Stereoselective Reactions. XXXIV.[1] Enantioselective Deprotonation of Prochiral 4-Substituted Cyclohexanones Using Chiral Bidentate Lithium Amides Having a Bulky Group Instead of a Phenyl Group on the Chiral Carbon

Masaharu TORIYAMA,[a] Keizo SUGASAWA,[b] Shigeyasu MOTOHASHI,[a] Norio TOKUTAKE,[a] and Kenji KOGA*,[c]

College of Pharmacy, Nihon University,[a] Narashinodai, Funabashi-shi, Chiba 274–8555, Japan, Institute for Drug Discovery Research, Yamanouchi Pharmaceutical Co., Ltd.,[b] 21 Miyukigaoka, Tsukuba-shi, Ibaraki 305–8585, Japan, and Research and Education Center for Materials Science, Nara Institute of Science and Technology,[c] Takayama-cho, Ikoma-shi, Nara 630–0101, Japan. Received January 5, 2001; accepted February 1, 2001

Using chiral bidentate lithium amides having a bulky group instead of a phenyl group on the chiral carbon, enantioselective deprotonation of prochiral 4-substituted cyclohexanones in the presence of excess trimethylsilyl chloride was examined in THF in the absence and in the presence of HMPA. It is shown that enantioselectivity of the reactions decreases as the substituent on the chiral carbon of the chiral lithium amides and the substituent at the 4-position of cyclohexanones become reasonably bulky. An eight-membered cyclic transition state model is proposed for this deprotonation reaction.

Key words chiral lithium amide; enantioselective deprotonation; ^{6}Li-NMR; ^{15}N-NMR; eight-membered cyclic transition state model

Lithium dialkylamides such as lithium diisopropylamide (LDA) are widely used in organic synthesis as strong bases with low nucleophilicity.[2] We have previously reported enantioselective deprotonation[3] of prochiral 4-substituted cyclohexanones (**1**) using chiral lithium amides in the presence of excess trimethylsilyl chloride (TMSCl) (Corey's internal quench method[4]) to isolate the corresponding lithium enolates (**2**) as trimethylsilyl enol ethers (**3**).[5] Among various chiral lithium amides examined, chiral bidentate lithium amides ((*R*)-**5a**, (*R*)-**5b**) having a phenyl group on the chiral carbon, a neopentyl or trifluoroethyl group on the amide nitrogen, and a piperidino group as an internal ligation site for the lithium give the products ((*R*)-**3**) in high ee's.[5b,c,i,l] By X-ray and NMR studies, it is shown that these chiral lithium amides ((*R*)-**5a**, (*R*)-**5b**) exist almost entirely as a chelated monomeric form ((*R*)-**6**) having a chiral amide nitrogen in tetrahydrofuran (THF) or dimethoxyethane (DME), and in THF, DME, ether, or toluene in the presence of 2 eq of hexamethylphosphoric triamide (HMPA).[5b,c,i,l] In this structure, the substituent (a neopentyl or trifluoroethyl group) on the amide nitrogen and the phenyl group on the chiral carbon are *trans*, presumably due to the steric repulsion between them. It is therefore reasonable to assume that bidentate chiral lithium amides ((*R*)-**12a**, **b**—(*R*)-**15a**, **b**, (*S*)-**16a**, **b**) having a bulkier substituent instead of a phenyl group on the chiral carbon would be more effective as chiral bases for enantioselective deprotonation. Based on this consideration, we prepared chiral bidentate amines ((*R*)-**7a**, **b**—(*R*)-**10a**, **b**, (*S*)-**11a**, **b**) for the preparation of their corresponding lithium amides.[1] The present paper describes the results of deprotonation reactions of 4-substituted cyclohexanones (**1a**—**d**) by these chiral bidentate lithium amides.

The reactions of **1a**—**d** were carried out under the fixed conditions, using 1.2 eq of lithium amide and 5 eq of TMSCl in the presence of 1.2 eq of HMPA in THF at −78 °C for 30 min.[6] The results using chiral lithium amides ((*R*)-**5a**, (*R*)-**11a**—(*R*)-**15a**, and (*S*)-**16a**) having a neopentyl group on the amide nitrogen are summarized in Table 1. It is shown that, except one case (run 20), chiral lithium amides having *R*-configuration give the products rich in *R*-enantiomer, while that having *S*-configuration gives the products rich in *S*-enantiomer. It is also shown that the enantioselectivities of the reactions are dependent on the bulkiness of both the substituent on the chiral carbon of the chiral lithium amides and the sub-

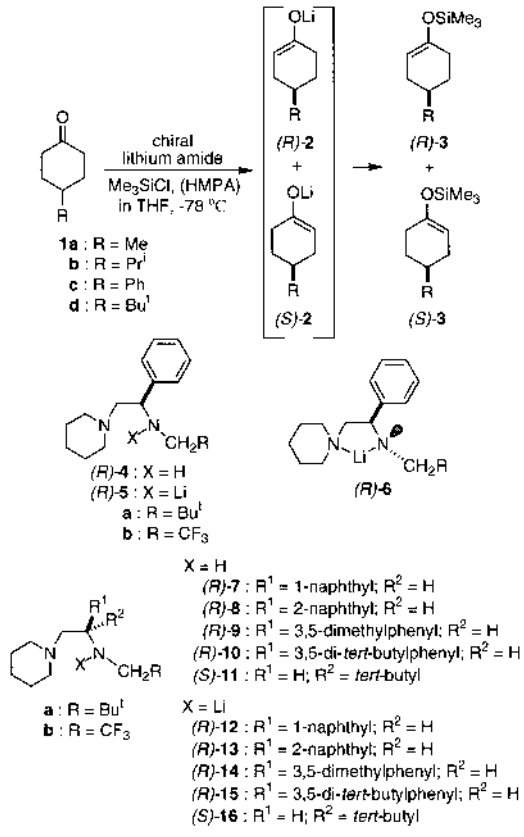


Chart 1

* To whom correspondence should be addressed. e-mail: kkoga@ms.aist-nara.ac.jp

Table 1. Enantioselective Deprotonation of **1** Using (*R*)-**5a**, (*R*)-**12a**—(*R*)-**15a**, and (*S*)-**16a**[a)]

Run	Ketone		Lithium amide			Product		
	Compound	R	Compound	R^1	R^2	Compound	Chem. y. (%)	E.e. (%)
1	**1a**	Me	(*R*)-**5a**	Ph	H	(*R*)-**3a**	77	92
2	**1b**	iso-Pr	(*R*)-**5a**	Ph	H	(*R*)-**3b**	91	89
3	**1c**	Ph	(*R*)-**5a**	Ph	H	(*R*)-**3c**	98	87
4	**1d**	*t*-Bu	(*R*)-**5a**	Ph	H	(*R*)-**3d**	96	83
5	**1a**	Me	(*R*)-**12a**	1-Naph	H	(*R*)-**3a**	87	94
6	**1b**	iso-Pr	(*R*)-**12a**	1-Naph	H	(*R*)-**3b**	91	93
7	**1c**	Ph	(*R*)-**12a**	1-Naph	H	(*R*)-**3c**	98	90
8	**1d**	*t*-Bu	(*R*)-**12a**	1-Naph	H	(*R*)-**3d**	87	85
9	**1a**	Me	(*R*)-**13a**	2-Naph	H	(*R*)-**3a**	78	92
10	**1b**	iso-Pr	(*R*)-**13a**	2-Naph	H	(*R*)-**3b**	93	87
11	**1c**	Ph	(*R*)-**13a**	2-Naph	H	(*R*)-**3c**	97	85
12	**1d**	*t*-Bu	(*R*)-**13a**	2-Naph	H	(*R*)-**3d**	95	75
13	**1a**	Me	(*R*)-**14a**	3,5-$Me_2C_6H_3$	H	(*R*)-**3a**	84	86
14	**1b**	iso-Pr	(*R*)-**14a**	3,5-$Me_2C_6H_3$	H	(*R*)-**3b**	95	80
15	**1c**	Ph	(*R*)-**14a**	3,5-$Me_2C_6H_3$	H	(*R*)-**3c**	99	74
16	**1d**	*t*-Bu	(*R*)-**14a**	3,5-$Me_2C_6H_3$	H	(*R*)-**3d**	99	47
17	**1a**	Me	(*R*)-**15a**	3,5-(*t*-Bu)$_2C_6H_3$	H	(*R*)-**3a**	67	66
18	**1b**	iso-Pr	(*R*)-**15a**	3,5-(*t*-Bu)$_2C_6H_3$	H	(*R*)-**3b**	85	33
19	**1c**	Ph	(*R*)-**15a**	3,5-(*t*-Bu)$_2C_6H_3$	H	(*R*)-**3c**	77	23
20	**1d**	*t*-Bu	(*R*)-**15a**	3,5-(*t*-Bu)$_2C_6H_3$	H	(*S*)-**3d**	85	16
21	**1a**	Me	(*S*)-**16a**	H	*t*-Bu	(*S*)-**3a**	65	27
22	**1b**	iso-Pr	(*S*)-**16a**	H	*t*-Bu	(*S*)-**3b**	78	17
23	**1c**	Ph	(*S*)-**16a**	H	*t*-Bu	(*S*)-**3c**	86	6
24	**1d**	*t*-Bu	(*S*)-**16a**	H	*t*-Bu	(*S*)-**3d**	77	12

a) A typical procedure is written in the Experimental.

stituent on the 4-position of cyclohexanones. Thus, by using (*R*)-**5a** having a phenyl group on the chiral carbon, enantioselectivities of the reactions decrease as the bulkiness of the substituent on the 4-position of cyclohexanones increases (runs 1—4). The same tendency is observed for the reactions using (*R*)-**12a** (runs 5—8), (*R*)-**13a** (runs 9—12), (*R*)-**14a** (runs 13—16), and (*R*)-**15a** (runs 17—19), having a 1-naphthyl, 2-naphthyl, 3,5-dimethylphenyl, and 3,5-di-*tert*-butylphenyl group, respectively, on the chiral carbon. It is also recognized that enantioselectivities of the reactions are generally higher by using chiral lithium amides having a phenyl or 1-naphthyl group on the chiral carbon ((*R*)-**5a** or (*R*)-**12a**), while they become lower by using chiral lithium amides having a more bulky substituent on the chiral carbon ((*R*)-**14a**, (*R*)-**15a**). As a result, the sense of asymmetric induction is reversed in the reaction of **1d** having a *tert*-butyl group by (*R*)-**15a** having a 3,5-di-*tert*-butylphenyl group, giving (*S*)-**3d** in low ee (run 20). On the other hand, the lithium amide ((*S*)-**16a**) having a *tert*-butyl group on the chiral carbon is not an efficient chiral base giving the products in low ee's (runs 21—24).

As summarized in Table 2, similar phenomena are observed for the reactions by chiral lithium amides ((*R*)-**5b**, (*R*)-**12b**—(*R*)-**15b**, (*S*)-**16b**) having a trifluoroethyl group on the amide nitrogen. Thus, except one case (run 20), the lithium amides having *R*-configuration give the products rich in *R*-enantiomer, while the lithium amide having *S*-configuration gives the products rich in *S*-enantiomer, and the enantioselectivities of the reactions lower as the bulkiness of both the aryl substituent at the chiral carbon of the chiral lithium amides and the substituent on the 4-position of cyclohexanones increases. The product of the reaction of **1d** having a *tert*-butyl group by (*R*)-**15b** having a 3,5-di-*tert*-butylphenyl group is almost racemic **3d** (run 20). Enantioselectivities of the reactions using (*S*)-**16b** (runs 21—24) are improved compared to those using (*S*)-**16a** (runs 21—24, Table 1), but are still lower than those using (*R*)-**5b**, (*R*)-**12b**, (*R*)-**13b**, and (*R*)-**14b** (runs 1—16).

These data clearly show that, for the reactions using chiral lithium amides having an aryl group on the chiral carbon ((*R*)-**5a**, **b**, (*R*)-**12a**, **b**—(*R*)-**15a**, **b**), severe steric interactions arise between the bulkier aryl substituent of the chiral lithium amides and the bulkier 4-substituent of cyclohexanones at the transition states of the reactions.

Two methods are available to convert the ketone to the corresponding silyl enol ether: the lithium amide and TMSCl are premixed prior to the addition of the ketone (internal quench method[4)]) and the lithium amide is allowed to react with the ketone before TMSCl is added (external quench method). It is shown that the internal quench method, in general, gives higher enantioselectivity than the external quench method, and that improvement in enantiomeric excess of the products under external quench conditions can be achieved by the presence of lithium halides in the reaction mixture at the deprotonation step.[5d,9,10)] We have previously observed a similar phenomenon in the deprotonation of **1d** using a monodentate chiral lithium amide, and shown that the formation of a 1 : 1 mixed dimer of the lithium amide and LiCl or LiBr is responsible for the improvement of enantioselectivities under the external quench conditions in the presence of these lithium halides at the deprotonation step.[5d)] All the reactions shown in Tables 1 and 2 are carried out under the internal quench method. As shown in Table 3, it is again recognized that enantioselectivities of the reactions of **1d** using (*R*)-**5a** and (*R*)-**12a** to give (*R*)-**3d** change by the reaction conditions employed. Thus, compared to the reactions under the internal

Table 2. Enantioselective Deprotonation of **1** Using (*R*)-**5b**, (*R*)-**12b**—(*R*)-**15b**, and (*S*)-**16b**[a)]

Run	Ketone		Lithium amide			Product		
	Compound	R	Compound	R^1	R^2	Compound	Chem. y. (%)	E.e. (%)
1	**1a**	Me	(*R*)-**5b**	Ph	H	(*R*)-**3a**	66	89
2	**1b**	iso-Pr	(*R*)-**5b**	Ph	H	(*R*)-**3b**	85	90
3	**1c**	Ph	(*R*)-**5b**	Ph	H	(*R*)-**3c**	91	88
4	**1d**	*t*-Bu	(*R*)-**5b**	Ph	H	(*R*)-**3d**	82	85
5	**1a**	Me	(*R*)-**12b**	1-Naph	H	(*R*)-**3a**	90	89
6	**1b**	iso-Pr	(*R*)-**12b**	1-Naph	H	(*R*)-**3b**	92	93
7	**1c**	Ph	(*R*)-**12b**	1-Naph	H	(*R*)-**3c**	96	91
8	**1d**	*t*-Bu	(*R*)-**12b**	1-Naph	H	(*R*)-**3d**	91	87
9	**1a**	Me	(*R*)-**13b**	2-Naph	H	(*R*)-**3a**	69	92
10	**1b**	iso-Pr	(*R*)-**13b**	2-Naph	H	(*R*)-**3b**	82	88
11	**1c**	Ph	(*R*)-**13b**	2-Naph	H	(*R*)-**3c**	90	86
12	**1d**	*t*-Bu	(*R*)-**13b**	2-Naph	H	(*R*)-**3d**	85	78
13	**1a**	Me	(*R*)-**14b**	3,5-$Me_2C_6H_3$	H	(*R*)-**3a**	68	91
14	**1b**	iso-Pr	(*R*)-**14b**	3,5-$Me_2C_6H_3$	H	(*R*)-**3b**	77	80
15	**1c**	Ph	(*R*)-**14b**	3,5-$Me_2C_6H_3$	H	(*R*)-**3c**	87	70
16	**1d**	*t*-Bu	(*R*)-**14b**	3,5-$Me_2C_6H_3$	H	(*R*)-**3d**	85	57
17	**1a**	Me	(*R*)-**15b**	3,5-(*t*-Bu)$_2C_6H_3$	H	(*R*)-**3a**	49	66
18	**1b**	iso-Pr	(*R*)-**15b**	3,5-(*t*-Bu)$_2C_6H_3$	H	(*R*)-**3b**	56	43
19	**1c**	Ph	(*R*)-**15b**	3,5-(*t*-Bu)$_2C_6H_3$	H	(*R*)-**3c**	46	30
20	**1d**	*t*-Bu	(*R*)-**15b**	3,5-(*t*-Bu)$_2C_6H_3$	H	(*RS*)-**3d**	54	~0
21	**1a**	Me	(*S*)-**16b**	H	*t*-Bu	(*S*)-**3a**	79	70
22	**1b**	iso-Pr	(*S*)-**16b**	H	*t*-Bu	(*S*)-**3b**	92	57
23	**1c**	Ph	(*S*)-**16b**	H	*t*-Bu	(*S*)-**3c**	95	54
24	**1d**	*t*-Bu	(*S*)-**16b**	H	*t*-Bu	(*S*)-**3d**	94	53

a) A typical procedure is written in the Experimental.

Table 3. Enantioselective Deprotonation of **1d** to Give (*R*)-**3d** under Different Conditons

Run	Lithium amide	Conditions[a)]	Product ((*R*)-**3d**)	
			Chem. y. (%)	E.e. (%)
1	(*R*)-**5a**	A	95	84
2	(*R*)-**5a**	B	88	77
3	(*R*)-**5a**	C	97	85
4	(*R*)-**12a**	A	84	86
5	(*R*)-**12a**	B	88	76
6	(*R*)-**12a**	C	94	87

a) All reactions were run in THF in the absence of HMPA. A: Internal quench method; B: External quench method; C: External quench conditions in the presence of LiBr at the deprotonation step.

quench method (runs 1 and 4), enantioselectivities of the reactions under the external quench method are somewhat lower (runs 2 and 5), but are improved to the level of the internal quench method under the external quench conditions in the presence of one equivalent of LiBr (runs 3 and 6).

Since LiCl is generated *in situ* as the silylation proceeds under the internal quench method, the solution structures of [^{6}Li, $^{15}N_2$]-(*R*)-**5a**[5i)] in THF-d_8 in the absence and in the presence of ^{6}LiCl were examined by ^{6}Li- and ^{15}N-NMR spectra. As already reported, [^{6}Li, $^{15}N_2$]-(*R*)-**5a** exists almost entirely as a chelated monomeric form (**17**) in the absence of ^{6}LiCl,[5i)] because the ^{6}Li-NMR spectrum shows a doublet of doublets, indicative of coupling with two ^{15}N nuclei, while the corresponding ^{15}N-NMR spectrum displays two sets of triplets, indicating that each nitrogen atom couples with one ^{6}Li nucleus[11)] (Fig. 1a). The new signals appear in the presence of ^{6}LiCl. They are the major signals in the presence of 0.9 eq of ^{6}LiCl (Fig. 1b), while they are the sole signals in the presence of 1.3 eq of ^{6}LiCl (Fig. 1c). The new signals are a doublet and a doublet of doublets for the ^{6}Li-NMR, while a triplet and a quintet-like triplet of triplets for the ^{15}N-NMR. These data mean that one ^{6}Li couples with one ^{15}N nucleus and the other ^{6}Li couples with two ^{15}N nuclei, while one ^{15}N couples with one ^{6}Li nucleus and the other ^{15}N couples with two ^{6}Li nuclei. Since the coordinating lone pair on the amide nitrogen of the chelated monomer (**17**) is known to be exclu-

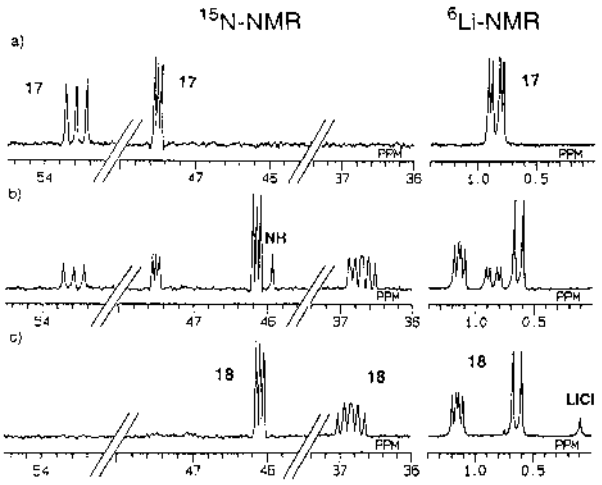
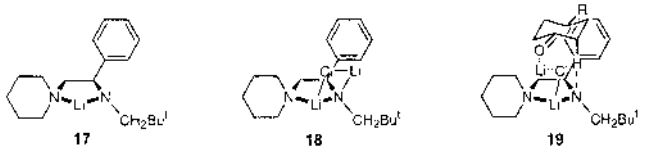


Fig. 1. NMR spectra of [^{6}Li,$^{15}N_2$]-(*R*)-**5a** in THF-d_8 (0.05 M, at −115 °C). a) Without ^{6}LiCl. b) With ^{6}LiCl (0.9 eq). c) With ^{6}LiCl (1.3 eq).



sively *cis* to the phenyl group in the chelated ring,[5i] a 1 : 1 mixed dimer (**18**) is proved to be formed in the presence of ^{6}LiCl, and is considered to be a responsible species for the deprotonation reactions under the internal quench method and under the external quench conditions in the presence of LiBr or LiCl.[5e]

We previously proposed the mechanism[12] of the present enantioselective deprotonation reactions based on Ireland's six-membered transition state model.[2,13] However, since the dimer (**18**) is considered to be responsible for the reactions under the internal quench method or under the external quench conditions in the presence of LiCl, it is reasonable to assume that the eight-membered cyclic transition state model (**19**) including LiCl[14] is a better explanation for (*R*)-**5a** to give the products (**3a**—**d**) rich in *R*-enantiomer. By this transition state model, it is possible to explain the severe steric interactions between the bulkier aryl substituent of the chiral bidentate lithium amides and the bulkier 4-substituent of cyclohexanones to reduce enantioselectivities of the reactions.

Experimental

General All boiling points are uncorrected. ^{6}Li- and ^{15}N-NMR spectra were recorded on a JEOL GSX-500 spectrometer (73.45 and 50.55 MHz, respectively) as reported, and the ^{6}Li- and ^{15}N chemical shifts are given in δ (ppm) using ^{6}LiCl in THF-d_8 (δ=0.0) and using [^{15}N]-aniline in THF-d_8 (δ=52.0) as external standards, respectively, as reported.[5i] The following abbreviations are used: d=doublet, dd=doublet of doublets, t=triplet, tt=triplet of triplets. Optical rotations were measured by a JASCO DIP-360 or a JASCO DIP-370 digital polarimeter using benzene as a solvent. The syntheses of (*R*)-**5a**, **b**,[7] (*R*)-**7a**, **b**—(*R*)-**10a**, **b**,[1] (*S*)-**11a**, **b**,[1] and [^{6}Li, $^{15}N_2$]-(*R*)-**5a**[5i] are reported. Maximum rotational values of (*R*)-**3a**, (*R*)-**3b**, (*R*)-**3c**, and (*R*)-**3d** in benzene are reported[8] to be $[\alpha]_{365}^{25}$ +238°, $[\alpha]_{365}^{25}$ +228°, $[\alpha]_{365}^{25}$ +146°, and $[\alpha]_{365}^{25}$ +237°, respectively.

Typical Procedures for Deprotonation Reactions a) Internal quench method (Table 1, run 6): A solution of *n*-BuLi in hexane (1.55 N, 1.55 ml, 2.40 mmol) was added to a solution of (*R*)-**12a** (811 mg, 2.50 mmol) in THF (50 ml) at −78 °C under argon atmosphere. The resulting solution was stirred for 30 min. After addition of HMPA (0.50 ml, 2.9 mmol), the whole was stirred at −78 °C for 20 min. A solution of **1b** (280 mg, 2.00 mmol) and TMSCl (1.27 ml, 10.0 mmol) in THF (4 ml) was added during 6 min, and the whole was stirred at −78 °C for 30 min. The reaction mixture was quenched by addition of triethylamine (4 ml) and saturated aqueous $NaHCO_3$ (10 ml) at −78 °C, and the whole was allowed to warm to room temperature. After addition of water, the whole was extracted with hexanes (50 ml×3). The organic extracts were combined, washed successively with water (20 ml×2), 0.1 N aqueous citric acid (80 ml×6), water (20 ml), saturated aqueous $NaHCO_3$ (20 ml), and brine (50 ml). Evaporation of the dried (Na_2SO_4) extracts gave a pale yellow oil (650 mg), which was purified by column chromatography (silica gel, hexane) followed by bulb-to-bulb distillation to give (*R*)-**3b** (387 mg, 91%) as a colorless oil of $bp_{0.4}$ 120 °C (bath temperature). $[\alpha]_{365}^{25}$ +211 (*c*=1.49), corresponding to be 93% ee.

b) External quench conditions in the presence of LiBr (Table 3, run 3): A solution of MeLi–LiBr in ether (1.50 N for MeLi, 1.60 ml, 2.40 mmol) was added to a solution of (*R*)-**4a** (686 mg, 2.50 mmol) in THF (50 ml) at −78 °C under argon atmosphere. The resulting solution was stirred for 30 min. A solution of **1d** (308 mg, 2.00 mmol) in THF (4 ml) was added during 5 min, and the whole was stirred at −78 °C for 10 min. TMSCl (1.27 ml, 10.0 mmol) was added, and the whole was stirred at −78 °C for 30 min. The reaction mixture was quenched by addition of triethylamine (4 ml) and saturated aqueous $NaHCO_3$ (10 ml) at −78 °C, and the whole was allowed to warm to room temperature. The work-up as described in a) above gave (*R*)-**3d** (437.5 mg, 97%) as a colorless oil of $bp_{0.7}$ 160 °C (bath temperature). $[\alpha]_{365}^{25}$ +201° (*c*=1.50), corresponding to be 85% ee.

c) External quench method (Table 3, run 5): A solution of *n*-BuLi in hexane (1.55 N, 1.55 ml, 2.40 mmol) was added to a solution of (*R*)-**7a** (811 mg, 2.50 mmol) in THF (50 ml) at −78 °C under argon atmosphere. The resulting solution was stirred for 30 min. A solution of **1d** (308 mg, 2.00 mmol) in THF (4 ml) was added during 5 min, and the whole was stirred at −78 °C for 10 min. TMSCl (1.27 ml, 10.0 mmol) was added, and the whole was stirred at −78 °C for 30 min. The reaction mixture was quenched by addition of triethylamine (4 ml) and saturated aqueous $NaHCO_3$ (10 ml) at −78 °C, and the whole was allowed to warm to room temperature. The work-up as described in a) above gave (*R*)-**3d** (400 mg, 88%) as a colorless oil of bp_1 150 °C (bath temperature). $[\alpha]_{365}^{25}$ +180° (*c*=1.50), corresponding to be 76% ee.

Rotational Values of the Products (3a—d) by the Reactions in Table 1 Run 1: $[\alpha]_{365}^{25}$ +219° (*c*=1.50); run 2: $[\alpha]_{365}^{25}$ +203° (*c*=1.49); run 3: $[\alpha]_{365}^{25}$ +128° (*c*=1.51); run 4: $[\alpha]_{365}^{25}$ +197° (*c*=1.51); run 5: $[\alpha]_{365}^{25}$ +223° (*c*=1.51); run 7: $[\alpha]_{365}^{25}$ +132° (*c*=1.48); run 8: $[\alpha]_{365}^{25}$ +201° (*c*=1.50); run 9: $[\alpha]_{365}^{25}$ +219° (*c*=1.50); run 10: $[\alpha]_{365}^{25}$ +198° (*c*=1.5); run 11: $[\alpha]_{365}^{25}$ +124° (*c*=1.50); run 12: $[\alpha]_{365}^{25}$ +177° (*c*=1.50); run 13: $[\alpha]_{365}^{25}$ +204° (*c*=1.51); run 14: $[\alpha]_{365}^{25}$ +182° (*c*=1.51); run 15: $[\alpha]_{365}^{25}$ +108° (*c*=1.50); run 16: $[\alpha]_{365}^{25}$ +111° (*c*=1.57); run 17: $[\alpha]_{365}^{25}$ +157° (*c*=1.50); run 18: $[\alpha]_{365}^{25}$ +74° (*c*=1.51); run 19: $[\alpha]_{365}^{25}$ +34.0° (*c*=1.51); run 20: $[\alpha]_{365}^{25}$ −38.5° (*c*=1.54); run 21: $[\alpha]_{365}^{25}$ −64.6° (*c*=1.51); run 22: $[\alpha]_{365}^{25}$ −38.0° (*c*=1.51); run 23: $[\alpha]_{365}^{25}$ −8.3° (*c*=1.50); run 24: $[\alpha]_{365}^{25}$ −28.4° (*c*=1.51).

Rotational Values of the Products (3a—d) by the Reactions in Table 2 Run 1: $[\alpha]_{365}^{25}$ +213° (*c*=1.51); run 2: $[\alpha]_{365}^{25}$ +205° (*c*=1.50); run 3: $[\alpha]_{365}^{25}$ +129° (*c*=1.50); run 4: $[\alpha]_{365}^{25}$ +202° (*c*=1.44); run 5: $[\alpha]_{365}^{25}$ +213° (*c*=1.42); run 6: $[\alpha]_{365}^{25}$ +212° (*c*=1.48); run 7: $[\alpha]_{365}^{25}$ +133° (*c*=1.50); run 8: $[\alpha]_{365}^{25}$ +205° (*c*=1.62); run 9: $[\alpha]_{365}^{25}$ +218° (*c*=1.50); run 10: $[\alpha]_{365}^{25}$ +200° (*c*=1.50); run 11: $[\alpha]_{365}^{25}$ +125° (*c*=1.50); run 12: $[\alpha]_{365}^{25}$ +185° (*c*=1.50); run 13: $[\alpha]_{365}^{25}$ +216° (*c*=1.49); run 14: $[\alpha]_{365}^{25}$ +182° (*c*=1.62); run 15: $[\alpha]_{365}^{25}$ +102° (*c*=1.52); run 16: $[\alpha]_{365}^{25}$ +135° (*c*=1.56); run 17: $[\alpha]_{365}^{25}$ +158° (*c*=1.43); run 18: $[\alpha]_{365}^{25}$ +97.8° (*c*=1.51); run 19: $[\alpha]_{365}^{25}$ +44.0° (*c*=1.51); run 20: $[\alpha]_{365}^{25}$ −0.5° (*c*=1.50); run 21: $[\alpha]_{365}^{25}$ −166° (*c*=1.49); run 22: $[\alpha]_{365}^{25}$ −130° (*c*=1.50); run 23: $[\alpha]_{365}^{25}$ −78.3° (*c*=1.51); run 24: $[\alpha]_{365}^{25}$ −125° (*c*=1.52).

Rotational Values of the Products (3d) by the Reactions in Table 3 Run 1: $[\alpha]_{365}^{25}$ +199° (*c*=1.51); run 2: $[\alpha]_{365}^{25}$ +183° (*c*=1.51); run 4: $[\alpha]_{365}^{25}$ +204° (*c*=1.42); run 6: $[\alpha]_{365}^{25}$ +205° (*c*=1.51).

^{6}Li- and ^{15}N-NMR Spectroscopic Analysis Solutions of [^{6}Li, $^{15}N_2$]-(*R*)-**5a** in THF-d_8 in the presence and in the absence of ^{6}LiCl were prepared according to the reported method.[5d,5i] Data are as follows. For [^{6}Li, $^{15}N_2$]-(*R*)-**5a** (Fig. 1a), ^{6}Li-NMR: 0.85 (dd, J_{Li-N}=7.0 and 2.4); ^{15}N-NMR: 47.5 (t, J_{N-Li}=2.4), 53.6 (t, J_{N-Li}=7.0). For [^{6}Li, $^{15}N_2$]-(*R*)-**5a** in the presence of 1.3 eq of ^{6}LiCl (Fig. 1c), ^{6}Li-NMR: 0.64 (d, J_{Li-N}=4.9), 1.14 (dd, J_{Li-N}=4.3 and 2.7). ^{15}N-NMR: 36.7 (tt, J_{Li-N}=4.3 and 4.9), 46.2 (t, J_{N-Li}=2.7).

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