Supporting Information

Efficient Synthesis of Chiral β-Hydroxy Sulfones via Iridium-Catalyzed Hydrogenation

Lin Tao,†a Congcong Yin,†a Xiu-Qin Dong,*a and Xumu Zhang*a,b

a Key Laboratory of Biomedical Polymers, Engineering Research Center of Organosilicon Compounds & Materials, Ministry of Education, College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, Hubei, 430072, P. R. China.
b Department of Chemistry and Shenzhen Grubbs Institute, Southern University of Science and Technology, Shenzhen, Guangdong, 518055, P. R. China.
† Lin Tao and Congcong Yin contributed equally to this work.
E-mail: zhangxm@sustc.edu.cn, xiuqindong@whu.edu.cn.

Contents

1. General remarks .............................................................................................................................................2
2. General procedure for synthesis of β-keto sulfones .........................................................................................2
3. General procedure for asymmetric hydrogenation ..........................................................................................3
4. NMR spectra ....................................................................................................................................................12
5. HPLC spectra ................................................................................................................................................31
6. Reference.........................................................................................................................................................67
1. General remarks

All reactions and manipulations which are sensitive to moisture or air were performed in an argon-filled glovebox or using standard Schlenk techniques. Hydrogen gas (99.999%) was purchased from Shanghai Regulator Factory Co., Ltd. Anhydrous hexane, THF, 1,4-dioxane and toluene was distilled from sodium benzophenone ketyl. Anhydrous i-PrOH, DCE, CHCl₃, CH₂Cl₂ were freshly distilled from calcium hydride. Anhydrous MeOH and EtOH were freshly distilled from Mg. Solvents were transferred by syringe. [Ir(COD)Cl]₂ was prepared according to the literature. ¹H and ¹³C spectra were recorded with a Bruker ADVANCE III (400 MHz) spectrometer with CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts are reported in parts per million (ppm, δ scale) downfield from TMS at 0.00 ppm and referenced to the CDCl₃ at 7.26 ppm (for ¹H NMR) or 77.00 ppm (for ¹³C NMR). Data are reported as: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in hertz (Hz) and signal area integration in natural numbers.¹³C NMR analyses were run with decoupling. Optical rotations [α]D were determined using a PERKIN ELMER polarimeter 343 instrument. HPLC analyses were performed using Daicel chiral column on an Agilent 1260 Series HPLC instrument.

2. General procedure for synthesis of β-keto sulfones

Method A:

\[
\begin{align*}
\text{R-} & \quad \text{Br} + \quad \text{PEG-400, rt, 3 h} \quad \text{PEG-400, rt, 3 h} \\
\text{O} & \quad \text{Br} \\
\text{S} & \quad \text{S} \\
\end{align*}
\]

In a 150 mL flask, bromoacetophenone (3.0 mmol) and sodium phenylsulfite (3.3 mmol) were added to the flask, and then 30 mL polyethylene glycol 400 was poured into the flask and stirred for 3 h at room temperature. The reaction system was extracted with ethyl acetate three times, then washed with water to remove polyethylene glycol three times, and then dried with anhydrous sodium sulfate. Then the reaction mixture was concentrated under reduced pressure, and the resulting residue was separated by column chromatography (petroleum ether:EtOAc = 6:1) to give the desired products.
The product can be further purified by recrystallization from dichloromethane.

**Method B:**

Bromoacetophenone (3.0 mmol) was added to a 150 mL flask, and then 20 mL 1,4-dioxane was added to dissolve it. Then 20 mL water solution of sodium methylene sulfite was added to the flask, and the reaction system was reacted at room temperature for 3 h. 1,4-Dioxane in the reaction system was removed by rotary evaporator, then a small amount of water was added, and then dichloromethane was used to extract the reaction system. Then the reaction mixture was concentrated under reduced pressure, and the resulting residue was separated by column chromatography (petroleum ether:EtOAc = 6:1) to give the desired products. The product can be further purified by recrystallization from dichloromethane.

Substrates 1a-1j, 1q-1r were prepared through method A.\(^1\) Substrates 1k-1p were prepared through method B.\(^2\) The absolute configuration of product 2a was determined by comparison of analytical data (optical rotation) with the literature.\(^{3-4}\) The absolute configuration of others were assigned by analogy.

1-(2-fluorophenyl)-2-(methylsulfonyl)ethanone 1l

![Structure of 1l](image)

White solid, 476.3 mg, 73% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.94 (td, \(J = 7.7, 1.9\) Hz, 1H), 7.67-7.61 (m, 1H), 7.32-7.28 (m, 1H), 7.23-7.18 (m, 1H), 4.68 (s, 2H), 3.18 (s, 3H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 187.1 (d, \(J = 3.0\) Hz), 162.1 (d, \(J = 254.0\) Hz), 136.6 (d, \(J = 10.0\) Hz), 131.1 (d, \(J = 1.0\) Hz), 125.0 (d, \(J = 4.0\) Hz), 124.2 (d, \(J = 11.0\) Hz), 117.0 (d, \(J = 24.0\) Hz), 64.9 (d, \(J = 9.0\) Hz), 42.3.

3. **General procedure for asymmetric hydrogenation**
General procedure (at S/C = 1 000): To a 4.0 mL vial was added the catalyst precursor [Ir(COD)Cl]₂ (1.4 mg, 2.0×10⁻³ mmol), ligand L₄ (3.3 mg, 4.2×10⁻³ mmol) and anhydrous isopropanol (2.0 mL) in the argon-filled glovebox. The mixture was stirred for 2.0 h at 25 °C giving orange red solution. And then 0.2 mmol β-keto sulfones, Na₂CO₃ (1.06 mg, 0.01 mmol) were added into a 5 mL hydrogenation vessel. 1.0 mL anhydrous toluene was added as solvent and a solution of Ir/f-Amphol L₄ in anhydrous isopropanol (100 μL) was added via an injection port. Then the vessel was placed in an autoclave, closed it and moved it out from glovebox. The autoclave quickly purged with hydrogen gas for three times, then pressurized to 20 atm H₂. The reaction solution was stirred at room temperature until for 12 h, then released pressure carefully. The solution of reaction mixture was purified by a flash chromatography on a silical gel with ethyl acetate and the solvent was removed under reduced pressure. The product was analyzed by NMR spectroscopy for conversion and chiral HPLC for ee values.

(S)-1-phenyl-2-(phenylsulfonyl)ethan-1-ol 2a

White solid, 99% yield, 51.9 mg; 95% ee; [α]_D^{25} = +27.2 (c = 1.50, CHCl₃). The enantiomeric excess was determined by HPLC on Chiracel OJ-H column, 220 nm, 20 °C, n-hexane: i-PrOH = 80:20; flow 1.0 mL/min; tᵣ (minor) = 31.6 min, tᵣ (major) = 33.6 min. ¹H NMR (400 MHz, CDCl₃) δ 7.99–7.96 (m, 2H), 7.72–7.68 (m, 1H), 7.63–7.68 (m, 2H), 7.35–7.28 (m, 5H), 5.30–5.27 (m, 1H), 3.68 (d, J = 2.1 Hz, 1H), 3.54–3.33 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 140.6, 139.1, 134.1, 129.5, 128.8, 128.4, 128.0, 125.6, 68.4, 63.9.

(S)-1-(2-methoxyphenyl)-2-(phenylsulfonyl)ethan-1-ol 2b
S/C = 500, 0.1 mmol substrate, Na₂CO₃ (10 mol%). White solid, 99% yield, 28.9 mg; >99% ee; [α]₀²⁵ = +24.3 (c = 1.50, CHCl₃). The enantiomeric excess was determined by HPLC on Chirapak AD-H column, 210 nm, 20 ºC, n-hexane: i-PrOH = 90:10; flow 1.0 mL/min; tᵣ (minor) = 34.6 min, tᵣ (major) = 41.0 min. \(^1\)H NMR (400 MHz, CDCl₃) δ 7.97–7.95 (m, 2H), 7.70–7.66 (m, 1H), 7.61–7.57 (m, 2H), 7.49–7.46 (m, 1H), 7.25–7.21 (m, 1H), 6.99–6.95 (m, 1H), 6.76–6.73 (m, 1H), 5.35-5.32 (m, 1H), 3.70 (d, J = 4.0 Hz, 1H), 3.60 (s, 3H), 3.58–3.40 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl₃) δ 155.2, 139.2, 133.7, 129.2, 129.0, 128.3, 128.1, 126.4, 120.9, 110.1, 64.4, 61.9, 55.0.

\((\text{S})\)-1-(3-methoxyphenyl)-2-(phenylsulfonyl)ethan-1-ol 2c

White solid, 98% yield, 57.3 mg; 96% ee; [α]₀²⁵ = +17.4 (c = 1.50, CHCl₃). The enantiomeric excess was determined by HPLC on Chiracel OJ-H column, 220 nm, 20 ºC, n-hexane: i-PrOH = 80:20; flow 1.0 mL/min; tᵣ (minor) = 34.5 min, tᵣ (major) = 43.9 min. \(^1\)H NMR (400 MHz, CDCl₃) δ 7.98–7.95 (m, 2H), 7.72–7.68 (m, 1H), 7.62-7.58 (m, 2H), 7.23 (t, J = 7.9 Hz, 1H), 6.88–6.79 (m, 3H), 5.27-5.25 (m, 1H), 3.78 (s, 3H), 3.67 (d, J = 2.2 Hz, 1H), 3.53–3.32 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl₃) δ 159.9, 142.2, 139.1, 134.1, 129.8, 129.5, 128.0, 117.8, 113.9, 111.1, 68.3, 63.9, 55.3.

\((\text{S})\)-1-(4-methoxyphenyl)-2-(phenylsulfonyl)ethan-1-ol 2d

White solid, 99% yield, 57.8 mg; 98% ee; [α]₀²⁵ = +13.9 (c = 1.50, CHCl₃). The enantiomeric excess was determined by HPLC on Chiracel AD-H column, 210 nm, 20
â€¢, n-hexane: i-PrOH = 90:10; flow 0.5 mL/min; t_R (major) = 132.5 min, t_R (minor) = 141.1 min. ^1H NMR (400 MHz, CDCl_3) δ 7.97–7.95 (m, 2H), 7.71–7.67 (m, 1H), 7.62–7.57 (m, 2H), 7.23–7.20 (m, 2H), 6.86–6.83 (m, 2H), 5.25-5.21 (m, 1H), 3.78 (s, 3H), 3.61 (d, J = 2.0 Hz, 1H), 3.54–3.30 (m, 2H). ^13C NMR (100 MHz, CDCl_3) δ 159.5, 139.2, 134.1, 132.7, 129.4, 128.0, 127.0, 114.1, 68.1, 63.9, 55.3.

(S)-1-(2-fluorophenyl)-2-(phenylsulfonyl)ethan-1-ol 2e

White solid, 97% yield, 54.4 mg; 90% ee; [â³]_D^{25} = +6.6 (c = 1.50, CHCl_3). The enantiomeric excess was determined by HPLC on Chiracel OJ-H column, 220 nm, 20 °C, n-hexane: i-PrOH = 80:20; flow 1.0 mL/min; t_R (major) = 25.3 min, t_R (minor) = 31.4 min. ^1H NMR (400 MHz, CDCl_3) δ 7.98–7.95 (m, 2H), 7.72–7.68 (m, 1H), 7.62–7.53 (m, 3H), 7.26–7.24 (m, 1H), 7.18-7.14 (m, 1H), 6.97-6.92 (m, 1H), 5.46-5.45 (m, 1H), 3.84 (d, J = 2.7 Hz, 1H), 3.50–3.48 (m, 2H). ^13C NMR (100 MHz, CDCl_3) δ 159.0 (d, J = 244.0 Hz), 138.8, 134.1, 129.8 (d, J = 8.0 Hz), 129.4, 128.0, 127.5 (d, J = 12.0 Hz), 127.3 (d, J = 4.0 Hz), 124.6 (d, J = 4.0 Hz), 115.3 (d, J = 21.0 Hz), 63.0 (d, J = 3.0 Hz), 62.2 (d, J = 1.0 Hz).

(S)-1-(4-fluorophenyl)-2-(phenylsulfonyl)ethan-1-ol 2f

White solid, 98% yield, 54.9 mg; 95% ee; [â³]_D^{25} = +24.8 (c = 1.50, CHCl_3). The enantiomeric excess was determined by HPLC on Chiracel OJ-H column, 220 nm, 20 °C, n-hexane: i-PrOH = 80:20; flow 1.0 mL/min; t_R (minor) = 27.3 min, t_R (major) = 33.3 min. ^1H NMR (400 MHz, CDCl_3) δ 7.98–7.95 (m, 2H), 7.73–7.68 (m, 1H), 7.63–7.58 (m, 2H), 7.30–7.26 (m, 2H), 7.03–6.99 (m, 2H), 5.29–5.27 (m, 1H), 3.76 (d, J = 2.1 Hz, 1H), 3.52–3.29 (m, 2H). ^13C NMR (100 MHz, CDCl_3) δ 162.5 (d, J = 246.0 Hz),
139.0, 136.4 (d, J = 4.0 Hz), 134.2, 129.5, 127.9, 127.4 (d, J = 8.0 Hz), 115.7 (d, J = 22.0 Hz), 67.8, 63.9.

(S)-1-(3-bromophenyl)-2-(phenylsulfonyl)ethan-1-ol 2g

White solid, 96% yield, 65.5 mg; 94% ee; [α]D25 = +21.5 (c = 1.50, CHCl3). The enantiomeric excess was determined by HPLC on Chirapak AD-H column, 210 nm, 20 °C, n-hexane: i-PrOH = 90:10; flow 1.0 mL/min; tR (minor) = 28.4 min, tR (major) = 34.9 min. 1H NMR (400 MHz, CDCl3) δ 7.97–7.95 (m, 2H), 7.73–7.69 (m, 1H), 7.63–7.59 (m, 2H), 7.42–7.39 (m, 1H), 7.24–7.17 (m, 2H), 5.29–5.25 (m, 1H), 3.81 (d, J = 2.1 Hz, 1H), 3.50–3.31 (m, 2H). 13C NMR (100 MHz, CDCl3) δ 142.8, 138.9, 134.3, 131.4, 130.3, 129.5, 128.8, 127.9, 124.3, 122.8, 67.8, 63.7.

(S)-1-(4-bromophenyl)-2-(phenylsulfonyl)ethan-1-ol 2h

White solid, 99% yield, 67.6 mg; 94% ee; [α]D25 = +24.5 (c = 1.50, CHCl3). The enantiomeric excess was determined by HPLC on Chiracel OJ-H column, 220 nm, 20 °C, n-hexane: i-PrOH = 80:20; flow 1.0 mL/min; tR (minor) = 39.7 min, tR (major) = 54.8 min. 1H NMR (400 MHz, CDCl3) δ 7.96–7.94 (m, 2H), 7.73–7.69 (m, 1H), 7.63–7.58 (m, 2H), 7.47–7.43 (m, 2H), 7.20–7.17 (m, 2H), 5.28–5.24 (m, 1H), 3.78 (d, J = 2.2 Hz, 1H), 3.49–3.29 (m, 2H). 13C NMR (100 MHz, CDCl3) δ 139.6, 138.9, 134.2, 131.9, 129.5, 127.9, 127.4, 122.2, 67.8, 63.7.

(S)-2-(phenylsulfonyl)-1-(p-tolyl)ethan-1-ol 2i
White solid, 99% yield, 54.7 mg; 96% ee; \([\alpha]_D^{25} = +18.5\) (c = 1.50, CHCl₃). The enantiomeric excess was determined by HPLC on Chiracel OJ-H column, 220 nm, 20 ℃, n-hexane: i-PrOH = 80:20; flow 1.0 mL/min; \(t_R\) (minor) = 23.6 min, \(t_R\) (major) = 28.2 min. \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.98–7.95 (m, 2H), 7.71–7.67 (m, 1H), 7.62–7.57 (m, 2H), 7.19–7.12 (m, 4H), 5.25–5.22 (m, 1H), 3.61 (d, \(J = 2.1\) Hz, 1H), 3.54–3.31 (m, 2H), 2.31 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl₃) \(\delta\) 139.2, 138.2, 137.6, 134.1, 129.4, 129.4, 128.0, 125.6, 68.3, 63.9, 21.1.

(S)-1-(4-chlorophenyl)-2-(phenylsulfonyl)ethan-1-ol 2j

White solid, 98% yield, 58.5 mg; 94% ee; \([\alpha]_D^{25} = +19.0\) (c = 1.50, CHCl₃). The enantiomeric excess was determined by HPLC on Chiracel OJ-H column, 220 nm, 20 ℃, n-hexane: i-PrOH = 80:20; flow 1.0 mL/min; \(t_R\) (minor) = 32.8 min, \(t_R\) (major) = 42.9 min. \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.97–7.94 (m, 2H), 7.73–7.69 (m, 1H), 7.63–7.58 (m, 2H), 7.31–7.28 (m, 2H), 7.26–7.22 (m, 2H), 5.29–5.26 (m, 1H), 3.78 (d, \(J = 2.2\) Hz, 1H), 3.49–3.29 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl₃) \(\delta\) 139.0, 138.9, 134.2, 134.1, 129.5, 128.9, 127.9, 127.0, 67.8, 63.8.

(S)-2-(methylsulfonyl)-1-phenylethan-1-ol 2k

S/C = 500, 0.2 mmol substrate, Na₂CO₃ (5 mol%). White solid, 99% yield, 39.6 mg; 97% ee; \([\alpha]_D^{25} = +49.9\) (c = 1.50, CHCl₃). The enantiomeric excess was determined by HPLC on Chiracel OJ-H column, 210 nm, 20 ℃, n-hexane: i-PrOH = 80:20; flow 1.0 mL/min; \(t_R\) (major) = 20.4 min, \(t_R\) (minor) = 30.9 min. \(^1\)H NMR (400 MHz, CDCl₃)
δ 7.42–7.31 (m, 5H), 5.36–5.32 (m, 1H), 3.45 (dd, J = 14.7, 10.3 Hz, 1H), 3.19–3.14 (m, 1H), 3.05 (s, 3H), 3.05-3.02 (m, 1H). 13C NMR (100 MHz, CDCl₃) δ 141.0, 129.0, 128.7, 125.6, 69.3, 62.4, 42.8.

(S)-1-(2-fluorophenyl)-2-(methylsulfonyl)ethan-1-ol 2l

White solid, 99% yield, 43.2 mg; 95% ee; [α]D²⁵ = +32.1 (c = 1.50, CHCl₃). The enantiomeric excess was determined by HPLC on Chiracel OJ-H column, 220 nm, 20 °C, n-hexane: i-PrOH = 80:20; flow 1.0 mL/min; tR (major) = 13.1 min, tR (minor) = 17.6 min. 1H NMR (400 MHz, CDCl₃) δ 7.57–7.53 (m, 1H), 7.35-7.30 (m, 1H), 7.23-7.19 (m, 1H), 7.10-7.05 (m, 1H), 5.61-5.58 (m, 1H), 3.48–3.40 (m, 2H), 3.34-3.29 (m, 1H), 3.07 (s, 3H). 13C NMR (100 MHz, CDCl₃) δ 159.2 (d, J = 244.0 Hz), 130.1 (d, J = 9.0 Hz), 127.8 (d, J = 13.0 Hz), 127.2 (d, J = 4.0 Hz), 124.8 (d, J = 4.0 Hz), 115.6 (d, J = 21.0 Hz), 63.8 (d, J = 3.0 Hz), 60.8 (d, J = 1.0 Hz), 42.6

(S)-1-(3-bromophenyl)-2-(methylsulfonyl)ethan-1-ol 2m

S/C = 500, 0.1 mmol substrate, Na₂CO₃ (10 mol%). White solid, 99% yield, 27.6 mg; 97% ee; [α]D²⁵ = +32.9 (c = 1.50, CHCl₃). The enantiomeric excess was determined by HPLC on Chiracel OJ-H column, 210 nm, 20 °C, n-hexane: i-PrOH = 80:20; flow 1.0 mL/min; tR (minor) = 32.3 min, tR (major) = 34.2 min. 1H NMR (400 MHz, CDCl₃) δ 7.58 (t, J = 1.8 Hz, 1H), 7.48-7.46 (m, 1H), 7.32–7.24 (m, 2H), 5.35-5.32 (m, 1H), 3.45–3.38 (m, 1H), 3.18-3.14 (m, 2H), 3.07 (s, 3H). 13C NMR (100 MHz, CDCl₃) δ 143.1, 131.7, 130.5, 128.8, 124.2, 123.1, 68.6, 62.2, 42.9.

(S)-2-(methylsulfonyl)-1-(p-tolyl)ethan-1-ol 2n
White solid, 98% yield, 50.0 mg; 98% ee; $[\alpha]_{D}^{25} = +34.1$ (c = 1.50, CHCl$_3$). The enantiomeric excess was determined by HPLC on Chiracel OD-H column, 220 nm, 20 °C, n-hexane: i-PrOH = 80:20; flow 1.0 mL/min; $t_{R}$ (major) = 11.4 min, $t_{R}$ (minor) = 13.4 min. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.28–7.26 (m, 2H), 7.20–7.18 (m, 2H), 5.32–5.28 (m, 1H), 3.48–3.42 (m, 1H), 3.17–3.12 (m, 1H), 3.04 (s, 3H), 2.94–2.93 (m, 1H), 2.35 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 138.5, 138.0, 129.6, 125.5, 69.2, 62.4, 42.8, 21.1.

(S)-1-(4-chlorophenyl)-2-(methylsulfonyl)ethan-1-ol 2o

White solid, 99% yield, 46.5 mg; 99% ee; $[\alpha]_{D}^{25} = +43.8$ (c = 1.50, CHCl$_3$). The enantiomeric excess was determined by HPLC on Chiracel OJ-H column, 220 nm, 20 °C, n-hexane: i-PrOH = 80:20; flow 1.0 mL/min; $t_{R}$ (major) = 27.7 min, $t_{R}$ (minor) = 31.9 min. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39–7.31 (m, 4H), 5.36–5.32 (m, 1H), 3.42 (dd, $J = 14.7$, 10.3 Hz, 1H), 3.16–3.12 (m, 2H), 3.07 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 139.4, 134.4, 129.1, 127.0, 68.6, 62.3, 42.9.

(S)-1-(4-methoxyphenyl)-2-(methylsulfonyl)ethan-1-ol 2p

White solid, 99% yield, 45.6 mg; 99% ee; $[\alpha]_{D}^{25} = +46.3$ (c = 1.50, CHCl$_3$). The enantiomeric excess was determined by HPLC on Chiracel OJ-H column, 220 nm, 20 °C, n-hexane: i-PrOH = 80:20; flow 1.0 mL/min; $t_{R}$ (major) = 42.2 min, $t_{R}$ (minor) = 60.0 min. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.32–7.28 (m, 2H), 6.93–6.89 (m, 2H), 5.30–5.27 (m, 1H), 3.81 (s, 3H), 3.49–3.42 (m, 1H), 3.14 (dd, $J = 14.7$, 2.0 Hz, 1H), 3.04 (s, 3H), 2.96–2.95 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 159.8, 133.1, 127.0, 114.3,
(S)-1-(furan-2-yl)-2-(phenylsulfonyl)ethanol 2q

\[
\begin{align*}
\text{S/C} &= 500, 0.2 \text{ mmol substrate, } \text{Na}_2\text{CO}_3 (5 \text{ mol\%}). \text{ White solid, 98\% yield, 49.4 mg; 86\% ee; } [\alpha]_D^{25} = +8.0 \text{ (c = 1.50, CHCl}_3). \text{ The enantiomeric excess was determined by HPLC on Chiracel OJ-H column, 220 nm, 20 \text{o}C, n-hexane: i-PrOH = 80:20; flow 1.0 mL/min; } t_R \text{ (major) = 38.1 min, } t_R \text{ (minor) = 36.0 min.} \quad \text{^1H NMR (400 MHz, CDCl}_3) \quad \delta 7.96-7.93 \text{ (m, 2H), 7.71-7.66 (m, 1H), 7.61-7.56 (m, 2H), 7.30 (dd, } J = 1.7, 1.0 \text{ Hz, 1H), 6.31-6.29 (m, 2H), 5.30-5.26 (m, 1H), 3.68 (dd, } J = 14.4, 9.4 \text{ Hz, 1H), 3.56-3.49 (m, 2H).} \quad \text{^13C NMR (100 MHz, CDCl}_3) \quad \delta 152.4, 142.6, 139.0, 134.1, 129.4, 128.0, 110.4, 107.4, 62.7, 60.5.
\end{align*}
\]

(S)-1-cyclohexyl-2-(phenylsulfonyl)ethan-1-ol 2r

\[
\begin{align*}
\text{S/C} &= 500, 0.2 \text{ mmol substrate, } \text{Na}_2\text{CO}_3 (5 \text{ mol\%}). \text{ Colorless liquid, 35\% yield, 18.9 mg; 90\% ee; } [\alpha]_D^{25} = +10.6 \text{ (c = 1.50, CHCl}_3). \text{ The enantiomeric excess was determined by HPLC on Chirapak AD-H column, 220 nm, 20 \text{o}C, n-hexane: i-PrOH = 80:20; flow 0.7 mL/min; } t_R \text{ (minor) = 18.9 min, } t_R \text{ (major) = 22.1 min.} \quad \text{^1H NMR (400 MHz, CDCl}_3) \quad \delta 7.94 \text{ (dd, } J = 8.3, 1.3 \text{ Hz, 2H), 7.69-7.67 (m, 1H), 7.62-7.58 (m, 2H), 3.96-3.95 (m, 1H), 3.26 (d, } J = 2.6 \text{ Hz, 1H), 3.26-3.22 (m, 2H), 1.74-1.63 (m, 5H), 1.46-1.36 (m, 1H), 1.27-0.99 (m, 5H).} \quad \text{^13C NMR (100 MHz, CDCl}_3) \quad \delta 139.2, 134.0, 129.4, 127.9, 69.7, 60.2, 43.1, 28.4, 27.5, 26.2, 25.9, 25.8.
\end{align*}
\]
4. NMR spectra
5. HPLC spectra

Data File: D:\DATA\GU...DYQG\INDOLE\DYQG-180723-Tri-Rac-1 2018-07-23 14:42-13\051-5601.D
Sample Name: TL-ph-ph-rac

========================================================================================================
Acq. Operator : Seq. Line : 56
Acq. Instrument : Instrument 2 Location : Viaf 51
Injection Date : 7/25/2018 12:27:43 AM Inj : 1
Inj Volume : 3.000 µl
Acq. Method : D:\DATA\GU...DYQG\INDOLE\DYQG-180723-Tri-Rac-1 2018-07-23 14:42-13
Analysis Method : D:\V6ETHD\DYQG\ANALYSIS\AD(1-6) 90-10-0.7UL-3UL-ALL-70MIN.M
Last changed : 8/21/2018 9:47:34 AM
(modified after loading)
Additional Info : Peak(s) manually integrated

![HPLC spectra diagram](image_url)

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

Area Percent Report

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

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 C, Sig=210.4 Ref-off (D:\DATA\GU...DYQG\INDOLE\DYQG-180723-Tri-Rac-1 2018-07-23 14:42-13\051-5601.D)

<table>
<thead>
<tr>
<th>Peak RetTime Type Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td>[min]</td>
<td>[nAU's]</td>
</tr>
<tr>
<td>1</td>
<td>30.993</td>
<td>BB</td>
<td>0.7358</td>
</tr>
<tr>
<td>2</td>
<td>33.632</td>
<td>BB</td>
<td>0.8511</td>
</tr>
</tbody>
</table>

Totals : 3.16755e+4 594.45883

Instrument 2 8/21/2018 9:47:36 AM
Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Use Multiplier & Dilution Factor with ISIDs

Signal 1: VW01 A, Wavelength=210 nm

<table>
<thead>
<tr>
<th>Peak RetTime Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td>[mAU’s]</td>
<td>[mAU]</td>
<td>%</td>
</tr>
<tr>
<td>1</td>
<td>34.438</td>
<td>0.8071</td>
<td>7703.96484</td>
<td>144.70210</td>
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<tr>
<td>2</td>
<td>41.035</td>
<td>0.9317</td>
<td>7703.17529</td>
<td>124.69363</td>
</tr>
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Totals: 1.54071e4 269.39573

Instrument 2 8/20/2018 9:14:32 PM
### Signal 1: VW01 A, Wavelength=210 nm

<table>
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<tr>
<th>Peak RetTime</th>
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<th>Width</th>
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<th>Area %</th>
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</thead>
<tbody>
<tr>
<td>34.592</td>
<td>MM</td>
<td>0.796</td>
<td>72.45431</td>
<td>1.51590</td>
<td>0.2449</td>
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<tr>
<td>40.994</td>
<td>BB</td>
<td>0.0404</td>
<td>2.9517444</td>
<td>476.07034</td>
<td>99.7551</td>
</tr>
</tbody>
</table>

**Totals:**
- Area: 2.96899e4
- Percentage: 477.58824
Data File D:\DATA\TL-6\TL-8 2018-07-09 21-09-18\023-0401.D
Sample Name: TL-3-MeO-ph-rac

Acq. Operator : Seq. Line : 4
Acq. Instrument : Instrument 2 Location : Vial 23
Injection Date : 7/9/2018 10:43:17 PM Inj : 1
Inj Volume : 3.000 μl
Acq. Method : D:\DATA\TL-6\TL-8 2018-07-09 21-09-18\023-0401.M
Last changed : 7/9/2018 9:15:39 PM
Analysis Method : D:\METHOD\LSD\DAD-AD(1-6)-95-5-1UL-2UL-ALL-20MIN.M
Last changed : 8/20/2018 9:42:06 PM (modified after loading)
Additional Info : Peak(s) manually integrated

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig-220.4 Ref-off
Peak RetTime Type Width Area Height Area
# | [min] | [min] | [nAUI's] | [nAUI] | %
---|-------|-------|--------|--------|---
1 34.122 BB 0.6078 3548.96901 63.91422 49.8698
2 44.206 BV 0.8612 3567.52515 49.01395 50.1302

Totals : 7116.51416 112.92818

Instrument 2 8/20/2018 9:42:08 PM Page 1 of 2
Signal 1: VW01 A, Wavelength=210 nm

<table>
<thead>
<tr>
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<th>Width</th>
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<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>132.457</td>
<td>2.6948</td>
<td>1,238,969</td>
<td>690,366,21</td>
<td>98.8335</td>
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<tr>
<td>2</td>
<td>141.066</td>
<td>2.5153</td>
<td>1,462,269</td>
<td>98,689</td>
<td>1.1665</td>
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Totals: 1,253,987 ± 702,0539

Instrument 2 12/18/2018 8:03:51 PM
Sort by : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs  

Signal 1: DAD1 B, Sig=220.4 Ref-off

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25.382</td>
<td>BB</td>
<td>0.5036</td>
<td>5049.20996</td>
<td>127.61078</td>
<td>49.7639</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>30.955</td>
<td>BV</td>
<td>0.6407</td>
<td>5097.11279</td>
<td>108.39634</td>
<td>50.2361</td>
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</tr>
</tbody>
</table>

Totals : 1.01488e4  235.99712
### Data File: D:\DATA\TL-6\TL-6 2018-07-09 21-09-18\022-0301.D
### Sample Name: TL-2-F-ph-ee

---

**Acq. Operator:** 3  
**Seq. Line:** 3  
**Acq. Instrument:** Instrument 2  
**Location:** Vial 22  
**Injection Date:** 7/9/2018 10:02:17 PM  
**Inj:** 1  
**Inj Volume:** 3.000 µl  
**Acq. Method:** D:\DATA\TL-6\TL-6 2018-07-09 21-09-18\022-0301.D  
**Last changed:** 7/9/2018 9:06:51 PM  
**Analysis Method:** D:\METHOD\LIM\DAD-AD(1-6)-95-5-1UL-2UL-ALL-1UL-IN.L  
**Last changed:** 8/20/2018 9:48:53 PM  
(modified after loading)  
**Additional Info:** Peak(s) manually integrated

---

**Sorted By:** Signal  
**Multiplier:** 1.0000  
**Dilution:** 1.0000  
**Use Multiplier & Dilution Factor with ISTDs**

**Signal 1: DAD1 B, Sig-220,4 Ref-off (D:\DATA\TL-6\TL-6 2018-07-09 21-09-18\022-0301.D)**

<table>
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<th></th>
<th>Area [mAU]</th>
<th>Height [mAU]</th>
<th>Width [min]</th>
<th>RetTime [min]</th>
<th>Type</th>
</tr>
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<tr>
<td>1</td>
<td>25,326</td>
<td>356,47754</td>
<td>0.6149</td>
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<td>BB</td>
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<td>2</td>
<td>31,441</td>
<td>777,33984</td>
<td>0.5417</td>
<td>31.441</td>
<td>BV</td>
</tr>
</tbody>
</table>

**Totals:** 1,604,504 mAU  
375,59930 mAU

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**Instrument 2 8/20/2018 9:48:56 PM**
Data File: D:\DATA\TL-TL-6\TL-8 2018-07-09 21-09-18\025-0601.D
Sample Name: TL-4-F-ph-rac

Acq. Operator: 
Seq. Line: 6
Acq. Instrument: Instrument 2
Location: Vial 25
Injection Date: 7/10/2018 12:35:15 AM
Injection: 1
Inj Volume: 3.000 µl
Acq. Method: D:\DATA\TL-TL-6\TL-8 2018-07-09 21-09-18\040-AQ-041(1-6)-80-20-1UL-3UL-ALL-45MIN.M
Last changed: 7/9/2018 9:24:11 PM
Analysis Method: D:\METHOD\LKW\DAD-AD(1-6)-95-5-1UL-2UL-ALL-20MIN.M
Last changed: 8/20/2018 9:44:38 PM
(modified after loading)
Additional Info: Peak(s) manually integrated

![Chemical Structure](image)

**Signal 1: DAD1 B, Sig-220,4 Ref-off**

<table>
<thead>
<tr>
<th>Peak RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
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</thead>
<tbody>
<tr>
<td>27.020</td>
<td>BV</td>
<td>0.6321</td>
<td>5188.89307</td>
<td>119.14967</td>
<td>49.8486</td>
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<tr>
<td>33.775</td>
<td>BB</td>
<td>0.6662</td>
<td>5220.41846</td>
<td>94.24884</td>
<td>50.1514</td>
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</tbody>
</table>

**Totals:** 1.04093e+4 213.39851

Instrument 2 8/20/2018 9:44:38 PM
Additional Info: Peak(s) manually integrated

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Use Multiplier & Dilution Factor with ISIDs

Signal 1: VW01 A, Wavelength=210 nm

<table>
<thead>
<tr>
<th>Peak RetTime Type Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 28.481 BB 0.6761</td>
<td>3.4914e4</td>
<td>783.19885</td>
<td>49.7706</td>
</tr>
<tr>
<td>2 35.037 BB 0.8215</td>
<td>3.5236e4</td>
<td>656.15796</td>
<td>50.2294</td>
</tr>
</tbody>
</table>

Totals: 7.0150e4 1439.35981

Instrument 2 8/20/2018 9:35:25 PM
**Data File**: D:\DATA\LHY-LHY-2-EE\LHY-3-477 2018-05-28 10-23-06\021-2591.D

**Sample Name**: ti-4-Br-ph-rac

---

**Additional Info**: Peak(s) manually integrated

---

**Sorted By**: Signal
**Multiplier**: 1.0000
**Dilution**: 1.0000

Use Multiplier & Dilution Factor with ISTDs

**Signal 1**: DAD1 B, Sig=220.4 Ref-off (D:\DATA\LHY-LHY-2-EE\LHY-3-477 2018-05-28 10:23 00261.4421)

---

**Peak RetTime** | **Type** | **Width** | **Area** | **Height** | **Area %**
--- | --- | --- | --- | --- | ---
1 | 39.187 BB | 0.9226 | 1.0220e4 | 133.58096 | 49.9718
2 | 55.500 BB | 1.2036 | 1.0323e4 | 93.43902 | 50.0282

**Totals**: 2.04525e4 227.01998

---

**Instrument 2** 11/6/2018 9:04:03 PM
Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Use Multiplier & Dilution Factor with ISIDs

Signal 1: DAD1 B, Sig=220.4 Ref-off

Peak RetTime Type Width Area Height Area %
----------- -------- -------- ------------ ------------ ------------
1 31.947 BB 0.7134 1.16421e4 188.17842 49.8995
2 42.395 BB 0.9343 1.16990e4 146.59465 50.1005

Totals: 2.33311e4 344.77307

Instrument 2 8/20/2018 9:08:19 PM
Data File: D:\DATA\GUAN_YQGYB-INDOLE\GYQB-180723-TRI-RAC-1 2018-07-23 14-42-13\021-2501.0
Sample Name: TL-ph-We-rac

Additional Info: Peak(s) manually integrated

Signal 1: DAD1 C, Sig-210.4 Ref-off

<table>
<thead>
<tr>
<th>Peak RetTime Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>[min]</td>
<td>[mAU's]</td>
<td>[mAU]</td>
<td>%</td>
</tr>
<tr>
<td>1</td>
<td>20.382</td>
<td>1.44845e+4</td>
<td>400.36893</td>
<td>49.9424</td>
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<td>2</td>
<td>30.291</td>
<td>1.45179e+4</td>
<td>271.13010</td>
<td>50.0576</td>
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Totals: 2.90025e+4 671.49902

Sorted By: Signal
Multiplier: 1.00000
Dilution: 1.00000
Use Multiplier & Dilution Factor with ISIDs
Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000

Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 C, Sig=210.4 Ref-off

<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>#</td>
<td>[min]</td>
<td>[min]</td>
<td>[mAU's]</td>
<td>[mAU]</td>
<td></td>
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<tr>
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<td>-----</td>
<td>------</td>
<td>--------</td>
<td>-------</td>
<td>--------</td>
</tr>
<tr>
<td>1</td>
<td>20.350</td>
<td>BB</td>
<td>0.5244</td>
<td>1.39998e4</td>
<td>392.25517</td>
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<tr>
<td>2</td>
<td>30.934</td>
<td>BB</td>
<td>0.5349</td>
<td>189.31180</td>
<td>4.23958</td>
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</table>

Totals:
1.41873e4 395.47515

Instrument 2 8/21/2018 9:43:49 AM

Page 1 of 2
Data File: D:\DATA\YCC\20180630\YCC-264-34 2018-07-12 18-34-01\073-1901.D
Sample Name: TL-2-F-Me-rac

Additional Info: Peak(s) manually integrated

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Use Multiplier & Dilution Factor with ISIDs

Signal 1: DAD1 B, Sig-220,4 Ref-off (D:\DATA\YCC\20180630\YCC 264-34 2018-07-12 18 34-01\073-1901.D)

<table>
<thead>
<tr>
<th>Peak RetTime</th>
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<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
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</thead>
<tbody>
<tr>
<td>13.247</td>
<td>BB</td>
<td>0.2888</td>
<td>855.37360</td>
<td>42.14367</td>
<td>49.7959</td>
</tr>
<tr>
<td>17.370</td>
<td>BB</td>
<td>0.3638</td>
<td>692.36811</td>
<td>31.28658</td>
<td>50.2041</td>
</tr>
</tbody>
</table>

Totals: 1717.75970 73.41025

Instrument 2 8/20/2018 10:03:59 PM
Sample Name: TL-4-Me-Me-rac

Acq. Operator : 2
Acq. Instrument : Instrument 2
Injection Date : 6/15/2018 8:07:15 PM
Inj : 1
Inj Volume : 3.000 μl
Last changed : 6/15/2018 8:44:57 PM
Analysis Method : D:\METHOD\Product\DAD-AD(1-6)-95-5-1UL-2UL-ALL-20UL.M
Last changed : 8/20/2018 9:04:12 PM

Additional Info : Peak(s) manually integrated

DAD1 B, Sig=220,4 Ref-off (D:\DATA\TL-3\TL-3 2018-06-15 20-55-12\011-0201.D)

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=220,4 Ref-off

Peak RetTime Type Width Area Height Area %
---|-----------|-----------|----------------|-----------|-------|--------||
1 11.394 BB | 0.3897 | 3879.39258 | 221.48277 | 50.0507
2 13.253 BB | 0.4544 | 5667.47217 | 197.69223 | 49.9493

Totals : 1.17489e4 419.58301

Instrument 2 8/20/2018 9:04:25 PM
Peak Ret Time Type Width Area Height Area
# [min] [min] [nAUs] [nAUs] %
1 28.038 BB 0.647 4075.72192 82.03175 50.1508
2 31.232 BB 0.633 4051.21313 76.32463 49.8492

Totals: 8126.93506 158.35638

Signal 1: DAD1 B, Sig=220.4 Ref-off (D:\DATA\TL\TL-6\TL-8 2018-07-09 21-09-18\025-1001.D)

Sort By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Additional Info : Peak(s) manually integrated
**Data File:** D:\DATA\TTL\TL-6\TL-8 2018-07-09 21-09-18\030-1101.D
**Sample Name:** TL-4-Cl-Me-ee

---

**Acq. Operator:**  
**Seq. Line:** 11

**Acq. Instrument:** Instrument 2  
**Location:** Vial 30

**Injection Date:** 7/10/2018 4:30:11 AM  
**Inj:** 1

**Acq. Method:** 0:\DATA\TTL\TL-6\TL-8 2018-07-09 21-09-18\030-1101.D  
**Inj Volume:** 3.000 μl

**Last changed:** 7/9/2018 9:06:51 PM

**Analysis Method:** 0:\METHOD\FROM\DAD-AD(1-6)-95-5-1UL-2UL-ALL-20UL.M

**Last changed:** 8/20/2018 9:32:02 PM  
(modified after loading)

**Additional Info:** Peak(s) manually integrated

---

**DAD1 B, Sig-220,4 Ref-off:**

---

**Sorted By:** Signal

**Multiplier:** 1.0000

**Dilution:** 1.0000

Use Multiplier & Dilution Factor with ISTDs

---

**Signal 1:** DAD1 B, Sig-220,4 Ref-off

---

**Peak RetTime**  
**Type**  
**Width**  
**Area**  
**Height**  
**Area**  
**%**

---

1 27.722 BB 0.7384 1.0730e+04 196.69144 99.2786
2 31.908 MM 0.8399 77.96723 1.54711 0.7214

**Totals:** 1.0638e+04 196.23854

---

**Instrument 2 8/20/2018 9:32:04 PM**

---

Page 1 of 2
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISIDs

Signal 1: DAD1 B, Sig-220.4 Ref-off (D:\DATA\YCC\20160830\YCC-264-34 2018-07-12 18-34-01\071-1601.D)

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<th>Height</th>
<th>Area [mAU]</th>
<th>%</th>
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</table>

Totals : 4.52010e4 476.87428

Instrument 2 8/20/2018 9:23:58 PM

Page 1 of 2
6. Reference


