Supporting Information for the Paper

Structurally Novel Bi- and Tricyclic β -Lactams via [2+2] Cycloaddition or Radical Reactions in 2-Azetidinone-Tethered Enallenes and Allenynes

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Table of Contents

General Procedure for the Preparation of Tricyclic β -Lactams 3 and 5	S1
Characterization of Tricyclic β -Lactam (+)- 3b	S2
Characterization of Tricyclic β -Lactam (+)- 3c	S2
Characterization of Tricyclic β -Lactam ($\pm$)- 5a	S2
General Procedure for the Preparation of Vinylic Stannanes 6	S2
Characterization of Bicyclic β -Lactam (–)- 6a	S3
Characterization of Bicyclic β -Lactam ($\pm$)- 6c	S3

General Procedure for the Preparation of Tricyclic β -Lactams **3 and **5**.** A solution of the corresponding enallene **2** (0.20 mmol) in toluene (10 mL) was heated in a sealed tube at 220 °C until disappearance of the starting material (TLC). The reaction mixture was allowed to cool to

room temperature, the solvent was removed under reduced pressure and after purification by flash chromatography tricycles **3** or **5** were obtained. Spectroscopic and analytical data for some representative forms of **3** and **5** follow.

Tricyclic β -Lactam (+)-3b. From 48 mg (0.21 mmol) of enallene (+)-**2b**, and after chromatography of the residue using hexanes/ethyl acetate (1:2) as eluent gave compound (+)-**3b** (27 mg, 56%) as a colorless oil. $[\alpha]_D = +136.3$ (*c* 1.9, CHCl_3). ^1H NMR (CDCl_3): δ 4.49 (d, 1H, *J* = 4.7 Hz), 4.10 (s, 1H), 4.01 (dd, 1H, *J* = 13.0, 5.9 Hz), 3.75 (d, 1H, *J* = 4.7 Hz), 3.64 (s, 3H), 3.59 (m, 1H), 3.16 (s, 1H), 2.74 (t, 1H, *J* = 13.0 Hz), 2.62 (m, 1H), 2.59 (m, 1H), 2.08 (m, 1H), 1.67 (m, 3H), 1.61 (m, 1H). ^{13}C NMR (CDCl_3): δ 165.6, 142.6, 128.9, 84.4, 72.7, 59.6, 59.3, 44.7, 40.4, 25.8, 20.3, 17.9. IR (CHCl_3 , cm^{-1}): ν 1740. MS (CI), *m/z*: 224 ($\text{M}^+ + 1$, 100), 223 (M^+ , 17). (Anal. Calcd. for $\text{C}_{12}\text{H}_{17}\text{NO}_3$: C, 64.55; H, 7.67; N, 6.27. Found: C, 64.47; H, 7.62; N, 6.30).

Tricyclic β -Lactam (+)-3c. From 45 mg (0.16 mmol) of enallene (+)-**2c**, and after chromatography of the residue using hexanes/ethyl acetate (1:2) as eluent gave compound (+)-**3c** (26 mg, 58%) as a colorless oil. $[\alpha]_D = +136.3$ (*c* 1.9, CHCl_3). ^1H NMR (CDCl_3): δ 7.34 (m, 2H), 7.26 (m, 3H), 4.68 (br s, 1H), 4.54 (dd, 1H, *J* = 4.6, 1.2 Hz), 4.08 (m, 1H), 3.93 (dd, 1H, *J* = 4.9, 0.9 Hz), 3.66 (s, 3H), 3.27 (d, 1H, *J* = 1.5 Hz), 2.91 (m, 3H), 2.20 (m, 1H), 1.75 (m, 1H). ^{13}C NMR (CDCl_3): δ 165.6, 147.2, 139.4, 133.9, 128.3, 128.0, 126.6, 84.6, 72.7, 59.7, 59.8, 44.5, 41.6, 27.8, 20.6. IR (CHCl_3 , cm^{-1}): ν 1735. MS (CI), *m/z*: 286 ($\text{M}^+ + 1$, 100), 285 (M^+ , 25). (Anal. Calcd. for $\text{C}_{17}\text{H}_{19}\text{NO}_3$: C, 71.56; H, 6.71; N, 4.91. Found: C, 71.67; H, 6.75; N, 4.89).

Tricyclic β -Lactam ($\pm$)-5a. From 45 mg (0.16 mmol) of enallene ($\pm$)-**2d**, and after chromatography of the residue using hexanes/ethyl acetate (1:2) as eluent gave compound ($\pm$)-**5a** (27 mg, 60%) as a colorless oil. ^1H NMR (CDCl_3): δ 7.40 and 6.89 (dd, each 2H, *J* = 6.8, 2.2 Hz), 4.96 (br s, 1H), 4.59 (t, 1H, *J* = 4.0 Hz), 4.19 (dd, 1H, *J* = 6.1, 4.4 Hz), 3.79 (s, 3H), 3.45 (m, 1H), 3.35 (t, 1H, *J* = 5.8 Hz), 2.70 (m, 2H), 2.49 (m, 1H), 1.77 (m, 3H), 1.82 (m, 1H). ^{13}C NMR (CDCl_3): δ 167.7, 156.1, 142.9, 131.9, 124.4, 117.5, 116.1, 114.7, 67.0, 56.2, 55.5, 53.5, 36.8, 29.0, 28.5, 16.0. IR (CHCl_3 , cm^{-1}): ν 1733. MS (CI), *m/z*: 286 ($\text{M}^+ + 1$, 100), 285 (M^+ , 27). (Anal. Calcd. for $\text{C}_{17}\text{H}_{19}\text{NO}_3$: C, 71.56; H, 6.71; N, 4.91. Found: C, 71.44; H, 6.74; N, 4.94).

General Procedure for the Synthesis of Vinylic Stannanes 6. A solution of the appropriate allenyne **2** (0.40 mmol), triphenyltin hydride (0.60 mmol) and AIBN (cat.) in benzene

(35 mL) was heated at reflux temperature until complete disappearance (TLC) of starting material (typically 45 min). The reaction mixture was allowed to cool to room temperature, the solvent was removed under reduced pressure and vinylstannanes **6** were obtained after purification by flash chromatography on silica gel using hexanes/ethyl acetate/triethylamine mixtures.

Bicyclic β -Lactam (–)-6a. From 51 mg (0.23 mmol) of allenyne (+)-**2f**, and after chromatography of the residue using hexanes/ethyl acetate (1:1 containing 1% of triethylamine) as eluent gave compound (–)-**6a** (85 mg, 64%) as a colorless oil. $[\alpha]_D = -1.3$ (c 0.4, CHCl₃). ¹H NMR (CDCl₃): δ 7.59 (m, 6H), 7.40 (m, 9H), 6.29 (s, 1H), 4.59 (m, 1H), 4.54 (d, 1H, $J = 5.0$ Hz), 4.29 (d, 1H, $J = 5.0$ Hz), 4.23 (d, 1H, $J = 13.9$ Hz), 3.64 (m, 1H), 3.59 (s, 3H), 3.09 (d, 1H, $J = 6.9$ Hz), 2.01 (s, 3H), 1.87 (s, 3H). ¹³C NMR (CDCl₃): δ 166.6, 160.7, 157.5, 138.0, 136.9, 136.8, 128.9, 128.7, 127.9, 83.7, 72.3, 59.3, 55.4, 48.9, 21.6, 16.8. IR (CHCl₃, cm⁻¹): ν 1740. MS (CI), m/z : 572 (M⁺, 3), 495 (M⁺ – 77, 100). (Anal. Calcd. for C₃₀H₃₁NO₃Sn: C, 62.96; H, 5.46; N, 2.45. Found: C, 62.82; H, 5.49; N, 2.42).

Bicyclic β -Lactam (±)-6c. From 30 mg (0.10 mmol) of allenyne (±)-**2h**, and after chromatography of the residue using hexanes/ethyl acetate (2:1 containing 1% of triethylamine) as eluent gave compound (±)-**6c** (31 mg, 47%) as a colorless oil. ¹H NMR (CDCl₃): δ 7.60 (m, 9H), 7.44 (m, 8H), 6.85 (dd, 1H, $J = 6.8, 2.0$ Hz), 6.22 (s, 1H), 4.88 (br s, 1H), 4.13 (dd, 1H, $J = 5.9, 2.2$ Hz), 3.79 (s, 3H), 3.28 (dd, 1H, $J = 15.4, 7.6$ Hz), 3.07 (q, 1H, $J = 6.0$ Hz), 2.59 (dd, 1H, $J = 15.4, 6.0$ Hz), 1.99 (d, 1H, $J = 4.3$ Hz), 1.74 (s, 3H), 1.56 (s, 3H). ¹³C NMR (CDCl₃): δ 166.6, 155.9, 138.4, 136.9, 131.8, 130.4, 129.1, 128.7, 128.4, 118.2, 114.3, 72.7, 56.6, 55.4, 29.7, 23.4, 20.4. IR (CHCl₃, cm⁻¹): ν 1731. MS (CI), m/z : 648 (M⁺, 6), 571 (M⁺ – 77, 100). (Anal. Calcd. for C₃₆H₃₅NO₃Sn: C, 66.69; H, 5.44; N, 2.16. Found: C, 66.82; H, 5.39; N, 2.13).