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Direct Access for the Regio- and Stereoselective Synthesis of *N*-Alkenylpyrazoles and Chromenopyrazoles

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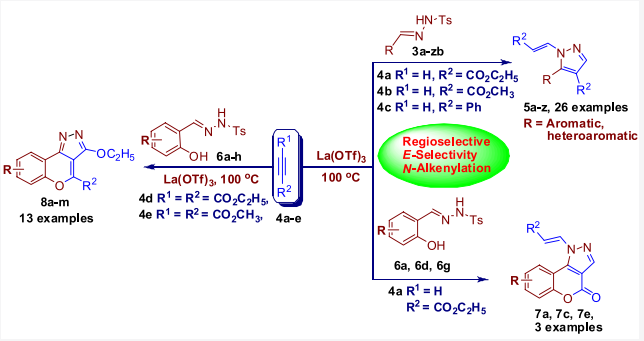
ABSTRACT: A highly regio- and stereoselective method was developed for the preparation of *N*-alkenylpyrazoles and chromenopyrazoles by the reaction of *N*-tosylhydrazones and salicyl *N*-tosylhydrazones with alkynes under neat conditions in the presence of La(OTf)$_3$. The present study was found to be efficient and convenient for direct access to *N*-alkenylpyrazoles and chromenopyrazoles through C−C, C−N, and C−O bond forming reactions. Structure assignment of *N*-alkenylpyrazole compound **5c** was confirmed by X-ray analysis.



INTRODUCTION

Pyrazole heterocyclic compounds are an attractive class of compounds[1] and are key components of several drug molecules (Celebrex, Viagra, Zometapine, Cyenopyrafen, Fenpyroximate, Tebufenpyrad, Apixaban) and insecticide (Fipronil).[2] Pyrazole compounds possess a broad spectrum of biological properties,[3a−d] serve as ligands in coordination chemistry, and act as optical brighteners.[3e,f] Therefore, synthesis of pyrazoles has become an important area of study. Two classical approaches are available for the synthesis of pyrazoles, namely, (1) Knorr condensation of 1,3-dicarbonyls with hydrazines[4] and (2) 1,3-dipolar cycloaddition of diazo compounds with alkynes or electron-deficient alkenes.[5] Later efforts have been made to achieve various pyrazoles from *N*-tosylhydrazones with ethynylbenzene, 2-bromo-3,3,3-trifluoroprop-1-ene, and activated alkynes.[6] These methods have one or more major drawbacks, such as hazardous reagents, limited substrate scope, and regioselectivity.

On the other hand, *N*-alkenylpyrazoles are predominantly heterocyclic compounds, and limited reports are available in the literature. These compounds are prepared by addition of alkynes to pyrazoles. In 2008, Tsuchimoto et al. reported[7] the Lewis acid-catalyzed addition of pyrazoles with alkynes (Figure 1). Das et al. developed the Ru-catalyzed regio- and stereoselective vinylation of pyrazoles with alkynes (Figure 1, A).[8] Later, Garg et al.[9] constructed (*E*)- and (*Z*)-vinylated pyrazoles by reacting pyrazoles with activated and unactivated alkynes in the presence of KOH/DMSO at 120 °C (Figure 1, B). There is no straightforward single-step method available in the literature for the synthesis of *N*-alkenylpyrazoles. Therefore, method developments for construction of *N*-alkenylpyrazoles have high priority and potential demand.

In a continuation of our research interest in the synthesis of heterocyclic compounds[10] and pyrazoles,[11] herein, we report a regio- and stereoselective synthesis of *N*- alkenylpyrazoles, chromenopyrazolyl acrylates, and chromenopyrazole-4-carboxylates starting from *N*-tosylhydrazones[12a−g] and salicyl *N*-tosylhydrazones[12h,i,16] with alkynes in the presence of La(OTf)$_3$[13] in one pot under neat conditions, and the results are discussed below.

RESULTS AND DISCUSSION

To establish the reaction conditions, we have chosen *N*′-benzylidene-4-methylbenzenesulfonohydrazide **3a** as a model substrate which was prepared from benzaldehyde **1a** and 4-methylbenzenesulfonohydrazide **2**. The substrate **3a** (1.0 equiv) was stirred with ethyl propiolate **4a** (1.0 equiv) in the presence of 5 mol % of La(OTf)$_3$ in toluene under reflux conditions. The usual workup gave compound **5a** in a 20% yield. Then the reaction was repeated with 2.0 equiv of **4a** under similar conditions, and compound **5a** was obtained with a 44% yield (Scheme 1). The compound structure was assigned as (*E*)-ethyl 1-(3-ethoxy-3-oxoprop-1-enyl)-5-phenyl-1*H*-pyrazole-4-carboxylate **5a** on the basis of spectral and

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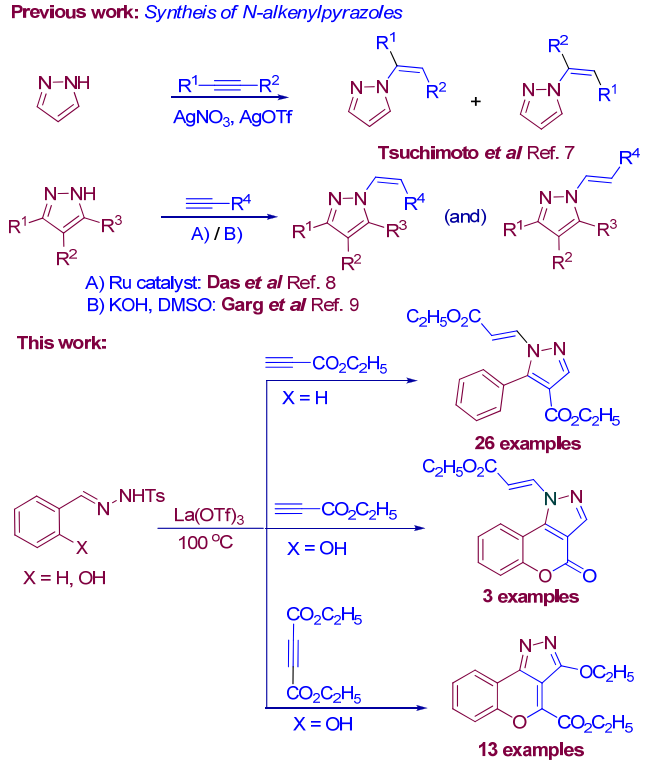
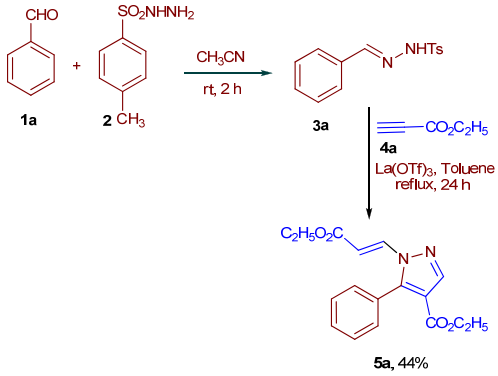


Figure 1. Previous approaches for preparation of *N*-alkenylpyrazoles and the present work.

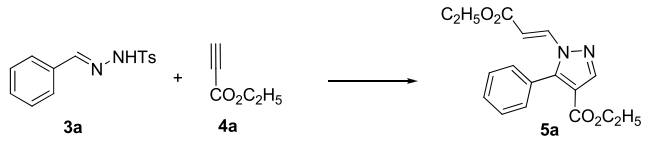
Scheme 1. Synthesis of (*E*)-Ethyl 1-(3-Ethoxy-3-oxoprop-1-enyl)-5-phenyl-1*H*-pyrazole-4-carboxylate 5a



analytical data (see SI). The pyrazole **5a** was formed in a regioselective manner with *E* (trans) geometry (see SI). This is the first example for the construction of *N*-alkenylpyrazoles with C−C and two C−N bond formations in one pot.

This interesting result prompted us to optimize the reaction conditions to obtain better yields, and the results are summarized in Table 1. The reaction at room temperature in toluene did not provide the compound (Table 1, entry 1). When the reaction was attempted using different solvents such as MeOH, THF, CH_3CN, and DCM under reflux conditions (Table 1, entries 3−6), **5a** was produced in moderate yields. Interestingly, compound **5a** was formed in 73% yield when the reaction was carried out under neat conditions at 100 °C (Table 1, entry 7). There was not much difference in the yield of **5a** when the reaction was carried out with either a higher (10 mol %) or a lower (3 mol %) amount of $La(OTf)_3$ (Table 1, entries 9 and 10). When the reaction time was extended to 8 h, an intractable mixture of products was observed. Lowering the temperature of the neat reaction to 80 °C led to a low yield (Table 1, entry 11), and no improvement of the yield was observed when the reaction was carried out at 120 °C or above (Table 1, entry 12).

Table 1. Optimization Study



entry	catalyst	quantity (mol %)	solvent	temp	time (h)	yield (%)[a]
1	$La(OTf)_3$	5	toluene	rt	48	
2	$La(OTf)_3$	5	toluene	reflux	24	44
3	$La(OTf)_3$	5	CH_3OH	reflux	24	40
4	$La(OTf)_3$	5	THF			32
5	$La(OTf)_3$	5	CH_3CN	reflux	24	35
6	$La(OTf)_3$	5	DCM	reflux	24	21
7	**$La(OTf)_3$**	**5**		**100 °C**	**5**	**73**
8	$La(OTf)_3$	5		100 °C	5	70
9	$La(OTf)_3$	10		100 °C	5	73
10	$La(OTf)_3$	3		100 °C	5	67
11	$La(OTf)_3$	5		80 °C	5	65
12	$La(OTf)_3$	5		120 °C	5	73
13	$Bi(OTf)_3$	5		100 °C	5	67
14	$Sc(OTf)_3$	5		100 °C	5	61
15	$Cu(OTf)_2$	5		100 °C	5	63
16	$Sn(OTf)_2$	5		100 °C	5	54
17	$Yb(OTf)_3$	5		100 °C	5	59
18	$In(OTf)_3$	5		100 °C	5	60
19	$AlCl_3$	5		100 °C	5	28
20	$FeCl_3$	5		100 °C	5	22
21	$InCl_3$	5		100 °C	5	17
22	CuI	5		100 °C	5	43
23	CuBr	5		100 °C	5	39
24	Ag_2CO_3	5		100 °C	5	48
25	$PdCl_2$	5		100 °C	5	49
26	$Pd(OAc)_2$	5		100 °C	5	52
27	$RuCl_3$	5		100 °C	5	68

[a]Isolated yields.

Having studied the reaction with various solvents, next, reaction of **3a** with **4a** was carried out at 100 °C in the presence of various catalysts (Table 1). The triflates have provided compound **5a** in the range of 54−67% yield (Table 1, entries 13−18). Al, Fe, In, and Cu halides and Ag_2CO_3 produced compound **5a** in moderate yield (entries 19−24). Compound **5a** was obtained in a moderate yield when the reaction was carried out with Pd and Ru catalysts (Table 1, entries 25−27). Finally, we found that $La(OTf)_3$ (5 mol %) at 100 °C is the most suitable condition to afford compound **5a** in very good yield (73%, Table 1, entry 7). We also carried out the reaction of **3a** with other terminal alkyne, methyl propiolate **4b** under optimized conditions. This provided compound **5b** in 71% yield (Table 2). Reaction with ethynyl benzene **4c** led to complete recovery of the starting material.

With the identification of the optimal conditions, we embarked to explore the present method with more substrates. Accordingly, the required benzenesulfonohydrazides **3b−n** have been prepared from benzaldehydes (**1b−n**) with **2** (see SI, Figure S1). Thus, obtained hydrazides **3b−n** were reacted

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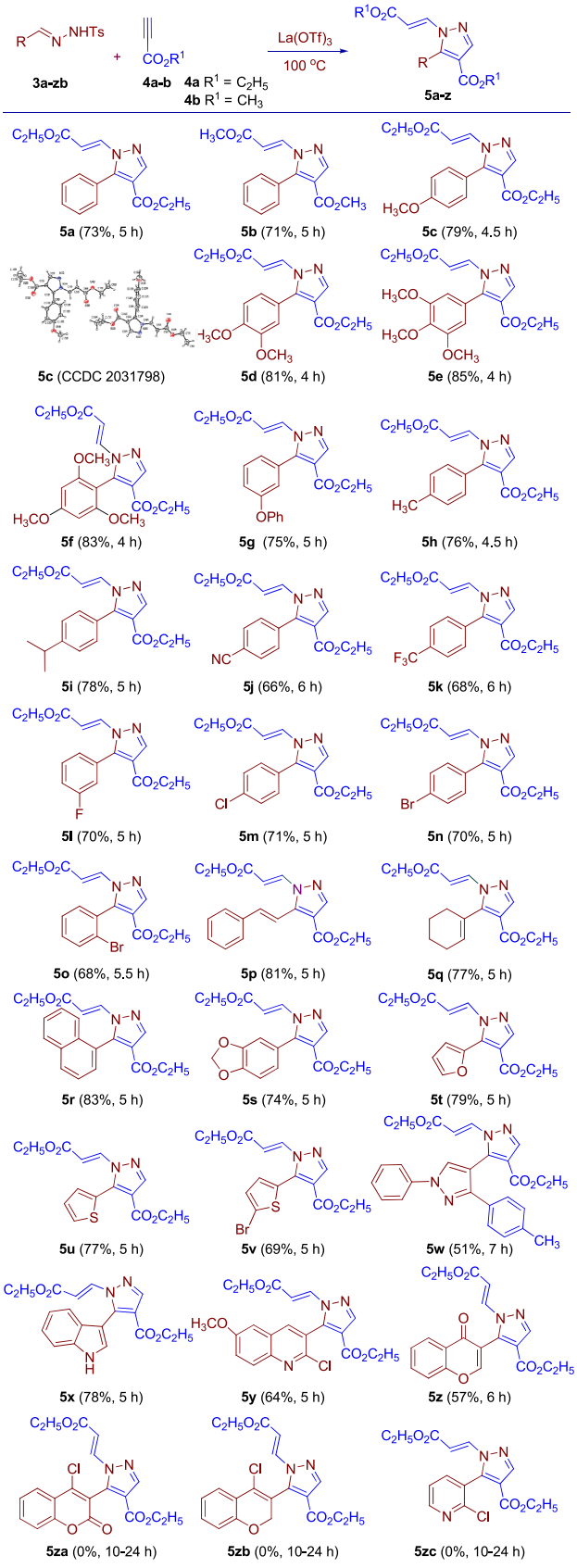
Table 2. Synthesis of *N*-Alkenyl 1*H*-Pyrazole-4-carboxylates 5a−z



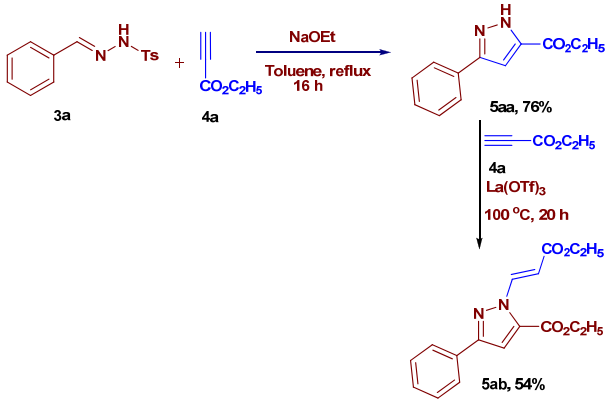
with ethyl propiolate **4a** under the optimized conditions, and the results are tabulated in Table 2. The electron-donating groups present on the substrate (**3b−3h**) were well tolerated and produced the *N*-alkenylpyrazoles **5c−i** in very good yields, whereas electron-withdrawing groups (**3i−3n**) produced compounds **5j−o** in moderate to good yields (Table 2). The structure of compound **5c** was confirmed by single-crystal X-ray diffraction analysis (CCDC 2031798, see SI, Figure S3). Further, we recorded the ^{19}F NMR data for **5k** and **5l** (see SI, ^{13}C NMR for **5k** and **5l**).[14]

Further, we demonstrated the method with a number of examples as shown in Table 2. We prepared the required hydrazides **3o−r** from cinnamaldehyde (**1o**), cyclohex-1-ene carbaldehyde (**1p**), 1-naphthaldehyde (**1q**), and benzo[*d*]-[1,3]dioxole-5-carbaldehyde (**1r**) with **2** (see SI, Figure S1). The hydrazides **3o−r** were reacted with **4a** under optimized reaction conditions to provide the corresponding compounds **5p−s** (Table 2, see SI).

After achieving the *N*-alkenylpyrazoles, the method was applied to heteroaromatic sulfonohydrazides **3s−zb**, which are depicted in Table 2 to show the diversity of the protocol. These hydrazides were prepared from heterocyclic aldehydes such as furan (**1s**), thiophene (**1t** and **1u**), pyrazole (**1v**), indole (**1w**), quinoline (**1x**), 4*H*-chromene (**1y**), 2*H*-chromenes (**1z** amd **1za**), and 2-chloronicotinaldehyde (**1zb**) with **2**. Hydrazides **3s−zb** were then reacted with **4a** under optimized conditions. The reactions proceeded smoothly with sulfonohydrazides **3s−y** to obtain the target compounds **5t−z** (Table 2, see SI). With sulfonohydrazides **3z−zb**, the reaction did not proceed and the starting materials were recovered.

To establish the reaction mechanism, we conducted the control experiment with **3a** and **4a** in the presence of NaOEt (3.0 equiv) under reflux conditions (Scheme 2).[6c] This

Scheme 2. Synthesis of 5aa and 5ab



provided the ethyl 3-phenyl-1*H*-pyrazole-5-carboxylate **5aa**.[6d] Then the obtained pyrazole **5aa** was subjected for *N*-alkenylation with **4a** in the presence of La(OTf)$_3$. This provided compound **5ab** with a 54% yield (see SI). In our present method we directly obtained altogether a different *N*-alkenylpyrazole compound **5a**. Compounds **5a** and **5ab** also have been analyzed by gNOESY and HPLC analyses (see SI).

A possible reaction pathway for the formation of **5a** is illustrated in Scheme 3.[15] Lewis scid [La(OTf)$_3$] activates the carbonyl functionality of the ester moiety of the ethyl propiolate **4a** and increases the electrophilic nature at the terminal carbon to undergo aza-Michael addition via addition

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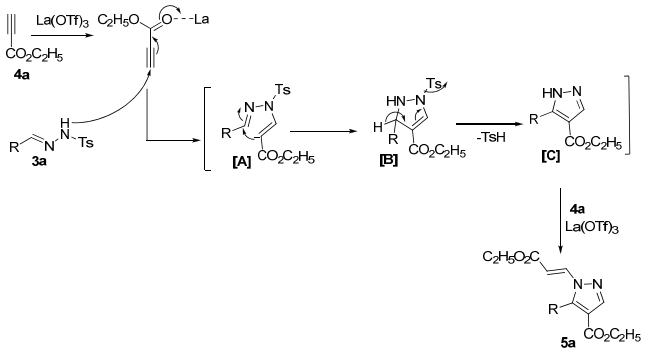
Scheme 3. Proposed Mechanism for the Formation of 5a

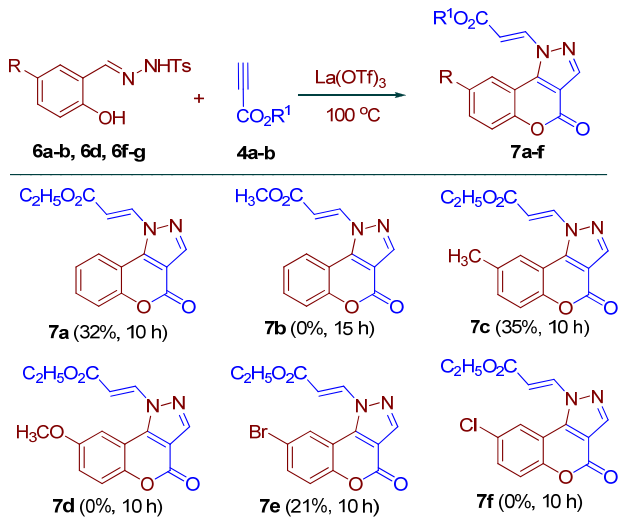


of *N*-tosylhydrazone **3a** to form intermediate **A**. Intramolecular cyclization of intermediate **A** led to *N*-tosylpyrazoline **B**, and subsequent elimination of TsH gives the pyrazole **C**. Another molecule of propiolate **4a** undergoes aza-Michael addition with the pyrazole **C** in the presence of the catalyst to give the *N*-alkenylpyrazole product **5a** with *E* (trans) selectivity.

The chromenopyrazoles are important bioactive compounds,[16] and we recently reported the synthesis of chromenopyrazolones and benzoylcoumarins.[17] To our knowledge, there is no report of a reaction between salicyl *N*-tosylhydrazones and activated alkynes for preparation of chromenopyrazolyl acrylates and chromenopyrazole-4-carboxylates. Therefore, a mild and one-pot method for the synthesis of chromenopyrazoles is very much needed. The *N*-alkenylpyrazole synthetic route prompted us to demonstrate this reaction toward the synthesis of chromenopyrazoles. Accordingly, salicyl *N*-tosylhydrazone **6a** was prepared from salicylaldehyde (**1zc**) with **2** as per our established procedure (see SI, Figure S2). Thus, the obtained hydrazone **6a** (1.0 equiv) was initially reacted with **4a** (2.0 equiv) under our optimized conditions (Table 3). Pleasingly, this provided fused heterocyclic compound (*E*)-ethyl 3-(4-oxochromeno[4,3-*c*]-pyrazol-1(4*H*)-yl)acrylate **7a** with moderate yield (32%).

To improve the yield of **7a**, a number of experiments between **6a** and **4a** were carried out under various reaction conditions. A maximum 32% yield was achieved in all of these

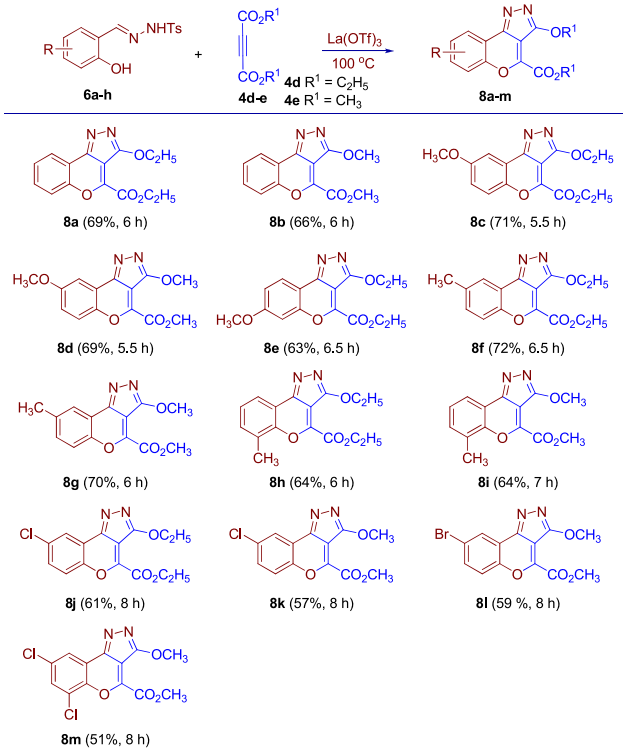
Table 3. Synthesis of (*E*)-Ethyl 3-(4-Oxochromeno[4,3-*c*]pyrazol-1(4*H*)-yl)acrylates 7a−f



experiments. Next, the reaction was screened with electron-donating and -withdrawing salicyl-*N*-tosylhydrazones (**6b**, **6d**, **6f**, and **6g**) with **4a** and **4b** as per the optimized conditions. The reactions with **6d** and **6g** proceeded smoothly and provided compounds **7c** and **7e** in moderate yields (Table 3, see SI). Compounds **7b**, **7d**, and **7f** were not obtained under the optimized reaction conditions, and the starting materials were recovered.

Since reaction with **4a** did not give better yields, we investigated the reaction with activated alkynes. Accordingly, **6a** was made to react with diethyl but-2-ynedioate **4d** under optimized conditions (Table 4). Interestingly, this reaction provided a different product which was confirmed as chromenopyrazole-4-carboxylate **8a** based on spectral data.

Table 4. Synthesis of Chromeno[4,3-*c*]pyrazole-4-carboxylates 8a−m



We were curious about this reaction, and the scope of the method was studied with more hydrazones **6b−h** with activated alkynes such as diethyl but-2-ynedioate **4d**, dimethyl but-2-ynedioate **4e**, ethyl 3-phenylpropiolate **4f**, and ethyl but-2-ynoate **4g** under optimized reaction conditions. The results are presented in Table 4 (see SI).

Reactions of **6b−h** with activated alkynes **4d** and **4e** proceeded smoothly and provided a series of chromenopyrazole-4-carboxylates **8b−m** (Table 4, see SI). However, alkynes such as **4f** and **4g** did not provide the pyrazoles under these conditions. It is noteworthy to mention here that the ester moiety is an essential component to furnish chromenopyrazole-4-carboxylates (Table 4, see SI).

A possible mechanism for the formation of **8a** is depicted in Scheme 4. Oxa−Michael addition of **6a** with La(OTf)$_3$ coordinates diethyl but-2-ynedioate to provide intermediate **B**. Intramolecular cyclization of **B** provides the chromene intermediate **C** with elimination of TsH. The imine present on

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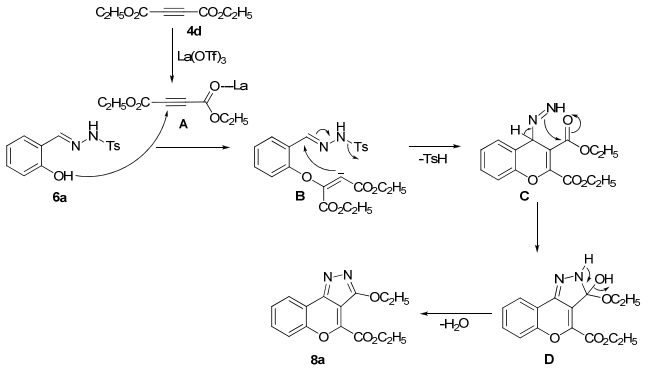
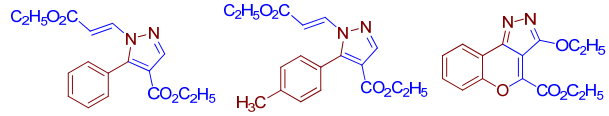
Scheme 4. Proposed Mechanism of Compound 8a



intermediate **C** reacts with ester carbonyl providing pyrazole intermediate **D**. Finally, intermediate **D** through aromatization with the loss of H_2O gives the chromenopyrazolecarboxylate **8a**.

To further demonstrate the present protocol, two *N*-alkenylpyrazoles **5a** and **5h** and one chromenopyrazole **8a** were prepared in gram scale by reaction of tosylhydrazones **3a** (1.0 g) with **4a** and **3g** (1.5 g) with **4a** and salicyl tosylhydrazone **6a** (1.2 g) with **4d** under our optimized reaction conditions. The results are depicted in Scheme 5.

Scheme 5. Gram Scale Preparation of Compounds 5a, 5h, and 8a



CONCLUSIONS

In summary, a highly regio- and stereoselective new protocol has been developed for the synthesis of *N*-alkenylpyrazoles, chromenopyrazolyl acrylates, and chromenopyrazole-4-carboxylates. The present method involves the synthesis of five-membered heterocyclic compounds including a fused one through C−C, two C−N, and C−O bond forming reactions in one pot. Due to the importance of these heterocyclic compounds, especially in pharmaceutical and medicinal chemistry, the present protocol can be extended for the synthesis of various scaffolds.

EXPERIMENTAL SECTION

General Information. Salicylaldehydes, activated alkynes, tosylhydrazine, and triflates were procured from Sigma-Aldrich. General chemicals, Lewis acids, and solvents were obtained from local suppliers. All of the reactions were carried at 100 °C using an oil bath. All of the reactions were monitored by thin layer chromatography (TLC) on precoated silica gel 60 F254 (mesh); spots were visualized under UV light. Merck silica gel (60−120 and 100−200 mesh) was used for column chromatography. ^{1}H NMR and ^{13}C NMR spectra were recorded on Avance 300, 400, and 500 MHz spectrometers in $CDCl_3$ using TMS as the internal standard. IR spectra were recorded on a Nicolet Nexus 670 FT spectrometer. ESI-MS results were obtained on a quarto micro spectrometer. HRMS data were measured on an Agilent Technologies 6510 by the Q-TOFLC/MS ESI-Technique. Melting points were determined in open glass capillary tubes on a Stuart melting point apparatus and are uncorrected. HPLC analysis was carried out by a Shimadzu SPD-M20A, PDA detector using a C-18 column, λ 200−500 nm. Eluent: CH_3CN:H_2O = 90:10. Flow rate: 0.5 mL/min. Structural assignments were made with additional information from gNOESY experiments.

Typical Procedure for Preparation of (*E*)-*N*′-Benzylidene-4-methylbenzenesulfonohydrazides (3a−zb). Tosylhydrazine **2** (877 mg, 4.72 mmol, 1.0 equiv) was added to a stirred solution of benzaldehyde **1a** (500 mg, 4.72 mmol, 1.0 equiv) in acetonitrile (5 mL) at room temperature, and the contents were stirred for 2 h (TLC). The solvent was removed under reduced pressure. The residue was purified by recrystallization with hexane and afforded (*E*)-*N*′-benzylidene-4-methylbenzenesulfonohydrazide **3a** as a colorless solid in 96% yield. The substituted tosylhydrazones **3b−zb** were prepared by reaction of aldehydes **1b−zb** with tosylhydrazine **2**. The tosylhydrazones **3a−d**, **3g−t**, **3w**, and **3zb** are known compounds and compared with the literature data.[12] The newly prepared tosylhydrazones **3e−f**, **3u−3v**, and **3x−3za** were characterized by spectral data.

*(E)-4-Methyl-N′-(2,4,6-trimethoxybenzylidene)-benzenesulfonohydrazide (**3e**).* Colorless solid (826 mg, 89% yield); mp 148−150 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.88 (s, 1H), 7.99 (s, 1H), 7.76 (d, J = 7.5 Hz, 2H), 7.41 (d, J = 7.8 Hz, 2H), 6.24 (d, J = 13.9 Hz, 2H), 3.78 (s, 3H), 3.74 (s, 6H), 2.38 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 162.2, 159.6, 142.9, 142.5, 136.4, 129.1, 127.3, 103.4, 90.9, 55.8, 55.3, 20.9. FT-IR (KBr): 3017, 2942, 1606, 1580, 1456, 1415, 1334, 1207, 1158, 1125, 751 cm^{-1}. MS (ESI) *m/z:* [M + H]$^+$ 365. HRMS (ESI) *m/z*: [M + H]$^+$ calcd for $C_{17}H_{21}N_2O_5S$, 365.1165; found, 365.1150.

*(E)-4-Methyl-N′-(3-phenoxybenzylidene)-benzenesulfonohydrazide (**3f**).* Colorless solid (785 mg, 85% yield); mp 124−126 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.49 (s, 1H), 7.88 (s, 1H), 7.70 (d, J = 8.1 Hz, 2H), 7.48−7.34 (m, 5H), 7.31 (d, J = 7.7 Hz, 1H), 7.21 (t, J = 7.4 Hz, 1H), 7.15 (s, 1H), 7.04 (d, J = 7.8 Hz, 3H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6): δ 157.2, 156.0, 146.1, 143.4, 135.9, 135.6, 130.5, 130.1, 129.6, 127.2, 123.9, 122.1, 120.0, 119.1, 115.4, 20.9. FT-IR (KBr): 3177, 1582, 1486, 1443, 1363, 1319, 1255, 1160, 1054, 913, 757 cm^{-1}. MS (ESI) *m/z*: [M + H]$^+$ 367. HRMS (ESI) *m/z*: [M + H]$^+$ calcd for $C_{20}H_{19}N_2O_3S$, 367.1110; found, 367.1102.

*(E)-N′-((5-Bromothiophen-2-yl)methylene)-4-methylbenzenesulfonohydrazide (**3u**).* Colorless solid (765 mg, 81% yield); mp 126−128 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.49 (s, 1H), 8.01 (d, J = 4.2 Hz, 1H), 7.78−7.62 (m, 2H), 7.42 (d, J = 8.2 Hz, 2H), 7.28−7.10 (m, 2H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 143.5, 141.2, 140.1, 135.8, 131.2, 131.1, 129.6, 127.1, 114.5, 20.92. FT-IR (KBr): 3190, 1598, 1444, 1354, 1322, 1202, 1158, 1050, 921, 751 cm^{-1}. MS (ESI) *m/z:* [M + H]$^+$ 359. HRMS (ESI) *m/z*: [M + H]$^+$ calcd for $C_{12}H_{121}N_2O_2BrS_2$, 358.9518; found, 358.9516.

*(E)-4-Methyl-N′-((1-phenyl-3-(p-tolyl)-1H-pyrazol-4-yl)-methylene)benzenesulfonohydrazide (**3v**).* Colorless solid (664 mg, 81% yield); mp 185−187 °C. ^{1}H NMR (400 MHz, DMSO- d_6): δ 11.20 (s, 1H), 8.83 (s, 1H), 8.01 (s, 1H), 7.96 (d, J = 7.9 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 7.52 (t, J = 7.1 Hz, 4H), 7.42−7.31 (m, 3H), 7.29 (d, J = 7.8 Hz, 2H), 2.37 (s, 3H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 151.2, 143.2, 140.7, 138.9, 137.9, 136.2, 129.5, 129.4, 129.0, 128.9, 128.2, 127.6, 127.2, 118.7, 116.1, 20.9, 20.8. FT-IR (KBr): 3212, 1602, 1540, 1451, 1405, 1351, 1221, 1164, 1089, 1037, 922, 759 cm^{-1}. MS (ESI) *m/z:* [M + H]$^+$ 431. HRMS (ESI) *m/z*: [M + H]$^+$ calcd for $C_{24}H_{23}N_4O_2S$, 431.1536; found, 431.1519.

*(E)-N′-((2-Chloro-6-methoxyquinolin-3-yl)methylene)-4-methylbenzenesulfonohydrazide (**3x**).* Colorless solid (704 mg, 80% yield); mp 203−205 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.00 (s, 1H), 8.64 (s, 1H), 8.32 (s, 1H), 7.84 (t, J = 9.5 Hz, 3H), 7.61 (d, J = 2.5 Hz, 1H), 7.45 (d, J = 7.7 Hz, 3H), 3.91 (s, 3H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (76 MHz, DMSO-d_6): δ 157.9, 145.3, 143.7, 143.1, 141.8, 136.1, 133.9, 129.8, 128.9, 127.9, 127.2, 125.3, 124.2, 106.3, 55.7, 20.9. FT-IR (KBr): 3672, 3568, 1497, 1229, 1164, 1061, 1016, 924, 763 cm^{-1}. MS (ESI) *m/z:* [M + H]$^+$ 390. HRMS (ESI) *m/z*: [M + H]$^+$ calcd for $C_{18}H_{17}N_3O_3ClS$, 390.0673; found, 390.0672.

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*(E)-4-Methyl-N′-((4-oxo-4H-chromen-3-yl)methylene)-benzenesulfonohydrazide (**3y**).* Colorless solid (904 mg, 92% yield); mp 221−223 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 11.55 (s, 1H), 8.63 (s, 1H), 8.15−8.03 (m, 1H), 8.02 (s, 1H), 7.83 (ddd, *J* = 13.7, 10.3, 4.9 Hz, 3H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.58−7.48 (m, 1H), 7.42 (d, *J* = 8.1 Hz, 2H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (76 MHz, DMSO-d_6): δ 174.7, 155.7, 154.4, 143.5, 139.5, 135.9, 134.7, 129.7, 127.2, 126.1, 125.1, 123.2, 118.7, 117.8, 20.9. FT-IR (KBr): 3114, 1618, 1589, 1461, 1353, 1311, 1226, 1163, 1095, 1050, 912, 763 cm^{-1}. MS (ESI) *m/z:* [M + H]$^+$ 343. HRMS (ESI) *m/z*: [M + H]$^+$ calcd for $C_{17}H_{15}N_2O_4S$, 343.0747; found, 343.0740.

*(E)-N′-((4-Chloro-2-oxo-2H-chromen-3-yl)methylene)-4-methylbenzenesulfonohydrazide (**3z**).* Colorless solid (804 mg, 89% yield); mp 161−163 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.97 (s, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.99 (s, 1H), 7.82 (d, *J* = 7.9 Hz, 2H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.44 (d, *J* = 7.7 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 1H), 2.39 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 161.5, 158.7, 153.9, 144.6, 134.9, 133.6, 129.9, 129.5, 127.8, 127.3, 125.2, 124.3, 122.8, 117.0, 21.0. FT-IR (KBr): 3669, 3483, 1729, 1573, 1403, 1219, 1024, 1007, 968, 731 cm^{-1}. MS (ESI) *m/z:* [M + H]$^+$ 377. HRMS (ESI) *m/z*: [M + H]$^+$ calcd for $C_{17}H_{14}N_2O_4ClS$, 377.0357; found, 377.0355.

*(E)-N′-((4-Chloro-2H-chromen-3-yl)methylene)-4-methylbenzenesulfonohydrazide (**3za**).* Colorless solid (867 mg, 93% yield); mp 192−194 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.79 (s, 1H), 8.03 (s, 1H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.47 (t, *J* = 6.9 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.94 (t, *J* = 15.3 Hz, 1H), 4.95 (s, 2H), 2.38 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 154.5, 143.6, 141.2, 135.6, 131.6, 129.7, 128.7, 127.1, 124.8, 123.5, 122.0, 120.5, 115.9, 64.5, 20.9. FT-IR (KBr): 3626, 3472, 1563, 1459, 1417, 1286, 1124, 1033, 1023, 973, 765 cm^{-1}. MS (ESI) *m/z:* [M + H]$^+$ 363. HRMS (ESI) *m/z*: [M + H]$^+$ calcd for $C_{17}H_{16}N_2O_3ClS$, 363.0564; found, 363.0557.

General Procedure for Preparation of (*E*)-Ethyl 1-(3-Ethoxy-3-oxoprop-1-en-1-yl)-5-phenyl-1*H*-pyrazole-4-carboxylates (5a−z). $La(OTf)_3$ (14 mg, 5 mol %) was added to the reaction mixture of (*E*)-*N*′-benzylidene-4-methylbenzenesulfonohydrazide **3a** (100 mg, 0.36 mmol, 1.0 equiv) and ethyl propiolate **4a** (72 mg, 0.73 mmol, 2.0 equiv) at room temperature. The contents were heated at 100 °C, and the reaction was monitored by TLC. After completion of the reaction (TLC, 5 h), the residue was purified by column chromatography using silica gel (60:120, ethyl acetate/hexane 10:90) and afforded (*E*)-ethyl 1-(3-ethoxy-3-oxoprop-1-en-1-yl)-5-phenyl-1*H*-pyrazole-4-carboxylate **5a** as a colorless solid in 73% yield. The oxopropenyl-1*H*-pyrazole-4-carboxylates **5b−z** were prepared by reaction of tosylhydrazones **3b−y** with ethyl propiolate **4a** under above optimized reaction conditions. The hydrazone **3a** was also reacted with methyl propiolate **4b** and provided compound **5b**. The newly prepared compounds **5a−z** were characterized by spectral data. Compound **5c** was dissolved in chloroform and kept for slow evaporation at room temperature. The crystals were grown after 3 days and analyzed by single-crystal X-ray diffraction.

*(E)-Ethyl 1-(3-ethoxy-3-oxoprop-1-en-1-yl)-5-phenyl-1H-pyrazole-4-carboxylate (**5a**).* Colorless solid (83 mg, 73% yield); mp 124−126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.93 (d, *J* = 13.9 Hz, 1H), 7.82 (dd, *J* = 2.5, 1.2 Hz, 1H), 7.80 (t, *J* = 3.0 Hz, 1H), 7.46−7.41 (m, 3H), 6.60 (d, *J* = 13.9 Hz, 1H), 4.31−4.24 (m, 4H), 1.35−1.28 (m, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 165.9, 162.1, 155.5, 138.5, 135.8, 131.1, 129.3, 129.1, 127.8, 114.9, 108.6, 60.8, 60.6, 14.2, 14.1. FT-IR (KBr): 3126, 2986, 1730, 1703, 1658, 1539, 1444, 1289, 1208, 1174, 1124, 1111, 1042, 966, 773 cm^{-1}. MS (ESI) *m/z*: [M + H]$^+$ 315. HRMS (ESI) *m/z*: [M + H]$^+$ calcd for $C_{17}H_{19}N_2O_4$ 315.1350; found, 315.1339.

*(E)-Methyl 1-(3-Methoxy-3-oxoprop-1-en-1-yl)-5-phenyl-1H-pyrazole-4-carboxylate (**5b**).* Colorless solid (74 mg, 71% yield); mp 164−166 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (s, 1H), 7.70 (d, *J* = 13.7 Hz, 1H), 7.5−7.49 (m, 3H), 7.41−7.38 (m, 2H), 6.66 (d, *J* = 13.7 Hz, 1H), 3.74 (s, 3H), 3.73 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 166.6, 162.5, 147.6, 144.0, 136.5, 130.4, 130.3, 128.6, 126.6, 114.8, 109.2, 51.8, 51.4. FT-IR (KBr): 2982, 2930, 1742, 1626, 1588, 1470, 1388, 1283, 1216, 1182, 1132, 1039, 755 cm^{-1}. MS (ESI) *m/z*: [M + H]$^+$ 287. HRMS (ESI) *m/z*: [M + H]$^+$ calcd for $C_{15}H_{15}N_2O_4$ 287.1028; found, 287.1026.

*(E)-Ethyl 1-(3-Ethoxy-3-oxoprop-1-enyl)-5-(4-methoxyphenyl)-1H-pyrazole-4-carboxylate (**5c**).* Colorless solid (89 mg, 79% yield); mp 116−118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (s, 1H), 7.74 (d, *J* = 13.7, 1H), 7.36−7.30 (m, 2H), 7.05−7.00 (m, 2H), 6.64 (d, *J* = 13.7 Hz, 1H), 4.20 (qd, *J* = 7.0, 3.3 Hz, 4H), 3.88 (s, 3H), 1.30−1.26 (m, 3H), 1.24−1.20 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 166.3, 162.1, 160.9, 147.5, 144.0, 136.5, 131.9, 118.6, 114.7, 113.9, 109.2, 60.5, 60.2, 55.3, 14.1, 14.0. FT-IR (KBr): 3416, 3045, 2967, 1718, 1792, 1459, 1369, 1301, 1234, 1170, 1146, 1084, 1019, 970, 714 cm^{-1}. MS (ESI) *m/z*: [M + H]$^+$ 345. HRMS (ESI) *m/z*: [M + H]$^+$ calcd for $C_{18}H_{21}N_2O_5$ 345.1449; found, 345.1445.

*(E)-Ethyl 5-(3,4-Dimethoxyphenyl)-1-(3-ethoxy-3-oxoprop-1-enyl)-1H-pyrazole-4-carboxylate (**5d**).* Colorless solid (91 mg, 81% yield); mp 132−134 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (s, 1H), 7.76 (d, *J* = 13.7 Hz, 1H), 6.97 (dt, *J* = 8.2, 5.1 Hz, 2H), 6.91 (d, *J* = 1.8 Hz, 1H), 6.64 (d, *J* = 13.7 Hz, 1H), 4.20 (q, *J* = 7.1, 4H), 3.96 (s, 3H), 3.90 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 166.3, 162.1, 150.5, 148.7, 147.4, 144.1, 136.6, 123.5, 118.8, 114.8, 113.5, 110.9, 109.3, 60.6, 60.3, 56.0, 55.9, 14.2, 14.1. FT-IR (KBr): 3395, 3129, 3103, 3072, 2985, 2936, 2838, 1712, 1653, 1605, 1563, 1523, 1465, 1438, 1357, 1261, 1168, 1125, 1030, 770 cm^{-1}. MS (ESI) *m/z*: [M + H]$^+$ 375. HRMS (ESI) *m/z*: [M + H]$^+$ calcd for $C_{19}H_{23}N_2O_6$ 375.1556; found, 375.1550.

*(E)-Ethyl 1-(3-Ethoxy-3-oxoprop-1-enyl)-5-(3,4,5-trimethoxyphenyl)-1H-pyrazole-4-carboxylate (**5e**).* Colorless solid (111 mg, 85% yield); mp 185−187 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (s, 1H), 7.77 (d, *J* = 13.7 Hz, 1H), 6.65 (d, *J* = 13.7 Hz, 1H), 6.59 (s, 2H), 4.24−4.18 (m, 4H), 3.95−3.94 (s, 3H), 3.87 (s, 6H), 1.30−1.26 (m, 3H), 1.24−1.20 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 166.3, 162.1, 153.1, 147.2, 144.0, 139.5, 136.5, 121.8, 115.0, 109.5, 107.9, 60.9, 60.7, 60.3, 56.3, 14.2, 14.1. FT-IR (KBr): 2981, 2941, 1714, 1652, 1615, 1589, 1469, 1420, 1293, 1274, 1230, 1205, 1157, 1033 cm^{-1}. MS (ESI) *m/z*: [M + H]$^+$ 405. HRMS (ESI) *m/z*: [M + H]$^+$ calcd for $C_{20}H_{25}N_2O_7$ 405.1685; found, 405.1656.

*(E)-Ethyl 1-(3-Ethoxy-3-oxoprop-1-enyl)-5-(2,4,6-trimethoxyphenyl)-1H-pyrazole-4-carboxylate (**5f**).* Colorless solid (92 mg, 83% yield); mp 148−150 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (s, 1H), 7.57 (d, *J* = 13.7, 1H), 6.59 (d, *J* = 13.7 Hz, 1H), 6.19 (s, 2H), 4.22−4.13 (m, 4H), 3.88 (s, 3H), 3.70 (s, 6H), 1.28 (dd, *J* = 9.2, 5.0 Hz, 3H), 1.17 (dd, *J* = 9.2, 5.0 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 166.7, 163.5, 162.2, 159.3, 144.0, 141.5, 137.3, 115.9, 107.6, 97.1, 90.6, 60.3, 59.7, 55.1, 55.3, 14.1, 14.0. FT-IR (KBr): 2981, 2940, 2845, 1715, 1652, 1616, 1589, 1469, 1421, 1294, 1275, 1230, 1205, 1158, 1033, 772 cm^{-1}. MS (ESI) *m/z*: [M + H]$^+$ 405. HRMS (ESI) *m/z*: [M + H]$^+$ calcd for $C_{20}H_{25}N_2O_7$ 405.1685; found, 405.1656.

*(E)-Ethyl 1-(3-Ethoxy-3-oxoprop-1-enyl)-5-(3-phenoxyphenyl)-1H-pyrazole-4-carboxylate (**5g**).* Colorless solid (83 mg, 75% yield); mp 108−110 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (s, 1H), 7.72 (d, *J* = 13.7 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.36 (dd, *J* = 8.4, 7.6 Hz, 2H), 7.18−7.12 (m, 2H), 7.11−7.08 (m, 3H), 7.04−7.00 (m, 1H), 6.64 (d, *J* = 13.7 Hz, 1H), 4.24−4.17 (m, 4H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 166.2, 161.9, 157.5, 156.3, 146.6, 144.0, 136.3, 129.9, 128.4, 124.9, 123.9, 120.4, 120.0, 119.4, 115.2, 109.7, 60.7, 60.4, 14.2, 14.0. FT-IR (KBr): 2982, 2933, 1713, 1651, 1580, 1562, 1490, 1456, 1279, 1228, 1153, 1120, 1038, 757 cm^{-1}. MS (ESI) *m/z*: [M + H]$^+$ 407. HRMS (ESI) *m/z*: [M + H]$^+$ calcd for $C_{23}H_{23}N_2O_5$ 407.1602; found, 407.1601.

*(E)-Ethyl 1-(3-Ethoxy-3-oxoprop-1-enyl)-5-p-tolyl-1H-pyrazole-4-carboxylate (**5h**).* Colorless solid (86 mg, 76% yield); mp 126−128 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (s, 1H), 7.92 (d, *J* = 13.8 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 6.56 (d, *J* = 13.8 Hz), 4.27 (qd, *J* = 7.1, 3.4 Hz, 4H), 2.40 (s, 3H), 1.32 (dt, *J* = 8.9, 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 165.9, 162.1, 155.5, 139.1, 138.5, 135.8, 129.1, 128.6, 128.2, 114.8, 108.4, 60.7,

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60.5, 21.3, 14.2. FT-IR (KBr): 2983, 2926, 1734, 1620, 1595, 1562, 1511, 1465, 1450, 1367, 1325, 1217, 1189, 1110, 1035, 753 cm^{-1}. MS (ESI) m/z: $[M + H]^+$ 329. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{21}N_2O_4$ 329.1511; found, 329.1495.

*(E)-Ethyl 1-(3-Ethoxy-3-oxoprop-1-enyl)-5-(4-isopropylphenyl)-1H-pyrazole-4-carboxylate (**5i**).* Colorless solid (88 mg, 78% yield); mp 120−122 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 8.20 (s, 1H), 7.92 (d, J = 13.8 Hz, 1H), 7.75 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 6.56 (d, J = 13.8 Hz, 1H), 4.32−4.23 (m, 4H), 2.95 (hept, J = 6.9 Hz, 1H), 1.32 (dt, J = 10.7, 7.1 Hz, 6H), 1.28 (d, J = 6.9 Hz, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 166.1, 162.2, 155.7, 150.1, 138.5, 135.7, 129.3, 128.6, 126.1, 114.9, 108.6, 60.8, 60.6, 34.0, 23.9, 14.3, 14.2. FT-IR (KBr): 3192, 2964, 1721, 1653, 1538, 1450, 1301, 1281, 1264, 1172, 1038, 777 cm^{-1}. MS (ESI) m/z: $[M + H]^+$ 357. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{25}N_2O_4$ 357.1828; found, 357.1808.

*(E)-Ethyl 5-(4-Cyanophenyl)-1-(3-ethoxy-3-oxoprop-1-enyl)-1H-pyrazole-4-carboxylate (**5j**).* Colorless solid (75 mg, 66% yield); mp 180−182 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 8.25 (s, 1H), 8.01 (d, J = 8.5 Hz, 2H), 7.93 (d, J = 13.9 Hz, 1H), 7.73 (d, J = 8.4 Hz, 2H), 6.59 (d, J = 13.9 Hz, 1H), 4.34−4.25 (m, 4H), 1.33 (q, J = 7.2 Hz, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 165.7, 161.8, 153.5, 138.1, 135.7, 136.0, 131.7, 130.0, 118.7, 115.2, 112.7, 109.7, 61.0, 60.9, 14.3, 14.2. FT-IR (KBr): 3139, 2984, 2919, 2227, 1713, 1655, 1537, 1462, 1287, 1268, 1176, 1132, 1037, 850, 773 cm^{-1}. MS (ESI) m/z: $[M + H]^+$ 340. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{18}N_3O_4$ 340.1297; found, 340.1304.

*(E)-Ethyl 1-(3-Ethoxy-3-oxoprop-1-enyl)-5-(4-(trifluoromethyl)-phenyl)-1H-pyrazole-4-carboxylate (**5k**).*[14] Colorless solid (76 mg, 68% yield); mp 96−98 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.79 (d, J = 8.1 Hz, 2H), 7.62 (d, J = 13.6 Hz, 1H), 7.55 (d, J = 8.0 Hz, 2H), 6.69 (d, J = 13.6 Hz, 1H), 4.23−4.17 (m, 4H), 1.28 (t, J = 7.1 Hz, 3H), 1.20 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): (ppm) 166.1, 161.8, 145.7, 144.0, 135.8, 132.3 (C−F, $2J_{C-F}$ = 33.0 Hz), 131.1, 130.6, 125.5, 123.6 (C−F, $1J_{C-F}$ = 272.4 Hz), 115.7, 110.4, 60.8, 60.6, 14.2, 14.0. ^{19}F NMR (377 MHz, $CDCl_3$): δ −62.99. FT-IR (KBr): 3105, 3066, 2983, 1706, 1651, 1623, 1565, 1518, 1465, 1417, 1333, 1273, 1245, 1131, 1070, 1029, 847 cm^{-1}. MS (ESI) m/z: $[M + H]^+$ 387. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{20}N_2O_4F_3$ 387.1227; found, 387.1213.

*(E)-Ethyl 1-(3-Ethoxy-3-oxoprop-1-enyl)-5-(3-fluorophenyl)-1H-pyrazole-4-carboxylate (**5l**).*[14] Colorless solid (80 mg, 70% yield); mp 140−142 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.92 (d, J = 13.9 Hz, 1H), 7.65 (ddd, J = 9.8, 5.4, 4.3 Hz, 1H), 7.59 (ddd, J = 10.1, 2.5, 1.6 Hz, 1H), 7.40 (td, J = 8.0, 5.9 Hz, 1H), 7.13 (tdd, J = 8.4, 2.6, 0.9 Hz, 1H), 6.57 (d, J = 13.9 Hz, 1H), 4.36−4.22 (m, 4H), 1.37−1.28 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): (ppm) 165.8, 162.3 (C−F, $1J_{C-F}$ = 244.3 Hz), 161.9, 154.1, 138.3, 135.9, 133.2 (C−F, $4J_{C-F}$ = 8.2 Hz), 129.4 (C−F, $4J_{C-F}$ = 8.2 Hz), 125.1 (C−F, $5J_{C-F}$ = 1.8 Hz), 116.6 (C−F, $2J_{C-F}$ = 23.6 Hz), 116.1 (C−F, $3J_{C-F}$ = 20.9 Hz), 115.1, 109.1, 60.9, 60.8, 14.2, 14.1. ^{19}F NMR (377 MHz, $CDCl_3$): δ −113.54. FT-IR (KBr): 2983, 2925, 2855, 1714, 1660, 1555, 1538, 1462, 1289, 1220, 1207, 1177, 1149, 1122, 1042, 774 cm^{-1}. MS (ESI) m/z: $[M + H]^+$ 333. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{18}N_2O_4F$ 333.1261; found, 333.1245.

*(E)-Ethyl 5-(4-Chlorophenyl)-1-(3-ethoxy-3-oxoprop-1-enyl)-1H-pyrazole-4-carboxylate (**5m**).* Colorless solid (80 mg, 71% yield); mp 120−122 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.14 (s, 1H), 7.65 (d, J = 13.6 Hz, 1H), 7.54−7.48 (m, 2H), 7.37−7.31 (m, 2H), 6.66 (d, J = 13.6 Hz, 1H), 4.23−4.17 (m, 4H), 1.28 (t, J = 7.1 Hz, 3H), 1.21 (t, J = 7.1 Hz). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 166.2, 161.9, 146.2, 144.1, 136.7, 136.0, 131.9, 128.9, 125.3, 115.3, 110.0, 60.8, 60.5, 14.2, 14.1. FT-IR (KBr): 2981, 2884, 1720, 1656, 1451, 1281, 1266, 1241, 1207, 1158, 1128, 1094, 1034, 775 cm^{-1}. MS (ESI) m/z: $[M + H]^+$ 349. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{18}N_2O_2Cl$ 349.0967; found, 349.0949.

*(E)-Ethyl 5-(4-Bromophenyl)-1-(3-ethoxy-3-oxoprop-1-enyl)-1H-pyrazole-4-carboxylate (**5n**).* Colorless solid (78 mg, 70% yield); mp 128−130 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 1H,), 7.91 (d, J = 13.9 Hz, 1H), 7.79−7.70 (m, 2H), 7.56 (d, J = 8.5 Hz, 2H), 6.57 (d, J = 13.9 Hz, 1H), 4.28 (qd, J = 7.1, 4.3 Hz, 4H), 1.32 (q, J = 7.1 Hz, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 165.9, 162.0, 154.4, 138.3, 135.9, 131.1, 130.9, 130.1, 123.7, 114.9, 109.1, 60.9, 60.8, 14.2. FT-IR (KBr): 2982, 2931, 1716, 1655, 1567, 1445, 1386, 1365, 1285, 1254, 1208, 1156, 1135, 1027, 769 cm^{-1}. MS (ESI) m/z: $[M + H]^+$ 393. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{18}N_2O_4Br$ 393.0470; found, 393.0444.

*(E)-Ethyl 5-(2-Bromophenyl)-1-(3-ethoxy-3-oxoprop-1-enyl)-1H-pyrazole-4-carboxylate (**5o**).* Colorless solid (76 mg, 68% yield); mp 118−120 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.73 (d, J = 13.6 Hz, 1H), 7.49−7.44 (m, 2H), 7.41 (td, J = 7.7, 1.8 Hz, 1H), 7.32 (dd, J = 7.4, 1.8 Hz, 1H), 6.65 (d, J = 13.6 Hz, 1H), 4.22−4.17 (m, 2H), 4.16−4.10 (m, 2H), 1.27 (t, J = 7.1 Hz, 3H), 1.11 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 166.1, 161.7, 145.7, 143.7, 135.9, 132.9, 132.0, 131.7, 128.8, 127.4, 124.2, 116.1, 109.9, 60.6, 60.3, 14.1, 13.8. FT-IR (KBr): 2982, 2927, 2854, 1714, 1652, 1566, 1444, 1284, 1253, 1207, 1154, 1119, 1061, 1025, 769 cm^{-1}. MS (ESI) m/z: $[M + H]^+$ 393. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{18}N_2O_4Br$ 393.0465; found, 393.0444.

*Ethyl 1-((E)-3-Ethoxy-3-oxoprop-1-enyl)-5-styryl-1H-pyrazole-4-carboxylate (**5p**).* Colorless solid (92 mg, 81% yield); mp 156−158 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.10 (s, 1H), 7.89 (d, J = 13.8 Hz, 1H), 7.63 (t, J = 7.3 Hz, 2H), 7.61−7.56 (m, 2H), 7.38 (dd, J = 10.1, 4.6 Hz, 2H), 7.33−7.28 (m, 1H), 6.59 (d, J = 13.8 Hz,), 4.35 (q, J = 7.1 Hz), 4.28 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H), 1.34 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 166.0, 162.4, 152.9, 138.4, 136.6, 134.9, 134.1, 128.7, 128.5, 127.2, 117.0, 115.1, 108.7, 60.8, 60.6, 14.3, 14.2. FT-IR (KBr): 3130, 2979, 1702, 1651, 1546, 1484, 1427, 1310, 1297, 1280, 1221, 1162, 1120, 1104, 778 cm^{-1}. MS (ESI) m/z: $[M + H]^+$ 341. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{21}N_2O_4$ 341.1501; found, 341.1495.

*(E)-Ethyl 5-cyclohexenyl-1-(3-ethoxy-3-oxoprop-1-enyl)-1H-pyrazole-4-carboxylate (**5q**).* Colorless solid (88 mg, 77% yield); mp 122−124 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.85 (d, J = 13.9 Hz, 1H), 6.47 (d, J = 13.9 Hz, 1H), 6.38 (dt, J = 5.7, 1.8 Hz, 1H), 4.27 (dq, J = 14.3, 7.1 Hz, 4H), 2.47−2.40 (m, 2H), 2.23 (dt, J = 6.1, 3.7 Hz, 2H), 1.81−1.74 (m, 2H), 1.73−1.66 (m, 2H), 1.33 (dt, J = 13.8, 7.1 Hz, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 166.1, 162.3, 157.6, 138.5, 135.4, 131.4, 129.6, 114.8, 108.0, 60.7, 60.5, 27.4, 25.6, 22.5, 21.8, 14.3, 14.2. FT-IR (KBr): 3395, 3126, 3072, 2925, 2858, 1714, 1648, 1529, 1450, 1337, 1267, 1162, 1114, 1026, 776 cm^{-1}. MS (ESI) m/z: $[M + H]^+$ 319. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{23}N_2O_4$ 319.1666; found, 319.1652.

*(E)-Ethyl 1-(3-Ethoxy-3-oxoprop-1-enyl)-5-(naphthalen-1-yl)-1H-pyrazole-4-carboxylate (**5r**).* Colorless solid (93 mg, 83% yield); mp 140−142 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 8.28 (s, 1H), 8.01 (t, J = 14.3 Hz, 1H), 7.99−7.89 (m, 1H), 7.58 (dt, J = 17.1, 8.5 Hz, 1H), 7.56−7.50 (m, 1H), 7.48−7.41 (m, 3H), 7.34 (d, J = 8.4 Hz, 1H), 6.66 (d, J = 13.7 Hz, 1H), 4.16−4.08 (m, 2H), 4.03−3.91 (m, 2H), 1.20 (t, J = 7.1 Hz, 3H), 0.82 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 166.1, 161.9, 145.7, 144.1, 136.3, 133.4, 132.1, 130.7, 128.9, 128.5, 127.2, 126.5, 124.9, 124.8, 124.6, 116.9, 109.6, 60.5, 60.1, 14.1, 13.5. FT-IR (KBr): 2983, 2824, 1720, 1652, 1583, 1559, 1463, 1385, 1279, 1256, 1240, 1216, 1154, 1140, 1085, 951, 775 cm^{-1}. MS (ESI) m/z: $[M + H]^+$ 365. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{21}N_2O_4$ 365.1520; found, 365.1495.

*(E)-Ethyl 5-(Benzo[d][1,3]dioxol-5-yl)-1-(3-ethoxy-3-oxoprop-1-enyl)-1H-pyrazole-4-carboxylate (**5s**).* Colorless solid (83 mg, 74% yield); mp 126−128 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 8.11 (s, 1H,), 7.73 (d, J = 13.7 Hz, 1H), 6.94 (d, J = 7.9 Hz, 1H), 6.89−6.80 (m, 2H), 6.64 (d, J = 13.7 Hz, 1H), 6.07 (s, 2H), 4.21 (qd, J = 7.1, 3.2 Hz, 4H), 1.28 (t, J = 7.1 Hz, 3H), 1.24 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 166.3, 162.1, 149.3, 147.8, 147.2, 144.0, 136.4, 124.8, 119.9, 115.0, 110.8, 109.5, 108.5, 101.7, 60.7, 60.3, 14.2, 14.1. FT-IR (KBr): 2924, 2853, 1711, 1650, 1567, 1504, 1461, 1278, 1231, 1203, 1151, 1118, 1098, 1031, 779 cm^{-1}. MS (ESI) m/z: $[M + H]^+$ 359. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{19}N_2O_6$ 359.1260; found, 359.1237.

*(E)-Ethyl 1-(3-Ethoxy-3-oxoprop-1-enyl)-5-(furan-2-yl)-1H-pyrazole-4-carboxylate (**5t**).* Colorless solid (91 mg, 79% yield); mp

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166−168 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (s, 1H), 7.94 (d, *J* = 13.9 Hz, 1H), 7.59 (d, *J* = 3.3 Hz, 1H), 7.57 (s, 1H), 6.58 (d, *J* = 13.9 Hz, 1H), 6.54 (dd, *J* = 3.2, 1.6 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.37 (q, *J* = 7.1 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 165.8, 161.6, 145.8, 145.4, 143.5, 138.3, 135.5, 114.4, 113.9, 111.6, 109.1, 60.8, 60.8, 14.3, 14.2. FT-IR (KBr): 3125, 2992, 1725, 1707, 1660, 1541, 1447, 1305, 1283, 1221, 1184, 1159, 1136, 1046, 1009, 774 cm^{-1}. MS (ESI) *m*/*z*: $[M + H]^+$ 305. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{15}H_{17}N_2O_5$ 305.1140; found, 305.1132.

*(E)-Ethyl 1-(3-Ethoxy-3-oxoprop-1-enyl)-5-(thiophen-2-yl)-1H-pyrazole-4-carboxylate (**5u**).* Colorless solid (88 mg, 77% yield); mp 140−142 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (s, 1H), 8.16 (d, *J* = 3.8 Hz, 1H), 7.87 (d, *J* = 13.8 Hz, 1H), 7.39 (d, *J* = 4.9 Hz, 1H), 7.16−7.07 (m, 1H), 6.57 (d, *J* = 13.8 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.35 (dt, *J* = 14.5, 7.1 Hz, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 165.9, 161.9, 149.5, 138.1, 136.1, 133.0, 130.2, 127.5, 114.1, 109.0, 60.9, 60.8, 14.3, 14.2. FT-IR (KBr): 3133, 2978, 1715, 1650, 1564, 1528, 1299, 1273, 1180, 1156, 1113, 772 cm^{-1}. MS (ESI) *m*/*z*: $[M + H]^+$ 321. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{15}H_{17}N_2O_6S$ 321.0915; found, 321.0903.

*(E)-Ethyl 5-(5-Bromothiophen-2-yl)-1-(3-ethoxy-3-oxoprop-1-enyl)-1H-pyrazole-4-carboxylate (**5v**).* Colorless solid (77 mg, 69% yield); mp 176−178 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (s, 1H), 7.95 (d, *J* = 4.0 Hz, 1H), 7.85 (d, *J* = 13.8 Hz, 1H), 7.05 (d, *J* = 4.0 Hz, 1H), 6.55 (d, *J* = 13.8 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.36 (dt, *J* = 14.1, 7.1 Hz, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 165.8, 161.9, 148.6, 137.9, 136.1, 134.7, 130.5, 130.2, 115.1, 113.9, 109.3, 60.9, 14.3, 14.2. FT-IR (KBr): 2925, 2853, 1721, 1707, 1648, 1532, 1470, 1296, 1267, 1225, 1174, 1111, 1063, 1021, 974, 774 cm^{-1}. MS (ESI) *m*/*z*: $[M + H]^+$ 399. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{15}H_{16}N_2O_4BrS$ 399.0010; found, 399.0008.

*(E)-Ethyl 2-(3-Ethoxy-3-oxoprop-1-enyl)-1′-phenyl-3′-p-tolyl-1′H,2H-3,4′-bipyrazole-4-carboxylate (**5w**).* Colorless solid (58 mg, 51% yield); mp 142−144 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 1H), 8.18 (s, 1H), 7.87 (d, *J* = 13.8 Hz, 1H), 7.85−7.78 (m, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.42 (d, *J* = 13.8 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.02 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 165.9, 161.9, 152.1, 148.3, 139.9, 138.4, 137.6, 135.0, 130.5, 129.4, 129.2, 128.7, 127.8, 126.5, 119.2, 116.3, 112.1, 108.7, 60.8, 60.6, 21.2, 14.2, 13.9. FT-IR (KBr): 2981, 2933, 1712, 1651, 1598, 1550, 1507, 1298, 1261, 1222, 1173, 1078, 1057, 963, 757 cm^{-1}. MS (ESI) *m*/*z*: $[M + H]^+$ 471. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{27}H_{27}N_2O_4$ 471.2064; found, 471.2026.

*(E)-Ethyl 1-(3-Ethoxy-3-oxoprop-1-enyl)-5-(1H-indol-3-yl)-1H-pyrazole-4-carboxylate (**5x**).* Colorless solid (88 mg, 78% yield); mp 172−174 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.09 (s, 1H), 8.22 (s, 1H), 7.98−7.86 (m, 1H), 7.32 (dd, *J* = 10.2, 4.0 Hz, 2H), 7.28 (dd, *J* = 6.1, 1.7 Hz, 1H), 7.23−7.13 (m, 2H), 6.72−6.64 (m, 1H), 4.19 (qd, *J* = 7.1, 3.7 Hz, 4H), 1.28−1.21 (m, 3H), 1.19−1.13 (m, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 166.1, 161.9, 144.1, 142.0, 136.7, 135.1, 126.6, 125.7, 122.2, 120.3, 118.7, 114.2, 111.1, 107.8, 100.6, 60.0, 59.7, 13.8, 13.4. FT-IR (KBr): 3347, 3272, 2982, 1709, 1649, 1580, 1524, 1435, 1423, 1291, 1264, 1222, 1159, 1088, 1026, 771 cm^{-1}. MS (ESI) *m*/*z*: $[M + H]^+$ 354. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{19}H_{20}N_3O_4$ 354.1472; found, 354.1448.

*(E)-Ethyl 5-(2-Chloro-6-methoxyquinolin-3-yl)-1-(3-ethoxy-3-oxoprop-1-enyl)-1H-pyrazole-4-carboxylate (**5y**).* Colorless solid (70 mg, 64% yield); mp 170−173 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 8.09 (d, *J* = 7.0 Hz, 1H), 8.02 (d, *J* = 13.6 Hz, 1H), 7.51 (ddd, *J* = 5.2, 4.7, 1.8 Hz, 2H), 7.12 (d, *J* = 2.7 Hz, 1H), 6.71 (d, *J* = 13.6 Hz, 1H), 4.22−4.12 (m, 4H), 3.95 (s, 3H), 1.25 (t, *J* = 6.9 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 165.9, 161.6, 158.8, 146.2, 144.3, 143.8, 142.5, 139.9, 135.5, 130.0, 127.1, 124.9, 120.9, 117.0, 110.4, 105.3, 60.7, 60.6, 55.7, 14.2, 13.9. FT-IR (KBr): 2981, 2932, 2824, 1717, 1655, 1562, 1497, 1348, 1293, 1272, 1254, 1229, 1203, 1159, 1083, 1027, 836 cm^{-1}. MS (ESI) *m*/*z*: $[M + H]^+$ 430. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{21}H_{21}N_3O_5Cl$ 430.1195; found, 430.1164.

*(E)-Ethyl 1-(3-Ethoxy-3-oxoprop-1-enyl)-5-(4-oxo-4H-chromen-3-yl)-1H-pyrazole-4-carboxylate (**5z**).* Colorless solid (64 mg, 57% yield); mp 118−120 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29 (dd, *J* = 8.0, 1.4 Hz, 1H), 8.22 (s, 1H), 8.15 (s, 1H), 7.93 (d, *J* = 13.9 Hz, 1H), 7.73−7.69 (m, 1H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 6.52 (d, *J* = 13.9 Hz, 1H), 4.29−4.25 (m, 2H), 4.22 (q, *J* = 6.7 Hz, 2H), 1.33 (t, *J* = 6.7 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 174.5, 166.3, 162.0, 157.8, 156.3, 144.1, 138.4, 136.5, 134.5, 126.4, 124.2, 124.0, 118.3, 116.3, 112.8, 109.7, 60.7, 60.6, 14.2, 14.1. FT-IR (KBr): 2986, 1717, 1657, 1613, 1559, 1552, 1465, 1368, 1289, 1246, 1191, 1050, 771 cm^{-1}. MS (ESI) *m*/*z*: $[M + H]^+$ 383. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{20}H_{19}N_2O_6$ 383.1262; found, 383.1237.

Typical Procedure for Preparation of (*E*)-*N*′-(2-Hydroxybenzylidene)-4-methylbenzenesulfonohydrazides (6a−h). Tosylhydrazine **2** (762 mg, 4.10 mmol, 1.0 equiv) was added to a stirred solution of salicylaldehyde **1zc** (500 mg, 4.10 mmol, 1.0 equiv) in acetonitrile (5 mL) at room temperature. The contents were stirred at the same temperature for 2 h. The reaction was monitored by TLC, after completion of the reaction; the solvent was removed under reduced pressure. The residue was purified by recrystallization with hexane and afforded (*E*)-*N*′-benzylidene-4-methylbenzenesulfonohydrazide **6a** as a colorless solid in 95% yield. The substituted tosylhydrazones **6b−g** were prepared by reaction of substituted salicylaldehyde **1zd-zj** with tosylhydrazine **2**. The prepared tosylhydrazones **6b−g** are known compounds and were compared with the literature data.[12]

General Procedure for the Preparation of (*E*)-Ethyl 3-(4-oxochromeno[4,3-*c*]pyrazol-1(4*H*)-yl)acrylate (7a). $La(OTf)_3$ (10 mg, 5 mol %) was added to the reaction mixture of ((*E*)-*N*′-(2-hydroxybenzylidene)-4-methylbenzenesulfonohydrazide **6a** (100 mg, 0.34 mmol, 1.0 equiv) and ethyl propiolate **4a** (68 mg, 0.69 mmol, 2.0 equiv) at room temperature, and the contents were heated at 100 °C. The reaction was monitored by TLC, and after completion of the reaction (10 h), the residue was purified by column chromatography using silica gel (60:120, ethyl acetate/hexane 5:95), affording (*E*)-ethyl 3-(4-oxochromeno[4,3-*c*]pyrazol-1(4*H*)-yl)acrylate **7a** as colorless solid in 32% yield. The chromenopyrazolyl acrylates **7c** and **7e** were prepared by reaction of hydrazones **6d** and **6g** with ethyl propiolate **4a** under the above optimized reaction conditions. The newly prepared compounds **7a**, **7c**, and **7e** were characterized by spectral data.

*(E)-Ethyl 3-(4-Oxochromeno[4,3-c]pyrazol-1(4H)-yl)acrylate (**7a**).* Colorless solid (31 mg, 32% yield); mp 176−178 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 1H), 8.10 (t, *J* = 11.7 Hz, 1H), 8.04 (d, *J* = 13.8 Hz, 1H), 7.54 (dd, *J* = 11.4, 4.2 Hz, 1H), 7.37 (dd, *J* = 15.7, 7.9 Hz, 2H), 6.79 (d, *J* = 13.8 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 165.4, 157.0, 153.3, 150.9, 138.2, 133.3, 131.5, 124.9, 123.3, 117.7, 113.8, 111.6, 110.3, 61.2, 14.2. FT-IR (KBr): 2954, 2358, 1720, 1705, 1662, 1565, 1453, 1405, 1297, 1280, 1241, 1217, 1162, 953, 776 cm^{-1}. MS (ESI) *m*/*z*: $[M + H]^+$ 285. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{15}H_{13}N_2O_4$ 285.0875; found, 285.0875.

*(E)-Ethyl 3-(8-Methyl-4-oxochromeno[4,3-c]pyrazol-1(4H)-yl)-acrylate (**7c**).* Colorless solid (33 mg, 35% yield); mp 145−147 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.76 (s, 1H), 7.85 (s, 1H), 7.37 (d, *J* = 10.9 Hz, 1H), 7.31 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.27 (d, *J* = 3.5 Hz, 1H), 5.77 (d, *J* = 10.9 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.44 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 164.1, 157.4, 151.4, 149.7, 136.3, 136.2, 134.5, 132.2, 122.9, 117.4, 113.4, 109.9, 108.7, 61.3, 20.8, 14.1. FT-IR (KBr): 3021, 1754, 1652, 1481, 1425, 1215, 1140, 1024, 761 cm^{-1}. MS (ESI) *m*/*z*: $[M + H]^+$ 299. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{16}H_{15}N_2O_4$ 299.1041; found, 299.1026.

*(E)-Ethyl 3-(8-Bromo-4-oxochromeno[4,3-c]pyrazol-1(4H)-yl)-acrylate (**7e**).* Colorless solid (21 mg, 21% yield); mp 244−246 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (s, 1H), 8.25 (s, 1H), 8.03 (d, *J* = 13.7 Hz, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 7.3 Hz, 1H),

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6.80 (d, J = 13.7 Hz, 1H), 4.32 (dd, J = 13.9, 6.8 Hz, 2H), 1.37 (t, J = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 165.3, 156.4, 152.2, 149.8, 138.0, 134.3, 133.4, 126.0, 119.5, 117.7, 115.5, 112.2, 110.1, 61.3, 14.2. FT-IR (KBr): 3660, 3296, 2984, 1765, 1720, 1654, 1596, 1467, 1263, 1219, 1181, 771 cm^{-1}. MS (ESI) m/z: $[M + H]^+$ 363. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{12}N_2O_4Br$ 362.9980; found, 362.9981.

General Procedure for the Preparation of Ethyl 3-Ethoxychromeno[4,3-*c*]pyrazole-4-carboxylates (8a−m). La$(OTf)_3$ (10 mg, 5 mol %) was added to the reaction mixture of ((*E*)-*N*′-(2-hydroxybenzylidene)-4-methylbenzenesulfonohydrazide **6a** (100 mg, 0.34 mmol, 1.0 equiv) and diethyl but-2-ynedioate **4d** (59 mg, 0.34 mmol, 1.0 equiv) at room temperature, and the contents were heated at 100 °C. The reaction was monitored by TLC, and after completion of the reaction (10 h), the residue was purified by column chromatography using silica gel (60:120, ethyl acetate/hexane 10:90), affording ethyl 3-ethoxychromeno[4,3-*c*]pyrazole-4-carboxylate **8a** as a colorless solid in 69% yield. The chromenopyrazole-4-carboxylates **8b−m** were prepared by reaction of hydrazones **6b−g** with activated alkynes **4d−e** under the above optimized reaction conditions. The newly prepared compounds **8a−m** were characterized by spectral data.

*Ethyl 3-Ethoxychromeno[4,3-c]pyrazole-4-carboxylate (**8a**).* Colorless solid (68 mg, 69% yield); mp 100−102 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.09 (dd, J = 7.8, 1.5 Hz, 1H), 7.48 (ddd, J = 8.7, 7.3, 1.6 Hz, 1H), 7.33 (ddd, J = 15.0, 8.4, 4.3 Hz, 2H), 4.65 (q, J = 7.2 Hz, 2H), 4.54 (q, J = 7.1 Hz, 2H), 1.58 (t, J = 7.2 Hz, 3H), 1.50 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 158.9, 155.7, 152.7, 148.3, 134.2, 130.5, 124.3, 122.5, 117.2, 114.2, 107.2, 62.8, 48.3, 15.8, 13.9. FT-IR (KBr): 2984, 2940, 2873, 1752, 1620, 1592, 1557, 1516, 1455, 1402, 1367, 1304, 1271, 1229, 1157, 1103, 1047, 1031, 968, 750 cm^{-1}. MS (ESI) m/z: $[M + H]^+$ 287. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{15}N_2O_4$ 287.1040; found, 287.1026.

*Methyl 3-Methoxychromeno[4,3-c]pyrazole-4-carboxylate (**8b**).* Colorless solid (59 mg, 66% yield); mp 168−170 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 7.7 Hz, 1H), 7.52−7.44 (m, 1H), 7.39−7.28 (m, 2H), 4.30 (s, 3H), 4.08 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 159.4, 155.5, 152.7, 148.3, 134.1, 130.6, 124.4, 122.5, 117.2, 113.9, 107.4, 53.2, 40.6. FT-IR (KBr): 2956, 2923, 2854, 1755, 1718, 1620, 1556, 1510, 1455, 1316, 1307, 1272, 1232, 1154, 1098, 1031, 972, 757 cm^{-1}. MS (ESI) m/z: $[M + H]^+$ 259. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{11}N_2O_4$ 259.0727; found, 259.0713.

*Ethyl 3-Ethoxy-8-methoxychromeno[4,3-c]pyrazole-4-carboxylate (**8c**).* Colorless solid (70 mg, 71% yield); mp 116−118 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 2.9 Hz, 1H), 7.30 (d, J = 9.1 Hz, 1H), 7.05 (dd, J = 9.1, 3.0 Hz, 1H), 4.65 (q, J = 7.2 Hz, 2H), 4.54 (q, J = 7.2 Hz, 2H), 3.91 (s, 3H), 1.58 (t, J = 7.0 Hz, 3H), 1.49 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 159.0, 156.2, 155.9, 134.3, 118.6, 118.4, 114.5, 107.4, 104.6, 62.8, 55.9, 48.3, 15.9, 13.9. FT-IR (KBr): 2994, 2943, 2837, 1747, 1603, 1556, 1521, 1485, 1462, 1432, 1391, 1367, 1302, 1232, 1216, 1156, 1092, 1052, 998, 770 cm^{-1}. MS (ESI) m/z: 317 $[M + H]^+$. HRMS (ESI) m/z: calcd for $C_{16}H_{17}N_2O_5$ $[M + H]^+$ 317.1139; found, 317.1132.

*Methyl 3,8-Dimethoxychromeno[4,3-c]pyrazole-4-carboxylate (**8d**).* Colorless solid (62 mg, 69% yield); mp 203−205 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.49 (d, J = 3.0 Hz, 1H), 7.32−7.28 (m, 1H), 7.08−7.03 (m, 1H), 4.31 (s, 3H), 4.08 (s, 3H), 3.89 (s, 3H) . $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 159.4, 156.2, 155.6, 148.3, 147.0, 134.2, 129.8, 114.2, 107.4, 104.4, 55.8, 53.2, 40.6. FT-IR (KBr): 2955, 2925, 2848, 1741, 1624, 1594, 1513, 1455, 1438, 1396, 1312, 1286, 1272, 1251, 1151, 1085, 1027, 989, 759 cm^{-1}. MS (ESI) m/z: $[M + H]^+$ 289. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{13}N_2O_5$ 289.0833; found, 289.0819.

*Ethyl 3-Ethoxy-7-methoxychromeno[4,3-c]pyrazole-4-carboxylate (**8e**).* Colorless solid (62 mg, 63% yield); mp 121−123 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 8.5 Hz, 1H), 6.88 (dt, J = 6.7, 2.3 Hz, 2H), 4.62 (q, J = 7.2 Hz, 2H), 4.53 (q, J = 7.1 Hz, 2H), 3.87 (s, 3H), 1.57 (t, J = 7.2 Hz, 3H), 1.49 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 161.6, 159.0, 155.9, 154.2, 148.6, 134.1, 123.5, 112.2, 107.2, 106.1, 101.4, 62.7, 55.6, 48.2, 15.8, 13.9. FT-IR (KBr): 2955, 2834, 1749, 1650, 1604, 1556, 1521, 1454, 1397, 1339, 1315, 1269, 1223, 1159, 1117, 1092, 1034, 825, 760 cm^{-1}. MS (ESI) m/z: $[M + H]^+$ 317. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{17}N_2O_5$ 317.1146; found, 317.1132.

*Ethyl 3-Ethoxy-8-methylchromeno[4,3-c]pyrazole-4-carboxylate (**8f**).* Colorless solid (71 mg, 72% yield); mp 142−144 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 0.8 Hz, 1H), 7.29−7.22 (m, 2H), 4.64 (q, J = 7.2 Hz, 2H), 4.57−4.50 (m, 2H), 2.43 (s, 3H), 1.58 (t, J = 7.2 Hz, 3H), 1.52−1.47 (m, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 159.0, 155.8, 150.9, 148.4, 134.2, 134.1, 131.4, 122.4, 116.9, 113.7, 107.3, 62.8, 48.3, 20.8, 15.8, 13.9. FT-IR (KBr): 2960, 2923, 2851, 1735, 1597, 1562, 1523, 1501, 1461, 1445, 1399, 1367, 1273, 1223, 1187, 1091, 1018, 914, 761 cm^{-1}. MS (ESI) m/z: $[M + H]^+$ 301. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{17}N_2O_4$ $[M + H]^+$ 301.1191; found, 301.1182.

*Methyl 3-Methoxy-8-methylchromeno[4,3-c]pyrazole-4-carboxylate (**8g**).* Colorless solid (62 mg, 70% yield); mp 196−198 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.86−7.82 (m, 1H), 7.30−7.23 (m, 2H), 4.29 (s, 3H), 4.08 (s, 3H), 2.43 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 159.4, 155.6, 150.7, 148.3, 134.1, 134.0, 131.4, 122.3, 116.8, 113.4, 107.3, 53.1, 40.5, 20.8. FT-IR (KBr): 2960, 2924, 2863, 1751, 1723, 1684, 1623, 1594, 1557, 1521, 1497, 1457, 1434, 1307, 1271, 1237, 1199, 1095, 1013, 926, 760 cm^{-1}. MS (ESI) m/z: $[M + H]^+$ 273. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{13}N_2O_4$ 273.0877; found, 273.0869.

*Ethyl 3-Ethoxy-6-methylchromeno[4,3-c]pyrazole-4-carboxylate (**8h**).* Colorless solid (63 mg, 64% yield); mp 93−95 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.93 (dd, J = 7.7, 0.9 Hz, 1H), 7.33 (dd, J = 7.4, 0.7 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 4.65 (q, J = 7.2 Hz, 2H), 4.53 (q, J = 7.1 Hz, 2H), 2.48 (s, 3H), 1.58 (s, 3H), 1.50 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 159.1, 155.7, 151.2, 148.8, 134.0, 131.8, 126.6, 123.9, 120.2, 113.9, 107.2, 62.7, 48.3, 16.1, 15.8, 13.9. FT-IR (KBr): 2984, 2924, 2854, 1754, 1618, 1558, 1523, 1457, 1423, 1393, 1368, 1307, 1248, 1227, 1190, 1149, 1125, 1038, 974, 745 cm^{-1}. MS (ESI) m/z: $[M + H]^+$ 301. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{17}N_2O_4$ 301.1191; found, 301.1182.

*Methyl 3-Methoxy-6-methylchromeno[4,3-c]pyrazole-4-carboxylate (**8i**).* Colorless solid (57 mg, 64% yield); mp 154−156 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.91 (dd, J = 7.8, 0.9 Hz, 1H), 7.33 (dd, J = 7.4, 0.7 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 4.30 (s, 3H), 4.08 (s, 3H), 2.48 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 159.5, 155.5, 151.1, 148.7, 134.0, 131.9, 126.6, 123.9, 120.0, 113.6, 107.4, 53.1, 40.6, 16.1. FT-IR (KBr): 2970, 2921, 2846, 1756, 1615, 1559, 1524, 1483, 1450, 1379, 1320, 1283, 1254, 1192, 1113, 1077, 1040, 946, 771 cm^{-1}. MS (ESI) m/z: $[M + H]^+$ 273. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{13}N_2O_4$ 273.0883; found, 273.0869.

*Ethyl 8-Chloro-3-ethoxychromeno[4,3-c]pyrazole-4-carboxylate (**8j**).* Colorless solid (60 mg, 61% yield); mp 110−112 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 2.5 Hz, 1H), 7.42 (dd, J = 8.8, 2.5 Hz, 1H), 7.33−7.27 (m, 1H), 4.65 (q, J = 7.2 Hz, 2H), 4.54 (q, J = 7.1 Hz, 2H), 1.58 (t, J = 7.2 Hz, 3H), 1.49 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 158.8, 155.1, 151.2, 147.4, 134.4, 130.5, 129.8, 122.3, 118.7, 115.4, 107.2, 62.9, 48.5, 15.8, 13.9. FT-IR (KBr): 2955, 2924, 2854, 1761, 1556, 1511, 1454, 1383, 1368, 1299, 1236, 1117, 1073, 1052, 989, 759 cm^{-1}. MS (ESI) m/z: $[M + H]^+$ 321. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{14}N_2O_2Cl$ 321.0654; found, 321.0636.

*Methyl 8-Chloro-3-methoxychromeno[4,3-c]pyrazole-4-carboxylate (**8k**).* Colorless solid (51 mg, 57% yield); mp 207−209 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 2.4 Hz, 1H), 7.43 (dd, J = 8.8, 2.4 Hz, 1H), 7.34−7.28 (m, 1H), 4.31 (s, 3H), 4.08 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 159.2, 154.9, 151.2, 147.2, 134.4, 130.6, 129.9, 122.2, 118.6, 115.2, 107.4, 53.3, 40.8. FT-IR (KBr): 2962, 2923, 2859, 1740, 1555, 1509, 1448, 1311, 1284, 1256, 1231, 1137, 1114, 1075, 1038, 999, 757 cm^{-1}. MS (ESI) m/z: $[M + H]^+$ 293. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{10}N_2O_4Cl$ 293.0339; found, 293.0323.

*Methyl 8-Bromo-3-methoxychromeno[4,3-c]pyrazole-4-carboxylate (**8l**).* Colorless solid (54 mg, 59% yield); mp 231−233 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 2.3 Hz, 1H), 7.56 (dd, J =

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8.8, 2.3 Hz, 1H), 7.28−7.22 (m, 1H), 4.31 (s, 3H), 4.08 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 159.2, 154.8, 151.6, 147.1, 134.4, 133.4, 125.2, 118.9, 117.2, 115.6, 107.4, 53.3, 40.8. FT-IR (KBr): 2957, 2941, 2863, 1744, 1692, 1614, 1586, 1554, 1509, 1449, 1378, 1311, 1284, 1257, 1230, 1134, 1109, 1038, 997, 753 cm^{-1}. MS (ESI) *m/z*: $[M + H]^+$ 337. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{13}H_{10}N_2O_4Br$ 336.9831; found, 336.9818.

*Methyl 6,8-Dichloro-3-methoxychromeno[4,3-c]pyrazole-4-carboxylate (**8m**).* Colorless solid (46 mg, 51% yield); mp 238−240 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 2.4 Hz, 1H), 7.54 (d, *J* = 2.4 Hz, 1H), 4.32 (s, 3H), 4.08 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 159.1, 153.6, 147.2, 146.9, 134.6, 130.8, 129.7, 123.1, 120.7, 116.3, 107.4, 53.4, 40.9. FT-IR (KBr): 2956, 2927, 2863, 1774, 1546, 1509, 1457, 1432, 1404, 1312, 1164, 1133, 1086, 1000, 827, 771 cm^{-1}. MS (ESI) *m/z*: $[M + H]^+$ 327. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{13}H_{14}N_2O_4Cl_2$ 326.9946; found, 326.9933.

*Ethyl 3-Phenyl-1H-pyrazole-5-carboxylate (**5aa**).* Colorless solid (60 mg, 76% yield); mp 108−109 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.75 (t, *J* = 6.5 Hz, 2H), 7.45−7.38 (m, 2H), 7.37−7.33 (m, 1H), 7.09 (s, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 160.6, 149.3, 139.1, 130.7, 128.9, 128.5, 125.7, 105.5, 61.3, 14.2. FT-IR (KBr): 3569, 3120, 2911, 1764, 1529, 1509, 1477, 1458, 1365, 1337, 1147, 1026 cm^{-1}. MS (ESI) *m/z*: $[M + H]^+$ 217. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{12}H_{13}N_2O_2$ 217.0971; found, 217.0968.

*(E)-Ethyl 1-(3-Ethoxy-3-oxoprop-1-en-1-yl)-3-phenyl-1H-pyrazole-5-carboxylate (**5ab**).* Colorless solid (78 mg, 54% yield); mp 138−140 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.97 (d, *J* = 13.7 Hz, 1H), 7.91−7.85 (m, 2H), 7.47−7.37 (m, 3H), 7.32 (s, 1H), 6.75 (d, *J* = 13.7 Hz, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 166.5, 158.9, 153.1, 137.9, 134.7, 131.2, 129.2, 128.8, 126.1, 111.5, 109.0, 61.8, 60.6, 14.32, 14.2. FT-IR (KBr): 3077, 2919, 2812, 1741, 1713, 1665, 1574, 1541, 1451, 1330, 1289, 1267, 1193, 1159, 1042 cm^{-1}. MS (ESI) *m/z*: $[M + H]^+$ 315. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{19}N_2O_4$ 315.1339; found, 315.1331.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02421.

^1H and ^{13}C NMR spectra, HRMS spectra, gNOESY spectra, structures of the tosylhydrazones **3a−zb** and **6a−h**, HPLC chromatograms, and X-ray crystallography data (PDF)

Accession Codes

CCDC 2031798 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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