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Catalytic Asymmetric Synthesis of Propranolol and Metoprolol Using a La–Li–BINOL Complex

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The La–Li–(*R*)-BINOL complex prepared from either lanthanum(III) chloride [$LaCl_3 \cdot 7H_2O$] or [$La(O\text{-}i\text{-}Pr)_3$] has made possible effective catalytic asymmetric syntheses of therapeutically important β-blockers such as propranolol and metoprolol. The possible stereochemical course of asymmetric nitroaldol reactions has been also clarified.

Keywords: lanthanum; asymmetric catalyst; bimetallic catalyst; nitroaldol; β-blockers

INTRODUCTION

Recently, considerable work concerning new reactions mediated by rare-earth metal reagents has been reported.[1] We too have investigated the reactivity of rare-earth metal complexes as basic reagents. We have found that rare-earth metal complexes such as $La_3(O\text{-}t\text{-}Bu)_9$, $Y_3(O\text{-}t\text{-}Bu)_8Cl$, $Y_5(O\text{-}i\text{-}Pr)_{13}O$, and $Sm(HMDS)_3$ (HMDS, hexamethyldisilazane) can be used as bases in catalytic aldol, cyanosilylation and nitroaldol reactions.[2a,g] Furthermore, we have succeeded in developing several asymmetric rare-earth metal–Li–BINOL complexes, which have been found to be quite effective in catalytic asymmetric nitroaldol reactions.[2] These complexes are stable at room temperature, without loss of their activity, over several months. Moreover, this catalytic asymmetric nitroaldol reaction does not require anhydrous conditions, and BINOL is readily recovered without racemization after the nitroaldol reaction, increasing the scope of this reaction for use in industrial processes. The La–Li–(*R*)-BINOL complex **1** (Fig. 1), one of the most effective catalysts for asymmetric nitroaldol reactions using aliphatic aldehydes, can be readily prepared from either $LaCl_3 \cdot 7H_2O$ or $La(O\text{-}i\text{-}Pr)_3$.[2b,d,e] On the other hand, quite recently we have found that the lithium-free La–BINOL complex prepared from $La(O\text{-}i\text{-}Pr)_3$ and (*R*)- or (*S*)-BINOL is highly efficient in catalytic asymmetric Michael reactions.[2f] Herein we report the catalytic asymmetric synthesis of propranolol and metoprolol using **1** as an asymmetric catalyst. For the preliminary communications, see Refs 2c and 2d.

RESULTS AND DISCUSSION

The nitroaldol reaction (Henry reaction) is a powerful synthetic method in organic synthesis, since the resulting nitroaldols can be easily transformed into various useful derivatives such as β-amino alcohols and α-hydroxy carbonyl compounds. β-Amino alcohols are found as important constituents of many bioactive compounds such

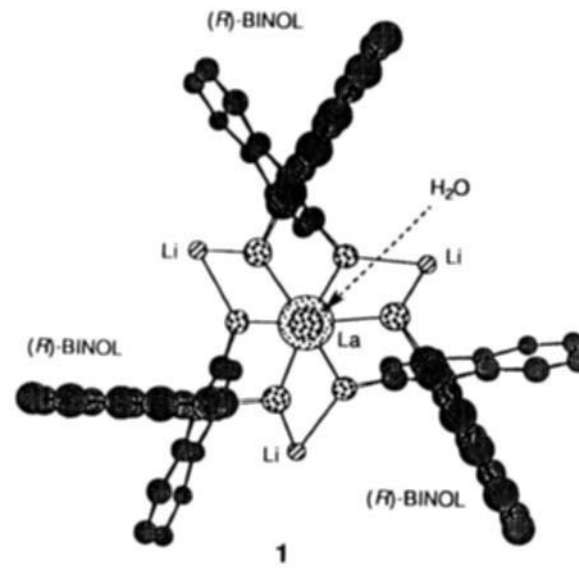

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Figure 1 La–Li–(*R*)-BINOL [(*R*)-LLB] catalyst.

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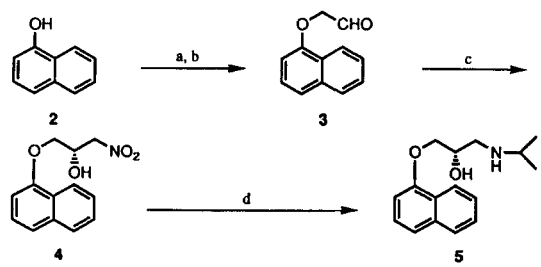
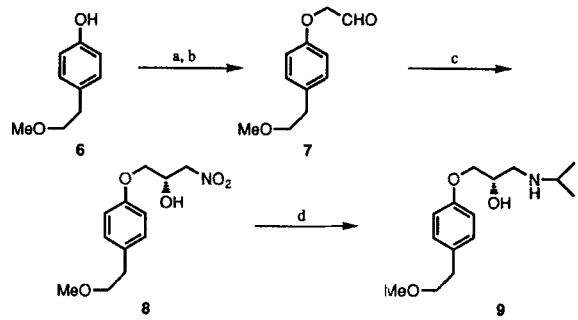
as α/β-adrenergic agonists or antagonists, HIV protease inhibitors and antifungal or antibacterial peptides. Despite their utility, nitroaldol reactions have not been well investigated until recently,[3] especially with respect to asymmetric control. As mentioned above, we have already shown that an asymmetric rare-earth metal–Li–BINOL complex, especially the La–Li–BINOL complex **1**, is quite a versatile catalyst for asymmetric nitroaldol reactions using aliphatic aldehydes. It was envisioned that **1** would be a useful catalyst for the asymmetric synthesis of β-blockers such as propranolol (**5**) and metoprolol (**9**). As with all other β-blockers, optically active (*S*)-propranolol **5** and (*S*)-metoprolol **9** show stronger β-blocking efficacy in cardiovascular diseases than either their (*R*) form or racemate.[4] Hence numerous methods for the synthesis of (*S*)-**5** and (*S*)-**9** have been published.[5] However, there has been no report in which a nitroaldol reaction is used as a key step. Thus, we planned to apply a catalytic asymmetric nitroaldol reaction using the La–Li–(*R*)-BINOL complex **1** as a new synthetic approach to **5** and **9**.

First of all, a catalytic asymmetric synthesis of (*S*)-propranolol **5** (Scheme 1) was carefully investigated. The requisite aldehyde (**3**) was readily prepared from α-naphthol (**2**) in two steps according to the reported procedure.[6] We were pleased to find that treatment of **3** with nitromethane at −50 °C in the presence of the asymmetric catalyst **1** (3 mol%), prepared from $LaCl \cdot 7H_2O$,[2b] gave the nitroaldol **4** at 92% ee in 80% yield. Even at −25 °C, use of this La–Li–(*R*)-BINOL complex gave **4** with high enantiomeric selectivity (87% ee, 62%). With the nitroaldol **4** at 92% ee are available, the stage was set for reduction of the nitro group to the corresponding primary amino functionality, followed by alkylation with retention of the absolute configuration. These desired conversions were best carried out by catalytic



(a) 3-chloro-1,2-propanediol, K_2CO_3, CH_3CN (83%); (b) silica gel, $NaIO_4$, CH_2Cl_2–H_2O (78%); (c) CH_3NO_2, (*R*)-LLB (3 mol %), THF; (d) PtO_2, H_2, MeOH then acetone

Scheme 1



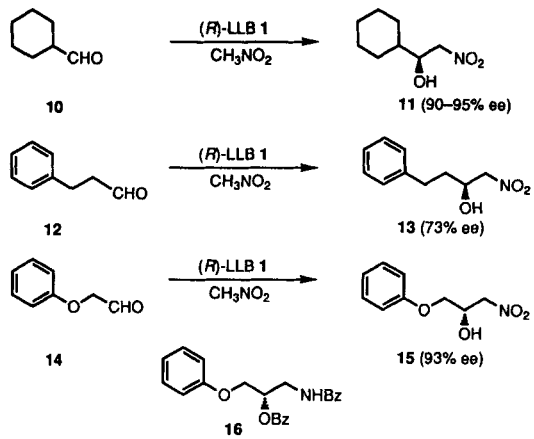
(a) 3-chloro-1,2-propanediol, K_2CO_3, CH_3CN; (b) silica gel, $NaIO_4$, CH_2Cl_2–H_2O; (c) CH_3NO_2, (*R*)-LLB (2 mol %), THF; (d) PtO_2, H_2, MeOH then acetone

Scheme 2

hydrogenation in the presence of PtO_2 followed by addition of acetone, affording (*S*)-propanolol **5** at 92% ee in 90% yield. Thus, a catalytic asymmetric synthesis of **5** (92% ee) has been achieved in a two-step sequence of reactions starting from **3** (72% overall yield). Furthermore, recrystallization of the HCl salt of propranolol (92% ee) from AcOEt–MeOH gave the optically pure drug.

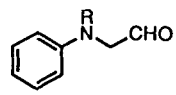
Having established a catalytic asymmetric synthesis of (*S*)-propranolol **5**, we then turned our attention to a catalytic asymmetric synthesis of (*S*)-metoprolol **9**, using the La–Li–(*R*)-BINOL complex **1**. The requisite aldehyde **7** was prepared starting with 4-(2-methoxyethyl)phenol (**6**) in two steps as shown in Scheme 2. It was found that treatment of **7** with nitromethane in the presence of **1** (2 mol%), prepared from $LaCl_3 \cdot 7H_2O$,[2b] afforded the nitroaldol **8** at 90% ee in 88% yield. Furthermore, exposure of **7** to nitromethane in the presence of **1** (5 mol%), prepared from $La(O\text{-}i\text{-}Pr)_3$,[2c] gave **8** at 94% ee in 90% yield (the use of the Pr–Li–BINOL catalyst (3 mol%) gave **8** at 91% ee in 82% yield[2d]). The nitroaldol **8** was readily transformed into (*S*)-metoprolol **9**, a β_1-selective β-blocker, in 80% yield. Thus, we have achieved highly efficient syntheses of two optically active β-blockers, **5** and **9**.

As previously observed,[2a,b,d] the La–Li–(*R*)-BINOL complex **1** generally affords nitroaldol adducts with (*S*) configuration (e.g. **10**→**11**, **12**→**13**; Scheme 3); the use of **1** and 4-(formylmethoxy)indole also gave the corresponding nitroaldol with (*S*) configuration. It is thus noteworthy that the enantiotopic face selection of the β-oxa-aldehydes used in propranolol (**5**) and metoprolol (**9**) syntheses is different from that of aldehydes employed in the usual catalytic asymmetric nitroaldol reactions, even if the absolute configuration of these nitroaldol adducts is the



Scheme 3

same in the system of nomenclature. In order to clarify this point, the neighboring group effect in the assymetric nitroaldol reaction was investigated using phenoxyacetaldehyde (**14**). It was found that use of phenoxyacetaldehyde **14** afforded the adduct **15** at 93% ee in 67% yield. Furthermore, as expected, the absolute configuration of the nitroaldol **15** was determined to be *S* by converting it to the corresponding dibenzoate **16** by the CD exciton chirality method. These results suggest that an oxygen atom at the β-position has a great influence not only on the enantiotopic face selection but also on the enantiomeric excess (Figure 2); the use of the aldehydes **i** and **ii** gave the corresponding nitroaldols with low enantiomeric excess.



i: R = $PhCH_2OCO$
ii: R = *t*-BuOCO

The catalytic asymmetric nitroaldol reaction appears to proceed through lithium nitronates coordinated to the phenolic oxygen. Although the precise mechanism is not clear at present, coordination of the β-oxygen to either the phenolic hydroxyl group through a hydrogen bond or the lithium cation would have a great effect in the asymmetric induction.

CONCLUSIONS

The La–Li–BINOL complex **1** prepared from either $LaCl_3 \cdot 7H_2O$ or $La(O\text{-}i\text{-}Pr)_3$ has been found to be quite useful for the catalytic asymmetric syntheses of propranolol (**5**) and metoprolol (**9**). These syntheses would be applicable to the industrial-scale preparation of therapeutically important β-blockers. Furthermore, we have found a general β-oxygen effect, which would be beneficial to understanding the reaction mechanism of the catalytic asymmetric nitroaldol reaction. Further studies along this line are under investigation.

EXPERIMENTAL

^1H and ^{13}C-NMR spectra were measured by JEOL EX270 or GSX400 with Me_4Si as an internal reference and $CDCl_3$ as the solvent. All solvents were dried prior to use.

(2*S*)-3-(α-Naphthoxy)nitropropan-2-ol (4)

α-Naphthoxyacetaldehyde (**3**) (560 mg, 3 mmol) and nitromethane (8 ml, 150 mmol) were added to 15 ml of THF at room temperature. After the

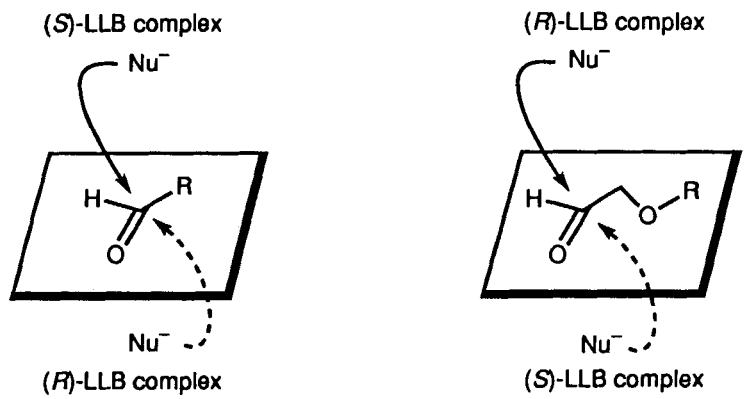


Figure 2 Stereochemical course of asymmetric nitroaldol reaction.

solution was cooled to −50 °C, 6 ml (0.1 mmol) of the La–Li–(*R*)-BINOL THF solution (*ca* 0.0167 M) was gradually added. The reaction mixture was stirred at −50 °C for 60 h, and then the reaction was quenched by the addition of 10 ml of 1 M HCl and extracted with ether. The organic layer was washed with brine, and dried over anhydrous Na_2SO_4. Removal of the solvent and flash column chromatography (CH_2Cl_2) yielded **4** (593 mg, 80%).

^{1}H NMR: δ 3.15 (d, J = 5.6 Hz, 1H), 4.20 (m, 2H), 4.70 (m, 2H), 4.80 (m, 1H), 6.74 (d, J = 7.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.40–7.50 (m, 3H), 7.80 (m, 1H), 8.10 (m, 1H): ^{13}C NMR: δ 67.4, 68.6, 78.0, 105.0, 121.4, 125.2, 125.6, 126.7, 127.7, 134.5, 153.4. IR ($CHCl_3$): ν 3575, 1597, 1460, 1216, 1105 cm^{-1}. MS: *m/z* 247 (M^+). The enantiomeric excess was determined to be 92% by HPLC analysis (Daicel Chiralpak AS: hexane/2-propanol (9:1)).

(*S*)-(−)-Propranolol HCl salt

To a solution of **4** (593 mg, 2.4 mmol) in methanol (50 ml) was added PtO_2 (100 mg). The reaction mixture was vigorously stirred at room temperature under a hydrogen atmosphere for 2 h. Acetone (170 µl, 2.9 mmol) was then added and the reaction mixture was stirred for an additional 16 h at 50 °C. After conversion to the HCl salt, by addition of ethereal HCl to an ether solution of the crude product, silica gel column chromatography (CH_2Cl_2/MeOH = 20:1→10:1) gave 650 mg of (*S*)-(−)-propranolol HCl salt (90%). The spectral data were identical to those previously reported by Sharpless and co-workers: $[\alpha]_D^{25}$ −27.9° (*c* 0.91, EtOH); lit.[5c] $[\alpha]_D^{25}$ −25.5° (*c* 1.05, EtOH).

2-Hydroxy-3-[4-(2-methoxyethyl)phenoxy]propanol

A mixture of 4-(2-methoxyethyl)phenol (5.0 g, 33 mmol), 3-chloro-1,2-propanediol (3.6 g, 33 mmol) and K_2CO_3 (23 g, 164 mmol) in CH_3CN (60 ml) was refluxed with stirring for 9.5 h. After being cooled to room temperature, the reaction mixture was filtered, and the filtrate was evaporated. The residue was purified by silica gel column chromatography (hexane/acetone = 2:1) to give the desired product (5.1 g, 69%) as a colorless viscous oil.

^{1}H NMR: δ 2.80 (1H, bs), 2.81 (2H, t, J = 6.9 Hz), 3.20 (1H, bs), 3.34 (3H, s), 3.56 (2H, t, J = 6.9 Hz), 3.60–3.90 (2H, m), 3.99 (2H, d, J = 4.6 Hz), 4.06 (1H, m), 6.83 (2H, d, J = 8.0 Hz), 7.12 (2H, d, J = 8.0 Hz). IR (neat): ν 3386, 2931, 2872, 1611, 1513, 1459, 1245, 1114, 1046, 829 cm^{-1}. MS: *m/z* 226 (M^+), 181 ($M^+ - MeOCH_2$), 107. High-resolution MS (HRMS): calcd for $C_{12}H_{18}O_4$ 226.1205; found 226.1219.

4-(2-Methoxyethyl)phenoxyacetaldehyde (7)

To a vigorously stirred suspension of silica gel (58 g) in CH_2Cl_2 (130 ml) was added 46 ml of $NaIO_4$ aqueous solution (0.65 M) and then 2-hydroxy-3-[4-(2-methoxyethyl)phenoxy]propanol (5.1 g, 22 mmol) in CH_2Cl_2 (100 ml) at room temperature, and the resulting mixture was further stirred vigorously at the same temperature for 1 h. Filtration and evaporation gave the residue, which was purified by silica column chromatography (hexane/acetone = 4:1) to afford **7** (3.7 g, 84%) as a colorless viscous oil.

^{1}H NMR: δ 2.84 (2H, t, J = 7.1 Hz), 3.35 (3H, s), 3.57 (2H, t, J = 7.1 Hz), 4.55 (2H, s), 6.82 (2H, d, J = 8.2 Hz), 7.16 (2H, d, J = 8.2 Hz), 9.86 (1H, s). IR (neat): ν 3383, 2929, 2869, 1737, 1611, 1510, 1458, 1382, 1298, 1247, 1114, 1063, 831 cm^{-1}. MS: *m/z* 194 (M^+), 149 ($M^+ - MeOCH_2$), 107. HRMS: calcd for $C_{11}H_{14}O_3$ 194.0943; found 194.0931.

(2*S*)-3-[4-(2-methoxyethyl)phenoxy]-nitropropan-2-ol (8)

To a stirred solution of **7** (106 mg, 0.55 mmol) and CH_3NO_2 (1.48 ml, 27.4 mmol) in THF (3 ml) was gradually added the La–Li–(*R*)-BINOL THF solution (0.66 ml, 0.011 mmol, *ca* 0.0167 M) at −50 °C, and the resulting mixture was stirred at the same temperature for 60 h. The reaction was quenched by the addition of 2 ml of 1 M HCl and extracted with ether. The organic layer was washed with brine, and dried over anhydrous Na_2SO_4. Removal of the solvent and silica gel column chromatography (CH_2Cl_2/MeOH = 200:1) gave **8** (123 mg, 88%) as a colorless viscous oil.

^{1}H NMR: δ 2.83 (2H, t, J = 6.9 Hz), 2.99 (1H, d, J = 5.6 Hz), 3.35 (3H, s), 3.57 (2H, t, J = 6.9 Hz), 4.03 (1H, dd, J = 4.0, 10.0 Hz), 4.07 (1H, dd,

$J = 5.0$, 10.0 Hz), 4.61 (1H, dd, $J = 8.0$, 12.0 Hz), 4.68 (1H, m), 4.70 (1H, m), 6.83 (2H, d, $J = 8.3$ Hz), 7.16 (2H, d, $J = 8.3$ Hz). ^{13}C NMR: δ 35.08, 58.53, 67.22, 68.41, 73.59, 77.97, 114.38, 129.88, 132.13, 156.30. IR (neat): ν 3382, 2932, 1612, 1556, 1514, 1383, 1244, 1114, 1049, 831 cm^{-1}. MS: m/z 255 (M^+), 210 ($M^+ - MeOCH_2$), 194, 107. The enantiomeric excess was determined to be 90% by HPLC analysis (Daicel Chiralpak AD: hexane/2-propanol, 9:1).

(*S*)-(+)-Metoprolol (9)

To a solution of **8** (64 mg, 0.25 mmol) in methanol (5 ml) was added PtO_2 (15 mg). The reaction mixture was vigorously stirred at 50 °C for 1 h. Acetone (18 µl, 0.30 mmol) was then added and the reaction mixture was stirred for an additional 15 h at 50 °C. After being cooled to room temperature, the mixture was filtered, and the filtrate was evaporated. The residue was purified by silica gel column chromatography (CH_2Cl_2/MeOH/30% aqueous NH_3, 100:20:1) to give **9** (54 mg, 80%); $[\alpha]_D^{22} + 5.9°$ (*c* 0.998, EtOH).

^{1}H NMR: δ 1.09 (6H, d, $J = 6.3$ Hz), 2.30 (2H, bs), 2.73 (1H, dd, $J = 5.4$, 9.0 Hz), 2.80–2.90 (2H, m), 2.84 (2H, t, $J = 7.1$ Hz), 3.35 (3H, s), 3.56 (2H, t, $J = 7.1$ Hz), 3.90 (2H, m), 4.00 (1H, m), 6.85 (2H, d, $J = 8.2$ Hz), 7.13 (2H, d, $J = 8.2$ Hz). ^{13}C NMR: δ 22.39, 22.45, 35.17, 49.08, 49.26, 58.51, 68.09, 70.46, 73.73, 114.39, 129.67, 131.29, 157.03. IR (neat): ν 3346, 2966, 2926, 2867, 2359, 1613, 1514, 1470, 1383, 1245, 1115, 827 cm^{-1}. MS: m/z 267 (M^+), 252 ($M^+ - CH_3$), 223, 107, 72. The enantiomeric excess of **9** was confirmed to be 90% by HPLC analysis (Daicel Chiralcel OD: hexane/2-propanol/Et_2NH, 90:10:0.1).

(2*S*)-1-Phenoxy-3-nitropropan-2-ol (15)

To a stirred solution of **14**[7] (75 mg, 0.55 mmol) and CH_3NO_2 (1.48 ml, 27.4 mmol) in THF (3 ml) was gradually added the La–Li–(*R*)-BINOL THF solution (1.1 ml, 0.018 mmol, *ca* 0.0167 M) at −50 °C, and the resulting mixture was stirred at the same temperature for 29 h. The reaction was quenched by the addition of 1 M HCl and extracted with ether. The organic layer was washed with brine, and dried over anhydrous Na_2SO_4. Removal of the solvent and silica gel column chromatography (hexane/acetone, 10:1) gave **15** (69 mg, 67%):

^{1}H NMR: δ 2.89 (d, $J = 5.6$ Hz, 1H), 4.07 (dd, $J = 5.2$, 9.7 Hz, 1H), 4.11 (dd, $J = 4.6$, 9.7 Hz, 1H), 4.60–4.70 (m, 2H), 4.65–4.80 (m, 1H), 6.90 (d, $J = 9.5$ Hz, 2H), 7.01 (t, $J = 8.0$ Hz, 1H), 7.31 (dd, $J = 8.0$, 9.5 Hz, 2H). ^{13}C NMR: δ 67.3, 68.2, 77.8, 114.5, 121.7, 130.0, 157.8. IR ($CHCl_3$): ν 3428, 2930, 1588, 1556, 1495, 1380, 1244 cm^{-1}. MS: m/z 197 (M^+), 137. HRMS calcd for $C_9H_{11}NO_4$ 197.0688; found 197.0695. $[\alpha]_D^{24} + 22.9°$ (*c* 1.889, EtOH). The enantiomeric excess of **15** was determined to be 93% by HPLC analysis (Daicel Chiralpak AS: hexane/2-propanol, 8:2).

(2*S*)-*N*-Benzoyl-2-benzoyloxy-3-phenoxy-1-propylamine (16)

To a stirred suspension of 10% Pd/C (62 mg) in MeOH (2 ml) was added a solution of **15** (99 mg, 0.5 mmol) in MeOH (2 ml) under an atmosphere of H_2. After being stirred overnight at room temperature, the mixture was filtered through celite. The solvent was evaporated and benzoyl chloride (0.10 ml, 0.85 mmol) was added to a solution of the residue in pyridine (0.5 ml). After being stirred for 2 h, the mixture was quenched with H_2O. The organic layer was separated and successively washed with 1 M HCl, sat. aq. $NaHCO_3$ and brine, and dried over anhydrous Na_2SO_4. Evaporation of the solvent and flash column chromatography (silica gel; hexane/AcOEt, 3:1) gave **16** (117 mg, 62%).

^{1}H NMR: δ 3.87–4.10 (m, 2H), 4.31 (d, $J = 5.2$ Hz, 2H), 5.58–5.62 (m, 1H), 6.92–6.99 (m, 4H), 7.25–7.56 (m, 8H), 7.74–7.77 (m, 2H), 8.02–8.07 (m, 2H). ^{13}C NMR: δ 41.3, 67.7, 72.0, 114.6, 121.4, 126.9, 128.3, 128.4, 128.6, 129.5, 129.8, 130.0, 131.5, 133.4, 134.1, 158.2, 166.6, 167.8. IR (KBr): ν 3300, 1727, 1643, 1599, 1537, 1274, 1245 cm^{-1}. MS: m/z 376 ($M^+ + 1$), 254 (base peak), 149, 105. M.p. 97–99 °C. $[\alpha]_D^{23} + 26.9°$ (*c* 1.15, $CHCl_3$). The CD spectrum showed a negative first Cotton effect at 239 nm and a positive second Cotton effect at 225 nm.

REFERENCES

1. For carbon–carbon bond-forming reactions, see: (a) G. A. Molander and J. O. Hoberg, *J. Am. Chem. Soc.* **114**, 3123 (1992); (b) G. A. Molander, *Chem. Rev.* **92**, 29 (1992); (c)

P. V. Weghe and J. Collin, *Tetrahedron Lett.* **34**, 3881 (1993); (d) T. Imamoto, N. Takiyama, K. Nakamura, T. Hatajima and Y. Kamiya, *J. Am. Chem. Soc.* **111**, 4392 (1989) and references cited therein. For carbon-nitrogen bond-forming reactions, see: (e) M. R. Gagne and T. J. Marks, *J. Am. Chem. Soc.* **111**, 4108 (1989); (f) M. R. Gagne, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.* **114**, 275 (1992). For Lewis acids, see: (g) S. Kobayashi, I. Hachiya, T. Takahori, M. Araki and H. Ishitani, *Tetrahedron Lett.* **33**, 6815 (1992); (h) S. Danishefsky and M. Bednarski, *Tetrahedron Lett.* **26**, 2507 (1985); (i) J.-H. Gu, M. Terada, K. Mikami and T. Nakai, *Tetrahedron Lett.* **33**, 1465 (1992); (j) S. Matsubara, T. Takai and K. Utimoto, *Chem. Lett.* 1447 (1991). For reductions, see: (k) K. Kusuda, J. Inanaga and M. Yamaguchi, *Tetrahedron Lett.* **30**, 2945 (1989); (l) A. L. Gemal and J. L. Luche, *J. Am. Chem. Soc.* **103**, 5454 (1981); (m) D. A. Evans and A. H. Hoveyda, *J. Am. Chem. Soc.* **112**, 6447 (1990); (n) D. Romo, S. D. Meyer, D. D. Johnson and S. L. Schreiber, *J. Am. Chem. Soc.* **115**, 7906 (1993).

2. (a) H. Sasai, T. Suzuki, S. Arai, T. Arai and M. Shibasaki, *J. Am. Chem. Soc.* **114**, 4418 (1992); (b)H. Sasai, T. Suzuki, N. Itoh, and M. Shibasaki, *Tetrahedron Lett.* **34**, 851 (1993); (c) H. Sasai, N. Itoh, T. Suzuki and M. Shibasaki, *Tetrahedron Lett.* **34**, 855 (1993); (d) H. Sasai, T. Suzuki, N. Itoh, S. Arai and M. Shibasaki, *Tetrahedron Lett.* **34**, 2657 (1993); (e) H. Sasai, T. Suzuki, N. Itoh, K. Tanaka, T. Date, K. Okamura and M. Shibasaki, *J. Am. Chem. Soc.* **115**, 10372 (1993); (f) H. Sasai, T. Arai and M. Shibasaki, *J. Am. Chem. Soc.* **116**, 1571 (1994); (g) H. Sasai, S. Arai and M. Shibasaki, *J. Org. Chem.* **59**, 2661 (1994).
3. (a) D. Seebach, E. R. Colvin, F. Lehr and T. Weller, *Chimia* **33**, 1 (1979); (b) G. Rosini and R. Ballini, *Synthesis*, 833 (1988).
4. R. Howe and R. G. Shanks, *Nature (London)* **210**, 1336 (1966).
5. (a) Y. Tsuda, K. Toshimoto and T. Nishikawa, *Chem. Pharm. Bull.* **29**, 3593 (1981); (b) Y. Terao, M. Murata and K. Achiwa, *Tetrahedron Lett.* **29**, 5173 (1988); (c) J. M. Klunder, S. Y. Ko and K. B. Sharpless. *J. Org. Chem.* **51**, 3710 (1986); (d) H. Takahashi, S. Sakuraba, H. Takeda and K. Achiwa, *J. Am. Chem. Soc.* **112**, 5876 (1990); (e) Z.-M. Wang, X.-L. Zhang and K. B. Sharpless, *Tetrahedron Lett.* **34**, 2267 (1993); (f) H. S. Bevinakatti and A. A. Banerji, *J. Org. Chem.* **56**, 5372 (1991).
6. A. Solladié-Cavallo and M. Bencheqroun, *Tetrahedron Lett.* **31**, 2157 (1990).
7. L. F. Hatch and S. S. Nesbitt, *J. Am. Chem. Soc.* **67**, 39 (1945).