Heteroannulation of 3-Bis(methylthio)acrolein with Aromatic Amines – A Convenient Highly Regioselective Synthesis of 2-(Methylthio)quinolines and their Benzo/Hetero Fused Analogs – A Modified Skraup Quinoline Synthesis

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Abstract: A simple and efficient synthesis of 2-(methylthio)quinolines and their condensed analogs has been developed through acid-induced cyclocondensation of their respective anilines or aromatic diamines with 3-bis(methylthio)acrolein. The 2-(methylthio) functionality in these quinolines could be either dethiomethylated or replaced by various nitrogen and carbon nucleophiles to afford 2-substituted quinolines.

Key words: heteroannulation, amines, regioselectivity, condensation, quinolines

Substituted quinolines and their benzo/hetero fused analogs represent an important class of heterocyclic compounds that have attracted considerable attention because of their presence in numerous natural products displaying wide range of physiological activities.[1,2] Several synthetic routes are well documented[3] for the formation of quinolines, since the quinoline nucleus plays an important role as an intermediate in many pharmacologically active compounds. The structural core of quinoline has generally been synthesized by various conventional named routes such as Skraup,[4] Doebner–Miller,[5] Conrad–Limpach,[6] Friedländer[7] and Pfitzinger[8] synthesis. The classical Skraup and Doebner–Miller synthesis are very similar, the former involves heating aniline with acrolein, generated in situ from glycerol and strong acid, whereas the latter method is based on generating a substituted acrolein, with both methods also requiring an oxidant. Inspite of their simplicity and generality, these syntheses suffer from several drawbacks such as harsh reaction conditions, requiring high temperature (>250 °C) and highly acidic conditions resulting in lower yields of the products due to the tedious isolation from complex reaction mixtures. Although subsequent work on these methods[9] has extended the scope of these reactions, the substitution patterns that can be obtained from the product quinolines are still limited along with the frequent formation of regioisomeric mixtures from *meta*- and 3,4-substituted quinolines.[4] During the course of our ongoing studies on polarized ketene *S*,*S*-acetals[10,11] we have recently developed a simple synthesis of 3-bis(methylthio)acrolein (**1**) from readily available starting materials.[12] In the present communication we report a mild and practical synthesis of substituted 2-(methylthio)quinolines,[13] employing 3-bis(methylthio)acrolein as a 'surrogate' acrolein in modified Skraup synthesis. The starting 3-bis(methylthio)acrolein (**1**) was prepared from vinyl acetate in improved yield (64%) by optimization of our earlier reported procedure.[12] Cyclization of anilines **2a**–**d** bearing a strong activating group *ortho* or *para* to the site of cyclization was first examined (Scheme 1). Thus the reaction of *m*-methoxyaniline and **1** proceeded smoothly in refluxing HOAc (8–10 h) to give a single product characterized as 7-methoxy-2-(methylthio)quinoline (**3a**) formed in 78% yield (method A). The corresponding 3,4-dimethoxy-, 3,5-dimethoxy- and 2,5-dimethoxyanilines (**2b**–**d**) similarly underwent facile cyclization under identical conditions furnishing the corresponding substituted 2-(methylthio)quinolines (**3b**–**d**) in overall high yields (Scheme 1).[14,15] Similarly, the 1-naphthylamine (**2e**) was efficiently transformed into the corresponding 2-(methylthio)benzo[*h*]quinoline (**3e**) in 70% yield. The structures and regiochemistry of all these newly synthesized quinolines **3a**–**e** were established with the help of spectral and analytical data and by NOE difference experiments.

The unsubstituted aniline however failed to yield the desired 2-(methylthio)quinoline (**3f**) when reacted with **1** in HOAc even under prolonged refluxing conditions (12 h). Reactions in the presence of other acid catalysts such as TFA, TfOH, H_2SO_4 or HCl also did not yield the desired quinoline under varying conditions and resulted in the formation of intractable reaction mixtures. However, subsequently it was found that the reaction of aniline (2.2 equiv) with **1** in the presence of TFA (0.23 mL) in CH_2Cl_2 at room temperature afforded the corresponding iminoenamine **4f** in nearly quantitative yield. The iminoenamine **4f** could be converted to 2-(methylthio)quinoline (**3f**, 50%) when subjected to cyclization in the presence of polyphosphoric acid at 90 °C.[16] Similarly the other substituted quinolines **3g**–**l** could also be obtained in moderate to good yields from the anilines **2g**–**l** following this two-step, one-pot procedure via iminoenamine intermediates **4g**–**l** (method B, Scheme 2).[17] Interestingly, the *o*-anisidine (**2m**) could also be converted to the corresponding

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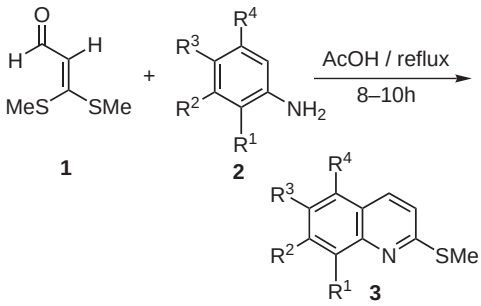
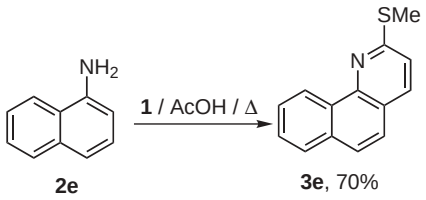
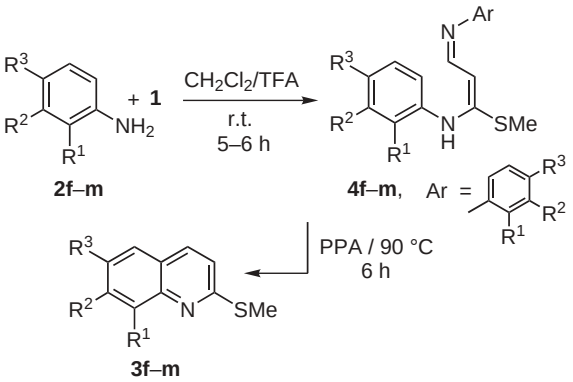


2a, **3a**, $R^1 = R^3 = R^4 = H$; $R^2 = OMe$, 78%
2b, **3b**, $R^1 = R^4 = H$; $R^2 = R^3 = OMe$, 86%
2c, **3c**, $R^1 = R^3 = H$; $R^2 = R^4 = OMe$, 68%
2d, **3d**, $R^2 = R^3 = H$; $R^1 = R^4 = OMe$, 62%



Scheme 1

2-(methylthio)-8-methoxyquinoline (**3m**) in 60% yield through this procedure in contrast to the reported failure of *o*-substituted anilines to afford 8-substituted quinolines (Table 1).[4a]

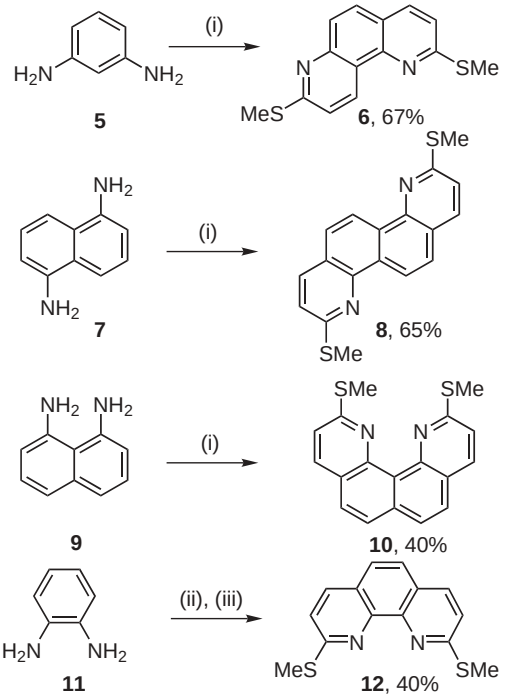


Scheme 2

Table 1 Synthesis of Quinolines

2, **3**, **4**	R^1	R^2	R^3	Yield (%) **3**
f	H	H	H	50
g	H	F	H	48
h	H	H	OMe	65
i	H	H	CI	50
j	H	H	Me	62
k	H	Me	H	65
l	H	CI	CI	66
m	OMe	H	H	60

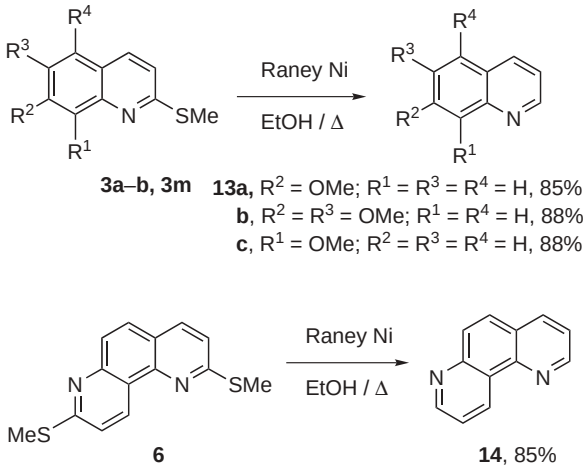
The new quinoline protocol could also be successfully implemented for the synthesis of tri- and tetracyclic pyrido-fused quinolines as depicted in Scheme 3. Thus treatment of *m*-phenylenediamine with 2.0 equivalents of **1** in refluxing acetic acid afforded the corresponding 2,8-bis(methylthio)pyrido[2,3-*h*]quinoline (**6**) in 67% yield, whereas the tetracyclic 3,9-bis(methylthio)quino[8,7-*h*]quinoline (**8**) was efficiently formed (65%) in one step by treatment of 1,5-diaminonaphthalene with **1** under identical conditions (Scheme 3). These successful results prompted us to extend this process to 1,8-diaminonaphthalene which yielded the novel 2,11-bis(methylthio)quino[7,8-*h*]quinoline (**10**) in moderate yield (Scheme 3).[18] Also the cyclocondensation of **1** with *o*-phenylenediamine under two steps reaction conditions (method B) provided the 2,9-bis(methylthio)pyrido[3,2-*h*]quinoline[19] (**12**) in the moderate yield of 40%. The structures of these condensed quinolines were confirmed with the help of spectral and analytical data.



Scheme 3 *Reagents and conditions*: (i) Method A: 1 (2.0 equiv), HOAc, 120 °C, 8–10 h; (ii) method B: **1** (0.67 equiv), CH_2Cl_2, TFA, r.t.; (iii) PPA, 90 °C, 6 h.

A few of the 2-(methylthio)quinolines **3a**,**b**,**m** and the fused quinoline **6** were converted to the sulfur free quinolines **13a**–**c** and **14** by treatment with Raney-Ni in refluxing ethanol (Scheme 4). Further utility of 2-methylthio functionality in these newly synthesized quinolines was demonstrated by its replacement with a few primary and secondary amines (Scheme 5). Thus the oxidation of 2-(methylthio)-7-methoxyquinoline (**3a**) with MCPBA afforded the 2-methylsulfonylquinoline[20] (**15a**) in 88% yield. The 2-methylsulfonyl group in **15a** could be easily substituted by morpholine, benzylamine and aniline under

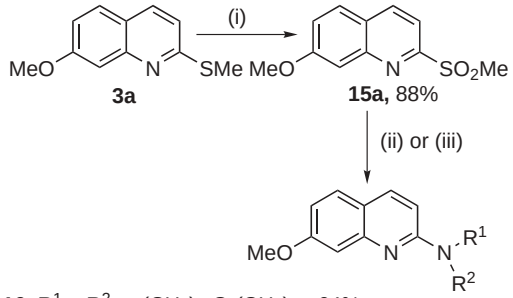
varying conditions yielding the respective 2-alkyl/arylaminoquinolines **16**–**18** in good yields (Scheme 5).[21] Also the 2-(methylthio) group in **3a** could be smoothly replaced by alkyl/aryl groups (Me, Ph) by treatment with either methyl or phenyl Grignard reagent in the presence of bis(triphenylphosphino)nickel dichloride to give 2-methyl- and 2-phenylquinolines **19** and **20** in good yields (Scheme 6).



3a–b, 3m **13a,** R^2 = OMe; R^1 = R^3 = R^4 = H, 85%
b, R^2 = R^3 = OMe; R^1 = R^4 = H, 88%
c, R^1 = OMe; R^2 = R^3 = R^4 = H, 88%

6 **14**, 85%

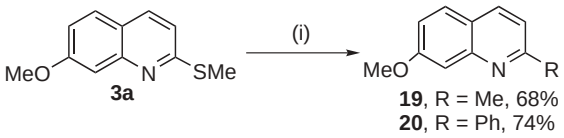
Scheme 4



3a **15a,** 88%

16, R^1 = R^2 = -$(CH_2)_2$-O-$(CH_2)_2$-, 64%
17, R^1 = H; R^2 = $PhCH_2$, 80%
18, R^1 = H; R^2 = Ph, 82%

Scheme 5 *Reagents and conditions*: (i) MCPBA, CH_2Cl_2, r.t.; (ii) morpholine, 120 °C, 5 h; (iii) benzylamine or aniline, sealed tube, 170 °C, 8 h.



3a **19**, R = Me, 68%
20, R = Ph, 74%

Scheme 6 *Reagents and conditions*: (i) RMgX, $(PPh_3)_2NiCl_2$, Et_2O, C_6H_6, 80 °C, 12 h.

In summary, a new mild variation of Skraup quinoline synthesis based on cyclocondensation of 3-bis(methylthio)acrolein with various anilines has been developed. The product 2-(methylthio)quinolines are formed in a highly regioselective fashion and the 2-(methylthio) functionality can be replaced by various nitrogen and carbon nucleophiles thus broadening its scope. Also the methodology could be extended to aryldiamines providing simple and practical routes to various pyrido-fused condensed quinolines.

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(14) All new compounds gave satisfactory spectral and analytical data.

(15) **General Procedure for the Synthesis of Substituted and Fused Quinolines 3a–e, 6, 8, 10: Method A:** A solution of 3-bis(methylthio)acrolein (**1**, 2.0 mmol, 0.3 g) and the appropriate anilines (2.2 mmol) or aryldiamines (1.1 mmol) in glacial HOAc (30 mL) was heated under reflux for 8–10 h (monitored by TLC). It was then cooled, quenched with sat. $NaHCO_3$ solution, extracted with $CHCl_3$ (3 × 30 mL), the combined organic layer was washed with H_2O (50 mL) and dried over Na_2SO_4. Removal of solvent gave crude products, which were purified by column chromatography over silica gel using hexane–EtOAc (9:1) as eluent. Data for compound **3a**: Yield 78%; light yellow solid; mp 43–44 °C; R_f = 0.4 (hexane–EtOAc, 9:1). IR (KBr): 2999, 2924, 1593 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.69 (s, 3 H, SMe), 3.94 (s, 3 H, OMe), 7.07 (dd, *J* = 2.4, 8.8 Hz, 1 H, ArH), 7.10 (d, *J* = 8.5 Hz, 1 H, ArH), 7.30 (d, *J* = 2.4 Hz, 1 H, ArH), 7.58 (d, *J* = 8.8 Hz, 1 H, ArH), 7.80 (d, *J* = 8.5 Hz, 1 H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.98, 55.45, 106.62, 117.74, 118.15, 120.73, 128.58, 134.89, 149.96, 160.17, 160.88. MS (EI): *m/z* (%) = 205 (100) [M^+], 159 (42.8). Anal. Calcd for $C_{11}H_{11}NOS$ (205.28): C, 64.36; H, 5.40; N, 6.82%. Found: C, 64.30; H, 5.45; N, 6.75%.
Data for compound **6**: Yield 67%; white solid; mp 125–126 °C; R_f = 0.7 (hexane–EtOAc, 9:1). IR (KBr): 2919, 1611, 1593 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.77 (s, 3 H, SMe), 2.80 (s, 3 H, SMe), 7.36 (d, *J* = 8.5 Hz, 1 H, ArH), 7.44 (d, *J* = 8.5 Hz, 1 H, ArH), 7.83 (d, *J* = 9.0 Hz, 1 H, ArH), 7.93 (d, *J* = 8.2 Hz, 2 H, ArH), 9.25 (d, *J* = 8.5 Hz, 1 H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.17, 13.31, 120.42, 120.93, 122.47, 123.06, 125.77, 129.32, 132.43, 135.24, 145.41, 148.99, 159.80, 161.44. MS (EI): *m/z* (%) = 273 (100) [M^+ + 1], 258 (10). Anal. Calcd for $C_{14}H_{12}N_2S_2$ (272.40): C, 61.73; H, 4.44; N, 10.28%. Found: C, 61.50; H, 4.35; N, 10.42%.
Data for compound **8**: Yield 65%; white solid; mp 225–226 °C; R_f = 0.7 (hexane–EtOAc, 9:1). IR (KBr): 3748, 3621, 2924, 1579 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.86 (s, 6 H, 2 × SMe), 7.41 (d, *J* = 8.6 Hz, 2 H, ArH), 7.87 (d, *J* = 8.8 Hz, 2 H, ArH), 8.03 (d, *J* = 8.6 Hz, 2 H, ArH), 9.25 (d, *J* = 8.8 Hz, 2 H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.26, 121.25, 121.77, 124.56, 125.66, 131.18, 135.49, 145.45, 158.96. MS (EI): *m/z* (%) = 323 (40) [M^+ + 1], 273 (10). Anal. Calcd for $C_{18}H_{14}N_2S_2$ (322.46): C, 67.05; H, 4.38; N, 8.69%. Found: C, 67.10; H, 4.25; N, 8.42%.

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(17) **General Procedure for the Synthesis of Substituted and Fused Quinolines 3f–m, 12: Method B:** To a solution of 3-bis(methylthio)acrolein (**1**, 2.0 mmol, 0.3 g) and respective anilines **2f**–**m** (4.4 mmol) or *o*-phenylenediamine (**11**, 3.0 mmol) in CH_2Cl_2 (20 mL), TFA (6.0 mmol, 0.46 mL) was added at r.t. and the reaction mixture was left for stirring at the same temperature for 5–6 h (monitored by TLC). It was then quenched with sat. $NaHCO_3$ solution (2 × 25 mL), extracted with CH_2Cl_2 (2 × 25 mL), dried over Na_2SO_4.The organic layer was distilled off under reduced pressure to give crude iminoenamines which were used as such for further reactions whereas few of the iminoenamines were purified by column chromatography over silica gel using hexane–EtOAc (9:1) as eluent for characterization. The crude iminoenamine (5 mmol) obtained was dissolved in PPA (20 mL) and the reaction mixture was heated with stirring at 90 °C for 6 h (monitored by TLC). It was then cooled, poured into ice-cold H_2O (50 mL), extracted with $CHCl_3$ (3 × 50 mL), the combined organic layer was washed with H_2O (3 × 50 mL) and dried over Na_2SO_4.The solvent was distilled off to give crude product, which was purified by column chromatography over silica gel using hexane–EtOAc (9:1) as eluent.
Data for compound **3m**: Yield 60%; yellow liquid; R_f = 0.8 (hexane–EtOAc, 8:2). IR (KBr): 2928, 2359, 1723, 1618 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.66 (s, 3 H, SMe), 3.96 (s, 3 H, OMe), 6.93 (dd, *J* = 1.4, 8.0 Hz, 1 H, ArH), 7.15–7.26 (m, 3 H, ArH), 7.76 (d, *J* = 8.8 Hz, 1 H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.91, 56.12, 108.80, 119.57, 120.90, 125.15, 126.82, 135.26, 139.94, 154.19, 159.04. MS (EI): *m/z* (%) = 206 (100) [M^+ + 1], 191 (20). Anal. Calcd for $C_{11}H_{11}NOS$ (205.28): C, 64.36; H, 5.40; N, 6.82%. Found: C, 64.58; H, 5.32; N, 6.60%.

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(19) Data for compound **12**: Yield 60%; yellow solid; mp 78 °C; R_f = 0.7 (hexane–EtOAc, 8:2). IR (KBr): 3371, 2925, 1628, 1597 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.51 (s, 6 H, 2 × SMe), 7.25 (d, *J* = 8.3 Hz, 2 H, ArH), 7.52 (s, 2 H, ArH), 7.70 (d, *J* = 8.3 Hz, 2 H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.71, 126.21, 127.20, 127.38, 129.90, 133.87, 135.40. MS (EI): *m/z* (%) = 273 (70) [M^+ + 1], 225 (30). Anal. Calcd for $C_{14}H_{12}N_2S_2$ (272.40): C, 61.73; H, 4.44; N, 10.28%. Found: C, 61.58; H, 4.32; N, 10.40%.

(20) Data for compound **15a**: Yield 88%; white solid; mp 160–161 °C; R_f = 0.5 (hexane–EtOAc, 8:2). IR (KBr): 3015, 2927, 1620, 1302 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.26 (s, 3 H, OMe), 3.89 (s, 3 H, SO_2Me), 7.26 (dd, *J* = 2.7, 9.0 Hz, 1 H, ArH), 7.40 (d, *J* = 2.7 Hz, 1 H, ArH), 7.71 (d, *J* = 9.0 Hz, 1 H, ArH), 7.89 (d, *J* = 8.3 Hz, 1 H, ArH), 8.24 (d, *J* = 8.3 Hz, 1 H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 39.99, 55.68, 107.38, 114.16, 122.89, 124.68, 128.72, 138.25, 149.02, 157.51, 161.93. MS (EI): *m/z* (%) = 238 (100) [M^+ + 1], 206 (30). Anal. Calcd for $C_{11}H_{11}NO_3S$ (237.28): C, 55.68; H, 4.67; N, 5.90%. Found: C, 55.60 H, 4.75; N, 5.85%.

(21) Data for compound **17**: Yield 80%; white low melting point solid; R_f = 0.6 (hexane–EtOAc, 8:2). IR (KBr): 3232, 2998, 2930, 1613 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.88 (s, 3 H, OMe), 4.69 (d, *J* = 5.1 Hz, 2 H, CH_2), 5.16 (br s, 1 H, NH), 6.47 (d, *J* = 8.6 Hz, 1 H, ArH), 6.86 (dd, *J* = 2.4, 8.6 Hz, 1 H, ArH), 7.08 (d, *J* = 2.4 Hz, 1 H, ArH), 7.27 (t, *J* = 7.0 Hz, 1 H, ArH), 7.33 (t, *J* = 7.0 Hz, 2 H, ArH), 7.39 (d, *J* = 7.0 Hz, 2 H, ArH), 7.45 (d, *J* = 8.8 Hz, 1 H, ArH), 7.72 (d, *J* = 8.8 Hz, 1 H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.89, 55.33, 105.40, 108.35, 114.23, 118.22, 127.28, 127.63, 128.44, 128.63, 137.21, 139.21, 149.48, 157.20, 161.10. MS (EI): *m/z* (%) = 265 (100) [M^+ + 1]. Anal. Calcd for $C_{17}H_{16}N_2O$ (264.33): C, 77.25; H, 6.10; N, 10.60%. Found: C, 77.15; H, 6.20; N, 10.65%.