Supporting Information for the Paper

Novel Carbonyl–Bromoallylation/Heck Reaction Sequence.

Stereocontrolled Access to Bicyclic β -Lactams

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General. General experimental data and procedures have been previously reported.⁷ NMR spectra were recorded in CDCl₃ solutions, except otherwise stated. Chemical shifts are given in ppm relative to TMS (¹H, 0.0 ppm), or CDCl₃ (¹³C, 76.9 ppm). Specific rotation [α]_D is given in deg cm² g^{–1} at 20 °C, and the concentration (*c*) is expressed in g per 100 mL. All commercially available compounds were used without further purification.

Bromohomoallyl Alcohol (+)-2c. From 286 mg (1.104 mmol) of 4-oxoazetidine-2-carbaldehyde (+)-**1c**, 278 mg (66%) of compound (+)-**2c** was obtained as a colorless oil after purification by flash chromatography (hexanes/ethyl acetate, 2/1). $[\alpha]_D = +131.2$ (c 0.8, CHCl_3). $^1\text{H-NMR}$: δ 2.58 (t, 1H, $J = 2.3$ Hz), 2.62 (m, 2H), 3.79 (s, 3H), 4.36 (dd, 1H, $J = 5.3, 4.5$ Hz), 4.44 (m, 1H), 4.53 (dd, 2H, $J = 4.4, 2.4$ Hz), 4.99 (d, 1H, $J = 5.1$ Hz), 5.53 (d, 1H, $J = 1.7$ Hz), 5.65 (dt, 1H, $J = 1.8, 0.9$ Hz), 6.87 and 7.39 (d, each 2H, $J = 9.0$ Hz). $^{13}\text{C-NMR}$: δ 164.3, 156.8, 130.2, 129.4, 120.4, 119.9, 114.1, 79.7, 78.1, 68.6, 60.0, 58.9, 55.3, 45.3. IR (CHCl_3 , cm^{-1}): ν 3431, 1742. MS (EI), m/z : 381 ($\text{M}^+ + 2$, 18), 379 (M^+ , 18), 149 (100). Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{NO}_4\text{Br}$: C, 53.70; H, 4.77; N, 3.68. Found: C, 53.80; H, 4.80; N, 3.66.

Bromohomoallyl Alcohol (+)-2d. From 168 mg (0.55 mmol) of 4-oxoazetidine-2-carbaldehyde (+)-**1d**, 183 mg (78%) of compound (+)-**2d** was obtained as a colorless oil after purification by flash chromatography (hexanes/ethyl acetate, 2/1). $[\alpha]_D = +145.7$ (c 1.0, CHCl_3). $^1\text{H-NMR}$: δ 2.36 (br s, 1H), 2.64 (m, 2H), 3.71 (s, 3H), 3.78 (s, 3H), 4.39 (m, 2H), 5.18 (d, 1H, $J = 4.6$ Hz), 5.56 (d, 1H, $J = 1.9$ Hz), 5.59 (d, 1H, $J = 13.2$ Hz), 5.69 (d, 1H, $J = 1.2$ Hz), 6.86 and 7.45 (d, each 2H, $J = 9.0$ Hz), 7.59 (d, 1H, $J = 12.2$ Hz). $^{13}\text{C-NMR}$: δ 167.1, 161.5, 159.7, 157.0, 130.1, 128.7, 120.5, 120.3, 114.1, 100.5, 80.7, 68.9, 60.1, 55.4, 51.3, 45.5. IR (CHCl_3 , cm^{-1}): ν 3430, 1742, 1715. MS (EI), m/z : 427 ($\text{M}^+ + 2$, 18), 425 (M^+ , 18), 149 (100). Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{NO}_6\text{Br}$: C, 50.72; H, 4.73; N, 3.29. Found: C, 50.80; H, 4.80; N, 3.26.

Preparation of Bromohomoallyl Alcohol ($\pm$)-2g. From 150 mg (0.617 mmol) of 4-oxoazetidine-2-carbaldehyde ($\pm$)-**1g** and after column chromatography eluting with hexanes/ethyl acetate (3:1), 140 mg (62%) of the more polar compound ($\pm$)-**2g** and 8 mg (4%) of the less polar compound, its *anti*-epimer were obtained.

Bromohomoallyl Alcohol *syn*-($\pm$)-2g. Colorless oil. $^1\text{H-NMR}$: δ 2.11 (t, 1H, $J = 2.7$ Hz), 2.71 (m, 4H), 3.58 (dt, 1H, $J = 9.2, 5.7$ Hz), 3.79 (s, 3H), 4.28 (dd, 1H, $J = 5.7, 4.8$ Hz), 4.51 (m, 1H), 5.57 (d, 1H, $J = 1.7$ Hz), 5.68 (m, 1H), 6.86 and 7.36 (d, each 2H, $J = 9.0$ Hz). $^{13}\text{C-NMR}$: δ 166.3, 157.1, 130.9, 129.3, 121.4, 120.7, 114.4, 91.4, 70.8, 68.5, 58.3, 55.7, 50.3, 47.8, 14.8. IR (CHCl_3 , cm^{-1}): ν 3429, 1742. MS (EI), m/z : 365 ($\text{M}^+ + 2$, 30), 363 (M^+ , 30), 149 (100). Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{NO}_3\text{Br}$: C, 56.06; H, 4.98; N, 3.85. Found: C, 56.15; H, 5.00; N, 3.83.

Bromohomoallyl Alcohol *anti*-(±)-2g. Colorless oil. $^1\text{H-NMR}$: δ 2.13 (t, 1H, $J = 2.7$ Hz), 2.30 (br s, 1H), 2.92 (m, 4H), 3.60 (q, 1H, $J = 5.2$ Hz), 3.80 (s, 3H), 4.26 (dd, 1H, $J = 5.6, 3.2$ Hz), 4.66 (m, 1H), 5.58 and 5.81 (d, each 1H, $J = 1.7$ Hz), 6.90 and 7.36 (d, each 2H, $J = 9.0$ Hz). $^{13}\text{C-NMR}$: δ 165.6, 156.7, 130.4, 129.4, 120.7, 119.5, 114.7, 82.3, 70.5, 66.6, 58.1, 55.6, 51.0, 45.6, 15.0. IR (CHCl_3 , cm^{-1}): ν 3430, 1742. MS (EI), m/z : 365 ($\text{M}^+ + 2$, 28), 363 (M^+ , 28), 149 (100). Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{NO}_3\text{Br}$: C, 56.06; H, 4.98; N, 3.85. Found: C, 55.95; H, 5.01; N, 3.88.

Preparation of Bromohomoallyl Alcohol (±)-2h. From 150 mg (0.612 mmol) of 4-oxoazetidine-2-carbaldehyde (±)-1h and after column chromatography eluting with hexanes/ethyl acetate (5:1), 153 mg (67%) of the more polar compound (±)-2h and 18 mg (8%) of the less polar compound, its *anti*-epimer were obtained.

Bromohomoallyl Alcohol *syn*-(±)-2h. Colorless oil. $^1\text{H-NMR}$: δ 1.94 (s, 3H), 2.19 (br s, 1H), 2.59 (m, 2H), 3.78 (s, 3H), 4.00 (d, 1H, $J = 5.1$ Hz), 4.28 (m, 2H), 5.21 (d, 1H, $J = 0.7$ Hz), 5.25 (t, 1H, $J = 1.5$ Hz), 5.54 (dd, 1H, $J = 1.7, 0.5$ Hz), 5.67 (m, 1H), 6.86 and 7.46 (d, each 2H, $J = 9.0$ Hz). $^{13}\text{C-NMR}$: δ 165.9, 156.9, 137.4, 131.2, 129.3, 121.1, 120.6, 118.9, 114.2, 69.7, 59.7, 57.7, 55.6, 46.1, 22.9. IR (CHCl_3 , cm^{-1}): ν 3434, 1744. MS (EI), m/z : 367 ($\text{M}^+ + 2$, 35), 365 (M^+ , 35), 149 (100). Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{NO}_3\text{Br}$: C, 55.75; H, 5.50; N, 3.82. Found: C, 55.89; H, 5.47; N, 3.80.

Bromohomoallyl Alcohol *anti*-(±)-2h. Colorless oil. $^1\text{H-NMR}$: δ 1.93 (s, 3H), 2.15 (br s, 1H), 2.47 (dd, 1H, $J = 14.4, 9.8$ Hz), 2.71 (d, 1H, $J = 14.1$ Hz), 3.80 (s, 3H), 4.10 (d, 1H, $J = 5.9$ Hz), 4.29 (m, 1H), 4.40 (dd, 1H, $J = 6.2, 3.8$ Hz), 5.25 (t, 1H, $J = 1.3$ Hz), 5.28 (d, 1H, $J = 1.0$ Hz), 5.53 (dd, 1H, $J = 1.7, 0.5$ Hz), 5.64 (m, 1H), 6.89 and 7.50 (d, each 2H, $J = 9.0$ Hz). $^{13}\text{C-NMR}$: δ 165.6, 156.6, 136.9, 131.3, 129.7, 120.7, 119.9, 117.7, 114.2, 68.3, 59.6, 57.7, 55.6, 46.0, 23.3. IR (CHCl_3 , cm^{-1}): ν 3430, 1745. MS (EI), m/z : 367 ($\text{M}^+ + 2$, 27), 365 (M^+ , 27), 149 (100). Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{NO}_3\text{Br}$: C, 55.75; H, 5.50; N, 3.82. Found: C, 55.62; H, 5.47; N, 3.84.

Bromohomoallyl Alcohol (+)-2i. From 100 mg (0.41 mmol) of 4-oxoazetidine-2-carbaldehyde (+)-1i, 95 mg (64%) of compound (+)-2i was obtained as a colorless oil after purification by flash chromatography (hexanes/ethyl acetate, 4/1). $[\alpha]_{\text{D}} = +82.3$ (c 1.3, CHCl_3). $^1\text{H-NMR}$: δ 1.78 (s, 3H), 2.34 (br s, 1H), 2.62 (ddd, 1H, $J = 14.2, 8.8, 0.7$ Hz), 2.80 (ddd, 1H, $J = 14.3, 3.7, 1.0$ Hz), 3.87 (dd, 1H, $J = 6.1, 5.1$ Hz), 3.90 and 4.07 (d, each 1H, $J = 15.5$ Hz), 4.39 (ddd, 1H,

$J = 8.8, 6.1, 3.7$ Hz), 4.96 and 4.99 (s, each 1H), 5.28 (d, 1H, $J = 5.1$ Hz), 5.59 (d, 1H, $J = 1.7$ Hz), 5.73 (m, 1H), 7.05 (m, 1H), 7.17 and 7.32 (m, each 2H). ^{13}C -NMR: δ 166.6, 157.5, 140.2, 129.8, 129.4, 122.8, 120.4, 116.0, 113.9, 80.3, 69.1, 60.6, 48.1, 46.0, 20.5. IR (CHCl_3 , cm^{-1}): ν 3428, 1742. MS (EI), m/z : 367 ($\text{M}^+ + 2$, 100), 366 (M^+ , 98). Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{NO}_3\text{Br}$: C, 55.75; H, 5.50; N, 3.82. Found: C, 55.88; H, 5.47; N, 3.85.

Bromohomoallyl Alcohol (+)-2k. From 96 mg (0.53 mmol) of 4-oxoazetidine-2-carbaldehyde (+)-**1k**, 146 mg (91%) of compound (+)-**2k** was obtained as a colorless oil after purification by flash chromatography (hexanes/ethyl acetate, 1/1). $[\alpha]_{\text{D}} = +47.5$ (c 0.9, CHCl_3). ^1H -NMR: δ 2.34 (m, 2H), 2.68 (m, 3H), 3.19 (m, 1H), 3.57 (m, 1H), 3.58 (s, 3H), 3.72 (t, 1H, $J = 5.0$ Hz), 4.15 (m, 1H), 4.44 (d, 1H, $J = 5.1$ Hz), 5.07 (m, 2H), 5.56 (d, 1H, $J = 1.7$ Hz), 5.72 (s, 1H), 5.75 (m, 1H). ^{13}C -NMR: δ 167.7, 134.8, 129.4, 120.0, 117.2, 82.8, 68.8, 59.8, 59.4, 45.7, 40.8, 31.8. IR (CHCl_3 , cm^{-1}): ν 3429, 1744. MS (EI), m/z : 305 ($\text{M}^+ + 2$, 100), 303 (M^+ , 98). Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{NO}_3\text{Br}$: C, 47.38; H, 5.96; N, 4.60. Found: C, 47.45; H, 5.93; N, 4.58.

Bromohomoallyl Alcohol (+)-2l. From 297 mg (1.78 mmol) of 4-oxoazetidine-2-carbaldehyde (+)-**1l**, 421 mg (82%) of compound (+)-**2l** was obtained as a colorless oil after purification by flash chromatography (hexanes/ethyl acetate, 1/1). $[\alpha]_{\text{D}} = +33.1$ (c 1.0, CHCl_3). ^1H -NMR: δ 2.31 (td, 1H, $J = 2.6, 0.5$ Hz), 2.70 (m, 3H), 3.61 (s, 3H), 3.86 (d, 1H, $J = 4.4$ Hz), 3.92 (dd, 1H, $J = 15.2, 2.6$ Hz), 4.24 (m, 1H), 4.38 (dd, 1H, $J = 17.7, 2.6$ Hz), 5.52 (d, 1H, $J = 4.9$ Hz), 5.57 (d, 1H, $J = 1.7$ Hz), 5.78 (d, 1H, $J = 1.2$ Hz). ^{13}C -NMR: δ 167.0, 129.5, 120.4, 83.6, 76.9, 73.2, 68.3, 59.7, 46.0, 31.1. IR (CHCl_3 , cm^{-1}): ν 3426, 1739. MS (EI), m/z : 289 ($\text{M}^+ + 2$, 100), 287 (M^+ , 98). Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{NO}_3\text{Br}$: C, 45.85; H, 4.90; N, 4.86. Found: C, 45.77; H, 4.92; N, 4.84.

Bromohomoallyl Alcohol (+)-2m. From 206 mg (1.14 mmol) of 4-oxoazetidine-2-carbaldehyde (+)-**1m**, 206 mg (60%) of compound (+)-**2m** was obtained as a colorless oil after purification by flash chromatography (hexanes/ethyl acetate, 1/2). $[\alpha]_{\text{D}} = +43.2$ (c 0.9, CHCl_3). ^1H -NMR: δ 2.02 (t, 1H, $J = 2.7$ Hz), 2.53 (td, 1H, $J = 6.8, 2.6$ Hz), 2.68 (m, 3H), 3.38 (m, 1H), 3.60 (s, 3H), 3.63 (m, 1H), 3.84 (t, 1H, $J = 5.4$ Hz), 4.21 (m, 1H), 4.51 (d, 1H, $J = 4.9$ Hz), 5.58 (d, 1H, $J = 1.7$ Hz), 5.74 (s, 1H). ^{13}C -NMR: δ 167.9, 129.5, 120.3, 83.2, 81.2, 70.5, 69.1, 60.6, 59.6, 45.9, 40.5,

18.0. IR (CHCl₃, cm⁻¹): ν 3428, 1742. MS (EI), m/z : 303 (M⁺ + 2, 100), 301 (M⁺, 98). Anal. Calcd for C₁₂H₁₆NO₃Br: C, 47.70; H, 5.34; N, 4.64. Found: C, 47.80; H, 5.31; N, 4.66.

General Procedure for the Preparation of the *O*-Acetylmandelates (+)-3 and (+)-4. The appropriate (*R*)- or (*S*)-*O*-acetylmandelic acid (0.10 mmol), 4-dimethylaminopyridine (DMAP) (cat.), and a solution of dicyclohexylcarbodiimide (DCC) (0.18 mmol) in dichloromethane (500 mL) were sequentially added at 0 °C to a solution of the alcohol (+)-2a (0.09 mmol) in dichloromethane (1.0 mL). The reaction mixture was allowed to warm to room temperature and stirred for 16 h. The solvent was removed under reduced pressure and diethyl ether was added. The mixture was then filtered and the filtrate was concentrated under reduced pressure. Chromatography of the residue eluting with hexanes/ethyl acetate mixtures gave analytically pure *O*-acetylmandelates.

(*R*)-*O*-Acetylmandelate (+)-3. From 25 mg (0.07 mmol) of homoallylic alcohol (+)-2a, 24 mg (65%) of compound (+)-3 was obtained as a colorless oil after purification by flash chromatography (hexanes/ethyl acetate, 2/1). [α]_D = +40.0 (*c* 1.2, CHCl₃). ¹H-NMR: δ 2.18 (s, 3H), 2.81 (dd, 1H, *J* = 15.0, 4.9 Hz), 3.01 (dd, 1H, *J* = 15.0, 7.9 Hz), 3.32 (s, 3H), 3.80 (s, 3H), 4.44 (m, 2H), 5.51 (d, 1H, *J* = 1.9 Hz), 5.66 (m, 2H), 5.86 (s, 1H), 6.81 (d, 2H, *J* = 9.0 Hz), 7.30 (m, 7H). ¹³C-NMR: δ 170.2, 168.0, 164.5, 156.8, 133.2, 129.9, 129.3, 128.8, 127.8, 127.6, 120.8, 119.6, 114.4, 83.1, 74.5, 71.0, 59.3, 56.7, 55.4, 42.0, 20.7. IR (CHCl₃, cm⁻¹): ν 3430, 1741, 1648. Anal. Calcd for C₂₅H₂₆NO₇Br: C, 56.40; H, 4.92; N, 2.63. Found: C, 56.51; H, 4.90; N, 2.61.

(*S*)-*O*-Acetylmandelate (+)-4. From 25 mg (0.07 mmol) of homoallylic alcohol (+)-2a, 30 mg (81%) of compound (+)-4 was obtained as a colorless oil after purification by flash chromatography (hexanes/ethyl acetate, 2/1). [α]_D = +93.3 (*c* 1.3, CHCl₃). ¹H-NMR: δ 2.14 (s, 3H), 2.64 (dd, 1H, *J* = 14.8, 3.3 Hz), 2.82 (dd, 1H, *J* = 15.0, 8.5 Hz), 3.63 (s, 3H), 3.80 (s, 3H), 4.49 (dd, 2H, *J* = 6.0, 5.0 Hz), 4.68 (d, 1H, *J* = 5.1 Hz), 5.05 (s, 1H), 5.09 (d, 1H, *J* = 1.7 Hz), 5.68 (m, 1H), 5.76 (s, 1H), 6.90 (d, 2H, *J* = 9.0 Hz), 7.36 (m, 7H). ¹³C-NMR: δ 169.8, 167.8, 164.4, 156.9, 133.6, 129.8, 129.2, 128.6, 127.8, 127.2, 120.4, 119.8, 114.4, 83.1, 74.1, 71.2, 59.6, 57.1, 55.4, 42.0, 20.6. IR (CHCl₃, cm⁻¹): ν 3432, 1742, 1645. Anal. Calcd for C₂₅H₂₆NO₇Br: C, 56.40; H, 4.92; N, 2.63. Found: C, 56.30; H, 4.89; N, 2.65.

Procedure for the Preparation of α,β -Unsaturated Ketone (+)-5. Palladium(II) acetate (2.5 mg, 0.011 mmol), potassium carbonate (20.2 mg, 0.146 mmol) and copper(II) acetate (46.5 mg, 0.256 mmol) were sequentially added to a stirred solution of the bromohomoallylic alcohol (+)-**2j**, (35 mg, 0.122 mmol) in acetonitrile (5 mL) under an argon atmosphere. The resulting suspension was stirred at reflux temperature for 9 h. The organic phase was diluted with brine (2 mL), extracted with ethyl acetate (5 x 5 mL), washed with brine (2 mL), dried (MgSO₄) and concentrated under reduced pressure. Chromatography of the residue eluting with hexanes/ethyl acetate (1:2) gave 13 mg (50%) of analytically pure ketone (+)-**5**.

α,β -Unsaturated Ketone (+)-5. $[\alpha]_D = +66.2$ (*c* 0.8, CHCl₃). ¹H-NMR: δ 2.32 (s, 3H), 3.47 (s, 3H), 3.60 (ddt, 1H, *J* = 15.5, 7.0, 1.1 Hz), 4.05 (ddt, 1H, *J* = 15.4, 5.4, 1.4 Hz), 4.31 (ddd, 1H, *J* = 8.4, 4.5, 0.6 Hz), 4.67 (d, 1H, *J* = 4.6 Hz), 5.20 (m, 2H), 5.71 (m, 1H), 6.28 (d, 1H, *J* = 16.1 Hz), 6.70 (dd, 1H, *J* = 16.2, 8.4 Hz). ¹³C-NMR: δ 197.2, 165.9, 140.1, 135.3, 130.7, 119.2, 85.6, 58.7, 58.6, 43.0, 26.9. IR (CHCl₃, cm⁻¹): ν 1744, 1674. MS (EI), *m/z*: 209 (M⁺, 100). Anal. Calcd for C₁₁H₁₅NO₃: C, 63.14; H, 7.23; N, 6.69. Found: C, 63.24; H, 7.20; N, 6.67.

Acetate (+)-6b. From 61 mg (0.16 mmol) of homoallylic alcohol (+)-**2b**, 59 mg (87%) of compound (+)-**6b** was obtained as a colorless solid after purification by flash chromatography (hexanes/ethyl acetate, 2/1). Mp: 105–106 °C (hexanes/ethyl acetate). $[\alpha]_D = +81.6$ (*c* 1.3, CHCl₃). ¹H-NMR: δ 1.76 (s, 3H), 2.86 (d, 2H, *J* = 5.8 Hz), 3.79 (s, 3H), 4.25 (dd, 1H, *J* = 12.7, 5.9 Hz), 4.44 (m, 2H), 4.78 (d, 1H, *J* = 5.1 Hz), 5.27 (dd, 1H, *J* = 10.5, 1.2 Hz), 5.38 (dd, 1H, *J* = 17.3, 1.5 Hz), 5.51 (d, 1H, *J* = 1.7 Hz), 5.63 (d, 1H, *J* = 1.0 Hz), 5.69 (dt, 1H, *J* = 7.8, 6.1 Hz), 5.96 (m, 1H), 6.86 and 7.37 (d, each 2H, *J* = 9.0 Hz). ¹³C-NMR: δ 169.5, 164.7, 156.7, 133.2, 130.0, 127.9, 120.2, 120.1, 118.1, 114.1, 80.3, 72.4, 70.7, 57.8, 55.4, 42.7, 20.5. IR (KBr, cm⁻¹): ν 1740, 1726. MS (EI), *m/z*: 425 (M⁺ + 2, 16), 423 (M⁺, 16), 149 (100). Anal. Calcd for C₁₉H₂₂NO₅Br: C, 53.79; H, 5.23; N, 3.30. Found: C, 53.70; H, 5.20; N, 3.28.

Acetate (+)-6d. From 107 mg (0.251 mmol) of homoallylic alcohol (+)-**2d**, 77 mg (65%) of compound (+)-**6d** was obtained as a colorless solid after purification by flash chromatography (hexanes/ethyl acetate, 2/1). Mp: 90–91 °C (hexanes/ethyl acetate). $[\alpha]_D = +112.8$ (*c* 1.0, CHCl₃). ¹H-NMR: δ 1.76 (s, 3H), 2.78 (m, 2H), 3.72 (s, 3H), 3.79 (s, 3H), 4.59 (dd, 1H, *J* = 7.3, 5.1 Hz), 5.22 (d, 1H, *J* = 5.1 Hz), 5.51 (d, 1H, *J* = 1.7 Hz), 5.59 (d, 1H, *J* = 12.4 Hz), 5.62 (s, 1H), 5.68 (m,

1H), 6.88 and 7.36 (d, each 2H, $J = 9.0$ Hz), 7.59 (d, 1H, $J = 12.4$ Hz). ^{13}C -NMR: δ 169.4, 167.1, 161.0, 159.8, 157.3, 129.4, 127.4, 120.7, 120.4, 114.4, 100.7, 81.0, 69.8, 57.6, 55.5, 51.4, 42.9, 20.5. IR (CHCl_3 , cm^{-1}): ν 1740, 1725, 1715. MS (EI), m/z : 469 ($\text{M}^+ + 2$, 20), 467 (M^+ , 20), 149 (100). Anal. Calcd for $\text{C}_{20}\text{H}_{22}\text{NO}_7\text{Br}$: C, 51.30; H, 4.74; N, 2.99. Found: C, 51.42; H, 4.70; N, 2.97.

Acetate ($\pm$)-6f. From 75 mg (0.205 mmol) of homoallylic alcohol ($\pm$)-**2f**, 55 mg (65%) of compound ($\pm$)-**6f** was obtained as a colorless oil after purification by flash chromatography (hexanes/ethyl acetate, 2/1). ^1H -NMR: δ 1.59 (s, 3H), 2.57 (q, 1H, $J = 7.7$ Hz), 2.74 (d, 2H, $J = 5.8$ Hz), 2.75 (m, 1H), 3.49 (td, 1H, $J = 7.7$, 5.6 Hz), 3.78 (s, 3H), 4.35 (dd, 1H, $J = 8.5$, 5.6 Hz), 5.17 (dq, 1H, $J = 10.2$, 1.4 Hz), 5.24 (dq, 1H, $J = 17.1$, 1.5 Hz), 5.51 (d, 1H, $J = 1.9$ Hz), 5.61 (m, 1H), 5.62 (s, 1H), 5.98 (m, 1H), 6.85 and 7.28 (d, each 2H, $J = 9.0$ Hz). ^{13}C -NMR: δ 169.5, 166.7, 156.3, 134.8, 130.2, 127.4, 121.1, 120.2, 117.2, 114.0, 70.1, 55.8, 55.4, 50.4, 44.0, 28.9, 20.3. IR (CHCl_3 , cm^{-1}): ν 1744, 1728. MS (EI), m/z : 409 ($\text{M}^+ + 2$, 17), 407 (M^+ , 17), 149 (100). Anal. Calcd for $\text{C}_{19}\text{H}_{22}\text{NO}_4\text{Br}$: C, 55.89; H, 5.43; N, 3.43. Found: C, 55.80; H, 5.46; N, 3.41.

Acetate *syn*-($\pm$)-6h. From 47 mg (0.128 mmol) of homoallylic alcohol *syn*-($\pm$)-**2h**, 36 mg (69%) of compound *syn*-($\pm$)-**6h** was obtained as a colorless oil after purification by flash chromatography (hexanes/ethyl acetate, 5/2). ^1H -NMR: δ 1.63 (s, 3H), 1.99 (d, 3H, $J = 0.5$ Hz), 2.71 (m, 2H), 3.79 (s, 3H), 4.04 (dd, 1H, $J = 5.9$, 0.5 Hz), 4.41 (dd, 1H, $J = 8.3$, 5.9 Hz), 5.24 (d, 1H, $J = 0.7$ Hz), 5.29 (q, 1H, $J = 1.5$ Hz), 5.50 (d, 1H, $J = 1.7$ Hz), 5.63 (m, 2H), 6.87 and 7.33 (d, each 2H, $J = 9.0$ Hz). ^{13}C -NMR: δ 169.4, 165.1, 156.7, 136.0, 130.1, 127.4, 121.0, 120.2, 119.2, 114.0, 70.2, 57.6, 56.5, 55.4, 43.3, 22.7, 20.3. IR (CHCl_3 , cm^{-1}): ν 1742, 1727. MS (EI), m/z : 409 ($\text{M}^+ + 2$, 100), 407 (M^+ , 98). Anal. Calcd for $\text{C}_{19}\text{H}_{22}\text{NO}_4\text{Br}$: C, 55.89; H, 5.43; N, 3.43. Found: C, 56.02; H, 5.46; N, 3.46.

Acetate *anti*-($\pm$)-6h. From 23 mg (0.063 mmol) of homoallylic alcohol *anti*-($\pm$)-**2h**, 23 mg (91%) of compound *anti*-($\pm$)-**6h** was obtained as a colorless oil after purification by flash chromatography (hexanes/ethyl acetate, 3/1). ^1H -NMR: δ 1.98 (s, 3H), 2.15 (s, 3H), 2.57 (dd, 3H, $J = 15.0$, 10.4 Hz), 2.80 (d, 1H, $J = 15.1$ Hz), 3.81 (s, 3H), 4.13 (d, 1H, $J = 6.6$ Hz), 4.37 (dd, 1H, $J = 6.5$, 1.4 Hz), 5.25 (d, 1H, $J = 0.7$ Hz), 5.32 (d, 1H, $J = 1.0$ Hz), 5.43 (dd, 1H, $J = 1.8$, 0.6 Hz), 5.50 (m, 2H), 6.90 and 7.46 (d, each 2H, $J = 9.0$ Hz). ^{13}C -NMR: δ 169.9, 164.8, 156.4, 136.0, 135.7, 131.5, 128.5, 119.9, 118.7, 117.5, 114.4, 70.0, 58.6, 57.6, 55.4, 41.9, 22.9, 20.9. IR (CHCl_3 , cm^{-1}):

ν 1745, 1728. MS (EI), m/z : 409 ($M^+ + 2$, 100), 407 (M^+ , 98). Anal. Calcd for $C_{19}H_{22}NO_4Br$: C, 55.89; H, 5.43; N, 3.43. Found: C, 55.74; H, 5.40; N, 3.40.

Acetate (+)-6i. From 46 mg (0.126 mmol) of homoallylic alcohol (+)-**2i**, 37 mg (73%) of compound (+)-**6i** was obtained as a colorless oil after purification by flash chromatography (dichloromethane/ethyl acetate, 30/1). $[\alpha]_D = +72.9$ (c 0.8, $CHCl_3$). 1H -NMR: δ 1.75 (s, 3H), 2.05 (s, 3H), 2.82 (ddd, 1H, $J = 14.9, 7.3, 0.7$ Hz), 2.93 (ddd, 1H, $J = 14.9, 4.6, 1.0$ Hz), 3.67 and 4.05 (d, each 1H, $J = 15.5$ Hz), 4.11 (dd, 1H, $J = 7.1, 5.1$ Hz), 4.90 and 4.97 (s, each 1H), 5.31 (d, 1H, $J = 5.1$ Hz), 5.54 (d, 1H, $J = 1.7$ Hz), 5.61 (m, 2H), 7.08 (m, 3H), 7.31 (m, 2H). ^{13}C -NMR: δ 169.4, 166.4, 157.3, 139.1, 129.5, 127.7, 122.4, 120.5, 115.7, 113.9, 79.9, 70.4, 58.1, 47.7, 43.4, 21.0, 20.1. IR ($CHCl_3$, cm^{-1}): ν 1744, 1730. MS (EI), m/z : 409 ($M^+ + 2$, 100), 407 (M^+ , 98). Anal. Calcd for $C_{19}H_{22}NO_4Br$: C, 55.89; H, 5.43; N, 3.43. Found: C, 56.92; H, 5.40; N, 3.41.

Acetate (+)-6j. From 75 mg (0.259 mmol) of homoallylic alcohol (+)-**2j**, 76 mg (88%) of compound (+)-**6j** was obtained as a colorless solid after purification by flash chromatography (hexanes/ethyl acetate, 3/2). Mp: 62–63 °C (hexanes/ethyl acetate). $[\alpha]_D = +29.4$ (c 0.9, $CHCl_3$). 1H -NMR: δ 2.05 (s, 3H), 2.76 (ddd, 1H, $J = 14.9, 7.1, 0.5$ Hz), 2.87 (ddd, 1H, $J = 14.9, 4.4, 1.0$ Hz), 3.58 (s, 3H), 3.62 (ddt, 1H, $J = 15.7, 6.7, 1.3$ Hz), 3.95 (dd, 1H, $J = 7.4, 5.0$ Hz), 4.06 (ddt, 1H, $J = 15.7, 5.3, 1.6$ Hz), 4.51 (d, 1H, $J = 4.9$ Hz), 5.18 (dq, 1H, $J = 5.7, 1.4$ Hz), 5.25 (q, 1H, $J = 1.2$ Hz), 5.41 (td, 1H, $J = 7.3, 4.4$ Hz), 5.52 (d, 1H, $J = 1.5$ Hz), 5.62 (m, 1H), 5.74 (m, 1H). ^{13}C -NMR: δ 169.7, 167.4, 131.5, 127.9, 120.5, 118.7, 83.2, 71.2, 59.3, 57.9, 44.0, 43.0, 21.1. IR (KBr, cm^{-1}): ν 1739, 1725. MS (EI), m/z : 333 ($M^+ + 2$, 100), 331 (M^+ , 98). Anal. Calcd for $C_{13}H_{18}NO_4Br$: C, 47.00; H, 5.46; N, 4.22. Found: C, 47.11; H, 5.41; N, 4.20.

Bicyclic β -Lactam (–)-7b. From 33 mg (0.081 mmol) of homoallylic acetate (+)-**6i**, 13 mg (48%) of compound (–)-**7b** was obtained as a colorless oil after purification by flash chromatography (hexanes/ethyl acetate, 5/1). Colorless oil. $[\alpha]_D = -14.4$ (c 0.5, $CHCl_3$). 1H -NMR: δ 1.90 (d, 3H, $J = 1.5$ Hz), 2.03 (s, 3H), 2.66 (dd, 1H, $J = 13.8, 6.2$ Hz), 2.79 (dd, 1H, $J = 13.9, 7.8$ Hz), 3.94 (d, 1H, $J = 14.6$ Hz), 4.07 (dd, 1H, $J = 4.9, 1.7$ Hz), 4.21 (d, 1H, $J = 15.1$ Hz), 5.02 and 5.07 (s, each 1H), 5.20 (d, 1H, $J = 4.9$ Hz), 5.36 (ddd, 1H, $J = 7.8, 6.2, 1.6$ Hz), 6.15 (s, 1H), 7.00 (m, 3H), 7.29 (m, 2H). ^{13}C -NMR: δ 170.0, 165.4, 157.6, 140.2, 131.5, 129.8, 129.6, 122.3, 119.8, 115.3, 79.2, 78.6, 57.6, 42.9, 39.0, 25.3, 21.1. IR ($CHCl_3$, cm^{-1}): ν 1740, 1724. MS (EI), m/z : 327

(M^+ , 100). Anal. Calcd for $C_{19}H_{21}NO_4$: C, 69.71; H, 6.47; N, 4.28. Found: C, 69.83; H, 6.42; N, 4.26.

Intramolecular Heck Reaction of Bromohomoallylic Acetate (+)-6j. Preparation of Bicycles (–)-8 and (+)-9. From 148 mg (0.446 mmol) of bromohomoallylic acetate (+)-6j on heating at 120 °C for 1 h, and after column chromatography eluting with dichloromethane/ethyl acetate (9:1), 8 mg (9%) of the less polar compound (+)-9 and 61 mg (55%) of the more polar compound (–)-8 were obtained.

Bicyclic β -Lactam (–)-8. Colorless oil. $[\alpha]_D = -25.0$ (c 0.5, $CHCl_3$). 1H -NMR: δ 2.07 (s, 3H), 2.77 (d, 2H, $J = 8.0, 0.7$ Hz), 3.44 (s, 3H), 3.87 (dd, 1H, $J = 4.8, 1.8$ Hz), 4.13 (d, 2H, $J = 7.5$ Hz), 4.43 (d, 1H, $J = 4.8$ Hz), 5.19 (s, 1H), 5.20 (s, 1H), 5.37 (td, 1H, $J = 8.2, 1.8$ Hz), 5.60 (dtd, 1H, $J = 11.9, 7.3, 0.7$ Hz), 6.34 (d, 1H, $J = 12.1$ Hz). IR ($CHCl_3$, cm^{-1}): ν 1737, 1724. MS (EI), m/z : 251 (M^+ , 100). Anal. Calcd for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57. Found: C, 62.06; H, 6.80; N, 5.59.

Intramolecular Heck Reaction of Bromohomoallylic Acetate (+)-6b. Preparation of Bicycles (+)-10 and (+)-11. From 102 mg (0.24 mmol) of bromohomoallylic acetate (+)-6b on heating at 95 °C for 26 h, and after column chromatography eluting with hexanes/ethyl acetate (2:1), 17 mg (21%) of the less polar compound (+)-10 and 22 mg (27%) of the more polar compound (+)-11 were obtained.

Bicyclic β -Lactam (+)-10. Colorless oil. $[\alpha]_D = +41.7$ (c 0.7, $CHCl_3$). 1H -NMR: δ 1.58 (s, 3H), 2.47 (dd, 1H, $J = 12.6, 10.6$ Hz), 2.80 (dd, 1H, $J = 12.9, 3.8$ Hz), 3.78 (s, 3H), 3.96 (d, 1H, $J = 11.9$ Hz), 4.25 (dd, 1H, $J = 9.8, 4.5$ Hz), 4.52 (d, 1H, $J = 11.5$ Hz), 4.68 (d, 1H, $J = 4.7$ Hz), 5.01 (d, 1H, $J = 1.4$ Hz), 5.11 (s, 1H), 5.24 (s, 1H), 5.26 (s, 1H), 5.33 (td, 1H, $J = 10.0, 3.8$ Hz), 6.85 and 7.38 (d, each 2H, $J = 8.8$ Hz). ^{13}C -NMR: δ 169.3, 163.4, 156.7, 147.4, 143.1, 130.4, 120.6, 116.6, 116.4, 113.9, 82.3, 78.6, 73.6, 62.5, 55.5, 43.5, 20.6. IR ($CHCl_3$, cm^{-1}): ν 1743, 1725. MS (ES), m/z : 366 ($M^+ + 23$, 100), 343 (M^+ , 11). Anal. Calcd for $C_{19}H_{21}NO_5$: C, 66.46; H, 6.16; N, 4.08. Found: C, 66.56; H, 6.12; N, 4.06.

Bicyclic β -Lactam (+)-11. Colorless oil. $[\alpha]_D = +130.7$ (c 1.1, $CHCl_3$). 1H -NMR: δ 1.75 (s, 3H), 2.48 (dd, 1H, $J = 14.2, 5.0$ Hz), 3.08 (dd, 1H, $J = 14.2, 4.7$ Hz), 3.78 (s, 3H), 4.29 (dd, 1H, $J = 14.7, 7.0$ Hz), 4.37 (dd, 1H, $J = 9.3, 5.0$ Hz), 4.63 (m, 1H), 4.77 (dd, 1H, $J = 5.0, 0.7$ Hz), 5.21 (s,

1H), 5.22 (s, 1H), 5.39 (dt, 1H, $J = 9.3, 4.6$ Hz), 5.59 (m, 1H), 6.29 (d, 1H, $J = 12.2$ Hz), 6.83 and 7.40 (d, each 2H, $J = 8.5$ Hz). ^{13}C -NMR: δ 169.4, 164.5, 156.5, 140.2, 136.9, 130.5, 124.4, 121.5, 120.0, 113.9, 81.2, 74.9, 67.6, 60.9, 55.5, 37.0, 20.9. IR (CHCl_3 , cm^{-1}): ν 1744, 1725. MS (ES), m/z : 366 ($\text{M}^+ + 23$, 100), 343 (M^+ , 19). Anal. Calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_5$: C, 66.46; H, 6.16; N, 4.08.

Bicyclic β -Lactam (–)-12. From 67 mg (0.143 mmol) of homoallylic acetate (+)-**6d**, 26 mg (47%) of compound (–)-**12** was obtained as a colorless solid after purification by flash chromatography (hexanes/ethyl acetate, 1/1). Mp: 174–175 °C (hexanes/ethyl acetate). $[\alpha]_{\text{D}} = -21.5$ (c 0.8, CHCl_3). ^1H -NMR: δ 1.91 (s, 3H), 2.52 (dd, 1H, $J = 14.4, 8.8$ Hz), 3.10 (dd, 1H, $J = 14.3, 6.7$ Hz), 3.75 (m, 1H), 3.77 (s, 3H), 3.80 (s, 3H), 4.44 (m, 1H), 5.14 (m, 1H), 5.35 (s, 1H), 5.52 (s, 1H), 5.58 (m, 1H), 6.86 and 7.44 (d, each 2H, $J = 8.5$ Hz). ^{13}C -NMR: δ 169.3, 165.0, 159.9, 156.9, 138.5, 130.1, 124.0, 123.0, 119.4, 114.2, 99.9, 79.9, 71.1, 58.4, 55.5, 51.4, 37.2, 20.9. IR (KBr, cm^{-1}): ν 1744, 1725, 1716. MS (ES), m/z : 410 ($\text{M}^+ + 23$, 100), 387 (M^+ , 11). Anal. Calcd for $\text{C}_{20}\text{H}_{21}\text{NO}_7$: C, 62.01; H, 5.46; N, 3.62. Found: C, 62.12; H, 5.42; N, 3.60.

Bicyclic β -Lactam ($\pm$)-14b. From 31 mg (0.076 mmol) of homoallylic acetate *syn*-($\pm$)-**6h**, 16 mg (65%) of compound ($\pm$)-**14b** was obtained as a colorless oil after purification by flash chromatography (hexanes/ethyl acetate, 5/1). ^1H -NMR: δ 1.74 (dd, 3H, $J = 1.5, 1.0$ Hz), 2.13 (s, 3H), 2.70 (d, 1H, $J = 18.1$ Hz), 2.96 (ddt, 1H, $J = 17.3, 5.1, 2.7$ Hz), 3.80 (s, 3H), 4.26 (d, 1H, $J = 1.5$ Hz), 5.14 (dt, 1H, $J = 2.9, 1.5$ Hz), 5.19 (d, 1H, $J = 3.2$ Hz), 5.25 (dd, 1H, $J = 1.7, 1.0$ Hz), 5.32 (d, 1H, $J = 4.9$ Hz), 5.52 (q, 1H, $J = 0.8$ Hz), 6.91 and 7.53 (d, each 2H, $J = 9.3$ Hz). ^{13}C -NMR: δ 170.6, 163.7, 156.3, 142.9, 137.5, 130.8, 117.9, 115.4, 114.6, 112.2, 73.5, 71.7, 66.0, 55.5, 36.9, 21.0, 20.0. IR (CHCl_3 , cm^{-1}): ν 1741, 1728. MS (ES), m/z : 350 ($\text{M}^+ + 23$, 100), 327 (M^+ , 11). Anal. Calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_4$: C, 69.71; H, 6.47; N, 4.28. Found: C, 69.82; H, 6.42; N, 4.31.

Bicyclic β -Lactam ($\pm$)-14c. From 20 mg (0.049 mmol) of homoallylic acetate *anti*-($\pm$)-**6h**, 10 mg (60%) of compound ($\pm$)-**14c** was obtained as a colorless oil after purification by flash chromatography (hexanes/ethyl acetate, 5/1). ^1H -NMR: δ 1.75 (dd, 3H, $J = 1.5, 1.0$ Hz), 1.85 (s, 3H), 2.86 (m, 2H), 3.80 (s, 3H), 4.60 (d, 1H, $J = 4.6$ Hz), 5.16 (m, 4H), 5.49 (q, 1H, $J = 0.8$ Hz), 6.87 and 7.36 (d, each 2H, $J = 9.3$ Hz). ^{13}C -NMR: δ 170.6, 164.3, 156.2, 139.8, 136.9, 131.3, 119.1, 115.4, 113.9, 112.3, 72.9, 72.7, 61.7, 55.3, 34.6, 20.6, 20.2. IR (CHCl_3 , cm^{-1}): ν 1742, 1727. MS

(ES), m/z : 350 ($M^+ + 23$, 100), 327 (M^+ , 9). Anal. Calcd for $C_{19}H_{21}NO_4$: C, 69.71; H, 6.47; N, 4.28. Found: C, 69.58; H, 6.43; N, 4.24.

Procedure for the Thermally-Promoted Isomerization of Bicyclic β -Lactam (+)-7a.

Preparation of Compound (–)-8. A solution of the bicyclic β -lactam (+)-7a (148 mg, 0.446 mmol) in toluene (5 mL) was heated in a sealed tube at 120 °C for 1 h. The reaction mixture was allowed to cool to room temperature, the solvent was removed under reduced pressure and after purification by flash chromatography (dichloromethane/ethyl acetate, 9/1), 111 mg (75%) of bicycle (–)-8 was obtained. Anal. Calcd for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57. Found: C, 62.25; H, 6.79; N, 5.60.

HMQC

H,H-COSY

H,H-COSY

HMQC

HMBC