Catalytic Asymmetric α-Iminol Rearrangement – New Chiral Platforms

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Supporting Information

Table of contents

1. General Information S-2
2. General Procedure for the Preparation of α-Hydroxy Aldehydes S-2
3. General Procedure for the Preparation of α-Iminols S-13
4. Procedure for the Preparation of Zr-VANOL Catalyst (R)-15 S-25
5. Procedures for the α-Iminol Rearrangement of Pre-formed Imines S-25
6. Procedure for the α-Iminol Rearrangement of in-situ Generated Imines S-45
7. Determination of the Absolute Stereochemistry of the Product 23a S-45
8. Synthesis of Amino Alcohols from Amino Ketones S-48
9. Crystal Structure of Zirconium Catalyst 28 S-52
10. Rearrangement of 22a with Crystals of Complex 28 S-86
11. Studies on the Stability of Catalyst 28 S-86
12. Studies on the Effect of Temperature on the α-Iminol Rearrangement of 22a S-87
13. Studies on the Effect of Solvent and Catalyst Composition on the α-Iminol Rearrangement of 22a S-88
14. References S-89
1. General information

Solvents for reactions were dried appropriately before use: toluene was dried by refluxing with sodium, THF was dried by refluxing with sodium and benzophenone as indicator. Both VAPOL and VANOL ligands are commercially available from Aldrich as well as Strem Chemicals (if desired, they could be purified using column chromatography on regular silica gel with 2:1 dichloromethane:hexanes, or recrystallized from 1:20 EtOAc:hexanes), or can be synthesized according to a literature procedure and was used as >99% ee material. All other reagents were directly used as purchased from either Aldrich or Alfa Aesar.

Melting points were measured on a Thomas Hoover capillary melting point apparatus. IR spectra were taken on a Galaxy series FTIR-3000 spectrometer. $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR were recorded on VXR-500 MHz instrument in CDCl$_3$. CDCl$_3$ was used as the internal standard for both $^1$H NMR ($\delta = 7.26$) and $^{13}$C NMR ($\delta = 77.0$). Thin-layer chromatography (TLC) was performed on silica gel plates with F-254 indicator. Visualization was by short wave (254 nm) and long wave (365 nm) ultraviolet light, or by staining with phosphomolybdic acid in ethanol. The silica gel for column chromatography was purchased from Sorbent Technologies with the following specifications: standard grade, 60 Å porosity, 230 X 400 mesh particle size, 500-600 m$^2$/g surface area and 0.4 g/mL bulk density. Chiral HPLC analysis was done using a Varian Prostar 210 Solvent Delivery Module with a Prostar 330 PDA Detector and a Prostar Workstation. Optical rotation was obtained on a Perkin-Elmer 341 polarimeter at a wavelength of 589 nm (Sodium D line) using a 1.0 decimeter cell with a total volume of 1.0 mL.

2. General Procedure for the Preparation of α-Hydroxyl Aldehydes (21).

\[
\begin{align*}
\text{Br–R} & \quad + \quad \text{Mg} \\
2.5 \text{ equiv} & \quad 2.5 \text{ equiv} \\
\text{1) THF, rt to 70 °C} & \quad \text{2) } 5\% \text{ HCl acetone} \\
\text{20 min} & \quad \text{70 °C, 1 h}
\end{align*}
\]

To a 50 mL clean and dry Schlenk flask was added Mg metal (40 mesh, 0.084 g, 3.5 mmol, 2.5 equiv), a small crystal of I$_2$ and 2 mL THF. While stirring, the appropriate aryl or alkyl bromide (3.5 mmol, 2.5 equiv) was added via a syringe (for solid bromides a solution was prepared by dissolving in a minimal
amount of THF). The flask was tightly sealed and the solution was stirred at room temperature for 10 min, then heated in a 70 °C oil bath until the Mg metal completely dissolved (usually it took less than 20 min). After being cooled down to room temperature, the flask was placed in a water bath and ethyl diethoxyacetate (0.25 mL in 2 mL THF, 1.4 mmol, 1 equiv.) was added dropwise and slowly via a syringe. The resulting mixture was stirred for another 30 min at room temperature then quenched with 5 mL saturated NH₄Cl solution. The two layers were separated and the aqueous layer was extracted with ether (5 mL x 3). The combined organic layer was concentrated under rotary evaporation and the crude residue was subjected to hydrolysis without purification.

The crude acetal intermediate was transferred to a 20 mL Schlenk flask with 0.5 mL 5% HCl (that is 1.7 M HCl) and enough acetone (usually it took 5 mL) to obtain a single layer homogenous solution. Thereafter, the flask was sealed and heated in a 70 °C oil bath for 1 h. After being cooled to room temperature, the solution was diluted with 10 mL CH₂Cl₂. The aqueous layer was separated and discarded; the organic layer was successively washed by NaHCO₃ solution and brine, dried over MgSO₄, filtered through filter paper in Büchner funnel and concentrated under rotary evaporation. The crude residue was purified by silica gel column chromatography with 20:1 hexanes:EtOAc as eluent.

2-hydroxy-2,2-diphenylacetaldehyde (21a)

Following the general procedure with a commercial 2M solution of phenylmagnesium chloride in THF (3.5 mL, 7.0 mmol, 2.5 equiv; 13.8 mL, 27.5 mmol and 50.0 mL, 100 mmol scale), the reaction afforded the product 21a as a white solid in 70-90% yield over several trials. mp = 55-57 °C (Lit¹b 52-55 °C). Spectral data for 21a: ¹H NMR (CDCl₃, 500 MHz) δ 4.41 (s, 1H), 7.38-7.42 (m, 10H), 10.00 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 83.45, 127.44, 128.51, 128.84, 139.29, 198.05; these NMR data are in agreement with the literature data.¹b
2-hydroxy-2,2-di-o-tolylacetaldehyde (21b).

Following the general procedure with 2-bromotoluene (0.42 mL, 3.5 mmol, 2.5 equiv), the reaction afforded the product 21b as a white wax-like solid (83%, 0.279 g, 1.16 mmol). mp = 46-49 °C. Spectral data for 21b: \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 2.08 (s, 6H), 4.36 (s, 1H), 7.17 (dd, \(J = 7.5, 1.5\) Hz, 2H), 7.21 (td, \(J = 7.5, 1.5\) Hz, 2H), 7.26 (td, \(J = 7.5, 1.5\) Hz, 2H), 7.30 (dd, \(J = 7.5, 1.5\) Hz, 2H), 10.09 (s, 1H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 21.30, 84.82, 126.33, 127.36, 128.53, 132.55, 137.13, 137.73, 197.99; IR (thin film) 3472s, 3063m, 3018m, 2930m, 2870m, 1716s, 1458s, 1336m, 1163m, 754s cm\(^{-1}\); HRMS (ESI-TOF) \(m/z\) found 223.1127 [(M-H\(_2\)O+H)\(^+\)]; calcd. 223.1123 for C\(_{16}\)H\(_{15}\)O.

2-hydroxy-2,2-bis(2-isopropylphenyl)acetaldehyde (21c).

The general procedure was followed with 1-bromo-2-isopropylbenzene (0.54 mL, 3.5 mmol, 2.5 equiv) and the Grignard reaction between the ester and 2-isopropylphenylmagnesium bromide was worked up and concentrated, the crude acetal was hydrolyzed with 0.5 g Amberlyst 15 ion-exchange resin (strongly acidic) in 10 mL 1:1 H\(_2\)O:acetone solution at room temperature for 24 h. The resulting mixture was neutralized with 10 mL saturated NaHCO\(_3\) and diluted with 20 mL CH\(_2\)Cl\(_2\). The aqueous layer was extracted with ether (10 mL x 3), the combined organic layer was washed with brine, dried over MgSO\(_4\), filtered through filter paper in Büchner funnel and concentrated under rotary evaporation. The crude product was purified by column chromatography with 20:1 hexanes:EtOAc as eluent. The product that was collected from the column was not pure by NMR, therefore it was washed with a small amount of hexanes. This afforded product 21c.
as a white solid (56%, 0.232 g, 0.784 mmol); mp = 119-121 °C. Spectral data for 21c: ¹H NMR (CDCl₃, 500 MHz) δ 1.01 (d, J = 7.0 Hz, 6H), 1.03 (d, J = 7.0 Hz, 6H), 3.15 (septet, J = 7.0 Hz, 2H), 4.46 (s, 1H), 7.19-7.23 (m, 3H), 7.34-7.40 (m, 5H), 10.22 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 24.08, 24.18, 29.84, 84.59, 125.96, 127.17, 127.92, 128.88, 137.51, 148.13, 198.98; IR (thin film) 3474br s, 3020m, 2966s, 2930s, 2868s, 1726s, 1483m, 1444m, 1153m, 1057m, 760s cm⁻¹; HRMS (ESI-TOF) m/z found 279.1749 [(M-H₂O+H)⁺]; calcd. 279.1749 for C₂₀H₂₃O.

2-hydroxy-2,2-di-m-tolylacetaldehyde (21d).

Following the general procedure with 3-bromotoluene (0.42 mL, 3.5 mmol, 2.5 equiv), the reaction afforded the product 21d as a white wax-like solid (77%, 0.261 g, 1.09 mmol). mp = 33-35 °C. Spectral data for 21d: ¹H NMR (CDCl₃, 500 MHz) δ 2.35 (s, 6H), 4.33 (s, 1H), 7.14-7.19 (m, 6H), 7.28 (t, J = 7.5 Hz, 2H), 9.96 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 21.51, 83.38, 124.51, 127.97, 128.62, 129.18, 138.62, 139.34, 198.18; IR (thin film) 3481br s, 3028m, 2922m, 2860m, 1722s, 1604m, 1487m, 1332m, 1155s, 702s cm⁻¹; HRMS (ESI-TOF) m/z found 223.1122 [(M-H₂O+H)⁺]; calcd. 223.1123 for C₁₆H₁₅O.

2,2-bis(3-chlorophenyl)-2-hydroxyacetaldehyde (21e).

The general procedure was followed with 1-bromo-3-chlorobenzene (0.50 mL, 4.1 mmol) with three exceptions: 1. The formation of the Grignard reaction was carried out in diethyl ether in a round bottom flask
with a condenser, 2. The hydrolysis of the acetal intermediate was carried out at 80 °C, and 3. The eluent was 8:1 hexane:EtOAc for the purification of the final product. This reaction afforded the product 21e (0.31 g, 1.1 mmol, 67%) as a wax-like white solid; mp = 42-43 °C. Spectral data for 21e: 1H NMR (CDCl3, 500 MHz) δ 4.44 (s, 1H), 7.23-7.27 (m, 2H), 7.34-7.39 (m, 6H), 9.95 (s, 1H); 13C NMR (CDCl3, 125 MHz) δ 82.55, 125.39, 127.46, 129.01, 130.20, 135.15, 140.80, 196.75; IR (thin film) 3456s, 1726s, 1653s, 1576m, 1473m, 1419m, 1180m, 1082m cm⁻¹; HRMS (ESI-TOF) m/z found 263.0024 [(M-H2O+H)+]; calcd. 263.0030 for C14H9OCl2.

2-hydroxy-2,2-di-p-tolylacetaldehyde (21f).

Following the general procedure with 4-bromotoluene (0.86 mL, 7.0 mmol, 2.5 equiv, the scale was doubled), this reaction afforded the product 21f as a colorless liquid (78%, 0.526 g, 2.18 mmol). Spectral data for 21f: 1H NMR (CDCl3, 500 MHz) δ 2.38 (s, 6H), 4.32 (s, 1H) 7.22 (d, J = 5.0 Hz, 4H), 7.25 (d, J = 5.0 Hz, 4H), 9.93 (s, 1H); 13C NMR (CDCl3, 125 MHz) δ 21.14, 83.21, 127.35, 129.48, 136.41, 138.32, 198.11; IR (neat) 3481br s, 3028m, 2922m, 1718s, 1510m, 1170m, 815m cm⁻¹; HRMS (ESI-TOF) m/z found 223.1121 [(M-H2O+H)+]; calcd. 223.1123 for C16H15O.

2,2-bis(4-n-butylphenyl)-2-hydroxyacetaldehyde (21g).

Following the general procedure with 1-bromo-4-n-butybenzene (0.62 mL, 3.5 mmol, 2.5 equiv), the reaction afforded the product 21g as a colorless liquid (73%, 0.332 g, 1.02 mmol). Spectral data for 21g: 1H
NMR (CDCl$_3$, 500 MHz) $\delta$ 0.92 (t, $J = 7.5$ Hz, 6H), 1.35 (sextet, $J = 7.5$ Hz, 4H), 1.59 (qt, $J = 7.5, 2.0$ Hz, 4H) 2.61 (t, $J = 7.5$ Hz, 4H), 4.29 (s, 1H), 7.20 (d, $J = 7.5$ Hz, 4H), 7.26 (d, $J = 7.5$ Hz, 4H), 9.93 (s, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 13.89, 22.32, 33.44, 35.26, 83.20, 127.31, 128.79, 136.57, 143.26, 198.10; IR (neat) 3487s, 3057s, 2930s, 2858s, 1718s, 1510s, 1414m, 1338m, 1170m, 831m cm$^{-1}$; HRMS (ESI-TOF) m/z found 307.2064 [(M-H$_2$O+H)$^+$]; calcd. 307.2062 for C$_{22}$H$_{27}$O.

2,2-bis(4-isopropylphenyl)-2-hydroxyacetaldehyde (21h).

Following the general procedure with 1-bromo-4-isopropylbenzene (0.53 mL, 3.5 mmol, 2.5 equiv), this reaction afforded the product 21h as a white solid (49%, 0.203 g, 0.686 mmol); mp = 80-81.5 °C. Spectral data for 21h: $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 1.25 (d, $J = 7.5$ Hz, 12H) 2.92 (septet, $J = 7.5$ Hz, 2H), 4.30 (s, 1H), 7.25 (d, $J = 7.5$ Hz, 4H), 7.29 (d, $J = 7.5$ Hz, 4H), 9.93 (s, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 23.86, 33.79, 83.19, 126.83, 127.39, 136.70, 149.14, 198.11; IR (thin film) 3406s, 3028m, 2961s, 2870s, 1718s, 1506m, 1458m, 1342m, 1178m, 825m cm$^{-1}$; HRMS (ESI-TOF) m/z found 279.1752 [(M-H$_2$O+H)$^+$]; calcd. 279.1749 for C$_{20}$H$_{23}$O.

2,2-bis(4-cyclohexylphenyl)-2-hydroxyacetaldehyde (21i).

Following the general procedure with 1-bromo-4-cyclohexylbenzene (0.65 mL, 3.5 mmol, 2.5 equiv), this reaction afforded the product 21i as a white solid (69%, 0.362 g, 0.966 mmol); mp = 155-156 °C. Spectral data for 21i: $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 1.22-1.28 (m, 2H), 1.34-1.44 (m, 8H), 1.73-1.76 (m, 2H), 1.82-1.87
(m, 8H), 2.48-2.53 (m, 2H), 4.29 (s, 1H), 7.22 (d, J = 7.0 Hz, 4H), 7.28 (d, J = 7.0 Hz, 4H), 9.92 (s, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz) δ 26.08, 26.81, 34.32, 44.22, 83.20, 127.20, 127.35, 136.65, 148.34, 198.11; IR (thin film) 3397s, 2920s, 2851s, 1720s, 1506m, 1448m, 1329m, 1170m cm$^{-1}$; HRMS (ESI-TOF) m/z found 359.2375 [(M-H$_2$O+H)$^+$]; calcd. 359.2375 for C$_{26}$H$_{31}$O).

2,2-bis(4-t-butylphenyl)-2-hydroxyacetaldehyde (21j).

Following the general procedure with 1-bromo-4-tert-butylbenzene (1.21 mL, 7.00 mmol, 2.5 equiv, the scale was doubled), the product was purified by recrystallization from hexanes to afford the product 21j as a white solid (61%, 0.555 g, 1.71 mmol); mp = 140-142 °C. Spectral data for 21j: $^1$H NMR (CDCl$_3$, 500 MHz) δ 1.32 (s, 18H), 4.30 (s, 1H), 7.30 (d, J = 8.5 Hz, 4H), 7.41 (d, J = 8.5 Hz, 4H), 9.94 (s, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz) δ 31.24, 34.57, 83.08, 125.69, 127.10, 136.28, 151.40, 198.11; IR (thin film) 3427br s, 2963s, 2868m, 1720s, 1506m, 1404m, 1109m, 823m cm$^{-1}$; HRMS (ESI-TOF) m/z found 307.2064 [(M-H$_2$O+H)$^+$]; calcd. 307.2062 for C$_{22}$H$_{27}$O).

2,2-di([1,1'-biphenyl]-4-yl)-2-hydroxyacetaldehyde (21k).

Following the general procedure with 4-bromobiphenyl (0.81g, 3.5 mmol, 2.5 equiv), the reaction afforded the product 21k as a white solid (77%, 0.393 g, 1.08 mmol); mp = 142-143 °C. Spectral data for 21k: $^1$H NMR (CDCl$_3$, 500 MHz) δ 4.44 (s, 1H), 7.37 (tt, J = 7.0, 1.5 Hz, 2H), 7.45 (tt, J = 8.0, 1.5 Hz, 4H), 7.49 (dt, J = 8.5, 2.0 Hz, 4H), 7.60 (dt, J = 8.5, 2.0 Hz, 4H), 7.65 (dt, J = 8.5, 2.0 Hz, 4H), 10.05 (s, 1H); $^{13}$C
NMR (CDCl$_3$, 125 MHz) $\delta$ 83.22, 127.12, 127.58, 127.62, 127.85, 138.18, 140.29, 141.48, 197.74; IR (thin film) 3596 br s, 3081 m, 3053 m, 3025 m, 1718 s, 1485 s, 1174 m, 1006 m, 827 m cm$^{-1}$; HRMS (ESI-TOF) $m/z$ found 347.1435 [(M-H$_2$O+H)$^+$]; calcd. 347.1436 for C$_{26}$H$_{19}$O.

2,2-bis(4-methoxyphenyl)-2-hydroxyacetaldehyde (21l). 

The general procedure was followed with 4-bromoanisole (0.44 mL, 3.5 mmol, 2.5 equiv) except the eluent for column chromatography was 3:1 to 2:1 hexanes:EtOAc. The reaction afforded the product 21l as a white solid (63%, 0.241 g, 0.882 mmol); mp = 90-91 °C. Spectral data for 21l: $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 3.81 (s, 6H), 4.26 (s, 1H), 6.91 (d, $J$ = 8.5 Hz, 4H), 7.27 (d, $J$ = 8.5 Hz, 4H), 9.88 (s, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 55.30, 82.79, 115.94 (d, $J$ = 21.8 Hz), 129.24 (d, $J$ = 8.5 Hz), 134.89, 162.73 (d, $J$ = 247.5 Hz), 197.23; $^{19}$F NMR (CDCl$_3$, 470 MHz) $\delta$ -112.79; IR (thin film) 3596 br s, 3081 m, 3053 m, 3025 m, 1718 s, 1485 s, 1174 m, 1006 m, 827 m cm$^{-1}$; HRMS (ESI-TOF) $m/z$ found 347.1435 [(M-H$_2$O+H)$^+$]; calcd. 347.1436 for C$_{26}$H$_{19}$O.

2,2-bis(4-fluorophenyl)-2-hydroxyacetaldehyde (21m). 

Following the general procedure with 1-bromo-4-fluorobenzene (0.39 mL, 3.5 mmol, 2.5 equiv), the reaction afforded the product 21m as a white wax-like solid (99%, 0.359 g, 1.39 mmol); mp = 24-25 °C. Spectral data for 21m: $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 4.40 (s, 1H), 7.11 (tt, $J$ = 9.0, 2.5 Hz, 4H), 7.34 (tt, $J$ = 9.0, 2.5 Hz, 4H), 9.93 (s, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 82.57, 115.94 (d, $J$ = 21.8 Hz), 129.24 (d, $J$ = 8.5 Hz), 134.89, 162.73 (d, $J$ = 247.5 Hz), 197.23; $^{19}$F NMR (CDCl$_3$, 470 MHz) $\delta$ -112.79; IR (thin film) 3596 br s, 3081 m, 3053 m, 3025 m, 1718 s, 1485 s, 1174 m, 1006 m, 827 m cm$^{-1}$; HRMS (ESI-TOF) $m/z$ found 347.1435 [(M-H$_2$O+H)$^+$]; calcd. 347.1436 for C$_{26}$H$_{19}$O.
2,2-bis(4-trifluoromethylphenyl)-2-hydroxyacetaldehyde (21n).

Th acetal intermediate of this substrate was synthesized via a different method: to a 100 mL clean and dry round bottom flask was added 10 mL THF and 1-bromo-4-(trifluoromethyl)benzene (0.49 mL, 3.5 mmol, 2.5 equiv). The flask was sealed by a septum with a N₂ balloon attached via a needle, and cooled to −78 °C in an acetone dry ice bath for 5 min. Then a solution of n-butyllithium (2.2 M in pentane, 1.60 mL, 3.5 mmol, 2.5 equiv) was added dropwise via a syringe. The resulting solution was stirred at −78 °C for another 10 min before addition of ethyl diethoxyacetate (0.30 mL in 2 mL THF, 1.68 mmol, 1.25 equiv). Thereafter, the solution was gradually warmed up to room temperature and allowed to stir for 30 min. It was then quenched with saturated NH₄Cl solution 10 mL. The two layers were separated and the aqueous layer was extracted with ether (5 mL x 3). The combined organic layer was concentrated under rotary evaporation and the crude residue was subjected to hydrolysis without purification. The hydrolysis followed the general procedure except that a 10% solution of HCl was used and the temperature was 80 °C. A mixture of 20:1 to 5:1 hexanes:EtOAc was employed as the eluent during column chromatography. The reaction afforded the product 21n as a white solid (53%, 0.31 g, 0.89 mmol); mp = 72-74 °C. Spectral data for 21n: ¹H NMR (CDCl₃, 500 MHz) δ 4.53 (s, 1H), 7.52 (d, J = 8.0 Hz, 4H), 7.70 (d, J = 8.0 Hz, 4H), 10.03 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 82.85, 123.71 (q, J = 270.8 Hz), 126.01 (q, J = 3.7 Hz), 127.68, 131.09 (q, J = 32.5 Hz), 142.62, 196.66; ¹⁹F NMR (CDCl₃, 470 MHz) δ −62.82; IR (thin film) 3395s, 1732s, 1329s, 1126s, 1070s, 833m cm⁻¹; HRMS (ESI-TOF) m/z found 331.0558 [(M-H₂O+H)⁺; calcd. 331.0558 for C₁₆H₉OF₆].
2,2-bis(4-acetylphenyl)-2-hydroxyacetaldehyde (21o).

Following the general procedure with 4-bromoacetophenone diethyl ketal (0.76 mL, 3.5 mmol, 2.5 equiv), the hydrolysis of all three acetals was carried out with 10% HCl at 80 °C for 1 h. A mixture of 4:1 to 2:1 hexanes:EtOAc was used as eluent for column chromatography. The reaction afforded the product 21o as a light yellow solid (55%, 0.228 g, 0.771 mmol); mp = 106-107 °C. Rf = 0.25 in 2:1 hexanes:EtOAc.

Spectral data for 21o: 1H NMR (CDCl3, 500 MHz) δ 2.59 (s, 6H), 4.59 (s, 1H), 7.47 (d, J = 8.5 Hz, 4H), 7.97 (d, J = 8.5 Hz, 4H), 10.02 (s, 1H); 13C NMR (CDCl3, 125 MHz) δ 26.70, 83.13, 127.47, 128.86, 137.12, 143.80, 196.92, 197.43; IR (thin film) 3443 br s, 3063w, 3005w, 2924w, 1732s, 1684s, 1603s, 1408s, 1359s, 1289s, 1190m, 1012m cm⁻¹; HRMS (ESI-TOF) m/z found 297.1134 [(M+H)+]; calcd. 297.1127 for C18H17O4.

2-hexyl-2-hydroxyoctanal (21p).

Following the general procedure with 1-bromohexane (0.49 mL, 3.5 mmol, 2.5 equiv), the reaction afforded the product 21p as a colorless liquid (71%, 0.227 g, 0.994 mmol). Spectral data for 21p: 1H NMR (CDCl3, 500 MHz) δ 0.86 (t, J = 7.0 Hz, 6H), 1.03-1.09 (m, 2H), 1.22-1.29 (m, 12H), 1.35-1.41 (m, 2H), 1.62-1.67 (m, 4H), 3.16 (s, 1H); 13C NMR (CDCl3, 125 MHz) δ 14.02. 22.50, 22.95, 29.55, 31.59, 36.25, 80.58, 204.69. IR (neat) 3516 br s, 2957s, 2930s, 2858s, 1732s, 1684s, 1603s, 1408s, 1359s, 1289s, 1190m, 1012m cm⁻¹. HRMS (ESI-TOF) m/z found 211.2051 [(M-H2O+H)+]; calcd. 211.2056 for C14H27O.
2-benzyl-2-hydroxy-3-phenylpropanal (21q).

Following the general procedure with commercial benzylmagnesium chloride (1M in ether, 7.0 mL, 7.0 mmol, 2.5 equiv, the scale was doubled), this reaction afforded the product 21q as a white solid (46%, 0.313 g, 1.29 mmol); mp = 66-70 °C. Spectral data for 21q: $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 3.00 (d, $J = 14.0$ Hz, 2H), 3.08 (s, 1H), 3.17 (d, $J = 14.0$ Hz, 2H), 7.19-7.21 (m, 4H), 7.26-7.32 (m, 6H), 9.66 (s, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 42.85, 80.86, 127.09, 128.40, 130.30, 134.75, 203.58; IR (thin film) 3493br s, 3086m, 3030s, 2928m, 1720s, 1641m, 1454s, 1109m, 814s, 752s, 700s cm$^{-1}$; HRMS (ESI-TOF) m/z found 223.1119 [(M-H$_2$O+H)$^+$]; calcd. 223.1123 for C$_{16}$H$_{15}$O.

2,2-dicyclohexyl-2-hydroxyacetaldehyde (21r)

Following the general procedure with commercial cyclohexylmagnesium chloride (2M in ether, 3.5 mL, 7.0 mmol, 2.5 equiv, the scale was doubled), this reaction afforded the product 21r as a white solid (57%, 0.359 g, 1.60 mmol); mp = 65-67 °C (lit. $^3$ 74.5 °C). Spectral data for 21r: $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 0.92 (qd, $J = 8.0$, 2.5 Hz, 2H), 1.06-1.15 (m, 2H), 1.17-1.25 (m, 6H), 1.52 (dd, $J = 6.0$, 2.5 Hz, 2H), 1.66 (d, $J = 12.5$ Hz, 2H), 1.75-1.86 (m, 8H), 3.21 (s, 1H), 9.58 (s, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 26.01, 26.27, 26.43, 26.59, 27.33, 40.36, 83.92, 206.61; IR (thin film) 3468 br s, 2930s, 2853s, 1720s, 1448s, 1329m, 1101m cm$^{-1}$; HRMS (ESI-TOF) m/z found 225.1852 [(M+H)$^+$]; calcd. 225.1855 for C$_{14}$H$_{25}$O$_2$. 
3. General Procedure for the Preparation of α-iminols.

To a 20 mL vial was added the appropriate α-hydroxyl aldehyde (0.3-0.5 mmol, 1 equiv), solid KHSO₄ (20 mol%), aniline (1.1 equiv) and toluene (1 mL). The vial was capped and the mixture was stirred at room temperature for 0.5 h. Upon completion, the reaction mixture was neutralized with 0.1 mL Et₃N and dried over MgSO₄, then it was filtered through a filter paper in Buchner funnel and concentrated under rotary evaporation. The crude solid iminols were purified by recrystallization from hexanes; crude oil iminols were purified by a short flash column chromatography, 10:1 hexanes:EtOAc as eluent.

1,1-diphenyl-2-(phenylimino)ethan-1-ol (22a).

Following the general procedure with 21a (0.5 mmol, 10 mmol and 40 mmol scale), the reaction afforded 78-100% yield of the product 22a as a white solid over several trials; mp = 86-88 °C. Spectral data for 22a: ¹H NMR (CDCl₃, 500 MHz) δ 5.74 (br s, 1H), 7.17 (d, J = 7.5 Hz, 2H), 7.25 (t, J = 7.0 Hz, 2H), 7.32 (tt, J = 7.5, 1.0 Hz, 2H), 7.35-7.39 (m, 5H), 7.44 (d, J = 7.0 Hz, 4H), 8.47 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 78.76, 121.17, 126.81, 127.19, 127.78, 128.52, 129.21, 143.23, 148.58, 164.92; IR (thin film) 3399s, 3059s, 3028s, 1647s, 1595s, 1487s, 1448s, 1385m, 1325m, 1170m cm⁻¹; HRMS (ESI-TOF) m/z found 270.1270 [(M-H₂O+H)⁺]; calcd. 270.1277 for C₂₀H₁₈N].
2-(phenylimino)-1,1-di-o-tolylethan-1-ol (22b).

Following the general procedure with 21b (0.117 g, 0.487 mmol), the reaction afforded the product 22b as a colorless liquid (88%, 0.135 g, 0.428 mmol). Spectral data for 22b: $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 2.12 (s, 6H), 5.78 (br s, 1H), 7.15-7.27 (m, 9H), 7.36-7.42 (m, 4H), 8.51 (s, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 21.47, 80.33, 115.15, 121.12, 126.01, 126.72, 127.12, 127.86, 129.23, 132.43, 136.90, 141.24, 164.43; IR (neat) 3395br s, 3061s, 3018s, 2964s, 2928s, 1693s, 1645s, 1611s, 1502s, 1487s, 1460s, 1381s, 1325s, 1161m, 998m, 970m, 868m cm$^{-1}$; HRMS (ESI-TOF) m/z found 298.1596 [(M-H$_2$O+H)$^+$; calcd. 298.1596 for C$_{22}$H$_{20}$N].

1,1-bis(2-isopropylphenyl)-2-(phenylimino)ethan-1-ol (22c).

Following the general procedure with 21c (0.101 g, 0.343 mmol), the formation of imine 22c was not complete after 19 h even in the presence of 0.30 g 4Å molecular sieves. The crude residue was a 1:3.2 mixture of aldehyde:imine as judged from the $^1$H NMR spectrum (δ 10.19 for the aldehyde and δ 8.59 for the imine). This crude imine was taken directly on to the next step.
2-(phenylimino)-1,1-di-m-tolylethan-1-ol (22d).

```
\[
\begin{align*}
\text{O} & \quad \text{H} & \quad \text{H} \\
\text{Ph} & \quad \text{CH}_3 & & & \quad \text{NH}_2 \\
\text{H} & \quad \text{H} & \quad \text{H}
\end{align*}
\]
\text{21d} + 20 \text{ mol\% KHSO}_4
\text{toluene, rt, 0.5 h}
\text{22d}
```

Following the general procedure with 21d (0.129 g, 0.533 mmol), the reaction afforded the product 22d as a colorless liquid (84\%, 0.142 g, 0.448 mmol). Spectral data for 22d: $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 2.36 (s, 6H), 5.71 (br s, 1H), 7.13-7.22 (m, 6H), 7.25-7.28 (m, 5H), 7.38 (t, $J = 8.0$ Hz, 2H), 8.47 (s, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 21.61, 78.69, 115.13, 121.20, 124.24, 126.74, 127.75, 128.31, 128.49, 129.19, 138.24, 143.27, 165.11; IR (neat) 3381br s, 3032s, 2920s, 1647s, 1603s, 1498s, 1487s, 1153m, 1026w, 873m cm$^{-1}$; HRMS (ESI-TOF) $m/z$ found 298.1583 [(M+H)$^+$; calcd. 298.1596 for C$_{22}$H$_{22}$NO].

1,1-bis(3-chlorophenyl)-2-(phenylimino)ethan-1-ol (22e).

```
\[
\begin{align*}
\text{O} & \quad \text{H} & \quad \text{Cl} & \quad \text{Cl} \\
\text{Ph} & \quad & & \\
\text{H} & \quad \text{H} & \quad \text{H}
\end{align*}
\]
\text{21e} + \text{KHSO}_4
\text{toluene, rt, 30 min}
\text{22e}
```

Following the general procedure with 21e (0.10 g, 0.35 mmol), this reaction afforded the product 22e (0.12g, 0.35 mmol, 100\%) as a colorless oil. Spectral data for 22e: $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 5.80 (s, 1H), 7.17 (dd, $J = 8.5$, 1.0 Hz, 2H), 7.27-7.36 (m, 7H), 7.39 (t, $J = 8.0$ Hz, 2H), 7.44-7.45 (m, 2H), 8.41 (s, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 78.04, 121.19, 125.21, 127.23, 127.26, 128.25, 129.31, 129.89, 134.72, 144.76, 147.88, 163.09; IR (thin film) 3409s, 1660s, 1448s, 1330m, 1190m, 1050m cm$^{-1}$; HRMS (ESI-TOF) $m/z$ found 356.0611 [(M+H)$^+$; calcd. 356.0609 for C$_{20}$H$_{15}$ONCl$_2$].
2-(phenylimino)-1,1-di-p-tolylethan-1-ol (22f).

Following the general procedure with 21f (0.087 g, 0.36 mmol), the reaction afforded the product 22f as a white solid (93%, 0.106 g, 0.334 mmol); mp = 116-119 °C. Spectral data for 22f: \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 2.36 (s, 6H), 5.66 (br s, 1H), 7.15-7.19 (m, 5H), 7.25-7.26 (m, 2H), 7.33 (d, \(J = 8.0\) Hz, 4H), 7.37 (t, \(J = 7.5\) Hz, 2H), 8.42 (s, 1H); \(^1^3\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 21.10, 78.49, 121.14, 126.65, 127.09, 129.16, 137.43, 140.42, 148.76, 165.20 (1 aromatic carbon was not located); IR (thin film) 3402br s, 3026s, 2922s, 1647s, 1595s, 1510s, 1487s, 1452m, 1410m, 1379m, 1327m, 1167s, 985s cm\(^{-1}\); HRMS (ESI-TOF) \(m/z\) found 298.1592 [(M-H\(_2\)O+H)\(^+\)]; calcd. 298.1596 for C\(_{22}\)H\(_{20}\)NO.

\[\text{N} \quad \text{H} \quad \text{HO} \quad \text{Ph} \quad 22f \quad \text{CH}_3 \quad \text{CH}_3\]

1,1-bis(4-butylphenyl)-2-(phenylimino)ethan-1-ol (22g).

Following the general procedure with 21g (0.114 g, 0.350 mmol), this reaction afforded the product 22g as a white solid (93%, 0.130 g, 0.325 mmol); mp = 75-77 °C. Spectral data for 22g: \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 0.94 (t, \(J = 7.5\) Hz, 6H), 1.37 (sextet, \(J = 7.5\) Hz, 4H), 1.61 (qt, \(J = 7.5, 2.5\) Hz, 4H), 2.62 (d, \(J = 7.5\) Hz, 4H), 5.68 (br s, 1H), 7.17-7.27 (m, 7H), 7.34-7.39 (m, 6H), 8.44 (s, 1H); \(^1^3\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 13.97, 22.39, 33.56, 35.29, 78.49, 121.18, 126.65, 127.06, 128.50, 129.16, 140.53, 142.42, 148.76, 165.27; IR (thin film) 3402s, 3024m, 2957s, 2930s, 2858s, 1647s, 1595m, 1508s, 1415m, 1167s, 981m cm\(^{-1}\); HRMS (ESI-TOF) \(m/z\) found 400.2638 [(M+H)\(^+\)]; calcd. 400.2640 for C\(_{28}\)H\(_{34}\)NO.
1,1-bis(4-isopropylphenyl)-2-(phenylimino)ethan-1-ol (22h).

Following the general procedure with 21h (0.106 g, 0.355 mmol), this reaction afforded the product 22h as a white solid (95%, 0.125 g, 0.337 mmol); mp = 138-139 °C. Spectral data for 22h: \( ^1H \) NMR (CDCl₃, 500 MHz) \( \delta \) 1.26 (d, \( J = 7.0 \) Hz, 12H), 2.92 (septet, \( J = 7.0 \) Hz, 2H), 5.68 (br s, 1H), 7.16-7.18 (m, 2H), 7.23-7.25 (m, 4H), 7.26-7.27 (m, 2H), 7.36-7.39 (m, 5H), 8.44 (s, 1H); \( ^13C \) NMR (CDCl₃, 125 MHz) \( \delta \) 23.95, 33.78, 78.44, 121.18, 126.52, 126.64, 127.11, 129.16, 140.66, 148.28, 148.77, 165.29; IR (thin film) 3412 br s, 2961s, 2870w, 1647s, 1484m, 1172m cm⁻¹; HRMS (ESI-TOF) \( m/z \) found 354.2220 \([\text{M-H}_2\text{O}+\text{H}]^+\); calcd. 354.2222 for C₂₆H₂₈N.

1,1-bis(4-cyclohexylphenyl)-2-(phenylimino)ethan-1-ol (22i).

Following the general procedure with 21i (0.105 g, 0.278 mmol), the reaction afforded the product 22i as a white solid (93%, 0.117 g, 0.259 mmol); mp = 153-155 °C. Spectral data for 22i: \( ^1H \) NMR (CDCl₃, 500 MHz) \( \delta \) 1.22-1.30 (m, 2H), 1.35-1.46 (m, 8H), 1.75 (dt, \( J = 12.5, 1.0 \) Hz, 2H), 1.84-1.89 (m, 8H), 2.48-2.53 (m, 2H), 5.68 (s, 1H), 7.16-7.18 (m, 2H), 7.21 (d, \( J = 8.0 \) Hz, 4H), 7.25 (tt, \( J = 7.5, 1.0 \) Hz, 2H), 7.35-7.39 (m, 5H), 8.44 (s, 1H); \( ^13C \) NMR (CDCl₃, 125 MHz) \( \delta \) 26.14, 26.88, 34.39, 44.21, 78.46, 121.20, 126.63, 126.90, 127.08, 129.15, 140.63, 147.51, 148.77, 165.30; IR (thin film) 3375 br s, 3032 w, 2924 s, 2851 s, 1603 s, 1498 m, 1448 m, 1278 m, 1172 m cm⁻¹; HRMS (ESI-TOF) \( m/z \) found 452.2957 \([\text{M+H}]^+\); calcd. 452.2953 for C₃₂H₃₈NO.
1,1-bis(4-t-butylphenyl)-2-(phenylimino)ethan-1-ol (22j).

Following the general procedure with 21j (0.137 g, 0.422 mmol), this reaction afforded the product 22j as a white solid (98%, 0.165 g, 0.414 mmol); mp = 137-140 °C. Spectral data for 22j: \(^1H\) NMR (CDCl\(_3\), 500 MHz) \(\delta\) 1.33 (s, 18H), 5.69 (br s, 1H), 7.18 (d, \(J = 7.5\) Hz, 2H), 7.24-7.27 (m, 2H), 7.36-7.41 (m, 9H), 8.46 (s, 1H); \(^{13}C\) NMR (CDCl\(_3\), 125 MHz) \(\delta\) 31.32, 34.53, 78.32, 121.19, 125.38, 126.63, 126.83, 129.16, 140.22, 148.78, 150.52, 150.78, 164.29; IR (thin film) 3402br s, 3032m, 2963s, 2905m, 1647s, 1597s, 1506s, 1404m, 1363s, 1269m, 1109s, 831m cm\(^{-1}\); HRMS (ESI-TOF) \(m/z\) found 382.2534 [(M-H\_2O+H)\(^+\)]; calcd. 382.2535 for C\(_{28}\)H\(_{32}\)N.

1,1-di([1,1'-biphenyl]-4-yl)-2-(phenylimino)ethan-1-ol (22k).

Following the general procedure with 21k (0.131 g, 0.360 mmol), the reaction afforded the product 22k as a white solid (95%, 0.150 g, 0.342 mmol); mp = 183-185 °C. Spectral data for 22k: \(^1H\) NMR (CDCl\(_3\), 500 MHz) \(\delta\) 5.82 (s, 1H), 7.22 (dt, \(J = 7.5, 1.0\) Hz, 2H), 7.28 (tt, \(J = 7.5, 1.0\) Hz, 2H), 7.35-7.42 (m, 4H), 7.46 (t, \(J = 7.5\) Hz, 4H), 7.57 (dt, \(J = 7.5, 1.0\) Hz, 4H), 7.61-7.65 (m, 7H), 8.55 (s, 1H); \(^{13}C\) NMR (CDCl\(_3\), 125 MHz) \(\delta\) 78.56, 121.21, 126.89, 127.14, 127.32, 127.44, 127.62, 128.80, 129.25, 140.60, 140.74, 142.17, 148.55, 164.61; IR (thin film) 3402br s, 1645s, 1485s, 1174m cm\(^{-1}\); HRMS (ESI-TOF) \(m/z\) found 440.2026 [(M+H)\(^+\)]; calcd. 440.2014 for C\(_{32}\)H\(_{26}\)NO.
1,1-bis(4-methoxylphenyl)-2-(phenylimino)ethan-1-ol (22l)

Following the general procedure with 21l (0.086 g, 0.308 mmol), the reaction afforded the product 22l as a white solid (97%, 0.104 g, 0.300 mmol); mp = 90-94 °C. Spectral data for 22l: ¹H NMR (CDCl₃, 500 MHz) δ 3.82 (s, 6H), 5.67 (br s, 1H), 6.92 (dt, J = 9.0, 3.0 Hz, 4H), 7.16-7.18 (m, 3H), 7.25-7.27 (m, 1H), 7.35-7.39 (m, 5H), 8.39 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 55.32, 78.15, 113.83, 115.12, 121.14, 126.67, 128.46, 129.20, 135.46, 159.07, 165.12; IR (thin film) 3385br s, 3034m, 3003m, 2934m, 1647s, 1606s, 1508s, 1302m, 1251s, 1172s, 1033s cm⁻¹; HRMS (ESI-TOF) m/z found 330.1492 [(M-H₂O+H)⁺]; calcd. 330.1494 for C₂₂H₂₀NO₂.

1,1-bis(4-fluorophenyl)-2-(phenylimino)ethan-1-ol (22m)

Following the general procedure with 21m (0.084 g, 0.36 mmol), this reaction afforded the product 22m as a colorless liquid (95%, 0.106 g, 0.346 mmol), which was purified by flash column chromatography on silica gel with a 10:1 mixture of hexanes:EtOAc. Spectral data for 22m: ¹H NMR (CDCl₃, 500 MHz) δ 5.78 (br s, 1H), 7.08 (tt, J = 9.0, 2.5 Hz, 4H), 7.16-7.20 (m, 3H), 7.26-7.30 (m, 1H), 7.38-7.42 (m, 5H), 8.40 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 78.00, 115.14, 115.48 (d, J = 20.9 Hz), 118.62, 121.17, 128.93 (d, J = 8.0 Hz), 129.29, 138.85 (d, J = 2.9 Hz), 162.32 (d, J = 245.6 Hz), 164.06; ¹⁹F NMR (CDCl₃, 470 MHz) δ –114.25; IR (neat) 3381br s, 3078s, 3029s, 1649s, 1603s, 1506s, 1224s, 1159s, 1091m, 1014m cm⁻¹; HRMS (ESI-TOF) m/z found 306.1090 [(M-H₂O+H)⁺]; calcd. 306.1094 for C₂₀H₁₄NF₂.
1,1-bis(4-trifluoromethylphenyl)-2-(phenylimino)ethan-1-ol (22n).

Following the general procedure with 21n (0.121 g, 0.349 mmol), the reaction afforded the product 22n as a white solid (90%, 0.133 g, 0.314 mmol); mp = 95-100 °C. Spectral data for 22n: \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 5.89 (br s, 1H), 7.18 (d, \(J = 8.5\) Hz, 2H), 7.29 (t, \(J = 8.5\) Hz, 1H), 7.40 (t, \(J = 8.5\) Hz, 2H), 7.56 (d, \(J = 8.5\) Hz, 4H), 7.66 (d, \(J = 8.5\) Hz, 4H), 8.47 (s, 1H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 78.30, 121.13, 123.89 (q, \(J = 270.0\) Hz), 125.69 (q, \(J = 3.7\) Hz), 126.66, 127.43, 129.38, 130.34 (q, \(J = 32.7\) Hz), 146.53, 147.76, 162.81; \(^{19}\)F NMR (CDCl\(_3\), 470 MHz) \(\delta\) –62.65; IR (thin film) 3391br s, 1653s, 1616s, 1489m, 1414s, 1325s, 1167s, 1126s, 1068s, 1018m, 841m cm\(^{-1}\); HRMS (ESI-TOF) \(m/\ell\) found 406.1040 [(M-H\(_2\)O+H)\(^+\)]; calcd. 406.1030 for C\(_{22}\)H\(_{14}\)NF\(_6\).

1,1'-((1-hydroxy-2-(phenylimino)ethane-1,1-diyl)bis(4,1-phenylene))bis(ethan-1-one) (22o).

Following the general procedure with 21o (0.0455 g, 0.154 mmol), the crude product was purified by flash column chromatography on silica gel with 10:1 CH\(_2\)Cl\(_2\):EtOAc as eluent. This reaction afforded the product 22o as a light yellow solid (88%, 0.0502 g, 0.136 mmol); mp = 168-169 °C. Spectral data for 22o: \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 2.62 (s, 6H), 5.88 (s, 1H), 7.18 (d, \(J = 8.5\) Hz, 2H), 7.30 (t, \(J = 8.5\) Hz, 1H), 7.40 (t, \(J = 8.5\) Hz, 2H), 7.55 (d, \(J = 8.5\) Hz, 4H), 7.99 (d, \(J = 8.5\) Hz, 4H), 8.50 (s, 1H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 26.72, 78.57, 121.15, 127.25, 127.33, 128.69, 129.35, 136.65, 147.75, 147.92, 163.00, 197.56; IR (thin film)
3387 br s, 1684s, 1603m, 1408m, 1267s cm⁻¹; HRMS (ESI-TOF) m/z found 372.1595 [(M+H)⁺; calcd. 372.1600 for C₂₄H₂₂NO₃].

7-((phenylimino)methyl)tridecan-7-ol (22p).

Following the general procedure with 21p (0.104 g, 0.458 mmol), this reaction afforded the product 22p as a colorless liquid (88%, 0.122 g, 0.402 mmol), which was purified by flash column chromatography on silica gel with a 10:1 mixture of hexanes:EtOAc. Spectral data for 22p: ¹H NMR (CDCl₃, 500 MHz) δ 0.87 (t, J = 7.5 Hz, 6H), 1.14-1.31 (m, 14H), 1.43-1.51 (m, 2H), 1.63 (td, J = 7.5, 5.0 Hz, 2H), 1.71 (td, J = 7.5, 5.0 Hz, 2H), 4.23 (br s, 1H), 7.08 (d, J = 7.5 Hz, 2H), 7.23 (t, J = 7.5 Hz, 1H), 7.36 (t, J = 7.5 Hz, 2H), 7.79 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 14.08, 22.60, 23.30, 29.76, 31.78, 39.07, 75.60, 120.77, 126.14, 129.12, 149.81, 168.47; IR (thin film) 3458br s, 3030w, 2930s, 2858s, 1653s, 1595s, 1489m, 1466m, 1396m, 1136m, 1072m, 868m cm⁻¹; HRMS (ESI-TOF) m/z found 286.2542 [(M-H₂O+H)⁺; calcd. 286.2535 for C₂₀H₃₂N].

2-benzyl-1-phenyl-3-(phenylimino)propan-2-ol (22q).

Following the general procedure with 21q (0.147 g, 0.606 mmol), the reaction afforded the product 22q as a light yellow oil (100%, 0.191 g, 0.606 mmol), which was purified by flash column chromatography on silica gel with a 10:1 mixture of hexanes:EtOAc. Spectral data for 22q: ¹H NMR (CDCl₃, 500 MHz) δ 3.13 (s, 4H), 4.15 (br s, 1H), 7.16-7.34 (m, 15H), 7.82 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 45.61, 76.03, 120.26, 125.78, 126.65, 128.04, 128.94, 130.58, 136.13, 150.15, 167.19; IR (neat) 3412 br s, 2063m, 3028s, 2920m,
1657m, 1599s, 1254s, 1086m, 1032m cm\(^{-1}\); HRMS (ESI-TOF) \(m/z\) found 316.1703 [(M+H)\(^+\)]; calcd. 316.1701 for C\(_{22}\)H\(_{22}\)NO].

1,1-dicyclohexyl-2-(phenylimino)ethan-1-ol (22r).

Following the general procedure with 21r (0.198 g, 0.882 mmol), the reaction afforded the product 22r as a white solid (88%, 0.246 g, 0.776 mmol); mp = 84-86 °C. Spectral data for 22r: \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 0.97-1.27 (m, 11H), 1.58-1.93 (m, 11H), 4.22 (br s, 1H), 7.07 (d, \(J = 8.0\) Hz, 2H), 7.21-7.25 (m, 1H), 7.36 (t, \(J = 8.0\) Hz, 2H), 7.83 (s, 1H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 26.38, 26.51, 26.61, 26.76, 27.52, 41.94, 78.92, 120.73, 126.04, 129.12, 150.07, 168.69; IR (thin film) 3447br s, 2928s, 2853s, 1651s, 1597m, 1487m, 1448m, 1425m, 1099m, 1074m cm\(^{-1}\); HRMS (ESI-TOF) \(m/z\) found 300.2338 [(M-H\(_2\)O+H)\(^+\)]; calcd. 300.2327 for C\(_{20}\)H\(_{30}\)NO].

2-((4-methoxyphenyl)imino)-1,1-diphenylethan-1-ol (22s).

Following the general procedure with 21a (0.961 g, 4.52 mmol) and 4-anisidine (0.607 g, 4.93 mmol, 1.1 equiv.), this reaction afforded the product 22s as a white solid (99%, 1.42 g, 4.48 mmol); mp = 77-79 °C. Spectral data for 22s: \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 3.82 (s, 3H), 5.85 (br s, 1H), 6.91 (dt, \(J = 9.0, 2.0\) Hz, 2H), 7.20 (dt, \(J = 9.0, 2.0\) Hz, 2H), 7.32 (tt, \(J = 7.5, 1.5\) Hz, 2H), 7.38 (tt, \(J = 7.5, 1.5\) Hz, 4H), 7.44 (dt, \(J = 7.0, 1.5\) Hz, 4H), 8.47 (s, 1H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 55.52, 78.62, 114.35, 122.63, 127.18, 127.68, 128.64,
141.13, 143.49, 158.81, 162.42; IR (thin film) 3385 br s, 3059 s, 3026 s, 2932 s, 1643 s, 1603 s, 1506 s, 1448 s, 1248 s, 1032 s cm⁻¹; HRMS (ESI-TOF) m/z found 318.1500 [(M+H)⁺]; calcd. 318.1494 for C₂₁H₂₀NO₂.

1,1-dicyclohexyl-2-((4-methoxyphenyl)imino)ethan-1-ol (22t).

The general procedure was followed with 21r (0.104 g, 0.465 mmol) and 4-anisidine (0.063 g, 0.51 mmol, 1.1 equiv) except that the reaction temperature was 50 °C for 2 h. The reaction afforded the product 22t as a light yellow solid (81%, 0.124 g, 0.377 mmol); mp = 94-97 °C. Spectral data for 22t: ¹H NMR (CDCl₃, 500 MHz) δ 1.00 (qd, J = 12.5, 3.5 Hz, 2H), 1.13 (td, J = 12.5, 3.5 Hz, 2H), 1.17-1.28 (m, 6H), 1.28 (d, J = 10.0 Hz, 2H), 1.67 (d, J = 12.5 Hz, 2H), 1.75-1.83 (m, 6H), 1.92 (d, J = 12.5 Hz, 2H), 3.82 (s, 3H), 4.33 (br s, 1H), 6.90 (d, J = 8.5 Hz, 2H), 7.10 (d, J = 8.5 Hz, 2H), 7.84 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 26.40, 26.52, 26.62, 26.78, 27.55, 42.01, 55.54, 78.87, 114.31, 122.03, 142.68, 158.27, 166.65; IR (thin film) 3437 br s, 2928 s, 2853 s, 1647 s, 1506 s, 1448 m, 1246 s, 1035 m cm⁻¹; HRMS (ESI-TOF) m/z found 330.2434 [(M+H)⁺]; calcd. 330.2433 for C₂₁H₃₂NO₂.

ethyl 4-((2-hydroxy-2,2-diphenylethylidene)amino)benzoate (22u).

Following the general procedure with 21a (0.041 g, 0.19 mmol), ethyl 4-aminobenzoate (0.034 g, 0.21 mmol), in the presence of 20 mol% pyrrolidine and 0.050 g 4Å molecular sieves (no KHSO₄ was added), the reaction afforded the product 22u as a colorless liquid (89%, 0.061 g, 0.17 mmol). Spectral data for 22u: ¹H NMR (CDCl₃, 500 MHz) δ 1.40 (t, J = 7.0 Hz, 3H), 4.38 (q, J = 7.0 Hz, 2H), 5.51 (s, 1H), 7.15 (dt, J = 8.0, 2.0
Hz, 2H), 7.33 (tt, J = 7.5, 2.0 Hz, 2H), 7.37-7.40 (m, 4H), 7.44 (dt, J = 7.0, 2.0 Hz, 4H), 8.05 (d, J = 9.0 Hz, 2H), 8.47 (s, 1H); 13C NMR (CDCl₃, 125 MHz) δ 14.31, 61.02, 78.94, 120.86, 126.09, 127.15, 127.91, 128.58, 130.81, 142.87, 152.80, 160.04, 166.73; IR (neat) 3449br s, 3059m, 2980m, 1714s, 1653m, 1603s, 1493m, 1448s, 1277s, 1170s, 1101s cm⁻¹; HRMS (ESI-TOF) m/z found 360.1602 [(M+H)+; calcd. 360.1600 for C₂₃H₂₂NO₃].

2-((3-(((tert-butyldimethylsilyl)oxy)methyl)phenyl)imino)-1,1-diphenylethan-1-ol (22v).

![Diagram of compound 22v]

Following the general procedure with 21a (0.15 g, 0.70 mmol, 1 equiv) and 3-(((tert-butyldimethylsilyl)oxy)methyl)aniline (0.18 g, 0.77 mmol, 1.1 equiv), the reaction afforded the product 22v as a colorless liquid (100%, 0.31 g, 0.77 mmol). Spectral data for 22v: ¹H NMR (CDCl₃, 500 MHz) δ 0.10 (s, 6H), 0.94 (s, 9H), 4.75 (s, 2H), 5.74 (s, 1H), 7.05 (d, J = 8.0 Hz, 1H), 7.13 (s, 1H), 7.20 (d, J = 8.0 Hz, 1H), 7.30-7.33 (m, 3H), 7.38 (t, J = 8.0 Hz, 4H), 7.44 (d, J = 8.0 Hz, 4H), 8.46 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 5.26, 18.41, 25.93, 64.46, 78.72, 118.41, 119.76, 124.20, 127.16, 127.73, 128.49, 129.02, 142.87, 143.26, 148.68, 164.89; IR (neat) 3393s, 2955s, 2932s, 2889s, 2856s, 1647s, 1601s, 1491s, 1375s, 1253s, 1172s, 1105s cm⁻¹; HRMS (ESI-TOF) m/z found 432.2365 [(M+H)+; calcd. 432.2359 for C₂₇H₃₄NO₂Si].

2-(benzylimino)-1,1-diphenylethan-1-ol (22w)

![Diagram of compound 22w]

Following the general procedure with 21a (0.12 g, 0.55 mmol, 1 equiv) and benzyl amine (66 µL, 0.60 mmol, 1.1 equiv), this reaction afforded the product 22w (0.13 g, 0.44 mmol, 80%) as a white solid; mp
= 78-80 °C. Spectral data for 22w: 1H NMR (CDCl₃, 500 MHz) δ 4.80 (s, 2H), 5.78 (br s, 1H), 7.27-7.33 (m, 5H), 7.35-7.40 (m, 10H), 8.33 (s, 1H); 13C NMR (CDCl₃, 125 MHz) δ 61.92, 78.28, 127.10, 127.27, 127.59, 127.81, 128.39, 128.60, 138.21, 143.62, 166.11; IR (thin film) 3408s, 1662s, 1448m, 1363m, 1172m, 1028w cm⁻¹; HRMS (ESI-TOF) m/z found 302.1532 [(M+H)+; calcd. 302.1545 for C₂₁H₂₀O₅N].

4. Procedure for the Preparation of the Zr-VANOL Catalyst (R)-15.

The Zr-VANOL catalyst (R)-15 was prepared as follows. (R)-VANOL (44 mg, 0.1 mmol, 2 equiv), Zr(OiPr)₄(HOiPr) zirconium(IV) isopropoxide isopropanol complex (19 mg, 0.05 mmol, 1 equiv) and 1 mL toluene were mixed under air at room temperature in a 20 mL vial, then N-methylimidazole (4 µL, 0.05 mmol, 1 equiv.) was added via a syringe. Soon after addition of N-methylimidazole, a white solid precipitate started to form. The resulting slurry was stirred at room temperature under air for 30 min before being used in the following asymmetric catalytic rearrangement of α-iminols. This catalyst solution (R)-15 could be stored in toluene for extended periods, with no compromise to the yield or ee of the rearranged product (see Section 11). Catalysts 14, 15, 16, 17, 18 and 19 could all be prepared via this method with the appropriate metal and ligand.

5. Procedures for the α-Iminol Rearrangement of Pre-formed Imines.

5.1. Procedure 1: Reaction with (S)-VANOL BOROX (1)

The catalyst (S)-VANOL BOROX 1 was prepared as follows. To a 20 mL flame dried Schlenk flask was added (S)-VANOL (0.0438 g, 0.1 mmol, 1 equiv.), B(OPh)₃ (0.0870 g, 0.3 mmol, 3 equiv) and toluene (1
mL), the flask was sealed and heated in an 80 °C oil bath under N₂ for 30 min. Then the reaction mixture was cooled to room temperature. This catalyst stock solution was directly used in the rearrangement reaction without further treatment.

To a 20 mL flame dried Schlenk flask was added the catalyst solution (0.25 mL, 0.025 mmol, 25 mol%), iminol 22a (0.0287 g, 0.100 mmol, 1 equiv) and 0.05 mL toluene. The flask was sealed and heated in a 75 °C oil bath under N₂ for 42 h. After being cooled to room temperature, the crude product was purified by silica gel column chromatography with 2:1 hexanes:CHCl₃ as eluent. The reaction afforded the product 23a as a yellow solid (60%, 0.0172 g, 0.0600 mmol); the optical purity was determined to be –17% ee as described in section 5.4. (the detailed analytical data for 23a are listed after procedure 4).

**5.2. Procedure 2: Reaction with (S)-VAPOL POH (7)**

To a 20 mL flame dried Schlenk flask was added the catalyst (S)-VAPOL POH 7 (0.015 g, 0.025 mmol, 25 mol%), iminol 22a (0.0287 g, 0.100 mmol, 1 equiv) and 0.3 mL CCl₄. The flask was sealed and heated in a 60 °C oil bath under N₂ for 14 h. After being cooled to room temperature, the crude product was purified by flash silica gel column chromatography with CHCl₃ as eluent. The reaction afforded the product 23a as a yellow solid (100%, 0.0287 g, 0.100 mmol), the optical purity was determined to be −8% ee as described in section 5.4 (the detailed analytical data for 23a are listed after procedure 4).

**5.3 Procedure 3: Reaction with (R)-VANOL Al (11)**

To a 20 mL flame dried Schlenk flask was added the catalyst (R)-VANOL Al 11 (3 mol%), iminol 22a (0.0287 g, 0.100 mmol, 1 equiv) and 0.3 mL toluene. The flask was sealed and heated in a 70 °C oil bath under N₂ for 8 h. After being cooled to room temperature, the crude product was purified by flash silica gel column chromatography with CHCl₃ as eluent. The reaction afforded the product 23a as a yellow solid (80%, 0.0287 g, 0.100 mmol), the optical purity was determined to be –8% ee as described in section 5.4 (the detailed analytical data for 23a are listed after procedure 4).
The catalyst (R)-VANOL Al 11 was prepared as follows. To a 10 mL flame dried round bottom flask was added (R)-VANOL (0.0219 g, 0.0500 mmol, 2 equiv) and THF (2.5 mL) under a nitrogen atmosphere, and then the solution was stirred for 1 min to dissolve the ligand. Then LiAlH₄ (0.0010 g, 0.025 mmol, 1 equiv) was added as a solid in one portion. The resulting solution was stirred at room temperature for 10 min before being used in the rearrangement reaction. Note: this aluminum catalyst solution was unstable for storage; it is necessary to prepare fresh catalyst for each reaction.

To a 20 mL flame dried Schlenk flask was added the catalyst solution 11 (0.3 mL, 0.003 mmol, 3 mol%), the solvent was carefully removed by high vacuum and then iminol 22a (0.0287 g, 0.100 mmol, 1 equiv.) and 0.3 mL toluene were added. The flask was sealed and heated in a 70 °C oil bath under N₂ for 8 h. After being cooled to room temperature, the crude product was purified by silica gel column chromatography with 2:1 hexanes:CHCl₃ as eluent. The reaction afforded the product 23a as a yellow solid (100%, 0.0287 g, 0.100 mmol), the optical purity was determined to be 68% ee as described in section 5.4 (the detailed analytical data for 23a are listed after procedure 4)

**Ligand Screen on Derivatives of Catalyst 11.** All reactions below were carried out according to procedure 3 at 85 °C under N₂ for 1h, with various VANOL ligands which have substituents at both the 7 and 7’ positions. All ligands were synthesized according to a literature procedure.⁴c

| entry | R          | % yield 23a | % ee 23a |
|-------|------------|-------------|----------|
| 1     | H          | 100         | 68       |
| 2     | tBu        | 100         | 88       |
| 3     | 4-tBuC₆H₄  | 63          | 74       |
| 4     | 3,5-(tBu)₂-4-MeOC₆H₄ | 96 | 71       |
| 5     | SiPh₂Bu    | 95          | 86       |
| 6     | 2,6-Me₂C₆H₃| 96          | 80       |
| 7     | 9-anthracenyl | 100  | 80       |
5.4. Procedure 4: General Procedure for Rearrangement with catalyst (R)-15

The rearrangement reaction was carried out with the following optimal conditions: To a 20 mL vial under air was added 0.25 mL toluene, appropriate α-iminol 22 (0.1 mmol, 1 equiv) and the Zr-VANOL complex catalyst solution (R)-15 (0.05 M in toluene, 50 µL, 2.5 x 10⁻⁵ mmol, 2.5 mol%, this white slurry was vigorously swirled and agitated while being drawn by a syringe). The vial was then capped, placed in a 60 °C oil bath and stirred under air for 1 h. Upon completion, the solution was cooled to room temperature and the crude product purified by flash column chromatography on silica gel with 3:1 to 1:1 hexanes:CHCl₃ as eluent. All the following substrates were synthesized via this procedure 4. Below is a photo of this reaction in a vial following procedure 4.
(S)-1,2-diphenyl-2-(phenylamino)ethan-1-one (23a).

This reaction was carried out with procedure 4 on 22a (0.0286 g, 0.100 mmol) and afforded the product (S)-23a as a yellow solid (94%, 0.0269 g, 0.0943 mmol); mp = 89-92 °C; the optical purity was determined to be 97% ee by Chiralcel OD-H column, 97:3 Hexane:PrOH, 1 mL/min flow rate, 245 nm, 11.4 min for the minor peak and 18.9 min for the major peak; Rf=0.60 in CHCl₃. Spectral data for (S)-23a: ¹H NMR (CDCl₃, 500 MHz) δ 5.62 (br s, 1H), 6.04 (s, 1H), 6.70-6.72 (m, 3H), 7.14 (t, J = 8.0 Hz, 2H), 7.21 (t, J = 7.5 Hz, 1H), 7.28 (t, J = 7.5 Hz, 2H), 7.42-7.46 (m, 4H), 7.52 (t, J = 7.5 Hz, 1H), 8.00 (dd, J = 7.5, 1.0 Hz, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 62.88, 113.72, 118.04, 125.28, 126.67, 126.99, 127.76, 128.17, 129.28, 130.92, 131.09, 131.23, 134.42, 136.59, 137.27, 137.64, 146.08, 201.35; IR (thin film) 3399s, 3053m, 2928s, 1698m, 1592s, 1449s, 1396s, 1353m, 1280m, 1189m, 1050s, 948m, 745s, 669m, 612m, 558m, 498w; [α]²⁰D = +132.1° (c = 1.0, CH₂Cl₂) on 97% ee. The NMR data is in agreement with the literature data.⁵

(S)-2-(phenylamino)-1,2-di-o-tolylethan-1-one (23b).

Following procedure 4 with 22b (0.0317 g, 0.101 mmol) afforded the product (S)-23b (88%, 0.0279 g, 0.0886 mmol) as a light yellow liquid. The optical purity was determined to be 84% ee by Chiralcel OD-H column, 97:3 Hexane:PrOH, 1 mL/min flow rate, 245 nm, 5.8 min for the minor peak and 9.5 min for the major peak; Rf=0.60 in CHCl₃. Spectral data for (S)-23b: ¹H NMR (CDCl₃, 500 MHz) δ 2.09 (s, 3H), 2.24 (s, 3H), 5.40 (br s, 1H), 5.94 (s, 1H), 6.59 (dd, J = 8.5, 0.5 Hz, 2H), 6.69 (dt, J = 8.5, 0.5 Hz, 1H), 7.06 (dd, J = 5.0, 3.5 Hz, 1H), 7.11-7.15 (m, 5H), 7.19 (t, J = 7.5 Hz, 1H), 7.31 (td, J = 7.5, 1.0 Hz, 1H) 7.34-7.39 (m, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 19.42, 19.57, 19.57, 62.65, 113.27, 117.80, 125.28, 126.67, 126.99, 127.76, 128.17, 129.28, 130.92, 131.09, 131.23, 134.42, 136.59, 137.27, 137.64, 146.08, 201.35; IR (thin film) 3399s, 3053m,
2926m, 1695s, 1603s, 1504s, 1300m, 1248m, 748m cm\(^{-1}\); HRMS (ESI-TOF) m/z found 316.1702 [(M+H)\(^+\); calcd. 316.1701 for C\(_{22}\)H\(_{22}\)NO]; \([\alpha]\)\(^D\) = +81.8° (c = 1.0, CH\(_2\)Cl\(_2\)) on 84% ee.

\((R)-1,2\text{-bis(2-isopropylphenyl)-2-(phenlamino)ethan-1-one (23c).}\)

![Diagram of reaction](image)

The reaction was performed with procedure 4 with catalyst (S)-15 on a sample of 22c (0.0522 g that was a mixture of 21c:22c (aldehyde:imine) = 1:3.2 (0.0422 g, 0.114 mmol of 22c). The reaction afforded the product \((R)-23c\) as a white semi-solid (95%, 0.0402 g, 0.108 mmol), the optical purity was determined to be 54% ee by Chiralcel OD-H column, 97:3 Hexane:iPrOH, 1 mL/min flow rate, 245 nm, 4.0 min for the major peak and 6.6 min for the minor peak; \(R_f\) = 0.60 in CHCl\(_3\). Spectral data for \((R)-23c:\) \(^1\text{H NMR (CDCl}_3, 500 MHz}\) δ 0.50 (d, \(J = 7.0\) Hz, 3H), 0.55 (d, \(J = 7.0\) Hz, 3H), 1.17 (d, \(J = 7.0\) Hz, 3H), 1.26 (d, \(J = 7.0\) Hz, 3H), 2.56 (septet, \(J = 7.0\) Hz, 1H), 3.24 (septet, \(J = 7.0\) Hz, 1H), 5.50 (d, \(J = 5.0\) Hz, 1H), 6.11 (d, \(J = 5.0\) Hz, 1H), 6.60 (d, \(J = 7.5\) Hz, 2H), 6.67 (t, \(J = 7.5\) Hz, 1H), 7.11 (t, \(J = 7.5\) Hz, 3H), 7.15-7.19 (m, 3H), 7.26 (t, \(J = 7.5\) Hz, 2H), 7.36 (t, \(J = 7.5\) Hz, 2H); \(^{13}\text{C NMR (CDCl}_3, 125 MHz}\) δ 23.25, 23.49, 24.46, 24.52, 28.54, 29.79, 62.03, 113.28, 117.65, 125.24, 125.90, 126.30, 126.38, 127.34, 128.52, 129.18, 130.78, 132.39, 137.71, 145.91, 147.39, 147.58, 202.07 (one aromatic carbon was not located); IR (thin film) 3402br s, 2964s, 2928s, 2868s, 1695s, 1606s, 1506s, 1487m, 1319m, 1032m, 760m cm\(^{-1}\); HRMS (ESI-TOF) m/z found 372.2331 [(M+H)\(^+\); calcd. 372.2327 for C\(_{26}\)H\(_{30}\)NO]; \([\alpha]\)\(^D\) = −39.3° (c = 0.66, CH\(_2\)Cl\(_2\)) on 54% ee.

\((S)-2-(phenlamino)-1,2\text{-di-m-tolylethan-1-one (23d).}\)

![Diagram of reaction](image)
Following procedure 4 with 22d (0.0310 g, 0.0985 mmol), the reaction afforded the product (S)-23d as a light yellow liquid (96%, 0.0298 g, 0.0946 mmol). The optical purity was determined to be 97.5% ee by Chiralcel OD-H column, 97:3 Hexane:iPrOH, 1 mL/min flow rate, 245 nm, 7.8 min for the minor peak and 11.7 min for the major peak; Rf = 0.60 in CHCl₃. Spectral data for (S)-23d: ¹H NMR (CDCl₃, 500 MHz) δ 2.28 (s, 3H), 2.38 (s, 3H), 5.42 (br s, 1H), 5.98 (s, 1H), 6.68 (d, J = 7.5 Hz, 2H), 6.69 (t, J = 7.5 Hz, 1H), 7.02 (d, J = 7.5 Hz, 1H), 7.10 (t, J = 7.5 Hz, 2H), 7.18 (t, J = 7.5 Hz, 1H), 7.24-7.28 (m, 2H), 7.32 (t, J = 8.0 Hz, 1H), 7.34 (t, J = 8.0 Hz, 1H), 7.82 (d, J = 7.5 Hz, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 21.37, 21.45, 62.6, 113.48, 117.76, 125.45, 126.07, 128.46, 128.50, 128.82, 128.91, 129.22, 129.44, 134.32, 135.03, 137.65, 138.55, 138.80, 146.23, 197.31; IR (neat) 3399s, 3051m, 2922m, 1682s, 1603s, 1506s, 1267m, 1151m, 748m cm⁻¹; HRMS (ESI-TOF) m/z found 316.1700 [(M+H)⁺; calcd. 316.1701 for C₂₂H₂₂NO]; [α]²⁰_D = +117.0° (c = 1.0, CH₂Cl₂) on 97.5% ee.

(R)-1,2-bis(3-chlorophenyl)-2-(phenylamino)ethan-1-one (23e).

General procedure 4 was followed with 22e (0.0356 g, 0.1 mmol) with three exceptions: 1. 5 mol% (S)-15 catalyst was used, 2. The reaction was at 70 °C for 6 h under N₂ atmosphere (reaction was done in a Schlenk flask under N₂ because the product was not stable under heat in presence of air). 3. The purification was as follows: hexanes (5 mL) was added to precipitate the catalyst after the reaction mixture was cooled to room temperature, and then the solid was removed by filtering through filter paper. The filtrate was concentrated on rotary vaporization and the residue was subjected to column chromatography with 1:1 hexane:CHCl₃. The reaction afforded the product (R)-23e (0.0327 g, 0.092 mmol, 92%) as a yellow oil. The optical purity was determined to be 93% ee with Chiralcel OD-H column, 90:10 hexane:iPrOH, 1 mL/min, 245 nm, 8.2 min for the major peak and 21.0 min for the minor peak. Spectral data for (R)-23e: ¹H NMR (CDCl₃, 500 MHz) δ 5.42 (br s, 1H), 5.95 (s, 1H), 6.67 (d, J = 7.5 Hz, 2H), 6.74 (t, J = 7.5 Hz, 1H), 7.17 (t, J = 7.5 Hz,


(S)-2-(phenylamino)-1,2-di-p-tolylethan-1-one (23f)

Following procedure 4 with 22e (0.0353 g, 0.112 mmol), the reaction afforded the product (S)-23e as a light yellow solid (92%, 0.0325 g, 0.103 mmol); mp = 96-98 °C. The optical purity was determined to be 98% ee by Chiralcel OD-H column, 97:3 Hexane:iPrOH, 1 mL/min flow rate, 245 nm, 8.4 min for the minor peak and 18.4 min for the major peak; Rf=0.60 in CHCl₃. Spectral data for (S)-23f: ¹H NMR (CDCl₃, 500 MHz) δ 2.25 (s, 3H), 2.38 (s, 3H), 5.44 (s, 1H), 5.99 (s, 1H), 6.68 (d, J = 8.5 Hz, 2H), 6.69 (t, J = 7.5 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 7.13 (t, J = 7.5 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.93 (d, J = 8.0 Hz, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 21.09, 21.69, 62.16, 113.47, 117.66, 127.98, 129.02, 129.19, 129.36, 129.73, 132.42, 134.87, 137.77, 144.44, 146.20, 196.58; IR (thin film) 3399 s, 3049 m, 2922 m, 1678 s, 1604 s, 1506 s, 1319 m, 1261 m, 1174 m, 748 m cm⁻¹; HRMS (ESI-TOF) m/z found 316.1700 [(M+H)+; calcd. 316.1701 for C₂₂H₂₂NO]; [α]²⁰D = +127.6° (c = 1.0, CH₂Cl₂) on 98% ee.

(S)-1,2-bis(4-n-butylphenyl)-2-(phenylamino)ethan-1-one (23g).
Following procedure 4 with 22g (0.0434 g, 0.109 mmol), the reaction afforded the product (S)-23f as a light yellow solid (95%, 0.0413 g, 0.104 mmol); mp = 75-77 °C. The optical purity was determined to be 99% ee by Chiralcel OD-H column, 95:5 Hexane:iPrOH, 1 mL/min flow rate, 245 nm, 5.5 min for the minor peak and 11.6 min for the major peak; Rf=0.60 in CHCl3; ¹H NMR (CDCl₃, 500 MHz) δ 0.89 (t, J = 7.5 Hz, 3H), 0.93 (t, J = 7.5 Hz, 3H), 1.27-1.39 (m, 4H), 1.53 (q, J = 8.0 Hz, 2H), 1.60 (q, J = 8.0 Hz, 2H), 2.52 (t, J = 8.0 Hz, 2H), 2.64 (t, J = 8.0 Hz, 2H), 5.38 (br s, 1H), 6.00 (s, 1H), 6.67-6.70 (m, 3H), 7.11 (t, J = 8.0 Hz, 2H), 7.14 (t, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.96 (d, J = 8.0 Hz, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 13.91, 13.93, 22.35, 22.40, 33.10, 33.37, 35.27, 35.71, 62.17, 113.44, 117.64, 127.96, 128.71, 128.89, 129.07, 129.20, 132.66, 135.03, 142.77, 146.32, 149.31, 196.67; IR (thin film) 3406s, 3051m, 2930s, 2858m, 1678s, 1604s, 1506s, 1317m, 1261m, 1174m, 748m cm⁻¹; HRMS (ESI-TOF) m/z found 400.2640 [(M+H)⁺]; calcd. 400.2640 for C₂₈H₃₄NO; [α]²₀D = +126.0° (c = 1.3, CH₂Cl₂) on 99% ee.

(S)-1,2-bis(4-isopropylphenyl)-2-(phenylamino)ethan-1-one (23h).

Following procedure 4 with 22h (0.0409 g, 0.110 mmol), the reaction afforded the product (S)-23h as a light yellow solid (98%, 0.0401 g, 0.108 mmol); mp = 72-74 °C. The optical purity was determined to be 99% ee by Chiralcel OD-H column, 97:3 Hexane:iPrOH, 1 mL/min flow rate, 245 nm, 12.1 min for the minor peak and 20.5 min for the major peak; Rf=0.60 in CHCl₃. Spectral data for (S)-23h: ¹H NMR (CDCl₃, 500 MHz) δ 1.18 (d, J = 6.5 Hz, 6H), 1.25 (d, J = 6.5 Hz, 6H), 2.83 (septet, J = 7.0 Hz, 1H), 2.94 (septet, J = 7.0 Hz, 1H), 5.44 (br s, 1H), 6.00 (s, 1H), 6.67-6.70 (m, 3H), 7.12-7.16 (m, 4H), 7.30 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.99 (d, J = 8.0 Hz, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 23.57, 23.58, 23.82, 33.69, 34.24, 62.15, 113.49, 117.71, 126.80, 127.16, 128.02, 128.88, 129.20, 132.80, 135.05, 146.26, 148.62, 155.07, 196.57 (one aliphatic carbon was not located); IR (thin film) 3406s, 3051s, 2961s, 2870m, 1678s, 1604s, 1506s, 1425s, 1362m, 1253m, 1174m, 744m cm⁻¹.
1315 m, 1176 m, 748 m \text{ cm}^{-1}; \text{ HRMS (ESI-TOF) } m/z \text{ found 372.2327 } [(\text{M+H})^+]; \text{ calcd. 372.2327 for } C_{26}H_{30}NO]. \\
[\alpha]_{D}^{20} = +107.9^\circ (c = 1.0, \text{ CH}_2\text{Cl}_2) \text{ on 99\% ee.}

(S)-1,2-bis(4-cyclohexylphenyl)-2-(phenylamino)ethan-1-one (23i).

Following procedure 4 with 22i (0.0446 g, 0.0990 mmol), the reaction afforded the product (S)-23i as a light yellow solid (97\%, 0.0433 g, 0.0960 mmol); mp = 170-171 °C. The optical purity was determined to be 94\% ee by Chiralcel OD-H column, 97:3 Hexane:iPrOH, 1 mL/min flow rate, 245 nm, 12.6 min for the minor peak and 26.0 min for the major peak; Rf =0.60 in CHCl3. Spectral data for (S)-23i: $^1\text{H}$ NMR (CDCl3, 500 MHz) $\delta$ 1.18-1.43 (m, 10H), 1.69-1.85 (m, 10H), 2.38-2.42 (m, 1H), 2.50-2.54 (m, 1H), 5.38 (br s, 1H), 5.97 (s, 1H), 6.65-6.68 (m, 3H), 7.10-7.13 (m, 4H), 7.26 (d, $J$ = 8.5 Hz, 2H), 7.36 (d, $J$ = 8.5 Hz, 2H), 7.96 (d, $J$ = 8.5 Hz, 2H); $^{13}\text{C}$ NMR (CDCl3, 125 MHz) $\delta$ 25.98, 26.07, 26.66, 26.80, 33.96, 34.24, 44.10, 44.65, 62.12, 113.44, 117.66, 127.5, 127.50, 127.96, 129.16, 129.18, 132.76, 135.03, 146.29, 147.85, 154.23, 196.59; IR (thin film) 3400 br s, 2924s, 2851s, 1672s, 1604s, 1508s, 1172m, 997m cm$^{-1}$; HRMS (ESI-TOF) $m/z$ found 434.2863 [(M-H$_2$O+H)$^+$]; calcd. 434.2848 for C$_{32}$H$_{36}$N]; [\alpha]_{D}^{20} = +69.3^\circ (c = 1.0, \text{ CH}_2\text{Cl}_2) \text{ on 94\% ee.}

(S)-1,2-bis(4-t-butylphenyl)-2-(phenylamino)ethan-1-one (23j).

Following procedure 4 with 22j (0.0426 g, 0.106 mmol), this reaction afforded the product (S)-23j as a light yellow solid (100\%, 0.0425 g, 0.106 mmol); mp = 151-153 °C. The optical purity was determined to
be >99% ee by Chiralcel OD-H column, 95:5 Hexane:iPrOH, 1 mL/min flow rate, 245 nm, 7.6 min for the minor peak and 11.8 min for the major peak; \( R_e = 0.60 \) in CHCl₃. Spectral data for (S)-23: \(^1\)H NMR (CDCl₃, 500 MHz) \( \delta \) 1.26 (s, 9H), 1.33 (s, 9H), 5.30 (br s, 1H), 6.01 (s, 1H), 6.65-6.70 (m, 3H), 7.14 (td, \( J = 8.0, 2.0 \text{ Hz}, 2H \)), 7.32 (dd, \( J = 8.0, 2.0 \text{ Hz}, 2H \)), 7.40 (dd, \( J = 8.0, 2.0 \text{ Hz}, 2H \)), 7.46 (dd, \( J = 8.0, 2.0 \text{ Hz}, 2H \)), 8.00 (dd, \( J = 8.0, 2.0 \text{ Hz}, 2H \)); ¹³C NMR (CDCl₃, 125 MHz) \( \delta \) 31.02, 31.25, 34.50, 34.17, 61.98, 113.39, 117.63, 125.67, 126.03, 127.73, 128.95, 129.21, 132.41, 134.72, 150.89, 157.31, 196.61; IR (thin film) 3408s, 2964s, 1678s, 1603s, 1506s, 1267m, 1109m, 748m cm⁻¹; HRMS (ESI-TOF) \( m/\text{z} \) found 400.2643 [(M+H)⁺]; calcd. 400.2640 for C₂₈H₃₄NO; \([\alpha]_{D}^{20} = +92.9^\circ \) (c = 1.0, CH₂Cl₂) on >99% ee.

\((S)-1,2\text{-di([1,1'-biphenyl]-4-yl)-2-(phenylamino)ethan-1-one (23k)}\)

\begin{center}
\begin{align*}
\text{Ph} & \quad \text{N} \\
\text{H} & \quad \text{O} \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\end{center}

\(2.5 \text{ mol\% (R)-VANOL Zr 15} \quad \text{toluene, 60 °C, 1 h} \)

Following procedure 4 with 22k (0.0343 g, 0.0779 mmol), this reaction afforded the product (S)-23k as a yellow solid (100%, 0.0342 g, 0.0779 mmol); mp = 196-199 °C. The optical purity was determined to be >99% ee by (R, R)-WHELK-O1 column, 99:1 Hexane:iPrOH, 1 mL/min flow rate, 245 nm, 63.0 min for the major peak and 69.2 min for the minor peak; \( R_e = 0.60 \) in CHCl₃. Spectral data for (S)-23k: \(^1\)H NMR (CDCl₃, 500 MHz) \( \delta \) 5.48 (br s, 1H), 6.12 (s, 1H), 6.70-6.75 (m, 3H), 7.17 (td, \( J = 7.5, 1.0 \text{ Hz}, 2H \)), 7.31 (tt, \( J = 7.5, 1.0 \text{ Hz}, 2H \)), 7.38-7.42 (m, 3H), 7.46 (tt, \( J = 7.5, 1.0 \text{ Hz}, 2H \)), 7.50-7.54 (m, 4H), 7.57 (dd, \( J = 6.5, 2.0 \text{ Hz}, 2H \)), 7.61 (dd, \( J = 7.5, 1.0 \text{ Hz}, 2H \)), 7.68 (dt, \( J = 8.5, 2.0 \text{ Hz}, 2H \)), 8.14 (dt, \( J = 8.5, 2.0 \text{ Hz}, 2H \)); ¹³C NMR (CDCl₃, 125 MHz) \( \delta \) 62.32, 113.51, 117.89, 127.01, 127.25, 127.36, 127.43, 127.84, 128.40, 128.53, 128.73, 128.97, 129.29, 129.56, 133.58, 136.73, 139.56, 140.32, 140.98, 146.10, 146.29, 196.38; IR (thin film) 3393s, 3031m, 2931m, 1666s, 1603s, 1506s, 1311m, 1170m, 743m cm⁻¹; HRMS (ESI-TOF) \( m/\text{z} \) found 440.2028 [(M+H)⁺]; calcd. 440.2014 for C₃₂H₂₈NO; \([\alpha]_{D}^{20} = -13.0^\circ \) (c = 1.0, CH₂Cl₂) on >99% ee.
(S)-1,2-bis(4-methoxylphenyl)-2-(phenylamino)ethan-1-one (23I)

Procedure 4 was followed with 22I (0.0332 g, 0.0961 mmol), except that the eluent for chromatography was CHCl₃ and the reaction was complete after 0.5 h. The reaction afforded the product (S)-23I as a light yellow solid (90%, 0.0300 g, 0.0865 mmol); mp = 96-97 °C. The optical purity was determined to be 98% ee by Chiralcel OD-H column, 95:5 Hexane:iPrOH, 1 mL/min flow rate, 245 nm, 16.9 min for the minor peak and 60.7 min for the major peak; R₁=0.10 in CHCl₃. Spectral data for (S)-23I: ¹H NMR (CDCl₃, 500 MHz) δ 3.72 (s, 3H), 3.84 (s, 3H), 5.19 (br s, 1H), 5.94 (s, 1H), 6.65-6.69 (m, 3H), 6.81 (d, J = 8.0 Hz, 2H), 6.91 (d, J = 8.0 Hz, 2H), 7.12 (t, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 8.01 (d, J = 8.0 Hz, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 55.18, 55.47, 61.50, 113.46, 113.88, 114.42, 115.23, 117.61, 127.77, 129.18, 130.07, 131.21, 146.25, 159.19, 163.73, 195.42; IR (thin film) 3399s, 2934w, 2837w, 1672s, 1603s, 1508s, 1257s, 1170s, 1030m, 750m cm⁻¹; HRMS (ESI-TOF) m/z found 348.1594 [(M+H)+]; calcd. 348.1600 for C₂₂H₂₂NO₃; [α]₃⁰D = +92.0° (c = 1.0, CH₂Cl₂) on 98% ee.

(R)-1,2-bis(4-fluorophenyl)-2-(phenylamino)ethan-1-one (23m)

Following procedure 4 with (S)-15 and 22m (0.0330 g, 0.102 mmol), this reaction afforded the product (R)-23m as a light yellow wax-like semi-solid (97%, 0.0320 g, 0.0991 mmol). The optical purity was determined to be >99% ee by Chiralcel OD-H column, 97:3 Hexane:iPrOH, 1 mL/min flow rate, 245 nm, 14.1 min for the major peak and 41.5 min for the minor peak; R₁=0.60 in CHCl₃. Spectral data for (S)-23m: ¹H NMR (CDCl₃, 500 MHz) δ 5.31 (br s, 1H), 5.97 (s, 1H), 6.65 (dd, J = 8.5, 1.0 Hz, 2H), 6.71 (td, J = 8.5, 1.0 Hz, 2H), 2.5 mol% (R)-15 toluene, 60 °C, 0.5 h
Hz, 1H) 6.98 (td, J = 8.5, 2.0 Hz, 2H), 7.10-7.16 (m, 4H), 7.42 (ddt, J = 8.5, 5.5, 2.0 Hz, 2H), 8.03 (ddt, J = 8.5, 5.5, 2.0 Hz, 2H); $^{13}$C NMR (CDCl$_3$, 125 MHz) δ 61.85, 113.49, 116.02 (d, J = 21.8 Hz) 116.11 (d, J = 21.8 Hz), 118.12, 129.29, 129.69 (d, J = 8.5 Hz), 131.46, 131.54, 133.36 (d, J = 8.5 Hz), 145.75, 162.38 (d, J = 246.3 Hz), 165.92 (d, J = 255.0 Hz), 195.29; $^{19}$F NMR (CDCl$_3$, 470 MHz) δ –103.54, –113.37; IR (thin film) 3402s, 1684s, 1601s, 1508s, 1263s, 1155m, 995m, 837m, 798m, 750m cm$^{-1}$. HRMS (ESI-TOF) m/z found 324.1199 [(M+H)$^+$/calcd. 324.1200 for C$_{20}$H$_{16}$NOF$_2$]; [α]$_{D}^{20}$ = –85.1° (c = 1.0, CH$_2$Cl$_2$) on >99% ee.

**(R)-2-(phenylamino)-1,2-bis(4-(trifluoromethyl)phenyl)ethan-1-one (23n).**

It was found necessary to perform the reaction of this substrate under an inert atmosphere. To a flame-dried Schlenk flask was added 22n (0.0444 g, 0.104 mmol), catalyst **(R)-15** (0.2 mL in toluene, 10 mol%) and 0.1 mL toluene. The flask was sealed and cooled in liquid N$_2$ for 5 min, then, the flask was connected to vacuum for 5 min and then sealed again. The flask was allowed to warm up to room temperature, which completed one cycle. The mixture was treated to three freeze-pump-thaw cycles and after the final warming to room temperature, the flask was filled with N$_2$ gas and sealed. The reaction mixture was heated in a 70 °C oil bath for 2.5 h, and then cooled to room temperature. The crude product was directly purified by silica gel column chromatography with 2:1 hexanes:CHCl$_3$ as eluent. The reaction afforded the product (**S**-23n) as a yellow semi-solid (74%, 0.0329 g, 0.0773 mmol). The optical purity was determined to be 73% ee on a (R,R)-WHELK-O1 column, 99:1 Hexane:iPrOH, 0.5 mL/min flow rate, 245 nm, 26.7 min for the major peak and 29.0 min for the minor peak; R$_f$=0.85 in CHCl$_3$. Spectral data for (**S**-23n): $^1$H NMR (CDCl$_3$, 500 MHz) δ 5.43 (br s, 1H), 6.08 (s, 1H), 6.65 (d, J = 7.5 Hz, 2H), 6.74 (t, J = 7.5 Hz, 1H), 7.16 (t, J = 7.5 Hz, 2H), 7.56 (s, 4H), 7.73 (d, J = 8.0 Hz, 2H), 8.07 (d, J = 8.0 Hz, 2H); $^{13}$C NMR (CDCl$_3$, 125 MHz) δ 62.71, 113.48, 118.54, 123.28 (q, J = 271.2 Hz), 123.69 (q, J = 270.2 Hz), 125.94 (q, J = 32.8 Hz), 135.07 (q, J = 3.7 Hz), 126.22 (q, J = 3.7 Hz), 128.13, 129.13, 129.41, 130.61 (q, J = 33.1 Hz), 135.07 (q, J = 32.8 Hz), 137.45, 141.14, 145.29,
\[ \text{[S]}-38 \]

195.60; \[^{19}F\text{NMR (CDCl}_3, 470 MHz) \delta -63.30, -62.78; IR (thin film) 3402 \text{br s, 3057m, 2928m, 1695s, 1604s, 1506s, 1325s, 1170s, 1128s, 1068s, 1018m cm}^{-1}; HRMS (ESI-TOF) m/z found 424.1136 [(M+H)^+; calcd. 424.1136 for C\text{22H}_{16}\text{NOF}_6]; \[\alpha\]_D^{20} = +15.2° (c = 1.0, CH\text{Cl}_2) on 73% ee.

Note: Exclusion of air is a must for this substrate because the product is sensitive to air under heat. If the reaction was performed with procedure 4, under air, an 18% yield of by-product \(24n\) was obtained as well as a 70% recovery of \(22n\). The desired product \(23n\) was not observed.

\((R)-1,1'-(\text{1-oxo-2-(phenylamino)ethane-1,2-diyl})\text{bis(4,1-phenylene))bis(ethan-1-one) (23o).}\)

The rearrangement of \(22o\) (0.0444 g, 0.120 mmol) was carried out with procedure 4 with the exception that 1 mL toluene was used due to the low solubility of the substrate \(22o\), and the reaction time was 3 h. The product was purified by column chromatography on silica gel with 8:1 to 3:1 hexanes:E\text{tOAc} as eluent to afford the product \((S)-23o\) as a yellow semi-solid (100%, 0.0444 g, 0.120 mmol). The optical purity was determined to be 97% ee by (R, R)-WHELK-O1 column, 70:30 Hexane:iPrOH, 2 mL/min flow rate, 254 nm, 24.2 min for the major peak and 31.5 min for the minor peak; \(R_t= 0.3\) in 2:1 Hexanes:E\text{tOAc}. Spectral data for \((S)-23o\): \(^1H\text{NMR (CDCl}_3, 500 MHz) \delta 2.52 (s, 3H), 2.62 (s, 3H), 5.54 (br s, 1H), 6.09 (s, 1H), 6.67 (d, \text{J} = 8.5 \text{Hz, 2H}), 6.72 (t, \text{J} = 8.5 \text{Hz, 1H}), 7.15 (t, \text{J} = 8.5 \text{Hz, 2H}), 7.54 (d, \text{J} = 8.5 \text{Hz, 2H}), 7.87 (d, \text{J} = 8.5 \text{Hz, 2H}), 8.00 (d, \text{J} = 8.5 \text{Hz, 2H}), 8.04 (d, \text{J} = 8.5 \text{Hz, 2H}); \(^{13}C\text{NMR (CDCl}_3, 125 MHz) \delta 26.60, 26.87, 62.99, 113.55, 118.38, 128.34, 128.58, 129.02, 129.15, 129.36, 136.91, 138.03, 140.55, 142.46, 145.41, 195.96, 197.12, 197.32; \text{IR (thin film) 3395} \text{br s, 3053m, 2924s, 2855m, 1684s, 1603s, 1506s, 1311m, 1265s cm}^{-1}.\)
HRMS (ESI-TOF) m/z found 372.1603 [(M+H)+; calcd. 372.1600 for C\textsubscript{24}H\textsubscript{22}NO\textsubscript{3}]; [α]\textsubscript{D}\textsuperscript{20} = +55.3° (c = 1.0, CH\textsubscript{2}Cl\textsubscript{2}) on 97% ee.

(S)-8-(phenylamino)tetradecan-7-one (23p).

Following procedure 4 with 22p (0.0333 g, 0.110 mmol), this reaction afforded the product (S)-23p as a colorless liquid (95%, 0.0317 g, 0.105 mmol). The optical purity was determined to be 89% ee by Chiralcel OD-H column, 99:1 Hexane:iPrOH, 1 mL/min flow rate, 245 nm, 5.3 min for the minor peak and 8.3 min for the major peak; R\textsubscript{i}=0.60 in CHCl\textsubscript{3}. Spectral data for (S)-23p: \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500 MHz) δ 0.86 (t, J = 6.5 Hz, 3H), 0.87 (t, J = 6.5 Hz, 3H), 1.24-1.38 (m, 14H), 1.55 (q, J = 7.5 Hz, 2H), 1.61-1.67 (m, 1H), 1.80-1.87 (m, 1H), 2.48 (t, J = 7.5 Hz, 2H), 3.99 (t, J = 7.0 Hz, 1H), 4.34 (br s, 1H), 6.56 (dd, J = 8.5, 1.0 Hz, 2H), 6.70 (td, J = 7.5, 1.0 Hz, 1H), 7.16 (td, J = 8.5, 2.0 Hz, 2H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 125 MHz) δ 14.02, 22.47, 22.54, 23.42, 25.26, 28.86, 29.17, 31.56, 31.59, 32.05, 38.72, 62.88, 113.00, 117.75, 129.35, 146.99, 212.50 (1 aliphatic carbon was not located); IR (neat) 3397s, 3053w, 2955s, 2930s, 2858s, 1713s, 1603s, 1317m, 748m cm\textsuperscript{-1}; HRMS (ESI-TOF) m/z found 304.2642 [(M+H)+; calcd. 304.2640 for C\textsubscript{20}H\textsubscript{34}NO]; [α]\textsubscript{D}\textsuperscript{20} = +19.4° (c = 1.0, CH\textsubscript{2}Cl\textsubscript{2}) on 89% ee.

(S)-1,4-diphenyl-3-(phenylamino)butan-2-one (23q).

Following procedure 4 with 22q (0.0330 g, 0.105 mmol), this reaction afforded the product (S)-23q as a yellow liquid (98%, 0.0324 g, 0.103 mmol). The optical purity was determined to be >99% ee by (R, R)-WHELK-O1 column, 95:5 Hexane:iPrOH, 1 mL/min flow rate, 245 nm, 13.3 min for the minor peak and 17.2 min for the major peak; R\textsubscript{i}=0.60 in CHCl\textsubscript{3}. Spectral data for (S)-23q: \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500 MHz) δ 3.01 (dd, J 2.5 mol% (R)-15 toluene, 60 °C, 1 h}
= 13.5, 7.0 Hz, 1H), 3.11 (dd, J = 13.5, 7.0 Hz, 1H), 3.66 (d, J = 16.0 Hz, 1H), 3.73 (d, J = 16.0 Hz, 1H), 4.24 (br s, 1H), 4.37 (t, J = 7.0 Hz, 1H), 6.51 (dd, J = 8.5, 1.0 Hz, 2H), 6.74 (tt, J = 7.5, 1.0 Hz, 1H), 7.07 (d, J = 8.5 Hz, 2H), 7.14-7.19 (m, 4H), 7.25-7.33 (m, 6H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 38.09, 47.19, 63.04, 113.34, 118.35, 127.08, 128.62, 128.78, 129.21, 129.42, 129.50, 129.63, 133.34, 136.45, 146.28, 209.26; IR (neat) 3400br s, 3062m, 3028m, 2924m, 1716s, 1603s, 1500s, 1496s, 1437m, 1317m cm\(^{-1}\); HRMS (ESI-TOF) m/z found 316.1699 [(M+H)\(^+\)]; calcd. 316.1701 for C\(_{22}\)H\(_{22}\)NO; \([\alpha]\)\(^{20}\) = +28.0° (c = 1.0, CH\(_2\)Cl\(_2\)) on >99% ee.

\((S)-1,2\text{-dicyclohexyl-2-(phenylamino)ethan-1-one (23r).}\)

Following procedure 4 with 22r (0.0308 g, 0.103 mmol), this reaction afforded the product \((S)-23r\) as a white solid (97%, 0.0299 g, 0.100 mmol); mp = 76-78 °C. The optical purity was determined to be 98% ee by Chiralcel OD-H column, 99.5:0.5 Hexane:iPrOH, 0.5 mL/min flow rate, 245 nm, 11.7 min for the minor peak and 15.6 min for the major peak; \(R_\ell=0.60\) in CHCl\(_3\). Spectral data for \((S)-23r\): \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 1.08-1.28 (m, 11H), 1.64-1.77 (m, 10H), 2.53-2.59 (m, 1H), 3.99 (d, J = 5.0 Hz, 1H), 4.41 (br s, 1H), 6.61 (dd, J = 8.5, 1.0 Hz, 2H), 6.70 (td, J = 8.5, 1.0 Hz, 1H), 7.14 (td, J = 8.5, 1.0 Hz, 2H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 25.36, 25.71, 25.90, 26.04, 26.15, 26.28, 27.74, 28.16, 29.21, 30.72, 40.66, 48.29, 66.77, 113.56, 117.68, 129.22, 148.05, 214.35; IR (thin film) 3395s, 2930s, 2855s, 1705s, 1603s, 1506s, 1450m, 1317m, 1255m, 748m cm\(^{-1}\); HRMS (ESI-TOF) m/z found 300.2332 [(M+H)\(^+\)]; calcd. 300.2327 for C\(_{20}\)H\(_{30}\)NO; \([\alpha]\)\(^{20}\) = +33.8° (c = 1.0, CH\(_2\)Cl\(_2\)) on 98% ee.
(S)-2-((4-methoxyphenyl)amino)-1,2-diphenylethan-1-one (23s).

The rearrangement of 22s (0.0317 g, 0.10 mmol) was carried out following procedure 4 except that the reaction temperature was at 80 °C, and the eluent for column chromatography was 8:1 to 4:1 hexanes:EtOAC. The reaction afforded the product (S)-23s as a yellow solid (98%, 0.0311 g, 0.098 mmol). mp = 90-94 °C. The optical purity was determined to be 98% ee by (R, R)-WHELK-O1 column, 95:5 Hexane:iPrOH, 1 mL/min flow rate, 245 nm, 23.7 min for the major peak and 27.1 min for the minor peak; Rf=0.10 in CHCl₃. Spectral data for (S)-23s: ¹H NMR (CDCl₃, 500 MHz) δ 3.71 (s, 3H), 5.14 (br s, 1H), 5.99 (s, 1H), 6.65 (dt, J = 9.0, 2.5 Hz, 2H), 6.74 (dt, J = 9.0, 2.5 Hz, 2H), 7.22 (t, J = 7.5 Hz, 1H), 7.30 (t, J = 7.5 Hz, 2H), 7.44 (t, J = 8.0 Hz, 4H), 7.54 (t, J = 7.5 Hz, 1H), 8.00 (d, J = 7.5 Hz, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 55.70, 63.77, 114.84, 115.03, 128.08, 128.12, 128.67, 128.83, 129.06, 133.47, 135.15, 137.85, 140.36, 152.36, 197.45; IR (thin film) 3397br s, 3062m, 2932m, 2833m, 1684s, 1514s, 1238s, 1176m, 1035m, 819m cm⁻¹. HRMS (ESI-TOF) m/z found 318.1507 [(M+H)+]; calcd. 318.1494 for C₂₁H₂₀NO₂; [α]²⁰_D = +151.1° (c = 1.0, CH₂Cl₂) on 98% ee.

A second run on much larger scale (45x) was carried out under air at 80 °C for 2 h, with 1.5 mol% (S)-15 in 14 mL toluene on a 1.42 gram scale (4.48 mmol) and produced the product (R)-23s as a yellow solid (1.22 g, 3.81 mmol, 85% yield); mp = 93-95 °C. The optical purity was determined to be 98% ee; [α]²⁰_D = −130.7° (c = 1.0, CH₂Cl₂) on 98% ee. A 7% yield of by-product 2-((4-methoxyphenyl)amino)-1,2-diphenylethan-1-one was also isolated.
A third run on much larger scale (41x) was carried out under N₂ atmosphere at 80 °C for 6 h, with 1 mol% \((R)-15\) on a 1.30 gram scale (4.10 mmol) and produced the product \((S)-23s\) as a yellow solid (1.22 g, 3.85 mmol, 94% yield) and the optical purity was determined to be 95% ee.

Notes: 1) A 7% yield of 2-((4-methoxyphenyl)imino)-1,2-diphenylethan-1-one was observed in this reaction as a by-product when air was present. 2) The product \(23s\) epimerized partially when it was left on the silica gel column over night: the ee dropped from 98% to 82%. 3) Recrystallization from 20:1 hexanes:EtOAc improved the ee from 95% to >99% with 82% recovery.

\((S)-1,2\text{-dicyclohexyl-2-((4-methoxyphenyl)amino)ethan-1-one (22t).}\)

The rearrangement of \(22t\) (0.0510 g, 0.154 mmol) was carried out with procedure 4 with the exception that the reaction temperature was 80 °C. After 2 h, the reaction afforded the product \((S)-23t\) as a pale yellow solid (97%, 0.0495 g, 0.150 mmol); mp = 103-106 °C. The optical purity was determined to be 94% ee by Chiralcel OD-H column, 99:1 Hexane:iPrOH, 1 mL/min flow rate, 245 nm, 3.8 min for the minor peak and 4.2 min for the major peak; \(R_t=0.10\) in CHCl₃. Spectral data for \((S)-23t\): \(^1\)H NMR (CDCl₃, 500 MHz) δ 1.07-1.43 (m, 11H), 1.57-1.76 (m, 10H), 2.53 (tt, \(J = 11.0, 3.5\) Hz, 1H), 3.72 (s, 3H), 3.85 (d, \(J = 5.0\) Hz, 1H), 4.11 (br s, 1H), 6.57 (d, \(J = 8.5\) Hz, 2H), 6.73 (d, \(J = 8.5\) Hz, 2H); \(^{13}\)C NMR (CDCl₃, 125 MHz) δ 25.35, 25.71, 25.90, 26.07, 26.17, 26.31, 27.68, 28.15, 29.08, 30.77, 40.54, 48.30, 55.70, 68.52, 114.74, 115.37, 142.39, 152.32, 215.02. IR (thin film) 3391br m, 2930s, 2855s, 1705s, 1512s, 1450m, 1238s, 1039m cm⁻¹. HRMS (ESI-TOF) \(m/z\) found 330.2436 [(M+H)⁺; calcd. 330.2433 for \(C_{21}H_{32}NO_2\)]; \([\alpha]^{20}_D = +30.0°\) (c = 1.0, CH₂Cl₂) on 94% ee.
ethyl (R)-4-((2-oxo-1,2-diphenylethyl)amino)benzoate (23u).

Following procedure 4 with (S)-15 and the imine 22u (0.0448 g, 0.125 mmol) this reaction was complete in 30 min and afforded the product (R)-23u as a white solid (88%, 0.0394 g, 0.110 mmol); mp = 145-147 °C. The optical purity was determined to be 96% ee by Chiralcel OD-H column, 90:10 Hexane:iPrOH, 1 mL/min flow rate, 287 nm, 9.1 min for the minor peak and 31.3 min for the major peak.

Spectral data for (R)-23u: \( ^1H \) NMR (CDCl\(_3\), 500 MHz) \( \delta 1.34 (t, J = 7.0 \text{ Hz}, 3H), 4.30 (q, J = 7.0 \text{ Hz}, 2H), 5.92 \) (br s, 1H), 6.08 (s, 1H), 6.65 (dt, \( J = 9.0, 2.5 \text{ Hz}, 2H \)), 7.22 (tt, \( J = 7.5, 2.0 \text{ Hz}, 1H \)), 7.30 (tt, \( J = 7.5, 2.0 \text{ Hz}, 2H \)), 7.46 (t, \( J = 7.5 \text{ Hz}, 4H \)), 7.56 (tt, \( J = 7.5, 2.0 \text{ Hz}, 2H \)), 7.84 (dt, \( J = 8.5, 2.0 \text{ Hz}, 2H \)), 8.02 (d, \( J = 7.5 \text{ Hz}, 2H \)); \( ^13C \) NMR (CDCl\(_3\), 125 MHz) \( \delta 14.43, 60.21, 61.96, 112.35, 119.33, 128.07, 128.36, 128.76, 128.93, 129.19, 131.43, 133.79, 134.57, 136.88, 149.53, 166.70, 196.02; IR (thin film) 3393brs, 3066m, 2926s, 1686s, 1606s, 1525s, 1448m, 1278s, 1174s, 1105s cm\(^{-1}\); HRMS (ESI-TOF) m/z found 360.1606 [(M+H)+]; calcd. 360.1600 for C\(_{23}\)H\(_{22}\)NO\(_3\); [\( \alpha \)]\(_{20}^D\) = –137.5° (c = 1.0, CH\(_2\)Cl\(_2\)) on 96% ee.

(S)-2-(((3-(((tert-butyldimethylsilyl)oxy)methyl)phenyl)amino)-1,2-diphenylethan-1-one (23v).

Following procedure 4 with imine 22v (0.0470 g, 0.1 mmol), this reaction afforded the product (S)-23v as a pale yellow liquid (91%, 0.0430 g, 0.09 mmol). The optical purity was determined to be 97% ee by (R, R)-WHELK-O1 column, 97:3 Hexane:iPrOH, 1 mL/min flow rate, 245 nm, 9.0 min for the major peak and 10.5 min for the minor peak. Spectral data for (S)-23v: \( ^1H \) NMR (CDCl\(_3\), 500 MHz) \( \delta 0.07 (s, 6H), 0.94 (s, 9H), 4.64 (s, 2H), 5.42 (d, \( J = 6.0 \text{ Hz}, 1H \)), 6.05 (d, \( J = 6.0 \text{ Hz}, 1H \)), 6.56 (d, \( J = 8.0 \text{ Hz}, 1H \)), 6.63 (d, \( J = 8.0 \text{ Hz}, 1H \),
1H), 6.70 (s, 1H), 7.09 (t, J = 8.0 Hz, 1H), 7.18-7.19 (m, 1H), 7.20-7.29 (m, 3H), 7.42-7.46 (m, 3H), 7.54 (t, J = 8.0 Hz, 1H), 8.00 (d, J = 9.0 Hz, 2H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) δ 5.23, 18.45, 26.01, 62.68, 64.99, 111.03, 112.09, 115.55, 128.05, 128.09, 128.67, 128.87, 129.02, 129.04, 133.49, 135.06, 137.74, 142.58, 146.18, 197.10; IR (neat) 3404s, 3061m, 2955s, 2928s, 2858s, 1688s, 1608s, 1491s, 1323m, 1253s, 1178m, 1101s, 1076s cm\(^{-1}\); HRMS (ESI-TOF) m/z found 432.2362 [(M+H)+]; calcd. 432.2359 for C\(_{27}\)H\(_{34}\)NO\(_2\)Si; [\(\alpha\)]\(_{20}^D\) = +90.8° (c = 1.0, CH\(_2\)Cl\(_2\)) on 97% ee.

(S)-2-(benzylamino)-1,2-diphenylethan-1-one (23w)

\[
\begin{align*}
\text{22w} & \quad \text{2.5 mol\%} \quad (S)-15 \quad \text{toluene, 120 °C, 2 h} \quad \text{23w} \\
\text{H} & \quad \text{N} & \quad \text{OH} \\
\text{Bn} & \quad \text{NH} & \quad \text{Bn}
\end{align*}
\]

The rearrangement of 22w (0.0300 g, 0.100 mmol) was performed following general procedure 4 with two exceptions: 1. The reaction conditions were 120 °C for 2 h under N\(_2\) atmosphere (reaction was done in a Schlenk flask because the product was not stable at 120 °C in presence of air). 2. The workup and purification was as follows: hexanes (5 mL) was added to precipitate the catalyst after the reaction mixture was cooled to room temperature, and then the solid was removed by filtering through filter paper. The filtrate was concentrated by rotary vaporization and the residue was subjected to column chromatography with 8:1 to 4:1 hexane:EtOAc. The reaction afforded the product (R)-23w (0.0285 g, 0.095 mmol, 95%) as a white semi-solid. The optical purity was determined to be 10% ee with (R, R) WHELK-O1 column, 95:5 hexane::iPrOH, 1 mL/min, 245 nm, 16.2 min for the major peak and 18.0 min for the minor peak. \(^1\)H NMR (CDCl\(_3\), 500 MHz) δ 2.74 (br s, 1H), 3.76 (s, 2H), 5.31 (s, 1H), 7.26-7.28 (m, 2H), 7.32-7.39 (m, 10H), 7.49 (tt, J = 7.5, 1.5 Hz, 1H), 7.90 (dd, J = 8.0, 1.0 Hz, 2H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) δ 51.01, 66.23, 127.07, 127.98, 128.24, 128.38, 128.42, 128.53, 128.69, 129.04, 133.16, 135.68, 138.24, 139.73, 198.92. [\(\alpha\)]\(_{20}^D\) = −2.5° (c = 1.0, CH\(_2\)Cl\(_2\)) on 10% ee. The \(^1\)H NMR and \(^{13}\)C NMR data are in partial agreement with literature.\(^6\)

Note: No rearrangement of 22w was observed at 80 °C after 19 h. The \(^1\)H NMR spectrum of the crude reaction mixture showed only the presence of the starting imine 22w and the presence of aldehyde 21a resulting from partial hydrolysis of 22w. The presence of (R)-23w was not detected. This is to be
compared with the rearrangement of 22a at 120 °C which gave 23a in 96% yield and 95% ee (See Section 12).

6. Procedure for the α-Iminol Rearrangement of in-situ Generated Imines.

\[
\begin{align*}
&\text{H}^+ - \text{C}^\equiv\text{N} - \text{Ph} - \text{t-Bu} + \text{NH}_2 \\
&\text{21j} \quad \text{1.1 equiv.} \\
&\text{toluene, 60 °C, 1 h} \\
&\rightarrow \text{Ph} = \text{O} - \text{NH} - \text{Ph} - \text{t-Bu} \\
&\text{23j}
\end{align*}
\]

To a 20 mL vial was added aldehyde 21i (0.0332 g, 0.102 mmol, 1 equiv), toluene 0.25 mL, (S)-15 catalyst solution (0.5 mL) prepared in section 4 and aniline (10 µL, 0.11 mmol, 1.1 equiv). The vial was capped and heated under air in a 60 °C oil bath for 1 h. Thereafter, the solution was cooled to room temperature and subjected to column chromatography on silica gel with 2:1 CHCl₃:hexanes as eluent. The reaction afforded the product (R)-23i as a light yellow solid (0.0400 g, 0.100 mmol, 98% yield). mp = 132-135 °C; The optical purity was determined to be >99%. The Chiral HPCL conditions were identical to that described in section 5 for (S)-23i; ¹H NMR and ¹³C NMR data were identical to that described in section 5 for (S)-23i; [α]²⁰D = –84.0° (c = 1.0, CH₂Cl₂).

7. Determination of the Absolute Stereochemistry of the Product 23a.

\[
\begin{align*}
&\text{Na}_2\text{CO}_3 \\
&1.5 \text{ equiv} \\
&\text{H}_2\text{O} \\
&\rightarrow \text{2 equiv PhB(OH)}_2 \\
&10 \text{ mol % Cu(OAc)}_2\cdot\text{H}_2\text{O} \\
&4 \text{ Å MS, CH}_2\text{Cl}_2 \quad \text{reflux, air} \\
&\rightarrow \text{Ph} - \text{CO}_2\text{Me} \\
&\text{NHPh} \\
&\text{(R)-31}
\end{align*}
\]

*Methyl-(R)-2-phenyl-2-(phenylamino)acetate 31*: To a 20 mL vial was added (R)-2-phenylglycine methyl ester hydrochloride (2.01 g, 10.0 mmol, 1 equiv) and Na₂CO₃ solution (2M, 7.5 mL, 15 mmol, 1.5 equiv) and 5 mL ether. The resulting mixture was stirred at room temperature for 10 min. The aqueous layer was extracted with EtOAc (5 mL x 3), and the combined organic layer was washed with brine, dried over
MgSO₄, filtered through filter paper in a Büchner funnel and concentrated under rotary evaporation. The crude amino ester was used in the next step without purification.

The following coupling reaction was done according to a literature procedure.⁷ To a three-necked round bottom flask equipped with a condenser was added copper(II) acetate monohydrate (0.11 g, 0.5 mmol, 10 mol%), 4 Å molecular sieves (3.05 g), PhB(OH)₂ (1.28 g, 10 mmol, 2 equiv.), and 40 mL CH₂Cl₂. The resulting mixture was stirred at room temperature for 5 min and then the crude amino ester (0.85 g, 5 mmol, 1 equiv.) was added. The two open necks were sealed by septa. A gentle air flow was introduced via a needle attached to one of the septa. The mixture was heated to reflux for 14 h, then cooled to room temperature, filtered through filter paper in Büchner funnel. The filtrate was concentrated under rotary evaporation. The product was purified by column chromatography on silica gel with 10:1 hexanes:EtOAc as eluent. The reaction afforded the product (R)-31 as a white solid (23%, 0.29 g, 2.3 mmol); mp = 51-52 °C; Rᵣ=0.45 in 4:1 hexanes:EtOAc. Spectral data for (R)-31: ¹H NMR (CDCl₃, 500 MHz) δ 3.73 (s, 3H), 5.08 (s, 1H), 5.39 (br s, 1H), 6.59 (d, J = 7.5 Hz, 2H), 6.72 (t, J = 7.5 Hz, 1H), 7.12 (tt, J = 7.5, 2.0 Hz, 2H), 7.30 (tt, J = 7.5, 2.0 Hz, 1H), 7.35 (tt, J = 7.5, 2.0 Hz, 2H), 7.49 (dt, J = 7.5, 2.0 Hz, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 52.85, 60.74, 113.42, 118.14, 127.26, 128.33, 128.89, 129.25, 137.57, 145.87, 172.31; [α]²⁰D = -93.8° (c = 1.0, CHCl₃), [lit.⁸ -20.2° (c = 1.0, CHCl₃) on 30% ee, and lit.⁹ +68.3° (c = 0.32, THF) on 98% ee for the (S)-enantiomer]. The ¹H NMR data are in agreement with the literature data.⁸

(R)-N-Methoxy-N-methyl-2-phenyl-2-(phenylamino)acetamide 32: To a 10 mL flame-dried round bottom flask was added N,O-dimethylhydroxylamine hydrochloride (0.10 g, 1.04 mmol, 2.5 equiv) and 2 mL THF at -45 °C in an acetonitrile dry ice bath for 5 min under a N₂ atmosphere. Then iPrMgCl (2M in THF, 1.04 mL, 2.08 mmol, 5 equiv) was added dropwise and stirred at the same temperature for 10 min. Then methyl (R)-2-phenyl-2-(phenylamino)acetate 31 (0.10 g in 1 mL THF, 0.41 mmol, 1 equiv) was added
dropwise via a syringe. The resulting mixture was kept at –45 °C for another 1 h before being quenched with saturated NH₄Cl solution. The solution was warmed up to room temperature, and extracted with EtOAc (5 mL x 3), dried over MgSO₄, filtered through filter paper in Büchner funnel and concentrated via rotary evaporation. The product was purified by column chromatography on silica gel with 4:1 to 2:1 hexanes:EtOAc as eluent. The reaction afforded the product (R)-32 as a yellow liquid (64%, 0.0722 g, 0.262 mmol); Rț=0.05 in 4:1 hexanes:EtOAc. Spectral data for (R)-32: ¹H NMR (CDCl₃, 500 MHz) δ 3.21 (s, 3H), 3.52 (s, 3H), 5.33 (br s, 1H), 5.51 (s, 1H), 6.66-6.71 (m, 3H), 7.13 (tt, J = 7.5, 2.0 Hz, 2H), 7.28 (tt, J = 7.5, 2.0 Hz, 1H), 7.35 (tt, J = 7.5, 2.0 Hz, 1H), 7.49 (dt, J = 7.5, 2.0 Hz, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 32.49, 57.73, 61.19, 113.64, 117.91, 127.92, 127.99, 128.71, 129.19, 138.40, 146.15 (the amide carbon was not located); [α]₂₀^D = −151.8° (c = 0.71, CH₂Cl₂). These NMR data are in agreement with the literature data.¹⁰

(R)-1,2-diphenyl-2-(phenylamino)ethan-1-one 23a: To a 10 mL flame-dried round bottom flask was added the Weinreb amide (R)-32 prepared above (0.0581 g, 0.21 mmol, 1 equiv) and 1 mL THF. The resulting solution was cooled to 0 °C for 5 min in an ice bath and then PhMgCl (2M in THF, 0.31 mL, 0.63 mmol, 3 equiv.) was added dropwise via a syringe. The resulting mixture was kept at 0 °C for 15 min before being quenched with saturated NH₄Cl solution. The solution was warmed up to room temperature, and extracted with EtOAc (5 mL x 3), dried over MgSO₄, filtered through filter paper in Büchner funnel and concentrated under rotary evaporation. The crude product was purified by column chromatography on silica gel with 1:1 hexanes:CHCl₃ as eluent. The reaction afforded the product (R)-23a as a yellow solid (65%, 0.0402 g, 0.137 mmol); mp = 76-81 °C. The ¹H and ¹³C NMR data were identical to the product (S)-23a from the rearrangement reaction of 22a in section 5.4. The optical purity was determined to be 90% ee by Chiralcel OD-H column, 97:3 Hexane:iPrOH, 1 mL/min flow rate, 245 nm, 11.4 min for the major peak and 18.9 min for the minor peak; [α]₂₀^D = −116.8° (c = 1.0, CH₂Cl₂) on 90% ee. The configuration of this compound is opposite to that of the product 23a obtained from the rearrangement using catalyst (R)-15.
8. Synthesis of Amino Alcohols from Amino Ketones.

\[
\text{(S)-23s} \quad \text{95% ee} \quad \text{H}_2\text{CO} \quad \text{NH} \quad \text{O} \quad \text{THF, } -78^\circ\text{C}, 15 \text{ min} \quad \text{Super-H} \\
\text{2 equiv } \quad \text{80% yield } \quad \text{92% ee } \quad >50:1 \text{ anti:syn} \quad \text{H}_2\text{CO} \quad \text{NH} \quad \text{OH} \quad \text{(1S,2R)-25} \quad \text{ee improved to >99% by crystallization with 87% recovery}
\]

\text{(1S,2R)-2-((4-methoxyphenyl)amino-1,2-diphenylethan-1-ol 25}: To a 10 mL flame-dried round bottom flask was added the amino ketone \text{(S)-23s} (0.0756 g, 0.24 mmol, 1 equiv, 95% ee) and 2 mL THF. The solution was cooled to \(-78^\circ\text{C}\) in dry ice/acetone bath for 5 min under a \text{N}_2\text{ atmosphere and lithium triethylborohydride (0.48 mL, 1M in THF, 0.48 mmol, 2 equiv.) was added dropwise via a syringe. The resulting mixture was kept at \(-78^\circ\text{C}\) for 15 min before being quenched with saturated NH\textsubscript{4}Cl solution. The solution was then gradually warmed up to room temperature and extracted with ether (5 mL x 3), dried over MgSO\textsubscript{4}, filtered through filter paper in Büchner funnel and concentrated under rotary evaporation. The anti:syn ratio was greater than 50:1 by \textsuperscript{1}H NMR analysis of the crude reaction mixture. The product was purified by flash column chromatography on silica gel with 8:1 to 4:1 hexanes:EtOAc as eluent to afford the product 25 as a light yellow solid (80%, 0.0605 g, 0.19 mmol); mp = 115-116 °C (lit\textsuperscript{11} 121-124 °C). The optical purity was determined to be 92% ee by Chiralcel OD-H column, 95:5 Hexane:iPrOH, 1 mL/min flow rate, 220 nm, 19.3 min for the minor peak and 23.7 min for the major peak. Spectral data for (1S,2R)-25 \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500 MHz) \(\delta\) 2.51 (br s, 1H), 3.68 (s, 3H), 4.24 (br s, 1H), 4.61 (d, \(J = 4.5\) Hz, 1H), 5.05 (d, \(J = 4.5\) Hz, 1H), 6.50 (d, \(J = 9.0\) Hz, 2H), 6.68 (d, \(J = 9.0\) Hz, 2H), 7.09-7.11 (m, 2H), 7.14-7.15 (m, 2H), 7.24-7.29 (m, 6H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 125 MHz) \(\delta\) 55.65, 64.65, 77.10, 114.67, 115.50, 126.58, 127.57, 127.90, 127.94, 128.19, 128.28, 138.67, 140.00, 140.71, 152.43; \([\alpha]_D^{20} = +50.7^\circ\) (c = 1.0, CHCl\textsubscript{3}) on 90% ee, \([\text{lit}^{11}]^+ +27.9^\circ, \text{c = 1.0, CHCl}_3, \text{on 93% ee}]\). The NMR data are in agreement with those in the literature\textsuperscript{11}

Note: The ee can be improved to >99% by crystallization from 10:1 hexanes:EtOAc with 87% recovery. Dissolution of 0.060 g product 25 (92% ee) in 1 mL EtOAc was followed by addition of 10 mL

S-48
hexanes. The clear solution was cooled in freezer at –20 °C for 1h. The white crystals were collected to give 0.052 g of 25 (87% recovery) that was >99% ee.

(S)-2-((4-methoxyphenyl)amino)-1,1,2-triphenylethanol 26: To a flame-dried 25 mL round bottom flask was added the amino ketone (S)-23s (0.0217 g, 0.068 mmol, 1 equiv, 95% ee) and 2 mL THF. The flask was sealed by a septum and a N₂ balloon was attached via a needle. The flask was cooled to 0 °C in an ice bath for 5 min. PhMgCl (2M in THF, 0.1 mL, 0.2 mmol, 3 equiv.) was added dropwise via a syringe. The resulting mixture was kept at 0 °C for 15 min then quenched with 3 mL of saturated NH₄Cl solution. The mixture was warmed up to room temperature, extracted with ether (4 mL x 2), dried over MgSO₄, filtered through filter paper in Büchner funnel and concentrated under rotary evaporation. The product was purified by column chromatography on silica gel with 16:1 to 10:1 hexanes:EtOAc as eluent to afford the product 26 as a white solid (76%, 0.0206 g, 0.0517 mmol); mp = 181-183 °C (lit.¹² 175-176 °C). The optical purity was determined to be 93% ee by Chiralcel OD-H column, 99:1 Hexane:iPrOH, 1 mL/min flow rate, 220 nm, 10.0 min for the minor peak and 31.2 min for the major peak. Spectral data for (S)-26: 

- NMR (CDCl₃, 500 MHz) δ 2.82 (s, 1H), 3.67 (s, 3H), 4.36 (br s, 1H), 5.21 (s, 1H), 6.39 (d, J = 9.0 Hz, 2H), 6.66 (d, J = 9.0 Hz, 2H), 7.01 (d, J = 8.5 Hz, 2H), 7.08-7.19 (m, 7H), 7.27 (t, J = 7.5 Hz, 2H), 7.34 (t, J = 7.5 Hz, 2H), 7.54 (d, J = 8.5 Hz, 2H);

- C NMR (CDCl₃, 125 MHz) δ 55.63, 65.07, 81.15, 114.68, 114.70, 125.90, 126.81, 126.91, 127.34, 127.39, 127.77, 127.91, 128.38, 128.72, 138.12, 140.85, 143.96, 144.72, 152.00; [α]²⁰ D = +196.1° (c = 1.0, CH₂Cl₂) on 93% ee. The NMR data are in agreement with those reported for the racemic compound;¹²

Note: The ee can be improved to >99% by crystallization from 10:1 hexanes:EtOAc with 82% recovery. A sample of 26 (0.0400 g, 93% ee) was dissolved in 1 mL EtOAc followed by addition of 10 mL
hexanes. The clear solution was cooled in freezer at –20 °C for 1 h. White crystals were collected to give 0.0328 g of 26 that was 82% recovery and >99% ee.

\[(S)-\text{N-}(4\text{-methoxyphenyl})\text{-N-}(2\text{-oxo-1,2-diphenylethyl})\text{acetamide 33:}\]

To a flame-dried 25 mL round bottom flask was added the amino ketone \((S)-23s\) (0.20 g, 0.64 mmol, 1 equiv, 95% ee) and 10 mL THF. The flask was sealed by a septum and a N\(_2\) balloon was attached via a needle. Acetyl chloride (65 µL, 0.95 mmol, 1.5 equiv.) was added dropwise via a syringe. The mixture was stirred at room temperature for 30 min and then quenched with 3 mL saturated Na\(_2\)CO\(_3\) solution. The aqueous layer was extracted with ether (5 mL x 2), and the combined organic layer was dried over MgSO\(_4\), filtered through filter paper in Büchner funnel and concentrated by rotary evaporation. The product was purified by flash column chromatography on silica gel with 4:1 to 2:1 hexanes:EtOAc as eluent to afford the product \((S)-33\) as a pale light yellow solid (75%, 0.17 g, 0.48 mmol); Rf = 0.05 in 4:1 hexanes:EtOAc; mp = 123-125 °C. Spectral data for \((S)-33:\)

\[\text{\textbf{1H NMR (CDCl}_3, 500 MHz) \delta 1.89 (s, 3H), 3.73 (s, 3H), 6.66 (br s, 3H), 7.01-7.03 (m, 2H), 7.10-7.13 (m, 3H), 7.18 (s, 1H), 7.35 (t, J = 7.5 Hz, 2H), 7.46 (t, J = 7.5 Hz, 1H), 7.94 (d, J = 7.5 Hz, 2H) (1 proton was not located); \textbf{13C NMR (CDCl}_3, 125 MHz) \delta 23.14, 55.28, 66.31, 113.67, 128.30, 128.43, 128.63, 128.84, 130.79, 131.84, 132.82, 132.91, 133.73, 135.57, 158.71, 171.39, 196.35; IR (thin film) 3063m, 2932m, 1695s, 1653s, 1516s, 1383m, 1248s, 1032m cm\(^{-1}\); HRMS (ESI-TOF) m/z found 360.1510 [(M+H)\(^+\)]; calcd. 360.1600 for C\(_{23}\)H\(_{22}\)NO\(_3\); [\(\alpha\)]\(_D\)\(^{20}\) = +169.6° (c = 1.0, CH\(_2\)Cl\(_2\)).
(1S,2S)-2-((4-methoxyphenyl)amino)-1,2-diphenylethan-1-ol 27: To a flame-dried 10 mL round bottom flask was added the acylated amino ketone (S)-33 (0.17g, 0.47 mmol, 1 equiv) prepared above and 5 mL THF. The solution was cooled in an ice bath for 5 min under a N₂ atmosphere and lithium triethylborohydride (1.9 mL, 1M in THF, 1.90 mmol, 4 equiv) was added dropwise via a syringe. The resulting mixture was stirred in an ice bath for 30 min before being quenched with 4 mL saturated NH₄Cl solution. The solution was then gradually warmed up to room temperature, and extracted with ether (5 mL x 3), dried over MgSO₄, filtered through filter paper in a Büchner funnel and concentrated under rotary evaporation. The product was subjected to the next step without purification. The crude product was transferred to a 25 mL Schlenk flask with 5 mL MeOH and KOH (0.078 g, 1.4 mmol, 3 equiv) was added. The flask was sealed and heated in a 65 °C oil bath for 30 min. Thereafter the solution was cooled to room temperature, which was followed by addition of 5 mL water. The mixture was extracted with ether (5 mL x 3). The syn:anti ratio was greater than 50:1 by ¹H NMR analysis of the crude reaction mixture. The combined ether layer was washed with brine and dried over MgSO₄, filtered through filter paper in a Büchner funnel and concentrated with rotary evaporation. The product was purified by silica gel column chromatography with 4:1 hexane:EtOAc as eluent to afford the product (1S,2S)-27 as a white solid (70% over two steps, 0.10 g, 0.32 mmol). The optical purity was determined to be 92% ee by Chiralcel OD-H column, 95:5 Hexane:iPrOH, 1 mL/min flow rate, 220 nm, 18.7 min for the major peak and 22.6 min for the minor peak. Spectral data for (1S,2S)-27: ¹H NMR (CDCl₃, 500 MHz) δ 2.90 (br s, 1H), 3.69 (s, 3H), 4.23 (br s, 1H), 4.42 (d, J = 7.0 Hz, 1H), 4.82 (d, J = 6.5 Hz, 1H), 6.53 (d, J = 9.0 Hz, 2H), 6.68 (d, J = 9.0 Hz, 2H), 7.17-7.18 (m, 2H), 7.22-7.28 (m, 8H); ¹³C NMR (CDCl₃, 125 MHz) δ 55.70, 66.17, 78.13, 114.64, 115.75, 126.70, 127.35, 127.46, 127.83, 128.17, 128.47, 140.21, 140.58, 141.30, 152.49; [α]D²⁰ = −35.5° (c = 0.9, CH₂Cl₂) on 92% ee (lit 13 +30.7 (c=1, CHCl₃) on 78% ee (1R,2R)-27). The NMR data are in agreement with those reported in the literature.¹³
Note: The ee can be improved to >99% by crystallization from 15:1 hexanes:EtOAc with 92% recovery. A sample of product 27 (92% ee, 0.10 g) was dissolved in 1 mL EtOAc and this was followed by addition of 15 mL hexanes. The clear solution was cooled in freezer at –20 °C for 1 h. White crystals were collected to give 0.092 g 27 that was a 92% recovery and >99% ee.

9. Crystal Structure of the Zirconium Catalyst 28.

A slurry of catalyst (S)-15 was generated from a 1:2:1 mixture of Zr(OiPr)_4(HOiPr), (S)-VANOL and N-methylimidazole in toluene as described in section 4 and was subjected to high vacuum to remove all volatiles. Then 1 mL of bromobenzene was added and the mixture was heated in a 100 °C oil bath for 5-10 min to dissolve the solids. After all solids were dissolved, the solution was allowed to very slowly cool to room temperature and the crystals that formed were subjected to analysis. An X-ray diffraction study revealed the presence of a homoleptic zirconium atom with three VANOL ligands consisting of a six-coordinate dianionic zirconium hexa-aryloxide that was charged balanced with two protonated N-methylimidazoles. The unit cell contains two zirconium centers and seven molecules of the bromobenzene solvent. The ratio of zirconium:VANOL:NMI was 1:3:2 instead of 1:2:1 in the solution from which the crystals were grown. Therefore, a second sample of crystals was prepared from a 1:3:2 mixture of Zr(OiPr)_4(HOiPr), (S)-VANOL and N-methylimidazole and X-ray analysis gave an identical unit cell to that above. These crystals did not melt up to 300 °C. At around 220 °C the color started to darken from light yellow to brown, and at around 260 °C the color become black. The hydrogens on the protonated imidazolium were located but the hydrogens on the water molecules in the unit cell were not located and were added at reasonable positions. This crystal structure has been deposited with the Cambridge Crystallographic Data Centre CCDC 1010777.
Figure 1. pdb structure of the molecules in the unit cell of the zirconium catalyst 28.
Table 1. Crystal data and structure refinement for 28.

| Description                          | Value                                |
|--------------------------------------|--------------------------------------|
| Identification code                  | wulff01                              |
| Empirical formula                    | C122 H92 Br3 N4 O7.50 Zr             |
| Formula weight                       | 2064.94                              |
| Temperature                          | 100(2) K                             |
| Wavelength                           | 1.54178 Å                            |
| Crystal system                       | Monoclinic                           |
| Space group                          | P 21                                 |
| Unit cell dimensions                 | a = 21.1863(13) Å, b = 19.5848(13) Å, c = 24.2104(15) Å |
| Volume                               | 9844.5(11) Å³                        |
| Z                                     | 4                                    |
| Density (calculated)                 | 1.393 Mg/m³                          |
| Absorption coefficient               | 2.832 mm⁻¹                           |
| F(000)                               | 4228                                 |
| Crystal size                         | 0.240 x 0.100 x 0.080 mm³            |
| Theta range for data collection      | 2.128 to 68.432°                     |
| Index ranges                         | -25 <= h <= 24, -23 <= k <= 23, -28 <= l <= 29 |
| Reflections collected                | 151698                               |
| Completeness to theta = 66.000°      | 100.0 %                              |
| Absorption correction                | Multi-scan                           |
| Refinement method                    | Full-matrix least-squares on F²      |
| Data / restraints / parameters       | 35613 / 1 / 2452                     |
| Goodness-of-fit on F²                | 1.023                                |
| Final R indices [I > 2sigma(I)]      | R1 = 0.0625, wR2 = 0.1753            |
| R indices (all data)                 | R1 = 0.0649, wR2 = 0.1793            |
| Absolute structure parameter         | 0.005(2)                             |
| Extinction coefficient               | n/a                                  |
| Largest diff. peak and hole          | 2.392 and -1.786 e.Å⁻³               |
Table 2. Atomic coordinates ($x \times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for wulff01. U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

|       | x         | y         | z         | U(eq)     |
|-------|-----------|-----------|-----------|-----------|
| Zr(1) | 9588(1)   | 5166(1)   | 1402(1)   | 27(1)     |
| Zr(2) | 6766(1)   | 4978(1)   | 5445(1)   | 28(1)     |
| Br(1) | 14037(1)  | 2412(1)   | 1550(1)   | 61(1)     |
| Br(2) | 7739(1)   | 9768(1)   | 3675(1)   | 86(1)     |
| Br(3) | 5216(1)   | 4978(1)   | 5445(1)   | 108(1)    |
| Br(4) | 4065(1)   | 7111(1)   | 126(1)    | 126(1)    |
| Br(5) | 4429(2)   | 5440(3)   | 1838(2)   | 279(3)    |
| Br(6) | 6322(3)   | 9967(2)   | 1269(2)   | 304(4)    |
| O(1S) | 9687(3)   | 6993(3)   | 552(2)    | 45(1)     |
| O(2S) | 6367(3)   | 3326(3)   | 6439(3)   | 53(1)     |
| O(3S) | 8687(3)   | 4799(4)   | 5214(3)   | 58(2)     |
| O(1C) | 8667(2)   | 5538(2)   | 1124(2)   | 33(1)     |
| O(1F) | 5872(2)   | 4502(3)   | 5358(2)   | 34(1)     |
| O(1E) | 7705(2)   | 5373(2)   | 5588(2)   | 31(1)     |
| O(2A) | 9967(2)   | 5638(2)   | 1124(2)   | 33(1)     |
| O(2B) | 6769(2)   | 3408(2)   | 5358(2)   | 34(1)     |
| O(2C) | 8667(2)   | 4512(2)   | 5367(3)   | 32(1)     |
| N(1A) | 8796(4)   | 7732(4)   | 1385(3)   | 52(2)     |
| N(1B) | 7955(2)   | 4073(2)   | 5874(2)   | 32(1)     |
| N(1C) | 9393(2)   | 2411(2)   | 983(2)    | 30(1)     |
| N(1F) | 8367(3)   | 4799(4)   | 5214(3)   | 58(2)     |
| O(1S) | 8687(3)   | 4799(4)   | 5214(3)   | 58(2)     |
| O(2S) | 6367(3)   | 3326(3)   | 6439(3)   | 53(1)     |
| O(3S) | 8687(3)   | 4799(4)   | 5214(3)   | 58(2)     |
| O(1C) | 8667(2)   | 5538(2)   | 1124(2)   | 33(1)     |
| O(1F) | 6769(2)   | 4512(2)   | 5367(3)   | 32(1)     |
| O(1E) | 8667(2)   | 4512(2)   | 5367(3)   | 32(1)     |
| O(2A) | 9967(2)   | 5638(2)   | 1124(2)   | 33(1)     |
| O(2B) | 6769(2)   | 3408(2)   | 5358(2)   | 34(1)     |
| N(2A) | 9593(3)   | 8932(3)   | 1168(3)   | 34(1)     |
| N(2B) | 8367(3)   | 4799(4)   | 5214(3)   | 58(2)     |
| N(2C) | 8687(3)   | 4799(4)   | 5214(3)   | 58(2)     |
| N(2D) | 7705(2)   | 5373(2)   | 5588(2)   | 31(1)     |
| C(1D) | 7733(3)   | 3408(3)   | 5367(3)   | 30(1)     |
| C(1E) | 8667(3)   | 3547(3)   | 1406(3)   | 29(1)     |
| C(1A) | 11089(3)  | 5011(3)   | 1633(3)   | 31(1)     |
| C(1F) | 5659(3)   | 4900(3)   | 6447(3)   | 32(1)     |
| C(1C) | 8586(3)   | 6729(4)   | 1279(3)   | 32(1)     |
| C(1B) | 11089(3)  | 5011(3)   | 1633(3)   | 31(1)     |
| C(2A) | 6769(3)   | 6229(3)   | 4667(3)   | 31(1)     |
| C(2F) | 6290(3)   | 5148(3)   | 6547(2)   | 30(1)     |
| C(2C) | 8476(3)   | 6165(3)   | 935(3)    | 33(1)     |
| C(2B) | 8411(3)   | 3861(3)   | 945(3)    | 29(1)     |
| C(2D) | 7640(3)   | 3729(3)   | 5857(3)   | 30(1)     |
| C(3A) | 11528(3)  | 4986(4)   | 2168(3)   | 34(1)     |
| C(3E) | 6453(4)   | 6312(3)   | 4095(3)   | 34(1)     |
| C(3F) | 6680(3)   | 5118(3)   | 7106(3)   | 33(1)     |
| C(3C) | 8095(3)   | 6220(4)   | 376(3)    | 33(1)     |
| C(3D) | 8102(3)   | 3652(3)   | 6373(3)   | 33(1)     |
C(3B)  8426(3) 3812(3) 393(3) 34(1)  
C(4A)  11354(4) 4676(4) 2639(3) 37(1)  
C(4E)  5838(3) 6021(4) 3885(3) 39(2)  
C(4C)  7863(5) 5640(4) 58(3) 37(1)  
C(4D)  7981(4) 3895(4) 6894(3) 36(1)  
C(4B)  8629(4) 4050(4) -91(3) 36(1)  
C(4F)  7291(3) 5429(4) 7222(3) 34(1)  
C(5A)  11797(4) 4612(4) 3144(3) 42(2)  
C(5E)  5530(4) 6108(4) 3330(3) 43(2)  
C(5D)  8418(4) 3802(4) 7757(3) 40(2)  
C(5B)  8219(4) 3996(4) -91(3) 36(1)  
C(5C)  7863(3) 5640(4) 58(3) 37(1)  
C(5F)  7863(4) 3895(4) 6894(3) 36(1)  
C(6B)  7613(4) 3707(4) -91(3) 44(2)  
C(6A)  12421(4) 4860(4) 3184(3) 45(2)  
C(6F)  7433(4) 5049(5) 7222(3) 45(2)  
C(6E)  5831(4) 6492(5) 2966(3) 51(2)  
C(6D)  8999(4) 3451(4) 7757(3) 40(2)  
C(6C)  7324(4) 6349(5) -91(3) 44(2)  
C(7B)  7408(4) 3469(4) -91(3) 42(2)  
C(7A)  12601(3) 5167(4) 2733(3) 40(2)  
C(7F)  6843(4) 4756(4) 8085(3) 44(2)  
C(7D)  9136(4) 3219(4) 6894(3) 39(2)  
C(7E)  6420(4) 6770(5) 2966(3) 51(2)  
C(7C)  7549(4) 6926(4) -91(3) 44(2)  
C(8B)  7820(3) 3507(4) -91(3) 34(1)  
C(8A)  12163(3) 5236(4) 2215(3) 36(1)  
C(8F)  6445(3) 4780(4) 7542(3) 37(1)  
C(8C)  7925(3) 6880(4) 144(3) 36(1)  
C(8E)  6752(4) 6695(4) 3719(3) 38(2)  
C(9B)  8686(3) 3313(3) 6373(3) 34(1)  
C(9A)  12330(3) 5544(4) 1735(3) 36(1)  
C(9F)  6445(3) 4780(4) 7542(3) 37(1)  
C(9C)  7925(3) 6880(4) 144(3) 36(1)  
C(9E)  6752(4) 6695(4) 3719(3) 38(2)  
C(10B) 8035(3) 3262(3) 1353(3) 35(1)  
C(10A) 11922(3) 5543(3) 1220(3) 33(1)  
C(10F) 8035(3) 3262(3) 1353(3) 35(1)  
C(10C) 8424(3) 7397(4) 1041(3) 35(1)  
C(10D) 8424(3) 7397(4) 1041(3) 35(1)  
C(10E) 7662(3) 6913(3) 4491(3) 31(1)  
C(11C) 9137(3) 3490(3) 1963(3) 29(1)  
C(11B) 9137(3) 3490(3) 1963(3) 29(1)  
C(11F) 5212(3) 5072(3) 5904(3) 32(1)  
C(11E) 7646(3) 6585(3) 5495(3) 30(1)  
C(11A) 10914(3) 5071(3) 579(2) 30(1)  
C(11D) 7191(3) 3315(4) 4873(3) 32(1)  
C(11B) 9137(3) 3490(3) 1963(3) 29(1)  
C(11F) 5212(3) 5072(3) 5904(3) 32(1)  
C(11E) 7646(3) 6585(3) 5495(3) 30(1)  
C(11A) 10914(3) 5071(3) 579(2) 30(1)  
C(11D) 7191(3) 3315(4) 4873(3) 32(1)  
C(11B) 9137(3) 3490(3) 1963(3) 29(1)
| C(12E) | 7872(3) | 6002(3) | 5796(3) | 29(1) |
|--------|---------|---------|---------|-------|
| C(12A) | 10281(3) | 5310(3) | 403(3) | 28(1) |
| C(13D) | 6449(4) | 3763(4) | 4035(3) | 38(2) |
| C(13B) | 9744(3) | 4008(4) | 2834(3) | 33(1) |
| C(13C) | 9654(4) | 6438(4) | 2733(3) | 38(2) |
| C(13F) | 4885(3) | 4976(4) | 4877(3) | 39(2) |
| C(13A) | 9952(3) | 5230(4) | -180(3) | 33(1) |
| C(13E) | 8324(3) | 6051(4) | 6324(3) | 33(1) |
| C(14Q) | 9955(4) | 4588(4) | 3165(3) | 39(2) |
| C(14B) | 10300(4) | 4522(4) | 3706(3) | 47(2) |
| C(14A) | 9360(3) | 5559(4) | -382(3) | 33(1) |
| C(14D) | 6185(4) | 4315(4) | 3690(3) | 40(2) |
| C(14E) | 8620(3) | 5469(4) | 6606(3) | 37(1) |
| C(14C) | 10275(4) | 6238(4) | 2977(3) | 41(2) |
| C(15B) | 10431(4) | 3879(5) | 3944(3) | 47(2) |
| C(15D) | 5790(4) | 4203(5) | 3178(3) | 50(2) |
| C(15A) | 9060(3) | 5494(4) | -946(3) | 36(1) |
| C(15E) | 9066(4) | 5530(4) | 7096(3) | 42(2) |
| C(15F) | 4543(4) | 4848(5) | 3869(3) | 45(2) |
| C(15C) | 10515(4) | 6301(5) | 3547(3) | 48(2) |
| C(16A) | 9335(3) | 5079(4) | -1307(3) | 38(2) |
| C(16E) | 9240(4) | 6178(5) | 7333(3) | 44(2) |
| C(16B) | 10431(4) | 3879(5) | 3944(3) | 47(2) |
| C(16D) | 5790(4) | 4203(5) | 3178(3) | 50(2) |
| C(16C) | 9060(3) | 5494(4) | -946(3) | 36(1) |
| C(16F) | 9066(4) | 5530(4) | 7096(3) | 42(2) |
| C(16A) | 9335(3) | 5079(4) | -1307(3) | 38(2) |
| C(16B) | 9488(4) | 6754(5) | 3674(3) | 46(2) |
| C(16D) | 5618(4) | 3532(5) | 2996(3) | 50(2) |
| C(16C) | 9488(4) | 6754(5) | 3674(3) | 46(2) |
| C(16F) | 9488(4) | 6754(5) | 3674(3) | 46(2) |
| C(17A) | 9907(4) | 4753(4) | -1111(3) | 39(2) |
| C(17B) | 9886(3) | 3354(4) | 3070(3) | 34(1) |
| C(17D) | 9886(3) | 3354(4) | 3070(3) | 34(1) |
| C(17C) | 9488(4) | 6754(5) | 3674(3) | 46(2) |
| C(17F) | 3934(4) | 5574(5) | 4363(4) | 52(2) |
| C(17E) | 8949(3) | 6755(4) | 7080(3) | 37(2) |
| C(17B) | 9886(3) | 3354(4) | 3070(3) | 34(1) |
| C(17D) | 9886(3) | 3354(4) | 3070(3) | 34(1) |
| C(17C) | 9488(4) | 6754(5) | 3674(3) | 46(2) |
| C(17F) | 3934(4) | 5574(5) | 4363(4) | 52(2) |
| C(17E) | 8949(3) | 6755(4) | 7080(3) | 37(2) |
| C(17B) | 9886(3) | 3354(4) | 3070(3) | 34(1) |
| C(17D) | 9886(3) | 3354(4) | 3070(3) | 34(1) |
| C(17C) | 9488(4) | 6754(5) | 3674(3) | 46(2) |
| C(17F) | 3934(4) | 5574(5) | 4363(4) | 52(2) |
| C(17E) | 8949(3) | 6755(4) | 7080(3) | 37(2) |

S-57
C(21D) 8506(3) 2829(4) 4835(3) 36(1)
C(21F) 4789(4) 4238(4) 6802(3) 37(1)
C(21B) 7776(3) 3009(4) 1836(3) 40(2)
C(22A) 12785(4) 5792(4) 681(3) 45(2)
C(22E) 8491(4) 4789(4) 6802(3) 37(1)
C(22B) 7480(4) 2364(5) 1799(4) 52(2)
C(23E) 9122(5) 8068(4) 4610(4) 50(2)
C(23D) 8889(4) 4371(4) 7186(3) 41(2)
C(23B) 7480(4) 2364(5) 1799(4) 52(2)
C(24E) 9595(4) 7686(5) 4941(3) 47(2)
C(24F) 3593(4) 3594(5) 6701(4) 53(2)
C(24D) 8861(4) 2320(6) 3867(4) 55(2)
C(24B) 7187(4) 2539(7) 2691(4) 66(3)
C(25E) 9448(4) 7043(4) 5130(3) 41(2)
C(25D) 8673(4) 2988(6) 3892(4) 54(2)
C(25A) 12012(5) 6671(5) 44(2) 59(2)
C(25F) 3987(5) 3444(5) 6325(4) 55(2)
C(25C) 9255(4) 8692(4) 2108(4) 48(2)
C(26C) 9147(4) 8121(4) 1778(3) 40(2)
C(26A) 11755(4) 6322(4) 364(3) 44(2)
C(26F) 4573(4) 3773(5) 6370(3) 47(2)
C(26E) 8820(3) 6799(4) 4988(3) 37(1)
C(26D) 8469(4) 3245(4) 4359(3) 42(2)
C(26B) 7782(4) 3413(5) 2320(3) 50(2)
C(27A) 11849(3) 4371(3) 344(3) 33(1)
C(27F) 4511(3) 5783(4) 6436(3) 36(2)
C(27E) 7449(4) 7866(4) 5505(3) 38(2)
C(27B) 9142(4) 2183(4) 1886(3) 40(2)
C(27D) 7251(3) 2022(4) 5011(4) 38(2)
C(27C) 7683(4) 7027(4) 2016(4) 48(2)
C(28A) 12069(4) 4029(4) 856(3) 37(2)
C(28B) 9348(4) 2045(4) 1393(3) 42(2)
C(28E) 6779(4) 7872(5) 5316(3) 50(2)
C(28F) 4981(4) 6083(4) 6859(3) 40(2)
C(28D) 7338(4) 1985(4) 5600(4) 43(2)
C(28C) 7306(4) 6567(5) 1669(4) 51(2)
C(29A) 12682(4) 3748(4) 981(3) 43(2)
C(29D) 7585(4) 1406(4) 5893(4) 48(2)
C(29F) 4824(4) 6329(4) 7351(4) 48(2)
C(29B) 9238(4) 1414(4) 1136(3) 46(2)
C(29E) 6476(6) 8487(6) 5121(4) 65(3)
C(29C) 6657(5) 6710(8) 1461(4) 76(3)
C(30A) 13086(4) 3809(4) 599(3) 45(2)
C(30D) 7759(4) 851(4) 5596(4) 50(2)
| Atom | Bond Type | Bond Length | Error |
|------|-----------|-------------|-------|
| C(30F) | 4205(4) | 6289(5) | 7434(4) | 51(2) |
| C(30B) | 8909(5) | 914(4) | 1362(4) | 50(2) |
| C(30E) | 6835(7) | 9070(5) | 5098(4) | 75(3) |
| C(30C) | 6393(5) | 7308(8) | 1606(4) | 75(3) |
| C(31A) | 12882(4) | 4134(4) | 91(4) | 43(2) |
| C(31F) | 3725(6) | 6001(5) | 7023(4) | 48(2) |
| C(31D) | 7671(4) | 866(4) | 5028(4) | 48(2) |
| C(31B) | 8695(5) | 1040(4) | 1852(4) | 49(2) |
| C(31E) | 7488(7) | 9059(5) | 5276(4) | 67(3) |
| C(31C) | 6753(6) | 7768(7) | 1949(4) | 71(3) |
| C(31Q) | 8095(5) | 1941(6) | 7329(4) | 60(2) |
| C(32A) | 12270(4) | 4414(4) | -30(3) | 39(2) |
| C(32D) | 7419(4) | 1453(4) | 4721(3) | 43(2) |
| C(32F) | 3884(4) | 5755(4) | 6522(3) | 42(2) |
| C(32Q) | 8821(4) | 1672(4) | 2121(3) | 43(2) |
| C(32E) | 7801(5) | 8458(4) | 5481(4) | 52(2) |
| C(32C) | 7405(7) | 7631(5) | 2172(4) | 58(2) |
| C(32B) | 8122(5) | 2494(6) | 8279(5) | 64(2) |
| C(33B) | 8546(6) | 2539(6) | 8757(4) | 67(3) |
| C(34B) | 8989(4) | 1923(4) | 8184(4) | 47(2) |
| C(41A) | 8242(5) | 7442(6) | -1781(5) | 69(3) |
| C(41C) | 4781(5) | 2466(8) | 4164(4) | 75(3) |
| C(42A) | 9005(4) | 7542(4) | -840(4) | 52(2) |
| C(42C) | 4834(5) | 1999(5) | 5137(4) | 59(2) |
| C(43A) | 9505(4) | 7946(4) | -628(4) | 50(2) |
| C(43C) | 5168(5) | 2159(5) | 5655(5) | 61(2) |
| C(44A) | 9160(4) | 8238(4) | -1500(4) | 46(2) |
| C(44C) | 5450(4) | 2894(6) | 5063(4) | 57(2) |
| C(51B) | 8625(4) | 10069(6) | 3825(5) | 65(2) |
| C(51A) | 13712(4) | 2604(5) | 2218(3) | 48(2) |
| C(51C) | 5927(6) | 2279(6) | 7859(7) | 91(4) |
| C(51D) | 4922(6) | 7281(9) | -429(6) | 89(4) |
| C(52A) | 13454(4) | 2075(5) | 2479(4) | 55(2) |
| C(52B) | 9005(5) | 9902(6) | 4336(5) | 67(3) |
| C(52D) | 5079(8) | 7904(10) | -156(7) | 99(4) |
| C(52C) | 6241(6) | 2167(7) | 8417(7) | 88(4) |
| C(53A) | 13206(5) | 2217(6) | 2957(5) | 65(2) |
| C(53B) | 9657(5) | 10089(7) | 4415(6) | 77(3) |
| C(53D) | 5680(7) | 8017(10) | 132(6) | 94(4) |
| C(53C) | 6009(8) | 2500(7) | 8859(6) | 98(5) |
| C(54B) | 9875(5) | 10403(7) | 3993(6) | 78(3) |
| C(54A) | 13216(5) | 2875(6) | 3148(4) | 64(2) |
| C(54D) | 6119(7) | 7506(8) | 160(6) | 83(3) |
| C(54C) | 5471(7) | 2964(9) | 8734(7) | 92(4) |
| C(55A) | 13474(5) | 3406(5) | 2898(4) | 59(2) |
| C(55B) | 9475(6) | 10560(7) | 3493(5) | 74(3) |
| C(55D) | 5983(7) | 6873(9) | -72(6) | 92(4) |
| C(55C) | 5177(6) | 3048(7) | 8187(8) | 93(5) |
| C(56B) | 8862(5) | 10381(6) | 3402(4) | 63(2) |
| C(56A) | 13719(5) | 3258(5) | 2407(4) | 56(2) |
| C(56D) | 5337(6) | 6761(8) | -374(6) | 84(4) |
| C(51E) | 5059(5) | 4887(6) | 1645(5) | 144(9) |
| C(52E) | 5679(7) | 5140(6) | 1683(6) | 129(7) |
|          |       |       |       |       |       |
|----------|-------|-------|-------|-------|-------|
| C(53E)  | 6174(5) | 4706(9) | 1606(6) | 450(60) |       |
| C(54E)  | 6048(6) | 4018(8) | 1493(6) | 140(9) |       |
| C(55E)  | 5428(7) | 3764(5) | 1456(5) | 140(9) |       |
| C(56E)  | 4934(5) | 4199(6) | 1532(5) | 99(4)  |       |
| C(51F)  | 5446(8) | 9933(10) | 839(7) | 186(14) |       |
| C(52F)  | 5344(9) | 9906(9) | 255(8) | 189(16) |       |
| C(53F)  | 4721(11) | 9898(10) | -62(6) | 260(20) |       |
| C(54F)  | 4198(8) | 9917(12) | 206(9) | 520(70) |       |
| C(55F)  | 4300(9) | 9943(12) | 791(9) | 630(70) |       |
| C(56F)  | 4924(11) | 9951(12) | 1107(6) | 220(19) |       |
| C(53C)  | 5386(6) | 2713(7) | 7738(7) | 87(4)  |       |
| C(81)   | 7208(7) | 5329(10) | 2803(6) | 101(5) |       |
| C(82)   | 8361(6) | 5165(7) | 3222(6) | 79(3)  |       |
| C(83)   | 8717(6) | 5101(9) | 3750(6) | 93(4)  |       |
| C(84)   | 7733(5) | 5160(6) | 3831(5) | 71(3)  |       |
Table 3. Bond lengths [Å] and angles [°] for wulff01.

| Bond                  | Length  |
|-----------------------|---------|
| Zr(1)-O(2B)           | 2.047(4)|
| Zr(1)-O(1A)           | 2.066(5)|
| Zr(1)-O(1C)           | 2.066(5)|
| Zr(1)-O(2C)           | 2.082(5)|
| Zr(1)-O(2A)           | 2.114(4)|
| Zr(1)-O(1B)           | 2.128(5)|
| Zr(2)-O(1E)           | 2.058(5)|
| Zr(2)-O(1F)           | 2.059(5)|
| Zr(2)-O(2F)           | 2.084(5)|
| Zr(2)-O(2D)           | 2.086(5)|
| Zr(2)-O(2E)           | 2.099(4)|
| Zr(2)-O(1D)           | 2.102(5)|
| Br(1)-C(51A)          | 1.915(8)|
| Br(2)-C(51B)          | 1.930(9)|
| Br(3)-C(51C)          | 1.874(18)|
| Br(4)-C(51D)          | 1.919(14)|
| Br(5)-C(51E)          | 1.850(11)|
| Br(6)-C(51F)          | 1.939(17)|
| O(1C)-C(2C)           | 1.344(8)|
| O(1F)-C(2B)           | 1.316(8)|
| O(1E)-C(2E)           | 1.346(8)|
| O(1A)-C(2A)           | 1.329(8)|
| O(1D)-C(2D)           | 1.345(8)|
| O(1B)-C(2B)           | 1.344(8)|
| O(2C)-C(12C)          | 1.335(8)|
| O(2F)-C(12F)          | 1.349(8)|
| O(2A)-C(12A)          | 1.336(8)|
| O(2E)-C(12E)          | 1.350(8)|
| O(2B)-C(12B)          | 1.344(8)|
| O(2D)-C(12D)          | 1.347(9)|
| N(1A)-C(44A)          | 1.319(11)|
| N(1A)-C(42A)          | 1.357(13)|
| N(1A)-C(41A)          | 1.473(13)|
| N(1C)-C(42C)          | 1.357(13)|
| N(1C)-C(44C)          | 1.368(13)|
| N(1C)-C(41C)          | 1.448(13)|
| N(1B)-C(34B)          | 1.354(12)|
| N(1B)-C(32B)          | 1.364(13)|
| N(1B)-C(31Q)          | 1.472(13)|
| N(1F)-C(82)           | 1.291(15)|
| N(1F)-C(84)           | 1.375(15)|
| N(1F)-C(81)           | 1.487(17)|
| N(2A)-C(44A)          | 1.320(11)|
| N(2A)-C(43A)          | 1.357(11)|
| N(2C)-C(44C)          | 1.293(13)|
| N(2C)-C(43C)          | 1.380(13)|
| N(2B)-C(34B)          | 1.314(12)|
| N(2B)-C(33B)          | 1.349(13)|
| N(2F)-C(84)           | 1.313(14)|
| N(2F)-C(83)           | 1.323(15)|
| C(1D)-C(2D)           | 1.391(9)|
C(1D)-C(10D)  1.434(9)
C(1D)-C(11D)  1.494(9)
C(1B)-C(2B)   1.381(9)
C(1B)-C(10B)  1.449(10)
C(1B)-C(11B)  1.502(9)
C(1E)-C(2E)   1.395(10)
C(1E)-C(10E)  1.433(9)
C(1E)-C(11E)  1.498(9)
C(1A)-C(2A)   1.398(9)
C(1A)-C(10A)  1.434(10)
C(1A)-C(11A)  1.493(8)
C(1F)-C(2F)   1.398(9)
C(1F)-C(10F)  1.432(9)
C(1F)-C(11F)  1.499(8)
C(2A)-C(3A)   1.437(9)
C(2E)-C(3E)   1.422(10)
C(2F)-C(3F)   1.440(8)
C(2C)-C(3C)   1.436(10)
C(2B)-C(3B)   1.447(9)
C(2D)-C(3D)   1.434(9)
C(3A)-C(4A)   1.406(10)
C(3A)-C(8A)   1.415(10)
C(3E)-C(4E)   1.419(10)
C(3E)-C(8E)   1.421(10)
C(3F)-C(4F)   1.405(10)
C(3F)-C(8F)   1.418(10)
C(3C)-C(4C)   1.405(10)
C(3C)-C(8C)   1.426(10)
C(3D)-C(8D)   1.403(10)
C(3D)-C(4D)   1.418(10)
C(3B)-C(8B)   1.400(10)
C(3B)-C(4B)   1.406(10)
C(4A)-C(5A)   1.390(10)
C(4E)-C(5E)   1.382(11)
C(4C)-C(5C)   1.372(11)
C(4D)-C(5D)   1.377(10)
C(4B)-C(5B)   1.385(10)
C(4F)-C(5F)   1.377(10)
C(5A)-C(6A)   1.394(12)
C(5E)-C(6E)   1.404(12)
C(5D)-C(6D)   1.415(11)
C(5F)-C(6F)   1.426(11)
C(5B)-C(6B)   1.387(12)
C(5C)-C(6C)   1.416(12)
C(6B)-C(7B)   1.370(12)
C(6A)-C(7A)   1.367(11)
C(6F)-C(7F)   1.353(12)
C(6E)-C(7E)   1.356(13)
C(6D)-C(7D)   1.351(11)
C(6C)-C(7C)   1.368(12)
C(7B)-C(8B)  1.429(10)
C(7A)-C(8A)  1.409(9)
C(7F)-C(8F)  1.413(10)
C(7D)-C(8D)  1.433(10)
C(7E)-C(8E)  1.417(11)
C(7C)-C(8C)  1.427(10)
C(8B)-C(9B)  1.414(11)
C(8A)-C(9A)  1.413(10)
C(8F)-C(9F)  1.399(11)
C(8C)-C(9C)  1.422(11)
C(8E)-C(9E)  1.392(11)
C(8D)-C(9D)  1.428(10)
C(9B)-C(10B) 1.377(10)
C(9D)-C(10D) 1.384(10)
C(9C)-C(10C) 1.372(10)
C(9F)-C(10F) 1.400(11)
C(9E)-C(10E) 1.386(10)
C(9A)-C(10A) 1.370(10)
C(10D)-C(21D) 1.482(10)
C(10A)-C(21A) 1.496(10)
C(10C)-C(21C) 1.489(10)
C(10B)-C(21B) 1.473(10)
C(10E)-C(21E) 1.500(10)
C(10F)-C(21F) 1.470(10)
C(11E)-C(12E) 1.386(9)
C(11E)-C(20E) 1.435(9)
C(11A)-C(12A) 1.403(9)
C(11A)-C(20A) 1.433(9)
C(11D)-C(12D) 1.390(10)
C(11D)-C(20D) 1.444(10)
C(11B)-C(12B) 1.386(10)
C(11B)-C(19B) 1.437(9)
C(11F)-C(12F) 1.384(9)
C(11F)-C(20F) 1.440(10)
C(11C)-C(12C) 1.379(11)
C(11C)-C(20C) 1.439(10)
C(12D)-C(13D) 1.438(10)
C(12C)-C(13C) 1.439(9)
C(12B)-C(13B) 1.439(9)
C(12F)-C(13F) 1.427(9)
C(12E)-C(13E) 1.441(9)
C(12A)-C(13A) 1.452(9)
C(13D)-C(14D) 1.414(11)
C(13D)-C(18D) 1.416(11)
C(13B)-C(14Q) 1.410(10)
C(13B)-C(17B) 1.411(10)
C(13C)-C(14C) 1.387(12)
C(13C)-C(18C) 1.442(11)
C(13F)-C(18F) 1.404(11)
C(13F)-C(14F) 1.418(11)
C(13A)-C(18A) 1.401(10)
C(13A)-C(14A) 1.408(10)
C(13E)-C(14E) 1.411(10)
C(13E)-C(18E) 1.431(10)
C(14Q)-C(14B) 1.373(11)
C(14B)-C(15B) 1.390(13)
C(14A)-C(15A) 1.392(9)
C(14D)-C(15D) 1.368(11)
C(14E)-C(15E) 1.365(10)
C(14C)-C(15C) 1.379(11)
C(14F)-C(15F) 1.370(11)
C(15B)-C(16B) 1.388(12)
C(15D)-C(16D) 1.411(14)
C(15A)-C(16A) 1.402(10)
C(15E)-C(16E) 1.412(12)
C(15F)-C(16F) 1.405(15)
C(15C)-C(16C) 1.408(13)
C(16A)-C(17A) 1.368(11)
C(16E)-C(17E) 1.372(12)
C(16B)-C(17B) 1.429(10)
C(16D)-C(17D) 1.358(14)
C(16C)-C(17C) 1.372(14)
C(16F)-C(17F) 1.351(14)
C(17A)-C(18A) 1.419(9)
C(17B)-C(18B) 1.420(10)
C(17D)-C(18D) 1.419(10)
C(17C)-C(18C) 1.432(10)
C(17F)-C(18F) 1.437(10)
C(17E)-C(18E) 1.425(9)
C(18B)-C(19B) 1.372(10)
C(18A)-C(19A) 1.409(10)
C(18F)-C(19F) 1.420(11)
C(18C)-C(19C) 1.378(13)
C(18D)-C(19D) 1.406(11)
C(18E)-C(19E) 1.411(10)
C(19D)-C(20D) 1.385(10)
C(19B)-C(27B) 1.493(10)
C(19A)-C(20A) 1.382(9)
C(19E)-C(20E) 1.382(10)
C(19F)-C(20F) 1.372(10)
C(19C)-C(20C) 1.358(12)
C(20E)-C(27E) 1.487(10)
C(20D)-C(27D) 1.479(11)
C(20A)-C(27A) 1.490(9)
C(20F)-C(27F) 1.487(10)
C(20C)-C(27C) 1.532(12)
C(21E)-C(22E) 1.382(11)
C(21E)-C(26E) 1.408(11)
C(21A)-C(22A) 1.389(11)
C(21A)-C(26A) 1.408(11)
C(21C)-C(26C) 1.394(12)
C(21C)-C(22C) 1.426(10)
C(21D)-C(22D) 1.375(11)
C(21D)-C(26D) 1.402(10)
C(21F)-C(26F) 1.394(12)
C(21F)-C(22F) 1.405(10)
C(21B)-C(22B) 1.405(12)  
C(21B)-C(26B) 1.412(13)  
C(22A)-C(23A) 1.387(12)  
C(22E)-C(23E) 1.392(12)  
C(22D)-C(23D) 1.400(11)  
C(22C)-C(23C) 1.383(12)  
C(22F)-C(23F) 1.390(12)  
C(22B)-C(23B) 1.390(12)  
C(23E)-C(24E) 1.373(14)  
C(23D)-C(24D) 1.373(14)  
C(23A)-C(24A) 1.399(15)  
C(23C)-C(24C) 1.390(14)  
C(23F)-C(24F) 1.381(14)  
C(23B)-C(24B) 1.347(16)  
C(24E)-C(25E) 1.396(12)  
C(24F)-C(25F) 1.382(14)  
C(24D)-C(25D) 1.372(15)  
C(24B)-C(25B) 1.385(17)  
C(24C)-C(25C) 1.393(13)  
C(24A)-C(25A) 1.356(15)  
C(25E)-C(26E) 1.391(11)  
C(25D)-C(26D) 1.382(12)  
C(25A)-C(26A) 1.394(12)  
C(25F)-C(26F) 1.384(13)  
C(25C)-C(26C) 1.366(12)  
C(25B)-C(26B) 1.369(13)  
C(27A)-C(32A) 1.396(10)  
C(27A)-C(28A) 1.405(10)  
C(27F)-C(32F) 1.386(11)  
C(27F)-C(28F) 1.408(11)  
C(27E)-C(32E) 1.385(12)  
C(27E)-C(28E) 1.403(12)  
C(27B)-C(28B) 1.375(11)  
C(27B)-C(32Q) 1.395(11)  
C(27D)-C(32D) 1.400(11)  
C(27D)-C(28D) 1.405(11)  
C(27C)-C(28C) 1.373(14)  
C(27C)-C(32C) 1.406(12)  
C(28A)-C(29A) 1.386(11)  
C(28B)-C(29B) 1.382(12)  
C(28E)-C(29E) 1.400(13)  
C(28F)-C(29F) 1.386(12)  
C(28D)-C(29D) 1.383(12)  
C(28C)-C(29C) 1.397(14)  
C(29A)-C(30A) 1.385(12)  
C(29D)-C(30D) 1.392(13)  
C(29F)-C(30F) 1.368(13)  
C(29B)-C(30B) 1.375(13)  
C(29E)-C(30E) 1.380(19)  
C(29C)-C(30C) 1.374(19)  
C(30A)-C(31A) 1.375(12)  
C(30D)-C(31D) 1.352(13)  
C(30F)-C(31F) 1.393(13)
| Bond                  | Distance (Å) |
|-----------------------|--------------|
| C(30B)-C(31B)         | 1.373(13)    |
| C(30E)-C(31E)         | 1.364(19)    |
| C(30C)-C(31C)         | 1.353(19)    |
| C(31A)-C(32A)         | 1.383(11)    |
| C(31F)-C(32F)         | 1.408(11)    |
| C(31D)-C(32D)         | 1.414(12)    |
| C(31B)-C(32Q)         | 1.400(11)    |
| C(31E)-C(32E)         | 1.394(14)    |
| C(31C)-C(32C)         | 1.405(15)    |
| C(32B)-C(33B)         | 1.320(17)    |
| C(42A)-C(43A)         | 1.339(14)    |
| C(42C)-C(43C)         | 1.349(15)    |
| C(51B)-C(56B)         | 1.370(16)    |
| C(51B)-C(52B)         | 1.377(16)    |
| C(51A)-C(56A)         | 1.359(14)    |
| C(51A)-C(52A)         | 1.381(13)    |
| C(51C)-C(52C)         | 1.40(2)      |
| C(51C)-C(56C)         | 1.410(18)    |
| C(51D)-C(56D)         | 1.33(2)      |
| C(51D)-C(52D)         | 1.40(2)      |
| C(52A)-C(53A)         | 1.394(15)    |
| C(52B)-C(53B)         | 1.404(16)    |
| C(52D)-C(53D)         | 1.34(2)      |
| C(52C)-C(53C)         | 1.42(2)      |
| C(53A)-C(54A)         | 1.367(17)    |
| C(53B)-C(54B)         | 1.352(19)    |
| C(53D)-C(54D)         | 1.36(2)      |
| C(53C)-C(54C)         | 1.44(2)      |
| C(54B)-C(55B)         | 1.367(19)    |
| C(54A)-C(55A)         | 1.369(15)    |
| C(54D)-C(55D)         | 1.37(2)      |
| C(54C)-C(55C)         | 1.36(2)      |
| C(55A)-C(56A)         | 1.420(14)    |
| C(55B)-C(56B)         | 1.322(16)    |
| C(55D)-C(56D)         | 1.44(2)      |
| C(55C)-C(56C)         | 1.41(2)      |
| C(51E)-C(52E)         | 1.3900       |
| C(51E)-C(56E)         | 1.3900       |
| C(52E)-C(53E)         | 1.3900       |
| C(53E)-C(54E)         | 1.3900       |
| C(54E)-C(55E)         | 1.3900       |
| C(55E)-C(56E)         | 1.3900       |
| C(51F)-C(52F)         | 1.3900       |
| C(51F)-C(56F)         | 1.3900       |
| C(52F)-C(53F)         | 1.3900       |
| C(53F)-C(54F)         | 1.3900       |
| C(54F)-C(55F)         | 1.3900       |
| C(55F)-C(56F)         | 1.3900       |
| C(82)-C(3)            | 1.355(19)    |

O(2B)-Zr(1)-O(1A)   93.93(18)
O(2B)-Zr(1)-O(1C)   88.76(18)
O(1A)-Zr(1)-O(1C)   175.08(19)
O(2B)-Zr(1)-O(2C)  95.04(17)
O(1A)-Zr(1)-O(2C)  97.63(18)
O(1C)-Zr(1)-O(2C)  86.22(18)
O(2B)-Zr(1)-O(2A)  176.72(18)
O(1A)-Zr(1)-O(2A)  82.85(18)
O(1C)-Zr(1)-O(2A)  94.49(18)
O(2B)-Zr(1)-O(1B)  84.76(17)
O(1A)-Zr(1)-O(1B)  81.96(18)
O(1C)-Zr(1)-O(1B)  94.20(18)
O(2C)-Zr(1)-O(1B)  179.5(2)
O(2A)-Zr(1)-O(1B)  95.38(17)
O(1E)-Zr(2)-O(1F)  87.26(18)
O(1E)-Zr(2)-O(2F)  98.59(19)
O(1F)-Zr(2)-O(2D)  87.35(17)
O(1F)-Zr(2)-O(2E)  94.73(18)
O(2F)-Zr(2)-O(2E)  174.03(18)
O(2D)-Zr(2)-O(2E)  85.35(19)
O(1E)-Zr(2)-O(1D)  177.94(18)
O(1F)-Zr(2)-O(1D)  94.22(18)
O(2F)-Zr(2)-O(1D)  94.87(18)
O(1F)-Zr(2)-O(2D)  82.97(19)
O(2F)-Zr(2)-O(2D)  127.6(4)
O(2D)-Zr(2)-O(1D)  129.2(4)
C(2A)-O(1A)-Zr(1)  133.5(4)
C(2D)-O(1D)-Zr(2)  127.6(4)
C(2B)-O(1B)-Zr(1)  124.5(4)
C(12C)-O(2C)-Zr(1)  124.0(4)
C(12F)-O(2F)-Zr(2)  121.9(4)
C(12A)-O(2A)-Zr(1)  125.0(4)
C(12E)-O(2E)-Zr(2)  124.5(4)
C(12B)-O(2B)-Zr(1)  130.9(4)
C(12D)-O(2D)-Zr(2)  127.9(4)
C(44A)-N(1A)-C(42A)  108.6(8)
C(44A)-N(1A)-C(41A)  125.1(9)
C(42A)-N(1A)-C(41A)  126.2(8)
C(42C)-N(1C)-C(44C)  108.6(8)
C(42C)-N(1C)-C(41C)  126.8(9)
C(44C)-N(1C)-C(41C)  124.5(9)
C(34B)-N(1B)-C(32B)  108.2(8)
C(34B)-N(1B)-C(31Q)  125.4(8)
C(32B)-N(1B)-C(31Q)  126.4(8)
C(82)-N(1F)-C(84)  109.4(10)
C(82)-N(1F)-C(81)  125.6(10)
C(84)-N(1F)-C(81)  125.0(10)
C(44A)-N(2A)-C(43A)  108.2(7)
C(44C)-N(2C)-C(43C)  110.5(9)
C(34B)-N(2B)-C(33B)  110.4(9)
C(84)-N(2F)-C(83)  108.3(10)
C(2D)-C(1D)-C(10D)  118.5(6)
C(2D)-C(1D)-C(11D)  121.4(6)
C(10D)-C(1D)-C(11D)  119.8(6)
C(2B)-C(1B)-C(10B)  118.9(6)
C(2B)-C(1B)-C(11B)  122.4(6)
C(10B)-C(1B)-C(11B)  118.7(6)
C(2E)-C(1E)-C(10E)  118.1(6)
C(2E)-C(1E)-C(11E)  123.1(6)
C(10E)-C(1E)-C(11E)  118.8(6)
C(2A)-C(1A)-C(10A)  118.1(6)
C(2A)-C(1A)-C(11A)  120.3(6)
C(10A)-C(1A)-C(11A)  121.1(6)
C(2F)-C(1F)-C(10F)  119.3(6)
C(2F)-C(1F)-C(11F)  119.4(6)
C(10F)-C(1F)-C(11F)  121.0(6)
C(2C)-C(1C)-C(10C)  119.2(6)
C(2C)-C(1C)-C(11C)  120.5(6)
C(10C)-C(1C)-C(11C)  120.0(6)
O(1A)-C(2A)-C(1A)  122.1(5)
O(1A)-C(2A)-C(3A)  117.0(6)
C(1A)-C(2A)-C(3A)  120.6(6)
O(1E)-C(2E)-C(1E)  120.2(6)
O(1E)-C(2E)-C(3E)  118.5(6)
C(1E)-C(2E)-C(3E)  121.1(6)
O(1F)-C(2F)-C(1F)  121.0(5)
O(1F)-C(2F)-C(3F)  118.9(6)
C(1F)-C(2F)-C(3F)  119.9(6)
O(1C)-C(2C)-C(1C)  121.6(6)
O(1C)-C(2C)-C(3C)  117.7(6)
C(1C)-C(2C)-C(3C)  120.4(6)
O(1B)-C(2B)-C(1B)  121.9(6)
O(1B)-C(2B)-C(3B)  117.3(6)
C(1B)-C(2B)-C(3B)  120.8(6)
O(1D)-C(2D)-C(1D)  121.4(6)
O(1D)-C(2D)-C(3D)  117.9(6)
C(1D)-C(2D)-C(3D)  120.5(6)
C(4A)-C(3A)-C(8A)  118.9(6)
C(4A)-C(3A)-C(2A)  121.2(6)
C(8A)-C(3A)-C(2A)  119.7(6)
C(4E)-C(3E)-C(8E)  118.4(7)
C(4E)-C(3E)-C(2E)  121.6(7)
C(8E)-C(3E)-C(2E)  120.0(7)
C(4F)-C(3F)-C(8F)  120.0(6)
C(4F)-C(3F)-C(2F)  120.2(6)
C(8F)-C(3F)-C(2F)  119.8(6)
C(4C)-C(3C)-C(8C)  119.0(6)
C(4C)-C(3C)-C(2C)  121.6(6)
C(8C)-C(3C)-C(2C)  119.3(6)
C(8D)-C(3D)-C(4D)  118.2(6)
C(8D)-C(3D)-C(2D)  119.9(6)
C(4D)-C(3D)-C(2D)  121.8(6)

S-68
C(8B)-C(3B)-C(4B)  120.1(6)
C(8B)-C(3B)-C(2B)  118.8(6)
C(4B)-C(3B)-C(2B)  121.1(6)
C(5A)-C(4A)-C(3A)  120.8(7)
C(5E)-C(4E)-C(3E)  121.4(7)
C(5C)-C(4C)-C(3C)  120.8(7)
C(5D)-C(4D)-C(3D)  121.7(7)
C(5B)-C(4B)-C(3B)  119.6(7)
C(5F)-C(4F)-C(3F)  120.4(6)
C(4A)-C(5A)-C(6A)  119.6(7)
C(4E)-C(5E)-C(6E)  119.4(7)
C(4D)-C(5D)-C(6D)  121.0(7)
C(4F)-C(5F)-C(6F)  119.5(7)
C(4B)-C(5B)-C(6B)  121.0(7)
C(4C)-C(5C)-C(6C)  119.7(8)
C(7B)-C(6B)-C(5B)  120.3(7)
C(7A)-C(6A)-C(5A)  120.6(6)
C(7F)-C(6F)-C(5F)  120.4(6)
C(7E)-C(6E)-C(5E)  120.4(7)
C(7D)-C(6D)-C(5D)  121.1(7)
C(7C)-C(6C)-C(5C)  120.6(7)
C(6B)-C(7B)-C(8B)  120.3(7)
C(6A)-C(7A)-C(8A)  121.0(7)
C(6F)-C(7F)-C(8F)  121.4(7)
C(6D)-C(7D)-C(8D)  120.3(7)
C(6E)-C(7E)-C(8E)  122.0(8)
C(6C)-C(7C)-C(8C)  120.5(7)
C(3B)-C(8B)-C(9B)  119.7(6)
C(3B)-C(8B)-C(7B)  118.7(6)
C(3B)-C(8B)-C(9B)  122.9(7)
C(7A)-C(8A)-C(9A)  122.9(7)
C(9A)-C(8A)-C(3A)  119.0(6)
C(9F)-C(8F)-C(7F)  122.5(7)
C(9F)-C(8F)-C(3F)  119.2(6)
C(7F)-C(8F)-C(3F)  118.3(6)
C(9C)-C(8C)-C(3C)  118.3(6)
C(9C)-C(8C)-C(7C)  123.1(7)
C(3C)-C(8C)-C(7C)  118.6(7)
C(9E)-C(8E)-C(7E)  123.9(7)
C(9E)-C(8E)-C(3E)  117.7(6)
C(7E)-C(8E)-C(3E)  118.4(7)
C(3D)-C(8D)-C(9D)  118.8(6)
C(3D)-C(8D)-C(7D)  119.6(6)
C(9D)-C(8D)-C(7D)  121.6(7)
C(10B)-C(9B)-C(8B)  121.6(7)
C(10D)-C(9D)-C(8D)  120.8(6)
C(10C)-C(9C)-C(8C)  121.5(7)
C(8F)-C(9F)-C(10F)  121.4(7)
C(10E)-C(9E)-C(8E)  123.0(6)
C(10A)-C(9A)-C(8A)  122.1(6)
C(9D)-C(10D)-C(1D)  120.6(6)
C(9D)-C(10D)-C(21D)  118.2(6)
| Bond Configuration | Angle (°) |
|--------------------|----------|
| C(1D)-C(10D)-C(21D) | 121.2(6) |
| C(9A)-C(10A)-C(1A) | 120.5(6) |
| C(9A)-C(10A)-C(21A) | 117.0(6) |
| C(1A)-C(10A)-C(21A) | 122.5(6) |
| C(9C)-C(10C)-C(1C) | 120.0(6) |
| C(9C)-C(10C)-C(21C) | 119.2(6) |
| C(1C)-C(10C)-C(21C) | 120.7(6) |
| C(9B)-C(10B)-C(1B) | 119.5(6) |
| C(9B)-C(10B)-C(21B) | 117.0(6) |
| C(1B)-C(10B)-C(21B) | 123.4(6) |
| C(9E)-C(10E)-C(1E) | 119.7(6) |
| C(9E)-C(10E)-C(21E) | 117.7(6) |
| C(1E)-C(10E)-C(21E) | 122.5(6) |
| C(9F)-C(10F)-C(1F) | 120.0(6) |
| C(9F)-C(10F)-C(21F) | 117.8(6) |
| C(1F)-C(10F)-C(21F) | 122.1(6) |
| C(12E)-C(11E)-C(20E) | 118.8(6) |
| C(12E)-C(11E)-C(1E) | 121.8(6) |
| C(20E)-C(11E)-C(1E) | 118.8(6) |
| C(12A)-C(11A)-C(20A) | 118.3(6) |
| C(12A)-C(11A)-C(1A) | 121.3(5) |
| C(20A)-C(11A)-C(1A) | 120.4(6) |
| C(12D)-C(11D)-C(20D) | 118.0(6) |
| C(12D)-C(11D)-C(1D) | 122.4(6) |
| C(20D)-C(11D)-C(1D) | 119.5(6) |
| C(12B)-C(11B)-C(19B) | 118.3(6) |
| C(12B)-C(11B)-C(1B) | 121.5(6) |
| C(19B)-C(11B)-C(1B) | 120.1(6) |
| C(12F)-C(11F)-C(20F) | 118.7(6) |
| C(12F)-C(11F)-C(1F) | 121.3(6) |
| C(20F)-C(11F)-C(1F) | 119.9(6) |
| C(12C)-C(11C)-C(20C) | 120.6(6) |
| C(12C)-C(11C)-C(1C) | 121.5(6) |
| C(20C)-C(11C)-C(1C) | 117.9(7) |
| O(2D)-C(12D)-C(11D) | 121.4(6) |
| O(2D)-C(12D)-C(13D) | 117.2(6) |
| C(11D)-C(12D)-C(13D) | 121.4(6) |
| O(2C)-C(12C)-C(11C) | 122.1(6) |
| O(2C)-C(12C)-C(13C) | 118.7(7) |
| C(11C)-C(12C)-C(13C) | 119.1(6) |
| O(2B)-C(12B)-C(11B) | 121.8(6) |
| O(2B)-C(12B)-C(13B) | 117.1(6) |
| C(11B)-C(12B)-C(13B) | 121.1(6) |
| O(2F)-C(12F)-C(11F) | 121.5(6) |
| O(2F)-C(12F)-C(13F) | 117.3(6) |
| C(11F)-C(12F)-C(13F) | 121.2(6) |
| O(2E)-C(12E)-C(11E) | 121.2(6) |
| O(2E)-C(12E)-C(13E) | 118.0(6) |
| C(11E)-C(12E)-C(13E) | 120.7(6) |
| O(2A)-C(12A)-C(11A) | 122.3(5) |
| O(2A)-C(12A)-C(13A) | 117.4(5) |
| C(11A)-C(12A)-C(13A) | 120.2(6) |
| C(14D)-C(13D)-C(18D) | 118.7(7) |
C(14D)-C(13D)-C(12D)  122.1(7)
C(18D)-C(13D)-C(12D)  119.1(7)
C(14Q)-C(13B)-C(17B)  118.9(6)
C(14Q)-C(13B)-C(12B)  122.0(6)
C(17B)-C(13B)-C(12B)  119.1(6)
C(14C)-C(13C)-C(12C)  121.7(7)
C(14C)-C(13C)-C(18C)  119.8(7)
C(12C)-C(13C)-C(18C)  118.4(7)
C(14F)-C(13F)-C(14D)  119.2(6)
C(14F)-C(13F)-C(12F)  118.9(6)
C(18F)-C(13F)-C(12F)  121.9(7)
C(18F)-C(14F)-C(13F)  119.3(6)
C(14A)-C(13A)-C(14A)  119.9(6)
C(14A)-C(13A)-C(12A)  119.3(6)
C(14A)-C(13A)-C(12A)  120.7(6)
C(14E)-C(13E)-C(16E)  118.9(6)
C(14E)-C(13E)-C(12E)  122.0(6)
C(18E)-C(13E)-C(12E)  119.1(6)
C(14B)-C(14Q)-C(13B)  121.0(7)
C(14Q)-C(14B)-C(15B)  120.3(8)
C(15A)-C(14A)-C(13A)  120.1(6)
C(15D)-C(14D)-C(13D)  120.9(8)
C(15E)-C(14E)-C(13E)  120.9(7)
C(15C)-C(14C)-C(13C)  122.1(8)
C(15F)-C(14F)-C(13F)  120.2(8)
C(16B)-C(15B)-C(14B)  121.0(7)
C(14D)-C(15D)-C(16D)  120.3(8)
C(14A)-C(15A)-C(16A)  119.9(6)
C(14E)-C(15E)-C(16E)  120.8(7)
C(14F)-C(15F)-C(16F)  120.7(8)
C(14C)-C(15C)-C(16C)  118.7(8)
C(17A)-C(16A)-C(15A)  120.3(6)
C(17E)-C(16E)-C(15E)  120.0(6)
C(15B)-C(16B)-C(17B)  119.1(7)
C(17D)-C(16D)-C(15D)  120.0(7)
C(17C)-C(16C)-C(15C)  121.4(7)
C(17F)-C(16F)-C(15F)  120.6(7)
C(16A)-C(17A)-C(18A)  120.9(7)
C(13B)-C(17B)-C(18B)  119.2(6)
C(13B)-C(17B)-C(16B)  119.6(7)
C(18B)-C(17B)-C(16B)  121.1(6)
C(16D)-C(17D)-C(18D)  121.1(8)
C(16C)-C(17C)-C(18C)  120.8(7)
C(16F)-C(17F)-C(18F)  120.3(8)
C(16E)-C(17E)-C(18E)  120.7(7)
C(19B)-C(18B)-C(17B)  120.9(6)
C(13A)-C(18A)-C(19A)  119.5(6)
C(13A)-C(18A)-C(17A)  118.7(6)
C(19A)-C(18A)-C(17A)  121.8(6)
C(13F)-C(18F)-C(19F)  119.3(6)
C(13F)-C(18F)-C(17F)  119.0(7)
C(19F)-C(18F)-C(17F)  121.7(7)
C(19C)-C(18C)-C(17C)  123.4(7)
C(19C)-C(18C)-C(13C)  119.4(7)
C(17C)-C(18C)-C(13C)  117.1(8)
C(19D)-C(18D)-C(13D)  119.1(6)
C(19D)-C(18D)-C(17D)  121.9(8)
C(13D)-C(18D)-C(17D)  118.9(7)
C(19E)-C(18E)-C(17E)  122.8(7)
C(19E)-C(18E)-C(13E)  118.6(6)
C(17E)-C(18E)-C(13E)  118.6(7)
C(20D)-C(19D)-C(18D)  121.5(7)
C(18B)-C(19B)-C(11B)  121.1(6)
C(18B)-C(19B)-C(27B)  116.4(6)
C(11B)-C(19B)-C(27B)  122.3(6)
C(20A)-C(19A)-C(18A)  121.3(6)
C(20E)-C(19E)-C(18E)  121.6(6)
C(20F)-C(19F)-C(18F)  121.4(7)
C(20C)-C(19C)-C(18C)  122.6(7)
C(19E)-C(20E)-C(11E)  120.4(6)
C(19E)-C(20E)-C(27E)  118.4(6)
C(11E)-C(20E)-C(27E)  121.2(6)
C(19D)-C(20D)-C(11D)  120.5(7)
C(19D)-C(20D)-C(27D)  117.7(6)
C(11D)-C(20D)-C(27D)  121.8(6)
C(19A)-C(20A)-C(11A)  120.7(6)
C(19A)-C(20A)-C(27A)  116.7(6)
C(11A)-C(20A)-C(27A)  122.6(6)
C(19F)-C(20F)-C(11F)  119.9(6)
C(19F)-C(20F)-C(27F)  117.8(6)
C(11F)-C(20F)-C(27F)  122.2(6)
C(19C)-C(20C)-C(11C)  119.0(7)
C(19C)-C(20C)-C(27C)  121.2(7)
C(11C)-C(20C)-C(27C)  119.6(7)
C(22E)-C(21E)-C(26E)  118.4(7)
C(22E)-C(21E)-C(10E)  121.6(7)
C(26E)-C(21E)-C(10E)  120.0(6)
C(22A)-C(21A)-C(26A)  118.3(7)
C(22A)-C(21A)-C(10A)  119.8(7)
C(26A)-C(21A)-C(10A)  121.9(7)
C(26C)-C(21C)-C(22C)  117.9(7)
C(26C)-C(21C)-C(10C)  123.5(7)
C(22C)-C(21C)-C(10C)  118.6(7)
C(22D)-C(21D)-C(26D)  118.6(7)
C(22D)-C(21D)-C(10D)  120.5(7)
C(26D)-C(21D)-C(10D)  120.8(7)
C(26F)-C(21F)-C(22F)  117.8(7)
C(26F)-C(21F)-C(10F)  122.7(7)
C(22F)-C(21F)-C(10F)  119.4(7)
C(22B)-C(21B)-C(26B)  119.1(8)
C(22B)-C(21B)-C(10B)  119.0(7)
C(26B)-C(21B)-C(10B)  121.7(7)
C(23A)-C(22A)-C(21A)  121.9(8)
C(21E)-C(22E)-C(23E)  120.8(8)
C(21D)-C(22D)-C(23D)  121.8(8)
C(23C)-C(22C)-C(21C)  119.4(8)
C(23F)-C(22F)-C(21F)  121.0(8)
C(30E)-C(29E)-C(28E)  120.3(10)
C(30C)-C(29C)-C(28C)  120.0(12)
C(31A)-C(30A)-C(29A)  120.7(7)
C(31D)-C(30D)-C(29D)  120.7(8)
C(29F)-C(30F)-C(31F)  120.2(8)
C(31B)-C(30B)-C(29B)  119.7(8)
C(31E)-C(30E)-C(29E)  120.5(9)
C(30A)-C(31A)-C(32A)  119.3(7)
C(30F)-C(31F)-C(32F)  119.3(7)
C(30D)-C(31D)-C(32D)  120.9(8)
C(30B)-C(31B)-C(32B)  119.8(8)
C(30E)-C(31E)-C(32E)  120.4(10)
C(30C)-C(31C)-C(32C)  120.1(10)
C(31A)-C(32A)-C(27A)  122.1(7)
C(27D)-C(32D)-C(31D)  119.5(7)
C(27F)-C(32F)-C(31F)  121.1(8)
C(27B)-C(32B)-C(31B)  120.4(7)
C(27E)-C(32E)-C(31E)  120.0(10)
C(31C)-C(32C)-C(27C)  119.3(10)
C(33B)-C(32B)-N(1B)  107.6(9)
C(32B)-C(33B)-N(2B)  107.4(9)
N(2B)-C(34B)-N(1B)  106.4(8)
C(43A)-C(42A)-N(1A)  106.9(7)
C(43C)-C(42C)-N(1C)  107.3(9)
C(42A)-C(43A)-N(2A)  107.6(8)
C(42C)-C(43C)-N(2C)  106.3(9)
N(1A)-C(44A)-N(2A)  108.7(8)
N(2C)-C(44C)-N(1C)  107.1(9)
C(56B)-C(51B)-C(52B)  122.8(9)
C(56B)-C(51B)-Br(2)  118.9(8)
C(52B)-C(51B)-Br(2)  118.0(9)
C(56A)-C(51A)-C(52A)  122.2(9)
C(56A)-C(51A)-Br(1)  119.2(7)
C(52A)-C(51A)-Br(1)  118.6(7)
C(52C)-C(51C)-C(56C)  120.3(16)
C(52C)-C(51C)-Br(3)  119.3(11)
C(56C)-C(51C)-Br(3)  120.4(12)
C(56D)-C(51D)-C(52D)  122.0(14)
C(56D)-C(51D)-Br(4)  117.1(12)
C(52D)-C(51D)-Br(4)  120.6(12)
C(51A)-C(52A)-C(53A)  118.6(10)
C(51B)-C(52B)-C(53B)  116.4(11)
C(53D)-C(52D)-C(51D)  120.2(17)
C(51C)-C(52C)-C(53C)  119.1(13)
C(54A)-C(53A)-C(52A)  119.0(10)
C(54B)-C(53B)-C(52B)  119.4(11)
C(52D)-C(53D)-C(54D)  118.2(17)
C(52C)-C(53C)-C(54C)  120.6(13)
C(53B)-C(54B)-C(55B)  121.8(11)
C(53A)-C(54A)-C(55A)  123.3(10)
C(53D)-C(54D)-C(55D)  124.2(15)
C(55C)-C(54C)-C(53C)  118.2(17)
C(54A)-C(55A)-C(56A) 117.3(9)
C(56B)-C(55B)-C(54B) 120.2(12)
C(54D)-C(55D)-C(56D) 116.7(15)
C(54C)-C(55C)-C(56C) 122.7(14)
C(55B)-C(56B)-C(51B) 119.2(11)
C(51A)-C(56A)-C(55A) 119.5(9)
C(51D)-C(56D)-C(55D) 118.4(15)
C(52E)-C(51E)-C(56E) 120.0
C(52E)-C(51E)-Br(5) 119.6(8)
C(56E)-C(51E)-Br(5) 119.9(8)
C(53E)-C(52E)-C(51E) 120.0
C(52E)-C(53E)-C(54E) 120.0
C(55E)-C(54E)-C(53E) 120.0
C(56E)-C(55E)-C(54E) 120.0
C(55E)-C(56E)-C(51E) 120.0
C(52F)-C(51F)-C(56F) 120.0
C(52F)-C(51F)-Br(6) 119.0(12)
C(56F)-C(51F)-Br(6) 121.0(12)
C(53F)-C(52F)-C(51F) 120.0
C(52F)-C(53F)-C(54F) 120.0
C(55F)-C(54F)-C(53F) 120.0
C(54F)-C(55F)-C(56F) 120.0
C(55F)-C(56F)-C(51F) 120.0
C(51C)-C(56C)-C(55C) 119.2(14)
N(1F)-C(82)-C(83) 106.6(10)
N(2F)-C(83)-C(82) 109.0(11)
N(2F)-C(84)-N(1F) 106.6(9)
Table 4. Anisotropic displacement parameters ($\hat{A}^2 \times 10^3$) for wulff01. The anisotropic displacement factor exponent takes the form: 

\[ -2\delta^2 [h^2 a^2 U_{11} + ... + 2h k a^* b^* U_{12} ] \]

|       | $u_{11}$ | $u_{22}$ | $u_{33}$ | $u_{23}$ | $u_{13}$ | $u_{12}$ |
|-------|----------|----------|----------|----------|----------|----------|
| Zr(1) | 33(1)    | 26(1)    | 23(1)    | -1(1)    | 5(1)     | 0(1)     |
| Zr(2) | 29(1)    | 27(1)    | 26(1)    | 1(1)     | 4(1)     | 0(1)     |
| Br(1) | 65(1)    | 69(1)    | 49(1)    | 7(1)     | 13(1)    | 11(1)    |
| Br(2) | 60(1)    | 87(1)    | 113(1)   | -20(1)   | 23(1)    | -8(1)    |
| Br(3) | 100(1)   | 93(1)    | 128(1)   | 25(1)    | 14(1)    | 4(1)     |
| Br(4) | 67(1)    | 126(2)   | 180(2)   | -10(1)   | 15(1)    | -10(1)   |
| Br(5) | 181(3)   | 284(5)   | 301(5)   | -170(4)  | -123(3)  | 128(3)   |
| Br(6) | 287(5)   | 427(8)   | 165(3)   | -43(4)   | -37(3)   | 244(6)   |
| O(1S) | 58(3)    | 36(3)    | 44(3)    | 1(2)     | 16(2)    | -3(2)    |
| O(2S) | 55(3)    | 47(3)    | 59(3)    | 4(3)     | 15(3)    | -7(3)    |
| O(3S) | 50(3)    | 63(4)    | 63(4)    | -12(3)   | 14(3)    | -7(3)    |
| O(1C) | 33(2)    | 24(2)    | 40(2)    | 2(2)     | 6(2)     | 1(2)     |
| O(1F) | 35(2)    | 33(2)    | 29(2)    | -2(2)    | 2(2)     | -4(2)    |
| O(1E) | 32(2)    | 32(2)    | 30(2)    | 4(2)     | 6(2)     | 1(2)     |
| O(1A) | 35(2)    | 34(2)    | 28(2)    | 0(2)     | 5(2)     | 0(2)     |
| O(1D) | 36(2)    | 30(2)    | 29(2)    | 4(2)     | 8(2)     | 3(2)     |
| O(1B) | 37(2)    | 26(2)    | 30(2)    | 0(2)     | 11(2)    | -3(2)    |
| O(2C) | 37(2)    | 32(2)    | 25(2)    | -3(2)    | 7(2)     | -4(2)    |
| O(2F) | 32(2)    | 37(2)    | 32(2)    | -2(2)    | 4(2)     | 0(2)     |
| O(2A) | 36(2)    | 31(2)    | 24(2)    | 1(2)     | 4(2)     | 4(2)     |
| O(2E) | 29(2)    | 27(2)    | 35(2)    | 1(2)     | -2(2)    | 1(2)     |
| O(2B) | 40(2)    | 26(2)    | 27(2)    | 0(2)     | 10(2)    | 3(2)     |
| N(1A) | 60(4)    | 42(4)    | 60(4)    | -15(3)   | 26(3)    | -11(3)   |
| N(1C) | 43(3)    | 61(4)    | 54(4)    | -3(3)    | 13(3)    | 5(3)     |
| N(1B) | 58(4)    | 45(4)    | 52(4)    | 7(3)     | 12(3)    | -2(3)    |
| N(1F) | 96(6)    | 45(4)    | 61(5)    | 0(4)     | 18(4)    | 19(4)    |
| N(2A) | 44(3)    | 35(3)    | 48(4)    | 2(3)     | 17(3)    | -3(3)    |
| N(2C) | 49(4)    | 47(4)    | 65(5)    | -4(3)    | 14(3)    | -2(3)    |
| N(2B) | 66(4)    | 47(4)    | 49(4)    | 5(3)     | 15(3)    | 10(3)    |
| N(2F) | 54(4)    | 56(5)    | 72(5)    | -1(4)    | 10(3)    | 0(4)     |
| C(1D) | 32(3)    | 24(3)    | 34(3)    | 2(2)     | 6(3)     | -1(2)    |
| C(1B) | 32(3)    | 29(3)    | 27(3)    | 3(2)     | 7(2)     | 1(2)     |
| C(1E) | 31(3)    | 27(3)    | 34(3)    | 3(2)     | 7(3)     | 5(2)     |
| C(1A) | 34(3)    | 28(3)    | 32(3)    | 0(3)     | 2(2)     | 3(3)     |
| C(1F) | 33(3)    | 28(3)    | 32(3)    | -1(2)    | 5(2)     | 4(3)     |
| C(1C) | 35(3)    | 33(3)    | 30(3)    | 4(3)     | 10(3)    | 2(3)     |
| C(2A) | 36(3)    | 27(3)    | 30(3)    | -2(2)    | 6(2)     | 4(3)     |
| C(2E) | 34(3)    | 27(3)    | 32(3)    | 4(2)     | 5(3)     | 5(2)     |
| C(2F) | 38(3)    | 27(3)    | 26(3)    | -3(2)    | 6(2)     | 6(3)     |
| C(2C) | 36(3)    | 32(3)    | 35(3)    | 7(3)     | 14(3)    | 3(3)     |
| C(2B) | 33(3)    | 25(3)    | 30(3)    | -2(2)    | 6(2)     | 2(2)     |
| C(2D) | 31(3)    | 26(3)    | 33(3)    | 2(2)     | 11(2)    | 0(2)     |
| C(3A) | 40(3)    | 32(3)    | 29(3)    | -1(3)    | 6(2)     | 3(3)     |
| C(3E) | 40(3)    | 30(3)    | 31(3)    | 0(3)     | 4(3)     | 3(3)     |
| C(3F) | 36(3)    | 32(3)    | 28(3)    | 0(3)     | 4(2)     | 5(3)     |
| C(3C) | 36(3)    | 33(3)    | 33(3)    | 4(3)     | 12(3)    | 5(3)     |
| C(3D) | 41(3)    | 24(3)    | 33(3)    | 4(2)     | 5(3)     | -4(3)    |
| C(3B) | 44(4) | 25(3) | 31(3) | 2(2) | 5(3) | 2(3) |
|-------|-------|-------|-------|------|------|------|
| C(4A) | 40(3) | 44(4) | 25(3) | 0(3) | 1(3) | 0(3) |
| C(4E) | 33(3) | 36(4) | 44(4) | 2(3) | 1(3) | -3(3) |
| C(4C) | 36(3) | 33(3) | 42(4) | -1(3) | 10(3) | 3(3) |
| C(4D) | 44(4) | 30(3) | 32(3) | 1(3) | 8(3) | -1(3) |
| C(4B) | 46(4) | 30(3) | 29(3) | -1(3) | 5(3) | -1(3) |
| C(4F) | 40(3) | 36(3) | 27(3) | -2(3) | 7(3) | 6(3) |
| C(5A) | 47(4) | 54(5) | 24(3) | 4(3) | 4(3) | 4(3) |
| C(5E) | 37(4) | 45(4) | 45(4) | 4(3) | 0(3) | -4(3) |
| C(5D) | 51(4) | 38(4) | 33(3) | 5(3) | 6(3) | 4(3) |
| C(5F) | 42(4) | 43(4) | 34(3) | -4(3) | 4(3) | 0(3) |
| C(5B) | 55(4) | 39(4) | 32(3) | 2(3) | 7(3) | -1(3) |
| C(5C) | 48(4) | 40(4) | 43(4) | 3(3) | 6(3) | 0(3) |
| C(6B) | 53(4) | 40(4) | 34(3) | -2(3) | -3(3) | 0(3) |
| C(6A) | 42(4) | 51(4) | 35(3) | 1(3) | -9(3) | 1(3) |
| C(6F) | 43(4) | 58(5) | 32(3) | -2(3) | -1(3) | 2(4) |
| C(6E) | 58(5) | 52(5) | 35(4) | 9(3) | -7(3) | 6(4) |
| C(6D) | 44(4) | 42(4) | 32(3) | 4(3) | -2(3) | 2(3) |
| C(6C) | 50(4) | 50(4) | 37(4) | 2(3) | 4(3) | 6(3) |
| C(7B) | 47(4) | 40(4) | 36(4) | 1(3) | -1(3) | -3(3) |
| C(7A) | 37(3) | 50(4) | 31(3) | -4(3) | 1(2) | -2(3) |
| C(7F) | 46(4) | 54(5) | 35(3) | 6(3) | 11(3) | 1(3) |
| C(7D) | 36(3) | 37(4) | 42(4) | 3(3) | 1(3) | 3(3) |
| C(7E) | 59(5) | 51(5) | 37(4) | 7(3) | 2(3) | -11(4) |
| C(7C) | 51(4) | 42(4) | 31(3) | 7(3) | 7(3) | 7(3) |
| C(8B) | 37(3) | 29(3) | 34(3) | 0(3) | 4(3) | -1(3) |
| C(8A) | 41(3) | 34(3) | 31(3) | -4(3) | 3(3) | 0(3) |
| C(8F) | 35(3) | 41(4) | 34(3) | 1(3) | 5(3) | 4(3) |
| C(8C) | 41(4) | 38(4) | 33(3) | 6(3) | 14(3) | 8(3) |
| C(8E) | 51(4) | 35(3) | 29(3) | 4(3) | 8(3) | 0(3) |
| C(8D) | 38(3) | 29(3) | 35(3) | -2(3) | 2(3) | -1(3) |
| C(9B) | 39(4) | 38(4) | 43(4) | 2(3) | 5(3) | -6(3) |
| C(9D) | 37(3) | 31(3) | 39(3) | 1(3) | 10(3) | 1(3) |
| C(9C) | 50(4) | 31(3) | 34(3) | 4(3) | 14(3) | 3(3) |
| C(9F) | 41(4) | 38(4) | 42(4) | 3(3) | 11(3) | -1(3) |
| C(9E) | 47(4) | 35(3) | 31(3) | 7(3) | 12(3) | -1(3) |
| C(9A) | 38(3) | 37(4) | 31(3) | -3(3) | 6(3) | -8(3) |
| C(10D) | 35(3) | 33(3) | 30(3) | -1(3) | 6(3) | -1(3) |
| C(10A) | 38(3) | 29(3) | 32(3) | -3(3) | 6(3) | -2(3) |
| C(10C) | 44(4) | 29(3) | 34(3) | 0(3) | 14(3) | 7(3) |
| C(10B) | 35(3) | 28(3) | 40(4) | 0(3) | 4(3) | -2(3) |
| C(10E) | 37(3) | 28(3) | 28(3) | 2(2) | 7(2) | -2(3) |
| C(10F) | 42(4) | 33(3) | 34(3) | 3(3) | 9(3) | 1(3) |
| C(11E) | 31(3) | 28(3) | 30(3) | 1(2) | 7(2) | 0(2) |
| C(11A) | 36(3) | 26(3) | 29(3) | -2(2) | 7(2) | -2(2) |
| C(11D) | 31(3) | 33(3) | 32(3) | 0(3) | 6(3) | -4(3) |
| C(11B) | 30(3) | 32(3) | 27(3) | 4(2) | 7(2) | 0(2) |
| C(11F) | 29(3) | 33(3) | 32(3) | -1(3) | 5(2) | -2(3) |
| C(11C) | 51(4) | 29(3) | 30(3) | -3(2) | 14(3) | 1(3) |
| C(12D) | 41(3) | 32(3) | 31(3) | -4(3) | 10(3) | 0(3) |
| C(12C) | 49(4) | 26(3) | 26(3) | -6(2) | 15(3) | -7(3) |
| C(12B) | 30(3) | 31(3) | 28(3) | 7(2) | 12(2) | 1(2) |
| C(12F) | 28(3) | 36(3) | 35(3) | 3(3) | 7(2) | -7(3) |
| C(21D) | 30(3) | 42(4) | 36(3) | 2(3) | 7(3) | -1(3) |
|--------|-------|-------|-------|------|------|-------|
| C(21F) | 39(4) | 35(3) | 35(3) | 7(3) | 8(3) | 4(3)  |
| C(21B) | 34(3) | 45(4) | 42(4) | 10(3) | 5(3) | 1(3)  |
| C(22A) | 44(4) | 46(4) | 44(4) | -3(3) | 9(3) | -9(3) |
| C(22E) | 52(4) | 34(4) | 44(4) | 0(3) | 5(3) | -8(3) |
| C(22D) | 35(3) | 45(4) | 39(4) | -6(3) | 8(3) | -4(3) |
| C(22C) | 55(4) | 37(4) | 37(4) | 5(3) | 10(3) | 14(3) |
| C(22F) | 41(4) | 41(4) | 41(4) | 4(3) | 11(3) | 2(3)  |
| C(22B) | 45(4) | 66(5) | 46(4) | 7(4) | 6(3) | -14(4) |
| C(23E) | 64(5) | 34(4) | 53(5) | -3(3) | 15(4) | -10(4) |
| C(23D) | 39(4) | 55(5) | 46(4) | -16(4) | 11(3) | -5(3) |
| C(23A) | 43(4) | 59(5) | 54(5) | -5(4) | 15(4) | -14(4) |
| C(23C) | 68(5) | 40(4) | 46(4) | 0(3) | 12(4) | 12(4) |
| C(23F) | 54(5) | 58(5) | 15(4) | 16(3) | -1(3) |
| C(23B) | 53(5) | 74(6) | 58(5) | 21(5) | 17(4) | -18(4) |
| C(24E) | 46(4) | 56(5) | 40(4) | -12(3) | 12(3) | -18(4) |
| C(24F) | 45(4) | 50(5) | 62(5) | 13(4) | 5(4) | -11(4) |
| C(24D) | 44(4) | 80(6) | 44(4) | -17(4) | 15(3) | -6(4)  |
| C(24B) | 45(4) | 97(8) | 63(6) | 10(5) | 26(4) | -12(5) |
| C(24C) | 81(6) | 32(4) | 52(5) | -2(3) | 14(4) | 7(4)  |
| C(24A) | 70(6) | 73(6) | 48(5) | 1(4) | 15(4) | -32(5) |
| C(25E) | 44(4) | 49(4) | 30(3) | -5(3) | 10(3) | -1(3) |
| C(25D) | 47(4) | 74(6) | 41(4) | 5(4) | 11(3) | 2(4)  |
| C(25A) | 63(5) | 66(6) | 44(4) | 13(4) | 1(4) | -23(4) |
| C(25F) | 61(5) | 57(5) | 44(4) | 5(4) | -1(4) | -18(4) |
| C(25C) | 59(5) | 37(4) | 49(4) | 5(3) | 12(3) | -3(3) |
| C(25B) | 50(5) | 100(8) | 37(4) | 5(4) | 13(3) | 11(5) |
| C(26C) | 45(4) | 30(3) | 48(4) | 10(3) | 14(3) | 1(3)  |
| C(26A) | 53(4) | 44(4) | 34(3) | 6(3) | 3(3) | -13(3) |
| C(26F) | 57(5) | 46(4) | 37(4) | 3(3) | 7(3) | -9(4) |
| C(26E) | 41(4) | 41(4) | 28(3) | 0(3) | 7(3) | -3(3) |
| C(26D) | 46(4) | 45(4) | 36(4) | 7(3) | 12(3) | 3(3)  |
| C(26B) | 41(4) | 68(5) | 40(4) | 9(4) | 7(3) | 3(4)  |
| C(27A) | 30(3) | 29(3) | 37(3) | -4(3) | 4(3) | -2(3) |
| C(27F) | 34(3) | 31(4) | 41(4) | 5(3) | 5(3) | 8(3)  |
| C(27E) | 50(4) | 32(3) | 32(3) | -3(3) | 7(3) | 6(3)  |
| C(27B) | 45(4) | 35(4) | 37(4) | 5(3) | 4(3) | 5(3)  |
| C(27D) | 38(3) | 34(3) | 43(4) | 0(3) | 10(3) | -7(3) |
| C(27C) | 56(5) | 45(4) | 53(5) | 14(4) | 32(4) | 15(4) |
| C(28A) | 42(4) | 34(4) | 35(3) | -4(3) | 8(3) | -1(3) |
| C(28B) | 48(4) | 38(4) | 40(4) | 2(3) | 11(3) | 4(3)  |
| C(28E) | 56(5) | 56(5) | 38(4) | 1(4) | 6(3) | 11(4) |
| C(28F) | 39(4) | 36(4) | 47(4) | -3(3) | 9(3) | 4(3)  |
| C(28D) | 44(4) | 36(4) | 49(4) | -1(3) | 11(3) | -5(3) |
| C(28C) | 39(4) | 67(5) | 48(4) | 11(4) | 9(3) | 3(4)  |
| C(29A) | 43(4) | 37(4) | 43(4) | 1(3) | -4(3) | 2(3)  |
| C(29D) | 57(5) | 42(4) | 43(4) | 7(3) | 6(3) | -8(3) |
| C(29F) | 49(4) | 41(4) | 51(4) | -5(3) | 4(3) | 5(3)  |
| C(29B) | 58(5) | 40(4) | 39(4) | 0(3) | 13(3) | 6(3)  |
| C(29E) | 81(7) | 66(6) | 46(5) | -2(4) | 9(4) | 42(5) |
| C(29C) | 55(5) | 123(10) | 48(5) | 6(6) | 3(4) | 9(6)  |
| C(30A) | 37(4) | 42(4) | 51(4) | -2(3) | 0(3) | 9(3)  |
| C(30D) | 49(4) | 31(4) | 68(5) | 7(3) | 10(4) | -6(3) |
|      | C(53E)    | C(54E)    | C(55E)    | C(56E)    | C(57E)    | C(58E)    | C(59E)    | C(60E)    | C(61E)    | C(62E)    | C(63E)    | C(64E)    | C(65E)    | C(66E)    | C(67E)    | C(68E)    | C(69E)    | C(70E)    | C(71E)    | C(72E)    | C(73E)    | C(74E)    | C(75E)    | C(76E)    | C(77E)    | C(78E)    | C(79E)    | C(80E)    | C(81E)    | C(82E)    | C(83E)    | C(84E)    |
|------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
|      | 79(13)    | 1150(180) | 126(19)   | -200(50)  | 26(12)    | -190(40)  |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |
| C(53E) | 120(14)   | 200(20)   | 115(14)   | -88(15)   | 46(12)    | -56(15)   |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |
| C(54E) | 230(30)   | 101(13)   | 106(13)   | 13(11)    | 67(16)    | 21(16)    |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |
| C(55E) | 101(10)   | 117(12)   | 79(8)     | -11(7)    | 19(7)     | -28(9)    |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |
| C(56E) | 200(30)   | 190(30)   | 200(30)   | 80(20)    | 90(20)    | 100(20)   |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |
| C(57E) | 370(50)   | 106(15)   | 122(16)   | 6(13)     | 120(20)   | 80(20)    |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |
| C(58E) | 210(30)   | 120(20)   | 400(60)   | -40(30)   | -50(40)   | 90(20)    |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |
| C(59E) | 530(80)   | 760(130)  | 190(30)   | -240(60)  | -140(40)  | 560(100)  |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |
| C(60E) | 480(60)   | 710(100)  | 890(120)  | 740(100)  | 600(80)   | 510(70)   |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |
| C(61E) | 350(50)   | 210(30)   | 140(20)   | 100(20)   | 140(30)   | 120(30)   |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |
| C(62E) | 57(6)     | 74(8)     | 118(11)   | 42(8)     | -11(6)    | -2(5)     |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |
| C(63E) | 93(9)     | 134(14)   | 78(8)     | 17(8)     | 20(7)     | 50(9)     |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |
| C(64E) | 82(7)     | 75(7)     | 92(8)     | -5(6)     | 43(6)     | -16(6)    |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |
| C(65E) | 69(6)     | 134(13)   | 80(7)     | -10(8)    | 27(6)     | -38(8)    |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |
| C(66E) | 60(5)     | 58(6)     | 102(8)    | -1(6)     | 31(5)     | 11(5)     |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |           |

S-81
Table 5. Hydrogen coordinates (× 10^4) and isotropic displacement parameters (Å^2 × 10^3) for wulf01.

|    | x   | y   | z   | U(eq) |
|----|-----|-----|-----|-------|
| H(1X) | 9630 | 6584 | 398 | 50    |
| H(1Y) | 9871 | 6940 | 930 | 50    |
| H(2X) | 6108 | 3701 | 6373| 50    |
| H(2Y) | 6718 | 3411 | 6292| 50    |
| H(3X) | 8418 | 4490 | 5013| 50    |
| H(3Y) | 8448 | 5045 | 5411| 50    |
| H(2AA) | 9890 | 8700 | -1012| 50    |
| H(2CA) | 5832 | 2901 | 5858| 64    |
| H(2BA) | 9436 | 2170 | 8944| 64    |
| H(2FA) | 8444 | 4481 | 73    |
| H(4AA) | 10928| 4508 | 2613| 45    |
| H(4EA) | 5635 | 5761 | 4131| 46    |
| H(4CA) | 7978 | 5199 | 210 | 44    |
| H(4DA) | 7589 | 1128 | 6900| 43    |
| H(4BA) | 9045 | 4246 | -62 | 43    |
| H(4FA) | 7477 | 5655 | 6929| 41    |
| H(5AA) | 11675| 4400 | 3460| 51    |
| H(5EA) | 5119 | 5909 | 3196| 52    |
| H(5DA) | 8330 | 3971 | 7736| 49    |
| H(5FA) | 8069 | 5629 | 7837| 48    |
| H(5BA) | 8356 | 4158 | -939| 50    |
| H(5CA) | 7310 | 5296 | -668| 53    |
| H(6BA) | 7338 | 3675 | -1024| 53    |
| H(6AA) | 12724| 4815 | 3528| 54    |
| H(6FA) | 7696 | 5015 | 8557| 54    |
| H(6EA) | 5619 | 6558 | 2585| 61    |
| H(6DA) | 9298 | 3377 | 7725| 49    |
| H(6CA) | 7064 | 6388 | -1072| 55    |
| H(7BA) | 6989 | 3278 | -235| 51    |
| H(7AA) | 13027| 5337 | 2768| 48    |
| H(7EA) | 6693 | 4530 | 8381| 53    |
| H(7DA) | 9533 | 2992 | 6895| 47    |
| H(7FA) | 6617 | 7024 | 2899| 60    |
| H(7CA) | 7455 | 7361 | -583| 50    |
| H(9BA) | 7202 | 3083 | 804 | 48    |
| H(9DA) | 9219 | 2865 | 5842| 42    |
| H(9CA) | 8053 | 7904 | 326 | 45    |
| H(9FA) | 5674 | 4257 | 7713| 48    |
| H(9EA) | 7572 | 7207 | 3679| 45    |
| H(9AA) | 12739| 5758 | 1772| 43    |
| H(14D) | 9857 | 5030 | 3011| 47    |
| H(14E) | 10451| 4918 | 3918| 56    |
| H(14F) | 9166 | 5826 | -134| 40    |
| H(14A) | 6283 | 4770 | 3814| 48    |
| H(14B) | 8508 | 5029 | 6454| 44    |
| H(14G) | 10543| 6052 | 2744| 49    |
| H(14C) | 5318 | 4392 | 4348| 54    |
| H(15D) | 10650 | 3841 | 4326 | 56  |
| H(15A) | 5630  | 4579 | 2943 | 60  |
| H(15E) | 8669  | 5730 | -1086| 43  |
| H(15B) | 9261  | 5132 | 7279 | 50  |
| H(15C) | 4593  | 4645 | 3524 | 61  |
| H(15F) | 10948 | 6177 | 3703 | 58  |
| H(16E) | 9124  | 5025 | -1689| 46  |
| H(16B) | 9559  | 6215 | 7669 | 52  |
| H(16D) | 10358 | 2854 | 3793 | 51  |
| H(16A) | 5333  | 4579 | 2943 | 60  |
| H(16C) | 4593  | 4645 | 3524 | 61  |
| H(16F) | 10948 | 6177 | 3703 | 58  |
| H(17E) | 5738  | 2541 | 3198 | 60  |
| H(17E) | 9222  | 6918 | 3918 | 56  |
| H(17C) | 3583  | 5878 | 4361 | 63  |
| H(17B) | 9054  | 7188 | 7250 | 45  |
| H(18A) | 8669  | 5730 | -1086| 43  |
| H(18B) | 9261  | 5132 | 7279 | 50  |
| H(19D) | 4593  | 4645 | 3524 | 61  |
| H(19E) | 10650 | 3841 | 4326 | 56  |
| H(19B) | 9222  | 6918 | 3918 | 56  |
| H(19C) | 5333  | 4579 | 2943 | 60  |
| H(19A) | 4593  | 4645 | 3524 | 61  |
| H(19F) | 10650 | 3841 | 4326 | 56  |
| H(22E) | 9124  | 5025 | -1689| 46  |
| H(22B) | 9559  | 6215 | 7669 | 52  |
| H(22D) | 10358 | 2854 | 3793 | 51  |
| H(22A) | 5333  | 4579 | 2943 | 60  |
| H(22C) | 4593  | 4645 | 3524 | 61  |
| H(22F) | 10650 | 3841 | 4326 | 56  |
| H(23B) | 9124  | 5025 | -1689| 46  |
| H(23D) | 9261  | 5132 | 7279 | 50  |
| H(23A) | 5333  | 4579 | 2943 | 60  |
| H(23C) | 4593  | 4645 | 3524 | 61  |
| H(23E) | 10650 | 3841 | 4326 | 56  |
| H(23F) | 9261  | 5132 | 7279 | 50  |
| H(24D) | 4593  | 4645 | 3524 | 61  |
| H(24E) | 10650 | 3841 | 4326 | 56  |
| H(24B) | 9261  | 5132 | 7279 | 50  |
| H(24C) | 5333  | 4579 | 2943 | 60  |
| H(24A) | 4593  | 4645 | 3524 | 61  |
| H(24F) | 10650 | 3841 | 4326 | 56  |
| H(25B) | 9124  | 5025 | -1689| 46  |
| H(25A) | 9261  | 5132 | 7279 | 50  |
| H(25C) | 5333  | 4579 | 2943 | 60  |
| H(25D) | 4593  | 4645 | 3524 | 61  |
| H(25F) | 10650 | 3841 | 4326 | 56  |
| H(26B) | 9261  | 5132 | 7279 | 50  |
| H(26A) | 5333  | 4579 | 2943 | 60  |
| H(26C) | 4593  | 4645 | 3524 | 61  |
| H(26D) | 10650 | 3841 | 4326 | 56  |
| H(28E) | 11795 | 3990 | 1121 | 44 |
|--------|-------|------|------|----|
| H(28D) | 9568  | 2387 | 1227 | 50 |
| H(28B) | 6534  | 7466 | 5320 | 60 |
| H(28C) | 5413  | 6117 | 6807 | 49 |
| H(28A) | 7225  | 2366 | 5803 | 51 |
| H(28F) | 7488  | 6152 | 1571 | 62 |
| H(29E) | 12824 | 3513 | 1327 | 51 |
| H(29A) | 7635  | 1387 | 6292 | 57 |
| H(29C) | 5148  | 6528 | 7633 | 57 |
| H(29D) | 9390  | 1324 | 800  | 55 |
| H(29B) | 6021  | 8502 | 5003 | 78 |
| H(29F) | 6397  | 6393 | 1219 | 91 |
| H(30E) | 13509 | 3625 | 688  | 54 |
| H(30A) | 7941  | 457  | 5796 | 60 |
| H(30C) | 4102  | 6458 | 7774 | 62 |
| H(30D) | 8830  | 484  | 1180 | 60 |
| H(30B) | 6627  | 9482 | 5003 | 78 |
| H(30F) | 5950  | 7400 | 1464 | 90 |
| H(31E) | 13157 | 4167 | -172 | 52 |
| H(31A) | 7780  | 478  | 4831 | 57 |
| H(31D) | 8463  | 699  | 2007 | 59 |
| H(31B) | 7730  | 9464 | 5261 | 81 |
| H(31F) | 6566  | 8183 | 2039 | 85 |
| H(31G) | 7663  | 2141 | 7235 | 90 |
| H(31H) | 8064  | 1444 | 7286 | 90 |
| H(31I) | 8361  | 2125 | 7076 | 90 |
| H(32E) | 12133 | 4642 | -380 | 47 |
| H(32A) | 7364  | 1461 | 4322 | 52 |
| H(32C) | 3556  | 5566 | 6237 | 50 |
| H(32D) | 8687  | 1753 | 2467 | 51 |
| H(32B) | 8256  | 8454 | 5605 | 63 |
| H(32F) | 7656  | 7944 | 2425 | 69 |
| H(32G) | 7705  | 2694 | 8201 | 77 |
| H(33A) | 8486  | 2768 | 9089 | 80 |
| H(33B) | 9285  | 1646 | 8037 | 57 |
| H(34A) | 9285  | 7932 | -255 | 103 |
| H(34B) | 8192  | 7677 | -2144| 103 |
| H(41B) | 7851  | 7502 | -1628| 103 |
| H(41C) | 8316  | 6954 | -1833| 103 |
| H(41D) | 4472  | 2095 | 4052 | 113|
| H(41E) | 5144  | 2414 | 3972 | 113|
| H(41F) | 4569  | 2905 | 4060 | 113|
| H(42A) | 8830  | 7190 | -646 | 63 |
| H(42B) | 4528  | 1641 | 5047 | 70 |
| H(43A) | 9752  | 7932 | -255 | 60 |
| H(43B) | 5142  | 1938 | 5999 | 73 |
| H(44A) | 9116  | 8463 | -1853| 55 |
| H(44B) | 5639  | 3272 | 4912 | 68 |
| H(52A) | 13447 | 1623 | 2334 | 66 |
| H(52B) | 8836  | 9672 | 4621 | 81 |
| H(52C) | 4760  | 8248 | -174 | 119|
| H(52D) | 6604  | 1873 | 8500 | 106|
| H(53A) | 13031 | 1862 | 3149 | 78|

S-84
| H      | 1st | 2nd  | 3rd | 4th |
|--------|-----|------|-----|-----|
| H(53B)| 9942| 9996 | 4762| 92  |
| H(53C)| 5796| 8444 | 310 | 113 |
| H(53D)| 6211| 2416 | 9240| 117 |
| H(54A)| 10319|10518 |4045| 94  |
| H(54B)| 13036|3204 | 9027| 110 |
| H(54C)| 6547| 7594 | 354 | 100 |
| H(54D)| 5327| 3204 | 9027| 77  |
| H(55A)| 13488|3855 | 3048| 70  |
| H(55B)| 9639| 10799|3210| 89  |
| H(55C)| 6301| 6525 | -35 | 110 |
| H(55D)| 4815| 3344 | 8102| 112 |
| H(56A)| 8588| 10467|3047| 75  |
| H(56B)| 13887|3614 | 2211| 68  |
| H(56C)| 5208| 6327 | -532| 101 |
| H(56D)| 13558|3611 | 1760| 154 |
| H(57E)| 6597| 4879 | 1632| 540 |
| H(57F)| 6386| 3721 | 1441| 168 |
| H(58E)| 5343| 3294 | 1379| 168 |
| H(58F)| 4510| 4025 | 1507| 119 |
| H(59F)| 5701| 9893 | 72  | 227 |
| H(59F)| 4651| 9879 | -462| 308 |
| H(59F)| 3772| 9911 | -11 | 627 |
| H(59F)| 3943| 9956 | 974 | 751 |
| H(59F)| 4993| 9970 | 1507| 264 |
| H(59F)| 5166| 2780 | 7360| 104 |
| H(60F)| 7357| 5346 | 2445| 152 |
| H(61F)| 6994| 5759 | 2859| 152 |
| H(61F)| 6904| 4950 | 2794| 152 |
| H(62F)| 8517| 5166 | 2880| 95  |
| H(63F)| 9173| 5068 | 3844| 111 |
| H(64F)| 7353| 5165 | 3983| 85  |
10. Catalysis of the Rearrangement of 22a with Crystals of Complex 28.

![](image)

Crystals of complex 28 (0.0040 g, 0.0025 mmol, 2.5 mol%) were added to a 20 mL vial along with a-iminol 22a (0.0287 g, 0.10 mmol) and toluene (0.3 mL) and an atmosphere of air according to Procedure 4. The vial was capped and heated in a 60 °C oil bath for 1 h. The solution was cooled to room temperature and the product purified by column chromatography on silica gel to afford the product 23a as a light yellow solid in 96% yield (0.0275 g, 0.0958 mmol). The optical purity was determined to be 98% ee as described on page S-29. The spectral data also matched those for compound 23a on page S-29.

11. Studies on the Stability of Catalyst 28.

The stability of the catalyst slurry (R)-15 that was prepared from section 4 was studied and summarized in the table below. All reactions were run according to procedure 4 with iminol 22a and the same batch of catalyst (R)-15 that had been stored as a solution in toluene in a vial (as shown) at room temperature under air for a period of up to 5 months and 10 days.
### Table 1: Yield and Ee of 23a

| Entry | Age of the Catalyst | Yield of 23a | Ee of 23a |
|-------|---------------------|--------------|-----------|
| 1     | Fresh               | 94%          | 97%       |
| 2     | 24 h old            | 97%          | 97%       |
| 3     | 6 days old          | 95%          | 97%       |
| 4     | 2 weeks old         | 98%          | 95%       |
| 5*    | 5 months 10 days old| 98%          | 97%       |

*The reaction time was 2.5 h.

12. **Studies on the Effect of Temperature on the $\alpha$-Iminol Rearrangement of 22a.**

The $\alpha$-iminol rearrangement of 22a was examined at temperatures from ambient to 160 °C and the results are presented in the table below. All reactions were performed with Procedure 4. The catalyst and substrate were mixed at room temperature and heated to the indicated temperature except the reaction in entry 9. This reaction was performed by heating the catalyst in mesitylene to 160 °C in the presence of air and then adding the substrate. The reaction was complete in 30 seconds and gave a 95% yield of (S)-23a with 89% ee.
13. Studies on the Effect of Solvent and Catalyst Composition on the α-Iminol Rearrangement of 22a.

The solvent can have a large effect on the rate of the reaction as illustrated by the data in Table 2. Coordinating solvents such as THF, EtOAc and CH₂CN provide only very low conversions under conditions where the reactions in aromatic solvents go to completion (60 °C, 1 h). Dichloroethane also provides low conversion in this timeframe and chloroform is also slower than the aromatic solvents. The components of the catalyst are the ligand, Zr(OiPr)₄(HOiPr), and N-methylimidazole and the amounts of each can have a dramatic effect, especially for the latter. Variations in the ratio of ligand to zirconium find that there is no change in induction when it is raised from 1:1 to 2:1 and to 3:1 but the yield does increase (entries 9, 11 and 15). However, the amount of N-methylimidazole has a dramatic effect on the rate of the reaction; without

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**Table.** Effect of Temperature on the α-Iminol Rearrangement of 22a.

| entry | temp (°C) | time (min) | solvent | % yield 23a | % ee 23a |
|-------|-----------|------------|---------|-------------|---------|
| 1     | 25        | 2880       | toluene | 55          | 97      |
| 2     | 40        | 480        | toluene | 98          | 98      |
| 3     | 50        | 150        | toluene | 95          | 97.5    |
| 4     | 60        | 60         | toluene | 94          | 97      |
| 5     | 70        | 60         | toluene | 95          | 97      |
| 6     | 80        | 30         | toluene | 97          | 97      |
| 7     | 100       | 10         | toluene | 100         | 95      |
| 8     | 120       | 5          | toluene | 96          | 95      |
| 9 a   | 160       | 0.5        | mesitylene | 95        | 89      |

a The substrate 22a was added to a solution of 15 in mesitylene that was pre-heated to 160 °C.
imidazole there is no reaction but with one equivalent the reaction goes to completion in one hour (entries 10 vs 11). Increasing the amount of N-methyl imidazole past one equivalent slows down the reaction; the yield drops to 70% with two equivalents and to 8% with twenty equivalents (entries 12 and 13).

Table. Optimization of Catalyst Composition and Solvent. a

| entry | solvent | % yield 23a | % ee 23a | entry | Ratio Zr:L:N | % yield 23a | % ee 23a |
|-------|---------|-------------|-----------|-------|--------------|-------------|---------|
| 1     | toluene | 94          | 97        | 9     | 1:1:1        | 67          | 97      |
| 2     | benzene | 100         | 97        | 10    | 1:2:0        | 0           | 0       |
| 3     | mesitylene | 96          | 94.5      | 11    | 1:2:1        | 94          | 97      |
| 4     | THF     | 6           | 94.5      | 12    | 1:2:2        | 70          | 97      |
| 5     | EtOAc   | 15          | 92        | 13    | 1:2:20       | 8           | 95.5    |
| 6     | CH₂CN   | 9           | 71        | 14    | 1:3:0        | 0           | 0       |
| 7     | CHCl₂CH₂Cl | 20         | 90        | 15    | 1:3:1        | 98          | 98      |
| 8     | CHCl₃   | 56          | 94        | 16    | 1:3:2        | 80          | 96      |

a Unless otherwise specified, all reactions were run with 2.5 mol% (R)-15 in the indicated solvent at 0.3 M in 22 (0.1 mmol) at 60 °C for 1 h under air and went to 100% completion. The catalyst was prepared by stirring a toluene solution of Zr(OiPr)₄(HOiPr) with 2 equiv of (R)-VANOL and 1 equiv of N-methylimidazole at 25 °C for 30 minutes. b Ratio of Zr:L:N is 1:2:1 c Isolated yield. d Determined by HPLC. e Solvent is toluene

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