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Synthesis of 1,3-Oxazine-4-thione Derivatives through an Efficient, Rapid and Green Method Catalyzed by L-Proline in Aqueous Medium

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The development of environmentally friendly and economical methods for the synthesis of biologically active heterocycles using readily available reagents remains a significant challenge in organic synthesis.[1–5] In this context, organocatalysis has emerged as a powerful methodology in organic synthesis for the preparation of both simple and complex bioactive heterocycles[6–11] Organocatalysts offer improved stability, lack of sensitivity to moisture and oxygen, ready availability, low cost, lower toxicity and metal-free reaction conditions. Among organocatalysts, L-proline is a readily obtainable naturally occurring amino acid and is easy to obtain in high enantiomeric purity. It has been reported as an eco-friendly catalyst for the synthesis of several heterocycles.[12–17]

Multi-component reactions (MCRs) have considerable ecological interest for use in the synthesis of biologically important compounds. The design of novel MCRs for the synthesis of diverse heterocycles has become as an important topic for medicinal and organic chemists.[18–22]

Heterocyclic compounds, especially nitrogen- and oxygen-containing heterocyclic molecules in five and six-membered rings, play key roles in medicinal chemistry.[23,24] Among them, oxazines and their derivatives are significant due a diversity of biological functions.[25–27] Both natural and synthetic oxazines exhibit a wide range of biological activities, including anticoagulant activity,[28] fungicidal activities,[29] α-amino-3-hydroxy-5-methyl-4-isoxazolepropionic acid receptor modulation activities,[30] as well as analgesic and antispasmodic activities.[31]

In continuation of our research on MCRs and our ongoing program for the synthesis of complex organic compounds based on green chemistry protocols,[32–36] we now report an efficient and green synthesis of 1,3-oxazine-4-thiones in the presence of

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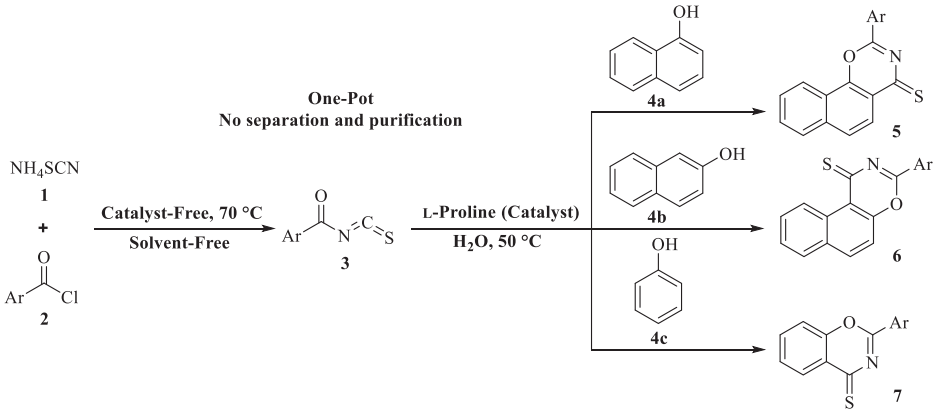

Scheme 1. Synthesis of 1,3-oxazine-4-thione derivatives.

L-proline as an effective and bifunctional organocatalyst in aqueous medium at 50 °C (*Scheme 1*).

1,3-Oxazine-4-thione derivatives were synthesized *via* a two-step procedure: in the first step, ammonium thiocyanate **1** (1 mmol) and acid chlorides **2** (1 mmol) were mixed at 70 °C (solvent-free) until, in less than 5 minutes, solids of benzoyl isothiocyanates **3** were formed. The second step involves the reaction between **3** and naphthols **4a-c** in the presence of L-proline in water to form the corresponding products **5**, **6** and **7**.

To find the best reaction conditions, the sequential one-pot three-component reaction of ammonium thiocyanate (1 mmol), 3-nitrobenzoyl chloride (1 mmol) and 1-naphthol (1 mmol) was selected as a model reaction in the presence of different catalytic systems. The yields and reaction times were monitored as functions of temperature and molar ratio of catalyst. As shown in *Table 1*, after extensive screening, we found that the best yields and time profiles were obtained when the reaction was carried out in the presence of 20 mol % of L-proline as catalyst in H_2O at 50 °C, which afforded the corresponding 2-(3-nitrophenyl)-4*H*-naphtho[2,1-*e*][1,3]oxazine-4-thione **5d** in 3 hours with 93% yield (*Table 1*, entry 8). The reaction did not proceed efficiently in the absence of solvent even after 4 hours at 50 °C (*Table 1*, entry 12).

With the optimized conditions in hand, the scope and efficiency of the reaction were explored for the synthesis of 1,3-oxazine-4-thione derivatives. The results are summarized in *Table 2*. The extensive structural range of benzoyl chlorides afforded the corresponding products in very good to excellent yields using L-proline as catalyst. Benzoyl chlorides containing electron-withdrawing groups increased the rate of reaction and gave higher yields (Entries 1-5, 10-13 and17-20) than those with electron-donating groups (Entries 7-9, 15 and 16).

We also investigated the recycling of the catalyst under optimal reaction conditions using a model reaction of ammonium thiocyanate, 3-nitrobenzoyl chloride and 1-naphthol (*Figure 1*). After completion of the reaction, the crude solid product was filtered and washed with H_2O (2×5 mL). The L-proline was thus removed from the reaction medium by washing with H_2O. Since the catalyst is soluble in water, the catalyst was recovered by evaporation of the water, and washed with diethyl ether and reused for the subsequent catalytic runs. The reactivity was without significant loss through the 2nd run. In the 3rd, 4th and 5th runs, product yield was reduced slightly. That may be due

Table 1
Optimization of the Reaction Conditions for the Synthesis of **5d**

Entry	Catalyst (mol %)	Reaction conditions	Time (h)	Yield (%)[a]
1	DABCO (20)	H_2O, 70 °C	2	54
2	Pyridine (20)	H_2O, 70 °C	2	37
3	Triethylamine (20)	H_2O, 70 °C	2	46
4	Imidazole (20)	H_2O, 70 °C	2	78
5	Caffeine (20)	H_2O, 70 °C	2	75
6	L-Proline(20)	H_2O, 70 °C	2	87
7	L-Proline(20)	H_2O, 100 °C	2	51
8	L-Proline(20)	H_2O, 50 °C	3	93
9	L-Proline(20)	H_2O, rt	8	Trace
10	L-Proline(30)	H_2O, 50 °C	3	91
11	L-Proline(10)	H_2O, 50 °C	3	72
12	L-Proline(20)	Solvent-free, 50 °C	4	Trace

[a]Isolated yield.

Table 2
Preparation of 1,3-oxazine-4-thione Derivatives in the Presence of L-proline (20 mol%) as Catalyst at 50 °C in H_2O

Entry	Naphthol	Ar group	Product	Time (h)	Yield (%)[a]	mp (Obs) (°C)	mp[Lit] (°C)
1	4a	4-NO_2-C_6H_4	**5a**	3	97	166-167	167-169[37]
2	4a	4-Cl-C_6H_4	**5b**	3	91	118-120	120-122[37]
3	4a	4-Br-C_6H_4	**5c**	3	96	124	122-124[37]
4	4a	3-NO_2-C_6H_4	**5d**	3	93	141-143	Present work
5	4a	3,5-$(NO_2)_2$-C_6H_3	**5e**	3	90	157-158	Present work
6	4a	C_6H_5	**5f**	3	95	105-106	107-109[37]
7	4a	4-Me-C_6H_4	**5g**	4	90	117-119	114-116[37]
8	4a	3-Me-C_6H_4	**5h**	4	88	111	Present work
9	4a	2-Me-C_6H_4	**5i**	4	86	125-127	Present work
10	4b	4-NO_2-C_6H_4	**6a**	3	95	170-172	169-171[37]
11	4b	4-Br-C_6H_4	**6b**	3	95	122-123	123-125[37]
12	4b	3-NO_2-C_6H_4	**6c**	3	93	149-150	Present work
13	4b	3,5-$(NO_2)_2$-C_6H_3	**6d**	3	91	172-174	Present work
14	4b	C_6H_5	**6e**	3	93	105	103-105[37]
15	4b	4-Me-C_6H_4	**6f**	4	88	132-134	132-134[37]
16	4b	2-Me-C_6H_4	**6g**	4	85	127-129	Present work
17	4c	4-NO_2-C_6H_4	**7a**	3	92	121	120-122[37]
18	4c	3-NO_2-C_6H_4	**7b**	3	88	108-110	Present work
19	4c	3,5-$(NO_2)_2$-C_6H_3	**7c**	3	87	130-131	Present work
20	4c	4-Br-C_6H_4	**7d**	3	90	146-148	Present work
21	4c	C_6H_5	**7e**	3	85	114-116	114-116[37]

[a]Isolated yield.

to some loss of catalyst during the recovery processes, likely a consequence of solubility in the wash solvents. Even so, the maximum decrease in yields through 5 runs was only 9% (*Figure 1*).

In summary, we have demonstrated an environmentally benign technique for the synthesis of functionalized 1,3-oxazine-4-thionederivatives in excellent yields and purities from readily available starting materials by using a catalytic amount of L-proline as a highly reactive, non-toxic and reusable catalyst, under conventional heating in aqueous medium.

Experimental Section

All melting points were determined on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded on a Shimadzu IR-470 spectrometer. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer at the Iranian Petroleum Central ResearchCompany. Mass spectra were recorded on an Agilent Technology (HP) spectrometer operating at an ionization potential of 70 eV. The ^{1}H nuclear magnetic resonance (NMR) and ^{13}C NMR spectra were recorded on Bruker Avance 400 MHz spectrometer Bruker DRX-400 MHz Avance instruments with $CDCl_3$ as solvent. Thin-layer chromatography (TLC) was performed on silica-gel Polygram SILG/UV 254 plates. All reagents and solvents were purchased from Merck and Aldrich and used without further purification.

General Procedure for the Synthesis of 1,3-Oxazine-4-thione Derivatives(5, 6, 7)

Ammonium thiocyanate **1** (1 mmol) and acid chloride **2** (1 mmol) were mixedat 70 °C (solvent-free) until in less than 5 minutes a solid of benzoyl isothiocyanate **3** was formed.[37–39] Then, 1-naphthol **4a** (1 mmol) was added into the reaction mixture and finally, a solution of L-proline (20 mol %) in water (5 mL) was added and the reaction mixture was stirred at 50 °C for an appropriate time as shown in *Table 2*. Upon completion of the reaction, monitored by TLC(eluent: ethyl acetate/hexane, 1:2), the reaction mixture was allowed to cool to room temperature. Then, the crude solid product was filtered and washed with H_2O (2×5 mL) to remove the catalyst. The resulting product was dried and subsequently washed with 10 mL of diethyl ether to give the pure solid. We also used 2-naphthol **4b** and phenol **4c** instead of 1-naphthol **4a** in this procedure (*Scheme 1*). The analytical and spectroscopic data for the unknown compounds are as follows.

2-(3-Nitrophenyl)-4H-naphtho[2,1-e][1,3]oxazine-4-thione (5d). Pale yellow powder; yield 93%, 0.311 g; mp 141-143 °C; IR (KBr) (ν_{max}, cm^{-1}): 1662, 1575, 1527, 1378, 1338, 1278, 1216, 1108, 1026, 760; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.41 (d, 1H, $J = 7.6$ Hz, Ar-H), 7.54-7.59 (m, 3H, Ar-H),7.81 (d, 1H, $J = 8.0$ Hz, Ar-H), 7.84-7.86 (m, 1H, Ar-H), 7.89-7.96 (m, 2H, Ar-H), 8.56-8.59 (m, 1H, Ar-H), 8.67 (d, 1H, $J = 7.6$ Hz, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 118.1, 120.9, 125.2, 125.4, 126.6, 126.7, 126.8, 128.2, 128.3, 130.0, 131.2, 134.7, 135.9, 146.3, 151.7, 163.2, 197.8; MS (m/z, %): 334 (M^+, 12).

Anal. Calcd for $C_{18}H_{10}N_2O_3S$: C, 64.66; H, 3.01; N, 8.38; S, 9.59. Found: C, 64.90; H, 3.18; N, 8.60; S, 9.72.

2-(3,5-Dinitrophenyl)-4H-naphtho[2,1-e][1,3]oxazine-4-thione (5e). Pale yellow powder; yield 90%, 0.341 g; mp 157-158 °C; IR (KBr) (ν_{max}, cm^{-1}): 1659, 1594, 1532,

1379, 1335, 1263, 1213, 1137, 1067, 766; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.43 (dd, 1H, $J_1 = 7.6$ Hz, $J_2 = 1.2$ Hz, Ar-H), 7.54-7.61 (m, 3H, Ar-H),7.84-7.89 (m, 2H, Ar-H), 7.95-7.98 (m, 1H, Ar-H), 8.36-8.39 (m, 1H, Ar-H), 8.45 (d, 1H, $J = 8.0$ Hz, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 118.0, 120.5, 123.1, 125.4, 126.1, 126.9, 127.0, 127.1, 128.3, 130.0, 133.1, 134.7, 145.9, 148.9, 161.3, 199.4; MS (m/z, %): 379 (M^+, 9).

Anal. Calcd for $C_{18}H_9N_3O_5S$: C, 56.99; H, 2.39; N, 11.08; S, 8.45. Found: C, 57.12; H, 2.43; N, 11.29; S, 8.70.

2-(m-Tolyl)-4H-naphtho[2,1-e][1,3]oxazine-4-thione (5h). Yellow powder; yield 88%, 0.267 g; mp 111 °C; IR (KBr) (ν_{max}, cm^{-1}): 1649, 1571, 1374, 1263, 1217, 1181, 1078, 762; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 2.39 (s, 3H, Me), 7.15 (s, 1H, Ar-H), 7.21-7.26 (m, 1H, Ar-H), 7.34-7.44 (m, 4H, Ar-H), 7.69 (d, 1H, $J = 8.0$ Hz, Ar-H), 7.79-7.85 (m, 1H, Ar-H), 8.06 (d, 1H, $J = 7.6$ Hz, Ar-H), 8.21 (d, 1H, $J = 8.0$ Hz, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 21.3, 118.3, 121.3, 125.5, 126.1, 126.2, 126.4, 126.5, 127.5, 128.6, 129.2, 130.8, 131.3, 134.6, 146.9, 152.2, 165.4, 198.6; MS (m/z, %): 303 (M^+, 23).

Anal. Calcd for $C_{19}H_{13}NOS$: C, 75.22; H, 4.32; N, 4.62; S, 10.57. Found: C, 75.11; H, 4.50; N, 4.91; S, 10.68.

2-(o-Tolyl)-4H-naphtho[2,1-e][1,3]oxazine-4-thione (5i). Yellow powder; yield 86%, 0.261 g; mp 125-127 °C; IR (KBr) (ν_{max}, cm^{-1}): 1646, 1585, 1377, 1273, 1215, 1149, 1076, 782; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 2.78 (s, 3H, Me),7.41-7.46 (m, 2H, Ar-H), 7.55-7.58 (m, 4H, Ar-H), 7.83 (d, 1H, $J = 8.0$ Hz, Ar-H), 7.94-8.01 (m, 2H, Ar-H), 8.44 (d, 1H, $J = 7.6$ Hz, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 22.1, 118.4, 121.3, 125.5, 126.2, 126.4, 126.5, 126.6, 127.1, 128.2, 128.8, 131.0, 131.3, 134.7, 146.9, 152.5, 165.8, 199.0; MS (m/z, %): 303 (M^+, 14).

Anal. Calcd for $C_{19}H_{13}NOS$: C, 75.22; H, 4.32; N, 4.62; S, 10.57. Found: C, 75.39; H, 4.45; N, 4.38; S, 10.34.

3-(3-Nitrophenyl)-1H-naphtho[1,2-e][1,3]oxazine-1-thione (6c). Pale yellow powder; yield 93%, 0.311 g; mp 149-150 °C; IR (KBr) (ν_{max}, cm^{-1}): 1653, 1612, 1581, 1527, 1344, 1294, 1156, 1056, 713; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.40 (dd, 1H, $J_1 = 8.8$ Hz, $J_2 = 2.4$ Hz, Ar-H), 7.52-7.58 (m, 2H, Ar-H), 7.75-7.76 (m, 1H, Ar-H), 7.79 (d, 1H, $J = 8.0$ Hz, Ar-H), 7.86-7.93 (m, 2H, Ar-H), 7.96 (d, 1H, $J = 8.8$ Hz, Ar-H), 8.53-8.61 (m, 2H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 118.6, 120.7, 125.1, 126.0, 126.8, 127.7, 127.8, 128.0, 129.7, 129.9, 131.4, 131.7, 133.7, 135.8, 148.1, 148.4, 163.3, 199.2; MS (m/z, %): 334 (M^+, 8).

Anal. Calcd for $C_{18}H_{10}N_2O_3S$: C, 64.66; H, 3.01; N, 8.38; S, 9.59. Found: C, 64.52; H, 3.14; N, 8.27; S, 9.71.

3-(3,5-Dinitrophenyl)-1H-naphtho[1,2-e][1,3]oxazine-1-thione (6d). Yellow powder; yield 91%, 0.345 g; mp 172-174 °C; IR (KBr) (ν_{max}, cm^{-1}): 1644, 1615, 1596, 1540, 1339, 1273, 1167, 1070, 756; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.40 (dd, 1H, $J_1 = 2.0$ Hz, $J_2 = 8.8$ Hz, Ar-H), 7.54-7.60 (m, 2H, Ar-H), 7.77 (d, 1H, $J = 1.6$ Hz, Ar-H), 7.88-7.94 (m, 2H, Ar-H), 7.98 (d, 1H, $J = 8.8$ Hz, Ar-H), 8.34-8.35 (m, 1H, Ar-H), 8.39 (d, 1H, $J = 2.0$ Hz, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 118.5, 120.2, 122.9, 126.4, 127.0, 127.8, 127.9, 129.9, 130.0, 131.8, 133.3, 133.6, 147.7, 148.8, 161.3, 198.9; MS (m/z, %): 379 (M^+, 10).

Anal. Calcd for $C_{18}H_9N_3O_5S$: C, 56.99; H, 2.39; N, 11.08; S, 8.45. Found: C, 57.14; H, 2.63; N, 11.25; S, 8.58.

3-(o-Tolyl)-1H-naphtho[1,2-e][1,3]oxazine-1-thione (6g). Yellow powder; yield 85%, 0.258 g; mp 127-129 °C; IR (KBr) (ν_{max}, cm^{-1}): 1639, 1593, 1501, 1296, 1233,

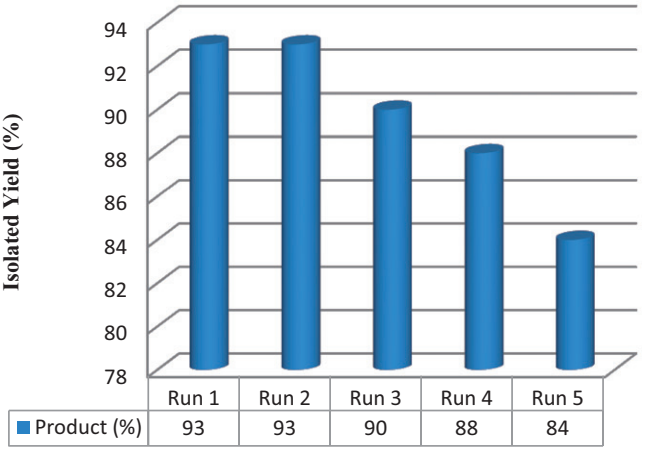

Figure 1. The investigation of the recycling of L-proline.

1150, 1041, 728; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 2.54 (s, 3H, CH_3), 7.36-7.40 (m, 2H, Ar-H), 7.50-7.55 (m, 2H, Ar-H), 7.71 (d, 1H, $J = 2.4$ Hz, Ar-H), 7.85-7.91 (m, 2H, Ar-H), 7.94 (d, 1H, $J = 8.8$ Hz, Ar-H), 8.06-8.09 (m, 1H, Ar-H), 8.26 (d, 1H, $J = 8.0$ Hz, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 22.0, 118.8, 121.4, 125.7, 125.9, 126.5, 127.0, 127.7, 128.5, 128.8, 129.4, 130.7, 131.8, 132.0, 134.8, 141.4, 148.5, 166.0, 199.3; MS (m/z, %): 303 (M^+, 5).

Anal. Calcd for $C_{19}H_{13}NOS$: C, 75.22; H, 4.32; N, 4.62; S, 10.57. Found: C, 75.39; H, 4.50; N, 4.46; S, 10.81.

2-(3-Nitrophenyl)-4H-benzo[e][1,3]oxazine-4-thione (7b). Yellow powder; yield 88%, 0.250 g; mp 108-110 °C; IR (KBr) (ν_{max}, cm^{-1}): 1650, 1591, 1522, 1339, 1316, 1290, 1248, 1108, 1054, 750; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.26 (d, 2H, $J = 8.0$ Hz, Ar-H), 7.34 (t, 1H, $J = 7.6$ Hz, Ar-H), 7.48 (t, 2H, $J = 8.0$ Hz, Ar-H), 7.76 (t, 1H, $J = 8.0$ Hz, Ar-H), 8.50-8.56 (m, 2H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 121.5, 122.9, 125.1, 126.6, 126.9, 128.0, 129.7, 129.9, 131.4, 135.8, 148.4, 150.5, 163.1, 199.6; MS (m/z, %): 284 (M^+, 19).

Anal. Calcd for $C_{14}H_8N_2O_3S$: C, 59.15; H, 2.84; N, 9.85; S, 11.28. Found: C, 59.37; H, 3.04; N, 9.89; S, 11.51.

2-(3,5-Dinitrophenyl)-4H-benzo[e][1,3]oxazine-4-thione (7c). Yellow powder; yield 87%, 0.286 g; mp 130-131 °C; IR (KBr) (ν_{max}, cm^{-1}): 1657, 1593, 1542, 1333, 1311, 1292, 1267, 1136, 1065, 756; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.27-7.29 (m, 2H, Ar-H), 7.35-7.39 (m, 1H, Ar-H), 7.48-7.50 (m, 2H, Ar-H), 7.79 (d, 1H, $J = 7.6$ Hz, Ar-H), 8.52-8.55 (m, 1H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 121.4, 122.9, 126.9, 128.7, 129.8, 129.9, 130.7, 131.4, 131.9, 133.3, 148.8, 150.1, 161.2, 198.4; MS (m/z, %): 329 (M^+, 7).

Anal. Calcd for $C_{14}H_7N_3O_5S$: C, 51.06; H, 2.14; N, 12.76; S, 9.74. Found: C, 51.39; H, 2.03; N, 12.83; S, 9.93.

2-(4-Bromophenyl)-4H-benzo[e][1,3]oxazine-4-thione (7d). Yellow powder; yield 90%, 0.286 g; mp 146-148 °C; IR (KBr) (ν_{max}, cm^{-1}): 1660, 1584, 1384, 1277, 1220, 1195, 1072, 743; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.22-7.24 (m, 1H, Ar-H),7.28-7.33 (m, 1H, Ar-H),7.44-7.48 (m, 2H, Ar-H),7.66-7.70 (m, 2H, Ar-H),8.07-8.10 (m, 2H, Ar-

H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 121.5, 121.6, 126.0, 128.4, 128.8, 129.5, 131.6, 131.8, 131.9, 135.4, 147.7, 150.7, 164.5, 199.2; MS (m/z, %): 318 (M^+, 15).

Anal. Calcd for $C_{14}H_8BrNOS$: C, 52.85; H, 2.53; N, 4.40; S, 10.08. Found: C, 53.07; H, 2.25; N, 4.14;S, 10.27.

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