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General Method and Materials

Chemical reagents and starting materials, unless otherwise noted, were purchased from commercial vendors and used without further purification. Most chemicals were from Sigma-Aldrich, except hafnium(IV) *tert*-butoxide was from Alfa Aesar. Anhydrous solvents were purchased from J. T. Baker, and purified by M. BRAUN solvent purification system (A2 alumina).

All epoxidation reactions were carried out in FisherbrandTM 16×100 mm test tubes sealed with sleeve stoppers and PTFE tape. FisherbrandTM 4×12 mm disposable PTFE stir bars were used. Reactions were monitored by thin-layer chromatography using Macherey-Nagel pre-coated silica gel glass plates (0.25 mm, $UV_{254} + UV_{366}$ indicator) and visualized using UV light (254 nm) and Cerium-ammonium-molybdate stain. Flash chromatography was performed on silica gel (ZEOprep 60 HYD 40-63 micron). Yields refer to chromatographically and spectrographically pure material, unless otherwise noted.

¹H and ¹³C NMR spectra were recorded on a Bruker DMX 500 spectrometer. Chemical shifts (δ scale) are reported in ppm relative to tetramethylsilane. The proton spectra are reported as follows: δ (multiplicity, coupling constant J, number of protons). Multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). High-performance liquid chromatography was performed on a Varian ProStar Series equipped with a variable wavelength detector using chiral stationary phases (Chirapak AD-H, AS-H, IB, IC, ID; 0.46 cm × 25 cm) from Daicel. Infrared spectra were recorded as thin films on sodium chloride plates using a Nicolet 20 SXB FTIR spectrometer. High-resolution mass spectra were acquired from a Agilent 6224 Tof-MS with 1290 UHPLC. The X-ray diffraction data were collected at 100 K on a Bruker D8 VENTURE with PHOTON 100 CMOS detector system equipped with a Cu-target X-ray tube ($\lambda = 1.54178$ Å).

Ligands (*R*, *R*)-L1, (*R*, *R*)-L2 and (*S*, *S*)-L2 were prepared according to previous literature.^{[1][2]} Ligand (+)-diisopropyl L-tartrate and (-)-diisopropyl D-tartrate were obtained from Sigma-Aldrich.

Derivation of the Kinetic Resolution Equation for Non-Racemic Mixture

$$R_0 + S_0 \longrightarrow R + R_p + S + S_p$$

Assume reaction starts with a known $\frac{R_o}{S_o}$, where $R_o > S_o$, thus

$$ee_o = \frac{(R_o - S_o)}{(R_o + S_o)}$$

$$conversion(c) = \frac{total \ product}{total \ starting \ material} = \frac{(R_o - R) + (S_o - S)}{(R_o + S_o)}$$

$$ee = \frac{product \ diff.}{total \ product} = \frac{(R_p - S_p)}{(R_p + S_p)} = \frac{(R_o - R) + (S_o - S)}{(R_o - R) + (S_o - S)}$$

S and R are expressed as a function of ee, c, R_0 and S_0 , and

$$R = \frac{(R_o + S_o)(1 + c - ee \cdot c) + (R_o - S_o)}{2}$$
$$S = \frac{(R_o + S_o)(1 + ee \cdot c - c) - (R_o - S_o)}{2}$$
$$seletivity = \frac{\ln(\frac{R}{R_o})}{\ln(\frac{S}{S_o})}$$
$$0 < c < 1$$

A plot of *ee* vs *c* is generated using Maplesoft, given the values of constants R_0 and S_0 , and *selectivity*.

When $R_0 = 0.5$, $S_0 = 0.5$ and *selectivity* = 50, $ee_0 = 0$. This is the standard scenario of a kinetic resolution of a racemic mixture, and the plot of *ee* vs *c* is depicted below.



When $R_0 = 0.9$, $S_0 = 0.1$ and *selectivity* = 50, $ee_0 = 0.8$. This is the case when reaction proceeds with an unequal mixture of R_0 and S_0 .



Intergrating the two plots above, one could see the advantage of running a kinetic resolution of non-racemic mixture.



Preparation and Characterization of Secondary Allylic Alcohols 1-10



Synthesis of substrates 1-3 and 6-10.

To a 100 ml flame-dried round-bottom flask of aryl bromide (20 mmol) in THF (20 ml) was purged with nitrogen and cooled to -78 °C in an acetone/dry ice bath. n-BuLi (1.6 M in THF, 20 mmol) was added dropwise to the solution and stirred at -78 °C for 1 hour. Aldehyde (20 mmol) in THF (20 ml) was then added and the reaction was slowly warmed up to room temperature and stirred overnight. The mixture was quenched with saturated NH₄Cl solution, extracted with diethyl ether and dried over sodium sulfate. The solvent was removed under reduced pressure to yield the crude product, which was purified using flash column chromatography (Hex:EtOAc=10:1).

Synthesis of substrates 4 and 5.

To a 100 ml flame-dried round-bottom flask of aldehyde (20 mmol) in THF (20 ml) at -78 °C was slowly added *n*-BuLi (1.6 M in THF, 20 mmol) and maintained at this temperature for 1 h. The reaction was then warmed up to room temperature overnight and quenched with saturated NH₄Cl solution, extracted with diethyl ether and dried over sodium sulfate. The solvent was removed under reduced pressure, and the crude mixture was purified by flash column chromatography (Hex:EtOAc=10:1).



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2: colorless oil. IR (film): 3345, 3085, 3062, 3029, 2958, 2929, 2872, 1493, 1453, 1379, 1338, 1193, 1192, 1072, 1030, 1005, 966, 914, 843, 757, 699, 634, 550 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ = 7.30-7.37 (m, 4 H), 7.22-7.26 (m, 1 H), 5.70-5.75 (m, 1 H), 5.61-5.66 (m, 1 H), 5.12 (d, J=6.65 Hz, 1 H), 2.23 (s, 1 H), 2.02 (g, J=7.08 Hz, 2 H), 1.40 (sext, J=7.37 Hz, 2 H), 0.89 (t, J=7.37 Hz, 3 H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ = 143.6, 132.6, 132.6, 128.5 (2 C), 127.5, 126.3 (2 C), 75.2, 34.3, 22.3, 13.8 ppm. HRMS (ESI): calcd. for $C_{12}H_{15}$ [M+H-H₂O]⁺: 159.1168 found: 159.1173.



6: colorless oil. IR (film): 2243, 2960, 2930, 2873, 1604, 1509, 1464, 1412, 1379, 1223, 1156, 1086, 1042, 1013, 968, 866, 836, 586, 549 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ = 7.29-7.32 (m, 2 H), 6.98-7.02 (m, 2 H), 5.68-5.74 (m, 1 H), 5.57-5.62 (m, 1 H), 5.10 (d, J=6.80 Hz, 1 H), 2.33 (s, 1 H), 2.02 (q, J=7.15 Hz, 2 H), 1.40 (sext, J=7.38 Hz, 2 H), 0.89 (t, J=7.37 Hz, 3 H) ppm; ¹³C

NMR (126 MHz, CDCl₃) δ = 162.2 (d, J=245 Hz, 1 C), 139.3 (d, J=3.08 Hz, 1 C), 132.8, 132.5, 127.9 (d, J=8.07 Hz, 2 C), 115.2 (d, J=21.3 Hz, 2 C), 74.6, 34.3, 22.3, 13.8 ppm. HRMS (ESI): calcd. for $C_{12}H_{14}F[M+H-H_2O]^+$: 177.1074 found: 177.1083.



7 : yellow oil. IR (film): 3335, 3049, 2957, 2928, 2871, 1597, 1510, 1456, 1436, 1395, 1378, 1260, 1228, 1165, 1092, 1074, 1049, 968, 798, 777, 734, 634, 570 cm^{-1} ; ¹H NMR (500 MHz, CDCl₃) $\delta = 8.10-8.12$ (m, 1 H), 7.81-7.83 (m, 1 H),7.73-7.75 (m, 1 H), 7.58-7.60 (m, 1 H), 7.40-7.48 (m, 3 H), 5.77-5.82 (m, 3 H), 2.26 (s, 1 H), 1.97-2.01 (m, 2 H), 1.36 (sext, J=7.37 Hz, 2 H), 0.85 (t, J=7.37 Hz, 3 H) ppm; 13 C NMR (126 MHz, CDCl₃) δ = 139.0, 134.0, 133.1, 131.9, 130.7, 128.8, 128.3, 126.0,

125.6, 125.5, 124.0, 123.6 ppm. HRMS (ESI): calcd. for $C_{16}H_{17}$ [M+H-H₂O]⁺: 209.1325 found: 209.1333.



8: colorless oil. IR (film): 3351, 3062, 3029, 2959, 2929, 2869, 1666, 1493, 1465, 1451, 1383, 1364, 1305, 1221, 1193, 1102, 1059, 1007, 969, 915, 760, 699, 634, 547 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ = 7.22-7.35 (m, 5 H), 5.68-5.72 (m, 1 H), 5.55-5.60 (m, 1 H), 5.10 (d, J=6.80 Hz, 1 H), 2.45 (s, 1 H), 2.29 (oct, J=6.58 Hz, 1 H), 0.99 $(d, J=6.75 \text{ Hz}, 3 \text{ H}), 0.98 (d, J=6.75 \text{ Hz}, 3 \text{ H}) \text{ ppm}; {}^{13}\text{C} \text{ NMR} (126 \text{ MHz}, \text{CDCl}_3) \delta =$

143.5, 139.5, 129.5, 128.5 (2 C), 127.4, 126.3 (2 C), 75.2, 30.7, 22.3, 22.2 ppm. HRMS (ESI): caled. for $C_{12}H_{15}$ [M+H-H₂O]⁺: 159.1168 found: 159.1172.



3: white solid. IR (film): 3340, 3059, 3082, 3027, 1600, 1494, 1449, 1391, 1300. 1191, 1092, 1067, 1009, 966, 915, 796, 745, 695, 638, 604, 544 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ = 7.21-7.42 (m, 10 H), 6.66-6.69 (m, 1 H), 6.35-6.40 (m, 1 H), 5.37 (d, *J*=5.90 Hz, 1 H), 2.10 (s, 1 H) ppm; ¹³C NMR (126 MHz, CDCl₃) $\delta = 142.9, 136.7, 131.7, 130.7, 128.8 (2 \text{ C}), 128.7 (2 \text{ C}), 127.9, 126.7 (2 \text{ C}), 126.5 (2 \text{ C}),$ C), 75.3 ppm. HRMS (ESI): calcd. for $C_{15}H_{13}$ [M+H-H₂O]⁺: 193.1012 found: 193.1008.



9: yellow oil. IR (film): 3335, 3030, 1601, 1559, 1540, 1508, 1455, 1418, 1228, 1158, 1070, 1013, 967, 857, 834, 763, 700, 668, 513 cm⁻¹; ¹H NMR (500 MHz, $CDCl_3$) $\delta = 7.26-7.41$ (m, 7 H), 6.95-6.98 (m, 2 H), 6.58-6.62 (m, 1 H), 6.24-6.29 (m, 1 H), 5.32 (d, *J*=6.45 Hz, 1 H), 2.36 (s, 1 H) ppm; ¹³C NMR (126 MHz, $CDCl_3$) $\delta = 162.4$ (d, J=247 Hz, 1 C), 142.8, 132.8, 131.4, 129.3, 128.6 (2 C),

128.2 (d, J=8.02 Hz, 2 C), 127.8, 126.4 (2 C), 115.5 (d, J=21.6 Hz, 2 C), 74.9 ppm. HRMS (ESI): calcd. for C₁₅H₁₂F [M+H-H₂O]⁺: 211.0918 found: 211.0927.



10: white solid. IR (film): 3334, 3061, 3028, 1653, 1559, 1487, 1453, 1419, 1400, 1298, 1190, 1071, 1008, 967, 850, 818, 790, 762, 699, 658, 634, 559 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ = 7.23-7.43 (m, 9 H), 6.61-6.64 (m, 1 H), 6.35- $6.39 \text{ (m, 1 H)}, 5.37 \text{ (d, } J=5.90 \text{ Hz}, 1 \text{ H)}, 2.06 \text{ (s, 1 H)} \text{ ppm}; {}^{13}\text{C} \text{ NMR} (126 \text{ MHz}, 1)$ $CDCl_3$) $\delta = 142.7, 135.6, 132.4, 131.8 (2 C), 129.4, 128.8 (2 C), 128.3 (2 C),$

128.1, 126.5 (2 C), 121.7, 75.1 ppm. HRMS (ESI): calcd. for C₁₅H₁₂Br [M+H-H₂O]⁺: 271.0117 found: 271.0121.



4 : colorless oil. IR (film): 3341, 2957, 2927, 2857, 1467, 1378, 1005, $1025, 967, 727 \text{ cm}^{-1}$; ¹H NMR (500 MHz, CDCl₃) $\delta = 5.59-5.65 \text{ (m, 1 H)},$ 5.42-5.47 (m, 1 H), 4.02 (q, J=6.71 Hz, 1 H), 2.02 (q, J=7.08 Hz, 2 H), 1.70 (s, 1 H), 1.23-1.59 (m, 15 H), 0.89 (q, *J*=7.28 Hz, 6 H) ppm; ¹³C NMR (126

MHz, CDCl₃) δ = 133.2, 132.2, 73.3, 37.2, 32.3, 31.8, 29.3, 28.9, 28.9, 27.8, 22.7, 22.7, 14.2 ppm. HRMS (ESI): calcd. for $C_{13}H_{25}$ [M+H-H₂O]⁺: 181.1951 found: 181.1943.



11: colorless oil. ¹H NMR (500 MHz, CDCl₃) δ = 5.55-.61 (m, 1 H), 5.42-5.47 (m, 1 H), 3.75 (t, *J*=7.00 Hz, 1 H), 2.18 (s, 1 H), 1.99-2.04 (m, 2 H), 1.84-1.88 (m, 1 H), 1.70-1.75 (m, 2 H), 1.64-1.68 (m, 2 H), 1.35-1.42 (m, 3 H), 1.16-1.25 (m, 2 H), 0.94-1.00 (m, 2 H), 0.90 (t, *J*=7.37 Hz, 3 H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ = 132.5, 131.8, 77.6, 43.7, 34.4, 28.8, 28.8, 26.6, 26.2, 22.4, 13.6 ppm.



5: yellow oil. ¹H NMR (500 MHz, CDCl₃) δ = 7.28-7.31 (m, 2 H), 6.95-6.98 (m, 2 H), 6.49 (d, *J*=15.90 Hz, 1 H), 6.11 (dd, *J*=15.90, 6.80 Hz, 1 H), 4.21-4.25 (m, 1 H), 3.05 (s, 1H), 1.55-1.66 (m, 2 H), 1.30-1.38 (m, 4 H), 0.89 (t, *J*=7.00 Hz, 3 H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ =162.3 (d, *J*=247 Hz, 1 C), 133.0, 132.5, 128.9, 128.0, 128.0 (d, *J*=7.97 Hz, 2 C), 115.4 (d, *J*=21.6 Hz, 2 C), 73.0, 37.1, 27.7, 22.7, 14.0 ppm.

General Procedure for the Kinetic Resolution of Secondary Allylic Alcohols By Enantioselective Epoxidation

Method a: Titanium-Tartrate Catalyzed Enantioselective Epoxidation

To a room temperature solution of substrate (1 mmol) and L-(+)-DIPT (28 mg, 0.12 mmol) in CH₂Cl₂ (4 ml) was added activated 3 Å molecular sieves (30 wt % of substrate) and cooled to -20 °C for 10 min. Ti(OiPr)₄(30 µl, 0.1 mmol) was added and stirred at -20 °C for 20-30 min. *tert*-Butyl hydroperoxide (127 µl, 0.7 mmol, ~5.5 M in decane) was added dropwise until 50 % conversion indicated by TLC analysis. The reaction was quenched with 6 ml of an aqueous solution (50 ml) of ammonia iron sulfate heptahydrate (16.5 g) and L-tartaric acid (5 g) at room temperature, and stirred vigorously until phase separation. The organic layer was dried over sodium sulfate and concentrated *in vacuo*. The product was purified by preparatory TLC (Hexane:EtOAc = 10:1). Procedure was similar to previous literature.^[3]

Method b: Titanium-Tartrate Catalyzed Enantioselective Epoxidation Similar to method A, except D-(-)-DIPT was used.

Method c: Tungsten-BHA Catalyzed Asymmetric Epoxidation

To a test tube was added substrate (0.4 mmol), (*R*, *R*)-L2 (17 mg, 0.012 mmol), WO₂(acac)₂ (4.1 mg, 0.01 mmol), NaCl (12 mg, 0.2 mmol) and CH₂Cl₂ (4 ml). H₂O₂ (30 wt %, 0.8 mmol) was added (solution turned from murky yellow to clear light yellow color after 10 min) and the reaction was stirred at room temperature for 24 hours. The mixture was diluted with CH₂Cl₂, dried over sodium sulfate and concentrated *in vacuo*. The crude product was purified using flash chromatography (Hexane:EtOAc = 10:1). The procedure was same as previous literature.^[2]

Method d: Hafnium-BHA Catalyzed Asymmetric Epoxidation

To a flame-dried test tube was added (*R*, *R*)-L1 (0.055 mmol, 29.4 mg) and MgO (0.2 mmol, 8 mg). $Hf(OtBu)_4$ (0.05 mmol, 20.2 µl, fresh out of the glove box) was dissolved in toluene (2.5 ml) and added to the test tube with L1, and stirred at room temperature for 2 h. Substrate (1 mmol) in toluene (2.5 ml) was added to complex at room temperature and cooled to 0 °C, cumene peroxide (80 %, 1 mmol, 184 µl) was added at once and stirred at 0 °C until approximately 50 % conversion. The mixture was quenched with methanol, filtered over a plug of silica, and concentrated *in vacuo*. The residue was purified by flash chromatography (100 % CH₂Cl₂) to furnish the epoxide. The procedure was similar to previous literature.^[4]



Asymmetric epoxidation, method a, 15 h. ¹H NMR (500 MHz, CDCl₃) δ = 7.33-7.41 (m, 5 H), 4.94 (d, *J*=2.75 Hz, 1 H), 3.23-3.25 (m, 1 H), 2.96-2.98 (m, 1 H), 2.76-2.77 (m, 1 H), 2.30 (s, 1 H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ = 139.5, 128.8 (2 C), 128.4, 126.5 (2 C), 70.8, 55.2, 43.6 ppm. HRMS (ESI): calcd. for C₉H₉O [M+H]⁺ [-H₂O]: 133.0648 found: 133.0649.



Asymmetric epoxidation: method a, 2 h, 50 % yield. ¹H NMR (500 MHz, CDCl₃) δ = 7.31-7.38 (m, 5 H), 4.86 (d, *J*=3.05 Hz, 1 H), 3.16-3.18 (m, 1 H), 2.96-2.97 (m, 1 H), 2.46 (s, 1 H), 1.35-1.55 (m, 4 H), 0.87 (t, *J*=7.25 Hz, 3 H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ = 139.8, 128.7 (2 C), 128.3, 126.5 (2 C), 71.1, 61.4, 55.2, 33.6, 19.4, 13.9 ppm. HRMS (ESI): calcd. for C₁₂H₁₆ Na O₂ [M+Na]⁺: 215.1043 found:

215.1007.



Asymmetric epoxidation: method a, 1 h, 43 % yield. ¹H NMR (500 MHz, CDCl₃) δ = 7.34-7.37 (m, 2 H), 7.04-7.07 (m, 2 H), 4.84 (d, *J*=2.95 Hz, 1 H), 3.13-3.16 (m, 1 H), 2.93-2.94 (m, 1 H), 2.54 (s, 1 H), 1.36-1.57 (m, 4 H), 0.88 (t, *J*=7.22 Hz, 3 H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ = 162.7 (d, *J*=246 Hz, 1 C), 135.6, 128.2 (d, *J*=8.16 Hz, 2 C), 115.6 (d, *J*=21.5 Hz, 2 C) 70.6, 61.3, 55.2, 33.6, 19.4,

13.9 ppm. HRMS (ESI): calcd. for $C_{15}H_{18}NO_2 [M+H]^+[-H_2O]$: 193.1023 found: 193.1017.



Asymmetric epoxidation: method a, 1 h, 39 % yield. ¹H NMR (500 MHz, CDCl₃) $\delta = 8.09$ (d, *J*=8.40 Hz, 1 H), 7.87 (d, *J*=7.85 Hz, 1 H), 7.81 (d, *J*=8.25 Hz, 1 H), 7.64 (d, *J*=7.10 Hz, 1 H), 7.46-7.54 (m, 3 H), 5.67 (d, *J*=2.50 Hz, 1 H), 3.18-3.22 (m, 2 H), 2.68 (s, 1 H), 1.34-1.1.50 (m, 4 H), 0.82 (t, *J*=7.27 Hz, 3 H) ppm; ¹³C NMR (126 MHz, CDCl₃) $\delta = 135.6, 133.9, 130.9, 129.0, 128.7, 126.4, 125.8,$

125.6, 123.8, 123.1, 67.6, 60.9, 55.5, 33.6, 19.3, 13.8 ppm. HRMS (ESI): calcd. for $C_{16}H_{19}O_2$ [M+H]⁺: 243.1380 found: 243.1381.



Asymmetric epoxidation: method a, 80 min, 52 % yield. ¹H NMR (500 MHz, CDCl₃) δ = 7.29-7.39 (m, 5 H), 4.85 (d, *J*=2.45 Hz, 1 H), 2.97-2.99 (m, 2 H), 2.53 (s, 1 H), 1.49-1.54 (m, 1 H), 0.99 (t, *J*=6.70 Hz, 3 H), 0.85 (t, *J*=6.90 Hz, 3 H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ = 139.9, 128.7 (2 C), 128.3, 126.6 (2 C), 71.1, 60.6, 60.5, 30.1, 19.1, 18.4 ppm. HRMS (ESI): calcd. for C₁₂H₁₇O₂ [M+H]⁺: 193.1223 found: 193.1201.



Asymmetric epoxidation: method a, 3 h, 48 % yield. ¹H NMR (500 MHz, CDCl₃) δ = 7.24-7.38 (m, 10 H), 4.99 (s, 1 H), 4.14 (d, *J*=1.95 Hz, 1 H), 3.28-3.29 (m, 1 H), 2.55 (d, *J*=2.05 Hz, 1 H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ = 139.3, 136.6, 128.8 (2 C), 128.6 (2 C), 128.5, 128.4, 126.7 (2 C), 125.9 (2 C), 71.3, 65.1, 55.1 ppm. HRMS (ESI): calcd. for C₁₅H₁₄NaO₂ [M+Na]⁺: 249.0886 found: 249.0881.



Asymmetric epoxidation: method a, 80 min, 39 % yield. ¹H NMR (500 MHz, CDCl₃) $\delta = 6.99$ -7.41 (m, 9 H), 5.00 (d, *J*=2.75 Hz, 1 H), 4.12 (d, *J*=1.80 Hz, 1 H), 3.25-3.26 (m, 1 H), 2.45 (s, 1 H) ppm; ¹³C NMR (126 MHz, CDCl₃) $\delta = 162.9$ (d, *J*=247 Hz, 1 C), 139.3, 132.4, 128.9 (2 C), 128.6, 127.6 (d, *J*=8.31 Hz, 2 C), 126.7 (2 C), 115.7 (d, *J*=21.7 Hz, 2 C), 71.3, 65.1, 54.6 ppm. HRMS (ESI): calcd. Ia1⁺: 267.0792 found: 267.0806

for C₁₅H₁₃FNaO₂ [M+Na]⁺: 267.0792 found: 267.0806.



Asymmetric epoxidation: method a, 1 h, 33 % yield. ¹H NMR (500 MHz, CDCl₃) δ = 7.30-7.41 (m, 7 H), 7.11 (d, *J*=8.40 Hz, 2 H), 5.00 (s, 1 H), 4.09 (d, *J*=1.85 Hz, 1 H), 3.22-3.23 (m, 1 H), 2.51 (s, 1 H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ = 139.2, 135.8, 131.8 (2 C), 128.9 (2 C), 128.6, 127.5 (2 C), 126.6 (2 C), 122.3, 71.3, 65.2, 54.6 ppm. HRMS (ESI): calcd. for C₁₅H₁₃BrNaO₂

[M+Na]⁺: 326.9991 found: 327.0046.



Asymmetric epoxidation: method a, 25 min, 44 % yield, 98:2 dr, major diastereomer *anti*-epoxy alcohol isolated for aminolysis. ¹H NMR (500 MHz, CDCl₃) δ = 3.78-3.79 (m, 1 H), 2.98-3.01 (m, 1 H), 2.76-.2.77 (m, 1

H), 2.00-2.01 (m, 1 H), 1.30-1.59 (m, 16 H), 0.87-0.94 (m, 6 H) ppm; 13 C NMR (126 MHz, CDCl₃) $\delta =$ 68.6, 61.2, 55.1, 33.4, 31.9, 31.7, 29.2, 27.6, 26.1, 22.9, 22.7, 14.2, 14.1 ppm. HRMS (ESI): calcd. for $C_{13}H_{27}O_2$ [M+H]⁺: 215.2006 found: 215.1987.

4d

Asymmetric epoxidation: method d, $15 h (0 \degree C) + 3 h (r.t.)$, 56 % yield, 1:2dr, major diastereomer syn-epoxy alcohol isolated for aminolysis. ¹H NMR $(500 \text{ MHz}, \text{CDCl}_3) \delta = 3.44-3.45 \text{ (m, 1 H)}, 2.91-2.92 \text{ (m, 1 H)}, 2.72-2.74$ (m, 1 H), 1.95 (m, 1 H), 1.55-1.58 (m, 4 H), 1.27-1.46 (m, 12 H), 0.87-0.93

(m, 6 H) ppm; 13 C NMR (126 MHz, CDCl₃) δ = 71.6, 62.0, 57.2, 34.2, 31.9, 31.8, 29.2, 27.6, 26.1, 22.8, 22.7, 14.2, 14.1ppm.



11d

Asymmetric epoxidation: method d, 24 h (r.t.), 49 % yield, 32:68 dr, major diastereomer syn-epoxy alcohol was isolated for aminolysis. ¹H NMR (500 MHz, $CDCl_3$) $\delta = 3.59$ (s, 1 H), 3.01-3.01 (m, 1 H), 2.82-2.83 (m, 1 H), 1.89 (s, 1 H), 1.14-1.76 (m, 14 H), 0.98 (t, J=7.17 Hz, 3 H) ppm; ¹³C NMR (126 MHz, CDCl₃) $\delta = 72.5$, 59.7, 55.0, 41.8, 33.8, 29.0, 28.4, 26.6, 26.3, 19.5, 14.1 ppm. HRMS (ESI): calcd. for

 $C_{12}H_{23}O_2$ [M+H]⁺: 199.1693 found: 199.1675.



Asymmetric epoxidation method a, 3 h, 49 % yield, 93:7 dr, major diastereomer *anti*-epoxy alcohol was isolated for aminolysis. ¹H NMR (500 MHz, CDCl₃) δ = 7.23-7.26 (m, 2 H), 7.02-7.05 (m, 2 H), 3.93-3.95 (m, 1 H), 3.03-3.04 (m, 1 H), 2.12 (s, 1 H), 1.33-1.64 (m, 6 H), 0.91 (t, *J*=7.22 Hz, 3 H) ppm; ¹³C NMR $(126 \text{ MHz}, \text{CDCl}_3) \delta = 162.9 \text{ (d}, J=247 \text{ Hz}, 1 \text{ C}), 132.9, 127.5 \text{ (d}, J=8.27 \text{ Hz}, 2 \text{ C})$ C), 115.6 (d, J=21.8 Hz, 2 C), 68.6, 65.1, 54.2, 33.2, 27.5, 22.8, 14.1 ppm. HRMS (ESI): calcd. for C₁₃H₁₈FO₂ [M+H]⁺: 225.1285 found: 225.1252.

S11

General Procedure for the Kinetic Resolution of Secondary Epoxy-Alcohols By Tungsten-Catalyzed Asymmetric Ring-Opening

Method e: Tungsten-Catalyzed Kinetic Resolution of Secondary Epoxy-Alcohols To a THF (2 ml) solution of substrate (0.15 mmol for all, except 0.2 mmol for **4d** and **11d**), W(OEt)₆ (4.5 mg, 0.01 mmol) and (*S*, *S*)-**L2** was added H₂O₂ (2.2 μ l, 0.02 mmol, 30 wt %) at stirred at 55 °C for 1.5 h. Amine (0.1 mmol) was added to reaction and it was stirred at 55 °C until completion. The product was purified using preparatory TLC (Hexane:EtOAc = 4:1). Procedure was similar to previous literature.^[5]

Method f: Tungsten-Catalyzed Kinetic Resolution of Secondary Epoxy-Alcohols Similar to method e, except (R, R)-L2 was used.



Enantioselective aminolysis: method e, 48 h, **2ae** was isolated as a white solid (27.3 mg, 94 %). IR (film): 3402, 3054, 3029, 2957, 2930, 2871, 1601, 1504, 1453, 1431, 1379, 1318, 1260, 1181, 1154, 1102, 1035, 910, 749, 694, 624, 508 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ = 7.31-7.39 (m, 5 H), 7.13-7.16 (m, 2 H), 6.69-6.72 (m, 1 H), 6.58-6.60 (m, 2 H), 4.71 (d, *J*=7.30 Hz, 1 H), 3.81-3.83 (m, 1 H), 3.67-3.69 (m, 1 H),

3.57 (s, 1 H), 2.88 (s, 1 H), 1.82 (s, 1 H), 1.76-1.77 (m, 1 H), 1.47-1.51 (m, 2 H), 1.32-1.33 (m, 1 H), 0.90 (t, *J*=7.27 Hz, 3 H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ = 147.7, 141.3, 129.5 (2 C), 128.8 (2 C), 128.5, 127.2 (2 C), 117.9, 114.0 (2 C), 76.0, 75.5, 55.0, 32.3, 19.3, 14.4 ppm. HRMS (ESI): calcd. for C₁₈H₂₄NO₂ [M+H]⁺: 286.1802 found: 286.1797.



Enantioselective aminolysis: method e, 24 h, **6ae** was isolated as a yellow oil (27.4 mg, 91 %). IR (film): 3400. 2958, 2931, 2871, 1602, 1509, 1467, 1431, 1380, 1317, 1224, 1156, 1035, 837, 786, 751, 693, 573 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ = 7.33-7.36 (m, 2 H), 7.14-7.17 (m, 2 H), 7.02-7.05 (m, 2 H), 6.70-6.73 (m, 1 H), 6.58-6.60 (m, 2 H), 4.72 (d, *J*=7.20 Hz, 1 H), 3.76-3.78 (m, 1 H), 3.62

(m, 1 H), 3.56 (s, 1 H), 2.99 (s, 1 H), 1.87 (s, 1 H), 1.74-1.77 (m, 1 H), 1.45-1.52 (m, 2 H), 1.30-1.32 (m, 1 H), 0.89 (t, J=7.27 Hz, 3 H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ = 162.8 (d, J=246 Hz, 1 C), 147.5, 137.1, 129.5 (2 C), 129.0 (d, J=8.07 Hz, 2 C), 118.2 (2 C), 115.6 (d, J=21.4 Hz, 2 C), 114.1 (2 C), 75.6, 75.4, 55.2, 32.5, 19.2, 14.3 ppm. HRMS (ESI): calcd. for C₁₈H₂₃FNO₂ [M+H]⁺: 304.1707 found: 304.1711.



Enantioselective aminolysis: method e, 44 h, **7ae** was isolated as an orange oil (19.6 mg, 58 %). IR (film): 3402, 3051, 2957, 2929, 2870, 1601, 1503, 1462, 1431, 1319, 1260, 1180, 1154, 1036, 992, 909, 801, 780, 749, 693 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ = 8.18-8.20 (m, 1 H), 7.86-7.88 (m, 1 H), 7.81 (d, *J*=8.25 Hz, 1 H), 7.69 (d, *J*=7.10 Hz, 1 H), 7.45-7.50 (m, 3 H), 7.08 (t, *J*=7.90 Hz, 2 H),

6.66 (t, J=7.32 Hz, 1 H), 6.51 (d, J=7.75 Hz, 2 H), 5.52 (d, J=7.65 Hz, 1 H), 4.14-4.17 (m, 1 H), 3.73-

3.75 (m, 1 H), 1.84-1.90 (m, 1 H), 1.47-1.58 (m, 2 H), 1.29-1.38 (m, 1 H), 0.90 (t, *J*=7.25 Hz, 3 H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ = 147.7, 137.2, 134.0, 131.4, 129.4 (2 C), 129.0, 128.9, 126.4, 125.9, 125.6, 124.8, 123.8, 117.8, 113.9 (2 C), 75.2, 73.3, 55.1, 31.9, 19.5, 14.3 ppm. HRMS (ESI): calcd. for C₂₂H₂₆NO₂ [M+H]⁺: 336.1958 found: 336.1948.



8ae

Enantioselective aminolysis: method e, 48 h, **8ae** was isolated as a yellow oil (4 mg, 14 %). IR (film): 3400, 3056, 3028, 2958, 2926, 2871, 1600, 1511, 1496, 1462, 1452, 1384, 1300, 1253, 1065, 1037, 748, 693 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ = 7.36-7.42 (m, 5 H), 7.16-7.20 (m, 2 H), 6.74-6.77 (m, 1 H), 6.65-6.67 (m, 2 H), 4.86 (d, *J*=6.25 Hz, 1 H), 3.84-3.86 (m, 1 H), 3.47-3.49 (m, 1 H), 2.24-2.29 (m, 1 H), 0.99 (d, *J*=6.85 Hz, 1 H), 0.94 (d, *J*=6.95 Hz, 1 H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ

=148.4, 140.8, 129.5 (2 C), 128.8 (2 C), 128.5, 127.8 (2 C), 118.4, 114.5 (2 C), 76.8, 75.2, 61.6, 30.1, 20.8, 17.1 ppm. HRMS (ESI): calcd. for $C_{18}H_{24}NO_2$ [M+H]⁺: 286.1802 found: 286.1794.



1 H), 4.37 (d, J=7.75 Hz, 1 H), 4.09 (dd, J=7.72, 4.77 Hz, 1 H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ = 146.7, 141.0, 139.1, 129.2 (2 C), 128.8 (2 C), 128.6 (2 C), 128.6, 128.3 (4 C), 127.8, 127.4 (2 C), 118.0, 114.2, 77.0, 75.4, 59.2 ppm. HRMS (ESI): calcd. for C₂₁H₂₂NO₂ [M+H]⁺: 320.1645 found: 320.1634.



Enantioselective aminolysis: method e, 24 h, **9ae** was isolated as a yellow oil (26.2 mg, 78 %). IR (film): 3400, 3053, 2922, 1601, 1509, 1503, 1452, 1432, 1315, 1222, 1157, 1089, 832, 750, 693 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ = 7.31-7.45 (m, 8 H), 7.00-7.10 (m, 4 H), 6.64-6.67 (m, 1 H), 6.53-6.55 (m, 2 H), 4.83 (dd, *J*=7.92, 4.42 Hz, 1 H), 4.68 (d, *J*=8.05 Hz, 1 H), 4.30 (dd, *J*=8.05, 2.70

Hz, 1 H), 4.09 (dt, J=9.12, 4.09 Hz, 1 H), 2.28 (d, J=3.05 Hz, 1 H), 1.53 (d, J=4.80 Hz, 1 H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ = 162.4 (d, J=246 Hz, 1 C), 146.6, 140.9, 134.7, 130.0 (d, J=8.01 Hz, 2 C), 129.3 (2 C), 129.0 (2 C), 128.8, 127.4 (2 C), 118.1, 115.4 (d, J=21.3 Hz, 2 C), 114.1 (2 C), 77.0, 75.4, 58.3 ppm. HRMS (ESI): calcd. for C₂₁H₂₁FNO₂ [M+H]⁺: 338.1551 found: 338.1545.



Enantioselective aminolysis: method e, 24 h, **10ae** was isolated as a white solid (31 mg, 78 %). IR (film): 3540, 3413, 3031, 2912, 1601, 1502, 1486, 1453, 1433, 1408, 1391, 1315, 1250, 1207, 1180, 1155, 1072, 1011, 909, 872, 847, 823, 793, 749, 734, 694, 613, 576 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ = 7.43-7.44 (m, 2 H), 7.29-7.34 (m, 7 H), 7.06-7.09 (m, 2 H), 6.64-6.67 (m, 1 H), 6.50-

6.52 (m, 2 H), 4.80 (d, J=3.45 Hz, 1 H), 4.69 (s, 1 H), 4.25 (d, J=8.10 Hz, 1 H), 4.07 (dd, J=8.07, 4.07 Hz, 1 H), 2.30 (s, 1 H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ = 146.4, 140.8, 138.1, 131.6 (2 C), 130.3 (2 C), 129.3 (2 C), 129.0 (2 C), 128.8, 127.4 (2 C), 121.6, 118.1, 114.0 (2 C), 76.9, 75.3, 58.3 ppm. HRMS (ESI): calcd. for C₂₁H₂₁BrNO₂ [M+H]⁺: 398.0750 found: 398.0707.



Enantioselective aminolysis: method e, 65 h, **3ae2** was isolated as a yellow oil (11 mg, 30 %). IR (film): 3396, 2923, 1653, 1576, 1540, 1519, 1479, 1456, 1379, 818, 790, 736, 702, 589 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ = 8.71 (dd, *J*=4.17, 1.52 Hz,

1 H), 8.03 (dd, J=8.25, 1.55 Hz, 1 H), 7.53 (d, J=7.30 Hz, 2 H), 7.21-7.39 (m, 10 H), 7.01 (d, J=7.90 Hz, 1 H), 6.53 (d, *J*=7.45 Hz, 1 H), 4.88 (m, 1H), 4.63 (d, *J*=7.25 Hz, 1 H), 4.34 (dd, *J*=7.20, 5.40 Hz, 1 H); ¹³C NMR (126 MHz, CDCl₃) δ = 147.2, 143.2, 140.9, 139.9, 139.2, 138.7, 136.1, 128.7 (2 C), 128.6 (2 C), 128.5, 128.4 (2 C), 127.8, 127.7, 127.5 (2 C), 121.5, 114.7, 106.8, 77.3, 75.3, 58.8 ppm. HRMS (ESI): calcd. for $C_{24}H_{23}N_2O_2 [M+H]^+$: 371.1754 found: 371.1726.



Enantioselective aminolysis: method e, 48 h, 2ae1 was isolated as a white solid (34.9 mg, 96 %). I13.0813R (film): 3407, 2957, 2928, 2871, 1594, 1495, 1454, 1400, 1318, 1294, 1257, 1179, 1097, 1074, 1035, 908, 813, 767, 733, 702, 556 cm^{-1} ; ¹H NMR (500 MHz, CDCl₃) δ = 7.33-7.38 (m, 5 H), 7.20-7.22 (m, 2 H), 6.44-6.46 (m, 2 H), 4.71 (d, J=7.35 Hz, 1 H), 3.81-3.82 (m, 1 H), 3.65 (m, 1 H), 2.47 (s, 1 H), 1.76-1.80 (m, 1 H), 1.46-1.53 (m, 2 H), 1.30-1.37 (m, 1 H), 0.91 (t, J=7.27 Hz, 3 H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ = 146.7, 141.1, 132.0 (2

C), 128.8 (2 C), 128.5, 127.0 (2 C), 115.2 (2 C), 109.0, 75.6, 75.5, 54.4, 31.9, 19.3, 14.2 ppm. HRMS (ESI): calcd. for $C_{18}H_{23}BrNO_2 [M+H]^+$ 364.0907 found: 364.0916.



Enantioselective aminolysis: method e, 48 h, 2ae2 was isolated as a white solid (29.7 mg, 98 %). IR (film): 3400, 2958, 2931, 2871, 1510, 1453, 1316, 1220, 1155, 1035, 821, 766, 702, 509 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ = 7.32-7.38 (m, 5 H), 6.84-6.87 (m, 2 H), 6.51-6.53 (m, 2 H), 4.70 (d, J=7.35 Hz, 1 H), 3.77 (dd, J=7.07, 4.52 Hz, 1 H), 3.57-3.59 (m, 1 H), 1.74-1.76 (m, 1 H), 1.46-1.51 (m, 2 H), 1.30-1.33 (m, 1 H), 0.90 (t, J=7.27 Hz, 3 H) ppm; ¹³C NMR (126 MHz, $CDCl_3$) $\delta = 156.1$ (d, J=236 Hz, 1 C), 144.0, 141.3, 128.8 (2 C), 128.5, 127.2 (2 C), 115.9 (d, J=22.2 Hz, 2 C), 115.0 (d, J=7.38 Hz, 2 C), 76.1, 75.4, 56.0, 32.3, 19.3, 14.3 ppm. HRMS

(ESI): calcd. for $C_{18}H_{23}FNO_2 [M+H]^+$: 304.1707 found: 304.1656.



Enantioselective aminolysis: method e, 48 h, 2ae3 was isolated as a colorless oil (31 mg, 98 %). IR (film): 3405, 2956, 2871, 2833, 1512, 1453, 1409, 1238, 1180, 1149, 1100, 1038, 910, 821, 765, 734, 702, 518 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ = 7.30-7.40 (m, 5 H), 6.75-6.76 (m, 2 H), 6.58-6.60 (m, 2H), 4.71 (d, J=7.30 Hz, 1 H), 3.74-3.76 (m, 4 H), 3.54 (s, 1 H), 3.47 (m, 1 H), 3.30-3.31 (m, 1 H), 1.84 (d, J=4.35 Hz, 1 H), 1.71-1.77 (m, 1 H), 1.43-1.52 (m, 2 H), 1.26-1.35 (m, 1 H), 0.88 (t, *J*=7.25 Hz, 3 H) ppm; ¹³C NMR (126 MHz, $CDCl_3$) $\delta = 152.8, 141.5, 141.4, 128.7 (2 C), 128.4, 127.3 (2 C), 116.0 (2 C), 115.1 (2 C), 76.6, 75.3, 141.4, 128.7 (2 C), 128.4, 127.3 (2 C), 116.0 (2 C), 115.1 (2 C),$ 57.2, 55.9, 32.7, 19.1, 14.4 ppm. HRMS (ESI): calcd. for $C_{19}H_{26}NO_3 [M+H]^+$: 316.1907 found: 316.1890.



Enantioselective aminolysis: method e, 48 h, 2ae4 was isolated as a colorless oil (30.5 mg, 98 %). IR (film): 3410, 2956, 2929, 2870, 1606, 1490, 1475, 1461, 1454, 1402, 1329, 1263, 1193, 1024, 742, 702, 585, 543, 513 cm⁻¹; ¹H NMR (500 MHz. $CDCl_3$) $\delta = 7.30-7.34$ (m, 5 H), 7.04 (d, J=7.10 Hz, 1 H), 6.98 (t, J=7.67 Hz, 1 H), 6.59 (t, J=7.30 Hz, 1 H), 6.23 (d, J=7.90 Hz, 1 H), 4.77 (dd, J=5.75, 2.95 Hz, 1 H), 3.95 (q, J=5.78 Hz, 1 H), 3.48-3.54 (m, 2 H), 3.43 (q, J=9.10 Hz, 1 H), 3.05 (s, 1 H), 2.88-3.01 (m, 2 H), 1.80 (s, 1 H), 1.67-1.77 (m, 2 H), 1.15-1.31 (m, 2 H), 0.83 (t,

J=7.35 Hz, 3 H) ppm; ¹³C NMR (126 MHz, CDCl₃) $\delta = 151.4$, 140.4, 129.3, 128.6 (2 C), 128.4, 127.6 (2 C), 127.3, 124.6, 117.1, 107.1, 76.7, 76.1, 56.5, 47.3, 29.9, 28.5, 20.5, 14.4 ppm. HRMS (ESI): calcd. for $C_{20}H_{26}NO_2 [M+H]^+$: 312.1958 found: 312.1948.



Enantioselective aminolysis: method e, 4 d. 4ae was isolated as a colorless solid (10 mg, 33 % yield) IR (film): 3383, 2956, 2927, 2855, 1601, 1510, 1466, 1432, 1378, 1324, 1262, 1130, 1073, 992 747, 692 cm⁻¹; ¹H NMR $(500 \text{ MHz}, \text{CDCl}_3) \delta = 7.15-7.18 \text{ (m. 2 H)}, 6.69-6.72 \text{ (m. 1 H)}, 6.64-6.66$ (m, 2 H), 3.65-3.72 (m, 2 H), 3.607-3.613 (m, 1 H), 2.02 (s, 1 H), 1.69-1.79

(m, 2 H), 1.58 (s, 1 H), 1.21-1.50 (m, 14 H), 0.91 (t, J=7.10 Hz, 3 H), 0.85 (t, J=6.82 Hz, 3 H) ppm;¹³C NMR (126 MHz, CDCl₃) δ = 147.9, 129.6 (2 C), 117.9, 113.8 (2 C), 75.3, 73.1, 55.4, 33.3, 31.9, 30.1, 29.6, 27.9, 26.2, 22.9, 22.7, 14.2, 14.2 ppm. HRMS (ESI): calcd. for C₁₉H₃₄NO₂ [M+H]⁺: 308.2584 found: 308.2596.



Enantioselective aminolysis: method f (W(OEt)₆/(R,R)-L2 / H₂O₂/ aniline / substrate = 0.2/0.24/0.2/1/2), 48 h. 4 df was isolated as a yellow oil (16 mg, 52 % vield). ¹H NMR (500 MHz, CDCl₃) δ = 7.15-7.18 (m, 2 H), 6.67-6.73 (m, 3 H), 3.75-3.78 (m, 1 H), 3.56-3.60 (m, 1 H), 3.49-3.50 (m, 1 H), 2.60 (s, 1 H), 1.21-1.60 (m, 17 H), 0.92 (t, J=7.05 Hz, 3 H), 0.85 (t, J=6.95 Hz, 3 H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ = 148.4, 129.5 (2 C), 118.0, 113.9 (2 C), 74.1, 71.3, 57.0, 34.1, 31.8, 31.8, 29.5, 28.0, 26.3, 22.8, 22.7, 14.2, 14.2 ppm.



Enantioselective aminolysis: method f (W(OEt)₆/(R,R)-L2 / H₂O₂/ aniline / substrate = 0.2/0.24/0.2/1/2, 48 h. **11df** was isolated as a yellow oil (10 mg, 35%). IR (film): 3393, 2922, 2851, 1601, 1501, 1450, 1033, 791, 745, 692 cm⁻¹; ¹H NMR (500 MHz, $CDCl_3$) $\delta = 7.15-7.18$ (m, 2 H), 6.68-6.73 (m, 3 H), 3.69 (m, 1 H), 3.59-3.63 (m, 1 H), 3.45-3.47 (m, 1 H), 2.63 (s, 1 H), 2.62 (s, 1 H), 1.00-1.93 (m, 14 H), 0.91 (t,

11df J=7.30 Hz, 1 H) ppm; ¹³C NMR (126 MHz, CDCl₃) $\delta = 148.6$, 129.5 (2 C), 118.0, 114.0 (2 C), 75.2, 71.1, 57.4, 40.9, 34.5, 29.6, 28.9, 26.5, 26.2, 26.1, 19.6, 14.3 ppm. HRMS (ESI): calcd. for C₁₈H₃₀NO₂ [M+H]⁺: 292.2271 found: 292.2270.



Enantioselective aminolysis: method e, 4 d. **5ae** was isolated as a yellow oil (12 mg, 38 %). IR (film): 3399, 2927, 2858, 1603, 1507, 1432, 1315, 1223, 1157, 1049, 840, 750, 693 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ =7.40-7.43 (m, 2 H), 7.08-7.11 (m, 2 H), 7.01-7.04 (m, 2 H), 6.65-6.68 (m, 1 H), 6.55-6.56 (m, 2 H), 4.77 (d, J=4.45 Hz, 1 H), 3.79 (m, 1 H), 3.35-3.38 (m, 1 H), 1.66 (s, 1 H), 1.56 (s, 1H), 1.42-1.48 (m, 2 H), 1.27-1.34 (m, 4 H), 0.89 (t, *J*=7.12 Hz, 3 H) ppm;

¹³C NMR (126 MHz, CDCl₃) δ =162.5 (d, *J*=246 Hz, 1 C), 146.6, 134.8, 129.7 (d, *J*=7.99 Hz, 2 C), 129.3 (2 C), 118.1, 115.8 (d, J=21.3 Hz, 2 C), 114.0 (2 C), 77.0, 73.1, 58.8, 33.4, 27.6, 22.9, 14.1 ppm. HRMS (ESI): calcd. for $C_{19}H_{25}FNO_2 [M+H]^+$: 318.1864 found: 318.1854.

HPLC Data

Epoxides		Conditions			
O OH	2a	HPLC (Chiralpak IB): Condition: Isopropanol/Hexane =			
Ph		5:95, flow rate = 0.75 mL/min; result: 11.6 min (major			
		diastereomer, major enantiomer), 12.9 min (major			
		diastereomer, minor enantiomer), 14.0 and 16.3 min (minor			
		diastereomer)			
OH OH	2b	HPLC (Chiralpak IC): Condition: Isopropanol/Hexane =			
		5:95, flow rate = 0.75 mL/min; result: 10.9 min (major			
		diastereomer, minor enantiomer), 13.0 min (major			
F		diastereomer major enantiomer) 18 0 and 24 0 min (minor			
		diastereomer)			
ОН	2c	HPLC (Chiralnak AS-H): Condition: Isopropanol/Hexane =			
	-0	10.90 flow rate = 0.75 mL/min ⁻ result: 12.6 min (major			
		diastereomer minor enantiomer) 16.5 min (major			
		diastereomer, major enantiomer), 18.8 min (major			
		diastereomer)			
OH	2d	HPLC (Chiralnak IC): Condition: Isopropanol/Heyane =			
	24	5.95 flow rate = 0.75 mL/min: result: 1.31 min (major			
		5:95, flow rate = 0.75 mL/min; result: 1.31 min (major			
		diastereomer, minor enantiomer), 19.0 min (major diastereomer, major enantiomer), 22.4 min (minor			
		diastereomer, major enantiomer), 22.4 min (minor			
OH	20	HDLC (Chiralnak IC): Condition: Isopropagal/Hayana =			
<u> </u>	26	FFLC (Childipak IC). Condition. Isopropanol/Hexale –			
── `Ph		3.95, now rate = 0.75 mL/mm, result. 18.9 mm (major			
		diastereomer, minor enantiomer), 25.0 min (major			
		diastereomer, major enantiomer), 31.9 min (minor			
	•	diastereomer)			
OH V	3a	HPLC (Chiralpak AD-H): Condition: Isopropanol/Hexane =			
		10:90, flow rate = 0.75 mL/min ; result: 15.7 min (major			
		diastereomer, minor enantiomer), 19.6 min (major			
		diastereomer, major enantiomer), 21.1 and 22.2 min (minor			
		diastereomer)			
, vo VH	9a HPLC (Chiralpak IC): Condition: Isopropanol/Hexane =				
	5:95, the rate = 0.75 mL/min; result: 15.5 min (major				
		diastereomer, minor enantiomer), 21.7 min (major			
		diastereomer, major enantiomer), 25.3 and 34.3 min (minor			
		diastereomer)			

Aminodiols		Conditions			
NHPHOH	1ae	HPLC (Chiralpak IC): Condition: Hexane/Isopropanol			
Ph		= 10.90, flow rate $= 0.5$ mL/min; result: 24.5 and 30.1			
ÖH		min (minor diastereomer), 32.6 min (major			
		diastereomer, minor enantiomer), 35.8 min (major			
		diastereomer, major enantiomer)			
NHPrOH	2ae	HPLC (Chiralpak IC): Condition: Isopropanol/Hexane			
		= 5:95, flow rate $= 0.75$ mL/min; result: 17.2 min			
ÖH		(major diastereomer, minor enantiomer), 18.3 min			
		(major diastereomer, major enantiomer), 23.3 min			
		(minor diastereomer)			
NHPhQH	2bf	HPLC (Chiralpak IC): Condition: Isopropanol/Hexane			
		= 5:95, flow rate $= 0.75$ mL/min; result: 17.1 min			
OH U		(major diastereomer, major enantiomer), 18.7 min			
×		(major diastereomer, minor enantiomer), 23.4 min			
		(minor diastereomer)			
NHPIOH	6ae	HPLC (Chiralpak ID): Condition: Isopropanol/Hexane			
		= 5:95, flow rate = 0.75 mL/min; result: 24.9 min			
он Ц		(major diastereomer, minor enantiomer), 26.1 min			
~ F		(minor diastereomer), 32.8 (major diastereomer, major			
		enantiomer)			
NHPrOH	7ae	HPLC (Chiralpak AD-H): Condition:			
		Isopropanol/Hexane = 2:8, flow rate = 0.75 mL/min;			
OH V		result: 16.1 min (major diastereomer, minor			
		enantiomer), 26.1 min (minor diastereomer), 32.8			
		(major diastereomer, major enantiomer)			
NHPIOH	8ae	HPLC (Chiralpak IC): Condition: Isopropanol/Hexane			
		= 5:95, flow rate = 0.75 mL/min; result: 16.7 min			
Öн 🥠		(major diastereomer, minor enantiomer), 18.5 min			
		(minor diastereomer), 30.1 min (major diastereomer,			
		major enantiomer)			
NHPrOH	3ae	HPLC (Chiralpak AD-H): Condition:			
		Isopropanol/Hexane = 2:8, flow rate = 0.75 mL/min;			
Он 🥠		result: 14.5 min (major diastereomer, minor			
		enantiomer), 16.3 and 25.3 min (minor diastereomer),			
		30.9 min (major diastereomer, major enantiomer)			
NHPrOH	9ae	HPLC (Chiralpak AS-H): Condition:			
		Isopropanol/Hexane = $2:8$, flow rate = 0.5 mL/min;			
БН		result: 16.3 min (major diastereomer, major			
'		enantiomer), 20.6 min (major diastereomer, minor			
		enantiomer), 23.8 and 30.0 min (minor diastereomer)			
	10ae	HPLC (Chiralpak IC): Condition: Isopropanol/Hexane			
		= 5:95, flow rate = 0.75 mL/min ; result: 15.6 min			
Br OH		(major diastereomer, minor enantiomer), 19.7 min			
		(major diastereomer, major enantiomer), 22.5 and 25.4			
		min (minor diastereomer)			

	3ae2	HPLC (Chiralpak IC): Condition: Isopropanol/Hexane	
		= 3.7 flow rate = 0.5 mL/min ⁻ result ⁻ 12.2 min (major	
		diastereomer minor enantiomer) 14.5 min (major	
NH OH		diastereomer, major enantiomer), 15.7 and 26.1 min	
		(minor diastereomer)	
		(minor diastereomer)	
Br	2ae1	HPLC (Chiralpak IB): Condition: Isopropanol/Hexane	
		= 1:9, flow rate = 0.5 mL/min ; result: 20.6 (major	
VI VI VI		diastereomer, minor enantiomer), 21.4 (minor	
		diastereomer), 22.8 (major diastereomer, major	
ŌH		enantiomer), 27.5 (minor diastereomer)	
F	2ae2	HPLC (Chiralpak IC): Condition: Isopropanol/Hexane	
		= 5:95, flow rate = 0.75 mL/min: result: 13.5 min	
🚿 мн он		(major diastereomer, minor enantiomer), 14.7 min	
		(major diastereomer, major enantiomer), 17.4 and 20.1	
ÖH L		min (minor diastereomer)	
MeQ	2003	HDLC (Chiralnak AD H): Condition:	
	2465	In LC (Childpak AD-11). Condition. Isopropopol/Hoyono = 2.8 flow rate = 0.5 mL/min:	
NH OH		regult: 20.2 min (moior diagtoreamon moior	
		result. 20.5 min (major diastereomer, major	
		enantiomer), 22.3 (major diastereomer, minor	
OH C		enantiomer), 24.0 and 37.5 (minor diastereomer)	
	2ae4	HPLC (Chiralpak AD-H): Condition:	
		Isopropanol/Hexane = 1:9, flow rate = 0.75 mL/min;	
		result: 13.3 min (major diastereomer, major	
		enantiomer), 14.5 (major diastereomer, minor	
Ōн		enantiomer), 15.3 and 18.6 (minor diastereomer)	
NHPrOH	4ae	HPLC (Chiralpak AS-H): Condition:	
		Isopropanol/Hexane = $6:94$, flow rate = 0.4 mL/min ;	
Ğн		result: 16.0 min (major enantiomer), 19.6 min (minor	
		enantiomer)	
NHPrOH	4df	HPLC (Chiralpak AS-H): Condition:	
		Isopronanol/Hexane = 6.94 flow rate = 0.4 mL/min [•]	
		result: 21.3 min (major enantiomer) 23.1 min (minor	
		enantiomer)	
NHPrOH	11df	HPLC (Chiralpak AD-H): Condition:	
	IIui	Isopronanol/Hexane = 1.9 flow rate = 0.5 mL/min ^o	
		result: 22 4 min (major enantiomer) 24 3 min (minor	
UH VH		nontiomor)	
	5	UDL C (Chinglach IC): Condition: Longroup 1/11	
	зае	5ac If LC (Chinaipak IC). Condition. Isopiopanoi/Hexane	
		= 5:95, flow rate = 0.75 mL/min; result: 10.3 min	
БН СН		(minor enantiomer), 12.5 min (major enantiomer)	

Determination of Absolute Stereochemistry of 2ae by X-ray Crystallography

Crystal growth of C₁₈**H**₂₃**NO**₂: Lan Luo (prof. Yamamoto's group). **Data collected**: Alexander S. Filatov, 02/11/2015 (X-ray Laboratory, Searle B013, Department of Chemistry, the University of Chicago, Chicago, Il). **Report prepared**: Alexander S. Filatov, 02/12/2015 (X-ray Laboratory, Searle B013, Department of Chemistry, the University of Chicago, Chicago, Il).

General information: A colorless plate (0.06 x 0.18 x 0.38 mm) was mounted on a Dual-Thickness MicroMounttm (MiTeGen) with 30 μ m sample aperture using grease to hold the crystal. The diffraction data were measured at 100 K on a Bruker D8 VENTURE with PHOTON 100 CMOS detector system equipped with a Cu-target X-ray tube ($\lambda = 1.54178$ Å). Data reduction and integration were performed with the Bruker APEX2 software package (Bruker AXS, version 2014.9-0, 2014). Data were corrected for absorption effects using the numerical scaling as implemented in SADABS (Bruker AXS, version 2014/4, 2014, part of Bruker APEX2 software package). The structure was solved by SHELXT (Sheldrick, G. M. *Acta Cryst.* **2015**, *A71*, 3-8) and refined by full-matrix least-squares procedure using Bruker SHELXTL (version 6.14) software package (XL refinement program version 2014/7, Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112-122; *Sheldrick, G. M. Acta Cryst.* **2015**, *C71*, 3-8). Crystallographic data and details of the data collection and structure refinement are listed in Table 1.

Specific details for structure refinement: All elements were refined anisotropically and hydrogen atoms were included in idealized positions for structure factor calculations except hydrogen atoms attached to O and N atoms. These H atoms were located at the difference Fourier map and their coordinates were allowed to be freely refined while their thermal parameters were constrained to be 1.2 or 1.5 times of the U_{eq} value of the N or O atoms, respectively. All structures are drawn with thermal ellipsoids at 40% probability.

Scheme



The configuration of **2b** was determined by Chiral HPLC to be *S* and compared with literature value¹. Since the configuration of this stereocenter was not changed, the absolute configuration of the compound **3** can be identified as (1S,2R,3R)-1-phenyl-3-(phenylamino)hexane-1,2-diol.



Thermal ellipsoids drawing with atoms labeling

¹ J. Am. Chem. Soc., 2006, 128 (46), pp 14808-14809





1D chain along [100] direction based on O-H^{...}O and O-H^{...}p intermolecular binding



Packing diagram showing unit cell content

Table 1. Crystal data and structure refinement	for 0055_Lan.		
Identification code	0055_Lan		
Empirical formula	$C_{18}H_{23}NO_2$		
Formula weight	285.37		
Temperature	100(2) K		
Wavelength	1.54178 Å		
Crystal system	Orthorhombic		
Space group	$P2_{1}2_{1}2_{1}$		
Unit cell dimensions	a = 5.2823(3) Å	α= 90°.	
	b = 10.7630(7) Å	β= 90°.	
	c = 27.6349(17) Å	$\gamma = 90^{\circ}$.	
Volume	1571.14(17) Å ³		
Ζ	4		
Density (calculated)	1.206 Mg/m ³		
Absorption coefficient	0.615 mm ⁻¹		
F(000)	616		
Crystal size	0.380 x 0.180 x 0.060 mm ³		
Theta range for data collection3.198 to 66.519°.			
Index ranges -6<=h<=5, -12<=k<=9, -26<=l<=			
Reflections collected 10178			
Independent reflections $2739 [R(int) = 0.0744]$			
Completeness to theta = 66.519°	99.2 %		
Absorption correction	Semi-empirical from equiva	lents	
Max. and min. transmission	0.753 and 0.561		
Refinement method	Full-matrix least-squares on	F^2	
Data / restraints / parameters	2739 / 0 / 206		
Goodness-of-fit on F ²	1.087		
Final R indices [I>2sigma(I)]	Final R indices $[I>2sigma(I)]$ R1 = 0.0510, wR2 = 0.1063		
R indices (all data)	(all data) $R1 = 0.0661, wR2 = 0.1134$		
solute structure parameter $0.3(3)$			
Extinction coefficient n/a			
Largest diff. peak and hole $0.177 \text{ and } -0.175 \text{ e.}\text{Å}^{-3}$			

$$\begin{split} R_{int} &= \Sigma \mid F_o^2 - \langle F_o^2 \rangle \mid / \Sigma \mid F_o^2 \mid \\ R1 &= \Sigma \mid \mid F_o \mid - \mid F_c \mid \mid / \Sigma \mid F_o \mid \\ wR2 &= [\Sigma \left[w \left(F_o^2 - F_c^2 \right)^2 \right] / \Sigma \left[w \left(F_o^2 \right)^2 \right] \right]^{1/2} \\ Goodness-of-fit &= [\Sigma \left[w \left(F_o^2 - F_c^2 \right)^2 \right] / (n-p)^{1/2} \end{split}$$

	Х	у	Z	U(eq)
C(1)	1745(6)	4164(4)	7821(1)	29(1)
C(2)	9(7)	4396(4)	8187(1)	32(1)
C(3)	-625(7)	5611(4)	8299(1)	33(1)
C(4)	497(7)	6592(4)	8054(1)	30(1)
C(5)	2208(7)	6345(4)	7686(1)	28(1)
C(6)	2844(6)	5131(3)	7564(1)	26(1)
C(7)	4530(6)	4881(4)	7131(1)	26(1)
C(8)	3185(6)	5257(4)	6660(1)	25(1)
C(9)	4715(6)	5049(3)	6196(1)	25(1)
C(10)	5191(7)	3688(3)	6074(1)	27(1)
C(11)	7128(7)	3528(4)	5669(1)	31(1)
C(12)	7622(8)	2186(4)	5538(1)	37(1)
C(13)	3239(6)	6932(4)	5746(1)	25(1)
C(14)	4989(7)	7742(3)	5947(1)	27(1)
C(15)	4808(7)	9008(3)	5859(1)	30(1)
C(16)	2885(7)	9490(4)	5580(1)	31(1)
C(17)	1094(7)	8685(4)	5388(1)	30(1)
C(18)	1256(6)	7430(4)	5466(1)	28(1)
N(1)	3439(5)	5643(3)	5788(1)	26(1)
O(1)	6827(4)	5605(3)	7149(1)	32(1)
O(2)	886(4)	4567(3)	6615(1)	29(1)

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³) for 0055_Lan. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table 3. Bond lengths	[Å] and angles [°] for	C(2)-C(3)-C(4)	120.4(4)
0055 Lan.		C(2)-C(3)-H(3)	119.8
-		C(4)-C(3)-H(3)	119.8
		C(5)-C(4)-C(3)	119.4(4)
$\overline{C(1)-C(6)}$	1.387(5)	C(5)-C(4)-H(4)	120.3
C(1)-C(2)	1.388(5)	C(3)-C(4)-H(4)	120.3
C(1)-H(1)	0.9500	C(4)-C(5)-C(6)	121.1(4)
C(2)-C(3)	1.386(5)	C(4)-C(5)-H(5)	119.5
C(2)-H(2)	0.9500	C(6)-C(5)-H(5)	119.5
C(3)-C(4)	1.387(5)	C(1)-C(6)-C(5)	118.6(3)
C(3)-H(3)	0.9500	C(1)-C(6)-C(7)	121.1(3)
C(4)-C(5)	1.386(5)	C(5)-C(6)-C(7)	120.1(3)
C(4)-H(4)	0.9500	O(1)-C(7)-C(6)	111.7(3)
C(5)-C(6)	1.391(5)	O(1)-C(7)-C(8)	106.0(3)
C(5)-H(5)	0.9500	C(6)-C(7)-C(8)	110.5(3)
C(6)-C(7)	1.516(5)	O(1)-C(7)-H(7)	111(2)
C(7)-O(1)	1.443(4)	C(6)-C(7)-H(7)	109(2)
C(7)-C(8)	1.537(5)	C(8)-C(7)-H(7)	109(2)
C(7)-H(7)	1.02(4)	O(2)-C(8)-C(9)	107.3(3)
C(8)-O(2)	1.429(4)	O(2)-C(8)-C(7)	109.3(3)
C(8)-C(9)	1.533(5)	C(9)-C(8)-C(7)	115.3(3)
C(8)-H(8)	1.05(4)	O(2)-C(8)-H(8)	110(2)
C(9)-N(1)	1 461(4)	C(9)-C(8)-H(8)	110(2)
C(9)-C(10)	1.524(5)	C(7)-C(8)-H(8)	105(2)
C(9)-H(9)	1 0000	N(1)-C(9)-C(10)	109(1(3))
C(10)- $C(11)$	1 526(5)	N(1)-C(9)-C(8)	109.8(3)
C(10)-H(10A)	0.9900	C(10)- $C(9)$ - $C(8)$	1143(3)
C(10)-H(10B)	0.9900	N(1)-C(9)-H(9)	107.8
C(11)-C(12)	1 512(5)	C(10)- $C(9)$ -H(9)	107.8
C(11)-H(11A)	0.9900	C(8)-C(9)-H(9)	107.8
C(11)-H(11B)	0.9900	C(9)-C(10)-C(11)	112.3(3)
C(12)-H(12A)	0.9800	C(9)-C(10)-H(10A)	109.1
C(12)-H(12R)	0.9800	C(11)-C(10)-H(10A)	109.1
C(12)-H(12C)	0.9800	C(9)-C(10)-H(10B)	109.1
C(12) - C(14)	1 387(5)	C(11)-C(10)-H(10B)	109.1
C(13)-O(14) C(13)-N(1)	1.307(5)	H(10A)-C(10)-H(10B)	107.9
C(13)-C(18)	1.57(5) 1.407(5)	C(12)-C(11)-C(10)	113 6(3)
C(14)-C(15)	1 387(5)	C(12)-C(11)-H(11A)	108.9
C(14)-C(15) C(14)-H(14)	0.9500	C(12)-C(11)-H(11A)	108.9
C(15)-C(16)	1 376(5)	C(12)-C(11)-H(11R)	108.9
C(15) + C(16)	0.9500	C(12)- $C(11)$ - $H(11B)$	108.9
$C(15)-\Gamma(15)$ C(16)-C(17)	1 388(5)	H(11A)-C(11)-H(11B)	103.9
C(16) + C(17)	0.9500	C(11) C(12) H(12A)	107.7
$C(10)-\Pi(10)$ C(17) $C(18)$	1.272(5)	C(11) - C(12) - H(12R) C(11) - C(12) - H(12R)	109.5
C(17) = C(18) C(17) = U(17)	1.372(3)	U(12) - U(12) - H(12B) U(12A) - U(12) - H(12B)	109.3
$C(17) - \Pi(17)$ $C(19) \Pi(19)$	0.9500	$\Gamma(12A) - C(12) - \Gamma(12B)$ $C(11) - C(12) - \Pi(12C)$	109.5
$V(10) - \Pi(10)$	0.9300	$U(12) - U(12) - \Pi(12U)$	109.5
$N(1) - \Pi(1A)$ O(1) U(1D)	0.89(4)	H(12R) - C(12) - H(12C) H(12R) - C(12) - H(12C)	109.5
$O(1) - \Pi(1D)$ $O(2) = \Pi(2A)$	0.88(4)	$\Gamma(12B)-C(12)-\Gamma(12C)$ C(14) C(12) N(1)	109.3 122.7(3)
$O(2) - \Pi(2A)$	0.87(4)	C(14) - C(13) - N(1)	122.7(3)
$\mathcal{O}(\mathcal{O})$ $\mathcal{O}(1)$ $\mathcal{O}(2)$	121.0(4)	C(14)- $C(13)$ - $C(18)$	118.5(3)
C(0) - C(1) - C(2)	121.0(4)	N(1)-U(13)-U(18) C(15) C(14) C(12)	118./(3)
$C(0) - C(1) - \Pi(1)$ $C(2) - C(1) - \Pi(1)$	119.3	C(15) - C(14) - C(15) C(15) - C(14) - U(14)	120.0(3)
C(2)- $C(1)$ - $H(1)$	119.5	C(13)-C(14)-H(14) C(12)-C(14)-H(14)	120.0
C(3) - C(2) - C(1)	119.3(4)	C(15) - C(14) - H(14)	120.0
C(3)-C(2)-H(2)	120.3	C(10) - C(15) - C(14)	121.3(3)
C(1)-C(2)-H(2)	120.3	C(10)-C(15)-H(15)	119.4

Table 3. Bond lengths [Å] and angles [°] for

C(14)-C(15)-H(15)	119.4
C(15)-C(16)-C(17)	118.8(4)
C(15)-C(16)-H(16)	120.6
C(17)-C(16)-H(16)	120.6
C(18)-C(17)-C(16)	120.8(4)
C(18)-C(17)-H(17)	119.6
C(16)-C(17)-H(17)	119.6
C(17)-C(18)-C(13)	120.5(3)
C(17)-C(18)-H(18)	119.7
C(13)-C(18)-H(18)	119.7
C(13)-N(1)-C(9)	122.3(3)
C(13)-N(1)-H(1A)	112(2)
C(9)-N(1)-H(1A)	113(2)
C(7)-O(1)-H(1B)	107(3)
C(8)-O(2)-H(2A)	107(3)

Symmetry transformations used to generate equivalent atoms:

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
C(1)	28(2)	28(2)	31(2)	1(2)	-5(2)	1(2)
C(2)	31(2)	37(3)	29(2)	7(2)	0(2)	-3(2)
C(3)	29(2)	42(3)	26(2)	0(2)	-2(2)	2(2)
C(4)	28(2)	32(2)	30(2)	-2(2)	-3(2)	3(2)
C(5)	25(2)	29(2)	29(2)	3(2)	-2(2)	-3(2)
C(6)	17(2)	35(2)	26(2)	2(2)	-6(1)	1(2)
C(7)	18(2)	28(2)	32(2)	-1(2)	0(1)	0(2)
C(8)	19(2)	27(2)	30(2)	-2(2)	-2(2)	0(1)
C(9)	21(2)	29(2)	26(2)	0(2)	-3(1)	-1(2)
C(10)	24(2)	27(2)	29(2)	3(2)	0(2)	-2(2)
C(11)	28(2)	31(2)	34(2)	-3(2)	2(2)	-4(2)
C(12)	43(2)	35(3)	34(2)	1(2)	7(2)	8(2)
C(13)	24(2)	30(2)	22(2)	2(2)	4(2)	1(2)
C(14)	22(2)	29(2)	31(2)	2(2)	0(2)	-1(2)
C(15)	26(2)	31(2)	35(2)	-2(2)	0(2)	-4(2)
C(16)	32(2)	27(2)	35(2)	3(2)	3(2)	1(2)
C(17)	30(2)	33(3)	26(2)	2(2)	0(2)	8(2)
C(18)	23(2)	35(3)	26(2)	2(2)	1(1)	0(2)
N(1)	21(2)	28(2)	29(2)	2(1)	-2(1)	-2(1)
O(1)	19(1)	49(2)	29(1)	-2(1)	-3(1)	-3(1)
O(2)	19(1)	38(2)	31(1)	-1(1)	1(1)	-5(1)

Table 4. Anisotropic displacement parameters (Å²x 10³) for 0055_Lan. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [h² a*²U¹¹ + ... + 2 h k a* b* U¹²]

	Х	У	Z	U(eq)
H(1)	2186	3331	7745	35
H(2)	-738	3726	8360	39
H(3)	-1835	5774	8546	39
H(4)	96	7425	8138	36
H(5)	2959	7015	7515	33
H(7)	4920(70)	3960(30)	7117(13)	31
H(8)	2780(70)	6210(40)	6702(13)	30
H(9)	6397	5462	6238	31
H(10A)	3576	3296	5976	32
H(10B)	5806	3254	6368	32
H(11A)	6517	3972	5378	37
H(11B)	8742	3917	5770	37
H(12A)	8145	1728	5828	56
H(12B)	8968	2145	5295	56
H(12C)	6073	1816	5407	56
H(14)	6312	7430	6146	33
H(15)	6035	9553	5994	36
H(16)	2784	10358	5521	38
H(17)	-260	9009	5200	36
H(18)	20	6891	5330	33
H(1A)	2010(70)	5270(30)	5705(13)	31
H(1B)	7450(80)	5530(40)	7445(15)	48
H(2A)	-220(80)	4910(40)	6809(14)	44

Table 5. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters (Å $^2x\ 10\ ^3$) for 0055_Lan.

C(6)-C(1)-C(2)-C(3)	-0.3(5)
C(1)-C(2)-C(3)-C(4)	-1.2(5)
C(2)-C(3)-C(4)-C(5)	1.8(5)
C(3)-C(4)-C(5)-C(6)	-0.9(5)
C(2)-C(1)-C(6)-C(5)	1.2(5)
C(2)-C(1)-C(6)-C(7)	-173.7(3)
C(4)-C(5)-C(6)-C(1)	-0.5(5)
C(4)-C(5)-C(6)-C(7)	174.3(3)
C(1)-C(6)-C(7)-O(1)	-133.5(3)
C(5)-C(6)-C(7)-O(1)	51.7(4)
C(1)-C(6)-C(7)-C(8)	108.7(4)
C(5)-C(6)-C(7)-C(8)	-66.1(4)
O(1)-C(7)-C(8)-O(2)	179.6(3)
C(6)-C(7)-C(8)-O(2)	-59.2(4)
O(1)-C(7)-C(8)-C(9)	58.6(4)
C(6)-C(7)-C(8)-C(9)	179.9(3)
O(2)-C(8)-C(9)-N(1)	68.2(4)
C(7)-C(8)-C(9)-N(1)	-169.8(3)
O(2)-C(8)-C(9)-C(10)	-54.8(4)
C(7)-C(8)-C(9)-C(10)	67.2(4)
N(1)-C(9)-C(10)-C(11)	67.7(4)
C(8)-C(9)-C(10)-C(11)	-169.0(3)
C(9)-C(10)-C(11)-C(12)	-179.5(3)
N(1)-C(13)-C(14)-C(15)	174.6(3)
C(18)-C(13)-C(14)-C(15)	-2.0(5)
C(13)-C(14)-C(15)-C(16)	1.2(6)
C(14)-C(15)-C(16)-C(17)	0.4(5)
C(15)-C(16)-C(17)-C(18)	-1.1(5)
C(16)-C(17)-C(18)-C(13)	0.3(5)
C(14)-C(13)-C(18)-C(17)	1.2(5)
N(1)-C(13)-C(18)-C(17)	-175.5(3)
C(14)-C(13)-N(1)-C(9)	27.5(5)
C(18)-C(13)-N(1)-C(9)	-155.9(3)
C(10)-C(9)-N(1)-C(13)	-165.9(3)
C(8)-C(9)-N(1)-C(13)	68.1(4)

Table 6. Torsion angles [°] for 0055_Lan.

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for 0055_Lan [Å and °].

D-HA	d(D-H)	d(HA)	d(DA)	<(DHA)
O(2)-H(2A)O(1)#1	0.87(4)	1.97(4)	2.833(3)	169(4)

Symmetry transformations used to generate equivalent atoms: #1 x-1,y,z

References

- [1] W. Zhang, A. Basak, Y. Kosugi, Y. Hoshino, H. Yamamoto, *Angew. Chemie Int. Ed.* **2005**, *44*, 4389–4391.
- [2] C. Wang, H. Yamamoto, J. Am. Chem. Soc. 2014, 136, 1222–1225.
- [3] Y. Gao, J. M. Klunder, R. M. Hanson, H. Masamune, S. Y. Ko, K. B. Sharpless, J. Am. Chem. Soc. **1987**, 109, 5765–5780.
- [4] J. L. Olivares-Romero, Z. Li, H. Yamamoto, J. Am. Chem. Soc. 2013, 135, 3411–3.
- [5] C. Wang, H. Yamamoto, Angew. Chem. Int. Ed. Engl. 2014, 53, 13920–13923.





7 316 7 316 7 316 7 316 7 316 7 316 7 316 7 316 7 316 6 996 6 993 7 5 7 5 7 5 7 5 7 5 7 5 6 5 7 5 <th>BRUKER</th>	BRUKER
B B B B B B B B B B B B B B B B B B B	Current Data Parameters NAME Lan_20150406_B6061 EXPNO 1 PROCNO 1 F2 - Acquisition Parameters Date_ 20150406 Time 18.38 INSTRUM spect PROBHD 5 mm PABBO BB/ PULPROG zg TD 59998 SOLVENT CDC13 NS 8 DS 0 SWH 10000.000 Hz FIDRES 0.166672 Hz AQ 2.999001 sec RG 8.83 DW 50.000 usec DE 6.50 usec TE 296.9 K D1 5.0000000 sec TD0 1
8 7 6 5 4 3 2 1 1075 1007 1007 1007 1007 1007 1007 1007	ppm





S36








142.903 136.662 131.660 130.697 128.698 127.927 126.749 126.483	75.263	E	BRUKER
			Current Data Parameters NAME Lan_20150406_B6203_C EXPNO 1 PROCNO 1 F2 - Acquisition Parameters Date_ 20150406 Time 19.53 INSTRUM spect PROBHD 5 mm PABBO BB/ PULPROG zgdc TD 187496 SOLVENT CDC13 NS 29 DS 0 SWH 31250.000 Hz FIDRES 0.166670 Hz AQ 2.9999361 sec RG 2050 DW 16.000 usec DE 6.50 usec TE 297.5 K D1 3.0000000 sec D1 0.03000000 sec TD0 1
170 160 150 140 130 120 110 1	vv 90 80 70 60 50	40 30 20 ppm	S41

























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7.377 7.371 7.355 7.557 7.557 7.557 7.557 7.557 7.5577 7.5577 7.55777 7.5577777777	4490 4400 4400 4400 4400 4400 4400 4400		1.441 441 427 1.427 1.416 1.416 1.385 1.385	Current NAME EXPNO PROCNO	Data Parameters Lan_20150915_B6089
		2a OH 2a		F2 - Acq Date_ Time INSTRUM PROBHD PULPROG TD SOLVENT NS DS SWH FIDRES AQ RG DW DE TE D1 TD0 	uisition Parameters 20150915 21.36 spect 5 mm PABBO BB/ 2g 59998 CDC13 8 0 10000.000 Hz 0.166672 Hz 2.9999001 sec 22.37 50.000 usec 6.50 usec 297.2 K 5.00000000 sec 1 CHANNEL f1 499.8730869 MHz 1H 10.75 usec
			⊥_M	PLW1 F2 - Pro SI SF WDW SSB LB GB PC	18.25000000 W cessing parameters 65536 499.8700146 MHz EM 0 0.30 Hz 0 1.00
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7	73.157 73.155 73.155 73.155 72.932 71.55420 55622 55652 71.55420 55652 71.55420 55652 703	5080738862244 5080737 5080737 5080737 5080737 5080737 5080737 5080737 5080737 5080737 5080737 5080738 5080737 5080738 5080758 50807578 5080750	1.414 1.414 1.381 1.381 1.363 1.363 0.894	Current Data Parameters NAME Lan_20150914_B6065
	<u>و و ال</u> 6a	F		$\begin{array}{ccccccc} \text{EXPNO} & 1 \\ \text{PROCNO} & 1 \\ \hline \\ \text{PROCNO} & 1 \\ \hline \\ \text{F2 - Acquisition Parameters} \\ \text{Date_ 20150914} \\ \text{Time 21.30} \\ \hline \\ \text{INSTRUM spect} \\ \hline \\ \text{PROBHD 5 mm PABBO BB/} \\ \text{PULPROG 2g} \\ \text{TD 59998} \\ \text{SOLVENT CDC13} \\ \text{NS 8} \\ \text{NS 8} \\ \text{DS 0} \\ \text{SWH 10000.000 Hz} \\ \hline \\ \text{FIDRES 0.166672 Hz} \\ \text{AQ 2.9999001 sec} \\ \text{RG 19.64} \\ \text{DW 50.000 usec} \\ \hline \\ \text{DE 6.50 usec} \\ \hline \\ \text{TE 295.8 K} \\ \text{D1 5.00000000 sec} \\ \hline \\ \text{TD0 1} \\ \end{array}$
	·····			SF01 499.8730869 MHz NUC1 1H P1 10.75 usec PLW1 18.25000000 W F2 Processing parameters SI 65536 SF 499.8700092 MHz WDW EM SSB 0 LB 0.30 Hz GB 0 PC 1.00
8.5 8.0 7.5 7.0 6.5	6.0 5.5 5.0 4.5 4.0	3.5 3.0 2.5 2.0 66:00 10 10 10 10 10	1.5 1.0 0.5 p	pm

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	~~~~~	OH Ta		F2 - Acquisition Parameters   Date_ 20150914   Time 21.58   INSTRUM spect   PROBHD 5 mm PABBO BB/   PULPROG zg   TD 59998   SOLVENT CDC13   NS 8   DS 0   SWH 10000.000 Hz   FIDRES 0.166672 Hz   AQ 2.9999001 sec   RG 16.71   DW 50.000 usec   DE 6.50 usec   TE 296.0 K   D1 5.00000000 sec   TD0 1
8.5 8.0 7.5 7.0 6.5 <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2600</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u>2000</u> <u></u>	6.0 5.5 5.0 4.5	4.0 3.5 3.0 2.5 2	2.0 1.5 1.0 0.5	ppm



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			F2 - Acquisition Parameters   Date_ 20150914   Time 22.13   INSTRUM spect   PROBHD 5 mm PABBO BB/   PULPROG zg   TD 59998   SOLVENT CDC13   NS 8   DS 0   SWH 10000.000 Hz   FIDRES 0.166672 Hz   AQ 2.9999001 sec   RG 15.35   DW 50.000 usec   DE 6.50 usec   TE 296.2 K   D1 5.00000000 sec   TD0 1   Image: CHANNEL f1
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5	5.0 4.5 4.0	) 3.5 3.0 2.5 2.0 1.5 1.0 0.5 p	pm

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a d d d d d d d d d d d d d d d d d d d	Current Data Parameters NAME Lan_20150915_B5303 EXPNO 1 PROCNO 1 F2 - Acquisition Parameters Date_ 20150915 Time 18.43 INSTRUM spect PROBHD 5 mm PABBO BB/ PULPROG 2g TD 59998 SOLVENT CDC13 NS 8 DS 0 SWH 10000.000 Hz FIDRES 0.166672 Hz AQ 2.9999001 sec RG 28.76 DW 50.000 usec DE 6.50 usec TE 296.1 K D1 5.0000000 sec TD0 1 
	SI F100essing parameters   SI 65536   SF 499.8700242 MHz   WDW EM   SSB 0   LB 0.30 Hz   GB 0   PC 1.00
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	4.088	$\overbrace{-2.512}^{3.230}$		Current Data Parameters NAME Lan_20150915_B6173 EXPNO 1 PROCNO 1
	Br 10a	OH		$F2$ - Acquisition Parameters   Date_ 20150915   Time 17.38   INSTRUM spect   PROBHD 5 mm PABBO BB/   PULPROG zg   TD 59998   SOLVENT CDC13   NS 8   DS 0   SWH 10000.000 Hz   FIDRES 0.166672 Hz   AQ 2.9999001 sec   RG 28.76   DW 50.000 usec   DE 6.50 usec   TE 295.7 K   D1 5.00000000 sec   TD0 1
				CHANNEL f1   SF01 499.8730869 MHz   NUC1 1H   P1 10.75 usec   PLW1 18.25000000 W   F2 - Processing parameters 65536   SF 499.8700186 MHz   WDW EM   SSB 0   LB 0.30 Hz   GB 0   PC 1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5	5.0 4.5 4.0 3	5.5 3.0 2.5 2.0	1.5 1.0 0.5 p	 om



				23.788	73.011 73.011 73.006 72.995 2.988	2.984 2.769 2.757 2.005 7.2005	//1.587 //1.568 //1.547	1.432 1.458 1.458		L. 295 LO. 935 LO. 921	BR	UKER
						<u>و OH</u> 4a	~		11		Current NAME EXPNO PROCNO F2 - Acq Date_ Time INSTRUM PROBHD PULPROG TD SOLVENT NS DS SWH FIDRES AQ DW DE TE D1 TD0	Data Parameters Lan_20150916_B6295anti 1 1 uisition Parameters 20150916 17.22 spect 5 mm PABBO BB/ 2g 59998 CDC13 8 0 10000.000 Hz 0.166672 Hz 2.9999001 sec 11.05 50.000 usec 6.50 usec 296.1 K 5.00000000 sec 1
6.5	6.0	5.5	5.0	4.5	4.0 3.5	3.0 2.5	5 2.0	1.5	1.0 0.5	l  DDM	SF01 NUC1 P1 PLW1 F2 - Proc SI SF WDW SSB LB GB PC	CHANNEL f1 499.8730869 MHz 1H 10.75 usec 18.25000000 W cessing parameters 65536 499.8700042 MHz EM 0 0.30 Hz 0 1.00
					1.00	<u></u>	1.06	16.27		ppm	l	







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7.258 7.254 7.254 7.241 7.234 7.230	L7.036 7.018 53.950 73.947 73.935	73.927 73.041 73.036 73.036 72.116	1.644 1.635 1.625 1.623 1.614 5014		71.502 71.486 71.428	1.408 1.397 1.392 1.392	1.356 1.356 1.342	1.339 1.325 1.325 1.0.927	BRI	JKER
									Current D NAME EXPNO PROCNO	ata Parameters Lan_20150916_B6299 1 1
		I	5a						F2 - Acqu Date_ Time INSTRUM PROBHD PULPROG TD SOLVENT NS DS SWH FIDRES AQ RG DW DE TE D1 TD0	isition Parameters 20150916 15.34 spect 5 mm PABBO BB/ 2g 59998 CDC13 8 0 10000.000 Hz 0.166672 Hz 2.9999001 sec 19.64 50.000 usec 6.50 usec 295.9 K 5.00000000 sec 1
				,					======= SF01 NUC1 P1 PLW1	CHANNEL f1 ======= 499.8730869 MHz 1H 10.75 usec 18.25000000 W
						Mund			F2 - Proc SI SF WDW SSB LB GB PC	essing parameters 65536 499.8700100 MHz EM ) 0.30 Hz ) 1.00
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146.429 140.794 138.147 131.618 130.265 129.316 128.957 128.836 127.369 118.098 114.008	76.892		Current NAME EXPNO PROCINO	Data Parameters Lan_20150407_B6195_C
	Br 10ae		F2 - AC Date_ Time INSTRUM PROBHD PULPROC TD SOLVENI NS DS SWH FIDRES AQ RG DW DE TE D1 D1 D11 TD0	cquisition Parameters 20150407 19.14 1 spect 5 mm PABBO BB/ CDC13 41 0 31250.000 Hz 0.166670 Hz 2.9999361 sec 2050 16.000 usec 6.50 usec 297.5 K 3.0000000 sec 0.03000000 sec 1
			SF01 NUC1 P1 PLW1 SF02 NUC2 CPDPRG PCPD2 PLW2 PLW12 F2 - Pr SI SF WDW SSB LB	<pre>CHANNEL f1 ====== 125.7049802 MHz 13C 10.00 usec 72.83999634 W = CHANNEL f2 ====== 499.8724993 MHz 1H 2 waltz16 80.00 usec 19.0000000 W 0.29688001 W cocessing parameters 1048576 125.6923982 MHz EM 0 0.30 Hz</pre>
<b>170 160 150 140 130 120 110 1</b>	100 90 80 70 60	50 40 30	олуницина 20 ррт	0 1.40



<pre>/ 147.174</pre>	143.212 140.870 139.903 139.152	136.109 136.109 128.732 128.597	128.493	127.738 127.544 121.469	114.659		77.338	58.834					I	Current NAME EXPNO PROCNO	Data Paramete Lan_20150507	<b>*</b> _B6265_C 1
									H OH	$\bigcirc$				F2 - Acc Date_ Time INSTRUM PROBHD PULPROG TD SOLVENT NS DS SWH FIDRES AQ RG DW DE TE D1 D11 TD0	Uisition Para 201505 17. spe 5 mm PABBO B 29 1874 CDC 1 31250.0 0.1666 2.99993 20 16.0 6. 296 3.000000 0.030000	meters 07 01 ct B/ dc 96 13 93 0 0 0 Hz 70 Hz 61 sec 50 usec 50 usec 50 usec 1
() and date of the state of the date of 19 11 11 11 11 11 11 11 11 11 11 11 11 1	11/12 & Start & J. 15. 14 (2010)				abula a ja ga ja ja Ista a ja a ja ja ja ja	and and the star			enid by provide income	1. 1		15, 4 12 1 4 8 44 16	la a., du Bilana, la 19 yezh 19 mar 19 mar 19	SF01 NUC1 P1 PLW1 SF02 NUC2 CPDPRG[2 PCPD2 PLW2 PLW12 F2 - Pro SI SF WDW SSB LB GB PC	CHANNEL f1 = 125.70498 1 10. 72.839996 CHANNEL f2 = 499.87249 waltz 80. 19.000000 0.296880 Cessing param 10485 125.69239 0 0 0 1.	22 MHz 3C 00 usec 34 W 93 MHz 1H 16 00 usec 00 W 01 W eters 76 30 MHz EM 30 Hz 40
170 16	60 150 ·	140 13	0 120	110	100	90 8	0 70	60	50	40	30	20	ppm	1	S93	

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7.379 7.372 7.359 7.354 7.354 7.354 7.333 7.333 7.333 7.333 6.455 6.455 6.455	4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.719 4.7194	BRUKER
		Current Data Parameters NAME Lan_20150405_B6153 EXPNO 1 PROCNO 1
	Br NH OH OH OH 2ae1	$\begin{array}{ccccc} F2 & - \ Acquisition \ Parameters \\ Date_ & 20150405 \\ Time & 18.47 \\ INSTRUM & spect \\ PROBHD & 5 \ mm \ PABBO \ BB/ \\ PULPROG & zg \\ TD & 59998 \\ SOLVENT & CDC13 \\ NS & 8 \\ DS & 0 \\ SWH & 10000.000 \ Hz \\ FIDRES & 0.166672 \ Hz \\ AQ & 2.9999001 \ sec \\ RG & 35.92 \\ DW & 50.000 \ usec \\ DE & 6.50 \ usec \\ TE & 297.5 \ K \\ D1 & 10.0000000 \ sec \\ TD0 & 1 \\ \end{array}$
		SF01 499.8730869 MHz   NUC1 1H   P1 10.75 usec   PLW1 18.25000000 W
	Mul	F2 - Processing parameters SI 65536 SF 499.8700144 MHz WDW EM SSB 0 LB 0.30 Hz GB 0 PC 1.00
<b>5</b> ,15 <b>5</b> ,15 <b>5</b> ,15 <b>5</b> ,15 <b>5</b> ,15 <b>5</b> ,15	5 4 3 2 1 00 10 10 10 10 10 10 10 10 10 10 10 10 1	0 ppm





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## HPLC Chromatograms











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Totals



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0.000



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No	r eak Ivallie	Kesun ()	Time (min)	Offset (min)	(counts)	Ret Time	Sep. Code	1/2 (sec)	Codes	Group
1		95.6432	21.267	0.000	249218080	0.00	BB	35.5		0
2		4.3568	23.080	0.000	11352630	0.00	BB	25.6		0
·	Totals	100.0000		0.000	260570704					









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