Supporting Information

Synthesis of 1,2-Amino Alcohols via Catalytic C–H Amidation of sp³ Methyl C–H Bonds

Taek Kang,^{ab} Heejeong Kim,^{ba} Jeung Gon Kim,^{*ab} and Sukbok Chang^{*ab}

^a Center for Catalytic Hydrocarbon Functionalizations, Institute for Basic Science, Daejeon 305-701, Korea
 ^b Department of Chemistry, Korea Advanced Institute of Science & Technology, Daejeon 305-701, Korea

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Spectral Copies of ¹H and ¹³C NMR of Compounds Obtained in This Study

I. General Methods

Unless otherwise stated, all commercial reagents and solvents were used without additional purification. Analytical thin layer chromatography (TLC) was performed on Merck pre-coated silica gel 60 F254 plates. Visualization on TLC was achieved by the use of UV light (254 nm), exposure to treatment with acidic anisaldehyde, phosphomolybdic acid, ninhydrin or ceric ammonium molydate stain followed by heating. Column chromatography was undertaken on Merck silica gel 60 (230-400 mesh) using a proper eluent system. ¹H NMR was recorded on Agilent Technologies DD2 (600 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br (broad), s (singlet), d (doublet), t (triplet), q (quartet), sep (septet), dd (doublet of doublet), td (triplet of doublet), ddd (doublet of doublet of doublet), m (multiplet). Coupling constants, J, were reported in hertz unit (Hz). ¹³C NMR was recorded on Agilent Technologies DD2 (150 MHz) and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center of a triplet at 77.0 ppm of chloroform-d. Infrared (IR) spectra were recorded on Bruker Alpha FT-IR Spectrometer. Frequencies are given in reciprocal centimeters (cm⁻¹) and only selected absorbance is reported. High resolution mass spectra were obtained from the Korea Basic Science Institute (Daegu, Korea) by using EI or FAB method, or from KAIST Research Analysis Center by using ESI method. Enantiomeric excess (ee) was measured using Agilent 1260 Infinity Series with UV detector. Optical rotation was measured with JASCO P-1020 polarimeter.

II. Experimental Procedure for the Preparation of Starting Materials

1. Preparation of Sulfonyl Azides

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To a solution of sodium azide (1.95 g, 30.0 mmol) in water (10 mL) was added dropwise over 1 h a solution of sulfonyl chloride (20.0 mmol) in acetone (20 mL) at 0 °C. The reaction mixture was warmed up to room temperature and stirred for 11 h. Acetone was removed under reduced pressure and the reaction mixture was extracted with EtOAc (30 mL x 3). The combined organic layers were dried over MgSO₄ and solvent was removed under reduced pressure. Crude product was used without further purification.

2. Preparation of Ketoximes

2-1. General Procedure for Ketoximes from Primary or Secondary Alcohols



To a stirred solution of primary or secondary alcohol (5.0 mmol, 1.0 equiv.), *N*-hydroxyphthalimide (6.0 mmol, 1.2 equiv.) and triphenylphosphine (6.0 mmol, 1.2 equiv.) in 20 mL THF was added diisopropyl azodicarboxylate (6.0 mmol, 1.2 equiv.) dropwise at 0 °C. Then the reaction was allowed to room temperature. After stirring for 3 h, the solvent was removed under reduced pressure. The resulting residue was purified by column chromatography on silica gel to give the corresponding *N*-alkoxyphthalimide.

To a solution of above *N*-alkoxyphthalimide (3.0 mmol, 1.0 equiv.) in MeOH (5 mL) was added hydrazine monohydrate (3.0 mmol, 1.0 equiv.) at room temperature slowly. After stirred for 30 min, cyclohexanone (9.0 mmol, 3.0 equiv.), sodium acetate (15 mmol, 5.0 equiv.), and water (2 mL) was added to the reaction mixture. The resulting mixture was heated to 65 °C, and stirred for 5 h. The mixture was cooled to room temperature, dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the corresponding ketoxime.

2-2. General Procedure for Ketoximes from Tertiary Alcohols



To a suspension of *N*-hydroxyphthalimide (20 mmol, 2 equiv.), tertiary alcohol (10 mmol, 1 equiv.) in 30 mL wet DCM (dichloromethane) ^(*), BF₃·OEt₂ (11 mmol, 1.1 equiv.) was added dropwise slowly at 0 °C. The reaction mixture was stirred for 1 h at room temperature. To the resulting mixture, DCM (10 mL) and saturated Na₂CO₃ solution in H₂O (50 mL) was added. The aqueous layer was extracted with DCM (10 mL x 3), the combined organic layers were dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give desired *N*-alkoxyphthalimide.

To a solution of above *N*-alkoxyphthalimide (3.0 mmol, 1.0 equiv.) in MeOH (5 mL) was added hydrazine monohydrate (3.0 mmol, 1.0 equiv.) at room temperature slowly. After stirred for 30 min,

cyclohexanone (9.0 mmol, 3.0 equiv.), sodium acetate (15 mmol, 5.0 equiv.), and water (2 mL) was added to reaction mixture. The resulting mixture was heated to 65 °C, and stirred for 5 h. The mixture was cooled to room temperature, dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the corresponding ketoxime.

(*) "Wet DCM" was prepared from extraction of dichloromethane with water (water content: 2,200 ppm measured by Karl Fischer titration). The reaction with HPLC grade DCM (water content: 70 ppm) resulted in lower product yields, when compared to those performed in wet DCM.

2-3. Spectroscopic Data of Prepared Ketoximes

Cyclohexanone O-(sec-butyl) oxime (Table 1, 1a)



Colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 4.04 (tq, J = 6.2, 6.2 Hz, 1H), 2.50-2.41 (m, 2H), 2.21-2.17 (m, 2H), 1.69-1.61 (m, 3H), 1.61-1.55 (m, 4H), 1.51–1.43 (m, 1H), 1.18 (d, J = 6.3 Hz, 3H), 0.90 (t, J = 7.5 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 159.5, 79.2, 32.3, 28.4, 27.1, 25.9, 25.8, 25.3, 19.1, 9.60; **IR** (cm⁻¹) 2965, 2929, 2858, 1640, 940; **HRMS** (EI) Calculated for C₁₀H₁₉NO:

169.1467, Found: 169.1467.

Cyclohexanone *O*-ethyl oxime (Table 1, 1b)



Colorless oil; ¹**H** NMR (600 MHz, CDCl₃) δ 4.07 (q, *J* = 7.0 Hz, 2H), 2.49–2.45 (m, 2H), 2.25-2.20 (m, 2H), 1.71-1.65 (m, 2H), 1.64-1.57 (m, 4H), 1.25 (t, J =6.9 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 160.5, 68.7, 32.2, 27.0, 25.8, 25.7, 25.3, 14.5; **IR** (cm⁻¹) 2975, 2929, 2859, 1640, 943; **HRMS** (EI) Calculated for C₈H₁₅NO: 141.1154, Found: 141.1153.

Cyclohexanone *O*-isopropyl oxime (Table 1, 1c)



Colorless oil; ¹**H NMR** (600 MHz, CDCl₃) δ 4.25 (sep, J = 6.2 Hz, 1H), 2.47–2.43 (m, 2H), 2.21–2.18 (m, 2H), 1.69–1.63 (m, 2H), 1.62–1.56 (m, 4H), 1.21 (d, J = 6.2 Hz, 6H); ¹³C NMR (150 MHz, CDCl₃) δ 159.6, 74.2, 32.3, 27.1, 25.9, 25.8, 25.3, 21.7 (2C); **IR** (cm⁻¹) 2972, 2930, 2858, 1641, 958; **HRMS** (EI) Calculated

for C₉H₁₇NO: 155.1310, Found:155.1312.

Cyclohexanone *O*-(*tert*-butyl) oxime (Table 1, 1d)



Colorless oil; ¹**H** NMR (600 MHz, CDCl₃) δ 2.47–2.43 (m, 2H), 2.23–2.18 (m, 2H), 1.67–1.62 (m, 2H), 1.60–1.56 (m, 4H), 1.26 (s, 9H); ¹³C NMR (150 MHz, CDCl₃) δ 158.2, 76.7, 32.4, 27.5 (3C), 27.1, 26.0, 25.8, 25.1; **IR** (cm⁻¹) 2974, 2930, 2858, 1643, 941; **HRMS** (EI) Calculated for C₁₀H₁₉NO: 169.1467, Found: 169.1467.

Cyclohexanone *O*-hexan-2-yl oxime (Table 1, 1e)



Colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 4.09 (tq, J = 6.3, 6.3 Hz, 1H), 2.49–2.41 (m, 2H), 2.22–2.17 (m, 2H), 1.69–1.61 (m, 3H), 1.61–1.55 (m, 4H), 1.46–1.39 (m, 1H), 1.38–1.26 (m, 4H), 1.19 (d, J = 6.3 Hz, 3H), 0.89 (t, J = 6.8Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 159.5, 78.1, 35.4, 32.3, 27.7, 27.1, 25.9, 25.8, 25.4, 22.8, 19.8, 14.1; IR (cm⁻¹) 2929, 2859, 1640, 946; **HRMS** (EI)

Calculated for C₁₂H₂₃NO: 197.1780, Found: 197.1778.

Cyclohexanone O-(4-methylpentan-2-yl) oxime (Table 1, 1f)



Colorless oil; ¹**H** NMR (600 MHz, CDCl₃) δ 4.27 (tq, J = 6.2, 6.2 Hz, 1H), 2.46–2.41 (m, 2H), 2.20–2.17 (m, 2H), 1.77–1.69 (m, 1H), 1.68–1.63 (m, 2H), 1.61–1.56 (m, 4H), 1.56–1.52 (m, 1H), 1.28–1.20 (m, 1H), 1.19 (d, J = 6.2 Hz, 3H), 0.91 (d, J = 6.7 Hz, 3H), 0.89 (d, J = 6.7 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 164.7, 76.5, 45.0, 32.3, 27.1, 25.9, 25.8, 25.4, 24.9, 22.9, 22.9, 20.4; **IR** (cm⁻¹) 2953, 2929, 2862, 1640, 942; **HRMS** (EI) Calculated for C₁₂H₂₃NO:

197.1780, Found: 197.1777.

Cyclohexanone O-(1-phenylpropan-2-yl) oxime (Table 1, 1g)



Colorless oil; ¹**H** NMR (600 MHz, CDCl₃) δ 7.29–7.25 (m, 2H), 7.22–7.17 (m, 3H), 4.43 (td, J = 6.9, 5.7, 1H), 3.02 (dd, J = 13.5, 5.7 Hz, 1H), 2.74 (dd, J = 13.6, 6.9 Hz, 1H), 2.50–2.39 (m, 2H), 2.24–2.20 (m, 2H), 1.72–1.63 (m, 2H), 1.63–1.55 (m, 4H), 1.18 (d, J = 6.3 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) 159.8, 138.8, 129.6 (2C), 128.0 (2C), 125.9, 78.7, 42.0, 32.3, 27.1, 25.9, 25.7, 25.5, 19.1; **IR** (cm⁻¹) 3027, 2928, 2857, 1642, 950; **HRMS** (EI) Calculated for C₁₅H₂₁NO: 231.1623, Found: 231.1626.

Cyclohexanone *O*-(3-methylbutan-2-yl) oxime (Table 1, 1h)



Colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 3.92 (td, J = 6.3, 6.3 Hz, 1H), 2.53–2.47 (m, 1H), 2.46–2.40 (m, 1H), 2.23–2.14 (m, 2H), 1.91–1.83 (m, 1H), 1.68–1.62 (m, 2H), 1.62–1.54 (m, 4H), 1.12 (d, J = 6.4 Hz, 3H), 0.90 (d, J = 6.9Hz, 3H), 0.87 (d, J = 6.9 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 159.4, 82.4, 32.3, 32.0, 27.1, 25.9, 25.8, 25.3, 18.6, 17.3, 15.7; **IR** (cm⁻¹) 2957, 2930, 2860, 1640, 943; **HRMS** (EI) Calculated for C₁₁H₂₁NO: 183.1623, Found: 183.1621.

Cyclohexanone O-(3-methylpentan-3-yl) oxime (Table 1, 1i)



Colorless oil; ¹**H** NMR (600 MHz, CDCl₃) δ 2.49–2.43 (m, 2H), 2.20–2.15 (m, 2H), 1.69–1.50 (m, 10H), 1.15 (s, 3H), 0.82 (t, *J* = 7.5 Hz, 6H); ¹³C NMR (150 MHz, CDCl₃) δ 158.7, 80.9, 32.5, 30.2 (2C), 27.3, 26.1, 26.0, 25.2, 22.1, 7.9 (2C); **IR** (cm⁻¹) 2968, 2932, 2880, 2857, 1639, 937; **HRMS** (EI) Calculated for C₁₂H₂₃NO: 197.1780, Found: 197.1779.

Cyclohexanone O-(tert-pentyl) oxime (Table 1, 1j)



Colorless oil; ¹**H** NMR (600 MHz, CDCl₃) δ 2.48–2.43 (m, 2H), 2.21–2.16 (m, 2H), 1.67–1.62 (m, 2H), 1.61–1.55 (m, 4H), 1.59 (q, *J* = 7.5 Hz, 2H), 1.21 (s, 6H), 0.84 (t, *J* = 7.5 Hz, 3H); ¹³**C** NMR (150 MHz, CDCl₃) δ 158.7, 78.9, 32.8, 32.5, 27.3, 26.0, 25.9, 25.2, 25.1 (2C), 8.3; **IR** (cm⁻¹) 2971, 2930, 2858, 1641, 940; **HRMS** (EI) Calculated for C₁₁H₂₁NO: 183.1623, Found: 183.1621.

Cyclohexanone *O*-(2-methyl-4-phenylbutan-2-yl) oxime (Table 1, 1k)



Pale yellow oil; ¹H NMR (600 MHz, CDCl₃) δ 7.29–7.25 (m, 2H), 7.21–7.14 (m, 3H), 2.63–2.59 (m, 2H), 2.50–2.46 (m, 2H), 2.25–2.22 (m, 2H), 1.92–1.88 (m, 2H), 1.70–1.64 (m, 2H), 1.61–1.58 (m, 4H), 1.31 (s, 6H); ¹³C NMR (150 MHz, CDCl₃) δ 159.4, 143.2, 128.3 (2C), 128.3 (2C), 125.5, 78.6, 42.3, 32.5, 30.4, 27.3, 26.0, 26.0, 25.7 (2C), 25.3; **IR** (cm⁻¹) 2973, 2930, 2857, 1641, 942; **HRMS** (EI) Calculated for C₁₇H₂₅NO:

259.1936, Found: 259.1934.

Cyclohexanone O-[(1R,3S,5r,7r)-2-methyladamantan-2-yl] oxime (Table 1, 1l)



White Soild; m.p. 47–49 °C; ¹H NMR (600 MHz, CDCl₃) δ 2.54–2.48 (m, 2H), 2.23–2.18 (m, 2H), 2.09–2.03 (m, 2H), 1.94–1.90 (m, 2H), 1.90–1.85 (m, 2H), 1.83–1.80 (m, 1H), 1.78–1.74 (m, 1H), 1.74–1.72 (m, 1H), 1.72–1.70 (m, 1H), 1.69–1.67 (m 2H), 1.67–1.63 (m, 2H), 1.62–1.57 (m,

4H), 1,48–1.45 (m, 1H), 1.45–1.43 (m, 1H), 1.41 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 159.1, 81.5, 38.5, 36.3 (2C), 34.7 (2C), 32.9 (2C), 32.5, 27.8, 27.3, 27.2, 26.1, 26.0, 25.4, 22.6; **IR** (cm⁻¹) 2918, 2856, 1640, 937; **HRMS** (EI) Calculated for C₁₇H₂₇NO: 261.2093, Found: 261.2094.

Cyclohexanone *O*-(1-methylcyclopentyl) oxime (Table 1, 1m)



Colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 2.46–2.42 (m, 2H), 2.22–2.19 (m, 2H), 1.98–1.92 (m, 2H), 1.73–1.67 (m, 2H), 1.67–1.63 (m, 2H), 1.60–1.54 (m, 6H), 1.50–1.44 (m, 2H), 1.38 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 159.6, 88.2, 37.9 (2C), 32.5, 27.3, 26.01 25.93, 25.3, 24.8, 24.5 (2C); **IR** (cm⁻¹) 2929, 2858, 1639, 935; **HRMS** (EI) Calculated for C₁₂H₂₁NO: 195.1623, Found: 195.1620.

Cyclohexanone O-(1-methylcyclohexyl) oxime (Table 1, 1n)



Colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 2.52–2.47 (m, 2H), 2.22–2.17 (m, 2H), 1.86–1.80 (m, 2H), 1.68–1.62 (m, 2H), 1.62–1.56 (m, 4H), 1.55–1.47 (m, 3H), 1.45–1.38 (m, 2H), 1.33 (ddd, *J* = 14.0, 11.1, 4.0 Hz, 2H), 1.28–1.25 (m, 1H), 1.24 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 159.0, 77.4, 36.2 (2C), 32.5, 27.3, 26.1, 26.0, 25.9, 25.8, 25.3, 22.3 (2C); **IR** (cm⁻¹) 2927, 2857, 1641, 942; **HRMS** (EI) Calculated for C₁₃H₂₃NO: 209.1780, Found: 209.1778.

Cyclohexanone O-(1-methylcycloheptyl) oxime (Table 1, 10)



Colorless oil; ¹**H** NMR (600 MHz, CDCl₃) δ 2.50–2.43 (m, 2H), 2.23–2.15 (m, 2H), 1.90 (dd, J = 13.2, 9.1 Hz, 2H), 1.68–1.62 (m, 2H), 1.62–1.53 (m, 10H), 1.53–1.46 (m, 2H), 1.41–1.32 (m, 2H), 1.26 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 159.0, 82.1, 39.5 (2C), 32.5, 30.0 (2C), 27.3, 27.3, 26.1, 25.9, 25.4, 22.7 (2C); **IR** (cm⁻¹) 2922, 2854, 1638, 935, 919; **HRMS** (EI) Calculated for C₁₄H₂₅NO: 223.1936, Found: 223.1938.

III. Experimental Procedure for Synthesis of 1,2-Amino Alcohols

1. General Procedure for the C-H Amidation of Ketoximes with Azides

1-1. General Procedure

To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added ketoxime (0.20 mmol, 1.0 equiv.), azide (0.40 mmol, 2.0 equiv.), [IrCp*Cl₂]₂ (8.0 mg, 0.010 mmol, 5 mol %), AgNTf₂ (15.6 mg, 0.040 mmol, 20 mol %), CsOAc (3.4 mg, 0.020 mmol, 10 mol %) and 1,2-dichloroethane (0.5 mL) under atmospheric conditions. The reaction mixture was stirred at 60 °C for 24 h, filtered through a pad of celite and then washed with ethyl acetate (5 mL x 3). Organic solvents were removed under reduced pressure and the residue was purified by chromatography on silica gel (*n*-hexane/EtOAc) to give the amidated product.

1-2. Spectroscopic Data of Amidated Products Obtained in This Study

N-[2-{(Cyclohexylideneamino)oxy}butyl]-4-methylbenzenesulfonamide (Table 1, 2a)



White solid; m.p. 51–53 °C; ¹H NMR (600 MHz, CDCl₃) 7.74–7.69 (m, 2H), 7.31-7.26 (m, 2H), 5.23 (s, 1H), 3.93-3.87 (m, 1H), 3.20 (dd, J = 12.8, 3.0 Hz)1H), 2.99 (dd, J = 12.7, 7.1 Hz, 1H), 2.41 (s, 3H), 2.39–2.30 (m, 2H), 2.14–2.09 (m, 2H), 1.66–1.60 (m, 2H), 1.60–1.51 (m, 5H), 1.48–1.41 (m, 1H), 0.85 (t, J $= 7.5 \text{ Hz}, 3\text{H}; {}^{13}\text{C} \text{ NMR} (150 \text{ MHz}, \text{CDCl}_3) \delta 161.1, 143.1, 136.9, 129.5 (2C),$ 127.0 (2C), 80.8, 46.6, 32.1, 26.9, 25.7 (2C), 25.2, 24.4, 21.4, 9.7; IR (cm⁻¹) 3276, 2971, 2927, 2859,

1642, 1317, 1157, 941, 820; **HRMS** (EI) Calculated for C₁₇H₂₆N₂O₃S: 338.1664, Found: 338.1662.

(S)-N-[2-{(Cyclohexylideneamino)oxy}butyl]-4-methylbenzenesulfonamide (Table 1, 2a-(S))





N-[2-{(Cyclohexylideneamino)oxy}propyl]-4-methylbenzenesulfonamide (Table 1, 2c)



Pale yellow oil; ¹**H NMR** (600 MHz, CDCl₃) 7.76–7.70 (m, 2H), 7.31–7.27 (m, 2H), 5.18 (dd, *J* = 6.9, 3.8 Hz, 1H), 4.19–4.12 (m, 1H), 3.19 (ddd, *J* = 12.7, 7.0, 3.0 Hz, 1H), 2.97 (ddd, *J* = 12.8, 7.2, 3.8 Hz, 1H), 2.41 (s, 3H), 2.40–2.35 (m, 1H), 2.35–2.29 (m, 1H), 2.17–2.06 (m, 2H), 1.66–1.60 (m, 2H), 1.59–1.52 (m, 4H), 1.14 (d, *J* = 6.5 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 161.0, 143.1,

137.0, 129.6 (2C), 127.0 (2C), 75.7, 48.2, 32.2, 26.9, 25.7, 25.7, 25.2, 21.5, 17.3; **IR** (cm⁻¹) 3278, 2930, 2857, 1639, 1325, 1159, 953, 814; **HRMS** (EI) Calculated for $C_{16}H_{24}N_2O_3S$: 324.1508, Found: 328.1507.

N-[2-{(Cyclohexylideneamino)oxy}-2-methylpropyl]-4-methylbenzenesulfonamide (Table 1, 2d)



Colorless solid; m.p. 106–108 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.73–7.69 (m, 2H), 7.31–7.27 (m, 2H), 5.11 (br, 1H), 3.04 (s, 2H), 2.41 (s, 3H), 2.38–2.33 (m, 2H), 2.11-2.07 (m, 2H), 1.63–1.59 (m, 2H), 1.58–1.53 (m, 4H), 1.20 (s, 6H); ¹³C NMR (150 MHz, CDCl₃) δ 160.8, 143.0, 137.0, 129.5 (2C), 127.0 (2C), 77.7, 51.3, 32.3, 27.0, 25.7 (2C), 25.2, 23.9 (2C), 21.5; **IR** (cm⁻¹) 3250,

2931, 1637, 1429, 1320, 1162, 1090, 925, 821; **HRMS** (ESI) Calculated for C₁₇H₂₆N₂O₃S [M+Na]⁺: 361.1562, Found: 361.1543.

N,N'-[2-{(Cyclohexylideneamino)oxy}-2-methylpropane-1,3-diyl]bis(4-methylbenzenesulfonamide) (Table 1, 2d')



White solid; m.p. 120–122 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.74–7.69 (m, 4H), 7.32–7.28 (m, 4H), 5.21–5.06 (m, 2H), 3.13–3.07 (m, 2H), 3.07–3.02 (m, 2H), 2.43 (s, 6H), 2.33–2.28 (m, 2H), 2.09–2.03 (m, 2H), 1.62–1.57 (m, 2H), 1.57–1.50 (m, 4H), 1.21 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 162.2, 143.4 (2C), 136.8 (2C), 129.7 (4C), 126.9 (4C), 79.5, 47.7 (2C), 32.3, 26.9,

25.6, 25.6, 25.2, 21.5 (2C), 20.3; **IR** (cm⁻¹) 3253, 2928, 1640, 1323, 1163, 973, 813; **HRMS** (EI) Calculated for $C_{24}H_{33}N_3O_5S_2$: 507.1862, Found: 507.1859.

N-[2-{(Cyclohexylideneamino)oxy}hexyl]-4-methylbenzenesulfonamide (Table 1, 2e)



Pale yellow oil; ¹H NMR (600 MHz, CDCl₃) 7.76–7.69 (m, 2H), 7.31–7.27 (m, 2H), 5.22 (s, 1H), 4.00–3.94 (m, 1H), 3.21 (dd, J = 12.7, 2.8 Hz, 1H), 3.00 (dd, J = 12.7, 7.0 Hz, 1H), 2.42 (s, 3H), 2.41–2.30 (m, 2H), 2.17–2.07 (m, 2H), 1.63 (d, J = 6.0 Hz, 2H), 1.60–1.52 (m, 5H), 1.43–1.35 (m, 1H), 1.29–1.21 (m, 4H), 0.85 (t, J = 6.8 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 161.1, 143.2,

137.0, 129.6 (2C), 127.1 (2C), 79.6, 47.1, 32.2, 31.1, 27.5, 27.0, 25.7 (2C), 25.3, 22.5, 21.5, 13.9; **IR** (cm⁻¹) 3275, 3255, 2929, 2857, 1640, 1325, 1161, 933, 813; **HRMS** (EI) Calculated for C₁₉H₃₀N₂O₃S: 366.1977, Found: 366.1979.

N-[2-{(Cyclohexylideneamino)oxy}-4-methylpentyl]-4-methylbenzenesulfonamide (Table 1, 2f)



Pale yellow oil; ¹**H NMR** (600 MHz, CDCl₃) δ 7.74–7.68 (m, 2H), 7.30–7.26 (m, 2H), 5.29 (dd, J = 7.0, 4.3 Hz, 1H), 4.07–3.99 (m, 1H), 3.19 (ddd, J = 12.7, 6.9, 2.9 Hz, 1H), 2.98 (ddd, J = 12.7, 6.8, 4.4 Hz, 1H), 2.40 (s, 3H), 2.39–2.29 (m, 2H), 2.16–2.04 (m, 2H), 1.66–1.59 (m, 3H), 1.59–1.52 (m, 4H), 1.48 (ddd, J = 14.6, 8.5, 6.4 Hz, 1H), 1.17 (ddd, J = 14.0, 7.7, 5.1 Hz, 1H), 0.83 (d, J = 6.6 Hz, 3H), 0.82 (d, J = 6.6 Hz, 3H); ¹³**C NMR** (150 MHz, CDCl₃) δ 161.0,

143.1, 137.0, 129.5 (2C), 127.1 (2C), 77.9, 47.5, 40.2, 32.2, 27.0, 25.69, 25.68, 25.2, 24.6, 22.9, 22.3, 21.4; **IR** (cm⁻¹) 3280, 2930, 2863, 1640, 1326, 1160, 935, 813; **HRMS** (EI) Calculated for C₁₉H₃₀N₂O₃S: 366.1977, Found: 366.1979.

N-[2-{(Cyclohexylideneamino)oxy}-3-phenylpropyl]-4-methylbenzenesulfonamide (Table 1, 2g)



Pale yellow oil; ¹**H NMR** (600 MHz, CDCl₃) δ 7.71–7.65 (m, 2H), 7.30–7.22 (m, 4H), 7.22–7.17 (m, 1H), 7.12–7.07 (m, 2H), 5.16 (br, 1H), 4.19 (dd, *J* = 6.8, 3.0 Hz, 1H), 3.21 (dd, *J* = 12.7, 3.0 Hz, 1H), 3.04 (dd, *J* = 12.8, 6.8 Hz, 1H), 2.93 (dd, *J* = 14.0, 6.6 Hz, 1H), 2.73 (dd, *J* = 14.0, 6.8 Hz, 1H), 2.42 (s, 3H), 2.40–2.28 (m, 2H), 2.17–2.10 (m, 2H), 1.69–1.61 (m, 2H), 1.60–1.50 (m, 4H); ¹³C NMR (150 MHz, CDCl₃) δ 161.6, 143.2, 137.4, 136.9, 129.6 (2C),

129.3 (2C), 128.3 (2C), 127.1 (2C), 126.3, 80.4, 46.0, 37.7, 32.1, 27.0, 25.7, 25.6, 25.4, 21.5; **IR** (cm⁻¹) 3277, 2928, 2856, 1639, 1325, 1159, 939, 813; **HRMS** (EI) Calculated for $C_{22}H_{28}N_2O_3S$: 400.1821, Found: 400.1823.

N-[2-{(Cyclohexylideneamino)oxy}-3-methylbutyl]-4-methylbenzenesulfonamide (Table 1, 2h)



Pale yellow oil; ¹**H NMR** (600 MHz, CDCl₃) & 7.73–7.69 (m, 2H), 7.30–7.26 (m, 2H), 5.29 (dd, *J* = 7.3, 4.0 Hz, 1H), 3.68 (td, *J* = 7.2, 2.6 Hz, 1H), 3.21 (ddd, *J* = 12.7, 7.2, 2.6 Hz, 1H), 3.02 (ddd, *J* = 12.6, 7.5, 3.9 Hz, 1H), 2.40 (s, 3H), 2.39–2.36 (m, 1H), 2.35–2.29 (m, 1H), 2.15–2.05 (m, 2H), 1.90–1.81 (m, 1H), 1.65–1.59 (m, 2H), 1.59–1.51 (m, 4H), 0.85 (d, *J* = 6.8 Hz, 3H), 0.82 (d,

 $J = 6.8 \text{ Hz}, 3\text{H}; {}^{13}\text{C NMR} (150 \text{ MHz}, \text{CDCl}_3) \delta 161.0, 143.1, 136.9, 129.5 (2C), 127.0 (2C), 84.4, 45.0, 32.1, 29.6, 26.9, 25.7, 25.7, 25.2, 21.4, 18.3, 18.3; IR (cm⁻¹) 3279, 2930, 2859, 1640, 1325, 1160, 934, 814; HRMS (EI) Calculated for C₁₈H₂₈N₂O₃S: 352.1821, Found: 352.1821.$

N-[2-{(Cyclohexylideneamino)oxy}-2-ethylbutyl]-4-methylbenzenesulfonamide (Table 1, 2i)



Colorless oil; ¹H NMR (600 MHz, CDCl₃) 7.73–7.68 (m, 2H), 7.30–7.26 (m, 2H), 5.28 (t, J = 5.9 Hz, 1H), 3.04 (d, J = 5.9 Hz, 2H), 2.41 (s, 3H), 2.40–2.36 (m, 2H), 2.10–2.05 (m, 2H), 1.67–1.45 (m, 10H), 0.76 (t, J = 7.5 Hz, 6H); ¹³C NMR (150 MHz, CDCl₃) δ 160.9, 143.0, 136.9, 129.5 (2C), 127.0 (2C), 82.1, 48.1, 32.4, 27.1, 25.9, 25.8, 25.2 (2C), 25.1, 21.4, 7.3 (2C); **IR** (cm⁻¹) 3280,

2932, 2881, 2857, 1640, 1449, 1326, 1160, 931, 813; **HRMS** (EI) Calculated for $C_{19}H_{30}N_2O_3S$: 366.1977, Found: 366.1977.

N-[2-{(Cyclohexylideneamino)oxy}-2-methylbutyl]-4-methylbenzenesulfonamide (Table 1, 2j)



White solid; m.p. 73–75 °C; ¹**H NMR** (600 MHz, CDCl₃) δ 7.73–7.68 (m, 2H), 7.29–7.26 (m, 2H), 5.24 (dd, J = 6.2, 5.7 Hz, 1H), 3.07 (dd, J = 12.1, 5.7 Hz, 1H), 3.00 (dd, J = 12.1, 6.2 Hz, 1H), 2.41 (s, 3H), 2.40–2.36 (m, 1H), 2.36–2.30 (m, 1H), 2.11–2.03 (m, 2H), 1.68–1.52 (m, 7H), 1.51–1.44 (m, 1H), 1.13 (s, 3H), 0.80 (t, J = 7.5 Hz, 3H); ¹³**C NMR** (150 MHz, CDCl₃) δ 160.8,

143.0, 137.0, 129.5 (2C), 127.0 (2C), 79.8, 50.0, 32.3, 29.2, 27.1, 25.8, 25.7, 25.1, 21.4, 20.6, 7.6; **IR** (cm⁻¹) 3261, 2931, 2859, 1643, 1448, 1321, 1162, 931, 820; **HRMS** (EI) Calculated for C₁₈H₂₈N₂O₃S: 352.1821, Found: 352.1818.

N-[2-{(Cyclohexylideneamino)oxy}-2-methyl-4-phenylbutyl]-4-methylbenzenesulfonamide (Table 1, 2k)



White solid; m.p. 97–99 °C; ¹**H NMR** (600 MHz, CDCl₃) δ 7.76–7.70 (m, 2H), 7.30–7.24 (m, 4H), 7.19–7.15 (m, 1H), 7.15–7.12 (m, 2H), 5.30 (dd, *J* = 6.2, 5.9 Hz, 1H), 3.16 (dd, *J* = 12.3, 5.9 Hz, 1H), 3.08 (dd, *J* = 12.3, 6.2 Hz, 1H), 2.64–2.51 (m, 2H), 2.48–2.42 (m, 1H), 2.41 (s, 3H), 2.39–2.32 (m, 1H), 2.17–2.07 (m, 2H), 1.96 (ddd, *J* = 13.8, 12.1, 5.0 Hz, 1H), 1.76 (ddd, *J* = 13.8, 12.0, 5.5 Hz, 1H), 1.69–1.51 (m, 6H), 1.26 (s,

3H); ¹³C NMR (150 MHz, CDCl₃) δ 161.0, 143.0, 142.2, 136.9, 129.5 (2C), 128.24 (2C), 128.21 (2C), 126.9 (2C), 125.7, 79.4, 50.3, 38.5, 32.3, 29.6, 27.1, 25.8, 25.7, 25.2, 21.4, 21.2; **IR** (cm⁻¹) 3257, 2929, 2857, 1643, 1495, 1451, 1324, 1162, 917, 814; **HRMS** (EI) Calculated for C₂₄H₃₂N₂O₃S: 428.2134, Found: 428.2132.

N-[[(1*r*,3*r*)-2-{(Cyclohexylideneamino)oxy}adamantan-2-yl]methyl]-4-methylbenzenesulfonamide (Table 1, 2l)



White solid; m.p. 107–109 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.74–7.69 (m, 2H), 7.30–7.26 (m, 2H), 5.24 (br, 1H), 3.33 (s, 2H), 2.47–2.43 (m, 2H), 2.42 (s, 3H), 2.12–2.07 (m, 2H), 2.03–2.00 (m, 2H), 1.96–1.92 (m, 2H), 1.83–1.80 (m, 1H), 1.79–1.74 (m, 3H), 1.70–1.68 (m, 1H), 1.67–1.65 (m, 3H), 1.64–1.61 (m, 2H), 1.59 (dt, *J* = 6.4, 3.1 Hz, 4H), 1.47 (dt, *J* = 12.6, 2.8 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 161.4, 142.9, 137.0, 129.5 (2C),

127.0 (2C), 82.0, 46.9, 38.1, 34.0 (2C), 32.6 (2C), 32.5 (2C), 32.5, 27.4, 27.22, 27.15, 26.1, 25.8, 25.4, 21.5; **IR** (cm⁻¹) 3325, 2922, 2856, 1643, 1457, 1353, 1160, 935, 813; **HRMS** (EI) Calculated for C₂₄H₃₄N₂O₃S: 430.2290, Found: 430.2287.





White solid; m.p. 99–101 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.73–7.67 (m, 2H), 7.28–7.24 (m, 2H), 5.34 (t, *J* = 5.6 Hz, 1H), 3.13 (d, *J* = 5.6 Hz, 2H), 2.39 (s, 3H), 2.36–2.31 (m, 2H), 2.09–2.03 (m, 2H), 1.85–1.79 (m, 2H), 1.67–1.56 (m, 4H), 1.56–1.49 (m, 8H); ¹³C NMR (150 MHz, CDCl₃) δ 161.1, 142.9, 136.9, 129.4 (2C), 126.9 (2C), 89.1, 50.1, 34.9 (2C), 32.3, 27.0, 25.8, 25.7,

25.1, 24.1 (2C), 21.4; **IR** (cm⁻¹) 3260, 2935, 2858, 1637, 1317, 1159, 946, 819; **HRMS** (EI) Calculated for C₁₉H₂₈N₂O₃S: 364.1821, Found: 364.1825.

N-[[1-{(Cyclohexylideneamino)oxy}cyclohexyl]methyl]-4-methylbenzenesulfonamide (Table 1, 2n)



Colorless oil; ¹**H NMR** (600 MHz, CDCl₃) δ 7.73–7.67 (m, 2H), 7.28–7.25 (m, 2H), 5.30 (t, *J* = 5.8 Hz, 1H), 3.04 (d, *J* = 5.8 Hz, 2H), 2.43–2.40 (m, 2H), 2.40 (s, 3H), 2.10–2.05 (m, 2H), 1.83–1.76 (m, 2H), 1.64–1.58 (m, 2H), 1.58–1.53 (m, 4H), 1.53–1.48 (m, 1H), 1.44–1.37 (m, 4H), 1.33–1.26 (m, 2H), 1.26–1.18 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 161.1, 142.9, 137.0, 129.4 (2C), 126.9

(2C), 78.0, 50.5, 32.4 (2C), 32.3, 27.1, 25.9, 25.7, 25.6, 25.2, 21.5 (2C), 21.4; **IR** (cm⁻¹) 3284, 2928, 2857, 1643, 1323, 1158, 939, 813; **HRMS** (EI) Calculated for $C_{20}H_{30}N_2O_3S$: 378.1977, Found: 378.1976.

N-[[1-{(cyclohexylideneamino)oxy}cycloheptyl]methyl]-4-methylbenzenesulfonamide (Table, 20)



White solid; m.p. 86–88 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.73–7.68 (m, 2H), 7.29–7.26 (m, 2H), 5.24 (br, 1H), 3.02 (s, 2H), 2.41 (s, 3H), 2.41–2.37 (m, 2H), 2.10–2.05 (m, 2H), 1.81–1.74 (m, 2H), 1.64–1.59 (m, 2H), 1.59–1.43 (m, 12H), 1.37–1.30 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 161.3, 142.9, 137.0, 129.5 (2C), 127.0 (2C), 83.0, 50.7, 35.1 (2C), 32.4, 30.1 (2C), 27.1, 25.9, 25.8, 25.3,

22.2 (2C), 21.4; **IR** (cm⁻¹) 3265, 2922, 2853, 1639, 1324, 1165, 991, 818; **HRMS** (FAB) Calculated for $C_{21}H_{32}N_2O_3S$ [M+H]⁺: 393.2212, Found: 393.2214.

N-[[1-{(Cyclohexylideneamino)oxy}cyclohexyl]methyl]benzenesulfonamide (Table 2, 3a)



White solid; m.p. 116–118 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.86–7.81 (m, 2H), 7.57–7.54 (m, 1H), 7.51–7.47 (m, 2H), 5.36 (br, 1H), 3.08 (s, 2H), 2.47–2.38 (m, 2H), 2.12–2.08 (m, 2H), 1.85–1.77 (m, 2H), 1.66–1.61 (m, 2H), 1.60–1.56 (m, 4H), 1.55–1.49 (m, 1H), 1.46–1.38 (m, 4H), 1.35–1.28 (m, 2H), 1.27–1.20 (m, 1H); ¹³C NMR (150 MHz,

CDCl₃) δ 161.4, 140.1, 132.3, 128.9 (2C), 127.0 (2C), 78.1, 50.7, 32.4 (2C), 32.4, 27.2, 26.0, 25.8, 25.7, 25.3, 21.6 (2C); **IR** (cm⁻¹) 3283, 2931, 2857, 1643, 1324, 1161, 939, 689; **HRMS** (EI) Calculated for C₁₉H₂₈N₂O₃S: 364.1821, Found: 364.1822.

N-[[1-{(Cyclohexylideneamino)oxy}cyclohexyl]methyl]-4-methoxybenzenesulfonamide (Table 2, 3b)



White solid; m.p. 104–106 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.79–7.74 (m, 2H), 6.97–6.93 (m, 2H), 5.19 (br, 1H), 3.86 (s, 3H), 3.04 (s, 2H), 2.45–2.41 (m, 2H), 2.13–2.09 (m, 2H), 1.81 (m, 2H), 1.66–1.60 (m, 2H), 1.60–1.56 (m, 4H), 1.55–1.49 (m, 1H), 1.45–1.39 (m, 4H), 1.34–1.28 (m, 2H), 1.27–1.21 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 162.6, 161.4, 131.7, 129.1 (2C), 114.0

(2C), 78.2, 55.6, 50.5, 32.5 (2C), 32.4, 27.2, 26.0, 25.8, 25.7, 25.3, 21.6 (2C); **IR** (cm⁻¹) 3284, 2930, 2856, 1642, 1323, 1155, 939, 832; **HRMS** (EI) Calculated for C₂₀H₃₀N₂O₄S: 394.1926, Found: 394.1926.

N-[[1-{(Cyclohexylideneamino)oxy}cyclohexyl]methyl]-4-fluorobenzenesulfonamide (Table 2, 3c)



White solid; m.p. 94–96 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.90–7.80 (m, 2H), 7.22–7.10 (m, 2H), 5.38 (br, 1H), 3.07 (s, 2H), 2.46–2.40 (m, 2H), 2.14–2.07 (m, 2H), 1.84–1.78 (m, 2H), 1.64–1.57 (m, 6H), 1.57–1.50 (m, 1H), 1.46–1.39 (m, 4H), 1.34–1.20 (m, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 164.9 (d, *J* = 254.9 Hz), 161.6, 136.2 (d, *J* = 3.7 Hz), 129.7 (d, *J* = 9.5 Hz, 2C),

116.1 (d, *J* = 23.3 Hz, 2C), 78.1, 50.7, 32.4 (3C), 27.2, 26.0, 25.8, 25.6, 25.3, 21.5 (2C); **IR** (cm⁻¹) 3282, 2931, 2857, 1641, 1332, 1168, 939, 838; **HRMS** (EI) Calculated for C₁₉H₂₇FN₂O₃S: 382.1726, Found: 382.1728.

N-[[1-{(Cyclohexylideneamino)oxy}cyclohexyl]methyl]naphthalene-1-sulfonamide (Table 2, 3d)



White solid; m.p. 129–131 °C; ¹H NMR (600 MHz, CDCl₃) δ 8.65–8.60 (m, 1H), 8.25–8.21 (m, 1H), 8.06–8.02 (m, 1H), 7.95–7.91 (m, 1H), 7.64–7.61 (m, 1H), 7.59–7.56 (m, 1H), 7.55–7.51 (m, 1H), 5.77 (br, 1H), 3.03 (s, 2H), 2.39–2.31 (m, 2H), 2.02–1.96 (m, 2H), 1.77–1.71 (m, 2H), 1.58–1.51 (m, 6H), 1.51–1.45 (m, 1H), 1.40–1.31 (m, 4H), 1.29–1.23 (m, 2H), 1.23–1.17 (m, 1H); ¹³C NMR (150 MHz,

CDCl₃) δ 161.3, 134.9, 134.3, 133.8, 129.2, 129.0, 128.3, 128.0, 126.6, 124.5, 124.1, 78.2, 50.9, 32.4 (2C), 32.3, 27.1, 25.9, 25.8, 25.6, 25.1, 21.6 (2C); **IR** (cm⁻¹) 3295, 2929, 2856, 1638, 1447, 1321, 1135, 939, 803; **HRMS** (EI) Calculated for C₂₃H₃₀N₂O₃S: 414.1977, Found: 414.1978.

N-[[1-{(Cyclohexylideneamino)oxy}cyclohexyl]methyl]methanesulfonamide (Table 2, 3e)



White solid; m.p. 87–89 °C; ¹H NMR (600 MHz, CDCl₃) δ 4.84 (br, 1H), 3.28 (s, 2H), 2.93 (s, 3H), 2.50–2.45 (m, 2H), 2.20–2.15 (m, 2H), 1.92–1.85 (m, 2H), 1.69–1.63 (m, 2H), 1.62–1.59 (m, 3H), 1.58–1.55 (m, 1H), 1.51–1.44 (m, 4H), 1.39–1.33 (m, 2H), 1.31–1.23 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 161.7, 78.2, 50.6, 39.8, 32.5, 32.4 (2C), 27.2, 26.0, 25.8, 25.7,

25.4, 21.6 (2C); **IR** (cm⁻¹) 3289, 2928, 2856, 1640, 1315, 1148, 939, 914; **HRMS** (EI) Calculated for C₁₄H₂₆N₂O₃S: 302.1664, Found: 302.1666.

N-[[1-{(Cyclohexylideneamino)oxy}cyclohexyl]methyl]-1-phenylmethanesulfonamide (Table 2, 3f)



White solid; m.p. 126–128 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.42–7.38 (m, 2H), 7.37–7.33 (m, 3H), 4.24 (s, 2H), 3.21 (s, 2H), 2.47–2.40 (m, 2H), 2.13–2.09 (m, 2H), 1.88–1.80 (m, 2H), 1.65–1.61 (m, 2H), 1.60–1.57 (m, 4H), 1.56–1.52 (m, 1H), 1.48–1.42 (m, 4H), 1.36–1.30 (m, 2H), 1.29–1.22 (m, 1H); ¹³C

NMR (150 MHz, CDCl₃) δ 161.5, 130.6 (2C), 129.7, 128.7 (2C), 128.5, 78.3, 58.2, 51.0, 32.4, 32.3 (2C), 27.2, 26.0, 25.8, 25.7, 25.3, 21.6 (2C); **IR** (cm⁻¹) 3282, 2932, 2855, 1465, 1399, 1157, 938, 913, 732; **HRMS** (EI) Calculated for C₂₀H₃₀N₂O₃S: 378.1977, Found: 378.1974.

N-[[1-{(Cyclohexylideneamino)oxy}cyclohexyl]methyl]-1-{(1*R*,4*R*)-7,7-dimethyl-2-oxobicyclo [2.2.1]heptan-1-yl}methanesulfonamide (Table 2, 3g)



Colorless oil; ¹**H NMR** (600 MHz, CDCl₃) δ 5.37 (br, 1H), 3.45 (d, J = 15.0 Hz, 1H), 3.36 (d, J = 12.4 Hz, 1H), 3.28 (d, J = 12.4 Hz, 1H), 2.91 (d, J = 15.0 Hz, 1H), 2.54–2.45 (m, 2H), 2.40–2.32 (m, 2H), 2.22–2.14 (m, 2H), 2.11–2.08 (m, 1H), 2.07–1.99 (m, 1H), 1.95–1.85 (m, 3H), 1.81 (ddd, J = 14.2, 9.4, 4.8 Hz, 1H), 1.68–1.62 (m, 2H), 1.62–1.52 (m, 5H), 1.52–1.45 (m, 4H), 1.44–1.35 (m, 3H), 1.32–1.26 (m, 1H), 1.07 (s, 3H), 0.89 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ

215.5, 161.2, 78.4, 58.8, 50.5, 49.0, 48.2, 42.84, 42.76, 32.5, 32.4, 32.2, 27.1, 27.0, 26.0, 25.9, 25.8, 25.7, 25.3, 21.7, 21.6, 19.9, 19.8; **IR** (cm⁻¹) 3290, 2929, 2857, 1738, 1641, 1324, 1145, 938, 731; **HRMS** (EI) Calculated for C₂₃H₃₈N₂O₄S: 438.2552, Found: 438.2554.

2. General Procedure for the Ketoxime Removals to 1,2-Amino Alcohols

1-1. General Procedure

To a stirred solution of amidated product (0.10 mmol, 1.0 equiv.) in Et_2O (1 mL) was added lithium aluminum hydride (LAH, 2.5 equiv.) at room temperature. The reaction mixture was stirred for 48 h at the same temperature. The resulting mixture was diluted with EtOAc (1 mL) and quenched with H₂O (30 µL). The slurry was filtered and inorganic salts were washed with EtOAc (2 mL x 3). The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography to give desired 1,2-amino alcohol.

1-2. Spectroscopic Data of Amidated Products Obtained in This Study

N-(2-Hydroxybutyl)-4-methylbenzenesulfonamide (Table 3, 4a)



White solid; m.p. 86–88 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.77–7.72 (m, 2H), 7.32–7.28 (m, 2H), 5.31–5.20 (m, 1H), 3.66–3.57 (m, 1H), 3.10–3.01 (m, 1H), 2.81–2.74 (m, 1H), 2.46–2.41 (m, 1H), 2.42 (s, 3H), 1.49–1.36 (m, 2H), 0.89 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 143.5, 136.7, 129.7 (2C), 127.1

(2C), 71.8, 48.3, 27.5, 21.5, 9.7; **IR** (cm⁻¹) 3511, 3277, 2968, 2928, 2879, 1450, 1321, 1155, 813; **HRMS** (FAB) Calculated for $C_{11}H_{17}NO_3S$ [M+H]⁺: 244.1007, Found: 244.1010.

(S)-N-(2-Hydroxybutyl)-4-methylbenzenesulfonamide (Table 3, 4a-(S))





N-(2-Hydroxypropyl)-4-methylbenzenesulfonamide (Table 3, 4b)



Colorless oil; ¹**H NMR** (600 MHz, CDCl₃) δ 7.77–7.72 (m, 2H), 7.32–7.29 (m, 2H), 5.43-5.34 (m, 1H), 3.93-3.86 (m, 1H), 3.05-2.97 (m, 1H), 2.81-2.71 (m, 1H), 2.58 (s, 1H), 2.42 (s, 3H), 1.13 (d, J = 6.3 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 143.5, 136.7, 129.7 (2C), 127.0 (2C), 66.6, 50.0, 21.5, 20.5; **IR** (cm⁻¹)

3485, 3277, 2972, 2924, 2873, 1318, 1154, 814; **HRMS** (FAB) Calculated for C₁₀H₁₅NO₃S [M+H]⁺: 230.0851, Found: 230.0848.

N-(2-Hydroxy-3-phenylpropyl)-4-methylbenzenesulfonamide (Table 3, 4c)



White solid; m.p. 87–89 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.75–7.69 (m, 2H), 7.31-7.28 (m, 3H), 7.28-7.25 (m, 1H), 7.24-7.20 (m, 1H), 7.15-7.12 (m, 2H), 5.16-5.10 (m, 1H), 3.93-3.87 (m, 1H), 3.15-3.07 (m, 1H), 2.90-2.83 (m, 1H), 2.75 (dd, J = 13.7, 5.1 Hz, 1H), 2.67 (dd, J = 13.7, 8.3 Hz, 1H), 2.42 (s, 3H), 2.20

(s, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 143.5, 137.0, 136.7, 129.7 (2C), 129.3 (2C), 128.7 (2C), 127.1 (2C), 126.8, 71.2, 48.0, 41.1, 21.5; **IR** (cm⁻¹) 3479, 3271, 3029, 2918, 1439, 1351, 1148, 810; **HRMS** (FAB) Calculated for C₁₆H₁₉NO₃S [M+H]⁺: 306.1164, Found: 306.1162.

N-(2-Hydroxyhexyl)-4-methylbenzenesulfonamide (Table 3, 4d)



Colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.78–7.72 (m, 2H), 7.33–7.28 (m, 2H), 5.31-5.21 (m, 1H), 3.72-3.62 (m, 1H), 3.09-3.00 (m, 1H), 2.81-2.73 (m, 1H), 2.42 (s, 3H), 2.38 (s, 1H), 1.42–1.36 (m, 2H), 1.35–1.20 (m, 4H), 0.86 (t, J = 6.9 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) 143.5, 136.7, 129.7 (2C), 127.1 (2C), 70.5, 48.7, 34.3, 27.5, 22.5, 21.5, 13.9; **IR** (cm⁻¹) 3484, 3278, 2955, 2929, 1320, 1154, 814;

HRMS (FAB) Calculated for C₁₃H₂₁NO₃S [M+H]⁺: 272.1320, Found: 272.1318.

N-(2-Ethyl-2-hydroxybutyl)-4-methylbenzenesulfonamide (Table 3, 4e)



White solid; m.p. 76–78 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.76–7.72 (m, 2H), 7.32-7.29 (m, 2H), 4.97 (s, 1H), 2.86-2.83 (m, 2H), 2.42 (s, 3H), 1.76 (s, 1H), 1.56–1.41 (m, 4H), 0.81 (t, J = 7.5 Hz, 6H); ¹³C NMR (150 MHz, CDCl₃) δ 143.4, 136.7, 129.7 (2C), 127.0 (2C), 74.3, 49.6, 28.7 (2C), 21.5, 7.6 (2C); **IR** (cm⁻¹) 3502,

3276, 2969, 2938, 1882, 1321, 1154, 814; **HRMS** (FAB) Calculated for C₁₃H₂₁NO₃S [M+H]⁺: 272.1320, Found: 272.1318.

N-(2-Hydroxy-2-methylpropyl)-4-methylbenzenesulfonamide (Table 3, 4f)



White solid; m.p. 69–71 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.75–7.72 (m, 2H), 7.31–7.29 (m, 2H), 5.19–5.14 (m, 1H), 2.85 (d, J = 6.6 Hz, 2H), 2.42 (s, 3H), 2.05 (s, 1H), 1.21 (s, 6H); ¹³C NMR (150 MHz, CDCl₃) δ 143.4, 136.8, 129.7 (2C), 127.0 (2C), 70.1, 53.4, 27.2 (2C), 21.5; **IR** (cm⁻¹) 3425, 3143, 2975, 2924, 1303, 1148, 814; **HRMS** (FAB)

Calculated for C₁₁H₁₇NO₃S [M+H]⁺: 244.1007, Found: 244.1006.

N-(2-Hydroxy-2-methylbutyl)-4-methylbenzenesulfonamide (Table 3, 4g)



Pale yellow oil; ¹H NMR (600 MHz, CDCl₃) δ 7.75–7.71 (m, 2H), 7.32–7.29 (m, 2H), 5.08-5.04 (m, 1H), 2.90-2.79 (m, 2H), 2.42 (s, 3H), 1.88 (s, 1H), 1.50 (q, J =7.5 Hz, 2H), 1.14 (s, 3H), 0.86 (t, J = 7.5 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 143.4, 136.8, 129.7 (2C), 127.0 (2C), 72.3, 51.7, 32.4, 24.0, 21.5, 8.0; **IR** (cm⁻¹) 3490,

3276, 2970, 2926, 2882, 1320, 1152, 813; **HRMS** (FAB) Calculated for C₁₂H₁₉NO₃S [M+H]⁺: 258.1164, Found: 258.1161.

N-(2-Hydroxy-2-methyl-4-phenylbutyl)-4-methylbenzenesulfonamide (Table 3, 4h)



Pale yellow oil; ¹H NMR (600 MHz, CDCl₃) δ 7.76–7.70 (m, 2H), 7.31–7.23 (m, 4H), 7.21-7.11 (m, 3H), 5.18-5.04 (m, 1H), 2.96-2.84 (m, 2H), 2.66-2.60 (m, 2H), 2.41 (s, 3H), 1.80–1.75 (m, 2H), 1.24 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 143.5, 141.7, 136.7, 129.7 (2C), 128.4 (2C), 128.3 (2C), 127.0 (2C), 125.9, 72.0,

52.1, 41.5, 30.0, 24.6, 21.5.; **IR** (cm⁻¹) 3492, 3271, 2972, 2924, 1320, 1154, 814; **HRMS** (FAB) Calculated for C₁₈H₂₃NO₃S [M+H]⁺: 334.1477, Found: 334.1479.

N-[{(1*r*,3*r*,5*r*,7*r*)-2-Hydroxyadamantan-2-yl}methyl]-4-methylbenzenesulfonamide (Table 3, 4i)



White solid; m.p. 147–149 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.76–7.72 (m, 2H), 7.32–7.28 (m, 2H), 5.05 (s, 1H), 3.13–3.09 (m, 2H), 2.42 (s, 3H), 2.09–2.01 (m, 2H), 1.95 (s, 1H), 1.83–1.77 (m, 4H), 1.76–1.71 (m, 2H), 1.70–1.64 (m, 4H), 1.60–1.55 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) 143.3, 136.9, 129.7 (2C), 127.0

(2C), 74.8, 49.4, 37.9, 35.0 (2C), 34.1 (2C), 32.5 (2C), 27.2, 26.9, 21.5; **IR** (cm⁻¹) 3541, 3515, 3259, 2946, 2899, 2856, 1326, 1153, 811; **HRMS** (FAB) Calculated for C₁₈H₂₅NO₃S [M+H]⁺: 336.1638, Found: 336.1629.

N-{(1-Hydroxycyclohexyl)methyl}-4-methylbenzenesulfonamide (Table 3, 4j)



White solid; m.p. 147–149 °C; ¹**H NMR** (600 MHz, CDCl₃) 7.76–7.71 (m, 2H), 7.32–7.27 (m, 2H), 5.17–5.09 (m, 1H), 2.87 (d, *J* = 6.5 Hz, 2H), 2.41 (s, 3H), 2.00–1.93 (m, 1H), 1.56–1.50 (m, 5H), 1.46–1.36 (m, 4H), 1.31–1.22 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 143.3, 136.9, 129.7 (2C), 127.0 (2C), 71.0, 52.2,

35.4 (2C), 25.5, 21.8 (2C), 21.5; **IR** (cm⁻¹) 3468, 3236, 2930, 2913, 2852, 1314, 1152, 809; **HRMS** (FAB) Calculated for C₁₄H₂₁NO₃S [M+H]⁺: 284.1320, Found: 284.1319.

N-{(1-Hydroxycyclohexyl)methyl}-4-methoxybenzenesulfonamide (Table 3, 4k)



White solid; m.p. 104–106 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.81–7.76 (m, 2H), 6.98–6.95 (m, 2H), 5.07 (s, 1H), 3.86 (s, 3H), 2.86 (s, 2H), 1.90 (s, 1H), 1.57-1.48 (m, 5H), 1.46–1.36 (m, 4H), 1.32–1.22 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 162.8, 131.5, 129.1 (2C), 114.2 (2C), 71.0, 55.6, 52.2, 35.4 (2C), 25.5, 21.8 (2C); **IR** (cm⁻¹)

3469, 3234, 2936, 2913, 1318, 1150, 833; **HRMS** (FAB) Calculated for C₁₄H₂₁NO₄S [M+H]⁺: 300.1270, Found: 300.1267.

IV. Experimental Procedure of Mechanistic Studies

1. Kinetic isotope effect test of substrate 1c



To a J-Young NMR tube were added substrate **1c** (31 mg, 0.20 mmol) or **1c**- d_6 (32mg, 0.20 mmol), [IrCp*Cl₂]₂ (8.0 mg, 0.010 mmol, 5 mol %), AgNTf₂ (16 mg, 0.040 mmol, 20 mol %), CsOAc (3.4 mg, 0.020 mmol, 10 mol %) and 1,2-dichloroethane- d_4 (0.5 mL). *p*-Toluenesulfonyl azide (79 mg, 0.4 mmol) was added and reaction progress was monitored by NMR spectroscopy. Conversion was measured with 1,1,2,2-tetrachloroethane as an internal standard every 25 min for 2.5 hr at 60 °C. The rate was obtained by plotting to give a KIE value of 10.8.



Cyclohexanone O-propan-2-yl-1,1,1,3,3,3-d6 oxime (1c-d₆)



Light yellow oil; ¹H NMR (600 MHz, CDCl₃) δ 4.21 (s, 1H), 2.47–2.43 (m, 2H), 2.21–2.18 (m, 2H), 1.69–1.63 (m, 2H), 1.62–1.56 (m, 4H); ¹³C NMR (150 MHz, CDCl₃) δ 159.4, 73.9, 32.3, 27.1, 25.9, 25.7, 25.3, 21.7 (m, 2C); HRMS (EI) Calculated for C₉H₁₁D₆NO: 161.1687, Found: 161.1685.

Appendix

Spectral Copies of ¹H and ¹³C NMR of Compounds Obtained in This Study



^{230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10} ppm

Cyclohexanone *O*-ethyl oxime (Table 1, 1b)











230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)





Cyclohexanone *O*-hexan-2-yl oxime (Table 1, 1e)

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Cyclohexanone O-(4-methylpentan-2-yl) oxime (Table 1, 1f)



Cyclohexanone *O*-(1-phenylpropan-2-yl) oxime (Table 1, 1g)





Cyclohexanone *O*-(3-methylbutan-2-yl) oxime (Table 1, 1h)





Cyclohexanone O-(3-methylpentan-3-yl) oxime (Table 1, 1i)



Cyclohexanone *O*-(*tert*-pentyl) oxime (Table 1, 1j)



Cyclohexanone *O*-(2-methyl-4-phenylbutan-2-yl) oxime (Table 1, 1k)





ppm



Cyclohexanone *O*-(1-methylcyclopentyl) oxime (Table 1, 1m)



Cyclohexanone *O*-(1-methylcyclohexyl) oxime (Table 1, 1n)



Cyclohexanone O-(1-methylcycloheptyl) oxime (Table 1, 1o)





N-[2-{(Cyclohexylideneamino)oxy}butyl]-4-methylbenzenesulfonamide (Table 1, 2a)



N-[2-{(Cyclohexylideneamino)oxy}propyl]-4-methylbenzenesulfonamide (Table 1, 2c)



N-[2-{(Cyclohexylideneamino)oxy}-2-methylpropyl]-4-methylbenzenesulfonamide (Table 1, 2d)

N,*N*'-[2-{(Cyclohexylideneamino)oxy}-2-methylpropane-1,3-diyl]bis(4-methylbenzenesulfonamide) (Table 1, 2d')





N-[2-{(Cyclohexylideneamino)oxy}hexyl]-4-methylbenzenesulfonamide (Table 1, 2e)





N-[2-{(Cyclohexylideneamino)oxy}-4-methylpentyl]-4-methylbenzenesulfonamide (Table 1, 2f)



N-[2-{(Cyclohexylideneamino)oxy}-3-phenylpropyl]-4-methylbenzenesulfonamide (Table 1, 2g)



N-[2-{(Cyclohexylideneamino)oxy}-3-methylbutyl]-4-methylbenzenesulfonamide (Table 1, 2h)



N-[2-{(Cyclohexylideneamino)oxy}-2-ethylbutyl]-4-methylbenzenesulfonamide (Table 1, 2i)



N-[2-{(Cyclohexylideneamino)oxy}-2-methylbutyl]-4-methylbenzenesulfonamide (Table 1, 2j)

N-[2-{(Cyclohexylideneamino)oxy}-2-methyl-4-phenylbutyl]-4-methylbenzenesulfonamide (Table 1, 2k)



N-[[(1*r*,3*r*)-2-{(Cyclohexylideneamino)oxy}adamantan-2-yl]methyl]-4-methylbenzenesulfonamide (Table 1, 2l)











^{230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10} ppm



N-[[1-{(cyclohexylideneamino)oxy}cycloheptyl]methyl]-4-methylbenzenesulfonamide (Table, 20)





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N-[[1-{(Cyclohexylideneamino)oxy}cyclohexyl]methyl]-4-methoxybenzenesulfonamide (Table 2, 3b)





N-[[1-{(Cyclohexylideneamino)oxy}cyclohexyl]methyl]-4-fluorobenzenesulfonamide (Table 2, 3c)



N-[[1-{(Cyclohexylideneamino)oxy}cyclohexyl]methyl]naphthalene-1-sulfonamide (Table 2, 3d)





230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm





N-[[1-{(Cyclohexylideneamino)oxy}cyclohexyl]methyl]-1-{(1*R*,4*R*)-7,7-dimethyl-2-oxobicyclo [2.2.1]heptan-1-yl}methanesulfonamide (Table 2, 3g)















230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

N-(2-Hydroxyhexyl)-4-methylbenzenesulfonamide (Table 3, 4d)







230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm



230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm



N-(2-Hydroxy-2-methylbutyl)-4-methylbenzenesulfonamide (Table 3, 4g)





230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm



230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm





110 100 90 ppm 230 220 210 200 190 180 170 160 150 140 130 120 -10





230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm