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REGIO- AND STEREOSELECTIVE ADDITION OF ORGANOLITHIUMS TO NAPHTHALENES. AN EFFICIENT SYNTHESIS OF 1,1,2-TRISUBSTITUTED AND *trans*-2-DISUBSTITUTED DIHYDRONAPHTHALENES#

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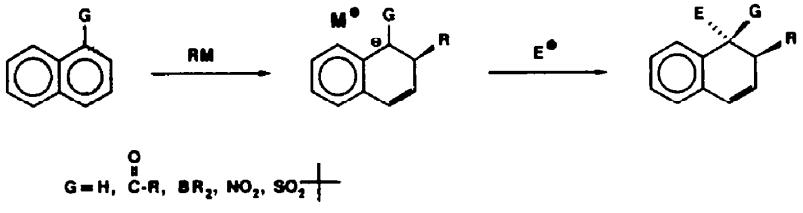
Abstract - The addition of a variety of organolithium reagents to 1-napthhthyloxazolines and 2-naphthyloxazolines followed by trapping with electrophiles leads to high yields of the title compounds. Very high stereoselectivity characterizes the present process in that the electrophile enters from the naphthalene face opposite to the entry of the organolithium reagent. A number of organolithiums have been investigated and it was found that *in situ* generation of the organolithiums from tetrasubstituted stannanes provides a superior reagent for nucleophilic addition to the naphthalene. Removal of the oxazoline efficiently led to either formyl or hydroxymethyl-1,2-dihydronaphthalenes.

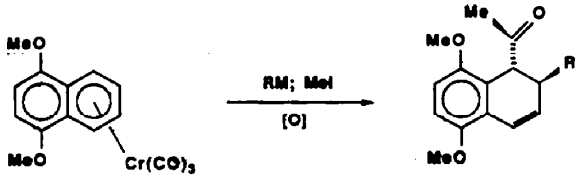
Direct introduction of substituents into the π-system of naphthalenes has been investigated over the past 40 years with little success. The value of such a process is obvious when one considers the rapid entry into a regio- and stereochemically substituted alicyclic moiety that would result (Scheme 1).

Scheme 1



A number of studies involving addition of alkyllithium to naphthalene,[1] Grignard addition to acylnaphthalenes,[2] nitronaphthalenes,[3] ate complexes of boranes,[4] and sulfonylnaphthalenes[5] have all shown limited success in reaching 1,2 or 1,1,2-substituted dihydronaphthalenes. More

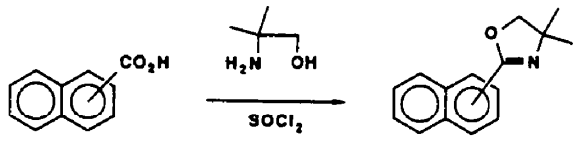
Scheme 2



#This paper is warmly dedicated to Professor Edward (Ted) C. Taylor on the occasion of his 65th birthday.

recently, Kündig[5] has demonstrated the ability to insert two adjacent substituents into the naphthalene system using an arene-chromium compound and this has considerable potential for achieving the goals mentioned above (Scheme 2).

We wish to describe our studies involving naphthalenes containing an oxazoline moiety at the 1 or 2-position (**3**, **4**), readily prepared from the corresponding 1- or 2-naphthoic acids (**1**, **2**).[7] We have found that naphthalenes equipped with this versatile heterocycle, have shown



1, 1-CO_2H

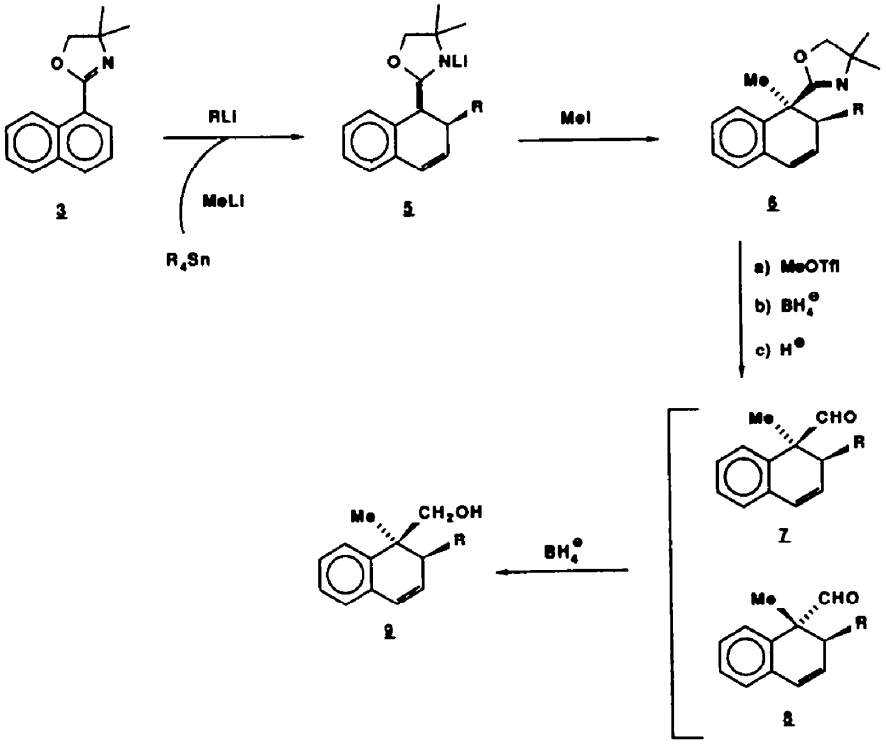
2, 2-CO_2H

3, 1-oxazoline

4, 2-oxazoline

considerable synthetic utility,[8] and allow a highly efficient entry into di- and trisubstituted dihydronaphthalenes[9] of the type described in Scheme 1.

Treatment of the 1-naphthyloxazoline **3** with alkyllithium reagents at -45° in THF, followed by addition of methyl iodide, furnished the tandem addition products **6** as a single diastereomer



in 60-99% yields. The *trans*-addition of the organolithium and methyl iodide was confirmed by single crystal X-ray studies of the product derived from *tert*-butyllithium and methyl iodide, **6d** (Fig. 1A). The ORTEP structure clearly shows the diaxial relationship of the newly entered *t*-butyl and methyl groups. Presumably, the azaenolate **5** is the initial product formed and entry of the electrophile (MeI) proceeds from the more accessible opposite face to that carrying the alkyl group. Table 1 shows the variety of organolithium reagents that have been successfully introduced.

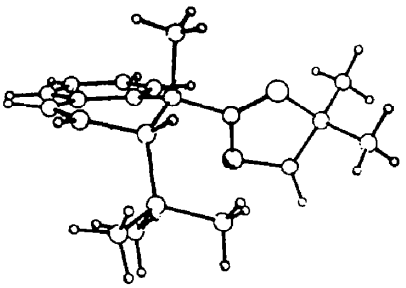


Figure 1A. ORTEP Structure of 6d

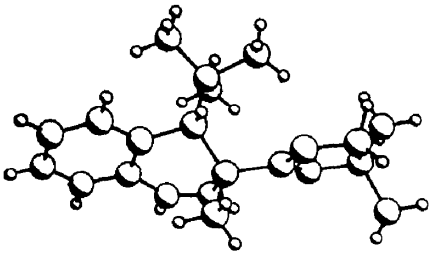
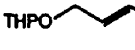


Figure 1B. ORTEP of 11c

TABLE 1. Tandem Addition of Organolithium Reagents and Methyl Iodide to 3

Entry	RLi[a]	Addition T°[c]	Yield % 6		Diastereomeric Ratio,[e] 6
a	MeLi	-20°	6a	65	>100:1
b	n-BuLi	-45°	6b	90	>100:1
c	s-BuLi	-45°	6c	94	>100:1
d	t-BuLi	-45°	6d	99	>100:1
e		-80°	6e	95	>100:1
f		-80°	6f	85	62:38
g	$PhCH_2Li$	-80°	6g	91	>100:1
h	$Ph-C\equiv C-CH_2Li$[b]	-40[d]	6h	90	70:30
i	 [b]	-40[d]	6i	74	84:16
j	$NCCH_2Li$	-80° to -10°	6j	No Rxn	
k	$C_3H_7C\equiv C-Li$	-80° to -10°	6k	No Rxn	

[a]Organolithium reagents, e-i, were all generated *in situ* from their corresponding tetrasubstituted stannanes. [b]Two equivalents of HMPA added to the solution of 3, and the stannane, prior to addition of methyllithium. [c]The addition of methyl iodide was optimized at -30° after the organolithium had added (4-8 h). [d]These reactions would only proceed at -40°, even in the presence of HMPA. [e]Determined by NMR.

There was a major modification to this process which was necessitated by the failure, in the early stages of this work, of a variety of organolithium reagents to add to the naphthalenes. Thus, although *s*-BuLi, *n*-BuLi, and *t*-BuLi behaved quite well as nucleophiles, MeLi was distinctly slower, requiring higher addition temperatures (-20°, -10°) and longer reaction times. This sluggishness, however, was to be used to great advantage (*vide infra*). More importantly, however, organolithium reagents such as allyl, benzyl, vinyl, etc. all failed to add to the π-system to furnish **5**. It was subsequently found that generation of the organolithium *in situ* from the tetrasubstituted stannane[10] and methyllithium in the presence of the naphthalene gave generally excellent yields of the tandem alkylation products **6**. The reason behind this enhanced behavior is not totally clear. The nucleophilic species could be an ate complex of tetraalkyl stannane and methyllithium which transfers the alkyl or vinyl groups *via* a different mechanistic pathway. On the other hand, the well-known *trans*-metalation[10] of tetrasubstituted stannanes to allyl, vinyl, or benzyllithium may give rise to halide free, unaggregated organolithium reagents with much higher reactivity[11] than aged or commercially available lithium reagents. The fact that these additions from the stannanes proceed at -80° as contrasted to organolithiums requiring -45 to

-20° C allowed the use of methyllithium to be used to effect the *trans*-metalation. In the case of lithioacetonitrile or 1-lithiobutyne, no addition to the naphthalene occurred. Furthermore, the vinyl lithium reagents (Table 1, entries h and i) would add extremely slowly at -20° to 0° C and provided only a 20% yield of tandem addition product after 8 hours. However, use of 2.0 equiv of hexamethylphosphoramide greatly increased the reaction rate and gave good yields of **6h** and **6i** after 6 hours at -40 to -50° C. Once again, the reason for this effect is not clear and the well known effect of additives on aggregation of organolithiums[11,12] may well be the cause.

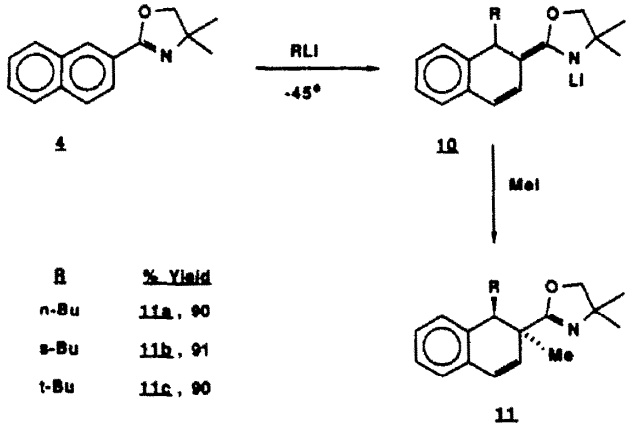
The adducts **6** were smoothly transformed into the carboxaldehydes **7** by sequential treatment with a) methyl trifluoromethylsulfonate, to quaternize the oxazoline nitrogen; b) sodium borohydride reduction to the oxazolidine; and c) acidic cleavage. In the cases where two diastereomers were present (**6f**, **6h**, **6i**) the oxazoline cleavage gave two carboxaldehydes **7** and **8**. These were not readily separable by chromatographic means and they were, therefore, reduced to the carbinols which were readily separated to afford pure **9** (Table 2). In the case of the tetrahydropyranyl derivative, **6i**, oxazoline cleavage expectedly afforded the allylic alcohol **7i**.

TABLE 2. Carboxaldehydes 7 and Carbinols 9 From Oxazolines 6

Entry	R	7 Aldehyde (%)	9 Carbinol (%)[c]
e		70[a]	94
f		84[b]	64
g	$PhCH_2$	90[a]	80
h	$PhC{\equiv}CCH_2-$	80[a,b]	58
i		89	

[a]Not completely characterized and carried directly to the corresponding carbinol **9**. [b]Mixtures of diastereomers which were separated at the carbinol stage. [c]Pure diastereomers.

The naphthyloxazoline **4** was also briefly studied and exhibited comparable addition behavior. Thus, alkyllithium addition at -45° produced the azaenolate **10** which was alkylated directly with methyl iodide affording a single product, **11**, in very high yield. No addition was observed to occur at the 3-position of the naphthalene ring and this is presumably due to the preservation of the aromaticity in **10**. Although **11** was not carried on to aldehydes as described for **6**, related non-racemic products have been carried further.[9] The stereochemical outcome of



4 **10**

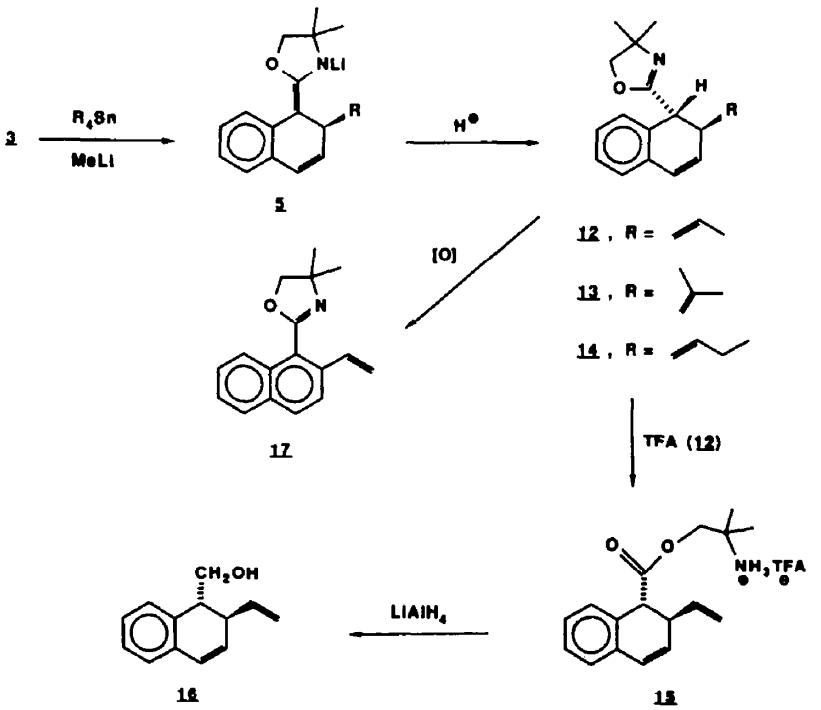
R	% Yield
n-Bu	**11a**, 90
s-Bu	**11b**, 91
t-Bu	**11c**, 90

11

the addition of **4** was once again confirmed by single crystal X-ray data (Fig. 1B) which clearly shows that the methyl group in the alkylation of **10** enters from the face opposite the *t*-butyl group.

The tandem addition was extended to the use of a proton as the trapping electrophile. Thus, the naphthalene **3** was treated with several tetraalkyl stannanes and subjected to the methyllithium addition. The intermediate azaenolate **5** was then treated with trifluoroacetic acid affording the disubstituted dihydronaphthalenes **12-14** as a single *trans* product in 86-90% yields. If the proton source was 2-propanol, a large amount of aromatization resulted and very little of **12** or **13** was isolated. However **14** and other non-vinylic substituents readily withstand the 2-propanol treatment which also leads to rapid and complete epimerization to the thermodynamic *trans* product.

To illustrate the crucial need for freshly generated vinyllithium and the type of proton quench required to provide good yields of adduct, a study was conducted using vinyllithium from tetravinyl stannane prepared in the presence of the naphthalene and vinyllithium allowed to age over several weeks prior to use. The results are summarized in Table 3. Thus, using vinyllithium generated from the tetravinyl stannane with methyllithium and allowed to remain in solution for 5 weeks prior to addition of the naphthalene, gave only aromatized material, 2-vinyl-1-oxazolinylnaphthalene **17** along with considerable amount of unreacted **3**. The use of vinyllithium generated in the presence of **3** with methyllithium gave more efficient addition to the

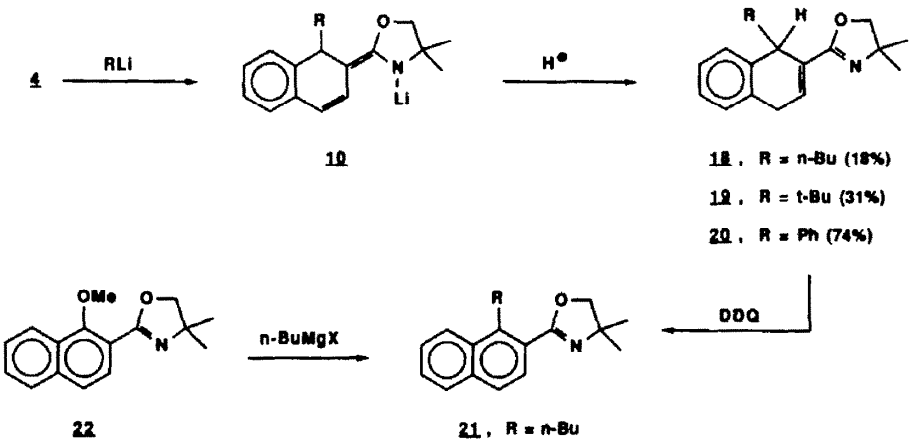


naphthalene, however quenching with 2-propanol resulted, once again, mainly in aromatization. This may be due to the lithium isopropoxide or lithium oxides which could be mediating base catalyzed aromatizations. The optimum conditions found are seen in the last entry in Table 3. The use of trifluoroacetic acid avoids the production of any basic material on quenching of **5** and allows for the isolation of good yields of adduct **15** as its trifluoroacetate salt. Direct reduction using lithium aluminum hydride furnished **16** as a single *trans*-isomer in 86% overall yield from **3**.

TABLE 3. Vinyllithium Addition - Proton Quench to 3

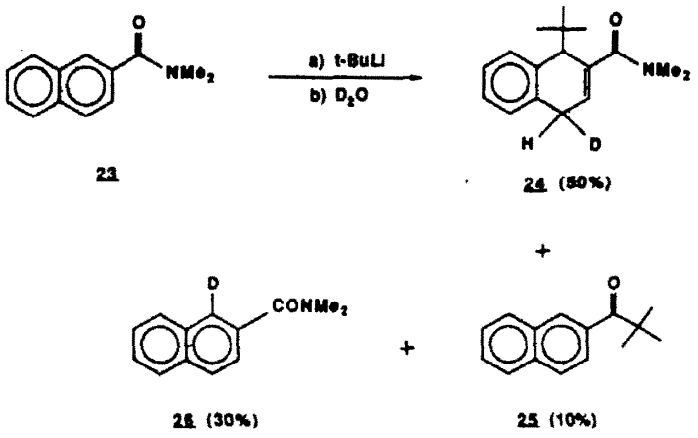
Nucleophile	Proton Source	T (°C)	Products (%)
Vinyl Li (5 weeks old)	i-PrOH-H_2O (1:1)	-30°	17 (54%) 3 (36%)
Vinyl Li (in situ)	i-PrOH-H_2O (1:1)	-30°	17 (89%) 3 (4%)
Vinyl Li (in situ)	CF_3CO_2H	-30°	12 (95%) 17 (4%)

Reaction of the 2-oxazolinylnaphthalene, **4** with various organolithium reagents followed by quenching with methanol or 2-propanol gave the dihydronaphthalenes **18-20** in varying yields. The major side reaction was aromatization to **21**. Furthermore, the adducts **18-20** were all products from double bond isomerization of the dihydronaphthalene. That the addition of



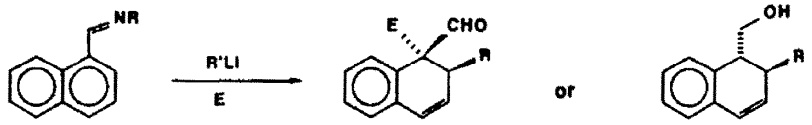
organolithiums had indeed occurred at the 1-position rather the 3-position in **4**, was verified by X-ray studies mentioned earlier (Fig. 1B). Additional evidence for the regioselectivity came earlier when the 2-methoxynaphthyloxazoline **22** was shown to react with the *n*-butylmagnesium bromide (as well as other nucleophiles)[7] and produced the identical product **21** obtained by aromatization of **18**.

Finally, we addressed the question of whether or not other electron-withdrawing groups would also serve to allow efficient addition to the naphthalene nucleus. The 2-naphthamide **23** was subjected to *t*-butyllithium at -45° C and gave the adduct **24** after quenching with deuterium oxide. Also obtained were 30-40% 1-deuteronaphthalene **26** and *t*-butylnaphthyl ketone **25** in 10% yield. The extensive studies by Snieckus[13] on metalation of naphthamides provided the background to these results. Ortho-metalation appears to be the major reaction pathway in the carboxamides when they are in the 1-position of naphthalene. In the 2-position, such as **23**, the metalation-alkylation reported by Snieckus[13] occurred in very poor yields (~ 4%). It is therefore quite likely that the latter reaction proceeded with high levels of addition to the naphthalene



nucleus. Unfortunately, spontaneous aromatization is very facile with adducts such as **24** which tends to limit their synthetic utility.

On the other hand, the adducts from 1-naphthyloxazolines, both alkyl or proton quenched, are obtained in good to excellent yields and may be further transformed into a variety of useful targets. Other 1-substituted electron-withdrawing groups have now been shown to behave in an analogous fashion. It was recently shown[14] that imines **27**, both chiral and achiral, lead to high yields of dihydronaphthalenes **28** or **29**.



27a, R = cyclohexyl
27b, R = (-)-valinol

28 29

EXPERIMENTAL

General

Melting points were determined in open capillary tubes and are uncorrected. MPLC utilized a column (30 x 2.5 cm) and packed with silica gel (Grace grade 951, 58 μ) with a pressure of 80-100 psi. HPLC utilized a Zorbax SII column (Dupont). Silica gel (Grace, grade 951, 58 μ) was used for flash chromatography. Tetrahydrofuran (THF) and ether were distilled from sodium benzophenone ketyl.

1-Naphthyloxazoline 3 - To a stirred suspension of 15.2 g (88 mmol) 1-naphthoic acid in 150 mL dichloromethane at 0° was added a solution of thionyl chloride (10.4 g, 6.4 mL, 150 mmols) in 100 mL dichloromethane. The mixture was warmed to room temperature and heated to reflux for 6 h and the solvent removed, *in vacuo*. The pale yellow crude acid chloride was redissolved in 250 mL dichloromethane and treated with a solution of 10.1 g (100 mmols) triethylamine, and 8.9 g (100 mmols) 2-amino-2-methylpropanol in 100 mL dichloromethane, which was slowly added at room temperature and then stirred for 15 h. The mixture was filtered and the filtrate concentrated to leave the amide as a white solid. The crude amido-alcohol was dissolved in 75 mL benzene and 150 mL dichloromethane and treated with 10.1 g thionyl chloride in 100 mL dichloromethane at 10-20° by dropwise addition. After completion of the addition, the mixture was heated to reflux for 1 h and allowed to stir at room temperature overnight. The reaction mixture was poured into cold 15% aqueous sodium hydroxide and extracted with dichloromethane, dried with K_2CO_3, and concentrated to give a crude product which was filtered through silica gel using hexane-ethyl acetate (4:1). Evaporation of the solvent gave 14.7 of a solid, mp 44-46° C (72%). The analytical sample was distilled (Kugelrohr), mp 46-48° C. IR (film) 1630, 1585 cm^{-1}. NMR ($CDCl_3$) δ 9.1-8.89 (m, 1), 8.07-7.1 (m, 6), 4.09 (s, 2), 1.46 (s, 2).
Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.88; H, 6.68.

2-Naphthyloxazoline, 4

Using the procedure described above, 20 g (120 mmols) of 2-naphthoic acid was transformed into 18.8 g (70%) of 4, mp 47-49° (recrystallized from hexane); IR (film) 1645, 1455 cm^{-1}; NMR ($CDCl_3$) δ 8.4 (br. s, 1), 8.0-7.45 (m, 6), 4.14 (s, 2) 1.48 (s, 6).
Anal. Calcd $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: 79.73; H, 6.60.

Organolithium Additions - Methyl Iodide Quench - General Procedure

To a cold (-45° C) stirred solution of the naphthyl oxazoline **3** or **4** (0.5 mmol) in tetrahydrofuran (0.25-0.4 M solution) was added dropwise, *via* syringe, 1.2 eq of the appropriate organolithium reagent. The resulting deep red reaction mixture was allowed to stir at -45° C for 1-3 hrs, quenched with methyl iodide, then warmed to room temperature. Extraction (Et_2O), drying (K_2CO_3), and concentration gave crude dihydronaphthalenes **6** or **11**. Purification was accomplished *via* preparative thin layer chromatography (silica gel, ethyl acetate/hexane).

1-(4,4-Dimethyl-2-oxazolinyl)-1,2-dimethyl-1,2-dihydronaphthalene, 6a

1-Naphthyloxazoline **3** (0.315 g, 1.4 mmol) in 4.2 mL of THF was treated with methyllithium (1.47 mL, 1.14 M in ether) at -45° C to 25° C for 4 h, followed by addition of methyl iodide (1.5 mL, 24 mmol), extraction and purification (ptlc, 25% EtOAc/hexane, silica gel) to give 0.232 g (65%) of **6a** as a clear colorless oil. NMR ($CDCl_3$) δ 7.44-6.83 (m, 4), 6.33 (d, J = 10 Hz, 1), 5.78 (dd, J = 10 Hz, J = 4 Hz, 1), 3.95 (s, 2), 2.85-2.30 (m, 1), 1.59 (s, 3), 1.29 and 1.27 (s, 6), 1.03 (d, J = 7 Hz, 6). IR (film) 2950, 1645, 1485, 1445 cm^{-1}.

Anal. Calcd for $C_{17}H_{21}NO$: C 79.96; H, 8.29, N, 5.49. Found: C, 79.80; H, 8.24.

1-(4,4-Dimethyl-2-oxazolinyl)-1-methyl-2-*n*-butyl-1,2-dihydronaphthalene, 6b

1-Naphthyloxazoline **3** (0.303 g, 1.35 mmol) in THF (1.7 mL) was treated with *n*-butyllithium (0.50 mL, 2.93 M in hexane) at -45° C for 2 h followed by addition of methyl iodide (0.20 mL, 3.2 mmol), extraction and purification (ptlc, silica gel, 20% EtOAc/hexane) to give 0.359 g, 90% of **6b** as a clear colorless oil. NMR ($CDCl_3$) δ 7.50-6.83 (m, 4), 6.34 (d, J = 10 Hz, 1), 5.93 (dd, J = 10 Hz, J = 4 Hz, 1), 3.90 (s, 2), 2.60-2.19 (m, 1), 1.77-0.69 (m, 9), 1.57 (s, 3), 1.26 (s, 3), 1.22 (s, 3). IR (film) 2960, 1645, 1450 cm^{-1}.

Anal. Calcd for $C_{20}H_{27}NO$: C, 80.76; H, 9.15; N, 4.17. Found: C, 80.60; H, 9.20.

1-(4-4-Dimethyl-2-oxazolinyl)-1-methyl-2-sec-butyl-1,2-dihydronaphthalene, 6c

In the usual manner, 1-naphthyloxazoline **3** (0.330 g, 1.46 mmol) in 5 mL of THF was treated with *sec*-BuLi (1.2 mL, 1.34 M in cyclohexane) at -45° C for 1.5 hr. The resulting deep red reaction mixture was quenched with methyl iodide (0.5 mL, 8 mmol), then subjected to extraction and purification (silica gel, 25% ethyl acetate/hexane) to give **6c** (0.410 g, 94%) as a clear, colorless oil. NMR ($CDCl_3$) δ 7.44-6.84 (m, 4), 6.48 (d, J = 10 Hz, 1), 5.76 (dd, J = 10 Hz, J = 5 Hz, 1), 3.93 (s, 2), 2.71-2.42 (m, 1), 1.60 (s, 3), 1.31 (s, 6), 1.80-0.60 (m, 9). IR (film) 3020-2860, 1645, 1485, 1455 cm^{-1}.

Anal. Calcd for $C_{20}H_{27}NO$: C, 80.76; H, 9.15: N, 4.71. Found: C, 80.95; H, 9.36.

1-(4,4-Dimethyl-2-oxazolinyl)-1-methyl-2-*t*-butyl-1,2-dihydronaphthalene, 6d

Similarly, treatment of a solution of 1-naphthyloxazoline **6d** (0.329 g, 1.46 mmol) in THF (5 mL) at -45° C with *t*-BuLi (0.95 mL, 1.7 M in pentane) for 1.5 h furnished a deep red/brown anionic solution which was quenched with methyl iodide (0.5 mL, 8 mmol). Extraction and purification (silica gel column 1 x 6 cm, ethyl acetate) gave 0.435 g (100%) **6d** as a white solid, mp 107.5-109° C. An analytical sample was recrystallized from hexane (mp 108-111°). NMR ($CDCl_3$ δ 7.72-7.55 (m, 1), 7.26-6.90 (m, 3), 6.43 (d, J = 10 Hz, 1), 5.94 (dd, J = 10 Hz, J = 6 Hz, 1), 3.90 (s, 2), 2.37 (d, J = 6 Hz, 1), 1.54 (s, 3), 1.37 (s, 3), 1.34 (s, 3), 0.89 (s, 9). IR (film) 2950, 1635, 1480, 1445 cm^{-1}. This was the sample submitted for X-ray determination (Fig. 1A).

Anal. Calcd for $C_{20}H_{27}NO$: C, 80.76; H, 9.15; N, 4.71. Found: C, 80.87; H 9.36.

Tetrasubstituted Stannanes[10] **- General Procedures**

To a suspension of magnesium (60 mmols, 1.44 g) in THF (30 mL) was added, dropwise, a solution of halide (50 mmols) in THF (30 mL). As soon as the reaction started, the mixture was cooled with a water bath (10 to 20° C). After the addition was completed, the mixture was stirred for 3 h at room temperature, then cannulated into a solution of $SnCl_4$ (12 mmols, 3.12 g) in benzene (20 mL). The mixture was heated at reflux overnight, cooled to room temperature, poured into water (50 mL) and extracted with ether (3 x 20 mL). The combined ethereal extracts were washed with water, dried over $MgSO_4$, and concentrated to give an oil which was filtered through silica gel with hexanes as the eluent. The products were used withour further purification for subsequent reactions.

Tetrasilyl stannane was obtained as a colorless oil, 2.8 g (82%).

Tetrabenzyl stannane was obtained as a colorless oil, 2.5 g (52%); ^{1}H-NMR: 7.16 (m, 2),7.0 (M, 1), 6.8 (M, 2), 2.18 (S, 2).

Tetra-(1-cyclopentenyl)stannane was obtained as a colorless oil 3.2 (70%); ^{1}H-NMR: 5.98 (m, 1), 2.49 (m, 2), 2.37 (m, 2), 1.82 (m, 2).

Tetra-(1-propenyl)stannane was obtained as a colorless oil, 3.0 g (90%), bp 100° C/18 mm Hg; ^{1}H-NMR 5.83 (s, 1), 5.22 (d, J = 1.3 Hz, 1), 2.02 (s, 3).

Organostannane-MeLi Additions - Methyl Iodide Quench - General Procedure for the Preparation of 6e-6l

To a solution of 1-naphthyloxazoline **3** (1 mmol) and tetrasubstituted stannane (0.4 mmol) in THF (20 mL) at -80° C was added, dropwise, a solution of methyllithium (1.2 mmols) in ether. The resulting red mixture was stirred for 24 h at -80° C and methyl iodide (2 mmols, 0.13 mL) was added. After 1 h the mixture was slowly allowed to warm to room temperature, washed twice with saturated aqueous ammonium chloride (10 mL), brine, dried ($MgSO_4$), and concentrated to give a yellow oil. Chromatography over silica gel with hexanes-ethyl acetate (9/1) yielded a colorless oil. No elemental analyses were performed on these materials (**6e-6l**) since they were prone to air oxidation.

1-(4,4-Dimethyl-2-oxazolinyl-)-1-methyl-2-(1-propenyl)-1,2-dihydronaphthalene, 6e

Using the procedure described above, at -80° to -30° C for 3 h, yielded a colorless oil (275 mg) 97%. ^{1}H-NMR: 7.15 (m, 4), 6.52 (d, 1 , J = 9.65 Hz), 5.75 (dd, 1, J = 5.9 and 9.65 Hz), 4.78 (m, 1), 4.62 (m, 1), 3.94 (d, 1, J = 7.97 Hz), 3.80 (d, 1, J = 7.9 Hz), 3.12 (d, 1, J = 5.9 Hz), 1.53 (s, 3), 1.46 (s, 3), 1.33 (s, 3). IR (neat): 3060, 3030, 3970, 2920, 2880, 1650 (C = N), 1480 (C = C), 1450, 1370, 1340, 1300, 1270, 1190, 1120, 1100, 1070 cm^{-1}.

1-(4,4-Dimethyl-2-oxazolinyl)-1-methyl-2-allyl-1,2-dihydronaphthalene, 6f

Using the procedure described above, at -80 to -30° C for 8 h, yielded a colorless oil (224 mg) 80%. Two diastereoisomers were detected by ^{1}H-NMR in a ratio of 68/32. ^{1}H-NMR: 7.23 (m, 4), 5.98 (m, 1), 5.75 (m, 2), 5.0 (m, 2), 3.85 (m, 2), 3.58 (m, 0.68 H), 3.45 (m, 0.32 H, 2.51 (m, 1), 2.41 (m, 1), 1.6 (s, 3), 1.3 (s, 6 x 0.68), 1.25 (s, 3 x 0.32), 1.24 (s, 3 x 0.32 H). IR (neat): 3080, 3020, 2980, 2920, 2880, 1650 (C = N), 1600 (C = C), 1480, 1460 1450, 1380, 1280, 1200, 1080, 980, 970, 910, 760 cm^{-1}.

1-(4,4-Dimethyl-2-oxazolinyl)-1-methyl-2-benzyl-1,2-dihydronaphthalene, 6g

Using the procedure described above, at -80 to -30° C for 8 h, yielded a colorless oil (300 mg) 91%. ^{1}H-NMR: 7.23 (m, 8), 6.99 (d, 1, J = 7.5 Hz), 5.88 (dd, 1, J = 4.15 and 10.1 Hz), 5.71 (d, 1, J = 10.1 Hz), 3.83 (m, 3), 3.05 (dd, 1, J = 4.09 and 13.2 Hz), 2.88 (dd, 1, J = 8.12 and 13.2 Hz), 1.3 (s, 3), 1.28 (s, 3), 1.26 (s, 3). IR (neat); 3060, 3020, 2960, 2920, 2880, 1650 (C = N), 1590 (C = C), 1480, 1440, 1380, 1270, 1190, 1170, 1030, 970, 960, 920, 740 cm^{-1}.

1-(4,4-Dimethyl-2-oxazolinyl)-1-methyl-2-(3-(-1-phenyl)-propynyl)-1,2-dihydronaph- thalene, 6h

To a solution of 1-phenyl-1-propyne (2.4 mmols, 278 mg) and HMPA (2.5 mmols, 447 mg) in THF (10 mL) at -80° C, *n*-BuLi (2 mmols, 1.1 mL, 1.8 M) was added. After 30 min the 1-naphthyloxazoline 3 (1 mmols, 225 mg) in THF (5 mL) was added dropwise. After 24 h at -80° C methyl iodide (3 mmols, 0.18 mL) was added and the general procedure described above was followed to furnish the product as a colorless oil (320 mg) 90%. Two diastereoisomers were detected by ^{1}H-NMR, in a ratio of 70:30. ^{1}H-NMR: 7.32 (m, 9), 6.28 (dd, 0.3 H, J = 4.2 and 11.2 Hz), 6.21 (dd, 0.7 Hz, J = 4.2 and 10.1 Hz), 5.9 (dd, 0.7 H, J = 1.2 and 10.1 Hz), 5.8 (dd, 0.3 H, J = 1.2 and 11.2 Hz), 3.85 (dd, 2, J = 8.1 and 17.6 Hz), 3.75 (m, 1), 2.87 (dd, 1, J = 5.4 and 16.6 Hz), 2.67 (dd, 1, J = 8.24 and 16.6 Hz), 1.66 (s, 3), 1.32 (s, 3 x 0.7), 1.31 (s, 3 x 0.7), 1.28 (s, 3 x 0.3), 1.25 (s, 3 x 0.3). IR (neat): 3040, 3020, 2960, 2920, 2880, 2240, 2200 (weak, C = C), 1640 (C = N), 1590 (C = C), 1480, 1450, 1360, 1280, 1200, 1070, 960, 900, 750.

1-(4,4-Dimethyl-2-oxazolinyl)-1-methyl-2-(1-propeny-3-tetrahydropyranyl)-1,2-dihydronaphthalene, 6i

To a solution of E-1-tri-*n*-butylstannyl-(1-propene-3-tetrahydropyranyl)[15] (1.5 mmols, 780 mg), HMPA (1.6 mmols, 0.29 mL) and 1-naphthyloxazoline 3 (1 mmol, 225 mg) in THF (20 mL) at -35° C, methyllithium (1.4 mmols, 1 mL, 1.4 M) was added dropwise. The mixture was stirred for 6 h at the same temperature, cooled to -80° C and methyl iodide (3 mmols) was added. The general procedure described above was followed and the product was isolated as a colorless oil (283 mg) 74%. ^{1}H-NMR: 7.22 (m, 3), 7.05 (m, 1), 6.41 (d, 1, J = 9.6 Hz), 5.81 (dd, 1, J = 5.3 and 9.5 Hz), 5.61 (m, 2), 4.59 (m, 1), 4.13 (m, 1), 3.85 (m, 4), 3.47 (m, 2), 3.0 (m, 1), 1.56 (m, 9), 1.3 (s, 6). IR (neat): 3020, 2960, 2930, 2880, 1640 (C = N), 1480 (C = C), 1450, 1360, 1350, 1270, 1200, 1120, 1020, 970 cm^{-1}.

Oxazoline Cleavage to Aldehydes, 7 - General Procedure

A solution of dihydronaphthalene 6 in dichloromethane (0.8 mmol in 2 mL) was treated dropwise with 0.86 mmols (0.1 mL) of methyl trifluoromethylsulfonate at room temperature. After 1 h, tlc examination showed only a baseline spot indicating complete quaternization of the oxazoline. A solution of sodium borohydride (0.9 mmol, 34 mg) in ethanol (2 mL) was slowly added to the dichloromethane solution and stirred for 6 h at room temperature. The mixture was poured into 20 mL water, extracted with ether (3 x 10 mL), the extracts concentrated to give a residue which was dissolved in THF (3 mL) and 2 N HCl (3 mL). This solution was stirred 16 h at room temperature and then extracted (3 x 10 mL) with ether. The ethereal extract was washed with water, brine, and dried ($MgSO_4$). Concentration gave an oil which was filtered through silica gel using hexane-ether (99:1) as eluent. The material obtained was analytically pure.

1-Methyl-2-allyl-1,2-dihydronaphthaldehyde, 7f

The procedure described above yielded a colorless oil (142 mg) 84% as a mixture of two diastereoisomers in the ratio, 68:32. These could not be separated on silica gel and were obtained as pure isomers in the form of the carbinol 9 (see below). ^{1}H-NMR: 9.34 (s, 1), 7.22 (m, 3), 7.02 (d, 1, J = 6.2 Hz), 6.11 (m, 1), 5.67 (m, 1), 5.53 (m, 1), 4.98 (m, 2), 3.6 (m, 1), 2.5 (m, 2), 1.52 (s, 3 x 0.32), 1.47 (s, 3 x 0.68). IR (neat): 3060, 3020, 2970, 2970, 2920, 2860, 2800, 2690, 1720 (C = O), 1640 (C = C), 1490, 1440, 1380, 980, 910 cm^{-1}.

Anal. Calcd for $C_{15}H_{16}O$: C, 84.86; H, 7.63. Found: C, 85.01; H, 7.63.

1-Methyl-2-(1-propene-3-ol)-1,2-dihydronaphthaldehyde, 7i

The procedure described above yielded a colorless oil (160 mg) 89%, as a single diastereomer, although the oxazoline 6i was an 84:16 mixture prior to cleavage. ^{1}H-NMR: 9.77 (s, 1), 7.18 (m, 4), 6.5 (dd, 1, J = 1.6 and 9.6 Hz), 5.81 (m, 3), 4.10 (d, 2, J = 4.5 Hz), 3.15 (m, 1), 1.57 (s broad, OH), 1.38 (s, 3). IR (neat): 3400 (broad), 3020, 2960, 2920, 2860, 2710, 1710 (C = O), 1480 1440, 1380, 1360, 1280, 1170, 1140, 1070 cm^{-1}.

Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.92; H, 7.05.

Reduction of Aldehydes 7 To Carbinols 9 - General Procedure

A solution of the dihydronaphthaldehydes 7 (0.6 mmol) in ethanol (1 mL) was treated with sodium borohydride (0.5 mmol, 19 mg). After 1 h the mixture was poured into water (5 mL) and extracted with ether (3 x 10 mL). The combined ether extracts were washed with water (5 mL), brine, dried ($MgSO_4$), and concentrated to give an oil. The material was purified and diastereomers readily separated on silica gel using hexane-ethylacetate (8:2) as eluent.

1-Hydroxymethyl-1-methyl-2-(2-propenyl)-1,2-dihydronaphthalene, 9a

Using the procedure described above yielded a colorless oil (98 mg) 94%. Only one diastereomer was detected. ^{1}H-NMR: 7.14 (m, 4), 6.52 (d, 1, J = 9.6 Hz), 5.76 (dd, 1, J = 5.9 and 9.6 Hz), 4.95 (s, 1), 4.77 (s, 1), 3.95 (m, 2), 3.04 (d, 1, J = 5.9 Hz), 1.8 (s, 1, O-H), 1.42 (s, 3), 1.27 (s, 3). IR (neat): 3080, 3020, 2980, 2920, 2880, 1650 (C = C), 1600, 1480, 1460, 1450, 1360, 1280, 1200, 1080, 980, 970, 910, 760 cm^{-1}.

Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.46. Found: C, 83.92, H, 8.56.

1-Hydroxymethyl-1-methyl-2-allyl-1,2-dihydronaphthalene, 9f

Using the procedure described above yielded a colorless oil (102 mg) 95%. After chromatography 64% (65 mg) of the major diastereoisomer was isolated. ^{1}H-NMR: 7.27 (m, 4), 6.0 (dd, 1, J = 3.85 and 10.2 Hz), 5.68 (m, 2), 5.00 (s, 1), 4.95 (m, 1), 3.83 (d, 1, J = 10.8 Hz), 3.53 (m, 2), 2.53 (m, 1), 2.39 (m, 1), 1.8 (s broad, 1, O-H), 1.28 (s, 3). IR (neat): 3400 (broad O-H), 3060, 3020, 2960, 2920, 2860, 1630, 1480, 1430, 1360, 1020, 900, 740 cm^{-1}.
Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.46. Found: C, 83.73; H, 8.51.

1-Hydroxymethyl-1-methyl-2-benzyl-1,2-dihydronaphthalene, 9g

The corresponding aldehyde 7g was not characterized, it was directly reduced after the oxazoline cleavage, using the procedure described above. A colorless oil was isolated (170 mg) 80% for the two steps. Only one diastereomer was detected. ^{1}H-NMR: 7.23 (m, 8), 6.95 (m, 1), 5.89 (dd, 1, J = 4.0 and 10.2 Hz), 5.55 (dd, 1, J = 1.1 and 10.2 Hz), 3.78 (d, m, 2, J = 10.8 Hz), 3.45 (d, 1, J = 10.8 Hz), 3.08 (dd, 1, J = 4.7 and 13.1 Hz), 2.85 (dd, 1, J = 8.0 and 13.1 Hz), 1.28 (s broad, O-H), 0.88 (s, 3). IR (neat): 3550, 3400 (O-H), 3050, 3020, 2950, 2910, 2850, 1590, 1480, 1440, 1360, 1060, 1020 cm^{-1}.
Anal. Calcd for $C_{19}H_{20}O$: C, 86.3; H, 7.62. Found: C, 85.65; H, 7.56.

1-Hydroxymethyl-1-methyl-2-(3-phenyl-1-propynyl)-1,2-dihydronaphthalene, 9h

The corresponding aldehyde was not characterized and was directly reduced after the oxazoline cleavage, using the procedure described above. A colorless oil was isolated (133 mg) 58%. After chromatography, 108 mg (47% overall from the major diastereoisomer) was isolated and 20 mg (9%) of the minor diastereoisomer (see below). ^{1}H-NMR: 7.30 (m, 9), 6.24 (dd, 1, J = 3.8 and 10.2 Hz), 5.75 (dd, 1, J = 1.5 and 10.2 Hz), 3.86 (d, 1, J = 10.8 Hz), 3.7 (m, 1), 3.57 (d, 1, J = 10.8 Hz), 2.88 (dd, 1, J = 5.0 and 16.6 Hz), 2.65 (dd, 1, J = 8.2 and 16.6 Hz). IR (neat): 3400 (broad, O-H), 3060, 3020, 2960, 2920, 2860, 1590, 1480, 1440, 1100, 1060, 1020, 900, 740 cm^{-1}.
Anal. Calcd for $C_{21}H_{20}O$: C, 87.46; H, 6.99. Found: C, 87.27; H, 7.13.

Minor Diastereoisomer in 9h

^{1}H-NMR: 7.31 (m, 9), 6.23 (dd, 1, J = 4.2 and 10.2 Hz), 5.69 (dd, 1, J = 1.4 and 10.2 Hz), 3.7 (d, m, 2, J = 10.6 Hz), 3.54 (d, 1, J = 10.6 Hz), 2.96 (dd, 1, J = 5.3 and 16.6 Hz), 2.69 (dd, 1, J = 8.4 and 16.6 Hz), 1.55 (s broad, 1, O-H), 1.35 (s, 3). The IR spectrum was virtually identical to the major isomer above.

1-*n*-Butyl-2-(4,4-dimethyl-2-oxazolinyl)-2-methyl-1,2-dihydronaphthalene, 11a

Using the procedure described earlier for addition to 3, 2-naphthyloxazoline 4 (0.390 g, 1.73 mmol) was treated with *n*-BuLi (0.71 mL, 2.92 M in hexane) in THF (5 mL) at -45° C for 1 h to give an orange-brown anion which was quenched with methyl iodide (0.3 mL, 4.82 mmol). Extractive workup and purification on silica gel using 15% ethyl acetate/hexane gave 0.467 g (90.6%) of a clear, colorless oil. ^{1}H-NMR ($CDCl_3$) δ 7.16-6.90 (m, 4), 6.25 (bs, 2), 3.89 (s, 2), 2.91-2.60 (m, 1), 1.62-0.70 (m, 18). IR (film): 2950, 1658, 1625, 1450 cm^{-1}.
Anal. Calcd for $C_{20}H_{27}NO$: C, 80.76; H, 9.15; N, 4.71. Found: C, 80.91; H, 8.91.

1-*s*-Butyl-2-(4,4-dimethyl-2-oxazolinyl)-2-methyl-1,2-dihydronaphthalene, 11b

As described above, 2-naphthyloxazoline 4 (0.398 g, 1.76 mmol) was treated with *sec*-BuLi (1.58 mL, 1.34 M in cyclohexane) in THF (4.5 mL) for 1 h at -45° C to give a mustard-colored anion which was quenched with 0.3 mL (4.82 mmol) of methyl iodide. Extraction and purification on silica gel (15% ethyl acetate/hexane) afforded 0.472 g (89.9%) of a clear, colorless oil which crystallized slowly on standing. ^{1}H-NMR ($CDCl_3$) δ 7.20-6.91 (m, 4), 6.31 (bs, 2), 2.94 (s, 2), 3.0-2.80 (m, 1), 1.70-0.61 (m, 18). IR (film): 2950, 1655, 1630, 1410 cm^{-1}.
Anal. Calcd for $C_{20}H_{27}NO$: C, 80.76; H, 9.15; N, 4.71. Found: C, 80.69; H, 9.25.

1-*t*-Butyl-2-(4,4-dimethyl-2-oxazolinyl)-2-methyl-1,2-dihydronaphthalene, 11c

In a similar manner, 2-naphthyloxazoline (0.391 g, 1.73 mmol) was treated with *t*-BuLi (1.22 mL, 1.7 M in pentane) in THF (10.5 mL) at -45° C for 1 h to give a thick, cloudy, mustard-colored anion suspension (the solution became very thick just after *t*-BuLi addition). Quenching with methyl iodide (0.3 mL, 4.82 mmol), extraction and purification on silica gel (15% ethyl acetate/hexane) gave 0.456 g (90.2%) of **11c** as a colorless solid, mp 59-65° C. ^{1}H-NMR ($CDCl_3$) δ 7.04 (m, 4), 6.64 (dd, J = 10 Hz, J_{BX} = 1 Hz, 1), 6.31 (d, J = 10 Hz, 1), 4.02 (d, J = 8 Hz, 1), 3.87 (d, J = 8 Hz, 1), 2.78 (d, J = 1 Hz, 1), 1.37 (s, 3), 1.25 (s, 3), 1.22 (s, 3), 0.95 (s, 9). IR (film): 2930, 1653, 1630, 1480, 1450 cm^{-1}. This sample was subjected to X-ray determination (Fig. 1B).
Anal. Calcd for $C_{20}H_{27}NO$: C, 80.76; H, 9.15; N, 4.71. Found: C, 81.03; H, 8.95.

Organostannane - MeLi Additions - Proton Quench - General Procedure for 12-14

To a solution of 3 (1 mmol) and the tetrasubstituted stannane (0.4 mmol) in 20 mL of THF, cooled to -80° C, was added in a dropwise manner, 1.2 mmols of methyllithium in ether. The red mixture was stirred for 20-24 h at -80° C and then the appropriate proton sources (trifluoroacetic acid, 2-propanol, or HCl) was added. The mixture was allowed to warm to room temperature, washed twice with saturated ammonium chloride, then brine, dried ($MgSO_4$) and concentrated. The residue was passed through silica gel using hexanes-ethyl/acetate (9:1) as eluent.

1-(4,4-Dimethyl-2-oxazolinyl-)-2-(1-propenyl)-1,2-dihydronaphthalene, 13

The procedure described above was used, at -80° to -30° C for 8 h and the reaction was quenched with a solution of HCl (2%, 0.5 mL). A colorless oil was isolated (240 mg) 90%. ^{1}H-NMR: 7.12 (m, 4), 6.5 (d, 1, J = 9.5 Hz), 5.83 (dd, 1, J = 2.6 and 9.6 Hz), 4.84 (s, 1), 4.83 (s, 2), 3.99 (m, 1), 3.94 (s, 2), 3.53 (d, 1, J = 11.4 Hz), 1.77 (s, 3), 1.34 (s, 3), 1.27 (s, 3). IR (neat): 3060, 3020, 2990, 2920, 2900, 1650 (C = N), 1490 (C = C), 1450, 1370, 1340, 1290, 1190, 1160, 1110, 1000, 910 cm^{-1}.

1-(4,4-Dimethyl-2-oxazolinyl-)-2-allyl-1,2-dihydronaphthalene, 14

Using the procedure described above and quenching with 1:1 water 2-propanol yielded a colorless oil (240 mg) 90%. ^{1}H-NMR: 7.96 (dd, 1, J = 1.9 and 7.4 Hz), 7.18 (m, 4), 6.77 (dd, 1,

J = 3.65 and 5.9 Hz), 5.77 (m, 1), 5.04 (s, 1), 4.99 (m, 1), 4.01 (d, 2, J = 1.9 Hz), 2.8 (m, 1), 2.38 (m, 3), 1.4 (s, 3), 1.39 (s, 3). IR (neat): 3080, 2980, 2920, 2890, 2860, 1650 (C = N), 1610 (C = C), 1490, 1450, 1360, 1340, 1290, 1190, 1160, 1110, 1000, 910.

1-Hydroxymethyl-2-vinyl-1,2-dihydronaphthalene, 16

The nucleophilic addition described above was used at -40° C and the reaction was quenched with trifluoroacetic acid (10 mmols, 0.77 mL) and stirred at room temperature for 1 h. To the mixture was added 500 mg Na_2SO_4, two drops of water, and stirred overnight (16 h). The salts were removed by filtration and the organic layer was dried ($MgSO_4$), concentrated, and kept under vacuum (0.3 mmHg) for 2 h. The residual yellow oil **15** was dissolved in ether (20 mL) and $LiAlH_4$ (190 mg, 5 mmols) was added. The mixture was stirred at room temperature for 1 h and quenched with $Na_2SO_4 \cdot 10\ H_2O$ (5 mmols, 1.6 g). The salts were removed by filtration, the mixture dried ($MgSO_4$), and concentrated. The product was purified by flash chromatography on silica gel using ethylacetate-hexane (1:4) and yielded 240 mg (86%) of a colorless oil. ^{1}H-NMR: 7.15 (m, 4), 6.47 (d, 1, J = 9.6 Hz), 5.85 (dd, 2, J = 5.9 and 9.6 Hz), 5.06 (dd, 1, J = 1.4 and 17.1 Hz), 4.92 (d, 1, J = 10.1 Hz), 3.65 (d, 2, J = 7.4 Hz), 3.14 (t, 1, J = 6.5 Hz), 2.91 (t, 1, J = 7.4 Hz), 1.47 (s broad, 1, OH). IR (neat): 3300 (OH), 3060, 3040, 2980, 2930, 1640, 1590, 1510, 1490, 1450, 1380, 1280.

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.57. Found: C, 83.38; H, 7.45.

1-*n*-Butyl-2-(4,4-dimethyl-2-oxazolinyl)-1,4-dihydronaphthalene, 18

Addition of 2-naphthyloxazoline **4** (0.48 g, 2.13 mmol) in 7 mL of THF to a solution of *n*-BuLi (1.13 mL, 2.07 M in hexane) in 2 mL of THF at -45° C, followed by stirring for 1 h, quenching with methanol, extraction and purification (2 x prep tlc, silica gel, 25% EtOAc/hexane) gave 0.111 g (18%) of **18** as an oil. ^{1}H-NMR ($CDCl_3$) δ 7.19-7.04 (m, 4), 6.78 (t, J = 4 Hz, 1), 4.20-3.85 (m, 1), 3.90 (s, 2), 3.54-3.33 (bt, 2), 1.48-0.56 (m, 9), 1.31 (s, 6). IR (film): 2960, 1665, 1620, 1460 cm^{-1}. The low yield was due to oxidation during purification, affording 60-70% yields of **21**.

1-*t*-Butyl-2-(4,4-dimethyl-2-oxazolinyl)-1,4-dihydronaphthalene, 19

Treatment of 2-naphthyloxazoline **4** (0.199 g, 0.884 mmol) in 4 mL of THF with *t*-BuLi (0.42 mL, 12.3 M in pentane) at -45° C for 1 h, followed by methanol quench, extraction and purification (prep tlc, silica gel 25% EtOAc/hexane) gave 0.079 g (31%) **19** as a clear colorless oil. ^{1}H-NMR ($CDCl_3$) δ 7.05-7.26 (m, 4), 6.98 (t, J = 2 Hz, 1), 3.89-3.81 (m, 3), 3.53-3.34 (bt, 2), 1.30 (s, 6), 0.89 (s, 9).

1-Phenyl-2-(4,4-dimethyl-2-oxazolinyl)-1,4-dihydronaphthalene, 20

2-Naphthyloxazoline **4** (0.298 g, 1.32 mmol) in 4 mL of THF was treated with PhLi (2.09 mL, 0.76 M in ether) at -45° C for 1 h, followed by methanol quench, extraction and purification (prep tlc, silica gel 25% EtOAc/hexane) to give 0.299 g (74%) of **20** as a clear colorless oil. ^{1}H-NMR ($CDCl_3$) δ 7.50-6.70 (m, 10), 5.33-5.11 (m, 1), 3.72 (s, 2), 3.70-3.35 (m, 2), 1.21 (s, 3), 1.10 (s, 3). IR (film): 2970, 1665, 1615, 1495, 1450 cm^{-1}.

Exposure to air over several months gave, by tlc, oxidized material corresponding to 1-phenyl-2-oxazolinyl-naphthalene, identical to material previously reported.[7]

Oxidation of Dihydronaphthalene, 18 to 21

To a solution of *n*-butyldihydronaphthyloxazoline **18** (0.111 g, 0.39 mmol) in 5 mL of toluene was added, with stirring 0.091 g (0.4 mmol) of dichlorodicyanobenzoquinone in 1 mL of toluene. The resulting solution was stirred at room temperature for 30 min. Ether was added and the mixture extracted four times with 12% aqueous NaOH (until washings were colorless). Drying (K_2CO_3) and concentration afforded 0.095 g of crude product. Preparative tlc (20% ethyl acetate/hexane; silica gel) gave 0.035 g of oxidized product which was identical in all respects to 1-*n*-butyl-2-oxazolinyl-naphthalene **21** reported earlier.[7]

1-*t*-Butyl-4-deutero-1,4-dihydro-2-naphthamide, 24

To a cold (-45° C) stirred solution of *t*-butyllithium (0.88 mL, 1.92 M in pentane) in THF (4 mL) was added a solution of N,N-dimethyl-2-naphthamide (0.306 g, 1.54 mmol) in THF (3 mL) dropwise, *via* syringe. The resulting deep red reaction mixture was stirred for 30 min at -45° C, then quenched with 2 mL of CH_3OD, followed by 2 mL of D_2O. The solution was stirred for 2 h at room temperature, followed by extractive workup, drying (K_2CO_3), and concentration to give 0.348 g of a pale yellow solid. Purification *via* preparative tlc (silica gel) using 20% ethyl acetate/hexane followed by a second separation using 30% acetone/hexane gave 0.215 g **24** in 55% yield. ^{1}H-NMR ($CDCl_3$) δ 7.24-7.07 (m, 4), 6.37 (d, 1, J = 6 Hz), 3.76 (s, 1), 3.27 (m, 1), 3.05 (s, 6), 1.88 (s, 9). The deuterium was identified by mass spectral analysis, m/e = (M + 1) 258.4407.

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