Experimental

(2S, 5R)-6,6-Dibromo-3,3-dimethyl-4,4,7-trioxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid (4); To a three-neck flask equipped with a paddle stirrer containing 6-aminopenicillanic acid (40 g, 0.18 mol) was added methylene chloride (300 mL) and bromine (88 g, 0.55 mol) and the mixture was cooled to 0^o C. 1.25 M Sulfuric acid (148 mL) was then added followed by sodium nitrite (25.6 g, 0.37 mol) potionwise to the mixture. This was added 6-aminopenicillanic acid portionwise over a period of 30 min and the resulting mixture was stirred for 30 min at that temperature. A solution of sodium bisulfite (~300 mL) was added slowly until the solution became a clear solution. After warming to room temperature, the organic layer was separated and the aqueous layer was extracted with methylene chloride. To the combined organic layer was added water (180 mL) followed by 1N sodium hyroxide (70 mL) dropwise to neutralize the reaction mixture. The aqueous layer was separated, cooled to -5^o C and was added portionwise a premixed solution of potassium permanganate (44 g), 85% phosphoric acid (13.3 mL) in water (380 mL) until the oxidation was complete. Ethyl acetate (300 mL) was added to the mixture and the pH of the solution was adjusted to 2 with 6N HCl. A solution of 1M sodium bisulfite solution was added to the mixture over a period of 20 min until a clear solution appeared. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layer was dried over anhydrous sodium sulfate and the solvent was removed *in vacuo* to obtain 40 g (56%) of the acid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.09(s, 3H), 1.60 (s, 3H), 4.58 (s, 1H), 4.62 (s, 1H), 9.00(brs, 1H).

(2S, 5R)-6,6-Dibromo-3,3-dimethyl-4,4,7-trioxo-4-thia-1- azabicyclo[3.2.0]heptane-2-carboxylic acid diphenylmethyl ester (5); To a solution of the acid **4** (28 g, 72 mmol) in acetone (100 mL) at 0^o C was added a solution of diphenyldiazomethane (15 g, 77 mmol) in acetone (50 mL) and the resulting mixture was stirred for 2 h at room temperature. The solvent was removed and the crude product was purified by silica gel chromatography to obtain 38 g (95%) of the product; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.09(s, 3H), 1.60 (s, 3H), 4.58 (s, 1H), 4.62 (s, 1H), 6.99 (s, 1H), 7.35 (m, 10H).

(2S, 5R, 6R)-6-Bromo-3,3-dimethyl-4,4,7-trioxo-6-(2-propenyl)-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid diphenylmethyl ester (6); To a solution of the dibromide **5** (6 g, 10.8 mmol) in toluene (80 mL) was added tributylallyltin (3.9 g, 11.8 mmol) followed by AIBN (195 mg, 1.2 mmol) and the resulting mixture was refluxed for 6 h. The solvent was removed and the crude product was purified by silica gel chromatography to obtain 4 g (72%) of the product; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.09(s, 3H), 1.60 (s, 3H), 3.05 (m, 2H), 4.58 (s, 1H), 4.62 (s, 1H), 5.26 (m, 2H), 5.85 (m, 1H), 6.99 (s, 1H), 7.35 (m, 10H).

(2S, 5R, 6R)-3,3-Dimethyl-4,4,7-trioxo-6-(2-propenyl)-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid diphenylmethyl ester (7); To a solution of the ally bromide **6** (4 g, 7.72 mmol) in toluene (80 mL) was added tributyltin hydride (2.1 mL, 7.72 mmol) followed by AIBN (127 mg, 0.77 mmol) and the resulting mixture was stirred for 3 h at room temperature. The solvent was removed and the crude product was purified by silica gel chromatography to obtain 2.5 g(75%) of the product; ^{1}H NMR(300 MHz, $CDCl_3$) δ 1.12 (s, 3H), 1.55 (s, 3H), 2.65 (m, 1H), 3.00 (m, 1H), 3.92 (m, 1H), 4.55 (s, 1H), 4.59 (d, 1H, J= 3.0 Hz), 5.20 (m, 2H), 5.84 (m, 1H), 6.96 (s, 1H), 7.38 (m, 10H)

(2S, 5R, 6R)-3,3-Dimethyl-4,4,7-trioxo-6-(2-oxo-ethyl)-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid diphenylmethyl ester (8); To a cooled (-78^o C) solution of the compound **7** (1.3 g, 2.96 mmol) in methylene chloride (100 mL) was passed ozone until blue color appeared and dimethyl sulfide (15 mL) was added and the resulting mixture was stirred for 15 h at room temperature. The solvent was removed and the crude product was purified by silica gel chromatography to obtain 1.1 g (85%) of the product; ^{1}H NMR(300 MHz, $CDCl_3$) δ 1.10 (s, 3H), 1.54 (s, 3H), 3.11 (dd, 1H, J_1= 6.0 Hz, J_2= 19.8 Hz), 3.59 (dd, 1H, J_1= 9.0 Hz, J_2= 19.8 Hz), 4.16 (m, 1H), 4.51 (s, 1H), 4.80 (d, 1H, J= 5.0 Hz), 6.98 (s, 1H), 7.30 (m, 10H), 9.81 (s, 1H); ^{13}C NMR(75 MHz, $CDCl_3$) δ 18.0, 19.7, 37.3, 45.8, 63.0, 64.6, 64.7, 79.2, 126.9, 127.7, 128.4, 128.7, 128.8, 138.7, 138.9, 166.0, 197.6.

(2S, 5R, 6R)-3,3-Dimethyl-4,4,7-trioxo-6-(2-hydroxylimino-ethyl)-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid diphenylmethyl ester (9); To a solution of aldehyde **8** (1.5 g, 3.4 mmol) in ethanol (15 mL) was added a solution of hydroxylamine hydrochloride (236 mg, 3.4 mmol) and sodium acetate (279 mg, 3.4 mmol) in ethanol (5 mL) and water (4 mL) and the resulting mixture was stirred for 5 h at room temperature. Methylene chloride and water were added and the organic layer was separated and dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* to obtain 1.4 g(90%) of the product; *major*; IR 3462, 2875, 1800, 1751, 1323, 1200, 1117, 701 cm^{-1}; ^{1}H NMR(300 MHz, $CDCl_3$) δ 1.08 (s, 1H), 1.52 (s, 3H), 2.70 (m, 1H), 3.21 (m, 1H), 4.09 (m, 1H), 4.52 (s, 1H), 4.73 (d, 1H, J= 5.1 Hz), 6.99(s, 1H), 7.34 (m, 10H), 7.52 (t, 1H, J= 3.6 Hz); HRMS Calcd. for $C_{23}H_{24}N_2O_6S$: 457.1433; Found, 457.1448. *minor;* ^{1}H NMR(300 MHz, $CDCl_3$) δ 1.08 (s, 1H), 1.52 (s, 3H), 2.70 (m, 1H), 3.21 (m, 1H), 4.09 (m, 1H), 4.55 (s, 1H), 4.61 (d, 1H, J= 5.1 Hz), 6.87 (t, 1H, J= 5.4 Hz), 6.99(s, 1H), 7.34 (m, 10H).

(2S, 5R, 6R)-3,3-Dimethyl-4,4,7-trioxo-6-(2-chloro-2-hydroxylimino-ethyl)-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid diphenylmethyl ester (10); To a solution of the oxime **9** (1.7 g, 3.73 mmol) in DMF (5 mL) was added N-chlorosuccinamide (498 mg, 3.73 mmol) portionwise and the resulting mixture was stirred for 2 h at room temperature. The mixture was poured into ice-cold water and extracted with ether, dried over anhydrous sodium sulfate. The removal of the solvent *in vacuo* gave 1.5 g (83%) of the product; IR 3494, 2927, 1800, 1756, 1324, 1184, 1118, 701 cm^{-1}; ^{1}H NMR(300 MHz, $CDCl_3$) δ 1.09(s, 3H), 1.54 (s, 3H), 2.95 (dd, 1H, J1= 5.4 Hz, J2= 17.1 Hz), 3.57 (dd, 1H, J_1= 11.4 Hz, J_2= 17.1 Hz), 4.16 (m, 1H), 4.53 (s, 1H), 4.70 (d, 1H, J= 4.8 Hz), 6.99 (s, 1H), 7.35 (m, 10H), 9.51 (brs, 1H); ^{13}C NMR(75 MHz, $CDCl_3$) δ 18.1, 20.0, 30.6, 49.6, 62.9, 64.9, 66.3, 79.5, 127.1, 128.0, 128.7, 129.1, 129.2, 137.4, 138.8, 139.1, 166.6, 173.4.

[2S, 5R, 6R, (5S)]-3,3-Dimethyl-4,4,7-trioxo-6-{(5S)-5-methoxycarbonyl-4, 5-dihydro-isoxazol-3-ylmethyl}-4-.lambda (6).-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid diphenylmethyl ester (12),

[2S, 5R, 6R, (5R)]-3,3-Dimethyl-4,4,7-trioxo-6-{(5R)-5-methoxycarbonyl-4, 5-dihydro-isoxazol-3-ylmethyl}-4-.lambda (6).-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid diphenylmethyl ester (13); To a cooled (0^o C) solution of hydroximic acid chloride **10** (200 mg, 0.41 mmol) in methylene chloride (2 mL) was added a mixture of methyl acrylate (35 mg, 0.41 mmol) and triethylamine (0.057 mL) in methylene chloride (2 mL) and the resulting mixture was stirred for 30 min at that temperature. The reaction mixture was added water and extracted with methylene chloride. The crude product was purified by silica gel chromatography to obtain 110 mg (50%) of the products as a 1:1 mixture of diastereoisomers; *Isomer* **12**; IR 3495, 2925, 1800, 1754, 1323, 1188, 700cm^{-1}; ^{1}H NMR(300 MHz, $CDCl_3$) δ 1.08 (s, 1H), 1.53 (s, 3H), 2.76 (m, 1H), 3.32 (m, 3H), 3.78 (s, 3H), 4.28 (m, 1H), 4.52 (s, 1H), 4.75 (m, 1H), 5.06 (m, 1H), 6.98 (s, 1H), 7.34 (m, 10H); ^{13}C NMR(75 MHz, $CDCl_3$) δ 18.2, 20.0, 21.8, 41.6, 49.6, 53.2, 63.1, 64.7, 64.9, 79.4, 127.1, 128.1, 128.7, 129.0, 129.1, 138.9, 139.2, 156.2, 166.5, 170.8, 173.9; MS (ES) 541.3 (M+H): *Isomer* **13**; IR 3474, 2926, 1800, 1752, 1323, 1189, 700^{-1}; ^{1}H NMR(300 MHz, $CDCl_3$) δ 1.09 (s, 3H), 1.53 (s, 3H), 2.75 (dd, 1H, J_1= 6.0 Hz, J_2= 17.7 Hz), 3.32 (m, 3H), 3.78 (s, 3H), 4.28 (m, 1H), 4.51 (s, 1H), 4.75 (d, 1H, J= 4.8 Hz), 5.05 (m, 1H), 6.98 (s, 1H), 7.36 9m, 10H); ^{13}C NMR(75 MHz, $CDCl_3$) δ 18.2, 20.0, 21.8, 41.6, 49.5, 53.2, 63.1, 64.7, 65.0, 66.2, 79.4, 127.1, 128.1, 128.7, 129.0, 129.1, 129.2, 138.9, 139.1, 156.0, 166.5, 171.0, 173.9; MS (ES) 541.2 (M+H).

[2S, 5R, 6R, (5R)]-3,3-Dimethyl-4,4,7-trioxo-6-{(5R)-5-benzenesulfonyl-4, 5-dihydro-isoxazol-3-ylmethyl}-4-.lambda (6).-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid diphenylmethyl ester (14),

[2S, 5R, 6R, (5S)]-3,3-Dimethyl-4,4,7-trioxo-6-{(5S)-5-benzenesulfonyl-4, 5-dihydro-isoxazol-3-ylmethyl}-4-.lambda (6).-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid diphenylmethyl ester (15); To a cooled (0^o C) solution of the hydroximic acid chloride **10** (150 mg, 0.31 mmol) in methylene chloride (1.5 mL) was added a mixture of phenylvinyl sulfone (52 mg, 0.31 mmol) and triethylamine (0.043 mL) in methylene chloride (1.5 mL) and the resulting mixture was stirred for 45 min at that temperature. The reaction mixture was added water and extracted ethyl acetate. The organic layer was dried over anhydrous sodium sulfate, the solvent was removed and the crude residue was

purified by silica gel chromatography to obtain 100 mg (52%) of the products as a 1:1 mixture of diastereoisomers; *Isomer* **14**; IR 2984, 1800, 1735, 1448, 1310, 1152, 1116, 700 cm^{-1}; ^1H NMR(300 MHz, $CDCl_3$) δ 1.05 (s, 3H), 1.51 (s, 3H), 2.72 (dd, 1H, J_1= 6.3 Hz, J_2= 18.0 Hz), 3.44 (m, 2H), 3.70 (m, 1H), 4.12 (m, 1H), 4.50 (s, 1H), 4.71 (d, 1H, J= 4.8 Hz), 5.44 (m, 1H), 6.97 (s, 1H), 7.33 (m, 10H), 7.62 (m, 3H), 7.94 (m, 2H); MS (ES) 640.2 (M+H): *Isomer* **15**; IR 3430, 2986, 1800, 1755, 1448, 1315, 1151, 700 cm^{-1}; ^1H NMR(300 MHz, $CDCl_3$) δ 1.09 (s, 3H), 1.56 (s, 3H), 2.90 (dd, 1H, J_1= 6.9 Hz, J_2= 17.4 Hz), 3.31 (m, 1H), 3.48 (m, 1H), 3.68 (m, 1H), 4.13 (m, 1H), 4.54 (s, 1H), 4.69 (m, 1H), 5.42 (m, 1H), 6.98 (s, 1H), 7.33 (m, 10H), 7.60 (m, 3H), 7.96 (m, 2H); HRMS Calcd. for $C_{31}H_{30}N_2O_8S_2$: 623.1522; Found, 623.1535.

[2S, 5R, 6R, (5R)]-3,3-Dimethyl-4,4,7-trioxo-6-{(5R)-5-phenylsulfanyl-4, 5-dihydro-isoxazol-3-ylmethyl}-4-.lambda (6).-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid diphenylmethyl ester (16),
[2S, 5R, 6R, (5S)]-3,3-Dimethyl-4,4,7-trioxo-6-{(5S)-5-phenylsulfanyl-4, 5-dihydro-isoxazol-3-ylmethyl}-4-.lambda (6).-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid diphenylmethyl ester (17); To a solution of hydroximic acid chloride **10** (100 mg, 0.2 mmol) in benzene (1 mL) was added a solution containing phenylvinyl sulfide (0.053 mL, 0.4 mmol) and bis(tributyltin) oxide (0.051 mL, 0.1 mmol) in benzene (1 mL) and the resulting mixture was stirred for 2 h at room temperature. The solvent was removed *in vacuo* and the crude residue was purified by silica gel chromatography to obtain 70 mg(59%) of the products as a 1:1 mixture of diastereomers; *Isomer* **16**; IR 2921, 1800, 1756, 1322, 1188, 701 cm^{-1}; ^1H NMR(300 MHz, $CDCl_3$) δ 1.07 (s, 3H), 1.52 (s, 3H), 2.65 (dd, 1H, J_1= 6.3 Hz, J_2= 18.0 Hz), 2.93 (dd, 1H, J_1= 4.5 Hz, J_2= 18.0 Hz), 3.27 (m, 1H), 3.49 (m, 1H), 4.17 (m, 1H), 4.44 (s, 1H), 4.74 (d, 1H, J= 4.8 Hz), 6.01 (m, 1H), 6.98 (s, 1H), 7.34 (m, 13H), 7.55 (m, 2H); ^{13}C NMR(75 MHz, $CDCl_3$) δ 17.8, 19.6, 21.6, 44.0, 49.1, 62.7, 64.3, 64.7, 79.0, 87.1, 126.8, 127.6, 128.2, 128.4, 128.8, 133.1, 138.6, 138.8, 156.9, 166.1, 173.5; HRMS Calcd. for $C_{31}H_{30}N_2O_6S_2$: 591.1618, Found; 591.1611: *Isomer* **17**; IR 2929, 1800, 1755, 1324, 1185, 1168, 700 cm^{-1}; ^1H NMR(300 MHz, $CDCl_3$) δ 1.04 (s, 3H), 1.48 (s, 3H), 2.70 (dd, 1H, J_1= 6.6 Hz, J_2= 18.0 Hz), 2.86 (dd, 1H, J_1= 5.4 Hz, J_2= 18.0 Hz), 3.30 (m, 2H), 4.11 (m, 1H), 4.46 (s, 1H), 4.66 (d, 1H, J= 5.1

Hz), 5.92 (m, 1H), 6.91 (s, 1H), 7.28 (m, 13H), 7.48 (m, 2H); ^{13}C NMR(75 MHz, $CDCl_3$) δ 17.8, 19.7, 21.5, 43.9, 49.1, 62.7, 64.5, 64.6, 77.2, 79.1, 87.2, 126.8, 127.7, 128.4, 128.8, 129.1, 132.9, 138.6, 138.8, 156.8, 166.1, 173.5; HRMS Calcd. for $C_{31}H_{30}N_2O_6S_2$: 591.1618, Found; 591.1611.

[2S, 5R, 6R, (5S)]-3,3-Dimethyl-4,4,7-trioxo-6-{(5S)-5-tert-butoxy-4, 5-dihydro-isoxazol-3-ylmethyl}-4-.lambda (6).-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid diphenylmethyl ester (18),
[2S, 5R, 6R, (5R)]-3,3-Dimethyl-4,4,7-trioxo-6-{(5R)-5-tert-butoxy-4, 5-dihydro-isoxazol-3-ylmethyl}-4-.lambda (6).-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid diphenylmethyl ester (19); To a solution of hydroximic acid chloride **10** (100 mg, 0.2 mmol) in benzene (1.5 mL) was added a solution containing ^{t}butyl vinyl ether (40 mg, 0.4 mmol) and bis(tributyltin) oxide (60 mg, 0.1 mmol) in benzene (1 mL) and the resulting mixture was stirred for 2 h at room temperature. The solvent was removed in vacuo and the crude residue was purified by silica gel chromatography to obtain 75 mg(68%) of the products as a 1:1 mixture of diastereomers; *Isomer* **18**; IR 2977, 1800, 1757, 1325, 1164, 701 cm^{-1}; ^{1}H NMR(300 MHz, $CDCl_3$) δ 1.15 (s, 3H), 1.26 (s, 9H), 1.54 (s, 3H), 2.65 (m, 1H), 2.85 (m, 1H), 3.06 (m, 1H), 3.32 (m, 1H), 4.25 (m, 1H), 4.53 (s, 1H), 4.77 (d, 1H, J= 4.8 Hz), 5.84 (m, 1H), 6.98 (s, 1H), 7.36 (m, 10H); ^{13}C NMR(75 MHz, $CDCl_3$) δ 17.8, 19.6, 21.7, 28.7, 44.4, 49.2, 62.7, 64.4, 64.7, 75.4, 79.0, 98.5, 126.8, 127.7, 128.4, 128.7, 128.8, 138.6, 138.8, 155.9, 166.2, 173.8; HRMS Calcd. for $C_{29}H_{34}N_2O_7S$: 555.2159, Found; 555.2155: *Isomer* **19**; IR 2977, 1800, 1758, 1323, 1165, 701 cm^{-1}; ^{1}H NMR(300 MHz, $CDCl_3$) δ 1.07 (s, 3H), 1.26 (s, 9H), 1.52 (s, 3H), 2.78 (m, 2H), 3.10 (m, 1H), 3.32 (m, 1H), 4.30 (m, 1H), 4.50 (s, 1H), 4.80 (d, 1H, J= 4.8 Hz), 5.85 (d, 1H, J= 6.0 Hz), 6.98 (s, 1H), 7.34 (m, 10H); ^{13}C NMR(75 MHz, $CDCl_3$) δ 18.1, 20.0, 22.3, 29.1, 44.6, 49.5, 63.0, 64.6, 65.3, 76.0, 79.3, 98.7, 127.1, 128.1, 128.7, 129.0, 129.2, 138.9, 139.2, 156.3, 166.5, 174.3; HRMS Calcd. for $C_{29}H_{34}N_2O_7S$: 555.2159, Found; 555.2155.

[2S, 5R, 6R, (5S)]-3,3-Dimethyl-4,4,7-trioxo-6-{(5S)-5-phenyl-4, 5-dihydro-isoxazol-3-ylmethyl}-4-.lambda (6).-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid diphenylmethyl ester (20),

[2S, 5R, 6R, (5R)]-3,3-Dimethyl-4,4,7-trioxo-6-{(5R)-5-phenyl-4, 5-dihydro-isoxazol-3-ylmethyl}-4-.lambda (6).-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid diphenylmethyl ester (21); To a solution of hydroximic acid chloride **10** (150 mg, 031 mmol) in benzene (1.5 mL) was added a solution containing styrene (64 mg, 061 mmol) and bis(tributyltin) oxide (93 mg, 0.16 mmol) in benzene (1.5 mL) and the resulting mixture was stirred for 2 h at room temperature. The solvent was removed *in vacuo* and the crude residue was purified by silica gel chromatography to obtain 93 mg(54%) of the products as a 1:1 mixture of diastereomers; *Isomer* **20**; IR 3032, 1800, 1756, 1323, 1186, 699 cm^{-1}; ^{1}H NMR(300 MHz, $CDCl_3$) δ 1.11 (s, 3H), 1.55 (s, 3H), 2.73 (dd, 1H, J_1= 4.5 Hz, J_2= 13.5 Hz), 2.95 (dd, 1H, J_1= 6.3 Hz, J_2= 12.6 Hz), 3.43 (m, 2H), 4.32 (m, 1H), 4.53 (s, 1H), 4.81 (d, 1H, J= 4.8 Hz), 5.62 (dd, 1H, J_1= 6.3 Hz, J_2= 7.1 Hz), 6.99 (s, 1H), 7.34 (m, 15H); ^{13}C NMR(75 MHz, $CDCl_3$) δ 17.8, 19.6, 21.8, 45.4, 49.3, 62.7, 64.4, 64.8, 77.2, 79.1, 82.1, 125.7, 126.8, 127.7, 128.2, 128.4, 128.7, 128.8, 128.8, 138.6, 138.8, 140.6, 155.7, 166.2, 173.7; HRMS Calcd. for $C_{31}H_{30}N_2O_6S$: 559.1897, Found; 559.1892: *Isomer* **21**; IR 3032, 1800, 1756, 1323, 1186, 699 cm^{-1}; ^{1}H NMR(300 MHz, $CDCl_3$) δ 1.12 (s, 3H), 1.55 (s, 3H), 2.76 (dd, 1H, J_1= 4.8 Hz, J_2= 13.5 Hz), 2.96 (dd, 1H, J_1= 6.3 Hz, J_2= 15.9 Hz), 3.35 (m, 2H), 4.34 (m, 1H), 4.53 (s, 1H), 4.82 (d, 1H, J= 4.2 Hz), 5.58 (dd, 1H, J_1= 6.6 Hz, J_2= 7.4 Hz), 6.99 (s, 1H), 7.34 (m, 15H); ^{13}C NMR(75 MHz, $CDCl_3$) δ 17.8, 19.6, 21.9, 45.7, 49.3, 62.7, 64.4, 64.8, 77.2, 79.1, 82.4, 126.0, 126.8, 127.7, 128.2, 128.4, 128.7, 128.8, 128.8, 138.6, 138.8, 140.7, 155.4, 166.2, 173.8; HRMS Calcd. for $C_{31}H_{30}N_2O_6S$: 559.1897, Found; 559.1892.

[2S, 5R, 6R]-3,3-Dimethyl-4,4,7-trioxo-6-(5-methoxycarbonyl-isoxazol-3-ylmethyl)-4-.lambda (6).-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid diphenylmethyl ester (22),

[2S, 5R, 6R]-3,3-Dimethyl-4,4,7-trioxo-6-(6-methoxycarbonyl-isoxazol-3-ylmethyl)-4-.lambda (6).-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid diphenylmethyl ester (23); To a solution of hydroximic acid chloride **10** (75 mg, 0.15 mmol) in benzene

(1 mL) was added a solution containing methyl propiolate (26 mg, 0.3 mmol) and bis(tributyltin) oxide (45 mg, 0.08 mmol) in benzene (1 mL) and the resulting mixture was stirred for 2 h at room temperature. The solvent was removed *in vacuo* and the crude residue was purified by silica gel chromatography to obtain 45 mg(56%) of the products as a 6:1 mixture of regioisomers; *Major isomer* **22**; IR 2956, 1800, 1747, 1323, 1283, 1183, 701 cm^{-1}; ^{1}H NMR(300 MHz, $CDCl_3$) δ 1.11 (s, 3H), 1.55 (s, 3H), 3.29 (dd, 1H, J_1= 5.1 Hz, J_2= 12.3 Hz), 3.73 (dd, 1H, J_1= 7.8 Hz, J_2= 12.3 Hz), 3.95 (s, 3H), 4.32 (m, 1H), 4.56 (s, 1H), 4.75 (d, 1H, J= 3.6 Hz), 6.92 (s, 1H), 6.99 (s, 1H), 7.36 (m, 10H); ^{13}C NMR(75 MHz, $CDCl_3$) δ 17.8, 19.6, 20.1, 50.1, 52.8, 62.8, 64.3, 64.6, 79.1, 109.4, 126.8, 127.7, 128.4, 128.7, 128.8, 128.8, 138.5, 138.7, 160.9, 166.0, 173.2; HRMS Calcd. for $C_{27}H_{26}N_2O_8S$: 539.1488, Found; 539.1505.

[2S, 5R, 6R]-3,3-Dimethyl-4,4,7-trioxo-6-(5-trimethylsilyl-isoxazol-3-ylmethyl)-4-.lambda (6).-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid diphenylmethyl ester (24); To a solution of hydroximic acid chloride **10** (100 mg, 0.2 mmol) in benzene (1 mL) was added a solution containing trimethylsilyl acetylene (40 mg, 0.4 mmol) and bis(tributyltin) oxide (60 mg, 0.1 mmol) in benzene (1 mL) and the resulting mixture was stirred for 2 h at room temperature. The solvent was removed *in vacuo* and the crude residue was purified by silica gel chromatography to obtain 50 mg(45%) of the product; IR 2959, 1800, 1757, 1322, 1184, 1171, 847, 760, 702 cm^{-1}; ^{1}H NMR(300 MHz, $CDCl_3$) δ 0.30 (s, 9H), 1.10 (s, 3H), 1.55 (s, 3H), 3.20 (dd, 1H, J_1= 6.3 Hz, J_2= 16.5 Hz), 3.70 (dd, 1H, J_1= 10.8 Hz, J_2= 16.5 Hz), 4.31 (m, 1H), 4.54 (s, 1H), 4.77 (d, 1H, J= 5.1 Hz), 6.40 (s, 1H), 6.99 (s, 1H), 7.39 (m, 10H); ^{13}C NMR(75 MHz, $CDCl_3$) δ -1.94, 17.8, 19.6, 19.7, 50.7, 62.7, 64.5, 64.7, 112.5, 126.8, 127.7, 128.4, 128.7, 128.8, 128.8, 138.6, 138.8, 158.3, 166.2, 173.8, 178.9; HRMS Calcd. for $C_{28}H_{32}N_2O_6SSi$: 553.1823, Found; 553.1819.

[2S, 5R, 6R]-3,3-Dimethyl-4,4,7-trioxo-6-[5-(4-methylphenylsulfonyl)-isoxazol-3-ylmethyl]-4-.lambda (6).-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid diphenylmethyl (25),

[2S, 5R, 6R]-3,3-Dimethyl-4,4,7-trioxo-6-[6-(4-methylphenylsulfonyl)-isoxazol-3-ylmethyl]-4-.lambda (6).-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid diphenylmethyl (26); To a solution of hydroximic acid chloride **10** (100 mg, 0.2 mmol) in benzene (1 mL) was added a solution containing p-tolylethynyl sulfone (72 mg, 0.4 mmol) and bis(tributyltin) oxide (0.051 mL, 0.1 mmol) in benzene (1 mL) and the resulting mixture was stirred for 2 h at room temperature. The solvent was removed *in vacuo* and the crude residue was purified by silica gel chromatography to obtain 70 mg(56%) of the products as a 2:1 mixture of regioisomers; *Isomer* **25**; ^{1}H NMR(300 MHz, $CDCl_3$) δ 1.08 (s, 3H), 1.54 (s, 3H), 2.45 (s, 3H), 3.26 (dd, 1H, J_1= 6.9 Hz, J_2= 16.8 Hz), 3.69 (dd, 1H, J_1= 10.2 Hz, J_2= 16.8 Hz), 4.23 (m, 1H), 4.54 (s, 1H), 4.70 (d, 1H, J= 5.1 Hz), 6.88 (s, 1H), 7.35 (m, 12H), 7.92 (d, 2H, J= 8.4 Hz): *Isomer* **26**; ^{1}H NMR(300 MHz, $CDCl_3$) δ 1.08 (s, 3H), 1.51 (s, 3H), 2.43 (s, 3H), 3.29 (dd, 1H, J_1= 6.0 Hz, J_2= 18.0 Hz), 3.73 (dd, 1H, J_1= 11.1 Hz, J_2= 18.0 Hz), 4.32 (m, 1H), 4.52 (s, 1H), 4.76 (d, 1H, J= 4.8 Hz), 6.98 (s, 1H), 7.37 (m, 12H), 7.82 (d, 2H, J= 8.4 Hz); ^{13}C NMR(75 MHz, $CDCl_3$) δ 15.6, 18.1, 19.3, 20.1, 22.1, 49.3, 64.8, 64.9, 66.2, 79.4, 124.4, 127.1, 127.8, 128.0, 128.7, 129.0, 129.1, 129.2, 130.7, 137.6, 138.9, 139.1, 157.2, 162.7, 166.4, 173.3.

[2S, 5R, 6R]-3,3-Dimethyl-4,4,7-trioxo-6-[5-(N'-tert-butoxycarbonyl-hydrazinocarbonyl)-isoxazol-3-ylmethyl]-4-.lambda (6).-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid diphenylmethyl (27), [2S, 5R, 6R]-3,3-Dimethyl-4,4,7-trioxo-6-[6-(N'-tert-butoxycarbonyl-hydrazinocarbonyl)-isoxazol-3-ylmethyl]-4-.lambda (6).-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid diphenylmethyl (28); To a solution of hydroximic acid chloride **10** (149 mg, 0.3 mmol) in benzene (2 mL) was added a solution containing N'-propynyl-hydrazinecarboxylic acid tert-butyl ester (112 mg, 0.6 mmol) and bis(tributyltin) oxide (45 mg, 0.3 mmol) in benzene (2 mL) and the resulting mixture was stirred for 2 h at room temperature. The solvent was removed *in vacuo* and the crude residue was purified by silica gel chromatography to obtain 85 mg(45%) of the products as a 1:1 mixture of regioisomers; *Isomer* **27**; IR 3345, 2979, 1799, 1747, 1703, 1325, 1161, 701 cm^{-1}; ^{1}H NMR(300 MHz, $CDCl_3$) δ 1.48 (s, 3H), 1.49 (s, 9H), 1.55 (s, 3H), 3.28 (dd, 1H, J_1= 6.0 Hz, J_2= 12.6 Hz), 3.74 (dd, 1H, J_1= 7.1 Hz, J_2= 12.6 Hz), 4.29 (m,

1H), 4.56 (s, 1H), 4.76 (d, 1H, J= 3.6 Hz), 6.59 (brs, 1H), 6.94 (s, 1H), 6.99 (s, 1H), 7.36 (m, 10H), 8.17 (brs, 1H); ^{13}C NMR(75 MHz, $CDCl_3$) δ 17.8, 19.6, 20.1, 28.1, 49.9, 62.8, 64.4, 64.6, 79.2, 82.6, 108.3, 121.0, 126.8, 127.7, 128.4, 128.7, 128.8, 128.8, 138.6, 138.8, 154.6, 161.3, 162.0, 166.1, 173.1; MS(ES); 639.8 (M+H). *Isomer* **28**; IR 3344, 2980, 1800, 1741, 1691, 1325, 1180, 700 cm^{-1}; ^{1}H NMR(300 MHz, $CDCl_3$) δ 1.49 (s, 12H), 1.54 (s, 3H), 3.42 (m, 1H), 3.87 (m,1H), 4.41 (m, 1H), 4.54 (s, 1H), 4.83 (d, 1H, J= 5.1 Hz), 6.68 (s, 1H), 6.99 (s, 1H), 7.35 (m, 10H), 8.86 (s, 1H); ^{13}C NMR(75 MHz, $CDCl_3$) δ 17.8, 19.6, 20.1, 28.1, 49.9, 62.8, 64.5, 64.8, 79.1, 82.7, 126.8, 127.7, 128.4, 128.4, 128.7, 128.8, 138.6, 138.9, 159.5, 166.1, 166.2, 173.1, 173.5; MS(ES); 639.8 (M+H).

[2S, 5R, 6R]-3,3-Dimethyl-4,4,7-trioxo-6-(5-benzoyl-isoxazol-3-ylmethyl)-4-.lambda (6).-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid diphenylmethyl (29); To a solution of hydroximic acid chloride **10** (100 mg, 0.2 mmol) in benzene (1 mL) was added a solution containing alkynyl phenyl ketone.... (52 mg, 0.4 mmol) and bis(tributyltin) oxide (0.051 mL, 0.1 mmol) in benzene (1 mL) and the resulting mixture was stirred for 2 h at room temperature. The solvent was removed *in vacuo* and the crude residue was purified by silica gel chromatography to obtain 58 mg(50%) of the product; IR 2934, 1800, 1756, 1662, 1323, 1264, 1117, 698 cm^{-1}; ^{1}H NMR(300 MHz, $CDCl_3$) δ 1.11 (s, 3H), 1.56 (s, 3H), 3.32 (dd, 1H, J_1= 6.6 Hz, J_2= 16.5 Hz), 3.78 (dd, 1H, J_1= 10.8 Hz, J_2= 16.8 Hz), 4.36 (m, 1H), 4.58 (s, 1H), 4.80 (d, 1H, J= 5.1 Hz), 6.99 (s, 2H), 7.34 (m, 10H), 7.50 (m, 2H), 7.62 (m, 1H), 8.10 (m, 2H); HRMS Calcd. for $C_{32}H_{28}N_2O_7S$: 585.1696, Found; 585.1710.

[2S, 5R, 6R]-3,3-Dimethyl-4,4,7-trioxo-6-(5-acetyl-isoxazol-3-ylmethyl)-4-.lambda (6).-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid diphenylmethyl (30); To a solution of hydroximic acid chloride **10** (100 mg, 0.2 mmol) in benzene (1 mL) was added a solution containing 3-butyne-2-one (52 mg, 0.4 mmol) and bis(tributyltin) oxide (0.051 mL, 0.1 mmol) in benzene (1 mL) and the resulting mixture was stirred for 2 h at room temperature. The solvent was removed *in vacuo* and the crude residue was purified by silica gel chromatography to obtain 52 mg(50%) of the product: IR 2926, 1800, 1757,

1702, 1323, 1183, 1117, 701 cm^{-1}; ^{1}H NMR(300 MHz, $CDCl_3$) δ 1.10 (s, 3H), 1.55 (s, 3H), 2.58 (s, 3H), 3.27 (dd, 1H, J_1= 6.6 Hz, J_2= 16.5 Hz), 3.73 (dd, 1H, J_1= 10.5 Hz, J_2= 16.8 Hz), 4.33 (m, 1H), 4.57 (s, 1H), 4.78 (d, 1H, J= 4.8 Hz), 6.86 (s, 1H), 6.99 (s, 1H), 7.36 (m, 10H); ^{13}C NMR(75 MHz, $CDCl_3$) δ 17.8, 19.6, 20.2, 27.2, 50.1, 62.8, 64.4, 64.6, 79.1, 107.1, 126.8, 127.7, 128.4, 128.7, 128.8, 128.8, 138.5, 138.8, 161.2, 166.1, 167.0, 173.1, 186.7; MS (ES)(M+H) 523.0.

[2S, 5R, 6R]-3-(2-Benzhydroxycarbonyl-3,3-dimethyl-4,4,7-trioxo-4-.lambda (6).-thia-1-azabicyclo[3.2.0]hept-6-ylmethyl)-isoxazole-4,5-dicarboxylic acid dimethyl ester (31); To a solution of hydroximic acid chloride **10** (100 mg, 0.2 mmol) in benzene (1 mL) was added a solution containing DMAD (57 mg, 0.4 mmol) and bis(tributyltin) oxide (0.051 mL, 0.1 mmol) in benzene (1 mL) and the resulting mixture was stirred for 2 h at room temperature. The solvent was removed *in vacuo* and the crude residue was purified by silica gel chromatography to obtain 50 mg(42%) of the product; IR 2955, 1800, 1750, 1324, 1181, 1116, 701 cm^{-1}; ^{1}H NMR(300 MHz, $CDCl_3$) δ 1.01 (s, 3H), 1.53 (s, 3H), 3.42 (dd, 1H, J_1= 6.0 Hz, J_2= 18.0 Hz), 3.89 (s, 3H), 3.99 (s, 3H), 4.38 (m, 1H), 4.55 (s, 1H), 4.81 (d, 1H, J= 4.8 Hz), 6.99 (s, 1H), 7.35 (m, 10H); HRMS Calcd. for $C_{28}H_{32}N_2O_6SSi$: 619.1362, Found; 619.1375.