Supporting Information for:

Two-Stage Optimization of a Supramolecular Catalyst for Catalytic Asymmetric Hydroboration

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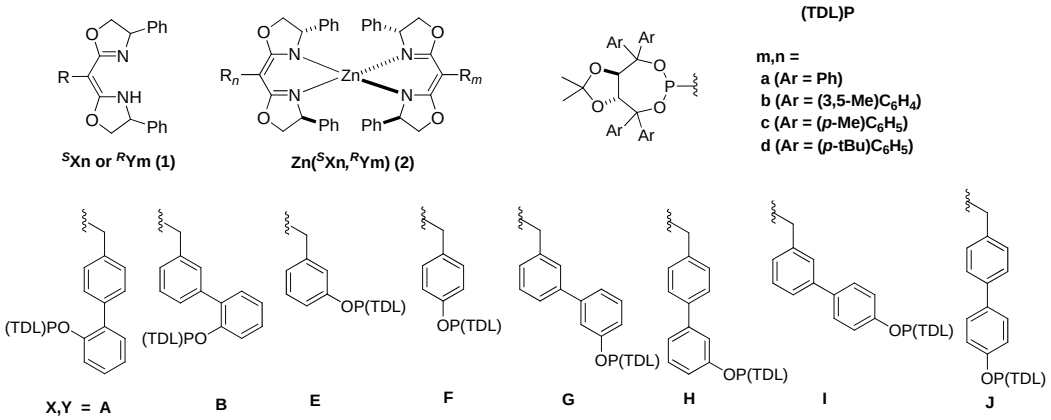
All reactions are carried out under an atmosphere of dry nitrogen. Dichloromethane, tetrahydrofuran (THF), and benzene were freshly distilled under the following conditions: benzene from sodium metal, THF from sodium/benzophenone and dichloromethane from calcium hydride. Pinacolborane was obtained from Aldrich Chemicals and distilled immediately prior to use. All other chemicals were used as received from the appropriate suppliers. NMR spectra were recorded on 300 or 400 MHz Bruker Avance NMR spectrometers using residue $CDCl_3$ (δ = 7.26) for ^1H NMR and the central $CDCl_3$ resonance (δ 77.16 ppm) for ^{13}C NMR. ^1H NMR spectra are reported as follows (s = singlet, d = doublet, t = triplet, q = quartet, m = unresolved multiplet). Flash chromatography was carried out using EMD Silica Gel 60 Geduran®. Thin Layer Chromatography analyses were performed on Analtech Silica Gel HLF (0.25 mm) precoated analytical plates and visualized with use of handheld short wavelength UV light, iodine stain (I_2 and EMD Silica Gel 60 Geduran®) and/or vanillin stain (Ethanol, H_2SO_4, and vanillin). Data were recorded and analyzed with ChromPerfect chromatography software (version 5.1.0). Chiral capillary GC analysis was performed on a Shimadzu GC14APFSC with a J&W Scientific 30.0 m x 0.25 mm ID Cyclosil β column, column temperature program 120 ^oC (1 min hold) to 130 ^oC @ 1 ^oC/min then 165^oC @ 2 ^oC/min). HRMS analyses were performed by the Nebraska Center for Mass Spectrometry. CD specs were recorded on JASCO J-815 CD spectrometer.



8 different tethers (A, B, E, F, G, H, I, & J) bearing TADDOL (a) were combined to create 64 supramolecular catalysts (combinations shown below). The data obtained with these catalysts were used to construct figure 2.

SXn/RXn	Aa	Ba	Ea	Fa	Ga	Ha	Ia	Ja
Aa	1	2	3	4	5	6	7	8
Ba	9	10	11	12	13	14	15	16
Ea	17	18	19	20	21	22	23	24
Fa	25	26	27	28	29	30	31	32
Ga	33	34	35	36	37	38	39	40
Ha	41	42	43	44	45	46	47	48
Ia	49	50	51	52	53	54	55	56
Ja	57	58	59	60	61	62	63	64

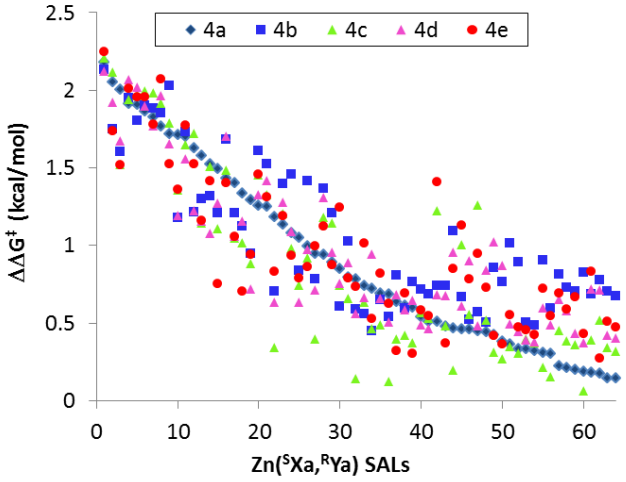
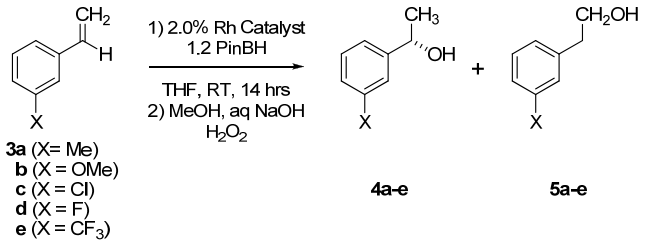


Figure 2. Enantioselectivity (expressed in terms of $\Delta\Delta G^{\ddagger}$) for CAHB leading to (*R*)- and (*S*)-**4a**–**e** with 64 supramolecular catalysts.



Literature best % ee for each meta-substituted styrenes are shown below:

3a: 91 %[1], 3b: NR, 3c: 89 %[2], 3d: 88 %[3], 3e: 83 %[2]

The following data shows that a change in TADDOL- phosphites lead to a change in reactivity.

% ee of **4**(% α-isomer **4**)

	^{S}**Xn**	^{R}**Xn**	**3a**	**3b**	**3c**	**3d**	**3e**
1	**Aa**	**Aa**	91(98)	90(92)	91(98)	92(94)	90(94)
2	**Ab**	**Ab**	91(91)	90(91)	90(86)	91(89)	91(93)
3	**Ac**	**Ac**	84(93)	92(95)	96(96)	95(98)	95(89)
4	**Ad**	**Ad**	57(96)	70(76)	75(97)	78(91)	83(94)
5[b]	**Ab**	**Ac**	94(98)	95(96)	94(93)	94(95)	94(97)
6[c]	**Ab**	**Ac**	94(93)	93(90)	94(89)	93(89)	93(87)
7	**Ac**	**Bc**	88(95)	95(97)	92(95)	92(90)	97(96)
8	**Bc**	**Ac**	90(95)	95(97)	92(95)	90(94)	95(96)
9	**Bc**	**Bc**	92(97)	93(96)	94(95)	96(95)	95(90)
10	**Bc**	**Cc**	88(95)	90(96)	90(93)	90(97)	90(93)

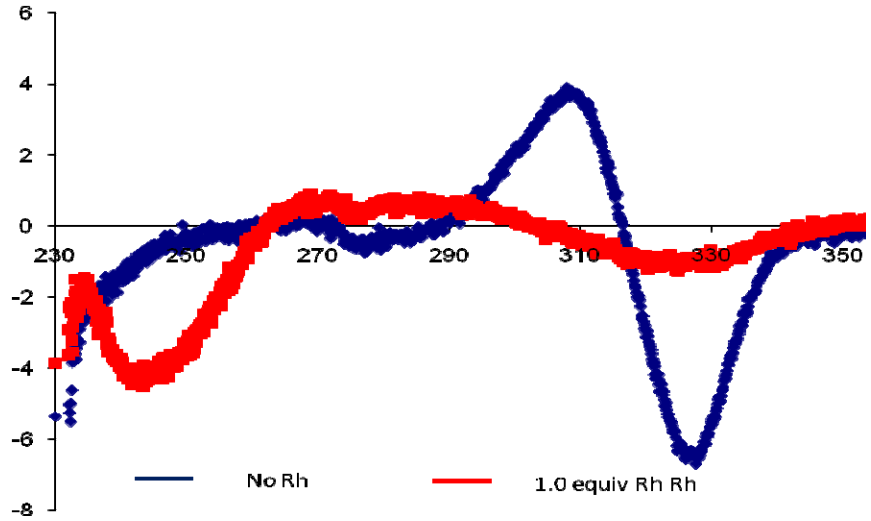
Table S2 (expanded). Subtle Variation of the Ligating Group Further Optimized the (SAL)Rh-Catalyzed CAHB of **3a-e**

[1]Stéphane Demay Dipl.-Ing, Florence Volant Dipl.-Chem, Paul Knochel, *Angew. Chem., Int. Ed.* **2001**, 40, 1235

[2] Henri Doucet, Elena Fernandez, Timothy P. Layzell, and John M. Brown, *Chemistry – A European Journal,* **1999**, 5, 1320-1330

[3] P. Veeraraghavan Ramachandran , Michael P. Jennings, *Journal of Fluorine Chemistry*, **2006**, 127, 1252-1255

CD spectra were recorded using JASCO J-815 CD spectrometer (serial number: A022061168). SALs were prepared in-situ (according to the procedure described in this supporting information) and the solution that contains $Rh(nbd)_2BF_4$ in dichloromethane was added to the SAL solution. Then the solution (0.000267μM) was stirred for 30 min and transferred into a cell for CD spec analysis. CD spectra were recorded range from 230 nm to 350 nm (0.1 nm interval).



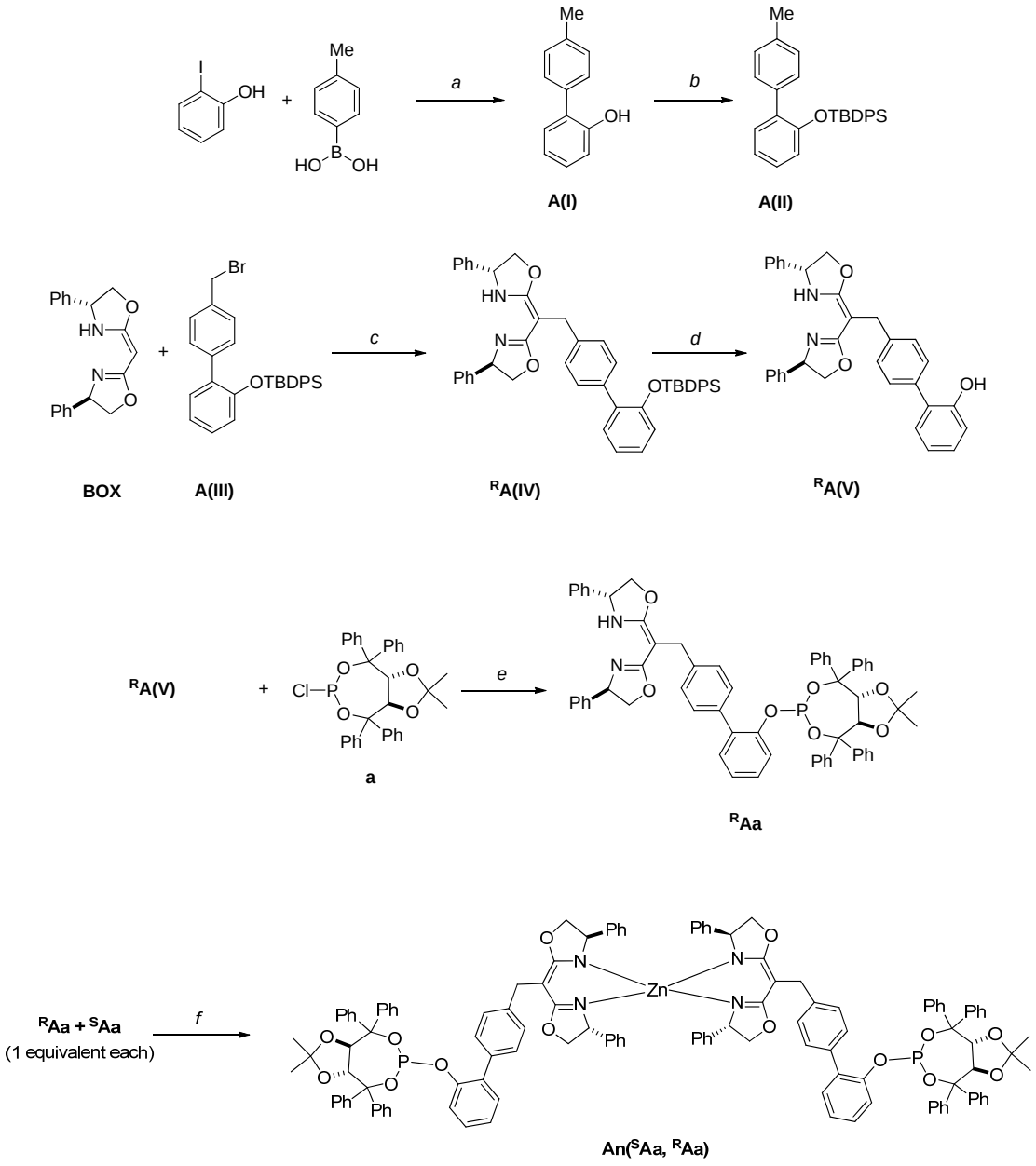
Figuire S3. CD spectral changes (230-350 nm in CH_2Cl_2) upon the addition of $Rh(nbd)_2BF_4$ to **Zn(**^{S}**Bc,**^{R}**Ac)** (blue curve) yielding [**Zn(**^{S}**Bc,**^{R}**Ac)**Rh(nbd)]BF_4 (red curve).

Gel Permeation chromatographic (GPC) analysis data:

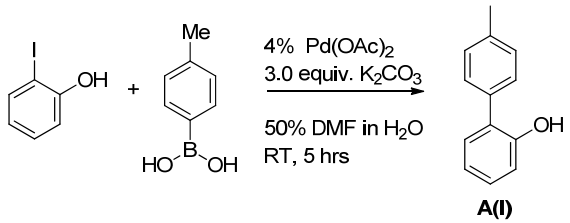
SAL	Without $Rh(nbd)_2BF_4$ Retention time (min)	With $Rh(nbd)_2BF_4$ Retention time (min)
Zn(^{S}Bc, ^{R}Ac)	8.60	8.76
Zn(^{S}Bc, ^{R}Cc)	8.57	8.79

Zinc complexes (**Zn(^{S}Bc, ^{R}Ac)** & **Zn(^{S}Bc, ^{R}Cc)**) were prepared in chloroform according to the procedure described in this supporting information. For Rh complex, the stock solution of Rh was made in chloroform and added to the solution that contains zinc complex. Then each sample was injected into GPC column (Jordi Gel fluorinated DVB 100 Å 250 x 4.6 mm column (serial number: 06171003)). The flow rate was 0.5 mL/min chloroform.

The syntheses of **^{R}Aa and ^{S}Aa** is illustrated by the preparation of the heterodimer **Zn(^{S}Aa, ^{R}Aa)** in the following scheme.



a) 4% $Pd(OAc)_2$, 3.0 equiv. K_2CO_3, 1:1 DMF:H_2O, RT 5 h. *b*) 1.1 equiv. TBDPSCl, 4.0 equiv. imidazole, DMF, 0°C to RT, 12 h. *c*) 1.0 equiv. NaHMDS, THF, -78 °C, 2 h, then 1.0 equiv. **BOX**, -78 °C to RT, 12h. *d*) 1.0 equiv. TBAF, THF, RT, 10 h. *e*) 1.2 equiv. **a**, 20 equiv. TEA, 5% DMAP, THF, RT, 12h. *f*) 1.0 equiv. $ZnEt_2$, DCM, RT, 5 min.

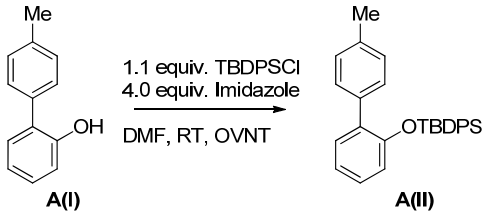


A(I)

***a*. Preparation of A(I) (*adapted from the procedure of Cowart, et al.*)[4].** To a 500 mL round-bottom flask was added 2-iodophenol (11.0 g, 50.0 mmol), 4-toluyl boronic acid (7.48 g, 55.0 mmol), and palladium acetate (0.455 g, 2.03 mmol). The mixture was dissolved in DMF (150 mL) and stirred at room temperature. Potassium carbonate (20.7 g, 150 mmol) was dissolved in 150 mL of degassed water, added to the reaction over 10 min and the resulting mixture was stirred at room temperature (5 h). Tthe mixture was extracted with ethyl acetate (3 x 100 mL) and the combined organic layers dried ($MgSO_4$) and concentrated. The **A(I)** was purified by flash chromatography on silica (ca 150 g, 10:90 ethyl acetate: hexane) to give **A(I)** (8.30 g, 90 %) as clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.38 (2H, m), 7.34-7.30 (2H, m), 7.28-7.25 (2H, m), 7.03-6.99 (2H, m), 2.45 ppm (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 137.7, 134.3, 130.4, 130.1, 129.1, 129.1, 128.3, 121.0, 116.0, 21.3 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{13}H_{12}O$ (M^+), 184.0888; found, 184.0893 *m/z*.

B(I) (8.90 g, 96 %) as clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.35 (1H, m), 7.32-7.25 (5H, m), 7.05-7.00 (2H, m), 2.46 ppm (3H, s); 13C NMR (100 MHz, $CDCl_3$) δ 152.6, 139.1, 137.2, 130.3, 130.0, 129.9, 129.3, 129.1, 128.7, 126.2, 120.9, 115.9, 21.6 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{13}H_{12}O$ (M^+), 184.0888; found, 184.0886 *m/z*.

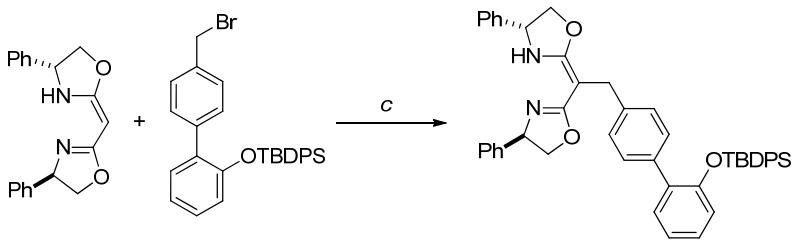
[4] M. Cowart, R. Faghih, M. P. Curtis, G. A. Gfesser, Y. L. Bennani, L. A. Black, L. Pan, K. C. Marsh, J. P. Sullivan, T. A. Esbenshade, G. B. Fox, A. A. Hancock , *J. Med. Chem.* **2005**, *48*, 38-55.



A(I) A(II)

***b*. Preparation of A(II).** To a cooled (0 °C) solution of **A(I)** (8.50 g, 46.1 mmol) and imidazole (9.35 g, 137 mmol) in DMF (130 mL) was added TBDPSCl (14.2 mL, 55.0 mmol) dropwise over 15 minutes. Upon complete addition, the cooling bath was removed and solution was stirred at ambient temperature overnight. Water (ca 50 mL) was added the mixture was extracted with diethyl ether (3 x 100 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated. The product **A(II)** was purified by flash chromatography on silica chromatographed (ca 150 g, 5:95 ethyl acetate:hexane) to give **A(II)** (17.5 g, 93 %) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.66 (4H, dd, *J* = 9.6 Hz, 1.8 Hz), 7.45-7.36 (11H, m), 6.96-6.86 (2H, m), 6.57-6.51 (1H, dd, *J* = 7.9, 1.3 Hz), 2.45 (3H, s), 0.89 ppm (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 136.4, 135.6, 135.3, 134.9, 133.0, 130.9, 129.9, 129.8, 129.7, 128.7, 127.8, 121.3, 119.9, 26.7, 21.4, 19.5 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{29}H_{30}OSiLi$ $[(M+Li)^+]$, 429.2226; found, 429.2215 *m/z*.

B(II) (18.3 g, 98 %) as clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.63 (4H, dd, *J* = 9.6, 1.9 Hz), 7.46-7.28 (10H, m), 7.18 (1H, d, *J* = 7.2 Hz), 6.96-6.88 (2H, m), 6.54-6.50 (1H, dd, *J* = 7.7, 1.5 Hz), 2.43 (3H, s), 0.88 ppm (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 139.1, 137.2, 135.6, 134.9, 133.2, 133.0, 130.9, 129.9, 129.3, 128.0, 127.8, 127.6, 126.9, 121.3, 119.8, 26.3, 21.6, 19.5 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{29}H_{30}OSiLi$ $[(M+Li)^+]$, 429.2226; found, 429.2217 *m/z*.



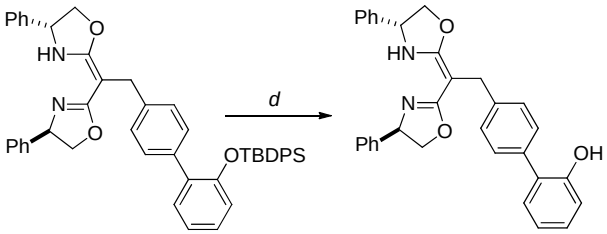
A(III) **^{R}A(IV)**

***c*. Preparation of A(III). Step *i*: Preparation of bromide A(III).** A solution of **A(II)** (5.50 g, 13.6 mmol), NBS (2.42 g, 13.6 mmol) and AIBN (111 mg, 0.68 mmol) in dry benzene (100 mL) was heated at reflux for 6 hours. The reaction mixture was cooled to room temperature during which time a solid precipitates. The mixture is filtered and the filtrate concentrated to give bromide **A(III)**, which was used without further purification.

Step *ii*: Preparation of substituted box derivative ^{R}A(IV). To a stirred, cooled (-78 ^{o}C) solution of 2,2'-methylenebis[(4*R*)-4-phenyl-4,5-dihydro-2-oxazole] (4.00 g, 13.1 mmol) in dry THF (10 mL) a solution of sodium bis(trimethylsilyl) amide (13.1 mL of a 1.0 *M* solution in THF, 13.1 mmol) was added dropwise. The resulting mixture was stirred (-78 ^{o}C, 2 h) then a solution of bromide **A(III)** in THF (15 mL) was added dropwise. The resulting reaction mixture was allowed to slowly warm to room temperature and stirred for a total of 12 h. The reaction was quenched by the addition water and extracted with CH_2Cl_2 (2 x 120 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$) and concentrated. Flash chromatography on silica (5:95 methanol:dichloromethane) gives **^{R}A(IV)** (8.11 g, 85 %) as a colorless solid: mp 84-85 ^{o}C; $[\alpha]D^{25}$ = +28.0 (c = 1.1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.65 (5H, m), 7.63-7.58 (2H, m), 7.44-7.24 (14H, m), 7.13-7.11 (2H, dd, *J* = 8.1, 8.0 Hz), 6.97-6.87 (2H, m), 6.57-6.54 (1H, dd, *J* = 8.0, 7.9 Hz), 5.28 and 5.22 (2H, overlapping t, *J*= 10.0, 10.0 Hz), 4.71 and 4.68 (2H, overlapping dd, *J*= 10.4, 10.3 Hz), 4.25-4.18 (1H, dd, *J* = 8.1, 8.1 Hz), 4.17-4.10 (2H, m), 3.59-3.51 (2H, m), 0.88 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.6, 152.6, 142.2, 142.2, 137.7, 136.7, 135.6, 132.91, 132.89, 132.7, 131.0, 130.2, 130.0,

128.9, 128.8, 128.1, 127.9, 127.7, 127.6, 126.8, 126.6, 121.4, 120.0, 75.5, 75.3, 69.80, 69.78, 41.6, 35.9, 26.5, 19.5 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{48}H_{47}N_2O_3Si$ [$(M+H)^+$], 727.3356; found, 727.3373 *m/z*.

^{R}B(IV) (7.78 g, 82 %) as a colorless solid: mp 89-90 ^{o}C; [α]D ^{25} = +24.2 (c = 0.8, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.54 (2H, m), 7.45-7.22 (17H, m), 7.09-7.07 (2H, dd, *J* = 7.9, 7.8 Hz), 6.92-6.90 (2H, m), 6.57-6.54 (2H, m), 5.28 and 5.20 (2H, overlapping t, *J*= 10.0, 10.0 Hz), 4.68 and 4.65 (2H, overlapping dd, *J*= 10.1, 10.1 Hz), 4.19-4.15 (1H, dd, *J* = 8.2, 8.1 Hz), 4.13-4.08 (2H, m), 3.57-3.46 (2H, m), 0.87 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.6, 152.5, 142.2, 139.5, 137.7, 135.5, 132.91, 132.88, 132.85, 130.9, 130.6, 129.9, 128.9, 128.7, 128.6, 128.13, 128.07, 127.8, 127.63, 127.57, 126.8, 126.7, 126.5, 121.3, 119.8, 75.5, 75.2, 69.72, 69.70, 41.5, 36.0, 26.34, 19.4 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{48}H_{47}N_2O_3Si$ [$(M+H)^+$], 727.3356; found, 727.3349 *m/z*.

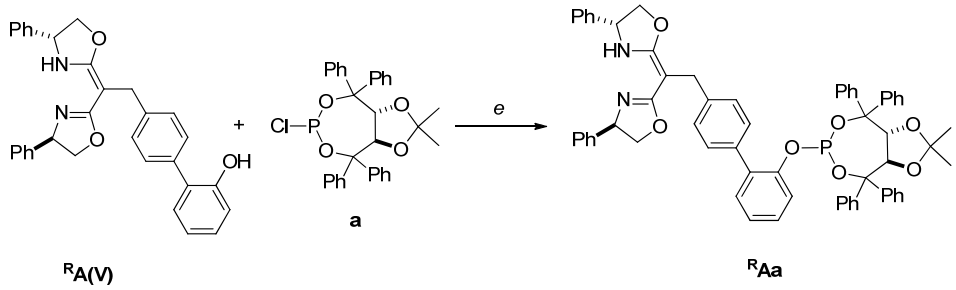


^{R}A(IV) **^{R}A(V)**

***d*. Preparation of ^{R}A(V).** To a solution of **^{R}A(IV)** (8.00 g, 11.0 mmol) in dry THF (100 mL) tetrabutylammonium fluoride (TBAF, 11.0 mL of a 1.0 *M* solution in THF, 11.0 mmol) was added dropwise. After 10 h, the mixture was partitioned between CH_2Cl_2 (80 mL)-water (80 mL). The organic layer was dried ($MgSO_4$) and concentrated. Chromatography on silica gel (10:90 methanol:dichloromethane) gave **^{R}A(V)** (5.17 g, 96%) as a colorless solid: mp 120-122 ^{0}C; [α]D ^{25} = +18.7 (c = 0.7, CH_2Cl_2); ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.50-7.41 (4H, dd, *J* = 19.6, 8.1 Hz), 7.36-7.19 (10H, m), 7.06-7.03 (2H, dd, *J* = 7.8, 7.0 Hz), 7.03-6.98 (1H, dd, *J* = 8.6,

8.4 Hz), 6.95-6.92 (1H, d, *J* = 8.0 Hz), 5.27-5.21 (2H, m), 4.74 and 4.68 (2H, overlapping dd, *J* = 8.5, 8.3 Hz), 4.24-4.19 (2H, dd, *J* = 8.2, 8.1 Hz), 4.15-4.10 (1H, dd, *J* = 8.5, 8.5 Hz), 3.54-3.43 ppm (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.9, 153.7, 141.8, 141.7, 136.9, 136.5, 130.5, 129.5, 129.3, 128.82, 128.78, 128.6, 128.2, 127.8, 127.7, 126.8, 126.7, 120.2, 116.3, 75.6, 75.4, 69.41, 69.38, 41.3, 35.6 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{32}H_{29}N_2O_3$ $[(M+H)^+]$, 489.2178; found, 489.2170 *m/z*.

^{R}B(V) (4.90 g, 91%) as a colorless solid: mp 124-126 ^{0}C; [α]D ^{25} = 18.8 (c = 0.6, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.20 (14H, m), 7.02-6.96 (4H, m), 5.24 and 5.20 (2H, overlapping t, *J* = 10.8, 10.8 Hz), 4.71 and 4.66 (2H, overlapping dd, *J* = 8.5, 8.5 Hz), 4.21-4.17 (1H, dd, *J* = 8.2, 8.1 Hz), 4.14-4.07 (2H, m), 3.55-3.43 ppm (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.7, 153.3, 141.9, 141.8, 138.3, 138.2, 130.4, 130.0, 129.1, 128.81, 128.77, 128.71, 128.2, 128.1, 127.8, 127.7, 127.6, 126.72, 126.69, 120.3, 116.3, 75.5, 75.3, 69.4 (2C), 41.3, 35.8 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{32}H_{29}N_2O_3$ $[(M+H)^+]$, 489.2178; found, 489.2180 *m/z*.



***e*. Preparation of ^{R}Aa (*adapted from the procedure of Kranich et al.*)[5].** (*R*,*R*)-TADDOL)PCl ((*R*)-**a**) was prepared according to the published procedure.[6] To a solution of **^{R}A(V)** (300 mg, 0.61 mmol), Et_3N (1.70 mL, 12.2 mmol), and DMAP (3.7 mg, 0.03 mmol) in dry THF (15 mL) was added dropwise a solution of

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[6] J. Sakaki, W. B. Schweizer, D. Seebach, *Helv. Chim. Acta* **1993**, *76*, 2654-2665.

(*R*,*R*)-TADDOL)PCl ((*R*)- **a**) (389 mg, 0.73 mmol) in dry THF (7 mL). The resulting milky suspension was stirred at room temperature (ca. 12 h) and then filtered under nitrogen through a short pad of celite. The celite was washed with degassed THF and the combined filtrates concentrated to dryness on a vacuum line using care to insure the product is kept at oxygen-free. Rapid chromatography of the residue on a short column of silica gel (5:95 methanol:dichloromethane) afforded ^{R}**Aa** (461 mg, 77%) as a colorless solid: mp 138-139 ^{0}C; [α]D ^{25} = -158.0 (c = 0.2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.12 (36H, m), 7.04-7.02 (2H, m), 5.23-5.18 (2H, m), 5.10 (2H, s), 4.66-4.60 (2H, m), 4.19-4.15 (1H, dd, *J* = 8.2, 8.2 Hz), 4.12-4.05 (2H, m), 3.57-3.45 (2H, m), 0.98 (3H, s), 0.39 ppm (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 165.47, 149.0, 145.5, 145.2, 142.1, 142.0, 141.39, 141.36, 140.7, 136.7, 136.6, 134.03, 134.01, 130.8, 130.1, 128.7, 128.69, 128.66, 128.2, 128.1, 127.8, 127.76, 127.6, 127.53, 127.50, 127.29, 127.26, 127.17, 127.07 126.99, 126.72, 126.70, 124.2, 122.1, 122.0, 113.2, 86.0 (d, J_{CP} = 8.9 Hz), 83.3, 82.1 (d, J_{CP} = 14.5 Hz), 80.9 (d, J_{CP} = 4.5 Hz), 75.4, 75.2, 69.7, 69.6, 41.4, 35.6, 27.1, 25.8 ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 134.9 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{63}H_{56}N_2O_7P$ [$(M+H)^+$], 983.3825; found, 983.3840 *m/z*.

^{S}**Aa** (462 mg, 77%) as a colorless solid: mp 139-140 ^{0}C; [α]D ^{25} = 142.0 (c = 0.4, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.21 (35H, m), 7.20 (1H, m), 7.05-7.03 (2H, m), 5.24-5.22 (2H, m), 5.13-5.12 (2H, m), 4.68-4.64 (2H, m), 4.19-4.07 (3H, m), 3.55-3.54 (2H, m), 0.98 (3H, s), 0.408 ppm (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.53, 165.50, 149.02, 145.54, 145.15, 142.08, 141.98, 141.41, 140.70, 136.73, 136.62, 133.99, 130.81, 130.07, 129.61, 128.78, 128.73, 128.67, 128.24, 128.07, 127.83, 127.79, 127.62, 127.54, 127.41, 127.31, 127.28, 127.20, 127.08, 127.00, 126.72, 126.52, 124.20, 121.95, 113.28, 86.05, 85.96, 83.30, 82.14, 82.00, 80.83, 80.79, 75.40, 75.21, 69.66, 41.31, 35.59, 27.15, 25.86 ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 134.7 ppm; HRMS (ESI) calcd. for $C_{63}H_{55}N_2O_7P$ [$(M+Na)^+$], 1005.3747; found, 1005.3635 *m/z*.

^{R}Bc (495 mg, 78%) as a colorless solid: mp 126-130 ^{0}C; [α]D ^{25} = -118.2 (c = 0.4, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.17 (22H, m), 7.09-7.00 (12H, m), 5.20-5.18 (2H, m), 5.00 (1H, d, *J* = 7.8 Hz), 4.91 (1H, d, *J* = 8.2 Hz), 4.63-4.60 (2H, m), 4.14-4.12 (1H, dd, *J* = 8.3, 8.3 Hz), 4.04-4.00 (2H, m), 3.36-3.34 (2H, m), 2.34-2.28 (12H, m) 1.10 (3H, s), 0.34 ppm (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.54, 165.51, 148.87, 148.85, 143.1, 142.5, 142.2, 142.1, 138.6, 138.5, 138.4, 138.0, 137.7, 137.2, 136.9, 136.6, 134.63, 134.60, 130.7,130.6, 128.8, 128.7, 128.6, 128.4, 128.1, 127.8, 127.6, 127.52, 127.46, 127.22, 126.8, 126.7, 124.3, 122.73, 122.66, 112.6 ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 135.3 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{67}H_{63}N_2O_7P$ [$(M+H)^+$], 1039.2001; found, 1039.4435 *m/z*.

^{S}Bc (514 mg, 81%) as a colorless solid: mp 126-129 ^{0}C; [α]D ^{25} = -103.5 (c = 0.4, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ7.37-7.13 (22H, m), 7.09-6.99 (12H, m), 5.22-5.17 (2H, m), 4.98 (1H, d, *J* = 7.8 Hz), 4.90 (1H, d, *J* = 8.2 Hz), 4.63-4.61 (2H, m), 4.13-4.10 (1H, dd, *J* = 8.3, 8.3 Hz), 4.05-4.03 (2H, m), 3.36-3.33 (2H, m), 2.34-2.29 (12H, m) 1.08 (3H, s), 0.34 ppm (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.55, 165.51, 148.9 (2C), 143.1, 142.6, 142.2, 142.1, 138.6, 138.53, 138.51, 138.1, 137.7, 137.2, 136.9, 136.6, 134.5, 130.7,130.6, 128.9, 128.7, 128.6, 128.4, 128.1, 127.8, 127.6, 127.52, 127.46, 127.2, 126.8, 126.68, 127.67, 124.2, 122.6, 122.5, 112.67, 85.0 (d, J_{CP} = 8.8 Hz), 82.9, 82.4 (d, J_{CP} = 14.3 Hz), 81.4 (d, J_{CP} = 4.4 Hz), 75.4, 75.1, 69.62, 69.60, 41.2, 35.8, 27.3, 25.7, 21.17, 21.14, 21.04, 21.02 ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 135.3 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{67}H_{63}N_2O_7P$ [$(M+H)^+$], 1039.2001; found, 1039.4435 *m/z*.

^{R}Cc (527 mg, 82%) as a colorless solid: mp 133-136 ^{0}C; [α]D ^{25} = -118.0 (c = 0.2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.43 (4H, m), 7.39-7.20 (18H, m), 7.15-7.13 (6H, m), 7.10-6.99 (6H, m), 5.32-5.19 (3H, m), 5.03 (1H, d, *J* = 8.2 Hz), 4.91-4.75 (2H, m), 4.66-4.65 (2H, m), 4.16-4.07 (3H, m), 3.53-3.47 (2H, m), 2.33 (3H, s), 2.32 (3H, s), 2.29 (3H, s), 2.28 (3H, s), 0.96 (3H, s), 0.61 ppm (3H, s); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 165.51, 165.48, 149.1, 143.0, 142.5, 142.1, 142.0, 138.6, 138.5, 138.0, 137.3, 136.90, 136.86, 136.72, 136.6, 136.5, 130.7,130.1, 128.8, 128.70, 128.64, 128.55, 128.37, 128.0, 127.8, 127.6, 127.5, 127.1, 126.9, 126.7, 124.2, 122.4, 122.3, 112.8, 85.3 (d, J_{CP} = 8.8 Hz), 83.0, 82.3 (d, J_{CP} = 14.3 Hz), 81.2 (d, J_{CP} = 4.4 Hz), 75.4, 75.2, 69.7, 69.6, 41.3, 35.6, 27.3, 25.8, 21.16, 21.12, 21.01 (2C) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 131.5 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{68}H_{65}N_2O_7P$ [$(M+H)^+$], 1053.2267; found, 1053.4563 *m/z*.

^{R}Ac (539 mg, 85%) as a colorless solid: mp 121-125 ^{0}C; [α]D ^{25} = -141.0 (c = 0.2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.40 (4H, m), 7.39-7.22 (18H, m), 7.08-6.98 (12H, m), 5.20-5.17 (2H, m), 5.01-4.96 (2H, m), 4.64-4.60 (2H, m), 4.18-4.14 (1H, dd, *J* = 8.1, 8.1 Hz), 4.09-4.03 (2H, m), 3.50-3.47 (2H, m), 2.31-2.25 (12H, m) 1.04 (3H, s), 0.36 ppm (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.55, 165.50, 149.1, 143.0, 142.5, 142.1, 142.0, 138.6, 138.5, 138.0, 137.3, 136.93, 136.87, 136.75, 136.6, 136.5, 134.2,130.7,130.1, 128.8, 128.70, 128.64, 128.59, 128.55,128.4, 128.0, 127.8, 127.6, 127.5, 127.1, 126.9, 126.7, 124.2, 122.4, 122.3, 112.8, 85.3 (d, J_{CP} = 8.8 Hz), 83.0, 82.3 (d, J_{CP} = 14.3 Hz), 81.2 (d, J_{CP} = 4.4 Hz), 75.4, 75.1, 69.7, 69.6, 41.3, 35.6, 27.3, 25.8, 21.16, 21.12, 21.01,14.2 (2C) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 136.4ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{67}H_{63}N_2O_7P$ [$(M+H)^+$], 1039.2001; found, 1039.4461 *m/z*.

^{S}Ac (520 mg, 82%) as a colorless solid: mp 120-125 ^{0}C; [α]D ^{25} = -128.7 (c = 0.2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.41 (4H, m), 7.40-7.20 (18H, m), 7.07-6.99 (12H, m), 5.22-5.20 (2H, m), 5.02-5.00 (2H, m), 4.63-4.62 (2H, m), 4.17-4.14 (1H, dd, *J* = 8.2, 8.2 Hz), 4.09-4.03 (2H, m), 3.50-3.47 (2H, m), 2.32-2.26 (12H, m) 1.05 (3H, s), 0.40 ppm (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.55, 165.51, 149.1, 143.0, 142.5, 142.1, 142.0, 138.66, 138.61, 138.1, 137.3, 136.9, 136.9, 136.8, 136.6, 136.5, 134.11, 134.08, 130.1, 128.8, 128.70, 128.65, 128.4, 128.0, 127.8, 127.6, 127.5, 127.2, 126.9, 126.7, 124.2, 122.33, 122.22, 112.9, 85.3 (d, J_{CP} = 8.8 Hz), 83.1, 82.4 (d, J_{CP} = 14.3 Hz), 81.2 (d, J_{CP} = 4.4 Hz), 75.4, 75.2, 69.7, 69.6, 41.3, 35.6,

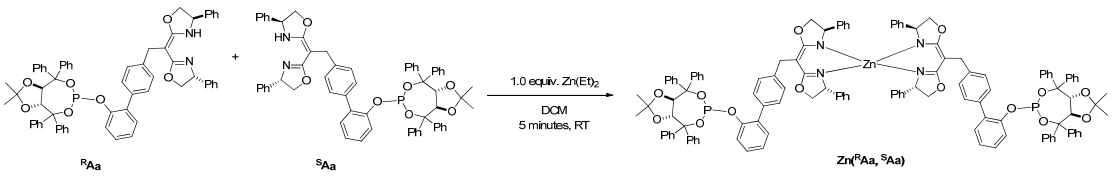
27.3, 25.8, 21.18, 21.14, 21.03 (2C) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 136.2 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{67}H_{63}N_2O_7P$ [$(M+H)^+$], 1039.2001; found, 1039.4430 *m/z*.

^{R}Ab (595 mg, 89%) as a colorless solid: mp 120-125 ^{0}C; [α]D ^{25} = -163.0 (c = 0.2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.21 (17H, m), 7.19-7.16 (2H, m), 7.13-7.05 (2H, m), 7.01-6.86 (9H, m), 5.07 (1H, d, *J* = 7.9 Hz), 4.96 (1H, d, *J* = 8.3 Hz), 4.67-4.59 (2H, m), 4.15-4.03 (3H, m), 3.36-3.27 (2H, m), 2.29-2.23 (24H, m) 1.17 (3H, s), 0.34 ppm (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 165.5, 149.1, 145.6, 145.3, 142.12, 142.11, 141.0, 140.9, 138.6, 137.50, 137.45, 136.8, 136.5, 136.2, 134.4, 130.8, 130.2, 129.5, 129.1, 129.0 128.8, 128.7, 128.5, 127.84, 127.76, 127.51, 127.46, 126.7, 126.6, 125.1, 124.9, 124.0, 122.2, 122.1, 112.7, 84.5 (d, J_{CP} = 8.3 Hz), 83.1, 82.3 (d, J_{CP} = 14.0 Hz), 82.0 (d, J_{CP} = 4.3 Hz), 75.4, 75.1, 69.61, 69.58, 41.2, 35.8, 27.4, 25.8, 21.65, 21.57, 21.53 (2C) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 134.7 ppm; HRMS (FAB, 3-NBA matrix) calcd. For $C_{71}H_{71}N_2O_7P$ [$(M+H)^+$], 1095.3064; found, 1095.5075 *m/z*.

^{S}Ab (581 mg, 87%) as a colorless solid: mp 120-125 ^{0}C; [α]D ^{25} = -149.0 (c = 0.2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.23 (17H, m), 7.12-7.09 (2H, m), 7.03-7.00 (2H, m), 6.94-6.82 (9H, m), 5.32-5.17 (2H, m), 5.07-5.05 (2H, m), 4.70-4.65 (2H, m), 4.21-4.17 (1H, dd, *J* = 8.3, 8.3 Hz), 4.10-4.08 (2H, m), 3.50-3.47 (2H, m), 2.29-2.23 (24H, m) 1.10 (3H, s), 0.35 ppm (3H, s); $_{13}$C NMR (100 MHz, $CDCl_3$) δ 165.51, 165.49, 149.3, 145.6, 145.2, 142.1, 142.0, 141.2, 137.4, 136.83, 136.76, 136.42, 136.35, 136.2, 133.68, 133.65, 130.9, 129.8, 129.5, 129.1, 129.0, 128.8, 128.70, 128.66, 127.8, 127.6, 127.5, 126.7, 126.4, 125.0, 124.9, 123.9, 121.7, 121.6, 112.9, 85.2 (d, J_{CP} = 8.8 Hz), 83.2, 82.6 (d, J_{CP} = 14.3 Hz), 81.2 (d, J_{CP} = 4.4 Hz), 75.4, 75.2, 69.65, 69.63, 41.3, 35.7, 27.3, 25.9, 21.63, 21.55, 21.52 (2C) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 136.4 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{71}H_{71}N_2O_7P$ [$(M+H)^+$], 1095.3064; found, 1095.5059 *m/z*.

^{R}Ad (569 mg, 80%) as a colorless solid: mp 123-127 ^{0}C; [α]D ^{25} = -141.0 (c = 0.2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.28 (23H, m), 7.24-7.23 (5H, m), 7.22-7.12 (2H, m), 7.06-7.03 (2H, m), 6.97-6.94 (2H, m), 6.67-6.63 (1H, m), 5.25-5.13 (2H, m), 4.69-4.64 (2H, m), 4.25-4.10 (3H, m), 3.60-3.47 (2H, m), 1.40 (18H, s), 1.33 (18H, s), 1.06 (3H, s), 0.45 ppm (3H,s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.97, 165.94, 157.13, 150.01, 149.79, 143.37, 142.32, 141.66, 141.58, 141.49, 139.73, 137.90, 129.61, 128.93, 128.80, 128.74, 128.39, 128.37, 128.03, 127.96, 127.76, 127.67, 127.43, 126.69, 126.64, 125.69, 124.93, 124.03, 118.59, 114.51, 109.27, 81.10, 75.67, 75.39, 69.27, 69.20, 41.28, 35.77, 34.48, 34.45, 31.49, 31.35, 27.05 ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 133.5 ppm; HRMS (ESI) calcd. for $C_{79}H_{83}N_2O_7P$ [$(M+Na)^+$], 1230.5085; found, 1230.7161 *m/z*

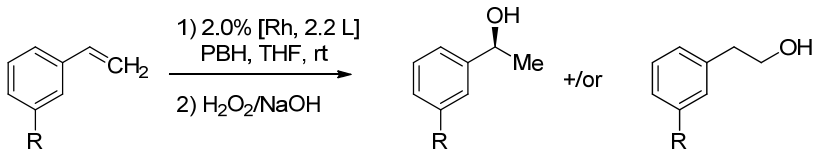
^{S}Ad (568 mg, 80%) as a colorless solid: mp 124-126 ^{0}C; [α]D ^{25} = -128.0 (c = 0.2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.52 (4H, m), 7.45-7.28 (20H, m), 7.26-7.22 (5H, m), 7.14-7.12 (1H, m), 7.07-7.04 (2H, m), 6.97-6.95 (2H, m), 5.25-5.22 (2H, m), 4.72-4.67 (2H, m), 4.27-4.22 (2H, m), 4.10 (1H, m), 3.63-3.62 (2H, m), 1.40 (18H, s), 1.34 (18H, s), 0.98 (3H, s), 0.53 ppm (3H,s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.99, 165.96, 157.15, 150.06, 149.81, 143.36, 142.32, 141.67, 141.61, 141.49, 139.69, 137.91, 129.61, 128.94, 128.82, 128.75, 128.40, 128.29, 128.02, 127.96, 127.78, 127.67, 127.38, 126.70, 126.65, 125.70, 124.96, 124.08, 118.58, 114.54, 114.51, 109.29, 81.27, 75.69, 75.41, 69.35, 69.23, 41.29. 35.79, 34.49, 34.46, 31.49, 31.36, 27.07 ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 133.6 ppm; HRMS (ESI) calcd. for calcd. for $C_{79}H_{83}N_2O_7P$ [$(M+Na)^+$], 1230.5085; found, 1230.7059 *m/z*



***f*. Preparation of Zn(^{S}Aa, ^{R}Aa).** Solutions of **^{S}Aa** (200 mg, 0.20 mmol) in DCM and **^{R}Aa** (200 mg, 0.20 mmol) in DCM were mixed and a solution of $ZnEt_2$ (25.9 mg, 0.20 mmol) in DCM was added. After the solution was stirred at room temperature (ca 5 mins), the solvent was evaporated and residue dried under vacuum (< 1 torr) to give **Zn(^{S}Aa, ^{S}Aa)** (398 mg, 99 %) as a white solid: mp 188-189 ^{0}C; [α]D ^{25} = -90.5 (c = 0.1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.42 (16H, m), 7.34-7.12 (52H, m), 7.03-6.98, (8H, m), 5.06 (4H, s), 4.02-3.98, (4H, m), 3.86-3.80 (4H, m), 3.76 (4H, s), 3.37-3.33 (4H, m), 0.99 (6H, s), 0.37 (3H, s), 0.35 ppm (3H, s);^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 149.0, 148.9, 145.7, 145.6, 145.3, 144.1, 143.7, 141.50, 141.45, 140.8, 140.7, 135.14, 135.05, 135.0, 134.9, 130.8, 129.3, 129.1, 128.81, 128.76, 128.4, 128.3, 127.8, 127.7, 127.6, 127.43, 127.39, 127.4, 127.3, 127.2, 127.1,, 127.0, 125.0, 124.2, 122.4, 122.2, 113.24, 113.1, 85.8, 85.7, 83.1, 83.0, 82.3, 82.1, 80.9, 80.8, 72.9, 65.6, 64.4, 64.3, 53.5, 31.1, 27.2, 25.79, 25.75; ^{31}P NMR (162 MHz, $CDCl_3$) δ 133.7, ppm; HRMS (FAB) calcd for $C_{126}H_{108}N_4O_{14}P_2Zn$ [$(M+H)^+$], 2026.6618; found: 2026.6674 *m/z*.

Zn(^{S}Ab, ^{R}Ac) (397 mg, 99%) as a white solid: mp 171-173 ^{0}C; [α]D ^{25} = -67.5 (c = 0.2, CH_2Cl_2); ^{1}H NMR (400 MHz, CDCl3) δ 7.47 – 6.91 (68H, m), 5.32 (1H, s), 5.04 – 4.99 (3H, m), 4.05 – 3.83 (4H, m), 3.86 – 3.80 (4H, m), 3.76 – 3.60 (4H, m), 3.38 – 3.33 (4H, m), 2.32 – 2.23 (36H, m), 1.13 (3H, s), 1.06 (3H, s), 0.39 (3H, s), 0.36 (3H, s) ^{13}C NMR (100MHz, $CDCl_3$) δ 169.9, 165.6, 149.5, 145.8, 145.3, 144.2, 143.9, 143.7, 143.2, 142.6, 142.1, 140.9, 138.8, 138.2, 137.5, 136.9, 136.5, 136.3, 135.2, 134.9, 134.8, 130.1, 129.8, 129.5, 129.4, 129.0, 128.8, 128.5, 128.1, 127.8, 127.6, 127.1, 126.9, 126.7, 126.5, 125.1, 125.0, 124.1, 112.7, 85.3, 85.1, 83.3, 83.0, 82.4, 81.7, 81.3, 75.4, 75.1, 72.9, 69.7, 65.7, 65.3, 64.7, 53.5, 41.3, 35.7,

31.3, 27.4, 27.3, 25.9, 25.8, 21.7, 21.4, 21.2, 20.9 ^{31}P NMR (162 MHz, $CDCl_3$) δ 135.5, 135.0; HRMS (ESI) calcd. for $C_{138}H_{132}N_4O_{14}P_2Zn$ $[(M+Li)^+]$, 2197.8508; found, 2197.8728 *m/z*.



General procedure employed for the preparative scales reactions reported in Table 2 illustrated for the preparation of 1-(3-methylphenyl) ethanol (4a). A solution of ^{S}**Ab** (21.6 mg, 19.6 x 10^{-3} mmol) and ^{R}**Ac** (20.4 mg, 19.6 x 10^{-3} mmol) in DCM (6 mL) was combined with a solution of $ZnEt_2$ (1.28mg, 19.6 x 10^{-3} mmol) in DCM (3mL) and stirred at ambient temperature (RT, ca. 5 min.) and then a solution of $Rh(nbd)_2BF_4$ (7.4 mg, 19.6 x 10^{-3} mmol) in DCM (2 mL) was added. The resulting mixture was stirred at ambient temperature (0.5 h) after which the volatile solvent was removed under vacuum. The residue was dissolved in THF (6 mL), stirred (0.5 h) and then 0.3mL aliquot of the solution was transferred into a 50 mL round bottom flask. 3-methylstyrene (132 mg, 0.98mmol) in THF (2.0mL) was added. The resulting mixture was cooled (0 ^{o}C) and a solution of pinacolborane (150.5 mg, 1.18 mmol) in THF (3.0 mL) added dropwise. The reaction mixture was gradually warmed to RT and stirred (12 h). The mixture was quenched by the addition of MeOH (10 mL), aq. NaOH (3.0 M, 15 mL), and aq. H_2O_2 (1 mL of a 30% solution) and stirred (1 h, RT). The solution was extracted with ethyl acetate (3 x 15 mL) and the combined organics were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude product was purified by chromatography on silica (10:90 ethyl acetate:hexane) to give 1-(3-methylphenyl) ethanol (124 mg, 93%) as a clear oil: Chiral GC analysis found peaks at 15.19 (2.8%, (R)) and 15.74 (97.2%, (S)); [α]D ^{25} = -65.3 (c = 1.00, $CHCl_3$) (lit.[5] [α]D ^{25} = -42.6 (84% ee (S), (c = 1.04, $CHCl_3$)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (1H, t, J = 7.6 Hz), 7.26 (1H, s), 7.22 (1H, dd, J = 9.6, 4.1 Hz), 7.13 (1H, d, J =

7.6 Hz), 4.89-4.84 (1H, q, J = 12.8, 6.4 Hz), 2.40 (3H, s) 1.51 ppm (3H, d, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) 145.9, 138.1, 128.4, 128.2, 126.2, 122.5, 70.4, 25.2, 21.5 ppm; HRMS (FAB) calcd for $C_9H_{12}O$ [$(M+H)^+$], 136.0888; found: 136.0886 m/z.

(*S*)-1-(3-methoxyphenyl) ethanol (4b). The title compound was prepared via the general procedure: The crude product was purified by chromatography on silica (10% EtOAc/Hex) to give 1-(3-methoxyphenyl)ethanol (135 mg, 90%) as a clear oil: chiral capillary GC analysis found peaks at 24.15 (2.5%, (*R*)) and 24.53 (97.5%, (*S*)); [α]D ^{25} = -40.4 (c = 1.1, $CHCl_3$) (lit.[4] [α]D ^{25} = +39.0 (96% ee (*R*), (c = 1.0, $CHCl_3$)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (1H, t, *J* = 8.0 Hz), 6.96-6.95 (2H, m), 6.84-6.82 (1H, dd, *J* = 7.7, 2.4 Hz), 4.89-4.84 (1H, q, *J* = 12.8, 6.4 Hz), 3.82 (3H, s) 1.49 ppm (3H, d, *J* = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) 159.7, 147.6, 129.5, 117.7, 112.9, 110.9, 70.3, 55.2, 25.1 ppm; HRMS (FAB) calcd for $C_9H_{12}O_2$ [$(M+H)^+$], 152.0837; found: 152.0835 *m/z*.

(S)-1-(3-chlorophenyl) ethanol (4c). The title compound was prepared via the general procedure. The crude product was purified by chromatography on silica (10% EtOAc/Hex) to give 1-(3-chlorophenyl)ethanol (134 mg, 89%) as a clear oil: chiral capillary GC analysis found peaks at 23.73 (1.8%, (R)) and 23.99 (98.2%, (S)) ; [α]D ^{25} = -50.3 (c = 1.20, MeOH) (lit.[6] [α]D ^{22} = +41.2 (94% ee (R), (c = 1.01, MeOH)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (1H, s), 7.30-7.21 (3H, m), 4.87-4.82 (1H, q, J = 12.8, 6.4 Hz), 1.46 ppm (3H, d, J = 6.4 Hz); $_{13}$C NMR (100 MHz, $CDCl_3$) 147.9, 134.2, 129.8, 127.5, 125.6, 123.6, 69.8, 25.2 ppm; HRMS (FAB) calcd for C_8H_9ClO [$(M+H)^+$], 156.0342; found: 156.10338 m/z.

(*S*)-1-(3-fluorophenyl) ethanol (4d). The title compound was prepared via the general procedure. The crude product was purified by chromatography on silica (10% EtOAc/Hex) to give 1-(3-fluorophenyl)ethanol (123 mg, 89%) as a clear oil: chiral capillary GC analysis found peaks at 13.23 (2.2%, (*R*)) and 13.52 (97.8%, (*S*));

[α]D ^{25} = -39.8 (c = 1.80, $CHCl_3$) (lit.[7] [α]D ^{25} = +36 (94% ee (*R*), (c = 1.80, $CHCl_3$)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (1H, dt, *J* = 8.0, 2.1 Hz), 7.13-7.07 (2H, m), 6.99-6.94 (1H, dt, *J* = 9.2, 3.6 Hz), 4.86 (1H, q, *J* = 12.8, 6.4 Hz), 1.48 ppm (3H, d, *J* = 6.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0 (d, J_{CF} = 245.5 Hz), 148.5 (d, J_{CF} = 7.0 Hz), 130.0 (t, J_{CF} = 14.1 Hz), 121.0 (d, J_{CF} = 2.0 Hz), 114.2 (d, J_{CF} = 21.1 Hz), 112.3 (d, J_{CF} = 22.1 Hz), 69.7 (d, J_{CF} = 2.0 Hz), 25.2 ppm; HRMS (FAB) calcd for C_8H_9FO [$(M+H)^+$], 140.0639; found: 140.0639 *m/z*.

(*S*)-1-(3-trifluoromethylphenyl) ethanol (4e). The title compound was prepared via the general procedure. The crude product was purified by chromatography on silica (10% EtOAc/Hex) to give 1-(3-trifluoromethylphenyl) ethanol (163 mg, 87%) as a clear oil: chiral capillary GC analysis found peaks at 13.34 (1.3%, (*R*)) and 13.59 (98.7%, (*S*)); [α]D ^{25} = -39.1 (c = 0.9, $CHCl_3$) (lit.[7] [α]D^{25} = +33.9 (91% ee (*R*), (c = 0.80, $CHCl_3$)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (1H, s), 7.55-7.53 (2H, m), 7.47 (1H, d, *J* = 7.7 Hz), 4.93 (1H, q, *J* = 12.8, 6.4 Hz), 2.37 (3H, s) 1.49 ppm (3H, d, *J* = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 130.7 (q, J_{CF} = 32.2 Hz), 128.9, 128.8, 124.2 (t, J_{CF} = 4.0 Hz), 125.5 (d, J_{CF} = 271.7 Hz), 122.2 (q, J_{CF} = 4.0 Hz), 69.8, 25.3 ppm; HRMS (FAB) calcd for $C_9H_9F_3O$ [$(M+H)^+$], 190.0606; found: 190.0599 *m/z*.

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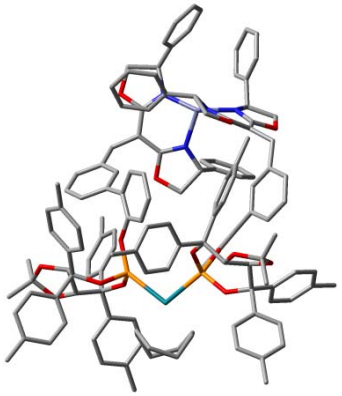
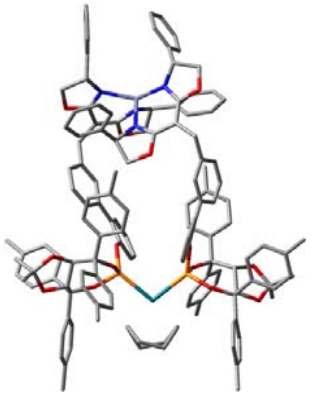
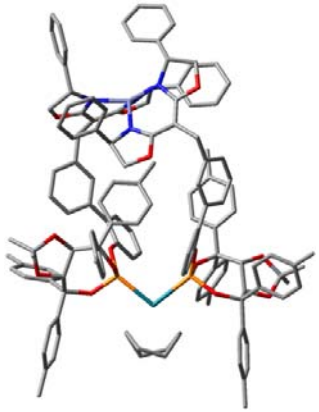
[7] S.T. Pickard and H.E. Smith, J. Am. Chem. Soc. 1990, 112, 5741.

[7] P.N. Liu, P.M. Gu, F. Wang, and Y.Q. Tu. Org. Lett., 2004, 6, 169.

Computational Details. The geometries of stationary points were optimized by using the B3LYP density functional methods (DFT), coupled with the 6-31G basis set for non-metal atoms and lanl2dz for metal atoms. All calculations were carried out by using the Gaussian 03 (revision D.01) program[8].

Possible conformers. Three possible conformers of the *cis*-[(Zn(^{S}Bc,^{R}Bc))Rh(cod)]$^{+}$ complex and relative energies were obtained by quantum chemical calculations, as shown in **Table S1**. It can be seen that conformer **a** is more stable than conformers **b** and **c**.

Table S1 Conformers and relative energies of [(Zn(^{S}Bc,^{R}Bc))Rh(cod)]$^{+}$, optimized at the B3LYP/6-31G level of theory

			
	conformer **a**	conformer **b**	conformer **c**
E[a]/Hartree	-7621.12788	-7621.11722	-7621.10835
ΔE[b]/(kcal/mol)	0.00	6.69	12.26

[a] E, total energy;

[b] ΔE, relative energy to that of conformer **a**.

Computational reference:

[8] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision D.01,Gaussian, Inc., Wallingford CT, **2004**.