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Heterocycle Synthesis

Synthesis of Structurally Diverse Benzotriazoles via Rapid Diazotization and Intramolecular Cyclization of 1,2-Aryldiamines

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Abstract: An operationally simple method has been developed for the preparation of *N*-unsubstituted benzotriazoles by diazotization and intramolecular cyclization of a wide range of 1,2-aryldiamines under mild conditions, using a polymer-supported nitrite reagent and *p*-tosic acid. The functional group tolerance of this approach was further demonstrated with effective activation and cyclization of *N*-alkyl, -aryl, and -acyl *ortho*-aminoanilines leading to the synthesis of N_1-substituted benzotriazoles. The synthetic utility of this one-pot heterocyclization process was exemplified with the preparation of a number of biologically and medicinally important benzotriazole scaffolds, including an α-amino acid analogue.

Introduction

Benzotriazoles are important heterocyclic scaffolds, widely used in medicinal chemistry,[1] organic synthesis[2] and material science.[3] Application of benzotriazole derivatives in medicinal chemistry is particularly widespread (Figure 1a) due to enzyme inhibition through π–π stacking or hydrogen bonding of the triazole unit.[1a] For example, antifungal benzotriazole derivatives have been discovered that inhibit the growth of fluconazole-insensitive *Cryptococcus neoformans*,[1b] while halogenated aryloxy-benzotriazoles inhibit isoniazid-resistant *Mycobacterium tuberculosis*.[1c] In organic synthesis, benzotriazoles have been used as precursors for the preparation of other heterocycles such as indoles, carbazoles as well as pyridoacridines,[4] and seminal work by Katritzky and co-workers demonstrated their application as auxiliaries for alkylation and benzannulation reactions.[2]

The general importance of benzotriazoles for a range of scientific applications has resulted in the development of various synthetic methods for the preparation of this benzannulated heterocycle. In recent years, base-mediated "click" type [3+2] cycloaddition reactions of benzynes and azides have allowed the synthesis of *N*-substituted benzotriazoles under mild conditions (Figure 1b).[5] A limitation of this approach is the formation of N_1- and N_3-benzotriazole regioisomers from unsymmetrically substituted benzynes, although this has been overcome using *ortho*-ether, boryl, and silyl directing groups.[5a,5e,5f] Regioselective synthesis of N_1-aryl-substituted benzotriazoles has been achieved by the transition metal-catalyzed cyclization of 1,3-diaryltriazenes.[6] For example, Ren and co-workers demonstrated such a process via a 1,7-palladium migration-cycliza-

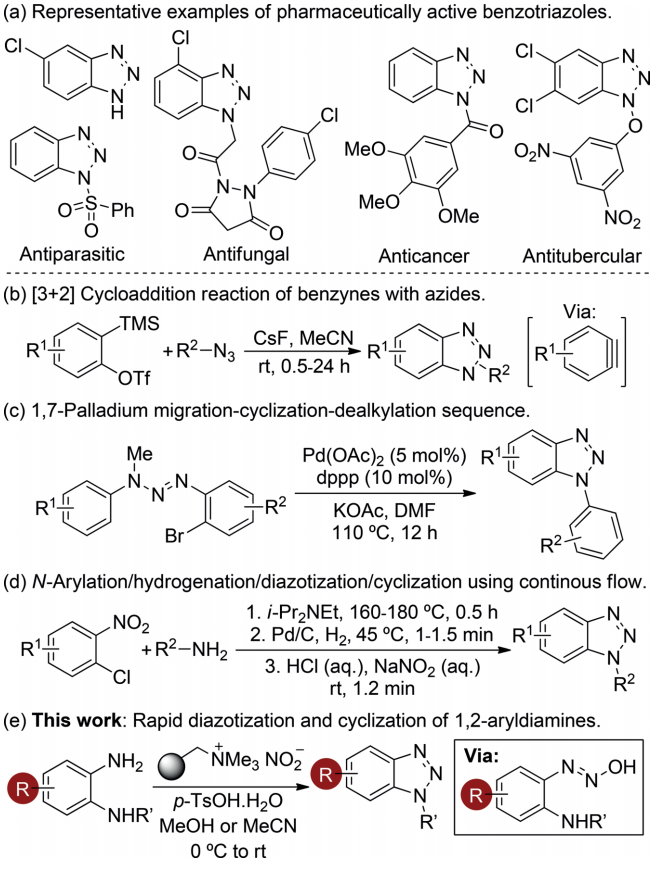

Figure 1. Pharmaceutically relevant benzotriazoles and some general methods for their synthesis.

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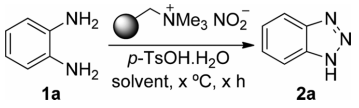
tion-dealkylation cascade (Figure 1c).[6b] Palladium-mediated oxidative addition of the aryl C-Br bond was followed by C–H activation and 1,7-palladium migration. Subsequent intramolecular amination and demethylation resulted in the regioselective preparation of a wide range of N_1-aryl-substituted benzotriazole derivatives. A more traditional approach for the preparation of benzotriazoles involves the diazotization and intramolecular cyclization of 1,2-aryldiamines using sodium nitrite and acidic conditions.[7] This reaction was incorporated into a multistep continuous flow process by Chen and Buchwald for the regioselective synthesis of N_1-substituted benzotriazoles from *ortho*-chloronitroarenes (Figure 1d).[8] Base-mediated S_NAr reaction of *ortho*-chloronitroarenes with amines was followed by reduction of the nitro group and diazotization of the resulting aniline with sodium nitrite and hydrochloric acid. Cyclization gave a range of N_1-substituted benzotriazoles in high overall yields. The scope of this process was further expanded by using a palladium-catalyzed Buchwald-Hartwig *N*-arylation reaction as the first step of the continuous flow process.

Despite these advances, there is still a need for a general method that can produce both unsubstituted benzotriazoles and the regioselective preparation of N_1-substituted benzotriazoles, while avoiding elevated temperatures, harsh acidic conditions and the use of sodium nitrite under these conditions, which can lead to the release of toxic nitrogen oxides.[9] In 2008, Filimonov and co-workers showed that a polymer-supported nitrite reagent in combination with less harsh acidic conditions (*p*-tosic acid) could be used for the preparation of stable aryl diazonium tosylate salts.[10] More recently, we have shown that this safe, mild and operationally simple method for aryl diazonium salt formation can be combined in one-pot multistep processes for (radio)iodination and Heck–Matsuda reactions of anilines.[11,12] We now report a general synthesis of benzotriazoles from 1,2-aryldiamines using a polymer-supported nitrite reagent, under mild conditions (Figure 1e). As well as exploring the scope of this process for the synthesis of both *N*-unsubstituted and N_1-substituted benzotriazoles, we also demonstrate the use of this approach for the facile preparation of pharmaceutically important benzotriazole containing compounds.

Results and Discussion

The study began by investigating whether benzotriazole formation could be achieved by activation and intramolecular cyclization of 1,2-diaminobenzene (**1a**) with a polymer-supported nitrite reagent and *p*-tosic acid (Table 1). The initial aim was to develop an operationally simple process with a short reaction time, that could be performed under mild reaction conditions. Another key objective was to show that the use of a polymer-supported nitrite reagent would facilitate work-up and purification of the benzotriazole product. In this study, the polymer-supported nitrite reagent was prepared by ion exchange of the tetraalkylammonium functionalized resin, Amberlyst A-26 with an aqueous solution of sodium nitrite.[10–12] Following our previous work,[11] diazotization and cyclization of **1a** was attempted using 3 equivalents of both the polymer-supported nitrite reagent and *p*-tosic acid in acetonitrile at 80 °C. After a reaction time of 1.5 hours, this gave benzotriazole **2a** in 46 % isolated yield (entry 1). Extending the reaction time to 18 hours, led to a more efficient process and a yield of 71 % (entry 2). In an attempt to improve the reaction conditions, the reaction solvent was switched to methanol. Crucially, 1,2-diaminobenzene (**1a**) was found to have better solubility in methanol, allowing the reaction to progress at much lower temperature. For example, cooling the reaction mixture to 0 °C, adding the reagents and warming the mixture to room temperature over 6 hours, gave benzotriazole **2a** in 66 % yield (entry 3). Longer reaction times showed no significant improvement in the overall yield (entry 4). Finally, the number of equivalents of reagents required was investigated. Using only 1 equivalent of both the polymer-supported nitrite reagent and *p*-tosic acid had a detrimental effect on the yield (entry 5), while increasing the number of equivalents to 6 showed no substantial benefit (entry 6). Therefore, the use of 3 equivalents of reagents in methanol at room temperature was deemed the most suitable procedure for this transformation (entry 3).

Table 1. Optimization of the diazotization and cyclization of **1a**.

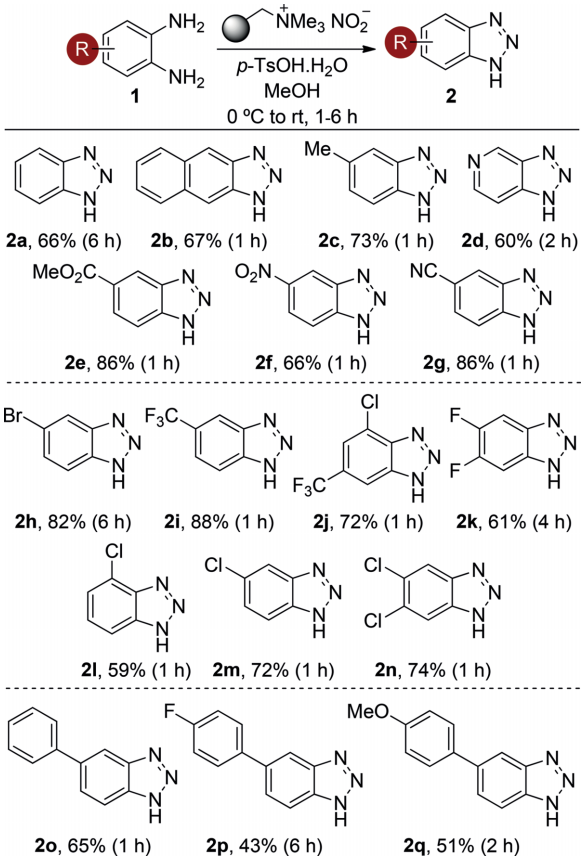


Entry	Reagent (equiv.)	Solvent	Temp (°C)	Time [h]	Yield [%][a]
1	3	MeCN	80	1.5	46
2	3	MeCN	80	18	71
3	3	MeOH	0 to rt	6	66
4	3	MeOH	0 to rt	48	69
5	1	MeOH	0 to rt	6	29
6	6	MeOH	0 to rt	6	62

[a] Isolated yield.

Using these optimized conditions, the substrate scope for the preparation of *N*-unsubstituted benzotriazoles was explored (Scheme 1). The method was found to be general and efficient for a wide range of commercially available 1,2-aryldiamines bearing both electron-deficient and electron-rich substituents. In addition, for the majority of substrates, the reaction was complete after 1 h, with the benzotriazoles easily isolated by filtration and purification using flash chromatography. As well as benzotriazoles bearing functional groups and a heterocyclic core (e.g. pyridine analogue **2d**), the method was applicable for the synthesis of various halogenated compounds (**2h–2n**). This included the efficient synthesis of antiparasitic agent **2m**, a compound that is active against the protozoan parasite *Entamoeba histolytica* and is more potent than metronidazole, which is used clinically for the treatment of amebiosis.[13] 5-Aryl derived benzotriazoles are excellent substrates for denitrogenative- and carbonylative-Suzuki coupling reactions[4f] and thus, we wanted to demonstrate that these could be accessed using this approach. 4-Bromo-2-nitroaniline was subjected to a Suzuki–Miyaura reaction with several boronic acids under standard conditions and the resulting 4-aryl analogues were reduced to 1,2-diaminobenzenes **1o–1q** using a combination of sodium borohydride and palladium on carbon.[14] The 4-aryl-

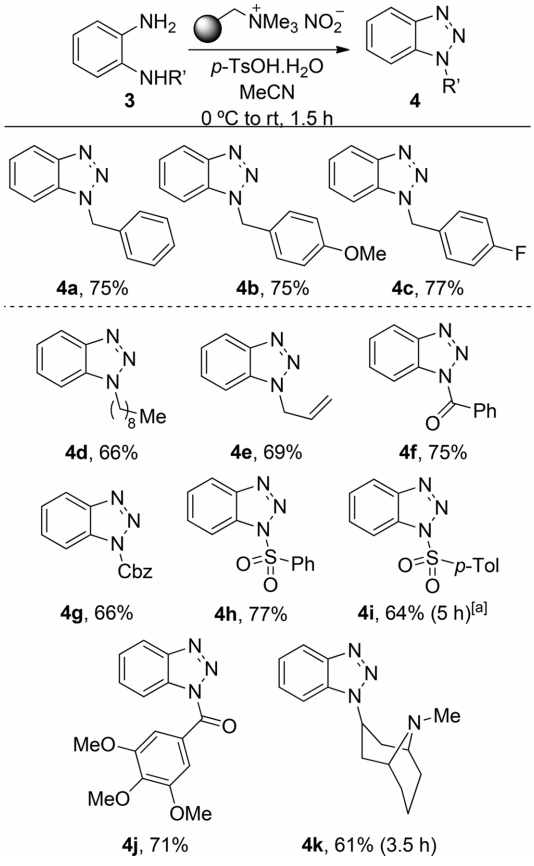
1,2-diaminobenzenes (**1o–1q**) were subjected to the one-pot diazotization and intramolecular cyclization and gave the corresponding benzotriazoles (**2o–2q**), cleanly and in moderate to good yields.



Scheme 1. Substrate scope for the synthesis of *N*-unsubstituted benzotriazoles.

Following the successful synthesis of a wide range of *N*-unsubstituted benzotriazoles, the general procedure was next investigated for the synthesis of N_1-substituted derivatives (Scheme 2). Initially, a series of *N*-benzyl 1,2-aryldiamines **3a–c** was prepared by nucleophilic aromatic substitution of 2-nitrofluorobenzene with various benzylamines, followed by chemoselective reduction of the nitro-group with zinc and acetic acid.[14] The resulting *N*-benzyl aryldiamines were activated and cyclized using the general procedure to give after 1.5 hours, benzotriazoles **4a–c** in good yields (75–77 %). It should be noted that acetonitrile was found to be the optimal solvent for the less polar *N*-substituted 1,2-aryldiamines.

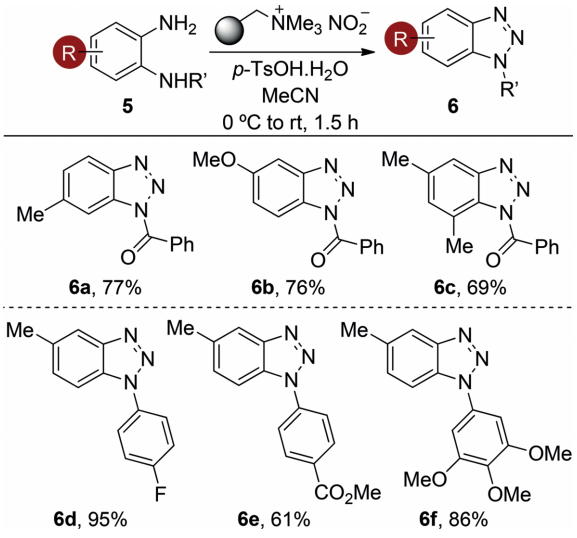
A second series of 1,2-aryldiamines bearing *N*-alkyl, -acyl or -sulfonyl groups were prepared from 2-nitroaniline by substitution of the amino group, followed by nitro-group reduction.[14] Subsequent treatment with the polymer-supported nitrite reagent and *p*-tosic acid gave the corresponding N_1-substituted benzotriazoles **4d–k** in good yields (61–77 %). From the range of substrates investigated, only two required modified procedures. *N*-Tosyl protected 1,2-diaminobenzene **3i**, for reasons that are not clear, required both an increase in the amounts of reagents (4.5 equiv.) and a longer reaction time (5 h), while synthesis of benzotriazole **4k**, bearing a bulky pseudopelletierine derived *N*-substituent, required a reaction time of 3.5 hours. As well as allowing the synthesis of a benzotriazole with an N_1-alkaloid substituent (e.g. **4k**), this method permitted the synthesis of a range of medicinally important compounds. For example, N_1-nonyl-substituted derivative **4d** is an antifungal agent, that can inhibit the growth of the fluconazole-insensitive organism *Cryptococcus neoformans*,[1b] while N_1-benzenesulfonyl-benzotriazole (**4h**) is highly active against the protozoan parasite, *Trypanosoma cruzi*, which is responsible for Chagas disease.[15] In addition, the 3,4,5-trimethoxybenzoyl derivative **4j** has antiproliferative activity against various human cancer cell lines, including stomach carcinoma MKN45.[16]



Scheme 2. Substrate scope for the synthesis of N_1-substituted benzotriazoles. [a] 4.5 equivalents of reagents were used.

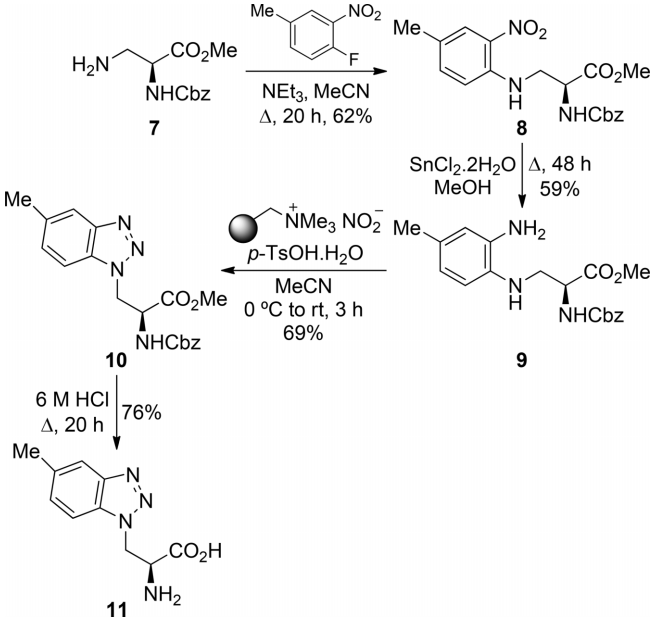
The next stage of this project then demonstrated how the regioselective issues associated with other methods,[5] could be overcome by the synthesis of selectively substituted 1,2-aryldiamines followed by the mild cyclization procedure, allowing the well-defined, efficient preparation of N_1-functionalized unsymmetrically substituted benzotriazoles (Scheme 3). Initially, a series of *N*-benzoyl protected 1,2-aryldiamines (**5a–c**) were prepared by the *N*-benzoylation of various 2-nitroanilines, followed by tin dichloride reduction.[14] Subsequent treatment with the polymer-supported nitrite reagent and *p*-tosic acid, under standard conditions completed the synthesis of benzotriazoles **6a–c** in good yields (69–77 %). The widespread pharmaceutical properties displayed by unsymmetrical benzotriazoles bearing *N*-aryl groups,[1,17] has meant that various synthetic strategies for their regioselective synthesis have been reported.[5d–5f,6,8,18]

In this study, an efficient approach for their synthesis has also been developed. Buchwald-Hartwig coupling of various anilines with 4-bromo-3-nitrotoluene using palladium acetate and (*S*)-BINAP,[19] followed by tin dichloride reduction of the nitro-group gave *N*-aryl 3,4-diaminotoluene analogues (**5d–f**).[14] These compounds were found to be excellent substrates for the polymer-supported nitrite and *p*-tosic acid mediated cyclization, giving the target N_1-aryl benzotriazoles **6d–f** in 61–95 % yields.



Scheme 3. Synthesis of N_1-functionalized unsymmetrically substituted benzotriazoles.

In the final stage of this project, we wanted to further demonstrate the compatible nature of the mild benzotriazole forming process for the synthesis of functionalized, biologically relevant targets. We have an interest in the development of new synthetic methods for the preparation of novel heterocycle-containing α-amino acids for biological applications,[20] and so the mild activation and cyclization process was investigated for the synthesis of a benzotriazole-containing α-amino acid (Scheme 4). Initially, the known L-3-aminoalanine derivative **7**,[21] was subjected to an S_NAr reaction with 4-fluoro-3-nitrotoluene under basic conditions, which gave coupled product **8** in 62 % yield.[22] Chemoselective reduction of the nitro-group with tin dichloride then gave key intermediate, 1,2-aryldiamine **9**. Reaction of **9** with the polymer-supported nitrite reagent and *p*-tosic acid under the standard conditions was complete after 3 hours and gave benzotriazole **10** in 69 % yield. Finally, removal of the protecting groups under acid-mediated conditions completed the synthesis of novel benzotriazole-containing α-amino acid **11**.



Scheme 4. Synthesis of benzotriazole-containing α-amino acid **11**.

Conclusions

In summary, a general and efficient process for the conversion of 1,2-aryldiamines to benzotriazoles has been developed. The particularly mild conditions involving a polymer-supported nitrite reagent and *p*-tosic acid are compatible with a range of substrates and functional groups, allowing easy purification of the targets by filtration and flash chromatography. This method avoids harsh reagents and the safety issues associated with more traditional approaches, as well as the regioselectivity challenges connected with some cycloaddition syntheses of N_1-functionalized unsymmetrically substituted benzotriazoles. The general nature of this method has been exemplified with the preparation of various medicinally important benzotriazoles and the synthesis of a new benzotriazole-containing α-amino acid.

Experimental Section

General Information: All reagents and starting materials were obtained from commercial sources and used as received. Methyl (2*S*)-2-[(benzyloxycarbonyl)amino]-3-aminopropanoate (**7**) was prepared according to the literature.[21] All dry solvents were purified using a PureSolv 500 MD solvent purification system. All reactions were performed under an atmosphere of argon unless otherwise mentioned. Brine refers to a saturated solution of sodium chloride. Flash column chromatography was carried out using Merck Geduran Si 60 (40–63 µm). Merck aluminium-backed plates pre-coated with silica gel 60 (UV_{254}) were used for thin layer chromatography and were visualized under ultraviolet light and by staining with $KMnO_4$ or ninhydrin. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AVI 400 or AVIII 400 spectrometer with chemical shift values in ppm relative to TMS (δ_H = 0.00 and δ_C = 0.0), residual chloroform (δ_H = 7.26 and δ_C = 77.2), methanol (δ_H = 3.31 and δ_C = 49.0) or dimethyl sulfoxide (δ_H = 2.50 and δ_C = 39.5) as standard. Assignment of ^1H and ^{13}C NMR signals are based on two-dimensional COSY, HSQC, and DEPT experiments. TFA was used to facilitate dissolution of various *N*-unsubstituted benzotriazoles when recording ^{13}C NMR spectra. Mass spectra were obtained using a JEOL JMS-700 spectrometer or a Bruker microTOFq High Resolution Mass Spectrometer. Infrared spectra were recorded on a Shimadzu FTIR-84005. Melting points were determined on a Gallenkamp melting point apparatus. Optical rotations were determined as solutions irradiating with the sodium D line (λ = 589 nm) using a polarimeter. $[\alpha]_D$ values are given in units 10^{-1} deg cm^2 g^{-1}.

General Procedure for the Preparation of the polymer-supported nitrite reagent: To a stirred solution of sodium nitrite (0.55 g, 8.00 mmol) in water (20 mL) was added Amberlyst® A26 hydroxide form resin (1.00 g, 4.00 mmol). The resulting mixture was stirred at room temperature for 0.5 h, and then polymer-supported resin was filtered and washed with water until the pH of filtrate became neutral. The content of prepared polymer-supported nitrite was 3.5 mmol of NO_2 per g of resin.[10a]

General Procedure for Synthesis of Benzotriazoles: To a stirred solution of the corresponding 1,2-phenylenediamines (1.0 equiv.) in methanol (**1a–1q**) or acetonitrile (all other substrates) (10 mL/mmol) at 0 °C was added polymer-supported nitrite (containing 3.0 equiv. of NO_2) and *p*-toluenesulfonic acid monohydrate (3.0 equiv.). The reaction mixture was stirred for 1 h at 0 °C (**1a–1q**) or 0.5 h at 0 °C (all other substrates). The reaction mixture was then warmed to room temperature and stirred until completion (1–6 h). The resin was filtered and washed with ethyl acetate (20 mL/mmol). The reaction mixture was concentrated in vacuo. Purification by silica gel flash column chromatography eluting with ethyl acetate in hexane or petroleum ether (40–60), diethyl ether in hexane or methanol in dichloromethane gave the benzotriazoles.

1*H*-Benzo[*d*][1.2.3]triazole (2a):[23] The reaction was carried out as described in the general procedure using 1,2-phenylenediamine (**1a**) (0.0500 g, 0.463 mmol), polymer-supported nitrite (0.396 g, containing 1.39 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.239 g, 1.39 mmol). The reaction was complete after 6 h. Purification by silica gel flash column chromatography eluting with 40 % ethyl acetate in hexane gave 1*H*-benzo[*d*][1.2.3]triazole (**2a**) (0.036 g, 66 %) as a white solid. Mp 94–96 °C (lit.[23] 97 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.43 (m, 2 H, 5-H and 6-H), 7.94 (dd, *J* = 6.2, 3.0 Hz, 2 H, 4-H and 7-H), 14.54 (br s, 1 H, 1-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 115.0 (2 × CH), 126.1 (2 × CH), 138.9 (2 × C). MS (ESI) *m/z* (%): 142 (100) $[M + Na]^+$.

1*H*-Naphtho-(2,3-*d*)[1.2.3]triazole (2b):[24] The reaction was carried out as described in the general procedure using 2,3-diaminonaphthalene (**1b**) (0.158 g, 1.00 mmol), polymer-supported nitrite (0.857 g, containing 3.00 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.517 g, 3.00 mmol). The reaction was complete after 1 h. Purification by silica gel flash column chromatography eluting with 50 % ethyl acetate in hexane gave 1*H*-naphtho-(2,3-*d*)-benzo[1.2.3]triazole (**2b**) (0.114 g, 67 %) as a pale yellow solid. Mp 178–180 °C (lit.[24] 186 °C). ^{1}H NMR (400 MHz, $[D_6]$DMSO + TFA): δ = 7.45–7.52 (m, 2 H, 6-H and 7-H), 8.12 (dd, *J* = 6.5, 3.3 Hz, 2 H, 5-H and 8-H), 8.53 (s, 2 H, 4-H and 9-H), 11.85 (br s, 1 H, 1-H). ^{13}C NMR (101 MHz, $[D_6]$DMSO + TFA): δ = 111.4 (2 × CH), 125.2 (2 × CH), 128.6 (2 × CH), 131.3 (2 × C), 137.8 (2 × C). MS (ESI) *m/z* (%): 170 (100) $[M + H]^+$.

5-Methyl-1*H*-benzo[*d*][1.2.3]triazole (2c):[25] The reaction was carried out as described in the general procedure using 3,4-diaminotoluene (**1c**) (0.122 g, 1.00 mmol), polymer-supported nitrite (0.857 g, containing 3.00 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.517 g, 3.00 mmol). The reaction was complete after 1 h. Purification by silica gel flash column chromatography eluting with 40 % ethyl acetate in hexane gave 5-methyl-1*H*-benzo-[*d*][1.2.3]triazole (**2c**) (0.097 g, 73 %) as an orange solid. Mp 78–80 °C (lit.[25] 80–83 °C). ^{1}H NMR (400 MHz, $[D_6]$DMSO + TFA): δ = 2.46 (s, 3 H, 5-CH_3), 7.23 (dd, *J* = 8.4, 1.2 Hz, 1 H, 6-H), 7.62 (d, *J* = 1.2 Hz, 1 H, 4-H), 7.80 (d, *J* = 8.4 Hz, 1 H, 7-H), 11.07 (br s, 1 H, 1-H). ^{13}C NMR (101 MHz, $[D_6]$DMSO + TFA): δ = 21.2 (CH_3), 112.9 (CH), 115.4 (CH), 127.1 (CH), 135.6 (C), 138.0 (C), 138.7 (C). MS (ESI) *m/z* (%): 156 (100) $[M + Na]^+$.

1*H*-[1.2.3]Triazolo-(4,5-*c*)pyridine (2d):[26] The reaction was carried out as described in the general procedure using 3,4-diaminopyridine (**1d**) (0.109 g, 1.00 mmol), polymer-supported nitrite (0.857 g, containing 3.00 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.517 g, 3.00 mmol). The reaction was complete after 2 h. Purification by silica gel flash column chromatography eluting with 5 % methanol in dichloromethane gave 1*H*-[1.2.3]triazolo-(4,5-*c*)pyridine (**2d**) (0.072 g, 60 %) as a white solid. Spectroscopic data were consistent with the literature.[26] Mp 171–174 °C. ^{1}H NMR (400 MHz, $[D_6]$DMSO): δ = 7.86 (dd, *J* = 5.8, 0.6 Hz, 1 H, 6-H), 8.45 (d, *J* = 5.8 Hz, 1 H, 7-H), 9.45 (br s, 1 H, 4-H). ^{13}C NMR (101 MHz, $[D_6]$DMSO): δ = 108.1 (CH), 139.7 (C), 140.6 (C), 142.1 (CH), 142.7 (CH). MS (EI) *m/z* (%): 120 (100) $[M]^+$, 92 (65), 66 (79).

Methyl 1*H*-benzo[*d*][1.2.3]triazole-5-carboxylate (2e):[27] The reaction was carried out as described in the general procedure using methyl-3,4-diaminobenzoate (**1e**) (0.0500 g, 0.301 mmol), polymer-supported nitrite (0.258 g, containing 0.903 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.155 g, 0.903 mmol). The reaction was complete after 1 h. Purification by silica gel flash column chromatography eluting with 50 % ethyl acetate in hexane gave methyl 1*H*-benzo[*d*][1.2.3]triazole-5-carboxylate (**2e**) (0.046 g, 86 %) as a white solid. Mp 166–168 °C (lit.[27] 169–170 °C). ^{1}H NMR (400 MHz, $CDCl_3$ + TFA): δ = 4.04 (s, 3 H, OCH_3), 8.09 (d, *J* = 8.8 Hz, 1 H, 7-H), 8.37 (dd, *J* = 8.8, 1.2 Hz, 1 H, 6-H), 8.79 (br s, 1 H, 4-H); ^{13}C NMR (101 MHz, $CDCl_3$ + TFA): δ = 53.5 (CH_3), 114.1 (CH), 117.4 (CH), 130.3 (CH), 131.1 (C), 135.8 (C), 136.9 (C), 166.3 (C). MS (ESI) *m/z* (%): 178 (100) $[M + H]^+$.

5-Nitro-1*H*-benzo[*d*][1.2.3]triazole (2f):[23] The reaction was carried out as described in the general procedure using 4-nitro-1,2-phenylenediamine (**1f**) (0.0500 g, 0.326 mmol), polymer-supported nitrite (0.280 g, containing 0.979 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.169 g, 0.979 mmol). The reaction was complete after 1 h. Purification by silica gel flash column chromatography eluting with 50 % ethyl acetate in hexane gave 5-nitro-1*H*-benzo[*d*][1.2.3]triazole (**2f**) (0.035 g, 66 %) as a white solid. Spectroscopic data were consistent with the literature.[23] Mp 188–190 °C. ^{1}H NMR (400 MHz, $CDCl_3$ + TFA): δ = 8.14 (d, *J* = 5.2 Hz, 1 H, 7-H), 8.54 (dd, *J* = 5.2, 1.6 Hz, 1 H, 6-H), 9.03 (d, *J* = 1.6 Hz, 1 H, 4-H). ^{13}C NMR (101 MHz, $CDCl_3$ + TFA): δ = 113.3 (CH), 114.9 (CH), 123.6 (CH), 138.1 (2 × C), 147.0 (C). MS (EI) *m/z* (%): 164 (95) $[M]^+$, 106 (42), 90 (25), 79 (26), 63 (100).

1*H*-Benzo[*d*][1.2.3]triazole-5-carbonitrile (2g):[28] The reaction was carried out as described in the general procedure using 3,4-diaminobenzonitrile (**1g**) (0.0500 g, 0.376 mmol), polymer-supported nitrite (0.322 g, containing 1.13 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.194 g, 1.13 mmol). The reaction was complete after 1 h. Purification by silica gel flash column chromatography eluting with 50 % ethyl acetate in hexane gave 1*H*-benzo[*d*][1.2.3]triazole-5-carbonitrile (**2g**) (0.047 g, 86 %) as an off-white solid. Spectroscopic data were consistent with the literature.[28] Mp 72–74 °C. ^{1}H NMR (400 MHz, $[D_6]$DMSO + TFA): δ = 7.68 (dd, *J* = 8.6, 1.4 Hz, 1 H, 6-H), 7.96 (d, *J* = 8.6 Hz, 1 H, 7-H), 8.12 (br s, 1 H, 4-H), 8.49 (br s, 1 H, 1-H). ^{13}C NMR (101 MHz, $[D_6]$DMSO + TFA): δ = 107.7 (C), 115.7 (CH), 119.3 (C), 123.5 (CH), 128.6 (CH), 138.6 (C), 140.6 (C). MS (EI) *m/z* (%): 144 (100) $[M]^+$, 116 (78), 69 (55), 57 (94).

5-Bromo-1*H*-benzo[*d*][1.2.3]triazole (2h):[25] The reaction was carried out as described in the general procedure using 4-bromo-1,2-phenylenediamine (**1h**) (0.0500 g, 0.267 mmol), polymer-supported nitrite (0.229 g, containing 0.802 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.138 g, 0.802 mmol). The reaction was complete after 6 h. Purification by silica gel flash column chromatography elut-

ing with 20 % ethyl acetate in hexane gave 5-bromo-1*H*-benzo[*d*][1.2.3]triazole (**2h**) (0.0440 g, 82 %) as a red solid. Mp 126–128 °C (lit.[25] 127–129 °C). ^{1}H NMR (400 MHz, $CDCl_3$ + TFA): δ = 7.88 (dd, *J* = 9.0, 1.2 Hz, 1 H, 6-H), 7.96 (d, *J* = 9.0 Hz, 1 H, 7-H), 8.24 (d, *J* = 1.2 Hz, 1 H, 4-H). ^{13}C NMR (101 MHz, $CDCl_3$ + TFA): δ = 115.5 (CH), 116.9 (CH), 123.7 (C), 133.1 (CH), 134.9 (C), 136.7 (C). MS (EI) *m/z* (%): 199 (72) [M]$^+$, 197 (73), 171 (50), 169 (52), 90 (50), 63 (100).

5-Trifluoromethyl-1*H*-benzo[*d*][1.2.3]triazole (2i):[25] The reaction was carried out as described in the general procedure using 4-trifluoromethyl-1,2-phenylenediamine (**1i**) (0.0500 g, 0.284 mmol), polymer-supported nitrite (0.243 g, containing 0.852 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.147 g, 0.852 mmol). The reaction was complete after 1 h. Purification by silica gel flash column chromatography eluting with 20 % ethyl acetate in hexane gave 5-trifluoromethyl-1*H*-benzo[*d*][1.2.3]triazole (**2i**) (0.0460 g, 88 %) as a yellow solid. Spectroscopic data were consistent with the literature.[25] Mp 94–96 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 7.73 (dd, *J* = 8.8, 1.2 Hz, 1 H, 6-H), 8.09 (d, *J* = 8.8 Hz, 1 H, 7-H), 8.41 (br s, 1 H, 4-H). ^{13}C NMR (101 MHz, [D$_6$]DMSO): δ = 115.2 (CH), 115.8 (CH), 122.7 (CH), 124.8 (q, $^1J_{C\text{-}F}$ = 272.2 Hz, C), 126.0 (q, $^2J_{C\text{-}F}$ = 33.5 Hz, C), 138.8 (C), 140.3 (C). MS (EI) *m/z* (%): 187 (55) [M]$^+$, 84 (81), 66 (100).

4-Chloro-6-(trifluoromethyl)-1*H*-benzo[*d*][1.2.3]triazole (2j): The reaction was carried out as described in the general procedure using 3-chloro-5-trifluoromethyl-1,2-phenylenediamine (**1j**) (0.0500 g, 0.237 mmol), polymer-supported nitrite (0.204 g, containing 0.712 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.230 g, 0.712 mmol). The reaction was complete after 1 h. Purification by silica gel flash column chromatography eluting with 50 % ethyl acetate in hexane gave 4-chloro-6-(trifluoromethyl)-1*H*-benzo[*d*][1.2.3]triazole (**2j**) (0.0390 g, 72 %) as a white solid. Mp 166–169 °C. IR (neat): $\tilde{\nu}_{max}$ = 2711, 1593, 1341, 1242, 1167, 1130, 1069, 874. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 7.90 (s, 1 H, 7-H), 8.40 (s, 1 H, 5-H), 16.75 (br s, 1 H, 1-H). ^{13}C NMR (101 MHz, [D$_6$]DMSO): δ = 113.2 (CH), 121.7 (CH), 123.9 (q, $^1J_{C\text{-}F}$ = 275.6 Hz, C), 126.8 (C), 127.6 (q, $^2J_{C\text{-}F}$ = 32.8 Hz, C), 139.4 (C), 139.4 (C). HRMS (EI) *m/z* [M]$^+$ calcd. for $C_7H_3{}^{35}ClF_3N_3$ 220.9968, found 220.9971.

5,6-Difluoro-1*H*-benzo[*d*][1.2.3]triazole (2k):[29] The reaction was carried out as described in the general procedure using 4,5-difluoro-1,2-phenylenediamine (**1k**) (0.144 g, 1.00 mmol), polymer-supported nitrite (0.857 g, containing 3.00 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.517 g, 3.00 mmol). The reaction was complete after 4 h. Purification by silica gel flash column chromatography eluting with 30 % ethyl acetate in hexane gave 5,6-difluoro-1*H*-benzo[*d*][1.2.3]triazole (**2k**) (0.0950 g, 61 %) as an off-white solid. Mp 176–178 °C (lit.[29] 183–184 °C). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.03 (dd, *J* = 8.8, 8.0 Hz, 2 H, 4-H and 7-H), 15.97 (br s, 1 H, 1-H). ^{13}C NMR (101 MHz, [D$_6$]DMSO): δ = 102.2 (2 × CH), 134.6 (2 × C), 149.2 (dd, $^1J_{C\text{-}F}$ = 248.1, $^2J_{C\text{-}F}$ = 17.7 Hz, 2 × C). MS (EI) *m/z* (%): 155 (100) [M]$^+$, 127 (47), 100 (58), 84 (32), 66 (40).

4-Chloro-1*H*-benzo[*d*][1.2.3]triazole (2l):[25] The reaction was carried out as described in the general procedure using 3-chloro-1,2-phenylenediamine (**1l**) (0.143 g, 1.00 mmol), polymer-supported nitrite (0.857 g, containing 3.00 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.517 g, 3.00 mmol). The reaction was complete after 1 h. Purification by silica gel flash column chromatography eluting with 30 % ethyl acetate in hexane gave 4-chloro-1*H*-benzo[*d*][1.2.3]triazole (**2l**) (0.0900 g, 59 %) as a white solid. Mp 160–162 °C (lit.[25] 168–170 °C). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 7.36–7.53 (m, 2 H, 6-H and 7-H), 7.76–7.90 (m, 1 H, 5-H), 16.13 (br s, 1 H, 1-H). ^{13}C NMR (101 MHz, [D$_6$]DMSO): δ = 113.1 (CH), 121.5 (C), 124.9 (CH), 127.4 (CH), 136.5 (C), 139.2 (C). MS (ESI) *m/z* (%): 154 (100) [M + H]$^+$.

5-Chloro-1*H*-benzo[*d*][1.2.3]triazole (2m):[25] The reaction was carried out as described in the general procedure using 4-chloro-1,2-phenylenediamine (**1m**) (0.143 g, 1.00 mmol), polymer-supported nitrite (0.857 g, containing 3.00 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.517 g, 3.00 mmol). The reaction was complete after 1 h. Purification by silica gel flash column chromatography eluting with 30 % ethyl acetate in hexane gave 5-chloro-1*H*-benzo[*d*][1.2.3]triazole (**2m**) (0.110 g, 72 %) as a white solid. Mp 125–128 °C (lit.[25] 129–131 °C). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 7.39 (dd, *J* = 8.8, 1.4 Hz, 1 H, 6-H), 7.92 (d, *J* = 8.8 Hz, 1 H, 7-H), 7.98 (d, *J* = 1.4 Hz, 1 H, 4-H), 15.87 (br s, 1 H, 1-H). ^{13}C NMR (101 MHz, [D$_6$]DMSO): δ = 114.7 (CH), 117.2 (CH), 126.4 (CH), 130.7 (C), 138.3 (C), 139.0 (C). MS (EI) *m/z* (%): 153 (100) [M]$^+$, 125 (74), 90 (39), 63 (88).

5,6-Dichloro-1*H*-benzo[*d*][1.2.3]triazole (2n):[23] The reaction was carried out as described in the general procedure using 4,5-dichloro-1,2-phenylenediamine (**1n**) (0.177 g, 1.00 mmol), polymer-supported nitrite (0.857 g, containing 3.00 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.517 g, 3.00 mmol). The reaction was complete after 1 h. Purification by silica gel flash column chromatography eluting with 30 % ethyl acetate in hexane gave 5,6-dichloro-1*H*-benzo[*d*][1.2.3]triazole (**2n**) (0.139 g, 74 %) as a white solid. Mp 249–252 °C (lit.[23] 267 °C). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.22 (s, 2 H, 4-H and 7-H), 15.99 (br s, 1 H, 1-H). ^{13}C NMR (101 MHz, [D$_6$]DMSO): δ = 116.9 (2 × CH), 128.9 (2 × C), 138.5 (2 × C). MS (EI) *m/z* (%): 189 (65) [M]$^+$, 187 (100), 161 (48), 159 (78), 97 (77), 66 (41).

5-Phenyl-1*H*-benzo[*d*][1.2.3]triazole (2o):[30] The reaction was carried out as described in the general procedure using [1,1′-biphenyl]-3,4-diamine (**1o**) (0.100 g, 0.543 mmol), polymer-supported nitrite (0.465 g, containing 1.63 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.281 g, 1.63 mmol). The reaction was complete after 1 h. Purification by silica gel flash column chromatography eluting with 20 % ethyl acetate in hexane gave 5-phenyl-1*H*-benzo[*d*][1.2.3]triazole (**2o**) (0.0690 g, 65 %) as a pale yellow solid. Mp 152–155 °C (lit.[30] 156 °C). ^{1}H NMR (400 MHz, [D$_6$]DMSO + TFA): δ = 7.38 (t, *J* = 7.4 Hz, 1 H, 4′-H), 7.48 (t, *J* = 7.4 Hz, 2 H, 3′-H and 5′-H), 7.70–7.77 (m, 3 H, 6-H, 2′-H and 6′-H), 7.98 (d, *J* = 8.8 Hz, 1 H, 7-H), 8.12 (br s, 1 H, 4-H); ^{13}C NMR (101 MHz, [D$_6$]DMSO + TFA): δ = 112.6 (CH), 116.0 (CH), 125.6 (CH), 127.8 (2 × CH), 128.0 (CH), 129.4 (2 × CH), 138.5 (C), 139.0 (C), 139.7 (C), 140.4 (C). MS (ESI) *m/z* (%): 218 (100) [M + Na]$^+$.

5-(4′-Fluorophenyl)-1*H*-benzo[*d*][1.2.3]triazole (2p): The reaction was carried out as described in the general procedure using 4′-fluoro-[1,1′-biphenyl]-3,4-diamine (**1p**) (0.120 g, 0.593 mmol), polymer-supported nitrite (0.509 g, containing 1.78 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.307 g, 1.78 mmol). The reaction was complete after 6 h. Purification by silica gel flash column chromatography eluting with 20 % ethyl acetate in hexane gave 5-(4′-fluorophenyl)-1*H*-benzo[*d*][1.2.3]triazole (**2p**) (0.0530 g, 43 %) as a pale yellow solid. Mp 176–179 °C. IR (neat): $\tilde{\nu}_{max}$ = 3460, 2250, 1053, 1024, 1005, 758. ^{1}H NMR (400 MHz, [D$_6$]DMSO + TFA): δ = 7.28–7.35 (m, 2 H, 3′-H and 5′-H), 7.72 (dd, *J* = 8.6, 2.2 Hz, 1 H, 6-H), 7.77–7.84 (m, 2 H, 2′-H and 6′-H), 7.98 (dd, *J* = 8.6, 0.6 Hz, 1 H, 7-H), 8.11 (br s, 1 H, 4-H), 8.90 (br s, 1 H, 1-H). ^{13}C NMR (101 MHz, [D$_6$]DMSO + TFA): δ = 112.7 (CH), 116.0 (CH), 116.2 (d, $^2J_{C\text{-}F}$ = 21.4 Hz, 2 × CH), 125.6 (CH), 129.8 (d, $^3J_{C\text{-}F}$ = 8.2 Hz, 2 × CH), 136.9 (d, $^4J_{C\text{-}F}$ = 3.1 Hz, C), 137.4 (C), 138.9 (C), 139.6 (C), 162.5 (d, $^1J_{C\text{-}F}$ = 244.7 Hz, C). HRMS (ESI) *m/z* [M + H]$^+$ calcd. for $C_{12}H_9FN_3$ 214.0775, found 214.0776.

5-(4′-Methoxyphenyl)-(1*H*)-benzo[*d*][1.2.3]triazole (2q):[31] The reaction was carried out as described in the general procedure using 4′-methoxy-[1,1′-biphenyl]-3,4-diamine (**1q**) (0.118 g, 0.551 mmol), polymer-supported nitrite (0.472 g, containing 1.65 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.284 g, 1.65 mmol). The reaction was complete after 2 h. Purification by silica gel flash column chromatography eluting with 20 % ethyl acetate in hexane gave 5-(4′-methoxyphenyl)-1*H*-benzo-[*d*][1.2.3]triazole (**2q**) (0.0630 g, 51 %) as a white solid. Spectroscopic data were consistent with literature.[31] Mp 181–183 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO + TFA): δ = 3.80 (s, 3 H, 4′-OCH$_3$), 7.02–7.07 (m, 2 H, 3′-H and 5′-H), 7.67–7.73 (m, 3 H, 6-H, 2′-H and 6′-H), 7.95 (d, *J* = 8.8 Hz, 1 H, 7-H), 8.03 (br s, 1 H, 4-H). ^{13}C NMR (101 MHz, [D$_6$]DMSO + TFA): δ = 55.6 (CH$_3$), 111.5 (CH), 114.9 (2 × CH), 116.1 (CH), 125.3 (CH), 128.9 (2 × CH), 132.7 (C), 138.3 (C), 139.0 (C), 139.4 (C), 159.5 (C). MS (ESI) *m/z* (%): 226 (100) [M + H]$^+$.

1-Benzyl-1*H*-benzo[*d*][1.2.3]triazole (4a):[32] The reaction was carried out as described in the general procedure using *N*-benzyl-1,2-phenylenediamine (**3a**) (0.112 g, 0.565 mmol), polymer-supported nitrite (0.484 g, containing 1.70 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.292 g, 1.70 mmol). The reaction was complete after 1.5 h. Purification by silica gel flash column chromatography eluting with 20 % diethyl ether in hexane gave 1-benzyl-1*H*-benzo[*d*][1.2.3]triazole (**4a**) (0.0890 g, 75 %) as a white solid. Mp 113–115 °C (lit.[32] 115–116 °C). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 5.85 (s, 2 H, 1′-H$_2$), 7.25–7.44 (m, 8 H, 8 × ArH), 8.07 (dt, *J* = 8.0, 1.2 Hz, 1 H, ArH). ^{13}C NMR (101 MHz, CDCl$_3$): δ = 52.3 (CH$_2$), 109.7 (CH), 120.1 (CH), 123.9 (CH), 127.4 (CH), 127.6 (2 × CH), 128.5 (CH), 129.0 (2 × CH), 132.8 (C), 134.8 (C), 146.4 (C). MS (ESI) *m/z* (%): 232 (100) [M + Na]$^+$.

1-(4′′-Methoxybenzyl)-1*H*-benzo[*d*][1.2.3]triazole (4b):[33] The reaction was carried out as described in the general procedure using *N*-(4′′-methoxybenzyl)-1,2-phenylenediamine (**3b**) (0.0630 g, 0.276 mmol), polymer-supported nitrite (0.237 g, containing 0.828 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.143 g, 0.828 mmol). The reaction was complete after 1.5 h. Purification by silica gel flash column chromatography eluting with 30 % diethyl ether in hexane gave 1-(4′′-methoxybenzyl)-1*H*-benzo[*d*][1.2.3]triazole (**4b**) (0.0490 g, 75 %) as a white solid. Mp 80–82 °C (lit.[33] 80–81 °C). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.76 (s, 3 H, 4′′-OCH$_3$), 5.77 (s, 2 H, 1′-H$_2$), 6.82–6.87 (m, 2 H, 3′′-H and 5′′-H), 7.21–7.27 (m, 2 H, 2′′-H and 6′′-H), 7.32 (ddd, *J* = 8.2, 6.4, 1.6 Hz, 1 H, 5-H), 7.34–7.36 (m, 1 H, 7-H), 7.39 (ddd, *J* = 8.4, 6.4, 1.2 Hz, 1 H, 6-H), 8.02–8.06 (m, 1 H, 4-H). ^{13}C NMR (101 MHz, CDCl$_3$) δ = 51.9 (CH$_2$), 55.3 (CH$_3$), 109.8 (CH), 114.3 (2 × CH), 120.0 (CH), 123.9 (CH), 126.8 (C), 127.3 (CH), 129.1 (2 × CH), 132.7 (C), 146.4 (C), 159.7 (C). MS (ESI) *m/z* (%): 262 (100) [M + Na]$^+$.

1-(4′′-Fluorobenzyl)-1*H*-benzo[*d*][1.2.3]triazole (4c):[34] The reaction was carried out as described in the general procedure using *N*-(4′′-fluorobenzyl)-1,2-phenylenediamine (**3c**) (0.200 g, 0.925 mmol), polymer-supported nitrite (0.793 g, containing 2.78 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.478 g, 2.78 mmol). The reaction was complete after 1.5 h. Purification by silica gel flash column chromatography eluting with 30 % diethyl ether in hexane gave 1-(4′′-fluorobenzyl)-1*H*-benzo[*d*][1.2.3]triazole (**4c**) (0.160 g, 77 %) as a white solid. Mp 98–100 °C (lit.[34] 99–101 °C). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 5.80 (s, 2 H, 1′-H$_2$), 6.97–7.04 (m, 2 H, 2′′-H and 6′′-H), 7.23–7.29 (m, 2 H, 3′′-H and 5′′-H), 7.31–7.37 (m, 2 H, 5-H and 7-H), 7.41 (ddd, *J* = 7.6, 5.6, 0.8 Hz, 1 H, 6-H), 8.04–8.07 (m, 1 H, 4-H). ^{13}C NMR (101 MHz, CDCl$_3$): δ = 51.5 (CH$_2$), 109.5 (CH), 116.0 (d, $^2J_{C\text{-}F}$ = 21.8 Hz, 2 × CH), 120.1 (CH), 124.0 (CH), 127.5 (CH), 129.4 (d, $^3J_{C\text{-}F}$ = 8.3 Hz, 2 × CH), 130.6 (d, $^4J_{C\text{-}F}$ = 3.3 Hz, C), 132.7 (C), 146.4 (C), 162.7 (d, $^1J_{C\text{-}F}$ = 247.6 Hz, C). MS (ESI) *m/z* (%): 250 (100) [M + Na]$^+$.

1-Nonyl-1*H*-benzo[*d*][1.2.3]triazole (4d):[1b] The reaction was carried out as described in the general procedure using *N*-nonyl-1,2-phenylenediamine (**3d**) (0.100 g, 0.427 mmol), polymer-supported nitrite (0.366 g, containing 1.28 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.220 g, 1.28 mmol). The reaction was complete after 1.5 h. Purification by silica gel flash column chromatography eluting with 35 % diethyl ether in hexane gave 1-nonyl-1*H*-benzo[*d*][1.2.3]triazole (**4d**) (0.0690 g, 66 %) as a white solid. Mp 34–35 °C (lit.[1b] 32–35 °C). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.86 (t, *J* = 6.8 Hz, 3 H, 9′-H$_3$), 1.19–1.39 (m, 12 H, 3′-H$_2$, 4′-H$_2$, 5′-H$_2$, 6′-H$_2$, 7′-H$_2$ and 8′-H$_2$), 1.95–2.05 (m, 2 H, 2′-H$_2$), 4.63 (t, *J* = 7.2 Hz, 2 H, 1′-H$_2$), 7.36 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1 H, 5-H), 7.47 (ddd, *J* = 8.4, 6.8, 1.0 Hz, 1 H, 6-H), 7.50–7.55 (m, 1 H, 7-H), 8.06 (br d, *J* = 8.4 Hz, 1 H, 4-H). ^{13}C NMR (101 MHz, CDCl$_3$): δ = 14.1 (CH$_3$), 22.6 (CH$_2$), 26.7 (CH$_2$), 29.0 (CH$_2$), 29.2 (CH$_2$), 29.3 (CH$_2$), 29.7 (CH$_2$), 31.8 (CH$_2$), 48.3 (CH$_2$), 109.3 (CH), 120.1 (CH), 123.7 (CH), 127.1 (CH), 133.0 (C), 146.0 (C). MS (ESI) *m/z* (%): 268 (100) [M + Na]$^+$.

1-Allyl-1*H*-benzo[*d*][1.2.3]triazole (4e):[35] The reaction was carried out as described in the general procedure using *N*-allyl-1,2-phenylenediamine (**3e**) (0.106 g, 0.715 mmol), polymer-supported nitrite (0.613 g, containing 2.15 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.370 g, 2.15 mmol). The reaction was complete after 1.5 h. Purification by silica gel flash column chromatography eluting with 30 % diethyl ether in hexane gave 1-allyl-1*H*-benzo[*d*][1.2.3]triazole (**4e**) (0.0790 g, 69 %) as a yellow oil. Spectroscopic data were consistent with the literature.[35] ^{1}H NMR (400 MHz, CDCl$_3$): δ = 5.21–5.34 (m, 4 H, 1′-H$_2$ and 3′-H$_2$), 6.05 (ddt, *J* = 16.8, 10.4, 6.0 Hz, 1 H, 2′-H), 7.35 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1 H, ArH), 7.45 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1 H, ArH), 7.50 (dt, *J* = 8.4, 1.2 Hz, 1 H, ArH), 8.05 (dt, *J* = 8.4, 1.2 Hz, 1 H, ArH). ^{13}C NMR (101 MHz, CDCl$_3$): δ = 50.9 (CH$_2$), 109.7 (CH), 119.3 (CH$_2$), 120.1 (CH), 123.9 (CH), 127.3 (CH), 131.2 (CH), 132.9 (C), 146.2 (C). MS (ESI) *m/z* (%): 182 (100) [M + Na]$^+$.

1-Benzoyl-1*H*-benzo[*d*][1.2.3]triazole (4f):[36] The reaction was carried out as described in the general procedure using *N*-benzoyl-1,2-phenylenediamine (**3f**) (0.0900 g, 0.424 mmol), polymer-supported nitrite (0.364 g, containing 1.27 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.219 g, 1.27 mmol). The reaction was complete after 1.5 h. Purification by silica gel flash column chromatography eluting with 20 % diethyl ether in hexane gave 1-benzoyl-1*H*-benzo[*d*][1.2.3]triazole (**4f**) (0.0700 g, 75 %) as a white solid. Mp 110–112 °C (lit.[36] 113–114 °C). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.52–7.62 (m, 3 H, 3 × ArH), 7.66–7.73 (m, 2 H, 2 × ArH), 8.15–8.24 (m, 3 H, 5-H, 6-H and 7-H), 8.39 (d, *J* = 8.0 Hz, 1 H, 4-H). ^{13}C NMR (101 MHz, CDCl$_3$): δ = 114.8 (CH), 120.2 (CH), 126.3 (CH), 128.4 (2 × CH), 130.4 (CH), 131.5 (C), 131.7 (2 × CH), 132.3 (C), 133.7 (CH), 145.8 (C), 166.7 (C). MS (ESI) *m/z* (%): 246 (100) [M + Na]$^+$.

1-Benzyloxycarbonyl-1*H*-benzo[*d*][1.2.3]triazole (4g):[37] The reaction was carried out as described in the general procedure using *N*-benzyloxycarbonyl-1,2-phenylenediamine (**3g**) (0.148 g, 0.611 mmol), polymer-supported nitrite (0.524 g, containing 1.83 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.315 g, 1.83 mmol). The reaction was complete after 1.5 h. Purification by silica gel flash column chromatography eluting with 20 % diethyl ether in hexane gave 1-benzyloxycarbonyl-1*H*-benzo[*d*][1.2.3]triazole (**4g**) (0.102 g, 66 %) as a white solid. Mp 108–110 °C (lit.[37] 108–110 °C). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 5.63 (s, 2 H, 1′-H$_2$), 7.36–7.45 (m, 3 H, 3 × ArH), 7.48 (ddd, *J* = 8.0, 7.2, 1.0 Hz, 1 H, ArH), 7.53–7.58 (m, 2 H, 2 × ArH), 7.63 (ddd, *J* = 8.4, 7.2, 1.0 Hz, 1 H, ArH), 8.08 (dt, *J* = 8.4, 1.2 Hz, 1 H, ArH), 8.12 (dt, *J* = 8.0, 1.2 Hz, 1 H, ArH). ^{13}C NMR (101 MHz, CDCl$_3$): δ = 70.4 (CH$_2$), 113.5 (CH), 120.5 (CH), 125.8 (CH), 128.9 (2 × CH), 128.9 (2 × CH), 129.2 (CH),

130.2 (CH), 131.8 (C), 134.0 (C), 145.9 (C), 148.9 (C). MS (ESI) *m/z* (%): 276 (100) [M + Na]$^+$.

1-Benzenesulfonyl-1*H*-benzo[*d*][1.2.3]triazole (4h):[32] The reaction was carried out as described in the general procedure using *N*-benzenesulfonyl-1,2-phenylenediamine (**3h**) (0.130 g, 0.524 mmol), polymer-supported nitrite (0.448 g, containing 1.57 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.270 g, 1.57 mmol). The reaction was complete after 1.5 h. Purification by silica gel flash column chromatography eluting with 20 % diethyl ether in hexane gave 1-benzenesulfonyl-1*H*-benzo[*d*][1.2.3]triazole (**4h**) (0.103 g, 77 %) as a white solid. Mp 106–109 °C (lit.[32] 108–110 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (ddd, *J* = 8.0, 7.2, 0.8 Hz, 1 H, ArH), 7.51–7.57 (m, 2 H, 2 × ArH), 7.62–7.69 (m, 2 H, 2 × ArH), 8.06–8.15 (m, 4 H, 4 × ArH). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 112.0 (CH), 120.6 (CH), 125.9 (CH), 128.0 (2 × CH), 129.7 (2 × CH), 130.3 (CH), 131.7 (C), 135.2 (CH), 137.2 (C), 145.5 (C). MS (ESI) *m/z* (%): 282 (100) [M + Na]$^+$.

1-(4′-Methylbenzenesulfonyl)-1*H*-benzo[*d*][1.2.3]triazole (4i):[32] The reaction was carried out as described in the general procedure using *N*-(2′-aminophenyl)-4-methylbenzenesulfonamide (**3i**) (0.0500 g, 0.190 mmol), polymer-supported nitrite (0.163 g, containing 0.570 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.0980 g, 0.570 mmol). After 0.5 h, further polymer-supported nitrite (0.081 g, containing 0.285 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.0490 g, 0.285 mmol) were added and the reaction was stopped after 5 h. Purification by silica gel flash column chromatography eluting with 50 % diethyl ether in hexane gave 1-(4′-methylbenzenesulfonyl)-1*H*-benzo[*d*][1.2.3]triazole (**4i**) (0.0330 g, 64 %) as a white solid. Mp 126–128 °C (lit.[32] 130–132 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3 H, 4′-CH_3), 7.29–7.33 (m, 2 H, 3′-H and 5′-H), 7.47 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1 H, ArH), 7.65 (ddd, *J* = 8.0, 7.2, 1.0 Hz, 1 H, ArH), 7.97–8.02 (m, 2 H, 2′-H and 6′-H), 8.07 (dt, *J* = 8.4, 0.8 Hz, 1 H, ArH), 8.10 (dd, *J* = 8.4, 0.8 Hz, 1 H, ArH). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 21.7 (CH_3), 112.1 (CH), 120.6 (CH), 125.8 (CH), 128.0 (2 × CH), 130.2 (CH), 130.3 (2 × CH), 131.6 (C), 134.1 (C), 145.5 (C), 146.8 (C). MS (ESI) *m/z* (%): 296 (100) [M + Na]$^+$.

1-(3′,4′,5′-Trimethoxybenzoyl)-1*H*-benzo[*d*][1.2.3]triazole (4j):[16] The reaction was carried out as described in the general procedure using *N*-(3′,4′,5′-trimethoxybenzoyl)-1,2-phenylenediamine (**3j**) (0.120 g, 0.397 mmol), polymer-supported nitrite (0.340 g, containing 1.19 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.205 g, 1.19 mmol). The reaction was complete after 1.5 h. Purification by silica gel flash column chromatography eluting with 60 % diethyl ether in hexane gave 1-(3′,4′,5′-trimethoxybenzoyl)-1*H*-benzo[*d*][1.2.3]triazole (**4j**) (0.0880 g, 71 %) as a white solid. Mp 124–126 °C (lit.[16] 126–128 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.93 (s, 6 H, 3′-OCH_3 and 5′-OCH_3), 3.97 (s, 3 H, 4′-OCH_3), 7.52 (ddd, *J* = 8.0, 7.2, 1.0 Hz, 1 H, ArH), 7.55 (s, 2 H, 2′-H and 6′-H), 7.68 (ddd, *J* = 8.4, 7.2, 1.0 Hz, 1 H, ArH), 8.13 (d, *J* = 8.4 Hz, 1 H, ArH), 8.33 (d, *J* = 8.0 Hz, 1 H, ArH). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 56.4 (2 × CH_3), 61.1 (CH_3), 109.6 (2 × CH), 114.8 (CH), 120.1 (CH), 125.9 (C), 126.3 (CH), 130.4 (CH), 132.6 (C), 143.2 (C), 145.6 (C), 152.9 (2 × C), 165.7 (C). MS (ESI) *m/z* (%) 336 (100) [M + Na]$^+$.

9-Methyl-9-azabicyclo[3.3.1]nonane-3-benzo[1.2.3]triazole (4k): The reaction was carried out as described in the general procedure using *N*-(2′-aminophenyl)-9-methyl-9-azabicyclo[3.3.1]nonan-3-amine (**3k**) (0.060 g, 0.24 mmol), *p*-toluenesulfonic acid monohydrate (0.14 g, 0.73 mmol), polymer-supported nitrite (0.21 g, containing 0.73 mmol of NO_2). The reaction was complete after 3.5 h. Purification by flash column chromatography eluting with 10 % methanol in dichloromethane and 1 % ammonium hydroxide gave 9-methyl-9-azabicyclo[3.3.1]nonane-3-benzo[1.2.3]triazole (**4k**) as a white solid (0.037 g, 61 %). Mp 78–80 °C. IR (neat): $\tilde{\nu}_{max}$ = 2922, 1451, 1310, 1229, 1150, 1061, 1026, 781, 743. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.12 (d, *J* = 13.5 Hz, 2 H, 6-*H*H and 8-*H*H), 1.64 (d, *J* = 13.5 Hz, 1 H, 7-*H*H), 2.07 (tt, *J* = 13.5, 3.8 Hz, 2 H, 6-H*H* and 8-H*H*), 2.25 (tt, *J* = 13.5, 3.8 Hz, 1 H, 7-H*H*), 2.35 (td, *J* = 13.5, 3.8 Hz, 2 H, 2-*H*H and 4-*H*H), 2.52–2.63 (m, 5 H, 2-H*H* and 4-H*H* and NCH_3), 3.19–3.27 (m, 2 H, 1-H and 5-H), 5.23–5.30 (m, 1 H, 3-H), 7.35 (ddd, *J* = 8.3, 6.9, 1.0 Hz, 1 H, 4′-H), 7.46 (ddd, *J* = 8.3, 6.9, 1.0 Hz, 1 H, 5′-H), 7.64 (br d, *J* = 8.3 Hz, 1 H, 6′-H), 8.05 (br d, *J* = 8.3 Hz, 1 H, 3′-H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.5 (CH_2), 23.1 (2 × CH_2), 32.9 (2 × CH_2), 39.8 (CH_3), 51.6 (2 × CH), 51.7 (CH), 109.8 (CH), 120.1 (CH), 123.8 (CH), 126.9 (CH), 133.0 (C), 146.1 (C). HRMS (ESI) *m/z* [M + H]$^+$ calcd. for $C_{15}H_{21}N_4$ 257.1761, found 257.1752.

1-Benzoyl-6-methyl-1*H*-benzo[*d*][1.2.3]triazole (6a):[38] The reaction was carried out as described in the general procedure using *N*-benzoyl-5-methyl-1,2-phenylenediamine (**5a**) (0.0900 g, 0.398 mmol), polymer-supported nitrite (0.524 g, containing 1.19 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.205 g, 1.19 mmol). The reaction was complete after 1.5 h. Purification by silica gel flash column chromatography eluting with 20 % diethyl ether in hexane gave 1-benzoyl-6-methyl-1*H*-benzo[*d*][1.2.3]triazole (**6a**) (0.0730 g, 77 %) as a white solid. Mp 122–123 °C (lit.[38] 122–123 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.60 (s, 3 H, 6-CH_3), 7.36 (dd, *J* = 8.4, 1.2 Hz, 1 H, 5-H), 7.54–7.60 (m, 2 H, 3′-H and 5′-H), 7.68 (tt, *J* = 7.6, 1.2 Hz, 1 H, 4′-H), 8.02 (d, *J* = 8.4 Hz, 1 H, 4-H), 8.17–8.23 (m, 3 H, 7-H, 2′-H and 6′-H). δ_C (101 MHz, $CDCl_3$): 22.1 (CH_3), 114.3 (CH), 119.6 (CH), 128.3 (CH), 128.4 (2 × CH), 131.6 (C), 131.7 (2 × CH), 132.8 (C), 133.6 (CH), 141.5 (C), 144.4 (C), 166.9 (C). MS (ESI) *m/z* (%): 260 (100) [M + Na]$^+$.

1-Benzoyl-5-methoxy-1*H*-benzo[*d*][1.2.3]triazole (6b):[39] The reaction was carried out as described in the general procedure using *N*-benzoyl-4-methoxy-1,2-phenylenediamine (**5b**) (0.0380 g, 0.157 mmol), polymer-supported nitrite (0.134 g, containing 0.470 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.0810 g, 0.470 mmol). The reaction was complete after 1.5 h. Purification by silica gel flash column chromatography eluting with 30 % diethyl ether in hexane gave 1-benzoyl-6-methyl-1*H*-benzo[*d*][1.2.3]triazole (**6b**) (0.0300 g, 76 %) as a white solid. Mp 114–116 °C (lit.[39] 116 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.93 (s, 3 H, 5-OCH_3), 7.32 (dd, *J* = 9.0, 2.2 Hz, 1 H, 6-H), 7.49 (d, *J* = 2.2 Hz, 1 H, 4-H), 7.57 (t, *J* = 7.5 Hz, 2 H, 3′-H and 5′-H), 7.68 (t, *J* = 7.5 Hz, 1 H, 4′-H), 8.19–8.23 (m, 2 H, 2′-H and 6′-H), 8.25 (d, *J* = 9.0 Hz, 1 H, 7-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 55.8 (CH_3), 99.8 (CH), 115.3 (CH), 121.9 (CH), 127.4 (C), 128.4 (2 × CH), 131.5 (C), 131.7 (2 × CH), 133.6 (CH), 147.0 (C), 158.6 (C), 166.5 (C). MS (ESI) *m/z* (%): 276 (100) [M + Na]$^+$.

1-Benzoyl-5,7-dimethyl-1*H*-benzo[*d*][1.2.3]triazole (6c):[40] The reaction was carried out as described in the general procedure using *N*-benzoyl-4,6-dimethyl-1,2-phenylenediamine (**5c**) (0.046 g, 0.19 mmol), polymer-supported nitrite (0.16 g, containing 0.57 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.098 g, 0.57 mmol). The reaction was complete after 1.5 h. Purification by silica gel flash column chromatography eluting with 25 % diethyl ether in hexane gave 1-benzoyl-5,7-dimethyl-1*H*-benzo[*d*][1.2.3]triazole (**6c**) (0.033 g, 69 %) as a white solid. Mp 109–111 °C (lit.[40] 111 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.53 (s, 3 H, CH_3), 2.66 (s, 3 H, CH_3), 7.30 (br s, 1 H, 6-H), 7.54–7.60 (m, 2 H, 3′-H and 5′-H), 7.71 (tt, *J* = 7.5, 1.4 Hz, 1 H, 4′-H), 7.77 (br s, 1 H, 4-H), 8.08–8.13 (m, 2 H, 2′-H and 6′-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 20.9 (CH_3), 21.3 (CH_3), 117.0 (CH), 123.9 (C), 128.5 (2 × CH), 130.7 (C), 132.0 (2 × CH), 132.0 (C), 133.9 (CH), 134.1 (CH), 136.6 (C), 147.4 (C), 166.2 (C); MS (ESI) *m/z* (%): 274 (100) [M + Na]$^+$.

1-(4′-Fluorophenyl)-5-methyl-1*H*-benzo[*d*][1.2.3]triazole (6d): The reaction was carried out as described in the general procedure using *N*-(4′-fluorophenyl)-4-methyl-1,2-phenylenediamine (**5d**) (0.0350 g, 0.162 mmol), polymer-supported nitrite (0.138 g, containing 0.486 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.0920 g, 0.486 mmol). The reaction was complete after 1.5 h. Purification by silica gel flash column chromatography eluting with 20 % ethyl acetate in petroleum ether (40–60) gave 1-(4′-fluorophenyl)-5-methyl-1*H*-benzo[*d*][1.2.3]triazole (**6d**) as a white solid (0.0350 g, 95 %). Mp 123–125 °C. IR (neat): $\tilde{\nu}_{max}$ = 3075, 2928, 1514, 1229, 1186, 1099, 1072, 829, 806. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.54 (s, 3 H, 4-CH_3), 7.29 (dd, *J* = 8.8, 8.2 Hz, 2 H, 3′-H and 5′-H), 7.38 (dd, *J* = 8.5, 1.1 Hz, 1 H, 6-H), 7.57 (d, *J* = 8.5 Hz, 1 H, 7-H), 7.74 (dd, *J* = 8.8, 4.7 Hz, 2 H, 2′-H and 6′-H), 7.89 (br s, 1 H, 4-H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.6 (CH_3), 109.7 (CH), 117.0 (d, $^2J_{C-F}$ = 23.1 Hz, 2 × CH), 119.4 (CH), 124.8 (d, $^3J_{C-F}$ = 8.6 Hz, 2 × CH), 130.6 (CH), 131.0 (C), 133.4 (d, $^4J_{C-F}$ = 3.1 Hz, C), 134.7 (C), 147.2 (C), 162.4 (d, $^1J_{C-F}$ = 249.0 Hz, C). HRMS (ESI) *m/z* [M + Na]$^+$ calcd. for $C_{13}H_{10}FN_3Na$ 250.0751, found 250.0747.

Methyl 4-*N*-(5′-methyl-1*H*-benzo[*d*][1.2.3]triazolo)benzoate (6e): The reaction was carried out as described in the general procedure using methyl 4-(4′-methyl-1,2-phenylenediamino)benzoate (**5e**) (0.0300 g, 0.101 mmol), polymer-supported nitrite (0.0871 g, containing 0.305 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.0580 g, 0.305 mmol). The reaction was complete after 1.5 h. Purification by silica gel flash column chromatography eluting with 20 % ethyl acetate in petroleum ether (40–60) gave methyl 4-*N*-(5′-methyl-1*H*-benzo[*d*][1.2.3]triazolo)benzoate (**6e**) as a white solid (0.0190 g, 61 %). Mp 156–157 °C. IR (neat): $\tilde{\nu}_{max}$ = 2951, 1721, 1609, 1516, 1437, 1290, 1117, 1059, 766. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.56 (s, 3 H, 5′-CH_3), 3.99 (s, 3 H, OCH_3), 7.43 (dd, *J* = 8.5, 1.0 Hz, 1 H, 6′-H), 7.70 (d, *J* = 8.5 Hz, 1 H, 7′-H), 7.91–7.95 (m, 3 H, 4′-H, 3-H and 5-H), 8.29 (d, *J* = 8.7 Hz, 2 H, 2-H and 6-H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.6 (CH_3), 52.6 (CH_3), 100.0 (CH), 119.7 (CH), 121.9 (2 × CH), 129.9 (C), 130.5 (C), 131.0 (CH), 131.5 (2 × CH), 135.0 (C), 140.9 (C), 147.5 (C), 166.2 (C). HRMS (ESI) *m/z* [M + Na]$^+$ calcd. for $C_{15}H_{13}N_3NaO_2$ 290.0900, found 290.0890.

1-(3′,4′,5′-Trimethoxyphenyl)-5-methyl-1*H*-benzo[*d*][1.2.3]triazole (6f): The reaction was carried out as described in the general procedure using *N*-(3′,4′,5′-trimethoxyphenyl)-4-methyl-1,2-phenylenediamine (**5f**) (0.0450 g, 0.156 mmol), polymer-supported nitrite (0.134 g, containing 0.468 mmol of NO_2) and *p*-toluenesulfonic acid monohydrate (0.0890 g, 0.468 mmol). The reaction was complete after 1.5 h. Purification by silica gel flash column chromatography eluting with 20 % ethyl acetate in petroleum ether (40–60) gave 1-(3′,4′,5′-trimethoxyphenyl)-5-methyl-1*H*-benzo[*d*][1.2.3]triazole (**6f**) as a white solid (0.0400 g, 86 %). Mp 136–137 °C. IR (neat): $\tilde{\nu}_{max}$ = 2940, 1601, 1508, 1464, 1229, 1128, 1070, 881. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.54 (s, 3 H, 5-CH_3), 3.92 (s, 3 H, 4′-OCH_3), 3.94 (s, 6 H, 3′-OCH_3 and 5′-OCH_3), 6.97 (s, 2 H, 2′-H and 6′-H), 7.38 (dd, *J* = 8.5, 1.2 Hz, 1H, 6-H), 7.61 (d, *J* = 8.5 Hz, 1 H, 7-H), 7.88 (br s, 1 H, 4-H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.6 (CH_3), 56.6 (2 × CH_3), 61.2 (CH_3), 100.8 (2 × CH), 109.9 (CH), 119.4 (CH), 130.5 (CH), 131.0 (C), 132.9 (C), 134.7 (C), 138.3 (C), 147.2 (C), 154.1 (2 × C). HRMS (ESI) *m/z* [M + Na]$^+$ calcd. for $C_{16}H_{17}N_3NaO_3$ 322.1162, found 322.1149.

Methyl (2*S*)-2-[(benzyloxycarbonyl)amino]-3-[(2′-nitro-4′-methylphenyl)amino]propanoate (8): To a solution of methyl (2*S*)-2-[(benzyloxycarbonyl)amino]-3-aminopropanoate (**7**) (2.85 g, 11.3 mmol) in acetonitrile (50 mL) was added 4-fluoro-3-nitrotoluene (5.26 g, 33.9 mmol) and triethylamine (4.72 mL, 33.9 mmol). The solution was heated under reflux and stirred under argon for 20 h. The solution was then cooled to room temperature and the solvent was removed in vacuo. The viscous residue was then dissolved in ethyl acetate (100 mL) and washed with a saturated solution of aqueous sodium hydrogen carbonate (200 mL). The aqueous layer was extracted with ethyl acetate (2 × 200 mL). The combined organic layers were washed with brine (200 mL), dried ($MgSO_4$), filtered, and concentrated. Purification by flash column chromatography eluting with 1 % methanol in dichloromethane gave methyl (2*S*)-2-[(benzyloxycarbonyl)amino]-3-[(2′-nitro-4′-methylphenyl)amino]propanoate (**8**) as a viscous orange oil (2.70 g, 62 %). IR (neat): $\tilde{\nu}_{max}$ = 3364, 2955, 1721, 1520, 1273, 1227, 1057. $[\alpha]_D^{24}$ = +50.4 (*c* = 1.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.26 (s, 3 H, 4′-CH_3), 3.68–3.84 (m, 5 H, OCH_3 and 3-H_2), 4.64 (q, *J* = 6.3 Hz, 1 H, 2-H), 5.10 (d, *J* = 12.4 Hz, 1 H, OC*H*HPh), 5.13 (d, *J* = 12.4 Hz, 1 H, OCH*H*Ph), 5.58 (d, *J* = 6.3 Hz, 1 H, NH), 6.90 (d, *J* = 8.5 Hz, 1 H, 6′-H), 7.24 (d, *J* = 8.5 Hz, 1 H, 5′-H), 7.28–7.41 (m, 5 H, Ph), 7.97 (s, 1 H, 3′-H), 8.09 (t, *J* = 6.3 Hz, 1 H, NH). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 20.1 (CH_3), 44.8 (CH_2), 53.1 (CH_3), 53.7 (CH), 67.5 (CH_2), 113.8 (CH), 126.1 (C), 126.4 (CH), 128.4 (2 × CH), 128.5 (CH), 128.7 (2 × CH), 132.6 (C), 136.1 (C), 137.9 (CH), 143.2 (C), 155.9 (C), 170.8 (C). HRMS (ESI) *m/z* [M + Na]$^+$ calcd. for $C_{19}H_{21}N_3NaO_6$ 410.1323, found 410.1313.

Methyl (2*S*)-2-[(benzyloxycarbonyl)amino]-3-(5′-methyl-1*H*-benzo[*d*][1.2.3]triazol-1′-yl)propanoate (10): To a solution of methyl (2*S*)-2-[(benzyloxycarbonyl)amino]-3-[(2′-nitro-4′-methylphenyl)amino]propanoate (**8**) (2.70 g, 6.96 mmol) in methanol (100 mL) was added tin(II) dichloride dihydrate (14.1 g, 62.7 mmol). The reaction mixture was heated under reflux and stirred under argon for 48 h. After cooling to room temperature, the reaction was quenched by addition of a saturated solution of aqueous sodium hydrogen carbonate (100 mL) and the product was extracted with ethyl acetate (3 × 100 mL). The combined organic layers were washed with brine (150 mL), dried ($MgSO_4$), filtered and concentrated in vacuo. Purification by flash column chromatography eluting with 10 % ethyl acetate in dichloromethane gave methyl (2*S*)-2-[(benzyloxycarbonyl)amino]-3-[(4′-methyl-2′-aminophenyl)amino]propanoate (**9**) as a viscous pale yellow oil (1.46 g, 59 %). This material was then used immediately for the next step. The reaction was carried out as described in the general procedure using methyl (2*S*)-2-[(benzyloxycarbonyl)amino]-3-[(4′-methyl-2′-aminophenyl)amino]propanoate (**9**) (1.40 g, 3.93 mmol), *p*-toluenesulfonic acid (2.24 g, 11.8 mmol) and polymer-supported nitrite (3.32 g, containing 11.8 mmol of NO_2). The reaction was complete after 3 h. Purification by flash column chromatography, eluting with 10 % ethyl acetate in dichloromethane gave methyl (2*S*)-2-[(benzyloxycarbonyl)amino]-3-(5′-methyl-1*H*-benzo[*d*][1.2.3]triazol-1′-yl)propanoate (**10**) as a white solid (0.997 g, 69 %). Mp 79–83 °C. IR (neat): $\tilde{\nu}_{max}$ = 3314, 2951, 1717, 1501, 1439, 1215, 1057, 1022, 741. $[\alpha]_D^{22}$ = +36.5 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.48 (s, 3 H, 5′-CH_3), 3.73 (s, 3 H, OCH_3), 4.86 (dt, *J* = 7.1, 4.6 Hz, 1 H, 2-H), 5.01–5.17 (m, 4 H, OCH_2Ph and 3-H_2), 5.68 (t, *J* = 7.1 Hz, 1 H, NH), 7.21 (dd, *J* = 8.5, 1.4 Hz, 1 H, 6′-H), 7.27–7.39 (m, 6 H, Ph and 7′-H), 7.76 (br s, 1 H, 4′-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 21.6 (CH_3), 48.6 (CH_2), 53.3 (CH_3), 54.3 (CH), 67.3 (CH_2), 108.7 (CH), 119.1 (CH), 128.3 (2 × CH), 128.4 (CH), 128.7 (2 × CH), 130.1 (CH), 132.4 (C), 134.2 (C), 136.1 (C), 146.4 (C), 155.8 (C), 169.5 (C). HRMS (ESI) *m/z* [M + Na]$^+$ calcd. for $C_{19}H_{20}N_4NaO_4$ 391.1377, found 391.1374.

(2*S*)-2-Amino-3-(5′-methyl-1*H*-benzo[*d*][1.2.3]triazol-1′-yl]-propanoic acid (11): A solution of methyl (2*S*)-2-[(benzyloxycarbonyl)amino]-3-[(5′-methyl)benzotriazole]propanoate (**10**) (0.185 g, 0.501 mmol) in 6 M hydrochloric acid solution (10 mL) was heated under reflux for 20 h. After cooling to room temperature, the reaction mixture was concentrated in vacuo. Recrystallization from methanol and diethyl ether gave (2*S*)-2-amino-3-(5′-methyl-

1*H*-benzo[*d*][1.2.3]triazol-1′-yl]propanoic acid (**11**) as a pale brown solid (0.0973 g, 76 %). Mp 180–184 °C. IR (neat): $\tilde{\nu}_{max}$ = 2916, 2862, 1744, 1505, 1435, 1227, 802. $[\alpha]_D^{19}$ = +17.9 (*c* = 1.0, MeOH). ^{1}H NMR (400 MHz, CD_3OD): δ = 2.52 (s, 3H, 5′-CH_3), 4.80 (dd, *J* = 5.6, 4.2 Hz, 1 H, 2-H), 5.25 (dd, *J* = 15.4, 4.2 Hz, 1 H, 3-*H*H), 5.34 (dd, *J* = 15.4, 5.6 Hz, 1 H, 3-H*H*), 7.47 (dd, *J* = 8.6, 1.5 Hz, 1 H, 6′-H), 7.73 (dd, *J* = 8.6, 0.8 Hz, 1 H, 7′-H), 7.77 (dd, *J* = 1.5, 0.8 Hz, 1 H, 4′-H). ^{13}C NMR (101 MHz, CD_3OD): δ = 21.4 (CH_3), 48.0 (CH_2), 53.5 (CH), 110.8 (CH), 119.0 (CH), 131.6 (CH), 133.4 (C), 136.6 (C), 147.2 (C), 168.9 (C). HRMS (ESI) *m/z* [M + Na]$^+$ calcd. for $C_{10}H_{12}N_4NaO_2$ 243.0852, found 243.0847.

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