Supplementary Material

Tandem Pummerer/Mannich Cyclization Cascade of α-Sulfinylamides as a Method to Prepare Aza-heterocycles

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Supporting Information Available: Spectroscopic and experimental procedures for compounds 9, 10, 12, 13, 26-34, and 42-46. $^1$H and $^{13}$C-NMR spectra for new compounds lacking elemental analyses together with ORTEP drawings for structures 10, 34 and 38. The authors have deposited atomic coordinates for these structures with the Cambridge Crystallographic Data Centre. This material is available free of charge via the Internet at http://pubs.acs.org.
Supplemental Experimental Section

Melting points are uncorrected. Mass spectra were determined at an ionizing voltage of 70eV. Unless otherwise noted, all reactions were performed in flame dried glassware under an atmosphere of dry nitrogen. Solutions were evaporated under reduced pressure with a rotary evaporator and the residue was chromatographed on a silica gel column using an ethyl acetate-hexane mixture as the eluent unless specified otherwise.

3-[(2-(3,4-Dimethoxyphenyl)ethyl]ethylsulfanylacetylamino)-2-methyl-but-2-enoic Acid Ethyl Ester (9). To a stirred solution containing 2.0 g (14 mmol) of ethyl 2-methylacetoacetate in 75 mL of toluene was added 2.5 g (14 mmol) of 3,4-dimethoxyphenethylamine. The resulting mixture was heated at reflux for 8 h in a flask equipped with a Dean-Stark trap. The solvent was removed under reduced pressure and the crude imine was taken up in 75 mL of CH$_2$Cl$_2$ and to this solution was added 1.1 g (14 mmol) of pyridine followed by 1.9 g (14 mmol) of ethylsulfenyl-acetyl chloride.$^1$ The mixture was stirred for 2 h at 25 °C and was washed with a saturated NaHCO$_3$ solution and dried over MgSO$_4$. Removal of the solvent under reduced pressure followed by silica gel chromatography afforded 3.1 g (55%) of 3-[(2-(3,4-dimethoxyphenyl)ethyl]ethylsulfanylacetylamino)-2-methyl-but-2-enoic acid ethyl ester as a clear oil which was used in the next step without further purification: IR (neat) 1709, 1652, 1517, and 1260 cm$^{-1}$; $^1$H-NMR (CDCl$_3$, 300 MHz) $\delta$ 1.27 (m, 6H), 1.96 (s, 6H), 2.71 (m, 3H), 2.86 (m, 1H), 3.24 (d, 1H, $J = 14.4$ Hz), 3.36 (d, 1H, $J = 14.4$ Hz), 3.56 (m, 2H), 3.85 (s, 3H), 3.89 (s, 3H), 4.16 (q, 2H, $J = 7.2$ Hz), and 6.77 (m, 3H); $^{13}$C-NMR (CDCl$_3$, 75 MHz) $\delta$ 14.0, 14.2, 15.9, 19.6, 26.4, 33.2, 33.6, 49.9, 55.8, 61.1, 111.1, 112.0, 120.6, 127.5, 131.5, 141.2, 147.4, 148.7, 149.9, 167.5, and 168.9.

To a stirred solution containing 0.4 g (1.8 mmol) of sodium periodate in a 2:1-methanol-H$_2$O mixture was added 0.7 g (1.6 mmol) of the above sulfide in 5 mL of methanol. The resulting mixture was stirred for 3 h at rt, diluted with water, extracted
with chloroform, and dried over MgSO₄. The solvent was removed under reduced pressure and the residue was subjected to silica gel chromatography to give 0.5 g (75%) of enamide 9 as a 1.5:1-mixture of rotamers in solution: IR (neat) 1709, 1652, 1509, and 1260 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) δ 1.27 (t, 3H, J = 7.2 Hz), 1.40 (t, 3H, J = 7.4 Hz), 1.96 (s, 3H), 1.88 (s, 3H), 2.70 (m, 1H), 2.86 (m, 2H), 3.15 (m, 1H), 3.57 (m, 2H), 3.77 (m, 1H), 3.85 (s, 3H), 3.87 (s, 3H), 3.88 (m, 1H), 4.18 (m, 2H), and 6.77 (m, 3H); ¹³C-NMR (CDCl₃, 75 MHz) δ 6.3, 6.6, 14.0, 15.9, 16.0, 19.5, 19.8, 33.4, 33.5, 46.1, 46.7, 49.3, 54.5, 55.7, 56.5, 61.2, 61.3, 111.1, 111.8, 120.5, 128.7, 130.9, 140.1, 140.2, 147.5, 148.8, 163.8, 164.2, 166.9, and 167.1; Anal. Calcd. for C₂₁H₃₁NO₆S: C, 59.27; H, 7.35; N, 3.29. Found: C, 59.13; H, 7.26; N, 3.08.

2-Ethylsulfenyl-8,9-dimethoxy-1-methyl-3-oxo-1,2,3,5,6,10b-hexahydropyrrolo[2,1-a]isoquinoline-1-carboxylic Acid Ethyl Ester (10). To a solution containing 0.09 g (0.5 mmol) of p-TsOH in 25 mL of benzene at 80 °C was added 0.1 g (0.2 mmol) of Z-enamide 9 in 1 mL of benzene. After heating at reflux for 20 min, the reaction mixture was cooled to rt, washed with a saturated NaHCO₃ solution and dried over MgSO₄. Removal of the solvent under reduced pressure followed by silica gel chromatography afforded 0.05 g (52%) of 10 as a white solid, mp 121-122 °C; IR (CCl₄) 1730, 1694, 1509, and 1260 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) δ 1.01 (s, 3H), 1.34 (t, 3H, J = 7.3 Hz), 1.35 (t, 3H, J = 7.3 Hz), 1.92 (s, 3H), 2.66 (m, 1H), 2.79 (m, 1H), 2.85 (q, 2H, J = 7.3 Hz), 3.01 (dt, 1H, J = 12.6 and 3.8 Hz), 3.18 (s, 1H), 3.85 (s, 6H), 4.28 (q, 2H, J = 7.1 Hz), 4.40 (m, 1H), 6.53 (s, 1H), and 7.39 (s, 1H); ¹³C-NMR (CDCl₃, 75 MHz) δ 14.1, 14.5, 25.0, 26.6, 28.8, 29.6, 34.2, 54.9, 55.7, 55.9, 56.4, 60.9, 66.3, 110.2, 110.9, 125.8, 130.6, 147.6, 147.9, 170.0, and 172.0; Anal. Calcd. for C₂₁H₂₉NO₅S: C, 61.89; H, 7.17; N, 3.44. Found: C, 61.98; H, 7.24; N, 3.36.

N-[2-(3,4-Dimethoxyphenyl)ethyl]-2-ethylsulfanyl-N-(2-phenylpropenyl)acetamide (12). To a stirred solution containing 1.0 g (7.5 mmol) of 2-
phenylpropionaldehyde in 40 mL of toluene was added 1.4 g (7.5 mmol) of 3,4-
dimethoxyphenethylamine and the resulting mixture was heated at reflux for 8 h in a
flask equipped with a Dean-Stark trap. The solvent was removed under reduced
pressure and the crude imine was taken up in 40 mL of CH₂Cl₂. To this solution was
added 0.6 g (7.5 mmol) of pyridine followed by 1.0 g (7.5 mmol) of ethylsulfenylacetyl
chloride. The mixture was stirred for 2 h at rt and was then washed with a saturated
NaHCO₃ solution and dried over MgSO₄. Removal of the solvent under reduced
pressure followed by silica gel chromatography gave 2.0 g (67%) of N-[2-(3,4-
dimethoxyphenyl)ethyl]-2-ethylsulfenyl-N-(2-phenylpropenyl)-acetamide as a
colorless oil which was used in the next step without further purification: IR (neat)
1652, 1516, and 1260 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) δ 1.27 (t, 3H, J = 7.3 Hz), 2.00
(s, 3H), 2.63 (q, 2H, J = 7.3 Hz), 2.86 (m, 2H), 3.24 (s, 2H), 3.80 (m, 2H), 3.86 (s, 6H),
6.40 (s, 1H), 6.79 (m, 3H), and 7.31 (m, 5H); ¹³C-NMR (CDCl₃, 75 MHz) δ 14.2, 15.6,
26.1, 33.4, 33.5, 49.6, 55.7, 111.1, 111.9, 120.6, 125.9, 126.2, 128.1, 128.4, 128.5,
131.4, 137.5, 139.3, 147.4, 148.7, and 169.5.

To a stirred solution containing 0.7 g (3.3 mmol) of sodium periodate in a 2:1
methanol/H₂O mixture was added 1.2 g (3.0 mmol) of the above sulfide in 5 mL of
methanol. The resulting mixture was stirred for 3 h at rt, diluted with H₂O, extracted
with chloroform, and dried over MgSO₄. The solvent was removed under reduced
pressure and the residue was subjected to silica gel chromatography to give 1.2 g
(96%) of E-enamide 12 as a colorless oil: IR (neat) 1652, 1509, 1417, and 1260
cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) δ 1.35 (t, 3H, J = 7.3 Hz), 2.03 (s, 3H), 2.87 (m, 4H),
3.74 (m, 4H), 3.85 (s, 6H), 6.35 (s, 1H), 6.78 (m, 3H), and 7.35 (m, 5H); ¹³C-NMR
(CDCl₃, 75 MHz) δ 6.2, 15.7, 33.1, 46.0, 49.2, 55.4, 111.0, 111.7, 120.5, 125.1, 125.8,
126.6, 128.4, 128.7, 130.7, 138.5, 139.4, 147.4, 148.7, and 164.3; Anal. Calcd. for
C₂₃H₂₉NO₄S: C, 66.48; H, 7.04; N, 3.37. Found: C, 66.37; H, 7.12; N, 3.28.
2-Ethylsulfenyl-8,9-dimethoxy-1-methyl-1-phenyl-1,5,6,10b-tetrahydro-2H-pyrrolo[2,1-a]isoquinolin-3-one (13). To a solution containing 0.9 g (4.9 mmol) of p-TsOH in 60 mL of benzene at 80 °C was added 0.9 g (2.4 mmol) of enamide 12 in 2 mL of benzene. After heating at reflux 20 min, the mixture was cooled to rt, washed with a saturated NaHCO₃ solution and dried over MgSO₄. Removal of the solvent under reduced pressure followed by silica gel chromatography afforded 0.4 g (49%) of 13 as a white solid, mp 127-128 °C; IR (CCl₄) 1687, 1509, 1417, and 1253 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) δ 1.35 (t, 3H, J = 7.3 Hz), 1.87 (s, 3H), 2.02 (m, 1H), 2.28 (m, 1H), 2.78 (dt, 1H, J = 12.5 and 3.1 Hz), 2.95 (m, 2H), 3.76 (s, 3H), 3.82 (s, 1H), 3.87 (s, 3H), 4.29 (dd, 1H, J = 12.5 and 4.6 Hz), 5.00 (s, 1H), 6.34 (s, 1H), 6.69 (s, 1H), and 7.02 (m, 5H); ¹³C-NMR (CDCl₃, 75 MHz) δ 14.2, 21.6, 25.5, 28.2, 37.4, 51.3, 55.3, 55.5, 55.9, 65.8, 109.0, 111.4, 123.9, 126.5, 127.4, 128.0, 141.6, 147.2, 147.5, and 172.8; Anal. Calcd. for C₂₃H₂₇NO₃S: C, 69.49; H, 6.85; N, 3.52. Found: C, 69.41; H, 6.93; N, 3.48.

2-Benzod[1,3]dioxol-5-yl-methyl-3-(benzylethane-sulfinylacetylamino)-but-2-enoic Acid Methyl Ester (26). To a stirred solution containing 1.4 g (5.6 mmol) of 2-benzo[1,3]dioxol-5-yl-methyl-3-oxo-butyric acid methyl ester² in 60 mL of toluene was added 0.6 g (5.6 mmol) of benzyl amine and the resulting mixture was heated at reflux for 8 h in a flask equipped with a Dean-Stark trap. The solvent was removed under reduced pressure and the crude imine was taken up in 50 mL of CH₂Cl₂. To this solution was added 0.4 g (5.6 mmol) of pyridine followed by 0.8 g (5.6 mmol) of ethylsulfenylacetyl chloride and the mixture was stirred at rt for 2 h. The reaction mixture was washed with a saturated NaHCO₃ solution and dried over MgSO₄. Removal of the solvent under reduced pressure followed by silica gel chromatography gave 1.2 g (49%) of 2-benzo[1,3]dioxol-5-yl-methyl-3-(benzyl-ethylsulfenyl-acetylamino)-but-2-enoic acid methyl ester as a clear oil which was used in the next step without further purification: IR (neat) 1716, 1652, 1488, and
1239 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) δ 1.27 (t, 3H, J = 7.4 Hz), 1.99 (s, 3H), 2.71 (m, 2H), 3.29 (d, 1H, J = 14.2 Hz), 3.39 (d, 1H, J = 14.2 Hz), 3.43 (s, 3H), 3.55 (s, 1H), 4.57 (d, 1H, J = 14.4 Hz), 4.73 (d, 1H, J = 14.4 Hz), 5.93 (s, 2H), 6.53 (m, 2H), 6.70 (m, 1H), and 7.27 (m, 5H); ¹³C-NMR (CDCl₃, 75 MHz) δ 14.2, 19.9, 26.5, 33.4, 35.2, 50.1, 100.9, 108.2, 108.6, 121.0, 127.5, 128.2, 129.3, 131.8, 136.8, 142.2, 146.1, 147.7, 150.0, 166.8, and 168.8.

To a stirred solution containing 0.6 g (3.0 mmol) of sodium periodate in a 2:1 methanol/H₂O mixture was added 1.2 g (2.7 mmol) of the above sulfide in 5 mL of methanol. The resulting mixture was stirred at rt for 3 h, diluted with H₂O, extracted with chloroform, and dried over MgSO₄. The solvent was removed under reduced pressure and the residue was subjected to silica gel chromatography to give 0.9 g (73%) of enamide 26 as a 2:1-mixture of rotamers in solution: IR (neat) 1716, 1652, 1488, and 1246 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) (major rotamer) δ 1.30 (t, 3H, J = 7.4 Hz), 1.95 (s, 3H), 2.83 (m, 2H), 3.32 (s, 3H), 3.57 (m, 2H), 3.75 (m, 2H), 4.34 (d, 1H, J = 14.3 Hz), 4.83 (d, 1H, J = 14.3 Hz), 5.88 (s, 2H), 6.47 (m, 2H), 6.65 (m, 1H), 7.23 (m, 5H); (minor rotamer) δ 1.30 (t, 3H, J = 7.4 Hz), 1.90 (s, 3H), 2.90 (m, 2H), 3.40 (s, 3H), 3.57 (m, 2H), 3.75 (m, 2H), 4.44 (d, 1H, J = 14.3 Hz), 4.73 (d, 1H, J = 14.3 Hz), 5.88 (s, 2H), 6.47 (m, 2H), 6.65 (m, 1H), and 7.23 (m, 5H); ¹³C-NMR (CDCl₃, 75 MHz) δ 6.3, 6.8, 19.8, 20.1, 35.2, 46.0, 46.6, 49.6, 49.9, 51.9, 52.0, 54.2, 57.1, 100.9, 108.2, 108.5, 121.0, 127.7, 128.3, 129.4, 130.8, 132.9, 135.8, 140.8, 141.4, 146.2, 147.7, 149.9, 163.6, 164.4, 166.5, and 166.6; Anal. Calcd. for C₂₄H₂₇NO₆S: C, 63.00; H, 5.95; N, 3.06. Found: C, 63.14; H, 5.88; N, 3.01.

3-Benzyl-1-ethylsulfenyl-3a-methyl-2-oxo-2,3,3a,9-tetrahydro-1H-5,7-dioxa-3-azo-cyclopenta[a]-5-indacene-9a-carboxyl Acid Methyl Ester (27). To a solution containing 0.3 g (1.8 mmol) of p-TsOH in 35 mL of benzene at 80 °C was added 0.4 g (0.9 mmol) of Z-enamide 26 in 2 mL of benzene. After heating at reflux for 20 min, the reaction was cooled to rt, washed with a saturated NaHCO₃
solution and dried over MgSO₄. Removal of the solvent under reduced pressure
followed by silica gel chromatography afforded 0.3 g (79%) of 27 as a white solid: mp
134-135 °C; IR (CCl₄) 1737, 1694, 1474, and 1246 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz)
δ 1.27 (t, 3H, J = 7.4 Hz), 1.28 (s, 3H), 2.74 (q, 2H, J = 7.4 Hz), 3.00 (d, 1H, J = 16.5
Hz), 3.37 (s, 1H), 3.59 (d, 1H, J = 16.5 Hz), 3.70 (s, 3H), 4.53 (d, 1H, J = 15.6 Hz), 4.96
(d, 1H, J = 15.6 Hz), 5.93 (m, 2H), 6.43 (s, 1H), 6.66 (s, 1H), and 7.31 (m, 5H); ¹³C-
NMR (CDCl₃, 75 MHz) δ 15.0, 21.9, 28.4, 36.3, 45.0, 51.7, 53.6, 65.6, 73.5, 101.4,
103.6, 105.5, 127.3, 127.7, 128.4, 131.2, 136.6, 138.5, 147.5, 148.3, 170.4, and
172.3; Anal. Calcd. for C₂₄H₂₅NO₅S: C, 65.59; H, 5.73; N, 3.19. Found: C, 65.50; H,
5.75; N, 3.13.

3-Benzyl-3a-methyl-2-oxo-2,3,3a,3b,8a,9-hexahydro-1H-5,7-dioxoa-3-
aza-cyclopenta[a]-s-indacene-9a-carboxylic Acid Methyl Ester (28). To a
solution containing 0.1 g (0.24 mmol) of 27 in 5 mL of a 1:1 THF/EtOH mixture was
added an excess of Raney nickel. The reaction mixture was stirred at room
temperature for 1 h and then filtered through a Celite plug. The plug was washed with
ethanol and the filtrate was concentrated under reduced pressure. Silica gel
chromatography provided 0.09 g (98%) of 28 as a white solid, mp 135-136 °C; IR
(KBr) 1723, 1688, 1474, and 1197 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ 1.23 (s, 3H),
2.62 (d, 1H, J = 17.1 Hz), 2.93 (d, 1H, J = 16.1 Hz), 3.35 (d, 1H, J = 17.1 Hz), 3.54 (d,
1H, J = 16.4 Hz), 3.68 (s, 3H), 4.21 (d, 1H, J = 15.6 Hz), 4.76 (d, 1H, 15.9 Hz), 5.94 (s,
1H), 5.97 (s, 1H), 6.62 (s, 1H), 6.69 (s, 1H), and 7.22 (m, 5H); ¹³C-NMR (75 MHz,
CDCl₃) δ 20.7, 39.4, 40.7, 43.4, 52.4, 59.0, 76.0, 101.3, 104.2, 105.1, 126.9, 127.1,
128.3, 134.6, 134.9, 138.1, 146.8, 148.3, 171.7, and 172.8; Anal. Calcd. For
C₂₂H₂₁NO₅: C, 69.63; H, 5.58; N, 3.69. Found: C, 69.55; H, 5.68; N, 3.66.

3-Benzyl-1-ethylsulfenyl-3a-methyl-2-thioxo-2,3,3a,3b,8a,9-hexahydro-
1H-5,7-dioxoa-3-aza-cyclopenta[a]-s-indacene-9a-carboxylic Acid Methyl
Ester (29). To a 1.7 g (3.9 mmol) sample of lactam 27 in toluene (40 mL) was
added 1.7 g (4.3 mmol) of Lawesson's reagent. The reaction mixture was heated at reflux for 5 h, and cooled to room temperature. After the solvent was removed under reduced pressure, silica gel chromatography provided 1.5 g (86%) of 29 as a white solid, mp 176-177 °C; IR (KBr) 1730, 1474, 1232, and 1033 cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.28 (s, 3H), 1.37 (t, 3H, \(J = 7.3\) Hz), 2.96 (m, 2H), 3.07 (d, 1H, \(J = 16.5\) Hz), 3.34 (d, 1H, \(J = 16.5\) Hz), 3.66 (s, 3H), 4.57 (d, 1H, \(J = 15.4\) Hz), 4.78 (s, 1H), 5.20 (d, 1H, \(J = 15.4\) Hz), 5.89 (d, 1H, \(J = 1.5\) Hz), 5.95 (d, 1H, \(J = 1.5\) Hz), 6.63 (s, 1H), 6.67 (s, 1H), and 7.19 (m, 5H); \(^13\)C-NMR (100 MHz, CDCl\(_3\)) \(\delta\) 14.5, 19.4, 28.0, 37.2, 48.5, 52.7, 60.4, 66.4, 81.4, 101.5, 104.6, 105.2, 127.0, 127.2, 128.4, 132.4, 136.2, 137.2, 146.9, 149.1, 171.9, and 199.9; Anal. Calcd. For C\(_{24}\)H\(_{25}\)NO\(_4\)S\(_2\): C, 63.27; H, 5.53; N, 3.07. Found: C, 63.37; H, 5.54; N, 3.03.

3a-Methyl-2,3\(a\),3\(b\),8\(a\),9-hexahydro-1\(H\)-5,7-dioxo-3-aza-cyclopenta[a]-s-indacene-9a-carboxylic Acid Methyl Ester (30). To a 0.5 g (1.2 mmol) sample of thiolactam 29 in ethanol (15 mL) was added an excess of Raney nickel. The reaction mixture was stirred at room temperature for 4 h and then filtered through a Celite plug. The plug was washed with ethanol and the solvent was removed under reduced pressure. The crude residue was subjected to column chromatography to give 0.2 g (70%) of 30 as a colorless oil: IR (neat) 1723, 1474, 1240, and 1033 cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.29 (s, 3H), 1.73 (m, 1H), 2.18 (br s, 1H), 2.57 (m, 2H), 2.83 (d, 1H, \(J = 16.1\) Hz), 3.10 (m, 1H), 3.64 (d, 1H, \(J = 16.1\) Hz), 3.74 (s, 3H), 5.91 (d, 1H, \(J = 1.5\) Hz), 5.93 (d, 1H, \(J = 1.5\) Hz), 6.60 (s, 1H), and 6.71 (s, 1H); \(^13\)C-NMR (100 MHz, CDCl\(_3\)) \(\delta\) 23.1, 39.4, 41.1, 46.2, 51.8, 63.3, 79.6, 101.0, 103.6, 104.7, 132.6, 139.0, 147.2, 147.8, and 176.3; Anal. Calcd. for C\(_{15}\)H\(_{17}\)NO\(_4\): C, 65.43; H, 6.23; N, 5.09. Found: C, 65.24; H, 6.09; N, 4.87.

2-[1-(Benzyl-ethylsulfinylacetyl-amino)-ethylidene]-4-trimethylsilyl-methyl-pent-4-enoic Acid Methyl Ester (31). To a stirred solution containing 1.0 g (8.6 mmol) of methyl acetoacetate in 35 mL of THF at 0 °C was added 0.4 g (8.6
mmol) of 60% NaH. The mixture was allowed to warm to rt and 1.9 g (8.6 mmol) of 2-[(methylsulphonyloxymethyl)-3-trimethylsilylprop-1-ene$^3$ and 1.3 g (8.6 mmol) of NaI were added in one portion. The reaction mixture was heated at reflux for 12 h, diluted with H$_2$O, extracted with ethyl acetate, and dried over MgSO$_4$. The solvent was removed under reduced pressure and the residue was subjected to silica gel chromatography to give 1.7 g (80%) of 2-acetyl-4-trimethylsilylmethyl-pent-4-enoic acid methyl ester as a clear oil: IR (neat) 1736, 1716, and 1489 cm$^{-1}$; $^1$H-NMR (CDCl$_3$, 300 MHz) $\delta$ 0.01 (s, 9H), 1.51 (s, 2H), 2.32 (s, 3H), 2.50 (m, 2H), 3.76 (s, 3H), 3.77 (m, 1H), and 4.61 (m, 2H); $^{13}$C-NMR (CDCl$_3$, 75 MHz) $\delta$ -1.4, 26.9, 29.0, 36.1, 52.4, 58.1, 108.7, 143.7, 149.9, and 169.9.

To a stirred solution containing 1.7 g (6.9 mmol) of the above ester in 75 mL of toluene was added 0.7 g (6.9 mmol) of benzylamine and the resulting mixture was heated at reflux for 8 h in a flask equipped with a Dean-Stark trap. The solvent was removed under reduced pressure and the crude imine was taken up in 50 mL of CH$_2$Cl$_2$. To this solution was added 0.5 g (6.9 mmol) of pyridine followed by 1.0 g (6.9 mmol) of ethylsulfenylacetyl chloride and the mixture was stirred at rt for 2 h. The solution was then washed with a saturated NaHCO$_3$ solution and dried over MgSO$_4$. Removal of the solvent under reduced pressure followed by silica gel chromatography gave 2.2 g (73%) of 2-[1-(benzylethylsulfenylacetyl-amino)-ethylidene]-4-trimethyl-silanylmethyl-pent-4-enoic acid methyl ester as a clear oil: IR (neat) 1723, 1652, 1431, and 1246 cm$^{-1}$; $^1$H-NMR (CDCl$_3$, 300 MHz) $\delta$ 0.01 (s, 9H), 1.27 (t, 3H, $J = 7.4$ Hz), 1.48-1.88 (m, 7H), 2.72 (m, 2H), 2.98 (m, 1H), 3.38 (m, 2H), 3.45 (s, 3H), 4.41-4.79 (m, 3H), and 7.26 (m, 5H); $^{13}$C-NMR (CDCl$_3$, 75 MHz) $\delta$ -1.4, 14.2, 19.8, 26.5, 27.2, 33.3, 38.2, 50.5, 51.8, 108.3, 115.8, 128.2, 129.0, 129.1, 131.0, 137.1, 142.0, 168.9, and 170.2; Anal. Calcd. for C$_{23}$H$_{35}$NO$_3$SSi: C, 63.71; H, 8.14; N, 3.23. Found: C, 63.64; H, 8.09; N, 3.17.
To a solution containing 1.1 g (5.3 mmol) of sodium periodate in a 2:1-methanol/H₂O mixture was added 2.1 g (4.8 mmol) of the above sulfide in 5 mL of methanol. The resulting mixture was stirred for 3 h at rt, diluted with H₂O, extracted with chloroform, and dried over MgSO₄. The solvent was removed under reduced pressure and the residue was subjected to silica gel chromatography to give 2.0 g (90%) of enamide 31 as a 2:1-mixture of rotamers in solution: IR (neat) 1716, 1652, 1431, and 1246 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) δ 0.03 (s, 9H), 1.26-1.53 (m, 5H), 1.62-2.04 (m, 4H), 2.87 (m, 2H), 3.12 (m, 2H), 3.47 (m, 3H), 3.75-4.13 (m, 2H), 4.42-4.76 (m, 3H), and 7.26 (m, 5H); ¹³C-NMR (CDCl₃, 75 MHz) δ -1.4, 4.6, 6.7, 19.8, 20.0, 20.3, 27.3, 31.0, 38.1, 46.2, 50.1, 50.4, 51.9, 52.0, 54.5, 56.8, 56.9, 108.4, 115.4, 127.6, 127.7, 128.3, 129.2, 129.3, 132.2, 136.0, 136.2, 138.6, 138.9, 141.4, 142.7, 142.9, 164.4, 164.7, 166.9, and 167.3; Anal. Calcd. for C₂₉H₃₅NO₄SSi: C, 61.44; H, 7.85; N, 3.12. Found: C, 61.35; H, 7.59; N, 3.04.

1-Benzyl-3-ethylsulfenyl-5,6a-dimethyl-2-oxo-2,3,6,6a-tetrahydro-1H-cyclopenta[b]pyrrole-3a-carboxylic Acid Methyl Ester (32). To a solution containing 0.3 g (1.7 mmol) of p-TsOH in 40 mL of benzene at 80 °C was added 0.4 g (0.8 mmol) of Z-enamide 31 in 2 mL of benzene. After heating at reflux for 20 min, the mixture was cooled to rt, washed with a saturated NaHCO₃ solution and dried over MgSO₄. Removal of the solvent under reduced pressure followed by silica gel chromatography afforded 0.2 g (61%) of 32 as a white solid, mp 91-92 °C; IR (CCl₄) 1737, 1694, 1396, and 1196 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) δ 1.08 (s, 3H), 1.49 (t, 3H, J = 7.4 Hz), 1.68 (s, 3H), 2.31 (d, 1H, J = 17.0 Hz), 2.77 (q, 2H, J = 7.4 Hz), 3.16 (d, 1H, J = 17.0 Hz), 3.35 (s, 1H), 3.70 (s, 3H), 4.49 (d, 1H, J = 15.4 Hz), 4.58 (d, 1H, J = 15.4 Hz), 4.90 (s, 1H), and 7.29 (m, 5H); ¹³C-NMR (CDCl₃, 75 MHz) δ 15.0, 16.7, 20.5, 28.5, 41.3, 44.6, 51.6, 55.4, 63.7, 74.7, 126.4, 127.3, 127.8, 128.3, 138.1, 138.7, 170.9, and 171.9; Anal. Calcd. for C₂₀H₂₅NO₃S: C, 66.82; H, 7.01; N, 3.90. Found: C, 66.93; H, 7.06; N, 3.87.
2-[1-(Benzy lethyl sulfinyl acet yl-amino) ethylidene]-hex-5-enoic Acid

Methyl Ester (33). A 1.2 g (10 mmol) sample of methyl acetoacetate was added to a suspension of 0.2 g (10 mmol) of NaH in 10 mL of THF at 0 °C and the mixture was stirred for 10 min. A 1.4 g (10 mmol) sample of 4-bromobutene was added and the mixture was heated at reflux for 48 h. The mixture was poured into water, separated and extracted with diethyl ether. The organic layer was dried over MgSO4, filtered and the residue was chromatographed on silica gel to give 0.8 g (49%) of 2-acetyl-hex-5-enoic acid methyl ester as a clear oil: IR (neat) 1740, 1715, 1441, and 1356 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) δ 1.87-2.09 (m, 4H), 2.18 (s, 3H), 3.43 (t, 1H, J = 6.7 Hz), 3.69 (s, 3H), 4.94-5.02 (m, 2H), and 5.65-5.75 (m, 1H); ¹³C-NMR (CDCl₃, 75 MHz) δ 27.0, 28.9, 31.2, 52.3, 58.5, 115.9, 136.8, 170.1, and 203.0.

A 0.6 g (3.6 mmol) sample of the above keto-ester and 0.4 g (3.8 mmol) of benzylamine in 40 mL of toluene was heated at reflux in a flask equipped with a Dean-Stark trap. The solvent was removed under reduced pressure and the residue was taken up in 30 mL of CH₂Cl₂. To this solution was added 0.6 mL (8 mmol) of pyridine followed by 0.5 g (3.8 mmol) of ethyl sulfenylacetyl chloride. After stirring for 1 h at rt, the mixture was washed with a saturated NaHCO₃ solution. The organic layer was separated, dried over MgSO₄, concentrated under reduced pressure and the residue was purified by silica gel chromatography to give 0.7 g (50%) of 2-[1-(benzyl-ethy lsulfinyl acet yl-amino) ethylidene]-hex-5-enoic acid methyl ester as a clear oil: IR (neat) 1720, 1653, 1429, and 1387 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) δ 1.22 (t, 3H, J = 7.3 Hz), 1.85 (s, 3H), 2.08-2.29 (m, 2H), 2.31-2.36 (m, 2H), 2.61-2.72 (m, 2H), 3.23-3.39 (m, 2H), 3.41 (s, 3H), 4.54 (s, 2H), 4.93-5.01 (m, 2H), 5.67-5.71 (m, 1H), and 7.12-7.23 (m, 5H); ¹³C-NMR (CDCl₃, 75 MHz) δ 14.1, 19.5, 26.4, 29.2, 32.1, 33.0, 50.2, 51.8, 115.8, 127.3, 128.1, 129.1, 132.5, 136.8, 136.9, 141.0, 167.1, and 168.8; Anal. Calcd. for C₂₀H₂₇NO₃S: C, 66.45; H, 7.53; N, 3.88. Found: C, 66.33; H, 7.47; N, 3.62.
A 0.6 g (1.8 mmol) sample of the above sulfide was dissolved in 20 mL of methanol and this was added to a solution containing 0.8 g (3.5 mmol) of NaIO₄ in 20 mL of water. The mixture was stirred for 1h at rt, extracted with chloroform, dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography to afford 0.5 g (82%) of Z-enamide 33 as a clear oil: IR (neat) 1717, 1650, 1433, and 1199 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) δ 1.34 (t, 3H, J = 7.6 Hz), 1.87 (s, 3H), 2.08-2.24 (m, 2H), 2.29-2.39 (m, 2H), 2.75-2.29 (m, 1H), 3.00-3.16 (m, 1H), 3.37 (s, 3H), 3.70-3.88 (m, 2H), 4.37-4.69 (m, 2H), 4.96-5.03 (m, 2H), 5.66-5.76 (m, 1H), and 7.21 (brs, 5H); ¹³C-NMR (CDCl₃, 75 MHz) δ 6.8, 19.6, 29.4, 32.1, 46.8, 49.9, 52.0, 56.9, 116.2, 127.7, 127.8, 128.4, 129.5, 136.0, 136.7, 139.8, 149.9, and 164.5; Anal. Calcd. for C₂₀H₂₇NO₄S: C, 63.63; H, 7.21; N, 3.71. Found: C, 63.55; H, 7.16; N, 3.66.

1-Benzyl-3-ethylsulfenyl-7a-methyl-2-oxo-6-(toluene-4-sulfonyloxy) octahydro-indole-3a-carboxylic Acid Methyl Ester (34). A solution containing 0.2 g (0.8 mmol) of p-TsOH in 30 mL of benzene was heated to 80 °C and 0.1 g (0.3 mmol) of the above sulfoxide in 5 mL of benzene was added. The mixture was heated at reflux for 25 min, cooled to rt and washed with a saturated NaHCO₃ solution. The organic layer was combined, dried over MgSO₄ and chromatographed on silica gel to give 0.1 g (87%) of 34 as a white solid, mp 145-146 °C; IR (neat) 1729, 1698, 1359, and 1177 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) _ 0.94 (s, 3H), 1.24 (t, 3H J = 7.4 Hz), 1.55 (t, 2H, J = 12.4 Hz), 1.90-2.16 (m, 4H), 2.42 (s, 3H), 2.67 (q, 2H, J = 7.4 Hz), 3.38 (s, 1H), 3.51 (s, 3H), 4.00 (d, 1H, J = 15.4 Hz), 4.31 (brs, 1H), 4.72 (d, 1H, J = 15.4 Hz), 7.21 (s, 5H), 7.30 (d, 2H, J = 8.0 Hz), and 7.70 (d, 2H, J = 8.0 Hz); ¹³C-NMR (CDCl₃, 75 MHz) _ 15.2, 21.6, 21.7, 23.3, 27.6, 28.6, 42.8, 43.4, 50.4, 51.8, 56.3, 62.8, 76.0, 127.3, 127.5, 127.8, 128.2, 129.9, 133.7, 138.1, 144.9, 171.2, and 171.8; Anal. Calcd. for C₂₇H₃₃NO₆S₂: C, 60.99; H, 6.26; N, 2.63: Found: C, 60.93; H, 6.34; N, 2.56.
2-[3-(Benzy1-ethylsulfanylacetyl-amino)-2-methoxycarbonyl-but-2-enyl]-indole-1-carboxylic Acid Methyl Ester (42). To a stirred solution containing 0.4 g (3.7 mmol) of methyl acetoacetate in 30 mL of THF at 0 °C was added 0.2 g (3.7 mmol) of 60% NaH. The mixture was allowed to warm to rt and 1.0 g (3.7 mmol) of methyl 2-bromomethyl-1-indolecarboxylate was added in one portion. After stirring for 3 h at rt, the reaction mixture was diluted with H2O, extracted with ethyl acetate, and dried over MgSO4. Concentration of the solution under reduced pressure followed by silica gel chromatography gave 0.8 g (67%) of 2-(2-methoxy-carbonyl-3-oxo-butyl)-indol-1-carboxylic acid methyl ester as a colorless oil: IR (neat) 1737, 1452, and 1331 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) δ 2.27 (s, 3H), 3.58 (m, 2H), 3.70 (s, 3H), 4.07 (s, 3H), 4.10 (m, 1H), 6.43 (s, 1H), 7.24 (m, 2H), 7.45 (m, 1H), and 8.03 (m, 1H); ¹³C-NMR (CDCl₃, 75 MHz) δ 27.9, 29.1, 52.2, 53.4, 58.5, 109.8, 115.4, 119.9, 122.7, 122.8, 123.7, 128.8, 135.9, 137.2, 152.0, and 169.1.

To a stirred solution containing 0.8 g (2.5 mmol) of the above ester in 50 mL of toluene was added 0.3 g (2.5 mmol) of benzylamine and the resulting mixture was heated at reflux for 8 h in a flask equipped with a Dean-Stark trap. The solvent was removed under reduced pressure and the crude imine was taken up in 50 mL of CH₂Cl₂. To this solution was added 0.2 g (2.5 mmol) of pyridine followed by 0.3 g (2.5 mmol) of ethylsulfenylacetyl chloride and the mixture was stirred at rt for 2 h. The solution was washed with a saturated NaHCO₃ solution and dried over MgSO₄. Removal of the solvent under reduced pressure followed by silica gel chromatography afforded 0.7 g (57%) of 2-[3-(benzylethylsulfenylacetyl-amino)-2-methoxy-carbonyl-but-2-enyl]-indole-1-carboxylic acid methyl ester as a clear oil: IR (neat) 1737, 1652, 1452, and 1324 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) δ 1.31 (t, 3H, J = 7.3 Hz), 1.98 (s, 3H), 2.74 (m, 2H), 3.45 (s, 3H), 3.48 (m, 2H), 4.04 (m, 2H), 4.07 (s, 3H), 4.66 (d, 1H, J = 14.5 Hz), 4.83 (d, 1H, J = 14.5 Hz), 6.01 (s, 1H), 7.33 (m, 8H), and 8.02 (d, 1H, J = 8.1 Hz); ¹³C-NMR (CDCl₃, 75 MHz) δ 14.1, 19.7, 26.4, 30.7, 33.3,
50.1, 51.9, 53.6, 108.3, 115.4, 119.9, 123.0, 123.8, 127.5, 128.2, 128.8, 129.1, 129.3, 136.1, 136.7, 136.9, 144.0, 152.3, 166.5, and 169.1; Anal. Calcd. for C_{27}H_{30}N_{2}O_{6}S: C, 65.56; H, 6.12; N, 5.67. Found: C, 65.42; H, 5.95; N, 5.58.

To a stirred solution containing 0.3 g (1.7 mmol) of sodium periodate in a 2:1-methanol/H_{2}O mixture was added 0.5 g (1.1 mmol) of the above sulfide in 2 mL of methanol. The resulting mixture was stirred at rt for 3 h, diluted with H_{2}O, extracted with chloroform, and dried over MgSO_{4}. The solvent was removed under reduced pressure and the residue was subjected to silica gel chromatography to give 0.5 g (88%) of enamide 42 as a 2:1-mixture of rotamers in solution: IR (neat) 1737, 1652, 1452, and 1324 cm^{-1}; \textsuperscript{1}H-NMR (CDCl_{3}, 300 MHz) (major rotamer) \delta 1.38 (t, 3H, J = 7.3 Hz), 2.01 (s, 3H), 2.90 (m, 1H), 3.12 (m, 1H), 3.37 (s, 3H), 3.84 (m, 4H), 4.05 (s, 3H), 4.47 (d, 1H, J = 14.5 Hz), 4.96 (d, 1H, J = 14.5 Hz), 6.00 (s, 1H), 7.32 (m, 8H), and 8.01 (d, 1H, J = 8.1 Hz); (minor rotamer) \delta 1.40 (t, 3H, J = 7.4 Hz), 1.97 (s, 3H), 2.90 (m, 1H), 3.12 (m, 1H), 3.42 (s, 3H), 3.84 (m, 4H), 4.05 (s, 3H), 4.58 (d, 1H, J = 14.4 Hz), 4.86 (d, 1H, J = 14.4 Hz), 6.05 (s, 1H), 7.32 (m, 8H), and 8.01 (d, 1H, J = 8.1 Hz); \textsuperscript{13}C-NMR (CDCl_{3}, 75 MHz) \delta 6.2, 6.6, 19.5, 19.8, 30.7, 30.8, 46.0, 46.6, 49.6, 49.8, 51.9, 52.0, 53.6, 54.4, 56.7, 108.7, 115.4, 119.9, 120.0, 122.9, 123.9, 127.7, 128.3, 128.6, 128.7, 129.2, 130.6, 130.7, 135.8, 135.9, 136.0, 136.3, 142.3, 142.5, 152.2, 152.3, 163.8, 164.4, 166.2, and 166.4; Anal. Calcd. for C_{27}H_{30}N_{2}O_{6}S: C, 63.51; H, 5.93; N, 5.49. Found: C, 63.44; H, 5.86; N, 5.31.

Dimethyl-1-benzyl-3-(ethylsulfenyl)-9c-methyl-2-oxo-2,3,4,9c-tetrahydro-1\textsuperscript{H}-pyrrolo[2',3',3,4]cyclopenta[1,2-b]indole-3a,5-dicarboxylate (43). To a solution containing 0.3 g (1.7 mmol) of p-TsOH in 40 mL of benzene at 80 °C was added 0.4 g (0.8 mmol) of Z-enamide 42 in 2 mL of benzene. After heating at reflux for 20 min, the reaction was cooled to rt, washed with a saturated NaHCO_{3} solution and dried over MgSO_{4}. Removal of the solvent under reduced pressure followed by silica gel chromatography afforded 0.3 g (80%) of 43 as a white solid; mp 201-202
°C; IR (CCl₄) 1737, 1701, 1445, and 1360 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) δ 1.28 (s, 3H), 1.32 (t, 3H, J = 7.4 Hz), 2.82 (m, 2H), 3.42 (d, 1H, J = 17.8 Hz), 3.60 (s, 1H), 3.74 (s, 3H), 3.93 (d, 1H, J = 17.8 Hz), 4.03 (s, 3H), 4.49 (d, 1H, J = 15.8 Hz), 5.30 (d, 1H, J = 15.8 Hz), 7.35 (m, 8H), and 8.24 (d, 1H, J = 8.0 Hz); ¹³C-NMR (CDCl₃, 75 MHz) δ 14.9, 21.2, 28.6, 34.6, 46.0, 51.6, 53.8, 55.2, 68.0, 70.7, 116.0, 118.7, 123.4, 123.9, 124.2, 125.1, 127.1, 127.2, 128.2, 138.1, 139.6, 139.8, 151.0, 169.7, and 172.0; Anal. Calcd. for C₂₇H₂₈N₂O₅S: C, 65.84; H, 5.73; N, 5.69. Found: C, 65.74; H, 5.74; N, 5.60.

**Dimethyl-1-benzyl-9c-methyl-2-oxo-2,3,4,9c-tetrahydro-1H-pyrrolo-[2',3',3,4]cyclopenta[1,2-b]indole-3a,5-dicarboxylate (44).** To a solution containing 0.2 g (0.4 mmol) of 43 in 5 mL of a 1:1 THF/EtOH mixture was added an excess of Raney nickel. The mixture was stirred at room temperature for 2 h and then filtered through a Celite plug. The plug was washed with ethanol and the filtrate was concentrated under reduce pressure. Silica gel chromatography afforded 0.17 g (99%) of 44 as a clear oil: IR (neat) 1737, 1688, 1437, 1360, and 1175 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ 1.35 (s, 3H), 2.72 (d, 1H, J = 17.3 Hz), 3.23 (d, 1H, J = 17.6 Hz), 3.52 (d, 1H, J = 17.3 Hz), 3.71 (s, 3H), 3.95 (d, 1H, J = 17.6 Hz), 4.03 (s, 3H), 4.21 (d, 1H, J = 16.1 Hz), 5.08 (d, 1H, J = 15.9 Hz), 7.29 (m, 7H), 7.48 (m, 1H), and 8.20 (d, 1H, J = 7.1 Hz); ¹³C-NMR (75 MHz, CDCl₃) δ 21.2, 38.7, 40.7, 44.9, 52.5, 53.9, 61.8, 73.3, 116.1, 118.2, 123.4, 123.9, 124.8, 124.9, 126.9, 127.0, 128.3, 138.1, 139.6, 142.0, 151.1, 171.9, and 172.5; Anal. Calcd. for C₂₅H₂₄N₂O₅: C, 69.42; H, 5.60; N, 6.48. Found: C, 69.33; H, 5.54; N, 6.47.

**3-(2,2-Diethylthio-N-benzylacetylamino)-2-(1-(methoxycarbonyl)indol-2-yl)methyl)but-3-enoic Acid Methyl Ester (45).** To a solution containing 7.0 g (23 mmol) of 2-(2-methoxycarbonyl-3-oxo-butyl)-indol-1-carboxylic acid methyl ester in 50 mL of toluene was added 2.5 mL (23 mmol) of benzylamine. The resulting solution was heated at reflux in a flask equipped with a Dean-Stark trap for 8 h. The
solvent was removed under reduced pressure and the crude enamide was taken up in 75 mL of CH₂Cl₂. To this solution was added 2.1 mL (26 mmol) of pyridine followed by 4.6 g (23 mmol) of bis-ethylsulfenyl-acetyl chloride. The reaction mixture was stirred for 2 h at rt and was then washed with a saturated NaHCO₃ solution. The organic layer was dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure. The crude residue was purified by silica gel chromatography to give 7.3 g (57%) of enamide 45 as a clear oil: IR (neat) 1745, 1645, 1453, and 1204 cm⁻¹; ¹H-NMR (DMSO-d₆, 400 MHz) δ 1.14 (m, 6H), 2.63 (m, 4H), 3.46 (m, 2H), 3.58 (s, 3H), 3.86 (m, 1H), 4.00 (s, 3H), 4.60 (m, 2H), 4.80 (s, 1H), 5.17 (s, 1H), 5.52 (s, 1H), 6.49 (s, 1H), 7.15 (m, 1H), 7.24 (m, 6H), 7.50 (m, 1H), and 8.02 (m, 1H); ¹³C-NMR (DMSO-d₆, 100 MHz) δ 13.8, 23.2, 23.4, 30.6, 48.9, 49.2, 52.0, 53.7, 109.4, 115.2, 118.0, 119.9, 122.8, 123.7, 126.9, 127.5, 127.9, 128.4, 135.7, 136.7, 136.9, 142.9, 151.5, 167.7, and 171.6; Anal. Calcd. for C₂₉H₃₄N₂O₅S₂: C, 62.79; H, 6.18; N, 5.05. Found: C, 62.70; H, 6.15; N, 4.93.

Methyl 12-Aza-3-ethythio-9-(methoxycarbonyl)-2-oxo-1-benzylspiro[pyrrolidine-5,3'-tricyclo[6.4.0.0².6]dodecane]a-6(13),7(11),14,16-tetraene-12-carboxylate (46). To a 0.1 g (0.3 mmol) sample of enamide 45 in 5 mL of CH₂Cl₂ at -40 °C was added 0.07 g (0.4 mmol) of DMTSF. The mixture was stirred for 1 h at -40 °C and was then warmed to 0 °C for 30 min. The solution was quenched with a saturated NaHCO₃ solution. The aqueous layer was extracted with diethyl ether and the combined organic phase was washed with brine and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure and the crude oil was crystallized to give 0.08 g (69%) of 46 as a white solid; mp 133-134 °C; IR (neat) 1738, 1695, 1446, and 1360 cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz) δ 1.33 (t, 3H, J = 7.6 Hz), 2.20 (dd, 1H, J = 14.4 and 10.4 Hz), 2.64 (dd, 1H, J = 14.4 and 8.8 Hz), 2.96 (m, 2H), 3.13 (dd, 1H, J = 17.2 and 8.4 Hz), 3.43 (dd, 1H, J = 17.2 and 7.2 Hz), 3.51 (dd, 1H, J = 8.0 and 7.6 Hz), 3.69 (dd, 1H, J = 10.0 and 8.8 Hz), 3.73 (s, 3H), 4.03 (s,
3H); 4.10 (d, 1H, J = 15.2 Hz), 4.85 (d, 1H, J = 15.2 Hz), 7.15 (m, 7H), 7.30 (m, 1H), and 8.18 (d, 1H, J = 8.0 Hz); $^{13}$C-NMR (CDCl$_3$, 100 MHz) δ 14.4, 25.4, 29.7, 36.5, 41.9, 44.6, 52.1, 53.9, 54.8, 70.9, 116.0, 117.9, 123.5, 123.7, 123.8, 124.4, 127.4, 128.3, 137.4, 140.2, 141.9, 151.2, 172.3, and 174.0; Anal. Calcd. for C$_{27}$H$_{28}$N$_2$O$_5$S: C, 65.83; H, 5.73; N, 5.69. Found: C, 65.76; H, 5.69; N, 5.66.

Experimental References:


