Stereochemical Control of Reductions. 9. Haptophilicity Studies with 1,1-Disubstituted 2-Methyleneacenaphthenes

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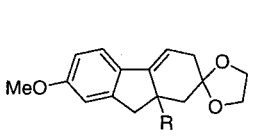
A series of 1-methyl-2-methyleneacenaphthenes has been synthesized, bearing an additional variable substituent (R) at the 1-position. These compounds have been hydrogenated in ethanol over a 5% Pd/C catalyst under standardized conditions in order to assess the haptophilicity of R, its ability to enforce addition of hydrogen from its own face of the molecule by coordination to the catalyst surface. The order of decreasing haptophilicity, assessed as the product epimer ratio, for the groups studied was R = CH_2NH_2, CH_2NMe_2, CH_2OH, CHNOH, CH_2OMe, CHO, $CONH_2$, $CH_2NHCOMe$, COOK, COMe, CN, CONHOH, COOH, COOMe, COONa, COOLi. Because knowledge of group haptophilicities offers potential for stereochemical control in such reductions, comparisons are provided with haptophilic orders found in other molecular systems. It is shown that absolute haptophilicities can be manipulated by varying the dielectric constant of the solvent employed.

Introduction

When reduction of unsaturation creates new stereocenters, the presence of other groups within the substrate offers the potential to control product stereochemistry. Beyond the more familiar steric hindrance effects, use of functional groups as reagent hinges or leashes is now common. Our own studies of the latter phenomenon have focused on the heterogeneous catalytic hydrogenation of alkenes,[1−9] where profound changes in product stereochemistry may be generated by simple changes in such "spectator" functional groups.[10−20] These stereochemical results bear little relationship to the usual measures of group size, basicity or polarity alone but apparently represent complex combinations of such properties, tempered by the shape and accessibility of the influencing group.[3] We term the *net* ability of such a group to enforce addition of hydrogen from its own face of the molecule "haptophilicity," and have established a haptophilic order for a dozen of the most common functional groups.[3,9] Knowledge of group haptophilicities offers promise of stereochemical control in such reductions, but for a haptophilic order to be generally useful, it must be shown to apply to a variety of substrate systems.



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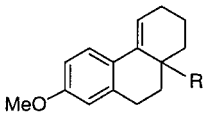

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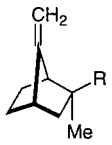

3

Our previous studies of these effects utilized systems **1**−**3**,[1,6,8] bearing several features in common. Each is a racemate without diastereomers and is reducible from either of two molecular faces, yielding only two epimers. Along with ease of construction, we have sought systems amenable to GC but large enough to make crystallinity likely. As our studies have evolved, we have also tried to choose systems with alkenes incapable of isomerizing, a potential complication with palladium catalysts,[3] and having uncluttered ^{1}H NMR spectra, since NMR is a principal tool for assessing product ratios. The subject of the present study is the system represented by **8**, which we have synthesized as shown in Scheme 1. Both this system and **3**[8,9] incorporate quaternary methyls to fix stereochemistry and act as ^{1}H NMR markers.

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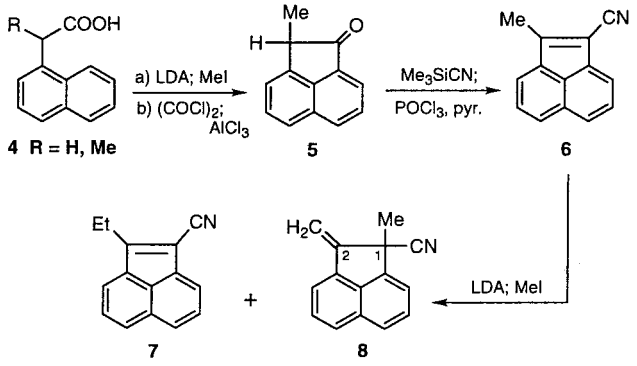
Scheme 1



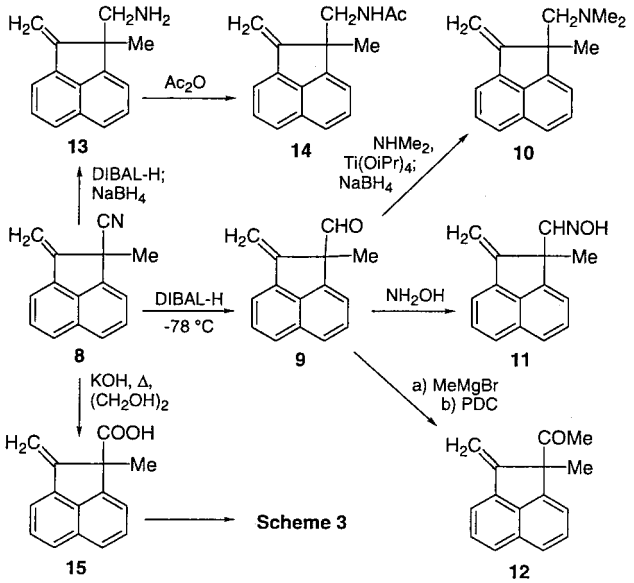
Results and Discussion

Syntheses. Commercially available **4** (R = H) was methylated in 96% yield through its dianion[21] and then cyclized in 77% yield via the acid chloride.[22] Treatment of **5** with Me_3SiCN and $BF_3{\cdot}OEt_2$ gave the protected cyanohydrin, which was not isolated but subjected directly to elimination by treatment with $SOCl_2$ and pyridine, providing a 65% yield of **6**.[23] Methylation of **6** in THF led to a product contaminated with up to 15% of the γ-methylated **7**, which was difficult to separate from **8**. This was overcome by careful temperature control, plus use of *N*,*N*′-dimethylpropyleneurea[24] as a cosolvent. This gave a 92% yield of **8** containing only ca. 5% of **7**, which could be removed in later steps.

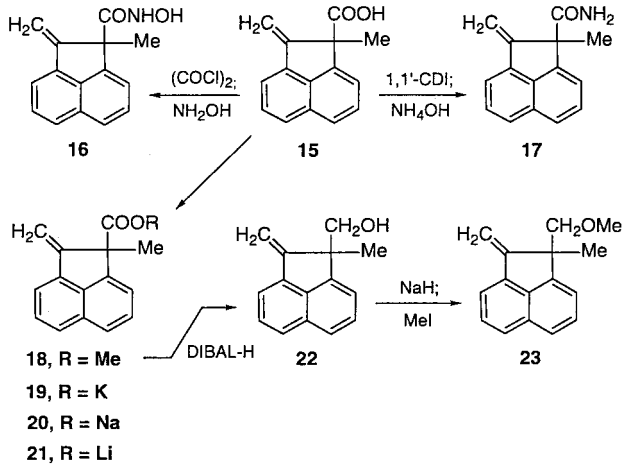
The transformations of nitrile **8** into the carboxylic acid **15** and the other functional groups required followed the routes outlined in Schemes 2 and 3. Hydrolysis of **8** to **15** could be carried out in good yield (92%) but illustrates the difficulties inherent in this molecular system. Acidic conditions could not be used because of the sensitivity of the styrene subunit, while, even with base, rather severe conditions were required because the R group is neopentyl. Several steps required careful control of reaction conditions.

Reduction of **8** with DIBAL-H at −78 °C[25] led in 82% yield to the aldehyde **9**, which could be transformed straightforwardly to **11** and **12**. However, attempts at further reduction of **8** to **13** with DIBAL-H led to multiple impurities, as did trials with $LiB(Et)_3H$, 9-BBN, and $(MeOCH_2CH_2O)_2AlH_2Na$. Attempts at producing **13** via the aldoxime **11** and by reductive amination of **9** with a variety of systems were equally unsuccessful. Interestingly, reductions of either **8** or carboxamide **17** with $LiAlH_4$ yielded products in which the double bond had suffered reduction. This was useful to us later in establishing the stereochemistry of the reduced species, but not for producing **13**. A poor yield of **13** could be achieved by converting alcohol **22** to its phthalimide derivative. Our success in reducing **8** to **9** had shown that these difficulties with **13** arose in further DIBAL-H reduction of the imine species. On this basis, we ultimately devised a tandem two-step reduction involving DIBAL-H followed by $NaBH_4$. With careful temperature control of the steps, this led in 82% yield to pure **13**, which could be transformed easily to its acetamide **14**. Reductive $NaBH_4$ amination of **9** using titanium isopropoxide[26] gave the dimethylamino species **10** in 60% yield; however, analogous reactions failed to provide the monomethylated amine or **13** (above), leading instead to double-bond loss; this is suspected to have involved internal nitrogen additions to the styrene system. Transformation of carboxylic acid **15** into the other species of Scheme 3 proceeded as outlined.

Scheme 2



Scheme 3



All the members of this series of compounds display unsplit pairs of singlets attributable to the exo-methylene function in the δ 5.2−6.1 region of their ^{1}H NMR spectra. A ^{1}H NOESY spectrum of methyl ester **18** established that the downfield member in the pair (δ 5.93, 5.45) has the cis relationship to the aromatic nucleus, consistent with expected deshielding effects. Although NOESY determinations were not made for the remainder of the series, the analogous assignment is fully consistent with every case. The average positions for the downfield and upfield singlets, respectively, are δ 5.95 ± 0.04 and 5.42 ± 0.11 (average separation = 0.53 ± 0.09 ppm), and the ranges for the two do not overlap. The methyl singlets appear at δ 1.62 ± 0.13.

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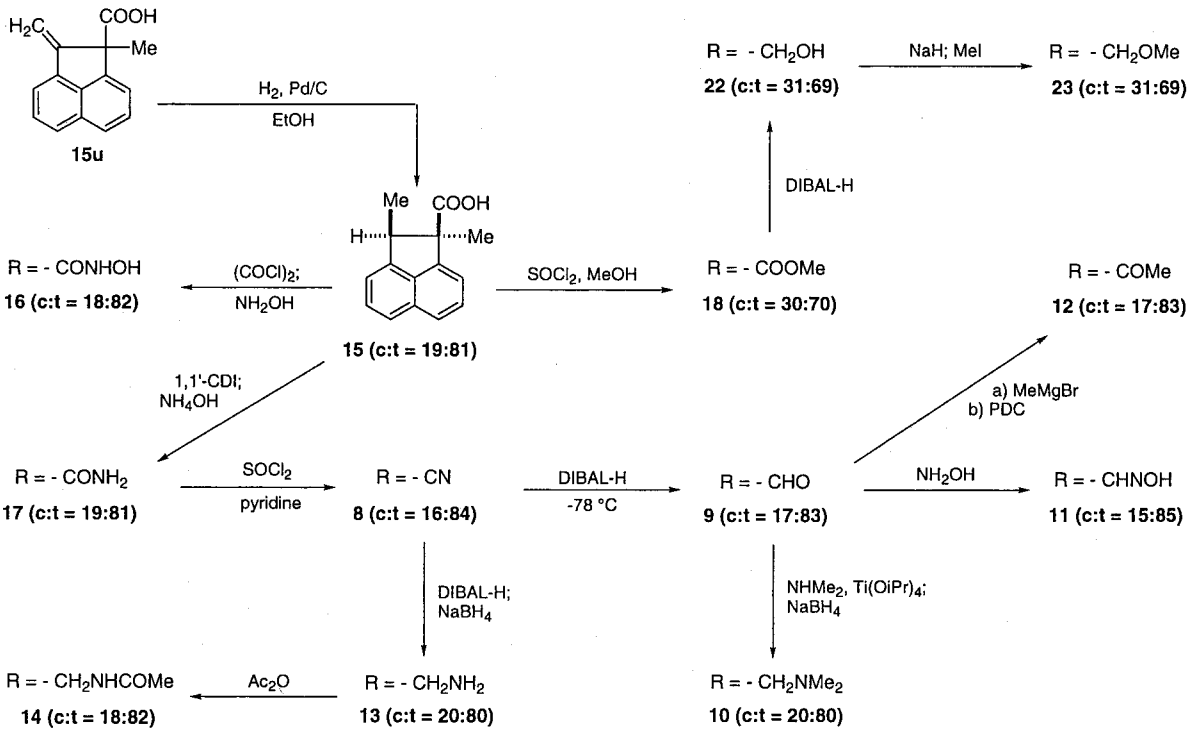
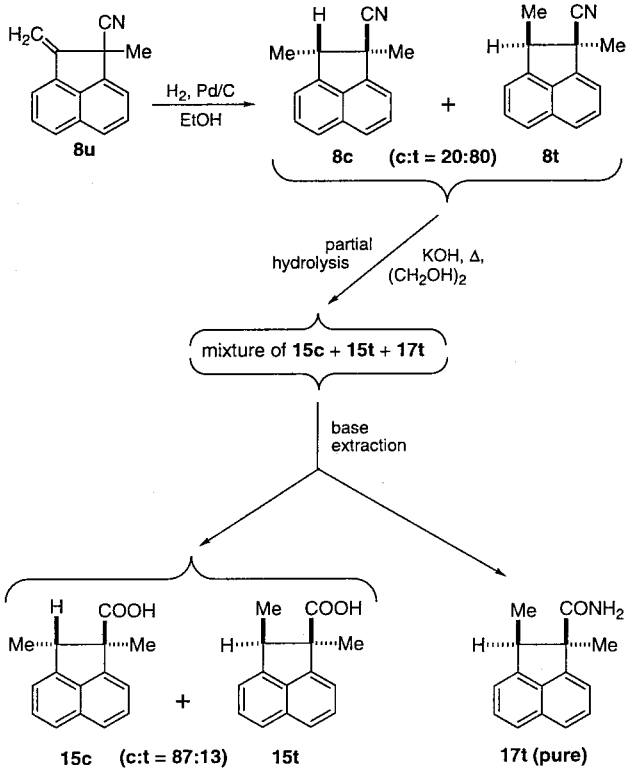
Scheme 4



Product Stereochemistry. We also needed to establish with certainty the stereochemistry of all our expected hydrogenation products via synthetic sequences independent of the individual hydrogenations. Our approach to this typically involves establishing unambiguous stereochemistry for at least one hydrogenation product, which is then used to synthesize the others in the same stereochemical series.[2,9] For this purpose, synthetic conversions such as R = COOH → CH_2NH_2 are obviously much easier to carry out than the reverse. Hence, even though we anticipated product ratios strongly favoring proximofacial[9] H_2 addition with R = CH_2NH_2, **13** was not a useful starting point for this process. However, hydrogenation of the unsaturated acid **15** provided a mixture rich in what was shown to be the distofacial[9] reduction product (**15c**:**15t** = 19:81). (The notations **c** (cis) and **t** (trans) specify the relative stereochemistry of the two methyl groups in the product, corresponding, respectively, to proximofacial and distofacial hydrogenation processes.) Although this product, like many of our cis/trans mixtures, was not readily separable, the absence of byproducts and the simplicity of the ^{1}H NMR spectra of its two components facilitated quantitation and enabled its direct use as a mixture for transformations to identify product stereochemistries by NMR.

The success of this approach depended on our being able, for every reduced mixture, to partition the integratable ^{1}H NMR signals and assign them to the individual diastereomers present. In practice, the peaks used were invariably the alkane signals, and most frequently the 1H benzylic quartet and the methyl doublet arising from reduction of the 2-methylene function, rather than the singlet for the 1-methyl group. Utilizing mixtures for the process of identifying these peaks in the first place would, of course, not be possible with mixtures close to 50:50. However, the 19:81 ratio for **15c**:**15t** offered us reasonable certainty that, e.g., the 19:81 ratio found for

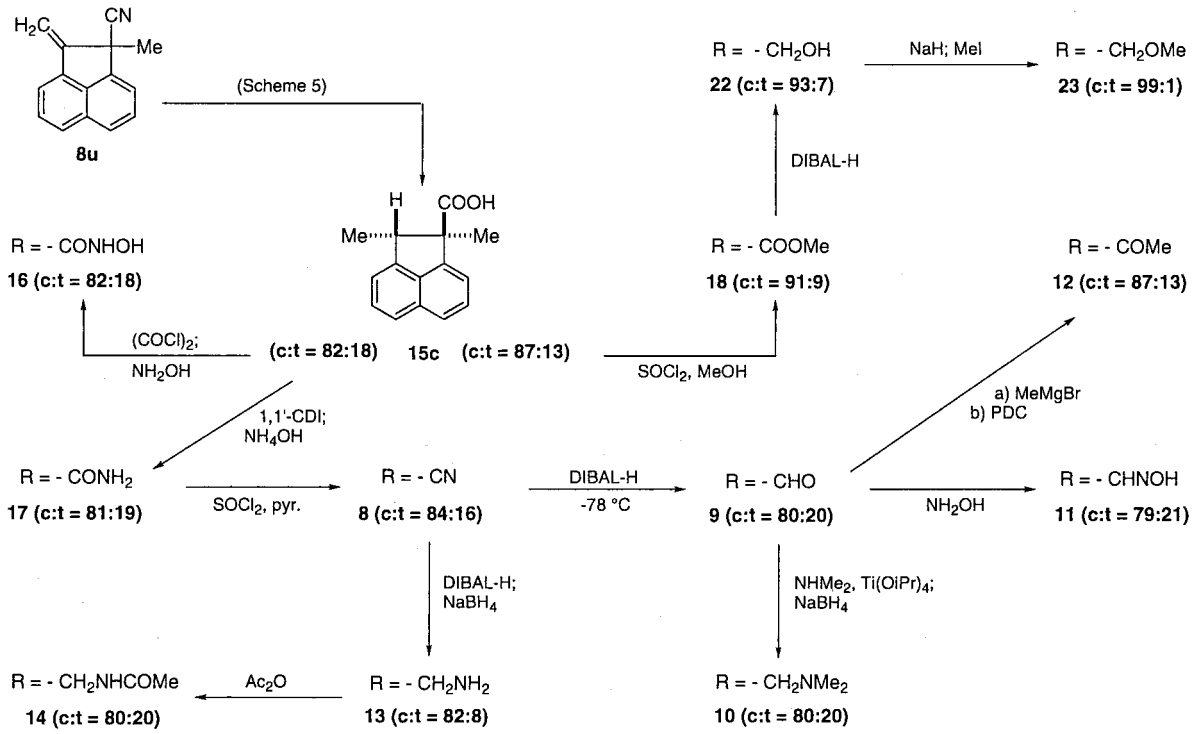
Scheme 5



the carboxamide mixture directly derived from **15c**:**15t** represented **17c**:**17t**, and not **17t**:**17c** (Scheme 4).

Fortunately, the ^{1}H NMR spectra of the mixtures produced in Scheme 4 were sufficiently clean that all peaks were readily assignable in every case. For each step in the set of transformations depicted, the cis:trans ratio for the product was thus readily assessable by ^{1}H NMR and remained quite close to that of its starting material. The sole exception involved the esterification **15** → **18**,

Scheme 6

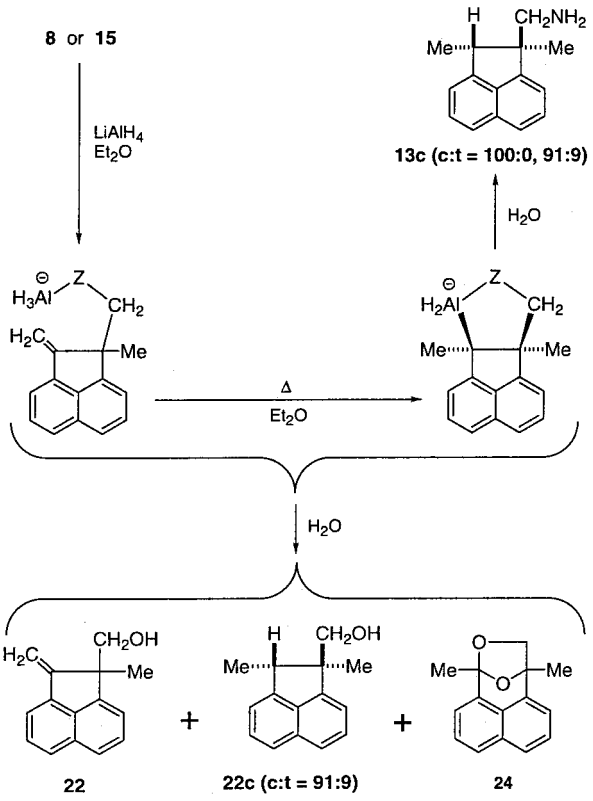


in which the ratio changed from 19:81 to 30:70. Although most of the actual proofs of stereochemistry for the reduced materials in our study hinged on compounds in the cis series (see below), this change is consistent with the assigned stereochemistries, which require greater hindrance about the substituent in **18t**.

This same hindrance about the substituent allowed us fortuitous entry into the cis series of reduced compounds via hydrogenation of the unsaturated nitrile **8** (Scheme 5), despite the fact that the initial binary product mix was rich in the trans diastereomer (**8c**:**8t** = 20:80). Selective hydrolysis gave a mixture from which all nitrile had been removed, but the cis amide **17c** was also essentially absent, as a result of its sterically less difficult hydrolysis compared to that of **17t**. The latter material persisted in the mixture and was separable in good purity from the reduced acids present by means of base extraction. The kinetically favored hydrolysis of **8c** and **17c** thus led to a recovered mixture of acids found to be rich in the cis diastereomer (**15c**:**15t** = 87:13), providing confirmation of our ^{1}H NMR assignments for the previous 19:81 mixture of **15c**:**15t**. Although the absolute yield of **15c** in this step was poor, its production gave us both confidence in our stereochemical assignments and enough material to carry forward the functional-group transformations shown in Scheme 6.

The transformations within Scheme 6 utilized reagents and conditions similar to those in the trans series (Scheme 4) but led to several alterations in the cis−trans product ratio, again consistent with greater hindrance about the functional group in the diastereomers assigned trans stereochemistry (Scheme 6). The sequence **15** → **18** → **22** → **23** produced a steady increase in cis content from 87 to 99%, while the transformation **9** → **12** gave a change in the cis:trans ratio from 80:20 to 87:13. Beyond these kinetic evidences, we were able to confirm the correctness of our stereochemical assignments by two other means.

Scheme 7



For two of our unsaturated materials, **8** and **15**, treatment with $LiAlH_4$ led to reduction of the alkene in addition to reduction of the functional group R (Scheme 7) and yielded **13c** and **22c**, respectively. Such internal delivery of hydride to alkenes by $LiAlH_4$ has been reported in several cases where combinations of favorable factors exist that have included strain in the alkene, advantageous ring size for the hydride delivery and

favorable ring size and/or carbanion stabilization for the (ultimately hydrolyzed) organoaluminum species formed.[6] A stereochemical study of one such case has demonstrated net syn addition of hydrogen, reflecting both internal hydride delivery and retention of configuration in the C−Al bond hydrolysis.[27]

Our previous demonstration of product stereochemistry consistent with such intramolecular hydride delivery in the case of **2** (R = CH_2OH) required high temperatures (142 °C).[6] In the present instance, the reactions of both **8** and **15** proceeded readily at 35 °C and both yielded 91:9 ratios of reduced-alkene products, consistent with the stereochemical assignments already made, i.e., cis:trans = 91:9. With **8**, lowering the hydride:substrate ratio from 5.5 to 2.5 equiv led to a product consisting entirely of **13c**, presumably by suppressing a minor intermolecular component of the reaction. In the case of **15**, although carboxyl reduction was complete, half of the product retained the alkene function, so that the product ratio for the entire isolated mixture was **22**:**22c**:**22t** = 49:44:4. Of the two obvious combinations of transition state plus organoaluminum intermediate for these processes, we have no direct evidence for but favor that involving seven-centered hydride delivery and five-membered organoaluminum species because of the benzylic stabilization the latter offers the polar C−Al bond.[6]

Further confirmation of our stereochemical assignments was achieved by means of a ^{1}H NOESY spectrum of a mixture of reduced oximes (**11c**:**11t** = 45:55). Of the six signals in the alkyl spectral region, we had assigned the 1H benzylic quartet (H-2) at δ 3.58, the methyl doublet at δ 1.42, and the methyl singlet at δ 1.64 all to **11t**. A NOESY cross-peak at δ 3.58-δ 1.42 confirmed this (vicinally coupled) relationship, and one at δ 3.58-δ 1.64 confirmed the cis stereochemical relationship between H-2 and the C-1 methyl, consistent with **11t**, where the distance between H-2 and the C-1 methyl carbon is ca. 2.45 Å. For **11c**, where this distance is ca. 3.15 Å, H-2 (δ 3.84) displayed a cross-peak with the methyl at C-2 but not with the methyl at C-1. These stereochemical assignments allowed reliable identification of all alkyl peaks in the ^{1}H NMR spectra of all our reduced compounds and revealed consistent patterns. The benzylic quartet in the cis isomers (av δ = 3.90) was invariably found farther downfield than in the corresponding trans species (av δ = 3.53), while the reverse was true for the methyl singlet (av δ = 1.61 for trans and 1.43 for cis).

We were now able to undertake the systematic hydrogenation of our unsaturated series **8**−**23** with confidence in our ability to assign correct stereochemistries and assess cis−trans ratios in our product mixtures. These hydrogenations were carried out at atmospheric pressure and room temperature, and the conditions, which employed absolute EtOH and the same batch of 5% Pd/C catalyst used previously with **1**−**3**, were chosen to allow as much comparison as possible with those systems.[3,9]

Hydrogenation Results. Table 1 shows the results of our hydrogenations of **8**−**23**, compared with those for our previously studied systems, including among the sixteen entries three functional groups we have never previously assessed (**10**, **14**, **23**). The entries are arranged in the "haptophilic order" found for **8**−**23**, i.e., decreasing content of proximofacial (cis) product. The previous case that this order most resembles (**3**) has only three nonzero entries, so that the internal haptophilic order is unknown for the remaining six R groups in that system, which are "off-scale" at the lower end. This was the result in **3** of an alkene so blocked at one face by the R group as to force exclusively distofacial hydrogenation wherever R did not provide strong haptophilic assistance.[9] This contrasts with system **2**, whose results may be viewed as off-scale at the opposite end (R = CH_2NH_2). With the present system, both diastereomers were detected in every product mixture, putting every group on scale.

Table 1. Percent Proximofacial[a] Product from Hydrogenation of Compounds 8−23 Compared with Results from Systems 1−3

			percent proximofcial product[b]			
compd	R	$P - 55$[c]	**8**−**23**[d]	**1**[e]	**2**[d,f]	**3**[d]
13	CH_2NH_2	33	87		100	63
10	CH_2NMe_2	115	62			
22	CH_2OH	21	48	95	9	19
11	CHNOH	36	45	65		
23	CH_2OMe	67	44			
9	CHO	10	42	93	95	18
17	$CONH_2$	37	33	10		0
14	CH_2NHAc	122	33			
19	$COO^- K^+$		30		76	0
12	COMe	49	22	14		
8	CN	11	20	75		
16	CONHOH	57	18		1	
15	COOH	20	17	18	26	0
18	COOMe	64	16	15	9	0
20	$COO^- Na^+$		10	55	70	0
21	$COO^- Li^+$		7	23	60	0

[a] "Proximofacial" and "distofacial" describe the stereochemistry of the reduction process itself, since cis/trans or syn/anti product nomenclature may not always accurately reflect this. [b] All hydrogenations were conducted at 25 °C and atmospheric pressure and assessed by NMR and/or GC. [c] Group parachors minus the value for methyl (55). [d] Solvent: absolute EtOH. [e] Solvent: 2-methoxyethanol. [f] Thompson, H. W.; O'Lenick, A. J., Jr. Unpublished results.

That the haptophilic effect depends strongly on basicity or electron availability is seen in the pattern for the carboxylate salts but is most evident from the positions of the amines (**13** and **10**) as compared to those of the amides (**17** and **14**) and all other groups, a result also observed in system **3**. It is also clear from **13** vs **10**, from **22** vs **23**, and from the acids vs their methyl esters that steric effects play a measurable role. Alongside the haptophilic order for **8**−**23**, Table 1 presents approximate steric volumes for the R groups, based on group parachors (P).[28] Because the two faces of our system differ only in the C-1 substituents, each product ratio represents a haptophilic competition between the R group present and methyl. We have therefore subtracted from each parachor the value for methyl (55), so that the resulting numbers simultaneously describe the relative group sizes and the size differences between R and methyl. The scatter of these tabulated parachors makes it evident that no explanation of haptophilicity is possible on the basis of size alone.

On the basis of the results from **8**−**23**, the functionalities involved may be divided, somewhat arbitrarily, into four groups, presenting high, moderate, low, and no haptophilicity. The two amino functions, **13** and **10**, both produce well over 50% of proximofacial product, clearly

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demonstrating an interaction with the catalyst that is strong and only modestly diminished by substitution. The alcohol, aldoxime, methyl ether, and aldehyde display little internal differentiation and give a proximofacial product in the range of 42−48%. Since the group sizes involved range from slightly to significantly larger than methyl, this result suggests moderate haptophilic behavior. The two amides and the potassium salt produce proximofacial/distofacial ratios in the range of 1:2, arguably not much different from what might be expected on the basis of steric effects alone, while the remaining groups all behave essentially as would be predicted on the basis of merely steric hindrance. In our previous discussions of the origins of haptophilicity, we have viewed it as a catalyst adsorption intermediate in strength and duration between poisoning and the sort of weak π "chemisorption" commonly invoked in the early stages of detailed hydrogenation mechanisms. It is noteworthy that amines are well-known as mild catalyst poisons, an effect that can be obviated by quaternization.

Hopes of controlling hydrogenation stereochemistry require that experimental haptophilicities be transferable in some degree from one molecular system to another. Hence, some importance becomes attached to the similarities and differences revealed by Table 1 among the haptophilic orders found in the four substrate systems so far employed. There appears to be good conformity between systems **8**−**23** and **3**, but this may mostly reflect the scant data on the internal ordering within **3**. For system **2**, the entries out of place in the present haptophilic ordering are the Na and Li carboxylates, plus CH_2OH. For system **1**, the entries most out of place with the present ordering are the same two carboxylates, plus $CONH_2$ and CN. The most striking consistencies overall involve CH_2NH_2, CHO, COMe, COOH, and COOMe, although data for specific entries are lacking for some of the systems. Taking into account the consistencies and inconsistencies in Table 1, together with the general utility of the various groups toward further synthetic transformations, it would appear that, in the absence of specific studies on any system of potential interest, the most generally useful group for inducing proximofacial H_2 addition may be CHO. At the other end of the scale, the group most generally useful for inducing distofacial H_2 addition is probably COOMe (or esters of even greater bulk). Below, we describe further experiments that extend the practical usefulness of the principle of haptophilicity.

Solvent Enhancement of Haptophilicity. Hydrogenation stereochemistry is sometimes markedly influenced by the solvent chosen.[29] Enhancement of haptophilicity by this means has been demonstrated in some cases[14] and is generally interpreted in terms of diminished solvent−substrate competition for the catalyst sites the haptophile must occupy in order to be effective. Our previous results in this area employed system **2** (R = CH_2OH), where we showed that a clear and progressive increase in haptophilic effectiveness accompanied a lowering of the solvent dielectric constant.[5] By extending this to the present system, we have now demonstrated significant solvent-based enhancements of haptophilicity not only for CH_2OH (**22**) but for the nitrile (**8**), carboxylic acid (**15**), and carboxamide (**17**) as well. Table 2 shows these results, which not only offer a means of significantly enhancing haptophilicities for several specific groups but also suggest that such solvent enhancement may be quite general. We have intentionally chosen the compounds tested here to reflect a broad range of haptophilic behavior (in EtOH), so it is worth noting that this solvent enhancement operates over the entire range of groups chosen, giving an average "improvement ratio" of roughly 2.1 ± 0.4. It should also be noted that the ordering of the groups is unchanged and that the improvement in haptophilicity is proportionally the greatest for the entries of low haptophilicity, although that may be in part simply because those species start from lower base values. The results suggest that low haptophilicities may in part reflect a poor ability to compete with polar solvents, particularly ones containing alcohol and ether functions, which are commonly used and are seen in system **8**−**23** as moderately effective haptophiles. It appears that, even for groups of low relative haptophilicity, their absolute haptophilicities may be considerably improved by suppressing this competition.

Table 2. Percent Cis Product from Hydrogenations Employing Solvents of Low Dielectric Constant[a]

compd	R	% cis in EtOH	solvent (ratio)	% cis	improvement[b]
22	CH_2OH	48	cyclohexane	75	1.56
17	$CONH_2$	33	cyclohexane/Et_2O (1:1)	57	1.73
8	CN	20	cyclohexane	54	2.7
15	COOH	17	hexane/$CHCl_3$ (9:1)	40	2.35

[a] Hydrogenations were conducted under standard conditions (5% Pd/C at 25 °C and atmospheric pressure) and assessed by NMR and/or GC. [b] Percent cis in the specified solvent divided by percent cis in EtOH.

Experimental Section

General Methods. Melting points were taken in open capillaries and are uncorrected. Unless otherwise specified, NMR spectra were taken on $CDCl_3$ solutions operating at 199.785 and 399.798 MHz for ^1H and 100.554 MHz for ^{13}C. ^1H NMR coupling constants (J) are given in hertz. Low-resolution electron-impact (EI) and isobutane chemical-ionization (CI) mass spectra were obtained by direct injection into a mass spectrometer at typical energies of 70 eV and an ionizing current of approximately 30 microamps. Fast-atom bombardment mass spectra (FABMS) utilized a matrix of 3-nitrobenzyl alcohol; the primary Xe beam had a maximum energy of 8 keV, and positive ions were accelerated over a potential of 7 keV. High-resolution mass spectra (HRMS) were obtained in the peak-matching mode using an instrument calibrated to a resolution of 10 000 with a 10% valley between peaks, using perfluorokerosene. Gas chromatograms (GC) were obtained using a system equipped with a 15 m × 0.20 mm × 0.33μ column and with the oven programmed from 100 to 325 °C. Flash chromatography employed a column packed with Silica Gel 60, pore size 60 Å, particle size 200−500 μm, or 40−140 mesh silica gel. Thin-layer chromatography (TLC) employed plates coated with Silica Gel 60 F_{254}; developed plates were visualized either with I_2 or a UV lamp.

1-(1-Naphthyl)propionic Acid (4, R = Me). To a stirred −78 °C solution of 200 mL (400 mmol) of $LiN(^iPr)_2$ in 800 mL of dry THF under Ar was added 37.24 g (200 mmol) of 1-naphthylacetic acid in 200 mL of dry THF dropwise over 25 min. The solution was stirred at 0 °C for 1 h and recooled to −78 °C, and a single portion of 18.75 mL (301 mmol) of MeI was added. After the mixture was stirred overnight at room temperature, the reaction was quenched with water; the mixture was vacuum-concentrated, and the residue was dis-

(29) (a) Augustine, R. L. *Catalytic Hydrogenation: Techniques and Applications in Organic Synthesis*; Marcel Dekker: New York, 1965; pp 45−49. (b) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; Benjamin/Cummings: Menlo Park, CA, 1972; pp 26−28.

solved in water. Extraction with Et_2O both before and after acidification yielded 38.38 g (96%) of **4** (R = Me) as a white solid: mp 141−143 °C (lit. 152−3 °C,[30] 140−142 °C[31]); IR ($CHCl_3$) 3500−2200 (br), 1747, 1710 cm^{-1}; ^1H NMR (400 MHz) δ 8.08 (1 H, d, J = 7.7), 7.87 (1 H, d, J = 8.5), 7.78 (1 H, d, J = 7.7), 7.50 (4 H, complex), 4.54 (1 H, q, J = 6.8), 1.67 (3 H, d, J = 6.8); MS (EI), *m/e* (relative intensity) 599.2 (13), 400.2 (24), 399.2 (100), 200.2 (6), 199.2 (43), 155.1(22); HRMS (EI) calcd for $C_{13}H_{12}O_2$ 200.0837, found 200.0841.

2-Methylacenaphthone (5). To a stirred 25 °C suspension of 38.38 g (191.8 mmol) of **4** (R = Me) in 650 mL of dry CH_2Cl_2 under Ar was added 21.8 mL (250 mmol) of $(COCl_2)_2$ dropwise over 30 min. After stirring at 25 °C for 3.5 h, the solution was vacuum-concentrated. To the residue, stirred in 550 mL of dry CH_2Cl_2 under a strong stream of Ar at −78 °C, was added 44.5 g (334 mmol) of $AlCl_3$ in portions. After the mixture was stirred overnight at room temperature, the reaction was quenched at −78 °C by dropwise addition of 200 mL of 4 N HCl. The organic layer combined with the CH_2Cl_2 extracts of the aqueous layer yielded a crude oil. Flash chromatography on silica gel afforded 27 g (77%) of **5** as a colorless oil, which solidified when chilled: mp 32−34 °C (lit.[29] 33−34 °C); IR ($CHCl_3$) 1717, 1626 cm^{-1}; ^1H NMR (400 MHz) δ 8.10 (1 H, d, J = 7.7), 7.97 (1 H, d, J = 6.8), 7.83 (1 H, d, J = 7.7), 7.73 (1 H, t, J = 7.7), 7.63 (1H, t, J = 6.8), 7.47 (1 H, d, J = 6.8), 3.75 (1 H, q, J = 7.7), 1.58 (3 H, d, J = 7.7); MS (EI), *m/e* (relative intensity) 182.1 (97), 167.1 (14), 154.2 (54), 153.1 (100), 139.1 (13), 76.1 (26), 63.0 (24); HRMS (EI) calcd for $C_{13}H_{10}O$ 182.0732, found 182.0730.

1-Cyano-2-methylacenaphthylene (6). To a stirred 25 °C mixture of 9.0 g (49 mmol) of ketone **5** and 9.0 mL (68 mmol) of Me_3SiCN under Ar was added 10 drops of $BF_3{\cdot}OEt_2$ dropwise. The mixture was heated to 60 °C, and another 10 drops of $BF_3{\cdot}OEt_2$ was added, followed by 45 mL of anhydrous pyridine and 9.0 mL (97 mmol) of $POCl_3$. The mixture was then heated at 100 °C for 1 h, cooled, poured onto 100 g of ice, and extracted with EtOAc. The combined extracts were washed with 1 N HCl and brine, dried, and vacuum-concentrated. Flash chromatography on silica gel afforded 6.13 g (65%) of **6** as a yellow powder: mp 108−110 °C; IR ($CHCl_3$) 2216, 1625 cm^{-1}; ^1H NMR (400 MHz) δ 7.99 (1 H, d, J = 7.7), 7.86 (1 H, d, J = 6.8), 7.84 (1H, d, J = 7.7), 7.75 (1 H, d, J = 6.8), 7.65 (1 H, t, J = 7.7), 7.59 (1 H, t, J = 6.8), 2.66 (3 H, s); ^{13}C NMR δ 153.28, 137.69, 136.07, 130.63, 128.26 (2C), 128.12, 127.72, 127.43, 125.249, 122.93, 115.86, 108.04, 12.97; MS (EI), *m/e* (relative intensity) 192.1 (6), 191.1 (58), 190.1 (100), 189.1 (5), 188.1 (7), 186.0 (6); HRMS (EI) calcd for $C_{14}H_9N$ 191.0735, found 191.0732.

1-Cyano-1-methyl-2-methyleneacenaphthene (8). To a stirred 0 °C solution of 25.3 mL (181 mmol) of $(^iPr)_2NH$ in 250 mL of dry THF under Ar was added 110 mL of *n*-BuLi (1.6 N in hexane, 176 mmol). After stirring for 15 min, the mixture was cooled to −78 °C and 16.78 g (87.8 mmol) of **6** in 100 mL of dry THF was added dropwise over 15 min. The mixture was stirred for 45 min at 0 °C and then recooled to −78 °C, and 11.6 mL (95.9 mmol) of *N,N′*-dimethylpropyleneurea was added, followed by 16.3 mL (262 mmol) of CH_3I in 65 mL of dry THF, added dropwise over 15 min. The mixture was stirred for 30 min, transferred to a −40 °C bath, and allowed to warm to −15 °C over 20 min. The cold bath was removed for 20 min, and the reaction was quenched with water; the mixture was then vacuum-concentrated and redissolved in CH_2Cl_2. After successive washes with 3% HCl and brine, the organic layer was dried and vacuum-concentrated. Flash chromatography on silica gel afforded 16.65 g (92%) of **8** as an oil that solidified when chilled: mp 54−57 °C; IR ($CHCl_3$) 2239, 1622 cm^{-1}; ^1H NMR (400 MHz) δ 7.79 (2 H, d, J = 6.0), 7.62 (3 H, complex), 7.53 (1 H, d, J = 6.8), 6.05 (1 H, s), 5.72 (1 H, s), 1.87 (3 H, s); ^{13}C NMR δ 150.28, 141.54, 136.77, 136.61, 131.39, 128.70, 128.36, 125.54, 125.06, 122.02, 122.02, 118.74, 117.40, 108.88, 28.25; MS (EI), *m/e* (relative intensity) 205.2 (42), 190.2 (100), 176.2 (5), 163.2 (9), 81.7 (7); HRMS (EI) calcd for $C_{15}H_{11}N$ 205.0891, found 205.0891.

1-Cyano-*trans*-1,2-dimethylacenaphthene (8t). Method A. To a stirred 25 °C solution of 200 mg (0.89 mmol) of the subsequently described mixture of carboxamides **17t** (84%) and **17c** (16%) in an anhydrous mixture of 25 mL of 4:1 THF/pyridine under N_2 was added 1.0 mL (14 mmol) of $SOCl_2$. The mixture was refluxed for 1 h, poured onto ice, and extracted with CH_2Cl_2. The combined organic layers were washed successively with 2 N NaOH and brine, dried, and vacuum-concentrated. Flash chromatography on silica gel afforded 140 mg (76%) of a mixture of **8t** (84%) and **8c** (16%) as a faintly yellowish solid: mp 46−49 °C; IR of the mixture (CH_2Cl_2) 2233, 1624 cm^{-1}; ^1H NMR of the major component (400 MHz) δ 7.76 (1 H, d, J = 8.1), 7.70 (1 H, d, J = 8.1), 7.58 (1 H, d, J = 7.1), 7.54 (2 H, complex), 7.30 (1 H, d, J = 6.8), 3.59 (1 H, q, J = 7.2), 1.83 (3 H, s), 1.67 (3 H, d, J = 7.1); MS (EI) of the mixture, *m/e* (relative intensity) 207.1 (67), 192.1 (89), 165.0 (100), 152.1 (13); MS (CI) of the mixture 208.1 (6), 181.1 (100), 81.1 (11), 71.1 (15), 70.1 (11), 69.1 (15); HRMS (EI) calcd for $C_{15}H_{13}N$ 207.1048, found 207.1044.

Method B. Catalytic hydrogenation of 1.0 g (4.9 mmol) of nitrile **8** under the standard conditions described below yielded a yellowish oil containing some solvent. The product was loaded onto a plug of silica gel; solvent was washed out, and the product was eluted, giving 1.0 g (99.5%) of a mixture of **8t** (80%) and **8c** (20%) as a faintly yellowish solid with NMR essentially identical to that obtained by Method A.

1-Cyano-*cis*-1,2-dimethylacenaphthene (8c). A stirred 25 °C solution of 270 mg (1.20 mmol) of a mixture of carboxamides **17c** (81%) and **17t** (19%) in 37.5 mL of anhydrous 4:1 THF/pyridine under N_2 was treated with 1.5 mL (21 mmol) of $SOCl_2$ and worked up as described above for **8t** (Method A), affording 200 mg (81%) of a mixture of **8c** (84%) and **8t** (16%) as a yellowish solid: mp 88−94 °C; IR (CH_2Cl_2) of the mixture 2233, 1603 cm^{-1}; ^1H NMR of the major component (200 MHz) δ 7.76 (1 H, d, J = 8.2), 7.70 (1 H, d, J = 8.1), 7.55 (3 H, complex), 7.26 (1 H, d, J = 7.3), 4.20 (1 H, q, J = 7.6), 1.61 (3 H, s), 1.58 (3 H, d, J = 7.6); ^{13}C NMR of the mixture δ 144.68, 144.52, 131.38, 128.60, 128.26, 124.91, 124.00, 123.63, 119.81, 119.43, 119.22, 119.09, 48.77, 29.71, 27.71, 23.30, 13.74; MS (EI) of the mixture, *m/e* (relative intensity) 207.1 (75), 192.1 (100), 165.0 (95), 152.1 (12); MS (CI) of the mixture 208.1 (5), 182.1 (9), 181.1 (100); HRMS (EI) calcd for $C_{15}H_{13}N$ 207.1048, found 207.1051.

1-Aminomethyl-1-methyl-2-methyleneacenaphthene (13). Method A. To a stirred −78 °C solution of 200 mg (0.98 mmol) of nitrile **8** in 6 mL of dry Et_2O under Ar was added 5.0 mmol of DIBAL-H (5.0 mL, 1.0 M in toluene). After the mixture was stirred for 25 min, 223 mg (5.8 mmol) of $NaBH_4$ was added and this mixture was stirred for 30 min. It was then allowed to warm to −15 °C, and an additional 200 mg (5.3 mmol) of $NaBH_4$ was added. This mixture was kept between −10 and −15 °C for 15 min and then cooled to −78 °C, and the reaction was quenched by slow, careful addition of MeOH, followed by saturated $NaHCO_3$. After filtration and CH_2Cl_2 extraction, the extracts were washed with NaOH and brine, dried, and concentrated. Flash chromatography afforded 140 mg (68%) of **13** as a faintly brownish oil: IR (CH_2Cl_2) 3361, 3296, 1660, 1615 cm^{-1}; ^1H NMR (400 MHz) δ 7.68 (2 H, complex), 7.58 (3 H, complex), 7.25 (1 H, d, J = 6.8), 5.93 (1 H, s), 5.28 (1 H, s), 3.03 (2 H, dd, J = 12, 8), 1.43 (3 H, s); MS (EI), *m/e* (relative intensity) 209.1 (6), 181.1 (17), 180.1 (100), 179.1 (67), 178.0 (55), 84.1 (44); HRMS (EI) calcd for $C_{15}H_{15}N$ 209.1204, found 209.1208.

Method B. To a stirred 25 °C solution of 210 mg (1.0 mmol) of alcohol **22**, 151 mg (1.03 mmol) of phthalimide, and 270 mg (1.03 mmol) of Ph_3P in 8 mL of freshly distilled THF was added 213 μL (1.03 mmol) of diethyl azodicarboxylate in 1 mL of toluene dropwise, and stirring was continued for 16 h. Concentration to a crude oil and flash chromatography afforded 150 mg of the *N*-phthalimidomethyl species as a white foam: IR (CH_2Cl_2) 1618 cm^{-1}; ^1H NMR (400 MHz) δ 7.79 (2 H, complex), 7.69 (4 H, complex), 7.59 (1 H, d, J = 6.8), 7.50 (2 H, overlapping t, J = 7.7, 8.5), 7.26 (1H, d, J = 6.8), 5.90 (1 H,

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s), 5.38 (1 H, s), 4.00 (2 H, s), 1.63 (3 H, s); MS (FAB+), *m/e* (relative intensity) 340.1 (58), 339.1 (57), 307.1 (27), 289.1 (14), 279.1 (24), 154.0 (100), 136 1(69); HRMS (EI) calcd for $C_{23}H_{17}NO_2$ 339.1259, found 339.1260.

To a stirred 25 °C solution of 87 mg (0.26 mmol) of the above *N*-phthalimidomethyl derivative in 8 mL of absolute EtOH was added 300 μL (2.6 mmol) of $N_2H_4 \cdot H_2O$. After 16 h of reflux, the mixture was concentrated to dryness and extracted with aqueous $NaHCO_3$ and Et_2O. The combined organic layers afforded 40 mg of crude product with ^{1}H NMR spectrum essentially identical to that of **13** produced by Method A.

1-Aminomethyl-*trans*-1,2-dimethylacenaphthene (13t). Method A. A stirred −78 °C solution of a mixture of nitriles **8t** (80%) and **8c** (20%) (300 mg, 1.45 mmol) in 10 mL of anhydrous THF under Ar was treated with 12.0 mmol of DIBAL-H (12.0 mL, 1.0 M in toluene) followed by a single portion of 78 mg (2.0 mmol) of $NaBH_4$, as described above for **13** (Method A). Workup afforded 123 mg (40%) of a mixture of **13t** (80%) and **13c** (20%) as a faintly yellowish oil: IR of the mixture (CH_2Cl_2) 3338 (br), 1666, 1603 cm^{-1}; ^{1}H NMR of the major component (400 MHz) δ 7.65 (1 H, d, J = 8.2), 7.62 (1 H, d, J = 8.1), 7.50 (2 H, complex), 7.25 (1 H, d, J = 7.6), 7.21 (1 H, d, J = 6.3), 3.44 (1 H, q, J = 7.4), 2.83 (2 H, broad), 1.52 (3 H, d, J = 7.4), 1.48 (3 H, s); MS (EI) of the mixture, *m/e* (relative intensity) 211.1 (4), 167.1 (64), 166.1 (40), 165.1 (100), 153.1 (13), 152.1 (26), 83.1 (10), 70.1 (31); MS (CI) of the mixture 212.1 (100), 183.1 (84), 181.0 (24); HRMS (EI) calcd for $C_{15}H_{17}N$ 211.1361, found 211.1352.

Method B. To a stirred solution of a mixture of 150 mg (0.67 mmol) of carboxamides **17t** (84%) and **17c** (16%) in 10 mL of anhydrous THF cooled in an ice bath was added 150 mg (3.95 mmol) of $LiAlH_4$, and the mixture was stirred for 1 h. An additional 10 mL of anhydrous THF and 150 mg (3.95 mmol) of $LiAlH_4$ were added, and the mixture was stirred for 1 h. The mixture was chilled; the reaction was quenched by slow addition of H_2O followed by 2 N NaOH, and then the mixture was extracted. The combined, washed, and dried organic portions were concentrated and flash-chromatographed to afford 100 mg (71%) of a mixture of **13t** (83%) and **13c** (17%) as a faintly yellowish oil with ^{1}H NMR essentially identical to that of the material obtained by Method A.

1-Aminomethyl-*cis*-1,2-dimethylacenaphthene (13c). Method A. A stirred −78 °C solution of a mixture of 65 mg (0.31 mmol) of nitriles **8c** (84%) and **8t** (16%) in 2.0 mL of anhydrous THF under Ar was treated with 2.0 mmol of DIBAL-H (2.0 mL, 1.0 M in toluene) followed by 148 mg (3.8 mmol) of $NaBH_4$ in two portions, as described above for **13** (Method A), to afford 30 mg (46%) of a mixture of **13c** (82%) and **13t** (18%) as a faintly yellowish oil: IR of the mixture (CH_2Cl_2) 3700−3100 (br), 1660, 1618 cm^{-1}; ^{1}H NMR of the major component (200 MHz) δ 7.69 (2 H, complex), 7.51 (2 H, complex), 7.32 (2 H, complex), 3.58 (1H, q, J = 7.4), 3.02 (2 H, broad), 1.38 (3 H, d, J = 7.1), 1.28 (3 H, s); MS (EI), *m/e* (relative intensity) 182.1 (69), 181.1 (100), 167.0 (23), 166.1 (37), 165.1 (94); MS (CI) 213.1 (14), 212.1 (100), 183.1 (4), 182.1 (2); HRMS (EI) calcd for $C_{15}H_{17}N$ 211.1361, found 211.1359.

Method B. Internal Delivery of Hydride Using $LiAlH_4$. To a 25 °C slurry of 100 mg (2.6 mmol) of $LiAlH_4$ in 5.0 mL of anhydrous Et_2O was added 100 mg (0.49 mmol) of nitrile **8** dropwise over 5 min. The reaction mixture was stirred for 15 min, refluxed for 1.5 h, and cooled, and the reaction was quenched by slow H_2O addition. Concentration of the dried extracts yielded 89 mg (87%) of a mixture of **13c** (91%) and **13t** (9%) as a crude oil with ^{1}H NMR essentially identical to that of **13c** obtained by Method A. A similar reaction carried out with only half as much $LiAlH_4$ produced **13c** exclusively.

1-Acetamidomethyl-1-methyl-2-methyleneacenaphthene (14). To a stirred 25 °C solution of 140 mg (0.67 mmol) of amine **13** in 2.5 mL of anhydrous MeOH under Ar was added 700 μL (7.4 mmol) of Ac_2O. After this solution had been stirred for 16 h and concentrated to dryness, the residue was dissolved in CH_2Cl_2 and washed with 6 N NaOH and then brine. The dried and concentrated organic layer yielded 140 mg (84%) of **14** as an off-white solid: mp 125−126 °C; IR ($CHCl_3$) 3289, 1654, 1550 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.72 (2 H, complex), 7.58 (3 H, complex), 7.30 (1 H, d, J = 6.8), 5.91 (1 H, s), 5.37 (1 H, s), 5.03 (1 H, broad), 3.80 (1 H, dd, J = 7.4), 3.67 (1H, dd, J = 7.8), 1.65 (3 H, s), 1.45 (3 H, s); MS (EI), *m/e* (relative intensity) 192.1 (39), 179.1 (100), 152.1 (11), 69.1 (15); HRMS (EI) calcd for $C_{17}H_{17}NO$ 251.1310, found 251.1321.

1-Acetamidomethyl-*trans*-1,2-dimethylacenaphthene (14t). Treatment of 60 mg (0.28 mmol) of a mixture of amines **13t** (83%) and **13c** (17%) with 500 μL (5.3 mmol) of Ac_2O as described above for **14** afforded 48 mg (68%) of a mixture of **14t** (82%) and **14c** (18%) as a white solid: mp 155−165 °C; IR of the mixture (CH_2Cl_2) 3285, 1661, 1566, cm^{-1}; ^{1}H NMR of the major component (400 MHz) δ 7.67 (1 H, d, J = 8.4), 7.64 (1 H, d, J = 8.4), 7.52 (2 H, overlapping t), 7.25 (2 H, complex), 4.85 (1 H, broad), 3.57 (1 H, dd, J = 6.0, 7.4), 3.45 (1 H, q, J = 7.3), 3.29 (1 H, dd, J = 5.7, 7.7), 1.73 (3 H, s), 1.51 (3 H, d, J = 7.4), 1.50 (3H, s); MS (EI), *m/e* (relative intensity) 253.1 (1), 194.1 (12), 183.1 (13), 182.1 (22), 181 (100), 167 (27), 166.1 (32), 165.1 (72) 153 (16.1), 153.1 (16), 152.1 (21), 83.1 (12), 71.1 (12), 57.1 (28), 55.1 (18); MS (CI) 255.1 (18), 254.1 (100), 226.1 (34), 181.1 (12), 91.1 (18); HRMS (EI) calcd for $C_{17}H_{19}NO$ 253.1467, found 253.1476.

1-Acetamidomethyl-*cis*-1,2-dimethylacenaphthene (14c). Treatment of 30 mg (0.14 mmol) of a mixture of amines **13c** (80%) and **13t** (20%) with 400 μL (4.2 mmol) of Ac_2O as described above for **14** afforded 27 mg (76%) of a mixture of **14c** (80%) and **14t** (20%) as a white solid: mp 170−177 °C; IR of the mixture (CH_2Cl_2) 3285, 3222, 2868, 1647, 1566, cm^{-1}; ^{1}H NMR of the major component (200 MHz) δ 7.71 (2 H, complex), 7.56 (2 H, complex), 7.27 (2 H, complex), 5.15 (1 H, broad), 3.85 (1 H, pair of doublets, J = 8.1, 8.1), 3.51 (1 H, q, J = 7.2), 3.45(1 H, pair of doublets, J = 4.4, 4.4), 1.78 (3 H, s), 1.38 (3 H, d, J = 7.1), 1.28 (3 H, s); MS (EI), *m/e* (relative intensity) 253.1 (4), 194 (30), 181.1 (100), 166.1 (22), 165.1 (53), 73.1 (13), 69.1 (13), 57.1 (24), 55.1 (18); MS (CI) 256.1 (6), 255.1 (15), 254.1 (100); HRMS (EI) calcd for $C_{17}H_{19}NO$ 253.1467, found 253.1468.

1-Methyl-2-methyleneacenaphthene-1-carboxaldehyde (9). Method A. To a stirred −78 °C solution of 1.0 g (4.9 mmol) of nitrile **8** in 30 mL of dry Et_2O under Ar was added 25.0 mmol of DIBAL-H (25.0 mL, 1.0 M in toluene). The solution was stirred for 30 min at −78 °C before the reaction was quenched by slow addition of EtOH. The warmed solution was filtered through a short layer of Celite, which was washed with excess Et_2O. The combined, concentrated organic portions were flash-chromatographed on 75 g of silica gel with 3:2 hexane/CH_2Cl_2 to afford 840 mg (82%) of **9** as a colorless oil: IR ($CHCl_3$) 2824, 1720, 1601 cm^{-1}; ^{1}H NMR (400 MHz) δ 9.32 (1 H, s), 7.77 (2 H, t, J = 8.5), 7.66 (1 H, d, J = 6.8), 7.60 (1 H, d, J = 7.7), 7.55 (1 H, t, J = 8.5), 7.25 (1 H, d, J = 6.8), 6.03 (1 H, s), 5.32 (1 H, s), 1.56 (3 H, s); MS (EI), *m/e* (relative intensity) 208.1 (56), 195.1 (54), 179.1 (100), 165.1 (29), 152.1 (23); HRMS (EI) calcd for $C_{15}H_{12}O$ 208.0888, found 208.0894.

Method B. To a stirred 25 °C solution of 575 mg (2.74 mmol) of alcohol **22** in 20 mL of anhydrous CH_2Cl_2 was added 1.38 g (3.65 mmol) of pyridinium dichromate, and the mixture was stirred for 16 h. The solution was diluted with CH_2Cl_2, filtered through Celite, washed alternately with brine and $NaHCO_3$, dried, and passed through a plug of silica gel to afford 200 mg (35%) of **9** as a colorless oil with ^{1}H NMR essentially identical to that produced by Method A.

***trans*-1,2-Dimethylacenaphthene-1-carboxaldehyde (9t).** After 300 mg (1.45 mmol) of a mixture of nitriles **8t** (84%) and **8c** (16%) had been treated with 8.0 mmol of DIBAL-H (8.0 mL, 1.0 M in toluene) and stirred for 30 min as described above for **9** (Method A), the mixture was kept at between −20 and −10 °C for 2.5 h and worked up to afford 170 mg (56%) of a mixture of **9t** (83%) and **9c** (17%) as a colorless oil: IR of the mixture (CH_2Cl_2) 2812, 2712, 1721, 1603 cm^{-1}; ^{1}H NMR of the major component (400 MHz) δ 9.44 (1 H, s), 7.72 (1 H, d, J = 8.5), 7.69 (1 H, d, J = 8.4), 7.54 (2 H, complex), 7.28 (1 H, d, J = 6.9), 7.18 (1 H, d, J = 7.0), 3.66 (1 H, q, J = 7.6), 1.60 (3 H, s), 1.52 (3 H, d, J = 7.7); MS (EI) of the mixture, *m/e* (relative intensity) 210.1 (8), 182 (7), 181.1 (100), 166.1

(24), 165.0 (64); MS (CI) of the mixture 212.1 (13), 211.1 (100), 181.1 (2); HRMS (EI) calcd for $C_{15}H_{14}O$ 210.1045, found 210.1037.

***cis*-1,2-Dimethylacenaphthene-1-carboxaldehyde (9c).** After 110 mg (0.53 mmol) of a mixture of nitriles **8c** (84%) and **8t** (16%) had been treated with 3.0 mmol of DIBAL-H (3.0 mL, 1.0 M in toluene) as described above for **9** (Method A), the solution was kept at between −20 and −10 °C for 30 min and worked up to afford 73 mg (66%) of a mixture of **9c** (80%) and **9t** (20%) as a colorless oil: IR of the mixture (CH_2Cl_2) 2871, 1720, 1596 cm^{-1}; ^1H NMR of the major component (200 MHz) δ 9.57 (1 H, s), 7.75 (2 H, overlapping d), 7.54 (2 H, overlapping t), 7.38 (1 H, d, J = 7.7), 7.23 (1 H, d, J = 7.2), 4.07 (1 H, q, J = 7.5), 1.48 (3 H, s), 1.40 (3 H, d, J = 7.1); MS (EI) of the mixture, *m/e* (relative intensity) 210.1 (8), 182.1 (12), 181.1 (100), 166.1 (23), 165.1 (63); MS (CI) of the mixture 212.1 (14), 211.1 (100), 197.1 (21), 181.1 (66); HRMS (EI) calcd for $C_{15}H_{14}O$ 210.1045, found 210.1042.

1-Methyl-2-methyleneacenaphthene-1-carboxaldoxime (11). To a stirred 25 °C solution of 140 mg (0.67 mmol) of aldehyde **9** in 25 mL of absolute EtOH under Ar was added 308 mg (3.37 mmol) of NaOAc and 257 mg (3.37 mmol) of $HONH_2$·HCl, and the mixture was refluxed for 16 h. After vacuum concentration, the mixture was extracted with water and CH_2Cl_2 and the combined organic layers were washed with 2 N HCl, dried, and concentrated to afford 106 mg (71%) of **11** as an off-white solid: mp 110−112 °C; IR ($CHCl_3$) 3583, 2846 cm^{-1}; ^1H NMR (400 MHz) δ 7.76 (1 H, d, J = 7.7), 7.72 (1 H, d, J = 7.7), 7.63 (1 H, d, J = 6.8), 7.56 (2 H, complex), 7.44 (1 H, s), 7.30 (1 H, d, J = 5.1), 5.95 (1 H, s), 5.36 (1 H, s), 1.67 (3 H, s), 1.25 (1 H, s); MS (EI), *m/e* (relative intensity) 223.1 (79), 206.1 (72), 191.1 (49), 179.1 (100), 152.1 (28); HRMS (EI) calcd for $C_{15}H_{12}O$ 223.0997, found 223.0989.

***trans*-1,2-Dimethylacenaphthene-1-carboxaldoxime (11t).** Treatment of 60 mg (0.28 mmol) of a mixture of aldehydes **9t** (83%) and **9c** (17%) with 150 mg (1.64 mmol) of NaOAc and 125 mg (1.64 mmol) of $HONH_2$·HCl as described above for **11** afforded 45 mg (71%) of a mixture of **11t** (85%) and **11c** (15%) as an off white solid: mp 94−96 °C; IR of the mixture (CH_2Cl_2) 3316, 2870, 1603 cm^{-1}; ^1H NMR of the major component (400 MHz) δ 7.68 (2 H, overlapping d, J = 8.3, 7.4), 7.51 (2 H, overlapping t, J = 7.6, 7.5), 7.45 (1 H, s, CHN), 7.25 (2 H, overlapping d), 3.58 (1 H, q, J = 7.5), 1.64 (3 H, s), 1.42 (3 H, d, J = 7.5), 1.26 (1H, s); MS (EI) of the mixture, *m/e* (relative intensity) 225.1 (36), 208.1 (48), 193.1 (88), 181 (57), 165.1 (100), 82.1 (31), 57.1 (13); MS (CI) of the mixture 227.1 (13), 226.1 (100), 181.1 (22); HRMS (EI) calcd for $C_{15}H_{15}NO$ 225.1154, found 225.1152.

***cis*-1,2-Dimethylacenaphthene-1-carboxaldoxime (11c).** Treatment of 20 mg (0.095 mmol) of a mixture of aldehydes **9c** (80%) and **9t** (20%) with 80 mg (0.87 mmol) of NaOAc and 60 mg (0.79 mmol) of $HONH_2$·HCl as described above for **11** afforded 21 mg (97%) of a mixture of **11c** (79%) and **11t** (21%) as a white solid: mp 83−87 °C; IR of the mixture (CH_2Cl_2) 3315, 2870, 1621, 1603 cm^{-1}; ^1H NMR of the major component (200 MHz) δ 7.77 (1 H, s), 7.68 (2 H, complex), 7.52 (2 H, overlapping t), 7.28 (2 H, complex), 3.84 (1 H, q, J = 7.4), 1.46 (3 H, d, J = 7.5), 1.41 (3 H, s), 1.28 (1 H, s); MS (EI) of the mixture, *m/e* (relative intensity) 225.1 (39), 208.3 (53), 193.1 (78), 181.1 (48), 165.2 (100); MS (CI) of the mixture 227.1 (15), 226.1 (91), 210.1 (100), 181.1 (78); HRMS (EI) calcd for $C_{15}H_{15}NO$ 225.1154, found 225.1154.

1-(*N*,*N*-Dimethylaminomethyl)-1-methyl-2-methyleneacenaphthene (10). To 270 mg (1.3 mmol) of aldehyde **9** under Ar at 25 °C was added 260 mg (2.6 mmol) of Et_3N in 1.0 mL of anhydrous EtOH followed by 741 mg (2.6 mmol) of Ti(IV) isopropoxide in 1.0 mL of anhydrous EtOH. To the resulting solution was added 214.5 mg (2.6 mmol) of Me_2NH·HCl, and the mixture was stirred for 9 h at 25 °C before the addition of 74.1 mg (1.95 mmol) of $NaBH_4$; the mixture was stirred for an additional 16 h. The mixture was worked up by adding 4 mL of 2 N NH_4OH and extracting with CH_2Cl_2. The combined extracts were washed with brine, dried, concentrated, and flash-chromatographed on silica gel with 9:1 CH_2Cl_2/MeOH, affording 185 mg (60%) of **10** as a faintly brownish oil: IR ($CHCl_3$) 1601 cm^{-1}; ^1H NMR (200 MHz, CD_3OD) δ 7.68 (3 H, complex), 7.55 (2 H, complex), 7.33 (1 H, d, J = 7.7), 5.95 (1 H, s), 5.35 (1 H, s), 2.90 (2 H, dd, J = 12, 8), 1.95 (6 H, s), 1.40 (3 H, s); MS (EI), *m/e* (relative intensity) 237.1 (36), 178.1 (32), 165.0 (23), 152.0 (19), 74.1 (30), 58.0 (100); HRMS (EI) calcd for $C_{17}H_{19}N$ 237.1518, found 237.1508.

1-(*N*,*N*-Dimethylaminomethyl)-*trans*-1,2-dimethylacenaphthene (10t). Treatment, as described above for **10**, of 25 mg (0.24 mmol) of a mixture of aldehydes **9t** (83%) and **9c** (17%) with 100 mg (1.0 mmol) of Et_3N, 160 mg (0.56 mmol) of Ti(IV) isopropoxide and 50 mg (0.6 mmol) of Me_2NH·HCl, followed by 150 mg (3.95 mmol) of $NaBH_4$, afforded 7 mg (12%) of a mixture of **10t** (72%) and **10c** (28%) as a yellowish oil: IR of the mixture (CH_2Cl_2) 1639 cm^{-1}; ^1H NMR of the major component (400 MHz) δ 7.60 (4 H, complex), 7.25 (2 H, complex), 3.39 (1 H, q, J = 7.5), 2.62 (2 H, overlapping d, J = 5.7), 1.94 (6 H, s), 1.48 (3 H, s), 1.47 (3 H, d, J = 7.4); MS (EI) of the mixture, *m/e* relative intensity) 165.1 (6), 59.1 (3), 58.1 (100); MS (CI) of the mixture 241.1 (12), 240.1 (100), 195.1 (4); HRMS (CI) calcd for $C_{17}H_{21}N$ 239.1674, found 239.1686.

1-(*N*,*N*-Dimethylaminomethyl)-*cis*-1,2-dimethylacenaphthene (10c). Treatment, as described above for **10**, of 27 mg (0.13 mmol) of a mixture of aldehydes **9c** (80%) and **9t** (20%) with 60 mg (0.6 mmol) of NEt_3, 150 mg (0.53 mmol) of Ti(IV) isopropoxide, and 42 mg (0.5 mmol) of $HNMe_2$·HCl, followed by 50 mg (1.32 mmol) of $NaBH_4$, afforded 15 mg (48%) of a mixture of **10c** (80%) and **10t** (20%) as a colorless oil: IR of the mixture (CH_2Cl_2) 1662, 1617, 1603 cm^{-1}; ^1H NMR of the major component (200 MHz) δ 7.63 (2 H, complex), 7.50 (2 H, complex), 7.28 (2 H, complex), 3.86 (1 H, q, J = 7.3), 2.62 (2 H, overlapping d, J = 4.4, 5.9), 2.17 (6 H, s), 1.42 (3 H, d, J = 7.5), 1.24 (3 H, s); MS (EI) of the mixture, *m/e* (relative intensity) 165.1 (4), 58.1 (100); MS (CI) of the mixture 241.1 (14), 240.1 (100), 195.1 (13), 181.0 (20); HRMS (CI) calcd for $C_{17}H_{21}N$ 239.1674, found 239.1671.

1-Acetyl-1-methyl-2-methyleneacenaphthene (12). To a stirred −78 °C solution of 121 mg (0.58 mmol) of aldehyde **9** in 4.0 mL of freshly distilled THF was added 1.0 mL (3.0 mmol) of 3.0 M MeMgBr in Et_2O. After 5 min of stirring at −78 °C, the reaction was quenched by slow addition of anhydrous CH_3OH. The solution was partitioned with CH_2Cl_2 and 3% HCl, dried, filtered through a plug of silica, and concentrated to yield 63 mg (0.28 mmol) of the alcohol as a faintly yellow oil. All of this alcohol in 2.0 mL of distilled Et_2O was oxidized at room temperature by adding 200 mg (0.53 mmol) of pyridinium dichromate (PDC) to the stirred solution. After 30 min, 7.0 mL of distilled CH_2Cl_2 was added, followed by an additional 300 mg (0.80 mmol) of PDC, and the mixture was stirred for 16 h. The mixture was diluted with CH_2Cl_2, filtered through Celite, concentrated under vacuum, and flash-chromatographed on silica gel. This afforded 30 mg (23%) of **12** as a faintly yellow oil: IR ($CHCl_3$) 1708 cm^{-1}; ^1H NMR (400 MHz) δ 7.72 (3 H, complex), 7.58 (1 H, d, J = 8.5), 7.53 (1 H, d, J = 8.5), 7.17 (1 H, d, J = 7.7), 5.92 (1 H, s), 5.26 (1 H, s), 1.72 (3 H, s), 1.59 (3 H, s); MS (EI), *m/e* (relative intensity) 223.1 (14), 222.1 (82), 179.1 (100), 178.0 (30), 152.0 (13); HRMS (EI) calcd for $C_{16}H_{14}NO$ 222.1044, found 222.1042.

1-Acetyl-*trans*-1,2-dimethylacenaphthene (12t). According to the procedure described above for **12**, 40 mg (0.19 mmol) of a mixture of aldehydes **9t** (83%) and **9c** (17%) was treated with 3.0 mmol of ethereal MeMgBr and the entire product (32 mg, 0.14 mmol) oxidized with two portions of PDC totalling 400 mg (1.05 mmol) to afford 25 mg (59%) of a mixture of **12t** (83%) and **12c** (17%) as a colorless oil: IR of the mixture (CH_2Cl_2) 1707, 1620, 1604 cm^{-1}; ^1H NMR of the major component (400 MHz) δ 7.71 (1 H, d, J = 8.6), 7.68 (1 H, d, J = 8.3), 7.52 (2 H, complex), 7.26 (1 H, d, J = 6.3), 7.19 (1 H, d, J = 6.7), 3.61 (1 H, q, J = 7.4), 1.63 (3 H, s), 1.59 (3 H, s), 1.43 (3 H, d, J = 7.5); MS (EI) of the mixture *m/e* (relative intensity) 224.1 (7), 182.1 (13), 181.1 (100), 166.1 (29), 165.1 (61); MS (CI) of the mixture 226.1 (12), 225.1 (100), 181.1 (2), 167.1 (4), 81.1 (2), 71.1 (2), 70.1 (2), 69.1 (2); HRMS (EI) calcd for $C_{16}H_{16}O$ 224.1201, found 224.1190.

1-Acetyl-*cis*-1,2-dimethylacenaphthene (12c). According to the procedure described above for **12**, 25 mg (0.12 mmol) of

a mixture of aldehydes **9c** (80%) and **9t** (20%) was converted to 19 mg (71%) of a mixture of **12c** (87%) and **12t** (13%) as a colorless oil: IR of the mixture (CH_2Cl_2) 1706, 1595, cm^{-1}; ^1H NMR of the major component (200 MHz) δ 7.75 (2 H, overlapping d, J = 8.1, 8.4), 7.55 (2 H, overlapping t, J = 7.0, 7.0), 7.28 (2 H, overlapping d, J = 7.0, 6.6), 3.94 (1 H, q, J = 7.4), 1.96 (3 H, s), 1.59 (3 H, s), 1.42 (3 H, d, J = 7.4); MS (EI) *m/e* (relative intensity) 224.1 (5), 182.0 (9), 181.1 (100), 166.1 (28), 165.1 (43); MS (CI) 226.1 (14), 225.1 (100), 207.1 (3), 181.0 (2), 167.1 (5); HRMS (EI) calcd for $C_{16}H_{16}O$ 224.1201, found 224.1197.

1-Carboxy-1-methyl-2-methyleneacenaphthene (15). A stirred mixture of 1.00 g (4.88 mmol) of nitrile **8** and 2.15 g (38.3 mmol) of KOH in 20 mL of ethylene glycol under Ar was heated at 105 °C for 16 h. The hot solution was poured onto ice and extracted with CH_2Cl_2, and the acidified aqueous layers were then extracted with CH_2Cl_2, dried, and concentrated to afford 1.0 g (92%) of **15** as a white solid: mp 149−151 °C; IR ($CHCl_3$) 3550−2550 (br), 1743 (shoulder), 1704 cm^{-1}; ^1H NMR (400 MHz) δ 7.73 (2 H, overlapping d, J = 8.5, 9.4), 7.62 (1 H, d, J = 6.8), 7.55 (2 H, complex), 7.36 (1 H, d, J = 6.8), 5.96 (1 H, s), 5.50 (1 H, s), 1.75 (3 H, s); ^{13}C NMR (100 MHz) δ 179.59, 151.86, 144.40, 138.67, 137.76, 131.37, 128.31, 128.13, 125.08, 124.12, 118.71, 116.73, 107.63, 57.30, 24.78; MS (EI), *m/e* (relative intensity) 448.1 (33), 447.1 (100), 285.1 (15), 241.0 (13), 223.1 (18); HRMS (EI) calcd for $C_{15}H_{12}O_2$ 224.0837, found 224.0836.

1-Carboxy-*trans*-1,2-dimethylacenaphthene (15t). Catalytic hydrogenation of acid **15** under the standard conditions described below provided a colorless oil shown to contain 81% of **15t** and 19% of **15c** by ^1H NMR: IR of the mixture (CH_2Cl_2) 3600−2400 (br), 1725 (shoulder), 1700, 1602 cm^{-1}; ^1H NMR of the major component (200 MHz) δ 7.68 (2 H, overlapping d, J = 7.7, 8.3), 7.52 (2 H, overlapping t), 7.30 (1 H, d, J = 7.7), 7.23 (1 H, d, J = 7.2), 3.60 (1 H, q, J = 7.2), 1.70 (3 H, s), 1.53 (3 H, d, J = 7.1); MS (EI) of the mixture, *m/e* (relative intensity) 226.1 (13), 198.1 (18), 196.1 (11), 183.1 (64), 182.0 (38), 181.1 (90), 171.1 (28), 169.1 (13), 168.1 (11), 167.1 (48), 166.0 (28), 165.1 (100), 153.1 (32), 152.1 (44), 151.1 (11), 115.1 (10), 82.0 (14), 76.0 (12); MS (CI) of the mixture 228.1 (14), 227.2 (100), 213.1 (8), 197.0 (23), 183.2 (17), 181.1 (63); HRMS (EI) calcd for $C_{15}H_{14}O_2$ 226.0994, found 226.0992.

1-Carboxy-*cis*-1,2-dimethyacenaphthene (15c). Selective Hydrolysis of a Mixture of Nitriles 8t and 8c. Catalytic hydrogenation of 1.0 g (4.9 mmol) of nitrile **8** under the standard conditions provided 1.0 g of a mixture of **8t** (80%) and **8c** (20%), which was heated with 5.0 g of KOH in 30 mL of ethylene glycol at 115 °C for 16 h. Workup as described above for the hydrolysis of **8** provided a 30% yield of carboxamide **17t** (described below) from the neutral fraction. The acidic portion afforded 255 mg (23%) of a mixture of **15c** (87%) and **15t** (13%) as a colorless oil: IR of the mixture (CH_2Cl_2) 3500−2300 (br), 1698, 1621, 1602 cm^{-1}; ^1H NMR of the major component (400 MHz) δ 7.69 (1 H, d, J = 7.8), 7.67 (1 H, d, J = 8.4), 7.49 (3 H, complex), 7.27 (1 H, d, J = 7.7), 4.27 (1 H, q, J = 7.2), 1.54 (3 H, s), 1.49 (3 H, d, J = 7.1); MS (EI) of the mixture, *m/e* (relative intensity) 226.1 (20), 181.1 (100), 166.0 (18), 165.1 (59), 83.1 (10), 69.1 (16), 57.1 (20), 55.1 (21); MS (CI) of the mixture, 228.1 (12), 227.1 (100), 181.1 (5); HRMS (EI) calcd for $C_{15}H_{14}O_2$ 226.0994, found 226.0996.

Lithium 1-Methyl-2-methyleneacenaphthene-1-carboxylate (21). A 25 °C suspension of 260 mg (1.16 mmol) of acid **15** and 46 mg (1.1 mmol) of LiOH in 10 mL of anhydrous MeOH was stirred under Ar for 16 h. The mixture was vacuum- concentrated to dryness and coevaporated three times with $CHCl_3$. The resulting solid was washed with hexane/petroleum ether to remove residual **15**, yielding 204 mg (80%) of **21** as an off-white solid: IR (KBr) 3042, 2974, 1575, 1386, 1356 cm^{-1}, no absorption was observed at 1700 cm^{-1}.

Sodium 1-Methyl-2-methyleneacenaphthene-1-carboxylate (20). A 25 °C suspension of 360 mg (1.61 mmol) of acid **15** and 63.0 mg (1.58 mmol) of NaOH in 13 mL of anhydrous MeOH plus 2 mL of anhydrous EtOH was stirred under Ar for 16 h. Vacuum-concentration and coevaporation (three times each) with CH_3OH and $CHCl_3$ gave a solid that was washed with hexane/petroleum ether to remove residual **15**, yielding 330 mg (83%) of **20** as an off-white solid: IR (KBr) 1644, 1576, 1454, 1363 cm^{-1}, no absorption was observed at 1700 cm^{-1}.

Potassium 1-Methyl-2-methyleneacenaphthene-1-carboxylate (19). A room-temperature suspension of 193 mg (0.86 mmol) of acid **15** and 51 mg (0.772 mmol) of KOH in 1.0 mL of anhydrous MeOH was stirred under Ar for 1 h. Vacuum-concentration, coevaporation (three times) with $CHCl_3$, and washing with hexane/petroleum ether to remove residual **15** provided 200 mg (89%) of **19** as an off-white solid: IR (KBr) 2966, 1594, 1490, 1378, 1340 cm^{-1}, no absorption was observed at 1700 cm^{-1}.

Methyl 1-Methyl-2-methyleneacenaphthene-1-carboxylate (18). To a stirred −78 °C solution of 2.50 g (11.2 mmol) of acid **15** in 250 mL of anhydous MeOH under Ar was added 3.3 mL (45 mmol) of $SOCl_2$ dropwise over 5 min. The mixture warmed to room temperature as it stirred overnight and then was vacuum-concentrated, coevaporated twice with EtOH, and flash-chromatographed on silica gel to afford 2.1 g (79%) of **18** as an off-white solid: mp 63−65 °C; IR ($CHCl_3$) 1728, 1642 cm^{-1}; ^1H NMR (400 MHz) δ 7.75 (1 H, d, J = 7.7), 7.72 (1 H, d, J = 8.5), 7.63 (1 H, d, J = 6.8), 7.54 (2 H, overlapping t), 7.32 (1 H, d, J = 6.8), 5.93 (1 H, s), 5.45 (1 H, s), 3.60 (3 H, s), 1.75 (3 H, s); ^{13}C NMR (100 MHz) δ 174.31, 152.45, 145.17, 138.91, 137.85, 131.38, 128.26, 128.14, 125.00, 123.86, 118.33, 116.68, 106.96, 57.43, 52.56, 25.13; MS (CI), *m/e* (relative intensity) 274.1 (M + $2NH_4$, 58), 256.1 (M + NH_4, 100), 239.1 (M + H, 94); HRMS (EI) calcd for $C_{16}H_{14}O_2$ 238.0994, found 238.0996.

Methyl *trans*-1,2-Dimethylacenaphthene-1-carboxylate (18t). Treatment of 250 mg (1.1 mmol) of a mixture of acids **15t** (81%) and **15c** (19%) with 25 mL of anhydrous MeOH and two portions of $SOCl_2$ totalling 0.90 mL (12.4 mmol), as described above for **18**, afforded 130 mg (49%) of a mixture of **18t** (70%) and **18c** (30%) as a white solid: mp 58−64 °C; IR of the mixture (CH_2Cl_2) 1729, 1603 cm^{-1}; ^1H NMR of the major component (400 MHz) δ 7.67 (2 H, complex), 7.50 (2 H, t, J = 7.7), 7.24 (2 H, complex), 3.56 (1 H, q, J = 7.4), 3.58 (3 H, s), 1.70 (3 H, s), 1.41 (3 H, d, J = 7.3); ^{13}C NMR of the mixture (100 MHz) δ 174.85, 147.43, 147.07, 137.15, 137.15, 131.32, 128.06, 127.98, 123.75, 123.58, 123.05, 122.94, 119.48, 118.89, 118.64, 118.39, 58.67, 52.37, 51.67, 45.89, 25.31, 22.92, 15.92, 14.56; MS (EI) of the mixture, *m/e* (relative intensity) 240 (18), 182 (10), 181 (100), 166 (20), 165 (48); MS (CI) of the mixture, 243.1 (3), 242.1 (10), 241.1 (100), 181.1 (11); HRMS (EI) calcd for $C_{16}H_{16}O_2$ 240.1150, found 240.1162.

Methyl *cis*-1,2-Dimethylacenaphthene-1-carboxylate (18c). Treatment of 120 mg (0.53 mmol) of a mixture of acids **15c** (87%) and **15t** (13%) in 12 mL of anhydrous MeOH plus 10 mL of $CHCl_3$ with 0.50 mL (6.9 mmol) of $SOCl_2$, as described above for **18**, afforded 81 mg (64%) of a mixture of **18c** (91%) and **18t** (9%) as a colorless oil: IR of the mixture (CH_2Cl_2) 1731, 1602 cm^{-1}; ^1H NMR of the major component (400 MHz) δ 7.68 (1 H, d, J = 8.3), 7.65 (1 H, d, J = 8.5), 7.50 (2 H, overlapping t, J = 7.0, 7.2), 7.41 (1 H, d, J = 7.2), 7.26 (1 H, d, J = 7.0), 4.26 (1 H, q, J = 7.5), 3.74 (3 H, s), 1.51 (3 H, s), 1.49 (3 H, d, J = 7.5); MS (EI) of the mixture, *m/e* (relative intensity) 240.3 (21), 181.2 (100), 180.2 (26), 165.2 (57); MS (CI) of the mixture, 241.1 (100), 240.1 (10), 181.1 96), 85.1 (2), 81.1 (3); HRMS (EI) calcd for $C_{16}H_{16}O_2$ 240.1150, found 240.1148.

1-Methyl-2-methyleneacenaphthene-1-hydroxamic Acid (16). To a stirred 25 °C solution of 112 mg (0.50 mmol) of acid **15** in 2 mL of distilled CH_2Cl_2 under Ar was added 300 μL (3.44 mmol) of $(COCl)_2$. After the mixture was refluxed for 3 h, an additional 300 μL (3.44 mmol) of $(COCl)_2$ was added and reflux was continued for 1 h before the mixture was stirred for 16 h at room temperature. Removal of $(COCl)_2$ with a stream of Ar yielded a white solid that was redissolved in 2 mL of CH_2Cl_2, and the drying was repeated. In a separate flask, 500 μL (3.6 mmol) of Et_3N was added to 200 mg (2.88 mmol) of a suspension of NH_2OH·HCl in 2 mL of anhydrous DMF; this solution was then cooled in an ice bath and transferred by syringe to the flask containing the acid chloride. After stirring for 16 h, the mixture was diluted with CH_2Cl_2

and the reaction was quenched with saturated $NaHCO_3$. The organic layer, washed with saturated $NaHCO_3$ and water, was dried and vacuum-concentrated. The resulting crude oil was loaded onto a plug of silica and washed with CH_2Cl_2 before elution with 9:1 CH_2Cl_2/MeOH afforded 95 mg (79%) of **16** as an off-white solid: mp 85−86 °C; IR ($CHCl_3$) 3290 (br), 1651 cm^{-1}; ^1H NMR (400 MHz) δ 8.15 (1 H, broad), 7.76 (2 H, complex), 7.59 (3 H, complex), 7.45 (1H, d, J = 8.5), 5.98 (1 H, s), 5.63 (1 H, s), 1.82 (3 H, s); MS (EI), *m/e* (relative intensity) 239.3 (39), 221.2 (88), 178.2 (100), 165.2 (58), 152.2 (50), 44.0 (48); HRMS (EI) calcd for $C_{15}H_{13}NO_2$ 239.0946, found 239.0941.

***trans*-1,2-Dimethylacenaphthene-1-hydroxamic Acid (16t).** Treatment of 100 mg (0.44 mmol) of a mixture of acids **15t** (81%) and **15c** (19%) with 800 μL (9.2 mmol) of $(COCl)_2$, as described above for **16**, provided the crude acid chloride, which was then treated with 500 μL (3.6 mmol) of Et_3N and 200 mg (2.88 mmol) of $NH_2OH{\cdot}HCl$ in anhydrous DMF to afford 16 mg (15%) of a mixture of **16t** (82%) and **16c** (18%) as a white solid: mp 90−92 °C; IR of the mixture (CH_2Cl_2) 3378, 3210 (br), 1660, 1603 cm^{-1}; ^1H NMR of the major component (400 MHz) δ 8.36 (1 H, broad), 7.76 (1 H, d, J = 8.5), 7.70 (1 H, d, J = 7.7), 7.55 (2 H, overlapping t, J = 7.2, 6.7), 7.33 (1 H, d, J = 7.1), 7.28 (1 H, d, J = 6.8), 3.56 (1 H, q, J = 7.4), 1.73 (3 H, s), 1.45 (3 H, d, J = 7.5); ^{13}C NMR of the mixture (100 MHz) δ 171.21, 128.9, 128.18, 124.82, 123.31, 119.68, 119.39, 57.11, 51.75, 25.01, 24.82; MS (EI) of the mixture, *m/e* (relative intensity) 241.1 (9), 182.1 (10), 181.1 (100), 180.1 (48), 179.1 (10), 166.1 (26), 165.1 (78), 164.1 (11), 152.1 (9), 86.1 (17), 85.0 (33), 84.1 (25), 83.1 (51), 82.1 (23); MS (CI) of the mixture 242.1 (100), 226.1 (14), 181.0 (38), 180.1 (24); HRMS (EI) calcd for $C_{15}H_{15}NO_2$ 241.1103, found 241.1108.

***cis*-1,2-Dimethylacenaphthene-1-hydroxamic Acid (16c).** Treatment of 100 mg (0.44 mmol) of a mixture of acids **15c** (87%) and **15t** (13%) with 400 μL (4.6 mmol) of $(COCl)_2$ and subsequent reaction with NH_2OH, as described above for **16**, yielded 40 mg (38%) of a mixture of **16c** (82%) and **16t** (18%) as a white solid: mp 141−144 °C; IR (CH_2Cl_2) 3227 (br), 1628, 1600 cm^{-1}; ^1H NMR (400 MHz) δ 8.0 (1 H, d, broad), 7.76 (1 H, d, J = 8.5), 7.69 (1 H, d, J = 8.3), 7.55 (2 H, overlapping t, J = 6.9), 7.35 (1 H, d, J = 6.9), 7.29 (1 H, d, J = 6.8), 3.91 (1 H, q, J = 7.3), 1.58 (3 H, s), 1.48 (3 H, d, J = 7.5); MS (EI) of the mixture, (relative intensity) 241.1 (96), 182.1 (10), 181.1 (100), 180.1 (19), 179.1 (12), 166.1 (27), 165.1 (98), 152.1 (9), 89.0 (5), 83.1 (6), 76.1 (5), 69.1 (8), 57.1 (15), 55.1 (9); MS (CI) 242 (100), 226 (77), 182 (12), 181 (91); HRMS (EI) calcd for $C_{15}H_{15}NO_2$ 241.1103, found 241.1100.

1-Methyl-2-methyleneacenaphthene-1-carboxamide (17). To a stirred 25 °C solution of 896 mg (4.0 mmol) of acid **15** in 12 mL of anhydrous DMF under Ar was added 988 mg (6.1 mmol) of 1,1′-carbonyldiimidazole in portions. The solution was stirred for 30 min at 25 °C, heated for 30 min at 40 °C, treated with 1.3 mL of concentrated NH_4OH dissolved in 2.7 mL of DMF and heated for 30 min at 80 °C. The mixture was cooled to 4 °C, and the reaction was quenched by slow addition of 15 mL of 2 N HCl. The crude product provided by CH_2Cl_2 extraction and vacuum-concentration was flash-chromatographed from 50 g of silica gel with 9:1 CH_2Cl_2/MeOH to afford 697 mg (78%) of **17** as an off-white solid: mp 122−123 °C; IR ($CHCl_3$) 3522, 3407, 1682, 1580 cm^{-1}; ^1H NMR (400 MHz) δ 7.78 (1 H, d, J = 8.5), 7.74 (1 H, d, J = 7.7), 7.66 (1 H, d, J = 6.8), 7.58 (2 H, complex), 7.44 (1 H, d, J = 6.8), 5.99 (1 H, s), 5.60 (1H, s), 5.30 (2 H, broad), 1.76 (3 H, s); ^{13}C NMR (100 MHz) δ 175.86, 153.03, 145.48, 138.52, 137.47, 131.42, 128.46 (2C), 125.22, 124.12, 118.92, 116.93, 107.87, 58.12, 24.94; MS (FAB+), *m/e* (relative intensity) 447.3 (60), 224 (52), 181.1 (100), 165.1 (26), 154.0 (32), 136.0 (22); HRMS (EI) calcd for $C_{15}H_{13}NO$ 223.0997, found 223.1000.

***trans*-1,2-Dimethylacenaphthene-1-carboxamide (17t). Method A.** Portionwise treatment of 900 mg (4.0 mmol) of a mixture of acids **15t** (81%) and **15c** (19%) in 3:1 DMF/CH_2Cl_2 with a total of 1.5 g (9.3 mmol) of 1,1′-carbonyldiimidazole, followed by 2.7 mL of concentrated NH_4OH, as described above for **17**, afforded 550 mg (61%) of a mixture of **17t** (84%) and **17c** (16%) as a colorless oil: IR of the mixture (CH_2Cl_2) 3475, 1673, 1600 cm^{-1}; ^1H NMR of the major component (400 MHz) δ 7.73 (1 H, d, J = 8.5), 7.68 (1 H, d, J = 8.5), 7.55 (2H, overlapping t), 7.30 (2H, complex), 5.33 (1 H, broad), 4.96 (1 H, broad), 3.56 (1 H, q, J = 7.3), 1.72 (3 H, s), 1.52 (3 H, d, J = 7.4); MS (EI) of the mixture, *m/e* (relative intensity) 225.1 (9), 182.1 (10), 181.1 (100), 166.1 (21), 165.1 (50); MS (CI) of the mixture, 228.1 (3), 227.1 (15), 226.1 (100), 181.1 (1), 89.1 (3), 74.1 (4); HRMS (EI) calcd for $C_{15}H_{15}NO$ 225.1154, found 225.1153.

Method B. Preparation of Pure 17t by Selective Hydrolysis of a Mixture of 8t and 8c. Catalytic hydrogenation of 1.0 g (4.9 mmol) of nitrile **8** under the standard conditions described below provided 1.0 g of a mixture of **8t** (80%) and **8c** (20%). Hydrolysis of this with KOH in $(CH_2OH)_2$, as described above for **15**, yielded a CH_2Cl_2-soluble neutral fraction that was washed, dried, vacuum-concentrated, and flash-chromatographed on silica gel. Elution with 9:1 CH_2Cl_2/acetone afforded 300 mg (30%) of pure **17t**: mp 109−111 °C; ^1H NMR was essentially identical to that of the major component of the **17t** /**17c** mixture produced by Method A above; ^{13}C NMR (100 MHz) δ 175.92, 147.66, 147.14, 131.54, 128.67 (2C), 128.28, 124.23, 123.19, 119.46, 119.13, 58.95, 51.34, 24.82, 15.21.

***cis*-1,2-Dimethylacenaphthene-1-carboxamide (17c).** Portionwise treatment of 300 mg (1.33 mmol) of a mixture of acids **15c** (87%) and **17t** (13%) with a total of 500 mg (3.1 mmol) of 1,1′-carbonyldiimidazole, followed by 0.6 mL of concentrated NH_4OH, as described above for **17**, afforded 300 mg (100%) of a mixture of **17c** (81%) and **17t** (19%) as a colorless oil: IR of the mixture (CH_2Cl_2) 3473, 1668, 1600, cm^{-1}; ^1H NMR of the major component (400 MHz) δ 7.73 (1 H, d, J = 8.1), 7.68 (1 H, d, J = 8.3), 7.55 (2 H, overlapping t), 7.36 (1 H, d, J = 6.9), 7.30 (1 H, d, J = 6.7), 5.42 (1 H, broad), 5.32 (1H, broad), 3.97 (1 H, q, J = 7.5), 1.54 (3 H, s), 1.49 (3 H, d, J = 7.4); MS (EI) of the mixture, *m/e* (relative intensity) 225 (14), 182 (15), 181 (100), 166 (25), 165 (53); MS (CI) of the mixture 228.1 (3), 227.1 (15), 226.1 (100), 181.1 (1), 89.1 (3), 74.1 (4); HRMS (EI) calcd for $C_{15}H_{15}NO$ 225.1154, found 225.1150.

1-Hydroxymethyl-1-methyl-2-methyleneacenaphthene (22). Method A. To a stirred −78 °C solution of 2.1 g (8.82 mmol) of methyl ester **18** in 53 mL of dry THF under Ar was added 40 mL (40 mmol) of DIBAL-H (1 M in THF) dropwise. The mixture was warmed to 25 °C over 1.5 h, and then the reaction was quenched at −78 °C by slowly adding 90 mL of 2 N HCl. Vacuum-concentration and CH_2Cl_2-extraction led to a crude product that was flash-chromatographed from silica gel with 7:3 CH_2Cl_2/hexane to afford 1.75 g (94%) of **22** as a colorless oil: IR ($CHCl_3$) 3550−3000 (br) cm^{-1}; ^1H NMR (400 MHz) δ 7.74 (1 H, d, J = 7.7), 7.69 (1 H, d, J = 8.5), 7.62 (1 H, d, J = 6.8), 7.55 (2 H, overlapping t), 7.32 (1 H, d, J = 6.8), 5.93 (1 H, s), 5.34 (1 H, s), 3.79 (2 H, m), 1.52 (3 H, s), 1.48 (1 H, t, J = 6.8); ^{13}C NMR (100 MHz) δ 153.77, 146.88, 139.55, 137.81, 131.30, 128.18, 128.16, 124.95, 123.53, 117.76, 116.45, 105.58, 70.71, 53.19, 22.90; MS(EI), *m/e* (relative intensity) 210.0 (70), 179.0 (100), 165.0 (10), 152.0 (11); HRMS (EI) calcd for $C_{15}H_{14}O$ 210.1045, found 210.1044.

Method B. To a stirred 25 °C solution of 1.16 g (5.2 mmol) of acid **15** in 16 mL of anhydrous DMF under Ar was added 1.2 g (7.4 mmol) of 1,1′-carbonyldiimidazole in portions. After stirring for 30 min at 25 °C and then 30 min at 40 °C, the warm solution was treated with 388 mg (10.3 mmol) of $NaBH_4$ in portions. The cooled mixture was quenched by slow addition of H_2O and then vacuum-concentrated. The residue in CH_2Cl_2 was washed with 1 N HCl and brine, dried, and vacuum-concentrated at 50 °C for 2 h to afford a yellowish oil. Flash chromatography on silica gel and elution with 1:1 CH_2Cl_2/hexane afforded 1.02 g (92%) of **22** as a colorless oil with ^1H NMR essentially identical to that described for Method A above.

1-Hydroxymethyl-*trans*-1,2-dimethylacenaphthene (22t). Treatment of 120 mg (0.5 mmol) of a mixture of methyl esters **18t** (70%) and **18c** (30%) in 6:5 THF/$CHCl_3$ with 5.0 mL (5.0 mmol) of DIBAL-H (1 M in toluene), as described above for **22**, afforded 67 mg (63%) of a mixture of **22t** (69%) and **22c** (31%) as a colorless oil: IR of the mixture (CH_2Cl_2) 3600−

3100 (br), 1620, 1604, 1593 cm^{-1}; ^1H NMR of the major component (400 MHz) δ 7.67 (1 H, d, J = 8.2), 7.63 (1 H, d, J = 8.2), 7.51 (2 H, overlapping t), 7.28 (1 H, d, J = 6.9), 7.24 (1 H, d, J = 7.0), 3.71 (1 H, d, J = 7.3), 3.69 (1H, d, J = 7.2), 3.45 (1 H, q, J = 7.5), 1.55 (3 H, d, J = 7.4), 1.49 (3 H, s); MS (EI) of the mixture, *m/e* (relative intensity) 212.1 (13), 181.2 (100), 166.1 (21), 165.0 (46), 152.1 (4); MS (CI) of the mixture 213.1 (52), 196.1 (10), 195.1 (100); HRMS (EI) calcd for $C_{15}H_{16}O$ 212.1201, found 212.1204.

1-Hydroxymethyl-*cis*-1,2-dimethylacenaphthene (22c). Treatment of 50 mg (0.21 mmol) of a mixture of methyl esters **18c** (91%) and **18t** (9%) in 2:1 THF/$CHCl_3$ with 3.0 mL (3.0 mmol) of DIBAL-H (1 M in toluene), as described for **22**, afforded 40 mg (90%) of a mixture of **22c** (93%) and **22t** (7%) as a white powder: mp 63−65 °C: IR (CH_2Cl_2) of the mixture 3368, 1604 cm^{-1}; ^1H NMR of the major component (400 MHz) δ 7.66 (1 H, d, J = 8.3), 7.63 (1 H, d, J = 8.2), 7.50 (2 H, overlapping t), 7.27 (1 H, d, J = 9.1), 7.25 (1 H, d, J = 7.5), 3.81 (1 H, d, J = 10.7), 3.69 (1 H, d, J = 11.0), 3.65 (1H, q, J = 7.4), 1.39 (3 H, d, J = 7.4), 1.31 (3 H, s); MS (EI) of the mixture, *m/e* (relative intensity) 212.1 (17), 181.1 (100), 166.1 (26), 165.0 (54), 152.1 (9); MS (CI) of the mixture 214.1 (5), 213.1 (43), 196.1 (13), 195.1 (100), 71.1 (4), 69.0 (4); HRMS (EI) calcd for $C_{15}H_{16}O$ 212.1201, found 212.1205.

Method B. Internal Delivery of Hydride Using Lithium Aluminum Hydride. To a 25 °C slurry of 200 mg (5.2 mmol) of $LiAlH_4$ in 5 mL of Et_2O was added 115 mg (0.51 mmol) of acid **15** in 4 mL of Et_2O dropwise over 10 min. The mixture was stirred at 25 °C for 15 min, refluxed for 10 min, and cooled to −78 °C, and the reaction was quenched by slow addition of H_2O. The combined $CHCl_3$ extracts were washed, dried, and vacuum-concentrated to afford 100 mg (93%) of a mixture of **22** (49%), **22c** (44%), and **22t** (4%), accompanied by ca. 3% of a byproduct shown to have structure **24** and presumed to arise by air-oxidation of an organoaluminum intermediate.

A similar reaction involving 500 mg (2.2 mmol) of acid **15**, refluxed for 3 h, yielded 140 mg (28%) of **24**, crystallized from MeCN/H_2O to afford a colorless solid: mp 94−96 °C; IR (KBr) 3450 (broad), 3049, 2991, 2939, 2892, 1602, 1504 cm^{-1}; ^1H NMR (400 MHz) δ 7.75 (2 H, complex), 7.45 (3 H, complex), 7.37 (1 H, d, J = 7.1), 3.91 (1 H, d, J = 6.7), 3.90 (1H, d, J = 6.6), 2.07 (3 H, s), 1.96 (3 H, s); ^{13}C NMR (100 MHz) δ 139.81, 137.56, 133.19, 127.85, 126.91, 125.72, 125.66, 118.65, 118.57, 106.98, 78.07, 77.31, 76.69, 20.86, 19.75; HRMS (EI) calcd for $C_{15}H_{14}O_2$ 226.0994, found 226.0992.

X-ray crystal data for **24**: $C_{15}H_{14}O_2$; M = 226.26; cell setting, orthorhombic; space group, *P*bca; a = 13.858(7) Å; b = 9.802(5) Å; c = 17.239(9) Å; V = 2342(2) $Å^3$; Z = 8; T = 293(2) K; d = 1.284 g/cm^3; total reflections, 2194; observed reflections, [$>2\sigma(I)$] 1097; parameters refined, 154; least squares R factor (all), 0.170; least squares R factor, [$>2\sigma(I)$] 0.072 (see Acknowledgments).

1-Methoxymethyl-1-methyl-2-methyleneacenaphthene (23). To a stirred 25 °C solution of 50 mg (0.24 mmol) of alcohol **22** in 2 mL of distilled THF under Ar was added 100 mg (2.5 mmol) of NaH (60% in mineral oil). After the mixture was heated for 1.5 h at 40 °C, 80 μL (1.29 mmol) of MeI was added to the warm solution and stirring was continued for 30 min. The mixture was cooled to 0 °C and diluted with CH_2Cl_2 followed by concentrated aqueous NH_4Cl. The CH_2Cl_2 extracts were washed, dried, and vacuum-concentrated to a crude oil. Elution from silica gel with 2:3 CH_2Cl_2/hexane afforded 45 mg (84%) of **23** as a colorless oil: IR (CH_2Cl_2) 3046, 2924, 2869, 1615 cm^{-1}; ^1H NMR (400 MHz) δ 7.71 (1 H, d, J = 7.9), 7.66 (1 H, d, J = 8.0), 7.59 (1 H, d, J = 6.4), 7.52 (2 H, complex), 7.35 (1 H, d, J = 6.85), 5.88 (1 H, s), 5.34 (1 H, s), 3.57 (1 H, d, J = 9.0), 3.50 (1 H, d, J = 9.0), 3.29 (3 H, s), 1.52 (3 H, s); MS (EI), *m/e* (relative intensity) 224 (14), 180 (13), 179 (100), 152 (9), 151 (4); HRMS (EI) calcd for $C_{16}H_{16}O$ 224.1201, found 224.1202.

1-Methoxymethyl-*trans*-1,2-dimethylacenaphthene (23t). Treatment of 50 mg (0.24 mmol) of a mixture of alcohols **22t** (69%) and **22c** (31%) with 100 mg (2.5 mmol) of 60% NaH followed by 100 μL (1.61 mmol) of MeI, as described above for **23**, afforded 26 mg (48%) of a mixture of **23t** (69%) and **23c** (31%) as a colorless oil: IR (CH_2Cl_2) of the mixture 2871, 2826, 1604 cm^{-1}; ^1H NMR of the major component (400 MHz) δ 7.64 (1 H, d, J = 7.6), 7.62 (1 H, d, J = 7.5), 7.48 (2 H, overlapping t, J = 7.2, 8.1), 7.27 (1 H, d, J = 6.9), 7.22 (1 H, d, J = 6.3), 3.50 (1 H, d, J = 7.7), 3.46 (1 H, d, J = 7.8), 3.41 (1 H, q, J = 7.2), 3.25 (3 H, s), 1.46 (3 H, s), 1.45 (3 H, d, J = 7.1); MS (EI) of the mixture, *m/e* (relative intensity) 226.1 (10), 181.1 (100), 166.2 (19), 165.1 (37); MS (CI) of the mixture, 227.1 (9), 195.2 (100); HRMS (EI) calcd for $C_{16}H_{18}O$ 226.1358, found 226.1365.

1-Methoxymethyl-*cis*-1,2-dimethylacenaphthene (23c). Treatment of 30 mg (0.14 mmol) of a mixture of alcohols **22c** (93%) and **22t** (7%) with 100 mg (2.5 mmol) of 60% NaH followed by 100 μL (1.61 mmol) of MeI, as described for **23**, afforded 20 mg (63%) of pure **23c** as a colorless oil: IR (CH_2Cl_2) 2869, 2823, 1604 cm^{-1}; ^1H NMR (400 MHz) δ 7.63 (1 H, d, J = 6.1), 7.61 (1 H, d, J = 6.0), 7.48 (2 H, overlapping t), 7.25 (1 H, d, J = 5.4), 7.24 (1 H, d, J = 6.9), 3.63 (1 H, q, J = 7.5), 3.53 (1 H, d, J = 9.1), 3.47 (1 H, d, J = 9.1), 3.34 (3 H, s), 1.39 (3 H, d, J = 7.4), 1.32 (3 H, s); MS (EI) of the mixture, *m/e* (relative intensity) 226.1 (14), 181.1 (100), 166.1 (29), 165.1 (46); MS (CI) of the mixture 228.1 (4), 227.1 (23), 226.1 (9), 196.2 (16), 195.2 (100); HRMS (EI) calcd for $C_{16}H_{18}O$ 226.1358, found 226.1347.

Procedure for Heterogeneous Catalytic Hydrogenations. Hydrogenations were carried out with a low-pressure apparatus at 1 atm (76 ± 2 cm) and room temperature (25 ± 2 °C) in absolute EtOH with 5% Pd/C for 25−56 min. The same lot of catalyst used previously for systems **1**−**3** was used for all reactions, in the ratio of 30 mg of Pd/C and 10 mL of solvent per mmol of olefin.

To a flask containing a Teflon-covered magnetic stirring bar and a solution of the olefin in absolute EtOH was added the appropriate quantity of catalyst. The flask was then alternately evacuated and filled with H_2 five times to displace air. The pressure was adjusted to 1 atm, and vigorous stirring was started. When at least the theoretical quantity of H_2 had been absorbed, the reaction mixture was filtered and the catalyst was washed several times with EtOH and $CHCl_3$. The solution was vacuum-concentrated at 50 °C for 2 h, redissolved in $CHCl_3$, and vacuum-concentrated (three times). For the metal carboxylates, the hydrogenation product was dissolved in water, the pH adjusted to 2 using 2 N HCl, and the product extracted with CH_2Cl_2, dried over $MgSO_4$, and vacuum-concentrated; volatiles were pumped off three times with $CHCl_3$. Recovered yields were 89−99%.

Analysis of Product Mixtures. The residue obtained from each hydrogenation was dissolved in $CDCl_3$ and used directly for ^1H NMR and GC analyses. The ratio of cis and trans products was determined by integrating the benzylic protons and confirmed by gas chromatography for most of the compounds.

Control Reactions, Using Standard Hydrogenation Conditions. Treatment of the pure trans nitrile **8t** with H_2 for 24 h gave 91% of recovered starting material, and ^1H NMR showed no trace of the cis isomer.

When the acid **15** was hydrogenated for five different time periods (25 min, 1 h, 3 h, 6 h, and 16 h), the cis/trans ratio was essentially identical for all five.

When the nitrile **8** was hydrogenated for three different time periods (1, 3, and 16 h), the cis/trans ratio was essentially identical for all three.

When the aldehyde **9** was hydrogenated for 40 min and for 4 h, the cis/trans ratio was essentially identical for both.

Hydrogenations Employing Solvents of Low Dielectric Constant. Compound **15**, hydrogenated in a 9:1 mixture of hexane and $CHCl_3$ under standard conditions, afforded a mixture of **15c** (40%) and **15t** (60%) in 91% yield.

Compound **8**, hydrogenated in cyclohexane under standard conditions, afforded a mixture of **8c** (54%) and **8t** (46%) in 99% yield.

Compound **17**, hydrogenated in a 1:1 mixture of cyclohexane and Et_2O under standard conditions, afforded a mixture of **17c** (57%) and **17t** (43%) in 97% yield.

Compound **22**, hydrogenated in cyclohexane under standard conditions, afforded a mixture of **22c** (75%) and **22t** (25%) in 92% yield.

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Supporting Information Available: ^{1}H NMR spectra for **4**−**6**, **8**−**18**, **22**, and **23** and for all the cis/trans mixtures described in Schemes 4 and 6. This material is available free of charge via the Internet at http://pubs.acs.org.

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