Mohammad Nikpassand*, Leila Zare Fekri and Hasti Taherkhorsand

Green synthesis of novel 2-pyrazolyl-1,3-thiazolidine-4-ones using 2-oxoimidazolidine-1,3-disulfonic acid

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Abstract: 2-Oxoimidazolidine-1,3-disulfonic acid (OImDSA) is a recoverable catalyst for the synthesis of 1,3-thiazolidine-4-ones at room temperature in a one-pot procedure without using any organic solvents. Moreover, the catalyst can be easily recovered and recycled for five runs without significant loss of catalytic activity. The structures of the synthesized 1,3-thiazolidine-4-one compounds were confirmed by ^{1}H NMR, ^{13}C NMR and FTIR spectral data and elemental analysis.

Keywords: one-pot reaction; solid acid; 1,3-thiazolidine-4-one; thioglycolic acid.

Introduction

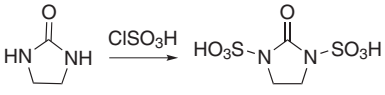
Thiazolidine compounds contribute to various pharmacological effects. Thiazolidines are used as anti-seizure, fungicidal, anti-bacterial, anti-tubercular, anti-inflammatory, anti-amoebic, anti-diabetic and local anesthetic agents [1, 2]. Some of these compounds have also shown anti-Parkinsonism [3], anti-oxidant [4], anti-convulsant [5], anti-cancer [6], hypoglycemic [7] and non-narcotic analgesic [8] activities. On the other hand, pyrazoles have shown anti-bacterial, anti-tumor, anti-viral, anti-fungal, anti-tubercular, anti-parasitic, anesthetic, anti-diabetic, anti-inflammatory, analgesic and insecticidal activities [9].

In recent years, silica gel [10], $SiCl_4$ [11], $Bi(SCH_2COOH)_3$ [12], $ZnCl_2$ [13], *N*,*N*,*N*′,*N*′-Tetramethyl-O-(1*H*-benzotriazol-1-yl)uronium hexafluorophosphate (HBTU) [14], [bmim][PF_6] [15], *Saccharomyces cerevisiae* [16], 1,3-dicyclohexylcarbodiimide (DCC) [17], supported protic acid [18] and nano-Fe_3O_4@SiO_2 supported ionic liquid [19] have been employed for the synthesis of 1,3-thiazolidine-4-ones. To the best of our knowledge, there is no report in the literature on the use of 2-oxoimidazolidine-1,3-disulfonic acid (OImDSA) as a catalyst for the green synthesis of pyrazolyl-1,3-thiazolidine-4-ones. In the search for eco-friendly alternatives to classical synthesis [10–22] and in continuation of our studies to synthesize heterocyclic and pharmaceutical compounds under mild and practical protocols [23–27], we report herein the synthesis of some novel pyrazolyl-1,3-thiazolidine-4-ones using OImDSA (Scheme 1).

Results and discussion

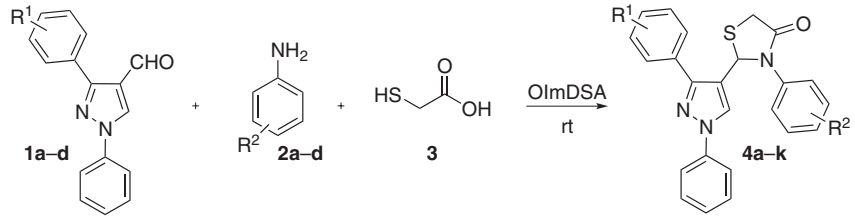
Pyrazolecarbaldehyde **1a**, 4-methoxyaniline **2a** and thioglycolic acid **3** were mixed with 10 mL of H_2O in the presence of a catalytic amount of HCl and various solid catalysts, namely montmorillonite K10, $ZnCl_2$, *L*-proline, nano-Fe_3O_4, nano-SiO_2 and OImDSA (Scheme 2) or under solvent-free condition using 2 mL of an ionic liquid such as [BMIM]Br, [BMIM]OH and [BMIM]SOH. In these experiments, OImDSA was the most efficient catalyst, not only in terms of high yield of pyrazolyl-1,3-thiazolidine-4-one **4a** but also high reaction rate (92% yield in 1 h). Moreover, our results showed that 0.1 g of OImDSA per 1 mmol of aldehyde **1a** is enough for the synthesis of **4a**. The optimal temperature for the synthesis of **4a** is room temperature. Increasing the temperature has no effect on the reaction time and yield.

Various pyrazolecarbaldehydes and anilines can be utilized in this protocol. It has been shown that aldehydes with electron-withdrawing groups react faster than the aldehydes with electron-releasing groups. The yields obtained with substrates having electron-withdrawing groups are also greater. To evaluate the reusability of the OImDSA, the catalyst was separated from the reaction medium by treatment with water. The aqueous solution



Scheme 1 Preparation of 2-oxoimidazolidine-1,3-disulfonic acid (OImDSA).

***Corresponding author: Mohammad Nikpassand,** Department of Chemistry, Rasht Branch, Islamic Azad University, Rasht, Iran, e-mail: Nikpassand@iaurasht.ac.ir
Leila Zare Fekri: Department of Chemistry, Payame Noor University, PO Box 19395-3697, Tehran, Iran
Hasti Taherkhorsand: Department of Chemistry, Rasht Branch, Islamic Azad University, Rasht, Iran



4a: R^1 = 4-Cl; R^2 = 4-OMe
4b: R^1 = H; R^2 = 4-OMe
4c: R^1 = H; R^2 = 2-Me-4-NO_2
4d: R^1 = 4-Cl; R^2 = 2-Me-4-NO_2
4e: R^1 = 3-NO_2; R^2 = 2-Me-4-NO_2
4f: R^1 = H; R^2 = H
4g: R^1 = H; R^2 = 4-NO_2
4h: R^1 = 4-Cl; R^2 = 4-NO_2
4i: R^1 = 3-NO_2; R^2 = 4-NO_2
4j: R^1 = H; R^2 = 4-Me
4k: R^1 = 4-OH; R^2= 4-NO_2

Scheme 2 Synthesis of compounds **4a–k**.

was fractionally distilled under reduced pressure and the recovered catalyst was reused in subsequent reactions. After five successive runs, OImDSA showed virtually no loss in efficiency regarding reaction time and yield.

Conclusions

An efficient protocol for the synthesis of compounds **4a–k** using OImDSA as an effective catalyst was developed. To the best of our knowledge, this is the first report on the synthesis of 1,3-thiazolidine-4-ones bearing pyrazole moiety in aqueous media.

Experimental

All commercial chemicals were used as received. Melting points were measured on an Electro-thermal 9100 apparatus and are uncorrected. ^{1}H nuclear magnetic resonance (NMR) (500 MHz) and ^{13}C NMR (125 MHz) spectra were obtained on a Bruker DRX 500 Avance spectrometer using $CDCl_3$ as solvent and TMS as the internal standard. Fourier transform infrared (FT-IR) spectra were recorded as KBr pellets on a Shimadzu FT-IR-8400S spectrometer. Elemental analyses were done on a Carlo-Erba EA1110CNNO-S analyzer.

Synthesis of 2-oxoimidazolidine-1,3-disulfonic acid (OImDSA)

A flask (500 mL) with imidazolidin-2-one (8.6 g, 0.1 mol) was equipped with a constant pressure dropping funnel containing chlorosulfonic acid (23.3 g, 0.2 mol) and a gas outlet tube which was dipped into water to dissolve the generated HCl gas during the reaction. The flask was placed into an ice bath and chlorosulfonic acid was added dropwise over a period of 20 min and the resulting mixture was stirred for an additional 20 min. The temperature of the mixture was brought up to the room temperature and stirring was continued for an additional 60 min. The mixture was triturated with *n*-hexane (20 mL) and then filtered. The solid residue was washed with *n*-hexane (20 mL) and dried under reduced pressure to give OImDSA as a white solid: mp >300°C; IR: 984 (S=O symmetric stretch), 1315 (S=O asymmetric stretch), 1661 (C=O stretch), 2963 (C-H aliphatic stretch), 3309 cm^{-1} (O-H stretch); ^{1}H NMR δ: 3.63 (s, 4H, N-$\underline{CH_2}$-$\underline{CH_2}$-N), 13.35 (s, br., 2H, -SO_3H); ^{13}C NMR: 51.4 (N-$\underline{CH_2}$-$\underline{CH_2}$-N), 152.5 (C=O). Anal. Calcd for $C_3H_6N_2O_7S_2$: C, 14.63; H, 2.46; N, 11.38. Found: C, 14.63; H, 2.47; N, 11.37.

General procedure for preparation of 4a–k

A mixture of a pyrazolecarbaldehyde **1** (1 mmol), an aniline **2** (1 mmol), thioglycolic acid **3** (1 mmol), H_2O (10 mL) and OImDSA (0.1 g) was stirred at room temperature for 1–2 h. The progress of the reaction was monitored by TLC (EtOAc/petroleum ether, 1:2). After completion of the reaction, the product was extracted with $CHCl_3$ and the aqueous phase containing catalyst OImDSA was fractionally distilled under reduced pressure. Then, the solution in $CHCl_3$ was concentrated under reduced pressure and the residue was purified by column chromatography (EtOAc/petroleum ether, 1:2). The product was crystallized from EtOH.

2-(3-(4-Chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-(4-methoxyphenyl)thiazolidin-4-one (4a) Reaction time 60 min; yield 92%; yellow solid, mp 242–244°C; IR: 1502, 1541, 1600 (C=C aromatic stretch), 1731 (C=O stretch), 2981 (C-H aliphatic stretch), 3126 cm^{-1} (C-H aromatic stretch); ^{1}H NMR: δ 3.28 (d, J = 15.3 Hz, 1H, CH_2-S), 3.50 (d, J = 15.3 Hz, 1H, CH_2-S), 3.52 (s, 3H, CH_3O), 5.48 (s, 1H, N-CH-S), 7.32 (t, J = 7.4 Hz, 1H, Ar), 7.43–7.49 (m, 4H, Ar), 7.73–7.80 (m, 4H, Ar), 8.22 (s, 1H, N-CH=C); ^{13}C NMR: δ 32.9, 40.4, 60.5, 118.0, 125.5, 127.4, 127.8, 128.4, 128.7, 129.5, 129.8, 133.6, 138.8, 143.1, 168.3 (C=O). Anal. Calcd for $C_{25}H_{20}ClN_3O_2S$: C, 65.00; H, 4.36; N, 9.10. Found: C, 65.02; H, 4.35; N, 9.08.

2-(3-(4-Chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-(4-methoxyphenyl)thiazolidin-4-one (4b) Reaction time 70 min, yield 90%; yellow solid; mp 231–233°C; IR: 1288 (C-O aromatic stretch), 1500, 1541, 1596 (C=C aromatic stretch), 1737 (C=O stretch), 2977 (C-H aliphatic stretch), 3058 cm^{-1} (C-H aromatic stretch); ^{1}H NMR: δ 3.29 (d, J = 15.2 Hz, 1H, CH_2-S), 3.49 (d, J = 15.2 Hz, 1H, CH_2-S), 3.58 (s, 3H, CH_3O), 5.49 (s, 1H, N-CH-S), 7.30 (td, J = 7.9, 0.7 Hz, 2H, CH=C- OCH_3), 7.37–7.41 (m, 2H, Ar), 7.45–7.48 (m, 6H, Ar), 7.76 (dd, J = 8.4 Hz and 0.6 Hz, 2H, Ar), 7.80 (d, J = 8.4 Hz, 2H, CH=C-Cl), 8.09 (s, 1H, N-CH=C);

^{13}C NMR δ: 32.9, 43.5, 60.5, 118.0, 125.7, 127.1, 127.3, 127.4, 127.5, 127.6, 128.4, 131.3, 138.6, 150.0, 168.8 (C=O). Anal. Calcd for $C_{25}H_{21}N_3O_2S$: C, 70.24; H, 4.95; N, 9.83. Found: C, 70.26; H, 4.97; N, 9.81.

2-(1,3-Diphenyl-1*H*-pyrazol-4-yl)-3-(2-methyl-4-nitrophenyl) thiazolidin-4-one (4c) Reaction time 75 min; yield 86% of yellow solid; mp 237–239°C; IR: 1363, 1541 (NO_2 stretch), 1450, 1500, 1596 (C=C aromatic stretch), 1730 (C=O stretch), 2981 (C-H aliphatic stretch), 3126 cm^{-1} (C-H aromatic stretch); ^{1}H NMR: δ 3.30 (d, J = 15.2 Hz, 1H, CH_2-S), 3.50 (d, J = 15.2 Hz, 1H, CH_2-S), 3.58 (s, 3H, CH_3), 5.50 (s, 1H, N-CH-S), 7.31 (t, J = 7.4 Hz, 1H, Ar), 7.40–7.42 (m, 1H, Ar), 7.45–7.49 (m, 7H, Ar), 7.75–7.78 (m, 2H, Ar), 7.80–7.82 (m, 2H, Ar), 8.23 (s, 1H, N-CH=C); ^{13}C NMR: δ 30.9, 40.4, 43.5, 60.5, 60.6, 118.0, 125.7, 127.1, 127.3, 127.4, 127.5, 127.6, 128.4, 131.3, 138.6, 150.0, 168.8 (C=O). Anal. Calcd for $C_{25}H_{20}N_4O_3S$: C, 65.77; H, 4.42; N, 12.27. Found: C, 65.75; H, 4.39; N, 12.29.

2-(3-(4-Chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-(2-methyl-4-nitrophenyl)thiazolidin-4-one (4d) Reaction time 60 min; yield 87% of yellow solid; mp 240–242°C; IR: 1400, 1539 (NO_2 stretch), 1454, 1500, 1598 (C=C aromatic stretch), 1731 (C=O stretch), 2981 (C-H aliphatic stretch), 3128 cm^{-1} (C-H aromatic stretch); ^{1}H NMR: δ 3.24 (d, J = 15.2 Hz, 1H, CH_2-S), 3.49 (d, J = 15.2 Hz, 1H, CH_2-S), 3.55 (s, 1H, CH_3), 5.45 (s, 1H, N-CH-S),7.26–7.30 (m, 2H, Ar),7.40–7.45 (m, 6H, Ar), 7.71–7.73 (m, 2H, Ar), 7.75–7.78 (m, 2H, CH=C-Cl), 8.20 (s, 1H, N-CH=C); ^{13}C NMR: δ 32.7, 40.3, 43.2, 60.4, 60.5, 117.8, 117.9, 125.7, 127.3, 127.6, 128.3, 128.6, 129.7, 133.1, 138.4, 148.7, 168.1 (C=O). Anal. Calcd for $C_{25}H_{19}ClN_4O_3S$, %: C, 61.16; H, 3.90; N, 11.41. Found: C, 61.14; H, 3.87; N, 11.39.

3-(2-Methyl-4-nitrophenyl)-2-(3-(3-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)thiazolidin-4-one (4e) Reaction time 70 min; yield 91% of yellow solid; mp 251–253°C; IR: 1353, 1533 (NO_2 stretch) 1456, 1595 (C=C aromatic stretch), 1731 (C=O stretch), 2981 (C-H aliphatic stretch), 3128 cm^{-1} (C-H aromatic stretch); ^{1}H NMR: δ 3.28 (d, J = 15.1 Hz, 1H, CH_2-S), 3.34 (d, J = 15.1 Hz, 1H, CH_2-S), 3.56 (s, 3H, CH_3), 5.52 (s, 1H, N-CH-S), 7.31–7.35 (m, 1H, Ar), 7.45–7.48 (m, 3H, Ar), 7.64–7.66 (m, 1H, Ar), 7.66–7.76 (m, 3H, Ar), 8.21 (d, J = 2.0 Hz, 1H, Ar), 8.23 (d, J = 2.0 Hz, 1H, CH_3-CH-CH=C-NO_2), 8.25 (s, 1H, N-CH=C), 8.72 (t, J = 1.8 Hz, 1H, Pyrazolyl-CH=C-NO_2); ^{13}C NMR δ: 32.8, 40.3, 60.4, 118.0, 118.3, 121.8, 122.3, 126.1, 127.7, 128.4, 128.5, 128.6, 133.1, 133.3, 138.3, 147.3, 147.4, 168.2 (C=O). Anal. Calcd for $C_{25}H_{19}N_5O_5S$: C, 59.87; H, 3.82; N, 13.96. Found: C, 59.85; H, 3.84; N, 13.95.

2-(1,3-Diphenyl-1*H*-pyrazol-4-yl)-3-phenylthiazolidin-4-one (4f) Reaction time 60 min; yield 89% of yellow solid; mp 221–223°C, IR: 1498, 1539, 1596 (C=C aromatic stretch), 1733 (C=O stretch), 2981 (C-H aliphatic stretch), 3058 cm^{-1} (C-H aromatic stretch); ^{1}H NMR: δ 3.29 (d, J = 15.1 Hz, 1H, CH_2-S), 3.52 (d, J = 15.1 Hz, 1H, CH_2-S), 5.53 (s, 1H, N-CH-S), 7.18–7.30 (m, 2H, Ar), 7.40–7.44 (m, 2H, Ar) 7.46–7.52 (m, 2H, Ar), 7.77 (d, J = 8.2, 2.4 Hz, 2H, Ar), 7.83 (dd, J = 8.2 Hz and 2.4 Hz, 2H, Ar), 8.26 (s, 1H, N-CH=C); ^{13}C NMR: δ 43.5, 44.5, 119.0, 119.1, 126.7, 128.2, 128.3, 128.4, 128.6, 129.4, 132.4, 139.7, 151.1, 169.8 (C=O). Anal. Calcd for $C_{24}H_{19}N_3OS$: C, 72.52; H, 4.82; N, 10.57. Found: C, 72.50; H, 4.79; N, 10.59.

2-(1,3-Diphenyl-1*H*-pyrazol-4-yl)-3-(4-nitrophenyl)thiazolidin-4-one (4g) Reaction time 75 min; yield 83% of yellow solid; mp 224–226°C; IR 1361 (NO_2 symmetric stretch), 1542 (NO_2 asymmetric stretch), 1730 (C=O stretch), 2981 (C-H aliphatic stretch), 3060 cm^{-1} (C-H aromatic stretch); ^{1}H NMR: δ 3.29 (d, J = 15.2 Hz, 1H, CH_2-S), 3.50 (d, J = 15.2 Hz, 1H, CH_2-S), 5.50 (s, 1H, N-CH-S), 7.28–7.32 (m, 2H, Ar), 7.39–7.42 (m, 2H, Ar), 7.44–7.49 (m, 6H, Ar), 7.76 (d, J = 7.9 Hz, 2H, CH-CH=C-NO_2), 7.82 (dd, J = 8.5 Hz and 1.4 Hz, 2H, CH=C-NO_2), 8.23 (s, 1H, N-CH=C); ^{13}C NMR δ: 32.9, 43.4, 117.3, 117.9, 118.0, 125.6, 126.7, 127.1, 127.2, 127.4, 127.5, 127.6, 127.7, 128.4, 131.2, 138.6, 150.0, 168.7 (C=O). Anal. Calcd for $C_{24}H_{18}N_4O_3S$: C, 65.14; H, 4.10; N, 12.66. Found: C, 65.12; H, 4.09; N, 12.63.

2-(3-(4-Chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-(4-nitrophenyl) thiazolidin-4-one (4h) Reaction time 80 min; yield 79% of yellow solid, mp 239–241°C; IR: 1380 (NO_2 symmetric stretch), 1544 (NO_2 asymmetric stretch), 1731 (C=O stretch), 2981 cm^{-1} (C-H aliphatic stretch); ^{1}H NMR: δ 3.31 (d, J = 15.2 Hz, 1H, CH_2-S), 3.53 (d, J = 15.2 Hz, 1H, CH_2-S), 5.51 (s, 1H, N-CH-S), 7.36–7.37 (m, 1H, Ar), 7.46–7.50 (m, 5H, Ar), 7.52 (dd, J = 5.6 Hz and 3.2 Hz, 1H, Ar), 7.75–7.85 (m, 6H, Ar), 8.26 (s, 1H, N-CH=C); ^{13}C NMR δ: 32.7, 44.0, 114.8, 118.2, 119.7, 123.9, 125.8, 128.4, 129.4, 129.8, 138.7, 150.3, 151.3, 170.3 (C=O). Anal. Calcd for $C_{24}H_{17}ClN_4O_3S$: C, 60.44; H, 3.59; N, 11.75. Found: C, 60.45; H, 3.61; N, 11.72.

3-(4-Nitrophenyl)-2-(3-(3-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)thiazolidin-4-one (4i) Reaction time 90 min; yield 84% of yellow solid, mp 263–265°C: IR: 1350 (NO_2 symmetric stretch), 1533 (NO_2 asymmetric stretch), 1598, 1627 (C=C aromatic stretch), 1731 (C=O stretch), 2923 cm^{-1} (C-H aliphatic stretch); ^{1}H NMR: δ 3.30 (d, J = 15.3 Hz, 1H, CH_2-S), 3.53 (d, J = 15.3 Hz, 1H, CH_2-S), 5.54 (s, 1H, N-CH-S), 7.35 (t, J = 7.4 Hz, 2H, Ar), 7.48–7.52 (m, 3H, Ar), 7.67 (t, J = 8.0 Hz, 2H, Ar), 7.76–7.80 (m, 3H, Ar), 8.24–8.76 (m, 4H, Ar); ^{13}C NMR: δ 43.3, 60.6, 118.1, 121.9, 122.4, 126.2, 127.8, 128.5, 128.6, 133.4, 168.7 (C=O). Anal. Calcd for $C_{24}H_{17}N_5O_5S$: C, 59.13; H, 3.51; N, 14.37. Found: C, 59.15; H, 3.49; N, 14.39.

2-(1,3-Diphenyl-1*H*-pyrazol-4-yl)-3-p-tolylthiazolidin-4-one (4j) Reaction time 90 min; yield 84% of yellow solid; mp 246–248°C; IR: 1350 (NO_2 symmetric stretch), 1533 (NO_2 asymmetric stretch), 1598, 1627 (C=C aromatic stretch), 1731 (C=O stretch), 2923 cm^{-1} (C-H aliphatic stretch); ^{1}H NMR δ: 3.32 (d, J = 15.2 Hz, 1H, CH_2-S), 3.54 (d, J = 15.2 Hz, 1H, CH_2-S), 3.63 (s, 3H, CH_3), 5.54 (s, 1H, N-CH-S), 7.34 (t, J = 7.6 Hz, 1H, Ar), 7.63 (t, J = 7.6 Hz, 1H, Ar), 7.48–7.55 (m, 6H, Ar), 7.80 (d, J = 7.6 Hz, 2H, Ar), 7.85 (dd, J = 7.6 Hz and 1.2 Hz, 2H, Ar), 8.27 (s, 1H, N-CH=C); ^{13}C NMR: δ 34.0, 41.48, 44.6, 119.0, 126.7, 128.2, 128.3, 128.5, 128.6, 129.0, 129.5, 129.7, 132.4, 139.7, 151.1, 169.8 (C=O). Anal. Calcd for $C_{25}H_{21}N_3OS$: C, 72.97; H, 5.14; N, 10.21. Found: C, 72.95; H, 5.15; N, 10.19.

2-(3-(4-Hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-(4-nitrophenyl)thiazolidin-4-one (4k) Reaction time 75 min, 87% of yellow solid, mp 254–256°C; IR: 1276 (C-O aromatic), 1502 (NO_2 symmetric stretch), 1533 (NO_2 asymmetric stretch), 1602 (C=C aromatic stretch), 1726 (C=O stretch), 2923 (C-H aliphatic stretch), 3425 cm^{-1} (O-H aliphatic stretch); ^{1}H NMR: δ 3.32 (d, J = 15.3 Hz, 1H, CH_2-S), 3.54 (d, J = 15.3 Hz, 1H, CH_2-S), 5.48 (s, 1H, N-CH-S), 6.91 (d, J = 8.4 Hz, 2H, CH=C-OH), 7.29–7.35 (m, 2H, Ar), 7.49–7.51 (m, 4H, Ar), 7.68 (d, J = 8.2 Hz, 2H, Ar), 7.75–7.78 (m, 3H, Ar), 8.22 (s, 1H, N-CH=C); ^{13}C NMR: δ 33.9, 44.6, 115.6, 118.7, 119.1, 124.4, 126.7, 128.1, 129.5, 129.9, 139.6, 151.1, 156.3, 170.0 (C=O). Anal. Calcd for $C_{24}H_{18}N_4O_4S$: C, 62.87; H, 3.96; N, 12.22. Found: C, 62.86; H, 3.97; N, 12.20.

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