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THREE-COMPONENT REACTION OF ARYNES, QUINOLINES, AND CHLOROFORM: TWO-STEP SYNTHESIS OF 2-QUINOLINONES FROM QUINOLINES

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Abstract – Reaction of quinoline with benzyne prepared from benzenediazonium-2-carboxylate and chloroform gave 1-phenyl-2-trichloromethyl-1,2-dihydroquinoline in 79% yield. Basic hydrolysis of dihydroquinoline by KOH resulted in the formation of 2-quinolinone in 85% yield.

INTRODUCTION

Arynes are powerful and useful reactive intermediates in organic chemistry, which can be easily converted into *ortho*-substituted arenes and benzo-annulated structures being hardly accessible by conventional methods.[1] Treatment of anthranilic acid (**1**) with alkyl nitrite affords benzenediazonium-2-carboxylate (**1'**), a popular benzyne precursor, which reacts with dienes and nucleophiles at elevated temperature to produce the corresponding adducts.[2] However, its explosive nature toward heating or solid surface replace other benzyne precursors such as 2-(trimethylsilyl)phenyl triflate (triflate) and phenyl(2-trimethylsilylphenyl)iodonium triflate, which form benzyne under very mild conditions (0 ºC to 80 ºC, neutral conditions).[3] By using triflate as a benzyne precursor, Chen and Jeganmohan,[4] Hu et al.,[5] Biju et al.,[6] and Tan et al.[7] have reported the reaction of benzyne derived from triflate with quinolines (**2**) and pronucleophiles to give the corresponding three-component products (Figure 1). However, reactions were generally performed under 0.5 mmol scale of reactants, which prevent further investigation of the obtained three-component products. Recently, by controlling in situ generation of benzyne from anthranilic acid **1** and isoamyl nitrite, we have accomplished the synthesis of 1-aryl-2-trichloromethyl-1,2-dihydroquinolines (**3**) from benzenediazonium-2-carboxylate **1'**, quinolines **2**, and chloroform up to 15 mmol scale.[8] Since large scale three-component reactions were achieved, we have interested in the reactivity of 1-aryl-2-trichloromethyl-1,2-dihydroquinolines **3**. This paper describes the full details of three-component reaction of quinolines and reaction of 1-phenyl-1,2-dihydroquinolines **3**.

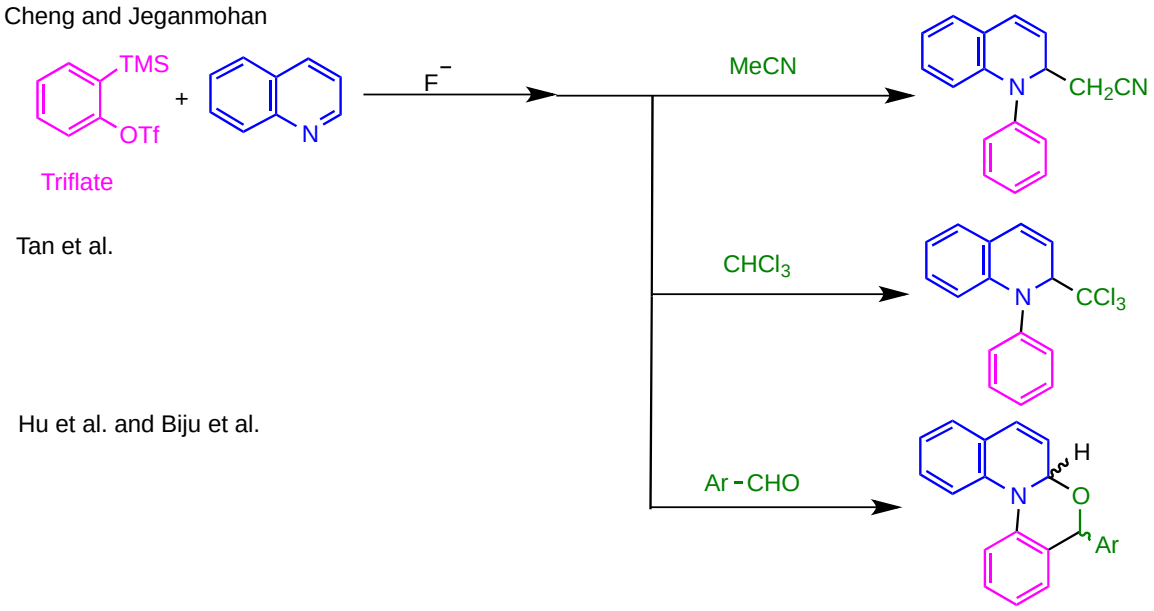
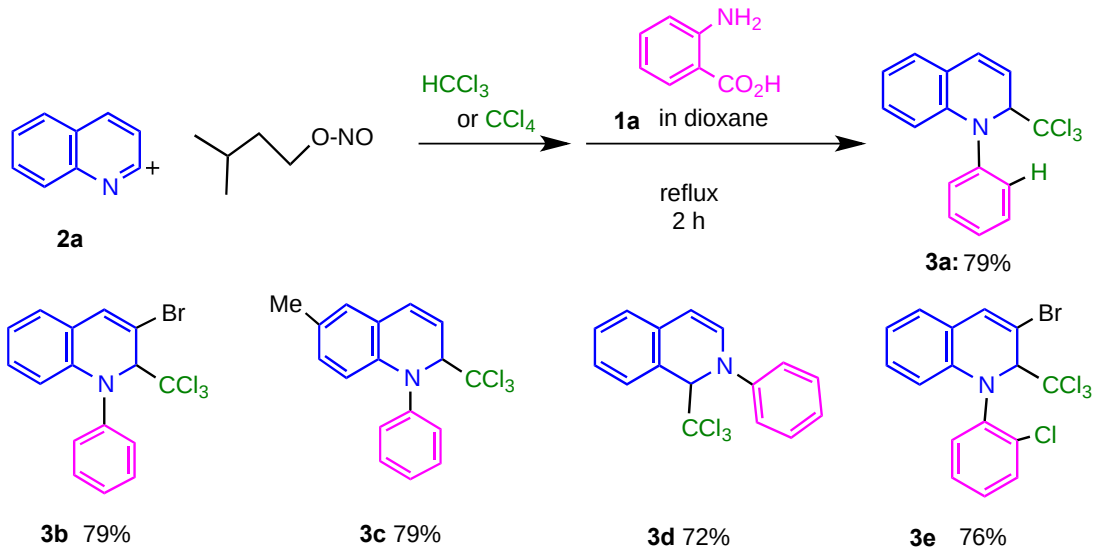


Figure 1. Three-component reaction of benzyne with quinolines and pronucleophiles

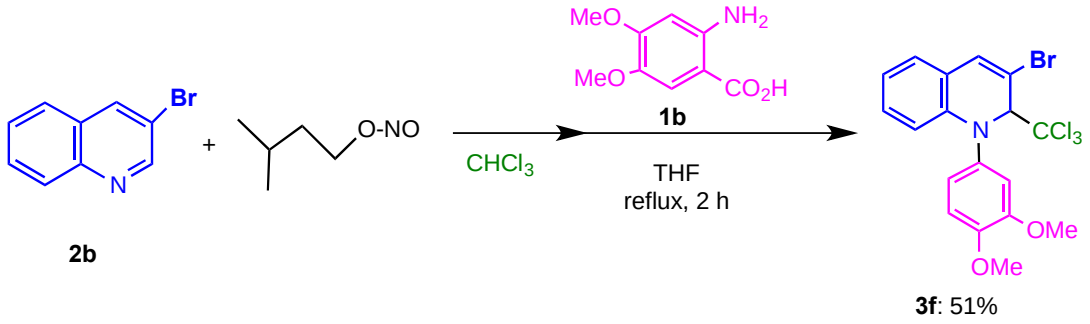
RESULTS AND DISCUSSION

Although intramolecular cyclization of benzyne with isoquinoline was reported by Kametani et al., there was no report on the reaction of quinoline with benzyne until the discovery of triflate.[9] By using triflate as a benzyne precursor, 1-aryl-2-trichloromethyl-1,2-dihydroquinolines **3** could be obtained by the reaction with quinolines and chloroform.[7] We have tried the reaction of quinolines with benzyne prepared from anthranilic acid **1** in the presence of chloroform whether three-component reaction would proceed, which would provide dihydroquinolines **3** in gram scale. As shown in Scheme 1, corresponding three-component product **3a** was obtained in 79% yield. Other quinolines also reacted with benzyne and chloroform to afford the corresponding three-component products **3b-3d**.



Scheme 1. Three-component reaction of benzyne with quinoline and chloroform or CCl_4

When carbon tetrachloride was used as a pronucleophile, the corresponding three-component product **3e** was obtained, whereas carbon tetrabromide, methyl propiolate, and acetonitrile gave a complex mixture (Scheme 1). When 2-amino-4,5-dimethoxybenzoic acid **1b** was used as an aryne precursor, 1-(3',4'-dimethoxyphenyl)-2-(trichloromethyl)-1,2-dihydroquinoline **3f** was obtained in 51% yield. When electron donating group such as dimethoxy group was substituted, yield of three-component product would be decreased (Scheme 2).



Scheme 2. Reaction of quinoline **2b** with 2-amino-4,5-dimethoxybenzoic acid **1b** and chloroform

Since large scale synthesis of 2-trichloromethyl-1,2-dihydroquinolines **3** was accomplished, we have interested in the reaction of these compounds. Kobayashi et al. and Hisaeda et al. reported that (trichloromethyl)benzene was easily converted to benzoic acid or esters.[10] Basic dehydrochlorination and hydrolysis of trichloromethyl group were also reported by Back et al. and Xu et al. (Figure 2).[11]

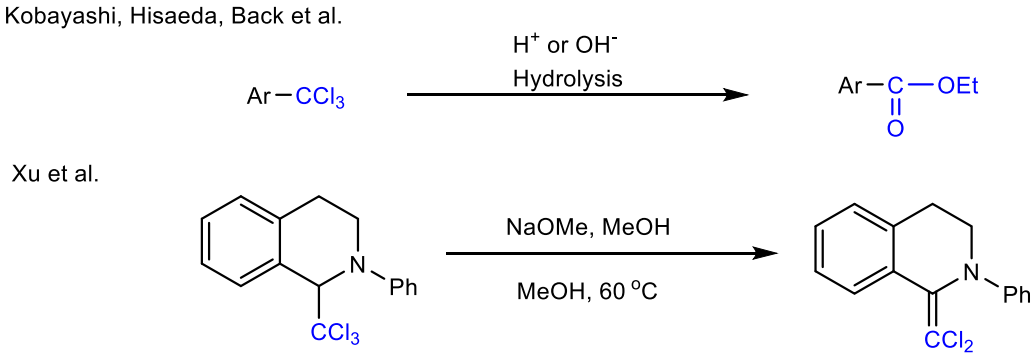
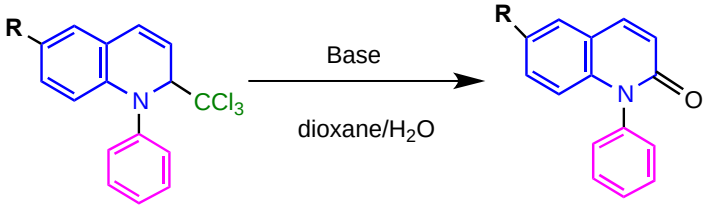


Figure 2. The reported examples for the reaction of trichlorides

Thus, we have tried the reaction of dihydroquinoline **3** with aqueous base whether dehydrochlorination or hydrolysis would proceed. When DBU and K_2CO_3 were treated with **3a** in refluxing dioxane, no reaction took place (Table 1, Entry1 and 2). When NaOH was used as a base (rt, 12 h) in dioxane/H_2O (8:1), 1-phenylquinolin-2-one **4a** was isolated in 15% yield (Entry 3). By using KOH as a base at this temperature, yield of quinolinone **4a** was improved to 36% (Entry 4). Finally, when the reaction was carried out in refluxing dioxane-H_2O (8:1) for 6 h, quinolinone **4a** was obtained in 79% yield (Entry 5).

6-Methyldihydroquinoline **3c** also reacted with KOH under these conditions to afford quinolinone **4c** in 59% yield along with small amount of 4-quinolinone derivative (Entry 6).

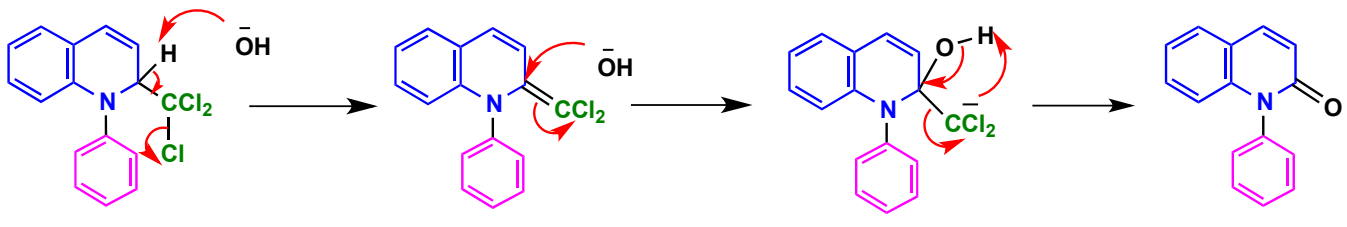
Table 1. Reaction of 1-Phenyl-1,2-dihydroquinoline **3** with Bases



3 **4**

Entry	**3**	R	Base	Temp.	**4**	Yield/%
1	**3a**	H	DBU	reflux	**4a**	0
2	**3a**	H	K_2CO_3	reflux	**4a**	0
3	**3a**	H	NaOH	rt	**4a**	15
4	**3a**	H	KOH	rt	**4a**	36
5	**3a**	H	KOH	reflux	**4a**	79
6	**3c**	Me	KOH	reflux	**4c**	59

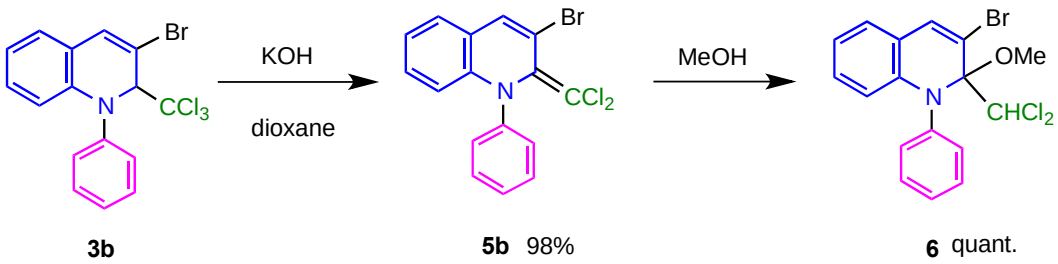
This result is quite different from the reported ones.[10,11] How can we explain these phenomena? Kobayashi, Hisaeda, Back et al. have reported the synthesis of carboxylic acid or esters from the corresponding trichlorides without any α-hydrogens such as (trichloromethyl)benzene, which resulted in the simple hydrolysis. Since dihydroquinolines **3** have α-hydrogens, dehydrochlorination is more likely to proceed than hydrolysis. Probably, cyclic amide is more stable than the corresponding dichloroalkene derivatives **5** under these conditions, quinolinones **4** would be final isolable products. Thus, reaction might proceed as follows: Initially formed dichloroalkene **5a** was attacked by OH^- to give the corresponding alcohol, which further attacked by OH^- to give the corresponding quinolinone **4a** (Scheme 3).



3a **5a** **4a**

Scheme 3. Plausible reaction mechanism on the formation of quinolinone **4**

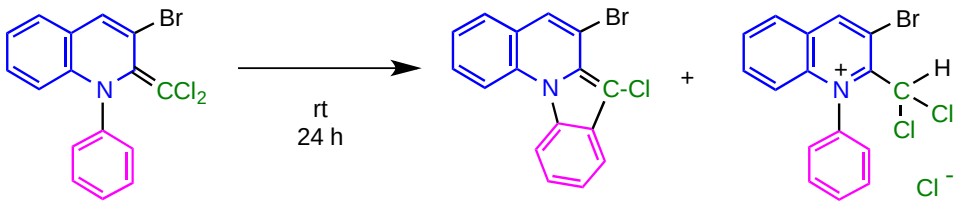
To confirm the formation of dichloroalkene derivative **5**, the reaction of 3-bromodihydroquinoline **3b** with KOH was carried out in dioxane, which resulted in the formation of dichloromethylene intermediate **5b**. Compound **5b** was further reacted with methanol to afford methoxy adduct **6b** in almost quantitative yield (Scheme 4). However, isolation of **5a** was failed due to its instability toward aqueous KOH.



3b **5b** 98% **6** quant.

Scheme 4. Reaction of **3b** with KOH

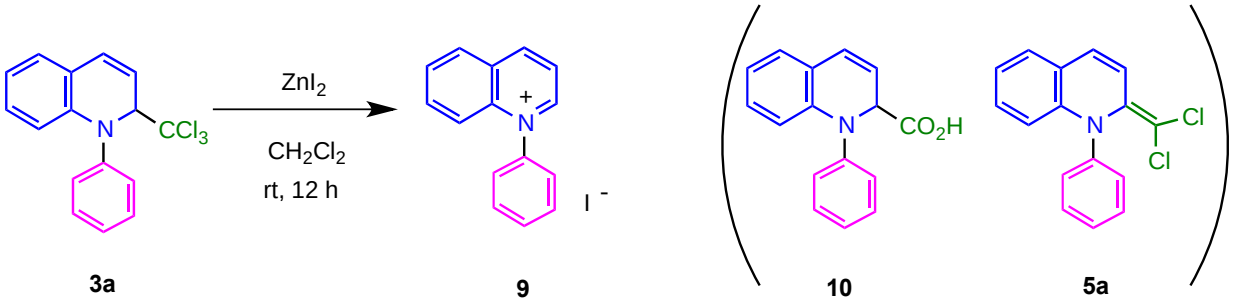
Interestingly, isolated dichloroalkene **5b** was relatively unstable, which easily disproportionated to give indoloquinoline **7** and quinolinium chloride **8** upon standing for 24 h (Scheme 5).



5b **7** 45% **8** 40%

Scheme 5. Disproportionation of **5b**

To confirm the stability of trichloromethyl group of dihydroquinoline **3**, we then investigated the reaction of **3a** under acidic conditions. Treatment of dihydroquinoline **3a** with trifluoromethanesulfonic acid at 60 °C in $CHCl_3$ resulted in a complex mixture, whereas when ZnI_2 was used as a Lewis acid, 1-phenylquinolinium iodide **9** was obtained in 64% yield, which clearly showed that quinolinium iodide **9** would be more stable than 1,2-dihydroquinoline-2-carboxylic acid **10** or 2-dichloromethylene-1,2-dihydroquinoline **5a** (Scheme 6).



3a **9** **10** **5a**

Scheme 6. Reaction of dihydroquinoline **3a** with ZnI_2

In summary, we have accomplished the three-component reaction of benzyne prepared from anthranilic acid **1** with quinolines **2** and chloroform in gram scale. The obtained 1-phenyl-2-trichloromethyldihydroqinolines **3a** and **3c** reacted with aqueous KOH to afford the corresponding 2-quinolinone derivatives **4**, which indicated that the direct two-step synthesis of 1-phenyl-2-quinolinones **4** from quinoline **2** was achieved. When dihydroquinoline **3b** was used as a reactant, dichloromethylene derivative **5b** was formed, however, which was easily disproportionated to give indoloquinoline **7** and quinolinium chloride **8**. Reaction of dihydroquinoline **3a** with ZnI_2 as a Lewis acid gave the corresponding 1-phenylquinolinium iodide **9**.

EXPERIMENTAL

Reaction of Quinoline 2a with benzyne prepared from anthranilic acid 1 and chloroform

To a refluxing suspension of quinoline **2a** (0.65 g, 5.0 mmol) and isoamyl nitrite (1.46 g, 12.5 mmol), and MS 4A (2 g) in $CHCl_3$ (10 mL) was added dropwise a solution of anthranilic acid **1** (1.37 g, 10 mmol) in dioxane (10 mL) over 2 h. After refluxing for 0.5 h, the reaction mixture was filtered and evaporated to give a pale brown oil, which was chromatographed over hexane to give 1-phenyl-2-(trichloromethyl)-1,2-dihydroquinoline **3a** (1.44 g, 4.45 mmol, 89%).

1-Phenyl-2-(trichloromethyl)-1,2-dihydroquinoline **3a**: colorless oil (lit,[7] yellow solid). ^{1}H NMR (400MHz, $CDCl_3$) δ = 4.98 (d, 1H, *J* = 6 Hz, CH), 6.12 (dd, 1H, *J* = 6 and 10 Hz, =CH), 6.96 - 6.88 (m, 2H), 7.00 (d, 1H, *J* = 8 Hz, ArH), 7.13 - 7.07 (m, 2H), 7.16 (d, 1H, *J* = 7 Hz, ArH), 7.28 (t, 2H, *J* = 8 Hz, ArH), 7.38 (d, 2H, *J* = 8 Hz, ArH). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 75.2, 104.3, 118.5, 121.6, 121.8, 124.8, 125.0, 125.5, 127.2, 128.9, 129.3, 130.4, 142.0, 150.1. MS (EI): Calcd for $C_{16}H_{12}Cl_3N$ *m/z* = 325.0 (M^+). Found; *m/z* = 325.1 (M^+).

3-Bromo-1-phenyl-2-(trichloromethyl)-1,2-dihydroquinoline **3b**: colorless crystals, mp 126-127 °C. ^{1}H NMR (400MHz, $CDCl_3$) δ = 5.24 (s, 1H, CH), 7.02 (dt, 1H, *J* = 1 and 7 Hz, ArH), 7.16 - 7.09 (m, 2H), 7.23 - 7.16 (m, 2H), 7.36 - 7.28 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 79.9, 102.5, 106.7, 122.8, 122.9, 123.0, 124.6, 126.3, 127.3, 129.2, 133.0, 139.0, 149.1. Anal. Calcd for $C_{16}H_{11}BrCl_3N$: C, 47.62; H, 2.75; N, 3.47%. Found; C, 47.66; H, 2.71; N, 3.40%.

6-Methyl-1-phenyl-2-(trichloromethyl)-1,2-dihydroquinoline **3c**: colorless crystals, mp 92-94 °C. ^{1}H NMR (400MHz, $CDCl_3$) δ = 2.30 (s, 3H, CH_3), 4.95 (dd, 1H, *J* = 1 and 6 Hz, CH), 6.13 (dd, 1H, *J* = 6 and 10 Hz, =CH), 6.91 (d, 1H, *J* = 10 Hz, =CH), 7.01 - 6.93 (m, 3H), 7.09 (tt, 1H, *J* = 1 and 7 Hz, ArH), 7.28 (t, 2H, *J* = 8 Hz, ArH), 7.38 - 7.33 (m, 2H), 7.36 (dd, 2H, *J* = 1 and 9 Hz, ArH). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 20.8, 75.2, 104.3, 118.7, 122.1, 124.1, 124.3, 125.7, 127.5, 129.3, 129.7, 130.4, 131.5, 139.3, 150.4. Anal. Calcd for $C_{17}H_{14}Cl_3N$: C, 60.29; H, 4.17; N, 4.14%. Found; C, 60.28; H, 4.40; N,

4.08%.

2-Phenyl-1-(trichloromethyl)-1,2-dihydroisoquinoline **3d**: colorless crystals, mp 130-131 °C (lit.[7] white solid). ^{1}H NMR (400MHz, $CDCl_3$) δ = 5.81 (d, 1H, *J* = 1 Hz, CH), 6.12 (d, 1H, *J* = 7 Hz, =CH), 6.78 (dd, 1H, *J* = 1 and 8 Hz, =CH), 7.05 (tt, 1H, *J* = 1 and 7 Hz, ArH), 7.30 - 7.19 (m, 4H), 7.41 - 7.31 (m, 3H), 7.47 (d, 1H, *J* = 8 Hz, ArH). ^{13}C NMR (101 MHz, $CDCl_3$) δ= 74.8, 105.0, 108.9, 118.8, 122.8, 123.7, 124.4, 126.0, 129.3, 129.4, 129.5, 130.2, 133.4, 147.0. Anal. Calcd for $C_{16}H_{12}Cl_3N$: C, 59.20; H, 3.73; N, 4.31%. Found; C, 59.10; H, 3.95; N, 4.23%.

3-Bromo-1-(2-chlorophenyl)-2-(trichloromethyl)-1,2-dihydroquinoline **3e**: Colorless crystals, mp 102-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.09 (s, 1H, CH), 6.74 (d, 1H, *J* = 8 Hz, ArH), 6.86 (dt, 1H, *J* = 1 and 7 Hz, ArH), 7.14 - 7.06 (m, 2H), 7.35 - 7.29 (m, 2H), 7.37 (dt, 1H, *J* = 2 and 8 Hz, ArH), 7.50 (dd, 1H, *J* = 2 and 8 Hz, ArH), 8.02 (d, 1H, *J* = 7 Hz, ArH). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 79.4, 103.7, 104.5, 116.1, 120.5, 123.9, 126.7, 127.0, 129.2, 129.2, 131.3, 133.6, 133.8, 136.0, 140.4, 143.6. MS (ESI): Calcd for $C_{16}H_{10}BrCl_4N$ *m/z* = 436.9 (M). Found; *m/z* = 437.8 ($M+H^+$).

3-Bromo-1-(3',4'-dimethoxyphenyl)-2-(trichloromethyl)-1,2-dihydroquinoline **3f**: colorless crystals, mp 125-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.81 (s, 3H), 3.86 (s, 3H), 5.17 (s, 1H), 6.79 (d, 1H, *J* = 8 Hz), 6.90 (d, 2H, *J* = 16 Hz), 6.93 - 6.86 (m, 2H), 6.96 (dt, 1H, *J* = 1 and 8 Hz), 7.04 (d, 1H, *J* = 8 Hz), 7.21 - 7.13 (m, 2H), 7.35 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 56.0, 56.1, 80.6, 102.6, 105.2, 109.2, 111.4, 117.3, 121.6, 122.0, 126.1, 126.2, 129.0, 133.0, 140.3, 142.9, 147.0, 149.2. Anal. Calcd for $C_{18}H_{15}BrCl_3NO_2$: C, 46.64; H, 3.26; N, 3.02%. Found; C, 46.37; H, 3.20; N, 3.05%.

Reaction of dihydroquinoline 3a with KOH in dioxane

A solution of KOH (0.54 g, 85%, 8.1 mmol) and dihydroquinoline **3a** (0.16 g, 0.50 mmol) in dioxane/water (8:1, 9 mL) was refluxed for 12 h. The reaction mixture was poured into water (15 mL), and extracted with CH_2Cl_2 (5 mL x 3), which was dried over sodium sulfate, filtered, and evaporated to give a dark brown oil, which was chromatographed over silica gel by elution with CH_2Cl_2:MeOH (30:1) to give a pale brown oil of 1-phenylquinoline-2-(1*H*)-4-one **4a** (0.087 g, 0.39 mmol).

1-Phenylquinolin-2(1*H*)-one **4a**: dark brown oil (lit.[12] brown solid), ^{1}H NMR (400MHz, $CDCl_3$) δ = 6.65 (1H, d, *J* = 9 Hz, ArH), 6.78 (1H, d, *J* = 9 Hz, CH), 7.20 (1H, t, *J* = 6 Hz, ArH), 7.27 - 7.36 (3H, m, ArH), 7.53 (1H, dd, *J* = 7 Hz, ArH), 7.56 - 7.63 (3H, m, ArH), 7.78 (1H, d, *J* = 9 Hz, CH). ^{13}C NMR (101 MHz, $CDCl_3$): δ= 115.9, 120.3, 122.2, 122.3, 128.3, 128.9, 130.2, 130.2, 137.7, 139.8, 141.2, 162.2. MS (ESI): Calcd for $C_{15}H_{11}NO$ m/z = 221.1 (M^+). Found; *m/z* = 222.0 ($M+H^+$).

Reaction of 6-methyl derivative **3c** was carried out in a similar manner.

6-Methyl-1-phenylquinolin-2(1*H*)-one **4c**: pale brown oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ= 2.39 (3H, s, CH_3), 6.55 (1H, d, *J* = 8 Hz, CH), 6.76 (1H, d, *J* = 10 Hz, CH), 7.14 (1H, dd, *J* = 2, 9 Hz, CH), 7.38 (1H,

s, CH), 7.49 - 7.63 (5H, m), 7.72 (1H, d, *J* = 10 Hz, CH). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 20.5, 115.9, 120.3, 122.2, 128.0, 128.8, 130.2, 131.4, 131.9, 137.8, 139.2, 139.6, 162.3. HRMS (ESI): Calcd for $C_{16}H_{13}NO$ *m/z* = 236.1070 ($M+H^+$). Found; *m/z* = 236.1065 ($M+H^+$).

Reaction of 3b with KOH in dioxane

To a solution of dihydroquinolne **3b** (403 mg, 1.0 mmol) in dioxane (5 mL) was added KOH (560 mg, 85%, 8.5 mmol) in water (0.6 mL). After being refluxed for 12 h, the solution was poured into water and extracted with CH_2Cl_2, which was dried over sodium sulfate, filtered and evaporated to give 3-bromo-2-(dichloromethylene)-1-phenyl-3-bromo-1,2-dihydroquinoline **5b** (360 mg, 0.98 mmol).

3-Bromo-2-(dichloromethylene)-1-phenyl-1,2-dihydroquinoline **5b**: yellow oil. ^{1}H NMR (400 MHz, DMSO) δ = 7.08 - 7.21 (m, 4H), 7.31 - 7.40 (m, 3H), 7.40 - 7.49 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 105.4, 120.8, 121.2, 124.0, 124.2, 126.3, 127.5, 129.1, 129.4, 133.7, 134.3, 139.5, 144.2. HRMS (EI): Calcd for $C_{16}H_{16}BrCl_2N$ *m/z* = 364.9374 (M^+). Found; *m/z* = 364.9362 (M^+).

Reaction of 5b with methanol

A solution of **5b** (360 mg, 0.98 mmol) in MeOH was stirred for 1day. After finishing the reaction, the solution was evaporated to give compound **6** (390 mg, 0.98 mmol).

3-Bromo-2-(dichloromethyl)-2-methoxy-1-phenyl-1,2-dihydroquinoline **6**: brown crystals, mp 127~129 °C. ^{1}H NMR (400 MHz, DMSO) δ = 3.39 (s, 3H), 5.92 (d, 1H, *J* = 10 Hz), 6.26 (s, 1H), 6.75 (dt, 1H, *J* = 1 and 7 Hz), 7.02 (ddd, 1H, *J* = 2, 7, and 9 Hz), 7.23 (dd, 1H, *J* = 2 and 8 Hz), 7.63 - 7.27 (m, 5H), 7.78 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 51.6, 74.4, 93.5, 110.4, 112.7, 116.7, 118.5, 127.5, 128.8, 129.7 (br), 130.0, 131.3 (br), 137.2, 138.3, 143.4. Anal. Calcd for $C_{17}H_{14}BrCl_2NO$: C, 51.16; H, 3.54; N, 3.51%. Found; C, 51.38; H, 3.44; N, 3.44%.

Disproportionation of 5b

Isolated **5b** was standing for 24 h at rt, 6-bromo-7-chloroindolo[1,2-*a*]quinoline **7** and 3-bromo-2-(dichloromethyl)-1-phenylquinolin-1-ium chloride **8** were obtained in 45% and 40% yields, respectively. 6-Bromo-7-chloroindolo[1,2-*a*]quinoline **7**: yellow crystals, mp 98~99 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31 (t, 1H, *J* = 7 Hz, ArH), 7.45 (s, 1H, ArH), 7.53 - 7.46 (m, 2H), 7.54 (dd, 1H, *J* = 2 and 8 Hz, ArH), 7.59 (ddd, 1H, *J* = 2, 7, and 9 Hz, ArH), 7.96 - 7.92 (m, 1H), 8.39 (d, 1H, *J* = 8 Hz, ArH), 8.47 (d, 1H, *J* = 8 Hz, ArH). ^{13}C NMR (101 MHz, DMSO) δ = 102.8, 110.5, 114.2, 115.5, 119.4, 122.8, 123.6, 123.9, 124.2, 127.4, 128.1, 128.4, 128.9, 129.3, 131.4, 135.8. Anal. Calcd for $C_{16}H_9BrClN$: C, 58.13; H, 2.74; N, 4.24%. Found; C, 57.80; H, 2.71; N, 4.18%.

3-Bromo-2-(dichloromethyl)-1-phenylquinolinium chloride **8**: colorless crystals, mp 210 °C. ^{1}H NMR (400 MHz, CD_3OD) δ = 7.17 (s, 1H, $CHCl_2$), 7.35 (d, 1H, *J* = 10 Hz, ArH), 7.82 (d, 2H, *J* = 8 Hz, ArH), 8.07 - 7.92 (m, 3H), 8.15 (t, 1H, *J* = 8 Hz, ArH), 8.23 (t, 1H, *J* = 8 Hz, ArH), 8.56 (d, 1H, *J* = 8 Hz, ArH),

10.01 (s, 1H, ArH). ^{13}C NMR (101 MHz, CD_3OD) δ = 66.0, 117.4, 122.5, 127.5, 130.8, 131.3, 132.9, 133.2, 134.3, 138.2, 139.2, 141.2, 151.4, 157.1. Anal. Calcd for $C_{16}H_{11}BrCl_3N$: C, 47.62; H, 2.75; N, 3.47%. Found; C, 47.31; H, 2.80; N, 3.40%.

Reaction of 3a with ZnI_2 in dichloromethane

A solution of ZnI_2 (0.32 g, 1.0 mmol) and dihydroquinoline **3a** (0.16 g, 0.50 mmol) in CH_2Cl_2 (5 mL) was stirred for 12 h at rt. The reaction mixture was concentrated to 1 mL and Et_2O (10 mL) was added to this solution. The precipitate was filtered to give dark brown solid, which was washed with ether to give 1-phenylquinolin-1-ium iodide **9** (0.11 g, 0.32 mmol).

1-Phenylquinolin-1-ium iodide **9**: dark brown solid (lit.[13]). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71 (1H, d, *J* = 9 Hz, CH), 7.75 - 7.83 (5H, m), 8.04 (1H, t, *J* = 8 Hz, CH), 8.11 (1H, t, *J* = 8 Hz, CH), 8.40 (1H, dd, *J* = 6 and 9 Hz, CH), 8.48 (1H, d, *J* = 9 Hz, CH), 9.30 - 9.33 (2H, m). ^{13}C NMR (101 MHz, $CDCl_3$): 119.9, 123.0, 126.6, 130.1, 131.0, 131.1, 131.2, 132.3, 136.3, 139.4, 139.5, 149.0, 149.2. MS (EI): Calcd for $C_{15}H_{12}N$ *m/z* = 206.1 (M^+). Found; *m/z* = 206.1 (M^+).

REFERENCES

1. Dehydrobenzene and cycloalkyne, W. R. Hoffmann, Academic Press, New York, 1967; Encyclopedia of Reagents for Organic Synthesis, ed. by L. A. Paquette, 1, 429-432, John & Wiley, Singapore, 2009; For reviews, C. Wentrup, *Aust. J. Chem*., 2010, **63**, 979; K. Okuma, *Heterocycles*, 2012, **85**, 515; P. M. Tadros and B. M. Stolz, *Chem. Rev.*, 2012, **112**, 3550.
2. M. Stiles and R. G. Miller, *J. Am. Chem. Soc*., 1960, **82**, 3802; L. Friedman and F. M. Logullo, *J. Am. Chem. Soc.*, 1963, **85**, 1549.
3. Y. Himeshima, T. Sonoda, and H. Kobayashi, *Chem. Lett.*, 1983, 1211; T. Kitamura and M. Yamane, *J. Chem. Soc., Chem. Commun.*, 1995, 983.
4. M. Jeganmohan and C.-H. Cheng, *Chem. Commun*., 2006, 2454.
5. P. Liu, M. Lei, and L. Hu, *Tetrahedron*, 2013, **69**, 10405.
6. A. Bhunia, D. Porwal, R. Gonnade, and A. T. Biju, *Org. Lett*., 2013, **15**, 4620.
7. J. Tan, B. Liu, and S. Su, *Org. Chem. Front.*, 2018, **5**, 3093.
8. K. Okuma, Y. X. Qu, N. Fujiie, and N. Nagahora, *Chem. Lett.*, 2020, **49**, 446.
9. T. Kametani, A. Ujiie, K. Takahashi, T. Nakano, T. Suzuki, and K. Fukumoto, *Chem. Pharm. Bull.*, 1973, **21**, 766.
10. M. Kobayashi and R. Kiritani, *Bull. Chem. Soc. Jpn*., 1966, **39**, 1782; H. Shimakoshi and Y. Hisaeda, *Angew. Chem. Int. Ed*., 2015, **54**, 15439.
11. C. Xu, Z. Zhu, Z. Jing, B. Gao, L. Zhao, and W.-K. Dong, *J. Org. Chem.*, 2019, **84**, 2234; D. Gao and T. G. Back, *Synlett*, 2013, **24**, 389.

12. R. Kancherla, T. Naveen, and D. Maiti, *Chem. Eur. J.*, 2015, **21**, 8360.
13. N. E. Shchepina, V. V. Avrorin, G. A. Badun, G. A. Alexandrova, S. E. Ukhanov, V. M. Fedoseev, S. B. Lewis, and I. I. Boiko, *Chem. Heterocycl. Compd*., 2009, **45**, 796.