

An Efficient Approach for the Esterification of 5-Chloroquinolin-8-ol through Steglich Reaction and their Antioxidant Applications

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Esterification of organic molecules offers a critical process for chemical modifications. Among the various methodologies, Steglich conditions gave easiest and mild pathways. O-Acylation of 5-chloro-8-hydroxyquinoline with different acylating counterparts has been investigated. Among the various catalysts used, *N,N*-dimethylpyridin-4-amine (DMAP) in the presence of *N,N'*-dicyclohexyl carbodiimide (DCC) displayed a plausible synthetic approach through the application of Steglich esterification reaction for the synthesis of 5-chloroquinolin-8-yl-benzoates (**3a-h**) with good yields. The structures of the synthesized compounds were characterized through NMR, IR and MS spectral data. In present study, 5-chloro-8-hydroxy quinoline and its derivatives (**3a-h**) bearing various substituents were investigated for their antioxidant activity by 2,2-diphenyl-1-picrylhydrazyl (DPPH) method. The findings revealed that the derivatives act as imminent candidates to be further developed as antioxidant agents.

Keywords: Steglich esterification, Acylation, 5-Chloroquinolin-8-yl-acetates, Catalysis.

INTRODUCTION

Functionalized quinoline derivatives with various side chain analogues represent an important class of heterocycles [1]. In particular, 8-hydroxyquinoline (8-HQ) and its derivatives are known for their varied bioactivities such as possession of a strong metal chelating properties [2], antitumor [3], antimalarial [4], antimicrobial activities [5]. Group transfer reactions are well-known chemical modifications or transformations in the synthetic organic chemistry [6]. One of the most studied reactions is the acetylation of alcohols [7]. There are numerous reports on attempts to improve the selectivity and efficiency of this transformation [8]. Substitution of a group on alcohol or amine is often typical due the steric-hindrance of core moiety [9,10]. Most of the studies revealed that 8-HQ reacted with electrophilic reagents at the both nitrogen and oxygen centers, which would lead to alkylated and acylated products [11].

Esterification of functional groups has a wide application in the synthetic chemistry particularly in the preparation of drug synthons to overcome the difficulties in structure activity relations (SAR) in medicinal chemistry [12]. Most of the procedures involved in the preparation of esters includes the use of

catalysts, such as silica chloride, iron chlorides, aluminium trichlorides, *etc.*, but all of these catalysts have been examined by long reaction time, less yield and side reactions, highly moisture sensitivity, less susceptibility with temperatures and product separation is highly difficult [13]. At higher temperatures or reflux conditions, sometimes there is a chance for the degradation and decomposition of reagents and products [14,15].

Very often used esterification method includes acid-catalyzed Fischer-Speier esterification, which includes use of various harsh acid catalysts to promote the synthesis [16-18]. However, the major drawback of this Fischer-Speier protocol is deviations of reactions due to acid sensitive reactants and intermediates. Steglich & Neises [19] and others [20,21] provide an alternate methodology for the esterification of functional groups in mild Reaction conditions such as utilization of *N,N'*-dicyclohexyl carbodiimide (DCC) and *N,N'*-dimethylpyridin-4-amine (DMAP) to boost the conversions. DMAP is a versatile catalyst for the group transfer modifications and extensively used for the esterification of alcohols and amines [22,23]. Currently, one of the major goals in the design of catalysts consists of finding asymmetric derivatives, which allow for an enantio-selective acetylation of racemates [24].

Wang *et al.* [25] reported the synthesis of 5-chloroquinolin-8-yl-acetate from benzoic acid and 5-chloro-8-hydroxyquinoline in the presence of triethylamine and thionyl chloride using dichloromethane as solvent with 62% yield. In present study, we quantitatively synthesized 5-chloroquinolin-8-yl-acetate derivatives in dichloromethane with DMAP in the presence of DCC as an efficient catalyst at room temperature and demonstrated that DMAP is highly efficient for the O-acylation with optimum yield.

EXPERIMENTAL

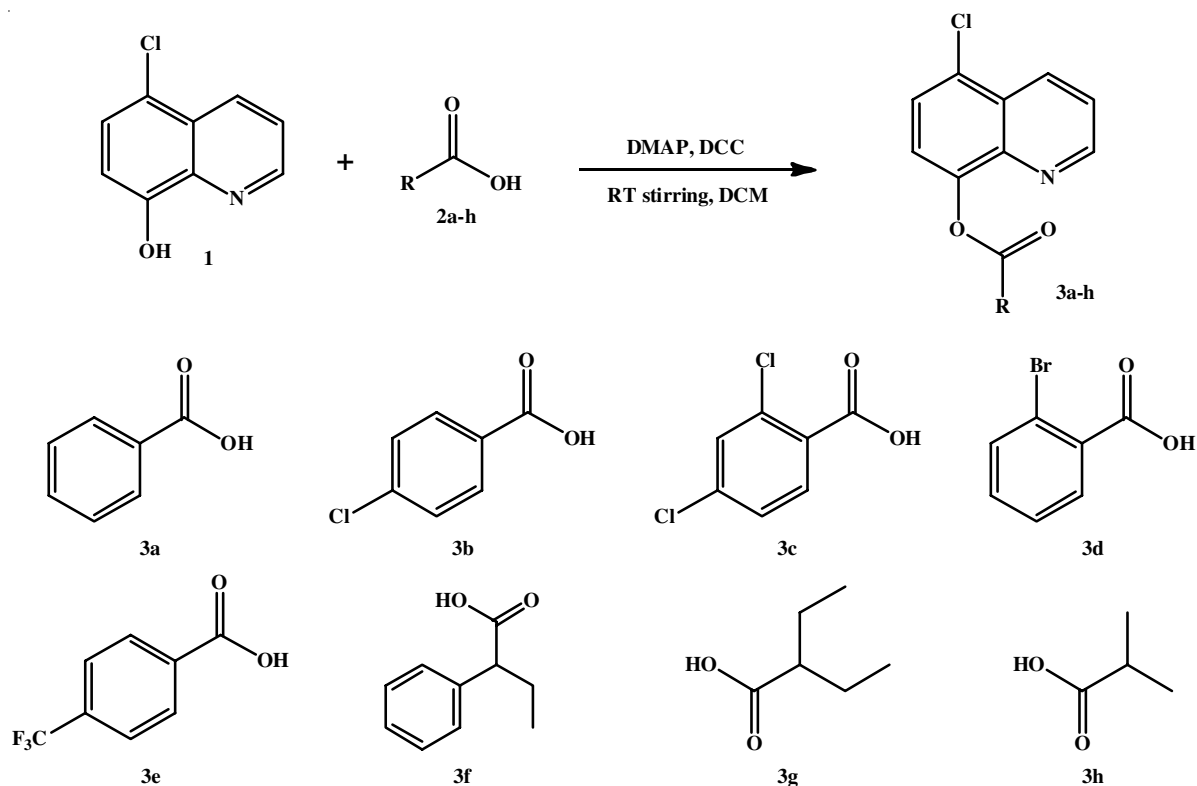
General method for synthesis of compounds (3a-h): In a 100 mL round bottom flask (RBF), an equivalent mixture of 5-chloroquinolin-8-ol (2.79 mmol) and acid reagents (2.79 mmol); DCC (4.05 mmol) and DMAP (0.027 mol) were added to 8.0 mL of dichloromethane and stirred at room temperature for 5-15 min. Progress of the reaction was monitored by TLC. After the completion of reaction, the reaction mixture was quenched with 10% cold HCl water and extracted with dichloromethane (DCM). The separated organic layer from the mother liquor was washed with 10% NaHCO₃ solution (15 mL × 2 times), followed by water wash (15 mL × 3 times) and dried over anhydrous sodium sulphate crystals (**Scheme-I**). Finally, organic layer was concentrated under reduced pressure to get desired compound and sent for analysis without further purification.

5-Chloroquinolin-8-ylbenzoate (3a): This compound was synthesized in two step process *via* acid chloride as reported by Wang *et al.* [25]. Off colourless solid, time: 5 min, yield: 98%, *m.w.*: C₁₆H₁₀NO₂Cl; m.p.: 153-155 °C. FT-IR (KBr disc,

cm⁻¹): 3095, 1739, 1276, 825; ¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.16 (t, 1H, *J* = 8.4 Hz), 7.25 (t, 1H, *J* = 7.2 Hz), 7.32 (t, 2H, *J* = 7.2 Hz), 7.42-7.48 (m, 4H, *J* = 7.2 Hz), 8.46 (d, 1H, *J* = 8.4 Hz), 8.81 (t, 1H, *J* = 2.0 Hz); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm): 121.72 (CH, C-7), 122.59 (CH, C-3), 126.33 (C, C-5, C-10), 127.45 (CH, C-6), 127.67 (CH, C-14), 129.03 (CH, C-16), 129.10 (CH, C-17), 132.02 (C, C-12, C-13), 133.64 (CH, C-4), 140.34 (CH, C-15), 141.41 (C, C-9), 146.45 (C, C-8), 151.01 (CH, C-2), 164.51 (C=O, C-11); Mass: *m/z* 284 (M+1).

5-Chloroquinolin-8-yl-4-chlorobenzoate (3b): Colourless solid, time: 5 min, yield: 97%, *m.w.*: C₁₆H₉NO₂Cl₂; m.p.: 81-82 °C. FT-IR (KBr disc, cm⁻¹): 3032, 1755, 1236, 798; ¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.49 (t, 1H, *J* = 4.4 Hz), 7.61 (d, 2H, *J* = 8.0 Hz), 7.74 (d, 2H, *J* = 8.4 Hz), 8.38 (d, 2H, *J* = 8.4 Hz), 8.45 (dd, 1H, *J*₁ = 8.4 Hz, *J*₂ = 1.4 Hz), 8.85 (dd, 1H, *J*₁ = 4.4 Hz, *J*₂ = 1.6 Hz); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm): 120.85 (CH, C-7), 122.02 (CH, C-3), 126.47 (C, C-5, C-10), 128.07 (CH, C-6), 128.84 (C, C-12), 129.66 (CH, C-14, C-16), 131.60 (CH, C-12), 132.37 (CH, C-17), 134.02 (CH, C-4), 140.12 (C, C-9), 145.10 (C, C-14), 149.95 (C, C-8), 159.78 (CH, C-2), 163.51 (C=O, C-11); Mass: *m/z* 317 (M+1).

5-Chloroquinolin-8-yl-2,4-dichlorobenzoate (3c): Off-white solid, time: 5 min, yield: 96%, *m.w.*: C₁₆H₈NO₂Cl₃; m.p.: 90-91 °C. FT-IR (KBr disc, cm⁻¹): 3032, 1755, 1236, 798; ¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.19 (s, 1H), 7.36 (dd, 1H, *J*₁ = 8.4 Hz, *J*₂ = 2 Hz), 7.47 (m, 3H), 7.60 (d, 1H, *J* = 8.4 Hz), 8.25 (d, 1H, *J* = 8.4 Hz), 8.52 (dd, 1H, *J*₁ = 8.8 Hz, *J*₂ = 1.6 Hz), 8.86 (dd, 1H, *J*₁ = 4.4 Hz, *J*₂ = 1.6 Hz); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm): 121.46 (CH, C-7), 122.61 (CH, C-3),



Scheme-I: DMAP catalyzed *o*-acylation of 5-chloroquinolin-8-yl-oate derivatives (**3a-h**); (Reaction condition: DCC, DMAP, dichloromethane, room temperature)

126.14 (CH, C-16), 127.20 (C, C-10), 127.25 (C, C-5), 127.44 (CH, C-6), 129.19 (C, C-12), 131.28 (C, C-14), 133.19 (CH, C-4), 133.72 (CH, C-17), 136.04 (C, C-13), 139.24 (C, C-9), 141.61 (C, C-15), 146.36 (C, C-8), 151.15 (CH, C-2), 163.02 (C=O, C-11); Mass: m/z 352 (M+1).

5-Chloroquinolin-8-yl-2-bromobenzoate (3d): Off-white solid, time: 6 min, yield: 92%; m.w.: $C_{16}H_9NO_2BrCl$, m.p.: 132-134 °C. FT-IR (KBr disc, cm^{-1}): 3097, 1737, 1274, 535; 1H NMR (400 MHz, $CDCl_3$) (δ , ppm): 7.42-7.50 (m, 4H), 7.60 (d, 1H, $J = 8.0$ Hz), 8.19 (d, 2H, $J = 8.4$ Hz), 8.54 (dd, 1H, $J_1 = 8.4$ Hz, $J_2 = 1.6$ Hz), 8.85 (d, 1H, $J = 2.8$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) (δ , ppm): 121.72 (CH, C-7), 122.59 (CH, C-3), 126.33 (C, C-13), 127.45 (CH, C-16), 127.67 (CH, C-6), 129.3 (C, C-12), 132.02 (CH, C-4), 133.62 (CH, C-17), 140.34 (CH, C-15), 141.42 (C, C-9), 146.45 (C, C-8), 151.01 (CH, C-2), 165.1 (C=O, C-11); Mass: m/z 362 (M+1).

5-Chloroquinolin-8-yl-4-(trifluoromethyl)benzoate (3e): Colourless solid, time: 10 min, yield: 89%, m.w.: $C_{17}H_9NO_2ClF_3$; m.p.: 84-86 °C. FT-IR (KBr disc, cm^{-1}): 3059, 1755, 1276, 829; 1H NMR (400 MHz, $CDCl_3$) (δ , ppm): 7.49 (t, 1H, $J = 4.4$ Hz), 7.61 (d, 2H, $J = 8.0$ Hz), 7.74 (d, 2H, $J = 8.4$ Hz), 8.38 (d, 2H, $J = 8.4$ Hz), 8.45 (dd, 1H, $J_1 = 8.4$ Hz, $J_2 = 1.2$ Hz), 8.85 (dd, 1H, $J_1 = 4.4$ Hz, $J_2 = 1.6$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) (δ , ppm): 121.56 (CH, C-7), 122.63 (CH, C-3), 124.99 (C, C-18), 126.27 (CH, C-14, C-16), 127.47 (C, C-5, C-10), 129.28 (CH, C-6), 131.01 (CH, C-12), 132.53 (CH, C-17), 133.50 (CH, C-13), 134.99 (CH, C-4), 146.41 (C, C-9), 151.05 (CH, C-2), 164.17 (C=O, C-11); Mass: m/z 352 (M+1).

5-Chloroquinolin-8-yl-2-phenylbutanoate (3f): Off-white solid, time: 5 min, yield: 90%; m.w.: $C_{19}H_{16}NO_2Cl$; m.p.: 93-94 °C. FT-IR (KBr disc, cm^{-1}): 3030, 1707, 1280, 783; 1H NMR (400 MHz, $CDCl_3$) (δ , ppm): 0.99-1.04 (m, 3H), 1.89-1.96 (m, 1H), 2.27-2.34 (m, 1H), 3.91 (t, 1H, $J = 7.6$ Hz), 7.16 (t, 1H, $J = 8.4$ Hz), 7.25 (t, 1H, $J = 7.2$ Hz), 7.32 (t, 2H, $J = 7.2$ Hz), 7.42-7.47 (m, 4H), 8.46 (dd, 1H, $J = 8.4$ Hz), 8.82 (t, 1H, $J = 2.4$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) (δ , ppm): 12.13 (CH₃, C-20), 27.02 (CH₂, C-19), 53.36 (CH, C-12), 121.25 (CH, C-7), 122.42 (CH, C-3), 126.06 (CH, C-16), 127.25 (CH, C-10, C-13), 127.37 (CH, C-14, C-18), 128.35 (CH, C-15, C-17), 128.65 (CH, C-6), 133.05 (CH, C-4), 138.74 (CH, C-5), 141.80 (CH, C-9), 146.71 (C, C-8), 150.84 (CH, C-2), 172.71 (C=O, C-11); Mass: m/z 326 (M+1).

5-Chloroquinolin-8-yl-2-ethylbutanoate (3g): Semi-solid, time: 12 min, yield: 94%; ($C_{15}H_{16}NO_2Cl$). FT-IR (KBr disc, cm^{-1}): 3062, 1707, 1282, 783. 1H NMR (400 MHz, $CDCl_3$) (δ , ppm): 1.01 (t, 6H, $J = 7.2$ Hz), 1.40-1.69 (m, 4H), 2.54-2.59 (m, 1H), 7.20 (d, 1H, $J = 8.4$ Hz), 7.39 (dd, 1H, $J_1 = 8.64$ Hz, $J_2 = 2.0$ Hz), 7.47 (dd, 1H, $J_1 = 7.6$ Hz, $J_2 = 1.6$ Hz), 8.42 (dd, 1H, $J_1 = 7.6$ Hz, $J_2 = 1.6$ Hz), 8.81 (t, 1H, $J = 2.0$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) (δ , ppm): 11.83 (CH₃, C-14, C-16), 25.03 (CH₂, C-15, C-13), 48.70 (CH, C-12), 121.50 (CH, C-7), 122.42 (CH, C-3), 127.28 (CH, C-6), 127.53 (C, C-10), 128.56 (CH, C-4), 133.11 (CH, C-5), 141.85 (CH, C-9), 146.71 (C, C-8), 150.81 (CH, C-2), 174.85 (C=O, C-11); Mass: m/z 278 (M+1).

5-Chloroquinolin-8-yl isobutyrate (3h): Pale yellow coloured liquid, time: 15 min, yield: 92%; m.w.: $C_{13}H_{12}NO_2Cl$;

FT-IR (KBr disc, cm^{-1}): 3068, 1280, 783. 1H NMR (400 MHz, $CDCl_3$) (δ , ppm): 1.34 (s, 3H), 2.97 (m, 1H), 7.26 (d, 1H, $J = 8.4$ Hz), 7.41 (dd, 1H, $J_1 = 8.4$ Hz, $J_2 = 4$ Hz), 7.50 (d, 1H, $J = 8$ Hz), 8.44 (d, 1H, $J = 8.8$ Hz), 8.83 (d, 1H, $J = 4.4$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) (δ , ppm): 19.20 (CH₃, C-13, C-14), 34.18 (CH, C-12), 121.40 (CH, C-7), 122.46 (CH, C-3), 126.16 (CH, C-6), 127.33 (C, C-10), 128.59 (CH, C-4), 133.13 (C, C-5), 141.86 (C, C-9), 148.61 (CH, C-8), 150.95 (CH, C-2), 175.87 (C=O, C-11); Mass: m/z 250 (M+1).

Biological screening

Antioxidant assay-DPPH radical scavenging assay: In present study, 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay was performed for 5-chloroquinolin-8-yl-acetates (**3a-h**). Compounds **3a-h**, 1 mg/mL were dissolved in methanol, mixed with freshly prepared 1 mL of 0.2 mM DPPH in methanol and the final volume was adjusted to 5 mL. Mixtures were vigorously shaken and left for 30 min in dark. The absorbance of ascorbic acid and compounds **3a-h** were measured at 517 nm and 1 mL of 0.2 mM DPPH diluted in 4 mL of methanol was used as control. The IC_{50} value represented as the concentration of compound that causes 50% of growth inhibition. The percentage of DPPH radical scavenging activity (%) of sample was calculated as follows:

$$\text{Inhibition (\%)} = \frac{A_b - A_s}{A_b} \times 100$$

where A_b = absorption of blank sample; A_s = absorption of sample.

RESULTS AND DISCUSSION

In current study, the esterification of 5-chloroquinolin-8-ol through Steglich reaction was conducted with good yield. The synthetic procedure was optimized in such way that no further purification was needed. These formations of compounds are confirmed by IR, NMR and mass spectral data.

In the quest to improve the reaction conditions, we have chosen compound **3a** as reference and optimized the procedure with different catalysts such as 2-methylpyridine, imidazole, pyrrolidine, *N*-methyl pyrrolidine, DMAP and DCC. Among various catalysts, DMAP was found to be a proficient catalyst for the synthesis of 5-chloroquinolin-8-yl-benzoate (**3a**) with good yield (98%) in a lesser time (Table-1) by acting as an acyl transfer reagent, leading to ester formation.

TABLE-1
OPTIMIZATION STUDIES FOR THE SYNTHESIS
OF COMPOUND **3a** USING DIFFERENT
ORGANOCATALYSIS AT ROOM TEMPERATURE

Catalyst	Time (h)	Yield (%)
2-Methylpyridine	12	38
Imidazole	8	10
Pyrrolidine	24	43
NMP	12	36
DMAP	0.15-0.30	98
L-Proline	6	60

Reaction condition: DCC (4.05 mmol), compound **1** (2.79 mmol), compound **2** (2.79 mmol), DMAP (0.027 mmol), dichloromethane (8.0 mL), room temperature.

Solvent optimization studies were also carried out with various solvents such as acetone, acetonitrile, chloroform, ethanol, dimethylformamide, tetrahydrofuran and dichloromethane (Table-2). Among the above solvents screened for the synthesis, dichloromethane with DMAP in the presence of DCC were found to be mild, effective and observed that the reaction was completed in less time.

Solvent	Yield (%)
Ethanol	No reaction
Acetonitrile	70
DMF	75
Acetone	58
Chloroform	85**
THF	82
Dichloromethane	98

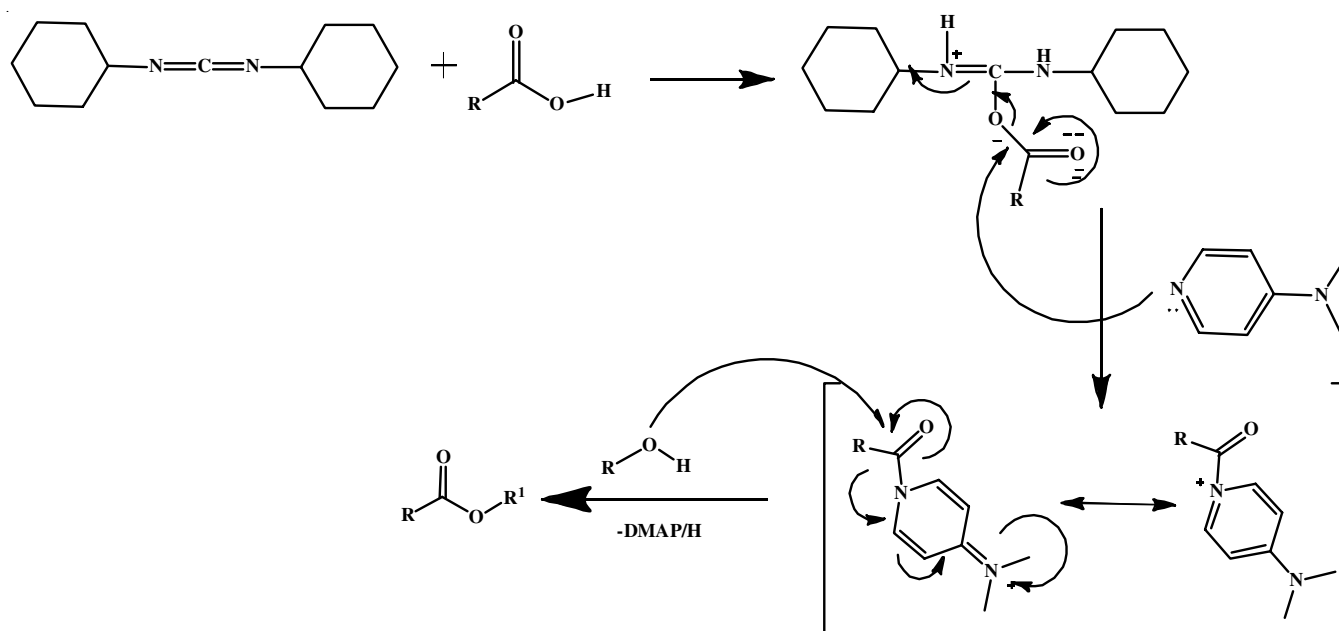
In the reaction of synthesis, at first DCC attacks on acid followed by DMAP and then upon alcohol, which leads to the formation of target molecules (**Scheme-II**). In this study, 5-chloroquinolin-8-ol is converted to 5-chloroquinolin-8-yl-benzoate when treated with acids in the presence of DCC and DMAP and the synthesized compounds were obtained 89-98%

yield in 5-15 min. The aforementioned process appears to be very similar to the Steglich esterification application and it was the first of its kind. However, in Steglich esterification alcohols to esters was synthesized in the presence of DCC, DMAP treated with acids.

DPPH assay: DPPH assay was performed for 5-chloroquinolin-8-yl-acetates (**3a-h**) to estimate the radical scavenging properties. The absorbance of the standard ascorbic acid and synthesized compounds **3a-h** were measured at 517 nm and the results obtained are tabulated in Table-3. Among the compounds screened, compounds **3g** and **3h** has exhibited percentage inhibition of 81.94 and 80.39 on par with the standard. All readings were triplicate to check the accuracy. Results were compared with the activity of standard, L-ascorbic acid.

Conclusion

In conclusion, an efficient strategy for the esterification of 5-chloro-8-hydroxyquinoline using DMAP as catalyst, DCM as solvent at room temperature was carried out. In spite of the mild reaction conditions, it is an easy process with excellent yields offering a significant advantage for the synthesis. This process avoids high temperature and metal free environments. It has been established that DMAP alone or mixed with triethylamine is an excellent acylation catalyst, with superior activity to pyridine. Among the synthesized molecules, **3a**, **3e**, **3f**, **3g** and **3h** displayed the optimum antioxidant properties.



Scheme-II: Plausible mechanism for the synthesis of 5-chloroquinolin-8-yl-benzoate derivatives (**3a-h**)

Conc. (μL)	Inhibition (%)								Ascorbic acid
	3a	3b	3c	3d	3e	3f	3g	3h	
20	22.19	11.56	15.64	21.05	18.61	17.28	23.51	20.54	26.51
40	29.05	19.12	22.06	28.08	22.74	22.13	29.84	28.19	35.45
60	34.56	31.26	26.29	36.33	30.89	31.62	38.67	32.16	42.16
80	44.14	50.25	38.50	47.11	42.14	48.55	55.63	52.05	59.67
100	76.22	72.85	66.78	74.58	74.89	76.35	81.94	80.38	90.84

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. S.M. Prajapati, K.D. Patel, R.H. Vekariya, S.N. Panchal and H.D. Patel, *RSC Adv.*, **4**, 24463 (2014); <https://doi.org/10.1039/C4RA01814A>
2. S. Srisung, T. Suksrichav, S. Prachayasi, S. Ruchirawat and V. Prachayasi, *Int. J. Pharmacol.*, **9**, 170 (2013); <https://doi.org/10.3923/ijp.2013.170.175>
3. K. Aggile, M. Alagumuthu, R.S. Mundre and A.A. Napoleon, *J. Heterocycl. Chem.*, **55**, 1669 (2018); <https://doi.org/10.1002/jhet.3202>
4. M. Akhter, R. Saha, O. Tanwar, M. Mumtaz Alam and M.S. Zaman, *Med. Chem. Res.*, **24**, 879 (2015); <https://doi.org/10.1007/s00044-014-1139-1>
5. M.R. Solanki, *Asian J. Res. Chem.*, **15**, 83 (2022); <https://doi.org/10.52711/0974-4150.2022.00013>
6. E. Kattnig and M. Albert, *Org. Lett.*, **6**, 945 (2004); <https://doi.org/10.1021/ol0364935>
7. M. Akcay, *Appl. Catal. A Gen.*, **269**, 157 (2004); <https://doi.org/10.1016/j.apcata.2004.04.010>
8. A. Sakakura, K. Kawajiri, T. Ohkubo, Y. Kosugi and K. Ishihara, *J. Am. Chem. Soc.*, **129**, 14775 (2007); <https://doi.org/10.1021/ja075824w>
9. P. Kumar, R.K. Pandey and M.S. Bodas, *J. Mol. Catal. Chem.*, **181**, 207 (2002); [https://doi.org/10.1016/S1381-1169\(01\)00365-X](https://doi.org/10.1016/S1381-1169(01)00365-X)
10. Y. Deng, F. Shi, J. Beng and K. Qiao, *J. Mol. Catal. Chem.*, **165**, 33 (2001); [https://doi.org/10.1016/S1381-1169\(00\)00422-2](https://doi.org/10.1016/S1381-1169(00)00422-2)
11. D. Sain, C. Kumari, A. Kumar, H.P. Nayek and S. Dey, *Dalton Trans.*, **45**, 9187 (2016); <https://doi.org/10.1039/C6DT00941G>
12. P. Ertl, E. Altmann and J.M. McKenna, *J. Med. Chem.*, **63**, 8408 (2020); <https://doi.org/10.1021/acs.jmedchem.0c00754>
13. H. Sharghi and M.H. Sarvari, *Tetrahedron*, **59**, 3627 (2003); [https://doi.org/10.1016/S0040-4020\(03\)00518-0](https://doi.org/10.1016/S0040-4020(03)00518-0)
14. K. Ishihara, S. Nakagawa and A. Sakakura, *J. Am. Chem. Soc.*, **127**, 4168 (2005); <https://doi.org/10.1021/ja050223v>
15. K. Komura, A. Ozaki, N. Ieda and Y. Sugi, *Synthesis*, 3407 (2008); <https://doi.org/10.1055/s-0028-1083175>
16. E. Fischer and A. Speier, Darstellung der ester. In Untersuchungen aus Verschiedenen Gebieten, Springer: Berlin, Heidelberg, pp. 285-291 (1924).
17. A.G.M. Barrett and D.C. Braddock, *Chem. Commun.*, **4**, 351 (1997); <https://doi.org/10.1039/a606484a>
18. G. Höfle, W. Steglich and H. Vorbrüggen, *Angew. Chem. Int. Ed. Engl.*, **17**, 569 (1978); <https://doi.org/10.1002/anie.197805691>
19. B. Neises and W. Steglich, *Angew. Chem. Int. Ed. Engl.*, **17**, 522 (1978); <https://doi.org/10.1002/anie.197805221>
20. H.M. Schotman, *Recl. Trav. Chim. Pays Bas*, **110**, 319 (1991); <https://doi.org/10.1002/recl.19911100704>
21. A. Das and P. Theato, *Macromolecules*, **48**, 8695 (2015); <https://doi.org/10.1021/acs.macromol.5b02293>
22. D. Su, Y. Wang and T. Yan, *Chem. Commun.*, 545 (1999); <https://doi.org/10.1039/a900577c>
23. C. Moberg, *Acc. Chem. Res.*, **49**, 2736 (2016); <https://doi.org/10.1021/acs.accounts.6b00396>
24. C.E. Anson, G. Dave and G.R. Stephenson, *Tetrahedron*, **56**, 2273 (2012); [https://doi.org/10.1016/S0040-4020\(99\)01110-2](https://doi.org/10.1016/S0040-4020(99)01110-2)
25. Y. Wang, F. Yu, X. Han, M. Li, Y. Tong, J. Ding and H. Hou, *Inorg. Chem.*, **56**, 5953 (2017); <https://doi.org/10.1021/acs.inorgchem.7b00653>