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ENANTIOSELECTIVE SYNTHESIS OF 2-SUBSTITUTED PYRROLIDINES FROM 4-HYDROXYNITRILES. APPLICATION TO THE SYNTHESIS OF THE DOPAMINE AGONIST RS-59022.†

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ABSTRACT: Two novel routes to optically active 4-hydroxynitriles and the subsequent cyclization to 2-substituted pyrrolidines are described. The methodology is applied to the synthesis of the key intermediate used in the synthesis of the dopamine agonist RS-59022. Unusual selectivity in the CBS reduction of 4-oxonitriles is explained through structural and mechanistic analysis.

RS-59022 is a potent, selective, orally active dopamine (DA_1/DA_2) receptor agonist which has been in development at Syntex for treatment of hypertension, acute and chronic renal failure, and congestive heart failure.[1] The key features of this symmetrical structure are the two (R)-3,4-dihydroxybenzylpyrrolidine rings and the six carbon linkage between them. Small quantities of the compound were prepared using a published procedure[1] in which the chirality was derived from the expensive unnatural amino acid (R)-proline. A different approach to the key intermediate **1**[2] from the cyclic sulfamate of (R)-prolinol was recently reported.[2b] Other enantioselective routes to 2-substituted pyrrolidines[3] suffer from modest enantioselectivity, a large number of steps or costly reagents making the

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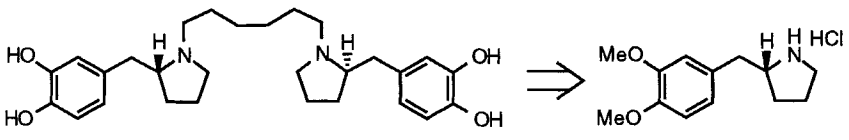
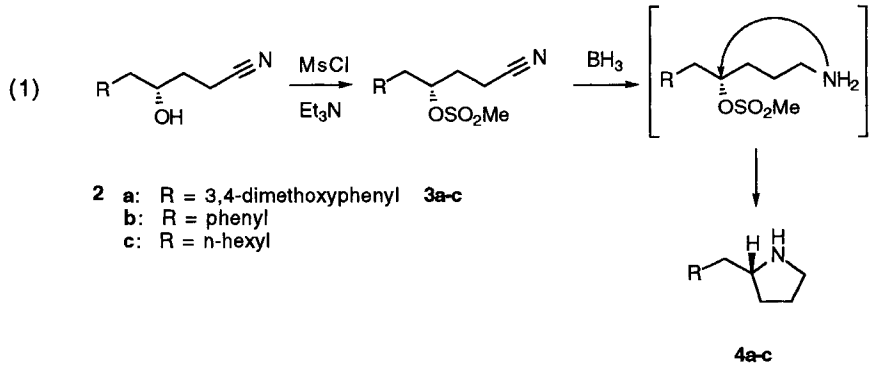


RS-59022 1

development of alternatives a worthwhile pursuit. We sought an alternative route to the key intermediate **1** which could be scaled-up and ultimately used for the economical commercial production of the compound. Herein we describe one approach involving the cyclization of an optically active masked amine derivative **3a** derived from the corresponding 4-hydroxynitrile **2a** as depicted in equation 1.

Chiral hydroxynitriles have served as precursors to a number of chiral lactones and spiroacetals. However, to the best of our knowledge their conversion to pyrrolidines is unprecedented. Enantioselective routes to hydroxynitriles include traditional optical resolution,[4] asymmetric synthesis,[5] as well as elaboration from carbohydrate precursors.[6] We investigated the synthesis of **2a** by asymmetric reduction[7] of the corresponding ketone **6a** as shown in equation 2 and by sequential dialkylation of glycidyl tosylate[8] as shown in scheme 1.

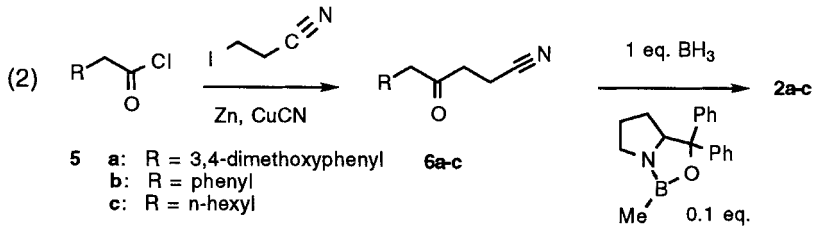


2 **a**: R = 3,4-dimethoxyphenyl **3a-c**
b: R = phenyl
c: R = n-hexyl

4a-c

An efficient and general enantioselective approach to chiral secondary alcohols is the oxazaborolidine catalyzed carbonyl reduction developed by Corey et al. (CBS reduction).[7a,b] The CBS reduction provides chiral alcohols with high ee

and predictable absolute stereochemistry based on the relative steric bulk of the ketone substituents. Although ketones **6a-c** do not appear to be ideal substrates for CBS reduction, a recent report[7c] described the CBS reduction of various ketones containing heteroatoms including 5-oxohexanenitrile which gave the alcohol in 74% ee despite comparable steric bulk of carbonyl substituents (-CH_3 vs -CH_2-CH_2-). Encouraged by this result we synthesized ketones **6a-c** and applied the CBS reduction as summarized in table 1.



5 **a**: R = 3,4-dimethoxyphenyl **6a-c**
b: R = phenyl
c: R = n-hexyl

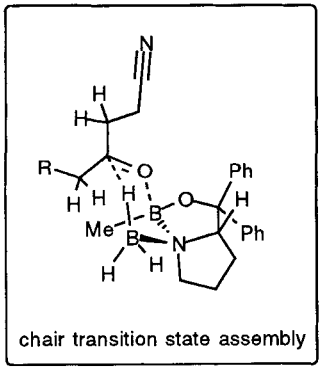
Table 1. Synthesis and CBS Reduction of 4-Oxonitriles **6a-c**

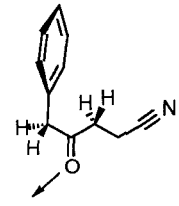
R	acylation product (yield)	reduction conditions	reduction product (yield)	ee
3,4-Dimethoxy-phenyl	**6a** (64%)	-15 °C, 15 min (R)-catalyst	ent-**2a** (88%)	82%
3,4-Dimethoxy-phenyl	-- --	-15 °C, 15 min (S)-catalyst	**2a** (100%)	80%
Phenyl	**6b** (69%)	0 °C, 30 min (S)-catalyst	**2b** (82%)	76%
n-Hexyl	**6c** (86%)	20 °C, 70 min (S)-catalyst	**2c** (90%)	26%

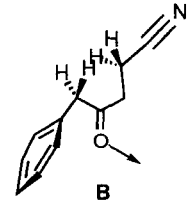
Treatment of the commercially available chlorides **5a-c** with the organocopper reagent derived from 3-iodopropionitrile according to Knochel[9] gave the desired 4-oxonitriles **6a-c** in 64-86% yield. CBS reduction of **6a** using 10 mol% of the (R)-catalyst (we assumed Ar-CH_2- would be the "large" substituent) afforded the corresponding alcohol as a 91:9 mixture of enantiomers.[10] Comparison with the alcohol prepared from (R)-glycidyl tosylate, *vide infra*,

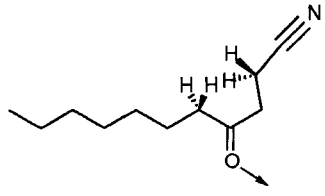
showed it to be predominantly the enantiomer of **2a**, i. e., the -CH_2CH_2CN acted as the large group relative to -CH_2-Ar! The same reduction carried out using the (S)-catalyst gave the desired enantiomer **2a** in 80% ee. Similarly, CBS reduction of **6b** using the (S)-catalyst gave the alcohol **2b** in 74% ee. With the -CH_2CH_2CN substituent acting as the "large" group in these cases and giving moderate enantioselectivity it seemed reasonable that a smaller group (than benzyl) would give higher ee. However, when the reduction was applied to **6c** the selectivity dropped to 26% ee.[11] In all three cases the -CH_2CH_2CN substituent behaved as the "large" group in the transition state assembly model used to predict stereochemical outcome.

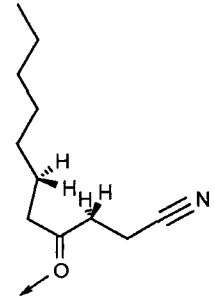
When ketone substituents are of similar size it is useful to consider more subtle conformational factors which can influence effective bulk.[12] The chair transition state assembly[13] that would lead to the observed enantioselectivity is shown below. The more accessible carbonyl lone pair *anti* to the "large" -CH_2CH_2CN substituent must be complexed to the catalyst prior to hydride attack. Complexation can only occur if the "small" -CH_2-R group points away from the





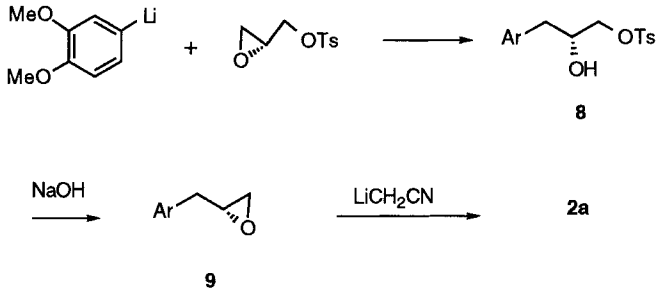






involved lone pair as in conformer **A.** In **A** the plane of the α-phenyl ring may be oriented perpendicular to the $C_\alpha COC_{\alpha'}$ plane reducing steric interaction with the two α'-H's. The alternative conformation **B** is clearly more sterically congested due to interactions of the two α–H's with the two β'–H's which must be at least partially eclipsed.[14] These effects may cause the seemingly "larger" $-CH_2$-Ar substituent to behave as the "small" group relative to $-CH_2CH_2CN$ for both **6a** and **6b**. In the case of **6c** the steric interactions in the two possible conformers **C** and **D** are nearly the same, leading to CBS reduction with poor enantioselectivity.

Scheme 1



Alternatively, enantiopure hydroxynitrile **2a** was prepared from (R)-glycidyl tosylate (Aldrich) as shown in scheme 1. Alkylation of the (R)-tosylate with veratryllithium gave tosylalcohol **8** in 53% yield. Treatment with K_2CO_3 in MeOH effected closure to epoxide **9** in 87% isolated yield. Alkylation of epoxide **9** with the anion derived from acetonitrile and butyllithium[15] afforded alcohol **2a** in 75% yield following an aqueous quench and chromatography. This material was determined to be enantiopure through NMR analysis of the MPTA ester. Since no inversion occurred at the asymmetric center, this material must posses the same absolute configuration as (R)-glycidyl tosylate from which it came. This provided the basis of the stereochemical assignments made for **2a** and ent-**2a**, *vide supra.*

Cyclization was effected in two steps according to equation 1. Alcohols **2a-c** were first converted into their corresponding mesylates in nearly quantitative yield by treatment with MsCl in the presence of Et_3N. Subsequent chemoselective

reduction of the nitrile function to the amine in the presence of the sulfonate ester was achieved using 4 equivalents of borane methyl sulfide complex in THF at reflux. A workup procedure involving *in situ* destruction of the excess reducing agent (MeOH) followed by concentration gave the entropically favored intramolecular cyclization, forming the pyrrolidines directly in good yields as tabulated below. The chiral purity of the 4-hydroxynitriles was conserved throughout these transformations as determined by comparison of optical rotation data with literature values. Pyrrolidine **2a** was upgraded to enantiopurity through a single crystallization of its HCl salt **1**. The resulting material was identical in every respect to an authentic sample prepared from (R)-proline.[1]

(1)

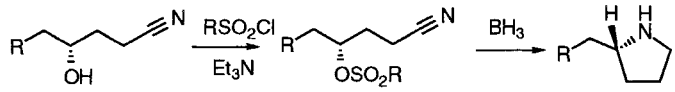


Table 2. Cyclization of 4-Hydroxynitriles **2a-c** to 2-Pyrrolidines **4a-c**

alcohol (ee)	mesylation product (yield)	cyclization product (yield)	$[\alpha]_D$ found	$[\alpha]_D$ reported	ee
2a (80%)	**3a** (96%)	**4a** (97%)	-6.7	-8.3	81%
2b (74%)	**3b** (97%)	**4b** (67%)	-15.1	+20.0*	76%
2c (26%)	**3c** (90%)	**4c** (82%)	+3.6	-13.8*	26%

* reported for the enantiomer, see experimental.

In summary, we have presented a short, efficient, and general enantioselective synthesis of 2-substituted pyrrolidines from 4-hydroxynitriles. Chirality was derived from the chiral pool (glycidyl tosylate) or by asymmetric carbonyl (CBS) reduction. The later is noteworthy due to the apparent reversal of stereochemical outcome, which was rationalized using the concept of effective steric bulk.[12] Pyrrolidines stereochemically related to (R)-proline were obtained without the use of the expensive unnatural amino acid. The **5a-c** to **4a-c** conversion represents a carboxylic acid to pyrollidine conversion in which the carboxylic carbon becomes the asymmetric 2-position of the new pyrrolidine ring.

EXPERIMENTAL

General: Elemental analysis were performed by the Institute of Analytical Research, Syntex Research. NMR spectra were recorded on a Bruker WM 300 spectrometer and *J* values are given in Hertz. THF was freshly distilled from sodium/benzophenone and methane sulfonyl chloride from P_2O_5. The (R) and (S) oxazaborolidine catalysts were prepared as previously described.[7d] All other reagents were commercially available and used as received. The 4-ketonitriles **6a-c** were prepared from the corresponding acid chlorides by an adaption of the procedure of Knochel[9] and were purified by silica gel column chromatography (CC) using ethyl acetate (EA) and hexanes (HEX).

5-(3,4-Dimethoxyphenyl)-4-oxopentanenitrile **6a** was prepared from 3,4-dimethoxyphenylacetyl chloride (18 mmol) and purified by elution with 50:50 EA/HEX affording 2.80 g (64%) as a crystalline solid. mp=38 °C, ^{1}H NMR δ 2.47 (t, *J* =7.05, 2 H), 2.78 (t, *J* =7.05, 2 H), 3.62 (s, 2 H), 3.74 (s, 3 H), 3.75 (s, 3 H), 6.69-6.84 (m, 3 H); ^{13}C NMR δ 11.61, 37.45, 49.38, 56.18, 56.20, 113.2, 114.4, 119.9, 122.4, 127.7, 149.9, 150.8, 204.7; MS *m/e* 233 (M+), 151 (P). Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.00. Found: C, 66.55; H, 6.42; N, 5.99.

5-Phenyl-4-oxopentanenitrile **6b** was prepared from phenylacetyl chloride (15 mmol) and purified by elution with 25:75 EA/HEX affording 1.79 g (69%) as a colorless oil. ^{1}H NMR δ 2.52 (t, *J* =7.16, 2H), 2.81 (*J* =7.16, 2 H), 3.73 (s, 2H), 7.18-7.38 (m, 5 H); ^{13}C NMR δ 11.46, 36.97, 49.77, 119.0, 127.5, 129.1 (2 C), 129.4 (2C), 133.2, 203.9; MS *m/e* 173 (M+), 91 (P). Anal. Calcd for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.09. Found: C, 76.55; H, 6.36; N, 7.89.

4-Oxoundecanenitrile **6c** was prepared from octanoyl chloride (15 mmol) and purified by elution with 20:80 EA/HEX affording 1.84 g (86%) as a colorless oil. ^{1}H NMR δ 0.88 (t, *J* =6.75, 3 H), 1.27 (m, 8 H), 1.60 (t, *J* =7.36, 2 H), 2.45 (t, *J* =7.36, 2 H), 2.58 (t, *J* =7.26, 2 H), 2.80 (t, *J* =7.26, 2 H); ^{13}C NMR δ 11.39, 14.07, 22.59, 23.70, 29.00, 29.10, 31.64, 37.67, 42.52, 119.1, 206.4; 181 (M+), 57 (P). Anal. Calcd for $C_{11}H_{19}NO$: C, 72.88; H, 10.56; N, 7.73. Found: C, 72.48; H, 10.32; N, 8.13.

General procedure asymmetric reduction of **6a-c.** The ketone (2 mmol) in 4 mL of THF was treated with a 1 molar toluene solution of (S)-oxazaborolidine catalyst[7d] (0.1 mmol) and the solution was cooled to the indicated temperature under N_2. Borane-DMS complex (2 mmol) was added dropwise and the solution was stirred until the reaction was judged complete by TLC (15-60 min). Treatment with MeOH (to destroy excess reducing agent) followed by concentration *in vacuo* gave the crude alcohols **2a-c** which were then purified by column chromatography.

(S)-5-(3,4-Dimethoxyphenyl)-4-hydroxypentanenitrile **2a.** Reaction temperature: -15 °C; TLC, 75:25 EA/HEX, CC: 35:65 EA/HEX; yield: 0.470 g (100%). $[\alpha]^{25}_D$ = -13.2 (c 0.68, EtOH); ^{1}H NMR δ 1.61-1.96 (m, 3 H), 2.54 (dd, *J* =6.46, 7.85, 2 H), 2.61, 2.80 (ddd, *J*=4.12, 8.74, 13.65, 2 H), 3.87 (s, 3 H), 3.89 (s, 3 H), 3.92 (m, 1 H), 6.72-6.85 (m, 3 H); ^{13}C NMR δ 13.85, 31.99, 43.58, 55.89, 55.94, 70.60, 111.5, 112.3, 119.8, 121.3, 129.6, 148.1, 149.3; MS *m/e* 235 (M+), 151 (P). Anal. calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.02; H, 7.46; N, 5.60.

(S)-5-Phenyl-4-hydroxypentanenitrile **2b** Reaction temperature: 0 °C ; TLC, 25:75 EA/HEX; CC, 25:75 EA/HEX; yield: 0.282 g (82%). $[\alpha]^{25}_D$ = -25.4 (c 1.7, EtOH); ^{1}H NMR δ 1.70–1.97 (m, 3 H), 2.52 (dd, *J*=6.46, 8.03, 2 H), 2.69, 2.84 (ddd, *J*=4.45, 8.40, 13.5, 2 H), 3.93 (m, 1 H), 7.18-7.36 (m, 5 H); ^{13}C NMR δ 13.86, 32.02, 44.04, 70.66, 119.8, 127.0, 128.9 (2C), 129.4 (2C), 137.3; MS *m/e* 175 (M+), 92 (P). Anal. calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.16; H, 7.59; N, 8.03.

(R)-4-Hydroxyundecanenitrile **2c.** Reaction temperature: 20 °C ; TLC, 20:80 EA/HEX; CC, 12:88 EA/Hex; yield: 0.328 g (90%). $[\alpha]^{25}_D$ = -6.52 (c 1.1, EtOH); ^{1}H NMR δ 0.88 (t, *J*=6.78, 3 H), 1.24-1.46 (m, 12 H), 1.62-1.90 (m, 3 H), 2.51 (t, *J*=6.80, 2 H), 3.72 (m, 1 H); ^{13}C NMR δ 13.71, 14.09, 22.64, 25.51, 29.21, 29.48, 31.76, 32.52, 37.47, 70.00, 120.0; MS *m/e* 183 (M+), 69 (P). Anal. calcd for: $C_{11}H_{21}NO$: C, 72.08; H, 11.55; N, 7.64. Found: C, 72.08; H, 11.94; N, 7.71.

Tosylalcohol **8.** A solution of veratryllithium was prepared by adding n-BuLi (6.6 mL, 1.6 M in hexanes) to a solution of 4-bromoveratrole (1.35 mL, 9.35 mmol) in THF (25 mL) at -70 °C and stirring 30 min. A solution of (R)-glycidyl tosylate (2.0 g, 8.7 mmol) in THF (10 mL) was cooled to -20 °C and treated with BF_3-

Et_2O (1.3 mL) followed by the veratryllithium solution. The mixture was stirred 30 min at -20 °C and quenched with saturated aqueous NH_4Cl. An extractive aqueous workup (EA) followed by CC (40:60 EA/Hex) afforded 1.7 g of **8** as a colorless oil (53%). $[\alpha]^{25}_D$ -5.06 (c 0.5, $CHCl_3$); ^1H NMR δ 2.45 (s, 3 H), 2.69 (m, 2 H), 3.84 (s, 6 H), 3.94-4.12 (m, 3 H), 6.66-6.79 (m, 3 H), 7.35 (d, *J*=8.1, 2 H), 7.79 (d, *J*=8.1, 2 H); ^{13}C NMR δ 21.67, 38.95, 55.89, 55.93, 70.40, 72.65, 111.4, 112.5, 121.3, 128.0 (2C), 129.1, 130.0 (2C), 132.7, 145.1, 148.0, 149.1; MS *m/e* 366 (m+), 151 (P). Anal. calcd for $C_{18}H_{21}O_6$: C, 59.00; H, 6.05. Found: C, 58.92; H, 6.15.

Epoxide **9.** To a MeOH solution of **8** was added excess K_2CO_3 and the suspension was stirred for 10 min. The mixture was filtered, concentrated, and the residue triturated with ethyl acetate. Concentration followed by CC (15:85 EA/Hex) afforded 0.66 g of the epoxide **9** as a crystalline solid (87%). mp=44-46 °C, $[\alpha]^{25}_D$ +9.7 (c 0.5 $CHCl_3$); ^1H NMR δ 2.54 (dd, *J*=5.0, 2.7, 1 H), 2.76-2.88 (m, 3 H), 3.14 (m, 1 H), 3.87 (s, 3 H), 3.89 (s, 3 H), 6.78-6.84 (m, 3 H); ^{13}C NMR δ 38.32, 46.81, 52.62, 55.89, 55.95, 111.3, 112.3, 121.0, 129.8, 147.9, 149.0; ms *m/e* 194 (M+), 151 (P). Anal. calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.25. Found: C, 67.90; H, 7.19.

Enantiopure **2a.** A solution of lithioacetonitrile was prepared by adding acetonitrile (0.24 mL, 4.53 mmol) to LDA (1.87 mL, 2.2 M in THF) in THF (3 mL) at -60 °C. A solution of **9** (0.40 g, 2.0 mmol) in THF (5 mL) was then added dropwise and the mixture was stirred at -20 °C for 1 hr and quenched with saturated aqueous NH_4Cl. An extractive aqueous workup followed by CC (40:60 EA/Hex) afforded 0.36 g of **2a** as a colorless oil (75%). $[\alpha]^{25}_D$ -15.6 (c 0.5 EtOH); Anal. calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.45; H, 7.23; N, 5.64: all other physical data were as those reported above.

General procedure for the preparation of mesylates **3a-c.** To a 0.5 M solution of the alcohol in CH_2Cl_2 at 0 °C was added Et_3N (2.0 equiv) and methanesulfonyl chloride (1.5 equiv). After stirring 30 min the mixture was subjected to a standard extractive aqueous workup, the organic solution was concentrated, and the oily residue purified by column chromatography.

Mesylate **3a** was prepared from 0.392 g (1.67 mmol) of alcohol **2a**. CC, 35:65 EA/HEX; Yield, 0.502 g colorless oil (96%). $[\alpha]^{25}_D$ -2.3 (c 0.3 MeOH); ^1H NMR

δ 1.65–2.15 (m, 2 H), 2.53 (dt, *J*=2.80, 7.35, 2 H), 2.67 (s, 3 H), 2.95, 3.03 (ddd, *J*=6.03, 7.41, 14.2, 2 H), 3.87 (s, 3 H), 3.89 (s, 3 H), 4.89 (m, 1 H), 6.75-6.84 (m, 3 H); ^{13}C NMR δ 13.69, 14.22, 30.36, 38.14, 40.74, 55.95, 56.02, 81.78, 111.4, 112.5, 118.9, 121.7, 148.4, 149.2. Anal. calcd for $C_{14}H_{19}NO_5S$: C, 53.66; H, 6.11; N, 4.47. Found: C, 53.59; H, 6.27; N, 4.14.

Mesylate **3b** was prepared from 0.152 g (0.868 mmol) of alcohol **2b**. CC, 20:80 EA/HEX; yield, 0.214 g colorless oil (97%). $[\alpha]^{25}_D$ -3.5 (c 0.2 MeOH); ^{1}H NMR δ 2.00–2.16 (m, 2 H), 2.53 (dt, *J*=3.15, 7.30, 2 H), 2.57 (s, 3 H), 3.00, 3.09 (ddd, *J*=5.95, 6.45, 14.1, 2 H), 4.90 (m, 1 H), 7.23-7.34 (m, 5 H); ^{13}C NMR δ 13.68, 30.56, 37.89, 41.12, 81.83, 118.8, 127.5, 128.9 (2 C), 129.6 (2C), 135.6. Anal. calcd for $C_{12}H_{15}NO_3S$: C, 56.90; H, 5.97; N, 5.53. Found: C, 56.72; H, 5.99; N, 5.34.

Mesylate **3c** was prepared from 0.177 g (0.967 mmol) of alcohol **2c**. CC, 15:85 ethyl acetate/hexanes; yield, 0.228 g colorless oil (90%). $[\alpha]^{25}_D$ -5.5 (c 0.4 MeOH); ^{1}H NMR δ 0.88(t, *J*=6.90, 3 H), 1.24-1.45 (m, 10 H), 1.60-1.81 (m, 2 H), 1.95-2.15 (m, 2 H), 2.52 (dt, *J*=2.05, 7.32, 2 H), 3.07 (s, 3 H), 4.78 (m, 1 H); ^{13}C NMR δ 13.50, 14.08, 22.61, 24.93, 29.06, 29.21, 30.21, 31.69, 34.47, 38.63, 80.63, 119.0. Anal. calcd for $C_{12}H_{23}NO_3S$: C, 55.14; H, 8.87; N, 5.36. Found: C, 55.09; H, 8.79; N, 5.24.

General procedure for nitrile reduction/cyclization of mesylates **3a-c**. To a 0.2 M solution of the mesylate in THF under N_2 was added 1 M BH_3 in THF (4 equiv). The mixture was heated under reflux for 30-40 min until reaction was judged complete by TLC. The cooled reaction mixture was diluted with MeOH (to destroy excess reducing agent), concentrated *in vacuo*, and purified by column chromatography.

2(R)-3,4-Dimethoxybenzyl pyrrolidine **4a** was prepared from 0.431 g (1.38 mmol) of mesylate **3a**. TLC, 88:10:2 (CH_2Cl_2/MeOH/ Et_3N); CC, 92:7:1 (CH_2Cl_2/MeOH/ Et_3N); yield, 0.298 g colorless oil (97%). $[\alpha]^{25}_D$ -6.7 (c 0.5 MeOH); observed for authenic sample prepared from (R)-proline as reported:[1] $[\alpha]^{25}_D$ -8.3 (c 1.1 MeOH). The hydrochloride salt **1** was obtained by treatment of an i-PrOH solution of 0.091 g **4a** with excess HCl gas followed by concentration and crystallization from i-PrOH/Et_2O affording 0.089 g of **1** as a white solid (84%). mp=129-131 °C, reported: mp 133-135; $[\alpha]^{25}_D$ -35.1 (c 0.4 MeOH),

reported: $[\alpha]^{25}_D$ -35.9 (c 1.2 MeOH); all other spectral data was identical to that reported.[1, 2b]

2(R)-Benzyl pyrrolidine **4b** was prepared from 0.160 g (0.632 mmol) of mesylate **3b**. TLC, 13:1:0.1 (CH_2Cl_2/MeOH/ NH_4OH); yield, 0.068 g colorless oil (67%). $[\alpha]^{25}_D$ -15.1 (c 0.6 MeOH); reported[3] for enantiomer: $[\alpha]^{25}_D$ +20.0 (c 0.3 MeOH). All other spectral data were identical to those reported.

2(S)-Heptyl pyrrolidine **4c** was prepared from 0.136 g (0.520 mmol) of mesylate **3c**. TLC, 13:1:0.1 (CH_2Cl_2/MeOH/ NH_4OH); yield, 0.072 g colorless oil (82%). $[\alpha]^{25}_D$ +3.6 (c 0.7 THF); reported[3] for enantiomer: $[\alpha]^{25}_D$ -13.8 (c 2.0 THF). All other spectral data were identical to those reported.

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