A New One-Pot, Three-Component Synthesis of 2,3,5-Substituted or Annulated-6-(Methylthio)pyridines

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Abstract: A new one-pot, three-component synthesis of 2,3,5-substituted (or 2,3-annulated)-6-(methylthio)pyridines by reacting acyclic or cyclic active methylene ketones, ammonium acetate, and bis(methylthio)acrolein (**1**) or its 2-phenyl analogue **8** (as 3-carbon-1,3-biselectrophilic components) in the presence of either AcOH–TFA (4:1) or $ZnBr_2$ (or ZnI_2) catalysts has been reported.

Key words: pyridines, cycloannulation, one-pot, three-component synthesis, bis(methylthio)acrolein, ammonium acetate

Substituted pyridines and their benzo/hetero-fused analogues represent an important class of heterocycles because of their presence in numerous natural products, along with useful biological and pharmacological activities[1] displayed by these compounds. In particular, the pyridine structural motif has assumed considerable importance because of its presence in enzymes (NADP), vitamins (niacin, pyridoxine), highly toxic alkaloids (nicotine),[2] agrochemicals,[3] and in several bioactive drugs (isoniazide, sulfapyridines, and COX-2 specific inhibitors).[4,5] In addition, pyridine derivatives are extensively utilized in preparative organic, coordination, analytical, and supramolecular chemistry.[6] Recently, certain pyridinium salts have been used as ionic liquids with potential scope in 'green' industrial applications.[2,7] Therefore development of new, efficient, and regiospecific methods for the synthesis of pyridine scaffolds with diverse functionalities and substituents remains an area of current interest. Several elegant general syntheses of pyridine ring systems[8,9] have been developed in recent years which have been elaborated in a review article published in 2004.[2]

Among the various routes towards substituted pyridines, a [3+3] approach involving cyclocondensation of a C–C–N fragment, more commonly an enaminone, enaminoester, or enaminonitrile and a 3-carbon-1,3-electrophilic component is the most useful and versatile,[2] since it allows construction of unsymmetrically substituted pyridines from relatively simple precursors. Several variations of this approach are available in the literature. Thus, Moody and Bagley have applied this approach for the preparation of a modified oxazole-thiazole pyridine core of the promothiocin/sulfomycin antibiotics[10] and for the synthesis of a library of functionalized pyridine scaffolds[11] by utilizing various enaminoesters and ethynyl ketones (Bohlmann–Ratz synthesis). In subsequent papers, Bagley and coworkers have further extended the scope and application by effecting this transformation in a one-pot, three-component reaction [3C+2C+N] at lower temperature using either a Brønsted/Lewis acid catalyst, bromine or iodine, or under neutral conditions.[12–14] Recently, Marcoux and Davies[15] have developed an efficient synthesis of 2,3-diaryl pyridines as COX-2 specific inhibitors involving vinamidinium salts[16] as three-carbon biselectrophilic partners in a one-step annulation with α-arylketones and ammonia [3C+2C+N approach]. Katritzky and coworkers have utilized α,β-unsaturated ketones as 1,3-electrophilic components in a [3+3] annulation with either α-benzotriazolylacetonitrile anion[17a] or iminophosphoranes[17b] as nucleophiles.

Our own interest in pyridine synthesis relies upon the synthetic application of α-oxoketene dithioacetal as 3-carbon-1,3-electrophilic component in aromatic and heteroaromatic annulation[18,19] and we have previously reported efficient and highly regiospecific synthesis of 2,3,4,5,6-substituted and 4,5-annulated (or 5,6-annulated) pyridines by [3+3] cyclocondensation of β-lithioaminoacrylonitriles[20] or lithioacetonitrile[21] with α-oxoketene dithioacetals. In an earlier study, Potts and coworkers[22] have demonstrated a useful [5+1] approach for 2,6-disubstituted pyridines via base-induced 1,4-addition of methyl ketones to α-oxoketene dithioacetals to give 1,5-enediones followed by their ring closure with ammonium acetate. We have recently reported the synthesis of bis(methylthio)acrolein[23] and its application as 'surrogate' acrolein in a modified Skraup synthesis of substituted 2-(methylthio)quinolines.[24] In continuation of these studies, we report herein a new general synthesis of 2,3,5-substituted/annulated-6-(methylthio)pyridines involving cycloannulation of 3-bis(methylthio)acrolein and its 2-phenyl analogue with various active methylene ketones in a three-component, one-pot process.

We first examined the two-step procedure by subjecting 4-methoxyacetophenone (**2a**) or the indane-1,3-dione (**5a**) to aldol condensation with bis(methylthio)acrolein (**1**) in the presence of sodium ethoxide in ethanol affording the aldol adducts **3a** and **6a** in high yields (Scheme 1). Subsequent heterocyclization of **3a** and **6a** to the respective pyridines (**4a** and **7a)** was investigated under various conditions in the presence of Brønsted/Lewis acids or ion-

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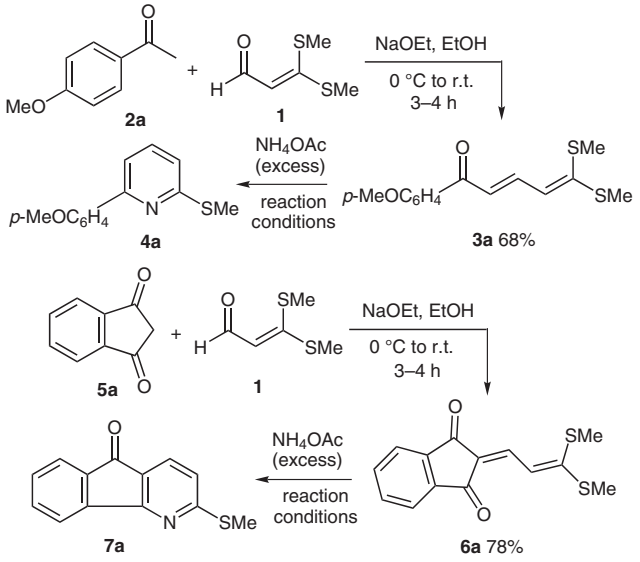
exchange resin (Scheme 1, Table 1). In all the reactions, the desired 2-(4-methoxyphenyl)-5-(methylthio)pyridine (**4a**) and the corresponding annulated pyridine **7a** were formed in varying yields under these conditions (Table 1).[25] Best yields of **4a** or **7a** were obtained either in refluxing AcOH–TFA (4:1, Table 1, entry 3) or in the presence of $ZnBr_2$ catalyst when the reaction was carried out in a sealed tube at higher temperature (110 °C, entry 6). In parallel experiments, we also investigated the possibility of devising a multicomponent condensation process with a view to develop a more efficient pyridine synthesis by reacting the active methylene ketone, bis(methylthio)acrolein (**1**) and ammonium acetate in a one-pot operation in the presence of various acid catalysts and the results are depicted in Scheme 2 and Tables 2 and 3.



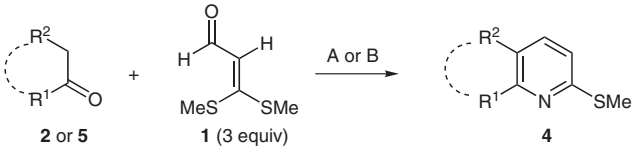
Scheme 1

Table 1 Two-Step Synthesis of Pyridines **4a** and **7a** under Different Reaction Conditions

Entry	Reaction conditions[a]	Yield of **4a** (%)	Yield of **7a** (%)
1	NH_4OAc, AcOH, Δ, 8–10 h	35	50
2	NH_4OAc, toluene–AcOH (5:1), Δ, 7–8 h	47	49
3	NH_4OAc, AcOH–TFA (4:1), Δ, 8–10 h	58	68
4	Amberlyst 15, toluene, Δ, 8–10 h	32	40
5	$ZnBr_2$ (15 mol%), toluene, Δ, 5–6 h	40	45
6	$ZnBr_2$ (15 mol%), sealed tube, 110 °C, 5–6 h	50	55

[a] General conditions: NH_4OAc (30 mol), **1** (3 equiv).

Thus, under optimized conditions, it was found that the pyridines **4a** and **7a** were formed in comparable yields to the two-step procedure when the ketone **2a** (or **5a**), **1** (3 equiv) and excess of ammonium acetate were reacted in refluxing AcOH–TFA (4:1) or in the presence of $ZnBr_2$ catalyst (15 mol%) in a sealed tube (Table 1, entries 3 and 6 vs. Table 2, entry 1 and Table 3, entry 1). These reaction conditions were employed for the synthesis of other substituted/annulated pyridines.[25,26] Thus, the active methylene ketones such as aryl/heteroaryl desoxybenzoins **2b–d** also underwent smooth cyclocondensation with **1** and ammonium acetate in refluxing AcOH–TFA (conditions A) to give 2,3-diarylpyridines **4b**,**c** and 2-(3-pyridyl)-3-phenylpyridine **4d** in moderate to good yields whereas in the presence of $ZnBr_2$ catalyst (conditions B) **4b–d** were obtained in decreased yield (Table 2, entries 2–4).



Scheme 2 *Reagents and conditions*: A: NH_4OAc (20 equiv), AcOH–TFA (4:1), reflux, 8–12 h; B: NH_4OAc (20 equiv), $ZnBr_2$ (15 mol%), 110 °C, 5–6 h, sealed tube.

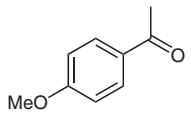
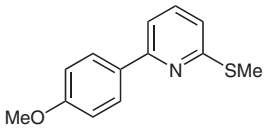
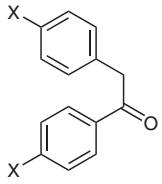
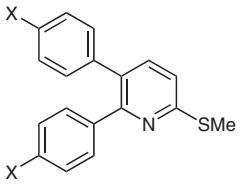
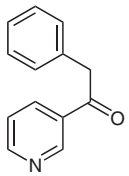
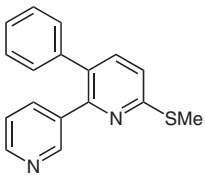
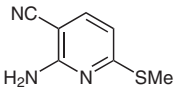
The versatility of this method was further demonstrated by extending the heteroannulation reaction to few benzo- and heterocyclic ketones **5a–d** furnishing the corresponding 2,3-annulated/heteroannulated pyridines **7a–d** in good yields under AcOH–TFA refluxing conditions (A) whereas yields were lower with $ZnBr_2$ catalyst (Scheme 2, Table 3, entries 1–4).[25,26]

In order to study the scope of this reaction and to establish its tolerance towards different substrates, a few of the active methylene compounds such as β-ketoesters (Table 2, entries 6 and 7) and malononitrile (entry 5) were reacted with bis(methylthio)acrolein and ammonium acetate following these standard conditions yielding the pyridines **4e–g** in moderate yields under refluxing AcOH–TFA. However, under $ZnBr_2$-catalyzed conditions, only intractable product mixtures were formed (Table 2, entries 5–7).[25]

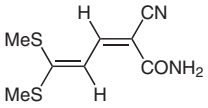
To further introduce a point of diversity at the 5-position of pyridine ring, this three-component reaction was elaborated to 2-phenyl-3-bis(methylthio)acrolein (**8**)[27] which was reacted with a range of active methylene ketones in the presence of excess of ammonium acetate in either refluxing AcOH–TFA (conditions A) or in the presence of $ZnBr_2$ (or ZnI_2) catalyst (conditions B)[28] yielding various substituted 5-phenyl pyridines **9** and **10c** as depicted in Scheme 3 and Table 4.[25]

A comparison of yields of product pyridines from bis(methylthio)acrolein (**1**, Tables 2 and 3) and those from 2-phenyl-3-bis(methylthio)acrolein (**8**, Table 4) shows that higher yields of 5-phenylpyridines **9** and **10c** are obtained in the presence of $ZnBr_2$ (or ZnI_2)[28] (conditions B) whereas in refluxing AcOH–TFA (conditions), they are markedly reduced, with the recovery of unreacted ketones. On the other hand, with bis(methylthio)acrolein (**1**), higher yields of product pyridines **4** and **7** are obtained in refluxing AcOH–TFA (conditions A) in comparison to $ZnBr_2$-catalyzed conditions (B, Tables 2 and 3).[29]

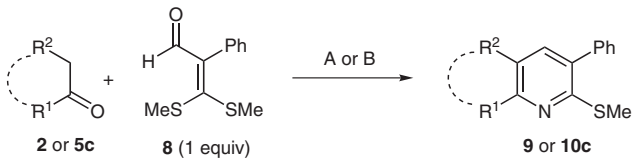
Table 2 Synthesis of 2,3-Substituted-6-(methylthio)pyridines **4**

Entry	Ketone **2**	**4**	Yield (%)	
			Conditions A	Conditions B
1	 **2a**	 **4a**	63	50
2	 **2b**, X = H	 **4b**, X = H	57	48
3	**2c**, X = MeO	**4c**, X = MeO	63	55
4	 **2d**	 **4d**	67	57
5	 **2e**	 **4e**	57[a]	–
6	**2f**, R = Ph	**4f**, R = Ph	42	–
7	**2g**, R = Me	**4g**, R = Me	47[b]	–

[a] Obtained as side product (24%):



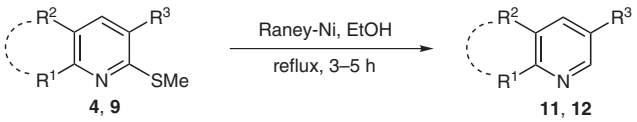
[b] Could not be isolated under conditions A but in refluxing in toluene–AcOH (5:1) for 6 h.



Scheme 3 *Reagents and conditions*: A: NH_4OAc (20 equiv), AcOH–TFA (4:1), reflux, 8–12 h; B: NH_4OAc (20 equiv), ZnI_2 or $ZnBr_2$ (15 mol%), 110 °C, 5–6 h, sealed tube.

A few of the selected 6-(methylthio)pyridines were dethiomethylated in the presence of Raney-Ni in refluxing ethanol to afford 6-unsubstituted sulfur-free pyridines **11** and **12** in excellent yields as shown in Scheme 4.[25,30]

Similarly, the parent tricyclic benzo[*h*][1,6]naphthyridine **14** could be prepared in high yield by aromatization of the corresponding *N*-sulfonyl derivative **7c** in the presence of NaOH and *n*-Bu_4NBr under refluxing conditions followed by desulfurization of the resulting product **13** with Raney-Ni in refluxing ethanol (Scheme 5).[25]



4c, **11c**: $R^1 = R^2 = 4\text{-}MeOC_6H_4$; $R^3 = H$; 93%
4d, **11d**: R^1 = 3-py; R^2 = Ph; R^3 = H; 95%
9h, **12h**: $R^1 = 4\text{-}ClC_6H_4$; R^2 = H; R^3 = Ph; 90%
9i, **12i**: R^1 = 3-py; R^2 = H; R^3 = Ph; 91%

Scheme 4

Table 3 Synthesis of 2,3-Annulated/Heteroannulated Pyridines **7a–d**

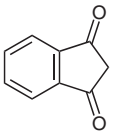
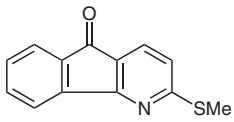
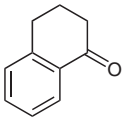
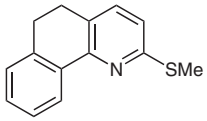
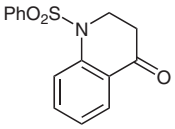
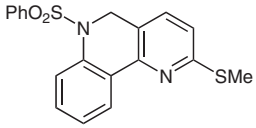
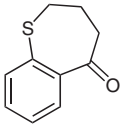
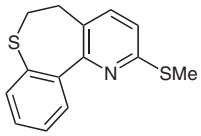
Entry	Cyclic ketone **5**	Product **7**	Yield of **7** (%)	
			Conditions A	Conditions B
1	 **5a**	 **7a**	78	55
2	 **5b**	 **7b**	64	55
3	 **5c**	 **7c**	70	60
4	 **5d**	 **7d**	63	51

Table 4 Synthesis of Pyridines **9** and **10c**

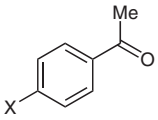
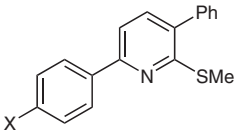
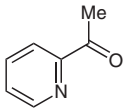
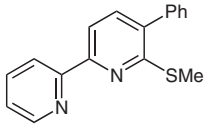
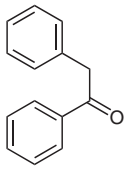
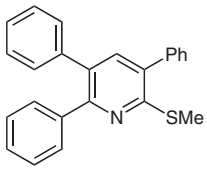
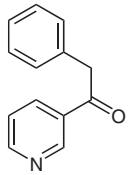
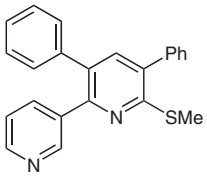
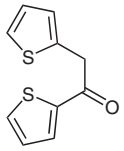
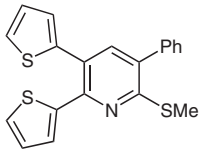
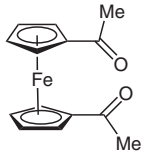
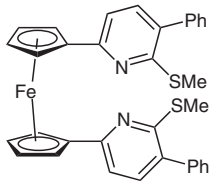
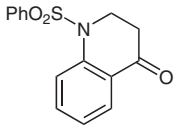
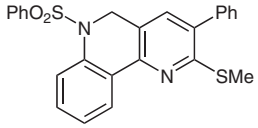
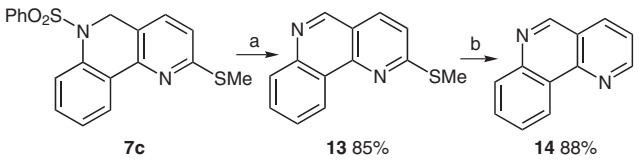
Entry	Ketone **2** or **5**	Product **9** or **10c**	Yield (%)	
			Conditions A	Conditions B
1	 **2a**, X = OMe	 **9a**, X = OMe	40	64
2	**2h**, X = Cl	**9h**, X = Cl	42	63
3	 **2i**	 **9i**	35	68
4	 **2b**	 **9b**	43	60
5	 **2d**	 **9d**	41	64

Table 4 Synthesis of Pyridines **9** and **10c** (continued)

Entry	Ketone **2** or **5**	Product **9** or **10c**	Yield (%)	
			Conditions A	Conditions B
6	 **2j**	 **9j**	37	57
7	 **2k**	 **9k**	36	55
8	 **5c**	 **10c**	44	66



Scheme 5 *Reagents and conditions*: (a) 50% NaOH, Bu_4NBr, toluene, reflux, 2 h; (b) Raney-Ni, EtOH, reflux, 3 h.

In conclusion, we have developed a novel one-pot, three component reaction for the synthesis of 2,3,5-substituted (or 2,3-annulated)-6-methylthiopyridines combining acyclic or cyclic active methylene ketones, ammonia, and bis(methylthio)acrolein or its 2-phenyl analogue (as 3-carbon 1,3-bielectrophilic component) in the presence of either protic acid or $ZnBr_2/ZnI_2$ as catalysts. These reactions proceed in moderate to high yields with total regiocontrol for either ketones or bis(methylthio)acroleins which can be considered as synthetic equivalents of vinamidinium salts. The 2-methylthio group in these newly synthesized pyridines can be replaced either by amines[24] or can be reacted with carbon nucleophiles through nickel chloride cross-coupling reactions.[19d] Further work to improve the yield of pyridine derivatives and to expand the scope of this heteroannulation reaction for acquiring more functional group diversity is in progress.

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(25) The structures of all newly synthesized compounds were confirmed with the help of spectral and analytical data.

(26) **General Procedure for One-Pot, Three-Component Synthesis of 2,3,5-Substituted or 2,3-Annulated-6-(methylthio)pyridines 4, 7, 9, and 10c**

Procedure A

A solution of appropriate ketone (1.0 mmol), bis(methylthio)acrolein (**1**, 3.0 mmol) or 2-phenyl-3-bis(methylthio)acrolein (**8**, 1.1 mmol), and NH_4OAc (20 mol) in AcOH–TFA (5 mL, 4:1) was heated with stirring at 110 °C for 8–10 h (monitored by TLC). The mixture was then neutralized with sat. $NaHCO_3$ solution (25 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were washed with H_2O (2 × 50 mL), brine (50 mL), dried (Na_2SO_4), and evaporated under reduced pressure to afford crude product which was purified by column chromatography over SiO_2 using EtOAc–hexane (1:9) as eluent.

Procedure B

A mixture of appropriate ketone (1.0 mmol), bis(methylthio)acrolein (**1**, 3.0 mmol) or 2-phenyl-3-bis(methylthio)acrolein (**8**, 1.1 mmol), NH_4OAc (20 mol), and $ZnBr_2$ or ZnI_2 (15 mol%) was heated in a sealed tube at 110 °C for 5–8 h (monitored by TLC). The residue was partitioned between sat. $NaHCO_3$ solution (30 mL) and $CHCl_3$ (30 mL), and was extracted with CH_2Cl_2 (3 × 15 mL). The organic layer was washed with H_2O (2 × 50 mL), brine (50 mL), dried (Na_2SO_4), and evaporated under reduced pressure to give crude product which was purified by column chromatography on SiO_2 using EtOAc–hexane (1:9) as eluent.

2-(4-Methoxyphenyl)-6-methylthiopyridine (4a)

Yield 63% (0.15 g); white solid; mp. 81–82 °C; R_f = 0.52 (hexane–EtOAc, 9:1). IR (KBr): 2919, 1602, 1555, 1448 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 9.0 Hz, 2 H, ArH), 7.49 (t, *J* = 7.8 Hz, 1 H, ArH), 7.35 (d, *J* = 7.6 Hz, 1 H, ArH), 7.05 (d, *J* = 7.8 Hz, 1 H, ArH), 6.92 (d, *J* = 8.8 Hz, 2 H, ArH), 3.85 (s, 3 H, OMe), 2.64 (s, 3 H, SMe). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.5, 159.1, 156.2, 136.6, 131.3, 128.1, 119.2, 114.8, 114.0, 55.3, 13.2. ESI-HRMS: *m/z* calcd for $C_{13}H_{14}NOS$ $[M + H]^+$: 232.0796; found: 232.0794.

2,3-Bis(4-methoxyphenyl)-6-methylthiopyridine (4c)

Yield 63% (0.21 g); white solid; mp 161–162 °C; R_f = 0.50 (hexane–EtOAc, 19.1). IR (KBr): 2950, 1684, 1509 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 8.1 Hz, 1 H, ArH), 7.35 (dd, *J* = 6.7, 2.1 Hz, 2 H, ArH), 7.14 (d, *J* = 8.3 Hz, 1 H, ArH), 7.07 (dd, *J* = 6.6, 2.2 Hz, 2 H, ArH), 6.74–6.81 (m, 4 H, ArH), 3.78 (s, 3 H, OMe), 3.77 (s, 3 H, OMe), 2.62 (s, 3 H, SMe). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7, 158.8, 157.5, 155.1, 139.7, 131.5, 131.4, 131.2, 130.5, 130.4, 119.3, 113.9, 113.3, 55.2, 55.1, 13.7. MS: *m/z* (%) = 337(100) $[M^+]$. Anal. Calcd (%) for $C_{20}H_{19}NO_2S$ (337.43):

C, 71.19; H, 5.68; N, 4.15. Found: C, 71.23; H, 5.70; N, 4.18.

2-Methylthioindeno[1,2-*b*]pyridin-5-one (7a)

Yield 78% (0.18 g); pale yellow solid; mp 145–146 °C; R_f = 0.54 (hexane–EtOAc, 9:1); IR (KBr): 2920, 1720, 1575, 1401 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 7.3 Hz, 1 H, ArH), 7.49 (d, *J* = 7.3 Hz, 1 H, ArH), 7.46 (d, *J* = 8.0 Hz, 1 H, ArH), 7.37 (t, *J* = 7.4 Hz, 1 H, ArH), 7.24 (t, *J* = 7.4 Hz, 1 H, ArH), 6.84 (d, *J* = 8.1 Hz, 1 H, ArH), 2.51 (s, 3 H, SMe). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.1, 167.1, 165.1, 142.7, 135.0, 134.4, 130.7, 130.3, 123.5, 123.4, 120.5, 119.8, 13.3. MS: *m/z* (%) = 227(100) [M^+]. Anal. Calcd (%) for $C_{13}H_9NOS$ (227.28): C, 68.70; H, 3.99; N, 6.16. Found: C, 68.76; H, 4.00; N, 6.18.

6-Methylthio-3,5-diphenyl-[2,3′]bipyridinyl (9d)

Yield 64% (0.23 g); light yellow solid; mp 160–161 °C; R_f = 0.45 (hexane–EtOAc, 5:1). IR (KBr): 2916, 1575, 1445, 1377 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.77 (br s, 1 H, ArH), 8.50 (dd, *J* = 4.9, 1.4 Hz, 1 H, ArH), 7.71 (dt, *J* = 8.0, 1.9 Hz, 1 H, ArH), 7.55–7.52 (m, 2 H, ArH), 7.51 (s, 1 H, ArH), 7.50–7.40 (m, 3 H, ArH), 7.33–7.27 (m, 3 H, ArH), 7.23–7.20 (m, 2 H, ArH), 7.17–7.15 (m, 1 H, ArH), 2.60 (s, 3 H, SMe). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.6, 151.4, 150.9, 148.7, 139.1, 138.9, 137.4, 137.1, 135.3, 135.0, 131.7, 129.5, 129.1, 128.7, 128.5, 128.4, 127.5, 122.6, 13.8. MS: *m/z* (%) = 355(100) [M + 1], 354(60) [M^+]. Anal. Calcd (%) for $C_{23}H_{18}N_2S$ (354.46): C, 77.93; H, 5.12; N, 7.90. Found: 77.97; H, 5.13; N, 7.93.

6-Methylthio-5-phenyl-[2,2′]bipyridinyl (9i)

Yield 68% (0.19 g); colorless solid; mp 100–101 °C; R_f = 0.47 (hexane–EtOAc, 19:1). IR (KBr): 2916, 1546, 1428, 1354 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.71 (dd, *J* = 4.9, 0.74 Hz, 1 H, ArH), 8.54 (d, *J* = 8.1 Hz, 1 H, ArH), 8.27 (d, *J* = 7.8 Hz, 1 H, ArH), 7.88 (td, *J* = 7.7, 1.7 Hz, 1 H, ArH), 7.56 (d, *J* = 7.8 Hz, 1 H, ArH), 7.49–7.40 (m, 5 H, ArH), 7.37–7.34 (m, 1 H, ArH), 2.62 (s, 3 H, SMe). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3, 155.2, 152.9, 148.3, 137.8, 137.3, 136.5, 129.1, 128.4, 128.3, 123.9, 121.4, 116.5, 13.8. MS: *m/z* (%): 279(100) [M + 1], 278(30). Anal. Calcd (%) for $C_{17}H_{14}N_2S$ (278.37): C, 73.35; H, 5.07; N, 10.06. Found: C, 73.32; H, 5.09; N, 10.09.

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(28) Comparable yields of pyridines **9** were obtained by using either $ZnBr_2$ or ZnI_2 catalyst.

(29) Lower yields of pyridines **4a–g** with $ZnBr_2$ (conditions B) catalyst at 110 °C are presumably due to the decomposition of bis(methylthio)acrolein(**1**) at higher temperature.

(30) The ^1H NMR of all desulfurized compounds **11c**,**d**, **12h**,**i** displayed a low field signal between δ = 8.63–8.96 ppm due to the pyridine H-6 proton which further confirmed the regiochemistry of the products.

2,3-Bis(4-methoxyphenyl)pyridine (11c)

Yield 93% (0.27 g); white solid; mp 82–83 °C; R_f = 0.5 (hexane–EtOAc, 19:1). IR (KBr): 2935, 2838, 1607, 1511, 1429 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.63 (dd, *J* = 4.6, 1.7 Hz, 1 H, ArH), 7.67 (dd, *J* = 7.6, 1.7 Hz, 1 H, ArH), 7.31 (dd, *J* = 6.7, 2.1 Hz, 2 H, ArH), 7.29–7.26 (m, 1 H, ArH), 7.11 (dd, *J* = 6.7, 2.1 Hz, 2 H, ArH), 6.83 (dd, *J* = 6.8, 1.9 Hz, 2 H, ArH), 6.78 (dd, *J* = 6.8, 1.9 Hz, 2 H, ArH), 3.81 (s, 3 H, OMe), 3.79 (s, 3 H, OMe). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2, 158.8, 156.7, 147.9, 138.4, 135.3, 132.8, 132.5, 131.1, 130.6, 121.6, 113.8, 113.3, 55.22, 55.18. MS: *m/z* (%) = 292(100) [M + 1], 291(40) [M^+]. Anal. Calcd (%) for $C_{19}H_{17}NO_2$ (291.34): C, 8.33; H, 5.88; N, 4.81. Found: C, 78.39; H, 5.90; N, 4.84.