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Metal-Free Tandem Oxidative Cyclization for the Synthesis of 1,2-Dihydropyridazines and Pyrazoles

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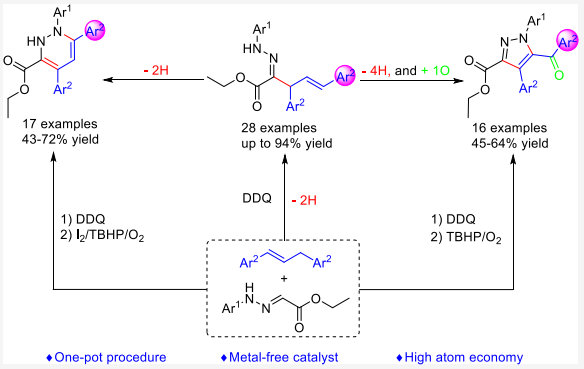
ABSTRACT: Mediated by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), a novel oxidative coupling of hydrazones and 1,3-diarylpropenes has been disclosed to generate appealing *β,γ*-unsaturated hydrazones, which further undergo 5-*exo*-trig or 6-*endo*-trig cascade cyclization to give the respective 1,2-dihydropyridazines or pyrazoles selectively under metal-free conditions. The mechanisms of the coupling and subsequent cyclization are proposed.



INTRODUCTION

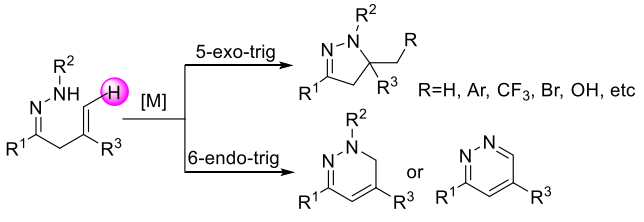
Tandem reactions consist of two or more successive independent steps performed in one pot,[1] which can save time, energy, labor, and minimize the generation of waste compared to the stepwise sequences.[2] Consequently, tandem reactions have become increasingly important for the preparation of complex products, including efficient and divergent synthesis of valuable N-heterocycles.[3] Among them, metal-free tandem cyclizations have played a pivotal role in the preparation of N-heterocycles because heavy transition-metal impurities could be avoided in the final products, and excellent progress has been achieved.[4] Owing to the importance of N-heterocycles in several fields, it is still desirable to develop more convenient and efficient tandem cyclizations for the construction of such compounds under metal-free conditions.

Dihydropyridazines and pyrazoles are important N-heterocycles and exist widely in natural products and pharmaceutically active compounds, and are used for selective inhibition of cyclooxygenase-2 (COX-2), and as spasmolytic, antimicrobial, antihypertensive, and anti-inflammatory agents.[5] These two types of N-heterocycles also serve as versatile intermediates in organic synthesis.[6] For these reasons, they have received much attention from synthetic and pharmaceutical chemists. Among the developed synthetic methodologies, the 5-*exo*-trig and 6-*endo*-trig cyclizations of *β,γ*-unsaturated hydrazones have emerged as attractive statics to construct these N-heterocycles. An extensive survey showed that transition-metal-catalyzed cyclizations of *β,γ*-unsaturated hydrazones are dominant in these transformations.[7] By comparison, the metal-free cyclizations of *β,γ*-unsaturated hydrazones are rarely reported. Besides, the reported transformations of *β,γ*-unsaturated hydrazones are mainly focused on those without substituents on the *γ*-position. Only the Sodeoka group[8] reported the $Cu(OAc)_2$-catalyzed cyclization of *β,γ*-unsaturated hydrazones containing an aryl group on the *γ*-position (Scheme 1).

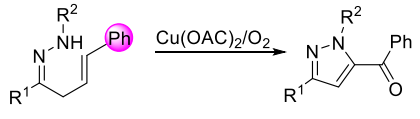
β,γ-Unsaturated hydrazones are valuable synthetic building blocks, which could undergo diverse synthetic transformations.[9] The common method to obtain the *β,γ*-unsaturated hydrazones

Scheme 1. Previous Works

a) Transition-metal-catalyzed cyclization of β,γ-unsaturated hydrazones:



b) Sodeoka's work:



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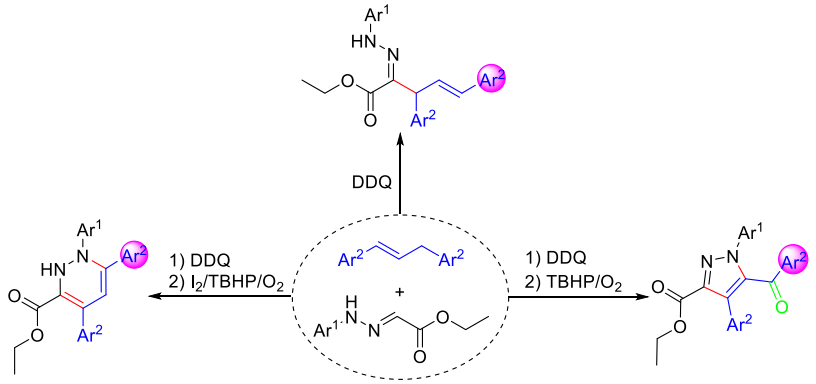
Scheme 2. This Work

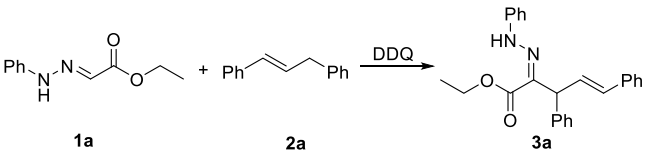


is allylation of aldehyde, followed by condensation with hydrazines.[10] The method requires the use of a functionalized substrate and a metal catalyst, thus may generate metal waste and cause environmental pollution. To our knowledge, there has been no report concerning the synthesis of β,γ-unsaturated hydrazones through the allylation of hydrazones via activation of the C−H bond under metal-free conditions. Recently, our group has developed various DDQ-mediated oxidative coupling/annulation reactions for the construction of carbon−carbon and carbon-heteroatom bonds and for the preparation of nitrogen-containing compounds utilizing push−pull enamines as the substrates.[11] In continuation of our previous work, herein we wish to report a metal-free coupling reaction between hydrazones and 1,3-diarylpropenes, which gives the corresponding γ-aryl substituted β,γ-unsaturated hydrazones, and generates 1,2-dihydropyridazines and pyrazoles via further intramolecular oxidative cyclization in one pot, respectively (Scheme 2).

RESULTS AND DISCUSSION

Initially, (*E*)-hydrazone **1a** and 1,3-diphenylpropene **2a** were chosen as model substrates (Table 1). The reaction was performed in CH_2Cl_2 at room temperature in the presence of 1.2 equiv of DDQ. To our expectation, the desired coupling product **3a** was obtained in 82% yield within 2 h (entry 1). From the downfield chemical shift of the N−H proton, **3a** should have a Z-configuration.[12] Other solvents such as dimethylformamide (DMF), CH_3CN, CH_3NO_2, $CHCl_3$, and 1,2-$ClCH_2CH_2Cl$ (DCE) were also investigated (entries 2−6). Both DCE and CH_2Cl_2 were found to be the most suitable. Subsequently, the dosages of DDQ and 1,3-diphenylpropene **2a** were examined, respectively. The yield of **3a** decreased slightly when the dosage of **2a** was increased to 1.5 equiv (entry 7), while an increase in the loading of DDQ to 1.3 equiv made the reaction system complicated and only 75% yield was obtained (entry 8). Finally, it was found that increasing the temperature to 60 °C afforded 94% yield of **3a** in DCE (entry 10).

Table 1. Optimization of the Reaction Conditions[a]

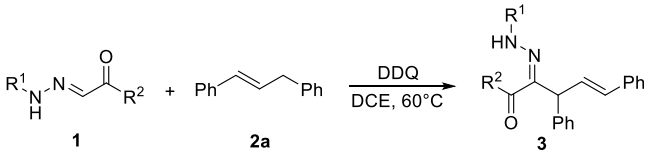


1a 2a 3a

entry	solvent	DDQ (equiv)	temperature (°C)	yield (%)[b]
1	CH_2Cl_2	1.2	r.t.	82
2	DMF	1.2	r.t.	63
3	CH_3CN	1.2	r.t.	70
4	CH_3NO_2	1.2	r.t.	73
5	$CHCl_3$	1.2	r.t.	58
6	DCE	1.2	r.t.	78
7	DCE	1.2	r.t.	74[c]
8	DCE	1.3	r.t.	75
9	DCE	1.2	40	86
10	DCE	1.2	60	94
11	DCE	1.2	0	–

[a]**2a** (0.6 mmol) and DDQ (0.6 mmol) in solvent (3 mL) were stirred for 10 min and **1a** (0.5 mmol) was added and stirred for 2 h. [b]Isolated yield. [c]0.75 mmol of **2a**.

Table 2. Coupling of Hydrazones 1 with 1,3-Diphenylpropene 2a[a]



1 2a 3

entry	R^1, R^2 **1**	product	yield (%)[b]
1	C_6H_5, OEt **1a**	**3a**	95
2	4-MeC_6H_4, OEt **1b**	**3b**	92
3	4-$MeOC_6H_4$, OEt **1c**	**3c**	64
4	4-FC_6H_4, OEt **1d**	**3d**	49
5	4-ClC_6H_4, OEt **1e**	**3e**	91
6	4-BrC_6H_4, OEt **1f**	**3f**	93
7	4-$O_2NC_6H_4$, OEt **1g**	**3g**	26
8	4-NCC_6H_4, OEt **1h**	**3h**	79
9	3-MeC_6H_4, OEt **1i**	**3i**	90
10	3-FC_6H_4, OEt **1j**	**3j**	96
11	3-ClC_6H_4, OEt **1k**	**3k**	94
12	3-BrC_6H_4, OEt **1l**	**3l**	94
13	2-MeC_6H_4, OEt **1m**	**3m**	76
14	3,4-$Me_2C_6H_3$, OEt **1n**	**3n**	94
15	3,5-$Me_2C_6H_3$, OEt **1o**	**3o**	90
16	*i*-Pr, OEt **1p**	**3p**	84
17	*t*-Bu, OEt **1q**	**3q**	84
18	C_6H_5, Ph **1r**	**3r**	79
19	C_6H_5, H **1s**	–	–
20	C_6H_5, Me **1t**	–	–

[a]**2a** (0.6 mmol) and DDQ (0.6 mmol) in DCE (3 mL) were stirred for 10 min and **1** (0.5 mmol) was added and stirred at 60 °C for 2 h. [b]Isolated yield.

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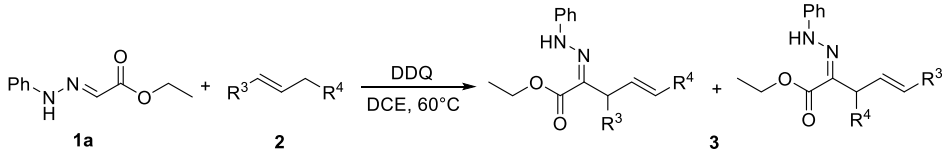
Table 3. Coupling of 1,3-Diarylpropenes 2 with Hydrazone 1a[a]

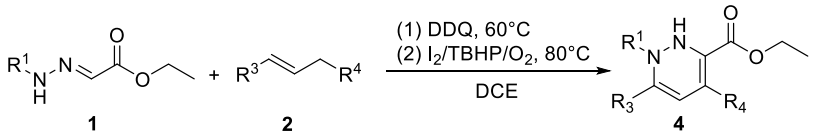


1a 2 3

entry	R^3, R^4 2	product	yield (%)[b]
1	4-MeC_6H_4, 4-MeC_6H_4 **2b**	**3s**	88
2	4-$MeOC_6H_4$, 4-$MeOC_6H_4$ **2c**	**3t**	65
3	4-ClC_6H_4, 4-ClC_6H_4 **2d**	**3u**	81
4	4-BrC_6H_4, 4-BrC_6H_4 **2e**	**3v**	85
5	3-MeC_6H_4, 3-MeC_6H_4 **2f**	**3w**	91
6	2-MeC_6H_4, 2-MeC_6H_4 **2g**	**3x**	92
7	4-MeC_6H_4, C_6H_5 **2h**	**3y** + **3y′**	95[c]
8	4-ClC_6H_4, C_6H_5 **2i**	**3z** + **3z′**	92[c]
9	C_6H_5, H **2j**	–	–
10	H, C_6H_5 **2k**	–	–

[a]**2** (0.6 mmol) and DDQ (0.6 mmol) in DCE (3 mL) were stirred for 10 min and **1a** (0.5 mmol) was added and stirred at 60 °C for 2 h. [b]Isolated yield. [c]Both α- and γ-positional isomeric products were obtained. According to the NMR, the ratio of isomers of **3y**/**3y′** is 50:50 and the ratio of isomers of **3z**/**3z′** is 45:55 or 55:45.

Table 4. Tandem Cyclization for Synthesizing 1,2-Dihydropyridazines 4[a]



1 2 4

entry	R^1 1	2	product	yield (%)[b]
1	C_6H_5 **1a**	**2a**	**4a**	[c,d]
2	**1a**	**2a**	**4a**	47[d]
3	**1a**	**2a**	**4a**	72
4	4-MeC_6H_4 **1b**	**2a**	**4b**	53
5	4-FC_6H_4 **1d**	**2a**	**4c**	63
6	4-ClC_6H_4 **1e**	**2a**	**4d**	66
7	4-BrC_6H_4 **1f**	**2a**	**4e**	67
8	3-MeC_6H_4 **1i**	**2a**	**4f**	43
9	3-FC_6H_4 **1j**	**2a**	**4g**	58
10	3-ClC_6H_4 **1k**	**2a**	**4h**	64
11	3-BrC_6H_4 **1l**	**2a**	**4i**	72
12	3,4-$Me_2C_6H_3$ **1n**	**2a**	**4j**	65
13	3,5-$Me_2C_6H_3$ **1o**	**2a**	**4k**	62
14	**1a**	**2b**	**4l**	72
15	**1a**	**2d**	**4m**	67
16	**1a**	**2e**	**4n**	70
17	**1a**	**2f**	**4o**	60
18	**1a**	**2g**	**4p**	63
19	**1a**	**2l**	**4q**	66

[a]**2** (0.6 mmol) and DDQ (0.6 mmol) in DCE (3 mL) were stirred for 10 min, **1** (0.5 mmol) was added and stirred at 60 °C for 2 h, then I_2 (0.5 mmol) and TBHP (0.75 mmol) were added and continued to be stirred at 80 °C for another 0.5 h in an atmosphere of dioxygen. [b]Isolated yield. [c]Extra 2.0 equiv of DDQ was added to the reaction mixture after the coupling and no expected product was obtained. [d]At 60 °C.

With the optimized conditions, the reaction was extended to a variety of substrates to explore the scope of this approach (Table 2). Hydrazones **1b**−**1m**, either substituted with electron-donating or electron-withdrawing groups on the benzene rings, could react with 1,3-diphenylpropene **2a** smoothly to give the corresponding coupling products **3b**−**3m** (entries 2−13). The yields ranged from 90 to 95% when the groups such as methyl, chloro, and bromo were linked to the para- or meta-position of the benzene ring, while only moderate yields could be obtained when a methoxyl or a fluoro group was attached to the para-position of the benzene ring (entries 3−4). The yield was 76% for the ortho-methyl-substituted **1m**, which indicates there was an obvious hindrance effect in the reaction (entries 2, 9, and 13). Hydrazones **1n**−**1o** having disubstituted groups were suitable candidates and generated the corresponding products **3n**−**3o** with excellent yields (entries 14−15). Notably, alkyl hydrazones **1p**−**1q** such as isopropyl and *t*-butyl were also good substrates in the reaction, producing the products **3p**−**3q** in 84% yields (entries 16−17). Besides, hydrazone **1r** could react with 1,3-diphenylpropene **2a** to give the product **3r** in 79% yield

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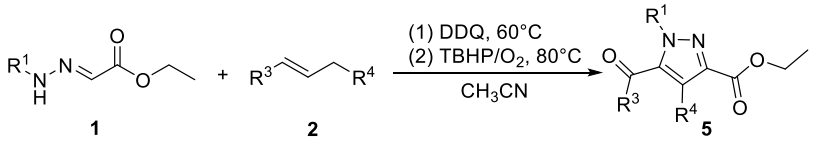
Table 5. Tandem Cyclization for Synthesizing Pyrazoles 5[a]



1 2 5

entry	R^1 1	2	product	yield (%)[b]
1	C_6H_5 **1a**	**2a**	**5a**	11[c,d]
2	**1a**	**2a**	**5a**	34[c]
3	**1a**	**2a**	**5a**	–[c,e]
4	**1a**	**2a**	**5a**	61
5	4-MeC_6H_4 **1b**	**2a**	**5b**	64
6	4-FC_6H_4 **1d**	**2a**	**5c**	57
7	4-ClC_6H_4 **1e**	**2a**	**5d**	60
8	4-BrC_6H_4 **1f**	**2a**	**5e**	62
9	3-MeC_6H_4 **1i**	**2a**	**5f**	58
10	3-FC_6H_4 **1j**	**2a**	**5g**	55
11	3-ClC_6H_4 **1k**	**2a**	**5h**	52
12	3-BrC_6H_4 **1l**	**2a**	**5i**	50
13	2-MeC_6H_4 **1m**	**2a**	**5j**	45
14	3,4-$Me_2C_6H_3$ **1n**	**2a**	**5k**	55
15	3,5-$Me_2C_6H_3$ **1o**	**2a**	**5l**	53
16	**1a**	**2d**	**5m**	53
17	**1a**	**2e**	**5n**	51
18	**1a**	**2f**	**5o**	50
19	**1a**	**2g**	**5p**	45

[a]**2** (0.6 mmol) and DDQ (0.6 mmol) in CH_3CN (3 mL) were stirred for 10 min, **1** (0.5 mmol) was added and stirred at 60 °C for 2 h, then TBHP (0.75 mmol) was added and continued to be stirred at 80 °C for another 8 h in the atmosphere of dioxygen. [b]Isolated yield. [c]DCE was used as a solvent. [d]In the atmosphere of air. [e]In the atmosphere of nitrogen.

(entry 18). The reactions of hydrazones **1s**–**1t** and 1,3-diphenylpropene **2a** were tried. Thin-layer chromatography indicated that the reaction mixtures were very complex. The desired coupling products could not be isolated (entries 19–20).

Several 1,3-diarylpropenes were also surveyed (Table 3). Symmetrical 1,3-diarylpropenes **2b**–**2g** with electron-donating or electron-withdrawing groups on the benzene rings could react with hydrazone **1a** smoothly, delivering the desired products **3s**–**3x** in 65–92% yields (entries 1–6). Unsymmetrical 1,3-diarylpropenes **2h**–**2i** (a mixture of α- and γ-isomers) were also prepared and subjected to the reaction, which gave the corresponding products **3y**–**3z** in 92–95% yields (entries 7 and 8). According to ^{1}H NMR spectroscopy, the obtained **3y**–**3z** were also a mixture of α- and γ-isomers. The ratios between isomers were different from those of the corresponding 1,3-diarylpropenes, which indicates that the allylic radicals or cations should generate in the reaction process. The reaction of hydrazone **1a** with (*E*)-prop-en-ylbenzene **2j** or allylbenzene **2k**, however, failed to afford the desired products (entries 9 and 10).

Based on the above results, the tandem cyclization of hydrazones and 1,3-diarylpropenes has been further explored to obtain the N-heterocycle 1,2-dihydropyridazine. First, 2.0 equiv of DDQ was added to the reaction mixture after the coupling of **1a** and **2a** and the reaction was continued to be stirred for another 0.5 h (Table 4, entry 1). Regretfully, the expected 1,2-dihydropyridazine could not be formed. To achieve this transformation, various metal-free oxidants such as benzoyl peroxide, *tert*-butyl peroxybenzoate, di-*tert*-butyl peroxide, I_2, *t*-butyl hydroperoxide (TBHP), and $PhI(OAc)_2$ have been examined. 1,2-Dihydropyridazine **4a** could be obtained in 47% yield when the reaction was performed at 60 °C in the presence of I_2/TBHP/O_2 (entry 2). Then, the solvent, temperature, and dosage of TBHP were surveyed to optimize the reaction conditions (see Supporting Information). To our delight, the yield was up to 72% when the temperature of intramolecular cyclization was increased to 80 °C (entry 3). With the optimal reaction conditions in hand, different hydrazones were subjected to react with 1,3-diphenylpropene **2a** and the corresponding 1,2-dihydropyridazines **4b**–**4k** were isolated in 43–72% yields (entries 4–13). 1,3-Diphenylpropenes with a halo or methyl substituent on the benzene rings also reacted with hydrazone **1a** successfully to give the products **4l**–**4q** in moderate yields (entries 14–19).

Interestingly, 5-*exo*-trig product pyrazole **5a** could be obtained in 11% yield when only 1.5 equiv of TBHP was added to the reaction mixture after completion of the coupling reaction (Table 5, entry 1). The yield was increased to 34% when the reaction was performed in the atmosphere of dioxygen (entry 2), while no cyclization product was isolated under a N_2 atmosphere (entry 3). These results showed that dioxygen was essential to further cyclization for the synthesis of pyrazoles. Screening the solvent found that CH_3CN was the suitable medium and the yield was improved to 61% (entry 4) (see Supporting Information). Subsequently, various hydrazones and 1,3-diarylpropenes were subjected to the developed tandem cyclization and the corresponding pyrazoles **5b**–**5p** were isolated in 45–64% yields (entries 5–19).

To examine the scalability of these developed tandem oxidative cyclizations, the reaction between hydrazone **1a** and 1,3-diphenylpropene **2a** was performed on a gram-scale in a single batch. The desired products **3a**, **4a**, and **5a** were obtained in 92, 60, and 52% yields (Scheme 3). These results indicated

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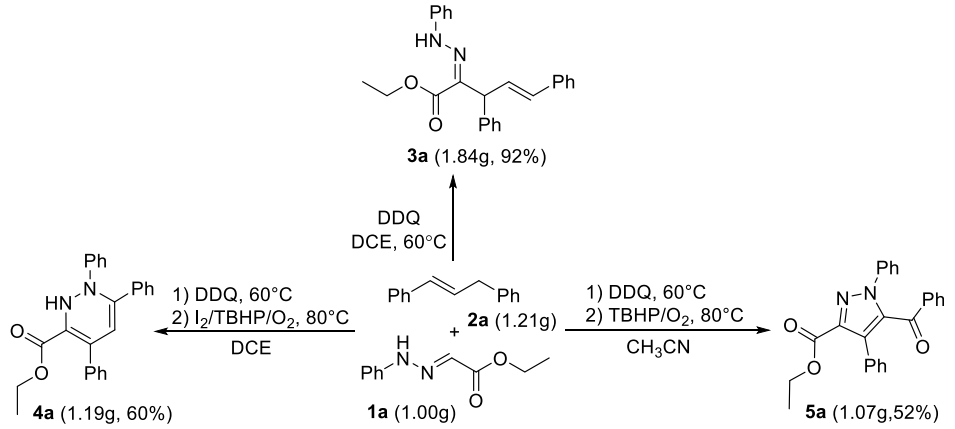
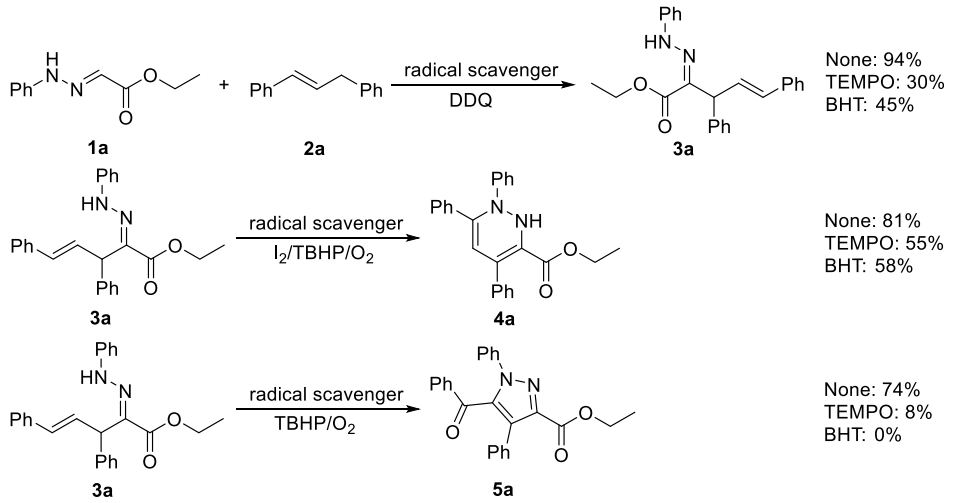
Scheme 3. Scalability of the Reaction to the Gram Scale



Scheme 4. Control Experiments



that the above tandem cyclizations possess a potential to be scaled up in industry.

In order to explore the reaction mechanism, several control experiments were conducted (Scheme 4). The coupling product **3a** was obtained in 30 and 45% yields, respectively, when 3.0 equiv of radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or 2,6-di-*tert*-butyl-4-methylphenol (BHT) was added to the reaction mixture of **1a** and **2a**. When **3a** was reacted in DCE at 80 °C in the presence of I_2/TBHP/O_2, the 6-*exo*-trig product **4a** was isolated in 81% yield within 0.5 h. Upon adding 3.0 equiv of TEMPO or BHT to the reaction mixture of **3a**, the obtained yields of **4a** were 55 and 58%, respectively. Additionally, when **3a** was reacted in CH_3CN at 80 °C in the presence of TBHP/O_2, the 5-*exo*-trig product **5a** was obtained in 74% yield within 8 h. Upon adding 3.0 equiv of TEMPO or BHT to the reaction mixture of **3a**, the yields of **5a** decreased to 8 and 0%, respectively, which indicates that the free radical pathway should be involved in the 5-*exo*-trig cyclization.

Based on the above experiment results and previous literature, a possible mechanism is proposed in Scheme 5. First, 1,3-diphenylpropene **2a** reacts with DDQ to generate the ion pair **A** through a charge-transfer (CT) complex. In our experiment, a color change from colorless to deep blue was observed, which may indicate the formation of a CT complex.[13] The nucleophilic hydrazone **1a** attacks the allyl cation in the ion pair **A**, giving the N-coupling intermediate **B**. The intermediate **B** undergoes a diaza-Cope rearrangement, followed by tautomerization to provide the product **3a**.[14] Subsequently, **3a** undergoes the electrophilic addition of iodine to generate iodonium ion **D**, which leads to the formation of 1,4-dihydropyridazine **F** through the 6-*exo*-trig cyclization and elimination of hydrogen iodide. Finally, 1,4-dihydropyridazine **F** goes through the rearrangement in the presence of TBHP/O_2, providing 1,2-dihydropyridazine **4a**. For the cyclization process of pyrazole **5a**, a hydrogen atom in **3a** is abstracted by TBHP to afford the N-center radical **G**, which generates the hydroxyl radical and *tert*-butyl alcohol. The N-center radical **G** undergoes the 5-*exo*-trig cyclization to produce the radical intermediate **H**. The radical intermediate **H** is captured by O_2 to provide the hydroperoxide radical **I**, which undergoes the 1,5-H shift to give the C-center radical **J**. The C-center radical **J** loses a hydrogen atom, and is further oxidized to generate pyrazole **5a**.

In conclusion, we have developed an oxidative coupling of readily available hydrazones and 1,3-diarylpropenes, which generates the corresponding γ-aryl-substituted β,γ-unsaturated hydrazones in good to excellent yields. Furthermore, two metal-free tandem oxidative cyclizations with hydrazones and 1,3-diarylpropenes as starting materials have been explored, which provide convenient and high atom-economy approaches for the synthesis of 1,2-dihydropyridazines and pyrazoles, respectively. These transformations involve the intermolecular oxidative coupling and a subsequent intramolecular cyclization reaction.

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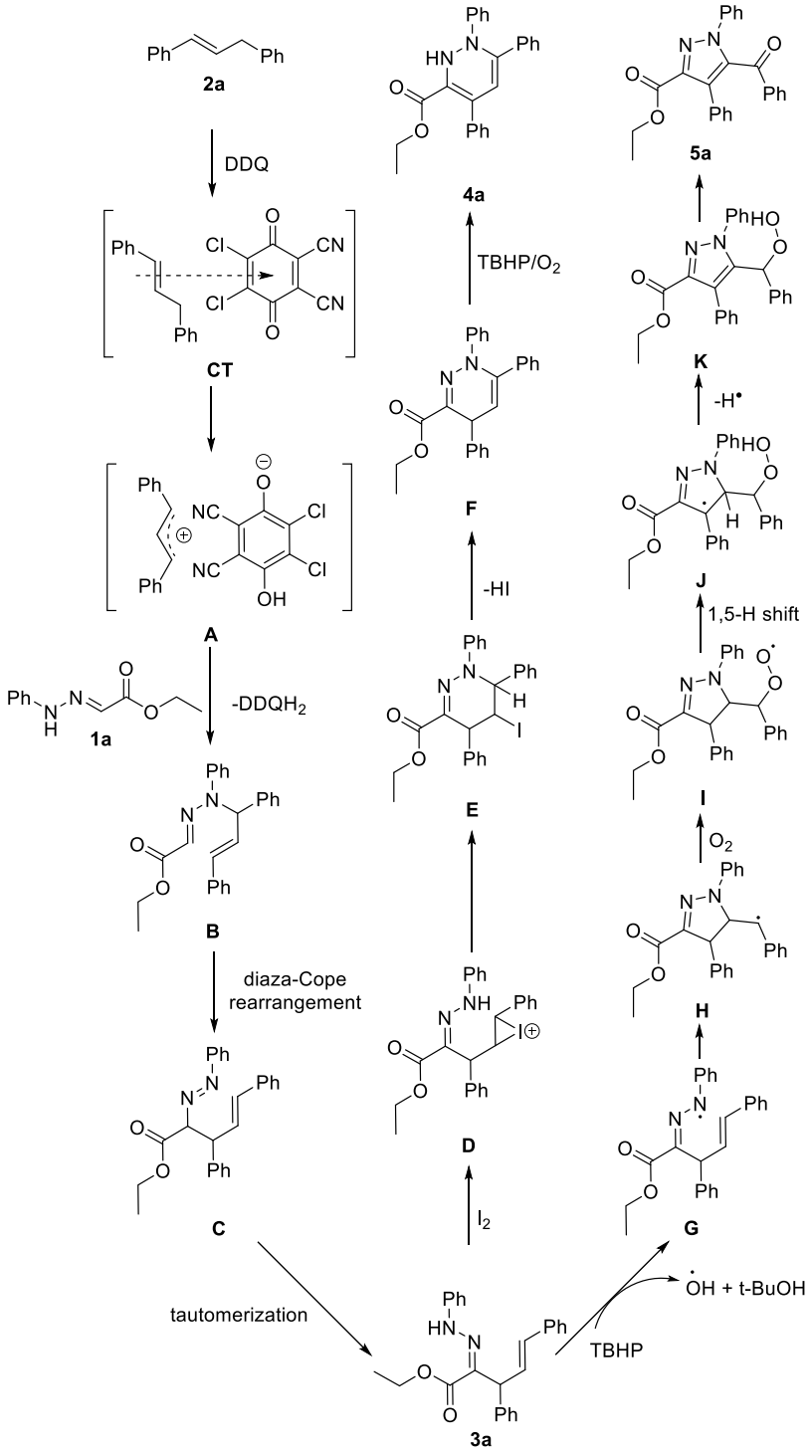
Scheme 5. Possible Mechanism



EXPERIMENTAL SECTION

General Information. Column chromatography was carried out on silica gel (200−300 mesh). The ^{1}H NMR spectra were recorded on a 400 MHz spectrometer (Bruker Magnet System 400′54 Ascend), a 500 MHz spectrometer (Bruker AVANCE III 500 MHz nuclear magnetic resonance Spectrometer), or a 600 MHz spectrometer (Bruker Ascend 600 MHz superconducting nuclear magnetic resonance spectrometer). ^{13}C NMR spectra were recorded on a 101 MHz spectrometer (Bruker Magnet System 400′54 Ascend), a 126 MHz spectrometer (Bruker AVANCE III 500 MHz nuclear magnetic resonance Spectrometer), or a 151 MHz spectrometer (Bruker Ascend 600 MHz superconducting nuclear magnetic resonance spectrometer). The measuring temperature for all NMR spectrometers is 300 K. Chemical shifts were reported in parts per million (δ) relative to the internal standard tetramethylsilane (0 ppm) for $CDCl_3$ or DMSO. The coupling constants, J, were reported in Hertz (Hz). High-resolution mass spectra (HRMS) were recorded on an electrospray ionization-time-of-flight spectrometer (Agilent 6210 TOF LC/MS). Melting points were measured with a SGW X-4. The reagents were purchased from commercial chemical reagent companies and used without further purification unless otherwise stated. Hydrazones **1**[15] and 1,3-diarylpropenes **2**[16] were prepared according to the literatures.

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General Procedure for the Synthesis of 3. To a solution of 1,3-diarylpropene **2** (0.6 mmol, 1.2 equiv) in DCE (3 mL, 0.17 M), DDQ (0.6 mmol, 0.1362 g, 1.2 equiv) was added. The mixture was stirred for 10 min, hydrazone **1** (0.5 mmol, 1.0 equiv) was added and stirred at 60 °C for 2 h in an oil bath. After completion of the reaction, the solvent was concentrated under reduced pressure. Purification was done by column chromatography on silica gel (200−300 mesh) with petroleum ether and ethyl acetate (40:1−45:1) as the eluent to give the pure product **3**.

General Procedure for the Synthesis of 4. To a solution of 1,3-diarylpropene **2** (0.6 mmol, 1.2 equiv) in DCE (3 mL, 0.17 M), DDQ (0.6 mmol, 0.1362 g, 1.2 equiv) was added. The mixture was stirred for 10 min, hydrazone **1** (0.5 mmol, 1.0 equiv) was added and stirred at 60 °C for 2 h in an oil bath. Then, I_2 (0.5 mmol, 0.1269 g, 1.0 equiv) and TBHP (0.75 mmol, 5.0 mol/L in decane, 0.15 mL, 1.5 equiv) were added and the mixture was stirred at 80 °C for another 0.5 h in the atmosphere of dioxygen. After completion of the reaction, the reaction mixture was washed with saturated solution of Na_2SO_3 and extracted with dichloromethane. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. Purification was done by column chromatography on silica gel (200−300 mesh) with petroleum ether and ethyl acetate (25:1) as the eluent to give the pure product **4**.

General Procedure for the Synthesis of 5. To a solution of 1,3-diarylpropene **2** (0.6 mmol, 1.2 equiv) in CH_3CN (3 mL, 0.17 M), DDQ (0.6 mmol, 0.1362 g, 1.2 equiv) was added. The mixture was stirred for 10 min, hydrazone **1** (0.5 mmol, 1.0 equiv) was added and stirred at 60 °C for 2 h in an oil bath. Then, TBHP (0.75 mmol, 5.0 mol/L in decane, 0.15 mL, 1.5 equiv) was added and the mixture was stirred at 80 °C for another 8 h in the atmosphere of dioxygen. After completion of the reaction, the solvent was concentrated under reduced pressure. Purification was done by column chromatography on silica gel (200−300 mesh) with petroleum ether and ethyl acetate (20:1) as the eluent to give the pure product **5**.

Procedure for the Gram Scale Synthesis of 3a. To a solution of 1,3-diphenylpropene **2a** (6.24 mmol, 1.21 g) in DCE (30.5 mL), DDQ (6.24 mmol, 1.416 g) was added. The mixture was stirred for 10 min, hydrazone **1a** (5.20 mmol, 1.00 g) was added and stirred at 60 °C for 2 h in an oil bath. After completion of the reaction, the solvent was concentrated under reduced pressure. Purification was done by column chromatography on silica gel (200−300 mesh) with petroleum ether and ethyl acetate (45:1) as the eluent to give the pure product **3a** (1.84 g, 92%).

Procedure for the Gram Scale Synthesis of 4a. To a solution of 1,3-diphenylpropene **2a** (6.24 mmol, 1.21 g) in DCE (30.5 mL), DDQ (6.24 mmol, 1.416 g) was added. The mixture was stirred for 10 min, hydrazone **1a** (5.20 mmol, 1.00 g) was added and stirred at 60 °C for 2 h in an oil bath. Then, I_2 (5.20 mmol, 1.32 g) and TBHP (7.8 mmol, 5.0 mol/L in decane, 1.56 mL) were added and the mixture was stirred at 80 °C for another 0.5 h in the atmosphere of dioxygen. After completion of the reaction, the reaction mixture was washed with saturated solution of Na_2SO_3 and extracted with dichloromethane. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. Purification was done by column chromatography on silica gel (200−300 mesh) with petroleum ether and ethyl acetate (25:1) as the eluent to give the pure product **4a** (1.19 g, 60%).

Procedure for the Gram Scale Synthesis of 5a. To a solution of 1,3-diphenylpropene **2a** (6.24 mmol, 1.21 g) in CH_3CN (30.5 mL), DDQ (6.24 mmol, 1.416 g) was added. The mixture was stirred for 10 min, hydrazone **1a** (5.20 mmol, 1.00 g) was added and stirred at 60 °C for 2 h in an oil bath. Then, TBHP (7.8 mmol, 5.0 mol/L in decane, 1.56 mL) was added and the mixture was stirred at 80 °C for another 8 h in the atmosphere of dioxygen. After completion of the reaction, the solvent was concentrated under reduced pressure. Purification was done by column chromatography on silica gel (200−300 mesh) with petroleum ether and ethyl acetate (20:1) as the eluent to give the pure product **5a** (1.07 g, 52%).

*Ethyl (2Z,4E)-3,5-Diphenyl-2-(2-phenylhydrazono)pent-4-enoate (**3a**).* Reaction time: 2 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (40:1) as the eluent. Yield: 0.1826 g (95%); colorless solid; mp 113−115 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.23 (s, 1H), 7.44−7.39 (m, 2H), 7.39−7.35 (m, 2H), 7.34−7.32 (m, 4H), 7.31 (d, J = 3.5 Hz, 2H), 7.25−7.23 (m, 1H), 7.23−7.19 (m, 3H), 6.98 (t, J = 7.3 Hz, 1H), 6.81 (dd, J = 15.8, 7.9 Hz, 1H), 6.41 (d, J = 15.8 Hz, 1H), 4.94 (d, J = 7.9 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 163.3, 143.6, 142.1, 137.6, 131.5, 130.4, 129.6, 129.3, 128.5, 128.4, 128.3, 127.2, 126.5, 126.3, 122.0, 113.8, 60.7, 51.2, 14.0. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{25}H_{25}N_2O_2$, 385.1911; found, 385.1921.

*Ethyl (2Z,4E)-3,5-Diphenyl-2-(2-(p-tolyl)hydrazono)pent-4-enoate (**3b**).* Reaction time: 2 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (40:1) as the eluent. Yield: 0.1833 g (92%); colorless solid; mp 117−118 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.22 (s, 1H), 7.42 (d, J = 7.6 Hz, 2H), 7.37 (d, J = 7.7 Hz, 2H), 7.35−7.30 (m, 4H), 7.26−7.20 (m, 2H), 7.13 (s, 4H), 6.83 (dd, J = 15.9, 8.0 Hz, 1H), 6.42 (d, J = 15.8 Hz, 1H), 4.94 (d, J = 8.0 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 2.33 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 163.3, 142.3, 141.3, 137.6, 131.6, 131.4, 130.2, 129.8, 128.9, 128.5, 128.4, 128.3, 127.1, 126.4, 126.3, 113.8, 60.6, 51.1, 20.7, 14.0. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{26}H_{27}N_2O_2$, 399.2067; found, 399.2075.

*Ethyl (2Z,4E)-2-(2-(4-Methoxyphenyl)hydrazono)-3,5-diphenylpent-4-enoate (**3c**).* Reaction time: 2 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (40:1) as the eluent. Yield: 0.1326 g (64%); colorless solid; mp 90−92 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.23 (s, 1H), 7.42−7.39 (m, 2H), 7.37−7.34 (m, 2H), 7.33−7.29 (m, 4H), 7.24−7.19 (m, 2H), 7.17−7.13 (m, 2H), 6.9−6.86 (m, 2H), 6.80 (dd, J = 15.9, 8.0 Hz, 1H), 6.41 (d, J = 15.8 Hz, 1H), 4.93 (d, J = 7.9 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.80 (s, 3H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 163.4, 155.2, 142.4, 137.7, 137.5, 131.7, 130.2, 128.5, 128.4, 128.4, 128.3, 127.1, 126.4, 126.3, 114.9, 114.8, 60.5, 55.7, 51.1, 14.0. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{26}H_{27}N_2O_3$, 415.2016; found, 415.2022.

*Ethyl (2Z,4E)-2-(2-(4-Fluorophenyl)hydrazono)-3,5-diphenylpent-4-enoate (**3d**).* Reaction time: 2 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (40:1) as the eluent. Yield: 0.0986 g (49%); colorless solid; mp 80−82 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.22 (s, 1H), 7.42−7.38 (m, 2H), 7.35−7.32 (m, 4H), 7.32−7.28 (m, 2H), 7.25−7.21 (m, 2H), 7.16−7.10 (m, 2H), 7.04−6.98 (m, 2H), 6.77 (dd, J = 15.9, 8.0 Hz, 1H), 6.40 (d, J = 15.8 Hz, 1H), 4.92 (d, J = 7.9 Hz, 1H), 4.19 (q, J = 6.9 Hz, 2H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 163.3, 158.34 (d, J = 240.0 Hz), 142.0, 139.9 (d, J = 2.4 Hz), 137.5, 131.3, 130.4, 129.6, 128.5, 128.3, 127.2, 126.5, 126.3, 116.1, 115.9, 114.8 (d, J = 7.6 Hz), 60.7, 51.1, 14.0. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{25}H_{24}FN_2O_2$, 403.1816; found, 403.1816.

*Ethyl (2Z,4E)-2-(2-(4-Chlorophenyl)hydrazono)-3,5-diphenylpent-4-enoate (**3e**).* Reaction time: 2 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (40:1) as the eluent. Yield: 0.1906 g (91%); colorless solid; mp 112−114 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.24 (s, 1H), 7.42−7.40 (m, 2H), 7.37−7.34 (m, 4H), 7.34−7.31 (m, 2H), 7.29−7.27 (m, 2H), 7.27−7.22 (m, 2H), 7.16−7.12 (m, 2H), 6.79 (dd, J = 15.9, 7.9 Hz, 1H), 6.42 (d, J = 15.8 Hz, 1H), 4.95 (d, J = 7.9 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 163.2, 142.2, 141.9, 137.5, 131.1, 130.5, 130.4, 129.3, 128.5, 128.4, 128.3, 127.2, 126.7, 126.5, 126.3, 114.9, 60.9, 51.2, 14.0. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{25}H_{23}ClN_2NaO_2$, 441.1340; found, 441.1333.

*Ethyl (2Z,4E)-2-(2-(4-Bromophenyl)hydrazono)-3,5-diphenylpent-4-enoate (**3f**).* Reaction time: 2 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (40:1) as the eluent. Yield: 0.1215 g (93%); colorless solid; mp 92−94 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.22 (s, 1H), 7.41 (d, J = 1.9 Hz, 2H), 7.40 (d, J = 1.8 Hz, 2H), 7.36−7.33 (m, 4H), 7.33−7.30 (m, 2H), 7.26−7.21 (m, 2H), 7.11−7.06 (m, 2H), 6.78 (dd, J = 15.9, 7.9 Hz, 1H), 6.41 (d, J = 15.8 Hz, 1H), 4.94 (d, J = 8.6 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz,

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$CDCl_3$): δ 163.2, 142.7, 141.8, 137.5, 132.2, 131.1, 130.6, 130.5, 128.5, 128.4, 128.3, 127.2, 126.5, 126.3, 115.4, 114.1, 60.9, 51.2, 14.0. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{25}H_{24}BrN_2O_2$, 463.1016; found, 463.1027.

*Ethyl (2Z,4E)-2-(2-(4-Nitrophenyl)hydrazono)-3,5-diphenylpent-4-enoate (**3g**).* Reaction time: 2 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (45:1) as the eluent. Yield: 0.0558 g (26%); colorless solid; mp 99−101 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.46 (s, 1H), 8.25−8.16 (m, 2H), 7.43−7.40 (m, 2H), 7.38−7.35 (m, 4H), 7.35−7.32 (m, 2H), 7.29−7.26 (m, 1H), 7.26−7.23 (m, 1H), 7.23−7.19 (m, 2H), 6.76 (dd, J = 15.9, 7.9 Hz, 1H), 6.44 (d, J = 15.8 Hz, 1H), 4.98 (d, J = 7.1 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 162.9, 148.6, 141.9, 141.0, 137.2, 134.4, 131.1, 130.2, 128.6, 128.5, 128.3, 127.4, 126.8, 126.3, 125.9, 113.1, 61.5, 51.4, 13.9. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{25}H_{24}N_3O_4$, 430.1761; found, 430.1763.

*Ethyl (2Z,4E)-2-(2-(4-Cyanophenyl)hydrazono)-3,5-diphenylpent-4-enoate (**3h**).* Reaction time: 2 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (45:1) as the eluent. Yield: 0.1617 g (79%); colorless solid; mp 140−142 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.35 (s, 1H), 7.59−7.55 (m, 2H), 7.42−7.39 (m, 2H), 7.35−7.33 (m, 4H), 7.33−7.30 (m, 2H), 7.27−7.23 (m, 2H), 7.22−7.19 (m, 2H), 6.75 (dd, J = 15.9, 7.9 Hz, 1H), 6.42 (d, J = 15.8 Hz, 1H), 4.96 (d, J = 8.9 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 1.24 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 163.0, 146.9, 141.2, 137.3, 133.70, 133.4, 130.9, 130.4, 128.6, 128.5, 128.3, 127.4, 126.8, 126.3, 119.5, 113.8, 104.1, 61.3, 51.3, 13.9. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{26}H_{24}N_3O_2$, 410.1863; found, 410.1868.

*Ethyl (2Z,4E)-3,5-Diphenyl-2-(2-(m-tolyl)hydrazono)pent-4-enoate (**3i**).* Reaction time: 2 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (40:1) as the eluent. Yield: 0.1793 g (90%); colorless solid; mp 72−74 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.21 (s, 1H), 7.46−7.43 (m, 2H), 7.40−7.37 (m, 2H), 7.37−7.32 (m, 4H), 7.26−7.20 (m, 3H), 7.09−7.02 (m, 2H), 6.84 (dd, J = 15.9, 8.0 Hz, 2H), 6.44 (d, J = 15.8 Hz, 1H), 4.96 (dd, J = 7.9, 1.1 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 2.37 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 163.3, 143.6, 142.2, 139.2, 137.7, 131.6, 130.4, 129.4, 129.2, 128.5, 128.41, 128.42, 127.2, 126.5, 126.3, 122.9, 114.6, 111.1, 60.7, 51.3, 21.6, 14.0. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{26}H_{27}N_2O_2$, 399.2067; found, 399.2067.

*Ethyl (2Z,4E)-2-(2-(3-Fluorophenyl)hydrazono)-3,5-diphenylpent-4-enoate (**3j**).* Reaction time: 2 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (40:1) as the eluent. Yield: 0.1932 g (96%); colorless solid; mp 84−86 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.27 (s, 1H), 7.48−7.43 (m, 2H), 7.41−7.33 (m, 6H), 7.30−7.25 (m, 3H), 7.06−7.01 (m, 1H), 6.92 (dd, J = 7.8, 1.6 Hz, 1H), 6.83 (dd, J = 15.9, 8.0 Hz, 1H), 6.76−6.65 (m, 1H), 6.46 (d, J = 15.8 Hz, 1H), 4.98 (d, J = 7.7 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 163.9 (d, J = 244.3 Hz), 163.2, 145.4 (d, J = 10.5 Hz), 141.8, 137.5, 131.0, 130.8, 130.6, 130.5 (d, J = 9.7 Hz), 128.5, 128.40, 128.39, 127.3, 126.6, 126.3, 109.5 (d, J = 2.7 Hz), 108.5 (d, J = 21.8 Hz), 101.0 (d, J = 26.5 Hz), 61.0, 51.3, 14.0. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{25}H_{24}FN_2O_2$, 403.1816; found, 403.1818.

*Ethyl (2Z,4E)-2-(2-(3-Chlorophenyl)hydrazono)-3,5-diphenylpent-4-enoate (**3k**).* Reaction time: 2 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (40:1) as the eluent. Yield: 0.1969 g (94%); colorless solid; mp 105−107 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.23 (s, 1H), 7.49−7.43 (m, 2H), 7.40−7.37 (m, 4H), 7.37−7.34 (m, 2H), 7.31−7.23 (m, 4H), 7.08−7.02 (m, 1H), 7.00−6.94 (m, 1H), 6.82 (dd, J = 15.9, 8.0 Hz, 1H), 6.46 (d, J = 15.8 Hz, 1H), 4.97 (d, J = 8.0 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 163.1, 144.8, 141.7, 137.5, 135.2, 131.0, 130.9, 130.6, 130.3, 128.5, 128.4, 128.3, 127.2, 126.6, 126.3, 121.8, 113.9, 112.0, 60.9, 51.3, 14.0. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{25}H_{24}ClN_2O_2$, 419.1521; found, 419.1528.

*Ethyl (2Z,4E)-2-(2-(3-Bromophenyl)hydrazono)-3,5-diphenylpent-4-enoate (**3l**).* Reaction time: 2 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (40:1) as the eluent. Yield: 0.2173 g (94%); colorless solid; mp 117−118 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.19 (s, 1H), 7.45−7.41 (m, 3H), 7.37−7.34 (m, 4H), 7.34−7.31 (m, 2H), 7.26−7.21 (m, 2H), 7.16 (t, J = 7.9 Hz, 1H), 7.11−7.05 (m, 2H), 6.79 (dd, J = 15.9, 8.0 Hz, 1H), 6.43 (d, J = 15.8 Hz, 1H), 4.94 (d, J = 8.0 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 1.23 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 163.2, 144.9, 141.8, 137.5, 131.0, 130.6, 128.6, 128.4, 128.4, 127.3, 126.6, 126.4, 124.7, 123.3, 116.8, 112.5, 61.0, 51.3, 14.0. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{25}H_{24}BrN_2O_2$, 463.1015; found, 463.1011.

*Ethyl (2Z,4E)-3,5-Diphenyl-2-(2-(o-tolyl)hydrazono)pent-4-enoate (**3m**).* Reaction time: 2 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (40:1) as the eluent. Yield: 0.1514 g (76%); colorless solid; mp 76−78 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.35 (s, 1H), 7.64 (d, J = 8.1 Hz, 1H), 7.44 (d, J = 7.7 Hz, 2H), 7.41 (d, J = 7.7 Hz, 2H), 7.38−7.30 (m, 5H), 7.26−7.22 (m, 2H), 7.16 (d, J = 7.5 Hz, 1H), 6.94 (t, J = 7.4 Hz, 1H), 6.87 (dd, J = 15.9, 8.0 Hz, 1H), 6.45 (d, J = 15.8 Hz, 1H), 5.00 (d, J = 7.9 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 2.34 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 163.4, 142.2, 141.6, 137.6, 131.5, 130.5, 130.4, 130.3, 128.5, 128.4, 128.3, 127.2, 127.1, 126.4, 126.3, 122.1, 121.6, 112.9, 60.7, 51.2, 17.0, 14.0. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{26}H_{27}N_2O_2$, 399.2067; found, 399.2064.

*Ethyl (2Z,4E)-2-(2-(3,4-Dimethylphenyl)hydrazono)-3,5-diphenylpent-4-enoate (**3n**).* Reaction time: 2 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (40:1) as the eluent. Yield: 0.1939 g (94%); colorless solid; mp 88−89 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.17 (s, 1H), 7.45−7.42 (m, 2H), 7.40−7.36 (m, 2H), 7.35−7.31 (m, 4H), 7.26−7.21 (m, 2H), 7.09 (d, J = 8.1 Hz, 1H), 7.04 (d, J = 2.3 Hz, 1H), 6.97 (dd, J = 8.2, 2.3 Hz, 1H), 6.84 (dd, J = 15.9, 8.0 Hz, 1H), 6.43 (d, J = 15.9 Hz, 1H), 4.95 (d, J = 7.9 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 2.27 (s, 3H), 2.24 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 163.3, 142.3, 141.6, 137.7, 137.5, 131.8, 130.3, 130.2, 130.1, 128.6, 128.5, 128.4, 128.3, 127.1, 126.4, 126.3, 115.3, 111.3, 60.5, 51.1, 20.1, 19.0, 14.0. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{27}H_{28}N_2NaO_2$, 435.2043; found, 435.2039.

*Ethyl (2Z,4E)-2-(2-(3,5-Dimethylphenyl)hydrazono)-3,5-diphenylpent-4-enoate (**3o**).* Reaction time: 2 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (40:1) as the eluent. Yield: 0.1856 g (90%); colorless solid; mp 118−120 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.14 (s, 1H), 7.47−7.43 (m, 2H), 7.40−7.36 (m, 2H), 7.35−7.31 (m, 4H), 7.26−7.21 (m, 2H), 6.87 (s, 2H), 6.86−6.80 (m, 1H), 6.66 (s, 1H), 6.43 (d, J = 15.9 Hz, 1H), 4.95 (d, J = 7.9 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 2.32 (s, 6H), 1.24 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 163.2, 143.6, 142.2, 139.0, 137.7, 131.7, 130.2, 129.1, 128.4, 128.4, 128.3, 127.1, 126.4, 126.3, 123.9, 111.8, 60.6, 51.2, 21.5, 14.0. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{27}H_{29}N_2O_2$, 413.2224; found, 413.2229.

*Ethyl (2Z,4E)-2-(2-Isopropylhydrazono)-3,5-diphenylpent-4-enoate (**3p**).* Reaction time: 2 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (40:1) as the eluent. Yield: 0.1472 g (84%); brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.18 (s, 1H), 7.40−7.38 (m, 2H), 7.33−7.31 (m, 4H), 7.31−7.28 (m, 2H), 7.23−7.19 (m, 2H), 6.76 (dd, J = 15.9, 8.1 Hz, 1H), 6.38 (d, J = 15.9 Hz, 1H), 4.82 (d, J = 8.5 Hz, 1H), 4.12 (q, J = 7.3 Hz, 2H), 3.75−3.69 (m, 1H), 1.28 (s, 3H), 1.27 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 163.1, 143.3, 137.9, 132.4, 129.6, 128.4, 128.14, 128.11, 126.9, 126.2, 126.1, 59.8, 51.4, 50.9, 22.1, 22.1, 14.0. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{22}H_{26}N_2NaO_2$, 373.1886; found, 373.1894.

*Ethyl (2Z,4E)-2-(2-(tert-Butyl)hydrazono)-3,5-diphenylpent-4-enoate (**3q**).* Reaction time: 2 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (40:1) as the eluent. Yield: 0.1531 g (84%); brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.21 (s, 1H), 7.40−7.38 (m, 2H), 7.33 (s, 1H), 7.33−7.32 (m, 2H) 7.31 (d, J = 1.8 Hz, 2H), 7.30 (d, J = 1.6 Hz, 1H),

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7.23−7.20 (m, 2H), 6.77 (dd, J = 15.9, 8.0 Hz, 1H), 6.37 (d, J = 15.8 Hz, 1H), 4.84 (d, J = 8.0 Hz, 1H), 4.16−4.12 (m, 2H), 1.33 (s, 9H), 1.22 (d, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 163.1, 143.3, 137.9, 132.7, 129.4, 128.4, 128.3, 128.1, 126.9, 126.2, 126.1, 125.6, 59.8, 54.7, 50.8, 28.8, 14.1. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{23}H_{29}N_2O_2$, 365.2152; found, 365.2151.

(2Z,4E)-1,3,5-Triphenyl-2-(2-phenylhydrazono)pent-4-en-one (**3r**). Reaction time: 2 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (40:1) as the eluent. Yield: 0.1645 g (79%); colorless solid; mp 104−106 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 8.52 (s, 1H), 8.07−8.02 (m, 2H), 7.60−7.56 (m, 1H), 7.52−7.48 (m, 2H), 7.48−7.45 (m, 3H), 7.45−7.41 (m, 3H), 7.36−7.32 (m, 3H), 7.30−7.27 (m, 1H), 7.22−7.18 (m, 2H), 6.93 (t, J = 7.4 Hz, 1H), 6.81 (d, J = 7.8 Hz, 2H), 6.79−6.74 (m, 1H), 6.65 (d, J = 16.1 Hz, 1H), 5.87 (d, J = 6.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 191.6, 142.7, 141.8, 138.5, 136.6, 133.9, 131.5, 130.7, 129.4, 129.3, 128.6, 127.9, 127.6, 127.5, 127.5, 126.5, 124.6, 122.4, 113.9, 44.3. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{29}H_{25}N_2O$, 417.1961; found, 417.1969.

Ethyl (2Z,4E)-2-(2-Phenylhydrazono)-3,5-di-p-tolylpent-4-enoate (**3s**). Reaction time: 2 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (40:1) as the eluent. Yield: 0.1815 g (88%); colorless solid; mp 117−119 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 12.27 (s, 1H), 7.40−7.33 (m, 4H), 7.32−7.25 (m, 4H), 7.22−7.13 (m, 4H), 7.06−6.99 (m, 1H), 6.80 (dd, J = 15.8, 7.9 Hz, 1H), 6.43 (d, J = 15.8 Hz, 1H), 4.95 (d, J = 7.6 Hz, 1H), 4.30−4.20 (m, 2H), 2.39 (s, 6H), 1.30 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 163.3, 143.6, 139.2, 136.8, 135.9, 134.9, 130.6, 130.0, 129.9, 129.3, 129.1, 129.0, 128.2, 126.2, 121.8, 113.8, 60.6, 50.7, 21.1, 21.0, 14.0. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{27}H_{28}N_2NaO_2$, 435.2043; found, 435.2041.

Ethyl (2Z,4E)-3,5-Bis(4-methoxyphenyl)-2-(2-phenylhydrazono)-pent-4-enoate (**3t**). Reaction time: 2 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (40:1) as the eluent. Yield: 0.1445 g (65%); colorless solid; mp 113−115 °C. ^1H NMR (600 MHz, $CDCl_3$): δ 12.21 (s, 1H), 7.38−7.34 (m, 2H), 7.34−7.30 (m, 2H), 7.30−7.27 (m, 2H), 7.24−7.20 (m, 2H), 6.99−6.97 (m, 1H), 6.90−6.86 (m, 4H), 6.66 (dd, J = 15.8, 7.8 Hz, 1H), 6.35 (d, J = 15.8 Hz, 1H), 4.89 (d, J = 7.8 Hz, 1H), 4.24−4.19 (m, 2H), 3.82, 3.81 (ss, 6H), 1.27 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 163.4, 158.9, 158.2, 143.7, 134.4, 130.5, 130.1, 129.7, 129.5, 129.4, 129.4, 127.4, 121.9, 113.9, 113.82, 113.76, 60.7, 55.3, 55.3, 50.3, 14.1. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{27}H_{29}N_2O_4$, 445.2050; found, 445.2051.

Ethyl (2Z,4E)-3,5-Bis(4-chlorophenyl)-2-(2-phenylhydrazono)-pent-4-enoate (**3u**). Reaction time: 2 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (40:1) as the eluent. Yield: 0.1836 g (81%); colorless solid; mp 124−125 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 12.23 (s, 1H), 7.33−7.30 (m, 4H), 7.30−7.28 (m, 3H), 7.28−7.26 (m, 3H), 7.20−7.16 (m, 2H), 7.01−6.97 (m, 1H), 6.72 (dd, J = 15.9, 7.7 Hz, 1H), 6.31 (d, J = 15.8 Hz, 1H), 4.89 (d, J = 7.6 Hz, 1H), 4.20 (q, J = 7.4 Hz, 2H), 1.24 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 163.0, 143.3, 140.4, 135.9, 132.9, 132.4, 131.6, 129.7, 129.5, 129.4, 128.8, 128.7, 128.5, 127.5, 122.3, 113.9, 60.9, 50.4, 14.0. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{25}H_{22}Cl_2N_2NaO_2$, 475.0951; found, 475.0953.

Ethyl (2Z,4E)-3,5-Bis(4-bromophenyl)-2-(2-phenylhydrazono)-pent-4-enoate (**3v**). Reaction time: 2 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (40:1) as the eluent. Yield: 0.2305 g (85%); colorless solid; mp 139−141 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 12.25 (s, 1H), 7.48−7.42 (m, 4H), 7.35−7.30 (m, 2H), 7.26 (d, J = 8.4 Hz, 2H), 7.24−7.21 (m, 2H), 7.21−7.17 (m, 2H), 7.02−6.98 (m, 1H), 6.74 (dd, J = 15.9, 7.7 Hz, 1H), 6.30 (d, J = 15.9 Hz, 1H), 4.89 (d, J = 7.6 Hz, 1H), 4.24−4.18 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 163.0, 143.3, 140.9, 136.3, 131.7, 131.6, 131.5, 130.1, 129.6, 129.4, 128.7, 127.8, 122.3, 121.0, 120.5, 113.8, 60.8, 50.4, 14.0. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{25}H_{22}Br_2N_2NaO_2$, 562.9940; found, 562.9937.

Ethyl (2Z,4E)-2-(2-Phenylhydrazono)-3,5-di-m-tolylpent-4-enoate (**3w**). Reaction time: 2 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (40:1) as the eluent. Yield: 0.1877 g (91%); colorless solid; mp 105−107 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 12.27 (s, 1H), 7.38−7.33 (m, 2H), 7.27−7.26 (m, 3H), 7.26−7.24 (m, 3H), 7.21−7.18 (m, 2H), 7.11−7.05 (m, 2H), 7.03−7.00 (m, 1H), 6.83 (dd, J = 15.8, 8.0 Hz, 1H), 6.42 (d, J = 15.8 Hz, 1H), 4.94 (d, J = 7.6 Hz, 1H), 4.27−4.21 (m, 2H), 2.39 (s, 6H), 1.28 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 163.3, 143.6, 142.1, 138.0, 137.8, 137.6, 131.4, 130.3, 129.7, 129.3, 129.1, 128.4, 128.2, 127.9, 127.2, 127.1, 125.5, 123.4, 121.9, 113.8, 60.7, 51.1, 21.5, 21.4, 14.0. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{27}H_{29}N_2O_2$, 413.2224; found, 413.2220.

Ethyl (2Z,4E)-2-(2-Phenylhydrazono)-3,5-di-o-tolylpent-4-enoate (**3x**). Reaction time: 2 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (40:1) as the eluent. Yield: 0.1898 g (92%); colorless solid; mp 113−115 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 12.27 (s, 1H), 7.54 (dd, J = 7.5, 1.3 Hz, 1H), 7.35−7.32 (m, 2H), 7.32−7.30 (m, 1H), 7.25−7.22 (m, 2H), 7.22−7.18 (m, 3H), 7.17−7.16 (m, 1H), 7.16−7.14 (m, 2H), 7.01−6.97 (m, 1H), 6.59−6.49 (m, 2H), 5.20 (d, J = 6.9 Hz, 1H), 4.21−4.14 (m, 2H), 2.50 (s, 3H), 2.30 (s, 3H), 1.21 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 163.3, 143.7, 140.2, 136.9, 135.9, 135.2, 132.4, 130.4, 130.1, 129.9, 129.4, 127.8, 127.7, 127.1, 126.4, 126.1, 125.9, 121.9, 113.8, 60.7, 47.1, 19.8, 19.6, 13.9. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{27}H_{29}N_2O_2$, 413.2224; found, 413.2218.

A 50:50 mixture of ethyl (2*Z*,4*E*)-3-phenyl-2-(2-phenylhydrazono)-5-(*p*-tolyl)pent-4-enoate (**3y**) and ethyl (2*Z*,4*E*)-5-phenyl-2-(2-phenylhydrazono)-3-(*p*-tolyl)pent-4-enoate (**3y′**) was used. Reaction time: 2 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (40:1) as the eluent. Yield: 0.1893 g (95%); colorless oil. ^1H NMR (500 MHz, $CDCl_3$): δ 12.26 (s, 50/100 × 1H), 12.25 (s, 50/100 × 1H), 7.46−7.42 (m, 1H), 7.40−7.37 (m, 1H), 7.37−7.32 (m, 5H), 7.29−7.23 (m, 4H), 7.17−7.14 (m, 2H), 7.02−6.98 (m, 2H), 6.84 (dd, J = 15.9, 8.0 Hz, 50/100 × 1H), 6.79 (dd, J = 15.9, 8.0 Hz, 50/100 × 1H), 6.44 (d, J = 15.9 Hz, 50/100 × 1H), 6.41 (d, J = 15.9 Hz, 50/100 × 1H), 5.01−4.88 (m, 1H), 4.28−4.18 (m, 2H), 2.37 (s, 3H), 1.28 (t, J = 6.4 Hz, 50/100 × 3H), 1.26 (t, J = 6.4 Hz, 50/100 × 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 163.3, 163.2, 143.6, 143.59, 142.3, 142.2, 139.1, 137.7, 136.9, 136.0, 134.8, 131.7, 130.4, 130.3, 130.1, 129.81, 129.80, 129.4, 129.2, 129.1, 128.5, 128.4, 128.34, 128.28, 127.3, 127.1, 126.4, 126.3, 126.2, 122.0, 121.9, 113.8, 60.72, 60.69, 51.2, 50.7, 21.2, 21.1, 14.1, 14.0. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{26}H_{27}N_2O_2$, 399.2067; found, 399.2067.

A mixture of 45:55 or 55:45 of ethyl (2*Z*,4*E*)-5-(4-chlorophenyl)-3-phenyl-2-(2-phenylhydrazono)pent-4-enoate (**3z**) and ethyl (2*Z*,4*E*)-3-(4-chlorophenyl)-5-phenyl-2-(2-phenylhydrazono)pent-4-enoate (**3z′**) was used. Reaction time: 2 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (40:1) as eluent. Yield: 0.1927 g (92%); colorless oil. ^1H NMR (500 MHz, $CDCl_3$): δ 12.27 (s, 45/100 × 1H), 12.26 (s, 55/100 × 1H), 7.44−7.42 (m, 1H), 7.38−7.36 (m, 2H), 7.36−7.33 (m, 3H), 7.33−7.31 (m, 3H), 7.31−7.27 (m, 2H), 7.25−7.23 (m, 2H), 7.04−6.99 (m, 1H), 6.81 (dd, J = 15.9, 7.9 Hz, 45/100 × 1H), 6.77 (dd, J = 15.9, 8.0 Hz, 55/100 × 1H), 6.41 (d, J = 15.9 Hz, 45/100 × 1H), 6.37 (d, J = 15.9 Hz, 55/100 × 1H), 4.98−4.92 (m, 1H), 4.26−4.19 (m, 1H), 1.27 (t, J = 6.4 Hz, 45/100 × 1H), 1.25 (t, J = 6.4 Hz, 55/100 × 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 163.2, 163.1, 143.5, 143.4, 141.9, 140.7, 137.4, 136.1, 132.7, 132.3, 130.9, 130.8, 129.8, 129.45, 129.41, 129.40, 129.13, 129.06, 128.7, 128.6, 128.5, 128.4, 128.39, 127.5, 127.4, 126.6, 126.3, 122.2, 122.1, 113.89, 113.86, 60.84, 60.76, 51.1, 50.5, 14.1, 14.0. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{25}H_{24}ClN_2O_2$, 419.1521; found, 419.1521.

Ethyl 1,4,6-Triphenyl-1,2-dihydropyridazine-3-carboxylate (**4a**). Reaction time: 0.5 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (25:1) as the eluent. Yield: 0.1377 g (72%); colorless solid; mp 106−108 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.81−7.78 (m, 2H), 7.55−7.52 (m, 2H), 7.42−7.35 (m, 5H), 7.33−7.30 (m, 1H), 7.22−7.17 (m, 2H), 6.93−6.88 (m, 1H), 6.56−6.52 (m, 2H), 6.50 (s, 1H), 4.07 (q, J =

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7.4 Hz, 2H), 1.02 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 161.4, 148.6, 139.4, 135.7, 133.3, 130.5, 129.6, 129.2, 128.5, 128.3, 128.1, 127.6, 127.1, 121.7, 118.2, 113.7, 108.6, 60.3, 13.7. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{25}H_{23}N_2O_2$, 383.1754; found, 383.1748.

*Ethyl 4,6-Diphenyl-1-(p-tolyl)-1,2-dihydropyridazine-3-carboxylate (**4b**).* Reaction time: 0.5 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (25:1) as the eluent. Yield: 0.1051 g (53%); colorless solid; mp 110−112 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.80−7.76 (m, 2H), 7.53−7.49 (m, 2H), 7.42−7.33 (m, 5H), 7.33−7.30 (m, 1H), 6.98 (d, J = 8.1 Hz, 2H), 6.47 (s, 1H), 6.43 (d, J = 8.4 Hz, 2H), 4.06 (q, J = 7.2 Hz, 2H), 2.23 (s, 3H), 1.01 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 161.4, 146.3, 139.3, 135.8, 133.2, 131.0, 130.5, 129.7, 129.6, 128.4, 128.3, 128.1, 127.6, 127.0, 113.8, 108.5, 77.3, 60.2, 20.6, 13.7. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{26}H_{25}N_2O_2$, 397.1911; found, 397.1920.

*Ethyl 1-(4-Fluorophenyl)-4,6-diphenyl-1,2-dihydropyridazine-3-carboxylate (**4c**).* Reaction time: 0.5 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (25:1) as the eluent. Yield: 0.1261 g (63%); colorless solid; mp 125−127 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.78−7.72 (m, 2H), 7.51−7.46 (m, 2H), 7.40−7.36 (m, 3H), 7.36−7.30 (m, 3H), 6.89−6.83 (m, 2H), 6.48−6.42 (m, 3H), 4.06 (q, J = 7.1 Hz, 2H), 1.00 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 161.5, 158.2 (d, J = 239.3 Hz), 144.6 (d, J = 2.3 Hz), 139.2, 135.7, 133.4, 130.4, 129.5, 128.4, 128.4, 128.2, 127.6, 127.1, 117.9, 115.8 (d, J = 22.8 Hz), 115.1 (d, J = 7.8 Hz), 108.7, 60.3, 13.7. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{25}H_{22}FN_2O_2$, 401.1660; found, 401.1658.

*Ethyl 1-(4-Chlorophenyl)-4,6-diphenyl-1,2-dihydropyridazine-3-carboxylate (**4d**).* Reaction time: 0.5 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (25:1) as the eluent. Yield: 0.1376 g (66%); colorless solid; mp 134−136 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.82−7.75 (m, 2H), 7.58−7.52 (m, 2H), 7.46−7.32 (m, 6H), 7.20−7.12 (m, 2H), 6.53 (s, 1H), 6.47 (d, J = 8.8 Hz, 2H), 4.11 (br, 2H), 1.05 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$): δ 161.4, 147.3, 139.4, 135.6, 133.6, 130.3, 129.6, 129.3, 128.5, 128.3, 127.7, 127.3, 126.7, 118.0, 115.0, 108.8, 60.4, 13.7. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{25}H_{22}ClN_2O_2$, 417.1364; found, 417.1366.

*Ethyl 1-(4-Bromophenyl)-4,6-diphenyl-1,2-dihydropyridazine-3-carboxylate (**4e**).* Reaction time: 0.5 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (25:1) as the eluent. Yield: 0.1546 g (67%); colorless solid; mp 127−129 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.71−7.65 (m, 2H), 7.46−7.41 (m, 2H), 7.34−7.27 (m, 5H), 7.23−7.20 (m, 3H), 6.41 (s, 1H), 6.33 (d, J = 8.7, 2H), 4.01 (q, J = 7.3 Hz, 2H), 0.96 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 161.4, 147.7, 139.3 135.6, 133.5, 132.1, 130.2, 129.6, 128.4, 128.3, 127.6, 127.2, 117.9, 115.5, 114.0, 108.7, 77.2, 60.3, 13.7. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{25}H_{22}BrN_2O_2$, 461.0859; found, 461.0864.

*Ethyl 4,6-Diphenyl-1-(m-tolyl)-1,2-dihydropyridazine-3-carboxylate (**4f**).* Reaction time: 0.5 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (25:1) as the eluent. Yield: 0.0852 g (43%); colorless solid; mp 117−119 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.96 (s, 1H), 7.82−7.74 (m, 2H), 7.53−7.47 (m, 2H), 7.39 (dd, J = 7.0, 1.7 Hz, 2H), 7.37−7.29 (m, 4H), 6.98 (d, J = 8.0 Hz, 2H), 6.47 (s, 1H), 6.43 (d, J = 8.4 Hz, 2H), 4.06 (q, J = 6.8 Hz, 2H), 2.23 (s, 3H), 1.01 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 161.4, 146.3, 139.3, 135.9, 133.2, 131.0, 130.6, 129.7, 129.6, 128.4, 128.3, 128.0, 127.6, 127.0, 118.1, 113.8, 108.5, 77.2, 60.2, 20.6, 13.7. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{26}H_{25}N_2O_2$, 397.1911; found, 397.1919.

*Ethyl 1-(3-Fluorophenyl)-4,6-diphenyl-1,2-dihydropyridazine-3-carboxylate (**4g**).* Reaction time: 0.5 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (25:1) as the eluent. Yield: 0.1161 g (58%); colorless solid; mp 105−107 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.80−7.70 (m, 2H), 7.54−7.47 (m, 2H), 7.42−7.29 (m, 6H), 7.15−7.06 (m, 1H), 6.61−6.51 (m, 1H), 6.47 (s, 1H), 6.36−6.28 (m, 1H), 6.21−6.12 (m, 1H), 4.06 (q, J = 6.8 Hz, 2H), 1.01 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 163.7 (d, J = 244.8 Hz), 161.3, 150.5 (d, J = 9.7 Hz), 139.3, 135.6, 133.5, 130.4 (d, J = 9.6 Hz), 130.2, 129.6, 128.38, 128.40, 128.2, 127.6, 127.2, 118.0, 109.4 (d, J = 2.8 Hz), 108.8, 108.5 (d, J = 21.5 Hz), 101.2 (d, J = 25.9 Hz), 60.3, 13.7. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{25}H_{22}FN_2O_2$, 401.1660; found, 401.1654.

*Ethyl 1-(3-Chlorophenyl)-4,6-diphenyl-1,2-dihydropyridazine-3-carboxylate (**4h**).* Reaction time: 0.5 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (25:1) as the eluent. Yield: 0.1334 g (64%); colorless solid; mp 110−112 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.76−7.71 (m, 2H), 7.54−7.49 (m, 2H), 7.42−7.37 (m, 3H), 7.37−7.31 (m, 3H), 7.08 (t, J = 8.1 Hz, 1H), 6.88−6.82 (m, 1H), 6.52 (s, 1H), 6.48 (s, 1H), 6.36 (dd, J = 8.1, 1.6 Hz, 1H), 4.08 (br s, 2H), 1.02 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 161.3, 149.8, 139.3, 135.6, 135.0, 133.5, 130.3, 130.2, 129.6, 128.4, 128.4, 128.3, 127.6, 127.2, 121.9, 117.9, 114.0, 111.9, 108.9, 60.3, 13.7. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{25}H_{21}ClNaN_2O_2$, 439.1184; found, 439.1194.

*Ethyl 1-(3-Bromophenyl)-4,6-diphenyl-1,2-dihydropyridazine-3-carboxylate (**4i**).* Reaction time: 0.5 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (25:1) as the eluent. Yield: 0.1661 g (72%); colorless solid; mp 144−146 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.80−7.69 (m, 2H), 7.59−7.48 (m, 2H), 7.43−7.38 (m, 3H), 7.38−7.34 (m, 2H), 7.34−7.31 (m, 1H), 7.07−6.98 (m, 2H), 6.73−6.70 (m, 1H), 6.49 (s, 1H), 6.43−6.34 (m, 1H), 4.09 (br s, 2H), 1.03 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 161.3, 149.9, 139.3, 135.6, 133.6, 130.6, 130.2, 129.6, 128.4, 128.3, 127.7, 127.6, 127.2, 124.8, 123.1, 117.9, 116.9, 112.3, 108.9, 60.4, 13.7. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{25}H_{22}BrN_2O_2$, 461.0859; found, 461.0867.

*Ethyl 1-(3,4-Dimethylphenyl)-4,6-diphenyl-1,2-dihydropyridazine-3-carboxylate (**4j**).* Reaction time: 0.5 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (25:1) as the eluent. Yield: 0.1334 g (65%); colorless solid; mp 110−112 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.94 (s, 1H), 7.80−7.75 (m, 2H), 7.52−7.49 (m, 2H), 7.40−7.29 (m, 6H), 6.91 (d, J = 8.1 Hz, 1H), 6.47 (s, 1H), 6.41 (d, J = 2.0 Hz, 1H), 6.20 (dd, J = 8.1, 2.6 Hz, 1H), 4.07 (q, J = 7.2 Hz, 2H), 2.16 (s, 3H), 2.14 (s, 3H), 1.02 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 161.4, 146.6, 139.3, 137.3, 135.9, 133.1, 130.7, 130.2, 129.8, 129.6, 128.4, 128.3, 128.0, 127.5, 127.0, 115.4, 111.0, 108.5, 77.2, 60.2, 20.0, 18.9, 13.7. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{27}H_{27}N_2O_2$, 411.2067; found, 411.2068.

*Ethyl 1-(3,5-Dimethylphenyl)-4,6-diphenyl-1,2-dihydropyridazine-3-carboxylate (**4k**).* Reaction time: 0.5 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (25:1) as the eluent. Yield: 0.1273 g (62%); colorless solid; mp 127−129 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.88 (s, 1H), 7.78−7.72 (m, 2H), 7.53−7.48 (m, 2H), 7.41−7.32 (m, 5H), 7.31−7.28 (m, 1H), 6.52 (s, 1H), 6.46 (s, 1H), 6.13 (s, 2H), 4.07 (q, J = 7.1 Hz, 2H), 2.19 (s, 6H), 1.01 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 161.4, 148.6, 139.3, 138.8, 135.9, 133.1, 130.6, 129.6, 128.4, 128.3, 128.0, 127.6, 127.0, 123.6, 111.6, 108.5, 60.2, 29.7, 21.4, 13.7. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{27}H_{27}N_2O_2$, 411.2067; found, 411.2069.

*Ethyl 1-Phenyl-4,6-di-p-tolyl-1,2-dihydropyridazine-3-carboxylate (**4l**).* Reaction time: 0.5 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (25:1) as the eluent. Yield: 0.1478 g (72%); colorless solid; mp 158−160 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (s, 1H), 7.70−7.61 (m, 2H), 7.45−7.36 (m, 2H), 7.24−7.13 (m, 6H), 6.93−6.83 (m, 1H), 6.54−6.46 (m, 2H), 6.42 (s, 1H), 4.06 (br s, 2H), 2.40 (s, 3H), 2.34 (s, 3H), 1.03 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 161.4, 148.7, 139.6, 138.0, 136.8, 133.4, 132.8, 129.5, 129.2, 129.1, 128.4, 128.4, 127.7, 121.6, 117.8, 113.7, 108.3, 60.2, 21.31, 21.30, 13.8. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{27}H_{27}N_2O_2$, 411.2067; found, 411.2074.

*Ethyl 4,6-Bis(4-chlorophenyl)-1-phenyl-1,2-dihydropyridazine-3-carboxylate (**4m**).* Reaction time: 0.5 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether

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and EtOAc (25:1) as the eluent. Yield: 0.1512 g (67%); colorless solid; mp 156−158 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.74−7.65 (m, 2H), 7.43−7.38 (m, 2H), 7.36−7.30 (m, 4H), 7.19−7.14 (m, 2H), 6.92−6.87 (m, 1H), 6.49−6.43 (m, 2H), 6.41 (s, 1H), 4.05 (q, J = 6.7 Hz, 2H), 1.01 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 161.1, 148.2, 138.2, 134.2, 134.0, 133.2, 131.9, 130.9, 129.6, 129.3, 128.7, 128.6, 127.8, 122.0, 113.7, 108.4, 77.2, 60.4, 13.7. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{25}H_{21}Cl_2N_2O_2$, 451.0975; found, 451.0967.

*Ethyl 4,6-Bis(4-bromophenyl)-1-phenyl-1,2-dihydropyridazine-3-carboxylate (**4n**).* Reaction time: 0.5 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (25:1) as the eluent. Yield: 0.1891 g (70%); colorless solid; mp 153−154 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.67−7.60 (m, 2H), 7.52−7.45 (m, 4H), 7.38−7.32 (m, 2H), 7.20−7.14 (m, 2H), 6.91−6.98 (m, 1H), 6.49−6.44 (m, 2H), 6.42 (s, 1H), 4.06 (q, J = 7.1 Hz, 2H), 1.02 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 161.0, 148.2, 138.2, 134.5, 131.9, 131.6, 131.2, 130.7, 129.9, 129.3, 129.2, 122.5, 122.1, 121.3, 113.6, 108.4, 77.2, 60.4, 13.8. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{25}H_{21}Br_2N_2O_2$, 538.9964; found, 538.9932.

*Ethyl 1-Phenyl-4,6-di-m-tolyl-1,2-dihydropyridazine-3-carboxylate (**4o**).* Reaction time: 0.5 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (25:1) as the eluent. Yield: 0.1232 g (60%); colorless solid; mp 142−144 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.64−7.59 (m, 2H), 7.37−7.32 (m, 2H), 7.31−7.27 (m, 2H), 7.23−7.13 (m, 4H), 6.92−6.89 (m, 1H), 6.57−6.51 (m, 2H), 6.49 (s, 1H), 4.09 (q, J = 7.1 Hz, 2H), 2.44 (s, 3H), 2.39 (s, 3H), 1.05 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 161.5, 148.7, 139.6, 137.8, 137.0, 135.6, 133.4, 130.4, 130.3, 129.2, 129.2, 128.9, 128.2, 127.8, 127.6, 126.7, 125.6, 121.7, 118.1, 113.7, 108.6, 60.2, 21.6, 21.5, 13.7. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{27}H_{27}N_2O_2$, 411.2067; found, 411.2064.

*Ethyl 1-Phenyl-4,6-di-o-tolyl-1,2-dihydropyridazine-3-carboxylate (**4p**).* Reaction time: 0.5 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (25:1) as the eluent. Yield: 0.1293 g (63%); colorless solid; mp 139−141 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (s, 1H), 7.46 (d, J = 7.3 Hz, 1H), 7.31 (d, J = 7.0 Hz, 1H), 7.30−7.24 (m, 5H), 7.22−7.16 (m, 3H), 6.93−6.86 (m, 1H), 6.50−6.44 (m, 2H), 6.20 (s, 1H), 3.97 (q, J = 7.1 Hz, 2H), 2.47 (s, 3H), 2.31 (s, 3H), 0.87 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 161.2, 149.1, 139.7, 137.6, 136.6, 136.4, 132.6, 131.0, 130.4, 130.2, 129.9, 129.3, 129.0, 128.6, 127.2, 125.4, 124.9, 121.5, 118.0, 113.2, 109.7, 59.8, 20.6, 20.3, 13.5. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{27}H_{27}N_2O_2$, 411.2067; found, 411.2063.

*Ethyl 4,6-Bis(4-fluorophenyl)-1-phenyl-1,2-dihydropyridazine-3-carboxylate (**4q**).* Reaction time: 0.5 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (25:1) as the eluent. Yield: 0.1380 g (66%); colorless solid; mp 144−146 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (s, 1H), 7.78−7.66 (m, 2H), 7.51−7.38 (m, 2H), 7.21−7.14 (m, 2H), 7.12−6.98 (m, 4H), 6.93−6.86 (m, 1H), 6.47 (d, J = 7.7 Hz, 2H), 6.38 (s, 1H), 4.04 (q, J = 7.1 Hz, 2H), 1.01 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 162.6 (d, J = 249.4 Hz), 162.2 (d, J = 246.8 Hz), 161.18, 148.3, 138.5, 132.3, 131.6 (d, J = 3.4 Hz), 131.2 (d, J = 8.0 Hz), 130.3 (d, J = 8.1 Hz), 129.3, 126.4 (d, J = 3.4 Hz), 121.9, 117.9, 115.4 (d, J = 21.6 Hz), 114.5 (d, J = 21.4 Hz), 113.6, 108.4, 60.4, 13.7. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{25}H_{20}F_2N_2NaO_2$, 441.1385; found, 441.1385.

*Ethyl 5-Benzoyl-1,4-diphenyl-1H-pyrazole-3-carboxylate (**5a**).* Reaction time: 8 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (20:1) as the eluent. Yield: 0.1209 g (61%); colorless solid; mp 115−117 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.66−7.58 (m, 2H), 7.47−7.45 (m, 2H), 7.39 (t, J = 7.4 Hz, 1H), 7.37−7.29 (m, 5H), 7.24−7.16 (m, 5H), 4.36 (q, J = 7.1 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 187.9, 161.9, 141.3, 139.7, 139.2, 136.1, 134.0, 130.3, 130.1, 129.7, 129.2, 128.8, 128.4, 127.8, 127.69, 127.71, 124.6, 61.2, 14.1. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{25}H_{21}N_2O_3$, 397.1538; found, 397.1542.

*Ethyl 5-Benzoyl-4-phenyl-1-(p-tolyl)-1H-pyrazole-3-carboxylate (**5b**).* Reaction time: 8 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (20:1) as the eluent. Yield: 0.1314 g (64%); colorless solid; mp 124−126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65−7.60 (m, 2H), 7.41−7.37 (m, 1H), 7.35−7.32 (m, 2H), 7.31−7.28 (m, 2H), 7.25−7.16 (m, 5H), 7.13 (d, J = 8.1 Hz, 2H), 4.35 (q, J = 7.1 Hz, 2H), 2.31 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 188.0, 162.0, 141.0, 139.6, 138.9, 136.8, 136.1, 134.0, 130.3, 130.2, 129.72, 129.70, 128.4, 127.8, 127.7, 127.6, 124.5, 61.2, 21.1, 14.2. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{26}H_{23}N_2O_3$, 411.1703; found, 411.1680.

*Ethyl 5-Benzoyl-1-(4-fluorophenyl)-4-phenyl-1H-pyrazole-3-carboxylate (**5c**).* Reaction time: 8 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (20:1) as the eluent. Yield: 0.1181 g (57%); colorless solid; mp 120−122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65−7.59 (m, 2H), 7.49−7.44 (m, 2H), 7.41 (t, J = 7.5 Hz, 1H), 7.33−7.28 (m, 3H), 7.25−7.18 (m, 4H), 7.09−7.01 (m, 2H), 4.37 (q, J = 7.1 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 187.7, 162.4 (d, J = 249.5 Hz), 161.8, 141.3, 139.7, 136.0, 135.3 (d, J = 3.2 Hz), 134.1, 130.2, 130.0, 129.7, 128.5, 127.8, 127.7, 126.7 (d, J = 8.8 Hz), 116.1 (d, J = 23.2 Hz), 61.3, 14.1. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{25}H_{20}FN_2O_3$, 415.1453; found, 415.1432.

*Ethyl 5-Benzoyl-1-(4-chlorophenyl)-4-phenyl-1H-pyrazole-3-carboxylate (**5d**).* Reaction time: 8 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (20:1) as the eluent. Yield: 0.1293 g (60%); colorless solid; mp 122−124 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67−7.62 (m, 2H), 7.46−7.41 (m, 3H), 7.38−7.34 (m, 2H), 7.32−7.28 (m, 3H), 7.26−7.18 (m, 4H), 4.38 (q, J = 7.1 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 187.7, 161.8, 141.4, 139.6, 137.6, 135.8, 134.8, 134.3, 130.2, 129.9, 129.7, 129.4, 128.6, 128.0, 127.9, 127.7, 125.9, 61.4, 14.1. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{25}H_{20}ClN_2O_3$, 431.1157; found, 431.1135.

*Ethyl 5-Benzoyl-1-(4-bromophenyl)-4-phenyl-1H-pyrazole-3-carboxylate (**5e**).* Reaction time: 8 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (20:1) as the eluent. Yield: 0.1474 g (62%); colorless solid; mp 135−137 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68−7.61 (m, 2H), 7.54−7.48 (m, 2H), 7.45−7.44 (m, 1H), 7.40−7.35 (m, 2H), 7.32−7.27 (m, 3H), 7.26−7.17 (m, 4H), 4.38 (q, J = 7.1 Hz, 2H), 1.30 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 187.7, 161.8, 141.5, 139.5, 138.1, 135.8, 134.3, 132.4, 130.2, 129.8, 129.7, 128.6, 128.02, 128.00, 127.7, 126.1, 122.8, 61.4, 14.1. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{25}H_{20}BrN_2O_3$, 475.0627; found, 475.0631.

*Ethyl 5-Benzoyl-4-phenyl-1-(m-tolyl)-1H-pyrazole-3-carboxylate (**5f**).* Reaction time: 8 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (20:1) as the eluent. Yield: 0.1190 g (58%); colorless solid; mp 135−137 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66−7.58 (m, 2H), 7.42−7.35 (m, 2H), 7.32−7.28 (m, 2H), 7.25−7.10 (m, 8H), 4.36 (q, J = 7.1 Hz, 2H), 2.32 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 187.9, 162.0, 141.0, 139.6, 139.5, 139.0, 136.1, 134.0, 130.3, 130.1, 129.7, 129.7, 128.9, 128.4, 127.8, 127.7, 127.7, 125.3, 121.6, 61.3, 21.3, 14.2. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{26}H_{23}N_2O_3$, 411.1703; found, 411.1677.

*Ethyl 5-Benzoyl-1-(3-fluorophenyl)-4-phenyl-1H-pyrazole-3-carboxylate (**5g**).* Reaction time: 8 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (20:1) as the eluent. Yield: 0.1140 g (55%); colorless solid; mp 128−130 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67−7.60 (m, 2H), 7.46−7.41 (m, 1H), 7.33−7.21 (m, 10H), 7.05 (m, 1H), 4.37 (q, J = 7.1 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 187.7, 162.6 (d, J = 248.8 Hz), 161.7, 141.6, 140.3, 139.6, 136.0, 134.2, 130.5, 130.4, 130.2, 129.8, 129.6, 128.5, 127.9, 127.7, 120.2 (d, J = 3.3 Hz), 115.8 (d, J = 21.0 Hz), 112.4 (d, J = 25.2 Hz), 61.3, 14.1. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{25}H_{20}FN_2O_3$, 415.1453; found, 415.1437.

*Ethyl 5-Benzoyl-1-(3-chlorophenyl)-4-phenyl-1H-pyrazole-3-carboxylate (**5h**).* Reaction time: 8 h; purification by column

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chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (20:1) as the eluent. Yield: 0.1120 g (52%); colorless solid; mp 155−157 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66−7.60 (m, 3H), 7.46−7.41 (m, 1H), 7.35−7.31 (m, 2H), 7.30−7.21 (m, 8H), 4.38 (q, J = 7.1 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 187.6, 161.7, 140.6, 140.1, 136.0, 135.0, 134.1, 130.2, 130.0, 129.9, 129.6, 129.0, 128.5, 128.0, 127.9, 127.7, 125.1, 122.7, 77.2, 61.3, 14.1. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{25}H_{20}ClN_2O_3$, 431.1157; found, 431.1131.

*Ethyl 5-Benzoyl-1-(3-bromophenyl)-4-phenyl-1H-pyrazole-3-carboxylate (**5i**).* Reaction time: 8 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (20:1) as the eluent. Yield: 0.1188 g (50%); colorless solid; mp 153−155 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (m, 1H), 7.66−7.62 (m, 2H), 7.50−7.46 (m, 1H), 7.45−7.41 (m, 1H), 7.36−7.33 (m, 1H), 7.3−7.20 (m, 8H), 4.38 (q, J = 7.1 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 187.6, 161.7, 141.7, 140.1, 139.6, 136.0, 134.1, 131.9, 130.2, 130.0, 129.9, 129.6, 128.5, 128.0, 127.9, 127.7, 123.1, 122.7, 77.2, 61.3, 14.1. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{25}H_{20}BrN_2O_3$, 475.0652; found, 475.0620.

*Ethyl 5-Benzoyl-4-phenyl-1-(o-tolyl)-1H-pyrazole-3-carboxylate (**5j**).* Reaction time: 8 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (20:1) as the eluent. Yield: 0.0924 g (45%); colorless solid; mp 129−131 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61−7.56 (m, 2H), 7.39−7.33 (m, 2H), 7.32−7.26 (m, 5H), 7.21−7.17 (m, 5H), 4.39 (q, J = 7.1 Hz, 2H), 2.24 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 187.2, 162.0, 140.8, 140.5, 138.4, 136.0, 135.5, 133.6, 130.9, 130.4, 130.3, 129.7, 129.6, 128.2, 127.7, 127.6, 127.5, 126.9, 126.3, 61.2, 17.7, 14.2. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{26}H_{23}N_2O_3$, 411.1703; found, 411.1675.

*Ethyl 5-Benzoyl-1-(3,4-dimethylphenyl)-4-phenyl-1H-pyrazole-3-carboxylate (**5k**).* Reaction time: 8 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (20:1) as the eluent. Yield: 0.1167 g (55%); colorless solid; mp 127−129 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66−7.59 (m, 2H), 7.39 (t, J = 7.4 Hz, 1H), 7.33−7.27 (m, 3H), 7.25−7.14 (m, 5H), 7.10−7.02 (m, 2H), 4.35 (q, J = 7.1 Hz, 2H), 2.21, 2.20 (ss, 6H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 188.0, 162.0, 140.8, 139.6, 137.9, 137.6, 136.9, 136.1, 133.9, 130.3, 130.2, 130.0, 129.7, 128.4, 127.72, 127.70, 127.5, 125.7, 121.8, 61.2, 19.8, 19.5, 14.2. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{27}H_{25}N_2O_3$, 425.1860; found, 425.1836.

*Ethyl 5-Benzoyl-1-(3,5-dimethylphenyl)-4-phenyl-1H-pyrazole-3-carboxylate (**5l**).* Reaction time: 8 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (20:1) as the eluent. Yield: 0.1125 g (53%); colorless solid; mp 135−137 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64−7.61 (m, 2H), 7.41 (t, J = 7.3 Hz, 1H), 7.31−7.20 (m, 7H), 7.07 (s, 2H), 6.94 (s, 1H), 4.37 (q, J = 7.1 Hz, 2H), 2.26 (s, 6H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 188.0, 162.0, 140.9, 139.6, 139.0, 138.9, 136.2, 133.9, 130.5, 130.3, 130.2, 129.6, 128.4, 127.8, 127.7, 122.3, 61.2, 21.2, 14.2. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{27}H_{25}N_2O_3$: 425.1860; found: 425.1840.

*Ethyl 5-(4-Chlorobenzoyl)-4-(4-chlorophenyl)-1-phenyl-1H-pyrazole-3-carboxylate (**5m**).* Reaction time: 8 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (20:1) as the eluent. Yield: 0.1233 g (53%); colorless solid; mp 146−148 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61−7.55 (m, 2H), 7.48−7.42 (m, 2H), 7.42−7.35 (m, 3H), 7.29−7.27 (m, 4H), 7.25−7.21 (m, 2H), 4.40 (q, J = 7.1 Hz, 2H), 1.34 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 186.4, 161.7, 141.2, 141.0, 139.3, 138.9, 134.2, 134.2, 131.5, 130.9, 129.4, 129.11, 129.10, 128.4, 128.1, 126.5, 124.5, 61.5, 14.21. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{25}H_{19}Cl_2N_2O_3$, 465.0782; found, 465.0788.

*Ethyl 5-(4-Bromobenzoyl)-4-(4-bromophenyl)-1-phenyl-1H-pyrazole-3-carboxylate (**5n**).* Reaction time: 8 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (20:1) as the eluent. Yield: 0.1413 g (51%); colorless solid; mp 157−159 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49−7.44 (m, 2H), 7.44−7.38 (m, 5H), 7.38−7.32 (m, 4H), 7.21−7.16 (m, 2H), 4.37 (q, J = 7.1 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 186.6, 161.7, 141.1, 139.1, 138.8, 134.6, 132.1, 131.8, 131.1, 130.9, 129.9, 129.4, 129.2, 128.8, 126.6, 124.5, 122.5, 61.5, 14.2. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{25}H_{19}Br_2N_2O_3$, 552.9757; found, 552.9732.

*Ethyl 5-(3-Methylbenzoyl)-1-phenyl-4-(m-tolyl)-1H-pyrazole-3-carboxylate (**5o**).* Reaction time: 8 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (20:1) as the eluent. Yield: 0.1061 g (50%); colorless solid; mp 117−119 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50−7.39 (m, 4H), 7.39−7.30 (m, 3H), 7.21−7.05 (m, 5H), 7.01−6.93 (m, 1H), 4.36 (q, J = 7.1 Hz, 2H), 2.22 (s, 6H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 187.9, 162.0, 141.2, 139.7, 139.3, 138.1, 137.1, 136.1, 134.7, 131.0, 130.3, 130.1, 129.1, 128.7, 128.5, 128.3, 127.8, 127.5, 127.3, 126.9, 124.7, 61.1, 21.2, 21.0, 14.1. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{27}H_{25}N_2O_3$, 425.1860; found, 425.1842.

*Ethyl 5-(2-Methylbenzoyl)-1-phenyl-4-(o-tolyl)-1H-pyrazole-3-carboxylate (**5p**).* Reaction time: 8 h; purification by column chromatography on silica gel (200−300 mesh) with petroleum ether and EtOAc (20:1) as the eluent. Yield: 0.0955 g (45%); colorless solid; mp 127−128 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53−7.46 (m, 2H), 7.40−7.32 (m, 3H), 7.29 (d, J = 7.8 Hz, 1H), 7.16 (t, J = 7.5 Hz, 1H), 7.10−6.96 (m, 6H), 4.27 (q, J = 7.1 Hz, 2H), 2.32 (s, 3H), 2.17 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 188.9, 161.7, 141.9, 141.0, 139.3, 139.1, 137.0, 136.4, 132.2, 131.4, 130.3, 130.1, 129.4, 129.1, 128.8, 128.02, 128.01, 125.1, 124.9, 124.7, 77.3, 61.1, 20.7, 20.3, 14.0. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{27}H_{25}N_2O_3$, 425.1860; found, 425.1845.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00020.

Screening of the reaction conditions for the synthesis of **4** and **5** and copies of the ^{1}H and ^{13}C NMR spectra of all isolated compounds (PDF)

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Notes

The authors declare no competing financial interest.

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