

Group IV-Metal-Catalyzed Aminolysis of *N*-Acyl-2-oxazolidinones: Applications to the Chemoselective and Enantioselective Carbonylation of Primary Alkylamines

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Reversible acyl transfer reactions catalyzed by enzymes such as lipase in organic solvent have great practical utility, in addition to being of theoretical interest, in asymmetric synthesis due to their facile chiral recognition.^{1,2} Such acyl transfer processes are also of practical utility in chemoselective acylation of polyheterofunctional compounds. These enzymatic reactions are recognized to proceed through acyl-enzyme complex 1, the enzyme moiety of which functions as chiral leaving group for achieving such facile selectivities (Figure 1).²

The Lewis acid-base complex 2, derived from *N*-acyl-2-oxazolidinone and a group IV metal catalyst, might be a suitable acyl-donor candidate possessing the similar function to that of the acyl-enzyme complex 1, since it is known that the complex 2 rigidly exists to provide enhanced electrophilicity of the carbonyl and nice chiral environment with the molecules upon applying chiral Lewis acids or 2-oxazolidinones.^{3ab} However, to the best of our knowledge, the complex 2 has never been applied to the selective acylation of heteroatomic nucleophiles as above.⁴ In this paper we report our preliminary results on group IV-metal-catalyzed aminolysis of *N*-acyl-2-oxazolidinones and its application to highly chemoselective acylation of straight-chain primary amines as well as enantiodiscrimination between α -phenylethylamine enantiomers.⁵

At first, aminolysis of *N*-benzoyloxazolidin-2-one (**3a**)⁶ and its analogs **3b–e**⁶ with 2-phenylethylamine was examined under the influence of easily available group IV-metal catalysts 4–7 including titanium or zirconium with a variety of ligands. The results are shown in Table 1. All reactions proceeded in the presence of a catalytic amount of the catalyst in tetrahydrofuran (THF) at room temperature to give the corresponding amides **8** [R = (CH₂)₂Ph] in high to modest yields. The rate of aminolysis was found to increase with increasing number of electron-donating η^5 -cyclopentadienyl (Cp) groups (entry 2 vs 3, Table 1) and with changing the metal from titanium to zirconium (entry 4 vs 5, Table 1). Alkoxytitanium catalyst

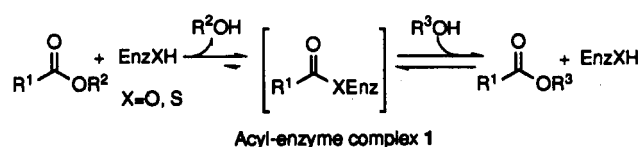


Figure 1. Reversible acyl transfer reactions catalyzed by enzymes.

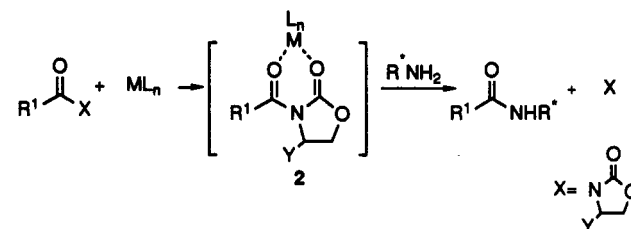
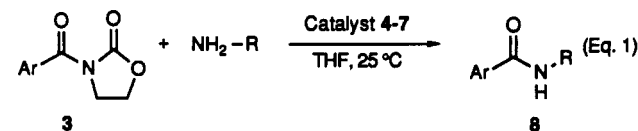


Figure 2. Aminolysis of Lewis acid-base complex 2 derived from *N*-acyl-2-oxazolidinones.

Table 1. Aminolysis of **3** with 2-Phenylethylamine Catalyzed by Group IV-Metal Catalysts 4–7

entry ^a	acyl donor 3	catalyst	time (h)	yield (%) ^b of 8 [R = (CH ₂) ₂ Ph]
1	3a	4	18	91 ^c
2	3a	5	18	64
3	3a	6	18	98
4	3a	7	2	95
5	3a	6	2	29
6	3b	6	2	91 ^d
7	3c	6	2	80 ^e
8	3d	6	2	70 ^f
9	3e	6	2	23 ^g

^a All reactions were carried out in THF at 25 °C in the presence of 20 mol % of the catalyst. ^b All compounds gave satisfactory elemental analysis. ^c mp 114–115 °C. ^d mp 163–165 °C. ^e mp 102–104 °C. ^f mp 134–136 °C. ^g mp 127–128 °C.



a: Ar=Ph; **b:** Ar=4-CF₃C₆H₄; **c:** Ar=3-ClC₆H₄;
d: Ar=4-ClC₆H₄; **e:** Ar=4-MeOC₆H₄

4: (i-PrO)₂TiCl₂; **5:** CpTiCl₃; **6:** Cp₂TiCl₂; **7:** Cp₂ZrCl₂

such as Cl₂Ti(Oi-Pr)₂ was also applicable to this reaction (entry 1, Table 1). Moreover, the rate of aminolysis strongly depends on aromatic substituents in acyl-donors **3** and the reactions accelerated with an electron-withdrawing aromatic substituent (entries 6, 7 vs 5, 9, Table 1).⁷

In order to explore the generality and scope of the above reaction, the aminolysis of *N*-acyl-2-oxazolidinone derivatives **3** was examined with various structural and functionally diverse primary alkyl- and arylamines (Table 2). It was soon realized that straight-chain primary amines are acylated quite generally to give the corresponding amides **8** in high yields upon treatment with **3a** in the presence of a catalytic amount of Cp₂TiCl₂ at room temperature (entries 1–6, Table 2). Alcohol and acetal functionalities in the molecule did not affect the reactions (entries 4–6). However, the reaction rates for acylations

(7) Linear Hammett plots with a positive ρ value (0.83, $r = 0.97$) for the relative reactivities were obtained.

(1) Recent reviews on enzyme-catalyzed asymmetric synthesis: (a) Zhu, L.-M.; Tedford, M. C. *Tetrahedron* 1990, 46, 6587. (b) Xie, Z.-F. *Tetrahedron: Asymmetry* 1992, 2, 733. (c) Tamm, C. *Pure Appl. Chem.* 1992, 64, 1187.

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(3) (a) Evans, D. A.; Chapman, K. T.; Bisaha, J. J. *Am. Chem. Soc.* 1988, 110, 1238. (b) Narasaka, K.; Iwasawa, N.; Inoue, M.; Yamada, T.; Nakashima, M.; Sugimori, J. J. *Am. Chem. Soc.* 1989, 111, 5340.

(4) Aminolysis of *N*-acetyl-2-oxazolidinones catalyzed by group IV-metal catalysts was briefly reported by Narasaka and co-workers without the detailed scope and limitation.^{3b}

(5) During preparation of this manuscript, magnesium-catalyzed enantioselective alcoholysis of *N*-acyl-2-oxazolidinone was reported: Evans, D. A.; Anderson, J. C.; Taylor, M. K. *Tetrahedron Lett.* 1993, 34, 5563.

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Table 2. Titanocene Dichloride (6) and Zirconocene Dichloride (7) Catalyzed Aminolysis of *N*-Acyl-2-oxazolidinones 3a,b with Various Amines

entry ^a	amine (R)	acyl donor 3	catalyst	% yield of 8 ^b (mp, °C)
1	CH ₂ Ph	3a	6	70 (101–103)
2	(CH ₂) ₄ Me	3a	6	98 (31–33)
3	CH ₂ - <i>c</i> -C ₆ H ₁₁	3a	6	86 (104–106)
4	CH ₂ CH(OEt) ₂	3a	6	65 (oil)
5	CH ₂ CH ₂ OH	3a	6	70 (60–61)
6	CH ₂ CHMeOH	3a	6	80 (88–89)
7	CHMe ₂	3a	6	18 (99–103)
8	CH(Me)Et	3a	6	10 (75–78)
9	CHMePh	3a	6	0
10	CHMePh	3a	7	30 (122–124)
11	CHMePh	3b	7	98 (152–154)
12	CHEt ₂	3a	6	0
13	CHEt ₂	3b	7	75 (122–123)
14	<i>c</i> -C ₆ H ₁₁	3a	6	0
15	3-MeC ₆ H ₄	3a	6	0

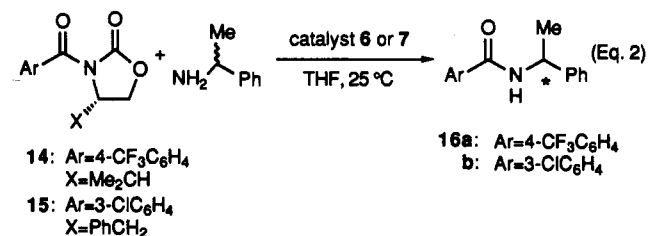
^a All reactions were carried out in THF at 25 °C in the presence of the catalyst (20 mol %) for 18 h. ^b All compounds gave satisfactory elemental analysis. ^c Determined by NMR analysis.

of α -alkyl-branched primary alkylamines and arylamines were found to be substantially slow under the identical conditions and most of starting amines remained unchanged (entries 7–9, 12, 14, and 15, Table 2). Such reactivities of α -alkyl-branched primary alkylamines to the reactions could be improved to give the corresponding amides in modest to high yields upon using 3b and Cp₂ZrCl₂ as an acyl donor reagent and a mediator, respectively (entries 10, 11, and 13, Table 2).

On the basis of the remarkable reaction rates differences observed above, we next examined the chemoselective carbonylation of straight-chain primary amines in the presence of α -alkyl-branched primary alkylamines and arylamines. Although several useful methods using a variety of reagent systems have been developed for chemoselective acylation of primary amines and alcohols containing secondary amines and alcohols,^{8a,b} practical and highly selective methods for discriminating sterically and electronically diverse primary amines with acylation are not available at present.^{9,10} Acylation of a 1:1 mixture of benzylamine and 1-phenylethylamine with 3a in the presence of Cp₂TiCl₂ (20 mol %) in THF proceeded chemoselectively to give *N*-benzylbenzamide (11) in 90% yield, while 1-phenylethylamine was recovered in virtually quantitative yield as expected (entry 4, Table 3). 1,2- and 1,3-Diamines were also acylated on *N*¹ primary amines under the same conditions to give mono-benzamides 9¹¹ and 10¹¹ in high chemoselectivity (entries 1, 2, and 3, Table 3). In the case of acylation for 1,2-diamine, a small amount of acylation products on *N*² primary amine and both amines were detected; moreover, the selectivity slightly depends upon the molar ratios of the diamine to the acyl

donor. The highest selectivity was obtained when a molar ratio of 2:1 of diamine to 3a was employed (entries 1 and 2, Table 3). Similar high chemoselectivity was observed with the acylation of *p*-aminobenzylamine (entry 5, Table 3).¹²

Finally the present acylation reaction was applied to an enantiodiscrimination between α -phenethylamine enantiomers using chiral *N*-acyl-2-oxazolidinones 14 and 15 as acyl-donor reagents (Table 4).⁵ In each of the indicated reactions employing Cp₂ZrCl₂ as a reaction mediator, acylation proceeded with a stereoregular kinetic preference for amidation of the (*R*) amine enantiomer in modest enantioselectivity and good yield (entries 1 and 3, Table 4). On the contrary, the use of Cp₂TiCl₂ induced the reversed enantioselectivity for amidation of the (*S*) amine enantiomer.



In conclusion this study has demonstrated that Lewis acid–base complexes derived from group IV-metal catalysts and *N*-acyl-2-oxazolidinones are mild acylating reagents for highly chemoselective carbonylation of primary amines as well as discrimination of chirality on primary alkylamines.

Experimental Section

General. Melting points are uncorrected. THF was distilled from sodium/benzophenone ketyl prior to use. Unless specified otherwise, reagent-grade amines and group IV metal catalysts were used as received from chemical suppliers. NMR spectra were recorded at 300 or 400 MHz for ¹H and at 100 MHz for ¹³C in CDCl₃ using residual chloroform as an internal reference (7.26 ppm for ¹H and 77.1 ppm for ¹³C). All reactions were carried out under nitrogen.

General Procedures for the Synthesis of *N*-Acyl-2-oxazolidinones (3, 14, and 15). *N*-Acyl-2-oxazolidinones 3a–e were prepared by the general method developed by Kunieda.¹⁴ The mixture of 2-oxazolidone and a catalytic amount of 4-(dimethylamino)pyridine (DMAP) in THF was treated with the corresponding acyl chloride (1.0 equiv) at room temperature for 18 h. Usual workup gave 3a–e in yields of >90%.

3-Benzoyl-2-oxazolidinone (3a): mp 168 °C (lit.⁶ mp 168 °C). Anal. Calcd for C₁₀H₉NO₃: C, 63.82; H, 4.75; N, 7.33. Found: C, 63.62; H, 4.52; N, 7.41.

3-[4-(Trifluoromethyl)benzoyl]-2-oxazolidinone (3b): mp 176 °C. Anal. Calcd for C₁₁H₉NO₃F₃: C, 50.97; H, 3.11; N, 5.41. Found: C, 51.06; H, 2.98; N, 5.38.

3-(3-Chlorobenzoyl)-2-oxazolidinone (3c): mp 171 °C. Anal. Calcd for C₁₀H₈NO₃Cl: C, 53.23; H, 3.57; N, 6.21. Found: C, 53.22; H, 3.53; N, 6.16.

3-(4-Chlorobenzoyl)-2-oxazolidinone (3d): mp 163 °C (lit.⁶ mp 163 °C). Anal. Calcd for C₁₀H₈NO₃Cl: C, 53.23; H, 3.57; N, 6.21. Found: C, 53.32; H, 3.43; N, 6.16.

3-(4-Methoxybenzoyl)-2-oxazolidinone (3d): mp 153 °C (lit.⁶ mp 153 °C). Anal. Calcd for C₁₀H₉NO₃Cl: C, 59.72; H, 5.01; N, 6.35. Found: C, 59.87; H, 4.95; N, 6.35.

(8) (a) Recent examples for chemoselective acylation of primary alcohols: Yamada, S. *J. Org. Chem.* 1992, 57, 1592. Ishihara, K.; Kurihara, H.; Yamamoto, H. *J. Org. Chem.* 1993, 58, 3791 and refs cited therein. (b) For selective acylation of primary alkylamines in the presence of secondary alkylamines. See Kikugawa, Y.; Mitsui, K.; Sakamoto, T.; Kawase, M.; Tamiya, H. *Tetrahedron Lett.* 1990, 31, 243. Akikusa, N.; Mitsui, K.; Sakamoto, T.; Kikugawa, Y. *Synthesis* 1992, 1058 and refs cited therein.

(9) Posner, G. H.; Oda, M. *Tetrahedron Lett.* 1981, 22, 5003.

(10) Lipase-catalyzed selective acylation of ϵ -primary amines in the dipeptide of L-Phe- α -L-Lys-O-*t*-Bu in organic solvent was reported: Gardossi, L.; Bianchi, D.; Klibanov, A. M. *J. Am. Chem. Soc.* 1991, 113, 6328.

(11) Structures of 9 and 10 were proved by their conversion to *N*-(2-hydroxypropyl)benzamide and *N*-(3-hydroxypentyl)benzamide, respectively (NaNO₂, AcOH, concd H₂SO₄, 25 °C).

(12) Selective acylation of *p*-aminobenzylamine was recently reported: King, J. F.; Rathore, R.; Lam, J. Y. L.; Guo, Z. R.; Klassen, D. F. *J. Am. Chem. Soc.* 1992, 114, 3028.

(13) Pirkle, W. H.; Sikkenga, D. J. *J. Org. Chem.* 1977, 42, 1370.

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Table 3. Chemoselective Acylation of Straight-Chain Alkylamines in the Presence of α -Alkyl-Branched Primary Amines and Aryl Amines

entry	diamine ^b	acyl donor	catalyst	product	% yield ^c (<i>N</i> ¹ -monoamide/ <i>N</i> ² -monoamide/diamine) ^d
1 ^e	1,2-Diaminopropane	3a	6	MeCH(NH ₂)CH ₂ NHCOPh (9)	83 (85:7:8)
2 ^e	1,2-Diaminopropane	3a	7	9	79 (81:9:10)
3	1,3-Diaminopentane	3a	6	EtCH(NH ₂)CH ₂ CH ₂ NHCOPh (10)	98 ^f
4 ^e	PhCH ₂ NH ₂ + PhCH(Me)NH ₂	3a	6	PhCH ₂ NHCOPh (11) PhCH(Me)NHCOPh (12)	90 2 ^h
5	4-NH ₂ C ₆ H ₄ CH ₂ NH ₂	3a	6	4-NH ₂ C ₆ H ₄ CH ₂ NHCOPh (13)	95 ^f

^a All reactions were carried out in THF in the presence of the catalyst (20 mol %) at room temperature for 18 h. ^b The molar ratio of diamine to acyl donor is 1.1:1 unless stated otherwise. ^c Yield based on acyl donor. ^d The ratios were determined by ¹H-NMR analysis of crude reaction mixtures. ^e The molar ratio of diamine to acyl donor is 2:1. ^f Diamide and the other isomers were not detected by ¹H- and ¹³C-NMR analysis of crude reaction mixture. ^g A 1:1 mixture of amines was used to substrate. ^h 1-Phenylethylamine was recovered in 90% yield.

Table 4. Enantioselective Acylation of α -Phenethylamine with Chiral 2-Oxazolidinones 14 and 15

entry ^a	acyl donor	catalyst	product	% yield ^b	[α] _D ^c	% ee ^d (config) ^e
1	14	7	16a	90	+8.07	43 (R)
2	14	6	16a	40	-4.37	23 (S)
3	15	7	16b	88	+6.94	55 (R)

^a All reactions were carried out in THF at 25 °C in the presence of 20 mol % of the catalyst for 18 h. ^b Yield based on 14 and 15. ^c Measured in CHCl₃ (c 1.0) at 20 °C. ^d Determined by NMR analysis with (*R*)-(-)-2,2,2-trifluoro-1-(9-anthryl)ethanol as chiral solvating agent.¹³ ^e Determined by comparison with authentic samples prepared from (+)- and (-)- α -phenethylamines.

N-Acyl-2-oxazolidinones 14 and 15 were prepared from the corresponding 2-oxazolidinone and acid chloride according to the general protocol (*n*-BuLi, THF, -78 °C) developed by Evans.^{3a}

(4*S*)-3-[4-(Trifluoromethyl)benzoyl]-4-(1-methylethyl)-2-oxazolidinone (14): mp 132–134 °C; [α]_D²⁰ +148.6° (c 1.0, CHCl₃); ¹H NMR (CDCl₃) δ 7.74 (2H, d, *J* = 8.5 Hz), 7.70 (2H, d, *J* = 8.5 Hz), 4.73–4.67 (1H, m), 4.43 (1H, dd, *J* = 9.1, 9.1 Hz), 4.39 (1H, dd, *J* = 9.1, 5.2 Hz), 2.45–2.55 (1H, m), 1.0 (6H, d, *J* = 6.9 Hz); MS *m/z* 301 (M⁺); IR (CHCl₃, cm⁻¹) 1795, 1695. Anal. Calcd for C₁₄H₁₄NO₃F₃: C, 58.32; H, 5.27; N, 5.23. Found: C, 58.44; H, 5.35; N, 5.27.

(4*S*)-3-(3-Chlorobenzoyl)-4-benzyl-2-oxazolidinone (15): mp 97–102 °C; [α]_D²⁰ +112.1° (c 1.0, CHCl₃); ¹H NMR (CDCl₃) δ 7.62 (1H, broad s), 7.59–7.46 (2H, m), 7.41–7.20 (6H, m), 4.94–4.85 (1H, m), 4.36 (1H, dd, *J* = 9.1, 9.1 Hz), 4.26 (1H, dd, *J* = 9.1, 5.5 Hz), 3.44 (1H, dd, *J* = 13.5, 3.6 Hz), 2.97 (1H, dd, *J* = 13.5, 8.9 Hz); MS *m/z* 315 (M⁺); IR (CHCl₃, cm⁻¹) 1790, 1690. Anal. Calcd for C₁₇H₁₄NO₃Cl: C, 64.66; H, 4.47; N, 4.53. Found: C, 64.71; H, 4.49; N, 4.53.

General Procedure for Group IV-Metal Catalyzed Aminolysis of *N*-Acyl-2-oxazolidinones. To a well-stirred solution of the *N*-acyl-2-oxazolidinones 3, 14, or 15 (4 mmol) in 8 mL of THF containing 20 mol % of the metal catalysts 4, 5, 6, or 7 were added the required amines (4.4 mmol) at room temperature. The mixture was stirred for several hours at the same temperature. The reaction was quenched with saturated aqueous KHSO₄ and extracted with CHCl₃. The organic layer was washed with brine, dried over Na₂SO₄, and evaporated to give the corresponding amides 8¹⁵ and 16.

N-(1-Phenylethyl)-4-(trifluoromethyl)benzamide (16a): mp 152–154 °C; ¹H NMR (CDCl₃) δ 7.89 (2H, d, *J* = 8.6 Hz), 7.70 (2H, d, *J* = 8.6 Hz), 7.45–7.27 (5H, m), 6.31 (1H, broad s), 5.30–

5.40 (1H, m), 1.64 (3H, d, *J* = 7.1 Hz); IR (CHCl₃, cm⁻¹) 3500, 1670; MS *m/z* 293 (M⁺). Anal. Calcd for C₁₆H₁₄NOF₃: C, 65.52; H, 4.81; N, 4.78. Found: C, 65.36; H, 4.83; N, 4.74.

N-(1-Phenylethyl)-3-chlorobenzamide (16b): mp 88–91 °C; ¹H NMR (CDCl₃) δ 7.60–7.80 (4H, m), 7.20–7.50 (5H, m), 6.20–6.30 (1H, m), 5.25–5.35 (1H, m), 1.63 (3H, d, *J* = 7.1 Hz); IR (CHCl₃, cm⁻¹) 3450, 1665; MS *m/z* 259 (M⁺). Anal. Calcd for C₁₅H₁₄NOCl: C, 69.36; H, 5.43; N, 5.39. Found: C, 69.14; H, 5.45; N, 5.42.

General Procedure for Monoacylation of Diamines. A mixture of 3 (4 mmol) and a catalyst 6 or 7 (0.8 mmol) in THF (8 mL) was treated with diamines (4–8 mmol) as above. The reactions were quenched with excess water and the mixture was extracted with CHCl₃ to give monoamides 9, 10, and 13.¹⁶

N-(2-Aminopropyl)benzamide (9): an oil; ¹H NMR (CDCl₃) δ 7.80 (2H, broad d, *J* = 6.8 Hz), 7.51–7.38 (3H, m), 6.92 (1H, broad s), 3.58–3.45 (1H, m), 3.20–3.10 (2H, m), 1.14 (3H, d, *J* = 5.9 Hz); ¹³C NMR (CDCl₃) δ 167.6, 134.7, 131.3, 128.4, 126.9, 47.3, 46.5, 22.1; IR (neat, cm⁻¹) 3300, 1640; HRMS calcd for C₁₀H₁₄N₂O *m/z* 178.1106, found 178.1094.

N-(3-Aminopentyl)benzamide (10): an oil; ¹³C NMR (CDCl₃) δ 167.0, 134.8, 131.0, 128.3, 126.9, 52.9, 38.8, 34.8, 31.8, 10.2; IR (neat, cm⁻¹) 3300, 1640; HRMS calcd for C₁₂H₁₇N₂O *m/z* 206.1419, found 206.1418.

N-(4'-Aminobenzyl)benzamide (13): mp 142–143 °C (lit.¹⁶ mp 142–143 °C); ¹H NMR (CDCl₃) δ 7.77 (2H, d, *J* = 8.3 Hz), 7.51–7.39 (3H, m), 7.16 (2H, d, *J* = 8.1 Hz), 6.68 (2H, d, *J* = 8.1 Hz), 4.53 (2H, d, *J* = 5.3 Hz). MS *m/z* 226 (M⁺).

Structural Proof of 9 and 10. Deamination of 9. A solution of amine 9 (4 mmol) in 15 mL of glacial acetic acid was treated with 30 mL of water, five drops of concd H₂SO₄, and a solution of NaNO₂ (3 g) in H₂O (3 mL) at 0 °C. The mixture was stirred for 18 h at room temperature and heated at 50 °C for 15 min. The reaction mixture was extracted with ether. The extract was dried (Na₂SO₄) and evaporated to give *N*-(2-hydroxypropyl)benzamide (mp 88–89 °C, 65% yield), which was identical to the authentic sample prepared by benzoylation of 1-amino-2-propanol.

Deamination of 10. Deamination of 10 as above gave *N*-(3-hydroxypentyl)benzamide in 55% yield, which was identical in all respects with the authentic sample prepared as follows: *N*-(3-hydroxypropyl)benzamide^{15c} (895 mg) was oxidized with DMSO (10 mmol), (COCl)₂ (5.5 mmol), and Et₃N (25 mmol) at -78 °C in CH₂Cl₂ according to the method of Swern¹⁷ to give an aldehyde which was treated with ethylmagnesium bromide (2 M solution in ether, 3 mL) in THF (10 mL) at 0 °C for 1 h. The reaction was quenched with saturated NH₄Cl and extracted with CHCl₃ to give *N*-(3-hydroxypentyl)benzamide in 76% yield as an oil: ¹³C NMR (CDCl₃) δ 168.2, 134.3, 131.4, 128.5, 126.9, 71.3, 37.5, 36.0, 30.2, 10.0.

(15) (a) Cline, G. W.; Hanna, S. B. *J. Am. Chem. Soc.* 1987, 109, 3087. (b) Well, M. J. M.; Clark, C. R. *J. Chromatogr.* 1982, 235, 43. (c) Arai, K.; Tamura, S.; Masumiya, T.; Kawai, K.; Nakajima, S.; Ueda, A. *Can. J. Chem.* 1990, 68, 903.

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