Trimethylsilyl Trifluoromethanesulfonate-Catalyzed Reaction of 2-[(Trimethylsilyl)oxy]furan with Nitrones

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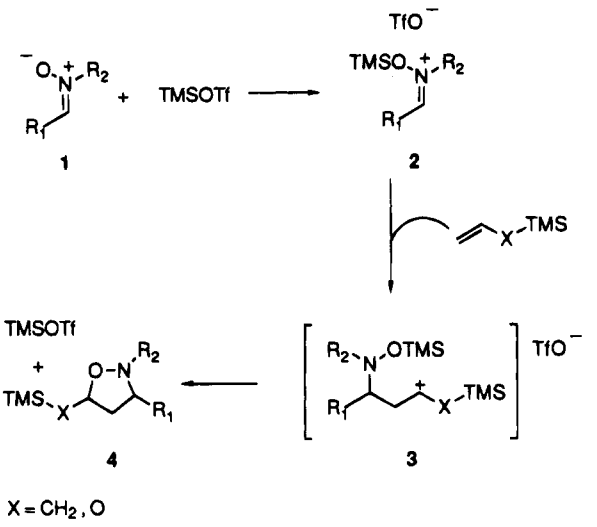
We have recently disclosed that trimethylsilyl trifluoromethanesulfonate (TMSOTf) promotes the formal [1,3]-dipolar cycloaddition of allyltrimethylsilane[1] and silyl enol ethers[2] with aldonitrones **1**. Reaction conditions are more mild than those required by the related thermal processes;[3] in fact, cycloadditions take place at −20 to 20 °C in chlorinated solvents in the presence of a slight molar excess of TMSOTf. We have shown that TMSOTf converts a nitrone into a highly electrophilic *N*-(silyloxy)-iminium ion **2**;[4] the overall process involves nucleophilic addition of the silylated nucleophile[5] to **2** to give the β-silylated carbonium ion **3** followed by a fast ring closure to the isoxazolidine **4**, as depicted in Scheme 1. Even though TMSOTf is regenerated in the cyclization step, it is tightly bound to isoxazolidine **4** and must be used in stoichiometric amount to get good conversions.

As an extension of our previous work, here we report a synthesis of bicyclic isoxazolidines **6** starting from nitrones **1a-j** and 2-[(trimethylsilyl)oxy]furan (**5**) (Scheme 2). 2-[(Trimethylsilyl)oxy]furan (**5**) has been recently recognized to act as a powerful reagent for straightforward syntheses of butenolides and for four-carbon elongation of aldoses;[6] in these reactions **5** undergoes aldolization as well as alkylation exclusively at the C-5 position.[7]

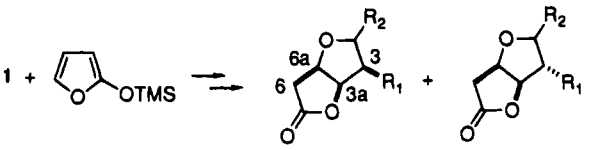
We found that **5** reacts with nitrones at −20 °C in dichloromethane in the presence of 5–35% of TMSOTf to give 2(5*H*)-furanone 5-*N*-hydroxymethanamines **8**. In order to account for the reaction mechanism, we propose the catalytic cycle depicted in Scheme 3.

Lactones **8** were detected, after hydrolysis with water, as the major components by IR (ν_{CO} at 1745 cm^{-1}), ^{1}H NMR (vinylic protons in the 5.5–6.5 ppm region) and GC-MS analysis[8] of the crude reaction mixture. Surprisingly, lactones **8** proved to be labile intermediates; in fact, any attempt to purify them by flash chromatography on silica gel failed, since silica almost quantitatively converted **8** into isoxazolidines **6**. With the exception of nitrone **1j**,[9] in general no more than traces of **8** are eluted from the column. In any case, the regioselectivity of the process is virtually complete since products deriving from attack

Scheme 1

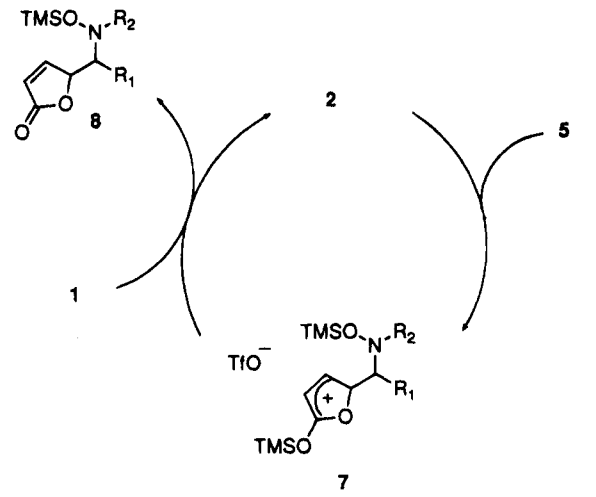


Scheme 2



	R_1	R_2		R_1	R_2
1a:	Ph	Me	**1f:**	Et	Bn
1b:	2-thienyl	Me	**1g:**	*i*-Pr	Bn
1c:	1-naphthyl	Me	**1h:**	*t*-Bu	Bn
1d:	*i*-Pr	Me	**1i:**	Ph	Bn
1e:	*t*-Bu	Me	**1j:**	2-thienyl	Bn

Scheme 3



(1) Dhavale, D. D.; Trombini, C. *Heterocycles* **1992**, *34*, 2253.

(2) (a) Dhavale, D. D.; Trombini, C. *J. Chem. Soc., Chem. Commun.* **1992**, 1268. (b) Camiletti, C.; Dhavale, D. D.; Gentilucci, L.; Trombini, C. *J. Chem. Soc., Perkin Trans. 1* **1993**, 3157.

(3) (a) Niwayama, S.; Dan, S.; Inouye, Y.; Kakisawa, H. *Chem. Lett.* **1985**, 957. (b) Hosomi, A.; Shoji, H.; Sakurai, H. *Chem. Lett.* **1985**, 1049.

(4) NMR spectra of silylated nitrones reveal the presence of a single isomer, whose configuration is *Z*, the same as the starting nitrone, on the basis of NOE evidence.

(5) Kita showed that the more reactive silyl ketene acetals do not require activation of nitrone and directly add to them to give β-(*N*-hydroxy)aminoesters at room temperature, while in the presence of a catalytic amount of ZnI_2 the reaction takes place at −78 °C. (a) Kita, Y.; Itoh, F.; Tamura, O.; Ke, Y. Y.; Tamura, Y. *Tetrahedron Lett.* **1987**, *28*, 1431. (b) Kita, Y.; Tamura, O.; Itoh, F.; Kishino, H.; Miki, T.; Kohno, M.; Tamura, Y. *J. Chem. Soc. Chem. Commun.* **1988**, 761.

(6) (a) Jefford, C. W.; Jaggi, D.; Boukouvalas, J. *Tetrahedron Lett.* **1987**, *28*, 364. (b) Jefford, C. W.; Jaggi, D.; Boukouvalas, J. *Tetrahedron Lett.* **1987**, *28*, 4037. (c) Casiraghi, G.; Colombo, L.; Rassu, G.; Spanu, P. *J. Org. Chem.* **1990**, *55*, 2565. (d) Casiraghi, G.; Colombo, L.; Rassu, G.; Spanu, P. *J. Org. Chem.* **1991**, *56*, 2135. (e) Yoshida, M.; Imai, R.; Komatsu, Y.; Morinaga, Y.; Kamigata, N.; Iyoda, M. *J. Chem. Soc., Perkin Trans. 1* **1993**, 501.

(7) It is worthy of note that the different reactivity of the boron derivative related to **5**, which regioselectively undergoes aldolization at C-3; see; Jefford, C. W.; Jaggi, D.; Boukouvalas.J. *J. Chem. Soc., Chem. Commun.* **1988**, 1595.

0022-3263/94/1959-6843$04.50/0

Table 1. Cycloaddition of 2-[(Trimethylsilyl)oxy]furan with Nitrones[a]

entry	nitrone	TMSOTf (equiv)	t (h)	yield of **6**[b] (%)	*syn*-**6**/*anti*-**6** ratio[b]
1	**1a**	0.062	3	96	84/16
2	**1b**	0.160	2[c]	84	96/4
3	**1c**	0.052	2	85	77/23
4	**1d**	0.259	3	55	45/55
5	**1e**	0.259	6	83	56/44
6	**1f**	0.129	2	65	23/77
7	**1g**	0.052	6	80	12/88
8	**1h**	0.345	24	46	29/71
9	**1i**	0.052	6	90	82/18
10	**1j**	0.166	4	48[d]	95/5

[a] Unless otherwise stated, reactions are carried out at −20 °C in dichloromethane. [b] Determined after purification by flash chromatography. [c] Reaction carried out at 0 °C. [d] The α,β-unsaturated lactone corresponding to desilylated **8j** was isolated in 25% yield (see ref 9).

to the nitrone by C-3 of **5** have never been detected. In order to optimize the recovery of bicyclic isoxazolidines **6** we have worked out a quenching procedure involving hydrolysis of the crude reaction mixture with aqueous trifluoroacetic acid (which in part induces cyclization to **6**), followed by flash chromatography of the crude concentrated extract on silica gel eluting with cyclohexane–ethyl ether mixtures. The results, in terms of isoxazolidines **6** obtained with a series of aliphatic and aromatic nitrones, are collected in Table 1.

Yields of compounds **6** are good to excellent, and in general diastereoisomers *syn*-**6** and *anti*-**6** are easily separated by flash chromatography, the *anti* isomer always showing the higher R_f.

The stereochemical outcome of these reactions deserves comment. While *C*-aryl-*N*-methyl nitrones **1a-c** preferentially lead to the *syn* product (entries 1–3), *C*-alkyl-*N*-benzylnitrones **1f-h** show an inverted preference for the *anti* product (entries 6–8), and *C*-alkyl-*N*-methylnitrones **1d,e** do not exhibit any appreciable selectivity (entries 4,5). Finally, *C*-aryl-*N*-benzylnitrones **1i,j** afford the same level of *syn* selectivity as *C*-aryl-*N*-methylnitrones **1a-c** (entries 9, 10). A possible rationale can be drawn by the analysis of the four conformers **A**–**D** (Figure 1), which correspond to Newman projections relatively to the incipient carbon–carbon bond and are considered as possible transition state (TS) models.

If we consider the *si* face of **5**, TS structures **A** and **B** refer to the attack to the *re* face of **2** and will lead, after cyclization, to *anti*-**6**, while **C** and **D** refer to the *si* face of **2** and lead to *syn*-**6**; **A** and **D** are antiperiplanar TS's, and **B** and **C** are synclinal TS's.

The most favored TS's should be **B** and **D** on purely steric grounds. The lack of selectivity observed when R_2 = Me and R_1 = alkyl means that **B** and **D** do not differ in energy using nitrones **1d-e**, while replacing Bn for Me substituent R_2 (nitrones **1f-h**) significantly favors TS **B**.

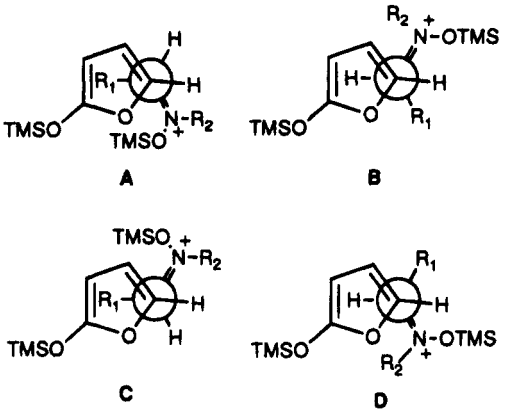


Figure 1. Proposed transition state structures for the coupling reaction of **5** with silylated nitrones **2**.

On the other hand, **C** becomes the lowest TS when R_1 is an aromatic ring (nitrones **1a,b,c,i,j**) thanks to the concurrence of two stabilizing effects, an attractive secondary orbital interaction between the stacked aromatic rings and an attractive electrostatic interaction between the developing positive charge on C-4 of the furan ring and the oxygen atom of **2**.

In conclusion, a simple route to bicyclic isoxazolidines **6** has been worked out starting from nitrones and 2-[(trimethylsilyl)oxy]furan; moreover, depending on the choice of substituents R_1 and R_2 of nitrone, complementary stereochemical courses of the cycloaddition reaction can be achieved. The interest for intermediates **6** lies in the fact that they are highly functionalized chiral building blocks, synthetic equivalents of stereodefined 5-amino-3,4-dihydroxyalkanoic acids.

Experimental Section

^{1}H-NMR and ^{13}C-NMR spectra of $CDCl_3$ solutions were recorded at 300 and 75 MHz, respectively, with a Varian Gemini 300 spectrometer. Chemical shifts are reported in ppm relative to internal standard Me_4Si (δ). NMR spectra of products **6** are reported in Tables 2 and 3. IR spectra were recorded on a Perkin Elmer PE 682 spectrophotometer. Gas chromatographic–mass spectrometric analyses (GC–MS) were performed with HP 5890 instrument connected to a quadrupole mass detector HP 5970 (cross-linked methyl silicone glass capillary column, 0.33-mm film thickness). Analytical thin-layer chromatography (TLC) was performed with Kieselgel 60 F_{254} plates using mixed solvents. Kiesegel 60 (230–400 mesh) was used for flash chromatography. Reactions were performed in oven-dried glassware under an atmosphere of dry argon. Dichloromethane was purified before use (water content 8 + 1 ppm). All nitrones were prepared according to literature procedures;[10] 2-[(trimethylsilyl)-oxy]furan was purchased by Aldrich.

Synthesis of Isoxazolidines *anti*- and *syn*-6a; Typical Procedure. To a stirred solution of nitrone **1a** (135 mg, 1 mmol) and 2-[(trimethylsilyl)oxy]furan (**5**) (0.2 mL, 1.2 mmol) in dry dichloromethane (8 mL) was added at −20 °C TMSOTf (11 μL, 0.062 mmol) in dichloromethane (2 mL). After 3 h, the reaction mixture was quenched with a solution of trifluoroacetic acid (50 μL) in water (1 mL); the two liquid layers were separated and the aqueous phase was extracted with diethyl ether (3 × 10 mL). The combined organic layers were washed with brine (1 mL),

(8) The TMSOTf-catalyzed condensation of nitrones with **5** cannot be properly analyzed by GC since lactones **8** also proved to be thermally unstable, and partially decompose in the injector of a GC–MS instrument (250 °C) into a complex mixture containing cyclized products **6** and products deriving from elimination of hydroxylamine from **8**.

(9) Data for the product deriving from desilylation of **8j**: R_f 0.31 (cyclohexane/diethyl ether 1:1); IR (neat) 3400, 2920, 2860, 1740, 1450, 1180, 1110, 845, 710 cm^{-1}; ^{1}H NMR δ 3.73 (d, 1H, J = 13 Hz, CH_2Ph), 3.91 (d, 1H, J = 13 Hz, CH_2Ph), 4.34 (d, 1H, J = 7.4 Hz, C*H*N), 5.67 (dt, 1H, J = 2.1, 2.1, 7.4 Hz, C*H*O), 6.02 (dd, 1H, J = 2.1, 7.4 Hz, C*H*C=O), 7.00–7.08 (m, 2H, 1ArH + C*H*=CHC=O), 7.25–7.38 (m, 7H, ArH); ^{13}C NMR δ 61.7 (CH_2Ph), 68.1 (*C*HO), 83.1 (*C*HN), 122.2 (*C*HC=O), 126.5, 126.9, 127.6, 128.4, 128.8, 129.5, 134.4, 136.6, (ArC), 155.1 (*C*H=CHC=O), 172.7 (C=O); MS m/z 178 (M^+ - HONBn, 100), 150 (18), 124 (13), 122 (46), 121 (27), 96 (39), 70 (10). Anal. Calcd for $C_{16}H_{15}NO_3S$: C, 63.77; H, 5.02; N, 4.65; S, 10.62. Found: C, 63.97; H, 4.92; N, 4.60; S, 10.39.

Table 2. ^{1}H NMR Data for Compounds 6a–j at 300 MHz

	H-3	H-3a	H-6a	H-6	others
syn-**6a**	3.44 (d, J = 4.3 Hz)	5.20 (dd, J = 4.3, 6.2 Hz)	5.02 (m)	2.87 (d, J = 5.5 Hz, 2H)	7.42–7.25 (m, 5H, PhH), 2.60 (s, 3H, NCH_3)
anti-**6a**	3.75–3.61 (m)	5.15–5.05 (bs)	4.95–4.85 (m)	2.80–2.75 (m, 2H)	7.47 7.32 (m, 5H, PhH), 2.66 (s, 3H, NCH_3)
syn-**6b**	3.76 (d, J = 4.1 Hz)	5.19 (dd, J = 4.1, 6.2 Hz)	5.04 (q, J = 6.2 Hz)	2.88 (d, J = 6.2 Hz, 2 H)	7.42–7.38 (m, 1H, ArH), 7.12–7.07 (m, 1H, ArH), 7.06–7.00 (m, 1H, ArH), 2.61 (s, 3H, NCH_3)
anti-**6b**[a]	4.08–3.93 (m)	5.18–5.01 (bm)	4.98–4.85 (m)	2.85–2.60 (m, 2H)	7.42–7.33 (m, 2H, ArH), 7.11–7.05 (m, 1H, ArH), 2.78 (s, 3H, NCH_3)
syn-**6c**	4.27 (d, J = 4.2 Hz)	5.48 (dd, J = 4.2, 6.6 Hz)	5.12 (dt, J = 3.6, 6.6 Hz)	2.92–2.86 (m, 2H)	8.06–7.93 (m, 1H, ArH), 7.93–7.80 (m, 2H, ArH), 7.60–7.44 (m, 4H, ArH)
anti-**6c**	4.85–4.40 (m)	5.10 (bt, J = 3.7 Hz)	4.90 (bdd, J = 3.7, 7.2 Hz)	2.82 (m, 2H)	8.28–8.20 (m, 1H, ArH), 7.93–7.82 (m, 2H, ArH), 7.72–7.68 (m, 3H, ArH), 7.65–7.42 (m, 1H, ArH)
syn-**6d**	2.29–2.20 (m)	5.21 (dd, J = 4.4, 6.0 Hz)	4.84 (ddd, J = 3.3, 6.0, 6.9 Hz)	2.84–2.64 (m, 2H)	2.69 (s, 3H, NCH_3), 2.04 (oct, J = 7.0 Hz, 1H, $CH(CH_3)_2$), 1.11 (d, J = 7.0 Hz, 3H, $CH(CH_3)_2$), 1.04 (d, J = 7.0 Hz, 3H, $CH(CH_3)_2$)
anti-**6d**	2.56 (dd, J = 2.0, 3.6 Hz)	4.93 (dd, J = 3.6, 4.9 Hz)	4.55 (dt, J = 1.2, 4.9 Hz)	2.84–2.64 (m, 2H)	2.71 (s, 3H, NCH_3), 1.86 (double heptet, J = 2.0, 6.8 Hz, 1H, $CH(CH_3)_2$), 1.06 (d, J = 6.8 Hz, 3H, $CH(CH_3)_2$), 0.97 (d, J = 6.8 Hz, 3H, $CH(CH_3)_2$)
syn-**6e**	2.36 (d, J = 4.7 Hz)	5.23 (bt, J = 4.7 Hz)	4.84 (m)	2.74–2.65 (m, 2H)	2.76 (s, 3H, NCH_3), 1.10 (s, 9H, $C(CH_3)_3$)
anti-**6e**	2.68 (d, J = 1.7 Hz)	4.99 (dd, J = 1.7, 4.3 Hz)	4.54 (dt, J = 1.3, 4.3 Hz)	2.74–2.67 (m, 2H)	2.83 (s, 3H, NCH_3), 1.01 (s, 9H, $C(CH_3)_3$)
syn-**6f**	2.90 (m)	4.90 (dd, J = 3.1, 5.1 Hz)	4.65 (ddd, J = 2.2, 5.1, 5,2 Hz)	2.73 (dd, J = 5.2, 19.0 Hz, 1 H), 2.66 (dd, J = 2.2, 19.0 Hz, 1H)	7.40–7.29 (m, 5H, PhH), 4.08 (d, J = 14.0 Hz, 1H, CH_2Ph), 3.88 (d, J = 14.0 Hz, 1H, CH_2Ph), 1.65–1.50 (m, 2H, CH_2CH_3), 1.09 (t, J = 7.6 Hz, 3H, CH_2CH_3)
anti-**6f**	2.54 (dt, J = 4.4, 8.9 Hz)	5.23 (dd, J = 4.4, 6.3 Hz)	4.86 (ddd, J = 3.2, 6.3, 7.9 Hz)	2.75 (dd, J = 7.9, 19.1 Hz, 1H), 2.65 (dd, J = 3.2, 19.1 Hz, 1H)	7.38–7.26 (m, 5H, PhH), 4.21 (d, J = 14.4 Hz, 1H, CH_2Ph), 3.66 (d, J = 14.4 Hz, 1H, CH_2Ph), 1.65–1.55 (m, 2H, CH_2CH_3), 1.10 (t, J = 7.5 Hz, 3H, CH_2CH_3)
syn-**6g**	2.61 (dd, J = 4.8, 6.9 Hz)	5.26 (dd, J = 4.8, 5.9 Hz)	4.85 (ddd, J = 3.0, 5.9, 6.7 Hz)	2.68 (m, 2H)	7.40–7.25 (m, 5H, PhH), 4.17 (d, J = 14.2 Hz, 1H, CH_2Ph), 3.71 (d, J = 14.2 Hz, 1H, CH_2Ph), 2.19 (oct, J = 6.9 Hz, 1H, $CH(CH_3)_2$), 1.18 (d, J = 6.9 Hz, 3H, $CH(CH_3)_2$), 1.12 (d, J = 6.9 Hz, 3H, $CH(CH_3)_2$)
anti-**6g**	2.88 (dd, J = 3.2, 4.8 Hz)	4.98 (dd, J = 3.2, 4.8 Hz)	4.56 (ddd, J = 2.0, 4.8, 4.8 Hz)	2.68 (m, 2H)	7.40–7.25 (m, 5H, PhH), 4.05 (d, J = 14.1 Hz, 1H, CH_2Ph), 3.87 (d, J = 14.1 Hz, 1H, CH_2Ph), 1.90 (double heptet, J = 4.9, 6.9 Hz, 1H, $CH(CH_3)_2$, 1.09 (d, J = 6.9 Hz, 3H, $CH(CH_3)_2$), 1.04 (d, J = 6.9 Hz, 3H, $CH(CH_3)_2$)
syn-**6h**	2.82 (d, J = 5.2 Hz)	5.30 (t, J = 5.2 Hz)	4.86 (ddd, J = 1.7, 5.2, 6.0 Hz)	2.70 (dd, J = 6.0, 18.6 Hz, 1H), 2.60 (dd, J = 1.7, 18.6 Hz, 1H)	7.42–7.25 (m, 5H, PhH), 4.10 (d, J = 14.0 Hz, 1H, CH_2Ph), 3.88 (d, J = 14.0 Hz, 1H, CH_2Ph), 1.15 (s, 9H, $C(CH_3)_3$)
anti-**6h**	3.07 (d, J = 1.0 Hz)	5.09 (dd, J = 1.0, 4.2 Hz)	4.64 (dt, J = 2.1, 4.2 Hz)	2.83–2.68 (m, 2H)	7.41–7.25 (m, 5H, PhH), 4.17 (d, J = 14.0 Hz, 1H, CH_2Ph), 4.07 (d, J = 14.0 Hz, 1H, CH_2Ph), 1.04 (s, 9H, $C(CH_3)_3$)
syn-**6i**	3.72 (d, J = 4.4 Hz)	5.23 (dd, J = 4.4, 6.2 Hz)	5.01 (dt, J = 4.4, 6.2 Hz)	2.91–2.76 (m, 2H)	7.49–7.22 (m, 10H, PhH), 4.10 (d, J = 14.6 Hz, 1H, CH_2Ph), 3.63 (d, J = 14.6 Hz, 1H, CH_2Ph)
anti-**6i**	4.01–3.90 (m)	5.12–5.05 (m)	4.90–4.83 (m)	2.85–2.70 (m, 2H)	7.49–7.22 (m, 10H, PhH), 3.96 (d, J = 14.3 Hz, 1H, CH_2Ph), 3.78 (d, J = 14.3 Hz, 1H, CH_2Ph)
syn-**6j**	4.05 (d, J = 4.3 Hz)	5.21 (dd, J = 4.3, 6.4 Hz)	5.03 (ddd, J = 3.9, 6.4, 7.9 Hz)	2.90–2.70 (m, 2H)	7.63–7.58 (m, 1H, ArH), 7.44–7.40 (m, 1H, ArH), 7.38–7.24 (m, 3H, ArH), 7.40–7.25 (m, 1H, ArH), 7.08–7.00 (m, 2H, ArH), 4.12 (d, J = 14.5 Hz, 1H, CH_2Ph), 3.62 (d, J = 14.5 Hz, 1H, CH_2Ph)
anti-**6j**[a]	4.10–3.90 (m)	5.18–5.02 (m)	4.98–4.82 (m)	2.84–2.67 (m, 2H)	7.39–7.23 (m, 6H, ArH), 7.12–7.05 (m, 2H, ArH), 4.52–4.25 (m, 1H, CH_2Ph), 3.78 (d, J = 14.0 Hz, 1H, CH_2Ph)

[a] *anti*-**6b** and **anti-6j** were not isolated in a pure form. ^{1}H NMR signals were drawn from the spectra of mixtures of *syn/anti* diastereoisomers enriched in the *syn* compound.

Table 3. ^{13}C NMR Data for Compounds 6a–j at 75 MHz

	C-3	C-3a	C-5	C-6	C-6a	others
syn-**6a**	76.6	87.5	175.0	35.6	75.3	132.6, 129.1, 128.9, 128.5 (PhC), 42.1 (NCH_3)
anti-**6a**	75.7	93.6	174.6	33.8	75.7	129.2, 129.0, 128.6, 127.9 (PhC), 42.9 (NCH_3)
syn-**6b**	72.2	86.5	174.7	35.5	75.5	133.6, 127.8, 127.4, 126.5 (PhC), 42.1 (NCH_3)
syn-**6c**	72.1	86.4	175.9	35.5	75.5	152.6, 133.6, 129.2, 128.5, 126.7, 126.4, 125.7, 125.5, 121.6, 121.5 (ArC), 42.5 (NCH_3)
anti-**6c**	77.2	93.4	174.6	33.7	76.0	134.2, 132.0, 131.5, 128.9, 128.8, 126.8, 126.1, 125.1, 124.6, 123.3 (ArC), 43.7 (NCH_3)
syn-**6d**	76.5[a]	88.0	174.9	35.2	74.6[a]	44.1 (NCH_3), 26.7 ($CH(CH_3)_2$), 20.0 ($CH(CH_3)_2$), 18.9 ($CH(CH_3)_2$)
anti-**6d**	80.0	88.2	174.9	34.0	75.5	44.0 (N-CH_3), 27.5 ($CH(CH_3)_2$), 20.0 ($CH(CH_3)_2$), 17.2 ($CH(CH_3)_2$)
syn-**6e**	79.9	89.0	174.9	35.0	74.5	46.0 (NCH_3), 32.6 ($C(CH_3)_3$) 28.1 ($C(CH_3)_3$)
anti-**6e**	82.5	90.5	174.6	35.1	76.4	48.2 (NCH_3), 32.6 ($C(CH_3)_3$, 26.9 ($C(CH_3)_3$)
syn-**6f**	75.4[a]	90.8	175.0	34.1	73.8[a]	136.9, 129.0, 128.6, 128.4, 128.3, 127.5 (PhC), 60.4 (NCH_2Ph), 20.9 (CH_2CH_3), 10.3 (CH_2CH_3)
anti-**6f**	71.3	86.3	175.7	35.3	74.5	136.9, 128.4, 128.3, 127.3 (PhC), 58.9 (NCH_2Ph), 19.3 (CH_2CH_3), 10.4 (CH_2CH_3)
syn-**6g**	74.1[a]	87.6	175.0	34.9	74.0[a]	137.2, 129.2, 128.7, 128.4, 128.3, 127.4 (PhC), 60.2 (NCH_2Ph), 27.2, ($CH(CH_3)_2$), 19.9 ($CH(CH_3)_2$), 18.7 ($CH(CH_3)_2$)
anti-**6g**	77.4	87.9	175.0	34.2	75.9	137.2, 128.6, 128.3, 127.4 (PhC), 61.1 (NCH_2Ph), 27.7 ($CH(CH_3)_2$, 19.9 ($CH(CH_3)_2$, 17.2 ($CH(CH_3)_2$)
syn-**6h**	78.0	88.7	174.7	34.2	75.1	137.6, 128.4, 128.3, 127.4 (PhC), 62.4 (NCH_2Ph), 33.6 ($C(CH_3)_3$), 28.1 ($C(CH_3)_3$)
anti-**6h**	79.0	89.9	174.7	35.7	77.4	137.5, 128.7, 128.4, 128.3, 127.4, (PhC), 64.6 (NCH_2Ph), 33.0 ($C(CH_3)_3$), 26.9 ($C(CH_3)_3$)
syn-**6i**	73.6	86.8	175.1	35.1	75.2	136.7, 132.5, 129.3, 129.1, 129.0, 128.8, 128.4, 128.2, 128.0, 127.8, 127.2, 127.1 (PhC), 58.1 (NCH_2Ph)
anti-**6i**	74.0[a]	87.0	175.1	35.5	75.4[a]	136.7, 132.5, 129.2, 129.0, 128.7, 128.6, 128.4, 128.3, 127.4, 127.3 (PhC), 58.4 (NCH_2Ph)
syn-**6j**	69.6	86.0	174.9	35.3	75.5	136.5, 133.7, 128.5, 128.4, 128.3, 128.2, 127.8, 127.5, 127.4, 126.5 (ArC), 58.2 (NCH_2Ph)

[a] The assignments may have to be interchanged.

dried (Na_2SO_4), and evaporated to dryness. Flash chromatography (cyclohexane/diethyl ether 70:30) of the residue gave the products *syn*-**6a** (0.176 g, 80.6%) and *anti*-**6a** (0.034 g, 15.4%).

anti-**6a**: oil; R_f 0.48 (cyclohexane/diethylether 1:1); IR (neat) 2900, 2860, 1765, 1455, 1370, 1175, 1060, 935, 770, 715 cm^{-1}; MS m/z (relative intensity) 219 (M^+, 18), 134 (100), 118 (14), 91 (13), 77 (12). Anal. Calcd for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N 6.39. Found: C, 65.82; H, 6.11; N, 6.21.

syn-**6a**: mp 117 °C (hexane); R_f 0.42 (cyclohexane/ether 1:1); IR (Nujol) 2900, 2850, 1770, 1450, 1380, 1170, 1060, 940, 770, 710 cm^{-1}; MS m/z (relative intensity) 219 (M^+, 17), 134 (100), 118 (16), 91 (12), 77 (14). Anal. Calcd for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.84; H, 5.91; N, 6.31.

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Supplementary Material Available: Table 4 of physical, spectral, and combustion analytical data of compounds **6b–j** (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.