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Synthesis and Crystal Structures of 4,5-Dihydroimidazo[1,5-*b*]-pyrazol-6-ones

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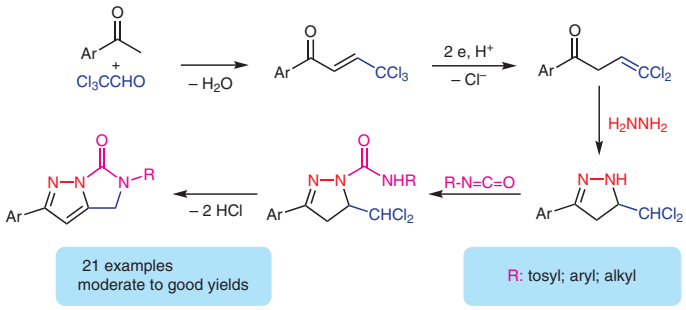

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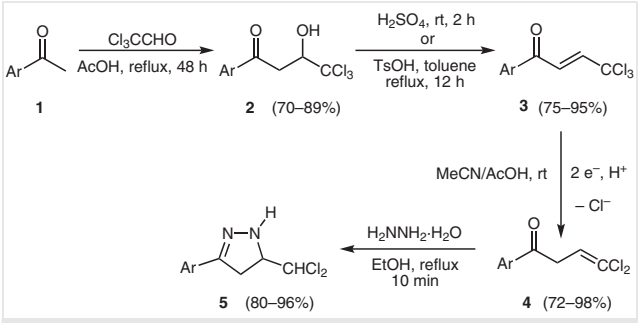
Abstract The synthesis of previously unattainable 2,5-disubstituted 4,5-dihydroimidazo[1,5-*b*]pyrazol-6-ones has been developed. Electrochemical reductions of readily available 2,2,2-trichloroethylideneacetophenones were followed by reaction with hydrazine, leading to 3-aryl-5-dichloromethyl-2-pyrazolines. These were treated with isocyanates to obtain the corresponding aminocarbonyl derivatives, which were found to be able to form an otherwise almost inaccessible imidazo[1,5-*b*]pyrazole ring system via a one-step reaction involving internal condensation followed by hydrogen chloride elimination and aromatization. The molecular structures of 2-(4-methylphenyl)-5-tosyl-4,5-dihydroimidazo[1,5-*b*]pyrazol-6-one, 5-dichloromethyl-*N*-(4-chlorophenyl)-4,5-dihydro-3-*p*-tolylpyrazole-1-carboxamide, and 5-(4-bromophenyl)-2-*p*-tolyl-4,5-dihydroimidazo[1,5-*b*]pyrazol-6-one were determined by X-ray crystallographic analysis.

Key words chloral, acetophenones, pyrazolines, heterocycles, imidazo-[1,5-*b*]pyrazolones

Recent reviews on the synthesis and properties of heterocycles condensed to a pyrazole core have reported that these are an important source of bioactive molecules.[1,2] Imidazopyrazoles have been recognized as substances of significant chemical, biological and medicinal interest.[3,4] By far, the most well-known compounds are those pertaining to the imidazo[1,2-*b*]pyrazole family, which have been described as possessing noteworthy anticancer,[4–6] antibacterial,[7,8] and anti-inflammatory[9,10] properties, among others. 5-Aminopyrazoles, the synthetic methods for which have been extensively reviewed,[11] are the main preparative intermediates for imidazo[1,2-*b*]pyrazoles.[12–29] The synthesis and properties of imidazo[4,5-*c*]pyrazoles have also received considerable attention.[30–42] 5-Aminopyrazoles have also been of great utility in preparing these compounds.[32,33,36,40,41] However, synthetic methodology for obtaining imidazo[1,5-*b*]pyrazole derivatives is notably lacking, and very little is known about these compounds.[3,4] Only a few individual examples having this uncommon ring fusion have been previously prepared; for example, by cyclodehydration of substituted pyrazolylmethylacetamides leading to 2,3-dihydroimidazo[1,5-*b*] derivatives related to cyclized histamine,[43] preparation of 2,3-dihydro-1*H*-imidazo[1,5-*b*]pyrazole-4,6(3a*H*,5*H*)-dione from 1-(benzylideneamino)-5-(2-hydroxyethyl)hydantoin,[44] and the synthesis of hexahydro-4,4-dimethyl-1,3a-diaryl-6-oxo-1*H*-imidazo[1,5-*b*]pyrazole-3-carbonitriles from α-aminoisobutyrophenone phenyl hydrazones.[45] Concerning imidazopyrazolones, studies on the synthesis, properties and usefulness of substances exhibiting [1,2-*b*],[46–50] [4,5-*c*],[51,52] and [3,4-*b*][45] ring systems have been successful. However, the synthesis of imidazo[1,5-*b*]pyrazol-6-ones remains to be achieved. To our knowledge, this paper describes the first synthetic approach to this class of compounds.

In an earlier work we synthesized novel 3-aryl-5-dichloromethyl-2-pyrazolines **5** starting from chloral, a cheap multipurpose starting material for organic synthesis,[53] and inexpensive, commercially available acetophenones. 2,2,2-Trichloroethylideneacetophenones **3** and 2,2-dichlorovinylacetophenones **4** were key intermediates (Scheme 1).[54,55] Taking into account the specific molecular arrangement of compounds **5** – two active centers of opposite polarity and the presence of an electrophilic dichloromethyl group attached to C-5 instead of the nucleophilic amino group present in 5-aminopyrazoles – we envisaged that compounds **5** could be of key interest as they offer privileged access to still unattainable imidazo[1,5-*b*]pyrazol-6-ones. The results of this study are detailed here, concluding in an effective

method for preparing hitherto unknown 2-aryl-5-tosyl-4,5-dihydroimidazo[1,5-*b*]pyrazol-6-ones **10**, as displayed in Scheme 2. Pyrazolines **5** were treated with toluenesulfonyl isocyanate to obtain the corresponding toluenesulfonylaminocarbonyl intermediates **7**, which were subjected to base treatment and directly provided the desired products (Table 1). The scope of this method could also be extended by using aryl and alkyl isocyanates, which allowed the synthesis of the target 2,5-diaryl- and 5-alkyl-2-aryl-4,5-dihydroimidazo[1,5-*b*]pyrazol-6-ones **12** (Table 2). It should be noted that, because of their utility for preparing a diversity of fused heterocyclic compounds, 5-aminopyrazoles have become key reagents for organic and medicinal chemistry.[56] However, these intermediates are not able to form an imidazo[1,5-*b*]pyrazole ring system. Conversely, we have overcome this limitation through 5-dichloromethylpyrazolines **5**. Furthermore, these appear to be promising agents offering many other possibilities to prepare a wide variety of fused heterocycles.



Scheme 1 Synthesis of 5-dichloromethyl-2-pyrazolines **5** through chloral derivatives. Ar: (**a**) C_6H_5; (**b**) 4-ClC_6H_4; (**c**) 4-BrC_6H_4; (**d**) 4-MeC_6H_4; (**e**) 4-$MeOC_6H_4$; (**f**) 4-$O_2NC_6H_4$; (**g**) 4-PhC_6H_4; (**h**) 2-$C_{10}H_7$; (**i**) 2,4-$Cl_2C_6H_3$; (**j**) 3-BrC_6H_4

A series of 3-aryl-5-dichloromethyl-2-pyrazolines **5** was prepared by applying our previously reported synthetic method,[54] which involves preparation and dehydration of chloralacetophenones **2** to obtain the corresponding 2,2,2-trichloroethylideneacetophenones **3**, selective electrochemical reduction[55,57] to give dichlorovinylacetophenones **4**, and treatment with hydrazine hydrate.

To investigate the first synthetic approach to products **10** through pyrazolines **5**, compound **5d** was selected as a model. Reaction with tosyl isocyanate led to the previously unknown 5-dichloromethyl-3-*p*-tolyl-*N*-tosyl-2-pyrazoline-1-carboxamide (**7d**; Ar = *p*-tolyl) in 96% yield (Scheme 2). Next, a cyclization process promoted by strong bases, such as potassium *tert*-butoxide or lithium diisopropylamide, was attempted, but provided disappointing results, since complex mixtures of unidentifiable products were observed. However, on heating to reflux in triethylamine, the progressive formation of a single product was observed. This was isolated and spectroscopically identified as the hitherto unknown 2-(4-methylphenyl)-5-toluenesulfonyl-4,5-dihydroimidazo[1,5-*b*]pyrazol-6-one (**10d**; yield 65%), the molecular structure of which was confirmed by X-ray crystallographic analysis (Figure 1).[58]

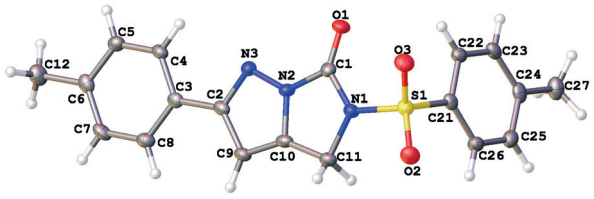
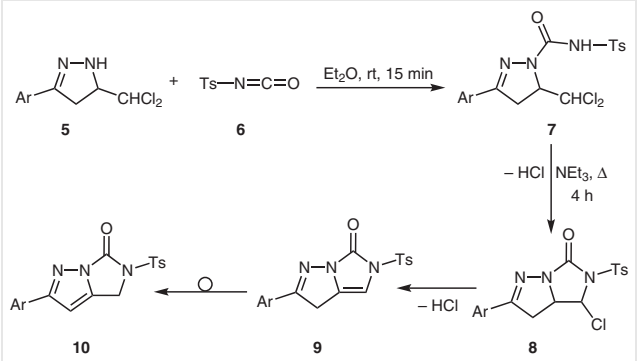


Figure 1 X-ray crystal structure of compound **10d** (thermal ellipsoids drawn at the 50% probability level)

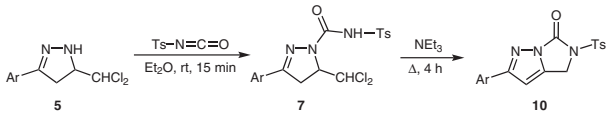


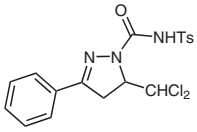
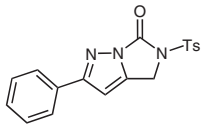
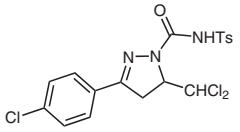
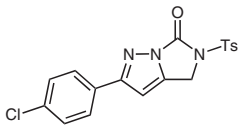
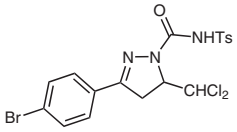
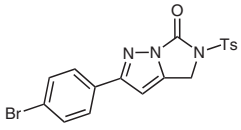
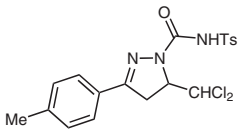
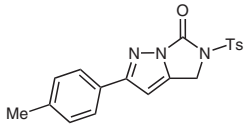
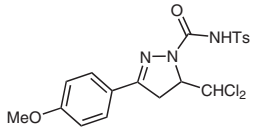
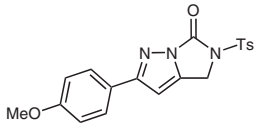
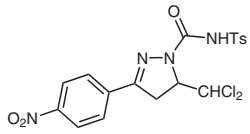
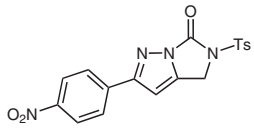
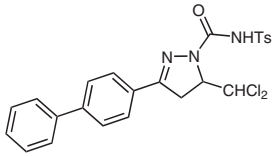
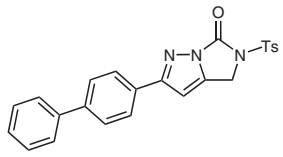
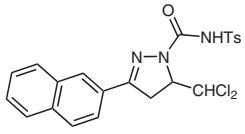
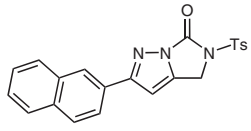
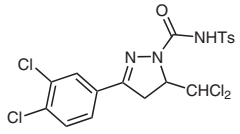
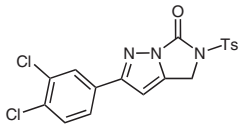
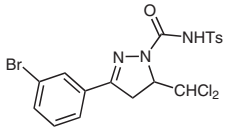
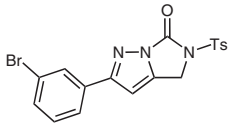
Scheme 2 Synthesis of 2-aryl-5-tosyl-4,5-dihydroimidazo[1,5-*b*]pyrazol-6-ones **10** from pyrazolines **5**

In view of this successful result, products **10a**, **10d**, **10e**, and **10h–j** were similarly obtained from their respective precursors **7** in boiling triethylamine; however, other conversions required operating at higher reaction temperature using a sealed vessel under pressure (Table 1). Successful results were also obtained with a more rapid and efficient one-pot preparative process. Thus, mixtures of compounds **5** with toluenesulfonyl isocyanate and triethylamine were heated at 130 °C for two hours, directly providing the desired products **10** in fair to good yields (Table 1). It is clear that the formation of these products is explicable by initial generation of intermediates **7**, which, under suitable basic experimental conditions, can undergo internal attack at the dichloromethyl group, leading to intermediates **8**, the chemical evolution of which would occur by hydrogen chloride elimination to give intermediates **9**. Finally, these would undergo an isomerization process to give the most stable products **10** (Scheme 2).

Once the synthesis of compounds **10** had been achieved, we focused on expanding the novel preparative method to obtain 2,5-diaryl- and 5-alkyl-2-aryl-4,5-dihydroimidazo[1,5-*b*]pyrazol-6-ones **12** by using aryl and alkyl isocyanates as acylating agents. Thus, reactions of a range of pyrazolines **5** with a variety of aryl and alkyl isocyanates were carried out to obtain novel derivatives **11** in moderate to good yields. The geometrical characteristics of these

Table 1 Preparation of Imidazo[1,5-*b*]pyrazol-6-ones **10**



Entry	Intermediate **7**	Yield (%)*	Product **10**	Yield (%)*
a		97		50[a] (63)[c]
b		92		63[b] (75)[c]
c		92		38[b] (57)[c]
d		96		65[a] (70)[c]
e		97		46[a] (77)[c]
f		93		55[b] (88)[c]
g		98		60[b] (68)[c]
h		83		78[a] (82)[c]
i		70		80[b] (85)[c]
j		80		65[a] (82)[c]

* Isolated yield
[a] At reflux temperature.
[b] At 130 °C.
[c] At 130 °C (one-pot process).

compounds were determined by X-ray crystallographic analysis of 5-dichloromethyl-*N*-(4-chlorophenyl)-4,5-dihydro-3-*p*-tolylpyrazole-1-carboxamide (**11f**; Figure 2).[59]

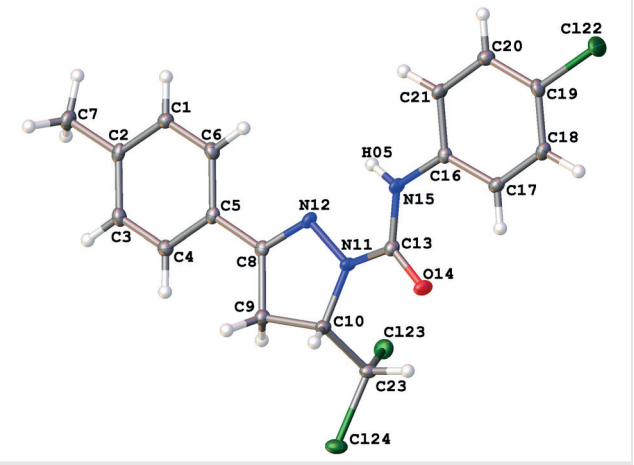


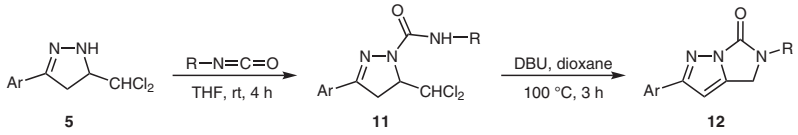
Figure 2 X-ray crystal structure of compound **11f** (thermal ellipsoids drawn at the 50% probability level)

Cyclizations of intermediates **11** promoted by potassium *tert*-butoxide, diisopropylamide or triethylamine were ineffective. Conversely, employing DBU as base afforded good results for the targeted dihydroimidazo[1,5-*b*]pyrazol-6-ones **12**, which were obtained in fair to good yields (Table 2).

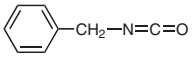
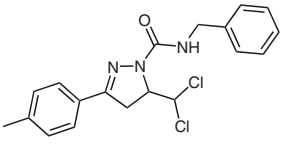
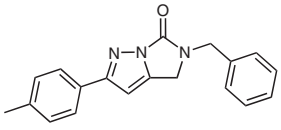
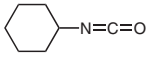
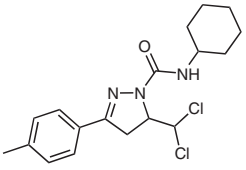
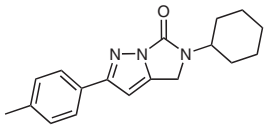
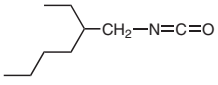
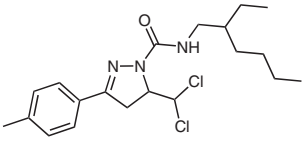
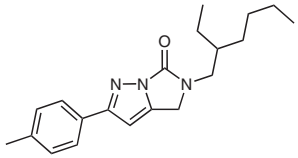
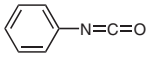
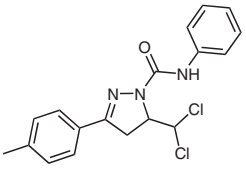
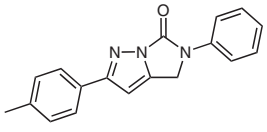
The molecular structure of one of these compounds: 5-(4-bromophenyl)-2-*p*-tolyl-4,5-dihydro-imidazo[1,5-*b*]-pyrazol-6-one (**12h**) was determined by X-ray crystallographic analysis (Figure 3).[60]

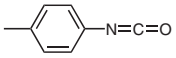
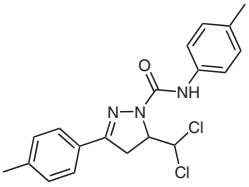
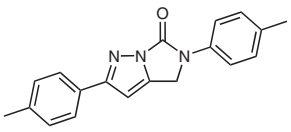
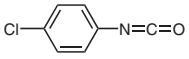
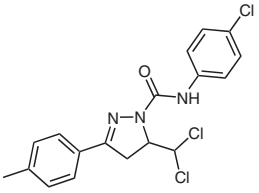
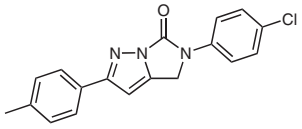
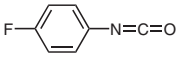
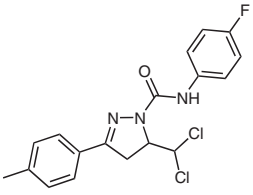
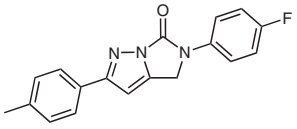
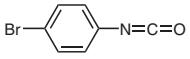
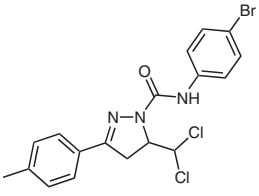
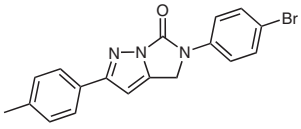
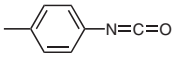
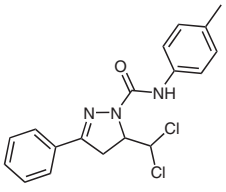
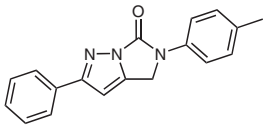
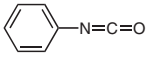
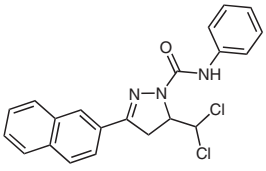
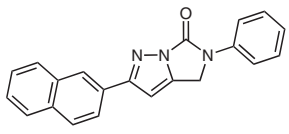
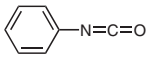
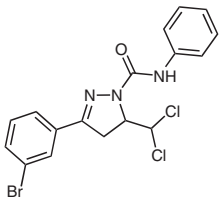
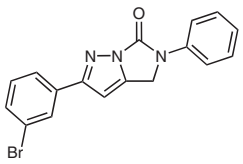
To conclude, a new and highly flexible synthetic method for preparing imidazo[1,5-*b*]pyrazoles is reported that provides straightforward access to previously unattainable 4,5-dihydroimidazo[1,5-*b*]pyrazol-6-ones through 5-dichloromethyl-2-pyrazolines. Given the previous scant progress in generating this type of ring fusion, these novel products are not only of high interest in themselves, but also in terms of exploring their possible biological properties. The development of syntheses for other classes of heterocyclic compounds by applying a similar strategy also appears feasible.

Table 2 Preparation of Imidazo[1,5-*b*]pyrazol-6-ones **12**



5 11 12

Entry	Isocyanate	Intermediate **11**	Yield (%)[a]	Product **12**	Yield (%)[a]
a			50		40
b			43		70
c			51		53
d			74		70

Entry	Isocyanate	Intermediate **11**	Yield (%)[a]	Product **12**	Yield (%)[a]
e			70		75
f			70		83
g			72		62
h			71		64
i			63		51
j			61		54
k			60		50

[a] Isolated yield.

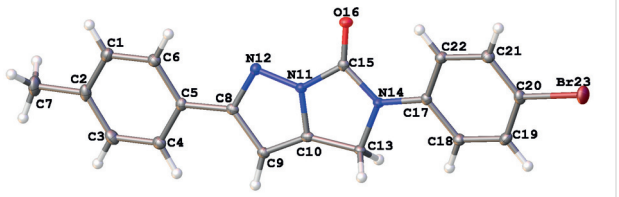


Figure 3 X-ray crystal structure of compound **12h** (thermal ellipsoids drawn at the 50% probability level)

NMR spectra were recorded with a Bruker AV-300 or Bruker AV-400 with tetramethylsilane as internal reference. High-resolution mass spectra (HRMS) were obtained with a time-of-flight (TOF) instrument equipped with electrospray ionization (ESI). IR spectra were recorded with Nicolet Impact 400 or Jasco FTIR-4700LE spectrophotometers. Microanalyses were performed with a Carlo Erba EA-1108 analyser. Melting points were determined with a Büchi Melting point B-540, and are uncorrected. 3-Aryl-5-dichloromethyl-2-pyrazolines **5** were prepared as previously described.[54]

Synthesis of 7; General Procedure

To a stirred suspension of compound **5** (2.5 mmol) in anhydrous diethyl ether (10 mL), a solution of toluenesulfonyl isocyanate (2.5 mmol) in anhydrous diethyl ether (10 mL) was slowly added dropwise (ca. 1 drop per second) under a nitrogen atmosphere. The stirring was continued for 10 min at r.t., and the precipitate was collected by filtration and crystallized from the appropriate solvent.

5-Dichloromethyl-3-phenyl-1-tosylaminocarbonyl-2-pyrazoline (7a)

Yield: 1.04 g (97%); white prisms; mp 168 °C (dec) (MeCN).

IR (Nujol): 3285, 1698, 1599, 1379, 1346, 1163, 1078, 895, 866, 848, 785, 673 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 2.44 (s, 3 H), 3.51 (dd, *J* = 18.3, 11.3 Hz, 1 H), 3.63 (dd, *J* = 18.3, 5.8 Hz, 1 H), 4.88 (ddd, *J* = 11.3, 5.8, 2.6 Hz, 1 H), 6.41 (d, *J* = 2.6 Hz, 1 H), 7.35 (d, *J* = 8.2 Hz, 2 H), 7.43–7.50 (m, 3 H), 7.72 (dd, *J* = 6.3, 1.8 Hz, 2 H), 7.99 (d, *J* = 8.2 Hz, 2 H), 8.67 (br s, 1 H).

^{13}C NMR ($CDCl_3$, 100.8 MHz): δ = 21.76 (CH_3), 35.15 (CH_2), 63.26 (CH), 71.11 ($CHCl_2$), 126.98 (CH), 128.42 (CH), 129.00 (CH), 129.62 (C), 129.67 (CH), 131.38 (CH), 136.04 (C), 145.00 (C), 148.41 (C=O), 155.12 (C=N).

MS: *m*/*z* (%) = 425 (0.5) $[M]^+$, 427 (0.4) $[M^+{+}2]$, 228 (11), 197 (12), 155 (29), 145 (100), 128 (18), 91 (70), 77 (22).

Anal. Calcd for $C_{18}H_{17}Cl_2N_3O_3S$: C, 50.71; H, 4.02; N, 9.86; S, 7.52. Found: C, 50.83; H, 3.96; N, 9.85; S, 7.50.

5-Dichloromethyl-3-(4-chlorophenyl)-1-tosylaminocarbonyl-2-pyrazoline (7b)

Yield: 1.06 g (92%); white needles; mp 224 °C (dec) (MeCN).

IR (Nujol): 3330, 1706, 1600, 1408, 1346, 1166, 1087, 821, 785, 664 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 2.44 (s, 3 H), 3.47 (dd, *J* = 18.3, 11.3 Hz, 1 H), 3.59 (dd, *J* = 18.3, 5.8 Hz, 1 H), 4.88 (ddd, *J* = 11.3, 5.8, 2.6 Hz, 1 H), 6.40 (d, *J* = 2.6 Hz, 1 H), 7.34 (d, *J* = 8.3 Hz, 2 H), 7.41 (d, *J* = 8.6 Hz, 2 H), 7.66 (d, *J* = 8.6 Hz, 2 H), 7.99 (d, *J* = 8.3 Hz, 2 H), 8.74 (br s, 1 H).

^{13}C NMR ($CDCl_3$, 100.8 MHz): δ = 21.76 (CH_3), 35.05 (CH_2), 63.43 (CH), 71.03 ($CHCl_2$), 128.12 (C), 128.22 (CH), 128.42 (CH), 129.30 (CH), 129.68 (CH), 135.96 (C), 137.50 (C), 145.07 (C), 148.35 (C=O), 154.00 (C=N).

MS: *m*/*z* (%) = 459 (0.2) $[M]^+$, 461 (0.2) $[M^+{+}2]$, 268 (10), 197 (20), 179 (100), 155 (35), 91 (77), 64 (20).

Anal. Calcd for $C_{18}H_{16}Cl_3N_3O_3S$: C, 46.92; H, 3.50; N, 9.12; S, 6.96. Found: C, 46.90; H, 3.49; N, 9.08; S, 7.00.

3-(4-Bromophenyl)-5-dichloromethyl-1-tosylaminocarbonyl-2-pyrazoline (7c)

Yield: 1.16 g (92%); white needles; mp 231 °C (dec) (MeCN).

IR (Nujol): 3331, 1706, 1593, 1404, 1347, 1166, 1072, 1009, 821, 784, 666 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 2.44 (s, 3 H), 3.47 (dd, *J* = 18.3, 11.1 Hz, 1 H), 3.59 (dd, *J* = 18.3, 6.0 Hz, 1 H), 4.88 (ddd, *J* = 11.1, 6.0, 2.4 Hz, 1 H), 6.40 (d, *J* = 2.4 Hz, 1 H), 7.58 (m, 4 H), 7.34 (d, *J* = 8.5 Hz, 2 H), 7.99 (d, *J* = 8.5 Hz, 2 H), 8.75 (br s, 1 H).

^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 21.76 (CH_3), 35.00 (CH_2), 63.46 (CH), 71.03 ($CHCl_2$), 125.90 (C), 128.38 (CH), 128.42 (CH), 128.57 (C), 129.69 (CH), 132.26 (CH), 135.98 (C), 145.08 (C), 148.35 (C=O), 154.09 (C=N).

MS: *m*/*z* (%) = 503 (0.15) $[M]^+$, 505 (0.18) $[M^+{+}2]$, 306 (7), 308 (11), 223 (85), 225 (77), 197 (34), 155 (61), 144 (82), 91 (100), 65 (32).

Anal. Calcd for $C_{18}H_{16}BrCl_2N_3O_3S$: C, 42.79; H, 3.19; N, 8.32; S, 6.35. Found: C, 42.81; H, 3.26; N, 8.30; S, 6.30.

5-Dichloromethyl-3-(4-methylphenyl)-1-tosylaminocarbonyl-2-pyrazoline (7d)

Yield: 1.06 g (96%); white prisms; mp 203 °C (dec) (MeCN).

IR (Nujol): 3293, 1696, 1350, 1168, 1072, 852, 782, 734, 668 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 2.40 (s, 3 H), 2.44 (s, 3 H), 3.48 (dd, *J* = 18.3, 11.2 Hz, 1 H), 3.59 (dd, *J* = 18.3, 5.6 Hz, 1 H), 4.85 (ddd, *J* = 11.2, 5.6, 2.3 Hz, 1 H), 6.41 (d, *J* = 2.3 Hz, 1 H), 7.25 (d, *J* = 7.8 Hz, 2 H), 7.34 (d, *J* = 8.1 Hz, 2 H), 7.61 (d, *J* = 7.8 Hz, 2 H), 7.99 (d, *J* = 8.1 Hz, 2 H), 8.71 (br s, 1 H).

^{13}C NMR ($CDCl_3$, 100.8 MHz): δ = 21.62 (CH_3), 21.75 (CH_3), 35.18 (CH_2), 63.16 (CH), 71.14 ($CHCl_2$), 126.85 (C), 126.94 (CH), 128.40 (CH), 129.65 (CH), 129.70 (CH), 136.07 (C), 141.96 (CH), 144.95 (C), 148.40 (C=O), 155.17 (C=N).

MS: *m*/*z* (%) = 439 (1) $[M]^+$, 441 (0.8) $[M^+{+}2]$, 242 (34), 244 (21), 197 (45), 159 (100), 155 (63), 132 (38), 115 (30), 91 (95), 89 (31), 65 (53).

Anal. Calcd for $C_{19}H_{19}Cl_2N_3O_3S$: C, 51.82; H, 4.35; N, 9.54; S, 7.28. Found: C, 52.02; H, 4.42; N, 9.52; S, 7.33.

5-Dichloromethyl-3-(4-methoxyphenyl)-1-tosylaminocarbonyl-2-pyrazoline (7e)

Yield: 1.10 g (97%); white needles; mp 217 °C (dec) (MeCN).

IR (Nujol): 3314, 1695, 1609, 1346, 1257, 1180, 1069, 832, 788, 733, 665 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 2.43 (s, 3 H), 3.44 (dd, *J* = 18.2, 11.3 Hz, 1 H), 3.58 (dd, *J* = 18.2, 5.7 Hz, 1 H), 3.86 (s, 3 H), 4.84 (ddd, *J* = 11.3, 5.7, 2.6 Hz, 1 H), 6.40 (d, *J* = 2.6 Hz, 1 H), 6.94 (d, *J* =8.9 Hz, 2 H), 7.32 (d, *J* = 8.4 Hz, 2 H), 7.65 (d, *J* = 8.9 Hz, 2 H), 7.98 (d, *J* = 8.4 Hz, 2 H), 8.62 (br s, 1 H).

^{13}C NMR ($CDCl_3$, 100.8 MHz): δ = 21.67 (CH_3), 35.55 (CH_2), 55.80 (CH_3), 63.35 (CH), 71.29 ($CHCl_2$), 114.59 (CH), 122.44 (C), 128.49 (CH), 128.73 (CH), 129.64 (CH), 136.55 (C), 144.84 (C), 148.53 (C=O), 154.81 (C=N), 162.37 (C).

MS: *m*/*z* (%) = 455 (0.3) [M]$^+$, 457 (0.2) [M$^+$+2], 258 (11), 260 (7), 197 (18), 175 (100), 155 (30), 160 (27), 91 (45), 65 (15).

Anal. Calcd for $C_{19}H_{19}Cl_2N_3O_4S$: C, 50.01; H, 4.20; N, 9.21; S, 7.03. Found: C, 50.04; H, 4.16; N, 9.18; S, 7.07.

5-Dichloromethyl-3-(4-nitrophenyl)-1-tosylaminocarbonyl-2-pyrazoline (7f)

Yield: 1.10 g (93%); yellow needles; mp 248 °C (dec) (MeCN).

IR (Nujol): 3329, 1709, 1596, 1586, 1517, 1350, 1167, 1087, 1069, 848, 665 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.39 (s, 3 H), 3.50 (dd, *J* = 18.5, 5.5 Hz, 1 H), 3.67 (dd, *J* = 18.5, 11.5 Hz, 1 H), 5.06 (ddd, *J* = 11.5, 5.5, 2.8 Hz, 1 H), 6.56 (d, *J* = 2.8 Hz, 1 H), 7.42 (d, *J* = 7.9 Hz, 2 H), 7.86 (d, *J* = 7.9 Hz, 2 H), 8.23 (d, *J* = 8.6 Hz, 2 H), 8.30 (d, *J* = 8.6 Hz, 2 H), 11.61 (br s, 1 H).

^{13}C NMR (DMSO-d_6, 100.8 MHz): δ = 21.02 (CH_2), 35.14 (CH_2), 63.98 (CH), 72.30 ($CHCl_2$), 123.72 (CH), 127.58 (CH), 128.36 (CH), 129.44 (CH), 136.24 (C), 136.86 (C), 144.02 (C), 148.25 (C), 148.96 (C=O), 152.66 (C=N).

MS: *m*/*z* (%) = 470 (0.12) [M]$^+$, 398 (6), 334 (25), 273 (4), 197 (22), 190 (61), 155 (61), 144 (34), 91 (100), 65 (32).

Anal. Calcd for $C_{18}H_{16}Cl_2N_4O_5S$: C, 45.87; H, 3.42; N, 11.89; S, 6.80. Found: C, 45.78; H, 3.40; N, 11.97; S, 6.81.

5-Dichloromethyl-3-(4-biphenylyl)-1-tosylaminocarbonyl-2-pyrazoline (7g)

Yield: 1.23 g (98%); yellow powder; mp 238 °C (dec) (MeCN/DMF).

IR (Nujol): 3275, 1692, 1594, 1344, 1162, 1076, 896, 841, 788, 732, 702, 663 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.39 (s, 3 H), 3.46 (dd, *J* = 18.4, 5.4 Hz, 1 H), 3.65 (dd, *J* = 18.4, 11.3 Hz, 1 H), 5.00 (ddd, *J* = 11.3, 5.4, 2.4 Hz, 1 H), 6.55 (d, *J* = 2.4 Hz, 1 H), 7.34–7.51 (m, 5 H), 7.68–7.79 (m, 4 H), 7.87 (d, *J* = 8.2 Hz, 2 H), 8.04 (d, *J* = 8.3 Hz, 2 H), 11.42 (1 H, br s).

^{13}C NMR (DMSO-d_6, 100.8 MHz): δ = 21.04 (CH_3), 34.38 (CH_2), 63.43 (CH), 72.46 ($CHCl_2$), 125.58 (C), 126.76 (CH), 127.60 (CH), 127.88 (CH), 128.01 (CH), 129.00 (CH), 129.20 (CH), 129.42 (CH), 137.02 (C), 139.15 (C), 142.09 (C), 143.93 (C), 148.93 (C=O), 154.10 (C=N).

MS: *m*/*z* (%) = 501 (1) [M]$^+$, 503 (0.8) [M$^+$+2], 429 (9), 304 (24), 306 (16), 221 (100), 197 (12), 155 (19), 91 (36).

Anal. Calcd for $C_{24}H_{21}Cl_2N_3O_3S$: C, 57.37; H, 4.21; N, 8.36; S, 6.38. Found: C, 57.45; H, 4.22; N, 8.41; S, 6.34.

5-Dichloromethyl-3-(2-naphthyl)-1-tosylaminocarbonyl-2-pyrazoline (7h)

Yield: 0.99 g (83%); white powder; mp 129–131 °C (dec) (Et_2O).

IR (ATR): 3243, 1695, 1597, 1440, 1376, 1067, 756, 780, 659 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.49 (s, 3 H), 3.62 (dd, *J* = 11.4, 18.4 Hz, 1 H), 3.76 (dd, *J* = 5.7, 18.4 Hz, 1 H), 4.93 (ddd, *J* = 2.6, 5.7, 11.4 Hz, 1 H), 6.45 (d, *J* = 2.6 Hz, 1 H), 7.35 (d, *J* = 8.3 Hz, 2 H), 7.56 (m, 2 H), 7.91 (m, 4 H), 8.03 (d, *J* = 8.1 Hz, 3 H), 8.75 (s, 1 H).

^{13}C NMR ($CDCl_3$, 100.8 MHz): δ = 22.56 (CH_3), 35.95 (CH_2), 64.18 (CH), 71.96 (CH), 123.87 (CH), 127.96 (CH), 128.75 (CH), 129.26 (CH), 129.45 (CH), 129.71 (CH), 130.47 (CH), 133.72 (C), 135.40 (C), 136.86 (C), 145.83 (C), 155.92 (C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{20}Cl_2N_3O_3S$: 476.0597; found: 476.0595.

5-Dichloromethyl-3-(3,4-dichlorophenyl)-1-tosylaminocarbonyl-2-pyrazoline (7i)

Yield: 0.87 g (70%); white powder; mp 205–207 °C (dec) (Et_2O).

IR (ATR): 3382, 1741, 1672, 1527, 1446, 1311, 855, 824, 749, 733, 688 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.39 (s, 3 H), 3.46 (dd, *J* = 10.7, 18.2 Hz, 1 H), 3.57 (dd, *J* = 5.5, 18.2 Hz, 1 H), 4.90 (m, 1 H), 6.39 (d, *J* = 1.8 Hz, 1 H), 7.35 (d, *J* = 7.9 Hz, 2 H), 7.54 (q, *J* = 7.8 Hz, 2 H), 7.80 (s, 1 H), 7.89 (d, *J* = 8.1 Hz, 2 H), 8.69 (s, 1 H).

^{13}C NMR (DMSO-d_6, 100.8 MHz): δ = 22.41 (CH_3), 35.74 (CH_2), 64.86 (CH), 73.88 (CH), 126.75 (CH), 129.25 (CH), 129.45 (CH), 130.38 (C), 130.50 (CH), 131.87 (CH), 134.40 (C), 136.40 (C), 136.67 (C), 145.96 (C), 149.05 (C), 153.71 (C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{16}Cl_4N_3O_3S$: 493.9661; found: 493.9679.

3-(3-Bromophenyl)-5-dichloromethyl-1-tosylaminocarbonyl-2-pyrazoline (7j)

Yield: 1.01 g (80%); white powder; mp 209–210 °C (dec) (Et_2O).

IR (ATR): 3240, 1716, 1696, 1442, 1420, 1170, 1072, 767, 664 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.43 (s, 3 H), 3.46 (dd, *J* =11.5, 18.4 Hz, 1 H), 3.57 (dd, *J* = 5.8, 11.5 Hz, 1 H), 4.89 (ddd, *J* = 2.6, 5.8, 11.5 Hz, 1 H), 6.40 (d, *J* = 2.6 Hz, 1 H), 7.3 (m, 3 H), 7.57 (dd, *J* = 7.7, 0.9 Hz, 1 H), 7.63 (d, *J* = 7.7 Hz, 1 H), 7.86 (t, *J* = 1.7 Hz, 1 H), 7.98 (d, *J* = 8.3 Hz, 2 H), 8.80 (s, 1 H).

^{13}C NMR ($CDCl_3$, 100.8 MHz): δ = 22.60 (CH_3), 35.78 (CH_2), 64.25 (CH), 71.84 (CH), 123.95, 126.39 (CH), 129.24 (CH), 130.50 (CH), 131.32 (CH), 132.43 (C), 134.96 (CH), 136.70 (C), 145.90 (C), 149.75 (C), 154.49 (C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{17}BrCl_2N_3O_3S$: 503.9546; found: 503.9537.

Synthesis of 10; General Procedures

Method (a): A suspension of **7** (0.5 mmol) in triethylamine (10 mL) was heated to reflux for 4 h. Then, the solvent was removed in vacuo and the residue was washed with cold water (25 mL), leaving a solid that was collected by filtration, dried and crystallized from the appropriate solvent.

Method (b): Compound **7** (0.5 mmol) and triethylamine (10 mL) were placed in a sealed pressurized reaction vessel and heated at 130 °C for 2 h. After cooling, the solvent was removed in vacuo and the residue was washed with cold water (25 mL), leaving a solid that was collected by filtration, dried and crystallized from the appropriate solvent.

One-Pot Procedure; Method (c): Pyrazoline **5** (0.6 mmol), toluenesulfonyl isocyanate (0.72 mmol) and triethylamine (10 mL) were placed in a sealed pressurized reaction vessel and heated at 130 °C for 2 h. After cooling, the solvent was removed in vacuo and the residue was washed with cold water (25 mL), leaving a solid that was collected by filtration, dried and crystallized from the appropriate solvent.

2-Phenyl-5-tosyl-4,5-dihydroimidazo[1,5-*b*]pyrazol-6-one (10a)

Yield: 88 mg (50%) (method A); 134 mg (63%) (method C); white needles; mp 237 °C (dec) (MeOH).

IR (Nujol): 3285, 1698, 1599, 1379, 1346, 1163, 1078, 895, 866, 848, 785, 673 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 2.44 (s, 3 H), 4.92 (s, 2 H), 6.58 (s, 1 H), 7.36–7.42 (m, 5 H), 7.85 (d, *J* = 6.7 Hz, 2 H), 8.01 (d, *J* = 7.9 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 100.8 MHz): δ = 21.80 (CH_3), 44.53 (CH_2), 99.69 (CH), 126.64 (CH), 128.30 (CH), 128.90 (CH), 129.73 (CH), 130.21 (CH), 131.45 (C), 134.46 (C), 140.90 (C), 144.99 (C=O), 146.23 (C), 160.96 (C=N).

MS: *m*/*z* (%) = 353 (33) $[M]^+$, 289 (37) $[M^+ - SO_2]$, 260 (14), 245 (10), 199 (9), 155 (19), 128 (100), 115 (29), 91 (98), 65 (34).

Anal. Calcd for $C_{18}H_{15}N_3O_3S$: C, 61.18; H, 4.28; N, 11.89; S, 9.07. Found: C, 61.28; H, 4.30; N, 11.95; S, 9.10.

2-(4-Chlorophenyl)-5-tosyl-4,5-dihydroimidazo[1,5-*b*]pyrazol-6-one (10b)

Yield: 122 mg (63%) (method b); 174 mg (63%) (method c); white needles; mp 263 °C (dec) ($MeOH/CHCl_3$).

IR (Nujol): 1790, 1598, 1584, 1565, 1434, 1318, 1169, 1110, 818, 731 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 2.45 (s, 3 H), 4.93 (s, 2 H), 6.56 (s, 1 H), 7.39 (br s, 4 H), 7.79 (d, *J* = 7.1 Hz, 2 H), 8.02 (d, *J* = 7.3 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 100.8 MHz): δ = 21.83 (CH_3), 44.51 (CH_2), 99.58 (CH), 127.89 (CH), 128.33 (CH), 129.18 (CH), 129.94 (C), 130.24 (CH), 134.28 (C), 135.75 (C), 141.06 (C), 144.90 (C=O), 146.33 (C), 159.82 (C=N).

MS: *m*/*z* (%) = 387 (36) $[M]^+$, 389 (14) $[M^+ + 2]$, 323 (30) $[M^+ - SO_2]$, 232 (4), 162 (49), 155 (22), 91 (100), 65 (29).

Anal. Calcd for $C_{18}H_{14}ClN_3O_3S$: C, 55.74; H, 3.64; N, 10.83; S, 8.27. Found: C, 55.68; H, 3.66; N, 10.78; S, 8.30.

2-(4-Bromophenyl)-5-tosyl-4,5-dihydroimidazo[1,5-*b*]pyrazol-6-one (10c)

Yield: 82 mg (38%) (method b); 147 mg (57%) (method c); white powder; mp 260 °C (dec) ($MeOH/Me_2CO$).

IR (Nujol): 1782, 1599, 1320, 1173, 1105, 954, 813, 799, 733, 684 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 2.44 (s, 3 H), 4.91 (d, *J* =1.0 Hz, 2 H), 6.53 (t, *J* = 1.0 Hz, 1 H), 7.36 (d, *J* = 8.2 Hz, 2 H), 7.54 (d, *J* = 8.5 Hz, 2 H), 7.71 (d, *J* = 8.5 Hz, 2 H), 8.01 (d, *J* = 8.2 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 100.8 MHz): δ = 21.75 (CH_3), 44.48 (CH_2), 99.47 (CH), 124.08 (C), 128.22 (CH), 128.46 (CH), 130.24 (CH), 130.67 (C), 132.21 (CH), 134.73 (C), 141.23 (C), 144.88 (C=O), 146.26 (C), 159.98 (C=N).

MS: *m*/*z* (%) = 431 (24) $[M]^+$, 433 (23) $[M^+ + 2]$, 367 (18) $[M^+ - SO_2]$, 277 (2), 206 (25), 169 (19), 155 (25), 127 (26), 91 (100), 65 (30).

Anal. Calcd for $C_{18}H_{14}BrN_3O_3S$: C, 50.01; H, 3.26; N, 9.72; S, 7.42. Found: C, 50.10; H, 3.30; N, 9.69; S, 7.35.

2-(*p*-Tolyl)-5-tosyl-4,5-dihydroimidazo[1,5-*b*]pyrazol-6-one (10d)

Yield: 121 mg (65%) (method a); 154 mg (70%) (method c); white needles; mp 241 °C (dec) (Me_2SO).

IR (Nujol): 1776, 1589, 1330, 1163, 1107, 951, 821, 800, 734, 686, 665 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 2.37 (s, 3 H), 2.43 (s, 3 H), 4.88 (d, *J* = 1.0 Hz, 2 H), 6.53 (t, *J* = 1.0 Hz, 1 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 7.35 (d, *J* = 8.2 Hz, 2 H), 7.73 (d, *J* = 8.0 Hz, 2 H), 7.99 (d, *J* = 8.2 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 100.8 MHz): δ = 21.42 (CH_3), 21.77 (CH_3), 44.51 (CH_2), 99.53 (CH), 126.53 (CH), 128.26 (CH), 128.64 (CH), 129.59 (C), 130.17 (CH), 134.40 (C), 139.87 (C), 140.84 (C), 145.01 (C=O), 146.15 (C), 161.03 (C=N).

MS: *m*/*z* (%) = 367 (51) $[M]^+$, 303 (47) $[M^+ - SO_2]$, 213 (27), 170 (28), 155 (35), 141 (100), 128 (37), 115 (50), 91 (70), 65 (42).

Anal. Calcd for $C_{19}H_{17}N_3O_3S$: C, 62.11; H, 4.66; N, 11.44; S, 8.73. Found: C, 62.20; H, 4.69; N, 11.40; S, 8.64.

2-(4-Methoxyphenyl)-5-tosyl-4,5-dihydroimidazo[1,5-*b*]pyrazol-6-one (10e)

Yield: 88 mg (46%) (method b); 176 mg (77%) (method c); white needles; mp 185 °C (dec) (MeOH).

IR (Nujol): 1787, 1756, 1616, 1570, 1529, 1332, 1316, 1284, 1251, 1162, 1104, 1034, 817, 731, 668 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 2.42 (s, 3 H), 3.83 (s, 3 H), 4.88 (d, *J* = 1.2 Hz, 2 H), 6.50 (t, *J* = 1.2 HZ, 1 H), 6.92 (d, *J* = 8.8 Hz, 2 H), 7.35 (d, *J* = 8.3 HZ, 2 H), 7.77 (d, *J* = 8.8 Hz, 2 H), 7.99 (d, *J* = 8.3 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 21.77 (CH_3), 44.50 (CH_2), 55.39 (CH_3), 99.30 (CH), 114.25 (CH), 123.98 (C), 128.00 (CH), 128.21 (CH), 130.15 (CH), 134.05 (C), 140.87 (C), 145.02 (C=O), 146.14 (C), 160.75 (C=N).

MS: *m*/*z* (%) = 383 (39) $[M]^+$, 319 (7) $[M^+ - SO_2]$, 228 (12), 172 (27), 158 (100), 143 (28), 115 (39), 91 (65), 65 (22).

Anal. Calcd for $C_{19}H_{17}N_3O_4S$: C, 59.52; H, 4.47; N, 10.96; S, 8.36. Found: C, 59.44; H, 4.35; N, 10.91; S, 8.43.

2-(4-Nitrophenyl)-5-tosyl-4,5-dihydroimidazo[1,5-*b*]pyrazol-6-one (10f)

Yield: 108 mg (55%) (method b); 211 mg (88%) (method c); white powder; mp 288 °C (dec) (Me_2SO).

IR (Nujol): 3121, 1784, 1576, 1517, 1340, 1310, 1164, 1105, 954, 731, 704, 685, 666 cm^{-1}.

^1H NMR (DMSO-d_6, 400 MHz): δ = 2.43 (s, 3 H), 5.15 (s, 2 H), 7.04 (s, 1 H), 7.49 (d, *J* = 8.2 Hz, 2 H), 7.98 (d, *J* = 8.2 Hz, 2 H), 8.14 (d, *J* = 8.4 Hz, 2 H), 8.28 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (DMSO-d_6, 100.8 MHz): δ = 20.46 (CH_3), 44.60 (CH_2), 99.97 (CH), 123.44 (CH), 126.85 (CH), 127.39 (CH), 129.43 (CH), 134.00 (C), 137.23 (C), 142.92 (C), 144.24 (C), 145.20 (C=O), 147.60 (C), 157.13 (C=N).

MS: *m*/*z* (%) = 398 (5) $[M]^+$, 334 (23) $[M^+ - SO_2]$, 243 (3), 173 (7), 155 (26), 114 (9), 91 (100), 65 (30).

Anal. Calcd for $C_{18}H_{14}N_4O_5S$: C, 54.27; H, 3.54; N, 14.06; S, 8.05. Found: C, 54.18; H, 3.51; N, 14.16; S, 8.08.

2-(4-Biphenylyl)-5-tosyl-4,5-dihydroimidazo[1,5-*b*]pyrazol-6-one (10g)

Yield: 129 mg (60%) (method b); 176 mg (68%) (method c); white powder; mp 276 °C (dec) ($MeOH/Me_2CO$).

IR (Nujol): 1788, 1774, 1594, 1326, 1175, 1106, 950, 801, 769, 727, 669 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 2.45 (s, 3 H), 4.94 (s, 2 H), 6.62 (s, 1 H), 7.35–7.39 (m, 3 H), 7.45 (t, *J* = 7.5 Hz, 2 H), 7.61 (d, *J* = 7.5 Hz, 2 H), 7.65 (d, *J* = 8.2 Hz, 2 H), 7.93 (d, *J* = 8.2 Hz, 2 H), 8.03 (d, *J* = 8.3 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 100.8 MHz): δ = 21.75 (CH_3), 44.51 (CH_2), 99.63 (CH), 127.16 (CH), 127.17 (CH), 127.63 (CH), 127.82 (C), 128.45 (CH), 128.97 (CH), 130.22 (CH), 130.58 (C), 134.78 (C), 140.55 (C), 141.04 (C), 142.67 (C), 144.97 (C=O), 146.19 (C), 160.79 (C=N).

MS: *m*/*z* (%) = 429 (71) [M]$^+$, 365 (18) [M$^+$ – SO_2], 275 (26), 218 (25), 204 (97), 189 (22), 155 (15), 91 (100), 65 (30).

Anal. Calcd for $C_{24}H_{19}N_3O_3S$: C, 67.12; H, 4.46; N, 9.78; S, 7.47. Found: C, 67.03; H, 4.44; N, 9.85; S, 7.50.

2-(Naphthalen-2-yl)-5-tosyl-4,5-dihydroimidazo[1,5-*b*]pyrazol-6-one (10h)

Yield: 157 mg (78%) (method a); 198 mg (82%) (method c); white powder; mp 250–251 °C (dec) (Et_2O).

IR (ATR): 1722, 1586, 1432, 1374, 1343, 1170, 1105, 780, 686, 661 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.40 (s, 3 H), 5.21 (s, 2 H), 7.11 (s, 1 H,), 7.49 (d, *J* = 8.4 Hz, 2 H), 7.54 (d, *J* = 8.4 Hz, 2 H), 7.98 (m, 5 H), 8.49 (s, 1 H).

^{13}C NMR (DMSO-d_6, 100.8 MHz): δ = 20.66 (CH_3), 44.77 (CH_2), 99.53 (CH), 125.32 (CH), 126.21 (CH), 126.38 (CH), 127.22 (CH), 127.53 (CH), 127.90 (CH), 128.10 (CH), 128.62 (CH), 129.59 (C), 132.63 (CH), 133.00 (C), 134.12 (C), 142.68 (C), 144.57 (C), 145.29 (C), 159.47 (C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{18}N_3O_3S$: 404.1063; found: 404.1051.

2-(3,4-Dichlorophenyl)-5-tosyl-4,5-dihydroimidazo[1,5-*b*]pyrazol-6-one (10i)

Yield: 169 mg (80%) (method b); 215 mg (85%) (method c); white powder; mp 252–253 °C (dec) (Et_2O).

IR (ATR): 1787, 1595, 1427, 1371, 1346, 1299, 1164, 1105, 1027, 814, 664 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.40 (s, 3 H), 5.17 (s, 2 H), 7.08 (s, 1 H), 7.48 (d, *J* = 4.4 Hz, 2 H), 7.71 (d, *J* = 6.6 Hz, 1 H), 7.88 (d, *J* = 6.6 Hz, 1 H), 7.97 (d, *J* = 4.4 Hz, 2 H), 8.13 (s, 1 H).

^{13}C NMR (DMSO-d_6, 100.8 MHz): δ = 22.48 (CH_3), 46.65 (CH_2), 101.34 (CH), 127.55 (CH), 129.18 (C), 124.41 (CH), 131.35 (CH), 132.59 (CH), 133.22 (CH), 133.34 (C), 135.43 (C), 144.81 (C), 146.22 (C), 147.15 (C), 158.56 (C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{14}Cl_2N_3O_3S$: 422.0127; found: 422.0146.

2-(3-Bromophenyl)-5-tosyl-4,5-dihydroimidazo[1,5-*b*]pyrazol-6-one (10j)

Yield: 143 mg (65%) (method a); 212 mg (82%) (method c); white powder; mp 202–203 °C (dec) (Et_2O).

IR (ATR): 1798, 1590, 1364, 1309, 1160, 1170, 782, 727, 686, 661 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.41 (s, 3 H), 5.18 (s, 2 H), 7.07 (s, 1 H), 7 (d, *J* = 8.2 Hz, 2 H), 7.63 (dd, *J* = 7.0, 14.1 Hz, 2 H), 7.90 (d, *J* = 7.0 Hz, 1 H), 7.97 (d, *J* = 8.1 Hz, 2 H), 8.07 (s, 1 H).

^{13}C NMR (DMSO-d_6, 100.8 MHz): δ = 22.49 (CH_3), 46.89 (CH_2), 101.24 (CH), 123.66 (C), 126.52 (CH), 129.41 (CH), 129.93 (CH), 131.35 (CH), 132.53 (CH), 133.54 (CH), 135.09 (C), 135.45 (C), 144.69 (C), 146.30 (C), 147.13 (C), 159.55 (C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{15}BrN_3O_3S$: 432.0012; found: 431.9999.

Synthesis of 11; General Procedure

To a solution of compound **5** (3 mmol) in anhydrous tetrahydrofuran (15 mL), the corresponding isocyanate (3.6 mmol) was added dropwise. The reaction mixture was stirred for 4 h at r.t. under a nitrogen atmosphere. Then, the solvent was evaporated under reduced pressure, obtaining a solid residue that was crystallized from the appropriate solvent. Product **11b** was prepared in EtOH instead of THF.

***N*-Benzyl-5-dichloromethyl-4,5-dihydro-3-*p*-tolylpyrazole-1-carboxamide (11a)**

Yield: 0.56 g (50%); off-white powder; mp 121–122 °C (dec) (EtOAc/pet ether).

IR (KBr): 3290, 3207, 6064, 2974, 1946, 1890, 1659, 1571, 1554, 1454, 1366, 1299, 1217, 111, 1080, 1028, 874, 818, 780, 745, 695 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.40 (s, 3 H), 3.47 (dd, *J* = 11.4, 18.2 Hz, 1 H), 3.59 (dd, *J* = 6.0, 18.2 Hz, 1 H), 4.39 (t, *J* = 6.0 Hz, 2 H), 4.99 (ddd, *J* = 2.4, 6, 11.4 Hz, 1 H), 6.43 (t, *J* = 6 Hz, 1 H), 6.63 (d, *J* = 2.4 Hz, 1 H), 7.23 (d, *J* = 8 Hz, 2 H), 7.30 (m, 1 H), 7.37 (m, 4 H), 7.60 (d, *J* = 8 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 100.8 MHz): δ = 22.39 (CH_3), 35.52 (CH_2), 44.84 (CH_2), 64.55 (CH), 73.46 (CH), 127.33 (CH), 128.26 (CH), 128.46 (CH), 128.79 (C), 129.55 (CH), 130.33 (CH), 139.85 (C), 141.60 (C), 153.09 (C), 155.47 (C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{20}Cl_2N_3O$: 376.0978; found: 376.0972.

***N*-Cyclohexyl-5-dichloromethyl-4,5-dihydro-3-*p*-tolylpyrazole-1-carboxamide (11b)**

Yield: 0.48 g (43%); white powder; mp 158–160 °C (dec) (EtOAc/pet ether).

IR (KBr): 3316, 2931, 2849, 1815, 650, 1595, 1528, 1514, 1449, 1415, 1392, 1326, 1253, 1160, 1134, 1079, 938, 871, 818, 752, 704, 646 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.20 (m, 3 H), 1.37 (m, 2 H), 1.63 (d, *J* = 12 Hz, 1 H), 1.74 (m, 2 H), 1.99 (t, *J* = 11.6 Hz, 2 H), 2.40 (s, 3 H), 3.45 (dd, *J* = 11.6, 18 Hz, 1 H), 3.65 (dd, *J* = 6, 18 Hz, 1 H), 3.68 (m, 1 H), 4.94 (m, 1 H), 5.91 (d, *J* = 8 Hz, 1 H), 6.55 (d, *J* = 2 Hz, 1 H), 7.23 (d, *J* = 8 Hz, 2 H), 7.60 (d, *J* = 8 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 100.8 MHz): δ = 22.45 (CH_3), 25.93 (CH_2), 26.47 (CH_2), 34.52 (CH_2), 34.73 (CH_2), 35.48 (CH_2), 49.87 (CH), 64.50 (CH), 73.62 (CH), 127.28 (CH), 128.92 (C), 130.30 (CH), 141.46 (C), 152.64 (C), 154.81 (C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{24}Cl_2N_3O$: 368.1291; found: 368.1297.

5-Dichloromethyl-*N*-(2-ethylhexyl)-4,5-dihydro-3-*p*-tolylpyrazole-1-carboxamide (11c)

Yield: 0.61 g (51%); pale-yellow oil (silica gel column chromatography; pet ether/EtOAc).

IR (KBr): 3604, 3437, 2730, 2019, 1725, 1681, 1528, 1513, 1466, 1376, 1319, 1296, 1251, 1166, 1136, 873, 813, 729, 720, 634 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.90 (m, 6 H), 1.32 (m, 9 H), 2.39 (s, 3 H), 3.25 (m, 2 H), 3.44 (dd, *J* = 11.6, 18.2 Hz, 1 H), 3.55 (dd, *J* = 6.2, 18.2 Hz, 1 H), 4.94 (ddd, *J* = 2.6, 6.2, 11.6 Hz, 1 H), 6.03 (d, *J* = 5.6, 1 H), 6.58 (d, *J* = 2.6 Hz, 1 H), 7.22 (d, *J* = 8 Hz, 2 H), 7.59 (d, *J* = 8 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 100.8 MHz): δ = 11.72 (CH_3), 15.04 (CH_3), 22.69 (CH_3), 23.83 (CH_2), 24.98 (CH_2), 29.82 (CH_2), 31.61 (CH_2), 35.68 (CH_2), 40.78 (CH), 44.10 (CH2), 64.54 (CH), 73.56 (CH), 127.23 (CH), 128.97 (C), 130.29 (CH), 1141.42 (C), 152.58 (C), 155.64 (C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{30}Cl_2N_3O$: 398.1760; found: 398.1775.

5-Dichloromethyl-*N*-phenyl-4,5-dihydro-3-*p*-tolylpyrazole-1-carboxamide (11d)

Yield: 0.80 g (74%); off-white powder; mp 149–150 °C (dec) (EtOAc/pet ether).

IR (KBr): 3317, 2989, 1938, 1891, 1665, 1594, 1533, 1501, 1448, 1391, 1329, 1313, 1234, 1144, 1112, 1029, 931, 868, 819, 760, 748, 701, 692, 643 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.42 (s, 3 H), 3.57 (dd, *J* = 11.4, 18 Hz, 1 H), 3.65 (dd, *J* = 6.1, 18 Hz, 1 H), 5.04 (ddd, *J* = 2.5, 6.1, 11.4 Hz, 1 H), 6.62 (d, *J* = 2.5 Hz, 1 H), 7.09 (t, *J* = 7.6 Hz, 1 H), 7.27 (t, *J* = 7.6 Hz, 2 H), 7.34 (t, *J* = 7.6 Hz, 2 H), 7.53 (d, *J* = 8.6 Hz, 2 H), 7.67 (d, *J* = 8.6 Hz, 2 H), 8.20 (s, 1 H).

^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 22.54 (CH_3), 35.89 (CH_2), 64.44 (CH), 73.26 (CH), 120.30 (CH), 124.41 (CH), 127.58 (CH), 128.66 (C), 130.02 (CH), 130.54 (CH), 139.01 (C), 142.08 (C), 152.68 (C), 153.78 (C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{18}Cl_2N_3O$: 362.0821; found: 362.0826.

5-Dichloromethyl-N-*p*-tolyl-4,5-dihydro-3-*p*-tolylpyrazole-1-carboxamide (11e)

Yield: 0.79 g (70%); off-white powder; mp 155–156 °C (dec) (EtOAc/pet ether).

IR (KBr): 3387, 2919, 1913, 1667, 1592, 1532, 1416, 1387, 1315, 1233, 1166, 1104, 1028, 933, 868, 812, 758, 748, 734, 698, 646 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.33 (s, 3 H), 2.42 (s, 3 H), 3.52 (dd, *J* = 11.4, 18.4 Hz, 1 H), 3.63 (dd, *J* = 6, 18.4 Hz, 1 H), 5.03 (ddd, *J* = 2.2, 6, 11.2 Hz, 1 H), 6.61 (d, *J* = 2.2 Hz, 1 H), 7.14 (d, *J* = 8 Hz, 2 H), 7.26 (d, *J* = 8 Hz, 2 H), 7.40 (d, *J* = 8 Hz, 2 H), 7.66 (d, *J* = 8 Hz, 2 H), 7.95 (s, 1 H).

^{13}C NMR ($CDCl_3$, 100.8 MHz): δ = 21.69 (CH_3), 22.43 (CH_3), 35.75 (CH_2), 64.33 (CH), 73.20 (CH), 120.37 (CH), 127.45 (CH), 128.57 (C), 130.41 (CH), 133.89 (C), 136.24 (C), 141.92 (C), 152.71 (C), 153.56 (C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{20}Cl_2N_3O$: 376.0978; found: 376.0980.

5-Dichloromethyl-*N*-(4-chlorophenyl)-4,5-dihydro-3-*p*-tolylpyrazole-1-carboxamide (11f)

Yield: 0.83 g (70%); white needles; mp 174–175 °C (dec) (EtOAc/pet ether).

IR (KBr): 3396, 3066, 1907, 1669, 1590, 1525, 1494, 1416, 1310, 1230, 1166, 1136, 1090, 1010, 935, 846, 757, 729, 673 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.43 (s, 3 H), 3.54 (dd, *J* = 11.6, 18.4 Hz, 1 H), 3.65 (dd, *J* = 5.6, 18.4 Hz, 1 H), 5.04 (m, 1 H), 6.60 (br s, 1 H), 7.29 (m, 4 H), 7.48 (d, *J* = 8.4 Hz, 4 H), 7.66 (d, *J* = 7.6 Hz, 2 H), 8.02 (s, 1 H).

^{13}C NMR ($CDCl_3$, 100.8 MHz): δ = 22.45 (CH_3), 35.84 (CH_2), 64.27 (CH), 72.99 (CH), 121.33 (CH), 127.50 (CH), 128.38 (C), 129.18 (C), 129.88 (CH), 130.46 (CH), 137.52 (C), 142.13 (C), 152.36 (C), 153.99 (C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{17}Cl_3N_3O$: 396.0432; found: 396.0434.

5-Dichloromethyl-*N*-(4-fluorophenyl)-4,5-dihydro-3-*p*-tolylpyrazole-1-carboxamide (11g)

Yield: 0.82 g (72%); off-white needles; mp 165 °C (dec) (Me_2CHOH).

IR (KBr): 3384, 3295, 3029, 1882, 1667, 1636, 1610, 1593, 1510, 1418, 13866, 1525, 1313, 1210, 1096, 849, 832, 767, 734, 703, 607 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.42 (s, 3 H), 3.54 (dd, *J* = 11.4, 18.1 Hz, 1 H), 3.64 (dd, *J* = 6.3, 18.1 Hz, 1 H), 5.03 (m, 1 H), 6.59 (d, *J* = 1.8 Hz, 1 H), 7.03 (t, *J* = 8.4 Hz, 2 H), 7.27 (d, *J* = 6.6 Hz, 2 H), 7.47 (dd, *J* = 4.5, 8.7 Hz, 2 H), 7.66 (d, *J* = 7.8 Hz, 2 H), 7.96 (s, 1 H).

^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 22.54 (CH_3), 35.92 (CH_2), 64.42 (CH), 73.17 (CH), 116.62 (d, *J* = 22.4 Hz, CH), 122.13 (d, *J* = 7.8 Hz, CH), 127.57 (CH), 128.57 (C), 130.55 (CH), 134.92 (d, *J* = 2.3 Hz, C), 142.16 (C), 152.77 (C), 153.94 (C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{17}Cl_2FN_3O$: 380.0727; found: 380.0735.

***N*-(4-Bromophenyl)-5-(dichloromethyl)-4,5-dihydro-3-*p*-tolylpyrazole-1-carboxamide (11h)**

Yield: 0.94 g (71%); white needles; mp 189–191 °C (dec) (EtOAc/pet ether).

IR (KBr): 3398, 1894, 1673, 1587, 1526, 1513, 1488, 1406, 1324, 1312, 1231, 1071, 1008, 843, 814, 805, 756, 729, 655 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.42 (s, 3 H), 3.54 (dd, *J* = 11.2, 18.3 Hz, 1 H), 3.65 (dd, *J* = 6.3, 18.3 Hz, 1 H), 5.02 (ddd, *J* = 2.6, 6.3, 11.2 Hz, 1 H), 6.58 (d, *J* = 2.6 Hz, 1 H), 7.27 (d, *J* = 8.0 Hz, 2 H), 7.43 (m, 4 H), 7.66 (d, *J* = 8.0 Hz, 2 H), 8.00 (s, 1 H).

^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 22.55 (CH_3), 35.95 (CH_2), 64.36 (CH), 73.07 (CH), 116.82 (C), 121.75 (CH), 127.61 (CH), 128.48 (C), 130.56 (CH), 132.93 (CH), 138.15 (C), 142.25 (C), 152.41 (C), 154.12 (C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{17}BrCl_2N_3O$: 439.9927; found: 439.9942.

5-Dichloromethyl-4,5-dihydro-*N*-*p*-tolyl-3-phenylpyrazole-1-carboxamide (11i)

Yield: 0.69 g (63%); white needles; mp 196 °C (dec) (EtOAc/pet ether).

IR (KBr): 3307, 1659, 1593, 1539, 1442, 1403, 1250, 1172, 933, 783, 764, 738, 689 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.34 (s, 3 H), 3.52 (dd, *J* = 11.3, 18.4 Hz, 1 H), 3.64 (dd, *J* = 6.3, 18.4 Hz, 1 H), 5.03 (ddd, *J* = 2.4, 6.3, 11.3 Hz, 1 H), 6.12 (d, *J* = 2.4 Hz, 2 H), 6.89 (d, *J* = 7.4 Hz, 1 H), 7.20 (t, *J* = 7.8 Hz, 2 H), 7.28 (d, *J* = 8.1 Hz, 1 H), 7.37 (s, 1 H), 7.45 (m, 3 H), 7.76 (dd, *J* = 3.4, 6.8 Hz, 2 H), 7.95 (s, 1 H).

^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 22.52 (CH_3), 35.81 (CH_2), 64.57 (CH_2), 73.20 (CH), 117.38 (CH), 120.93 (CH), 125.29 (CH), 127.60 (CH), 129.82 (CH), 131.45 (C), 131.61 (CH), 138.85 (C), 139.94 (C), 152.66 (C), 153.61 (C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{18}Cl_2N_3O$: 362.0821; found: 362.0821.

5-Dichloromethyl-4,5-dihydro-3-(naphthalen-3-yl)-*N*-phenylpyrazole-1-carboxamide (11j)

Yield: 0.73 g (61%); off-white powder; mp 146–146 °C (dec) (EtOAc/pet ether).

IR (KBr): 3382, 1741, 1672, 1595, 1527, 1466, 1323, 825, 749, 688 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.65 (dd, *J* = 11.2, 18.1 Hz, 1 H), 3.78 (dd, *J* = 6.0, 18.1 Hz, 1 H), 5.09 (ddd, *J* = 2.4, 6.0, 11.2 Hz, 1 H), 7.08 (t, *J* = 7.4 Hz, 1 H), 7.34 (t, *J* = 8.1 Hz, 2 H), 7.54 (m, 4 H), 7.88 (m, 3 H), 8.02 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 35.80 (CH_2), 64.80 (CH), 73.31 (CH), 120.36 (CH), 124.01 (CH), 124.51 (CH), 127.94 (CH), 128.34 (CH), 128.49 (CH), 128.82 (CH), 128.97 (C), 129.48 (CH), 129.62 (CH), 130.04 (CH), 133.98 (C), 135.24 (C), 138.94 (C), 152.59 (C), 153.70 (C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{18}Cl_2N_3O$: 398.0821; found: 398.0834.

3-(3-Bromophenyl)-5-dichloromethyl-4,5-dihydro-*N*-phenylpyrazole-1-carboxamide (11k)

Yield: 0.77 g (61%); off-white powder; mp 138–140 °C (dec) (EtOAc/pet ether).

IR (KBr): 3308, 1597, 1663, 1530, 1446, 1315, 1233, 873, 764, 750, 688 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.59 (dd, *J* = 11.3, 18.1 Hz, 1 H), 3.64 (dd, *J* = 5.9, 18.1 Hz, 1 H), 5.01 (m, 1 H), 6.62 (d, *J* = 1.8 Hz, 2 H), 7.10 (t, *J* = 7.4 Hz, 1 H), 7.35 (t, *J* = 7.6 Hz, 2 H), 7.59 (d, *J* = 6.9 Hz, 1 H), 7.37 (d, *J* = 7.6 Hz, 1 H), 7.95 (d, *J* = 9.8 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 100.8 MHz): δ = 35.56 (CH_2), 64.60 (CH), 72.92 (CH), 120.31 (CH), 123.95 (C), 124.52 (CH), 126.05 (CH), 129.64 (CH), 130.29 (CH), 131.24 (CH), 133.39 (C), 134.33 (CH), 138.63 (C), 152.16 (C), 152.36 (C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{15}BrCl_2N_3O$: 425.977; found: 425.980.

Synthesis of 12; General Procedure

A mixture of **11** (3 mmol), dioxane (5 mL), and DBU (9 mmol) was stirred for 3 h at 100 °C. The solvent was then evaporated under reduced pressure, leaving a solid residue that was crystallized from the appropriate solvent.

5-Benzyl-2-*p*-tolyl-4,5-dihydroimidazo[1,5-*b*]pyrazol-6-one (12a)

Yield: 0.36 g (40%); white powder; mp 202–203 °C (dec) (Me_2CHOH/H_2O).

IR (KBr): 3476, 3031, 1948, 1746, 1585, 1495, 1467, 1445, 1406, 1314, 1298, 1246, 1077, 986, 930, 826, 806, 746, 699, 657, 623 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.37 (s, 3 H), 4.24 (br s, 2 H), 4.69 (br s, 2 H), 7.22 (d, *J* = 6.8 Hz, 2 H), 7.33 (m, 5 H), 7.79 (d, *J* = 6.8 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 100.8 MHz): δ = 22.20 (CH_3), 44.16 (CH_2), 48.78 (CH_2), 99.08 (CH), 127.12 (CH), 129.12 (CH), 129.91 (CH), 130.27 (CH), 130.43 (C), 136.40 (C), 139.76 (C), 142.66 (C), 150.76 (C), 159.69 (C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{18}N_3O$: 304.1444; found: 304.1443.

5-Cyclohexyl-2-*p*-tolyl-4,5-dihydroimidazo[1,5-*b*]pyrazol-6-one (12b)

Yield: 0.62 g (70%); beige powder; mp 201–203 °C (dec) (Me_2CHOH/H_2O).

IR (KBr): 3326, 2930, 2851, 1753, 1626, 1575, 1445, 1317, 1298, 1229, 1088, 892, 804, 741, 641 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 1.50 (t, *J* = 9.2 Hz, 2 H), 1.63 (m, 2 H), 1.76 (d, *J* = 9.6 Hz, 2 H), 1.79 (s, 1 H), 2.32 (s, 3 H), 3.77 (s, 1 H), 4.52 (s, 2 H), 5.56 (d, *J* = 7.2 Hz, 1 H), 6.83 (s, 1 H), 7.24 (d, *J* = 7.6 Hz, 2 H), 7.77 (d, *J* = 7.6 Hz, 2 H).

^{13}C NMR (DMSO-d_6, 100.8 MHz): δ = 22.19 (CH_3), 25.78 (CH_2), 26.31 (CH_2), 26.66 (CH_2), 31.43 (CH_2), 34.67 (CH_2), 48.83 (CH_2), 53.54 (CH), 99.23 (CH), 127.09 (CH), 130.71 (CH), 131.08 (C), 139.48 (C), 144.76 (C), 149.91 (C), 158.49 (C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{22}N_3O$: 296.1757; found: 296.1757.

5-(2-Ethylhexyl)-2-*p*-tolyl-4,5-dihydroimidazo[1,5-*b*]pyrazol-6-one (12c)

Yield: 0.52 g (53%); off-white powder; mp 106–107 °C (dec) (Me_2CHOH/H_2O).

IR (KBr): 3399, 2960, 2927, 1748, 1674, 1633, 1586, 1529, 1466, 1445, 1406, 1315, 1297, 1236, 1117, 1100, 108, 804, 739, 665 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.25 (m, 13 H), 2.38 (s, 3 H), 3.09 (d, *J* = 4 Hz, 2 H), 3.43 (t, *J* = 6.8 Hz, 2 H), 4.38 (s, 2 H), 6.52 (s, 1 H), 7.24 (d, *J* = 8 Hz, 2 H), 7.79 (d, *J* = 8 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 100.8 MHz): δ = 11.33 (CH_3), 11.76 (CH_3), 14.96 (CH_3), 22.22 (CH), 23.91 (CH_2), 24.48 (CH_2), 25.00 (CH_2), 29.44 (CH_2), 29.78 (CH_2), 31.23 (CH_2), 31.81 (CH_2), 38.88 (CH), 40.61 (CH), 44.33 (CH_2), 45.20 (CH_2), 48.61 (CH_2), 98.92 (CH), 127.09 (CH), 130.28 (CH), 130.43 (C), 139.73 (C), 142.53 (C), 151.04 (C), 159.50 (C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{28}N_3O$: 326.2227; found: 326.2235.

5-Phenyl-2-*p*-tolyl-4,5-dihydroimidazo[1,5-*b*]pyrazol-6-one (12d)

Yield: 0.61 g (70%); white powder; mp 260–261 °C (dec) (Me_2CHOH/H_2O).

IR (KBr): 3063, 1932, 1742, 1599, 1591, 1505, 1459, 1443, 1386, 1324, 1298, 1274, 1173, 1113, 1082, 1065, 953, 856, 836, 812, 745, 686, 656 cm^{-1}.

^{1}H NMR (DMSO-d_6, 300 MHz): δ = 2.32 (s, 3 H), 5.09 (s, 2 H), 6.94 (s, 1 H), 7.19 (m, 1 H), 7.20 (d, *J* = 9.8 Hz, 2 H), 7.44 (t, *J* = 9.8 Hz, 2 H), 7.73 (d, *J* = 10.6 Hz, 2 H), 7.81 (d, *J* = 10.6 Hz, 2 H).

^{13}C NMR (DMSO-d_6, 75.4 MHz): δ = 22.35 (CH_3), 46.19 (CH_2), 99.65 (CH), 120.44 (CH), 125.95 (CH), 127.36 (CH), 130.59 (C), 130.91 (CH), 139.95 (C), 143.86 (C), 148.77 (C), 159.44 (C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{16}N_3O$: 290.1288; found: 290.1293.

2,5-Di-*p*-tolyl-4,5-dihydroimidazo[1,5-*b*]pyrazol-6-one (12e)

Yield: 0.68 g (75%); off-white powder; mp 230–231 °C (dec) (Me_2CHOH/H_2O).

IR (KBr): 3304, 2916, 1894, 1748, 1640, 1594, 1564, 1516, 1442, 1384, 1325, 1297, 1239, 1168, 1065, 953, 860, 813, 731, 627 cm^{-1}.

^{1}H NMR (DMF-d_7, 400 MHz, 100 °C): δ = 2.37 (s, 3 H), 2.97 (3 H, s), 5.11 (s, 2 H), 6.84 (s, 1 H), 7.29 (d, *J* = 2.0 Hz, 2 H), 7.31 (d, *J* = 2.0 Hz, 2 H), 7.55 (d, *J* = 8.2 Hz, 2 H), 7.87 (d, *J* = 8.2 Hz, 2 H).

^{13}C NMR (DMF-d_7, 100.8 MHz, 100 °C): δ = 20.82 (CH_3), 21.30 (CH_3), 45.98 (CH_2), 98.94 (CH), 120.67 (CH), 127.08 (CH), 130.29 (CH), 130.49 (C), 131.21 (CH), 135.34 (C), 137.47 (C), 139.60 (C), 143.50 (C), 148.65 (C), 159.63 (C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{18}N_3O$: 304.1444; found: 304.1453.

5-(4-Chlorophenyl)-2-*p*-tolyl-4,5-dihydroimidazo[1,5-*b*]pyrazol-6-one (12f)

Yield: 0.81 g (83%); white needles; mp 298–299 °C (dec) (Me_2NCHO).

IR (KBr): 3296, 1914, 1744, 1633, 1590, 1561, 1496, 1443, 1394, 1328, 1299, 1288, 1098, 954, 859, 823, 801, 732, 629 cm^{-1}.

^{1}H NMR (DMF-d_7, 400 MHz, 110 °C): δ = 2.52 (s, 3 H), 5.27 (s, 2 H), 6.96 (s, 1 H), 7.42 (d, *J* = 7.6 Hz, 2 H), 7.63 (d, *J* = 8.8 Hz, 2 H), 7.97 (d, *J* = 8.8 Hz, 2 H), 7.98 (d, *J* = 7.6 Hz, 2 H).

^{13}C NMR (DMF-d_7, 100.8 MHz): δ = 21.35 (CH_3), 46.07 (CH_2), 99.39 (CH), 122.15 (CH), 127.25 (CH), 130.06 (CH), 130.38 (CH), 131.30 (C), 139.11 (C), 139.86 (C), 143.59 (C), 148.78 (C), 160.14 (C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{15}ClN_3O$: 324.0898; found: 324.0892.

5-(4-Fluorophenyl)-2-*p*-tolyl-4,5-dihydroimidazo[1,5-*b*]pyrazol-6-one (12g)

Yield: 0.57 g (62%); white needles; mp 300 °C (dec) (Me_2NCHO).

IR (KBr): 3150, 2926, 1870, 1743, 1581, 1564, 1512, 1442, 1398, 1327, 1299, 1230, 1174, 1116, 1066, 954, 865, 823, 797, 732, 610 cm^{-1}.

^{1}H NMR (DMF-d_7, 400 MHz, 110 °C): δ = 2.38 (m, 3 H), 5.12 (s, 2 H), 6.82 (s, 1 H), 7.26 (m, 4 H), 7.88 (m, 4 H).

^{13}C NMR (DMF-d_7, 100.8 MHz): δ = 26.48 (CH_3), 51.50 (CH_2), 104.26 (CH), 121.80 (d, *J* = 22.9 Hz, CH), 128.2 (d, *J* = 8.1 Hz, CH), 132.34 (CH), 135.50 (CH), 136.43 (C), 141.54 (C), 144.89 (C), 148.75 (C), 154.01 (C), 164.79 (C), 165.07 (C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{15}FN_3O$: 308.1194; found: 308.1196.

5-(4-Bromophenyl)-2-*p*-tolyl-4,5-dihydroimidazo[1,5-*b*]pyrazol-6-one (12h)

Yield: 0.71 g (64%); white needles; mp 306–307 °C (dec) (Me_2NCHO).

IR (KBr): 3297, 1892, 11744, 1634, 1589, 1558, 1488, 1443, 1391, 1327, 1299, 1284, 1237, 1173, 1070, 1064, 1005, 954, 857, 823, 800, 732, 629 cm^{-1}.

^{1}H NMR ($CDCl_3$+TFA-d_1, 400 MHz): δ = 2.52 (s, 3 H), 5.12 (s, 2 H), 7.52 (d, *J* = 4 Hz, 1 H), 7.52 (m, 4 H), 7.71 (d, *J* = 8.2 Hz, 2 H), 7.84 (d, *J* = 8.2 Hz, 2 H).

^{13}C NMR ($CDCl_3$+TFA-d_1, 100.8 MHz): δ = 22.57 (CH_3), 49.88 (CH_2), 103.38 (C), 124.71 (C), 125.12 (CH), 129.71 (CH), 133.26 (CH), 135.64 (CH), 136.29 (C), 147.37 (C), 148.88 (C), 149.67 (C), 160.41 (C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{15}BrN_3O$: 368.0393; found: 368.0404.

5-*p*-Tolyl-2-phenyl-4,5-dihydroimidazo[1,5-*b*]pyrazol-6-one (12i)

Yield: 0.44 g (51%); white powder; mp 130–133 °C (dec) (Me_2CHOH/H_2O).

IR (KBr): 3467, 1735, 1589, 1495, 1440, 1389, 1328, 1199, 083, 955, 776, 733, 697 cm^{-1}.

^{1}H NMR ($CDCl_3$+TFA-d_1, 400 MHz): δ = 2.38 (s, 3 H), 4.97 (s, 2 H), 6.72 (s, 1 H), 7.27 (s, 2 H), 7.55 (m, 4 H), 7.76 (m, 2 H).

^{13}C NMR ($CDCl_3$+TFA-d_1, 100.8 MHz): δ = 21.73 (CH_3), 46.94 (CH_2), 100.67 (CH), 121.61 (CH), 127.64 (CH), 130.05 (CH), 131.11 (CH), 134.88 (C), 137.77 (C), 142.65 (C), 148.77 (C), 160.75 (C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{16}N_3O$: 290.1288; found: 290.1294.

2-(Naphthalen-3-yl)-5-phenyl-4,5-dihydroimidazo[1,5-*b*]pyrazol-6-one (12j)

Yield: 0.53 g (54%); white powder; mp 170–172 °C (dec) ($CHCl_3$/pet ether).

IR (ATR): 2961, 1740, 1583, 1501, 1436, 1385, 1366, 1293, 1171, 970, 862, 794, 681 cm^{-1}.

^{1}H NMR (DMF-d_7, 400 MHz): δ = 5.23 (s, 2 H), 7.11 (s, 1 H), 7.27 (t, *J* = 7.1 Hz, 2 H), 7.51 (t, *J* = 7.7 Hz, 2 H), 7.57 (m, 2 H), 7.86 (d, *J* = 8.3 Hz, 2 H), 7.98 (d, *J* = 7.0 Hz, 1 H), 8.00 (s, 2 H), 8.17 (d, *J* = 8.6 Hz, 1 H), 8.54 (s, 1 H).

^{13}C NMR (DMF-d_7, 100.8 MHz): δ = 45.95 (CH_2), 99.48 (CH), 120.40 (CH), 124.94 (CH), 125.60 (CH), 126.31 (CH), 127.43 (CH), 128.65 (CH), 129.25 (CH), 129.36 (CH), 130.05 (CH), 131.32 (C), 134.59 (C), 134.65 (C), 139.97 (C), 143.74 (C), 148.62 (C), 159.58 (C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{16}N_3O$: 326.1288; found: 326.1278.

2-(3-Bromophenyl)-5-phenyl-4,5-dihydroimidazo[1,5-*b*]pyrazol-6-one (12k)

Yield: 0.53 g (50%); white needles; mp 132–133 °C (dec) (EtOH).

IR (ATR): 3064, 1714, 1598, 1502, 1391, 1311, 1203, 1065, 785, 751, 679 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 5.13 (s, 2 H), 7.08 (s, 1 H), 7.22 (t, *J* = 6.4 Hz, 1 H), 7.45 (q, *J* = 8.5 Hz, 3 H), 7.61 (d, *J* = 7.9 Hz, 1 H), 7.76 (d, *J* = 7.8 Hz, 2 H), 7.97 (d, *J* = 7.3 Hz, 1 H), 8.13 (s, 1 H).

^{13}C NMR (DMSO-d_6, 100.8 MHz): δ = 46.21 (CH_2), 100.06 (CH), 119.40 (C), 120.49 (CH), 123.64 (C), 126.00 (CH), 126.29 (CH), 129.73 (CH), 129.96 (C), 130.49 (CH), 132.46 (CH), 132.99 (CH), 139.67 (C), 144.02 (C), 148.50 (C), 157.68 (C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{13}BrN_3O$: 354.0237; found: 354.0244.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0040-1707304.

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