Supporting Information

A Complementary Approach to 3,5-Substituted Pyrazoles with Tosylhydrazones and Terminal Alkynes Mediated by TfOH.

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General experimental methods:
Solvents were distilled from the appropriate drying agents before use. All the reagents were purchased from Acros, Alfa Aesar, and National Chemical Reagent Group Co.Ltd., P.R.China and used as received. The progress of the reactions was monitored by TLC (silica-coated glass plates and visualized under UV light or in iodine). NMR samples were recorded in CDCl₃ or DMSO-d₆ (to some samples, a drop of conc. HCl were added) on 400 MHz spectrometers. Chemical shifts (δ) are reported in ppm using TMS (δ = 0.0) as an internal standard. Multiplicities of NMR signals are designated as s (singlet), d (doublet), t (triplet), q (quartet), br (broad), m (multiplet, for unresolved lines), etc. ¹³C NMR spectra were recorded on a 100 MHz spectrometer. HRMS spectra were recorded on Finnigan-Mat-95 mass spectrometer, equipped with ESI source. Flash column chromatography was performed on silica gel (300-400 mesh) with petroleum ether and EtOAc.

**General Procedure for the synthesis of tosylhydrazones 1a-m and 6:**

\[
\text{TsNH₂} + \text{R₁CHO} \xrightarrow{\text{MeOH}, \text{r.t.}} \text{TsN=NR₁}
\]

A solution of pure TsNHNH₂ (1.024 g, 5.5 mmol) in methanol (5 mL) was heated to 60°C until the TsNHNH₂ was completely dissolved. The mixture was cooled to room temperature, and then aldehydes (5.0 mmol) were dropped to the mixture slowly. After approximately 30 minutes the crude products could be obtained as precipitates. The precipitates were washed by hexane then removed in vacuum to afford the pure products.

**Experimental Procedures for the Synthesis of 1n:**

\[
\text{TsNH₂} + \text{CF₃OH} \xrightarrow{\text{MeOH, 60°C, 10h}} \text{TsN-CF₃}
\]

A solution of pure TsNHNH₂ (1.024 g, 5.5 mmol) in methanol (3 mL) was heated to 60 °C until the TsNHNH₂ was completely dissolved, and then 2,2,2-trifluoro-1-methoxyethanol (1.033 g, 7.15 mmol, 90% purity) were dropped to the mixture slowly. After heating at 60°C for 10h, the reaction mixture was concentrated under reduced pressure. The residue was recrystallized with ether/hexane to afford 1n as white solid.

**Experimental Procedures for the Synthesis of 1y:**
To a solution of triphenylphosphine (1.049 g, 4.0 mmol) in THF (5 mL, dry) was added dropwise DEAD (0.627 g, 3.6 mmol) at 0 °C (ice bath). After 15 min, the mixture was added a THF (5 mL, dry) solution consisting of hydrazone (0.549 g, 2.0 mmol) and isopropanol (0.18 g, 3.0 mmol). The resultant mixture is stirred at 0 °C for 12h and concentrated under reduced pressure. The residue was purified by silica gel chromatography (petroleum ether/EtOAc = 20:1) to afford the product 1y.

**General Procedure for TfOH- mediated 1,3-Dipolar-Cycloaddition Reaction of Tosylhydrazones with Terminal Alkynes:**

To a solution of tosylhydrazones (0.5 mmol, 1.0eq.) in DCE (2 mL, dry) was added TfOH (0.5 mmol, 1.0eq.) dropwise at room temperature under Ar atmosphere. After stirring for about 10 min, the alkynes (0.75 mmol, 1.5eq.) was added. The reaction flask was refluxed for 12 hours, and then it was cooled to room temperature and quenched with sat. Na₂CO₃ (5 mL) and extracted with EtOAc (3×10 mL) three times. The combined organic layers were washed with brine (10 mL), dried over Na₂SO₄ and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (petroleum ether/EtOAc = 4:1) to afford the corresponding product 3. In some cases, 4 can be obtained by basic Al₂O₃ (100-200 mesh) column chromatography (petroleum ether/EtOAc = 6:1). Some of the pyrazoles are known products and we did not describe their HRMS data. In some cases, quaternary carbons were not recorded in ¹³C NMR spectrums, probably due to longer relaxation times which is a consequence of the neighboring nitrogen atoms present in highly conjugated systems.

**Experimental Procedures for the Synthesis of 11a:**

![Chemical structure of compound 1y](image)
Method A: To a solution of NaH (39 mg, 1.3 mmol, 80%) in THF (5 mL, dry) was added 3a (0.220 g, 1.0 mmol) at room temperature. After 30 min, to the mixture was added CH₃I (0.213 g, 1.5 mmol). The resultant mixture was stirred for 16h and concentrated under reduced pressure. The residue was purified by silica gel chromatography (petroleum ether/EtOAc = 8:1) to afford the product 11a.

Method B: As per Method A except K₂CO₃ (0.104 g, 1.5 mmol) as base and DMSO (2 mL, dry) as solvent.

Spectra Data of the products:

\[ \text{N'-(benzylidene)-4-methylbenzenesulfonohydrazide (1a).} \]

Yield: 87%; \(R_f = 0.23\) (petroleum ether/EtOAc = 4:1); white solid. \(^1\)H NMR (400 MHz, CDCl₃): \(\delta = 8.24\) (br, 1 H), 7.88 (d, \(J = 8.1\) Hz, 2 H), 7.77 (s, 1 H), 7.56 - 7.58 (m, 2 H), 7.30 - 7.36 (m, 5 H), 2.40 (s, 3 H) ppm. ESI-LRMS: \(m/z\) 275.2 [M + H]⁺.

\[ \text{N'-(4-methylbenzylidene)-4-methylbenzenesulfonohydrazide (1b):} \]

Yield: 88%; \(R_f = 0.38\) (petroleum ether/EtOAc = 3:1); white solid. \(^1\)H NMR (400 MHz, CDCl₃): \(\delta = 8.08\) (br, 1 H), 7.87 (d, \(J = 8.2\) Hz, 2 H), 7.73 (s, 1 H), 7.47 (d, \(J = 7.8\) Hz, 2 H), 7.30 (d, \(J = 8.0\) Hz, 2 H), 7.16 (d, \(J = 7.6\) Hz, 2 H), 2.40 (s, 3 H), 2.35 (s, 3 H) ppm. ESI-LRMS: \(m/z\) 289.0 [M + H]⁺.

\[ \text{N'-(4-methoxybenzylidene)-4-methylbenzenesulfonohydrazide (1c):} \]

Yield: 80%; \(R_f = 0.56\) (petroleum ether/EtOAc = 2:1); white solid. \(^1\)H NMR (400 MHz, CDCl₃): \(\delta = 8.11\) (br, 1 H), 7.87 (d, \(J = 8.2\) Hz, 2 H), 7.73 (s, 1 H), 7.51 (d, \(J = 8.8\) Hz, 2 H), 7.30 (d, \(J = 8.0\) Hz, 2 H), 6.86 (d, \(J = 8.8\) Hz, 2 H), 3.81 (s, 3 H), 2.40 (s, 3 H) ppm. ESI-LRMS: \(m/z\) 305.0 [M + H]⁺.
**N’-(4-fluorobenzylidene)-4-methylbenzenesulfonohydrazide (1d):**

Yield: 78%; $R_f = 0.43$ (petroleum ether/EtOAc = 3:1); white solid. $^1H$ NMR (400 MHz, CDCl$_3$): $\delta = 8.33$ (br 1 H), 7.87 (d, $J = 8.3$ Hz, 2 H), 7.76 (d, $J = 6.9$ Hz, 1 H), 7.54 - 7.58 (m, 2 H), 7.32 (d, $J = 8.0$ Hz, 2 H), 7.01 - 7.06 (m, 2 H), 2.41 (s, 3 H). **ESI-LRMS:** $m/z$ 292.9 [M + H]$^+$. 

**N’-(4-chlorobenzylidene)-4-methylbenzenesulfonohydrazide (1e):**

Yield: 94%; $R_f = 0.40$ (petroleum ether/EtOAc = 3:1); white solid. $^1H$ NMR (400 MHz, CDCl$_3$): $\delta = 8.31$ (br, 1 H), 7.87 (d, $J = 8.1$ Hz, 2 H), 7.73 (s, 1 H), 7.50 (d, $J = 8.2$ Hz, 2 H), 7.31 (d, $J = 8.0$ Hz, 4 H), 2.41 (s, 3 H) ppm. **ESI-LRMS:** $m/z$ 309.0 [M + H]$^+$. 

**N’-(4-bromobenzylidene)-4-methylbenzenesulfonohydrazide (1f):**

Yield: 97%; $R_f = 0.41$ (petroleum ether/EtOAc = 3:1); white solid. $^1H$ NMR (400 MHz, CDCl$_3$): $\delta = 8.09$ (br, 1 H), 7.86 (d, $J = 8.1$ Hz, 2 H), 7.70 (s, 1 H), 7.49 (d, $J = 8.6$ Hz, 2 H), 7.44 (d, $J = 8.3$ Hz, 2 H), 7.32 (d, $J = 8.1$ Hz, 2 H), 2.41 (s, 3 H) ppm. **ESI-LRMS:** $m/z$ 353.0 [M + H]$^+$. 

**N’-(3-nitrobenzylidene)-4-methylbenzenesulfonohydrazide (1g):**

Yield: 92%; $R_f = 0.45$ (petroleum ether/EtOAc = 2:1); light yellow solid. $^1H$ NMR (400 MHz, DMSO-d$_6$): $\delta = 11.84$ (s, 1 H), 8.37 (br, 1 H), 8.22 (m, 1 H), 8.07 (s, 1 H), 8.02 (d, $J = 7.8$ Hz, 1 H), 7.79 (d, $J = 8.3$ Hz, 2 H), 7.69 (t, $J = 8.0$ Hz, 1 H), 7.43 (d, $J = 8.1$ Hz, 2 H), 2.37 (s, 3 H) ppm. **ESI-LRMS:** $m/z$ 319.9 [M + H]$^+$.
N’-(3-(trifluoromethyl)benzylidene)-4-methylbenzenesulfonohydrazide (1h):
Yield: 93%; $R_f = 0.38$ (petroleum ether/EtOAc = 3:1); white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.73$ (br, 1 H), 7.90 (d, $J = 8.1$ Hz, 2 H), 7.83 (s, 1 H), 7.73 - 7.77 (m, 2 H), 7.59 (d, $J = 7.8$ Hz, 1 H), 7.45 (t, $J = 7.7$ Hz, 1 H), 7.32 (d, $J = 8.1$ Hz, 2 H), 2.40 (s, 3 H) ppm. ESI-LRMS: $m/z$ 343.0 [M + H]$^+$.  

4-methyl-N’-(naphthalen-1-ylmethylene)benzenesulfonohydrazide (1i):
Yield: 84%; $R_f = 0.54$ (petroleum ether/EtOAc = 3:1); light yellow solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.61$ (br, 1 H), 8.55 (d, $J = 8.0$ Hz, 1 H), 8.39 (s, 1 H), 7.95 (d, $J = 8.3$ Hz, 2 H), 7.83 (d, $J = 8.0$ Hz, 2 H), 7.69 (d, $J = 7.2$ Hz, 1 H), 7.45 - 7.53 (m, 2 H), 7.40 (m, 1 H), 7.29 (d, $J = 8.0$ Hz, 2 H), 2.35 (s, 3 H) ppm. ESI-LRMS: $m/z$ 325.0 [M + H]$^+$.  

4-methyl-N’-(thiophen-2-ylmethylene)benzenesulfonohydrazide (1j):
Yield: 86%; $R_f = 0.31$ (petroleum ether/EtOAc = 3:1); white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.18$ (s, 1 H), 7.99 (s, 1 H), 7.85 (d, $J = 8.3$ Hz, 2 H), 7.29 - 7.35 (m, 3 H), 7.18 (m, 1 H), 6.99 (dd, $J = 5.0$, 3.7 Hz, 1 H), 2.40 (s, 3 H) ppm. ESI-LRMS: $m/z$ 280.9 [M + H]$^+$.  

N’-(furan-2-ylmethylene)-4-methylbenzenesulfonohydrazide (1k):
Yield: 58%; $R_f = 0.35$ (petroleum ether/EtOAc = 3:1); white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.20$ (s, 1 H), 7.86 (d, $J = 8.3$ Hz, 2 H), 7.73 (s, 1 H), 7.45 (d, $J = 1.1$ Hz, 1 H), 7.31 (d, $J = 8.1$ Hz, 2 H), 6.67 (d, $J = 3.4$ Hz, 1 H), 6.43 (dd, $J = 3.4$, 1.7 Hz, 1 H), 2.41 (s, 3 H) ppm. ESI-LRMS: $m/z$ 265.0 [M + H]$^+$.  

N’-(cyclohexylmethylene)-4-methylbenzenesulfonohydrazide (1l):
Yield: 85%; $R_f = 0.38$ (petroleum ether/EtOAc = 3:1); white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.80$ (d, $J = 8.3$ Hz, 2 H), 7.74 (br, 1 H), 7.31 (d, $J = 8.0$ Hz, 2 H),
7.06 (d, $J = 5.4$ Hz, 1 H), 2.43 (s, 3 H), 2.18 (m, 1 H), 1.61 - 1.70 (m, 5 H), 1.10 - 1.34 (m, 5 H) ppm. **ESI-LRMS**: $m/z$ 281.0 [M + H]$^+$.  

![N'-(2-ethylbutylidene)-4-methylbenzenesulfonohydrazide (1m):](image)

Yield: 87%; $R_f = 0.49$ (petroleum ether/EtOAc = 3:1); white solid. **$^1$H NMR** (400 MHz, CDCl$_3$): $\delta = 7.81$ (d, $J = 8.3$ Hz, 2 H), 7.71 (s, 1 H), 7.30 (d, $J = 8.0$ Hz, 2 H), 6.94 (d, $J = 7.2$ Hz, 1 H), 2.42 (s, 3 H), 2.05 (m, 1 H), 1.24 - 1.51 (m, 4 H), 0.70 (t, $J = 7.5$ Hz, 6 H). **ESI-LRMS**: $m/z$ 269.2 [M + H]$^+$.  

![4-methyl-N'-(2,2,2-trifluoroethylidene)benzenesulfonohydrazide (1n):](image)

Yield: 94%; $R_f = 0.39$ (petroleum ether/EtOAc = 3:1); white solid. **$^1$H NMR** (400 MHz, DMSO-d$_6$): $\delta = 12.49$ (br, 1 H), 7.71 (d, $J = 8.3$ Hz, 2 H), 7.50 (q, $J = 4.0$ Hz, 1 H), 7.45 (d, $J = 8.1$ Hz, 2 H), 2.40 (s, 3H) ppm. **$^{13}$C NMR** (100 MHz, DMSO-d$_6$): $\delta = 144.2$, 135.1, 132.9 (q, $J_{CF} = 37.5$ Hz), 129.8, 127.0, 119.8 (q, $J_{CF} = 271.1$ Hz), 20 ppm. **ESI-LRMS**: $m/z$ 267.0 [M + H]$^+$.  

![N'-benzylidene-N-isopropyl-4-methylbenzenesulfonohydrazide (1y):](image)

Yield: 93%; $R_f = 0.51$ (petroleum ether/EtOAc = 8:1); light yellow solid. **$^1$H NMR** (400 MHz, CDCl$_3$): $\delta = 8.62$ (s, 1 H), 7.69 - 7.75 (m, 4 H), 7.40 - 7.47 (m, 3 H), 7.29 (d, $J = 8.1$ Hz, 2 H), 4.45 - 4.52 (m, 1 H), 2.42 (s, 3 H), 1.08 (d, $J = 6.7$ Hz, 6 H) ppm. **ESI-LRMS**: $m/z$ 317.0 [M + H]$^+$.  

![3,5-diphenyl-1H-pyrazole (3a).](image)

Yield: 78%; m.p. 197 - 199 °C, $R_f = 0.31$ (petroleum ether/EtOAc = 4:1); light yellow solid. **$^1$H NMR** (400 MHz, CDCl$_3$): $\delta = 7.71$ (d, $J = 7.3$ Hz, 4 H), 7.25 - 7.38 (m, 6 H), 6.82 (s, 1 H) ppm. **$^{13}$C NMR** (100 MHz, CDCl$_3$): $\delta = 128.9$, 128.2, 125.6, 100.1 ppm. **ESI-LRMS**: $m/z$ 221.2 [M + H]$^+$.  

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5-phenyl-3-p-tolyl-1H-pyrazole (3b).
Yield: 66%; m.p. 170 - 172 °C, Rf = 0.51 (petroleum ether/EtOAc = 3:1); light yellow solid. $^1$H NMR (400 MHz, CDCl₃): $\delta$ = 7.72 (d, $J$ = 7.3 Hz, 2 H), 7.59 (d, $J$ = 8.0 Hz, 2 H), 7.29 - 7.39 (m, 3 H), 7.18 (d, $J$ = 7.9 Hz, 2 H), 6.79 (s, 1 H), 2.37 (s, 3 H) ppm. $^{13}$C NMR (100 MHz, CDCl₃): $\delta$ = 138.2, 129.6, 128.8, 128.1, 125.6, 125.5, 99.8, 21.3 ppm. ESI-LRMS: m/z 235.0 [M + H]$^\dagger$.

3-(4-methoxyphenyl)-5-phenyl-1H-pyrazole (3c).
Yield: 66%; m.p. 156 - 158 °C, Rf = 0.31 petroleum ether/EtOAc = 3:1); light yellow solid. $^1$H NMR (400 MHz, CDCl₃): $\delta$ = 7.71 - 7.73 (m, 2 H), 7.61 - 7.65 (m, 2 H), 7.37 - 7.41 (m, 2 H), 7.33 (m, 1 H), 6.90 - 6.93 (m, 2 H), 6.75 (s, 1 H), 3.83 (s, 3 H) ppm. $^{13}$C NMR (100 MHz, CDCl₃): $\delta$ = 159.7, 131.5, 128.8, 128.1, 126.9, 125.6, 123.9, 114.3, 99.5, 55.3 ppm. ESI-LRMS: m/z 251.2 [M + H]$^\dagger$.

3-(4-fluorophenyl)-5-phenyl-1H-pyrazole (3d).
Yield: 66%; m.p. 178 - 180 °C, Rf = 0.40 (petroleum ether/EtOAc = 3:1); light yellow solid. $^1$H NMR (400 MHz, DMSO-d₆): $\delta$ = 13.37 (br, 1 H), 7.80 - 7.90 (m, 4H), 7.26 - 7.48 (m, 5H), 7.18 (s, 1 H) ppm. $^{13}$C NMR (100 MHz, DMSO-d₆): $\delta$ = 162.6 (d, $J_{CF}$ = 247.4 Hz), 128.9, 128.3, 127.4, 127.3, 125.5, 115.8, 115.6, 99.9 ppm. ESI-LRMS: m/z 239.1 [M + H]$^\dagger$.

3-(4-chlorophenyl)-5-phenyl-1H-pyrazole (3e).
Yield: 60%; m.p. 214 - 215 °C, Rf = 0.51 (petroleum ether/EtOAc = 3:1); light yellow solid. $^1$H NMR (400 MHz, DMSO-d₆ with a drop of conc. HCl): $\delta$ = 7.97 (d, $J$ = 8.6 Hz, 2 H), 7.93 (d, $J$ = 7.3 Hz, 2 H), 7.56 (d, $J$ = 8.5 Hz, 2 H), 7.51 (t, $J$ = 7.5 Hz, 2 H),
7.43 (d, J = 7.3 Hz, 1 H), 7.40 (s, 1 H) ppm. $^{13}$C NMR (100 MHz, DMSO-d$_6$ with a drop of conc. HCl): $\delta$ = 147.2, 147.1, 133.4, 130.1, 129.9, 129.4, 129.4, 129.1, 127.8, 126.0, 101.0 ppm. **ESI-LRMS**: m/z 255.1 [M + H]$^+$. 

3-(4-bromophenyl)-5-phenyl-1H-pyrazole (3f).

Yield: 63%; m.p. 212 - 214 °C, $R_f$ = 0.49 (petroleum ether/EtOAc = 3:1); light yellow solid. $^1$H NMR (400 MHz, DMSO-d$_6$ with a drop of conc. HCl): $\delta$ = 7.90 - 7.95 (m, 4 H), 7.70 (d, J = 8.4 Hz, 2 H), 7.52 (t, J = 7.6 Hz, 2 H), 7.41 - 7.45 (m, 2 H) ppm. $^{13}$C NMR (100 MHz, DMSO-d$_6$ with a drop of conc. HCl): $\delta$ = 147.0, 146.9, 132.1, 129.8, 129.7, 129.3, 129.1, 127.9, 125.9, 122.0, 100.9 ppm. **ESI-LRMS**: m/z 299.0 [M + H]$^+$. 

![3-(4-bromophenyl)-5-phenyl-1H-pyrazole (3f).](image)

3-(3-nitrophenyl)-5-phenyl-1H-pyrazole (3g).

Yield: 66%; m.p. 206 - 207 °C, $R_f$ = 0.32 (petroleum ether/EtOAc = 3:1); yellow solid. $^1$H NMR (400 MHz, DMSO-d$_6$ with a drop of conc. HCl): $\delta$ = 8.71 (t, J = 1.6 Hz, 1 H), 8.36 (d, J = 7.9 Hz, 1 H), 8.21 (dd, J = 8.2, 1.5 Hz, 1 H), 7.91 - 7.93 (m, 2 H), 7.78 (t, J = 8.0 Hz, 1 H), 7.49 - 7.53 (m, 3 H), 7.40 (t, J = 7.4 Hz, 1 H) ppm. $^{13}$C NMR (100 MHz, DMSO-d$_6$ with a drop of conc. HCl): $\delta$ = 148.8, 147.4, 146.5, 134.1, 132.0, 130.9, 130.2, 129.4, 128.9, 125.8, 122.8, 119.8, 101.2 ppm. **ESI-LRMS**: m/z 266.0 [M + H]$^+$. 

![3-(3-nitrophenyl)-5-phenyl-1H-pyrazole (3g).](image)

5-phenyl-3-(3-(trifluoromethyl)phenyl)-1H-pyrazole (3h).

Yield: 47%; m.p. 194 - 196 °C, $R_f$ = 0.50 (petroleum ether/EtOAc = 3:1); white solid. $^1$H NMR (400 MHz, DMSO-d$_6$ with a drop of conc. HCl): $\delta$ = 8.27 (s, 1 H), 8.24 (t, J = 4.3 Hz, 1 H), 7.94 (d, J = 7.4 Hz, 2 H), 7.74 (d, J = 4.8 Hz, 2 H), 7.50 - 7.54 (m, 3 H), 7.42 (t, J = 7.3 Hz, 1 H) ppm. $^{13}$C NMR (100 MHz, DMSO-d$_6$ with a drop of conc. HCl): $\delta$ = 149.0, 147.3, 133.2, 130.9, 130.7, 129.4, 128.9, 125.8, 122.8, 119.8, 101.2 ppm. **ESI-LRMS**: m/z 282.0 [M + H]$^+$. 

![5-phenyl-3-(3-(trifluoromethyl)phenyl)-1H-pyrazole (3h).](image)
HCl): $\delta = 147.1$, 146.7, 132.4, 130.3, 130.1, 130.0, 129.8, 129.5, 129.2, 128.8, 125.7, 124.9, 123.0, 121.9, 101.0 ppm. **ESI-LRMS:** $m/z$ 289.1 [$M + H]^+$. **ESI-HRMS:** calculated for $C_{16}H_{12}F_{3}N_{2}^+$ [$M + H]^+$ 289.0953, found 289.0950.

3-(naphthalen-1-yl)-5-phenyl-1H-pyrazole (3i).
Yield: 63%; m.p. 140 - 142 °C, $R_f = 0.47$ (petroleum ether/EtOAc = 3:1); white solid. **$^1H$ NMR** (400 MHz, DMSO-d$_6$ with a drop of conc. HCl): $\delta = 8.36$ - 8.39 (m, 1 H), 8.00 - 8.07 (m, 4 H), 7.78 (dd, $J = 7.1$, 0.9 Hz, 1 H), 7.60 - 7.66 (m, 3 H), 7.52 (t, $J = 7.5$ Hz, 2 H), 7.43 (t, $J = 7.4$ Hz, 1 H), 7.27 (s, 1 H) ppm. **$^{13}C$ NMR** (100 MHz, DMSO-d$_6$ with a drop of conc. HCl): $\delta = 147.0$, 146.9, 133.9, 130.9, 130.4, 129.6, 129.4, 129.1, 128.9, 128.5, 127.9, 127.4, 126.7, 126.2, 125.9, 125.8, 104.4 ppm. **ESI-LRMS:** $m/z$ 271.1 [$M + H]^+$. **ESI-HRMS:** calculated for $C_{19}H_{15}N_{2}^+$ [$M + H]^+$ 271.1235, found 271.1211.

5-phenyl-3-(thiophen-2-yl)-1H-pyrazole (3j).
Yield: 35%; m.p. 187 - 188 °C, $R_f = 0.41$ (petroleum ether/EtOAc = 3:1); white solid. **$^1H$ NMR** (400 MHz, CDCl$_3$): $\delta = 11.73$ (br, 1 H), 7.64 (d, $J = 6.8$ Hz, 2 H), 7.27 - 7.37 (m, 4 H), 7.23 (dd, $J = 5.0$, 1.0 Hz, 1 H), 7.01 (dd, $J = 5.0$, 3.6 Hz, 1 H), 6.68 (s, 1 H) ppm. **$^{13}C$ NMR** (400 MHz, CDCl$_3$): $\delta = 128.9$, 128.5, 127.6, 125.6, 124.9, 124.1, 100.1 ppm. **ESI-LRMS:** $m/z$ 227.1 [$M + H]^+$.

3-(furan-2-yl)-5-phenyl-1H-pyrazole (3k).
Yield: 37%; m.p. 170 - 172 °C, $R_f = 0.38$ (petroleum ether/EtOAc = 3:1); white solid. **$^1H$ NMR** (400 MHz, CDCl$_3$): $\delta = 10.93$ (br, 1 H), 7.72 (d, $J = 7.4$ Hz, 2 H), 7.39 - 7.45 (m, 3 H), 7.34 (m, 1 H), 6.77 (s, 1 H), 6.66 (d, $J = 3.3$ Hz, 1 H), 6.48 (dd, $J = 3.3$, 1.8 Hz, 1 H) ppm. **$^{13}C$ NMR** (400 MHz, CDCl$_3$): $\delta = 142.1$, 128.9, 128.4, 125.6, 111.5, 106.4, 99.4 ppm. **ESI-LRMS:** $m/z$ 211.1 [$M + H]^+$.
3-cyclohexyl-5-phenyl-1H-pyrazole (3l).
Yield: 90%; m.p. 135 - 137 °C, \( R_f = 0.35 \) (petroleum ether/EtOAc = 3:1); light yellow solid. \( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta = 10.58 \) (br, 1 H), 7.74 (d, \( J = 4.7 \) Hz, 2 H), 7.37 - 7.40 (m, 2 H), 7.28 - 7.32 (m, 1 H), 6.36 (s, 1 H), 2.67 (tt, \( J = 11.4, 3.5 \) Hz, 1 H), 2.01 - 2.04 (m, 2 H), 1.79 - 1.84 (m, 2 H), 1.73 (m, 1 H), 1.21 - 1.50 (m, 5 H) ppm. \( ^{13}C \) NMR (400 MHz, CDCl\(_3\)): \( \delta = 128.7, 127.7, 125.6, 99.3, 35.8, 32.9, 26.1, 25.9 \) ppm. ESI-LRMS: \( m/z \) 227.2 [M + H]\(^+\).

3-(pentan-3-yl)-5-phenyl-1H-pyrazole (3m).
Yield: 90%; m.p. 123 - 124 °C, \( R_f = 0.30 \) (petroleum ether/EtOAc = 3:1); light yellow solid. \( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.77 \) (d, \( J = 7.5 \) Hz, 2 H), 7.39 (t, \( J = 7.5 \) Hz, 2 H), 7.30 (t, \( J = 7.4 \) Hz, 1 H), 6.35 (s, 1 H), 2.52 (m, 1 H), 1.54 - 1.75 (m, 4 H), 0.83 - 0.87 (m, 6 H) ppm. \( ^{13}C \) NMR (400 MHz, CDCl\(_3\)): \( \delta = 128.7, 127.7, 125.5, 99.9, 41.2, 28.0, 11.9 \) ppm. ESI-LRMS: \( m/z \) 215.2 [M + H]\(^+\).

3-phenyl-5-p-tolyl-1H-pyrazole (3o).
Yield: 59%; m.p. 170 - 172 °C, \( R_f = 0.51 \) (petroleum ether/EtOAc = 3:1); light yellow solid. \( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.72 \) (d, \( J = 7.2 \) Hz, 2 H), 7.59 (d, \( J = 7.4 \) Hz, 2 H), 7.30 - 7.39 (m, 3 H), 7.18 (d, \( J = 7.3 \) Hz, 2 H), 6.79 (s, 1 H), 2.37 (s, 3 H) ppm. ESI-LRMS: \( m/z \) 235.0 [M + H]\(^+\).

3-(4-bromophenyl)-5-p-tolyl-1H-pyrazole (3p).
Yield: 68%; m.p. 239 - 241 °C, \( R_f = 0.49 \) (petroleum ether/EtOAc = 3:1); white solid. \( ^1H \) NMR (400 MHz, DMSO-d\(_6\) with a drop of conc. HCl): \( \delta = 7.90 \) (d, \( J = 8.6 \) Hz, 2 H), 7.82 (d, \( J = 8.1 \) Hz, 2 H), 7.70 (d, \( J = 8.6 \) Hz, 2 H), 7.40 (s, 1 H), 7.32 (d, \( J = 8.0 \) Hz, 2 H), 7.09 (d, \( J = 8.5 \) Hz, 2 H), 6.89 (s, 1 H), 2.35 (s, 3 H) ppm. ESI-LRMS: \( m/z \) 263.0 [M + H]\(^+\).
3-(4-bromophenyl)-5-(4-fluorophenyl)-1H-pyrazole (3r).

Yield: 52%; m.p. 228 - 229 °C, R_{f} = 0.58 (petroleum ether/EtOAc = 3:1); white solid.

{^1}H NMR (400 MHz, DMSO-d_{6} with a drop of conc. HCl): \( \delta = 7.95 - 7.99 \) (m, 2 H), 7.88 (d, \( J = 8.5 \) Hz, 2 H), 7.69 (d, \( J = 8.5 \) Hz, 2 H), 7.32 - 7.37 (m, 3 H) ppm. \n
{^{13}C} NMR (100 MHz, DMSO-d_{6} with a drop of conc. HCl): \( \delta = 162.6 \) (d, \( J_{CF} = 245.7 \) Hz), 146.9, 146.6, 132.3, 130.1, 128.2 (d, \( 3J_{CF} = 8.4 \) Hz), 128.0, 127.1 (d, \( 4J_{CF} = 3.1 \) Hz), 122.0, 116.3 (d, \( 2J_{CF} = 21.8 \) Hz), 100.91 ppm.

ESI-LRMS: \( m/z = 313.0 \) [M + H]^+.

ESI-HRMS: calculated for C_{16}H_{14}BrN_{2}^+ [M + H]^+ 313.0340, found 313.0337.

3-(4-bromophenyl)-5-(3-chlorophenyl)-1H-pyrazole (3s).

Yield: 40%; m.p. 191 - 193 °C, R_{f} = 0.54 (petroleum ether/EtOAc = 3:1); white solid.

{^1}H NMR (400 MHz, DMSO-d_{6} with a drop of conc. HCl): \( \delta = 7.97 \) (t, \( J = 1.7 \) Hz, 1 H), 7.85 - 7.89 (m, 3 H), 7.69 (d, \( J = 8.5 \) Hz, 2 H), 7.52 (t, \( J = 7.9 \) Hz, 1 H), 7.43 - 7.45 (m, 2 H) ppm. \n
{^{13}C} NMR (100 MHz, DMSO-d_{6} with a drop of conc. HCl): \( \delta = 146.7, 146.5, 134.1, 133.2, 132.3, 131.3, 130.3, 128.4, 127.8, 125.4, 124.4, 121.8, 101.3 \) ppm.

ESI-LRMS: \( m/z = 333.0 \) [M + H]^+.

ESI-HRMS: calculated for C_{15}H_{11}BrClN_{2}^+ [M + H]^+ 332.9794, found 332.9780.

3-(4-bromophenyl)-5-butyl-1H-pyrazole (3t).

Yield: 42%; m.p. 91 - 92 °C, R_{f} = 0.37 (petroleum ether/EtOAc = 3:1); white solid.

{^1}H NMR (400 MHz, CDCl_{3}): \( \delta = 7.61 \) (d, \( J = 8.5 \) Hz, 2 H), 7.48 - 7.51 (m, 2 H), 6.34 (s, 1 H), 2.63 (t, \( J = 7.6 \) Hz, 2 H), 1.60 - 1.67 (m, 2 H), 1.32 - 1.42 (m, 2 H), 0.92 (t, \( J = 7.3 \) Hz, 3 H) ppm. \n
{^{13}C} NMR (400 MHz, CDCl_{3}): \( \delta = 131.7, 127.1, 121.6, 100.9, 95.5, 58.3, 37.6, 21.7, 14.0 \) ppm.
31.2, 25.8, 22.2, 13.7 ppm. **ESI-LRMS**: \( m/z \) 279.0 \([M + H]^+\). **ESI-HRMS**: calculated for \( C_{13}H_{16}BrN_2^+ \) \([M + H]^+\) 279.0497, found 279.0484.

![5-(4-fluorophenyl)-3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (4d).](image)

**5-(4-fluorophenyl)-3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (4d).**
Yield: 25%; \( R_f = 0.35 \) (petroleum ether/EtOAc = 5:1); white solid. **\(^1H\) NMR** (400 MHz, CDCl\(_3\)): \( \delta = 7.75 \) (d, \( J = 8.3 \) Hz, 2 H), 7.67 - 7.69 (m, 2 H), 7.35 - 7.45 (m, 5 H), 7.27 (d, \( J = 8.6 \) Hz, 2 H), 7.00 - 7.05 (m, 2 H), 4.90 (dd, \( J = 11.2, 9.3 \) Hz, 1 H), 3.52 (dd, \( J = 17.3, 11.3 \) Hz, 1 H), 3.09 (dd, \( J = 17.3, 9.2 \) Hz, 1 H), 2.39 (s, 3 H) ppm. **\(^{13}C\) NMR** (400 MHz, CDCl\(_3\)): \( \delta = 162.4 \) (d, \( J_{CF} = 246.8 \) Hz), 156.4, 144.2, 136.6, 132.5, 130.7, 130.6, 129.5, 128.7, 128.5, 128.4, 126.9, 115.6 (d, \( J_{CF} = 21.7 \) Hz), 64.6, 43.8, 21.6 ppm. **ESI-LRMS**: \( m/z \) 394.9 \([M + H]^+\). **ESI-HRMS**: calculated for \( C_{22}H_{20}FN_2O_2S^+ \) \([M + H]^+\) 395.1230, found 395.1247.

![5-(4-chlorophenyl)-3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (4e).](image)

**5-(4-chlorophenyl)-3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (4e).**
Yield: 13%; \( R_f = 0.36 \) (petroleum ether/EtOAc = 5:1); white solid. **\(^1H\) NMR** (400 MHz, CDCl\(_3\)): \( \delta = 7.75 \) (d, \( J = 8.2 \) Hz, 2 H), 7.67 - 7.69 (m, 2 H), 7.37 - 7.45 (m, 3 H), 7.30 - 7.35 (m, 4 H), 7.27 (d, \( J = 8.8 \) Hz, 2 H), 4.88 (dd, \( J = 11.2, 9.3 \) Hz, 1 H), 3.53 (dd, \( J = 17.2, 11.4 \) Hz, 1 H), 3.08 (dd, \( J = 17.3, 9.3 \) Hz, 1 H), 2.40 (s, 3 H) ppm. **\(^{13}C\) NMR** (400 MHz, CDCl\(_3\)): \( \delta = 156.4, 144.3, 139.3, 133.8, 132.4, 130.7, 130.5, 129.5, 128.9, 128.7, 128.5, 128.1, 126.9, 64.5, 43.7, 21.6 ppm. **ESI-LRMS**: \( m/z \) 411.0 \([M + H]^+\). **ESI-HRMS**: calculated for \( C_{22}H_{20}ClN_2O_2S^+ \) \([M + H]^+\) 411.0934, found 411.0945.
5-(4-bromophenyl)-3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (4f).
Yield: 14%; $R_f = 0.38$ (petroleum ether/EtOAc = 5:1); white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.74$ (d, $J = 8.2$ Hz, 2 H), 7.66 - 7.68 (m, 2 H), 7.47 (d, $J = 8.3$ Hz, 2 H), 7.37 - 7.43 (m, 3 H), 7.26 - 7.28 (m, 4 H), 4.87 (dd, $J = 11.1$, 9.5 Hz, 1 H), 3.53 (dd, $J = 17.2$, 11.3 Hz, 1 H), 3.08 (dd, $J = 17.2$, 9.2 Hz, 1 H), 2.40 (s, 3 H) ppm. $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta = 156.4$, 144.3, 139.8, 132.4, 131.9, 130.7, 130.5, 129.5, 128.7, 128.5, 128.5, 126.9, 122.0, 64.6, 43.7, 21.6 ppm. ESI-LRMS: $m/z$ 454.9 [M + H]$^+$. ESI-HRMS: calculated for C$_{22}$H$_{20}$BrN$_2$O$_2$S$^+$ [M + H]$^+$ 455.0429, found 455.0447.

3-phenyl-5-(thiophen-2-yl)-1-tosyl-4,5-dihydro-1H-pyrazole (4j).
Yield: 12%; $R_f = 0.32$ (petroleum ether/EtOAc = 5:1); white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.74$ (d, $J = 8.1$ Hz, 2 H), 7.68 - 7.70 (m, 2 H), 7.37 - 7.45 (m, 3 H), 7.22 - 7.26 (m, 3 H), 7.11 (d, $J = 3.2$ Hz, 1 H), 6.94 - 6.96 (m, 1 H), 5.31 (dd, $J = 11.0$, 8.1 Hz, 1 H), 3.54 (dd, $J = 17.1$, 11.1 Hz, 1 H), 3.26 (dd, $J = 17.2$, 8.1 Hz, 1 H), 2.39 (s, 3 H) ppm. $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta = 156.6$, 144.1, 143.5, 132.8, 130.7, 130.6, 129.4, 128.7, 128.5, 126.9, 126.7, 126.0, 125.5, 60.7, 43.9, 21.6 ppm. ESI-LRMS: $m/z$ 383.0 [M + H]$^+$. ESI-HRMS: calculated for C$_{20}$H$_{19}$N$_2$O$_2$S$_2$$^+$ [M + H]$^+$ 383.0888, found 383.0897.
5-(4-bromophenyl)-3-p-tolyl-1-tosyl-4,5-dihydro-1H-pyrazole (4p).
Yield: 9%; $R_f = 0.35$ (petroleum ether/EtOAc = 5:1); light yellow solid. $^1H$ NMR (400 MHz, CDCl$_3$): $\delta$ = 7.74 (d, $J = 8.2$ Hz, 2 H), 7.56 (d, $J = 8.1$ Hz, 2 H), 7.46 (d, $J = 8.4$ Hz, 2 H), 7.25 - 7.28 (m, 4 H), 7.19 (d, $J = 8.0$ Hz, 2 H), 4.84 (dd, $J = 11.1$, 9.3 Hz, 1 H), 3.49 (dd, $J = 17.2$, 11.3 Hz, 1 H), 3.05 (dd, $J = 17.2$, 9.2 Hz, 1 H), 2.39 (s, 3 H), 2.37 (s, 3 H) ppm. $^{13}C$ NMR (400 MHz, CDCl$_3$): $\delta$ = 156.5, 144.2, 141.2, 139.9, 132.4, 131.8, 129.5, 129.4, 128.5, 128.5, 127.7, 126.8, 121.9, 64.5, 43.7, 21.6, 21.5 ppm. ESI-LRMS: $m/z$ 469.0 [M + H]$^+$. ESI-HRMS: calculated for C$_{23}$H$_{22}$BrN$_2$O$_2$S$^+$ [M + H]$^+$ 469.0585, found 469.0587.

5-(4-bromophenyl)-3-(4-fluorophenyl)-1-tosyl-4,5-dihydro-1H-pyrazole (4r).
Yield: 14%; $R_f = 0.34$ (petroleum ether/EtOAc = 5:1); white solid. $^1H$ NMR (400 MHz, CDCl$_3$): $\delta$ = 7.73 (d, $J = 7.7$ Hz, 2 H), 7.65 - 7.68 (m, 2 H), 7.47 (d, $J = 8.0$ Hz, 2 H), 7.25 - 7.32 (m, 4 H), 7.08 (t, $J = 8.1$ Hz, 2 H), 4.89 (t, $J = 10.2$ Hz, 1 H), 3.51 (dd, $J = 17.2$, 11.4 Hz, 1 H), 3.06 (dd, $J = 17.2$, 9.2 Hz, 1 H), 2.41 (s, 3 H) ppm. $^{13}C$ NMR (400 MHz, CDCl$_3$): $\delta$ = 164.1 (d, $^1J_{CF}= 251.9$ Hz), 155.31, 144.4, 139.7, 132.5, 131.9, 129.5, 128.9 (d, $^3J_{CF}= 8.5$ Hz), 128.5, 128.5, 126.8 (d, $^4J_{CF}= 3.2$ Hz), 122.1, 115.9 (d, $^2J_{CF}= 22.0$ Hz), 64.6, 43.7, 21.6 ppm. ESI-LRMS: $m/z$ 473.0 [M + H]$^+$. ESI-HRMS: calculated for C$_{22}$H$_{19}$BrFN$_2$O$_2$S$^+$ [M + H]$^+$ 473.0335, found 473.0334.
N′-(5-bromo-2-(prop-2-ynyloxy)benzylidene)-4-methylbenzenesulfonohydrazide (6).
Yield: 90%; $R_f = 0.32$ (petroleum ether/EtOAc = 3:1); white solid. $^1H$ NMR (400 MHz, CDCl$_3$): $\delta = 8.07$ (br, 1 H), 8.06 (s, 1 H), 7.94 (d, $J = 2.5$ Hz, 1 H), 7.87 (d, $J = 8.3$ Hz, 2 H), 7.41 (dd, $J = 8.8$, 2.5 Hz, 1 H), 7.33 (d, $J = 8.1$ Hz, 2 H), 6.86 (d, $J = 8.9$ Hz, 1 H), 4.68 (d, $J = 2.3$ Hz, 2 H), 2.52 (t, $J = 2.3$ Hz, 1 H), 2.42 (s, 3 H) ppm. ESI-LRMS: $m/z$ 407.0 [M + H]$^+$. 

![Chemical structure of N\'-(5-bromo-2-(prop-2-ynyloxy)benzylidene)-4-methylbenzenesulfonohydrazide (6)](image)

3-(5-bromo-2-(prop-2-ynyloxy)phenyl)-5-phenyl-1H-pyrazole (9).
Yield: 62%; m.p. 74 - 76 °C, $R_f = 0.38$ (petroleum ether/EtOAc = 3:1); light yellow solid. $^1H$ NMR (400 MHz, CDCl$_3$): $\delta = 7.84$ - 7.88 (m, 3 H), 7.39 - 7.45 (m, 3 H), 7.34 (m, 1 H), 6.96 - 7.00 (m, 2 H), 4.83 (d, $J = 2.4$ Hz, 2 H), 2.62 (t, $J = 2.4$ Hz, 1 H) ppm. $^{13}C$ NMR (400 MHz, CDCl$_3$): $\delta = 152.9$, 131.6, 130.8, 128.7, 127.9, 125.6, 114.8, 114.8, 100.9, 56.9 ppm. ESI-LRMS: $m/z$ 353.0 [M + H]$^+$. ESI-HRMS: calculated for C$_{18}$H$_{14}$BrN$_2$O$^+$ [M + H]$^+$ 353.0290, found 353.0273. 

![Chemical structure of 3-(5-bromo-2-(prop-2-ynyloxy)phenyl)-5-phenyl-1H-pyrazole (9)](image)

methyl-3,5-diphenyl-1H-pyrazole (11a).
Yield: 99%; $R_f = 0.65$ (petroleum ether/EtOAc = 3:1); colorless semi-solid. $^1H$ NMR (400 MHz, CDCl$_3$): $\delta = 7.86$ - 7.80 (m, 2 H), 7.51 - 7.37 (m, 7 H), 7.34 - 7.27 (m, 1 H), 6.61 (s, 1 H), 3.93 (s, 3 H) ppm. $^{13}C$ NMR (100 MHz, CDCl$_3$): $\delta = 150.5$, 145.1, 133.4, 130.7, 128.8, 128.7, 128.7, 128.6, 127.6, 125.5, 103.3, 37.6 ppm. ESI-LRMS: $m/z$ 235.1 [M + H]$^+$. 

![Chemical structure of methyl-3,5-diphenyl-1H-pyrazole (11a)](image)
$^{1}H$ spectrum of 1n

$^{13}C$ spectrum of 1n
$^{13}$C spectrum of $3g$

$^1$H spectrum of $3h$
Compound 4p, NOESY, in CDCl₃, 400MHz

Compound 4p, II-III COSY, in CDCl₃, 400MHz
Key HMBC and NOESY correlations and $^1$H, $^{13}$C-NMR data of compounds 4p