Asymmetric and Nonasymmetric Addition of RLi and RMgX to 3-Methoxynaphthalen-2-yl Oxazolines and Imines. An Approach to Substituted 2-Tetralones†

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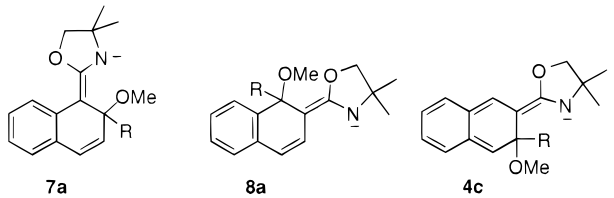
Chiral and achiral 3-methoxynaphthalen-2-yl oxazolines **4a**,**b** failed to undergo an aromatic nucleophilic displacement of the 3-methoxy group with organolithium reagents and instead afforded dihydronaphthalenes **9** and **14** in 30−95% yield. Dihydronaphthalenes **9** (racemic) and **14** (nonracemic) were easily converted into the corresponding aldehydes **15**. Alternatively, aldehydes **15** were prepared via tandem addition of Grignard reagents to imines **17** in 50−65% yield. Aldehydes **15** served as precursors to 3,3,4-trisubstituted 2-tetralones **16**. Use of methyl chloroformate to trap the azaenolate derived from **17f** and *i*-PrMgCl afforded, in 65% yield, a versatile synthetic intermediate **23** which may serve to access 4-alkyl-, 3,4-dialkyl-, 3,4-disubstituted and 3,3,4-trisubstituted 2-tetralones with diverse substitution patterns.

Conjugate addition of organolithium and Grignard reagents to a naphthalene nucleus, activated by electron-withdrawing groups, has been shown to be an attractive approach to dihydronaphthalenes.[1] However, use of naphthalenes having a methoxy substituent in the activated ring for the addition has been only sparsely studied. One example of such a study involved addition of a series of organolithium reagents to chiral naphthyloxazoline[1h] **1** to afford methyl vinyl ethers **2** which were converted into nonracemic highly substituted 1-tetralones **3** in good chemical and optical yields (Scheme 1). A study was, therefore, initiated to examine the feasibility of a similar approach to the corresponding 2-tetralones in direct analogy to the process documented for **1**. 2-Tetralones are known precursors to 2-aminotetralins which display a variety of biological activities.[2] This report is concerned with addition of certain organometallics to 3-methoxynaphthalen-2-yl oxazolines **4** and imines **5** in an effort to access chiral, nonracemic dihydronaphthalenes **6** which might further be elaborated, after hydrolysis, into chiral substituted 2-tetralones with diverse substitution patterns, in high enantiomeric purity.

In earlier studies[3,4] we found that addition of organolithium or Grignard reagents to oxazolines **7** and **8** resulted in substitution of the methoxy group rather than addition to the naphthalene nucleus. A distinct feature of **7** and **8** is that their methoxy groups are found in the 1- or 2-position of the naphthalene ring which allows them to undergo nucleophilic addition followed by their displacement. Of further interest in the additions to **4a** and **4b** was the general question "will conjugate addition still occur at the 1-position or would the methoxy group at C-3 still be displaced?" Nucleophilic addition of alkyl anions (R) to **7** and **8** produces the σ-complexes **7a** and **8a**, respectively, yet these intermediates still contain an unperturbed benzene ring in a conjugated styrene π-system. The addition of a nucleophile to **4** would produce σ-complex **4c** having a cross-conjugated *o*-quinone methide moiety providing a transition state of higher energy than the potential energy of the isomeric styrene systems in **7a** and **8a**. Invoking the concept of "partial bond fixation",[5] the addition of nucleophiles to **4** should, therefore, take place at the 1-position leaving the methoxy enol ether unaffected.



† The paper is dedicated to the memory of Lendon N. Pridgen.

(1) (a) For the use of a hindered ester as an activating group for naphthalene additions, see: Shindo, M.; Koga, K.; Asano, Y.; Tomioka, K. *Tetrahedron* **1999**, *55*, 4955−4968. For the use of a carboxylate as an activating group for naphthalene additions, see: (b) Plunain, B.; Mortier, J.; Vaultier, J.; *J. Org. Chem.* **1996**, *61*, 5206−5207. For the use of oxazolidine/imine system as an activating group for naphthalene additions, see: (c) Pridgen, L. N.; Mokhallatie, M. K.; Wu, M.-J. *J. Org. Chem.* **1992**, *57*, 1237−1241. (d) Mokhallatie, M. K.; Muralidharan, K. R.; Pridgen, L. N. *Tetrahedron Lett.* **1994**, *35*, 4267−4270. For the use of imine as an activating group for naphthalene additions, see: (e) Meyers, A. I.; Brown, J. D.; Laucher, D. *Tetrahedron Lett.* **1987**, *28*, 5279−5282. (f) Meyers, A. I.; Brown, J. D.; Laucher, D. *Tetrahedron Lett.* **1987**, *28*, 5283−5286. (g) Tomioka, K.; Shindo, M.; Koga, K.; *J. Am. Chem. Soc.* **1989**, *111*, 8266−8268. For the use of 1,3-oxazoline as an activating group for naphthalene additions, see: (h) Meyers, A. I.; Roth, G. P.; Hoyer, D.; Barner, B. A.; Laucher, D. *J. Am. Chem. Soc.* **1988**, *110*, 4611−4624. (i) Rawson, D. J.; Meyers, A. I. *J. Org. Chem.* **1991**, *56*, 2292−2294.

(2) (a) Mellin, C.; Björk, L.; Karlén, A.; Johansson, A. M.; Sundell, S.; Kenne, L.; Nelson, D. L.; Andén, N.-E.; Hacksell, U. *J. Med. Chem.* **1988**, *31*, 1130−1140. (b) Johansson, A. M.; Mellin, C.; Hacksell, U. *J. Org. Chem.* **1986**, *51*, 5252−5258. See, also: Malmberg, A.; Nordvall, G.; Johansson, A. M.; Mohell, N.; Hacksell, U. *Mol. Pharmacol.* **1994**, *46*, 299−312; *Chem. Abstr.* **1994**, *121*, 194983h. Horn, A. S.; Dijkstra, D.; Feenstra, M. G. P.; Grol, C. J.; Rollema, H.; Westerink, B. H. C. *Eur. J. Med. Chem.-Chem. Ther.* **1980**, *15*, 387−92; *Chem. Abstr.* **1981**, *94*, 103044n. Beaulieu, M.; Itoh, Y.; Tepper, P.; Horn, A. S.; Kebabian, J. W. *Eur. J. Pharmacol.* **1984**, *105*, 15−21. *Chem. Abstr.* **1985**, *102*, 437x.

(3) For reviews on oxazolines chemistry, see: (a) Gant, T. G.; Meyers, A. I. *Tetrahedron* **1994**, *50*, 2297−2360. (b) Meyers, A. I. *J. Heterocycl. Chem.* **1998**, *35*, 991−1002.

(4) (a) Gant, T. G.; Meyers, A. I. *J. Am. Chem. Soc.* **1992**, *114*, 1010−1015. (b) Meyers, A. I.; Lutomski, K. A. *Synthesis* **1983**, 105−107. (c) Meyers, A. I.; Flanagan, M. E. *Organic Syntheses*; Wiley: New York, 1998; Coll. Vol. IX, pp 258−262.

(5) *Advanced Organic Chemistry*, 3rd ed.; March, J., Ed.; John Wiley & Sons: New York, 1985; pp 39−41.

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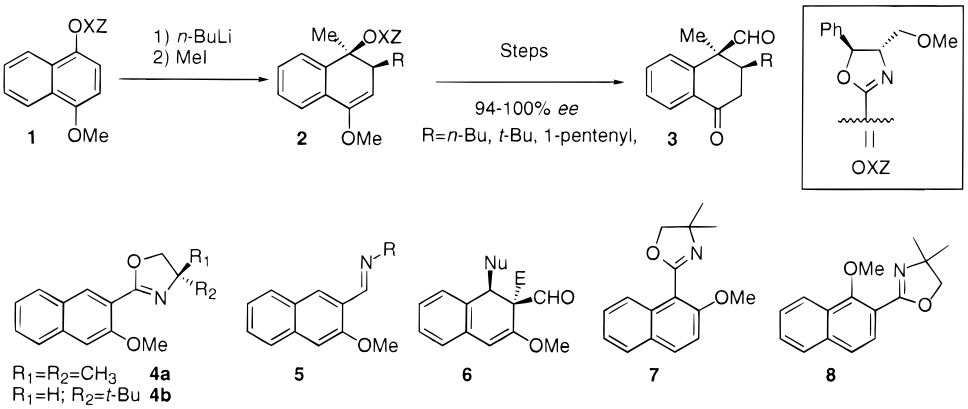
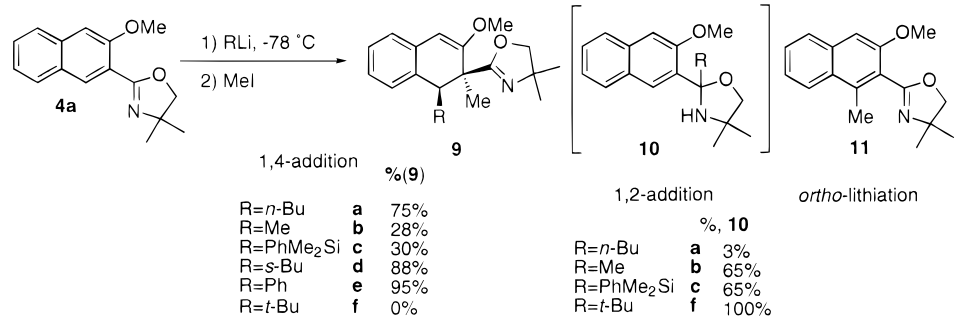
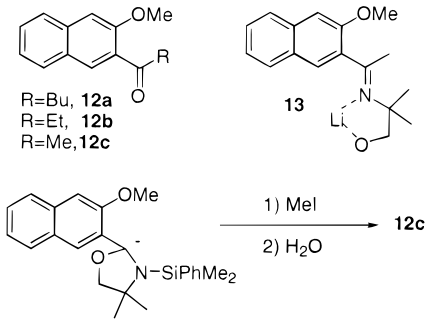
Scheme 1



Scheme 2



Scheme 3



When *n*-BuLi was added to **4a** in THF at −78 °C, the reaction resulted in the 1,4-addition product (**9a**) and the 1,2-addition product (**10a**) in 75% and 3% yield, respectively (Scheme 2). Formation of oxazoline **11** arising from a directed *ortho*-metalation of **4a** *ortho* to the oxazolinyl moiety was also observed in 5% yield.[3a] On treatment of the reaction mixture with dilute acid, oxazolidine **10a** was hydrolyzed to the methyl ketone **12a** which was isolated and characterized. Thus, the hypothesis of the high energy transition state leading to **4c** appears valid, and no methoxy group displacement products were observed.

When methyllithium was added to **4a**, the ethyl ketone **12b**, unexpectedly, was the major product and the 1,4-addition product **9b** was obtained in only 28% yield after methyl iodide quench (Scheme 3). Such poor yields of MeLi−MeI addition to naphthyloxazolines have been observed earlier.[1h] The yields of ethyl ketone **12b** and oxazoline **9b** were not dependent on whether MeLi or a complex of MeLi·LiBr was used in the reaction. A possible pathway for the unexpected formation of ethyl ketone **12b** may involve an initial 1,2-addition of MeLi to the C=N link of the oxazoline moiety to form oxazolidine **10b** with concomitant ring-chain tautomerism of the oxazolidine to its imine form **13**. The imine may be deprotonated by MeLi and alkylated with MeI to give ethyl ketone **12b** on acidic hydrolysis. In the case of *n*-BuLi addition only the *n*-butyl ketone **12a** was obtained, after aqueous hydrolysis of **10a**. The addition of *tert*-butyllithium−MeI to **4a** afforded only 2-*tert*-butyloxazolidine **10f**.

The reaction of phenyldimethylsilyllithium[6] with naphthyloxazoline **4a** followed by MeI quench afforded methyl ketone **12c** as a major product in 65% yield, while dihydronaphthalene **9c** was isolated in only 30% yield. Ketone **12c** may be a result of an aza-Brook rearrangement of **10c** and alkylation of the intermediate benzylic carbanion with methyl iodide (Scheme 3). A related aza-Brook of (α-silylallyl)amines was reported by Mori and Honda.[7]

s-Butyllithium cleanly added to **4a** to give 88% of the desired dihydronaphthalene **9d** as a 2:1 mixture of diastereomers at the *s*-Bu stereogenic center. Phenyllithium also cleanly afforded the corresponding dihydronaphthalene **9e** in 95% yield. Crystal structure[8] determination of **9e** (Figure 1) confirmed the relative

(6) (a) Fleming, I.; Newton, T. W.; Roessler, F. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2527−2532. (b) Hulme, A. N.; Henry, S. S.; Meyers, A. I. *J. Org. Chem.* **1995**, *60*, 1265−1270.

(7) Honda, T.; Mori, M. *J. Org. Chem.* **1996**, *61*, 1196−1197.

(8) Crystal structure analysis of **9e**: $C_{23}H_{25}NO_2$, M_r 347.44, 0.18 × 0.28 × 0.40 mm, monoclinic, $P2_1/c$, a = 13.5764(6), b = 8.0560(4), c = 19.1666(8) Å, $\alpha = \gamma = 90°$, β = 109.7530(10)°, V = 1972.9(2) Å^3, Z = 4, ρ_{calc} = 1.170 g/cm^3, Mo Kα (λ = 0.71073 Å), T = 171(2) K; μ = 0.074 mm^{-1}. Area detector data collected on a Siemens SMART CCD diffractomerer. A total of 12551 reflections were collected ($1.59 < \Theta < 28.33°$); independent reflections 4748 (R_{int} = 0.0657). Structure solved by direct methods (SHELXTL) and refined by full-matrix least-squares on $|F|^2$. Final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0556, w$R2$ = 0.0962. GOF = 0.912. Residual electron densitry (e·Å^{-3}) 0.246/−0.209.

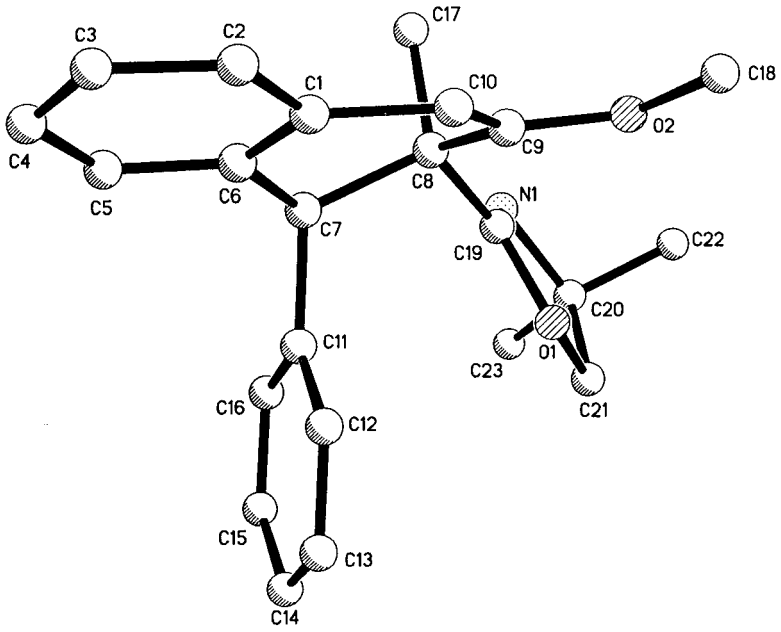
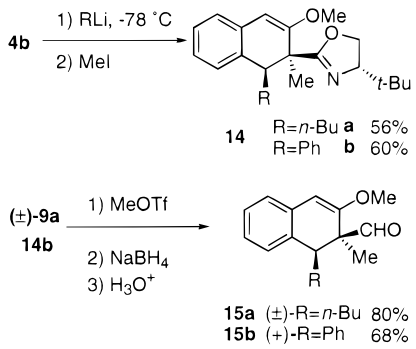


Figure 1. Crystal structure of **9e**.

Scheme 4



stereochemistry of the process as being an overall *trans*-addition. This finding is in agreement with the one previously reported[1h,i] and implies that the 3-methoxy group does not change the relative stereochemical outcome of this tandem addition process.

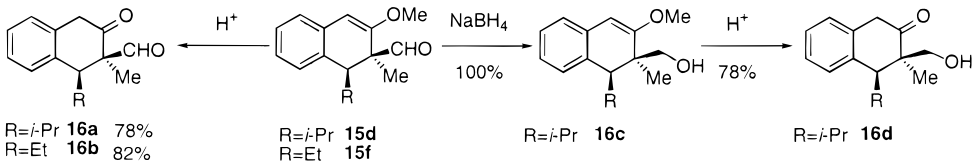
The use of chiral nonracemic naphthyloxazoline **4b** in place of **4a** was also investigated for the addition of organolithium reagents in anticipation of reaching enantiomerically pure adducts. Reaction of *n*-BuLi and PhLi with oxazoline **4b** afforded **14a** and **14b** as single diastereomers in 56% and 60% yield, respectively (Scheme 4). The absolute stereochemistry of **14** is believed to be as shown and is based on analogy to the previously reported[1h,i] observation that the incoming organolithium reagent approaches the face which is opposite to the sterically demanding 4-*tert*-butyl group of the oxazolinyl moiety.

We have previously reported that products from the addition of organolithiums to naphthyloxazolines such as **9** and **14** can be readily converted into carboxaldehydes.[1h,4c] Both oxazolines **9a** and **14b** were smoothly transformed into the corresponding aldehydes **15a**,**b** in 80% and 68% yield, respectively.

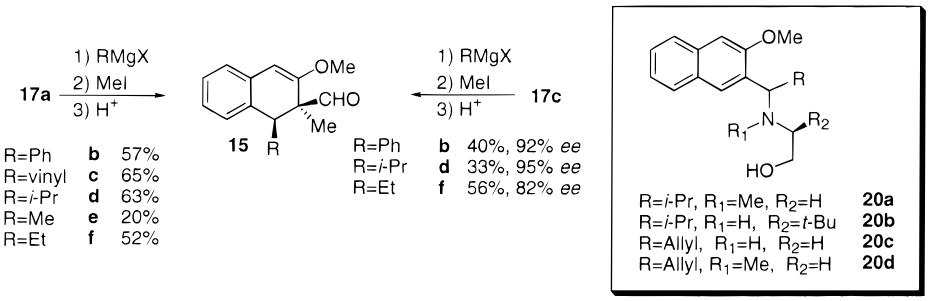
To demonstrate the accessibility of highly substituted chiral 2-tetralones from **15**, enol ethers **15d** and **15f** (R = *i*-Pr, Et, respectively; synthesis vide infra) was subjected to acidic hydrolyses. Surprisingly, enol ethers **15d**,**f** were found to be stable in 10% aqueous hydrochloric acid in THF (ca. 1:1, v/v) at room temperature. The unusual stability of the enol ethers may be due to the adjacent quaternary center. Deprotection of the methyl vinyl ethers **15d**,**f** was subsequently achieved in a mixture of THF, TFA, and a small amount of trifluoromethanesulfonic acid which afforded the 2-tetralones **16a**,**b** in 78% and 82% yield, respectively (Scheme 5). It was observed that aldehydes **15** are shelf-stable compounds for several days at room temperature before decomposition products are detected by TLC, whereas the corresponding neat 2-tetralones such as **16a** decompose to unidentified products over the same period of time and should be stored in a freezer. Aldehyde **15d** was converted to the alcohol **16c** with sodium borohydride which was qualitatively more shelf-stable than starting aldehyde **15d**. The enol ether **16c** was transformed to the tetralone **16d** under the same conditions as above. Furthermore, when **15d** was treated with DDQ in refluxing dioxane, it underwent simultaneous deformylation and aromatization to isopropylnaphthalene **16e**.

To further explore the synthetic utility of dihydronaphthalene adducts such as **15** and capitalize on the fact that no displacement of the 3-methoxy group in naphthalenes **4** was observed, an alternative route to aldehydes **15** was investigated. This was based on the use of an imine as the activating group for addition to the naphthalene nucleus. It was earlier reported from these laboratories that chiral nonracemic and achiral naphthylimines treated with organolithium reagents furnished dihydronaphthalenes **19b** after aqueous hydrolysis in 60−90% yield.[1e,f] An extension of this methodology was later communicated by Pridgen who was able to effect highly diastereoselective addition of Grignard reagents to a chiral tautomeric mixture of oxazolidine/imine **19a** derived from (*R*)-phenylglycinol and 1-naphthylcarboxaldehyde. Chiral, nonracemic addition adducts (**19b**) were obtained in good

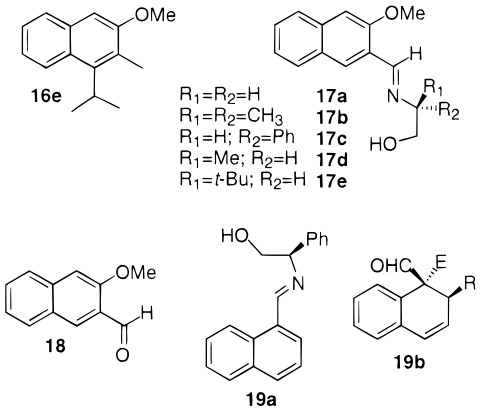
Scheme 5



Scheme 6



chemical yields and >90% ee.[1c,d]



The requisite imines **17a**−**e** were readily obtained by heating naphthaldehyde **18** either with an excess or equimolar amount of the corresponding 2-amino alcohol with azeotropic removal of water. The reaction was followed by the disappearance of the aldehyde proton ($\delta(CDCl_3) = 10.3$ ppm) in **18**. *gem*-Dimethyl imine **17b** existed as its oxazolidine tautomer in solution while the unsubstituted derivative **17a** existed primarily as its imine form. Furthermore, it is known that aldimines exist almost exclusively in the *E*-configuration[9] whereas the remaining derivatives, **17c**−**e**, were found to consist of an equilibrating mixture of imine and both diastereomeric oxazolidines in solution (^{1}H NMR).[1c]

A variety of Grignard reagents added readily to achiral imine **17a** in THF, and the intermediate aza-enolates were trapped with MeI. The relative stereochemistry of 2-methylaldehydes **15** is shown in Scheme 6. This stereochemistry is based on the analogy to the results reported from this laboratory[1e,f] and by Pridgen and co-workers.[1c,d] In all previous cases of the tandem addition to chiral and achiral activated naphthalenes, the entry of the electrophile on the planar lithio or magnesio enolate or azaenolate occurs from the side opposite to the group entering as the nucleophile.[1] The yields of aldehydes **15** obtained ranged from 50% to 65% with the exception of MeMgCl which gave aldehyde **15e** in a poor 20% yield when the addition was conducted at 0 °C.[1d] A competing process in the addition of Grignard reagents to naphthalenes **17** involved addition to the C=N linkage furnishing **20.** Naphthylamine **20a** was isolated in 20% yield and fully characterized.[10,11]

The addition of *i*-PrMgCl, EtMgBr, PhMgBr to (*R*)-phenylglycinol imine **17c** afforded enantiomerically enriched aldehydes **15b**,**d**,**f** in 33−56% yield and in 82−95% ee as determined by HPLC (Scheme 6). Addition of *i*-PrMgCl to (*S*)-alaninol imine **17d** gave the opposite enantiomer of **15d** in 78% ee and 45% chemical yield. The 1-phenylaldehyde **15b** obtained by the addition of PhMgBr to imine **17c** had identical spectral characteristics and specific rotation to aldehyde **15b** obtained from enantiomerically pure oxazoline **4b** which suggests that the absolute stereochemistry of **15b** is as shown and the entry of the nucleophile occurs from the side opposite the phenyl moiety in the chelated imine intermediate, as reported earlier by Pridgen and co-workers[1c,d] for a related system.

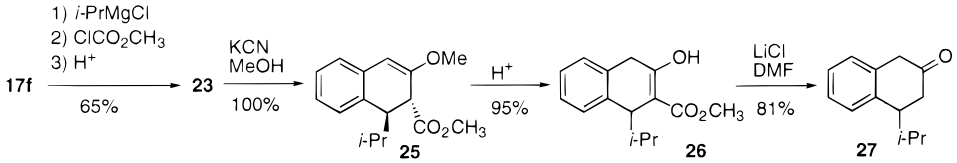
In an effort to increase the yield of the desired aldehydes **15** addition of *i*-PrMgCl to a series of imines **17** having various alkyl substituent in the amino alcohol fragment was investigated. The results of this study suggested an interesting trend in the influence of a 2-alkyl substituent of the 1,2-amino alcohol on the yield of the recovered tandem addition product **15**. Namely, increasing the bulk of the 2-alkyl substituent results in lower yields of aldehyde **15**. This observation was confirmed by the addition of *i*-PrMgCl to imines **17b** and **17e** having a *gem*-dimethyl group and *t*-Bu substituent, respectively. The reaction of **17b** with *i*-PrMgCl gave a low yield of tandem addition product **15d** (12−15%). In

(9) (a) Bjørgo, J.; Boyd, D. R.; Watson, C. G.; Jennings, W. B.; Jerina, D. M.; *J. Chem. Soc., Perkin Trans. 2* **1974**, 1080−1084. (b) Karabatsos, G. J.; Lande, S. S. *Tetrahedron* **1968**, *24*, 3907−3922.

(10) Use of excess of MeI resulted in partial methylation of the imine addition adducts such as **20c** and **20d**, making their purification difficult because of very close R_f values. Addition of Grignard reagents to chiral nonracemic **17** may also suffer from poor diastereoselectivity, resulting in the formation of two diastereomers at the newly created stereogenic center which subsequently may get partially methylated. Therefore, except for **20a**−**d**, purification of the imine addition adducts was not attempted, however, ^{1}H NMR of the mixtures of the crude adducts supported their identity.

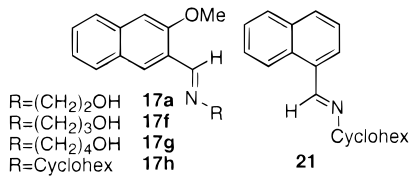
(11) For the asymmetric addition of Grignard reagents to imines, see: (a) Enders, D.; Reinhold: U. *Tetrahedron: Asymmetry* **1997**, *8*, 1895−1946. (b) Suzuki, Y.; Takahshi, H. *Chem. Pharm. Bull.* **1983**, *31*, 31−40. (c) Takahshi, H.; Suzuki, Y.; Inagaki, H. *Chem. Pharm. Bull.* **1982**, *30*, 3160−3166.

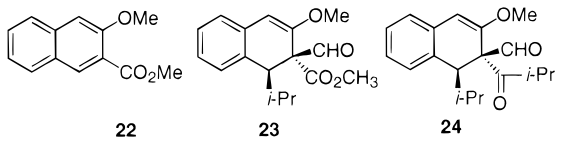
Scheme 7



the case of *tert*-leucinol imine **17e** exclusive addition to the imine was observed. Amine **20b** was formed in quantitative yield upon aqueous NH_4Cl quench of the latter reaction mixture. For characterization purposes, amine **20b** was converted into a cyclic oxazolidone using carbonyldiimidazole. Addition of allylmagnesium chloride to **17a** also gave exclusively a mixture of imine addition adducts **20c** and **20d**. Benzylmagnesium chloride was unreactive toward **17a** and 95% of **18** was recovered after the acidic hydrolysis.

To assess the importance of the appended hydroxyl group in imines **17** and its influence on the addition of Grignard reagents, imines **17f**,**g**, having the hydroxyl group spaced from the imine nitrogen by three and four methylene groups, respectively, were prepared. Addition of *i*-PrMgCl to **17f**,**g** followed by MeI quench gave 27% and 44% yield of the addition product **15d**, respectively. This suggested that the appended hydroxyl group might not be necessary for the tandem addition to naphthalene to occur. This notion was supported by the fact that imine **17h** having no appended hydroxyl gave 39% of dihydronaphthalene **15d** and 23% of unreacted naphthylaldehyde **18** when 2 equiv of *i*-PrMgBr in THF at 0 °C were employed. However, the same finding implies that the appended hydroxy group increased the rate of the addition. It was further found that using a 3-fold excess of *i*-PrMgBr and raising the temperature from 0 °C to room temperature afforded dihydronaphthalene **15d** in 65% yield. Use of EtMgBr in place of *i*-PrMgBr under the latter conditions afforded 42% yield of **15f**, and 58% of **18** was also recovered. We reported earlier that imine **21** readily added organolithium reagents to afford the corresponding dihydronaphthalenes after aqueous hydrolysis.[1e,f] In the present study it was found that use of 3 equiv of a Grignard reagent at room temperature drastically accelerated the rates of addition and tandem additions to imine **17h**.





In all examples shown thus far, methyl iodide was utilized as an electrophilic quenching reagent to form 2-methyl aldehydes **15**. However, we also employed methyl chloroformate as an electrophile to trap the azaenolate obtained from **17f** and *i*-PrMgCl. This gave, after hydrolysis, a 65% yield of aldehyde **23** (Scheme 7). Interestingly, when **17a** was treated with *i*-PrMgCl followed by methyl chloroformate quench and hydrolysis, an inseparable 1:2 mixture of **23** and **24** was obtained in 50% combined yield. The isopropyl ketone **24** undoubtedly arose from addition of *i*-PrMgCl to the ester group of the intermediate imine which was converted to **23** after aqueous hydrolysis. The formyl group in **23** was readily removed with potassium cyanide in refluxing methanol to afford ester **25**. The relative stereochemistry of **25** was supported by a small J_{H-H} coupling of H-3 and H-4 of 1.3 Hz which implies a trans relationship between 4-isopropyl and 3-carboxymethyl groups. Examination of ester **25** revealed it to be a product of a tandem addition of *i*-PrMgCl or *i*-PrLi to 3-methoxy-2-carbomethoxynaphthalene (**22**) followed by a proton quench. Such a synthetic transformation is normally not possible because organolithium or Grignard reagents chemoselectively react with the ester moiety and not the naphthalene nucleus.[1a] However, this transformation would be highly desirable since 1,2-disubstituted-1,2-dihydronaphthalenes are found in a number of natural products.[1h]

As above, the methoxyvinyl ether in **25** was transformed, under acidic conditions, to 2-tetralone **26** which existed in its enol form as evidenced by ^1H NMR. The carbomethoxy group of **26** was cleanly removed under Krapcho conditions[12] to provide 4-isopropyl- 2-tetralone (**27**) in 85% yield.[13,14]

To access a 3,4-dialkyl disubstituted 2-tetralone **30**, the ester **25** was first deprotonated with LiHMDS and the corresponding enolate was alkylated with MeI. The vinylmethyl ether of **28** was first hydrolyzed and the ester was decarbomethoxylated with LiCl in refluxing DMF. The desired 4-isopropyl-3-methyl-2-tetralone (**30**) (Scheme 7) was obtained in 81% yield and was found to exist as a 3:1 mixture of trans- and cis-isomers, respectively. It should be noted that reduction of the carboxaldehyde moiety of **23** to a methyl group would produce the 3-epimer of dihydronaphthlene **28**.

In conclusion, we have demonstrated that (3-methoxy-2-naphthyl)oxazolines **4** do not undergo aromatic nucleophilic substitution of the 3-methoxy group with organolithium reagents and afford, instead, dihydronaphthalenes **9** and **14**. Dihydronaphthalenes **9** and **14** were readily converted into the corresponding aldehydes, **15**. The latter were also prepared via a tandem addition of

(12) Krapcho, A. P. *Synthesis* **1982**, 805−822 and 893−914.

(13) For an example of an alternative synthesis of 4-alkyl-2-tetralones, see: (a) Vebrel, J.; Carrié, R. *Bull. Soc. Chim. Fr.* **1982**, II, 116−124. (b) Vebrel, J.; Carrié, R. *Bull. Soc. Chim. Fr.* **1982**, II, 161−166.

(14) For general approaches to 2-tetralones, see: (a) Burckhalter, J. H.; Campbell, J. R.; *J. Org. Chem.* **1961**, *26*, 4232−4235. (b) Rosowsky, A.; Battaglia, J.; Chen, K. K. N.; Modest, E. J.; *J. Org. Chem.* **1968**, *33*, 4288−4290. (c) Sims, J. J.; Cadogan, M.; Selman, L. H. *Tetrahedron Lett.* **1971**, 951−954. (d) Simms, J. J.; Selman, L. H.; Cadogan, M. *Organic Syntheses*; Wiley: New York, 1988; Coll. Vol. VI, pp 744−746. (e) Shner, V. F.; Przhiyaglovskaya, N. M. *Russ. Chem. Rev. (Engl. Transl.)* **1966**, *35*, 523−531. (f) Rosowsky, A.; Chen, K. K. N.; Papathanasopoulos, N.; Modest, E. J. *J. Heterocycl. Chem.* **1972**, *9*, 263−273. (g) Soffer, M. D.; Bellis, M. P.; Gellerson, H. E.; Stewart, R. A. *Organic Syntheses*; Wiley: New York, 1963; Coll. Vol. IV, pp 903−906.

Grignard reagents to imines **17**. It was further demonstrated that aldehydes **15**, possessing an enol ether residue, serve as precursors to 3,3,4-trisubstituted 2-tetralones **16**. The appended hydroxy group in imines **17** may not be essential for the addition of Grignard reagents to the aromatic ring since cyclohexyl imine **21** also reacted with Grignard reagents in this manner. However, lack of the appended hydroxy group in **21** required higher temperatures and a larger excess of the Grignard reagents. Use of methyl chloroformate to trap the azaenolate derived from **17f** and *i*-PrMgCl afforded, in 65% yield, a highly versatile synthetic intermediate **23** which served as an example of a precursor to 4-alkyl-substituted and 3,4-dialkyl-substituted 2-tetralones.

Experimental Section[15]

4,4-Dimethyl-2-(2-(3-methoxynaphthyl))oxazoline (4a). Yield 85% from the corresponding acid. White crystals: mp 125−127 °C. ^{1}H NMR δ 8.29 (1H, s), 7.83 (1H, d, J = 8.0), 7.75 (1H, d, J = 8.0), 7.51 (1H, m), 7.37 (1H, m), 7.21 (1H, s), 4.19 (2H, s), 4.00 (3H, s), 1.47 (6H, s). ^{13}C NMR δ 161.1, 155.4, 135.3, 132.0, 128.1, 127.7, 127.5, 126.2, 124.0, 119.1, 106.3, 79.0, 67.5, 56.0, 28.3. IR 1631, 1468, 1195. MS 255. Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49; O, 12.53. Found: C, 75.44; H, 6.72; N, 5.60.

(−)-(*S*)-4-*tert*-Butyl-2-(2-(3-methoxynaphthyl))oxazoline (4b). Yield 75% from the corresponding acid. A yellowish oil: ^{1}H NMR δ 8.26 (1H, s), 7.83 (1H, d, J = 8.0), 7.75 (1H, d, J = 8.4), 7.50 (1H, m), 7.40 (1H, m), 7.21 (1H, s), 4.43 (1H, m), 4.32 (1H, m), 4.16 (1H, m), 4.00 (3H, s), 1.06 (9H, s). ^{13}C NMR δ 162.1, 155.3, 135.3, 131.7, 128.1, 127.7, 127.5, 126.2, 124.0, 119.2, 106.2, 76.2, 68.5, 55.9, 34.0, 25.8. $[\alpha]_D$ = −50.8 (CH_2Cl_2, *c* 1.25). MS 283.

Typical Procedures for the Addition of RLi to 4. (±)-1,2-Dihydro-1-*s*-butyl-2-methyl-2-(5-(3,3-dimethyloxazolinyl))-3-methoxynaphthalene (9d). To a magnetically stirred clear solution of 255 mg (1 mmol) of **4a** in 9 mL of dry THF cooled to −78 °C was added dropwise 2.2 mL (2.64 mmol) of *s*-BuLi (1.2 M/cyclohexane). After the addition of the organolithium was complete, the resulting red clear solution was stirred at −78 °C for 2 h and quenched with 0.5 mL (8 mmol) of neat MeI added dropwise. The resulting orange solution was stirred at −78 °C for 30 min and allowed to warm to room temperature at which time an orange solid formed. The orange suspension was stirred for 30 min while immersed into a room-temperature water bath. The resulting yellowish suspension was partitioned between water and dichloromethane. The collected organic layer was dried (Na_2SO_4), and decanted, and the solvent was rotoevaporated to dryness. The resulting yellowish oil was chromatographed over silica gel eluting with 1% AcOEt/CH_2Cl_2 to yield 290 mg (88%) of the desired **9d** as a yellowish oil: ^{1}H NMR δ (major) 7.30−7.03 (4H, m), 5.50 (1H, s), 3.93 (2H, m), 3.73 (3H, s), 2.81 (1H, d, J = 1.6), 2.00−1.00 (3H, series of multiplets), 1.40 (3H, s), 1.37 (3H, s), 1.34 (3H, s), 0.92 (3H, t, J = 7.0), 0.67 (3H, d, J = 6.7). MS 327. IR 1643.

(±)-1,2-Dihydro-1-*n*-butyl-2-methyl-2-(2-(4,4-dimethyloxazolinyl))-3-methoxynaphthalene (9a). To a magnetically stirred clear solution of 1.02 g (4 mmol) of **4a** in a mixture of 40 mL of THF and 10 mL of diethyl ether cooled to −95 °C (acetone/dry ice/L N_2) was added dropwise 3.0 mL (7.5 mmol) of *n*-BuLi (2.5 M/hexanes). After the addition of the organolithium was complete, the resulting orange clear solution was stirred at −78 °C for 6 h and quenched with 0.5 mL (8 mmol) of neat MeI added dropwise and warmed to room-temperature overnight. The solvent was rotoevaporated, and the residue was partitioned between water and dichloromethane. The collected organic layer was dried (Na_2SO_4) and decanted, and the solvent was concentrated. The residue was dissolved in 25 mL of THF and 5 mL of water, and 720 mg oxalic acid dihydrate was added. The solution was stirred at room temperature for 4 h, the solvent rotoevaporated, and the residue was partitioned between dichloromethane and water. The collected organic layer was dried (Na_2SO_4), decanted, and mixed with 20 mL of silica gel. After concentration, the product was placed on silica gel packed in 10%AcOEt/hexanes and eluted with the same solvent increasing percentage of AcOEt to 50%AcOEt/hexanes to neat AcOEt to 5%MeOH/AcOEt to afford 980 mg (75%) of **9a** as a colorless oil: ^{1}H NMR δ 7.30−7.03 (4H, m), 5.57 (1H, s), 3.95 (2H, AB-q), 3.74 (3H, s), 2.70 (1H, m), 1.80−1.10 (6H, series of m), 1.41 (3H, s), 1.35 (3H, s), 1.33 (3H, s), 0.85 (3H, t, J = 7.0); ^{13}C NMR δ 167.4, 160.7, 133.6, 133.0, 128.0, 126.3, 124.8, 124.1, 96.3, 78.6, 66.5, 55.5, 51.0, 46.5, 30.7, 30.0, 28.4, 28.2, 23.5, 22.9, 14.0. MS 327. HRMS Calcd for $C_{21}H_{29}NO_2$ 327.2202; Found 327.2198. IR 1644.

Also recovered: 30 mg (3%, highest R_f) of 2-pentanoyl-3-methoxynaphthalene **(12a)** as a yellowish oil: ^{1}H NMR δ 8.09 (1H, s), 7.86 (1H, d, J = 8.0), 7.76 (1H, d, J = 8.0), 7.53 (1H, m),7.40 (1H, m), 7.20 (1H, s), 4.02 (3H, s), 3.06 (2H, m), 1.73 (1H, m), 1.56 (1H, m), 0.98 (3H, t, J = 7.3). ^{13}C NMR δ 203.8, 155.1, 135.7, 130.4, 130.3, 128.8, 128.0, 127.8, 126.2, 124.2, 106.1, 55.5, 43.4, 26.6, 22.5, 14.0. MS 242. IR 1679. Positive 2,4-DNP test on TLC.

50 mg (5%, lowest R_f) of 4,4-dimethyl-2-(2-(1-methyl-3-methoxynaphthyl))oxazoline **(11)** as a yellowish oil: ^{1}H NMR δ 8.00 (1H, d, J = 8.0), 7.75 (1H, d, J = 7.7), 7.49 (1H, m), 7.41 (1H, m), 7.05 (1H, s), 4.19 (2H, s), 3.94 (3H, s), 2.69 (3H, s), 1.49 (6H, s). MS 269.

(±)-1,2-Dihydro-1,2-dimethyl-2-(2-(4,4-dimethyloxazolinyl))-3-methoxynaphthalene (9b). Using a procedure analogous to that for **9a**, 2.5 mL of MeLi (3.5 mmol, 1.4 M/diethyl ether) was added to 255 mg (1 mmol) of **4a** in 5 mL of THF at −78 °C. The resulting orange solution was stirred for 20 min at −78 °C and overnight at −30 °C. The reaction was quenched with 0.5 mmol (8 mmol) of MeI. The workup as for **9a** and column chromatography (5% AcOEt/hexanes to 10% AcOEt/hexanes) afforded 80 mg (28%) of **9b** as a yellowish oil: ^{1}H NMR δ 7.30−7.03 (4H, m), 5.65 (1H, s), 3.88 (2H, AB-q), 3.76 (3H, s), 3.00 (1H, q, J = 7.0), 1.50 (3H, s), 1.31 (6H, s), 1.31 (3H, d, J = 7.0); ^{13}C NMR δ 167.0, 160.0, 135.7, 133.0, 126.3, 125.9, 125.0, 124.7, 96.8, 78.8, 66.5, 55.5, 45.5, 44.7, 28.4, 28.2, 23.0, 17.0. MS 285. IR 1644.

There were also recovered 100 mg (47%) of 2-propanoyl-3-methoxynaphthalene (**12b**) as a yellowish oil: ^{1}H NMR δ 8.13 (1H, s), 7.86 (1H, d, J = 8.0), 7.76 (1H, d, J = 8.0), 7.54 (1H, m),7.30 (1H, m), 7.22 (1H, s), 4.02 (3H, s), 3.09 (2H, t, J = 7.3), 1.25 (3H, t, J = 7.3). ^{13}C NMR δ 203.8, 155.1, 135.6, 130.4, 130.3, 128.8, 128.0, 127.7, 126.2, 124.2, 106.0, 55.4, 36.9, 8.5. MS 214. IR 1681. Positive 2,4-DNP test on TLC.

(±)-1,2-Dihydro-1-(phenyldimethylsilyl)-2-methyl-2-(2-(4,4-dimethyloxazolinyl))-3-methoxynaphthalene (9c). A mixture of 550 mg (3.2 mmol) of dimethylphenylsilane and 230 mg (33 mmol) of Li metal was sonicated for 2 h at room temperature. The resulting deep red solution was cannulated to a solution of 255 mg (1 mmol) of **4a** in 8 mL of THF cooled to −78 °C, and the mixture was allowed to react overnight at −78 °C and quenched with 0.8 mL (13 mmol) of MeI. The products were chromatographed over silica gel (CH_2Cl_2 to 20%AcOEt/CH_2Cl_2) to afford 120 mg (30%) of the desired **9c** as a yellowish oil that crystallized on standing: mp 114−116 °C. ^{1}H NMR δ 7.40−7.20 (5H, m), 7.20−6.80 (4H, m), 5.46 (1H, s), 3.62 (3H, s), 3.59 (1H, d, J = 7.8), 2.70 (2H, m), 1.35 (3H, s), 1.09 (3H, s), 0.79 (3H, s), 0.32 (3H, s), −0.24 (3H, s); ^{13}C NMR δ 167.0, 161.9, 140.4, 133.1, 132.9, 132.3, 128.8, 127.9, 127.5, 125.2, 124.3, 123.9, 96.6, 77.9, 65.9, 55.5, 44.6, 41.5, 29.0, 27.1, 24.3, 1.8, −3.4. HRMS Calcd for $C_{25}H_{31}SiNO_2$ 405.2118; Found 405.2124.

There was also recovered 130 mg (65%) of 2-acetyl-3-methoxynaphthalene (**12c**) as a yellowish oil: ^{1}H NMR δ 8.15 (1H, s), 7.82 (1H, d, J = 8.0), 7.71 (1H, d, J = 8.0), 7.54 (1H, m), 7.30 (1H, m), 7.16 (1H, s), 3.98 (3H, s), 2.66 (3H, s). MS 200. IR 1679. Positive 2,4-DNP test on TLC.

(15) *tert*-Leucinol was prepared by $NaBH_4$−I_2 reduction of *tert*-leucine; cf. McKennon, M. J.; Meyers, A. I. *J. Org. Chem.* **1993**, *58*, 3568−3571.

(±)-1,2-Dihydro-1-phenyl-2-methyl-2-(2-(4,4-dimethyloxazolinyl))-3-methoxynaphthalene (9e). Using a procedure analogous to that for **9d**, 255 mg (1 mmol) of **4a** was treated with 1.5 mL (2.7 mmol) of PhLi (1.8 M cyclohexane/diethyl ether) at −22 °C overnight, cooled to −78 °C, and quenched with 0.5 mL (8 mmol) of MeI. Purified by column chromatography over silica gel (2% AcOEt/CH_2Cl_2) to afford 330 mg (95%) of **9e** as an off-white solid: mp 141−143 °C (heptane). ^{1}H NMR δ 7.30−6.87 (9H, m), 5.75 (1H, s), 4.10 (1H, s), 3.77 (3H, s), 3.70 (1H, d, J = 7.7), 3.25 (1H, d, J = 7.7), 1.58 (3H, s), 1.20 (3H, s), 1.15 (3H, s); ^{13}C NMR δ 166.5, 159.9, 141.0, 133.6, 133.4, 129.5, 128.3, 127.9, 126.8, 125.3, 125.0, 97.4, 78.8, 66.3, 57.4, 55.6, 46.9, 28.6, 27.7, 24.3. MS 347. IR 1644. Anal. Calcd for $C_{23}H_{25}NO_2$: C, 79.51; H, 7.25; N, 4.03; O, 9.21. Found: C, 79.47; H, 7.18; N, 4.03.

(±)-4,4-Dimethyl-2-*tert*-butyl-2-(2-(3-methoxynaphthyl))oxazolidine (10f). Using a procedure analogous to that for **9d**, 255 mg (1 mmol) of **4a** was treated with 1.5 mL (2.55 mmol) of *t*-BuLi (1.7 pentane). The product was purified by column chromatography over silica gel (5% hexanes/CH_2Cl_2) to afford 315 mg (96%) of **10f** as an off-white solid: mp 119−121 °C (hexane). ^{1}H NMR δ 8.07 (1H, s), 7.86 (1H, d, J = 8.0), 7.78 (1H, d, J = 8.0), 7.49 (1H, m),7.43 (1H, m), 7.23 (1H, s), 4.00 (3H, s), 3.85 (1H, s br), 3.76 (1H, d J = 7.6), 3.47 (1H, d J = 7.6), 1.32 (3H, s), 1.04 (3H, s), 1.03 (9H, s). ^{13}C NMR δ 156.3, 133.6, 131.9, 129.0, 128.2, 128.0, 126.1, 125.8, 123.7, 106.1, 103.0, 57.2, 55.0, 39.7, 29.9, 27.2, 26.0. Anal. Calcd for $C_{20}H_{27}NO_2$: C, 76.64; H, 8.68; N, 4.47; O, 10.21. Found: C, 76.60; H, 8.66; N, 4.45.

(+)-(*S*,*S*,*S*)-1,2-Dihydro-1-*n*-butyl-2-methyl-2-(2-(4-*tert*-butyloxazolinyl))-3-methoxynaphthalene (14a). Using a procedure analogous to that for **9d**, 255 mg (0.9 mmol) of **4b** in 9 mL of THF was treated with 1.0 mL (2.5 mmol) of *n*-BuLi (2.5 M/ hexanes) at −78 °C for 10 min, −30 °C for 10 min, and 0 °C for 10 min. The resulting red solution was cooled to −78 °C and quenched with 0.8 mL (13 mmol) of MeI. Purified by column chromatography over silica gel as for **9d** (2% AcOEt/CH_2Cl_2) to afford 180 mg (56%) of the desired **14a** as colorless oil. Further purification of **14a** was achieved by thin-layer preparative radial chromatography (3% AcOEt/hexanes): ^{1}H NMR δ 7.30−7.03 (4H, m), 5.57 (1H, s), 4.15 (2H, m), 3.84 (1H, m), 3.72 (3H, s), 2.73 (1H, m), 1.65 (2H, m), 1.45 (3H, s), 1.31−1.11 (4H, m), 0.94 (9H, s), 0.85 (3H, t, J = 7.0); ^{13}C NMR δ 169.0, 160.9, 133.9, 133.1, 128.0, 126.3, 124.8, 124.1, 96.3, 74.9, 68.3, 55.4, 51.0, 46.7, 33.8, 31.0, 30.2, 25.7, 23.6, 22.9, 14.0. MS 355. HRMS Calcd for $C_{23}H_{33}NO_2$ 355.2516; Found 355.2511. IR 1643.8. $[\alpha]_D$ = +35.0 (*c* 1.6, CH_2Cl_2).

(−)-(*S*,*S*,*S*)-1,2-Dihydro-1-phenyl-2-methyl-2-(2-(4-*tert*-butyloxazolinyl))-3-methoxynaphthalene (14b). Using a procedure analogous to that for **9d**, 517 mg (1.81 mmol) of **4b** was treated with 2.5 mL (4.5 mmol) of PhLi (1.8 M cyclohexane/diethyl ether) at −78 °C for 6 h and quenched with 0.5 mL (8 mmol) of MeI. Purified by column chromatography over silica gel as for **9a** (5% AcOEt/CH_2Cl_2 to 25% AcOEt/CH_2Cl_2) to afford 400 mg (59%) of the desired **14b** as colorless oil. Further purification of **14b** was achieved by thin-layer preparative radial chromatography (5% AcOEt/hexanes to 25% AcOEt/hexanes): ^{1}H NMR δ 7.30−6.80 (4H, m), 5.73 (1H, s), 4.13 (1H, s), 3.86 (1H, m), 3.71 (3H, s), 3.64 (1H, m), 3.38 (1H, m), 1.61 (3H, s), 0.85 (9H, s); ^{13}C NMR δ 168.0, 19.9, 141.2, 133.8, 133.4, 129.2, 128.3, 127.9, 126.8, 126.7, 125.2, 125.0, 97.2, 74.5, 68.5, 57.1, 55.4, 47.4, 33.8, 25.5, 24.2. MS 375. $[\alpha]_D$ = −173.0 (c 2.0, CH_2Cl_2). Anal. Calcd for $C_{23}H_{25}NO_2$: C, 79.96; H, 7.78; N, 3.75; O, 8.52. Found: C, 79.68; H, 7.80; N, 3.76.

There were also recovered 140 mg (27%) of the starting **4b**.

Typical Procedure for the Synthesis of Imines 17. 2-(2-(3-Methoxynaphthyl)methylenamino))ethanol (17a). A mixture of 3.05 g (16.4 mmol) of **18** and 3.3 g (54 mmol) of 2-aminoethanol in 60 mL of benzene was heated to reflux overnight with concomitant removal of water with the aid of a Dean−Stark trap. ^{1}H NMR indicated the reaction to be complete (disappearance of the aldehyde proton (δ = 10.6)). The solvent was rotoevaporated, and the yellow residue obtained was subjected to short-path Kugelrohr distillation at ca. 1 mmHg heating the pot to <120 °C to remove excess of amino alcohol and traces of benzene. The residual oil was dissolved in 50 mL of 40% CH_2Cl_2/hexanes, and the solvent was allowed to evaporate slowly while the solution was sitting in the hood at which time the imine crystallized. The material was suspended in a mixture of 50 mL of hexanes and 5 mL of CH_2Cl_2 and filtered to afford 3.1 g (82%) of the desired **17a** as a solid: mp 71−73 °C. ^{1}H NMR δ (imine) 8.83 (1H, s), 8.42 (1H, s), 7.85 (1H, d, J = 8.5), 7.72 (1H, d, J = 8.0), 7.48 (1H, m), 7.38 (1H, m), 7.08 (1H, s), 3.98 (2H, m), 3.89 (3H, s), 3.84 (2H, m). ^{13}C NMR δ 159.3, 155.9, 135.5, 128.7, 128.1, 127.4, 127.2, 126.2, 125.1, 123.9, 105.2, 63.8, 62.3, 55.2. MS 229. IR 3359.

The yields for other imines **17** were close to quantitative.

3,3-Dimethyl-5-(2-(3-methoxynaphthyl))oxazolidine (17b). An off-white solid: mp 99−101 °C. ^{1}H NMR δ (oxazolidine) 8.04 (1H, s), 7.83 (1H, d, J = 8.0), 7.77 (1H, d, J = 8.0), 7.49 (1H, m), 7.41 (1H, m), 7.18 (1H, s), 5.96 (1H, s), 4.00 (3H, s), 3.82 (1H, d J = 7.3), 3.70 (1H, d J = 7.0), 2.40 (1H, br s), 1.40 (6H, s), 1.04 (3H, s), 1.03 (9H, s).

^{1}H NMR δ (imine) 8.91 (1H, s), 8.45 (1H, s), 7.86 (1H, d, J = 8.8), 7.75 (1H, d, J = 8.8), 7.17 (1H, s), 3.63 (1H, s), 1.35 (3H, s). MS 257. IR 3387.

(+)-(*R*)-2-Phenyl-2-(1-(3-methoxynaphthyl)methylenamino))ethanol (17c). An off-white solid: mp 98−100 °C. ^{1}H NMR δ (imine) 8.96 (1H, s), 8.63 (1H, d, J = 8.4), 7.94 (1H, d, J = 8.1), 7.75 (1H, d, J = 8.1), 7.60−7.20 (7H, m), 7.09 (1H, s), 4.65 (1H, m), 4.15 (1H, m), 4.03 (1H, m), 3.86 (3H, s), 3.00 (1H, br s). $[\alpha]_D$ = +162.2 (c 3.5, CH_2Cl_2) after 15 min equilibration in solution. Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59; O, 10.48. Found: C, 78.44; H, 6.13; N, 4.71.

(+)-(*S*)-2-Methyl-2-(1-(3-methoxynaphthyl)methylenamino))ethanol (17d). An off-white solid: mp 135−137 °C. ^{1}H NMR δ (imine) 8.87 (s, 1H), 8.47 (s, 1H), 7.88 (1H, d, J = 7.7), 7.73 (1H, d, J = 8.4), 7.40 (1H, m), 7.37 (1H, m), 7.10 (1H, s), 3.90 (3H, s), 3.80 (m), 3.75 (m), 1.32 (3H, d, J = 6.2). $[\alpha]_D$ = +33.8 (*c* 1.6, CH_2Cl_2) after 15 min equilibration in solution.

(−)-(*S*)-2-*tert*-Butyl-2-(1-(3-methoxynaphthyl)methylenamino))ethanol (17e). A yellowish oil. ^{1}H NMR δ (imine and two diastereomeric oxazolidines) 8.83 (s), 8.52 (s), 7.93 (s), 7.90 (d, J = 8.1), 7.82 (d, J = 8.0), 7.77 (d, J = 8.0), 7.76 (d, J = 8.0), 7.50 (m), 7.39 (m), 7.20 (s), 7.18 (s), 7.16 (s), 5.88 (s), 5.75 (s), 4.00 (s), 3.97 (s), 3.93 (m), 3.75 (t, J = 8.0), 3.35 (t, J = 7.7), 3.07 (t, J = 6.2), 1.07 (s), 1.04 (s), 1.03 (s). $[\alpha]_D$ = −20.2 (*c* 2.5, CH_2Cl_2)

3-(2-(3-Methoxynaphthyl)methylenamino))-1-propanol (17f). A yellowish oil: ^{1}H NMR δ (imine) 8.81 (1H, t, J = 1.4), 8.38 (1H, s), 7.86 (1H, d, J = 7.3), 7.75 (1H, d, J = 8.0), 7.48−7.34 (2H, m), 7.17 (1H, s), 4.00 (3H, s), 3.95 (2H, m), 3.89 (2H, m), 3.25 (2H, m). ^{1}H NMR δ (cyclic) 8.00 (1H, s), 7.82 (1H, d, J = 8.0), 7.75 (1H, d, J = 8.0), 7.48−7.34 (2H, m), 7.17 (1H, s), 5.60 (1H, s), 4.38 (1H), 4.01 (3H, s), 3.45 (1H, m), 2.02 (4H, m).

3-(2-(3-Methoxynaphthyl)methylenamino))-1-butanol (17g). A yellowish oil. ^{1}H NMR δ (imine) 8.86 (1H, t, J = 1.3), 8.39 (1H, s), 7.89 (1H, d, J = 8.0), 7.75 (1H, d, J = 8.4), 7.48−7.34 (2H, m), 7.18 (1H, s), 4.02 (3H, s), 3.76 (4H, m), 1.86 (4H, m). ^{13}C NMR δ 157.5, 156.1, 135.5, 128.9, 128.3, 127.8, 127.4, 126.37, 125.2, 124.1, 105.5, 62.8, 61.7, 55.7, 33.7, 28.9.

Cyclohexyl Imine of 18 (17h). A yellowish oil. ^{1}H NMR δ 8.90 (1H, s), 8.48 (1H, s), 7.89 (1H, d, J = 8.0), 7.75 (1H, d, J = 8.0), 7.48−7.34 (2H, m), 7.16 (1H, s), 4.00 (3H, s), 3.35 (1H, m), 2.00−1.60 (6H, m), 1.40 (4H, m). ^{13}C NMR δ 156.1, 154.9, 135.3, 128.7, 128.4, 127.2, 127.0, 126.2, 126.0, 123.8, 105.3, 70.4, 55.4, 34.5, 25.7, 25.0.

General Procedure for the Addition of Grignard Reagents to 17. To a magnetically stirred solution of 2 mmol of **17** in 8−9 mL of dry THF cooled to −78 °C was added dropwise 3 mL (6 mmol) of a Grignard reagent (2 M/THF). In cases where 1 M solutions of a Grignard in THF were used, 6 mL (6 mmol) of a Grignard reagent (1 M/THF) were added to **17** with concomitant decrease of THF to 5 mL. After the addition of the Grignard reagent was complete, the resulting amber solution was stirred at −78 °C for 5 min and transferred to −30 °C bath and stirred for 2 h and 10−14 h (overnight) at

0 °C at which time the solution became darker. The solution was cooled to −30 °C, quenched with 1 mL (16 mmol) of neat MeI, and allowed to warm to 0 °C. The resulting suspension was stirred at 0 °C for 3 h, and 2 h at room temperature. The resulting white suspension was quenched by the addition of 8 mL of water followed by 8 mL of 10% aq HCl, and the resulting mixture was stirred for 10 h (overnight) at room temperature and partitioned between water and dichloromethane. The collected organic layer was dried (Na_2SO_4), decanted, and mixed with 20 mL of silica gel. The solvent was removed and the residue loaded on silica gel. Elution with 5% EtOAc/hexane gradually increasing to 10% AcOEt and further to 20% AcOEt/hexanes. Elution of the column with 10% MeOH/acetone or 10% MeOH/CH_2Cl_2 provided crude imine addition products as oils which were further purified by preparative radial thin-layer chromatography (Chromatotron) over silica gel eluting with 2% MeOH/CH_2Cl_2. Analogously, the crude dihydronaphthalenes obtained as above were further purified by preparative radial thin-layer chromatography (Chromatotron) over silica gel eluting with a gradient of Et_2O in hexanes (hexanes to 3% Et_2O/hexanes to 10% Et_2O/hexanes) to afford the desired products **15** as yellowish oils.

Additions to imine **17h** followed the same general procedure as for **17a**−**g** except that (a) the addition of the Grignard reagent was done at room temperature, (b) the reaction was carried out at room temperature for 18 h, (c) hydrolysis of the tandem addition products after the alkylation step to remove the cyclohexylimine was carried out with 10% aq HCl instead of 1/1 (v/v) 10% aq HCl/water.

(±)-1,2-Dihydro-1-*n*-butyl-2-methyl-3-methoxynaphthalene-2-carboxaldehyde (15a). The desired **15a** was obtained in 80% from **9a** by the earlier procedure as a colorless oil: ^{1}H NMR δ 10.19 (1H, s), 7.30−7.03 (4H, m), 5.66 (1H, s), 3.80 (3H, s), 2.73 (1H, dd, J = 3.6, J = 9.8), 1.80−1.61 (2H, m), 1.40−1.00 (4H, m), 1.17 (3H, s), 0.77 (3H, t, J = 7.3); ^{13}C procedure[1h,2e] NMR δ 205.6, 160.5, 133.1, 132.7, 128.5, 126.7, 125.2, 124.5, 96.2, 55.4, 53.3, 50.2, 29.9, 29.7, 22.7, 19.0, 13.9. MS 258. IR 1724. Positive 2,4-DNP test on TLC.

(±)-1,2-Dihydro-1-phenyl-2-methyl-3-methoxynaphthalene-2-carboxaldehyde (15b). For the synthesis of racemic **15b** from **17a**, the reaction was carried out at room-temperature overnight rather than at (−30 °C to 0 °C). Yield 57% as a yellowish oil: ^{1}H NMR δ 9.37 (1H, s), 7.30−6.90 (8H, m), 5.90 (1H, s), 4.11 (1H, s), 3.79 (3H, s), 1.33 (3H, m); ^{13}C NMR δ 203.0, 158.5, 138.6, 133.4, 133.0, 129.3, 128.6, 128.3, 127.3, 127.2, 125.7, 125.4, 98.3, 55.8, 55.6, 54.4, 18.4. MS 278. IR 1725. Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52; O 11.50. Found: C, 81.82; H, 6.60. Positive 2,4-DNP test on TLC.

Nonracemic (+)-(*S*,*S*) **15b** obtained in 40% yield from **17c**: 92% ee by HPLC, $[\alpha]_D$ = +52.7 (*c* 1.3, CH_2Cl_2); nonracemic (+)-(*S*,*S*)-**15b** obtained in 58% yield from **14b**: $[\alpha]_D$ = +60.3 (*c* 2.0, CH_2Cl_2).

(±)-1,2-Dihydro-1-vinyl-2-methyl-3-methoxynaphthalene-2-carboxaldehyde (15c). 65% Yield as a yellowish oil: ^{1}H NMR δ 9.71 (1H, s), 7.30−7.03 (4H, m), 5.97 (1H, m), 5.80 (1H, s), 5.21 (2H, m), 3.78 (3H, s), 3.49 (1H, d, J = 9.9), 1.25 (3H, m); ^{13}C NMR δ 202.9, 158.5, 135.3, 133.0, 131.9, 127.3, 125.6, 125.2, 118.6, 97.0, 55.4, 54.5, 53.6, 16.5. Positive 2,4-DNP test on TLC.

(±)-1,2-Dihydro-1-isopropyl-2-methyl-3-methoxynaphthalene-2-carboxaldehyde (15d). 63% Yield as a yellowish oil: ^{1}H NMR δ 10.24 (1H, s), 7.30−7.03 (4H, m), 5.62 (1H, s), 3.80 (3H, s), 2.73 (1H, d, J = 3.3), 2.15 (1H, m), 1.19 (3H, s), 0.89 (3H, d, J = 6.6), 0.83 (3H, d, J = 6.6); ^{13}C NMR δ 205.8, 161.1, 134.7, 130.1, 129.1, 127.0, 124.9, 124.2, 97.0, 56.1, 55.6, 52.6, 30.3, 22.7, 20.4, 18.2. MS 244. HRMS Calcd for $C_{16}H_{20}O_2$ 244.1463; Found 244.1463. IR 1720. Positive 2,4-DNP test on TLC.

The reaction of **16a** and *i*-PrMgCl also afforded 20% of *N*-(2-hydroxyethyl)-*N*-methyl-1-(3-methoxynaphthyl)-2-methylpropylamine (**20a**) as a yellowish oil: ^{1}H NMR δ 7.81 (1H, d, J = 8.8), 7.77 (1H, d, J = 8.4), 7.63 (1H, s), 7.47 (1H, m), 7.38 (1H, m), 7.20 (1H, s), 4.06 (1H, d, J = 9.0), 3.96 (3H, s), 3.70 (1H, m), 3.60 (1H, m), 2.80 (1H, br), 2.68 (1H, m), 2.46 (2H, m), 2.22 (3H, s), 1.22 (3H, d, J = 6.2), 0.77 (3H, d, J = 6.5). ^{13}C NMR δ 156.8, 133.3, 128.0, 127.8, 127.6, 127.5, 126.1, 125.0, 123.5, 105.0, 65.0, 57.9, 55.5, 55.3, 35.3, 29.0, 20.9, 20.5. HRMS Calcd for ($C_{18}H_{25}NO_2 \cdot H^+$) 288.1968; Found 288.1963. IR 3416 cm^{-1}.

Nonracemic (+)-(*S*,*S*)-**15d** obtained from **17c** in 33% yield: 98% ee by HPLC, $[\alpha]_D$ = +190.5 (*c* 0.8, CH_2Cl_2); nonracemic (−)-(*R*,*R*) obtained from **17d** in 45% yield: 73% *ee* by HPLC, $[\alpha]_D$ = −132.0 (*c* 1.6, CH_2Cl_2)

(±)-1,2-Dihydro-1,2-dimethyl-3-methoxynaphthalene-2-carboxaldehyde (15e). Yield 20% as a yellowish oil: ^{1}H NMR δ 9.92 (1H, s), 7.30−7.03 (4H, m), 5.75 (1H, s), 3.80 (3H, s), 3.0 (1H, q, J = 7.0), 1.32 (3H, d, J = 7.3), 1.24 (3H, s); ^{13}C NMR δ 204.4, 159.2, 135.4, 132.6, 126.8, 126.4, 125.6, 125.2, 97.1, 55.5, 53.6, 43.9, 17.7, 16.3. MS 216. Positive 2,4-DNP test on TLC.

There were also recovered 64% of the starting **18**.

(±)-1,2-Dihydro-1-ethyl-2-methyl-3-methoxynaphthalene-2-carboxaldehyde (15f). Yield 52% as a yellowish oil: ^{1}H NMR δ 10.19 (1H, s), 7.30−7.03 (4H, m), 5.66 (1H, s), 3.80 (3H, s), 2.65 (1H, dd, J = 3.5, J = 9.8), 1.73 (2H, m), 1.18 (3H, s), 0.83 (3H, t, J = 6.6); ^{13}C NMR δ 205.8, 160.6, 132.8, 132.6, 128.9, 126.8, 125.2, 124.4, 96.3, 55.5, 53.3, 51.8, 22.9, 19.1, 12.3. MS 230. IR 1725. Positive 2,4-DNP test on TLC.

Nonracemic (+)-(*S*,*S*)-**15f** obtained from **17c** in 56% yield: 82% ee by HPLC, $[\alpha]_D$ = +155.0 (*c* 0.7, CH_2Cl_2).

(±)-1,2-Dihydro-1-isopropyl-2-methyl-2-(hydroxymethyl)-3-methoxynaphthalene (16c). The desired **16c** was obtained by reduction of 320 mg (1.33 mmol) of **15d** with 82 mg (2.2 mmol) of $NaBH_4$ in 25 mL of MeOH at room temperature. The extractive workup gave 318 mg (100%) of **16c** as a colorless oil: ^{1}H NMR δ 7.20−6.90 (4H, m), 5.49 (1H, s), 4.14 (1H, dd, J = 3.7, J = 15.0), 3.75 (3H, s), 3.70 (1H, d, J = 8.8, J = 11.4), 2.49 (1H, d, J = 3.3), 2.37 (1H, m), 2.18 (1H, m), 1.13 (3H, s), 0.90 (3H, d, J = 7.0), 0.68 (3H, d, J = 7.0); ^{13}C NMR δ 164.3, 135.2, 130.6, 130.1, 126.4, 124.3, 123.7, 96.6, 66.4, 55.2, 54.5, 42.1, 28.3, 23.0, 22.9, 17.4. MS 246. IR 3404.

1-Isopropyl-2-methyl-3-methoxynaphthalene (16e). A mixture of 130 mg (0.5 mmol) of **15d**, 130 mg (0.6 mmol) of DDQ in 3 mL of dry dioxane was heated for 5 h. Chromatographic purification over silica gel afforded 60 mg (53%) of the desired **16e** as an oil: ^{1}H NMR δ 8.26 (1H, d, J = 8.0), 7.79 (1H, d, J = 8.0), 7.44 (2H, m), 7.08 (1H, s), 4.00 (3H, s), 2.50 (3H, s), 1.60 (6H, d, J = 5.5). In ^{13}C NMR there were observed several unresolved resonances possibly due to hindered rotation of the isopropyl group. MS 214. HRMS Calcd for $C_{15}H_{18}O$ 214.1357; Found 214.1358. Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47; O, 7.47. Found: C, 84.18; H, 8.49.

(±)-1,2-Dihydro-1-isopropyl-2-formyl-2-carbomethoxy-3-methoxynaphthalene (23). The general procedure for aldehydes **15** was followed except that 6 equiv of methyl chloroformate were added at −78 °C as an electrophilic quenching agent. The resulting reddish solution was kept at −78 °C for 2 h, at −25 °C for 2 and 1 h at room temperature. A yellowish solid: mp 91−93 °C. ^{1}H NMR δ 10.11 (1H, s), 7.20−7.01 (4H, m), 5.75 (1H, s), 3.86 (3H, s), 3.72 (1H, d, J = 3.7), 3.64 (3H, s), 2.22 (1H, m), 0.98 (3H, d, J = 7.0), 0.85 (3H, d, J = 7.0); ^{13}C NMR δ 198.6, 168.7, 153.8, 133.7, 129.5, 127.2, 125.2, 124.8, 99.8, 99.7, 65.3, 56.0, 52.9, 51.5, 29.2, 22.7, 18.6. MS 288. IR 1746, 1719. Positive 2,4-DNP test on TLC.

(±)-*N*-(2-Hydroxyethyl)-1-(3-methoxynaphthyl)-3-butenamine (20c). The reaction of allylmagnesium chloride and **17a**, following the general procedure with the exception that it was run at room temperature, afforded 53% of **20c** as a yellowish oil: ^{1}H NMR δ 7.79 (1H, d, J = 8.8), 7.77 (1H, d, J = 9.2), 7.73 (1H, s), 7.47 (1H, m), 7.38 (1H, m), 7.18 (1H, s), 5.76 (1H, m), 5.10 (1H, d, J = 20.8), 5.05 (1H, d, J = 14.3), 4.24 (1H, t, J = 7.0), 4.00 (3H, s), 3.75 (1H, m), 3.63 (1H, m), 3.49 (2H, s br), 2.75 (m, 4H). ^{13}C NMR δ 155.8, 135.0, 133.7, 130.5, 128.4, 127.7, 127.5, 126.2, 123.8, 117.4, 105.6, 60.3, 58.2, 55.4, 48.7, 39.8. IR 3321.3 cm^{-1}.

There was also recovered 18% of (±)-*N*-(2-hydroxyethyl)-*N*-methyl-1-(3-methoxynaphthyl)-3-butenamine **(20d)** as a colorless oil: ^{1}H NMR δ 7.83 (1H, d, J = 7.7), 7.78 (1H, d, J = 8.0), 7.72 (1H, s), 7.49 (1H, m), 7.40 (1H, m), 7.21 (1H, s), 5.84 (1H,

m), 5.10 (1H, m), 5.04 (1H, m), 4.46 (1H, t, $J = 7.0$), 4.00 (3H, s), 3.62 (2H, m), 3.35 (1H, br), 2.76 (m, 5H), 2.24 (3H, s). ^{13}C NMR δ 156.1, 135.9, 133.5, 128.8, 127.9, 127.7, 127.5, 126.0, 123.6, 117.3, 116.5, 105.5, 59.8, 58.1, 56.0, 55.2, 35.7, 33.3. HRMS Calcd for ($C_{18}H_{24}NO_2 \cdot H^+$) 286.1807; Found 286.1807. IR 3416 cm^{-1}.

(−)-*N*-(1(*S*)-*tert*-Butyl-2-hydroxyethyl)-1-(3-methoxynaphthyl)-2-methylpropylamine (20b). Following the general procedure, 375 mg (1.3 mmol) of **17e** were treated with 2 mL (4 mmol) of *i*-PrMgCl (2 M/THF). The reaction was quenched with a solution of 4 g of NH_4Cl in 10 mL of water to afford 325 mg (100%) of **20b** as a colorless oil after extractive workup with CH_2Cl_2: ^{1}H NMR δ 7.81 (1H, d, $J = 8.4$), 7.53 (1H, s br), 7.49 (1H, m), 7.41 (1H, m), 7.18 (1H, s), 3.98 (3H, s), 3.70 (2H, m), 3.40 (1H, br), 2.30 (1H, br), 2.05 (1H, d, $J = 4.4$), 1.27 (3H, d, $J = 6.6$), 0.88 (9H, s), 0.75 (3H, d, $J = 6.5$). ^{13}C NMR contained several broad unresolved signals and only 14 carbon resonances. $[\alpha]_D = -36.0$ (*c* 0.7, CH_2Cl_2).

(−)-Carbamate of (−)-*N*-(1(*S*)-*tert*-Butyl-2-hydroxyethyl)-1-(3-methoxynaphthyl)-2-methylpropylamine (20b). Obtained by treating the amine **20b** with 360 mg (2.2 mmol) of carbonyldiimidazole in 10 mL of dry CH_2Cl_2 at room-temperature overnight. Purified by column chromatography over silica gel (10% AcOEt/hexanes) to afford 320 mg (69% from **17e**) as a colorless oil: ^{1}H NMR δ 8.11 (1H, s), 7.83 (1H, d, $J = 7.7$), 7.76 (1H, d, $J = 8.5$), 7.45 (1H, m), 7.39 (1H, m), 7.13 (1H, s), 3.93 (3H, s), 2.92 (1H, d, $J = 5.3$), 2.23 (1H, m), 1.86 (1H, d, $J = 3.7$), 1.42 (1H, d, $J = 6.6$), 1.20−1.16 (1H, m), 1.14 (3H, d, $J = 6.7$), 0.83 (3H, d, $J = 6.5$). 0.63 (9H, s). ^{13}C NMR δ 156.0, 133.7, 133.2, 129.0, 128.7, 127.6, 126.2, 125.6, 123.3, 104.2, 55.2, 46.6, 35.5, 32.5, 29.9, 27.0, 20.4, 19.4. IR 1623, 1592. $[\alpha]_D = -126.8$ (*c* 2.1, CH_2Cl_2).

Typical Procedure for the Deprotection of the Methyl Vinyl Ether in Dihydronaphthalene Adducts. (±)-1,4-Dihydro-4-isopropyl-3-carbomethoxy-2-hydroxynaphthalene (26). To a clear solution of 400 mg (1.5 mmol) of **25** in 4 mL of THF were added 230 mg of water, 455 mg of TFA, and 280 mg of trifluoromethanesulfonic acid. The resulting yellowish solution was stirred for 2 h at room temperature. The solvent was rotoevaporated, and the yellowish oil was partitioned between dichloromethane and water. The collected organic layer was dried (Na_2SO_4) and decanted, and the solvent was rotoevaporated. The yellow oil obtained was purified by preparative thin-layer radial chromatography over silica gel (hexanes to 3% Et_2O/hexanes to 10% Et_2O/hexanes to 20% Et_2O/hexanes) to afford 360 mg (95%) of **26** as a yellowish oil: ^{1}H NMR δ 12.47 (1H, s), 7.24 (4H, m), 3.88 (3H, s), 3.80 (2H, m), 3.50 (1H, m), 2.01 (1H, m), 0.98 (3H, d, $J = 6.6$), 0.73 (3H, d, $J = 6.9$); ^{13}C NMR δ 172.3, 172.1, 137.0, 133.1, 128.8, 127.5, 126.0, 125.6, 100.0, 51.4, 45.2, 35.9, 35.3, 20.8, 18.6. MS 260. IR 1656 cm^{-1}. Positive 2,4-DNP test on TLC.

No attempts at obtaining elemental analysis on **26** and other 2-tetralones discribed in this account were made due to decomposition over 1−2 days at room temperature. As for some known unsubstituted 2-tetralones[14d,g] all 2-tetralones described herein should be kept in a freezer for prolonged storage.

(±)-4-Isopropyl-3-methyl-3-formyl-2-tetralone (16a). Yield 78% as a colorless oil: ^{1}H NMR δ 10.40 (1H, s), 7.30−7.25 (4H, m), 3.77 (2H, AB-q), 3.10 (1H, d, $J = 4.0$), 2.12 (1H, m), 1.13 (3H, s), 0.93 (3H, d, $J = 7.0$), 0.69 (3H, d, $J = 6.6$); ^{13}C NMR δ 211.5, 203.6, 133.7, 132.5, 131.0, 128.5, 127.1, 126.2, 59.0, 56.6, 42.1, 31.0, 23.1, 21.0, 18.2. MS 230. HRMS Calcd for $C_{15}H_{18}O_2$ 230.1306; Found 230.1303. IR 1722, 1705 cm^{-1}. Positive 2,4-DNP test on TLC.

(±)-4-Ethyl-3-methyl-3-formyl-2-tetralone (16b). Yield 82% as a colorless oil: ^{1}H NMR δ 10.26 (1H, s), 7.30−7.25 (4H, m), 3.75 (2H, AB-q), 3.00 (1H, dd, $J = 3.6$, $J = 11.4$), 1.80 (1H, m), 1.65 (1H, m), 1.11 (3H, s), 0.85 (3H, t, $J = 7.2$); ^{13}C NMR δ 210.2, 203.0, 136.6, 131.0, 129.7, 128.3, 127.1, 126.5, 60.1, 50.3, 42.4, 24.7, 20.1, 12.3. MS 216. IR 1723, 1709 cm^{-1}. Positive 2,4-DNP test on TLC.

(±)-4-Isopropyl-3-methyl-3-(hydroxymethyl)-2-tetralone (16d). Yield 78% from **15d** as a colorless oil. ^{1}H NMR δ 7.30−7.13 (4H, m), 4.23 (1H, d, $J = 11.3$), 3.66 (2H, AB-q), 2.86 (1H, d, $J = 3.3$), 2.76 (1H, br s), 2.23 (1H, m), 1.14 (3H, s), 0.95 (3H, d, $J = 7.0$), 0.55 (3H, d, $J = 7.0$); ^{13}C NMR δ 217.0, 134.3, 133.3, 131.1, 127.8, 126.6, 125.7, 66.0, 56.0, 50.9, 42.1, 29.1, 23.0, 21.8, 16.8. MS 232. HRMS Calcd for $C_{15}H_{20}O_2$ 232.1463; Found 232.1463. IR 3454, 1699 cm^{-1}. Positive 2,4-DNP test on TLC.

(±)-1,2-Dihydro-1-isopropyl-2-carbomethoxy-3-methoxynaphthalene (25). To a clear solution of 440 mg (1.53 mmol) of **23** in 8 mL of anhydrous methanol was added all at once 120 mg (1.85 mmol) of solid KCN. The clear yellow solution was refluxed for 2 h, and the solvent was rotoevaporated. The residue was partitioned between water and dichloromethane, the collected organic layer was dried (Na_2SO_4), and the solvent was rotoevaporated. The oily residue was purified by preparative thin-layer radial chromatography over silica gel (hexanes to 3% Et_2O/hexanes to 10% Et_2O/hexanes to 20% Et_2O/hexanes) to afford 390 mg (99%) of **25** as yellowish oil: ^{1}H NMR δ 7.20−7.01 (4H, m), 5.67 (1H, s), 3.80 (3H, s), 3.64 (3H, s), 3.34 (1H, d, $J = 1.1$), 2.97 (1H, dd, $J = 1.1$, $J = 7.2$), 1.96 (1H, m), 0.98 (3H, d, $J = 6.6$), 0.89 (3H, d, $J = 6.9$); ^{13}C NMR δ 172.5, 154.9, 133.6, 132.7, 128.9, 126.7, 125.2, 124.4, 98.1, 55.3, 52.2, 49.0, 46.7, 32.2, 20.9, 20.0. MS 260. IR 1732. Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 74.02; H, 7.77.

(±)-4-Isopropyl-2-tetralone (27). A clear solution of 340 mg (1.38 mmol) of **26** and 560 mg (13.1 mmol) of LiCl in 3 g of DMF was refluxed for 3 h. The solution was cooled to room temperature and partitioned between 10% Et_2O/hexanes and water. The collected organic layer was dried (Na_2SO_4) and decanted, and the solvent was rotoevaporated. The yellow oil obtained was purified by preparative thin-layer radial chromatography over silica gel (hexanes to 3% Et_2O/hexanes to 10% Et_2O/hexanes) to afford 210 mg (81%) of the desired **27** as yellowish oil: ^{1}H NMR δ 7.30−7.15 (4H, m), 3.62 (2H, AB-q), 2.85 (2H, m), 2.65 (1H, m), 1.83 (1H, m), 0.99 (3H, d, $J = 6.6$), 0.91 (3H, d, $J = 6.9$); ^{13}C NMR δ 210.6, 139.1, 132.9, 128.9, 128.5, 126.5, 126.0, 46.7, 43.6, 42.1, 31.7, 21.4, 19.8. MS 188. IR 1701 cm^{-1}.

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Supporting Information Available: Tables of X-ray data and ORTEP for **9e**; carbon-13 and proton spectra for 15 compounds: **4b**, **9d,e**, **14a**, **16a,c,d**, **17a,f**, **20c**, **26**. This material is available free of charge via the Internet at http://pubs.acs.org.

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