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2-Aminothiophenol as building blocks for novel heterocycles

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RESEARCH ARTICLE

2-Aminothiophenol as building blocks for novel heterocycles

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Herein, the chemistry of 2-aminothiophenol has been utilized in the synthesis of several interesting products such as oxidation and reaction with π-deficient compounds. On oxidizing 2-aminothiophenol by sodium hypochlorite furnishes 2-[(2-aminophenyl)-dithio]aniline. Treatment of the obtained product with acetyl chloride affords *N*-(2-[2-(acetylamino)-phenyl-disulphanyl)-phenyl]acetamide. Reaction of the former acetamide with $POCl_3$ yields 2-methyl-1,3-benzothiazole. Moreover, (3,4,8,9)-dibenzo-2,7-dithia-5,10-diaza[4,4,4]propellane is formed on reacting the target 2-aminothiophenol with cyclohexane-1,2-dione, whereas its reactions with electron π-acceptors such as 2,3-dichloro-1,4-naphthoquinone (DCHNQ), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), tetra-cyanoethylene (TCNE), and 1-(dicyanomethylen)acenaphthen-2-one yield various heterocycles.

Keywords: 2-Aminothiophenol; Sodium hypochlorite; Cyclohexane-1,2-dione; Electron acceptors

1. Introduction

It was known that the oxidation of thiol yields the corresponding disulphide, this conversion is a useful transformation and is of importance both from a biological and from a practical point of view [1]. The oxidizing agents known for the former interconversion were described, in the literature, such as hydrogen peroxide [2], dimethyl sulphoxide [3], lead(IV)acetate [4, 5], nitric oxide and nitrogen dioxide [6], thallium(III)acetate [7], iodine in ethanol [8], nickel peroxide [9], sodium chlorite [10], Fe(III) ion exchanged montmorillonite [11], enzyme catalysis [12], potassium superoxide [13], as well as benzyltriphenylphosphonium peroxodisulphate [14].

There were no attempts to use hypochlorite solution as an oxidizing agent. It was reported that, condensation of either ethanolamine or 2-aminophenol with cyclohexane-1,2-dione gave heteropropellanes [15]. In this publication, we aimed to synthesis propellane derivative using 2-aminothiophenol (**1**) using cyclohexane-1,2-dione. The formal reaction gave heteropropellane **5** as shown in outlined scheme 1. The structure of **5**, in 60% yield, was confirmed from its spectroscopic data (see Experimental Section). It was found that 2-aminothiophenol was condensed with several aldehydes or ketones in (1:1) ratio to form 2-(R-substituted)benzo-thiazolines [16, 17].

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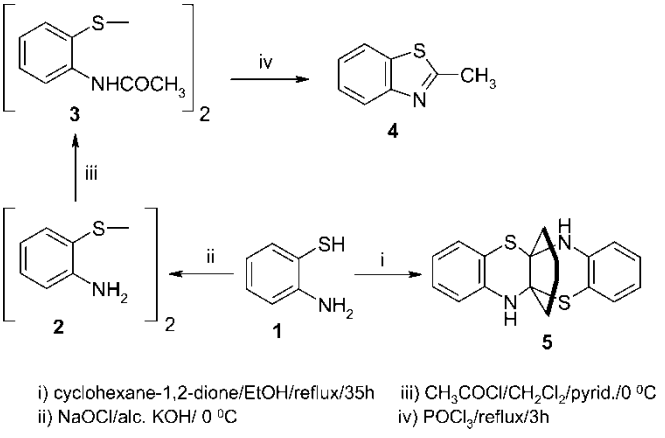
Organic molecules containing electron donor and acceptor moieties constitute a very interesting topic due to their electronic properties [18]. The chemistry of quinones is of considerable interest, the class includes many natural products and numerous important synthetic products [19]. Therefore, 2-aminophenol was subjected to π-acceptor quinones along with tetracyanoethylene in order to synthesize various classes of heterocycles which might have biological and pharmaceutical interest.

2. Results and discussion

We recently found that hypochlorite oxidation of 4,15-diamino[2.2]paracyclophane furnishes 4,15-azo[2.2]paracyclophane, the first multi-bridged cyclophane with a bridge consisting only of heteroatoms [20]. Whereas, on oxidizing any organic compound that has both thiol and amino groups, the priority for oxidation is for thiol groups. Thus, oxidation of the target **1** with sodium hypochlorite in the presence of alcoholic potassium hydroxide produces 2-[(2-aminophenyl)-dithio]aniline (**2**).

Acetylation of **2** by acetyl chloride in the presence of pyridine furnishes *N*-(2-[2-(acetylamino)-phenyl-disulphanyl)-phenyl]acetamide (**3**) (scheme 1). The structure of **3** was proved by spectral data. Mass spectrometry and elemental analysis proved the molecular formula of **3** as $C_{16}H_{16}N_2S_2O_2$. The IR spectrum of **3** revealed an absorption assigned to the carbonyl group at $\tilde{\nu}_{max} = 1690\,cm^{-1}$, in addition to a strong absorption band at $\tilde{\nu}_{max} = 3391\,cm^{-1}$ corresponding to the absorption of NH-group (the NH-proton resonated in the ^1H NMR spectrum at δ_H 8.90). The ^{13}C {H} NMR spectrum proved the symmetrical structure of **3** by the appearance of only eight carbon signals. Ring closure of **3** was succeeded during its reaction with phosphorus oxychloride and 2-methyl-1,3-benzothiazole (**4**) was obtained in a good yield (scheme 1).

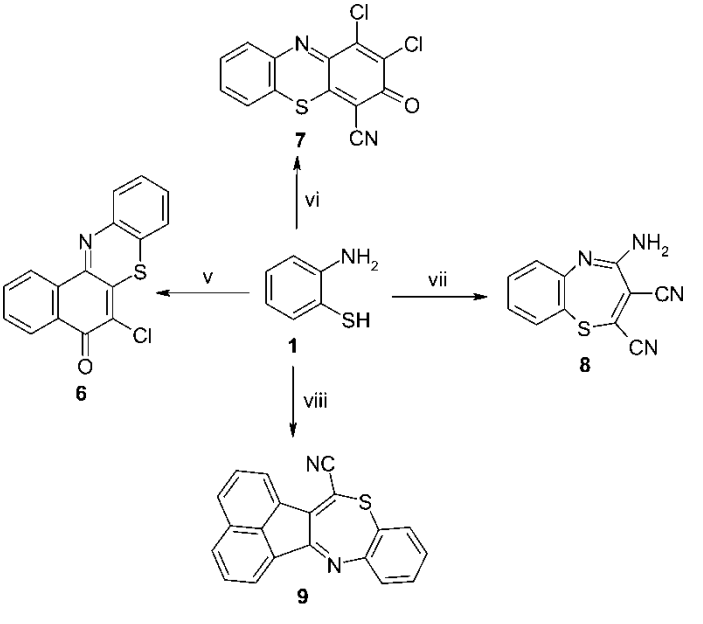


SCHEME 1 Reactivity of **1** towards cyclohexane-1,2-dione, NaOCl and CH_3COCl.

On refluxing **1** with cyclohexane-1,2-dione the reaction proceeded to afford (3,4,8,9)-dibenzo-2,7-dithia-5,10-diaza[4.4.4]propellane (**5**) as shown in scheme 1. The structure of **5** was proved by spectral data and elemental analysis. The molecular formula of **5** was elucidated to be $C_{18}H_{18}N_2S_2$ utilized by mass spectrometry and elemental analysis. The IR spectrum of **5** did not reveal any absorption bands for both carbonyl and amino groups. While the NH-group absorption band appears at $\tilde{\nu}_{max} = 3329\,cm^{-1}$ (the NH-proton resonated in ^1H NMR spectrum at δ_H 7.25). The symmetrical structure of **5** was proved by ^{13}C {H} NMR spectrum, which

reveals only nine carbon signals. Where, one of the nine signals characteristic for the aliphatic quaternary carbon atoms (HN-*C*-S) that resonated at δ_C 81.2 ppm, while the two methylene groups resonated at δ_C 22.5 ppm and 32.3 ppm respectively.

Previously, the chemistry of 2-aminothiophenol and 3-amino-2-hydroxy-pyridine was investigated towards various selected π-acceptors such as 3,4,5,6-tetrachloro-1,2-benzoquinone (CHL-*o*), 2,3,5,6-tetrachloro-1,4-benzoquinone (CHL-*p*), 2,3-dicyano-1,4-naphthoquinone (DCNQ), and 2-dicyanomethyleneindane-1,3-dione (CNIND) and heterocycles represented by benzothiazine and benzothiazepines were obtained [21]. The aforementioned results encouraged us to reinvestigate the chemistry of **1** towards other electron π-deficient compounds. Scheme 2 outlines the reactivity of **1** towards DCHNQ, DDQ, TCNE and 1-(dicyano-methylen)acenaphthen-2-one. It is interesting to note that the reactions of **1** with these π-acceptors were carried out in either absolute acetonitrile or ethyl acetate at room temperature, leading to complex formation that gradually disappeared to give the products. The reaction of **1** with DCHNQ was carried out in acetonitrile at room temperature for 24 h. After chromatographic purification compound **6** was obtained and recrystallized from methanol.



v) DCHNQ/CH_3CN, rt, overnight vi) DDQ/CH_3CN, rt, overnight
vii) TCNE/Ethylacetate, rt, overnight
viii) 1-(dicyanomethylen)-acenaphthen-2-one/CH_3CN, rflux 5h

SCHEME 2 Reaction of **1** with some selected π-acceptors.

The structural assignment of **6** was supported by the following spectral data: The IR spectrum showed an absorption band at $\tilde{\nu}_{max} = 1725\,cm^{-1}$ characteristic for the carbonyl group, which was further confirmed by $^{13}C\{H\}$ NMR spectrum where it resonated at δ_C 187.6 ppm. In addition, the imino group, which was observed in the IR spectrum at $\tilde{\nu}_{max} = 1602\,cm^{-1}$, was absorbed in the $^{13}C\{H\}$ NMR spectrum at δ_C 164.2 ppm. The structure of **6** was identified as 6-chloro-benzo[*a*]phenothiazin-5-one.

In an attempt to carry out the reaction of **1** with DDQ under the same reaction conditions, the reaction produced 1,2-dichloro-3-oxo-3*H*-phenothiazin-4-carbonitrile (**7**). The molecular

formula of **7** was elucidated by mass spectrum and elemental analysis as $C_{13}H_4Cl_2N_2OS$. The ^{1}H NMR spectrum of **7** is in accordance with the suggested structure. Most indicatively, the ^{13}C {H} NMR spectra of **7** revealed three distinctive carbon signals at δ_C 116.1, 165.0 and 189.0 corresponding to th C≡N, C=N and C=O groups, respectively.

The reaction of **1** with TCNE in ethyl acetate at room temperature furnishes the formation of 4-Amino-benzo[*b*][1,4]thiazepine-2,3-dicarbonitrile (**8**) in 77% yield (scheme 2). The ^{1}H NMR spectrum revealed a broad singlet at δ_H 7.30 related to the NH_2-protons. While the aromatic protons resonated in the ^{1}H NMR as two multiplets (see the Experimental Section). In the ^{13}C {H} NMR of **8** the azomethine carbon resonated at δ_C 163.7 ppm. Besides, the two cyano groups, which absorbed in the IR spectrum at $\tilde{\nu}_{max} = 2210, 2202\,cm^{-1}$ and appeared in the ^{13}C {H} NMR spectrum at δ_C 116.1 ppm and 116.8 ppm.

Interestingly, upon treatment of **1** with 1-(dicyanomethylen)acenaphthen-2-one under the reaction conditions mentioned before, the reaction afforded compound **9** in good yield (scheme 2). The structural proof of **9** was based upon the mass, ^{1}H NMR, ^{13}C {H} NMR and IR spectra as well as elemental analysis. Mass spectrometry and elemental analysis proved the molecular formula of **9** as $C_{20}H_{10}N_2S$. The IR spectrum of **9** revealed an absorption band at $\tilde{\nu}_{max} = 2178\,cm^{-1}$ characteristic for C≡N group. This group resonated in the ^{13}C {H} NMR spectrum at δ_C 117.2. The ^{1}H NMR spectrum is in accordance with the suggested structure and showed eight discernible sets of aromatic protons, which appeared as multiplets.

In conclusion, we have demonstrated convenient procedures for the novel synthesis of both benzothiazine and benzothiazepine as well as propellane derivatives. The advantages of these methodologies are the high yield of the desired products and the facility of the routes.

3. Experimental section

3.1 *General consideration*

Melting points are uncorrected. ^{1}H NMR and ^{13}C {H} NMR spectra (Bruker AM 400 spectrometer with TMS as internal standard, ^{1}H: 400.13 MHz, ^{13}C: 100.6 MHz) were obtained from $CDCl_3$ and DMSO-d_6 solutions. Coupling constants are expressed in Hz. IR spectra were run on a Shimadzu 470 spectrometer using KBr pellets. Mass spectra were run at 70 eV electron impact mode using a Finnigan MAT 8430 spectrometer. For preparative layer chromatography (plc), glass plates (20 × 48 cm) were covered with a slurry of silica gel Merck PF_{254} and air-dried, using the solvents listed for development. Zones were detected by quenching of indicator fluorescence upon exposure to 254 nm UV light. Elemental analyses were performed by Microanalytical unit at Cairo university, Cairo, Egypt.

3.2 *Starting materials*

2-Aminothiophenol, DDQ, and TCNE (Aldrich), cyclohexane-1,2-dione, acetyl chloride and DCHNQ (Fluka). While 1-(dicyanomethylen)acenaphthen-2-one was prepared according to reference [22].

3.2.1 2-[(2-aminophenyl)-dithio]aniline (2). A 100-ml flask equipped with a magnetic stirrer is charged with (125 mg, 1 mmol) of 2-aminothiophenol (**1**). 0.5 g KOH dissolved in 20 ml EtOH was added. The reaction mixture is cooled in ice at 0 °C. Freshly prepared solution of NaOCl (15 ml, 13%) was added in one portion with constant stirring. A precipitate was obtained which poured on ice-H_2O and extracted with 50 ml CH_2Cl_2 the extract washed

with $NaHCO_3$ and NaCl solutions to remove acidic components and dried over $MgSO_4$. The solvent evaporated and the solid product was recrystallized from ethanol to give colourless crystals (231 mg, 93%) mp 93 °C, (Lit. [13, 23], mp 93 °C).

3.2.2 N-[2-(2-acetylamino-phenyldisulphanyl)-phenyl]acetamide (3). In a conical flask immersed in an ice-bath, (248 mg, 1 mmole) of 2-[(2-aminophenyl)-dithio]aniline (**2**) dissolved in 20 ml CH_2Cl_2 was added. Few drops of pyridine was added to the reaction followed by dissolving (156 mg, 2 mmole) of acetyl chloride dissolved in CH_2Cl_2 was added dropwise with constant shaking. The reaction mixture left to warm to room temperature and the formed precipitate filtered, dried, to form colourless crystals (0.299 g, 90%), mp 182–183 °C (EtOH).
δ_H (400 MHz, $CDCl_3$): 1.91 (6 H, s, 2 CH_3), 6.86–6.89 (2 H, m), 7.21–7.26 (4 H, m), 7.80 (2 H, d, $J = 7.2$ Hz), 8.90 (2 H, br.-s, 2 N*H*). δ_C (100.6 MHz, $CDCl_3$): 17.6 ($2CH_3$), 120.7 (2Ar-CH), 124.1 (2Ar-C), 124.4 (2Ar-CH), 125.5 (2Ar-CH), 129.4 (2Ar-CH), 141.5 (2Ar-C), 168.2 (2CO). $\tilde{\nu}_{max}$ (cm^{-1}): 3391 (NH, s), 1690 (CO, s), 1497–1486 (C=C, m). EI + mass spectrum (m/z, %): 332 ([M^+], 100%), 317 ([M^+-CH_3], 46%), 302 (18%), 216 (62%), 166 (28%), 96 (32%), 75 (10%), 69 (22%). C, H, N (%): found C, 57.55; H, 4.71; N, 8.27; S, 19.01. $C_{16}H_{16}N_2S_2O_2$ requires C, 57.81; H, 4.85; N, 8.43; S, 19.29.

3.2.3 (3,4,8,9)-Dibenzo-2,7-dithia-5,10-diaza[4.4.4]propellane (5). In a round bottomed flask fitted with a reflux condenser (112 mg, 1 mmol) of cyclohexane-1,2-dione and (250 mg, 2 mmol) a solution of **1** dissolved in 20 ml absolute ethanol was added. The reaction mixture was heated under reflux conditions for 35 h. The reaction was monitored by TLC analysis. The solvent was concentrated in vacuu to give pale brown crystals (0.199 g, 61%), mp 264–266 °C (EtOH).
δ_H (400 MHz, DMSO-d_6): 1.40–1.45 (4 H, m, 2 CH_2), 1.87–1.93 (4 H, m, 2 CH_2), 6.38–6.45 (4 H, m), 6.83–6.90 (4 H, m), 7.25 (2 H, br.-s, 2 N*H*). δ_C (100.6 MHz, DMSO-d_6): 22.5 ($2CH_2$), 32.3 ($2CH_2$), 81.2 (2 HN-*C*-S), 113.8 (2Ar-CH), 114.9 (2Ar-CH), 118.5 (2Ar-CH), 120.5 (2Ar-CH), 129.3 (2 HN-*C*=CH), 140.7 (2 S-*C*=CH). $\tilde{\nu}_{max}$ (cm^{-1}): 3329 (NH, s), 2920–2896 (aliph.-CH, m), 1500 (C=C, s). EI + mass spectrum (m/z, %): 326 ([M^+], 66%), 235 (22%), 207 (100%), 157 (34%), 120 (14%), 93 (40%), 65 (10%).
C, H, N (%): found C, 65.89; H, 5.40; N, 8.39; S, 19.37. $C_{18}H_{18}N_2S_2$ requires C, 66.22; H, 5.56; N, 8.58; S, 19.64.

3.2.4 6-Chloro-benzo[a]phenothiazin-5-one (6). An equimolar amounts of 2,3-dichloro-1,4-naphthoquinone (227 mg, 1 mmol), and 2-aminothiophenol (125 mg, 1 mmol) were dissolved in acetonitrile (20 mL), the colour of the reaction mixture becomes red and changed to yellow after 1 h. The reaction mixture left overnight at room temperature. The solvent was concentrated under reduced pressure and the residue was subjected to chromatographic plates using CH_2Cl_2 as eluent to get the product as Yellow crystal (0.172 g, 58%), mp 203–205 °C (CH_3OH).
δ_H (400 MHz, $CDCl_3$): 7.00–7.04 (1 H, m), 7.10–7.18 (2 H, m), 7.20–7.23 (1 H, m), 7.47–7.51 (2 H, m), 7.76–7.84 (2 H, m). δ_C (100.6 MHz, DMSO-d_6): 122.3 (Ar-CH), 124.0 (Ar-C), 126.1 (Ar-C), 126.3 (Ar-CH), 127.3 (Ar-CH), 129.2 (Ar-CH), 129.8 (Ar-CH), 130.5 (Ar-CH), 131.3 (A-CH), 132.4 (Ar-C), 134.1 (Ar-CH), 137.2 (Ar-C), 140.0 (Ar-C), 153.6 (Ar-C), 164.2 (C=N), 187.6 (CO). $\tilde{\nu}_{max}$ (cm^{-1}): 3080–3000 (Ar-CH, m), 1725 (C=O, s), 1602 (C=N, s). EI + mass spectrum (m/z, %): 299 ([M^{+2}], 10%), 297 ([M^+], 68%), 261 (84%), 243 (6%), 184 (16%), 154 (8%), 126 (30%), 108 (24%), 100 (14%), 76 (52%). C, H, N (%): found: C,

64.33; H, 2.72; Cl, 11.66; N, 4.57; S, 10.53. $C_{16}H_8ClNOS$ requires C, 64.54; H, 2.71; Cl, 11.91; N, 4.70; S, 10.77.

3.2.5 1,2-Dichloro-3-oxo-3H-phenothiazin-4-carbonitrile (7). An equimolar quantities of 2-aminothiophenol (125 mg, 1 mmol), and DDQ (227 mg, 1 mmol) were dissolved in acetonitrile (30 ml), the colour of the solution changes into green then changed into blue with forming a precipitate after 5 min. (dihydro), the reaction mixture left overnight at room temp., the precipitate. was filtered and the filterate was subjected to chromatographic plates using EA: toluene (1:1) to get the product as Blue crystals (0.190 g, 62%), mp 220–222 °C (EtOH).
δ_H (400 MHz, $CDCl_3$): 7.43–7.58 (3 H, m), 7.64–7.71 (1 H, m). δ_C (100.6 MHz, $CDCl_3$): 106.6 (Ar-C), 116.1 (CN), 122.2 (Ar-CH), 126.1 (Ar-CH), 127.3 (Ar-CH), 127.9 (Ar-CH), 129.0 (Ar-C), 129.36 (Ar-C), 132.0 (Ar-C), 142.3 (Ar-C), 147.4 (Ar-C), 165.0 (C=N), 189.3 (CO). $\tilde{\nu}_{max}$ (cm^{-1}): 3095–3020 (Ar-CH, m), 2165 (C≡N, s), 1730 (CO, s), 1645 (C=N, s), 1497 (C=C, s). EI + mass spectrum (m/z, %): 310 ([M^{+4}], 17%), 308 ([M^{+2}], 23%), 306 ([M^+], 46%), 281 (16%), 247 (80%), 186 (12%), 174 (52%), 136 (14%), 124 (80%), 97 (62%), 76 (30%), 55 (85%). C, H, N (%): found: C, 50.67; H, 1.22; Cl, 22.79; N, 8.97; S, 10.23. $C_{13}H_4Cl_2N_2OS$ requires C, 50.84; H, 1.31; Cl, 23.08; N, 9.12; S, 10.44.

3.2.6 4-Amino-benzo[b][1,4]thiazepine-2,3-dicarbonitrile (8). An equimolar amounts of 1,1,2,2-tetracyanoethylene (128 mg, 1 mmol) and 2-aminothiophenol (125 mg, 1 mmol) were dissolved in ethyl acetate (20 ml), the reaction mixture colour becomes red and changed to yellow with time. the reaction mix. left overnight at room temp.. The solvent was concentrated under reduced pressure and the residue was subjected to chromatographic plates using CH_2Cl_2 as eluent to get the product as yellow crystals (0.174 g, 77%), mp 139–140 °C ($CHCl_3$).
δ_H (400 MHz, $CDCl_3$): 6.85–7.12 (1 H, m), 7.30 (2 H, br.-s, NH_2), 7.37–7.46 (3 H, m). δ_C (100.6 MHz, $CDCl_3$): 102.9 (Ar-C), 116.1 (CN), 116.8 (CN), 122.0 (Ar-CH), 126.6 (Ar-CH), 127.3 (Ar-CH), 127.9 (Ar-CH), 129.1 (Ar-C), 139.4 (Ar-C), 147.1 (Ar-C), 163.7 (C=N). $\tilde{\nu}_{max}$ (cm^{-1}): 3349, 3309 (NH_2, m), 2210 (C≡N, s), 2202 (C≡N, s), 1645 (C=N, s). EI + mass spectrum (m/z, %): 226 ([M^+], 46%), 210 ([M^+ - NH_2], 31%), 199 ([M^+ - CN], 12%) 175 ([M^+ - 2CN], 18%), 160 (32%), 134 (8%), 123 (14%), 108 (62%), 96 (40%), 83 (22%), 75 (34%). C, H, N (%): found C, 58.13; H, 2.51; N, 24.57; S, 13.95. $C_{11}H_6N_4S$ requires C, 58.39; H, 2.67; N, 24.76; S, 14.17.

3.2.7 Reaction of 1 with 1-(dicyanomethylen)acenaphthen-2-one. In a round bottomed flask fitted with a reflux condenser was added 1 mmol of 1-(dicyanomethylen)acenaphthen-2-one and (125 mg, 1 mmol) of compound **1** dissolved in 30 ml absolute acetonitrile. The reaction mixture was heated under reflux conditions for 5 h. It is followed by TLC using toluene/ethyl acetate (2:1) as an eluent. The solvent was concentrated under reduced pressure and the residue was recrystallized from ethanol to give compound **9** as bluish-green crystals (0.217 g, 70%), mp>340 °C (DMF/$CHCl_3$).
δ_H (400 MHz, DMSO-d_6): 6.92–6.95 (1 H, m), 7.10–7.15 (1 H, m), 7.20–7.23 (2 H, m), 7.27–7.30 (1 H, m), 7.36–7.40 (1 H, m), 7.50–7.53 (2 H, m), 7.91–7.94 (1 H, m), 7.96–7.98 (1 H, m). δ_C (100.6 MHz, DMSO-d_6): 110.7 (Ar-C), 117.2 (CN), 122.3 (Ar-CH), 123.4 (Ar-CH), 125.8 (Ar-CH), 126.0 (Ar-CH), 126.2 (Ar-CH), 126.5 (Ar-C), 127.0 (Ar-C), 127.3 (Ar-CH), 127.9 (Ar-CH), 129.1 (Ar-C), 130.3 (Ar-CH), 131.5 (Ar-C), 131.8 (Ar-CH), 133.1 (Ar-CH), 133.4 (Ar-C), 135.7 (Ar-C), 152.8 (Ar-C), 164.7 (C=N). $\tilde{\nu}_{max}$ (cm^{-1}): 3109–3045 (Ar-CH, m), 2178 (C≡N, s), 1645 (C=N, s). EI + mass spectrum (m/z, %): 310 ([M^+], 56%), 284

([M^+- CN], 100%), 162 (42%), 146 (20%), 122 (64%), 90 (12%), 84 (8%), 76 (18%). C, H, N (%): found C, 77.25; H, 3.10; N, 8.80; S, 10.07. $C_{20}H_{10}N_2S$ requires C, 77.40; H, 3.25; N, 9.03; S, 10.33.

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