



Supporting Information

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Iron-catalyzed Enantioselective Hydrosilylation of Ketones

*Nadim S. Shaikh, Stephan Enthaler, Kathrin Junge, and Matthias Beller**

Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Straße
29a, D-18059 Rostock, Germany

matthias.beller@catalysis.de

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Materials and Methods: All reactions were conducted under argon atmosphere using standard Schlenk techniques. All the substrates were purchased from commercial sources and were distilled over CaH_2 and stored under argon. Solid substrates were used as received. $\text{Fe}(\text{OAc})_2$ was purchased from Aldrich with 99.995% purity. Phosphine Ligands were purchased from Strem Chemical Company. $(\text{EtO})_2\text{MeSiH}$ and other silanes used were purchased from Aldrich and distilled under vacuum and stored under argon. PMHS was purchased from Aldrich and degassed before use. (PMHS: MW 1900, a 29mer, with one hydride per monomeric unit. Monomer weight = 60).¹ THF and Toluene were dried over sodium benzophenone, distilled and stored under argon. Melting points were determined on a Leica galen III melting point apparatus and were uncorrected. Optical rotations were measured on a Perkin Elmer 343 polarimeter at 25 °C in a 1-dm cell. Absolute configuration of product alcohols were assigned by comparison of the sign of optical rotation with reported values. NMR spectra were recorded on a Bruker ARX 300 spectrometer, operating at 300 MHz for ^1H NMR, 75 MHz for ^{13}C NMR. NMR spectra were reported downfield from CDCl_3 (d: 7.27 ppm) for ^1H NMR. For ^{13}C NMR chemical shifts were reported in the scale relative to the solvent of CDCl_3 (d: 77.0 ppm). Mass spectra were recorded on an AMD 402/3 or a HP 5989A mass selective detector. GC analyses were performed with a Hewlett Packard HP 6890 spectrometer. Column chromatography was performed with silica gel Merck 60 (70-230 mesh ASTM)

using solvents of commercial grade. Isolated products were characterized by comparison of NMR data with reported values and GC-MS (showed >95% purity).

(Ligands **La**, **Lb** and **Lk** were obtained from Aldrich. Ligands **Lc-Lj** were prepared by the known procedure).^[2]

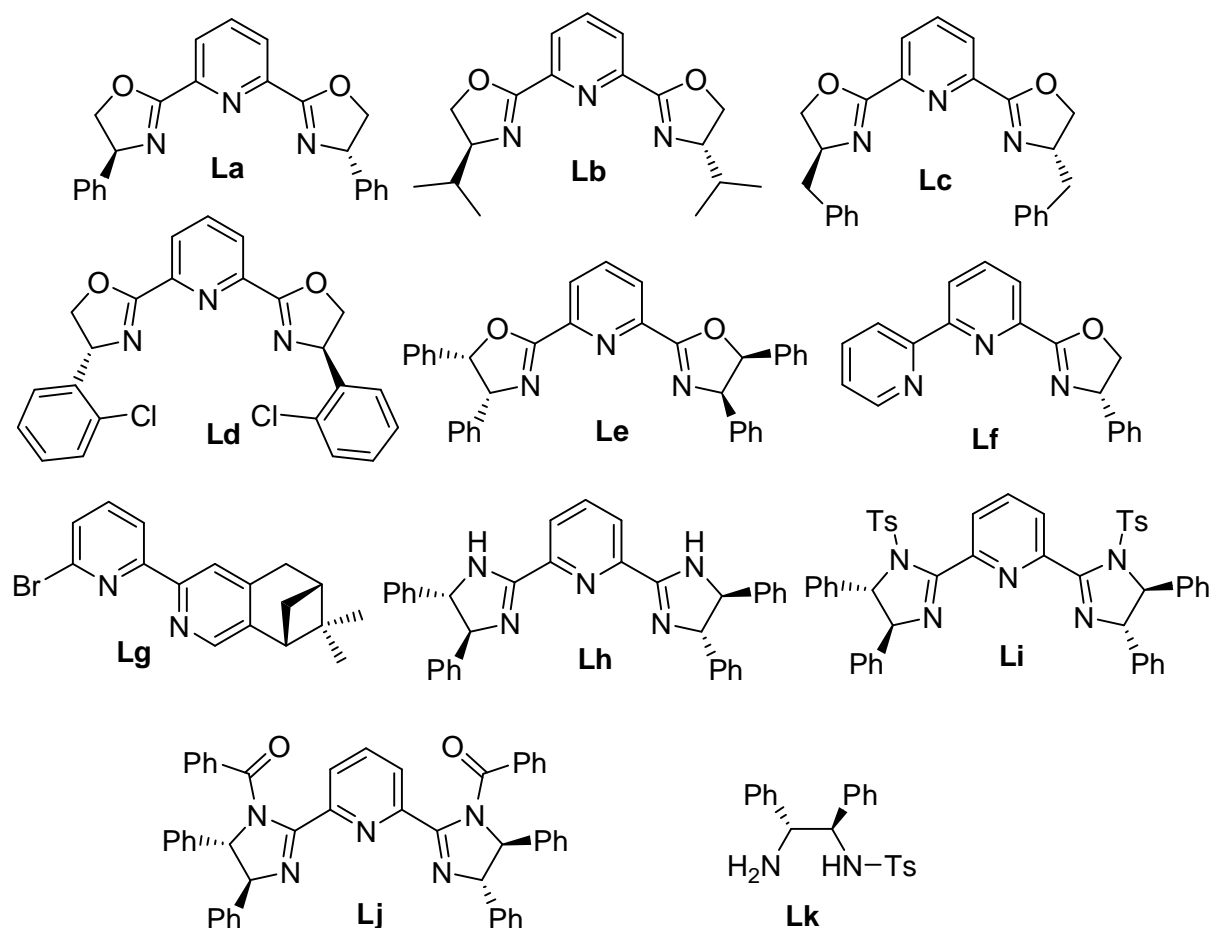
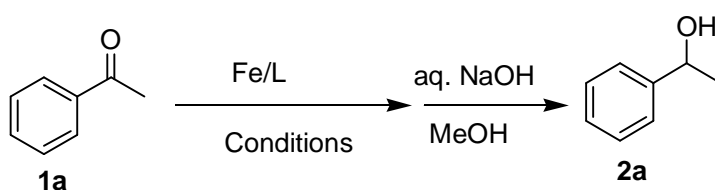


Fig. 1: Ligands studied in the asymmetric hydrosilylation of acetophenone

Table 1. Asymmetric hydrosilylation of acetophenone - ligand screening^[a]



Entry	Catalyst [mol%]	Ligand [mol%]	Silane [equiv.]	Conditions	Conv. ^[b] [%]	ee ^[c] [%]
1	Fe(acac) ₂ (20)	La (20)	Ph ₂ SiH ₂ (2)	Toluene, 100 °C, 20h.	68	22
2	Fe(acac) ₂ (5)	La (10)	Ph ₂ SiH ₂ (2)	THF, 100 °C, 20h.	5	1
3	Fe(acac) ₂ (5)	La (10)	(EtO) ₂ MeSiH (2)	THF, 65 °C, 20h.	28	34
4	Fe(OAc) ₂ (5)	Lb (10)	(EtO) ₂ MeSiH (2)	THF, 65 °C, 20h.	94	24
5	Fe(OAc) ₂ (5)	Lc (10)	(EtO) ₂ MeSiH (2)	THF, 65 °C, 20h.	98	36
6	Fe(OAc) ₂ (5)	Lc +PPh ₃ (10)	(EtO) ₂ MeSiH (2)	THF, 65 °C, 20h.	97	35
7	Fe(OAc) ₂ (5)	Ld (10)	(EtO) ₂ MeSiH (2)	THF, 65 °C, 20h.	94	7
8	Fe(OAc) ₂ (5)	Le (10)	(EtO) ₂ MeSiH (2)	THF, 65 °C, 20h.	97	6
9	Fe(OAc) ₂ (5)	Lf (10)	(EtO) ₂ MeSiH (2)	THF, 65 °C, 20h.	98	24
10	Fe(OAc) ₂ (5)	Lg (10)	(EtO) ₂ MeSiH (2)	THF, 65 °C, 20h.	31	1
11	Fe(OAc) ₂ (5)	Lh (10)	(EtO) ₂ MeSiH (2)	THF, 65 °C, 20h.	15	2
13	Fe(OAc) ₂ (5)	Li (10)	(EtO) ₂ MeSiH (2)	THF, 65 °C, 20h.	5	0
14	Fe(OAc) ₂ (5)	Lj (10)	(EtO) ₂ MeSiH (2)	THF, 65 °C, 20h.	96	3
15	Fe(OAc) ₂ (5)	Lk (10)	(EtO) ₂ MeSiH (2)	THF, 65 °C, 20h.	12	10
16	Fe(OAc) ₂ (5)	none	(EtO) ₂ MeSiH (2)	THF, 65 °C, 24h.	24	0

[a] Reactions were carried out under argon atmosphere using general conditions. [b] Determined by GC-FID using diethyleneglycol dimethyl ether as an internal standard. [c] Determined by GC with chiral phase.

Table 2. Asymmetric hydrosilylation of acetophenone using Fe(OAc)₂ (mixed ligand system)^[a]

Entry	Ligand	Silane [equiv.]	Conditions	Conv. ^[b]	ee ^[c]
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	[mol%]			[%]	[%]
1	(<i>S,S</i>)-Me-DuPHOS (10)	(EtO) ₂ MeSiH (2)	THF, 65 °C, 20h.	>99	75
2	(<i>S,S</i>)-Me-DuPHOS + TMEDA(10)	(EtO) ₂ MeSiH (2)	THF, 65 °C, 20h.	>99	73
3	(<i>S,S</i>)-Me-DuPHOS + PPh ₃ (10)	(EtO) ₂ MeSiH (2)	THF, 65 °C, 20h.	>99	75
4	(<i>S,S</i>)-Me-DuPHOS + Lc (10)	(EtO) ₂ MeSiH (2)	THF, 65 °C, 20h.	>99	71

[a] Reactions were carried out under argon atmosphere using general conditions. [b] Determined by GC-FID using diethyleneglycol dimethyl ether as an internal standard. [c] Determined by GC with chiral phase.

Table 3. Asymmetric hydrosilylation of acetophenone - additive effect^[a]

Entry	Additive [mol %]	Temp [°C]	Conv. ^[b] [%]	<i>ee</i> ^[c] [%]
1	AcOH (1)	65	12	76
2	TFA (1)	65	10	66
3	KOtBu (1)	65	>99	5
4	4A-Molecular Sieves	65	>99	76
5	H ₂ O (10)	65	42	73
6	Air	50	75	7
7	Acetone (5)	65	67	75
8	Acetone (10)	65	33	76
9	Acetone (25)	65	10	76

[a] Reactions were carried out under argon atmosphere using general conditions. Additive was added at the beginning of the reaction followed by addition of the solvent. [b] Determined by GC-FID using diethyleneglycol dimethyl ether as an internal standard. [c] Determined by GC with chiral phase.

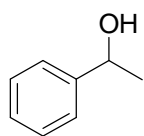
Table 4. Asymmetric hydrosilylation of acetophenone using Fe(OAc)₂ - catalyst loading^[a]

Entry	Fe(OAc) ₂ [mol%]	(<i>S,S</i>)-Me-DuPHOS [mol%]	Temp [°C], <i>t</i> [h]	Conv. ^[b] [%]	<i>ee</i> ^[c] [%]
1	1	1	65 (16)	8	7
2	1	2	65 (16)	6	60

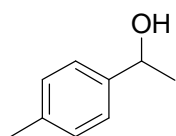
3	2	1	65 (16)	80	36
4	3	3	65 (16)	90	71
5	5	15	65 (16)	100	75
6	5	10	65 (16)	100	75
7	5	8	65 (16)	94	70
8	5	5	65 (16)	>99	70
9	2.5	5	65 (16)	>99	74
10	5	10	0 (32)	18	64
11	5	10	-78 (32)	6	78
12	5	10	RT (16)	45	79
13	5	10	RT (48)	88	79

[a] Reactions were carried out under argon atmosphere using general conditions. [b] Determined by GC-FID using diethyleneglycol dimethyl ether as an internal standard. [c] Determined by GC with chiral phase.

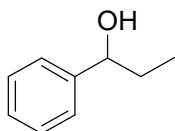
Spectroscopic and analytical data (compounds from Table 4 and Scheme 1):



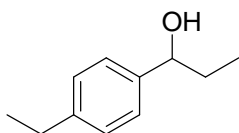
(*R*)-1-Phenylethanol (2a):^[3] Obtained as clear liquid. ¹H NMR *d* 7.28-7.4 (m, 5H), 4.89 (q, *J* = 6.5 Hz, 1H), 2.05 (br. s, 1H), 1.5 (d, *J* = 6.5 Hz, 3H); ¹³C NMR *d* 145.8, 128.4, 127.4, 125.3, 70.3, 25.1; MS (EI): *m/z* 122 (*M*⁺). The *ee* (79%, table 4, entry 1) was determined using GC with chiral column (25 m Lipodex E, 70-180 °C): *t_R* (min) = 58.8 (minor), 59.6 (major).



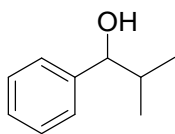
(R)-1-(4-Methylphenyl)ethanol (2b):^[4] Obtained as clear liquid. ¹H NMR *d* 7.28 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 4.87 (q, *J* = 6.5 Hz, 1H), 2.37 (s, 3H), 1.93 (br s, 1H), 1.5 (d, *J* = 6.5 Hz, 3H); ¹³C NMR *d* 142.8, 137.1, 129.1, 125.3, 70.2, 25.0, 21.1; MS (EI): *m/z* 136 (*M*⁺). The *ee* (81%) was determined using chiral HPLC (Chiralcel OJ-H, n-heptane-isopropanol (95:5; 0.5 ml/min.): *t*_R (min) = 26.3 (minor), 29.6 (major).



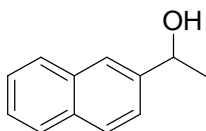
(R)-1-Phenylpropanol (2c):^[4] Obtained as clear liquid. ¹H NMR *d* 7.26-7.40 (m, 5H), 4.6 (t, *J* = 6.5 Hz, 1H), 1.99 (br s, 1H), 1.70-1.91 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); ¹³C NMR *d* 144.5, 128.4, 127.4, 125.9, 76.0, 31.8, 10.1; MS (EI): *m/z* 136 (*M*⁺). The *ee* (78%) was determined using chiral HPLC (Chiralcel OB-H, n-heptane-ethanol (98:2; 1 ml/min.): *t*_R (min) = 7.9 (minor), 10.1 (major).



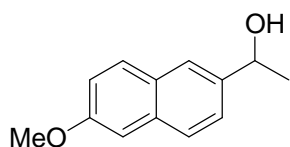
(R)-1-(4-Ethylphenyl)propanol (2d): Obtained as clear liquid. ¹H NMR *d* 7.33 (dd, *J* = 8.2 Hz, 4H), 4.57 (t, *J* = 6.9 Hz, 1H), 2.67 (q, *J* = 7.6 Hz, 2H), 1.94 (br s, 1H), 1.79 (m, 2H), 1.25 (t, *J* = 7.61, 3H), 0.93 (t, *J* = 7.4 Hz, 3H); ¹³C NMR *d* 143.5, 141.8, 127.8, 125.9, 75.9, 31.7, 28.5, 15.6, 10.2; MS (EI): *m/z* 164 (*M*⁺). The *ee* (82%) was determined using chiral HPLC (Chiralpak AD-H, n-heptane-ethanol (95:5; 0.8 ml/min.): *t*_R (min) = 9.1 (major), 9.6 (minor).



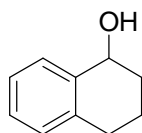
(R)-2-Methyl-1-phenylpropan-1-ol (2e):^[5] Obtained as clear liquid. ¹H NMR *d* 7.25-7.33 (m, 5H), 4.36 (d, *J* = 6.9 Hz, 1H), 1.91-2.03 (m, 2H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.81 (d, *J* = 6.8 Hz, 3H); ¹³C NMR *d* 143.6, 128.2, 127.4, 126.5, 80.0, 35.2, 18.9, 18.2; MS (EI): *m/z* 150 (*M*⁺); The *ee* (67%) was determined using chiral HPLC (Chiralpak AD-H, n-heptane-ethanol (99.5:0.5; flow rate: 1 ml/min.): *t*_R (min) = 13.2 (major), 14.9 (minor).



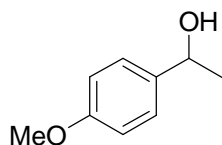
(R)-1-(Naphthalen-2-yl)ethanol (2f):^[6] Obtained as thick liquid. ¹H NMR *d* 7.75-7.90 (m, 4H), 7.45-7.57 (m, 3H), 5 (q, *J* = 6.5 Hz, 1H), 2.85 (br s, 1H), 1.58 (d, *J* = 6.5 Hz, 3H); ¹³C NMR *d* 143.1, 133.2, 132.7, 128.1, 127.8, 127.5, 125.9, 125.6, 123.7, 123.6, 70.2, 24.9; MS (EI): *m/z* 172 (*M*⁺). The *ee* (70%) was determined using chiral HPLC (Chiralcel OD-H, n-hexane-ethanol (95:5; 1 ml/min.): *t_R* (min) = 7.5 (minor), 8.3 (major).



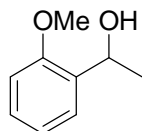
(R)-1-(6-Methoxynaphthalen-2-yl)ethanol (2g):^[7] Obtained as white solid. mp 110-112 °C; ¹H NMR *d* 7.70-7.76 (m, 3H), 7.48 (dd, *J* = 8.7 & 1.8 Hz, 1H), 7.13-7.18 (m, 2H), 5.04 (q, *J* = 6.5 Hz, 1H), 3.93 (s, 3H), 1.99 (br s, 1H), 1.58 (d, *J* = 6.5 Hz, 3H); ¹³C NMR *d* 157.6, 140.9, 134.0, 129.4, 128.7, 127.1, 124.3, 123.7, 118.9, 105.6, 70.5, 55.3, 25.0; MS (EI): *m/z* 202 (*M*⁺). The *ee* (79%) was determined using chiral HPLC (Chiralpak AD-H, n-heptane-ethanol (95:5; flow rate: 1 ml/min.): *t_R* (min) = 11.4 (minor), 12.7 (major).



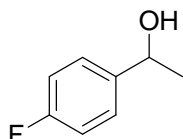
(R)-1,2,3,4-Tetrahydronaphthalen-1-ol (2h):^[8] Obtained as clear liquid. ¹H NMR *d* 7.36-7.48 (m, 1H), 7.18-7.26 (m, 2H), 7.08-7.16 (m, 1H), 4.78 (t, *J* = 4.5 Hz, 1H), 2.67-2.91 (m, 2H), 1.72-2.1 (m, 5H); ¹³C NMR *d* 138.7, 137.1, 128.9, 128.6, 127.5, 126.1, 68.0, 32.2, 29.2, 18.7; MS (EI): *m/z* 148 (*M*⁺). The *ee* (75%) was determined using chiral HPLC (Chiralcel OJ-H, n-heptane-isopropanol (95:5; 0.5 ml/min.): *t_R* (min) = 21.6 (minor), 31.3 (major).



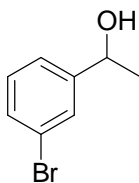
(R)-1-(4-Methoxyphenyl)ethanol (2i):^[6] Obtained as clear liquid. ¹H NMR *d* 7.27-7.33 (m, 2H), 6.85-6.91 (m, 2H), 4.85 (q, *J* = 6.5 Hz, 1H), 3.81 (s, 3H), 1.92 (br s, 1H), 1.48 (d, *J* = 6.5 Hz, 3H); ¹³C NMR *d* 158.9, 137.9, 126.6, 113.8, 69.9, 55.6, 25.0; MS (EI): *m/z* 152 (*M*⁺). The *ee* (78%) was determined using chiral HPLC (Chiralcel OB-H, n-heptane-ethanol (98:2; 2 ml/min.): *t_R* (min) = 13.1 (minor), 16.1 (major).



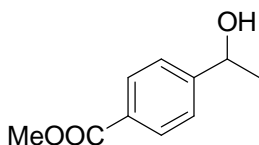
(*R*)-1-(2-Methoxyphenyl)ethanol (2j):^[6] Obtained as clear liquid. ¹H NMR *d* 7.35 (dd, *J* = 7.9 & 1.9 Hz, 1H), 7.26 (ddd, *J* = 7.8 & 1.9 Hz, 1H), 6.86-7.04 (m, 2H), 5.1 (q, *J* = 6.5 Hz, 1H), 3.87 (s, 3H), 2.7 (br s, 1H), 1.52 (d, *J* = 6.5 Hz, 3H); ¹³C NMR *d* 156.5, 133.6, 128.2, 126.0, 120.7, 110.4, 66.5, 55.4, 22.8; MS (EI): *m/z* 152 (M⁺). The *ee* (77%) was determined using chiral HPLC (Chiralcel OB-H, Heptane-ethanol (98:2; 1 ml/min.): *t_R* (min) = 9.2 (minor), 16.7 (major).



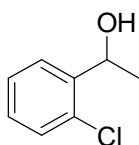
(*R*)-1-(4-Fluorophenyl)ethanol (2k):^[9] Obtained as clear liquid. ¹H NMR *d* 7.3-7.37 (m, 2H), 6.99-7.1 (m, 2H), 4.88 (q, *J* = 6.5 Hz, 1H), 1.99 (br s, 1H), 1.48 (d, *J* = 6.5 Hz, 3H); ¹³C NMR *d* 162.1 (d, *J*_{C-F} = 245 Hz), 141.5 (d, *J*_{C-F} = 3.2 Hz), 127 (d, *J*_{C-F} = 8.3 Hz), 115.2 (d, *J*_{C-F} = 21.2 Hz), 69.7, 25.3; MS (EI): *m/z* 140 (M⁺). The *ee* (62%) was determined using GC with chiral column (50 m Lipodex E, 70-180 °C): *t_R* (min) = 16.7 (major), 18.8 (minor).



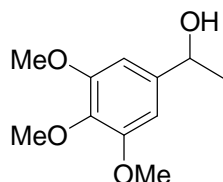
(*R*)-1-(3-Bromophenyl)ethanol (2l):^[10] Obtained as clear liquid. ¹H NMR *d* 7.52-7.55 (m, 1H), 7.38-7.43 (m, 1H), 7.19-7.31 (m, 2H), 4.87 (q, *J* = 6.5 Hz, 1H), 2.0 (br s, 1H), 1.48 (d, *J* = 6.5 Hz, 3H); ¹³C NMR *d* 148.1, 130.5, 130.1, 128.5, 124, 122.6, 69.7, 25.2; MS (EI): *m/z* 200 (M⁺). The *ee* (49%) was determined using chiral GC (50 m Lipodex E, 120-180 °C): *t_R* (min) = 36.2 (major), 38.2 (minor).



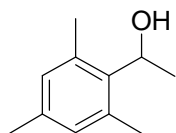
Methyl 4-(1-hydroxyethyl)benzoate (2m):^[11] Obtained as thick liquid. ¹H NMR *d* 8.0 (m, 2H), 7.43 (m, 2H), 4.95 (q, *J* = 6.5 Hz, 1H), 3.9 (s, 3H), 2.2 (br s, 1H), 1.49 (d, *J* = 6.5 Hz, 3H); ¹³C NMR *d* 167.0, 150.9, 129.8, 129.2, 125.3, 69.9, 52.1, 25.3; MS (EI): *m/z* 180 (M⁺). The *ee* (48%) was determined using chiral GC (50 m Lipodex E, 100-180 °C): *t_R* (min) = 49.1 (major), 50.0 (minor).



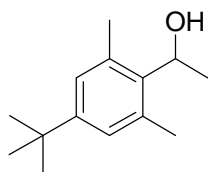
(R)-1-(2-Chlorophenyl)ethanol (2n):^[6] Obtained as clear liquid. ¹H NMR *d* 7.53-7.57 (m, 1H), 7.12-7.38 (m, 3H), 5.25 (q, *J* = 6.5 Hz, 1H), 2.18 (br s, 1H), 1.45 (d, *J* = 6.5 Hz, 3H); ¹³C NMR *d* 143.0, 131.6, 129.4, 128.3, 127.2, 126.4, 66.9, 23.5; MS (EI): *m/z* 156 (*M*⁺). The *ee* (55%) was determined using chiral GC (50 m Lipodex E, 70-180 °C): *t*_R (min) = 38.4 (minor), 39.3 (major)



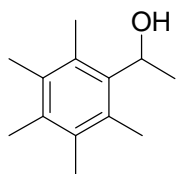
(R)-1-(3,4,5-Trimethoxyphenyl)ethanol (2o):^[12] Obtained as a viscous liquid. ¹H NMR *d* 6.6 (s, 2H), 4.83 (q, *J* = 6.5 Hz, 1H), 3.87 (s, 6H), 3.84 (s, 3H), 1.97 (br s, 1H), 1.49 (d, *J* = 6.5 Hz, 3H); ¹³C NMR *d* 153.2, 141.7, 137.0, 102.2, 70.6, 60.8, 56.0, 25.2; MS (EI): *m/z* 212 (*M*⁺). The *ee* (89%) was determined using chiral HPLC (Chiralpak AD-H, n-hexane-ethanol (95:5; flow rate: 1 ml/min.): *t*_R (min) = 30.1 (major), 31.7 (minor).



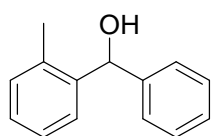
(R)-1-Mesitylethanol (2p):^[13] Obtained as white solid. mp 65-67 °C; ¹H NMR *d* 6.85 (s, 2H), 5.38 (q, *J* = 6.8 Hz, 1H), 2.44 (s, 6H), 2.28 (s, 3H), 1.86 (br s, 1H), 1.54 (d, *J* = 6.8 Hz, 3H); ¹³C NMR *d* 137.6, 136.3, 135.6, 130.1, 67.4, 21.5, 20.6, 20.5; MS (EI): *m/z* 164 (*M*⁺). The *ee* (99%) was determined using HPLC with chiral column (Chiralpak-AD-H, n-heptane-ethanol, 98:2; flow rate: 0.8 ml/min.): *t*_R (min) = 6.2 (major), 6.9 (minor).



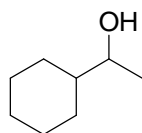
(R)-1-(4-tert-Butyl-2,6-dimethylphenyl)ethanol (2q):^[14] Obtained as white solid. mp 104-106 °C; ¹H NMR *d* 7.03 (s, 2H), 5.38 (q, *J* = 6.2 Hz, 1H), 2.47 (s, 6H), 1.79 (br s, 1H), 1.55 (d, *J* = 6.8 Hz, 3H), 1.32 (s, 9H); ¹³C NMR *d* 149.5, 137.6, 135.3, 126.4, 67.5, 34.1, 31.3, 21.4, 20.9. MS (EI): *m/z* 206 (*M*⁺). The *ee* (99%) was determined using HPLC with chiral column (Chiralpak-AD-H, n-heptane-ethanol, 99:1; flow rate: 1 ml/min.): *t*_R (min) = 11.2 (minor), 12.1 (major). The absolute configuration for this compound is tentatively assigned on the basis of other substrates in table 4.



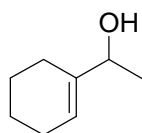
(R)-1-(2,3,4,5,6-Pentamethylphenyl)ethanol (2r): Obtained as white solid. mp (86-88) °C; ^1H NMR d 5.55 (q, J = 6.7 Hz, 1H), 2.45 (s, 6H), 2.32 (s, 3H), 2.30 (s, 6H), 2.0 (br s, 1H), 1.64 (d, J = 6.8 Hz, 3H); ^{13}C NMR d 138.2, 133.9, 133.3, 131.4, 67.9, 21.9, 16.9, 16.8, 16.5. MS (EI): m/z 192 (M^+). The ee (99%) was determined using HPLC with chiral column (Chiralcel-OD-H, n-heptane-ethanol, 99:1; flow rate: 1 ml/min.): t_R (min) = 9.2 (minor), 11.2 (major). The absolute configuration for this compound is tentatively assigned on the basis of other substrates in table 4.



(R)-Phenyl(*o*-tolyl)methanol (2s):^[15] Obtained as white solid. mp 95-97 °C; ^1H NMR d 7.52-7.56 (m, 4H), 7.71-7.35 (m, 8H), 6.02 (d, J = 3.5 Hz, 1H), 2.27 (s, 3H), 2.17 (d, J = 3.5 Hz, 1H); ^{13}C NMR d 142.8, 141.4, 135.4, 130.5, 128.5, 127.6, 127.5, 127.1, 126.2, 126.1, 73.3, 19.4. MS (EI): m/z 198 (M^+). The ee (51%) was determined using HPLC with chiral column (Chiralpak-AD-H, n-heptane-ethanol, 99:1; flow rate: 1 ml/min.): t_R (min) = 27.9 (major), 30.3 (minor)



(R)-1-Cyclohexylethanol (2t):^[10,16] Obtained as clear liquid. ^1H NMR d 3.54 (m, 1H), 1.62-1.88 (m, 5H), 1.43 (br s, 1H), 0.93-1.32 (m, 9H); ^{13}C NMR d 72.2, 45.1, 28.7, 28.3, 26.5, 26.2, 26.1, 20.4; MS (EI): m/z 128 (M^+). The ee (45%) was determined using GC with chiral column (25 m Lipodex E, 60-180 °C): t_R (min) = 74.6 (minor), 76.9 (major).



(R)-1-(1-Cyclohexenyl)ethanol (2u):^[39] Obtained as viscous liquid. ^1H NMR d 5.62-5.67 (m, 1H), 4.14 (q, J = 6.4 Hz, 1H), 1.93-2.07 (m, 4H), 1.5-1.68 (m, 5H), 1.23 (d, J = 6.5 Hz, 3H); ^{13}C NMR d 141.2, 121.4, 72.1, 24.9, 23.6, 22.6, 22.5, 21.4. MS (EI): m/z 126. The ee (79%) was determined using chiral GC (25m, Lipodex E, 70-180 °C); t_R (min) = 27.6 (minor), 28.4 (major).

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