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A novel approach to 12-chloro-3-thio-4*H*-quino[3,2-*e*][1,3]diazocines *via* Vilsmeier Haack reaction

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The Vilsmeier Haack reaction on 4-hydroxyquinaldines lead to potential intermediate 4-chloro-3-formyl-2-(2-hydroxy-ethene-1-yl)quinolines. The intermediate is further utilized to prepare quino[3,2-*e*][1,3]diazocines on treatment with thiourea. The structures of the new compounds are determined by the analytical and spectroscopic data.

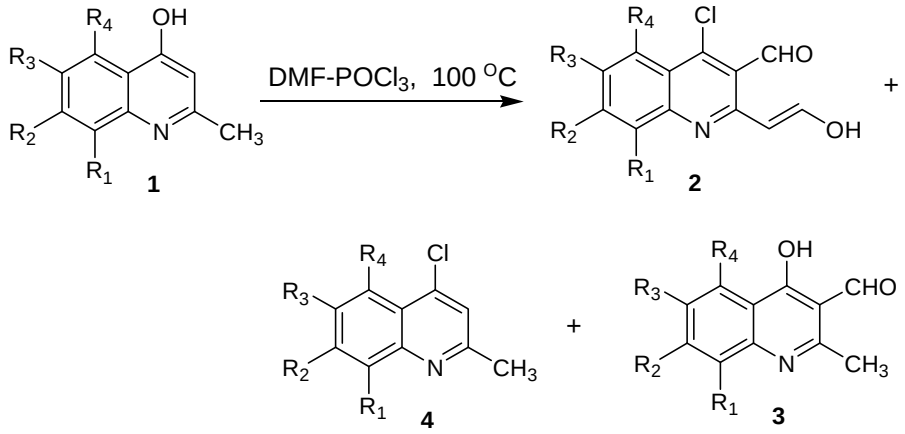
Keywords: Vilsmeier Haack reaction, 4-hydroxyquinaldines, diazocines

A literature search on recent years suggest that there has been sustained interest in the application of Vilsmeier Haack reagent in organic synthesis. It has proved to be a mild and efficient reagent for the formylation of reactive aromatic and heteroaromatic substrates[1-3]. The versatility of the reaction has been further extended as an activating agent for acylhalo addition[4] and ring annulation[5-7]. Besides aromatic formylation, a wide variety of alkene derivatives[8], carbonyl compounds[9], activated methyl and methylene groups[10] as well as oxygen and nitrogen nucleophiles[11] efficiently react with Vilsmeier Haack reagent to yield the corresponding iminium salts. The intramolecular cyclisation potential of halomethyleniminium salts formed under Vilsmeier condition and microwave induced Vilsmeier conditions were reported[12-24]. The classical Vilsmeier Haack reaction involves electrophilic substitution of an activated aromatic ring with a halo-methyleniminium salt to yield the corresponding iminium species, which facilitates easy entry into large number of novel heterocyclic systems. The capability of the reagent to generate a broad-spectrum of iminium species has been explored further to hitherto unknown quinoline, as a part of our objective towards the construction of [*c*] annelated nitrogen and oxygen heterocycles *via* 4-chloro-3-formylquinaldines which is obtainable from 4-hydroxyquinaldines[25] by Vilsmeier Haack reaction.

Results and Discussion

It was presumed that the Vilsmeier Haack reaction on 4-hydroxyquinaldines **1**, (previously prepared from corresponding aniline and ethyl acetoacetate followed by subsequent cyclization of the β-anilinocrotonates) could provide an utility intermediate for the preparation of several substituted [*c*] annelated heterocyclic compounds[26-28]. The reaction was carried out at 100°C for 15-20 hr, using the Vilsmeier Haack reagent derived from phosphorus oxychloride-dimethyl formamide *in situ*. The reaction yielded a mixture of products. These were isolated using silica gel column chromatography. The analytical and spectroscopic data confirmed the products as 4-chloro-3-formyl-2-(2-hydroxy-ethene-1-yl)quinoline **2**, 4-hydroxy-3-formylquinaldine **3** and 4-chloro-quinaldine **4** in good yields (**Scheme I**).

The Vilsmeier Haack reagents are usually applied for the formylation of aromatic and heteroaromatic compounds. These are the chloromethyleniminium species responsible for the formylation. As in our reaction, the chloromethyleniminium species obtained *in situ* from phosphorus oxychloride-dimethylformamide reacts with the active methyl group of 4-hydroxy-quinaldine. Another formylation occurs at the aromatic C_3 of the quinaldine leading to the iminium compound. Since these iminium salts having the special capability to replace the hydroxyl group at aromatic C_4 by the nucleophiles like chlorine, bromine etc., they have led the formation of 4-chloroquinaldine **4** in minor yields



1-4 : a) $R_1 = R_2 = R_3 = R_4 = H$
b) $R_1 = CH_3$, $R_2 = R_3 = R_4 = H$
c) $R_2 = CH_3$, $R_1 = R_3 = R_4 = H$
d) $R_3 = Cl$, $R_1 = R_2 = R_4 = H$
e) $R_1 = R_4 = CH_3$, $R_2 = R_3 = H$

Scheme I

and also in the conversion of hydroxy moiety to the chloro moiety in case of 4-chloro-3-formyl-2-(2-hydroxy-ethene-1-yl)quinoline **2**. In the case of 4-hydroxyquinaldine **1a** and 8-methyl-4-hydroxyquinaldine **1b** the reaction got completed within 15 hr and with 5,8-dimethyl-4-hydroxyquinaldine **1e**, in 20 hr, monitored by the TLC.

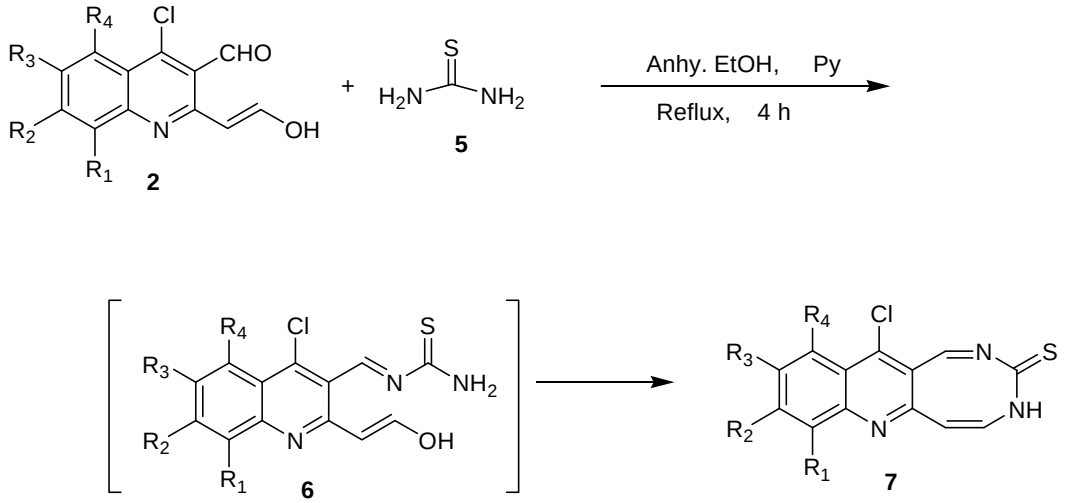
Having prepared the new intermediates, **2a-e** we were able to start the intended synthesis of some annulated quinolines. The corresponding vinyl derivative was treated with thiourea in anhydrous ethanol with 2 mL of pyridine and refluxed for four hours. The silica gel column chromatography afforded the desired compounds **7a-e** using pet.ether-ethyl acetate as eluents (**Scheme II**).

The reaction proceeded *via* the corresponding hydrazone and the subsequent aromatization has yielded the diazocine. The yields, reaction time and the temperature at which the reaction carried out are shown in **Table I**.

Experimental Section

General: Thin layer chromatography was used to assess the reactions and the purity of products. Melting points were determined on a Boetius Microheating Table (Japan) and are uncorrected. IR spectra were recorded with a Shimadzu – 8201FT instrument (Japan) in KBr discs and only noteworthy absorption levels (reciprocal centimeter) are listed. ^{1}H NMR spectra were recorded with a Bruker - AMX-400 MHz spectrometer (US) in $CDCl_3$ solution; chemical shifts are expressed in ppm (δ) relative to TMS, coupling constants (*J*) in Hz. Signal multiplicities are represented by bs (broad singlet), s (singlet), d (doublet), t (triplet) and m (multiplet). ^{13}C NMR spectra were recorded on Bruker - AMX-100 MHz spectrometer (US) in $CDCl_3$ with TMS as internal standard. Mass spectra were recorded using a Jeol –D- 300 mass spectrometer (70 eV) (Japan). C H N analyses were carried out on a Perkin-Elmer Model 240 analysers (UK).

Vilsmeier Haack reaction on 4-hydroxyquinaldine: The Vilsmeier reagent was prepared by taking *N*,*N*-dimethylformamide (3.86 mL, 0.05 mole) in a round bottomed flask in ice cold condition (0–5°C) with constant stirring. To this, phosphorus oxychloride (13.04 mL, 0.014 mole) was added dropwise for a period of 30 min and the resultant mixture was stirred for further one hour. The appropriate 4-hydroxyquinaldines **1a-e** were added to the Vilsmeier reagent and stirred again for 30 min and the reaction mixture was kept on a water-bath at 100°C for the period of time stated in **Table I**. After the reaction, followed by TLC, has been completed, the reaction mixture was poured into 500 g of crushed ice with constant manual stirring. The reaction mixture was kept aside for overnight. After neutralization with 4*N* NaOH, the precipitate obtained was washed well with water and extracted using ethyl acetate. The combined organic layers were collected and dried over anhyd. Na_2SO_4. The silica gel chromatography of the reaction mixture afforded three products **4**, **3**



2,6,7: a) $R_1 = R_2 = R_3 = R_4 = H$
b) $R_1 = CH_3$, $R_2 = R_3 = R_4 = H$
c) $R_2 = CH_3$, $R_1 = R_3 = R_4 = H$
d) $R_3 = Cl$, $R_1 = R_2 = R_4 = H$
e) $R_1 = R_4 = CH_3$, $R_2 = R_3 = H$

Scheme II

Table I — Vilsmeier Haack reaction of 4-hydroxyquinaldines **1a-e** and synthesis of quino[3,2-*e*][1,3]diazocines **7a-e**

Entry	Substrates	R_1	R_2	R_3	R_4	Reaction time hr.	Yield (%)			
							2	**3**	**4**	**7**
1	**1a**	H	H	H	H	15	70	15	10	-
2	**1b**	CH_3	H	H	H	12.5	73.5	18	5	-
3	**1c**	H	CH_3	H	H	16	55	12	17	-
4	**1d**	H	H	Cl	H	17.5	78	12	5	-
5	**1e**	CH_3	H	H	CH_3	20	65	10	15	-
6	**2a**	H	H	H	H	3	-	-	-	76
7	**2b**	CH_3	H	H	H	4	-	-	-	80
8	**2c**	H	CH_3	H	H	3.5	-	-	-	72.5
9	**2d**	H	H	Cl	H	3.5	-	-	-	67
10	**2e**	CH_3	H	H	CH_3	4.5	-	-	-	82.5

and **2** using pet.ether (100), pet.ether-ethyl acetate (94:6) and pet.ether-ethyl acetate (85:15) respectively. The products were recrystallized with methanol. The products were identified by the analytical and spectroscopic data.

Preparation of 12-chloro-3-thio-4*H*-quino[3,2-e][1,3]diazocines: Thiourea (0.002 mole) and the appropriate 4-chloro-3-formyl-2-(2-hydroxy-ethene-1-yl)quinoline (0.002 mole) were dissolved in 50 mL of anhydrous ethanol along with 2 mL of pyridine. They were kept at the refluxing temperature for 4 hr. The completion of the reaction was indicated by the tlc analysis and the ethanol was removed under reduced pressure. The remaining residual mass was completely washed with dil HCl (1:1) for 4 to 5 times and extracted with ethyl acetate. The combined organic layers were then dried over anhydrous sodium sulfate and silica gel column chromatography yielded the product (Petroleum ether/EtOAc).

4-Chloro-3-formyl-2-(2-hydroxy-ethene-1-yl)quinoline 2a: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.7(d, 1H, C_8-H, J = 8.1 Hz), 7.6(t, 1H, C_7-H, J = 8.3 Hz), 7.9(t, 1H, C_6-H, J = 7.3 Hz), 8.2(d, 1H, C_5-H, J = 8.3 Hz), 9.2(s, 1H, C_3-CHO), 9.4 and 9.6(2s, 2H, vinylic

protons), 16.5(bs, vinylic–OH, D_2O exchangeable); ^{13}C NMR($CDCl_3$, 100 MHz): δ 192.41, 189.33, 189.08, 146.24, 137.30, 135.90, 133.32, 126.93, 125.21, 122.61, 119.32, 118.99; MS(70 eV, *m/z*, M^+): 233, (M+2): 235; IR(KBr): 3438, 1664, 1595 cm^{-1}. Anal. Found: C, 61.62; H, 3.38; N, 5.92. Calcd. for $C_{12}H_8O_2NCl$: C, 61.69; H, 3.45; N, 5.99; m.p. 155°C.

3-Formyl-4-hydroxyquinaldine 3a: ^1H NMR ($CDCl_3$, 400 MHz): δ 2.4(s, 3H, CH_3), 7.3(d, 1H, C_8-H, *J* = 7.84 Hz), 7.5(t, 1H, C_7-H, *J* = 7.58 Hz), 7.7(t, 1H, C_6-H, *J* = 7.6 Hz), 8.2(d, 1H, C_5-H, *J* = 8.28 Hz), 9.4(s, 1H, CHO), 14.1(bs, 1H, OH); MS(70 eV, *m/*z, M^+): 187; IR(KBr): 3520, 1695, 1610 cm^{-1}. Anal. Found: C, 70.54; H, 4.81; N, 7.43. Calcd. for $C_{11}H_9O_2N$: C, 70.58; H, 4.85; N, 7.48; m.p. 140°C.

4-Chloroquinaldine 4a: ^1H NMR ($CDCl_3$, 400 MHz): δ 2.5(s, 3H, CH_3), 7.3(s, 1H, C_3-H), 8.1(d, 1H, C_5-H, *J* = 8.2 Hz), 7.7(t, 1H, C_6-H, *J* = 7.54 Hz), 7.9(t, 1H, C_7-H, *J* =7.82 Hz), 7.5(d, 1H, C_8-H, *J* = 8.14 Hz); IR(KBr): 1590 cm^{-1}. m.p.; 65°C.

12-Chloro-3-thio-4*H*-quino[3,2-*e*][1,3]diazocine 7a: ^1H NMR ($CDCl_3$, 400 MHz): δ 5.6 (s, 1H, NH), 7.1-8.2 (m, 7H, Ar-H); MS(70 eV, *m/z*, M^+): 273 (M+2): 275; IR(KBr): 3350, 1590, 1575, 1325 cm^{-1}. Anal. Found: C, 57.11; H, 2.81; N, 15.24. Calcd. for $C_{13}H_8N_3SCl$: C, 57.04; H, 2.95; N, 15.35; m.p. 220°C.

4-Chloro-3-formyl-8-methyl-2-(2-hydroxy-ethene-1-yl)quinoline 2b: ^1H NMR ($CDCl_3$, 400 MHz): δ 2.8(s, 3H, CH_3), 7.5(t, 1H, C_6-H, *J* = 7.92 Hz), 7.7(d, 1H, C_7-H, *J* = 7.16 Hz), 8.1(d, 1H, C_5-H, *J* = 8.24 Hz), 9.2(s, 1H, C_3-CHO), 9.4 and 9.5(2s, 2H, vinylic protons), 16.5(bs, vinylic–OH, D_2O exchangeable); ^{13}C NMR($CDCl_3$, 100 MHz): δ 192.35, 189.45, 189.01, 147.22, 136.94, 133.95, 130.23, 126.61, 126.39, 122.99, 121.96, 118.59, 18.45; MS(70 eV, *m/z*, M^+): 247 (16.5 %) (M+2): 249 (5.2 %), 220 (66.7 %), 203 (100 %), 178(36.5 %); IR(KBr): 3450, 1660, 1595 cm^{-1}. Anal. Found: C, 62.02; H, 3.98; N, 5.63. Calcd. for $C_{13}H_{10}O_2NCl$: C, 63.04; H, 4.07; N, 5.66; m.p. 132°C.

3-Formyl-4-hydroxy-8-methylquinaldine 3b:. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.6(s, 6H, 2×CH_3), 7.4(t, 1H, C_6-H, *J* = 7.6 Hz), 7.6(d, 1H, C_7-H, *J* = 7.28 Hz), 8.0(d, 1H, C_5-H, *J* = 8.24 Hz), 9.3(s, 1H, CHO), 15.3(bs, 1H, OH); MS(70 eV, *m/z*, M^+): 201; IR(KBr): 3500, 1710, 1590 cm^{-1}. Anal. Found: C, 71.58; H, 5.44; N, 6.98. Calcd. for $C_{12}H_{11}O_2N$: C, 71.63; H, 5.51; N, 6.96; m.p. 195°C.

4-Chloro-8-methylquinaldine 4b: ^1H NMR ($CDCl_3$, 400 MHz): δ 2.7(s, 3H, C_2-CH_3), 2.8(s, 3H, C_8-CH_3), 7.4(s, 1H, C_3-H), 8.1(d, 1H, C_5-H, *J* = 7.92 Hz), 7.4(t, 1H, C_6-H, *J* = 7.2 Hz), 7.6(d, 1H, C_7-H, *J* = 6.28 Hz); IR: 1570. m.p. 47°C.

12-Chloro-8-methyl-3-thio-4*H*-quino[3,2-*e*][1,3]diazocine 7b: ^1H NMR ($CDCl_3$, 400 MHz): δ 2.6 (s, 3H, CH_3), 5.7 (s, 1H, NH), 7.0-8.1 (m, 6H, Ar-H); MS(70 eV, *m/z*, M^+): 287 (M+2): 289; IR(KBr): 3320, 1587, 1571, 1321 cm^{-1}. Anal. Found: C, 58.24; H, 3.41; N, 14.73. Calcd. for $C_{14}H_{10}N_3SCl$: C, 58.43; H, 3.50; N, 14.66; m.p. 195°C.

4-Chloro-3-formyl-7-methyl-2-(2-hydroxy-ethene-1-yl)quinoline 2c: ^1H NMR ($CDCl_3$, 400 MHz): δ 2.6(s, 3H, CH_3), 7.6(d, 1H, C_6-H, *J* = 7.56 Hz), 7.8(s, 1H, C_8-H), 8.1(d, 1H, C_5-H, *J* = 8.16 Hz), 9.2(s, 1H, -CHO), 9.3 and 9.5(2s, 2H, vinylic protons), 16.5(bs, vinylic–OH, D_2O exchangeable); ^{13}C NMR($CDCl_3$, 100 MHz): δ 192.28, 189.41, 189.09, 145.26, 135.68, 134.06, 131.22, 126.28, 126.05, 122.75, 122.34, 119.70, 19.52; MS(70 eV, m/z, M^+): 247 (M+2): 249; IR(KBr): 3480, 1670, 1590 cm^{-1}. Anal. Found: C, 62.98; H, 4.01; N, 5.59. Calcd. for $C_{13}H_{10}O_2NCl$: C, 63.04; H, 4.07; N, 5.66; m.p. 148°C.

3-Formyl-4-hydroxy-7-methylquinaldine 3c: ^1H NMR ($CDCl_3$, 400 MHz): δ 2.5(s, 6H, 2×CH_3), 7.6(d, 1H, C_6-H, *J* = 7.14 Hz), 7.8(s, 1H, C_8-H), 8.0(d, 1H, C_5-H, *J* = 8.20 Hz), 9.4(s, 1H, CHO), 15.1(bs, 1H, OH); MS(70 eV, m/z, M^+): 201; IR(KBr): 3350, 1700, 1600 cm^{-1}. Anal. Found: C, 71.61; H, 5.46; N, 6.94. Calcd. for $C_{12}H_{11}O_2N$: C, 71.63; H, 5.51; N, 6.96; m.p. 215°C.

4-Chloro-7-methylquinaldine 4c: ^1H NMR ($CDCl_3$, 400 MHz): δ 2.6(s, 6H, 2 × CH_3), 7.3(s, 1H, C_3-H), 7.5(s, 1H, C_8-H), 7.8(d, 1H, C_6-H, *J* = 7.24 Hz), 8.1(d, 1H, C_5-H, *J* = 8.06 Hz); IR(KBr): 1585 cm^{-1}. m.p. 92°C.

12-Chloro-9-methyl-3-thio-4*H*-quino[3,2-*e*][1,3]-diazocine 7c: ^1H NMR ($CDCl_3$, 400 MHz): δ 2.5 (s, 3H, CH_3), 5.9 (s, 1H, NH), 7.3-8.2 (m, 6H, Ar-H)); MS(70 eV, *m/z*, M^+): 287 (M+2): 289; IR(KBr): 3295, 1593, 1578, 1330 cm^{-1}. Anal. Found: C, 58.54; H, 3.67; N, 14.58. Calcd. for $C_{14}H_{10}N_3SCl$: C, 58.43; H, 3.50; N, 14.66; m.p. 248°C.

4,6-Dichloro-3-formyl-2-(2-hydroxy-ethene-1-yl)-quinoline 2d: ^1H NMR ($CDCl_3$, 400MHz): δ 7.3(d, 1H, C_7-H, *J* = 7.68 Hz), 7.5(d, 1H, C_8-H, *J* = 7.96 Hz), 8.1(s, 1H, C_5-H), 9.2(s, 1H, C_3-CHO), 9.3 and 9.5(2s, 2H, vinylic protons), 16.5(bs, vinylic–OH, D_2O exchangeable); ^{13}C NMR($CDCl_3$, 100 MHz):

δ 192.27, 189.26, 189.08, 133.90, 133.21, 129.80, 129.04, 124.41, 121.13, 120.86, 119.87, 118.34; MS(70 eV, *m/z*, M^+): 267, (M+2): 269, (M+4): 271; IR(KBr): 3470, 1670, 1590 cm^{-1}. Anal. Found: C, 53.71; H, 2.65; N, 5.22. Calcd. for $C_{12}H_7O_2NCl_2$: C, 53.76; H, 2.63; N, 5.26; m.p. 180°C.

6-Chloro-3-formyl-4-hydroxyquinaldine 3d: ^1H NMR ($CDCl_3$, 400 MHz): δ 2.5(s, 3H, CH_3), 7.4(d, 1H, C_7-H, *J* = 8.76 Hz), 7.7(d, 1H, C_8-H, *J* = 7.64 Hz), 8.2(s, 1H, C_5-H), 9.4(s, 1H, CHO), 14.2(bs, 1H, OH); MS(70 eV, *m/z*, M^+): 221; IR(KBr): 3480, 1715, 1595 cm^{-1}. Anal. Found: C, 59.52; H, 3.57; N, 6.27. Calcd. for $C_{11}H_8O_2NCl$: C, 59.61; H, 3.64; N, 6.32; m.p. 230°C.

4,6-Dichloroquinaldine 4d: ^1H NMR ($CDCl_3$, 400 MHz): δ 2.4(s, 3H, CH_3), 7.4(s, 1H, C_3-H), 7.7-8.0(m, 3H, Ar-H); IR: 1575 cm^{-1}. m.p. 74°C.

10,12-Dichloro-3-thio-4*H*-quino[3,2-*e*][1,3]diazocine 7d: ^1H NMR ($CDCl_3$, 400 MHz): δ 6.0 (s, 1H, NH), 7.2-7.9 (m, 6H, Ar-H); MS(70 eV, *m/z*, M^+): 307 (M+2): 309: (M+4): 311; IR(KBr): 3372, 1605, 1585, 1327 cm^{-1}. Anal. Found: C, 50.59; H, 2.21; N, 13.57. Calcd. for $C_{13}H_7N_3SCl_2$: C, 50.67; H, 2.29; N, 13.63; m.p. 125°C.

5,8-Dimethyl-4-chloro-3-formyl-2-(2-hydroxy-ethene-1-yl)quinoline 2e: ^1H NMR ($CDCl_3$, 400 MHz): δ 2.6(s, 6H, 2×CH_3), 7.6(d, 1H, C_6-H, *J* = 7.46 Hz), 7.9(d, 1H, C_7-H, *J* = 7.96 Hz), 9.3(s, 1H, -CHO), 9.4 and 9.5(2s, 2H, vinylic protons), 16.5(bs, vinylic–OH, D_2O exchangeable); ^{13}C NMR($CDCl_3$, 100 MHz): δ 192.34, 189.38, 189.07, 144.34, 136.38, 133.86, 130.95, 127.54, 126.01, 123.11, 122.45, 118.60, 19.80, 18.95; MS(70 eV, *m/z*, M^+): 261 (M+2): 263; IR(KBr): 3525, 1680, 1595 cm^{-1}. Anal. Found: C, 64.21; H, 4.57; N, 5.28. Calcd. for $C_{14}H_{12}O_2NCl$: C, 64.25; H, 4.62; N, 5.35; m.p. 170°C.

3-Formyl-4-hydroxy-5,8-dimethylquinaldine 3e: ^1H NMR ($CDCl_3$, 400 MHz): δ 2.7(s, 9H, 3×CH_3), 7.5(d, 1H, C_6-H, *J* = 7.84 Hz), 7.7(d, 1H, C_7-H, *J* = 7.68 Hz), 9.2(s, 1H, CHO), 14.5(bs, 1H, OH); MS(70 eV, *m/z*, M^+): 215; IR(KBr): 3510, 1702, 1610 cm^{-1}. Anal. Found: C, 72.47; H, 6.01; N, 6.42. Calcd. for $C_{13}H_{13}O_2N$: C, 72.54; H, 6.09; N, 6.51; m.p. 155°C.

4-Chloro-5,8-dimethylquinaldine 4e: ^1H NMR ($CDCl_3$, 400 MHz): δ 2.6(s, 9H, 3 × CH_3), 7.4(s, 1H, C_3-H), 7.6-7.8(m, 2H, Ar-H); IR(KBr): 1580 cm^{-1}. m.p. 80°C.

12-Chloro-8,11-dimethyl-3-thio-4*H*-quino[3,2-*e*]-[1,3]diazocine 7e: ^1H NMR ($CDCl_3$, 400 MHz): δ 2.3 (s, 6H, 2 × CH_3), 5.6 (s, 1H, NH), 6.9-7.7 (m, 5H, Ar-H); MS(70 eV, *m/z*, M^+): 301 (M+2): 303; IR(KBr): 3275, 1590, 1565, 1323 cm^{-1}. Anal. Found: C, 59.81; H, 4.13; N, 13.81. Calcd. for $C_{15}H_{11}N_3SCl$: C, 59.70; H, 4.01; N, 13.92; m.p. 275°C.

Conclusion

In conclusion, we have demonstrated the utility of Vilsmeier Haack reaction on 4-hydroxyquinaldine resulting in some efficient and potential intermediate 4-chloro-3-formyl-2-(2-hydroxy-ethene-1-yl)quinolines, which is further utilized for the synthesis of novel diazocines.

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