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Electroreductive five- and six-membered cyclization of aromatic β- and γ-imino esters derived from (*S*)-aspartic acid and (*S*)-glutamic acid

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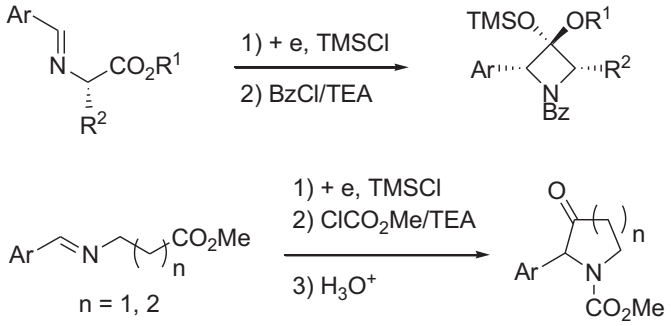
ABSTRACT

The electroreduction of aromatic β-dimethylcarbamoyl-β-imino esters, prepared from (*S*)-aspartic acid, in the presence of chlorotrimethylsilane gave five-membered cyclized products, 1-benzoyl-4-hydroxy-5-aryl-*N*,*N*-dimethylpyrrolidine-2-carboxamides and 5-(dimethylcarbamoyl)-2-aryl-1*H*-pyrrol-3-yl benzoates, depending on the post-treatment after the electroreduction. The electroreduction of aromatic γ-dialkylcarbamoyl-γ-imino and γ-methoxylmethyl-γ-imino esters, prepared from (*S*)-glutamic acid, and following transformation gave six-membered cyclized products, 1-benzoyl-5-hydroxy-*N*,*N*-dialkyl-6-phenylpiperidine-2-carboxamides and 3-hydroxy-6-(methoxymethyl)-2-phenylpiperidin-1-yl)(phenyl) methanones, respectively.

1. Introduction

Reductive intramolecular coupling of imino esters is a efficient method for the synthesis of cyclic amines and has been realized by us using electroreduction in the presence of chlorotrimethylsilane (TMSCl). That is, we have reported that the electroreductive intramolecular coupling of aromatic α-, β-, and γ-imino esters gave cyclized products as azetidines,[1] pyrrolidines,[2] and piperidines,[2] respectively (Scheme 1). We also disclosed that the electroreductive coupling of aromatic imino diesters prepared from (*S*)-aspartic acid and (*S*)-glutamic acid dimethyl diesters afforded azetidines, in particular, exclusively in the latter case (Scheme 2).[3] These results show that the four-membered cyclization is equivalent to the five-membered cyclization and much more favorable than the six-membered cyclization in the electroreductive intramolecular coupling of the imino esters.[4] Therefore, we investigated the other β- and γ-imino esters derived from (*S*)-aspartic and (*S*)-glutamic acids as the substrates for the electroreductive intramolecular coupling in order to obtain five- and six-membered cyclized products selectively. In this paper, we report that the electroreduction of aromatic β-dimethylcarbamoyl-β-imino esters prepared from (*S*)-aspartic acid gave five-membered cyclized products exclusively. The cyclized products were obtained as 5-aryl-2-(dimethylcarbamoyl)pyrrolidine-4-ones and 5-(dimethylcarbamoyl)-2-aryl-1*H*-pyrrol-3-yl benzoates depending on the post-treatment after the electroreduction (Scheme 3). Although the six-membered cyclization of imino esters was presumed to be more difficult from the results in Scheme 2, we also found that the electroreduction of aromatic γ-dialkylcarbamoyl-γ-imino and γ-methoxylmethyl-γ-imino esters prepared from (*S*)-glutamic acid formed six-membered cyclized products, piperidine-5-ones (Scheme 4).



Scheme 1. Electroreductive intramolecular coupling of α-, β-, and γ-imino esters.

2. Results and discussion

According to our reported method,[3] the electroreduction of β-dimethylcarbamoyl-β-imino ester **1a**, prepared from (*S*)-aspartic

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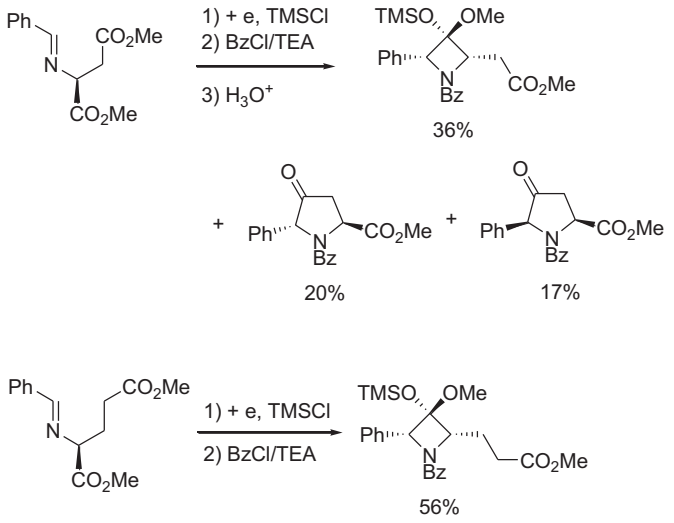
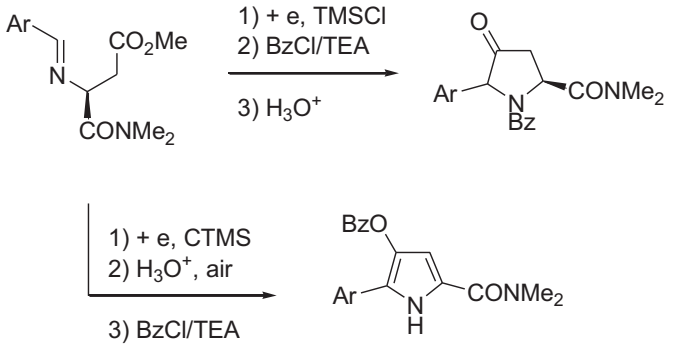
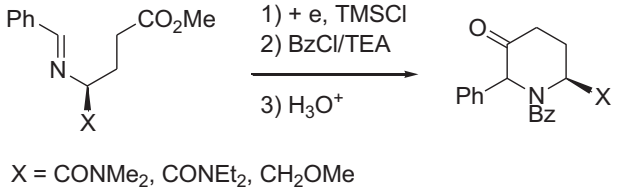


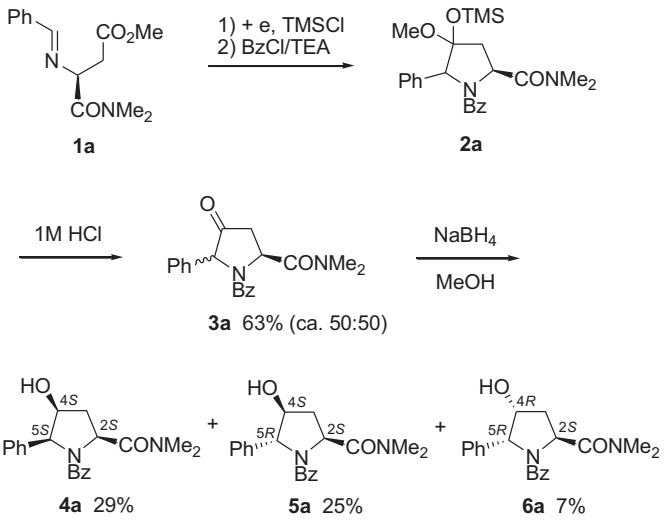
Scheme 2. Electroreductive intramolecular coupling of imino diesters prepared from (*S*)-aspartic acid and (*S*)-glutamic acid dimethyl esters.



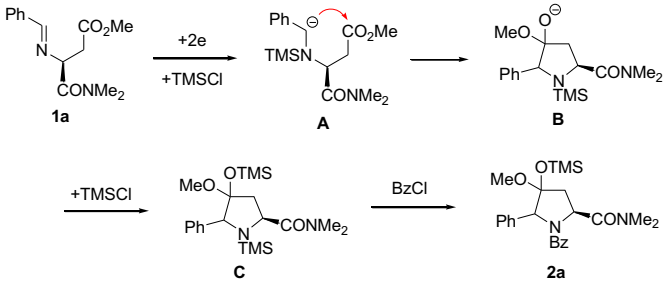
Scheme 3. Electroreductive intramolecular coupling of β-dimethylcarbamoyl-β-imino esters prepared from (*S*)-aspartic acid.



Scheme 4. Electroreductive intramolecular coupling of γ-dialkylcarbamoyl- and γ-methoxymethyl-γ-imino esters prepared from (*S*)-glutamic acid.



Scheme 5. Electroreductive cyclization of **1a** and subsequent transformation of **2a** to **3a**, **4a**, **5a**, and **6a**.



Scheme 6. Reaction mechanism of electroreductive cyclization of **1a**.

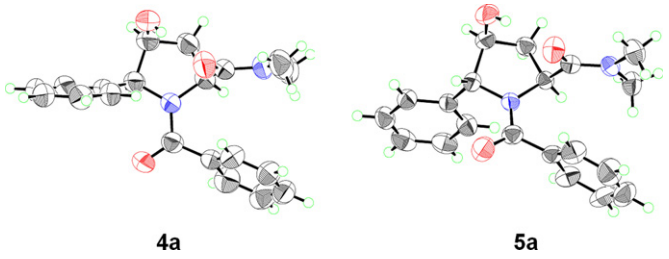


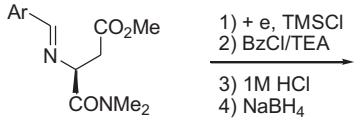
Fig. 1. X-ray crystal structures of **4a** and **5a**.

acid and benzaldehyde, and subsequent N-benzoylation of the resulting mixture were carried out to give five-membered cyclized product as mixed ketal **2a** (Scheme 5). The reaction mechanism of the electroreductive cyclization of **1a** is speculated as illustrated in Scheme 6. Two electron transfer and N-silylation to **1a** generate carbanion **A**. Cyclization of **A** and successive O-silylation of resulting **B** form **C**. Subsequent treatment of **C** with benzoyl chloride gives **2a**. The diastereomeric mixture of **2a** was transformed to ketone **3a** (63% yield from **1a**) by treatment with 1 M HCl (Scheme 5). Since the two diastereomers of **3a** (ca. 50:50 mixture) could not be separated, the mixture of **3a** was reduced to alcohols with $NaBH_4$ in methanol. Three diastereomeric alcohols **4a**, **5a**, and **6a** were isolated by column chromatography in 29%, 25%, and 7% yields from **1a**, respectively. Of the three diastereomers, the stereostructures of **4a** and **5a** were confirmed to be 2*S*,4*S*,5*S* and 2*S*,4*S*,5*R*, respectively, by X-ray crystallography (Fig. 1). The stereoconfiguration of **6a** was assigned to be 2*S*,4*R*,5*R* as described below. Thus, the cis:trans ratio at 2,5-positions was 48:52 (**4a**:**5a**+**6a**).

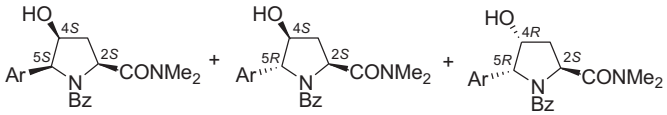
We therefore examined the electroreduction of a variety of aromatic β-dimethylcarbamoyl-β-imino esters **1b**–**h** and the subsequent sequential treatments; N-benzoylation, acid hydrolysis, and reduction with $NaBH_4$. The results are summarized in Table 1. In all cases, three diastereomeric five-membered cyclized products **4**, **5**, and **6** were obtained in 46–65% combined yields from **1**. The cis:trans ratios at 2,5-positions (**4**:**5**+**6**) were about 50:50 in most cases, although the electroreduction of electron-withdrawing *p*-fluoro and *p*-cyano substituted imino esters **1e** and **1f** brought about 64% and 81% 2,5-*trans* selectivities, respectively. The increase of the diastereoselectivity is presumed to be due to the stabilization of the intermediate carbanion corresponding to **B** in Scheme 6. Of the cyclized products **4**–**6**, the stereostructures of **4e**, **4g**, **5b**, **6c**, and **6h** were determined by X-ray crystallography (Fig. 2). The stereostructures of the other products were assigned by the correlation of their ^1H NMR spectra as shown in Tables 2–4.

On the other hand, the electroreduction of **1a** and following hydrolysis with 1 M HCl in contact with the atmosphere produced

Table 1
Electroreduction of **1** and subsequent transformation to **4**, **5**, and **6**



1a-h



4a-h **5a-h** **6a-h**

1	Ar	Yield[a] (%)				2,5-cis:trans
		4	5	6	4+5+6	
1a	Ph	29	25	7	61	48:52
1b	*p*-MeOC$_6$H$_4$	25	16	5	46	54:46
1c	*m*-MeOC$_6$H$_4$	31	28	5	64	48:52
1d	*o*-MeOC$_6$H$_4$	32	23	8	63	51:49
1e	*p*-FC$_6$H$_4$	20	29	7	56	36:64
1f	*p*-NCC$_6$H$_4$	10	34	8	52	19:81
1g	1-Naphthyl	25	23	7	55	45:55
1h	2-Naphthyl	37	21	7	65	57:43

[a] Isolated yields from **1a**–**h**.

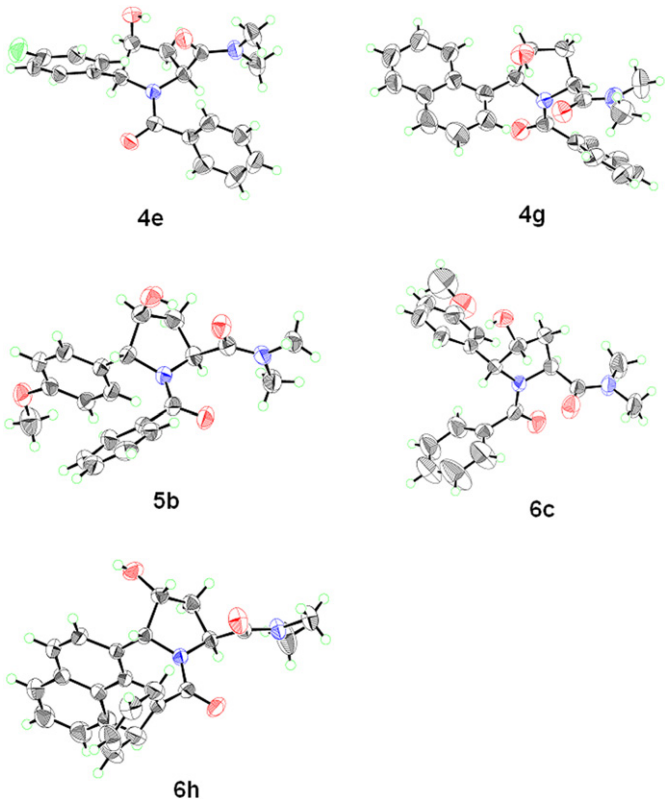


Fig. 2. X-ray crystal structures of **4e**. **4g**, **5b**, **6c**, and **6h**.

4-hydroxypyrrole **7a** in 52% isolated yield from **1a**. Alternatively, to facilitate the isolation of the somewhat unstable **7a**, the crude **7a** was treated with benzoyl chloride to give 4-benzyloxypyrrole **8a** in 54% yield from **1a** (Scheme 7). The pyrroles **7a** and **8a** were identified by X-ray crystallography (Fig. 3). The other β-dimethylcarbamoyl-β-imino esters **1b**–**h** were electrolyzed, hydrolyzed, and then *O*-benzoylated in a similar manner. The results are summarized in Table 5. In most cases, 4-benzyloxypyrroles **8** were

Table 2
^{1}H NMR chemical shifts (δ, ppm) of **4a**–**h**

4	Chemical shift (multitude)2-H, 4-H, 5-H
4a[a]	4.28–5.44 (m)
4b	4.17–5.40 (m)
4c	4.31–5.43 (m)
4d	4.17–5.30 (m), 5.51–5.72 (m)
4e[a]	4.21–5.53 (m)
4f	4.27–5.81(m)
4g[a]	4.20–5.47 (m), 5.88–6.26 (m)
4h	4.23–5.54 (m)

[a] The stereostructure was confirmed by X-ray crystallography.

Table 3
^{1}H NMR chemical shifts (δ, ppm) of **5a**–**h**

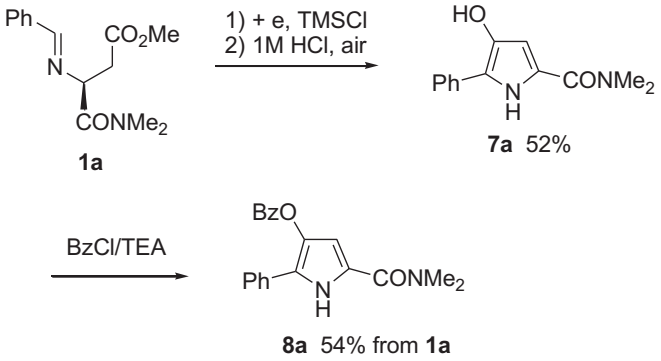
5	Chemical shift (multitude)		
	2-H	4-H	5-H
5a[a]	5.35 (d)	4.18 (dd)	6.76 (d)
5b[a]	5.32 (d)	4.13 (dd)	6.69 (d)
5c	5.32 (d)	4.19 (dd)	6.76 (d)
5d	5.34 (d)	4.17 (dd)	6.58 (d)
5e	5.35 (d)	4.14 (d)	6.99 (d)
5f	5.38 (d)	4.12–4.20 (m)	6.88 (d)
5g	5.46 (d)	4.35 (dd)	6.82 (d)
5h	5.45 (d)	4.27 (dd)	6.80 (d)

[a] The stereostructure was confirmed by X-ray crystallography.

Table 4
^{1}H NMR chemical shifts (δ, ppm) of **6a**–**h**

6	Chemical shift (multitude)		
	2-H	4-H	5-H
6a	5.35 (dd)	4.78–4.86 (m)	5.07–5.11 (m)
6b	5.27–5.31 (m)	4.74 (dd)	4.99 (d)
6c[a]	5.32 (dd)	4.76–4.84 (m)	5.00–5.08 (m)
6d	5.30–5.36 (m)	4.58 (dd)	5.63 (d)
6e	5.34 (dd)	4.80 (dd)	5.06–5.10 (m)
6f	5.34 (dd)	4.88 (dd)	5.12 (d)
6g	5.33–5.41 (m)	4.77–5.00 (m)	5.92–6.04 (m)
6h[a]	5.46 (dd)	4.89–4.97 (m)	5.28 (d)

[a] The stereostructure was confirmed by X-ray crystallography.



1a **7a** 52%

8a 54% from **1a**

Scheme 7. Electroreductive cyclization of **1a** and subsequent transformation to **7a** and **8a**.

obtained in moderate yields. However, the yields of electron-donating *p*- and *o*-methoxy substituted products **8b** and **8d** were relatively low, since 4-hydroxypyrroles **7b** and **7d** were probably unstable to the atmospheric conditions.

Next, we examined the electroreduction of aromatic γ-dialkylcarbamoyl-γ-imino esters **9a**,**b** and γ-methoxylmethyl-γ-imino ester **9c**, prepared from (*S*)-glutamic acid and benzaldehyde, and

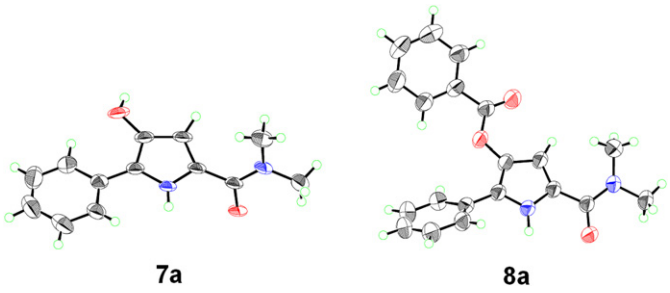
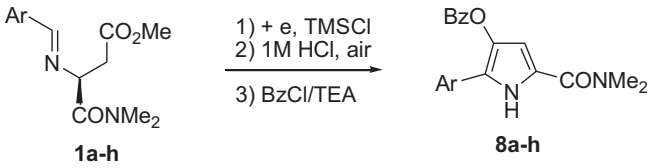


Fig. 3. X-ray crystal structures of **7a** and **8a**.

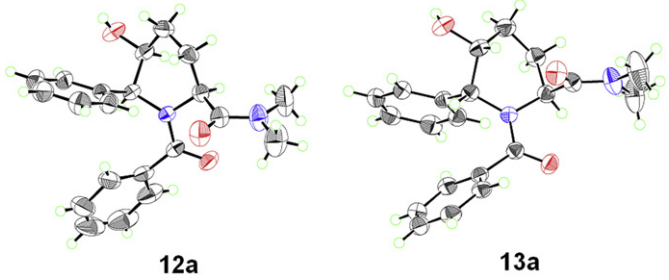
Table 5
Electroreduction of **1** and subsequent transformation to **8**



1	Ar	Yield of 8[a] (%)
1a	Ph	54
1b	*p*-$MeOC_6H_4$	20
1c	*m*-$MeOC_6H_4$	53
1d	*o*-$MeOC_6H_4$	23
1e	*p*-FC_6H_4	56
1f	*p*-NCC_6H_4	48
1g	1-Naphthyl	44
1h	2-Naphthyl	52

[a] Isolated yields from **1a**–**h**.

subsequent N-benzoylation and acid hydrolysis. Six-membered cyclized products piperidine-5-ones **10a**–**c** were obtained as mixtures of two diastereomers together with uncyclized products **11a**–**c**. Since the diastereomers of **10a**–**c** could not be separated, the mixtures of **10a**–**c** were treated with $NaBH_4$ to give two diastereomeric alcohols **12a**–**c** and **13a**–**c**. The results are summarized in Table 6. From **9a** and **9b**, the piperidines **12a**,**b** and **13a**,**b** were obtained in poor yields, 12% and 20% combined yields, respectively. On the contrary, the reaction of **9c** afforded the cyclized piperidines **12c** and **13c** in 44% combined yield, although the ratio



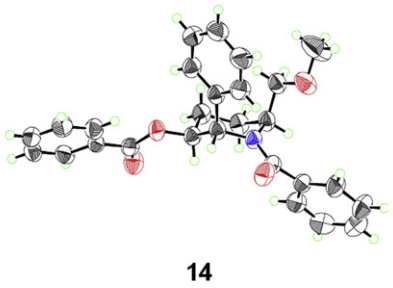


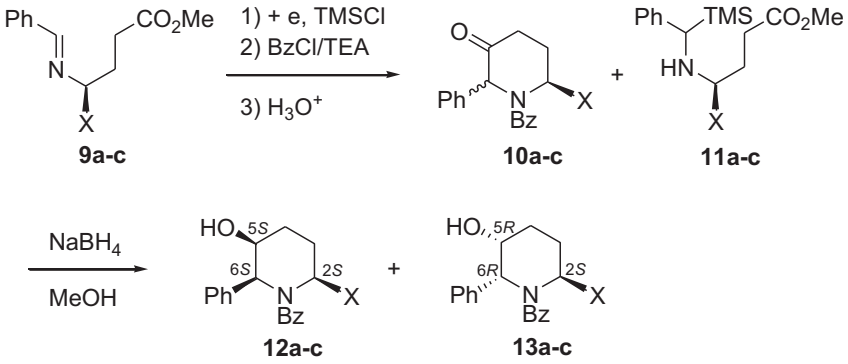
Fig. 4. X-ray crystal structures of **12a**, **13a**, and **14**.

of the diastereomers was 50:50. The stereostructures of **12a** and **13a** were determined to be 2*S*,5*S*,6*S* and 2*S*,5*R*,6*R* by X-ray crystallography, respectively (Fig. 4). The stereoconfigurations of **12b** and **13b** were assigned by their ^1H NMR correlation with those of **12a** and **13a**. Since the cyclized products **12c** and **13c** could not be still separated, these alcohols were further transformed to separable benzoates **14** and **15** (Scheme 8). The stereostructure of **14** was confirmed to be 2*S*,3*S*,6*S* by X-ray crystallography (Fig. 4). The stereoconfiguration of **13c** was assigned to be 2*R*,3*R*,6*S* by ^1H NMR (difNOE and COSY) analyses for the pure sample obtained by the hydrolysis of **15** (Scheme 8).

3. Conclusion

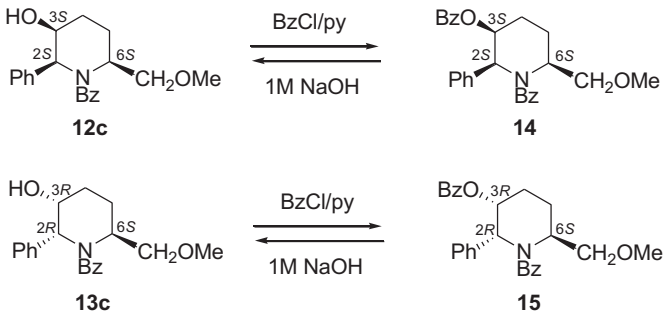
This paper describes that the electroreductive intramolecular coupling of aromatic β-dimethylcarbamoyl-β-imino esters **1a**–**h** prepared from (*S*)-aspartic acid in the presence of TMSCl followed by N-benzoylation, acid hydrolysis, and reduction with $NaBH_4$

Table 6
Electroreduction of **9** and subsequent transformation to **12** and **13**



9	X	Yield[a] (%)		
		12	**13**	**11**
9a	$CONMe_2$	9	3	34
9b	$CONEt_2$	15	5	24
9c	CH_2OMe	22	22	8

[a] Isolated yields from **9a**–**c**.



Scheme 8. Benzoylation of **12c** and **13c** and hydrolysis of **14** and **15**.

produced five-membered cyclized products 1-benzoyl-4-hydroxy-5-aryl-*N*,*N*-dimethylpyrrolidine-2-carboxamides as mixtures of three diastereomers, **4a**–**h**, **5a**–**h**, and **6a**–**h**. On the other hand, the electroreduction of **1a**–**h** followed by acid hydrolysis under open-air conditions and O-benzoylation gave 5-(dimethylcarbamoyl)-2-aryl-1*H*-pyrrol-3-yl benzoates **8a**–**h** as the cyclized products. In addition, the electroreduction of aromatic γ-dialkylcarbamoyl-γ-imino and γ-methoxylmethyl-γ-imino esters **9a**–**c** prepared from (*S*)-glutamic acid followed by N-benzoylation, acid hydrolysis, and reduction with $NaBH_4$ afforded six-membered cyclized products 1-benzoyl-5-hydroxy-*N*,*N*-dialkyl-6-phenylpiperidine-2-carboxamides, **12a**,**b** and **13a**,**b**, and 3-hydroxy-6-((methoxymethyl)-2-phenylpiperidin-1-yl)(phenyl)methanones, **12c** and **13c**, as mixtures of two diastereomers.

4. Experimental section

4.1. General

Column chromatography was performed on silica gel 60. THF and 1,4-dioxane were distilled from sodium benzophenone ketyl radical. TMSCl, TEA, and DMF were distilled from CaH_2.

4.2. Starting materials

Aromatic β- and γ-imino esters were prepared by treatment of ω-methyl esters derived from (*S*)-aspartic acid and (*S*)-glutamic acid with aromatic aldehydes in dichloromethane in the presence of magnesium sulfate at 25 °C and isolated by recrystallization from hexanes/ethyl acetate or used without purification.

*4.2.1. (S,E)-Methyl 3-(benzylideneamino)-4-(dimethylamino)-4-oxobutanoate (**1a**).* Pale yellow solid; mp 92–93 °C (recryst from hexanes/ethyl acetate=2:1); $[\alpha]_D^{20}$ −120 (*c* 1.01, $CHCl_3$); IR (KBr) 1733, 1637, 1579, 1498, 761, 744, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.74 (dd, 1H, *J*=6.0, 16.5 Hz), 3.00 (s, 3H), 3.09 (s, 3H), 3.16 (dd, 1H, *J*=7.8, 16.5 Hz), 3.67 (s, 3H), 5.00–5.04 (m, 1H), 7.39–7.48 (m, 3H), 7.73–7.78 (m, 2H), 8.34 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 35.8 (q), 36.9 (q), 37.2 (t), 51.5 (q), 64.4 (d), 128.2 (d), 128.4 (d), 131.1 (d), 135.5 (s), 163.1 (d), 169.7 (s), 171.7 (s).

*4.2.2. (S,E)-Methyl 4-(dimethylamino)-3-(4-methoxybenzylideneamino)-4-oxobutanoate (**1b**).* Colorless paste; $[\alpha]_D^{22}$ −108 (*c* 1.32, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.71 (dd, 1H, *J*=16.5, 6.2 Hz), 2.99 (s, 3H), 3.08 (s, 3H), 3.14 (dd, 1H, *J*=16.5, 8.3 Hz), 3.67 (s, 3H), 3,84 (s, 3H), 4.16 (dd, 1H, *J*=8.3, 6.2 Hz), 6.90–6.95 (m, 2H), 7.67–7.72 (m, 2H), 8.26 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 35.9 (q), 37.0 (q), 37.4 (t), 51.6 (q), 55.3 (q), 64.4 (d), 113.9 (d), 128.6 (s), 130.0 (d), 162.1 (s), 162.4 (d), 170.1 (s), 172.0 (s).

*4.2.3. (S,E)-Methyl 4-(dimethylamino)-3-(3-methoxybenzylideneamino)-4-oxobutanoate (**1c**).* Colorless paste; $[\alpha]_D^{20}$ −104 (*c* 1.22, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.73 (dd, 1H, *J*=16.5, 6.4 Hz), 3.00 (s, 3H), 3.08 (s, 3H), 3.16 (dd, 1H, *J*=16.5, 7.6 Hz), 3.67 (s, 3H), 3.84 (s, 3H), 5.01 (dd, 1H, *J*=7.6, 6.4 Hz), 6.97–7.02 (m, 1H), 7.24–7.37 (m, 3H), 8.31 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 36.0 (q), 37.0 (q), 37.3 (t), 51.7 (q), 55.3 (q), 64.4 (d), 111.6 (d), 118.0 (d), 121.8 (d), 129.5 (d), 137.0 (s), 159.8 (s), 163.1 (d), 169.8 (s), 171.9 (s).

*4.2.4. (S,E)-Methyl 4-(dimethylamino)-3-(2-methoxybenzylideneamino)-4-oxobutanoate (**1d**).* Colorless paste; $[\alpha]_D^{21}$ −126 (*c* 1.15, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.68 (dd, 1H, *J*=16.9, 6.1 Hz), 2.99 (s, 3H), 3.08 (s, 3H), 3.20 (dd, 1H, *J*=16.9, 8.3 Hz), 3.67 (s, 3H), 3.86 (s, 3H), 4.97 (dd, 1H, *J*=8.3, 6.1 Hz), 6.88–7.06 (m, 2H), 7.35–7.43 (m, 1H), 7.94–8.01 (m, 1H), 8.79 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 36.0 (q), 37.0 (q), 37.5 (t), 51.7 (q), 55.4 (q), 65.3 (d), 110.9 (d), 120.7 (d), 124.1 (s), 127.3 (d), 132.5 (d), 158.9 (s), 159.4 (d), 170.1 (s), 172.0 (s).

*4.2.5. (S,E)-methyl 4-(dimethylamino)-3-(4-fluorobenzylideneamino)-4-oxobutanoate (**1e**).* Pale yellow solid; $[\alpha]_D^{21}$ −109 (*c* 1.16, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.74 (dd, 1H, *J*=16.9, 6.2 Hz), 3.00 (s, 3H), 3.09 (s, 3H), 3.14 (dd, 1H, *J*=16.9, 7.7 Hz), 3.67 (s, 3H), 4.98–5.04 (m, 1H), 7.06–7.14 (m, 2H), 7.71–7.80 (m, 2H), 8.31 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 35.9 (q), 37.0 (q), 37.2 (t), 51.7 (q), 64.3 (d), 115.6 (d, J_{CC}=22.1 Hz), 130.3 (d, J_{CCCF}=8.6 Hz), 131.9 (s, J_{CCCCF}=2.9 Hz), 161.6 (d), 164.5 (s, J_{CF}=251.9 Hz), 169.8 (s), 171.8 (s).

*4.2.6. (S,E)-Methyl 4-(dimethylamino)-3-(4-cyanobenzylideneamino)-4-oxobutanoate (**1f**).* Pale yellow paste; $[\alpha]_D^{23}$ −77.7 (*c* 1.10, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.77 (dd, 1H, *J*=17.2, 7.0 Hz), 3.00 (s, 3H), 3.10 (s, 3H), 3.14 (dd, 1H, *J*=17.2, 7.0 Hz), 3.68 (s, 3H), 5.10 (t, 1H, *J*=7.0 Hz), 7.69–7.73 (m, 2H), 7.84–7.88 (m, 2H), 8.37 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 36.0 (q), 37.0 (t), 37.0 (q), 51.8 (d), 64.2 (q), 114.5 (s), 118.3 (s), 128.8 (d), 132.4 (d), 139.3 (s), 161.2 (d), 169.4 (s), 171.7 (s).

*4.2.7. (S,E)-Methyl 4-(dimethylamino)-3-(naphthalen-1-ylmethyleneamino)-4-oxobutanoate (**1g**).* Pale yellow paste; $[\alpha]_D^{22}$ −99.4 (*c* 1.09, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.85 (dd, 1H, *J*=16.6, 6.9 Hz), 3.02 (s, 3H), 3.12 (s, 3H), 3.24 (dd, 1H, *J*=16.6, 6.9 Hz), 3.68 (s, 3H), 5.10 (t, 1H, *J*=6.9 Hz), 7.47–7.63 (m, 3H), 7.83–7.95 (m, 3H), 8.86–8.91 (m, 1H), 8.99 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 36.0 (q), 37.1 (q), 37.5 (t), 51.7 (q), 65.7 (d), 124.2 (d), 125.1 (d), 126.1 (d), 127.4 (d), 128.6 (d), 129.5 (d), 130.9 (s), 131.1 (s), 131.7 (d), 133.7 (s), 163.5 (d), 169.9 (s), 172.0 (s).

*4.2.8. (S,E)-Methyl 4-(dimethylamino)-3-(naphthalen-2-ylmethyleneamino)-4-oxobutanoate (**1h**).* Pale yellow solid; $[\alpha]_D^{22}$ −108 (*c* 1.05, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.79 (dd, 1H, *J*=16.6, 6.3 Hz), 3.01 (s, 3H), 3.11 (s, 3H), 3.20 (dd, 1H, *J*=16.6, 7.7 Hz), 3.68 (s, 3H), 5.05–5.10 (m, 1H), 7.48–7.56 (m, 2H), 7.81–8.08 (m, 5H), 8.49 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 36.0 (q), 37.1 (q), 37.4 (t), 51.7 (q), 64.6 (d), 123.6 (d), 126.6 (d), 127.4 (d), 127.8 (d), 128.5 (d), 128.7 (d), 130.7 (d), 132.9 (s), 133.3 (s), 134.9 (s), 163.2 (d), 169.9 (s), 172.0 (s).

*4.2.9. (S,E)-Methyl 4-(benzylideneamino)-5-(dimethylamino)-5-oxopentanoate (**9a**).* Pale yellow paste; $[\alpha]_D^{20}$ −44.3 (*c* 1.20, $CHCl_3$); IR (neat) 1733, 1699, 1647, 1579, 1497, 758, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.12–2.20 (m, 1H), 2.26–2.34 (m, 1H), 2.38–2.44 (m, 2H), 2.98 (s, 3H), 3.13 (s, 3H), 3.65 (s, 3H), 4.50–4.53 (m, 1H), 7.38–7.47 (m, 3H), 7.73–7.78 (m, 2H), 8.30 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 28.1 (t), 30.2 (t), 35.8 (q), 36.8 (q), 51.4 (q), 68.8 (d), 128.2 (d), 128.4 (d), 130.9 (d), 135.5 (s), 162.5 (d), 170.5 (s), 173.4 (s).

*4.2.10. (S,E)-Methyl 4-(benzylideneamino)-5-(diethylamino)-5-oxopentanoate (**9b**).* Pale yellow paste; $[\alpha]_D^{22}$ −32.3 (*c* 1.03, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.13 (t, 3H, *J*=7.2 Hz), 1.16 (t, 3H, *J*=7.1 Hz), 2.10–2.50 (m, 4H), 3.28–3.60 (m, 4H), 3.65 (s, 3H), 4.51 (t, 1H, *J*=7.0 Hz), 7.38–7.47 (m, 3H), 7.73–7.78 (m, 2H), 8.31 (s, 1H); ^{13}C

NMR ($CDCl_3$) δ 12.7 (q), 14.4 (q), 28.4 (t), 30.2 (t), 40.2 (t), 41.3 (t), 51.2 (q), 68.0 (d), 128.1 (d), 128.3 (d), 130.8 (d), 135.6 (s), 162.0 (d), 169.7 (s), 173.3 (s).

*4.2.11. (S,E)-Methyl 4-(benzylideneamino)-5-methoxypentanoate (**9c**).* Pale yellow paste; $[\alpha]_D^{25}$ −65.7 (*c* 1.04, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.90–2.06 (m, 2H), 2.23–2.39 (m, 2H), 3.33 (s, 3H), 3.39–3.55 (m, 3H), 3.62 (s, 3H), 7.37–7.44 (m, 3H), 7.71–7.79 (m, 2H), 8.27 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 27.6 (t), 30.6 (t), 51.4 (q), 58.9 (q), 69.7 (d), 76.0 (t), 128.2 (d), 128.4 (d), 130.6 (d), 135.9 (s), 161.8 (d), 173.7 (s).

4.3. Typical procedure for electroreduction of imino esters 1 and subsequent transformation to 4, 5, and 6

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**) (262 mg, 1 mmol), TMSCl (0.64 mL, 5 mmol), and TEA (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 25 °C, the catholyte was evaporated in vacuo. The residue was dissolved in Et_2O (20 mL) and insoluble solid was filtered off. After removal of the solvent, the residue was dissolved in THF (5 mL). To the solution were added benzoyl chloride (0.12 mL, 1 mmol) and TEA (0.21 mL, 1.5 mmol) at 25 °C. After the suspended mixture was stirred for 2 h, 1 M HCl (5 mL) was added to the mixture. The mixture was stirred at 25 °C for 1 h, diluted with H_2O (10 mL), and then extracted with ethyl acetate three times. After the solvent was removed, the residue was purified by column chromatography on silica gel (hexanes/ethyl acetate) to give **3a** in 63% yield as a about 50:50 mixture of two diastereomers. Recrystallization of the mixture from hexane/ethyl acetate=1:5 gave ***trans*-3a** as a pure solid.

To a solution of the crude **3a** in methanol (5 mL) was added $NaBH_4$ (38 mg, 1.0 mmol) at 0 °C. After being stirred for 30 min at this temperature, the mixture was diluted with water (10 mL) and extracted with ethylacetate three times. After the solvent was removed, the residue was column chromatographed on silica gel (hexanes/ethyl acetate) to give alcohols **4a**, **5a**, and **6a** in 29%, 25%, and 7% yields, respectively.

*4.3.1. (2S,5R)-1-Benzoyl-N,N-dimethyl-4-oxo-5-phenylpyrrolidine-2-carboxamide (**trans-3a**).* White solid; R_f 0.25 (hexane/ethyl acetate=1:5); mp 220–221 °C (recryst from hexane/ethyl acetate=1:5); $[\alpha]_D^{20}$ −166 (*c* 0.86, $CHCl_3$); IR (KBr) 1749, 1635, 1600, 1577, 1492, 731, 704 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.62 (d, 1H, *J*=17.9 Hz), 3.00 (dd, 1H, *J*=10.1, 17.9 Hz), 3.04 (s, 3H), 3.35 (s, 3H), 5.19 (s, 1H), 5.80 (d, 1H, *J*=10.1 Hz), 6.87–6.93 (m, 2H), 7.07–7.21 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 35.6 (q), 35.8 (q), 36.1 (q), 37.0 (q), 38.2 (t), 52.1 (d), 68.1 (d), 125.6 (d), 126.0 (d), 127.1 (d), 127.4 (d), 127.5 (d), 128.0 (d), 128.3 (d), 129.1 (d), 129.4 (d), 135.3 (s), 136.0 (s), 137.2 (s), 171.3 (s), 171.4 (s), 205.9 (s). Anal. Calcd for $C_{20}H_{20}N_2O_3$: C, 71.41%; H, 5.99%; N, 8.33%. Found: C, 71.46%; H, 6.02%; N, 8.18%.

*4.3.2. (2S,4S,5S)-1-Benzoyl-4-hydroxy-N,N-dimethyl-5-phenylpyrrolidine-2-carboxamide (**4a**).* White solid; R_f 0.25 (ethyl acetate); mp 194–196 °C (recryst from ethyl acetate); $[\alpha]_D^{24}$ 194 (*c* 1.06, $CHCl_3$); IR (KBr) 3368, 1645, 1628, 1601, 1497, 789, 758, 743, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.08–2.62 (m, 2H), 2.89–3.51 (m, 6H), 4.28–5.44 (m, 4H), 6.83–7.77 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 35.2 (t), 36.3 (q), 37.5 (q), 56.3 (d), 69.4 (d), 74.0 (d), 126.4 (d), 126.7 (d), 127.5 (d), 128.3 (d), 129.1 (d), 135.9 (s), 137.2 (s), 171.0 (s), 173.0 (s). Anal. Calcd for $C_{20}H_{22}N_2O_3$: C, 70.99%; H, 6.55%; N, 8.28%. Found: C, 70.97%; H, 6.56%; N, 8.15%.

*4.3.3. (2S,4S,5S)-1-Benzoyl-4-hydroxy-5-(4-methoxyphenyl)-N,N-dimethylpyrrolidine-2-carboxamide (**4b**).* White solid; R_f 0.3 (ethyl acetate/ethanol=10:1); mp 182–183 °C (recryst from ethyl acetate); $[\alpha]_D^{21}$ 146 (*c* 1.10, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.94–2.67 (m, 2H), 2.80–3.89 (m, 9H), 4.17–5.40 (m, 4H), 6.47–7.76 (m, 9H); ^{13}C NMR (DMSO-d_6) δ 33.0 (t), 36.0 (q), 36.5 (q), 37.1 (q), 55.2 (d), 66.3 (d), 71.3 (d), 113.1 (d), 127.0 (d), 127.9 (d), 129.97 (d), 130.04 (d), 131.9 (s), 136.4 (s), 158.4 (s), 170.9 (s), 171.4 (s). Anal. Calcd for $C_{21}H_{24}N_2O_4$: C, 68.46%; H, 6.57%; N, 7.60%. Found: C, 68.57%; H, 6.64%; N, 7.45%.

*4.3.4. (2S,4S,5S)-1-Benzoyl-4-hydroxy-5-(3-methoxyphenyl)-N,N-dimethylpyrrolidine-2-carboxamide (**4c**).* Colorless paste; R_f 0.3 (ethyl acetate/ethanol=10:1); $[\alpha]_D^{24}$ 124 (*c* 1.20, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.11–2.27 (m, 1H), 2.38–2.67 (m, 1H), 2.94–3.95 (m, 9H), 4.31–5.43 (m, 4H), 6.54–7.63 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 35.0 (t), 36.2 (q), 37.4 (q), 54.9 (q), 56.1 (d), 68.9 (d), 73.7 (d), 112.8 (d), 113.7 (d), 120.7 (d), 126.4 (d), 127.3 (d), 128.5 (d), 129.2 (d), 135.7 (s), 138.9 (s), 158.9 (s), 171.0 (s), 172.6 (s); HRMS (ESI) calcd for $C_{21}H_{25}N_2O_4$ $(M+H)^+$ 369.1816, found 369.1808.

*4.3.5. (2S,4S,5S)-1-Benzoyl-4-hydroxy-5-(2-methoxyphenyl)-N,N-dimethylpyrrolidine-2-carboxamide (**4d**).* Colorless paste; R_f 0.45 (ethyl acetate/ethanol=10:1); $[\alpha]_D^{24}$ 89.0 (*c* 1.13, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.98–3.96 (m, 11H), 4.17– 5.30 (m, 3H), 5.51–5.72 (m, 1H), 6.44–7.96 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 35.9 (t), 36.5 (q), 37.8 (q), 55.1 (d), 56.6 (q), 62.8 (d), 73.2 (d), 109.5 (d), 120.3 (d), 125.2 (s), 126.3 (d), 127.2 (d), 128.0 (d), 129.1 (d), 130.2 (d), 136.1 (s), 155.7 (s), 170.9 (s), 173.4 (s); HRMS (ESI) calcd for $C_{21}H_{25}N_2O_4$ $(M+H)^+$ 369.1816, found 369.1809.

*4.3.6. (2S,4S,5S)-1-Benzoyl-5-(4-fluorophenyl)-4-hydroxy-N,N-dimethylpyrrolidine-2-carboxamide (**4e**).* White solid; R_f 0.3 (ethyl acetate/ethanol=10:1); mp 259–260 °C (recryst from CH_2Cl_2); $[\alpha]_D^{24}$ 182 (*c* 1.10, $CHCl_3$); IR (KBr) 3372, 1643, 1628, 1603, 1578, 1508, 866, 831, 812, 745, 731, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.02–2.74 (m, 2H), 2.83–3.63 (m, 6H), 4.21–5.53 (m, 4H), 6.60–7.80 (m, 9H); ^{13}C NMR (DMSO-d_6) δ 33.0 (t), 35.6 (q), 36.8 (q), 54.9 (d), 65.9 (d), 71.0 (d), 113.8 (d, J_{CCF}=22.1 Hz), 126.5 (d), 127.5 (d), 129.5 (d), 130.3 (d, J_{CCCF}=6.7 Hz), 135.6 (s), 136.1 (s), 161.2 (s, J_{CF}=246.2 Hz), 170.3 (s), 171.1 (s). Anal. Calcd for $C_{20}H_{21}FN_2O_3$: C, 67.40%; H, 5.94%; N, 7.86%. Found: C, 67.48%; H, 5.92%; N, 7.74%.

*4.3.7. (2S,4S,5S)-1-Benzoyl-5-(4-cyanophenyl)-4-hydroxy-N,N-dimethylpyrrolidine-2-carboxamide (**4f**).* White solid; R_f 0.35 (ethyl acetate/ethanol=10:1); mp 289–291 °C (recryst from CH_2Cl_2); $[\alpha]_D^{22}$ 215 (*c* 1.00, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.04–3.56 (m, 8H), 4.27–5.81 (m, 4H), 6.85–7.92 (m, 9H); ^{13}C NMR (DMSO-d_6) δ 33.2 (t), 35.6 (q), 36.7 (q), 54.9 (d), 66.1 (d), 71.0 (d), 109.4 (s), 119.2 (s), 126.4 (d), 127.8 (d), 129.0 (d), 129.6 (d), 131.2 (d), 136.2 (s), 145.8 (s), 170.2 (s), 171.0 (s). Anal. Calcd for $C_{21}H_{21}N_3O_3$: C, 69.41%; H, 5.82%; N, 11.56%. Found: C, 69.40%; H, 5.85%; N, 11.38%.

*4.3.8. (2S,4S,5S)-1-Benzoyl-4-hydroxy-N,N-dimethyl-5-(naphthalen-1-yl)pyrrolidine-2-carboxamide (**4g**).* White solid; R_f 0.3 (ethyl acetate/ethanol=10:1); mp 269–271 °C (recryst from CH_2Cl_2); $[\alpha]_D^{25}$ 9.1 (*c* 1.13, $CHCl_3$); IR (KBr) 3406, 1647, 1624, 1597, 1576, 800, 791, 731 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.10–3.61 (m, 8H), 4.20–5.47 (m, 3H), 5.88–6.26 (m, 1H), 6.65–8.36 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 35.8 (t), 36.2 (q), 36.5 (q), 37.3 (q), 37.7 (q), 38.3 (t), 56.5 (d), 59.0 (d), 65.3 (d), 65.4 (d), 72.5 (d), 73.4 (d), 121.6 (d), 122.4 (d), 124.1 (d), 125.0 (d), 125.4 (d), 125.6 (d), 126.8 (d), 127.2 (d), 127.5 (d), 128.2 (d), 128.6 (d), 128.9 (d), 130.5 (d), 130.7 (s), 132.4 (s), 133.0 (s), 133.7 (s), 135.7 (s), 136.9 (s), 171.0 (s), 171.9 (s), 173.2 (s), 174.5(s). Anal. Calcd for

$C_{24}H_{24}N_2O_3$: C, 74.21%; H, 6.23%; N, 7.21%. Found: C, 74.20%; H, 6.18%; N, 7.09%.

*4.3.9. (2S,4S,5S)-1-Benzoyl-4-hydroxy-N,N-dimethyl-5-(naphthalen-2-yl)pyrrolidine-2-carboxamide (**4h**).* White solid; R_f 0.4 (ethyl acetate/ethanol=10:1); mp 194–195 °C (recryst from CH_2Cl_2); $[\alpha]_D^{22}$ 214 (*c* 1.08, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.09–2.59 (m, 2H), 2.93–3.48 (m, 6H), 4.23–5.54 (m, 4H), 6.74–8.14 (m, 12H); ^{13}C NMR (DMSO-d_6) δ 33.2 (t), 36.0 (q), 37.1 (q), 55.4 (d), 66.9 (d), 71.6 (d), 125.7 (d), 125.9 (d), 126.7 (d), 126.9 (d), 127.3 (d), 127.5 (d), 127.6 (d), 127.8 (d), 128.1 (d), 130.0 (d), 132.4 (s), 133.0 (s), 136.3 (s), 137.8 (s), 170.8 (s), 171.5 (s). Anal. Calcd for $C_{24}H_{24}N_2O_3$: C, 74.21%; H, 6.23%; N, 7.21%. Found: C, 74.25%; H, 6.16%; N, 7.10%.

*4.3.10. (2S,4S,5R)-1-Benzoyl-4-hydroxy-N,N-dimethyl-5-phenylpyrrolidine-2-carboxamide (**5a**).* White solid; R_f 0.45 (ethyl acetate); mp 206–207 °C (recryst from hexanes/ethyl acetate=1:2); $[\alpha]_D^{22}$ −55.4 (*c* 1.12, $CHCl_3$); IR (KBr) 3341, 1640, 1626, 1599, 1493, 783, 766, 754, 710, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.91 (d, 1H, *J*=14.5 Hz), 2.35–2.42 (m, 1H), 3.10 (s, 3H), 3.44 (s, 3H), 4.18 (dd, 1H, *J*=4.1, 11.4 Hz), 5.16 (s, 1H), 5.35 (d, 1H, *J*=9.6 Hz), 6.76 (d, 1H, *J*=11.3 Hz), 7.03–7.07 (m, 2H), 7.17–7.31 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 33.2 (t), 36.6 (q), 38.0 (q), 55.9 (d), 73.9 (d), 78.8 (d), 125.0 (d), 126.4 (d), 127.3 (d), 127.8 (d), 128.6 (d), 129.6 (d), 135.7 (s), 140.4 (s), 171.4 (s), 173.7 (s). Anal. Calcd for $C_{20}H_{22}N_2O_3$: C, 70.99%; H, 6.55%; N, 8.28%. Found: C, 71.04%; H, 6.53%; N, 8.20%.

*4.3.11. (2S,4S,5R)-1-Benzoyl-4-hydroxy-5-(4-methoxyphenyl)-N,N-dimethylpyrrolidine-2-carboxamide (**5b**).* White solid; R_f 0.25 (ethyl acetate); mp 201–202 °C (recryst from ethyl acetate); $[\alpha]_D^{22}$ −89.3 (*c* 1.05, $CHCl_3$); IR (KBr) 3198, 3187, 1636, 1618, 1584, 1578, 1506, 849, 808, 795, 731, 704 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.89 (d, 1H, *J*=14.3 Hz), 2.34–2.42 (m, 1H), 3.09 (s, 3H), 3.43 (s, 3H), 3.77 (s, 3H), 4.13 (dd, 1H, *J*=11.5, 4.1 Hz), 5.10 (s, 1H), 5.32 (d, 1H, *J*=9.4 Hz), 6.69 (d, 1H, *J*=11.5 Hz), 6.78–6.84 (m, 2H), 6.93–6.98 (m, 2H), 7.17–7.31 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 33.3 (t), 36.7 (q), 38.2 (q), 55.2 (q), 56.0 (d), 73.5 (d), 79.0 (d), 114.1 (d), 126.4 (d), 126.6 (d), 127.9 (d), 129.7 (d), 132.7 (s), 135.8 (s), 158.8 (s), 171.6 (s), 173.8 (s). Anal. Calcd for $C_{21}H_{24}N_2O_4$: C, 68.46%; H, 6.57%; N, 7.60%. Found: C, 68.51%; H, 6.56%; N, 7.53%.

*4.3.12. (2S,4S,5R)-1-Benzoyl-4-hydroxy-5-(3-methoxyphenyl)-N,N-dimethylpyrrolidine-2-carboxamide (**5c**).* White solid; R_f 0.5 (ethyl acetate/ethanol=10:1); mp 192–194 °C (recryst from ethyl acetate/ethanol=1:1); $[\alpha]_D^{23}$ −50.7 (*c* 1.10, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.90 (d, 1H, *J*=14.2 Hz), 2.35–2.43 (m, 1H), 3.10 (s, 3H), 3.43 (s, 3H), 3.75 (s, 3H), 4.19 (dd, 1H, *J*=11.4, 4.0 Hz), 5.12 (s, 1H), 5.32 (d, 1H, *J*=9.6 Hz), 6.56–6.67 (m, 2H), 6.74–6.78 (m, 2H), 7.17–7.23 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 33.4 (t), 36.7 (q), 38.2 (q), 55.1 (q), 56.1 (d), 73.9 (d), 79.0 (d), 111.3 (d), 112.3 (d), 117.3 (d), 126.6 (d), 127.9 (d), 129.7 (d), 129.8 (d), 135.8 (s), 142.3 (s), 159.8 (s), 171.5 (s), 173.8 (s). Anal. Calcd for $C_{21}H_{24}N_2O_4$: C, 68.46%; H, 6.57%; N, 7.60%. Found: C, 68.59%; H, 6.66%; N, 7.58%.

*4.3.13. (2S,4S,5R)-1-Benzoyl-4-hydroxy-5-(2-methoxyphenyl)-N,N-dimethylpyrrolidine-2-carboxamide (**5d**).* White solid; R_f 0.6 (ethyl acetate/ethanol=10:1); mp 179–180 °C (recryst from hexanes/ethyl acetate=1:5); $[\alpha]_D^{24}$ −9.8 (*c* 1.07, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.88 (d, 1H, *J*=13.8 Hz), 2.29–2.37 (m, 1H), 3.10 (s, 3H), 3.43 (s, 3H), 3.70 (s, 3H), 4.17 (dd, 1H, *J*=11.5, 4.6 Hz), 5.34 (d, 1H, *J*=9.2 Hz), 5.39 (s, 1H), 6.58 (d, 1H, *J*=11.5 Hz), 6.75–6.79 (m, 1H), 6.89–7.04 (m, 2H), 7.14–7.29 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 33.6 (t), 36.7 (q), 38.1 (q), 55.2 (q), 56.2 (d), 69.5 (d), 77.0 (d), 110.5 (d), 120.4 (d), 125.4 (d), 126.6 (d), 127.8 (d), 128.66 (d), 128.73 (s), 129.5 (d), 135.8 (s), 155.8 (s), 171.4 (s), 173.9 (s). Anal. Calcd for $C_{21}H_{24}N_2O_4$: C, 68.46%; H, 6.57%; N, 7.60%. Found: C, 68.49%; H, 6.53%; N, 7.42%.

*4.3.14. (2S,4S,5R)-1-Benzoyl-5-(4-fluorophenyl)-4-hydroxy-N,N-dimethylpyrrolidine-2-carboxamide (**5e**).* White solid; R_f 0.3 (ethyl acetate); mp 213–214 °C (ethyl acetate/ethanol=1:1); $[\alpha]_D^{22}$ −50.4 (*c* 1.08, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.93 (d, 1H, *J*=14.4 Hz), 2.34–2.41 (m, 1H), 3.10 (s, 3H), 3.43 (s, 3H), 4.14 (d, 1H, *J*=4.6 Hz), 5.14 (s, 1H), 5.35 (d, 1H, *J*=9.6 Hz), 6.94–7.02 (m, 4H), 7.18–7.33 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 32.3 (t), 36.7 (q), 38.2 (q), 56.0 (d), 73.4 (d), 78.9 (d), 115.6 (d, J_{CCF}=21.1 Hz), 126.4 (d), 126.8 (d, J_{CCCF}=7.7 Hz), 128.0 (d), 129.8 (d), 135.7 (s), 136.3 (s, J_{CCCCF}=2.9 Hz), 161.8 (s, J_{CF}=246.7 Hz), 171.6 (s), 173.6 (s). Anal. Calcd for $C_{20}H_{21}FN_2O_3$: C, 67.40%; H, 5.94%; N, 7.86%. Found: C, 67.51%; H, 6.00%; N, 7.75%.

*4.3.15. (2S,4S,5R)-1-Benzoyl-5-(4-cyanophenyl)-4-hydroxy-N,N-dimethylpyrrolidine-2-carboxamide (**5f**).* White solid; R_f 0.5 (ethyl acetate/ethanol=10:1); mp 242–243 °C (recryst from CH_2Cl_2); $[\alpha]_D^{22}$ −143 (*c* 1.17, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.92 (d, 0.1H, *J*=14.2 Hz), 1.97 (d, 0.9H, *J*=14.5 Hz), 2.23–2.37 (m, 0.9H), 2.39–2.46 (m, 0.1H), 2.50 (s, 0.3H), 2.69 (s, 0.3H), 3.10 (s, 2.7H), 3.44 (s, 2.7H), 4.12–4.20 (m, 1H), 5.03 (d, 0.1H, *J*=9.7 Hz), 5.21 (s, 0.9H), 5.38 (d, 0.9H *J*=9.8 Hz), 5.65 (d, 0.1H, *J*=12.2 Hz), 5.72 (s, 0.1H), 6.88 (d, 0.9H, *J*=11.9 Hz), 7.13–7.70 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 33.3 (t), 36.7 (q), 38.1 (q), 56.0 (d), 73.8 (d), 78.8 (d), 111.4 (s), 118.1 (s), 126.0 (d), 126.3 (d), 128.1 (d), 129.9 (d), 132.5 (d), 135.4 (s), 145.7 (s), 171.3 (s), 173.4 (s). Anal. Calcd for $C_{21}H_{21}N_3O_3$: C, 69.41%; H, 5.82%; N, 11.56%. Found: C, 69.45%; H, 5.77%; N, 11.43%.

*4.3.16. (2S,4S,5R)-1-Benzoyl-4-hydroxy-N,N-dimethyl-5-(naphthalen-1-yl)pyrrolidine-2-carboxamide (**5g**).* White solid; R_f 0.5 (ethyl acetate/ethanol=10:1); mp 222–224 °C (recryst from CH_2Cl_2); $[\alpha]_D^{22}$ 44.3 (*c* 1.13, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.96 (d, 1H, *J*=14.3 Hz), 2.31–2.38 (m, 1H), 3.12 (s, 3H), 3.46 (s, 3H), 4.35 (dd, 1H, *J*=11.7, 4.1 Hz), 5.46 (d, 1H, *J*=9.7 Hz), 5.84 (s, 1H), 6.82 (d, 1H, *J*=11.7 Hz), 7.05–7.50 (m, 9H), 7.73–7.96 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 33.6 (t), 36.7 (q), 38.2 (q), 56.5 (d), 71.8 (d), 77.7 (d), 122.1 (d), 122.9 (d), 125.0 (d), 126.0 (d), 126.4 (d), 126.5 (d), 127.9 (d), 128.3 (d), 128.6 (d), 129.7 (d and s), 133.6 (s), 135.6 (s), 136.1 (s), 171.5 (s), 173.9 (s). Anal. Calcd for $C_{24}H_{24}N_2O_3$: C, 74.21%; H, 6.23%; N, 7.21%. Found: C, 74.32%; H, 6.22%; N, 7.13%.

*4.3.17. (2S,4S,5R)-1-Benzoyl-4-hydroxy-N,N-dimethyl-5-(naphthalen-2-yl)pyrrolidine-2-carboxamide (**5h**).* White solid; R_f 0.3 (ethyl acetate); mp 255–256 °C (recryst from CH_2Cl_2); $[\alpha]_D^{21}$ −209 (*c* 1.05, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.93 (d, 1H, *J*=14.2 Hz), 2.37–2.45 (m, 1H), 3.12 (s, 3H), 3.47 (s, 3H), 4.27 (dd, 1H, *J*=11.5, 4.2 Hz), 5.32 (s, 1H), 5.45 (d, 1H, *J*=9.5 Hz), 6.80 (d, 1H, *J*=11.5 Hz), 7.11–7.91 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 33.3 (t), 36.7 (q), 38.2 (q), 56.2 (d), 74.0 (d), 78.8 (d), 123.4 (d), 123.5 (d), 126.1 (d), 126.48 (d), 126.52 (d), 127.6 (d), 127.7 (d), 127.9 (d), 128.7 (d), 129.7 (d), 132.5 (s), 133.1 (s), 135.7 (s), 138.1 (s), 171.7 (s), 178.8 (s). Anal. Calcd for $C_{24}H_{24}N_2O_3$: C, 74.21%; H, 6.23%; N, 7.21%. Found: C, 74.26%; H, 6.25%; N, 7.05%.

*4.3.18. (2S,4R,5R)-1-Benzoyl-4-hydroxy-N,N-dimethyl-5-phenylpyrrolidine-2-carboxamide (**6a**).* White solid; R_f 0.1 (ethyl acetate); mp 218–219 °C (recryst from ethyl acetate); $[\alpha]_D^{25}$ −56.6 (*c* 1.03, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.45 (d, 0.8H, *J*=7.6 Hz), 1.52 (d, 0.2H, *J*=4.8 Hz), 2.12–2.24 (m, 2H), 2.56 (s, 0.6H), 2.62 (s, 0.6H), 3.04 (s, 2.4H), 3.26 (s, 2.4H), 4.59–4.65 (m, 0.2H), 4.78–4.86 (m, 0.8H), 5.07–5.11 (m, 1H), 5.35 (dd, 0.8H, *J*=3.8, 8.4 Hz), 5.49 (d, 0.2H, *J*=5.8 Hz), 6.95–7.50 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 34.2 (t), 36.2 (q), 37.3 (q), 55.4 (d), 66.6 (d), 71.4 (d), 126.4 (d), 127.60 (d), 127.62 (d), 128.2 (d), 129.2 (d), 136.5 (s), 137.6 (s), 171.2 (s), 171.5 (s). Anal. Calcd

for $C_{20}H_{22}N_2O_3$: C, 70.99%; H, 6.55%; N, 8.28%. Found: C, 71.08%; H, 6.60%; N, 8.12%.

*4.3.19. (2S,4R,5R)-1-Benzoyl-4-hydroxy-5-(4-methoxyphenyl)-N,N-dimethylpyrrolidine-2-carboxamide (**6b**).* White solid; R_f 0.2 (ethyl acetate/ethanol=10:1); mp 165–167 °C (recryst from hexanes/ethyl acetate=1:5); $[\alpha]_D^{21}$ −75.2 (*c* 1.21, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.22–1.30 (m, 0.2H), 2.00–2.31 (m, 2.8H), 2.54 (s, 0.6H), 2.57 (s, 0.6H), 3.00 (s, 2.4H), 3.22 (s, 2.4H), 3.74 (s, 2.4H), 3.78 (s, 0.6H), 4.54–4.60 (m, 0.2H), 4.74 (dd, 0.8H, *J*=14.4, 7.0 Hz), 4.99 (d, 0.8H, *J*=7.0 Hz), 5.03 (dd, 0.2H, *J*=7.8, 5.2 Hz), 5.27–5.31 (m, 0.8H), 5.42 (d, 0.2H, *J*=6.0 Hz), 6.70–7.46 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 34.1 (t), 36.1 (q), 37.2 (q), 55.1 (q), 55.3 (d), 66.0 (d), 71.3 (d), 113.7 (d), 126.4 (d), 127.6 (d), 128.7 (d), 129.1 (s), 129.5 (d), 136.5 (s), 159.0 (s), 171.2 (s), 171.5 (s). Anal. Calcd for $C_{21}H_{24}N_2O_4$: C, 68.46%; H, 6.57%; N, 7.60%. Found: C, 68.47%; H, 6.57%; N, 7.54%.

*4.3.20. (2S,4R,5R)-1-Benzoyl-4-hydroxy-5-(3-methoxyphenyl)-N,N-dimethylpyrrolidine-2-carboxamide (**6c**).* White solid; R_f 0.25 (ethyl acetate/ethanol=10:1); mp 197–198 °C (recryst from CH_2Cl_2); $[\alpha]_D^{24}$ −87.3 (*c* 1.00, $CHCl_3$); IR (KBr) 3430, 1636, 1613, 1603, 1582, 795, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.68 (d, 1H, *J*=4.2 Hz), 2.08–2.31 (m, 2H), 2.56 (s, 0.6H), 2.59 (s, 0.6H), 3.02 (s, 2.4H), 3.25 (s, 2.4H), 3.72 (s, 2.4H), 3.81 (s, 0.6H), 4.59–4.65 (m, 0.2H), 4.76–4.86 (m, 0.8H), 5.00–5.08 (m, 1H), 5.32 (dd, 0.8H, *J*=7.6, 4.4 Hz), 5.44–5.48 (m, 0.2H), 6.45–7.51 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 34.4 (t), 36.2 (q), 37.3 (q), 55.2 (q), 55.4 (d), 66.5 (d), 71.6 (d), 113.1 (d), 113.6 (d), 119.9 (d), 126.5 (d), 127.7 (d), 129.2 (d), 129.5 (d), 136.6 (s), 139.2 (s), 159.6 (s), 171.2 (s), 171.5 (s). Anal. Calcd for $C_{21}H_{24}N_2O_4$: C, 68.46%; H, 6.57%; N, 7.60%. Found: C, 68.40%; H, 6.55%; N, 7.51%.

*4.3.21. (2S,4R,5R)-1-Benzoyl-4-hydroxy-5-(2-methoxyphenyl)-N,N-dimethylpyrrolidine-2-carboxamide (**6d**).* White solid; R_f 0.3 (ethyl acetate/ethanol=10:1); mp 171–172 °C (recryst from hexanes/ethyl acetate=1:5); $[\alpha]_D^{24}$ −37.2 (*c* 1.06, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.93 (br s, 1H), 2.06–2.30 (m, 2H), 2.57 (s, 0.6H), 2.61 (s, 0.6H), 3.04 (s, 2.4H), 3.26 (s, 2.4H), 3.61 (s, 2.4H), 3.90 (s, 0.6H), 4.77 (dd, 0.2H, *J*=12.3, 6.2 Hz), 4.85 (dd, 0.8H, *J*=14.1, 6.8 Hz), 5.06 (dd, 0.2H, *J*=8.2, 5.0 Hz), 5.30–5.36 (m, 0.8H), 5.63 (d, 0.8H, *J*=6.8 Hz), 5.93 (d, 0.2H, *J*=6.2 Hz), 6.65–7.51 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 34.3 (t), 36.2 (q), 37.4 (q), 55.58 (d), 55.60 (q), 70.1 (d), 71.5 (d), 110.7 (d), 120.9 (d), 126.3 (s), 126.4 (d), 127.4 (d), 128.2 (d), 128.9 (d), 129.0 (d), 136.6 (s), 156.6 (s), 171.1 (s), 171.6 (s). Anal. Calcd for $C_{21}H_{24}N_2O_4$: C, 68.46%; H, 6.57%; N, 7.60%. Found: C, 68.50%; H, 6.58%; N, 7.67%.

*4.3.22. (2S,4R,5R)-1-Benzoyl-5-(4-fluorophenyl)-4-hydroxy-N,N-dimethylpyrrolidine-2-carboxamide (**6e**).* White solid; R_f 0.3 (ethyl acetate/ethanol=10:1); mp 243–245 °C (recryst from ethyl acetate/ethanol=1:1); $[\alpha]_D^{24}$ −74.8 (*c* 0.82, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 2.11–2.31 (m, 2H), 2.56 (s, 0.6H), 2.61 (s, 0.6H), 3.03 (s, 2.4H), 3.25 (s, 2.4H), 4.60 (dd, 0.2H, *J*=11.5, 5.2), 4.80 (dd, 0.8H, *J*=14.3, 6.7 Hz), 5.06–5.10 (m, 1H), 5.34 (dd, 0.8H, *J*=7.7, 3.1 Hz), 5.46 (d, 0.2H, *J*=6.6 Hz), 6.86–7.48 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 34.3 (t), 36.2 (q), 37.3 (q), 55.4 (d), 66.1 (d), 71.5 (d), 115.3 (d, J_{CCF}=21.1 Hz), 126.4 (d), 127.1 (d), 127.8 (d), 129.3 (d, J_{CCCF}=8.6 Hz), 133.4 (s, J_{CCCCF}=2.6 Hz), 136.5 (s), 162.2 (s, J_{CF}=247.4 Hz), 171.3 (s), 171.5 (s). Anal. Calcd for $C_{20}H_{21}FN_2O_3$: C, 67.40%; H, 5.94%; N, 7.86%. Found: C, 67.56%; H, 6.09%; N, 7.72%.

*4.3.23. (2S,4R,5R)-1-Benzoyl-5-(4-cyanophenyl)-4-hydroxy-N,N-dimethylpyrrolidine-2-carboxamide (**6f**).* White solid; R_f 0.35 (ethyl acetate/ethanol=10:1); mp 247–248 °C (recryst from CH_2Cl_2); $[\alpha]_D^{23}$ −107 (*c* 1.06, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.21–1.36 (m, 1H), 2.09–2.40 (m, 2H), 2.56 (s, 0.9H), 2.60 (s, 0.9H), 3.01 (s, 2.1H), 3.52 (s, 2.1H), 4.66 (dd, 0.3H, *J*=11.3, 5.6 Hz), 4.88 (dd, 0.7H, *J*=14.3, 6.9 Hz), 5.08 (dd, 0.3H, *J*=7.7, 5.6 Hz), 5.12 (d, 0.7H, *J*=6.9 Hz), 5.34 (dd, 0.7H, *J*=8.3, 3.4 Hz), 5.46 (d, 0.3H, *J*=5.6 Hz), 7.02–7.72 (m, 9H); ^{13}C NMR (DMSO-d_6) δ 33.7 (t), 35.6 (q), 36.1 (q), 36.5 (t), 36.6 (q), 37.1 (q), 55.7 (d), 57.9 (d), 64.9 (d), 66.4 (d), 69.7 (d), 70.7 (d), 109.7 (s), 110.0 (s), 119.1 (s), 119.4 (s), 126.4 (d), 127.1 (d), 128.1 (d), 128.2 (d), 128.8 (d), 129.1 (d), 129.6 (d), 130.0 (d), 131.6 (d), 131.7 (d), 136.9 (s), 145.3 (s), 170.5 (s), 171.1 (s), 171.4 (s), 171.6 (s). Anal. Calcd for $C_{21}H_{21}N_3O_3$: C, 69.41%; H, 5.82%; N, 11.56%. Found: C, 69.50%; H, 5.83%; N, 11.40%.

*4.3.24. (2S,4R,5R)-1-Benzoyl-4-hydroxy-N,N-dimethyl-5-(naphthalen-1-yl)pyrrolidine-2-carboxamide (**6g**).* Colorless paste; R_f 0.3 (ethyl acetate/ethanol=10:1); $[\alpha]_D^{25}$ 39.9 (*c* 1.16, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.95–2.33 (m, 3H), 2.52 (s, 0.6H), 2.59 (s, 0.6H), 3.00 (s, 2.4H), 3.22 (s, 2.4H), 4.77–5.00 (m, 1H), 5.08–5.17 (m, 0.2H), 5.33–5.41 (m, 0.8H), 5.92–6.04 (m, 0.8H), 6.34 (d, 0.2H, *J*=5.5 Hz), 6.79–7.91 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 34.3 (t), 35.7 (q), 36.2 (q), 36.5 (q), 37.1 (t), 37.3 (q), 55.5 (d), 58.1 (d), 62.2 (d), 70.4 (d), 71.5 (d), 122.8 (d), 123.4 (d), 124.8 (d), 125.1 (d), 125.6 (d), 125.7 (d), 126.1 (d), 126.2 (d), 127.1 (d), 127.2 (d), 127.4 (d), 127.9 (d), 128.1 (d), 128.3 (d), 128.4 (d), 128.7 (d), 128.9 (d), 129.8 (d), 131.3 (s), 133.2 (s), 133.9 (s), 134.1 (s), 136.2 (s), 171.2 (s), 171.4 (s), 171.6 (s); HRMS (ESI) calcd for $C_{24}H_{25}N_2O_3$ $(M+H)^+$ 389.1867, found 389.1860.

*4.3.25. (2S,4R,5R)-1-Benzoyl-4-hydroxy-N,N-dimethyl-5-(naphthalen-2-yl)pyrrolidine-2-carboxamide (**6h**).* White solid; R_f 0.3 (ethyl acetate/ethanol=10:1); mp >300 °C (recryst from ethanol); $[\alpha]_D^{22}$ −158.5 (*c* 0.10, methanol); IR (KBr) 3430, 1645, 1628, 1601, 1578, 835, 764, 706 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.04–1.40 (m, 1H), 2.17–2.43 (m, 2H), 2.59 (s, 0.6H), 2.66 (s, 0.6H), 3.07 (s, 2.4H), 3.31 (s, 2.4H), 4.69–4.73 (m, 0.2H), 4.89–4.97 (m, 0.8H), 5.17–5.21 (m, 0.2H), 5.28 (d, 0.8H, *J*=7.0 Hz), 5.46 (dd, 0.8H, *J*=8.3, 3.7 Hz), 5.67 (d, 0.2H, *J*=5.7 Hz), 6.98–7.18 (m, 5H), 7.37–7.56 (m, 4H), 7.70–7.91 (m, 3H). Anal. Calcd for $C_{24}H_{24}N_2O_3$: C, 74.21%; H, 6.23%; N, 7.21%. Found: C, 74.17%; H, 6.30%; N, 7.16%.

*4.3.26. (4S)-Methyl 5-(dimethylamino)-5-oxo-4-(phenyl(trimethylsilyl)methylamino)pentanoate (**11a**) (8:2 diastereomeric mixture).* Pale yellow paste; R_f 0.75 (hexanes/ethyl acetate=1:1); ^{1}H NMR ($CDCl_3$) δ −0.03 (s, 7.2H), −0.02 (s, 1.8H), 1.57–1.87 (m, 2H), 2.18–2.47 (m, 2H), 2.63 (s, 0.6H), 2.73 (s, 0.6H), 2.77 (s, 2.4H), 3.00 (s, 2.4H), 3.07 (s, 0.8H), 3.23 (s, 0.2H), 3.38–3.47 (m, 1H), 3.63 (s, 2.4H), 3.69 (s, 0.6H), 7.03–7.30 (m, 5H).

*4.3.27. (4S)-Methyl 5-(diethylamino)-5-oxo-4-(phenyl(trimethylsilyl)methylamino)pentanoate (**11b**) (7:3 diastereomeric mixture).* Pale yellow paste; R_f 0.55 (hexanes/ethyl acetate=2:1); ^{1}H NMR ($CDCl_3$) δ −0.04 (s, 2.7H), −0.03 (s, 6.3H), 0.70 (t, 0.9H, *J*=7.3 Hz), 0.82 (t, 2.1H, *J*=7.3 Hz), 0.97 (t, 0.9H, *J*=7.3 Hz), 1.10 (t, 2.1H, *J*=7.3 Hz), 1.60–1.75 (m, 2H), 2.35–2.76 (m, 2H), 2.85–2.95 (m, 1H), 3.01–3.31 (m, 4H), 3.56–3.64 (m, 3.1H), 3.68 (s, 0.9H), 7.03–7.23 (m, 5H); ^{13}C NMR ($CDCl_3$) major: δ −4.0 (q), 13.0 (q), 14.2 (q), 28.5 (t), 30.2 (t), 40.31 (t), 40.9 (t), 51.3 (q), 54.8 (d), 55.6 (d), 125.0 (d), 126.9 (d), 127.7 (d), 142.5 (s), 173.9 (s), 174.0 (s), minor: δ −3.7 (q), 12.7 (q), 13.6 (q), 29.2 (t), 29.6 (t), 40.27 (t), 41.3 (t), 51.3 (q), 56.7 (d), 56.8 (d), 125.1 (d), 127.0 (d), 127.8 (d), 143.2 (s), 174.2 (s), 174.5 (s).

*4.3.28. (2S,5S,6S)-1-Benzoyl-5-hydroxy-N,N-dimethyl-6-phenylpiperidine-2-carboxamide (**12a**).* White solid; R_f 0.25 (ethyl acetate); mp 179–181 °C (recryst from ethyl acetate); $[\alpha]_D^{22}$ 106 (*c* 0.83, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.86–1.95 (m, 1H), 1.97–2.06 (m, 2H), 2.19–2.29 (m, 1H), 2,86 (s, 3H), 3.08 (s, 3H), 3.89 (br s, 1H), 4.12–4.19 (m, 1H), 5,04 (d, 1H, *J*=5.1 Hz), 5.20–5.25 (m, 1H), 7.18–7.34 (m, 8H), 7.56–7.61 (m, 2H); ^{13}C NMR δ 21.5 (t), 26.2 (t), 36.3 (q), 37.2 (q), 49.6 (d), 63.3 (d), 68.6 (d), 126.5 (d), 127.0 (d), 127.9 (d), 128.2 (d), 129.8 (d), 135.9 (s), 138.6 (s), 172.9 (s), 173.5 (s). Anal.

Calcd for $C_{21}H_{24}N_2O_3$: C, 71.57%; H, 6.86%; N, 7.95%. Found: C, 71.60%; H, 6.85%; N, 7.88%.

*4.3.29. (2S,5S,6S)-1-Benzoyl-5-hydroxy-N,N-diethyl-6-phenylpiperidine-2-carboxamide (**12b**).* White solid; R_f 0.3 (hexanes/ethyl acetate=1:2); mp 179–180 °C (recryst from ethyl acetate); $[\alpha]_D^{21}$ 125 (*c* 0.75, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.19 (t, 3H, *J*=7.3 Hz), 1.24 (t, 3H, *J*=7.3 Hz), 1.85–1.97 (m, 2H), 2.11–2.28 (m, 2H), 3.27–3.48 (m, 3H), 3.65–3.76 (m, 1H), 4.16–4.23 (m, 1H), 4.61 (d, 1H, *J*=9.2 Hz), 5.00 (d, 1H, *J*=5.0 Hz), 5.22 (t, 1H, *J*=7.3 Hz), 7.14–7.21 (m, 5H), 7.22–7.30 (m, 3H), 7.48–7.53 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 12.7 (q), 14.3 (q), 21.6 (t), 26.3 (t), 41.3 (t), 42.2 (t), 50.0 (d), 64.1 (d), 68.0 (d), 126.5 (d), 126.7 (d), 127.7 (d), 127.9 (d), 128.0 (d), 129.6 (d), 136.1 (s), 139.6 (s), 172.9 (s), 174.1 (s). Anal. Calcd for $C_{23}H_{28}N_2O_3$: C, 72.60%; H, 7.42%; N, 7.36%. Found: C, 72.68%; H, 7.45%; N, 7.20%.

*4.3.30. ((2S,3S,6S)-3-Hydroxy-6-(methoxymethyl)-2-phenylpiperidin-1-yl)(phenyl)methanone (**12c**).* Colorless paste; R_f 0.3 (hexanes/ethyl acetate=1:1); $[\alpha]_D^{23}$ 91.1 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.66–1.92 (m, 3H), 2.19–2.31 (m, 1H), 2.77–3.02 (m, 5H), 4.08–4.24 (m, 2H), 5.84–6.33 (m, 1H), 7.17–7.74 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 24.4 (t), 24.7 (t), 52.5 (d), 54.9 (d), 58.0 (q), 70.2 (d), 72.0 (t), 126.3 (d), 126.7 (d), 127.9 (d), 128.3 (d), 128.4 (d), 129.2 (d), 136.6 (s), 138.8 (s), 172.8 (s); HRMS (ESI) calcd for $C_{20}H_{24}NO_3$ $(M+H)^+$ 326.1758, found 326.1754.

*4.3.31. (2S,5R,6R)-1-Benzoyl-5-hydroxy-N,N-dimethyl-6-phenylpiperidine-2-carboxamide (**13a**).* White solid; R_f 0.25 (ethyl acetate); mp 215–216 °C (recryst from ethyl acetate); $[\alpha]_D^{22}$ −58.3 (*c* 1.03, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.62 (br s, 1H), 1.36–1.56 (m, 3H), 1.78–1.88 (m, 1H), 2.13 (br s, 3H), 2.66 (br s, 3H), 4.49–4.57 (m, 1H), 5.02–5.08 (m, 1H), 5.21–5.27 (m, 1H), 6.91–7.23 (m, 10H). Anal. Calcd for $C_{21}H_{24}N_2O_3$: C, 71.57%; H, 6.86%; N, 7.95%. Found: C, 71.65%; H, 6.89%; N, 7.82%.

*4.3.32. (2S,5R,6R)-1-Benzoyl-5-hydroxy-N,N-diethyl-6-phenylpiperidine-2-carboxamide (**13b**).* White solid; R_f 0.4 (hexanes/ethyl acetate, 1:5); mp 183–184 °C (recryst from ethyl acetate); $[\alpha]_D^{21}$ −66.0 (*c* 1.01, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.05–2.07 (m, 9H), 2.29–2.47 (m, 1H), 3.16–3.69 (m, 4H), 4.37–4.69 (m, 1H), 4.92–5.40 (m, 2H), 7.03–7.43 (m, 10H); ^{13}C NMR δ ($CDCl_3$) δ 12.7 (q), 13.8 (q), 22.3 (t), 25.0 (t), 40.8 (t), 41.9 (t), 51.6 (d), 62.2 (d), 67.3 (d), 126.6 (d), 126.8 (d), 127.6 (d), 127.9 (d), 128.0 (d), 129.1 (d), 136.5 (s), 139.9 (s), 171.5 (s), 174.2 (s). Anal. Calcd for $C_{23}H_{28}N_2O_3$: C, 72.60%; H, 7.42%; N, 7.36%. Found: C, 72.74%; H, 7.51%; N, 7.21%.

*4.3.33. ((2S,3R,6R)-3-Hydroxy-6-(methoxymethyl)-2-phenylpiperidin-1-yl)(phenyl)methanone (**13c**).* Colorless paste; R_f 0.3 (hexanes/ethyl acetate=1:1); $[\alpha]_D^{24}$ −122 (*c* 1.01, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.50–1.96 (m, 3H), 2.07–2.17 (m, 1H), 3.41 (s, 3H), 3.54–3.64 (m, 1H), 3.80–3.85 (m, 1H), 4.29–4.36 (m, 1H), 4.42–4.50 (m, 1H), 4.70–4.78 (m, 1H), 7.19–7.73 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 21.4 (t), 24.6 (t), 27.4 (d), 59.1 (q), 67.7 (d), 70.2 (d), 72.2 (t), 126.3 (d), 126.8 (d), 128.2 (d), 128.4 (d), 129.9 (d), 130.7 (d), 135.6 (s), 138.5 (s), 175.8 (s); HRMS (ESI) calcd for $C_{20}H_{24}NO_3$ $(M+H)^+$ 326.1758, found 326.1751.

4.4. O-Benzoylation of 12c and 13c

To the 1:1 mixture of **12c** and **13c** (143 mg, 0.44 mmol) was added pyridine (1 mL) and benzoyl chloride (0.12 mL, 1 mmol). The solution was stirred at 25 °C for 12 h and then evaporated in vacuo. The residue was purified by column chromatography on silica gel (hexanes/ethyl acetate) to give **14** and **15** in quantitative yields, respectively.

*4.4.1. (2S,3S,6S)-1-Benzoyl-6-(methoxymethyl)-2-phenylpiperidin-3-yl benzoate (**14**).* White solid; R_f 0.6 (hexanes/ethyl acetate=2:1); mp 114–115 °C (recryst from hexanes/ethyl acetate=2:1); $[\alpha]_D^{20}$ 76 (*c* 1.07, $CHCl_3$); IR (KBr) 1715, 1628, 1601, 1582, 727, 718, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.81–1.98 (m, 2H), 2.12–2.21 (m, 1H), 2.40–2.54 (m, 1H), 2.79–2.97 (m, 5H), 4.00–4.59 (m, 1H), 5.48–5.61 (m, 1H), 6.10–6.60 (m, 1H), 7.24–8.01 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 22.3 (t), 24.9 (t), 52.4 (d), 58.0 (q), 71.6 (t), 72.2 (d), 126.5 (d), 127.0 (d), 128.0 (d), 128.1 (d), 128.3 (d), 128.4 (d), 129.3 (d), 129.5 (d), 129.7 (s), 133.1 (d), 136.3 (s), 138.5 (s), 165.3 (s), 172.4 (s). Anal. Calcd for $C_{27}H_{27}NO_4$: C, 75.50%; H, 6.34%; N, 3.26%. Found: C, 75.52%; H, 6.31%; N, 3.20%.

*4.4.2. (2S,3R,6R)-1-Benzoyl-6-(methoxymethyl)-2-phenylpiperidin-3-yl benzoate (**15**).* Colorless paste; R_f 0.5 (hexanes/ethyl acetate=2:1); $[\alpha]_D^{21}$ −56.8 (*c* 1.24, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.87–2.21 (m, 4H), 3.37 (s, 3H), 3.66–3.94 (m, 2H), 4.24–4.36 (m, 1H), 5.23 (d, 1H, *J*=4.5 Hz), 5.58–5.66 (m, 1H), 7.11–8.10 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 21.3 (t), 23.0 (t), 52.6 (d), 58.9 (q), 60.3 (d), 71.2 (d), 73.6 (t), 126.95 (d), 127.05 (d), 128.2 (d), 128.26 (d), 128.29 (d), 129.4 (d), 129.7 (s), 129.87 (d), 129.90 (d), 130.0 (d), 136.5 (s), 138.4 (s), 165.3 (s), 174.2 (s); HRMS (ESI) calcd for $C_{27}H_{28}NO_4$ $(M+H)^+$ 430.2020, found 430.2011.

4.5. Typical procedure for electroreduction of imino esters 1 and subsequent transformation to 8

After electroreduction of **1a** (1 mmol) was carried out as described above, the catholyte was evaporated in vacuo. The residue was dissolved in Et_2O (20 mL) and insoluble solid was filtered off. After the solvent was removed, the residue was dissolved in dioxane (5 mL) and 1 M HCl (5 mL). The mixture was stirred at 25 °C for 12 h with vigorous stirring under open-air conditions, and then the solvent was evaporated in vacuo. The residue was purified by column chromatography on silica gel (hexanes/ethyl acetate) to give **7a** in 52% yield.

To a solution of the crude **7a** in dioxane (5 mL) were added benzoyl chloride (0.12 mL, 1 mmol) and TEA (0.21 mL, 1.5 mmol) at 25 °C. The mixture was stirred for 6 h, diluted with water (10 mL), and then extracted with ethyl acetate three times. After the solvent was removed, the residue was purified by column chromatography on silica gel (hexanes/ethyl acetate) to give **8a** in 54% yield.

*4.5.1. 4-Hydroxy-N,N-dimethyl-5-phenyl-1H-pyrrole-2-carboxamide (**7a**).* Pale yellow solid; R_f 0.5 (hexanes/ethyl acetate=1:5); mp 246–248 °C (recryst from methanol); IR (KBr) 3229, 1605, 1568, 1539, 1526, 1489, 773, 745, 698, 691, 662 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 2.86 (br s, 6H), 5.89–5.93 (m, 1H), 6.84–6.90 (m, 1H), 7.04–7.11 (m, 2H), 7.64–7.69 (m, 2H), 8.67 (s, 1H), 10.63 (br s, 1H); ^{13}C NMR (DMSO-d_6) δ 37.3 (q), 103.4 (d), 116.9 (s), 121.2 (s), 124.5 (d), 125.0 (d), 128.3 (d), 132.1 (s), 142.1 (s), 162.3 (s). Anal. Calcd for $C_{20}H_{18}N_2O_3$: C, 71.84%; H, 5.43%; N, 8.38%. Found: C, 71.89%; H, 5.41%; N, 8.28%.

*4.5.2. 5-(Dimethylcarbamoyl)-2-phenyl-1H-pyrrol-3-yl benzoate (**8a**).* White solid; R_f 0.65 (hexanes/ethyl acetate=1:5); mp 181–183 °C (recryst from ethyl acetate); IR (KBr) 3204, 1728, 1601, 1570, 1520, 1489, 826, 760, 704, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.15 (br s, 3H), 3.34 (br s, 3H), 6.80–6.88 (m, 1H), 7.24–7.32 (m, 1H), 7.35–7.44 (m, 2H), 7.48–7.57 (m, 2H), 7.61–7.71 (m, 3H), 8.18–8.26 (m, 2H), 10.08 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 36.8 (q), 38.9 (q), 107.4 (d), 121.5 (s), 123.5 (s), 126.1 (d), 127.2 (d), 128.57 (d), 128.60 (d), 129.4 (s), 130.0 (s), 130.1 (d), 133.5 (d), 134.0 (s), 162.2 (s), 164.6 (s). Anal. Calcd for $C_{27}H_{22}N_2O_4$: C, 73.96%; H, 5.06%; N, 6.39%. Found: C, 74.07%; H, 5.10%; N, 6.25%.

*4.5.3. 5-(Dimethylcarbamoyl)-2-(4-methoxyphenyl)-1H-pyrrol-3-yl benzoate (**8b**).* White solid; R_f 0.6 (hexanes/ethyl acetate=1:5); mp 147–149 °C (recryst from hexanes/ethyl acetate=1:5); ^{1}H NMR

($CDCl_3$) δ 3.23 (br s, 6H), 3.80 (s, 3H), 6.78–6.98 (m, 3H), 7.47–7.68 (m, 5H), 8.16–8.24 (m, 2H), 10.08 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 36.9 (q), 38.4 (q), 55.2 (q), 107.4 (d), 114.2 (d), 120.9 (s), 122.8 (s), 123.5 (s), 127.5 (d), 128.6 (d), 129.5 (s), 130.0 (d), 133.4 (s), 133.5 (d), 158.9 (s), 162.2 (s), 164.7 (s). Anal. Calcd for $C_{28}H_{24}N_2O_5$: C, 71.78%; H, 5.16%; N, 5.98%. Found: C, 71.82%; H, 5.18%; N, 5.85%.

*4.5.4. 5-(Dimethylcarbamoyl)-2-(3-methoxyphenyl)-1H-pyrrol-3-yl benzoate (**8c**).* White solid; R_f 0.6 (hexanes/ethyl acetate=1:5); mp 81–83 °C (recryst from hexanes/ethyl acetate=1:5); ^{1}H NMR ($CDCl_3$) δ 3.02–3.49 (m, 6H), 3.74 (s, 3H), 6.79–6.86 (m, 2H), 7.17–7.68 (m, 6H), 8.18–8.25 (m, 2H), 9.83 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 36.8 (q), 38.8 (q), 55.1 (q), 107.5 (d), 111.0 (d), 113.6 (d), 118.3 (d), 121.5 (s), 123.2 (s), 128.6 (d), 129.4 (s), 129.8 (d), 130.1 (d), 131.2 (s), 133.6 (d), 134.3 (s), 159.9 (s), 162.0 (s), 164.6 (s). Anal. Calcd for $C_{28}H_{24}N_2O_5$: C, 71.78%; H, 5.16%; N, 5.98%. Found: C, 71.77%; H, 5.21%; N, 5.92%.

*4.5.5. 5-(Dimethylcarbamoyl)-2-(2-methoxyphenyl)-1H-pyrrol-3-yl benzoate (**8d**).* White solid; R_f 0.65 (hexanes/ethyl acetate=1:5); mp 143–144 °C (recryst from hexanes/ethyl acetate=1:5); ^{1}H NMR ($CDCl_3$) δ 3.26 (br s, 6H), 3.93 (s, 3H), 6.73–7.87 (m, 9H), 8.17–8.25 (m, 1H), 10.43 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 37.6 (q), 55.6 (q), 106.5 (d), 111.4 (d), 118.5 (s), 120.26 (s), 120.34 (s), 121.0 (d), 128.1 (d), 128.3 (d), 128.6 (d), 129.5 (s), 130.0 (d), 133.5 (d), 134.5 (s), 155.6 (s), 161.9 (s), 164.6 (s). Anal. Calcd for $C_{28}H_{24}N_2O_5$: C, 71.78%; H, 5.16%; N, 5.98%. Found: C, 71.92%; H, 5.16%; N, 5.80%.

*4.5.6. 5-(Dimethylcarbamoyl)-2-(4-fluorophenyl)-1H-pyrrol-3-yl benzoate (**8e**).* Yellow solid; R_f 0.5 (hexanes/ethyl acetate=1:5); mp 194–195 °C (recryst from hexanes/ethyl acetate=1:2); ^{1}H NMR ($CDCl_3$) δ 3.12 (br s, 3H), 3.34 (br s, 3H), 6.78–6.84 (m, 1H), 7.02–7.12 (m, 2H), 7.48–7.71 (m, 5H), 8.14–8.24 (m, 2H), 10.44 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 37.1 (q), 39.0 (q), 107.4 (d), 115.5 (d, J_{CCF}=22.1 Hz), 121.5 (s), 123.0 (s), 126.4 (s, J_{CCCCF}=2.9 Hz), 128.1 (d, J_{CCCF}=7.7 Hz), 128.6 (d), 129.3 (s), 130.0 (d), 133.5 (d), 133.8 (s), 161.9 (s, J_{CF}=247.8 Hz), 162.3 (s), 164.6 (s). Anal. Calcd for $C_{27}H_{21}FN_2O_4$: C, 71.04%; H, 4.64%; N, 6.14%. Found: C, 71.18%; H, 4.71%; N, 6.12%.

*4.5.7. 5-(Dimethylcarbamoyl)-2-(4-cyanophenyl)-1H-pyrrol-3-yl benzoate (**8f**).* White solid; R_f 0.55 (hexanes/ethyl acetate=1:5); mp 233–234 °C (recryst from hexanes/ethyl acetate=1:5); ^{1}H NMR ($CDCl_3$) δ 3.11 (br s, 3H), 3.38 (br s, 3H), 6.82–6.85 (m, 1H), 7.51–7.87 (m, 7H), 8.16–8.29 (m, 2H), 11.08 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 36.9 (q), 39.1 (q), 107.7 (d), 110.0 (s), 118.8 (s), 121.7 (s), 123.2 (s), 126.3 (d), 128.7 (d), 129.0 (s), 130.0 (d), 132.3 (d), 133.8 (d), 134.5 (s), 135.6 (s), 162.2 (s), 164.3 (s). Anal. Calcd for $C_{28}H_{21}N_3O_4$: C, 72.56%; H, 4.57%; N, 9.07%. Found: C, 72.48%; H, 4.49%; N, 8.97%.

*4.5.8. 5-(Dimethylcarbamoyl)-2-(naphthalen-1-yl)-1H-pyrrol-3-yl benzoate (**8g**).* White solid; R_f 0.65 (hexanes/ethyl acetate=1:5); mp 236–238 °C (recryst from ethyl acetate); ^{1}H NMR ($CDCl_3$) δ 2.70–3.60 (m, 6H), 5.00–5.25 (m, 0.3H), 6.33–6.37 (m, 0.3H), 6.88–6.91 (m, 0.7H), 7.24–8.07 (m, 11.7H), 9.47–9.62 (m, 0.3H), 10.00–10.21 (m, 0.7H); ^{13}C NMR ($CDCl_3$) δ 36.7 (q), 38.5 (q), 106.7 (d), 121.9 (s), 122.8 (s), 125.2 (d), 125.9 (d), 126.0 (d), 126.5 (d), 127.8 (s), 128.0 (d), 128.2 (d), 128.3 (d), 128.7 (d), 129.3 (s), 129.9 (d), 131.5 (s), 133.2 (d), 133.7 (s), 134.7 (s), 162.0 (s), 164.6 (s). Anal. Calcd for $C_{31}H_{24}N_2O_4$: C, 76.21%; H, 4.95%; N, 5.73%. Found: C, 76.20%; H, 4.92%; N, 5.68%.

*4.5.9. 5-(Dimethylcarbamoyl)-2-(naphthalen-2-yl)-1H-pyrrol-3-yl benzoate (**8h**).* White solid; R_f 0.6 (hexanes/ethyl acetate=1:5); mp 183–185 °C (recryst from hexanes/ethyl acetate=1:5); ^{1}H NMR ($CDCl_3$) δ 3.15 (br s, 3H), 3.35 (br s, 3H), 6.87–6.93 (m, 1H), 7.40–7.91 (m, 9H), 8.08–8.14 (m, 1H), 8.21–8.29 (m, 2H), 10.16 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 36.4 (q), 38.8 (q), 107.5 (d), 121.8 (s), 123.7 (s), 124.3 (d), 125.1 (d), 125.9 (d), 126.2 (d), 127.52 (d), 127.54 (s), 127.9 (d), 128.1 (d), 128.6 (d), 129.4 (s), 130.0 (d), 132.3 (s), 133.3 (s), 133.5 (d), 134.5 (s), 162.3 (s), 164.5 (s). Anal. Calcd for $C_{31}H_{24}N_2O_4$: C, 76.21%; H, 4.95%; N, 5.73%. Found: C, 76.32%; H, 5.02%; N, 5.63%.

4.6. 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 SIR-97 and refined with SHELXL-97. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. All calculations were performed with the YADOKARI-XG software package. Crystal data are as follows: CCDC 862781–862792 contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

*4.6.1. Crystal data for **4a** (CCDC 862784).* $C_{20}H_{22}N_2O_3$, FW=338.40, mp 194–196 °C, orthorhombic, $P2_12_12_1$ (no. 19), colorless block, a=6.2349(12) Å, b=9.3862(16) Å, c=29.881(5) Å, V=1748.7(5) Å^3, T=298 K, Z=4, D_{calcd}=1.285 g/cm^3, μ=0.87 cm^{-1}, GOF=0.923.

*4.6.2. Crystal data for **4e** (CCDC 862785).* $C_{20}H_{21}FN_2O_3$, FW=356.39, mp 259–260 °C, orthorhombic, $P2_12_12_1$ (no. 19), colorless block, a=6.2101(7) Å, b=9.4330(13) Å, c=29.665(3) Å, V=1737.8(4) Å^3, T=298 K, Z=4, D_{calcd}=1.362 g/cm^3, μ=0.99 cm^{-1}, GOF=1.015.

*4.6.3. Crystal data for **4g** (CCDC 862786).* $C_{24}H_{24}N_2O_3$, FW=388.45, mp 269–271 °C, orthorhombic, $P2_12_12_1$ (no. 19), colorless block, a=9.4429(13) Å, b=9.5870(14) Å, c=22.697(3) Å, V=2054.7(5) Å^3, T=296 K, Z=4, D_{calcd}=1.256 g/cm^3, μ=0.83 cm^{-1}, GOF=0.946.

*4.6.4. Crystal data for **5a** (CCDC 862787).* $C_{20}H_{22}N_2O_3$, FW=338.40, mp 206–207 °C, orthorhombic, $P2_12_12_1$ (no. 19), colorless block, a=5.8642(10) Å, b=9.5412(17) Å, c=31.703(5) Å, V=1773.8(5) Å^3, T=298 K, Z=4, D_{calcd}=1.267 g/cm^3, μ=0.86 cm^{-1}, GOF=1.020.

*4.6.5. Crystal data for **5b** (CCDC 862788).* $C_{21}H_{24}N_2O_4$, FW=368.42, mp 201–202 °C, orthorhombic, $P2_12_12_1$ (no. 19), colorless block, a=16.140 Å, b=6.064 Å, c=19.062 Å, V=1865.7 Å^3, T=298 K, Z=4, D_{calcd}=1.312 g/cm^3, μ=0.91 cm^{-1}, GOF=1.043.

*4.6.6. Crystal data for **6c** (CCDC 862789).* $C_{21}H_{24}N_2O_4$, FW=368.42, mp 197–198 °C, orthorhombic, $P2_12_12_1$ (no. 19), colorless block, a=9.681(3) Å, b=13.873(6) Å, c=14.908(7) Å, V=2002.3(15) Å^3, T=298 K, Z=4, D_{calcd}=1.222 g/cm^3, μ=0.85 cm^{-1}, GOF=1.017.

*4.6.7. Crystal data for **6h** (CCDC 862790).* $C_{24}H_{24}N_2O_3$, FW=388.45, mp >300 °C, orthorhombic, $P2_12_12_1$ (no. 19), colorless block, a=14.1824(9) Å, b=14.2274(11) Å, c=10.1258(7) Å, V=2043.2(2) Å^3, T=298 K, Z=4, D_{calcd}=1.263 g/cm^3, μ=0.84 cm^{-1}, GOF=1.015.

*4.6.8. Crystal data for **7a** (CCDC 862791).* $C_{13}H_{14}N_2O_2$, FW=230.26, mp 246–248 °C, orthorhombic, *Pbcn* (no. 60), colorless block, a=9.5243(7) Å, b=11.1522(7) Å, c=22.0081(13) Å, V=2337.6(3) Å^3, T=298 K, Z=8, D_{calcd}=1.309 g/cm^3, μ=0.90 cm^{-1}, GOF=1.053.

*4.6.9. Crystal data for **8a** (CCDC 862792).* $C_{20}H_{18}N_2O_3$, FW=334.36, mp 181–183 °C, triclinic, *P*-1 (no. 2), colorless block, a=8.880(9) Å, b=9.593(6) Å, c=10.110(7) Å, α=108.13(8), β=92.52(8), γ=96.80(7), V=809.7(11) Å^3, T=298 K, Z=2, D_{calcd}=1.371 g/cm^3, μ=0.93 cm^{-1}, GOF=1.068.

*4.6.10. Crystal data for **12a** (CCDC 862781).* $C_{21}H_{24}N_2O_3$, FW=352.42, mp 179–181 °C, orthorhombic, $P2_12_12_1$ (no. 19),

colorless block, a=7.9183(4) Å, b=12.2737(8) Å, c=20.0040(10) Å, V=1944.13(19) Å^3, T=298 K, Z=4, D_{calcd}=1.204 g/cm^3, μ=0.81 cm^{-1}, GOF=1.019.

4.6.11. Crystal data for ***13a*** *(CCDC 862782).* $C_{21}H_{24}N_2O_3$, FW=352.42, mp 215–216 °C, monoclinic, $P2_1$ (no. 4), colorless block, a=19.323(5) Å, b=7.8956(14) Å, c=19.226(5) Å, β=18.399(3), V=925.8(4) Å^3, T=298 K, Z=4, D_{calcd}=1.264 g/cm^3, μ=0.85 cm^{-1}, GOF=1.044.

4.6.12. Crystal data for ***14*** *(CCDC 862783).* $C_{27}H_{27}NO_4$, FW=429.50, mp 114–115 °C, monoclinic, $P2_1$ (no. 4), colorless block, a=8.73(3) Å, b=8.26(3) Å, c=16.35(6) Å, β=101.8(3), V=1155(7) Å^3, T=298 K, Z=2, D_{calcd}=1.235 g/cm^3, μ=0.83 cm^{-1}, GOF=1.051.

References and notes

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