Supporting Information-I

Stereoselective Synthesis of Cyclopentanone-fused Benzosultams through Tomita Zipper Cyclization

Dhevalapally B. Ramachary,* Patoju M. Krishna, and T. Prabhakar Reddy

Catalysis Laboratory, School of Chemistry, University of Hyderabad, Central University (P.O.), Hyderabad 500 046, India

E-mail: ***ramsc@uohyd.ac.in*** or ***ramchary.db@gmail.com***

General Methods: The ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively. The chemical shifts are reported in ppm downfield to TMS ($\delta = 0$) for ^{1}H NMR and relative to the central $CDCl_3$ resonance ($\delta = 77.0$) for ^{13}C NMR. *In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 or CH_3) was determined by recording the DEPT-135 experiment, and is given in parentheses.* The coupling constants *J* are given in Hz. Column chromatography was performed using Acme's silica gel (particle size 0.063-0.200 mm). High-resolution mass spectra (HRMS) were recorded on ESI-TOF maXis. GCMS mass spectrometry was performed on Shimadzu GCMS-QP2010 mass spectrometer. IR spectra were recorded on JASCO FT/IR-5300. Elemental analyses were recorded on a Thermo Finnigan Flash EA 1112 analyzer. Mass spectra were recorded on either VG7070H mass spectrometer using EI technique or Shimadzu-LCMS-2010 A mass spectrometer. The X-ray diffraction measurements were carried out at 298 K on an automated Enraf-Nonious MACH 3 diffractometer using graphite monochromated, Mo-Kα ($\lambda = 0.71073$ Å) radiation with CAD4 software or the X-ray intensity data were measured at 298 K on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo-Kα fine-focus sealed tube ($\lambda = 0.71073$ Å). For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were

visualized by irradiation with UV light and/or by treatment with a solution of *p*-anisaldehyde (23 mL), conc. H_2SO_4 (35 mL), acetic acid (10 mL), and ethanol (900 mL) followed by heating.

Materials: All solvents and commercially available chemicals were used as received. Ynones **1a-g** and olefins **2a-d** were prepared according to the literature procedure.[1]

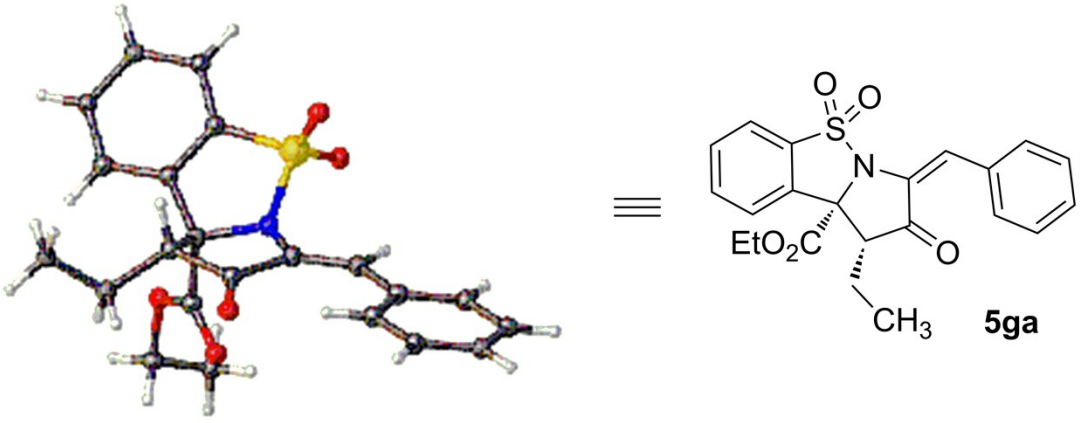

Figure S1: X-Ray crystal structure of (1*R**,9b*S**,*E*)-ethyl 3-benzylidene-1-ethyl-2-oxo-1,2,3,9b-tetrahydrobenzo[*d*]pyrrolo[1,2-*b*]isothiazole-9b-carboxylate 5,5-dioxide (**5ga**).

General Experimental Procedures

Procedure A: **General Procedure for Phosphine-Catalyzed TZC [3+2]-Cycloaddition of Ynones with Cyclic *N*-Sulfonyl α-Iminoesters:** In an ordinary glass vial equipped with a magnetic stirring bar was taken a mixture phosphine catalyst **3a** (20 mol-%) and acetic acid **4e** (20 mol-%) in dichloroethane. Then 0.6 mmol of ynone **1**, 0.3 mmol of cyclic *N*-sulfonyl α-iminoesters **2** were added sequentially to the reaction mixture was stirred at ambient temperature for 3-9 h. The reaction mixture was concentrated and pure products **5** and **6** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

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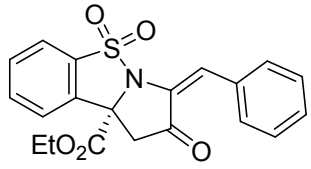
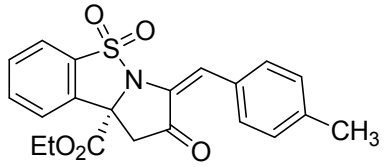
(*S*,E*)-Ethyl 3-benzylidene-2-oxo-1,2,3,9b-tetrahydrobenzo[d]pyrrolo[1,2-b]isothiazole-9b-carboxylate 5,5-dioxide (5aa): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as off white solid.



5aa

Mp 102 °C; *dr* = 2.2:1; IR (KBr): ν_{max} 2919, 1742, 1636, 1606, 1444, 1323, 1181, 1126, 1070, 858, 757, 691, 611 and 580 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, major isomer) δ 7.98 (1H, d, *J* = 7.2 Hz), 7.90 (1H, d, *J* = 7.6 Hz), 7.87-7.85 (1H, m), 7.74 (1H, d, *J* = 7.6 Hz), 7.69 (1H, d, *J* = 7.2 Hz), 7.62 (1H, d, *J* = 7.6 Hz), 7.38-7.37 (3H, m), 7.00 (1H, s), 4.25 (2H, q, *J* = 6.8 Hz), 3.57 (1H, d, *J* = 18.0 Hz), 2.89 (1H, d, *J* = 18.0 Hz), 1.24 (3H, t, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135, major isomer) δ 194.6 (C, *C*=O), 168.9 (C, *O-C=O*), 135.7 (C), 134.3 (CH), 133.9 (C), 132.4 (C), 131.0 (2 x CH), 130.6 (CH), 130.1 (CH), 129.3 (C), 128.6 (CH), 128.2 (2 x CH), 125.0 (CH), 122.3 (CH), 69.6 (C), 63.5 (CH_2), 47.2 (CH_2), 13.9 (CH_3); ^1H NMR ($CDCl_3$, 400 MHz, minor isomer) δ 7.87-7.85 (3H, m), 7.78-7.76 (2H, m), 7.65 (1H, d, *J* = 7.2 Hz), 7.43-7.40 (3H, m), 7.22 (1H, s), 4.32-4.23 (2H, m), 3.57 (1H, d, *J* = 18.0 Hz), 2.79 (1H, d, *J* = 18.4 Hz), 1.28 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135, minor isomer) δ 196.6 (C, *C*=O), 169.0 (C, *O-C=O*), 135.6 (C), 134.3 (CH), 133.9 (C), 132.4 (C), 131.0 (2 x CH), 130.5 (CH), 130.1 (CH), 129.1 (C), 128.65 (2 x CH), 128.56 (CH), 124.8 (CH), 122.0 (CH), 70.8 (C), 63.5 (CH_2), 45.3 (CH_2), 13.9 (CH_3); HRMS m/z 406.0727 ($M + Na^+$), calcd for $C_{20}H_{17}NO_5SNa$ 406.0725.

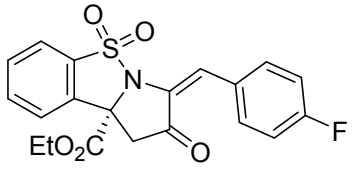
(*S*,E*)-Ethyl 3-(4-methylbenzylidene)-2-oxo-1,2,3,9b-tetrahydrobenzo[d]pyrrolo[1,2-b]isothiazole-9b-carboxylate 5,5-dioxide (5ba): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as semi off white solid; *dr* = 3.6:1; IR (KBr): ν_{max} 2919, 1737, 1631, 1611, 1505, 1449, 1323, 1181, 1060, 904, 813, 757, 590 and 570 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, major isomer) δ 7.90-7.88 (1H, m), 7.79 (2H, d, *J* = 8.4 Hz), 7.75-7.71 (1H, m), 7.67 (1H, d, *J* = 7.2 Hz), 7.61 (1H, d, *J* = 8.0 Hz), 7.18 (2H, d, *J* = 8.0 Hz), 6.95 (1H, s), 4.24 (2H, q, *J* = 7.2 Hz), 3.55 (1H, d, *J* = 18.0 Hz), 2.87 (1H, d, *J* = 18.0 Hz), 2.37 (3H, s), 1.23 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135, major isomer) δ 194.4 (C, *C*=O), 168.8 (C, *O-C=O*), 140.6 (C), 135.6 (C), 134.1 (CH), 133.8 (C), 131.0 (2 x CH), 130.9 (CH), 129.7 (C), 129.1 (CH), 128.9 (2 x CH), 128.5 (C), 124.9 (CH), 122.2 (CH), 69.5 (C), 63.3 (CH_2),



5ba

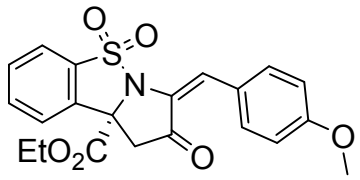
47.2 (CH_2), 21.5 (CH_3), 13.8 (CH_3); HRMS m/z 420.0882 ($M + Na^+$), calcd for $C_{21}H_{19}NO_5SNa$ 420.0882.

(*S,*E*)-Ethyl 3-(4-fluorobenzylidene)-2-oxo-1,2,3,9b-tetrahydrobenzo[d]pyrrolo[1,2-b]isothiazole-9b-carboxylate 5,5-dioxide (5ca):** Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as off white solid. Mp 106 °C; *dr* = 3.4:1; IR (KBr): ν_{max} 1732, 1641, 1601, 1505, 1323, 1237, 1186, 1065, 833, 752, 595 and 570 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, major isomer) δ 7.91-7.87 (3H, m), 7.77-7.73 (1H, m), 7.69 (1H, d, *J* = 7.2 Hz), 7.62 (1H, d, *J* = 7.6 Hz), 7.05 (2H, t, *J* = 8.8 Hz), 6.92 (1H, s), 4.25 (2H, q, *J* = 7.2 Hz), 3.57 (1H, d, *J* = 18.0 Hz), 2.89 (1H, d, *J* = 18.0 Hz), 1.23 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135, major isomer) δ 194.6 (C, *C*=O), 168.8 (C, *O-C=O*), 163.5 (C, d, *J* = 251.0 Hz), 135.6 (C), 134.2 (CH), 133.8 (C), 133.2 (2 x CH, d, *J* = 8.0 Hz), 130.0 (CH), 128.8 (C, d, *J* = 33.0 Hz), 127.4 (CH), 124.9 (CH + C), 122.3 (CH), 115.3 (2 x CH, d, *J* = 22.0 Hz), 69.6 (C), 63.5 (CH_2), 47.2 (CH_2), 13.8 (CH_3); HRMS m/z 424.0633 ($M + Na^+$), calcd for $C_{20}H_{16}FNO_5SNa$ 424.0631.



5ca

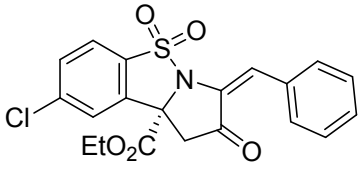
(*S,*E*)-Ethyl 3-(4-methoxybenzylidene)-2-oxo-1,2,3,9b-tetrahydrobenzo[d]pyrrolo[1,2-b]isothiazole-9b-carboxylate 5,5-dioxide (5da):** Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as semi solid; *dr* = 1.7:1; IR (Neat): ν_{max} 2974, 2944, 1737, 1636, 1601, 1510, 1338, 1257, 1166, 1025, 858,757 and 626 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, major isomer) δ 7.95 (2H, d, *J* = 8.8 Hz), 7.90 (1H, d, *J* = 7.6 Hz), 7.74-7.72 (1H, m), 7.69-7.67 (1H, m), 7.61 (1H, d, *J* = 7.6 Hz), 6.94 (1H, s), 6.90 (2H, d, *J* = 8.8 Hz), 4.24 (2H, q, *J* = 7.2 Hz), 3.84 (3H, s), 3.56 (1H, d, *J* = 17.6 Hz), 2.88 (1H, d, *J* = 18.0 Hz), 1.23 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135, major isomer) δ 194.5 (C, *C*=O), 168.9 (C, *O-C=O*), 161.3 (C), 135.7 (C), 134.1 (CH), 133.8 (C), 133.3 (2 x CH), 130.9 (CH), 129.9 (CH), 127.5 (C), 125.4 (C), 124.8 (CH), 122.3 (CH), 113.7 (2 x CH), 69.8 (C), 63.4 (CH_2), 55.3 (CH_3), 47.3 (CH_2), 13.8 (CH_3); ^1H NMR ($CDCl_3$, 400 MHz, minor isomer) δ 8.00 (2H, d, *J* = 9.2 Hz), 7.79 (1H, d, *J* = 8.0 Hz), 7.76-7.72 (1H, m), 7.69-7.65 (2H, m), 7.23 (1H, s), 6.94 (2H, d, *J* = 8.8 Hz), 4.30-4.22 (2H, m), 3.84 (3H, s), 3.53 (1H, d, *J* = 18.0 Hz), 2.76 (1H, d, *J* = 18.4 Hz), 1.25 (3H, t, *J* = 8.0 Hz); ^{13}C



5da

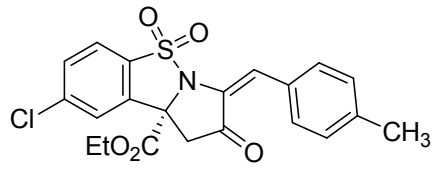
NMR ($CDCl_3$, DEPT-135, minor isomer) δ 196.5 (C, *C*=O), 169.0 (C, *O*-*C*=*O*), 161.5 (C), 135.6 (C), 134.2 (CH), 133.8 (C), 132.8 (2 x CH), 130.9 (CH), 127.2 (C), 126.0 (CH), 124.8 (CH), 124.6 (C), 122.0 (CH), 114.1 (2 x CH), 71.0 (C), 63.4 (CH_2), 55.3 (CH_3), 45.3 (CH_2), 13.8 (CH_3); HRMS m/z 436.0835 ($M + Na^+$), calcd for $C_{21}H_{19}NO_6SNa$ 436.0831.

(*S*,E*)-Ethyl 3-benzylidene-8-chloro-2-oxo-1,2,3,9b-tetrahydrobenzo[d]pyrrolo[1,2-b]isothiazole-9b-carboxylate 5,5-dioxide (5ab): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as semi solid; *dr* = 1.5:1; IR (Neat): ν_{max} 3085, 2924, 2843, 1732, 1621, 1449, 1328, 1267, 1181, 1090, 823, 757 and 701 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, major isomer) δ 7.96-7.94 (1H, m), 7.86-7.82 (2H, m), 7.71-7.59 (2H, m), 7.44-7.37 (3H, m), 6.96 (1H, s), 4.36-4.23 (2H, m), 3.52 (1H, d, *J* = 18.0 Hz), 2.89 (1H, d, *J* = 18.0 Hz), 1.26 (3H, t, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135, major isomer) δ 193.8 (C, *C*=O), 168.3 (C, *O*-*C*=*O*), 140.7 (C), 137.4 (C), 132.3 (C), 132.2 (C), 131.5 (CH), 130.9 (2 x CH), 130.4 (CH), 129.0 (C), 128.8 (CH), 128.2 (2 x CH), 125.3 (CH), 123.5 (CH), 69.0 (C), 63.7 (CH_2), 47.0 (CH_2), 13.8 (CH_3); ^1H NMR ($CDCl_3$, 400 MHz, minor isomer) δ 7.86-7.82 (2H, m), 7.71-7.59 (3H, m), 7.44-7.37 (3H, m), 7.22 (1H, s), 4.36-4.23 (2H, m), 3.52 (1H, d, *J* = 18.0 Hz), 2.79 (1H, d, *J* = 18.4 Hz), 1.29 (3H, t, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135, minor isomer) δ 195.8 (C, *C*=O), 168.5 (C, *O*-*C*=*O*), 140.8 (C), 137.3 (C), 132.3 (C), 132.2 (C), 131.5 (CH), 130.5 (CH), 130.1 (2 x CH), 128.8 (C), 128.6 (2 x CH), 125.2 (CH), 125.0 (CH), 123.2 (CH), 70.2 (C), 63.7 (CH_2), 45.1 (CH_2), 13.8 (CH_3); LRMS m/z 417.30 (M^+), calcd for $C_{20}H_{16}ClNO_5S$ 417.04; Anal. calcd for $C_{20}H_{16}ClNO_5S$ (417.04): C, 57.49; H, 3.86; N, 3.35. Found: C, 57.36; H, 3.92; N, 3.41%.



5ab

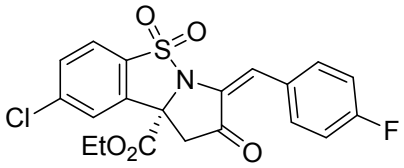
(*S*,E*)-Ethyl 8-chloro-3-(4-methylbenzylidene)-2-oxo-1,2,3,9b-tetrahydrobenzo[d]pyrrolo[1,2-b]isothiazole-9b-carboxylate 5,5-dioxide (5bb): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as off white solid. Mp 98 °C; *dr* = 1.3:1; IR (Neat): ν_{max} 2914, 1737, 1636, 1601, 1338, 1262, 1181, 1141, 1085, 1035 and 813 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, major isomer) δ 7.83 (1H, d, *J* = 8.4 Hz), 7.80 (2H, d, *J* = 8.0 Hz), 7.72-7.60 (2H, m), 7.19 (2H, d, *J* = 8.0 Hz), 6.95



5bb

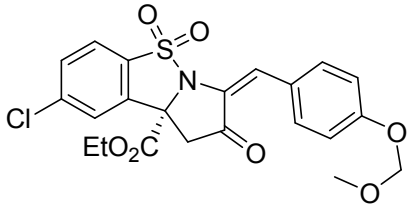
(1H, s), 4.34-4.21 (2H, m), 3.51 (1H, d, *J* = 18.0 Hz), 2.89 (1H, d, *J* = 17.6 Hz), 2.38 (3H, s), 1.26 (3H, t, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135, major isomer) δ 193.8 (C, *C*=O), 168.4 (C, *O*-*C*=*O*), 140.9 (C), 140.7 (C), 137.5 (C), 132.4 (C), 131.5 (CH), 131.1 (2 x CH), 129.61 (CH), 129.57 (C), 129.0 (2 x CH), 128.3 (C), 125.3 (CH), 123.5 (CH), 69.2 (C), 63.7 (CH_2), 47.1 (CH_2), 21.6 (CH_3), 13.8 (CH_3); ^{1}H NMR ($CDCl_3$, 400 MHz, minor isomer) δ 7.87 (2H, d, *J* = 8.4 Hz), 7.72-7.60 (3H, m), 7.23 (2H, d, *J* = 7.2 Hz), 7.22 (1H, s), 4.34-4.21 (2H, m), 3.51 (1H, d, *J* = 18.4 Hz), 2.78 (1H, d, *J* = 18.4 Hz), 2.38 (3H, s), 1.29 (3H, t, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135, minor isomer) δ 195.9 (C, *C*=O), 168.6 (C, *O*-*C*=*O*), 141.3 (C), 140.8 (C), 137.4 (C), 132.4 (C), 131.5 (CH), 130.6 (2 x CH), 129.4 (2 x CH), 129.2 (C), 128.1 (C), 125.7 (CH), 125.2 (CH), 123.2 (CH), 70.3 (C), 63.7 (CH_2), 45.2 (CH_2), 21.7 (CH_3), 13.8 (CH_3); HRMS m/z 432.0673 (M + H^+), calcd for $C_{21}H_{18}ClNO_5SH$ 432.0672.

(*S,*E*)-Ethyl 8-chloro-3-(4-fluorobenzylidene)-2-oxo-1,2,3,9b-tetrahydrobenzo[d]pyrrolo[1,2-b]isothiazole-9b-carboxylate 5,5-dioxide (5cb):** Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as semi solid; *dr* = 1.5:1; IR (KBr): ν_{max} 3096, 2944, 1732, 1595, 1510, 1318, 1282, 1237, 1090, 1065, 853, 833, 757 and 727 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, major isomer) δ 7.91-7.88 (2H, m), 7.83 (1H, d, *J* = 8.0 Hz), 7.67-7.62 (2H, m), 7.08-7.04 (2H, m), 6.91 (1H, s), 4.38-4.22 (2H, m), 3.53 (1H, d, *J* = 17.6 Hz), 2.90 (1H, d, *J* = 17.6 Hz), 1.31-1.24 (3H, m); ^{13}C NMR ($CDCl_3$, DEPT-135, major isomer) δ 194.0 (C, *C*=O), 168.3 (C, *O*-*C*=*O*), 163.6 (C, d, *J* = 251.0 Hz), 140.8 (C), 137.4 (C), 133.27 (2 x CH, d, *J* = 9.0 Hz), 132.3 (C), 131.6 (CH), 128.7 (C), 128.5 (C, d, *J* = 3.0 Hz), 127.8 (CH), 125.3 (CH), 123.5 (CH), 115.3 (2 x CH, d, *J* = 22.0 Hz), 69.1 (C), 63.8 (CH_2), 47.0 (CH_2), 13.9 (CH_3); ^{1}H NMR ($CDCl_3$, 400 MHz, minor isomer) δ 7.98-7.95 (2H, m), 7.73-7.70 (3H, m), 7.18 (1H, s), 7.13-7.08 (2H, m), 4.38-4.22 (2H, m), 3.51 (1H, d, *J* = 18.4 Hz), 2.79 (1H, d, *J* = 18.4 Hz), 1.31-1.24 (3H, m); ^{13}C NMR ($CDCl_3$, DEPT-135, minor isomer) δ 195.7 (C, *C*=O), 168.4 (C, *O*-*C*=*O*), 163.7 (C, d, *J* = 251.0 Hz), 140.9 (C), 137.3 (C), 132.7 (2 x CH, d, *J* = 9.0 Hz), 132.2 (C), 131.6 (CH), 128.8 (C), 128.3 (C, d, *J* = 3.0 Hz), 125.3 (CH), 124.0 (CH), 123.3 (CH), 115.9 (2 x CH, d, *J* = 21.0 Hz), 70.3 (C), 63.8 (CH_2), 45.2 (CH_2), 13.9 (CH_3); HRMS m/z 436.0422 (M + H^+), calcd for $C_{20}H_{15}ClFNO_5SH$ 436.0422.



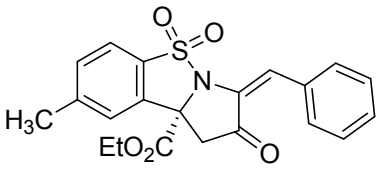
5cb

(*S*,E*)-Ethyl 8-chloro-3-(4-(methoxymethoxy)benzylidene)-2-oxo-1,2,3,9b-tetrahydrobenzo[d]pyrrolo[1,2-b]isothiazole-9b-carboxylate 5,5-dioxide (5eb): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as semi solid; *dr* = 1.6:1; IR (Neat): ν_{max} 2934, 1727, 1631, 1606, 1510, 1333, 1242, 1176, 1146, 1080, 989, 853, 828 and 752 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, major isomer) δ 7.91 (2H, d, *J* = 8.8 Hz), 7.82 (1H, d, *J* = 8.4 Hz), 7.64-7.59 (2H, m), 7.03 (2H, d, *J* = 8.8 Hz), 6.91 (1H, s), 5.23-5.18 (2H, m), 4.31-4.22 (2H, m), 3.52-3.46 (1H, m), 3.46 (3H, s), 2.89 (1H, d, *J* = 18.0 Hz), 1.24 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135, major isomer) δ 193.8 (C, *C*=O), 168.4 (C, *O*-*C*=*O*), 158.9 (C), 140.6 (C), 137.4 (C), 133.2 (2 x CH), 132.4 (C), 131.4 (CH), 129.6 (CH), 127.2 (C), 126.2 (C), 125.2 (CH), 123.5 (CH), 115.7 (2 x CH), 94.0 (CH_2), 69.2 (C), 63.6 (CH_2), 56.1 (CH_3), 47.1 (CH_2), 13.8 (CH_3); ^1H NMR ($CDCl_3$, 400 MHz, minor isomer) δ 7.95 (2H, d, *J* = 8.8 Hz), 7.72-7.68 (2H, m), 7.64-7.59 (1H, m), 7.21 (1H, s), 7.06 (2H, d, *J* = 8.8 Hz), 5.23-5.18 (2H, m), 4.31-4.22 (2H, m), 3.52-3.46 (4H, m), 2.76 (1H, d, *J* = 18.4 Hz), 1.26 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135, minor isomer) δ 195.8 (C, *C*=O), 168.5 (C, *O*-*C*=*O*), 159.2 (C), 140.7 (C), 137.5 (C), 132.6 (2 x CH), 132.2 (C), 131.5 (CH), 127.6 (C), 125.8 (CH), 125.5 (C), 125.2 (CH), 123.2 (CH), 116.1 (2 x CH), 94.1 (CH_2), 70.4 (C), 63.6 (CH_2), 56.1 (CH_3), 45.1 (CH_2), 13.8 (CH_3); LRMS m/z 498.75 (M^+), calcd for $C_{22}H_{20}ClNO_7S$ 498.06; Anal. calcd for $C_{22}H_{20}ClNO_7S$ (498.06): C, 55.29; H, 4.22; N, 2.93. Found: C, 55.37; H, 4.28; N, 2.86%.



5eb

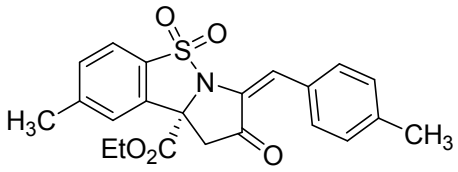
(*S*,E*)-Ethyl 3-benzylidene-8-methyl-2-oxo-1,2,3,9b-tetrahydrobenzo[d]pyrrolo[1,2-b]isothiazole-9b-carboxylate 5,5-dioxide (5ac): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as off white solid. Mp 118 °C; *dr* = 2.9:1; IR (KBr): ν_{max} 2924, 1732, 1636, 1595, 1459, 1318, 1161, 808, 757 and 696 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, major isomer) δ 7.86-7.84 (2H, m), 7.77 (1H, d, *J* = 8.0 Hz), 7.48-7.36 (5H, m), 6.96 (1H, s), 4.30-4.23 (2H, m), 3.55 (1H, d, *J* = 17.6 Hz), 2.87 (1H, d, *J* = 18.0 Hz), 2.50 (3H, s), 1.24 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135, major isomer) δ 194.6 (C, *C*=O), 169.0 (C, *O*-



5ac

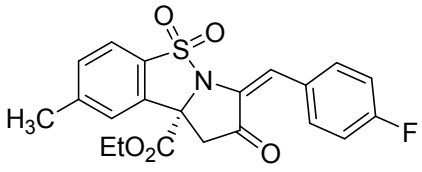
C=*O*), 145.5 (C), 135.9 (C), 132.4 (C), 131.9 (CH), 131.1 (C), 130.9 (2 x CH), 129.9 (CH), 129.3 (C), 128.3 (CH), 128.1 (2 x CH), 125.0 (CH), 121.9 (CH), 69.4 (C), 63.4 (CH_2), 47.2 (CH_2), 21.8 (CH_3), 13.8 (CH_3); ^{1}H NMR ($CDCl_3$, 400 MHz, minor isomer) δ 7.98 (2H, d, *J* = 7.2 Hz), 7.64 (1H, d, *J* = 8.0 Hz), 7.48-7.36 (5H, m), 7.21 (1H, s), 4.33-4.23 (2H, m), 3.55 (1H, d, *J* = 17.6 Hz), 2.76 (1H, d, *J* = 18.8 Hz), 2.50 (3H, s), 1.29-1.22 (3H, m); ^{13}C NMR ($CDCl_3$, DEPT-135, minor isomer) δ 196.7 (C, *C*=O), 169.1 (C, *O*-*C*=*O*), 145.5 (C), 135.8 (C), 132.3 (C), 131.9 (CH), 131.1 (C), 130.5 (2 x CH), 130.3 (CH), 129.1 (C), 128.5 (2 x CH), 124.9 (CH), 124.6 (CH), 121.7 (CH), 70.6 (C), 63.4 (CH_2), 45.3 (CH_2), 21.8 (CH_3), 13.8 (CH_3); HRMS m/z 420.0884 (M + Na^+), calcd for $C_{21}H_{19}NO_5SNa$ 420.0882.

(*S,*E*)-Ethyl 8-methyl-3-(4-methylbenzylidene)-2-oxo-1,2,3,9b-tetrahydrobenzo[d]pyrrolo[1,2-b]isothiazole-9b-carboxylate 5,5-dioxide (5bc):** Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as brown solid. Mp 132 °C; *dr* = 2.3:1; IR (KBr): ν_{max} 1736, 1632, 1600, 1353, 1323, 1161, 860, 810, 684, 602 and 553 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, major isomer) δ 7.80-7.76 (3H, m), 7.48-7.45 (1H, m), 7.39 (1H, s), 7.19 (2H, d, *J* = 8.0 Hz), 6.94 (1H, s), 4.26-4.22 (2H, m), 3.55 (1H, d, *J* = 17.6 Hz), 2.86 (1H, d, *J* = 17.6 Hz), 2.50 (3H, s), 2.37 (3H, s), 1.24 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135, major isomer) δ 194.6 (C, *C*=O), 169.1 (C, *O*-*C*=*O*), 145.5 (C), 140.6 (C), 136.0 (C), 131.9 (CH), 131.2 (C), 131.1 (2 x CH), 129.1 (CH), 128.9 (2 x CH), 128.7 (C), 125.3 (C), 124.9 (CH), 122.0 (CH), 69.5 (C), 63.4 (CH_2), 47.3 (CH_2), 21.9 (CH_3), 21.6 (CH_3), 13.8 (CH_3); ^{1}H NMR ($CDCl_3$, 400 MHz, minor isomer) δ 7.90 (2H, d, *J* = 8.0 Hz), 7.65 (1H, d, *J* = 8.0 Hz), 7.48-7.45 (2H, m), 7.24-7.21 (3H, m), 4.26-4.22 (2H, m), 3.54 (1H, d, *J* = 18.4 Hz), 2.75 (1H, d, *J* = 18.0 Hz), 2.50 (3H, s), 2.37 (3H, s), 1.27 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135, minor isomer) δ 196.7 (C, *C*=O), 169.2 (C, *O*-*C*=*O*), 145.6 (C), 141.0 (C), 135.9 (C), 131.9 (CH), 130.7 (2 x CH), 129.7 (CH), 129.44 (C), 129.37 (2 x CH), 128.4 (C), 124.9 (C), 124.8 (CH), 121.7 (CH), 70.7 (C), 63.4 (CH_2), 45.3 (CH_2), 21.9 (CH_3), 21.7 (CH_3), 13.8 (CH_3); HRMS m/z 412.1218 (M + H^+), calcd for $C_{22}H_{21}NO_5SH$ 412.1219.



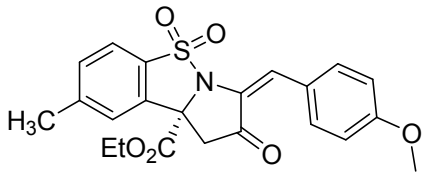
5bc

(*S*,E*)-Ethyl 3-(4-fluorobenzylidene)-8-methyl-2-oxo-1,2,3,9b-tetrahydrobenzo[d]pyrrolo[1,2-b]isothiazole-9b-carboxylate 5,5-dioxide (5cc): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as off white solid. Mp 110 °C; *dr* = 3.6:1; IR (KBr): ν_{max} 2919, 2848, 1732, 1641, 1595, 1515, 1292, 1227, 1161, 1065, 833, 752 and 676 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, major isomer) δ 7.91-7.87 (2H, m), 7.77 (1H, d, *J* = 8.0 Hz), 7.49-7.44 (1H, m), 7.39 (1H, s), 7.12-7.03 (2H, m), 6.90 (1H, s), 4.27-4.21 (2H, m), 3.56 (1H, d, *J* = 17.6 Hz), 2.87 (1H, d, *J* = 17.6 Hz), 2.51 (3H, s), 1.29-1.22 (3H, m); ^{13}C NMR ($CDCl_3$, DEPT-135, major isomer) δ 194.8 (C, *C*=O), 169.0 (C, *O-C=O*), 163.5 (C, d, *J* = 251.0 Hz), 145.6 (C), 135.9 (C), 133.2 (2 x CH, d, *J* = 8.0 Hz), 132.0 (CH), 131.1 (C), 129.1 (C), 128.7 (C), 127.3 (CH), 125.0 (CH), 122.0 (CH), 115.2 (2 x CH, d, *J* = 21.0 Hz), 69.4 (C), 63.4 (CH_2), 47.2 (CH_2), 21.9 (CH_3), 13.8 (CH_3); HRMS m/z 416.0968 ($M + H^+$), calcd for $C_{21}H_{18}FNO_5SH$ 416.0968.



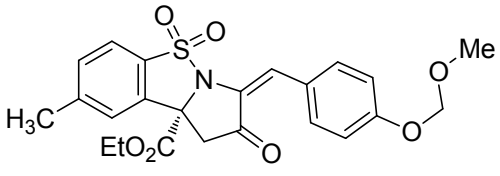
5cc

(*S*,E*)-Ethyl 3-(4-methoxybenzylidene)-8-methyl-2-oxo-1,2,3,9b-tetrahydrobenzo[d]pyrrolo[1,2-b]isothiazole-9b-carboxylate 5,5-dioxide (5dc): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as semi solid; *dr* = 6.7:1; IR (KBr): ν_{max} 2974, 2924, 2858, 2353, 1732, 1626, 1601, 1570, 1318, 1262, 1171, 1025, 883, 833, 686 and 575 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, major isomer) δ 8.00 (2H, d, *J* = 8.8 Hz), 7.66 (1H, d, *J* = 8.8 Hz), 7.45 (2H, s), 7.22 (1H, s), 6.93 (2H, d, *J* = 8.8 Hz), 4.33-4.20 (2H, m), 3.84 (3H, s), 3.51 (1H, d, *J* = 18.4 Hz), 2.74 (1H, d, *J* = 18.4 Hz), 2.51 (3H, s), 1.25 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135, major isomer) δ 196.7 (C, *C*=O), 169.2 (C, *O-C=O*), 161.5 (C), 145.6 (C), 135.9 (C), 132.8 (2 x CH), 131.9 (CH), 131.2 (C), 127.3 (C), 125.9 (CH), 124.8 (CH), 124.7 (C), 121.8 (CH), 114.1 (2 x CH), 70.9 (C), 63.3 (CH_2), 55.3 (CH_3), 45.3 (CH_2), 21.9 (CH_3), 13.9 (CH_3); HRMS m/z 428.1165 ($M + H^+$), calcd for $C_{22}H_{21}NO_6SH$ 428.1168.



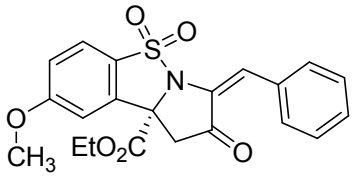
5dc

(*S,*E*)-Ethyl 3-(4-(methoxymethoxy)benzylidene)-8-methyl-2-oxo-1,2,3,9b-tetrahydrobenzo[d]pyrrolo[1,2-b]isothiazole-9b-carboxylate 5,5-dioxide (5ec):** Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as semi solid; *dr* = 1.7:1; IR (Neat): ν_{max} 2954, 2919, 1737, 1631, 1601, 1510, 1328, 1242, 1166, 1080, 989, 929, 858, 737 and 681 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, major isomer) δ 7.92 (2H, d, *J* = 8.8 Hz), 7.76 (1H, d, *J* = 8.0 Hz), 7.45-7.43 (1H, m), 7.38 (1H, s), 7.02 (2H, d, *J* = 8.8 Hz), 6.91 (1H, s), 5.21 (2H, s), 4.30-4.21 (2H, m), 3.54 (1H, d, *J* = 18.0 Hz), 3.47 (3H, s), 2.86 (1H, d, *J* = 18.0 Hz), 2.50 (3H, s), 1.23 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135, major isomer) δ 194.7 (C, *C*=O), 169.1 (C, *O*-*C*=*O*), 158.8 (C), 145.5 (C), 136.0 (C), 133.1 (2 x CH), 131.9 (CH), 131.2 (C), 129.2 (CH), 128.0 (C), 126.4 (C), 124.9 (CH), 122.0 (CH), 115.7 (2 x CH), 94.1 (CH_2), 69.6 (C), 63.3 (CH_2), 56.1 (CH_3), 47.3 (CH_2), 21.9 (CH_3), 13.8 (CH_3); ^1H NMR ($CDCl_3$, 400 MHz, minor isomer) δ 7.98 (2H, d, *J* = 8.4 Hz), 7.66 (1H, d, *J* = 8.8 Hz), 7.48-7.43 (2H, m), 7.21 (1H, s), 7.06 (2H, d, *J* = 8.8 Hz), 5.23-5.18 (2H, m), 4.30-4.21 (2H, m), 3.52 (1H, d, *J* = 18.0 Hz), 3.47 (3H, s), 2.74 (1H, d, *J* = 18.4 Hz), 2.50 (3H, s) 1.25 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135, minor isomer) δ 196.7 (C, *C*=O), 169.2 (C, *O*-*C*=*O*), 159.1 (C), 145.6 (C), 135.9 (C), 132.7 (2 x CH), 131.9 (CH), 131.1 (C), 127.6 (C), 125.7 (C), 125.5 (CH), 124.8 (CH), 121.8 (CH), 116.1 (2 x CH), 94.1 (CH_2), 70.8 (C), 63.3 (CH_2), 56.1 (CH_3), 45.3 (CH_2), 21.9 (CH_3), 13.8 (CH_3); HRMS m/z 480.1093 ($M + Na^+$), calcd for $C_{23}H_{23}NO_7SNa$ 480.1093.



5ec

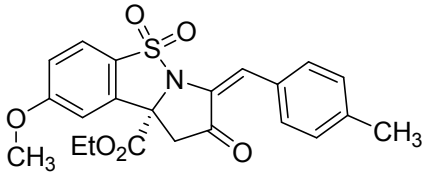
(*S,*E*)-Ethyl 3-benzylidene-8-methoxy-2-oxo-1,2,3,9b-tetrahydrobenzo[d]pyrrolo[1,2-b]isothiazole-9b-carboxylate 5,5-dioxide (5ad):** Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as semi solid; *dr* = 3.2:1; IR (Neat): ν_{max} 2919, 2858, 1732, 1590, 1479, 1464, 1323, 1292, 1247, 1176, 1070, 752 and 691 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, major isomer) δ 7.87-7.85 (2H, m), 7.79 (1H, d, *J* = 8.4 Hz), 7.41-7.36 (3H, m), 7.17-7.08 (1H, m), 7.01 (1H, s), 6.95 (1H, s), 4.29-4.22 (2H, m), 3.91 (3H, s), 3.55 (1H, d, *J* = 17.6 Hz), 2.89 (1H, d, *J* = 17.6 Hz), 1.25 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$,



5ad

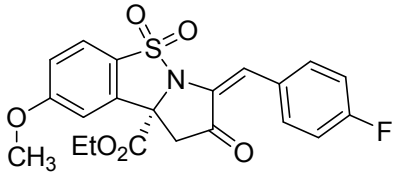
DEPT-135, major isomer) δ 194.6 (C, *C*=O), 168.9 (C, *O*-*C*=*O*), 164.3 (C), 138.1 (C), 132.4 (C), 130.9 (2 x CH), 130.0 (CH), 129.4 (C), 128.5 (CH), 128.1 (2 x CH), 125.7 (C), 123.8 (CH), 117.8 (CH), 108.8 (CH), 69.3 (C), 63.4 (CH_2), 56.1 (CH_3), 47.2 (CH_2), 13.9 (CH_3); HRMS m/z 436.0833 ($M + Na^+$), calcd for $C_{21}H_{19}NO_6SNa$ 436.0831.

(*S,*E*)-Ethyl 8-methoxy-3-(4-methylbenzylidene)-2-oxo-1,2,3,9b-tetrahydrobenzo[d]pyrrolo[1,2-b]isothiazole-9b-carboxylate 5,5-dioxide (5bd):** Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as semi solid; *dr* = 5.5:1; IR (Neat): ν_{max} 2959, 2924, 2853, 1732, 1590, 1515, 1313, 1282, 1156, 868 and 823 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, major isomer) δ 7.80-7.79 (3H, m), 7.23-7.11 (3H, m), 7.00 (1H, d, *J* = 2.0 Hz), 6.94 (1H, s), 4.29-4.21 (2H, m), 3.91 (3H, s), 3.54 (1H, d, *J* = 18.0 Hz), 2.89 (1H, d, *J* = 17.6 Hz), 2.37 (3H, s), 1.24 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135, major isomer) δ 194.6 (C, *C*=O), 169.0 (C, *O*-*C*=*O*), 164.3 (C), 140.7 (C), 138.2 (C), 131.1 (2 x CH), 129.8 (C), 129.2 (CH), 128.9 (2 x CH), 128.7 (C), 125.7 (C), 123.8 (CH), 117.8 (CH), 108.7 (CH), 69.4 (C), 63.4 (CH_2), 56.1 (CH_3), 47.3 (CH_2), 21.6 (CH_3), 13.9 (CH_3); HRMS m/z 450.0988 ($M + Na^+$), calcd for $C_{22}H_{21}NO_6SNa$ 450.0987.



5bd

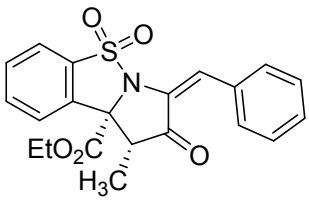
(*S,*E*)-Ethyl 3-(4-fluorobenzylidene)-8-methoxy-2-oxo-1,2,3,9b-tetrahydrobenzo[d]pyrrolo[1,2-b]isothiazole-9b-carboxylate 5,5-dioxide (5cd):** Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as off white solid. Mp 120 °C; *dr* = 2.9:1; IR (KBr): ν_{max} 2924, 1732, 1606, 1464, 1328, 1166, 1010, 914, 813, 681 and 590 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, major isomer) δ 7.92-7.88 (2H, m), 7.80 (1H, d, *J* = 8.8 Hz), 7.19-7.16 (1H, m), 7.13-7.04 (2H, m), 7.02-7.00 (1H, m), 6.91 (1H, s), 4.33-4.23 (2H, m), 3.92 (3H, s), 3.56 (1H, d, *J* = 18.0 Hz), 2.90 (1H, d, *J* = 17.6 Hz), 1.30-1.22 (3H, m); ^{13}C NMR ($CDCl_3$, DEPT-135, major isomer) δ 194.8 (C, *C*=O), 168.9 (C, *O*-*C*=*O*), 164.3 (C), 163.4 (C, d, *J* = 251.0 Hz), 138.1 (C), 133.2 (2 x CH, d, *J* = 7.0 Hz), 129.1 (C), 128.7 (C, d, *J* = 3.0 Hz), 127.4 (CH), 125.6 (C), 123.8 (CH), 117.9 (CH), 115.3 (2 x CH, d, *J* = 17.0 Hz),



5cd

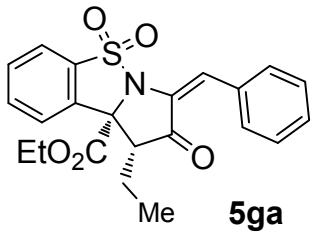
108.7 (CH), 69.3 (C), 63.5 (CH_2), 56.1 (CH_3), 47.2 (CH_2), 13.9 (CH_3); HRMS m/z 454.0736 (M + Na^+), calcd for $C_{21}H_{18}FNO_6SNa^+$ 454.0737.

(1*R,9b*S**,*E*)-Ethyl 3-benzylidene-1-methyl-2-oxo-1,2,3,9b-tetrahydrobenzo[d]pyrrolo[1,2-b]isothiazole-9b-carboxylate 5,5-dioxide (5fa):** Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as gummy solid; *dr* = 2.1:1, c*is*:*trans* = 2.8:1; IR (KBr): ν_{max} 2924, 1737, 1641, 1454, 1333, 1232, 1181, 1025, 757, 691 and 575 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, major isomer) δ 7.98-7.82 (3H, m), 7.79-7.63 (3H, m), 7.42-7.37 (3H, m), 7.00 (1H, s), 4.32-4.21 (2H, m), 2.76 (1H, q, *J* = 6.8 Hz), 1.40-1.29 (3H, m), 1.27-1.23 (3H, m); ^{13}C NMR ($CDCl_3$, DEPT-135, major isomer) δ 196.8 (C, *C*=O), 166.5 (C, *O*-*C*=*O*), 134.4 (C), 133.7 (CH), 133.6 (C), 132.5 (C), 130.7 (2 x CH), 130.8 (CH), 130.4 (CH), 129.7 (CH), 129.5 (C), 128.1 (2 x CH), 127.0 (CH), 122.1 (CH), 73.2 (C), 63.0 (CH_2), 54.1 (CH), 14.0 (CH_3), 9.3 (CH_3); ^1H NMR ($CDCl_3$, minor isomer) δ 7.98-7.82 (3H, m), 7.79-7.63 (3H, m), 7.42-7.37 (3H, m), 7.00 (1H, s), 4.32-4.21 (2H, m), 2.76 (1H, q, *J* = 6.8 Hz), 1.40-1.29 (3H, m), 1.27-1.23 (3H, m); ^{13}C NMR ($CDCl_3$, DEPT-135, minor isomer) δ 198.8 (C, *C*=O), 166.5 (C, *O*-*C*=*O*), 134.6 (C), 133.7 (CH), 133.4 (C), 132.5 (C), 130.8 (2 x CH), 130.6 (CH), 130.2 (CH), 129.3 (C), 128.5 (2 x CH), 128.1 (CH), 126.4 (CH), 122.4 (CH), 73.7 (C), 62.9 (CH_2), 51.9 (CH), 13.8 (CH_3), 9.7 (CH_3); HRMS m/z 415.1329 (M + NH_4^+), calcd for $C_{21}H_{19}NO_5SNH_4$ 415.1328.



5fa

(1*R,9*bS**,*E*)-Ethyl 3-benzylidene-1-ethyl-2-oxo-1,2,3,9b-tetrahydrobenzo[d]pyrrolo[1,2-b]isothiazole-9b-carboxylate 5,5-dioxide (5ga):** Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as off white solid. Mp 118 °C; *dr* = 11.1:1; IR (KBr): ν_{max} 2959, 2929, 1737, 1611, 1449, 1388, 1328, 1186, 1141, 1065, 934, 762, 696 and 580 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, major isomer) δ 7.94-7.91 (1H, m), 7.87-7.85 (3H, m), 7.78 (1H, dt, *J* = 7.5, 1.0 Hz), 7.71 (1H, dt, *J* = 8.0, 1.0 Hz), 7.41-7.36 (3H, m), 6.97 (1H, s), 4.25 (2H, dq, *J* = 7.5, 2.0 Hz), 2.60 (1H, dd, *J* = 8.5, 4.0 Hz), 1.94-1.87 (1H, m), 1.76-1.68 (1H, m), 1.25 (3H, t, *J* = 7.5 Hz), 1.17 (3H, t, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135, major isomer) δ 197.3 (C, *C*=O), 166.7 (C, *O*-*C*=*O*), 134.5 (C), 133.7 (CH), 132.6 (C), 130.8 (CH), 130.7 (2 x CH, C), 129.7 (CH, C), 128.1 (2 x



5ga

CH), 127.0 (CH), 126.6 (CH), 122.2 (CH), 73.0 (C), 63.1 (CH_2), 60.2 (CH), 19.1 (CH_2), 13.9 (CH_3), 12.9 (CH_3); HRMS m/z 434.1037 ($M + Na^+$), calcd for $C_{22}H_{21}NO_5SNa$ 434.1038.

References:

1. (a) S. R.Gagne, C. Curutchet, F. Grenier, G. D. Scholes, *Tetrahedron* **2010**, *66,* 4230-4242; (b) A. Zanka, *Organic Process Research & Development* **1998**, *2,* 60-62; (c) H. Wang, T. Jiang and M.-H. Xu, *J. Am. Chem. Soc*., **2013**, *135*, 971-974.