Supporting Information

Palladium-Catalyzed Asymmetric Hydrogenation of 2-Aryl Cyclic Ketones for the Synthesis of *trans* Cycloalkanols through Dynamic Kinetic Resolution under Acidic Conditions

Xiang Li, Zi-Biao Zhao, Mu-Wang Chen, Bo Wu, Han Wang, Chang-Bin Yu,* Yong-Gui Zhou*

Zhang Dayu School of Chemistry, Dalian University of Technology, 2 Linggong Road, Dalian 116024, P. R. China and State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China.

Email: cbyu@dicp.ac.cn; ygzhou@dicp.ac.cn

Table of Contents

1. General and Materials..........................................................S1
2. General Procedure for Synthesis of 2-Aryl Cyclic Ketones.............S1-2
3. Pd-Catalyzed Hydrogenation of 2-Aryl Cyclic Ketones..................S3-7
4. Synthetic Transformations.....................................................S8-9
5. References.............................................................................S9-10
6. Copy of NMR and HPLC..........................................................S11-90
1. General and Materials

Commercially available reagents were used without further purification. Solvents were treated prior to use according to the standard methods. $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra were recorded at room temperature in CDCl$_3$ on 400 MHz instrument with TMS (tetramethylsilane) as internal standard. Enantiomeric excess was determined by HPLC analysis, using chiral column described below in detail. Optical rotations were measured by polarimeter. Flash column chromatography was performed on silica gel (200-300 mesh). All reactions were monitored by TLC analysis or NMR analysis.

Materials: Commercially available reagents were used throughout without further purification. The anhydrous solvents for asymmetric hydrogenation were also purchased without the further purification.

2. General Procedure for Synthesis of 2-Aryl Cyclic Ketones

2-Aryl cyclic ketones 1a-1q, 1s-1t can be conveniently synthesized according to the known literature procedures.$^{[1]}$ The compound 1r is commercially available. The compounds 1a-1e, 1g-1p, 1s-1t are the known compounds.$^{[2]}$ The compounds 1f, 1q are the new compounds.

The 2-aryl cyclic ketones 1 could be synthesized from 2-aryl cyclic alcohols 2 and Dess-Martin periodinane according to the known literature procedure. The intermediate 2-aryl cyclic alcohols 2 were synthesized from the commercially available 7-oxabicyclo[4.1.0]heptane and arylmagnesium bromide in the presence of cuprous iodide according to the known literature procedure.$^{[1]}$

Magnesium shavings (0.432 g, 18.0 mmol) were stirred in dry tetrahydrofuran (5 mL) and iodine (trace amount) was added. RBr solution (15.0 mmol, 25 mL THF) was added dropwise under nitrogen atmosphere. The reaction was stirred at 80 °C for 4 hours. The solution was cooled to 0 °C and then cuprous iodide (0.095 g, 0.5 mmol) was added. 7-Oxabicyclo[4.1.0]heptane (1.0 mL, 10.0 mmol) was dissolved in 20 mL of ether and added dropwise to the reaction mixture. The resultant solution was stirred for overnight, and then quenched with water (10 mL). The reaction mixture was transferred to a separatory funnel containing 100 mL of water. The organic phase was collected and the aqueous phase was extracted with ether (50 mL×3). The combined organic solution was dried over anhydrous sodium sulphate, and concentrated under the reduced pressure. Purification was performed by flash column chromatography on silica gel using hexanes/ethyl acetate (30/1-20/1) as eluent to provide the pure trans compounds (+/-)-2.
The above compounds (+/-)-2f (1.300 g, 5.3 mmol) and Dess-Martin periodinane (3.371 g, 8.0 mmol) were dissolved in dichloromethane (10 mL) and stirred. Dichloromethane (5 mL) was saturated with water (0.53 mmol) and added dropwise as the solution slowly became clear. The resultant solution was stirred for overnight. When TLC indicated that the reaction was finished, then quenched with saturated sodium thiosulfate solution (10 mL). The two phases were separated, and the aqueous phase was extracted with dichloromethane (10 mL×3). The combined organic phases were dried by anhydrous sodium sulfate and concentrated under reduced pressure. Purification was performed by column chromatography on silica gel using hexanes and ethyl acetate as eluent to provide the pure compounds 1f. Using the analogous experimental procedures, its congener 1q was prepared.

2-(4-Fluoronaphthalen-1-yl)cyclohexan-1-one (1f): The reaction was conducted by using 2-(4-fluoronaphthalen-1-yl)cyclohexan-1-ol (+/-)-2f (1.300 g, 5.3 mmol), affording the 1f 0.870 g, 68%, white solid, mp = 146-147 °C, known compound,[26] R_f = 0.37 (hexanes/ethyl acetate 10/1). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.20-8.09 (m, 1H), 7.75-7.63 (m, 1H), 7.57-7.47 (m, 2H), 7.29-7.25 (m, 1H), 7.17-7.08 (m, 1H), 4.33-4.24 (m, 1H), 2.69-2.57 (m, 2H), 2.45-2.33 (m, 1H), 2.30-2.17 (m, 2H), 2.16-2.08 (m, 1H), 2.01-1.80 (m, 2H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 210.1, 158.2 (d, \(J = 249\) Hz), 133.2 (d, \(J = 4.0\) Hz), 131.2 (d, \(J = 4.0\) Hz), 127.0, 125.8 (d, \(J = 2.0\) Hz), 125.1 (d, \(J = 8.0\) Hz), 124.1 (d, \(J = 16.0\) Hz), 123.5 (d, \(J = 3.0\) Hz), 121.5 (d, \(J = 6.0\) Hz), 109.0 (d, \(J = 20.0\) Hz), 53.2, 42.8, 34.5, 28.0, 26.1. \(^1^9\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -124.54. HRMS: Calculated for C\(_{16}\)H\(_{16}\)FO [M+H]^+ 243.1180, found: 243.1178.

2-(2,4-Dimethylphenyl)cyclohexan-1-one (1q): The reaction was conducted by using 2-(2,4-dimethylphenyl)cyclohexan-1-ol (+/-)-2q (1.432 g, 7.0 mmol), affording the 1q 1.166 g, 82%, yellow oil, new compound, R_f = 0.51 (hexanes/ethyl acetate 10/1). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.09-6.93 (m, 3H), 3.80-3.66 (m, 1H), 2.59-2.41 (m, 2H), 2.29 (s, 3H), 2.27-2.17 (m, 2H), 2.16 (s, 3H), 2.09-1.96 (m, 2H), 1.90-1.71 (m, 2H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 210.3, 136.4, 136.0, 134.4, 131.3, 127.6, 126.8, 53.6, 42.6, 34.3, 27.9, 26.0, 21.1, 19.8. HRMS: Calculated for C\(_{14}\)H\(_{19}\)O [M+H]^+ 203.1430, found: 203.1432.
3. Pd-Catalyzed Hydrogenation of 2-Aryl Cyclic Ketones

Pd(OCOCF₃)₂ (5.0 mg, 0.015 mmol) and (R)-SegPhos (11.0 mg, 0.018 mmol) were placed in a dried Schlenk tube under nitrogen atmosphere, and degassed anhydrous acetone was added. The mixture was stirred at room temperature for 1 hour. The solvent was removed under vacuum to give the catalyst. This catalyst was taken into a glove box filled with nitrogen and dissolved in 2,2,2-trifluoroethanol (TFE, 1.0 mL). To the mixture of 2-aryl cyclic ketones 1 (0.3 mmol) and p-toluenesulfonic acid monohydrate (28.5 mg, 0.15 mmol) in 2,2,2-trifluoroethanol (2.0 mL) was added this catalyst solution, and then the mixture was transferred to an autoclave, which was charged hydrogen gas (100 psi). The autoclave was stirred at 30 °C for 24 hours. After release of the hydrogen gas, the autoclave was opened and the reaction mixture was evaporated. Purification was performed by column chromatography on silica gel using hexanes/dichloromethane/ethyl acetate (2/2/0.1) as the eluent to give the chiral reductive products 2.

Racemates of 2 were prepared by the reduction of the corresponding 2-aryl cyclic ketones 1 catalyzed by palladium catalyst with racemic ligand.

(-)-(1R,2S)-2-(Naphthalen-1-yl)cyclohexan-1-ol (2a): 62 mg, 91% yield, white solid, known compound,[3a] R₉ = 0.44 (hexanes/dichloromethane/ethyl acetate 2/2/0.1), 97% ee, [α]°D = -75.32 (c 1.24, MeOH), [lit.[3a]: [α]°D = -60 (c 1.46, MeOH) for 85% ee]. 1H NMR (400 MHz, CDCl₃) δ 8.20 (d, J = 8.4 Hz, 1H), 7.92-7.84 (m, 1H), 7.79-7.72 (m, 1H), 7.56-7.45 (m, 1H), 4.11-3.86 (m, 1H), 3.53-3.26 (m, 1H), 2.29-2.16 (m, 1H), 2.04-1.89 (m, 1H), 1.86-1.77 (m, 1H), 1.64-1.46 (m, 1H). 13C NMR (100 MHz, CDCl₃) δ 139.7, 134.2, 132.7, 129.0, 127.1, 126.1, 125.8, 125.7, 123.3, 122.8, 74.3, 46.7, 34.8, 34.0, 26.5, 25.2. HPLC: Chiracel IC column, 230 nm, 30 °C, n-Hexane/i-PrOH = 96/4, flow = 0.7 mL/min, retention time 19.1 min (major) and 20.4 min.

cis-2-(Naphthalen-1-yl)cyclohexan-1-ol (2a'): the known compound,[3b] R₉ = 0.50 (hexanes/dichloromethane/ethyl acetate 2/2/0.1), 94% yield, white solid, known compound,[3a] [α]°D = -21.09 (c 1.28, CHCl₃), [lit.[3a]: [α]°D = -20.2 (c 1.035, CHCl₃) for 70% ee]. 1H NMR (400 MHz, CDCl₃) δ 7.91-7.85 (m, 1H), 7.76 (d, J = 7.8 Hz, 1H), 7.58-7.41 (m, 1H), 3.68-3.59 (m, 1H), 2.39-2.26 (m, 1H), 1.89-1.73 (m, 2H), 1.71-1.48 (m, 4H). 13C NMR (100 MHz, CDCl₃) δ 139.5, 134.3, 131.5, 129.3, 127.4, 126.1, 125.7, 125.6, 124.4, 123.1, 69.1, 43.3, 32.9, 26.9, 25.0, 20.0.

(−)-2-(Naphthalen-2-yl)cyclohexan-1-ol (2b): 64 mg, 94% yield, white solid, the known compound,[3a] R₉ = 0.32 (hexanes/dichloromethane/ethyl acetate 2/2/0.1), 92% ee, [α]°D = -21.09 (c 1.28, CHCl₃), [lit.[3a]: [α]°D = -20.2 (c 1.035, CHCl₃) for 70% ee]. 1H NMR (400 MHz, CDCl₃) δ 7.87-7.73 (m, 3H), 7.72-7.66 (m, 1H), 7.50-7.40 (m, 2H), 7.38 (dd, J = 8.5, 1.6 Hz, 1H), 3.81-3.67 (m, 1H), 2.65-2.51 (m, 1H), 2.20-2.07 (m, 1H), 1.96-1.71 (m, 3H), 1.68-1.53 (m, 2H), 1.51-1.29 (m, 3H). 13C NMR (100 MHz, CDCl₃) δ 140.8, 133.7, 132.7, 128.6, 127.74, 127.71, 126.8, 126.2, 126.0, 125.6, 74.3, 53.4, 34.6, 33.4, 26.2, 25.2. HPLC: Chiracel IC column, 230 nm, 30 °C, n-Hexane/i-PrOH = 98/2, flow = 0.8 mL/min, retention time 33.3 min (major) and 36.5 min.
(-)-2-(Phenanthren-9-yl)cyclohexan-1-ol (2c): 69 mg, 83% yield, white solid, the known compound,[4a] Rf = 0.42 (hexanes/dichloromethane/ethyl acetate 2/2/0.1), 91% ee, [α]D = -109.85 (c 1.36, CHCl3). 1H NMR (400 MHz, CDCl3) δ 8.75-8.70 (m, 1H), 8.64 (d, J = 8.0 Hz, 1H), 8.29-8.20 (m, 1H), 7.87-7.80 (m, 1H), 7.74-7.69 (m, 1H), 7.68-7.53 (m, 4H), 4.17-4.01 (m, 1H), 3.48-3.29 (m, 1H), 2.28-2.17 (m, 1H), 2.11-1.99 (m, 1H), 1.97-1.74 (m, 3H), 1.63-1.43 (m, 4H). 13C NMR (100 MHz, CDCl3) δ 137.8, 131.8, 131.7, 131.0, 129.7, 128.4, 126.82, 126.78, 126.49, 126.46, 123.9, 123.4, 122.6, 73.8, 46.8, 34.8, 34.0, 34.0, 26.5, 25.2. HPLC: Chiracel IC column, 254 nm, 30 °C, n-Hexane/i-PrOH = 95/5, flow = 1.0 mL/min, retention time 19.2 min (major) and 21.2 min.

(-)-2-(4-Methoxynaphthalen-1-yl)cyclohexan-1-ol (2d): 64 mg, 83% yield, white solid, mp = 108-109 °C, new compound, Rf = 0.38 (hexanes/dichloromethane/ethyl acetate 2/2/0.1), 97% ee, [α]D = -77.73 (c 1.28, CHCl3). 1H NMR (400 MHz, CDCl3) δ 8.32 (dd, J = 8.3, 1.1 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.57-7.45 (m, 2H), 7.37 (d, J = 8.0 Hz, 1H), 6.81 (d, J = 8.0 Hz, 1H), 3.98 (s, 3H), 3.97-3.86 (m, 1H), 3.35-3.21 (m, 1H), 2.26-2.16 (m, 1H), 1.99-1.86 (m, 2H), 1.84-1.75 (m, 1H), 1.73-1.67 (m, 1H), 1.57-1.40 (m, 4H). 13C NMR (100 MHz, CDCl3) δ 154.3, 133.5, 131.2, 126.6, 126.1, 125.1, 123.1, 122.7, 103.7, 74.3, 55.5, 46.2, 34.8, 34.1, 26.5, 25.2. HPLC: Chiracel IC column, 230 nm, 30 °C, n-Hexane/i-PrOH = 95/5, flow = 1.0 mL/min, retention time 20.8 min (major) and 31.4 min. HRMS: Calculated for C17H24NO [M+NH4]+ 274.1802, found: 274.1803.

(-)-2-(4-Methylnaphthalen-1-yl)cyclohexan-1-ol (2e): 64 mg, 89% yield, colorless oil, new compound, Rf = 0.37 (hexanes/dichloromethane/ethyl acetate 2/2/0.1), 98% ee, [α]D = -80.23 (c 1.26, CHCl3). 1H NMR (400 MHz, CDCl3) δ 8.24-8.18 (m, 1H), 8.05-8.00 (m, 1H), 7.56-7.49 (m, 2H), 7.36 (d, J = 7.3 Hz, 1H), 7.31 (d, J = 7.4 Hz, 1H), 4.03-3.82 (m, 1H), 3.40-3.22 (m, 1H), 2.67 (s, 3H), 2.25-2.14 (m, 1H), 2.01-1.86 (m, 2H), 1.82-1.75 (m, 1H), 1.71-1.64 (m, 1H), 1.59-1.41 (m, 4H). 13C NMR (100 MHz, CDCl3) δ 137.7, 133.2, 132.9, 132.7, 126.6, 125.7, 125.5, 125.0, 123.8, 122.4, 74.2, 46.5, 34.8, 34.1, 26.5, 25.2, 19.6. HPLC: Chiracel IC column, 230 nm, 30 °C, n-Hexane/i-PrOH = 95/5, flow = 0.8 mL/min, retention time 13.0 min (major) and 16.9 min. HRMS: Calculated for C17H24NO [M+NH4]+ 258.1852, found: 258.1851.

(-)-2-(4-Fluoronaphthalen-1-yl)cyclohexan-1-ol (2f): 64 mg, 88% yield, colorless oil, new compound, Rf = 0.39 (hexanes/dichloromethane/ethyl acetate 2/2/0.1), 97% ee, [α]D = -57.58 (c 1.24, CHCl3). 1H NMR (400 MHz, CDCl3) δ 8.24-8.11 (m, 2H), 7.62-7.51 (m, 2H), 7.42-7.34 (m, 1H), 7.19-7.09 (m, 1H), 4.00-3.82 (m, 1H), 3.40-3.22 (m, 1H), 2.26-2.13 (m, 1H), 2.00-1.72 (m, 3H), 1.64-1.60 (m, 1H), 1.59-1.39 (m, 4H). 13C NMR (100 MHz, CDCl3) δ 157.7 (d, J = 249.0 Hz), 135.5, 134.0, 127.0, 126.1, 124.3 (d, J = 16.0 Hz), 123.4, 122.6, 121.3 (d, J = 6.0 Hz), 109.2 (d, J = 19.0 Hz), 74.4, 46.4, 35.0, 34.1, 26.4, 25.2. 19F NMR (376 MHz, CDCl3) δ -125.05. HPLC: Chiracel IC column, 230 nm, 30 °C, n-Hexane/i-PrOH = 95/5, flow = 0.8 mL/min, retention time 13.0 min (major) and 16.9 min. HRMS: Calculated for C16H21FNO [M+NH4]+ 262.1602, found: 262.1601.

(-)-2-Phenylcyclohexan-1-ol (2g): 48 mg, 91% yield, white solid, the known compound,[4b] Rf = 0.39 (hexanes/dichloromethane/ethyl acetate 2/2/0.1), 97% ee, [α]D = -26.74 (c 0.92, CHCl3), [lit.[4b]: [α]D = -20.9 (c 1.0, CHCl3) for 86% ee]. 1H NMR (400 MHz, CDCl3) δ 7.38-7.28 (m, 3H), 6.91-6.78 (m, 1H), 7.04 (d, J = 7.9 Hz, 1H).
2H), 7.27-7.19 (m, 3H), 3.69-3.58 (m, 1H), 2.48-2.35 (m, 1H), 2.15-2.03 (m, 1H), 1.91-1.80 (m, 2H), 1.79-1.71 (m, 1H), 1.67-1.57 (m, 1H), 1.56-1.43 (m, 1H), 1.42-1.24 (m, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.4, 128.8, 128.0, 126.9, 74.5, 53.3, 34.5, 33.4, 26.2, 25.2. HPLC: Chiracel IC column, 220 nm, 30 $^\circ$C, $n$-Hexane/i-PrOH = 99/1, flow = 1.0 mL/min, retention time 11.6 min (major) and 12.6 min.

(-)-2-(2-Methoxyphenyl)cyclohexan-1-ol (2h): 48 mg, 77% yield, colorless oil, known compound,[3a] $R_f = 0.28$ (hexanes/dichloromethane/ethyl acetate 2/2/0.1), 93% ee, $[\alpha]^20_D = -64.75$ (c 0.82, MeOH), [lit.[3a]: $[\alpha]^20_D = -5$ (c 1.52, MeOH) for 15% ee]. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.27-7.17 (m, 2H), 7.00-6.92 (m, 1H), 6.89 (d, $J = 8.2$ Hz, 1H), 3.82 (s, 3H), 3.78-3.69 (m, 1H), 3.06-2.95 (m, 1H), 2.18-2.08 (m, 1H), 1.88-1.70 (m, 4H), 1.55-1.32 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.8, 131.6, 127.5, 127.4, 121.1, 110.9, 74.1, 55.6, 45.1, 34.8, 26.3, 25.2. HPLC: Chiracel IC column, 220 nm, 30 $^\circ$C, $n$-Hexane/i-PrOH = 97/3, flow = 0.7 mL/min, retention time 17.1 min (major) and 18.1 min.

(-)-2-(2-(Trifluoromethyl)phenyl)cyclohexan-1-ol (2i): 29 mg, 40% yield, colorless oil, new compound, $R_f = 0.35$ (hexanes/dichloromethane/ethyl acetate 2/2/0.1), 86% ee, $[\alpha]^20_D = -54.78$ (c 0.46, MeOH). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.65 (d, $J = 7.9$ Hz, 1H), 7.58-7.48 (m, 2H), 7.35-7.28 (m, 1H), 3.90-3.79 (m, 1H), 2.99-2.85 (m, 1H), 2.21-2.11 (m, 1H), 1.95-1.84 (m, 2H), 1.79-1.70 (m, 1H), 1.51-1.29 (m, 5H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.1, 132.3, 129.7 (q, $J = 29.0$ Hz), 127.7, 126.5, 126.2 (q, $J = 6.0$ Hz), 124.7 (q, $J = 272.0$ Hz), 74.3, 48.3, 35.5, 34.8, 26.0, 25.2. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -57.98. HPLC: Chiracel IA column, 220 nm, 30 $^\circ$C, $n$-Hexane/i-PrOH = 96/4, flow = 0.7 mL/min, retention time 13.4 min and 16.3 min (major). HRMS: Calculated for C$_{13}$H$_{19}$F$_3$NO [$M+NH_4]^+$ 262.1413, found: 262.1414.

(-)-2-($o$-Tolyl)cyclohexan-1-ol (2j): 49 mg, 86% yield, colorless oil, known compound, [3a] $R_f = 0.36$ (hexanes/dichloromethane/ethyl acetate 2/2/0.1), 94% ee, $[\alpha]^20_D = -64.49$ (c 0.98, CHCl$_3$), [lit.[3a]: $[\alpha]^20_D = -42$ (c 1.28, CHCl$_3$) for 65% ee]. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.27-7.23 (m, 1H), 7.22-7.14 (m, 2H), 7.13-7.08 (m, 1H), 3.83-3.71 (m, 1H), 2.83-2.68 (m, 1H), 2.36 (s, 3H), 2.18-2.07 (m, 1H), 1.94-1.70 (m, 3H), 1.69-1.59 (m, 1H), 1.51-1.27 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 141.5, 137.2, 126.6, 126.4, 125.6, 74.4, 47.9, 34.6, 33.2, 26.4, 25.2. HPLC: Chiracel IC column, 220 nm, 30 $^\circ$C, $n$-Hexane/i-PrOH = 97/3, flow = 0.7 mL/min, retention time 9.8 min (major) and 10.9 min.

(-)-2-($m$-Tolyl)cyclohexan-1-ol (2k): 45 mg, 79% yield, colorless oil, known compound,[3a] $R_f = 0.42$ (hexanes/dichloromethane/ethyl acetate 2/2/0.1), 89% ee, $[\alpha]^20_D = -35.28$ (c 0.36, CHCl$_3$), [lit.[3a]: $[\alpha]^20_D = -9$ (c 0.90, CHCl$_3$) for 36% ee]. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.26-7.25 (m, 1H), 7.21-7.14 (m, 2H), 7.13-7.08 (m, 1H), 3.83-3.71 (m, 1H), 2.83-2.68 (m, 1H), 2.36 (s, 3H), 2.18-2.07 (m, 1H), 1.94-1.70 (m, 3H), 1.69-1.59 (m, 1H), 1.51-1.27 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.3, 138.4, 128.8, 128.7, 127.7, 125.0, 74.5, 53.3, 34.5, 33.4, 26.2, 25.2, 21.6. HPLC: Chiracel IC column, 220 nm, 30 $^\circ$C, $n$-Hexane/i-PrOH = 96/4, flow = 0.7 mL/min, retention time 15.2 min (major) and 17.4 min.

(-)-2-($p$-Tolyl)cyclohexan-1-ol (2l): 49 mg, 86% yield, white solid, known compound,[5a] $R_f = 0.41$ (hexanes/dichloromethane/ethyl acetate 2/2.0/1), 92% ee, $[\alpha]^20_D = -48.47$ (c 0.98, MeOH), [lit.[5a]: $[\alpha]^23_D = -58.05$ (c 1.0, MeOH) for > 99% ee]. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.17-7.10 (m,
(-)-2-(4-Methoxyphenyl)cyclohexan-1-ol (2m): 51 mg, 82% yield, white solid, the known compound,[3a] Rf = 0.27 (hexanes/dichloromethane/ethyl acetate 2/2/0.1), 88% ee, [α]20 = -24 (c 1.46, MeOH) for 44% ee. [lit.[3a]: [α]20 = -24 (c 1.46, MeOH) for 44% ee].

1H NMR (400 MHz, CDCl3) δ 7.21-7.12 (m, 2H), 6.91-6.83 (m, 2H), 3.79 (s, 3H), 3.65-3.52 (m, 1H), 2.44-2.31 (m, 1H), 2.16-2.03 (m, 1H), 1.91-1.72 (m, 1H), 1.58-1.23 (m, 4H). 13C NMR (100 MHz, CDCl3) δ 158.6, 135.3, 128.9, 114.3, 74.7, 53.1, 35.0, 33.4, 26.0, 25.1.

19F NMR (376 MHz, CDCl3) δ -116.35. HPLC: Chiracel AD-H column, 220 nm, 30 °C, n-Hexane/i-PrOH = 95/5, flow = 1.0 mL/min, retention time 8.7 min and 12.6 min (major).

(-)-2-(4-(Trifluoromethyl)phenyl)cyclohexan-1-ol (2n): 61 mg, 84% yield, white solid, the known compound,[5b] Rf = 0.45 (hexanes/dichloromethane/ethyl acetate 2/2/0.1), 82% ee, [α]20 = -40.60 (c 1.16, MeOH), [lit.[5b]: [α]20 = -42.9 (c 1.0, MeOH) for > 99% ee].

1H NMR (400 MHz, CDCl3) δ 7.58 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 3.76-3.58 (m, 1H), 2.61-2.41 (m, 1H), 2.16-2.03 (m, 1H), 1.97-1.72 (m, 1H), 1.58-1.23 (m, 5H). 13C NMR (100 MHz, CDCl3) δ 148.0, 129.1 (q, J = 32.0 Hz), 128.3, 125.7 (q, J = 4.0 Hz), 124.4 (q, J = 270.0 Hz), 74.3, 53.1, 35.0, 33.4, 26.0, 25.1.

19F NMR (376 MHz, CDCl3) δ -62.39. HPLC: Chiracel AD-H column, 220 nm, 30 °C, n-Hexane/i-PrOH = 95/5, flow = 1.0 mL/min, retention time 9.5 min and 11.1 min (major).

(-)-2-(4-Fluorophenyl)cyclohexan-1-ol (2o): 42 mg, 72% yield, white solid, known compound,[3a] Rf = 0.39 (hexanes/dichloromethane/ethyl acetate 2/2/0.1), 81% ee, [α]20 = -49.16 (c 0.60, MeOH). [lit.[3a]: [α]20 = -12.3 (c 1.52, MeOH) for 53% ee].

1H NMR (400 MHz, CDCl3) δ 7.25-7.16 (m, 2H), 7.07-6.96 (m, 2H), 3.67-3.53 (m, 1H), 2.48-2.35 (m, 1H), 2.14-2.04 (m, 1H), 1.91-1.71 (m, 3H), 1.65-1.53 (m, 1H), 1.52-1.25 (m, 4H). 13C NMR (100 MHz, CDCl3) δ 161.8 (d, J = 243.0 Hz), 139.1 (d, J = 3.0 Hz), 129.3 (d, J = 7.0 Hz), 115.6 (d, J = 21.0 Hz), 74.6, 52.5, 34.7, 33.6, 26.1, 25.1.

19F NMR (376 MHz, CDCl3) δ -116.35. HPLC: Chiracel AD-H column, 220 nm, 30 °C, n-Hexane/i-PrOH = 95/5, flow = 1.0 mL/min, retention time 9.5 min and 11.1 min (major).

(-)-2-(4-Chlorophenyl)cyclohexan-1-ol (2p): 58 mg, 92% yield, white solid, known compound,[5c] Rf = 0.45 (hexanes/dichloromethane/ethyl acetate 2/2/0.1), 83% ee, [α]20 = -46.25 (c 1.12, MeOH). 1H NMR (400 MHz, CDCl3) δ 7.32-7.26 (m, 2H), 7.21-7.15 (m, 2H), 3.66-3.54 (m, 1H), 2.47-2.33 (m, 1H), 2.14-2.04 (m, 1H), 1.91-1.71 (m, 3H), 1.65-1.53 (m, 1H), 1.52-1.24 (m, 4H).

13C NMR (100 MHz, CDCl3) δ 142.1, 132.5, 129.3, 128.9, 74.4, 52.6, 34.8, 33.5, 26.0, 25.1. HPLC: Chiracel AD-H column, 220 nm, 30 °C, n-Hexane/i-PrOH = 95/5, flow = 1.0 mL/min, retention time 10.6 min and 13.3 min (major).

(-)-2-(2,4-Dimethylphenyl)cyclohexan-1-ol (2q): 56 mg, 92% yield, colorless oil, new compound, Rf = 0.52 (hexanes/dichloromethane/ethyl acetate 2/2/0.1), 95% ee, [α]20 = -61.98 (c 1.06, CHCl3). 1H NMR (400 MHz, CDCl3) δ 7.14 (d, J = 7.8 Hz, 1H), 7.05-6.97 (m, 2H), 3.81-3.68 (m,
(-)-2-Benzylcyclohexan-1-ol (2r): 16 mg, 28% yield, white solid, known compound, [5d] Rf = 0.30 (hexanes/dichloromethane/ethyl acetate 2/2/0.1), 9% ee, \([\alpha]^{20}_D = -5.62 (c 0.32, CHCl_3)\].

1H NMR (400 MHz, CDCl3) \(\delta\) 7.30-7.25 (m, 2H), 7.21-7.16 (m, 3H), 3.35-3.25 (m, 1H), 3.17 (dd, \(J = 13.3, 4.0\) Hz, 1H), 2.36 (dd, \(J = 13.3, 9.2\) Hz, 1H), 2.03-1.95 (m, 1H), 1.74-1.46 (m, 5H), 1.34-1.18 (m, 2H), 1.15-1.02 (m, 1H), 0.97-0.85 (m, 1H).

13C NMR (100 MHz, CDCl3) \(\delta\) 140.9, 129.6, 128.3, 125.9, 74.7, 49.3, 39.2, 36.0, 30.1, 25.6, 25.1. HPLC: Chiracel IC column, 220 nm, 30 °C, n-Hexane/i-PrOH = 98/2, flow = 0.7 mL/min, retention time 17.8 min (major) and 21.9 min.

(-)-2-(Naphthalen-1-yl)cyclopentan-1-ol (2s): 40 mg, 63% yield, colorless oil, the known compound, [5e] Rf = 0.40 (hexanes/dichloromethane/ethyl acetate 2/2/0.1), 77% ee, \([\alpha]^{20}_D = 26.48 (c 0.74, CHCl_3)\). 1H NMR (400 MHz, CDCl3) \(\delta\) 8.20 (d, \(J = 8.2\) Hz, 1H), 7.84 (d, \(J = 7.8\) Hz, 1H), 7.71 (d, \(J = 8.0\) Hz, 1H), 7.55-7.33 (m, 4H), 4.49-4.34 (m, 1H), 3.80-3.68 (m, 1H), 2.40-2.27 (m, 1H), 2.19-2.07 (m, 1H), 2.03-1.69 (m, 5H). 13C NMR (100 MHz, CDCl3) \(\delta\) 139.6, 134.1, 132.6, 128.9, 126.9, 126.0, 125.7, 125.6, 123.9, 122.6, 79.5, 49.3, 34.2, 31.9, 22.1. HPLC: Chiracel IC column, 230 nm, 30 °C, n-Hexane/i-PrOH = 95/5, flow = 1.0 mL/min, retention time 10.1 min (major) and 11.2 min.

(+)-2-Phenylcycloheptan-1-ol (trans-2t): 22 mg, 39% yield, colorless oil, known compound, [4c] Rf = 0.30 (hexanes/dichloromethane/ethyl acetate 2/2/0.1), 72% ee, \([\alpha]^{20}_D = -3.95 (c 0.38, CHCl_3)\). [lit.[4c]: \([\alpha]^{20}_D = -0.852 (c 7.06, CHCl_3)\) for 84% ee]. 1H NMR (400 MHz, CDCl3) \(\delta\) 7.36-7.28 (m, 2H), 7.26-7.18 (m, 3H), 3.83-3.68 (m, 1H), 2.62-2.50 (m, 1H), 2.08-1.97 (m, 1H), 1.89-1.51 (m, 10H). 13C NMR (100 MHz, CDCl3) \(\delta\) 146.0, 128.9, 127.8, 126.8, 77.7, 55.5, 35.5, 32.2, 27.5, 26.9, 22.0. HPLC: Chiracel IC column, 220 nm, 30 °C, n-Hexane/i-PrOH = 99/1, flow = 0.5 mL/min, retention time 21.9 min (major) and 23.7 min.

(-)-2-Phenylcycloheptan-1-ol (cis-2t'): 8 mg, 14% yield, colorless oil, the known compound, [5f] Rf = 0.30 (hexanes/dichloromethane/ethyl acetate 2/2/0.1), 73% ee, \([\alpha]^{20}_D = -21.25 (c 0.16, CHCl_3)\). [lit.[5f]: \([\alpha]^{20}_D = -98.8 (c 1.14, CHCl_3)\) for > 99:1 er]. 1H NMR (400 MHz, CDCl3) \(\delta\) 7.36-7.28 (m, 2H), 7.26-7.18 (m, 3H), 3.83-3.71 (m, 1H), 2.62-2.50 (m, 1H), 2.08-1.97 (m, 1H), 1.89-1.51 (m, 10H). 13C NMR (100 MHz, CDCl3) \(\delta\) 145.6, 128.7, 128.2, 126.5, 73.8, 51.8, 35.3, 29.0, 28.2, 26.9, 21.7. HPLC: Chiracel IC column, 220 nm, 30 °C, n-Hexane/i-PrOH = 99/1, flow = 0.5 mL/min, retention time 14.5 min and 15.6 min (major).
4. Synthetic Transformations

To a stirred mixture of trans-(-)-2-(naphthalen-1-yl)cyclohexan-1-ol 2a (45.2 mg, 0.2 mmol), NCS (53.4 mg, 0.4 mmol) and triphenylphosphine (78.7 mg, 0.3 mmol) were added dry THF (2 mL). The mixture was stirred at room temperature for one hour. The THF was removed by rotary evaporation and the resulting residue was purified by silica gel column chromatography (hexanes/ethyl acetate 50/1) to provide pure (+)-1-(2-chlorocyclohexyl)naphthalene 4. [6a]

(S,S)-(+)1-(2-Chlorocyclohexyl)naphthalene (4): 41 mg, 84% yield, white solid, the known compound,[6b] Rf = 0.80 (hexanes/ethyl acetate 20/1), 95% ee, [α]D20 = +167.67 (c 0.56, CHCl3).

1H NMR (400 MHz, CDCl3) δ 7.94 (d, J = 8.4 Hz, 1H), 7.90-7.84 (m, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.54-7.43 (m, 3H), 4.74-4.67 (m, 1H), 3.82-3.74 (m, 1H), 2.48-2.35 (m, 1H), 2.25-2.08 (m, 2H), 1.88-1.71 (m, 1H). 13C NMR (100 MHz, CDCl3) δ 138.6, 134.0, 131.2, 129.5, 127.4, 126.1, 125.4, 125.3, 122.3, 64.8, 43.3, 35.2, 26.7, 25.4, 20.0. HPLC: Chiracel AD-H column, 230 nm, 30 °C, n-Hexane/i-PrOH = 99.5/0.5, flow = 0.5 mL/min, retention time 10.5 min (major) and 11.9 min.

To a stirred mixture of trans-(-)-2-(naphthalen-1-yl)cyclohexan-1-ol 2a (113.1 mg, 0.5 mmol, 97% ee) and triethylamine (0.28 mL, 2.0 mmol) in dry dichloromethane (4 mL) were cooled at -20 °C, and methanesulfonyl chloride (MeSO2Cl, 117.0 µL, 1.5 mmol) was added dropwise while the temperature was maintained -20 °C for 3 hours. After the reaction was moved to room temperature for 18 hours. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography (hexanes/dichloromethane/ethyl acetate 2/2/0.1) to provide the pure compound A (149.0 mg, 98%) for the next step.

A mixture of compound A (149.0 mg, 0.49 mmol) and sodium azide (96.0 mg, 1.47 mmol) in reagent grade DMF (4 mL) was heated at 90 °C for 69 hours. The mixture was diluted with water (5 mL), and then extracted with dichloromethane (5 mL×3). The organic layer was separated and washed repeatedly with water (10 mL×3) to remove the DMF, dried by anhydrous sodium sulfate and filtered. The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography (hexanes/dichloromethane/ethyl acetate 2/2/0.1) to provide the pure compound 5 (102.0 mg, 83%).[7]

(S,S)-(+)1-(2-Azidocyclohexyl)naphthalene (5): 102 mg, 81% yield (two steps), colorless oil, new compound, Rf = 0.80 (hexanes/ethyl acetate 10/1), 97% ee, [α]D20 = +175.59 (c 1.98, CHCl3).

1H NMR (400 MHz, CDCl3) δ 7.97 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 7.9 Hz, 1H), 7.79-7.74 (m, 1H), 7.55-7.42 (m, 4H), 4.14-4.10 (m, 1H), 3.65-3.56 (m, 1H), 2.32-2.18 (m, 1H), 2.15-2.06 (m,
S9

1H), 2.02-1.94 (m, 1H), 1.92-1.82 (m, 1H), 1.76-1.63 (m, 3H), 1.58-1.44 (m, 1H). 13C NMR (100 MHz, CDCl3) δ 138.6, 134.0, 131.2, 129.5, 127.4, 126.1, 125.6, 125.4, 125.0, 122.5, 62.9, 42.0, 31.1, 26.6, 25.9, 20.6. HPLC: Chiracel OD-H column, 230 nm, 30 °C, n-Hexane /i-PrOH = 99/1, flow = 0.7 mL/min, retention time 12.0 min and 14.9 min (major). HRMS: Calculated for C16H21N4 [M+NH4]+ 269.1761, found: 269.1744.

5. References


6. Copy of NMR and HPLC

$^1$H NMR XL-4-78 in CDCl$_3$
$^{13}$C NMR XL-4-78 in CDCl$_3$
19F NMR XL-4-78 in CDCl3

19F NMR (376 MHz, CDCl3)
$^1$H NMR XL-5-24 in CDCl$_3$
$^{13}$C NMR XL-5-24 in CDCl$_3$

$^{13}$C NMR (100 MHz, CDCl$_3$)
1\textsuperscript{H} NMR XL-4-81-trans in CDCl\textsubscript{3}

2a \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})
$^{13}$C NMR XL-4-81-trans in CDCl₃

2a $^{13}$C NMR (100 MHz, CDCl₃)
$^1$H NMR XL-4-45A·ds in CDCl$_3$

2a' $^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR XL-4-45A-cis in CDCl$_3$

$^{2a'}{}^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR XL-4-84-trans in CDCl$_3$

2b $^1$H NMR (400 MHz, CDCl$_3$)

S20
$^{13}$C NMR XL-4-84-trans in CDCl$_3$

2b $^{13}$C NMR (100 MHz, CDCl$_3$)

S21
$^{1}H$ NMR XL-4-93-trans in CDCl$_3$
$^{13}$C NMR XL-4-93-trans in CDCl$_3$
$^{1}H$ NMR XL-4-90-trans in CDCl$_3$

$^{2}$H NMR (400 MHz, CDCl$_3$)
13C NMR XL-4-90-trans in CDCl3

2d $^{13}$C NMR (100 MHz, CDCl3)
$^1$H NMR XL-4-85-trans in CDCl$_3$
$^{13}$C NMR XL-4-85-trans in CDCl$_3$

$^{2}$H$_{$\text{NMR}}^{13}$C (100 MHz, CDCl$_3$)
$^1$H NMR XL-4-89-trans in CDCl$_3$
13C NMR XL-4-89-trans in CDCl3

2f\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3})
$^{19}$F NMR XL-4-89-trans in CDCl₃

$^{29}$F $^{19}$F NMR (376 MHz, CDCl₃)
$^1$H NMR XL-4-75-trans in CDCl$_3$
$^{13}$C NMR XL-4-75-trans in CDCl$_3$

![NMR spectrum](image)
$^{1}H$ NMR XL-5-5-trans in CDCl$_3$

2h $^{1}H$ NMR (400 MHz, CDCl$_3$)

S33
13C NMR XL-5-5-trans in CDCl3

$2h^{13}C$ NMR (100 MHz, CDCl3)
$1^H$ NMR XL-5-8-trans in CDCl$_3$
13C NMR XL-5-8-trans in CDCl₃

21³C NMR (100 MHz, CDCl₃)
$^{19}$F NMR XL-5-8-trans in CDCl$_3$

2i $^{19}$F NMR (376 MHz, CDCl$_3$)

OH

$\text{CF}_3$

f1 (ppm)

20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
$^1$H NMR XL-4-88-trans in CDCl$_3$
$^{13}$C NMR XL-4-88-trans in CDCl$_3$

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR XL-5-6-trans in CDCl$_3$

$^2$H$^1$HNMR (400 MHz, CDCl$_3$)
$^{13}$C NMR XL-5,6-trans in CDCl$_3$

$^{2}$H NMR (100 MHz, CDCl$_3$)
1H NMR XL-4-94-trans in CDCl3
$^{13}$C NMR XL-4-94-trans in CDCl$_3$

$^{21}{^{13}}$C NMR (100 MHz, CDCl$_3$)

S43
$^1$H NMR XL-5-19-trans in CDCl$_3$
$^{13}$C NMR XL-5-19-trans in CDCl$_3$

$2m^{13}$C NMR (100 MHz, CDCl$_3$)
1H NMR XL-5-27-trans in CDCl3

$\text{OH}$

$\text{CF}_3$

$2n \text{ } ^1\text{H NMR (400 MHz, CDCl}_3)$

\begin{align*}
\text{H} & \quad \text{Chemical Shift (ppm)} \\
1.97 & \quad 1.88 \\
2.00 & \quad 1.99 \\
2.89 & \quad 3.05 \\
5.37 & \quad \\
\end{align*}
$^{13}$C NMR XL-5-27-trans in CDCl$_3$

$^{2n}$ $^{13}$C NMR (100 MHz, CDCl$_3$)
$^{19}$F NMR XL-5-27-trans in CDCl$_3$
$^1$H NMR XL-5-18-trans in CDCl$_3$

![NMR spectrum](image-url)
13C NMR XL-5-18-trans in CDCl3

2o $^{13}$C NMR (100 MHz, CDCl₃)
19F NMR XL-5-18-trans in CDCl3

2o $^{19}$F NMR (376 MHz, CDCl3)
\[1H \text{NMR Xl-5-26-trans in CDCl}_3\]

\[2\text{p }^1H\text{NMR (400 MHz, CDCl}_3)\]
$^1$H NMR (500 MHz, CDCl$_3$)

$^1$C NMR (125 MHz, CDCl$_3$)
$^1$H NMR XL-5-28-trans in CDCl$_3$
$^{13}$C NMR XL-5-28-trans in CDCl$_3$

$^{2}$q $^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR XL-6-4-trans in CDCl$_3$
13C NMR XL-6-4-trans in CDCl3

2r$^{13}$C NMR (100MHz, CDCl3)
$^{1}$H NMR XL-5-81-trans in CDCl$_3$
13C NMR XL-5-81-trans in CDCl3

$2s^{13}C$ NMR (100 MHz, CDCl3)
$^1$H NMR XL-5-99-trans in CDCl$_3$

**trans-2t $^1$H NMR (400 MHz, CDCl$_3$)**
$^{13}$C NMR XL-5-99-trans in CDCl$_3$

trans-2t$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR XL-5-99-cis in CDCl$_3$

**cis-2t** $^1$H NMR (400 MHz, CDCl$_3$)
13C NMR XL-5-99-cis in CDCl₃

cis-2t \textsuperscript{13}C NMR (100 MHz, CDCl₃)
$^1$H NMR XL-5-87 in CDCl$_3$

4 $^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR XL-5-87 in CDCl$_3$

$^4$ $^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR XL-6-10 in CDCl$_3$

5 $^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR XL-6-10 in CDCl$_3$

$^5$ $^{13}$C NMR (100 MHz, CDCl$_3$)
Data File (C:\CHEM2\1\DATA\190310\0103100197.D)
Sample Name: OL-4-0l-tesos-(-)-1

Additional Info: Peaks(s) manually integrated

Area Percent Report

Sorted By: Signal
Multiplicities: 1.0000
Solution: 1.0000
Use Multiplier x Dilution Factor with IS0s

Signal 1: VDI 1, Wavelength: 200 nm

Peak RetTime Type Width Area Height Area
# [min] [min] [nA/min] [nA/min]
1 20.397 20.397 3528.247 3528.247

Totals: 4270.184

Area Percent Report

Sorted By: Signal
Multiplicities: 1.0000
Solution: 1.0000
Use Multiplier x Dilution Factor with IS0s

Signal 1: VDI 1, Wavelength: 200 nm

Peak RetTime Type Width Area Height Area
# [min] [min] [nA/min] [nA/min]
1 19.141 19.141 321156 321156
2 20.414 20.414 520792 520792

Totals: 84193150 32706530

*** End of Report ***
Area Percent Report

Sorted By : Signal
Multiplier: 1.0000
Solution: 1.0000
Use Multiplier x Dilution Factor with ISVs

Signal 1: Wavelength=354 nm

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Width</th>
<th>Area</th>
<th>Width</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(min)</td>
<td>(min)</td>
<td>(AUFS)</td>
<td>(AUFS)</td>
<td>(AU)</td>
</tr>
<tr>
<td>1</td>
<td>20.370</td>
<td>0.613</td>
<td>1.045x64</td>
<td>286.7548</td>
<td>49.9935</td>
</tr>
<tr>
<td>2</td>
<td>21.021</td>
<td>0.466</td>
<td>1.041x64</td>
<td>333.2765</td>
<td>50.0035</td>
</tr>
</tbody>
</table>

Totals: 2.0914x64 599.9930

*** End of Report ***
Data File (C:\CHEMO21\DATA\19031903003217.D)
Sample Name: 06-4-85-tams (+/−)

Acq. Operator:  
Location:  Vial 1
Injection Date:  5/22/19 20:43:08
Injection Volume:  5.000 µl

Acq. Method:  C:\CHEMO21\METHODS\DEP_LC111.M
Last changed:  5/22/19 20:43:11
(modified after loading)

Analysis Method:  C:\CHEMO21\METHODS\DEP_LC111.M
Last changed:  5/22/19 20:43:11
(modified after loading)

Sample Info:  IC, n-hexane/i-PrOH = 95/5, 0.8 ml/min, 30 oC, 230 nm

---

Additional Info: Peaks(s) manually integrated

---

Area Percent Report

Sorted By:  Signal
Multiplier:  1.0000
Solution:  1.0000
Use Multiplier x Solution Factor with IDTs

Signal: UV1 a, Wavelength=230 nm

Peak RetTime Type Width Area Height Area
# [min] [min] [µm²] [µm²]
1 13.03 VB 0.2280 3256.7617 223.6496 48.7932
2 16.893 BV 0.3048 3324.1447 169.4759 50.2363

Totals: 6620.9049 399.1176

---

End of Report

---
Data File: c:\CHEMO211\DATA\HID191300003233.D
Sample Name: GL-4-09-001-30

=================================================================================================
Acq. Operator:  
Acq. Instrument:  
Location: Vial 1  
Injection Date: 6/25/19 15:07:44  
Injection Volume: 5.00 µl  
Acq. Method: c:\CHEMO211\METHODS\HID191300003233.M  
Last changed: 6/25/19 14:00:19  
(modified after loading)  
Analysis Method: c:\CHEMO211\METHODS\HID191300003233.M  
Last changed: 6/25/19 14:00:19  
(modified after loading)  
Sample Info: IC, n-hexane/i-PROH = 95/5, 1.0 mL/min, 50 oC, 230 nm

Additional Info: Peak(s) manually integrated

=================================================================================================
Area Percent Report
=================================================================================================
Sorted By: Signal  
Multiplicies: 1  
Dilutions: 1  
Use Multiplier x Dilution Factor with ISDBs

Signal 1: UV1 A, Wavelength=230 nm

Peak Set/Type Width Area Height Area
# [min] [min] [UFLt] [UFT] ^  
1 0.500 0.1757 4464.74072 402.84938 49.9729
2 9.346 0.1941 4553.67011 363.73563 50.0271
Totals: 9102.41943 766.57666

=================================================================================================

Additional Info: Peak(s) manually integrated

=================================================================================================
Area Percent Report
=================================================================================================
Sorted By: Signal  
Multiplicies: 1  
Dilutions: 1  
Use Multiplier x Dilution Factor with ISDBs

Signal 1: UV1 A, Wavelength=230 nm

Peak Set/Type Width Area Height Area
# [min] [min] [UFLt] [UFT] ^  
1 0.392 0.1670 3369.32377 312.15062 92.2965
2 9.913 0.2068 4766.58992 4.633267 1.7934
Totals: 3427.71290 322.79129

=================================================================================================

Page 1 of 1
### Area Percent Report

**Sorted By**: Signal

**Multiplier**: 1.0000

**Dilution**: 1.0000

**Use Multiplier x Dilution Factor with HTM**

**Signal**: 240 nm, Wavelength=200 nm

**Peak RetTime**: Width, Area, Height, Area

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17.033</td>
<td>0.359</td>
<td>2754.49408</td>
<td>101.12083</td>
</tr>
<tr>
<td>2</td>
<td>18.206</td>
<td>0.319</td>
<td>3764.43726</td>
<td>183.43100</td>
</tr>
</tbody>
</table>

**Totals**: 7516.84175 374.66993

***End of Report***
Additional Info: Peaks manually integrated

Area Percent Report

Sorted By: Signal
Multiplier: = 1.0000
Division: = 1.0000
Use Multiplier x Division Factor with ISTDs

Signal I: Wavelength=220 nm

<table>
<thead>
<tr>
<th>Peak RetTime Type Width Area</th>
<th>Width</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.979 VY</td>
<td>0.2460</td>
<td>4.055, 52785</td>
</tr>
<tr>
<td>2.081 VY</td>
<td>0.2460</td>
<td>4.055, 6991</td>
</tr>
</tbody>
</table>

Totals: 8201.22754, 518.39029

*** End of Report ***
<table>
<thead>
<tr>
<th>Peak RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.53</td>
<td>VWD1</td>
<td>0.228</td>
<td>295.4989</td>
<td>4.9587</td>
<td></td>
</tr>
<tr>
<td>2.07</td>
<td>VWD1</td>
<td>0.246</td>
<td>317.3252</td>
<td>50.0433</td>
<td></td>
</tr>
</tbody>
</table>

Totals: 853.2370 563.03740

Area Percent Report

<table>
<thead>
<tr>
<th>Sorted By</th>
<th>Signal Multiply:</th>
<th>1.0000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dilution:</td>
<td>1.0000</td>
<td></td>
</tr>
</tbody>
</table>

Use Multiplier + Dilution Factor with IDTBs

Signal: VWD1, Wavelength=200 nm

<table>
<thead>
<tr>
<th>Peak RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.53</td>
<td>VWD1</td>
<td>0.228</td>
<td>295.4989</td>
<td>4.9587</td>
<td></td>
</tr>
<tr>
<td>2.07</td>
<td>VWD1</td>
<td>0.246</td>
<td>317.3252</td>
<td>50.0433</td>
<td></td>
</tr>
</tbody>
</table>

Totals: 853.2370 563.03740

Area Percent Report

<table>
<thead>
<tr>
<th>Sorted By</th>
<th>Signal Multiply:</th>
<th>1.0000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dilution:</td>
<td>1.0000</td>
<td></td>
</tr>
</tbody>
</table>

Use Multiplier + Dilution Factor with IDTBs

Signal: VWD1, Wavelength=200 nm

<table>
<thead>
<tr>
<th>Peak RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.53</td>
<td>VWD1</td>
<td>0.228</td>
<td>295.4989</td>
<td>4.9587</td>
<td></td>
</tr>
<tr>
<td>2.07</td>
<td>VWD1</td>
<td>0.246</td>
<td>317.3252</td>
<td>50.0433</td>
<td></td>
</tr>
</tbody>
</table>

Totals: 853.2370 563.03740

Area Percent Report

<table>
<thead>
<tr>
<th>Sorted By</th>
<th>Signal Multiply:</th>
<th>1.0000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dilution:</td>
<td>1.0000</td>
<td></td>
</tr>
</tbody>
</table>

Use Multiplier + Dilution Factor with IDTBs

Signal: VWD1, Wavelength=200 nm
Data File (C:\CHEM321\DATA\H00019\30003351.D)
Sample Name: AD-8, n-butanethiol/1-OctOH = 95/5, 1.0 mL/min, 90°C, 220 nm

Additional Info: Peaks(s) manually integrated

Area Percent Report

**End of Report**

Data File (C:\CHEM321\DATA\H00019\30003499.D)
Sample Name: AD-8, n-butanethiol/1-OctOH = 95/5, 1.0 mL/min, 90°C, 220 nm

Additional Info: Peaks(s) manually integrated

Area Percent Report

**End of Report**
Data File (C:\CHEM21\DATA\13000019300003603.B)
Sample Name: GL-6-4-trons-(+/-)

Additional Info: Peaks(s) manually integrated

Area Percent Report

Sorted By : Signal
Multipies: 1.0000
Dilution: 1.0000
Use Multiplier x Dilution Factor with ISTDs

Signal 1: VOD, Wavelength=220 nm

Peak RetTime Width Area Height Area
# [min] [min] [WAVT] [WAVT] [AHT] [AHT]
1 17.913 0.384 3545.0745 49.7151
2 21.964 0.545 3550.7125 129.8318 50.2849

Totals: 7130.7970 276.82552

Page 1 of 1

S85