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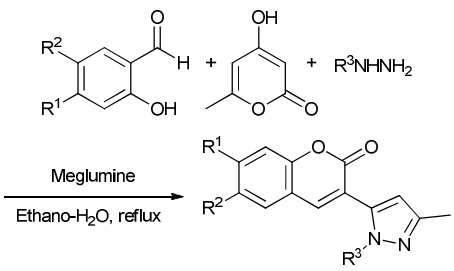
• **Graphical Abstract:**



Meglumine catalyzed one-pot, three-component combinatorial synthesis of pyrazoles bearing a coumarin unit

Xiao-Tang Li, Yu-Heng Liu, Xin Liu, and Zhan-Hui Zhang*

Meglumine has been found to be an efficient catalyst for the synthesis of pyrazolylcoumarins by one-pot three-component reaction of salicylaldehyde, 4-hydroxy-6-methyl-2H-pyran-2-one, and hydrazine.

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Meglumine catalyzed one-pot, three-component combinatorial synthesis of pyrazoles bearing a coumarin unit

Xiao-Tang Li[a], Yu-Heng Liu[b], Xin Liu[a], Zhan-Hui Zhang[a,*]

A simple, efficient, and eco-friendly procedure for synthesis of a wide range of pyrazoles bearing a coumarin unit has been developed by one-pot three-component reaction of salicylaldehyde, 4-hydroxy-6-methyl-2*H*-pyran-2-one, and hydrazine using meglumine as a catalyst in aqueous-ethanol media. This new protocol offers several advantages including the use of biodegradable and inexpensive catalyst, short reaction time, high yields, and simple work-up procedure.

Introduction

Currently, multicomponent reactions (MCRs) are becoming powerful and valuable synthetic strategy in modern organic and medicinal chemistry because they make multistep synthesis to be conducted in a single procedural step to provide novel and highly functionalized organic molecules and biologically active heterocyclic compounds from simple and readily accessible starting materials. These reactions hold the possibility for convenient, safe, atom-economic, high-yielding, and environmentally benign procedures and reduce generation of chemical waste.[1-4] On the other hand, catalysts based on biodegradable materials such as chitosan,[5] starch,[6] cellulose,[7] xanthan,[8] polysaccharides,[9] gluconic acid[10] and eggshell[11] have received much attention. Meglumine is an amino sugar derived from sorbitol and can be widely used in pharmaceuticals and medicine due to its peculiar physical and chemical properties such as low toxicity, bio-compatibility and bio-degradability, low cost and non-corrosion nature. It was early reported by Gu as a promoting medium with gluconic acid aqueous solution for hydroxymethylation of β-ketosulfones with formaldehyde.[12] Meglumine contains amino group, primary and secondary hydroxyl groups. Therefore, it can activate the reaction components by not only base centers but also hydrogen bonding. Recently, it has been demonstrated that meglumine is a highly active catalyst for some organic transformations.[13] Therefore, the combination of MCRs and meglumine will make the chemical reaction more economical and environmentally friendly.

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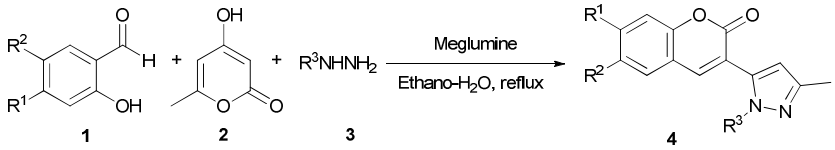
It is well known that pyrazole nucleus is an important core of various products and medicinal agents. They exhibit broad spectra of biological activities such as anticancer,[14] antibacterial,[15] antitubercular,[16] antimicrobial,[17] antioxidant,[18] and kinase inhibitors.[19] In addition, coumarins represent another important moiety occurring frequently in numerous natural products, pharmaceuticals, agrochemicals, dyes, and functional materials.[20] Due to the importance of these two structural frameworks, the development of a simple procedure for the synthesis of aesthetically appealing molecular architecture containing both the pyrazole moiety and coumarin framework using biodegradable material as a catalyst and green solvent is still desirable and challenging task.

In view of the above points and as a continuation of our ongoing work on the development of multicomponent reactions[21] and environmentally friendly methodologies,[22] attempts were made to construct pyrazolylcoumarins via one-pot, three-component coupling (TCC) reaction of salicylaldehyde, 4-hydroxy-6-methyl-2*H*-pyran-2-one and hydrazine using meglumine as a biodegradable catalyst (Scheme 1).



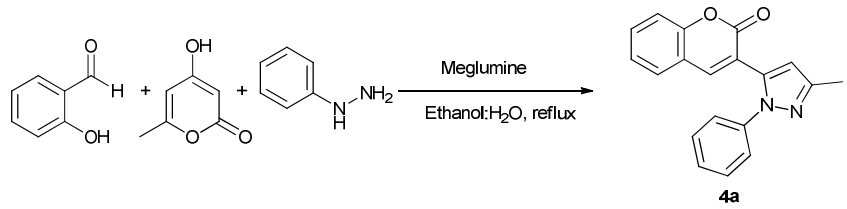
Scheme 1 One-pot, three-component synthesis of pyrazolylcoumarins catalyzed by meglumine

Results and discussion

Initially, salicylaldehydes, 1,4-hydroxy-6-methyl-2*H*-pyran-2-one and phenylhydrazine served as model substrates for optimization of reaction conditions. Some of the key results are summarized in Table 1. In the control experiments, no anticipated product was observed in the absence any catalyst (Table 1, entries 1 and 2). Little product was obtained when the reaction was performed using Fe_2O_3 or *L*-proline as catalyst in a mixture of EtOH/H_2O. When $CaCO_3$, piperidine, 1,3-dimethylurea, chitosan, betaine HCl, mannitol, DMAP, Et_3N or DABCO was employed as the catalyst, the reaction took place, however, the yield of the target compound **4a** was not satisfactory (entries 3-14). When the reaction was carried out in deep eutectic solvents (DES) such as choline chloride: urea or citric acid: DMU, no improvement was observed (entries 15 and 16). Further experiments found that meglumine was the best catalyst for this three-component reaction and afforded the desired product **4a** in an isolated yield of 80% within 1.5 h (Table 1, entry 17).

Subsequently, the reaction media, amounts of catalyst and reaction times were also examined. The reaction did not proceed satisfactorily in water, possibly due to incomplete homogeneity of the reaction mixture. Further studies showed that aqueous-ethanol (1:1, v/v) was the best choice of solvent for this transformation. The reaction was also carried out using different amounts of the catalyst and the results showed that 20 mol% of catalyst was the best choice. Decreasing the amount of catalyst to 10 mol% relative to substrate, the yield of product decreased (entry 25). When the reaction was conducted with increasing amounts of meglumine or by prolonging the reaction times, the yield of **4a** could not be further increased. From the above investigations, the optimized reaction conditions were established by employing salicylaldehyde, 4-hydroxy-6-methyl-2*H*-pyran-2-one (1 mmol), and phenylhydrazine (1 mmol) with meglumine (0.2 mmol) in aqueous-ethanol (1:1 v/v, 4 ml) under reflux for 1.5 h (Table 1, entry 17).

Table 1 Optimization of the reaction conditions for the synthesis of **4a**.[a]



4a

Entry	Catalyst	Solvent	Temp (°C)	Time (min)	Yield (%)[b]
1	None	Ethanol	Reflux	720	0
2	None	Ethanol: H_2O (1: 1)	Reflux	720	0
3	Fe_2O_3	Ethanol: H_2O (1: 1)	Reflux	720	Trace
4	L-Proline	Ethanol: H_2O (1: 1)	Reflux	720	Trace
5	$CaCO_3$	Ethanol: H_2O (1: 1)	Reflux	360	20
6	Piperidine	Ethanol: H_2O (1: 1)	Reflux	360	40
7	1,3-Dimethylurea	Ethanol: H_2O (1: 1)	Reflux	360	38
8	Chitosan	Ethanol: H_2O (1: 1)	Reflux	360	35
9	Betaine HCl	Ethanol: H_2O (1: 1)	Reflux	360	20
10	Mannitol	Ethanol: H_2O (1: 1)	Reflux	360	30
11	DMAP	Ethanol: H_2O (1: 1)	Reflux	360	42
12	DBU	Ethanol: H_2O (1: 1)	Reflux	360	60
13	Et_3N	Ethanol: H_2O (1: 1)	Reflux	360	56
14	DABCO	Ethanol: H_2O (1: 1)	Reflux	360	68
15	Choline chloride: urea (1: 2)		80	360	42
16	Citric acid: DMU (40: 60)		80	360	30
17	Meglumine	Ethanol: H_2O (1: 1)	Reflux	90	80
18	Meglumine	H_2O	Reflux	720	Trace
19	Meglumine	Glycerin	Reflux	720	40
20	Meglumine	Glycerin: ethanol (1: 2)	Reflux	720	48
21	Meglumine	Glycerin : H_2O (1: 3)	Reflux	360	56

22	Meglumine	PEG400	100	360	45
23	Piperidine	CH_3CN	Reflux	360	36
24	Meglumine	Ethanol	Reflux	90	70
25	Meglumine (0.1 mmol)	Ethanol: H_2O (1: 1)	Reflux	90	65
26	Meglumine (0.4 mmol)	Ethanol: H_2O (1: 1)	Reflux	60	60
27	Meglumine (0.4 mmol)	Ethanol: H_2O (1: 1)	Reflux	90	80
28	Meglumine (0.4 mmol)	Ethanol: H_2O (1: 1)	Reflux	360	80
29	Meglumine (0.3 mmol)	Ethanol: H_2O (1: 1)	Reflux	90	80

[a] Experimental conditions: salicylaldehyde (1 mmol), 4-hydroxy-6-methyl-2*H*-pyran-2-one (1 mmol), phenylhydrazine (1 mmol), catalyst (0.2 mmol), solvent (4 ml). [b] Isolated yield.

Under the optimized reaction conditions, the scope of this three-component reaction was considerably expanded and the results are summarized in Figure 1. Various arylhydrazines bearing electron-donating group (EDG) and electron-withdrawing group (EWG) underwent the reaction with salicylaldehydes and 4-hydroxy-6-methyl-2*H*-pyran-2-one to afford the desired products in good to high yields. The influence of substituents on the benzene ring of phenylhydrazine was also examined. In general, substituents possessing an EDG tended to afford better yields than those bearing EWG. However, for phenylhydrazine with a strong EWG such as (4-nitrophenyl)hydrazine, no expected product was obtained. In addition to arylhydrazines, we found that hydrazine was compatible and furnished the desired product **4g** in good yield. The 2-hydrazinylpyridine worked well, providing high yield of expected **4h**. Fortunately, 2-hydrazinylbenzo[*d*]thiazole also proceeded efficiently, producing the corresponding product **4n** in 70% isolated yield.

Inspired by these encouraging results, we next explored the scope of this MCR process with respect to salicylaldehydes. As anticipated, salicylaldehydes bearing either electron-donating or electron-withdrawing groups such as hydroxyl, methoxy, NEt_2, chloro, bromo and nitro were all tolerated and afforded the respective products in good to high yields. Generally, the electron-withdrawing substituted salicylaldehydes showed better reactivity than the electron-donating substituted salicylaldehydes. Furthermore, 2-hydroxy-1-naphthaldehyde participated in the reaction smoothly and delivered the products **4ab**-**4ae** in 70-86% yield, respectively.

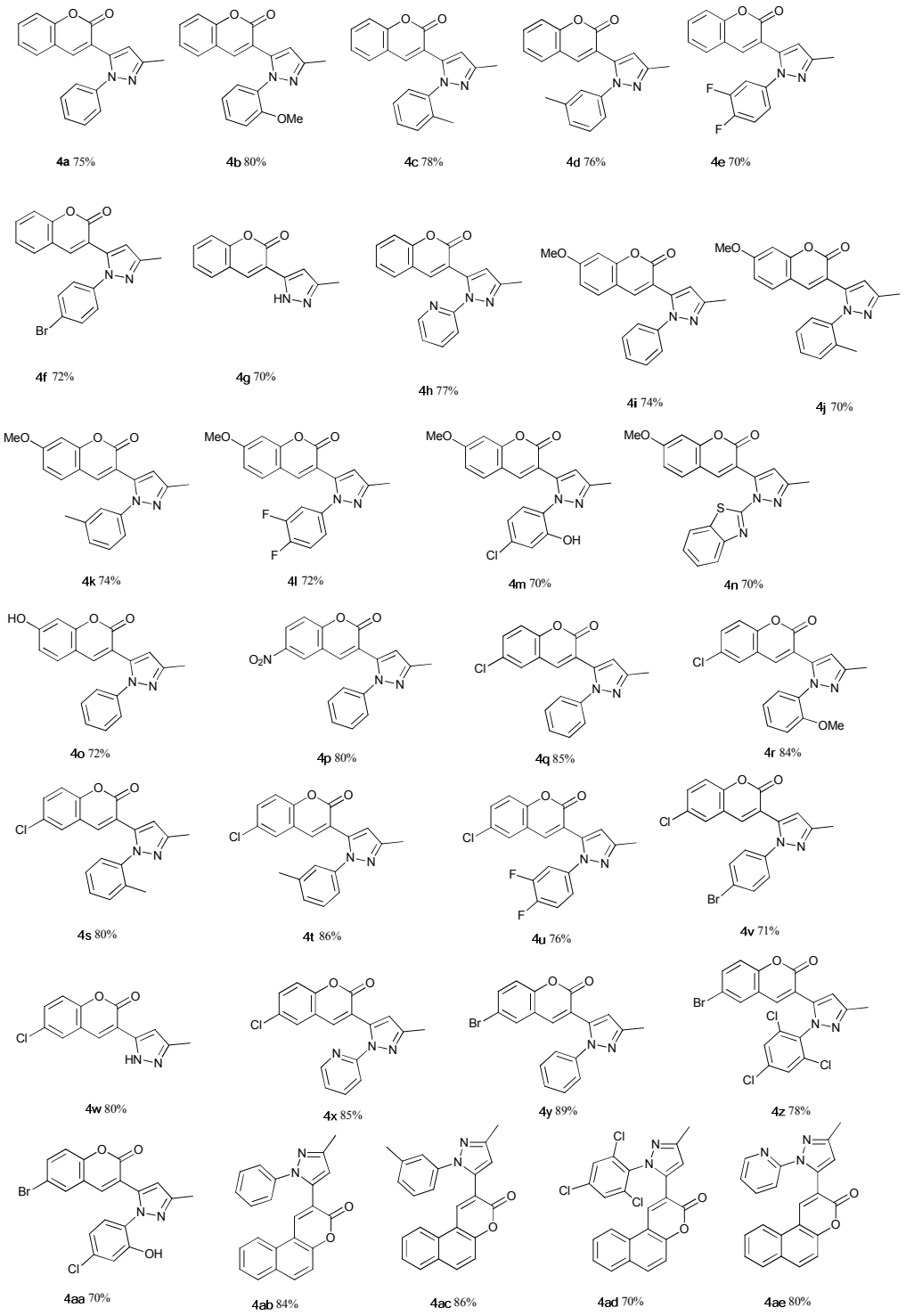
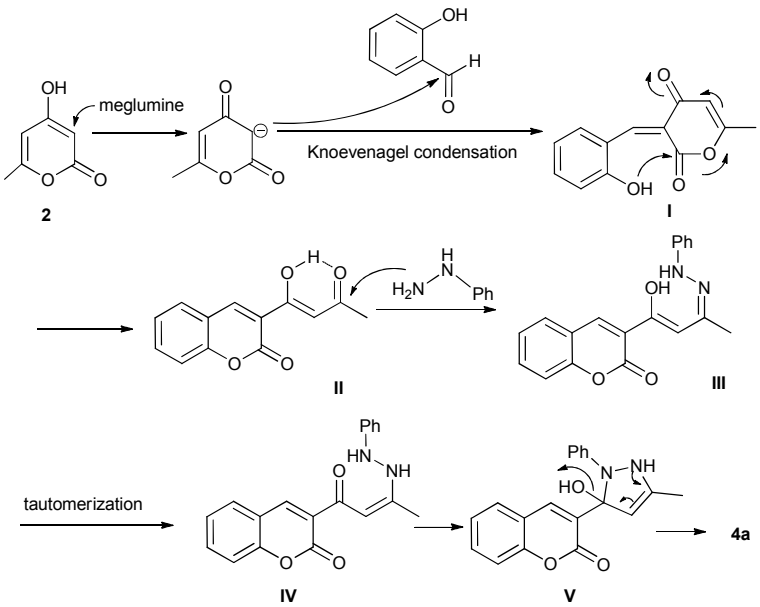


Figure 1 Scope of pyrazolylcoumarin synthesis.

A proposed mechanism for the synthesis of 3-(3-methyl-1-phenyl-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (**4a**) from salicylaldehyde, 4-hydroxy-6-methyl-2*H*-pyran-2-one, and phenylhydrazine catalyzed by meglumine is shown in Scheme 2. We reasoned that in the presence of meglumine, Knoevenagel

condensation of salicylaldehyde and 4-hydroxy-6-methyl-2*H*-pyran-2-one would occur first to produce the intermediate **I**. The intermediate **I** could then undergo intramolecular cyclization by the nucleophilic addition of enolate oxygen to carbonyl group to afford the intermediate **II**. The intermediate **II** further reacted with phenylhydrazine to form the intermediate **IV,** which then tautomerized to intermediate **IV**. Finally, an intramolecular cyclization of intermediate **IV** promoted by meglumine would happen to give the target product **4a** by eliminating one molecule of water.



Scheme 2. Plausible mechanism for synthesis of product **4a**.

Conclusion

In summary, a novel, highly efficient and green procedure has been successfully developed for the synthesis of a series of pyrazoles bearing a coumarin unit via one-pot three-component reaction of salicylaldehyde, 4-hydroxy-6-methyl-2*H*-pyran-2-one, and hydrazine by using meglumine as an inexpensive, biodegradable catalyst in aqueous-ethanol media. Environmental acceptability, economic viability, short reaction time, high yields, and cleaner reaction profiles are important features of this protocol. This strategy opens a new opportunity for the preparation of libraries of a wide variety of pyrazolylcoumarin derivatives for biological screening.

Experimental section

General information

All chemicals were purchased from commercial sources and used without further purification. Melting

points were determined using an X-4 apparatus and are uncorrected. IR spectra were taken as KBr discs with a Thermo Fisher Scientific Nicolet iS50 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 spectrometer at 500 MHz and 125 MHz in $CDCl_3$, respectively. Elemental analyses were carried out on a Vario EL III CHNOS instrument. Mass spectra were recorded on a 3200 Qtrap instrument with an ESI source.

General procedure for the synthesis of pyrazolesubstituted derivatives

To a mixture of ethyl salicylaldehyde (1 mmol) and 4-hydroxy-6-methyl-2*H*-pyran-2-one (1 mmol) in ethanol-H_2O (1:1) (4 mL) was added hydrazine (1 mmol), and meglumine (0.2 mmol) at room temperature. The reaction mixture was stirred under reflux and monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature. The solid product was separated, washed with ether and purified by column chromatography on silica gel (eluent: EtOAc–hexane 1:9).

Characterization data

3-(3-Methyl-1-phenyl-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (4a). White solid, 130-131 °C (Lit. 126-127 °C)[23]; IR (KBr): 3032, 1780, 1680, 1620, 1500, 1465, 1386, 1012 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm: 7.55-7.52 (m, 1H), 7.46 (s, 1H), 7.42-7.40 (m, 3H), 7.38 (s, 1H), 7.34-7.31 (m, 3H), 7.24 (d, *J* = 7.5 Hz, 1H), 6.61 (s, 1H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 157.0, 155.1, 153.1, 143.1, 139.6, 129.6, 121.2, 118.8, 117.4, 116.6, 116.4, 114.7, 114.5, 112.7, 28.9; Anal. Calcd for $C_{19}H_{14}N_2O_2$: C, 75.48; H, 4.67; N, 9.27. Found: C, 75.65; H, 4.50; N, 9.44; ESI-MS: m/z = 303 $(M+1)^+$.

3-(1-(2-Methoxyphenyl)-3-methyl-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (4b). White solid, 191-192 °C; IR (KBr): 3015, 1738, 1661, 1613, 1516, 1453, 1389, 1163, 756, 693 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm: 8.50 (s, 1H), 7.51 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 5.5 Hz, 2H), 7.39 (d, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 1H), 6.91 (s, 1H), 6.83 (s, 1H), 3.83 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 160.1, 154.7, 148.8, 142.2, 136.3, 133.6, 131.0, 130.5, 129.5, 128.3, 127.9, 127.6, 126.9, 126.4, 125.8, 120.7, 117.3, 112.3, 29.7, 14.1; Anal. Calcd for $C_{20}H_{16}N_2O_3$: C, 72.28; H, 4.85; N, 8.43. Found: C, 72.45; H, 4.68; N, 8.60; ESI-MS: m/z = 333 $(M+1)^+$.

3-(3-Methyl-1-(o-tolyl)-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (4c). White solid, 149-150 °C; IR (KBr): 3119, 1745, 1638, 1612, 1496, 1454, 1398, 1165, 750, 709 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm: 8.50 (s, 1H), 7.52 (t, *J* = 7.0 Hz, 2H), 7.41 (t, *J* = 7.0 Hz, 1H), 7.38 (s, 1H), 7.37 (d, *J* = 5.0 Hz, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.10 (s, 1H), 2.17 (s, 3H), 2.13 (s, 3H); ^{13}C

NMR (125 MHz, $CDCl_3$) δ ppm: 160.1, 153.4, 145.2, 140.9, 138.5, 137.3, 136.1, 131.1, 129.5, 128.9, 127.7, 126.7, 124.5, 120.7, 119.7, 116.4, 107.0, 17.3, 11.5; Anal. Calcd for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 76.10; H, 4.93; N, 9.03; ESI-MS: m/z = 317 $(M+1)^+$.

3-(3-Methyl-1-(m-tolyl)-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (4d). White solid, 164 °C; IR (KBr): 3001, 1767, 1654, 1630, 1496, 1460, 1384, 1048 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ ppm: 8.51 (s, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.40-7.35 (m, 2H), 7.34 (s, 1H), 7.28 (d, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.06 (s, 1H), 2.44 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 160.0, 153.4, 145.2, 140.1, 137.4, 131.2, 129.0, 128.9, 128.1, 125.9, 124.5, 122.1, 120.6, 119.6, 116.4, 108.3, 21.4, 12.5; Anal. Calcd for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 76.10; H, 4.93; N, 9.03; ESI-MS: m/z = 317 $(M+1)^+$.

3-(1-(3,4-Difluorophenyl)-3-methyl-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (4e).

White solid, 209-210 °C; IR (KBr): 3032, 1750, 1668, 1600, 1502, 1543, 1381, 1050, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ ppm: 8.47 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.30-7.27 (m, 2H), 7.07 (s, 1H), 6.99-6.89 (m, 1H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 159.9, 153.5, 150.2 (dd, J_{FC} = 249.5, 13.6 Hz), 149.9 (dd, J_{FC} = 248.9, 12.5 Hz), 145.9, 140.1, 137.8, 136.0 (dd, J_{FC} = 8.0, 3.5 Hz), 131.4, 128.2, 124.6, 120.9 (dd, J_{FC} = 6.4, 3.7 Hz), 120.2, 119.5, 117.6 (d, J_{FC} = 18.5 Hz), 116.4, 114.7 (d, J_{FC} = 19.6 Hz), 109.0, 12.5; Anal. Calcd for $C_{19}H_{12}F_2N_2O_2$: C, 67.45; H, 3.58; N, 8.28. Found: C, 67.62; H, 3.41; N, 8.45; ESI-MS: m/z = 339 $(M+1)^+$.

3-(1-(4-Bromophenyl)-3-methyl-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (4f). White solid, 212-213 °C; IR (KBr): 3013, 1724, 1661, 1611, 1494, 1454, 1340, 1070, 753, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ ppm: 8.51 (s, 1H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.11 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 160.0, 153.5, 145.8, 140.1, 138.7, 137.7, 132.4, 131.3, 128.5, 128.2, 126.5, 126.2, 124.5, 121.8, 120.4, 119.6, 116.4, 108.9, 12.5; Anal. Calcd for $C_{19}H_{13}BrN_2O_2$: C, 59.86; H, 3.44; N, 7.35. Found: C, 60.03; H, 3.27; N, 7.52; ESI-MS: m/z = 381 $(M+1)^+$.

3-(3-Methyl-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (4g). White solid, 180-181 °C (Lit. 182 °C)[23]; IR (KBr): 3432, 2954, 1728, 1713, 1610, 1554, 1459, 1394, 1032 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ ppm: 8.03 (d, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 7.0 Hz, 1H), 7.43 (s, 1H), 7.03 (t, *J* = 8.5 Hz, 1H), 6.98 (d, *J* = 7.0 Hz, 1H), 6.91 (s, 1H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 159.8, 150.9, 146.0, 135.5, 131.1, 127.8, 125.2, 123.4, 117.8, 114.4, 32.0; Anal. Calcd for $C_{13}H_{10}N_2O_2$: C, 69.02; H, 4.46; N, 12.38. Found: C,

69.19; H, 4.29; N, 12.55; ESI-MS: m/z = 227 $(M+1)^+$.

3-(3-Methyl-1-(pyridin-2-yl)-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (4h). White solid, 158-160 °C; IR (KBr): 3018, 1735, 1640, 1600, 1593, 1475, 1384, 1054 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ ppm: 8.18 (d, *J* = 4.5 Hz, 1H), 7.94 (s, 1H), 7.65 (t, *J* = 7.0 Hz, 1H), 7.55-7.51 (m, 1H), 7.37-7.33 (m, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.08 (s, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.84 (t, *J* = 6.0 Hz, 1H), 2.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 157.2, 155.5, 147.8, 147.2, 142.9, 139.2, 138.6, 130.5, 129.8, 119.6, 118.2, 116.7, 116.4, 106.6, 30.9; Anal. Calcd for $C_{18}H_{13}N_3O_2$: C, 71.28; H, 4.32; N, 13.85. Found: C, 71.45; H, 4.15; N, 14.02; ESI-MS: m/z = 304 $(M+1)^+$.

7-Methoxy-3-(3-methyl-1-phenyl-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (4i). Yellow oil; IR (KBr): 3047, 1726, 1604, 1503, 1458, 1383, 1074, 776, 695 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ ppm: 8.48 (s, 1H), 7.75-7.73 (m, 1H), 7.56-7.54 (m, 1H), 7.54-7.53 (m, 3H), 7.48-7.44 (m, 2H), 7.06 (s, 1H), 6.89 (s, 1H), 3.91 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 162.6, 155.3, 145.8, 140.0, 137.9, 132.3, 130.9, 129.2, 129.1, 128.8, 127.9, 125.1, 112.9, 108.2, 100.4, 65.6, 19.2; Anal. Calcd for $C_{20}H_{16}N_2O_3$: C, 72.28; H, 4.85; N, 8.43. Found: C, 72.45; H, 4.68; N, 8.60; ESI-MS: m/z = 333 $(M+1)^+$.

6-Methoxy-3-(3-methyl-1-(o-tolyl)-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (4j). White solid, 148-150 °C; IR (KBr): 3003, 1742, 1663, 1609, 1514, 1454, 1333, 1088, 778, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ ppm: 8.09 (s, 1H), 7.71 (d, *J* = 9.0 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 7.0 Hz, 2H), 7.09 (s, 1H), 3.85 (s, 3H), 2.40 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 161.7, 153.2, 151.9, 150.5, 149.6, 145.7, 140.0, 138.1, 137.1, 132.3, 131.6, 130.9, 128.8, 127.2, 126.2, 122.4, 117.7, 113.3, 29.7, 19.2, 13.7; Anal. Calcd for $C_{21}H_{18}N_2O_3$: C, 72.82; H, 5.24; N, 8.09. Found: C, 72.99; H, 5.07; N, 8.26; ESI-MS: m/z = 347 $(M+1)^+$.

7-Methoxy-3-(3-methyl-1-(m-tolyl)-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (4k). White solid, 163-165 °C; IR (KBr): 3007, 1735, 1700, 1631, 1507, 1465, 1384, 1049, 728, 695 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ ppm: 7.61 (s, 1H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.53-7.42 (m, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 6.5 Hz, 1H), 7.13 (d, *J* = 8.5 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 6.65 (s, 1H), 3.81 (s, 3H), 2.43 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 159.3, 151.8, 146.2, 139.1, 138.3, 130.8, 128.8, 126.7, 121.6, 117.9, 111.4, 111.0, 102.3, 29.7, 21.8, 12.8; Anal. Calcd for $C_{21}H_{18}N_2O_3$: C, 72.82; H, 5.24; N, 8.09. Found: C, 72.99; H, 5.07; N, 8.26; ESI-MS: m/z = 347 $(M+1)^+$.

3-(1-(3,4-Difluorophenyl)-3-methyl-1*H*-pyrazol-5-yl)-7-methoxy-2*H*-chromen-2-one (4l). Yellow oil; IR (KBr): 3103, 1739, 1658, 1610, 1520, 1454, 1398, 1025, 777, 697 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ

ppm: 7.57 (s, 1H), 7.46-7.38 (m, 1H), 7.11 (d, J = 9.0 Hz, 2H), 7.11 (d, J = 5.5 Hz, 1H), 6.86 (d, J = 8.5 Hz, 1H), 6.82-6.81 (m, 1H), 6.46 (s, 1H), 3.88 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 163.6, 159.2 (dd, J_{FC} = 274.7, 13.2 Hz), 158.1 (dd, J_{FC} = 252.9, 10.5 Hz), 155.8, 150.0, 142.9, 138.1, 137.2, 129.2 (dd, J_{FC} = 10.4, 3.1 Hz), 120.2 (dd, J_{FC} = 6.4, 3.7 Hz), 117.5 (d, J_{FC} = 17.7 Hz), 115.0, 114.0 (d, J_{FC} = 20.0 Hz), 113.3, 112.9, 112.1, 110.2, 108.7, 55.9, 13.5; Anal. Calcd for $C_{20}H_{14}F_2N_2O_3$: C, 65.22; H, 3.83; N, 7.61. Found: C, 65.39; H, 3.66; N, 7.78; ESI-MS: m/z = 369 $(M+1)^+$.

3-(1-(4-Chloro-2-hydroxyphenyl)-3-methyl-1*H*-pyrazol-5-yl)-7-methoxy-2*H*-chromen-2-one (4m). Yellow oil; IR (KBr): 3431, 2919, 1730, 1661, 1622, 1558, 1476, 1384, 1075, 715, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm: 8.60 (s, 1H), 7.62-7.47 (m, 3H), 7.33-7.29 (m, 1H), 6.98 (s, 1H), 6.90 (d, J = 7.5 Hz, 1H), 6.83 (s, 1H), 3.91 (s, 3H), 2.71 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 164.9, 158.4, 156.8, 146.0, 145.6, 142.2, 134.2, 131.8, 130.8, 129.1, 128.8, 118.3, 118.1,116.9, 113.7, 112.4, 100.9, 100.2, 56.0, 27.2; Anal. Calcd for $C_{20}H_{15}ClN_2O_4$: C, 62.75; H, 3.95; N, 7.32. Found: C, 62.92; H, 3.78; N, 7.49; ESI-MS: m/z = 383 $(M+1)^+$.

3-(1-(Benzo[d]thiazol-2-yl)-3-methyl-1*H*-pyrazol-5-yl)-7-methoxy-2*H*-chromen-2-one (4n). Yellow oil; IR (KBr): 3047, 1754, 1676, 1601, 1500, 1454, 1386, 1089, 756, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm: 8.53 (s, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.11 (s, 1H), 6.90 (d, J = 9.0 Hz, 2H), 6.87 (s, 1H), 6.84-6.83 (m, 1H), 3.91 (s, 3H), 2.88 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 159.5, 154.7, 151.9, 147.8, 147.1, 145.8, 142.6, 141.6, 140.4, 139.3, 133.9, 130.9, 128.5, 126.3, 124.1, 122.7, 119.0, 117.3, 106.1, 22.7, 14.1; Anal. Calcd for $C_{21}H_{15}N_3O_3S$: C, 64.77; H, 3.88; N, 10.79. Found: C, 64.94; H, 3.71; N, 10.96; ESI-MS: m/z = 390 $(M+1)^+$.

7-Hydroxy-3-(3-methyl-1-phenyl-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (4o). White solid, 150-151 °C; IR (KBr): 3489, 3125, 1722, 1646, 1601, 1496, 1449, 1384, 1075, 750, 687 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm: 7.30-7.28 (m, 5H), 7.24-7.23 (m, 3H), 6.89 (s, 1H), 6.87 (s, 1H), 1.62 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 156.0, 143.0, 139.2, 134.7, 132.4, 131.3, 129.6, 125.1, 121.3 120.3, 118.5, 112.7, 111.1, 29.7; Anal. Calcd for $C_{19}H_{14}N_2O_3$: C, 71.69; H, 4.43; N, 8.80. Found: C, 71.86; H, 4.26; N, 8.97; ESI-MS: m/z = 319 $(M+1)^+$.

3-(3-Methyl-1-phenyl-1*H*-pyrazol-5-yl)-6-nitro-2*H*-chromen-2-one (4p). White solid, 168-170 °C; IR (KBr): 3041, 1727, 1635, 1599, 1502, 1464, 1383, 1046, 712, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm: 7.38 (s, 1H), 7.37 (s, 3H), 7.34-7.31 (m, 1H), 7.29 (t, J = 4.5 Hz, 1H), 7.25-7.24 (m, 1H), 7.23-7.21 (m, 1H), 7.00-6.97 (m, 1H), 6.62 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 157.0, 155.1,

153.1, 143.1, 139.6, 129.6, 121.2, 118.8, 118.7, 117.5, 117.4, 116.6, 116.4, 114.7, 114.5, 112.7,21.4; Anal. Calcd for $C_{19}H_{13}N_3O_4$: C, 65.70; H, 3.77; N, 12.10. Found: C, 65.87; H, 3.60; N, 12.27; ESI-MS: m/z = 348 $(M+1)^+$.

6-Chloro-3-(3-methyl-1-phenyl-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (4q). White solid, 175-177 °C; IR (KBr): 3158, 1752, 1701, 1617, 1493, 1437, 1384, 1073, 713, 689 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ ppm: 7.94 (d, *J* = 8.0 Hz, 1H), 7.74-7.72 (m, 1H), 7.55-7.53 (m, 2H), 7.49 (s, 1H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.37 (s, 1H), 7.09 (t, *J* = 8.5 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 156.9, 154.1, 149.6, 142.9, 140.9, 136.9, 134.7, 131.1, 127.8, 126.9, 122.6, 118.2, 117.6, 114.9, 112.1, 104.5, 21.0; Anal. Calcd for $C_{19}H_{13}ClN_2O_2$: C, 67.76; H, 3.89; N, 8.32. Found: C, 67.93; H, 3.72; N, 8.49; ESI-MS: m/z = 337 $(M+1)^+$.

7-Chloro-3-(1-(2-methoxyphenyl)-3-methyl-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (4r). White solid, 223-224 °C; IR (KBr): 3042, 1740, 1663, 1608, 1507, 1454, 1392, 1080, 778, 683 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ ppm: 8.41 (s, 1H), 7.47 (d, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 9.0 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 8.5 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.07-7.05 (m, 2H), 3.83 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 154.6, 151.7, 145.0, 142.3, 135.8, 130.9, 130.7, 129.1, 127.1, 121.8 121.0, 120.8, 117.8, 112.1, 107.2, 29.7, 11.4; Anal. Calcd for $C_{20}H_{15}ClN_2O_3$: C, 65.49; H, 4.12; N, 7.64. Found: C, 65.66; H, 4.29; N, 7.81; ESI-MS: m/z = 367 $(M+1)^+$.

6-Chloro-3-(3-methyl-1-(*o*-tolyl)-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (4s). White solid, 150-151 °C; IR (KBr): 3095, 1740, 1661, 1602, 1502, 1454, 1380, 1083, 729, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ ppm: 8.37 (s, 1H), 7.44 (s, 1H), 7.41 (t, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 7.0 Hz, 1H), 7.35 (d, *J* = 7.0 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.27 (t, *J* = 4.5 Hz, 1H), 7.06 (s, 1H), 2.14 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 159.4, 151.7, 144.7, 141.0, 138.4, 136.0, 135.7, 131.2, 131.0, 129.7, 129.6, 127.7, 127.1, 126.8, 121.8, 120.7, 117.8, 107.2, 17.3, 11.5; Anal. Calcd for $C_{20}H_{15}ClN_2O_2$: C, 68.48; H, 4.31; N, 7.99. Found: C, 68.65; H, 4.14; N, 8.16; ESI-MS: m/z = 351 $(M+1)^+$.

6-Chloro-3-(3-methyl-1-(m-tolyl)-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (4t). White solid, 167-169 °C; IR (KBr): 2923, 1731, 1608, 1592, 1495, 1479, 1370, 1032, 695, 649 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ ppm: 8.44 (s, 1H), 7.50-7.48 (m, 1H), 7.44 (d, *J* = 9.0 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 6.5 Hz, 1H), 7.24 (s, 1H), 7.06 (s, 1H), 2.44 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 159.4, 157.8, 144.7, 140.5, 139.5, 136.3, 131.6, 129.8, 129.2, 129.0, 127.3, 126.0, 122.2, 121.4, 120.7, 117.8, 108.6, 21.4, 12.5; Anal. Calcd for $C_{20}H_{15}ClN_2O_2$: C, 68.48; H, 4.31; N, 7.99. Found: C, 68.65; H, 4.14; N, 8.16; ESI-MS: m/z = 351 $(M+1)^+$.

6-Chloro-3-(1-(3,4-difluorophenyl)-3-methyl-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (4u). White solid, 223-225 °C; IR (KBr): 3020, 1750, 1702, 1623, 1500, 1465, 1384, 1038, 717, 696 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ ppm: 8.40 (s, 1H), 7.53-7.52 (m, 1H), 7.46 (d, J = 8.5 Hz, 1H), 7.42-7.39 (m, 1H), 7.31 (d, J = 8.5 Hz, 2H), 7.23-7.17 (m, 1H), 7.08 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 163.2 (dd, J_{FC} = 258.6, 11.1 Hz), 159.4 (dd, J_{FC} = 258.2, 14.5 Hz), 159.3, 151.8, 145.4, 140.3, 136.3, 131.3, 129.8, 127.3, 121.3, 121.0 (dd, J_{FC} = 6.4, 3.7 Hz), 120.6, 117.9 (dd, J_{FC} = 7.5, 3.1 Hz), 117.7 (d, J_{FC} = 18.5 Hz), 114.8 (d, J_{FC} = 19.6 Hz), 109.1, 12.5; Anal. Calcd for $C_{19}H_{11}ClF_2N_2O_2$: C, 61.22; H, 2.97; N, 7.52. Found: C, 61.39; H, 2.80; N, 7.69; ESI-MS: m/z = 373 $(M+1)^+$.

3-(1-(4-Bromophenyl)-3-methyl-1*H*-pyrazol-5-yl)-6-chloro-2*H*-chromen-2-one (4v). White solid, 227-229 °C; IR (KBr): 3030, 1745, 1666, 1600, 1505, 1460, 1381, 1080, 755, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ ppm: 8.43 (s, 1H), 7.67 (d, J = 8.5 Hz, 2H), 7.54 (s, 1H), 7.48 (d, J = 9.0 Hz, 1H), 7.42 (d, J = 9.0 Hz, 2H), 7.33 (d, J = 9.0 Hz, 1H), 7.10 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 159.4, 151.8, 145.3, 140.2, 136.1, 132.4, 131.2, 129.8, 128.5, 127.2, 126.5, 121.9, 121.5, 120.6, 117.8, 109.1, 12.5; Anal. Calcd for $C_{19}H_{12}BrClN_2O_2$: C, 54.90; H, 2.91; N, 6.74. Found: C, 55.07; H, 2.74; N, 6.91; ESI-MS: m/z = 415 $(M+1)^+$.

6-Chloro-3-(3-methyl-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (4w). White solid, 177-179 °C; IR (KBr): 3415, 3055, 1740, 1612, 1554, 1465, 1377, 1018, 731, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ ppm: 8.55 (s, 1H), 7.62 (d, J = 2.0 Hz, 1H), 7.58-7.56 (m, 1H), 7.31 (d, J = 9.0 Hz, 1H), 7.00 (s, 1H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 164.1, 157.4, 152.7, 144.0, 133.8, 130.3, 128.5, 121.8, 119.5, 118.0, 101.9, 29.7; Anal. Calcd for $C_{13}H_9ClN_2O_2$: C, 59.90; H, 3.48; N, 10.75. Found: C, 60.07; H, 3.31; N, 10.92; ESI-MS: m/z = 261 $(M+1)^+$.

6-Chloro-3-(3-methyl-1-(pyridin-2-yl)-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (4x). White solid, 168-169 °C; IR (KBr): 2962, 1735, 1629, 1593, 1580, 1476, 1383, 1035, 713, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ ppm: 8.30 (d, J = 4.5 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.85 (t, J = 7.5 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.72-7.70 (m, 1H), 7.53-7.51 (m, 1H), 7.31 (s, 1H), 7.12-7.09 (m, 1H), 6.16 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 156.9, 140.9, 138.0, 135.7, 131.1, 129.5, 129.2, 127.0 123.2, 121.7, 120.8, 119.9, 118.9, 116.4, 112.7, 101.4, 27.2; Anal. Calcd for $C_{18}H_{12}ClN_3O_2$: C, 64.01; H, 3.58; N, 12.44. Found: C, 64.18; H, 3.41; N, 12.61; ESI-MS: m/z = 338 $(M+1)^+$.

7-Bromo-3-(3-methyl-1-phenyl-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (4y). White solid, 162-163 °C (Lit. 160-162 °C)[23]; IR (KBr): 3030, 1773, 1628, 1598, 1500, 1443, 1390, 1071, 748, 691 cm^{-1}; ^1H NMR

($CDCl_3$, 500 MHz) δ ppm: 7.81 (s, 1H), 7.36 (s, 1H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.00 (d, *J* = 8.5 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.47 (s, 1H), 6.39 (s, 1H), 2.71 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 156.5, 150.3, 146.1, 143.5, 140.1, 138.7, 133.7, 131.5, 129.1, 126.0, 125.7, 124.7, 121.3, 116.7, 113.7, 111.4, 30.8; Anal. Calcd for $C_{19}H_{13}BrN_2O_2$: C, 59.86; H, 3.44; N, 7.35. Found: C, 60.03; H, 3.27; N, 7.52; ESI-MS: m/z = 381 $(M+1)^+$

6-Bromo-3-(3-methyl-1-(2,4,6-trichlorophenyl)-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (4z). White solid, 170-172 °C; IR (KBr): 3015, 1735, 1640, 1593, 1561, 1476, 1384, 1054, 780, 737, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm: 7.73 (s, 1H), 7.46 (s, 1H), 7.21 (d, *J* = 6.5 Hz, 1H), 7.16 (d, *J* = 5.5 Hz, 2H), 6.75 (d, *J* = 8.5 Hz, 2H), 2.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 156.7, 143.5, 135.7, 133.3, 132.0, 129.3, 129.1, 127.1, 119.5, 118.7, 110.9, 30.7; Anal. Calcd for $C_{19}H_{10}BrCl_3N_2O_2$: C, 47.10; H, 2.08; N, 5.78. Found: C, 47.27; H, 1.91; N, 5.95; ESI-MS: m/z = 483 $(M+1)^+$.

7-Bromo-3-(1-(4-chloro-2-hydroxyphenyl)-3-methyl-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (4aa). Yellow oil; IR (KBr): 3516, 2975, 1727, 1685, 1611, 1501, 1474, 1360, 1080, 770, 639 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm: 8.41 (s, 1H), 7.93 (s, 1H), 7.74-7.73 (m, 1H), 7.71-7.70 (m, 1H), 7.47 (d, *J* = 5.0 Hz, 1H), 7.44 (s, 1H), 7.41 (s, 1H), 6.45 (d, *J* = 9.5 Hz, 1H), 2.71 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 153.4, 152.5, 147.1, 142.2, 137.2, 136.3, 134.6, 134.3, 131.6, 131.2, 130.2, 129.1, 128.2, 126.4, 118.7, 118.5, 101.6, 15.3; Anal. Calcd for $C_{19}H_{12}BrClN_2O_3$: C, 52.87; H, 2.80; N, 6.49. Found: C, 53.04; H, 2.63; N, 6.66; ESI-MS: m/z = 413 $(M+1)^+$.

2-(3-Methyl-1-phenyl-1*H*-pyrazol-5-yl)-3*H*-benzo[f]chromen-3-one (4ab). White solid, 186-188 °C; IR (KBr): 2976, 1732, 1713, 1605, 1495, 1468, 1384, 1049 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm: 8.77 (s, 1H), 8.37 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 9.0 Hz, 1H), 7.98 (d, *J* = 9.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.77-7.71 (m, 3H), 7.60 (t, *J* = 7.0 Hz, 1H), 7.50-7.45 (m, 2H), 7.22 (d, *J* = 9.0 Hz, 1H), 7.09 (s, 1H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 159.9, 155.4, 151.3, 149.1, 147.5, 146.9, 145.0, 143.9, 138.4, 130.9, 128.8, 117.9, 114.4, 110.6, 107.6, 30.9; Anal. Calcd for $C_{23}H_{16}N_2O_2$: C, 78.39; H, 4.58; N, 7.95. Found: C, 78.56; H, 4.41; N, 8.12; ESI-MS: m/z = 353 $(M+1)^+$.

2-(3-Methyl-1-(m-tolyl)-1*H*-pyrazol-5-yl)-3*H*-benzo[f]chromen-3-one (4ac). White solid, 201-202 °C; IR (KBr): 3120 ,1731, 1663, 1600, 1517, 1454, 1397, 1050, 740, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm: 9.28 (s, 1H), 8.43 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 9.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 9.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.39 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.27 (s, 1H), 7.14 (s, 1H), 2.47 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ

ppm: 160.1, 153.0, 145.6, 140.1, 139.6, 139.4, 133.3, 132.5, 130.4, 129.3, 128.9, 128.8, 128.0, 126.0, 122.2, 119.6, 113.9, 108.4, 21.4, 12.5; Anal. Calcd for $C_{24}H_{18}N_2O_2$: C, 78.67; H, 4.95; N, 7.65. Found: C, 78.84; H, 4.78; N, 7.82; ESI-MS: m/z = 367 $(M+1)^+$.

2-(3-Methyl-1-(2,4,6-trichlorophenyl)-1*H*-pyrazol-5-yl)-3*H*-benzo[f]chromen-3-one (4ad). White solid, 200-201 °C; IR (KBr): 3057, 1760, 1698, 1601, 1500, 1466, 1384, 1034, 778, 725 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ ppm: 8.37 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 9.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 9.0 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.15 (s, 1H), 7.11 (s, 1H), 2.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 158.3, 141.1, 135.8, 129.8, 129.2, 129.1, 127.5, 126.6, 126.5, 126.3, 123.5, 121.8, 117.8, 116.5, 113.1, 109.5, 101.5, 27.4; Anal. Calcd for $C_{23}H_{13}Cl_3N_2O_2$: C, 60.62; H, 2.88; N, 6.15. Found: C, 60.79; H, 2.71; N, 6.32; ESI-MS: m/z = 455 $(M+1)^+$.

2-(3-Methyl-1-(pyridin-2-yl)-1*H*-pyrazol-5-yl)-3*H*-benzo[f]chromen-3-one (4ae). White solid, 198-200 °C; IR (KBr): 3015, 1732, 1667, 1610, 1512, 1454, 1400, 1075 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ ppm: 9.35 (s, 1H), 8.51 (t, *J* = 5.0 Hz, 1H), 8.46 (d, *J* = 8.5 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.89 (t, *J* = 7.0 Hz, 1H), 7.71 (s, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 9.0 Hz, 1H), 7.48 (d, *J* = 9.0 Hz, 1H), 7.14 (s, 1H), 2.75 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 154.4, 147.8, 138.5, 138.4, 133.8, 131.0, 129.5, 129.0, 128.3, 127.9, 127.7, 126.3, 126.2, 125.8, 123.1, 121.7, 118.3, 116.7, 109.4, 14.1; Anal. Calcd for $C_{22}H_{15}N_3O_2$: C, 74.78; H, 4.28; N, 11.89. Found: C, 74.95; H, 4.11; N, 12.06; ESI-MS: m/z = 354 $(M+1)^+$.

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