Supplementary Information for:

Asymmetric Hydrosilylation of Ketones Catalyzed by Complexes Formed from *trans*-Diaminocyclohexane-based Diamines and Diethylzinc

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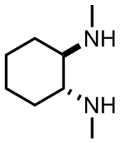
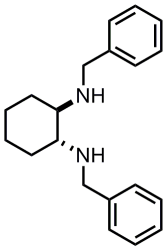
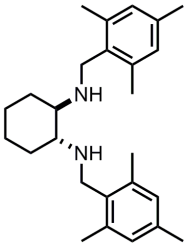
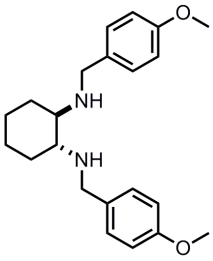
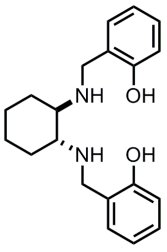
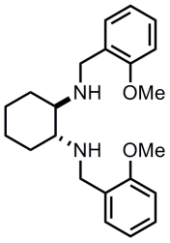
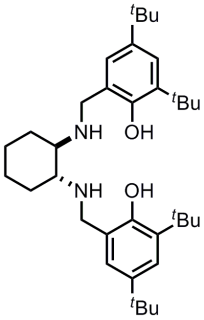
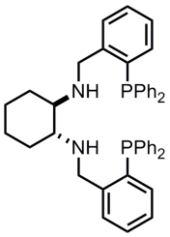
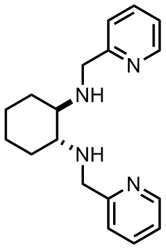
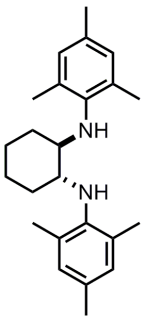
Table SI1. Conditions and retention times for HPLC separation of enantiomers of ArCH(OH)R alcohols using a Chiralpak IA column.

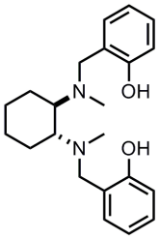
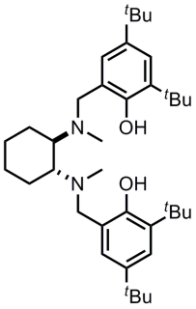
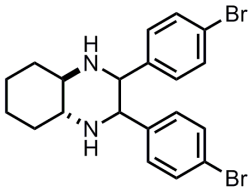
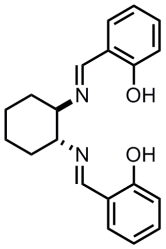
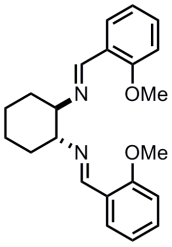
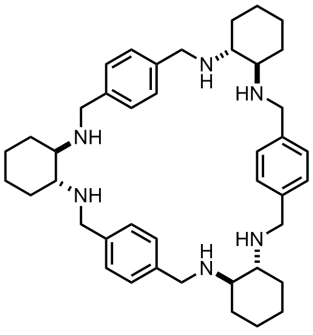
Ar	R	Flow [ml·min^{-1}]	Hexane [%]	2-Propanol [%]	Retention time [min]	
					Minor	Major
Ph	Me	0.5	95	5	23.12	23.87
Ph	Et	0.5	95	5	16.76	17.29
Ph	Cy	0.5	95	5	22.29	20.95
4-Me-C_6H_4	Me	0.5	95	5	18.61	19.89
4-MeO-C_6H_4	Me	0.5	90	10	16.44	17.32
4-CN-C_6H_4	Me	0.55	90	10	16.75	17.36
4-F-C_6H_4	Me	1.0	99	1	21.97	22.87
3,5-CF_3-C_6H_3	Me	0.55	90	10	13.48	15.57
Ph	CF_3	0.5	95	5	19.89	21.13
4-F-C_6H_4	CF_3	0.5	95	5	18.35	19.91
2,4,6-$Me_3C_6H_2$	CF_3	0.5	95	5	15.41	13.81
3-Me-C_6H_4	Ph	0.55	99	1	55.00	51.79
4-Me-C_6H_4	Ph	0.5	95	5	18.24	19.49
2-Cl-C_6H_4	Ph	0.5	95	5	31.97	33.72
4-Cl-C_6H_4	Ph	0.5	95	5	44.83	41.28
1-Indanol		0.5	90	10	26.45	24.35

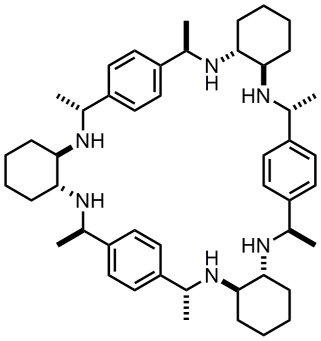
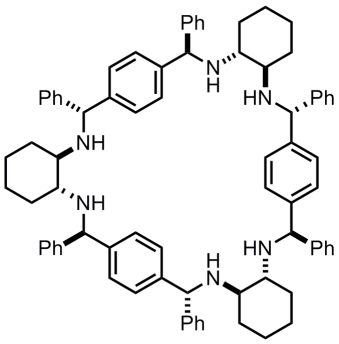
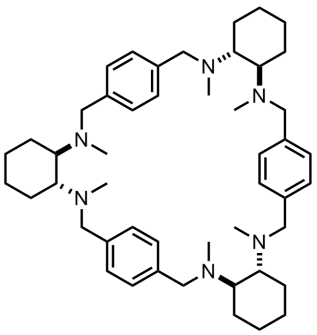
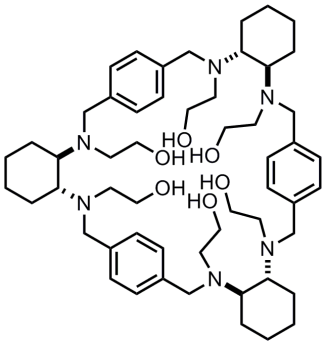
α-Tetralol	0.5	90	10	26.89	24.09
β-Tetralol	0.5	90	10	28.45	32.05

Table SI2. Systematic names, melting points and references to the NMR data for ligands **L1**-**L23**.

Ligand	Melting point and reference to the NMR data
L1 	(*R*,*R*)-*N*,*N'*-Dimethyl-1,2-diaminocyclohexane Commercial product; E.-K. Lee, S.-H. Kim, B.-H. Jung, W.-S. Ahn, G.-J. Kim, *Tetrahedron Letters***2003**, *44*, 1971.
L2 	(*R*,*R*)-*N*,*N'*-Dibenzyl-1,2-diaminocyclohexane Oil; E.-K. Lee, S.-H. Kim, B.-H. Jung, W.-S. Ahn, G.-J. Kim, *Tetrahedron Letters* **2003**, *44*, 1971.
L3 	(*R*,*R*)-*N,N'*-Bis[(2,4,6-trimethylphenyl)methyl]-1,2-cyclohexanediamine White solid, mp: 164 °C; J. Etxebarria, H. Degenbeck, A.-S. Felten, S. Serres, N. Nieto, A. Vidal-Ferran, *J. Org. Chem.* **2009**,*74*, 8794.
L5 	(*R*,*R*)-*N*,*N'*-Bis[(4-methoxyphenyl)methyl]-1,2-cyclohexanediamine Oil; T. Kylmälä, N. Kuuloja, Y. Xu, K. Rissanen, R. Franzén, *Eur. J. Org. Chem.* **2008**, 4019.
L7 	(*R*,*R*)-*N*,*N*'-Bis(salicyl)cyclohexane-1,2-diamine Oil; J. Sun, C. Zhu, Z. Dai, M. Yang, Y. Pan, H. Hu, *J. Org. Chem.* **2004**, *69*, 8500.

L8		(*R,R)-N,N'*-Bis[(2-methoxyphenyl)methyl]-1,2-cyclohexanediamine Oil; T. Kylmälä, N. Kuuloja, Y. Xu, K. Rissanen, R. Franzén, *Eur. J. Org. Chem.* **2008**, 4019.
L9		(*R,R*)-*N,N'*-Bis(3,5-di-*tert*-butylsalicyl)cyclohexane-1,2-diamine White solid, m.p. 140-141 ˚C; J. Sun, C. Zhu, Z. Dai, M. Yang, Y. Pan, H. Hu, *J. Org. Chem.* **2004**, *69*, 8500.
L10		(*R,R*)-*N,N*'-Bis[*o*-(diphenylphosphino)benzyl]cyclohexane-1,2-diamine White solid, m.p. 53-55 °C; J.-X.Gao, X.-D. Yi, P.-P.Xu, C.-L. Tang, H.-L. Wan, T.Ikariya, *J. Organometal. Chem.* **1999**, *592*, 290.
L11		*N,N'*-Bis(2-pyridylmethyl)-(1*R*,2*R*)-cyclohexane-1,2-diamine Oil; W. Park, M. H. Shin, J. H. Chung, J. Park, M.S. Lahc, D. Lim, *Tetrahedron Letters* **2006**, *47*, 8841.
L12		(*R,R*)-*N,N'*-Dimesityl-1,2-cyclohexanediamine Yellow solid, m.p. 122 °C; T. J. Seiders, D. W. Ward, R. H. Grubbs, *Org. Lett.* **2001**, *3*, 3225.

L13		(*R*,*R*)-*N*,*N*'-Dimethyl-*N*,*N'*-bis(salicyl)cyclohexane-1,2-diamine White solid, m.p. 119-120 °C; J. Sun, C. Zhu, Z. Dai, M. Yang, Y. Pan, H. Hu, *J. Org. Chem.* **2004**, *69*, 8500.
L14		(*R*,*R*)-*N*,*N'*-Dimethyl-*N*,*N'*-bis(3,5-di-*tert*-butylsalicyl)cyclohexane-1,2-diamine White solid, m.p. 100 °C; J. Balsells, P. J. Carroll, P. J. Walsh, *Inorg. Chem.* **2001,** *40,* 5568.
L15		(4*αR*,8*αR*)-2,3-Bis(4-bromophenyl)decahydroquinoxaline Yellow solid, m.p. 149-150 °C; P. Hesemann, J. J. E. Moreau, T. Soto, *Synth. Commun.* **2003**, *33*, 183.
L16		(*R*,*R*)-*N*,*N'*-Bis(salicylidene)-1,2-cyclohexanediamine White solid, m.p. 118-119 °C; T. Kylmälä, N. Kuuloja, Y. Xu, K. Rissanen, R. Franzén, *Eur. J. Org. Chem.* **2008**, 4019.
L17		(*R*,*R*)-*N*,*N'*-Bis[(2-methoxyphenyl)methylene]-1,2-cyclohexanediamine Yellowish solid; m.p. 107-108 °C; T. Kylmälä, N. Kuuloja, Y. Xu, K. Rissanen, R. Franzén, *Eur. J. Org. Chem.* **2008**, 4019.
L18		(2*R*,3*R*,12*R*,13*R*,22*R*,23*R*)-1,4,11,14,21,24-Hexa-aza-(2,3:12,13:22,23)-tributano-(6,9:16,19:26,29)-trietheno-(1*H*,2*H*,3*H*,4*H*,5*H*,10*H*,11*H*,12*H*,13*H*,14*H*,15*H*,20*H*,21*H*,22*H*,23*H*,24*H*,25*H*,30*H*)-octadecahydro-(30)-annulene White solid, m.p. 154–156 °C; J. Gawroński, K. Gawrońska, J. Grajewski, M. Kwit,

		A.Plutecka, U. Rychlewska, *Chem. Eur. J.* **2006**, *12*, 1807.
L21		(2*R*,3*R*,5*R*,10*R*,12*R*,13*R*,15*R*,20*R*,22*R*,23*R*,25*R*,30*R*)-1,4,11,14,21,24-Hexa-aza-(2,3:12,13:22,23)-tributano-(6,9:16,19:26,29)-trietheno-(1*H*,2*H*,3*H*,4*H*,11*H*,12*H*,13*H*,14*H*,21*H*,22*H*,23*H*,24*H*)-dodecahydro-(5,10,15,20,25,30)-hexamethyl-(30)-annulene White solid, m.p. 87–88 ˚C; D. Savoia, A. Gualandia, H. Stoeckli-Evans, *Org. Biomol. Chem.* **2010**, *8*, 3992.
L22		(2*R*,3*R*,5*R*,10*R*,12*R*,13*R*,15*R*,20*R*,22*R*,23*R*,25*R*,30*R*)-1,4,11,14,21,24-Hexa-aza-(2,3:12,13:22,23)-tributano-(6,9:16,19:26,29)-trietheno-(1*H*,2*H*,3*H*,4*H*,11*H*,12*H*,13*H*,14*H*,21*H*,22*H*,23*H*,24*H*)-dodecahydro-(5,10,15,20,25,30)-hexaphenyl-(30)-annulene White crystals, m.p. 136–137 ˚C; D. Savoia, A. Gualandia, H. Stoeckli-Evans, *Org. Biomol. Chem.* **2010**, *8*, 3992.
L23		(2*R*,3*R*,12*R*,13*R*,22*R*,23*R*)-1,4,11,14,21,24-Hexa-aza-1,4,11,14,21,24-hexamethyl-(2,3:12,13:22,23)-tributano-(6,9:16,19:26,29)-trietheno-(1*H*,2*H*,3*H*,4*H*,5*H*,10*H*,11*H*,12*H*,13*H*,14*H*,15*H*,20*H*,21*H*,22*H*,23*H*,24*H*,25*H*,30*H*)-octadecahydro-(30)-annulene White solid, m.p. 182–186 °C; J. Gawroński, K. Gawrońska, J. Grajewski, M. Kwit, A. Plutecka, U. Rychlewska, *Chem. Eur. J.* **2006**, *12*, 1807.
L24		(2*R*,3*R*,12*R*,13*R*,22*R*,23*R*)-1,4,11,14,21,24-Hexa-aza-1,4,11,14,21,24-hexa(2-hydroxyethyl)-(2,3:12,13:22,23)-tributano-(6,9:16,19:26,29)-trietheno-(1*H*,2*H*,3*H*,4*H*,5*H*,10*H*,11*H*,12*H*,13*H*,14*H*,15*H*,20*H*,21*H*,22*H*,23*H*,24*H*,25*H*,30*H*)-octadecahydro-(30)-annulene Glassy product; J. Gawroński, K. Gawrońska, J. Grajewski, M.

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Chem. Eur. J. **2006**, *12*, 1807.

Table SI3. Systematic names, melting points and references to the NMR data for the products of hydrosilylation reactions.

Systematic name	Known compound	Melting point [°C]	Reference to melting point in literature	Reference to NMR data in literature
(*S*)-1-Phenylethanol	Yes	oil	–	1
(*S*)-1-Phenylpropan-1-ol	Yes	oil	–	1
(*S*)-Cyclohexylphenyl-methanol	Yes	48-50	2	1
(*S*)-1-(4-Methylphenyl)-ethanol	Yes	oil	–	3
(*S*)-1-(4-Methoxyphenyl)-ethanol	Yes	oil	–	1
(*S*)-1-(4-Cyanophenyl)-ethanol	Yes	oil	–	4
(*S*)-1-(4-Fluorophenyl)-ethanol	Yes	oil	–	3
(*S*)-1-[3,5-Bis(trifluoromethyl)phenyl]-ethanol	Yes	oil	–	5
(*R*)-2,2,2-Trifluoro-1-phenylethanol	Yes	oil	–	6
(*R*)-2,2,2-Trifluoro-1-(4-fluoro-phenyl)-ethanol	Yes	oil	–	7
(*R*)-2,2,2-Trifluoro-1-(2,4,6-trimethylphenyl)-ethanol	Yes	oil	–	6
(*S*)-(3-Methylphenyl)phenyl-methanol	Yes	51-52	8	8
(*S*)-(4-Methylphenyl)phenyl-methanol	Yes	59-60	9	9
(*S*)-(2-Chlorophenyl)phenyl-methanol	Yes	oil	9	9
(*S*)-(4-Chlorophenyl)phenyl-methanol	Yes	54-55	9	9
(*S*)-1-Indanol	Yes	71-72	10a	10b
(*S*)-α-Tetralol	Yes	oil	–	11
(*S*)-β-Tetralol	Yes	oil	–	11

Reference

1. Morris DJ, Hayes AM, Wills M (2006) J Org Chem 71:7035
2. Belén Díaz-Valenzuela M, Phillips SD, France MB, Gunn ME, Clarke ML (2009) Chem Eur J 15:1227.
3. Utsukihara T, Misumi O, Kato N, Kuroiwa T, Horiuchi CA (2006) Tetrahedron Asymmetry 17:1179
4. Shuanglong L; Christian W (2007) Org Lett 9:2965
5. Singh RP, Twamley B, Fabry-Asztalos L, Matteson DS, Shreeve JM (2000) J Org Chem 65:8123
6. Yong KH, Chong JM (2002) Org Lett 4:4139
7. Xu Q, Zhou H, Geng X, Chen P (2009) Tetrahedron 65:2232
8. Stanchev S, Rakovska R, Berova N, Snatzke G (1995) Tetrahedron Asymmetry 6:183
9. Wu X, Liu X, Zhao G (2005) Tetrahedron Asymmetry 16:2299
10. a) Siden T, Gerard J (1980) J Organomet Chem 197:199; b) Aupoix A, Bournaud C, Vo-Thanh G (2011) Eur J Org Chem 15:2772
11. Palmer M, Walsgrove T, Wills M (1997) J Org Chem 62:5226