Derivative 55PS: slighly yellow oil; eluent, cyclohexane/AcOEt = 95/5; yield = 91%; ^{31}P NMR (C_6D_6) δ 97.457 ($\Delta\delta$ = 0.065); ^{1}H NMR ($CDCl_3$) δ 0.8–1.00 (m, 6 H, $CH_3CH_2CHCH_3$), 1.1–2.15 (m, 11 H, $NCHCH_2CH_2CH_2CH_2CHN$ and $CH_3CH_2CHCH_3$), 2.5–2.9 (m, 10 H, $PNCH_3$, PNCH, and $PSCH_2$); ^{13}C NMR ($CDCl_3$) δ 11.43 (CH_2CH_3), 19.01, 19.09 ($CHCH_3$), 24.34, 24.41 ($NCHCH_2CH_2CH_2CH_2CHN$), 28.13, 28.33 (CH_2CH_3), 28.39 ($PNCH_3$), 28.68, 28.77, 28.85, 28.94 ($NCHCH_2CH_2CH_2CH_2CHN$), 29.08 ($PNCH_3$), 35.85, 35.93, 36.04 ($CHCH_3$), 41.36, 41.43 ($PSCH_2$), 64.55, 64.63, 64.69 (PNCH).

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Registry No. 7, 137943-76-1; 8, 137943-77-2; 9, 137943-78-3; 9S, 137943-79-4; 10, 137943-80-7; (±)-11, 15892-23-6; 11Pa, 137943-81-8; 11Pb, 138051-22-6; 11'Pb, 138051-23-7; 11Pc, 137943-82-9; 11'Pc, 138051-24-8; 11POb, 137943-83-0; 11'POb, 138051-25-9; 11POc, 137943-84-1; 11'POc, 138051-26-0; 11POd, 137943-85-2; 11'POd, 138124-49-9; 11PSa, 137943-86-3; 11'PSa, 138051-27-1; 11PSb, 138051-28-2; 11'PSb, 138051-29-3; 11PSc, 137943-87-4; 11'PSc, 138051-30-6; (±)-12, 4128-31-8; (S)-12, 6169-06-8; 12P, 131897-19-3; 12'P, 131780-03-5; 12PO, 137943-88-5; 12'PO, 138051-31-7; 12PS, 131780-20-6; 12'PS, 131898-25-4; (±)-13, 70116-68-6; 13PO, 137943-89-6; 13'PO, 138051-32-8; (±)-14, 65337-13-5; 14PO, 137943-90-9; 14'PO, 138051-33-9; (±)-15, 21632-19-9; (S)-15, 33652-83-4; 15P, 137943-91-0; 15'P, 138051-34-0; 15PO, 137943-92-1; 15'PO, 138051-35-1; 15PS, 137943-93-2; 15'PS, 138051-36-2; (±)-16, 37911-28-7; 16PO, 137943-94-3; 16'PO, 138051-37-3; (±)-17, 119046-43-4; 17P, 137943-95-4; 17'P, 138124-50-2; 17PO, 137943-96-5; 17'PO, 138124-51-3; (±)-18, 67738-25-4; 18P, 137943-97-6; 18'P, 138051-38-4; 18PS, 137943-98-7; 18-PS, 138051-39-5; (±)-19, 22564-99-4; 19P, 138124-52-4; 19'P, 138125-58-3; 19PS, 138124-53-5; 20, 137943-99-8; 21, 137944-00-4; 22, 91633-80-6; (±)-22, 138051-40-8; 22S, 137944-01-5; (±)-24, 13323-81-4; 24P, 137944-02-6; 24'P, 138051-41-9; 24PS, 138125-59-4; 24'PS, 137944-03-7; (±)-25, 6118-14-5; 25P, 138051-42-0; 25'P, 138051-43-1; 25PS, 138051-44-2; 25'PS, 138051-45-3; (−)-26, 2216-51-5; 26P, 138051-46-4; 26'P, 138051-47-5; 26PS, 138051-48-6; 26'PS, 138051-49-7; (+)-27, 2216-52-6; 27P, 131897-22-8; 27'P, 131897-11-5; 27PS, 131897-32-0; 27'PS, 131897-12-6; (−)-28, 464-45-9; 28P, 137944-04-8; 28'P, 138051-50-0; 28PS, 138125-60-7; 28'PS, 137944-05-9; (±)-29, 56007-85-3; 29P, 137944-06-0; 29'P, 138051-51-1; 29PS, 137944-07-1; 29'PS, 138051-52-2; (±)-30, 18826-95-4; (S)-31, 687-47-8; 31P, 131897-23-9; 31'P, 131780-08-0; 31PS, 131897-33-1; 31'PS, 131780-09-1; (S)-32, 5928-67-6; 32P, 131897-24-0; 32'P, 131780-10-4; 32PS, 131897-34-2; 32'PS, 131780-11-5; (±)-33, 105120-61-4; 33P, 138125-61-8; 33'P, 137944-08-2; 33PS, 137944-09-3; 33'PS, 138051-53-3; (±)-34, 93059-59-7; 34P, 137944-10-6; 34'P, 138051-54-4; 34PS, 137944-11-7; 34'PS, 138051-55-5; (+)-35, 42151-56-4; 35P, 137944-12-8; 35'P, 138051-56-6; 35PS, 137944-13-9; 35'PS, 138051-57-7; (±)-36, 138051-58-8; 36P, 137944-14-0; 36PS, 137944-15-1; (±)-37, 19641-57-7; 37P, 137944-16-2; 37'P, 138051-59-9; 37PS, 137944-17-3; 37'PS, 138051-60-2; (±)-38, 34713-94-5; 38P, 137944-18-4; 38'P, 138051-61-3; 38PS, 137944-19-5; (±)-39, 98103-87-8; 39P, 137964-59-1; 39'P, 138125-62-9; 39PS, 137964-60-4; (±)-40, 111767-94-3; 40P, 137944-20-8; 40'P, 138051-62-4; 40PS, 137944-21-9; (±)-41, 86495-15-0; 41P, 137944-22-0; 41'P, 138051-63-5; 41PS, 137944-23-1; (S)-42, 7540-51-4; 42P, 131897-17-1; 42'P, 131779-97-0; 42PS, 138124-54-6; (±)-43, 111768-05-9; 43P, 137944-24-2; 43PS, 137944-25-3; (S)-44, 22323-82-6; 44P, 131897-15-9; 44'P, 131779-93-6; 44PS, 138051-64-6; (±)-45, 138051-65-7; 45P, 137944-26-4; 45'P, 138051-66-8; 45PS, 137944-27-5; 46, 134931-07-0; 46P, 138051-67-9; 46'P, 138051-68-0; 46PS, 138124-55-7; 46'PS, 138124-56-8; (±)-47, 131780-19-3; 47P, 138051-69-1; 47'P, 138051-70-4; 47PS, 138051-71-5; 47'PS, 138051-72-6; (±)-48, 52949-66-3; 49P, 137944-28-6; 49PS, 137944-29-7; erythro-(±)-51, 138124-57-9; threo-(±)-51, 138124-58-0; 51P (isomer 1), 137944-30-0; 51P (isomer 2), 138124-59-1; 51P (isomer 3), 138124-60-4; 51P (isomer 4), 138124-61-5; erythro-(±)-52, 138124-62-6; threo-(±)-52, 138124-63-7; 52P (isomer 1), 137944-31-1; 52P (isomer 2), 138124-64-8; 52P (isomer 3), 138124-65-9; 52P (isomer 4), 138124-66-0; erythro-(±)-53, 138051-73-7; threo-(±)-53, 114180-72-2; 53P (isomer 1), 137944-32-2; 53P (isomer 2), 138051-74-8; 53P (isomer 3), 138051-75-9; 53P (isomer 4), 138051-76-0; 53PS (isomer 1), 138125-63-0; 53PS (isomer 2), 137944-33-3; 53PS (isomer 3), 138124-67-1; 53PS (isomer 4), 138124-68-2; (±)-54, 91840-99-2; 54P, 137944-34-4; 54'P, 138051-77-1; 54PS, 137944-35-5; 54'PS, 138051-78-2; (±)-55, 110549-12-7; 55P, 137944-36-6; 55'P, 138051-79-3; 55PS, 137944-37-7; HMPT, 1608-26-0; Cl_3OP, 10025-87-3; Cl_3PS, 3982-91-0; (R,R)-N,N'-dimethylcyclohexane-1,2-diamine, 68737-65-5; (R,R)-N,N'-diisopropylcyclohexane-1,2-diamine, 137944-38-8; (R,R)-(−)-cyclohexane-1,2-diamine, 20439-47-8; (R,R)-diethyl 1,2-cyclohexanediylbiscarbamate, 75730-13-1; (R,R)-N,N'-dimethyl-1,2-diphenylethylene-1,2-diamine, 118628-68-5; (R,R)-N,N'-dimethyl-1,2-[bis(m-trifluoromethyl)phenyl]ethylene-1,2-diamine, 137944-39-9.

Supplementary Material Available: ^{1}H and ^{13}C NMR data for products 7, 10, 21, 12PO, 15PO, 16PO, 19PS, 24PS, 25PS, 29PS, 34PS, 38PS, 40PS, 42PS, 44PS, 45PS, 46PS, and 47PS and ^{31}P, ^{1}H, and ^{13}C NMR spectra of products 15P, 15PS, 16PO, 18P, 18PS, 19P, 19PS, 22, 22PS, 25P, 25PS, 27P, 27PS, 31P, 31PS, 32P, 32PS, 33P, 33PS, 34P, 34PS, 35P, 35PS, 39P, 39PS, 42P, 42PS, 44P, 44PS, 45P, 45PS, 47PS, 48PS, 54P, 54PS (78 pages). Ordering information is given on any current masthead page.

1,2- vs 1,4-Addition of Nucleophilic Organometallics to Nonracemic 2-(1-Naphthyl)- and 2-Cinnamyl-1,3-oxazolidines

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We herein report our results where the addition of organomagnesium reagents to 2-(1-naphthyl)- and 2-cinnamyl-1,3-oxazolidines *occurred consistently in a 1,4-conjugate manner, while lithium, cerium, and copper organometallic reagents added in a 1,2-fashion.* The 1,4-conjugate addition pathway was primarily exploited by using (4*R*)-2-(1-naphthyl)-4-phenyl-1,3-oxazolidine (4) as a substrate to obtain, after $NaBH_4$ reduction of the intermediate aldehyde, *trans*-disubstituted 1,2-dihydronaphthalenes with enantiomeric excesses of 93–94%. The amino alcohol products resulting from 1,2-addition were oxidatively cleaved to afford enantiomeric enriched (*R*)-α-(1-naphthyl)alkylamines **6a** and **6b** in >99% ee.

We have previously reported our results concerning nucleophilic addition to (4*R*)-2-aryl-4-phenyl-1,3-oxazolidines **1** wherein diastereomerically enriched amino alcohols **2** were obtained in moderate to good yields.[3a,b] In that

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Scheme I

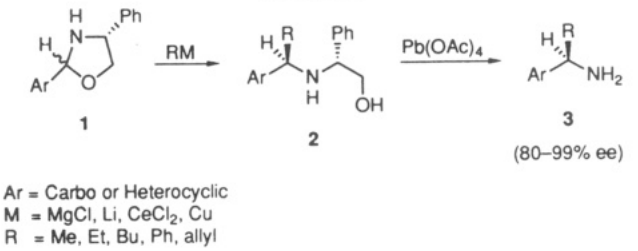
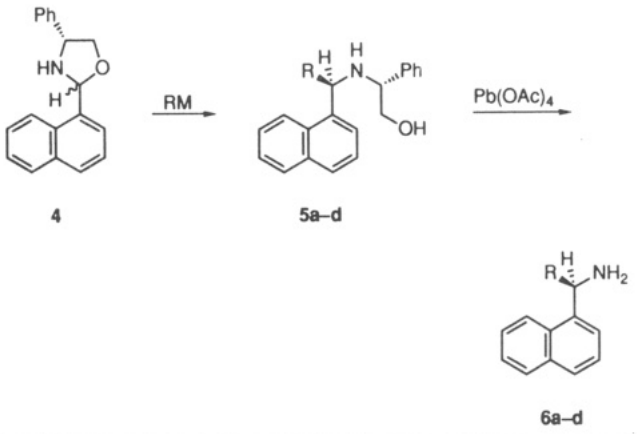


Table I. 1,2-Addition of Organometallic Reagents to (4*R*)-2-(1-Naphthyl)-4-phenyl-1,3-oxazolidine (4) and Oxidative Cleavage Results



entry	compd	RM (°C)	yield, % 5	de,[a] %	yield, % 6	ee,[b] %
1	**a**	CH_3Li (−78)	46	95		
2	**a**	CH_3CeCl_2 (−45)	75	96	61	>99
3	**a**	$CH_3Cu{\cdot}BF_3$ (−78)	71	52	80	54
4	**b**	$C_2H_5CeCl_2$ (−45)	75	>99	57	>99
5	**c**	BuLi (−78)	81	26		
6	**d**	PhLi (−78)	48	>99		

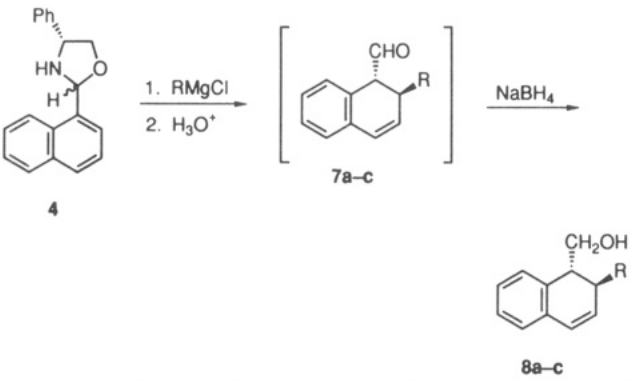
[a] Diastereomeric ratios were determined by 400-MHz ^1H NMR. [b] The enantiomeric excess was determined using (*R*)-BNPPA as the shift reagent as reported by Shapiro.[9]

study, we demonstrated how one could subsequently obtain, via oxidative cleavage of **2** (Scheme I), α-arylalkylamines **3** in high enantiomeric excess.

We now report that during the course of that study, we observed that 2-(1-naphthyl) derivatives of **1** underwent exclusively *1,4-addition with Grignard reagents and 1,2-addition with lithium, cerium, and copper organometallic reagents* (Tables I and II). Such a result, particularly, for the latter metal was highly surprising in light of its propensity for predominantly conjugate-type addition. Two of the amino alcohol products resulting from the 1,2-addition were ultimately converted via oxidative cleavage to enantiomerically enriched α-(1-naphthyl)alkylamines analogous to the aryl examples previously reported.[3a,b] The 1,4-conjugate addition products, which are enantiomerically enriched trans-disubstituted 1,2-dihydronaphthalenes, have been previously reported by Meyers[4] and demonstrated by him to be valuable intermediates in syntheses of the natural products (+)-phyltetralin,[4c] (−)-podophyllotoxin,[4e] and the AB-ring of aklavinone.[4f] Tomioka has also formed these same dihydronaphthalenes by organolithium addition to the cyclohexylimine of 1-naphthalenecarboxaldehyde in the presence of a enantiomerically enriched diether cocatalyst.[5b] The majority of the previous work on organometallic addition to optically active α,β-unsaturated imines[6] and/or oxazolines originated from the laboratories of Tomioka[7] and Meyers.[8]

Organometallic addition to the naphthalene nucleus has been limited so far to lithium reagents.[4,5] In Tomioka's

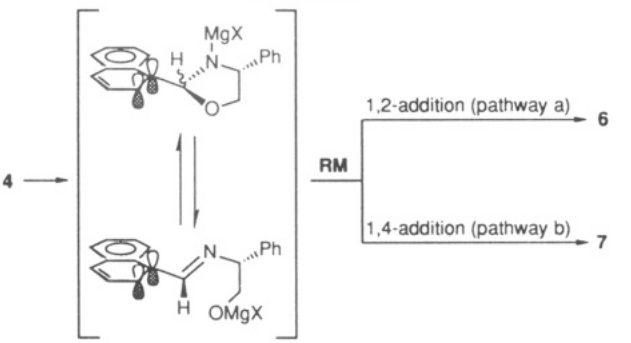
Table II. 1,4-Addition of Grignard Reagents to (4*R*)-2-(1-Naphthyl)-4-phenyl-1,3-oxazolidine (4)



entry	compd	R	yield, % 8	ee %
1	**a**	Ph	50	93[a] (94)[b]
2	**b**	Bu	83	93[a]
3	**c**	Et	65	96[b]

[a] Optical purity was determined by comparison to literature reported optical rotation.[4b,c] [b] Optical purity was determined by ^{19}F NMR of the Mosher ester.[10]

Scheme II



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(2) SmithKline Beecham Post-Doctoral Fellow, 1989–1990.

(3) (a) Wu, M.-J.; Pridgen, L. N. *J. Org. Chem.* **1991**, *56*, 1340. (b) Wu, M.-J.; Pridgen, L. N. *Synlett.* **1990**, 636. (c) For a recently reported relevant study see also: Takahashi, H.; Hsieh, B. C.; Higashiyama, K. *Chem. Pharm. Bull.* **1990**, *38*, 2429.

(4) (a) Meyers, A. I.; Barner, B. A. *J. Am. Chem. Soc.* **1984**, *106*, 1865. (b) Meyers, A. I.; Barner, B. A. *J. Org. Chem.* **1986**, *51*, 120. (c) Meyers, A. I.; Roth, G. P.; Hoyer, D.; Barner, B. A.; Laucher, D. *J. Am. Chem. Soc.* **1988**, *110*, 4611. (d) Meyers, A. I.; Licini, G. *Tetrahedron Lett.* **1989**, *30*, 4049. (e) Andrews, R. C.; Teague, S. J.; Meyers, A. I. *J. Am. Chem. Soc.* **1988**, *110*, 7854. (f) Meyers, A. I.; Higashiyama, K. *J. Org. Chem.* **1987**, *52*, 4592. (g) Meyers, A. I.; Hoyer, D. *Tetrahedron Lett.* **1984**, *25*, 3667. (h) Meyers, A. I.; Rawson, D. J. *J. Org. Chem.* **1991**, *56*, 2292.

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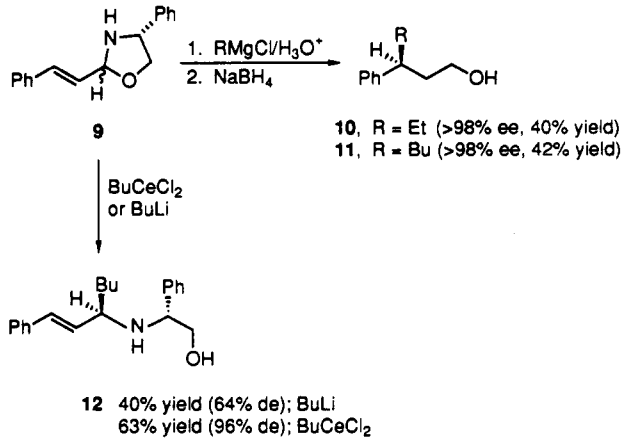
Scheme III



report of organolithium addition to naphthalene carboxylates, predominantly cis addition products were obtained, although epimerization to trans derivatives were easily accomplished with sodium methylate in THF. We herein report that organomagnesium reagents also add to the naphthalene ring in THF yielding trans-disubstituted 1,2-dihydronaphthalenes. To the best of our knowledge, this is the first report of organomagnesium reagents adding to the naphthalene nucleus.

Oxazolines,[8] imines,[5b,d,6] carboxylates,[5a,c] and now apparently oxazolidines activate through induction the ortho position of naphthyl rings toward nucleophilic attack. Thus, the proposed mode of addition accounting for the subsequently obtained absolute stereochemistry of the resulting products is the same as that previously reported (Scheme II).[3] The strong Lewis basicity character of both the imino nitrogen and amino alcohol oxygen results in very strong complexation to at least 0.5 equiv of Grignard reagent, thus limiting the flexibility of the transition state. Consequently, nucleophilic attack occurs predominantly from the less sterically demanding face, that opposite the 4-phenyl. Attack by lithium, cerium, and copper reagents occurs at the hard aminal/imino carbon (pathway a) leading to 1,2-addition products (Table I).[13] The resulting disubstituted amino alcohols were readily cleaved as previously described[3a,b] to enantiomerically enriched α-(1-naphthyl)alkylamines. Pathway b requires attack at the softer electrophilic γ-carbon and is the exclusive pathway for Grignard addition in this ring system (Table II).

Lithium, cerium, and magnesium organometallic reagents exhibited similar addition behaviors when reacted with oxazolidine **9**, the cinnamyl derivative of **4**. Scheme III shows our results where the former two reagents added in a 1,2-fashion while Grignard reagents afforded the 1,4-addition products. Reaction of **9** with ethyl- and butylorganomagnesium reagents yielded **10** (40% yield, 96% ee) and **11** (42% yield, 98% ee), respectively.[11,12] Conversely, reaction of **9** with butyllithium or butylcerium chloride gave **12** in 40% yield (64% de) and 63% yield (96% de), respectively.

In summary, we have demonstrated how important the choice of metal becomes in adding organometallics to 2-(1-naphthyl)-1,3-oxazolidines or to 2-cinnamyl-1,3-oxazolidines. Either conjugate addition or products resulting from addition at the aminal/imino carbon are obtained in high stereoselectivity. The stereoselectivities reported herein for the Grignard 1,4-additions are comparable to those reported by Meyers[8] and Tomioka.[7] Moreover, this work, as well as the previously reported study from this laboratory,[3a,b] have established organoceriums as the organometallics of choice for nucleophilic 1,2-addition to 2-substituted 1,3-oxazolidines. Studies designed to explore the conjugate addition pathway and extend the realm of nucleophiles that selectively add in this manner are underway.

Experimental Section

For information on solvents, reagents, analytical instruments, and a description of chromatographic reagents, see ref 3a unless otherwise noted. All Grignard (MeMgCl, EtMgCl, BuMgCl, and PhMgCl; 2 M solutions in THF) and organolithium (CH_3Li, 1.4 M in Et_2O; BuLi, 2.5 M in hexanes; PhLi, 1.8 M in cyclohexane/Et_2O (7/3, v/v)) reagents used in this study were purchased from Aldrich Chemical Co. and titrated by the method of Ogura.[14] Moisture-sensitive reactions were carried out in predried glassware and under nitrogen atmosphere.

General Procedure for the Preparation of the Oxazolidines 4 and 9.[3] An equimolar solution of the appropriate aldehyde and (*R*)-(−)-2-amino-2-phenylethanol in $CHCl_3$ (1 M) containing 1 equiv of anhydrous $MgSO_4$ was stirred under reflux overnight. The solid was filtered off, and the solvent was removed in vacuo. The residual solid was purified by recrystallization. Oxazolidines are known to exist in solution as a tautomeric mixture of its imino alcohol and oxazolidine forms.[3] We found that compound **4** exists in $CDCl_3$ in an 3:1 ratio of both forms, respectively, as determined by ^1H NMR peak integration of the imino proton at δ 9.05 and the aminal proton at δ 6.24. Only spectral data for the imino form are reported below. Compound **9** was found to exist in $CDCl_3$ in only its imino alcohol form.

(4*R*)-2-(1-Naphthyl)-4-phenyl-1,3-oxazolidine (4): 14.9 g, 75% yield; pale yellow crystals; $[\alpha]^{25}_D$ +54.17° (*c* 1.0, $CHCl_3$); mp 83–84 °C (from $CHCl_3$–hexanes); IR (KBr) 3414 (br, OH), 1633, 1601, 1333, 1052, 810, 777, 744, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.05 (s, 1 H), 9.02 (d, 1 H, J = 8.7 Hz), 8.0–7.3 (m, 11 H), 4.59 (dd, 1 H, J = 8.4, 4.4 Hz), 4.05 (dd, 1 H, J = 11.2, 8.4 Hz), 3.97 (dd, 1 H, J = 11.2, 4.4 Hz); ^{13}C NMR ($CDCl_3$) δ 162.7, 140.8, 133.8, 131.5, 131.3, 131.2, 129.7, 128.7, 128.6(2), 127.5(2), 127.4, 127.3, 126.1, 125.2, 124.4, 77.5, 68.0; MS (CI) *m/e* (relative intensity) 276 [(M + 1)$^+$, 100]. Anal. Calcd for $C_{19}H_{17}NO$: C, 82.88; H, 6.22; N, 5.09. Found: C, 82.34; H, 6.26; N, 5.25.

(4*R*)-2-((*E*)-2-Phenylethenyl)-4-phenyl-1,3-oxazolidine (9): 7.33 g, 77% yield; colorless crystals; $[\alpha]^{25}_D$ −65.54° (*c* 1.0, $CHCl_3$); mp 103–103.5 °C (from $CHCl_3$–hexanes); IR (KBr) 3226 (br, OH), 1638, 1449, 1169, 1075, 1058, 1003, 756, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.09 (d, 1 H, J = 8.8 Hz), 7.45–7.20 (m, 10 H) 6.94 (dd, 1 H, J = 16.1, 8.8 Hz), 6.81 (d, 1 H, J = 16.1 Hz), 4.39 (dd, 1 H, J = 9.1, 4.0 Hz), 4.02 (dd, 1 H, J = 11.6, 9.1 Hz), 3.89 (dd, 1 H, J = 11.6, 4.0 Hz); ^{13}C NMR ($CDCl_3$) δ 164.7, 143.1, 140.5, 135.3, 129.3, 128.7(2), 128.6(2), 127.4, 127.3(2), 127.2, 127.1(2), 77.0, 67.5; MS (CI) *m/e* (relative intensity) 252 [(M + 1)$^+$, 100]. Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 80.93; H, 6.61; N, 5.53.

General Procedure for 1,4-Addition of Grignard Reagents to (4*R*)-2-(1-Naphthyl)-4-phenyl-1,3-oxazolidine (4). To a magnetically stirred solution of oxazolidine (10 mmol) in dry THF (20 mL) was added 3 equiv of the appropriate Grignard reagent (THF solution) dropwise through an addition funnel at −45 °C. The resulting red-brown solution was stirred for 7 h at −45 °C and at rt overnight. Aqueous HCl (3 N, 30 mL) was then added

(11) (a) Hashimoto, S.-I.; Yamada, S.-I.; Koga, K. *J. Am. Chem. Soc.* **1976**, *98*, 7450. (b) Ahlbrecht, H.; Bonnet, G.; Enders, D.; Zimmerman, G. *Tetrahedron Lett.* **1980**, *21*, 3175.

(12) Optical purities were determined by ^1H NMR on the acetoxy analogues. The peak height of the acetate methyl was measured using the chiral shift reagent tris[((3-heptafluoropropyl)hydroxymethylene)-(+)-camphorato]europium(III). The racemic analog was prepared in order to ensure that peak discrimination had been obtained.

(13) Entries 5 and 6 of Table I were added as a result of comments offered by a reviewer who felt that 1,2-addition of methyllithium may not be representative of other organolithiums by analogy to work reported in ref 6 wherein only methyllithium added in a 1,2-fashion to *N*-cyclohexylimine of naphthaldehyde. However, as presented in Table I, *all the organolithiums employed gave exclusively 1,2-addition products*, with butyllithium being almost nonselective.

(14) Aso, Y.; Yomashita, H.; Otsubo, T.; Ogura, F. *J. Org. Chem.* **1989**, *54*, 5627.

and the reaction mixture stirred for 2 h. After dilution of the reaction mixture with ether, the organic layer was separated, washed with H_2O, saturated $NaHCO_3$ solution, and brine, and then dried ($MgSO_4$) and concentrated in vacuo. The remaining crude aldehyde was dissolved in methanol (30 mL), and the solution was cooled to 0 °C. Sodium borohydride (1.14 g, 30 mmol) was added and the solution stirred for 1 h. The mixture was then poured into a 3 N aqueous HCl (50 mL) and extracted with ether. The combined and dried ($MgSO_4$) ether extracts were concentrated to yield the known alcohols **8a** and **8b**[4b,c] which were obtained as colorless oils after flash column chromatography using 20% Et_2O in hexanes as eluent.

(1*R*,2*S*)-(+)-*trans*-1-(Hydroxymethyl)-2-phenyl-1,2-dihydronaphthalene (8a): 1.19 g, 50% yield; $[\alpha]^{25}_D$ +519° (*c* 1.4, $CHCl_3$), 94% ee;[4b,c] IR (neat) 3360 (br, OH), 3015, 1601, 1490, 1455, 755, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25–7.05 (m, 8 H), 6.95 (d, 1 H, J = 7.3 Hz), 6.54 (d, 1 H, J = 9.6 Hz), 5.92 (dd, 1 H, J = 9.6, 5.7 Hz), 3.73 (d, 1 H, J = 5.7 Hz), 3.68–3.55 (m, 2 H), 3.01 (t, 1 H, J = 7.1 Hz), 2.42 (br s, 1 H, OH); ^{13}C NMR ($CDCl_3$) δ 142.8, 133.4, 133.0, 129.1, 129.0, 128.4(2), 127.5(2), 127.4, 127.2, 126.9, 126.41, 126.37, 65.6, 48.7, 41.1; ^{19}F NMR (376 MHz, of Mosher ester, C_6F_6 as an internal standard) major δ 90.52 (97%), minor δ 90.34 (3%); MS (CI) m/e (relative intensity) 237 [$(M + 1)^+$, 1], 219 [$(M - H_2O + 1)^+$, 100].

(1*R*,2*S*)-(+)-*trans*-1-(Hydroxymethyl)-2-butyl-1,2-dihydronaphthalene (8b): 1.79 g, 83% yield; $[\alpha]^{25}_D$ +380° (*c* 0.95, $CHCl_3$), 93% ee;[4b,c] IR (neat) 3360 (br, OH) 2960, 2920, 1455, 1050, 790, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.2–7.0 (m, 4 H), 6.35 (d, 1 H, J = 9.6 Hz), 5.93 (m, 1 H), 3.53 (m, 2 H), 2.78 (t, 1 H, J = 7.5 Hz), 2.37 (m, 1 H), 1.82 (br s, 1 H, OH), 1.4–1.2 (m, 6 H), 0.85 (t, 3 H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 134.4, 132.8, 131.4, 129.3, 126.9(2), 126.2, 125.4, 65.0, 45.8, 34.9, 33.6, 29.1, 22.7, 13.9; MS (CI) m/e (relative intensity) 217 [$(M + 1)^+$, 6], 199 [$(M - H_2O + 1)^+$, 100].

(1*R*,2*S*)-(+)-*trans*-1-(Hydroxymethyl)-2-ethyl-1,2-dihydronaphthalene (8c): 1.22 g, 65% yield; $[\alpha]^{25}_D$ +362° (*c* 1.1, $CHCl_3$), 96% ee; IR (neat) 3360 (br, OH), 2960, 2920, 2880, 1480, 1455, 1050, 780, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.15–6.95 (m, 4 H), 6.34 (d, 1 H, J = 9.6 Hz), 5.91 (dd, 1 H, J = 9.6, 6.0 Hz), 3.48 (m, 2 H), 2.77 (t, 1 H, J = 7.5 Hz), 2.38 (br s, 1 H, OH), 2.29 (q, 1 H, J = 6.8 Hz), 1.48–1.22 (m, 2 H), 0.88 (t, 3 H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$) δ 134.4, 132.8, 131.1, 129.3, 126.9(2), 126.1, 125.6, 65.2, 45.5, 36.6, 26.7, 11.3; ^{19}F NMR (376 MHz, of Mosher ester, C_6F_6 as an internal standard) major δ 90.29 (98%), minor δ 90.19 (2%); MS (CI) m/e (relative intensity) 189 [$(M + 1)^+$, 4], 171 [$(M - H_2O + 1)^+$, 100]; HRMS (CI) calcd for $C_{13}H_{16}O$ 188.1201 (M^+), found 188.1207.

General Procedure for 1,4-Addition of Grignard Reagents to (4*R*)-2-((*E*)-2-Phenylethenyl)-4-phenyl-1,3-oxazolidine (9). The oxazolidine (10 mmol in 30 mL of dry THF) was cooled to −45 °C and treated with 3 equiv of the appropriate Grignard reagent (THF solution). The resulting red-brown solution was stirred at −45 °C for 5 h and at rt overnight. The reaction mixture was poured into a solution of oxalic acid (4.5 g) in 70 mL of THF/H_2O (50/20, v/v) and was stirred overnight. The reaction mixture was then diluted with ether, and the organic layer was separated and washed with H_2O, saturated $NaHCO_3$, and brine and then dried ($MgSO_4$). After concentration, the crude aldehyde was dissolved in methanol (30 mL) and the solution was cooled to 0 °C. Sodium borohydride (1.14 g, 30 mmol) was added, and the resulting solution was stirred for 1 h. The reaction mixture was diluted with ether and then washed with 3 N aqueous HCl. The acidic aqueous layer was back-washed with ether. The combined ether extracts were dried ($MgSO_4$) and concentrated in vacuo to afford the known alcohols **10** and **11** which were obtained as colorless oils after flash column chromatography (20% Et_2O in hexanes).

(*S*)-3-Phenyl-1-pentanol (10): 0.65 g, 40% yield; $[\alpha]^{25}_D$ −7.0° (*c* 0.95, $CHCl_3$), >98% ee;[11,12] IR (neat) 3340 (br, OH), 3030, 2930, 2880, 1450, 1045, 755, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.3–7.05 (m, 5 H), 3.5–3.3 (m, 2 H), 2.93 (br s, 1 H, OH), 2.53 (m, 1 H), 1.86 (m, 1 H), 1.75–1.5 (m, 3 H), 0.75 (t, 3 H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$) δ 144.8, 128.1(2), 127.5(2), 125.8, 60.5, 43.9, 39.0, 29.5, 11.9; MS (CI) m/e (relative intensity) 182 [$(M + NH_4)^+$, 100] HRMS (CI) calcd for $C_{11}H_{16}O$ 164.1201 (M^+), found 164.1196; ^1H NMR (400 MHz) analysis of the acetate derivative showed only one methyl peak at δ 2.28 using the chiral shift reagent tris[((3-heptafluoropropyl)hydroxymethylene)-(+)-camphorato]europium(III).

(*S*)-3-Phenyl-1-heptanol (11): 0.53 g, 42% yield; $[\alpha]^{25}_D$ +1.98° (*c* 1, $CHCl_3$), >98% ee;[11,12] IR (neat) 3330 (br, OH), 2956, 2929, 2872, 2858, 1453, 1047, 1028, 760, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.3–7.05 (m, 5 H), 3.45–3.3 (m, 2 H), 2.62 (m, 1 H), 2.46 (br s, 1 H, OH), 1.87 (m, 1 H), 1.77 (m, 1 H), 1.68–1.45 (m, 2 H), 1.35–1.05 (m, 4 H), 0.81 (t, 3 H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 145.2, 128.3(2), 127.5(2), 125.9, 60.7, 42.3, 39.5, 29.6, 22.6, 13.9; MS (CI) m/e (relative intensity) 193 [$(M + 1)^+$, 5], 175 [$(M - H_2O + 1)^+$, 79], 147 (100); HRMS (CI) calcd for $C_{13}H_{20}O$ 192.1514 (M^+), found 192.1508; ^1H NMR (400 MHz) analysis of the acetate derivative showed only one methyl peak at δ 2.51 using the chiral shift reagent tris [((3-heptafluoropropyl)hydroxymethylene)-(+)-camphorato]europium(III).

General Procedure A: Addition of Organolithium to Oxazolidines 4 and 9. To a dry ice/acetone bath cooled (−78 °C) solution of the oxazolidine (10 mmol) in 20 mL of dry THF was added a solution of 3 equiv of the appropriate organolithium dropwise through an addition funnel. The resulting dark-green solution was stirred at −78 °C for 2 h. The reaction mixture was quenched with saturated NH_4Cl solution and extracted with ether. The ether extracts were dried ($MgSO_4$) and concentrated. The residual oil was purified by flash column chromatography.

General Procedure B: Addition of Organocerium to Oxazolidines 4 and 9. Anhydrous $CeCl_3$ (3 equiv) was stirred in THF (5 mL per gram of $CeCl_3$) for 2 h. The suspension was cooled to −45 °C and then treated with 3 equiv of the appropriate Grignard reagent (THF solution) and stirred for 1 h at −45 °C. A solution of the oxazolidine in THF (0.5 M) was added into the stirred suspension dropwise via an addition funnel. The resulting suspension was stirred at −45 °C for 6 h and at room temperature overnight. The reaction mixture was then poured into ice/water and extracted with ether. The ether extracts were combined, dried ($MgSO_4$), and then concentrated in vacuo, and the residual oil was purified by flash column chromatography.

General Procedure C: Addition of Organocuprate to Oxazolidine 4. To a suspension of CuI (15 mmol) in dry THF (30 mL) was added Grignard reagent (15 mmol) dropwise at −50 °C. After being stirred for 30 min at this temperature, the solution was cooled to −78 °C. Boron trifluoride etherate (15 mmol) was added, and the solution was stirred for an additional 10 min. A solution of oxazolidine **4** (5 mmol) in dry THF (10 mL) was added at −78 °C, and the reaction mixture was allowed to warm to rt and stirred for 3 h. Aqueous NaOH (10%, 20 mL) was added to the reaction mixture which was then extracted with ether. The ether extracts were combined, dried ($MgSO_4$), and concentrated in vacuo. The crude product was purified by flash column chromatography.

(1*R*,1′*R*)-*N*-2′-Hydroxy-1′-(phenylethyl)-1-(1-naphthyl)-ethylamine (5a). Prepared by adding methylcerium chloride to **4** using general procedure B (2.18 g, 75% yield, 96% de) as a thick orange oil (flash chromatography, 50% Et_2O in hexanes): $[\alpha]^{25}_D$ −74.92° (*c* 1, $CHCl_3$); IR (neat) 3380 (br; NH, OH), 2980, 2930, 1450, 1030, 780, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.2 (m, 12 H), 4.50 (q, 1 H, J = 6.5 Hz), 4.00 (dd, 1 H, J = 8.2, 4.6 Hz), 3.76 (dd, 1 H, J = 10.8, 4.6 Hz), 3.54 (dd, 1 H, J = 10.8, 8.2 Hz), 1.85 (br s, 2 H, NH, OH), 1.53 (d, 3 H, J = 6.5 Hz); ^{13}C NMR δ ($CDCl_3$) 141.1, 140.6, 133.8, 130.8, 128.9, 128.7(2), 127.7, 127.6, 127.2(2), 125.9, 125.6, 125.4, 123.1, 122.8, 66.0, 61.5, 49.6, 21.8; MS (CI) m/e (relative intensity) 292 [$(M + 1)^+$, 11], 274 [$(M + H - H_2O)^+$, 7], 155 (100); HRMS (CI) calcd for $C_{20}H_{22}NO$ 292.1701 $(M + H)^+$, found 292.1711.

Prepared from **4** using general procedure A in 46% yield (95% de) as a thick orange oil.

Prepared from **4** using general procedure C in 71% yield (52% de) as a thick orange oil.

(1*R*,1′*R*)-*N*-2′-Hydroxy-1′-(phenylethyl)-1-(1-naphthyl)-propylamine (5b). Prepared by adding ethylcerium chloride to **4** using general procedure B (2.31 g, 75% yield, >99% de) as a thick orange oil (flash chromatography, 30% EtOAc in hexanes): $[\alpha]^{25}_D$ −89.95° (*c* 1.2, $CHCl_3$) IR (neat) 3360 (br; NH, OH), 2970, 2930, 2880, 1455, 1030, 780, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.1 (m, 12 H), 4.37 (t, 1 H, J = 6.6 Hz), 3.83 (dd, 1 H, J = 7.4, 4.6 Hz), 3.69 (dd, 1 H, J = 10.8, 4.6 Hz), 3.44 (dd, 1 H, J = 10.8, 7.4

Hz), 2.18 (br s, 2 H, NH, OH), 1.95–1.8 (m, 2 H), 0.73 (t, 3 H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 141.1, 139.6, 133.9, 131.5, 128.9, 128.6(2), 127.51, 127.5, 127.1(2), 125.8, 125.4(2), 123.8, 123.1, 65.7, 61.4, 56.3, 28.7, 10.4; MS (CI) m/e (relative intensity) 306 [$(M + 1)^+$, 100]; HRMS calcd for $C_{21}H_{24}NO$ 306.1858 $(M + H)^+$, found 306.1851.

***N*-2′-Hydroxy-1′-(phenylethyl)-1-(1-naphthyl)pentylamine (5c).** Prepared by adding butyllithium to **4** using general procedure A in 81% yield (flash chromatography, 15 → 20% EtOAc in hexanes) as a thick red-golden oil (de 26%). A pure sample of each diastereomer was obtained by careful flash chromatography (CH_2Cl_2). The first isomer eluted was **5c** (1*S*,1′*R*): $[\alpha]^{25}_D$ −115.46° (*c* 1, $CHCl_3$); IR (neat) 3360 (br; NH, OH), 2955, 2929, 2870, 2858, 1454, 1026, 778, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.9–7.1 (m, 12 H), 4.32 (br s, 1 H), 3.58–3.45 (m, 3 H), 2.28 (br s, 2 H, NH, OH), 1.79 (br s, 2 H), 1.4–1.1 (m, 4 H), 0.79 (t, 3 H, J = 7.2 Hz); ^{13}C NMR [$(CD_3)_2SO$, 67.5 MHz] δ 142.2, 140.6 (br), 133.5, 131.4, 128.7, 128.0(2), 127.6(2), 126.9, 126.7, 125.7, 125.6, 125.2, 123.1 (br), 122.5 (br), 66.7, 61.8, 53.3 (br), 38.1, 28.3, 22.1, 13.9; HRMS (CI) calcd for $C_{23}H_{28}NO$ 334.2171 $(M + H)^+$, found 334.2169. The second isomer was **5c** (1*R*,1′*R*): $[\alpha]^{25}_D$ −78.17° (*c* 1, $CHCl_3$); IR (neat) 3340 (br; NH, OH), 3061, 2955, 2930, 2870, 1454, 1050, 779, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.0–7.1 (m, 12 H), 4.49 (t, 1 H, J = 6.5 Hz), 3.89 (dd, 1 H, J = 7.2, 4.6 Hz), 3.76 (dd, 1 H, J = 10.8, 4.6 Hz), 3.50 (dd, 1 H, J = 10.8, 7.2 Hz), 2.1 (br s, 2 H, NH, OH), 1.91 (m, 2 H), 1.35–1.0 (m, 4 H), 0.80 (t, 3 H, J = 7.0 Hz); ^{13}C NMR δ ($CDCl_3$, 67.5 MHz) 141.1, 139.9, 133.8, 131.4, 128.8, 128.5(2), 127.4(2), 127.1(2), 125.7, 125.4, 125.3, 123.8, 123.0, 65.5, 61.4, 55.1 (br), 35.9, 28.3, 22.7, 13.9; HRMS (CI) calcd for $C_{23}H_{28}NO$ 334.2171 $(M + H)^+$, found 334.2163.

(1*R*,1′*R*)-*N*-2′-Hydroxy-1′-(phenylethyl)-1-(1-naphthyl)-1-phenylmethylamine (5d). Prepared by adding phenyllithium to **4** using general procedure A (1.71 g, 48% yield, >99% de) as a white oily solid (flash chromatography, 10 → 20% EtOAc in hexanes): $[\alpha]^{25}_D$ −19.12° (*c* 1, $CHCl_3$); IR (KBr) 3420 (br; NH, OH), 3058, 2924, 2871, 1509, 1452, 1052, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.85–7.15 (m, 17 H), 5.53 (s, 1 H), 3.85 (dd, 1 H, J = 8.7, 4.7 Hz), 3.71 (dd, 1 H, J = 10.8, 4.7 Hz), 3.65 (dd, 1 H, J = 10.8, 8.7 Hz), 2.35 (br s, 2 H, NH, OH); ^{13}C NMR ($CDCl_3$) δ 142.0, 140.1, 139.4, 133.9, 130.8, 128.8, 128.76(2), 128.6(2), 128.2(2), 127.93, 127.87, 127.6(2), 127.2, 126.0, 125.47, 125.45, 124.9, 123.2, 66.5, 61.7, 58.8; MS (CI) m/e (relative intensity) 354 [$(M + H)^+$, 49], 336 [$(M + H - H_2O)^+$, 3], 322 (4), 217 (100); HRMS (CI) calcd for $C_{25}H_{24}NO$ 354.1858 $(M + H)^+$, found 354.1855.

(1*R*,1′*R*)-*N*-2′-Hydroxy-1′-(phenylethyl)-1-((*E*)-2-phenylethenyl)pentylamine (12). Prepared by adding butylcerium chloride to **9** using general procedure B (1.95 g, 63% yield, 96% de) as a thick orange oil (flash chromatography, 50% Et_2O in hexanes): $[\alpha]^{25}_D$ +2.96° (*c* 1, $CHCl_3$); IR (neat) 3400 (br, NH, OH), 2960, 2930, 2860, 1492, 1450, 1060, 970, 750, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.4–7.1 (m, 10 H), 6.34 (d, 1 H, J = 15.8 Hz), 5.89 (dd, 1 H, J = 15.8, 8.4 Hz), 3.90 (dd, 1 H, J = 7.3, 4.7 Hz, 3.73 (dd, 1 H, J = 10.8, 4.7), 3.54 (dd, 1 H, J = 10.8, 7.3 Hz), 3.23 (m, 1 H), 2.08 (br s, 1 H, NH, OH), 1.65 (m, 1 H), 1.47 (m, 1 H), 1.30 (m, 4 H), 0.87 (m, 3 H); ^{13}C NMR δ ($CDCl_3$) 141.3, 136.9, 132.9, 130.9, 128.6(2), 128.4(2), 127.5, 127.4, 127.2(2), 126.3(2), 65.6, 61.3, 59.0, 34.9, 27.9, 22.7, 14.0; MS (CI) m/e (relative intensity) 310 [$(M + 1)^+$, 37], 292 [$(M + H - H_2O)^+$, 7], 173 (100); HRMS (CI) calcd for $C_{21}H_{28}NO$ 310.2171 $(M + H)^+$, found 310.2178.

Prepared from **9** using general procedure A in 40% yield (64% de).

Oxidative Cleavage of Amino Alcohol 5 and Hydrolysis to Amine 6. To a stirred solution of amino alcohol **5** (0.05 M) in CH_2Cl_2/MeOH (2/1, v/v) at 0 °C was added in one portion 1 equiv of lead tetraacetate. The reaction mixture was stirred for 4 min, whereupon 15% aqueous NaOH (5 mL) was added. The reaction mixture was extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic extracts were concentrated in vacuo. The remaining crude oil was dissolved in ether (100 mL) and stirred with an equal volume of 3 N aqueous HCl solution overnight. The aqueous phase was separated, basified with Na_2CO_3, and then extracted with ether. The ether extracts were combined, dried ($MgSO_4$), and concentrated in vacuo to give the amines **6a** and **6b** which were obtained as colorless oils after flash column chromatography (Et_2O).

(*R*)-α-(1-Naphthyl)ethylamine (6a):[15,16] 1.04 g, 61% yield; $[\alpha]^{25}_D$ + 32.8° (*c* 1.2, $CHCl_3$); IR (neat) 3370, 3300 (NH) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.15–7.45 (m, 7 H), 4.96 (q, 1 H, J = 6.6 Hz), 1.63 (br s, 2 H), 1.55 (d, 3 H, J = 6.6 Hz); MS (CI) m/e (relative intensity) 172 [$(M + 1)^+$, 100].

(*R*)-α-(1-Naphthyl)propylamine (6b):[16] 0.63 g, 57% yield: $[\alpha]^{25}_D$ + 21.08° (*c* 1, $CHCl_3$); IR (neat) 3371, 2961, 2930, 2872, 1510, 798, 778 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.14 (d, 1 H, J = 8.2 Hz), 7.86 (d, 1 H, J = 8.6 Hz), 7.74 (d, 1 H, J = 8.2 Hz), 7.61 (d, 1 H, J = 7.1 Hz), 7.56–7.42 (m, 3 H), 4.69 (dd, 1 H, J = 7.5, 5.5 Hz), 1.96 (m, 1 H), 1.80 (m, 1 H), 1.68 (s, 2 H), 0.99 (t, 3 H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$) 142.1, 133.8, 131.0, 128.8, 127.1, 125.7, 125.4, 125.3, 122.9, 122.3, 52.3, 31.5, 11.1; MS (CI) m/e (relative intensity) 203 [$(M + NH_4)^+$, 3], 186 [$(M + H)^+$, 100], 169 (93), 156 (18). Anal. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56. Found: C, 83.98; H, 8.09; N, 7.14.

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Registry No. **4**, 132313-01-0; **5a**, 138234-64-7; **5b**, 138234-65-8; (1*R*,1′*R*)-**5c**, 138234-66-9; (1*S*,1′*R*)-**5c**, 138234-67-0; **5d**, 138258-94-3; **6a**, 3886-70-2; **6b**, 22038-83-1; **6c**, 138234-68-1; **6d**, 3789-61-5; **8a**, 99797-48-5; **8b**, 99797-47-4; **8c**, 138234-69-2; **9**, 138234-70-5; **10**, 2845-25-2; **11**, 137623-81-5; **12**, 138234-71-6; $CeCl_3$, 7790-86-5; CuI, 7681-65-4; CH_3Li, 917-54-4; CH_3CeCl_2, 94616-84-9; $CH_3Cu{\cdot}BF_3$, 65139-98-2; $C_2H_5CeCl_2$, 135738-30-6; BuLi, 109-72-8; PhLi, 591-51-5; PhMgCl, 100-59-4; BuMgCl, 693-04-9; EtMgCl, 2386-64-3; (*R*)-(−)-2-amino-2-phenylethanol, 56613-80-0; 1-naphthylaldehyde, 66-77-3; cinnamaldehyde, 104-55-2.

(15) Commercially available from Norse Laboratories; Newbury Park, CA.

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