### **Supplementary Information**

### Rhodium-catalyzed asymmetric addition of arylboroxines to $\beta$ -alkoxyacrylate esters

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### 1. General

All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen. NMR spectra were recorded on a JEOL JNM ECA-600 spectrometer (600 MHz for <sup>1</sup>H, 150 MHz for <sup>13</sup>C). Chemical shifts are reported in  $\delta$  (ppm) referenced to the residual peaks of CDCl<sub>3</sub> ( $\delta$  7.26), C<sub>6</sub>D<sub>6</sub> ( $\delta$  7.16), and CD<sub>3</sub>OD ( $\delta$  3.31) for <sup>1</sup>H NMR and CDCl<sub>3</sub> ( $\delta$  77.00) for <sup>13</sup>C NMR. The following abbreviations are used; s: singlet, d: doublet, t: triplet, q: quartet, sept: septet, m: multiplet, br: broad. Optical rotations were measured on a JASCO P-2200 polarimeter. High-resolution mass spectra were obtained with a Bruker micrOTOF spectrometer.

### 2. Materials

Dichloromethane was distilled over CaH<sub>2</sub> under N<sub>2</sub>. Methanol was distilled over Mg under N<sub>2</sub>. Rhodium complexes, [RhCl(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>]<sub>2</sub>, <sup>1</sup> [[Rh(OH)((*R*)-binap)]<sub>2</sub> (CAS: 805323-12-0), <sup>2</sup> [Rh(OH)((*R*,*R*)-L3)]<sub>2</sub> (CAS: 1235989-05-5),<sup>3</sup> and [Rh(OH)((*R*,*R*)-L4)]<sub>2</sub> (CAS: 1204591-09-2 for the (*S*,*S*)-complex)<sup>4</sup> were prepared according to the reported procedures.  $\beta$ -Alkoxyacrylate esters were prepared according to the reported procedures.<sup>5</sup>

### 3. Preparation of [Rh(OH)((*S*,*S*)-L2)]<sub>2</sub> (CAS: 1204591-10-5)



To a solution of  $[RhCl((S,S)-L2)]_2$  (CAS: 1196788-92-7)<sup>6</sup> (315 mg, 0.22 mmol) in THF (20 mL) was added 1 N KOH (aq) (4.0 mL, 4.0 mmol) at room temperature, and the mixture was stirred for 1 h. After most of THF was removed under reduced pressure,  $CH_2Cl_2$  (10 mL) was added. The mixture was washed with deoxygenated H<sub>2</sub>O (5 mL × 4), dried by passing through a short Na<sub>2</sub>SO<sub>4</sub> column, and concentrated under vacuum to give  $[Rh(OH)((S,S)-L2)]_2$  (301 mg, 0.21 mmol, 98%), which was used without further purifications. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  –1.00 (br s, 2H), 2.56 (d, *J* = 6.1 Hz, 4H), 3.61–3.64 (m, 4H), 3.92–3.95 (m, 4H), 4.01–4.05 (m, 4H), 4.03 (s, 16H), 4.10–4.13

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(m, 4H), 4.40 (s, 4H), 5.60 (d, J = 6.1 Hz, 4H).

### **4.** Preparation of β-alkoxyacrylate esters

 $\beta$ -Alkoxyacrylate esters **1a–1i** were prepared according to the reported procedures as follows.<sup>5</sup>



To a solution of propiolic acid esters **s1** (2.0 mmol) and alcohol (R'OH) (1 equiv for MeOH, EtOH, benzyl alcohol, and *p*-methoxybenzyl alcohol; 5 equiv for 2-propanol and cyclohexanol) in  $CH_2Cl_2$  (10 mL) was added 1,4-diazabicyclo[2.2.2]octane (DABCO) (22 mg, 0.20 mmol) at 0 °C, and the mixture was stirred at the same temperature for 0.5 h. The mixture was passed through a short column of silica gel with  $Et_2O$  and the mixture was concentrated on a rotary evaporator. The residue was subjected to flash column chromatography on silica gel with hexane/ethyl acetate to give **1**. *t*-Butyl propiolate (**s1a**) and methyl propiolate (**s1b**) were purchased and used as received. 2,6-Dimthylphenyl propiolate (**s1c**) (CAS: 114251-41-1) and 2,6-dimthoxyphenyl propiolate (**s1d**) were prepared according to the reported procedures.<sup>4</sup>

### 5. Characterization of β-alkoxyacrylate esters



**Compound 1a**: 60% yield; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.28 (d, *J* = 5.9 Hz, 6H), 1.47 (s, 9H), 4.19 (sept, *J* = 5.9 Hz, 1H), 5.15 (d, *J* = 12.5 Hz, 1H), 7.43 (d, *J* = 12.5 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  22.0, 28.3, 75.1, 79.5, 98.7, 160.8, 167.7. HRMS (ESI) calcd for C<sub>10</sub>H<sub>18</sub>NaO<sub>3</sub> (M+Na)<sup>+</sup> 209.1148, found 209.1153.



**Compound 1b** (CAS: 89941-50-4): 62% yield; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.30 (d, *J* = 5.9 Hz, 6H), 3.69 (s, 3H), 4.23 (sept, *J* = 5.9 Hz, 1H), 5.24 (d, *J* = 12.5 Hz, 1H), 7.53 (d, *J* = 12.5 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  21.8, 50.8, 75.5, 96.7, 161.6, 168.4. HRMS (ESI) calcd for C<sub>7</sub>H<sub>12</sub>NaO<sub>3</sub> (M+Na)<sup>+</sup> 167.0679, found 168.0678.



1c

**Compound 1c**: 90% yield; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.36 (d, *J* = 6.1 Hz, 6H), 2.16 (s, 6H), 4.32 (sept, *J* = 6.1 Hz, 1H), 5.47 (d, *J* = 12.6 Hz, 1H), 7.01–7.08 (m, 3H), 7.75 (d, *J* = 12.6 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  16.3, 22.0, 76.2, 96.0, 125.5, 128.4, 130.5, 148.2, 163.1, 165.8. HRMS (ESI) calcd for C<sub>14</sub>H<sub>18</sub>NaO<sub>3</sub> (M+Na)<sup>+</sup> 257.1148, found 257.1145.



**Compound s1d.** A solution of propiolic acid (2.80 g, 40.0 mmol) and 2,6-dimethoxyphenol (4.62 g, 30.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) was cooled to -18 °C (ice/salt bath), and 4-(dimethylamino)pyridine (DMAP) (37 mg, 0.30 mmol) and dicyclohexylcarbodiimide (DCC) (8.25 g, 40.0 mmol) were added. The mixture was stirred at -18 °C for 1 h, before it was slowly warmed up to room temperature (over 4 h). The mixture was filtered through a short column of silica gel with hexane/ethyl acetate (1/1), and the solution was concentrated on a rotary evaporator. The residue was subjected to column chromatography on silica gel with hexane/CHCl<sub>3</sub> (3/1–1/3) to give **s1d** (2.18 g, 10.6 mmol, 35% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.04 (s, 1H), 3.84 (s, 6H), 6.62 (d, *J* = 8.7 Hz, 2H), 7.17 (t, *J* = 8.7 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  56.1, 74.1, 76.5, 104.8, 127.0, 127.5, 150.2, 152.1. HRMS (ESI) calcd for C<sub>11</sub>H<sub>10</sub>NaO<sub>4</sub> (M+Na)<sup>+</sup> 229.0471, found 229.0471.



**Compound 1d**: 90% yield; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.34 (d, *J* = 5.9 Hz, 6H), 3.82 (s, 6H), 4.31 (sept, *J* = 5.9 Hz, 1H), 5.51 (d, *J* = 12.8 Hz, 1H), 6.62 (d, *J* = 8.3 Hz, 2H), 7.12 (t, *J* = 8.3 Hz, 1H), 7.73 (d, *J* = 12.8 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  22.0, 56.2, 75.9, 95.8, 104.9, 125.9, 128.8, 152.7, 163.2, 165.9. HRMS (ESI) calcd for C<sub>14</sub>H<sub>18</sub>NaO<sub>5</sub> (M+Na)<sup>+</sup> 289.1046, found 289.1050.



1e

**Compound 1e**: 89% yield; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.25–1.38 (m, 3H), 1.48–1.60 (m, 3H), 1.75–1.82 (m, 2H), 1.92–1.99 (m, 2H), 3.82 (s, 6H), 4.01 (tt, *J* = 9.2, 4.1 Hz, 1H), 5.52 (d, *J* = 12.6 Hz, 1H), 6.61 (d, *J* = 8.1 Hz, 2H), 7.12 (t, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 12.6 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  23.5, 25.2, 31.8, 56.2, 81.1, 95.8, 104.9, 125.9, 128.8, 152.7, 163.4, 165.9. HRMS (ESI) calcd for C<sub>17</sub>H<sub>22</sub>NaO<sub>5</sub> (M+Na)<sup>+</sup> 329.1359, found 329.1352.



**Compound 1f**: 90% yield; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.38 (t, *J* = 7.1 Hz, 3H), 3.82 (s, 6H), 3.99 (q, *J* = 7.1 Hz, 2H), 5.48 (d, *J* = 12.6 Hz, 1H), 6.62 (d, *J* = 8.3 Hz, 2H), 7.13 (t, *J* = 8.3 Hz, 1H), 7.79 (d, *J* = 12.6 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  14.4, 56.1, 66.8, 95.1, 104.9, 126.0, 128.7, 152.6, 163.9, 165.6. HRMS (ESI) calcd for C<sub>13</sub>H<sub>16</sub>NaO<sub>5</sub> (M+Na)<sup>+</sup> 275.0890, found 275.0893.



**Compound 1g**: 85% yield; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.77 (s, 3H), 3.83 (s, 6H), 5.49 (d, *J* = 13.1 Hz, 1H), 6.22 (d, *J* = 8.2 Hz, 2H), 7.13 (t, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 13.1 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  56.2, 57.4, 94.8, 104.9, 126.0, 128.7, 152.6, 164.6, 165.3. HRMS (ESI) calcd for C<sub>12</sub>H<sub>14</sub>NaO<sub>5</sub> (M+Na)<sup>+</sup> 261.0733, found 261.0740.



1h

**Compound 1h**: 83% yield; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.83 (s, 6H), 4.97 (s, 2H), 5.62 (d, *J* = 12.9 Hz, 1H), 6.63 (d, *J* = 8.1 Hz, 2H), 7.14 (t, *J* = 8.1 Hz, 1H), 7.35–7.45 (m, 5H), 7.90 (d, *J* = 12.9 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  56.2, 72.9, 96.1, 104.9, 126.0, 127.8, 128.6, 128.67, 128.71, 135.1, 152.6, 163.6, 165.3. HRMS (ESI) calcd for C<sub>18</sub>H<sub>18</sub>NaO<sub>5</sub> (M+Na)<sup>+</sup> 337.1046, found 337.1046.



1i

**Compound 1i**: 92% yield; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.812 (s, 6H), 3.814 (s, 3H), 4.89 (s, 2H), 5.59 (d, *J* = 12.8 Hz, 1H), 6.61 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 8.3 Hz, 2H), 7.12 (t, *J* = 8.6 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.87 (d, *J* = 12.8 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  55.3, 56.2, 72.9, 95.9, 104.9, 114.1, 126.0, 127.1, 128.7, 129.7, 152.6, 159.9, 163.6, 165.4. HRMS (ESI) calcd for C<sub>19</sub>H<sub>20</sub>NaO<sub>6</sub> (M+Na)<sup>+</sup> 367.1152, found 367.1147.

# 6. A general procedure for rhodium-catalyzed asymmetric 1,4-addition of phenylboroxine (2m) to β-alkoxyacrylate esters 1 (Table 1)

[Rh(OH)(diene)]<sub>2</sub> (3.0  $\mu$ mol, 6.0  $\mu$ mol of Rh) and phenylboroxine (**2m**) (52.0 mg, 0.167 mmol) were placed in a Schlenk tube under N<sub>2</sub>, and triethylamine (for conditions C) (28  $\mu$ L, 0.20 mmol), **1** (0.200 mmol), and solvent (0.8 mL) were added successively. The mixture was stirred at 30 °C for 3 h, and it was passed through a short column of silica gel with Et<sub>2</sub>O as eluent. The solvent was evaporated on a rotary evaporator and the residue was dried under vacuum. <sup>1</sup>H NMR of the crude mixture was measured using nitromethane as an internal standard. After isolation of the product **3** by use of preparative TLC on silica gel with CHCl<sub>3</sub>/ethyl acetate, the ee was measured by chiral HPLC analysis.

# 7. A general procedure for rhodium-catalyzed asymmetric 1,4-addition of arylboroxines 2 to β-alkoxyacrylate esters 1 (Table 2)

[Rh(OH)((S,S)-L2)]<sub>2</sub> (4.3 mg, 3.0 µmol, 6.0 µmol of Rh) and arylboroxine 2 (0.167 mmol)

were placed in a Schlenk tube under  $N_2$ , and triethylamine (28 µL, 0.20 mmol), **1** (0.200 mmol), MeOH (0.4 mL), and CH<sub>2</sub>Cl<sub>2</sub> (0.4 mL) were added successively. The mixture was stirred at 30 °C for 3 h, and it was passed through a short column of silica gel with Et<sub>2</sub>O as eluent. The solvent was evaporated on a rotary evaporator and the residue was subjected to preparative TLC on silica gel with CHCl<sub>3</sub>/ethyl acetate to give **3**.

### 8. Characterization of the products



**Compound 3am.** The ee was measured by HPLC (Chiralcel OF column, hexane/2-propanol = 100/1, flow 0.5 mL/min, 224 nm,  $t_1 = 14.8 \text{ min}(R)$ ,  $t_2 = 20.6 \text{ min}(S)$ );  $[\alpha]_{D}^{20}$  -64 (*c* 0.98, CHCl<sub>3</sub>) for 98% ee (*S*). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.04 (d, *J* = 6.1 Hz, 3H), 1.15 (d, *J* = 6.1 Hz, 3H), 1.43 (s, 9H), 2.46 (dd, *J* = 14.6, 4.4 Hz, 1H), 2.64 (dd, *J* = 14.6, 9.2 Hz, 1H), 3.50 (sept, *J* = 6.1 Hz, 1H), 4.81 (dd, *J* = 9.2, 4.4 Hz, 1H), 7.24–7.28 (m, 1H), 7.30–7.37 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  21.2, 23.3, 28.0, 45.4, 69.4, 76.0, 80.4, 126.6, 127.6, 128.3, 142.3, 170.3. HRMS (ESI) calcd for C<sub>16</sub>H<sub>24</sub>NaO<sub>3</sub> (M+Na)<sup>+</sup> 287.1618, found 287.1616.



3bm

**Compound 3bm**. The ee was measured by HPLC (Chiralcel OD-H column × 2, hexane/2-propanol = 95/5, flow 0.45 mL/min, 224 nm,  $t_1 = 43.1 \text{ min } (R)$ ,  $t_2 = 46.8 \text{ min } (S)$ );  $[\alpha]_D^{20}$  -83 (*c* 1.10, CHCl<sub>3</sub>) for >99.5% ee (*S*). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.05 (d, *J* = 6.1 Hz, 3H), 1.14 (d, *J* = 6.1 Hz, 3H), 2.55 (dd, *J* = 15.3, 4.3 Hz, 1H), 2.75 (dd, *J* = 15.5, 9.5 Hz, 1H), 3.49 (sept, *J* = 6.1 Hz, 1H), 3.68 (s, 3H), 4.86 (dd, *J* = 9.5, 4.3 Hz, 1H), 7.26–7.29 (m, 1H), 7.32–7.37 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  21.1, 23.3, 44.0, 51.5, 69.5, 75.6, 126.4, 127.7, 128.4, 142.1, 171.5. HRMS (ESI) calcd for C<sub>13</sub>H<sub>18</sub>NaO<sub>3</sub> (M+Na)<sup>+</sup> 245.1148, found 245.1151.



3cm

**Compound 3cm**. The ee was measured by HPLC (Chiralpak AD-H column × 2, hexane/2-propanol = 98/2, flow 0.5 mL/min, 224 nm,  $t_1 = 24.6 \min(S)$ ,  $t_2 = 31.2 \min(R)$ );  $[\alpha]_{D}^{20}$ 

-63 (*c* 1.20, CHCl<sub>3</sub>) for >99.5% ee (*S*). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.09 (d, *J* = 6.1 Hz, 3H), 1.17 (d, *J* = 6.1 Hz, 3H), 2.12 (br s, 6H), 2.84 (dd, *J* = 15.7, 4.8 Hz, 1H), 3.09 (dd, *J* = 15.7, 9.5 Hz, 1H), 3.56 (sept, *J* = 6.1 Hz, 1H), 5.02 (dd, *J* = 9.5, 4.8 Hz, 1H), 7.02–7.09 (m, 3H), 7.29–7.34 (m, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.44 (d, *J* = 7.5 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 16.3, 20.9, 23.4, 43.5, 69.1, 75.2, 125.8, 126.7, 127.9, 128.46, 128.53, 130.2, 141.8, 148.2, 169.0. HRMS (ESI) calcd for  $C_{20}H_{24}NaO_3$  (M+Na)<sup>+</sup> 335.1618, found 335.1617.



**Compound 3dm**. The ee was measured by HPLC (Chiralcel OD-H column, hexane/2-propanol = 4/1, flow 0.5 mL/min, 224 nm,  $t_1 = 12.1 \text{ min}(S)$ ,  $t_2 = 16.2 \text{ min}(R)$ );  $[\alpha]^{20}{}_{D}$  -43 (*c* 1.02, CHCl<sub>3</sub>) for >99.5% ee (*S*). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.09 (d, *J* = 6.1 Hz, 3H), 1.20 (d, *J* = 6.1 Hz, 3H), 2.87 (dd, *J* = 15.7, 4.8 Hz, 1H), 3.10 (dd, *J* = 15.7, 8.9 Hz, 1H), 3.60 (sept, *J* = 6.1 Hz, 1H), 3.78 (s, 6H), 5.01 (dd, *J* = 8.9, 4.8 Hz, 1H), 6.60 (d, *J* = 8.7 Hz, 2H), 7.12 (t, *J* = 8.7 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.45 (d, *J* = 7.2 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  21.2, 23.3, 43.5, 56.0, 69.6, 75.5, 104.9, 126.2, 126.6, 127.6, 128.3, 128.8, 142.3, 152.3, 168.8. HRMS (ESI) calcd for C<sub>20</sub>H<sub>24</sub>NaO<sub>5</sub> (M+Na)<sup>+</sup> 367.1516, found 367.1514.



3dn

**Compound 3dn**. The ee was measured by HPLC (Chiralcel OD-H column, hexane/2-propanol = 4/1, flow 0.5 mL/min, 224 nm,  $t_1 = 14.3 \min(S)$ ,  $t_2 = 20.6 \min(R)$ );  $[\alpha]^{20}_D - 43$  (*c* 1.01, CHCl<sub>3</sub>) for >99.5% ee (*S*). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.09 (d, *J* = 6.1 Hz, 3H), 1.19 (d, *J* = 6.1 Hz, 3H), 2.36 (s, 3H), 2.85 (dd, *J* = 15.5, 4.4 Hz, 1H), 3.09 (dd, *J* = 15.5, 9.3 Hz, 1H), 3.58 (sept, *J* = 6.1 Hz, 1H), 3.79 (s, 6H), 4.98 (dd, *J* = 9.3, 4.4 Hz, 1H), 6.60 (d, *J* = 8.6 Hz, 2H), 7.12 (t, *J* = 8.6 Hz, 1H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  21.1, 21.2, 23.3, 43.5, 56.0, 69.4, 75.3, 104.9, 126.1, 126.6, 128.8, 129.0, 137.2, 139.2, 152.3, 168.8. HRMS (ESI) calcd for C<sub>21</sub>H<sub>26</sub>NaO<sub>5</sub> (M+Na)<sup>+</sup> 381.1672, found 381.1667.



#### 3do

**Compound 3do**. The ee was measured by HPLC (Chiralcel OD-H column, hexane/2-propanol = 4/1, flow 0.5 mL/min, 224 nm,  $t_1 = 11.5 \min(S)$ ,  $t_2 = 15.0 \min(R)$ );  $[\alpha]_D^{20} -50$  (*c* 1.01, CHCl<sub>3</sub>) for >99.5% ee (*S*). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.10 (d, *J* = 6.1 Hz, 3H), 1.20 (d, *J* = 6.1 Hz, 3H), 2.37 (s, 3H), 2.86 (dd, *J* = 15.7, 4.8 Hz, 1H), 3.08 (dd, *J* = 15.7, 8.9 Hz, 1H), 3.60 (sept, *J* = 6.1 Hz, 1H), 3.79 (s, 6H), 4.98 (dd, *J* = 8.9, 4.8 Hz, 1H), 6.61 (d, *J* = 8.1 Hz, 2H), 7.09–7.14 (m, 2H), 7.23–7.28 (m, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  21.2, 21.4, 23.3, 43.5, 56.0, 69.6, 75.5, 104.9, 123.7, 126.2, 127.3, 128.2, 128.3, 128.8, 137.9, 142.3, 152.3, 168.8. HRMS (ESI) calcd for C<sub>21</sub>H<sub>26</sub>NaO<sub>5</sub> (M+Na)<sup>+</sup> 381.1672, found 381.1665.



3dp

**Compound 3dp.** The ee was measured by HPLC (Chiralcel OD-H column, hexane/2-propanol = 4/1, flow 0.5 mL/min, 224 nm,  $t_1 = 11.2 \text{ min } (S)$ ,  $t_2 = 14.6 \text{ min } (R)$ );  $[\alpha]_{D}^{20} -71$  (*c* 1.25, CHCl<sub>3</sub>) for >99.5% ee (S). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.10 (d, J = 6.1 Hz, 3H), 1.21 (d, J = 6.1 Hz, 3H), 2.43 (s, 3H), 2.83 (dd, J = 15.7, 3.6 Hz, 1H), 3.02 (dd, J = 15.7, 9.3 Hz, 1H), 3.56 (sept, J = 6.1 Hz, 1H), 3.80 (s, 6H), 5.25 (dd, J = 9.3, 3.6 Hz, 1H), 6.61 (d, J = 8.9 Hz, 2H), 7.13 (t, J = 8.9 Hz, 1H), 7.15 (d, J = 7.8 Hz, 1H), 7.19 (t, J = 7.8 Hz, 1H), 7.25 (t, J = 7.8 Hz, 1H), 7.57 (d, J = 7.8 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  19.0, 21.3, 23.3, 42.2, 56.0, 69.6, 72.2, 104.9, 126.1, 126.2, 126.3, 127.2, 128.8, 130.3, 134.9, 140.4, 152.4, 169.0. HRMS (ESI) calcd for C<sub>21</sub>H<sub>26</sub>NaO<sub>5</sub> (M+Na)<sup>+</sup> 381.1672, found 381.1670.



ouq

Compound 3dq. The ee was measured by HPLC (Chiralcel OD-H column,

hexane/2-propanol = 4/1, flow 0.5 mL/min, 224 nm,  $t_1 = 14.8 \text{ min } (S)$ ,  $t_2 = 23.9 \text{ min } (R)$ );  $[\alpha]^{20}_{D} -35$ (*c* 1.01, CHCl<sub>3</sub>) for >99.5% ee (*S*). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.07 (d, *J* = 6.1 Hz, 3H), 1.18 (d, *J* = 6.1 Hz, 3H), 2.84 (dd, *J* = 15.3, 4.8 Hz, 1H), 3.09 (dd, *J* = 15.3, 8.8 Hz, 1H), 3.56 (sept, *J* = 6.1 Hz, 1H), 3.78 (s, 6H), 3.81 (s, 3H), 4.95 (dd, *J* = 8.8, 4.8 Hz, 1H), 6.60 (d, *J* = 8.2 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 7.11 (t, *J* = 8.2 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  21.2, 23.3, 43.5, 55.2, 56.0, 69.3, 75.0, 104.9, 113.7, 126.2, 127.9, 128.8, 134.3, 152.3, 159.1, 168.8. HRMS (ESI) calcd for C<sub>21</sub>H<sub>26</sub>NaO<sub>6</sub> (M+Na)<sup>+</sup> 397.1622, found 397.1620.



3dr

**Compound 3dr**. The ee was measured by HPLC (Chiralcel OD-H column, hexane/2-propanol = 4/1, flow 0.5 mL/min, 224 nm,  $t_1 = 17.5 \text{ min}(S)$ ,  $t_2 = 28.3 \text{ min}(R)$ );  $[\alpha]^{20}{}_{D} - 34$  (*c* 1.00, CHCl<sub>3</sub>) for >99.5% ee (*S*). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.08 (d, *J* = 6.1 Hz, 3H), 1.19 (d, *J* = 6.1 Hz, 3H), 2.84 (dd, *J* = 15.5, 5.4 Hz, 1H), 3.08 (dd, *J* = 15.5, 8.4 Hz, 1H), 3.57 (sept, *J* = 6.1 Hz, 1H), 3.77 (s, 6H), 4.97 (dd, *J* = 8.4, 5.4 Hz, 1H), 6.60 (d, *J* = 8.7 Hz, 2H), 7.12 (t, *J* = 8.7 Hz, 1H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  21.3, 23.2, 43.3, 56.0, 69.8, 74.8, 104.8, 126.3, 128.1, 128.5, 128.6, 133.3, 140.8, 152.3, 168.5. HRMS (ESI) calcd for C<sub>20</sub>H<sub>23</sub>ClNaO<sub>5</sub> (M+Na)<sup>+</sup> 401.1126, found 401.1127.



3ds

**Compound 3ds**. The ee was measured by HPLC (Chiralcel OD-H column, hexane/2-propanol = 4/1, flow 0.5 mL/min, 224 nm,  $t_1 = 12.7 \text{ min } (S)$ ,  $t_2 = 22.0 \text{ min } (R)$ );  $[\alpha]^{20}{}_{D} -37$  (*c* 1.01, CHCl<sub>3</sub>) for >99.5% ee (*S*). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.10 (d, *J* = 6.1 Hz, 3H), 1.21 (d, *J* = 6.1 Hz, 3H), 2.88 (dd, *J* = 15.6, 5.5 Hz, 1H), 3.11 (dd, *J* = 15.6, 8.2 Hz, 1H), 3.59 (sept, *J* = 6.1 Hz, 1H), 3.77 (s, 6H), 5.06 (dd, *J* = 8.2, 5.5 Hz, 1H), 6.60 (d, *J* = 8.3 Hz, 2H), 7.13 (t, *J* = 8.3 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  21.3, 23.2, 43.2, 55.9, 70.2, 75.0, 104.8, 124.1 (q, *J*<sub>F-C</sub> = 272 Hz), 125.3 (q, *J*<sub>F-C</sub> = 3 Hz), 126.3, 127.0, 128.6, 129.9 (q, *J*<sub>F-C</sub> = 33 Hz),

146.5, 152.2, 168.4. HRMS (ESI) calcd for  $C_{21}H_{23}F_3NaO_5$  (M+Na)<sup>+</sup> 435.1390, found 435.1393.



**Compound 3dt**. The ee was measured by HPLC (Chiralcel OD-H column × 2, hexane/2-propanol = 4/1, flow 0.5 mL/min, 224 nm,  $t_1 = 34.4 \text{ min } (S)$ ,  $t_2 = 39.9 \text{ min } (R)$ );  $[\alpha]_D^{20} - 35$  (*c* 1.01, CHCl<sub>3</sub>) for >99.5% ee (*S*). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.12 (d, J = 6.1 Hz, 3H), 1.25 (d, J = 6.1 Hz, 3H), 2.99 (dd, J = 15.7, 5.3 Hz, 1H), 3.22 (dd, J = 15.7, 8.7 Hz, 1H), 3.67 (sept, J = 6.1 Hz, 1H), 3.72 (s, 6H), 5.19 (dd, J = 8.7, 5.3 Hz, 1H), 6.60 (d, J = 8.7 Hz, 2H), 7.12 (t, J = 8.7 Hz, 1H), 7.47–7.53 (m, 2H), 7.62 (dd, J = 8.1, 1.4 Hz, 1H), 7.84–7.92 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  21.2, 23.3, 43.3, 55.9, 69.7, 75.7, 104.8, 124.4, 125.80, 125.84, 126.0, 126.2, 127.6, 127.9, 128.3, 128.7, 133.1, 133.2, 139.6, 152.3, 168.7. HRMS (ESI) calcd for C<sub>24</sub>H<sub>26</sub>NaO<sub>5</sub> (M+Na)<sup>+</sup> 417.1672, found 417.1671.



**Compound 3em.** The ee was measured by HPLC (Chiralcel OD-H column, hexane/2-propanol = 4/1, flow 0.5 mL/min, 224 nm,  $t_1 = 20.3 \text{ min } (S)$ ,  $t_2 = 25.0 \text{ min } (R)$ );  $[\alpha]_D^{20} - 42$  (*c* 1.01, CHCl<sub>3</sub>) for >99.5% ee (*S*). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.10–1.56 (m, 6H), 1.65–1.80 (m, 3H), 1.95–2.03 (m, 1H), 2.87 (dd, J = 15.7, 4.6 Hz, 1H), 3.11 (dd, J = 15.7, 9.1 Hz, 1H), 3.25–3.33 (m, 1H), 3.79 (s, 6H), 5.07 (dd, J = 9.1, 4.6 Hz, 1H), 6.61 (d, J = 8.5 Hz, 2H), 7.13 (t, J = 8.5 Hz, 1H), 7.30 (t, J = 7.3 Hz, 1H), 7.37 (t, J = 7.3 Hz, 2H), 7.45 (d, J = 7.3 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  23.8, 24.0, 25.8, 31.2, 33.4, 43.5, 56.0, 75.1, 75.5, 104.8, 126.1, 126.5, 127.5, 128.3, 128.7, 142.5, 152.3, 168.8. HRMS (ESI) calcd for C<sub>23</sub>H<sub>28</sub>NaO<sub>5</sub> (M+Na)<sup>+</sup> 407.1829, found 407.1819.



Compound 3fm. The ee was measured by HPLC (Chiralcel OD-H column,

hexane/2-propanol = 4/1, flow 0.5 mL/min, 224 nm,  $t_1 = 14.4 \text{ min } (S)$ ,  $t_2 = 19.6 \text{ min } (R)$ );  $[\alpha]_D^{20} - 30$ (*c* 1.02, CHCl<sub>3</sub>) for >99.5% ee (S). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.21 (t, J = 7.1 Hz, 3H), 2.91 (dd, J = 15.5, 5.0 Hz, 1H), 3.13 (dd, J = 15.5, 8.8 Hz, 1H), 3.46 (q, J = 7.1 Hz, 2H), 3.78 (s, 6H), 4.90 (dd, J = 8.8, 5.0 Hz, 1H), 6.60 (d, J = 8.7 Hz, 2H), 7.12 (t, J = 8.7 Hz, 1H), 7.31 (t, J = 7.5 Hz, 1H), 7.37 (t, J = 7.5 Hz, 2H), 7.43 (d, J = 7.5 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  15.2, 43.1, 56.0, 64.5, 78.1, 104.9, 126.2, 126.6, 127.8, 128.4, 128.7, 141.4, 152.3, 168.7. HRMS (ESI) calcd for C<sub>19</sub>H<sub>22</sub>NaO<sub>5</sub> (M+Na)<sup>+</sup> 353.1359, found 353.1352.



**Compound 3gm**. The ee was measured by HPLC (Chiralcel OD-H column, hexane/2-propanol = 4/1, flow 0.5 mL/min, 224 nm,  $t_1 = 19.0 \text{ min } (S)$ ,  $t_2 = 30.2 \text{ min } (R)$ );  $[\alpha]_D^{20} - 24$  (*c* 1.01, CHCl<sub>3</sub>) for >99.5% ee (S). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.91 (dd, J = 15.7, 4.8 Hz, 1H), 3.12 (dd, J = 15.7, 8.9 Hz, 1H), 3.31 (s, 3H), 3.78 (s, 6H), 4.79 (dd, J = 8.9, 4.8 Hz, 1H), 6.60 (d, J = 8.7 Hz, 2H), 7.12 (t, J = 8.7 Hz, 1H), 7.32 (t, J = 7.3 Hz, 1H), 7.38 (t, J = 7.3 Hz, 2H), 7.42 (d, J = 7.3 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  43.0, 56.1, 56.9, 80.0, 104.9, 126.2, 126.7, 127.9, 128.5, 128.7, 140.7, 152.3, 168.6. HRMS (ESI) calcd for C<sub>18</sub>H<sub>20</sub>NaO<sub>5</sub> (M+Na)<sup>+</sup> 339.1203, found 339.1199.



3hm

**Compound 3hm**. The ee was measured by HPLC (Chiralcel OD-H column, hexane/2-propanol = 4/1, flow 0.5 mL/min, 224 nm,  $t_1 = 18.9 \text{ min}(S)$ ,  $t_2 = 24.4 \text{ min}(R)$ );  $[\alpha]_D^{20} - 39$  (*c* 1.00, CHCl<sub>3</sub>) for >99.5% ee (*S*). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.98 (dd, J = 15.8, 4.8 Hz, 1H), 3.24 (dd, J = 15.8, 8.9 Hz, 1H), 3.72 (s, 6H), 4.45 (d, J = 11.6 Hz, 1H), 4.49 (d, J = 11.6 Hz, 1H), 5.05 (dd, J = 8.9, 4.8 Hz, 1H), 6.60 (d, J = 8.2 Hz, 2H), 7.13 (t, J = 8.2 Hz, 1H), 7.24–7.28 (m, 1H), 7.29–7.37 (m, 5H), 7.38–7.43 (m, 2H), 7.46–7.50 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  43.0, 56.0, 70.9, 78.1, 104.8, 126.2, 126.9, 127.4, 127.5, 128.0, 128.2, 128.5, 128.7, 138.3, 140.8, 152.3, 168.5. HRMS (ESI) calcd for C<sub>24</sub>H<sub>24</sub>NaO<sub>5</sub> (M+Na)<sup>+</sup> 415.1516, found 415.1515.



#### 3im

**Compound 3im**. The ee was measured by HPLC (Chiralcel OD-H column, hexane/2-propanol = 4/1, flow 0.5 mL/min, 224 nm,  $t_1 = 24.2 \text{ min}(S)$ ,  $t_2 = 33.5 \text{ min}(R)$ );  $[\alpha]_{D}^{20} - 33$  (*c* 1.01, CHCl<sub>3</sub>) for >99.5% ee (*S*). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.97 (dd, J = 15.6, 4.8 Hz, 1H), 3.23 (dd, J = 15.6, 8.9 Hz, 1H), 3.74 (s, 6H), 3.80 (s, 3H), 4.39 (d, J = 11.2 Hz, 1H), 4.43 (d, J = 11.2 Hz, 1H), 5.03 (dd, J = 8.9, 4.8 Hz, 1H), 6.61 (d, J = 8.3 Hz, 2H), 6.86 (d, J = 9.1 Hz, 2H), 7.13 (t, J = 8.3 Hz, 1H), 7.27 (d, J = 9.1 Hz, 2H), 7.34 (t, J = 7.3 Hz, 1H), 7.41 (t, J = 7.3 Hz, 2H), 7.48 (d, J = 7.3 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  42.9, 55.2, 56.0, 70.5, 77.7, 104.8, 113.6, 126.2, 126.9, 127.9, 128.5, 128.7, 129.2, 130.4, 140.9, 152.3, 159.0, 168.6. HRMS (ESI) calcd for C<sub>25</sub>H<sub>26</sub>NaO<sub>6</sub> (M+Na)<sup>+</sup> 445.1622, found 445.1618.

### 9. Transformations of compounds 3dm and 3im



**Compound 5.** To a solution of **3dm** (170 mg, 0.49 mmol) in THF (5.0 mL) and MeOH (5.0 mL) was added LiOH·H<sub>2</sub>O (63 mg, 1.5 mmol) in H<sub>2</sub>O (5.0 mL) and the mixture was stirred at room temperature for 6.5 h. The mixture was acidified with 1 N HCl (aq) and the mixture was extracted with Et<sub>2</sub>O. The combined extract was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated on a rotary evaporator. The residue was subjected to GPC with CHCl<sub>3</sub> as eluent to give **5** (88 mg, 0.42 mmol, 86% yield). The ee of **5** was determined by chiral HPLC analysis of the methyl ester **3bm** derived from **5**.  $[\alpha]_{D}^{20} -91$  (*c* 1.00, CHCl<sub>3</sub>) for >99.5% ee (*S*). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.09 (d, *J* = 6.2 Hz, 3H), 1.19 (d, *J* = 6.2 Hz, 3H), 2.63 (dd, *J* = 15.8, 4.1 Hz, 1H), 2.82 (dd, *J* = 15.8, 9.6 Hz, 1H), 3.55 (sept, *J* = 6.2 Hz, 1H), 4.89 (dd, *J* = 9.6, 4.1 Hz, 1H), 7.28–7.40 (m, 5H), 11.31 (br s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  20.9, 23.2, 43.9, 69.6, 75.3, 126.4, 127.8, 128.5, 141.6, 176.8. HRMS (ESI) calcd for C<sub>12</sub>H<sub>16</sub>NaO<sub>3</sub> (M+Na)<sup>+</sup> 231.0992, found 231.0986.



**Compound 6.** To a solution of **3dm** (74.1 mg, 0.215 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) was added dropwise  $(i-\text{Bu})_2$ AlH (1 M solution in hexane, 0.47 mL, 0.47 mmol) at 0 °C and the mixture was stirred for 15 min. 10% NaOH solution (1.4 mL) was slowly added, and the mixture was extracted with Et<sub>2</sub>O. The organic layer was washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated on a rotary evaporator. The residue was subjected to preparative TLC on silica gel with CHCl<sub>3</sub>/MeOH (10/1) to give **6** (40.0 mg, 0.206 mmol, 96%). The ee was measured by HPLC (Chiralcel OJ-H column × 2, hexane/2-propanol = 4/1, flow 0.5 mL/min, 224 nm,  $t_1 = 18.7$  min (*R*),  $t_2 = 22.4$  min (*S*));  $[\alpha]^{20}{}_{\text{D}} - 125$  (*c* 1.01, CHCl<sub>3</sub>) for >99.5% ee (*S*). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.10 (d, *J* = 6.1 Hz, 3H), 1.19 (d, *J* = 6.1 Hz, 3H), 1.81–1.87 (m, 1H), 1.96–2.03 (m, 1H), 3.00 (br s, 1H), 3.51 (sept, *J* = 6.1 Hz, 1H), 3.73–3.83 (m, 2H), 4.64 (dd, *J* = 9.2, 3.7 Hz, 1H), 7.25–7.29 (m, 1H), 7.31–7.37 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  21.0, 23.5, 40.6, 61.4, 69.1, 79.3, 126.3, 127.5, 128.4, 142.7. HRMS (ESI) calcd for C<sub>12</sub>H<sub>18</sub>NaO<sub>2</sub> (M+Na)<sup>+</sup> 217.1199, found 217.1198.



**Compounds 7 and 8.** A mixture of **3im** (73.7 mg, 0.174 mmol) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (58.6 mg, 0.258 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.9 mL) and H<sub>2</sub>O (0.1 mL) was stirred at room temperature for 3.5 h. The mixture was filtered and the filtrate was washed with 5% NaHCO<sub>3</sub> (aq), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated on a rotary evaporator. The residue was subjected to preparative TLC on silica gel with hexane/ethyl acetate (2/1) to give **7** (47.7 mg, 0.158 mmol, 90%). The ee of **7** was measured by HPLC (Chiralcel AD-H column, hexane/2-propanol = 2/1, flow 0.5 mL/min, 224 nm,  $t_1 = 17.7 \text{ min}$  (*R*),  $t_2 = 22.4 \text{ min}$  (*S*));  $[\alpha]^{20}_{\text{ D}}$  –43 (*c* 1.01, CHCl<sub>3</sub>) for >99.5% ee (*S*). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.04 (dd, *J* = 15.6, 8.9 Hz, 1H), 3.07 (dd, *J* = 15.6, 4.0 Hz, 1H), 3.62 (d, *J* = 2.7 Hz, 1H), 3.84 (s, 6H), 5.28–5.37 (m, 1H), 6.64 (d, *J* = 8.3 Hz, 2H), 7.17 (t, *J* = 8.3 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.47 (d, *J* = 7.5 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  43.9, 56.1, 70.5, 104.9, 125.7, 126.5, 127.7, 128.3, 128.5,

142.1, 152.1, 169.6. HRMS (ESI) calcd for C<sub>17</sub>H<sub>18</sub>NaO<sub>5</sub> (M+Na)<sup>+</sup> 325.1046, found 325.1043. The basic hydrolysis of **7** with LiOH·H<sub>2</sub>O gave β-hydroxycarboxylic acid (*S*)-**8** in 77% yield, whose absolute configuration was determined by comparison of its specific rotation with the value reported previously (lit.  $[\alpha]_{D}^{23}$  –21.9 (*c* 4, MeOH)).<sup>7</sup> Compound **8**:  $[\alpha]_{D}^{20}$  –20 (*c* 0.50, MeOH); <sup>1</sup>H NMR (CD<sub>3</sub>OD) δ 2.65 (dd, *J* = 15.3, 4.8 Hz, 1H), 2.71 (dd, *J* = 15.3, 8.5 Hz, 1H), 5.09 (dd, *J* = 8.5, 4.8 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 7.5 Hz, 2H).

<sup>7</sup> O. Pàmies and J.-E. Bäckvall, Adv. Synth. Catal., 2002, 344, 947.



### 10. <sup>1</sup>H and <sup>13</sup>C NMR spectra and chiral HPLC charts

### Electronic Supplementary Material (ESI) for Chemical Communications This journal is O The Royal Society of Chemistry 2011















































































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![](_page_60_Figure_1.jpeg)

![](_page_61_Figure_1.jpeg)

![](_page_61_Figure_2.jpeg)

![](_page_62_Figure_1.jpeg)

![](_page_63_Figure_1.jpeg)