Beckmann Rearrangement of *O*-4-Pentenyl Oxime through *N*-Bromosuccinimide-Mediated Activating Process

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Beckmann rearrangement of *O*-4-pentenyl oxime derivatives proceeds in good yield under mild conditions through the formation of a cationic tetrahydrofuranium intermediate in the halocyclization reaction with *N*-bromosuccinimide.

Key words Beckmann rearrangement; halocyclization; tetrahydrofuranium; *N*-bromosuccinimide; *O*-4-pentenyl oxime

Hydrolysis of *O*-4-pentenylacetal and glycosidation of *O*-4-pentenylglycoside through an activating process mediated by an electrophilic halogenating reagent have been investigated by Fraser-Reid *et al.* (Chart 1).[1] Although these reactions proceed in good yield *via* cationic haloetherification intermediates under neutral conditions, this method is only applicable to the activation of acetal compounds. In the course of our ongoing project to develop synthetic organic reactions using an iodine-mediated activating process,[2] we have focused our attention on this activating process of the *O*-4-pentenyl system in order to apply it to other reactions.[3] In this paper, we report Beckmann rearrangement through an *N*-bromosuccinimide (NBS)-mediated activating process of *O*-4-pentenyl oxime.

Since the discovery of Beckmann rearrangement, the acid-mediated rearrangement of oximes to amides, in 1886, various modifications of the reagents and the reaction conditions have been reported.[4] As a new method for activation in Beckmann rearrangement, we expected that the reaction of *O*-4-pentenyl oxime with an electrophilic halogenating reagent might proceed under neutral conditions through the formation of a cationic tetrahydrofuranium intermediate, followed by elimination of halomethyltetrahydrofuran and migration of the alkyl group (Chart 2). *O*-4-Pentenyl oxime derivatives **1** could be prepared in good yields by the reaction of the corresponding oxime Na salts with 4-pentenyl bromide. In the presence of various halogenating reagents, Beckmann rearrangement of *O*-4-pentenyl acetophenone oxime in aqueous CH_3CN was examined. The reactions using I_2 and IDPC (iodonium dicollidine perchlorate) as reagents hardly proceeded, and the starting material **1a** was quantitatively recovered (entries 1—3). The use of NIS (*N*-iodosuccinimide) gave acetanilide **2a** in low yield with recovery of **1a** (entries 4, 5). As a halogenating reagent, NBS was found to work well, and the concentration of H_2O in CH_3CN influenced the yield of **2a**. For example, in 10% aqueous CH_3CN, the reaction of **1a** with NBS gave **2a** in 68% yield, with the competitive formation of the bromohydrin (15% yield) as a by-product (entry 6). Under the optimized reaction conditions of 1.5 eq of NBS in 3% aqueous CH_3CN, **2a** was obtained in 88% yield without the formation of the bromohydrin (entry 7). CH_3CN was the most effective solvent; for example, in tetrahydrofuran (THF), the rearrangement product **2a** was hardly obtained and **1a** was recovered.

The Beckmann rearrangement with various *O*-4-pentenyl oximes using this activating method was further

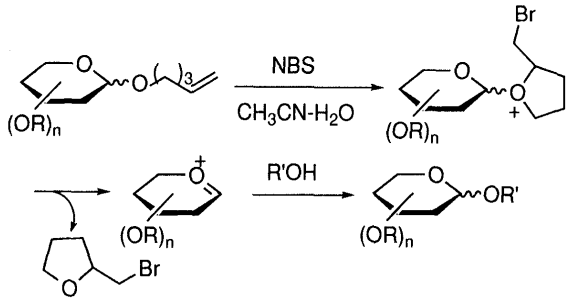

Chart 1

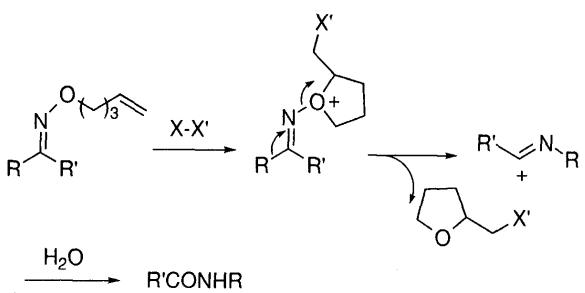

Chart 2

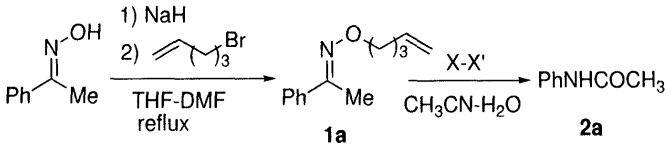

Chart 3

Table 1. Beckmann Rearrangement of Acetophenone Oxime **1a**[a]

Entry	X–X'	$CH_3CN:H_2O$	**2a** yield (%)[b]
1	I_2 (1.1 eq)	10:1	Trace
2	I_2 (1.1 eq)–pyridine	100:1	Trace
3	IDPC[c] (1.1 eq)	10:1	Trace
4	NIS (1.1 eq)	100:1	27
5	NIS (1.1 eq)	10:1	31
6	NBS (1.1 eq)	10:1	68
7	NBS (1.5 eq)	30:1	88

a) Beckmann rearrangement: oxime (0.3 mmol), solvent (3—3.3 ml) rt, 1—3 h. *b*) Isolated yield. *c*) Iodonium dicollidine perchlorate.

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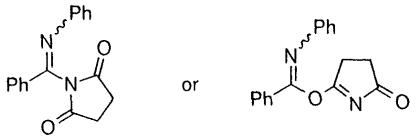
Table 2. Beckmann Rearrangement of *O*-4-Pentenyl Oximes[a]

Entry	Oxime	Amide	Yield (%)[b]
1	RON=(t-Bu) **1b**	HN(O=)(t-Bu) **2b**	87
2	RON=(Ph)(Ph) **1c**	PhCONHPh **2c**	65[c]
3	RO,N,Ph **1d** (*Z*:*E*=2:1)	*i*-PrCONHPh **2d**	23
		PhCONH*i*-Pr **2d'**	52
4	N(OR),Ph *E*-**1e**	MeCON(H)Ph **2e**	68
5	RO,N,Ph *Z*-**1e**	Ph,CONHMe **2e'**	12[d]

a) Beckmann rearrangement: oxime (R=4-pentenyl, 0.3 mmol), NBS (0.45 mmol), H_2O (0.1 ml), CH_3CN (3 ml), rt, 1 h. *b*) Isolated yield. *c*) After the reaction, the reaction mixture was treated with 2% HCl. *d*) With 70% recovery of the starting material.



3c or **3c'**

examined (Table 2). As in the case of **1a**, the reaction of 4-*tert*-butylcyclohexanone oxime **1b** proceeded in good yield to give ε-caprolactam **2b** (entry 1). In the case of benzophenone oxime **1c**, the product **3c** or **3c'** formed by the attack of succinimide anion on the nitrilium ion intermediate was also obtained together with benzanilide **2c**. Compound **3c** or **3c'** could be easily hydrolyzed and **2c** was obtained in 65% yield by treating the reaction mixture with 2% aqueous HCl (entry 2). The reaction of **1d**, a mixture of *E*- and *Z*-isomers (*Z*:*E*=2:1), gave a mixture of the anilide **2d** (23%) and the benzamide **2d'** (52%) in a ratio similar to that of **1d** (entry 3). For the further confirmation of this stereospecificity, the reactions of the easily separable *O*-pentenyl oximes *E*-**1e** and *Z*-**1e** were performed. The reaction of *E*-**1e** smoothly proceeded to give **2e** in 68% yield without the formation of **2e'** (entry 4), while the reaction of *Z*-**1e** gave **2e'** in low yield (12%) due to lower migratory aptitude of the methyl group (entry 5). In the latter case, the starting material *Z*-**1e** was recovered in 70% yield without isomerization of the oxime double bond, so the present reaction should proceed with complete stereospecificity. In the reaction of *O*-4-pentenoyl oxime **4b**, which would proceed through a cationic halolactonization intermediate in the activating process, ε-caprolactam **2b** was obtained in lower yield than that of **1b** (Chart 4).[5]

As shown in Chart 5, this activating method can be applied to *O*-Me 3-butenyl phenyl ketone oxime **5** to give the functionalized amide **6** in good yield through the formation of a 6-membered cyclic cationic halocyclization

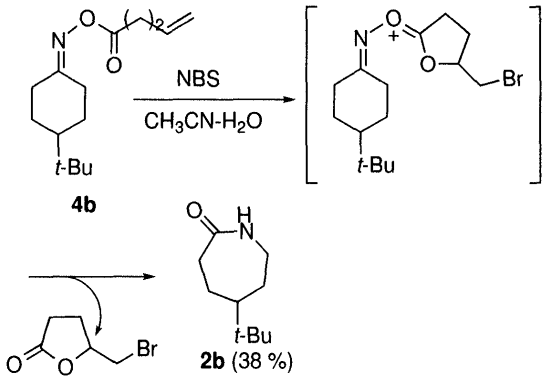


Chart 4

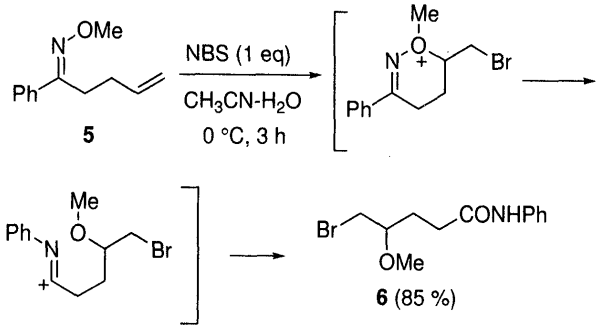


Chart 5

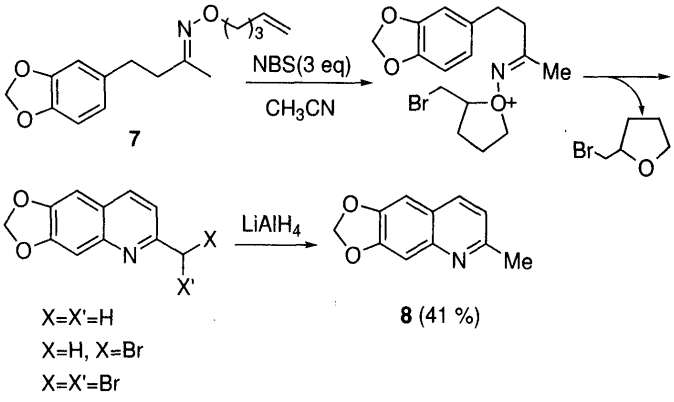


Chart 6

intermediate.

Recently, Narasaka *et al.* reported that in the Beckmann rearrangement catalyzed by tetrabutylammonium perrhenate(VII),[6] benzylacetone oxime derivatives give quinoline derivatives *via* intramolecular substitution reaction on the nitrogen atom by a phenyl group having an electron-donating group.[7] They pointed out that the substitution process prior to the migration of the alkyl group on the nitrogen atom depends on the nature of the oxime oxygen as a leaving group.[8] As an application to this reaction system, the NBS-promoted reaction of *O*-pentenyl benzylacetone oxime **7** was investigated. The reaction of **7** with NBS resulted in a mixture of the corresponding quinolines, including brominated derivatives, and successive $LiAlH_4$ reduction of the reaction mixture gave the methylquinoline **8** in 41% yield.

In conclusion, we have shown that the Beckmann rearrangement of *O*-4-pentenyl oximes can be carried out

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under mild conditions through an NBS-mediated activating process.

Experimental

The ^{1}H- and ^{13}C-NMR spectra were recorded on a 400- and 300-MHz spectrometer; chemical shifts were expressed in δ (ppm) downfield from $CHCl_3$ (7.26 ppm) and $CDCl_3$ (77.0 ppm), respectively. Mass spectra were recorded in the electron impact mode. Column chromatography was performed on silica gel, Wakogel C-200 (75—150 μm). Medium-pressure liquid chromatography (MPLC) was performed on a 30 × 4 cm i.d. prepacked column (silica gel, 50 μm) with a UV detector.

General Procedure for Preparation of *O*-4-Pentenyl Oximes (1) A THF solution (20 ml) of acetophenone oxime (1.28 g, 9.51 mmol) was added to a suspension of NaH (274 mg, 11.4 mmol) in THF (50 ml)–DMF (5 ml) at 0 °C. The mixture was stirred for 30 min at room temperature, then 5-bromo-1-pentene (1.2 ml, 9.51 mmol) was added and the whole was refluxed overnight at 100 °C. The mixture was poured into water and extracted with AcOEt. The AcOEt extracts were washed with brine, dried over $MgSO_4$, and evaporated to dryness. The residue was purified by column chromatography (hexane only) to give **1a** (1.873 g, 97%).

***(E)*-*O*-4-Pentenyl Acetophenone Oxime (1a)** **1a**: Colorless oil. IR (neat): 2933, 1641 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.84 (2H, quint, J=6.6 Hz), 2.13—2.25 (2H, m), 2.24 (3H, s), 4.22 (2H, t, J=6.6 Hz), 4.99 (1H, br d, J=9.0 Hz), 5.07 (1H, br d, J=16.0 Hz), 5.87 (1H, m). ^{13}C-NMR ($CDCl_3$) δ: 12.4, 28.4, 30.1, 73.3, 114.7, 125.8, 128.2, 128.7, 136.7, 138.0, 153.9. MS m/z: 202 ($M^+ - H^+$), 134, 118, 104, 77. HRMS m/z: Calcd for $C_{13}H_{17}NO$ (M^+), 203.1310. Found: 203.1297.

***O*-4′-Pentenyl 4-*tert*-Butylcyclohexanone Oxime (1b)** This was prepared from 4-*tert*-butylcyclohexanone oxime (845 mg, 5 mmol) in accordance with the general procedure. Purification by column chromatography (hexane only) gave **1b** (998 mg, 84%).

1b: Colorless oil. IR (neat): 2952, 1642 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.89 (s, 9H), 1.05—1.30 (3H, m), 1.65—1.70 (3H, m), 1.85—2.20 (5H, m), 2.41 (1H, br d, J=12.6 Hz), 3.29 (1H, br d, J=14.5 Hz), 4.01 (2H, t, J=6.6 Hz), 4.95 (1H, br d, J=11.0 Hz), 5.02 (1H, br d, J=16.3 Hz), 5.83 (1H, m). ^{13}C-NMR ($CDCl_3$) δ: 24.8, 26.3, 27.4, 27.6, 28.2, 30.1, 31.8, 32.3, 47.4, 72.3, 114.5, 138.0, 159.4; MS m/z: 237 (M^+), 222, 180, 57. *Anal.* Calcd for $C_{15}H_{26}NO$: C, 75.90; H, 11.46; N, 5.90. Found: C, 75.92; H, 11.35; N, 6.04.

***O*-4-Pentenyl Benzophenone Oxime (1c)** This was prepared from benzophenone oxime (723 mg, 3.7 mmol) in accordance with the general procedure. Purification by column chromatography (hexane only) gave **1c** (327 mg, 35%).

1c: Colorless oil. IR (neat): 2933, 1641 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.81 (2H, quint, J=6.9 Hz), 2.12 (2H, q, J=7.0 Hz), 4.20 (2H, t, J=6.6 Hz), 4.94—5.08 (2H, m), 5.83 (m, 1H), 7.30—7.52 (10H, m). ^{13}C-NMR ($CDCl_3$) δ: 28.4, 30.1, 73.9, 114.8, 127.8, 127.9, 128.1, 128.6, 129.1, 129.2, 133.4, 136.6, 138.1, 156.3. MS m/z: 265 (M^+), 196, 180, 77. *Anal.* Calcd for $C_{18}H_{19}NO$: C, 81.48; H, 7.22; N, 5.28. Found: C, 81.01; H, 7.38; N, 5.24.

***(Z)*- and *(E)*-*O*-4-Pentenyl Isopropyl Phenyl Ketone Oxime (*Z*- and *E*-1d)** This was prepared from isopropyl phenyl ketone oxime (187 mg, 1.15 mmol) in accordance with the general procedure. Purification by column chromatography (hexane only) gave a mixture of *Z*- and *E*-**1d** (197 mg, 76%) in a ratio of Z/E=2.

1d: Colorless oil. IR (neat): 2966, 1641 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: (*Z*)-**1d** 1.19 (6H, d, J=7.2 Hz), 1.81 (2H, quint, J=6.6 Hz), 2.18 (2H, q, J=7.1 Hz), 3.50 (1H, sept, J=7.2 Hz), 4.15 (2H, t, J=6.6 Hz), 4.90—5.10 (2H, m), 5.70—5.92 (1H, m), 7.18—7.43 (5H, m), (*E*)-**1d** 1.11 (6H, d, J=6.9 Hz), 1.69 (2H, quint, J=6.6 Hz), 2.03 (2H, q, J=7.0 Hz), 2.81 (1H, sept, J=6.9 Hz), 4.01 (2H, t, J=6.6 Hz), 4.90—5.10 (2H, m), 5.70—5.92 (1H, m), 7.18—7.43 (5H, m). ^{13}C-NMR ($CDCl_3$) δ: (*E*, *Z* mixture): 19.4, 20.2, 28.3, 28.4, 30.0, 30.2, 34.3, 72.8, 73.2, 114.5, 114.7, 127.5, 127.6, 127.7, 127.8, 127.9, 128.2, 134.4, 136.0, 138.0, 138.1, 162.0, 163.6. MS m/z: 231 (M^+), 200, 104, 77. *Anal.* Calcd for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.05. Found: C, 77.45; H, 8.98; N, 6.05.

***(E)*- and *(Z)*-*O*-4-Pentenyl Benzylacetone Oxime (*E*- and *Z*-1e)** *E*- and *Z*-**1e** were prepared from benzylacetone oxime (619 mg, 3.8 mmol) in accordance with the general procedure. Purification by column chromatography (hexane only) and then MPLC (hexane : AcOEt = 10 : 1) gave *E*-**1e** (less polar, 472 mg, 54%) and *Z*-**1e** (more polar, 171 mg, 19%).

(*E*)-**1e**: Colorless oil. IR (neat): 2927, 1641 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.66—1.82 (2H, m), 1.86 (3H, s), 2.12 (2H, q, J=7.0 Hz), 2.45—2.53 (2H, m), 2.80—2.87 (2H, m), 4.03 (2H, t, J=6.5 Hz), 4.94—5.10 (2H, m), 5.83 (m, 1H), 7.15—7.30 (5H, m). ^{13}C-NMR ($CDCl_3$) δ: 14.2, 28.3, 30.1, 32.7, 37.6, 72.5, 114.6, 125.9, 128.2, 128.2, 138.1, 141.1, 156.2. MS m/z: 231 (M^+), 146, 132, 105, 91. *Anal.* Calcd for $C_{15}H_{21}NO$: C; 77.88, H; 9.15, N, 6.05. Found: C, 77.67; H, 9.03; N, 5.98.

(*Z*)-**1e**: Colorless oil. IR (neat): 2927, 1641 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.70—1.85 (2H, m), 1.80 (3H, s), 2.14 (2H, q, J=7.0 Hz), 2.60—2.70 (2H, m), 2.80—2.90 (2H, m), 4.02 (2H, t, J=6.5 Hz), 4.97 (1H, br d, J=10.2 Hz), 5.04 (1H, br d, J=15.7 Hz), 5.85 (m, 1H), 7.15—7.35 (5H, m). ^{13}C-NMR ($CDCl_3$) δ: 20.3, 28.3, 30.2, 31.3, 31.7, 72.5, 114.7, 126.0, 128.2, 128.3, 138.1, 141.2, 157.0. MS m/z: 231 (M^+), 146, 132, 104, 91. *Anal.* Calcd for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.05. Found: C, 77.57; H, 8.95; N, 6.00.

General Procedure of Beckmann Rearrangement A solution of *O*-4-pentenyl acetophenone oxime **1a** (61 mg, 0.3 mmol) in 3% aqueous CH_3CN (3 ml) was treated with NBS (80 mg, 0.45 mmol) under stirring at room temperature for 1 h. The mixture was poured into aqueous $Na_2S_2O_3$ solution and the whole was extracted with AcOEt. The AcOEt extracts were washed with brine, dried over $MgSO_4$, and evaporated to dryness. The residue was purified by column chromatography (hexane : AcOEt = 5 : 1) to give acetanilide **2a** (36 mg, 88%). The amides **2a** (commercially available), **2c** (commercially available), **2d**,[9] **2d′**,[9] **2e**[10] and **2e′**,[11] and the lactam **2b**[12] are known compounds.

***E*-*O*-Methyl 3-Butenyl Phenyl Ketone Oxime (5)** A THF (5 ml)–dimethyl formamide (DMF) (1 ml) solution of 3-butenyl phenyl ketone oxime (152 mg, 0.87 mmol) was added to a suspension of NaH (22 mg, 0.9 mmol) in THF (2 ml). The mixture was stirred for 20 min at room temperature, then MeI (213 mg, 1.5 mmol) was added and whole was stirred for 6 h at room temperature, poured into 2% HCl and extracted with AcOEt. The AcOEt extracts were washed with brine, dried over $MgSO_4$ and evaporated to dryness. The residue was purified by column chromatography (hexane : AcOEt = 50 : 1) and then MPLC (hexane : AcOEt = 30 : 1) to give **5** (115 mg, 70%).

5: Colorless oil. IR ($CHCl_3$): 2944, 1604 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.23—2.34 (2H, m), 2.78—2.88 (2H, m), 3.98 (3H, s), 4.95—5.10 (2H, m), 5.84 (1H, ddt, J=17.0, 10.4, 6.6 Hz), 7.33—7.40 (3H, m), 7.57—7.65 (2H, m). ^{13}C-NMR ($CDCl_3$) δ: 26.1, 30.5, 61.9, 115.0, 126.3, 128.5, 129.0, 137.6, 158.0. MS m/z: 189 (M^+), 158, 144, 131, 104. HRMS Calcd for $C_{12}H_{15}NO$ (M^+) 189.1154. Found: 189.1162.

***N*-Phenyl 4-Methoxy-5-bromopentanamide (6)** A solution of the *O*-Me oxime **5** (111 mg, 0.59 mmol) in 3% aqueous CH_3CN was treated with NBS (107 mg, 0.6 mmol) under stirring for 3 h at 0 °C. The mixture was poured into aqueous $Na_2S_2O_3$ solution and extracted with AcOEt. The AcOEt extracts were washed with brine, dried over $MgSO_4$, and evaporated to dryness. The residue was purified by column chromatography (hexane : AcOEt = 5 : 1) to give the amide **6** (143 mg, 85%).

6: Colorless oil. IR (neat): 3304, 2936, 1666 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.85—2.17 (2H, m), 2.48 (2H, t, J=7.2 Hz), 3.38—3.54 (3H, m), 3.42 (3H, s), 7.10 (1H, t, J=7.4 Hz), 7.31 (2H, t, J=7.9 Hz), 7.50 (2H, d, J=7.7 Hz), 7.65 (1H, br s). ^{13}C-NMR ($CDCl_3$) δ: 28.6, 32.7, 33.9, 57.1, 78.8, 120.0, 124.1, 128.7, 137.8, 171.1. MS m/z: 287 (M^+ Br^{81}), 285 (M^+ Br^{79}), 206, 192, 93, 71. *Anal.* Calcd for $C_{12}H_{16}BrNO_2$: C, 50.37; H, 5.64; N, 4.89. Found: C, 50.04; H, 5.70; N, 5.06.

2-Methyl-6,7-methylenedioxyquinoline (8)[7] A solution of *O*-4-pentenyl oxime **7** (83 mg, 0.3 mmol) in CH_3CN (5 ml) was treated with NBS (160 mg, 0.9 mmol) under stirring for 2 h at room temperature. The mixture was poured into aqueous $Na_2S_2O_3$ solution and extracted with AcOEt. The AcOEt extracts were washed with brine, dried over $MgSO_4$, and evaporated to dryness. A THF solution (5 ml) of the residue was added to a suspension of $LiAlH_4$ (23 mg, 0.3 mmol) in THF (5 ml) and the mixture was stirred for 3 h at room temperature. The reaction mixture was poured into water and extracted with AcOEt. The AcOEt extracts were washed with brine, dried over $MgSO_4$, and evaporated to dryness. The residue was purified by column chromatography (hexane : AcOEt = 5 : 1—3 : 1) to give **8** (23 mg, 41%).

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