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Synthesis of Multi-substituted Dihydropyrazoles by Copper-Mediated [4+1] Cycloaddition Reaction of *N*-Sulfonylhydrazones and Sulfoxonium Ylides

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Abstract. A general and expeditious approach for the copper mediated synthesis of multi-functionalized dihydropyrazoles from *N*-sulfonylhydrazones and sulfoxonium ylides has been achieved under aerobic oxidative conditions. The formal [4+1] cycloaddition reaction exhibits many notable features and can be easily scaled up to gram scale.

Keywords: sulfoxonium ylides; 1,2-diaza-1,3-diene; [4+1] cycloaddition reaction; dihydropyrazoles; *N*-heterocyclic compounds

Introduction

Dihydropyrazoles, as highly privileged heterocyclic scaffolds, have been found wide applications in natural products and pharmacologically active compounds as well as versatile building blocks in organic synthesis (**Figure 1**).[1] The conventional methods and many recent methods for the construction of dihydropyrazoles have mainly focused on thermal cycloaddition and catalytic cyclization reactions.[2] In recent years, Xiao's group reported a series of reactions regarding the intramolecular cyclization of *β,γ*-unsaturated hydrazones for the synthesis of various dihydropyrazoles.[3] Considering the great significance of dihydropyrazole skeletons in various application fields, the development of more general, mild and operationally easy approach for the synthesis of the dihydropyrazole structure is highly desirable.

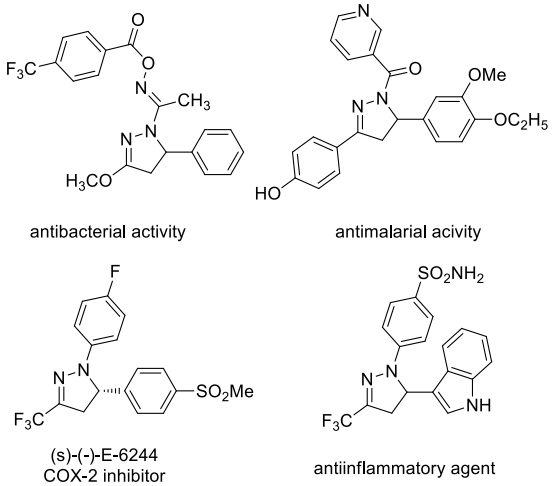

Figure 1. Biologically Active Dihydropyrazole Molecules.

1,2-Diaza-1,3-dienes, which are usually in situ generated from *α*-halogeno ketohydrazones, have been extensively applied as versatile four-unit synthons in a range of cyclization reactions for the assembly of structurally diverse nitrogen-containing heterocycles.[4] Sulfur ylide and sulfoxonium ylide have been known as key one-carbon units in numerous cyclic process for the preparation of carbo- and heterocycles.[5] Compared with another common carbene precursor diazo compounds, the ylides are generally stable solids and easy to prepare.[6] Therefore, the strategy of combination of the powerful 1,2-diaza-1,3-diene and sulfur ylide synthon into one procedure provides an expeditious pathway to access to dihydropyrazoles. In 2012, Bolm's group reported a copper-catalyzed asymmetric formal [4+1] cycloaddition of in situ-generated azoalkenes with sulfur ylides for the synthesis of enantioenriched dihydropyrazoles.[2c] Very recently, Fang, Wang and co-workers developed a catalyst-free [4+1]-annulation of α-halo hydrazones with fluorinated sulfur ylides to produce 5-(trifluoromethyl)dihydropyrazoles.[7] In the meantime, Shao and co-workers demonstrated the substrate-controlled reactions to construct spirocyclopropylpyrazolones and bicyclic 4,5-dihydropyrazoles from 1,2-diaza-1,3-dienes and sulfur ylides.[8]

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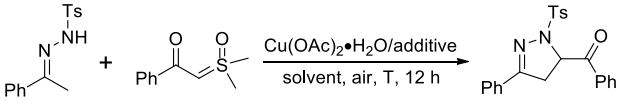
In 2013, Zhang's group reported a copper mediated tandem C-N and N-N bond formation to synthesize 1,2,3-triazoles from readily available *N*-tosylhydrazones and amines.[9] In the transformation, the key 1,2-diaza-1,3-diene intermediate (1-tosyl-2-vinyldiazene) was proposed to be in situ generated from *N*-tosylhydrazone through C-H cleavage for the first time. Compared with commonly used α-halo hydrazones, the employment of *N*-tosylhydrazones to generate 1,2-diaza-1,3-dienes through direct dehydrogenation avoid environmentally unfriendly halogenation and dehalogenation process, exhibiting good atom-economy and operational simplicity. The use of *N*-tosylhydrazone as the precursor of 1,2-diaza-1,3-diene through C-H cleavage to construct other valuable nitrogen-containing heterocycles had been subsequently disclosed.[10] Inspired by the conductive work and our continuous effort on the construction of structurally diversified nitrogen-containing heterocycles,[11] we demonstrate herein an efficient copper mediated formal [4+1] cycloaddition of *N*-sulfonylhydrazones and sulfoxonium ylides to lead to a variety of highly substituted 4,5-dihydropyrazoles.

Results and Discussion

We initially started our investigation with *N*-sulfonylhydrazone **1a** and sulfoxonium ylide **2a** as model substrates, in the presence of $Cu(OAc)_2 \cdot H_2O$ (1.0 equiv) and K_2CO_3 (2.0 equiv) in toluene at 100 °C (Table 1, entry 1). Unfortunately, no product was detected. Other organic or inorganic bases could also not give the desired product (Table 1, entry 1). The switch of base into acidic additive HOAc failed to enable positive results, but the use of PivOH could afford the desired dihydropyrazole product **3a** in 60% yield (Table 1, entries 2-3). We also tested other copper species, such as CuI, CuBr, $CuBr_2$, $CuCl_2$, CuO or $Cu(OTf)_2$, and the inferior results were obtained. (Table 1, entry 4). Control experiments indicated that the absence of PivOH slightly inhibited the reaction efficiency and the lack of $Cu(OAc)_2 \cdot H_2O$ totally shut down the reaction (Table 1, entries 5-6). The solvent effect was tested by the employment of diverse solvents, and toluene showed the optimal result, affording the highest yield (Table 1, entries 7-14). Further optimization towards the reaction temperature revealed that the reaction did not occur at room temperature and 60 °C. Moderate yield was obtained when the reaction was performed at 80 °C. Further increasing the temperature to 120 °C enabled the reaction to undergo other transformation, affording some unidentified products, perhaps due to the decomposion of *N*-tosylhydrazone in the presence of copper catalyst at high temperture (Table 1, entries 12-14). When the catalytic amount of $Cu(OAc)_2 \cdot H_2O$ was employed, only trace of dihydropyrazole product was observed (Table 1, entry 15). To our delight, increasing amount of $Cu(OAc)_2 \cdot H_2O$ to 2.0 equiv could clearly enhance the yield to 87% during 4 hours (Table 1, entry 16). Notably, an inert atmosphere could suppress the reaction to a great extent (Table 1, entry 17). Intriguingly, when we applied the sulfur ylide ($PhCOCH=SMe_2$) to replace **2a** under the standard reaction conditions, only trace of desired product was detected (Table 1, entry 18).

Table 1. Optimization of reaction conditions.[a]



1a **2a** **3a**

Entry	Additive. (equiv)	Solvent (mL)	Temperature (°C)	Yield[b] (%)
1	bases[c]	toluene	100	ND
2	HOAc	toluene	100	trace
3	PivOH	toluene	100	60
4	PivOH	toluene	100	ND-26[d]
5	--	toluene	100	45
6	PivOH	toluene	100	ND[e]
7	PivOH	DMSO	100	27
8	PivOH	DMF	100	trace
9	PivOH	DCE	100	43
10	PivOH	1,4-dioxane	100	ND
11	PivOH	CH_3CN	100	ND
12	PivOH	toluene	25 or 60	ND
13	PivOH	toluene	80	57
14	PivOH	toluene	120	ND
15	PivOH	toluene	100	trace[f]
16	PivOH	toluene	100	87[g]
17	PivOH	toluene	100	35[g,h]
18	PivOH	toluene	100	trace[i]

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $Cu(OAc)_2 \cdot H_2O$ (1.0 equiv) and additive (2.0 equiv) in solvent (2.0 mL) under air at specified temperature for 12 h.
[b] Isolated yields.
[c] Inorganic or organic bases were used, including K_2CO_3, Cs_2CO_3, KO*t*-Bu and NEt_3.
[d] Other copper species were used in the reaction. The use of $CuCl_2$ could afford the product **3a** in 26% yield. No product was detected in the presence of other copper species, including CuI, CuBr, $CuBr_2$, CuO or $Cu(OTf)_2$.
[e] In the absence of $Cu(OAc)_2 \cdot H_2O$.
[f] $Cu(OAc)_2 \cdot H_2O$ (0.2 equiv) was used.
[g] The reaction was performed with $Cu(OAc)_2 \cdot H_2O$ (2.0 equiv) for 4 h.
[h] N_2 atmosphere. ND = No detection of the product.
[i] The reaction was performed with sulfur ylide ($PhCOCH=SMe_2$) instead of sulfoxonium ylide **2a**.

With the optimal reaction conditions in hand, the generality and limitation of the formal [4+1] cycloaddition reaction was next studied (Table 2). A variety of *N*-tosylhydrazones derived from different

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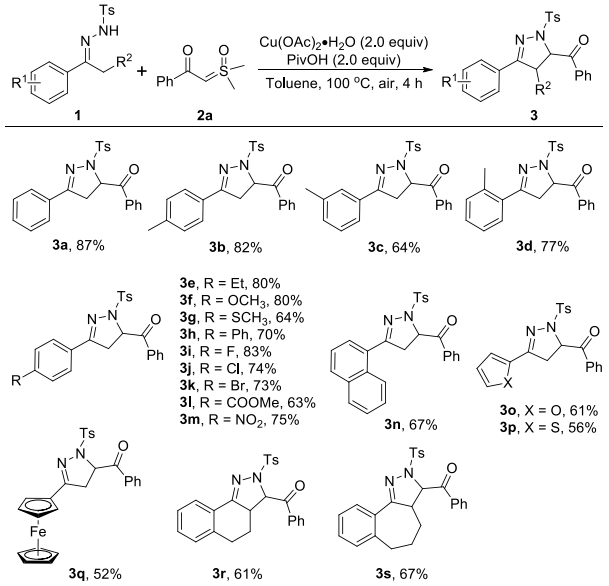
Table 2. The Scope of *N*-tosylhydrazones Derived from Different Ketones.[a,b]

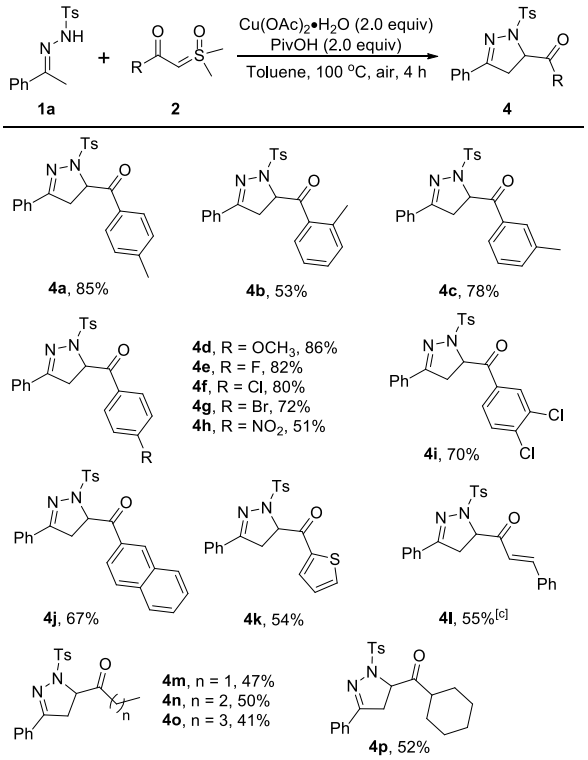


[a] Reaction conditions: **1** (0.2 mmol), **2a** (0.4 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.4 mmol) and PivOH (0.4 mmol) in toluene (2.0 mL) under air at 100 °C for 4 h.
[b] Isolated yields.

ketones were subjected to the standard conditions and moderate to good yields were achieved. In general, the electronic nature of the aryl ring had little influence on the reaction, as exemplified by the comparable yields of *N*-tosylhydrazones bearing electron-donating or -withdrawing groups (**3a-m**). Noteworthy was that the steric hindrance also exerted a marginal effect on the reaction (**3b-d**). Apart from the common halogen groups, some strong electron-withdrawing groups attached in the aryl ring, including ester and nitro group, were well tolerated under the optimized conditions (**3i-m**). Furthermore, the naphthalene, furan, thiophene and ferrocene ring could also be incorporated into the dihydropyrazole product with acceptable reactivity (**3n-q**). It should be noted that the *N*-tosylhydrazones derived from 3,4-dihydronaphthalen-1(*2H*)-one and 6,7,8,9-tetrahydro-*5H*-benzo[7]annulen-5-one, could be compatible with the reaction to deliver the corresponding poly-substituted dihydropyrazoles in 61-67% yield (**3r-s**), further extending the structural diversity of the obtained dihydropyrazole frameworks.

The compatibility of the protocol was explored by the employment of a wide range of sulfoxonium ylides (Table 3). Benzoyl-substituted sulfoxonium ylides bearing electron-donating and -withdrawing groups on the phenyl ring all reacted smoothly with *N*-tosylhydrazone **1a** to afford the relevant dihydropyrazole products in moderate to excellent yields (**4a-k**). The orientation of substituents on the aromatic ring had an obvious impact on the efficacy of the transformation, owing to the inferior efficiency of *ortho* methyl substituted sulfoxonium ylide (**4b**). The reaction proceeded smoothly with the tolerance of diverse halogenated substituents, as well as strong

Table 3. The Scope of Sulfoxonium Ylides.[a,b]



[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.4 mmol) and PivOH (0.4 mmol) in toluene (2.0 mL) under air at 100 °C for 4 h.
[b] Isolated yields.
[c] The reaction was performed at 90 °C for 2 h.

electron-withdrawing group (**4e-i**). Moreover, sulfoxonium ylides possessing naphthalene or thiophene were also investigated to provide the corresponding dihydropyrazoles in reasonable yields (**4j-k**). The scope of the methodology was further extended by the fact that sulfoxonium ylides were not limited to aryl substitution, and several alkenyl and alkyl substituents were also applicable to the reaction, giving rise to the products **4l-p** in moderate yields. The structure of the dihydropyrazole **4a** was unambiguously confirmed by single X-ray diffraction analysis[12] (Figure 2).

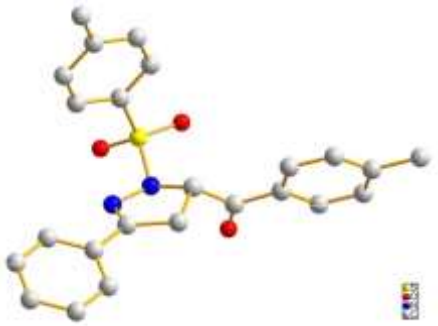
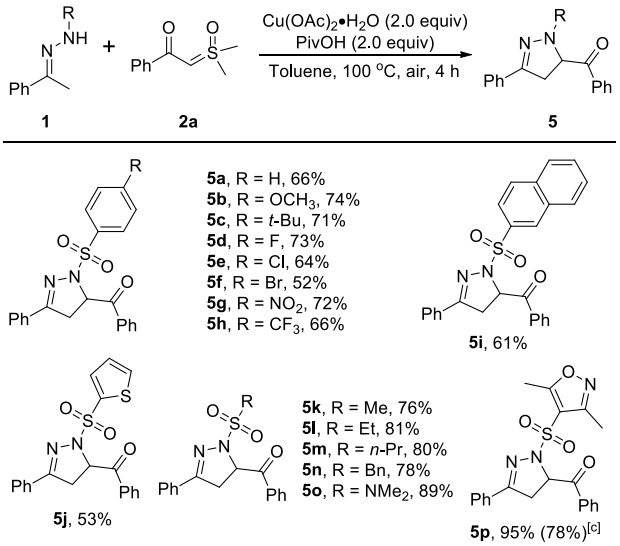


Figure 2. The X-ray Structure of Product **4a**.

The *N*-sulfonylhydrazones derived from diverse sulfonyl hydrazines could be successfully applied to the present cycloaddition protocol (Table 4). At this stage, both electron-donating and -withdrawing

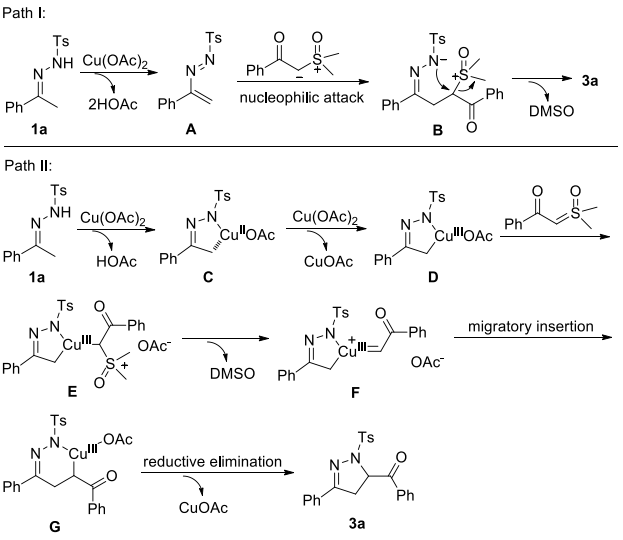
Table 4. The Scope of *N*-sulfonylhydrazones Derived from Diverse Sulfonyl hydrazines.[a,b]



[a] Reaction conditions: **1** (0.2 mmol), **2a** (0.4 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.4 mmol) and PivOH (0.4 mmol) in toluene (2.0 mL) under air at 100 °C for 4 h.
[b] Isolated yields.
[c] The reaction was performed on 3.5 mmol scale.

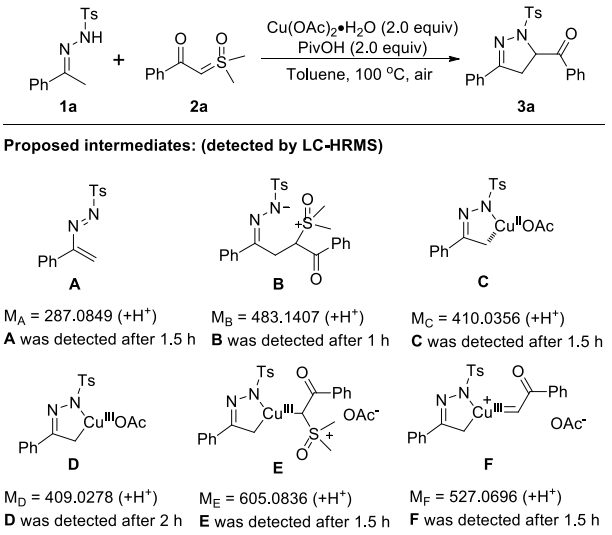
groups at the *para*-positions of the phenyl ring were well tolerated (**5a-h**). The reaction was also amenable to the incorporation of naphthalene and thiophene into dihydropyrazoles, giving the corresponding cyclized products in favorable yields (**5i-j**). Furthermore, the *N*-sulfonylhydrazones derived from alkyl sulfonyl hydrazines readily participated in this transformation to furnish a series of alkyl substituted dihydropyrazoles in good yields (**5k-n**). More importantly, the *N*,*N*-dimethyl group and isoxazole ring could be smoothly incorporated into the dihydropyrazole products (**5o-p**) with high reactivity. As for product **5p**, the reaction was easily reproducible on a gram scale in 78% yield, providing the possibility for the scale production of structurally diverse dihydropyrazoles. Unfortunately, the hydrazones prepared from benzohydrazide or phenylhydrazine did not participate in the transformation.

On the basis of the observation data from the preliminary mechanistic investigations and in previous literatures,[5g-k, 8, 9] two plausible reaction pathways were proposed as depicted in Scheme 1. Initially, *N*-tosylhydrazones **1a** underwent an oxidative dehydrogenation process or a concerted metalation–deprotonation (CMD) process in the presence of $Cu(OAc)_2$ and PivOH to give the key intermediate 1,2-diaza-1,3-diene **A**.[9] Then, the 1,4-conjugated addition of sulfoxonium ylide **2a** on **A** to furnish the intermediate **B**.[8] The intramolecular nucleophilic attack of **B** could generate the final product **3a** with the release of DMSO (Path I). Another possible pathway was the coordination of *N*-tosylhydrazones **1a** to $Cu(OAc)_2$ to deliver complex **C**, which could be oxidized to Cu^{III} complex **D** by



Scheme 1. Plausible Reaction Mechanism.

oxygen or by the process of disproportionation of the Cu^{II} complex.[10a] The subsequent coordination of sulfoxonium ylide **2a** gave a Cu^{III} species **E**, which underwent α-elimination of DMSO afford a reactive copper α-oxo carbine **F**. Migratory insertion of the Cu–C bond could produce a six-membered metallacyclic intermediate **G**.[5g-k] The final dihydropyrazole product **3a** was afforded by the reductive elimination of complex **G** with the release of Cu^{I} species (Path II).



Scheme 2. Control Experiment.

To gain some evidence of the proposed reaction mechanism, a control experiment was implemented as shown in Scheme 2. The reaction of substrate **1a** and **2a** was performed under the standard reaction conditions, and the reaction process was monitored by LC-HRMS. During 2 hours, the sample was tested at half-hour intervals. Fortunately, the proposed intermediates **A, B, C, D, E** and **F** were detected by LC-HRMS. It is speculated that these intermediates are presumably

involved in the reaction process. We also attempt to isolate the 1,2-diaza-1,3-diene **A**, but unfortunately, the active intermediate was very unstable and could not be isolated during the reaction. According to the previous literature,[8] the relatively stable 1,2-diaza-1,3-diene species were that possessing greater conjugated system. In addition, the *N*-sulfonylhydrazones derived from aliphatic ketones failed to form the desired products, which further verified the above viewpoint. It is supposed that the 1,2-diaza-1,3-diene generated from alkyl *N*-tosylhydrazone is extremely unstable due to the lack of conjugated system.

Conclusion

In conclusion, we have developed an attractive and expeditious protocol for the synthesis of diverse multi-functionalized dihydropyrazoles through copper-mediated formal [4+1] cycloaddition reaction of readily available *N*-sulfonylhydrazones and sulfoxonium ylides. The transformation exhibits many notable features, including readily accessible starting materials, convenient operating conditions, a broad substrate scope, and high efficiency. The reaction can be easily scaled up to gram scale. Further study towards the reaction mechanism and practical application are underway.

Experimental Section

General Information

Unless otherwise stated, all reactions were performed under air in a flame-dried reaction flask. Toluene, DCE, 1,4-Dioxane, CH_3CN and DMF were dried by calcium hydride and freshly distilled. DMSO was used without further purification. The other materials and solvents were purchased from Adamas-beta and other commercial suppliers, and used without additional purification. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ^{1}NMR spectra were recorded on a Bruker Avance operating at for ^{1}H NMR at 400 MHz, and ^{13}C NMR at 100 MHz using TMS as internal standard. Mass spectroscopy data of the products were collected on an HRMS-TOF instrument or Waters TOFMS GCT Premier using EI or ESI ionization. Melting points were measured with WRR digital point apparatus and not corrected. The sulfoxonium ylides were synthesized according to the previous literature.[13]

Synthesis of *N*-Sulfonylhydrazones

A solution of sulfonyl hydrazine (10 mmol) in methanol (10 mL) was stirred and heated to 60 °C until the sulfonyl hydrazine dissolved. The mixture was cooled to room temperature and the carbonyl compound was dropped to the mixture slowly. After approximately 5 minutes the crude products could be obtained as solid precipitates. The precipitations were washed by petroleum ether, and were then kept in desiccator under vacuum to afford pure products **2**. The yields were around 80% - 95% in general.

General Procedure for the Synthesis of Dihydropyrazoles (Tables 2-4)

$Cu(OAc)_2 \cdot H_2O$ (80 mg, 0.4 mmol) and PivOH (40.8 mg, 0.4 mmol) were added to a solution of substrate **1** (0.2 mmol) and sulfoxonium ylide **2** (0.4 mmol) in toluene (2 mL). The mixture was stirred at 100 °C under air for 4 h. After the completion of the reaction (monitored by TLC), the reaction mixture was cooled to ambient temperature and the solvent was removed in vacuo to provide a crude product, which was purified by column chromatography on silica gel with petroleum ether/EtOAc as eluent to afford the products **3**, **4** or **5**.

phenyl(3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)methanone (3a): Yield: 87%; 70.5 mg, white solid; m.p = 178-180 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.07 (d, 2H, *J* = 7.2 Hz), 7.87 (d, 2H, *J* = 8.0 Hz), 7.64 (m, 3H), 7.51 (t, 2H, *J* = 7.4 Hz), 7.39 (m, 3H), 7.33 (d, 2H, *J* = 7.6 Hz), 5.27 (t, 1H, *J* = 11.2 Hz), 3.53 (dd, 1H, J_1 = 16.6 Hz, J_2 = 12.2 Hz), 3.33 (dd, 1H, J_1 = 16.8 Hz, J_2 = 10.4 Hz), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.6, 155.8, 144.6, 134.4, 133.8, 132.7, 130.8, 130.3, 129.6, 129.1, 128.9, 128.8, 128.7, 127.0. HRMS (ES^+-TOF) calcd for $C_{23}H_{21}N_2O_3S^+$ ($M+H^+$): 405.1267, found: 405.1278.

phenyl(3-(p-tolyl)-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)methanone (3b): Yield: 82%; 68.7 mg, white solid; m.p = 131-132 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.06 (d, 2H, *J* = 7.6 Hz), 7.86 (d, 2H, *J* = 8.0 Hz), 7.62 (t, 1H, *J* = 7.4 Hz), 7.55 (d, 2H, *J* = 8.4 Hz), 7.51 (t, 2H, *J* = 7.6 Hz), 7.32 (d, 2H, *J* = 8.0 Hz), 7.18 (d, 2H, *J* = 8.0 Hz), 5.20 (t, 1H, *J* = 11 Hz), 3.50 (dd, 1H, J_1 = 17 Hz, J_2 = 11.8 Hz), 3.31 (dd, 1H, J_1 = 16.8 Hz, J_2 = 10.4 Hz), 2.41 (s, 3H) , 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.6, 156.0, 144.5, 141.3, 134.4, 133.8, 132.5, 130.1, 129.6, 129.4, 129.2, 128.8, 128.7, 127.5, 126.9, 64.9, 39.1, 21.6, 24.5. HRMS (ES^+-TOF) calcd for $C_{24}H_{23}N_2O_3S^+$ ($M+H^+$): 419.1424, found: 419.1428.

phenyl(3-(m-tolyl)-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)methanone (3c): Yield: 64%; 53.8 mg, white solid; m.p = 127-128 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.05 (d, 2H, *J* = 7.6 Hz), 7.86 (d, 2H, *J* = 8.4 Hz), 7.62 (t, 2H, *J* = 7.2 Hz), 7.63 (m, 3H), 7.42 (d, 1H, *J* = 7.2 Hz), 7.32 (d 2H, *J* = 8.0 Hz), 7.24 (m, 2H), 5.22 (t, 1H, *J*= 11.2 Hz), 3.52 (dd, 1H, J_1 = 17.0 Hz, J_2 = 11.8 Hz), 3.31 (dd, 1H, J_1 = 16.8 Hz, J_2 = 10.4 Hz), 2.41 (s, 3H), 2.35 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.5, 156.0, 144.5, 138.4, 134.3, 133.8, 132.6, 131.6, 130.1, 129.6, 129.1, 128.8, 128.7, 128.5, 127.5, 124.1, 64.8, 39.1, 21.6, 21.3. HRMS (ES^+-TOF) calcd for $C_{24}H_{23}N_2O_3S^+$ ($M+H^+$): 419.1424, found: 419.1429.

phenyl(3-(o-tolyl)-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)methanone (3d): Yield: 77%; 64.5 mg, white solid; m.p = 126-128 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.08 (d, 2H, *J* = 7.6 Hz), 7.87 (d, 2H, *J* = 8.4 Hz), 7.63 (t, 1H, *J* = 7.4 Hz), 7.52 (t, 2H, *J* = 7.6 Hz), 7.34 (d, 2H, *J* = 8.4 Hz), 7.26 (m, 2H), 7.19 (m, 2H), 5.23 (t, 1H, *J*= 11.2 Hz), 3.55 (dd, 1H, J_1 = 16.8 Hz, J_2 = 12.0 Hz), 3.42 (dd, 1H, J_1 = 16.8 Hz, J_2 = 10.4 Hz), 2.56 (s, 3H), 2.43 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.8, 156.4, 144.6, 138.5, 134.5, 133.8, 132.8, 131.8, 129.9, 129.5, 129.1, 128.8, 128.7, 125.8, 64.0, 41.3, 23.2, 21.6. HRMS (ES^+-TOF) calcd for $C_{24}H_{23}N_2O_3S^+$ ($M+H^+$): 419.1424, found: 419.1431.

(3-(4-ethylphenyl)-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)(phenyl)methanone (3e): Yield: 80%; 69.2 mg, white solid; m.p = 123-125 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.06 (d, 2H, *J* = 7.6 Hz), 7.85 (d, 2H, *J* = 6.8 Hz), 7.60 (m, 3H), 7.50 (t, 2H, *J* = 6.8 Hz), 7.31 (d, 2H, *J* = 7.2 Hz), 7.21 (d, 2H, *J* = 6.4 Hz), 5.19 (t, 1H, *J* = 10.6 Hz), 3.50 (dd, 1H, J_1 = 17 Hz, J_2 = 11.8 Hz), 3.31 (dd, 1H, J_1 = 16.8 Hz, J_2 = 10.4 Hz), 2.66 (q, 2H, *J* = 6.9 Hz), 2.41 (s, 3H), 1.23 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.6, 156.0, 147.5, 144.5, 134.3, 133.8, 132.5, 129.6, 129.1, 129.0, 128.8, 128.7, 128.2, 127.6, 127.0, 64.9, 39.1, 28.8, 21.6, 15.3. HRMS (ES^+-TOF) calcd for $C_{25}H_{25}N_2O_3S^+$ ($M+H^+$): 433.1580, found: 433.1583.

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(3-(4-methoxyphenyl)-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)(phenyl)methanone (3f): Yield: 80%; 69.3 mg, white solid; m.p = 146-147 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.07 (d, 2H, *J* = 7.2 Hz), 7.85 (d, 2H, *J* = 8.4 Hz), 7.61 (m, 3H), 7.50 (t, 2H, *J* = 7.8 Hz), 7.32 (d, 2H, *J* = 8.0 Hz), 6.88 (d, 2H, *J* = 8.8 Hz), 5.18 (dd, 1H, J_1 = 11.6 Hz, J_2 = 10.4 Hz), 3.83 (s, 3H), 3.47 (dd, 1H, J_1 = 16.8 Hz, J_2 = 12 Hz), 3.31 (dd, 1H, J_1 = 17 Hz, J_2 = 10.2 Hz), 2.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.7, 161.7, 155.8, 144.5, 134.4, 133.8, 132.5, 129.6, 129.2, 128.8, 128.7, 128.6, 122.8, 114.1, 64.9, 55.4, 39.1, 21.6. HRMS (ES^+-TOF) calcd for $C_{24}H_{23}N_2O_4S^+$ ($M+H^+$): 435.1373, found: 435.1381.

(3-(4-(methylthio)phenyl)-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)(phenyl)methanone (3g): Yield: 64%; 57.4 mg, white solid; m.p = 166-168 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.06 (d, 2H, *J* = 7.2 Hz), 7.85 (d, 2H, *J* = 8.0 Hz), 7.62 (t, 1H, *J* = 7.2 Hz), 7.56 (d, 2H, *J* = 8.0 Hz), 7.51 (t, 2H, *J* = 7.8 Hz), 7.32 (d, 2H, *J* = 8.0 Hz), 7.20 (d, 2H, *J* = 8.4 Hz), 5.24 (t, 1H, *J* = 11.0 Hz), 3.49 (dd, 1H, J_1 = 17.0 Hz, J_2 = 11.8 Hz), 3.29 (dd, 1H, J_1 = 17.0 Hz, J_2 = 10.2 Hz), 2.49 (s, 3H) , 2.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.6, 155.5, 144.6, 142.6, 134.3, 133.8, 132.6, 129.6, 129.1, 128.8, 128.7, 127.2, 126.6, 125.6, 64.8, 38.9, 21.6, 15.1. HRMS (ES^+-TOF) calcd for $C_{24}H_{23}N_2O_3S_2^+$ ($M+H^+$): 451.1145, found: 451.1150.

(3-([1,1'-biphenyl]-4-yl)-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)(phenyl)methanone (3h): Yield: 70%; 67.1 mg, white solid; m.p = 143-145 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.08 (d, 2H, *J* = 7.6 Hz), 7.89 (d, 2H, *J* = 8.4 Hz), 7.73 (d, 2H, *J* = 8.0 Hz), 7.61 (m, 5H), 7.52 (t, 2H, *J* = 7.8 Hz), 7.46 (t, 2H, *J* = 7.6 Hz), 7.39 (d, 1H, *J* = 7.6 Hz), 7.34 (d, 2H, *J* = 8.4 Hz), 5.28 (t, 1H, *J* = 11.0 Hz), 3.57 (dd, 1H, J_1 = 17.0 Hz, J_2 = 11.8 Hz), 3.36 (dd, 1H, J_1 = 17.2 Hz, J_2 = 10.4 Hz), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.5, 155.5, 144.6, 143.5, 139.9, 134.3, 133.9, 132.6, 129.6, 129.1, 129.0, 128.9, 128.8, 128.7, 128.0, 127.4, 127.3, 127.0, 64.9, 39.1, 21.6. HRMS (ES^+-TOF) calcd for $C_{29}H_{25}N_2O_3S^+$ ($M+H^+$): 481.1580, found: 481.1585.

(3-(4-fluorophenyl)-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)(phenyl)methanone (3i): Yield: 83%; 70.2mg, white solid; m.p = 155-159 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.05 (d, 2H, *J* = 7.6 Hz), 7.85 (d, 2H, *J* = 8.0 Hz), 7.64 (m, 3H), 7.51 (t, 2H, *J* = 7.6 Hz), 7.33 (d, 2H, *J* = 8.0 Hz), 7.06 (t, 2H, *J* = 8.6 Hz), 5.32 (t, 1H, *J* = 10.8 Hz), 3.51 (dd, 1H, J_1 = 17.0 Hz, J_2 = 11.8 Hz), 3.30 (dd, 1H, J_1 = 17.0 Hz, J_2 = 10.2 Hz), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.5, 164.2 (d, J_{C-F} = 250.5 Hz), 154.8, 144.6, 134.3, 133.9, 132.7, 129.6, 129.1, 129.0 (d, J_{C-F} = 8.6 Hz), 128.9, 128.7, 126.5 (d, J_{C-F} = 3.1 Hz), 115.9 (d, J_{C-F} = 21.8 Hz), 64.6, 39.0, 21.6. HRMS (ES^+-TOF) calcd for $C_{23}H_{20}FN_2O_3S^+$ ($M+H^+$): 423.1173, found: 423.1180.

(3-(4-chlorophenyl)-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)(phenyl)methanone (3j): Yield: 74%; 65.1 mg, white solid; m.p = 162-163 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.05 (d, 2H, *J* = 7.6 Hz), 7.86 (d, 2H, *J* = 8.0 Hz), 7.64 (t, 1H, *J* = 7.4 Hz), 7.58 (d, 2H, *J* = 8.4 Hz), 7.52 (t, 2H, *J* = 7.6 Hz), 7.34 (m, 4H), 5.35 (dd, 1H, J_1 = 11.6 Hz, J_2 = 10.4 Hz), 3.51 (dd, 1H, J_1 = 16.8 Hz, J_2 = 12.0 Hz), 3.29 (dd, 1H, J_1 = 17.0 Hz, J_2 = 10.2 Hz), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.4, 154.7, 144.7, 136.9, 134.4, 134.0, 132.8, 129.7, 129.1, 129.0, 128.9, 128.7, 128.2, 64.6, 39.0, 21.7. HRMS (ES^+-TOF) calcd for $C_{23}H_{20}ClN_2O_3S^+$ ($M+H^+$): 439.0878, found: 439.0881.

(3-(4-bromophenyl)-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)(phenyl)methanone (3k): Yield: 73%; 70.5 mg, white solid; m.p = 169-171 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.05 (d, 2H, *J* = 7.6 Hz), 7.86 (d, 2H, *J* = 8.4 Hz), 7.64 (t, 1H, *J* = 7.4 Hz), 7.51 (m, 6H), 7.33 (d, 2H, *J* = 8.4 Hz), 5.35 (dd, 1H, J_1 = 11.6 Hz, J_2 = 10.0 Hz), 3.51 (dd, 1H, J_1 = 16.8 Hz, J_2 = 12.0 Hz), 3.29 (dd, 1H, J_1 = 17.0 Hz, J_2 = 10.2 Hz), 2.43 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.4, 154.7, 144.7, 134.3, 134.0, 132.8, 131.9, 129.7, 129.2, 129.1, 128.9, 128.7, 128.3, 125.2, 64.6, 38.8, 21.7. HRMS (ES^+-TOF) calcd for $C_{23}H_{20}BrN_2O_3S^+$ ($M+H^+$): 483.0373, found: 483.0380.

methyl 4-(5-benzoyl-1-tosyl-4,5-dihydro-1H-pyrazol-3-yl)benzoate (3l): Yield: 63%; 58.6 mg, white solid; m.p = 157-160 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.03 (t, 4H, *J* = 8.8 Hz), 7.87 (d, 2H, *J* = 8.4 Hz), 7.70 (d, 2H, *J* = 8.4 Hz), 7.63 (t, 1H, *J* = 7.4 Hz), 7.51 (t, 2H, *J* = 7.6 Hz), 7.33 (d, 2H, *J* = 8.4 Hz), 5.42 (dd, 1H, J_1 = 11.6 Hz, J_2 = 10.4 Hz), 3.91(s,3H), 3.58 (dd, 1H, J_1 = 16.8 Hz, J_2 = 12.0 Hz), 3.31 (dd, 1H, J_1 = 16.8 Hz, J_2 = 10.0 Hz), 2.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.3, 166.2, 154.5, 144.7, 134.3, 134.0, 132.9, 131.7, 129.8, 129.7, 129.0, 128.9, 128.6, 126.8, 64.5, 52.3, 38.9, 21.6. HRMS (ES^+-TOF) calcd for $C_{25}H_{23}N_2O_5S^+$ ($M+H^+$): 463.1322, found: 463.1327.

(3-(4-nitrophenyl)-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)(phenyl)methanone (3m): Yield: 75%; 67.1 mg, white solid; m.p = 161-163 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.23 (d, 2H, *J* = 8.8 Hz), 8.05 (d, 2H, *J* = 7.2 Hz), 7.89 (d, 2H, *J* = 8.0 Hz), 7.80 (d, 2H, *J* = 8.8 Hz), 7.66 (t, 1H, *J* = 7.4 Hz), 7.54 (t, 2H, *J* = 7.8 Hz), 7.36 (d, 2H, *J* = 8.0 Hz), 5.58 (dd, 1H, J_1 = 12.2 Hz, J_2 = 9.8 Hz), 3.62 (dd, 1H, J_1 = 17.0 Hz, J_2 = 12.2 Hz), 3.33 (dd, 1H, J_1 = 17.0 Hz, J_2 = 9.8 Hz), 2.44 (s, 3H). ^{13}C NMR (DMSO, 100 MHz) δ (ppm) 194.7, 155.2, 148.8, 145.2, 136.4, 134.7, 134.6, 133.2, 130.4, 129.5, 129.3, 128.6, 128.5, 124.4, 64.9, 39.1, 21.6. HRMS (ES^+-TOF) calcd for $C_{23}H_{20}N_3O_5S^+$ ($M+H^+$): 450.1118, found: 450.1121.

(3-(naphthalen-1-yl)-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)(phenyl)methanone (3n): Yield: 67%; 60.5 mg, white solid; m.p = 173-175 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 9.08 (d, 2H, *J* = 8.4 Hz), 8.11 (d, 2H, *J* = 7.6 Hz), 7.95 (d, 2H, *J* = 8.0 Hz), 7.86 (t, 2H, *J* = 7.0 Hz), 7.64 (t, 2H, *J* = 7.4 Hz), 7.55 (m, 3H), 7.41 (m, 2H), 7.33 (d, 2H, *J* = 8.0 Hz), 5.35 (t, 1H, *J* = 11.0 Hz), 3.70 (dd, 1H, J_1 = 16.8 Hz, J_2 = 11.6 Hz), 3.56 (dd, 1H, J_1 = 16.8 Hz, J_2 = 10.4 Hz), 2.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.8, 156.2, 144.7, 134.5, 133.9, 132.9, 131.7, 130.5, 129.7, 129.2, 128.9, 128.8, 128.6, 128.3, 127.8, 126.9, 126.5, 124.6, 63.9, 41.8, 21.7. HRMS (ES^+-TOF) calcd for $C_{27}H_{23}N_2O_3S^+$ ($M+H^+$): 455.1424, found: 455.1431.

(3-(furan-2-yl)-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)(phenyl)methanone (3o): Yield: 61%; 48.4 mg, light yellow solid; m.p = 149-151 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.05 (d, 2H, *J* = 7.6 Hz), 7.85 (d, 2H, *J* = 8.0 Hz), 7.63 (t, 1H, *J* = 7.2 Hz), 7.51 (m, 3H), 7.33 (d, 2H, *J* = 7.6 Hz), 6.81 (d, 1H, *J* = 2.8 Hz), 6.48 (s, 1H), 5.24 (t, 1H, *J* = 11.0 Hz), 3.48 (dd, 1H, J_1 = 17.2 Hz, J_2 = 12.0 Hz), 3.29 (dd, 1H, J_1 = 17.0 Hz, J_2 = 10.2 Hz), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.3, 147.7, 145.8, 144.9, 144.6, 134.3, 133.9, 132.6, 129.6, 129.1, 128.9, 128.8, 112.9, 112.1, 64.1, 38.9, 21.6. HRMS (ES^+-TOF) calcd for $C_{21}H_{19}N_2O_4S^+$ ($M+H^+$): 395.1060, found: 395.1072.

phenyl(3-(thiophen-2-yl)-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)methanone (3p): Yield: 56%; 45.7 mg, white solid; m.p = 144-146 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.06 (d, 2H, *J* = 7.6 Hz), 7.84 (d, 2H, *J* = 8.0 Hz), 7.63 (t, 1H, *J* = 7.4 Hz), 7.51 (t, 2H, *J* = 7.6 Hz), 7.43 (d, 1H, *J* = 5.2 Hz), 7.32 (d, 2H, *J* = 8.0 Hz), 7.60 (d, 1H, *J* = 3.6 Hz), 7.02 (t, 1H, *J* = 4.2 Hz), 5.22 (t, 1H, *J* = 10.8 Hz), 3.48 (dd, 1H, J_1 = 16.8 Hz, J_2 = 11.6 Hz), 3.35 (dd, 1H, J_1 = 16.6 Hz, J_2 = 10.2 Hz), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.3, 151.7, 144.6, 134.3, 133.9, 133.6, 132.4, 129.6, 129.3, 129.2, 128.8, 127.5, 64.9, 39.6, 21.6. HRMS (ES^+-TOF) calcd for $C_{21}H_{19}N_2O_3S_2^+$ ($M+H^+$): 411.0832, found: 411.0837.

(3-ferrocenyl-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)(phenyl)methanone (3q): Yield: 52%; 52.9 mg, red

solid; m.p = 189-191 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.12 (d, 2H, *J* = 6.8 Hz), 7.85 (d, 2H, *J* = 7.6 Hz), 7.62 (t, 1H, *J* = 6.4 Hz), 7.51 (t, 2H, *J* = 6.8 Hz), 7.35 (d, 2H, *J* = 7.2 Hz), 4.98 (t, 1H, *J* = 10.6 Hz), 4.60 (d, 2H, *J* = 7.2 Hz), 4.39 (s, 2H), 4.00 (s, 5H), 3.27 (d, 2H, *J* = 10.8 Hz), 2.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.8, 159.2, 144.6, 133.8, 129.5, 129.3, 128.9, 128.8, 70.8, 69., 68.2, 67.9, 64.9, 40.1, 21.6. HRMS (ES$^+$-TOF) calcd for $C_{27}H_{25}FeN_2O_3S^+$ (M+H$^+$): 513.0930, found: 513.0936.

phenyl(2-tosyl-3,3a,4,5-tetrahydro-2H-benzo[g]indazol-3-yl)methanone (3r): Yield: 61%; 60.1 mg, white solid; m.p = 182-184 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.16 (d, 2H, *J* = 7.6 Hz), 8.04 (d, 1H, *J* = 7.6 Hz), 7.82 (d, 2H, *J* = 8.0 Hz), 7.62 (t, 1H, *J* = 7.4 Hz), 7.51 (t, 2H, *J* = 7.6 Hz), 7.32 (m, 4H), 7.13 (d, 1H, *J* = 7.6 Hz), 4.52 (d, 1H, *J* = 12.4 Hz), 3.57 (dt, 1H, J_1 = 12.8 Hz, J_2 = 2.4 Hz), 2.85 (m, 2H), 2.16 (m, 1H), 1.61 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.8, 157.3, 144.7, 134.7, 133.7, 131.2, 131.1, 130.1, 129.6, 129.4, 129.1, 128.9, 128.7, 128.4, 126.9, 126.2, 125.8, 72.9, 51.2, 28.8, 27.5, 21.6. HRMS (ES$^+$-TOF) calcd for $C_{25}H_{23}N_2O_3S^+$ (M+H$^+$): 431.1424, found: 431.1423.

phenyl(2-tosyl-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazol-3-yl)methanone (3s): Yield: 67%; 59.4 mg, white solid; m.p = 93-95 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.10 (d, 2H, *J* = 7.6 Hz), 7.88 (d, 2H, *J* = 7.2 Hz), 7.84 (d, 2H, *J* = 8.4 Hz), 7.62 (t, 1H, *J* = 7.4 Hz), 7.51 (t, 2H, *J* = 7.8 Hz), 7.34 (d, 2H, *J* = 8.0 Hz), 7.31 (t, 1H, *J* = 7.2 Hz), 7.25 (m, 1H), 7.10 (d, 1H, *J* = 7.2 Hz), 4.67 (d, 1H, *J* = 10.4 Hz), 5.51 (dt, 1H, J_1 = 11.0 Hz, J_2 = 4.0 Hz), 2.86 (m, 1H), 2.60 (m, 1H), 2.44 (s, 3H), 1.99 (m, 1H), 1.79 (m, 1H), 1.28 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.9, 161.9, 144.6, 140.9, 134.6, 133.8, 131.9, 130.7, 130.3, 129.5, 129.4, 129.3, 128.9, 128.8, 126.7, 72.5, 52.7, 34.7, 31.1, 24.9, 21.7. HRMS (ES$^+$-TOF) calcd for $C_{26}H_{25}N_2O_3S^+$ (M+H$^+$): 445.1580, found: 445.1587.

(3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)(p-tolyl)methanone (4a): Yield: 85%; 71.5 mg, white solid; m.p = 152-154 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.96 (d, 2H, *J* = 8.4 Hz), 7.86 (d, 2H, *J* = 8.0 Hz), 7.65 (m, 2H), 7.40 (m, 3H), 7.31 (t, 4H, *J* = 7.8 Hz), 5.24 (dd, 1H, J_1 = 11.6 Hz, J_2 = 10.4 Hz), 3.51 (dd, 1H, J_1 = 17.0 Hz, J_2 = 11.8 Hz), 3.31 (dd, 1H, J_1 = 17.2 Hz, J_2 = 10.4 Hz), 2.43 (s, 3H), 2.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.7, 175.9, 155.6, 144.5, 138.8, 134.7, 134.4, 132.8, 130.7, 130.3, 129.6, 128.8, 128.6, 126.9, 126.2, 64.6, 39.1, 21.6, 21.4. HRMS (ES$^+$-TOF) calcd for $C_{24}H_{23}N_2O_3S^+$ (M+H$^+$): 419.1424, found: 419.1430.

(3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)(o-tolyl)methanone (4b): Yield: 53%; 44.6 mg, white solid; m.p = 126-128 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.80 (d, 2H, *J* = 8.4 Hz), 7.70 (d, 1H, *J* = 7.6 Hz), 7.65 (d, 2H, *J* = 8.0 Hz), 7.41 (m, 4H), 7.31 (m, 4H), 5.24 (dd, 1H, J_1 = 11.6 Hz, J_2 = 10.0 Hz), 3.49 (dd, 1H, J_1 = 16.8 Hz, J_2 = 12.0 Hz), 3.32 (dd, 1H, J_1 = 17.0 Hz, J_2 = 9.8 Hz), 2.54 (s, 3H), 2.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 198.1, 155.7, 144.5, 139.5, 135.5, 132.9, 132.1, 131.9, 130.7, 130.2, 129.6, 128.6, 128.4, 126.9, 125.6, 65.7, 38.7, 21.6, 21.1. HRMS (ES$^+$-TOF) calcd for $C_{24}H_{23}N_2O_3S^+$ (M+H$^+$): 419.1424, found: 419.1428.

(3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)(m-tolyl)methanone (4c): Yield: 78%; 65.2 mg, white solid; m.p = 120-121 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.86 (m, 4H), 7.66 (d, 2H, *J* = 6.8 Hz), 7.39 (m, 5H), 7.30 (d, 2H, *J* = 8.4 Hz), 5.35 (t, 1H, *J* = 11.2 Hz), 3.53 (dd, 1H, J_1 = 17.0 Hz, J_2 = 11.8 Hz), 3.31 (dd, 1H, J_1 = 17.2 Hz, J_2 = 10.4 Hz), 2.43 (s, 3H), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.1, 155.8, 144.9, 144.5, 132.7, 131.8, 130.7, 130.3, 129.6, 129.5, 129.2, 128.7, 128.6, 126.9, 64.7, 39.1, 21.7, 21.6. HRMS (ES$^+$-TOF) calcd for $C_{24}H_{23}N_2O_3S^+$ (M+H$^+$): 419.1424, found: 419.1429.

(4-methoxyphenyl)(3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)methanone (4d): Yield: 86%; 74.4 mg, white solid; m.p = 164-166 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.07 (d, 2H, *J* = 9.2 Hz), 7.87 (d, 2H, *J* = 8.4 Hz), 7.66 (d, 2H, *J* = 6.8 Hz), 7.40 (m, 3H), 7.32 (d, 2H, *J* = 8.0 Hz), 6.98 (d, 2H, *J* = 9.2 Hz), 5.19 (t, 1H, *J* = 11.0 Hz), 3.89 (s, 3H), 3.50 (dd, 1H, J_1 = 17.0 Hz, J_2 = 12.2 Hz), 3.33 (dd, 1H, J_1 = 16.8 Hz, J_2 = 10.4 Hz), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 193.0, 164.1, 155.9, 144.5, 132.6, 131.6, 130.7, 130.3, 129.6, 128.7, 128.6, 127.2, 126.9, 114.1, 64.7, 55.6, 39.2, 21.6. HRMS (ES$^+$-TOF) calcd for $C_{24}H_{23}N_2O_4S^+$ (M+H$^+$): 435.1373, found: 435.1381.

(4-fluorophenyl)(3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)methanone (4e): Yield: 82%; 69.1 mg, white solid; m.p = 166-168 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.12 (m, 2H), 7.84 (d, 2H, *J* = 8.4 Hz), 7.66 (d, 2H, *J* = 6.8 Hz), 7.40 (m, 3H), 7.32 (d, 2H, *J* = 8.4 Hz), 7.17 (d, 2H, J = 8.6 Hz), 5.16 (dd, 1H, J_1 = 11.6 Hz, J_2 = 10.8 Hz), 3.51 (dd, 1H, J_1 = 17.0 Hz, J_2 = 11.8 Hz), 3.33 (dd, 1H, J_1 = 16.8 Hz, J_2 = 10.4 Hz), 2.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 193.1, 166.1 (d, J_{C-F} = 255.1 Hz), 156.2, 144.7, 132.3, 132.0 (d, J_{C-F} = 9.5 Hz), 130.8, 130.7, 130.1, 129.7, 128.7 (d, J_{C-F} = 2.4 Hz), 127.0, 116.0 (d, J_{C-F} = 21.9 Hz), 65.0, 38.9, 21.6. HRMS (ES$^+$-TOF) calcd for $C_{23}H_{20}FN_2O_3S^+$ (M+H$^+$): 423.1173, found: 423.1171.

(4-chlorophenyl)(3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)methanone (4f): Yield: 80%; 70.1 mg, white solid; m.p = 159-161 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.03 (d, 2H, *J* = 8.4 Hz), 7.84 (d, 2H, *J* = 8.4 Hz), 7.66 (d, 2H, *J* = 6.8 Hz), 7.48 (d, 2H, *J* = 8.4 Hz), 7.40 (m, 3H), 7.33 (d, 2H, J = 8.0 Hz), 5.14 (t, 1H, *J* = 11.2 Hz), 3.51 (dd, 1H, J_1 = 17.0 Hz, J_2 = 11.8 Hz), 3.34 (dd, 1H, J_1 = 16.8 Hz, J_2 = 10.4 Hz), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 193.6, 166.6, 156.1, 144.7, 140.4, 132.6, 132.3, 130.9, 130.6, 130.1, 129.7, 129.2, 128.8, 128.7, 127.0, 65.1, 61.2, 38.9, 21.6. HRMS (ES$^+$-TOF) calcd for $C_{23}H_{20}ClN_2O_3S^+$ (M+H$^+$): 439.0878, found: 439.0880.

(4-bromophenyl)(3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)methanone (4g): Yield: 72%; 69.2 mg, white solid; m.p = 175-177 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.94 (d, 2H, *J* = 8.4 Hz), 7.84 (d, 2H, *J* = 8.0 Hz), 7.65 (t, 4H, *J* = 6.8 Hz), 7.40 (m, 3H), 7.32 (d, 2H, *J* = 8.0 Hz), 5.14 (t, 1H, *J* = 11.2 Hz), 3.51 (dd, 1H, J_1 = 17.0 Hz, J_2 = 12.2 Hz), 3.33 (dd, 1H, J_1 = 16.8 Hz, J_2 = 10.4 Hz), 2.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 193.8, 156.2, 144.7, 133.0, 132.3, 132.2, 130.9, 130.7, 130.1, 130.0, 129.2, 128.7, 128.7, 127.0, 65.0, 38.9, 21.6. HRMS (ES$^+$-TOF) calcd for $C_{23}H_{19}BrN_2O_3S$ (M+H$^+$): 483.0373, found: 483.0374.

(4-nitrophenyl)(3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)methanone (4h): Yield: 51%; 46.2 mg, yellow solid; m.p = 135-137 °C; ^{1}H NMR (DMSO, 400 MHz) δ (ppm) 8.45 (d, 2H, *J* = 8.8 Hz), 8.36 (d, 2H, *J* = 8.8 Hz), 7.83 (d, 2H, *J* = 8.0 Hz), 7.69 (d, 2H, *J* = 6.8 Hz), 7.48 (m, 5H), 5.62 (t, 1H, *J* = 10.8 Hz), 3.85 (dd, 1H, J_1 = 17.6 Hz, J_2 = 12.0 Hz), 3.49 (dd, 1H, J_1 = 17.6 Hz, J_2 = 9.6 Hz), 2.41 (s, 3H). ^{13}C NMR (DMSO, 100 MHz) δ (ppm) 194.6, 157.5, 150.9, 145.1, 139.4, 132.6, 131.4, 130.8, 130.4, 130.3, 129.3, 128.8, 127.4, 124.5, 64.9, 39.0, 21.6. HRMS (ES$^+$-TOF) calcd for $C_{23}H_{20}N_3O_5S^+$ (M+H$^+$): 450.1118, found: 450.1129.

(3,4-dichlorophenyl)(3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)methanone (4i): Yield: 70%; 66.0 mg, white solid; m.p = 171-173 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.15 (s, 1H), 7.92 (d, 1H, *J* = 8.8 Hz), 7.83 (d, 2H, *J* = 8.4 Hz), 7.66 (d, 2H, *J* = 6.8 Hz), 7.58 (d, 1H, *J* = 8.4 Hz), 7.40 (m, 3H), 7.33 (d, 2H, *J* = 8.0 Hz), 5.11 (t, 1H, *J* = 11.0 Hz), 3.51 (dd, 1H, J_1 = 17.0 Hz, J_2 = 11.8 Hz), 3.33 (dd, 1H, J_1 = 17.0 Hz, J_2 = 10.6 Hz), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 192.7, 156.3, 144.9, 138.5, 133.8, 133.6, 132.1, 131.1, 131.0, 130.9, 129.9,

129.7, 128.7, 128.1, 127.0, 64.9, 38.7, 21.6. HRMS (ES^+-TOF) calcd for $C_{23}H_{19}Cl_2N_2O_3S^+$ ($M+H^+$): 473.0488, found: 473.0485.

naphthalen-2-yl(3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)methanone (4j): Yield: 67%; 61.3 mg, white solid; m.p = 178-179 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.61 (s, 1H), 8.09 (dd, 1H, J_1 = 8.6 Hz, J_2 = 1.4 Hz), 7.98 (d, 1H, J = 8.0 Hz), 7.93 (d, 1H, J = 8.8 Hz), 7.89 (d, 3H, J = 8.4 Hz), 7.66 (m, 3H), 7.57 (d, 1H, J = 7.2 Hz), 7.39 (m, 3H), 7.32 (d, 2H, J = 8.4 Hz), 5.44 (dd, 1H, J_1 = 11.6 Hz, J_2 = 10.4 Hz), 3.60 (dd, 1H, J_1 = 17.2 Hz, J_2 = 12.0 Hz), 3.40 (dd, 1H, J_1 = 17.2 Hz, J_2 = 10.4 Hz), 2.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.6, 156.0, 144.6, 135.9, 132.4, 131.8, 131.1, 130.8, 130.3, 129.9, 129.7, 129.0, 128.8, 128.7, 127.8, 127.0, 124.4, 64.7, 39.2, 21.7. HRMS (ES^+-TOF) calcd for $C_{27}H_{23}N_2O_3S^+$ ($M+H^+$): 455.1424, found: 455.1430.

(3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)(thiophen-2-yl)methanone (4k): Yield: 54%; 44.1 mg, white solid; m.p = 178-179 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.02 (d, 1H, J = 3.2 Hz), 7.85 (d, 2H, J = 8.4 Hz), 7.73 (d, 1H, J = 4.8 Hz), 7.66 (d, 2H, J = 7.6 Hz), 7.41 (m, 3H), 7.32 (d, 2H, J = 8.0 Hz), 7.18 (t, 1H, J = 4.4 Hz), 4.85 (t, 1H, J = 11.2 Hz), 3.51 (dd, 1H, J_1 = 17.2 Hz, J_2 = 11.6 Hz), 3.38 (dd, 1H, J_1 = 17.2 Hz, J_2 = 11.0 Hz), 2.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 187.9, 156.5, 144.8, 139.8, 135.3, 134.2, 131.8, 130.9, 130.0, 129.7, 128.8, 128.7, 128.5, 127.0, 66.5, 39.4, 21.6. HRMS (ES^+-TOF) calcd for $C_{21}H_{19}N_2O_3S_2^+$ ($M+H^+$): 411.0832, found: 411.0838.

(E)-3-phenyl-1-(3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)prop-2-en-1-one (4l): Yield: 55%; 46.9 mg, white solid; m.p = 125-127 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.83 (m, 3H), 7.66 (m, 4H), 7.41 (m, 7H), 7.31 (d, 2H, J = 8.4 Hz), 4.51 (dd, 1H, J_1 = 11.4 Hz, J_2 = 9.8 Hz), 3.38 (dd, 1H, J_1 = 17.4 Hz, J_2 = 9.8 Hz), 3.26 (dd, 1H, J_1 = 17.6 Hz, J_2 = 11.6 Hz), 2.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.6, 158.2, 145.9, 144.8, 134.3, 131.6, 131.0, 130.1, 129.7, 128.9, 128.8, 128.7, 127.1, 120.3, 67.8, 37.4, 21.6. HRMS (ES^+-TOF) calcd for $C_{25}H_{23}N_2O_3S^+$ ($M+H^+$):431.1424, found: 431.1432.

1-(3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)propan-1-one (4m): Yield: 47%; 33.3 mg, white solid; m.p = 156-157 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.78 (d, 2H, J = 8.0 Hz), 7.65 (d, 2H, J = 7.2 Hz), 7.40 (m, 3H), 7.29 (d, 2H, J = 8.0 Hz), 4.32 (t, 1H, J = 10.6 Hz), 3.21 (m, 2H), 3.05 (dd, 1H, J_1 = 19.2 Hz, J_2 = 7.6 Hz), 2.88 (dd, 1H, J_1 = 19.2 Hz, J_2 = 7.2 Hz), 2.39 (s, 3H), 1.14 (t, 3H, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 208.0, 158.1, 144.8, 131.4, 131.0, 130.0, 129.7, 128.7, 127.1, 67.9, 37.3, 31.9, 21.6, 7.3. HRMS (ES^+-TOF) calcd for $C_{19}H_{21}N_2O_3S^+$ ($M+H^+$):357.1267, found: 357.1277.

1-(3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)butan-1-one (4n): Yield: 50%; 37.2 mg, white solid; m.p = 149-151 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.78 (d, 2H, J = 8.0 Hz), 7.65 (d, 2H, J = 6.8 Hz), 7.41 (m, 3H), 7.29 (d, 2H, J = 8.0 Hz), 4.30 (t, 1H, J = 10.6 Hz), 3.20 (m, 2H), 3.00 (m, 1H), 2.82 (m, 1H), 2.39 (s, 3H), 1.67 (m, 2H), 0.96 (t, 3H, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 207.1, 158.0, 144.8, 131.4, 131.0, 130.0, 129.7, 128.8, 128.7, 127.0, 68.0, 40.3, 37.2, 21.6, 16.6, 13.6. HRMS (ES^+-TOF) calcd for $C_{20}H_{23}N_2O_3S^+$ ($M+H^+$): 371.1424, found: 371.1430.

1-(3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)pentan-1-one (4o): Yield: 41%; 31.9 mg, white solid; m.p = 154-156 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.78 (d, 2H, J = 8.4 Hz), 7.65 (d, 2H, J = 6.8 Hz), 7.41 (m, 3H), 7.29 (d, 2H, J = 8.0 Hz), 4.30 (dd, 1H, J_1 = 11.2 Hz, J_2 = 8.0 Hz), 3.19 (m, 2H), 2.97 (m, 1H), 2.85 (m, 1H), 2.39 (s, 3H), 1.62 (m, 2H), 1.36 (m, 2H), 0.93 (t, 3H, J = 7.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 207.4, 158.0, 144.8, 131.3, 131.0, 130.0, 129.7, 128.8, 128.7, 127.0, 68.1, 38.2, 37.2, 25.2, 22.2, 21.6, 13.9. HRMS (ES^+-TOF) calcd for $C_{21}H_{25}N_2O_3S^+$ ($M+H^+$): 385.1580, found: 385.1586.

cyclohexyl(3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazol-5-yl)methanone (4p): Yield: 52%; 42.6 mg, white solid; m.p = 144-146 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.79 (d, 2H, J = 8.4 Hz), 7.65 (d, 2H, J = 6.8 Hz), 7.40 (m, 3H), 7.29 (d, 2H, J = 8.0 Hz), 4.47 (dd, 1H, J_1 = 11.6 Hz, J_2 = 9.2 Hz), 3.25 (dd, 1H, J_1 = 17.2 Hz, J_2 = 9.2 Hz), 3.15 (dd, 1H, J_1 = 17.0 Hz, J_2 = 11.8 Hz), 2.39 (s, 3H), 2.04 (d, 1H, J = 7.2 Hz), 1.79 (m, 4H), 1.41 (m, 4H), 1.25 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 209.6, 158.0, 144.7, 131.8, 130.1, 129.6, 128.7, 128.6, 127.1, 66.6, 46.8, 37.4, 29.1, 28.5, 25.8, 25.5, 25.5, 21.6. HRMS (ES^+-TOF) calcd for $C_{23}H_{27}N_2O_3S^+$ ($M+H^+$): 411.1737, found: 411.1739.

phenyl(3-phenyl-1-(phenylsulfonyl)-4,5-dihydro-1H-pyrazol-5-yl)methanone (5a): Yield: 66%; 51.3 mg, white solid; m.p = 164-166 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.06 (d, 2H, J = 8.0 Hz), 7.99 (d, 2H, J = 7.6 Hz), 7.66 (d, 2H, J = 7.2 Hz), 7.62 (t, 2H, J = 6.2 Hz), 7.52 (m, 4H), 7.40 (m, 3H), 5.32 (dd, 1H, J_1 = 11.6 Hz, J_2 = 10.4 Hz), 3.55 (dd, 1H, J_1 = 16.8 Hz, J_2 = 12.0 Hz), 3.33 (dd, 1H, J_1 = 17.0 Hz, J_2 = 10.2 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.5, 156.0, 135.9, 134.3, 134.0, 133.6, 130.9, 129.1, 129.0, 128.9, 128.7, 127.0, 64.7, 39.1. HRMS (ES^+-TOF) calcd for $C_{22}H_{19}N_2O_3S^+$ ($M+H^+$): 391.1111, found: 391.1118.

(1-((4-methoxyphenyl)sulfonyl)-3-phenyl-4,5-dihydro-1H-pyrazol-5-yl)(phenyl)methanone (5b): Yield: 74%; 62.4 mg, white solid; m.p = 188-190 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.07 (d, 2H, J = 7.6 Hz), 7.92 (d, 2H, J = 9.2 Hz), 7.65 (m, 3H), 7.51 (t, 2H, J = 7.6 Hz), 7.40 (m, 3H), 6.99 (d, 2H, J = 9.2 Hz), 5.24 (dd, 1H, J_1 = 11.6 Hz, J_2 = 10.4 Hz), 3.85 (s, 3H), 3.54 (dd, 1H, J_1 = 16.8 Hz, J_2 = 12.0 Hz), 3.33 (dd, 1H, J_1 = 16.8 Hz, J_2 = 10.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.6, 163.7, 155.8, 134.3, 133.8, 130.9, 130.8, 130.2, 129.1, 128.8, 128.7, 126.9, 114.2, 64.9, 55.6, 39.0. HRMS (ES^+-TOF) calcd for $C_{23}H_{21}N_2O_4S^+$ ($M+H^+$): 421.1217, found: 421.1220.

(1-((4-(tert-butyl)phenyl)sulfonyl)-3-phenyl-4,5-dihydro-1H-pyrazol-5-yl)(phenyl)methanone (5c): Yield: 71%; 63.7 mg, white solid; m.p = 192-194 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.07 (d, 2H, J = 7.2 Hz), 7.91 (d, 2H, J = 8.0 Hz), 7.67 (d, 2H, J = 6.8 Hz), 7.63 (t, 1H, J = 7.4 Hz), 7.52 (m, 4H), 7.39 (m, 3H), 5.30 (t, 1H, J = 11.0 Hz), 3.57 (dd, 1H, J_1 = 17.0 Hz, J_2 = 11.8 Hz), 3.34 (dd, 1H, J_1 = 16.8 Hz, J_2 = 10.4 Hz), 1.33 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.6, 157.4, 155.7, 134.3, 133.8, 132.7, 130.7, 130.3, 129.1, 128.8, 128.6, 128.5, 127.0, 126.0, 64.7, 39.0, 32.2, 31.0. HRMS (ES^+-TOF) calcd for $C_{26}H_{27}N_2O_3S^+$ ($M+H^+$): 447.1737, found: 447.1741.

(1-((4-fluorophenyl)sulfonyl)-3-phenyl-4,5-dihydro-1H-pyrazol-5-yl)(phenyl)methanone (5d): Yield: 73%; 59.8 mg, white solid; m.p = 193-195 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.04 (m, 4H), 7.65 (m, 3H), 7.52 (t, 2H, J = 7.8 Hz), 7.40 (m, 3H), 7.22 (t, 2H, J = 8.6 Hz), 5.39 (dd, 1H, J_1 = 12.0 Hz, J_2 = 10.0 Hz), 3.62 (dd, 1H, J_1 = 17.2 Hz, J_2 = 12.0 Hz), 3.34 (dd, 1H, J_1 = 17.0 Hz, J_2 = 9.8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.4, 165.8 (d, J_{C-F} = 261.7 Hz), 155.9, 134.0, 131.5 (d, J_{C-F} = 9.7 Hz), 130.1, 129.0 (d, J_{C-F} = 13.1 Hz), 128.7, 126.9, 116.3 (d, J_{C-F} = 22.4 Hz), 64.5, 39.1. HRMS (ES^+-TOF) calcd for $C_{22}H_{18}FN_2O_3S^+$ ($M+H^+$): 409.1017, found: 409.1021.

(1-((4-chlorophenyl)sulfonyl)-3-phenyl-4,5-dihydro-1H-pyrazol-5-yl)(phenyl)methanone (5e): Yield: 64%; 54.6 mg, white solid; m.p = 196-198 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.04 (d, 2H, J = 7.6 Hz), 7.94 (d, 2H, J = 8.4 Hz), 7.64 (t, 3H, J = 6.6 Hz), 7.52 (t, 4H, J = 7.6 Hz), 7.40 (m, 3H), 5.40 (dd, 1H, J_1 = 12.0 Hz, J_2 = 10.0 Hz), 3.62 (dd, 1H, J_1 = 16.8 Hz, J_2 = 12.0 Hz), 3.33 (dd, 1H, J_1 = 17.0 Hz, J_2 = 9.8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ

(ppm) 194.2, 155.9, 140.2, 134.7, 134.2, 134.0, 130.9, 130.1, 130.0, 129.3, 129.0, 128.9, 128.7, 126.9, 64.5, 39.1. HRMS (ES^+-TOF) calcd for $C_{22}H_{18}ClN_2O_3S^+$ ($M+H^+$): 425.0721, found: 425.0724.

(1-((4-bromophenyl)sulfonyl)-3-phenyl-4,5-dihydro-1H-pyrazol-5-yl)(phenyl)methanone (5f): Yield: 52%; 49.1 mg, white solid; m.p = 202-204 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.04 (d, 2H, J = 7.6 Hz), 7.86 (d, 2H, J = 8.4 Hz), 7.66 (m, 5H), 7.52 (t, 2H, J = 7.6 Hz), 7.40 (m, 3H), 5.40 (t, 1H, J = 10.8 Hz), 3.62 (dd, 1H, J_1 = 16.8 Hz, J_2 = 12.0 Hz), 3.33 (dd, 1H, J_1 = 17.0 Hz, J_2 = 10.2 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.2, 155.9, 135.2, 134.2, 134.0, 132.3, 130.9, 130.1, 130.0, 129.0, 128.9, 128.8, 128.7, 126.9, 64.5, 39.1. HRMS (ES^+-TOF) calcd for $C_{22}H_{18}BrN_2O_3S^+$ ($M+H^+$): 469.0216, found: 469.0221.

(1-((4-nitrophenyl)sulfonyl)-3-phenyl-4,5-dihydro-1H-pyrazol-5-yl)(phenyl)methanone (5g): Yield: 72%; 62.4 mg, white solid; m.p = 182-184 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.39 (d, 2H, J = 8.0 Hz), 8.22 (d, 2H, J = 8.0 Hz), 8.00 (d, 2H, J = 7.2 Hz), 7.65 (m, 3H), 7.54 (t, 2H, J = 7.2 Hz), 7.40 (m, 3H), 5.68 (t, 1H, J = 10.2 Hz), 3.72 (dd, 1H, J_1 = 16.2 Hz, J_2 = 13.0 Hz), 3.31 (dd, 1H, J_1 = 16.8 Hz, J_2 = 8.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 193.9, 155.8, 150.4, 142.9, 134.3, 133.9, 131.1, 129.8, 129.1, 129.0, 128.8, 126.9, 124.0, 64.0, 39.1. HRMS (ES^+-TOF) calcd for $C_{22}H_{18}N_3O_5S^+$ ($M+H^+$): 436.0962, found: 436.0963.

phenyl(3-phenyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)-4,5-dihydro-1H-pyrazol-5-yl)methanone (5h): Yield: 66%; 60.6 mg, white solid; m.p = 177-179 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.15 (d, 2H, J = 8.4 Hz), 8.03 (d, 2H, J = 7.2 Hz), 7.82 (d, 2H, J = 8.4 Hz), 7.66 (m, 3H), 7.53 (t, 2H, J = 7.6 Hz), 7.40 (m, 3H), 5.53 (dd, 1H, J_1 = 12.2 Hz, J_2 = 9.4 Hz), 3.67 (dd, 1H, J_1 = 17.0 Hz, J_2 = 12.2 Hz), 3.33 (dd, 1H, J_1 = 17.0 Hz, J_2 = 9.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.1, 155.9, 140.2, 135.1, 134.8, 134.1, 134.0, 129.9, 129.0, 128.0 (q, $J_{C\text{-}CF3}$ = 218.4 Hz), 126.0 (q, $J_{C\text{-}CF3}$ = 3.5 Hz), 121.8, 64.2, 39.1. HRMS (ES^+-TOF) calcd for $C_{23}H_{18}F_3N_2O_3S^+$ ($M+H^+$): 459.0985, found: 459.0991.

(1-(naphthalen-2-ylsulfonyl)-3-phenyl-4,5-dihydro-1H-pyrazol-5-yl)(phenyl)methanone (5i): Yield: 61%; 53.8 mg, white solid; m.p = 219-221 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.54 (s, 1H), 8.08 (d, 2H, J = 7.2 Hz), 7.99 (m, 3H), 7.90 (d, 2H, J = 8.0 Hz), 7.63 (m, 5H), 7.52 (d, 2H, J = 7.6 Hz), 7.38 (m, 3H), 5.35 (dd, 1H, J_1 = 11.8 Hz, J_2 = 10.6 Hz), 3.54 (dd, 1H, J_1 = 17.2 Hz, J_2 = 12.0 Hz), 3.34 (dd, 1H, J_1 = 17.2 Hz, J_2 = 10.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.5, 155.9, 135.2, 134.3, 133.9, 132.7, 132.0, 130.8, 130.3, 130.1, 129.5, 129.2, 129.1, 128.9, 128.6, 127.9, 127.5, 126.9, 123.6, 64.8, 39.1. HRMS (ES^+-TOF) calcd for $C_{26}H_{21}N_2O_3S^+$ ($M+H^+$): 441.1267, found: 441.1272.

phenyl(3-phenyl-1-(thiophen-2-ylsulfonyl)-4,5-dihydro-1H-pyrazol-5-yl)methanone (5j): Yield: 53%; 42.4 mg, white solid; m.p = 184-186 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.06 (d, 2H, J = 7.2 Hz), 7.70 (m, 4H), 7.63 (t, 1H, J = 7.2 Hz), 7.42 (m, 3H), 7.14 (t, 1H, J = 4.4 Hz), 5.24 (t, 1H, J = 11.0 Hz), 3.55 (dd, 1H, J_1 = 16.6 Hz, J_2 = 11.8 Hz), 3.39 (dd, 1H, J_1 = 16.6 Hz, J_2 = 10.6 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.2, 156.8, 134.5, 134.3, 134.0, 131.1, 130.0, 129.1, 128.9, 128.7, 127.5, 127.1, 65.0, 39.3. HRMS (ES^+-TOF) calcd for $C_{20}H_{17}N_2O_3S_2^+$ ($M+H^+$): 397.0675, found: 397.0678.

(1-(methylsulfonyl)-3-phenyl-4,5-dihydro-1H-pyrazol-5-yl)(phenyl)methanone (5k): Yield: 76%; 49.9 mg, white solid; m.p = 173-175 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.01 (d, 2H, J = 7.2 Hz), 7.69 (d, 2H, J = 7.2 Hz), 7.64 (t, 1H, J = 7.4 Hz), 7.52 (t, 2H, J = 7.8 Hz), 7.38 (m, 3H), 5.90 (dd, 1H, J_1 = 12.4 Hz, J_2 = 7.6 Hz), 3.78 (dd, 1H, J_1 = 17.0 Hz, J_2 = 12.6 Hz), 3.35 (s, 3H), 3.30 (dd, 1H, J_1 = 17.2 Hz, J_2 = 7.6 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.7, 154.5, 134.1, 130.6, 130.2, 129.0, 128.9, 128.6, 126.8, 62.8, 39.5, 38.9. HRMS (ES^+-TOF) calcd for $C_{17}H_{17}N_2O_3S^+$ ($M+H^+$): 329.0954, found: 329.0959.

(1-(ethylsulfonyl)-3-phenyl-4,5-dihydro-1H-pyrazol-5-yl)(phenyl)methanone (5l): Yield: 81%; 55.7 mg, white solid; m.p = 162-164 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.02 (d, 2H, J = 7.6 Hz), 7.69 (d, 2H, J = 7.2 Hz), 7.64 (t, 1H, J = 7.2 Hz), 7.52 (t, 2H, J = 7.6 Hz), 7.40 (m, 3H), 5.92 (dd, 1H, J_1 = 12.4 Hz, J_2 = 8.4 Hz), 3.77 (dd, 1H, J_1 = 17.2 Hz, J_2 = 12.4 Hz), 3.55 (m, 2H), 3.30 (dd, 1H, J_1 = 17.2 Hz, J_2 = 8.4 Hz), 1.52 (t, 3H, J = 7.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 195.0, 154.7, 134.2, 134.1, 130.6, 130.3, 129.0, 128.9, 128.7, 126.8, 61.9, 47.1, 38.9, 7.74. HRMS (ES^+-TOF) calcd for $C_{18}H_{19}N_2O_3S^+$ ($M+H^+$): 343.1111, found: 343.1121.

phenyl(3-phenyl-1-(propylsulfonyl)-4,5-dihydro-1H-pyrazol-5-yl)methanone (5m): Yield: 80%; 56.8 mg, white solid; m.p = 151-153 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.01 (d, 2H, J = 7.6 Hz), 7.69 (d, 2H, J = 7.2 Hz), 7.63 (t, 1H, J = 7.4 Hz), 7.51 (t, 2H, J = 7.8 Hz), 7.39 (m, 3H), 5.91 (dd, 1H, J_1 = 12.4 Hz, J_2 = 8.4 Hz), 3.76 (dd, 1H, J_1 = 17.0 Hz, J_2 = 12.2 Hz), 3.48 (m, 2H), 3.28 (dd, 1H, J_1 = 17.0 Hz, J_2 = 8.2 Hz), 2.01 (m, 2H), 1.10 (t, 3H, J = 7.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 195.0, 154.6, 134.2, 134.0, 130.6, 130.3, 128.9, 128.6, 126.8, 62.0, 54.1, 38.9, 16.8, 13.0. HRMS (ES^+-TOF) calcd for $C_{19}H_{21}N_2O_3S^+$ ($M+H^+$): 357.1267, found: 357.1277.

(1-(benzylsulfonyl)-3-phenyl-4,5-dihydro-1H-pyrazol-5-yl)(phenyl)methanone (5n): Yield: 78%; 62.7 mg, white solid; m.p = 192-193 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.86 (d, 2H, J = 7.6 Hz), 7.69 (d, 2H, J = 6.2 Hz), 7.61 (t, 1H, J = 7.4 Hz), 7.41 (m, 10H), 5.46 (dd, 1H, J_1 = 12.4 Hz, J_2 = 8.0 Hz), 4.76 (dd, 2H, J_1 = 50.6 Hz, J_2 = 13.8 Hz), 3.55 (dd, 1H, J_1 = 17.2 Hz, J_2 = 12.4 Hz), 3.21 (dd, 1H, J_1 = 17.0 Hz, J_2 = 7.8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.6, 154.76, 134.0, 133.9, 131.2 130.7, 130.3, 128.9, 128.8, 128.7, 128.1, 126.8, 63.5, 58.4, 38.8. HRMS (ES^+-TOF) calcd for $C_{23}H_{21}N_2O_3S^+$ ($M+H^+$): 405.1267, found: 405.1267.

5-benzoyl-N,N-dimethyl-3-phenyl-4,5-dihydro-1H-pyrazole-1-sulfonamide (5o): Yield: 89%; 63.7 mg, white solid; m.p = 174-176 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.03 (d, 2H, J = 7.6 Hz), 7.68 (d, 2H, J = 6.4 Hz), 7.62 (t, 2H, J = 7.4 Hz), 7.50 (t, 2H, J = 7.6 Hz), 7.40 (m, 3H), 5.71 (dd, 1H, J_1 = 11.6 Hz, J_2 = 10.0 Hz), 3.71 (dd, 1H, J_1 = 16.8 Hz, J_2 = 12.0 Hz), 3.28 (dd, 1H, J_1 = 17.0 Hz, J_2 = 10.2 Hz), 3.04 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 195.5, 154.9, 134.9, 133.8, 130.5, 128.8, 128.7, 128.6, 126.8, 63.2, 38.8, 38.6. HRMS (ES^+-TOF) calcd for $C_{18}H_{20}N_3O_3S^+$ ($M+H^+$): 358.1220, found: 358.1231.

(1-((3,5-dimethylisoxazol-4-yl)sulfonyl)-3-phenyl-4,5-dihydro-1H-pyrazol-5-yl)(phenyl)methanone (5p): Yield: 95%; 77.9 mg, white solid; m.p = 179-181 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.04 (d, 2H, J = 7.6 Hz), 7.64 (d, 2H, J = 7.2 Hz), 7.52 (t, 2H, J = 7.6 Hz), 7.42 (m, 3H), 5.51 (t, 1H, J = 10.8 Hz), 3.76 (dd, 1H, J_1 = 17.0 Hz, J_2 = 12.2 Hz), 3.37 (dd, 1H, J_1 = 17.0 Hz, J_2 = 9.6 Hz), 2.68 (s, 3H) , 2.48 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.1, 175.5, 158.7, 156.3, 134.1, 134.0, 131.1, 1299.9, 1299.0, 128.9, 128.8, 126.9, 113.3, 63.8, 39.2, 13.0, 11.1. HRMS (ES^+-TOF) calcd for $C_{21}H_{20}N_3O_4S^+$ ($M+H^+$): 410.1169, found: 410.1172.

The Control Experiment

$Cu(OAc)_2 \cdot H_2O$ (80 mg, 0.4 mmol) and PivOH (40.8 mg, 0.4 mmol) were added to a solution of substrate **1a** (0.2 mmol) and **2a** (0.4 mmol) in toluene (2 mL). The mixture was stirred at 100 °C under air. During 1-2 hours, the sample of the reaction was tested by LC-HRMS at half-

hour intervals. The proposed intermediate **A, B, C, D, E** and **F** (See the Scheme 1-2) could be detected at different periods of time.

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[12] Compound **4a** was determined by X-ray crystallography. See the Supporting Information for full details. CCDC 1888422 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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FULL PAPER

Synthesis of Multi-substituted Dihydropyrazoles by Copper-Mediated [4+1] Cycloaddition Reaction of *N*-Sulfonylhydrazones and Sulfoxonium Ylides

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