[bmim]PF_6/KOH: a recyclable catalytic system for an azide–arylacetaldehyde [3 + 2] cycloaddition

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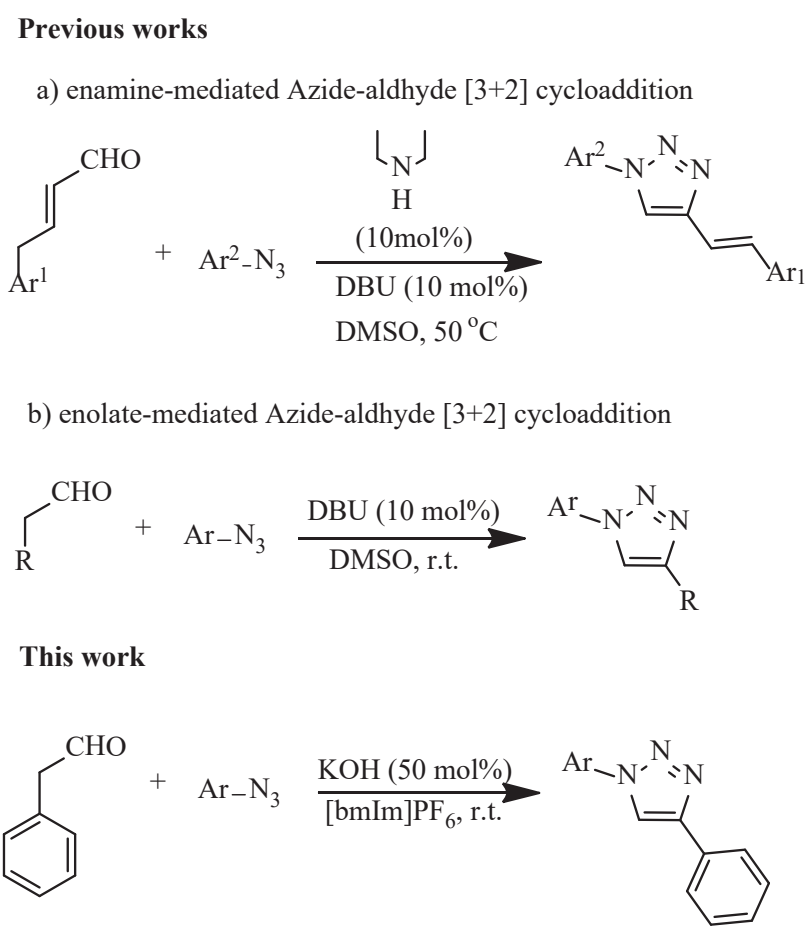
A fast and green protocol for the synthesis of 1,4-disubstituted 1,2,3-triazoles from azides and arylacetaldehydes at room temperature was developed using [bmim]PF_6/KOH as the reaction medium. It was found that the *in situ*-generated carbene from [bmim]PF_6/KOH acted as the catalyst. In the absence of a transition-metal catalyst and organic solvent, this azide–arylacetaldehyde [3 + 2] cycloaddition proceeds efficiently, with high levels of regioselectivity, broad range of substrates, excellent yields and simple operation under mild conditions.

Keywords: 1,4-disubstituted 1,2,3-triazoles, ionic liquid [bmim]PF_6/KOH, arylacetaldehydes

1,4-Disubstituted-1,2,3-triazoles are widely used in the pharmaceutical industry due to their considerable biological activity. The best-known regioselective formation of 1,4-disubstituted-1,2,3-triazoles is the copper(ı)-catalysed azide–alkyne cycloaddition (CuAAC) reaction. Compared with the classical thermal Huisgen reaction,[1] the CuAAC reaction is considered to be a very reliable and straightforward method for the regioselective synthesis of 1,4-disubstituted-1,2,3-triazoles.

Although the CuAAC reaction has been widely used in organic synthesis, medicinal chemistry, surface and polymer chemistry, and bioconjugation applications, its use in chemical biology has some limitations due to the cytotoxicity of copper ions in living organisms. For this reason, a metal-free catalytic azide–aldehyde [3 + 2] cycloaddition has been developed (Scheme 1, previous work).[2,3] In 2013, Wang and co-workers developed[2] an inverse-electron-demand 1,3-dipolar cycloaddition reaction between various azides and unsaturated aldehydes catalysed by diethylamine in DMSO at 50 ºC using DBU as the base. This has been used to synthesise 1,4-disubstituted 1,2,3-triazoles with high levels of regioselectivity. In the following year, Ramachary and co-workers reported[3] a DBU-catalysed azide–aldehyde [3 + 2] 1,3-dipolar cycloaddition reaction in DMSO at room temperature between azides and enolisable aldehydes to form 1,4-disubstituted 1,2,3-triazoles. Such metal-free



Scheme 1 Azide–aldehyde [3 + 2] cycloaddition reaction for synthesis of 1,4-disubstituted 1,2,3-triazoles.

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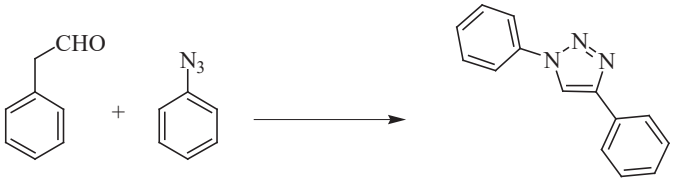
azide–aldehyde [3 + 2] 1,3-dipolar cycloaddition reactions are considered to be alternatives to the previous CuAAC reactions due to their high rate and regioselectivity, mild reaction conditions, easily available substrates and excellent yields. However, the use of organic solvents (DMSO) and catalysts (DBU and diethylamine) could potentially cause various health and environmental concerns due to their volatility and toxicity. The preferred green solvents used for the synthesis of 1,4-disubstituted 1,2,3-triazoles are water,[4–7] supercritical carbon dioxide ($ScCO_2$)[8–10] and ionic liquids.[11–13]

An ionic liquid is a salt in the liquid state, which presents unique properties, such as high thermal stability, good solvating ability, negligible vapour pressure and ease of recyclability. Among them, the room temperature ionic liquids usually consisting of bulky and asymmetric organic cations, such as 1-alkyl-3-methylimidazolium, 1-alkylpyridinium, *N*-methyl-*N*-alkylpyrrolidinium or ammonium ions, have shown great promise as attractive alternatives to conventional volatile and toxic organic solvents. To the best of our knowledge, the azide–aldehyde [3 + 2] 1,3-dipolar cycloaddition reaction for the synthesis of 1,4-disubstituted 1,2,3-triazoles performed in a green ionic liquid has not been reported previously. Thus, taking into account the economic and environmental aspects, we decided to synthesise 1,4-disubstituted 1,2,3-triazoles in ionic liquids using an inorganic base as the catalyst. Following our previous work on the synthesis of 1,4-disubstituted 1,2,3-triazoles,[4,5] the main work described in this paper reveals a green protocol using [bmim]PF_6/KOH as the reaction medium and catalyst for the azide–aldehyde [3 + 2] cycloaddition reaction with a much easier work-up and purification (Scheme 1, this work).

Results and discussion

The reaction between phenylacetaldehyde and phenyl azide was selected as the model reaction for optimising the reaction conditions (Scheme 2). First, in the light of economic and environmental concerns, the reaction conditions were established as follows. The results of the reaction of phenylacetaldehyde (1.0 mmol), phenyl azide (1.0 mmol), catalyst (10 mol%) and [bmim]PF_6 (5.0 mL) at room temperature to screen suitable inorganic base catalysts are shown in Table 1. The model reaction was initially carried out in the absence of inorganic bases for 30 min and no products were obtained (Table 1, entry 1). Meanwhile, when using a weak inorganic base as the catalyst, such as Na_2CO_3, K_2CO_3 or $KHCO_3$ (Table 1, entries 2–4), the model reaction yielded the products in less than 5%, which indicated that the phenylacetaldehyde could not be enolised by weak bases. Therefore, the strong inorganic base KOH (10 mol%) was used and the yield increased to 20% in 30 min. When increasing the catalyst loading of KOH to 40 mol% (Table 1, entries 5–8), the yield reached 90%. A further increase in the catalyst loading of KOH to 50 mol% (Table 1, entry 9) gave almost the same yield in 10 min. According to these results, it was concluded that the stronger the alkaline, the more loading of the catalyst, the faster the reaction rate. The selected catalyst loading of KOH was 40 mol%.



Scheme 2 Model reaction for optimising the reaction conditions.

Table 1 The model reaction was performed in [bmim]PF_6 at room temperature[a]

Entry	Catalyst	Catalyst loading (mol%)	Time (min)	Yield (%)[b]
1	–	–	30	–
2	Na_2CO_3	10	30	<5
3	K_2CO_3	10	30	<5
4	$KHCO_3$	10	30	<5
5	KOH	10	30	20
6	KOH	20	30	42
7	KOH	30	30	58
8	KOH	40	10	90
9	KOH	50	10	91

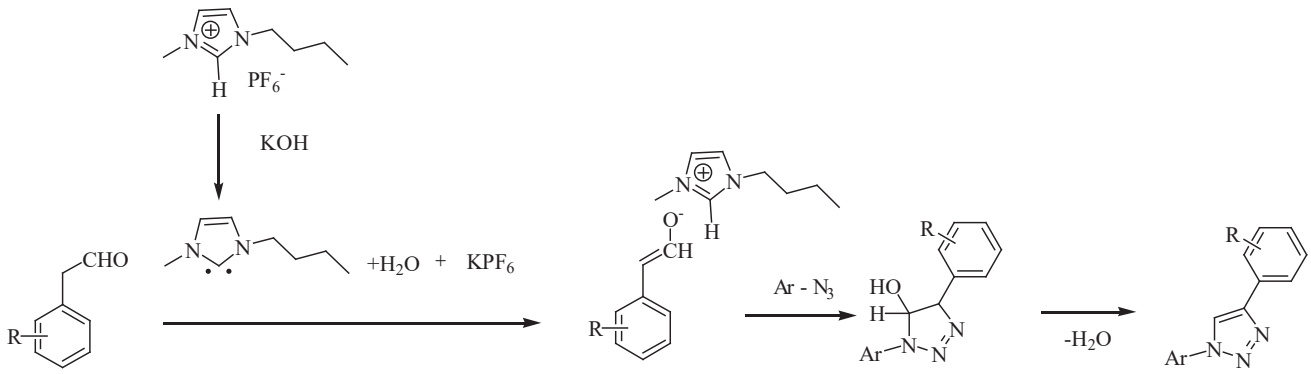
[a]Reaction conditions: phenylacetaldehyde (1.0 mmol), phenyl azide (1.0 mmol), [bmim]PF_6 (5.0 mL) and room temperature.
[b]Isolated yields.

A mechanism for the azide–aldehyde [3 + 2] cycloaddition reaction in [bmim]PF_6 in the presence of KOH was also proposed and studied (Scheme 3). First, the [bmim]PF_6 could react with KOH to produce a mixture of carbene and water. Second, the generated carbene could convert the aldehyde to its corresponding enolate. Then the enolate reacted with aryl azides to form the adduct 1,2,3-triazolines. The adducts subsequently underwent elimination and were converted to the 1,4-disubstituted 1,2,3-triazoles.[3] To provide some experimental support for the mechanistic proposal, the ^{1}H NMR spectra of [bmim]PF_6 in [D_6]DMSO before and after the addition of KOH were determined and the results are shown in ESI Fig. 1. It can be seen from ESI Fig. 1a that the signal at 9.1 ppm was assigned to the C_2–H in [bmim]PF_6. The disappearance of the signal at 9.1 ppm in ESI Fig. 1b was clearly observed, which indicated that OH^- is removing the C_2–H in [bmim]PF_6 to generate the corresponding carbene.[14,15] In addition, the stability of the generated carbene was tested by adding extra water to the system containing [bmim]PF_6 and KOH in [D_6]DMSO. It can be seen from ESI Fig. 1c that the signal at 9.1 ppm did not recover and the signal of H_2O could be seen at 3.8 ppm, which indicated that this carbene was stable in the presence of water.

Furthermore, it was confirmed by comparison of the ^{1}H NMR spectrum of [bmim]PF_6 + KOH before and after addition of phenylacetaldehyde in [D_6]DMSO that the *in situ*-generated carbene converted the aldehyde to its corresponding enolate. The results are shown in ESI Fig. 2. As shown in ESI Fig. 2a,b, the signals at 9.7 ppm and 9.1 ppm were assigned to the proton in the aldehyde of phenylacetaldehyde and the C_2–H in [bmim]PF_6, respectively. When KOH was added to [bmim]PF_6, the C_2–H in [bmim]PF_6 was removed and the corresponding carbene generated (ESI Fig. 2c). At this time, phenylacetaldehyde was added. It can be seen from ESI Fig. 2d that the signal at 9.7 ppm disappeared and the signal at 9.1 ppm appeared. This indicated that the generated carbene converted the aldehyde to its corresponding enolate.

In considering the economic and environmental aspects, the lifetime and re-use of the ionic liquid and the catalyst are very significant factors. The re-use of ionic liquids usually involves the following procedures.[6] After reaction completion, the products are quantitatively recovered by simple pump filtration system. At the same time, the catalytic carbene remains in the reaction mixture. Fresh quantities of reactants are then introduced for another reaction cycle. As can be seen from Table 2, the activity of the remaining carbene was not lost after five cycles. No significant loss of ionic liquid was observed.

Finally, we considered that the optimised conditions are: KOH (40 mol%), phenylacetaldehyde (1.0 mmol), phenyl azide (1.0 mmol) and room temperature. With the optimised conditions

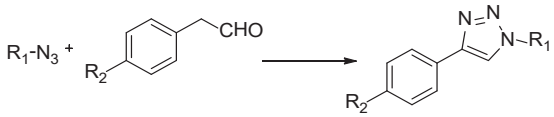


Scheme 3 Proposed mechanism for the azide–aldehyde [3 + 2] cycloaddition catalysed by [bmim]PF_6/KOH.

Table 2 The reusablity of the ionic liquid system

Cycle	1	2	3	4	5
Yield (%)	95	94	93	94	90

Table 3 Synthesis of 1,4-disubstituted 1,2,3-triazoles catalysed by KOH in [bmim]PF_6[a]



Entry	R_1	R_2	Product	Time (min)	Yield (%)[b]
1	C_6H_5	H	**a**	10	90
2	$C_6H_5CH_2$	H	**b**	60	86
3	*o*-FC_6H_4	H	**c**	30	90
4	*o*-$F_3CC_6H_4$	H	**d**	30	93
5	*o*-ClC_6H_4	H	**e**	30	91
6	*o*-MeC_6H_4	H	**f**	30	86
7	*p*-MeC_6H_4	H	**g**	30	90
8	2,4,6-MeC_6H_4	H	**h**	60	87
9	C_6H_5	*p*-MeO	**i**	40	92
10	$EtOOCCH_2$	H	**j**	90	87
11	$C_6H_5CH_2$	*p*-MeO	**k**	70	86
12	$C_6H_5CH_2$	*p*-EtO	**l**	70	88
13	$C_6H_5CH_2$	*p*-Cl	**m**	60	93
14	$C_6H_5CH_2$	*p*-F	**n**	60	90
15	C_6H_5	*p*-EtO	**o**	30	95
16	$C_6H_5CH_2$	*p*-Me	**p**	60	89
17	C_6H_5	*p*-Me	**q**	30	92
18	2-Me-5-$NO_2C_6H_5$	*p*-Me	**r**	30	90

[a]Reaction conditions: azide (1.0 mmol), aldehyde (1.0 mmol), KOH (40 mol%) and room temperature

[b]Isolated yields

in hand, a series of 1,4-disubstituted 1,2,3-triazole derivatives were synthesised (Table 3). Azides and aldehydes with various substituents, including electron-donating groups and electron-withdrawing groups, were all compatible with the optimal reaction conditions.

In summary, we have developed a rapid, efficient and green protocol for the synthesis of 1,2,3-triazoles from various azides and arylacetaldehydes. It is noteworthy that the reaction proceeds efficiently in ionic liquid [bmim]PF_6 in the presence of KOH. Obvious features of this transformation include the operational simplicity, the low cost of reagents, and the high rate and regioselectivity. This should arouse more research on the green synthesis of triazoles.

Experimental

All reagents were purchased from commercial sources and used without further treatment, unless otherwise indicated. The products were characterised using ^{1}H NMR and ^{13}C NMR (Bruker Avance/400) with $CDCl_3$ as the solvent and TMS as internal standard at room temperature (20 ± 2 ºC). Data are presented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, dd = double of doublets, t = triplet, q = quartet, m = multiplet, br = broad) and coupling constants (*J*) in Hertz (Hz).

Synthesis of triazoles; general procedure

The ionic liquid [bmim]PF_6 (5.0 mL) was treated with KOH (40 mol%, 22.4 mg), azides (1.0 mmol) and aldehydes (1.0 mmol). Then the reaction mixture was vigorously stirred at room temperature and monitored by TLC. The products were filtrated from the reaction mixtures and recrystallised using pentane (PE)/ethyl acetate (EA) as the solvent. All the known compounds were characterised by their ^{1}H NMR and ^{13}C NMR spectra.

*1,4-Diphenyl-1*H*-1,2,3-triazole* (**a**):[16] White solid; m.p. 180–182 °C (lit.[17] 183–184 °C); IR (KBr) (υ_{max} cm^{-1}): 3122, 3098, 2360, 1505, 1384; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (t, *J* = 7.7 Hz, 2H), 7.50–7.43 (m, 3H), 7.38 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 137.1, 130.3, 129.8, 128.9, 128.4, 125.9, 120.5, 117.6. MS (ESI) *m/z*: 222 $[M + H]^+$.

*1-(3-Chlorobenzyl)-4-phenyl-1*H*-1,2,3-triazole* (**b**):[16] White solid; m.p. 107–109 °C (lit.[18] 108–110 °C); IR (KBr) (υ_{max} cm^{-1}): 3084, 3064, 2359, 1460, 1437, 1223, 1078, 1047, 765, 754, 694; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 7.1 Hz, 2H), 7.63 (s, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.28–7.20 (m, 4H), 7.09 (d, *J* = 6.9 Hz, 1H), 5.46 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 135.6, 134.0, 129.4, 129.3, 128.0, 127.8, 127.2, 127.0, 125.0, 124.7, 118.5, 52.5. MS (ESI) *m/z*: 270 $[M + H]^+$.

*1-(2-Fluorophenyl)-4-phenyl-1*H*-1,2,3-triazole* (**c**):[19] White solid; m.p. 99–101 °C (lit.[19] 101–102 °C); IR (KBr) (υ_{max} cm^{-1}): 3149, 3067, 2360, 2342, 1511, 1474, 1244, 1214, 1038, 1022, 817, 763, 691; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, *J* = 2.8 Hz, 1H), 7.98–7.92 (m, 1H), 7.87–7.81 (m, 2H), 7.39 (t, *J* = 7.6 Hz, 3H), 7.32–7.26 (m, 2H), 7.25–7.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.5, 152.0, 148.2, 130.4, 130.0, 129.0, 128.5, 125.9, 125.3, 124.8, 120.7, 117.2, 117.0. MS (ESI) *m/z:* 240 $[M + H]^+$.

*4-Phenyl-1-(2-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole* (**d**):[20] White solid; m.p. 206–208 °C (lit.[20] 204–205 °C); IR (KBr) (υ_{max} cm^{-1}): 3132, 3080, 2360, 1606, 1512, 1463, 1316, 1271, 1137, 768, 693, 639; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.90 (dd, *J* = 11.3, 8.3 Hz, 3H), 7.73 (dt, *J* = 27.0, 7.5 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 134.9, 133.1, 130.5, 130.0, 129.0, 128.5, 127.4, 126.4, 125.9, 124.0, 122.2, 121.3, 100.0. MS (ESI) *m/z*: 290 $[M + H]^+$.

*1-(2-Chlorophenyl)-4-phenyl-1*H*-1,2,3-triazole* (**e**):[21] White solid; m.p. 128–129 °C (lit.[22] 128–130 °C); IR (KBr) (υ_{max} cm^{-1}): 3131, 3080, 2360, 1606, 1512, 1316, 1271, 1235, 1137, 768, 711, 693, 639; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 1H), 7.95–7.90 (m, 2H), 7.68 (dd, *J* = 6.1,

3.4 Hz, 1H), 7.62–7.57 (m, 1H), 7.50–7.43 (m, 4H), 7.37 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 134.9, 130.8, 130.2, 129.0, 128.5, 128.0, 127.8, 125.9, 121.6. MS (ESI) *m/z*: 256 $[M + H]^+$.

*4-Phenyl-1-(*o-*tolyl)-1*H*-1,2,3-triazole* (**f**):[21] White solid; m.p. 72–73 °C (lit.[22] 73 °C); IR (KBr) (υ_{max} cm^{-1}): 3131, 2920, 2361, 1505, 1480, 1461, 1229, 1046, 1035, 773, 765, 691; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.94–7.91 (m, 2H), 7.40–7.35 (m, 7H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 136.5, 133.8, 131.6, 130.4, 130.0, 129.0, 128.4, 126.9, 125.9, 121.2, 18.0. MS (ESI) *m/z*: 236 $[M + H]^+$.

*4-Phenyl-1-(*p-*tolyl)-1*H*-1,2,3-triazole* (**g**):[19] White solid; m.p. 156–158 °C (lit.[19] 159–160 °C); IR (KBr) (υ_{max} cm^{-1}): 3131, 3080, 2360, 1606, 1512, 1482, 1463, 1316, 1271, 1235, 1169, 1137, 768, 711, 693, 639; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.91 (d, *J* = 7.1 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.35 (dd, *J* = 16.8, 7.9 Hz, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3, 138.9, 134.8, 130.3, 128.9, 128.4, 125.9, 120.4, 117.7, 21.1. MS (ESI) *m/z*: 236 $[M + H]^+$.

*1-Mesityl-4-phenyl-1*H*-1,2,3-triazole* (**h**):[20] White solid; m.p. 113–115 °C (lit.[17] 113–116 °C); IR (KBr) (υ_{max} cm^{-1}): 3137, 2956, 2922, 2360, 1607, 1494, 1477, 1438, 1380, 1222, 1072, 1034, 768, 989, 856, 817, 767, 693; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95–7.91 (m, 2H), 7.84 (s, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.40–7.33 (m, 1H), 7.01 (s, 2H), 2.37 (s, 3H), 2.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 140.1, 135.1, 133.5, 130.5, 129.0, 128.3, 125.8, 121.5, 21.2, 17.4. MS (ESI) *m/z*: 264 $[M + H]^+$.

*4-(4-Methoxyphenyl)-1-phenyl-1*H*-1,2,3-triazole* (**i**):[16] White solid; m.p. 158–159 °C (lit.[17] 160–161 °C); IR (KBr) (υ_{max} cm^{-1}): 3106, 3059, 3004, 2360, 1616, 1560, 1493, 1507, 1464, 1248, 1176, 1034, 837, 815, 764, 690; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 1H), 7.82 (d, *J* = 8.7 Hz, 2H), 7.77 (d, *J* = 7.7 Hz, 2H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 148.3, 137.1, 129.8, 128.7, 127.2, 122.9, 120.4, 116.8, 114.3, 55.3. MS (ESI) *m/z*: 252 $[M + H]^+$.

*Ethyl 2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)acetate* (**j**):[23] White solid; m.p. 97–99 °C (lit.[24] 93–95 °C); IR (KBr) (υ_{max} cm^{-1}): 3134, 3004, 2361, 1606, 1755, 1467, 1442, 1347, 1216, 1199, 1144, 1076, 1050, 1016, 766, 694; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (s, 1H), 7.77 (d, *J* = 7.1 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 1H), 5.13 (s, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 146.9, 129.3, 127.8, 127.3, 124.8, 120.0, 61.3, 49.9, 13.0. MS (ESI) *m/z*: 232 $[M + H]^+$.

*1-Benzyl-4-(4-methoxyphenyl)-1*H*-1,2,3-triazole* (**k**):[25] White solid; m.p. 145–146 °C (lit.[26] 143–144 °C); IR (KBr) (υ_{max} cm^{-1}): 3136, 2927, 2836, 2361, 1616, 1558, 1500, 1455, 1349, 1251, 1217, 1171, 1070, 1049, 1028, 834, 796, 720; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.7 Hz, 2H), 7.60 (s, 1H), 7.41–7.28 (m, 5H), 6.94 (d, *J* = 8.7 Hz, 2H), 5.55 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 148.1, 134.8, 129.1, 128.7, 128.1, 127.0, 123.3, 118.8, 114.2, 55.3, 54.2. MS (ESI) *m/z*: 266 $[M + H]^+$.

*1-Benzyl-4-(4-ethoxyphenyl)-1*H*-1,2,3-triazole* (**l**):[26] White solid; m.p. 136–138 °C (lit.[26] 139–140 °C); IR (KBr) (υ_{max} cm^{-1}): 3088, 2972, 2932, 2360, 1618, 1502, 1452, 1251, 1176, 1116, 1046, 835, 815, 716; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.8 Hz, 2H), 7.59 (s, 1H), 7.42–7.34 (m, 3H), 7.33–7.28 (m, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 5.55 (s, 2H), 4.05 (q, *J* = 7.0 Hz, 2H), 1.43 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 148.1, 134.8, 129.1, 128.7, 128.0, 127.0, 123.1, 118.7, 114.8, 63.5, 54.2, 14.8. MS (ESI) *m/z*: 280 $[M + H]^+$.

*1-Benzyl-4-(4-chlorophenyl)-1*H*-1,2,3-triazole* (**m**):[26] White solid; m.p. 131–133 °C (lit.[26] 130–132 °C); IR (KBr) (υ_{max} cm^{-1}): 3442, 3117, 3039, 2360, 1479, 1452, 1433, 1226, 1186, 1135, 1091, 1069, 1051, 813, 708, 698, 514; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.69 (s, 1H), 7.45–7.29 (m, 7H), 5.58 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.5, 133.9, 129.2, 129.1, 129.0, 128.9, 128.1, 126.9, 54.3. MS (ESI) *m/z*: 270 $[M + H]^+$.

*1-Benzyl-4-(4-fluorophenyl)-1*H*-1,2,3-triazole* (**n**):[25] White solid; m.p. 113–115 °C (lit.[26] 109–110 °C); IR (KBr) (υ_{max} cm^{-1}): 3151, 3102, 3082, 2360, 1496, 1452, 1223, 1157, 1046, 846, 833, 799, 730, 715, 523; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.65 (s, 1H), 7.36 (m, 5H), 7.09 (t, *J* = 8.7 Hz, 2H), 5.57 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.9, 161.4, 147.4, 134.6, 129.2, 128.9, 128.1, 127.5, 127.4, 126.8, 119.3, 115.9, 115.7, 54.3. MS (ESI) *m/z*: 254 $[M + H]^+$.

*4-(4-Ethoxyphenyl)-1-phenyl-1*H*-1,2,3-triazole* (**o**):[26] White solid; m.p. 161–163 °C (lit.[27] 164.7 °C); IR (KBr) (υ_{max} cm^{-1}): 3432, 3136, 2971, 2360, 1617, 1496, 1474, 1246, 1230, 1182, 1045, 845, 755; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (s, 1H), 7.79 (dd, *J* = 18.4, 8.2 Hz, 4H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 8.7 Hz, 2H), 4.06 (q, *J* = 7.0 Hz, 2H), 1.43 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 148.3, 137.1, 129.8, 128.6, 127.2, 122.8, 120.4, 116.8, 114.9, 77.4, 77.1, 76.8, 63.5, 14.8. MS (ESI) *m/z*: 266 $[M + H]^+$.

*1-Benzyl-4-(*p-*tolyl)-1*H*-1,2,3-triazole* (**p**):[28] White solid; m.p. 153–154 ºC (lit.[29] 155–157 °C); IR (KBr) (υ_{max} cm^{-1}): 3143, 3018, 2917, 2361, 1496, 1457, 1348, 1223, 1182, 1136, 1066, 1047, 973, 828, 793, 721, 513; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 7.9 Hz, 2H), 7.62 (s, 1H), 7.38 (d, *J* = 5.5 Hz, 3H), 7.30 (d, *J* = 5.8 Hz, 2H), 7.20 (d, *J* = 7.7 Hz, 2H), 5.55 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 137.1, 133.8, 128.6, 128.2, 127.8, 127.1, 126.8, 124.7, 118.3, 53.3, 20.4. MS (ESI) *m/z*: 250 $[M + H]^+$.

*1-Phenyl-4-(*p-*tolyl)-1*H*-1,2,3-triazole* (**q**):[19] White solid; m.p. 162–155 ºC (lit.[17] 166–169 °C); IR (KBr) (υ_{max} cm^{-1}): 3109, 3061, 2916, 1599, 1508, 1495, 1463, 1238, 1228, 1042, 814, 756, 686, 536; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (s, 1H), 7.78 (dd, *J* = 7.8, 5.9 Hz, 4H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.26 (d, *J* = 8.1 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.7, 138.5, 137.3, 129.9, 129.8, 128.0, 127.6, 125.9, 120.7, 117.5, 21.5. MS (ESI) *m/z*: 236 $[M + H]^+$.

*1-(2-Methyl-5-nitrophenyl)-4-(*p-*tolyl)-1*H*-1,2,3-triazole* (**r**):[10] White solid; m.p. 102–103 ºC (lit.[10] 128–130 °C); IR (KBr) (υ_{max} cm^{-1}): 3135, 3117, 3065, 3030, 2980, 2921, 2859, 1633, 1600, 1521, 1440, 1380, 1350, 810, 797, 739, 706; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 6.8 Hz, 2H), 8.02 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 9.1 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 2H), 2.44 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 146.3, 141.5, 138.5, 136.7, 132.5, 129.6, 126.8, 125.6, 124.1, 121.0, 120.6, 21.2, 18.5. MS (ESI) *m/z*: 295 $[M + H]^+$.

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