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# Conversion of homochiral amines and α-amino esters to their chiral 1,2,3,5-substituted pyrrole derivatives via gold-catalysed amination/annulation reactions of 2-propynyl-1,3-dicarbonyl compounds

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**Abstract**—Homochiral primary amines, amino alcohols and α-amino esters have been reacted with 2-propynyl-1,3-dicarbonyl compounds under gold catalysis leading to 1,2,5-trisubstituted 3-acylpyrrole derivatives in moderate to high yields and high enantiomeric excess. 

## 1. Introduction

Pyrrole derivatives represent a class of heterocycles of great importance because they very frequently display biological activity and are also versatile building blocks in organic synthesis.[1] Although many efficient syntheses of pyrroles have been reported, developing new synthetic methods remains an attractive goal.[2a–g] Special attention is devoted to the asymmetric synthesis of heterocyclic compounds due to the enantiospecificity shown by most biological systems in their responses to drugs and to the regulatory pressure[3] on the pharmaceutical industry to market chiral drugs as single enantiomers.[4] Chiral pyrrole derivatives of amines and amino acids are important starting materials for the synthesis of many different biologically active compounds. A short, enantiogenic syntheses[5] of (−)-indolizidine 167B, (+)-monomorine and indolizidine alkaloids[6] based on the reaction of pyrrole derivatives of amino acids has been reported. However, there are limited reports on the preparation of enantiomers of pyrrole derivatives having **1-N** directly linked to the stereogenic center.[7a–c] 1,2,5-Trisubstituted-3-acylpyrrole derivatives[8] were found to show potent inhibiting activity of platelet aggregation[9] and were worthy of clinical testing as antihypertensive agents.[10] During the course of structure–activity relationship studies on these pharmaceutically relevant compounds, we became interested in developing methodologies for the preparation of pyrrole derivatives in homochiral form for subsequent biological evaluation following the new regulatory guidelines.

We describe herein the extension of a new synthetic methodology of the target 1,2,5-trisubstituted pyrroles through gold-catalysed sequential amination/annulation reactions[11] for the preparation of these compounds in homochiral form.

## 2. Results and discussion

Enantiomerically pure amines, β-amino alcohols and α-amino esters **2a**–**2i** were used as the starting materials for the synthesis of the chiral pyrrole derivatives **3a**–**3j** (Scheme 1, Table 1).

The reaction of primary amines with 2-propynyl-1,3-dicarbonyls led to enaminone derivatives[12] **4**, which undergo regioselective cycloamination to pyrroles **3** under the catalytic action of $NaAuCl_4 \cdot 2H_2O$ (Scheme 2). The above formation of **3** has been suggested to proceed by the *anti*-addition of nitrogen and gold moieties in a 5-*exo*-*dig* manner to the acetylenic bond to

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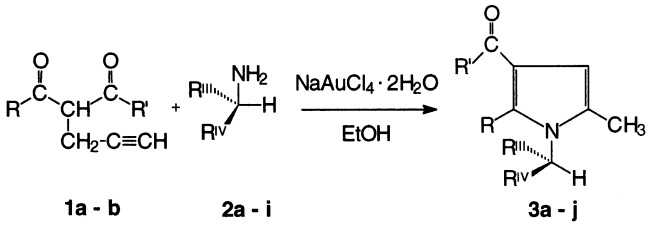
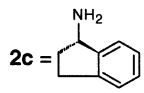



**1a**: R = $R^{II}$ = -$CH_3$
**1b**: R = -$CH_3$; $R^{II}$ = OEt
**2a**: $R^{III}$ = -Ph; $R^{IV}$ = -$CH_3$
**2b**: $R^{III}$ = -$CH_3$; $R^{IV}$ = -Ph
**2d**: $R^{III}$ = -$CH_2$-OH; $R^{IV}$ = -$CH_2$-$CH_3$
**2e**: $R^{III}$ = -COOEt; $R^{IV}$ = -CH-$(CH_3)_2$
**2f**: $R^{III}$ = -COOEt; $R^{IV}$ = -$CH_2$-$CH_2$-COOEt
**2g**: $R^{III}$ = -$COOCH_2Ph$; $R^{IV}$ = -$(CH_2)_4$-NH-$COOCH_2Ph$
**2h**: $R^{III}$ = -$COOCH_3$; $R^{IV}$ = $CH_2$-$CH_2$-S-$CH_3$
**2i**: $R^{III}$ = -$COOCH_2Ph$; $R^{IV}$ = -$CH_2$-$C_6H_4$-*p*-OH




**Scheme 1.**

give the vinylaurate species **5**. Subsequent protonolysis of the $Csp^2$–Au bond and isomerization reactions afford the pyrroles **3**.

Regio- and chemosolective interaction with the acetylenic bond is one of the interesting features of gold(III) catalysis.[13] Even though various metal salts have been reported to effectively catalyse the intramolecular addition of the amine to the alkyne,[14] gold catalysts have been reported to show higher activity in the condensation step of ketones with amines compared to other transition metal catalysts.[11] The absolute stereochemistry of **3a**–**3j** can be assigned based on the assumption that the stereogenic centre in the starting amine is not affected during this transformation. It should be pointed out that the enantiomeric excess of the resulting products **3** was always identical with that of the corresponding starting amine derivatives, thus demonstrating the complete stereospecificity of the reaction sequence. E.e.s were determined by enantioselective HPLC analyses (Fig. 1). During the condensation reaction of 1,4-dicarbonyl compounds and their masked equivalents[15] with α-amino esters for the formation of the pyrrole ring (Paal–Knorr synthesis), partial racemization often occurs. The mild reaction conditions of this new methodology avoid this drawback.

## 3. Conclusion

In conclusion, we have developed a new simple and efficient synthetic methodology for the preparation of 1,2,5-trisubstituted-4-acylpyrroles in homochiral form through sequential gold-catalysed amination/annulation reactions of 2-propynyl-1,3-dicarbonyl compounds with chiral amines, amino alcohols and α-amino esters. In this synthetic procedure readily available compounds are used and the reactions proceed under mild conditions.

## 4. Experimental

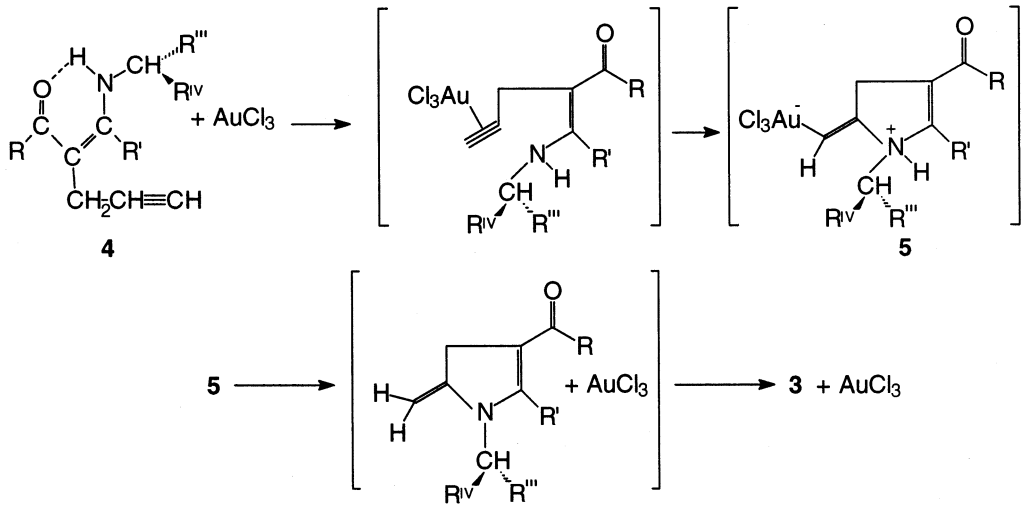
### 4.1. General methods

Optical rotations were measured on a Perkin Elmer R 241 polarimeter. $^1H$ and $^{13}C$ NMR spectra were recorded with a Bruker AC 200 E spectrometer. EI (70 eV) mass spectra were recorded with a Saturn 2100T GC/MS Varian instrument and APCI/Ms-Ms spectra with a TSQ 700 Finnigan/Mat instrument. IR spectra were recorded with a Perkin–Elmer 683 spectrometer. Only the most significant IR absorptions are given. CHN analyses were recorded with a Eurovector EA3000 instrument. All starting materials, $NaAuCl_4 \cdot 2H_2O$ (Aldrich), and solvents if not otherwise stated, are commercially available and were used as purchased, without further purification. The 2-propynyl-1,3-dicarbonyl derivatives **1a**–**1b** were prepared[16] by alkylation reaction of 1,3-dicarbonyl compounds with propargyl bromide and DBU in toluene. All reactions

**Table 1.** Preparation of 1,2,5-trisubstituted-3-acylpyrroles

| Entry | Compound **1** | Compound **2** | Product **3** | Time (h) | Yield[a] (%) | E.e.[b] (%) | $[\alpha]_D^{20}$ (c)[c] |
|---|---|---|---|---|---|---|---|
| 1 | **1a** | **2a** | (*S*)-**3a** | 2 | 98 | 99 | −12.8 (0.6) |
| 2 | **1a** | **2b** | (*R*)-**3b** | 2 | 96 | 97 | +12.8 (0.6) |
| 3 | **1a** | **2c** | (*R*)-**3c** | 5 | 95 | 98 | −1.5 (0.9) |
| 4 | **1a** | **2d** | (*S*)-**3d** | 3 | 86 | 98 | −16.4 (0.7) |
| 5 | **1b** | **2a** | (*S*)-**3e** | 12 | 80 | 98 | −35.8 (0.4) |
| 6 | **1a** | **2e**[d] | (*S*)-**3f** | 8 | 88 | 99 | −108.7 (0.6) |
| 7 | **1a** | **2f**[d] | (*S*)-**3g** | 7 | 64 | 96 | −60.2 (0.5) |
| 8 | **1a** | **2g**[d] | (*S*)-**3h** | 7 | 74 | 99 | −29.1 (0.9) |
| 9 | **1a** | **2h**[d] | (*S*)-**3i** | 7 | 64 | 96 | −77.7 (0.4) |
| 10 | **1a** | **2i**[e] | (*S*)-**3j** | 7 | 50 | 98 | −101.7 (0.6) |

[a] Yields refer to isolated and purified materials.
[b] Determined by enantioselective HPLC.
[c] Measured in $CHCl_3$ solution.
[d] As hydrochloride salt.
[e] As *p*-toluenesulfonate salt.




**Scheme 2.**

were carried out under nitrogen. Temperatures are reported as bath temperature. Solvents used in extraction and purification were distilled prior to use. Compounds were visualised on analytical thin-layer chromatograms (TLC) by UV light (254 nm). The products, after usual work-up, were purified by flash chromatography on silica gel (230–400 mesh) eluting with *n*-hexane/ethyl acetate mixtures. HPLC analyses were performed on a Chiralcel OD column (250×4.6 mm) or on a Chiralpak AD column (250×4.6 mm); mobile phase hexane/*iso*-propanol 85:15 or 95:5; flow rate 0.8 ml/min; *T* 30°C; detection wavelength 280 or 230 nm.

### 4.2. General procedure for the synthesis of 1,2,3,5-substituted pyrroles 3a–3j

To a solution of **1a**–**1b** and amine **2a**–**2d** in ethanol, $NaAuCl_4{\cdot}2H_2O$ was added at room temperature under a nitrogen atmosphere using the following molar ratios: **1**:**2**:$NaAuCl_4{\cdot}2H_2O$ = 1:1.5:0.05. The reaction mixture was heated (40°C) and stirred for an additional period, monitoring the reaction by TLC. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel ($SiO_2$, hexane/ethyl acetate mixtures), to give **3a**–**3e**.

To a solution of **1a**, α-amino ester salt (hydrochloride or *p*-toluenesulfonate) **2e**–**2i** and sodium ethoxide in ethanol, was added $NaAuCl_4{\cdot}2H_2O$ at room temperature under a nitrogen atmosphere using the following molar ratios: **1**:**2**:NaOEt:$NaAuCl_4{\cdot}2H_2O$ = 1:1.5:1.5:0.05. The reaction mixture was heated (60°C) and stirred for an additional period, while monitoring the reaction by TLC. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel ($SiO_2$, hexane/ethyl acetate mixtures), to give **3f**–**3j**.

Selected data for these compounds are as follows.

**4.2.1. (*S*)-(−)-1-[2,5-Dimethyl-1-(1-phenyl-ethyl)-1*H*-pyrrol-3-yl]ethanone 3a**. $[\alpha]_D = -12.8$; IR (film): $\nu = 1650$ $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$): $\delta = 7.33$–$7.25$ (m, 3H, Ar-H), 7.08–7.02 (m, 2H, Ar-H), 6.24 (s, 1H, =C-H), 5.54 (q, $J = 8.4$ Hz, 1H, HC(Ph)-$CH_3$), 2.46 (s, 3H, 2-$CH_3$), 2.38 (s, 3H, $CH_3$-CO), 2.02 (s, 3H, 5-$CH_3$), 1.86 (d, $J = 8.4$ Hz, 3H, $CH_3$-CH-Ph); $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta = 195.1$ (C=O), 140.7, 135.7, 129.2, 128.6, 127.8, 127.2, 125.8, 109.5, 52.4 (CH(Ph)-$CH_3$), 28.6 ($CH_3$-CO), 18.7 ($CH_3$-CH-Ph), 13.6 ($CH_3$), 12.6 ($CH_3$); MS (APCI/Ms-Ms): 242 ($M^+$+1), 200, 138, 105; anal. calcd for $C_{16}H_{19}NO$: C, 79.63; H; 7.94; N, 5.80; found: C, 79.60; H, 7.98; N, 5.72%.

**(*R*)-(+)-1-[2,5-Dimethyl-1-(1-phenyl-ethyl)-1*H*-pyrrol-3-yl]ethanone 3b** has been previously described.[11]

**4.2.2. (*R*)-(−)-1-(1-Indan-1-yl-2,5-dimethyl-1*H*-pyrrol-3-yl)ethanone 3c**. $[\alpha]_D = -1.5$; IR (film): $\nu = 1680$ $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$): $\delta = 7.26$–$7.19$ (m, 3H, Ar-H), 6.94–6.90 (m, 1H, Ar-H), 6.20 (s, 1H, =C-H), 5.82 (m, 1H, HC(Ph)-$CH_2$), 3.14–3.04 (m, 2H, -$CH_2$-CH-N), 2.68 (s, 3H, 2-$CH_3$), 2.44 (s, 6H, $CH_3$-CO+5-$CH_3$), 2.34–2.15 (m, 2H, -$CH_2$-$CH_2$); $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta = 194.8$ (C=O), 142.3, 1141.9, 141.3, 128.0, 127.7, 126.9, 125.0, 124.7, 123.8, 110.5, 59.7 (CH(Ph)-$CH_2$), 30.2 (-$CH_2$-CH-N), 28.5 ($CH_3$-CO), 27.9 (-$CH_2$-$CH_2$), 13.9 ($CH_3$), 13.0 ($CH_3$); MS: $m/z$ (%) = 253 (36) [$M^+$], 137 (49), 117 (100), 91 (18); anal. calcd for $C_{17}H_{19}NO$: C, 80.60; H, 7.56; N, 5.53; found: C, 80.55; H, 7.63; N, 5.49.

**4.2.3. (*S*)-(−)-1-[1-(Hydroxymethyl-propyl)-2,5-dimethyl-1*H*-pyrrol-3-yl]ethanone 3d**. $[\alpha]_D = -16.4$; IR (film): $\nu =$ 3350, 1650 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$): $\delta = 6.14$ (s, 1H, =C-H), 4.20–4.05 (m, 1H, HC($CH_2$)-$CH_2OH$), 3.93–3.77 (m, 2H, -$CH_2OH$) 2.54 (s, 3H, 2-$CH_3$), 2.26 (s, 3H, $CH_3$-CO), 2.25 (s, 3H, 5-$CH_3$), 1.95–1.73 (m, 2H, -$CH_2$-$CH_3$), 0.84 (t, $J = 7.4$ Hz, 3H, -$CH_2CH_3$) $^{13}C$

NMR (50 MHz, $CDCl_3$): $\delta = 196.1$ (C=O), 136.1, 130.1, 120.1, 108.5, 63.8 (-$CH_2$OH), 61.1 (HC($CH_2$)-$CH_2$OH), 28.1, 23.5, 20.6, 13.4 10.8; MS: $m/z$ (%) = 209 (94) [$M^+$], 194 (43), 137 (54), 122 (100); anal. calcd for $C_{12}H_{19}NO_2$: C, 68.87; H, 9.15; N, 6.69; found: C, 68.91; H, 9.03; N, 6.75%.

**4.2.4. (*S*)-(−)-2,5-Dimethyl-l(1-phenyl-ethyl)-1*H*-pyrrole-3-carboxylic acid ethyl ester 3e**. $[\alpha]_D = -35.8$; IR (film): $\nu = 1720$ cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$): $\delta = 7.32$–7.24 (m, 3H, Ar-H), 7.07–7.02 (m, 2H, Ar-H), 6.28 (s, 1H, =C-H), 5.54 (q, $J = 7.0$ Hz, 1H, -CH(Ph)$CH_3$), 4.23 (q, $J = 7.1$ Hz, 2H, -O$CH_2CH_3$), 2.42 (s, 3H, 2-$CH_3$),

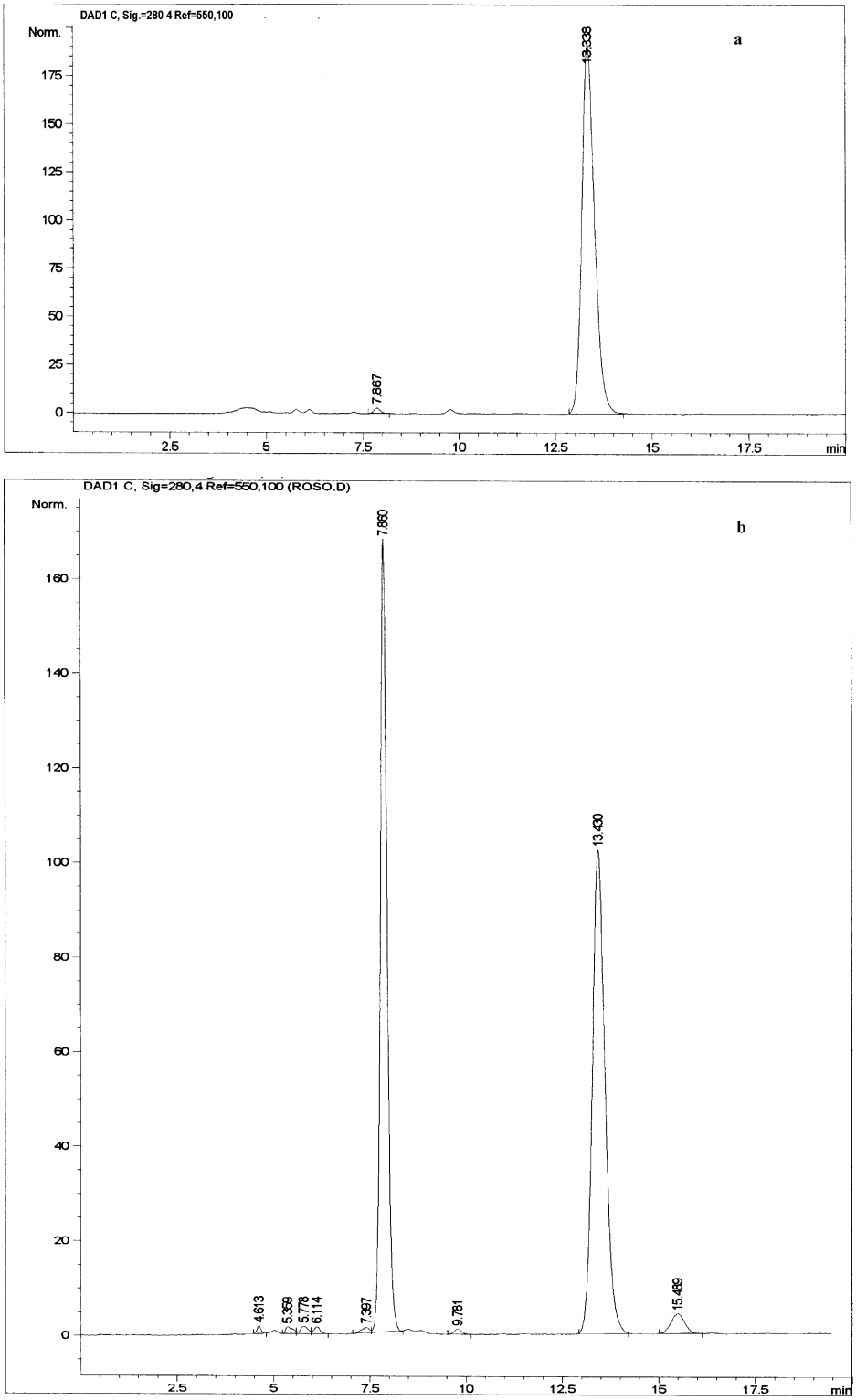



**Figure 1.** Chromatogram of (*S*)-**3a**: (a) in comparison with an (*RS*) mixture; (b) (Chiracel OD column, Daicel Chemichal Co., Ltd, 250×4.6 mm, eluant: *n*-hexane/*iso*-propanol 85/15, flow rate: 0.8 mL/min).

1.99 (s, 3H, 5-$CH_3$), 1.86 (d, $J=7.0$ Hz, 3H, $\underline{CH_3}$-CH(Ph)), 1.29 (t, $J=7.1$ Hz, 3H, -$CH_2\underline{CH_3}$); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta=165.7$ (OC=O), 141.0, 135.7, 128.6, 128.0, 127.1, 125.8, 111.1, 108.6, 59.1 ($\underline{CH}$(Ph)-$CH_3$), 52.6 ($\underline{CH_2}$O-CO), 21.7, 18.8, 14.5, 13.9; MS: $m/z$ (%)=271 (49) [M$^+$], 226 (15), 167 (51), 105 (100); anal. calcd for $C_{17}H_{21}NO_2$: C, 75.25; H, 7.80; N, 5.16; found: C, 75.17; H, 7.84; N, 5.21%.

**4.2.5. (*S*)-(−)-2-(3-Acetyl-2,5-dimethyl-pyrrol-1-yl)-3-methyl-butyric acid ethyl ester 3f**. $[\alpha]_D=-108.7$; IR (film): $\nu=1735$, 1640 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$): $\delta=6.21$ (s, 1H, =C-H), 4.27 (d, $J=11.0$ Hz, 1H, -$\underline{CH}$(N)CH), 4.17 (q, $J=7.1$ Hz, 2H, -O$\underline{CH_2}CH_3$), 2.57 (s, 3H, 2-$CH_3$), 2.36 (s, 3H, $CH_3$CO), 2.22 (s, 3H, 5-$CH_3$), 1.21 (t, $J=7.1$ Hz, 3H, -$CH_2\underline{CH_3}$), 1.18–1.16 (m, 1H, -$\underline{CH}(CH_3)_2$), 1.15 (d, $J=6.3$ Hz, 3H, $\underline{CH_3}$-CH), 0.64 (d, $J=6.3$ Hz, 3H, $\underline{CH_3}$-CH); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta=195.2$ (C=O), 169.4 (O-C=O), 135.6, 128.1, 120.1, 109.5, 63.7 (O$\underline{CH_2CH_3}$), 61.5 (CH(N)), 28.7, 21.3, 18.6, 14.0, 13.3, 12.2; MS: $m/z$ (%)=265 (100) [M$^+$], 250 (68), 222 (38), 208 (62), 137 (94); anal. calcd for $C_{15}H_{23}NO_3$: C, 67.90; H, 8.74; N, 5.28; found: C, 67.82; H, 8.80; N, 5.31%.

**4.2.6. (*S*)-(−)-2-(3-Acetyl-2,5-dimethyl-pyrrol-1-yl)-pentanedioic acid diethyl ester 3g**. $[\alpha]_D=-60.2$; IR (film): $\nu=1740$, 1660 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$): $\delta=6.24$ (s, 1H, =C-H), 4.95 (m, 1H, -$\underline{CH}$(N)$CH_2$), 4.22 (q, $J=7.1$ Hz, 2H, -O$\underline{CH_2}CH_3$), 4.09 (q, $J=7.2$ Hz, 2H, -O$\underline{CH_2}CH_3$), 2.38 (s, 3H, 2-$CH_3$), 2.32 (s, 3H, $CH_3$CO), 2.26–2.22 (m, 4H, -$CH_2CH_2$), 2.20 (s, 3H, 5-$CH_3$), 1.23 (dt, $J=7.2$, 7.1 Hz, 6H, -O$CH_2\underline{CH_3}$); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta=195.0$ (C=O), 172.3 (O-C=O), 169.7 (O-C=O), 135.3, 127.9, 120.5, 109.6, 62.0 (O$\underline{CH_2}CH_3$), 60.7 (CH(N)), 55.8 (O$\underline{CH_2}CH_3$), 29.8, 28.6, 25.8, 14.1, 14.0, 13.0, 12.3; MS: $m/z$ (%)=323 (100) [M$^+$], 308 (88), 280 (57); anal. calcd for $C_{17}H_{25}NO_5$: C, 63.14; H, 7.79; N, 4.33; found: C, 63.42; H, 7.64; N, 4.23%.

**4.2.7. (*S*)-(−)-2-(3-Acetyl-2,5-dimethyl-pyrrol-1-yl)-6-phenoxycarbonylamino-hexanoic acid benzyl ester 3h**. $[\alpha]_D=-29.1$; IR (film): $\nu=3350$, 1750, 1660 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$): $\delta=10.3$ (bs, 1H, NH), 7.42–7.20 (m, 10H, Ar-H), 6.20 (s, 1H, =C-H), 5.14 (s, 2H, -$OCH_2$-Ph), 5.04 (s, 2H, -$OCH_2$-Ph), 4.56–4.53 (m, 1H, -$\underline{CH}$(N)$CH_2$), 3.40–3.10 (m, 2H, -$\underline{CH_2}$NH), 2.41 (s, 3H, 2-$CH_3$), 2.33 (s, 3H, $CH_3$CO), 2.12–201 (m, 2H, -$CH_2$-$CH_2$), 2.07 (s, 3H, 5-$CH_3$), 1.51–090 (m, 4H, -$CH_2$-$CH_2$); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta=195.2$ (C=O), 169.8 (O-C=O), 156.4 (HN-C=O), 135.3, 135.0, 128.5, 128.4, 128.1, 128.0, 127.8, 120.3, 109.5, 108.0, 67.3 (O$\underline{CH_2}$Ph), 66.4 (O$\underline{CH_2}$Ph), 57.1 (CH(N)), 40.5 (HN-$\underline{CH_2}CH_2$-), 30.3, 29.4, 28.5, 23.2, 13.1, 12.4; MS/MS: $m/z$ (%)=490 (100) [M$^+$], 475 (59); anal. calcd for $C_{29}H_{34}N_2O_5$: C, 71.00; H, 6.99; N, 5.71; found: C, 70.95; H, 7.05; N, 5.63%.

**4.2.8. (*S*)-(−)-2-(3-Acetyl-2,5-dimethyl-pyrrol-1-yl)-4-methylsulfanylbutyric acid methyl ester 3i**. $[\alpha]_D=-77.7$; IR (film): $\nu=1700$, 1660 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$): $\delta=6.24$ (s, 1H, =C-H), 5.15–5.05 (m, 1H, -$\underline{CH}$(N)$CH_2$), 3.75 (s, 3H, -$OCH_3$), 2.36 (s, 3H, 2-$CH_3$), 2.30 (s, 3H, $CH_3$CO), 2.27–2.09 (m, 4H, -$CH_2$-$CH_2$), 2.27 (s, 3H, S-$CH_3$), 2.25 (s, 3H, 5-$CH_3$); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta=195.0$ (C=O), 170.5 (O-C=O), 135.2, 127.9, 120.5, 109.54.9 ($OCH_3$), 52.9 (CH(N)), 32.0, 30.3, 29.9, 28.6, 15.2, 13.1; MS: $m/z$ (%)=283 (100) [M$^+$], 194 (91); anal. calcd for $C_{14}H_{21}NO_3S$: C, 59.34; H, 7.47; N, 4.94; found: C, 59.49; H, 7.25; N, 4.70%.

**4.2.9. (*S*)-(−)-2-(3-Acetyl-2,5-dimethyl-pyrrol-1-yl)-3-(4-hydroxy-phenyl)-propionic acid phenylester 3j**. $[\alpha]_D=-101.7$. Oil; IR (film): $\nu=$, 3440, 1740, 1650 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$): $\delta=7.32–7.28$ (m, 5H, Ar-H), 6.67 (m, 4H, Ar-H), 6.22 (s, 1H, =C-H), 5.20 (s, 2H, -$OCH_2$Ph), 4.95–4.75 (m, 1H, -$\underline{CH}$(N)$CH_2$), 3.51–3.49 (m, 1H, -Ar-$\underline{CH_2}$-CH), 3.05–3.15 (m, 1H, -Ar-$\underline{CH_2}$-CH), 2.34 (s, 3H, 2-$CH_3$), 2.17 (s, 3H, $CH_3$CO), 1.85 (s, 3H, 5-$CH_3$); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta=196.2$ (C=O), 169.6 (O-C=O), 155.7, 134.8, 130.0, 128.5, 128.3, 127.4, 120.0, 115.6, 109.3, 67.5 ($OCH_2$Ph), 59.4 (CH(N)), 36.1, 28.4, 12.7, 12.4; MS: $m/z$ (%)=391 (82) [M$^+$], 376 (15), 137 (76), 91 (100); anal. calcd for $C_{24}H_{25}NO_4$: C, 73.64; H, 6.44; N, 3.58; found: C, 73.34; H, 6.65; N, 3.43%.

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