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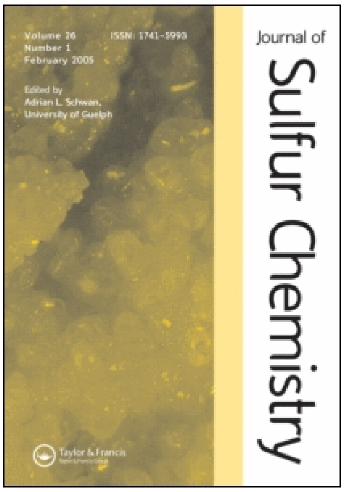

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Zn(Pro) $_2$-promoted CuI-catalyzed synthesis of diphenyl sulfide derivations in ionic liquid

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Zn(Pro)$_2$-promoted CuI-catalyzed synthesis of diphenyl sulfide derivations in ionic liquid

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We report a mild, palladium-free synthetic protocol for the cross-coupling reaction of aryl chlorides and thiols under the assistance of Zn complexes of proline and CuI, with K_2CO_3 as the base, performed at 110 °C in ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4). This protocol is particularly noteworthy given its experimental simplicity, high generality, and the exceptional level of functional group tolerations and low cost of the catalyst system.

Keywords: thiols; cross-coupling reaction; room temperature ionic liquid; Zn-proline

1. Introduction

Transition-metal-catalyzed coupling is one of the most important tools to form a carbon–hetero atom bond (*1*). Among these, the formation of the carbon–sulfur bond has received much attention due to the occurrence of this bond in many molecules that are of biological, pharmaceutical, and material interests (*2*).

Traditional copper-catalyzed cross-coupling reactions of aryl and vinyl halides with thiols suffered from drawbacks such as high reaction temperatures, the use of copper salts in greater than stoichiometric amounts, sensitivity to functional groups on the aryl halide, and irreproducibility. These cross-coupling reactions that form a carbon–sulfur bond would be even more useful and efficient if performed catalytically, rather than stoichiometrically (*3*). More recently, the palladium-catalyzed cross-coupling reactions of aryl and vinyl halides with thiols are versatile synthetic methods in the processes of carbon–sulfur bond-forming transformations (*4–6*). Buchwald (*1*) reported Cu(I) salts as catalysts in glycol based on the K_2CO_3 method for the formation of aryl carbon–sulfur bond, and Takahiro (*2*) reported palladium-catalyzed coupling of aryl bromides and thiols; however, the two methods are still using expensive reagents such as aryl iodides or palladium catalysts. Moreover, promising catalytic systems for less expensive or readily available unactivated aryl chlorides have been studied extensively. There has been a resurgence in interest in developing mild synthetic methods based on copper-based catalysts as an alternative to palladium(0) catalysts for the formation of carbon-sulfur (*7–9*) and carbon-nitrogen (*10–14*) bonds and this method remains as the reactions of choice in large- and industrial-scale syntheses.

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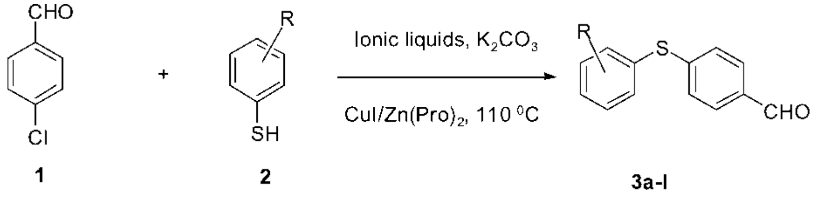
Ionic liquids (ILs) as the novel “solutions” for transition metal catalysis have been extensively studied in recent years (*15–19*). Various metal-catalyzed reactions, including copper-catalyzed cross-coupling reaction, have been demonstrated in ILs, and excellent results have been obtained. To the best of our knowledge, the method of using air-stable transition-metal complexes (Zn-proline) and CuI in ILs as catalysts to promote the cross-coupling reaction has never been reported. Here we wish to report a cross-coupling of aryl chlorides with thiols catalyzed by Zn-proline complexes and CuI in room temperature ionic liquids.

2. Results and discussion

In the course of our research, we first chose to study the efficacy of 10 mol% of CuI and 20 mol% of L-proline catalysts in the cross-coupling reaction between 4-chloro-benzaldehyde and thiophenol in ionic liquids. The reaction proceeded well and the diaryl sulfide was obtained in good yield, but the side-products of diaryl disulfides were found in this method; when we used Zn complexes of L-proline as a catalyst, a slightly higher yield was obtained and the byproducts of diaryl sulfide compounds were not found (Scheme 1, Table 3). The reaction was very slow when the reaction temperature was lowered to 70 °C, such as in alcohol and acetonitrile solvents. Hence, alcohol and acetonitrile were infective for the coupling reaction and the yields were less than 35% after reflux for 24 h, probably due to the low boiling point of these solvents; we also scanned the effects of other high boiling point organic solvents. Both DMF and DMSO were more effective, but the best yields were obtained from ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4) and this was consistent with our previous idea (Scheme 1, Table 1).



Scheme 1.

Table 1. The effects of different solvents in the coupling of 4-chloro-benzaldehyde with thiophenol catalyzed by CuI/Zn$(Pro)_2$.[a]

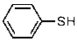
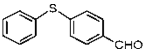
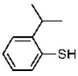
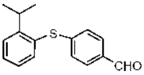
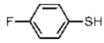
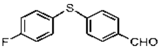
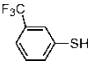
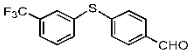
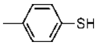
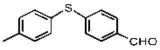
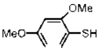
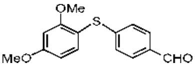
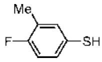
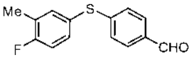
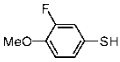
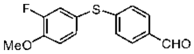
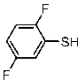
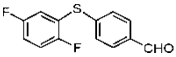
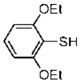
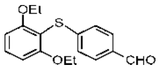
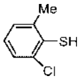
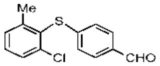
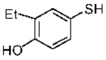
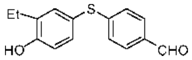
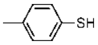
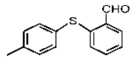
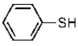
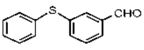
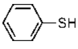
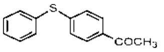
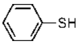
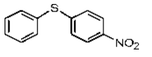
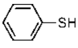
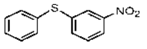
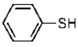
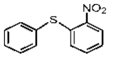
Entry	Solvent	Base	Temperature	Time	% Yield[b]
1	EtOH	K_2CO_3	Reflux	24	35
2	CH_3CN	K_2CO_3	Reflux	24	24
3	DMF	K_2CO_3	110 °C	24	55
4	DMSO	K_2CO_3	110 °C	24	60
5	DMSO	K_3PO_4	110 °C	24	62
6	[Bmim]BF_4	*t*-BuOK	110 °C	12	85
7	[Bmim]BF_4	Na_2CO_3	110 °C	12	75
8	[Bmim]BF_4	Cs_2CO_3	110 °C	12	92
9	[Bmim]BF_4	K_2CO_3	110 °C	12	90
10	[Bmim]BF_4	K_3PO_4	110 °C	12	87
11	[Bmim]BF_4	DBU	110 °C	24	45
12	[Bmim]BF_4	Et_3N	110 °C	24	28

Notes: [a]Reaction conditions: 4-chloro-benzaldehyde (10 mmol), thiophenol (12 mmol), 5 mol% of CuI, 10 mol% of Zn$(Pro)_2$, 2.0 equiv of K_2CO_3, in 5 ml of [Bmim]BF_4 at 110 °C under nitrogen atmosphere. [b]Isolated yield (average of two runs).

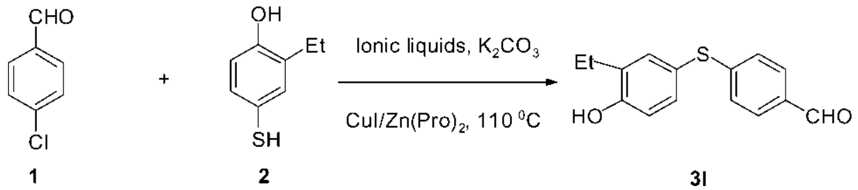
Cu(I) complexes generally gave superior results compared with Cu(II) sources in terms of conversion and yield of the desired product (*3*); we chose to focus on the use of CuI due to its stability to air and as it is inexpensive. The choice of the base is also critical. All bases such as Cs_2CO_3, K_2CO_3, K_3PO_4, and *t*-BuOK were found to be effective for this cross-coupling reaction; the use of other bases such as Na_2CO_3, DBU, and Et_3N gave somewhat lower yields (Table 1).

Using this protocol, the reaction of aryl chlorides coupled with thiophenols that contained either electron-rich (–OH) or electron-poor function group (–CF_3) gave excellent yields (Table 2); and the presence of substituted groups in the ortho, para, or meta position of the thiophenols was

Table 2. CuI/Zn(Pro)$_2$-catalyzed carbon–sulfur bond formation.[a]

Entry	Thiols	Aryl sulfide	Product	*t*/*h*	*T*/°C	% Yield[b]
1			**3a**	10	110	88
2			**3b**	11	110	90
3			**3c**	13	110	85
4			**3d**	15	120	72
5			**3e**	10	110	89
6			**3f**	10	110	88
7			**3g**	14	120	83
8			**3h**	15	120	81
9			**3i**	16	120	78
10			**3j**	12	110	75
11			**3k**	12	110	85
12			**3l**	11	105	82
13			**3m**	12	120	38
14			**3n**	12	120	43
15			**3o**	12	120	57
16			**3p**	8	110	85
17			**3q**	8	110	82
18			**3r**	8	110	75

Notes: [a]Reaction conditions: 4-chloro-benzaldehyde (10 mmol), thiophenol (12 mmol), 5 mol% of CuI, 10 mol% of Zn(Pro)$_2$, 2.0 equiv of K_2CO_3, in 5 ml of [Bmim]BF_4 at 110 °C under nitrogen atmosphere.
[b]Isolated yield (average of two runs).



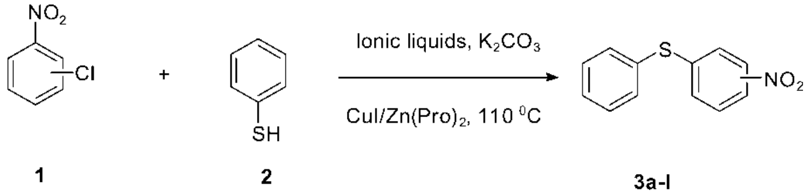
Scheme 2.

tolerated, *e.g.* 2-isopropylthiophenol gave the corresponding aryl sulfides in very good yields (entry 2). Also of interest is the result in entry 12 in which chemoselective carbon-sulfur bond formation occurs in the presence of a phenolic OH group (Scheme 2).

We also explored different benzaldehydes to couple with thiols, such as the 2-chloro-benzaldehyde and 3-chloro-benzaldehyde, but the results were poor (entries 13 and 14, Table 2); the yield was slightly better when we used 4-chloro-phenethanone to couple with thiophenol (entry 15, Table 2). The nitrobenzene compounds, such as 1-chloro-4-nitro-benzene, 1-chloro-3-nitro-benzene, and 1-chloro-2-nitro-benzene, can react with thiols under mild conditions and the yields were also excellent (Scheme 3, entries 16–18, Table 2).

The amino acids were found to act as highly effective ligands in the coupling reactions catalyzed by CuI recently (*11–15*). In this reaction, we found that the Zn complexes of L-proline as an additive could promote this cross-coupling reaction than only using pure L-proline, and the Zn complexes of L-proline can reduce the formation of the byproduct (especially the diaryl disulfide compounds). Some more Zn amino acid complexes were also screened and proved to be effective, but the best yield was obtained when Zn complexes of L-proline were additive. If no amino acid or Zn complex of amino acid was added, almost no coupling product was produced (Table 3).

Another merit of this protocol is that the ionic liquid, Zn amino acid complex, and CuI system can be reused after simple treatment. As the metal catalysts were immobilized in IL, and the separation of products from reaction mixture by extraction will not remove the ionic liquid or Zn



Scheme 3.

Table 3. The effects of different zinc(II) complexes in the coupling of 4-chloro-benzaldehyde with *p*-methyl thiophenol.[a]

Entry	Additive	Time (h)	Yield (%)[b]
1	Zinc L-proline	6	92
2	Zinc L-glycine	8	84
3	Zinc *N*-methylglycine	8	85
4	Zinc L-lysine	9	73
5	L-proline	8	52
6	No	8	Trace

Notes: [a]Reaction conditions: 4-chloro-benzaldehyde (10 mmol), thiophenol (12 mmol), 5 mol% of CuI, 10 mol% of Zn(Pro)$_2$, 2.0 equiv of K_2CO_3, in 5 ml of [Bmim]BF$_4$ at 110 °C under nitrogen atmosphere.
[b]Isolated yield (average of two runs).

amino acid complex or CuI, and the IL–Zn(Pro)$_2$–CuI mixture was dried under reduced pressure after the product was separated, it could be reused again three to five times without any decrease in the yields.

In conclusion, we have developed a CuI and Zn amino acid complex-catalyzed system for the synthesis of diaryl sulfide derivatives in good yields using a combination of 5 mol% of CuI, 10 mol% of Zn(Pro)$_2$, 2.0 equiv. of K_2CO_3, in 5 ml of [Bmim]BF_4 at 110 °C under nitrogen atmosphere. This method tolerates a wide range of functional groups; additionally, the reaction requires the free usage of expensive palladium and/or air-sensitive additives.

3. Experimental

^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance-300 spectrometer with tetramethylsilane (TMS) as internal standard. Infra red (IR) spectra were determined on a Vector-55 instrument. Silica gel GF254 was used for analytical and preparative thin-layer chromatography (TLC). All products were characterized by comparison with authentic samples using IR, ^{1}H NMR, and mass spectrometry (MS).

3.1. *General procedure for the synthesis of 3a–3l*

In a 25-mL beaker, 5 mL of IL was placed; then 5 mol% of CuI and 10 mol% of Zn(Pro)$_2$ were added and stirred for 0.5 h at 60 °C; the mixture was then cooled to room temperature. This was followed by the addition of 10 mmol of 4-chloro benzaldehyde, 12 mmol of thiophenol, and 20 mmol of $K_2CO_3$to the IL mixture, heated to 110 °C for 10–16 h under nitrogen atmosphere. The cooled mixture was extracted with ether (15 ml × 3), concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel with cyclohexane and ethyl acetate ($V : V = 10 : 1$) as eluent.

3.2. *Data*

3a: Yellow crystals (from EtOH). Mp: 51–54 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ : 7.25 (d, $J = 4.6$ Hz, 2H), 7.44 (m, 3H), 7.52 (m, 2H), 7.71 (q, $J = 8.6$ Hz, $J = 4.6$ Hz, 2H), 9.91 (s, 1H). IR (KBr) ν : 2750, 1652, 1535, 785 cm^{-1}. ^{13}C NMR (75 MHz, $CDCl_3$): 127.33, 129.15, 129.82, 130.13, 131.44, 133.82, 134.34, 147.19, 191.11. MS (70 eV) m/z (%): 215 ($[M + 2]^+$, 5.8), 214 (M^+, 70), 213 ($[M - 1]^+$ 100), 186 (28), 78 (55), 34 (35). Anal. calcd. for $C_{13}H_{10}OS$: C 72.87, H 4.70; found C 72.69, H 4.75.
3b: Yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.18 (s, 3H), 1.20 (s, 3H), 3.58 (q, 1H), 7.12 (d, $J = 8.3$ Hz, 2H), 7.27 (m, 1H), 7.45 (d, $J = 4.2$ Hz, 2H), 7.52 (d, $J = 8.3$ Hz, 1H), 7.71 (d, $J = 8.3$ Hz, 2H), 9.89 (s, 1H).^{13}C NMR (75 MHz, $CDCl_3$): 23.74, 31.02, 126.52, 126.74, 127.14, 130.11, 130.48, 130.57, 133.37, 136.73, 148.38, 152.75, 191.20. IR (film) ν: 2970, 2720, 1682, 1500, 785 720 cm^{-1}; MS (70 eV) m/z (%): 256 (M^+, 50), 255 ($[M - 1]^+$ 70), 152 (100), 105 (58), 91 (55), 29 (45). Anal. calcd. for $C_{16}H_{16}OS$: C 74.96, H 6.29; found C 74.39, H 7.05.
3c: Yellow crystals (from EtOH). Mp: 63–65 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.18 (m, 4H), 7.22 (m, 2H), 7.32 (q, $J = 6.7$ Hz, $J = 1.8$ Hz, 2H), 9.90 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) 116.97, 117.26, 126.79, 130.17, 133.80, 136.82, 136.94, 147.32, 161.81, 165.13, 191.06. IR (KBr) ν: 2716, 1685, 1550 ,785, 760 cm^{-1}. MS (70 eV) m/z (%): 232 (M^+, 50), 231 ($[M - 1]^+$ 70), 128 (100), 108 (34), 77 (15), 29 (28). Anal. calcd. for $C_{13}H_9FOS$: C 67.22, H 3.91; found C 68.19, H 3.85.

3d: Oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.37 (q, $J = 8.8$ Hz, $J = 1.6$ Hz, 2H), 7.56 (m, 1H), 7.66 (m, 2H), 7.77 (m, 3H), 9.94 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 125.50, 128.53, 129.44, 129.90, 130.18, 130.48, 130.91, 133.89, 134.46, 136.53, 144.87, 191.17. IR (film) ν: 2716, 1685, 1550, 785, 760 cm^{-1}. MS (70 eV) m/z (%): 282 (M^+, 65), 283 ($[M + 1]^+$, 5.8), 253 (68), 146 (35), 110 (100), 108 (37), 28 (39). Anal. calcd. for $C_{14}H_9F_3OS$: C 59.57, H 3.21; found C 60.32, H 3.25.

3e: Yellow solid. Mp: 53–53 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.36 (s, 3H), 7.20 (m, 4H), 7.43 (q, $J = 8.0$ Hz, $J = 1.90$ Hz, 2H), 7.70 (q, $J = 8.2$ Hz, $J = 1.7$ Hz, 2H), 9.81 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 21.30, 126.64, 128.59, 129.47, 129.80, 130.08, 130.66, 134.83, 139.70, 148.15, 191.15. IR (KBr) ν: 2780, 1602, 1565, 785, 767 cm^{-1}. MS (70 eV) m/z (%):228 (M^+, 75), 227 ($[M - 1]^+$, 85), 123 (55), 91 (100), 77 (35), 28 (35). Anal. calcd. for $C_{14}H_{12}OS$: C 73.65, H 5.30; found C 73.24, H 5.39.

3f: White solid. Mp: 124–126 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.79 (s, 3H), 3.87 (s, 3H), 6.62 (m, 2H), 7.11 (q, $J = 6.8$ Hz, $J = 4.8$ Hz, 2H), 7.53 (m, 1H), 7.74 (m, 2H), 9.87 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 55.56, 56.01, 99.58, 105.81, 125.49, 129.92, 133.15, 136.66, 148.37, 160.39, 161.28, 191.22. IR (KBr) ν: 2765, 2545, 1650, 1565, 1260, 785, 767 cm^{-1}. MS (70 eV) m/z (%): 274 (M^+, 45), 273 ($[M - 1]^+$, 65), 246 (55), 169 (25), 123 (70), 77 (100), 28 (78), 15 (45). Anal. calcd. for $C_{15}H_{14}O_3S$: C 65.67; H 5.14; found C 66.14, H 5.05.

3g: White solid, Mp: 76–78 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.29 (d, $J = 1.8$, 3H), 7.04 (t, 1H), 7.16 (q, $J = 7.0$ Hz, 2H), 7.42 (m, 2H), 7.72 (q, $J = 6.6$ Hz, 2H), 9.90 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 17.51, 116.48, 126.61, 127.79, 130.14, 133.67, 134.29, 138.19, 147.73, 160.46, 163.76, 191.11. IR (KBr) ν: 2775, 2345, 1655, 1555, 1230, 782, 750 cm^{-1}. MS (70 eV) m/z (%): 246 (M^+, 100), 245 ($[M - 1]^+$, 45), 218 (58), 109 (88), 91 (89), 77 (68). Anal. calcd. for $C_{14}H_{11}FOS$: C 68.27, H 4.50; found C 68.24, H 4.55.

3h: White solid. Mp: 74–76 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.93 (s, 3H), 7.02 (t, $J = 8.4$ Hz, 1H), 7.17 (q, $J = 7.0$ Hz, 1H), 7.42 (m, 3H), 7.72 (q, $J = 6.9$ Hz, 2H), 9.90 (s, 1H).^{13}C NMR (75 MHz, $CDCl_3$): 56.32, 114.24, 122.68, 126.51, 130.15, 131.67, 133.72, 147.60, 149.19, 150.84, 154.66, 191.09. IR (KBr) ν: 2785, 2245, 1690, 1555, 1230, 798, 750 cm^{-1}. MS (70 eV) m/z (%): 262 (M^+, 47), 233 (100), 126 (65), 109 (68), 107 (38), 94 (85), 15 (27). Anal. calcd. for $C_{14}H_{11}FO_2S$: C 64.11, H 4.23; found C 64.22, H 4.35.

3i: White solid. Mp: 50–52 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.19 (m, 3H), 7.34 (q, $J = 8.2$ Hz, 1H), 7.80 (q, $J = 6.7$ Hz, 2H), 9.95 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 117.20, 117.53, 117.92, 128.47, 130.32, 134.67, 143.28, 156.98, 160.25, 190.99. IR (KBr)ν: 2220, 1685, 1475, 1260, 758, 750, 650 cm^{-1}. MS (70 eV) m/z (%):250 (M^+, 18), 249 (54), 221 (100), 126 (65), 109 (100), 77 (85), 35(18). Anal. calcd for $C_{13}H_8F_2OS$: C 62.39, H 3.22; found C 62.87, H 3.31.

3j: Oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.16 (t, 3H), 1.28 (t, 3H), 3.96 (q, 4H), 6.89 (m, 2H), 7.12 (m, 1H), 7.23 (q, $J = 8.4$ Hz, 2H), 7.71 (q, $J = 8.5$ Hz, 2H), 9.91 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 15.58, 58.71, 103.21, 106.57, 128.22, 130.17, 131.33, 135.61, 137.52, 161.92, 191.12. IR (KBr) ν: 2350, 2150, 1645, 1575, 1230, 758, 670, 550 cm^{-1}. MS (70 eV) m/z (%): 305 (M^+, 15), 274 (35), 197 (75), 165 (100), 137 (80), 77 (85), 28 (58). Anal. calcd. for $C_{17}H_{18}O_3S$: C 67.52, H 6.00; found C 67.25, H 6.12.

3k: White crystals (from EtOH). Mp: 42–44 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.28 (s, 3H), 7.11 (q, $J = 6.8$ Hz, 2H), 7.34 (m, 2H), 7.45 (d, $J = 2.1$ Hz, 1H), 7.80 (q, $J = 8.3$ Hz, 2H), 9.87 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 20.10, 127.11, 129.76, 132.10, 132.15, 132.32, 133.99, 134.86, 140.37, 145.51, 190.99. IR (KBr) ν: 2360, 1685, 1515, 1260, 750, 680, 520 cm^{-1}. MS (70 eV) m/z (%): 262 (M^+, 55), 233 (15), 158 (35), 112 (100), 77 (85), 48 (27). Anal. calcd. for $C_{14}H_{11}ClOS$: C 64.00, H 4.22; found C 65.05, H 4.47.

3l: White solid. Mp: 78–80 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.24 (t,3H), 2.35 (q, 2H), 5.13 (b, 1H), 7.14 (m, 3H), 7.36(q, $J = 8.4$ Hz, 2H), 7.55 (q, $J = 8.5$ Hz, 2H), 8.97 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 16.43, 19.18, 116.79, 124.56, 128.12, 129.24, 130.36, 131.69, 131.89, 135.80, 137.86, 155.38, 191.05. IR (KBr) ν: 3023, 2350, 2150, 1645, 1575, 1230, 758 cm^{-1}. MS (70 eV) m/z (%): 240 (15), 216 (35), 106 (75), 76 (100), 28 (58). Anal. calcd. for $C_{15}H_{14}O_2S$: C 69.74, H 5.46; found C 69.25, H 5.19.

3m: Yellow oil. ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 2.38 (s, 3H), 7.07 (m, 3H), 7.23 (q, $J = 8.6$ Hz, 2H), 7.36 (q, $J = 8.8$ Hz, 2H), 7.83 (m, 1H), 10.36 (s, 1H). ^{13}C NMR (75 MHz, CDCl$_3$): 20.13, 127.51, 128.56, 130.12, 130.21, 130.32, 131.54, 133.84, 134.56, 136.87, 140.12, 190.49. IR (film) ν: 2825, 1692, 1555, 788, 660 cm^{-1}. MS (70 eV) m/z (%): 228 (M$^+$, 52), 123 (45), 106 (65), 91 (100), 28 (39), 15 (34). Anal. calcd. for $C_{14}H_{12}OS$: C 73.65, H 5.30; found C 73.56, H 5.26.

3n(*2*)**:** Colorless oil. ^{1}H NMR(CDCl$_3$, 300 MHz) δ: 7.38 (m, 3H), 7.45 (m, 3H), 7.52 (m, 1H), 7.71 (m, 1H), 7.76 (dt, $J = 1.8$ Hz, 1H), 9.93 (s, 1H). ^{13}C NMR (75 MHz, CDCl$_3$): 128.03, 128.57, 129.98, 130.11, 131.03, 132.89, 134.03, 135.76, 137.52, 139.22, 192.16. IR (film) ν: 3040, 3016, 2948, 2914, 2828, 2716, 1675 cm^{-1}. Anal. calcd. for $C_{13}H_9FOS$: C 67.22, H 3.91; found C 67.28, H 3.88.

3o(*2*)**:** White solid. Mp: 66–67 °C. ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 2.55 (s, 3H). 7.21 (dd, $J = 6.8$ Hz, $J = 1.8$ Hz, 2H,), 7.42 (m, 3H), 7.50 (dd, $J = 7.8$ Hz, $J = 1.8$ Hz, 2H), 7.82 (dd, $J = 6.7$ Hz, $J = 1.8$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl$_3$): 26.57, 127.50, 128.82, 128.91, 129.59, 132.23, 133.67, 134.12, 144.92, 198.73. IR (KBr) ν: 3060, 3012, 2942, 2910, 2821, 1680. Anal. calcd. for $C_{14}H_{12}OS$: C 73.65, H 5.30; found C 73.58, H 5.38.

3p(*2*)**:** Yellow crystal (from EtOH). Mp: 54–56 °C. ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 7.18 (dd, $J = 7.0$ Hz, $J = 2.0$ Hz, 2H), 7.45 (m, 1H), 7.48 (d, $J = 2.4$ Hz, 2H), 7.54 (m, 2H), 8.06 (dd, $J = 7.0$ Hz, $J = 2.0$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl$_3$): 124.04, 126.76, 129.67, 130.04, 130.54, 134.73, 145.42, 148.48. IR (KBr) ν: 3065, 1577, 1515, 1475, 1430, 1082, 851, 741, 691, 514 cm^{-1}.

3q(*2*)**:** Yellow oil. ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 7.42 (m, 2H), 7.51 (m, 3H), 8.02 (m, 4H). ^{13}C NMR (CDCl$_3$, 75 MHz): 120.93, 123.17, 128.40, 128.96, 128.98, 129.68, 129.87, 132.14, 133.45, 134.26. IR (film) ν: 3053, 1674, 1620, 1527, 1466, 1348, 1126, 1026, 875, 752, 691.

3r(*2*)**:** Yellow crystal (from EtOH). Mp: 79–81 °C. ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 6.87, 7.21, 7.33, 7.48, 7.58, 8.21. ^{13}C NMR (75 MHz, CDCl$_3$): 124.94, 125.71, 128.36, 129.99, 130.09, 131.06, 133.37, 135.87, 139.40, 145.08. IR (KBr) ν: 3099, 1565, 1474, 1453, 1057, 998, 782, 655 cm^{-1}. MS (70 eV) m/z (%):231.04 (100), 185.23 (76), 154.15 (52), 109.01 (61), 77.02 (67). Anal. calcd. for $C_{12}H_9NO_2S$: C 62.32, H 3.92; found C 63.28, H 3.99.

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