

Table 2

Entry	Ketone	Alcohol ^a	Time (d)	%ee	yield (%)
1			0.9	97 ^b	73
2			0.8	91 ^c	77
3			8	94 ^{c,d}	51
4			2	90 ^b	78
5			1	95 ^c	88
6			0.9	96 ^c	84
7			2	94 ^c	85
8			0.8	87 ^c	62
9			1	96 ^b	75
10			1	97 ^c	89
11			8	65 ^{d,e}	66

^a Reactions were run using 4.5 mol % **1** as the (*R,R,R*)-diastereomer. The absolute configuration was determined by comparison of the optical rotation with literature sources. ^b Percent ee determined by GC analysis using a cyclodex-B column. ^c Percent ee determined by HPLC analysis using a Chiralcel OB HPLC column. ^d Did not go to completion. ^e Percent ee determined by ¹⁹F NMR of the Mosher ester.

Table 3

Entry	Ketone	Alcohol ^a	Time (d)	%ee	yield (%)
1			1	95 ^b	96
2			4.5	92 ^{b,c}	79
3			2.5	94 ^b	78
4			2.5	82 ^{b,d}	88
5			1	82 ^{b,d}	88
6			1.6	92 ^b	68
7			3.5	91 ^b	92

^a Reactions were run using 4.5 mol % **1** as the (*R,R,R*)-diastereomer. The absolute configuration was determined by comparison of the optical rotation with literature sources. ^b Percent ee determined by HPLC analysis using a Chiralcel OB HPLC column. ^c Reaction run with 10 mol % **1** and 10 equiv of silane. ^d 1.5 equiv of PhSiH₃ as silane.

entry 11) was reduced to the corresponding alcohol with only a moderate level of enantioselectivity. Addition of 9,10-dihydroanthracene¹⁰ increased the enantioselectivity of the reaction to 81–91%, but did not increase the reaction rate. This provides evidence that the catalyst, in this case, is being converted, by a radical process, into a species which also hydrosilylates ketones but with little or no enantioselectivity. This hydrosilylation procedure tolerates aromatic bromides,

(10) Narayanan, B. A.; Amatore, C.; Casey, C. P.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 6351.

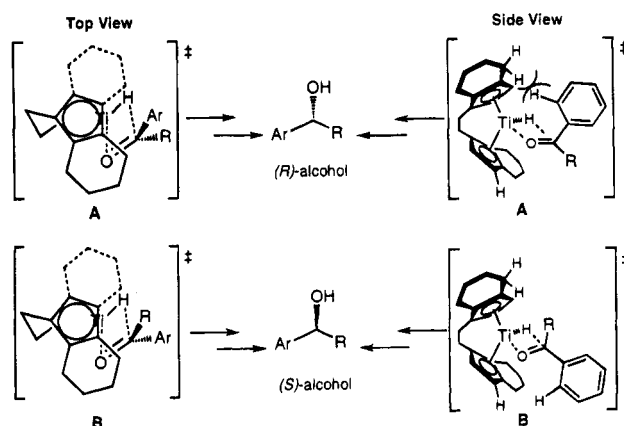


Figure 1.

unlike the related hydrogenation of imines.¹¹ Both *o*- and *p*-bromoacetophenone (Table 2, entries 3 and 9) are reduced to the corresponding alcohols with high levels of enantioselectivity. However, the reduction of *o*-bromoacetophenone does not proceed to completion. Initially we presumed that catalyst deactivation was due to a side reaction operating via a radical mechanism, but the addition of 9,10-dihydroanthracene¹⁰ had no effect on the rate, enantioselectivity, or degree of conversion of the reaction. While earlier reports suggested that a titanium(III) hydride species would reductively cleave an aromatic bromide,¹² neither acetophenone nor 1-phenylethanol was detected by GC analysis of the crude reaction mixtures. Possible explanations for these conflicting observations are (1) that there are different titanium species involved in each reaction or (2) that different hydrogen sources affect the reactivity of the titanium catalyst.

We have also examined how the size of the alkyl group of the alkyl aryl ketone affects the hydrosilylation reaction. A variety of ketones with branched aliphatic groups were hydrosilylated (Table 3). All ketones were reduced to the (*S*)-enantiomers of the corresponding alcohols with moderate to good levels of enantioselectivity. Bulkier substrates required the use of additional catalyst and/or longer reaction times. Aryl cyclobutyl and aryl cyclohexyl ketones (Table 3, entries 4 and 5) were transformed with better enantioselectivity when phenylsilane was used in place of polymethylhydrosiloxane.

It has been postulated,^{4,6,7,13} that the active species in these reductions is a titanium(III) hydride. To account for the stereoselectivity of this reaction, we propose the transition state model¹⁴ shown in Figure 1. Analysis of the metallocene orbitals as determined by Lauher and Hoffmann¹⁶ indicates that the ketone should approach the titanium complex from the side. If one assumes that the aromatic (or olefinic) group and the carbonyl group remain in conjugation throughout the reaction,¹⁷

(11) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 8952.

(12) Colomer, E.; Corriu, R. *J. Organomet. Chem.* **1974**, *82*, 367.

(13) (a) Sato, F.; Jinbo, T.; Sato, M. *Tetrahedron Lett.* **1980**, *21*, 2171. (b) Nakano, T.; Nagai, Y. *Chem. Lett.* **1988**, 481.

(14) We have been unable to identify the exact nature of the catalytic species in this reaction. It is possible that a variety of titanium species are present in the solution including titanium(III) hydrides, silyl titanium(IV) hydrides, bimetallic silyl titanium hydrides, and bimetallic titanium hydrides. All of these have been previously reported in the literature¹⁵ and may be capable of reducing ketones. However, our basic model does not change whether the catalyst is a titanium(III) hydride or a titanium(IV) hydrido silyl species.

(15) (a) Harrod, J. F.; Mu, Y.; Samuel, E. *Can. J. Chem.* **1992**, *2980*. (b) Harrod, J. F.; Ziegler, T.; Tschinke, V. *Organomet.* **1990**, *9*, 897. (c) Samuel, E.; Mu, Y.; Harrod, J. F.; Dromzee, Y.; Jeannin, Y. *J. Am. Chem. Soc.* **1990**, *112*, 3435. (d) Aitken, C. T.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059.

(16) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

the aromatic group should not rotate to minimize interactions with the catalyst. The ketone thus prefers to approach the complex as shown in transition state B to minimize steric interactions between the cyclohexyl portion of the tetrahydroindenyl ligand and the aromatic ring of the ketone. Reaction through transition state B results in the (*S*)-alcohol as observed. In transition state A, the aromatic group of the ketone would be forced into close contact with the cyclohexyl portion of the tetrahydroindenyl ligand, thus destabilizing A relative to B. The observed configuration of products is consistent with this model. For unconjugated ketones (e.g., Table 1, entry 2) rotation of the side chain can occur upon approach to the catalyst to minimize steric interactions. In these cases the sizes of the groups on the ketone are similar and poor enantioselectivity is observed.

In summary, we have presented the first method to hydrosilylate aromatic ketones with high enantioselectivity using an early transition metal catalyst. Further efforts to design asymmetric catalysts for the reduction of prochiral substrates are underway.

Experimental Section

General Techniques. Reactions were generally run under an atmosphere of argon in sealed Schlenk flasks that were base washed and dried in an oven at 150 °C overnight. Benzene was distilled under nitrogen from sodium benzophenone ketyl. The ketones and the silanes were passed through a plug of neutral alumina prior to use. Melting points were obtained using a Haake Buchler melting point apparatus in an open capillary tube and are uncorrected. Proton nuclear magnetic resonance (¹H NMR) spectra were recorded on a Bruker AC-250 (250 MHz) or a Varian XL-300 (300 MHz) instrument. Chemical shifts are reported in δ units, parts per million (ppm) downfield from tetramethylsilane (TMS). Coupling constants are reported in hertz (Hz). Infrared spectra (IR) were obtained on a Perkin-Elmer 1600 Series FTIR and are recorded in cm⁻¹. Optical rotations were recorded on a Perkin-Elmer polarimeter 241. Enantiomeric excesses were determined by GC analysis using a cyclodex-B column, HPLC analysis using a Chiralcel OB or OD column, or ¹⁹F NMR (Varian VXR-500, 470.268 MHz) of the Mosher ester.¹⁸

General Procedure for the Hydrosilylation of Ketones. A solution of *n*-butyllithium in hexanes (0.090 mmol) was added to the center of a solution of **1**^{5,19} (0.045 mmol) in anhydrous benzene (1.0 mL) under an atmosphere of argon in a Schlenk tube. After 5 min, polymethylhydrosiloxane (5.0 mmol) was added and formation of a precipitate was observed. After an additional 5 min, ketone (1.0 mmol) was added, the precipitate disappeared, and bubbling occurred. The reaction was monitored by TLC or GC analysis until complete. The reaction mixture was diluted with THF (5 mL) and quenched with a solution of 1.0 M TBAF in THF (6.0 mL). **CAUTION:** vigorous bubbling! After 2 h the reaction was concentrated *in vacuo*, diluted with ether (25 mL), washed with 0.5 M aqueous HCl (25 mL), 0.5 M aqueous NaOH (25 mL), and saturated aqueous NaCl (12 mL), dried (MgSO₄), and concentrated *in vacuo* to give an oil. The product was purified by flash column chromatography²⁰ (ether–pentane) and characterized by ¹H NMR and optical rotation. The results reported in this paper are the average of at least two runs.

Alternative Workup. The reaction mixture was diluted with acetone (5 mL) and quenched with 10% aqueous HCl (1 mL). After 2 h the reaction mixture was concentrated *in vacuo*, diluted with ether (25 mL), washed with water (10 mL), 0.5 M aqueous NaOH (10 mL), and saturated aqueous NaCl (10 mL), dried (MgSO₄), and concentrated

in vacuo to give an oil. The product was purified by flash column chromatography²⁰ (ether–pentane) and Kugelrohr distillation and characterized by ¹H NMR and optical rotation.

(S)-1-Phenylethanol: 0.9 day; 97% ee; 73% yield; ¹H NMR (CDCl₃, 250 MHz) 1.48 (d, *J* = 6.47 Hz, 3 H), 2.04 (br s, 1 H), 4.87 (q, *J* = 6.34 Hz, 1 H), 7.23–7.36 (m, 5 H); IR (neat) 606, 699, 761, 899, 997, 1011, 1029, 1078, 1099, 1204, 1303, 1369, 1451, 1493, 2875, 2927, 2973, 3028, 3062, 3085, 3356 cm⁻¹; [α]_D -49.5° (c 0.0489, CH₂Cl₂) (lit.²¹ [α]_D 48.6° (c 1.0, CH₂Cl₂), 96.2% ee (*R*)).

(R)-1-Cyclohexylethanol: 4 days; 24% ee; 67% yield; ¹H NMR (CDCl₃, 250 MHz) 1.02–1.34 (m, 6H), 1.16 (d, *J* = 6.34 Hz, 3 H), 1.38 (br s, 1 H), 1.65–1.88 (m, 5 H), 3.50–3.57 (m, 1 H); IR (neat) 892, 938, 1043, 1062, 1098, 1128, 1269, 1373, 1449, 2852, 2924, 2969, 3356 cm⁻¹; [α]_D -1.6° (c 0.0368, CHCl₃) (lit.²² [α]_D -3.4° (c 1.1, CHCl₃), 94% ee (*R*)).

(S)-1-(1-Cyclohexenyl)ethanol:²³ 1 day; 9 mol % **1**, 10 equiv of silane; 90% ee; 72% yield; ¹H NMR (CDCl₃, 300 MHz) 1.26 (d, *J* = 6.42 Hz, 3 H), 1.39 (br s, 1 H), 1.54–1.67 (m, 4 H), 1.89–2.05 (m, 4 H), 4.16 (q, *J* = 6.38 Hz, 1 H), 5.67 (br s, 1 H).

(R)-4-Phenyl-2-butanol: 0.8 day; 12% ee; 88% yield; ¹H NMR (CDCl₃, 250 MHz) 1.23 (d, *J* = 6.34 Hz, 3 H), 1.43 (br s, 1 H), 1.67–1.87 (m, 2 H), 2.61–2.82 (m, 2 H), 3.75–3.90 (br m, 1 H), 7.15–7.37 (m, 5 H); IR (neat) 699, 746, 954, 1031, 1055, 1082, 1128, 1373, 1454, 1485, 1603, 1603, 2927, 2965, 3026, 3062, 3084, 3355 cm⁻¹; [α]_D -2.1° (c 0.0621, CHCl₃) (lit.²⁴ [α]_D 17.45° (c 2.04, CHCl₃), >95% ee (*S*)).

(S)-1-(2-Naphthyl)ethanol: 3 days; 95% ee; 84% yield; ¹H NMR (CDCl₃, 300 MHz) 1.23 (d, *J* = 6.34 Hz, 3 H), 1.43 (br s, 1 H), 1.67–1.87 (m, 2 H), 2.61–2.82 (m, 2 H), 3.75–3.90 (br m, 1 H), 7.15–7.37 (m, 5 H); [α]_D -52.3° (c 0.0520, CHCl₃) (lit.^{1b} [α]_D 49.6° (c 1.1, CHCl₃), 89% ee (*R*)); mp 69.7–70.5 °C (lit.²⁵ mp 71–72 °C).

(S)-1-(2'-Methoxyphenyl)ethanol: 0.8 day; 91% ee; 77% yield; ¹H NMR (CDCl₃, 250 MHz) 1.51 (d, *J* = 6.55 Hz, 3 H), 2.62 (d, *J* = 5.30 Hz, 1 H), 3.89 (s, 3 H), 5.09 (qd, *J* = 6.21, 6.21 Hz, 1 H), 6.88 (d, *J* = 8.19 Hz, 1 H), 6.96 (t, *J* = 7.49 Hz, 1 H), 7.22–7.35 (m, 2 H); IR (neat) 582, 612, 754, 802, 898, 1030, 1050, 1078, 1125, 1161, 1175, 1194, 1236, 1284, 1365, 1403, 1483, 1492, 1587, 1601, 2836, 2929, 2969, 3033, 3060, 3384 cm⁻¹; [α]_D -57.6° (c 0.0363, toluene) (lit.²¹ [α]_D 48.9° (c 1.1, toluene), 81.5% ee (*R*)).

(S)-1-(2'-Bromophenyl)ethanol:²⁶ 9 days; alternative workup; 94% ee; 59% yield; ¹H NMR (CDCl₃, 300 MHz) 1.49 (d, *J* = 6.36 Hz, 3 H), 1.99 (d, *J* = 3.36 Hz, 1 H), 5.25 (qd, *J* = 6.38, 3.63 Hz, 1 H), 7.13 (dt, *J* = 7.65, 1.65 Hz, 1 H), 7.35 (dt, *J* = 7.43, 1.03 Hz, 1 H), 7.52 (dd, *J* = 7.92, 1.20 Hz, 1 H), 7.60 (dd, *J* = 7.76, 1.61 Hz, 1 H); IR (neat) 608, 668, 723, 754, 900, 1008, 1024, 1045, 1071, 1091, 1128, 1200, 1268, 1346, 1368, 1440, 1469, 1568, 2927, 2973, 3064, 3345 cm⁻¹; [α]_D -50.5° (c 0.0305, CHCl₃); mp 51.0–52.4 °C.

(S)-1-(2'-Chlorophenyl)ethanol: 2 days; 90% ee; 78% yield; ¹H NMR (CDCl₃, 250 MHz) 1.49 (d, *J* = 6.42 Hz, 3 H), 2.01 (br s, 1 H), 5.29 (qd, *J* = 6.29, 2.46 Hz, 1 H), 7.17–7.35 (m, 3 H), 7.60 (dd, *J* = 7.73, 1.81 Hz, 1 H); IR (neat) 609, 692, 729, 754, 900, 1009, 1036, 1048, 1073, 1094, 1133, 1202, 1266, 1348, 1369, 1437, 1474, 1574, 1595, 2929, 2975, 3088, 3354 cm⁻¹; [α]_D -56.5° (c 0.0463, CHCl₃) (lit.²⁷ [α]_D 18.5° (neat), 70% ee (*R*)).

(S)-1-(2'-Methylphenyl)ethanol: 1 day; 95% ee; 88% yield; ¹H NMR (CDCl₃, 250 MHz) 1.47 (d, *J* = 6.41 Hz, 3 H), 1.74 (d, *J* = 2.66 Hz, 1 H), 2.35 (s, 3 H), 5.14 (qd, *J* = 6.32, 3.07 Hz, 1 H), 7.12–7.28 (m, 3 H), 7.52 (d, *J* = 7.31 Hz, 1 H); IR (neat) 727, 759, 896, 1006, 1050, 1077, 1128, 1271, 1368, 1460, 1488, 2927, 2971, 3345 cm⁻¹; [α]_D -58.6° (c 0.0665, ethanol) (lit.²⁸ [α]_D -14° (c 0.4, ethanol), 25% ee (*S*)).

(21) Hayashi, T.; Matsumoto, Y.; Ito, Y. *Tetrahedron: Asymmetry* **1991**, 2, 601.

(22) Janssen, A. J. M.; Klunder, A. J. H.; Zwanenburg, B. *Tetrahedron* **1991**, 47, 7645.

(23) Brown, H. C.; Pai, G. G. *J. Org. Chem.* **1985**, 50, 1384.

(24) Burgess, K.; Jennings, L. D. *J. Am. Chem. Soc.* **1991**, 113, 6129.

(25) *Dictionary of Organic Compounds*, 5th ed.; Buckingham, J., Ed.; Chapman and Hall: New York, 1982.

(26) Kitamura, M.; Tokunaga, M.; Ohkuma, T.; Noyori, R. *Tetrahedron Lett.* **1991**, 32, 4163.

(27) Pickard, S. T.; Smith, H. E. *J. Am. Chem. Soc.* **1990**, 112, 5741.

(28) Holland, H. L.; Kindermann, M.; Kumaresan, S.; Stefanac, T. *Tetrahedron: Asymmetry* **1993**, 4, 1353.

(17) The RHF/6-31G* barrier for rotation of the carbonyl group of acetophenone was calculated to be 6.5 kcal/mol (Petillo, P. A. Unpublished results).

(18) (a) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, 34, 2543. (b) Yamaguchi, S. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1983; Vol. 1, Chapter 7.

(19) The addition of *n*-butyllithium to the center of the reaction solution is important for reproducibility. Variable enantioselectivity was observed if the *n*-butyllithium was allowed to run down the side of the reaction flask.

(20) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, 43, 2923.

(S)-1-(4'-Methylphenyl)ethanol: 0.9 day; 96% ee; 84% yield; ¹H NMR (CDCl₃, 250 MHz) 1.48 (d, *J* = 6.48 Hz, 3 H), 1.78 (br s, 1 H), 2.35 (s, 3 H), 4.87 (qd, *J* = 6.43, 2.33 Hz, 1 H), 7.22 (AB, *J* = 7.89 Hz, Δ*ν* = 25.92 Hz, 4 H); IR (neat) 819, 899, 1010, 1089, 1117, 1202, 1368, 1415, 1451, 1514, 2868, 2924, 2972, 3021, 3356 cm⁻¹; [α]_D -54.1° (c 0.0532, CHCl₃) (lit.²¹ [α]_D 51.6° (c 1.0, CHCl₃), 93.8% ee (R)).

(S)-1-(4'-Chlorophenyl)ethanol: 2 days; 94% ee; 85% yield; ¹H NMR (CDCl₃, 300 MHz) 1.43 (d, *J* = 6.93 Hz, 3 H), 1.78 (br s, 1 H), 4.84 (br q, 1 H), 7.27 (s, 4 H); IR (neat) 778, 829, 898, 1013, 1089, 1112, 1201, 1272, 1295, 1338, 1371, 1408, 1453, 1493, 2886, 2928, 2973, 3346 cm⁻¹; [α]_D -48.9° (c 0.0613, ether) (lit.²⁹ [α]_D 45.61° (c 1.5, ether), 90% ee (R)).

(S)-1-(4'-Methoxyphenyl)ethanol: 0.8 day; 87% ee; 62% yield; ¹H NMR (CDCl₃, 250 MHz) 1.48 (d, *J* = 6.44 Hz, 3 H), 1.79 (br s, 1 H), 3.81 (s, 3 H), 4.86 (q, *J* = 6.40 Hz, 1 H), 7.10 (AB, *J* = 8.63 Hz, Δ*ν* = 105 Hz, 4 H); IR (neat) 808, 832, 898, 1006, 1035, 1088, 1116, 1176, 1204, 1245, 1302, 1369, 1455, 1513, 1586, 1612, 2836, 2931, 2969, 3382 cm⁻¹; [α]_D -46.2° (c 0.0273, CHCl₃) (lit.²² [α]_D 52.1° (c 1.0, CHCl₃), 87% ee (R)).

(S)-1-(4'-Bromophenyl)ethanol: 1 day; 96% ee; 75% yield; ¹H NMR (CDCl₃, 250 MHz) 1.47 (d, *J* = 6.52 Hz, 3 H), 1.88 (br s, 1 H), 4.87 (q, *J* = 6.32 Hz, 1 H), 7.36 (AB, *J* = 8.43 Hz, Δ*ν* = 54.8 Hz, 4 H); IR (neat) 772, 824, 899, 1009, 1086, 1112, 1201, 1271, 1295, 1370, 1403, 1448, 1489, 2877, 2926, 2973, 3346 cm⁻¹; [α]_D -37.5° (c 0.0666, CHCl₃) (lit.³⁰ [α]_D 37.71° (c 5.4, CHCl₃), 90% ee (R)).

(S)-1-(4'-Fluorophenyl)ethanol: 1 day; 97% ee; 89% yield; ¹H NMR (CDCl₃, 300 MHz) 1.44 (d, *J* = 6.32 Hz, 3 H), 1.74 (d, *J* = 3.25 Hz, 1 H), 4.85 (qd, *J* = 6.43, 3.25 Hz, 1 H), 6.96–7.03 (m, 2 H), 7.27–7.33 (m, 2 H); IR (neat) 570, 836, 899, 1013, 1084, 1157, 1223, 1371, 1509, 1604, 2974, 3346 cm⁻¹; [α]_D -47.4° (c 0.0576, CHCl₃) (lit.³⁰ [α]_D -41.0° (c 1.30, CHCl₃), >97% ee (S)).

(S)-1-[4'-(Trifluoromethyl)phenyl]ethanol: 6 days; alternative workup; 61% ee; 67% yield; ¹H NMR (CDCl₃, 250 MHz) 1.51 (d, *J* = 6.45 Hz, 3 H), 1.87 (br d, *J* = 3.26 Hz, 1 H), 4.96 (qd, *J* = 6.36, 3.51 Hz, 1 H), 7.55 (AB, *J* = 8.20 Hz, Δ*ν* = 28.48 Hz, 4 H); IR (neat) 605, 630, 738, 842, 900, 1016, 1068, 1124, 1206, 1327, 1372, 1416, 1451, 1621, 2881, 2932, 2978, 3346 cm⁻¹; [α]_D -10.8° (c 0.0578, MeOH) (lit.³¹ [α]_D -24.7° (c 1.9, MeOH), 84% ee (S)).

(S)-1-Phenylpropanol: 1 day; 95% ee; 96% yield; ¹H NMR (CDCl₃, 250 MHz) 0.92 (t, *J* = 7.39 Hz, 3 H), 1.69–1.83 (m, 2 H), 1.87 (d, *J* = 2.94 Hz, 1 H), 4.59 (td, *J* = 6.59, 3.07 Hz, 1 H), 7.39–7.23 (m, 5 H); IR (neat) 700, 766, 974, 1013, 1045, 1097, 1201, 1270, 1331, 1378, 1453, 1493, 2876, 2932, 3964, 3029, 3062, 3362 cm⁻¹; [α]_D -46.7° (c 0.0409, CHCl₃) (lit.²² [α]_D 49.0° (c 1, CHCl₃), 96% ee (R)).

(S)-2-Methyl-1-phenylpropanol: 4.5 days; 10 mol % 1; 10 equiv of silane; 92% ee; 79% yield; ¹H NMR (CDCl₃, 300 MHz) 0.76 (d, *J*

= 7.09 Hz, 3 H), 0.96 (d, *J* = 6.72 Hz, 3 H), 1.78 (br d, *J* = 3.30 Hz, 1 H), 1.92 (dsept, *J* = 6.73, 6.73 Hz, 1 H), 4.32 (dd, *J* = 6.84, 3.19 Hz, 1 H), 7.20–7.33 (m, 5 H); IR (neat) 701, 760, 1022, 1124, 1366, 1383, 1453, 1468, 2872, 2930, 2959, 3029, 3386 cm⁻¹; [α]_D -45.7° (c 0.0623, ether) (lit.³² [α]_D 34.8° (c 4.90, ether), 73% ee (R)).

(S)-3-Methyl-1-phenylbutanol: 2.5 days; 94% ee; 78% yield; ¹H NMR (CDCl₃, 300 MHz) 0.91 (d, *J* = 6.49 Hz, 3 H), 0.91 (d, *J* = 6.56 Hz, 3 H), 1.45–1.53 (m, 1 H), 1.62–1.75 (m, 2 H), 1.73 (d, *J* = 3.14 Hz, 1 H), 4.68–4.74 (m, 1 H), 7.20–7.33 (m, 5 H); IR (CDCl₃) 1047, 1368, 1385, 1454, 1467, 1493, 2870, 2928, 2959, 3605 cm⁻¹; [α]_D -39.9° (c 0.0504, *n*-heptane) (lit.³³ [α]_D -28.7° (c 16.6, *n*-heptane), 95% ee (S)); mp 49.6–50.6 °C (lit.³⁵ 50.0–50.5 °C).

(S)-1-Cyclohexyl-1-phenylmethanol: 2.5 days; 1.5 equiv of PhSiH₃; 82% ee; 88% yield; ¹H NMR (CDCl₃, 300 MHz) 0.82–1.29 (m, 7 H), 1.30–1.49 (br d, 1 H), 1.51–1.75 (m, 3 H), 1.75 (d, *J* = 3.45 Hz, 1 H), 4.33 (dd, *J* = 7.30, 3.34 Hz, 1 H), 7.19–7.32 (m, 5 H); [α]_D -20.9° (c 0.0507, PhH) (lit.³⁵ [α]_D -28.27° (c 3.29, PhH) (S)); mp 63.1–69.1 °C.

(S)-1-Cyclobutyl-1-phenylmethanol: 36 1 day; 1.5 equiv of PhSiH₃; 82% ee; 88% yield; ¹H NMR (CDCl₃, 250 MHz) 1.79–2.14 (m, 7 H), 2.55–2.68 (m, 1 H), 4.58 (dd, *J* = 7.93, 3.17 Hz, 1 H), 7.24–7.39 (m, 5 H); IR (neat) 699, 754, 1008, 1028, 1049, 1133, 1194, 1282, 1430, 1452, 1492, 3028, 3061, 3374 cm⁻¹; [α]_D -29.7° (c 0.0519, CHCl₃).

(S)-1-Indanol: 1.6 days; 92% ee; 68% yield; ¹H NMR (CDCl₃, 250 MHz) 1.76 (d, *J* = 6.67 Hz, 1 H), 1.88–2.01 (m, 1 H), 2.42–2.56 (m, 1 H), 2.76–2.88 (m, 1 H), 3.00–3.12 (m, 1 H), 5.24 (td, *J* = 6.33, 5.85 Hz, 1 H), 7.22–7.42 (m, 4 H); [α]_D 28.7° (c 0.0230, CHCl₃) (lit.^{1b} [α]_D -29.8° (c 1.1, CHCl₃) (S)); mp 71.6–72.6 °C (lit.²⁵ mp 72 °C).

(S)-1-Tetralol: 3.5 days; 91% ee; 92% yield; ¹H NMR (CDCl₃, 300 MHz) 1.58–1.99 (m, 5 H), 2.63–2.84 (m, 2 H), 4.74 (br s, 1 H), 7.05–7.09 (m, 1 H), 7.13–7.21 (m, 2 H), 7.37–7.42 (m, 1 H); [α]_D 29.0° (c 0.0462, CHCl₃) (lit.³⁷ [α]_D 25.8° (c 3.1, CHCl₃) (S)); mp 32.9–34.9 °C (lit.³⁸ mp 33 °C).

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(32) Niwa, S.; Soai, K. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2717.

(33) von dem Bussche-Hünnefeld, J. L.; Seebach, D. *Tetrahedron* **1992**, 48, 5719.

(34) MacLeod, R.; Welch, F. J.; Mosher, H. S. *J. Am. Chem. Soc.* **1960**, 82, 876.

(35) Ojima, I.; Kogure, T.; Kumagai, M.; Horiuchi, S.; Sato, T. *J. Organomet. Chem.* **1976**, 122 (1), 83.

(36) Racemic: Dupont, A. C.; Audia, V. H.; Waid, P. P.; Carter, J. P. *Synth. Commun.* **1990**, 20, 1011.

(37) Kim, Y. H.; Park, D. H.; Byun, I. S.; Yoon, I. K.; Park, C. S. *J. Org. Chem.* **1993**, 58, 4511.

(38) Mentzer, M. C.; Billet, M. D. *Bull. Soc. Chim. Fr.* **1948**, 835.

(29) Basavaiah, D.; Raju, S. B. *Synth. Commun.* **1991**, 21, 1859.

(30) Nieduzak, T. R.; Margolin, A. L. *Tetrahedron: Asymmetry* **1991**, 2, 113.

(31) Soai, K.; Hirose, Y.; Niwa, S. *J. Fluorine Chem.* **1992**, 59, 5.