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Selective Buchwald–Hartwig arylation of *C*-amino-1,2,4-triazoles and other coordinating aminoheterocycles enabled by bulky NHC ligands and TPEDO activator†

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C-Amino-1,2,4-triazoles are challenging polynitrogen substrates for metal-catalyzed arylation due to their multidentate character, enhanced coordinating ability and decreased nucleophilicity of the amino group. In the present study, the Buchwald–Hartwig cross-coupling of diverse 3(5)-amino-1,2,4-triazoles with aryl chlorides and bromides delivering (hetero)arylamino-1,2,4-triazoles in good-to-excellent yields under Pd/NHC catalysis was developed. The use of Pd complexes with bulky NHC ligands such as IPr^{*OMe} and TPEDO (1,1,2,2-tetraphenylethane-1,2-diol) as an *in situ* Pd(II) to Pd(0) reductant enabled the selective arylation of the NH_2 group even in acidic NH unprotected substrates and deactivated 1-substituted 5-amino- and 4-substituted 3-amino-1,2,4-triazoles. The reaction mechanism and structure–activity relationships were studied with DFT calculations. A significant effect of the position of the N-substituent in the 1,2,4-triazole ring on the favorable reaction pathways was revealed.

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1. Introduction

Palladium-catalyzed Buchwald–Hartwig amination has become an indispensable tool for the construction of (hetero)aromatic amine frames in the pharma industry, agrochemistry and material sciences.[1–7] Despite the great progress in the development of efficient catalytic systems for a wide combination of amines and electrophiles, polynitrogen heteroaromatic compounds still remain challenging substrates for Buchwald–Hartwig cross-coupling.[8–12] The decreased reactivity of polynitrogen aminoheterocycles can usually be explained by the low nucleophilicity of amino groups combined with the multidentate character of these substrates as well as their arylation products, which are prone to coordinate with metal centers *via* endocyclic N atoms and thus hinder reductive elimination, oxidative addition, and Pd(II) to Pd(0) reduction at the activation stage.[9–13]

1,2,4-Triazole is a highly demanded scaffold in medicinal chemistry[14–20] and material sciences.[21–24] For example, arylamino-1,2,4-triazoles, such as the anticancer[25–28] and anti-SARS-CoV-2[29–32] drug Bemcentinib (**R428**), anticancer agents **JNJ-7706621**[33,34] and **K00546**,[34,35] and antidepressant **JNJ-39393406**,[36–38] are currently under clinical trials (Fig. 1). In addition, many other 3(5)-arylamino-1,2,4-triazoles have been reported as compounds revealing potential anticancer,[39–41]

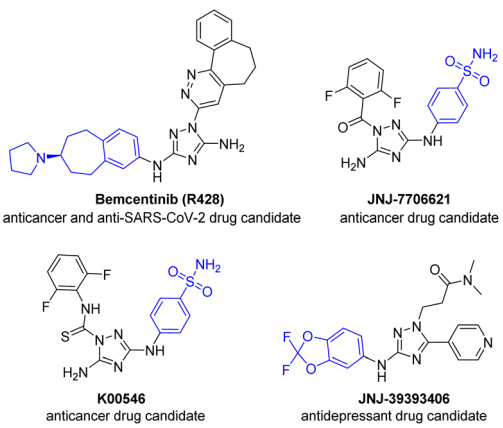

Fig. 1 Medicinally important 3(5)-arylamino-1,2,4-triazoles under clinical trials.

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antibacterial,[42] anti-HIV,[43,44] anti-inflammatory[45,46] and antimalarial[47,48] activities. Moreover, 3-arylamino-1,2,4-triazoles were recently studied as promising photoactive compounds possessing aggregation-induced emission (AIE)[49] and precursors for N-heterocyclic carbene ligands.[50–52]

Although various methods based on the cyclization of acyclic precursors[42,53–57] or amination of 3(5)-bromo-1,2,4-triazoles[58–60] have been reported in the literature, arylation of easily available *C*-amino-1,2,4-triazoles[19,61] may be considered one of most efficient pathways to diverse 3(5)-arylamino-1,2,4-triazoles. However, noncatalytic arylation of *C*-amino-1,2,4-triazoles is limited to activated arylating agents such as nitrochloroarenes,[62] whereas metal-catalyzed arylation is encumbered by the strongly coordinating character of these substrates and the low nucleophilicity of the amino group. For example, Cu-catalyzed arylation of aminotriazoles with boronic acids (Chan–Lam reaction) required using over-stoichiometric loadings of Cu salts and a large excess of quite expensive boronic acids,[63,64] whereas Pd-catalyzed arylation with aryl halides was only possible in the presence of expensive bulky phosphine ligands at high Pd loadings.[65,66]

Complexes of palladium with N-heterocyclic carbene ligands (Pd/NHC) were recently reported as efficient catalysts for the selective arylation of various polynitrogen aminoheterocycles. Organ and co-workers described the use of Pd-PEPPSI-IPent^{Cl} precatalyst for the (het)arylation of aminopyridines,[10] Wu, Qiu and co-workers reported new precatalyst (SIPr)^{Ph2}Pd(cin)Cl efficient in room temperature Buchwald–Hartwig cross-coupling of various (hetero)aryl chlorides with multinitrogen heteroaryl amines,[11] and Szostak, Liu and co-workers successfully applied Pd-BIAN-NHC complexes for catalysis of (hetero)arylation of various coordinating aminoheterocycles.[12]

However, to the best of our knowledge, arylation of *C*-amino-1,2,4-triazoles under catalysis with Pd/NHC complexes has never been studied before. Herein, we report a facile approach to diverse 3(5)-(hetero)arylamino-1,2,4-triazoles *via* Pd/NHC-catalyzed (hetero)arylation of 3(5)-amino-1,2,4-triazoles enabled by the bulky NHC-ligand and new efficient Pd (II) to Pd(0) reductant (Scheme 1). The developed catalytic system can also be employed in the N-(hetero)arylation of other coordinating aminoheterocycles.

2. Results and discussion

2.1 Experimental study of arylation of *C*-amino-1,2,4-triazoles

The structures of the Pd/NHC complexes (**1a–i**) used in the present study are shown in Fig. 2. For comparison, Pd/phosphine catalytic systems consisting of palladium acetate and phosphine ligands presented in Fig. 2 were also evaluated. Arylation of 3-amino-1-*tert*-butyl-1,2,4-triazole **2a** with 4-chlorotoluene **3a** in 1,4-dioxane at 105 °C (Bu^{t}OK as base) was used as a model reaction for the preliminary evaluation of catalytic activities (Table 1 and Tables S1–S4†).

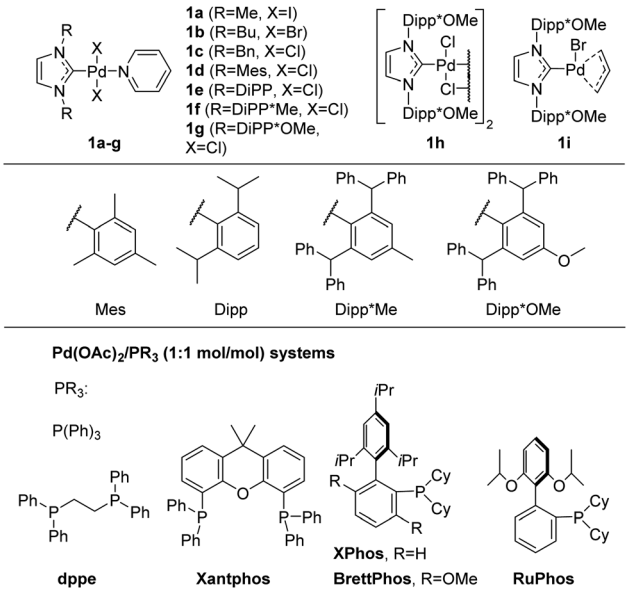
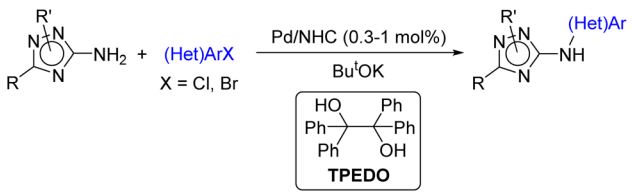


Fig. 2 Pd/NHC complexes and phosphine ligands used in this study.

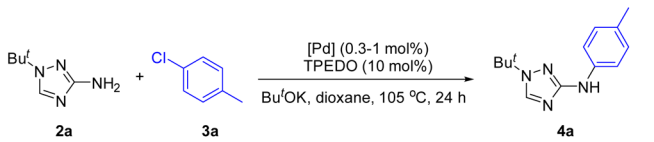
Initially, the efficiency of various precatalysts was studied at 1 mol% Pd loading. Complexes **1a–c** were inactive in the studied conditions (Table S1,† entries 1–3). In addition, fast formation of Pd-black was observed in the reaction mixtures containing precatalysts **1a–c**. Apparently, complexes **1a–c** suffer facile decomposition *via* O-NHC,[52,67] N-NHC,[68] H-NHC and C-NHC coupling reactions.[69–72] More stable complexes **1d** and **1e** with bulkier NHC ligands provided 6% and 19% yields of **4a**, respectively (Table 1, entries 1 and 2). The yields of **4a** with bromo- and iodoarenes were slightly higher under catalysis with precatalysts **1d** and **1e**; however, the formation of a side *N*,*N*-diarylation product **4a′** was observed (Table S1,† entries 4 and 5, compare results for X = Cl, Br). Complexes **1f–i** with the bulkiest NHC ligands, such as Dipp^{*Me} and Dipp^{*OMe}, furnished 68–99% yields of **4a** at 1 mol% Pd loading (Table 1, entries 3–6). Close results were obtained when 4-bromo- and 4-iodotoluene were used as arylating agents with precatalysts **1g–i** (Table S1†). Obviously, an increase in NHC steric bulkiness enhances the selectivity of arylation with more active aryl bromides and iodides. Remarkably, all the studied Pd/phosphine systems (Fig. 2), except Pd(OAc)$_2$/XPhos, were significantly less efficient (Table 1, entries 17–23).

Encouraged by the results obtained with Pd/NHC complexes **1g–i**, we further optimized the reaction conditions to reduce Pd loading. Reducing the Pd loading to 0.5 mol% resulted in a slight decrease in the yield of **4a** with complexes **1g** and **1h** (Table 1, entries 7 and 8), whereas the yield provided



Scheme 1 Arylation of diverse 3(5)amino-1,2,4-triazoles (this work).

Table 1 Optimization of reaction conditions of the studied arylation reaction[a]



2a 3a 4a

Entry	[Pd] precatalyst (Pd loading, mol%)	Activator	Yield of **4a** [b], %
1	**1d** (1)	No	6
2	**1e** (1)	No	19
3	**1f** (1)	No	68
4	**1g** (1)	No	96
5	**1h** (1)	No	92
6	**1i** (1)	No	99
7	**1g** (0.5)	No	94
8	**1h** (0.5)	No	89
9	**1i** (0.5)	No	99
10	**1g** (0.3)	No	75
11	**1h** (0.3)	No	85
12	**1i** (0.3)	No	95
13	**1g** (0.3)	TPEDO	99
14	**1h** (0.3)	TPEDO	99
15	**1i** (0.3)	TPEDO	89
16	**1g** (0.2)	TPEDO	87
17	$Pd(OAc)_2/PPh_3$ (1)	No	6
18	$Pd(OAc)_2$/dppe (1)	No	22
19	$Pd(OAc)_2$/XantPhos (1)	No	36
20	$Pd(OAc)_2$/XPhos (1)	No	93
21	$Pd(OAc)_2$/XPhos (0.5)	No	66
22	$Pd(OAc)_2$/BrettPhos (1)	No	49
23	$Pd(OAc)_2$/RuPhos (1)	No	37

[a] Reaction conditions: **2a** (0.2 mmol), tolyl chloride **3a** (0.2 mmol), ButOK (0.5 mmol), palladium precatalyst (0.6–2 μmol, 0.3–1 mol%), TPEDO (0.02 mmol, 10 mol%) if required, dioxane (1 mL), 105 °C, 24 h. [b] The yields of **4a** were determined by GC-MS.

by complex **1i** remained the same (entry 9). Remarkably, Pd $(OAc)_2$/XPhos furnished a significantly decreased yield of **4a** (66%) at 0.5 mol% Pd loading (Table 1, entry 21). Further decreasing Pd loadings to 0.3 mol% (Table 1) resulted in a more appreciable decrease in the **4a** yield in the case of precatalysts **1g** (75%, Table 1, entry 10) and **1h** (85%, Table 1, entry 11) and a smaller decrease in the yield in the case of precatalyst **1i** (95%, entry 12). It should be noted that complex **1i** contains a sacrificial allylic ligand that serves as internal Pd(II) to Pd(0) reductant in basic media and most likely provides more efficient precatalyst activation.[73–75] Apparently, the rate of Pd(II) to Pd(0) reduction has an appreciable effect on the efficiency of Pd/NHC catalytic systems under the studied conditions. Therefore, we explored the possibility of applying external Pd(II) to Pd(0) reductants to enhance the efficiency of Pd/NHC catalytic systems.

A number of potential Pd(II) to Pd(0) reductants[76–80] were studied in the conditions of the model reaction between **2a** and **3a** (Table S2†). Among them, TPEDO (1,1,2,2-tetraphenylethane-1,2-diol) was found to be the most efficient activator (Table S2,† entry 10). The use of TPEDO reduced the loading of complexes **1g** and **1h** up to 0.3 mol% with the retention of 99% yield of **4a** (Table 1, entries 13 and 14). It should be noted that TPEDO and analogous diols were used previously for the reduction of Ni(II) to Ni(0)[78,81] complexes and as a source of hydrogen for the hydrogenation of alkenes in the presence of Pd catalysts.[82] To the best of our knowledge, the use of TPEDO for Pd/NHC precatalyst activation has not been reported previously.

Further lowering the Pd loading to 0.2 and 0.1 mol% caused a decrease in the **4a** yield in the case of all precatalysts even in the presence of TPEDO, which was less intensive than in the absence of the activator (Table 1, entry 16; Table S3†). Kinetic experiments also confirmed the significant promoting effect of TPEDO (Fig. 3 and Fig. S2–S5†). It is interesting to note that the use of TPEDO was inefficient in the case of precatalyst **1i**, even though a slight decrease in **4a** yield was observed (Table 1, compare entries 15 and 16; Fig. S5†).

Variation of the reaction conditions (base, solvent, TPEDO loading) was further studied for more easily available precatalyst **1g** (Table S4†). The conditions of the experiment of entry 13 in Table 1 were accepted as optimal.

With the optimized reaction conditions in hand, we evaluated the efficiency of the catalytic system in the arylation of 1-substituted 3-amino-1,2,4-triazoles **2a–g** by (hetero)aryl chlorides and bromides (Scheme 2 and Fig. S1†).

Diverse 1-substituted 3-(hetero)arylamino-1,2,4-triazoles **4a–ae** were obtained in good to excellent yields *via* the (hetero)arylation of 1-substituted 3-amino-1,2,4-triazoles **2a–g** under the optimized conditions (Scheme 2). Even sterically hindered deactivated aryl chlorides provided good yields of products **4t**, **u**. Remarkably, arylation of 3,5-diamino-1-phenyl-1,2,4-triazole **2g** (R = NH_2, R^1 = Ph) afforded monoarylation product **4o** owing to the higher nucleophilicity of the 3-NH_2 group.[61] Compounds **4p–r** were isolated as tetrafluoroborate salts due to the high solubility of free bases in organic solvents and difficulties with their purification.

However, attempts at the arylation of 3(5)-amino-1,2,4-triazoles **5b–k** with unsubstituted N-atoms of the triazole ring, as well as 1-substituted 5-amino-1,2,4-triazoles **6a–d** and 4-substituted 3-amino-1,2,4-triazoles **7a–c** (Scheme 3) using the same

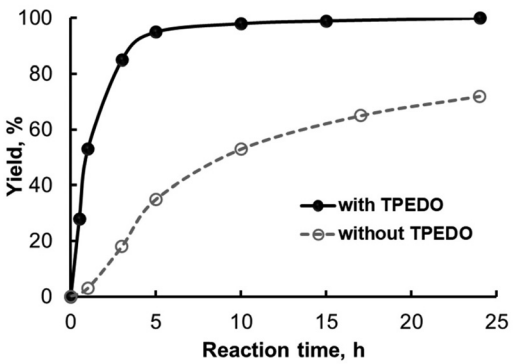
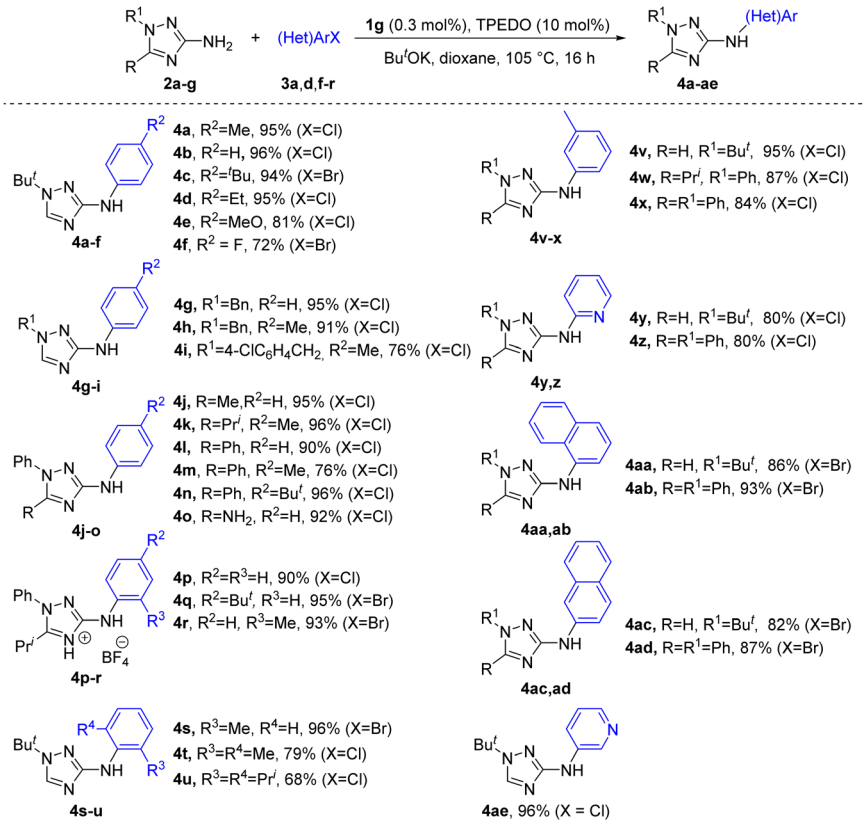


Fig. 3 Kinetic curves for the formation of product **4a** in the reaction between **2a** and **3a**. Reaction conditions: **2a** (0.2 mmol), **3a** (0.2 mmol), ButOK (0.5 mmol), precatalyst **1g** (0.6 μmol, 0.3 mol%), TPEDO (0.02 mmol, 10 mol%) if required, dioxane (1 mL), 105 °C.



Scheme 2 Arylation of 1-substitited 3-amino-1,2,4-triazoles **2a–g**.

reaction conditions as in Scheme 2, resulted in low yields of arylated products (~10–40%). The lowered reactivity of triazoles **5b–k** can presumably be explained by the capture of Pd active species by triazole anions formed *via* deprotonation of the endocyclic NH in basic conditions into less active complexes. This inhibiting effect of acidic endocyclic NH-groups in various azoles is a known phenomenon in metal-catalyzed reactions (see also discussion in further section).[8,13] In addition, deprotonation of endocyclic nitrogen should significantly decrease the acidity of the NH_2 group and therefore hinder the formation of amide-type intermediates required for further reductive elimination. The decreased reactivity of triazoles **6a–d** and **7a–c** can be explained by the lowered nucleophilicity of the NH_2 group in these compounds, as follows from DFT calculations (see below). We found that deactivated substrates **5**, **6** and **7** can be successfully arylated at enhanced to 1 mol% Pd loading (Scheme 3). Remarkably, no formation of endocyclic nitrogen arylation products from substrates **5b–k** was detected by GC-MS and NMR analyses of the reaction mixtures.

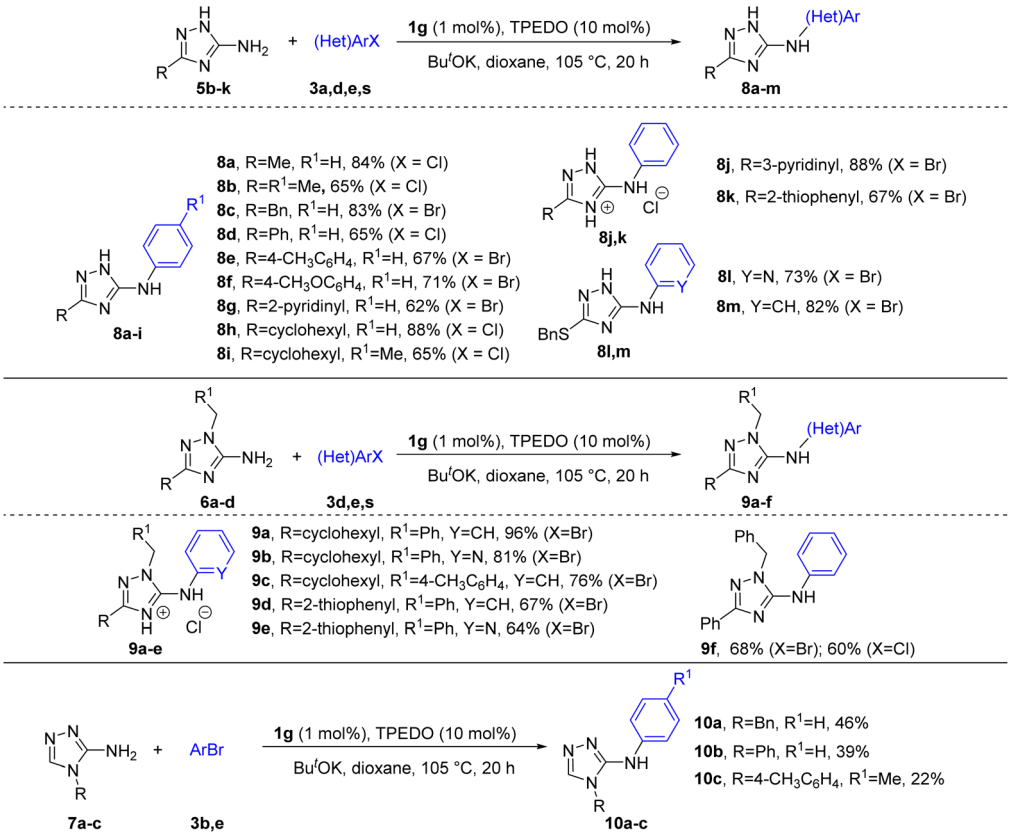
The developed catalytic system is also applicable for the selective *N*-arylation of other nitrogen heteroaryl amines. Compounds **11a–g** were successfully arylated to give the desired products in good to excellent yields (Scheme 4).

The structures of the arylation products **4a–ae**, **8a–m**, **9a–f**, **10a–c**, and **12a–q** were confirmed by ^{1}H and ^{13}C NMR spectra, including 2D experiments for some compounds and HRMS. Single crystal X-ray analyses were performed for compounds **4h**, **4u** and **9f** (see ESI for details†).

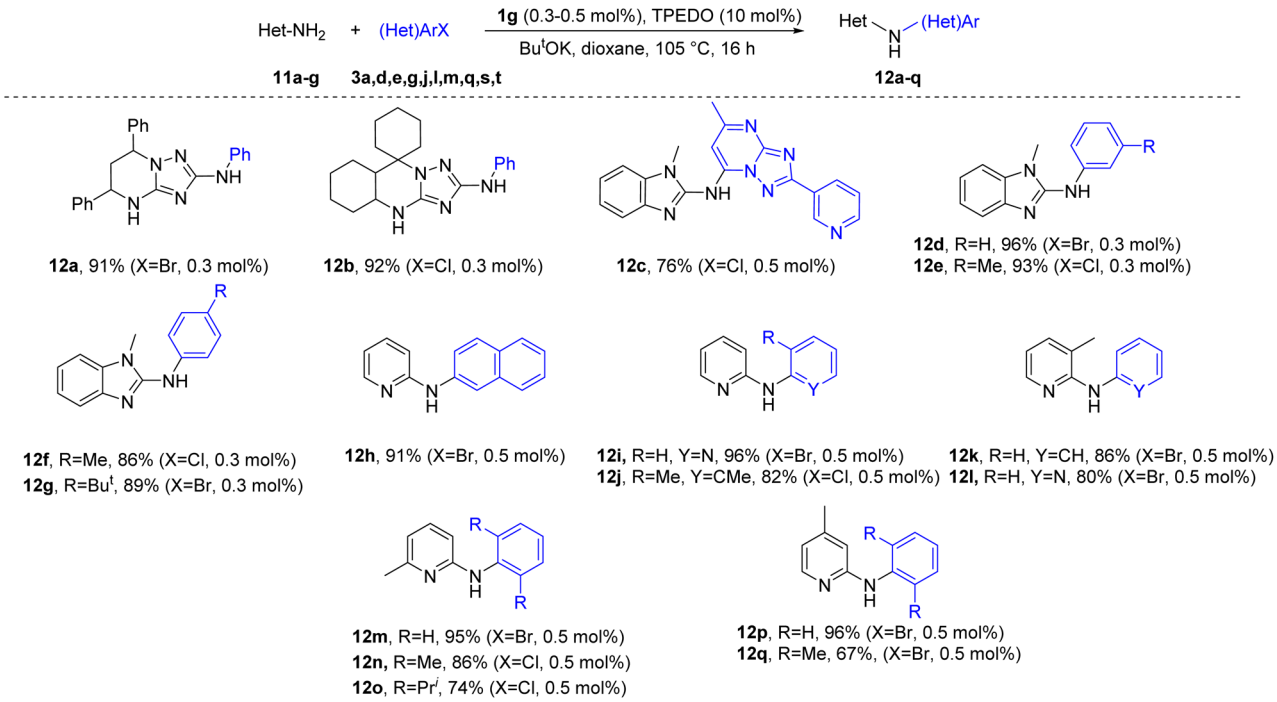
2.2 Theoretical study of the arylation of *C*-amino-1,2,4-triazoles

To obtain an insight into the reaction mechanism, we performed a theoretical investigation of the arylation reaction using DFT calculations at the PBE1PBE/def2svp level of theory. Complex (NHC)PdPy (NHC = IPr, Py = pyridine) was selected as a model catalyst. The potassium *tert*-butoxide dimer was selected as a model base since metal alcoholates in low-polarity solvents are prone to the formation of dimers and oligomers.[83]

The free energy profile of a model reaction between aminotriazole **2a** and chlorobenzene is presented in Fig. 4 (detailed consideration of the reaction routes from starting compounds to **TS-IIA** and **TS-IIB** is provided in Fig. S7 and S8†). Oxidative addition (OA) of PhCl to the starting complex is preceded by pyridine displacement with chlorobenzene molecules to form intermediate **IA**, which then undergoes oxidative addition *via* transition state **TS-IIA** to form oxidative addition intermediate **II**, which can then capture a pyridine molecule to form more stable intermediate **III**. The total energy barrier of the oxidative addition process $\Delta G^{\ddagger}_{OA}$ is 21.1 kcal mol^{-1}. It should be noted that OA can also proceed through an alternative pathway without preliminary displacement of a pyridine ligand *via*



Scheme 3 Arylation of *C*-amino-1,2,4-triazoles **5b–k**, **6a–d**, **7a–c**.



Scheme 4 Arylation of aminoheterocycles **11a–g**.

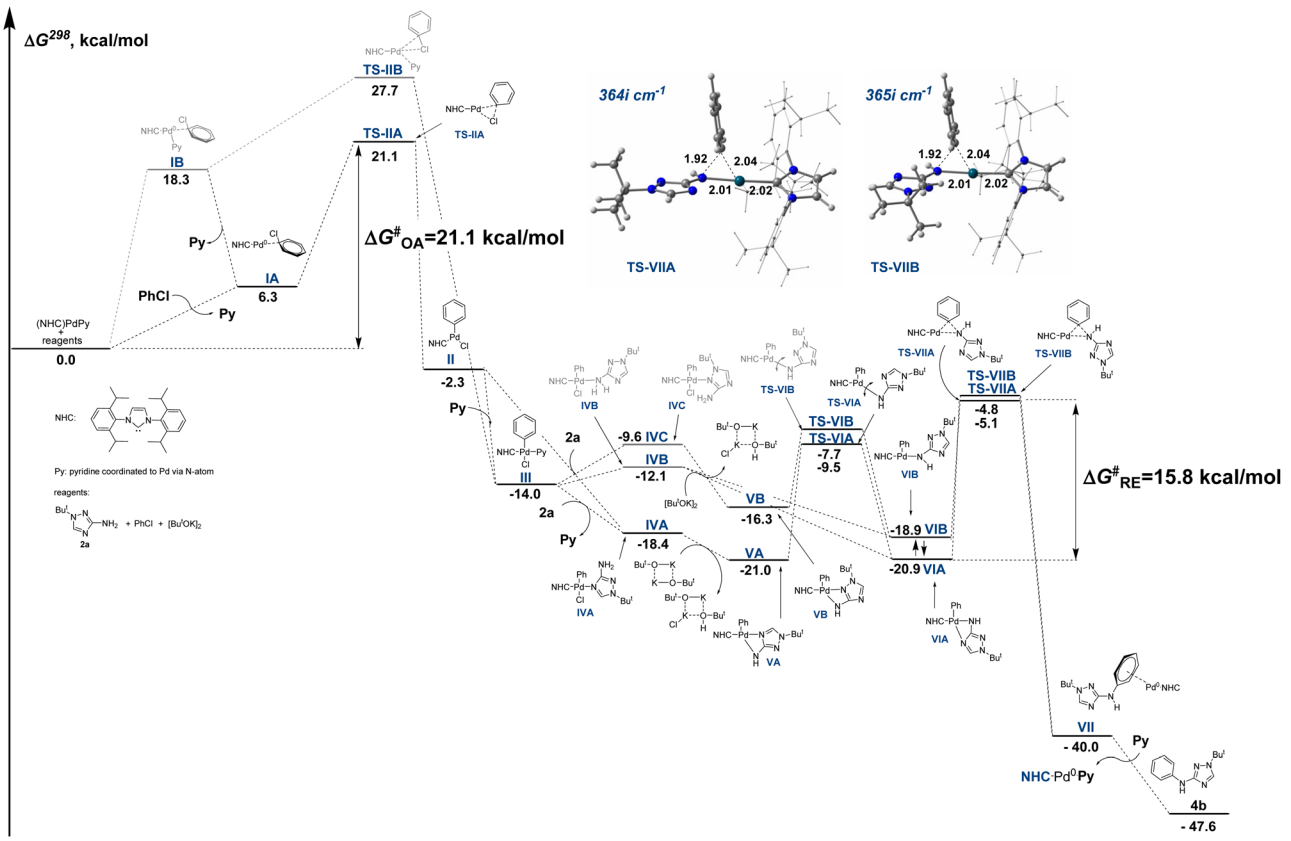


Fig. 4 Relative Gibbs free energies of intermediates and transition states of the C–N coupling reaction between aminotriazole **2a** and chlorobenzene computed at the PBE1PBE/def2svp level. For details of the reaction routes from starting compounds to **TS-IIA** and **TS-IIB**, see Fig. S7 and S8.†

intermediates **IB** and **TS-IIB** (Fig. 4 and Fig. S7, S8†). However, the alternative pathway is characterized by a significantly higher energy barrier of 27.7 kcal mol^{-1} and seems less probable. Remarkably, it was reported that oxidative addition of PhI to a similar complex (IPr)Pd(DMF) also required pushing out the DMF coligand from the coordination sphere of palladium upon oxidative addition.[84]

Then, the catalytic process should involve the coordination of the **2a** molecule and subsequent deprotonation and reductive elimination steps. However, aminotriazoles are polydentate molecules that can form coordination compounds due to binding with metals by various N atoms, including the NH_2 group as well as different N atoms of the triazole ring.[21,22] Molecule **2a** can coordinate to intermediate **II** or to intermediate **III** (with the displacement of the pyridine coligand) to give intermediates **IVA**, **IVB** and **IVC** (Fig. 4 and Fig. S9†). The intermediate **IVA** is 6.3 and 8.8 kcal mol^{-1} more stable than intermediates **IVB** and **IVC**, respectively (Fig. S6†). In addition, the electrostatic potential of the **2a** molecule is localized predominantly on the N4 atom of the triazole ring rather than on the NH_2 group or N2 (Fig. S6†), so the formation of the thermodynamically more stable **IVA** should proceed faster than the formation of intermediates **IVB** and **IVC**.

Deprotonation of **IVA** leads to an intermediate **VA**, which then rearranges *via* **TS-VIA** into a key intermediate **VIA**. Deprotonation of the intermediate **IVB** leads directly to the key intermediate **VIA** or **VIB**, whereas deprotonation of **IVC** leads to an intermediate **VB**, which then rearranges into an alternative key intermediate **VIB**. The intermediate **VIA** is 2.0 kcal mol^{-1} more stable than **VIB**. Both deprotonated intermediates **VIA** and **VIB** are amenable for the reductive elimination (RE) step to give intermediate **VII**. The RE from **VIA** proceeds through a transition state **TS-VIIA** and is accompanied by a cleavage of a bond between Pd and endocyclic N atom, whereas the RE from **VIB** proceeds through a transition state **TS-VIIB**. These transition states differ in conformation of the triazole moiety (Fig. 4). The pathway from **VIA** to **VII** through **TS-VIIA** is only 0.3 kcal mol^{-1} energetically more profitable than the alternative pathway from **VIB** through **TS-VIIB**. Intermediate **VII** then undergoes displacement of the Pd-coordinated arylated aminotriazole molecule by pyridine and transforms into the starting complex (NHC)PdPy and reaction product **4b**.

It should be noted that aminotriazole is used in a large molar excess relative to the starting complex (NHC)PdPy; therefore, replacement of the pyridine coligand by the **2a** molecule can lead to new starting active complexes (NHC)PdL, in which L is a Pd-coordinated molecule of aminotriazole. Therefore, the alternative reaction pathway through the more stable complex (NHC)PdL should not be excluded. We studied the alternative reaction pathway (Fig. S9†) starting from the

complex (NHC)Pd(L) in which aminotriazole (L) is coordinated to the Pd atom *via* the N4 atom of the triazole ring (the most stable coordination isomer) and found that this reaction pathway is energetically very similar to the pathway starting from the complex (NHC)PdPy. The main difference is that the displacement of the aminotriazole ligand by the chlorobenzene molecule to give the intermediate **IA** slightly enhances the barrier of the oxidative addition by 1.8 kcal mol^{-1} ($\Delta G^{\ddagger}_{OA}$ = 22.9 kcal mol^{-1}, Fig. S9†).

According to the results of the DFT calculations (Fig. 4), the oxidative addition of chlorobenzene to the starting complex (NHC)PdPy ($\Delta G^{\ddagger}_{OA}$ = 21.1 kcal mol^{-1}) should be the rate-determining step in the arylation of compound **2a.** Calculations taking into account solvation effect of 1,4-dioxane using IEFPCM approximation afforded similar results ($\Delta G^{\ddagger}_{OA}$ = 20.4 kcal mol^{-1}, $\Delta G^{\ddagger}_{RE}$ = 16.7 kcal mol^{-1}, Fig. S10†). It should be noted that the energy barriers of the OA stage may be lower with precatalysts **1f–i** containing bulkier IPr* and IPr^{*OMe} ligands because bulkier ligands can facilitate a pyridine or L coligand pushing out and stabilize the OA transition state *via* attractive noncovalent interactions with aryl chloride.[85] Therefore, the effect of aryl halide on the yield of arylation product **4a** may be less pronounced under catalysis with precatalysts **1f–i**.

On the other hand, the experimentally observed significant effects of the structures of the studied *C*-amino-1,2,4-triazoles (Schemes 2 and 3), especially the position of a substituent on a nitrogen atom of the triazole ring, on the yields of arylation products suggest that the rate-determining step may depend on the aminotriazole substrate. Therefore, we computed corresponding energy profiles for the arylation of isomeric 3(5)-amino-1(4)-methyl-1,2,4-triazoles **2h**, **6e**, **7d** (Fig. 5 and Fig. S13, S15, S17†). The energy barrier of the OA stage is the same ($\Delta G^{\ddagger}_{OA}$ = 21.1 kcal mol^{-1}) for all reactions, as presented in Fig. 5, because the OA stage does not involve the participation of the aminotriazole substrates. However, the computed energy barriers of the reductive elimination stage ($\Delta G^{\ddagger}_{RE}$) differ significantly and amount to 15.9 kcal mol^{-1}, 21.2 kcal mol^{-1} and 23.7 kcal mol^{-1} for the arylation of isomeric substrates **2h**, **6e** and **7d**, respectively. In other words, reductive elimination becomes the rate-determining stage in the arylation of compound **7d.** In the case of the arylation of compound **6e**, the computed energy barriers of the OA and RE stage are very close (21.1 and 21.2 kcal mol^{-1}, respectively). It can be presumed, that the rate determining stage in the arylation of 1-substituted 5-amino-1,2,4-triazoles **6** can depend on the variation of substrate structure and reaction conditions.

The computed order of the RE energy barriers (Fig. 5 and Fig. S13, S15, S17, Table S5†) correlates well with the experimentally found reactivity of *C*-amino-1,2,4-triazoles: 1-substitud 3-amino-1,2,4-triazoles **2** are the most reactive substrates, which require only 0.3 mol% Pd loading (Scheme 2), whereas 1-substituted 5-amino-1,2,4-triazoles **6** and, especially, 4-substituted 3-amino-1,2,4-triazoles **7** are less reactive and require 1 mol% Pd loading (Scheme 3). Remarkably, the observed differences in the reactivity of 1-substituted 3-amino-1,2,4-triazoles **2** and 5-amino-1,2,4-triazoles **6** agree with the differences in nucleophilicity of the NH_2-group in isomeric 1-substituted *C*-amino-1,2,4-triazoles: the 3-NH_2 group is significantly more nucleophilic than the 5-NH_2 group.[61]

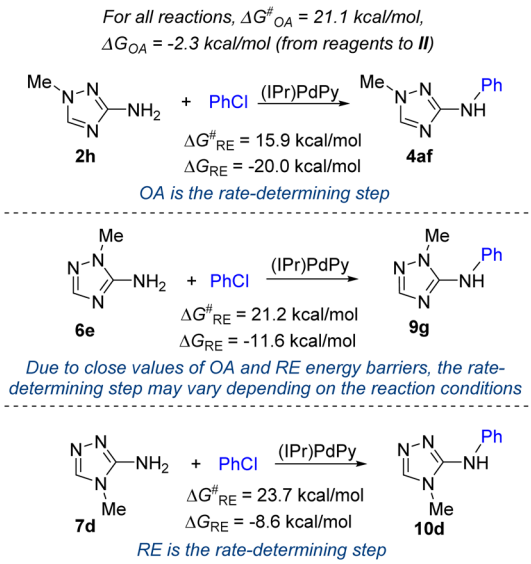


Fig. 5 Gibbs free energy barriers ($\Delta G^{\ddagger}_{RE}$) and energies (ΔG_{RE}) of the reductive elimination stage in the arylation of isomeric 1-methyl- and 4-methyl-3(5)-amino-1,2,4-triazoles with chlorobenzene computed at the PBE1PBE/def2svp level.

Arylation of aminotriazoles **5** unsubstituted at the endocyclic nitrogen atoms deserves special discussion. These substrates exist and can react in several tautomeric forms possessing different reactivities (Fig. S19†).[86–91] According to previous theoretical and experimental studies, a less reactive 5-amino-1*H*-tautomeric form can dominate in polar media.[86,89,91] In addition, these substrates are quite acidic and can eliminate the proton from the endocyclic NH in strong alkaline media.[92,93] The formed triazole N-anions can coordinate to Pd species to give quite stable complexes that can represent the catalyst resting state (for example, **XXXIIA**, Fig. S20†). Obviously, for these reasons, aminotriazoles **5** unsubstituted at the endocyclic nitrogen atoms demonstrate lower reactivity than 1-substituted 3-amino-1,2,4-triazoles **2** (Schemes 2 and 3). Another question is why these substrates do not form products of arylation at the triazole ring N atoms? The answer to this question is obvious from the consideration of the RE stage (Fig. 6 and Fig. S21†). The lowest energy barrier for the arylation of the NH_2 group to give product **8n** amounts to 16.0 kcal mol^{-1}, whereas energy barriers for the formation of N1, N2 and N4 arylation products **2i**, **6f** and **7b** amount to 21.2 kcal mol^{-1}, 21.9 kcal mol^{-1} and 24.0 kcal mol^{-1}, respectively (Fig. 6 and Fig. S21†). Apparently, the kinetics of the RE step determine the selectivity of the arylation of substrates **5**.

Although theoretical calculations provided some useful insights into the reaction mechanism, one should take into account the limitations in the model applied and limitations in the accuracy of calculations. The present results should be taken as preliminary, and more investigations are required for

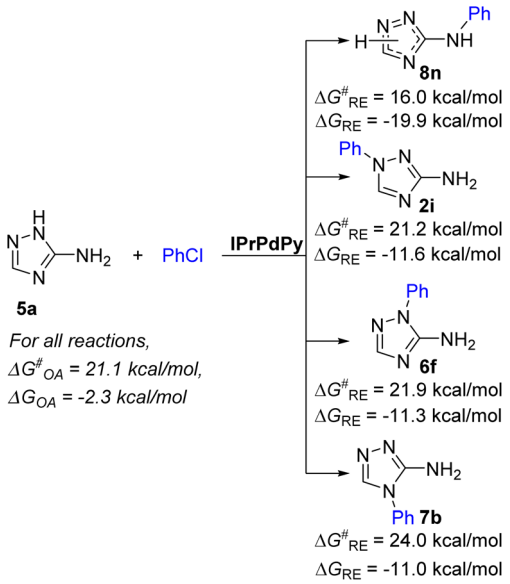


Fig. 6 Gibbs free energy barriers ($\Delta G^{\ddagger}_{RE}$) and reaction energies (ΔG_{RE}) of the reductive elimination stages leading to isomeric products in the arylation of 3-amino-1,2,4-triazole **5a** computed at the PBE1PBE/def2svp level.

a better description of reaction pathways. In particular, the discussion on the rate-determining stages and accurate barriers may be further continued.

3. Conclusion

In summary, a new efficient approach for the selective arylation of NH_2 groups in diverse *C*-amino-1,2,4-triazoles and other coordinating polynitrogen heteroaryl amines by (hetero) aryl chlorides and bromides has been developed. The approach relies on the use of a Pd/NHC precatalyst containing a bulky IPr^{*OMe} NHC ligand and 1,1,2,2-tetraphenylethane-1,2-diol (TPEDO) as an *in situ* activator. The use of TPEDO significantly enhanced the yields of arylation products in comparison with experiments without the use of the Pd(II) reductant. The developed approach provides excellent selectivity for NH_2 group arylation even in substrates containing unprotected endocyclic NH moieties.

The reactivity of *C*-amino-1,2,4-triazoles in the arylation decreases in the order 1-substituted 3-amino-1,2,4-triazoles > 3(5)-amino-1,2,4-triazoles unsubstituted at the endocyclic N atoms ~1-substituted 5-amino-1,2,4-triazoles > 4-substituted 3-amino-1,2,4-triazoles. A theoretical study of the reaction mechanism with the use of DFT calculations revealed a significant effect of the *C*-amino-1,2,4-triazole structure on the energy barrier of the reductive elimination (RE) stage. The rate of the arylation of more nucleophilic 1-substituted 3-amino-1,2,4-triazoles is most likely limited by the oxidative addition of aryl chloride. In the arylation of less nucleophilic 1-substituted 5-amino-1,2,4-triazoles, the rate determining stage may vary due to closeness of the oxidative addition and reductive elimination energy barriers. However, in the arylation of 4-substituted 3-amino-1,2,4-triazoles, the reductive elimination stage is anticipated to be the rate determining stage. The arylation of 3(5)-amino-1,2,4-triazoles unsubstituted at the endocyclic N atoms, due to their proneness to prototropy, can proceed *via* a few reaction channels. The decreased reactivity of these substrates may be explained by their high coordinating ability and the formation of coordination complexes with Pd species that are too stable. The observed high selectivity of the arylation of the N atom of the NH_2 group is determined by the kinetics of the reductive elimination step, namely, by the significantly lower energy barrier of the reductive elimination of the arylamino-product relative to the energy barriers of the reductive elimination of triazole ring *N*-arylated products.

4. Experimental section

4.1 General information

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded using a Bruker Avance Neo NMR spectrometer at 300 MHz for ^{1}H and 75 MHz for ^{13}C spectra. ^{1}H and ^{13}C chemical shifts are presented in ppm relative to the residual peak of the solvent signal (δ 7.26 for trace $CHCl_3$ in $CDCl_3$, δ 2.50 for trace DMSO-d_5 in DMSO-d_6; δ 77.2 for $CDCl_3$, δ 39.5 for DMSO-d_6).

High-resolution mass spectra were obtained on a Bruker maXis Q TOF spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with an electrospray ionization (ESI) ion source. The measurements were conducted in positive (+) MS ion mode (HV Capillary: 4500 V; Spray Shield: −500 V) with a scan range of *m*/*z* 50–1500. External calibration of the mass spectrometer was performed using a low-concentration Agilent tuning mix solution. Direct syringe injection was applied to the analyzed solutions at a flow rate of 3 μL min^{-1}. N_2 was applied as the nebulizer gas (0.4 bar) and dry gas (4.0 L min^{-1}, the dry temperature was 250 °C). All the mass spectra were recorded with a 1 Hz frequency and processed using Bruker Data Analysis 4.0 software.

GC-MS analyses were performed using an Agilent 7890A gas chromatograph equipped with an Agilent 5975C mass-selective detector (EI, 70 eV) and an HP-5MS column (30 m × 0.25 mm × 0.25 μm film) using He as the carrier gas at a flow rate of 1.0 mL min^{-1}.

Melting points were determined in a Thiele apparatus in open capillary tubes and were uncorrected.

Precatalysts **1a**,[94] **1b**,[95] **1c**,[96] **1d**,[97] **1e**,[97] **1f**,[98] **1g**,[76] and starting compounds 1-alkyl-1*H*-1,2,4-triazol-3-amines (**2a–c**, **g**),[88,99–105] 1-unsubstituted 1*H*-1,2,4-triazol-3(5)-amines (**5b–k**),[88,99–105] 4-benzyl-4*H*-1,2,4-triazol-3-amines (**7a**),[106] 4-phenyl-4*H*-1,2,4-triazol-3-amines (**7b**),[107] 5,7-diaryl-4,5,6,7-tetrahydro-[1,2,4]triazolo[1,5-*a*]pyrimidin-2-amine (**11a**, **b**)[26] and 4a′,5′,6′,7′,8′,8a′-hexahydro-4′*H*-spiro[cyclohexane-1,9′-[1,2,4]triazolo[5,1-*b*]quinazolin]-2′-amine (**11c**)[108] were synthesized *via* procedures adapted from the literature. Other chemicals were obtained from commercial sources. Solvents were distilled and dried by standard methods prior to use.

Bis{1,3-bis[2,6-bis(diphenylmethyl)-4-methoxyphenyl]-1,3-dihydro-2*H*-imidazol-2-ylidene}(di-μ-chloro)dichlorodipalladium (1h). Compound **1h** was synthesized *via* procedure adapted from the literature (see Scheme S1†). A solution of concentrated H_2SO_4 (75 mg, 0.75 mmol) in 1,4-dioxane (1 mL) was added dropwise to a vigorously stirred suspension of complex **1g** (97 mg, 0.075 mmol) in 1,4-dioxane (4 mL). The mixture was heated within 12 h at 100 °C under stirring. After cooling to 20 °C, the precipitate formed was collected by filtration, washed with water, dried at 60 °C, then dissolved in CH_2Cl_2. The solution was filtered through a shot pad of silica gel, evaporated to a small volume (~1 mL) and diluted by pentane (~2 mL). The precipitate formed was collected by filtration, recrystallized from a mixture of CH_2Cl_2-Et_2O (1 : 2) and dried at 60 °C *in vacuo*. Yield 60 mg (66%), light-yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz) (as a mixture of dimer and monomer): δ 3.38 and 3.53 (two s, 12H, 4CH_3O), 4.60 and 4.64 (two s, 4H, 4CH), 5.47 (s, 2H, C$\underline{H}Ph_2$), 6.19 (s, 2H, C$\underline{H}Ph_2$), 6.35 (s, 2H, C$\underline{H}Ph_2$), 6.47 (s, 2H, C$\underline{H}Ph_2$), 6.49–6.50 (m, 3H, Ar), 6.57–6.61 (m, 7H, Ar), 6.71–6.77 (m, 11H, Ar), 6.87–7.11 (m, 40H, Ar), 7.18–7.32 (m, 19H, Ar), 7.41–7.44 (m, 4H, Ar), 7.48–7.50 (m, 4H, Ar). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ ^{13}C NMR (75 MHz, $CDCl_3$) δ 51.2, 51.4, 55.2, 114.6, 116.4, 124.2, 126.0, 126.2, 126.4, 126.6, 128.1, 128.2, 128.3, 128.8, 129.2, 129.4, 129.6, 129.7, 130.7, 130.9, 142.9, 143.5, 143.8, 144.18, 144.24, 144.5, 144.7, 145.1, 146.0, 159.7. Anal. calcd for $C_{138}H_{112}Cl_4N_4O_4Pd_2$, %: C 73.83, H 5.03, N 2.50. Found, %: C 73.90, H 4.99, N 2.54.

{1,3-Bis[2,6-bis(diphenylmethyl)-4-methoxyphenyl]-1,3-dihydro-2*H*-imidazol-2-ylidene}(bromo)prop-2-en-1-ylpalladium (1i). Synthesis was performed in argon atmosphere. A mixture of 1,3-bis[2,6-bis(diphenylmethyl)-4-methoxyphenyl]-1,3-dihydro-2*H*-imidazol-2-ium chloride (IPr^{*OMe}·HCl),[109] (216 mg, 0.22 mmol) and Bu^tOK (28 mg, 0.24 mmol) in THF (16 mL) was magnetically stirred at room temperature within 4 h. Then $[Pd(allyl)(\mu\text{-}Br)]_2$ (50 mg, 0.11 mmol) was added to the reaction mixture which was then stirred overnight at room temperature. Then the reaction mixture was evaporated in a rotary evaporator. The residue was extracted by CH_2Cl_2 (3 × 5 mL), the extract was passed through a shot pad of silica gel, evaporated to a small volume (~2 mL) and diluted by in pentane. A precipitate formed after cooling to ~5 °C was collected by filtration. Yield 206 mg (80%), light-yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.34–1.48 (m, 2H, CH_2), 3.08–3.14 (m, 2H, CH_2), 3.70 (s, 6H, 2OCH_3), 4.32–4.33 (m, 1H, CH), 4.71–4.72 (m, 1H, CH), 5.34 (s, 2H, 2CH), 5.45 (s, 2H, 2CH), 6.03–6.05 (m, 4H, Ar), 6.69 (s, 4H, Ar), 6.98–7.01 (m, 10H, Ar), 7.33–7.48 (m, 27H, Ar). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 51.76, 51.78, 54.8, 55.2, 66.0, 71.1, 114.5, 114.8, 115.0, 123.4, 126.5, 126.7, 128.3, 128.4, 129.3, 130.57, 130.61, 131.7, 143.2, 143.4, 143.5, 144.3, 144.4, 158.9, 184.5. Anal. calcd for $C_{72}H_{61}BrN_2O_2Pd$, %: C 73.75, H 5.24, N 2.39. Found, %: C 73.68, H 5.31, N 2.41.

4.2 General procedure for the synthesis of compounds 2d–f (see Scheme S2†)

A solution of acyl chloride or acetic anhydride (36 mmol) in dry MeCN (10 mL) was added dropwise while stirring to a solution of *S*-methylisothiuronium sulfate $[(NH_2)_2CSMe]_2SO_4$ (2.5 g, 9 mmol) and Et_3N (4.55 g, 45 mmol) in dry MeCN (20 mL). Then, the resulting mixture was heated under reflux with stirring for 2 h and cooled to room temperature. Then, phenyl hydrazine (1.95 g, 18 mmol) was added to the reaction mixture, and the resulting solution was additionally heated at 80 °C with stirring for 2 h and then evaporated to dryness *in vacuo*. The oily residue was suspended in a 5% aqueous acetic acid solution (20 mL) and extracted with $CHCl_3$ (3 × 10 mL). The extract was washed with distilled water (2 × 10 mL), dried over anhydrous Na_2SO_4 and evaporated to dryness *in vacuo*. The residue obtained was dissolved in a mixture of concentrated HCl (1 mL) and EtOH (20 mL). The solution was heated under reflux within 5 h, evaporated to a small volume (~5 mL), neutralized with a saturated aqueous solution of $NaHCO_3$ (to pH 8–9) and extracted with $CHCl_3$ (3 × 10 mL). The extract was dried over anhydrous Na_2SO_4, evaporated to a small volume and subjected to column chromatography on silica gel using $CHCl_3$ as the eluent. Product **2** was finally purified by crystallization from an EtOH–Et_2O mixture (1 : 5).

5-Methyl-1-phenyl-1*H*-1,2,4-triazol-3-amine (2d). Yield 1.19 g (38%), colorless needles, mp 183–184 °C (lit[110]: 183–185 °C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.42 (s, 3H, CH_3), 4.13 (s, 2H, NH_2), 7.35–7.49 (m, 5H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 13.4, 124.3, 128.2, 129.4, 137.7, 151.6, 162.4. HRMS (ESI) calcd for $C_9H_{11}N_4$ $[M + H]^+$ *m*/*z* 175.0978, found *m*/*z* 175.0986.

1-Phenyl-5-(propan-2-yl)-1*H*-1,2,4-triazol-3-amine (2e). Yield 1.35 g (37%), yellowish needles, mp 162–164 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.28 (d, J = 6.8 Hz, 6H, 2CH_3), 3.03 (hept, J = 6.8 Hz, 1H, CH), 4.18 (s, 2H, NH_2), 7.36–7.50 (m, 5H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 21.7, 25.9, 125.4, 128.7, 129.5, 137.6, 160.6, 162.4. HRMS (ESI) calcd for $C_{11}H_{15}N_4$ $[M + H]^+$ *m*/*z* 203.1291, found *m*/*z* 203.1301.

1,5-Diphenyl-1*H*-1,2,4-triazol-3-amine (2f). Yield 1.78 g (42%), yellowish needles, mp 150–152 °C (lit[111]: 150–152 °C). HRMS (ESI) calcd for $C_{14}H_{13}N_4$ $[M + H]^+$ *m*/*z* 237.1135, found *m*/*z* 237.1143. The NMR spectra of the obtained compound are identical to those described in the literature.[111,112]

4.3 General procedure for the synthesis of compounds 6a–d (see Scheme S3†)

A mixture of the appropriate triazole **5c**, **e**, **h** (3.0 mmol) and MeONa (168 mg, 3.1 mmol) in DMSO (5 mL) was stirred at room temperature for 30 min. Then, the appropriate alkyl halide (3.0 mmol) was added dropwise to the stirred reaction mixture. The mixture was additionally stirred at room temperature within 16 h, diluted with water (20 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The extract was washed with water (3 × 10 mL), dried over anhydrous Na_2SO_4 and evaporated *in vacuo* to a small volume (~0.5 mL). The residue was diluted with Et_2O (3 mL) and cooled to 0–5 °C. The precipitate formed was collected by filtration, washed with a small amount of Et_2O, recrystallized from the appropriate solvent and dried *in vacuo* at 50 °C.

1-Benzyl-3-cyclohexyl-1*H*-1,2,4-triazol-5-amine (6a). Yield 546 mg (71%), colorless needles, mp 139–141 °C (from

CH_3CN). ^1H NMR (DMSO-d_6, 300 MHz): δ 1.11–1.45 (m, 5H, cyclohexyl), 1.60–1.71 (m, 3H, cyclohexyl), 1.80–1.84 (m, 2H, cyclohexyl), 2.38 (tt, J = 11.0, 3.5 Hz, 1H, CH cyclohexyl), 5.03 (s, 2H, CH_2), 6.18 (s, 2H, NH_2), 7.16–7.19 (m, 2H, Ar), 7.23–7.35 (m, 3H, Ar). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75 MHz): δ 25.6, 25.8, 31.4, 37.1, 48.7, 127.2, 127.3, 128.4, 137.4, 155.3, 164.0. HRMS (ESI) calcd for $C_{15}H_{21}N_4$ $[M + H]^+$ m/z 257.1761, found m/z 257.1773.

3-Cyclohexyl-1-(4-methylbenzyl)-1*H*-1,2,4-triazol-5-amine (6b). Yield 543 mg (67%), colorless needles, mp 167–168 °C (from CH_3CN). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.17–1.55 (m, 5H, cyclohexyl), 1.67–1.81 (m, 3H, cyclohexyl), 1.95–1.99 (m, 2H, cyclohexyl), 2.33 (s, 3H, CH_3), 2.57 (tt, J = 11.6, 3.4 Hz, 1H, CH cyclohexyl), 4.37 (s, 2H, NH_2), 5.03 (s, 2H, CH_2), 7.08–7.16 (m, 4H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 21.2, 26.2, 26.3, 32.0, 37.9, 50.8, 127.2, 129.9, 132.2, 138.2, 154.1, 165.3. HRMS (ESI) calcd for $C_{16}H_{23}N_4$ $[M + H]^+$ m/z 271.1917, found m/z 271.1922.

1-Benzyl-3-phenyl-1*H*-1,2,4-triazol-5-amine (6c). Yield 556 mg (74%), colorless needles, mp 168–169 °C (from EtOH). ^1H NMR ($CDCl_3$, 300 MHz): δ 4.67 (s, 2H, NH_2), 5.20 (s, 2H, CH_2), 7.25–7.27 (m, 2H, Ar), 7.32–7.43 (m, 6H, Ar), 7.97–8.00 (m, 2H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 51.3, 126.1, 127.2, 128.5, 128.6, 129.0, 129.3, 131.4, 135.0, 154.9, 158.7. HRMS (ESI) calcd for $C_{11}H_{15}N_4$ $[M + H]^+$ m/z 203.1291, found m/z 203.1287.

1-Benzyl-3-(thiophen-2-yl)-1*H*-1,2,4-triazol-5-amine (6d). Yield 492 mg (64%), colorless needles, mp 145–146 °C (from CH_3CN). ^1H NMR ($CDCl_3$, 300 MHz): δ 4.80 (s, 2H, NH_2), 5.16 (s, 2H, CH_2), 7.05 (dd, J = 5.0, 3.6 Hz, 1H, Ar), 7.23–7.39 (m, 6H, Ar), 7.54 (dd, J = 3.6, 1.1 Hz, 1H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 51.2, 125.5, 125.9, 127.2, 127.7, 128.5, 129.3, 134.5, 134.8, 154.8, 154.9. HRMS (ESI) calcd for $C_{13}H_{13}N_4S$ $[M + H]^+$ m/z 257.0855, found m/z 257.0858.

4.4 Procedure for the synthesis of 4-(4-methylphenyl)-4*H*-1,2,4-triazol-3-amine (7c)

A solution of 4-methylaniline (338 mg, 3.15 mmol) in EtOH (5 mL) was added with stirring to the *S*-methyl-isothiosemicarbazide hydroiodide $[NH_2NH(NH_2)CSMe]I$ (700 mg, 3 mmol). Then, the resulting mixture was heated under reflux with stirring for 6 h and evaporated to dryness *in vacuo*. The oily residue was washed with Et_2O (3 × 5 mL) and evaporated to dryness *in vacuo*. The resulting residue was dissolved in concentrated HCOOH (5 mL). The solution was boiled for 2 h, slowly evaporated for 1 h at 140 °C, neutralized with a saturated aqueous $NaHCO_3$ solution (to pH 8–9), and extracted with $CHCl_3$ (5 × 10 ml). The extract was dried over anhydrous Na_2SO_4, evaporated to a small volume, and precipitated with Et_2O. The precipitate formed was collected by filtration, washed with a small amount of Et_2O, recrystallized from EtOH–Et_2O (1 : 5) and dried *in vacuo* at 50 °C.

4-(4-Methylphenyl)-4*H*-1,2,4-triazol-3-amine (7c). Yield 213 mg (43%), colorless needles, mp 228–230 °C. ^1H NMR (DMSO-d_6, 300 MHz): δ 2.36 (s, 3H, Me), 5.73 (s, 2H, NH_2), 7.34 (pseudo s, 4H, Ar), 8.13 (s, 1H, CH). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75 MHz): δ 20.6, 124.3, 130.1, 131.3, 137.6, 139.7, 153.6. HRMS (ESI) calcd for $C_9H_{11}N_4$ $[M + H]^+$ m/z 175.0978, found m/z 175.0987.

4.5 Study of *N*-arylation of compound 2a

A 4 mL screw-capped glass tube equipped with a magnetic stirring bar was charged with the corresponding base (0.5 mmol), aryl halide (0.2 mmol), 1-*tert*-butyl-1*H*-1,2,4-triazol-3-amine (**2a**) (28 mg, 0.2 mmol), appropriate Pd precatalyst (0.2–2 μmol, 0.1–1 mol%), and, if needed, appropriate NHC proligand and 1,1,2,2-tetraphenylethane-1,2-diol (TPEDO, 11 mg, 0.03 mmol, Table 1 and Table S1†). Then, the appropriate solvent (1 mL, Table 1 and Tables S1, S2†) was added to the resulting mixture, and the tube was purged with argon, sealed with a screw cap fitted with a rubber septum, placed in a thermostated oil bath and heated with vigorous stirring at the corresponding temperature for 24 h. Then, the glass tubes were cooled to room temperature, and a solution of AcOH (30 mg, 0.5 mmol) and naphthalene (12.8 mg, 0.1 mmol, an internal standard in 1 mL of acetonitrile) was added by syringe through the septum. An aliquot (5–10 μl) of the reaction mixture was dissolved in 1 ml of CH_3CN and analyzed by GC-MS (Fig. S2–S5,† Table 1 and Tables S1–S4†).

4.6 General procedure for the synthesis of compounds 4a–ae, 8a–m, 9a–f, 10a–c, and 12a–q

A 7 mL screw-capped glass tube equipped with a magnetic stirring bar was charged with Bu^{t}OK (224 mg, 2.0 mmol), aryl halide (0.8 mmol), corresponding aminotriazole (**2a–g**, **5b–k**, **6a–d**, **7a–c**) or compound **11a–g** (0.8 mmol), 1,1,2,2-tetraphenylethane-1,2-diol (TPEDO, 30 mg, 0.08 mmol, 10 mol%) and Pd precatalyst **1g** (2.9 mg, 2.4 μmol, 0.3 mol% for the arylation compounds **2a–g**, **11a–c** (see Schemes 2 and 4), or 4–8 μmol, 0.5–1 mol% for the arylation of compounds **5–7**, **11d–g** (see Schemes 3 and 4). Then, 1,4-dioxane (4 mL) was added to the resulting mixture, and the tube was purged with argon, sealed with a screw cap fitted with a septum, placed in a thermostated oil bath and stirred at 105 °C for 20 h. After cooling to room temperature, the tube was opened, and the reaction mixture was neutralized with AcOH (~0.2 g) and evaporated to dryness *in vacuo*.

To isolate compounds **4a–o**, **s–ae**, **9f** and **12h–q**, the residue obtained after evaporation of the reaction mixture was dissolved in CH_2Cl_2 (10 mL). The solution was washed with water (3 × 10 mL), dried over anhydrous Na_2SO_4, evaporated to a small volume (0.5–1.0 mL) and subjected to column chromatography on silica gel using CH_2Cl_2 as the eluent. Products **4a–o**, **s–ae**, **9f** and **12h–q** were finally purified by recrystallization from the appropriate solvent and dried *in vacuo* at 50 °C overnight.

To isolate compounds **8a–i**, **l**, **m**, **10a–c**, and **12a–g** the residue obtained after evaporation of the reaction mixture was dissolved in EtOH (7 mL). The solution was passed through a short layer of Celite, evaporated to a small volume (~1 mL), diluted with water (~1 mL) and cooled to 0–5 °C. A precipitate formed was collected by filtration and recrystallized from the appropriate solvent and then dried *in vacuo* at 50 °C.

To isolate hydrochlorides **9a–e**, **8j**, **k** and hydrotetrafluoroborates **4p–r**, the residue obtained after evaporation and column chromatography of the reaction mixture was dissolved in hot C_2H_5OH (0.1 mL) and acidified by the addition of concentrated HCl or 40% aqueous HBF_4 solution. Then, the resulting acidic solution was diluted with Et_2O (1 mL) and cooled to −10 °C. A precipitate formed was collected by filtration, washed with cold ether, recrystallized from the appropriate solvent and dried *in vacuo* at 80 °C overnight.

1-*tert*-Butyl-*N*-(4-methylphenyl)-1*H*-1,2,4-triazol-3-amine (4a). Yield 175 mg (95%), colorless needles, mp 139–140 °C (from EtOH–H_2O 5 : 1 mixture). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.60 (s, 9H, $3CH_3$), 2.29 (s, 3H, CH_3), 6.55 (s, 1H, NH), 7.09 (d, J = 8.2 Hz, 2H), 7.35–7.38 (m, 2H, Ar), 7.82 (s, 1H, CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 20.8, 29.4, 58.0, 116.3, 129.6, 129.7, 138.2, 139.0, 160.6. HRMS (ESI) calcd for $C_{13}H_{19}N_4$ $[M + H]^+$ m/z 231.1604, found m/z 231.1608.

1-*tert*-Butyl-*N*-phenyl-1*H*-1,2,4-triazol-3-amine (4b). Yield 166 mg (96%), colorless needles, mp 144–146 °C (from EtOH–H_2O 5 : 1 mixture). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.61 (s, 9H, $3CH_3$), 6.73 (s, 1H, NH), 6.88–6.93 (m, 1H, Ph), 7.26–7.32 (m, 2H, Ph), 7.46–7.50 (m, 2H, Ph), 7.84 (s, 1H, CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 29.4, 58.0, 116.1, 120.4, 129.2, 138.2, 141.4, 160.3. HRMS (ESI) calcd for $C_{12}H_{17}N_4$ $[M + H]^+$ m/z 217.1448, found m/z 217.1453. The spectral data of compound **4b** are consistent with the literature data.[56]

1-*tert*-Butyl-*N*-(4-*tert*-butylphenyl)-1*H*-1,2,4-triazol-3-amine (4c). Yield 205 mg (94%), colorless needles, mp 149–151 °C (from EtOH). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.31 (s, 9H, $3CH_3$), 1.60 (s, 9H, $3CH_3$), 6.58 (s, 1H, NH), 7.30–7.34 (m, 2H, Ar), 7.39–7.43 (m, 2H, Ar), 7.82 (s, 1H, CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 29.4, 31.6, 34.2, 58.0, 116.0, 125.9, 138.1, 138.9, 143.2, 160.6. HRMS (ESI) calcd for $C_{16}H_{25}N_4$ $[M + H]^+$ m/z 273.2074, found m/z 273.2072.

1-*tert*-Butyl-*N*-(4-ethylphenyl)-1*H*-1,2,4-triazol-3-amine (4d). Yield 185 mg (95%), colorless needles, mp 85–86 °C (from Pr^iOH–H_2O 5 : 1 mixture). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.22 (t, J = 7.6 Hz, 3H, CH_3), 1.61 (s, 9H, $3CH_3$), 2.60 (q, J = 7.6 Hz, 2H, CH_2), 6.85 (s, 1H, NH), 7.11–7.14 (m, 2H, Ar), 7.39–7.42 (m, 2H, Ar), 7.83 (s, 1H, CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 15.9, 28.2, 29.3, 57.8, 116.2, 128.3, 136.1, 138.0, 139.2, 160.5. HRMS (ESI) calcd for $C_{14}H_{21}N_4$ $[M + H]^+$ m/z 245.1761, found m/z 245.1765.

1-*tert*-Butyl-*N*-(4-methoxyphenyl)-1*H*-1,2,4-triazol-3-amine (4e). Yield 159 mg (81%), colorless needles, mp 113–115 °C (from EtOH–H_2O 5 : 1 mixture). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.60 (s, 9H, $3CH_3$), 3.78 (s, 3H, CH_3), 6.58 (s, 1H, NH), 6.87 (d, J = 9.0 Hz, 2H, Ar), 7.41 (d, J = 9.0 Hz, 2H, Ar), 7.81 (s, 1H, CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 29.4, 55.8, 57.9, 114.5, 117.7, 135.2, 138.2, 153.9, 160.8. HRMS (ESI) calcd for $C_{13}H_{19}N_4O$ $[M + H]^+$ m/z 247.1553, found m/z 247.1558.

1-*tert*-Butyl-*N*-(4-fluorophenyl)-1*H*-1,2,4-triazol-3-amine (4f). Yield 135 mg (72%), colorless needles, mp 154–156 °C (from EtOH–H_2O 5 : 1 mixture). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.61 (s, 9H, $3CH_3$), 6.66 (s, 1H, NH), 6.96–7.02 (m, 2H, Ar), 7.40–7.45 (m, 2H, Ar), 7.83 (s, 1H, CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 29.4, 58.1, 115.6 (d, $^2J_{CF}$ = 22.4 Hz), 117.4 (d, $^3J_{CF}$ = 7.5 Hz), 137.6 (d, $^4J_{CF}$ = 2.1 Hz), 138.3, 157.3 (d, $^1J_{CF}$ = 238.0 Hz), 160.4. HRMS (ESI) calcd for $C_{12}H_{16}FN_4$ $[M + H]^+$ m/z 235.1354, found m/z 235.1353.

1-Benzyl-*N*-phenyl-1*H*-1,2,4-triazol-3-amine (4g). Yield 190 mg (95%), colorless needles, mp 123–125 °C (from EtOH–Et_2O 1 : 5 mixture). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.24 (s, 2H, CH_2), 6.77 (s, 1H, NH), 6.89–6.94 (m, 1H, Ar), 7.29–7.47 (m, 9H, Ar), 7.75 (s, 1H, CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 53.7, 116.4, 120.7, 128.2, 128.7, 129.1, 129.2, 135.0, 141.0, 141.7, 161.0. HRMS (ESI) calcd for $C_{15}H_{15}N_4$ $[M + H]^+$ m/z 251.1291, found m/z 251.1294.

1-Benzyl-*N*-(4-methylphenyl)-1*H*-1,2,4-triazol-3-amine (4h). Yield 193 mg (91%), colorless needles, mp 141–143 °C (from EtOH–H_2O 2 : 1 mixture). ^{1}H NMR ($CDCl_3$, 300 MHz): 2.29 (s, 3H, CH_3), 5.23 (s, 2H, CH_2), 6.61 (s, 1H, NH), 7.08–7.11 (m, 2H, Ar), 7.29–7.42 (m, 7H, Ar), 7.73 (s, 1H, CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 20.8, 53.6, 116.6, 128.2, 128.6, 129.1, 129.7, 130.1, 135.0, 138.6, 141.7, 161.3. HRMS (ESI) calcd for $C_{16}H_{17}N_4$ $[M + H]^+$ m/z 265.1448, found m/z 265.1452.

1-(4-Chlorobenzyl)-*N*-(4-methylphenyl)-1*H*-1,2,4-triazol-3-amine (4i). Yield 182 mg (76%), colorless needles, mp 143–145 °C (from $CHCl_3$–*n*-hexane 1 : 10 mixture). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.29 (s, 3H, CH_3), 5.19 (s, 2H, CH_2), 6.75 (s, 1H, NH), 7.08–7.11 (m, 2H, Ar), 7.23–7.26 (m, 2H, Ar), 7.32–7.37 (m, 4H, Ar), 7.76 (s, 1H, CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 20.8, 52.8, 116.6, 129.3, 129.4, 129.7, 130.2, 133.6, 134.6, 138.5, 141.7, 161.4. HRMS (ESI) calcd for $C_{16}H_{16}ClN_4$ $[M + H]^+$ m/z 299.1058, found m/z 299.1062.

5-Methyl-*N*,1-diphenyl-1*H*-1,2,4-triazol-3-amine (4j). Yield 190 mg (95%), colorless needles, mp 176–179 °C (from EtOH–H_2O 1 : 2 mixture). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.50 (s, 3H, CH_3), 6.83 (s, 1H, NH), 6.90–6.94 (m, 1H, Ar), 7.27–7.32 (m, 2H, Ar), 7.38–7.44 (m, 1H, Ar), 7.49–7.52 (m, 6H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 13.5, 116.5, 120.7, 124.4, 128.2, 129.2, 129.5, 137.8, 141.0, 150.9, 159.6. HRMS (ESI) calcd for $C_{15}H_{15}N_4$ $[M + H]^+$ m/z 251.1291, found m/z 251.1292.

***N*-(4-Methylphenyl)-1-phenyl-5-(propan-2-yl)-1*H*-1,2,4-triazol-3-amine (4k).** Yield 225 mg (96%), colorless needles, mp 142–145 °C (from $CHCl_3$–*n*-hexane 1 : 10 mixture). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.32 (d, J = 6.8 Hz, 6H, $2CH_3$), 2.28 (s, 3H, CH_3), 3.11 (hept, J = 6.8 Hz, 1H, CH), 6.58 (s, 1H, NH), 7.07–7.09 (m, 2H, Ar), 7.37 (d, J = 8.3 Hz, 2H, Ar), 7.43–7.51 (m, 5H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 20.8, 21.8, 25.9, 116.5, 125.5, 128.6, 129.5, 129.6, 129.8, 137.8, 138.6, 159.8 (signals of two aromatic carbons overlap). HRMS (ESI) calcd for $C_{18}H_{21}N_4$ $[M + H]^+$ m/z 293.1761, found m/z 293.1770.

***N*,1,5-Triphenyl-1*H*-1,2,4-triazol-3-amine (4l).** Yield 225 mg (90%), colorless needles, mp 200–202 °C (from $CHCl_3$–*n*-hexane 1 : 10 mixture). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.89–6.94 (m, 1H, Ar), 7.17 (s, 1H, NH), 7.24–7.42 (m, 11H, Ar), 7.49–7.52 (m, 4H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 116.5, 120.7, 125.4, 128.0, 128.5, 128.7, 129.0, 129.2, 129.4, 130.2, 138.4, 140.9, 152.4, 160.1. HRMS (ESI) calcd for $C_{20}H_{17}N_4$ $[M + H]^+$ m/z 113.1448, found m/z 313.1458.

***N*-(4-Methylphenyl)-1,5-diphenyl-1*H*-1,2,4-triazol-3-amine (4m).** Yield 198 mg (76%), colorless needles, mp 196–198 °C (from $CHCl_3$–*n*-hexane 1 : 10 mixture). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.30 (s, 3H, CH_3), 6.72 (s, 1H, NH), 7.08–7.11 (m, 2H, Ar), 7.31–7.44 (m, 10H, Ar), 7.48–7.51 (m, 2H, Ar). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 20.8, 116.7, 125.4, 128.1, 128.4, 128.7, 129.0, 129.4, 129.7, 130.11, 130.13, 138.4, 138.5, 152.4, 160.2. HRMS (ESI) calcd for $C_{21}H_{19}N_4$ $[M + H]^+$ *m*/*z* 327.1604, found *m*/*z* 327.1618.

***N*-(4-*tert*-Butylphenyl)-1,5-diphenyl-1*H*-1,2,4-triazol-3-amine (4n).** Yield 283 mg (96%), colorless needles, mp 202–204 °C (from Pr^iOH). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.31 (s, 9H, $3CH_3$), 6.90 (s, 1H, NH), 7.29–7.46 (m, 12H, Ar), 7.49–7.53 (m, 2H, Ar). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 31.6, 34.2, 116.5, 125.4, 126.0, 128.1, 128.4, 128.7, 129.0, 129.3, 130.1, 138.4, 138.5, 143.5, 152.4, 160.3. HRMS (ESI) calcd for $C_{24}H_{25}N_4$ $[M + H]^+$ *m*/*z* 369.2074, found *m*/*z* 369.2089.

***N*^{3},1-Diphenyl-1*H*-1,2,4-triazole-3,5-diamine (4o).** Yield 185 mg (92%), colorless needles, mp 189–190 °C (from hexane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.06 (s, 2H, NH_2), 6.86–6.92 (m, 1H, Ar), 7.23–7.56 (m, 10H, Ar + NH). ^{13}C{1H} NMR ($CDCl_3$, 75 MHz): δ 116.7, 120.5, 122.8, 127.3, 129.1, 129.8, 137.3, 141.1, 152.3, 157.8. HRMS (ESI) calcd for $C_{14}H_{14}N_5$ $[M + H]^+$ *m*/*z* 252.1244, found *m*/*z* 252.1239.

1-Phenyl-3-(phenylamino)-5-(propan-2-yl)-1*H*-1,2,4-triazol-4-ium tetrafluoroborate (4p). Yield 263 mg (90%), colorless needles, mp 149–150 °C (from Et_2O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.44 (d, J = 7.0 Hz, 6H, $2CH_3$), 3.29 (sept, J = 7.0 Hz, 1H, CH), 7.01–7.06 (m, 1H, Ar), 7.26–7.31 (m, 2H, Ar), 7.45–7.48 (m, 2H, Ar), 7.53–7.55 (m, 2H, Ar), 7.64–7.66 (m, 3H, Ar), 8.40 (s, 1H, NH) (N^4H signal is broadened and merged into the background). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 20.3, 25.9, 118.1, 123.4, 125.6, 129.3, 130.4, 131.6, 134.8, 137.6, 150.9, 155.4. HRMS (ESI) calcd for $C_{17}H_{19}N_4$ $[M - BF_4^-]^+$ *m*/*z* 279.1604, found *m*/*z* 279.1617.

3-[(4-*tert*-Butylphenyl)amino]-1-phenyl-5-(propan-2-yl)-1*H*-1,2,4-triazol-4-ium tetrafluoroborate (4q). Yield 320 mg (95%), colorless needles, mp 198–200 °C (from Et_2O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.28 (s, 9H, $3CH_3$), 1.46 (d, J = 7.0 Hz, 6H, $2CH_3$), 3.30 (sept, J = 7.0 Hz, 1H, CH), 7.30–7.33 (m, 2H, Ar), 7.39–7.42 (m, 2H, Ar), 7.50–7.53 (m, 2H, Ar), 7.64–7.66 (m, 3H, Ar), 8.39 (s, 1H, NH), 12.50 (br. s, 1H, N^4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 20.3, 25.9, 31.5, 34.4, 118.2, 125.5, 126.2, 130.5, 131.7, 134.6, 134.8, 146.7, 150.6, 155.1. HRMS (ESI) calcd for $C_{21}H_{27}N_4$ $[M - BF_4^-]^+$ *m*/*z* 335.2230, found *m*/*z* 335.2243.

3-[(2-Methylphenyl)amino]-1-phenyl-5-(propan-2-yl)-1*H*-1,2,4-triazol-4-ium tetrafluoroborate (4r). Yield 282 mg (93%), colorless needles, mp 168–170 °C (from Et_2O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.47 (d, J = 7.0 Hz, 6H, $2CH_3$), 2.35 (s, 3H, CH_3), 3.29 (sept, J = 7.0 Hz, 1H, CH), 6.98–7.03 (m, 1H, Ar), 7.14–7.19 (m, 2H, Ar), 7.49–7.52 (m, 2H, Ar), 7.61–7.65 (m, 3H, Ar), 7.82–7.84 (m, 1H, Ar), 7.95 (s, 1H, NH), 12.48 (br. s, 1H, N^4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 17.7, 20.2, 25.9, 119.5, 124.4, 125.6, 126.8, 128.3, 130.4, 131.0, 131.7, 134.6, 135.6, 151.0, 155.4. HRMS (ESI) calcd for $C_{18}H_{21}N_4$ $[M - BF_4^-]^+$ *m*/*z* 293.1761, found *m*/*z* 293.1770.

1-*tert*-Butyl-*N*-(2-methylphenyl)-1*H*-1,2,4-triazol-3-amine (4s). Yield 177 mg (96%), colorless needles, mp 100–102 °C (from Et_2O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.62 (s, 9H, $3CH_3$), 2.30 (s, 3H, CH_3), 6.37 (s, 1H, NH), 6.83–6.88 (m, 1H, Ar), 7.13 (d, J = 7.3 Hz, 1H, Ar), 7.20–7.25 (m, 1H, Ar), 7.85 (s, 1H, CH), 8.15 (d, J = 7.8 Hz, 1H, Ar). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 18.0, 29.4, 58.0, 115.9, 120.4, 123.5, 127.1, 130.3, 138.2, 139.6, 160.5. HRMS (ESI) calcd for $C_{13}H_{19}N_4$ $[M + H]^+$ *m*/*z* 231.1604, found *m*/*z* 231.1615.

1-*tert*-Butyl-*N*-(2,6-dimethylphenyl)-1*H*-1,2,4-triazol-3-amine (4t). Yield 154 mg (79%), colorless needles, mp 110–112 °C (from *n*-hexane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.53 (s, 9H, $3CH_3$), 2.27 (s, 6H, $2CH_3$), 5.73 (s, 1H, NH), 7.02–7.10 (m, 3H, Ar), 7.73 (s, 1H, CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 18.8, 29.3, 57.6, 125.5, 128.4, 134.7, 137.9, 138.7, 162.6. HRMS (ESI) calcd for $C_{14}H_{21}N_4$ $[M + H]^+$ *m*/*z* 245.1761, found *m*/*z* 245.1768.

1-*tert*-Butyl-*N*-[2,6-di(propan-2-yl)phenyl]-1*H*-1,2,4-triazol-3-amine (4u). Yield 164 mg (68%), colorless needles, mp 113–115 °C (from *n*-hexane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.16 (d, J = 6.8 Hz, 12H, $4CH_3$), 1.49 (s, 9H, $3CH_3$), 3.27 (sept, J = 6.8 Hz, 2H, 2CH), 5.58 (s, 1H, NH), 7.16–7.18 (m, 2H, Ar), 7.25–7.28 (m, 1H, Ar), 7.71 (s, 1H, CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 23.9, 28.5, 29.3, 57.6, 123.6, 127.2, 134.9, 138.6, 146.9, 164.1. HRMS (ESI) calcd for $C_{18}H_{29}N_4$ $[M + H]^+$ *m*/*z* 301.2387, found *m*/*z* 301.2390.

1-*tert*-Butyl-*N*-(3-methylphenyl)-1*H*-1,2,4-triazol-3-amine (4v). Yield 175 mg (95%), colorless needles, mp 108–110 °C (from EtOH–H_2O 5 : 1 mixture). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.61 (s, 9H, $3CH_3$), 2.34 (s, 3H, CH_3), 6.59 (s, 1H, NH), 6.71–6.74 (m, 1H, Ar), 7.18 (t, J = 7.8 Hz, 1H, Ar), 7.24 (br. s, 1H, Ar), 7.32–7.35 (m, 1H, Ar), 7.83 (s, 1H, CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 21.8, 29.4, 58.0, 113.3, 116.9, 121.3, 129.0, 138.2, 138.9, 141.4, 160.4. HRMS (ESI) calcd for $C_{13}H_{19}N_4$ $[M + H]^+$ *m*/*z* 231.1604, found *m*/*z* 231.1608.

***N*-(3-Methylphenyl)-1-phenyl-5-(propan-2-yl)-1*H*-1,2,4-triazol-3-amine (4w).** Yield 204 mg (87%), colorless needles, mp 128–130 °C (from $CHCl_3$–*n*-hexane 1 : 10 mixture). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.32 (d, J = 6.8 Hz, 6H, $2CH_3$), 2.33 (s, 3H, CH_3), 3.11 (sept, J = 6.8 Hz, 1H, CH), 6.60 (s, 1H, NH), 6.72–6.74 (m, 1H, Ar), 7.14–7.20 (m, 1H, Ar), 7.22 (br. s, 1H, Ar), 7.34–7.38 (m, 1H, Ar), 7.42–7.54 (m, 5H, Ar). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 21.8 (three $\underline{C}H_3$), 25.9, 113.5, 117.0, 121.5, 125.5, 128.6, 129.1, 129.5, 137.8, 138.9, 141.0, 159.7, 159.8. HRMS (ESI) calcd for $C_{18}H_{21}N_4$ $[M + H]^+$ *m*/*z* 293.1761, found *m*/*z* 293.1766.

***N*-(3-Methylphenyl)-1,5-diphenyl-1*H*-1,2,4-triazol-3-amine (4x).** Yield 219 mg (84%), colorless needles, mp 132–134 °C (from $CHCl_3$–*n*-hexane 1 : 10 mixture). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.17 (s, 3H, CH_3), 6.58–6.62 (m, 1H, Ar), 6.73 (s, 1H, NH), 7.01–7.11 (m, 3H, Ar), 7.17–7.29 (m, 6H, Ar), 7.34–7.35 (m, 2H, Ar), 7.36–7.37 (m, 2H, Ar). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 21.8, 113.7, 117.2, 121.7, 125.4, 128.1, 128.4, 128.7, 129.0, 129.1, 129.4, 130.1, 138.5, 139.0, 140.9, 152.5, 160.1. HRMS (ESI) calcd for $C_{21}H_{19}N_4$ $[M + H]^+$ *m*/*z* 327.1604, found *m*/*z* 327.1616.

***N*-(1-*tert*-Butyl-1*H*-1,2,4-triazol-3-yl)pyridin-2-amine (4y).** Yield 139 mg (80%), colorless needles, mp 129–130 °C (from

EtOH). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.62 (s, 9H, $3CH_3$), 6.80–6.84 (m, 1H, Ar), 7.61–7.67 (m, 1H, Ar), 7.90 (s, 1H, CH), 8.01–8.04 (m, 1H, Ar), 8.32–8.34 (m, 1H, Ar), 8.40 (s, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 29.4, 58.2, 110.0, 115.9, 138.2, 138.5, 148.2, 154.1, 159.2. HRMS (ESI) calcd for $C_{11}H_{16}N_5$ $[M + H]^+$ m/z 218.1400, found m/z 218.1409.

***N*-(1,5-Diphenyl-1*H*-1,2,4-triazol-3-yl)pyridin-2-amine (4z).** Yield 200 mg (80%), colorless needles, mp 208–210 °C (from $CHCl_3$–*n*-hexane 1 : 10 mixture). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.84–6.88 (m, 1H, Ar), 7.32–7.44 (m, 8H, Ar + NH), 7.50–7.54 (m, 2H, Ar), 7.63–7.69 (m, 1H, Ar), 8.13–8.17 (m, 1H, Ar), 8.37–8.39 (m, 2H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 110.5, 116.3, 125.5, 128.0, 128.6, 128.7, 129.1, 129.4, 130.2, 138.3, 138.4, 148.2, 152.8, 153.7, 159.0. HRMS (ESI) calcd for $C_{19}H_{16}N_5$ $[M + H]^+$ m/z 314.1400, found m/z 314.1414.

1-*tert*-Butyl-*N*-(naphthalen-1-yl)-1*H*-1,2,4-triazol-3-amine (4aa). Yield 183 mg (86%), colorless needles, mp 137–139 °C (from Et_2O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.64 (s, 9H, $3CH_3$), 7.36 (s, 1H, NH), 7.47–7.51 (m, 4H, Ar), 7.84–7.87 (m, 1H, Ar), 7.90 (s, 1H, CH), 8.00–8.03 (m, 1H, Ar), 8.23–8.26 (m, 1H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 29.4, 58.2, 111.9, 120.2, 120.9, 124.3, 125.5, 125.8, 126.5, 128.9, 134.4, 136.4, 138.4, 160.7. HRMS (ESI) calcd for $C_{16}H_{19}N_4$ $[M + H]^+$ m/z 267.1604, found m/z 267.1599.

***N*-(Naphthalen-1-yl)-1,5-diphenyl-1*H*-1,2,4-triazol-3-amine (4ab).** Yield 270 mg (93%), colorless needles, mp 188–189 °C (from Pr^iOH). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 7.42–7.52 (m, 14H, Ar), 7.86–7.89 (m, 1H, Ar), 8.16–8.18 (m, 1H, Ar), 8.48–8.51 (m, 1H, Ar), 9.36 (s, 1H, NH). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75 MHz): δ 113.1, 120.7, 122.4, 124.9, 125.0, 125.6, 125.8, 126.1, 127.8, 128.1, 128.61, 128.63, 129.5, 130.0, 133.9, 137.0, 138.1, 152.1, 160.5. HRMS (ESI) calcd for $C_{24}H_{19}N_4$ $[M + H]^+$ m/z 363.1604, found m/z 363.1594.

1-*tert*-Butyl-*N*-(naphthalen-2-yl)-1*H*-1,2,4-triazol-3-amine (4ac). Yield 175 mg (82%), colorless needles, mp 174–175 °C (from Et_2O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.66 (s, 9H, $3CH_3$), 7.13 (s, 1H, NH), 7.26–7.32 (m, 1H, Ar), 7.38–7.44 (m, 2H, Ar), 7.73–7.78 (m, 3H, Ar), 7.91 (s, 1H, CH), 8.14–8.15 (m, 1H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 29.4, 58.2, 110.8, 118.6, 123.3, 126.3, 127.1, 127.7, 128.8, 128.9, 134.8, 138.2, 138.9, 160.3. HRMS (ESI) calcd for $C_{16}H_{19}N_4$ $[M + H]^+$ m/z 267.1604, found m/z 267.1609.

***N*-(Naphthalen-2-yl)-1,5-diphenyl-1*H*-1,2,4-triazol-3-amine (4ad).** Yield 252 mg (87%), colorless needles, mp 208–209 °C (from Pr^iOH). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 7.24–7.29 (m, 1H, Ar), 7.36–7.55 (m, 11H, Ar), 7.63–7.81 (m, 4H, Ar), 8.21 (m, 1H, Ar), 9.77 (s, 1H, NH). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75 MHz): δ 109.8, 118.9, 122.9, 125.6, 126.2, 126.5, 127.4, 127.8, 128.0, 128.3, 128.6, 128.7, 129.5, 130.0, 134.2, 138.1, 139.3, 151.9, 159.8. HRMS (ESI) calcd for $C_{24}H_{19}N_4$ $[M + H]^+$ m/z 363.1604, found m/z 363.1598.

***N*-(1-*tert*-Butyl-1*H*-1,2,4-triazol-3-yl)pyridin-3-amine (4ae).** Yield 167 mg (96%), colorless needles, mp 138–140 °C (from $CHCl_3$–*n*-hexane 1 : 10 mixture). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.62 (s, 9H, $3CH_3$), 7.21–7.25 (m, 1H, Ar), 7.92 (s, 1H, CH), 7.99 (s, 1H, Ar), 8.07–8.15 (m, 2H, Ar), 8.66 (s, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 29.4, 58.3, 122.5, 123.8, 138.25, 138.33, 138.6, 141.2, 159.9. HRMS (ESI) calcd for $C_{11}H_{16}N_5$ $[M + H]^+$ m/z 218.1400, found m/z 218.1407.

3-Methyl-*N*-phenyl-1*H*-1,2,4-triazol-5-amine (8a). Yield 117 mg (84%), colorless needles, mp 142–145 °C (from EtOH–H_2O 3 : 1 mixture). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 2.27 (s, 3H, CH_3), 6.73–6.78 (m, 1H, Ar), 7.15–7.21 (m, 2H, Ar), 7.48–7.52 (m, 2H, Ar), 8.95 (s, 1H, NH), 12.78 (s, 1H, NH). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75 MHz): δ 11.7, 115.5, 118.6, 128.6, 142.4, 150.9, 160.2. HRMS (ESI) calcd for $C_9H_{11}N_4$ $[M + H]^+$ m/z 175.0978, found m/z 175.0980.

3-Methyl-*N*-(4-methylphenyl)-1*H*-1,2,4-triazol-5-amine (8b). Yield 98 mg (65%), colorless needles, mp 136–138 °C (from Et_2O). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 2.20 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 6.98–7.01 (m, 2H, Ar), 7.38–7.41 (m, 2H, Ar), 8.82 (s, 1H, NH), 12.72 (s, 1H, NH). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75 MHz): δ 9.7, 20.3, 115.6, 122.6, 129.0, 143.2, 167.0, 169.0. HRMS (ESI) calcd for $C_{10}H_{13}N_4$ $[M + H]^+$ m/z 189.1135, found m/z 189.1143.

3-Benzyl-*N*-phenyl-1*H*-1,2,4-triazol-5-amine (8c). Yield 166 mg (83%), colorless needles, mp 218–220 °C (from EtOH–H_2O 5 : 1 mixture). ^{1}H NMR (DMSO-d_6, 300 MHz) (two tautomers): δ 3.87 and 4.00 (two s, 2H, CH_2), 6.72–6.77 (m, 1H, Ar), 7.15–7.35 (m, 7H, Ar), 7.48–7.51 (m, 2H, Ar), 9.01 and 9.25 (two s, 1H, NH), 12.29 and 13.01 (two s, 1H, NH). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75 MHz): δ 32.0, 115.5, 118.7, 126.6, 128.5, 128.6, 128.7, 137.1, 142.3, 153.5, 160.3. HRMS (ESI) calcd for $C_{15}H_{15}N_4$ $[M + H]^+$ m/z 251.1291, found m/z 251.1299.

***N*,3-Diphenyl-1*H*-1,2,4-triazol-5-amine (8d).** Yield 123 mg (65%), colorless needles, mp 222–224 °C (from EtOH). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 6.80–6.85 (m, 1H, Ar), 7.22–7.28 (m, 2H, Ar), 7.48–7.55 (m, 3H, Ar), 7.58–7.61 (m, 2H, Ar), 7.97–8.00 (m, 2H, Ar), 9.31 (s, 1H, NH), 13.54 (s, 1H, NH). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75 MHz): δ 115.9, 119.3, 123.7, 125.7, 128.7, 128.9, 142.1, 152.6, 160.6 (one signal of aromatic carbon is broadened and merged into the background or overlapped). HRMS (ESI) calcd for $C_{14}H_{13}N_4$ $[M + H]^+$ m/z 237.1135, found m/z 237.1145.

3-(4-Methylphenyl)-*N*-phenyl-1*H*-1,2,4-triazol-5-amine (8e). Yield 134 mg (67%), colorless needles, mp 220–222 °C (from EtOH–H_2O 3 : 1 mixture). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 2.36 (s, 3H, CH_3), 6.78–6.83 (m, 1H, Ar), 7.21–7.26 (m, 2H, Ar), 7.30–7.33 (m, 2H, Ar), 7.57–7.60 (m, 2H, Ar), 7.85–7.88 (m, 2H, Ar), 9.42 (s, 1H, NH), 13.57 (s, 1H, NH). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75 MHz): δ 21.0, 115.8, 119.2, 125.7, 128.7, 129.4, 139.1, 142.0, 153.7, 158.8 (one signal of aromatic carbon is broadened and merged into the background or overlapped). HRMS (ESI) calcd for $C_{15}H_{15}N_4$ $[M + H]^+$ m/z 251.1291, found m/z 251.1301.

3-(4-Methoxyphenyl)-*N*-phenyl-1*H*-1,2,4-triazol-5-amine (8f). Yield 151 mg (71%), colorless needles, mp 230–231 °C (from EtOH–H_2O 3 : 1 mixture). ^{1}H NMR (DMSO-d_6, 300 MHz) (two tautomers): δ 3.82 (s, 2H, CH_2), 6.75–6.80 (m, 1H, Ar), 7.00–7.11 (m, 2H, Ar), 7.19–7.24 (m, 2H, Ar), 7.57–7.59 (m, 2H, Ar), 7.89–7.92 (m, 2H, Ar), 9.16 and 9.39 (two s, 1H, NH), 12.53 and 13.49 (two s, 1H, NH). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75 MHz):

δ 55.3, 114.5, 115.6, 118.8, 120.0, 127.4, 128.6, 128.9, 142.3, 152.2, 160.6. HRMS (ESI) calcd for $C_{15}H_{15}N_4O$ $[M + H]^+$ *m*/*z* 267.1240, found *m*/*z* 267.1232.

***N*-Phenyl-3-(pyridin-2-yl)-1*H*-1,2,4-triazol-5-amine (8g).** Yield 118 mg (62%), colorless needles, mp 181–183 °C (from EtOH–H_2O 1 : 1 mixture). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 6.77–6.82 (m, 1H, Ar), 7.21–7.26 (m, 2H, Ar), 7.50–7.54 (m, 1H, Ar), 7.54–7.61 (m, 2H, Ar), 8.00–8.01 (m, 2H, Ar), 8.69–8.70 (m, 1H, Ar), 9.25 (s, 1H, NH), 14.02 (s, 1H, NH). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz): δ 115.7, 119.1, 121.1, 124.9, 128.7, 137.9, 142.2, 146.3, 149.6, 151.7, 160.9. HRMS (ESI) calcd for $C_{13}H_{12}N_5$ $[M + H]^+$ *m*/*z* 238.1087, found *m*/*z* 238.1095.

3-Cyclohexyl-*N*-phenyl-1*H*-1,2,4-triazol-5-amine (8h). Yield 170 mg (88%), colorless needles, mp 210–212 °C (from EtOH–H_2O 3 : 1 mixture). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 1.19–1.51 (m, 5H, cyclohexyl), 1.63–1.78 (m, 3H, cyclohexyl), 1.91–1.96 (m, 2H, cyclohexyl), 2.62–2.69 (m, 1H, cyclohexyl), 6.72–6.77 (m, 1H, Ar), 7.15–7.21 (m, 2H, Ar), 7.48–7.52 (m, 2H, Ar), 9.12 (s, 1H, NH), 12.93 (s, 1H, NH). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz): δ 25.3, 25.5, 31.0, 35.5, 115.5, 118.6, 128.6, 142.3, 159.1, 161.0. HRMS (ESI) calcd for $C_{14}H_{19}N_4$ $[M + H]^+$ *m*/*z* 243.1604, found *m*/*z* 243.1597.

3-Cyclohexyl-*N*-(4-methylphenyl)-1*H*-1,2,4-triazol-5-amine (8i). Yield 133 mg (65%), colorless needles, mp 212–214 °C (from EtOH–H_2O 3 : 1 mixture). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 1.16–1.53 (m, 5H, cyclohexyl), 1.64–1.77 (m, 3H, cyclohexyl), 1.91–1.95 (m, 2H, cyclohexyl), 2.20 (s, 3H, CH_3), 2.63–2.70 (m, 1H, cyclohexyl), 6.97–7.00 (m, 2H, Ar), 7.38–7.41 (m, 2H, Ar), 8.85 (s, 1H, NH), 12.70 (s, 1H, NH). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz): δ 20.3, 25.3, 25.5, 30.9, 35.3, 115.5, 127.0, 129.0, 140.0, 158.7, 160.0. HRMS (ESI) calcd for $C_{15}H_{21}N_4$ $[M + H]^+$ *m*/*z* 257.1761, found *m*/*z* 257.1751.

5-(Phenylamino)-3-(pyridin-3-yl)-1*H*-1,2,4-triazol-4-ium chloride (8j). Yield 192 mg (88%), colorless needles, mp 189–190 °C (from Et_2O). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 6.89–6.93 (m, 1H, Ar), 7.27–7.32 (m, 2H, Ar), 7.60–7.63 (m, 2H, Ar), 8.07 (s, 1H, Ar), 8.92–8.94 (m, 2H, Ar), 9.30 (s, 1H, Ar), 9.73 (s, 1H, NH) (two NH signals are broadened and merged into the background). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz): δ 116.6, 120.6, 127.2, 128.9, 129.4, 139.7, 140.3, 140.7, 142.7, 152.7, 155.5. HRMS (ESI) calcd for $C_{13}H_{12}N_5$ $[M - Cl^-]^+$ *m*/*z* 238.1087, found *m*/*z* 238.1096.

5-(Phenylamino)-3-(thiophen-2-yl)-1*H*-1,2,4-triazol-4-ium chloride (8k). Yield 149 mg (67%), colorless needles, mp 102–104 °C (from Et_2O). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 6.83–6.88 (m, 1H, Ar), 7.17–7.20 (m, 1H, Ar), 7.23–7.28 (m, 2H, Ar), 7.52–7.54 (m, 2H, Ar), 7.66–7.69 (m, 2H, Ar), 9.43 (s, 1H, NH) (two NH signals are broadened and merged into the background). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz): δ 116.3, 119.9, 126.3, 127.8, 128.1, 128.8, 131.3, 141.3, 150.1, 157.3. HRMS (ESI) calcd for $C_{12}H_{11}N_4S$ $[M - Cl^-]^+$ *m*/*z* 243.0699, found *m*/*z* 243.0709.

***N*-[5-(Benzylsulfanyl)-1*H*-1,2,4-triazol-3-yl]pyridin-2-amine (8l).** Yield 165 mg (73%), colorless needles, mp 182–183 °C (from EtOH–H_2O 3 : 1 mixture). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 4.32 (s, 2H, CH_2), 6.89–7.01 (m, 2H, Ar), 7.21–7.33 (m, 3H, Ar), 7.36–7.42 (m, 2H, Ar), 7.65–7.71 (m, 1H, Ar), 8.22–8.24 (m, 1H, Ar), 10.69 (s, 1H, NH), 13.07 (s, 1H, NH). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz): δ 35.0, 110.5, 116.1, 127.1, 128.4, 128.8, 138.2, 138.3, 147.2, 151.7, 152.8, 155.7. HRMS (ESI) calcd for $C_{14}H_{14}N_5S$ $[M + H]^+$ *m*/*z* 284.0964, found *m*/*z* 284.0967.

5-(Benzylsulfanyl)-*N*-phenyl-1*H*-1,2,4-triazol-3-amine (8m). Yield 185 mg (82%), colorless needles, mp 147–149 °C (from EtOH–H_2O 3 : 1 mixture). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.34 (s, 2H, CH_2), 6.96–7.00 (m, 2H, Ar), 7.22–7.39 (m, 9H, Ar + NH) (one NH signal is broadened and merged into the background). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 37.8, 117.6, 122.0, 127.9, 128.9, 129.0, 129.5, 137.1, 140.4, 153.2, 159.1. HRMS (ESI) calcd for $C_{15}H_{15}N_4S$ $[M + H]^+$ *m*/*z* 283.1012, found *m*/*z* 283.1024.

1-Benzyl-3-cyclohexyl-5-(phenylamino)-1*H*-1,2,4-triazol-4-ium chloride (9a). Yield 283 mg (96%), colorless needles, mp 170–171 °C (from CH_2Cl_2–hexane 1 : 10 mixture). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 1.17–1.51 (m, 5H, cyclohexyl), 1.62–1.75 (m, 3H, cyclohexyl), 1.89–1.93 (m, 2H, cyclohexyl), 2.57–2.67 (m, 1H, cyclohexyl), 5.49 (s, 2H, CH_2), 7.08–7.13 (m, 1H, Ar), 7.29–7.39 (m, 7H, Ar), 7.50–7.53 (m, 2H, Ar), 10.46 (s, 1H, NH) (one NH signal is broadened and merged into the background). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz): δ 25.2, 25.4, 30.5, 35.8, 50.0, 120.0, 123.5, 127.5, 127.8, 128.6, 129.2, 135.8, 138.7, 149.2, 159.1. HRMS (ESI) calcd for $C_{21}H_{25}N_4$ $[M\text{-}Cl^-]^+$ *m*/*z* 333.2074, found *m*/*z* 333.2081.

1-Benzyl-3-cyclohexyl-5-(pyridin-2-ylamino)-1*H*-1,2,4-triazol-4-ium chloride (9b). Yield 239 mg (81%), colorless needles, mp 112–115 °C (from CH_2Cl_2–hexane 1 : 10 mixture). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.17–1.61 (m, 5H, cyclohexyl), 1.72–1.86 (m, 3H, cyclohexyl), 2.02–2.06 (m, 2H, cyclohexyl), 2.71–2.81 (m, 1H, cyclohexyl), 5.87 (s, 2H, CH_2), 7.10–7.14 (m, 1H, Ar), 7.27–7.35 (m, 3H, Ar), 7.62–7.66 (m, 2H, Ar), 7.91–7.97 (m, 1H, Ar), 8.09–8.11 (m, 1H, Ar), 8.53–8.56 (m, 1H, Ar) (two NH signals are broadened and merged into the background). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 25.8, 31.3, 36.8, 52.0, 116.8, 117.6, 128.4, 128.8, 129.0, 134.8, 138.3, 142.8, 146.8, 150.6, 160.5 (signals of two aliphatic carbons overlap). HRMS (ESI) calcd for $C_{20}H_{24}N_5$ $[M - Cl^-]^+$ *m*/*z* 334.2026, found *m*/*z* 334.2040.

3-Cyclohexyl-1-(4-methylbenzyl)-5-(phenylamino)-1*H*-1,2,4-triazol-4-ium chloride (9c). Yield 232 mg (76%), colorless needles, mp 155–157 °C (from CH_2Cl_2–hexane 1 : 10 mixture). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.22–1.51 (m, 5H, cyclohexyl), 1.67–1.70 (m, 1H, cyclohexyl), 1.77–1.80 (m, 2H, cyclohexyl), 1.99–2.02 (m, 2H, cyclohexyl), 2.30 (s, 3H, CH_3), 2.63–2.68 (m, 1H, cyclohexyl), 5.32 (s, 2H, CH_2), 7.01–7.23 (m, 9H, Ar), 10.54 (s, 1H, NH) (one NH signal is broadened and merged into the background). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 21.3, 25.52, 25.55, 30.4, 35.3, 52.6, 121.2, 125.5, 128.4, 129.6, 130.4, 136.2, 138.6, 146.7, 155.8, 170.8. HRMS (ESI) calcd for $C_{22}H_{27}N_4$ $[M - Cl^-]^+$ *m*/*z* 347.2230, found *m*/*z* 347.2240.

1-Benzyl-5-(phenylamino)-3-(thiophen-2-yl)-1*H*-1,2,4-triazol-4-ium chloride (9d). Yield 138 mg (47%), colorless needles, mp 174–176 °C (from Et_2O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.28 (s, 2H, CH_2), 6.06 (br. s, 1H, NH), 7.00–7.09 (m, 3H, Ar), 7.26–7.37

(m, 9H, Ar), 7.70 (s, 1H, Ar) (one NH signal is broadened and merged into the background). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 52.3, 118.3, 122.9, 126.4, 126.5, 127.6, 127.8, 128.8, 129.5, 133.9, 134.5, 139.4, 151.4, 154.9 (signals of two aromatic carbons overlap). HRMS (ESI) calcd for $C_{19}H_{17}N_4S$ $[M - Cl^-]^+$ m/z 333.1168, found m/z 333.1168.

1-Benzyl-5-(pyridin-2-ylamino)-3-(thiophen-2-yl)-1*H*-1,2,4-triazol-4-ium chloride (9e). Yield 160 mg (54%), colorless needles, mp 191–193 °C (from Et_2O). ^1H NMR ($CDCl_3$, 300 MHz): δ 5.80 (s, 2H, CH_2), 7.09–7.15 (m, 3H, Ar), 7.30–7.35 (m, 4H, Ar), 7.62–7.70 (m, 3H, Ar), 7.98–8.11 (m, 2H, Ar), 8.74 (s, 1H, NH) (one NH signal is broadened and merged into the background). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz)(two tautomers): δ 51.9, 116.8 and 117.1, 126.9 and 127.1, 127.9, 128.4, 128.7, 128.9, 132.8, 135.0, 136.0, 144.8, 148.0 and 148.5, 150.0, 154.3 and 154.6, 159.9 (signals of two aromatic carbons overlap). HRMS (ESI) calcd for $C_{18}H_{16}N_5S$ $[M - Cl^-]^+$ m/z 334.1121, found m/z 334.1136.

1-Benzyl-*N*,3-diphenyl-1*H*-1,2,4-triazol-5-amine (9f). Yield 178 mg (68%), colorless needles, mp 150–152 °C (from Et_2O). ^1H NMR ($CDCl_3$, 300 MHz): δ 5.31 (s, 2H, CH_2), 5.82 (s, 1H, NH), 6.96–7.02 (m, 1H, Ar), 7.28–7.47 (m, 12H, Ar), 8.12–8.15 (m, 2H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 51.7, 117.5, 122.4, 126.3, 127.4, 128.6, 128.8, 129.1, 129.4, 129.5, 131.4, 134.8, 139.9, 151.7, 159.1. HRMS (ESI) calcd for $C_{21}H_{19}N_4$ $[M + H]^+$ m/z 327.1604, found m/z 327.1602.

4-Benzyl-*N*-phenyl-4*H*-1,2,4-triazol-3-amine (10a). Yield 92 mg (46%), colorless needles, mp 195–197 °C (from CH_2Cl_2–Et_2O 1 : 1 mixture). ^1H NMR (DMSO-d_6, 300 MHz): δ 5.26 (s, 2H, CH_2), 6.84–6.89 (m, 1H, Ar), 7.20–7.37 (m, 7H, Ar), 7.53–7.56 (m, 2H, Ar), 8.27, 8.69 (two s, 2H, CH + NH). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75 MHz): δ 45.5, 116.5, 120.3, 127.1, 127.8, 128.7, 128.8, 136.5, 141.1, 141.5, 150.5. HRMS (ESI) calcd for $C_{15}H_{15}N_4$ $[M + H]^+$ m/z 251.1291, found m/z 251.1300.

***N*,4-Diphenyl-4*H*-1,2,4-triazol-3-amine (10b).** Yield 74 mg (39%), colorless needles, mp 213–215 °C (from Et_2O). ^1H NMR (DMSO-d_6, 300 MHz): δ 6.81–6.87 (m, 1H, Ar), 7.18–7.24 (m, 2H, Ar), 7.38–7.44 (m, 2H, Ar), 7.50–7.57 (m, 5H, Ar), 8.49, 8.49 (two s, 2H, CH + NH). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75 MHz): δ 116.6, 120.2, 125.3, 128.6, 128.7, 129.8, 133.3, 141.4, 141.9, 149.9. HRMS (ESI) calcd for $C_{14}H_{13}N_4$ $[M + H]^+$ m/z 237.1135, found m/z 237.1138.

***N*,4-Bis(4-methylphenyl)-4*H*-1,2,4-triazol-3-amine (10c).** Yield 46 mg (22%), colorless needles, mp 232–234 °C (from *n*-hexane). ^1H NMR ($CDCl_3$, 300 MHz): δ 2.29 (s, 3H, CH_3), 2.46 (s, 3H, CH_3), 5.92 (s, 1H, NH), 7.08–7.11 (m, 2H, Ar), 7.25–7.28 (m, 2H, Ar), 7.37–7.40 (m, 4H, Ar), 7.96 (s, 1H, CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 20.8, 21.4, 117.5, 125.7, 129.8, 130.1, 131.3, 131.7, 137.0, 140.0, 140.4, 150.6. HRMS (ESI) calcd for $C_{16}H_{17}N_4$ $[M + H]^+$ m/z 265.1448, found m/z 265.1445.

***N*,5,7-Triphenyl-4,5,6,7-tetrahydro[1,2,4]triazolo[1,5-*a*]pyrimidin-2-amine (12a).** Yield 267 mg (91%), colorless needles, mp 270–271 °C (from EtOH). ^1H NMR (DMSO-d_6, 300 MHz): δ 2.01–2.13 (m, 1H, C^6H), 2.41–2.50 (m, 1H, C^6H), 4.68–4.72 (m, 1H, C^5H), 5.29–5.34 (m, 1H, C^7H), 6.68 (t, J = 7.3 Hz, 1H, NH), 7.07–7.12 (m, 2H, Ar), 7.24–7.40 (m, 11H, Ar), 7.45–7.47 (m, 2H, Ar), 8.83 (s, 1H, NH). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75 MHz): δ 42.7, 53.9, 58.3, 115.5, 118.5, 126.6, 127.0, 127.5,127.6, 128.3, 128.4, 128.5, 140.6, 141.9, 142.4, 154.5, 157.4. HRMS (ESI) calcd for $C_{23}H_{22}N_5$ $[M + H]^+$ m/z 368.1870, found m/z 368.1872.

***N*-Phenyl-4a′,5′,6′,7′,8′,8a′-hexahydro-4′*H*-spiro[cyclohexane-1,9′-[1,2,4]triazolo[5,1-*b*]quinazolin]-2′-amine (12b).** Yield 248 mg (92%), colorless needles, mp 240–242 °C (from EtOH). ^1H NMR (DMSO-d_6, 300 MHz): δ 0.96–2.17 (m, 19H, aliphatic CH), 3.74–3.75 (m, 1H, H-4a′), 6.68–6.73 (m, 2H, Ph + NH), 7.12–7.17 (m, 2H, Ph), 7.46–7.50 (m, 2H, Ph), 8.64 (s, 1H, NH). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75 MHz): δ 19.2, 20.3, 21.6, 21.8, 24.9, 25.2, 29.8, 31.7, 35.7, 36.7, 44.9, 58.8, 115.4, 118.2, 128.4, 142.7, 151.4, 156.7. HRMS (ESI) calcd for $C_{20}H_{28}N_5$ $[M + H]^+$ m/z 338.2339, found m/z 338.2348.

5-Methyl-*N*-(1-methyl-1*H*-benzimidazol-2-yl)-2-(pyridin-3-yl)[1,2,4]triazolo[1,5-*a*]pyrimidin-7-amine (12c). Yield 217 mg (76%), colorless needles, mp 190–192 °C (from EtOH). ^1H NMR (DMSO-d_6, 300 MHz): δ 2.48 (s, 3H, CH_3), 3.69 (s, 3H, CH_3), 6.73 (s, 1H, Ar), 7.22–7.35 (m, 4H, Ar), 7.45–7.58 (m, 2H, Ar), 8.43–8.47 (m, 1H, Ar), 8.67 (br. s, 1H, NH), 9.29 (br. s, 1H, Ar). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75 MHz): δ 24.4, 28.7, 96.8, 109.6, 111.1, 122.5, 122.8, 124.0, 128.4, 129.2, 129.6, 131.5, 134.0, 147.7, 150.1, 150.2, 150.7, 157.1, 160.3. HRMS (ESI) calcd for $C_{19}H_{17}N_8$ $[M + H]^+$ m/z 357.1571, found m/z 357.1570.

1-Methyl-*N*-phenyl-1*H*-benzimidazol-2-amine (12d). Yield 171 mg (96%), colorless needles, mp 198–200 °C (from EtOH). ^1H NMR (DMSO-d_6, 300 MHz): δ 3.71 (s, 3H, CH_3), 6.95 (t, J = 7.3 Hz, 1H, Ar), 7.02–7.09 (m, 2H, Ar), 7.28–7.40 (m, 4H, Ar), 7.86–7.88 (m, 2H, Ar), 8.91 (s, 1H, NH). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75 MHz): δ 29.0, 108.0, 116.1, 117.9, 119.6, 120.8, 121.0, 128.6, 134.2, 141.0, 141.7, 150.5. HRMS (ESI) calcd for $C_{14}H_{14}N_3$ $[M + H]^+$ m/z 224.1182, found m/z 224.1190.

1-Methyl-*N*-(3-methylphenyl)-1*H*-benzimidazol-2-amine (12e). Yield 177 mg (93%), colorless needles, mp 207–209 °C (from EtOH). ^1H NMR (DMSO-d_6, 300 MHz): δ 2.31 (s, 3H, CH_3), 3.69 (s, 3H, CH_3), 6.76–6.79 (m, 1H, Ar), 7.04–7.08 (m, 2H, Ar), 7.17–7.23 (m, 1H, Ar), 7.27–7.30 (m, 1H, Ar), 7.37–7.40 (m, 1H, Ar), 7.64–7.70 (m, 2H, Ar), 8.83 (br. s, 1H, NH). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75 MHz): δ 21.4, 29.0, 108.0, 115.2, 116.0, 118.4, 119.7, 120.8, 121.8, 128.5, 134.2, 137.7, 140.9, 141.6, 150.4. HRMS (ESI) calcd for $C_{15}H_{16}N_3$ $[M + H]^+$ m/z 238.1339, found m/z 238.1338.

1-Methyl-*N*-(4-methylphenyl)-1*H*-benzimidazol-2-amine (12f). Yield 163 mg (86%), colorless needles, mp 180–182 °C (from EtOH). ^1H NMR (DMSO-d_6, 300 MHz): δ 2.26 (s, 3H, CH_3), 3.69 (s, 3H, CH_3), 7.02–7.05 (m, 2H, Ar), 7.11–7.14 (m, 2H, Ar), 7.26–7.29 (m, 1H, Ar), 7.34–7.37 (m, 1H, Ar), 7.73–7.78 (m, 2H, Ar), 8.79 (br. s, 1H, NH). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75 MHz): δ 20.4, 28.9, 107.9, 116.0, 118.0, 119.5, 120.7, 129.0, 129.7, 134.3, 138.4, 141.9, 150.7. HRMS (ESI) calcd for $C_{15}H_{16}N_3$ $[M + H]^+$ m/z 238.1339, found m/z 238.1335.

***N*-(4-*tert*-Butylphenyl)-1-methyl-1*H*-benzimidazol-2-amine (12g).** Yield 199 mg (89%), colorless needles, mp 220–222 °C (from EtOH). ^1H NMR (DMSO-d_6, 300 MHz): δ 1.28 (s, 9H, $3CH_3$), 3.69 (s, 3H, CH_3), 7.00–7.07 (m, 2H, Ar), 7.26–7.36 (m, 4H, Ar), 7.72–7.77 (m, 2H, Ar), 8.81 (s, 1H, NH). $^{13}C\{^1H\}$ NMR (DMSO-

d_6, 75 MHz): δ 28.9, 31.3, 33.9, 107.9, 116.0, 117.8, 119.5, 120.7, 125.2, 134.3, 138.4, 141.9, 143.3, 150.8. HRMS (ESI) calcd for $C_{18}H_{22}N_3$ $[M + H]^+$ m/z 280.1808, found m/z 280.1810.

***N*-(Naphthalen-2-yl)pyridin-2-amine (12h).** Yield 160 mg (91%), colorless needles, mp 138–140 °C (from EtOH). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.76–6.80 (m, 1H, Ar), 6.97–7.01 (m, 1H, Ar), 7.24 (br. s, 1H, NH), 7.38–7.53 (m, 4H, Ar), 7.74–7.84 (m, 4H, Ar), 8.26–8.29 (m, 1H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 108.7, 115.3, 115.6, 121.5, 124.4, 126.6, 127.1, 127.7, 129.2, 130.1, 134.5, 137.9, 138.3, 148.5, 156.2. HRMS (ESI) calcd for $C_{15}H_{13}N_2$ $[M + H]^+$ m/z 221.1073, found m/z 221.1074.

***N*-(Pyridin-2-yl)pyridin-2-amine (12i).** Yield 131 mg (96%), yellow prism, mp 89–91 °C. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 7.22–7.26 (m, 2H, Ar), 7.34–7.37 (m, 2H, Ar), 8.02–8.08 (m, 2H, Ar), 8.37–8.39 (m, 2H, Ar), 11.52 (s, 1H, NH). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75 MHz): δ 114.0, 117.6, 141.7, 142.2, 151.6. HRMS (ESI) calcd for $C_{10}H_{10}N_3$ $[M + H]^+$ m/z 172.0869, found m/z 172.0873.

***N*-(2,6-Dimethylphenyl)pyridin-2-amine (12j).** Yield 130 mg (82%), yellow prism, mp 115–117 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.23 (s, 6H, $2CH_3$), 6.02–6.06 (m, 1H, Ar), 6.63–6.67 (m, 2H, Ar + NH), 7.14 (s, 3H, Ar), 7.37–7.43 (m, 1H, Ar), 8.09–8.12 (m, 1H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 18.5, 106.4, 113.7, 127.2, 128.8, 136.1, 136.8, 138.7, 147.1, 157.4. HRMS (ESI) calcd for $C_{13}H_{15}N_2$ $[M + H]^+$ m/z 199.1230, found m/z 199.1238.

3-Methyl-*N*-phenylpyridin-2-amine (12k). Yield 127 mg (86%), colorless prism, mp 114–116 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.25 (s, 3H, CH_3), 6.12 (br. s, 1H, NH), 6.69–6.74 (m, 1H, Ar), 6.97–7.03 (m, 1H, Ar), 7.28–7.38 (m, 3H, Ar), 7.54–7.57 (m, 2H, Ar), 8.11–8.13 (m, 1H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 17.5, 115.4, 119.7, 122.1, 123.0, 129.1, 138.0, 141.0, 145.6, 154.1. HRMS (ESI) calcd for $C_{12}H_{13}N_2$ $[M + H]^+$ m/z 185.1073, found m/z 185.1071.

3-Methyl-*N*-(pyridin-2-yl)pyridin-2-amine (12l). Yield 119 mg (80%), yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.31 (s, 3H, CH_3), 6.77–6.81 (m, 1H, Ar), 6.87–6.90 (m, 1H, Ar), 7.17 (br. s, 1H, NH), 7.39–7.43 (m, 1H, Ar), 7.63–7.69 (m, 1H, Ar), 8.15–8.17 (m, 1H, Ar), 8.21–8.23 (m, 1H, Ar), 8.40–8.43 (m, 1H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 17.6, 112.5, 116.4, 117.1, 119.2, 138.2, 138.3, 145.1, 147.6, 152.7, 153.8. HRMS (ESI) calcd for $C_{11}H_{12}N_3$ $[M + H]^+$ m/z 186.1026, found m/z 186.1021.

6-Methyl-*N*-phenylpyridin-2-amine (12m). Yield 140 mg (95%), yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.40 (s, 3H, CH_3), 6.54–6.57 (m, 1H, Ar), 6.67–6.70 (m, 2H, Ar + NH), 6.96–7.02 (m, 1H, Ar), 7.21–7.37 (m, 5H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 24.3, 105.0, 114.5, 120.4, 122.8, 129.4, 138.3, 140.8, 155.6, 157.3. HRMS (ESI) calcd for $C_{12}H_{13}N_2$ $[M + H]^+$ m/z 185.1073, found m/z 185.1079.

***N*-(2,6-Dimethylphenyl)-6-methylpyridin-2-amine (12n).** Yield 146 mg (86%), colorless needles, mp 91–92 °C (from hexane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.23 (s, 6H, $2CH_3$), 2.42 (s, 3H, CH_3), 5.75–5.78 (m, 1H, Ar), 6.10 (br. s, 1H, NH), 6.49–6.51 (m, 1H, Ar), 7.12–7.13 (m, 3H, Ar), 7.23–7.28 (m, 1H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 18.6, 24.4, 102.5, 113.2, 126.8, 128.7, 136.7, 137.0, 138.4, 157.3, 157.4. HRMS (ESI) calcd for $C_{14}H_{17}N_2$ $[M + H]^+$ m/z 213.1386, found m/z 213.1387.

***N*-(2,6-Diisopropylphenyl)-6-methylpyridin-2-amine (12o).** Yield 158 mg (74%), colorless needles, mp 123–125 °C (from hexane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.13 (d, J = 6.9 Hz, 12H, $4CH_3$), 2.41 (s, 3H, CH_3), 3.22 (sept, J = 6.9 Hz, 2H, 2CH), 5.73–5.76 (m, 1H, Ar), 6.16 (br. s, 1H, NH), 6.46–6.48 (m, 1H, Ar), 7.20–7.32 (m, 4H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 24.0, 24.5, 28.4, 102.5, 113.0, 124.1, 128.1, 133.7, 138.2, 148.1, 157.2, 159.0. HRMS (ESI) calcd for $C_{18}H_{25}N_2$ $[M + H]^+$ m/z 269.2012, found m/z 269.2018.

4-Methyl-*N*-phenylpyridin-2-amine (12p). Yield 141 mg (96%), colorless needles, mp 105–107 °C (from hexane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.26 (s, 3H, CH_3), 6.57–6.59 (m, 1H, Ar), 6.71–6.72 (m, 1H, Ar), 6.76 (br. s, 1H, NH), 7.02–7.07 (m, 1H, Ar), 7.30–7.34 (m, 4H, Ar), 8.06–8.08 (m, 1H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 21.4, 108.6, 116.7, 120.6, 122.8, 129.4, 140.8, 148.2, 149.0, 156.3. HRMS (ESI) calcd for $C_{12}H_{13}N_2$ $[M + H]^+$ m/z 185.1073, found m/z 185.1073.

N-(2,6-Dimethylphenyl)-4-methylpyridin-2-amine (12q). Yield 114 mg (67%), colorless needles, mp 86–87 °C (from hexane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.15 (s, 3H, CH_3), 2.23 (s, 6H, $2CH_3$), 5.80–5.81 (m, 1H, Ar), 6.13 (br. s, 1H, NH), 6.46–6.48 (m, 1H, Ar), 7.13–7.14 (m, 3H, Ar), 7.99–8.01 (m, 1H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 18.6, 21.3, 106.0, 115.4, 126.8, 128.7, 136.7, 136.9, 148.2, 149.1, 158.0. HRMS (ESI) calcd for $C_{14}H_{17}N_2$ $[M + H]^+$ m/z 213.1386, found m/z 213.1386.

4.7 X-ray crystal structure determination of compounds 4h, 4u and 9f

Details of the X-ray structure determinations are presented in ESI, section S3.†

Crystallographic data for **4h**, **4u** and **9f** have been deposited with the Cambridge Crystallographic Data Center. CCDC 2194495 (**4h**), CCDC 2194496 (**4u**) and CCDC 2194497 (**9f**) contain the supplementary crystallographic data for this paper.

5. Computational details

All geometry optimizations were performed by the PBE1PBE method[113,114] using the def2svp basis set[115] in the Gaussian 09[116] software package. The PBE1PBE method is one of the cost-effective and reliable DFT methods often used for describing chemical reactions involving transition metal complexes.[117–120] The calculations were performed both in vacuum and in dioxane medium (in the IEF PCM approximation).[121,122] The IPr ligand was used in the calculations instead of bulkier IPr^{*OMe} to reduce computational time. Although IPr provides lower catalytic efficiency, the general regularities of the arylation reaction were similar for both ligands according to the experimental data. For optimized molecular structures, the thermodynamic parameters were calculated at a temperature of 298 K. In the vibrational spectrum of each transition state, there is one imaginary fre-

quency corresponding to the vibration along the reaction coordinate. Molecular structures and MESP density isosurfaces were visualized using Chemcraft software.[123]

Conflicts of interest

There are no conflicts to declare.

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