Concise Synthesis of Coscinamide B, a Bisindolic Enamide from Marine Sponge

Manas Chakrabarty,*[a] Ramkrishna Basak,[a] Yoshihiro Harigaya[b]

[a] Department of Chemistry, Bose Institute, 93/1, A.P.C. Road, Kolkata 700009, India
Fax +91(33)23506790; E-mail: chakmanas@yahoo.co.in

[b] School of Pharmaceutical Sciences, Kitasato University, Minato-ku, Tokyo 108, Japan

Received 22 April 2003; revised 16 June 2003

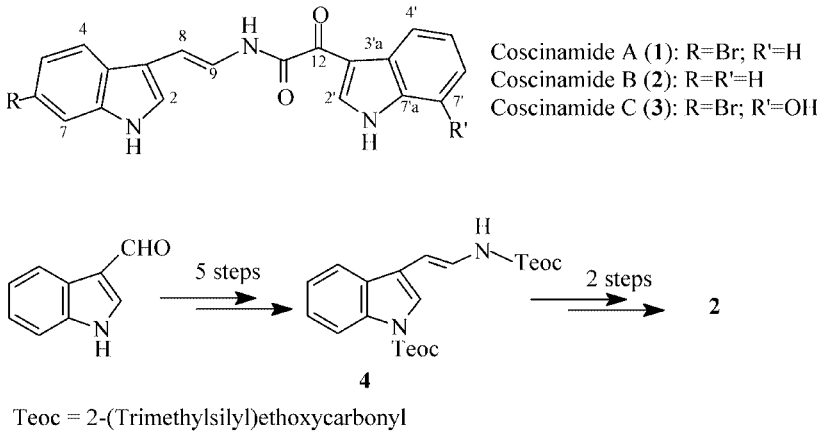
Abstract: An efficient, four-step synthesis of coscinamide B (**2**) from tryptamine is reported, in which a one-pot benzylic bromination and subsequent in situ dehydrobromination in the absence of an added base is the key step.

Key words: coscinamide B, bisindolic enamide, synthesis, tryptamine, in situ dehydrobromination

Indolic enamides constitute a small group of natural products of both plant and marine origins.[1a–e] Bisindolic enamides, however, are quite rare,[2] and recently three new bisindolic enamides, coscinamides A–C (**1**–**3**), showing partial cytoprotection against HIV in the NCI assay, were isolated from a marine sponge, a *Coscinoderma sp*.[3] A Japanese group has subsequently reported the synthesis of coscinamide B (**2**) by a seven-step strategy using an *N*-protected indolylalkenyl carbamate **4**, prepared in situ from the corresponding indolylalkenyl acid azide by Curtius rearrangement (Scheme 1).[4]

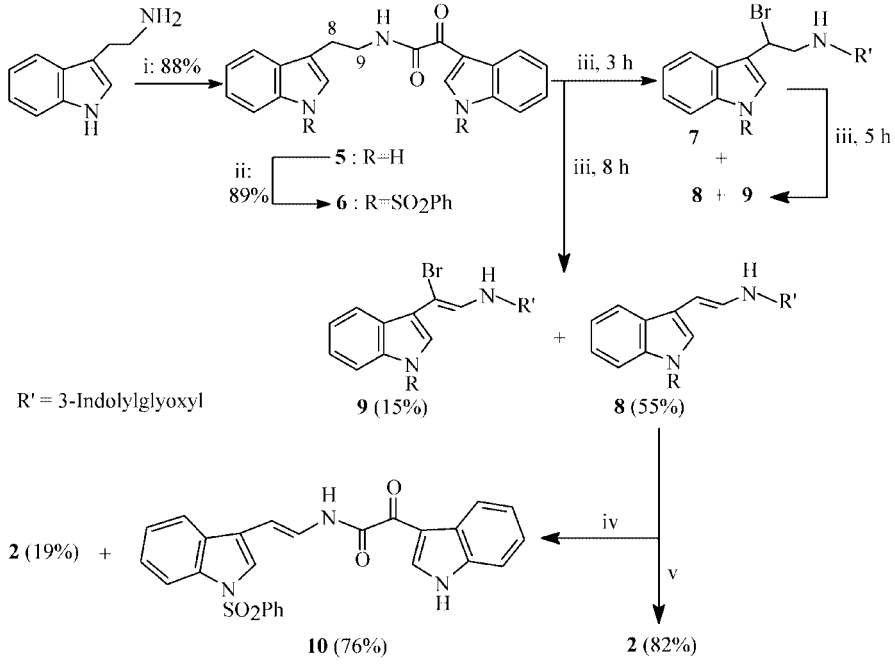
This multistep synthesis of **4** and the reported low overall yield of **2** prompts us to report herein an alternate, concise and efficient synthesis of **2**, which we embarked upon much earlier than the publication of the synthesis by the Japanese group. Our method of synthesis of **2** is outlined in Scheme 2.

Our plan was to first prepare 8,9-dihydrocoscinamide B (**5**) from tryptamine in one-step and subject it to benzylic bromination and finally dehydrobrominate the resulting 8-bromo derivative by treatment with a base. Accordingly, tryptamine was condensed with 3-indolylglyoxyl chloride[5] to give **5** in high yield. When the corresponding *N*,*N*′-bis(benzenesulfonyl) derivative **6**, derived from **5** in the usual manner,[6] was refluxed with *N*-bromosuccinimide (NBS) in carbon tetrachloride in the presence of a catalytic amount of benzoyl peroxide, *N*,*N*′-bis(benzenesulfonyl)coscinamide B (**8**), instead of the expected 8-bromodihydro derivative **7**, was unexpectedly formed as the major product along with the corresponding 8-bromo enamide **9** as the minor byproduct. The coupling constant (J = 15 Hz) for the NMR signal H-8 (δ = 6.504, d) demonstrated **8** to be the *E*-isomer, as in coscinamide B.[3] The direct formation of **8** from **6** in the absence of an added base strongly suggests that the 8-bromo derivative **7** was initially formed, which, upon subsequent in situ dehydrobromination in solution, furnished **8**. Although a few instances of free radical elimination in solution have been previously documented,[7a,b] this type of one-pot benzylic bromination and subsequent in situ dehydrobromination in presence of NBS/benzoyl peroxide is, to the best of our knowledge, undocumented as yet. Also, our assumption regarding the formation of **8** from **6** via the in-



Scheme 1

Synthesis 2003, No. 13, Print: 18 09 2003. Web: 19 08 2003.
Art Id.1437-210X,E;2003,0,13,2011,2014,ftx,en;P03403SS.pdf.
DOI: 10.1055/s-2003-41022



Scheme 2 *Reagents and conditions*: i) 3-indolylglyoxyl chloride, MeCN, r.t., 4 h; ii) $BzEt_3NCl$ (2 mol%), NaOH (3 equiv), $PhSO_2Cl$, CH_2Cl_2, r.t., 1 h; iii) NBS (1.1 equiv), $(PhCO_2)_2O$ (cat), CCl_4, reflux; iv) K_2CO_3, MeOH–H_2O (4:1), 40–50 °C, 2 h; v) K_2CO_3, MeOH–H_2O (4:1), reflux, 7 h

termediacy of **7** received support when we isolated **7** along with **8** and **9** by terminating the reaction of **6** with NBS and benzoyl peroxide in carbon tetrachloride under reflux after 3 hours, instead of 8 hours. In **7**, C-8 could be easily ascertained as the site of substitution by bromine since substitution only at this site can explain the observed mutiplicities of the ^{1}H NMR signals of H-8, H-9 and the amidic NH (dd, ddd, ddd and dd, respectively) (see Experimental). Moreover, when **7** was refluxed with NBS and benzoyl peroxide in carbon tetrachloride for 5 hours, both **8** and **9** were formed. This experiment confirms our view, stated earlier, that **8** is indeed formed via the intermediacy of **7**. Since our objective was to develop an efficient, concise synthesis of **2**, we did not carry out any further experiment to find out the exact course of formation of **9**. However, the formation of 8,8-dibromo derivative of **6** (not isolated), followed by elimination of a molecule of hydrogen bromide, may be the route to the formation of **9**. In **9**, the site of substitution by bromine (i.e., C-8) was obvious because only in that case each of the amidic NH and H-9 would be a doublet having a common coupling constant (J = 11 Hz), which was indeed observed. In the final step, mild alkaline hydrolysis of **8** afforded *N*-(benzenesulfonyl)coscinamide B (**10**) and coscinamide B (**2**) as the major and the minor products, respectively. Nevertheless, alkaline hydrolysis of **8** under a harsher condition furnished only **2** in very good yield. The spectral data of the synthetic product were in agreement with those reported for coscinamide B in the literature.[3]

In conclusion, we have developed a concise synthesis of coscinamide B with higher overall yield (35% as against 13%[4]) from simple building blocks. Furthermore, this one-pot benzylic bromination and in situ dehydrobromination in the absence of any added base opens up the possibility of a new general synthesis of bisindolic enamides, which we intend to explore in near future.

All solvents were dried and purified using standard techniques. Et_2O was stored over sodium wire. The glass apparatus for the anhydrous reactions were dried in an oven and assembled hot before use. Melting points were determined on a Toshniwal apparatus. IR spectra were recorded on a Nicolet Impact 410 spectrophotometer. LR EI-MS was performed using an AEI MS 30 spectrometer and LR EI-MS and HR FAB-MS (*m*-nitrobenzyl alcohol as a liquid matrix) were carried out on Jeol JMS-AX505HA and Jeol JMS-700 M Station mass spectrometers. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra, both 1D and 2D, including DEPT-135 were recorded on a Bruker DRX 500 NMR spectrometer. Individual ^{1}H and ^{13}C NMR assignments, wherever made, are based on HMQC and HMBC spectral analyses. Both analytical and preparative TLC were carried out on silica gel G (Merck, India) plates. Petroleum ether used had bp 60–80 °C. Elemental analyses were performed in a Dr. Hans Hoesli Analyser (Type A1, No.1058).

8,9-Dihydrocoscinamide B (5)

A solution of freshly distilled oxalyl chloride (0.93 mL, 11 mmol) in Et_2O (20 mL) was added dropwise with stirring to a solution of indole (1.17 g, 10 mmol) in Et_2O (5 mL) at 0 °C and the solution stirred at 0 °C for 1 h, producing a yellow precipitate. Et_2O was then distilled off and the residue was washed with a large excess of anhyd petroleum ether and dried. The resulting 3-indolylglyoxyl chloride was dissolved in MeCN (20 mL), cooled to 0 °C, and to this was added dropwise with stirring a solution of tryptamine (1.76 g, 11 mmol) in MeCN (10 mL) during 10–15 min. The stirring was continued at r.t. for 4 h, the solution was then poured into H_2O and extracted with EtOAc (3 × 25 mL). The organic phase was further

washed with H_2O and dried (Na_2SO_4). The solvent was distilled off and the residue was crystallised from EtOAc–petroleum ether to furnish **5** (2.92 g, 88%) as reddish brown crystals; mp 198–200 °C.

IR (KBr): 3388, 3354, 3278, 1662, 1618, 1504, 1436, 1234, 738 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 2.941 (t, 2 H, *J* = 7.5 Hz, H-8), 3.506 (dt, 2 H, *J* = 7, 7 Hz, H-9), 6.967 (t, 1 H, *J* = 7.5 Hz, H-5), 7.051 (td, 1 H, *J* = 7.5, 1 Hz, H-6), 7.18 (d, 1 H, *J* = 2 Hz, H-2), 7.229 (td, 1 H, *J* = 7, 2 Hz, H-5′), 7.248 (td, 1 H, *J* = 7, 2 Hz, H-6′), 7.327 (d, 1 H, *J* = 8 Hz, H-7), 7.5–7.537 (m, 1 H, H-7′), 7.585 (d, 1 H, *J* = 7.5 Hz, H-4), 8.2–8.24 (m, 1 H, H-4′), 8.75 (d, 1 H, *J* = 3 Hz, H-2′) , 8.786 (t, 1 H, *J* = 5.5 Hz, NHCO), 10.803 (br s, 1 H, NH-1), 12.208 (br s, 1 H, NH-1′).

^{13}C NMR (DMSO-d_6): δ = 25.7 (CH_2-8), 40.2 (CH_2-9), 112.2 (CH-7), 113.4 (CH-7′), 119.13 and 119.19 (CH-4, 5), 121.8 (CH-6), 122.1 (CH-4′), 123.3 (CH-2), 123.5 (CH-5′), 124.2 (CH-6′), 139.3 (CH-2′), 112.4 (C-3), 113.0 (C-3′), 127.1 (C-3′a), 128.0 (C-3a), 137.1 (2 × C-7a, 7′a), 164.3 (NHCO), 183.0 (Ar*C*O).

MS: *m*/*z* (%) = 331 (M^+, 31), 144 (100), 143 (98), 130 (60), 116 (15), 89 (9), 77 (3).

Anal. Calcd for $C_{20}H_{17}N_3O_2$: C, 72.50; H, 5.17; N, 12.68. Found: C, 72.54; H, 5.18; N, 12.65.

1,1′-Bis(benzenesulfonyl)dihydrocoscinamide B (6)

To a solution **5** (1.66 g, 5 mmol) in CH_2Cl_2 (50 mL) was added $BnEt_3NCl$ (23 mg, 0.10 mmol, 2 mol%), followed by powdered NaOH (0.6 g, 15 mmol), and the mixture was stirred at r.t. for 1 h. Benzenesulfonyl chloride (1.92 mL, 15 mmol) was then added to this suspension and the mixture was stirred at r.t. for another 1 h. The reaction mixture was poured into H_2O and extracted with CH_2Cl_2 (3 × 20 mL). The CH_2Cl_2 extract was dried (Na_2SO_4) and evaporated. The residue was crystallised from CH_2Cl_2–petroleum ether to furnish **6** (2.72 g, 89%) as a white amorphous solid; mp 162–164 °C.

IR (Nujol): 3270, 1692, 1653, 1520, 1175, 1135, 976, 751 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 3.009 (t, 2 H, *J* = 7 Hz, H-8), 3.711 (dt, 2 H, *J* = 7, 7 Hz, H-9), 7.267 (t, 1 H, *J* = 7.5 Hz, H-5), 7.342 (t, 1 H, *J* = 7.5 Hz, H-6), 7.387 (t, 1 H, *J* = 7.5 Hz, H-5′), 7.402 (t, 2 H, *J* = 7.5 Hz, H-3‴, 5‴), 7.417 (t, 1 H, *J* = 7.5 Hz, H-6′), 7.43 (t, 1 H, *J* = 7.5 Hz, CONH), 7.463 (m, 1 H, H-4‴), 7.504 [t, 2 H (out of 3 H), *J* = 7.5 Hz, H-3″, 5″], 7.504 [s, 1 H (out of 3 H), H-2], 7.542 (d, 1 H, *J* = 7.5 Hz, H-4), 7.597 (t, 1 H, *J* = 7.5 Hz, H-4″), 7.873 (d, 2 H, *J* = 7.5 Hz, H-2‴, 6‴), 7.986–8.05 (m, 4 H, H-7, 7′, 2″, 6″), 8.34 (d, 1 H, *J* = 7 Hz, H-4′), 9.444 (s, 1 H, H-2′).

^{13}C NMR ($CDCl_3$): δ = 25.4 (CH_2-8), 38.9 (CH_2-9), 113.6 (CH-7′), 114.2 (CH-7), 119.7 (CH-4), 123.1 (CH-4′), 123.8 and 123.9 (CH-2, 5), 125.4 (CH-6), 125.6 (CH-5′), 126.4 (CH-6′), 127.1 (2 ×, CH-2‴, 6‴), 127.7 (2 ×, CH-2″, 6″), 129.7 (2 ×, CH-3‴, 5‴), 130.1 (2 ×, CH-3″, 5″), 134.1 (CH-4‴), 135.0 (CH-4″), 138.9 (CH-2′), 116.5 (C-3′), 119.8 (C-3), 128.5 (C-3′a), 130.8 (C-3a), 134.6 (C-7′a), 135.7 (C-7a), 137.8 (C-2″), 138.4 (C-2‴), 161.5 (NHCO), 181.9 (Ar*C*O).

MS: *m*/*z* (%) = 611 (M^+, 21), 284 (75), 283 (100), 70 (13), 141 (16), 77 (18).

Anal. Calcd for $C_{32}H_{25}N_3O_6S_2$: C, 62.84; H, 4.12; N, 6.87. Found: C, 62.76; H, 4.14; N, 6.85

1,1′-Bis(benzenesulfonyl)coscinamide B (8) and 8-Bromo-1,1′-bis(benzenesulfonyl)coscinamide B (9)

To a solution of **6** (0.306 g, 0.5 mmol) in CCl_4 (50 mL) was added NBS (0.1 g, 0.55 mmol) and benzoyl peroxide (6 mg), and the mixture was refluxed for 8 h when the solution gradually turned yellow. It was then cooled and the precipitated succinimide was filtered off. The filtrate was concentrated and the residue was purified by preparative TLC on silica gel (benzene) to furnish **8** as light orange flakes (0.168 g, 55%); mp 204–206 °C (CH_2Cl_2–petroleum ether) and **9** as yellow needles (52 mg, 15%); mp 222–224 °C (CH_2Cl_2–petroleum ether).

8

IR (Nujol): 3337, 1686, 1646, 1175, 764, 724 cm^{-1}.

^1H NMR ($CDCl_3$): δ= 6.504 (d, 1 H, *J* = 15 Hz), 7.312 and 7.371 (t each, 1 H, *J* = 7.5 Hz), 7.412, 7.449 and 7.512 (t each, 2 H, *J* = 7.5 Hz), 7.527 and 7.542 (t each, 1 H, *J* = 7.5 Hz), 7.601 (m, 1 H), 7.611 (s, 1 H), 7.743 (d, 1 H, *J* = 7.5 Hz), 7.9 (d, 2 H, *J* = 7.5 Hz), 7.95–8.08 (m, 4 H), 8.363 (d, 1 H, *J* = 7.5 Hz), 9.164 (d, 1 H, *J* = 10.5 Hz), 9.461 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 108.0, 122.2 (both olefinic CH), 113.7, 114.2, 120.7, 123.2, 123.7, 124.2, 125.6, 125.7, 126.6, 127.2 (2 ×), 127.7 (2 ×), 129.7 (2 ×), 130.1 (2 ×), 134.3, 135.1, 139.1 (ArCH), 116.4, 119.1, 128.4, 129.0, 134.7, 135.9, 137.8, 138.4 (ArC), 158.2 (NHCO), 180.9 (Ar*C*O).

MS: *m*/*z* (%) = 609 (M^+, 34), 284 (100), 141 (26), 77 (44).

HRMS: *m*/*z* calcd for $C_{32}H_{23}N_3O_6S_2$: 609.1029; found: 609.1033 (M^+).

9

IR (Nujol): 3350, 1699, 1653, 1182, 731 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.349 and 7.401 (t each, 1 H, *J* = 7.5 Hz), 7.416, 7.488 and 7.519 (t each, 2 H, *J* = 7.5 Hz), 7.580 and 7.618 (t each, 1 H, *J* = 7.5 Hz), 7.747 (d, 1 H, *J* = 11 Hz), 7.822 (s, 1 H), 7.846 (d, 1 H, *J* = 8 Hz), 7.936 (d, 2 H, *J* = 8 Hz), 7.955–8.058 (m, 4 H), 8.388 (d, 1 H, *J* = 7.5 Hz), 9.42 (s, 1 H), 9.507 (d, 1 H, *J* = 11 Hz).

^{13}C NMR ($CDCl_3$): δ = 121.4 (=CH), 113.7, 114.3, 120.9, 123.2, 124.5, 125.8, 126.0, 126.7, 127.1, 127.3 (2 ×), 127.7 (2 ×), 129.9 (2 ×), 130.1 (2 ×), 134.6, 135.2, 138.9 (ArCH), 102.8 (=CBr) 116.3, 120.7, 127.5, 128.4, 134.7, 135.8, 137.7, 138.2 (ArC), 158.2 (NHCO), 180.1 (Ar*C*O).

MS: *m*/*z* (%) = 689 (37), 687 (M^+, 34), 608 (100), 468 (45), 351 (27), 326 (66), 284 (13), 141 (16), 77 (91).

HRMS: *m*/*z* calcd for $C_{32}H_{22}Br^{79}N_3NaO_6S_2$: 710.0031; found: 710.0035 (M + Na) $^+$; *m*/*z* calcd for $C_{32}H_{22}Br^{81}N_3NaO_6S_2$: 712.0010; found: 712.0021 (M + Na) $^+$.

1,1′-Bis(benzenesulfonyl)-8-bromodihydrocoscinamide B (7)

To a solution of **6** (0.2 g, 0.32 mmol) in CCl_4 (40 mL) was added NBS (63 mg, 0.35 mmol), followed by benzoyl peroxide (5 mg), and the mixture was refluxed for 3 h, when the solution, as before, slowly became yellow. After workup as before, followed by purification by preparative TLC on silica gel (EtOAc–benzene, 1:9), furnished **7** as a yellowish brown solid (88 mg, 39%); mp 158–160 °C along with a mixture (TLC) of **8** and **9** (76 mg) which were not further separated.

7

IR (Nujol): 3356, 1692, 1653, 1527, 1454, 1175, 970, 751 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 3.527 (ddd, 1 H, *J* = 13, 6.5, 6.5 Hz, H-9), 3.662 (ddd, 1 H, *J* = 12, 6.5, 5.5 Hz, H-9), 5.064 (dd, 1 H, *J* = 11, 5.5 Hz, H-8), 7.256 (t, 1 H, *J* = 7.5 Hz, H-5), 7.327 (t, 1 H, *J* = 7.5 Hz, H-6), 7.43 (t, 1 H, *J* = 7.5 Hz, H-5′), 7.455 (t, 2 H, *J* = 7.5 Hz, H-3‴, 5‴), 7.469 (t, 1 H, *J* = 7.5 Hz, H-6′), 7.541 (t, 1 H, *J* = 7.5 Hz, H-4″), 7.628 (t, 2 H, *J* = 7.5 Hz, H-3″, 5″), 7.729 (s, 1 H, H-2), 7.744 (t, 1 H, *J* = 7.5 Hz, H-4‴), 7.764 (d, 1 H, *J* = 7.5 Hz, H-4), 7.917 (d, 3 H, *J* = 8 Hz, H-7, 2″, 6″), 7.983 (d, 1 H, *J* = 8 Hz, H-7′), 8.121 (d, 2 H, *J* = 7.5 Hz, H-2‴, 6‴), 8.242 (d, 1 H, *J* = 7.5 Hz, H-4′), 8.921(dd, 1 H, *J* = 5.5, 5.5 Hz, CONH), 9.125 (s, 1 H, H-2′).

^{13}C NMR (DMSO-d_6): δ = 45.8 (CH_2-9), 65.5 (CHBr-8), 114.0 (2 ×, CH-7, 7′), 121.7 (CH-4), 123.0 (CH-4′), 123.9 (CH-2), 124.1 (CH-5), 125.7 (CH-6), 126.2 (CH-5′), 127.1 (CH-6′), 127.4 (2 ×, CH-2″, 6″), 128.2 (2 ×, CH-2‴, 6‴), 130.5 (2 ×, CH-3‴, 5‴), 131.1 (2 ×, CH-3″, 5″), 135.3 (CH-4″), 136.4 (CH-4‴), 138.0 (CH-2′), 116.6 (C-3′), 125.5 (C-3), 128.3 (C-3′a), 129.9 (C-3a), 134.2 (C-7′a), 135.5 (C-7a), 136.9 (C-1″), 137.9 (C-1‴), 162.7 (NHCO), 183.5 (ArCO).

MS: *m*/*z* = 691, 689 (M^+), 610, 284, 141, 77.

Anal. Calcd for $C_{32}H_{24}Br^{79+81}N_3O_6S_2$: C, 55.64; H, 3.50; N, 6.08. Found: C, 55.54; H, 3.51; N, 6.11.

Conversion of 1,1′-Bis(benzenesulfonyl)-8-bromodihydrocosinamide B (7) to 8 and 9

To a solution of **7** (70 mg, 0.1 mmol) in CCl_4 (30 mL) was added NBS (20 mg, 0.11 mmol) followed by a pinch of benzoyl peroxide, and the mixture was refluxed for 5 h. Following a similar workup as in the two previous experiments, a solid residue (41 mg) comprising a mixture (TLC) of **8** and **9** was obtained.

1-Benzenesulfonylcoscinamide B (10) and Coscinamide B (2)

To a solution of **8** (0.123 g, 0.2 mmol) in MeOH (20 mL) was added K_2CO_3 (0.164 g, 1.2 mmol) in H_2O (5 mL), and the mixture was heated to 40–50 °C for 2 h, concentrated to one third of its volume under vacuum, poured into H_2O and extracted with EtOAc (2 × 25 mL). The combined EtOAc extracts were dried (Na_2SO_4), evaporated and the residue was purified by preparative TLC (petroleum ether–EtOAc, 13:7), followed by crystallisation from CH_2Cl_2–petroleum ether, to furnish **10** as yellow flakes (72 mg, 76%); mp 126–128 °C along with **2** as an orange solid (13 mg, 19%).

10

IR (Nujol): 3376, 3277, 1686, 1626, 1175, 1122, 744 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 6.744 (d, 1 H, *J* = 15 Hz), 7.265–7.283 (m, 2 H), 7.339 (t, 1 H, *J* = 7.5 Hz), 7.391 (t, 1 H, *J* = 7.5 Hz), 7.57 (t, 2 H, *J* = 7.5 Hz), 7.517–7.632 (m, 2 H), 7.659 (d, 1 H, *J* = 7.5 Hz), 7.68 (d, 1 H, *J* = 7.5 Hz), 7.974 (d, 1 H, *J* = 8 Hz), 7.994 (s, 1 H), 8.001 (d, 2 H, *J* = 7.5 Hz), 8.259 (m, 1 H), 8.79 (s, 1 H), 11.041 (d, 1 H, *J* = 10 Hz), 12.339 (br s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 106.7, 113.5, 114.3, 120.9, 122.1, 123.6, 123.8, 124.4, 124.6, 124.8, 126.0, 127.6 (2 ×), 130.6 (2 ×), 135.4, 139.6 (CH), 113.0, 120.1, 127.0, 129.4, 135.6, 137.2, 137.7 (C), 161.7 (NHCO), 181.5 (ArCO).

MS: *m*/*z* (%) = 469 (M^+, 26), 329 (17), 298 (5), 270 (9), 157 (23), 144 (100), 116 (12), 89 (6), 77 (12).

HRMS: *m*/*z* calcd for $C_{26}H_{19}N_3O_4S$: 469.1115; found: 469.1096 (M^+).

Conversion of 8 to 2

In a second set of experiment, a solution of **8** (0.123 g, 0.2 mmol) in aq methanolic K_2CO_3 (as above) was refluxed for 7 h. After the workup as before, followed by crystallization from EtOAc–petroleum ether, furnished only **2** (55 mg, 82%) as orange crystals; mp 228–230 °C (dec).

IR (KBr): 3323, 3288, 3230, 2922, 2850, 1625, 1581, 1517, 1431, 1242, 1124, 744 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 6.841 (d, 1 H, *J* = 15 Hz), 7.086 (t, 1 H, *J* = 7.5 Hz), 7.127 (t, 1 H, *J* = 7.5 Hz), 7.208 (t, 1 H, *J* = 8 Hz), 7.24 (t, 1 H, *J* = 8 Hz), 7.387 (d, 1 H, *J* = 7 Hz), 7.408 (dd, 1 H, *J* = 15, 10 Hz), 7.474 (s, 1 H), 7.509 (d, 1 H, *J* = 7.5 Hz), 7.678 (d, 1 H, *J* = 7.5 Hz), 8.26 (m, 1 H), 8.82 (s, 1 H), 10.796 (d, 1 H, *J* = 10 Hz), 11.204 (br s, 1 H), 12.332 (br s, 1 H).

MS: *m*/*z* (%) = 329 (M^+, 29), 327 (60), 158 (30), 144 (100), 116 (25), 89 (16), 77 (6).

HRMS : *m*/*z* calcd for $C_{20}H_{16}N_3O_2$: 330.1242; found: 330.1194 $(M + H)^+$.

Acknowledgments

The authors express their sincere thanks to the Director, Bose Institute for providing laboratory facilities, to Mr. B. Majumdar, NMR Facilities, Bose Institute for recording the spectra and to the C.S.I.R., Govt. of India for providing an ad-hoc fellowship (R.B.).

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