doi:10.1016/j.tetasy.2015.10.004

Tetrahedron: *Asymmetry* xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Tetrahedron: *Asymmetry*

journal homepage: www.elsevier.com/locate/tetasy

Synthesis and enantiomeric recognition studies of optically active acridone bis(urea) and bis(thiourea) derivatives

Dávid Pál [a], Ildikó Móczár [a], Attila Kormos [a], Péter Baranyai [b], László Óvári [a], Péter Huszthy [a,*]

[a] *Department of Organic Chemistry and Technology, Budapest University of Technology and Economics, PO Box 91, H-1521 Budapest, Hungary*
[b] *'Lendület' Supramolecular Chemistry Research Group, Institute of Organic Chemistry, Research Centre of Natural Sciences, Hungarian Academy of Sciences, PO Box 286, H-1519 Budapest, Hungary*

ARTICLE INFO

Article history:
Received 24 August 2015
Accepted 9 October 2015
Available online xxxx

ABSTRACT

Novel optically active acridone bis(urea) and bis(thiourea) derivatives were synthesized and their enantiomeric recognition abilities towards the enantiomers of tetrabutylammonium salts of α-hydroxy and *N*-protected α-amino acids were examined in acetonitrile–DMSO 99:1 using fluorescence spectroscopy.

1. Introduction

Enantiomeric recognition as a special case of molecular recognition, is a frequently occurring and vital phenomenon in Nature. Examples of its action include the metabolism of single enantiomeric forms of amino acids and sugars in biosynthetic pathways. Since each enantiomer of a biologically active chiral compound may have different physiological properties to the other, the determination of the enantiomeric composition of chiral organic compounds has great importance.

The carboxyl group is a very common functional group in amino acids, enzymes, metabolic intermediates and several biologically active molecules. Therefore, the synthesis and studies of sensor and selector molecules, which are able to discriminate between the enantiomers of chiral carboxylic acids, are of great interest. The enantiomers of chiral carboxylic acids can not only be differentiated in their neutral forms, and also as their carboxylates by enantioselective anion sensors.[1–18]

Amino acid, BINOL, steroid and monosaccharide units are the most frequently used chiral building blocks in anion sensors,[1–13,18] while 1-arylethyl[19–22] moieties have also been applied as sources of chirality. Urea and thiourea units are often used as the receptor parts of these sensor molecules because of their high affinity towards anions due to hydrogen bond formation.[9] Some chiral anion sensors containing two urea or thiourea moieties have a fluorescent signalling unit, which allows for the examination of the anion recognition process by the spectroscopy.[9,22–31] Using an acridone fluorophore unit in a sensor molecule is very advantageous because of its strong fluorescence[32–35] and great photostability.[36] Acridone[37] and certain amide, urea, thiourea[38–40] and pyridyloxadiazole[41] functionalized achiral derivatives proved to be efficient receptors for different anions.

Herein we report the synthesis of novel acridone bis(urea) and bis(thiourea) derivatives containing (*S*)-1-phenylethyl units (*S*,*S*)-**1** and (*S*,*S*)-**2** (Scheme 1), and our studies on their enantiomeric recognition abilities towards the enantiomers of different optically active tetrabutylammonium carboxylates in acetonitrile containing 1% DMSO.

2. Results and discussion

2.1. Synthesis

The synthesis of new acridone bis(urea) and bis(thiourea) derivatives containing (*S*)-1-phenylethyl units (*S*,*S*)-**1** and (*S*,*S*)-**2** was carried out as outlined in Scheme 1. Diaminoacridone **3** was reacted with the appropriate, commercially available optically active isocyanate (*S*)-**4** and isothiocyanate (*S*)-**5** in DMF to give acridone derivatives (*S*,*S*)-**1** and (*S*,*S*)-**2**.

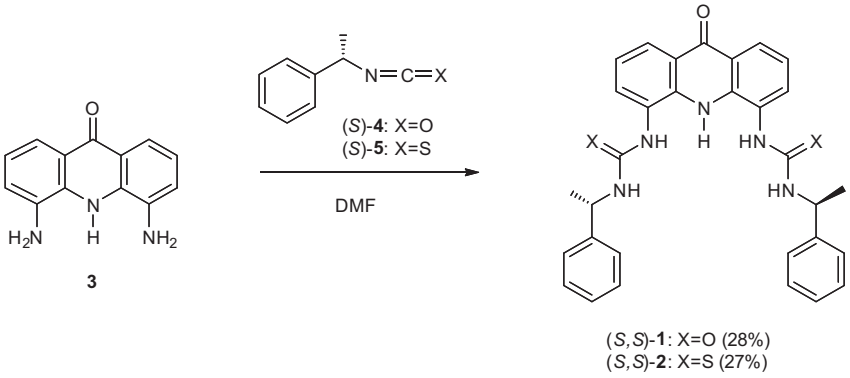
Diaminoacridone **3** was synthesized from dinitroacridone **4**[42–45] by catalytic hydrogenation (yield: 97%, Scheme 2) as a more efficient and convenient method than the ones published in the literature (reduction with stannous chloride and hydrochloric acid, yields: 51–78%[42–45] and reduction with sodium hydrosulfite, yield: 63%[43]).

2.2. Enantiomeric recognition studies

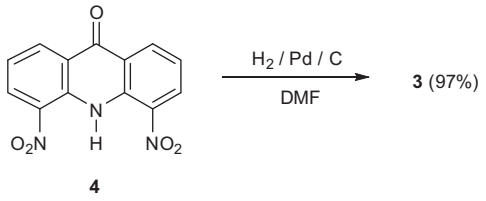
The enantiomeric recognition abilities of receptors (*S*,*S*)-**1** and (*S*,*S*)-**2** towards the enantiomers of tetrabutylammonium salts of mandelic acid (Man), *tert*-butoxycarbonyl-protected phenylglycine

* Corresponding author. Tel.: +36 1 463 1071; fax: +36 1 463 3297.
E-mail address: huszthy@mail.bme.hu (P. Huszthy).

http://dx.doi.org/10.1016/j.tetasy.2015.10.004
0957-4166/



Scheme 1. Synthesis of receptors (*S*,*S*)-**1** and (*S*,*S*)-**2**.



Scheme 2. Synthesis of diaminoacridone **3**.

(Boc-Phg), *tert*-butoxycarbonyl-protected phenylalanine (Boc-Phe) and *tert*-butoxycarbonyl-protected alanine (Boc-Ala) (Fig. 1) were studied in acetonitrile containing 1% DMSO by UV–vis and fluorescence spectroscopies.

Since basic anions often cause the deprotonation of neutral anion sensors, we recorded the UV–vis and fluorescence spectra of the deprotonated forms of receptors (*S*,*S*)-**1** and (*S*,*S*)-**2** using tetrabutylammonium hydroxide as a strong base (Fig. 2).

We also determined the fluorescence quantum yields of the neutral and deprotonated forms of receptors (*S*,*S*)-**1** and (*S*,*S*)-**2** and acridone as a reference compound (Table 1). When comparing the quantum yields of the neutral forms, a considerably lower value is observed in the case of thiourea derivative (*S*,*S*)-**2**, which can be attributed to the quenching effect of the sulfur atoms in the molecule. It can also be seen that the urea moieties did not significantly influence the quantum yield of the acridone core. The quantum yields of acridone and receptor (*S*,*S*)-**1** show a slight decrease, while that of receptor (*S*,*S*)-**2** shows a significant increase upon deprotonation. Thus, the quantum yields of the deprotonated forms are similar.

Upon the addition of carboxylate anions to receptors (*S*,*S*)-**1** and (*S*,*S*)-**2**, the absorption spectral showed changes due to complexation and in most cases, little to no spectra characteristic changes to deprotonation were observed (Fig. 3A and B). There was an exception [(*S*,*S*)-**1** + Boc-Ala], in which case the absorption spectra changes due to deprotonation were more significant (Fig. 3C).

For the investigation of the complexation properties of receptors (*S*,*S*)-**1** and (*S*,*S*)-**2** by fluorescence spectroscopy, excitation wavelengths (375 nm and 385 nm, respectively) were chosen from the absorption ranges where the absorbances of the deprotonated receptors were lower than those of the neutral forms. In this way, the fluorescence titration spectra upon the addition of the various chiral carboxylates showed mainly the spectral characteristic changes to the complexation process, and the deprotonation could be neglected during the evaluation. The titration series of spectra, which showed 10–40% emission decreases upon addition of carboxylates (Fig. 4), could be fitted satisfactorily by assuming a 1:1 complex formation and the enantioselectivity values were calculated (Table 2).

Based on these results, receptor (*S*,*S*)-**1** had an appreciable enantiomeric recognition ability towards (*S*)-Boc-Ala over its (*R*)-isomer (Fig. 4). However, in the cases of other chiral carboxylates (Man, Boc-Phg and Boc-Phe) containing a phenyl or benzyl group at their stereogenic centres, receptor (*S*,*S*)-**1** showed practically no enantiomeric discrimination. This can be attributed to an additional π–π interaction between the phenyl or benzyl moiety and one of the urea carbonyl units beside the hydrogen bonded interactions between the carboxylate and the NH groups. Presumably, the complexes with the enantiomers of Boc-Ala containing an aliphatic and less bulky methyl group had a different structure relative to the complexes with Man, Boc-Phg and Boc-Phe, thus it can render much higher enantiomeric recognition for the former.

It can also be seen that the stability constants of the complexes of receptors (*S*,*S*)-**1** and (*S*,*S*)-**2** with Boc-Phe containing a benzyl group are larger than those with Boc-Phg and Man containing a phenyl group. The change of the urea moieties to thiourea ones had a significant effect on the enantiomeric recognition, that is, receptor (*S*,*S*)-**2** showed moderate selectivity towards the enantiomers of most chiral anions studied (the only exception was Boc-Phe). The opposite (homochiral) enantioselectivity preference in the case of Boc-Ala can also be explained by a probably different binding mode to the receptor relative to Man and Boc-Phg.

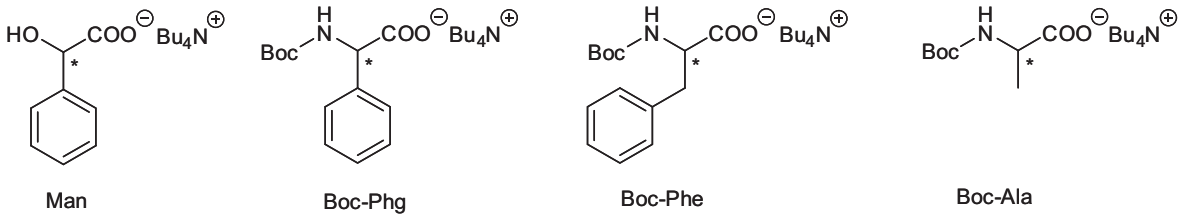


Figure 1. Optically active tetrabutylammonium carboxylates used in the enantiomeric recognition studies.

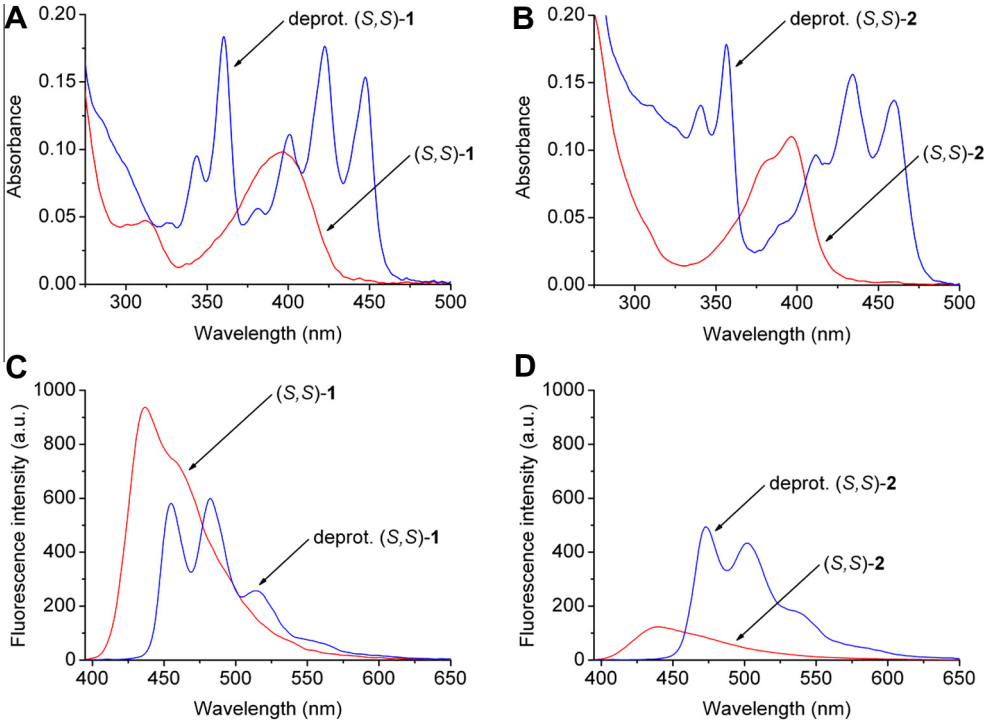


Figure 2. Absorption spectra of (*S*,*S*)-**1**, (*S*,*S*)-**2** and their deprotonated forms (10 μM) in MeCN–DMSO 99:1, optical path length: 1 cm (A and B); fluorescence emission spectra of (*S*,*S*)-**1**, (*S*,*S*)-**2** and their deprotonated forms (10 μM) in MeCN–DMSO 99:1, λ_{ex} = 366 nm for (*S*,*S*)-**1** and deprot. (*S*,*S*)-**1**, λ_{ex} = 364 nm for (*S*,*S*)-**2** and deprot. (*S*,*S*)-**2** (C and D).

Table 1
Fluorescence quantum yields of acridone, (*S*,*S*)-**1**, (*S*,*S*)-**2** and their deprotonated forms in MeCN–DMSO 99:1

	Φ_f	
	Neutral form	Deprotonated form
Acridone	0.42	0.31
(*S*,*S*)-**1**	0.47	0.30
(*S*,*S*)-**2**	0.071	0.25

Table 2
Stability constants for complexes of (*S*,*S*)-**1** and (*S*,*S*)-**2** with the enantiomers of optically active tetrabutylammonium carboxylates and the degrees of enantiomeric differentiation in MeCN–DMSO 99:1

	(*S*,*S*)-**1**		(*S*,*S*)-**2**	
	log*K*	Δlog*K*	log*K*	Δlog*K*
(*R*)-Man	5.37 ± 0.04	−0.01	5.52 ± 0.04	0.20
(*S*)-Man	5.38 ± 0.04		5.32 ± 0.05	
(*R*)-Boc-Phg	5.81 ± 0.09	0.08	5.80 ± 0.05	0.26
(*S*)-Boc-Phg	5.73 ± 0.06		5.54 ± 0.06	
(*R*)-Boc-Phe	6.38 ± 0.06	0.05	6.43 ± 0.11	0.06
(*S*)-Boc-Phe	6.33 ± 0.05		6.37 ± 0.10	
(*R*)-Boc-Ala	6.08 ± 0.03	−0.56	6.18 ± 0.08	−0.25
(*S*)-Boc-Ala	6.64 ± 0.07		6.43 ± 0.07	

3. Conclusion

Herein we have studied the enantiomeric recognition abilities of the newly synthesized acridone bis(urea) (*S*,*S*)-**1** and acridone bis(thiourea) (*S*,*S*)-**2** towards the enantiomers of tetrabutylammonium salts of α-hydroxy and *N*-protected α-amino acids. The highest enantioselectivity was observed in the case of receptor (*S*,*S*)-**1** and Boc-Ala. The presence of a phenyl or benzyl group in the carboxylate anion had a significant effect on the enantiomeric recognition ability of receptor (*S*,*S*)-**1**. The type of the receptor units (urea or thiourea) in the anion sensors also influenced the enantiomeric discrimination.

4. Experimental

4.1. General

Starting materials were purchased from Sigma–Aldrich Corporation unless otherwise noted. Silica gel 60 F_{254} (Merck) plates were used for TLC. The ratios of the solvents for the eluents are given in volumes (mL/mL). Solvents were dried and purified according to well established methods.[46] Evaporations were carried out under reduced pressure.

Melting points were taken on a Boetius micro-melting point apparatus and are uncorrected. Optical rotations were taken on a Perkin–Elmer 241 polarimeter, which was calibrated by measuring the specific rotations of both enantiomers of menthol. IR spectra were recorded on a Bruker Alpha-T FT-IR spectrometer. ^{1}H (500 MHz) NMR spectra were obtained on a Bruker DRX-500 Avance spectrometer. ^{1}H (300 MHz) and ^{13}C (75.5 MHz) NMR spectra were obtained on a Bruker 300 Avance spectrometer. NMR spectra were taken at 298 K unless otherwise indicated. The signals of NH protons in the ^{1}H NMR spectra were helped to identify by shaking the NMR samples with D_2O. Mass spectra were recorded on an Agilent-6120 Single Quadrupole LC/MS instrument using ESI method. Elemental analyses were performed in the Microanalytical Laboratory of the Department of Organic Chemistry, Institute for Chemistry, L. Eötvös University, Budapest, Hungary.

UV–vis spectra were taken on a Unicam UV4-100 spectrophotometer. Quartz cuvettes with path length of 1 cm and 4 cm were used. Fluorescence spectra were recorded on a Perkin–Elmer LS 50B luminescent spectrometer. Emission spectra were corrected by the spectrometer software. Quartz cuvettes with path length of 1 cm were used. Fluorescence quantum yields were determined relative to quinine sulfate (Φ_f = 0.53 in 0.1 M H_2SO_4).[31] Stability

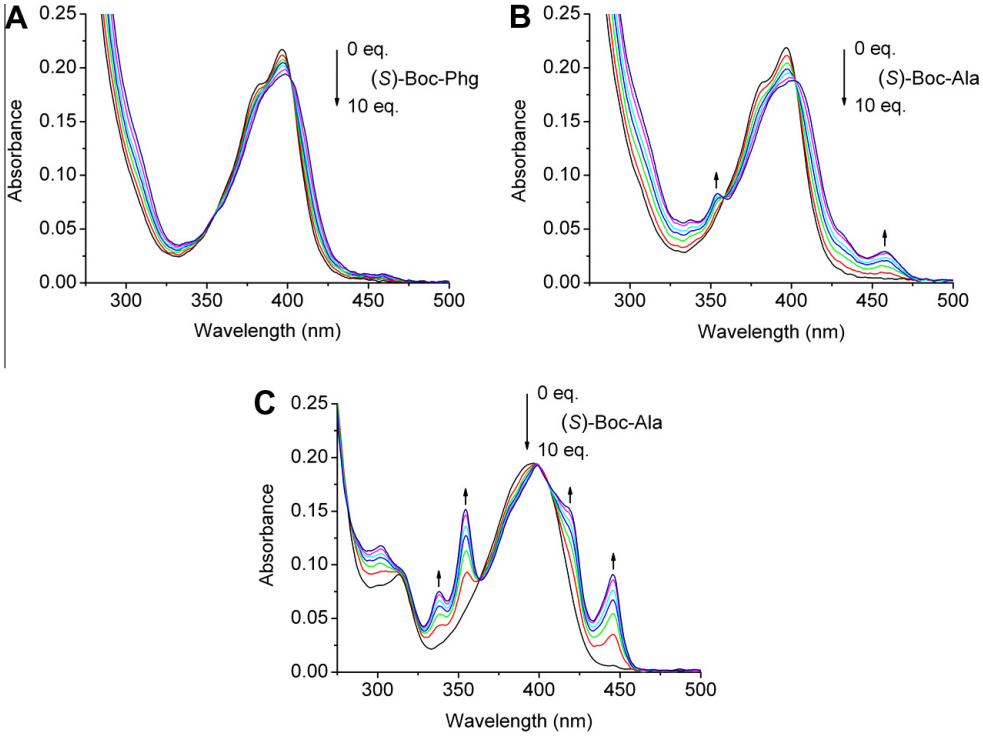


Figure 3. Series of absorption spectra upon titration of (*S*,*S*)-**2** (5 μM) with (*S*)-Boc-Phg (0–10 equiv) (A), (*S*,*S*)-**2** (5 μM) with (*S*)-Boc-Ala (0–10 equiv) (B) and (*S*,*S*)-**1** (5 μM) with (*S*)-Boc-Ala (0–10 equiv) (C) in MeCN–DMSO 99:1, optical path length: 4 cm.

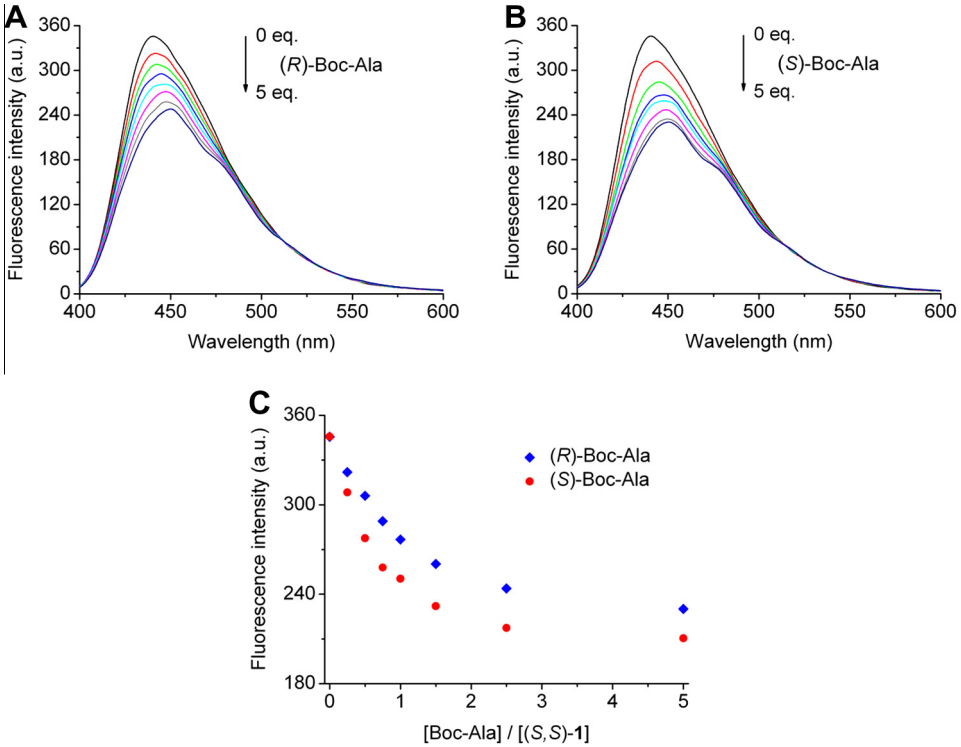


Figure 4. Series of fluorescence emission spectra upon titration of (*S*,*S*)-**1** (2 μM) with (*R*)-Boc-Ala (0–5 equiv) (A) and (*S*)-Boc-Ala (0–5 equiv) (B) in MeCN–DMSO 99:1, λ_{ex} = 375 nm. Titration curves with (*R*)-Boc-Ala and (*S*)-Boc-Ala (0–5 equiv) at 440 nm (C).

constants of the complexes were determined by global nonlinear regression analysis using SPECFIT/32™ software.

The enantiomers of mandelic acid and Boc-protected amino acids were purchased from Sigma–Aldrich Corporation. The tetrabutylammonium salts of the anions were prepared by adding 1 equiv of carboxylic acid to 1 equiv of Bu_4NOH dissolved in MeOH. After evaporating MeOH, the salts were dried under reduced pressure over P_2O_5. During the fluorescence titrations, the concentrations of

receptors (*S*,*S*)-**1** and (*S*,*S*)-**2** were 2 μM and the concentrations of the titrant solutions of chiral carboxylates were 0.5 mM.

4.2. 1,1′-(9-Oxo-9,10-dihydroacridine-4,5-diyl)bis{3-[(1*S*)-1-phenylethyl]urea} (*S*,*S*)-1

To a solution of diaminoacridone **3** (200 mg, 0.888 mmol) in DMF (3 mL) was added a solution of isocyanate (*S*)-**4** (274 mg, 1.862 mmol) in DMF (2 mL) under Ar at rt. The mixture was stirred at rt for 30 min. The precipitate was filtered off, washed with water and ethanol, and then triturated with butyl acetate. The crude product was recrystallized from DMF to yield acridone derivative (*S*,*S*)-**1** (129 mg, 28%) as off-white crystals. Mp: >360 °C; R_f: 0.26 (silica gel TLC, MeOH–CH_2Cl_2 1:20); $[\alpha]_D^{25} = -28$ (*c* 0.15, DMF); IR (KBr) ν_{max} 3402, 3316, 3262, 3062, 3029, 2980, 2965, 2931, 1635, 1605, 1572, 1524, 1441, 1329, 1264, 1237, 1215, 749, 698, 516 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 1.43 (d, J = 7 Hz, 6H), 4.82–4.99 (m, 2H), 6.90 (d, J = 7 Hz, 2H, NH), 7.15–7.43 (m, 12H), 7.62 (d, J = 7 Hz, 2H), 8.02 (d, J = 8 Hz, 2H), 8.54 (s, 2H, NH), 10.83 (s, 1H, NH); ^{13}C NMR (75.5 MHz, DMSO-d_6) δ 23.03, 49.10, 120.98, 121.45, 121.67, 125.88, 126.72, 127.47, 128.02, 128.33, 134.93, 144.72, 155.62, 176.92; MS calcd for $C_{31}H_{29}N_5O_3$: 519.2, found $(M+H)^+$: 520.2; Anal. calcd for $C_{31}H_{29}N_5O_3 \cdot H_2O$: C, 69.26; H, 5.81; N, 13.03. Found: C, 69.51; H, 5.60; N, 13.25.

4.3. 1,1′-(9-Oxo-9,10-dihydroacridine-4,5-diyl)bis{3-[(1*S*)-1-phenylethyl]thiourea} (*S*,*S*)-2

To a solution of diaminoacridone **3** (200 mg, 0.888 mmol) in DMF (3 mL) was added a solution of isothiocyanate (*S*)-**5** (304 mg, 1.862 mmol) in DMF (2 mL) under Ar at rt. The mixture was stirred at rt for 10 days. The solvent was removed, and the residue was triturated with water, ethanol and then butyl acetate. The crude product was recrystallized from DMF–ethanol to yield acridone derivative (*S*,*S*)-**2** (132 mg, 27%) as yellow crystals. Mp: 233–237 °C (decomp.); R_f: 0.39 (silica gel TLC, MeOH–CH_2Cl_2 1:20); $[\alpha]_D^{25} = -21$ (*c* 0.15, DMF); IR (KBr) ν_{max} 3406, 3313, 3261, 3062, 3029, 2976, 2936, 1618, 1579, 1531, 1494, 1439, 1371, 1338, 1327, 1288, 1222, 759, 702, 659, 558, 543, 511 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 1.49 (d, J = 7 Hz, 6H), 5.61 (br s, 2H), 7.17–7.43 (m, 12H), 7.62 (br s, 2H), 8.16 (d, J = 8 Hz, 2H), 8.38 (br s, 2H, NH), 9.16 (s, 1H, NH), 9.43 (br s, 2H, NH); ^1H NMR (300 MHz, DMSO-d_6, 360 K) δ 1.54 (d, J = 7 Hz, 6H), 5.56–5.69 (m, 2H), 7.18–7.44 (m, 12H), 7.62 (d, J = 7 Hz, 2H), 8.04 (d, J = 6 Hz, 2H, NH), 8.19 (d, J = 8 Hz, 2H), 9.14 (br s, 3H, NH); ^{13}C NMR (75.5 MHz, DMSO-d_6) δ 21.69, 53.42, 121.14, 121.39, 124.41, 126.27, 126.72, 127.39, 128.27, 132.59, 136.71, 143.61, 176.85, 181.96; MS calcd for $C_{31}H_{29}N_5OS_2$: 551.2, found $(M+H)^+$: 552.2; Anal. calcd for $C_{31}H_{29}N_5OS_2 \cdot H_2O$: C, 65.35; H, 5.48; N, 12.29. Found: C, 65.10; H, 5.19; N, 12.25.

4.4. 4,5-Diaminoacridin-9(10*H*)-one 3

Dinitroacridone **4**[42–45] (350 mg, 1.227 mmol) was hydrogenated in DMF (28 mL) at 60 °C in the presence of Pd/C catalyst (35 mg, 10% palladium on charcoal, activated). After the reaction was completed, the catalyst was filtered off and the solvent was evaporated to give diaminoacridone **3** (267 mg, 97%) as a green solid which was used without purification. Mp: >360 °C [lit. mp: 340–342 °C[42] and >320 °C[43,44]]; R_f: 0.22 (silica gel TLC, AcOH–acetone–toluene 1:2:10); IR (KBr) ν_{max} 3379 (NH_2 as), 3307 (NH), 3193 (NH_2 s), 3078, 3025, 1656, 1615, 1549, 1528, 1482, 1294, 1239, 827, 743, 589, 548, 495, 435 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 5.71 (s, 4H, NH), 6.96–7.06 (m, 4H), 7.48–7.57 (m, 2H), 8.74 (s, 1H, NH); ^{13}C NMR (75.5 MHz, DMSO-d_6) δ 114.20, 116.56, 121.59, 121.99, 129.92, 137.46, 177.89; MS calcd for $C_{13}H_{11}N_3O$: 225.1, found $(M+H)^+$: 226.1; Anal. calcd for $C_{13}H_{11}N_3O \cdot H_2O$: C, 64.19; H, 5.39; N, 17.27. Found: C, 64.47; H, 5.17; N, 17.48.

Acknowledgements

The financial supports of the Hungarian Scientific Research Fund/National Research, Development and Innovation Office, Hungary (OTKA/NKFIH Nos. K 112289 and PD 104618), the New Széchenyi Development Plan (TÁMOP-4.2.1/B-09/1/KMR-2010-0002) and the Zsuzsanna Szabó Research Fellowship are gratefully acknowledged. The authors express their appreciation to Dr. György Tibor Balogh and Dr. Eszter Riethmüller for taking mass spectra, and for Dr. András Simon for helpful discussion.

References

1. Stibor, I.; Zlatušková, P. *Top. Curr. Chem.* **2005**, *255*, 31–63.
2. Kubik, S. *Chem. Soc. Rev.* **2009**, *38*, 585–605.
3. Brotherhood, P. R.; Davis, A. P. *Chem. Soc. Rev.* **2010**, *39*, 3633–3647.
4. Dieng, P. S.; Sirlin, C. *Int. J. Mol. Sci.* **2010**, *11*, 3334–3348.
5. Accetta, A.; Corradini, R.; Marchelli, R. *Top. Curr. Chem.* **2011**, *300*, 175–216.
6. Zhou, Y.; Yoon, J. *Chem. Soc. Rev.* **2012**, *41*, 52–67.
7. Granda, J. M.; Jurczak, J. In *SPR—Carbohydrate Chemistry*; Rauter, A. P., Lindhorst, T. K., Queneau, Y., Eds.; RSC: Cambridge, UK, 2014; Vol. 40, pp 445–460.
8. Granda, J. M.; Jurczak, J. *Curr. Org. Chem.* **2014**, *18*, 1886–1896.
9. Zhang, X.; Yin, J.; Yoon, J. *Chem. Rev.* **2014**, *114*, 4918–4959.
10. Li, Q.; Xu, K.; Song, P.; Dai, Y.; Yang, L.; Pang, X. *Dyes Pigm.* **2014**, *109*, 169–174.
11. Xu, K.-X.; Kong, H.-J.; Li, P.; Yang, L.; Zhanga, J.-L.; Wangb, C.-J. *New J. Chem.* **2014**, *38*, 1004–1010.
12. Ulatowski, F.; Jurczak, J. *Tetrahedron: Asymmetry* **2014**, *25*, 962–968.
13. Ema, T.; Okuda, K.; Watanabe, S.; Yamasaki, T.; Minami, T.; Esipenko, N. A.; Anzenbacher, P., Jr. *Org. Lett.* **2014**, *16*, 1302–1305.
14. Xu, K.; Kong, H.; Zu, F.; Yang, L.; Wang, C. *Spectrochim. Acta, Part A* **2014**, *118*, 811–815.
15. Botha, F.; Budka, J.; Eigner, V.; Hudeček, O.; Vrzal, L.; Císařová, I.; Lhoták, P. *Tetrahedron* **2014**, *70*, 477–483.
16. Mačková, M.; Mikšátko, J.; Budka, J.; Eigner, V.; Cuřínová, P.; Lhoták, P. *New J. Chem.* **2015**, *39*, 1382–1389.
17. Akdeniz, A.; Mosca, L.; Minami, T.; Anzenbacher, P., Jr. *Chem. Commun.* **2015**, 5770–5773.
18. Ulatowski, F.; Jurczak, J. *J. Org. Chem.* **2015**, *80*, 4235–4243.
19. Gunnlaugsson, T.; Davis, A. P.; Hussey, G. M.; Tierney, J.; Glynn, M. *Org. Biomol. Chem.* **2004**, *2*, 1856–1863.
20. Griesbeck, A. G.; Hanft, S.; Miara, Y. D. *Photochem. Photobiol. Sci.* **2010**, *9*, 1385–1390.
21. Trejo-Huizar, K. E.; Ortiz-Rico, R.; Peña-González, M. A.; Hernández-Rodríguez, M. *New J. Chem.* **2013**, *37*, 2610–2613.
22. Zhou, X.-B.; Yip, Y.-W.; Chan, W.-H.; Lee, A. W. M. *Beilstein J. Org. Chem.* **2011**, *7*, 75–81.
23. Wei, L.-H.; He, Y.-B.; Xu, K.-X.; Liu, S.-Y.; Meng, L.-Z. *Chin. J. Chem.* **2005**, *23*, 757–761.
24. Liu, S.-Y.; He, Y.-B.; Chan, W. H.; Lee, A. W. M. *Tetrahedron* **2006**, *62*, 11687–11696.
25. Costero, A. M.; Colera, M.; Gaviña, P.; Gil, S.; Kubinyi, M.; Pál, K.; Kállay, M. *Tetrahedron* **2008**, *64*, 3217–3224.
26. Kim, Y. K.; Lee, H. N.; Singh, N. J.; Choi, H. J.; Xue, J. Y.; Kim, K. S.; Yoon, J.; Hyun, M. H. *J. Org. Chem.* **2008**, *73*, 301–304.
27. Huang, X.-H.; He, Y.-B.; Chen, Z.-H.; Hu, C.-G.; Qing, G.-Y. *Can. J. Chem.* **2008**, *86*, 170–176.
28. Hu, C.; He, Y.; Chen, X.; Huang, Z. *Tetrahedron: Asymmetry* **2009**, *20*, 104–110.
29. Costero, A. M.; Llaosa, U.; Gil, S.; Parra, M.; Colera, M. *Tetrahedron: Asymmetry* **2009**, *20*, 1468–1471.
30. Wang, F.; Nandhakumar, R.; Hu, Y.; Kim, D.; Kim, K. M.; Yoon, J. *J. Org. Chem.* **2013**, *78*, 11571–11576.
31. Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, 3rd ed.; Springer Science +Business Media: New York, NY, 2006.
32. Albert, A. *The Acridines*, 2nd ed.; Edward Arnold: London, UK, 1966.
33. Acheson, R. M., In *The Chemistry of Heterocyclic Compounds*, 2nd ed.; Weissberger, A., Taylor, E. C., Eds.; Wiley: New York, NY, 1973; Vol. 9.
34. Siegmund, M.; Bendig, J. *Ber. Bunsen-Ges. Phys. Chem.* **1978**, *82*, 1061–1068.
35. Móczár, I.; Huszthy, P.; Mezei, A.; Kádár, M.; Nyitrai, J.; Tóth, K. *Tetrahedron* **2010**, *66*, 350–358.
36. Rothman, J. H.; Still, W. C. *Bioorg. Med. Chem. Lett.* **1999**, *9*, 509–512.
37. Miyaji, H.; Sessler, J. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 154–157.
38. Blázquez, M. T.; Muniz, F. M.; Sáez, S.; Simón, L. M.; Alonso, Á.; Raposo, C.; Lithgow, A.; Alcázar, V.; Morán, J. R. *Heterocycles* **2006**, *69*, 73–81.

39. García-Garrido, S. E.; Caltagirone, C.; Light, M. E.; Gale, P. A. *Chem. Commun.* **2007**, 1450–1452.
40. Lin, C.; Simov, V.; Drueckhammer, D. G. *J. Org. Chem.* **2007**, *72*, 1742–1746.
41. Mashraqui, S. H.; Tripathi, S.; Betkar, R.; Chandiramani, M. *Chem. Lett.* **2010**, *39*, 650–651.
42. Goldberg, A. A.; Kelly, W. *J. Chem. Soc.* **1947**, 595–597.
43. Klein, E. R.; Lahey, F. N. *J. Chem. Soc.* **1947**, 1418–1419.
44. Dixon, R. P.; Snyder, J. S.; Bradley, L.; Linnenbrink, J. *Org. Prep. Proced. Int.* **2000**, *32*, 573–577.
45. Santini, V.; Boyer, G.; Galy, J.-P. *Heterocycl. Commun.* **2003**, *9*, 265–270.
46. Riddick, J. A.; Bunger, W. B.; Sakano, T. K., In *Techniques of Chemistry*, 4th ed.; Weissberger, A., Ed.; Wiley-Interscience: New York, NY, 1986; Vol. 2.

Please cite this article in press as: Pál, D.; et al. *Tetrahedron: Asymmetry* (2015), http://dx.doi.org/10.1016/j.tetasy.2015.10.004