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One-Pot Synthesis of 5-Amino-1,2,3-triazole Derivatives via Dipolar Azide–Nitrile Cycloaddition and Dimroth Rearrangement under Solvent-Free Conditions

Pavel S. Gribanov,*[a] Edita M. Atoian,[a] Anna N. Philippova,[a] Maxim A. Topchiy,[b] Andrey F. Asachenko,[b] and Sergey N. Osipov[a, c]

An efficient one-pot methodology for the preparation of 5-amino-1,2,3-triazole derivatives based on the combination of dipolar azide–nitrile cycloaddition with Dimroth rearrangement under solvent-free conditions has been developed.

Introduction

Due to their unique physicochemical properties, 1,2,3-triazole-containing compounds have been the subject of intensive research over the past two decades. This important class of heterocycles has found many applications in various fields: as precursors in organic synthesis,[1] ligands in homogeneous catalysis,[2] components of optoelectronic devices,[3] polymeric materials,[4] and building blocks in agricultural chemicals.[5]

Despite the fact that 1,2,3-triazoles have not yet been found in any natural source,[6] this class of molecules is often used in the design of biologically active molecules[7] and is actively investigated in medicinal chemistry along with 1,2,4-triazoles[8] in the development of a number of new potential drugs.[9]

Biologically active 1,2,3-triazoles primarily include 1,4-disubstituted 5-amino 1,2,3-triazoles[10] and 5-alkyl(aryl)amino derivatives of 1,2,3-triazole.[11] The presence of an amino group at position 5 is often responsible for the manifestation of the maximum biological activity.[6,12] Thus, derivatives of 5-amino-1,2,3-triazoles are used in the treatment of pulmonary fibrosis,[13] kidney diseases,[14] and a number of other pathologies (Figure 1).[12c,15]

The presence of an active amino group at position 5 of 1,2,3-triazole core makes the main approaches based on Cu(I)-, ruthenium- or iridium- catalyzed azide–alkyne cycloaddition,[16] organocatalytic azide–carbonyl cycloadditon,[17] reactions of *N*-tosylhydrazones with anilines[18] and other syntheses of fully substituted 1,2,3-triazoles[19] inapplicable to this type of functionalized triazoles. In this regard, the set of existing methods for the preparation of these compounds is still essentially limited to rare examples.

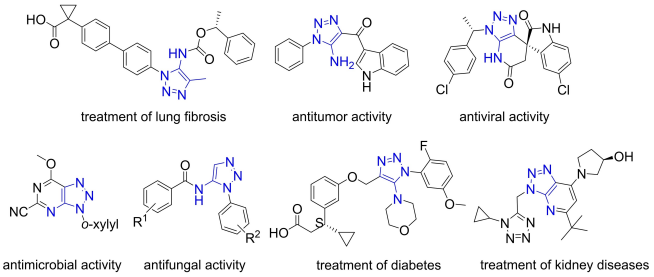

Figure 1. 5-Amino 1,2,3-triazoles and their derivatives used in medicinal chemistry.

The main synthetic route to them is dipolar [3 + 2]-cycloaddition reaction (DCR) between arylazides and monosubstituted acetonitriles, conducted in a sodium alkoxide/alcohol medium,[20] or with a catalytic amount of *tert*-amines or carbonate salts in DMSO/H_2O mixture,[10] or by generating lithium carbanion by the addition of BuLi to alkyl nitriles in THF (Figure 2).[6]

Also, a method for the preparation of aminotriazoles by one-pot cycloaddition/Raney-Ni reduction of 1-alkynyltriazenes with aryl and alkylazides has recently been described.[21]

Subsequent thermal isomerization of 5-amino-1,2,3-triazoles by Dimroth reaction has been also demonstrated on a few examples in solution.[10,20a,b] It was found that the reaction occurs irreversibly only under basic conditions, the absence of base leads to equilibrium between starting and final products.[20b]

Given the extreme importance of 5-amino-1,2,3-triazoles and their derivatives in medicinal chemistry, an important issue is the development of robust and highly efficient, and atom-economical methods for their synthesis, which would allow excluding the use of chemical reagents that cause the formation of hazardous wastes and to get the target products *via* a shorter way with maximum efficiency and selectivity.[22]

Taking into account modern environmental problems, avoiding the use of toxic organic solvents, which account for

[a] *Dr. P. S. Gribanov, E. M. Atoian, A. N. Philippova, Prof. S. N. Osipov*
A. N. Nesmeyanov Institute of Organoelement compounds
Russian Academy of Sciences
Vavilov str. 28, 119991 Moscow, Russian Federation
E-mail: gribanovps@mail.ru
https://istina.msu.ru/profile/gribanovps/
[b] *Dr. M. A. Topchiy, Prof. A. F. Asachenko*
A. V. Topchiev Institute of Petrochemical Synthesis
Russian Academy of Sciences
Leninsky Prospect 29, Moscow, 119991, Russian Federation
[c] *Prof. S. N. Osipov*
Peoples' Friendship University of Russia (RUDN University)
Miklukho-Maklaya Str. 6, 117198 Moscow, Russian Federation

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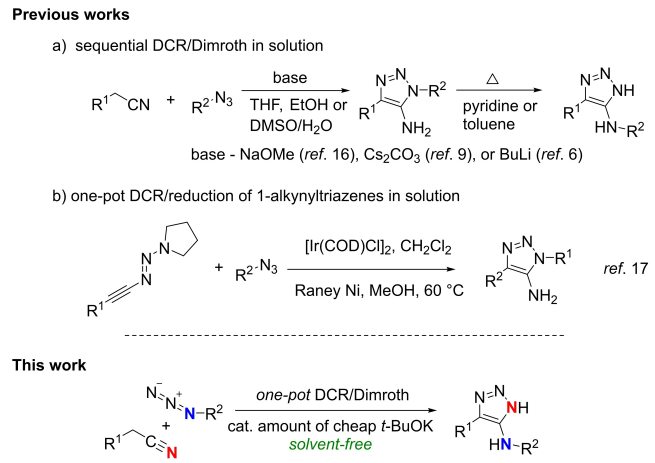


Figure 2. Synthetic approaches to 5-Amino 1,2,3-triazoles and their derivatives.

about 80% of chemical industry waste, is one of the most important tasks in organic chemistry.[23] In this regard, a number of industries started introducing methods of "green" chemistry, such as the application of more effective catalysts, reduction of the volume of traditional organic solvents, using ecologically-safe ones instead, or, ideally, complete avoidance of the solvents in the reaction media.[24] Currently, the development of solvent-free methodologies is a rapidly developing field of synthetic organic chemistry. Highly efficient protocols for Suzuki-Miyaura,[25] Buchwald-Hartwig,[26] and Stille,[27] cross-coupling of aryl lithium compounds,[28] borylation reactions,[29] and "click" reactions,[30] amide synthesis,[31] and hydrohydrazination of acetylenes[32] are reported to date.

Here we wish to disclose an efficient method for the preparation of different 5-amino-1,2,3-triazole derivatives using a one-pot two-step strategy based on the combination of dipolar cycloaddition reaction (DCR) of azides and monosubstituted acetonitriles with Dimroth rearrangement under solvent-free conditions. We have consistently investigated the azide–nitrile DCR, Dimroth, and one-pot DCR/Dimroth reactions under the above-mentioned conditions in the presence of catalytic amounts of cheap bases without the usage of an inert atmosphere. To the best of our knowledge, the combination of solvent-free azide–nitrile cycloaddition with Dimroth rearrangement in a one-pot manner has never been reported before.

Results and Discussion

As a model reaction, we chose the [3 + 2]-cycloaddition of 2-phenylacetonitrile (**1a**) with phenylazide (**2a**) to optimize the conditions in the absence of any solvents. The corresponding base was added in portions to a mixture of the starting compounds homogenously mixed at room temperature. After 24 h, the reaction mixture was dissolved in ethyl acetate/H_2O mixture, the aqueous mixture was extracted with ethyl acetate, and the product was purified by flash chromatography. A primary test with cesium carbonate, which was previously identified to be the most effective base in a similar reaction in solution,[10] resulted in an unsatisfactory result. The target 1,4-diphenyl-1*H*-1,2,3-triazol-5-amine (**3a**) was isolated just in 6% yield (Table 1, entry 1).

Replacing Cs_2CO_3 with K_2CO_3 or Na_2CO_3 (Table 1, entries 2 and 3), or with organic bases such as DBU or DABCO (Table 1, entries 4 and 5) did not significantly increase the yield. Switching to NaOH and KOH (entries 6 and 7) improved the yields to moderate. Finally, potassium *tert*-butoxide was found to be the most effective base for this reaction (entry 10) to afford the target 5-amino-triazole **3a** in 70% yield.

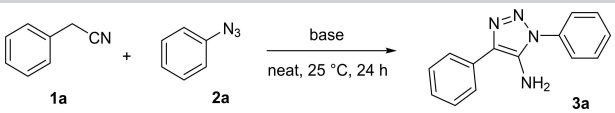
In order to determine the scope of the dipolar azide–nitrile cycloaddition under optimized solvent-free conditions, we performed a series of reactions between different aryl/alkyl azides and monosubstituted acetonitriles to access a variety of 1,4-disubstituted 5-amino-1,2,3-triazoles (Table 2).

As a result, the target 1,4-disubstituted 5-amino-1,2,3-triazoles **3** were obtained in high to almost quantitative yields with the only exceptions for bisaminotriazoles **3z** (35%) and **3aa** (30%) due to extremely low solubility of the reaction partners and the products in the reaction media. The method allows one to efficiently obtain the corresponding 5-amino-triazoles from various alkyl and aryl azides bearing donor (**3a–j**), acceptor (**3k**, **3n–s**) or sterically hindered (**3e**, **3i**, **3j**, **3l**, **3m**) substituents and both aryl and hetaryl acetonitriles without the use of any solvents.

After the cycloaddition step, the presence of an amino group at position 5 of the 1,2,3-triazole product polarizes the N–N bond in the triazole ring, which enables the Dimroth rearrangement[33] (the triazole opens, the atoms rotate around the C–C bond followed by ring closure, thus exo- and endocyclic nitrogen atoms of the 1,2,3-triazole ring are swapped) (Scheme 1).

Despite the fact that this approach was used to prepare some heterocyclic compounds including fused heterocycles,[34] there are only several sporadic examples in the literature that involve prolonged heating of an aminotriazole in dry pyridine[16b,b] or toluene at 180 °C.[10] Therefore, the search for less laborious methods that would significantly simplify the synthetic availability of biologically relevant *N*-aryl-substituted aminotriazoles is of current interest.[12b,35]

Table 1. Optimization of the reaction conditions.[a]

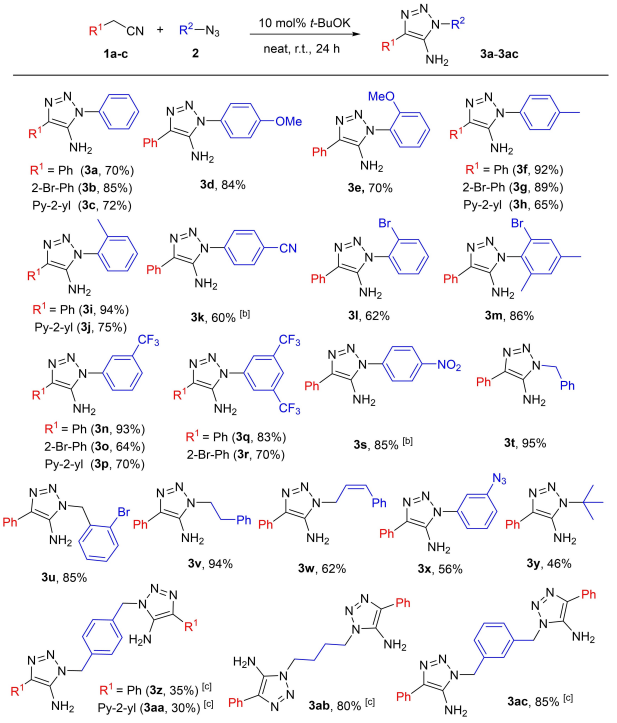


1a 2a 3a

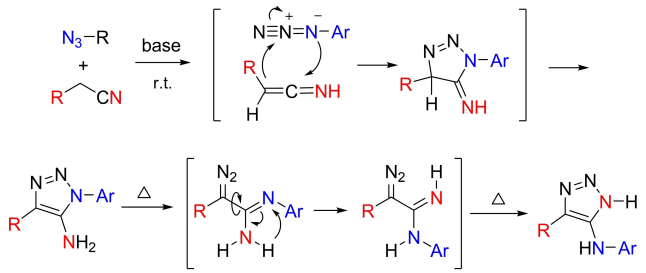
Entry	Base	Yield [%]	Entry	Base	Yield [%]
1	Cs_2CO_3	6	6	KOH	53
2	K_2CO_3	0	7	NaOH	56
3	Na_2CO_3	0	8	*t*-BuOLi	29
4	DBU	25	9	*t*-BuONa	59
5	DABCO	0	**10**	***t*-BuOK**	**70**

[a] Reaction conditions: 2-Phenylacetonitrile **1a** (1 mmol), phenyl azide **2a** (1.1 mmol), base (10 mol%), neat, 25 °C, 24 h, 700 RPM. Isolated yield.

Table 2. Solvent-free DCR of azides and acetonitriles.[a]



[a] Conditions: acetonitrile **1a–c** (1 mmol), aryl (alkyl) azide **2** (1.1 mmol), *t*-BuOK (10 mol%), neat, 25 °C, 24 h. [b] aryl azide (1 mmol), 2-Phenylacetonitrile (3 mmol). [c] acetonitrile **1a** or **1c** (2 mmol), alkyl azide (1 mmol), *t*-BuOK (20 mol%).

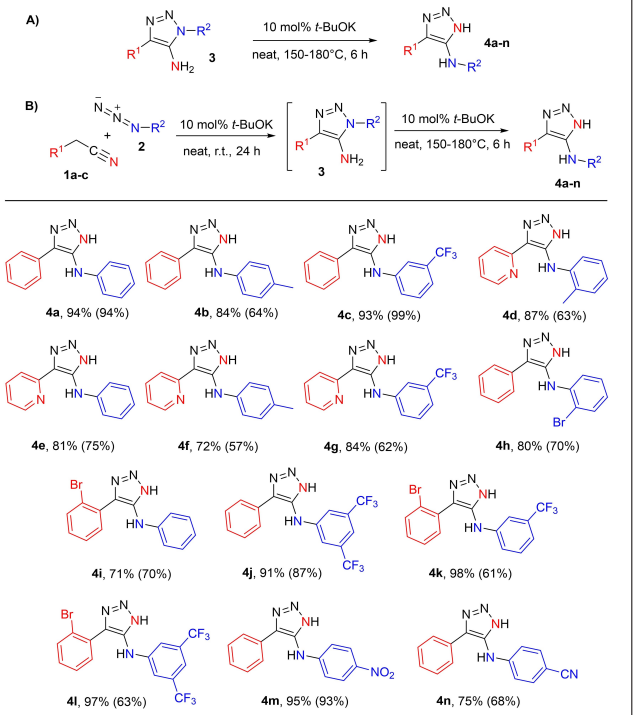


Scheme 1. Proposed mechanism for one-pot two-step DCR/Dimroth reaction.

Thus, the heating of a mixture of the previously obtained 1,4-diphenyl-5-amino-1,2,3-triazole **3a** and 10 mol% of powdered potassium *tert*-butoxide under aerobic and solvent-free conditions at 180 °C for 6 h allowed to obtain the product of Dimroth rearrangement **4a** in 94% yield (Table 3, route **A**). Based on this result, we investigated the reactivity of the other *N*-aryl-substituted 5-amino-triazoles **3** in Dimroth reaction under found conditions (route **A**). As a result, the target *N*-aryl-substituted aminotriazoles **4** containing substituents of different steric and electronic nature were obtained in excellent yields.

Given modern trends in the development of new ecologically benign methodologies for the synthesis of diversified organic compounds including biologically relevant

Table 3. Dimroth rearrangement of 5-amino-1,2,3-triazoles (route A) and one-pot two-step DCR/Dimroth reaction (route B) under solvent-free conditions.[a]



[a] Conditions: *1) Route A*: 5-Amino-1,2,3-triazole **3** (1 mmol), *t*-BuOK (10 mol%), neat, 150–180 °C (depending on melting point of 5-amino-1,2,3-triazole), 6 h. *2) Route B* (yields in parenthesis): *DCR step*: acetonitrile **1a–c** (1 mmol), aryl azide **2** (1.1 mmol), *t*-BuOK (10 mol%), neat, 25 °C, 24 h. *Dimroth step*: *t*-BuOK (10 mol%), neat, 150–180 °C, 6 h.

heterocycles,[36] we investigated the feasibility fof the one-pot preparation of 5-amino-1,2,3-triazoles **4** (Table 3, route **B**).

Thus, after completion of cycloaddition step (TLC control) a new portion of *t*-BuOK was added to the same flask and the resulting mixture was heated for 6 h to afford desired Dimroth products **4** (route **B**).

The new one-pot protocol demonstrates a broad substrate scope, good tolerance towards functional groups (CN, NO_2, Br), and higher overall yields of *N*-aryl-substituted aminotriazoles compared to the two-step protocol.

Conclusion

In conclusion, we developed a robust, highly efficient, and environmentally benign methodology for the preparation of 5-amino-1,2,3-triazole derivatives based on the combination of dipolar azide–nitrile cycloaddition with Dimroth rearrangement under solvent-free conditions. The elaborated protocol has various advantageous features, such as broad substrate scope, operational simplicity, and step economy. The reactions can be easily performed under relatively mild aerobic conditions to afford a variety of biologically relevant aminotriazoles with excellent regioselectivity and good to excellent yields. To our

knowledge, this work is the first solvent-free methodology for the preparation of 5-amino-1,2,3-triazoles.

Experimental Section

General information

All reagents were purchased from commercial sources and were used as received. Analytical TLC was performed with Merck silica gel 60 F 254 plates; visualization was accomplished with UV light or iodine vapors. Chromatography was carried out using Merck silica gel (Kieselgel 60, 0.063–0.200 mm) and petroleum ether/ethyl acetate as an eluent. The NMR spectra were obtained with Bruker AV-400 (400 MHz ^{1}H, 101 MHz ^{13}C, 376 MHz ^{19}F) and AV-600 (600 MHz ^{1}H, 151 MHz ^{13}C) spectrometers using TMS and CCl_3F as references for ^{1}H and ^{19}F NMR spectra respectively. High-resolution mass spectra (HRMS) were measured using AB Sciex TripleTOF 5600 + equipped with TurboV electrospray ionization (ESI) source. Melting points were determined on a melting point apparatus and are uncorrected.

General procedure for solvent-free preparation of 1,4-disubstituted-5-amino-1,2,3-triazoles 3 *via* dipolar azide–nitrile cycloaddition (DCR). A screw-cap vial equipped with a magnetic stir bar was charged with 1 mmol of arylacetonitrile and 1.1 equiv. of corresponding azide. The reaction vial was placed into a water bath (room temperature) and 10 mol% of powdered potassium tert-butoxide was added portionwise. The reaction mixture was allowed to stir (750 RPM) for 24 h at room temperature. After 24 h, the reaction mixture was dissolved in EtOAc/H_2O mixture (1:1, 10 mL), the organic phase was separated, and the aqueous mixture was extracted with ethyl acetate (3×5 mL). The organic extract was evaporated to dryness in vacuo. Purification by chromatography using petroleum ether/ethyl acetate as eluent yielded an analytically pure product.

General procedure for solvent-free Dimroth rearrangement of 3 into 4 (Route A). A screw-cap vial equipped with a magnetic stir bar was charged with 1 mmol of 1,4-disubstituted-5-amino-1,2,3-triazole and 10 mol% of powdered potassium tert-butoxide was replaced into a preheated oil bath (150–180 °C, depending on appropriate 5-amino-1,2,3-triazole melting temperature) and allowed to stir (750 RPM) for 6 h at this temperature. After 6 h the reaction mixture was cooled, dissolved in EtOAc/H_2O mixture (1:1, 10 mL), the organic phase was separated, and the aqueous mixture was extracted with ethyl acetate (3×5 mL). The organic extract was evaporated to dryness in vacuo. Purification by chromatography using petroleum ether/ethyl acetate as eluent gave the analytically pure product.

General procedure for one-pot solvent-free azide–nitrile DCR/Dimroth rearrangement (Route B). A screw-cap vial equipped with a magnetic stir bar was charged with 1 mmol of arylacetonitrile and 1.1 equiv. of the corresponding azide. The reaction vial was placed into a water bath (room temperature) and 10 mol% of powdered potassium tert-butoxide was added portionwise. The reaction mixture was allowed to stir (750 RPM) for 24 h at room temperature. After 24 h new powdered potassium *tert*-butoxide portion (10 mol%) was added and the reaction vial was replaced into a preheated oil bath (150–180 °C, depending on appropriate 5-amino-1,2,3-triazole melting temperature) and allowed to stir for 6 h at this temperature. After 6 h the reaction mixture was cooled, dissolved in EtOAc/H_2O mixture (1:1, 10 mL), the organic phase was separated, and the aqueous mixture was extracted with ethyl acetate (3×5 mL). The organic extract was evaporated to dryness in vacuo. Purification by chromatography using petroleum ether/ethyl acetate as eluent afforded pure product.

N,4-diphenyl-1*H*-1,2,3-triazol-5-amine (4 a). Following Route **A** (221 mg, 94% yield) and Route **B** (223 mg, 94% yield), **4 a** was obtained as a white solid, m.p. 163–165 °C. ^{1}H NMR (400 MHz, DMSO-d_6 + NaOH/D_2O) δ 7.73 (d, J = 7.7 Hz, 2H), 7.20 (t, J = 7.6 Hz, 2H), 7.08–6.95 (m, 3H), 6.61–6.48 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6 + NaOH/D_2O) δ 148.3, 140.9, 135.1, 134.9, 129.2, 128.6, 125.4, 125.3, 116.9, 113.8. IR (υ/cm^{-1}): 689 (VS), 747 (VS), 765 (S), 875 (W), 994 (M), 1022 (M), 1118 (M), 1175 (S), 1246 (M), 1297 (M), 1442 (S), 1498 (S), 1533 (S), 1602 (S), 2911 (M), 2934 (M), 3031 (M), 3050 (M), 3146 (M), 3217 (M), 3277 (S). HRMS (ESI) calc. for $C_{14}H_{13}N_4$ $[M+H]^+$: 237.1135, found: 237.1139; calc. for $C_{14}H_{12}N_4Na$ $[M+Na]^+$: 259.0954, found: 259.0959.

4-phenyl-N-p-tolyl-1*H*-1,2,3-triazol-5-amine (4 b). Following Route **A** (211 mg, 84% yield) and Route **B** (159 mg, 64% yield), **4 b** was obtained as a white solid, m.p. 147–149 °C. ^{1}H NMR (400 MHz, DMSO-d_6 + NaOH/D_2O) δ 7.78 (d, J = 7.6 Hz, 2H), 7.37 (t, J = 6.6 Hz, 2H), 7.30–7.22 (m, 1H), 6.92 (d, J = 7.2 Hz, 2H), 6.79 (d, J = 6.4 Hz, 2H), 2.16 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6 + NaOH/D_2O) δ 143.2, 142.8, 135.0, 131.2, 129.4, 128.7, 127.2, 126.7, 126.1, 114.6, 20.3. IR (υ/cm^{-1}): 689 (VS), 762 (VS), 807 (VS), 971 (VS), 994 (S), 1022 (S), 1048 (S), 1072 (S), 1183 (S), 1198 (S), 1243 (S), 1289 (S), 1311 (S), 1399 (S), 1439 (VS), 1505 (S), 1535 (VS), 1617 (S), 2916 (S), 3021 (M), 3133 (M), 3356 (M). HRMS (ESI) calc. for $C_{15}H_{15}N_4$ $[M+H]^+$: 251.1291; found: 251.1288.

4-phenyl-N-(3-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazol-5-amine (4 c). Following Route **A** (282 mg, 93% yield) and Route **B** (302 mg, 99% yield), **4 c** was obtained as a white solid, m.p. 128–129 °C. ^{1}H NMR (400 MHz, Benzene-d_6) δ 11.75 (s, 1H), 7.68 (d, J = 7.4 Hz, 2H), 7.29 (s, 1H), 7.15 (d, J = 8.2 Hz, 2H), 7.07 (t, J = 7.4 Hz, 1H), 6.98 (d, J = 7.4 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 6.88 (t, J = 7.8 Hz, 1H), 5.60 (s, 1H). ^{13}C{^{1}H} NMR (101 MHz, Benzene-d_6) δ 144.2, 143.4, 131.7 (q, J = 32.0 Hz), 129.9, 129.4, 128.8, 127.4, 126.4, 123.7, 118.9, 117.0 (q, J = 3.9 Hz), 112.8 (q, J = 3.9 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ −61.29. IR (υ/cm^{-1}): 698 (VS), 777 (VS), 873 (S), 916 (S), 984 (S), 1072 (S), 1099 (S), 1126 (VS), 1166 (VS), 1336 (VS), 1447 (S), 1458 (S), 1490 (S), 1557 (S), 1571 (S), 1620 (S), 2925 (M), 3085 (M), 3168 (M), 3412 (M). HRMS (ESI) calc. for $C_{15}H_{12}F_3N_4$ $[M+H]^+$: 305.1008, found: 305.1011.

4-(pyridin-2-yl)-N-o-tolyl-1*H*-1,2,3-triazol-5-amine (4 d). Following Route **A** (219 mg, 87% yield) and Route **B** (158 mg, 63% yield), **4 d** was obtained as a white solid, m.p. 174–175 °C. ^{1}H NMR (400 MHz, Benzene-d_6) δ 9.99 (s, 1H), 9.84 (s, 1H), 8.85–8.75 (m, 1H), 8.10 (d, J = 4.9 Hz, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.39 (t, J = 7.9 Hz, 1H), 7.05 (t, J = 7.9 Hz, 1H), 6.93 (t, J = 7.5 Hz, 1H), 6.51 (t, J = 6.1 Hz, 1H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, Benzene-d_6) δ 148.1, 136.6, 130.5, 127.6, 121.5, 120.5, 120.1, 116.2, 18.3. IR (υ/cm^{-1}): 746 (VS), 787 (VS), 981 (S), 994 (S), 1049 (S), 1066 (S), 1097 (S), 1153 (S), 1261 (S), 1280 (S), 1302 (S), 1316 (S), 1344 (S), 1416 (S), 1450 (S), 1464 (S), 1480 (S), 1518 (S), 1553 (VS), 1576 (VS), 1596 (VS), 2911 (M), 3055 (M), 3121 (M), 3183 (M), 3256 (M). HRMS (ESI) calc. for $C_{14}H_{14}N_5$ $[M+H]^+$: 252.1243; found: 252.1244.

N-phenyl-4-(pyridin-2-yl)-1*H*-1,2,3-triazol-5-amine (4 e). Following Route **A** (192 mg, 81% yield) and Route **B** (178 mg, 75% yield), **4 e** was obtained as a white solid, m.p. 168–170 °C. ^{1}H NMR (400 MHz, Benzene-d_6) δ 10.09 (s, 1H), 9.89 (s, 1H), 8.21 (d, J = 5.5 Hz, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.83 (d, J = 7.9 Hz, 2H), 7.29 (t, J = 7.8 Hz, 2H), 7.05 (t, J = 7.8 Hz, 1H), 6.90 (t, J = 7.6 Hz, 1H), 6.57–6.47 (m, 1H). ^{13}C{^{1}H} NMR (151 MHz, Benzene-d_6) δ 152.6, 148.2, 142.3, 136.6, 131.1, 129.5, 128.3, 121.6, 120.7, 120.2, 117.2. IR (υ/cm^{-1}): 695 (VS), 746 (VS), 788 (VS), 981 (VS), 1152 (S), 1280 (S), 1443 (S), 1499 (S), 1517 (S), 1554 (VS), 1576 (VS), 1601 (VS), 2918 (M), 3050 (M), 3118 (M),

3183 (M). HRMS (ESI) calc. for $C_{13}H_{12}N_5$ $[M+H]^+$: 238.1087; found: 238.1087.

4-(pyridin-2-yl)-N-p-tolyl-1*H*-1,2,3-triazol-5-amine (4f). Following Route **A** (180 mg, 72% yield) and Route **B** (166 mg, 57% yield), **4f** was obtained as a white solid, m.p. 191–193 °C. ^{1}H NMR (400 MHz, Benzene-d_6) δ 10.06 (s, 1H), 9.86 (s, 1H), 8.22 (d, J=5.0 Hz, 1H), 8.03 (d, J=8.1 Hz, 1H), 7.79 (d, J=8.0 Hz, 2H), 7.12 (d, J=8.2 Hz, 3H), 7.04 (t, J=7.8 Hz, 1H), 6.54–6.47 (m, 1H), 2.17 (s, 3H). ^{13}C{^{1}H} NMR (151 MHz, Benzene-d_6) δ 148.2, 140.0, 136.5, 130.0, 129.7, 128.4, 121.5, 120.2, 117.3, 20.8. IR (υ/cm^{-1}): 785 (VS), 822 (VS), 981 (VS), 994 (VS), 1276 (S), 1341 (S), 1517 (VS), 1554 (S), 1573 (S), 1599 (VS), 2914 (M), 3120 (M), 3185 (M), 3271 (M), 3368 (M). HRMS (ESI) calc. for $C_{14}H_{14}N_5$ $[M+H]^+$: 252.1244; found: 252.1245.

4-(pyridin-2-yl)-N-(3-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazol-5-amine (4g). Following Route **A** (257 mg, 84% yield) and Route **B** (190 mg, 62% yield), **4g** was obtained as a white solid, m.p. 150–152 °C. ^{1}H NMR (400 MHz, Benzene-d_6) δ 9.95 (s, 1H), 9.72 (s, 1H), 8.30 (s, 1H), 8.16–8.11 (m, 1H), 7.98 (d, J=8.0 Hz, 1H), 7.59 (d, J=7.6 Hz, 1H), 7.08 (d, J=7.7 Hz, 1H), 7.02 (td, J=8.0, 1.7 Hz, 2H), 6.50 (ddd, J=7.5, 5.0, 1.2 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, Benzene-d_6) δ 155.9, 148.2, 148.0, 136.8, 129.8, 121.8, 120.2, 119.9, 116.9 (q, J=3.6 Hz), 113.4 (q, J=3.5 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ −61.17. IR (υ/cm^{-1}): 786 (VS), 865 (VS), 920 (VS), 981 (VS), 1068 (VS), 1120 (VS), 1164 (VS), 1236 (S), 1338 (VS), 1460 (S), 1559 (VS), 1586 (VS), 1606 (VS), 2942 (M), 3057 (M), 3121 (M), 3182 (M). HRMS (ESI) calc. for $C_{14}H_{11}F_3N_5$ $[M+H]^+$: 306.0967; found: 306.0970.

N-(2-bromophenyl)-4-phenyl-1*H*-1,2,3-triazol-5-amine (4h). Following Route **A** (257 mg, 84% yield) and Route **B** (190 mg, 62% yield), **4g** was obtained as a grey solid, m.p. 123–125 °C. ^{1}H NMR (400 MHz, Benzene-d_6) δ 7.89 (d, J=8.3 Hz, 1H), 7.83 (d, J=7.6 Hz, 2H), 7.30 (d, J=7.9 Hz, 1H), 7.14 (s, 1H), 7.05 (t, J=7.2 Hz, 1H), 6.97 (t, J=7.7 Hz, 1H), 6.78 (s, 1H), 6.43 (t, J=7.6 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, Benzene-d_6) δ 144.1, 140.5, 136.9, 132.6, 130.4, 129.3, 128.8, 128.6, 127.2, 121.3, 116.4, 111.1. IR (υ/cm^{-1}): 697 (VS), 735 (VS), 765 (VS), 985 (VS), 1021 (VS), 1050 (S), 1316 (VS), 1445 (VS), 1469 (S), 1558 (VS), 1597 (VS), 2917 (M), 3060 (M), 3163 (M), 3410 (M). HRMS (ESI) calc. for $C_{14}H_{12}BrN_4$ $[M+H]^+$: 315.0240, 317.0219, found: 315.0244, 317.0224.

4-(2-bromophenyl)-N-phenyl-1*H*-1,2,3-triazol-5-amine (4i). Following Route **A** (224 mg, 71% yield) and Route **B** (220 mg, 70% yield), **4i** was obtained as a grey solid, m.p. 124–125 °C. ^{1}H NMR (400 MHz, Benzene-d_6) δ 7.34 (dd, J=8.1, 1.2 Hz, 1H), 7.25 (dd, J=7.6, 1.7 Hz, 1H), 7.22–7.18 (m, 2H), 7.13 (d, J=8.6 Hz, 1H), 6.86 (td, J=7.6, 1.2 Hz, 1H), 6.81 (tt, J=7.2, 1.2 Hz, 1H), 6.67 (td, J=7.8, 1.7 Hz, 1H), 5.69 (s, 1H). ^{13}C{^{1}H} NMR (101 MHz, Benzene-d_6) δ 146.1, 142.5, 133.5, 132.8, 131.8, 130.5, 129.3, 123.9, 120.8, 116.5. IR (υ/cm^{-1}): 695 (VS), 735 (VS), 766 (VS), 916 (M), 982 (S), 1025 (S), 1070 (M), 1160 (M), 1217 (M), 1283 (S), 1317 (M), 1372 (S), 1425 (S), 1455 (S), 1515 (VS), 1573 (S), 1599 (VS), 1624 (VS), 2851 (W), 2924 (W), 3061 (M), 3187 (M), 3317 (S), 3425 (M). HRMS (ESI) calc. for $C_{14}H_{12}BrN_4$ $[M+H]^+$: 315.0240, 317.0219, found: 315.0241, 317.0222.

N-(3,5-bis(trifluoromethyl)phenyl)-4-phenyl-1*H*-1,2,3-triazol-5-amine (4j). Following Route **A** (338 mg, 91% yield) and Route **B** (355 mg, 87% yield), **4j** was obtained as a grey solid, m.p. 154–156 °C. ^{1}H NMR (400 MHz, Benzene-d_6) δ 11.18 (s, 1H), 7.58 (d, J=7.4 Hz, 2H), 7.35 (d, J=13.1 Hz, 3H), 7.20 (d, J=7.3 Hz, 2H), 7.10 (t, J=7.4 Hz, 1H), 5.58 (s, 1H). ^{13}C{^{1}H} NMR (101 MHz, Benzene-d_6) δ 143.8, 143.5, 142.6, 132.6 (q, J=33.0 Hz), 129.9, 129.5, 129.1, 127.5, 125.4, 122.7, 120.0, 115.7, 115.7, 113.5 (p, J=3.9 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ −61.85. IR (υ/cm^{-1}): 766 (S), 870 (S), 956 (S), 997 (S), 1026 (S), 1052 (S), 1129 (VS), 1176 (VS), 1276 (VS), 1387 (VS), 1471 (S), 1499 (S), 1595 (S), 1624 (S), 2858 (M), 2919 (M), 3309 (M). HRMS (ESI) calc. for $C_{16}H_{11}F_6N_4$ $[M+H]^+$: 373.0882, found: 373.0889.

4-(2-bromophenyl)-N-(3-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazol-5-amine (4k). Following Route **A** (374 mg, 98% yield) and Route **B** (234 mg, 61% yield), **4k** was obtained as a white solid, m.p. 146–148 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.44 (s, 1H), 7.72 (d, J=8.0 Hz, 1H), 7.59 (s, 1H), 7.47 (dd, J=13.6, 5.9 Hz, 3H), 7.35 (t, J=7.1 Hz, 2H), 7.00 (d, J=7.6 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 144.6, 143.8, 133.4, 132.8, 132.4, 131.8, 130.3, 129.7, 129.5 (q, J=30.8 Hz), 127.6, 124.5 (q, J=272.1 Hz), 123.7, 118.5, 114.4 (q, J=3.8 Hz), 110.6 (q, J=3.7 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ −61.30. IR (υ/cm^{-1}): 699 (VS), 754 (VS), 872 (VS), 992 (VS), 1019 (VS), 1069 (VS), 1125 (VS), 1166 (VS), 1337 (VS), 1475 (S), 1541 (S), 1571 (S), 1604 (S), 2914 (M), 3120 (M), 3256 (M). HRMS (ESI) calc. for $C_{15}H_{11}F_3BrN_4$ $[M+H]^+$: 383.0113, 385.0093, found: 383.0118, 385.0099.

N-(3,5-bis(trifluoromethyl)phenyl)-4-(2-bromophenyl)-1*H*-1,2,3-triazol-5-amine (4l). Following Route **A** (439 mg, 97% yield) and Route **B** (284 mg, 63% yield), **4l** was obtained as a white solid, m.p. 135–136 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.06 (s, 1H), 7.97 (s, 2H), 7.77 (d, J=8.0 Hz, 1H), 7.49 (d, J=3.6 Hz, 2H), 7.42 (ddd, J=8.9, 5.4, 3.5 Hz, 1H), 7.35 (s, 1H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 145.3, 143.4, 133.3, 132.9, 132.5, 131.4, 131.0, 130.8 (q, J=32.2 Hz), 130.5, 123.8, 123.6 (q, J=272.9 Hz), 114.4, 110.5. ^{19}F NMR (376 MHz, DMSO-d_6) δ −61.25. IR (υ/cm^{-1}): 681 (VS), 699 (VS), 737 (S), 760 (S), 871 (S), 956 (S), 1019 (S), 1073 (S), 1122 (VS), 1168 (VS), 1281 (VS), 1388 (VS), 1435 (S), 1471 (S), 1543 (S), 1588 (S), 1627 (S), 3272 (M), 3446 (M). HRMS (ESI) calc. for $C_{16}H_{10}F_6BrN_4$ $[M+H]^+$: 450.9987, 452.9967, found: 450.9988, 452.9968.

N-(4-nitrophenyl)-4-phenyl-1*H*-1,2,3-triazol-5-amine (4m). Following Route **A** (267 mg, 95% yield) and Route **B** (261 mg, 93% yield), **4m** was obtained as a yellow solid, m.p. 145–147 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.31 (s, 1H), 8.07 (d, J=8.7 Hz, 2H), 7.75 (d, J=8.2 Hz, 2H), 7.44 (t, J=7.6 Hz, 2H), 7.35 (t, J=7.4 Hz, 1H), 6.98 (d, J=8.9 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 151.9, 140.5, 138.2, 136.0, 129.6, 128.9, 128.1, 126.3, 126.0, 113.4. IR (υ/cm^{-1}): 749 (VS), 764 (VS), 842 (VS), 987 (VS), 1112 (VS), 1188 (VS), 1303 (VS), 1326 (VS), 1442 (S), 1505 (S), 1546 (S), 1576 (S), 1602 (VS), 2914 (M), 3153 (M), 3396 (M). HRMS (ESI) calc. for $C_{14}H_{12}N_5O_2$ $[M+H]^+$: 282.0986; found: 282.0997.

4-(4-phenyl-1*H*-1,2,3-triazol-5-ylamino)benzonitrile (4n). Following Route **A** (196 mg, 75% yield) and Route **B** (179 mg, 68% yield), **4n** was obtained as a light-brown solid, m.p. 144–146 °C. ^{1}H NMR (400 MHz, DMSO-d_6 + NaOH/D_2O) δ 7.69 (d, J=7.7 Hz, 2H), 7.34 (d, J=8.5 Hz, 2H), 7.22 (t, J=7.7 Hz, 2H), 7.05 (t, J=7.9 Hz, 1H), 6.63 (d, J=8.5 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6 + NaOH/D_2O) δ 152.7, 139.7, 134.8, 134.8, 133.5, 128.5, 125.3, 121.5, 113.7, 96.6, 95.5. IR (υ/cm^{-1}): 696 (M), 766 (M), 830 (M), 986 (M), 1021 (W), 1047 (W), 1174 (M), 1249 (M), 1324 (M), 1443 (M), 1511 (S), 1543 (S), 1596 (VS), 1606 (VS), 2216 (S), 2911 (M), 3065 (M), 3160 (M), 3396 (M). HRMS (ESI) calc. for $C_{15}H_{12}N_5$ $[M+H]^+$: 262.1087, found: 262.1093.

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Conflict of Interest

The authors declare no conflict of interest.

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[1] a) A. V. Gulevich, V. Gevorgyan, *Angew. Chem. Int. Ed. Engl.* **2013**, *52*, 1371–1373; b) B. Chattopadhyay, V. Gevorgyan, *Angew. Chem. Int. Ed. Engl.* **2012**, *51*, 862–872; c) Q. Gu, H. H. Al Mamari, K. Graczyk, E. Diers, L. Ackermann, *Angew. Chem. Int. Ed. Engl.* **2014**, *53*, 3868–3871.

[2] H. Duan, S. Sengupta, J. L. Petersen, N. G. Akhmedov, X. Shi, *J. Am. Chem. Soc.* **2009**, *131*, 12100–12102.

[3] a) M. Ichikawa, S. Mochizuki, H.-G. Jeon, S. Hayashi, N. Yokoyama, Y. Taniguchi, *J. Mater. Chem.* **2011**, *21*, 11791; b) G. de Miguel, M. Wielopolski, D. I. Schuster, M. A. Fazio, O. P. Lee, C. K. Haley, A. L. Ortiz, L. Echegoyen, T. Clark, D. M. Guldi, *J. Am. Chem. Soc.* **2011**, *133*, 13036–13054.

[4] a) J. E. Hein, V. V. Fokin, *Chem. Soc. Rev.* **2010**, *39*, 1302–1315; b) M. A. Azagarsamy, K. S. Anseth, *ACS Macro Lett.* **2013**, *2*, 5–9; c) J. A. Johnson, M. G. Finn, J. T. Koberstein, N. J. Turro, *Macromol. Rapid Commun.* **2008**, *29*, 1052–1072; d) M. Meldal, C. W. Tornoe, *Chem. Rev.* **2008**, *108*, 2952–3015.

[5] P. Sharma, A. Kumar, S. Upadhyay, J. Singh, V. Sahu, *Med. Chem. Res.* **2010**, *19*, 589–602.

[6] A. Gomes, P. Martins, D. R. Rocha, M. Neves, V. Ferreira, A. Silva, J. Cavaleiro, F. da Silva, *Synlett* **2013**, *24*, 41–44.

[7] a) A. Lauria, R. Delisi, F. Mingoia, A. Terenzi, A. Martorana, G. Barone, A. M. Almerico, *Eur. J. Org. Chem.* **2014**, *2014*, 3289–3306; b) E. Bonandi, M. S. Christodoulou, G. Fumagalli, D. Perdicchia, G. Rastelli, D. Passarella, *Drug Discovery Today* **2017**, *22*, 1572–1581.

[8] a) B. Kahveci, F. Yılmaz, E. Menteşe, F. Ş. Beriş, *J. Chem. Res.* **2012**, *36*, 484–488; b) B. Kahveci, E. Mentese, E. Akkaya, F. Yilmaz, I. S. Dogan, A. Ozel, *Arch. Pharm. Chem. Life Sci.* **2014**, *347*, 449–455; c) B. Kahveci, F. Yilmaz, E. Mentese, S. Ulker, *Arch. Pharm. Chem. Life Sci.* **2017**, *350*, 1600369; d) E. Mentese, F. Yilmaz, N. Baltas, O. Bekircan, B. Kahveci, *J. Enzyme Inhib. Med. Chem.* **2015**, *30*, 435–441.

[9] a) Y. C. Duan, Y. C. Ma, E. Zhang, X. J. Shi, M. M. Wang, X. W. Ye, H. M. Liu, *Eur. J. Med. Chem.* **2013**, *62*, 11–19; b) H. Elamari, R. Slimi, G. G. Chabot, L. Quentin, D. Scherman, C. Girard, *Eur. J. Med. Chem.* **2013**, *60*, 360–364; c) I. E. Glowacka, J. Balzarini, A. E. Wroblewski, *Eur. J. Med. Chem.* **2013**, *70*, 703–722; d) O. A. Phillips, E. E. Udo, A. A. M. Ali, N. Al-Hassawi, *Bioorg. Med. Chem.* **2003**, *11*, 35–41; e) C. Bengtsson, A. E. Lindgren, H. Uvell, F. Almqvist, *Eur. J. Med. Chem.* **2012**, *54*, 637–646; f) R. Cannalire, M. L. Barreca, G. Manfroni, V. Cecchetti, *J. Med. Chem.* **2016**, *59*, 16–41; g) M. J. Giffin, H. Heaslet, A. Brik, Y. C. Lin, G. Cauvi, C. H. Wong, D. E. McRee, J. H. Elder, C. D. Stout, B. E. Torbett, *J. Med. Chem.* **2008**, *51*, 6263–6270.

[10] P. M. Krishna, D. B. Ramachary, S. Peesapati, *RSC Adv.* **2015**, *5*, 62062–62066.

[11] a) M.-T. Ren, M. Li, A.-J. Wang, J. Gao, X.-X. Zhang, W.-M. Shu, *Eur. J. Org. Chem.* **2020**, *2020*, 2233–2236; b) T. Weide, S. A. Saldanha, D. Minond, T. P. Spicer, J. R. Fotsing, M. Spaargaren, J. M. Frere, C. Bebrone, K. B. Sharpless, P. S. Hodder, V. V. Fokin, *ACS Med. Chem. Lett.* **2010**, *1*, 150–154.

[12] a) J. R. E. Hoover, A. R. Day, *J. Am. Chem. Soc.* **1956**, *78*, 5832–5836; b) G. Biagi, V. Calderone, I. Giorgi, O. Livi, V. Scartoni, B. Baragatti, E. Martinotti, *Eur. J. Med. Chem.* **2000**, *35*, 715–720; c) X. Zhao, B. W. Lu, J. R. Lu, C. W. Xin, J. F. Li, Y. Liu, *Chin. Chem. Lett.* **2012**, *23*, 933–935.

[13] Y. Qian, M. Hamilton, A. Sidduri, S. Gabriel, Y. Ren, R. Peng, R. Kondru, A. Narayanan, T. Truitt, R. Hamid, Y. Chen, L. Zhang, A. J. Fretland, R. A. Sanchez, K. C. Chang, M. Lucas, R. C. Schoenfeld, D. Laine, M. E. Fuentes, C. S. Stevenson, D. C. Budd, *J. Med. Chem.* **2012**, *55*, 7920–7939.

[14] Y. Liao, Q. Lu, G. Chen, Y. Yu, C. Li, X. Huang, *ACS Catal.* **2017**, *7*, 7529–7534.

[15] a) N. Pokhodylo, O. Shyyka, V. Matiychuk, *Med. Chem. Res.* **2013**, *23*, 2426–2438; b) P. G. Baraldi, M. G. Pavani, M. d. C. Nuñez, P. Brigidi, B. Vitali, R. Gambari, R. Romagnoli, *Bioorg. Med. Chem.* **2002**, *10*, 449–456.

[16] a) V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2002**, *41*, 2596–2599; *Angew. Chem.* **2002**, *114*, 2708–2711; b) C. W. Tornoe, C. Christensen, M. Meldal, *J. Org. Chem.* **2002**, *67*, 3057–3064; c) L. K. Rasmussen, B. C. Boren, V. V. Fokin, *Org. Lett.* **2007**, *9*, 5337–5339; d) B. C. Boren, S. Narayan, L. K. Rasmussen, L. Zhang, H. Zhao, Z. Lin, G. Jia, V. V. Fokin, *J. Am. Chem. Soc.* **2008**, *130*, 8923–8930; e) S. Ding, G. Jia, J. Sun, *Angew. Chem. Int. Ed.* **2014**, *53*, 1877–1880; *Angew. Chem.* **2014**, *126*, 1908–1911; f) E. Rasolofonjatovo, S. Theeramunkong, A. Bouriaud, S. Kolodych, M. Chaumontet, F. Taran, *Org. Lett.* **2013**, *15*, 4698–4701.

[17] a) M. Belkheira, D. El Abed, J. M. Pons, C. Bressy, *Chem. Eur. J.* **2011**, *17*, 12917–12921; b) D. B. Ramachary, A. B. Shashank, S. Karthik, *Angew. Chem. Int. Ed.* **2014**, *53*, 10420–10424; *Angew. Chem.* **2014**, *126*, 10588–10592; c) W. Li, J. Wang, *Angew. Chem. Int. Ed.* **2014**, *53*, 14186–14190; *Angew. Chem.* **2014**, *126*, 14410–14414; d) S. S. Ramasastry, *Angew. Chem. Int. Ed.* **2014**, *53*, 14310–14312; *Angew. Chem.* **2014**, *126*, 14536–14538.

[18] a) Z. Chen, Q. Yan, Z. Liu, Y. Xu, Y. Zhang, *Angew. Chem. Int. Ed.* **2013**, *52*, 13324–13328; *Angew. Chem.* **2013**, *125*, 13566–13570; b) Z. J. Cai, X. M. Lu, Y. Zi, C. Yang, L. J. Shen, J. Li, S. Y. Wang, S. J. Ji, *Org. Lett.* **2014**, *16*, 5108–5111.

[19] a) J. Ma, S. Ding, *Asian J. Org. Chem.* **2020**, *9*, 1872–1888; b) F. Wei, W. Wang, Y. Ma, C. H. Tung, Z. Xu, *Chem. Commun.* **2016**, *52*, 14188–14199; c) Z. Chen, Z. Liu, G. Cao, H. Li, H. Ren, *Adv. Synth. Catal.* **2017**, *359*, 202–224.

[20] a) E. Lieber, T. S. Chao, C. N. R. Rao, *Org. Synth.* **1957**, *37*, 26; b) E. Lieber, T. S. Chao, C. N. R. Rao, *J. Org. Chem.* **1957**, *22*, 654–662; c) N. T. Pokhodylo, V. S. Matiychuk, N. B. Obushak, *Chem. Heterocycl. Compd.* **2009**, *45*, 483–488; d) N. Pokhodylo, V. Matiychuk, M. Obushak, *Synthesis* **2009**, *2009*, 2321–2323.

[21] L. Zeng, Z. Lai, C. Zhang, H. Xie, S. Cui, *Org. Lett.* **2020**, *22*, 2220–2224.

[22] C. Torborg, M. Beller, *Adv. Synth. Catal.* **2009**, *351*, 3027–3043.

[23] a) V. Polshettiwar, A. Decottignies, C. Len, A. Fihri, *ChemSusChem* **2010**, *3*, 502–522; b) R. A. Sheldon, *Chem. Commun.* **2008**, 3352–3365; c) A. F. Asachenko, *Ineos Open* **2020**, *3*, 80–91.

[24] C. Capello, U. Fischer, K. Hungerbühler, *Green Chem.* **2007**, *9*, 927.

[25] a) A. F. Asachenko, K. R. Sorochkina, P. B. Dzhevakov, M. A. Topchiy, M. S. Nechaev, *Adv. Synth. Catal.* **2013**, *355*, 3553–3557; b) P. S. Gribanov, G. A. Chesnokov, P. B. Dzhevakov, N. Y. Kirilenko, S. A. Rzhevskiy, A. A. Ageshina, M. A. Topchiy, M. V. Bermeshev, A. F. Asachenko, M. S. Nechaev, *Mendeleev Commun.* **2019**, *29*, 147–149.

[26] a) M. A. Topchiy, A. F. Asachenko, M. S. Nechaev, *Eur. J. Org. Chem.* **2014**, *2014*, 3319–3322; b) M. A. Topchiy, P. B. Dzhevakov, M. S. Rubina, O. S. Morozov, A. F. Asachenko, M. S. Nechaev, *Eur. J. Org. Chem.* **2016**, *2016*, 1908–1914; c) G. A. Chesnokov, P. S. Gribanov, M. A. Topchiy, L. I. Minaeva, A. F. Asachenko, M. S. Nechaev, E. V. Bermesheva, M. V. Bermeshev, *Mendeleev Commun.* **2017**, *27*, 618–620; d) A. A. Ageshina, G. K. Sterligov, S. A. Rzhevskiy, M. A. Topchiy, G. A. Chesnokov, P. S. Gribanov, E. K. Melnikova, M. S. Nechaev, A. F. Asachenko, M. V. Bermeshev, *Dalton Trans.* **2019**, *48*, 3447–3452.

[27] a) P. S. Gribanov, Y. D. Golenko, M. A. Topchiy, L. I. Minaeva, A. F. Asachenko, M. S. Nechaev, *Eur. J. Org. Chem.* **2018**, *2018*, 120–125; b) P. S. Gribanov, Y. D. Golenko, M. A. Topchiy, A. N. Philippova, N. Y. Kirilenko, N. V. Krivoshchapov, G. K. Sterligov, A. F. Asachenko, M. V. Bermeshev, M. S. Nechaev, *Mendeleev Commun.* **2018**, *28*, 323–325.

[28] E. B. Pinxterhuis, M. Giannerini, V. Hornillos, B. L. Feringa, *Nat. Commun.* **2016**, *7*, 11698.

[29] P. B. Dzhevakov, M. A. Topchiy, D. A. Zharkova, O. S. Morozov, A. F. Asachenko, M. S. Nechaev, *Adv. Synth. Catal.* **2016**, *358*, 977–983.

[30] a) G. A. Chesnokov, M. A. Topchiy, P. B. Dzhevakov, P. S. Gribanov, A. A. Tukov, V. N. Khrustalev, A. F. Asachenko, M. S. Nechaev, *Dalton Trans.* **2017**, *46*, 4331–4345; b) M. A. Topchiy, A. A. Ageshina, G. A. Chesnokov, G. K. Sterligov, S. A. Rzhevskiy, P. S. Gribanov, S. N. Osipov, M. S. Nechaev, A. F. Asachenko, *ChemistrySelect* **2019**, *4*, 7470–7475.

[31] S. A. Rzhevskiy, A. A. Ageshina, G. A. Chesnokov, P. S. Gribanov, M. A. Topchiy, M. S. Nechaev, A. F. Asachenko, *RSC Adv.* **2019**, *9*, 1536–1540.

[32] O. S. Morozov, P. S. Gribanov, A. F. Asachenko, P. V. Dorovatovskii, V. N. Khrustalev, V. B. Rybakov, M. S. Nechaev, *Adv. Synth. Catal.* **2016**, *358*, 1463–1468.

[33] a) O. Dimroth, *Justus Liebigs Ann. Chem.* **1909**, *364*, 183–226; b) O. Dimroth, W. Michaelis, *Justus Liebigs Ann. Chem.* **1927**, *459*, 39–46.

[34] a) A. Krajczyk, J. Boryski, *Curr. Org. Chem.* **2017**, *21*, 2515; b) A. Baykal, D. Zhang, J. Knelles, I. T. Alt, B. Plietker, *Chem. Asian J.* **2019**, *14*, 3003–3010; c) A. Champire, C. Vala, A. Laabid, A. Benharref, M. Marchivie, K. Ple, S. Routier, *J. Org. Chem.* **2016**, *81*, 12506–12513; d) H. M. E. Hassaneen, I. A. Abdelhamid, *J. Heterocycl. Chem.* **2017**, *54*, 1048–1053; e) A. L. Odom, T. J. McDaniel, *Acc. Chem. Res.* **2015**, *48*, 2822–2833; f) M.-X. Liu, J.-R. Li, K. Zheng, H. Yao, Q. Zhang, D.-X. Shi, *Tetrahedron* **2015**, *71*, 7658–7662; g) A. A. Dissanayake, R. J. Staples, A. L. Odom, *Adv. Synth. Catal.* **2014**, *356*, 1811–1822.
[35] G. Biagi, I. Giorgi, O. Livi, V. Scartoni, S. Velo, P. L. Barili, *J. Heterocycl. Chem.* **1996**, *33*, 1847–1853.
[36] a) M. Trujillo, C. Hull-Crew, A. Outlaw, K. Stewart, L. Taylor, L. George, A. Duensing, B. Tracey, A. Schoffstall, *Molecules* **2019**, *24*, 973; b) A. Daştan, A. Kulkarni, B. Török, *Green Chem.* **2012**, *14*, 17–37.

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