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Molecular Recognition: Studies on the Synthesis of Methylene Pivotal Bisthiophene Carboxamide Derivatives as Ditopic Receptors for Suberic Acid

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New molecular receptors with diphenylmethane with dithiophene as spacer containing functional groups complementary to suberic acid have been developed.

Keywords: Binding; Receptor; Dicarboxylic acid

INTRODUCTION

Supramolecular chemistry based on molecular recognition is one of the most popular and rapidly growing subjects and has added a new dimension to chemistry [1–5]. Both mono- and dicarboxylic acids and carboxylates are important targets in the area of molecular recognition because of their presence in a large number of antibiotics, analgesics, anti-inflammatory agents and other biologically active molecules. Thus, host–guest complexation studies of the carboxylic acids and their derivatives with suitable receptors have become the central focus of molecular recognition studies aiming to mimic biochemical processes. As a result, studies of supramolecular systems designed as receptors with the capability to bind carboxylic acids have recently received much attention and a number of important works in this area have been documented [6–23].

With the aim of generating new spacers, we have designed and executed a new type of receptor with a carbon pivotal forceps-type molecule having amide functionality at the end to selectively bind appropriate sized dicarboxylic acids. The success of these systems largely depends on proper orientation of the binding groups of the receptors to complement those of the intended substrates or the guest molecules. We herein report the selective recognition of suberic acid through multipoint hydrogen bonds of the bisthiophene-5-carboxamide derivative, **1** (Fig. 1).

In this receptor, the 2-aminopyridine moiety has been used as a hydrogen-bonding motif and the two pyridine units are angularly disposed by a diphenylmethane spacer. A methylene ($-CH_2-$) spacer has been deliberately chosen so that it can increase the π-acceptor nature of the amide proton to enhance the complex formation with a π-donor acid. Interestingly, the introduction of two thiophene moieties will allow us to synthesize receptors with high fluorescence intensity in comparison to some other recently reported molecules [11]. All the hydrogen-bonding groups are presumably arranged in a concave orientation and in the solution phase three theoretical conformations (in–in, in–out, out–out) of comparable energy values are expected. Detailed energy minimization studies showed that the distances between the two amide protons and two pyridine nitrogen atoms in receptor **1** (E_{min} = 19.67 kcal mol^{-1}) are 14.38 and 17.02 Å, respectively. The corresponding distance between the carbonyl oxygens (C=O) was found to be 16.43 Å. Another non-specific receptor **2** (Fig. 1) was also synthesized, having comparable shape and size to receptor **1**, lacking only the 2-aminopyridine moiety. In **2** (E_{min} = 14.55 kcal mol^{-1}), the corresponding NH–HN and CH_3O-OCH_3 distances are 14.38 and 16.04 Å, respectively. The corresponding distance between the carbonyl oxygens (C=O) was found to be 16.57 Å.

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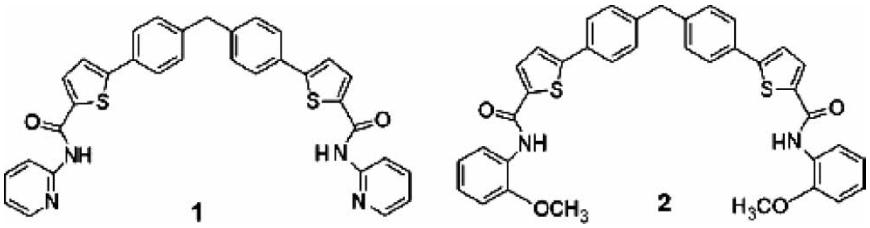


FIGURE 1 Structures of the receptors **1** and **2**.

The energy minimized structures (Fig. 2) of these receptors were generated from molecular mechanics studies (MM2 calculation) by using CS Chem 3D Pro (Version 5.0), 1999 software [24]. Detailed energy minimization studies of the receptors were performed with different dicarboxylic acids, namely, suberic acid, benzene 1,3-dipropanoic acid, benzene-1,3-dibutanoic acid, sebacic acid, adipic acid and glutaric acid. However, only suberic acid ($E_{min} = 26.01\,kcal\,mol^{-1}$), benzene 1,3-dipropanoic acid ($E_{min} = 29.82\,kcal\,mol^{-1}$) and benzene-1,3-dibutanoic acid ($E_{min} = 30.33\,kcal\,mol^{-1}$) were found to fit well into the cavity of these receptors. A proposed mode of complexation of **1** with suberic acid is presented in Fig. 3a and a host–guest energy minimized structure is shown in Fig. 3b.

RESULTS AND DISCUSSION

The receptor **1** was synthesized in six steps starting from diphenylmethane (Scheme 1). Thus, Friedel–Crafts acylation of **3** with an excess of acetyl chloride/anhydrous $AlCl_3$ in dry carbon disulfide produced diketone **4** in 83% yield. The diketone **4** on treatment with $POCl_3$/DMF at 0°C for 2 days afforded 4,4′-bis(1-chloro-2-formylethenyl)phenylmethane **5** in 86% yield as a yellow solid. The bis-chloroaldehyde on condensation with methyl thioglycolate/Et_3N in pyridine followed by ring closure with 50% KOH solution in a one-pot reaction produced the bis-thiophene-5-carboxylic ester derivative **6**. Subsequent hydrolysis of bis-ester **6** with aqueous ethanolic KOH afforded bis-carboxylic acid **7** in 51% yield. Reaction of this bis-acid with oxalyl chloride formed the bis-acid chloride derivative that, on treatment with 2-aminopyridine and triethylamine in dry dichloromethane, resulted in the formation of receptor **1** in moderate yield. The reaction of the bis-acid chloride with *o*-anisidine under identical conditions furnished receptor **2**.

The association constant K_a [25] for suberic acid with **1** was determined by an NMR titration experiment. From the ^1H NMR spectra, upon addition of the guest, a downfield shift of the amide resonance proton was observed and the binding constant of **1** with suberic acid was found to be $(3.16 \pm 0.4) \times 10^3\,M^{-1}$. This result is comparable to the binding data of some of the other recently published receptor molecules [8,11,26]. A corresponding ΔG ($-RT \ln K_a$) was calculated to be $-4.82\,kcal\,mol^{-1}$ at 25°C. Proton NMR titration with the host was carried out at 25°C by increasing addition of a solution of the suberic acid (in dry $CDCl_3$ containing 2% of dry DMSO-d_6) to a solution of **1** (in dry $CDCl_3$) and recording the NMR spectrum after each addition [27,28]. Addition was continued until the complexation was complete, that is until no further change in the amide proton was observed. A blank titration was also performed by the addition of a dry DMSO-d_6 solution to a solution of **1** in dry $CDCl_3$, which resulted in a negligible shift of the amide resonance proton indicating a very small effect in the NMR spectral shift by the presence of

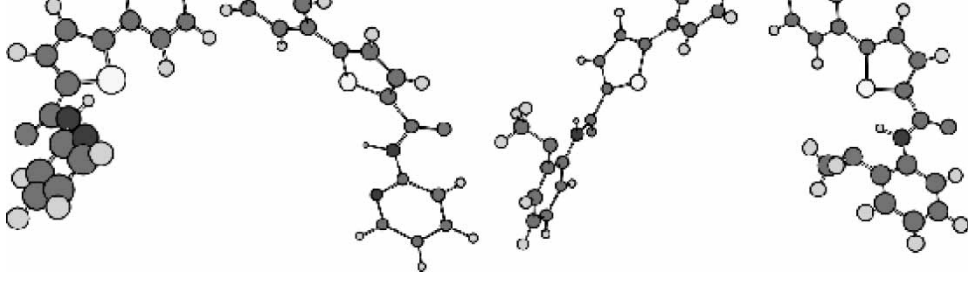


FIGURE 2 Energy minimized MM2 structures of the receptors **1** and **2**.

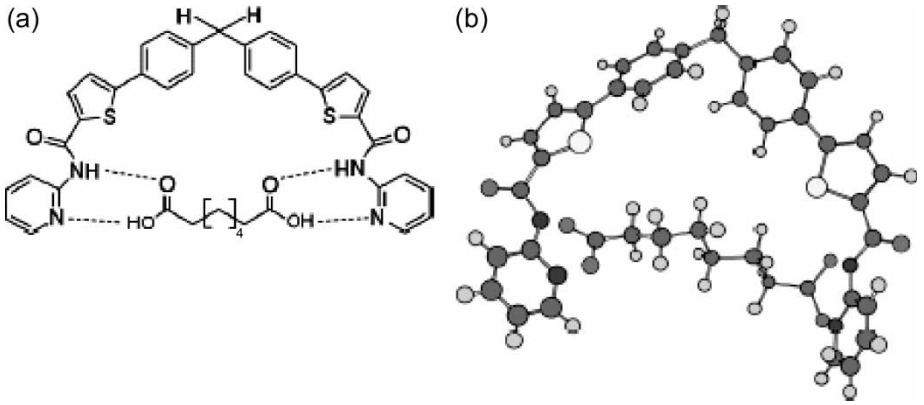
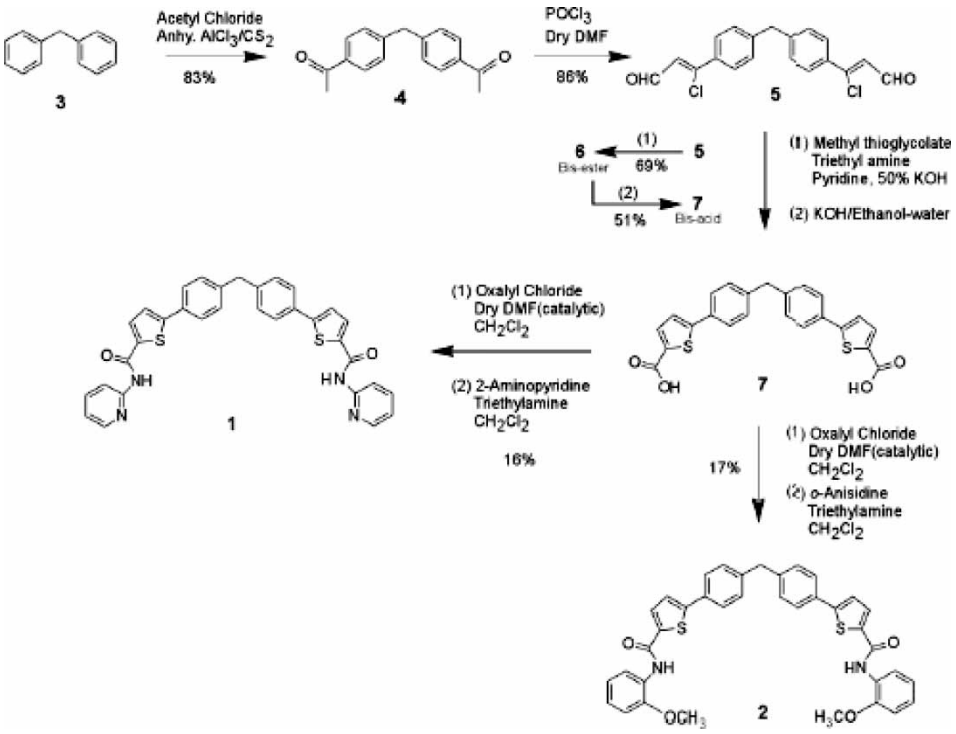


FIGURE 3 (a) Proposed mode of complexation of receptor **1** with suberic acid and (b) energy minimized structure of receptor **1** and suberic acid.

DMSO. The change in chemical shift (Δδ) values was calculated by subtracting the chemical shift at each point from the chemical shift value of the pure host. A titration curve of (Δδ) *vs.* concentration ratio of guest (G) and host (H) was plotted (Fig. 4a) and the break in the titration curve (Δδ *vs.* [G]/[H]) [27,28] clearly established a 1:1 stoichiometry for the suberic acid with **1**.

The 1:1 stoichiometry of **1** and suberic acid was further supported by integration of the signals of the 1:1 complex in the ^{1}H NMR spectrum. Interestingly, the result obtained from the proton NMR titration experiment was also supported by a fluorescence titration experiment. The fluorescence titration experiment was carried out by successive addition of the guest solution (in $CHCl_3$ containing 2% dry DMSO) to the solution of receptor (in $CHCl_3$) and a change in the fluorescence emission intensity (monitored at $\lambda_{emission} = 430$ nm) was recorded (Fig. 4b). The receptor was excited at 330 nm and the titration experiment was carried out at 25°C. A higher affinity for suberic acid with **1** was also noted, with a considerable change in the fluorescence intensity. K_a was calculated from the titration curve (a plot of emission intensity against the concentration of suberic acid) and was found to be $(2.85 \pm 0.7) \times 10^3\ M^{-1}$. This result is consistent with the binding data obtained from the ^{1}H NMR titration experiment. The methoxy derivative **2**, however, was found to be a very poor receptor for suberic acid compared to **1**, presumably because of the absence of any specific binding site for the dicarboxylic acid.



SCHEME 1 Synthesis of ditopic receptors **1** and **2**.

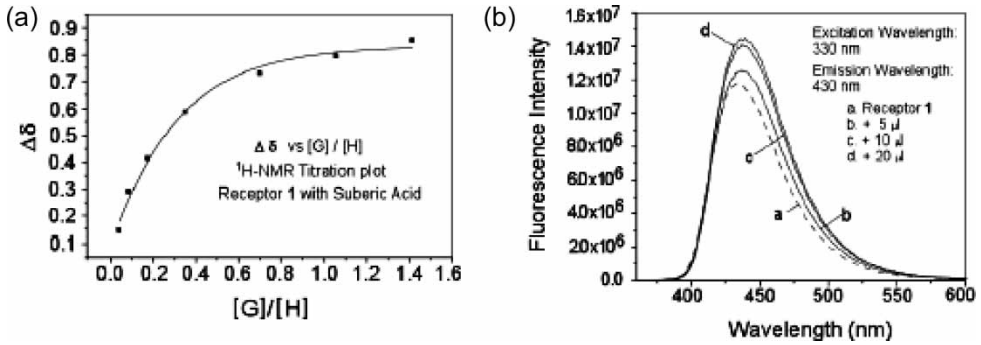


FIGURE 4 (a) ^{1}H NMR titration curve for suberic acid with receptor **1**. (b) Fluorescence emission spectra of **1** with suberic acid at 25°C; $\lambda_{excitation} = 330$ nm.

Unfortunately, **1** was also found to be a very poor receptor for the other two dicarboxylic acids. The binding constants from the ^{1}H NMR titration experiment of **1** with benzene-1,3-dipropanoic acid and benzene-1,3-dibutanoic acid were determined to be of the order of 10^2.

In summary, we have successfully developed a route to synthesize a novel class of bis-thiophene-5-carboxamide derivatives based on a non-rigid pivotal methylene ($-CH_2-$) linkage, hinged with two symmetrical arms of *p*-substituted phenyl with a thiophene moiety as a core structure. We have also demonstrated that these receptors are capable of forming strong complexes with suitable dicarboxylic acids. This work also opens up the possibility of synthesizing new macrocylic receptor molecules with a rigid framework by a slight modification of the methodology described.

EXPERIMENTAL

Solvents and reagents were used as obtained from commercial suppliers or purified according to standard procedures. NMR spectra were recorded on a 200 MHz Bruker spectrometer in $CDCl_3$ (dried with 4 Å molecular sieves) or DMSO-d_6 as solvent with TMS as an internal standard. Coupling constant (*J*) values are given in Hz. All melting points are uncorrected and recorded in one-side open glass capillaries using a paraffin oil bath. IR spectra were recorded on a Perkin-Elmer 800 instrument. Mass spectral data were obtained from IICB, Kolkata.

4,4′-Diacetylphenylmethane (4)

To a stirred solution of diphenylmethane (4 g, 23.8 mmol) and acetyl chloride (4.23 mL, 0.07 mol) in dry carbondisulfide (75 mL), anhydrous $AlCl_3$ (15 g, 11.23 mmol) was added in four batches at 0–5°C. The reaction mixture was allowed to reach room temperature gradually and then stirred for 12 h. The mixture was then refluxed for 2 h, cooled to room temperature and quenched with crushed ice with stirring. The aqueous layer was extracted with $CHCl_3$. The organic layer was successively washed with water and then dried over anhydrous Na_2SO_4. Removal of solvent afforded the crude product **4**, which was recrystallized from a $CHCl_3$–petroleum ether mixture to furnish 5 g (83%) of the diketone as a brown solid, mp 100°C (chloroform). IR (KBr) ν_{max}: 1670 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.52 (s, 6H), 4.08 (s, 2H), 7.25 (brd, 4H, $J = 8.2$ Hz), 7.88 (brd, 4H, $J = 8.2$ Hz). ^{13}C NMR ($CDCl_3$): δ 26.60, 41.89, 128.84, 129.20, 135.65, 145.67, 197.70. Anal. Calcd. for $C_{17}H_{16}O_2$(%): C, 80.95; H, 6.35. Found: C, 81.12; H 6.55.

4,4′-Bis(1-chloro-2-formylethenyl) phenylmethane (5)

To an ice-cold solution of DMF (3 mL), $POCl_3$ (0.66 mL, 7.24 mmol) was added dropwise and stirred for 10 min at 0°C. To this stirred mixture at 0–5°C, a solution of the ketone **4** (4 g, 15.87 mmol) in DMF (2–3 mL) was injected slowly. Stirring was continued at 0–5°C for 2 h and then at room temperature for 2 days. Then the reaction mixture was decomposed with an excess of ice-cold sodium acetate solution and extracted with CH_2Cl_2. The organic layer was washed successively with water, $NaHCO_3$ (5%) solution and finally thoroughly with water and then dried over anhydrous Na_2SO_4. Removal of solvent afforded compound **5** as a yellow solid. The crude product was purified by column chromatography using silica/hexane:ethyl acetate (8:1) to furnish 4.66 g (86%) of **5** as a yellow solid, mp 136°C (from dichloromethane–diethyl ether mixture). IR (KBr) ν_{max}: 1670 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 4.08 (s, 2H), 6.65 (d, 2H, $J = 6.1$ Hz), 7.27 (dd, 4H, $J = 7.5$ and 8.3 Hz), 7.70 (dd, 4H, $J = 1.8$ and 8.3 Hz), 10.20 (d, 2H, $J = 6.8$ Hz); ^{13}C NMR ($CDCl_3$): δ 41.41, 124.35, 127.57, 129.42, 144.30, 151.87, 191.35; Anal. Calcd. for $C_{19}H_{14}O_2Cl_2$(%) C, 66.28; H, 4.07. Found: C, 66.78; H, 4.27.

4,4′-Bis(5-carbomethoxy-2-thienyl) phenylmethane (6)

To a stirred solution of chloroaldehyde **5** (500 mg, 1.45 mmol) and methyl thioglycolate (0.285 mL, 3.19 mmol) in 3–4 mL pyridine at 0°C, triethylamine (0.62 mL, 4.35 mmol) was added dropwise. The reaction mixture was gradually allowed to attain room temperature and then stirred at 45–50°C for an additional 30 min. Then it was cooled to 10–15°C and 6 mL 50% aq. KOH was added. Stirring was continued at 10–15°C for 20 min. The reaction mixture was then poured into ice-water and extracted with CH_2Cl_2. The organic layer was successively washed with dilute HCl and water and then dried over anhydrous Na_2SO_4. Removal of solvent followed by purification by column chromatography (silica gel/benzene) afforded 450 mg (69%) of **6** as a light yellow solid, mp 178–179°C (chloroform). IR (KBr) ν_{max}: 1700 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.90 (s, 6H), 4.02 (s, 2H), 7.20–7.26 (m, 6H), 7.55 (dd, 4H, $J = 1.7$ and 8.3 Hz), 7.74 (d, 2H, $J = 3.9$ Hz); ^{13}C NMR ($CDCl_3$): δ 31.99, 41.42, 52.20, 123.48, 126.53, 129.69, 131.88, 134.48, 141.54, 151.20; EI-MS (m/z): 448, 417, 137, 109, 95, 82; Anal. Calcd. for $C_{25}H_{20}O_4S_2$(%): C, 66.96; H, 6.66. Found: C, 67.12; H 6.86.

4,4′-Bis(5-carboxy-2-thienyl) phenylmethane (7)

To a solution of bis-ester **6** (500 mg, 1.116 mmol) in 60 mL of ethanol, KOH (250 mg) in 20 mL of water was added and was allowed to reflux for 4 h. Excess of ethanol was distilled off and the residue was diluted with ice-cold water, and extracted with ethyl acetate to remove neutral matter (if any). The aqueous part was treated with active charcoal and filtered while hot. Acidification of the cold filtrates with cold dilute HCl precipitated the desired product, which was isolated by filtration, washed well with water and dried to produce 440 mg (51%) of compound **7**, mp 250°C. IR (KBr) ν_{max}: 1668 cm^{-1}; ^1H NMR (DMSO-d_6): δ 4.0 (s, 2H), 7.33 (d, 4H, $J = 8.2$ Hz), 7.51 (d, 2H, $J = 3.9$ Hz), 7.64–7.70 (m, 6H); Anal. Calcd. for $C_{23}H_{16}O_4S_2$(%): C, 65.71; H, 3.8. Found: C, 65.91; H, 4.12.

4,4′-Bis[(5-pyridine-2-aminocarboxyl)-2-thienyl] phenylmethane (1)

To a suspension of the bis-acid **7** (210 mg, 0.5 mmol) in dry CH_2Cl_2 (30 mL), oxalyl chloride (0.2 mL, 2.25 mmol) and dry DMF (catalytic) were added and the mixture stirred at room temperature for 7 h. The solvent was removed under reduced pressure to furnish the acid chloride as an orange–brown solid, which was used without further purification. It was immediately dissolved in 50 mL of dry CH_2Cl_2 and stirred at 0–5°C. To this stirred solution at 0–5°C, a solution of 2-aminopyridine (94 mg, 1.0 mmol) and triethylamine (0.17 mL, 1.25 mmol) in CH_2Cl_2 (100 mL) was added dropwise. The mixture was stirred at room temperature for 24 h and was then refluxed for 2 h. The reaction mixture was then allowed to cool to room temperature, decomposed with ice-water and extracted thoroughly with ethyl acetate. The organic layer was washed successively with water, 10% $NaHCO_3$ solution, finally with water for several times and dried over anhydrous Na_2SO_4. Removal of solvent followed by purification with preparative TLC (silica gel/benzene:ethyl acetate, 2:1) furnished 40 mg (16%) of the bis-amide **1** as a pale yellow solid, mp 190–195°C (chloroform, petroleum ether). IR (KBr) ν_{max}: 1650, 3440 (brd) cm^{-1}; ^1H NMR ($CDCl_3$): δ 4.01 (s, 2H), 7.12 (m, 2H), 7.41 (m, 6H), 7.79 (m, 2H), 7.94 (dd, 4H, $J = 1.7$ and 8.3 Hz), 8.15 (d, 2H, $J = 3.9$ Hz), 8.27 (d, 2H, $J = 8.2$ Hz), 8.38 (d, 2H, $J = 6$ Hz), 9.76 (s, 2H); Anal. Calcd. for $C_{33}H_{24}N_4O_2S_2$(%): C, 69.23; H, 4.19. Found: C, 69.68; H, 4.20.

4,4′-Bis[5-(2-methoxyanilido)-2-thienyl] phenylmethane (2)

To a suspension of the bis-acid **7** (300 mg, 0.72 mmol) in dry CH_2Cl_2 (20 mL), oxalyl chloride (0.32 mL, 3.56 mmol) and dry DMF (catalytic) were added and the mixture stirred at room temperature for 7 h. The solvent was then removed under reduced pressure to furnish the acid chloride as an orange brown solid, which was used without further purification. It was immediately dissolved in dry CH_2Cl_2 (50 mL) and stirred at 0–5°C. To this stirred solution at 0–5°C, a solution of *o*-anisidine (0.17 mL, 1.42 mmol) and triethylamine (0.3 mL, 2.14 mmol) in CH_2Cl_2 (50 mL) was added. The mixture was stirred at room temperature for 24 h and then refluxed for 2 h. The reaction mixture was then cooled to room temperature, decomposed with ice-water and extracted thoroughly with ethyl acetate. The organic layer was washed successively with water, 10% $NaHCO_3$ solution, finally with water several times and dried over anhydrous Na_2SO_4. Removal of solvent followed by purification with preparative TLC (silica gel/benzene: ethyl acetate, 2:1) furnished 70 mg (15%) of the bis-amide **2** as a pale yellow solid, mp 210°C (chloroform, petroleum ether). IR (KBr) ν_{max}: 1656, 3370, 3420 (brd.) cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.95 (s, 3H), 3.95 (s, 3H), 4.01 (s, 2H), 6.91–7.18 (m, 8H), 7.27 (d, 2H, $J = 4$ Hz), 7.59 (d, 2H, $J = 4$ Hz), 7.65 (brd, 4H, $J = 8.5$ Hz), 8.41–8.49 (m, 4H), 9.96 (brd. 2H); Anal. Calcd. for $C_{37}H_{30}N_2O_2S_2$(%): C, 74.24; H, 5.01. Found: C, 74.34; H, 5.04.

Acknowledgements

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