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Efficient and rapid synthesis of regioselective functionalized potassium 1,2,3-triazoletrifluoroborates via 1,3-dipolar cycloaddition

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ABSTRACT

In this study, we present a previously unreported method of preparing regiospecific organo-[1,2,3]-triazol-1-aryl-trifluoroborates from haloaryltrifluoroborates via a one-pot 1,3-dipolar cycloaddition reaction. We found that the use of either electron-rich or electron-deficient *haloaryltrifluoroborates* led to the desired cycloaddition products with good to excellent yields. Furthermore, we successfully carried out the cross-coupling reactions of the obtained triazoles with various aryl halides by means of the Suzuki–Miyaura reaction in the presence of 3 mol % of $Pd(PPh_3)_4$ catalyst in a 20% aqueous 1,4-dioxane solution at 100 °C; all these reactions yielded complete conversion to the corresponding products. Besides providing a high level of personnel safety, our highly versatile approach allows the preparation of functionalized organotrifluoborates containing 1,2,3-triazoles with retained functionality.

1. Introduction

The increasing demand in generating libraries for biological screening in the areas of drug discovery and medicinal chemistry has led to the research and development of simpler and more efficient methods for synthesizing heterocylic compounds that are used in these areas. The 1,2,3-triazole class of heterocycles has attracted considerable interest because of its anti-microbial,[1a] antibacterial,[1b] and anti-HIV[1c] properties and its wide applications in various fields, such as organic synthesis,[1d] material science,[1e] and medicinal chemistry.[1f,g] The method of using Huisgen 1,3-dipolar cycloaddition of azides and terminal alkynes is widely used in forming 1,2,3-triazole rings.[2a–d] Sharpless[2e] and Meldal[2f] have initially and independently proposed that the Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) reaction significantly enhances the cycloaddition between alkynes and azides, exclusively affording 1,4-disubstituted 1,2,3-triazole. One of the numerous features of the CuAAC is its association with the Suzuki–Miyaura cross-coupling reaction.

Over the past few years, organotrifluoroborate salts have been considered as valuable alternatives to boronic acids and boronate esters used as precursors in the Suzuki–Miyaura cross-coupling reaction.[3] Organotrifluoroborates are inert and stable under various reaction conditions, and are thus suitable for the preparation of more complex organotriflouroborates that may not be easily obtained by conventional syntheses of organoboron reagents.[3b–d,4] These organotrifluoroborate substrates do not undergo undesirable side reactions with commonly employed organic bases, acids, and nucleophiles. Moreover, potassium organotrifluoroborate salts exhibit enhanced stability, and thus they can be prepared and stored for long periods of time.[3a,5]

In 2010, Frost and co-workers[6] demonstrated the use of azidoboronate ester motif in a cycloaddition reaction. However, this example utilizes only benzylazido-boronate ester in the formation of 1,2,3-triazole. Organic azides are considered explosive in nature; thus, the isolation or purification of lower organic azides or polyazides is difficult.[7] Therefore, an appropriate method of the in situ generation of azides from suitable precursors is required; such a method can avoid the necessary isolation of organic azides in conventional methods.

2. Results and discussion

In a recent report, we have demonstrated an efficient method for the preparation of potassium azidoaryltrifluoroborates from the corresponding haloaryltrifluoroborates (Scheme 1).[8]

During our research in the preparation of functionalized potassium organotrifluoroborates, we felt that our method of preparing organo-[1,2,3]-triazol-1-aryl-trifluoroborates from haloaryltrifluoroborates via the in situ formation of azidoaryltrifluoroborates

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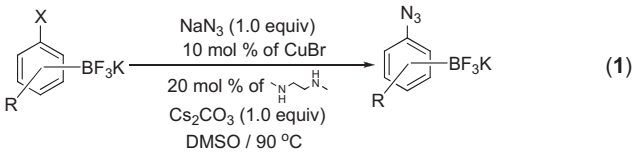


(1)

Scheme 1. Preparation of potassium azidoaryltrifluoroborates.

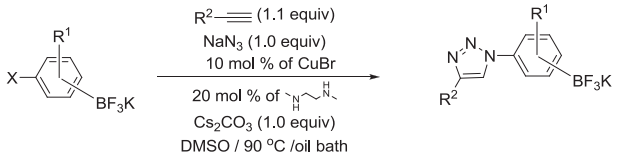
could further be developed into an efficient one-pot procedure. This method would reduce the safety concerns raised from working with organic azides. The lack of examples detailing a practical method for our objective and the limitations associated with other boron derivatives prompted us to investigate and explore a general, mild, and convenient method for the preparation of organo-[1,2,3]-triazol-1-aryl-trifluoroborates. In this study, we report a one-pot synthesis of organo-[1,2,3]-triazol-1-aryl-trifluoroborates with a broad range of alkynes and various haloaryltrifluoroborates. Our approach (which is the first of its kind) is highly versatile; it allows the preparation of functionalized organotrifluoborate containing 1,2,3-triazoles with retained functionality.

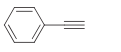
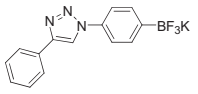
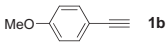
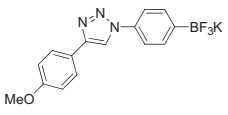
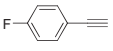
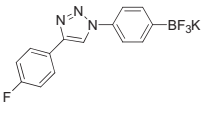
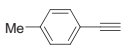
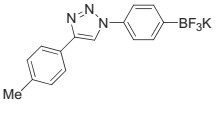
Firstly, we examined whether our catalyst system for the azidation of haloaryltrifluoroborates has a catalytic effect on the 1,3-dipolar addition between azidoaryltrifluoroborates and terminal alkynes. Initially, we carried out the reaction of potassium 4-iodophenyltrifluoroborate (0.25 mmol) with phenylacetylene (**1a**, 0.28 mmol) in the presence of NaN_3 (0.25 mmol), 10 mol % of CuBr and 20 mol % of *N*,*N*′-dimethylethylenediamine (DMEDA) in DMSO-d_6 as a solvent at 90 °C in an oil bath using a nuclear magnetic resonance (NMR) tube for 1 h. The conversion of the reaction was monitored by ^{1}H NMR at various intervals of time. It was observed that the conversion reached its end point after 1 h. Subsequent to the removal of the solvent under high vacuum at 60–70 °C, the desired salt product was obtained. It is noteworthy that the reaction could be scaled to 2 mmol, thereby providing product **2a** in 98% yield (Table 1, entry 1). However, when 4-bromophenyltrifluoroborate was used as a starting material, reaction time was extended to 8.5 h (see Experimental section). Our results clearly proved that the catalytic system is effective for both the azidation and the 1,3-dipolar cycloaddition. Therefore, a similar two-step one-pot method can be employed in the preparation of 1-aryl 1,2,3-triazoles from the corresponding haloaryltrifluoroborates.

In order to explore the scope of the 1,3-dipolar cycloaddition reaction in our study, we tested other haloaryltrifluoroborates with different substituents and a selection of terminal alkynes. The results are summarized in Table 1. As can be observed in Table 1, a variety of terminal alkynes were tolerated in this one-pot reaction. Aryl alkynes bearing electron-withdrawing groups such as flouro and bromo groups (Table 1, entries 3, 7, and 8) underwent the 1,3-dipolar cycloaddition with a good overall reaction rate and sufficient yield. However, the electron-withdrawing group present at the *meta*-position (e.g., the chloro group) showed a slight decrease in yield (Table 1, entry 6). In a similar fashion, aryl alkynes bearing electron-donating groups such as methoxy, methyl, and *n*-pentyl groups (Table 1, entries 2, 4, and 5) were obtained in good yields. On the other hand, alkyl acetylenes also showed higher reactivity with a variety of functional group tolerances (Table 1, entries 9–14). However, the only the exception is entry 10, where the reaction with prop-2-ynylcyclohexane resulted in a moderate yield of 66% due to the steric hindrance. In addition, the strong electron-withdrawing nitrile group was well tolerated (Table 1, entry 11). Alkyl acetylenes containing electron-donating groups such as methoxy and hydroxy groups (Table 1, entries 12–14) completed the reaction in identical time spans when 1.5 equiv of methyl propargyl ether was used.

The reaction involving 2-methylbut-3-yn-2-ol sterically hindered hydroxyl group by methyl groups exhibited sufficient reactivity (Table 1, entry 14); a 95% yield was obtained within 1.5 h. Moreover, with regards to electromeric effects, the haloaryltrifluoroborates showed a decline in product yield and observed longer reaction time with *meta*-BF_3K as compared with BF_3K positioned at the *para*-position (Table 1, entries 1, 8, and 15). The scope of the reaction regarding the substituent effect on haloaryltrifluoroborates was then examined and found that with methoxy group higher yield was obtained in less time than with methyl substituent (Table 1,

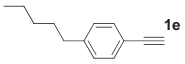
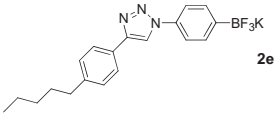
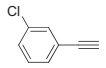
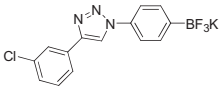
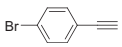
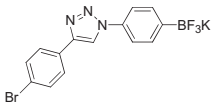
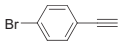
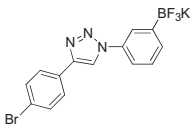
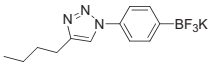
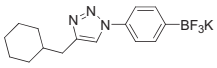
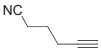
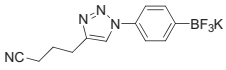
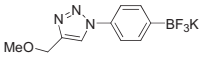
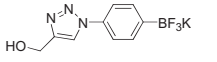
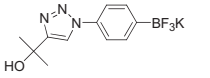
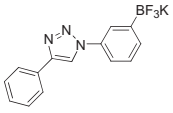
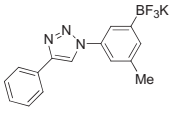
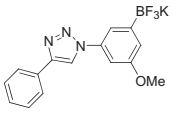
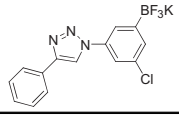
Table 1
One-pot 1,3-dipolar cycloaddition reactions[a]



Entry	Alkyne	Reaction time (h)	Product	Isolated yield (%)
1	 **1a**	1.0 (from I) 8.5 (from Br)	 **2a**	98[b] 95[c]
2	 **1b**	1.0	 **2b**	90
3	 **1c**	1.5	 **2c**	94
4	 **1d**	1.5	 **2d**	92

(*continued on next page*)

Table 1 (*continued*)

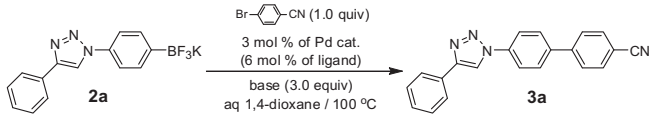
Entry	Alkyne	Reaction time (h)	Product	Isolated yield (%)
5	 **1e**	1.5	 **2e**	91
6	 **1f**	1.5	 **2f**	86
7	 **1g**	1.0	 **2g**	98
8	 **1g**	7.0	 **2h**	94[c]
9	 **1h**	1.5	 **2i**	80
10	 **1i**	1.5	 **2j**	66
11	 **1j**	1.5	 **2k**	82[b]
12[d]	 **1k**	1.5	 **2l**	94
13	 **1l**	1.5	 **2m**	82
14	 **1m**	1.5	 **2n**	95
15[c]	 **1a**	7.0 (from I) 11.0 (from Br)	 **2o**	75 65
16[c]	 **1a**	8.5 (from Br)	 **2p**	80
17[c]	 **1a**	4.5 (from Br)	 **2q**	92
18[c]	 **1a**	12.5 (from Br)	 **2r**	75

[a] All reactions were performed on a 0.25 mmol scale in 1.0 mL of DMSO and monitored by ^{1}H NMR in DMSO-d_6.
[b] Reactions were performed on a 2.0 mmol scale.
[c] Initially converted into azide and then alkyne was added, see experimental part for more details.
[d] Methyl propargyl ether (1.5 equiv) as a starting material was used.

entries 16 and 17). When haloaryltrifluoroborates containing electron-withdrawing substituent, such as chloride was chosen for the reaction process, the reaction went to completion after 12.5 h (Table 1, entry 18). And, the productivity in these cases was lower than those obtained with electron-donating substituents (Table 1, entries 16–18). It was found that the use of either electron-rich or electron-deficient haloaryltrifluoroborates led to the desired cycloaddition products with good to excellent yields.

Next, we attempted to optimize the cross-coupling reaction conditions using these organotrifluoroborates. As observed in the optimization studies (Table 2), a 32% yield of the cross-coupling compound **3a** was obtained by using **2a** as a model substrate with 4-bromobenzonitrile under typical conditions when reacting with $Pd(OAc)_2$ (3 mol %), and K_2CO_3 as a base in 20% aqueous 1,4-dioxane solvent system at 80 °C (Table 2, entry 1). When we attempted to increase the reaction temperature under identical reaction conditions, the desired product **3a** was obtained with a satisfactory yield of 65% (Table 2, entry 2). However, the use of $Pd(dba)_2$ as a catalyst in the above reaction resulted in a low yield (Table 2, entry 3). When further optimization studies were carried out for the production of **3a**, the target compound was obtained in yields of 72%, 62%, 57%, and 74% using $Pd(OAc)_2/PPh_3$, $Pd(OAc)_2$/Xphos, $PdCl_2(dppf)\cdot CH_2Cl_2$, and $Pd(PPh_3)_4$, respectively (Table 2, entries 4–7). However, when the reaction was performed with $Pd(PPh_3)_4$ and Cs_2CO_3 as a base under identical conditions, the isolated yield of **3a** increased to 79% (Table 2, entry 8). Our examination of solvent effects showed that a 20% aqueous 1,4-dioxane solution proved to be the optimal solvent system (Table 2, entries 9–11).

Table 2
Optimization of reaction conditions for the cross-coupling reaction with triazole-containing organotrifluoroborates[a]



Entry	3 mol % Pd cat./6 mol % ligand	Base	Reaction time (h)	Isolated yield (%)
1[b]	$Pd(OAc)_2$	K_2CO_3	4	32
2	$Pd(OAc)_2$	K_2CO_3	4	65
3	$Pd(dba)_2$	K_2CO_3	4	52
4	$Pd(OAc)_2/PPh_3$	K_2CO_3	4	72
5	$Pd(OAc)_2$/XPhos	K_2CO_3	4	62
6	$PdCl_2(dppf)\cdot CH_2Cl_2$	K_2CO_3	4	57
7	$Pd(PPh_3)_4$	K_2CO_3	2	74
8	$Pd(PPh_3)_4$	Cs_2CO_3	2	79
9[c]	$Pd(PPh_3)_4$	Cs_2CO_3	2	47
10[d]	$Pd(PPh_3)_4$	Cs_2CO_3	2	Trace
11[e]	$Pd(PPh_3)_4$	Cs_2CO_3	2	27

[a] All reaction was performed on a 0.1 mmol scale in 0.6 mL of 20% aqueous 1,4-dioxane at 100 °C in an oil bath.
[b] Reaction temperature was 80 °C.
[c] Reaction was performed in methanol at 65 °C.
[d] Reaction solvent was 20% aqueous toluene.
[e] Reaction solvent was 20% aqueous DMF.

Having obtained the above optimal reaction conditions, we examined the Suzuki–Miyaura cross-coupling reaction of various triazoles containing organotrifluoroborates with aryl, pyridyl and alkenyl bromides. All the reactions yielded complete conversion to the corresponding products. The results are presented in Table 3.

As expected, the coupling reactions led to the corresponding products in good to excellent yields within short reaction times. In the case of 4-bromoanisole (Table 3, entry 2), there is slight decrease in yield when compared with that of 4-bromobenzonitrile (Table 3, entry 1), thereby showing the impact of the electron releasing effects involved in the former reaction. In order to study the efficiency of this cross-coupling condition, when 2-bromopyridine was used to couple with **2a** to produce **3c**, a slight decrease in yield was observed in this case (Table 3, entry 3). When we used triazole **2k**, a higher yield was obtained with the previously used 4-bromobenzonitrile compound (Table 3, entry 4). Finally, when we tested the reactivity of the triazole **2k** with bromotriphenylethylene, it was noteworthy that though the reaction completed within 2 h with an 87% product yield (Table 3, entry 5), the chosen halide exhibited an enormous steric effect.

3. Conclusion

In conclusion, regiospecific potassium organo-[1,2,3]-triazol-1-aryl-trifluoroborates were prepared for the first time from haloaryltrifluoroborates via one-pot 1,3-dipolar cycloaddition reactions with retained functionality. Further, their C–C bond formation by the Suzuki–Miyaura cross-coupling reaction was explored with various aryl bromides. Our reaction conditions allow the simple and effective synthesis of potassium organotrifluoroborate containing 1,2,3-triazoles. In addition, our method provides the distinct advantage of high purity and yields over current methods.

4. Experimental

4.1. General considerations

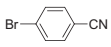
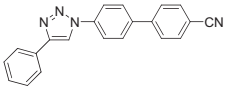
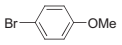
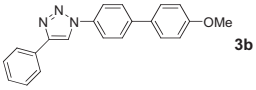
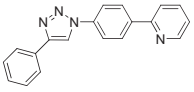
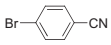
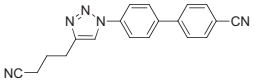
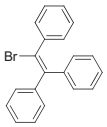
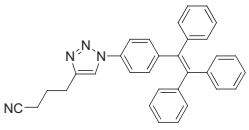
^1H, ^{13}C, and ^{19}F NMR spectra were recorded at 400, 100, and 376 MHz, respectively using Bruker UltraShield Plus 400 MHz/54 mm instrument. ^{19}F NMR chemical shifts were referenced to external $CFCl_3$ (0.0 ppm). ^{11}B NMR spectra at 128 MHz were obtained on a spectrometer equipped with the appropriate decoupling accessories. All ^{11}B NMR chemical shifts were referenced to external $BF_3\cdot OEt_2$ (0.0 ppm) with a negative sign indicating an up field shift. Mass spectra of potassium 1,2,3-triazoletrifluoroborates were recorded on LCQ Fleet Ion Trap Mass Spectrometer (ESI-MS) using negative ESI mode at the mass spectrometry facilities in KIST-Gangneung Institute. IR spectra were obtained using Nicolet iS10 FT-IR spectrometer. Reactions were performed in glass vessels (capacity 10 mL) sealed with a septum. Melting points were performed on recrystallized solids and recorded on Stanford Research Systems OptiMelt MPA100 melting point apparatus and are uncorrected. Commercially available reagents were used without purification unless noted otherwise.

4.2. General procedure I (one-pot 1,3-dipolar cycloaddition reactions) Table 1

To a solution of potassium haloaryltrifluoroborate (0.25 mmol), NaN_3 (16.3 mg, 0.25 mmol), CuBr (3.6 mg, 10 mol %), Cs_2CO_3 (81.5 mg, 0.25 mmol), and *N*,*N*′-dimethylethylenediamine (4.4 mg, 20 mol %) in DMSO-d_6 (1 mL) was added corresponding alkyne (0.28 mmol, 1.1 equiv) under atmospheric conditions. The reaction mixture was heated in an oil bath at 90 °C until the ^1H NMR (in DMSO-d_6) indicated completion of the reaction (see Table 1). After completion of the reaction, the solvent was removed in vacuum at 60–70 °C. The residual product was dissolved in dry acetone (3 mL), and the insoluble salts were removed by filtration through Celite. The solvent was concentrated on a rotary evaporator. The addition of Et_2O led to the precipitation of the product. The product was filtered and dried in vacuum to afford the desired pure product.

*4.2.1. Potassium 4-(4-phenyl-1H-1,2,3-triazol-1-yl)phenyltrifluoroborate (**2a**, 2.0 mmol scale reaction from I).* General procedure I was used employing potassium 4-iodophenyltrifluoroborate (620 mg, 2.0 mmol), NaN_3 (130.0 mg, 2.0 mmol), CuBr (28.7 mg, 10 mol %), Cs_2CO_3 (651.8 mg, 2.0 mmol), *N*,*N*′-dimethylethylenediamine (35.3 mg, 20 mol %), and ethynylbenzene (**1a**, 225 mg, 2.2 mmol) in DMSO-d_6 (8 mL), to give the desired product in 98% yield (641 mg, a light brown solid). Mp=206–208 °C ^1H NMR (400 MHz, acetone-d_6) δ 8.89 (s, 1H), 8.02 (d, 2H, J=6.8 Hz), 7.69 (m, 4H), 7.48 (t, 2H, J=7.6 Hz), 7.38 (m, 1H). ^{13}C NMR (100 MHz, acetone-d_6) δ 147.4, 135.0, 132.7, 131.2, 128.7, 127.8, 125.4, 118.4, 118.1. ^{19}F NMR (376 MHz, acetone-d_6) δ −142.3. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.43. FT-IR

Table 3
Suzuki–Miyaura cross-coupling reactions[a]

Entry	Triazole/BF_3K	R-Br	Product	Reaction time (h)	Isolated yield (%)
1	**2a**		 **3a**	2	79
2	**2a**		 **3b**	2	75
3	**2a**		 **3c**	3	65
4	**2k**		 **3d**	3	82
5	**2k**		 **3e**	2	87

[a] All reaction were performed on a 0.5 mmol scale in 2.0 mL of 20% aqueous 1,4-dioxane according to the optimized conditions of entry 8 in Table 2.

(ATR): 3129, 2081, 1603, 1514, 1482, 1455, 1428, 1396, 1215, 1094, 965, 828, 759, 690 cm^{-1}. ESI-MS: *m/z* calcd for $C_{14}H_{10}BF_3N_3$ $[M-K^+]^-$ 288.09, found 288.29.

*4.2.2. Potassium 4-(4-phenyl-1H-1,2,3-triazol-1-yl)phenyltrifluoroborate (**2a**, 0.25 mmol scale reaction from Br).* A solution of potassium 4-bromophenyltrifluoroborate (65.7 mg, 0.25 mmol), NaN_3 (16.2 mg, 0.25 mmol), CuBr (3.6 mg, 10 mol %), Cs_2CO_3 (81.4 mg, 0.25 mmol), and *N*,*N*′-dimethylethylenediamine (4.4 mg, 20 mol %) in DMSO-d_6 (1 mL) was heated in an oil bath at 90 °C for 7 h monitored by the ^1H NMR (in DMSO-d_6) until the complete conversion of the starting material into azide[8] and then added ethynylbenzene (**1a**, 28.6 mg, 0.28 mmol) into the reaction mass and continued for another 1.5 h (see Table 1). After completion of the reaction, work-up was adopted as mentioned in General procedure I, to give the desired product in 95% yield (65.9 mg, a light brown solid).

*4.2.3. Potassium 4-(4-(4-methoxyphenyl)-1H-1,2,3-triazol-1-yl)phenyltrifluoroborate (**2b**).* General procedure I was used employing potassium 4-iodophenyltrifluoroborate (77.5 mg, 0.25 mmol) and 1-ethynyl-4-methoxybenzene (**1b**, 37.0 mg, 0.28 mmol), to give the desired product in 90% yield (80.4 mg, a light brown solid). Mp=195 °C (dec). ^1H NMR (400 MHz, acetone-d_6) δ 8.77 (s, 1H), 7.94 (d, 2H, *J*=8.4 Hz), 7.66 (m, 4H), 7.04 (d, 2H, *J*=8.8 Hz), 3.86 (s, 3H). ^{13}C NMR (100 MHz, acetone-d_6) δ 160.5, 147.6, 135.8, 133.5, 127.6, 124.7, 118.9, 118.3, 115.0, 55.6. ^{19}F NMR (376 MHz, acetone-d_6) δ −142.4. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.22. FT-IR (ATR): 3621, 3136, 2942, 2838, 2206, 2164, 2037, 1605, 1563, 1496, 1467, 1439, 1396, 1306, 1219, 1178, 1108, 1093, 1027, 965, 830, 611, 536 cm^{-1}. ESI-MS: *m/z* calcd for $C_{15}H_{12}BF_3N_3O$ $[M-K^+]^-$ 318.10, found 318.18.

*4.2.4. Potassium 4-(4-(4-fluorophenyl)-1H-1,2,3-triazol-1-yl)phenyltrifluoroborate (**2c**).* General procedure I was used employing potassium 4-iodophenyltrifluoroborate (77.5 mg, 0.25 mmol) and 1-ethynyl-4-fluorobenzene (**1c**, 33.6 mg, 0.28 mmol), to give the desired product in 94% yield (81.1 mg, a light gray solid). Mp=247–251 °C. ^1H NMR (400 MHz, acetone-d_6+DMSO-d_6) δ 8.93 (s, 1H), 8.76 (dd, 2H, *J*=8.8, 5.2 Hz), 7.69 (d, 2H, *J*=8.4 Hz), 7.66 (d, 2H, *J*=8.4 Hz), 7.26 (t, 2H, *J*=8.8 Hz). ^{13}C NMR (100 MHz, acetone-d_6+DMSO-d_6) δ 162.4 (d, $^1J_{CF}$=243.4 Hz), 146.5, 134.8, 132.7, 127.8, 127.4 (d, $^3J_{CF}$=8.1 Hz), 118.5, 118.1, 115.5 (d, $^2J_{CF}$=21.7 Hz). ^{19}F NMR (376 MHz, acetone-d_6+DMSO-d_6) δ −115.7, −141.7. ^{11}B NMR (128 MHz, acetone-d_6+DMSO-d_6) δ 3.24. FT-IR (ATR): 3135, 2916, 2849, 1603, 1559, 1494, 1438, 1397, 1207, 1158, 1026, 1010, 957, 822 cm^{-1}. ESI-MS: *m/z* calcd for $C_{14}H_9BF_4N_3$ $[M-K^+]^-$ 306.08, found 306.11.

*4.2.5. Potassium (4-p-tolyl-1H-1,2,3-triazol-1-yl)phenyltrifluoroborate (**2d**).* General procedure I was used employing potassium 4-iodophenyltrifluoroborate (77.5 mg, 0.25 mmol) and 1-ethynyl-4-methylbenzene (**1d**, 32.5 mg, 0.28 mmol), to give the desired product in 92% yield (78.5 mg, a light brown solid). Mp=204–210 °C. ^1H NMR (400 MHz, acetone-d_6) δ 8.81 (s, 1H), 7.90 (d, 2H, *J*=8.0 Hz), 7.69 (d, 2H, *J*=8.4 Hz), 7.66 (d, 2H, *J*=8.4 Hz), 7.29 (d, 2H, *J*=8.0 Hz), 2.38 (s, 3H). ^{13}C NMR (100 MHz, acetone-d_6) δ 147.5, 137.4, 134.9, 132.7, 129.3, 128.5, 125.4, 118.1, 118.0, 20.3. ^{19}F NMR (376 MHz, acetone-d_6) δ −142.3. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.07. FT-IR (ATR): 3408, 3131, 3043, 2918, 2855, 2258, 2120, 1914, 1604, 1496, 1436, 1396, 1377, 1343, 1215, 1110, 1026, 961, 826 cm^{-1}. ESI-MS: *m/z* calcd for $C_{15}H_{12}BF_3N_3$ $[M-K^+]^-$ 302.10, found 302.07.

*4.2.6. Potassium 4-(4-(4-pentylphenyl)-1H-1,2,3-triazol-1-yl)phenyltrifluoroborate (**2e**).* General procedure I was used employing potassium 4-iodophenyltrifluoroborate (77.5 mg, 0.25 mmol) and 1-ethynyl-4-pentylbenzene (**1e**, 48.2 mg, 0.28 mmol), to give the desired product in 91% yield (90.4 mg, an ivory solid). Mp=257–262 °C. ^1H NMR (400 MHz, acetone-d_6) δ 8.81 (s, 1H), 7.92 (d, 2H, *J*=8.4 Hz), 7.69 (d, 2H, *J*=8.4), 7.65 (9d, 2H, *J*=8.4 Hz), 7.31 (d, 2H, *J*=8.4 Hz), 2.67 (t, 2H, *J*=7.2 Hz), 1.67 (m, 2H), 1.36 (m, 4H), 0.91(t, 3H, *J*=6.8 Hz). ^{13}C NMR (100 MHz, acetone-d_6) δ 147.5, 142.5, 134.9, 132.7 (x2), 128.7, 125.4, 118.0 (x2), 35.3, 31.3, 31.0, 22.2, 13.3. ^{19}F NMR (376 MHz, acetone-d_6) δ −141.6. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.24. FT-IR (ATR): 3127, 2947, 2927, 2855, 1603, 1514, 1495, 1436, 1396, 1207, 1026, 1010, 965, 830 cm^{-1}. ESI-MS: *m/z* calcd for $C_{19}H_{20}BF_3N_3$ $[M-K^+]^-$ 358.17, found 358.13.

*4.2.7. Potassium 4-(4-(3-chlorophenyl)-1H-1,2,3-triazol-1-yl)phenyltrifluoroborate (**2f**).* General procedure I was used employing potassium 4-iodophenyltrifluoroborate (77.5 mg, 0.25 mmol) and 1-chloro-3-ethynylbenzene (**1f**, 38.2 mg, 0.28 mmol), to give the

desired product in 86% yield (77.7 mg, a light purple solid). Mp=252 °C (dec). ^{1}H NMR (400 MHz, acetone-d_6) δ 8.98 (s, 1H), 8.05 (s, 1H), 7.98 (d, 1H, J=7.6 Hz), 7.70 (d, 2H, J=8.4 Hz), 7.67 (d, 2H, J=8.4 Hz), 7.51 (t, 1H, J=8.0 Hz), 7.40 (m, 1H). ^{13}C NMR (100 MHz, acetone-d_6) δ 148.6, 146.0, 134.2, 133.3, 132.7, 130.5, 127.6, 125.1, 123.8, 119.2, 118.15. ^{19}F NMR (376 MHz, acetone-d_6) δ −141.7. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.29. FT-IR (ATR): 3648, 3607, 3128, 2357, 1603, 1573, 1515, 1473, 1442, 1395, 1215, 1104, 1079, 1025, 961, 826, 771, 730, 685, 629, 570 cm^{-1}. ESI-MS: m/z calcd for $C_{14}H_9BClF_3N_3$ [M−K$^+$]$^-$ 322.05, found 322.06.

*4.2.8. Potassium 4-(4-(4-bromophenyl)-1H-1,2,3-triazol-1-yl)phenyltrifluoroborate (**2g**).* General procedure I was used employing potassium 4-iodophenyltrifluoroborate (77.5 mg, 0.25 mmol) and 1-bromo-4-ethynylbenzene (**1 g**, 50.6 mg, 0.28 mmol), to give the desired product in 98% yield (99.5 mg, a brown solid). Mp=267 °C (dec). ^{1}H NMR (400 MHz, acetone-d_6) δ 8.94 (s, 1H), 7.97 (d, 2H, J=8.4 Hz), 7.69 (d, 2H, J=8.4 Hz), 7.67 (d, 2H, J=8.4 Hz), 7.65 (d, 2H, J=8.0 Hz). ^{13}C NMR (100 MHz, acetone-d_6) δ 146.3, 134.7, 132.7, 131.8, 130.5, 127.3, 121.0, 118.8, 118.1. ^{19}F NMR (376 MHz, acetone-d_6) δ −142.1. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.30. FT-IR (ATR): 3426, 3127, 2933, 2200, 2129, 2040, 1603, 1548, 1515, 1479, 1436, 1397, 1218, 1071, 1027, 969, 827, 739, 718, 627 cm^{-1}. ESI-MS: m/z calcd for $C_{14}H_9BBrF_3N_3$ [M−K$^+$]$^-$ 366.00, found 366.23.

*4.2.9. Potassium 3-(4-(4-bromophenyl)-1H-1,2,3-triazol-1-yl)phenyltrifluoroborate (**2h**).* General procedure I was used employing potassium 3-iodophenyltrifluoroborate (77.5 mg, 0.25 mmol), NaN_3 (16.3 mg, 0.25 mmol), CuBr (3.6 mg, 10 mol %), Cs_2CO_3 (81.4 mg, 0.25 mmol), and *N*,*N*′-dimethylethylenediamine (4.4 mg, 20 mol %) in DMSO-d_6 (1 mL) was heated in an oil bath at 90 °C for 6 h monitored by the ^{1}H NMR (in DMSO-d_6) until the complete conversion of the starting material into azide[8] and then added 1-bromo-4-ethynylbenzene (**1g**, 50.6 mg, 0.28 mmol) into the reaction mass and continued for another 1 h (see Table 1). After completion of the reaction, work-up was adopted as mentioned in General procedure I, to give the desired product in 94% yield (95.4 mg, a brown solid). Mp=264 °C (dec). ^{1}H NMR (400 MHz, acetone-d_6) δ 8.97 (s, 1H), 8.01 (d, 2H, J=8.4 Hz), 7.66 (d, 2H, J=8.4 Hz), 7.62 (m, 2H), 7.34 (t, 1H, J=7.6 Hz). ^{13}C NMR (100 MHz, acetone-d_6) δ 146.3, 135.8, 132.2, 131.8, 130.6, 127.4, 127.3, 123.1, 121.0, 119.0, 117.1. ^{19}F NMR (376 MHz, acetone-d_6) δ −142.8. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.32. FT-IR (ATR): 3392, 3071, 2132, 2010, 1579, 1461, 1237, 1209, 1178, 1100, 1068, 1023, 1009, 964, 882, 848, 811, 784, 759, 697, 669, 607 cm^{-1}. ESI-MS: m/z calcd for $C_{14}H_9BBrF_3N_3$ [M−K$^+$]$^-$ 366.00, found 366.21.

*4.2.10. Potassium 4-(4-butyl-1H-1,2,3-triazol-1-yl)phenyltrifluoroborate (**2i**).* General procedure I was used employing potassium 4-iodophenyltrifluoroborate (77.5 mg, 0.25 mmol) and 1-hexyne (**1h**, 23.0 mg, 0.28 mmol), to give the desired product in 80% yield (61.4 mg, an ivory solid). Mp=251−255 °C. ^{1}H NMR (400 MHz, acetone-d_6) δ 8.17 (s, 1H), 7.64 (d, 2H, J=8.4 Hz), 7.57 (d, 2H, J=8.0 Hz), 2.75 (t, 2H, J=7.6 Hz), 1.70 (m, 2H), 1.43 (m, 2H) 0.96 (t, 3H, J=7.2 Hz). ^{13}C NMR (100 MHz, acetone-d_6) δ 148.0, 135.2, 132.6, 119.0, 117.9, 31.4, 25.0, 22.0, 13.2. ^{19}F NMR (376 MHz, acetone-d_6) δ −141.7. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.35. FT-IR (ATR): 3139, 2958, 2931, 2860, 1928, 1603, 1552, 1513, 1465, 1432, 1395, 1220, 1191, 962, 826, 730, 625 cm^{-1}. ESI-MS: m/z calcd for $C_{12}H_{14}BF_3N_3$ [M−K$^+$]$^-$ 268.12, found 268.14.

*4.2.11. Potassium 4-(4-(cyclohexylmethyl)-1H-1,2,3-triazol-1-yl)phenyltrifluoroborate (**2j**).* General procedure I was used employing potassium 4-iodophenyltrifluoroborate (77.50 mg, 0.25 mmol) and prop-2-ynylcyclohexane (**1i**, 34.2 mg, 0.28 mmol), to give the desired product in 66% yield (57.3 mg, an ivory solid). Mp=210−212 °C. ^{1}H NMR (400 MHz, acetone-d_6) δ 8.17 (s, 1H), 7.64 (d, 2H, J=8.4 Hz), 7.58 (d, 2H, J=8.4 Hz), 2.63 (d, 2H, J=7.2 Hz), 1.72 (m, 6H), 1.24 (m, 3H), 1.02 (m, 2H). ^{13}C NMR (100 MHz, acetone-d_6) δ 146.5, 135.1, 132.6, 119.6, 117.9, 38.0, 33.1, 32.8, 26.2, 26.0. ^{19}F NMR (376 MHz, acetone-d_6) δ −142.0. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.31. FT-IR (ATR): 3374, 3135, 3037, 2920, 2849, 2660, 2125, 2007, 1603, 1515, 1447, 1397, 1223, 1193, 955, 817, 726 cm^{-1}. ESI-MS: m/z calcd for $C_{15}H_{18}BF_3N_3$ [M−K$^+$]$^-$ 308.15, found 308.16.

*4.2.12. Potassium 4-(4-(3-cyanopropyl)-1H-1,2,3-triazol-1-yl)phenyltrifluoroborate (**2k**, 2.0 mmol scale reaction).* General procedure I was used employing potassium 4-iodophenyltrifluoroborate (620 mg, 2.0 mmol), NaN_3 (130.0 mg, 2.0 mmol), CuBr (28.7 mg, 10 mol %), Cs_2CO_3 (651.8 mg, 2.0 mmol), *N*,*N*′-dimethylethylenediamine (35.3 mg, 20 mol %), and hex-5-ynenitrile (**1j**, 205 mg, 2.2 mmol) in DMSO-d_6 (8 mL), to give the desired product in 82% yield (522 mg, a light brown solid). Mp=208 °C (dec). ^{1}H NMR (400 MHz, acetone-d_6+DMSO-d_6) δ 8.33 (s, 1H), 7.65 (d, 2H, J=8.4 Hz), 7.59 (d, 2H, J=8.0 Hz), 2.91 (t, 2H, J=7.6 Hz), 2.62 (t, 2H, J=7.2 Hz), 2.09 (m, 2H). ^{13}C NMR (100 MHz, acetone-d_6+DMSO-d_6) δ 151.8, 146.2, 135.0, 132.6, 119.8, 119.7, 118.0, 53.2, 25.2, 24.2, 15.8. ^{19}F NMR (376 MHz, acetone-d_6+DMSO-d_6) δ −141.9. ^{11}B NMR (128 MHz, acetone-d_6+DMSO-d_6) δ 3.28. FT-IR (ATR): 3420, 3120, 3083, 3039, 2945, 2245, 1601, 1552, 1519, 1463, 1436, 1419, 1340, 1325, 1226, 1212, 1189, 1057, 1025, 964, 939, 844, 823 cm^{-1}. ESI-MS: m/z calcd for $C_{12}H_{11}BF_3N_4$ [M−K$^+$]$^-$ 279.10, found 279.33.

*4.2.13. Potassium 4-(4-(methoxymethyl)-1H-1,2,3-triazol-1-yl)phenyltrifluoroborate (**2l**).* General procedure I was used employing potassium 4-iodophenyltrifluoroborate (77.5 mg, 0.25 mmol) and 3-methoxyprop-1-yne (**1k**, 26.6 mg, 0.38 mmol), to give the desired product in 94% yield (70.0 mg, a light purple solid). Mp=195−198 °C. ^{1}H NMR (400 MHz, acetone-d_6) δ 8.38 (s, 1H), 7.66 (d, 2H, J=8.4 Hz), 7.59 (d, 2H, J=8.0 Hz), 4.58 (s, 2H), 3.37 (s, 3H). ^{13}C NMR (100 MHz, acetone-d_6) δ 145.0, 134.9, 132.7, 132.6, 121.1, 118.2, 65.4, 57.0. ^{19}F NMR (376 MHz, acetone-d_6) δ −140.4. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.29. FT-IR (ATR): 3668, 3612, 3605, 3585, 3565, 3530, 3497, 3486, 3456, 3430, 3415, 3387, 3348, 3139, 2933, 2899, 1603, 1515, 1456, 1437, 1369, 1207, 1189, 1100, 1048, 955, 826, 803, 771 cm^{-1}. ESI-MS: m/z calcd for $C_{10}H_{10}BF_3N_3O$ [M−K$^+$]$^-$ 256.08, found 256.41.

*4.2.14. Potassium 4-(4-(hydroxymethyl)-1H-1,2,3-triazol-1-yl)phenyltrifluoroborate (**2m**).* General procedure I was used employing potassium 4-iodophenyltrifluoroborate (77.5 mg, 0.25 mmol) and prop-2-yn-1-ol (**1l**, 15.7 mg, 0.28 mmol), to give the desired product in 82% yield (57.6 mg, a light brown solid). Mp=212 °C (dec). ^{1}H NMR (400 MHz, acetone-d_6+DMSO-d_6) δ 8.32 (s, 1H), 7.66 (d, 2H, J=8.0 Hz), 7.58 (d, 2H, J=8.0 Hz), 4.72 (s, 2H). ^{13}C NMR (100 MHz, acetone-d_6+DMSO-d_6) δ 149.0, 135.0, 132.7, 120.2, 118.1, 55.7. ^{19}F NMR (376 MHz, acetone-d_6+DMSO-d_6) δ −140.8. ^{11}B NMR (128 MHz, acetone-d_6+DMSO-d_6) δ 3.21. FT-IR (ATR): 3149, 2876, 1913, 1602, 1580, 1516, 1466, 1435, 1399, 1215, 1193, 1063, 955, 938, 825, 813, 760, 733, 624, 553 cm^{-1}. ESI-MS: m/z calcd for $C_9H_8BF_3N_3O$ [M−K$^+$]$^-$ 242.07, found 242.46.

*4.2.15. Potassium 4-(4-(2-hydroxypropan-2-yl)-1H-1,2,3-triazol-1-yl)phenyltrifluoroborate (**2n**).* General procedure I was used employing potassium 4-iodophenyltrifluoroborate (77.5 mg, 0.25 mmol) and 2-methylbut-3-yn-2-ol (**1m**, 23.5 mg, 0.28 mmol), to give the desired product in 95% yield (73.4 mg, a brown solid). Mp=253 °C (dec). ^{1}H NMR (400 MHz, acetone-d_6+DMSO-d_6) δ 8.24 (s, 1H), 7.65 (d, 2H, J=8.4 Hz), 7.58 (d, 2H, J=8.0 Hz), 4.40 (br s, 1H), 1.61 (s, 6H). ^{13}C NMR (100 MHz, acetone-d_6+DMSO-d_6) δ 156.8, 135.1, 132.7, 118.1, 118.0, 67.5, 30.3. ^{19}F NMR (376 MHz, acetone-d_6+DMSO-d_6) δ −141.2. ^{11}B NMR (128 MHz, acetone-d_6+DMSO-d_6)

δ 3.28. FT-IR (ATR): 3270, 3153, 2982, 2934, 2120, 1601, 1508, 1462, 1392, 1377, 1363, 1206, 1170, 1054, 1027, 956, 827, 804, 730, 613, 566 cm^{-1}. ESI-MS: *m*/*z* calcd for $C_{11}H_{12}BF_3N_3O$ $[M-K^+]^-$ 270.10, found 270.10.

*4.2.16. Potassium 3-(4-phenyl-1H-1,2,3-triazol-1-yl)phenyltrifluoroborate (**2o** from I).* A solution of potassium 3-iodophenyltrifluoroborate (77.5 mg, 0.25 mmol), NaN_3 (16.3 mg, 0.25 mmol), CuBr (3.6 mg, 10 mol %), Cs_2CO_3 (81.5 mg, 0.25 mmol), and *N*,*N*′-dimethylethylenediamine (4.4 mg, 20 mol %) in DMSO-d_6 (1 mL) was heated in an oil bath at 90 °C for 6 h monitored by the ^{1}H NMR (in DMSO-d_6) until the complete conversion of the starting material into azide[8] and then added ethynylbenzene (**1a**, 28.6 mg, 0.28 mmol) into the reaction mass and continued for another 1 h (see Table 1). After completion of the reaction, work-up was adopted as mentioned in General procedure I, to give the desired product in 75% yield (61.3 mg, a brown solid). Mp=243 °C (dec). ^{1}H NMR (400 MHz, acetone-d_6+DMSO-d_6) δ 8.99 (s, 1H), 8.06 (m, 2H), 7.94 (m, 1H), 7.62 (m, 2H), 7.47 (t, 2H, *J*=7.6 Hz), 7.36 (m, 2H). ^{13}C NMR (100 MHz, acetone-d_6+DMSO-d_6) δ 147.4, 136.0, 132.1, 131.3, 128.7, 127.8, 127.4, 125.5, 123.1, 118.8, 117.1. ^{19}F NMR (376 MHz, acetone-d_6+DMSO-d_6) δ −141.5. ^{11}B NMR (128 MHz, acetone-d_6+DMSO-d_6) δ 3.09. FT-IR (ATR): 3393, 3150, 2110, 2043, 1644, 1606, 1582, 1474, 1446, 1429, 1248, 1213, 1175, 1072, 1022, 960, 884, 822, 791, 755, 693, 602 cm^{-1}. ESI-MS: *m*/*z* calcd for $C_{14}H_{10}BF_3N_3$ $[M-K^+]^-$ 288.09, found 287.98.

*4.2.17. Potassium 3-(4-phenyl-1H-1,2,3-triazol-1-yl)phenyltrifluoroborate (**2o** from Br).* A solution of potassium 3-bromophenyltrifluoroborate (65.7 mg, 0.25 mmol), NaN_3 (16.3 mg, 0.25 mmol), CuBr (3.6 mg, 10 mol %), Cs_2CO_3 (81.5 mg, 0.25 mmol), and *N*,*N*′-dimethylethylenediamine (4.4 mg, 20 mol %) in DMSO-d_6 (1 mL) was heated in an oil bath at 90 °C for 9 h monitored by the ^{1}H NMR (in DMSO-d_6) until the complete conversion of the starting material into azide[8] and then added ethynylbenzene (**1a**, 28.6 mg, 0.28 mmol) into the reaction mass and continued for another 3 h (see Table 1). After completion of the reaction, work-up was adopted as mentioned in General procedure I, to give the desired product in 65% yield (53.1 mg, a brown solid).

*4.2.18. Potassium 3-methyl-5-(4-phenyl-1H-1,2,3-triazol-1-yl)phenyltrifluoroborate (**2p**).* A solution of potassium 3-bromo-5-methylphenyltrifluoroborate (69.2 mg, 0.25 mmol), NaN_3 (16.3 mg, 0.25 mmol), CuBr (3.6 mg, 10 mol %), Cs_2CO_3 (81.5 mg, 0.25 mmol), and *N*,*N*′-dimethylethylenediamine (4.4 mg, 20 mol %) in DMSO-d_6 (1 mL) was heated in an oil bath at 90 °C for 8 h monitored by the ^{1}H NMR (in DMSO-d_6) until the complete conversion of the starting material into azide[8] and then added ethynylbenzene (**1a**, 28.6 mg, 0.28 mmol) into the reaction mass and continued for another 0.5 h (see Table 1). After completion of the reaction, work-up was adopted as mentioned in General procedure I, to give the desired product in 80% yield (68.2 mg, a dark brown solid). Mp=238.0 °C (dec). ^{1}H NMR (400 MHz, acetone-d_6) δ 8.85 (s, 1H), 8.04 (d, 2H, *J*=7.6 Hz), 7.72 (s, 1H), 7.47 (m, 4H), 7.35 (t, 1H, *J*=7.6 Hz), 2.38 (s, 3H). ^{13}C NMR (100 MHz, acetone-d_6) δ 147.3, 136.7, 136.0, 133.0, 131.4, 128.7, 127.7, 125.4, 120.3, 118.5, 117.7, 20.6. ^{19}F NMR (376 MHz, acetone-d_6) δ −141.9. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.33. FT-IR (ATR): 3612, 3150, 3061, 2921, 2853, 2358, 1608, 1590, 1467, 1434, 1377, 1352, 1276, 1236, 1171, 1024, 993, 970, 868, 763, 694, 614 cm^{-1}. ESI-MS: *m*/*z* calcd for $C_{15}H_{12}BF_3N_3$ $[M-K^+]^-$ 302.10, found 302.06.

*4.2.19. Potassium 3-methoxy-5-(4-phenyl-1H-1,2,3-triazol-1-yl)phenyltrifluoroborate (**2q**).* A solution of potassium 3-bromo-5-methoxyphenyltrifluoroborate (73.2 mg, 0.25 mmol), NaN_3 (16.3 mg, 0.25 mmol), CuBr (3.6 mg, 10 mol %), Cs_2CO_3 (81.5 mg, 0.25 mmol), and *N*,*N*′-dimethylethylenediamine (4.4 mg, 20 mol %) in DMSO-d_6 (1 mL) was heated in an oil bath at 90 °C for 4 h monitored by the ^{1}H NMR (in DMSO-d_6) until the complete conversion of the starting material into azide[8] and then added ethynylbenzene (**1a**, 28.6 mg, 0.28 mmol) into the reaction mass and continued for another 0.5 h (see Table 1). After completion of the reaction, work-up was adopted as mentioned in General procedure I, to give the desired product in 92% yield (82.2 mg, a dark brown solid). Mp=253 °C (dec). ^{1}H NMR (400 MHz, acetone-d_6+metanol-d_4) δ 8.91 (s, 1H), 8.01 (d, 2H, *J*=7.6 Hz), 7.56 (s, 1H), 7.46 (t, 2H, *J*=7.2 Hz), 7.35 (t, 1H, *J*=7.2 Hz), 7.25 (s, 1H), 7.20 (s, 1H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, acetone-d_6+metanol-d_4) δ 159.5, 147.5, 136.8, 130.9, 128.7, 127.9, 125.4, 118.8, 117.2, 115.3, 103.3, 54.6. ^{19}F NMR (376 MHz, acetone-d_6+metanol-d_4) δ −141.8. ^{11}B NMR (128 MHz, acetone-d_6+metanol-d_4) δ 3.30. FT-IR (ATR): 3166, 2936, 2832, 1661, 1582, 1441, 1428, 1397, 1319, 1279, 1250, 1220, 1171, 1099, 1023, 987, 859, 794, 766, 695, 618 cm^{-1}. ESI-MS: *m*/*z* calcd for $C_{15}H_{12}BF_3N_3O$ $[M-K^+]^-$ 318.10, found 318.39.

*4.2.20. Potassium 3-chloro-5-(4-phenyl-1H-1,2,3-triazol-1-yl)phenyltrifluoroborate (**2r**).* A solution of potassium 3-bromo-5-chlorophenyltrifluoroborate (74.3 mg, 0.25 mmol), NaN_3 (16.3 mg, 0.25 mmol), CuBr (3.6 mg, 10 mol %), Cs_2CO_3 (81.5 mg, 0.25 mmol), and *N*,*N*′-dimethylethylenediamine (4.4 mg, 20 mol %) in DMSO-d_6 (1 mL) was heated in an oil bath at 90 °C for 12 h monitored by the ^{1}H NMR (in DMSO-d_6) until the complete conversion of the starting material into azide[8] and then added ethynylbenzene (**1a**, 28.6 mg, 0.28 mmol) into the reaction mass and continued for another 0.5 h (see Table 1). After completion of the reaction, work-up was adopted as mentioned in General procedure I, to give the desired product in 75% yield (67.8 mg, a greenish brown solid). Mp=253 °C (dec). ^{1}H NMR (400 MHz, acetone-d_6) δ 9.02 (s, 1H), 8.05 (d, 2H, *J*=7.6 Hz), 7.89 (s, 1H), 7.73 (s, 1H), 7.57 (s, 1H), 7.48 (t, 3H, *J*=7.6 Hz), 7.37 (t, 1H, *J*=7.2 Hz). ^{13}C NMR (100 MHz, acetone-d_6) δ 148.5, 137.9, 134.0, 132.4, 131.9, 129.8, 129.7, 129.4, 128.8, 128.0, 126.4, 122.0, 119.6, 117.8. ^{19}F NMR (376 MHz, acetone-d_6) δ −141.1. ^{11}B NMR (128 MHz, acetone-d_6) δ 2.63. FT-IR (ATR): 3156, 3061, 1576, 1473, 1424, 1393, 1211, 1168, 1099, 1026, 1000, 979, 872, 788, 763, 690, 612, 559 cm^{-1}. ESI-MS: *m*/*z* calcd for $C_{14}H_9BClF_3N_3$ $[M-K^+]^-$ 322.05, found 322.64.

4.3. General procedure II (Suzuki–Miyaura cross-coupling reactions) Table 3

To a 16×90 mm glass vessel containing a stirring bar were added potassium 1,2,3-triazoletrifluoroborate (**2a** or **2k**, 0.5 mmol), Cs_2CO_3 (195 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3.5 mg, 3 mol %), and aryl bromide (0.5 mmol). The mixture was dissolved in 20% aqueous 1,4-dioxane (2 mL). The reaction was stirred in an oil bath at 100 °C. After the aryl bromide was totally consumed (the reaction was monitored by TLC), then cooled to room temperature. The reaction mixture was extracted with ethyl acetate and then combined organic layers were washed with H_2O. Finally organic layer was dried over $MgSO_4$. The solvent was filtered off through silica gel. The solvent was concentrated on a rotary evaporator. The crude product was purified by preparative TLC (0.5 mm, elution with hexane/EtOAc=3:1). The pure compound **3** was obtained as a white solid.

*4.3.1. 4′-(4-Phenyl-1H-1,2,3-triazol-1-yl)biphenyl-4-carbonitrile (**3a**).* General procedure II was used employing potassium 4-(4-phenyl-1H-1,2,3-triazol-1-yl)phenyltrifluoroborate (**2a**, 163.5 mg, 0.5 mmol) and 4-bromobenzonitrile (91 mg, 0.5 mmol) to give the desired product in 79% yield (127.3 mg, an ivory solid). Mp=215–218 °C (lit.[8] mp=215–219 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.87 (m, 4H), 7.69 (m, 6H), 7.41 (t, 2H, *J*=7.6 Hz), 7.32 (t, 1H, *J*=7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 138.5, 136.1, 131.7,

129.0, 127.9, 127.5, 127.3, 126.6, 124.8, 119.9, 117.6, 116.2, 110.6. FT-IR (ATR): 3097, 2962, 2924, 2853, 2222, 1604, 1499, 1455, 1396, 1228, 1095, 1022, 992, 858, 818, 799, 772, 693, 539 cm^{-1}. ESI-MS: *m/z* calcd for $C_{21}H_{14}N_4$ $[M+H]^+$ 323.12, found 322.97.

*4.3.2. 1-(4′-Methoxybiphenyl-4-yl)-4-phenyl-1H-1,2,3-triazole (**3b**).* General procedure II was used employing potassium 4-(4-phenyl-1*H*-1,2,3-triazol-1-yl)phenyltrifluoroborate (**2a**, 163.5 mg, 0.5 mmol) and 4-bromoanisole (93.5 mg, 0.5 mmol) to give the desired product in 75% yield (122.7 mg, a light yellow solid). Mp=208–213 °C °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.93 (d, 2H, *J*=7.2 Hz), 7.84 (d, 2H, *J*=8.4 Hz), 7.71 (d, 2H, *J*=8.4 Hz), 7.57 (d, 2H, *J*=8.8 Hz), 7.47 (t, 2H, *J*=7.6 Hz), 7.38 (t, 1H, *J*=7.6 Hz), 7.02 (d, 2H, *J*=8.8 Hz), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 148.4, 141.4, 135.6, 132.1, 130.2, 128.9, 128.4, 128.1, 127.8, 127.1, 125.8, 120.8, 117.4, 114.4, 55.4. FT-IR (ATR): 3119, 3094, 3062, 2959, 2922, 2922, 2839, 1736, 1608, 1574, 1505, 1480, 1454, 1441, 1417, 1400, 1293, 1281, 1256, 1228, 1181, 1095, 1073, 1040, 1019, 992, 912, 820, 759, 737, 689, 659, 606 cm^{-1}. ESI-MS: *m/z* calcd for $C_{21}H_{17}N_3O$ $[M+H]^+$ 328.13, found 328.01.

*4.3.3. 2-(4-(4-Phenyl-1H-1,2,3-triazol-1-yl)phenyl)pyridine (**3c**).* General procedure II was used employing potassium 4-(4-phenyl-1*H*-1,2,3-triazol-1-yl)phenyltrifluoroborate (**2a**, 163.5 mg, 0.5 mmol) and 2-bromopyridine (79 mg, 0.5 mmol) to give the desired product in 65% yield (97 mg, a light brown solid). Mp=181–188 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, 1H, *J*=4.8 Hz), 8.29 (s, 1H), 8.22 (d, 2H, *J*=8.8 Hz), 7.95 (m, 4H), 7.84 (m, 2H), 7.50 (t, 2H, *J*=7.2 Hz), 7.41 (t, 1H, *J*=7.6 Hz), 7.33 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 155.8, 149.9, 148.5, 139.7, 137.3, 137.0, 130.4, 130.3, 130.1, 128.9, 128.5, 128.3, 127.4, 125.9, 125.8, 122.7, 122.4, 120.6, 120.5, 117.8, 117.4, 116.4. FT-IR (ATR): 3132, 3098, 3062, 2922, 2851, 2360, 1939, 1736, 1606, 1585, 1566, 1520, 1472, 1455, 1436, 1429, 1408, 1231, 1182, 1152, 1114, 1096, 1073, 1043, 1026, 990, 968, 921, 859, 809, 778, 757, 740, 721, 694, 667, 616, 569 cm^{-1}. ESI-MS: *m/z* calcd for $C_{19}H_{14}N_4[M+H]^+$ 299.14, found 299.57.

*4.3.4. 4′-(4-(3-Cyanopropyl)-1H-1,2,3-triazol-1-yl)biphenyl-4-carbonitrile (**3d**).* General procedure II was used employing potassium 4-(4-(3-cyanopropyl)-1*H*-1,2,3-triazol-1-yl)phenyltrifluoroborate (**2k**, 159 mg, 0.5 mmol) and 4-bromobenzonitrile (91 mg, 0.5 mmol) to give the desired product in 82% yield (128.5 mg, an ivory solid). Mp=122–126 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (m, 3H), 7.77 (m, 6H), 3.02 (t, 2H, *J*=7.2 Hz), 2.51 (t, 2H, *J*=7.2 Hz), 2.19 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 142.9, 138.4, 136.0, 131.7, 127.5, 126.6, 119.8, 118.3, 118.2, 117.6, 110.6, 23.7, 23.1, 15.5. FT-IR (ATR): 3127, 3057, 2930, 2853, 2248, 2223, 1904, 1726, 1678, 1603, 1553, 1528, 1497, 1437, 1418, 1398, 1325, 1309, 1209, 1191, 1180, 1119, 1044, 997, 988, 856, 814, 753, 720, 693, 537 cm^{-1}. ESI-MS: *m/z* calcd for $C_{19}H_{15}N_5$ $[M+H]^+$ 314.13, found 313.95.

*4.3.5. 4-(1-(4-(1,2,2-Triphenylvinyl)phenyl)-1H-1,2,3-triazol-4-yl)butanenitrile (**3e**).* General procedure II was used employing potassium 4-(4-(3-cyanopropyl)-1H-1,2,3-triazol-1-yl)phenyltrifluoroborate (**2k**, 159 mg, 0.5 mmol) and bromotriphenylethylene (167.6 mg, 0.5 mmol) to give the desired product in 87% yield (202 mg, an ivory solid). Mp=211–213 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.47 (d, 2H, *J*=8.8 Hz), 7.28 (s, 2H), 7.14 (m, 9H), 7.08 (m, 6H), 2.97 (t, 2H, *J*=7.2 Hz), 2.47 (t, 2H, *J*=7.2 Hz), 2.16 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 132.6, 131.3, 131.2, 127.9, 127.8, 127.7, 126.9, 126.8, 126.7, 119.6, 24.7, 24.1, 16.4. FT-IR (ATR): 3128, 3078, 3028, 2922, 2852, 2247, 1897, 1736, 1598, 1574, 1546, 1516, 1491, 1460, 1443, 1409, 1317, 1294, 1235, 1178, 1152, 1112, 1073, 1050, 1029, 997, 978, 916, 848, 821, 762, 754, 719, 696, 626, 582, 569 cm^{-1}. ESI-MS: *m/z* calcd for $C_{32}H_{26}N_4$ $[M+H]^+$ 467.21, found 467.00.

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Supplementary data

Supplementary data contain the copies of ^1H, ^{13}C, ^{19}F, and ^{11}B NMR spectra of all new compounds. Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2011.05.126.

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