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MIRC reactions of 2-bromo-5-(*l*-menthyloxy)furan-2(5*H*)-one with stabilized anions. Preparation of homochiral bicyclic γ-butyrolactones †

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Abstract

Homochiral (5*R*)-4-bromo-5-(*l*-menthyloxy)furan-2(5*H*)-one with stabilized carbanions (from nitroalkanes, malononitrile and ethyl acetoacetate) afforded enantiopure bicyclic compounds in good yield (70–90%). 3-Oxabicyclic[3.1.0]hexan-2-one derivatives were obtained with nitromethane and malonic acid derivatives. However, dihydrofuro[3,4-d]isoxazol-6-one and dihydrofuro[3,4-b]furan-6(4*H*)-one derivatives were obtained from nitroethane and ethyl acetoacetate, respectively.

1. Introduction

5-Alkoxyfuran-2(5*H*)-ones have attracted considerable attention since its skeleton comprises a cyclic structure, a latent carbonylic functionality on C-5 and the α,β-unsaturated ester moiety. They also have a high conformational rigidity and the steric requirements of the alkoxy group brings about an important shielding of one of the faces of the conjugated system.

Some years ago we reported that bromine addition to the double bond of 5-methoxyfuran-2(5*H*)-one followed by HBr elimination under different experimental conditions affords a regioselective synthesis of 3- and 4-bromo derivatives.[1,2] The 3-bromo-5-methoxyfuran-2(5*H*)-one **1**[1] behaves as an excellent Michael acceptor towards oxygen,[3,4] nitrogen,[4,5] sulfur[4,5] and stabilized carbon nucleophiles,[4,6] while 4-bromo-5-methoxyfuran-2(5*H*)-one is a suitable substrate for the preparation of the 4-alkylamino and 4-alkylthio furanones by nucleophilic substitution of the halogen.[7]

Due to the synthetic versatility of these haloderivatives we prepared the corresponding enantiomerically pure menthol analogues. In this sense, we obtained homochiral (5*S*)-4-bromo-5-(*l*-menthyloxy)furan-2(5*H*)-one[8] from the 4-bromo-5-methoxyfuran-2(5*H*)-one. Since the publication of

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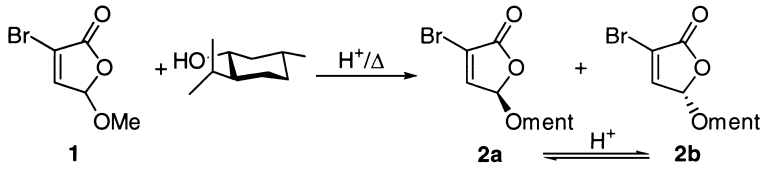
our report, the synthesis of other diastereoisomerically pure halogenated menthyloxyfuranones, such as the 4-chloro-,[9] the 3,4-dibromo-[10] and the (5*R*)-3-bromo-5-(*l*-menthyloxy)furan-2(5*H*)-one **2a**,[11] have appeared in the literature. The recent communication of Chen and Huang[11] describing the synthesis and the reactions with alcohols of enantiomerically pure furanone **2a** in a solid–liquid two-phase system, previously reported by us for the racemic methoxy analogue **1**,[4] prompted us to present our results on the preparation of (5*R*)-3-bromo-5-(*l*-menthyloxy)furan-2(5*H*)-one **2a** and its use in the synthesis of enantiomerically pure bicyclic systems containing the 2(5*H*)-furanone ring by MIRC (Michael Initiated Ring Closure) reactions. We describe herein the reactions of **2a** with stabilized carbon nucleophiles from nitroalkanes, ethyl acetoacetate and malonic acid derivatives. These reagents have similar pK_a values and at least two acidic protons, that allow them to act twice as nucleophiles by successive deprotonations and therefore behave as excellent MIRC reagents.

2. Results and discussion

We prepared menthyloxy bromofuranone **2** by transacetalization of 3-bromo-5-methoxyfuran-2(5*H*)-one **1**[1] with *l*-menthol in the presence of *p*-toluenesulfonic acid, by heating at 60°C in toluene solution (Scheme 1). The crystallization from hexane at −18°C of the 54:46 epimeric mixture of **2a**:**2b** afforded **2a** as a single diastereoisomer. The mother liquor that contained the mixture of both compounds (enriched in **2b**) had been epimerized by heating, in the presence of *p*-toluenesulfonic acid as catalyst, to obtain additional amounts of **2a**. A global yield of 55% in pure (5*R*)-bromofuranone **2a** was obtained by this procedure.



Scheme 1.

The reactions of furanone **2a** with nitromethane (Table 1, entries 1–3) and malononitrile (Table 1, entries 4 and 5) anions afforded cyclopropane-furanones **3** and **4**, respectively, as sole products (Scheme 2), although with variable yield according to the procedure used. The best results were obtained in THF at −18°C, with NaH as the base and in a 1:3:3 ratio of **2a**:nucleophile:base. However, in all of the tested conditions (Table 1, entries 6–8), the major product from the reaction of **2a** with diethyl malonate anion was the spiro-cyclopropane derivative **6**, although the reaction at room temperature yielded a significant amount of bicyclic cyclopropane-furanone **5**.

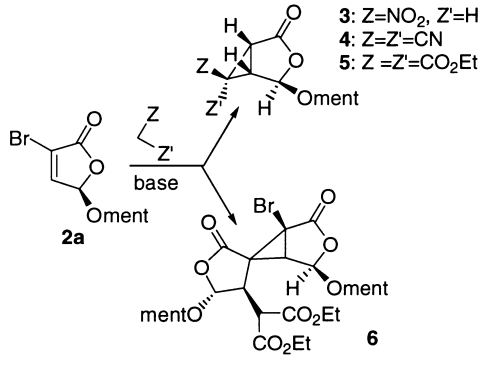
Unlike the above nucleophiles, the reactions of nitroethane and ethyl acetoacetate anions with furanone **2a** exclusively afforded diastereoisomerically pure dihydroisoxazole *N*-oxide **7** and dihydrofuro[3,4-d]furanone **8**, respectively (Scheme 3 and Table 2). It is important to mention the different behaviour of these nucleophiles giving *O*-alkylation instead of *C*-alkylation as above. On the other hand, DBU in THF instead of NaH/DMF (suitable for preparing cyclopropane derivatives) is preferred to obtain these [3.3.0] bicyclic compounds (Table 2, entries 3 and 6).

Compound **7** was deoxygenated by hydrogenolysis in the presence of Pd–C to yield the furodihydroisoxazole derivative **9** which, according to the literature, is the opposite regioisomer to the one obtained by 1,3-dipolar cycloaddition of acetonitrile oxide to the 5-(*l*-menthyloxy)furan-2(5*H*)-one.[12] Therefore, this procedure represented a complementary process to 1,3-cycloaddition reactions of non-halogenated furanones.

Table 1
Reaction of **2a** with Z-CH_2-Z′

Entry	Z	Z'	Proc[a].	T (°C)	Product (%)
1	H	NO_2	A	rt	**3** (26)
2			B	-18	**3** (90)
3			C	0	**3** (53)
4	CN	CN	A	rt	**4** (63)
5			B	-18	**4** (70)[c]
6	CO_2Et	CO_2Et	A	rt	**5** (16) **6** (27)
7			B	-18	**6** (50)
8			B	rt[b]	**5** (40) **6** (50)

[a] Procedure: A) Ratio **2a**:Nu:K_2CO_3:TBAB 1:1:5:0.05 in CH_3CN. B) Ratio **2a**:Nu:NaH 1:3:3 in DMF. C) Ratio **2a**:Nu:DBU 1:1.5:3 in THF. [b] The same result is obtained at 60 °C. [c] A 10% of the malononitrile 1,4-adduct is isolated.

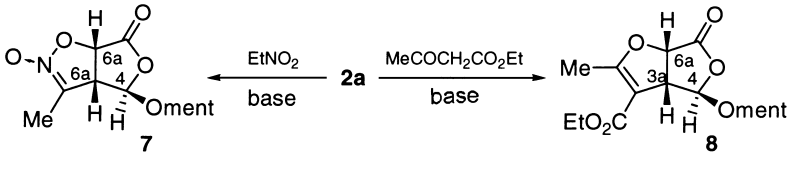


Scheme 2.

Table 2
Reaction of **2a** with nitroethane and ethyl acetoacetate

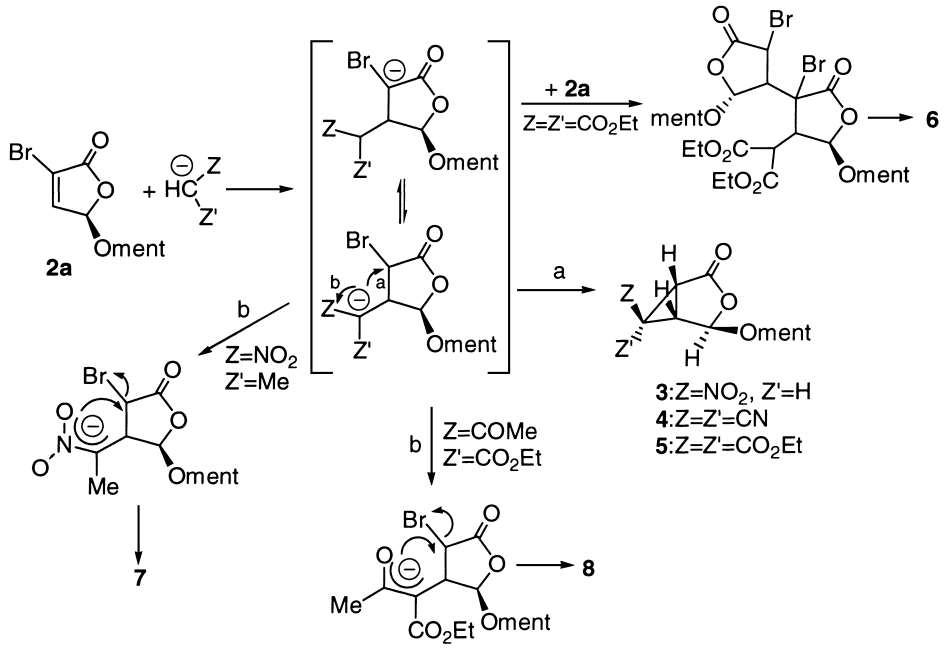
Entry	Nucleophile	Proc[a].	T (°C)	Product (Yield %)
1	$EtNO_2$	A	rt	**7** (traces)
2		B	-18	**7** (46)
3		C	-40	**7** (86)
4	CH_3COCO_2Et	A	rt	**8** (60)
5		B	-18	**8** (50)
6		C	-40	**8** (75)

[a]Procedure: A) Ratio **2a**:Nu:K_2CO_3:TBAB 1:1:5:0.05 in CH_3CN. B) Ratio **2a**:Nu:NaH 1:3:3 in DMF. C) Ratio **2a**:Nu:DBU 1:1.5:3 in THF.



Scheme 3.

The structure of all the above compounds was determined according to their spectral and analytical data. A rationalization of the results is presented in Scheme 4.



Scheme 4.

In conclusion, the presence of the halogen atom on the menthyloxyfuranone skeleton considerably increased the reactivity and the synthetic potential of these conjugated systems, providing a convenient route to different enantiomerically pure bicyclic systems.

3. Experimental

Melting points were determined on a Gallenkamp apparatus. NMR spectra were recorded on a Bruker WP-200-SY instrument. Optical rotations were measured on a Perkin–Elmer 241-MC polarimeter. Mass spectra were registered on a VG AutoSpec instrument in the electron impact mode (EI) at 70 eV unless stated otherwise. IR spectra were obtained in a Philips PU-9716. All reactions were monitored by TLC, that was performed on precoated sheets of silica gel 60 (F_{254}), and flash chromatography was effected with silica gel 60 (230–400 mesh). The apparatus for inert atmosphere experiments was dried by flaming in a stream of dry argon. Dry THF was obtained by distillation from sodium/benzophenone under argon. DMF was distilled and dried over 4 Å molecular sieves.

*3.1. (5*R*)-3-Bromo-5-(*l*-menthyloxy)furan-2(5*H*)-one **2a***[11]

(−)-Menthol (9.74 g, 62.66 mmol) was added to a solution of 3-bromo-5-methoxyfuran-2(5*H*)-one (**1**, 7.115 g, 36.86 mmol) and *p*-toluenesulfonic acid (2.13 g, 11.16 mmol) in toluene (35 mL) and the mixture was maintained for 4 days at 60°C. The solvent was evaporated in vacuo, the crude mixture was dissolved in ethyl acetate and the solution washed with a saturated solution of sodium hydrogen carbonate. The organic extracts were dried (Na_2SO_4) and the solvent evaporated. The crude product was mainly a diastereoisomeric mixture (54:46) of **2a**:**2b** and recovered **1**. Compounds **2a**:**2b** were isolated

by column chromatography (hexane:ethyl acetate, 30:1). Pure **2a** was separated as a white solid by crystallization of the diastereoisomeric mixture with hexane at −18°C. Additional amounts of pure **2a** were recovered from the remained diastereoisomeric mixture by successive epimerization at 70°C in toluene using *p*-toluenesulfonic acid as a catalyst, followed by the above-mentioned hexane treatment. Global yield 55%. Mp 92–94°C; $[\alpha]_D$ −134.1 (*c* 1, $CHCl_3$). Anal. calcd for $C_{14}H_{21}O_3Br$: C, 53.01; H, 6.67; Br, 25.19. Found: C, 53.14; H, 6.69; Br, 24.94.

3.2. Reaction with nucleophiles: general procedure

Procedure A: bromofuranone (**2a**, 50 mg, 0.16 mmol) was added to a mixture of anhydrous potassium carbonate (109 mg, 0.79 mmol), tetrabutylammonium bromide (2.5 mg, 0.0079 mmol) and the nucleophile (0.16 mmol) in acetonitrile (1 mL). The mixture was vigorously stirred at room temperature until the starting bromofuranone disappeared or a practically constant concentration was obtained (1–2 days). The salts were filtered after dilution with ethyl acetate or acetonitrile, and were washed with the same solvent. The solution was evaporated under reduced pressure to yield the crude mixture.

Procedure B: to a solution of NaH (23 mg, 0.95 mmol) in dry DMF (2.5 mL) under argon at −18°C, the nucleophile (0.95 mmol) was slowly added. The reaction mixture was stirred at the indicated temperature (Tables 1 and 2) for ca. 30 min and furanone **2a** (100 mg, 0.32 mmol) in DMF (1 mL) was added. After completion (0.5–2 h), the mixture was added onto an NH_4Cl saturated solution (containing some drops of 10% aqueous HCl) and was extracted with ether. Organic extracts were dried (Na_2SO_4) and removed in vacuo.

Procedure C: to a DBU (146 mg, 0.96 mmol) solution in dry THF (1 mL) at 0°C under argon the nucleophile (0.48 mmol) was slowly added. The mixture was stirred on an ice bath for ca. 30 min and the temperature was taken down to −40°C (Table 2, entries 3 and 6) or maintained at 0°C (Table 1, entry 3) before the addition of **2a** (100 mg, 0.32 mmol) in THF (1 mL). The reaction was stirred at the same temperature until consumption of **2a** (15 min). The reaction work-up was effected as in procedure B.

3.3. Reaction with nitroalkanes

*3.3.1. (1*R,*4*R,*5*S,*6*R*)-4-(*l*-Menthyloxy)-6-nitro-3-oxabicyclo[3.1.0]hexan-2-one **3***

The compound was obtained diastereoisomerically pure from nitromethane following the general procedure B at −18°C (Table 1, entry 2). Column chromatography on silica gel (hexane:acetone, 5:1) afforded pure **3** as a white solid (yield 90%). Mp 147–149°C; $[\alpha]_D^{25}$ −116.8 (*c* 1, $CHCl_3$). Anal. calcd for $C_{15}H_{23}NO_5$: C, 60.59; H, 7.80; N, 4.71. Found: C, 60.23; H, 7.81; N, 4.50. ^{1}H NMR: 5.65 (s, 1H), 4.33 (dd, 1H, *J*=2.1, 1.6), 3.6 (dt, 1H, ment., *J*=10.7 and 4.2), 3.19 (m, 2H), 2.2–0.8 (m, 18H, ment.); ^{13}C NMR: 168.0, 98.2, 78.3, 58.5, 47.5, 39.9, 34.0, 31.4, 29.7, 26.6, 25.3, 23.0, 22.1, 20.8, 15.5. IR ($CHCl_3$): 3100, 1790, 1560, 1365, 1340. MS (15 eV) *m/z* (relative intensity): 251 (M^+−46, 1), 223 (4), 212 (4), 138 (100), 95 (33), 81 (56).

*3.3.2. (3a*R,*4*R,*6a*S*)-4-(*l*-Menthyloxy)-3-methyl-3a,6a-dihydrofuro[3,4-d]isoxazol-6-(4*H*)-one* N-*oxide **7***

The compound was obtained as a sole diastereomer from nitroethane following the general procedure C (Table 2, entry 3). Purification was effected by column chromatography (hexane:acetone:ether, 7:1:1) (yield 86%). Mp 117–119°C; $[\alpha]_D^{25}$ −83.7 (*c* 1, $CHCl_3$). Anal. calcd for $C_{16}H_{25}NO_5$: C, 61.72; H, 8.09; N, 4.50. Found: C, 61.72; H, 8.03; N, 4.58. ^{1}H NMR: 5.69 (s, 1H,), 5.20 (d, 1H, *J*=9.1), 4.0 (dq, 1H, *J*=9.1 and 2.0), 3.58 (dt, 1H, ment., *J*=10.7 and 4.3), 2.09 (d, 3H, *J*=2.0), 2.2–0.7 (m, 18H, ment.); ^{13}C

NMR: 170.7, 108.0, 98.8, 77.8, 70.1, 54.3, 47.4, 39.4, 34.0, 31.2, 25.4, 22.9, 22.1, 20.7, 15.4, 10.8. IR ($CHCl_3$): 1800, 1785, 1650. MS (15 eV) *m/z* (relative intensity): 312 (M^++1, 9), 268 (2), 239 (6), 139 (100), 138 (24), 123 (3), 99 (36), 83 (65), 81 (18).

3.4. Reaction with malononitrile

*3.4.1. (1*S*,4*R*,5*R*)-6,6-Dicyano-4-(*l*-menthyloxy)-3-oxabicyclo[3.1.0]hexan-2-one **4***

The compound prepared according to the general procedure A was purified by column chromatography (hexane:acetone, 9:1), yield 63% (Table 1, entry 4). Pure **4** (yield 70%) was also obtained following the general procedure B by (hexane:acetone, 10:1) chromatographic separation (Table 1, entry 5). Mp 200–202°C; $[\alpha]_D^{25}$ −194.7 (*c* 1, $CHCl_3$). Anal. calcd for $C_{17}H_{22}N_2O_3$: C, 67.53; H, 7.33; N, 9.26. Found: C, 67.26; H, 7.35; N, 9.08. ^{1}H NMR: 5.73 (s, 1H), 3.68 (dt, 1H, *J*=10.9 and 4.7), 3.32, 3.24 (AB system, 2H, *J*=5.5), 2.2–0.7 (m, 18 H); ^{13}C NMR: 165.3, 110.9, 97.8, 79.5, 47.5, 39.8, 36.1, 33.9, 31.8, 31.3, 25.4, 22.9, 20.7, 15.5, 9.2. MS *m/z* (relative intensity): 257 (M^+−45, 1), 217 (11), 138 (43), 123 (40), 95 (67), 81 (100).

3.5. Reaction with diethyl malonate

Following the general procedure B at 25°C, a 42:51:7 mixture (^{1}H NMR) of compounds **5**, **6** and unreacted diethyl malonate was obtained (Table 1, entry 8). The separation of the mixture was obtained by column chromatography (hexane:acetone, 5:0.3) to afford compounds **5** (40%) and **6** (50%). Compound **6** was obtained as sole product at lower temperature (−18°C) with the same yield (50%) (Table 1, entry 7).

*3.5.1. (1*S*,4*R*,5*R*)-6.6-Diethoxycarbonyl-4-(*l*-menthyloxy)-3-oxabicyclo[3.1.0]hexan-2-one **5***

^{1}H NMR: 5.61 (s, 1H), 4.22 (m, 4H), 3.52 (dt, 1H, *J*=10.2 and 4.3), 2.88 (s, 2H) 1.30 (t, 6H, *J*=7.2), 2.2–0.7 (m, 18H); ^{13}C NMR: 166.6, 165.9, 98.2, 77.9, 62.9, 62.6, 47.6, 41.6, 40.0, 34.5, 34.1, 31.3, 29.7, 25.3, 23.0, 20.8, 15.5, 14.0, 13.8, 13.7. MS *m/z* (relative intensity): 323 (M^+−73, 1), 241 (100), 213 (61), 185 (66), 167 (25), 139 (40), 138 (35), 123 (30), 95 (73), 81 (55).

*3.5.2. (1*S*,4*R*,4′*R*,5*S*,5′*R*,6*S*)1-Bromo-4,5′-di(*l*-menthyloxy)-2-oxo-4′-[bis(ethoxycarbonyl]methyl)-3-oxabicyclo[3.1.0]hexane-6-spiro-tetrahydrofuran-2-one **6***

Mp 57–59°C; $[\alpha]_D^{25}$ −99.0 (*c* 1, $CHCl_3$). Anal. calcd for $C_{35}H_{53}O_{10}Br$: C, 58.90; H, 7.49; Br, 11.20. Found: C, 59.17; H, 7.45; Br, 11.18. ^{1}H NMR: 5.95 (s, 1H), 5.75 (s, 1H), 4.22 (m, 4H), 3.61, 3.52 (2dt, 2×1H, *J*=10.2 and 4.3), 3.35 (d, 1H, *J*=4.3), 3.05 (s, 1H), 2.72 (d, 1H, *J*=4.3), 1.30, 1.35 (t, 2×3H, *J*=7.1), 2.3–0.7 (m, 18H); ^{13}C NMR: 168.7, 167.4, 166.2, 166.0, 100.0, 95.9, 78.0, 76.0, 62.6, 62.2, 50.6, 47.1, 44.2, 39.6, 38.8, 38.5, 37.2, 34.2, 33.8, 33.7, 31.0, 25.2, 24.3, 22.9, 22.4, 21.8, 21.7, 20.6, 20.3, 15.3, 15.1, 13.6, 13.4. IR ($CHCl_3$): 1780, 1740, 1720. MS *m/z* (relative intensity): 712–714 (M^++1, 0.2), 557–559 (7), 249 (7), 161 (25), 139 (58), 138 (49), 123 (30), 95 (91), 83 (100), 81 (84).

3.6. Reaction with ethyl acetoacetate

*3.6.1. (3a*R*,4*R*,6a*S*)-3-Ethoxycarbonyl-4-(*l*-menthyloxy)-2-methyl-3a,6a-dihydrofuro[3,4-b]furan-6(4*H*)-one **8***

The compound was obtained as a sole diastereoisomer following procedures A (yield 60%), B (yield 50%) or C (yield 75%) (Table 2, entries 4–6). Purification was effected by column chromatography on

silica gel (hexane:ether, 4:0.5). Mp 97–99°C; $[\alpha]_D^{25}$ −22.0 (*c* 1, $CHCl_3$). Anal. calcd for $C_{20}H_{30}O_6$: C, 65.55; H, 8.25. Found: C, 65.30; H, 8.38. ^{1}H NMR: 5.78 (s, 1H), 5.17 (d, 1H, *J*=9.1), 4.2 (m, 2H), 3.85 (dq, 1H, *J*=9.1 and 2.2), 3.54 (dt, 1H, *J*=10.2 and 3.8), 2.28 (d, 3H, *J*=2.2), 1.30 (t, 3H, *J*=7.2), 2.3–0.7 (m, 18H); ^{13}C NMR: 172.6, 169.6, 164.3, 103.5, 78.1, 77.9, 60.1, 51.2, 47.6, 39.8, 34.2, 31.3, 25.4, 23.0, 22.1, 20.8, 15.5, 14.3, 14.0. IR ($CHCl_3$): 1780, 1680, 1620. MS *m/z* (relative intensity): 321 (M^+−45, 2), 182 (7), 154 (100), 138 (10), 137 (12), 126 (17), 125 (16), 123 (8), 109 (24), 95 (30), 81 (28).

3.7. Hydrogenolysis of the N*-oxide* ***7***

*3.7.1. (3a*R*,4*R*,6a*S*)-4-(*l*-Menthyloxy)-3-methyl-3a,6a-dihydrofuro[3,4-d]isoxazol-6-(4*H*)-one* ***9***

To a stirred 10% suspension of Pd–C (10 mg) in ethyl acetate (2 mL), isoxazol *N*-oxide **7** (0.05 g, 0.16 mmol) was added. The reaction was maintained for 24 h at room temperature under a hydrogen balloon at atmospheric pressure. The catalyst was filtered and washed with the solvent, and the solution was evaporated in vacuo to afford **9** (yield 90%). Mp 132–134°C; $[\alpha]_D$ +161.6 (*c* 0.5, MeOH). Anal. calcd for $C_{16}H_{25}NO_4$: C, 65.06; H, 8.53; N, 4.74. Found: C, 65.33; H, 8.55; N, 4.81. ^{1}H NMR: 5.55 (s, 1H, H_4), 4.83 (d, 1H, *J*=7.3), 3.50 (dt, 1H, ment., *J*=10.2, 3.8), 3.22 (d, 1H, *J*=7.3), 2.2–0.7 (m, 18H, ment.), 1.97 (s, 3H); ^{13}C NMR: 176.1, 153.2, 98.3, 77.3, 68.1, 51.6, 47.2, 39.1, 33.8, 30.9, 25.2, 22.6, 21.8, 20.5, 15.1, 13.8. IR ($CHCl_3$): 1800, 1700. MS *m/z* (relative intensity): 296 (M^++1, 1), 240 (5), 158 (12), 139 (15), 138 (32), 123 (30), 95 (96), 83 (98), 81 (83), 55 (100).

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