

# An Efficient, Stereoselective Approach to *syn*-1,2-Diols Protected as Cyclic Carbonates

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**Preparation of 6a:** The general procedure for the synthesis of alkyl 4-hydroxybut-2-ynyl carbonates was followed for: Zn(OTf)<sub>2</sub> (200 mg, 0.55 mmol), (–)-NME (108 mg, 0.60 mmol), toluene (1 mL) and Et<sub>3</sub>N (84  $\mu$ L, 0.60 mmol) at rt for 2 h 30 min. Alkyne **3**<sup>1</sup> (92.9 mg, 0.5 mmol), toluene (0.5 mL) at rt for 30 min. Cyclohexanecarbaldehyde (73  $\mu$ L, 0.60 mmol) for 4 h. Purification by flash chromatography with gel (CH<sub>2</sub>Cl<sub>2</sub>/MeOH : 99/1) gave **6a** (137.2 mg, 93%) as a colorless oil: [ $\alpha$ ]<sub>D</sub><sup>25</sup> +2.62 (c 0.98, CHCl<sub>3</sub>) for 98% ee;<sup>2</sup> IR (film) 3444, 2929, 1752, 1451, 1391, 1263 cm<sup>–1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  7.40–7.35 (5H, m), 5.19 (2H, s), 4.79 (2H, d, *J* = 1.8 Hz), 4.18 (2H, dt, *J* = 6.2, 1.8 Hz), 1.85–1.51 (7H, m), 1.32–0.99 (5H, m); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>)  $\delta$  154.5, 134.9, 128.6, 128.5, 128.3, 87.7, 78.9, 70.0, 67.1, 55.8, 43.9, 28.4, 28.1, 26.3, 25.8, 25.8; HRMS(ESI) calcd for C<sub>18</sub>H<sub>22</sub>NaO<sub>4</sub> (M + Na<sup>+</sup>) 325.1416, found 325.1413.

**Preparation of 7a:** The general procedure for the synthesis of alkyl 4-hydroxybut-2-ynyl carbonates was followed for: Zn(OTf)<sub>2</sub> (200 mg, 0.55 mmol), (–)-NME (108 mg, 0.60 mmol), toluene (1 mL), and Et<sub>3</sub>N (84  $\mu$ L, 0.60 mmol) at rt for 2 h 30 min. Alkyne **4**<sup>3</sup> (58.0 mg, 0.5 mmol), toluene (0.5 mL) at rt for 30 min. Cyclohexanecarbaldehyde (73  $\mu$ L, 0.60 mmol) for 5 h. Purification by flash chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/MeOH : 99/1) gave **7a** (100.3 mg, 87%) as a colorless oil: [ $\alpha$ ]<sub>D</sub><sup>25</sup> +3.17 (c 1.12, CHCl<sub>3</sub>) for 97% ee;<sup>2</sup> IR (film) 3436, 2929, 1756, 1447, 1376, 1270 cm<sup>–1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  4.78 (2H, d, *J* = 1.7 Hz), 4.19 (1H, dt, *J* = 6.1, 1.7 Hz), 3.82 (3H, s), 1.85–1.50 (7H, m), 1.32–0.99 (5H, m); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>)  $\delta$  155.1, 87.6, 78.9, 67.0, 55.7, 55.1, 43.9, 28.4, 28.1, 26.3, 25.8, 25.8; HRMS(ESI) calcd for C<sub>12</sub>H<sub>18</sub>NaO<sub>4</sub> (M + Na<sup>+</sup>) 249.1103, found 249.1100.

**General procedure for the synthesis of alkyl (Z)-4-hydroxybut-2-enyl carbonates (8a–d, 8f, 9a, 10a, and 13e):** the alkyl 4-hydroxybut-2-ynyl carbonate, Pd/CaCO<sub>3</sub> (5%) poisoned with lead, quinoline, and AcOEt were added in a flask which was purged with N<sub>2</sub> and then with H<sub>2</sub>. The reaction mixture was shaken and monitored for completion by TLC. The mixture was filtered through a short pad of Celite. The organic layer was washed with aqueous HCl 2 N and brine, dried over MgSO<sub>4</sub>, and evaporated under reduced pressure. The mixture was purified by flash chromatography on silica gel to give the (Z)-alkene.

**Compound 8a:** The general procedure was followed for: alkyne **5a** (95.9 mg, 0.36 mmol), Pd/CaCO<sub>3</sub> (27.0 mg), quinoline (8  $\mu$ L), and AcOEt (2.5 mL) for 90 min. Purification of the crude mixture by flash chromatography on silica gel (Hexane/AcOEt : 80/20) gave **8a** (81.2 mg, 84%) as a colorless oil: [ $\alpha$ ]<sub>D</sub><sup>25</sup>

<sup>1</sup> Zhang, H. X.; Guibé, F.; Balavoine, G. *Tetrahedron Lett.* **1988**, 29, 619–622.

<sup>2</sup> Determined by HPLC of the corresponding Mosher's esters.

<sup>3</sup> Allcock, S. J.; Gilchrist, T. L.; Shuttleworth, S. J.; King, F. D. *Tetrahedron* **1991**, 47, 10053–10064.

–14.7 (c 1.71, CHCl<sub>3</sub>) for >96% ee; IR (film) 3427, 2927, 1743, 1451, 1370, 1277 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  5.67 (2H, m), 4.82 (1H, dd, *J* = 12.6, 6.6 Hz), 4.50 (1H, dd, *J* = 12.6, 4.0 Hz), 4.19 (1H, t, *J* = 7.2 Hz), 1.97–0.82 (12H, m), 1.48 (9H, s); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>)  $\delta$  153.5, 136.3, 125.1, 82.4, 71.6, 62.7, 43.4, 28.7, 28.5, 27.7, 26.5, 26.0, 25.9; HRMS(ESI) calcd for C<sub>15</sub>H<sub>26</sub>NaO<sub>4</sub> (M + Na<sup>+</sup>) 293.1729, found 291.1739.

**Compound 8b:** The general procedure was followed for: alkyne **5b** (39.0 mg, 0.17 mmol), Pd/CaCO<sub>3</sub> (7.0 mg), quinoline (2.8  $\mu$ L), and AcOEt (1.3 mL) for 30 min. Purification of the crude mixture by flash chromatography on silica gel (Hexane/Et<sub>2</sub>O : 9/1) gave **8b** (32.8 mg, 83%) as a colorless oil:  $[\alpha]_D^{25}$  –2.26 (c 1.00, CHCl<sub>3</sub>) for 96% ee; IR (film) 3467, 2964, 1742, 1457, 1370 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.71–5.63 (2H, m), 4.83 (1H, dd, *J* = 12.7, 7.2 Hz), 4.52 (1H, dd, *J* = 12.7, 4.3 Hz), 4.18 (1H, dd, *J* = 7.8, 6.8 Hz), 1.72 (1H, oct, *J* = 6.7 Hz), 1.48 (9H, s), 0.98 (3H, d, *J* = 6.7 Hz), 0.87 (3H, d, *J* = 6.8 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  153.6, 136.2, 125.4, 82.5, 72.4, 62.7, 33.7, 27.7, 18.1, 18.1; HRMS(ESI) calcd for C<sub>12</sub>H<sub>22</sub>NaO<sub>4</sub> (M + Na<sup>+</sup>) 253.1416, found 253.1413.

**Compound 8c:** The general procedure was followed for: alkynol **5c** (32.9 mg, 0.136 mmol), Pd/CaCO<sub>3</sub> (6.5 mg), and quinoline (4  $\mu$ L) in AcOEt (1.3 mL) for 30 min. Purification of the crude mixture by flash chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>) gave **8c** (27.5 mg, 83%) as a colorless oil:  $[\alpha]_D^{25}$  –18.0 (c 1.31, CHCl<sub>3</sub>) for 89% ee; IR (film) 3436, 2958, 1742, 1459, 1370, 1279 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.69–5.56 (2H, m), 4.85 (1H, ddt, *J* = 12.7, 8.2, 1.1 Hz), 4.58 (1H, td, *J* = 7.0, 6.0 Hz), 4.52 (1H, ddd, *J* = 12.7, 5.7, 1.2 Hz), 2.11 (1H, bs), 1.72 (1H, m), 1.53 (1H, m), 1.48 (9H, s), 1.28, (1H, m), 0.94 (3H, d, *J* = 6.6 Hz), 0.92 (3H, d, *J* = 6.6 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  153.6, 138.3, 124.3, 82.5, 65.5, 62.5, 45.9, 27.7, 24.4, 23.0, 22.4; HRMS(ESI) calcd for C<sub>13</sub>H<sub>24</sub>NaO<sub>4</sub> (M + Na<sup>+</sup>) 267.1572, found 267.1609.

**Compound 8d:** The general procedure was followed for: alkynol **5d** (82.5 mg, 0.314 mmol), Pd/CaCO<sub>3</sub> (25 mg), and quinoline (16  $\mu$ L) in AcOEt (5 mL). Purification of the crude mixture by flash chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/MeOH : 99/1) gave **8d** (74.7 mg, 90%) as a colorless oil:  $[\alpha]_D^{25}$  –105.1 (c 0.95, CHCl<sub>3</sub>) for >96% ee; IR (film) 3446, 2981, 1740, 1457, 1370, 1277 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.41–7.28 (5H, m), 5.88 (1H, ddt, *J* = 11.0, 8.5, 1.2 Hz), 5.69 (1H, m), 5.62 (1H, bd, *J* = 8.8 Hz), 4.95 (1H, ddd, *J* = 12.8, 8.2, 1.2 Hz), 4.63 (1H, ddd, *J* = 12.8, 5.9, 1.2 Hz), 1.49 (9H, s); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  153.6, 142.5, 136.9, 128.6, 127.6, 126.0, 124.6, 82.6, 69.5, 62.5, 27.7; HRMS(ESI) calcd for C<sub>15</sub>H<sub>20</sub>NaO<sub>4</sub> (M + Na<sup>+</sup>) 287.1259, found 287.1281.

**Compound 8f:** The general procedure was followed for: alkynol **5f** (42.4 mg, 0.16 mmol), Pd/CaCO<sub>3</sub> (12.4 mg), and quinoline (3.5  $\mu$ L) in AcOEt (1.5 mL) for 2 h. Washings with HCl 2 N were substituted by washings with a 7% aqueous citric acid solution. Purification of the crude mixture by flash chromatography on silica gel (Hexane/AcOEt : 7/3) gave **8f** (38.9 mg, 91%) as a colorless oil:  $[\alpha]_D^{25} +19.5$  (c 1.00, CHCl<sub>3</sub>); IR (film) 3467, 2985, 1740, 1456, 1372, 1277 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.76 (1H, ddt, *J* = 11.2, 7.9, 1.1 Hz), 5.65 (1H, dddd, *J* = 11.2, 7.9, 5.7, 1.1 Hz), 4.82 (1H, ddd, *J* = 12.9, 7.9, 1.1 Hz), 4.60–4.54 (2H, m), 4.11–4.02 (2H, m), 3.94 (1H, dd, *J* = 8.1, 6.1 Hz), 1.48 (9H, s), 1.43 (3H, s), 1.36 (3H, s); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>)  $\delta$  153.4, 132.6, 127.4, 109.4, 82.6, 77.9, 67.8, 65.6, 62.7, 27.8, 26.5, 25.1; HRMS(ESI) calcd for C<sub>14</sub>H<sub>24</sub>NaO<sub>6</sub> (M + Na<sup>+</sup>) 311.1471, found 311.1486.

**Compound 9a:** The general procedure was followed for: alkyne **6a** (90.2 mg, 0.36 mmol), Pd/CaCO<sub>3</sub> (27.0 mg), quinoline (8  $\mu$ L), and AcOEt (2.5 mL) for 2 h. Purification of the crude mixture by flash chromatography on silica gel (Hexane/AcOEt : 80/20) gave **9a** (72.3 mg, 80%) as a colorless oil:  $[\alpha]_D^{25} -19.5$  (c 1.74, CHCl<sub>3</sub>) for >96% ee;<sup>4</sup> IR (film) 3444, 2929, 1752, 1451, 1391, 1263 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  7.39–7.32 (5H, m), 5.67 (2H, m), 5.15 (2H, s), 4.87 (1H, m), 4.57 (1H, m), 4.17 (1H, t, *J* = 7.3 Hz), 2.25 (1H, bs), 1.95–1.59 (5H, m), 1.47–0.86 (6H, m); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>)  $\delta$  155.0, 136.7, 135.0, 128.5, 128.5, 128.2, 124.6, 71.7, 69.7, 63.7, 43.4, 28.6, 28.5, 26.4, 26.0, 25.9; HRMS(ESI) calcd for C<sub>18</sub>H<sub>24</sub>NaO<sub>4</sub> (M + Na<sup>+</sup>) 327.1572, found 327.1565.

**Compound 10a:** The general procedure was followed for: alkyne **7a** (34.0 mg, 0.15 mmol), Pd/CaCO<sub>3</sub> (5.7 mg), quinoline (4.5  $\mu$ L), and AcOEt (1.4 mL) for 1 h. Purification of the crude mixture by flash chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/MeOH : 99/1) gave **10a** (31.9 mg, 93%) as a colorless oil:  $[\alpha]_D^{25} -20.3$  (c 0.93, CHCl<sub>3</sub>) for 97% ee;<sup>2</sup> IR (film) 3435, 2927, 1750, 1447, 1362, 1270 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  5.68 (2H, m), 4.87 (1H, dd, *J* = 12.4, 7.2 Hz), 4.58 (1H, dd, *J* = 12.4, 4.0 Hz), 4.20 (1H, t, *J* = 7.3 Hz), 3.78 (3H, s), 2.19 (1H, bs), 1.97–1.60 (5H, m), 1.44–0.88 (6H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  155.8, 136.7, 124.8, 71.7, 63.6, 54.8, 43.4, 28.6, 28.5, 26.4, 26.0, 25.9; HRMS(ESI) calcd for C<sub>12</sub>H<sub>20</sub>NaO<sub>4</sub> (M + Na<sup>+</sup>) 251.1259, found 251.1263.

**Compound 13e:** The general procedure was followed for: alkynol **5e** (67.5 mg, 0.26 mmol), Pd/CaCO<sub>3</sub> (12.0 mg), and quinoline (4  $\mu$ L) in AcOEt (2 mL) for 30 min. Purification of the crude mixture by flash chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>) gave (2*Z*,4*S*)-4-hydroxynon-2-enyl benzoate (**13e**, 60.7 mg, 89%) as a colorless oil:  $[\alpha]_D^{25} -27.4$  (c 0.82, CHCl<sub>3</sub>) for 80% ee; IR (film) 3423, 2930,

<sup>4</sup> Determined by <sup>1</sup>H and <sup>19</sup>F NMR of the corresponding Mosher's esters.

1721, 1603, 1272  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (2H, m), 7.56 (1H, m), 7.43 (2H, m), 5.70 (2H, m), 5.08 (1H, m), 4.79 (1H, dd,  $J = 12.7, 4.5$  Hz), 4.59 (1H, q,  $J = 6.7$  Hz), 1.64 (2H, m), 1.53–1.28 (6H, m), 0.88 (3H, d,  $J = 6.8$  Hz);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  166.5, 137.8, 133.0, 129.6, 129.6, 128.3, 124.6, 67.6, 60.8, 37.0, 31.8, 25.0, 22.6, 14.0; HRMS(ESI) calcd for  $\text{C}_{16}\text{H}_{22}\text{NaO}_3$  ( $\text{M} + \text{Na}^+$ ) 285.1467, found 285.1458.

**Cyclization of 8a catalyzed by 0.5%  $\text{Pd}(\text{PPh}_3)_4$ :** A solution of  $\text{Pd}(\text{PPh}_3)_4$  (2.31 mg, 0.002 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.4 mL) was added to a flask (sealed with a septum) that contained the alkenol **8a** (108.1 mg, 0.4 mmol) under  $\text{N}_2$ . Then,  $\text{Et}_3\text{N}$  (11  $\mu\text{L}$ , 0.08 mmol) was added and the mixture was stirred for 24 h at rt. The solvent was removed in vacuo and the crude mixture was purified by flash chromatography on silica gel ( $\text{CH}_2\text{Cl}_2/\text{Hexane} : 1/1$ ) to afford a mixture 84:16 of *trans*-**1a** and *cis*-**1a** as a colorless oil (23.8 mg, 30%) and starting material **8a** (47.8 mg, 44%). Spectra of *cis*-**1a**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.92 (1H, ddd,  $J = 17.1, 10.4, 7.4$  Hz), 5.52 (1H, dt,  $J = 17.1, 1.0$  Hz), 5.50 (1H, dt,  $J = 10.4, 1.0$  Hz), 5.04 (1H, ddt,  $J = 7.4, 7.1, 1.0$  Hz), 4.36 (1H, dd,  $J = 9.0, 7.1$  Hz), 1.92–1.63 (5H, m), 1.35–1.00 (6H, m);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.6, 129.2, 122.0, 83.9, 80.2, 37.2, 28.8, 28.1, 25.9, 25.1, 25.0.

**Isomerization of *cis*-1a:** The above mixture of *trans*-**1a** and *cis*-**1a** (84:16, 23.8 mg, 0.12 mmol) was dissolved in  $\text{CDCl}_3$  (1.0 mL) and  $\text{Pd}(\text{PPh}_3)_4$  (7.0 mg, 0.006 mmol) was added. The isomerization rate at rt was: 16% *cis*-**1a** at 0 min, 9.6% at 30 min, 8.5% at 1 h, 5.9% at 5 h, 3.7% at 24 h.

**Preparation of *E*-8a:** A 1.6M solution of BuLi in hexanes (13.75 mL, 22 mmol) was added to a solution of 2-propyn-1-ol (561 mg, 10.0 mmol) in anhyd THF (20 mL) at  $-78^\circ\text{C}$ . Cyclohexanecarbaldehyde (1.45 mL, 12.0 mmol) was added and the mixture was warmed up to rt and stirred for additional 20 min. The reaction was quenched with an aqueous saturated solution of  $\text{NH}_4\text{Cl}$  and extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with brine and dried with anhyd  $\text{MgSO}_4$ . Then, the crude mixture can be purified by flash chromatography on silica gel (from  $\text{CH}_2\text{Cl}_2$  to  $\text{CH}_2\text{Cl}_2/\text{MeOH} : 95/5$ ) to afford 1-cyclohexylbut-2-yne-1,4-diol as colorless oil (1.379 g, 82%). Alternatively, the above crude mixture (without chromatography) was dissolved in anhyd  $\text{Et}_2\text{O}$  (30 mL) and  $\text{LiAlH}_4$  (1.33 g, 35 mmol) was added at  $0^\circ\text{C}$ . The suspension was quenched with a saturated solution of Rochelle salt and was extracted with  $\text{Et}_2\text{O}$ . The organic layer was washed with brine and was dried with anhyd  $\text{MgSO}_4$ . The crude mixture was purified by flash chromatography on silica gel (from  $\text{CH}_2\text{Cl}_2$  to  $\text{CH}_2\text{Cl}_2/\text{MeOH} : 95/5$ ) to afford (*E*)-1-cyclohexylbut-2-ene-1,4-diol as colorless oil (377 mg, 22% for the two steps). The purified diol (128 mg, 0.75 mmol) was dissolved in anhyd THF (2 mL) at  $-78^\circ\text{C}$ . A 1.6 M solution of BuLi in hexanes (516  $\mu\text{L}$ , 0.83 mmol) was added and stirred for 10 min. Then, a solution of  $\text{Boc}_2\text{O}$  (180

mg, 0.83 mmol) in THF (2 mL) was added at  $-78\text{ }^{\circ}\text{C}$  and stirred for 45 min. The reaction mixture was quenched by addition of an aqueous saturated solution of  $\text{NH}_4\text{Cl}$  and extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with brine and dried over anhyd  $\text{MgSO}_4$ . The crude mixture was purified by flash chromatography on silica gel (from  $\text{CH}_2\text{Cl}_2$  to  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  : 99/1) to afford *tert*-butyl (*E*)-4-cyclohexyl-4-hydroxybut-2-enyl carbonate (**E-8a**) as a colorless oil (128 mg, 63%), IR (film) 3436, 2981, 1742, 1451, 1370, 1279  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.85–5.74 (2H, m), 4.56 (2H, dd,  $J$  = 5.4, 1.0 Hz), 3.88 (1H, t,  $J$  = 6.1 Hz), 1.85–0.94 (11H, m), 1.49 (9H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.3, 136.5, 125.0, 82.2, 76.5, 66.7, 43.5, 28.7, 28.3, 27.7, 26.4, 26.1, 26.0. HRMS(ESI) calcd for  $\text{C}_{15}\text{H}_{26}\text{NaO}_4$  ( $\text{M} + \text{Na}^+$ ) 293.1729, found 293.1738.

**Preparation of 12e:** A solution of  $\text{Et}_2\text{Zn}$  (1.1M) in toluene (909  $\mu\text{L}$ , 1.00 mmol) was added at rt to a solution of **11**<sup>5</sup> (163.6 mg, 1.00 mmol) in anhyd toluene (1 mL), and the mixture was refluxed for 1 h. A catalyst solution of (*R*)-BINOL (28.6 mg, 0.1 mmol), phenol (9.4 mg, 0.1mmol),  $\text{Ti}(\text{iPrO})_4$  (74  $\mu\text{L}$ , 0.25 mmol) in anhyd  $\text{Et}_2\text{O}$  (3 mL) was stirred for 30 min. This solution was added to the reaction mixture and it was stirred for one additional hour at rt before adding hexanal (30  $\mu\text{L}$ , 0.25 mmol). The reaction mixture was stirred for 4 h at rt. Finally, the reaction was quenched with  $\text{NH}_4\text{Cl}$ , the organic layer was washed with HCl (2 N),  $\text{NaHCO}_3$ , brine, dried over  $\text{MgSO}_4$ , and evaporated under reduced pressure. The crude mixture was purified on silica gel ( $\text{CH}_2\text{Cl}_2/\text{MeOH}$  : 99/1) to give (*S*)-4-hydroxynon-2-ynyl benzoate (**12e**, 65.1 mg, 100%) as colorless oil:  $[\alpha]_D^{25} +1.16$  ( $c$  0.97,  $\text{CHCl}_3$ ) for 80% ee;<sup>2</sup> IR (film) 3440, 2932, 1726, 1269, 712  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (2H, m), 7.58 (1H, m), 7.45 (2H, m), 4.96 (2H, d,  $J$  = 1.6 Hz), 4.43 (1H, tt,  $J$  = 6.6, 1.6 Hz), 2.11 (1H, bs), 1.72 (2H, m), 1.46 (2H, m), 1.31 (4H, m), 0.88 (3H, t,  $J$  = 6.9 Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.9, 133.3, 129.8, 129.5, 128.4, 88.0, 78.8, 62.4, 52.8, 37.5, 31.4, 24.7, 22.5, 13.9; HRMS(ESI) calcd for  $\text{C}_{16}\text{H}_{20}\text{NaO}_3$  ( $\text{M} + \text{Na}^+$ ) 283.1310, found 283.1300.

**Synthesis of 1e:** Potassium *tert*-butyl carbonate was prepared by bubbling  $\text{CO}_2$  through a solution of potassium *tert*-butoxide (224 mg, 2.00 mmol) in anhyd THF (20 mL) for 2 h at rt. A solution of  $\text{Pd}(\text{PPh}_3)_4$  (6.5 mg, 0.006 mmol) and alkenol **8e** (23.5 mg, 0.11 mmol) in  $\text{CH}_2\text{Cl}_2$  (1 mL) was added to another solution of potassium *tert*-butyl carbonate (88 mg, 0.56 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.8 mL) under  $\text{N}_2$  atmosphere. The mixture was stirred at rt until TLC showed complete disappearance of **8e**. The reaction mixture was quenched with an aqueous phosphate buffer (pH=7). The organic layer was washed with brine, dried over  $\text{MgSO}_4$ , and evaporated under reduced pressure. The crude mixture was purified by

<sup>5</sup> Bandgar, B. P.; Kamble, V. T.; Sadavarte, V. S.; Uppalla, L. S. *Synlett* **2002**, 735–738.

flash chromatography on silica gel (hexane/Et<sub>2</sub>O : 9/1) to afford **1e** as a colorless oil (16.3 mg, 80%);  $[\alpha]_D^{25}$  -38.5 (*c* 0.98, CHCl<sub>3</sub>) for 80% ee; IR (film) 2931, 1806, 1459, 1366, 1266 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  5.87 (1H, ddd, *J* = 17.1, 10.5, 7.1 Hz), 5.49 (1H, d, *J* = 17.1 Hz), 5.43 (1H, dt, *J* = 10.5 Hz), 4.64 (1H, t, *J* = 7.2, 1.0 Hz), 4.30 (1H, td, *J* = 7.6, 5.1 Hz), 1.72 (2H, m), 1.56–1.30 (6H, m), 0.90 (3H, t, *J* = 7.0 Hz); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  154.3, 132.2, 121.2, 82.6, 81.9, 32.9, 31.3, 24.3, 22.3, 13.9.

**Formation of 14f:** Cyclic carbonate **1f** (18.0 mg, 0.084 mmol) was stirred in a mixture of NaOH 1 M (1 mL) and 1,4-dioxane (1 mL) for 2 h. A saturated solution of NH<sub>4</sub>Cl was added and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with brine and dried over anhyd MgSO<sub>4</sub>. The solvent was evaporated in vacuo and the crude mixture was purified by flash chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/MeOH from 98:2 to 95:5) to afford **14f** (7.6 mg, 48%) as a colorless oil:<sup>6</sup>  $[\alpha]_D^{25}$  +23.4 (*c* 0.63, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.96 (1H, ddd, *J* = 17.4, 10.6, 5.7 Hz), 5.39 (1H, dt, *J* = 17.4, 1.5 Hz), 5.28 (1H, dt, *J* = 10.6, 1.4 Hz), 4.27 (1H, m), 4.16 (1H, q, *J* = 6.3 Hz), 4.08 (1H, dd, *J* = 8.4, 6.3 Hz), 3.97 (1H, dd, *J* = 8.4, 6.3 Hz), 3.62 (1H, m), 2.34 (1H, d, *J* = 4.2 Hz), 2.28 (1H, d, *J* = 4.2 Hz), 1.43 (3H, s), 1.37 (3H, s); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>)  $\delta$  137.2, 117.1, 109.2, 76.0, 73.7, 72.1, 66.0, 26.7, 25.2.

<sup>6</sup> (a) Sato, A.; Ito, H.; Taguchi, T. *J. Org. Chem.* **2000**, *65*, 918–921. (b) Yadav, J. S.; Reddy, B. V. S.; Reddy, K. S. *Tetrahedron*, **2003**, *59*, 5333–5336. (c) Lee, H. W.; Yoon, H. K.; Lee, I.-Y. *C. Bull. Korean Chem. Soc.* **1998**, *19*, 916–917.











































































































