Pergamon

Tetrahedron: *Asymmetry* 13 (2002) 2099–2104

TETRAHEDRON: *ASYMMETRY*

Diethylzinc-mediated 1,3-dipolar cycloaddition reaction of chiral azomethine ylides: asymmetric synthesis of ferrocenyl-substituted pyrrolidine derivatives

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Received 22 July 2002; accepted 18 September 2002

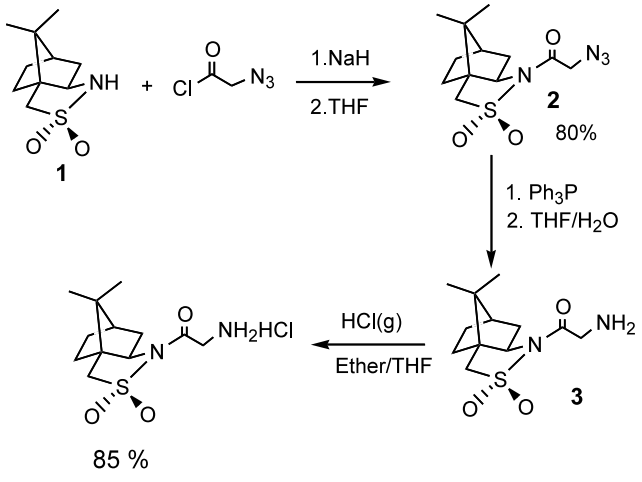
Abstract—Asymmetric synthesis of ferrocenyl-substituted pyrrolidine derivatives was successfully achieved by diethylzinc-mediated 1,3-dipolar cycloaddition reactions of chiral azomethine ylides with a number of electron-deficient dipolarophiles. Chiral azomethine ylides were formed by condensing glycyl sultam with ferrocenecarboxaldehyde via imine tautomerization and complexation with diethylzinc. All of the cycloaddition reactions gave ferrocenyl-substituted pyrrolidine derivatives with very high regio- and diastereoselectivity in reasonable yields.

1. Introduction

Pyrrolidine derivatives are of great interest and potential due to their wide spectrum of biological activity.[1] They are present in a variety of natural products and drugs, such as cephalotoxin, kainic acid, domoic acid, and quinocarcin. Ferrocenyl-substituted organic molecules are also important due to their unusual biological activities[2] and their application in asymmetric catalysis,[3] and in material science.[4] The asymmetric synthesis of new biologically active pyrrolidine derivatives is currently an active research area in organic chemistry and we are particularly interested in synthesizing new ferrocenyl-substituted chiral pyrrolidine derivatives. We recently reported the synthesis of racemic ferrocenyl-substituted pyrrolidine derivatives through 1,3-dipolar cycloaddition reactions of azomethine ylides obtained by imine tautomerization method.[5] A key feature of this work was our use of Et_2Zn as a catalyst precursor. In this work, we applied our protocol for the asymmetric synthesis of pyrrolidine derivatives by employing Oppolzer's sultam,[6] which serves as a chiral auxiliary. Garner and Dogan used this auxiliary to create chiral azomethine ylides.[7] They also showed that this auxiliary controls the stereoselectivity of 1,3-dipolar cycloaddition reactions of azomethine ylides. However, these reactions were performed at 80–85°C. Herein, we report full details of our diethylzinc-catalyzed version of the Garner method for asymmetric synthesis of ferrocenyl-substituted pyrrolidine derivatives.

2. Results and discussion

The starting glycyl sultam **1** was synthesized by a new and efficient method. The camphor sultam **1** was treated with NaH then reacted with azidoacetyl chlo-



Scheme 1.

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PII: S0957-4166(02)00576-1

ride to afford azidoacetyl sultam **2** in 80% isolated yield. Staudinger reaction of compound yielded crude glycyl sultam **3** (which was directly converted to its hydrochloride salt) in 85% yield (Scheme 1).

In order to create chiral azomethine ylides, glycyl sultam **3** was reacted with ferrocenecarboxaldehyde to yield imine **4**, which tautomerizes at room temperature in the presence of a zinc catalyst to give azomethine ylide **5**. Diethylzinc serves as a base, removing the α-proton and facilitating azomethine ylide formation.[8] It also forms a complex with the azomethine ylide, thus lowering the HOMO level of the dipole so that the reaction takes place at room temperature. If diethylzinc is not used, it is necessary to reflux the reaction mixture in benzene or toluene. When the ylide **5** was trapped with *N*-phenylmaleimide **6**, the reaction gave cycloadduct **8** as the only isolable cycloadduct of the reaction in 64% yield (Scheme 2, Table 1, entry 1). We carefully analyzed the crude reaction product by ^{1}H NMR and did not observe any other isomer(s) of cycloadduct **8**. When *N*-methylmaleimide **7** was used as the dipolarophile, the cycloaddition reaction gave cycloadduct **9** again as the only isolable cycloaddition product in good yield (Scheme 2, Table 1, entry 2). The absolute stereochemistry of both cycloadducts was determined by the coupling constants of H-3 ($J_{3,3a}=8.4$ Hz for **8** and $J_{3,3a}=7.9$ Hz for **9**) and H-1 ($J_{1,6a}=6.5$ Hz for **8** and $J_{1,6a}=6.9$ Hz for **9**). When the same protons are *trans* to H-3a and H-6a, respectively, the same coupling constants are either zero or closer to zero, which is in agreement with the literature values for similar compounds.[9]

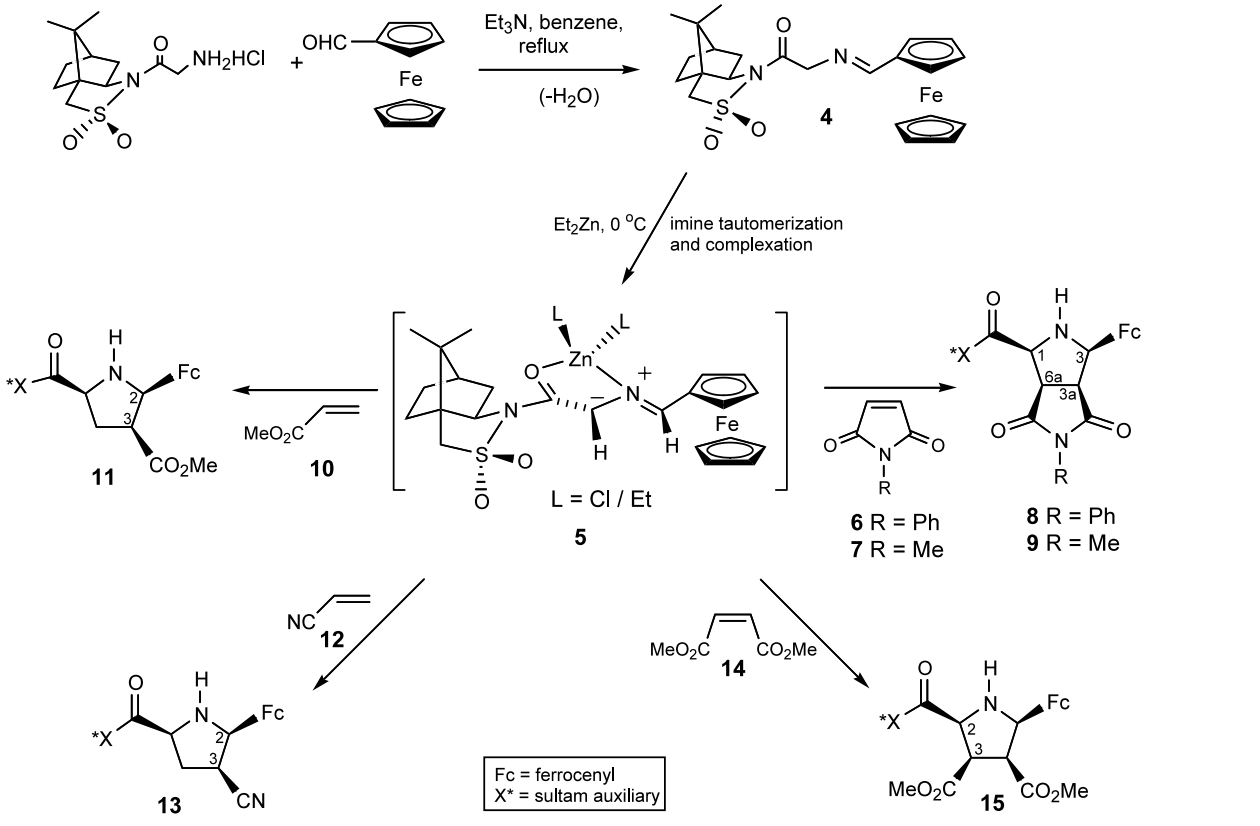
Dipolar cycloaddition reaction of ylide **5** to methyl acrylate **10** gave compound **11** as the only cycloadduct in reasonable yield (Scheme 2, Table 1, entry 3). The absolute stereochemistry of the cycloadduct **11** was unambiguously determined by X-ray analysis, which showed that all the pyrrolidine substituents were *cis* to each other (Fig. 1).[10]

With acrylonitrile **12** as the dipolarophile, cycloadduct **13** was obtained as the only cycloaddition product, in acceptable yield (Scheme 2, Table 1, entry 4). Again, the absolute stereochemistry of the cycloadduct 13 was unambiguously determined by X-ray analysis, which showed that all the pyrrolidine substituents had a *cis* relationship to each other as in the previous case (Fig. 2).[10]

Finally, the dipolar cycloaddition reaction of ylide **5** with dimethyl maleate **14** resulted in the formation of

Table 1. Dipolar cycloadditions of azomethine ylide **5**

Entry	Azomethine ylide	Dipolarophile	Product	Yield (%)
1	**5**	**6**	**8**	64
2	**5**	**7**	**9**	76
3	**5**	**10**	**11**	59
4	**5**	**12**	**13**	52
5	**5**	**14**	**15**	51



Scheme 2.

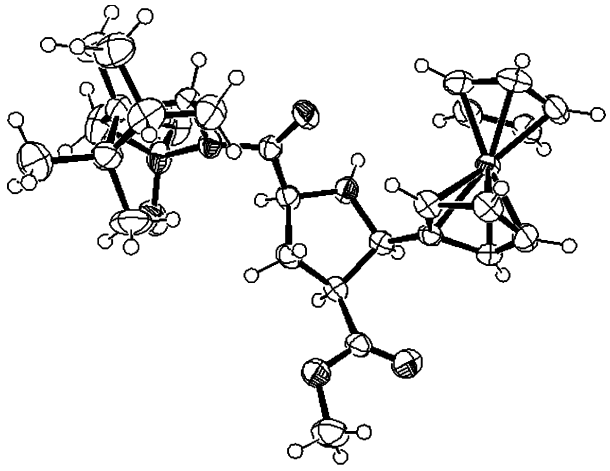


Figure 1. ORTEP drawing of cycloadduct **11**.

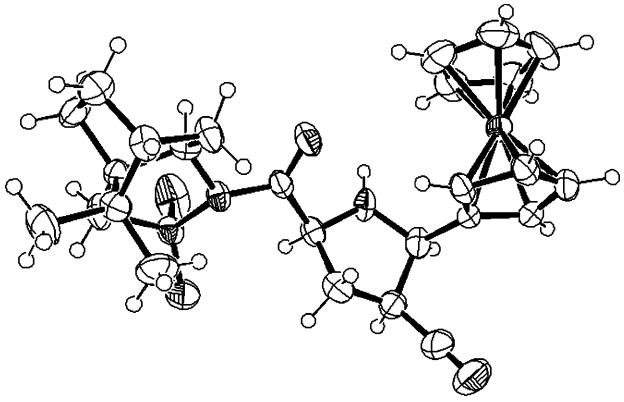


Figure 2. ORTEP drawing of cycloadduct **13**.

the pyrrolidine derivative **15** as the only cycloadduct in 55% yield. The absolute stereochemistry of this cycloadduct was easily determined by the characteristic upfield shift of the 4-CO_2Me ^1H NMR signal due to the shielding effect of the *cis*-ferrocenyl group.[8] Also, the stereochemistry of the previous cycloadducts which are resulted from transition state proposed in Fig. 3 strongly support the absolute stereochemistry of cycloadduct **15**. The transition state in Fig. 3 is based on the Oppolzer–Curran model on the selectivity of this

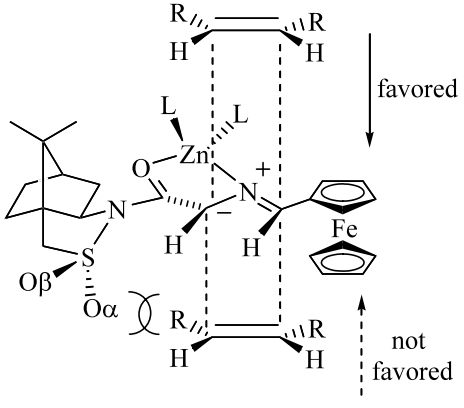


Figure 3. Possible transition state based on the Oppolzer–Curran model.

sultam auxiliary. In this transition state, dipolarophiles approach the *E*,*E*-ylide **5** in an *endo* mode from the upper face to give the *cis* arrangement of all substituents.

In the literature study, a phenyl group is used in place of the ferrocenyl group and the diastereofacial selectivity is in the range 4/1–8/1, which is the usual selectivity of this auxiliary. The very high diastereofacial selectivity observed in this study can therefore be attributed to the ferrocenyl group, which adds more steric hindrance to the *re*-face of the ylide **5**, thus the approach of the dipolarophile from this side is almost forbidden. Although diethylzinc is used as the Lewis acid, we believe that the ligands on the zinc in the transition state are chlorides from $Et_3N{\cdot}HCl$ formed at the very beginning of the reaction. As mentioned above, one ethyl group of diethylzinc reacts with $Et_3N{\cdot}HCl$ and the other ethyl group reacts with the imine to remove the α-proton. This also explains why no ethyl group transfer from diethylzinc to the ester functionality of the cycloadducts takes place.

In conclusion, a Lewis acid (diethylzinc)-mediated version of the auxiliary controlled 1,3-dipolar cycloaddition reactions of chiral azomethine ylides was successfully applied to the asymmetric synthesis of ferrocenyl-substituted pyrrolidine derivatives. All new pyrrolidine derivatives were characterized by ^1H and ^{13}C NMR, IR, and mass spectroscopic techniques. Products were obtained in reasonable yields (52–76%) with very high regio- and stereoselectivities.

3. Experimental

Melting points (mp) are uncorrected and were recorded on a Reichter 7905 apparatus. Optical rotations were measured on a Rudolph Research Analytical Automatic Polarimeter (AUTOPOL IV). Elemental analysis was recorded on a Elemental Analysis Instrument CHNS-932 (LECO). IR spectra were recorded on a Perkin Elmer 1600 series FT-IR spectrometer and reported in reciprocal centimeters (cm^{-1}). ^1H and ^{13}C NMR spectra were obtained in CCl_4–$CDCl_3$ (2/3) solvent system and recorded with a Bruker Spectrospin Avance DPX-400 Ultrashield instrument. Chemical shifts are given in parts per million (δ) downfield from tetramethylsilane as internal standard. The numbering system used in the experimental corresponds to the current CA index names. All the reactions were carried out under an argon atmosphere unless stated. Air sensitive liquids were transferred via syringe through rubber septa. Degassing was performed under vacuum. Reagent grade solvents were used for all extraction and chromatography. The following solvents and reagents were purified and dried beyond commercial reagent grade as follows: tetrahydrofuran, dimethylformamide, triethylamine were distilled from CaH_2. Thin layer chromatography (TLC) analysis was performed on E. Merck 0.25 mm precoated silica gel 60 F-254 and visualized with UV illumination followed by charging with either 5% anisaldehyde in (95:5:1) EtOH–AcOH–

H_2SO_4 or 0.3% ninhydrin in (97:3) *n*-BuOH–AcOH. Preparative TLC separations were performed on the same type of plates (layer thickness 0.5 mm). Flash column chromatography was carried out using E. Merck silica gel 60 (Merck 60, 0.040–0.060 nm). R_f values were determined in hexane/EtOAc (1/1 or 3/1) mixed solvent systems.

3.1. Synthesis of glycyl sultam, 3

To a stirred solution of the Oppolzer's Sultam **6** (4.4 g, 20.5 mmol) in dry THF (~0.3 M) at 0 °C was added NaH (820 mg, 20.5 mmol, 60% oil dispersion). The reaction mixture was stirred for 30 min at this temperature and then cooled to –40°C. To this mixture was added azidoacetyl chloride (2.83 g, 23.6 mmol) dropwise. When all the sultam **1** was consumed, monitored by TLC, the reaction mixture was quenched with water, organic phase was separated and the aqueous phase was extracted with EtOAc (3×20 mL). The combined organic layers were dried over $MgSO_4$, concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (10:1 hexane/EtOAc) to give pure azido acetyl sultam **2** in 80% yield; R_f=0.68 in 2:1 hexane/EtOAc; ^{1}H NMR ($CDCl_3$): δ 4.22 (d, J=17.3 Hz, 1H, 0.5 CH_2N_3), 4.18 (d, J=17.3 Hz, 1H, 0.5 CH_2N_3), 3.90 (m, 1H, H-7a), 3.45 (d, J=13.7 Hz, 1H, 0.5 CH_2SO_2), 3.43 (d, J=13.8 Hz, 1H, 0.5 CH_2SO_2), 2.24–2.09 (m, 2H), 1.93–1.87 (m, 3H), 1.47–1.35 (m, 3H), 1.14 (s, 3H), 0.98 (s, 3H).

Azidoacetyl sultam **2** (4.23 g, 14.2 mmol) was dissolved in THF (60 mL) and stirred with Ph_3P (4.77 g, 14.2 mmol) and H_2O (1 mL) at room temperature for 12 h. TLC analysis showed the complete consumption of the starting material. The mixture was diluted with THF (60 mL) and acidified with HCl (1N, 20 mL). The aqueous layer was separated, extracted with EtOAc (5×50 mL), neutralized with $NaHCO_3$ and extracted with CH_2Cl_2 (5×50 mL). The combined organic layers were dried over $MgSO_4$ and concentrated. The crude product was dissolved in THF+Et_2O (10+90 mL) and HCl gas (obtained by dropwise addition of 37.5% HCl to 98% H_2SO_4) was bubbled into the solution until cloudy mixture becomes clear by precipitation of white solids). The solid was filtered and washed with ether to give desired glycyl sultam **3** as its HCl salt in 85% yield; ^{1}H NMR (D_2O): δ 3.94 (m, 2H), 3.82 (t, J=5.2 Hz, 1H), 3.63 (d, J=14.4 Hz, 1H, 0.5 CH_2SO_2), 3.51 (d, J=14.3 Hz, 1H, 0.5 CH_2SO_2), 1.98 (m, 1H), 1.76 (m, 4H), 1.23 (m, 1H), 1.10 (m, 1H), 0.86 (s, 3H), 0.75 (s, 3H).

3.2. General procedure for 1,3-dipolar cycloaddition reactions

Glycyl sultam **3** salt (250 mg, 0.81 mmol), Et_3N (0.13 mL) and ferrocenecarboxaldehyde (174 mg, 0.81 mmol) were mixed in benzene (11 mL) at reflux temperature for 2 h. The reaction mixture was cooled to 0°C and dry THF (0.50 mL), Et_2Zn (0.78 mL of 1.1 M, Et_2Zn in hexanes or toluene, 0.85 mmol) and *N*-phenylmaleimide (**6**, 280 mg, 1.62 mmol), *N*-methylmaleimide (**7**, 180 mg, 1.62 mmol), methyl acrylate (**10**, 0.146 mL, 1.62 mmol), acrylonitrile (**12**, 0.232 mL, 3.50 mmol), or dimethyl maleate (**14**, 0.10 mL, 0.81 mmol) was added. After stirring the reaction mixture at this temperature for 15 min, the flask was warmed to rt and stirred for about 20 h. The reaction mixture was hydrolyzed with water. The organic phase was separated and the aqueous phase was extracted with EtOAc (3×20 mL). The combined organic layers were dried over $MgSO_4$, concentrated in vacuo and the residue was purified by flash column chromatography

3.3. [1*S*-[(1*S**,3*R**,3a*S**,6a*R**),3aα,6α,7aβ]]-3*H*-3a,6-Methano-2,1-benzisothiazole, hexahydro-8,8-dimethyl-1-[(hexahydro-4,6-diaxo-3-ferrocenyl-5-phenylpyrrolo[3,4-*c*]pyrrol-1-yl)carbonyl]-2,2-(S_S)-dioxide, 8

Azomethine ylide **5** was trapped with *N*-phenylmaleimide as described in the general experimental procedure to give cycloadduct **8**. Flash column chromatography (SiO_2 2:1 hexane/EtOAc) 64% yield; R_f= 0.15 in 3:1 hexane/EtOAc; mp 236–38°C; $[\alpha]_D^{29}$=–28.7° (*c* 0.67, CH_2Cl_2, *d*=0.5 dm); ^{1}H NMR: δ 7.33–7.09 (m, 5H, Ph), 4.59 (d, J=6.5, 1H, H-1), 4.44 (d, J=8.9, 1H, H-3), 4.27 (s, 1H, ferrocene), 4.21 (s, 1H, ferrocene), 4.15 (s, 1H, ferrocene), 4.15 (s, 5H, ferrocene), 4.13 (s, 1H), 3.99 (t, J=6.8 Hz, 1H), 3.99 (s, 1H, H-6a), 3.51 (d, J=13.6 Hz, 1H, 0.5 CH_2SO_2), 3.56 (d, J=13.6 Hz, 1H, 0.5 CH_2SO_2), 3.40 (t, J=8.4 Hz, 1H, H-3a), 2.60 (d, J=2.42 Hz, 1H), 2.60 (s, 1H, N-H), 2.02 (m, 1H), 1.92 (m, 3H), 1.50–1.34 (m, 2H), 1.28 (s, 3H), 0.98 (s, 3H); ^{13}C NMR: δ 174.4, 173.3, 167.5, 131.6, 128.6, 127.9, 126.0, 84.3, 68.7 (5C), 68.5, 68.3, 67.8, 65.5, 64.8, 62.5, 60.6, 53.0, 50.7, 48.6, 47.8, 44.4, 37.1, 32.8, 26.6, 20.2, 20.1; IR ($CDCl_3$): 2962.8, 2252.0, 1717.3, 1598.8, 1500.2, 1267.6, 1134.8, 796.1, 782 cm^{-1}. Anal. calcd for $C_{33}H_{35}FeN_3O_5S$: C, 61.78; H, 5.50; N, 6.55; S, 5.00. Found: C, 61.65; H, 5.30; N, 6.50; S, 5.08%.

3.4. [1*S*-[(1*S**,3*R**,3a*S**,6a*R**),3aα,6α,7aβ]]-3*H*-3a,6-Methano-2,1-benzisothiazole, hexahydro-8,8-dimethyl-1-[(hexahydro-4,6-diaxo-3-ferrocenyl-5-methylpyrrolo[3,4-*c*]pyrrol-1-yl)carbonyl]-2,2-(S_S)-dioxide, 9

Trapping the ylide **5** with *N*-methylmaleimide furnished cycloadduct **9**. Flash column chromatography (SiO_2 2:1 hexane/EtOAc) 76% yield; R_f=0.51 in 1:1 hexane/EtOAc; mp 242–44°C; $[\alpha]_D^{29}$=–18.7 (*c* 0.67, CH_2Cl_2); ^{1}H NMR: δ 4.45 (brs, 1H, H-1), 4.33 (brs, 1H, H-7a), 4.23 (s, 1H, ferrocene), 4.19 (s, 2H, ferrocene), 4.15 (s, 4H, ferrocene), 4.11 (s, 1H, ferrocene), 4.07 (t, J=5.0 Hz, 1H), 3.80 (t, J=6.8 Hz, 1H, H-6a), 3.54 (d, J=13.5 Hz, 1H, 0.5 CH_2SO_2), 3.47 (d, J=13.5 Hz, 1H, 0.5 CH_2SO_2), 3.47 (t, J=7.9 Hz, 1H, H-3a), 2.89 (brs, 1H), 2.73 (s, 3H, N-Me), 2.64 (d, J=13.2 Hz, 1H), 2.06 (m, 1H), 1.94 (m, 3H), 1.53 (m, 1H), 1.40 (m, 1H), 1.29 (s, 3H), 0.99 (s, 3H); ^{13}C NMR: δ 176.09, 174.94, 168.19, 77.59, 77.27, 76.95, 69.6 (5C), 65.9, 62.9, 60.6, 53.6, 50.7, 50.3, 49.1, 48.3, 45.1, 37.5, 33.3, 27.1, 25.2, 20.7, 20.6; IR ($CDCl_3$): 1707.8, 1543.4, 1332.8, 1244.4, 1132, 1047.2, 804.7, 785.8, 775.9, 772, 726.5, 534.5, 494.1, 478.2, 457.9 cm^{-1}. Anal. calcd for $C_{28}H_{33}FeN_3O_5S$: C, 58.03; H, 5.74; N, 7.25; S, 5.20. Found: C, 57.90; H, 5.78; N, 7.12; S, 5.08%.

3.5. [3a*S*-[(2*R**,3*S**,5*S**),3aα,6α,7aβ]]-3-Pyrrolidinecarboxylic acid, 2-ferrocenyl-5-[(tetrahydro-8,8-dimethyl-3*H*-3a,6-methano-2,1-benzisothiazol-1(4*H*)carbonyl] methyl ester (S_S)-dioxide, 11

Azomethine ylide **5** was trapped with methyl acrylate as described in the general experimental procedure to give cycloadduct **11**. Flash column chromatography (SiO_2 6:1 hexane/EtOAc) 59% yield; R_f = 0.71 in 1:1 hexane/EtOAc; mp 210–12°C; $[\alpha]_D^{29}$ = +7.8 (*c* 0.67, CH_2Cl_2); ^{1}H NMR: δ 4.34–4.28 (brs, 3H, ferrocene+H-2+H-5), 4.19 (s, 5H, ferrocene), 4.13 (s, 1H, ferrocene), 4.08 (s, 1H, ferrocene), 4.03 (s, 1H, ferrocene), 3.97 (t, *J* = 6.1 Hz, 1H, H-7a), 3.52 (d, *J* = 13.4 Hz, 1H, 0.5 CH_2SO_2), 3.45 (d, *J* = 13.6 Hz, 1H, 0.5 CH_2SO_2), 3.34 (s, 3H, 3-COOMe), 3.25 (m, 1H, H-3), 2.94 (brs, 1H, N-H), 2.52–2.32 (m, 1H, H-4), 2.16 (brs, 2H), 2.11–2.03 (m, 1H, H-4), 1.92 (brs, 3H), 1.53–1.41 (m, 2H), 1.15 (s, 3H), 0.98 (s, 3H); ^{13}C NMR: δ 173.3, 172.1, 88.5, 69 (5C), 68.8, 68.4, 68.1, 65.8, 65.5, 61.2, 61.1, 53.3, 51.5, 50.8, 49.1, 48.2, 44.9, 38.7, 34.1, 33.1, 27.0, 21.2, 20.3; IR ($CHCl_3$): 3023.9, 2956.8, 1732.1, 1457.5, 1336.1, 1272.7, 1229.1, 1168.3, 1134.1, 820.6, 772, 756.5, 740.1, 535.8, 493.9, 478 cm^{-1}. Anal. calcd for $C_{27}H_{34}FeN_2O_5S$: C, 58.49; H, 6.18; N, 5.05; S, 5.78. Found: C, 58.34; H, 6.23; N, 5.08; S, 5.75%.

3.6. [3a*S*-[2*R**,3*S**,5*S**),3aα,6α,7aβ]]-5-[(Tetrahydro-8,8-dimethyl-3*H*-3a,6-methano-2,1-benzisothiazol-1(4*H*)carbonyl]-2-ferrocenylpyrrolidine-3-carbonitrile (S_S)-dioxide, 13

Glycycl sultam and ferrocenecarboxaldehyde were refluxed in toluene to give azomethine ylide **5** that was trapped with acrylonitrile under similar reaction conditions as explained in the general experimental procedure to give cycloadduct **13**. Flash column chromatography (SiO_2 2:1 hexane/EtOAc) 52% yield; R_f = 0.6 in 1:1 hexane/EtOAc; mp 192–93°C; $[\alpha]_D^{29}$ = −23.8 (*c* 0.67, CH_2Cl_2); ^{1}H NMR: δ 4.46 (s, 1H, ferrocene), 4.35 (t, *J* = 7.1 Hz, 1H, H-5), 4.22–4.13 (brs, 10H, ferrocene and H-2), 3.97 (t, *J* = 6.0 Hz, 1H, H-7a), 3.47 (d, *J* = 14.1 Hz, 1H, 0.5 CH_2SO_2), 3.43 (d, *J* = 14.2 Hz, 1H, 0.5 CH_2SO_2), 3.11 (m, 1H, H-3), 2.66 (m, 1H, H-4), 2.25 (m, 1H, H-4), 2.14 (brs, 2H), 1.91 (brs, 3H), 1.48 (m, 1H), 1.40 (m, 1H), 1.15 (s, 3H), 0.99 (s, 3H); ^{13}C NMR: δ 172.3, 119.2, 86.5, 77.6, 77.3, 76.9, 69.2 (5C), 68.7, 66.4, 65.7, 61.2, 60.4, 53.3, 49.2, 48.2, 44.9, 38.5, 33.6, 36.4, 33.1, 26.9, 21.1, 20.3; IR ($CDCl_3$): 2250.9, 1696, 1339.8, 1271, 1135.4, 998.9, 915.3, 816.2, 786.2, 771.8, 755.8, 740.9, 726.2, 538.4, 494.2, 478 cm^{-1}. Anal. calcd for $C_{26}H_3FeN_3O_3S$: C, 59.89; H, 5.99; N, 8.06; S, 6.15. Found: C, 60.01; H, 6.11; N, 8.02; S, 5.97%. Anal. calcd for $C_{26}H_{31}FeN_3O_3S$: C, 59.89; H, 5.99; N, 8.06; S, 6.15. Found: C, 59.80; H, 6.02; N, 8.20; S, 6.10%.

3.7. [2*S*-[(2*S**,3*R**,4*S**,5*R**)]]-3,4-Pyrrolidine carboxylic acid, 2-ferrocenyl-5-[(tetrahydro-8,8-dimethyl-3*H*-3a,6-methano-2,1-benzisothiazol-1(4*H*)-yl)carbonyl] dimethyl ester (S_S)-dioxide, 15

Azomethine ylide **5** was trapped with dimethylmaleate as described in the general experimental procedure to give cycloadduct **15**. Flash column chromatography (SiO_2 2:1 hexane/EtOAc) 51% yield; R_f = 0.4 in 1:1 hexane/EtOAc; mp 218–20°C; $[\alpha]_D^{29}$ = −3.4 (*c* 0.67, CH_2Cl_2); ^{1}H NMR: δ 4.41 (brs, 1H, H-2), 4.16–4.04 (9H, ferrocene, H-5, and H-7a), 3.84 (t, *J* = 17.2 Hz, 1H, H-3), 3.56 (s, 3H, 3-COOMe), 3.50 (d, *J* = 13.6 Hz, 1H, 0.5 CH_2SO_2), 3.38 (d, *J* = 13.6 Hz, 1H, 0.5 CH_2SO_2), 3.30 (s, 4H, 4-CO_2M_e+ H-4), 2.47 (m, 1H), 2.21 (m, 1H), 1.89 (m, 3H), 1.51 (m, 1H), 1.39 (m, 1H), 1.29 (s, 3H), 1.01 (s, 3H); ^{13}C NMR: δ 171.5, 170.5, 168.8, 84.1, 77.6, 77.3, 77.1, 69.3 (5C), 68.1, 67.9, 67.6, 66.9, 65.8, 62.3, 61.2, 60.5, 54.3, 53.3, 53.1, 52.1, 51.5, 49.1, 48.1, 45.4, 39.133.5, 26.8, 22.1, 20.4; IR ($CDCl_3$): 1742.3, 1545, 1437.4, 1334, 1242.1, 1204.1, 1134.8, 1053.9, 800.7, 786, 771.9, 755.8, 740.4, 730.2, 537.5, 494.1, 478.1 cm^{-1}. Anal. calcd for $C_{29}H_{36}FeN_2O_7S$: C, 56.87; H, 5.92; N, 4.57; S, 5.24. Found: C, 56.95; H, 6.14; N, 4.48; S, 5.20%.

Acknowledgements

We thank the Scientific and Technical Research Council of Turkey (TUBITAK, Grant No. TBAG-2119) and Middle East Technical University Research Foundation for the financial support.

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10. Inquiries concerning the X-ray structures of **11** and **13** should be addressed to Ü. Dinçer and C. Arici. Crystallographic data for structures **11** and **13** have been deposited with the CCDC as supplementary publication no. CCDC 190152 and 190153, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).