New β,β-Bis(benzo[*b*]thienyl)dehydroalanine Derivatives: Synthesis and Cyclization

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The methyl ester of β,β-dibromo-*N*-(*tert*-butoxycarbonyl)-dehydroalanine was synthesized by treating the methyl ester of *N*,*N*-bis(*tert*-butoxycarbonyl)dehydroalanine with trifluoroacetic acid, *N*-bromosuccinimide and triethylamine. This compound was then used in Suzuki cross-coupling reactions with several (benzo[*b*]thienyl)boronic acids to give the corresponding β,β-bis(benzo[*b*]thienyl)dehydroalanine derivatives in good to high yields (55–90 %). After several experiments, the best conditions were shown to be: (benzo[*b*]thienyl)boronic acid (5 equiv.), $[Pd(PPh)_2Cl_2]$ (20 mol %), Na_2CO_3 (4 equiv.) in DME/H_2O (10:1). The Suzuki cross-coupling products were treated with $Pd(OAc)_2$ and $Cu(OAc)_2$ in DMF at 160 °C to give the (benzo[*b*]thienyl)pyrroles in moderate to good yields (25–62 %). Other attempts were carried out using only $Cu(OAc)_2$, the thienylpyrroles being, in some cases, isolated in lower yields. Preliminary fluorescence studies show that the (benzo[*b*]thienyl)pyrroles can be used as biomarkers. All of these compounds are non-proteinogenic amino acids that can have biological activity or can be used in conformational studies in order to establish structure-activity relationships.

Introduction

Dehydroamino acids are an important class of compounds that can be biologically active or can be used in structure-activity studies due to the conformational constraints they impose.[1] These compounds are also valuable substrates for the synthesis of non-proteinogenic amino acids.[2] Recently, we used β-bromodehydroamino acids as substrates for the synthesis, in good yields, of several sulfur analogues of tryptophan. The former were synthesized in a one-pot procedure from the methyl ester of *N*,*N*-bis(*tert*-butoxycarbonyl)dehydroalanine with trifluoroacetic acid, *N*-bromosuccinimide and triethylamine. These compounds were coupled with several (benzo[*b*]thienyl)boronic acids under the Suzuki cross-coupling conditions giving the corresponding β-substituted dehydroamino acids in good to high yields.[3] The benzo[*b*]thiophenes are important heterocycles, either as biologically active molecules or as sensors, due to their luminescent properties.[4] With this in mind, we had linked the benzo[*b*]thiophene moiety by either the benzene or the thiophene ring to dehydroamino acids using Michael addition or sequential Michael addition and palladium-catalyzed C−C and C−N cross-couplings.[5] Now, we describe the synthesis of β,β-bis(benzo[*b*]thienyl)dehydroalanines from β,β-dibromodehydroalanine and several (benzo[*b*]thienyl)boronic acids. The cross-coupling products were *N*-deprotected and cyclized to (benzo[*b*]thienyl)pyrroles in the presence of $Pd(OAc)_2$ and $Cu(OAc)_2$.

Preliminary fluorescence studies were preformed on one of these compounds. The results obtained indicate that it is possible to use it as a biomarker. Since the compounds obtained are non-proteinogenic amino acids, they can be biologically active or can be used in the development of peptidomimetics.

Results and Discussion

Recently, we described the synthesis of the methyl ester of β,β-dibromo-*N*-(*tert*-butoxycarbonyl)dehydroalanine (**2**) [Boc-ΔAla(β,β-Br)-OMe] from the methyl ester of *N*,*N*-bis-(*tert*-butoxycarbonyl)dehydroalanine[6] [Boc_2-ΔAla-OMe] with TFA, NBS and triethylamine using a one-pot procedure in 52 % yield (Scheme 1).[7] This compound was also obtained in a higher overall yield (81 %) in two steps (Scheme 1). Kolar et al. had already described the synthesis of the methyl ester of *N*-acetyl-β,β-dichlorodehydroalanine in 54 % yield, from the corresponding β-chlorodehydroalanine using chlorine followed by treatment with DABCO.[8]

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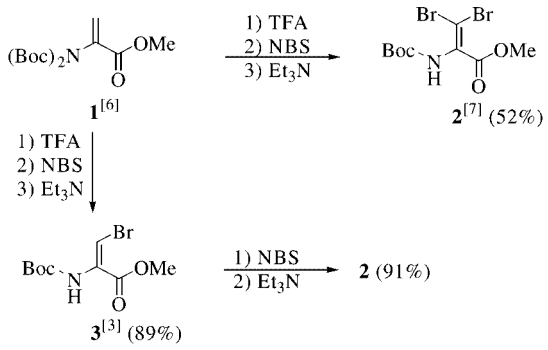
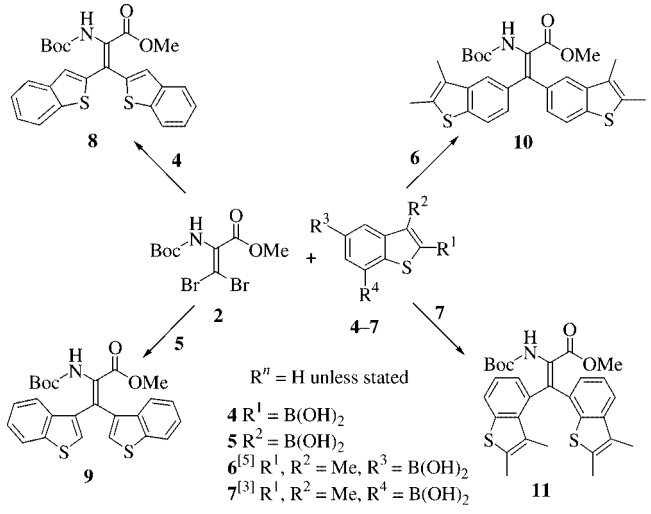


Scheme 1

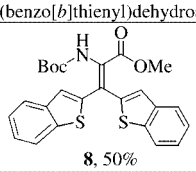
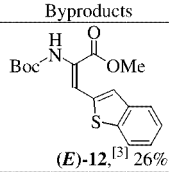
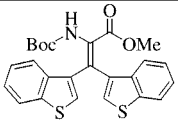
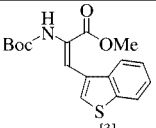
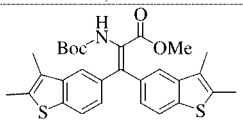
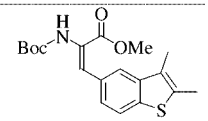
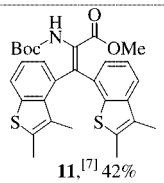
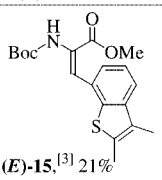
Substituted 1,1-dibromoalkenes have been used as electrophiles in palladium-catalyzed reactions giving the corresponding tetrasubstituted alkenes.[9] In this work, the β,β-dibromodehydroalanine ester **2** was used in Suzuki cross-couplings with several (benzo[*b*]thienyl)boronic acids **4**−**7** (Scheme 2, Table 1). Compounds **6** and **7** were synthesized from the corresponding bromobenzo[*b*]thiophenes as already described by us.[3,5]



Scheme 2

After several experiments, the best conditions for the synthesis of the β,β-(benzo[*b*]thienyl)dehydroalanine derivatives **8**−**11** were shown to be 5 equiv. of the (benzo[*b*]thienyl)boronic acids **4**−**7**, 4 equiv. of Na_2CO_3, 20 mol % of $[PdCl_2(PPh_3)_2]$ in DME/H_2O (10:1) (Table 1). Using $[Pd(PPh_3)_4]$ as catalyst and different amounts of the (benzo[*b*]thienyl)boronic acids (2.6 or 5 equiv.) and base (4 or 8 equiv.), the yields of the β,β-disubstituted dehydroalanines were lower (40−50 %). Using these conditions, the (*E*) isomers of the corresponding monosubstituted dehydroalanines were also isolated in moderate yields (21−39 %) together with small amounts of the benzo[*b*]thiophene dimers. The formation of the (*E*) isomer could be due to the fact that the first oxidative addition occurs on the less hindered side of the carbon−halogen bonds as observed by other authors with 1,1-dibromo-1-alkene.[10] Compounds **(*E*)-12**, **(*E*)-13** and **(*E*)-15** had already been obtained by us and their stereochemistry was determined by NOE difference experiments, irradiating the α-NH proton and observing an NOE on the β-CH proton.[3] The same method was used to establish the stereochemistry of the new compound **(*E*)-14**.

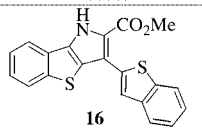
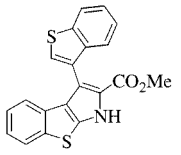
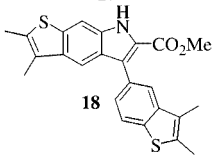
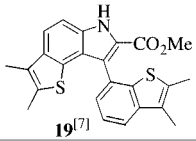
Table 1. Results obtained in the synthesis of β,β-bis(benzo[*b*]thienyl)dehydroalanine derivatives; A: 2.6 equiv. of (benzo[*b*]thienyl)-boronic acid, 8 equiv. of Na_2CO_3, 20 mol % of $[Pd(PPh_3)_4]$, DME/H_2O (10:1); B: 2.6 equiv. of (benzo[*b*]thienyl)boronic acid, 4 equiv. of Na_2CO_3, 20 mol % of $[Pd(PPh_3)_4]$, DME/H_2O (10:1); C: 5 equiv. of (benzo[*b*]thienyl)boronic acid. 4 equiv. of Na_2CO_3, 20 mol % of $[Pd(PPh_3)_4]$, DME/H_2O (10:1); D: 5 equiv. of (benzo[*b*]thienyl)-boronic acid, 4 equiv. of Na_2CO_3, 20 mol % of $[PdCl_2(PPh_3)_2]$, DME/H_2O (10:1)

Conditions	β,β-Bis(benzo[*b*]thienyl)dehydroalanines	Byproducts
A	 **8**, 50%	 (*E*)-**12**,[3] 26%
C	**8**, 43%	(*E*)-**12**, 21%
D	**8**, 90%	—
A	 **9**, 42%	 (*E*)-**13**,[3] 22%
B	**9**, 55%	*E*-**13**, 29%
D	**9**, 90%	—
D	 **10**, 55%	 (*E*)-**14**, 24%
A	 **11**,[7] 42%	 (*E*)-**15**,[3] 21%
B	**11**, 40%	(*E*)-**15**, 39%
D	**11**, 80%	—

The β,β-bis(benzo[*b*]thienyl)dehydroalanine derivatives **8**−**11** were treated with $Pd(OAc)_2$ and $Cu(OAc)_2$ in DMF at 160 °C affording, after intramolecular cyclization and *N*-deprotection, (benzo[*b*]thienyl)pyrroles (dehydroprolines) in moderate to good yields (Table 2). From compound **10**, only the product resulting from cyclization on position 6 was obtained as shown by ^{1}H NMR spectroscopy.

Treatment of compound **9** using only $Cu(OAc)_2$ (3 equiv.) in DMF at 160 °C gave the (benzo[*b*]thienyl)pyrrole **17** in a similar yield, while the same conditions applied to compound **11**[7] gave a lower yield (22 %) of the (benzo[*b*]thienyl)indole **19**.[7] These results indicate that the cyclization in the thiophene ring is not affected by the presence of $Pd(OAc)_2$. However, the same is not true for the cyclization in the benzene ring, where its presence increases significantly the product yield (60 %). In the synthesis of compound **19**, several amounts of $Pd(OAc)_2$ (10, 20, 30 and 50 mol %) were tested, the better product yield being obtained when 50 mol % was used.

Table 2. Yields obtained in the cyclization reactions to (benzo[*b*]thienyl)pyrroles; reaction conditions: $Pd(OAc)_2$ (50mol %), $Cu(OAc)_2$ (3 equiv.), DMF, 160 °C

Reagent	Product	Yield (%)
8	 **16**	30
9	 **17**	25
10	 **18**	62
11[7]	 **19**[7]	60

The absorption and fluorescence properties of compound **19** were studied with the aim of using this type of compound as a biomarker. The absorption spectrum in dichloromethane (Figure 1) shows a λ_{max} at 324 nm and a shoulder at 275 nm. The fluorescence spectrum (Figure 2) was independent of the excitation wavelength showing λ_{em} = 420 nm. The quantum yield was 0.040 ± 0.004 and the decay time was 0.60 ns (λ_{exc} at 325 nm; λ_{em} at 420 nm).

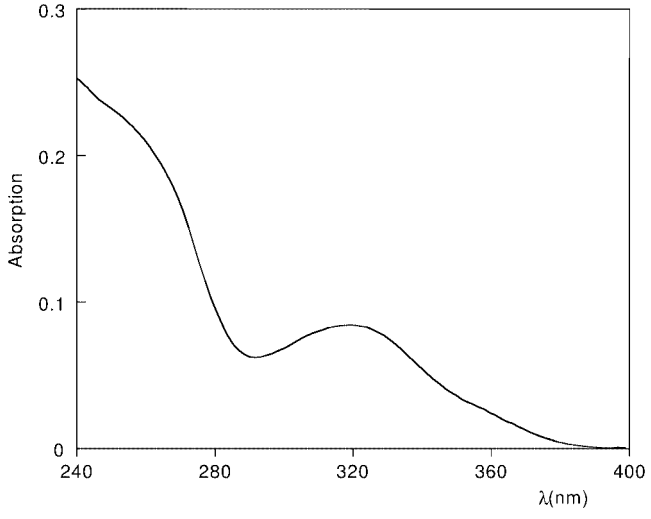


Figure 1. Absorption spectra of compound **19** in CH_2Cl_2

Conclusion

New β,β-bis(benzo[*b*]thienyl)dehydroalanines were prepared in high yields using Suzuki cross-couplings of a β,β-dibromodehydroalanine derivative with several (benzo[*b*]-thienyl)boronic acids. Their intramolecular cyclization afforded dehydroprolines in moderate to good yields using $Cu(OAc)_2$ with or without $Pd(OAc)_2$.

Absorption and fluorescence properties of one of the cyclized products indicate the possible application of this type of compound as a biomarker. All the dehydroamino acids prepared can also show biological activity or be used in conformational studies.

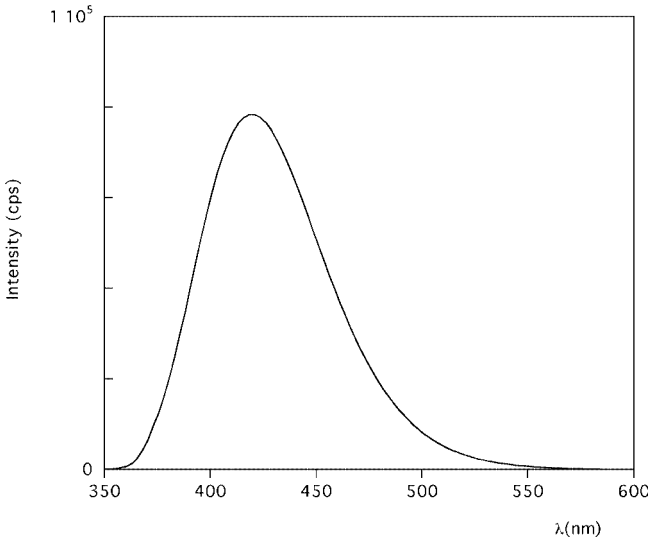


Figure 2. Fluorescence spectrum of compound **19** in CH_2Cl_2

Experimental Section

General Remarks: Melting points were determined with a Gallenkamp apparatus and are uncorrected. The ^1H NMR spectra were measured with a Varian Unity Plus at 300 MHz. Spin-spin decoupling techniques were used to assign the signals. NOE experiments were performed to determine the stereochemistry of the products. The ^{13}C NMR spectra were measured with the same instrument at 75.4 MHz (using DEPT θ 45°). Elemental analyses were determined with a LECO CHNS 932 elemental analyzer. MS (EI and FAB) and HRMS data were recorded by the mass spectrometry service of University of Vigo, Spain. Steady-state fluorescence experiments were carried out with a Fluoromax Spectrofluorometer (Spex, Jobyn-Yvon), operating in Single Photon Counting (SPC) mode. Nanosecond decays were measured by a CD900 SPC lifetime apparatus from Edinburgh Instruments (U.K.). All fluorescence experiments were carried out in quartz cells, using freshly prepared solutions, thermostatted at 25 °C. Quantum yields were determined using anthracene in ethanol as a reference compound (q.y. = 0.27 ± 0.03). Column chromatography was performed on Macherey−Nagel silica gel 230−400 mesh. The petroleum ether used had a boiling range of 40−60 °C. When a solvent gradient was used, the increase in polarity was done gradually from pure petroleum ether to mixtures of diethyl ether and petroleum ether, successively adding 10 % of diethyl ether until the isolation of the product. The benzo[*b*]thienylboronic acids **4** and **5** are commercial, and **6**[5] and **7**[3] were already described by us. The dehydroamino acids **1**,[6] **2**,[7] **3**,[3] **11**[7] were already prepared by us. The thienylpyrrole **19**[7] was already described by us. DME = 1,2-dimethoxyethane.

General Procedure for the Synthesis of Suzuki Cross-Coupling Products: To a solution of compound **2** (0.05 M) in DME/H_2O (10:1) were added the boronic acid (5 equiv.), Na_2CO_3 (4 equiv.) and $[PdCl_2(PPh_3)_2]$ (20 mol %), and the mixture was heated at 90 °C while the reaction was monitored by TLC. The DME was removed under reduced pressure and the residue was dissolved in ethyl acetate (15 mL). The organic layer was then washed with water and brine (2 × 5 mL each), dried with $MgSO_4$ and the solvents were evaporated at reduced pressure to give an oil.

Boc-ΔAla[β,β-bis(benzo[*b*]thien-2-yl)]-OMe (8): The procedure described above was applied using compound **2** (0.280 mmol, 0.100 g) and the benzo[*b*]thienylboronic acid **4**, and heating for 1 h. Column chromatography using a solvent gradient from pure petroleum ether to 40 % diethyl ether in petroleum ether, gave compound **8** (0.117 g, 90 %) as a white solid. Recrystallization from diethyl ether/petroleum ether gave colourless crystals, m.p. 193.4−195.0 °C. ^{1}H NMR ($CDCl_3$): δ = 1.51 (s, 9 H, CH_3 Boc), 3.62 (s, 3 H, OCH_3), 6.71 (s, 1 H, NH), 7.29−7.41 (m, 6 H, ArH), 7.72−7.85 (m, 4 H, ArH) ppm. ^{13}C NMR ($CDCl_3$): δ = 28.10 [C(*C*H_3)$_3$], 52.55 (OCH_3), 82.09 [O*C*(CH_3)$_3$], 122.14 (CH), 122.16 (CH), 123.78 (CH), 124.13 (CH), 124.40 (CH), 124.72 (CH), 124.77 (CH), 125.14 (CH), 125.41 (CH), 127.18 (CH), 128.55 (C), 138.95 (C), 139.06 (C), 139.17 (C), 140.53 (C), 140.60 (C), 140.82 (C), 152.07 (C=O), 165.43 (C=O) ppm. $C_{25}H_{23}NO_4S_2$ (465.58): calcd. C 64.49, H 4.98, N 3.01, S 13.77; found C 64.54, H 5.30, N 2.96, S 13.37.

Boc-ΔAla[β,β-bis(benzo[*b*]thien-3-yl)]-OMe (9): The procedure described above was applied using compound **2** (0.280 mmol, 0.100 g) and the benzo[*b*]thienylboronic acid **5**, and heating for 1 h. Column chromatography using a solvent gradient from pure petroleum ether to 30 % diethyl ether in petroleum ether, gave compound **9** (0.117 g, 90 %) as a white solid. Recrystallization from diethyl ether/petroleum ether gave colourless crystals, m.p. 159.0−159.9 °C. ^{1}H NMR ($CDCl_3$): δ = 1.43 (s, 9 H, CH_3 Boc), 3.51 (s, 3 H, OCH_3), 6.03 (s, 1 H, NH), 7.08−7.18 (m, 2 H, ArH), 7.24−7.30 (m, 2 H, ArH), 7.40−7.46 (m, 3 H, ArH), 7.78−7.82 (m, 2 H, ArH), 7.90−7.94 (m, 1 H, ArH) ppm. ^{13}C NMR ($CDCl_3$): δ = 28.05 [C(*C*H_3)$_3$], 52.30 (OCH_3), 81.52 [O*C*(CH_3)$_3$], 122.59 (CH), 122.83 (CH), 123.04 (CH), 123.25 (CH), 124.31 (CH), 124.46 (CH), 124.86 (CH), 124.91 (CH), 125.31 (CH), 128.60 (C), 128.85 (CH), 132.53 (C), 134.82 (C), 135.97 (C), 138.01 (C), 139.80 (C), 140.29 (C), 152.57 (C=O), 166.04 (C=O) ppm. $C_{25}H_{23}NO_4S_2$ (465.58): calcd. C 64.49, H 4.98, N 3.01, S 13.77; found C 64.36, H 5.11, N 3.05, S 13.54.

Boc-ΔAla[β,β-bis(2,3-dimethylbenzo[*b*]thien-5-yl)]-OMe (10) and Boc-(*E*)-ΔAla[β-(2,3-dimethylbenzo[*b*]thien-5-yl)]-OMe [(*E*)-14]: The procedure described above was applied using compound **2** (0.200 mmol, 70.0 mg) and the benzo[*b*]thienylboronic acid **6**, and heating for 90 min. Column chromatography using a solvent gradient from pure petroleum ether to 30 % diethyl ether in petroleum ether gave compound **10** (60.0 mg, 55 %) as a white solid, followed by compound **(*E*)-14** (17.0 mg, 24 %). Recrystallization of compound **10** from diethyl ether/petroleum ether gave colourless crystals, m.p. 204.1−205.2 °C. ^{1}H NMR ($CDCl_3$): δ = 1.47 (s, 9 H, CH_3 Boc), 2.22 (s, 3 H, Ar-CH_3), 2.24 (s, 3 H, Ar-CH_3), 2.48 (s, 3 H, Ar-CH_3), 2.50 (s, 3 H, Ar-CH_3), 3.53 (s, 3 H, OCH_3), 6.15 (s, 1 H, NH), 7.03 (dd, *J* = 8.1, 1.2 Hz, 1 H, 6-H), 7.07 (broad d, 1 H, 6′-H), 7.39 (d, *J* = 1.2 Hz, 1 H, 4-H), 7.57 (broad s, 1 H, 4′-H), 7.64 (d, *J* = 8.1 Hz, 1 H, 7-H), 7.72 (d, *J* = 8.1 Hz, 1 H, 7′-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 11.32 (CH_3), 11.35 (CH_3), 13.81 (CH_3), 13.84 (CH_3), 28.18 [C(*C*H_3)$_3$], 52.09 (OCH_3), 81.05 [O*C*(CH_3)$_3$], 121.63 (CH), 121.78 (CH), 122.34 (CH), 122.62 (CH) 124.88 (CH), 125.31 (C), 125.47 (CH), 127.17 (C), 127.26 (C), 134.44 (C), 134.47 (C), 134.99 (C), 135.78 (C), 137.74 (C), 138.06 (C), 140.88 (C), 141.14 (C), 153.01 (C=O), 167.05 (C=O) ppm. $C_{29}H_{31}NO_4S_2$ (521.69): calcd. C 66.77, H 5.99, N 2.68, S 12.29; found C 67.06, H 6.27, N 2.66, S 11.94. Recrystallization of compound **(*E*)-14** from diethyl ether/petroleum ether gave colourless crystals, m.p. 150.3−151.0 °C. ^{1}H NMR ($CDCl_3$): δ = 1.42 (s, 9 H, CH_3 Boc), 2.29 (s, 3 H, Ar-CH_3), 2.49 (s, 3 H, Ar-CH_3), 3.88 (s, 3 H, OCH_3), 6.23 (s, 1 H, NH), 7.44 (s, 1 H, 4-H), 7.50 (d, *J* = 8.1 Hz, 1 H, 6- or 7-H), 7.71 (d, *J* = 8.1 Hz, 1 H, 7- or 6-H), 7.75 (s, 1 H, β-CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 11.24 (CH_3), 13.78 (CH_3), 28.09 [C(*C*H_3)$_3$], 52.52 (OCH_3), 80.81 [O*C*(CH_3)$_3$], 121.88 (CH), 122.94 (CH), 124.57 (CH), 127.15 (C) 129.73 (C), 131.37 (CH), 134.70 (C), 139.11 (C), 141.04 (C), 152.87 (C=O), 166.19 (C=O) ppm. $C_{19}H_{23}NO_4S$ (361.46): calcd. C 63.14, H 6.41, N 3.88, S 8.87; found C 62.97, H 6.41, N 3.87, S 8.60.

General Procedure for the Synthesis of Benzo[*b*]thienylpyrroles 16−18: To a solution of the β,β-bis(benzo[*b*]thienyl)dehydroalanine derivative **8**−**10** (0.1 M) in DMF were added $Pd(OAc)_2$ (50 mol %) and $Cu(OAc)_2·H_2O$ (3 equiv.), and the mixture was heated at 160 °C, monitoring the reaction by TLC. Ethyl acetate (50 mL) was then added and the organic layer washed with water and brine (2 × 25 mL each), dried with $MgSO_4$ and the solvents were evaporated at reduced pressure to give an oil that was submitted to column chromatography.

Methyl 3-(Benzo[*b*]thien-2-yl)-1*H*-benzo[*b*]thieno[3,2-*b*]pyrrole-2-carboxylate (16): The procedure described above was applied using compound **8** (0.200 mmol, 94.0 mg), and heating for 90 min. Column chromatography using a solvent gradient from pure petroleum ether to 30 % diethyl ether in petroleum ether, gave compound **16** (21.0 mg, 30 %) as a brown solid. Recrystallization from diethyl ether/petroleum ether gave beige crystals, m.p. 221.1−222.1 °C. ^{1}H NMR ($CDCl_3$): δ = 4.01 (s, 3 H, OCH_3), 7.30−7.50 (m, 4 H, ArH), 7.85−7.90 (m, 4 H, ArH), 7.97 (s, 1 H, ArH), 9.67 (s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$): δ = 51.89 (OCH_3), 118.30 (C), 119.78 (CH), 121.16 (C), 122.00 (CH), 123.73 (CH), 124.28 (CH), 124.38 (CH), 124.41 (CH), 124.47 (CH), 124.70 (CH), 124.91 (C), 125.39 (CH), 125.71 (C), 134.32 (C), 135.10 (C), 139.96 (C), 139.98 (C), 143.79 (C), 161.06 (C=O) ppm. MS: *m*/*z* (%) = 363 (66) [M^+], 331 (100) [M^+ − OMe], 302 (58). HRMS: calcd. for $C_{20}H_{13}NO_2S_2$ [M^+] 363.0388; found 363.0382.

Methyl 3-(Benzo[*b*]thien-3-yl)-1*H*-benzo[*b*]thieno[2,3-*b*]pyrrole-2-carboxylate (17): The procedure described above was applied using compound **9** (0.200 mmol, 94.0 mg), and heating for 90 min. Column chromatography using a solvent gradient from 50 % dichloromethane/petroleum ether to 90 % dichloromethane/petroleum ether gave compound **17** (19.0 mg, 25 %) as a brown solid, m.p. 242.9−243.7 °C. ^{1}H NMR ($CDCl_3$): δ = 3.68 (s, 3 H, OCH_3), 7.10−7.13 (m, 2 H, ArH), 7.19−7.24 (m, 1 H, ArH), 7.27−7.33 (m, 1 H, ArH), 7.40 (td, *J* = 7.8, 0.9 Hz, 1 H, ArH), 7.54 (d, *J* = 8.1 Hz, 1 H, ArH), 7.60 (s, 1 H, ArH), 7.73 (d, *J* = 8.1 Hz, 1 H, ArH), 7.98 (d, *J* = 7.8 Hz, 1 H, ArH), 9.88 (s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$): δ = 51.61 (OCH_3), 118.32 (C), 121.64 (CH), 122.63 (CH), 123.49 (CH), 123.53 (CH), 123.94 (CH), 124.12 (CH), 124.30 (CH), 124.34 (C), 124.82 (CH), 125.75 (CH), 127.22 (C), 128.79 (C), 131.40 (C), 135.83 (C), 138.64 (C), 139.61 (C), 139.83 (C), 161.53 (C=O) ppm. MS: *m*/*z* (%) = 363 (61) [M^+], 331 (100) [M^+ − OMe], 302 (32). HRMS: calcd. for $C_{20}H_{13}NO_2S_2$ [M^+] 363.0388; found 363.0384.

Methyl 3-(2,3-Dimethylbenzo[*b*]thien-5-yl)-1*H*-5,6-dimethylbenzo[*b*]thieno[6,5-*b*]pyrrole-2-carboxylate (18): The procedure described above was applied using compound **10** (0.228 mmol, 0.119 g), and

heating for 2 h. Recrystallization from diethyl ether gave compound **18** (62.0 mg, 62 %) as a brown solid. Recrystallization from chloroform/petroleum ether gave light brown crystals that melted with decomposition. ^{1}H NMR ($CDCl_3$): δ = 2.24 (s, 3 H, Ar-CH_3), 2.33 (s, 3 H, Ar-CH_3), 2.47 (s, 3 H, Ar-CH_3), 2.54 (s, 3 H, Ar-CH_3), 3.81 (s, 3 H, OCH_3), 7.52 (d, J = 8.1 Hz, 1 H, ArH), 7.78 (s, 1 H, ArH), 7.79 (s, 1 H, ArH), 7.83 (s, 1 H, ArH), 7.87 (d, J = 8.1 Hz, 1 H, ArH), 8.85 (s, 1 H, NH) ppm. MS: *m*/*z* (%) = 419 (84) [M^+], 387 (100) [M^+ − OMe], 344 (41). HRMS: calcd. for $C_{24}H_{21}NO_2S_2$ [M^+] 419.1014; found 419.1024.

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