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PAPER

Coumarin-based chiral fluorescence sensor incorporating a thiourea unit for highly enantioselective recognition of *N*-Boc-protected proline†

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New coumarin-based chiral thiourea sensor **1** was found to be an enantioselective fluorescent chemosensor for *N*-Boc-protected proline. The chiral sensor shows lower background fluorescence, and higher fluorescence enhancement with 18 nm blue shifts. Job plot analysis result indicates that sensor **1** can form a 1 : 1 stoichiometric complex and it could be used as a fluorescence sensor for the determination of enantiomer composition of *N*-Boc-protected proline.

Introduction

Molecular recognition, especially chiral recognition, is one of the most fundamental properties of various natural systems.[1] It is of particular significance for understanding the interactions of biological molecules and the designing of asymmetric catalysis systems.[2] With the increasingly successful application to smart artificial systems, chiral recognition has gained greater scientific maturity as a broader and more commonly used 'tool'. More and more attention has been paid to fluorescence-based enantioselective sensors due to their high selectivity and potential application in analytical, biological, clinical and biochemical environments.[3] They can effectively provide a real-time analytical tool for chiral compound assay. Using these sensors can not only facilitate rapid determination of enantiomeric composition of chiral compounds, but also allow a rapid screening of high-throughput catalysts for their asymmetric synthesis.[4] To date, reports of successful enantiodiscriminating sensors are mainly focused on a variety of optically active 1,1′-bi-2-naphthol (BINOL) derivatives,[5] chiral macrocycles (fluorophore-modified calixarenes, cyclodextrins and crown ethers), dendrimers and oligomers.[6]

Amino acids are found to be the structural units of many natural products and drug molecules. They can also serve as multifunctional precursors for a variety of organic compounds.[7] The molecular recognition of amino acids by synthetic receptor molecules has been attracting much attention, due to the frequent use of the basic amino acids (*e.g.*, Lys, Arg, His, Ala) for biological processes and therapeutic drugs made from chiral amino acids intermediates.[8]

Proline is a widely used organocatalyst as it is readily available and inexpensive. It has been employed in a variety of asymmetric organic reactions including aldol, Michael addition and Mannich reactions.[9] Proline also can be employed as an effective ligand for Ullmann type coupling reactions, which has been developed by Ma.[10] Although its versatile catalytic characteristics are fully reported in previous literature, there is no report on its chiral promoting effect on a fluorescence system. For this purpose, the design of fluorescent sensors for the enantioselective recognition of chiral organic molecules and the rapid determination of their enantiomeric composition is highly desirable.[11]

Urea and thiourea derivatives[12] are fascinating compounds, and have been widely utilized in the field of anion recognition because of their strong hydrogen bonding ability.[13] More recent studies have described a great deal of enantioselective as well as diastereoselective reactions catalyzed by urea or thiourea derivatives.[14]

Although the chiral recognition of amino acids[15] and their derivatives (especially *N*-Boc-protected amino acids[16] and *N*-Cbz-protected amino acids[6c,17]) with high ef (*i.e.*, the enantiomeric fluorescence difference ratio, ef = $(I_D - I_0)/(I_L - I_0)$),[18] has been reported recently, there have been very few reports on chiral fluorescence sensors incorporating a thiourea moiety for chiral molecular recognition. Chiral recognition requires multiple-point interaction.[19] We envision that by using an additional interaction, *e.g.*, hydrogen binding, the chiral thiourea unit could be enantioselective toward amino acids. With this concept in mind we designed and synthesized sensor **1** featuring thiourea and coumarin moieties.

Results and discussion

The syntheses of compounds **1a** and **1b** are readily achieved in several steps (Scheme 1). *tert*-Butyl 2,2′-thiocarbonyl bis-

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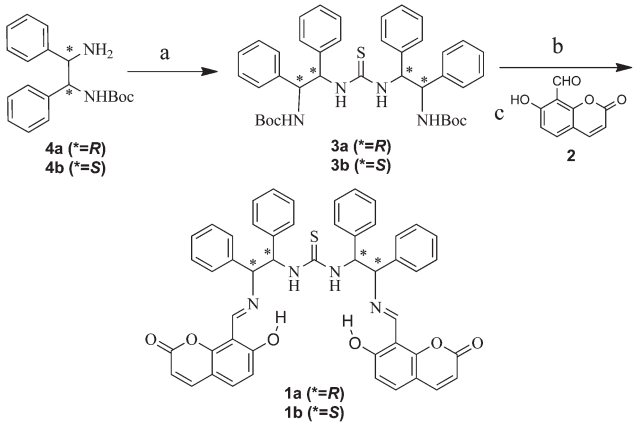
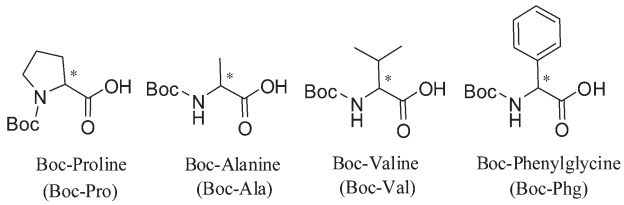


Scheme 1 Synthesis of the chiral sensor **1**. *Reagents and conditions*: (a) EtOH, CS_2, reflux, 20 h, 78% yield; (b) TFA, CH_2Cl_2, 12 h; (c) **2**, CH_3OH, 2 h, 80% yield.



Scheme 2 *N*-Boc amino acids used in this study.

(azanediyl) bis(1,2-diphenyl-ethane-2,1-diyl) dicarbamate **3** was synthesized from *N*-Boc-protected-1,2-diphenyldiamine **4** in 78% yield.[20] Then **3** reacted with **2**[21] in methanol to afford the chiral sensor **1** in 80% yield. The *N*-Boc-protected amino acids (Scheme 2) are chosen as sensing substrates and the chiral recognition of sensor **1** toward them has been investigated.

The concentration effect on the UV-vis spectrum of **1a** was studied (see ESI, Fig. S1†). In the concentration range from 1×10^{-7} to 1×10^{-4} mol dm^{-3}, the UV-vis spectra of **1a** in toluene obey the Lambert–Beer law well. The CD spectra of **1a** and **1b** are approximately mirror-images of each other. **1a** exhibits intense positive Cotton effects at 448 nm, 380 nm and 337 nm, whereas **1b** shows opposite Cotton effects at the corresponding wavelengths (Fig. 1).

Firstly we investigated the recognition of **1a** (1.0×10^{-5} mol dm^{-3}) toward enantiomers of Boc-proline (Boc-Pro) in toluene solution. Kinetic study of sensor **1a** with Boc-D-Pro shows that the complex proceeds to completion within a set time interval (6 hours) for our measurements (see ESI, Fig. S2†).

The free sensor **1a** can emit a weak fluorescence situated at 520 nm (Fig. 2a). While chiral recognition of Boc-Pro was carried out, **1a** can exhibit a pronounced fluorescence enhancement the concentration of the Boc-Pro increases. Meanwhile, in the fluorescence spectra of **1a** 18 nm blue shifts appear gradually from 520 nm to 502 nm (Fig. 3), which could be ascribed to the intramolecular charge transfer (ICT) effect. The chiral sensor can form a strong intramolecular hydrogen bond between the C=N group and the phenol proton. While the *N*-protected amino acid as guest molecule forms a complex with the host chiral sensor *via* the stronger acid and base interaction between the C=N

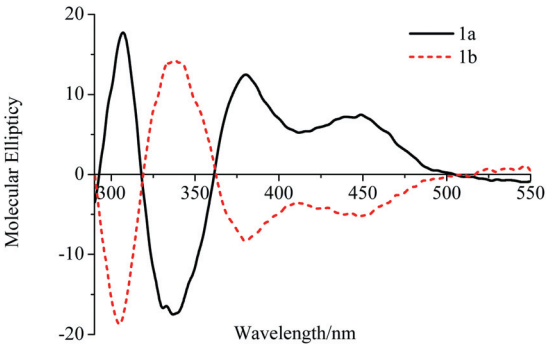


Fig. 1 CD spectra of **1a** and **1b** in toluene. [**1a**] = 1.0×10^{-4} mol dm^{-3}, [**1b**] = 1.0×10^{-4} mol dm^{-3}.

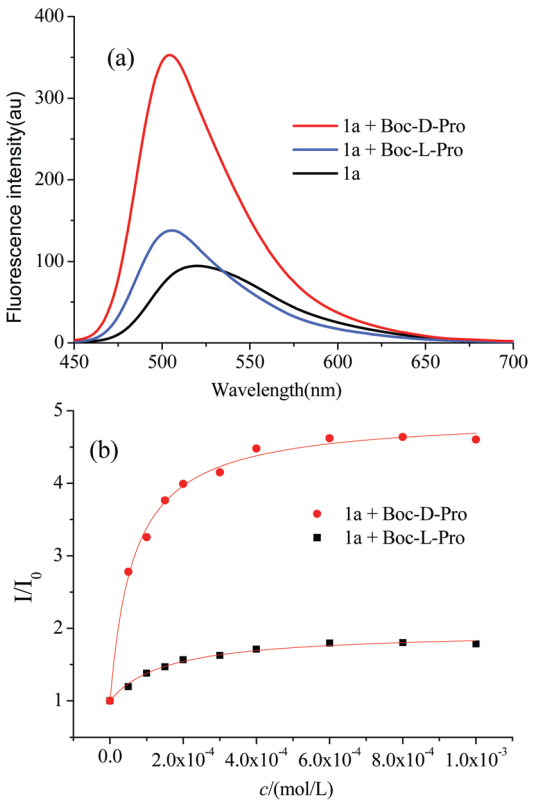


Fig. 2 (a) Fluorescence spectra of **1a** (1.0×10^{-5} mol dm^{-3} in toluene) with Boc-(L or D)-Pro (1.0×10^{-3} mol dm^{-3}) and (b) the plots of (I/I_0) *versus* the concentration of acid during the titration of **1a** with Boc-(L or D)-Pro (λ_{ex} = 430 nm, λ_{em} = 502 nm).

group and the carboxyl group of the *N*-protected amino acid, the intramolecular hydrogen bond is destroyed and the electron density of the conjugated structure of the chiral sensor is decreased, leading to the obvious fluorescence enhancement response and the blue shift of the fluorescent emission wavelength. Remarkable differences in fluorescence enhancement could be observed as demonstrated, Boc-D-Pro can lead to an obvious increase in the fluorescence intensity of **1a**, but Boc-L-Pro has much less fluorescence increase. The net fluorescence intensity increase of **1a** by Boc-D-Pro was found to be 4.55 times that by Boc-L-Pro (*i.e.*, the enantiomeric fluorescence

difference ratio, ef = $(I_D - I_0)/(I_L - I_0)$, was 4.55),[18] which indicates that **1a** can exhibit a highly enantioselective response toward Boc-D-Pro.

To ascertain whether the different fluorescence responses of sensor **1a** toward the two enantiomers of Boc-Pro arise from chiral recognition, sensor **1b**, the enantiomer of **1a**, was synthesized. The fluorescence responses of **1b** toward L- and D-Boc-Pro appear as a mirror image of that for **1a**, which confirms that the observed fluorescence responses are indeed due to the enantioselective recognition.

The stability constants (K) of fluorescence sensors **1a** and **1b** with Boc-Pro, Boc-alanine (Boc-Ala), Boc-phenylglycine (Boc-Phg) and Boc-valine (Boc-Val) were calculated by fitting the emission intensity at 502 nm *versus* the concentration of *N*-Boc-protected amino acids (Fig. 2b and Table 1). With **1a**, a binding constant (K) of $(1.54 \pm 0.10) \times 10^4$ M^{-1} was observed for Boc-D-Pro, *versus* $K = (6.57 \pm 0.65) \times 10^3$ M^{-1} for Boc-L-Pro ($K_D : K_L = 2.3 : 1.0$). To prove the enantioselectivity, **1b** was also titrated with Boc-Pro (see ESI, Fig. S3 and S4†). A mirror effect was observed ($K_D : K_L = 1.0 : 2.1$).

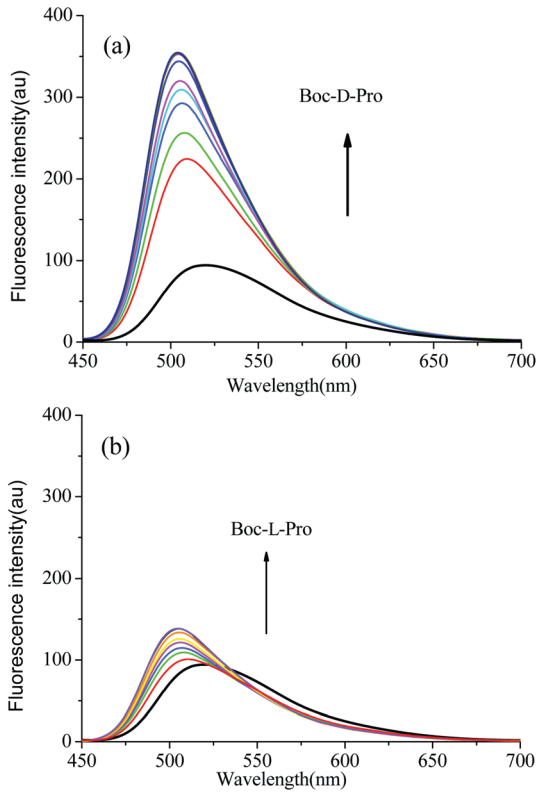


Fig. 3 Fluorescence spectra of **1a** (1.0×10^{-5} mol dm^{-3} in toluene solution) with (a) Boc-D-Pro and (b) Boc-L-Pro; concentrations of Boc-(L or D)-Pro are from 5.0×10^{-5} mol dm^{-3} to 1.0×10^{-3} mol dm^{-3} ($\lambda_{ex} = 430$ nm).

Enantioselective recognition of Boc-Ala and Boc-Phg is more challenging (see ESI, Fig. S5–S10†), because the methyl group in Boc-Ala is less bulky, and the phenyl group in Boc-Phg maybe less flexible than that in Boc-Pro, respectively. The minor steric hindrance may attenuate the enantioselectivity. As shown in Table 1, with Boc-D-Ala, $K = (4.78 \pm 0.56) \times 10^3$ M^{-1} was observed for **1a**, whereas for **1b**, $K = (4.25 \pm 0.37) \times 10^3$ M^{-1} ($K_R : K_S = 1.12 : 1.0$). Boc-L-Ala was also tested, and a mirror effect was observed. With Boc-D-Phg, $K = (6.38 \pm 0.99) \times 10^3$ $M^{-1}$was observed for **1a**, whereas for **1b**, $K = (4.36 \pm 0.46) \times 10^3$ M^{-1} ($K_R : K_S = 1.46 : 1.0$). Boc-L-Phg was also tested, and a mirror effect was observed. With Boc-D-Val, $K = (9.87 \pm 0.89) \times 10^3$ M^{-1} was observed for **1a**, whereas for **1b**, $K = (8.26 \pm 0.69) \times 10^3$ M^{-1} ($K_R : K_S = 1.19 : 1.0$). Boc-L-Val was also tested, and a mirror effect was observed.

The influence of the enantiomeric composition of Boc-D-Pro on the fluorescence intensity was investigated (Fig. 4). A fair linear relationship ($R > 0.98$) between the fluorescence intensity and the percent of the Boc-D-Pro component is observed, which indicates that **1a** can be effectively applied for the enantiomer composition determination.[23] From the Job plot (Fig. 5) a maximum is observed at 50% indicating that sensor **1a** forms a 1 : 1 complex with Boc-D-Pro.

Conclusions

In conclusion, a coumarin-based chiral fluorescence sensor **1** incorporating a thiourea unit has been prepared. Sensor **1** is highly enantioselective towards *N*-Boc-protected proline. Job plot analysis indicates that sensor **1** can form a 1 : 1 stoichiometric complex with Boc-Pro and it could be used as a fluorescence sensor for the determination of enantiomer composition of *N*-Boc-protected proline. We believe that our system will

Table 1 Stability constants, fluorescence enhancement (F) on binding and enantioselectivity ($K_R : K_S$) of sensors **1a**, and **1b**[a]

	K		F[b]			
Analytes	**1a**	**1b**	**1a**	**1b**	$K_R : K_S$	Response selectivity[c]
Boc-D-Pro	$(1.54 \pm 0.10) \times 10^4$	$(6.45 \pm 0.63) \times 10^3$	4.93 ± 0.06	1.93 ± 0.03	2.39 : 1.00	6.1 : 1.0
Boc-L-Pro	$(6.57 \pm 0.65) \times 10^3$	$(1.35 \pm 0.02) \times 10^4$	1.95 ± 0.02	4.97 ± 0.10	1.00 : 2.05	1.0 : 5.2
Boc-D-Ala	$(4.78 \pm 0.56) \times 10^3$	$(4.25 \pm 0.37) \times 10^3$	2.54 ± 0.06	1.75 ± 0.02	1.12 : 1.00	1.6 : 1.0
Boc-L-Ala	$(4.33 \pm 0.52) \times 10^3$	$(4.49 \pm 0.40) \times 10^3$	1.68 ± 0.02	2.53 ± 0.04	1.00 : 1.04	1.0 : 1.6
Boc-D-Phg	$(6.38 \pm 0.99) \times 10^3$	$(4.36 \pm 0.46) \times 10^3$	1.89 ± 0.04	1.41 ± 0.01	1.46 : 1.00	1.9 : 1.0
Boc-L-Phg	$(4.37 \pm 0.56) \times 10^3$	$(5.90 \pm 0.58) \times 10^3$	1.47 ± 0.03	1.88 ± 0.03	1.00 : 1.35	1.0 : 1.7
Boc-D-Val	$(9.87 \pm 0.89) \times 10^3$	$(8.26 \pm 0.69) \times 10^3$	2.87 ± 0.04	2.11 ± 0.03	1.19 : 1.00	1.6 : 1.0
Boc-L-Val	$(8.05 \pm 0.94) \times 10^3$	$(9.90 \pm 0.75) \times 10^3$	2.20 ± 0.02	2.78 ± 0.03	1.00 : 1.23	1.0 : 1.6

[a] Constants determined by fitting a 1 : 1 binding model to I/I_0;[22] determination coefficients $r^2 > 0.98$ in most cases. [b] Maximum fluorescence enhancement. [c] Response selectivity = $(K_{(R)}F_{(R)})/(K_{(S)}F_{(S)})$.

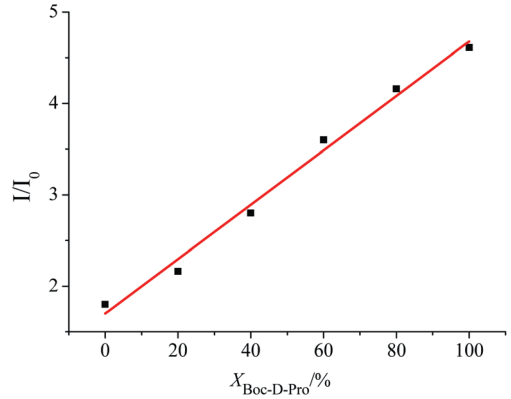


Fig. 4 Fluorescence enhancement of **1a** (1.0×10^{-5} mol dm^{-3} in toluene solution) *vs.* the enantiomeric composition of Boc-Pro (1.0×10^{-3} mol dm^{-3}), λ_{ex} = 430 nm, λ_{em} = 502 nm.

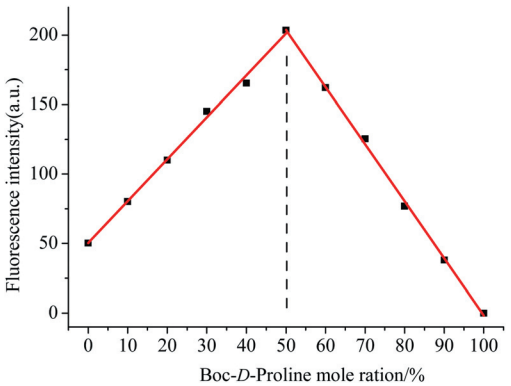


Fig. 5 Job plot of **1a** with Boc-D-Pro at a constant total concentration *c* (**1a**) + *c* (Boc-D-Pro) of 5.0×10^{-5} mol dm^{-3} in toluene solution, λ_{ex} = 430 nm, λ_{em} = 502 nm.

guide the design of new chiral sensors for amino acids with practical utility.

Experimental section

General

All solvents and reagents were commercially available and analytical reagent grade. TLC analyses were performed on silica gel 60 F_{254}. Column chromatographic purifications were carried out on silica gel (HG/T2354-92). Nuclear magnetic resonance spectra were run in either chloroform-d or DMSO-d_6. ^{1}H NMR spectra were recorded at 300 MHz, and ^{13}C {^{1}H} NMR spectra at 75 MHz. Chemical shifts (δ) are expressed in parts per million and are reported relative to the residual solvent peak or to tetramethylsilane as an internal standard in ^{1}H and ^{13}C {^{1}H} NMR spectra The multiplicities and general assignments of the spectroscopic data are denoted as: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quin), doublet of doublets (dd), doublet of triplets (dt), triplet of triplets (tt), unresolved multiplet (m), broad (br) and aryl (Ar). Coupling constants (*J*) are expressed in hertz. Electrospray ionization mass spectra (ESI-MS) were measured on a LCQ Fleet system. UV-vis absorption spectra were recorded on a Shimadzu 3600 spectrophotometer. Fluorescence emission spectra were measured on a Perkin Elmer LS-55 luminescence spectrometer. Samples for absorption and emission measurements were contained in 1 cm × 1 cm quartz cuvettes.

tert-Butyl (1*R*,1′*R*,2*R*,2′*R*)-2,2′-thiocarbonylbis(azanediyl)-bis-(1,2-diphenylethane-2,1-diyl)-dicarbamate (3a)

A solution of carbon disulfide (0.1 mL, 1.66 mmol) and **4a** (1.04 g, 3.32 mmol) in ethanol (6 mL) was refluxed during 20 h. The precipitate obtained was filtered off, washed with hexane and ether, and allowed to dry in air affording **3a** as white needles (0.862 g, 78%). ^{1}H NMR (300 MHz, DMSO-d_6) δ_H: 1.27 (s, 9H), 4.90 (m, 2H), 5.69 (m, 2H), 7.02–7.39 (m, 20H), 8.04 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 183.36, 155.61, 140.84, 128.13, 127.67, 127.13, 78.45, 61.90, 59.07, 28.51; ESI-MS: *m*/*z* 665.3357 ([M − H]$^+$, $C_{39}H_{45}N_4O_4S$ requires 665.3162).

tert-Butyl (1*S*,1′*S*,2*S*,2′*S*)-2,2′-thiocarbonylbis(azanediyl)-bis(1,2-diphenylethane-2,1-diyl)-dicarbamate (3b)

A similar procedure is followed as **3a**. A solution of carbon disulfide (0.1 mL, 1.66 mmol) and **4b** (1.04 g, 3.32 mmol) in ethanol (6 mL) was refluxed during 20 h. The precipitate obtained was filtered off, washed with hexane and ether, and allowed to dry in air affording **3b** as white needles (0.857 g, 78%). ^{1}H NMR (300 MHz, DMSO-d_6) δ_H: 1.29 (s, 9H), 4.93 (m, 2H), 5.71 (m, 2H), 7.05–7.42 (m, 20H), 8.06 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 183.36, 155.61, 140.85, 128.13, 127.67, 127.13, 78.45, 61.91, 59.04, 28.51; ESI-MS: *m*/*z* 665.3279 ([M − H]$^+$, $C_{39}H_{45}N_4O_4S$ requires 665.3162).

Synthesis of compound 1a

Compound **3a** (266.4 mg, 0.4 mmol) was then treated with TFA (3 mL) and DCM (3 mL) for 12 h at room temperature. Then the excess TFA was evaporated. Compound **2**[21,24] (152.0 mg, 0.8 mmol) dissolved in 5 mL methanol was added. The obtained solution was stirred at r.t. for 2 h. The solvent was then removed by a rotary evaporator. The crude product was recrystallized from methanol to afford a yellow solid **1a** (227 mg, 80% yield). $[\alpha]_D^{25} = -12 \pm 1$ (c = 10 mg mL^{-1}, CH_3OH : DCM = 1 : 1); ^{1}H NMR (300 MHz, DMSO-d_6) δ_H: 5.13 (d, J = 4.0, 1H), 6.07 (d, J = 4.0, 1H), 6.19–7.91 (m, 14H), 8.25 (br, 1H), 8.88 (s, 1H) 14.69 (br, 1H); ^{13}C NMR(75 Hz, DMSO-d_6) δ_C: 183.39, 168.13, 160.31, 159.87, 155.10, 145.29, 139.35, 139.24, 133.47, 128.72, 128.17, 127.63, 127.38, 115.81, 111.00, 109.34, 105.26, 74.85, 62.26; ESI-MS: *m*/*z* 811.2585 ([M + H]$^+$, $C_{49}H_{39}N_4O_6S$ requires 811.2546).

Synthesis of compound 1b

A similar procedure was followed to that for **1a**. Compound **3b** (266.4 mg, 0.4 mmol) was then treated with TFA (3 mL) and DCM (3 mL) for 12 h at room temperature. Then the excess TFA was evaporated. Compound **2** (152.0 mg, 0.8 mmol) dissolved in 5 mL methanol was added. The solution obtained was

stirred at r.t. for 2 h. The solvent was then removed by a rotary evaporator. The crude product was recrystallized from methanol to afford a yellow solid **1b** (226 mg, 80% yield). $[\alpha]_D^{25} = +12 \pm 1$ (c = 10 mg mL^{-1}, CH_3OH : DCM = 1 : 1); ^{1}H NMR (300 MHz, DMSO-d$_6$) δ_H: 5.12 (d, J = 4.0, 1H), 6.04 (d, J = 4.0, 1H), 6.16–7.90 (m, 14H), 8.36 (br, 1H), 8.86 (s, 1H) 14.66 (br, 1H); ^{13}C NMR (75 Hz, DMSO-d$_6$) δ_C: 183.67, 168.41, 160.31, 159.89, 155.22, 145.30, 139.34, 139.24, 133.45, 128.71, 128.13, 127.71, 127.36, 115.85, 111.96, 109.32, 105.29, 74.94, 62.33; ESI-MS: m/z 811.2567 ([M + H]$^+$, $C_{49}H_{39}N_4O_6S$ requires 811.2546).

Acknowledgements

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