

# A green synthetic route to antimalarial and antibacterial agent CJ-15,801 and its isomer cis-CJ-15,801

K. Kashinath, Pandrangi Siva Swaroop, D. Srinivasa Reddy\*

CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune, 411008, India.

\*Corresponding author:

Dr. D. Srinivasa Reddy

National Chemical Laboratory (CSIR, India),

Division of Organic Chemistry,

Dr. Homi Bhabha Road,

Pune 411008, Maharashtra,

India.

E-mail: ds.reddy@ncl.res.in

Tel. +91 20 25902445

Fax. +91 20 25902629

## Supporting Information

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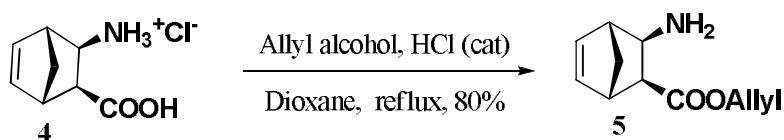
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## General information:

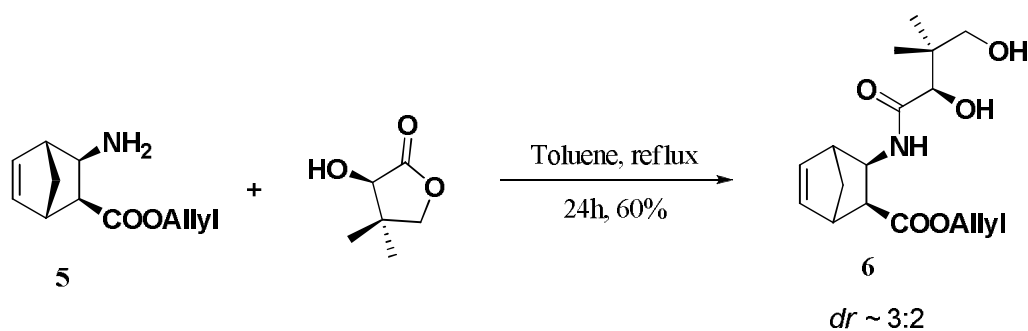
All reactions were carried out in oven-dried glassware under a positive pressure of argon or nitrogen unless otherwise mentioned with magnetic stirring. Air sensitive reagents and solutions were transferred via syringe or cannula and were introduced to the apparatus *via* rubber septa. All reagents, starting materials, and solvents were obtained from commercial suppliers and used as such without further purification. Reactions were monitored by thin layer chromatography (TLC) with 0.25 mm pre-coated silica gel plates (60 F<sub>254</sub>). Visualization was accomplished with either UV light, or by immersion in ethanolic solution of phosphomolybdic acid (PMA), or KMnO<sub>4</sub> followed by heating on a heat gun for ~15 sec. Column chromatography was performed on silica gel (100-200 or 230-400 mesh size). Deuterated solvents for NMR spectroscopic analyses were used as received. All <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained using a 200 MHz (200 MHz for <sup>1</sup>H and 50 MHz for <sup>13</sup>C), 400 MHz (400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C) and 500 MHz (500 MHz for <sup>1</sup>H and 125 MHz for <sup>13</sup>C) spectrometer. Coupling constants were measured in Hertz. All chemical shifts were quoted in ppm, relative to CDCl<sub>3</sub>, using the residual solvent peak as a reference standard. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, app = apparent. Mass spectra were measured with ESI ionization in MSQ LCMS mass spectrometer. HRMS Mass spectra were recorded on MALDI-TOF using 2,5-dihydroxybenzoic acid as the solid matrix. Infrared (IR) spectra were recorded on a FT-IR spectrometer as a thin film. Optical rotation values were recorded on P-2000 polarimeter at 589 nm. Chemical nomenclature was generated using Chem Draw.

## Experimental procedures:



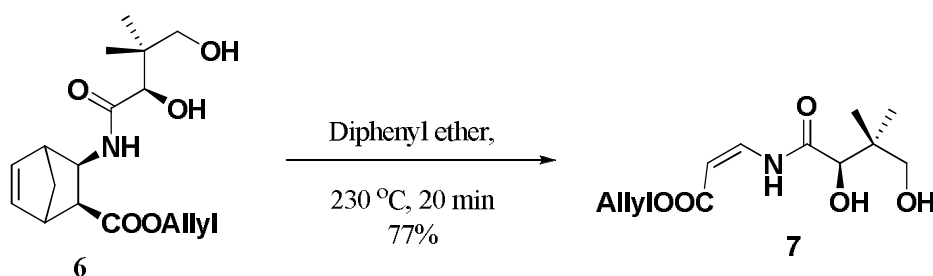
**(1S\*,2S\*,3R\*,4R\*)-Allyl 3-aminobicyclo[2.2.1]hept-5-ene-2-carboxylate (4):** To a mixture containing **4**<sup>1</sup> (1.0 g, 5.2 mmol) and allyl alcohol (3.6 mL, 52 mmol) in dioxane (20 mL) was added 10N HCl (cat) (0.5 mL) and heated to reflux. After 4h, the dioxane was removed under vacuum from the reaction mixture and adjusted to pH 8 with saturated aq. NaHCO<sub>3</sub>. The aqueous

layer was extracted with ethyl acetate (2 X 100 mL) and the combined organic layers were washed with water (1 X 50 mL), brine (1 X 25 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated under reduced pressure to afford crude **5** as brown thick mass (800 mg, 80%), which was forwarded to next reaction without any further purification. IR  $\nu_{\text{max}}$  (film): 3383, 3063, 2979, 2882, 1728, 1647 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  6.11 (2H, m), 5.90 (1H, ddt,  $J = 17.0, 10.3, 5.8$  Hz), 5.30 (1H, dd,  $J = 17.0, 1.5$  Hz), 5.20 (1H, dd,  $J = 10.3, 1.2$  Hz), 4.57 (2H, m), 3.21 (1H, dd,  $J = 7.9, 1.2$  Hz), 2.93 (1H, m), 2.53 (1H, m), 2.45 (1H, dd,  $J = 7.9, 1.8$  Hz), 2.04 (1H, m), 1.51 (1H, m), 1.46 (2H, br s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  173.7, 138.0, 137.2, 132.2, 118.3, 65.0, 54.6, 50.1, 48.9, 44.6, 43.9; LCMS [M+H]<sup>+</sup>: 194; HRMS calculated for C<sub>11</sub>H<sub>15</sub>NNaO<sub>2</sub><sup>+</sup> [M+Na]<sup>+</sup>: 216.1000, found 216.1003.

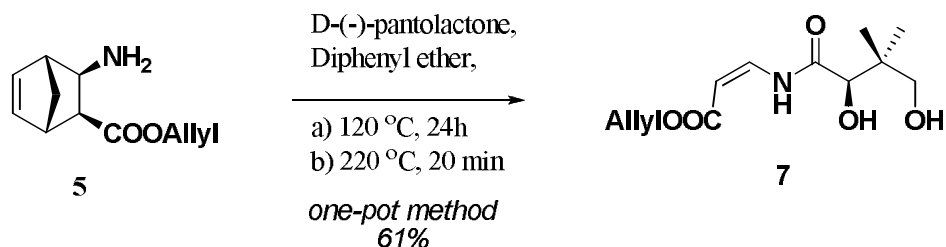


**(1*S*,2*S*,3*R*,4*R*)-Allyl 3-((*R*)-2,4-dihydroxy-3,3-dimethylbutanamido)bicyclo[2.2.1]hept-5-ene-2-carboxylate and (1*R*,2*R*,3*S*,4*S*)-Allyl 3-((*R*)-2,4-dihydroxy-3,3-dimethylbutanamido)bicyclo[2.2.1]hept-5-ene-2-carboxylate (**6**):** A mixture of **5** (200 mg, 1 mmol), and D (-)-pantolactone (270 mg, 2 mmol) in toluene (10 mL) were heated to reflux for 24 h and the reaction progress was monitored through TLC. After considerable amount of compound **5** was consumed with no further progress in the reaction, toluene was removed under vacuum. The crude mixture was diluted with ethyl acetate (20 mL) and the organic layer was washed with 1N HCl (1 X 5 mL), water (1 X 10 mL), brine (1 X 5 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum. The crude residue was purified by silica gel column chromatography by eluting with methanol: DCM (2:98) to afford a yellow gummy mass of **6** (198 mg, 60%) as inseparable diastereomeric mixture. The diastereomeric ratio of **6** (~ 3:2) was determined by <sup>1</sup>H NMR and HPLC analysis. (IR  $\nu_{\text{max}}$  (film): 3386, 2977, 2877, 1721, 1648, 1521

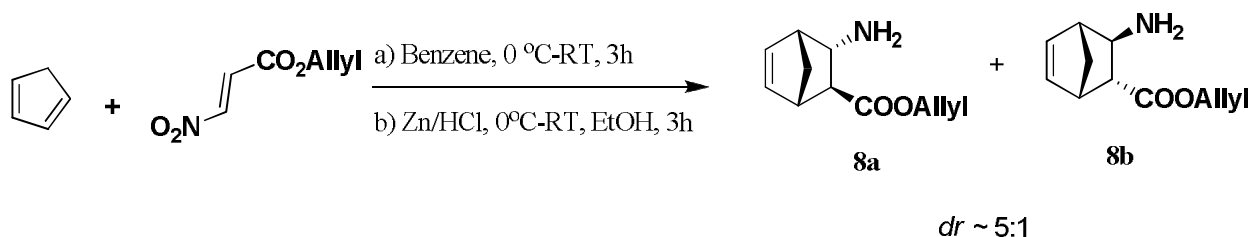
$\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) : (mixture)  $\delta$  7.67 (1H, m), 6.20 (1H, m), 6.18 (1H, m), 5.86 (1H, ddt,  $J = 17.0, 10.3, 5.8$  Hz), 5.26 (1H, m), 5.20 (1H, m), 4.53 (2H, m), 4.13 (1H, m), 3.94 (1H, d,  $J = 7.3$  Hz), 3.43 (2H, m), 2.96 (1H, m), 2.69 (1H, m), 2.62 (1H, m), 1.97 (1H, m), 1.54 (1H, m), 0.94 (3H, d,  $J = 14.0$  Hz), 0.86 (3H, d,  $J = 18.3$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ): (mixture)  $\delta$  173.9 (2C overlapped), 172.8, 172.7, 138.3 (2C overlapped), 137.1, 137.0, 131.7, 131.6, 118.7, 118.6, 77.6, 77.3, 71.2, 70.9, 65.6, 65.5, 50.7 (2C), 48.5 (2C overlapped), 46.4, 46.3, 45.9, 45.8, 44.3 (2C overlapped), 39.2, 39.1, 21.0, 20.9, 20.2 (2C); LCMS  $[\text{M}+\text{Na}]^+$ : 346; HRMS calculated for  $\text{C}_{17}\text{H}_{25}\text{NNaO}_5^+$   $[\text{M}+\text{Na}]^+$ : 346.1630, found 346.1613.



**(R, Z)-Allyl 3-(2,4-dihydroxy-3,3-dimethylbutanamido)acrylate (7):** A diastereomeric mixture of **6** (50 mg, 0.2 mmol) in diphenyl ether (5 mL) was heated to  $\sim 230$  °C by inserting the reaction mixture in a pre-heated oil bath for 20 min.<sup>2</sup> The crude reaction mixture was cooled to room temperature and purified through silica gel column chromatography by eluting with methanol: DCM (3:97) to afford (30 mg, 77%) of **7** as a brown colored mass. IR  $\nu_{\text{max}}$  (film): 3408, 2962, 1695, 1634  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.25 (1H, br d,  $J = 11.6$  Hz), 7.46 (1H, dd,  $J = 11.6, 8.8$  Hz), 5.93 (1H, ddt,  $J = 17.2, 10.4, 5.6$  Hz), 5.32 (1H, ddd,  $J = 17.2, 2.9, 1.3$  Hz), 5.24 (1H, overlapped dd,  $J = 10.4, 1.3$  Hz), 5.22 (1H, d,  $J = 8.8$  Hz), 4.63 (2H, m), 4.20 (1H, s), 3.58 (1H, d,  $J = 10.8$  Hz), 3.53 (1H, d,  $J = 10.8$  Hz), 1.03 (3H, s), 0.98 (3H, s);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  171.8, 168.2, 136.9, 131.9, 118.4, 97.5, 78.1, 71.4, 64.8, 39.3, 20.9, 20.2; LCMS  $[\text{M}+\text{Na}]^+$ : 280.  $[\alpha]_{\text{D}}^{23} = +26.2$  ( $c = 0.8, \text{CHCl}_3$ ). Spectral data compared with that of reported data and was found to be identical.<sup>5a</sup>



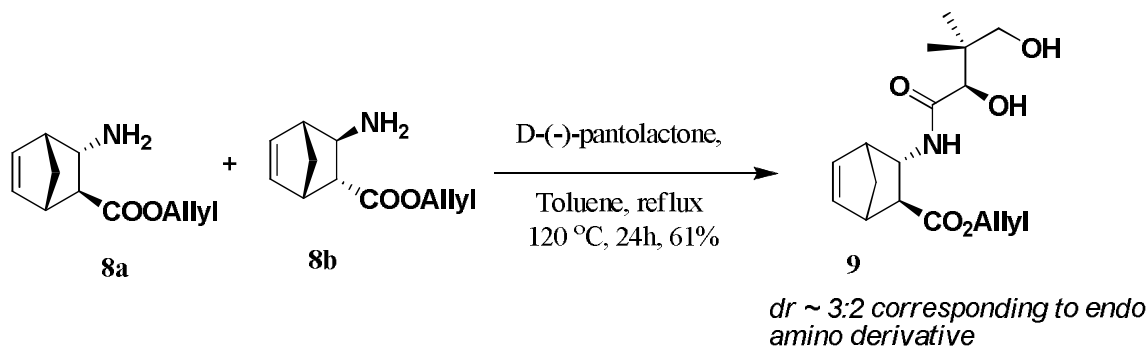
**One-pot procedure:** A mixture of **5** (250 mg, 1.3 mmol) and D (-)-pantolactone (340 mg, 2.6 mmol) in diphenyl ether (15 mL) were heated to ~120 °C for 24 h and the progress of the reaction was monitored through TLC. After considerable amount of compound **5** was consumed with no further progress in the reaction, the reaction mixture was further heated to ~220 °C for 20 min.<sup>2</sup> The crude reaction mixture was cooled to room temperature and purified by silica gel column chromatography eluting with methanol: DCM (3:97) to afford the desired product **7** (202 mg, 61%).



**(1S\*,2S\*,3S\*,4R\*)-Allyl 3-aminobicyclo[2.2.1]hept-5-ene-2-carboxylate and (1S\*,2R\*,3R\*,4R\*)-Allyl 3-aminobicyclo[2.2.1]hept-5-ene-2-carboxylate (8a and 8b):** To a solution of  $\beta$ -nitro allyl acrylate<sup>3</sup> (4.0 g, 25 mmol) in dry benzene (40 mL) at 0 °C, was added slowly cyclopentadiene (2.1 mL, 25 mmol) (freshly prepared by cracking dicyclopentadiene dimer) and the resulting mixture was allowed to stir at room temperature for 3h. The benzene was removed under vacuum to afford the crude diastereomeric mixture (~ 5.6 g) was carried forward for the next step. <sup>1</sup>H NMR analysis of a diastereomeric mixture revealed ~ 5:1 ratio of the endo and exo the nitro cyclo adducts. IR  $\nu_{\text{max}}$  (film): 3419, 2954, 1732, 1621,  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ ): (major)  $\delta$  6.48 (1H, dd,  $J = 5.6, 3.2$  Hz), 6.08 (1H, dd,  $J = 5.6, 2.7$  Hz), 5.93 (1H, ddt,  $J = 17.0, 10.3, 5.8$  Hz), 5.41 (1H, m), 5.34 (1H, dd,  $J = 17.0, 1.5$  Hz), 5.28 (1H, dd,  $J = 10.3, 1.2$  Hz), 4.65 (2H, d,  $J = 5.8$  Hz), 3.61 (1H, m), 3.25 (1H, m), 3.07 (1H, m), 1.69 (1H, app d,  $J = 9.4$  Hz), 1.62 (1H, ddd,  $J = 9.4, 3.9, 1.8$  Hz); <sup>13</sup>C NMR (125 MHz,  $\text{CDCl}_3$ ):

(major)  $\delta$  171.8, 139.2, 133.6, 131.5, 118.9, 87.6, 66.1, 48.9, 47.7, 47.3, 46.2; HRMS calculated for  $C_{11}H_{14}NO_4^+$   $[M+H]^+$ : 224.0923, found 224.0924.

The above diastereomeric mixture (~ 5.6 g, 25 mmol) was placed in 250 mL round bottom flask together with ethanol (100 mL) and the resulting solution was charged with 10N HCl (30 mL) and zinc (13.0 g, 200 mmol) which was added portion wise slowly to the reaction mixture and was allowed to stir for 3h. The reaction mixture was filtered through a short pad of celite bed and was washed with ethanol. The filtrate was concentrated under vacuum, diluted with water (50 mL), basified with  $NaHCO_3$  to pH 8 and extracted with ethyl acetate (2 X 100 mL). The combined organic layers were washed with water (2 X 50 mL), brine (1 X 10 mL) and dried over  $Na_2SO_4$  and concentrated under vacuum to afford **8a** and **8b** (~ 5:1) (3.9 g, 80 %) as pale brown gummy mass. IR  $\nu_{max}$  (film): 3438, 2974, 2878, 1729, 1646  $cm^{-1}$ ;  $^1H$  NMR (500 MHz,  $CDCl_3$ ): (major)  $\delta$  6.39 (1H, dd,  $J = 5.4, 3.0$  Hz), 6.20 (1H, dd,  $J = 5.4, 2.7$  Hz), 5.93 (1H, ddt,  $J = 17.0, 10.3, 5.8$  Hz), 5.30 (1H, dd,  $J = 17.0, 1.5$  Hz), 5.22 (1H, dd,  $J = 10.3, 1.2$  Hz), 4.58 (2H, app d,  $J = 5.8$  Hz), 3.69 (1H, app t,  $J = 3.6$  Hz), 2.98 (1H, m), 2.83 (1H, m), 1.77 (1H, dd,  $J = 3.6, 2.4$  Hz), 1.70 (1H, app d,  $J = 8.8$  Hz), 1.48 (1H, dd,  $J = 8.8, 1.9$  Hz), 1.41 (2H, br s).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ) : (major)  $\delta$  174.7, 138.8, 134.1, 132.2, 118.1, 65.2, 57.6, 55.1, 48.4, 47.3, 47.0; LCMS  $[M+H]^+$ : 194; HRMS calculated for  $C_{11}H_{15}NNaO_2^+$   $[M+Na]^+$ : 216.1000, found 216.0986.

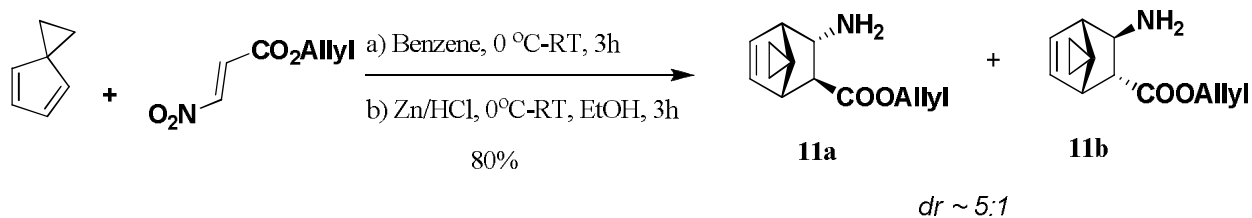


**(1*S*,2*S*,3*S*,4*R*)-Allyl3-((*R*)-2,4-dihydroxy-3,3-dimethylbutanamido)bicyclo[2.2.1]hept-5-ene-2-carboxylate** and **(1*R*,2*R*,3*R*,4*S*)-Allyl3-((*R*)-2,4-dihydroxy-3,3-dimethylbutanamido)bicyclo[2.2.1]hept-5-ene-2-carboxylate (9)**: Prepared from the mixture **8a** and **8b** (0.5 g, 2.6 mmol) and D-(-) pantolactone (0.67 g, 5.2 mmol) in 61% yield as a mixture of four diastereomers by following the procedure for the synthesis of **6**. The *endo* (9):*exo* (9) diastereomeric ratio (96:4) was determined by HPLC analysis (Chiralcel-OJ-H column, 220 nm,

95:5 Petroleum ether/*i*-PrOH, 1.0 mL/min,  $\tau$  exo 7.4, 8.8 and endo 9.6, 11.3); IR  $\nu_{\max}$  (film): 3407, 2960, 2876, 1732, 1651  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): (major)  $\delta$  6.65 (1H, m), 6.41 (1H, m), 5.88 (1H, m), 5.28 (1H, m), 5.20 (1H, m), 4.68 (1H, m), 4.58 (2H, m), 3.92 (1H, d,  $J = 1.5$  Hz), 3.42 (2H, d,  $J = 8.5$  Hz), 3.03 (2H, m), 1.94 (1H, ddd,  $J = 21.3, 3.9, 2.1$  Hz), 1.78 (1H, m), 1.50 (1H, m), 0.92 (3H, d,  $J = 10.0$  Hz), 0.83 (3H, d,  $J = 13.4$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ): (major)  $\delta$  173.7, 173.5, 173.1, 173.0, 139.6, 139.4, 134.1, 133.9, 131.9 (2C overlapped), 118.3, 118.2, 77.0 (2C overlapped), 71.0 (2C overlapped), 65.5, 65.4, 53.7, 53.4, 52.4, 52.6, 47.3, 47.0, 46.3, 46.2, 46.1, 45.8, 39.2 (2C overlapped), 21.1, 21.0, 20.0 (2C); LCMS  $[\text{M}+\text{Na}]^+$ : 346; HRMS calculated for  $\text{C}_{17}\text{H}_{25}\text{NNaO}_5^+$   $[\text{M}+\text{Na}]^+$ : 346.1630 found 346.1618 (3.46 ppm).

### Preparation of CJ-15,801 (1):

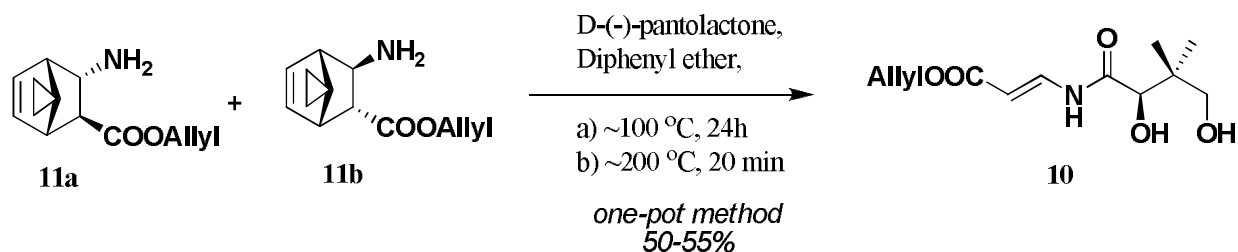
To the crude mixture<sup>4</sup> containing **9** and **10** (8:2) (20 mg) in dioxane/water (4:1) was added  $\text{Pd}(\text{PPh}_3)_4$  (0.2 eq) and stirred overnight. After the completion of reaction (TLC monitoring), the reaction mixture was dried ( $\text{Na}_2\text{SO}_4$ ) and purified through preparative TLC by eluting with methanol:DCM (1:9) afforded ~1 mg of **1** as a brown colored mass.  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  7.78 (1H, d,  $J = 14.1$  Hz), 5.71 (1H, d,  $J = 14.1$  Hz), 3.98 (1H, s), 3.49 (1H, d,  $J = 10.8$  Hz), 3.42 (1H, d,  $J = 10.8$  Hz), 0.94 (3H, s), 0.93 (3H, s). The  $^1\text{H}$  NMR data was compared with the reported data<sup>5</sup> and found to be identical.



**(1*S*\*,4*S*\*,5*S*\*,6*S*\*)-Allyl5-aminospiro[bicyclo[2.2.1]hept[2]ene-7,1'-cyclopropane]-6-carboxylate and (1*S*\*,4*S*\*,5*R*\*,6*R*\*)-Allyl5-aminospiro[bicyclo[2.2.1]hept[2]ene-7,1'-cyclopropane]-6-carboxylate (**11a** and **11b**):** The nitro adduct was prepared from allyl  $\beta$ -nitroacrylate (1.0 g, 6.3 mmol) and spiro[2.4]hepta-4,6-diene<sup>6</sup> (0.6 mL, 6.3 mmol) as inseparable diastereomeric mixture (5:1; determined by NMR analysis) by following the procedure for the synthesis of **7**. IR  $\nu_{\max}$  (film): 3076, 3022, 1733, 1647  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): (major)  $\delta$  6.51 (1H, m), 6.10 (1H, m), 5.87 (1H, m), 5.57 (1H, app t,  $J = 3.7$  Hz), 5.30 (1H, dd,  $J$

= 17.3, 1.2 Hz), 5.22 (1H, app d,  $J = 10.2$  Hz), 4.58 (2H, br d,  $J = 5.7$  Hz), 3.19 (1H, br d,  $J = 3.3$  Hz), 2.99 (1H, m), 2.79 (1H, m), 0.50 (2H, m), 0.43 (2H, m);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ): (major)  $\delta$  170.5, 139.1, 133.2, 131.5, 118.8, 87.2, 65.8, 52.6, 51.1, 50.6, 43.3, 8.1, 4.5; HRMS calculated for  $\text{C}_{13}\text{H}_{15}\text{NNaO}_4^+$   $[\text{M}+\text{Na}]^+$ : 272.0899, found 272.0890.

The above obtained nitro adduct (1.3 g) was reduced to corresponding amine **11a** and **11b** (1.1 g) as a brown liquid in 80% yield by following the procedure for the synthesis of **8**. IR  $\nu_{\text{max}}$  (film): 3684, 3584, 3020, 1722, 1524  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): (major)  $\delta$  6.47 (1H, m), 6.27 (1H, dd, 5.7, 2.7 Hz), 5.89 (1H, m), 5.29 (1H, dd,  $J = 17.0, 1.5$  Hz), 5.21 (1H, app d,  $J = 10.0$  Hz), 4.58 (2H, d,  $J = 5.5$  Hz), 3.94 (1H, m), 2.57 (1H, m), 2.26 (1H, m), 1.97 (1H, d,  $J = 3.9$  Hz), 1.81 (2H, br s), 0.47 (1H, m), 0.39 (2H, m), 0.32 (1H, m);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ): (major)  $\delta$  173.3, 138.6, 133.8, 132.2, 118.2, 65.1, 57.0, 55.5, 54.0, 51.0, 43.8, 8.2, 4.3; LCMS  $[\text{M}+\text{H}]^+$ : 220; HRMS calculated for  $\text{C}_{13}\text{H}_{17}\text{NNaO}_2^+$   $[\text{M}+\text{Na}]^+$ : 242.1156, found 242.1177.



**(*R,E*)-allyl 3-(2,4-dihydroxy-3,3-dimethylbutanamido)acrylate (10)**: Prepared by following the procedure<sup>7</sup> for the synthesis of **7** by using **11a/b** (100 mg, 0.4 mmol) and D (-) - pantolactone (118 mg, 0.8 mmol) in 52% yield (55 mg). IR  $\nu_{\text{max}}$  (film): 3344, 2964, 2931, 2877, 1687, 1633  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ , 3.31):  $\delta$  7.98 (1H, d,  $J = 14.3$  Hz), 5.98 (1H, ddt,  $J = 17.3, 10.5, 5.5$  Hz), 5.78 (1H, d,  $J = 14.3$  Hz), 5.34 (1H, dd,  $J = 17.3, 1.5$  Hz), 5.24 (1H, dd,  $J = 10.5, 1.2$  Hz), 4.65 (2H, app dt,  $J = 6.7, 5.5$  Hz), 4.05 (1H, s), 3.50 (1H, d,  $J = 10.8$  Hz), 3.39 (1H, d,  $J = 10.8$  Hz), 0.96 (3H, s), 0.95 (3H, s);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  171.3, 167.1, 136.8, 132.2, 118.1, 102.3, 77.9, 71.51, 64.9, 39.3, 20.9, 20.1; LCMS  $[\text{M}+\text{Na}]^+$ : 280.  $[\alpha]_{\text{D}}^{24} = +73.2^\circ$  ( $c = 0.75$ ,  $\text{CH}_3\text{CN}$ ); Lit.<sup>5c</sup>  $[\alpha]_{\text{D}}^{25} = +80.0^\circ$  ( $c = 0.12$ ,  $\text{CH}_3\text{CN}$ ). All the spectral data compared with that of reported data and found to be identical.<sup>5c</sup>



### NMR data comparison of *cis*-CJ-15,801 allyl ester (7)

<sup>1</sup> H NMR (ppm)		<sup>13</sup> C NMR (ppm)	
Reported (400 MHz) (CDCl <sub>3</sub> at 7.25 ppm) <sup>5a</sup>	Synthesized (500 MHz) (CDCl <sub>3</sub> at 7.25 ppm)	Reported (100 MHz) (CDCl <sub>3</sub> at 77.0 ppm) <sup>5a</sup>	Synthesized (125 MHz) (CDCl <sub>3</sub> at 77.0 ppm)
11.22 (1H, br d, <i>J</i> = 10.6 Hz)	11.25 (1H, br d, <i>J</i> = 11.6 Hz)	171.5	171.8
7.47 (1H, dd, <i>J</i> = 11.7, 8.9 Hz),	7.46 (1H, dd, <i>J</i> = 11.6, 8.8 Hz)	168.2	168.2
5.93 (1H, m),	5.93 (1H, ddt, <i>J</i> = 17.2, 10.4, 5.6 Hz)	136.9	136.9
5.32 (1H, d, <i>J</i> = 17.2 Hz),	5.32 (1H, ddd, <i>J</i> = 17.2, 2.9, 1.3 Hz)	131.9	131.3
5.22 (2H, m)	5.24 (1H, overlapped dd, <i>J</i> = 10.4, 1.3 Hz)	118.4	118.4
	5.22 (1H, d, <i>J</i> = 8.8 Hz)	97.6	97.5
4.63 (2H, d, <i>J</i> = 7.9 Hz),	4.63 (2H, m)	78.2	78.1
4.19 (1H, s)	4.20 (1H, s)	71.6	71.4
3.88 (1H, s),		64.9	64.8
3.60 (1H, d, <i>J</i> = 10.8 Hz)	3.58 (1H, d, <i>J</i> = 10.8 Hz)	39.4	39.3
3.53 (1H, d, <i>J</i> = 10.8 Hz)	3.53 (1H, d, <i>J</i> = 10.8 Hz)	20.9	20.9
1.03 (3H, s),	1.03 (3H, s)	20.3	20.2
0.97 (3H, s)	0.98 (3H, s)		

### NMR data comparison of CJ-15,801 allyl ester (10)

<sup>1</sup> H NMR (ppm)		<sup>13</sup> C NMR (ppm)	
Reported (400 MHz) (CD <sub>3</sub> OD at 3.31 ppm) <sup>5c</sup>	Synthesized (400 MHz) (CD <sub>3</sub> OD at 3.31 ppm)	Reported (100 MHz) (CD <sub>3</sub> OD at 49.15 ppm) <sup>5c</sup>	Synthesized (50 MHz) (CDCl <sub>3</sub> at 77.0 ppm)
7.99 (1H, d, <i>J</i> = 14.4 Hz)	7.98 (1H, d, <i>J</i> = 14.3 Hz)	175.3	171.3
6.01 (1H, ddt, <i>J</i> = 17.2, 10.4, 5.6 Hz),	5.98 (1H, ddt, <i>J</i> = 17.3, 10.5, 5.5 Hz)	169.3	167.1
5.78 (1H, d, <i>J</i> = 14.4 Hz),	5.78 (1H, d, <i>J</i> = 14.3 Hz)	139.3	136.8
5.34 (1H, d, <i>J</i> = 17.2 Hz)	5.34 (1H, dd, <i>J</i> = 17.3, 1.5 Hz)	134.2	132.8
5.22 (1H, d, <i>J</i> = 10.4 Hz),	5.24 (1H, dd, <i>J</i> = 10.5, 1.2 Hz)	118.4	118.1
4.63 (2H, d, <i>J</i> = 5.6 Hz),	4.65 (2H, app dt, <i>J</i> = 6.78, 5.53 Hz)	102.7	102.3
4.02 (1H, s),	4.05 (1H, s)	77.2	77.9
3.50 (1H, d, <i>J</i> = 10.8 Hz),	3.50 (1H, d, <i>J</i> = 10.8 Hz)	69.9	71.5
3.39 (1H, d, <i>J</i> = 10.8 Hz)	3.39 (1H, d, <i>J</i> = 10.8 Hz)	66.0	64.9
0.93 (3H, s)	0.96 (3H, s)	40.9	39.3
0.92 (3H, s)	0.95 (3H, s)	21.6	20.9
		20.6	20.1

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7. Except the heating carried out at slightly lower temperatures (initially heating at ~100 °C for 24 h followed by heating at ~200 °C for 20 min.).

## Copies of $^1\text{H}$ & $^{13}\text{C}$ NMR spectra:

