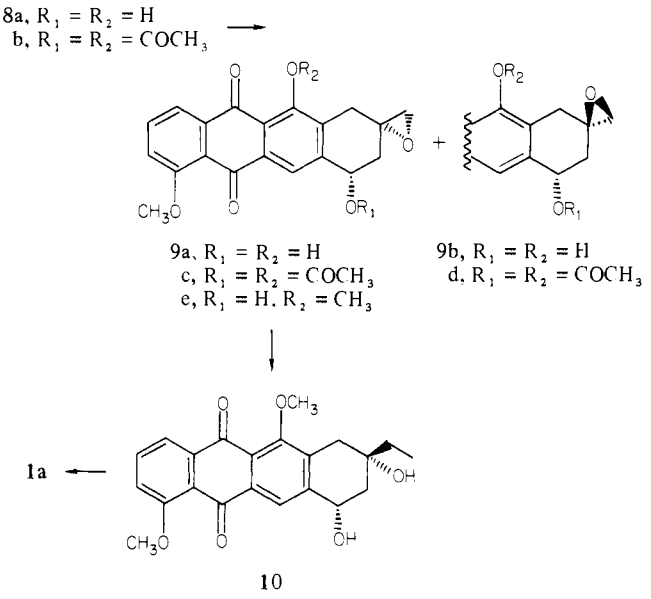
Scheme II



as an intermediate to γ-citromycinone (**1a**), is shown in Scheme I. Condensation[10] of the phthalidylsulfone **2**[11] (3 equiv of LiO-*t*-Bu, THF; initially at −78 °C and then at reflux) with **3**[12] gave the regiospecifically constructed tetrahydronaphthacene **4** which was directly transformed to the anthraquinone **5**[13] (55% overall yield) upon heating in DMF under an oxygen atmosphere[14] (100 °C, 12 h). Reaction of **5** with 2-(chloromethyl)propene (K_2CO_3, acetone; 95%) gave the allyl ether intermediate that was deacetylated (NaOH, H_2O–THF; 98%) to furnish the hydroxymethylanthraquinone **6**. Claisen rearrangement[15] of **6** ($Na_2S_2O_4$, DMF; 94%) followed by oxidation[16] of the hydroxymethyl group ($BaMnO_4$, CH_2Cl_2; 92%) gave the olefinic aldehyde **7**.

Treatment of **7** in methylene chloride with stannic chloride pentahydrate (0.5 equiv) resulted in instantaneous formation of **8a** as the sole regioisomer of reaction in 93% yield. The *exo*-methylene protons in the ^1H NMR spectrum of **8a** appeared as two singlets centered at 5.08 and 5.15 ppm. The C-7 proton at 4.75 ppm became a triplet (J = 4 Hz) upon exchange (D_2O) indicating that the C-7 hydroxyl group is axially oriented and therefore antiperiplanar with respect to the aromatic fragment.

The use of the seven hydroxyl group to effect stereocontrolled manipulation of the C-9, 13 olefinic group was straightforwardly realized as shown in Scheme II. Epoxidation of **8a** and the diacetate derivative **8b** with MCPBA (CH_2Cl_2; 89%) gave a 4:1 and 1:1 ratio of the corresponding *cis*- (**9a,c**) and *trans*-epoxides (**9b,d**), respectively. Ultimately, Sharpless epoxidation[17] of **8a** ($VO(AcAc)_2$, *t*-BuOOH, CH_2Cl_2) furnished **9a** as the sole stereoisomer of reaction (66%[18]).

Methylation of **9a** (Me_2SO_4, K_2CO_3, acetone; 91%) gave the methyl ether intermediate **9e**,[19] which was reacted with excess methyl copper[20] (2CuCN, 12MeLi; THF, 0 °C; 84%) to construct the ethylcarbinol fragment from the epoxide and furnished **10**. Demethylation of **10** (BCl_3, CH_2Cl_2, 86%) completed the synthesis of γ-citromycinone (**1a**). A direct comparison with an authentic sample was not possible due to its rarity; however, the mass spectrum of the synthetic material[21] was in excellent agreement with that reported for natural γ-citromycinone.[6]

Studies to establish the generality of this plan as a route for enantio- and stereospecific synthesis of other classes of anthracyclinones are being conducted.

Acknowledgment. We thank Dr. Bruce Lipschutz for helpful discussions. This work was generously supported by the National Cancer Institute of the National Institutes of Health (Grant 18141).

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(13) Compounds **1a**, **5**, **6**, **7**, **8a**, **9a**, and **10** gave satisfactory combustion analyses (C ≤ 0.2%; H ≤ 0.3%). Melting points and ^1H NMR spectra of selected intermediates are given below. **5**: mp 178–180 °C; ^1H NMR ($CDCl_3$) δ 12.43 (s, 1 H), 7.98 (d, 1 H, J = 8.0 Hz), 7.73 (t, 1 H, J = 8.0 Hz), 7.72 (s, 1 H), 7.30 (d, 1 H, J = 8.0 Hz), 7.2 (s, 1 H), 5.18 (s, 2 H), 4.04 (s, 3 H), 2.16 (s, 3 H). **6**: ^1H NMR ($CdCl_3$) δ 7.88 (dd, 1 H, J = 7.5, 1.3 Hz) 7.73 (s, 1 H), 7.67 (t, 1 H, J = 7.5 Hz), 7.28 (s, 1 H), 7.23 (dd, 1 H, J = 7.5, 1.3 Hz), 5.35 (br s, 1 H), 5.06 (br s, 1 H), 4.78 (s, 1 H), 4.56 (s, 1 H), 4.01 (s, 3 H), 2.6 (br s, 1 H), 1.90 (s, 3 H). **7**: mp 187–189 °C; ^1H NMR ($CDCl_3$) δ 12.93 (s, 1 H), 10.32 (s, 1 H), 8.26 (s, 1 H), 8.00 (d, 1 H, J = 7.5 Hz), 7.76 (t, 1 H, J = 7.5 Hz), 7.40 (d, 1 H, J = 7.5 Hz), 4.82 (br s, 1 H), 4.39 (br s, 1 H), 4.07 (s, 3 H), 3.88 (br s, 2 H), 1.89 (s, 3 H). **8a**: mp 199–201 °C; ^1H NMR ($CDCl_3$) δ 12.81 (s, 1 H), 7.96 (dd, 1 H, J = 7.5, 1.3 Hz), 7.86 (s, 1 H), 7.71 (t, 1 H, J = 7.5 Hz), 7.35 (dd, 1 H, J = 7.5, 1.3 Hz), 5.15 (br s, 1 H), 5.08 (br s, 1 H), 4.8 (m, 1 H), 4.04 (s, 3 H), 3.53 (s, 2 H), 2.69 (unresolved dd, 2 H), 2.22 (d, 1 H, J = 8.0 Hz). **9a**: ^1H NMR ($CDCl_3$) δ 12.79 (s, 1 H), 7.91 (dd, 1 H, J = 7.9, 1.3 Hz), 7.90 (s, 1 H), 7.71 (t, 1 H, J = 7.9 Hz), 7.36 (dd, J = 7.9, 1.3 Hz), 4.99 (br s, 1 H), 4.05 (s, 3 H), 3.12 (d, 1 H, J = 19 Hz), 2.86 (s, 2 H), 2.82 (d, 1 H, J = 19 Hz), 2.26 (dd, 1 H, J = 14.0, 4.8 Hz), 2.02 (dd, 1 H, J = 14.0, 4.8 Hz). **10**: mp 167–170 °C; ^1H NMR ($CDCl_3$) δ 8.15 (s, 1 H), 7.84 (d, 1 H, J = 8.0 Hz), 7.65 (t, 1 H, J = 8.0 Hz), 7.25 (d, 1 H, J = 8.0 Hz), 4.92 (m, 1 H), 4.24 (d, 1 H, J = 8.0, D_2O exchangeable), 4.00 (s, 3 H), 3.88 (s, 3 H), 3.16 (br d, 1 H, J = 18.4 Hz), 3.00 (s, 1 H, D_2O exchangeable), 2.64 (d, 1 H, J = 18.4 Hz), 2.31 (br d, J = 16.0 Hz), 1.84 (unresolved dd, 1 H, J = 16.0, 4.4 Hz), 1.68 (q, 2 H, J = 7.0 Hz), 1.06 (t, 3 H, J = 7.0 Hz). **1a**: mp 215 °C dec; ^1H NMR (pyridine-d_5) δ 13.2 (br s, 2 H, D_2O exchangeable), 8.42 (s, 1 H), 7.88 (dd, 1 H, J = 7.5, 1.3 Hz), 7.61 (t, 1 H, J = 7.5 Hz), 7.35 (dd, 1 H, J = 7.5, 1.3 Hz), 5.11 (t, 1 H, J = 4.8 Hz), 5.10 (br s, 2 H, D_2O exchangeable), 3.40 (d, 1 H, J = 18.0 Hz), 2.97 (d, 1 H, J = 18.0 Hz), 2.46 (dd, 1 H, J = 14.5, 4.8 Hz), 2.22 (dd, 1 H, J = 14.5, 4.8 Hz), 1.79 (q, 2 H, J = 7.0 Hz), 1.16 (t, 3 H, J = 7.0 Hz); mass spectrum, m/z (relative intensity) 354 (6.4), 326 (30), 318 (5.5), 307 (12), 282 (37), 280 (100), 279 (22), 254 (21).
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(21) The mass spectrum of the synthetic material is given in ref 13. For a comparison of these data with those reported for natural γ-citromycinone, see ref 6.

Mechanism of Hydroboration of Alkenes with Borane–Lewis Base Complexes. Evidence That the Mechanism of the Hydroboration Reaction Proceeds through a Prior Dissociation of Such Complexes

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Ever since our discovery that ether solvents powerfully catalyze the hydroboration of alkenes with diborane,[2] we have been interested in understanding the mechanism of this reaction and the actual role of the ether solvents on the mechanism.[3-10] Unfor-

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Table I. Rate Data for the Hydroboration of 1-Octene (20 mmol) with $BH_3 \cdot NR_1R_2R_3$ (6.67 mmol) in Toluene[a]

amine, $R_1R_2R_3N$	temp, °C	$t_{1/2}$[b]	comments
Et_3N	75	26 h	standard
$PhNEt_2$	75	instantaneous[c]	base weakened by resonance contribution of phenyl
	25	26 min	
	75	32 h	base strengthened by decreased steric effect of ring
	75	3.25 h	base weakened by −I effect of oxygen substituent
	75	~5 min[c]	base weakened by greater steric requirements of *i*-Pr

[a] In 20.0 mL of the solution. [b] Time for the first 50% of the reaction. [c] The reaction was exothermic on the addition of 1-octene to the solution of the reagent at 75 °C.

tunately, the complexity of the reaction[11] impeded rigorous kinetic studies. However, simplifications could be made.[10,12] By studying the kinetics of hydroboration of representative alkenes with well-characterized dialkylborane dimers, we established that, in general, the dialkylborane dimer initially dissociates into the monomer, which subsequently reacts with the alkene.[10] More importantly, we studied the mechanism of hydroboration of alkenes with 9-borabicyclo[3.3.1]nonane–Lewis base complexes.[8] All of our data convincingly pointed out that the 9-BBN–Lewis base complex reacts with the alkene via a prior dissociation mechanism (eq 1 and 2).[8] These studies also provided a reasonable explanation for the catalytic role of ether solvents on the hydroboration reaction.[8] Very recently, we established that the hydroboration of alkenes with dibromoborane–methyl sulfide also proceeds via the dissociation mechanism.[13]

$$\text{9-BBN·LB} \rightleftharpoons \text{9-BBN} + \text{LB} \quad (1)$$

$$\text{9-BBN} + \text{alkene} \rightarrow \text{product} \quad (2)$$

Recently, Schleyer and co-workers have proposed on the basis of ab initio calculations that the reaction of ethylene with $BH_3 \cdot OH_2$ (model for BH_3·THF) proceeds by an S_N2-type direct displacement of the Lewis base by the alkene.[14] Pasto and co-workers had studied the kinetics of hydroboration of 2,3-dimethyl-2-butene with BH_3·THF in THF at 0 °C. They observed second-order kinetics. On the basis of the observed entropy of activation, they also proposed a direct-attack mechanism for this reaction.[12] We were intrigued by the difference between our conclusions and theirs. Indeed, Schleyer had argued that BH_3–Lewis base complexes might behave differently from 9-BBN–Lewis base or Br_2BH–Lewis base complexes. Consequently, we decided to test the applicability of the dissociation mechanism to BH_3–Lewis base complexes by studying the hydroboration characteristics of representative BH_3–Lewis base complexes. The results clearly support the dissociation mechanism.

First, we studied the rates of hydroboration of 1-octene (3 equiv) with several BH_3–amine complexes (1 equiv). The rates vary inversely and remarkably with the stability of the adduct (Table I). For example, BH_3·$NPhEt_2$ reacts far faster with 1-octene than does BH_3·NEt_3. BH_3–*N*-ethylpiperidine reacts slower and BH_3–*N*-ethylmorpholine faster than BH_3·NEt_3. Again, BH_3·NEt-*i*-Pr_2 reacts much faster than BH_3·NEt_3. Thus any factor, either steric or electronic, that decreases the stability of the adduct increases the rate of hydroboration. Unfortunately, however, these observations cannot totally rule out the direct-attack mechanism since any factor that decreases the stability of the adduct may, at least in principle, be expected to increase the leaving tendency of the ligand in a bimolecular mechanism.

Table II. Effect of Adding Excess Lewis Base on the Rate of Hydroboration of Alkenes with BH_3–Lewis Base Complex in Toluene

alkene, mmol	BH_3·LB (mmol)	molar equiv of LB added	temp, °C	$t_{1/2}$[a]
1-octene[b] (20 mmol)	$BH_3 \cdot NEt_3$[b] (6.67)	0	75	26 h
		1		54 h
		2		86 h
1-octene[c] (10 mmol)	$BH_3 \cdot SMe_2$[c] (3.33)	0	25	200 s
		1		315 s
		2		375 s
2,3-dimethyl-2-butene[c] (5 mmol)	$BH_3 \cdot SMe_2$[c] (5)	0	0	34 min
		1		52 min
		2		69 min

[a] Time for the first 50% of the reaction. [b] In 20 mL of the solution. [c] In 25 mL of the solution.

Table III. Rate Data for the Reaction of 2,3-Dimethyl-2-butene with $BH_3 \cdot SMe_2$ in Toluene at 0 °C, with and without Added Me_2S[a]

No added Me_2S			$[Me_2S] = 0.400$ M		
time, s	[TME], M	$10^3k_2''$, M^{-1} s^{-1}	time, s	[TME], M	$10^3k_2''$,[a] M^{-1} s^{-1}
258	0.169	3.55	774	0.169	1.19
498	0.157	2.75	1086	0.160	1.15
978	0.137	2.35	1494	0.149	1.15
1698	0.115	2.18	3174	0.114	1.19
3378	0.083	2.10	4374	0.097	1.21
6018	0.059	2.00	5814	0.085	1.17
				$k_{graphical}$	1.19

[a] For all data in table [TME] = 0.200 M and [BMS] = 0.200 *M*. [b] For the reaction of 0.20 M TME with 0.20 M BMS in the presence of 0.20 M Me_2S, the rate constant still decreased with extent of reaction ($k_{graphical} \approx 1.56 \times 10^{-3}$ M^{-1} s^{-1}). For the reaction of 0.30 M TME with 0.30 M BMS in the presence of 0.60 M Me_2S, $k_{graphical} = 1.13 \times 10^{-3}$ M^{-1} s^{-1}.

We thought that a more rigorous way to distinguish between the dissociation and the direct-attack mechanisms would be to study the effect of excess complexing agent on the rate of hydroboration of alkenes with BH_3–Lewis base complexes. The dissociation mechanism requires that the rate be depressed by excess complexing agent while, for the direct-attack mechanism, the effect should be negligible or none.

Indeed, we find that the presence of 1 and 2 equiv of triethylamine represses significantly the rate of hydroboration of 1-octene (3 equiv) with BH_3·NEt_3 (1 equiv) in toluene at 75 °C (Table II). Similarly, 1 and 2 equiv of Me_2S represses the rate of hydroboration of 1-octene (3 equiv) with BH_3·SMe_2 (1 equiv) in toluene at 25 °C (Table II). To test whether such a rate repression is observable in the first step of hydroboration, we studied the effect of Me_2S on the rate of hydroboration of 2,3-dimethyl-2-butene with BH_3·SMe_2 in toluene at 0 °C. Here again we observe a significant rate retardation[15] (Table II). It may be noted that excess complexing agent also represses the rates of hydroboration of alkenes with 9-BBN·NMe_3,[8] Br_2BH·SMe_2,[13] and

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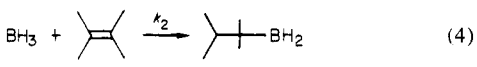
(15) We find the magnitude of the rate retardation to be greater in the case of BH_3·NEt_3 than in the case of BH_3·SMe_2. This is to be anticipated on the basis of the dissociation mechanism since the extent of the rate retardation produced by excess complexing agent depends on both the concentration of the complexing agent and the inherent stability of the complex, BH_3–Lewis base.

thexylchloroborane–methyl sulfide.[16] In our view, these results clearly establish that the hydroboration of alkenes with BH_3–Lewis base complexes must involve a prior dissociation of the complex followed by reaction of the free borane with the alkene.

As mentioned time and again,[10] kinetic studies of the reaction of BH_3–Lewis base complexes with simple alkenes such as 1-octene have been practically impossible due to the complexity of the reaction. However, the reaction of BH_3·SMe_2 with 2,3-dimethyl-2-butene (TME) stops at the first stage (RBH_2), making possible a rigorous kinetic analysis of the reaction. The rate equation for the dissociation mechanism (eq 3 and 4) derived

$$BH_3 \cdot SMe_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} BH_3 + SMe_2 \qquad (3)$$



(4)

by steady-state treatment predicts complex kinetic behavior. The direct-attack mechanism, on the other hand, requires clean second-order kinetics to be exhibited. Our kinetic analysis of the rate data for the reaction of TME (0.200 M) with BH_3·SMe_2 (0.200 M) in toluene at 0 °C yielded second-order rate constants decreasing in magnitude with the progress of the reaction, as predicted by eq 5 (Table III). When the reaction is done in the

$$\frac{dp}{dt} = \frac{k_1 k_2[\mathrm{BMS}][\mathrm{TME}]}{k_{-1}[\mathrm{SMe_2}] + k_2[\mathrm{TME}]} \qquad (5)$$

presence of excess Me_2S, $k_{-1}[SMe_2] >> k_2[TME]$, simplifying the rate equation to eq 6.[17] Since Me_2S is in excess, its concentration will be fairly constant, leading to reasonable pseudo-second-order kinetic behavior. We observe this behavior. For the reaction of TME (0.200 M) with BMS (0.200 M) in the presence of excess Me_2S (0.400 M) in toluene at 0 °C, good second-order rate constants are observed (Table III).

$$\frac{dp}{dt} = \frac{k_1 k_2[\mathrm{BMS}][\mathrm{TME}]}{k_{-1}[\mathrm{SMe_2}]} \qquad (6)$$

It is interesting to note that these results can explain Pasto's results on the reaction of TME with BH_3·THF in THF at 0 °C.[12] Since the reaction was done in the presence of a large excess of THF (solvent), k_{-1}[THF] will be very large and thus be constant. A pseudo-second-order kinetics will obtain, as was indeed observed. (An expression similar to eq 6 should be applicable.)

Thus, our results on the reaction of 2,3-dimethyl-2-butene with BH_3·SMe_2 provide strong evidence for the dissociation mechanism.

We also wish to draw attention to the important observation made by Klein and co-workers.[18] They noted that the hydroboration of aged solutions of *m*-methoxystyrene with BH_3·THF exhibited a considerable induction period. They attributed this induction period to the diversion of a reactive intermediate by an impurity, probably peroxide. Only after all of the impurity had reacted would the hydroboration itself begin. This experiment clearly shows that the complex, BH_3·THF, is *not* the hydroborating species involved in the actual hydroboration step.

Thus, our present studies and that of Klein indicate that the mechanism of hydroboration of alkenes with BH_3–Lewis base complexes proceeds via a prior dissociation of the complex. They do not support the direct-attack mechanism proposed by Schleyer and co-workers on the basis of ab initio calculations.[14]

The rate studies were performed by monitoring the disappearance of the B–H stretching absorbance of the BH_3–Lewis base complex (~4.0–4.3 μm) using a quantiative IR procedure.[5,8]

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(17) The term k_2[TME] in eq 6 may still contribute to a minor extent, since a sufficiently large excess of Me_2S to eliminate the competition would have altered the medium. As a result, the observed pseudo-second-order rate constants k_2'' in Table III are not strictly inversely proportional to [Me_2S].

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Asymmetric Addition to Chiral Naphthyloxazolines. A Facile Route to 1,1,2-Trisubstituted-1,2-dihydronaphthalenes in High Enantiomeric Excess

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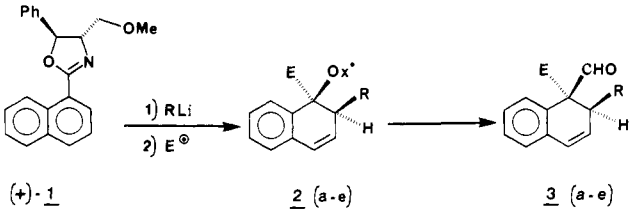
The increasingly important role of asymmetric synthesis has been manifested by the large number of reports on this subject over the past 10 years.[2] Prominent among these studies has been the use of chiral oxazolines as auxiliaries for a wide range of enantiomerically enriched compounds.[3] We now describe a novel asymmetric route to chiral 1,1,2-trisubstituted-1,2-dihydronaphthalenes with very high enantioselectivity.[4] The process involves the nucleophilic addition of various organolithium reagents to the chiral 1-naphthyloxazoline **1**[5] followed by trapping of the intermediate azaenolate with several electrophiles to furnish the dihydronaphthalene **2**. This tandem alkylation sequence affords



2 with a high degree of diastereofacial selectivity thus incorporating two asymmetric centers in a one-pot reaction.[6] Furthermore, a mild, high-yield procedure for removal of the oxazoline moiety is described, producing enantiomerically pure 1,2-dihydronaphthalene aldehydes **3**.

Treatment of a THF solution containing (+)-**1** (−45 °C) with an organolithium reagent followed by additin of an electrophile (−45 °C) produced the adducts **2a–e** as a mixture of diastereomers, whose ratios were readily assessed by HPLC analysis (Table I). In each example, the two diastereomers formed were the result of sequential trans addition,[7] thus the diastereomeric ratios reflect only the facial selectivity of the initial lithium nucleophile. The absolute configuration as well as the trans addition were confirmed by X-ray diffraction studies on pure **2c**. Since the oxazoline is known to contain the 4*S*,5*S* configuration,[8] the organolithium enters mainly at the β-face followed by electrophile entry at the α-face of the naphthalene ring. The diastereomers of **2** were easily separated by flash chromatography providing enantiomerically pure aldehydes **3** after removal of the oxazoline (vide infra).

(1) National Research Service Award Postdoctoral Fellow (N1H-1F-32CA07333).

(2) A comprehensive review on asymmetric synthesis has been compiled: Morrison, J. D. "Asymmetric Synthesis"; Academic Press: New York, 1983; Vol. 1–4, in press.

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(4) Aryl borate anions have been shown to furnish *trans*-1,2-disubstituted-1,2-dihydronaphthalenes (Negishi, E.; Merrill, R. E. *Chem. Commun.* **1974**, 860.

(5) Prepared in 62% yield from 1-naphthoic acid following the procedure reported previously: Meyers, A. I.; Lutomski, K. A. *J. Am. Chem. Soc.* **1982**, *104*, 879. For other derivatives of aryloxazolines, see: Meyers, A. I.; Hanagan, M. A.; Trefonas, L. M.; Baker, R. J. *Tetrahedron* **1983**, *39*, 1991. $[\alpha]^{25}_D$ of **1** 53.0° (*c* 7.50, $CHCl_3$).

(6) Organolithium reagents add to simple, achiral naphthalene oxazolines and may be trapped to *trans*-1,1,2-trisubstituteddihydronaphthalenes (confirmed by X-ray analysis). Lutomski, K. A., unpublished results.

(7) The trans alignment of R to E in **2c** as well as the absolute configuration are given with the X-ray details in the supplementary material.

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