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1,3-Dipolar Cycloaddition of Alkyne-Tethered *N*-Tosylhydrazones: Synthesis of Fused Polycyclic Pyrazoles

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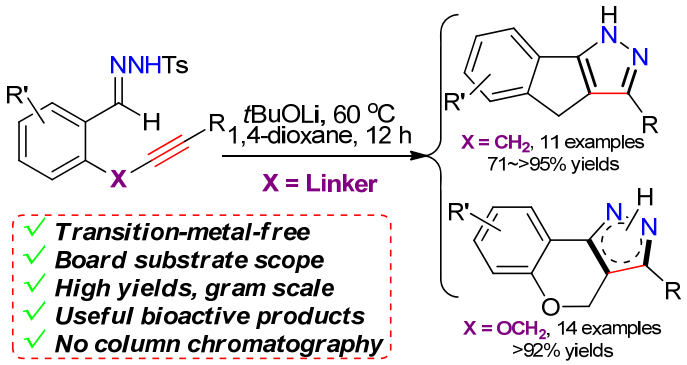
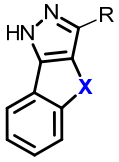


ABSTRACT: A general and transition-metal-free access to the fused polycyclic pyrazoles *via* an intramolecular 1,3-dipolar cycloaddition reaction of alkyne-tethered tosylhydrazones has been reported. The pure solid products could be obtained without column chromatography in high to excellent yields, and the obtained products are useful bioactive molecules or could be used as the key intermediate for synthesis of these compounds in one or two steps. Additionally, a [3+2]-cycloaddition followed by a direct *H*-shift aromatization reaction mechanism was proposed, which is different from previously reported aryl or alkyl sequential [1,5]-sigmatropic rearrangement pathway.

INTRODUCTION

The fused polycyclic pyrazole motif is a core structure in various important heterocycles, which show broad bioactivities and are extensively applied in pharmacology.[1-4] For example, compound **A** is an important KDR kinase inhibitor,[2a] and its also works as a vascular endothelial growth factor (VEGF);[2b] the ketone

variant **B** shows anti-depression and antitumor activities;[3] and molecule **C** works as an effective benzodiazepine receptor (BZR) ligand (Figure 1).[4] During the past decades, methods are developed for the pyrazoles construction, especially for the multi-substituted and fused polycyclic structure.[5-11] Among these works, stepwise condensation of 1,3-dicarbonyl compounds with hydrazines, which is known as Knorr pyrazole synthesis, is a classic access to these library of compounds.[5] Recently, Joksović[5e] and Banerjee[5f] disclosed two eco-friendly processes of this transformation by carrying out the reactions "in water" or "in one-pot" individually.



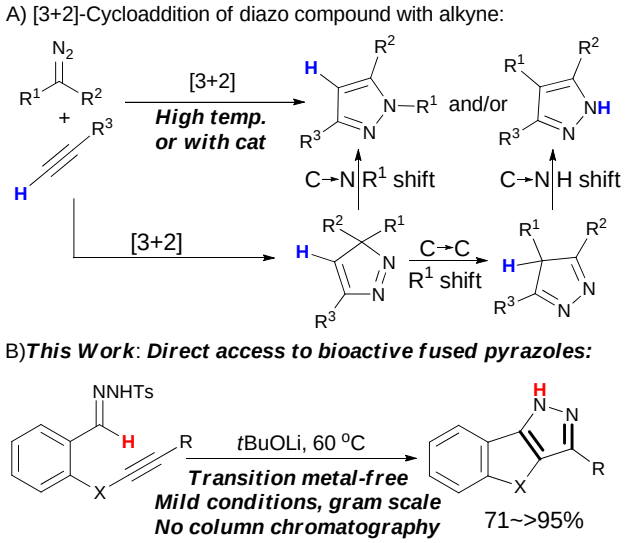
A, **X = CH_2**, R = Ar,
KDR kinase inhibitor
B, **X = CO**, R = Ar,
Antidepressive and antitumor activity
C, **X = OCO**, R = Ph or Me,
Benzodiazepine receptors (BZR) ligand

Figure 1. Selected examples of bioactive fused polycyclic pyrazoles.

On the other hand, 1,3-dipolar cycloaddition of diazo compounds, hydrazones or their equivalents, with C-C double or triple bonds is a complementary approach to the pyrazole framework (Scheme 1).[7-12] Breakthroughs have been disclosed recently in this context, for example, 1,3-dipolar cycloaddition of diazo compounds to electron-deficient alkynes were reported by Li[7a] and Legros[7b], which were carried out in water or under catalyst-free conditions individually. In addition, Valdés reported a one-step approach with *N*-tosylhydrazones and alkynes, which broadly expended the substrate scope of the 1,3-dipoles.[8] Nevertheless, challenges remain in these reactions, for example, the migration preference in the dipolar cycloaddition reaction (Scheme 1A, R^1 vs R^2 shift; and/or C→N vs C→C migration).[8] Meanwhile, high temperature (>100 ^oC),[8] or catalysts[9] are inescapable to promote these transformations, and even using transition-metal catalyst in some case.[10] In addition, substrate limitation is another shortcoming in this cycloaddition reaction. Although the diazo compound part is extended *via* applying hydrazones as their stable precursor by Valdés in this [3+2]-cycloaddition,[8] only terminal alkynes[8,9,10a,10b] or alkynes with carbonyl group[10c,10d] are reported in these transformations. And reaction with internal alkynes, which have two different substitutions on each carbon, is rare.[13] Additionally, direct approaches to the fused polycyclic pyrazole frameworks are under development[6] compared with the method to the multi-substituted pyrazoles. Inspired by these works,

and in our continuing interest in bioactive fused polycyclic structure synthesis,[14] we disclose here a direct access to fused polycyclic pyrazoles *via* an intramolecular [3+2]-cycloaddition reaction of alkyne-tethered tosylhydrazones under mild conditions (60 °C, transition-metal-free) with high to excellent yields (Scheme 1B). Besides, it takes a few of steps to prepare these polycyclic bioactive molecules with other methods.[2-4]

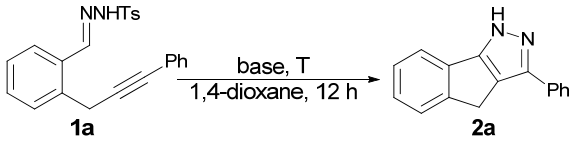
Scheme 1. [3+2]-Cycloaddition for the Pyrazole Synthesis



RESULTS AND DISCUSSION

The condition optimization is summarized in Table 1. Initially, substrate **1a** was treated with lithium *tert*-butoxide (*t*BuOLi) in 1,4-dioxane at 50 °C and the corresponding fused prazole product **2a** was obtained in 41% yield (Table 1, entry 1). Elevating the reaction temperature can promote the conversion and 60 °C was found to be the best temperature, which gave the product **2a** in 95% yield (Table 1, entry 2). The reaction also occurs at room temperature and much longer time is needed to get full conversion. It should be noted that the pure product could be obtained in similar yield without column chromatography (entry 2, in parentheses),[15] and this is the first example of intramolecular [3+2]-cycloaddition of hydrazones with unsymmetrical internal alkynes with high selectivity control. Encouraged by these results, other bases were also investigated, and only inferior results were obtained due to their solubility and/or basicity under current conditions (Table 1, entries 4-7).[16] Notably, the pure solid product could be obtained *via* filtration and followed by washing with DCM with comparable yield (entry 2, result in parentheses).

Table 1. Optimization of Reaction Conditions[a]



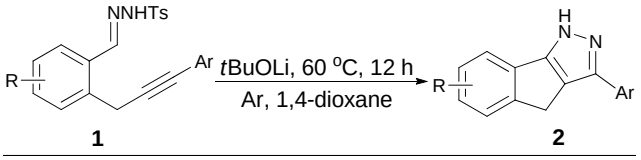
1a **2a**

Entry	Base	Temp (°C)	Yield (%)[b]
1	*t*BuOLi	50	41[c]
2	***t*BuOLi**	**60**	**95 (94)**[d]
3	*t*BuOLi	70	87
4	CsF	60	70
5	NaOMe	60	59
6	NaOH	60	45
7	K_2CO_3	60	50

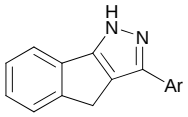
[a] Reaction conditions: **1a** (0.15 mmol), base (1.2 equiv) in 2.0 mL of 1,4-dioxane under an atmosphere of argon at indicated temperature for 12 h. [b] Isolated yields after chromatography. [c] Unreacted **1a** was recovered. [d] Yields after washing the filtered solid product with DCM three times (3.0 mL× 3).

Under the optimized conditions, the substrate generality was tested, and the results were shown in Table 2. The transformation proceeded smoothly with a wide range of substrates and gave the desired products **2** in high to excellent yields. Higher yield is obtained for substrates with *para*-substituted aryl at the terminal alkyne **2f**) compared to the *ortho*- or *meta*-substituted ones (**2g**-**2h**). The naphthyl-substituted compound **1i** and the substrates with fluorinated aryl linker are also well tolerated under these conditions (**2i**-**2k**, >91% yields). The structure of this fused compound was confirmed by the X-ray diffraction of its bromo-derivative **2e**.[17]

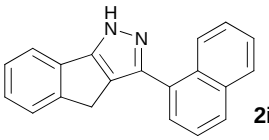
Table 2. [3+2]-Cycloaddition for the Construction of 6,5,5-Tricyclic Pyrazoles[a]



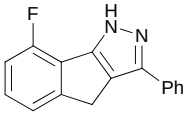
1 **2**



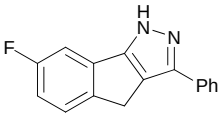
2a, Ar = Ph, 95%
2b, Ar = 4-$CF_3C_6H_4$, >95%
2c, Ar = 4-FC_6H_4, 85%
2d, Ar = 4-ClC_6H_4, >95%
2e, Ar = 4-BrC_6H_4, >95%
2f, Ar = 4-MeC_6H_4, >95%
2g, Ar = 2-MeC_6H_4, 71%
2h, Ar = 3-MeC_6H_4,72%



2i, 92%



2j, 91%

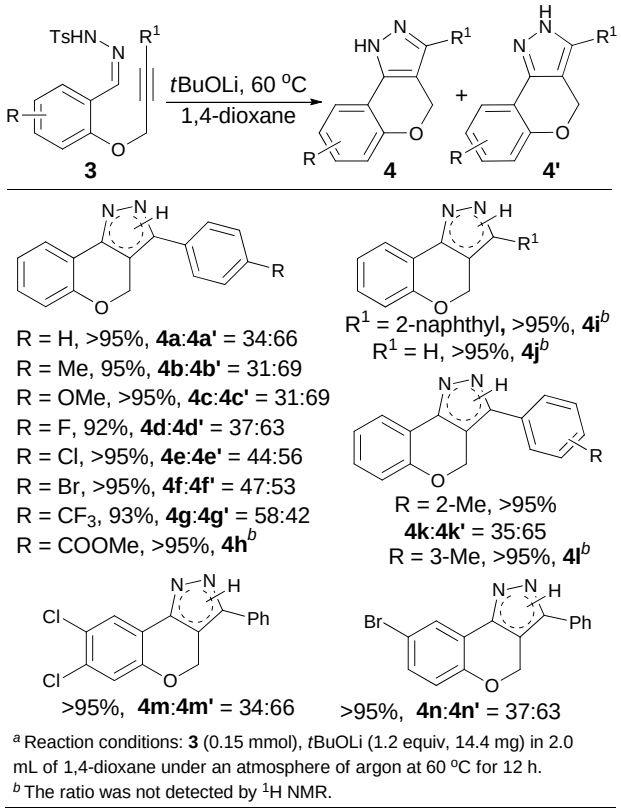


2k, >95%

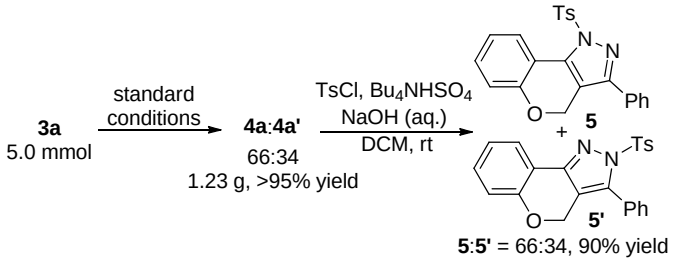
[a] Reaction conditions: **1** (0.15 mmol), *t*BuOLi (1.2 equiv, 14.4 mg) in 2.0 mL of 1,4-dioxane under an atmosphere of argon for 12 h.

To further explore the potential of this methodology, substrates using an ether linker instead of methylene were also tested under the optimized conditions (Table 3). In general, all the tested substrates gave the desired products in excellent yields (>92% yields). Notably, substrate with terminal alkyne also proceeded very well, and gave the corresponding product in >95% yield (**4j**). The tautomers with the proton on the two different nitrogen-atoms were existing in the products, which are inseparable by column chromatography.[18] To distinguish these two isomers, gram scale pure product **4a** was prepared in >95% yield without column chromatography under the standard conditions (Scheme 2). Then the product was treated with *p*-toluenesulfonyl chloride (TsCl) under basic conditions to give **5** and **5'** in 66:34 ratio (determined by ^{1}H-NMR, and the ratio is identical to **4a**:**4a'**), which could be separated by column chromatography. The structure of **5** was unambiguously determined by the X-ray diffraction, and the structure of **4a** could be deduced.[17]

Table 3. [3+2]-Cycloaddition for the Construction of 6,6,5-Tricyclic Pyrazoles[a]



Scheme 2.



In order to gain insight into the reaction mechanism, a control reaction was carried out in an NMR tube with d^8-dioxane as the solvent (Figure 2). A corresponding proton signal of diazo compound intermediate **D** was detected at 5.43 ppm.[19] Based on this observation and according to the previous reports,[7-11, 19-20] a plausible reaction mechanism is proposed in Scheme 3. First, the diazo compound **D** was generated under basic conditions from *N*-tosylhydrazone.[20] Then intramolecular 1,3-dipolar cycloaddition directly provided **E**. The desired products **2** or **4** were formed *via* a direct H-shift aromatization (Scheme 2, path a), which was different from previous aryl or alkyl [1,5]-sigmatropic rearrangement and aromatization process reported by Valdés (Scheme 1A).[8] In contrast, a stepwise pathway involving base captured a proton from the hydrazone to generate anion **A** followed by addition

with alkynyl and aromatization to give the final product could be totally ruled out so far.[21]

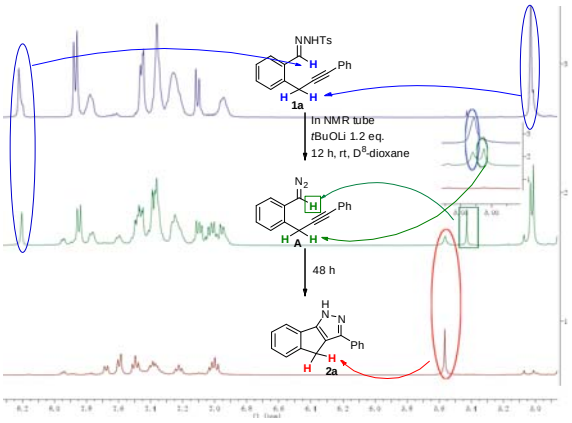
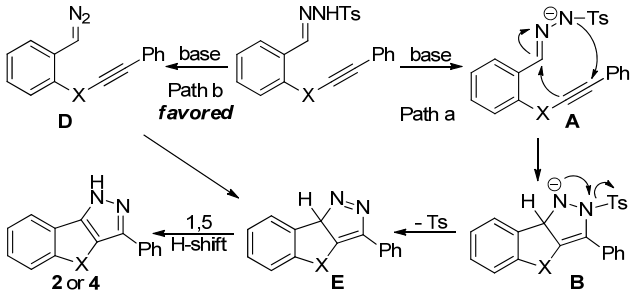


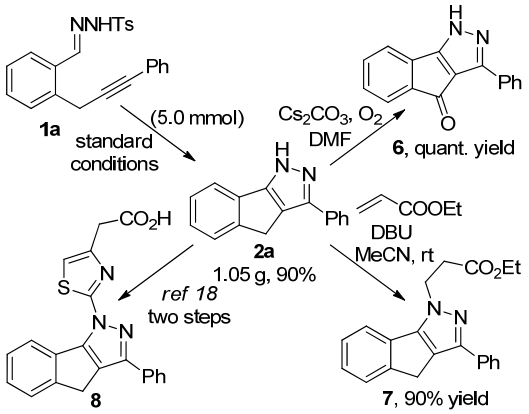
Figure 2. Control experiments.

Scheme 3. Proposed Reaction Mechanism



In addition, product **2a** was prepared on a gram scale under the optimization condition in 90% yield without column chromatography (Scheme 4). And the utility of this fused polycyclic pyrazole was demonstrated by various transformations to give the corresponding derivatives. For example, the conversion of **2a** to ketone **6** under mild oxidative conditions proceeds in quantitative yield.[3a] Aza-Michael addition of **2a** with ethyl acrylate produced **7** in 90% yield in the presence of DBU.[22] Besides, compound **8** was reported to be synthesized from **2a** in two steps, which is a promising candidates in developing OAB drugs.[23]

Scheme 4. The Derivatization of 2a



In conclusion, we have developed an intramolecular 1,3-dipolar cycloaddition reaction of alkyne-tethered tosylhydrazones, which lead to a direct approach to the selective synthesis of fused polycyclic pyrazoles in high to excellent yields. This transition metal-free reaction is carried out under mild conditions and the pure products are obtained without column chromatography. Notably, the reaction could be carried out on gram scale with almost the same yields. The obtained polycyclic products are very useful bioactive molecules, which take a few of steps to prepare by other methods. And some of these could be used as a practical material to the bioactive compounds in one or two steps.

EXPERIMENTAL SECTION

General. All reactions were carried out in oven-dried glassware under an atmosphere of dry argon. Solvents were dried and degassed by the standard methods. Flash column chromatography was performed using silica gel (300-400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200-300 mesh silica gel impregnated with a fluorescent indicator (254 nm). ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a 400 MHz spectrometer; chemical shifts are reported in ppm with the solvent signals as reference, and coupling constants (*J*) are given in Hertz. The peak information is described as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite. High-resolution mass spectra (HRMS) were recorded on a commercial apparatus (ESI or CI Source).

General Procedure for the Synthesis of Alkyne-tethered *N*-Tosylhydrazones 1.

Alkyne-tethered aldehydes were prepared from corresponding 2-bromobenzaldehyde according to the procedures of the reported literature.[24]

Synthesis of **1**: To a 50-mL oven-dried flask containing a magnetic stirring bar, alkyne-tethered aldehydes (3.0 mmol), *p*-toluenesulfonhydrazide (3.3 mmol, 613.8 mg) and methanol (15.0 mL) were added in sequence, and the reaction mixture was stirred at 65 ^{o}C for 12 h. After the reaction was completed, the solvent was evaporated and the residue was purified by column chromatography on silica gel (Hexanes:EtOAc = 10:1~5:1) to provide the pure compound **1** as yellow solid (80-90% yield).

General Procedure for the Synthesis of Alkyne-tethered *N*-Tosylhydrazones 3.

Propargyl alcohol tethered aldehydes were prepared from corresponding *o*-hydroxybenzaldehydes according to the procedures of the reported literature.[25]

Synthesis of **3**: To a 50-mL oven-dried flask containing a magnetic stirring bar, propargyl alcohol tethered aldehydes (3.0 mmol), *p*-toluenesulfonhydrazide (3.3 mmol, 613.8 mg) and methanol (15.0 mL) were added in sequence, and the mixture was stirred at 65 ^{o}C for 12 h. After the reaction completed, half of the solvent was evaporated and the residue was precipitated out from the cold methanol. The pure compound **3** were obtained as white solid after filtration (> 90% yield).

4-Methyl-N'-[2-(3-phenylprop-2-yn-1-yl)benzylidene]benzenesulfonohydrazide ***(1a).*** 954.5 mg, 82% yield. Yellow solid, mp: 82.9-83.8 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 8.10 (s, 1 H), 7.90-7.87 (m, 2H), 7.63 (d, J = 7.3 Hz, 1H), 7.55 (d, J = 7.3 Hz, 1H), 7.40-7.25 (comp, 10H), 3.90 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 146.9, 144.4, 135.7, 135.3, 131.7, 130.9, 130.3, 129.8, 129.5, 128.7, 128.3, 128.1, 128.0, 127.2, 123.5, 87.1, 83.7, 24.2, 21.7. HRMS (TOF MS CI^{+}) calculated for $C_{23}H_{21}N_2O_2S$ $[M+H]^{+}$: 389.1324, found 389.1319.

4-Methyl-N'-{2-[3-(4-(trifluoromethyl)phenyl]prop-2-yn-1-yl}benzylidene)benzenesulfonohydrazide ***(1b).*** 1101.4 mg, 82% yield. White solid, mp: 124.0-125.9 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 8.07 (s, 1H), 7.98 (s, 1H), 7.88 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 7.7 Hz, 1H), 7.55-7.47 (comp, 5H), 7.39-7.37 (m, 1H), 7.31-7.28 (comp, 3H), 3.94 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 146.9, 144.5, 135.3, 135.2, 132.0, 131.0, 130.5, 129.9, 129.62, 129.57, 129.0, 128.1, 127.4, 125.4,

125.2 (q, *J* = 3.7 Hz), 122.7, 89.9, 82.4, 24.4, 21.7. HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{20}F_3N_2O_2S$ $[M+H]^+$: 457.1198, found 451.1189.

*N'-{2-[3-(4-Fluorophenyl)prop-2-yn-1-yl]benzylidene}-4-methylbenzenesulfonohydrazide (**1c**).* 974.4 mg, 80% yield. White solid, mp: 131.0-132.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 8.11 (s, 1H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.37-7.31 (comp, 3H), 7.28-7.25 (comp, 4H), 6.95 (m, 2H), 3.86 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 162.2 (d, *J* = 250.1 Hz), 146.9, 144.4, 135.7, 135.3, 133.6 (d, *J* = 8.3 Hz), 131.0, 130.4, 129.8, 129.5, 128.7, 128.1, 127.2, 119.6 (d, *J* = 3.5 Hz), 115.5 (d, *J* =21.8 Hz), 86.8, 82.6, 24.2, 21.7. HRMS (TOF MS CI$^+$) calculated for $C_{23}H_{20}FN_2O_2S$ $[M+H]^+$: 407.1230, found 407.1229.

*N'-{2-[3-(4-Chlorophenyl)prop-2-yn-1-yl]benzylidene}-4-methylbenzenesulfonohydrazide (**1d**).* 1101.4 mg, 87% yield. White solid, mp: 118.4-119.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 8.40 (s, 1H), 8.10 (s, 1H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 7.4 Hz, 1H), 7.50 (d, *J* = 7.4 Hz, 1H), 7.35-7.29 (comp, 4H), 7.27-7.22 (comp, 4H), 3.88 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 146.9, 144.5, 135.5, 135.2, 133.9, 132.9, 131.0, 130.4, 129.8, 129.5, 128.8, 128.6, 128.1, 127.3, 122.0, 88.2, 82.6, 24.3, 21.7. HRMS (TOF MS ESI$^+$) calculated for $C_{23}H_{20}ClN_2O_2S$ $[M+H]^+$: 423.0934, found 423.0942.

N'-{2-[3-(4-bromophenyl)prop-2-yn-1-yl]benzylidene}-4-methylbenzenesulfonohydrazide (1e). 1202.3 mg, 86% yield. White solid, mp: 123.4-124.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 8.07 (s, 1H), 8.00 (s, 1H), 7.89-7.86 (m, 2H), 7.63-7.61 (m, 1H), 7.52-7.51 (m, 1H), 7.43-7.40 (m, 2H), 7.38-7.34 (m, 1H), 7.33-7.28 (comp, 3H), 7.25-7.23 (m, 2H), 3.89 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 146.1, 143.9, 134.9, 134.7, 132.6, 131.0, 130.3, 129.9, 129.3, 129.1, 128.3, 128.2, 127.5, 126.8, 121.6, 87.1, 82.1, 23.8, 21.1. HRMS (TOF MS ESI$^+$) calculated for $C_{23}H_{20}BrN_2O_2S$ $[M+H]^+$: 467.3782, found 467.3785.

*4-Methyl-N'-{2-[3-(p-tolyl)prop-2-yn-1-yl]benzylidene}benzenesulfonohydrazide (**1f**).* 1025.1 mg, 85% yield. White solid, mp: 121.9-122.5 °C.^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 8.15 (s, 1H), 8.10 (s, 1H), 7.89 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 6.8 Hz, 1H), 7.54 (d, *J* = 6.8 Hz, 1H), 7.34 (m, 1H), 7.30-7.27 (comp, 5H), 7.09 (d, *J* = 8.3 Hz, 2H), 3.88 (s, 2H), 2.38 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 146.8, 144.5, 138.2, 136.0, 135.3, 131.6, 130.9, 130.5, 129.9, 129.7, 129.2, 128.7, 128.2, 127.2, 100.0, 86.2, 83.9, 24.3, 21.7, 21.6. HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{23}N_2O_2S$ $[M+H]^+$: 403.1480, found 403.1484.

*4-Methyl-N'-{2-[3-(o-tolyl)prop-2-yn-1-yl]benzylidene}benzenesulfonohydrazide (**1g**).* 976.9 mg, 81% yield. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 8.12 (s, 1H), 7.89 (d, *J* = 8.3 Hz, 2H), 7.62-7.58 (m, 2H), 7.37-7.32 (comp, 3H), 7.28-7.25 (comp, 4H), 7.19-7.15 (m, 2H), 3.93 (s, 2H), 2.36 (comp, 6H). ^{13}C NMR (100 MHz, $CDCl_3$)

(δ, ppm) δ 146.8, 144.5, 140.2, 136.0, 135.3, 132.0, 130.8, 130.5, 129.9, 129.6, 129.5, 128.8, 128.2, 128.1, 127.2, 125.6, 123.3, 90.9, 82.8, 24.5, 21.7, 20.9. HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{22}N_2NaO_2S$ $[M+Na]^+$: 425.1300, found 425.1288.

*4-Methyl-N'-{2-[3-(m-tolyl)prop-2-yn-1-yl]benzylidene}benzenesulfonohydrazide (**1h**).* 988.9 mg, 82% yield. White solid, mp: 124.0-125.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 8.43 (s, 1H), 8.14 (s, 1H), 7.93-7.91 (m, 2H), 7.64 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.58 (d, *J* = 7.1 Hz, 1H), 7.39-7.36 (m, 2H), 7.32-7.28 (m, 4H), 7.22-7.18 (m, 2H), 7.14-7.12 (m, 1H), 3.91 (s, 2H), 2.41 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 146.8, 144.5, 138.1, 135.9, 135.3, 132.3, 130.9, 130.5, 129.9, 129.6, 129.0, 128.8, 128.7, 128.3, 128.2, 127.2, 123.3, 86.6, 86.4, 24.3, 21.7, 21.3. HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{23}N_2O_2S$ $[M+H]^+$: 403.1480, found 403.1486.

*4-Methyl-N'-{2-[3-(naphthalen-1-yl)prop-2-yn-1-yl]benzylidene}benzenesulfonohydrazide (**1i**).* 1182.6 mg, 90% yield. White solid, mp: 165.7-166.5 °C. ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 11.62 (s, 1H), 8.33 (s, 1H), 8.15-8.13 (m, 1H), 7.95-7.90 (m, 2H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 2H), 7.55 (d, *J* = 6.1 Hz, 3H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.40-7.36 (m, 1H), 7.32-7.29 (m, 3H), 4.08 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, DMSO) (δ, ppm) δ 145.3, 143.4, 136.2, 135.4, 132.8, 132.6, 131.4, 130.2, 130.1, 129.62, 129.60, 128.5, 128.4, 127.3, 127.2, 127.1, 127.0, 126.6, 125.48, 125.46, 120.3, 93.1, 80.5, 23.2, 20.9. HRMS (TOF MS ESI$^+$) calculated for $C_{27}H_{23}N_2O_2S$ $[M+H]^+$: 439.1480, found 439.1489.

*N'-[2-Fluoro-6-(3-phenylprop-2-yn-1-yl)benzylidene]-4-methylbenzenesulfonohydrazide (**1j**).* 1084.0 mg, 89% yield. White solid, mp: 114.1-115.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 8.13-8.12 (comp, 2H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.46-7.44 (comp, 2H), 7.34-7.30 (m, 6H), 7.00-6.95 (m, 1H), 4.00 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 162.2 (d, *J* = 250.1 Hz), 144.6, 141.8 (d, *J* = 8.1 Hz), 138.2, 135.1, 131.7, 131.1 (d, *J* = 9.7 Hz), 129.9, 128.4, 128.2, 128.0, 125.3 (d, *J* = 3.1 Hz), 123.7, 118.9 (d, *J* = 9.2 Hz), 114.0 (d, *J* = 22.1 Hz), 87.0, 83.8, 25.3, 21.7. HRMS (TOF MS ESI$^+$) calculated for $C_{23}H_{20}FN_2O_2S$ $[M+H]^+$: 407.1230, found 407.1227.

*N'-[5-Fluoro-2-(3-phenylprop-2-yn-1-yl)benzylidene]-4-methylbenzenesulfonohydrazide (**1k**).* 1084.0 mg, 89% yield. White solid, mp: 117.9-118.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 8.46 (s, 1H), 8.08 (d, *J* = 0.8 Hz, 1H), 7.89 (d, *J* = 8.3 Hz, 2H), 7.47 (dd, *J* = 8.5, 5.5 Hz, 1H), 7.39-7.36 (comp, 3H), 7.30-7.27 (comp, 5H), 7.03 (m, 1H), 3.81 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ161.8 (d, *J* = 244.3 Hz), 144.81, 144.78, 144.7, 135.1, 132.8 (d, *J* = 7.7 Hz), 131.7, 131.5 (d, *J* = 3.0 Hz), 131.3 (d, *J* = 7.9 Hz), 129.9, 128.4, 128.1, 123.3, 117.3 (d, *J* = 21.4 Hz), 114.4 (d, *J* = 23.0 Hz), 86.7, 83.9, 23.5, 21.7. HRMS (TOF MS ESI$^+$) calculated for $C_{23}H_{20}FN_2O_2S$ $[M+H]^+$: 407.1230, found 407.1225.

*4-Mmethyl-N'-{2-[(3-phenylprop-2-yn-1-yl)oxy]benzylidene}benzenesulfonohydrazide (**3a**).* 1151.4 mg, 95% yield. White solid, mp: 125.1-126.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 8.21 (s, 1H), 7.88-7.86 (comp, 4H), 7.41-7.28 (comp, 8H), 7.05-6.97 (comp, 2H), 4.91 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 156.2, 144.2, 143.7, 135.5, 131.9, 131.7, 129.8, 129.0, 128.5, 128.1, 126.9, 122.5, 122.1, 121.8, 112.8, 87.8, 83.4, 57.3, 21.7. HRMS (TOF MS ESI$^+$) calculated for $C_{23}H_{21}N_2O_3S$ $[M+H]^+$: 405.1273, found 405.1268.

*4-Methyl-N'-{2-[(3-(p-tolyl)prop-2-yn-1-yl)oxy]benzylidene}benzenesulfonohydrazide (**3b**).* 1203.8 mg, 96% yield. White solid, mp: 153.7-154.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 8.20 (s, 1H), 7.88-7.85 (comp, 3H), 7.37-7.28 (comp, 5H), 7.10 (d, J = 8.0 Hz, 2H), 7.05-6.97 (m, 2H), 4.90 (s, 2H), 2.39 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 156.3, 144.2, 143.7, 139.2, 135.5, 131.8, 131.7, 129.8, 129.2, 128.1, 126.8, 122.5, 121.73, 119.0, 112.9, 88.0, 82.7, 57.4, 21.7, 21.6. HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{23}N_2O_3S$ $[M+H]^+$: 419.1429, found 419.1411.

*N'-{2-[(3-(4-Methoxyphenyl)prop-2-yn-1-yl)oxy]benzylidene}-4-methylbenzenesulfonohydrazide (**3c**).* 1276.0 mg, 98% yield. White solid, mp: 181.6-182.9 °C. ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 11.42 (s, 1H), 8.25 (s, 1H), 7.75(d, J = 8.2 Hz, 2H), 7.63 (d, J = 8.3 Hz, 1H), 7.41-7.36 (comp, 5H), 7.18 (d, J = 8.3 Hz, 1H), 7.00 (t, J = 7.5 Hz, 1H), 6.93 (d, J = 8.2 Hz, 2H), 5.06 (s, 2H), 3.76 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, DMSO) (δ, ppm) δ 159.8, 155.6, 143.4, 142.2, 136.2, 133.2, 131.4, 129.7, 127.2, 125.3, 122.3, 121.5, 114.4, 113.5, 113.3, 86.9, 83.0, 57.0, 55.3, 21.0. HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{23}N_2O_4S$ $[M+H]^+$: 435.1379, found 435.1380.

*N'-{2-[(3-(4-Fluorophenyl)prop-2-yn-1-yl)oxy]benzylidene}-4-methylbenzenesulfonohydrazide (**3d**).* 1164.7 mg, 92% yield. White solid, mp: 163.8-164.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 8.20 (s, 1H), 7.89-7.85 (comp, 4H), 7.40-7.35 (comp, 3H), 7.29 (d, J = 8.0 Hz, 2H), 7.03-6.96 (comp, 4H), 4.89 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ163.0 (d, J = 248.9 Hz), 156.2, 144.3, 143.6, 135.5, 133.9 (d, J = 8.5 Hz), 131.7, 129.8, 128.1, 126.9, 122.5, 121.9, 118.1 (d, J = 3.5 Hz), 115.8 (d, J = 21.9 Hz), 112.8, 86.8, 83.1, 57.3, 21.7. HRMS (TOF MS ESI$^+$) calculated for $C_{23}H_{20}FN_2O_3S$ $[M+H]^+$: 423.1179, found 423.1159.

*N'-{2-[3-(4-Chlorophenyl)prop-2-yn-1-yl)oxy]benzylidene}-4-methylbenzenesulfonohydrazide (**3e**).* 1235.2 mg, 94% yield. White solid, mp: 177.0-178.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 8.20 (s, 1H), 8.01 (s, 1H), 7.88-7.85 (m, 3H), 7.34-7.25 (m, 7H), 7.02-6.97 (m, 2H), 4.89 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 156.2, 144.2, 143.7, 135.5, 135.1, 133.1, 131.7, 129.8, 128.8, 128.1, 126.9, 122.6, 121.9, 120.5, 112.8, 86.7, 84.4, 57.2, 21.7. HRMS (TOF MS ESI$^+$) calculated for $C_{23}H_{20}ClN_2O_3S$ $[M+H]^+$: 439.0883, found 439.0872.

N'-{2-[(3-(4-Bromophenyl)prop-2-yn-1-yl)oxy]benzylidene}-4-methylbenzenesulfonoh

*ydrazide (**3f**).* 1344.8 mg, 93% yield. White solid, mp: 179.0-180.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 8.19 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 3H), 7.78 (s, 1H), 7.45-7.41 (m, 2H), 7.37-7.33 (m, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.24 (s, 1H), 7.03-6.98 (m, 2H), 4.89 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 156.2, 144.3, 143.6, 135.5, 133.3, 131.8, 131.7, 129.8, 128.1, 127.0, 123.4, 122.6, 121.9, 121.0, 112.8, 86.8, 84.6, 57.3, 21.7. HRMS (TOF MS ESI$^+$) calculated for $C_{23}H_{20}BrN_2O_3S$ $[M+H]^+$: 483.0378, found 483.0381.

*4-Methyl-N'-{2-[(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)oxy]benzylidene}benzenesulfonohydrazide (**3g**).* 1316.8 mg, 93% yield. White solid, mp: 160.6-161.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 8.22 (s, 1H), 7.87 (comp, 3H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.02 (m, 2H), 4.94 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 156.1, 144.3, 143.6, 135.5, 132.2, 131.7, 130.9, 130.6, 129.8, 128.1, 127.0, 125.9, 125.3 (q, *J* = 16.0 Hz), 122.6, 122.0, 112.8, 86.4, 85.8, 57.2, 21.7. HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{20}F_3N_2O_3S$ $[M+H]^+$: 473.1147, found 473.1158.

*4-Methyl-{3-[2-((2-tosylhydrazono)methyl)phenoxy]prop-1-yn-1-yl}benzoate (**3h**).* 1344.4 mg, 97% yield. White solid, mp: 202.8-203.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 8.20 (s, 1H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.88-7.86 (comp, 3H), 7.76 (s, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.38-7.34 (m, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.04-6.99 (m, 2H), 4.93 (s, 2H), 3.91 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 166.5, 156.2, 144.3, 143.8, 135.5, 131.9, 131.8, 130.3, 129.8, 129.6, 128.1, 127.1, 126.7, 122.4, 122.0, 112.78, 87.0, 86.2, 57.2, 52.5, 21.7. HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{23}N_2O_5S$ $[M+H]^+$: 463.1328, found 463.1329.

*4-Methyl-N'-{2-[(3-(naphthalen-1-yl)prop-2-yn-1-yl)oxy]benzylidene}benzenesulfonohydrazide (**3i**).* 1297.0 mg, 95% yield. White solid, mp: 156.9-157.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 8.25 (s, 1H), 8.15-8.12 (m, 1H), 7.90-7.82 (comp, 6H), 7.63 (d, *J* = 7.1 Hz, 1H), 7.51-7.49 (m, 2H), 7.42-7.36 (m, 2H), 7.27-7.25 (m, 2H), 7.15 (d, *J* = 8.3 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 5.07 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 156.2, 144.2, 143.7, 135.5, 133.4, 133.2, 131.7, 131.0, 129.8, 129.5, 128.5, 128.1, 127.1, 126.9, 126.7, 126.0, 125.2, 122.7, 121.9, 119.7, 113.1, 88.2, 86.1, 57.5, 21.7. HRMS (TOF MS ESI$^+$) calculated for $C_{27}H_{23}N_2O_3S$ $[M+H]^+$: 455.1429, found 455.1421.

*4-Methyl-N'-[2-(prop-2-yn-1-yloxy)benzylidene]benzenesulfonohydrazide (**3j**).* 934.8 mg, 95% yield. White solid, mp: 89.9-91.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 8.16 (s, 1H), 7.88-7.84 (comp, 3H), 7.36-7.27 (comp, 3H), 7.01-6.95 (m, 2H), 4.69 (d, *J* = 2.4 Hz, 2H), 2.50 (t, *J* = 2.4 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 155.9, 144.3, 143.5, 135.5, 131.6, 129.8, 128.1, 126.9, 122.6, 122.0, 112.7, 78.1, 76.2, 56.4, 21.7. HRMS (TOF MS ESI$^+$) calculated for $C_{17}H_{17}N_2O_3S$ $[M+H]^+$: 329.0960, found 329.0961.

*4-Methyl-N'-{2-[(3-(o-tolyl)prop-2-yn-1-yl)oxy]benzylidene}benzenesulfonohydrazide (**3k**).* 1141.1 mg, 91% yield. White solid, mp: 162.7-163.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 8.21 (s, 1H), 7.87 (comp, 3H), 7.37-7.33 (m, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.25-7.07 (comp, 5H), 7.00 (t, *J* = 7.6 Hz, 1H), 4.97 (s, 2H), 2.39 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 156.2, 144.3, 143.7, 140.6, 135.5, 132.3, 131.7, 129.8, 129.6, 129.0, 128.1, 126.9, 125.7, 122.5, 121.9, 121.8, 113.0, 87.2, 86.9, 57.3, 21.7, 20.7. HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{23}N_2O_3S$ $[M+H]^+$: 419.1429, found 419.1409.

*4-Methyl-N'-{2-[(3-(m-tolyl)prop-2-yn-1-yl)oxy]benzylidene}benzenesulfonohydrazide (**3l**).* 1128.6 mg, 90% yield. White solid, mp: 134.7-135.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 8.21 (s, 1H), 7.88-7.85 (comp, 3H), 7.37-7.33 (m, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.23-7.18 (comp, 3H), 7.15 (t, *J* = 7.0 Hz, 1H), 7.05-6.97 (m, 2H), 4.90 (s, 2H), 2.39 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 156.3, 144.3, 143.7, 138.2, 135.5, 132.5, 131.7, 129.9, 129.8, 129.0, 128.4, 128.1, 126.9, 122.5, 121.9, 121.8, 112.8, 88.0, 83.0, 57.4, 21.7, 21.3. HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{23}N_2O_3S$ $[M+H]^+$: 419.1429, found 419.1426.

*N'-{4,5-Dichloro-2-[(3-phenylprop-2-yn-1-yl)oxy]benzylidene}-4-methylbenzenesulfonohydrazide (**3m**).* 1359.4 mg, 96% yield. White solid, mp: 101.7-102.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 8.20 (s, 1H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.78 (d, *J* = 2.6 Hz, 1H), 7.42 (d, *J* = 2.6 Hz, 1H), 7.36-7.28 (comp, 7H), 4.95 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 150.7, 144.0, 141.1, 134.7, 131.1, 131.0, 130.3, 130.2, 129.3, 128.7, 128.6, 128.0, 127.4, 124.2, 121.0, 88.8, 82.3, 61.9, 21.2. HRMS (TOF MS ESI$^+$) calculated for $C_{23}H_{19}Cl_2N_2O_3S$ $[M+H]^+$: 473.0493, found 473.0496.

*N'-{5-Bromo-2-[(3-phenylprop-2-yn-1-yl)oxy]benzylidene}-4-methylbenzenesulfonohydrazide (**3n**).* 1359.2 mg, 94% yield. White solid, mp: 143.0-143.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 8.11 (comp, 2H), 7.94 (d, *J* = 2.5 Hz, 1H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.43-7.37 (comp, 3H), 7.33-7.29 (comp, 5H), 6.93 (d, *J* = 8.3 Hz, 1H), 4.89 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 155.1, 144.5, 142.0, 135.4, 134.0, 131.9, 129.9, 129.3, 129.1, 128.5, 128.1, 124.4, 121.8, 114.7, 114.5, 88.2, 82.9, 57.5, 21.7. HRMS (TOF MS ESI$^+$) calculated for $C_{23}H_{20}BrN_2O_3S$ $[M+H]^+$: 483.0378, found 483.0382.

General Procedure for 1,3-Dipolar [3+2]-Cycloaddition Reactions. To a 10-mL oven-dried vial containing a magnetic stirring bar, compound **1** (or **3**, 0.15 mmol), the base *t*BuOLi (1.2 equiv, 14.4 mg) and 1,4-dioxane (2.0 mL) were added in sequence under an atmosphere of argon, and the mixture was stirred at 60 °C for 12 h. After the reaction was completed, the mixture was quenched by the addition of saturated brine

and extracted with EtOAc (3×10 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo* to provide a crude residue, which was purified by washing with dichloromethane for three times (3.0 mL×3) to give the pure product in high yields. Further purification is necessary in some cases by recrystalization in DCM, including **2c**, **2g** and **2h** (the crude product was dissolved in 5~10 mL of warm DCM, and after most of the solvent was volatilize under open air at room temperature, about 1-2 mL left over, the pure product was obtained by filtration).

*3-Phenyl-1, 4-dihydroindeno[1, 2-c]pyrazole (**2a**).* 33.1 mg, 95% yield. Yellow solid, mp: 238.9-241.9 °C.[26a] ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 13.24 (s, 1H), 7.84-7.82 (m, 2H), 7.69-7.67 (m, 1H), 7.57-7.56 (m, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.38-7.33 (m, 2H), 7.31-7.27 (m, 1H), 3.86 (s, 2H); ^{13}C NMR (100 MHz, DMSO) (δ, ppm) δ 159.8, 148.3, 135.7, 134.8, 129.6, 129.1, 127.7, 126.9, 126.3, 126.1, 125.2, 120.6, 119.3, 29.2. HRMS (TOF MS ESI$^+$) calculated for $C_{16}H_{13}N_2$ $[M+H]^+$: 233.1079, found 233.1086.

*3-[4-(Trifluoromethyl)phenyl]-1,4-dihydroindeno[1,2-c]pyrazole (**2b**).* 44.1 mg, >95% yield. Yellow solid, mp: 278.5-279.6 °C. ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 13.48 (s, 1H), 8.02 (s, 2H), 7.84 (s, 2H), 7.69 (s, 1H), 7.58-7.56 (m, 1H), 7.39-7.36 (m, 1H), 7.32-7.28 (m, 1H), 3.89 (s, 2H); ^{13}C NMR (100 MHz, DMSO) (δ, ppm) δ 160.0, 148.2, 137.7, 134.5, 133.4, 131.3, 126.9, 126.5-125.7 (multi-C), 122.9, 122.0, 119.4, 118.9, 29.2. HRMS (TOF MS ESI$^+$) calculated for $C_{17}H_{12}F_3N_2$ $[M+H]^+$: 301.0953, found 301.0963.

*3-(4-Fluorophenyl)-1, 4-dihydroindeno[1, 2-c]pyrazole (**2c**).* 31.9 mg, 85% yield. Yellow solid, mp: 239.7-242.3 °C. ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 13.24 (s, 1H), 7.86 (s, 2H), 7.67 (s, 1H), 7.58-7.56 (m, 1H), 7.39-7.27 (comp, 4H), 3.85 (s, 2H); ^{13}C NMR (100 MHz, DMSO) (δ, ppm) δ161.6 (d, *J* = 243.3 Hz), 159.8, 148.3, 134.8 (d, *J* = 10.6 Hz), 127.3, 127.2, 126.9, 126.3, 126.2, 126.1, 120.4 (d, *J* = 9.8 Hz), 119.3, 116.0 (d, *J* = 21.2 Hz), 29.1. HRMS (TOF MS ESI$^+$) calculated for $C_{16}H_{12}FN_2$ $[M+H]^+$: 251.0985, found 251.0976.

*3-(4-Chlorophenyl)-1, 4-dihydroindeno[1, 2-c]pyrazole (**2d**).* 39.2 mg, >95% yield. Yellow solid, mp: 262.3-263.9 °C. ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 13.29 (s, 1H), 7.83-7.81 (m, 2H), 7.70-7.56 (comp, 4H), 7.39-7.35 (m, 1H), 7.32-7.28 (m, 1H), 3.87 (s, 2H); ^{13}C NMR (100 MHz, DMSO) (δ, ppm) δ 159.9, 148.2, 134.6, 132.2, 129.1, 128.8, 128.5, 126.9, 126.8, 126.4, 126.1, 121.0, 119.3, 29.1. HRMS (TOF MS ESI$^+$) calculated for $C_{16}H_{12}ClN_2$ $[M+H]^+$: 267.0689, found 267.0679.

*3-(4-Bromophenyl)-1, 4-dihydroindeno[1, 2-c]pyrazole (**2e**).* 46.2 mg, >95% yield. Yellow solid. ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 13.34 (s, 1H), 7.78-7.68 (comp, 5H), 7.57-7.56 (m, 1H), 7.39-7.35 (m, 1H), 7.31-7.27 (m, 1H), 3.85 (s, 2H); ^{13}C NMR (100 MHz, DMSO) (δ, ppm) δ 159.8, 148.2, 134.6, 132.0, 129.1, 128.8, 127.2, 126.9, 126.4, 126.1, 121.0, 120.7, 119.3, 29.1. HRMS (TOF MS ESI^{+}) calculated for $C_{16}H_{12}BrN_2$ $[M+H]^{+}$: 311.0184, found 311.0179.

*3-(p-Tolyl)-1, 4-dihydroindeno[1, 2-c]pyrazole (**2f**).* 36.6 mg, >95% yield. Yellow solid, mp: 254.1-255.5 ^{o}C.[26b] ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 13.14 (s, 1H), 7.71–7.67 (comp, 3H), 7.58-7.56 (m, 1H), 7.38-7.27 (comp, 4H), 3.85 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, DMSO) (δ, ppm) δ 159.7, 148.3, 137.2, 135.8, 134.8, 129.6, 126.9, 126.3, 126.1, 125.2, 125.1, 120.1, 119.3, 29.1, 20.9. HRMS (TOF MS ESI^{+}) calculated for $C_{17}H_{15}N_2$ $[M+H]^{+}$: 247.1235, found 247.1227.

*3-(o-Tolyl)-1, 4-dihydroindeno[1, 2-c]pyrazole (**2g**).* 26.2 mg, 71% yield. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 7.77 (d, J = 7.4 Hz, 1H), 7.51-7.47 (m, 2H), 7.38-7.28 (comp, 5H), 3.69 (s, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 148.5, 136.5, 134.8, 131.13, 131.10, 129.9, 129.3, 128.9, 127.1, 126.9, 126.3, 125.9, 122.9, 120.4, 120.3, 30.0, 20.8. HRMS (TOF MS ESI^{+}) calculated for $C_{17}H_{15}N_2$ $[M+H]^{+}$: 247.1235, found 247.1248.

*3-(m-Tolyl)-1, 4-dihydroindeno[1, 2-c]pyrazole (**2h**).* 26.6 mg, 72% yield. Yellow solid, mp: 230.4-232.9 ^{o}C. ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 13.17 (s, 1H), 7.65-7.56 (comp, 4H), 7.39-7.35 (m, 2H), 7.31-7.27 (m, 1H), 7.18-7.16 (m, 1H), 3.87 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, DMSO) (δ, ppm) δ 159.7, 148.3, 138.2, 135.7, 134.8, 129.6, 128.9, 128.3, 126.9, 126.2, 126.1, 125.8, 122.3, 120.5, 119.2, 29.3, 21.2. HRMS (TOF MS ESI^{+}) calculated for $C_{17}H_{15}N_2$ $[M+H]^{+}$: 247.1235, found 247.1236.

*3-(Naphthalen-1-yl)-1,4-dihydroindeno[1,2-c]pyrazole (**2i**).* 39.0 mg, 92% yield. Yellow solid, mp: 91.4-98.6 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 11.37 (br, 1H), 8.10 (d, J = 8.1 Hz, 1H), 7.93-7.88 (m, 2H), 7.65-7.63 (m, 1H), 7.55-7.44 (comp, 5H), 7.29-7.20 (m, 2H), 3.66 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 159.0, 147.9, 136.6, 134.0, 133.3, 130.7, 128.7, 128.1, 127.8, 126.7, 126.4, 126.23, 126.16, 125.8, 125.3, 125.0, 124.9, 123.3, 119.7, 29.2. HRMS (TOF MS ESI^{+}) calculated for $C_{20}H_{15}N_2$ $[M+H]^{+}$: 283.1235, found 283.1244.

*8-Fluoro-3-phenyl-1, 4-dihydroindeno[1, 2-c]pyrazole (**2j**).* 34.2 mg, 91% yield. Yellow solid, mp: 272.1-273.6 ^{o}C. ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 13.37 (s, 1H), 7.83-7.81 (m, 2H), 7.51-7.49 (m, 2H), 7.49-7.32 (comp, 3H), 7.22-7.18 (m, 1H), 3.96 (s, 2H); ^{13}C NMR (100 MHz, DMSO) (δ, ppm) δ 166.9, 156.8, 151.5, 135.7, 131.7 (d, J = 14.4 Hz), 129.4, 129.1, 128.7, 128.1 (d, J = 28.8 Hz), 125.3, 122.3, 120.4, 113.8 (d, J = 19.0 Hz), 29.5. HRMS (TOF MS ESI^{+}) calculated for $C_{16}H_{12}FN_2$

$[M+H]^+$: 251.0985, found 251.0986.

*7-Fluoro-3-phenyl-1, 4-dihydroindeno[1, 2-c]pyrazole (**2k**).* 37.2 mg, >95% yield. Yellow solid, mp: 272.1-273.6. ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 13.36 (s, 1H), 7.83-7.81 (m, 2H), 7.59-7.56 (m, 1H), 7.53-7.45 (comp, 3H), 7.39-7.35 (m, 1H), 7.14-7.09 (m, 1H), 3.86 (s, 2H); ^{13}C NMR (100 MHz, DMSO) (δ, ppm) δ161.8 (d, J = 239.2 Hz), 157.1, 144.0, 138.0, 136.5 (d, J = 9.4 Hz), 131.0, 129.0, 127.4, 127.2 (d, J = 9.1 Hz), 125.1, 122.3, 112.2 (d, J = 22.5 Hz), 106.0 (d, J = 23.8 Hz), 28.8. HRMS (TOF MS ESI$^+$) calculated for $C_{16}H_{12}FN_2$ $[M+H]^+$: 251.0985, found 251.0995.

(4a+4a')[27] 36.9 mg, >95% yield. White solid, mp: 254.4-256.1. **4a:** ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 13.39 (s, 1H), 7.66-6.95 (comp, 9H), 5.52 (s, 2H); **4a':** ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 13.54, (s, 1H), 7.66-6.95 (comp, 9H), 5.52 (s, 2H); ^{13}C NMR (100 MHz, DMSO, + Cs_2CO_3) (δ, ppm) δ 152.9, 140.2 131.6 128.9 (2C), 128.6, 127.4, 126.0, 121.7, 121.5, 118.2, 116.6, 107.9, 64.6. HRMS (TOF MS ESI$^+$) calculated for $C_{16}H_{13}N_2O$ $[M+H]^+$: 249.1082, found 249.1088.

(4b+4b'). 37.4 mg, 95% yield. White solid, mp: 273.7-274.6 ^{o}C. **4b:** ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 13.30 (s, 1H), 7.66-6.95 (comp, 8H), 5.50 (s, 2H), 2.34 (s, 3H); **4b':** ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 13.48 (s, 1H), 7.66-6.95 (comp, 8H), 5.50 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, DMSO, + Cs_2CO_3) (δ, ppm) δ 153.0, 140.3, 137.0, 129.5, 128.7, 128.3, 125.9, 121.7, 121.5, 118.1, 116.7, 107.7, 64.45, 20.83. HRMS (TOF MS ESI$^+$) calculated for $C_{17}H_{15}N_2O$ $[M+H]^+$: 263.1184, found 263.1183.

(4c+4c'). 40.9 mg, >95% yield. White solid, mp: 228.1-229.7 ^{o}C. **4c:** ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 13.23 (s, 1H), 7.66-6.94 (comp, 8H), 5.47 (s, 2H), 3.80 (s, 3H); **4c':** ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 13.44 (s, 1H), 7.66-6.94 (comp, 8H), 5.55 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, DMSO, + Cs_2CO_3) (δ, ppm) δ 158.2, 152.6, 141.0, 140.4, 127.8, 127.1, 125.5, 121.5, 121.3, 119.4, 116.4, 114.2, 106.8, 65.10, 55.15. HRMS (TOF MS ESI$^+$) calculated for $C_{17}H_{15}N_2O_2$ $[M+H]^+$: 279.1134, found 279.1148.

(4d+4d'). 36.7 mg, 92% yield. White solid, mp: 267.6-269.6 ^{o}C. **4d:** ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 13.35 (s, 1H), 7.62-6.95 (comp, 8H), 5.49 (s, 2H); **4d':** ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 13.55 (s, 1H), 7.62-6.95 (comp, 8H), 5.56 (s, 2H); ^{13}C NMR (100 MHz, DMSO, + Cs_2CO_3) (δ, ppm) δ161.8 (d, J = 243.9 Hz), 153.0, 144.0, 141.3, 129.3, 128.3 (d, J = 8.2 Hz), 123.8, 121.8, 121.6, 116.8, 116.0 (d, J = 21.7 Hz), 108.1, 99.5, 64.1. HRMS (TOF MS ESI$^+$) calculated for $C_{16}H_{12}FN_2O$ $[M+H]^+$: 267.0934, found 267.0948.

(4e+4e'). 40.7 mg, >95% yield. White solid, mp: 262.1-267.9 ^{o}C. **4e:** ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 13.35 (s, 1H), 7.53-6.83 (comp, 8H), 5.41 (s, 2H); **4e':** ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 13.55 (s, 1H), 7.53-6.83 (comp, 8H), 5.41 (s,

2H); ^{13}C NMR (100 MHz, DMSO, + Cs_2CO_3) (δ, ppm) δ 153.0, 140.0, 139.7, 132.5, 129.4, 129.0 (2C), 127.8, 124.1, 121.8, 121.6, 116.8, 108.4, 64.1. HRMS (TOF MS ESI$^+$) calculated for $C_{16}H_{12}ClN_2O$ $[M+H]^+$: 283.0638, found 283.0646.

(4f+4f'). 48.6 mg, >95% yield. White solid, mp: 275.7-277.8 ^{o}C. **4f:** ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 13.47 (s, 1H), 7.66-6.94 (comp, 8H), 5.49 (s, 2H); **4f':** ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 13.70 (s, 1H), 7.66-6.94 (comp, 8H), 5.56 (s, 2H); ^{13}C NMR (100 MHz, DMSO, + Cs_2CO_3) (δ, ppm) δ 152.9, 140.3, 139.5, 131.9, 130.8, 129.3, 129.2, 128.1, 121.8, 121.6, 120.9, 116.7, 108.3, 64.2. HRMS (TOF MS ESI$^+$) calculated for $C_{16}H_{12}BrN_2O$ $[M+H]^+$: 327.0133, found 327.0139.

(4g+4g'). 44.1 mg, 93% yield. White solid, mp: 237.7-246.5 ^{o}C. **4g:** ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 13.61 (s, 1H), 7.81-6.96 (comp, 8H), 5.60 (s, 2H); **4g':** ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 13.75 (s, 1H), 7.81-6.96 (comp, 8H), 5.60 (s, 2H); ^{13}C NMR (100 MHz, DMSO, + Cs_2CO_3) (δ, ppm) δ 152.9, 140.4, 139.2, 135.4, 129.4, 128.0, 127.7, 126.7, 125.9-125.6 (multi-C), 125.6, 122.9, 121.8, 121.6, 116.8, 109.0, 64.3. HRMS (TOF MS ESI$^+$) calculated for $C_{17}H_{12}F_3N_2O$ $[M+H]^+$: 317.0902, found 317.0901.

(4h). 44.6 mg, >95% yield. White solid, mp: 263.3-264.9 ^{o}C. ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 13.70 (br, 1H), 8.04-6.95 (comp, 8H), 5.58 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, DMSO, + Cs_2CO_3) (δ, ppm) δ 165.9, 152.9, 135.5, 129.9, 129.5-129.4 (3C), 128.6, 126.2, 121.9, 121.7, 116.8, 106.3, 94.8, 64.2, 52.2. HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{15}N_2O_3$ $[M+H]^+$: 307.1083, found 307.1085.

(4i). 44.3 mg, >95% yield. White solid, mp: 97.3-101.0 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 10.75 (br, 1H), 7.87-6.75 (comp, 8H), 5.15 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 154.1, 142.8, 138.7, 133.8, 131.2, 129.7, 129.6, 128.7, 127.7, 127.1, 127.0, 126.4, 125.3, 124.9, 122.6, 122.0, 117.8, 117.2, 111.2, 64.1. HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{15}N_2O$ $[M+H]^+$: 299.1184, found 299.1185.

(4j). 25.6 mg, >95% yield. White solid, mp: 158.4-163.1 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 7.68-6.95 (comp, 5H), 5.31 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 154.1, 142.0, 129.6, 125.8, 122.3, 121.9, 117.8, 117.4, 111.7, 63.9. HRMS (TOF MS ESI$^+$) calculated for $C_{10}H_9N_2O$ $[M+H]^+$: 173.0715, found 173.0718.

(4k+4k'). 39.0 mg, >95% yield. White solid, mp: 221.0-222.9 ^{o}C. **4k:** ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 13.32 (s, 1H), 7.69-6.95 (comp, 8H), 5.50 (s, 2H), 2.37 (s, 3H); **4k':** ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 13.53 (s, 1H), 7.69-6.95 (comp, 8H), 5.59 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, DMSO, + Cs_2CO_3) (δ, ppm) δ 153.1, 140.3, 138.3, 129.2, 128.9, 128.7, 126.6, 126.4, 123.3, 121.8, 121.6, 116.8, 116.7, 108.2, 107.8, 64.2, 21.1. HRMS (TOF MS ESI$^+$) calculated for $C_{17}H_{15}N_2O$ $[M+H]^+$: 263.1184, found 263.1196.

(4l). 39.0 mg, >95% yield. White solid, mp: 103.7-105.2. **4l:** ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 9.06 (br, 1H), 7.57-6.88 (comp, 8H), 5.22 (s, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 154.1, 142.8, 139.4, 136.8, 130.9, 129.8, 129.7, 129.3, 128.9, 126.2, 122.6, 122.0, 118.0, 117.3, 110.5, 64.0, 20.0. HRMS (TOF MS ESI$^+$) calculated for $C_{17}H_{15}N_2O$ $[M+H]^+$: 263.1184, found 263.1185.

(4m+4m'). 47.1 mg, >95% yield. White solid, mp: 278.1-278.9 ^{o}C. **4m:** ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 13.80 (s, 1H), 7.90-7.41 (comp, 8H), 5.67 (s, 2H); **4m':** ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 14.10 (s, 1H), 7.90-7.41 (comp, 8H), 5.76 (s, 2H); ^{13}C NMR (100 MHz, DMSO, + Cs_2CO_3) (δ, ppm) δ 147.5, 138.6, 129.6, 129.0, 128.3, 127.9, 127.8, 126.1, 125.2, 121.7, 120.7, 120.0, 108.1, 65.7. HRMS (TOF MS ESI$^+$) calculated for $C_{16}H_{11}Cl_2N_2O$ $[M+H]^+$: 317.0248, found 317.0240.

(4n+4n'). 48.5 mg, >95% yield. White solid, mp: 275.7-277.8 ^{o}C. **4n:** ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 13.54 (s, 1H), 7.76-6.93 (comp, 8H), 5.55 (s, 2H); **4n':** ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 13.59 (s, 1H), 7.76-6.93 (comp, 8H), 5.60 (s, 2H); ^{13}C NMR (100 MHz, DMSO, + Cs_2CO_3) (δ, ppm) δ152.3, 139.5, 132.3, 131.0, 129.3, 127.7, 126.3, 124.2, 121.1, 119.2, 113.3, 108.3, 92.2, 65.5. HRMS (TOF MS ESI$^+$) calculated for $C_{16}H_{12}BrN_2O$ $[M+H]^+$: 327.0133, found 327.0140.

Procedure for the Synthesis of 5 and 2bb:

The obtained products **2**/**4** (0.30 mmol) and tetrabutylammonium hydrogen sulfate (0.03 mmol, 10 mol %) was dissolved in CH_2Cl_2 (5.0 mL), and 50% NaOH aqueous solution (150 μL) was added to the above reaction mixture. After the mixture was stirred for a few minutes, TsCl (0.45 mmol, 1.5 equiv) was added to the reaction mixture and the solution was then stirred vigorously at room temperature. When the reaction was completed (monitored by TLC plates), the solution was poured into water and extracted with dichloromethane. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography to afford the *N*-Ts protected products.

3-Phenyl-1-tosyl-1,4-dihydrochromeno[4, 3-c]pyrazole ***(5).*** 71.7 mg, 60% yields. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 8.36-8.34 (m, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.53-7.51 (m, 2H), 7.45-7.40 (comp, 3H), 7.33-7.29 (m, 1H), 7.25-7.23 (m, 2H), 7.16-7.12 (m, 1H), 7.04-7.02 (m, 1H), 5.21 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 153.7, 151.1, 145.2, 139.8, 133.9, 130.32, 130.30, 129.3, 128.9, 128.4, 127.5, 127.1, 126.7, 121.9, 117.1, 116.9, 115.6, 63.1, 21.2. HRMS (TOF MS ESI$^+$) calculated for $C_{23}H_{19}N_2O_3S$ $[M+H]^+$: 403.1116, found 403.1112.

3-Phenyl-2-tosyl-2,4-dihydrochromeno[4, 3-c]pyrazole ***(5').*** 36.9 mg, 30% yields. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 7.96-7.93 (m, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.51-7.46 (comp, 3H), 7.33-7.29 (m, 1H), 7.35-7.33 (m, 2H), 7.30-7.25 (m, 1H), 7.21

(d, J = 8.4 Hz, 1H), 7.06-7.02 (m, 1H), 6.94-6.92 (m, 1H), 5.00 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 157.4, 147.5, 144.9, 141.4, 134.2, 130.9, 129.4, 129.2, 127.71, 127.67, 127.5, 123.6, 121.7, 117.0, 116.1, 116.0, 62.2, 21.2. HRMS (TOF MS ESI$^+$) calculated for $C_{23}H_{19}N_2O_3S$ $[M+H]^+$: 403.1116, found 403.1119.

*1-tosyl-3-[4-(trifluoromethyl)phenyl]-1,4-dihydroindeno[1,2-c]pyrazole (**2bb**).* 111.7 mg, 82% yields. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 8.46-8.45 (m, 1H), 8.06 (d, J = 8.2 Hz, 2H), 8.01-7.99 (m, 2H), 7.79-7.77 (m, 1H), 7.73 (d, J = 8.2 Hz, 2H), 7.62-7.56 (m, 2H), 7.54-7.51 (m, 1H), 7.45-7.42 (m, 1H), 7.33-7.31 (m, 2H), 3.82 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 167.8, 152.4, 148.9, 148.8, 145.9, 134.7, 132.5, 131.3, 131.0, 130.1, 129.0, 128.4, 128.1, 127.8, 127.7, 127.0, 126.0, 125.6 (q, J = 3.8 Hz), 30.1, 21.8. HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{18}F_3N_2O_2S$ $[M+H]^+$: 455.1041, found 455.1049.

General Procedure for Scale Up:

To a 50-mL oven-dried vial containing a magnetic stirring bar, compound **1a** (5.0 mmol, 1.94 g), base *t*BuOLi (1.2 equiv, 480.0 mg) and 1,4-dioxane (50 mL) were added in sequence under an atmosphere of argon, and the mixture was stirred at 60 ^{o}C for 12 h. After the reaction was completed, the mixture was quenched by the addition of saturated brine and extrated with EtOAc (3×80 mL). The combined organic extracts were dried over Na_2SO_4, filtered and concentrated reduced pressure to provide a crude residue which was purified by washing with dichloromethane for three times (15 mL×3) to give the pure product **2a** (1.05 g, 90% yield).

To a 50-mL oven-dried vial containing a magnetic stirring bar, compound **3a** (5.0 mmol, 2.02 g), the base *t*BuOLi (1.2 equiv, 480.0 mg) and 1,4-dioxane (50 mL) were added in sequence under an atmosphere of argon, and the mixture was stirred at 60 ^{o}C for 12 h. After the reaction was completed, the mixture was quenched by the addition of saturated brine and extracted with EtOAc (3×80 mL). The combined organic extracts were dried over Na_2SO_4, filtered and concentrated *in vacuo* to provide a crude residue which was purified by washing with dichloromethane for three times (15 mL ×3) to give the pure product **4** (**4a** and **4a'**, 1.23 g, >95% yield).

Compound **6** was synthesized from **2a** *via* reported procedure.[3a]

Procedure for the Synthesis of 7:

The obtained **2a** (1.0 mmol, 232.3 mg) and methyl acrylate (1.5 mmol, 150.2 mg) was dissolved in CH_3CN (2.0 ml), and DBU (0.5 mmol) was added to the reaction mixture at room temperature. After 6 h, the mixture was concentrated reduced pressure. The resulting residue was purified by silica gel column chromatography, and the pure product **7** was isolated in 90% yield (299.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 7.95-7.93 (m, 2H), 7.69 (d, J = 7.6 Hz, 1H), 7.58 (d, J = 8.1 Hz, 1H), 7.52-7.48 (m, 2H), 7.46-7.42 (m, 1H), 7.40-7.31 (m, 2H), 4.75 (t, J = 7.0 Hz, 2H), 4.19 (q, J = 7.1

Hz, 2H), 3.80 (s, 2H), 3.13 (t, J = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 171.0, 149.8, 149.1, 144.9, 133.7, 131.9, 128.7, 127.5, 126.9, 126.2, 126.1, 125.8, 123.5, 118.8, 60.9, 46.5, 35.1, 30.1, 14.2. HRMS (TOF MS ESI$^+$) calculated for $C_{21}H_{21}N_2O_2$ $[M+H]^+$: 333.1603, found 333.1607.

ASSOCIATED CONTENT

Supporting Information

^{1}H, and ^{13}C NMR spectra for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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