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FULL PAPER

One-pot Allan-Robinson/Friedländer route to Chromen-/Quinolin-4-one via Domino Acetylative Cyclisation of 2-Hydroxy-/2-Aminobenzaldehyde

Vijai K. Rai,* [a] Fooleswar Verma,[a] Ganeshwar P. Sahu,[a] Manorama Singh[a] and Ankita Rai[b]

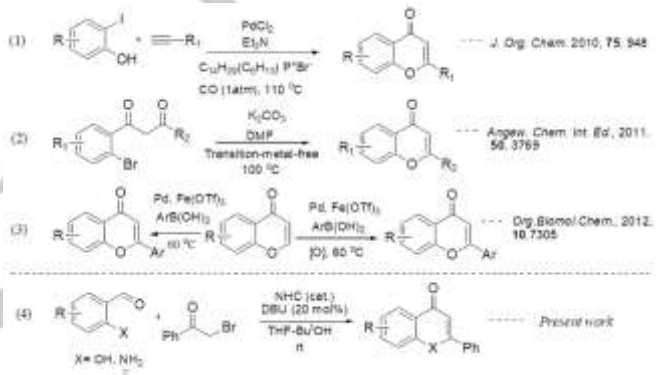
Abstract: Domino synthesis of 2-phenyl-4H-chromen-4-ones and quinolin-4-ones via acetylation of 2-hydroxy/-2-aminobenzaldehyde with α-haloketones followed by intramolecular oxa-/azaheterocyclization is reported. The envisaged method is novel extension of Allan-Robinson and Friedländer reaction using N-heterocyclic carbene catalysis to construct target molecules in good to excellent yield; 86-95% of chromen-4-ones and 83-96% of quinolin-4-ones and has advantage of its operational simplicity, no by-product formation, and ambient reaction conditions.

Introduction

On demand, there are scores of natural products has concerned 2-phenyl-*4H*-chromen-4-ones moiety, also called flavones which represent a fundamental function in natural products,[1] drugs,[2] and contribute a wide variety of considerable biologically activities.[3] From synthetic point of view, flavones have been well utilized as platform chemical for expansion of different types of their derivatives to generate a library of drugs and natural products.[4-5] Literature reports a good number of synthetic strategies (Scheme 1)[5-8] for construction of 2-phenyl-*4H*-chromen-4-ones employing various types of reagents *viz.,* Rh, Pd/IL, $Fe(OTf)_3$, microwave irradiation, additional oxidants, base, $PhI(OAc)_2$, $I_2/SbCl_3$ etc.[9,10] However, these reported methods undergo one or more drawbacks such as harsh reaction conditions, poor substituent scope, multistep synthesis, low yield of pure products and thus construction of 2-phenyl-*4H*-chromen-4-one is still challenging task in organic synthesis.

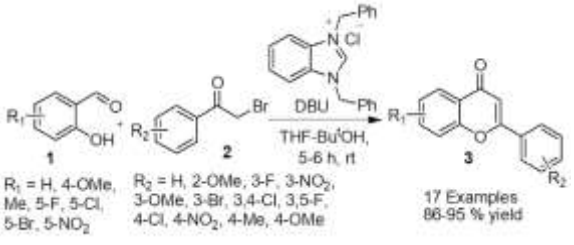
N-Heterocyclic carbene (NHC) catalyst has cooperated tremendous job for coupling of carbon-carbon bond, especially activation of aldehydes, α-functionalized aldehydes, ketones, and enals to development of new scaffolds and new reactions.[11] The umpolung strategy for conversion of electrophilic into nucleophilic aldehydes has the valuable beauty of NHC-catalyst,[12] which cultivates a new carbon-carbon bond and shortens the usual synthetic corridor in organic synthesis.[13] Since 1924, Allan-Robinson reaction[1] has been explored for synthesis of 2-phenyl-*4H*-chromen-4-one (flavones),[1-5] which involves base catalyzed condensation between *o*-hydroxyaryl ketones and an anhydride of aromatic acid. Later on, substrate scope of this method was tolerated by *o*-acyl phenols and carboxylic acid derivatives.

Allan–Robinson reaction is still attractive process to fabricate flavone ring due to presence of a variety of functional group in the substrates. Though, a broad range of functional groups is recognized on the aromatic ring in *o*-hydroxy aldehyde constituent, the construction of the reactive species has been



Scheme 1. Various routes to substituted 2-phenyl-*4H*-chromen-4-one.

short of regiocontrol. Keeping this point in mind, we chose α-haloketone as an alternative ketone component of Allan–Robinson reaction, which would not only avoid the problem of regiocontrol but would also be a novel and potential substrate for intramolecular oxa-heterocyclization affording a library of 2-phenyl-*4H*-chromen-4-ones. Herein, we disclose an NHC-catalyzed efficient synthesis of 2-phenyl-*4H*-chromen-4-ones *via* acetylation of 2-hydroxybenzaldehyde **1** with α-haloketones **2** followed by intramolecular *oxa*-heterocyclization cascades (Scheme 2). The envisaged protocol is hitherto unreported and is the outcome of our interest to expand synthetically useful processes for biologically and pharmaceutically important molecules.[14,15]



Scheme 2. Synthesis of substituted 2-phenyl-*4H*-chromen-4-one **3**.

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Supporting information for this article is given via a link at the end of the document.

Results and Discussion

In model experiment, salicylaldehyde **1a** (2 mmol) and phenacyl bromide **2a** (2mmol) were taken as substrate and different NHC inventor **4a-f** catalyst (Figure 1), stirring in hot air-dried round bottom flask at room temperature and results are sum up in Table 1. NHC-catalyst **4c** was found to be the most efficient among different NHC precursors **4a-f** for synthesis of product **3a** (Table 1, entries 1-6). To generate the NHC, 20% of DBU was used as base with 20 mol % of pre-catalyst **4c** for the best result (Table 1, entries 1-6). Furthermore, we have screened various solvents for the formation of **3a** and THF-Bu^{t}OH was found the best solvent system among THF-H_2O, THF-Bu^{t}OH, DCM and THF-MeOH (Table 1, entries 6-9). However, for conversion of product **3a**, we have also monitored the role of pre-catalyst in model reaction. On increasing the amount of pre-catalyst up to 25 mol %, yield of product **3a** was same (Table 1, entry 10), while on decreasing the amount of pre-catalyst from 20 to 15 mol %, the yield of product **3a** was also reduced (Table 1, entry 11). Next, we also checked the role of pre-catalyst in present conversion and a reaction was set up containing a mixture of salicylaldehyde **1a** (2.0 mmol) and phenacyl bromide **2a** (2.0 mmol) in 10 mL of THF-Bu^{t}OH under positive pressure of nitrogen followed by addition of DBU (0.4 mmol) in absence of benzimidazolium salt **4c**. No product formation even after prolonged reaction time confirms not only the essential role of pre-catalyst **4c** but also rules out the possibility of amine catalysis in the present conversion (Table 1, entry 12). Thus, 20 mol % of each pre-catalyst **4c** and DBU in THF-Bu^{t}OH has been found the best reaction condition for preparation of 2-phenyl-*4H*-chromen-4-one **3a** (Table 1).

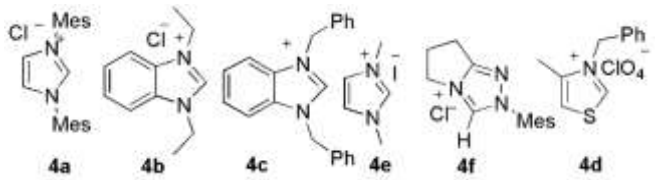
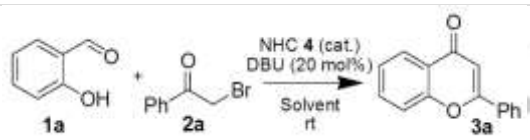


Figure 1. Screening of catalyst **4a-f**.

Table 1. Optimization experiment for synthesis of **3a** [a].



Entry	Pre-catalyst 4 (mol %)	Solvent [b]	Time (h)[c]	Yield (%)[d,e]
1	**4a** (20)	THF-Bu^{t}OH	5	41
2	**4b** (20)	THF-Bu^{t}OH	5	27
3	**4d** (20)	THF-Bu^{t}OH	5	38
4	**4e** (20)	THF-Bu^{t}OH	5	36
5	**4f** (20)	THF-Bu^{t}OH	5	50
6	**4c** (20)	THF-Bu^{t}OH	5	90
7	**4c** (20)	DCM	6	42
8	**4c** (20)	THF-MeOH	5	65
9	**4c** (20)	THF-H_2O	5	62
10	**4c** (25)	THF-Bu^{t}OH	5	90
11	**4c** (15)	THF-Bu^{t}OH	5	79
12	-	THF-Bu^{t}OH	6	00

[a] For the detail pl see the general method of preparation. [b] THF-MeOH (10:01) and THF-H_2O (10:01) were used. [c] Time for stirring at room temperature. [d] Yield of isolated and purified product. [e] All compounds gave C and H analyses within ± 0.37 %, and satisfactory spectral (^{1}H NMR, ^{13}C NMR and EIMS) data.

After optimization of reaction conditions, we next investigated the substrate scope for the envisaged reaction and a variety of substituted salicyldehyde **1** and phenacyl bromide **2** were used employing present reaction condition affording good to excellent yield of target molecule **3** (Figure 2). The substituent on the benzene ring of substrate did not show any specific effect over the product outcome as well as conversion rate (Fig. 2). For generality of the envisaged process, total 17 products have been synthesized with the highest yield (95%) of product **3j**. The formation of product was confirmed by their ^{1}H NMR and ^{13}C spectral analysis.

The formation of 2-phenyl-*4H*-chromen-4-one **3** may be explained (Scheme 3) presumably by nucleophilic attack of carbene **4** to carbonyl carbon of salicyldehyde **1** followed by proton shift in **5** generating homoenolate **6**. The homoenolate **6** (d^1 nucleophile) then attacked to phenacyl bromide **2**, resulting adduct **7** which further underwent intramolecular *oxa*-

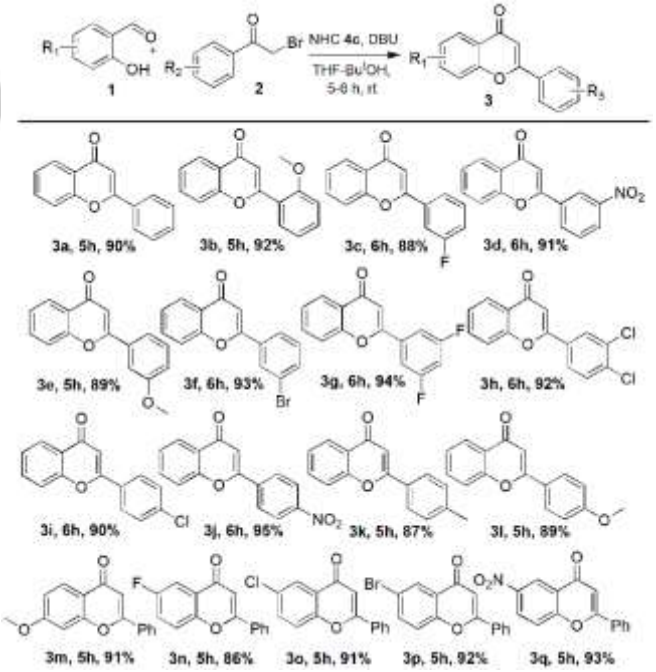
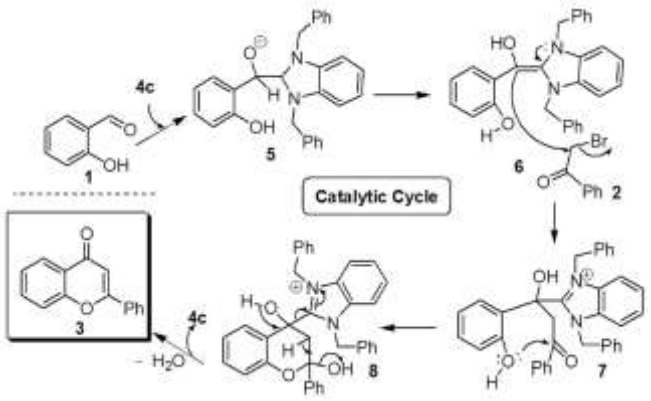


Figure 2. Substrate scope for the formation of 2-phenyl-4H-chromen-4-one **3**.



Scheme 3. Plausible mechanism for the formation of Flavones **3**.

heterocyclization proton shifting cascades to produce adduct **8**. In the last step, presumably enhanced stability of conjugated double bond of **3** has been the driving force for dehydration of **8** (Scheme 3).

Quinolines are the most common structural motifs found in natural (cinchona alkaloids) and synthetic products, displaying a wide range of biological activities[16,17] with enhanced electronic and photonic functions.[18] Literature documents a good number of synthetic routes for construction of quinoline ring including Skraup, Doebner-von Miller, Friedländer and Combes methods.[19-29] Friendläender reaction is still attractive method to construct quinoline ring due to the observed broad range of functional group is tolerated on the aromatic ring in aromatic *o*-amino aldehyde component, lack of regiocontrol in functional group compatibility in the substrates. Though, a wide the formation of the reactive species, derived from the ketone component still opens up new substrate hope with α-metylene carbonyl moiety. As a probe to check the general validity of the envisaged synthetic methodology and to construct quinoline ring keeping in mind, we extended the scope of aldehyde component from *o*-hydroxy- to *o*-amino benzaldehyde for synthesis of quinolin-4-ones **10**. Thus, after preliminary experimentation, 2-aminobenzaldehyde **9** (2 mmol), phenacyl bromide **2** (2mmol), pre-catalyst **4c** (20 mol%) and DBU (20 mol%) were taken in THF-Bu^{t}OH for synthesis of quinoline **10** (Figure 3). Total 12 products were synthesized in good to excellent yield with the highest yield of **10e** as 96%. Both electron releasing (-Me, -OMe, -NH_2) as well as electron withdrawing (-Br, -Cl, -F, -NO_2) groups tolerated the product yield good to excellent in this conversion. All the synthesized products **10** were confirmed by their ^{1}H NMR and ^{13}C NMR spectra.

Conclusions

We have developed a domino synthesis of 2-phenyl-*4H*-chromen-4-one and quinolin-4-one *via* dehydrative acetylation of different *o*-substituted aldehyde with α-haloketone followed by intramolecular heterocyclization, which is hitherto unknown and has advantage of its operational simplicity, atom economy, no by-product formation and ambient reaction conditions. Furthermore,

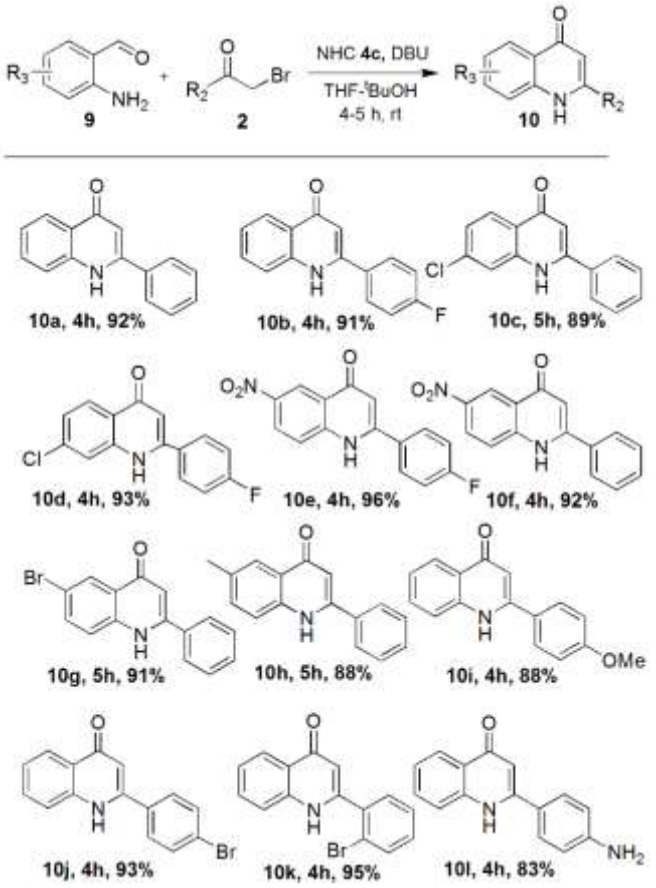


Figure 3. Substrate scope for the formation of quinoline-4-ones **10**.

the synthesized molecules may serve platform chemical for generating a library of biologically relevant molecules and would be a practical alternative to the existing procedures for their preparations.

Experimental Section

General: All chemicals were purchased from Aldrich, Sd-Fine and Hi-Media (India) and used as received, except all solvents which were used after distillation. All reactions were carried out with oven-dried glassware under air. Distilled *n*- hexane and ethyl acetate were used for column chromatography. Analytical TLC was performed on Merck 60F254 silica gel plates (0.25 mm thickness). Column chromatography was performed on silica gel (60-120 mesh size, Hi-Media (India). ^{1}H NMR spectra were recorded on Bruker AV 400.

The ^{1}H NMR chemical shifts are reported relative to the centre of solvent resonance ($CDCl_3$: 7.26 (1H). Chemical shifts are expressed in parts per million (δ) and the signals were reported as s (singlet), d (doublet), dd (double doublet), t (triplet), tt (triplet triplet), dt (doublet triplet), q (quartet), m (multiplet) and coupling constants *J* were given in Hz. ^{13}C NMR spectra were recorded at 100 MHz in $CDCl_3$ and DMSO-d_6 solution. Chemical shifts are expressed in parts per million (δ) and are referenced to $CDCl_3$ (δ = 77.16) as internal standard.

Experiment procedure for 2-phenyl-*4H*-chromen-4-one (3): The 2-hydroxybenzaldehyde 1 (2.0 mmol), phenacyl bromide 2 (2.0 mmol) were taken in the hot air-dried round bottom flask. Benzimidazolium salt 4c (0.4 mmol) and 10 mL of THF/Bu^{t}OH; 10:1 under positive pressure of nitrogen followed by addition of DBU (0.4 mmol) with a syringe. The resulting solution was stirred for 5-6 h at room temperature. After completion of the reaction (monitored by TLC), the reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using *n*-hexane/EtOAc (8:2) as eluent to afford analytically pure product 3. Characterization data of the representative compounds are:

2-Phenyl-*4H*-chromen-4-one (3a): Colourless solid (90%); mp 95-96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.95–7.45 (m, 8H$_{arom.}$), 7.06 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 164.5, 156.4, 134.4, 132.1, 131.3, 129.1, 126.5, 125.7, 125.6, 123.1, 118.1, 106.9; IR (KBr): 1640, 1605, 1375, 1130 cm^{-1}; Anal. Calcd for $C_{15}H_{10}O_2$: C, 81.07, H, 4.54%; Found: C, 81.26, H, 4.65%.

2-(2-Methoxyphenyl)-*4H*-chromen-4-one (3b): Colourless solid (92%); mp 97–100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.89 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.65 (td, *J* = 8.7, 7.1, 1.7 Hz, 1H), 7.52 (d, 1H), 7.45 (td, 1H), 7.38 (td, *J* = 8.1, 7.1, 1.1 Hz, 1H), 7.12 (s, 1H), 7.09 (td, *J* = 7.6, 1.0 Hz, 1H), 7.02 (d, 1H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 160.8, 158.0, 156.5, 133.6, 132.4, 129.2, 125.6, 124.9, 123.8, 120.8, 120.7, 118.0, 112.6, 111.7, 55.9; IR (KBr): 1638, 1615, 1462 cm^{-1}; Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18, H, 4.79%; Found: C, 76.55, H, 4.65%.

2-(3-Fluorophenyl)-*4H*-chromen-4-one (3c): Colourless solid (88%); mp 97–98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.68-7.24 (m, 7H$_{arom.}$), 6.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.7, 163.0 (d, *J* = 241.7 Hz), 156.1, 134.0, 133.9, 133.9, 130.7 (d, *J* = 8.1 Hz), 125.7, 125.4, 123.9, 121.9 (d, *J* = 3.1 Hz), 118.5 (d, *J* = 21.2), 118.0, 113.3 (d, *J* = 23.9 Hz), 108.2; IR (KBr): 1664, 1642, 1510, 1376 cm^{-1}; Anal. Calcd for $C_{15}H_9FO_2$: C, 75.00, H, 3.78%; Found: C, 75.25, H, 3.85%.

2-(3-Nitrophenyl)-*4H*-chromen-4-one (3d): Colourless solid (91%); mp 196–198 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (t, *J* = 2.0 Hz, 1H), 8.37 (ddd, *J* = 8.2, 2.4, 1.0 Hz, 1H), 8.22 (dq, *J* = 7.8, 1.7 Hz, 2H), 7.76–7.70 (m, 2H$_{arom.}$), 7.63 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.45 (td, *J* = 8.1, 7.0, 1.1 Hz, 1H), 6.89 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 161.0, 156.8, 148.5, 134.3, 133.6, 131.7, 130.3, 125.9, 125.8, 125.7, 123.9, 121.2, 118.1, 108.8; IR (KBr): 1661, 1619, 1459, 1369 cm^{-1}; Anal. Calcd for $C_{15}H_9NO_4$: C, 67.42, H, 3.39, N, 5.24%; Found: C, 67.25, H, 3.45, N, 5.15%.

2-(3-Methoxyphenyl)-*4H*-chromen-4-one (3e): Colourless solid (89%); mp 125–127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.69 (td, *J* = 8.7, 7.0, 1.7 Hz, 1H), 7.55 (d, 1H), 7.49 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.44 (d, *J* = 3.2 Hz, 1H), 7.43–7.39 (m, 2H$_{arom.}$), 7.06 (ddd, *J* = 8.1, 2.6, 1.1 Hz, 1H), 6.81 (s, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 163.1, 159.7, 156.2, 133.7, 133.0, 130.1, 125.6, 125.2, 123.9, 118.7, 118.1, 117.1, 111.4, 107.7, 55.9; IR (KBr): 1650, 1605, 1464, 867, 767, 693 cm^{-1}; Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18, H, 4.79%; Found: C, 75.95, H, 5.16%.

2-(3-Bromophenyl)-*4H*-chromen-4-one (3f): Yellowish solid (93%); mp 85–89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.05 (t, *J* = 1.9 Hz, 1H), 7.79-7.35 (m, 6H$_{arom.}$), 6.68 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 161.6, 156.0, 134.4, 133.9, 133.7, 130.5, 129.2, 125.7, 125.4, 124.8, 123.9, 123.2, 118.0, 108.1; IR (KBr): 1642, 1605, 1470, 1366 cm^{-1}; Anal. Calcd for $C_{15}H_9BrO_2$: C, 59.83, H, 3.01%; Found: C, 60.15, H, 3.06%.

2-(3,5-Difluorophenyl)-*4H*-chromen-4-one (3g): Yellowish solid (94%); mp 146–147 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.58–7.42 (m, 5H$_{arom.}$), 6.98 (tt, 1H), 6.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.1, 164.6, 162.1, 160.6, 156.1, 135.1 (d, *J* = 9.4 Hz), 134.2, 125.8, 123.8, 118.1, 109.5, 108.5, 107.1; IR (KBr): 1640, 1378, 1122 cm^{-1}; Anal. Calcd for $C_{15}H_8F_2O_2$: C, 69.77, H, 3.12%; Found: C, 69.47, H, 3.49%.

2-(3,4-Dichlorophenyl)-*4H*-chromen-4-one (3h): Yellowish solid (92%); mp 196–199 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.01 (d, *J* = 2.2 Hz, 1H), 7.72 (td, *J* = 8.5, 6.5, 1.9 Hz, 2H), 7.63 (td, *J* = 9.3, 8.0 Hz, 2H), 7.42 (td, 1H), 6.69 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.1, 160.8, 156.0, 135.9, 134.1, 133.7, 131.7, 131.1, 128.0, 125.8, 125.5, 125.2, 123.9, 118.0, 108.2; ; IR (KBr): 1663, 1605, 1470, 1131 cm^{-1}; Anal. Calcd for $C_{15}H_8Cl_2O_2$: C, 61.88, H, 2.77%; Found: C, 61.77, H, 2.85.

2-(4-Chlorophenyl)-*4H*-chromen-4-one (3i): Colourless solid (90%); mp 177–178 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.86 (d, 2H), 7.70 (td, *J* = 8.7,0 7.1, 1.7 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.49 (d, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 6.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.1, 162.6, 156.2, 137.8, 133.9, 130.2, 129.3, 127.5, 125.7, 125.3, 123.9, 117.1, 108.0; IR (KBr): 1660, 1375, 1093, 827, 754 cm^{-1}; Anal. Calcd for $C_{15}H_9ClO_2$: C, 70.19, H, 3.53%; Found: C, 70.56, H, 3.16%.

2-(4-Nitrophenyl)-*4H*-chromen-4-one (3j): Yellowish solid (95%); mp 232–235 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 9.0 Hz, 2H), 8.24 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.11 (d, *J* = 8.9 Hz, 1H), 7.74 (td, *J* = 8.6, 7.1, 1.7 Hz, 1H), 7.60 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.45 (td, *J* = 8.2, 7.1, 1.1 Hz, 1H), 6.80 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 164.1, 159.1, 144.8, 132.3 130.7, 129.2, 128.1, 126.4, 124.2, 122.4, 119.8, 107.8; IR (KBr): 1660, 1523, 1347, 857 cm^{-1}; Anal. Calcd for $C_{15}H_9NO_4$: C, 67.42, H, 3.39, N, 5.24%; Found: C, 67. 24, H, 3.46, N, 5.18%.

2-(p-Tolyl)-*4H*-chromen-4-one (3k): Yellowish solid (87%); mp 105–107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.82-7.24 (m, 7H$_{arom.}$), 6.93 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 164.3 156.3, 142.7, 134.0, 129.8, 128.6, 126.4, 125.6, 125.4, 123.3, 118.1, 106.4, 21.5; IR (KBr): 1642, 1468, 815 cm^{-1}; Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.34, H, 5.12%; Found: C, 81.44, H, 5.02%.

2-(4-Methoxyphenyl)-*4H*-chromen-4-one (3l): Yellowish solid (89%); mp 151–152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.92 (d, 2H), 7.73 (td, *J* = 8.7, 7.1, 1.7 Hz, 1H), 7.60 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.44 (td, *J* = 8.0, 7.1, 1.0 Hz, 1H), 7.11 (bs, 1H), 7.01 (d, 2H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.1, 165.4, 163.3, 156.3, 134.6, 128.7, 125.8, 125.6, 123.1, 122.3, 118.1, 114.7, 104.8, 55.6; IR (KBr): 1642, 1378, 827 cm^{-1}; Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18, H, 4.79%; Found: C, 76.44, H, 5.02%.

7-Methoxy-2-phenyl-*4H*-chromen-4-one (3m): Colourless solid (91%); mp 86–88 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12-8.05 (m, 1H$_{arom.}$), 7.92 (dd, *J* = 7.8, 1.9 Hz, 2H), 7.50–7.48 (m, 3H), 6.99-6.96 (m, 2H$_{arom.}$), 6.92 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 164.5, 163.7, 158.1, 131.7, 131.5, 129.0, 127.0, 126.3, 117.3, 114.9, 106.8, 100.1, 55.9; IR (KBr): 1650, 1627, 1445, 1152, 1018 cm^{-1}; Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18, H, 4.79%; Found: C, 76.25, H, 4.95%.

6-Fluoro-2-phenyl-*4H*-chromen-4-one (3n): Yellowish solid (86%); mp 125–127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.82 (m, 3H$_{arom.}$), 7.56–7.50 (m, 5H$_{arom.}$), 6.80 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 163.6, 160.8, 158.4, 152.5, 131.6 (d, *J* = 30.6 Hz), 129.1, 126.3, 125.1 (d, *J* = 7.1 Hz), 121.9 (d, *J* = 25.4 Hz), 120.1 (d, *J* = 8.1 Hz), 110.6 (d, *J* = 23.6 Hz),

106.9; IR (KBr): 1658, 1357 cm^{-1}; Anal. Calcd for $C_{15}H_9FO_2$: C, 75.00, H, 3.78%; Found: C, 75.30, H, 3.65%.

6-Chloro-2-phenyl-*4H*-chromen-4-one (3o): Yellowish solid (91%); mp 177–180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 2.5 Hz, 1H), 7.89 (dd, 2H), 7.60–7.50 (m, $5H_{arom.}$), 6.87 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 163.8, 154.6, 133.9, 131.8, 131.4, 131.2, 129.1, 126.3, 125.1, 124.9, 119.1, 107.5; IR (KBr): 1651, 1604, 1433, 1130, 679 cm^{-1}; Anal. Calcd for $C_{15}H_9ClO_2$: C, 70.19, H, 3.53%; Found: C, 70.50, H, 3.45%.

6-Bromo-2-phenyl-*4H*-chromen-4-one (3p): Yellowish solid (92%); mp 172–175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 2.4 Hz, 1H), 7.91 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.78 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.54–7.46 (m, $4H_{arom.}$), 6.84 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 163.9, 155.1, 137.0, 132.0, 131.3, 129.1, 128.4, 126.4, 125.1, 120.0, 118.8, 107.4; IR (KBr): 1650, 1598, 1453, 1435 cm^{-1}; Anal. Calcd for $C_{15}H_9BrO_2$: C, 59.83, H, 3.01%; Found: C, 60.12, H, 3.15%.

6-Nitro-2-phenyl-*4H*-chromen-4-one (3q): Yellowish solid (93%); mp 185–187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (d, *J* = 2.8 Hz, 1H), 8.53(dd, *J* = 9.2, 2.8 Hz, 1H), 7.91 (dd, *J* = 8.2, 1.6 Hz, 2H), 7.71 (d, *J* = 9.2 Hz, 1H), 7.56–7.52 (m, $4H_{arom.}$), 6.90 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 164.0, 159.0, 144.6, 132.3, 130.7, 129.2, 128.1, 126.4, 124.0, 122.4, 119.8, 107.8; IR (KBr): 1648, 1614, 1510, 1456, 1337, 1018 cm^{-1}; Anal. Calcd for $C_{15}H_9NO_4$: C, 67.42, H, 3.39%; Found: C, 67.54, H, 3.51%.

Experiment procedure for 2-Phenylquinolin-4-one (10): A hot oven dried round bottom flask was charged with benzimidazolium salt 4c (0.4 mmol). 2-aminobenzaldehyde 9 (2.0 mmol), phenacyl bromide 2 (2.0 mmol) and 10 mL of THF/Bu^tOH; 10:1 under positive pressure of nitrogen followed by addition of DBU (0.4 mmol) with a syringe. The resulting yellow solution was stirred for 4-5 h at room temperature. After completion of the reaction (monitored by TLC), the reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using *n*-hexane/EtOAc (8:2) as eluent to afford analytically pure product 10. Characterization data of the representative compounds are:

2-Phenylquinolin-4-one (10a): Solid (92%) m.p. 251–254 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.31 (d, *J* = 8.0 Hz, 1H), 8.28 (d, *J* = 8.0, 1H), 7.83-7.77 (m, $3H_{arom.}$), 7.75 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 1H), 6.61 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 176.5, 150.9, 140.0, 134.7, 131.8, 130.4, 129.0, 127.4, 124.9, 124.7, 123.2, 118.7, 107.7; IR (KBr): 1629, 3259 cm^{-1}; Anal. Calcd for $C_{15}H_{11}NO$: C, 81.43, H, 5.01, N, 6.33%; Found: C, 81.25, H, 5.15, N, 6.50%.

2-(4-Fluorophenyl)quinolin-4-one (10b): Solid (91%), m.p. 317-319 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.71 (br, s, 1H), 8.12 (d, *J* = 12 Hz, 1H), 7.92 (d, *J* = 12 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.69 (t, *J* = 7.2 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 1H), 6.33 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 176.1, 163.4 (d, *J* = 248.2 Hz), 149.4, 140.5, 131.9, 130.7 (d, *J* = 3.1 Hz), 129.9 (d, *J* = 8.8 Hz), 124.8, 124.7, 123.3, 118.7, 116.0 (d, *J* = 21.8 Hz), 107.0; Anal. Calcd for $C_{15}H_{10}FNO$: C, 75.30, H, 4.21, N, 7.94%; Found: C, 75.24, H, 4.35, N, 7.90%.

7-Chloro-2-phenylquinolin-4-one (10c): Solid (89%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.47 (d, *J* = 12.0 Hz, 1H), 8.35 (d, *J* = 8.0 Hz, 1H), 7.99−7.96 (m, $2H_{arom.}$), 7.68−7.60 (m, $4H_{arom.}$), 7.45 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 170.7, 157.4, 142.0, 141.2, 133.4, 131.5, 130.1 129.3, 129.0, 126.0, 119.9, 118.7, 104.0; Anal. Calcd for $C_{15}H_{11}ClNO$: C, 70.46, H, 3.94, N, 5.48%; Found: C, 70.81, H, 3.69, N, 5.36%.

7-Chloro-2-(4-fluorophenyl) quinolin-4-one (10d): Solid (93%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.73 (br s, 1H), 8.12 (d, *J* = 8.6 Hz, 1H), 7.92−7.89 (m, $2H_{arom.}$), 7.78 (s, 1H), 7.46 (t, *J* = 8.8 Hz, 2H), 7.37 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.30 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.6, 141.9, 131.3, 131.2, 128.2, 125.4, 119.0, 118.2, 116.6, 116.4, 104.0; Anal. Calcd for $C_{15}H_{10}ClFNO$: C, 65.83, H, 3.31, N, 6.94%; Found: C, 65.63, H, 3.66, N, 6.75%.

2-(4-Fluorophenyl)-6-nitroquinolin-4-one (10e): Yellowish solid (96%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.48 (d, *J* = 2.7 Hz, 1H), 7.95 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.67 (s, 1H), 7.28−7.15 (m, $4H_{arom.}$), 6.68 (d, *J* = 9.2 Hz, 1H), 5.67 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 187.6, 163.6 (d, *J* = 244.4 Hz), 161.8, 155.3, 134.3, 133.1 (d, *J* = 3.5 Hz), 130.1 (d, *J* = 8.3 Hz), 126.9, 126.7, 120.0, 115.8, 115.2 (d, *J* = 21.6 Hz), 93.3; Anal. Calcd for $C_{15}H_{10}FN_2O_3$: C, 63.38, H, 3.19, N, 6.68%; Found: C, 63.21, H, 3.01, N, 7.03%.

6-Nitro-2-phenylquinolin-4-one (10f): Yellowish solid (92%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.42 (s, 1H), 7.92 (d, *J* = 12.0 Hz, 1H), 7.39–7.22 (m, $4H_{arom.}$), 6.60 (d, *J* = 8.0 Hz, 1H), 5.82 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 187.5, 162.8, 155.3, 136.8, 134.3, 128.1, 128.0, 127.5, 126.8, 126.7, 120.1, 115.8, 93.8; IR (KBr): 3019, 1615, 1513, 1319 cm^{-1}; Anal. Calcd for $C_{15}H_{10}N_2O_3$: C, 67.67, H, 3.79, N, 10.52%; Found: C, 67.48, H, 3.67, N, 10.65%.

6-Bromo-2-phenylquinolin-4-one (10g): Yellowish solid (91%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.31 (s, 1H), 8.22 (d, *J* = 8.0 Hz, 1H) 7.88 (d, *J* = 8.0 Hz, 1H) 7.85–7.81 (m, $2H_{arom.}$), 7.48-7.42 (m, $3H_{arom.}$), 7.34 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.2, 156.8, 138.7, 137.9, 132.7, 130.8, 129.5, 128.4, 126.0, 121.8, 121.6, 120.7, 104.7; Anal. Calcd for $C_{15}H_{10}BrNO$: C, 60.02, H, 3.36, N, 4.67%; Found: C, 60.37, H, 3.07, N, 4.65%.

6-Methyl-2-phenylquinolin-4-one (10h): Solid (88%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.05 (d, *J* = 8.0 Hz, 1H), 7.71-7.43 (m, $7H_{arom.}$), 6.71 (s, 1H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 179.7, 151.6, 139.1, 134.7, 134.6, 134.4, 131.0, 129.4, 127.7, 125.0, 124.6, 118.7, 107.0, 21.6; Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68, H, 5.57, N, 5.95%; Found: C, 81.99, H, 5.37, N, 5.67%.

2-(4-Methoxyphenyl)quinolin-4-one (10i): Brown solid (88%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.52 (br, s, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.84 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.79 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.36−7.32 (m, $2H_{arom.}$), 7.18−7.14 (m, $2H_{arom.}$), 6.33 (s, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 176.0, 161.8, 149.6, 140.1, 131.6, 128.8, 126.2, 124.8, 124.7, 123.1, 118.6, 114.4, 106.4, 55.5; Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48, H, 5.21, N, 5.57%; Found: C, 76.58, H, 5.37, N, 5.47%.

2-(4-Bromophenyl)quinolin-4-one (10j): Solid (93%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.5 (br, s, 1H), 8.17 (d, *J* = 8.0 Hz, 2H), 7.80 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.70−7.50 (m, $3H_{arom.}$), 7.17 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 176.9, 148.5, 140.5, 133.3, 131.9, 131.9, 129.5, 124.9, 124.7, 124.0, 123.3, 118.7, 107.5; Anal. Calcd for $C_{15}H_{10}BrNO$: C, 60.02, H, 3.36, N, 4.67%; Found: C, 60.12, H, 3.37, N, 4.47%.

2-(2-Bromophenyl)quinolin-4-one (10k): Red solid (95%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.69−7.61 (m, $2H_{arom.}$), 7.43 (td, *J* = 7.5, 1.2 Hz, 1H), 7.32 (ddd, *J* = 8.0, 7.4, 1.8 Hz, 1H), 7.24 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.08 (ddd, *J* = 8.4, 7.1, 1.5 Hz, 1H), 6.60 (dd, *J* = 8.3, 1.2 Hz, 1H), 6.50 (ddd, *J* = 8.1, 7.1, 1.2 Hz, 1H), 6.41 (br s, 1H), 5.67 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 188.5, 158.8, 149.8, 138.3, 132.0, 131.3, 129.6, 129.4, 129.4,

127.4, 121.9, 121.7, 116.3, 114.7, 93.8; Anal. Calcd for $C_{15}H_{11}BrNO$: C, 60.02, H, 3.36, N, 4.67%; Found: C, 60.22, H, 3.47, N, 4.27%.

2-(4-Aminophenyl)quinolin-4-one (10l): Yellowish solid (83%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.7 (br s, 1H), 8.3 (dd, J = 8.1, 1.5 Hz, 1H), 7.8 (d, J = 8.3 Hz, 1H), 7.7−7.6 (m, 3H$_{arom.}$), 7.3 (ddd, J = 8.0, 6.9, 1.1 Hz, 1H), 6.7- 6.6 (m, 2H$_{arom.}$), 6.6 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 176.8, 151.8, 150.6, 140.4, 131.4, 128.3, 124.5, 122.9, 120.1, 118.5, 113.6, 104.4; 1629; IR 3428 cm^{-1}; Anal. Calcd for $C_{15}H_{13}N_2O$: C, 76.25, H, 5.12, N, 11.86%; Found: C, 76.12, H, 5.25, N, 11.82%.

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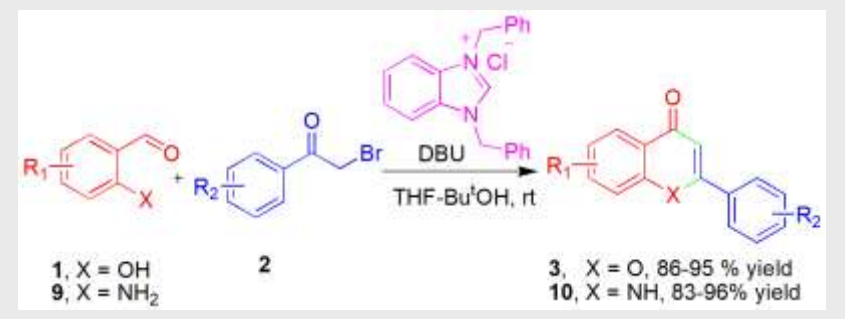

NHC-Catalysis*

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One-pot Allan-Robinson/Friedländer route to Chromen-/Quinolin-4-one via Domino Acetylative Cyclisation of 2-Hydroxy-/2-Aminobenzaldehyde