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A novel one-pot oxidative cyclization of 2′-amino and 2′-hydroxychalcones employing $FeCl_3 \cdot 6H_2O$–methanol. Synthesis of 4-alkoxy-2-aryl-quinolines and flavones

Kalvi Hemanth Kumar and Paramasivan T. Perumal*

Organic Chemistry Division, Central Leather Research Institute, Adyar, Chennai-600 020, Tamil Nadu, India

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Abstract—A simple, inexpensive, and efficient oxidative cyclization of 2′-amino and 2′-hydroxychalcones has been carried out by employing $FeCl_3 \cdot 6H_2O$–methanol under mild conditions. This method has been investigated for the synthesis of 2-(1,3-diphenyl-1*H*-pyrazol-4-yl)-4-methoxyquinolines.
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1. Introduction

Quinolines are widely distributed in the plant family *Rutaceae*. The alkaloid (entry 4, Table 2) has been isolated as a natural product from *Lunarira amara*.[1,2] The synthesis of 4-alkoxy-2-aryl-quinoline derivatives continues to attract attention due to their biological activities.[1,3] Only a few methods for the synthesis of these compounds are available in literature and most involve multiple steps[2,4] or corrosive and toxic reagents.[5–7]

2. Result and discussion

In continuation of our studies on the synthesis of heterocyclic compounds with medicinal potential from 2′-amino and 2′-hydroxychalcones,[8] in this paper we wish to describe an efficient oxidative cyclization of 2′-amino and 2′-hydroxychalcones under mild condition employing $FeCl_3 \cdot 6H_2O$–methanol.

Recently $FeCl_3 \cdot 6H_2O$ has been utilized in a wide variety of organic reactions such as the oxidation of benzoin[9] and Hantzsch 1,4-dihydropyridine[10] synthesis and as a catalyst for Biginelli[11] condensations and Michael[12] and esterification[13] reactions. The oxidation of 2′-aminochalcones to 3-(β-styryl)-2,1-benzisoxazoles[14] with $PhI(OAc)_2$–KOH–methanol prompted us to investigate the oxidation of 2′-aminochalcone using $FeCl_3 \cdot 6H_2O$.

The objective is to synthesize 3-(β-styryl)-2,1-benzisoxazoles by using a mild, safe, and inexpensive reagent in good yields. The treatment of 2′-aminochalcone (entry 4, Table 1) with 2.5 equiv of $FeCl_3 \cdot 6H_2O$ in methanol affords a white solid upon purification, that is not the expected 3-(β-styryl)-2,1-benzisoxazole. Analysis of the spectral data (IR, ^1H NMR, and ^{13}C NMR) of the product ruled out the possible formation of 3-(β-styryl)-2,1-benzisoxazole. The structural features of the white product imply the sole formation of 2-phenyl-4-methoxyquinoline (Scheme 1).

A screening study carried out with the 2′-aminochalcone (entry 4, Table 1) to assess the efficacy of different oxidizing agents revealed that $Mn(OAc)_3$, CAN, copper(II)acetate–manganese(III)acetate, copper(II) acetate–$K_2S_2O_8$, PCC, NBS, $Co(NO_3)_2$–$K_2S_2O_8$, and iodine failed to oxidize the substrates to 2-phenyl-4-methoxyquinoline. Among the oxidizing agents screened in this work $FeCl_3 \cdot 6H_2O$ in methanol was found to be a mild, inexpensive, and efficient oxidizing agent for the effective oxidative cyclization. The generality of the new transformation was examined by treating a wide range of substituted and structurally diverse 2′-aminochalcones and pyrazole analogs of 2′-aminochalcones (entries 1–9, Table 1).

The success encountered in the oxidative cyclization of 2′-aminochalcones prompted us to study the action of $FeCl_3 \cdot 6H_2O$ on 2′-hydroxychalcones (Scheme 2). When we treated the 2′-hydroxychalcone with 2.5 equiv of $FeCl_3 \cdot 6H_2O$ in methanol in oil-bath at reflux for 8 h interestingly the corresponding flavones were obtained in moderate yields. The results are presented in Table 2.

In conclusion, this procedure promoted by $FeCl_3 \cdot 6H_2O$–methanol provides a simple, inexpensive, safe, and efficient synthesis of biologically important 4-alkoxy-2-aryl-quinolines and flavones.

* Corresponding author. Fax: +91 (44) 4911589; e-mail: ptperumal@gmail.com

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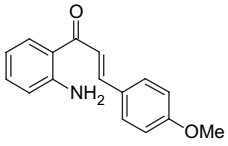
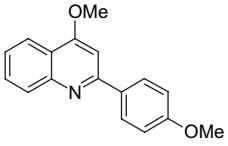
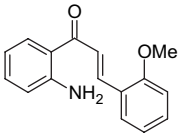
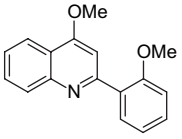
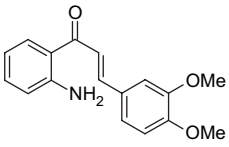
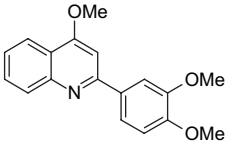
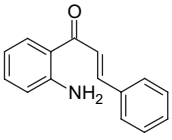
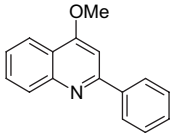
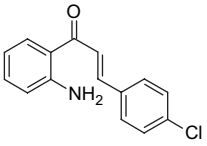
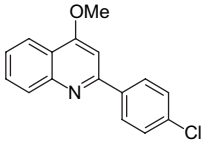
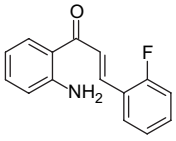
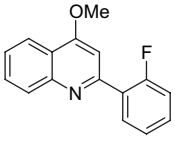
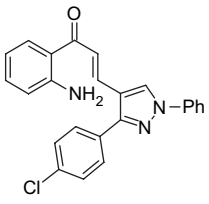
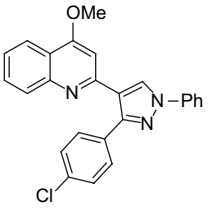
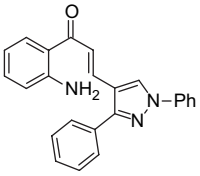
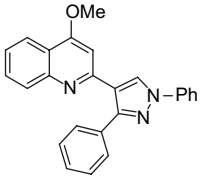
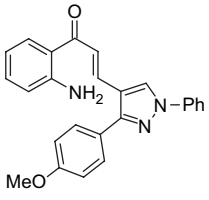
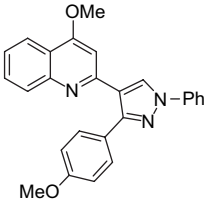
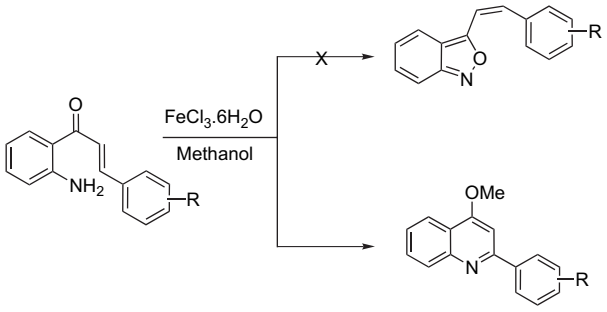
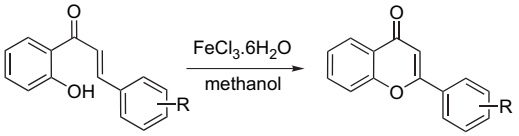
Table 1. $FeCl_3 \cdot 6H_2O$–methanol mediated oxidative cyclization of 2′-aminochalcones and pyrazole analogs of 2′-aminochalcones

Entry	Substrate	Product[a]	Time (h)	Yield[b] (%)
1			6	65
2			5	58
3			5	68
4			6	62
5			7	60
6			7	55
7			7	64
8			6	60
9			6	72

[a] All products were characterized by IR, ^{1}H NMR, and mass spectra.
[b] Yield of isolated products.

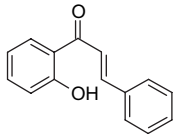
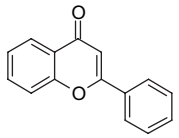
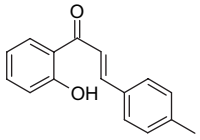
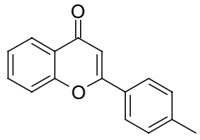
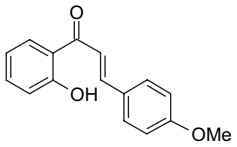
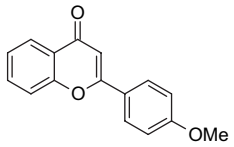
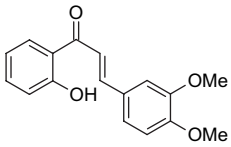
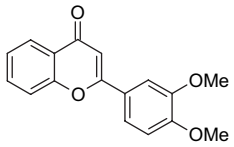


Scheme 1.



Scheme 2.

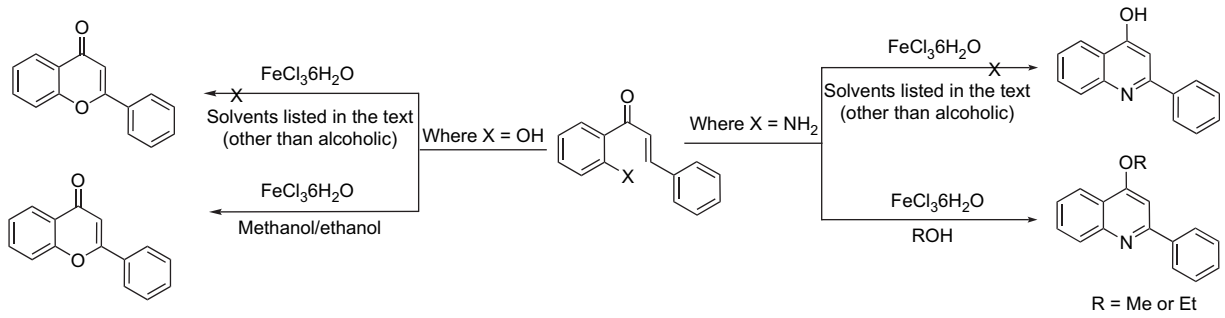
Table 2. $FeCl_3 \cdot 6H_2O$–methanol mediated oxidative cyclization of 2′-hydroxychalcones

Entry	Substrate	Product[a]	Time (h)	Yield[b] (%)
1			10	55
2			10	55
3			8	58
4			9	62

[a] All products were characterized by IR, ^{1}H NMR, and mass spectra.
[b] Yield of isolated products.

2.1. Effect of solvent

To study the effect of the solvent on the $FeCl_3 \cdot 6H_2O$ mediated oxidative cyclization of 2′-amino and 2′-hydroxy chalcones. We used various solvents apart from alcoholic solvents (methanol and ethanol), such as acetonitrile, DMF, DMSO, ethylacetate, THF, and toluene to carry out the oxidative cyclization of the 2′-aminochalcone (entry 4, Table 1) to get the corresponding 4-hydroxyquinoline, interestingly we did not get the required product and we recovered the aminochalcone. Among all the solvents, alcoholic solvents (methanol and ethanol) found to give the



Scheme 3.

4-methoxy-2-phenylquinoline and 4-ethoxy-2-phenylquinoline in 62 and 58% yields, respectively. In case of 2′-hydroxychalcone (entry 1, Table 2) also we got the corresponding flavone only with the alcoholic solvents (methanol and ethanol) and with other solvents (DMF, DMSO, ethylacetate, THF and toluene) the reaction did not proceed to give the respective flavone, we recovered the starting material. The results are summarized in the Scheme 3.

3. Experimental section

3.1. General

$FeCl_3 \cdot 6H_2O$ was purchased from SRL, India. Tetrahydroquinolones, benzofurodihydropyridinones, 2′-amino and hydroxychalcones were synthesized according to the procedure reported in literature.[15] Melting points were determined in capillary tubes and are uncorrected. Analytical TLC was performed on precoated plastic sheets of silica gel G/UV-254 of 0.2 mm thickness (Macherey-Nagel, Germany). IR spectra were recorded as KBr pellets for solids on a Perkin–Elmer Spectrum RXI FTIR. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded in $CDCl_3$ solutions with TMS as an internal standard on a JEOL instrument. Mass spectra were recorded using JEOL DX-303 in EI ionization mode at 70 eV. Elemental analysis data were recorded using Thermo Finnigan FLASH EA 1112 CHN analyzer. Column chromatography was performed on silica gel (100–200 mesh, SRL, India).

3.2. General procedure for the oxidative cyclization of 2′-aminochalcones (entries 1–9, Table 1)

2′-Aminochalcone (1 mmol) was dissolved in 15 mL of methanol and to this $FeCl_3 \cdot 6H_2O$ (675 mg, 2.5 mmol) was added. The mixture was refluxed in an oil-bath until TLC showed completion of the reaction. Then ice-cold water (50 mL) was added to the reaction mixture and it was extracted with ethyl acetate (4×20 mL) and the extract was dried over anhydrous sodium sulfate. Removal of the solvent under vacuum gave the crude product, which was further purified by column chromatography on silica gel (100–200 mesh) with ethyl acetate–hexane (1:9) as eluant to afford pure product.

3.3. General procedure for the oxidative cyclization of 2′-hydroxychalcones (entries 1–4, Table 2)

To a solution of 2′-hydroxychalcone (1 mmol) in 15 mL of methanol was added $FeCl_3 \cdot 6H_2O$ (675 mg, 2.5 mmol) and the reaction mixture was refluxed (oil-bath) until completion of the reaction as indicated by TLC. Then ice-cold water (50 mL) was added to the reaction mixture and it was extracted with ethyl acetate (4×20 mL) and the extract was dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure gave the crude product, which was further purified by column chromatography on silica gel (100–200 mesh) with ethyl acetate–hexane (2:8) as eluant to afford pure product.

3.3.1. 4-Methoxy-2-(4-methoxyphenyl)quinoline (entry 1, Table 1). White solid. Mp: 94–95 °C (lit. 93–94 °C).[5] R_f: 0.4 with 2:8 ethylacetate–pet. ether. FTIR (KBr) ν_{max} cm^{-1}: 1578, 1418, 1206, 1139. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.86 (s, 3H, OCH_3), 4.07 (s, 3H, OCH_3), 7.10 (s, 1H, H-3), 7.41–7.47 (m, 1H), 7.65–7.70 (m, 1H), 8.06–8.07 (m, 3H), 8.08 (d, J=7.68 Hz, 2H), 8.14 (d, J=8.0 Hz, 1H, H-5). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 55.5, 55.7, 95.5, 114.2, 120.3, 121.7, 125.1, 128.9, 129.1, 129.9, 132.9, 135.8, 149.3, 158.4, 162.8. MS m/z: 265 (M^+). Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.64; H, 5.49; N, 5.22.

3.3.2. 4-Methoxy-2-(2-methoxyphenyl)quinoline (entry 2, Table 1). White solid. Mp: 82–83 °C. R_f: 0.45 with 2:8 ethylacetate–pet. ether. FTIR (KBr) ν_{max} cm^{-1}: 1586, 1425, 1204, 1126. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.70 (s, 3H, OCH_3), 7.01 (s, 1H, H-3), 7.37–7.41 (m, 1H), 7.44–7.50 (m, 1H), 7.66–7.78 (m, 4H), 8.14 (d, J=8.45 Hz, 1H, H-8), 8.18 (dd, J=1.5, 8.0 Hz, 1H, H-8). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 55.8, 102.5, 111.59, 120.4, 121.3, 121.7, 125.6, 128.6, 129.7, 129.9, 130.5, 131.4, 148.6, 157.1, 158.3, 161.9. MS m/z: 265 (M^+). Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.64; H, 5.49; N, 5.22.

3.3.3. 2-(3,4-Dimethoxyphenyl)-4-methoxyquinoline (entry 3, Table 1). White solid. Mp: 125–126 °C. R_f: 0.45 with 2:8 ethylacetate–pet. ether. FTIR (KBr) ν_{max} cm^{-1}: 1589, 1420, 1200, 1110. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.95 (s, 3H, OCH_3), 4.01 (s, 3H, OCH_3), 4.04 (s, 3H, OCH_3), 6.97 (d, J=8.6 Hz, 1H, H′-5), 7.1 (s, 1H, H-3), 7.44 (t, J=7.45 Hz, 1H, H-7), 7.57 (dd, J=1.7, 8.0 Hz, 1H, H′-6), 7.68 (t, J=8.0 Hz, 1H, H-6), 7.82 (d, J=2.3 Hz, 1H, H′-2), 8.06 (d, J=8.6 Hz, 1H, H-8), 8.15 (d, J=8.05 Hz, 1H, H-5). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 55.7, 56.1, 56.2, 97.6, 110.7, 110.9, 120.2, 120.4, 121.7, 125.2, 129.07, 130.0, 133.4, 149.2, 149.4, 150.4, 158.4, 162.8. MS m/z: 295 (M^+). Anal. Calcd for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N, 4.74. Found: C, 73.01; H, 5.49; N, 4.42.

3.3.4. 4-Methoxy-2-phenylquinoline (entry 4, Table 1). White solid. Mp: 67–68 °C (lit. 68–69 °C).[6] R_f: 0.48 with 2:8 ethylacetate–pet. ether. FTIR (KBr) ν_{max} cm^{-1}: 1588, 1411, 1205, 1100. ^1H NMR (500 MHz, $CDCl_3$) δ: 4.07 (s, 3H, OCH_3), 7.15 (s, 1H, H-3), 7.44–7.53 (m, 4H), 7.69–7.7 (m, 1H, H-7), 8.10–8.12 (m, 3H), 8.19 (d, J=8.05 Hz, 1H, H-5). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 55.8, 98.1, 120.4, 121.7, 125.5, 127.6, 128.9, 129.3, 129.4, 130.1, 140.5, 149.3, 159.0, 162.9. MS *m/z*: 235 (M^+). Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.48; H, 5.58; N, 5.78.

3.3.5. 2-(4-Chlorophenyl)-4-methoxyquinoline (entry 5, Table 1). White solid. Mp: 111–112 °C (lit. 110–111 °C).[6] R_f: 0.4 with 2:8 ethylacetate–pet. ether. FTIR (KBr) ν_{max} cm^{-1}: 1583, 1429, 1210, 1122. ^1H NMR (500 MHz, $CDCl_3$) δ: 4.0 (s, 3H, OCH_3), 7.11 (s, 1H, H-3), 7.47–7.50 (m, 3H), 7.64–7.72 (m, 1H), 8.05–8.08 (m, 3H), 8.17 (d, J=8.40 Hz, 1H, H-5). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 55.8, 97.7, 120.5, 121.8, 125.7, 128.9, 129.0, 129.2, 130.3, 135.5, 138.81, 149.2, 157.6, 163.1. MS *m/z*: 269 (M^+) and 271 (M+2). Anal. Calcd for $C_{16}H_{12}ClNO$: C, 71.25; H, 4.48; N, 5.19. Found: C, 71.34; H, 4.28; N, 5.32.

3.3.6. 2-(2-Fluorophenyl)-4-methoxyquinoline (entry 6, Table 1). White solid. Mp: 115–116 °C. R_f: 0.4 with 2:8 ethylacetate–pet. ether. FTIR (KBr) ν_{max} cm^{-1}: 1579, 1419, 1205, 1120. ^1H NMR (500 MHz, $CDCl_3$) δ: 4.0 (s, 3H, OCH_3), 7.10 (s, 1H, H-3), 7.39–7.44 (m, 1H), 7.49–7.52 (m, 1H), 8.0–8.12 (m, 5H), 8.19 (d, J=7.45 Hz, 1H, H-5). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 55.9, 101.6, 121.8, 124.8, 124.8, 125.8, 129.3, 129.8, 130.0, 131.6, 132.3, 140.3, 149.2, 155.3, 159.7, 161.7. MS *m/z*: 253 (M^+). Anal. Calcd for $C_{16}H_{12}FNO$: C, 75.88; H, 4.78; N, 5.53. Found: C, 75.78; H, 4.89; N, 5.49.

3.3.7. 2-[3-(4-Chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl]-4-methoxyquinoline (entry 7, Table 1). White solid. Mp: 156–157 °C. R_f: 0.32 with 2:8 ethylacetate–pet. ether. FTIR (KBr) ν_{max} cm^{-1}: 1592, 1419, 1212, 1134. ^1H NMR (500 MHz, $CDCl_3$) δ: 3.74 (s, 3H, OCH_3), 6.63 (s, 1H, H-3), 7.31 (t, J=6.90 Hz, 1H, H-7), 7.36–7.50 (m, 5H), 7.63–7.85 (m, 5H), 8.02 (d, J=8.4 Hz, 1H, H-8), 8.13 (d, J=6.9 Hz, 1H, H-5), 8.55 (s, 1H, pyrazole CH). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 55.6, 100.6, 119.3, 120.3, 121.8, 123.7, 125.5, 127.0, 128.6, 128.7, 128.8, 129.6, 130.2, 130.6, 131.8, 134.4, 139.8, 149.3, 150.2, 153.3, 162.2. MS *m/z*: 412 (M^+). Anal. Calcd for $C_{25}H_{18}ClN_3O$: C, 72.90; H, 4.40; N, 10.20. Found: C, 72.68; H, 4.29; N, 10.43.

3.3.8. 2-(1,3-Diphenyl-1*H*-pyrazol-4-yl)-4-methoxyquinoline (entry 8, Table 1). White solid. MP: 172–174 °C. R_f: 0.36 with 2:8 ethylacetate–pet. ether. FTIR (KBr) ν_{max} cm^{-1}: 1598, 1415, 1218, 1143. ^1H NMR (500 MHz, $CDCl_3$) δ: 3.73 (s, 3H, OCH_3), 6.63 (s, 1H, H-3), 7.32 (t, J=7.60 Hz, 1H, H-7), 7.36–7.52 (m, 5H), 7.63–7.85 (m, 6H), 8.01 (d, J=8.4 Hz, 1H, H-8), 8.13 (d, J=8.4 Hz, 1H, H-5), 8.55 (s, 1H, pyrazole CH). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 55.6, 100.6, 119.3, 120.3, 121.8, 123.7, 125.5, 127.0, 128.6, 128.70, 128.7, 129.6, 130.2, 130.7, 131.8, 134.4, 139.8, 148.9, 150.2, 153.3, 162.1. MS *m/z*: 377 (M^+). Anal. Calcd for $C_{25}H_{19}N_3O$: C, 79.55; H, 5.07; N, 11.13. Found: C, 79.48; H, 5.29; N, 11.43.

3.3.9. 2-[3-(4-Methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl]-4-methoxyquinoline (entry 9, Table 1). White solid. Mp: 128–129 °C. R_f: 0.3 with 2:8 ethylacetate–pet. ether. FTIR (KBr) ν_{max} cm^{-1}: 1586, 1419, 1217, 1140. ^1H NMR (500 MHz, $CDCl_3$) δ: 3.65 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 6.62 (s, 1H, H-3), 7.32 (t, J=7.84 Hz, 1H, H-7), 7.40–7.55 (m, 5H), 7.57–7.86 (m, 5H), 8.02 (d, J=8.0 Hz, 1H, H-8), 8.11 (d, J=8.45 Hz, 1H, H-5), 8.56 (s, 1H, pyrazole CH). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 54.4, 55.6, 100.6, 119.3, 119.3, 120.3, 121.8, 125.5, 127.0, 128.5, 128.6, 128.8, 129.6, 130.1, 130.2, 131.8, 134.4, 138.3, 149.2, 150.1, 153.7, 162.2. MS *m/z*: 407 (M^+). Anal. Calcd for $C_{26}H_{21}N_3O_2$: C, 76.64; H, 5.19; N, 10.31. Found: C, 76.48; H, 5.20; N, 10.21.

3.3.10. 2-(4-Methoxyphenyl)-4*H*-chromen-4-one (entry 1, Table 2). Pale white solid. Mp: 156–157 °C (lit. 157–158 °C).[16] R_f: 0.2 with 2:8 ethylacetate–pet. ether. FTIR (KBr) ν_{max} cm^{-1}: 1662, 1420, 1200, 1110. ^1H NMR (500 MHz, $CDCl_3$) δ: 3.87 (s, 3H, OCH_3), 6.97 (s, 1H, H-3), 6.99 (d, J=8.55 Hz, 2H), 7.37 (m, 1H), 7.52 (d, J=8.6 Hz, 1H, H-8), 7.65 (m, 1H), 7.85 (d, J=8.6 Hz, 2H), 8.2 (d, J=8 Hz, 1H, H-5). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 55.5, 106.2, 114.6, 118.0, 118.1, 124.0, 125.1, 125.8, 128.1, 133.7, 156.3, 162.5, 163.5, 178.5. MS *m/z*: 252 (M^+). Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79. Found: C, 76.01; H, 4.92.

3.3.11. 2-(4-Methylphenyl)-4*H*-chromen-4-one (entry 2, Table 2). White solid. Mp: 108–109 °C (lit. 110–111 °C).[16] R_f: 0.2 with 2:8 ethylacetate–pet. ether. FTIR (KBr) ν_{max} cm^{-1}: 1668, 1417, 1228, 1016. ^1H NMR (500 MHz, $CDCl_3$) δ: 2.37 (s, 3H, CH_3), 6.79 (s, 1H, H-3), 7.30 (d, J=8.05 Hz, 2H), 7.39–7.42 (m, 1H), 7.54–7.56 (m, 2H), 7.81 (d, J=8.0 Hz, 2H), 8.21 (dd, J=1.7, 8.0 Hz, 1H, H-5). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 21.6, 107.1, 118.1, 124.1, 125.2, 125.8, 126.3, 129.0, 129.8, 133.8, 142.4, 156.3, 163.7, 178.6. MS *m/z*: 236 (M^+). Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.10; H, 4.92.

3.3.12. 2-(4-Methoxyphenyl)-4*H*-chromen-4-one (entry 3, Table 2). White solid. Mp: 156–157 °C (lit. 157–158 °C).[16] R_f: 0.2 with 2:8 ethylacetate–pet. ether. FTIR (KBr) ν_{max} cm^{-1}: 1662, 1420, 1200, 1110. ^1H NMR (500 MHz, $CDCl_3$) δ: 3.87 (s, 3H, OCH_3), 6.97 (s, 1H, H-3), 6.99 (d, J=8.55 Hz, 2H), 7.37 (m, 1H), 7.52 (d, J=8.6 Hz, 1H, H-8), 7.65 (m, 1H), 7.85 (d, J=8.6 Hz, 2H), 8.2 (d, J=8 Hz, 1H, H-5). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 55.5, 106.2, 114.6, 118.0, 118.1, 124.0, 125.1, 125.8, 128.1, 133.7, 156.3, 162.5, 163.5, 178.5. MS *m/z*: 252 (M^+). Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79. Found: C, 76.01; H, 4.92.

3.3.13. 2-(3,4-Dimethoxyphenyl)-4*H*-chromen-4-one (entry 4, Table 2). White solid. Mp: 178–179 °C. R_f: 0.25 with 2:8 ethylacetate–pet. ether. FTIR (KBr) ν_{max} cm^{-1}: 1672, 1430, 1212, 1019. ^1H NMR (500 MHz, $CDCl_3$) δ: 3.93 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 6.73 (s, 1H, H-3), 6.94–7.54 (m, 4H), 7.64–7.69 (m, 1H), 7.52 (d, J=8.6 Hz, 1H, H-8), 8.18 (dd, J=1.55, 8.4 Hz, 1H, H-5). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 56.2, 106.5, 108.8, 111.20, 118.07, 120.08, 124.0, 124.3, 125.2, 125.7, 133.7, 149.3, 152.1, 156.2, 163.4, 178.5. MS *m/z*: 282 (M^+). Anal. Calcd for $C_{17}H_{14}O_4$: C, 72.33; H, 5.00. Found: C, 72.01; H, 4.94.

3.3.14. 4-Ethoxy-2-phenylquinoline (Scheme 3). Mp: 74–75 °C (lit. 73–74 °C).[5] R_f: 0.55 with 2:8 ethylacetate–pet. ether. FTIR (KBr) ν_{max} cm^{-1}: 1585, 1414, 1206, 1113. ^1H NMR (500 MHz, $CDCl_3$) δ: 1.58 (t, J=6.82 Hz, 3H), 4.32 (q, J=7.45, 6.80 Hz, 2H), 7.14 (s, 1H, H-3), 7.45–7.58 (m, 4H), 7.6–8.1 (m, 4H), 8.2 (dd, J=1.15, 8.6 Hz, 1H, H-5). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 14.7, 64.1, 98.6, 120.6, 121.9, 125.4, 127.7, 128.8, 129.3, 129.3, 130.0, 140.6, 149.3, 158.9, 162.2. MS m/z: 249 (M^+). Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.82; H, 6.10; N, 5.56.

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