(1*S*,3*R*,4*R*)-2-Azanorbornylmethanol, an Efficient Ligand for Ruthenium-Catalyzed Asymmetric Transfer Hydrogenation of Ketones

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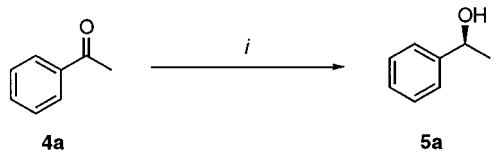
Ruthenium-catalyzed hydrogen transfer from 2-propanol to ketones is an efficient method for the preparation of secondary alcohols.[1] In contrast to hydrogenation using molecular hydrogen, the transfer hydrogenation of ketones is carried out in a very simple way and does not require the use of reactive metal hydrides or hydrogen. As a consequence, much effort has been put into the development of asymmetric versions of the reaction. Very recently, Noyori developed an efficient and highly enantioselective catalyst using diamines as chiral ligands to ruthenium.[2] Other types of chiral phosphorus and/or nitrogen ligands have also been used, however, with rather varying levels of yields and selectivity.[3]

Despite the progress recently being made on this catalytic enantioselective process, there are only a few examples that use simple amino alcohols as chiral ligands for asymmetric transfer hydrogenation of ketones.[4] We have recently reported the use of 2-azanorbornyl derivatives as ligands in asymmetric catalysis.[5] The promising results obtained prompted us to apply some of these rigid proline analogues to the catalytic hydrogen-transfer process.[6] Herein we present our preliminary results for this reaction.

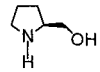
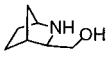
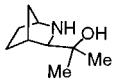
Scheme 1[a]



4a **5a**

[a] Reagents and conditions: (i) 0.25 mol % $[RuCl_2(HMB)]_2$, 2 mol % L* (**1**−**3**), 2.5 mol % *i*-PrOK, *i*-PrOH.

Table 1. Hydrogen-Transfer Reduction of Acetophenone Using Ligands 1−3

entry	ligand (L*)	yield (%)[a]	time (h)	ee (%)[b]	config[c]
1	 **1**	16	6.5	8	*S*
2	 **2**	92	5	95	*S*
3	 **3**	85	16[d]	rac.	--

[a] Determined by GLC and 300 MHz ^{1}H NMR analysis. [b] Determined by HPLC analysis (ChiralCel OD-H; 5% of *i*-PrOH in hexane; 0.5 mL/min). [c] Determined from the sign of rotation of the isolated product. [d] The reaction was run at 83 °C.

To study the effect of the ligand backbone, (*S*)-2-pyrrolidinemethanol (**1**) was compared with the conformationally constrained (1*S*,3*R*,4*R*)-3-(hydroxymethyl)-2-azabicyclo[2.2.1]heptane (**2**) and (1*S*,3*R*,4*R*)-3-(2-hydroxy-2-propyl)-2-azabicyclo[2.2.1]heptane (**3**) in the reduction of acetophenone **4a** (Scheme 1). In a typical experiment, a solution of the ketone (1 equiv, 0.1 M in dry 2-propanol), the ruthenium complex ($[RuCl_2(HMB)]_2$;[7] 0.25 mol %), the chiral amino alcohol (2 mol %), and *i*-PrOK (2.5 mol %) was stirred under argon at room temperature for 5−16 h in dry *i*-PrOH. The use of **1** gave rise to a rather slow and unselective reaction for reasons not yet fully understood (16% conversion and 8% ee over the unexpected enantiomer, after 6.5 h; entry 1, Table 1). However, amino alcohol **2** gave an excellent result (92% conversion and 95% ee after 5 h; entry 2, Table 1). In the presence of the sterically more hindered ligand **3** no reaction was observed at room temperature. For some hindered systems, it has been observed that the reactions may be carried out at higher temperatures without significant loss of enantioselectivity.[3m] In the case of ligand **3**, however, carrying the reaction out at reflux led to the formation of racemic product (entry 3, Table 1). It therefore seems that 2-azanorbornyl carbinols with tertiary alcohol moieties are not useful in this catalytic system.

The bicyclic ligand structure is particularly attractive as it is easily prepared in either enantiomeric forms and on a multigram scale with the use of only inexpensive

(1) (a) Sasson, Y.; Blum, J. *Tetrahedron Lett.* **1971**, *24*, 2167. (b) Sasson, Y.; Blum, J. *J. Org. Chem.* **1975**, *40*, 1887. (c) Linn, D. E.; Halpern, G. *J. Am. Chem. Soc.* **1987**, *109*, 2969. (d) Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, *23*, 345. (e) Chowdhury, R. L.; Bäckvall, J. E. *J. Chem. Soc., Chem. Commun.* **1991**, 1063.

(2) (a) Hashiguchi, S.; Fujii, A.; Takehara, J.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1995**, *117*, 7562. (b) Fujii, A.; Hashiguchi, S.; Uematsu, N.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 2521. (c) Haack, K. J.; Hashiguchi, S.; Fujii, A.; Ikariya, T.; Noyori, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 285. (d) Matsumura, K.; Hashiguchi, S.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1997**, *119*, 8738.

(3) (a) For a review see: Zassinovich, G.; Mestroni, G.; Gladiali, S. *Chem. Rev.* **1992**, *92*, 1051. (b) Gladiali, S.; Pinna, L.; Delogu, G.; De Martin, S.; Zassinovich, G.; Mestroni, G. *Tetrahedron: Asymmetry* **1990**, *1*, 635. (c) Muller, D.; Umbricht, G.; Weber, B.; Pfaltz, A. *Helv. Chim. Acta* **1991**, *74*, 232. (d) Genet, J.-P.; Ratovelomonana-Vidal, V.; Pinel, C. *Synlett* **1993**, *34*, 478. (e) Krasik, P.; Alper, H. *Tetrahedron* **1994**, *50*, 4347. (f) Yang, H.; Alvarez, M.; Lugan, N.; Mathieu, R. *J. Chem. Soc., Chem. Commun.* **1995**, 1721. (g) Langer, T.; Helmchen, G. *Tetrahedron Lett.* **1996**, *37*, 1381. (h) Langer, T.; Janssen, J.; Helmchen, G. *Tetrahedron: Asymmetry* **1996**, *7*, 1599. (i) Jiang, Q.; Van Plew, D.; Mutuza, S.; Zhang, X. *Tetrahedron Lett.* **1996**, *37*, 797. (j) Puntener, K.; Schwink, L.; Knochel, P. *Tetrahedron Lett.* **1996**, *37*, 8165. (k) Gamez, P.; Dunjic, B.; Lemaire, M. *J. Org. Chem.* **1996**, *61*, 5196. (l) Jiang, Y.; Jiang, Q.; Zhu, G.; Zhang, X. *Tetrahedron Lett.* **1997**, *38*, 215. (m) Sammakia, T.; Stangeland, E. L. *J. Org. Chem.* **1997**, *62*, 6104.

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(5) Södergren, M. J.; Andersson, P. G. *Tetrahedron Lett.* **1996**, *37*, 7577.

(6) During the progress of this work, Wills et al. reported on the use of conformationally rigid 2-indanol derivatives as chiral ligands for the asymmetric transfer hydrogenation of ketones; see: Palmer, M.; Walsgrove, T.; Wills, M. *J. Org. Chem.* **1997**, *62*, 5226.

(7) HMB = hexamethylbenzene. For the synthesis of the Ru complexes see: (a) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233. (b) Bennett, M. A.; Matheson, T. W.; Robertson, G. B.; Smith, A. K.; Tucker, P. A. *Inorg. Chem.* **1980**, *19*, 1014.

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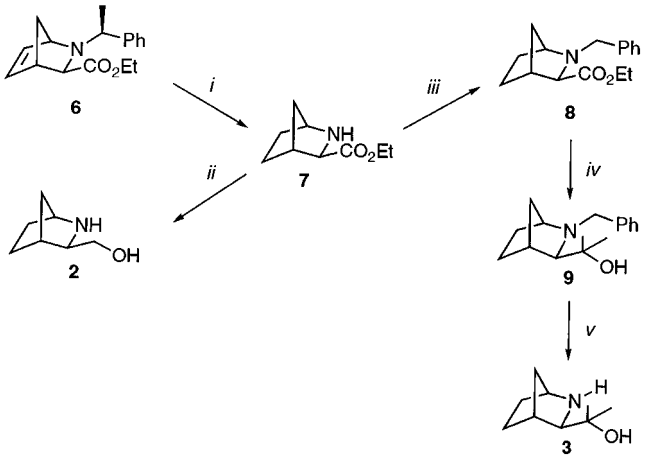
Scheme 2[a]



[a] Reagents and conditions: (i) H_2 (150 psi), 5% Pd−C, EtOH, 98%, 97% ee;[12] (ii) $LiAlH_4$, THF, 90%; (iii) $PhCH_2Br$, K_2CO_3, CH_3CN, 78%; (iv) MeMgBr, THF, 84%; (v) H_2 (150 psi), 5% Pd−C, EtOH, 98%.

reagents (Scheme 2). Adduct **6** is prepared in high yield via a highly exo and diastereoselective aza-Diels−Alder reaction employing either (+)- or (−)-phenylethylamine as the source of chirality.[8] Hydrogenation/hydrogenolysis[9] and subsequent reduction with $LiAlH_4$ affords amino alcohol **2** in 92% overall yield from **6**.

Next, we wanted to investigate whether the very promising results obtained with **2** could be extended to other substrates, and indeed, it was found that a variety of prochiral ketones could be reduced with high enantioselectivity (Table 2, Scheme 3). In accordance with Noyori's observations,[4a] ketones with a bulky substituent adjacent to the carbonyl reacted very slowly under the reaction conditions (entry 7, Table 2).

Finally, we also studied the influence of the arene ligand in the ruthenium complex. It was found that the use of $[RuCl_2(p\text{-cymene})]_2$ instead of $[RuCl_2(\text{hexamethylbenzene})]_2$ resulted in a higher rate and improved selectivity for all the substrates studied (compare entries 1−6 with 8−13, Table 2). Using this complex, the secondary alcohols were obtained with ee's ranging from 92 to 97%.

In conclusion, we have demonstrated that ruthenium complexes having 2-azanorbornylmethanol as chiral ligand are efficient catalysts for the enantioselective transfer hydrogenation of aromatic ketones, affording the corresponding secondary alcohols in excellent ee's. Studies are in progress in order to further improve the enantioselectivity and also to rationalize the origin of the asymmetric induction observed with this new catalytic system.

Experimental Section

For general experimental information see ref 13.

Flash chromatography was preformed on silica gel (Matrex 60A, 37−70 μm). When mentioned, deactivated silica gel means that it was treated with 5% Et_3N in pentane and the column was eluted with the same solvent mixture until the coming eluent was basic according to pH paper. TLC's were prefomed on precoated plates, SIL G-60 UV_{254}, purchased from Macherey-Nagel. When mentioned, deactivated silica gel means that the TLC plate was eluted with 5% Et_3N in pentane and dried before applying the sample. HPLC analyses were carried out using a chiral column (ChiralCelOD-H), a 254 nm UV detector, and a flow rate of 0.5 mL/min.

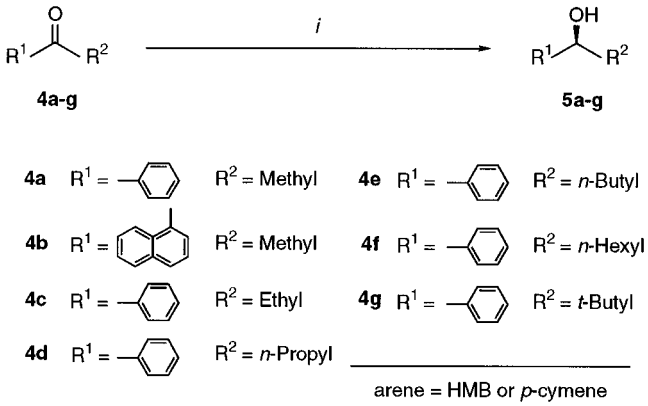
Ethyl (1*S*,3*R*,4*R*)-2-[[(*S*)-1-Phenylethyl]amino]-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate (6). Compound **6** was prepared via an aza-Diels−Alder reaction between cyclopenta-

Table 2. Hydrogen Transfer Reduction of Ketones 4a−g Using Ligand 2[a]

				product			
entry	ketone	$[RuCl_2(\text{arene})]_2$	time (h)	no.	yield[b] (%)	ee[c] (%)	config[d]
1	**4a**	HMB	5	**5a**	92	95	*S*[e]
2	**4b**	HMB	3	**5b**	100 (98)[f]	94	*S*[e]
3	**4c**	HMB	5	**5c**	81	83	*S*[e]
4	**4d**	HMB	5	**5d**	81	90	*S*[e]
5	**4e**	HMB	5	**5e**	70	89	*S*[g]
6	**4f**	HMB	5	**5f**	17	83	*S*[h]
7	**4g**	HMB	5	**5g**	*i*	*j*	
8	**4a**	*p*-cymene	1.5	**5a**	91	94	*S*
9	**4b**	*p*-cymene	1.5	**5b**	92	97	*S*
10	**4c**	*p*-cymene	1.5	**5c**	81	93	*S*
11	**4d**	*p*-cymene	1.5	**5d**	60	92	*S*
12	**4e**	*p*-cymene	1.5	**5e**	78	95	*S*[g]
13	**4f**	*p*-cymene	1.5	**5f**	53	95	*S*[h]

[a] General procedure for the hydrogen-transfer reduction: The ruthenium complex dimer (10 μmol) and **2** (80 μmol) were weighed into a round-bottom flask, and any moisture was azeotropically removed via evaporation of benzene (5 × 5 mL) at reduced pressure. A condenser was attached, and the residue was dissolved in dry *i*-PrOH (5 mL). The solution was refluxed under argon for 30 min before it was cooled to rt and transferred to a flask containing a solution of the ketone (4 mmol) and potassium isopropoxide (100 μmol) in *i*-PrOH (35 mL). The resulting solution was then stirred for the time indicated at rt under argon (monitored by GC and/or ^1H NMR), neutralized with 1 M solution of HCl, and concentrated in vacuo to give the crude product, which was purified by flash column chromatography (SiO_2, EtOAc/pentane 90/10). [b] Yield was determined by GLC and 300 MHz ^1H NMR analysis. [c] Determined by HPLC analysis (ChiralCel OD-H; 5% of *i*-PrOH in hexane; 0.5 mL/min). [d] Determined from the sign of rotation of the isolated product. [e] Commercially available compounds. [f] Isolated yield after flash chromatography (silica gel, pentane/EtOAc 90/10). [g] See ref 10. [h] See ref 11. [i] Less than 5% of conversion was obtained after 5 h. [j] Not determined.

Scheme 3[a]



[a] Reagents and conditions: (i) 0.25 mol % $[RuCl_2(\text{arene})]_2$, 2 mol % **2** (97% ee[12]), 2.5 mol % *i*-PrOK, *i*-PrOH.

(8) (a) Stella, L.; Abraham, M.; Feneau-Dupont, J.; Tinant, B.; Declercq, J. P. *Tetrahedron Lett.* **1990**, *18*, 2603. (b) Waldmann, H.; Braun, M. *Liebigs Ann. Chem.* **1991**, 1045.

(9) Nakano, H.; Kumagai, N.; Matsuzaki, H.; Kabuto, C.; Hongo, H. *Tetrahedron: Asymmetry* **1997**, *9*, 1391.

(10) Watanabe, M.; Araki, S.; Butsugan, Y. *J. Org. Chem.* **1991**, *56*, 2218.

(11) Mori, K.; Bernotas, R. *Tetrahedron: Asymmetry* **1990**, *1*, 87.

(12) Determined by HPLC analysis of the *N*-benzoyl derivative of ethyl (1*S*,3*R*,4*R*)-2-azabicyclo[2.2.1]heptane-3-carboxylate (**7**).

(13) Bedekar, A. V.; Koroleva, E. B.; Andersson, P. G. *J. Org. Chem.* **1997**, *62*, 2518.

diene, an iminium ion derived from ethyl glyoxylate and (*S*)-1-phenylethylamine, following a literature procedure.[14] Purification by flash chromatography (deactivated silica gel, pentane/Et_2O 95/5−80/20) afforded pure compound **6** (60% yield). All the physical and spectroscopic data for compound **6** were in complete agreement with the reported data for its enantiomer,[14] except for the sign of the optical rotation.

Ethyl (1*S*,3*R*,4*R*)-2-Azabicyclo[2.2.1]heptane-3-carboxylate (7). A solution of the Diels−Alder adduct **6** (7.87 g, 29.0 mmol) in absolute ethanol (50 mL) was stirred under a hydrogen pressure of 100 psi at room temperature for 48 h in the presence of 5% Pd−C (1.57 g, 20 wt %). The Pd−C was removed by filtration through Celite and evaporation of the solvent yielded 4.81 g (98% yield) of the pure NH amino ester: R_f 0.53 (pentane/acetone 1/1; deactivated silica gel); $[\alpha]^{24}_D = -28.2$ (c = 1.26, $CHCl_3$); IR (neat, cm^{-1}) 3310, 1728, 1206; ^1H NMR δ 1.21 (1 H, br d, J = 9.8 Hz), 1.25 (3 H, t, J = 7.1 Hz), 1.34−1.66 (5 H, m), 2.18 (1 H, br s), 2.59, 3.27, 3.50 (1 H each, 3 br s), 4.15 (2 H, q, J = 7.1 Hz); ^{13}C NMR δ 14.2, 28.4, 31.1, 35.7, 41.7, 56.2, 61.0, 63.6, 174.5; MS (EI) m/z (rel intensity) 169 (M^+, 8), 131 (26), 73 (23), 69 (100), 57 (25), 55 (40). Anal. Calcd for $C_9H_{15}NO_2 \cdot 0.1H_2O$: C, 63.21; H, 8.96; N, 8.19. Found: C, 62.98; H, 9.06; N, 8.11.

(1*S*,3*R*,4*R*)-3-(Hydroxymethyl)-2-azabicyclo[2.2.1]-heptane (2). A solution of ethyl (1*S*,3*R*,4*R*)-2-azabicyclo[2.2.1]-heptane-3-carboxylate (2.60 g, 15.4 mmol) in dry THF (20 mL) was added to a suspension of $LiAlH_4$ (1.17 g, 30.8 mmol) in dry THF (20 mL) at 0 °C under argon. After completion according to TLC, the reaction was quenched by adding consecutively 1.2 mL of water, 1.2 mL of 5% NaOH solution, and 3.6 mL of water. The mixture was then stirred for 30 min at room temperature. Filtration and solvent evaporation afforded 1.77 g of pure compound **2** as a white solid (90% yield) that was recrystallized from hexane: mp = 43−45 °C; R_f 0.22 (methanol; deactivated silica gel); $[\alpha]^{25.6}_D = -62.9$ (c = 1.03, $CHCl_3$); IR (neat, cm^{-1}) 3383; ^1H NMR δ 1.15 (1 H, dt, J = 9.8, 1.4 Hz), 1.40−1.30 (2 H, m), 1.72−1.53 (3 H, m), 2.17 (1 H, m), 2.89−2.79 (3 H, m), 3.17 (1 H, dd, J = 10.7, 8.2 Hz), 3.40 (1 H, dd, J = 10.7, 5.4 Hz), 3.43 (1 H, br s); ^{13}C NMR δ 28.8, 32.9, 34.7, 38.8, 55.8, 62.2, 65.3; MS (EI) m/z (rel intensity) 127 (M^+, 2), 96 (49), 68 (100). Anal. Calcd for $C_7H_{13}NO$: C, 66.11; H, 10.30; N, 11.01. Found: C, 65.18; H, 10.37; N, 10.85.

Ethyl (1*S*,3*R*,4*R*)-2-Benzyl-2-azabicyclo[2.2.1]heptane-3-carboxylate (8). Anhydrous K_2CO_3 (335 mg, 2.4 mmol) was added to a solution of ethyl (1*S*,3*R*,4*R*)-2-azabicyclo[2.2.1]-heptane-3-carboxylate (339 mg, 2.0 mmol) and benzyl bromide (0.29 mL, 2.4 mmol) in CH_3CN (10 mL) at room temperature, and the reaction mixture was stirred for 32 h. The solvent was then evaporated, water was added, and the resultant mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated and the residue purified by flash chromatography (pentane/Et_2O 99/1 to 95/5) to afford 407 mg (78% yield) of the pure benzyl ester: R_f 0.53 (pentane/Et_2O 1/1); $[\alpha]^{25}_D = -0.9$ (c = 1.06, $CHCl_3$), $[\alpha]^{25}_{365} = -8.1$ (c = 1.06, $CHCl_3$); IR (neat, cm^{-1}) 1742, 1155; ^1H NMR δ 1.13 (3 H, t, J = 7.1 Hz), 1.24 (1 H, dt, J = 9.4, 1.4 Hz), 1.30−1.44, 1.61−1.71, 1.92−2.05 (2, 1 and 2 H, respectively, 3 m), 2.50−2.54 (1 H, m), 2.67 (1 H, s), 3.31−3.33 (1 H, m), 3.72, 3.76 (2H, 2 d, J = 12.9 Hz), 4.00 (2 H, q, J = 7.1 Hz), 7.18−7.37 (5 H, m); ^{13}C NMR δ 14.2, 22.4, 29.3, 36.6, 42.4, 55.5, 59.6, 60.2, 69.9, 126.8, 128.1, 129.0, 139.4, 173.5; MS (EI) m/z (rel intensity) 259 (M^+, <1), 186 (39), 158 (32), 91 (100), 65 (21). Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16; N, 5.40. Found: C, 73.89; H, 8.17; N, 5.37.

(1*S*,3*R*,4*R*)-2-Benzyl-3-(2-hydroxy-2-propyl)-2-azabicyclo-[2.2.1]heptane (9). To a solution of ethyl (1*S*,3*R*,4*R*)-2-benzyl-2-azabicyclo[2.2.1]heptane-3-carboxylate (1.5 mmol) in dry THF at −30 °C was added dropwise a 3 M solution of MeMgBr (3.75 mmol) in dry Et_2O (4 mL). The reaction was stirred for 7 h, allowing the temperature to rise to room temperature. Then, the reaction mixture was hydrolyzed with water and extracted with ethyl acetate (3 × 20 mL). The organic layer was dried over $MgSO_4$ and evaporated and the residue purified by flash chromatography (pentane/acetone 95/5) to afford 311 mg (84% yield) of pure product: mp = 48−50 °C; R_f 0.40 (pentane/acetone 4/1); $[\alpha]^{25}_D = +31.5$ (c = 1.09, $CHCl_3$); IR (KBr, cm^{-1}) 3482; ^1H NMR δ 1.07 (1 H, br d, J = 9.5 Hz), 1.21, 1.23 (3 H each, 2 s), 1.19−1.30, 1.57−1.66, 1.83−1.89, 2.01−2.09 (2, 1, 1 and 1 H, respectively, 4 m), 2.01 (1 H, s), 2.38−2.42 (1 H, m), 3.12 (1 H, br s), 3.18 (1 H, br s), 3.70, 4.02 (2H, 2 d, J = 14.0 Hz), 7.22−7.38 (5 H, m); ^{13}C NMR δ 22.1, 26.5, 29.8, 30.3, 36.0, 39.5, 55.5, 58.0, 71.2, 76.3, 126.8, 128.3 (4 C), 140.0; MS (EI) m/z (rel intensity) 230 ($M^+ - 15$, 2), 186 (56), 158 (45), 91 (100), 65 (18). Anal. Calcd for $C_{16}H_{23}NO$: C, 78.32; H, 9.45; N, 5.71. Found: C, 78.34; H, 9.42; N, 5.69.

(1*S*,3*R*,4*R*)-3-(2-Hydroxy-2-propyl)-2-azabicyclo[2.2.1]-heptane (3). A solution of (1*S*,3*R*,4*R*)-2-benzyl-3-(2-hydroxy-2-propyl)-2-azabicyclo[2.2.1]heptane (259 mg, 1.05 mmol) in absolute ethanol (25 mL) was submitted to hydrogenolysis in the presence of 5% Pd−C (51 mg, 20 wt %) under a hydrogen pressure of 150 psi at room temperature for 24 h. The Pd−C was removed by filtration through Celite, and evaporation of the solvent afforded 160 mg of the desired product (98% yield) as a low-melting-point white solid that was recrystallized from pentane/ether: R_f 0.24 (pentane/ether 1/1); $[\alpha]^{24.2}_D = -37.3$ (c = 0.71, $CHCl_3$); IR (KBr, cm^{-1}) 3284, 3176; ^1H NMR δ 1.02−1.40 (9 H, m with 2 s at 1.05 and 1.15), 1.42−1.76 (3 H, m), 2.39 (1 H, br s), 2.47 (1 H, s), 2.90 (1 H, br s), 3.46 (1 H, br s); ^{13}C NMR δ 25.3, 28.7, 30.1, 32.4, 34.8, 37.7, 55.4, 68.8, 70.4; MS (EI) m/z (rel intensity) 140 ($M^+ - 15$, 2), 96 (18), 68 (100), 67 (41), 59 (34).

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Supporting Information Available: HPLC traces for compounds **5a**−**f** (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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