# **Supporting Information**

## Doubly Stereocontrol in Asymmetric Aldol Reaction Catalyzed by Bifunctional N-Prolyl Sulfinamides under Solvent-free Conditions

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#### **Experimental section**

#### Materials and reagents

4-Nitrobenzaldehyde, 3-Nitrobenzaldehyde, 4-Cyanobenzalde-hyde, 4-(Trifluoromethyl) benzaldehyde, 2,4-Dichlorobenz-aldehyde, 4-Chlor benzaldehyde were obtained by TCI. 2-Nitrobenzaldehyde, 2-naphthaldehyde and 4-bromobenz-aldehyde were bought from Acros. Cyclohexanone and cyclopentanone, cycloheptanone were purchased from Aldrich. Other commercially available chemicals were laboratory grade reagents from local suppliers. They were used without further purification, except for aromatic aldehyde, which was purified by distillation.

#### Methods

<sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra were recorded in CDCl<sub>3</sub> or CD<sub>3</sub>COCD<sub>3</sub> on a Bruker AV-500 spectrometer. Chemical shifts for <sup>1</sup>H NMR spectra are reported in ppm relative to residual CHCl<sub>3</sub> as internal reference (<sup>1</sup>H:  $\delta$ 7.26) downfield from TMS, chemical shifts for <sup>13</sup>C NMR spectra are reported in ppm relative to internal chloroform ( $\delta$  77.23 ppm for <sup>13</sup>C), and chemical shifts for <sup>19</sup>F NMR spectra are reported in ppm downfield from internal fluorotrichloro methane (CFCl<sub>3</sub>). Coupling constants (J) are given in Hertz (Hz). The terms m, s, d, t, q refer to multiplet, singlet, doublet, triplet, quartlet respectively; br refers to a broad signal. Infrared spectra (IR) were recorded on AVATAR 370 FT-IR spectrometer, absorbance frequencies are given at maximum of intensity in cm<sup>-1</sup>. Single-crystal XRD was performed with graphite-monochromated Mo-Ka radiation ( $\lambda = 0.71073$  Å) with a Bruker Smart ApexII CCD diffractometer at T = 273(2) K. The structures were solved by direct methods with the SHELXS-97 program and refined by full-matrix least-squares on F2 with the SHELXL-97 program. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located and included at their calculated position. Mass spectra were recorded on Agilent 5975N GC-MS. Elemental analyses were performed using an

Elemental	Vario	EL	III	instrument.	HPLC	analysis	was	performed	at	Shimadzu	1100
apparatus v	with Da	nicel	Chi	iralpak AD-H	H and C	hiralpak (	OD-H	I, PC-1 colu	ımr	1.	

Table S1. Screening results of aldol reaction with catalyst 4a additives. <sup>a</sup>							
$ \begin{array}{c} \begin{array}{c} \begin{array}{c} CHO \\ \hline \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $							
Entry	Additive	Yield <sup>b</sup>	dr <sup>c</sup>	ee <sup>e</sup>			
		(%)	anti/syn	(%)			
1	NR	97	86:14	82			
2	HCl	64	/	/			
3	HOAc	89	/	30			
4	CF <sub>3</sub> COOH	95	94:6	95			
5	CF <sub>3</sub> COOH (10 %) <sup>b</sup>	91	65:35	58			
6	S-BINOL	78	43:87	29			
7	Benzonic acid	95	58:42	30			
8	4-Nitrobenzonic acid	98	/	35			
9	3,5-Dinitrobenzonic acid	97	/	27			
10	<i>p</i> -Toluenesulfonicacid	90	/	63			

<sup>&</sup>lt;sup>a</sup> The reaction were performed with 0.5 mmol of *p*-nitrobenzaldehyde, 2.5 mmol of cyclohexanone, 5 mol% of catalyst **4a**, 5 mol% of Brønsted acid additive at 0 °C temperature in three days. <sup>b</sup> 10 % TFA was loaded. <sup>c</sup> Isolated yield. <sup>d</sup> Determined by <sup>1</sup>H NMR of the crude product. <sup>e</sup> Determined by chiral-phase HPLC analysis for *anti* isomer.

#### Representative procedure of (S, or R)-tert-butyl 2-(S)-tert-butyl sulfinyl-

#### carbamoyl) pyrrolidine-1-carboxylate 3a- 3d (Sp1)

To a solution of the (*S*, *or R*)-2-Methyl-2-propanesulfinamide (10 mmol) in dry THF (25mL) at 0 °C was added NaH (0.48 g, 12mmol, 60%) under nitrogen atmosphere. The reaction mixture was stirred for 0.5 h and then compound (*S*)-1 or (*R*)-1 (1.21 g, 0.01 mol) was added. After the resulting mixture was stirred for another 48 h, it was poured into saturated aqueous NH<sub>4</sub>Cl solution, and extracted with EtOAc ( $4 \times 30$  ml). The EtOAc extracts were successively washed with saturated aqueous NaHCO<sub>3</sub> solution and brine, dried over MgSO<sub>4</sub>, and evaporated to dryness. Purification of the residue by column chromatography (2:1 petroleum: ethyl acetate) gave a

colorless compound 3 in about 70% yield.

(S)-tert-butyl 2-((R)-tert-butylsulfinylcarbamoyl)pyrrolidine-1-carboxylate (3a)



The title compound was obtained according to **SP1** (2.48g, 78% isolated yield). White solid .<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  (ppm)):  $\delta$  = 9.47 (br, 1H), 4.33 (t, *J* = 7.8 Hz, 1H), 3.42-3.28(m, 1H), 2.54-2.48 (m, 1H), 2.04-1.97 (m, 1H), 1.46 (s, 9H), 1.28 (s, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 172.6, 156.9, 81.5, 60.2, 56.4, 47.4, 28.4, 26.9, 24.6, 22.3; elemental analysis calcd (%) for C<sub>14</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub>S: C, 52.81; H, 8.23; N, 8.80; Found: C, 52.80; H, 8.42; N, 8.90.

#### (R)-tert-butyl 2-(((S)-tert-butylsulfinyl)carbamoyl)pyrrolidine-1-carboxylate (3c)



The title compound was obtained according to **SP1** (2.29g, 72% isolated yield). White solid .<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  (ppm)):  $\delta$  = 9.55 (br, 1H), 4.35 (t, *J* = 8.1 Hz, 1H), 3.35-3.27(m, 2H), 2.54-2.49 (m, 1H), 1.91-1.87 (m, 3H), 1.46 (s, 9H), 1.24 (s, 9H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>,  $\delta$  (ppm)): 172.3, 156.4, 80.9, 60.0, 56.2, 47.2, 28.3, 26.5, 24.5, 22.0. elemental analysis calcd (%) for C<sub>14</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub>S: C, 52.81; H, 8.23; N, 8.80; Found: C, 52.87; H, 8.25; N, 8.63.

#### (R)-tert-butyl 2-((R)-tert-butylsulfinylcarbamoyl)pyrrolidine-1-carboxylate (3d)



The title compound was obtained according to **SP1** (2.42g, 76% isolated yield). White solid .<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  (ppm)):  $\delta$  = 9.45 (br, 1H), 4.29 (t, *J* = 7.5 Hz, 1H), 3.38-3.24 (m, 2H), 2.48-2.45 (m, 1H), 1.87-1.83 (m, 3H), 1.42 (s, 9H), 1.23 (s, 9H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>,  $\delta$  (ppm)): 172.6, 156.9, 81.5, 60.2, 56.4, 47.4, 28.4, 26.9, 24.5, 22.3. elemental analysis calcd (%) for C<sub>14</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub>S: C, 52.81; H, 8.23; N, 8.80; Found: C, 52.79; H, 8.36; N, 8.87.

#### Synthesis of catalyst 4a

#### (S)-N-((R)-tert-butylsulfinyl)pyrrolidine-2-carboxamide (4a)<sup>1</sup>

A mixture of **3a** (400mg, 1.3 mmol), 0.3mL HCl in 1,4-dioxane (5mL) was stirred for 2 h at room temperature. The reaction mixture were successively washed with solid NaHCO<sub>3</sub>, and then evaporated to dryness. Purification of the residue by flash column chromatography (10:1 Dichloromethane: methanol) on silica gel gave a colorless solid of organocatalyst **4a** (0.23g) in 81% yield.

#### (S)-N-((R)-tert-butylsulfinyl)pyrrolidine-2-carboxamide (4a)



The title compound was obtained according to **SP2**. White solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 7.09 (1H, s), 4.20-4.17 (dd, J = 8.5 Hz, 1H), 3.36-3.31 (m, 1H), 3.24-3.19 (m, 1H), 2.25-2.21 (m, 1H), 2.04-1.97 (m, 1H), 1.86-1.82 (m, 2H), 1.15 (s, 9H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): <math>\delta = 177.3, 61.4, 53.8, 46.9, 30.8, 25.3, 22.2;$  IR (KBr):  $v^{\sim} = 3643, 3476, 2975, 1580, 1533, 1360 \text{ cm}^{-1};$ MS (ESI): m/z 219.21 [M+H]<sup>+</sup>. elemental analysis calcd (%) for C<sub>9</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>S: C 49.51, H 8.31, N 12.83, Found: C 49.36, H 8.49, N 12.77.

#### Representative procedure of catalyst 4b-4d (SP2)

A mixture of **3** (2.0 g, 6.3 mmol), trifluoroacetic acid (1 ml) in dichloromethane (20mL) was stirred for 10 h at room temperature. After the reaction mixture were directly evaporated to

dryness, purification of the residue by flash column chromatography (4:1 dichloromethane: methanol) and recryallization from MeOH gave a white solid of organocatalyst **4b-4d** in a good yield.

#### (S)-2-((R)-tert-butylsulfinylcarbamoyl)pyrrolidinium 2,2,2-trifluoroacetate (4b)



The title compound was obtained according to **SP2** (1.51g, 72% isolated yield). White solid; m.p. 182-183 °C;  $[\alpha]_D{}^{20} = -43.2$  (c = 1.0 in MeOH); <sup>1</sup>H NMR (500 MHz, d<sub>6</sub>-DMSO):  $\delta = 8.70$ -10.72 (br, 3H), 4.43 (t, J = 8.5 Hz, 1H), 3.25 (t, J = 8.5 Hz, 2H), 2.36 (m, J = 7.5 Hz, 1H), 1.91 (m, 3H), 1.20 (s, 9H); <sup>13</sup>C NMR (125 MHz, d<sub>6</sub>-DMSO):  $\delta = 170.7$ , 159.3 (q, <sup>2</sup> $J_{C-F} = 32.5$  Hz), 118.6 (q, <sup>1</sup> $J_{C-F} = 296$  Hz), 59.7, 57.0, 46.1, 29.8, 23.8, 22.1; <sup>19</sup>F NMR (470 MHz, d<sub>6</sub>-DMSO) :  $\delta = -73.89$ (CF<sub>3</sub>, s); IR (KBr): v = 3431, 2983, 1679, 1474, 1397, 1207, 583 cm<sup>-1</sup>; elemental analysis calcd (%) for C<sub>11</sub>H<sub>19</sub>F<sub>3</sub>N<sub>2</sub>O<sub>4</sub>S: C 39.75, H 5.76, N 8.43; Found: C 39.56, H 5.89, N 8.57.

#### (R)-2-((S)-tert-butylsulfinylcarbamoyl)pyrrolidinium 2,2,2-trifluoroacetate (4c)



The title compound was obtained according to **SP2** (1.36g, 65% isolated yield). White solid; m.p.: 183-184 °C; [a]<sub>D</sub><sup>20</sup> =41.9 (c= 1.0 in MeOH); <sup>1</sup>H NMR (500 MHz, d6-DMSO):  $\delta$  = 9.75 (br, 3H), 4.38 (t, *J* = 8.4 Hz, 1H), 3.24 (t, *J* = 7.2 Hz, 2H), 2.39-2.33 (m, 1H), 1.93-1.86 (m, 3H), 1.20 (s, 9H); <sup>13</sup>C NMR (125 MHz, d6-DMSO):  $\delta$  = 170.7, 159.3 (q, <sup>2</sup>*J*<sub>C-*F*</sub> = 31.2 Hz), 118.6 (q, <sup>*I*</sup>*J*<sub>C-*F*</sub> = 296.3 Hz), 59.8, 57.0, 46.2, 29.7, 23.7, 22.1.; <sup>19</sup>F NMR (470 MHz, d6-DMSO) :  $\delta$  = -73.90 (CF3, s); IR (KBr):  $\tilde{v}$  = 3435, 2980, 1682, 1474, 1395, 1187cm<sup>-1</sup>; elemental analysis calcd (%) for C<sub>11</sub>H<sub>19</sub>F<sub>3</sub>N<sub>2</sub>O<sub>4</sub>S: C 39.75, H 5.76, N 8.43; Found: C 39.76, H 5.79, N 8.47. (*R*)-2-((*R*)-tertbutylsulfinylcarbamoyl)pyrrolidinium 2,2,2-trifluoroacetate (4d)



The title compound was obtained according to **SP2** (1.25g, 60% isolated yield). White solid; m.p: 93-95 °C;  $[a]_D^{20} = -13.4$  (c= 1.0 in MeOH);. <sup>1</sup>H NMR (500 MHz, d<sub>6</sub>-DMSO,  $\delta$  (ppm)):  $\delta =$ 9.78 (br, 3H), 4.45 (t, J = 8.0 Hz, 1H), 3.24 (t, J = 7.1 Hz, 2H), 2.37-2.33 (m, 1H), 1.90-1.80 (m, 3H), 1.19 (s, 9H); <sup>13</sup>C NMR (125 MHz, d<sub>6</sub>-DMSO,  $\delta$  (ppm)): 171.0 159.7 (q, <sup>2</sup> $J_{C-F} = 32.5$  Hz), 118.6 (q, <sup>1</sup> $J_{C-F} = 296.3$  Hz), 59.7, 56.8, 46.0, 30.1, 23.8, 22.1. <sup>19</sup>F NMR (470 MHz, d<sub>6</sub>-DMSO,  $\delta$ (ppm)): -73.91 (CF<sub>3</sub>, s). IR (KBr): v = 3433, 2982, 1680, 1474, 1396, 1197cm<sup>-1</sup>; elemental analysis calcd (%) C<sub>11</sub>H<sub>19</sub>F<sub>3</sub>N<sub>2</sub>O<sub>4</sub>S: C, 39.75; H, 5.76; N, 8.43; Found: C, 39.52; H, 5.74; N, 8.39.

#### General Procedure for Aldol Reaction of Ketones with Aldehydes (SP3)

A catalytic amount of *N*-prolyl sulfinamide was added to a vial containing 4-nitrobenzaldehyde (0.0760 g, 0.5 mmol, 1.0 equiv), cyclohexanone (0.26 mL, 2.5mmol, 5 equiv) in a closed system. The reaction mixture was stirred at indicated temperature and subsequently poured into an extraction funnel that contained brine (10 ml). The aqueous phase was extracted with ethyl acetate ( $3 \times 15$  ml). The combined organic extracts were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The crude aldol product was purified by silica-gel column chromatography to give the aldol product **7a-7o**.

All the aldol products in the paper are known compounds that exhibited spectroscopic data identical to those reported in the literature.

#### Spectra data of aldol products

#### (2S, 1'R)-2-(Hydroxy-(p-nitrophenyl)methyl)cyclohexan-1-one (7a1)<sup>2,3</sup>





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Prepared according to **SP3** (241mg, 97% isolated yield). Orangish solid. Purified by flash chromatography (Hex/EtOAc, 3:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$  (ppm)): 8.21 (2H, d, J = 8.5 Hz), 7.51 (2H, m), 4.90 (1H, dd, J = 8.0, 3.0 Hz), 4.06 (1H, d, J = 3.0 Hz), 2.59-2.58 (1H, m), 2.49-2.37 (1H, m), 2.36-2.35 (1H, m), 2.13-2.10 (1H, m), 1.84-1.81 (1H, m), 1.68-1.56 (3H, m), 1.42-1.36 (1H, m). Chiral HPLC conditions: Daicel Chiralpak AD-H. n-Hexane: *i*-PrOH, 90:10, 1 mL/ min, 254 nm: *anti*: *t*R (major) = 30.54 min; *t*R (minor) = 23.09 min. *syn*: *t*R (major) = 20.66 min; *t*R (minor) = 18.01 min.

(2R, 1'S)-2-(Hydroxy-(p-nitrophenyl)methyl)cyclohexan-1-one (7a2)<sup>2,3</sup>



Prepared according to **SP3** (237mg, 95% isolated yield). Orangish solid. Purified by flash chromatography (Hex/EtOAc, 3:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$  (ppm)): 8.20 (2H, d, J = 9.0 Hz), 7.52 (2H, d, J = 8.5 Hz),4.90 (1H, dd, J = 8.0, 3.0 Hz), 4.08 (1H, d, J = 8.0 Hz), 3.17-3.16 (1H, m), 2.61-2.58 (1H, m), 2.51-2.49 (1H, m), 2.37-2.36 (1H, m), 2.13-2.10 (1H, m), 1.84-1.82 (1H, m), 1.69-1.55 (2H, m), 1.40-1.37 (1H, m). Chiral HPLC conditions: Daicel Chiralpak AD-H. n-Hexane: *i*-PrOH, 90:10, 1 mL/ min, 254 nm: *anti*:  $t_R$  (major) = 23.34 min;  $t_R$  (minor) = 31.05 min. *syn*:  $t_R$  (major) = 18.32 min;  $t_R$  (minor) = 20.94 min.

#### (2S, 1'R)-2-(Hydroxy-(m-nitrophenyl)methyl)cyclohexan-1-one (7b1)<sup>3,4</sup>



Prepared according to **SP3** (234mg, 94% isolated yield). Yellow solid. Purified by flash chromatography (Hex/EtOAc, 3:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, δ (ppm)): 8.21 (1H, s), 8.17 (1H, d, *J* = 8.0 Hz), 7.68 (1H, d, *J* = 8.0 Hz), 7.53 (1H, t, *J* = 8.0 Hz), 4.90 (1H, dd, *J* = 8.5, 3.0 Hz),

4.11 (1H, d, J = 3.5 Hz), 2.62--2.61 (1H, m), 2.49-2.48 (1H, m), 2.38-2.36 (1H, m), 2.11-2.10 (1H, m), 1.85-1.82 (1H, m), 1.69-1.57 (3H, m), 1.40-1.37 (1H, m). Chiral HPLC conditions: Daicel Chiralpak AD-H. n-Hexane: *i*-PrOH, 90:10, 1 mL/ min, 254 nm: *anti*:  $t_R$  (major) = 19.58 min;  $t_R$  (minor) = 24.43 min. *syn*:  $t_R$  (major) = 16.44 min;  $t_R$  (minor) = 17.35 min.

#### (2R, 1'S)-2-(Hydroxy-(m-nitrophenyl)methyl)cyclohexan-1-one (7b2)<sup>3,4</sup>



Prepared according to **SP3** (229mg, 92% isolated yield). Yellow solid. Purified by flash chromatography (Hex/EtOAc, 3:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$  (ppm)): 8.21 (1H, s), 8.17 (1H, d, *J* = 8.5 Hz), 7.68 (1H, d, *J* = 7.5 Hz), 7.53 (1H, t, *J* = 7.5 Hz), 4.90 (1H, dd, *J* = 8.5, 2.0 Hz), 4.11 (1H, d, *J* = 3.0 Hz), 2.62-2.51 (1H, m), 2.49-2.48 (1H, m), 2.40-2.37 (1H, m), 2.13-2.10 (1H, m), 1.84-1.82 (1H, m), 1.68-1.58 (3H, m), 1.40-1.38 (1H, m). Chiral HPLC conditions: Daicel Chiralpak AD-H. n-Hexane: *i*-PrOH, 90:10, 1 mL/ min, 254 nm: *anti*: *t*<sub>R</sub> (major) = 24.05 min; *t*<sub>R</sub> (minor) = 19.04 min. *syn*: *t*<sub>R</sub> (major) = 17.05 min; *t*<sub>R</sub> (minor) = 16.05 min.

#### (2S, 1'R)-2-(Hydroxy-(o-nitrophenyl)methyl)cyclohexan-1-one (7c1)<sup>2,3,4</sup>



Prepared according to **SP3** (237mg, 95% isolated yield). Yellow solid. Purified by flash chromatography (Hex/EtOAc, 3:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$  (ppm)): 7.81 (1H, d, J = 9.0 Hz), 7.74 (1H, d, J = 9.0 Hz), 7.60 (1H, t, J = 7.0 Hz), 7.40 (1H, t, J = 7.5 Hz), 5.42 (1H, d, J = 7.0 Hz), 4.20 (1H, s), 2.75-2.73 (1H, m), 2.40-2.31 (2H, m), 2.05-2.04 (1H, m), 1.82-1.58 (5H, m). Chiral HPLC conditions: Daicel Chiralpak AD-H. n-Hexane: *i*-PrOH, 95:5, 1 mL/min, 254 nm: *anti*:  $t_{\rm R}$  (major) = 31.54 min;  $t_{\rm R}$  (minor) = 33.26 min.

#### (2R, 1'S)-2-(Hydroxy-(o-nitrophenyl)methyl)cyclohexan-1-one (7c2)<sup>2,3,4</sup>



Prepared according to **SP3** (231mg, 93% isolated yield). Yellow solid. Purified by flash chromatography (Hex/EtOAc, 3:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$  (ppm)): 7.83 (1H, dd, J = 15, 1.0 Hz), 7.75 (1H, d, J = 1.5 Hz), 7.64-7.61 (1H, m), 7.44-7.40 (1H, m), 5.44 (1H, dd, J = 7.0, 5.0 Hz), 4.20 (1H, d, J=4.5Hz), 2.76-2.74 (1H, m), 2.46-2.32 (2H, m), 1.75-1.74 (1H, m), 1.70-1.60 (5H, m). Chiral HPLC conditions: Daicel Chiralpak AD-H. n-Hexane: *i*-PrOH, 95:5, 1 mL/ min, 254 nm: *anti*:  $t_{\rm R}$  (major) = 33.39 min;  $t_{\rm R}$  (minor) = 31.48 min.





Prepared according to **SP3** (217mg, 95% isolated yield). White solid. Purified by flash chromatography (Hex/EtOAc, 3:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$  (ppm)): 7.65 (2H, m), 7.45 (2H, d, J = 8.5 Hz), 4.84 (1H, d, J = 8.1 Hz), 4.05 (1H, d, J = 2.5 Hz), 2.57-2.47 (2H, m), 2.36-2.35(1H, m), 2.10-2.09 (1H, m), 1.84-1.81 (1H, m), 1.57-1.54 (3H, m), 1.36-1.33 (1H, m). Chiral HPLC conditions: Daicel Chiralpak AD-H. n-Hexane: *i*-PrOH, 90:10, 1.0 mL/ min, 254 nm: *anti*:  $t_{\rm R}$  (major) = 27.97 min;  $t_{\rm R}$  (minor) = 21.97 min. *syn*:  $t_{\rm R}$  (major) = 16.23 min;  $t_{\rm R}$  (minor) = 19.04 min.

(2R, 1'S)-2-(Hydroxy-(p-cyanophenyl)methyl)cyclohexan-1-one (7d2)<sup>5</sup>



Prepared according to **SP3** (218mg, 95% isolated yield). White solid. Purified by flash chromatography (Hex/EtOAc, 3:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$  (ppm)): 7.65 (2H, d, J = 7.0 Hz), 7.45 (2H, d, J = 8.0Hz), 4.84 (1H, d, J = 8.5 Hz), 4.05 (1H, s), 2.56-2.47 (2H, m), 2.36-2.34 (1H, m), 2.10-2.08 (1H, m), 1.84-1.80 (1H, m), 1.57-1.54 (3H, m), 1.38-1.33 (1H, m). Chiral HPLC conditions: Daicel Chiralpak AD-H. n-Hexane: *i*-PrOH, 90:10, 1.0 mL/ min, 254 nm: *anti*:  $t_R$  (major) = 22.1 min;  $t_R$  (minor) = 27.40 min. *syn*:  $t_R$  (major) = 19.01 min;  $t_R$  (minor) = 16.25 min.





7e1

Prepared according to **SP3** (180mg, 66% isolated yield). Yellow solid. Purified by flash chromatography (Hex/EtOAc, 3:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$  (ppm)): 7.61 (2H, d, J = 8.0 Hz), 7.43 (2H, d, J = 8.0 Hz), 4.85 (1H, d, J = 8.5 Hz), 4.05 (1H, s), 2.60-2.47 (1H, m), 2.37-2.35 (1H, m), 2.11-2.08 (1H, m), 1.81-1.79 (1H, m), 1.67-1.65 (2H, m), 1.58-1.53 (2H, m). Chiral HPLC conditions: Daicel Chiralpak AD-H. n-Hexane: *i*-PrOH, 90:10, 1 mL/min, 254 nm: *anti*:  $t_R$  (major) = 12.76 min;  $t_R$  (minor) = 10.36 min.

#### (2R, 1'S)-2-(Hydroxy-(p-(trifluoromethyl)phenyl)methyl)cyclohexan-1-one (7e2)<sup>2,5,6</sup>



7e2

Prepared according to **SP3** (193mg, 71% isolated yield). Yellow solid. Purified by flash chromatography (Hex/EtOAc, 3:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$  (ppm)): 7.61 (2H, d, J = 8.0 Hz), 7.43 (2H, d, J = 8.0 Hz), 4.85 (1H, d, J = 8.5 Hz), 4.05 (1H, d, J = 3.0 Hz), 2.60-2.47 (2H, m), 2.40-2.35 (1H, m), 2.11-2.08 (1H, m), 1.83-1.80 (1H, m), 1.60-1.55(4H, m). Chiral HPLC conditions: Daicel Chiralpak AD-H. n-Hexane: *i*-PrOH, 90:10,1 mL/min, 254 nm: *anti*:  $t_R$  (major) = 10.40 min;  $t_R$  (minor) = 12.65 min.

(2S, 1'R)-2-(Hydroxy-(2,4-dichlorophenyl)methyl)cyclohexan-1-one (7f1)<sup>7,8,9</sup>



Prepared according to **SP3** (180mg, 66% isolated yield). Yellow solid. Purified by flash chromatography (Hex/EtOAc, 3:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$  (ppm)): 7.50 (1H, d, J = 8.5 Hz), 7.35 (1H, d, J = 2.0 Hz), 7.30-7.28 (1H, m), 5.29 (1H, dd, J = 8.0, 4.0 Hz), 4.05 (1H, d, J = 4.0 Hz), 2.65-2.60 (1H, m), 2.48-2.45 (1H, m), 2.34-2.33 (1H, m), 2.11-2.10 (1H, m), 1.84-1.67 (1H, m), 1.66-1.58 (4H, m). Chiral HPLC conditions: Daicel Chiralpak Phenomenex amylose-2 column. n-Hexane: *i*-PrOH, 90:10, 1 mL/ min, 220nm: *anti*:  $t_R$  (major) = 13.39 min;  $t_R$  (minor) = 17.57 min. *syn*:  $t_R$  (major) = 8.74 min;  $t_R$  (minor) = 7.36 min.

#### (2R, 1'S)-2-(Hydroxy-(2,4-dichlorophenyl)methyl)cyclohexan-1-one (7f2)<sup>7,8,9</sup>

Prepared according to **SP3** (190.4mg, 70% isolated yield). Yellow solid. Purified by flash chromatography (Hex/EtOAc, 3:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$  (ppm)): 7.50 (1H, d, J = 8.5 Hz), 7.35 (1H, d, J = 2.0 Hz), 7.30-7.28 (1H, m), 5.29 (1H, dd, J = 8.0, 4.0 Hz), 4.05 (1H, d, J = 4.0 Hz), 2.65-2.60 (1H, m), 2.48-2.45 (1H, m), 2.34-2.32 (1H, m), 2.11-2.08 (1H, m), 1.85-1.66 (1H, m), 1.66-1.58 (4H, m). Chiral HPLC conditions: Daicel Chiralpak Phenomenex amylose-2 column. n-Hexane: *i*-PrOH, 90:10, 1 mL/ min, 220nm: *anti*:  $t_R$  (major) = 17.34 min;  $t_R$  (minor) = 13.87min. *syn*:  $t_R$  (major) = 7.43 min;  $t_R$  (minor) = 8.85 min.  $t_R$  (minor) = 13.87min. *syn*:  $t_R$  (minor) = 8.85 min.

(2S, 1'R)-2-(Hydroxy-(p-bromophenyl)methyl)cyclohexan-1-one (7g1)<sup>4,5,10</sup>



Prepared according to **SP3** (150mg, 53% isolated yield). Yellow solid. Purified by flash chromatography (Hex/EtOAc, 3:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$  (ppm)): 7.47 (2H, d, J = 8.0 Hz), 7.20 (2H, d, J = 8.0 Hz), 4.75 (1H, d, J = 9.0 Hz), 3.99 (1H, d, J = 2.0 Hz), 2.56-2.46 (2H, m), 2.38-2.34 (1H, m), 2.11-2.07 (1H, m), 1.81-1.78 (1H, m), 1.57-1.55 (3H, m), 1.30-1.27 (1H, m). Chiral HPLC conditions: Daicel Ch iralpak AD-H. n-Hexane: *i*-PrOH, 95:5, 1.0 mL/ min, 220 nm: *anti*:  $t_{\rm R}$  (major) = 28.76 min;  $t_{\rm R}$  (minor) = 24.79 min. *syn*: (major) = 13.81 min;  $t_{\rm R}$  (minor) = 16.94 min.





Prepared according to **SP3** (127mg, 45% isolated yield). Yellow solid. Purified by flash chromatography (Hex/EtOAc, 3:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$  (ppm)): 7.47 (2H, d, J =8.5Hz), 7.20 (2H, d, J = 8.5Hz), 4.75 (1H, d, J = 8.5 Hz), 3.99 (1H, s), 2.56-2.46 (2H, m), 2.37-2.34 (1H, m), 2.11-2.07 (1H, m), 1.81-1.78 (1H, m), 1.59-1.55 (3H, m), 1.30-1.27 (1H, m). Chiral HPLC conditions: Daicel Chiralpak AD-H column. n-Hexane: *i*-PrOH, 95:5, 1.0 mL/ min, 220 nm: *anti*:  $t_{\rm R}$  (major) = 25.18 min;  $t_{\rm R}$  (minor) = 29.28 min. *syn*: (major) = 17.24 min;  $t_{\rm R}$  (minor) = 14.09 min.

#### (2S, 1'R)-2-(Hydroxy-(p-chlorophenyl)methyl)cyclohexan-1-one (7h1)<sup>9,10</sup>



Prepared according to **SP3** (95mg, 40% isolated yield). Yellow solid. Purified by flash chromatography (Hex/EtOAc, 3:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$  (ppm)): 7.32 (2H, d, J = 8.5 Hz), 7.26 (2H, t, J = 7.0 Hz), 4.76 (1H, dd, J = 8.5, 2.0 Hz), 3.99 (1H, d, J = 3.0 Hz), 2.55-2.34 (3H, m), 2.11-2.07 (1H, m),1.81-1.78 (1H, m), 157-1.52 (3H, m), 1.30-1.28 (1H, m). Chiral HPLC conditions: Daicel Chiralpak AD-H. n-Hexane: *i*-PrOH, 90:10,1 mL/min, 220 nm: *anti*:  $t_R$  (major) = 16.19 min;  $t_R$  (minor) = 14.37 min. *syn*: (major) = 9.21 min;  $t_R$  (minor) = 10.67 min.

#### .(2R, 1'S)-2-(Hydroxy-(p-chlorophenyl)methyl)cyclohexan-1-one (7h2)<sup>9,10</sup>



Prepared according to **SP3** (90.4mg, 38% isolated yield). Yellow solid. Purified by flash chromatography (Hex/EtOAc, 3:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$  (ppm)): 7.32 (2H, d, J = 8.5 Hz), 7.26 (2H, d, J = 8.0 Hz), 4.76 (1H, d, J = 8.0 Hz), 3.99 (1H, s), 2.55-2.32 (3H, m), 2.11-2.08 (1H, m), 1.85-1.78(1H, m), 1.64-1.55 (3H, m), 1.33-1.25 (1H, m). Chiral HPLC conditions: Daicel Chiralpak AD-H. n-Hexane: *i*-PrOH, 90:10,1 mL/ min, 220 nm: *anti*:  $t_R$  (major) = 14.27 min;  $t_R$  (minor) = 16.12 min. *syn*: (major) = 10.62 min;  $t_R$  (minor) = 9.17 min.

#### (2S, 1'R)-2-(Hydroxy(naphthalen-2-yl)methyl)cyclohexan-1-one (7i1)<sup>9,10</sup>





Prepared according to **SP3** (114mg, 45% isolated yield). Yellow solid. Purified by flash chromatography (Hex/EtOAc, 3:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$  (ppm)): 7.85-7.82 (3H, m), 7.75 (1H, s), 7.48-7.47 (3H, m), 4.96 (1H, dd, J = 9.0, 2.0 Hz), 4.06 (1H,d, J = 2.0 Hz), 2.74-2.69 (1H, m), 2.52 (1H, d, J = 8.5 Hz), 2.39-2.37 (1H, d, J = 8.5 Hz), 2.10-2.07 (1H, m), 1.74-1.51 (5H, m). Chiral HPLC conditions: Daicel Chiralpak Phenomenex amylose-2 column. n-Hexane: *i*-PrOH, 90:10,1 mL/min, 254 nm: *anti*:  $t_R$  (major) = 33.04 min;  $t_R$  (minor) = 44.80 min. *syn*: (major) = 19.58 min;  $t_R$  (minor) = 18.21 min.

(2S, 1'R)-2-(Hydroxy(naphthalen-2-yl)methyl)cyclohexan-1-one (7i2)<sup>9,10</sup>



Prepared according to **SP3** (127mg, 50% isolated yield). Yellow solid. Purified by flash chromatography (Hex/EtOAc, 3:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$  (ppm)): 7.82 (3H, t, J = 3.5 Hz), 7.75 (1H, s), 7.49-7.47 (3H, m), 4.96 (1H, dd, J = 9.0, 2.5 Hz), 4.06 (1H, d, J = 2.5 Hz), 2.75-2.69 (1H, m), 2.52-2.49 (1H, t, J = 4.5 Hz), 2.40-2.39 (1H, m), 2.10-2.07 (1H, m), 1.58-1.33 (5H, m). Chiral HPLC conditions: Daicel Chiralpak Phenomenex amylose-2 column. n-Hexane: *i*-PrOH, 90:10,1 mL/ min, 254 nm: *anti*:  $t_R$  (major) = 42.66min;  $t_R$  (minor) = 32.91 min. *syn*: (major) = 17.52 min;  $t_R$  (minor) = 18.81 min.

(2S, 1'R)-2-(Hydroxy(phenyl)methyl)cyclohexan-1-one (7j1)<sup>3,4,9,10</sup>



Prepared according to **SP3** (163mg, 80% isolated yield). Yellow solid. Purified by flash chromatography (Hex/EtOAc, 6:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, δ (ppm)): 7.35-7.29 (5H, m), 4.80 (1H, d, *J* =8.5 Hz), 3.97 (1H, s), 2.62-2.56 (1H, m), 2.47-2.46 (1H, m), 2.36-2.35 (1H, m), 2.08-2.07 (1H, m), 1.77-1.76(1H, m), 1.67-1.53 (2H, m), 1.33-1.25 (2H, m). Chiral HPLC conditions: **16**/94

Daicel Chiralpak OJ-H. n-Hexane: *i*-PrOH, 90:10, 1.0 mL/ min, 220 nm: *anti*:  $t_R$  (major) = 15.84 min;  $t_R$  (minor) = 23.32 min. *syn*: (major) = 13.05 min;  $t_R$  (minor) = 14.41 min.

#### (2R, 1'S)-2-(Hydroxy(phenyl)methyl)cyclohexan-1-one (7j2) 3,4,9,10



Prepared according to **SP3** (170mg, 83% isolated yield). Yellow solid. Purified by flash chromatography (Hex/EtOAc, 6:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$  (ppm)): 7.35-7.31 (5H, m), 4.80 (1H, dd, J = 8.5, 2.0 Hz), 3.97 (1H, d, J = 3.0 Hz), 2.62-2.60 (1H, m), 2.47-2.46 (1H, m), 2.38-2.34 (1H, m), 2.08-2.07 (1H, m), 1.79-1.76 (1H, m), 1.67-1.55 (2H, m), 1.31-1.28 (2H, m). Chiral HPLC conditions: Daicel Ch iralpak OJ-H. n-Hexane: *i*-PrOH, 90:10, 1.0 mL/ min, 220 nm: *anti*:  $t_{\rm R}$  (major) =21.43 min;  $t_{\rm R}$  (minor) = 16.00 min. *syn*: (major) = 14.45 min;  $t_{\rm R}$  (minor) = 13.09 min.

#### (2S, 1'R)-2-(Hydroxy-(p-methoxyphenyl)methyl)cyclohexan-1-one(7k1)<sup>9,10,11</sup>



Prepared according to **SP3** (84mg, 36% isolated yield). Yellow solid. Purified by flash chromatography (Hex/EtOAc, 6:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$  (ppm)): 7.23 (2H, s), 6.88-6.86 (2H, m), 4.74 (1H, dd, J = 9.0, 2.0 Hz), 3.92 (1H, t, J = 2.0 Hz), 3.80 (3H, s), 2.59-2.58 (1H, m), 2.50-2.46 (1H, m), 2.36-2.35 (1H, m), 2.10-2.06 (1H, m), 1.80-1.78 (1H, m), 1.70-1.57 (3H, m), 1.28-1.24 (1H, m). Chiral HPLC conditions: Daicel Ch iralpak OJ-H. n-Hexane: *i*-PrOH, 90:10, 1.0 mL/ min, 254 nm: *anti*:  $t_{\rm R}$  (major) = 18.50 min;  $t_{\rm R}$  (minor) = 27.22 min. *syn*: (major) = 9.28 min;  $t_{\rm R}$  (minor) = 7.50 min.

#### (2R, 1'S)-2-(Hydroxy-(p-methoxyphenyl)methyl)cyclohexan-1-one(7k2)<sup>9,10,11</sup>



Prepared according to **SP3** (140mg, 60% isolated yield). Yellow solid. Purified by flash chromatography (Hex/EtOAc, 6:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$  (ppm)): 7.24 (2H, q, J = 2.0 Hz), 6.88 (2H, dd, J = 7.0, 2.0 Hz), 4.74 (1H, d, J = 9.0 Hz), 3.89 (1H, t, J = 5.5 Hz), 3.80 (3H, s), 2.61-2.58 (1H, m), 2.50-2.46 (1H, m), 2.38-2.35 (1H, m), 2.10-2.07 (1H, m), 1.80-1.77 (1H, m), 1.70-1.57 (3H, m), 1.28-1.24 (1H, m). Chiral HPLC conditions: Daicel Ch iralpak OJ-H. n-Hexane: *i*-PrOH, 90:10, 1.0 mL/ min, 254 nm: *anti*:  $t_R$  (major) =29.78 min;  $t_R$  (minor) = 19.90 min. *syn*: (major) = 7.46 min;  $t_R$  (minor) = 9.62 min.

#### (2S, 1'R)-2-(Hydroxy-(furan-2-yl)propyl)cyclohexan-1-one (7l1)<sup>10</sup>



Prepared according to **SP3** (136mg, 70% isolated yield). Yellow solid. Purified by flash chromatography (Hex/EtOAc, 3:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$  (ppm)): 7.34 (1H, t, *J* = 1.0 Hz), 6.33 (1H, m), 6.27 (1H, dd, *J* = 6.5, 3.0 Hz), 4.83 (1H, d, J = 8.5 Hz), 3.89 (1H, s), 2.91-2.80 (1H, m), 2.45-2.36 (2H, m), 2.11-2.10 (1H, m), 1.84-1.82 (2H, m), 1.67-1.65 (2H, m), 1.42-1.32 (1H, m). Chiral HPLC conditions: Daicel Ch iralpak AD-H. n-Hexane: *i*-PrOH, 90:10, 0.5 mL/min, 210 nm: *anti*:  $t_R$  (major) =30.63 min;  $t_R$  (minor) = 34.01 min. *syn*: (major) = 23.42 min;  $t_R$  (minor) = 22.13 min.

#### (2R, 1'S)-2-(Hydroxy-(furan-2-yl)propyl)cyclohexan-1-one (7l2)<sup>10</sup>



Prepared according to SP3 (120mg, 62% isolated yield). Yellow solid. Purified by flash

chromatography (Hex/EtOAc, 3:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$  (ppm)): 7.38-7.34 (1H, m), 6.32 (1H, dd, J = 3.5, 3.0 Hz), 6.28 (1H, d, J = 3.0 Hz), 4.83 (1H, dd, J = 8.0, 3.5 Hz), 3.89 (1H, d, J = 1.5 Hz), 2.93-2.89 (1H, m), 2.45-2.36 (2H, m), 2.11-2.10 (1H, m), 1.84-1.82 (2H, m), 1.67-1.61 (2H, m), 1.36-1.33 (1H, m). Chiral HPLC conditions: Daicel Chiralpak AD-H. n-Hexane: *i*-PrOH, 90:10,0.5 mL/ min, 210 nm: *anti*:  $t_R$  (major) =34.19 min;  $t_R$  (minor) = 30.80 min. *syn*: (major) = 22.20 min;  $t_R$  (minor) = 23.51 min.

*R*-4-hydroxy-4-(4-nitrophenyl)butan-2-one (7m1)<sup>9,10</sup>



Prepared according to **SP3** (66mg, 40% isolated yield). Orangish solid. Purified by flash chromatography (Hex/EtOAc, 3:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$  (ppm)): 8.20 (2H, d, J = 8.5 Hz), 7.54 (2H, d, J = 8.5 Hz), 5.28-5.25 (1H, m), 3.57 (1H, d, J = 3.5 Hz), 2.86 (2H, t, J = 6.0 Hz), 2.22 (3H, s). Chiral HPLC conditions: Daicel Chiralpak OJ-H. n-Hexane: *i*-PrOH, 90:10, 1.0 mL/min, 254 nm:  $t_R$  (major) = 28.47 min;  $t_R$  (minor) = 32.95 min.

#### (2S, 1'S)-2-(Hydroxy-(p-nitrophenyl)methyl)cyclopentan-1-one (7n1)<sup>9,10</sup>



Prepared according to **SP3** (223mg, 95% isolated yield). Yellow solid. Purified by flash chromatography (Hex/EtOAc, 3:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$  (ppm)): 8.21 (2H, dd, J = 9.0, 2.5 Hz), 7.52 (2H, t, J = 9.0 Hz), 4.85 (1H, d, J = 9.5 Hz), 4.75 (1H, s), 2.48-2.16 (3H, m), 2.15-2.03 (1H, m), 1.74-1.61 (3H, m). Chiral HPLC conditions: Daicel Chiralpak AD-H. n-Hexane: *i*-PrOH, 90:10, 1.0 mL/min, 254 nm: *syn*:  $t_R$  (major) =21.23 min;  $t_R$  (minor) = 24.01 min.

#### (2S, 1'R)-2-(Hydroxy-(p-nitrophenyl)methyl)cycloheptan-1-one (701)<sup>10</sup>



Prepared according to **SP3** (118mg, 45% isolated yield). Yellow solid. Purified by flash chromatography (Hex/EtOAc, 6:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$  (ppm)): 8.20 (2H, d, *J* = 8.5 Hz), 7.53 (2H, d, *J* = 8.5 Hz), 4.92 (1H, dd, *J* = 7.5, 5.0 Hz), 3.72 (1H, d, *J* = 5.0 Hz), 2.98-2.97 (1H, m), 2.50-2.48 (2H, m), 1.88-1.71 (4H, m), 1.38-1.25 (4H, m). Chiral HPLC conditions: Daicel Chiralpak AD-H. n-Hexane: *i*-PrOH, 90:10, 1.0 mL/min, 220 nm: *anti*:  $t_R$  (major) = 19.84 min;  $t_R$  (minor) = 9.96 min. *syn*:  $t_R$  (major) = 8.28 min;  $t_R$  (minor) = 7.13min.

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### <sup>1</sup>H and <sup>13</sup>C NMR spectra

(S)-tert-butyl 2-(((R)-tert-butylsulfinyl)carbamoyl)pyrrolidine-1-carboxylate (3a)





(R)-tert-butyl 2-(((S)-tert-butylsulfinyl)carbamoyl)pyrrolidine-1-carboxylate (3c)









(S)-2-((R)-tert-butylsulfinylcarbamoyl)pyrrolidinium 2,2,2-trifluoroacetate (4b)





(R)-2-((S)-tert-butylsulfinylcarbamoyl)pyrrolidinium 2,2,2-trifluoroacetate (4c)





(R)-2-((R)-tert-butylsulfinylcarbamoyl)pyrrolidinium 2,2,2-trifluoroacetate (4d)











(2R, 1'S)-2-(Hydroxy-(p-nitrophenyl)methyl)cyclohexan-1-one (7a2)



(2S, 1'R)-2-(Hydroxy-(m-nitrophenyl)methyl)cyclohexan-1-one (7b1)



(2R, 1'S)-2-(Hydroxy-(m-nitrophenyl)methyl)cyclohexan-1-one (7b2)

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(2S, 1'R)-2-(Hydroxy-(o-nitrophenyl)methyl)cyclohexan-1-one (7c1)





(2S, 1'R)-2-(Hydroxy-(p-cyanophenyl)methyl)cyclohexan-1-one (7d1)



(2R, 1'S)-2-(Hydroxy-(p-cyanophenyl)methyl)cyclohexan-1-one (7d2)



(2S, 1'R)-2-(Hydroxy-(p-(trifluoromethyl)phenyl)methyl)cyclohexan-1-one (7e1)



(2R, 1'S)-2-(Hydroxy-(p-(trifluoromethyl)phenyl)methyl)cyclohexan-1-one (7e2)



(2S, 1'R)-2-(Hydroxy-(2,4-dichlorophenyl)methyl)cyclohexan-1-one (7f1)






(2S, 1'R)-2-(Hydroxy-(p-bromophenyl)methyl)cyclohexan-1-one (7g1)



(2R, 1'S)-2-(Hydroxy-(p-bromophenyl)methyl)cyclohexan-1-one (7g2)



(2S, 1'R)-2-(Hydroxy-(p-chlorophenyl)methyl)cyclohexan-1-one (7h1)



.(2R, 1'S)-2-(Hydroxy-(p-chlorophenyl)methyl)cyclohexan-1-one (7h2)



(2S, 1'R)-2-(Hydroxy(naphthalen-2-yl)methyl)cyclohexan-1-one (7i1)



(2S, 1'R)-2-(Hydroxy(naphthalen-2-yl)methyl)cyclohexan-1-one (7i2)



(2S, 1'R)-2-(Hydroxy(phenyl)methyl)cyclohexan-1-one (7j1)



(2R, 1'S)-2-(Hydroxy(phenyl)methyl)cyclohexan-1-one (7j2)



(2S, 1'R)-2-(Hydroxy-(p-methoxyphenyl)methyl)cyclohexan-1-one (7k1)



(2R, 1'S)-2-(Hydroxy-(p-methoxyphenyl)methyl)cyclohexan-1-one (7k2)



(2S, 1'R)-2-(Hydroxy-(furan-2-yl)propyl)cyclohexan-1-one (711)



(2R, 1'S)-2-(Hydroxy-(furan-2-yl)propyl)cyclohexan-1-one (7l2)



R-4-hydroxy-4-(4-nitrophenyl)butan-2-one (7m1)







(2S, 1'R)-2-(Hydroxy-(p-nitrophenyl)methyl)cycloheptan-1-one (701)



==== Shimadzu LCsolution Analysis Report ====





Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %
1	19.245	1192818	44336	6.807	9.669
2	21.882	1188146	37174	6.780	8.107
3	24.402	7580015	214139	43.254	46.700
4	32.086	7563349	162893	43.159	35.524
Total		17524328	458542	100.000	100.000



Batch Name

Report Name

Modified Date

Acquisition Date

: Default.lcr

: 2012-9-11 14:37:18 : 2012-9-11 15:16:04

Operator	: Admin
Sample	; gw20120911-23
Sample ID	: gw20120911-23
Vial#	:
Inj. Volume	: 10 uL
Data Name	: gw20120911-23.lcd
Method Name	: yuyu.lcm

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Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %
1	18.012	365192	14433	1.699	2.917
2	20.664	826355	26766	3.845	5.410
3	23.088	479248	14525	2.230	2.936
4	30.537	19821749	439006	92.226	88.736
Total		21492544	494731	100.000	100.000







Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %
1	18.324	804005	30737	3.041	4.050
2	20.944	773048	24858	2.924	3.276
3	23.388	24066939	684935	91.029	90.253
4	31.046	794882	18378	3.006	2.422
Total		26438873	758908	100.000	100.000







Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %
1	16.007	8146128	351281	18.154	21.861
2	17.045	8316086	334273	18.533	20.802
3	19.042	14197192	514061	31.640	31.990
4	23.964	14212260	407306	31.673	25.347
Total		44871666	1606921	100.000	100.000





Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %
1	16.442	738789	31135	1.376	1.709
2	17.352	491419	18016	0.916	0.989
3	19.577	51710747	1748398	96.346	95.944
4	24.434	731029	24762	1.362	1.359
Total	0	53671984	1822311	100.000	100.000







Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %
1	16.048	939678	41581	1.925	2.901
2	17.048	1156102	48421	2.368	3.378
3	19.042	1470676	59514	3.013	4.152
4	24.047	45248618	1283855	92.694	89.569
Total		48815075	1433371	100.000	100.000







1 PDA 多色谱图 1/254nm 4nm

Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %
1	32.226	4020473	91346	49.459	50.988
2	34.167	4108503	87807	50.541	49.012
Total		8128976	179153	100.000	100.000





Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %
1	31.542	20276157	461419	97.660	97.451
2	33.260	485912	12068	2.340	2.549
Total		20762069	473486	100.000	100.000





PDA Ch1 254nm 4nm							
Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %		
1	31.480	585185	14566	5.088	5.813		
2	33.394	10915802	236027	94.912	94.187		
Total		11500987	250593	100.000	100.000		





Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %
1	16.265	1243500	50112	31.135	37.777
2	19.030	1277100	42627	31.976	32.135
3	21.970	730410	21925	18.288	16.528
4	27.347	742922	17988	18.601	13.560
Total	•	3993932	132651	100.000	100.000



Operator Sample Sample ID Vial# Inj. Volume Data Name Method Name : Admin GW20120927-35 GW20120927-35 : 10 uL GW20120927-35.lcd

: yuyu.icm

Batch Name : Default.lcr Report Name 2012-9-27 13:57:47 2012-9-27 14:43:09 Acquisition Date Modified Date

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Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %
1	16.234	771504	30879	3.763	7.470
2	19.037	482813	16200	2.355	3.919
3	21.969	511052	15079	2.493	3.648
4	27.966	18737015	351220	91.389	84.963
Total		20502.384	413377	100.000	100.000





Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %
1	16.250	326938	13148	2.935	4.044
2	19.006	1291612	43109	11.597	13.260
3	22.101	8765235	250485	78.700	77.049
4	27.402	753721	18355	6.767	5.646
Total		11137506	325098	100.000	100.000





Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %
1	7.036	111065	10856	2.292	4.511
2	8.043	162573	12592	3.355	5.232
3	10.358	156766	9822	3.235	4.081
4	12.762	4415322	207386	91.118	86.175
Total		4845726	240655	100.000	100.000





#### PDA Ch2 254nm 4nm

Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %
1	7.090	149307	14212	3.170	4.903
2	8.086	218089	9869	4.631	3.405
3	10.404	4213951	259392	89.475	89.491
4	12.649	128313	6380	2.724	2.201
Total		4709659	289853	100.000	100.000



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Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %
1	7.324	3987700	197132	1.804	5.062
2	8.672	2759426	149814	1.249	3.847
3	12.979	89698833	1809960	40.589	46.480
4	16.226	124546682	1737115	56.358	44.610
Total		220992641	3894021	100.000	100.000





Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %
1	7.363	1605333	84949	3.267	4.685
2	8.739	2407333	160627	4.899	8.859
3	13.389	43501986	1513750	88.519	83.484
4	17.569	1629451	53884	3.316	2.972
Total		49144103	1813211	100.000	100.000



Operator Sample Sample ID Vial# Inj. Volume Data Name Method Name

: Admin : gw20121123-42-2 : gw20121123-42-2 : : 10 uL : gw20121123-42-2.lcd : yuyu.icm Batch Name Report Name Acquisition Date Modified Date

: Default.lcr 2012-11-23 19:10:11 2012-11-23 19:34:45



Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %
1	7.430	2394909	122574	4.379	8.336
2	8.847	1803283	116337	3.297	7.912
3	13.873	1538699	66439	2.814	4.518
4	17.343	48950468	1165093	89.510	79.234
Total		54687359	1470443	100.000	100.000





Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %
1	13.917	34882185	1567329	17.662	27.672
2	16.941	36205780	1275523	18.332	22.520
3	25.082	62547739	1491037	31.670	26.325
4	29.253	63861871	1330040	32.336	23.483
Total		197497574	5663929	100.000	100.000





Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %
1	13.810	902866	39379	2.349	4.442
2	16.935	569187	24884	1.481	2.807
3	24.788	1673642	48791	4.355	5.504
4	28.758	35286255	773401	91.815	87.246
Total		38431950	886455	100.000	100.000







Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %
1	14.094	926004	38355	1.981	3.155
2	17.244	1061649	38420	2.271	3.161
3	25.184	42490258	1085683	90.903	89.315
4	29.275	2264427	53112	4.844	4.369
Total		46742339	1215570	100.000	100.000





Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %
1	9.485	13843125	974861	26.313	34.160
2	10.977	14092651	840106	26.787	29.438
3	14.829	12309635	552489	23.398	19.360
4	16.712	12364149	486369	23.502	17.043
Total		52609560	2853825	100.000	100.000





: Admin : gw20121204-45-1 : gw20121204-45-1 : : 10 uL : gw20121204-45-1.lcd : yuyu.icm Batch Name : Report Name : Default.lcr Acquisition Date : 2012-12-4 15:06:58 Modified Date : 2012-12-4 15:34:30



Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %
1	9.206	440769	33431	2.262	4.209
2	10.673	293531	19498	1.506	2.455
3	14.374	1090497	52127	5.596	6.563
4	16.189	17660972	689247	90.635	86.774
Total	•	19485769	794302	100.000	100.000





PDA Ch1 220nm 4nm							
Peak#	Resolution Time	Area	Height	Area %	Height %		
1	9.168	744568	57170	2.063	3.767		
2	10.623	974003	66261	2.699	4.366		
3	14.268	32097094	1300748	88.939	85.703		
4	16.119	2273030	93552	6.298	6.164		

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100.000

Peak#	Resol	utior

Total

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100.000




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Operator Sample Sample ID	Admin gw20121123-41-1 gw20121123-41-1	Batch Name Report Name Acquisition Date Modified Date	: Default.lcr 2012-11-23 16:41:55 2012-11-23 17:34:48
Vial#	- 10 ul	Modified Date	2012-11-20 11:04:40
inj. volume	. 10 UL		
Data Name	: gw20121123-41-1.lcd		
Method Name	: yuyu.icm		

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### PDA Ch2 254nm 4nm

Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %
1	18.208	285319	8908	2.070	4.456
2	19.581	416053	11918	3.019	5.961
3	33.040	12666509	173535	91.897	86.797
4	44.803	415431	5571	3.014	2.787
Total		13783312	199932	100.000	100.000







PDA Ch2 254nm 4nm								
Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %			
1	17.521	503355	15067	5.262	11.921			
2	18.807	487643	13660	5.098	10.808			
3	32.921	594888	9589	6.219	7.587			
4	42.657	7979277	88075	83.420	69.685			
Total		9565164	126391	100.000	100.000			



Acquired by Sample Name Sample ID Vail # Injection Volume Data File Name

: Admin : gw20121201-40 : gw20121201-40 : -1 : 5 uL : gw20121201-40.lcd Method File Name Batch File Name Report File Name Data Acquired Data Processed : 1.lcm : : Default.lcr : 2012-12-1 18:42:44 : 2012-12-1 19:24:43



1 Det.A Ch1/220nm

Detector A Ch1 220nm						
Peak#	Ret. Time	Area	Height	Area %	Height %	
1	13.116	9949870	310767	26.625	34.027	
2	14.484	10096330	284220	27.017	31.120	
3	16.056	8626258	203161	23.083	22.245	
4	22.400	8698321	115147	23.276	12.608	
Total		37370778	913295	100.000	100.000	



: 1.lcm

: Default.lcr : 2012-12-1 19:29:35 : 2012-12-1 19:56:14

Acquired by: AdminMethod File NameSample Name: gw20121201-40-1'Batch File NameSample ID: gw20121201-40-1'Report File NameVail #: -1Data AcquiredInjection Volume: 5 uLData ProcessedData File Name: gw20121201-40-1'1.lcd



PeakTable

Detector A	Ch1 220nm				
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.051	7247132	230541	14.507	21.217
2	14.411	3822223	113047	7.651	10.404
3	15.838	32901511	657249	65.861	60.488
4	22.318	5985424	85747	11.981	7.891
Total		49956290	1086583	100.000	100.000





1 Det.A Ch1/220nm

Detector A (	"h1 220mm		. cuntin		
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.087	4300325	138943	9.066	18.649
2	14.445	6009598	174085	12.669	23.366
3	15.999	4748133	120783	10.010	16.212
4	21.432	32377071	311221	68.255	41.773
Total		47435127	745032	100.000	100.000





PeakTable

		1 Ca	KT able		
Detector A (	Ch1 220nm				
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.640	4216043	122077	7.451	15.285
2	9.844	5732868	225763	10.132	28.268
3	19.303	25822428	306524	45.635	38.380
4	30.329	20812857	144289	36.782	18.067
Total		56584196	798653	100.000	100.000





PeakTable

Distanton A	Ch1 220mm		untraore		
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.498	16765662	191487	6.507	4.142
2	9.277	17333239	712399	6.728	15.408
3	18.492	198906971	3383510	77.202	73.180
4	27.220	24637367	336138	9.563	7.270
Tota	1	257643238	4623534	100.000	100.000





Detector A	Ch1 220nm				
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.456	283680	5529	3.877	5.437
2	9.618	53799	1437	0.735	1.413
3	19.903	1443846	31566	19.732	31.041
4	29.782	5536005	63158	75.656	62.108
Total		7317330	101690	100.000	100.000





PDA Ch1	210nm 4nm				
Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %
1	22.018	7325396	237412	5.562	8.230
2	23.322	7604139	224399	5.774	7.779
3	30.542	57957104	1267980	44.005	43.955
4	33.896	58820131	1154941	44.660	40.036
Total		131706769	2884732	100.000	100.000





#### PDA Ch1 210nm 4nm

Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %
1	22.126	4640911	154095	10.284	13.375
2	23.422	10736975	321962	23.791	27.946
3	30.631	23127906	536105	51.248	46.534
4	34.013	6623800	139913	14.677	12.144
Total		45129592	1152074	100.000	100.000



711





### PDA Ch1 210nm 4nm

Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %
1	22.195	14733430	478829	22.339	29.738
2	23.510	7083717	203511	10.740	12.639
3	30.800	10130587	232899	15.360	14.464
4	34.188	34006556	694932	51.561	43.159
Total		65954290	1610170	100.000	100.000



712



Detector A	Ch1 254nm				
Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.990	28233907	282300	50.065	53.415
2	32.243	28160068	246202	49.935	46.585
Total	10 1	56393976	528502	100.000	100.000







Detector A	Ch1 254nm				
Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.465	20674965	211862	74.950	74.207
2	32.953	6910068	73640	25.050	25.793
Total		27585033	285502	100.000	100.000





PDA	Ch2	254nm	4nm
1 1/1	<u> </u>	20-11111	

Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %
1	21.920	7964797	172397	48.947	51.402
2	23.857	8307547	162991	51.053	48.598
Total		16272344	335388	100.000	100.000







F DA UNZ 234000 400	PDA	Ch2	254nm	4nm
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Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %
1	21.277	34849780	641440	88.690	88.526
2	24.013	4444056	83137	11.310	11.474
Total		39293836	724578	100.000	100.000



Operator Sample Sample ID Vial# Inj. Volume Data Name Method Name

: Admin : gw-48-1 : gw-48-1 : : 10 uL : gw-48.lcd : yuyu.lcm Batch Name Report Name Acquisition Date Modified Date

: Default.lcr 2013-5-7 15:41:47 2013-5-7 16:19:03



### PDA Ch1 220nm 4nm

Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %
1	7.775	7957077	667483	23.803	34.093
2	8.934	7738484	564041	23.149	28.809
3	10.601	8692468	505049	26.003	25.796
4	20.621	9041122	221278	27.046	11.302
Total		33429152	1957850	100.000	100.000



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PDA Ch1	220nm 4nm				(
Peak#	<b>Resolution Time</b>	Area	Height	Area %	Height %
1	7.128	6961029	559224	12.889	22.990
2	8.283	9697300	642608	17.955	26.418
3	9.957	12029549	672764	22.273	27.658
4	19.839	25321262	557875	46.883	22.935
Total		54009139	2432470	100.000	100.000

