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Method for the Synthesis of Phenothiazines via a Domino Iron-Catalyzed C−S/C−N Cross-Coupling Reaction

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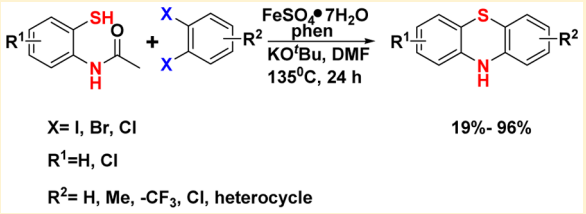
Supporting Information

ABSTRACT: An environmentally benign and efficient method has been developed for the synthesis of phenothiazines via a tandem iron-catalyzed C−S/C-N cross-coupling reaction. Some of the issues typically encountered during the synthesis of phenothiazines in the presence of palladium and copper catalysts, including poor substrate scope, long reaction times and poor regioselectivity, have been addressed using this newly developed iron-catalyzed method.



INTRODUCTION

In recent years, transition metals have been the main force in cross-coupling reactions, which play an important role in the formation of C−N bonds and C−S bonds of some important compounds in biological, pharmaceutical, and materials sciences,[1] especially iron, which is an essential trace element in human beings. Since the pioneering work of Tamura and Kochi,[2] iron salts as catalysts have attracted widespread attention. In the past few years, there has been a significant increase in the number of reports pertaining to the development of iron-catalyzed reactions in organic synthesis, where iron has shown several significant advantages over other metals, such as being more abundant, commercially inexpensive and environmentally friendly.[3] Compared with palladium, the use of iron is particularly suitable for reactions involving the preparation of therapeutic agents for human consumption. The iron-catalyzed formation of C−N bonds and C−S bonds has been reported several times.[4,5] However, it is rare that one iron-catalyzed system is effective for both C−N coupling and C−S coupling, because every catalyzed system has its own compound specificity.

Phenothiazines represent an important class of heterocyclic compounds which play an important role in the treatment of mental illnesses[6] and have also been used as anodynes, peroxidation inhibitors and optoelectronic materials.[7] In recent years, some new methods for the synthesis of phenothiazines have been reported.[8−11] Compared with traditional methods,[12] those methods indeed solved some problems such as toxicity (e.g., H_2S byproduct) and low regioselectivity. For example, Jørgensen's group reported an elegant method for the synthesis of substituted phenothiazines via the palladium-catalyzed three-component coupling reaction of substituted 1-bromo-2-iodobenzenes with primary amines and 2-bromobenzenethiol in 2008.[10] In 2010, Ma et al.[11a] reported a CuI/L-proline-catalyzed C−S/C−N bond formation of 2-iodoanilines and 2-bromobenzenethiols by controlling the reaction temperature and time (i.e., 90 °C for 24−48 h followed by 110 °C for 48−96 h). Although many catalyzed systems have been reported for the synthesis of phenothiazines, no iron-catalyzed versions have been studied. With this in mind, it was envisaged that an iron-catalyzed reaction could be developed for the synthesis of substituted phenothiazines. Herein we report the results of our preliminary investigations toward the development of this protocol.

RESULTS AND DISCUSSION

Given that there are no reports in the literature to date pertaining to the use of iron as a catalyst for the coupling reaction of an arylamine and aryl halide, we used an acyl-protected arylamine[14] to investigate this reaction because it could be readily removed upon completion of the coupling reaction.[13] The reaction of **1a** with 1,2-dibromobenzene was used as the model transformation to identify the optimum reaction conditions by screening a variety of different iron salts, bases, ligands and solvents (Table 1). Several iron salts were screened in this reaction, including Fe_2O_3, $FeSO_4{\cdot}7H_2O$, $Fe_2(SO_4)_3$, $Fe(acac)_3$, $FeCl_3$, $FeCl_2{\cdot}4H_2O$ and $Fe(NO_2)_3{\cdot}9H_2O$. $FeSO_4{\cdot}7H_2O$ was found to give the best results with the desired product **3a** being formed in a yield of 52% (Table 1, entries 1−7). Several other bases, including $NaOCH_3$, K_2CO_3, Cs_2CO_3 and NaOAc were also evaluated under the same conditions using $FeSO_4{\cdot}7H_2O$, but all of these bases failed to provide results better than that of KO^{t}Bu (Table 1, entries 8−11).

Several ligands were also screened in the model reaction, and the results revealed that the nature of the ligand has a dramatic impact on the yield of the reaction. For example, the use of 1,10-phenanthroline gave 10*H*-phenothiazine in 70% yield, whereas DABCO, bis-pyridyl and L-proline provided much lower yields of 11%, 19% and 14%, respectively (Table 1, entries 12−15). The reaction was also conducted in a variety of

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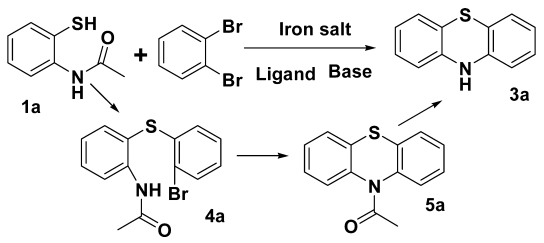
Table 1. Optimization of the Reaction of 1a with 1,2-Dibromobenzene[a]



entry	iron salt	L[c]	base	solvent	yield (%)[b]
1	Fe_2O_3	A	KO^{t}Bu	DMF	42
2	$FeSO_4{\cdot}7H_2O$	A	KO^{t}Bu	DMF	52
3	$Fe_2(SO_4)_3$	A	KO^{t}Bu	DMF	44
4	$Fe(acac)_3$	A	KO^{t}Bu	DMF	46
5	$FeCl_3$	A	KO^{t}Bu	DMF	47
6[d]	$FeCl_2{\cdot}4H_2O$	A	KO^{t}Bu	DMF	44
7	$Fe(NO_2)_3{\cdot}9H_2O$	A	KO^{t}Bu	DMF	35
8	$FeSO_4{\cdot}7H_2O$	A	NaOMe	DMF	40
9	$FeSO_4{\cdot}7H_2O$	A	K_2CO_3	DMF	32
10	$FeSO_4{\cdot}7H_2O$	A	Cs_2CO_3	DMF	37
11	$FeSO_4{\cdot}7H_2O$	A	NaOAc	DMF	29
12	$FeSO_4{\cdot}7H_2O$	B	KO^{t}Bu	DMF	11
13	$FeSO_4{\cdot}7H_2O$	C	KO^{t}Bu	DMF	70
14	$FeSO_4{\cdot}7H_2O$	D	KO^{t}Bu	DMF	19
15	$FeSO_4{\cdot}7H_2O$	E	KO^{t}Bu	DMF	14
16	$FeSO_4{\cdot}7H_2O$	C	KO^{t}Bu	PhMe	trace
17	$FeSO_4{\cdot}7H_2O$	C	KO^{t}Bu	DMSO	17
18	$FeSO_4{\cdot}7H_2O$	C	KO^{t}Bu	MeCN	trace
19	$FeSO_4{\cdot}7H_2O$	C	KO^{t}Bu	EtOH	0
20	$FeSO_4{\cdot}7H_2O$	C	KO^{t}Bu	THF	0
21	$FeSO_4{\cdot}7H_2O$	C	none	DMF	0
22	none	C	KO^{t}Bu	DMF	0
23	none	none	KOH	DMSO	trace
24[e]	$FeSO_4{\cdot}7H_2O$	C	KO^{t}Bu	DMF	73
25[f]	$FeSO_4{\cdot}7H_2O$	C	KO^{t}Bu	DMF	60

[a]Reaction conditions: **1a** (0.3 mmol), 1,2-dibromobenzene (1.5 equiv), iron salt (20 mmol %), base (4 equiv) and ligand (20 mmol %) were added to a solvent (2 mL) and reacted at 135 °C for 24 h under N_2. [b]A yield based on **1a** after silica gel chromatography. [c]A = TMEDA, B = DABCO, C = 1,10-phenanthroline, D = dipyridyl, E = L-proline. [d]$FeCl_2{\cdot}4H_2O$ in a purity of 99.99%. [e]$FeSO_4{\cdot}7H_2O$ in a purity of 99.999% from Alfa. [f]With iron salt in a dosage of 10 mmol %.

different solvents to determine the impact of the solvent on the outcome of the reaction. DMF was found to be the best solvent for the transformation, because it provided a much higher yield of the desired product than toluene, DMSO or acetonitrile (Table 1, entries 16–18). Some clean solvents, including ethanol and THF, were applied in the reaction, but no product was obtained (Table 1, entries 19 and 20).

Control experiments were taken in the absence of $FeSO_4{\cdot}7H_2O$ or KO^{t}Bu, respectively; no product was obtained (Table, entries 21 and 22). In view of the fact that trace metals in catalysts sometimes play an important role in the reaction,[15] high-purity $FeSO_4{\cdot}7H_2O$ (99.999%) was applied in the reaction (Table 1, entry 24). The product was formed in a yield of 73% which was similar to that of $FeSO_4{\cdot}7H_2O$ (99%). Finally, the dosage of $FeSO_4{\cdot}7H_2O$ was reduced to 10 mmol %, but only 60% yield was obtained (Table 1, entry 25). Taken together, the results of these screening experiments revealed that the optimal conditions for the reaction were $FeSO_4{\cdot}7H_2O$ (20 mol %), 1,10-phenanthroline (20 mol %) and KO^{t}Bu in DMF at 135 °C.

It is noteworthy that the intermediate product **4a** was formed as a byproduct under the optimized conditions via the C–S cross-coupling reaction of *N*-(2-mercaptophenyl)acetamide (**1a**) with 1,2-dibromobenzene. Furthermore, the subsequent intramolecular C–N cross coupling of **4a** gave the N-acetylated phenothiazine **5a**. These results demonstrated that the one-pot reaction includes three different processes, which are shown in Table 1.

With the optimized reaction conditions in hand, we proceeded to investigate the substrate scope of the reaction using a variety of different aryl 1,2-dihalobenzenes (Table 2). *N*-(2-Mercaptophenyl)acetamide was reacted with a variety of 1,2-dihalobenzene substrates, including 1-bromo-2-chlorobenzene, 1-chloro-2-iodobenzene, 1,2-dibromobenzene, 1-bromo-2-iodobenzene and 1,2-dichlorobenzene under the optimized conditions, with the desired 10*H*-phenothiazine being formed in moderate to excellent yields (Table 2, entries 1–5). Even the least reactive of these substrates, 1,2-dichlorobenzene, provided the desired product under the optimized conditions, albeit in a low yield of 20% (Table 2, entry 5). The optimized conditions were also applied to a series of substituted 1,2-dihalobenzenes, including 2-bromo-1-iodo-4-methylbenzene and 2-bromo-4-(trifluoromethyl)-1-iodobenzene, with the corresponding substituted phenothiazines being formed in only 19% and 40% yields, respectively (Table 2, entries 6 and 7). Byproducts were observed, and we believe that the methyl and trifluoromethyl groups affect the C–N cross-coupling process by lowering the activity of the halogen in the meta position. It is noteworthy that the reactions of 2-bromo-4-chloro-1-iodobenzene and 4-chloro-1,2-diiodobenzene resulted in a mixture of two regioisomers in both cases in a high total yield (Table 2, entries 8 and 9). The result may be caused by the diminution of the gap of activity between two reaction centers.

Several exciting results were obtained when the substrate scope was expanded to evaluate the use of *N*-(5-chloro-2-mercaptophenyl)acetamide under the optimized conditions. Most of the 1,2-dihalobenzene substrates, including 1-bromo-2-chlorobenzene, 1-chloro-2-iodobenzene, 1,2-dibromobenzene, 1-bromo-2-iodobenzene and 1,2-dichlorobenzene, reacted smoothly with *N*-(5-chloro-2-mercaptophenyl)acetamide to give 2-chloro-10*H*-phenothiazine in yields of up to 92% (Table 2, entries 10–14). High total yields were also obtained when *N*-(5-chloro-2-mercaptophenyl)acetamide was reacted with 2-bromo-4-chloro-1-iodobenzene and 4-chloro-1,2-diiodobenzene (Table 2, entries 15 and 16).

The use of heterocyclic compounds as substrates for this reaction was also investigated using 2,3-dibromopyridine, 2,3-dibromo-5-methylpyridine and 2,3-dibromoquinoxaline. Pleasingly, the corresponding heterocyclic phenothiazines were obtained in good yields when 2,3-dibromopyridine and 2,3-dibromo-5-methylpyridine were used as substrates (Table 2, entries 17–20). Furthermore, 2,3-dibromoquinoxaline reacted smoothly with both *N*-(2-mercaptophenyl)acetamide and *N*-(5-chloro-2-mercaptophenyl)acetamide to afford the corresponding coupling products in 90% and 96% yields, respectively (Table 2, entries 21 and 22). This work therefore represents the first reported example of the synthesis of phenothiazines from a quinoxaline.

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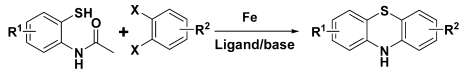
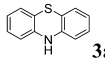
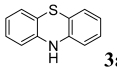
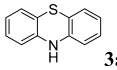
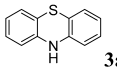
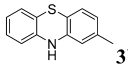
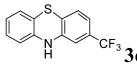
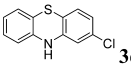
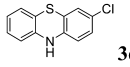
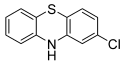
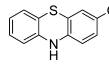
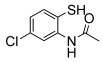
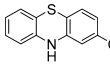
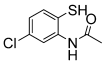
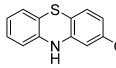
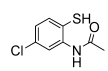
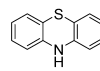
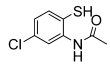
Table 2. Reagent Scope of the Reaction[a]



Entry	Substrate 1	Substrate 2	Product	Y(%)
1			 **3a**	72
2			 **3a**	70
3			 **3a**	81
4			 **3a**	80
5			 **3a**	20
6			 **3b**	19
7			 **3c**	40
8			 **3d**	50
			 **3e**	21
9			 **3d**	70
			 **3e**	14
10			 **3d**	80
11			 **3d**	92
12			 **3d**	69
13			**3d**	85
14			**3d**	35
15			**3f**	63
			3g	32
16			**3f**	65
			3g	20
17			**3h**	63
18			**3i**	70
19			**3j**	60
20			**3k**	78
21			**3l**	90
22			**3m**	96

[a]Reaction conditions: Substrate **1** (0.3 mmol), substrate **2** (0.45 mmol), $FeSO_4{\cdot}7H_2O$ (0.06 mmol), phen (0.06 mmol), KO*t*Bu (1.2 mmol) and DMF (2 mL) at 135 °C for 24 h.

CONCLUSION

In summary, an efficient method has been developed for the synthesis of phenothiazines using an iron salt as a catalyst. This method has been successfully applied to the C−N coupling of aryl amines and aryl halides for the synthesis of serviceable compounds. Work is in progress to understand the mechanism.

EXPERIMENTAL SECTION

General Details. All of the reagents and solvents were used directly as obtained commercially unless otherwise noted. Petroleum ether (PE) refers to the 60−90 °C boiling point fraction of petroleum. Column chromatography was performed with 300−400 mesh silica gel using flash column techniques. ^1H and ^{13}C NMR spectra were determined in $CDCl_3$ or DMSO-d_6 on a 400 MHz spectrometer, and chemical shifts were measured relative to the signals for residual chloroform (7.26 ppm) or DMSO (2.50 ppm) in the deuterated solvent, unless otherwise stated. Chemical shifts in ^{13}C NMR spectra are reported relative to the central line of DMSO (δ = 40.00 ppm).

Synthesis of 10*H*-Phenothiazine. *N*-(2-Mercaptophenyl)-acetamide (50.1 mg, 0.3 mmol), $FeSO_4{\cdot}7H_2O$ (16.68 mg, 0.06 mmol), 1,10-phenanthroline (10.08 mg, 0.06 mmol) and KO^{t}Bu (134.4 mg, 1.2 mmol) were weighed into an oven-dried Schlenk tube which was sealed with a plug, and an nitrogen atmosphere was established. Then 1,2-dibromobenzene (53.8 μL,0.45 mmol) and DMF (2 mL) were added via syringe. The Schlenk tube was heated to 135 °C and stirred for 24 h. When the reaction was complete, the homogeneous mixture was cooled to room temperature and diluted with water and ether. The organic solution was washed with brine, dried (Na_2SO_4), and purified by column chromatography (ethyl acetate: petroleum ether = 1:80) to give desired 10*H*-phenothiazine.

*10H-Phenothiazine (**3a**).*[11a] obtained as a celadon solid; mp 184−185 °C. ^1H NMR (400 MHz, DMSO-d_6) (ppm): 8.58 (s, 1H), 7.00−6.96 (m, 2H), 6.91−6.89 (d, J = 7.6, 2H), 6.76−6.68 (m, 4H). $^{13}C\{^1H\}$-NMR (100 MHz, DMSO-d_6, δ ppm): 142.6, 128.0, 126.7, 122.2, 116.8, 114.9. LC-MS: $[M + H]^+$ m/z = 200.0.

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*2-Methyl-10H-phenothiazine (**3b**).*[11a] obtained as a obtained as a rufous solid; isolated yield: 12.14 mg (19%); mp 186−187.5 °C. ^{1}H NMR (400 MHz, DMSO-d_6) (ppm): 8.50 (s, 1H), 6.99−6.95 (m, 1H), 6.90−6.88 (m, 1H), 6.79−6.67 (m, 3H), 6.59−6.51 (m, 2H), 2.15 (s, 3H). ^{13}C{^{1}H}-NMR (100 MHz, DMSO-d_6, δ ppm): 142.6, 142.5, 137.4, 127.9, 126.7, 126.5, 123.0, 122.1, 117.1, 115.6, 114.9, 113.4, 21.1. LC-MS: $[M + H]^+$ m/z = 214.1.

*2-(Trifluoromethyl)-10H-phenothiazine (**3c**).*[11a] obtained as a yellow solid; isolated yield: 32.04 mg (40%); mp 188−190 °C. ^{1}H NMR (400 MHz, DMSO-d_6) (ppm): 8.88 (s, 1H), 7.12−7.00 (m, 3H), 6.94−6.89 (m, 2H), 6.79 (t, J = 7.52, 1H), 6.65 (d, J = 8, 1H). ^{13}C{^{1}H}-NMR (100 MHz, DMSO-d_6, δ ppm): 143.1, 141.4, 128.6 ($^2J_{CF}$ = 31 Hz), 128.0, 126.7, 125.8 (q, $^1J_{CF}$ = 270.34 Hz), 123.1, 123.0, 122.5, 118.5, 115.7, 115.21, 110.2. LC-MS: $[M + H]^+$ m/z = 268.0.

*2-Chloro-10H-phenothiazine (**3d**).*[11a] obtained as a rufous solid; mp196−198 °C. ^{1}H NMR (400 MHz, DMSO-d_6) (ppm): 8.78 (s, 1H), 7.02−6.98 (m, 1H), 6.92−6.90 (d, J = 8.08, 2H), 6.80−6.76 (m, 2H), 6.70−6.66 (m, 2H). ^{13}C{^{1}H}-NMR (100 MHz, DMSO-d_6, δ ppm): 144.0, 141.6, 132.3, 128.3, 127.9, 126.8, 122.8, 121.7, 116.5, 116.0, 115.1, 114.2. LC-MS: $[M + H]^+$ m/z = 234.1.

*3-Chloro-10H-phenothiazine (**3e**).*[10] obtained as a rufous solid; mp 200−201 °C. ^{1}H NMR (400 MHz, DMSO-d_6) (ppm): 8.73 (s, 1H), 7.03−6.98 (m, 3H), 6.93−6.91 (m, 1H), 6.79−6.75 (m, 1H), 6.68−6.65 (m, 2H). ^{13}C{^{1}H}-NMR (100 MHz, DMSO-d_6, δ ppm): 142.1, 141.6, 128.3, 127.7, 126.8, 125.9, 125.4, 122.6, 119.1, 116.0, 115.9, 115.1. LC-MS: $[M + H]^+$ m/z = 234.1.

*2,8-Dichloro-10H-phenothiazine (**3f**).*[15] obtained as a yellow solid; mp 267−268.5 °C. ^{1}H NMR (400 MHz, DMSO-d_6) (ppm): 8.94 (s, 1H), 6.94−6.92 (d, J = 8.2, 2H), 6.82−6.80 (m, 2H), 6.67 (s, 2H). ^{13}C{^{1}H}-NMR (100 MHz, DMSO-d_6, δ ppm):143.0, 132.5, 128.1, 122.3, 115.7, 114.5. LC-MS: $[M + H]^+$ m/z = 268.9.

*2,7-Dichloro-10H-phenothiazine (**3g**).*[16] obtained as a yellow solid; mp 214−215.5 °C. ^{1}H NMR (400 MHz, DMSO-d_6) (ppm): 8.90 (s, 1H), 7.05−7.03 (m, 2H), 6.94−6.92 (d, J = 8.24, 1H), 6.81−6.78 (m, 1H), 6.68−6.63 (m, 2H). ^{13}C{^{1}H}-NMR (100 MHz, DMSO-d_6, δ ppm): 143.5, 140.6, 132.6, 128.1, 128.0, 126.1, 126.0, 122.0, 118.8, 116.2, 115.2, 114.4. LC-MS: $[M + H]^+$ m/z = 268.9.

*5H-Pyrido[2,3-b][1,4]benzothiazine (**3h**).*[17] obtained as a yellow solid; isolated yield: 37.8 mg (63%); mp 112−113 °C. ^{1}H NMR (400 MHz, DMSO-d_6) (ppm): 9.19 (s, H), 7.80 (d, J = 3.8, 1H), 7.26 (d, J = 7.16, 1H), 7.01−6.90 (m, 2H), 6.83−6.70 (m, 3H). ^{13}C{^{1}H}-NMR (100 MHz, DMSO-d_6, δ ppm): 153.7, 146.1, 141.3, 134.3, 128.2, 126.4, 123.0, 118.4, 115.8, 115.7, 112.7. LC-MS: $[M + H]^+$ m/z = 201.1.

*7-Chloro-5H-pyrido[2,3-b][1,4]benzothiazine (**3i**) (new).* obtained as a yellow solid; isolated yield: 49.14 mg (70%); mp 217−218.5 °C. ^{1}H NMR (400 MHz, DMSO-d_6) (ppm): 9.34 (s, 1H), 7.83−7.81 (m, 1H), 7.29 (d, J = 7.48, 1H), 6.93 (d, J = 8.2, 1H), 6.85−6.74 (m, 3H). ^{13}C{^{1}H}-NMR (100 MHz, DMSO-d_6, δ ppm): 152.9, 146.3, 142.8, 134.5, 132.5, 127.7, 122.4, 118.9, 115.0, 114.9, 112.4. LC-MS: $[M + H]^+$ m/z = 235.0. HRMS (ESI/TOF-Q) m/z: $[M + H]^+$ calcd for $C_{11}H_7ClN_2SH$ 235.0091; found 235.0100.

*3-Methyl-5H-pyrido[2,3-b][1,4]benzothiazine (**3j**) (new).* obtained as a light yellow solid; isolated yield: 38.52 mg (60%); mp 163.5−164,5 °C. ^{1}H NMR (400 MHz, DMSO-d_6) (ppm): 9.04 (s, 1H), 7.63 (s, 1H), 7.12 (s, 1H), 6.97 (t, J = 7.32, 1H), 6.90 (d, J = 7.64, 1H), 6.81−6.73 (m, 2H). ^{13}C{^{1}H}-NMR (100 MHz, DMSO-d_6, δ ppm): 151.5, 145.6, 141.7, 134.9, 128.2, 127.3, 126.4, 122.7, 115.7, 115.5, 112.3, 17.3. LC-MS: $[M + H]^+$ m/z = 215.1. HRMS (ESI/TOF-Q) m/z: $[M + H]^+$ calcd for $C_{12}H_{10}N_2SH$ 215.0637; found 215.0629

*3-Methyl-7-chloro-5H-pyrido[2,3-b][1,4]benzothiazine (**3k**) (new).* obtained as a light yellow solid; isolated yield: 58.03 mg (78%); mp 219−220 °C. ^{1}H NMR (400 MHz, DMSO-d_6) (ppm): 9.20 (s, 1H), 7.65 (s, 1H), 7.15 (s, 1H), 6.92 (d, J = 8.2, 1H), 6.82−6.77 (m, 2H). ^{13}C{^{1}H}-NMR (100 MHz, DMSO-d_6, δ ppm): 150.7, 145.8, 143.2, 135.1, 132.5, 127.9, 127.7, 122.1, 114.9, 114.8, 112.1, 17.3. LC-MS: $[M + H]^+$ m/z = 248.9.HRMS (ESI/TOF-Q) m/z: $[M + H]^+$ calcd for $C_{12}H_9ClN_2SH$ 249.0248; found 249.0244.

*12H-Quinoxalino[2,3-b][1,4]benzothiazine(**3l**).*[18] obtained as a yellow solid; isolated yield: 67.77 mg (90%); mp 281−282.5 °C. ^{1}H NMR (400 MHz, DMSO-d_6) (ppm): 10.22 (s, 1H), 7.52−7.29 (m, 4H), 7.05−6.99 (m, 2H), 6.87−6.79 (m, 2H). ^{13}C{^{1}H}-NMR (100 MHz, DMSO-d_6, δ ppm): 146.0, 145.6, 140.8, 139.6, 136.9, 129.7, 128.4, 127.2, 126.3, 126,2, 126.0, 123.0, 116.4, 115.6. LC-MS: $[M + H]^+$ m/z = 252.0.

*2-Chloro-12H-quinoxalino[2,3-b][1,4]benzothiazine (**3m**).*[18] obtained as a yellow solid; isolated yield: 82.08 mg (96%); mp 289−290 °C. ^{1}H NMR (400 MHz, DMSO-d_6) (ppm): 10.32 (s, 1H), 7.52−7.31 (m, 4H), 7.02 (d, J = 8.12, 1H), 6.84 (t, J = 7.32, 2H). ^{13}C{^{1}H}-NMR (100 MHz, DMSO-d_6, δ ppm): 145.4, 145.0, 140.6, 139.7, 138.4, 132.5, 129.8, 127.7, 127,3, 126.6, 126.2, 122.4, 115.6, 114.83. LC-MS: $[M + H]^+$ m/z = 286.0.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra for all compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00568.

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Notes

The authors declare no competing financial interest.

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