f 0.5 (hexanes−ethyl acetate, 1:1); IR (neat) 1759, 1699, 1510, 797, 775, 731 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.66−2.89 (m, 2 H), 3.59 (brs, 3 H), 4.01−4.28 (m, 2 H), 5.85 (s, 1 H), 7.29 (d, 1 H, J = 7.3 Hz), 7.42 (t, 1 H, J = 7.6 Hz), 7.48−7.64 (m, 2 H), 7.76−7.90 (m, 2 H), 8.27 (d, 1 H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 35.0 (t), 42.3 (t), 52.8 (q), 62.5 (d), 121.8 (d), 124.2 (d), 125.0 (d), 125.9 (d), 126.3 (d), 128.4 (d), 128.5 (d), 130.7 (s), 132.8 (s), 134.0 (s), 207.4 (s). Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.40; H, 5.68; N, 5.03.

1-MOC-2-(2-naphthyl)pyrrolidin-3-one (3i): colorless paste; R_f 0.25 (hexanes−ethyl acetate, 2:1); IR (neat) 1761, 1705, 1601, 1508, 816, 773, 733 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.62−2.84 (m, 2 H), 3.66 (brs, 3 H), 3.94−4.07 (m, 1 H), 4.11−4.28 (m, 1 H), 5.12 (s, 1 H), 7.41 (dd, 1 H, J = 1.6, 8.6 Hz), 7.44−7.52 (m, 2 H), 7.69 (s, 1 H), 7.78−7.87 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 35.2 (t), 42.3 (t), 52.8 (q), 65.6 (d), 123.5 (d), 124.3 (d), 126.0 (d), 126.2 (d), 127.5 (d), 127.8 (d), 128.6 (d), 132.8 (s), 133.1 (s), 133.7 (s), 155.6 (s), 208.6 (s). Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.48; H, 5.66; N, 5.07.

1-BOC-2-(2-naphthyl)pyrrolidin-3-one (4i): colorless paste; R_f 0.64 (hexanes−ethyl acetate, 1:1); IR (neat) 1757, 1686, 1599, 1508, 1475, 866, 822, 754, 727 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.22 (brs, 9 H), 2.67−2.80 (m, 2 H), 3.95−4.02 (m, 1 H), 4.07−4.15 (m, 1 H), 5.04 (brs, 1 H), 7.37−7.42 (m, 1 H), 7.44−7.51 (m, 2 H), 7.68 (brs, 1 H), 7.79−7.86 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 27.9 (q), 35.2 (t), 41.7 (t), 65.8 (t), 80.3 (s), 123.6 (d), 124.5 (d), 125.8 (d), 126.1 (d), 127.5 (d), 127.7 (d), 128.4 (d), 132.7 (s), 133.1 (s), 134.7 (s), 154.3 (s), 209.3 (s). Anal. Calcd for $C_{19}H_{21}NO_3$: C, 73.29; H, 6.80; N, 4.50. Found: C, 73.40; H, 6.92; N, 4.29.

1-MOC-2-(2-furyl)pyrrolidin-3-one (3j): pale yellow paste; R_f 0.32 (hexanes−ethyl acetate, 2:1); IR (neat) 1767, 1705, 1502, 978, 930, 773, 745 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.63−2.86 (m, 2 H), 3.71 (s, 3 H), 3.80−3.92 (m, 1 H), 4.00−4.17 (m, 1 H), 5.00 (brs, 1 H), 6.32−6.35 (m, 2 H), 7.34 (t, 1 H, J = 1.4 Hz); ^{13}C NMR ($CDCl_3$) δ 35.8 (t), 42.0 (t), 52.7 (q), 59.5 (d), 108.6 (d), 110.3 (d), 142.6 (d), 149.0 (s), 155.0 (s), 207.0 (s). Anal. Calcd for $C_{10}H_{11}NO_4$: C, 57.41; H, 5.30; N, 6.70. Found: C, 57.44; H, 5.39; N, 6.51.

1-MOC-2-phenylpiperidin-3-one (7a): colorless paste; R_f 0.42 (hexanes−ethyl acetate, 2:1); IR (neat) 1701, 1601, 1495, 959, 770, 731, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.84−2.08 (m, 2 H), 2.38−2.56 (m, 2 H), 3.30−3.45 (m, 1 H), 3.74 (s, 3 H), 3.97−4.28 (m, 1 H), 5.71 (brs, 1 H), 7.19−7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 22.6 (t), 37.0 (t), 40.3 (t), 52.8 (q), 65.7 (d), 125.0 (d), 127.4 (d), 128.6 (d), 134.7 (s), 155.9 (s), 204.3 (s). Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.00. Found: C, 66.88; H, 6.54; N, 5.87.

1-BOC-2-phenylpiperidin-3-one (8a):[5] colorless paste; R_f 0.33 (hexanes−ethyl acetate, 5:1); IR (neat) 1722, 1693, 1601, 1583, 1495, 972, 897, 860, 758, 727, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.43 (brs, 9 H), 1.86−2.02 (m, 2 H), 2.40−2.52 (m, 2 H), 3.26−3.38 (m, 1 H), 3.95−4.20 (m, 1 H), 5.22−5.88 (m, 1 H), 7.20−7.23 (m, 2 H), 7.27−7.31 (m, 1 H), 7.34−7.38 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.7 (t), 28.1 (q), 37.2 (t), 39.7 (t), 66.3 (d), 80.6 (s), 125.2 (d), 127.5 (d), 128.8 (d), 135.4 (s), 154.8 (s), 205.3 (s). Anal. Calcd for $C_{16}H_{21}NO_3$: C, 69.79; H, 7.69; N, 5.09. Found: C, 69.86; H, 7.72; N, 4.82.

1-MOC-2-(4-methoxyphenyl)piperidin-3-one (7b): colorless paste; R_f 0.31 (hexanes−ethyl acetate, 2:1); IR (neat) 1699, 1611, 1510, 961, 768, 669 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.86−2.07 (m, 2 H), 2.47 (t, 2 H, J = 6.8 Hz), 3.29−3.42 (m, 1 H), 3.74 (s, 3 H), 3.79 (s, 3 H), 3.97−4.25 (m, 1 H), 5.66 (s, 1 H), 6.85−6.92 (m, 2 H), 7.09−7.16 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.7 (t), 37.0 (t), 40.2 (t), 52.9 (q), 55.1 (q), 65.3 (d), 114.1 (d), 126.4 (d), 126.7 (s), 156.0 (s), 158.9 (s), 204.7 (s). Anal. Calcd for $C_{14}H_{17}NO_4$: C, 63.87; H, 6.51; N, 5.32. Found: C, 63.79; H, 6.57; N, 5.14.

1-BOC-2-(4-methoxyphenyl)piperidin-3-one (8b): colorless paste; R_f 0.44 (hexanes−ethyl acetate, 2:1); IR (neat) 1722, 1693, 1609, 1583, 1510, 972, 899, 870, 827, 770 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.44 (s, 9 H), 1.87−2.01 (m, 2 H), 2.41−2.51 (m, 2 H), 3.26−3.34 (m, 1 H), 3.80 (s, 3 H), 3.97−4.16 (m, 1 H), 5.59 (brs, 1 H), 6.86−6.91 (m, 2 H), 7.09−7.14 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.6 (t), 28.0 (q), 36.9 (t), 39.6 (t), 54.9 (q), 65.5 (d), 80.3 (s), 114.0 (d), 126.4 (d), 127.2 (s), 154.7 (s), 158.8 (s), 205.3 (s). Anal. Calcd for $C_{17}H_{23}NO_4$: C, 66.86; H, 7.59; N, 4.59. Found: C, 66.91; H, 7.62; N, 4.38.

1-MOC-2-(3-methoxyphenyl)piperidin-3-one (7c): colorless paste; R_f 0.4 (hexanes−ethyl acetate, 2:1); IR (neat) 1705, 1599, 1583, 1489, 961, 768, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.86−2.03 (m, 2 H), 2.47 (t, 2 H, J = 6.2 Hz), 3.31−3.47 (m, 1 H), 3.74 (brs, 3 H), 3.79 (s, 3 H), 3.95−4.25 (m, 1 H), 5.57−5.85 (m, 1 H), 6.75−6.86 (m, 3 H), 7.28 (t, 1 H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 22.7 (t), 37.1 (t), 40.5 (t), 53.0 (q), 55.1 (q), 65.7 (d), 111.2 (d), 112.7 (d), 117.2 (d), 129.8 (d), 136.4 (s), 156.0 (s), 159.9 (s), 204.3 (s). Anal. Calcd for $C_{14}H_{17}NO_4$: C, 63.87; H, 6.51; N, 5.32. Found: C, 63.85; H, 6.52; N, 5.24.

1-BOC-2-(3-methoxyphenyl)piperidin-3-one (8c): colorless paste; R_f 0.52 (hexanes−ethyl acetate, 2:1); IR (neat) 1699, 1601, 1585, 976, 856, 772, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.43 (brs, 9 H), 1.86−2.02 (m, 2 H), 2.41−2.51 (m, 2 H), 3.26−3.40 (m, 1 H), 3.79 (S, 3 H), 3.94−4.18 (m, 1 H), 5.59 (brs, 1 H), 6.75−6.85 (m, 3 H), 7.27 (t, 1 H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$) δ 22.6 (t), 28.1 (q), 37.1 (t), 39.6 (t), 55.0 (q), 66.1 (d), 80.5 (s), 111.0 (d), 112.8 (d), 117.3 (d), 129.8 (d), 137.0 (d), 154.8 (s), 160.0 (s), 205.1 (s). Anal. Calcd for $C_{17}H_{23}NO_4$: C, 66.86; H, 7.59; N, 4.59. Found: C, 67.05; H, 7.63; N, 4.40.

1-MOC-2-(2-methoxyphenyl)piperidin-3-one (7d): colorless paste; R_f 0.41 (hexanes−ethyl acetate, 1:1); IR (neat) 1701, 1601, 1587, 1493, 961, 756, 731 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.00−2.13 (m, 2 H), 2.51−2.71 (m, 2 H), 3.35−3.48 (m, 1 H), 3.69 (s, 3 H), 3.78 (m, 3 H), 4.07−4.22 (m, 1 H), 5.60 (s, 1 H), 6.85−6.91 (m, 1 H), 6.91−6.99 (m, 1 H), 7.23−7.32 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 23.0 (t), 36.8 (t), 40.3 (t), 52.6 (q), 55.1 (q), 64.1 (d), 111.2 (d), 120.6 (d), 126.3 (s), 129.1 (d), 130.3 (d),155.8 (s), 156.2 (s), 205.4 (s). Anal. Calcd for $C_{14}H_{17}NO_4$: C, 63.87; H, 6.51; N, 5.32. Found: C, 63.65; H, 6.62; N, 5.06.

1-BOC-2-(2-methoxyphenyl)piperidin-3-one (8d): white solid; R_f 0.33 (hexanes−ethyl acetate, 2:1); mp 73−75 °C; IR (KBr) 1719, 1680, 1599, 1495, 961, 907, 858, 845, 845, 773, 752 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.40 (s, 9 H), 2.00−2.13 (m, 2 H), 2.52−2.65 (m, 2 H), 3.33−3.40 (m, 1 H), 3.78 (s, 3 H), 4.07−4.17 (m, 1 H), 5.61 (brs, 1 H), 6.88 (d, 1 H, J = 8.5 Hz), 6.92−6.96 (m, 1 H), 7.24−7.29 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.8 (t), 28.0 (q), 36.7 (t), 39.9 (t), 55.0 (d), 63.8 (d), 80.0 (s), 111.1 (d), 120.4 (d), 126.8 (s), 128.9 (d), 129.7 (d), 154.5 (s), 156.4 (s),

205.9 (s). Anal. Calcd for $C_{17}H_{23}NO_4$: C, 66.86; H, 7.59; N, 4.59. Found: C, 67.13; H, 7.60; N, 4.47.

1-MOC-2-(3,4-dimethoxyphenyl)piperidin-3-one (7e): colorless paste; R_f 0.17 (hexanes−ethyl acetate, 2:1); IR (neat) 1697, 1591, 1514, 962, 941, 858, 812, 768 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.90−2.04 (m, 2 H), 2.48 (t, 2 H, J = 6.8 Hz), 3.34−3.46 (m, 1 H), 3.75 (s, 3 H), 3.85 (s, 3 H), 3.87 (s, 3 H), 4.00−4.24 (m, 1 H), 5.66 (brs, 1 H), 6.69−6.77 (m, 2 H), 6.84 (d, 1 H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 22.6 (t), 37.0 (t), 40.4 (t), 52.9 (q), 55.7 (q), 65.3 (d), 108.6 (d), 111.2 (d), 117.0 (d), 127.1 (s), 148.3 (s), 149.1 (s), 156.0 (s), 204.6 (s). Anal. Calcd for $C_{15}H_{19}NO_5$: C, 61.42; H, 6.53; N, 4.78. Found: C, 61.30; H, 6.51; N, 4.62.

1-BOC-2-(3,4-dimethoxyphenyl)piperidin-3-one (8e): colorless paste; R_f 0.30 (hexanes−ethyl acetate, 2:1); IR (neat) 1720, 1693, 1591, 1516, 976, 916, 897, 858, 812, 766, 733 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.45 (s, 9 H), 1.87−2.02 (m, 2 H), 2.47 (t, 2 H, J = 6.5 Hz), 3.27−3.38 (m, 2 H), 3.85 (s, 3 H), 3.87 (s, 3 H), 4.01−4.15 (m, 1 H), 5.59 (brs, 1 H), 6.69−6.76 (m, 2 H), 6.82−6.86 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 22.3 (t), 27.8 (q), 36.7 (t), 39.6 (t), 55.3 (q), 55.4 (q), 65.4 (d), 80.0 (s), 108.3 (d), 110.9 (d), 116.9 (d), 127.5 (s), 148.1 (s), 148.9 (s), 154.5 (s), 205.0 (s). Anal. Calcd for $C_{18}H_{25}NO_5$: C, 64.46; H, 7.51; N, 4.18. Found: C, 64.57; H, 7.54; N, 4.05.

1-MOC-2-(4-fluorophenyl)piperidin-3-one (7f): colorless paste; R_f 0.41 (hexanes−ethyl acetate, 2:1); IR (neat) 1701, 1603, 1508, 961, 833, 770 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.84−2.10 (m, 2 H), 2.38−2.58 (m, 2 H), 3.29−3.43 (m, 1 H), 3.75 (s, 3 H), 3.98−4.25 (m, 1 H), 5.68 (brs, 1 H), 7.00−7.09 (m, 2 H), 7.16−7.25 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.5 (t), 37.1 (t), 40.5 (t), 53.1 (q), 65.2 (d), 115.7 (d, J_{CCF} = 21.7 Hz), 127.0 (d, J_{CCCF} = 8.3 Hz), 130.7 (s, J_{CCCCF} = 2.8 Hz), 156.1 (s), 162.1 (s, J_{CF} = 244.9 Hz), 204.4 (s). Anal. Calcd for $C_{13}H_{14}FNO_3$: C, 62.14; H, 5.62; N, 5.57. Found: C, 62.07; H, 5.58; N, 5.30.

1-BOC-2-(4-fluorophenyl)piperidin-3-one (8f): colorless paste; R_f 0.71 (hexanes−ethyl acetate, 2:1); IR (neat) 1724, 1697, 1603, 1508, 972, 901, 833, 769 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.43 (brs, 9 H), 1.84−2.08 (m, 2 H), 2.38−2.55 (m, 2 H), 3.24−3.40 (m, 1 H), 3.95−4.20 (m, 1 H), 5.48−5.78 (m, 1 H), 7.02−7.08 (m, 1 H), 7.16−7.22 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 22.3 (t), 27.9 (q), 37.0 (t), 39.9 (t), 65.2 (t), 80.5 (s), 115.5 (d, J_{CCF} = 21.0 Hz), 126.9 (d, J_{CCCF} = 7.6 Hz), 131.3 (s), 154.6 (s), 161.9 (s, J_{CF} = 245.1 Hz), 205.0 (s). Anal. Calcd for $C_{16}H_{20}FNO_3$: C, 65.51; H, 6.87; N, 4.78. Found: C, 65.40; H, 6.73; N, 4.63.

1-MOC-2-(4-cyanophenyl)piperidin-3-one (7g): colorless paste; R_f 0.41 (hexanes−ethyl acetate, 1:1); IR (neat) 2230, 1705, 1607, 1502, 959, 772, 733 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.83−2.13 (m, 2 H), 2.36−2.61 (m, 2 H), 3.32−3.46 (m, 1 H), 3.76 (s, 3 H), 4.02−4.25 (m, 1 H), 5.74 (brs, 1 H), 7.36−7.42 (m, 2 H), 7.63−7.69 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.0 (t), 37.2 (t), 40.8 (t), 53.1 (q), 60.1 (q), 65.5 (d), 111.5 (s), 118.0 (s), 126.1 (d), 132.4 (d), 140.6 (s), 155.8 (s), 203.3 (s). Anal. Calcd for $C_{14}H_{14}N_2O_3$: C, 65.11; H, 5.46; N, 10.85. Found: C, 65.22; H, 5.50; N, 10.68.

1-BOC-2-(4-cyanophenyl)piperidin-3-one (8g): colorless paste; R_f 0.43 (hexanes−ethyl acetate, 2:1); IR (neat) 3373, 2230, 1682, 1607, 1502, 972, 905, 878, 853, 767, 733 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.42 (brs, 9 H), 1.83−1.95 (m, 1 H), 1.97−2.08 (m, 1 H), 2.37−2.45 (m, 1 H), 2.49−2.57 (m, 1 H), 3.29−3.40 (m, 1 H), 3.96−4.19 (m, 1 H), 5.66 (brs, 1 H), 7.36−7.39 (m, 2 H), 7.64−7.68 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.0 (t), 28.1 (q), 37.3 (t), 40.4 (t), 65.7 (d), 81.1 (s), 111.5 (s), 118.3 (s), 126.2 (d), 132.5 (d), 141.4 (s), 154.6 (s), 204.2 (s). Anal. Calcd for $C_{17}H_{20}N_2O_3$: C, 67.98; H, 6.71; N, 9.33. Found: C, 68.11; H, 6.82; N, 9.12.

1-MOC-2-(1-naphthyl)piperidin-3-one (7h): white solid; R_f 0.21 (hexanes−ethyl acetate = 5:1); IR (KBr) 1726, 1686, 1595, 1508, 978, 945, 800, 781 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.07−2.26 (m, 2 H), 2.47−2.70 (m, 2 H), 3.68 (s, 3 H), 3.57−3.78 (m, 1 H), 4.04−4.23 (m, 1 H), 6.39 (brs, 1 H), 7.38−7.65 (m, 4 H), 7.77−7.89 (m, 2 H), 8.36 (d, 1 H, J = 8.6 Hz); ^{13}C NMR ($CDCl_3$) δ 22.4 (t), 37.3 (t), 41.5 (t), 53.2 (q), 64.5 (d), 123.7 (d), 124.5 (d), 124.7 (d), 125.9 (d), 126.5 (d), 128.5 (d), 128.9 (d), 131.3 (s), 133.4 (s), 134.0 (s), 156.1 (s), 205.1 (s). Anal. Calcd for $C_{17}H_{17}NO_3$: C, 72.07; H, 6.05; N, 4.94. Found: C, 72.12; H, 6.04; N, 4.77.

1-MOC-2-(2-naphthyl)piperidin-3-one (7i): colorless paste; R_f 0.3 (hexanes−ethyl acetate = 5:1); IR (neat) 1701, 1632, 1599, 1508, 953, 820, 754, 733 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.88−2.11 (m, 2 H), 2.41−2.60 (m, 2 H), 3.41−3.52 (m, 1 H), 3.77 (brs, 3 H), 4.00−4.33 (m, 1 H), 5.86 (brs, 1 H), 7.37 (dd, 1 H, J = 1.6, 8.4 Hz), 7.44−7.53 (m, 2 H), 7.63 (s, 1 H), 7.77−7.87 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 22.7 (t), 37.2 (t), 40.6 (t), 53.0 (q), 66.0 (d), 123.0 (d), 124.0 (d), 126.0 (d), 126.2 (d), 127.3 (d), 127.7 (d), 128.7 (d), 132.3 (s), 132.5 (s), 133.0 (s), 156.1 (s), 204.5 (s). Anal. Calcd for $C_{17}H_{17}NO_3$: C, 72.07; H, 6.05; N, 4.94. Found: C, 72.18; H, 6.09; N, 4.73.

1-BOC-2-(2-naphthyl)piperidin-3-one (8i): colorless paste; R_f 0.56 (hexanes−ethyl acetate, 2:1); IR (neat) 1682, 1634, 1601, 1508, 976, 955, 910, 857, 822, 754, 737 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.43 (brs, 9 H), 1.89−2.04 (m, 2 H), 2.43−2.56 (m, 2 H), 3.36−3.45 (m, 1 H), 4.00−4.25 (m, 1 H), 5.79 (brs, 1 H), 7.34−7.39 (m, 1 H), 7.46−7.52 (m, 2 H), 7.62 (s, 1 H), 7.78−7.87 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 22.8 (t), 28.1 (q), 37.3 (t), 40.0 (t), 66.4 (d), 80.7 (s), 123.2 (d), 124.1 (d), 126.1 (d), 126.3 (d), 127.5 (d), 127.8 (d), 128.7 (d), 132.6 (s), 133.0 (s), 133.2 (s), 154.9 (s), 205.3 (s). Anal. Calcd for $C_{20}H_{23}NO_3$: C, 73.82; H, 7.12; N, 4.30. Found: C, 73.96; H, 7.24; N, 4.05.

1-MOC-2-(2-furyl)piperidin-3-one (7j): pale yellow paste; R_f 0.35 (hexanes−ethyl acetate = 5:1); IR (neat) 1705, 1501, 961, 937, 922, 885, 766, 746 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.93−2.18 (m, 2 H), 2.51−2.74 (m, 2 H), 3.32−3.50 (m, 1 H), 3.74 (s, 3 H), 3.96−4.24 (m, 1 H), 5.52−5.82 (m, 1 H), 6.27 (s, 1 H), 6.35 (dd, 1 H, J = 1.9, 3.2 Hz), 7.37 (dd, 1 H, J = 0.8, 1.9 Hz); ^{13}C NMR ($CDCl_3$) δ 22.8 (t), 37.6 (t), 40.3 (t), 53.1 (q), 60.9 (d), 108.4 (d), 110.5 (d), 142.7 (d), 149.2 (s), 155.7 (s), 202.5 (s). Anal. Calcd for $C_{11}H_{13}NO_4$: C, 59.19; H, 5.87; N, 6.27. Found: C, 59.28; H, 5.96; N, 6.02.

Reduction of Ketones 3, 4, 7, and 8 with $NaBH_4$. To a solution of a ketone (1.0 mmol) in methanol (5 mL) was added $NaBH_4$ (38 mg, 1.0 mmol) at 5 °C. After being stirred for 30 min at this temperature, the solvent was removed in vacuo. The residue was column chromatographed on silica gel (hexanes−ethyl acetate) to give the corresponding *cis*-alcohol.

1-MOC-*cis*-2-phenylpyrrolidin-3-ol (13a): white solid; R_f 0.10 (hexanes−ethyl acetate, 2:1); mp 134−136 °C; IR (KBr) 3368, 1670, 1555, 1495, 1464, 779, 756, 700, 660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.16 (brs, 1 H), 1.83−2.00 (m, 1 H), 2.08−2.16 (m, 1 H), 3.51 (s, 1.5 H), 3.62−3.80 (m, 3.5 H), 4.39−4.48 (m, 1 H), 4.91 (brs, 0.5 H), 4.96 (brs, 0.5 H), 7.16−7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 30.8 (t), 31.8 (t), 44.6 (t), 52.3 (q), 52.3 (q), 64.2 (d), 65.1 (d), 72.1 (d), 72.7 (d), 126.9 (d), 127.5 (d), 128.3 (d), 136.9 (s), 137.4 (s), 155.5 (s), 155.9 (s). Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 65.18; H, 6.80; N, 6.29.

1-MOC-*cis*-2-(4-methoxyphenyl)pyrrolidin-3-ol (13b): colorless paste; R_f 0.31 (hexanes−ethyl acetate, 1:2); IR (neat) 3437, 1684, 1600, 1589, 1491, 773, 756 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.17 (brs, 1 H), 1.81−2.00 (m, 1 H), 2.07−2.15 (m, 1 H), 3.53 (s, 1.5 H), 3.62−3.76 (m, 3.5 H), 3.80 (s, 3 H), 4.36−4.43 (m, 1 H), 4.86 (brs, 0.5 H), 4.91 (brs, 0.5 H), 6.89−6.93 (m, 2 H), 7.06−7.20 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 30.7 (t), 31.7 (t), 44.5 (t), 52.3 (q), 55.1 (q), 63.6 (d), 64.6 (d), 72.1 (d), 72.6 (d), 113.8 (d), 113.9 (d), 128.0 (d), 128.7 (s), 129.2 (s), 155.4 (s), 155.9 (s), 159.0 (s). Anal. Calcd for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57. Found: C, 62.21; H, 6.85; N, 5.50.

1-BOC-*cis*-2-(4-methoxyphenyl)pyrrolidin-3-ol (14b): white solid; R_f 0.29 (hexanes−ethyl acetate, 1:1); mp 85−87 °C; IR (KBr) 3423, 1668, 1611, 1587, 1514, 1479, 862, 808, 766 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.16 (brs, 6.3 H), 1.44 (brs, 2.7 H), 1.86−1.97 (m, 1 H), 2.05−2.13 (m, 1 H), 3.56−3.76 (m, 2 H), 3.81 (s, 3 H), 4.35−4.40 (m, 1 H), 4.78 (brs, 0.7 H), 4.89 (brs, 0.3 H), 6.88−6.92 (m, 2 H), 7.10−7.15 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 27.9 (q), 28.2 (q), 31.1 (t), 31.4 (t), 44.1 (t), 44.5 (t),

55.0 (q), 63.8 (d), 64.7 (d), 72.0 (d), 72.7 (d), 79.1 (s) 113.4 (d), 113.7 (d), 127.9 (d), 128.1 (d), 130.2 (s), 154.5 (s), 158.7 (s). Anal. Calcd for $C_{16}H_{23}NO_4$: C, 65.51; H, 7.90; N, 4.77. Found: C, 65.45; H, 7.88; N, 4.63.

1-MOC-*cis*-2-(3-methoxyphenyl)pyrrolidin-3-ol (13c): white solid; R_f 0.16 (hexanes−ethyl acetate, 1:1); mp 125−127 °C; IR (KBr) 3396, 1674, 1612, 1585, 1487, 972, 862, 789, 775, 758, 704 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.08−1.21 (m, 1 H), 1.83−2.02 (m, 1 H), 2.07−2.16 (m, 1 H), 3.54 (brs, 1.5 H), 3.62−3.78 (m, 3.5 H), 3.81 (s, 3 H), 4.40−4.47 (m, 1 H), 4.84−4.97 (m, 1 H), 6.70−6.87 (m, 3 H), 7.30 (t, 1 H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 30.9 (t), 31.9 (t), 44.7 (t), 52.4 (q), 55.1 (q), 64.3 (d), 65.1 (d), 72.2 (d), 72.8 (d), 112.7 (d), 113.0 (d), 119.2 (d), 129.5 (d), 129.6 (d), 138.5 (s), 139.1 (s), 155.5 (s), 155.9 (s), 159.7 (s). Anal. Calcd for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57. Found: C, 62.30; H, 6.90; N, 5.38.

1-BOC-*cis*-2-(3-methoxyphenyl)pyrrolidin-3-ol (14c): colorless paste; R_f 0.16 (hexanes−ethyl acetate, 2:1); IR (neat) 3425, 1674, 1603, 1587, 783, 758, 740, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.16 (brs, 6 H), 1.44 (brs, 3 H), 1.86−1.97 (m, 1 H), 2.03−2.12 (m, 1 H), 3.55−3.76 (m, 2 H), 3.79 (s, 3 H), 4.36−4.42 (m, 1 H), 4.78 (brs, 0.67 H), 4.89 (brs, 0.33 H), 6.74 (brs, 1 H), 6.76−6.84 (m, 2 H), 7.23−7.29 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 27.9 (q), 28.3 (q), 31.4 (t), 31.7 (t), 44.3 (t), 44.7 (t), 55.1 (q), 64.4 (d), 65.5 (d), 72.2 (d), 73.0 (d), 79.3 (s), 112.7 (d), 112.7 (d), 119.4 (d), 119.1 (d), 129.2 (d), 129.4 (d), 140.0 (s), 154.5 (s), 159.5 (s). Anal. Calcd for $C_{16}H_{23}NO_4$: C, 65.51; H, 7.90; N, 4.77. Found: C, 65.35; H, 7.81; N, 4.56.

1-MOC-*cis*-2-(2-methoxyphenyl)pyrrolidin-3-ol (13d): colorless paste; R_f 0.22 (hexanes−ethyl acetate, 1:1); IR (neat) 3423, 1678, 1610, 1585, 1512, 829, 810, 773 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.84−1.98 (m, 1 H), 1.99 (brs, 1 H), 2.04−2.13 (m, 1 H), 3.53 (s, 1.5 H), 3.63−3.77 (m, 3.5 H), 3.87 (s, 3 H), 4.56 (brs, 1 H), 5.31 (brs, 0.5 H), 5.38 (brs, 0.5 H), 6.91 (d, 1 H, J = 7.8 Hz), 6.97 (t, 1 H, J = 7.8 Hz), 7.09 (d, 1 H, J = 7.4 Hz), 7.22−7.30 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 30.5 (t), 31.3 (t), 44.4 (t), 44.5 (t), 52.2 (q), 55.3 (q), 59.8 (d), 60.3 (d), 71.4 (d), 72.1 (d), 110.1 (d), 110.3 (d), 120.7 (d), 125.2 (s), 125.9 (s), 126.9 (d), 128.3 (d), 155.3 (s), 155.8 (s), 156.2 (s), 156.4 (s). Anal. Calcd for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57. Found: C, 62.28; H, 6.91; N, 5.38.

1-BOC-*cis*-2-(2-methoxyphenyl)pyrrolidin-3-ol (14d): colorless paste; R_f 0.33 (hexanes−ethyl acetate, 1:1); IR (neat) 3439, 1693, 1603, 1589, 1493, 1479, 903, 754, 733 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.15 (brs, 5.8 H), 1.45 (brs, 3.2 H), 1.85−2.12 (m, 2 H), 3.56−3.74 (m, 2 H), 3.85 (s, 3 H), 4.50−4.58 (m, 1 H), 5.25 (brs, 0.65 H), 5.36 (brs, 0.35 H), 6.90 (d, 1 H, J = 8.5 Hz), 6.97 (t, 1 H, J = 7.0 Hz), 7.05−7.18 (m, 1 H), 7.22−7.31 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 27.7 (q), 28.1 (q), 31.1 (t), 31.2 (t), 44.0 (t), 44.4 (t), 55.3 (q), 59.5 (d), 60.0 (d), 71.3 (d), 71.9 (d), 78.7 (s), 79.0 (s), 110.0 (d), 120.2 (d), 120.5 (d), 125.5 (s), 126.6 (s), 126.7 (d), 127.5 (d), 127.9 (d), 128.0(d), 154.0 (s), 154.2 (s), 156.4 (s). Anal. Calcd for $C_{16}H_{23}NO_4$: C, 65.51; H, 7.90; N, 4.77. Found: C, 65.63; H, 7.97; N, 4.53.

1-MOC-*cis*-2-(3,4-dimethoxyphenyl)pyrrolidin-3-ol (13e): white solid; R_f 0.13 (hexanes−ethyl acetate, 1:1); mp 144−145 °C; IR (KBr) 3452, 1674, 1609, 1593, 1512, 966, 791, 773, 756 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.05−1.20 (m, 1 H), 1.81−2.03 (m, 1 H), 2.08−2.16 (m, 1 H), 3.55 (s, 1.5 H), 3.63−3.79 (m, 3.5 H), 3.89 (s, 6 H), 4.37−4.45 (m, 1 H), 4.81−4.96 (m, 1 H), 6.67−6.84 (m, 2 H), 6.88 (d, 1 H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 30.7 (t), 31.7 (t), 44.5 (t), 52.3 (q), 55.7 (q), 63.9 (d), 64.8 (d), 72.0 (d), 72.6 (d), 110.0 (d), 110.3 (d), 110.9 (d), 111.1 (d), 118.8 (d), 129.2 (s), 129.7 (s), 148.3 (s), 148.7 (s), 155.4 (s), 155.9 (s). Anal. Calcd for $C_{14}H_{19}NO_5$: C, 59.78; H, 6.81; N, 4.98. Found: C, 59.85; H, 6.88; N, 4.74.

1-BOC-*cis*-2-(3,4-dimethoxyphenyl)pyrrolidin-3-ol (14e): colorless paste; R_f 0.18 (hexanes−ethyl acetate, 1:1); IR (neat) 3435, 1693, 1609, 1595, 1518, 800, 760, 733 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.17 (brs, 6 H), 1.45 (brs, 3 H), 1.89−1.98 (m, 1 H), 2.04−2.13 (m, 1 H), 3.57−3.79 (m, 2 H), 3.87 (s, 3 H), 3.89 (brs, 3 H), 4.35−4.41 (m, 1 H), 4.78 (brs, 0.67 H), 4.88 (brs, 0.33 H), 6.71−6.79 (m, 2 H), 6.87 (d, 1 H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 27.8 (q), 28.2 (q), 31.2 (t), 31.5 (t), 44.2 (t), 44.6 (t), 55.6 (q), 64.2 (d), 65.0 (d), 72.0 (d), 72.8 (d), 79.1 (s), 110.1 (d), 110.67 (d), 111.1 (d), 118.7 (d), 119.1 (d), 129.5 (s), 130.7 (s), 148.0 (s), 148.6 (s), 154.5 (s). Anal. Calcd for $C_{17}H_{25}NO_5$: C, 63.14; H, 7.79; N, 4.33. Found: C, 63.25; H, 7.86; N, 4.14.

1-MOC-*cis*-2-(4-fluorophenyl)pyrrolidin-3-ol (13f): white solid; R_f 0.22 (hexanes−ethyl acetate, 1:1); mp 151−152 °C; IR (KBr) 3368, 1670, 1605, 1508, 837, 820, 772, 658 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.30 (brs, 1 H), 1.80−1.99 (m, 1 H), 2.07−2.16 (m, 1 H), 3.52 (s, 1.5 H), 3.60−3.78 (m, 3.5 H), 4.37−4.66 (m, 1 H), 4.83−4.97 (m, 1 H), 7.03−7.08 (m, 2 H), 7.11−7.23 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 30.6 (t), 31.5 (t), 44.5 (t), 52.32 (q), 52.34 (q), 63.6 (d), 64.4 (d), 71.9 (d), 72.5 (d), 115.0 (d, J_{CCF} = 20.0 Hz), 128.5 (d, J_{CCCF} = 6.7 Hz), 132.9 (s), 133.4 (s), 155.5 (s), 155.8 (s), 162.0 (s, J_{CF} = 244.2 Hz). Anal. Calcd for $C_{12}H_{14}FNO_3$: C, 62.24; H, 5.90; N, 5.85. Found: C, 60.29; H, 5.91; N, 5.77.

1-BOC-*cis*-2-(4-fluorophenyl)pyrrolidin-3-ol (14f): white solid; R_f 0.42 (hexanes−ethyl acetate, 1:1); mp 155−157 °C; IR (KBr) 3354, 1655, 1605, 1508, 862, 822, 773, 754 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.15 (s, 6 H), 1.44 (s, 3 H), 1.59 (brs, 1 H), 1.84−2.00 (m, 1 H), 2.06−2.15 (m, 1 H), 3.58−3.78 (m, 2 H), 4.38−4.45 (m, 1 H), 4.75−4.98 (m, 1 H), 7.03−7.09 (m, 2 H), 7.16−7.22 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 27.9 (q), 28.2 (q), 31.2 (t), 44.2 (t), 44.6 (t), 63.7 (d), 64.7 (d), 72.0 (d), 72.8 (d), 79.4 (s), 114.8 (d, J_{CCF} = 21.0 Hz), 128.6 (d), 133.2 (s), 134.3 (s), 154.4 (s), 162.0 (s, J_{CF} = 244.2 Hz). Anal. Calcd for $C_{15}H_{20}FNO_3$: C, 64.04; H, 7.17; N, 4.98. Found: C, 64.05; H, 7.22; N, 4.92.

1-MOC-*cis*-2-(4-cyanophenyl)pyrrolidin-3-ol (13g): white solid; R_f 0.39 (hexanes−ethyl acetate, 1:1); mp 134−135 °C; IR (KBr) 3468, 2237, 1703, 1605, 1499, 833, 777 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.43 (d, 1 H, J = 5.5 Hz), 1.82−2.03 (m, 1 H), 2.11−2.19 (m, 1 H), 3.51 (s, 1.5 H), 3.62−3.80 (m, 3.5 H), 4.46−4.56 (m, 1 H), 4.88−4.99 (m, 1 H), 7.28−7,39 (m, 2 H), 7.63−7.67 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 30.9 (t), 31.8 (t), 44.6 (t), 52.5 (q), 64.2 (d), 64.9 (d), 72.0 (d), 72.6 (d), 110.6 (s), 118.5 (s), 127.8 (d), 128.0 (d), 131.7 (d), 143.6 (s), 144.0 (s), 155.5 (s). Anal. Calcd for $C_{13}H_{14}N_2O_3$: C, 63.40; H, 5.73; N, 11.38. Found: C, 63.44; H, 5.73; N, 11.30.

1-BOC-*cis*-2-(4-cyanophenyl)pyrrolidin-3-ol (14g): colorless paste; R_f 0.20 (hexanes−ethyl acetate, 1:1); IR (neat) 3489, 2237, 2224, 1672, 1607, 1502, 1477, 837, 737, 725 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.13 (brs, 6 H), 1.43 (brs, 3 H), 1.74 (brs, 1 H), 1.85−1.98 (m, 1 H), 2.08−2.17 (m, 1 H), 3.60−3.77 (m, 2 H), 4.44−4.52 (m, 1 H), 4.83 (brs, 0.67 H), 4.92 (brs, 0.33 H), 7.34 (d, 2 H, J = 8.2 Hz), 7.63 (d, 2 H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$) δ 27.9 (q), 28.2 (q), 31.7 (t), 44.4 (t), 44.7 (t), 64.4 (d), 65.4 (d), 72.1 (d), 72.9 (d), 79.9 (s), 110.6 (s), 118.6 (s), 126.3 (d), 128.0 (d), 131.6 (d), 132.1 (d), 144.0 (s), 145.0 (s), 154.3 (s). Anal. Calcd for $C_{16}H_{20}N_2O_3$: C, 66.65; H, 6.69; N, 9.72. Found: C, 66.71; H, 7.00; N, 9.68.

1-MOC-*cis*-2-(2-naphthyl)pyrrolidin-3-ol (13i): colorless paste; R_f 0.48 (hexanes−ethyl acetate, 1:1); IR (neat) 3418, 1682, 1634, 1601, 1508, 820, 773, 729 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.18 (brs, 1 H), 1.87−2.06 (m, 1 H), 2.09−2.18 (m, 1 H), 3.48 (s, 1.5 H), 3.61−3.89 (m, 3.5 H), 4.45−4.54 (m, 1 H), 5.01−5.16 (m, 1 H), 7.28−7.38 (m, 1 H), 7.42−7.54 (m, 2 H), 7.61−7.71 (m, 1 H), 7.77−7.88 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 30.5 (t), 31.5 (t), 44.5 (t), 52.2 (q), 64.1 (d), 65.1 (d), 72.1 (d), 72.6 (d), 125.2 (d), 125.4 (d), 125.6 (d), 126.0 (d), 127.4 (d), 127.6 (d), 127.7 (d), 132.6 (s), 132.7 (s), 133.0 (s), 134.7 (s), 135.3 (s), 155.4 (s), 155.8 (s), 171.0 (s). Anal. Calcd for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32; N, 5.16. Found: C, 70.96; H, 6.34; N, 5.01.

1-BOC-*cis*-2-(2-naphthyl)pyrrolidin-3-ol (14i): colorless paste; R_f 0.39 (hexanes−ethyl acetate, 1:1); IR (neat) 3441, 1668, 1601, 1510, 1477, 864, 822, 772, 750, 735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.08 (brs, 6 H), 1.45 (brs, 3 H), 1.94−2.02 (m, 1 H), 2.09−2.18 (m, 1 H), 3.63−3.87 (m, 2 H), 4.46−4.52 (m, 1 H), 5.00 (brs, 0.67 H), 5.10 (brs, 0.33 H), 7.32−7.36 (m, 1 H), 7.42−

7.52 (m, 2 H), 7.66 (brs, 1 H), 7.79−7.87 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 27.9 (q), 28.3 (q), 31.3 (t), 31.7 (t), 44.3 (t), 44.8 (t), 64.7 (d), 65.4 (d), 72.3 (d), 73.0 (d), 79.3 (s), 125.1 (d), 125.4 (d), 125.6 (d), 125.7 (d), 126.0(d), 127.5 (d), 127.6 (d), 132.7 (s),133.0 (s), 135.1 (s), 136.0 (s), 154.5 (s). Anal. Calcd for $C_{19}H_{23}NO_3$: C, 72.82; H, 7.40; N, 4.47. Found: C, 72.88; H, 7.43; N, 4.39.

1-MOC-*cis*-2-phenylpiperidin-3-ol (15a): White solid; R_f 0.46 (hexanes−ethyl acetate, 2:1); mp 72−75 °C; IR (KBr) 3470, 1678, 1603, 1582, 1499, 957, 858, 818, 788, 766, 735, 706 cm^{-1};. ^{1}H NMR ($CDCl_3$) δ 1.63−1.74 (m, 2 H), 1.75−1.89 (m, 3 H), 3.04 (dt, 1 H, J = 4.2, 13.1 Hz), 3.69 (s, 3 H), 4.01−4.13 (m, 2 H), 5.43 (d, 1 H, J = 5.5 Hz), 7.25−7.30 (m, 1 H), 7.32−7.37 (m, 2 H), 7.46−7.51 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 23.6 (t), 27.4 (t), 39.3 (t), 52.7 (q), 58.4 (d), 70.0 (d), 126.8 (d), 128.1 (d), 128.4 (d), 137.5 (s), 156.5 (s). Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.39; H, 7.30; N, 5.85.

1-MOC-*cis*-2-(4-methoxyphenyl)piperidin-3-ol (15b): colorless paste; R_f 0.13 (hexanes−ethyl acetate, 2:1); IR (neat) 3431, 1678, 1611, 1582, 1512, 962, 862, 833, 770, 735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.61−1.72 (m, 2 H), 1.74−1.90 (m, 3 H), 3.01 (dt, 1 H, J = 3.7, 13.3 Hz), 3.69 (s, 3 H), 3.80 (s, 3 H), 3.99−4.09 (m, 2 H), 5.39 (d, 1 H, J = 6.0 Hz), 6.86−6.89 (m, 2 H), 7.40−7.43 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 23.7 (t), 27.5 (t), 39.2 (t), 52.7 (q), 55.0 (q), 57.9 (d), 70.1 (d), 113.5 (d), 129.4 (s), 129.6 (d), 156.5 (s), 158.4 (s). Anal. Calcd for $C_{14}H_{19}NO_4$: C, 63.38; H, 7.22; N, 5.28. Found: C, 63.45; H, 7.26; N, 5.06.

1-BOC-*cis*-2-(4-methoxyphenyl)piperidin-3-ol (16b): colorless paste; R_f 0.33 (hexanes−ethyl acetate, 2:1); IR (neat) 3427, 1666, 1611, 1581, 1512, 964, 881, 827, 802, 764, 735, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.39 (s, 9 H), 1.61−1.88 (m, 4 H), 3.00 (dt, 1 H, J = 3.5, 13.0 Hz), 3.81 (s, 3 H), 3.99 (dt, 1 H, J = 6.0, 13.5 Hz), 4.01−4.08 (m, 1 H), 5.30 (d, 1H, J = 6.0 Hz), 6.85−6.89 (m, 2 H), 7.36−7.40 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 23.5 (t), 27.5 (t), 28.1 (q), 39.0 (t), 54.9 (q), 57.9 (d), 70.0 (d), 79.6 (s), 113.3 (d), 129.5 (d), 130.0 (s), 155.2 (s), 158.2 (s). Anal. Calcd for $C_{17}H_{25}NO_4$: C, 66.43; H, 8.20; N, 4.56. Found: C, 66.63; H, 8.34; N, 4.29.

1-MOC-*cis*-2-(3-methoxyphenyl)piperidin-3-ol (15c): colorless paste; R_f 0.10 (hexanes−ethyl acetate, 2:1); IR (neat) 3431, 1678, 1600, 1583, 1491, 970, 789, 770, 735, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.62−1.88 (m, 5 H), 3.07 (dt, 1 H, J = 4.2, 13.3 Hz), 3.69 (s, 3 H), 3.80 (s, 3 H), 4.01−4.11 (m, 2 H), 5.38 (d, 1 H, J = 5.5 Hz), 6.80−6.84 (m, 1 H), 7.04−7.07 (m, 2 H), 7.24−7.29 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.4 (t), 27.5 (t), 39.5 (t), 52.7 (q), 55.0 (q), 58.6 (d), 70.0 (d), 112.0 (d), 114.6 (d), 120.6 (d), 129.2 (d), 139.2 (s), 156.5 (s), 159.4 (s). Anal. Calcd for $C_{14}H_{19}NO_4$: C, 63.38; H, 7.22; N, 5.28. Found: C, 63.27; H, 7.20; N, 5.11.

1-BOC-*cis*-2-(3-methoxyphenyl)piperidin-3-ol (16c): colorless paste; R_f 0.30 (hexanes−ethyl acetate, 2:1); IR (neat) 3435, 1666, 1601, 1583, 970, 868, 787, 754, 731, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.38 (s, 9 H), 1.63−1.73 (m, 1 H), 1.75−1.86 (m, 3 H), 3.04 (dt, 1 H, J = 4.2, 12.8 Hz), 4.05−4.11 (m, 1 H), 5.29 (d, 1 H, J = 5.5 Hz), 6.80−6.83 (m, 1 H), 7.01−7.05 (m, 2 H), 7.26 (t, 1 H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$) δ 23.3 (t), 27.5 (t), 28.2 (q), 39.2 (t), 54.9 (q), 59.0 (d), 70.0 (d), 79.8 (s), 112.0 (d), 114.2 (d), 120.5 (d), 129.0 (d), 139.9 (s), 155.2 (s), 159.3 (s). Anal. Calcd for $C_{17}H_{25}NO_4$: C, 66.43; H, 8.20; N, 4.56. Found: C, 66.55; H, 8.31; N, 4.38.

1-MOC-*cis*-2-(2-methoxyphenyl)piperidin-3-ol (15d): white solid; R_f 0.13 (hexanes−ethyl acetate, 2:1); mp 144−146 °C; IR (KBr) 3456, 1672, 1599, 1493, 955, 903, 847, 775, 660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.70−1.87 (m, 4 H), 2.41 (brs, 1 H), 3.38−3.47 (m, 1 H), 3.61 (s, 3 H), 3.87 (s, 3 H), 4.15−4.24 (m, 2 H), 5.66 (d, 1 H, J = 6.0 Hz), 6.91 (d, 1 H, J = 7.8 Hz), 6.94−6.99 (m, 1 H), 7.23−7.29 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.2 (t), 25.5 (t), 40.3 (t), 52.5 (q), 54.7 (d), 55.5 (q), 68.2 (d), 110.7 (d), 120.7 (d), 127.2 (s), 127.5 (d), 128.2 (d), 156.4 (s), 156.7 (s). Anal. Calcd for $C_{14}H_{19}NO_4$: C, 63.38; H, 7.22; N, 5.28. Found: C, 63.39; H, 7.24; N, 5.20.

1-BOC-*cis*-2-(2-methoxyphenyl)piperidin-3-ol (16d): colorless paste; R_f 0.26 (hexanes−ethyl acetate, 2:1); IR (neat) 3450, 1682, 1601, 1589, 1461, 962, 878, 754, 731 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 9 H), 1.64−1.89 (m, 4 H), 3.35−3.42 (m, 1 H), 3.86 (s, 3 H), 4.08−4.14 (m, 1 H), 4.15−4.20 (m, 1 H), 5.60 (d, 1 H, J = 6.0 Hz), 6.90 (d, 1 H, J = 8.5 Hz), 6.95 (t, 1 H, J = 8.0 Hz), 7.22−7.28 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.1 (t), 25.5 (t), 27.9 (q), 40.1 (t), 54.4 (d), 55.3 (q), 68.2 (d), 79.1 (s), 110.2 (d), 120.6 (d), 127.4 (d), 127.9 (d), 128.3 (s), 155.2 (s), 156.6 (s). Anal. Calcd for $C_{17}H_{25}NO_4$: C, 66.43; H, 8.20; N, 4.56. Found: C, 66.48; H, 8.30; N, 4.35.

1-MOC-*cis*-2-(3,4-dimethoxyphenyl)piperidin-3-ol (15e): colorless paste; R_f 0.16 (hexanes−ethyl acetate, 2:1); IR (neat) 3435, 1674, 1607, 1589, 1522, 974, 926, 885, 858, 812, 768, 733, 704 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.60−1.90 (m, 4 H), 1.99 (brs, 1 H), 3.00 (dt, 1 H, J = 1.3, 13.3 Hz), 3.70 (s, 3 H), 3.86 (s, 3 H), 3.87 (s, 3 H), 3.98−4.09 (m, 1 H), 5.39 (d, 1 H, J = 5.5 Hz), 6.83 (d, 1 H, J = 8.7 Hz), 7.03 (dd, 1 H, J = 1.9, 8.7 Hz), 7.06 (d, 1 H, J = 1.9 Hz); ^{13}C NMR ($CDCl_3$) δ 23.5 (t), 27.6 (t), 39.4 (t), 52.8 (q), 55.7 (q), 55.8 (q), 58.3 (d), 70.1 (d), 110.8 (d), 112.0 (d), 120.5 (d), 129.9 (s), 148.0 (s), 148.6 (s), 156.5 (s). Anal. Calcd for $C_{15}H_{21}NO_5$: C, 61.00; H, 7.17; N, 4.74. Found: C, 60.88; H, 7.20; N, 4.50.

1-BOC-*cis*-2-(3,4-dimethoxyphenyl)piperidin-3-ol (16e): colorless paste; R_f 0.26 (hexanes−ethyl acetate, 2:1); IR (neat) 3435, 1670, 1609, 1591, 1516, 972, 876, 812, 766, 733 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.40 (s, 9 H), 1.62−1.72 (m, 1 H), 1.75−1.88 (m, 3 H), 2.99 (dt, 1 H, J = 4.0, 13.0 Hz), 3.87 (s, 3 H), 3.88 (s, 3 H), 3.96−4.02 (m, 1 H), 4.03−4.10 (m, 1 H), 5.30 (d, 1 H, J = 5.5 Hz), 6.83 (d, 1 H, J = 9.0 Hz), 6.98−7.04 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 23.5 (t), 27.3 (t), 28.0 (q), 38.9 (t), 55.3 (q), 57.6 (d), 70.0 (d), 79.5 (s), 110.4 (d), 111.7 (d), 120.2 (d), 130.4 (s), 147.4 (s), 148.1 (s), 155.0 (s). Anal. Calcd for $C_{18}H_{27}NO_5$: C, 64.07; H, 8.07; N, 4.15. Found: C, 64.21; H, 8.20; N, 3.98.

1-MOC-*cis*-2-(4-fluorophenyl)piperidin-3-ol (15f): colorless paste; R_f 0.20 (hexanes−ethyl acetate, 2:1); IR (neat) 3431, 1678, 1605, 1508, 962, 864, 837, 772 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.60−1.94 (m, 4 H), 2.90−2.97 (m, 1 H), 3.70 (s, 3 H), 3.97−4.05 (m, 1 H), 4.06−4.12 (m, 1 H), 5.44 (d, 1 H, J = 6.0 Hz), 6.99−7.05 (m, 2 H), 7.46−7.51 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 23.7 (t), 27.4 (t), 39.2 (t), 52.8 (q), 57.7 (d), 70.1 (d), 114.8 (d, J_{CCF} = 21.0 Hz), 130.1 (d, J_{CCCF} = 7.6 Hz), 133.2 (s, J_{CCCCF} = 3.8 Hz), 156.5 (s), 161.6 (s, J_{CF} = 244.2 Hz). Anal. Calcd for $C_{13}H_{16}FNO_3$: C, 61.65; H, 6.37; N, 5.53. Found: C, 61.70; H, 6.39; N, 5.48.

1-BOC-*cis*-2-(4-fluorophenyl)piperidin-3-ol (16f): colorless paste; R_f 0.50 (hexanes−ethyl acetate, 2:1); IR (neat) 3431, 1666, 1605, 1508, 966, 881, 864, 833, 814, 764, 733 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.39 (S, 9 H), 1.60−1.88 (m, 4 H), 2.90−2.98 (m, 1 H), 3.95−4.01 (m, 1 H), 4.05−4.11 (m, 1 H), 5.34 (d, 1 H, J = 5.5 Hz), 6.99−7.05 (m, 2 H), 7.42−7.47 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 23.6 (t), 27.4 (t), 28.2 (q), 39.2 (t), 57.8 (d), 70.1 (d), 80.0 (s), 114.8 (d, J_{CCF} = 21.0 Hz), 130.0 (d, J_{CCCF} = 7.6 Hz), 133.9 (s, J_{CCCCF} = 2.9 Hz), 155.3 (s), 161.5 (s, J_{CF} = 244.2 Hz). Anal. Calcd for $C_{16}H_{22}FNO_3$: C, 65.07; H, 7.51; N, 4.74. Found: C, 65.24; H, 7.46; N, 4.51.

1-MOC-*cis*-2-(4-cyanophenyl)piperidin-3-ol (15g): colorless paste; R_f 0.20 (hexanes−ethyl acetate, 2:1); IR (neat) 3443, 2230, 1686, 1609, 1504, 959, 868, 841, 772, 737, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.61−1.92 (m, 4 H), 2.25 (brs, 1 H), 2.80−2.88 (m, 1 H), 3.72 (s, 3 H), 3.97−4.07 (m, 1 H), 4.10−4.18 (m, 1 H), 5.51 (d, 1 H, J = 5.1 Hz), 7.60−7.63 (m, 2 H), 7.65−7.69 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 23.6 (t), 27.6 (t), 39.6 (t), 53.0 (q), 58.2 (d), 70.1 (d), 110.6 (s), 118.7 (s), 129.2 (d), 131.8 (d), 143.6 (s), 156.5 (s). Anal. Calcd for $C_{14}H_{16}N_2O_3$: C, 64.60; H, 6.20; N, 10.76. Found: C, 64.52; H, 6.29; N, 10.53.

1-BOC-*cis*-2-(4-cyanophenyl)piperidin-3-ol (16g): colorless paste; R_f 0.31 (hexanes−ethyl acetate, 2:1); IR (neat) 3437, 2230, 1674, 1609, 1504, 1477, 966, 883, 862, 829, 771, 737, 704 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.40 (s, 9 H), 1.59−1.78 (m, 3 H), 1.82−1.90 (m, 1 H), 2.77−2.85 (m, 1 H), 3.93−4.01 (m, 1

H), 4.09−4.16 (m, 1 H), 5.43 (d, 1 H, J = 5.1 Hz), 7.58−7.65 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 23.5 (t), 27.8 (t), 28.2 (q), 39.6 (t), 58.2 (d), 70.2 (d), 80.5 (s), 110.6 (s), 118.8 (s), 129.1 (d), 131.8 (d), 144.4 (s), 155.2 (s). Anal. Calcd for $C_{17}H_{22}N_2O_3$: C, 67.53; H, 7.33; N, 9.26. Found: C, 67.72; H, 7.40; N, 9.09.

1-MOC-*cis*-2-(2-naphthyl)piperidin-3-ol (15i): colorless paste; R_f 0.53 (hexanes−ethyl acetate, 1:1); IR (neat) 3460, 1678, 1601, 1506, 972, 947, 820, 758, 735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.66−1.99 (m, 4 H), 2.05 (s, 1 H), 3.10 (dt, 1 H, J = 4.2, 13.1 Hz), 3.70 (s, 3 H), 4.05−4.13 (m, 1 H), 4.16−4.22 (m, 1 H), 5.59 (d, 1 H, J = 5.5 Hz), 7.44−7.50 (m, 2 H), 7.56 (m, 1 H, J = 1.9, 8.7 Hz), 7.79−7.85 (m, 3 H), 7.99 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.6 (t), 27.5 (t), 39.5 (t), 52.8 (q), 70.2 (d), 125.8 (d), 125.9 (d), 126.4 (d), 127.3 (d), 127.8 (d), 128.0 (d), 132.3 (s), 133.0 (s), 135.1 (s), 156.6 (s). Anal. Calcd for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71; N, 4.91. Found: C, 71.65; H, 6.75; N, 4.77.

1-BOC-*cis*-2-(2-naphthyl)piperidin-3-ol (16i): colorless paste; R_f 0.32 (hexanes−ethyl acetate, 2:1); IR (neat) 3425, 1666, 1601, 1506, 970, 951, 889, 858, 820, 758, 737, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.38 (s, 9 H), 1.64−1.83 (m, 2 H), 1.83−1.95 (m, 2 H), 3.05 (dt, 1 H, J = 3.7, 12.9 Hz), 4.03 (dd, 1 H, J = 3.7, 13.8 Hz), 4.13−4.20 (m, 1 H), 5.51 (d, 1H, J = 5.5 Hz), 7.44−7.49 (m, 2 H), 7.54 (dd, 1 H, J = 1.9, 8.7 Hz), 7.78−7.84 (m, 3 H), 7.97 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.4 (t), 27.6 (t), 28.3 (q), 39.5 (t), 58.9 (d), 70.2 (d), 80.0 (s), 125.7 (d), 125.9 (d), 126.5 (d), 127.2 (d), 127.4 (d), 127.8 (d), 128.0 (d), 132.4 (s), 133.1 (s), 135.8 (s), 155.4 (s). Anal. Calcd for $C_{20}H_{25}NO_3$: C, 73.37; H, 7.70; N, 4.28. Found: C, 73.52; H, 7.76; N, 4.21.

X-ray Crystallographic Analysis. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo Kα radiation. The structure was solved by direct methods with SIR92 and expanded by using Fourier techniques with DIRDIF99. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. All calculations were performed with the CrystalStructure crystallographic software package.

Crystal data for 13a: $C_{12}H_{15}O_3N$, FW = 221.26, monoclinic, $P2_{1/c}$ (no. 14), colorless block, a = 13.831(2) Å, b = 8.845(1) Å, c = 13.595(2) Å, β = 42.811(4)°, V = 1130.2(2) Å^3, T = 298 K, Z = 4, D_{calcd} = 1.300 g/cm^3, μ = 0.93 cm^{-1}, GOF = 1.003. The final cycle of full-matrix least-squares refinement on F was based on 1494 observed reflections and 160 variable parameters and converged with unweighted and weighted agreement factors of R = 0.040 and R_w = 0.049.

Crystal data for 13f: $C_{13}H_{14}O_3N_2$, FW = 246.27, monoclinic, $P2_{1/a}$ (no. 14), colorless block, a = 9.9726(6) Å, b = 12.5133(6) Å, c = 10.5966(7) Å, β = 110.642(2)°, V = 1237.5(1) Å^3, T = 298 K, Z = 4, D_{calcd} = 1.322 g/cm^3, μ = 0.95 cm^{-1}, GOF = 0.995. The final cycle of full-matrix least-squares refinement on F was based on 2317 observed reflections and 220 variable parameters and converged with unweighted and weighted agreement factors of R = 0.038 and R_w = 0.063.

Crystal data for 13g: $C_{12}H_{14}O_3NF$, FW = 239.25, monoclinic, $P2_{1/c}$ (no. 14), colorless block, a = 13.994(3) Å, b = 8.865(3) Å, c = 13.764(4) Å, β = 42.472(6)°, V = 1153.0(5) Å^3, T = 298 K, Z = 4, D_{calcd} = 1.378 g/cm^3, μ = 1.09 cm^{-1}, GOF = 1.002. The final cycle of full-matrix least-squares refinement on F was based on 1850 observed reflections and 211 variable parameters and converged with unweighted and weighted agreement factors of R = 0.037 and R_w = 0.050.

Crystal data for 15a: $C_{13}H_{15}O_7N$, FW = 235.28, monoclinic, $P2_{1/a}$ (no. 14), colorless block, a = 15.495(4) Å, b = 10.946(3) Å, c = 15.325(3) Å, β = 27.877(5)°, V = 1215.3(5) Å^3, T = 298 K, Z = 4, D_{calcd} = 1.286 g/cm^3, μ = 0.91 cm^{-1}, GOF = 0.998. The final cycle of full-matrix least-squares refinement on F was based on 1609 observed reflections and 171 variable parameters and converged with unweighted and weighted agreement factors of R = 0.041 and R_w = 0.042.

Crystal data for 15d: $C_{14}H_{19}O_4N$, FW = 265.31, monoclinic, $P2_{1/c}$ (no. 14), colorless block, a = 9.717(2) Å, b = 9.665(2) Å, c = 14.758(3) Å, β = 105.305(8)°, V = 1336.8(4) Å^3, T = 298 K, Z = 4, D_{calcd} = 1.318 g/cm^3, μ = 0.96 cm^{-1}, GOF = 1.000. The final cycle of full-matrix least-squares refinement on F was based on 2031 observed reflections and 249 variable parameters and converged with unweighted and weighted agreement factors of R = 0.031 and R_w = 0.036.

Supporting Information Available: A drawing of the electrolysis cell, ^{1}H and ^{13}C NMR spectra of **2a′**, **2a″**, **6a′**, and **6a″**, and X-ray crystallographic structures (ORTEP) of **13a**,**f**,**g** and **15a**,**d**, as well as crystallographic files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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