Supporting Information

Ruthenium-Catalyzed Selective Hydrogenation of Epoxides to Secondary Alcohols

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General Experimental: All catalytic reactions were performed in H₂ atmosphere using Buchi tinyclave steel vessel with a Teflon sleeve (25 mL) high-pressure reactors. All stoichiometric reactions were performed in nitrogen atmosphere MBRAUN glove box. Ru-MACHO [Carbonylchlorohydrido {bis[2-(diphenylphosphinomethyl)ethyl]amino} ethyl]amino} ruthenium(II)] and KO'Bu were purchased from Sigma-Aldrich and stored inside glove box. Epoxides were purchased from Acros, Sigma-Aldrich, Alfa-aesar, TCI chemicals and used without further purification. Epoxides required for the secondary alcohol products 2b, 2c and 2s were prepared by epoxidation of corresponding alkenes using m-CPBA.¹ Dry solvents were prepared according to standard procedures. Infrared (IR) spectra were recorded in Perkin-Elmer FT-IR and Thermo-Nicolet FT-IR spectrophotometers. Mass spectra (ESI-MS) were obtained on Bruker micrOTOF-Q II Spectrometer and are reported as m/z (relative intensity). Nuclear magnetic resonance spectra (¹H NMR and ¹³C NMR) were recorded at Bruker AV-400 and JEOL-400 (¹H at 400 MHz, ¹³C at 100.6 MHz). ¹H NMR chemical shifts are referenced in parts per million (ppm) with respect to tetramethyl silane (TMS) (δ 0.00 ppm) and ¹³C {¹H} NMR chemical shifts are referenced in parts per million (ppm) with respect to CDCl₃ (δ 77.160 ppm). Coupling constants are reported in Hertz (Hz). ¹H NMR spectroscopy abbreviations: s, Singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; dt, doublet of triplets; dq, doublet of quartets; td, triplet of doublets; qd, quartets of doublets; ddd, doublets of doublets; m, multiplet; br, broad. Assignment of spectra was done based on one-dimensional (dept-135) NMR techniques.

GC Method: Gas chromatography data were obtained using a gas chromatograph equipped with a SH-Rtx-1 capillary column (30 m × 250 μ m). The instrument was set to an injection volume of 1 μ L, an inlet split ratio of 10:1, and inlet and detector temperatures of 300 and 330 °C, respectively. The temperature program used for all of the analyses is as follows: 50 °C, 1 min; 12 °C/min to 320 °C, 7 min. Response factor for all of the necessary compounds with respect to standard benzene was calculated from the average of three independent GC runs.

General Optimization Procedure for Regioselective Hydrogenation of Styrene oxide:

A Buchi tinyclave steel high-pressure reactor containing a teflon sleeve (25 mL) was equipped with a stirring bar, catalyst 1 (0.01-0.005 mmol), base (0.02-0.01 mmol), styrene oxide (0.5 mmol) and toluene (1.5 mL) under nitrogen atmosphere inside the glove box. The pressure reactor was taken out of the glove box, charged with H_2 and heated at indicated temperature (using preheated oil bath) with stirring for 24 h. After cooling to room temperature, the H_2 pressure was released. Benzene internal standard (0.5 mmol) was added into the reaction mixture. The conversion of styrene oxide was calculated using GC analysis. Further, the solvent was evaporated and crude reaction mixture was purified by column chromatography over silica-gel (100-200 mesh) using ethyl acetate/hexane mixture as an eluent. Yields were calculated for isolated pure products of A and B.

Procedure for 1 mmol Scale Reaction of Regioselective Hydrogenation of Styrene oxide:

A Buchi tinyclave steel high-pressure reactor containing a teflon sleeve (25 mL) was equipped with a stirring bar, catalyst **1** (0.01 mmol), base (0.02 mmol), styrene oxide (1 mmol) and toluene (1.5 mL) under nitrogen atmosphere inside the glove box. The pressure reactor was taken out of the glove box, charged with H_2 (50 bar) and heated at indicated temperature (using preheated oil bath) with stirring for 24 h. After cooling to room temperature, the H_2 pressure was released. Benzene internal standard (1 mmol) was added into the reaction mixture. The conversion of styrene oxide was calculated using GC analysis. Further, the solvent was evaporated and crude reaction mixture was purified by column chromatography over silica-gel (100-200 mesh) using ethyl acetate/hexane mixture as an eluent. The reaction provided a complete conversion of styrene oxide and 97 % yield isolated as the mixtures A and B (94:6 selectivity).

General Procedure for Regioselective Hydrogenation of Epoxides:

A Buchi tinyclave steel high-pressure reactor containing a teflon sleeve (25 mL) was equipped with a stirring bar, catalyst **1** (0.01 mmol), base (0.02 mmol), epoxide (0.5 mmol) and toluene (1.5 mL) under nitrogen atmosphere inside the glove box. The pressure reactor was taken out of the glove box, charged with H₂ gas (50 bar) and heated at 75 °C (using preheated oil bath) with stirring for 24 h. After cooling to room temperature, the H₂ pressure was released. Benzene internal standard (0.5 mmol) was added into the reaction mixture. The conversion of epoxides was calculated using GC analysis. Further, the solvent was evaporated and crude reaction mixture was purified by column chromatography over silica-gel (100-200 mesh) using ethyl acetate/hexane mixture as an eluent. Yields were calculated for isolated pure products.

Spectral Data of the Secondary Alcohol Products:

1-Phenylethan-1-ol (2a):² Purified by silica gel column chromatography using ethyl acetate/hexane



(20:80) mixture as an eluent. Colorless liquid. Isolated as a mixture of isomers A and B, ca. 96:4 ratio. Yield: 60 mg, 99% (for 0.5 mmol scale)

and 118 mg, 97% (for 1 mmol scale). IR (DCM): 3413, 3054, 2976, 1452, 1265, 896, 745 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.14-7.26 (m, 5H, ArC*H*), 4.74 (q, *J* = 6.4 Hz, 1H, C*H*-isomer-A), 3.69 (t, *J* = 6.6 Hz, 2H, C*H*₂-isomer-B), 2.72 (t, *J* = 6.7 Hz, 2H, C*H*₂- isomer-B), 2.39 (s, 1H, O*H*), 1.36 (d, *J* = 6.5 Hz, 3H, C*H*₃-isomer-A). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 145.87, 128.47, 127.41, 125.42, 70.29, 63.56, 39.15, 25.15. MS (ESI) m/z calcd for C₈H₁₀O (M+H)⁺: 123.08, found: 123.08.

1-(*p***-Tolyl)ethan-1-ol (2b):²** Purified by silica gel column chromatography using ethyl acetate/hexane (20:80) mixture as an eluent. Colorless liquid. Yield: 49 mg, 72%. IR (DCM): 3506, 3026, 2921, 1495, 1217, 911, 729 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.14 (d, *J* = 7.9 Hz, 2H, ArC*H*), 7.04 (d, *J* = 7.8 Hz, 2H, ArC*H*), 4.71 (q, *J* = 6.2 Hz, 1H, C*H*), 2.24

(s, 4H, Ar-CH₃ & OH), 1.35 (d, J = 6.4 Hz, 3H, CH₃). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 142.98, 137.08, 129.17, 125.44, 70.18, 25.11, 21.13. MS (ESI) m/z calcd for C₉H₁₂O (M+H)⁺: 137.09, found: 137.09.

1-(4-(*tert*-Butyl)phenyl)ethan-1-ol (2c):² Purified by silica gel column chromatography using ethyl \rightarrow acetate/hexane (20:80) mixture as an eluent. Colorless liquid. Yield: 37.4 mg, 42%. IR (DCM): 3419, 3053, 2965, 1265, 1086, 741 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.28-7.33 (m, 2H, ArCH), 7.21-7.26 (m, 2H, ArCH), 4.80 (q, *J* = 6.5 Hz, 1H, CH), 1.83 (s, 1H, OH), 1.42 (d, *J* = 6.5 Hz, 3H, CH₃), 1.25 (s, 9H, 3×CH₃). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 150.59, 142.89, 125.54, 125.30, 70.32, 34.63, 31.48, 25.03. MS (ESI) m/z calcd for C₁₂H₁₈O (M+H)⁺: 179.14, found: 179.14.

1-(4-Fluorophenyl)ethan-1-ol (2d):² Purified by silica gel column chromatography using ethyl OH acetate/hexane (20:80) mixture as an eluent. Colorless liquid. Yield: 67 mg, 96%. IR (DCM): 3425, 3052, 2963, 2905, 1259, 1089, 801, 746 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.22 (dd, $J_1 = 7.8$ Hz, $J_2 = 5.8$ Hz, 2H, ArCH), 6.92 (t, J = 8.6 Hz, 2H, ArCH), 4.76 (q, J = 6.4 Hz, 1H, CH), 2.21 (s, 1H, OH), 1.36 (d, J = 6.4 Hz, 3H, CH₃). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 163.41, 160.98, 141.64 (d, J = 3.1 Hz), 127.15 (d, J = 8.0 Hz), 115.31 (d, J = 21.3 Hz), 69.80, 25.33. MS (ESI) m/z calcd for C₈H₉FO (M+H)⁺: 141.07, found: 141.07.

1-(4-Chlorophenyl)ethan-1-ol (2e):² Purified by silica gel column chromatography using ethyl OH acetate/hexane (20:80) mixture as an eluent. Colorless liquid. Yield: 31 mg, 40%. IR (DCM): 3446, 3053, 2985, 1492, 1265, 742, 735 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.18 (q, *J* = 8.3 Hz, 4H, ArC*H*), 4.72 (q, *J* = 6.4 Hz, 1H, C*H*), 2.39 (s, 1H, O*H*), 1.34 (d, *J* = 6.4 Hz, 3H, C*H*₃). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 144.33, 133.06, 128.63, 126.88, 69.70, 25.27. MS (ESI) m/z calcd for C₈H₉ClO (M+H)⁺: 157.04, found: 157.04. 1-(4-Bromophenyl)ethan-1-ol (2f):² Purified by silica gel column chromatography using ethyl OH acetate/hexane (20:80) mixture as an eluent. Colorless liquid. Yield: 37 mg, 37%. IR (DCM): 3413, 3053, 2968, 2932, 1435, 1376, 1265, 746 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.34 (d, *J* = 8.0 Hz, 2H, ArC*H*), 7.10 (d, *J* = 8.1 Hz, 2H, ArC*H*), 4.70 (dd, *J*₁ = 11.0 Hz, *J*₂ = 4.7 Hz, 1H, C*H*), 2.48 (s, 1H, O*H*), 1.32 (d, *J* = 6.4 Hz, 3H, C*H*₃). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 144.78, 131.51, 127.19, 121.09, 69.65, 25.18. MS (ESI) m/z calcd for C₈H₉BrO (M+H)⁺: 200.99, found: 200.99.

1-Phenylpropan-2-ol (2g):³ Purified by silica gel column chromatography using ethyl acetate/hexane (20:80) mixture as an eluent. Colorless liquid. Yield: 64.6 mg, 95%. IR (DCM): 3372, 3061, 2967, 2928, 1452, 1120, 741 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.19-7.23 (m, 2H, ArC*H*), 7.10-7.15 (m, 3H, ArC*H*), 3.90 (ddd, $J_1 = 7.7$ Hz, $J_2 = 6.2$ Hz, $J_3 = 5.1$ Hz, 1H, C*H*), 2.63 (qd, $J_1 = 13.4$ Hz, $J_2 = 6.4$ Hz, 2H, C*H*₂), 1.81 (s, 1H, O*H*), 1.13 (d, J = 6.2 Hz, 3H, C*H*₃). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 138.65, 129.48, 128.58, 126.50, 68.91, 45.82, 22.80. MS (ESI) m/z calcd for C₉H₁₂O (M+H)⁺: 137.09, found: 137.09.

1-(Benzyloxy)propan-2-ol (2h):⁴ Purified by silica gel column chromatography using ethyl acetate/hexane (20:80) mixture as an eluent. Colorless liquid. Yield: 81 mg, 98%. IR (DCM): 3446, 3053, 2973, 2863, 1453, 1265, 1096, 743 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.18-7.28 (m, 5H, ArCH), 4.45 (s, 2H, CH₂), 3.87-3.91 (s, 1H, CH), 3.35 (dd, J₁ = 9.4 Hz, J₂ = 3.2 Hz, 1H, CH₂), 3.19 (dd, J₁ = 9.4 Hz, J₂ = 8.0 Hz, 1H, CH₂), 2.69 (s, 1H, OH), 1.04 (d, J = 6.4 Hz, 3H, CH₃). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 138.01, 128.47, 127.78, 75.85, 73.28, 66.45, 18.73. MS (ESI) m/z calcd for C₁₀H₁₄O₂ (M+H)⁺: 167.10, found: 167.10.

1-Phenoxypropan-2-ol (2i):³ Purified by silica gel column chromatography using ethyl OH acetate/hexane (20:80) mixture as an eluent. Colorless liquid. Yield: 74.5 mg, 98%. IR (DCM): 3392, 3054, 2937, 2856, 1447, 1265, 895, 747 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.19 (t, J = 7.8 Hz, 2H, ArCH), 6.87 (t, J = 7.3 Hz, 1H, ArCH), 6.81 (d, J = 8.2 Hz, 2H, ArCH), 4.05-4.13 (m, 1H, CH), 3.82 (dd, J_1 = 9.2 Hz, J_2 = 3.0 Hz, 1H, CH₂), 3.68-3.72 (m, 1H, CH₂), 2.55 (s, 1H, OH), 1.18 (d, J = 6.4 Hz, 3H, CH₃). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 158.64, 129.58, 121.16, 114.64, 73.29, 66.30, 18.87. MS (ESI) m/z calcd for C₉H₁₂O₂ (M+H)⁺: 153.09, found: 153.09.

1-(*o***-Tolyloxy)propan-2-ol (2j):**⁵ Purified by silica gel column chromatography using ethyl acetate/hexane (20:80) mixture as an eluent. Colorless liquid. Yield: 80.6 mg, 97%. IR (DCM): 3421, 3052, 2975, 2928, 1495, 1265, 1051, 741 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.02-7.10 (m, 2H, ArC*H*), 6.79 (td, $J_1 = 7.4$ Hz, $J_2 = 1.0$ Hz, 1H, ArC*H*), 6.68-6.75 (m, 1H, ArC*H*), 4.04-4.23 (m, 1H, C*H*), 3.83 (dd, $J_1 = 9.2$ Hz, $J_2 = 3.5$ Hz, 1H, C*H*₂), 3.71 (dd, $J_1 = 9.2$ Hz, $J_2 = 7.4$ Hz, 1H, C*H*₂), 2.46 (s, 1H, O*H*), 2.15 (s, 3H, C*H*₃), 1.21 (d, J = 6.4 Hz, 3H, C*H*₃). ¹³C {¹H} NMR (100.6 MHz, CDCl₃): δ 156.65, 130.85, 126.94, 126.77, 120.87, 111.27, 73.31, 66.49, 18.96, 16.33. MS (ESI) m/z calcd for C₁₀H₁₄O₂ (M+H)⁺: 167.10, found: 167.10.

1-(2-Methoxyphenoxy)propan-2-ol (2k):⁶ Purified by silica gel column chromatography using ethyl acetate/hexane (20:80) mixture as an eluent. Colorless liquid. Yield: 61 mg, 67%. IR (DCM): 3485, 2971, 2931, 2837, 1732, 1504, 1027, 742 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 6.80-6.91 (m, 4H, ArC*H*), 4.08-4.13 (m, 1H, C*H*), 3.92 (dd, $J_1 = 9.7$ Hz, $J_2 = 3.0$ Hz, 1H, C*H*₂), 3.77 (s, 3H, OC*H*₃), 3.72 (dd, $J_1 = 9.6$ Hz, $J_2 = 8.4$ Hz, 1H, C*H*₂), 2.95 (s, 1H, O*H*), 1.16 (d, J = 6.4 Hz, 3H, C*H*₃). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 150.00, 148.27, 122.20, 121.15, 115.38, 112.04, 75.93, 66.05, 55.90, 18.50. MS (ESI) m/z calcd for C₁₀H₁₄O₃ (M+H)⁺: 183.10, found: 183.10.

1-(4-Methoxyphenoxy)propan-2-ol (21):⁷ Purified by silica gel column chromatography using ethyl

OH acetate/hexane (20:80) mixture as an eluent. Colorless liquid. Yield: 88 mg, 97%. IR (DCM): 3586, 3053, 2934, 2835, 1508, 1265, 1041, 741 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 6.74-6.79 (m, 4H, ArC*H*), 4.07-4.12 (m, 1H, C*H*), 3.82 (dd, $J_1 = 9.2$ Hz, $J_2 = 2.9$ Hz, 1H, C*H*₂), 3.65-3.69 (m, 4H, OC*H*₃ & C*H*₂), 2.37 (s, 1H, O*H*), 1.19 (d, J = 6.4 Hz, 3H, C*H*₃). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 154.24, 152.87, 115.72, 114.82, 74.23, 66.45, 55.85, 18.83. MS (ESI) m/z calcd for C₁₀H₁₄O₃ (M+H)⁺: 183.10, found: 183.10.

1-(2,4-Dibromophenoxy)propan-2-ol (2m):⁸ Purified by silica gel column chromatography using ethyl acetate/hexane (20:80) mixture as an eluent. Colorless liquid. Yield: 101 mg, 65%. IR (DCM): 3521, 3054, 2983, 2853, 1734, 1244, 1047, 911, 735 cm⁻¹. ¹ H NMR (400 MHz, CDCl₃): δ 7.60 (d, J = 2.4 Hz, 1H, ArCH), 7.29 (dd, $J_1 = 8.7$ Hz, $J_2 = 2.4$ Hz, 1H, ArCH), 6.70 (d, J = 8.7 Hz, 1H, ArCH), 4.16 (dqd, $J_1 = 13.0$ Hz, $J_2 = 6.5$ Hz, $J_3 = 3.2$ Hz, 1H, CH), 3.92 (dd, $J_1 = 9.1$ Hz, $J_2 = 3.2$ Hz, 1H, CH₂), 3.74 (dd, $J_1 = 9.0$ Hz, $J_2 = 7.5$ Hz, 1H, CH₂), 2.10 (s, 1H, OH), 1.23 (d, J = 6.4 Hz, 3H, CH₃). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 154.26, 135.52, 131.34, 114.83, 113.61, 113.32, 74.86, 66.09, 18.64. MS (ESI) m/z calcd for C₉H₁₀Br₂O₂ (M+H)⁺: 308.91, found: 308.91

1-([1,1'-Biphenyl]-2-yloxy)propan-2-ol (2n):⁹ Purified by silica gel column chromatography using ethyl acetate/hexane (20:80) mixture as an eluent. Colorless liquid. Yield: 112 mg, 98%. IR (DCM): 3582, 3053, 2983, 1583, 1434, 1265, 744 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.37-7.40 (m, 2H, ArC*H*), 7.24-7.29 (m, 2H, ArC*H*), 7.14-7.21 (m, 3H, ArC*H*), 6.89-6.94 (m, 1H, ArC*H*), 6.82 (d, *J* = 8.2 Hz, 1H, ArC*H*), 3.84-3.90 (m, 1H, C*H*), 3.78 (dd, *J*₁ = 9.2 Hz, *J*₂ = 3.5 Hz, 1H, C*H*₂), 3.58-3.63 (m, 1H, C*H*₂), 2.24 (s, 1H, O*H*), 1.02 (dd, *J*₁ = 6.4 Hz, *J*₂ = 2.0 Hz, 3H, C*H*₃). ¹³C NMR (100.6 MHz, CDCl₃): δ 155.44, 138.45, 131.37, 130.89, 129.47, 128.73, 128.09, 127.05, 121.58, 113.31, 74.20, 66.12, 18.72. MS (ESI) m/z calcd for C₁₅H₁₆O₂ (M+H)⁺: 229.12, found: 229.12.

Octan-2-ol (20):¹⁰ Purified by silica gel column chromatography using ethyl acetate/hexane (20:80) mixture as an eluent. Colorless liquid. Yield: 64 mg, 98%. IR (DCM): 3430, 3052, 2987, 1460, 1267,

OH $747 \text{ cm}^{-1} \cdot {}^{1}\text{H} \text{ NMR} (400 \text{ MHz, CDCl}_3): \delta 3.68-3.76 (m, 1H, CH), 1.85 (s, 1H, OH),$ $1.32-1.41 (m, 2H, CH_2), 1.22-1.30 (m, 8H, CH_2), 1.11 (dd, J_1 = 6.2 \text{ Hz}, J_2 = 0.6 \text{ Hz}, 3H,$ $CH_3), 0.81 (t, J = 6.7 \text{ Hz}, 3H, CH_3). {}^{13}\text{C} \text{ NMR} (100.6 \text{ MHz}, \text{CDCl}_3): \delta 68.31, 39.51,$ $31.96, 29.44, 25.86, 23.60, 22.73, 14.20. \text{ MS} (\text{ESI}) \text{ m/z} \text{ calcd for } C_8H_{18}\text{O} (\text{M}+\text{H})^+: 131.14, \text{ found:}$ 131.14.

OH **Decan-2-ol (2p):**¹⁰ Purified by silica gel column chromatography using ethyl acetate/hexane (20:80) mixture as an eluent. Colorless liquid. Yield: 78 mg, 99%. IR (DCM): 3432, 3052, 2928, 2855, 1466, 1264, 909, 731 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 3.67-3.72 (m, 1H, CH), 1.79 (s, 1H, OH), 1.31-1.38 (m, 2H, CH₂), 1.20-1.26 (m, 12H, CH₂), 1.10 (d, J = 6.1 Hz, 3H, CH₃), 0.81 (t, J = 6.7 Hz, 3H, CH₃). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 68.15, 39.45, 31.97, 29.76, 29.68, 29.37, 25.88, 23.50, 22.75, 14.16. MS (ESI) m/z calcd for C₁₀H₂₂O (M+H)⁺: 159.17, found: 159.17.

Dodecan-2-ol (2q):¹⁰ Purified by silica gel column chromatography using ethyl acetate/hexane OH (20:80) mixture as an eluent. Colorless liquid. Yield: 91 mg, 98%. IR (DCM): 446, 3053, 2927, 2854, 1436, 1263, 895, 720 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 3.69-3.76 (m, 1H, CH), 1.96 (s, 1H, OH), 1.22-1.46 (m, 17H, CH₂), 1.13 (dd, $J_1 = 6.2$ Hz, $J_2 = 0.9$ Hz, 3H, CH₃), 0.84 (t, J = 6.8 Hz, 3H, CH₃). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 68.10, 39.44, 31.99, 29.76, 29.71, 29.42, 25.87, 23.47, 22.75, 14.15. MS (ESI) m/z calcd for C₁₂H₂₆O (M+H)⁺: 187.20, found: 187.20.

Hexadecan-2-ol (2r):¹¹ Purified by silica gel column chromatography using ethyl acetate/hexane OH (20:80) mixture as an eluent. Colorless liquid. Yield: 75 mg, 62%. IR (DCM): 3447, 3053, 2927, 2854, 1421, 1265, 895, 738 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 3.66-3.77 (m, 1H, CH), 1.49 (s, 1H, OH), 1.30-1.42 (m, 2H, CH₂), 1.19-1.26 (m, 23H, CH₂), 1.11 (d, J = 6.2 Hz, 3H, CH₃), 0.81 (t, J = 6.9 Hz, 3H, CH₃). ¹³C {¹H} NMR (100.6 MHz, CDCl₃): δ 68.32, 39.52, 32.06, 29.80, 29.50, 25.92, 23.59, 22.83, 14.24. MS (ESI) m/z calcd for C₁₆H₃₄O (M+H)⁺: 243.27, found: 243.27.

2-Phenylpropan-2-ol (2s):¹² Purified by silica gel column chromatography using ethyl acetate/hexane (20:80) mixture as an eluent. Colorless liquid. Yield: 31.2 mg, 46%. IR (DCM): 3447, 3058, 3003, 1450, 1267, 895, 747, 703 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.37 -7.39 (m, 2H, ArC*H*), 7.23 (t, *J* = 7.6 Hz, 2H, ArC*H*), 7.13 (t, *J* = 7.3 Hz, 1H, ArC*H*), 2.05 (s, 1H, O*H*), 1.47 (s, 6H, C*H*₃). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 149.22, 128.26, 126.72, 124.48, 72.56, 31.77. MS (ESI) m/z calcd for C₉H₁₂O (M+H)⁺: 136.08, found: 136.08.

1,1'-((Propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(propan-2-ol) (3a):¹³ Purified by silica gel column chromatography using ethyl acetate/hexane (20:80) mixture as an eluent. Colorless liquid. Yield: 170.5 mg, 99%. IR (DCM): 3438, 3052, 2971, 2932, 1607, 1510, 1249, 1306, 744 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.03-7.07 (m, 4H, ArCH), 6.70-6.75 (m, 4H, ArCH), 4.06-4.10 (m, 2H, CH), 3.82 (dd, $J_1 = 9.3$ Hz, $J_2 = 3.3$ Hz, 2H, CH₂), 3.69 (dd, $J_1 = 9.3$ Hz, $J_2 = 7.7$ Hz, 2H, CH₂), 2.48 (s, 2H, OH), 1.55 (s, 6H, CH₃), 1.18 (d, J = 6.4 Hz, 6H, CH₃). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 156.50, 143.66, 127.88, 114.05, 73.37, 66.36, 41.82, 31.13, 18.87. MS (ESI) m/z calcd for C₂₁H₂₈O₄ (M+H)⁺: 345.20, found: 345.20.

1,1'-(((9*H***-Fluorene-9,9-diyl)bis(4,1-phenylene))bis(oxy))bis(propan-2-ol) (3b):¹⁴** Purified by silica gel column chromatography using ethyl acetate/hexane (20:80) mixture as an eluent. Colorless white solid. Yield: 226 mg, 97%. IR (DCM): 3433, 3053, 2977, 2929, 1507, 1265, 1038, 739 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.66 (d, J = 7.4 Hz, 2H, ArCH), 7.26 (dd, $J_1 = 14.6$ Hz, $J_2 = 7.5$ Hz, 4H, ArCH), 7.17 (t, J = 7.3 Hz, 2H, ArCH), 7.03 (d, J = 8.6 Hz, 4H, ArCH), 6.67 (d, J = 8.6 Hz, 4H, ArCH), 3.95-4.23 (m, 2H, CH), 3.78 (dd, $J_1 = 9.2$ Hz, $J_2 = 2.9$ Hz, 2H, CH₂), 3.64 (t, J = 8.5 Hz, 2H, CH₂), 2.29 (s, 2H, OH), 1.16 (d, J = 6.3 Hz, 6H, CH₃). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 157.42, 151.79, 140.06, 138.70, 129.34, 127.83, 127.50, 126.09, 120.28, 114.31, 73.34, 66.36, 64.27, 18.85. MS (ESI) m/z calcd for C₃₁H₃₀O₄ (M+H)⁺: 467.22, found: 467.22.

Octane-2,7-diol (3c):³ Purified by silica gel column chromatography using ethyl acetate/hexane (20:80) mixture as an eluent. Colorless liquid. Yield: 71 mg, 97%. IR (DCM): 3470, 3052, 2987, 1572, 1267, 895, 747 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 3.67-3.70 (m, 2H, C*H*), 2.72 (s, 2H, O*H*),

OH 1.23-1.41 (m, 8H, CH₂), 1.09 (dd, $J_1 = 6.2$ Hz, $J_2 = 1.1$ Hz, 6H, CH₃). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 67.73, 67.64, 39.16, 25.75, 25.66, 23.41. MS (ESI) m/z calcd for C₈H₁₈O₂ (M+H)⁺: 147.14, found: 147.14.

NMR Spectra of the Secondary Alcohol Products:

¹H NMR spectrum of 1-phenylethan-1-ol (**2a**):



¹H NMR spectrum of 1-(*p*-tolyl)ethan-1-ol (**2b**):



¹³C NMR spectrum of 1-(*p*-tolyl)ethan-1-ol (**2b**):







¹³C NMR spectrum of 1-(4-(*tert*-butyl)phenyl)ethan-1-ol (**2c**):



¹H NMR spectrum of 1-(4-fluorophenyl)ethan-1-ol (**2d**):



¹³C NMR spectrum of 1-(4-fluorophenyl)ethan-1-ol (**2d**):



¹H NMR spectrum of 1-(4-chlorophenyl)ethan-1-ol (**2e**):



¹³C NMR spectrum of 1-(4-chlorophenyl)ethan-1-ol (2e):



¹H NMR spectrum of 1-(4-bromophenyl)ethan-1-ol (**2f**):



¹³C NMR spectrum of 1-(4-bromophenyl)ethan-1-ol (**2f**):







¹H NMR spectrum of 1-phenylpropan-2-ol (**2g**):



¹H NMR spectrum of 1-(benzyloxy)propan-2-ol (**2h**):

¹³C NMR spectrum of 1-(benzyloxy)propan-2-ol (**2h**):



¹H NMR spectrum of 1-phenoxypropan-2-ol (2i):





¹H NMR spectrum of 1-(*o*-tolyloxy)propan-2-ol (2j):





¹³C NMR spectrum of 1-(2-methoxyphenoxy)propan-2-ol (2k):



¹H NMR spectrum of 1-(4-methoxyphenoxy)propan-2-ol (21):



¹³C NMR spectrum of 1-(4-methoxyphenoxy)propan-2-ol (21):





¹H NMR spectrum of 1-(2,4-dibromophenoxy)propan-2-ol (**2m**):







¹H NMR spectrum of 1-([1,1'-biphenyl]-2-yloxy)propan-2-ol (**2n**):

¹³C NMR spectrum of 1-([1,1'-biphenyl]-2-yloxy)propan-2-ol (**2n**):



¹H NMR spectrum of octan-2-ol (20):



¹H NMR spectrum of decan-2-ol (**2p**):



¹H NMR spectrum of dodecan-2-ol (**2q**):







¹H NMR spectrum of 2-phenylpropan-2-ol (**2s**):



¹³C NMR spectrum of 2-phenylpropan-2-ol (2s):



¹H NMR spectrum of 1,1'-((propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(propan-2-ol) (**3a**):



¹³C NMR spectrum of 1,1'-((propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(propan-2-ol) (**3a**):





¹H NMR spectrum of octane-2,7-diol (3c):



¹³C NMR spectrum of octane-2,7-diol (3c):



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