

## PAPER

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# Combined inorganic base promoted N-addition/[2,3]-sigmatropic rearrangement to construct homoallyl sulfur-containing pyrazolones†

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The first sequentially combined inorganic base promoted N-addition/[2,3]-sigmatropic rearrangement reaction of  $\alpha$ -alkylidene pyrazolinones and propargyl sulfonium salts has been reported to construct homoallyl sulfur-containing pyrazolones with moderate to excellent yields.  $\alpha$ -Alkylidene pyrazolinones function as N-nucleophilic agents distinguished from the reported C-addition reactions. Propargyl sulfonium salts were first involved in the [2,3]-sigmatropic rearrangement protocol differentiated from the well-established annulation reactions. The excellent regioselectivity, the broad scope of substrates, gram-scale synthesis and convenient transformation embody the synthetic superiority of this cascade process.

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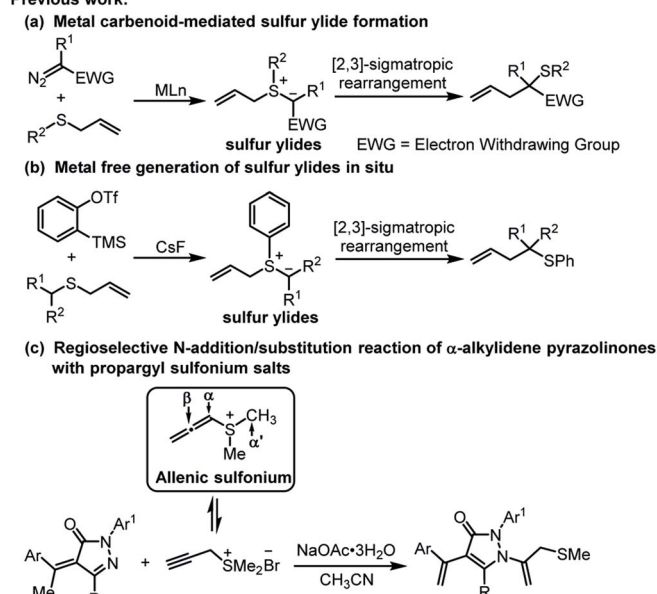
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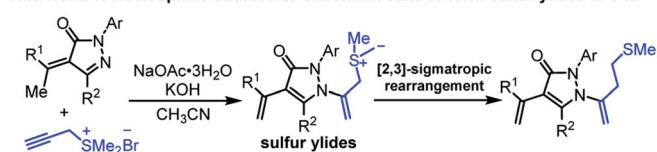
## Introduction

Organosulfur compounds that exist broadly in biologically active natural products as well as pharmaceuticals and are engaged in numerous chemical transformations, have been attracting vivid interest from academia and industry.<sup>1</sup> Sulfur ylides are among the most versatile class of structural motifs, having widespread applications ranging from classical cyclopropanation, epoxidation and aziridination to more complicated  $[n + 1]$ -cycloadditions, domino reactions and rearrangement reactions based on transition metal catalysis, organocatalysis and photocatalysis.<sup>2</sup> As an efficient C–C bond-forming strategy, [2,3]-sigmatropic rearrangements of sulfur ylides have been widely explored and applied since their discovery in the late 1960s.<sup>3,4</sup> The transition metal carbenoid-mediated rearrangement reactions between allyl sulfides and diazo species named Doyle–Kirmse reactions are representative examples and have made impressive progress especially in to the content of catalytic and asymmetric variants in the past decade (Scheme 1a).<sup>5</sup> Metal-free generation of sulfur ylides *in situ* between allyl thioethers and arynes followed by [2,3]-sigmatropic rearrangements are also alternative methods (Scheme 1b).<sup>6</sup> Despite the aforementioned excellent work, the

### Previous work:



### This work: N-Nucleophilic addition to sulfonium salts to form sulfur ylides *in situ*



**Scheme 1** [2,3]-Sigmatropic rearrangements of sulfur ylides (a and b) and N-2 initiating nucleophilic reaction of  $\alpha, \beta$ -unsaturated pyrazolone (c).

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† Electronic supplementary information (ESI) available: Copies of <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR and ESI-HRMS spectra for compounds. CCDC 1943758. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9ra07610g



attempt to utilize propargyl sulfonium salts to form key species of sulfur ylides accompanied by subsequent [2,3]-sigmatropic rearrangements process has not been achieved.

Propargyl sulfonium salts, because of their easy acquisitions and multiple reaction sites, are versatile and promising building blocks. Generally, propargyl sulfonium salts can isomerize to allenic sulfonium salts in the presence of the base, which are active forms and possess three reactive sites of  $\alpha$ -carbon,  $\beta$ -carbon and  $\alpha'$ -carbon (Scheme 1c). Kanematsu's,<sup>7</sup> Huang's<sup>8</sup> and our group<sup>9</sup> have reported the  $[n + 2]$  or  $[n + 1]$  cascade annulation reactions based on  $\alpha$ -carbon and  $\beta$ -carbon sites. Meanwhile, pyrazolones represent a class of privileged heterocycles that exhibit extensive physiological and pharmacological activities and are valuable drug candidates.<sup>10</sup> Accordingly, fruitful protocols have been explored to access versatile pyrazolones architectures based on the multiple reactive sites of pyrazolin-5-ones and  $\alpha,\beta$ -unsaturated pyrazolones.<sup>11,12</sup> As to  $\alpha,\beta$ -unsaturated pyrazolones having  $\gamma$ -H, the preferential  $\gamma$ -C nucleophilic property facilitates their functioning as C3 synthons to construct spiro-pyrazolones by  $[3 + n]$  annulation.<sup>13</sup> In contrast, the N-2 initiating nucleophilic reaction of  $\alpha,\beta$ -unsaturated pyrazolones was less investigated. Recently our group reported the first regioselective NaOAc·3H<sub>2</sub>O-promoted N-addition/substitution reaction between  $\alpha$ -alkylidene pyrazolinones and propargyl sulfonium salts (Scheme 1c).<sup>14</sup> Accidentally, we found that strong inorganic bases can efficiently promoted the rearrangement of sulfur salts. Based on our

processive interests on constructing functionalized pyrazolones and exploring the diverse reactive pathway of propargyl sulfonium salts,<sup>9,15</sup> we herein report the realization of regioselective NaOAc·3H<sub>2</sub>O/KOH-promoted N-addition/[2,3]-sigmatropic rearrangement reaction of  $\alpha$ -alkylidene pyrazolinones and propargyl sulfonium salts, delivering bioactive homoallyl sulfur-containing pyrazolones in moderate to excellent yields (Scheme 1d).

## Results and discussion

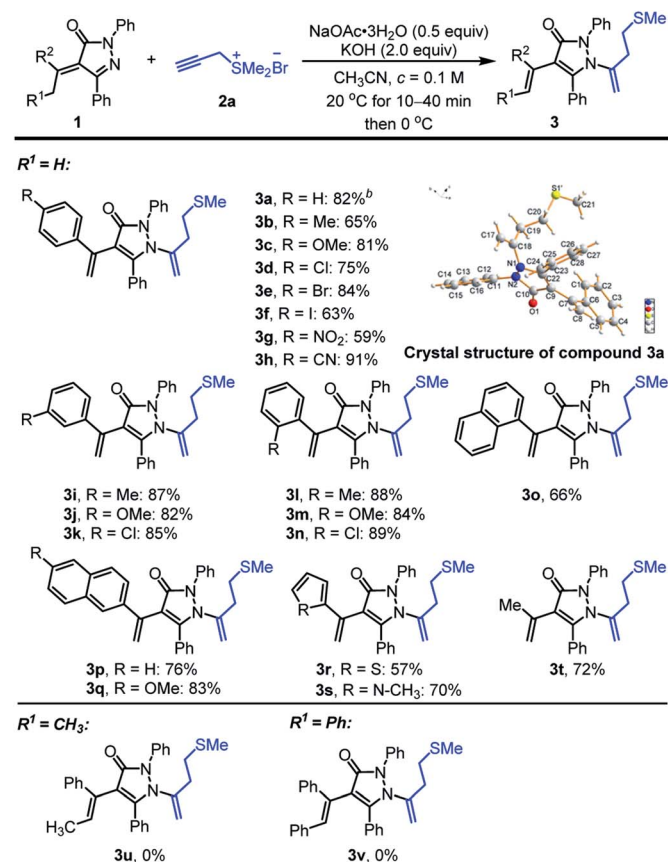
We began our investigation by selecting  $\alpha$ -alkylidene pyrazolinone **1a** and propargyl sulfonium salt **2a** as model substrates (Table 1). When **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.24 mmol, 1.2 equiv.) and NaOAc·3H<sub>2</sub>O (0.1 mmol, 0.5 equiv.) in CH<sub>3</sub>CN (2 mL) were mixed and stirred for 10 minutes at 20 °C, the  $\alpha$ -alkylidene pyrazolinone **1a** was consumed completely. After the reaction temperature was decreased to 0 °C, KOH (0.4 mmol, 2.0 equiv.) was added and the reaction was stirred for 6 h at 0 °C to afford N-addition/[2,3]-sigmatropic rearrangement product **3a** with 82% yield (Table 1, entry 4). When the mixture of NaOAc·3H<sub>2</sub>O and KOH was added in one portion,  $\alpha$ -alkylidene pyrazolinone could not be consumed completely even after 12 h and the operation caused decreased yield. Extensive exploration of a range of bases indicated that NaOAc·3H<sub>2</sub>O or anhydrous NaOAc was most efficient to promote the process (entries 4–5 vs. 1–3 and 6–10 in Table 1). The combined usage of bases NaOAc·3H<sub>2</sub>O and KOH was

Table 1 Optimization of the reaction conditions<sup>a</sup>

Entry	Base1/base2	Solvent	1a : 2a : base1 : base2	Yield <sup>b</sup> (%)
1	Na <sub>2</sub> CO <sub>3</sub> /KOH	CH <sub>3</sub> CN	1 : 1.2 : 0.5 : 2	69
2	K <sub>2</sub> CO <sub>3</sub> /KOH	CH <sub>3</sub> CN	1 : 1.2 : 0.5 : 2	58
3	Cs <sub>2</sub> CO <sub>3</sub> /KOH	CH <sub>3</sub> CN	1 : 1.2 : 0.5 : 2	75
4	NaOAc·3H <sub>2</sub> O/KOH	CH <sub>3</sub> CN	1 : 1.2 : 0.5 : 2	82
5	NaOAc/KOH	CH <sub>3</sub> CN	1 : 1.2 : 0.5 : 2	82
6	KOAc/KOH	CH <sub>3</sub> CN	1 : 1.2 : 0.5 : 2	68
7	NEt <sub>3</sub> /KOH	CH <sub>3</sub> CN	1 : 1.2 : 0.5 : 2	39
8	DABCO <sup>c</sup> /KOH	CH <sub>3</sub> CN	1 : 1.2 : 0.5 : 2	68
9	DBU <sup>d</sup> /KOH	CH <sub>3</sub> CN	1 : 1.2 : 0.5 : 2	60
10	DMAP <sup>e</sup> /KOH	CH <sub>3</sub> CN	1 : 1.2 : 0.5 : 2	75
11	NaOAc·3H <sub>2</sub> O	CH <sub>3</sub> CN	1 : 1.2 : 0.5 : 0	0
12	KOH	CH <sub>3</sub> CN	1 : 1.2 : 0 : 2	46
13	NaOAc·3H <sub>2</sub> O/NaOH	CH <sub>3</sub> CN	1 : 1.2 : 0.5 : 2	74
14	NaOAc·3H <sub>2</sub> O/LiOH	CH <sub>3</sub> CN	1 : 1.2 : 0.5 : 2	68
15	NaOAc·3H <sub>2</sub> O/KOH	CH <sub>2</sub> Cl <sub>2</sub>	1 : 1.2 : 0.5 : 2	74
16	NaOAc·3H <sub>2</sub> O/KOH	CHCl <sub>3</sub>	1 : 1.2 : 0.5 : 2	53
17	NaOAc·3H <sub>2</sub> O/KOH	MeOH	1 : 1.2 : 0.5 : 2	64
18	NaOAc·3H <sub>2</sub> O/KOH	THF	1 : 1.2 : 0.5 : 2	48
19	NaOAc·3H <sub>2</sub> O/KOH	Toluene	1 : 1.2 : 0.5 : 2	36
20	NaOAc·3H <sub>2</sub> O/KOH	CH <sub>3</sub> CN	1 : 2.0 : 0.5 : 2	83
21	NaOAc·3H <sub>2</sub> O/KOH	CH <sub>3</sub> CN	1 : 1.2 : 0.25 : 2	80
22	NaOAc·3H <sub>2</sub> O/KOH	CH <sub>3</sub> CN	1 : 1.2 : 1.0 : 2	82
23	NaOAc·3H <sub>2</sub> O/KOH	CH <sub>3</sub> CN	1 : 1.2 : 0.5 : 4	81
24	NaOAc·3H <sub>2</sub> O/KOH	CH <sub>3</sub> CN	1 : 1.2 : 0.5 : 2	78

<sup>a</sup> Unless otherwise noted, the reactions were performed under air and  $\alpha$ -alkylidene pyrazolinones **1** (0.2 mmol, 1.0 equiv.), sulfonium salt **2a** (0.24 mmol, 1.2 equiv.) and NaOAc·3H<sub>2</sub>O (0.1 mmol, 0.5 equiv.) in CH<sub>3</sub>CN (2.0 mL) were mixed and stirred for 10–40 minutes at 20 °C until starting material **1a** disappeared (monitored by TLC), then the reaction temperature was decreased to 0 °C and KOH (2.0 equiv.) was added to keep stirring at 0 °C for 6–10 h. <sup>b</sup> Isolated yield.

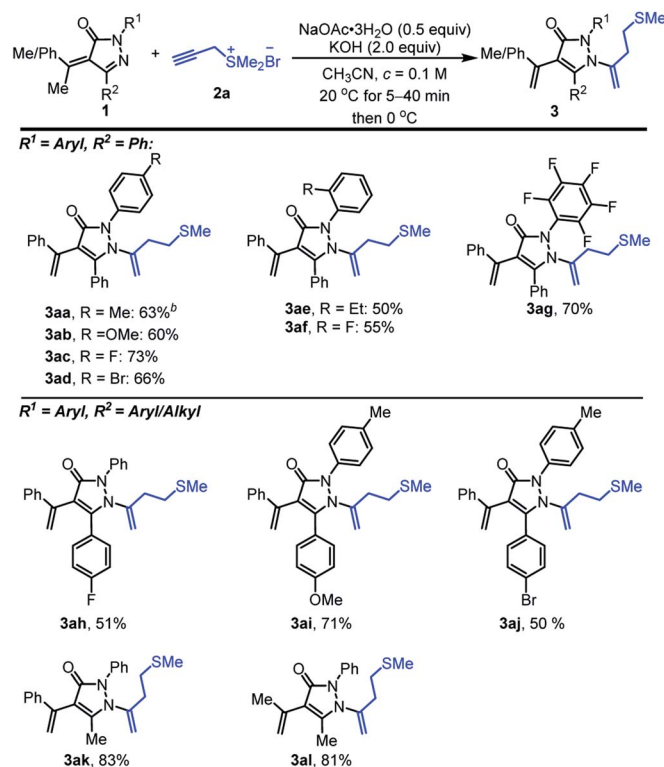




**Scheme 2** Scope of Disubstituted  $\alpha$ -Alkylidene Pyrazolinones.<sup>a</sup> Unless otherwise noted, the reactions were performed under air and  $\alpha$ -alkylidene pyrazolinones **1** (0.2 mmol, 1.0 equiv.), sulfonium salt **2a** (0.24 mmol, 1.2 equiv.) and NaOAc·3H<sub>2</sub>O (0.1 mmol, 0.5 equiv.) in CH<sub>3</sub>CN (2.0 mL) were mixed, stirred for 10–40 minutes at 20 °C until starting material **1a** disappeared (monitored by TLC), then the reaction temperature was decreased to 0 °C and KOH (2.0 equiv.) was added to keep stirring at 0 °C for 6–10 h.<sup>b</sup> Isolated yield.

crucial for the high efficiency while NaOAc·3H<sub>2</sub>O or KOH was utilized separately to give the desired **3a** in 0% and 46% yields, respectively (Table 1, entries 11–12). Replacement of KOH with NaOH or LiOH gave related 74% and 68% yields (Table 1, entries 13–14). Screening of solvents including CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, MeOH, THF and toluene did not give a better yield (entries 4 vs. 15–19). We also probed the influence of the amount of sulfonium salts **2a**, NaOAc·3H<sub>2</sub>O and KOH. Increasing the content of propargyl sulfonium salt **2a** to 2.0 equiv. has little influence on yield (entry 20). Decreasing the amount of NaOAc·3H<sub>2</sub>O to 0.25 equiv. or increasing to 1.0 equiv. had a slight effect on yield (entries 21–22). Increasing the quantities of KOH to 4.0 equiv. did not improve the yield (entry 23). The yield was declined from 82% to 78% when the reaction was stirred at 20 °C (entry 24).

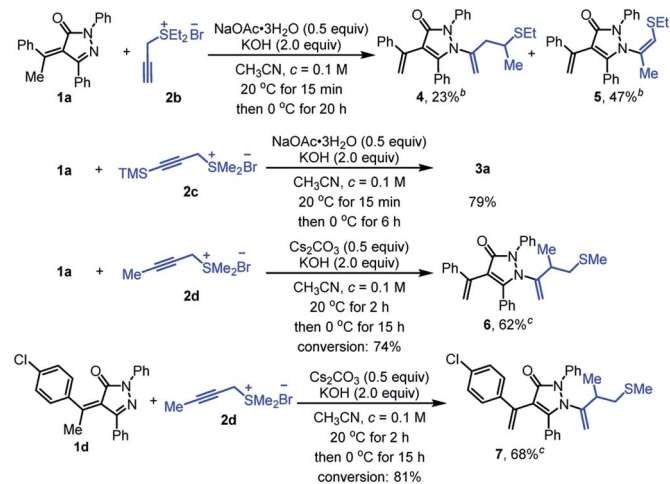
Having established the optimized conditions (Table 1, entry 4), we commenced to explore the substrate scope of the reaction (Scheme 2). Generally, the existence of methyl group (R<sup>1</sup> = H) at  $\alpha$ -position of alkylidene pyrazolinones was pivotal for the success of the reaction and various aryl and alkyl-substituted alkylidene pyrazolinones **1** was adaptable to the



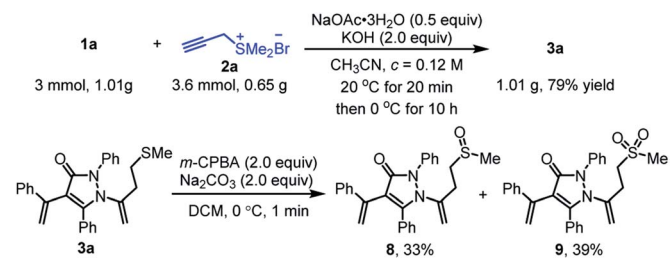
**Scheme 3** Scope of  $\alpha$ -alkylidene pyrazolinones on the pyrazolinone ring.<sup>a</sup> Unless otherwise noted, the reactions were performed under air and  $\alpha$ -alkylidene pyrazolinones **1** (0.2 mmol, 1.0 equiv.), sulfonium salt **2a** (0.24 mmol, 1.2 equiv.) and NaOAc·3H<sub>2</sub>O (0.1 mmol, 0.5 equiv.) in CH<sub>3</sub>CN (2.0 mL) were mixed and stirred for 10–40 minutes at 20 °C until starting material **1** disappeared (monitored by TLC), then the reaction temperature was decreased to 0 °C and KOH (2.0 equiv.) was added to keep stirring at 0 °C for 6–10 h.<sup>b</sup> Isolated yield.

transformation. Acetophenones derived alkylidene pyrazolinones **1** with methyl, methoxy, chloro-, bromo-, iodo-, nitro- and cyano-groups on *ortho*-, *meta*- or *para*-positions, could react effectively with propargyl sulfonium salt **2a** to furnish the related homoallyl sulfur-containing pyrazolinones in 59–91% yields (**3a–3n** in Scheme 2). As to the same substituent on phenyl group, such as methyl, methoxy and chloro-, *ortho*- and *meta*-positions exhibited higher yields than *para*-position (**3b** vs. **3i**, **3l**; **3c** vs. **3j**, **3m**; **3d** vs. **3k**, **3n**). Naphthyl-substituted  $\alpha$ -alkylidene pyrazolinones were well-tolerated to provide **3o**, **3p** and **3q** in 66, 76 and 83% yields, respectively. Hetero-aromatic unsaturated pyrazolinones containing thiophene and N-methyl protected pyrrole could participate in the reaction to afford corresponding product **3r** and **3s** in 57 and 70% yields, respectively. Double alkyl-substituted alkylidene pyrazolinone could also be engaged in the reaction to produce the predicted **3t** with 72% yield. In contrast, when the methyl group was replaced by ethyl (R<sup>1</sup> = CH<sub>3</sub>) or benzyl groups (R<sup>1</sup> = Ph), the desired reaction was sluggish, abundant alkylidene pyrazolinones were recovered and no target products **3u** or **3v** could be separated. In addition, the structure of homoallyl sulfur-containing pyrazolinone derivative **3a** was assigned unambiguously by using single crystal X-ray analysis.<sup>16</sup>

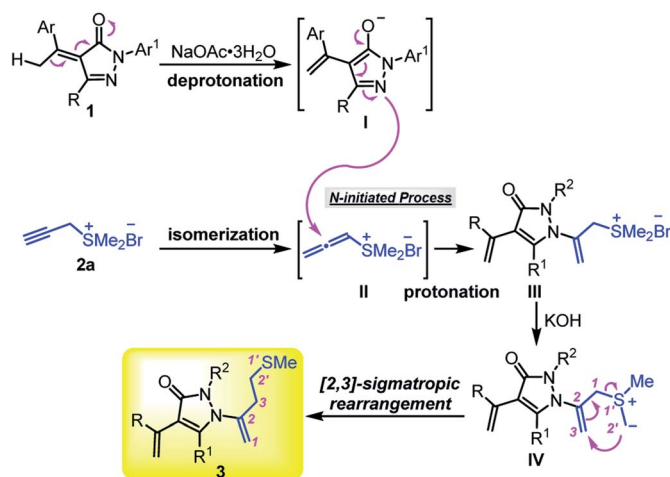




**Scheme 4** Scope of propargyl sulfonium salts.<sup>a</sup> Unless otherwise noted, the reactions were performed under air and  $\alpha$ -alkylidene pyrazolinone **1a** or **1d** (0.2 mmol, 1.0 equiv.), sulfonium salts **2b**, **2c** or **2d** (0.24 mmol, 1.2 equiv.) and NaOAc·3H<sub>2</sub>O (0.1 mmol, 0.5 equiv.) in CH<sub>3</sub>CN (2.0 mL) were mixed and stirred at 20 °C until starting material **1a** or **1d** disappeared (monitored by TLC), then the reaction temperature was decreased to 0 °C and KOH (2.0 equiv.) was added to keep stirring at 0 °C for related time. <sup>b</sup>Isolated yield. <sup>c</sup> Cs<sub>2</sub>CO<sub>3</sub> (0.1 mmol, 0.5 equiv.) was utilized instead of NaOAc·3H<sub>2</sub>O under the standard condition and the reaction was kept stirring at 0 °C for 15 h.



**Scheme 5** Gram-scale synthesis and further transformation of **3a**.



**Scheme 6** Plausible reaction mechanism.

Subsequently, we went on to evaluate the effect of different substituents on pyrazolinone ring (Scheme 3).  $\alpha$ -Alkylidene pyrazolinones **1** with the *para*-substituted phenyl-ring of R<sup>1</sup> worked well to deliver the corresponding products **3aa**, **3ab**, **3ac** and **3ad** with moderate yields of 63, 60, 73 and 66%, respectively. Electron-withdrawing groups on the phenyl group gave better yields than electron-donating groups (**3ac**, **3ad** vs. **3aa**, **3ab**). *ortho*-Ethyl, fluoro-substituted phenyl ring of R<sup>1</sup> gave relatively lower yields of 50 and 55% partially because of the instability of **1**. It is noteworthy that the substrate having electron-withdrawing group C<sub>6</sub>F<sub>5</sub>- supplied the desired product **3ag** with a moderate yield of 70%.  $\alpha$ -Alkylidene pyrazolinones **1** with 4-fluoro-, 4-methoxy and 4-bromo-substituted phenyl ring of R<sup>2</sup> could also be applied to the reaction and provide the related homoallyl sulfur-containing pyrazolones **3ah**, **3ai** and **3aj** with 51, 71 and 50% yields.  $\alpha$ -Alkylidene pyrazolinones **1** including alkyl group of R<sup>2</sup> showed excellent compatibility and afforded **3ak** with 83% yield. Moreover, trimethyl involved alkylidene pyrazolinone displayed proof of tolerance and 81% yield was obtained (**3al**).

To further broaden the scope of the reaction, other representative propargyl sulfonium salts were also investigated (Scheme 4). Diethyl thioether derived propargyl sulfonium salt **2b** was adaptable to give the predicted homoallyl sulfur-containing pyrazolone **4** in 23% yield, together with additional isomerization product **5** in 47% yield. Trimethylsilyl-containing propargyl sulfonium salt **2c** can also be applied to the reaction but the desilylation product **3a** was obtained with a yield of 79%. Methyl substituted propargyl sulfonium salt **2d** did not engage in the reaction under standard condition, mainly because NaOAc·3H<sub>2</sub>O was not suitable to transform propargyl sulfonium salt **2d** into active allenic form and alkylidene pyrazolinone **1a** was nearly fully recovered after stirred at 20 °C for 20 h. When NaOAc·3H<sub>2</sub>O was replaced by Cs<sub>2</sub>CO<sub>3</sub>, the reaction could proceed to afford the desired product **6** with 62% yield. Substrate **1d** could also react with **2d** smoothly to provide **7** with 68% yield under the same conditions.

To demonstrate the further synthetic utility of this protocol, we performed the large-scale operation using  $\alpha$ -alkylidene pyrazolinone **1a** (1.01 g, 3 mmol) and propargyl sulfonium salt **2a** (1.2 equiv.) as the representative substrates under the optimized conditions, providing the related product **3a** (1.00 g) with 79% yield (Scheme 5). The typical transformation was also conducted by oxidation of **3a** with *m*-chloro peroxybenzoic acid (2.0 equiv.), sulfinyl product **8** and sulfonyl product **9** were obtained in Scheme 5 with 33% and 39% yields, respectively.

According to the experimental observations and previous reports,<sup>8,9,14</sup> a possible mechanism is proposed to account for the formation of homoallyl sulfur-containing pyrazolone derivatives **3** (Scheme 6). Under the activation of inorganic base NaOAc·3H<sub>2</sub>O,  $\alpha$ -alkylidene pyrazolinone **1** can form intermediate **I** and propargyl sulfonium salt **2a** can isomerize to allenic sulfonium salts **II**. The N-nucleophilic attack of **I** to allenic sulfonium salts **II** initiates the reaction and gives intermediate **III** after protonation. Subsequently, the deprotonation of methyl-carbon by KOH provides the key sulfur ylide **IV**. Finally,



the [2,3]-sigmatropic rearrangement of key species **IV** affords the desired product **3**.

## Conclusions

In summary, we have developed a sequentially combined inorganic bases promoted N-addition/[2,3]-sigmatropic rearrangement reaction between  $\alpha$ -alkylidene pyrazolinones and propargyl sulfonium salts for the first time, delivering bioactive homoallyl sulfur-containing pyrazolones in moderate to excellent yields. In this reaction,  $\alpha$ -alkylidene pyrazolinones function as N-nucleophilic agents distinguished from reported C-addition reactions. Meanwhile, propargyl sulfonium salts were first involved in [2,3]-sigmatropic rearrangement protocols differentiated from the well-established annulation reactions. Gram-scale synthesis and convenient transformations are furnished. The proposed mechanism is also discussed. Excellent regioselectivity, the broad scope of substrates, gram-scale synthesis and convenient transformation embody the synthetic superiority of this reaction process.

## Experimental

### General information

All reactions were performed in oven-dried or flame-dried round-bottom flasks and vials. Stainless steel syringes and cannula were used to transfer air- and moisture-sensitive liquids. Flash chromatography was performed using silica gel 60 (230–400 mesh) from Aladdin. Commercial reagents were purchased from Aladdin, J&K, Macklin and Merck and used as received. All solvents were used after being freshly distilled unless otherwise noted. Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra and carbon nuclear magnetic resonance ( $^{13}\text{C}$  NMR) spectra were recorded on Bruker UltraShield-600 (600 MHz). The mass spectroscopic data were obtained using a Micromass Platform II single quadrupole instrument. Infrared (IR) spectra were obtained using a PerkinElmer Spectrum 100 FT-IR spectrometer.

### General procedure for the synthesis of $\alpha$ -alkylidene pyrazolinones (**1**)

$\alpha$ -Alkylidene pyrazolinones **1** were prepared through a known procedure.<sup>12b,13b,14,17</sup> Aryl formyl acetate (5.5 mmol, 1.1 equiv.) was slowly added to the mixture of the corresponding hydrazine (5 mmol, 1.0 equiv.) in glacial acetic acid (2 mL). The mixture was stirred at room temperature for 24 h.  $\text{NEt}_3$  (5 mmol, 1.0 equiv.) was added to neutralize the hydrochloride while phenylhydrazine hydrochloride was used. After the reaction was completed, ethyl (50 mL) was added. The precipitate was filtered and washed with 5 mL of ether (three times). The corresponding pyrazolone products were obtained as solid and used in the following step.

Under nitrogen atmosphere, a mixture of pyrazolone (5 mmol, 1.0 equiv.), acetophenone (6 mmol, 1.2 equiv.) and pyridine (0.8 mL, 10 mmol) in THF (10 mL) was stirred for 10 min followed by slow addition (30 min) of Titanium

isopropoxide (4.3 mL, 15 mmol). The mixture was stirred at room temperature for 24 h. The resulting reaction mixture was diluted with EtOAc (100 mL) and washed with 1 N aqueous HCl, saturated aqueous solution of  $\text{NaHCO}_3$  and brine. The organic layer was dried over  $\text{Na}_2\text{SO}_4$ , concentrated, and purified by column chromatography to provide  $\alpha$ -alkylidene pyrazolinone derivatives **1**. If the products are mixed with excess liquid acetophenones, they can be further purified by washing with petroleum ether.

Propargyl Sulfonium Salts (**2a**, **2b**, **2c**, **2d** and **2e**) were prepared through a known procedure.<sup>18</sup>

### General procedure for the reaction of unsaturated pyrazolones with propargyl sulfide ylide

To a flame-dried sealable 3-dram vial equipped with a stir bar was added unsaturated pyrazolinones **1** (0.2 mmol, 1.0 equiv.),  $\text{NaOAc} \cdot 3\text{H}_2\text{O}$  (0.1 mmol, 0.5 equiv.) and **2a** (44 mg, 0.24 mmol, 1.2 equiv.) under air. Subsequently treated  $\text{CH}_3\text{CN}$  (2 mL,  $c = 0.1$  M) was added to vial *via* syringe. The reaction mixture was stirred for 10–40 min at 20 °C until unsaturated pyrazolones **1** was fully consumed (monitored by TLC). Then the reaction was stirred at 0 °C for 6–10 h. The organic solvent was removed under reduced pressure and purified through column chromatography (eluent: petroleum ether and EtOAc) to afford the desired product **3**.

### 1-(4-(Methylthio)but-1-en-2-yl)-2,5-diphenyl-4-(1-phenylvinyl)-1,2-dihydro-3H-pyrazol-3-one (**3a**)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3a** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a white solid (75 mg, 85% yield). mp 174.7–175.6 °C. IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 3062, 2985, 1677, 1568, 1452, 1391, 1183, 1026, 955;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.62 (dd,  $J = 1.2, 7.8$  Hz, 2H), 7.47 (t,  $J = 7.8$  Hz, 2H), 7.34–7.29 (m, 5H), 7.26 (d,  $J = 7.2$  Hz, 1H), 7.23 (t,  $J = 7.2$  Hz, 2H), 7.17 (t,  $J = 7.8$  Hz, 2H), 7.13 (t,  $J = 7.2$  Hz, 1H), 5.69 (d,  $J = 1.2$  Hz, 1H), 5.65 (d,  $J = 1.2$  Hz, 1H), 5.45 (s, 1H), 5.06 (s, 1H), 2.24 (t,  $J = 7.8$  Hz, 2H), 2.05 (t,  $J = 7.8$  Hz, 2H), 1.94 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.6, 155.6, 145.1, 140.2, 138.3, 135.9, 130.0, 129.6, 129.2, 128.7, 127.9, 127.9, 127.2, 126.9, 126.4, 124.2, 118.9, 117.9, 114.3, 31.3, 31.1, 15.3. HRMS (ESI-TOF,  $m/z$ ): calcd for  $\text{C}_{28}\text{H}_{26}\text{N}_2\text{NaOS}^+$ ,  $[\text{M} + \text{Na}]^+$ , 461.1658, found 461.1662.

### 1-(4-(Methylthio)but-1-en-2-yl)-2,5-diphenyl-4-(1-(*p*-tolyl)vinyl)-1,2-dihydro-3H-pyrazol-3-one (**3b**)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3b** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (59 mg, 65% yield). IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 3102, 2899, 1698, 1571, 1433, 1367, 1256, 1142, 1030, 979;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.62 (dd,  $J = 0.6, 8.4$  Hz, 2H), 7.46 (t,  $J = 7.8$  Hz, 2H), 7.36 (d,  $J = 8.4$  Hz, 2H), 7.31–7.30 (m, 2H), 7.28–7.23 (m, 4H), 7.00 (d,  $J = 7.8$  Hz, 2H), 5.64 (d,  $J = 1.2$  Hz, 1H), 5.49 (d,  $J = 1.2$  Hz, 1H), 5.44 (s, 1H), 5.06 (s, 1H), 2.28 (s, 3H), 2.26 (t,  $J = 7.8$  Hz, 2H), 2.06 (t,  $J = 7.8$  Hz, 2H), 1.95 (s, 3H);



$^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.7, 155.6, 145.3, 138.2, 137.4, 137.0, 136.1, 130.1, 129.6, 129.4, 128.7, 127.9, 126.8, 126.4, 124.1, 118.0, 117.8, 114.8, 31.4, 31.1, 21.0, 15.4. HRMS (ESI-TOF,  $m/z$ ): calcd for  $\text{C}_{29}\text{H}_{28}\text{N}_2\text{ONa}^+$ ,  $[\text{M} + \text{Na}]^+$ , 475.1815, found 475.1812.

#### 4-(1-(4-Methoxyphenyl)vinyl)-1-(4-(methylthio)but-1-en-2-yl)-2,5-diphenyl-1,2-dihydro-3H-pyrazol-3-one (3c)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3c** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (76 mg, 81% yield). IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 3087, 2977, 1664, 1582, 1456, 1361, 1129, 1057, 933, 854;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.62 (d,  $J = 7.2$  Hz, 2H), 7.46 (t,  $J = 7.8$  Hz, 2H), 7.36 (d,  $J = 7.2$  Hz, 2H), 7.30–7.24 (m, 6H), 6.72 (d,  $J = 9.0$  Hz, 2H), 5.60 (d,  $J = 1.2$  Hz, 1H), 5.48 (d,  $J = 1.2$  Hz, 1H), 5.45 (s, 1H), 5.06 (s, 1H), 3.75 (s, 3H), 2.24 (t,  $J = 7.8$  Hz, 2H), 2.05 (t,  $J = 7.8$  Hz, 2H), 1.94 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.5, 159.1, 155.5, 145.1, 137.6, 135.9, 132.8, 129.9, 129.5, 129.2, 128.6, 127.9, 127.8, 126.3, 124.0, 117.8, 117.1, 114.6, 113.5, 55.2, 31.3, 31.0, 15.3. HRMS (ESI-TOF,  $m/z$ ): calcd for  $\text{C}_{29}\text{H}_{29}\text{N}_2\text{O}_2\text{S}^+$ ,  $[\text{M} + \text{H}]^+$ , 469.1944, found 469.1943.

#### 4-(1-(4-Chlorophenyl)vinyl)-1-(4-(methylthio)but-1-en-2-yl)-2,5-diphenyl-1,2-dihydro-3H-pyrazol-3-one (3d)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3d** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (71 mg, 75% yield). IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 3073, 2956, 1680, 1479, 1364, 1182, 1036, 937;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.60 (dd,  $J = 1.2, 8.4$  Hz, 2H), 7.47 (t,  $J = 8.4$  Hz, 2H), 7.30 (d,  $J = 8.4$  Hz, 4H), 7.25 (d,  $J = 7.8$  Hz, 2H), 7.23–7.21 (m, 2H), 7.11 (d,  $J = 8.4$  Hz, 2H), 5.69 (d,  $J = 1.2$  Hz, 1H), 5.65 (d,  $J = 1.2$  Hz, 1H), 5.44 (s, 1H), 5.06 (s, 1H), 2.23 (t,  $J = 7.8$  Hz, 2H), 2.04 (t,  $J = 7.8$  Hz, 2H), 1.93 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.3, 155.5, 144.9, 138.8, 137.3, 135.7, 133.1, 130.0, 129.7, 129.1, 128.8, 128.2, 128.0, 126.5, 124.2, 119.3, 118.0, 113.6, 31.2, 15.3. HRMS (ESI-TOF,  $m/z$ ): calcd for  $\text{C}_{28}\text{H}_{26}\text{ClN}_2\text{OS}^+$ ,  $[\text{M} + \text{H}]^+$ , 473.1449, found 473.1451.

#### 4-(1-(4-Bromophenyl)vinyl)-1-(4-(methylthio)but-1-en-2-yl)-2,5-diphenyl-1,2-dihydro-3H-pyrazol-3-one (3e)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3e** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (87 mg, 84% yield). IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 3102, 2941, 1668, 1603, 1490, 1377, 1268, 1146, 1021, 919, 832;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.60 (d,  $J = 7.8$  Hz, 2H), 7.46 (t,  $J = 7.8$  Hz, 2H), 7.31–7.26 (m, 5H), 7.25–7.22 (m, 3H), 7.15 (d,  $J = 8.4$  Hz, 2H), 5.69 (d,  $J = 0.6$  Hz, 1H), 5.64 (d,  $J = 0.6$  Hz, 1H), 5.42 (s, 1H), 5.05 (s, 1H), 2.23 (t,  $J = 7.8$  Hz, 2H), 2.04 (t,  $J = 7.8$  Hz, 2H), 1.93 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.3, 155.4, 144.8, 139.3, 137.3, 135.7, 131.0, 129.9, 129.7, 129.0, 128.7, 128.5, 128.0, 126.5, 124.1, 121.2, 119.2, 118.0, 113.4, 31.2, 15.3. HRMS (ESI-TOF,  $m/z$ ): calcd for  $\text{C}_{28}\text{H}_{26}\text{BrN}_2\text{OS}^+$ ,  $[\text{M} + \text{H}]^+$ , 517.0944, found 517.0945.

#### 4-(1-(4-Iodophenyl)vinyl)-1-(4-(methylthio)but-1-en-2-yl)-2,5-diphenyl-1,2-dihydro-3H-pyrazol-3-one (3f)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3f** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (71 mg, 63% yield). IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 3082, 2986, 1677, 1598, 1465, 1343, 1188, 1067, 962;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.60 (dd,  $J = 1.2, 7.8$  Hz, 2H), 7.48–7.45 (m, 4H), 7.32–7.28 (m, 4H), 7.25 (d,  $J = 7.2$  Hz, 2H), 7.03 (d,  $J = 8.4$  Hz, 2H), 5.67 (d,  $J = 1.2$  Hz, 1H), 5.64 (d,  $J = 1.2$  Hz, 1H), 5.42 (s, 1H), 5.06 (s, 1H), 2.23 (t,  $J = 7.8$  Hz, 2H), 2.04 (t,  $J = 7.8$  Hz, 2H), 1.93 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.3, 155.5, 144.9, 139.9, 137.5, 137.0, 135.8, 130.0, 129.7, 129.1, 128.8, 128.7, 128.0, 126.5, 124.2, 119.3, 117.9, 113.4, 92.7, 31.2, 15.3. HRMS (ESI-TOF,  $m/z$ ): calcd for  $\text{C}_{28}\text{H}_{25}\text{IN}_2\text{ONa}^+$ ,  $[\text{M} + \text{Na}]^+$ , 587.0624, found 587.0620.

#### 1-(4-(Methylthio)but-1-en-2-yl)-4-(1-(4-nitrophenyl)vinyl)-2,5-diphenyl-1,2-dihydro-3H-pyrazol-3-one (3g)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3g** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (57 mg, 59% yield). IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 3076, 2977, 1668, 1599, 1472, 1338, 1169, 1027, 912, 835;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.98 (d,  $J = 9.0$  Hz, 2H), 7.60 (dd,  $J = 1.2, 8.4$  Hz, 2H), 7.49 (t,  $J = 7.8$  Hz, 2H), 7.39 (d,  $J = 8.4$  Hz, 2H), 7.33 (t,  $J = 7.8$  Hz, 1H), 7.27–7.25 (m, 3H), 7.22 (t,  $J = 7.2$  Hz, 2H), 5.96 (d,  $J = 0.6$  Hz, 1H), 5.77 (d,  $J = 0.6$  Hz, 1H), 5.45 (s, 1H), 5.08 (s, 1H), 2.23 (t,  $J = 7.8$  Hz, 2H), 2.04 (t,  $J = 7.8$  Hz, 2H), 1.94 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.1, 155.4, 147.1, 144.7, 137.0, 135.7, 130.1, 130.0, 128.9, 128.2, 128.0, 127.9, 126.8, 124.4, 123.2, 121.9, 118.2, 112.5, 31.5, 31.3, 15.4. HRMS (ESI-TOF,  $m/z$ ): calcd for  $\text{C}_{28}\text{H}_{25}\text{N}_3\text{O}_3\text{Na}^+$ ,  $[\text{M} + \text{Na}]^+$ , 506.1509, found 506.1509.

#### 4-(1-(1-(4-(Methylthio)but-1-en-2-yl)-3-oxo-2,5-diphenyl-2,3-dihydro-1H-pyrazol-4-yl)vinyl) benzonitrile (3h)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3h** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (84 mg, 91% yield). IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 3065, 2963, 2023, 1672, 1564, 1491, 1336, 1287, 1142, 1053, 965;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.58 (d,  $J = 7.2$  Hz, 2H), 7.48 (t,  $J = 7.8$  Hz, 2H), 7.39 (d,  $J = 7.2$  Hz, 2H), 7.30–7.34 (m, 3H), 7.28 (d,  $J = 3.6$  Hz, 1H), 7.27–7.25 (m, 2H), 7.22 (d,  $J = 7.2$  Hz, 2H), 5.90 (s, 1H), 5.72 (s, 1H), 5.44 (s, 1H), 5.07 (s, 1H), 2.22 (t,  $J = 7.8$  Hz, 2H), 2.03 (t,  $J = 7.8$  Hz, 2H), 1.92 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.1, 155.4, 145.1, 144.7, 137.2, 135.7, 131.7, 130.0, 128.9, 128.1, 127.7, 126.8, 124.3, 121.4, 118.7, 118.2, 112.5, 110.9, 31.4, 31.2, 15.4. HRMS (ESI-TOF,  $m/z$ ): calcd for  $\text{C}_{29}\text{H}_{25}\text{N}_3\text{ONa}^+$ ,  $[\text{M} + \text{Na}]^+$ , 486.1611, found 486.1610.

#### 1-(4-(Methylthio)but-1-en-2-yl)-2,5-diphenyl-4-(1-(*m*-tolyl)vinyl)-1,2-dihydro-3H-pyrazol-3-one (3i)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3i** was purified through column



chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (79 mg, 87% yield). IR  $\nu_{\max}$  (neat)/cm<sup>-1</sup>: 3106, 2932, 1688, 1492, 1356, 1149, 1028, 972, 855; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.64 (dd,  $J$  = 1.2, 8.4 Hz, 2H), 7.47 (t,  $J$  = 7.8 Hz, 2H), 7.34 (d,  $J$  = 7.2 Hz, 2H), 7.29 (t,  $J$  = 7.8 Hz, 1H), 7.26 (d,  $J$  = 7.2 Hz, 1H), 7.23 (t,  $J$  = 7.2 Hz, 2H), 7.13 (d,  $J$  = 7.8 Hz, 1H), 7.09 (d,  $J$  = 6.0 Hz, 1H), 7.06 (d,  $J$  = 7.2 Hz, 1H), 6.94 (d,  $J$  = 7.2 Hz, 1H), 5.67 (d,  $J$  = 1.2 Hz, 1H), 5.64 (d,  $J$  = 1.2 Hz, 1H), 5.44 (s, 1H), 5.05 (s, 1H), 2.26 (t,  $J$  = 7.8 Hz, 2H), 2.25 (s, 3H), 2.06 (t,  $J$  = 7.8 Hz, 2H), 1.95 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  164.6, 155.5, 145.1, 140.1, 138.4, 137.2, 136.0, 130.0, 129.5, 129.3, 128.7, 128.0, 127.8, 127.8, 127.7, 126.3, 124.1, 118.5, 117.8, 114.3, 31.3, 31.1, 21.2, 15.3. HRMS (ESI-TOF,  $m/z$ ): calcd for C<sub>29</sub>H<sub>29</sub>N<sub>2</sub>OS<sup>+</sup>, [M + H]<sup>+</sup>, 453.1995, found 453.1993.

#### 4-(1-(3-Methoxyphenyl)vinyl)-1-(4-(methylthio)but-1-en-2-yl)-2,5-diphenyl-1,2-dihydro-3H-pyrazol-3-one (3j)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3j** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (77 mg, 82% yield). IR  $\nu_{\max}$  (neat)/cm<sup>-1</sup>: 3088, 2898, 1667, 1584, 1492, 1336, 1177, 1062, 946; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.62 (d,  $J$  = 7.2 Hz, 2H), 7.46 (t,  $J$  = 7.8 Hz, 2H), 7.34 (d,  $J$  = 7.2 Hz, 2H), 7.30–7.26 (m, 2H), 7.23 (t,  $J$  = 7.2 Hz, 2H), 7.08 (t,  $J$  = 7.8 Hz, 1H), 6.92 (d,  $J$  = 7.8 Hz, 1H), 6.83 (s, 1H), 6.68 (dd,  $J$  = 1.8, 7.8 Hz, 1H), 5.68 (d,  $J$  = 1.2 Hz, 1H), 5.67 (s, 1H), 5.43 (s, 1H), 5.05 (s, 1H), 3.74 (s, 3H), 2.24 (t,  $J$  = 7.8 Hz, 2H), 2.05 (t,  $J$  = 7.8 Hz, 2H), 1.94 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  164.5, 159.4, 155.5, 145.1, 141.7, 138.2, 135.9, 130.0, 129.6, 129.2, 128.9, 128.7, 127.8, 126.4, 124.1, 119.7, 118.9, 117.9, 114.2, 113.0, 112.9, 55.1, 31.3, 31.1, 15.3. HRMS (ESI-TOF,  $m/z$ ): calcd for C<sub>29</sub>H<sub>28</sub>N<sub>2</sub>NaO<sub>2</sub>S<sup>+</sup>, [M + Na]<sup>+</sup>, 491.1764, found 491.1764.

#### 4-(1-(3-Chlorophenyl)vinyl)-1-(4-(methylthio)but-1-en-2-yl)-2,5-diphenyl-1,2-dihydro-3H-pyrazol-3-one (3k)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3k** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (80 mg, 85% yield). IR  $\nu_{\max}$  (neat)/cm<sup>-1</sup>: 3074, 2973, 1679, 1563, 1455, 1383, 1257, 1061, 977; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.61 (d,  $J$  = 7.2 Hz, 2H), 7.47 (t,  $J$  = 7.8 Hz, 2H), 7.31–7.30 (m, 3H), 7.29–7.21 (m, 4H), 7.15 (dt,  $J$  = 1.8, 4.8 Hz, 1H), 7.05 (d,  $J$  = 4.8 Hz, 2H), 5.81 (d,  $J$  = 1.2 Hz, 1H), 5.66 (d,  $J$  = 1.2 Hz, 1H), 5.42 (s, 1H), 5.05 (s, 1H), 2.23 (t,  $J$  = 7.8 Hz, 2H), 2.04 (t,  $J$  = 7.8 Hz, 2H), 1.94 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  164.3, 155.4, 144.8, 142.2, 137.2, 135.8, 133.8, 130.0, 129.7, 129.1, 128.8, 127.9, 127.3, 127.1, 126.5, 125.2, 124.2, 119.8, 118.0, 113.1, 31.3, 31.2, 15.3. HRMS (ESI-TOF,  $m/z$ ): calcd for C<sub>28</sub>H<sub>25</sub>ClN<sub>2</sub>NaOS<sup>+</sup>, [M + Na]<sup>+</sup>, 495.1268, found 495.1265.

#### 1-(4-(Methylthio)but-1-en-2-yl)-2,5-diphenyl-4-(1-(*o*-tolyl)vinyl)-1,2-dihydro-3H-pyrazol-3-one (3l)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3l** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as

a foam solid (80 mg, 88% yield). IR  $\nu_{\max}$  (neat)/cm<sup>-1</sup>: 3106, 3023, 2984, 1688, 1492, 1356, 1149, 1028, 972, 855; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.59 (d,  $J$  = 7.2 Hz, 2H), 7.47 (t,  $J$  = 7.2 Hz, 2H), 7.30 (t,  $J$  = 7.2 Hz, 1H), 7.19–7.16 (m, 1H), 7.12–7.09 (m, 4H), 6.95 (dd,  $J$  = 1.2, 7.2 Hz, 1H), 6.90 (dt,  $J$  = 1.2, 7.2 Hz, 1H), 6.86 (t,  $J$  = 7.2 Hz, 1H), 6.81 (d,  $J$  = 7.8 Hz, 1H), 6.25 (d,  $J$  = 1.8 Hz, 1H), 5.37 (d,  $J$  = 1.8 Hz, 1H), 5.22 (s, 1H), 4.93 (s, 1H), 2.20 (t,  $J$  = 7.8 Hz, 2H), 2.10 (s, 3H), 2.00 (t,  $J$  = 7.8 Hz, 2H), 1.93 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  164.2, 154.4, 144.5, 141.1, 138.3, 135.9, 135.7, 134.8, 129.7, 129.6, 129.5, 129.1, 128.7, 127.3, 126.7, 126.4, 124.9, 124.0, 120.1, 117.0, 112.9, 31.5, 31.0, 19.9, 15.2. HRMS (ESI-TOF,  $m/z$ ): calcd for C<sub>29</sub>H<sub>28</sub>N<sub>2</sub>NaOS<sup>+</sup>, [M + Na]<sup>+</sup>, 475.1815, found 475.1813.

#### 4-(1-(2-Methoxyphenyl)vinyl)-1-(4-(methylthio)but-1-en-2-yl)-2,5-diphenyl-1,2-dihydro-3H-pyrazol-3-one (3m)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3m** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (79 mg, 84% yield). IR  $\nu_{\max}$  (neat)/cm<sup>-1</sup>: 3078, 2983, 1660, 1576, 1469, 1337, 1147, 1053, 983; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.59 (d,  $J$  = 7.2 Hz, 2H), 7.45 (t,  $J$  = 7.8 Hz, 2H), 7.27–7.25 (m, 3H), 7.21 (t,  $J$  = 7.2 Hz, 1H), 7.15 (t,  $J$  = 7.2 Hz, 2H), 7.13 (d,  $J$  = 7.2 Hz, 1H), 7.04 (dt,  $J$  = 1.8, 8.4 Hz, 1H), 6.75 (dt,  $J$  = 0.6, 7.2 Hz, 1H), 6.53 (d,  $J$  = 8.4 Hz, 1H), 6.03 (d,  $J$  = 1.8 Hz, 1H), 5.44 (d,  $J$  = 1.8 Hz, 1H), 5.30 (s, 1H), 4.96 (s, 1H), 3.68 (s, 3H), 2.22 (t,  $J$  = 7.8 Hz, 2H), 2.02 (t,  $J$  = 7.8 Hz, 2H), 1.93 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  164.6, 156.4, 154.4, 145.1, 136.2, 130.6, 130.1, 129.4, 129.1, 128.6, 128.4, 127.3, 126.1, 123.9, 120.2, 117.1, 113.8, 110.5, 55.3, 31.2, 15.2. HRMS (ESI-TOF,  $m/z$ ): calcd for C<sub>29</sub>H<sub>28</sub>N<sub>2</sub>NaO<sub>2</sub>S<sup>+</sup>, [M + Na]<sup>+</sup>, 491.1764, found 491.1766.

#### 4-(1-(2-Chlorophenyl)vinyl)-1-(4-(methylthio)but-1-en-2-yl)-2,5-diphenyl-1,2-dihydro-3H-pyrazol-3-one (3n)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3n** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (84 mg, 89% yield). IR  $\nu_{\max}$  (neat)/cm<sup>-1</sup>: 3056, 2933, 1679, 1586, 1453, 1332, 1175, 1026, 944; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.58 (d,  $J$  = 7.2 Hz, 2H), 7.45 (t,  $J$  = 7.2 Hz, 2H), 7.29 (t,  $J$  = 7.2 Hz, 1H), 7.23–7.18 (m, 3H), 7.17 (d,  $J$  = 6.6 Hz, 2H), 7.07 (dd,  $J$  = 1.8, 6.6 Hz, 1H), 7.03 (dd,  $J$  = 1.8, 6.6 Hz, 1H), 6.96–6.92 (m, 2H), 6.23 (d,  $J$  = 1.2 Hz, 1H), 5.43 (d,  $J$  = 1.2 Hz, 1H), 5.24 (s, 1H), 4.94 (s, 1H), 2.22 (t,  $J$  = 7.8 Hz, 2H), 2.02 (t,  $J$  = 7.8 Hz, 2H), 1.93 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  164.2, 154.2, 144.5, 139.9, 136.5, 135.9, 132.3, 131.3, 129.9, 129.2, 129.1, 128.7, 128.0, 127.5, 126.4, 126.0, 124.1, 121.1, 117.1, 112.0, 31.7, 31.0, 15.2. HRMS (ESI-TOF,  $m/z$ ): calcd for C<sub>28</sub>H<sub>25</sub>ClN<sub>2</sub>NaOS<sup>+</sup>, [M + Na]<sup>+</sup>, 495.1268, found 495.1270.

#### 1-(4-(Methylthio)but-1-en-2-yl)-4-(1-(naphthalen-2-yl)vinyl)-2,5-diphenyl-1,2-dihydro-3H-pyrazol-3-one (3o)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3o** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and



obtained as a foam solid (65 mg, 66% yield). IR  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$ : 3113, 2965, 1680, 1566, 1473, 1357, 1121, 1073, 961;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.87 (dd,  $J = 2.4, 7.2$  Hz, 1H), 7.62 (d,  $J = 4.8$  Hz, 1H), 7.61 (t,  $J = 7.2$  Hz, 2H), 7.49 (t,  $J = 7.2$  Hz, 2H), 7.44 (d,  $J = 7.8$  Hz, 1H), 7.38–7.36 (m, 2H), 7.32 (t,  $J = 7.2$  Hz, 1H), 7.13–7.08 (m, 2H), 6.95 (t,  $J = 7.2$  Hz, 1H), 6.79 (t,  $J = 7.2$  Hz, 2H), 6.68 (d,  $J = 7.8$  Hz, 2H), 6.61 (d,  $J = 2.4$  Hz, 1H), 5.58 (d,  $J = 2.4$  Hz, 1H), 5.06 (s, 1H), 4.83 (s, 1H), 2.16 (t,  $J = 7.8$  Hz, 2H), 1.98 (t,  $J = 7.8$  Hz, 2H), 1.91 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.3, 154.8, 144.3, 139.5, 137.4, 136.0, 133.4, 131.4, 129.5, 128.8, 128.7, 127.9, 127.3, 127.0, 126.8, 126.5, 126.0, 125.5, 125.2, 124.8, 124.1, 120.8, 116.7, 112.9, 32.0, 31.1, 15.3. HRMS (ESI-TOF,  $m/z$ ): calcd for  $\text{C}_{32}\text{H}_{28}\text{ClN}_2\text{NaOS}^+$ ,  $[\text{M} + \text{Na}]^+$ , 511.1815, found 511.1818.

#### 1-(4-(Methylthio)but-1-en-2-yl)-4-(1-(naphthalen-2-yl)vinyl)-2,5-diphenyl-1,2-dihydro-3H-pyrazol-3-one (3p)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3p** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (74 mg, 76% yield). IR  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$ : 3039, 2976, 1677, 1562, 1473, 1390, 1124, 973, 837;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.76 (d,  $J = 4.8$  Hz, 2H), 7.74 (d,  $J = 7.2$  Hz, 1H), 7.68–7.65 (m, 3H), 7.51–7.48 (m, 3H), 7.44–7.40 (m, 2H), 7.38–7.37 (m, 2H), 7.31 (t,  $J = 7.2$  Hz, 1H), 7.16–7.14 (m, 3H), 5.84 (s, 1H), 5.74 (s, 1H), 5.47 (s, 1H), 5.07 (s, 1H), 2.29 (t,  $J = 7.8$  Hz, 2H), 2.11 (t,  $J = 7.8$  Hz, 2H), 1.97 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.6, 155.7, 145.1, 138.3, 137.7, 135.9, 133.2, 132.8, 129.9, 129.5, 129.1, 128.7, 128.1, 127.8, 127.5, 127.3, 126.4, 126.0, 125.7, 125.6, 125.1, 124.1, 119.2, 117.9, 114.3, 31.3, 31.2, 15.3. HRMS (ESI-TOF,  $m/z$ ): calcd for  $\text{C}_{32}\text{H}_{28}\text{ClN}_2\text{NaOS}^+$ ,  $[\text{M} + \text{Na}]^+$ , 511.1815, found 511.1816.

#### 4-(1-(6-Methoxynaphthalen-2-yl)vinyl)-1-(4-(methylthio)but-1-en-2-yl)-2,5-diphenyl-1,2-dihydro-3H-pyrazol-3-one (3q)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3q** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (86 mg, 83% yield). IR  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$ : 3027, 2917, 1673, 1510, 1445, 1307, 1011, 904, 816;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.69–7.65 (m, 4H), 7.56 (d,  $J = 9.0$  Hz, 1H), 7.50–7.47 (m, 3H), 7.39–7.38 (m, 2H), 7.30 (t,  $J = 7.2$  Hz, 1H), 7.17–7.16 (m, 4H), 7.11 (dd,  $J = 2.4, 9.0$  Hz, 1H), 7.05 (d,  $J = 2.4$  Hz, 1H), 5.81 (d,  $J = 0.6$  Hz, 1H), 5.67 (s, 1H), 5.47 (s, 1H), 5.07 (s, 1H), 3.89 (s, 3H), 2.28 (t,  $J = 7.8$  Hz, 2H), 2.10 (t,  $J = 7.8$  Hz, 2H), 1.96 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.5, 157.6, 155.6, 145.0, 138.2, 135.9, 135.4, 133.9, 129.8, 129.5, 129.1, 128.7, 127.7, 126.4, 126.3, 125.7, 125.4, 124.0, 118.4, 118.4, 117.9, 114.5, 105.8, 55.1, 31.2, 31.1, 15.3. HRMS (ESI-TOF,  $m/z$ ): calcd for  $\text{C}_{33}\text{H}_{30}\text{N}_2\text{NaO}_2\text{S}^+$ ,  $[\text{M} + \text{Na}]^+$ , 541.1920, found 541.1922.

#### 1-(4-(Methylthio)but-1-en-2-yl)-2,5-diphenyl-4-(thiophen-2-yl)-1,2-dihydro-3H-pyrazol-3-one (3r)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3r** was purified through

column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (51 mg, 57% yield). IR  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$ : 3032, 2987, 1681, 1527, 1397, 1262, 1098, 1002, 935, 882;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.63 (d,  $J = 7.8$  Hz, 2H), 7.48–7.45 (m, 4H), 7.37–7.29 (m, 4H), 7.09 (d,  $J = 5.4$  Hz, 1H), 6.95 (d,  $J = 3.6$  Hz, 1H), 6.84 (dd,  $J = 3.6, 5.4$  Hz, 1H), 5.73 (s, 1H), 5.48 (s, 1H), 5.34 (s, 1H), 5.08 (s, 1H), 2.26 (t,  $J = 7.8$  Hz, 2H), 2.06 (t,  $J = 7.8$  Hz, 2H), 1.94 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.1, 155.7, 145.0, 143.9, 135.8, 131.8, 129.8, 129.6, 129.0, 128.7, 128.0, 127.0, 126.4, 125.1, 124.9, 124.4, 124.3, 124.2, 118.1, 117.5, 114.2, 31.2, 31.0, 15.3. HRMS (ESI-TOF,  $m/z$ ): calcd for  $\text{C}_{26}\text{H}_{25}\text{N}_2\text{OS}^+$ ,  $[\text{M} + \text{H}]^+$ , 445.1403, found 445.1405.

#### 4-(1-(1-Methyl-1H-pyrrol-2-yl)vinyl)-1-(4-(methylthio)but-1-en-2-yl)-2,5-diphenyl-1,2-dihydro-3H-pyrazol-3-one (3s)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3s** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (62 mg, 70% yield). IR  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$ : 3072, 2976, 1672, 1476, 1331, 1229, 1152, 1034, 913, 826;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.59 (d,  $J = 7.8$  Hz, 2H), 7.46 (t,  $J = 7.8$  Hz, 2H), 7.31 (t,  $J = 7.8$  Hz, 4H), 7.28–7.25 (m, 2H), 6.29 (t,  $J = 2.4$  Hz, 1H), 5.92 (dd,  $J = 1.8, 3.0$  Hz, 1H), 5.85 (d,  $J = 1.8$  Hz, 1H), 5.84 (s, 1H), 5.43 (d,  $J = 1.8$  Hz, 1H), 5.38 (s, 1H), 5.02 (s, 1H), 3.42 (s, 3H), 2.22 (t,  $J = 7.8$  Hz, 2H), 2.01 (t,  $J = 7.8$  Hz, 2H), 1.93 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.3, 155.0, 144.9, 135.8, 133.2, 129.7, 129.5, 128.7, 127.6, 126.4, 124.1, 122.8, 119.4, 117.7, 114.0, 109.8, 107.2, 34.5, 31.2, 15.3. HRMS (ESI-TOF,  $m/z$ ): calcd for  $\text{C}_{27}\text{H}_{27}\text{N}_3\text{NaOS}^+$ ,  $[\text{M} + \text{Na}]^+$ , 464.1767, found 464.1772.

#### 1-(4-(Methylthio)but-1-en-2-yl)-2,5-diphenyl-4-(prop-1-en-2-yl)-1,2-dihydro-3H-pyrazol-3-one (3t)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3t** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (54 mg, 72% yield). IR  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$ : 3051, 2982, 1672, 1568, 2448, 1379, 1253, 1062, 937, 784;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.55 (d,  $J = 7.8$  Hz, 2H), 7.47–7.43 (m, 7H), 7.28 (t,  $J = 7.2$  Hz, 1H), 5.46 (s, 1H), 5.31 (s, 1H), 5.15 (s, 1H), 4.98 (s, 1H), 2.21 (t,  $J = 7.8$  Hz, 2H), 1.99 (t,  $J = 7.8$  Hz, 2H), 1.93 (s, 3H), 1.77 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.3, 153.7, 144.9, 135.9, 133.8, 130.2, 129.8, 128.7, 128.2, 126.4, 124.1, 117.4, 117.2, 114.7, 31.3, 31.2, 22.6, 15.3. HRMS (ESI-TOF,  $m/z$ ): calcd for  $\text{C}_{23}\text{H}_{25}\text{N}_2\text{OS}^+$ ,  $[\text{M} + \text{H}]^+$ , 377.5255, found 377.5256.

#### 1-(4-(Methylthio)but-1-en-2-yl)-2,5-diphenyl-4-(thiophen-2-yl)-1,2-dihydro-3H-pyrazol-3-one (3aa)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3aa** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (57 mg, 63% yield). IR  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$ : 3022, 2918, 1672, 1580, 1397, 1301, 1189, 1011, 934, 781;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.49 (d,  $J = 8.4$  Hz, 2H), 7.34–7.30 (m, 4H), 7.28–7.24 (m, 3H), 7.21 (t,  $J = 7.2$  Hz, 2H), 7.16 (t,  $J =$



7.2 Hz, 2H), 7.11 (t,  $J = 7.2$  Hz, 1H), 5.68 (d,  $J = 1.2$  Hz, 1H), 5.67 (d,  $J = 1.2$  Hz, 1H), 5.41 (s, 1H), 5.04 (s, 1H), 2.40 (s, 3H), 2.25 (t,  $J = 7.8$  Hz, 2H), 2.05 (t,  $J = 7.8$  Hz, 2H), 1.95 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.5, 155.1, 145.1, 140.3, 138.4, 136.3, 133.4, 130.0, 129.5, 129.3, 127.8, 127.8, 127.1, 126.9, 124.3, 118.7, 117.8, 114.1, 31.2, 20.9, 15.3. HRMS (ESI-TOF,  $m/z$ ): calcd for  $\text{C}_{29}\text{H}_{28}\text{N}_2\text{NaOS}^+$ ,  $[\text{M} + \text{Na}]^+$ , 475.1815, found 475.1817.

#### 2-(4-Methoxyphenyl)-1-(4-(methylthio)but-1-en-2-yl)-5-phenyl-4-(1-phenylvinyl)-1,2-dihydro-3H-pyrazol-3-one (3ab)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3ab** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (56 mg, 60% yield). IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 3030, 2944, 1677, 1589, 1491, 1270, 1086, 933, 812;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.50 (d,  $J = 9.0$  Hz, 2H), 7.32–7.30 (m, 4H), 7.25 (t,  $J = 7.2$  Hz, 1H), 7.20 (t,  $J = 7.2$  Hz, 2H), 7.15 (t,  $J = 7.2$  Hz, 2H), 7.11 (t,  $J = 7.2$  Hz, 1H), 6.99 (d,  $J = 9.0$  Hz, 2H), 5.67 (s, 1H), 5.66 (s, 1H), 5.39 (s, 1H), 5.05 (s, 1H), 3.84 (s, 3H), 2.25 (t,  $J = 7.8$  Hz, 2H), 2.04 (t,  $J = 7.8$  Hz, 2H), 1.95 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.7, 158.5, 154.7, 145.1, 140.4, 138.5, 130.0, 129.5, 129.4, 128.9, 127.9, 127.8, 127.2, 127.0, 126.3, 118.7, 118.0, 114.3, 114.0, 55.5, 31.3, 15.3. HRMS (ESI-TOF,  $m/z$ ): calcd for  $\text{C}_{29}\text{H}_{29}\text{N}_2\text{OS}^+$ ,  $[\text{M} + \text{H}]^+$ , 469.1944, found 469.1946.

#### 2-(4-Fluorophenyl)-1-(4-(methylthio)but-1-en-2-yl)-5-phenyl-4-(1-phenylvinyl)-1,2-dihydro-3H-pyrazol-3-one (3ac)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3ac** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (67 mg, 73% yield). IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 3037, 2975, 1658, 1589, 1452, 1358, 1284, 1031, 982;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.60–7.57 (m, 2H), 7.32 (dd,  $J = 7.2$ , 8.4 Hz, 2H), 7.29 (t,  $J = 6.6$  Hz, 2H), 7.26 (d,  $J = 7.2$  Hz, 1H), 7.22 (t,  $J = 7.2$  Hz, 2H), 7.18–7.15 (m, 4H), 7.13 (t,  $J = 7.2$  Hz, 1H), 5.68 (d,  $J = 1.2$  Hz, 1H), 5.64 (d,  $J = 1.2$  Hz, 1H), 5.42 (s, 1H), 5.07 (s, 1H), 2.26 (t,  $J = 7.8$  Hz, 2H), 2.04 (t,  $J = 7.8$  Hz, 2H), 1.95 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.8, 161.9, 160.3, 155.7, 145.2, 140.2, 138.4, 132.1, 130.0, 129.7, 129.2, 128.0, 127.3, 126.9, 126.1, 126.1, 119.0, 118.0, 115.8, 115.6, 114.3, 31.4, 31.1, 15.4.  $^{19}\text{F}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  –114.98. HRMS (ESI-TOF,  $m/z$ ): calcd for  $\text{C}_{28}\text{H}_{26}\text{FN}_2\text{OS}^+$ ,  $[\text{M} + \text{H}]^+$ , 457.1744, found 457.1746.

#### 2-(4-Bromophenyl)-5-(4-methoxyphenyl)-1-(4-(methylthio)but-1-en-2-yl)-4-(1-phenylvinyl)-1,2-dihydro-3H-pyrazol-3-one (3ad)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3ad** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (68 mg, 66% yield). IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 3033, 2989, 1668, 1565, 1487, 1312, 1220, 1101, 979, 856;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.59 (d,  $J = 7.8$  Hz, 2H), 7.52 (d,  $J = 8.4$  Hz, 2H), 7.33 (d,  $J = 7.2$  Hz, 2H), 7.30 (d,  $J = 7.2$  Hz, 2H), 7.26 (d,  $J = 7.2$  Hz, 1H), 7.23 (t,  $J = 7.2$  Hz, 2H), 7.17 (t,  $J = 7.2$  Hz, 2H), 7.13 (t,  $J = 7.2$  Hz, 1H), 5.68 (d,  $J = 0.6$  Hz, 1H), 5.62 (d,  $J = 0.6$  Hz, 1H), 5.44 (s, 1H), 5.08 (s, 1H), 2.26 (t,  $J = 7.8$  Hz, 2H), 2.04

(t,  $J = 7.8$  Hz, 2H), 1.95 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.5, 156.1, 145.2, 140.1, 138.2, 135.1, 131.9, 130.0, 129.8, 129.7, 129.0, 127.9, 127.3, 126.9, 125.3, 119.8, 119.0, 118.0, 114.5, 31.4, 30.9, 15.4. HRMS (ESI-TOF,  $m/z$ ): calcd for  $\text{C}_{28}\text{H}_{25}\text{BrN}_2\text{NaOS}^+$ ,  $[\text{M} + \text{Na}]^+$ , 539.0763, found 539.0763.

#### 2-(2-Ethylphenyl)-1-(4-(methylthio)but-1-en-2-yl)-5-phenyl-4-(1-phenylvinyl)-1,2-dihydro-3H-pyrazol-3-one (3ae)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3ae** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (47 mg, 50% yield). IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 3038, 2933, 1681, 157, 1392, 1267, 1083, 962, 828;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.42 (d,  $J = 6.6$  Hz, 1H), 7.39 (dt,  $J = 1.2$ , 7.2 Hz, 1H), 7.35 (d,  $J = 7.2$  Hz, 1H), 7.32–7.29 (m, 5H), 7.23 (d,  $J = 7.2$  Hz, 1H), 7.19 (t,  $J = 7.2$  Hz, 2H), 7.13 (t,  $J = 7.2$  Hz, 2H), 7.09 (t,  $J = 7.2$  Hz, 1H), 5.74 (d,  $J = 1.2$  Hz, 1H), 5.72 (d,  $J = 1.2$  Hz, 1H), 5.20 (s, 1H), 4.99 (s, 1H), 2.91–2.84 (m, 1H), 2.73–2.67 (m, 1H), 2.27–2.24 (m, 2H), 2.11–2.07 (m, 2H), 1.94 (s, 3H), 1.34 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.6, 154.1, 144.8, 142.8, 140.5, 138.5, 134.4, 129.8, 129.5, 129.4, 129.0, 127.9, 127.8, 127.1, 127.0, 126.2, 118.8, 118.0, 113.0, 32.1, 31.1, 23.9, 15.4, 14.0. HRMS (ESI-TOF,  $m/z$ ): calcd for  $\text{C}_{30}\text{H}_{30}\text{N}_2\text{NaOS}^+$ ,  $[\text{M} + \text{Na}]^+$ , 489.1971, found 489.1972.

#### 2-(2-Fluorophenyl)-1-(4-(methylthio)but-1-en-2-yl)-5-phenyl-4-(1-phenylvinyl)-1,2-dihydro-3H-pyrazol-3-one (3af)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3af** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (50 mg, 55% yield). IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 3062, 2983, 1668, 1549, 1433, 1327, 1252, 1098, 972, 819;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.51 (t,  $J = 6.0$  Hz, 1H), 7.41–7.37 (m, 1H), 7.33–7.25 (m, 4H), 7.23 (d,  $J = 7.8$  Hz, 3H), 7.20 (t,  $J = 7.2$  Hz, 2H), 7.13 (t,  $J = 7.2$  Hz, 2H), 7.09 (t,  $J = 7.2$  Hz, 1H), 5.74 (d,  $J = 1.2$  Hz, 1H), 5.70 (d,  $J = 1.2$  Hz, 1H), 5.39 (s, 1H), 5.05 (s, 1H), 2.27 (t,  $J = 7.8$  Hz, 2H), 2.08 (t,  $J = 7.8$  Hz, 2H), 1.94 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.2, 158.8, 157.2, 155.2, 144.8, 140.3, 138.3, 130.1, 130.0, 129.8, 129.6, 129.1, 127.9, 127.8, 127.1, 127.0, 124.3, 118.8, 118.4, 116.8, 116.7, 113.1, 31.5, 31.2, 15.3.  $^{19}\text{F}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  –118.90. HRMS (ESI-TOF,  $m/z$ ): calcd for  $\text{C}_{28}\text{H}_{25}\text{FN}_2\text{NaOS}^+$ ,  $[\text{M} + \text{Na}]^+$ , 479.1564, found 479.1566.

#### 1-(4-(Methylthio)but-1-en-2-yl)-2-(perfluorophenyl)-5-phenyl-4-(1-phenylvinyl)-1,2-dihydro-3H-pyrazol-3-one (3ag)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3ag** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (74 mg, 70% yield). IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 3066, 2952, 1561, 1445, 1270, 1184, 1077, 977, 835;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.32 (d,  $J = 6.6$  Hz, 2H), 7.28–7.26 (m, 3H), 7.20 (t,  $J = 7.2$  Hz, 2H), 7.14 (dd,  $J = 6.0$ , 7.8 Hz, 2H), 7.10 (t,  $J = 7.2$  Hz, 1H), 5.75 (d,  $J = 1.2$  Hz, 1H), 5.71 (d,  $J = 1.2$  Hz, 1H), 5.40 (s, 1H), 5.14 (s, 1H), 2.33 (t,  $J = 7.8$  Hz, 2H), 2.11 (t,  $J = 7.8$  Hz, 2H), 1.96 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):



$\delta$  165.9, 157.2, 145.9, 145.3, 144.2, 141.3, 139.9, 138.9, 137.8, 137.2, 130.2, 130.0, 129.7, 129.6, 128.6, 128.1, 128.0, 127.4, 126.9, 119.3, 118.5, 113.1, 111.8, 31.1, 31.1, 15.3.  $^{19}\text{F}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  -142.99, -143.02, -151.13, -151.17, -151.21, -161.11, -161.14, -161.14, -161.18. HRMS (ESI-TOF,  $m/z$ ): calcd for  $\text{C}_{28}\text{H}_{21}\text{F}_5\text{N}_2\text{NaOS}^+$ ,  $[\text{M} + \text{Na}]^+$ , 551.1187, found 551.1188.

#### 5-(4-Fluorophenyl)-1-(4-(methylthio)but-1-en-2-yl)-2-phenyl-4-(1-phenylvinyl)-1,2-dihydro-3H-pyrazol-3-one (3ah)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3ah** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (47 mg, 51% yield). IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 3036, 2942, 1670, 1589, 1433, 1362, 1098, 937, 828;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.61 (d,  $J$  = 7.8 Hz, 2H), 7.47 (t,  $J$  = 7.8 Hz, 2H), 7.32–7.30 (m, 3H), 7.27 (dd,  $J$  = 1.2, 7.8 Hz, 2H), 7.17–7.13 (m, 3H), 6.90 (t,  $J$  = 9.0 Hz, 2H), 5.72 (d,  $J$  = 1.2 Hz, 1H), 5.70 (d,  $J$  = 1.2 Hz, 1H), 5.44 (s, 1H), 5.08 (s, 1H), 2.24 (t,  $J$  = 7.8 Hz, 2H), 2.03 (t,  $J$  = 7.8 Hz, 2H), 1.95 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.5, 164.2, 162.5, 154.3, 145.2, 140.2, 138.2, 135.9, 132.0, 132.0, 128.8, 128.0, 127.4, 127.0, 126.5, 125.3, 124.2, 119.1, 118.2, 115.2, 115.1, 114.5, 31.3, 31.0, 15.4.  $^{19}\text{F}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  -110.07. HRMS (ESI-TOF,  $m/z$ ): calcd for  $\text{C}_{28}\text{H}_{26}\text{FN}_2\text{OS}^+$ ,  $[\text{M} + \text{H}]^+$ , 457.1744, found 457.1744.

#### 5-(4-Methoxyphenyl)-1-(4-(methylthio)but-1-en-2-yl)-4-(1-phenylvinyl)-2-(*p*-tolyl)-1,2-dihydro-3H-pyrazol-3-one (3ai)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3ai** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (69 mg, 71% yield). IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 3052, 2989, 1671, 1489, 1345, 1287, 1176, 1044, 929, 817;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.48 (d,  $J$  = 8.4 Hz, 2H), 7.33 (d,  $J$  = 7.2 Hz, 2H), 7.27 (t,  $J$  = 8.4 Hz, 4H), 7.17 (t,  $J$  = 7.2 Hz, 2H), 7.13 (t,  $J$  = 7.2 Hz, 1H), 6.73 (d,  $J$  = 8.4 Hz, 2H), 5.70 (d,  $J$  = 1.2 Hz, 1H), 5.64 (s, 1H), 5.43 (s, 1H), 5.06 (s, 1H), 3.75 (s, 3H), 2.39 (s, 3H), 2.25 (t,  $J$  = 7.8 Hz, 2H), 2.04 (t,  $J$  = 7.8 Hz, 2H), 1.95 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.8, 160.6, 155.1, 145.4, 140.2, 138.5, 136.2, 133.5, 131.4, 129.3, 127.8, 127.1, 126.8, 124.3, 121.4, 118.5, 117.9, 113.4, 55.1, 31.3, 31.0, 20.9, 15.3. HRMS (ESI-TOF,  $m/z$ ): calcd for  $\text{C}_{30}\text{H}_{30}\text{N}_2\text{NaO}_2\text{S}^+$ ,  $[\text{M} + \text{Na}]^+$ , 505.1920, found 505.1920.

#### 5-(4-Bromophenyl)-1-(4-(methylthio)but-1-en-2-yl)-4-(1-phenylvinyl)-2-(*p*-tolyl)-1,2-dihydro-3H-pyrazol-3-one (3aj)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3aj** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (53 mg, 50% yield). IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 3039, 2962, 1670, 1527, 1363, 1299, 1108, 1036, 898;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.46 (d,  $J$  = 8.4 Hz, 2H), 7.35 (d,  $J$  = 8.4 Hz, 2H), 7.28–7.26 (m, 4H), 7.19–7.16 (m, 5H), 5.69 (s, 1H), 5.68 (s, 1H), 5.40 (s, 1H), 5.07 (s, 1H), 2.40 (s, 3H), 2.25 (t,  $J$  = 7.8 Hz, 2H), 2.02 (t,  $J$  = 7.8 Hz, 2H), 1.96 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.4, 153.7, 145.2, 140.3, 138.3, 136.6,

133.3, 132.0, 131.5, 131.2, 131.1, 129.5, 128.3, 128.1, 127.4, 127.0, 124.4, 124.2, 124.1, 119.1, 118.8, 118.1, 114.8, 31.4, 31.2, 21.0, 15.4. HRMS (ESI-TOF,  $m/z$ ): calcd for  $\text{C}_{29}\text{H}_{28}\text{BrN}_2\text{OS}^+$ ,  $[\text{M} + \text{H}]^+$ , 531.1100, found 531.1103.

#### 5-Methyl-1-(4-(methylthio)but-1-en-2-yl)-2-phenyl-4-(1-phenylvinyl)-1,2-dihydro-3H-pyrazol-3-one (3ak)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3ak** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (62 mg, 83% yield). IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 3072, 2916, 1667, 1539, 1420, 1331, 1298, 1032, 919, 827;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.49 (d,  $J$  = 7.2 Hz, 2H), 7.49–7.40 (m, 2H), 7.34 (t,  $J$  = 7.2 Hz, 2H), 7.29 (t,  $J$  = 7.2 Hz, 1H), 7.25 (t,  $J$  = 7.2 Hz, 1H), 5.73 (d,  $J$  = 1.2 Hz, 1H), 5.66 (d,  $J$  = 1.2 Hz, 1H), 5.38 (s, 1H), 5.27 (s, 1H), 2.36 (t,  $J$  = 7.2 Hz, 2H), 2.23 (t,  $J$  = 7.2 Hz, 2H), 2.03 (s, 3H), 1.98 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.8, 152.1, 143.7, 141.0, 138.6, 136.4, 128.7, 128.3, 127.5, 126.9, 126.0, 123.2, 117.9, 115.4, 110.8, 32.6, 30.9, 15.4, 13.0. HRMS (ESI-TOF,  $m/z$ ): calcd for  $\text{C}_{23}\text{H}_{25}\text{N}_2\text{OS}^+$ ,  $[\text{M} + \text{H}]^+$ , 377.1682, found 377.1686.

#### 5-Methyl-1-(4-(methylthio)but-1-en-2-yl)-2-phenyl-4-(prop-1-en-2-yl)-1,2-dihydro-3H-pyrazol-3-one (3al)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **3al** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (51 mg, 81% yield). IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 3046, 2982, 1670, 1533, 1478, 1324, 1278, 1109, 1082, 952;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.43–7.39 (m, 4H), 7.25–7.22 (m, 1H), 5.38 (s, 1H), 5.27 (s, 1H), 5.20 (d,  $J$  = 1.2 Hz, 1H), 5.09 (d,  $J$  = 1.2 Hz, 1H), 2.32 (s, 3H), 2.31 (t,  $J$  = 7.8 Hz, 2H), 2.18 (t,  $J$  = 7.8 Hz, 2H), 2.14 (s, 3H), 2.00 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.7, 150.4, 144.0, 136.4, 135.9, 128.7, 126.0, 123.3, 115.8, 115.3, 112.5, 32.5, 31.0, 22.3, 15.4, 12.8. HRMS (ESI-TOF,  $m/z$ ): calcd for  $\text{C}_{18}\text{H}_{22}\text{N}_2\text{NaOS}^+$ ,  $[\text{M} + \text{Na}]^+$ , 337.1345, found 337.1345.

#### Reaction of unsaturated pyrazolones **1a** with propargyl sulfide ylide **2b**

To a flame-dried sealable 3-dram vial equipped with a stir bar was added unsaturated pyrazolinones **1a** (68 mg, 0.2 mmol, 1.0 equiv.),  $\text{NaOAc} \cdot 3\text{H}_2\text{O}$  (14 mg, 0.1 mmol, 0.5 equiv.) and **2b** (50 mg, 0.24 mmol, 1.2 equiv.) under air. Subsequently treated  $\text{CH}_3\text{CN}$  (2 mL,  $c$  = 0.1 M) was added to vial *via* syringe. The reaction mixture was stirred for 15 min at 20 °C until unsaturated pyrazolones **1a** was fully consumed (monitored by TLC). Then the reaction was stirred at 0 °C for 20 h. The organic solvent was removed under reduced pressure and purified through column chromatography (eluent: petroleum ether and EtOAc) to afford the desired product **4** (23% yield, 22 mg) and **5** (47% yield, 41 mg).



### 1-(4-(Ethylthio)pent-1-en-2-yl)-2,5-diphenyl-4-(1-phenylvinyl)-1,2-dihydro-3H-pyrazol-3-one (4)

IR  $\nu_{\max}$  (neat)/cm<sup>-1</sup>: 3082, 2977, 2864, 1705, 1594, 1466, 1272, 1042, 967, 832; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.63 (dd,  $J$  = 1.2, 8.4 Hz, 2H), 7.47 (t,  $J$  = 7.8 Hz, 2H), 7.36 (d,  $J$  = 8.4 Hz, 2H), 7.32–7.25 (m, 4H), 7.22 (t,  $J$  = 7.2 Hz, 2H), 7.17–7.11 (m, 3H), 5.69 (d,  $J$  = 1.2 Hz, 1H), 5.63 (d,  $J$  = 1.2 Hz, 1H), 5.52 (s, 1H), 5.09 (s, 1H), 2.64–2.59 (m, 1H), 2.41 (q,  $J$  = 7.8 Hz, 2H), 2.19 (dd,  $J$  = 4.8, 15.6 Hz, 1H), 1.77 (dd,  $J$  = 9.6, 15.6 Hz, 1H), 1.18 (t,  $J$  = 7.2 Hz, 3H), 0.78 (d,  $J$  = 7.2 Hz, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  164.7, 155.6, 144.1, 140.3, 138.4, 136.2, 130.3, 129.7, 129.3, 128.7, 128.0, 127.9, 127.3, 127.0, 126.4, 124.2, 119.2, 118.9, 114.3, 39.2, 36.4, 24.6, 20.5, 14.7. HRMS (ESI-TOF,  $m/z$ ): calcd for C<sub>30</sub>H<sub>30</sub>N<sub>2</sub>NaOS<sup>+</sup>, [M + Na]<sup>+</sup>, 489.1971, found 489.1972.

### (E)-1-(1-(ethylthio)prop-1-en-2-yl)-2,5-diphenyl-4-(1-phenylvinyl)-1,2-dihydro-3H-pyrazol-3-one (5)

IR  $\nu_{\max}$  (neat)/cm<sup>-1</sup>: 3057, 2973, 2824, 1698, 1572, 1376, 1269, 1187, 1028, 932; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.58 (d,  $J$  = 7.2 Hz, 2H), 7.46 (t,  $J$  = 7.8 Hz, 2H), 7.33–7.30 (m, 5H), 7.26 (t,  $J$  = 7.2 Hz, 1H), 7.21 (t,  $J$  = 7.2 Hz, 2H), 7.16 (t,  $J$  = 7.2 Hz, 2H), 7.12 (t,  $J$  = 7.2 Hz, 1H), 6.34 (s, 1H), 5.69 (d,  $J$  = 1.2 Hz, 1H), 5.67 (d,  $J$  = 1.2 Hz, 1H), 2.53 (q,  $J$  = 7.2 Hz, 2H), 1.38 (s, 3H), 1.03 (t,  $J$  = 7.2 Hz, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  164.4, 155.5, 140.4, 138.6, 135.9, 133.3, 130.5, 129.8, 129.6, 129.5, 128.7, 127.9, 127.2, 127.1, 126.5, 124.7, 118.8, 114.8, 28.1, 15.4, 13.5. HRMS (ESI-TOF,  $m/z$ ): calcd for C<sub>28</sub>H<sub>27</sub>N<sub>2</sub>OS<sup>+</sup>, [M + H]<sup>+</sup>, 439.1839, found 439.1838.

### Reaction of unsaturated pyrazolones 1a with trimethylsilyl propargyl sulfide ylide 2c

To a flame-dried sealable 3-dram vial equipped with a stir bar was added unsaturated pyrazolinones **1a** (68 mg, 0.2 mmol, 1.0 equiv.), NaOAc·3H<sub>2</sub>O (14 mg, 0.1 mmol, 0.5 equiv.) and **2c** (61 mg, 0.24 mmol, 1.2 equiv.) under air. Subsequently treated CH<sub>3</sub>CN (2 mL,  $c$  = 0.1 M) was added to vial *via* syringe. The reaction mixture was stirred for 15 min at 20 °C until unsaturated pyrazolones **1a** was fully consumed (monitored by TLC). Then the reaction was stirred at 0 °C for 6 h. The organic solvent was removed under reduced pressure and purified through column chromatography (eluent: petroleum ether and EtOAc) to afford the desired product **3a** (79% yield, 70 mg).

### Reaction of unsaturated pyrazolones 1a with methyl propargyl sulfide ylide 2d

To a flame-dried sealable 3-dram vial equipped with a stir bar was added unsaturated pyrazolinones **1a** (68 mg, 0.2 mmol, 1.0 equiv.), Cs<sub>2</sub>CO<sub>3</sub> (33 mg, 0.1 mmol, 0.5 equiv.) and **2d** (47 mg, 0.24 mmol, 1.2 equiv.) under air. Subsequently treated CH<sub>3</sub>CN (2 mL,  $c$  = 0.1 M) was added to vial *via* syringe. The reaction mixture was stirred for 2 h at 20 °C until unsaturated pyrazolones **1a** was fully consumed (monitored by TLC). Then the reaction was stirred at 0 °C for 15 h. The organic solvent was removed under reduced pressure and purified through column

chromatography (eluent: petroleum ether and EtOAc) to afford the desired product **6** (36 mg, 62% yield, conversion: 74%).

### 1-(3-Methyl-4-(methylthio)but-1-en-2-yl)-2,5-diphenyl-4-(1-phenylvinyl)-1,2-dihydro-3H-pyrazol-3-one (6)

The reaction was carried out on a 0.2 mmol scale following the General procedure. The product **6** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (56 mg, 62% yield). IR  $\nu_{\max}$  (neat)/cm<sup>-1</sup>: 3062, 2933, 1668, 1574, 1379, 1259, 1149, 1028, 932, 834; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.63 (d,  $J$  = 7.2 Hz, 2H), 7.47 (t,  $J$  = 7.8 Hz, 2H), 7.36 (t,  $J$  = 7.2 Hz, 2H), 7.32 (t,  $J$  = 7.2 Hz, 2H), 7.29–7.22 (m, 4H), 7.17 (t,  $J$  = 7.2 Hz, 2H), 7.13 (t,  $J$  = 7.2 Hz, 1H), 5.68 (d,  $J$  = 1.2 Hz, 1H), 5.60 (d,  $J$  = 1.2 Hz, 1H), 5.51 (s, 1H), 5.10 (s, 1H), 2.19 (dd,  $J$  = 2.4, 13.2 Hz, 1H), 2.13–2.10 (m, 1H), 1.97 (dd,  $J$  = 10.2, 13.2 Hz, 1H), 1.89 (s, 3H), 0.81 (d,  $J$  = 6.6 Hz, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  164.8, 155.6, 150.6, 140.3, 138.4, 136.2, 130.4, 129.6, 129.3, 128.7, 128.0, 127.9, 127.3, 126.9, 126.3, 124.1, 123.2, 118.8, 117.0, 114.0, 40.4, 35.1, 18.8, 15.9. HRMS (ESI-TOF,  $m/z$ ): calcd for C<sub>29</sub>H<sub>28</sub>N<sub>2</sub>NaOS<sup>+</sup>, [M + Na]<sup>+</sup>, 475.1815, found 475.1818.

### Reaction of unsaturated pyrazolones 1d with methyl propargyl sulfide ylide 2d

To a flame-dried sealable 3-dram vial equipped with a stir bar was added unsaturated pyrazolinones **1d** (72 mg, 0.2 mmol, 1.0 equiv.), Cs<sub>2</sub>CO<sub>3</sub> (33 mg, 0.1 mmol, 0.5 equiv.) under air. Subsequently treated CH<sub>3</sub>CN (2 mL,  $c$  = 0.1 M) was added to vial *via* syringe. The reaction mixture was stirred for 2 h at 20 °C until unsaturated pyrazolones **1d** was fully consumed (monitored by TLC). Then the reaction was stirred at 0 °C for 15 h. The organic solvent was removed under reduced pressure and purified through column chromatography (eluent: petroleum ether and EtOAc) to afford the desired product **7** (65 mg, 68% yield, conversion: 81%).

### 4-(1-(4-Chlorophenyl)vinyl)-1-(3-methyl-4-(methylthio)but-1-en-2-yl)-2,5-diphenyl-1,2-dihydro-3H-pyrazol-3-one (7)

The reaction was carried out on a 0.2 mmol scale. The product **7** was purified through column chromatography (PE/EtOAc: from 6 : 1 to 4 : 1) and obtained as a foam solid (64 mg, 66% yield). IR  $\nu_{\max}$  (neat)/cm<sup>-1</sup>: 3086, 2982, 1688, 1559, 1437, 1322, 1251, 1067, 972, 853; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.61 (d,  $J$  = 7.8 Hz, 2H), 7.47 (t,  $J$  = 7.8 Hz, 2H), 7.33 (d,  $J$  = 7.2 Hz, 2H), 7.32–7.30 (m, 2H), 7.25 (d,  $J$  = 7.2 Hz, 2H), 7.22 (t,  $J$  = 7.2 Hz, 2H), 7.12 (d,  $J$  = 8.4 Hz, 2H), 5.65 (s, 1H), 5.64 (s, 1H), 5.50 (s, 1H), 5.10 (s, 1H), 2.18 (dd,  $J$  = 1.8, 7.2 Hz, 1H), 2.12–2.08 (m, 1H), 1.97 (dd,  $J$  = 10.8, 13.2 Hz, 1H), 1.88 (s, 3H), 0.81 (t,  $J$  = 6.6 Hz, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  164.5, 155.5, 150.4, 138.9, 137.4, 136.1, 133.2, 130.3, 129.8, 129.1, 128.8, 128.3, 128.1, 128.0, 126.5, 124.1, 119.3, 117.1, 113.3, 40.4, 35.3, 18.7, 15.9. HRMS (ESI-TOF,  $m/z$ ): calcd for C<sub>29</sub>H<sub>27</sub>ClN<sub>2</sub>NaOS<sup>+</sup>, [M + Na]<sup>+</sup>, 509.1425, found 509.1425.



### Gram-scale synthesis of 3a

To a flame-dried sealable 3-dram vial equipped with a stir bar was added unsaturated pyrazolinones **1a** (1.01 g, 3.0 mmol, 1.0 equiv.), NaOAc·3H<sub>2</sub>O (204 mg, 1.5 mmol, 0.5 equiv.) and **2a** (0.65 g, 3.6 mmol, 1.2 equiv.) under air. Subsequently treated CH<sub>3</sub>CN (25 mL, *c* = 0.12 M) was added to vial *via* syringe. The reaction mixture was stirred for 20 min at 20 °C until unsaturated pyrazolinones **1a** was fully consumed (monitored by TLC). Then the reaction was stirred at 0 °C for 10 h. The organic solvent was removed under reduced pressure and purified through column chromatography (eluent: petroleum ether and EtOAc) to afford the desired product **3a** with a yield of 79% (1.01 g).

### Oxidation of 3a with *m*-CPBA

To a flame-dried sealable 2-dram vial equipped with a stir bar was added pyrazolones **3a** (302 mg, 0.68 mmol, 1.0 equiv.), Na<sub>2</sub>CO<sub>3</sub> (145 mg, 1.36 mmol, 3 equiv.) and CH<sub>2</sub>Cl<sub>2</sub> (5 mL, *c* = 0.14 M). After stirred at 0 °C for 10 min, *m*-CPBA (313 mg, 1.36 mmol, 75%, 2.0 equiv.) was added to the mixture slowly. The reaction mixture was kept stirring for 1 min at 0 °C until unsaturated pyrazolones **3a** was fully consumed (monitored by TLC). The reaction was quenched with aqueous Na<sub>2</sub>CO<sub>3</sub> and extracted with CH<sub>2</sub>Cl<sub>2</sub> (5 mL × 3). The combined organic solvent was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, removed under reduced pressure and purified through column chromatography (eluent: petroleum ether and EtOAc) to afford the desired product **8** (101 mg, 33%) and **9** (125 mg, 39%).

### 1-(4-(Methylsulfinyl)but-1-en-2-yl)-2,5-diphenyl-4-(1-phenylvinyl)-1,2-dihydro-3H-pyrazol-3-one (**8**)

IR  $\nu_{\max}$  (neat)/cm<sup>-1</sup>: 3162, 2958, 1672, 1587, 1421, 1356, 1151, 1077, 946; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.60 (d, *J* = 7.8 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 2H), 7.31 (d, *J* = 7.2 Hz, 3H), 7.29–7.24 (m, 3H), 7.21 (t, *J* = 7.2 Hz, 2H), 7.13 (t, *J* = 7.2 Hz, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 5.68 (s, 2H), 5.52 (s, 1H), 5.11 (s, 1H), 2.41 (t, *J* = 6.6 Hz, 2H), 2.36 (s, 3H), 2.22 (t, *J* = 6.6 Hz, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  164.6, 155.5, 143.9, 140.1, 138.2, 135.8, 129.9, 129.8, 128.8, 128.1, 128.0, 127.9, 127.2, 126.9, 126.5, 124.1, 119.1, 114.5, 51.5, 38.4, 23.9. HRMS (ESI-TOF, *m/z*): calcd for C<sub>28</sub>H<sub>26</sub>N<sub>2</sub>NaO<sub>2</sub>S<sup>+</sup>, [*M* + Na]<sup>+</sup>, 477.1607, found 477.1609.

### 1-(4-(Methylsulfonyl)but-1-en-2-yl)-2,5-diphenyl-4-(1-phenylvinyl)-1,2-dihydro-3H-pyrazol-3-one (**9**)

IR  $\nu_{\max}$  (neat)/cm<sup>-1</sup>: 3055, 2985, 1663, 1578, 1412, 1365, 1155, 1062, 964; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.61 (d, *J* = 1.2 Hz, 2H), 7.60 (d, *J* = 1.2 Hz, 2H), 7.48 (t, *J* = 7.8 Hz, 3H), 7.34–7.27 (m, 3H), 7.23 (t, *J* = 7.2 Hz, 2H), 7.15 (t, *J* = 7.2 Hz, 2H), 7.12 (t, *J* = 7.2 Hz, 1H), 5.70 (s, 2H), 5.54 (s, 1H), 5.09 (d, *J* = 0.6 Hz, 1H), 2.73 (t, *J* = 8.4 Hz, 2H), 2.68 (s, 3H), 2.29 (t, *J* = 8.4 Hz, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  164.7, 155.5, 143.2, 140.1, 138.1, 135.8, 130.0, 129.0, 128.2, 128.0, 127.4, 127.0, 126.8, 124.1, 119.3, 115.1, 52.4, 40.5, 24.0. HRMS (ESI-TOF, *m/z*): calcd for C<sub>28</sub>H<sub>26</sub>N<sub>2</sub>NaO<sub>3</sub>S<sup>+</sup>, [*M* + Na]<sup>+</sup>, 493.1556, found 493.1558.

## Conflicts of interest

The authors declare no competing financial interest.

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## References

- For related reviews and books, see: (a) T. Kondo and T.-A. Mitsudo, *Chem. Rev.*, 2000, **100**, 3205–3220; (b) H. Liu and X. Jiang, *Chem.-Asian J.*, 2013, **8**, 2546–2563; (c) M. Feng, B. Tang, S. Liang and X. Jiang, *Curr. Top. Med. Chem.*, 2016, **16**, 1200–1216; (d) N. Kharasch, *The Chemistry of Organic Sulfur Compounds*, Pergamon, London, 1996; (e) L. A. Damani, *Sulfur-Containing Drugs and Related Organic Compounds: Chemistry, Biochemistry, And Toxicology*, Ellis Horwood, Ltd., Chichester, U.K., 1989, vol. 1, part B.
- For related reviews, see: (a) A.-H. Li, L.-X. Dai and V. K. Aggarwal, *Chem. Rev.*, 1997, **97**, 2341–2372; (b) L.-X. Dai, X.-L. Hou and Y.-G. Zhou, *Pure Appl. Chem.*, 1999, **71**, 369–376; (c) V. K. Aggarwal and C. L. Winn, *Acc. Chem. Res.*, 2004, **37**, 611–620; (d) E. M. McGarrigle, E. L. Myers, O. Illa, M. A. Shaw, S. L. Riches and V. K. Aggarwal, *Chem. Rev.*, 2007, **107**, 5841–5883; (e) X.-L. Sun and Y. Tang, *Acc. Chem. Res.*, 2008, **41**, 937–948; (f) L.-Q. Lu, J.-R. Chen and W.-J. Xiao, *Acc. Chem. Res.*, 2012, **45**, 1278–1293; (g) A. C. B. Burtoloso, R. M. P. Dias and I. A. Leonarczyk, *Eur. J. Org. Chem.*, 2013, **23**, 5005–5016; (h) L.-Q. Lu, T.-R. Li, Q. Wang and W.-J. Xiao, *Chem. Soc. Rev.*, 2017, **46**, 4135–4149; (i) J. D. Neuhaus, R. Oost, J. Merad and N. Maulide, *Top. Curr. Chem.*, 2018, **376**, 15; (j) D. Kaiser, I. Klose, R. Oost, J. Neuhaus and N. Maulide, *Chem. Rev.*, 2019, **119**, 8701–8780; (k) X.-P. Wu, S. Sun, J.-T. Yu and J. Cheng, *Synlett*, 2019, **30**, 21–29; (l) J. Vaitla and A. Bayer, *Synthesis*, 2019, **51**, 612–628. For selected synthetic applications of sulfur-containing compounds, see: (m) S. Peng, Y.-X. Song, J.-Y. He, S.-S. Tang, J.-X. Tan, Z. Cao, Y.-W. Lin and W.-M. He, *Chin. Chem. Lett.*, 2019, DOI: 10.1016/j.cclet.2019.08.002; (n) Z. Cao, Q. Zhu, Y.-W. Lin and W.-M. He, *Chin. Chem. Lett.*, 2019, DOI: 10.1016/j.cclet.2019.09.041; (o) L.-Y. Xie, S. Peng, F. Liu, G.-R. Chen, W. Xia, X. Yu, W.-F. Li, Z. Cao and W.-M. He, *Org. Chem. Front.*, 2018, **5**, 2604–2609; (p) W.-H. Bao, Z. Wang, X. Tang, Y.-F. Zhang, J.-X. Tan, Q. Zhu, Z. Cao, Y.-W. Lin and W.-M. He, *Chin. Chem. Lett.*, 2019, DOI: 10.1016/j.cclet.2019.06.052; (q) C. Wu, L.-H. Lu, A.-Z. Peng, G.-K. Jia, C. Peng, Z. Cao, Z. Tang, W.-M. He and X. Xu, *Green Chem.*, 2018, **20**, 3683–3688.



- 3 (a) J. E. Baldwin, R. E. Hackler and D. P. Kelley, *J. Am. Chem. Soc.*, 1968, **90**, 4758–4759; (b) G. M. Blackburn, W. D. Ollis, J. D. Plackett, C. Smith and I. O. Sutherland, *J. Chem. Soc., Chem. Commun.*, 1968, 186–188; (c) J. E. Baldwin, R. E. Hackler and D. P. Kelley, *J. Chem. Soc., Chem. Commun.*, 1968, 537–538; *J. Chem. Soc., Chem. Commun.*, 1968, 538–539.
- 4 For related reviews, see: (a) M. P. Doyle and D. C. Forbes, *Chem. Rev.*, 1998, **98**, 911–936; (b) D. M. Hodgson, F. Y. T. M. Pierard and P. A. Stupp, *Chem. Soc. Rev.*, 2001, **30**, 50–61; (c) S. Braverman and M. Cherkinsky, *Top. Curr. Chem.*, 2006, **275**, 67–101; (d) M. Reggelin, *Top. Curr. Chem.*, 2007, **275**, 1–65; (e) Y. Zhang and J. Wang, *Coord. Chem. Rev.*, 2010, **254**, 941–953; (f) S.-F. Zhu and Q.-L. Zhou, *Natl. Sci. Rev.*, 2014, **1**, 580–603; (g) T. H. West, S. S. M. Spoehrle, K. Kasten, J. E. Taylor and A. D. Smith, *ACS Catal.*, 2015, **5**, 7446–7479; (h) Z. Sheng, Z. Zhang, C. Chu, Y. Zhang and J. Wang, *Tetrahedron*, 2017, **73**, 4011–4022.
- 5 For selected examples, see: (a) M. P. Doyle, J. H. Griffin, M. S. Chinn and D. Van Leusen, *J. Org. Chem.*, 1984, **49**, 1917–1925; (b) T. Fukuda and T. Katsuki, *Tetrahedron Lett.*, 1997, **38**, 3435–3438; (c) D. S. Carter and D. L. Van Vranken, *Org. Lett.*, 2000, **2**, 1303–1305; (d) K. L. Greenman, D. S. Carter and D. L. Van Vranken, *Tetrahedron*, 2001, **57**, 5219–5225; (e) C.-Y. Zhou, W.-Y. Yu, P. W. H. Chan and C.-M. Che, *J. Org. Chem.*, 2004, **69**, 7072–7082; (f) M. Ma, L. Peng, C. Li, X. Zhang and J. Wang, *J. Am. Chem. Soc.*, 2005, **127**, 15016–15017; (g) L. Peng, X. Zhang, M. Ma and J. Wang, *Angew. Chem., Int. Ed.*, 2007, **46**, 1905–1908; (h) I. Aviv and Z. Gross, *Chem.–Eur. J.*, 2008, **14**, 3995–4005; (i) M. Liao, L. Peng and J. Wang, *Org. Lett.*, 2008, **10**, 693–696; (j) P. W. Davies, S. J.-C. Albrecht and G. Assanelli, *Org. Biomol. Chem.*, 2009, **7**, 1276–1279; (k) Y. Li, Y. Shi, Z. Huang, X. Wu, P. Xu, J. Wang and Y. Zhang, *Org. Lett.*, 2011, **13**, 1210–1213; (l) M. S. Holzwarth, I. Alt and B. Plietker, *Angew. Chem., Int. Ed.*, 2012, **51**, 5351–5354; (m) V. Tyagi, G. Sreenilayam, P. Bajaj, A. Tinoco and R. Fasan, *Angew. Chem., Int. Ed.*, 2016, **55**, 13562–13566; (n) K. J. Hock and R. M. Koenigs, *Angew. Chem., Int. Ed.*, 2017, **56**, 13566–13568; (o) Z. Zhang, Z. Sheng, W. Yu, G. Wu, R. Zhang, W.-D. M. Chu, Y. Zhang and J. Wang, *Nat. Chem.*, 2017, **9**, 970–976; (p) K. J. Hock, L. Mertens, R. Hommelsheim, R. Spitzner and R. M. Koenigs, *Chem. Commun.*, 2017, **53**, 6577–6580; (q) X. Lin, Y. Tang, W. Yang, F. Tan, L. Lin, X. Liu and X. Feng, *J. Am. Chem. Soc.*, 2018, **140**, 3299–3305; (r) H. Zhang, B. Wang, H. Yi, Y. Zhang and J. Wang, *Org. Lett.*, 2015, **17**, 3322–3325; (s) X. Zhang, Z. Qu, Z. Ma, W. Shi, X. Jin and J. Wang, *J. Org. Chem.*, 2002, **67**, 5621–5625.
- 6 (a) M. Thangaraj, R. N. Gaykar, T. Roy and A. T. Biju, *J. Org. Chem.*, 2017, **82**, 4470–4476; (b) J. Tan, T. Zheng, K. Xu and C. Liu, *Org. Biomol. Chem.*, 2017, **15**, 4946–4950.
- 7 (a) M. Aso, M. Sakamoto, N. Urakawa and K. Kanematsu, *Heterocycles*, 1990, **31**, 1003–1006; (b) M. Aso, A. Ojida, G. Yang, O.-J. Cha, E. Osawa and K. Kanematsu, *J. Org. Chem.*, 1993, **58**, 3960–3968; (c) A. Ojida, F. Tanoue and K. Kanematsu, *J. Org. Chem.*, 1994, **59**, 5970–5976.
- 8 (a) P. Jia, Q. Zhang, H. Jin and Y. Huang, *Org. Lett.*, 2017, **19**, 412–415; (b) P. Jia, Q. Zhang, Q. Ou and Y. Huang, *Org. Lett.*, 2017, **19**, 4664–4667; (c) P. Jia, Q. Zhang, Y. Zhuge, X. Liwei and Y. Huang, *Adv. Synth. Catal.*, 2018, **360**, 438–443; (d) P. Jia and Y. Huang, *Adv. Synth. Catal.*, 2018, **360**, 3044–3048.
- 9 S. Shen, Y. Yang, J. Duan, Z. Jia and J. Liang, *Org. Biomol. Chem.*, 2018, **16**, 1068–1072.
- 10 For an excellent book on pyrazolone chemistry, see: (a) G. Varvounis, *Pyrazol-3-ones. Part IV: Synthesis and Applications*, in *Advances in Heterocyclic Chemistry*, ed. A. R. Katritzky, Academic Press, New York, 2009, vol. 98, pp. 143–224. For related reviews, see: (b) B. Ke, M. Tian, J. Li, B. Liu and G. He, *Med. Res. Rev.*, 2016, **36**, 983–1035; (c) V. Kumar, K. Kaur, G. K. Gupta and A. K. Sharma, *Eur. J. Med. Chem.*, 2013, **69**, 735–753; (d) S. Fustero, M. Sánchez-Roselló, P. Barrio and A. Simón-Fuentes, *Chem. Rev.*, 2011, **111**, 6984–7034; (e) A. Schmidt and A. Dreger, *Curr. Org. Chem.*, 2011, **15**, 1423–1463; (f) S. Sondhi, M. Dinodia, J. Singh and R. Rani, *Curr. Bioact. Compd.*, 2007, **3**, 91–108; (g) D. A. Horton, G. T. Bourne and M. L. Smythe, *Chem. Rev.*, 2003, **103**, 893–930, and the references therein. For selected synthetic applications of N-heterocycles, see: (h) Z. Yang, Z. Song, L. Jie, L. Wang and X. Cui, *Chem. Commun.*, 2019, **55**, 6094–6097; (i) L.-Y. Xie, S. Peng, T.-G. Fan, Y.-F. Liu, M. Sun, L.-L. Jiang, X.-X. Wang, Z. Cao and W.-M. He, *Science China Chemistry*, 2019, **62**, 460–464; (j) L.-Y. Xie, L.-L. Jiang, J.-X. Tan, Y. Wang, X.-Q. Xu, B. Zhang, Z. Cao and W.-M. He, *ACS Sustainable Chem. Eng.*, 2019, **7**, 14153–14160; (k) K. Sun, S. Wang, R. Feng, Y. Zhang, X. Wang, Z. Zhang and B. Zhang, *Org. Lett.*, 2019, **21**, 2052–2055; (l) K. Sun, Z. Shi, Z. Liu, B. Luan, J. Zhu and Y. Xue, *Org. Lett.*, 2018, **20**, 6687–6690; (m) K. Sun, B. Luan, Z. Liu, J. Zhu, J. Du, E. Bai, Y. Fang and B. Zhang, *Org. Biomol. Chem.*, 2019, **17**, 4208–4211; (n) X. Wang, C. Li, Y. Zhang, B. Zhang and K. Sun, *Org. Biomol. Chem.*, 2019, **17**, 8364–8368.
- 11 For recent reviews, see: (a) P. Chauhan, S. Mahajan and D. Enders, *Chem. Commun.*, 2015, **51**, 12890–12907; (b) S. Liu, X. Bao and B. Wang, *Chem. Commun.*, 2018, **54**, 11515–11529; (c) X. Xie, L. Xiang, C. Peng and B. Han, *Chem. Rec.*, 2019, **19**, 1–28; (d) X. Xie, W. Huang, C. Peng and B. Han, *Adv. Synth. Catal.*, 2018, **360**, 194–228; (e) R. Rios, *Chem. Soc. Rev.*, 2012, **41**, 1060–1074.
- 12 For recent selected asymmetric examples: see: (a) J.-X. Zhang, N.-K. Li, Z.-M. Liu, X.-F. Huang, Z.-C. Geng and X.-W. Wang, *Adv. Synth. Catal.*, 2013, **355**, 797–808; (b) X. Han, W. Yao, T. Wang, Y. R. Tan, Z. Yan, J. Kwiatkowski and Y. Lu, *Angew. Chem., Int. Ed.*, 2014, **53**, 5643–5647; (c) P. Chauhan, S. Mahajan, C. C. J. Loh, G. Raabe and D. Enders, *Org. Lett.*, 2014, **16**, 2954–2957; (d) S. Wang, C. Rodriguez-Esrich and M. A. Pericas, *Org. Lett.*, 2016, **18**, 556–559; (e) C. Ni and X. Tong, *J. Am. Chem. Soc.*, 2016, **138**, 7872–7875; (f) D. Hack, A. B. Dürr, K. Deckers, P. Chauhan, N. Seling, L. Rübenach, L. Mertens, G. Raabe, F. Schoenebeck and D. Enders, *Angew. Chem., Int. Ed.*,



- 2016, **55**, 1797–1800; (g) F. Vetica, S. Bailey, P. Chauhan, M. Turberg, A. Ghaur, G. Raabe and D. Enders, *Adv. Synth. Catal.*, 2017, **359**, 3729–3734; (h) U. Kaya, P. Chauhan, S. Mahajan, K. Deckers, A. Valkonen, K. Rissanen and D. Enders, *Angew. Chem., Int. Ed.*, 2017, **56**, 15358–15362; (i) J. Zheng, S.-B. Wang, C. Zheng and S.-L. You, *Angew. Chem., Int. Ed.*, 2017, **56**, 4540–4544; (j) S.-W. Li, Q. Wan and Q. Kang, *Org. Lett.*, 2018, **20**, 1312–1315; (k) X. Bao, S. Wei, J. Qu and B. Wang, *Chem. Commun.*, 2018, **54**, 2028–2031; (l) B.-L. Zhao and D.-M. Du, *Org. Lett.*, 2018, **20**, 3797–3800; (m) X. Bao, S. Wei, X. Qian, J. Qu, B. Wang, L. Zou and G. Ge, *Org. Lett.*, 2018, **20**, 3394–3398; (n) B. Mondal, R. Maity and S. C. Pan, *J. Org. Chem.*, 2018, **83**, 8645–8654; (o) S. Meninno, A. Mazzanti and A. Lattanzi, *Adv. Synth. Catal.*, 2019, **361**, 79–84.
- 13 (a) G. Rassu, V. Zambrano, L. Pinna, C. Curti, L. Battistini, A. Sartori, G. Pelosi, G. Casiraghi and F. Zanardi, *Adv. Synth. Catal.*, 2014, **356**, 2330–2336; (b) S. R. Yetra, S. Mondal, S. Mukherjee, R. G. Gonnade and A. T. Biju, *Angew. Chem., Int. Ed.*, 2016, **55**, 268–272; (c) S. Mondal, S. Mukherjee, S. R. Yetra, R. G. Gonnade and A. T. Biju, *Org. Lett.*, 2017, **19**, 4367–4370; (d) J.-Y. Liu, J. Zhao, J.-L. Zhang and P.-F. Xu, *Org. Lett.*, 2017, **19**, 1846–1849; (e) W. Yang, W. Sun, C. Zhang, Q. Wang, Z. Guo, B. Mao, J. Liao and H. Guo, *ACS Catal.*, 2017, **7**, 3142–3146; (f) H.-J. Leng, Q.-Z. Li, R. Zeng, Q.-S. Dai, H.-P. Zhu, Y. Liu, W. Huang, B. Han and J.-L. Li, *Adv. Synth. Catal.*, 2018, **360**, 229–234; (g) J. Zheng, P. Li, M. Gu, A. Lin and H. Yao, *Org. Lett.*, 2017, **19**, 2829–2832; (h) H. Li, R. Gontla, J. Flegel, C. Merten, S. Ziegler, A. P. Antonchick and H. Waldmann, *Angew. Chem., Int. Ed.*, 2019, **58**, 307–311; (i) J. Xu, L. Hu, H. Hu, S. Ge, X. Liu and X. Feng, *Org. Lett.*, 2019, **21**, 1632–1636.
- 14 S.-J. Shen, X.-L. Du, X.-L. Xu, Y.-H. Wu, M.-G. Zhao and J.-Y. Liang, *J. Org. Chem.*, 2019, **84**, 12520–12531.
- 15 J.-Y. Liang, S.-J. Shen, X.-Q. Chai and T. Lv, *J. Org. Chem.*, 2018, **83**, 12744–12752.
- 16 Crystallographic data for **3a** has been deposited with the Cambridge Crystallographic Data Centre as deposition number CCDC 1943758.†
- 17 Y. Liu, Y. Yang, Y. Huang, X.-H. Xu and F.-L. Qing, *Synlett*, 2015, **26**, 67–72.
- 18 A. Terada and Y. Kishida, *Chem. Pharm. Bull.*, 1969, **17**, 966–973.

