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Palladium-Catalyzed Direct Diarylation of 2-Benzyl-1,2,3-triazole: a Simple Access to 4-Aryl- or 4,5-Diaryl-2-benzyl-1,2,3-triazoles and Phenanthro[9,10-*d*][1,2,3]triazoles

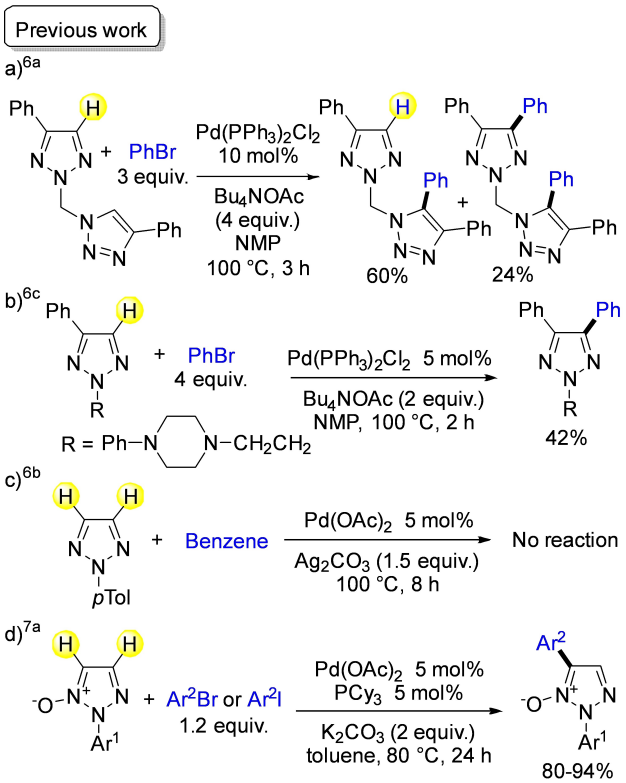
Xinzhe Shi,[a] Jian Zhang,[a] Thierry Roisnel,[a] Jean-François Soulé,*[a] and Henri Doucet*[a]

The reactivity of 2-benzyl-1,2,3-triazole in palladium-catalyzed direct arylation was studied. The reaction conditions for the selective synthesis of 2-benzyl-4-aryl-1,2,3-triazoles in moderate to high yields using phosphine-free $Pd(OAc)_2$ catalyst and inexpensive KOAc base have been found. Then, from these 4-aryl-1,2,3-triazoles, the palladium-catalyzed C–H bond functionalization of the C5-position allowed the synthesis of the corresponding 4,5-diarylated 2-benzyl-1,2,3-triazoles. This selective 4,5-diarylation of 2-benzyl-1,2,3-triazole was successfully applied for the straightforward building of the π-extended polycyclic heteroaromatic structures phenanthro[9,10-*d*][1,2,3]triazoles through Pd-catalyzed C4- and C5-intermolecular arylations followed by Pd-catalyzed C–H intramolecular arylation.

Introduction

Pd-catalyzed so-called direct arylation of 5-membered ring heteroaromatics, *via* a C–H bond cleavage step,[1,2] has led in recent years to a revolution in bi(hetero)aryl and poly(hetero) aromatic synthesis methods. These couplings are very attractive, compared to the more classical reactions catalyzed by palladium such as Stille, Suzuki or Negishi couplings, because they do not require the prior synthesis of organometallic derivatives.[2] Several examples of Pd-catalyzed direct arylations of various heteroarenes such as pyrazoles,[3] or imidazoles[4] with aryl halides have been reported. A few groups have also reported examples of Pd-catalyzed direct arylations of 1-substituted 1,2,3-triazoles.[5] For example, in 2007, Gevorgyan group described the first Pd-catalyzed direct arylations of 1-benzyl- and 1-alkyl-1,2,3-triazoles.[5a] They observed a strong preference for C5- *vs* C4-arylation. The same year, similar results were reported by Oshima and Yorimitsu,[5b] for the arylation of 1-benzyl-1,2,3-triazoles using aryl chlorides under microwave irradiation. In 2008, Ackermann's group reported another procedure for the C4-arylation of 1,5-disubstituted 1,2,3-triazoles, and C5-arylation of 1,4-disubstituted 1,2,3-triazoles.[5c]

In contrast, to our knowledge, the metal-catalyzed direct arylation of 2-substituted 1,2,3-triazoles has attracted much less attention (Scheme 1).[6] In 2008, Fokin *et al.* studied the direct arylation of a compound containing both 1-substituted 4-phenyl-1,2,3-triazole and 2-substituted 4-phenyl-1,2,3-triazole units (Scheme 1a).[6a] They employed $Pd(PPh_3)_2Cl_2$ as the catalyst and Bu_4NOAc as the base. Their study revealed that the 1-substituted 4-phenyl-1,2,3-triazole unit is the most reactive, affording the mono-arylation product in 60% yield; whereas the diarylated compound – arylation of both types of triazole rings – was only obtained in 24% yield.



Scheme 1. Pd-catalyzed direct arylations of 2-substituted 1,2,3-triazoles and 1,2,3-triazole *N*-oxides.

This procedure was recently employed by Ko et al. for the arylation of another 2-substituted 4-phenyl-1,2,3-triazole (Scheme 1b).[6c] In 2013, in the course of their study on the arylation of 2-substituted 1,2,3-triazole *N*-oxides, Kuang *et al.*

[a] X. Shi, J. Zhang, Dr. T. Roisnel, Dr. J.-F. Soulé, Dr. H. Doucet
ISCR-UMR 6226,
Univ Rennes,
35000 Rennes, France
E-mail: jean-francois.soule@univ-rennes1.fr
henri.doucet@univ-rennes1.fr

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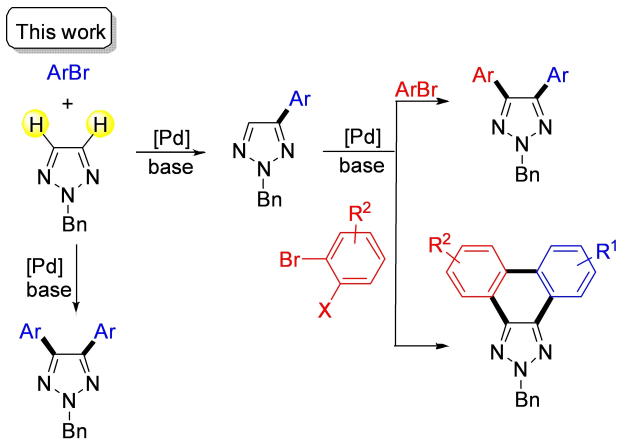
attempted to arylate 2-benzyl-1,2,3-triazole with benzene under Pd-catalyzed oxidative coupling conditions, but the reaction was unsuccessful (Scheme 1c).[6b] A few examples of C5-arylations of 2-substituted 1,2,3-triazole *N*-oxides have also been described (Scheme 1d).[7] However, the use of such 1,2,3-triazole *N*-oxides requires two more steps due to the nitrogen protection/deprotection sequence.

As the discovery of an effective procedure, for the arylation of 1,2,3-triazole derivatives, using readily available catalyst and base is desirable, the reactivity of 2-benzyl-1,2,3-triazole in direct arylation in the presence of palladium catalysts needed to be investigated. Here, we report (i) conditions for the palladium-catalyzed direct arylation of 1,2,3-triazoles; (ii) on the scope of the reaction; (iii) on the subsequent reactivity of these 4-aryl-1,2,3-triazoles in Pd-catalyzed C–H bond functionalization for access to 4,5-diaryl-1,2,3-triazoles; and (iv) on the synthesis of the π-extended molecules phenanthro[9,10-*d*][1,2,3]triazoles *via* Pd-catalyzed intermolecular arylations followed by a C–H intramolecular arylation (Scheme 2).



Scheme 2. Pd-catalyzed direct arylation of 2-substituted 1,2,3-triazoles.

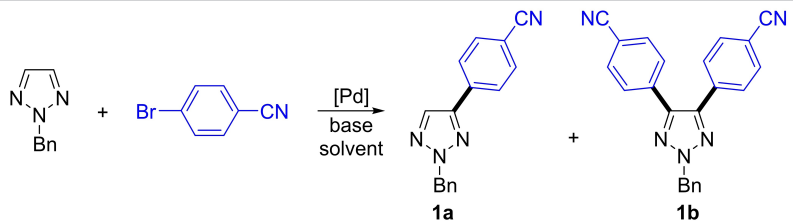
Results and Discussion

4-Bromobenzonitrile (1 equiv.) and 2-benzyl-1,2,3-triazole (2 equiv.) were employed as model substrates for our study (Table 1). We initially examined the influence of the base on the aryl bromide conversion and on the selectivity (mono- *vs* di-arylation) using 2 mol% $Pd(OAc)_2$ catalyst and DMA as the solvent. We had previously observed that this combination of catalyst and solvent promoted very effectively the direct arylation of some heteroarenes.[2j] Cs_2CO_3 was ineffective and 4-bromobenzonitrile was recovered (Table 1, entry 1).

K_2CO_3 or NaOAc as bases, afforded the desired product **1a** in quite low yields due to a partial conversion of 4-bromobenzonitrile and also to the formation of [1,1′-biphenyl]-4,4′-dicarbonitrile as side-product (Table 1, entries 2 and 3). Conversely, the use of KOAc gave **1a** in a high 66% yield with a complete conversion of the aryl bromide (Table 1, entry 4). This result is consistent with a concerted metallation deprotonation mechanism.[8,9] CsOAc and KOPiv were found to be less effective bases for this reaction, as **1a** was obtained in 54% and 60% yield respectively, due to a lower selectivity (mono- *vs* di-arylation) (Table 1, entries 5 and 6). The use of $PdCl(C_3H_5)$(dppb) catalyst[10] instead of $Pd(OAc)_2$, or the reaction performed in DMF afforded **1a** in lower yields (Table 1, entries 7 and 8). Finally, a lower catalyst loading (1 mol%) or a lower reaction temperature led to partial conversions of 4-bromobenzonitrile (Table 1, entries 9 and 10).

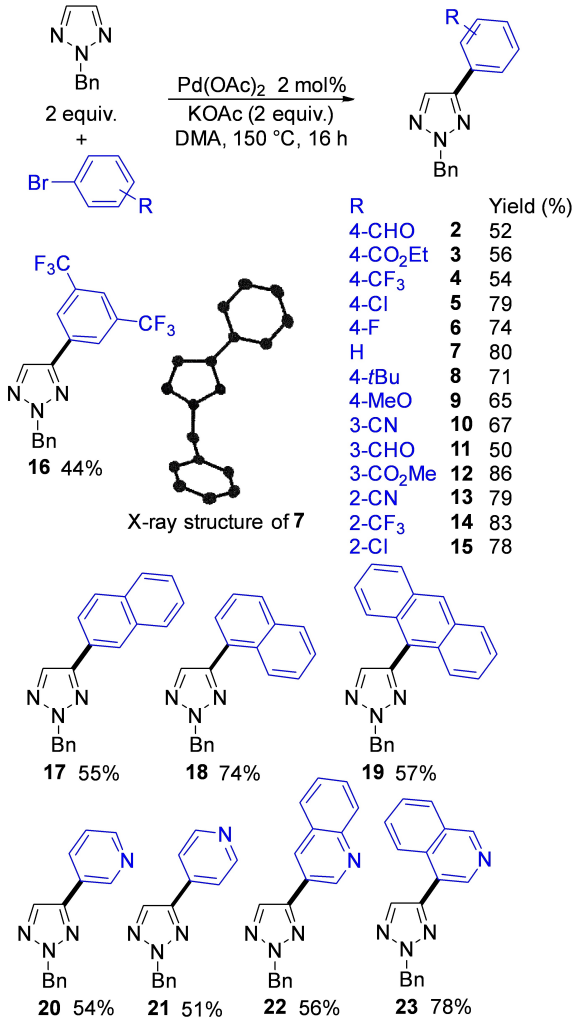
Then, 2-benzyl-1,2,3-triazole was coupled with a set of aryl bromides in the presence of 2 mol% $Pd(OAc)_2$, KOAc as the base in DMA (Scheme 3). Moderate yields in the desired C4-arylation products **2**–**4** were obtained using aryl bromides

Table 1. Influence of the reaction conditions on the Pd-catalyzed C4-arylation of 2-benzyl-1,2,3-triazole with 4-bromobenzonitrile.[a]



Entry	Catalyst (mol%)	Solvent	Base	Conv. [%]	Ratio **1a**:**1b**	Yield in **1a** [%]
1	$Pd(OAc)_2$ (2)	DMA	Cs_2CO_3	–	–	0
2	$Pd(OAc)_2$ (2)	DMA	K_2CO_3	64	93:7	31
3	$Pd(OAc)_2$ (2)	DMA	NaOAc	82	93:7	25[b]
4	$Pd(OAc)_2$ (2)	DMA	KOAc	100	84:16	66
5	$Pd(OAc)_2$ (2)	DMA	CsOAc	93	74:26	54
6	$Pd(OAc)_2$ (2)	DMA	KOPiv	100	68:32	60
7	$PdCl(C_3H_5)$(dppb) (2)	DMA	KOAc	100	75:25	45
8	$Pd(OAc)_2$ (2)	DMF	KOAc	100	80:20	42
9	$Pd(OAc)_2$ (1)	DMA	KOAc	87	93:7	55
10	$Pd(OAc)_2$ (2)	DMA	KOAc	74	87:13	53[c]

[a] Conditions: 4-Bromobenzonitrile (1 equiv.), 2-benzyl-1,2,3-triazole (2 equiv.), base (2 equiv.), 16 h, 150 °C, conversion of 2-benzyl-1,2,3-triazole, isolated yields. [b] A large amount of homocoupling of 4-bromobenzonitrile was also observed. [c] 120 °C.

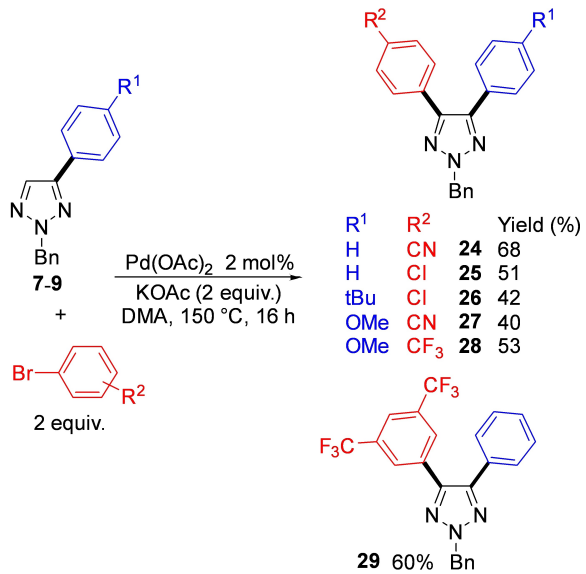


Scheme 3. Scope of the direct C4-arylation of 2-benzyl-1,2,3-triazole.

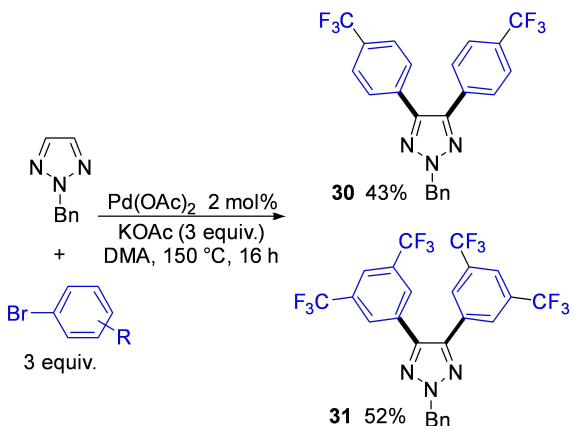
bearing formyl, ester or trifluoromethyl *para*-substituents. With 4-(trifluoromethyl)bromobenzene, a significant amount of 4,5-diarylated triazole was observed by GC/MS and ^{1}H NMR analysis of the crude mixtures. Higher yields were obtained for the coupling of the more electron-rich aryl bromides, 4-bromochlorobenzene, 4-bromofluorobenzene and bromobenzene leading to products **5**–**7** in 74–80% yields. The structure of **7** was confirmed by X-ray analysis.[11] *tert*-Butyl- and methoxy-substituents at *para*-position on the aryl bromides were also tolerated giving rise to products **8** and **9** in 71% and 65% yield, respectively. Nitrile-, formyl- and acyloxy-substituents at *meta*-position on the aryl bromide were also tolerated providing the C4-arylated triazoles **10**–**12** in moderate to high yields. Reactions with the more hindered substrates, 2-bromobenzonitrile, 2-(trifluoromethyl)bromobenzene, 2-bromochlorobenzene and 1-bromonaphthalene were also successful affording the products **13**–**15** and **18** in 74–83% yields. Even the very congested 9-bromoanthacene was successfully coupled with 2-benzyl-1,2,3-triazole to give **19** in 57% yield. The use of the *N*-containing heterocycles, 3- or 4-bromopyridines, 3-bromoquinoline and 4-bromoisoquinoline also afforded the desired C4-arylated triazole derivatives **20**–**23** in 51–78% yields.

The reactivity for arylation of the C5-position of 4-arylated 2-benzyl-1,2,3-triazoles was then examined (Scheme 4). As seen in the Table 1, the 4,5-diarylation of 2-benzyl-1,2,3-triazoles using only one equiv. of aryl bromide was generally observed in low yield, revealing that the second arylation is challenging but possible. The reaction of 2-benzyl-4-phenyl-1,2,3-triazole **7** (1 equiv.) with 4-bromobenzonitrile or 4-bromochlorobenzene (2 equiv.) in the presence of 2 mol% $Pd(OAc)_2$ catalyst afforded the desired products **24** and **25** in 68% and 51% yield, respectively. Lower yields in **27** and **28** were obtained from the more electron-rich 2-benzyl-4-(4-methoxyphenyl)-1,2,3-triazole **9** using 4-bromobenzonitrile and 4-(trifluoromethyl) bromobenzene as the coupling partners.

The one pot synthesis of 4,5-diarylated 1,2,3-triazoles from 2-benzyl-1,2,3-triazole was then examined (Scheme 5). As described in the Table 1, the 4,5-diarylation was generally



Scheme 4. Scope of the direct C5-arylation of 4-aryl-2-benzyl-1,2,3-triazoles.



Scheme 5. C4,C5-Diarylation of 2-benzyl-1,2,3-triazole.

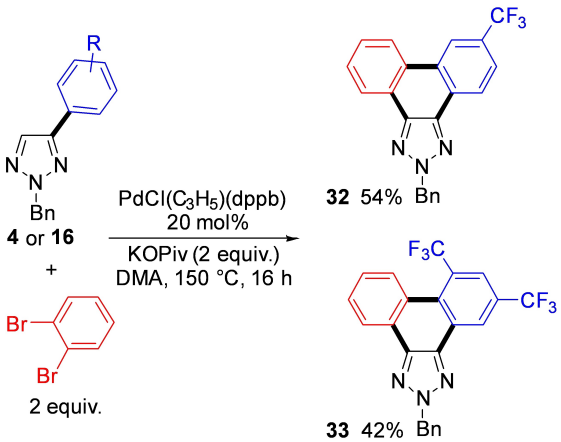
observed in quite low yield in the presence of 1 equiv. of aryl bromide. Conversely, the use of an excess (3 equiv.) of the electron-poor aryl bromides, 4-(trifluoromethyl)bromobenzene or 3,5-bis(trifluoromethyl)bromobenzene in the presence of 2 mol% $Pd(OAc)_2$ catalyst and 3 equiv. of KOAc afforded the desired 4,5-diarylated triazoles **30** and **31** in 43% and 52% yield, respectively.

Palladium-catalyzed intermolecular arylation associated with an intramolecular C–H bond arylation represents a straightforward method for the step-economic synthesis of π-extended (hetero)polyaromatic structures.[12a] Therefore, we applied the Pd-catalyzed triazoles 4,5-diarylation methodology to the synthesis of phenanthro[9,10-*d*][1,2,3]triazoles (Scheme 6 and Scheme 7). From 2-benzyl-4-(4-(trifluoromethyl)phenyl)-1,2,3-triazole **4** and 1,2-dibromobenzene in the presence of $PdCl(C_3H_5)$(dppb) catalyst, the targeted 2-benzyl-6-(trifluoromethyl)-phenanthro[9,10-*d*][1,2,3]triazole **32** was obtained in 54% yield (Scheme 6). A lower yield in the π-extended triazole **33** was obtained using **16** as the triazole source.

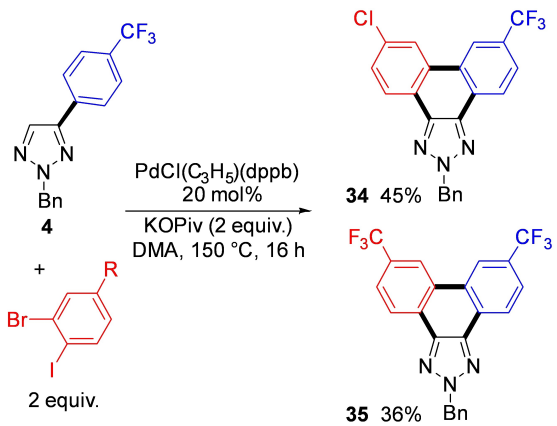
It should be mentioned that the one pot synthesis of 2-benzylphenanthro[9,10-*d*][1,2,3]triazole from 2,2′-dibromobiphenyl (1 equiv.) and 2-benzyl-1,2,3-triazole (1 equiv.) was also attempted.[12b] However, using the reaction conditions of Scheme 6, with 3 equiv. of base during 24 h, no trace of the desired product was detected in the NMR of the crude mixture.

The use of 1-bromo-2-iodobenzene reagents instead of 1,2-dibromobenzenes should allow to introduce regioselectively a substituent on the phenanthro[9,10-*d*][1,2,3]triazoles, as the oxidative addition to palladium is generally faster for the C–I bond than for the C–Br bond. Thus, using 2-benzyl-4-(4-(trifluoromethyl)phenyl)-1,2,3-triazole **4** and 2-bromo-4-chloro-1-iodobenzene, we introduced of a chloro-substituent at C6-position of the phenanthro[9,10-*d*][1,2,3]triazole **34** potentially allowing for further functionalization (Scheme 7). Similarly, the reaction of 2-benzyl-4-(4-(trifluoromethyl)phenyl)-1,2,3-triazole **4** with 2-bromo-1-iodo-4-(trifluoromethyl)benzene afforded the symmetrical CF_3-substitued phenanthro[9,10-*d*][1,2,3]triazole **35**.

Several methods for the deprotection of benzyl-substituted heteroarenes have been reported,[13] and on this basis, the deprotection of 4-phenyl-2-benzyl-1,2,3-triazole **7** was performed (Scheme 8). The reaction of **7** with *t*BuOK and O_2 bubbling during 2 hours at 60 °C afforded the desired 4-phenyl-1,2,3-triazole **36** in 93% yield.



Scheme 6. Synthesis of 2-benzyl-phenanthro[9,10-*d*][1,2,3]triazoles.



Scheme 7. Synthesis of 2-benzyl-phenanthro[9,10-*d*][1,2,3]triazoles.

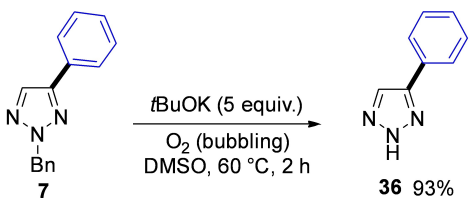
Conclusion

In summary, we demonstrated that the direct arylation of triazoles is not limited to 1-substituted 1,2,3-triazoles. Using only 2 mol% of easily available $Pd(OAc)_2$ catalyst precursor and KOAc as inexpensive bases, 2-benzyl-1,2,3-triazole can be arylated at C4-position affording a wide variety of 4-(hetero) arylated 2-benzyl-1,2,3-triazoles in good yields. The access to symmetrical and non-symmetrical 4,5-diaryl-2-benzyl-1,2,3-triazoles in moderate yields *via* two C–H bond functionalizations is also described. Finally, this new C–H arylation method was applied to the easy synthesis of π-extended phenanthro[9,10-*d*][1,2,3]triazoles by using two Pd-catalyzed intermolecular arylations associated to an intramolecular C–H bond arylation.

Experimental Section

General procedure for palladium-catalyzed direct C4-arylations of 2-benzyl-1,2,3-triazole: products 1a, 2–23

The reaction of the aryl bromide (1 mmol), 2-benzyl-1,2,3-triazole (0.318 g, 2 mmol), KOAc (0.196 g, 2 mmol) in the presence of $Pd(OAc)_2$ (2.4 mg, 0.02 mmol) in DMA (4 mL) at 150 °C during 16 h, under argon affords the coupling products **1a**, **2**–**23** after



Scheme 8. Deprotection of 4-phenyl-2-benzyl-1,2,3-triazole.

evaporation of the solvent and purification on silica gel. Eluent heptane:diethyl ether 7:3 for compounds **1a**, **1b**, **2**, **13**; heptane: diethyl ether 4:1 for compounds **3**, **4**, **7**, **9**–**12**, **14**, **19**; heptane: diethyl ether 9:1 for compounds **5**, **6**, **8**, **17**, **18**; heptane:diethyl ether 19:1 for compounds **15** and **16**; heptane:diethyl ether 3:7 for compounds **20** and **22**; heptane:diethyl ether 1:9 for compound **21**; heptane:diethyl ether 2:3 for compound **23**.

4-(2-Benzyl-1,2,3-triazol-4-yl)benzonitrile (1a): From 4-bromobenzonitrile (0.182 g, 1 mmol), 2-benzyl-1,2,3-triazole (0.318 g, 2 mmol) and KOAc (0.196 g, 2 mmol), product **1a** was obtained in 66% yield (0.172 g) as a white solid: mp 101–103 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.89 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.37–7.32 (m, 5H), 5.64 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 135.0, 134.9, 132.8, 132.1, 129.0, 128.6, 128.2, 126.5, 118.8, 112.0, 59.2. HRMS calcd for $[M+Na]^+$ $C_{16}H_{12}N_4Na$ 283.0954, found 283.0954.

4,4′-(2-Benzyl-1,2,3-triazole-4,5-diyl)dibenzonitrile (1b) was also isolated in low yield as a white solid: mp 111–113 °C: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 8.4 Hz, 4H), 7.62 (d, J = 8.4 Hz, 4H), 7.47–7.32 (m, 5H), 5.65 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 135.1, 134.5, 132.7, 129.1 128.9, 128.8, 128.5, 118.5, 112.6, 59.4. HRMS calcd for $[M+Na]^+$ $C_{23}H_{15}N_5Na$ 384.1220, found 384.1224.

4-(2-Benzyl-1,2,3-triazol-4-yl)benzaldehyde (2): From 4-bromobenzaldehyde (0.185 g, 1 mmol), 2-benzyl-1,2,3-triazole (0.318 g, 2 mmol) and KOAc (0.196 g, 2 mmol), product **2** was obtained in 52% yield (0.137 g) as a white solid: mp 88–90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.03 (s, 1H), 7.99-7.90 (m, 5H), 7.40–7.32 (m, 5H), 5.65 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.8, 146.9, 136.3, 136.2, 135.1, 132.3, 130.5, 129.0, 128.6, 128.2, 126.5, 59.2. HRMS calcd for $[M+Na]^+$ $C_{16}H_{13}N_3ONa$ 318.1213, found 318.1210.

Ethyl 4-(2-benzyl-1,2,3-triazol-4-yl)benzoate (3): From ethyl 4-bromobenzoate (0.229 g, 1 mmol), 2-benzyl-1,2,3-triazole (0.318 g, 2 mmol) and KOAc (0.196 g, 2 mmol), product **3** was obtained in 56% yield (0.172 g) as a white solid: mp 82–84 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 8.4 Hz, 2H), 7.92 (s, 1H), 7.85 (d, J = 8.4 Hz, 2H), 7.39–7.32 (m, 5H), 5.64 (s, 2H), 4.39 (q, J = 7.6 Hz, 2H), 1.41 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 147.2, 135.2, 134.7, 132.1, 130.4, 130.3, 129.0, 128.6, 128.2, 125.8, 61.2, 59.1, 14.5. HRMS calcd for $[M+Na]^+$ $C_{18}H_{17}N_3O_2Na$ 330.1213, found 330.1214.

2-Benzyl-4-(4-(trifluoromethyl)phenyl)-1,2,3-triazole (4): From 4-bromobenzotrifluoride (0.225 g, 1 mmol), 2-benzyl-1,2,3-triazole (0.318 g, 2 mmol) and KOAc (0.196 g, 2 mmol), product **4** was obtained in 54% yield (0.164 g) as a yellow solid: mp 55–57 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.80 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.39–7.32 (m, 5H), 5.65 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.8, 135.1, 133.9, 131.9, 130.3 (q, J = 32.5 Hz), 128.9, 128.6, 128.2, 126.2, 125.9 (q, J = 3.8 Hz), 124.1 (q, J = 272.0 Hz), 59.0. HRMS calcd for $[M+Na]^+$ $C_{16}H_{12}F_3N_3Na$ 326.0875, found 326.0873.

2-Benzyl-4-(4-chlorophenyl)-1,2,3-triazole (5): From 4-bromochlorobenzene (0.191 g, 1 mmol), 2-benzyl-1,2,3-triazole (0.318 g, 2 mmol) and KOAc (0.196 g, 2 mmol), product **5** was obtained in 79% yield (0.212 g) as a white solid: mp 60–62 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (s, 1H), 7.71 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.37–7.32 (m, 5H), 5.62 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 135.3, 134.5, 134.3, 131.5, 129.2, 128.9, 128.5, 128.1, 127.3, 59.0. HRMS calcd for $[M+Na]^+$ $C_{15}H_{12}ClN_3Na$ 292.0612, found 292.0615.

2-Benzyl-4-(4-fluorophenyl)-1,2,3-triazole (6): From 4-bromofluorobenzene (0.175 g, 1 mmol), 2-benzyl-1,2,3-triazole (0.318 g, 2 mmol) and KOAc (0.196 g, 2 mmol), product **6** was obtained in 74% yield (0.187 g) as a white solid: mp 53–55 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (s, 1H), 7.76 (dd, J = 8.4, 5.3 Hz, 2H), 7.39–7.32 (m, 5H), 7.11 (t, J = 8.4 Hz, 2H), 5.62 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.0 (d, J = 247.8 Hz), 147.3, 135.4, 131.3, 128.9, 128.5, 128.1, 127.8 (d, J = 8.3 Hz), 126.7 (d, J = 3.3 Hz), 116.0 (d, J = 21.8 Hz), 58.9. HRMS calcd for $[M+Na]^+$ $C_{15}H_{12}FN_3Na$ 276.0908, found 276.0908.

2-Benzyl-4-phenyl-1,2,3-triazole (7):[14] From bromobenzene (0.157 g, 1 mmol), 2-benzyl-1,2,3-triazole (0.318 g, 2 mmol) and KOAc (0.196 g, 2 mmol), product **7** was obtained in 80% yield (0.188 g) as a white solid: mp 78–80 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (s, 1H), 7.78 (d, J = 8.4 Hz, 2H), 7.43 (t, J = 7.8 Hz, 2H), 7.39–7.32 (m, 6H), 5.63 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2, 135.5, 131.6, 130.5, 129.0, 128.9, 128.6, 128.4, 128.1, 126.1, 58.9. HRMS calcd for $[M+Na]^+$ $C_{15}H_{13}N_3Na$ 258.1002, found 258.1000.

2-Benzyl-4-(4-(*tert*-butyl)phenyl)-1,2,3-triazole (8): From 1-bromo-4-*tert*-butylbenzene (0.213 g, 1 mmol), 2-benzyl-1,2,3-triazole (0.318 g, 2 mmol) and KOAc (0.196 g, 2 mmol), product **8** was obtained in 71% yield (0.207 g) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.78 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.39–7.32 (m, 5H), 5.66 (s, 2H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.6, 148.1, 135.6, 131.4, 128.8, 128.3, 128.0, 127.7, 125.8, 125.7, 58.7, 34.7, 31.4. HRMS calcd for $[M+Na]^+$ $C_{19}H_{21}N_3Na$ 314.1628, found 314.1630.

2-Benzyl-4-(4-methoxyphenyl)-1,2,3-triazole (9): From 4-bromoanisole (0.187 g, 1 mmol), 2-benzyl-1,2,3-triazole (0.318 g, 2 mmol) and KOAc (0.196 g, 2 mmol), product **9** was obtained in 65% yield (0.172 g) as a white solid: mp 79–81 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (s, 1H), 7.72 (d, J = 8.4 Hz, 2H), 7.37-7.32 (m, 5H), 6.96 (d, J = 8.4 Hz, 2H), 5.62 (s, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 148.0, 135.6, 131.0, 128.8, 128.3, 128.0, 127.3, 123.2, 114.4, 58.7, 55.4. HRMS calcd for $[M+Na]^+$ $C_{16}H_{15}N_3ONa$ 288.1107, found 288.1110.

3-(2-Benzyl-1,2,3-triazol-4-yl)benzonitrile (10): From 3-bromobenzonitrile (0.182 g, 1 mmol), 2-benzyl-1,2,3-triazole (0.318 g, 2 mmol) and KOAc (0.196 g, 2 mmol), product **10** was obtained in 67% yield (0.174 g) as a white solid: mp 80–82 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.89 (s, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.54 (t, J = 7.8 Hz, 1H), 7.37–7.32 (m, 5H), 5.63 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.1, 135.0, 131.8, 131.7, 131.6, 130.1, 129.8, 129.5, 129.0, 128.6, 128.2, 118.6, 113.3, 59.1. HRMS calcd for $[M+Na]^+$ $C_{16}H_{12}N_4Na$ 283.0954, found 283.0956.

3-(2-Benzyl-1,2,3-triazol-4-yl)benzaldehyde (11): From 3-bromobenzaldehyde (0.185 g, 1 mmol), (0.182 g, 1 mmol), 2-benzyl-1,2,3-triazole (0.318 g, 2 mmol) and KOAc (0.196 g, 2 mmol), product **11** was obtained in 50% yield (0.132 g) as a white solid: mp 85–87 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.07 (s, 1H), 8.29 (s, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.94 (s, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.59 (t, J = 7.8 Hz, 1H), 7.39–7.32 (m, 5H), 5.64 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.1, 146.9, 137.0, 135.2, 131.8, 131.7, 131.6, 129.7, 129.6, 129.0, 128.5, 128.2, 127.1, 59.0. HRMS calcd for $[M+Na]^+$ $C_{16}H_{13}N_3ONa$ 286.0951, found 286.0953.

Methyl 3-(2-benzyl-1,2,3-triazol-4-yl)benzoate (12): From methyl 3-bromobenzoate (0.215 g, 1 mmol), 2-benzyl-1,2,3-triazole (0.318 g, 2 mmol) and KOAc (0.196 g, 2 mmol), product **12** was obtained in 86% yield (0.252 g) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (s, 1H), 8.01 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.93 (s, 1H), 7.50 (t, J = 7.8 Hz, 1H), 7.39-7.32 (m, 5H), 5.64 (s, 2H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 147.3, 135.3, 131.7, 131.0, 130.9, 130.4, 129.6, 129.1, 129.0, 128.5, 128.2, 127.1, 59.0, 52.4. HRMS calcd for $[M+Na]^+$ $C_{17}H_{15}N_3O_2Na$ 316.1057, found 316.1059.

2-(2-Benzyl-1,2,3-triazol-4-yl)benzonitrile (13): From 2-bromobenzonitrile (0.182 g, 1 mmol), 2-benzyl-1,2,3-triazole (0.318 g, 2 mmol)

and KOAc (0.196 g, 2 mmol), product **13** was obtained in 79% yield (0.205 g) as a white solid: mp 58–60 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.65 (t, J = 7.9 Hz, 1H), 7.46-7.32 (m, 6H), 5.66 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.7, 134.9, 134.1, 133.6, 133.4, 133.1, 128.9, 128.7, 128.6, 128.5, 128.3, 118.8, 109.7, 59.1. HRMS calcd for $[M+K]^+$ $C_{16}H_{12}N_4K$ 299.0693, found 299.0687.

2-Benzyl-4-(2-(trifluoromethyl)phenyl)-1,2,3-triazole (14): From 2-bromobenzotrifluoride (0.225 g, 1 mmol), 2-benzyl-1,2,3-triazole (0.318 g, 2 mmol) and KOAc (0.196 g, 2 mmol), product **14** was obtained in 83% yield (0.251 g) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (s, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.59 (t, J = 7.9 Hz, 1H), 7.49 (t, J = 7.9 Hz, 1H), 7.39–7.32 (m, 5H), 5.67 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.5, 135.3, 134.3 (q, J = 4.2 Hz), 132.0, 131.9, 131.8, 129.6 (q, J = 1.8 Hz), 128.9, 128.5 (q, J = 32.5 Hz), 128.0, 126.4 (q, J = 5.6 Hz), 124.0 (q, J = 273.5 Hz), 58.8. HRMS calcd for $[M+Na]^+$ $C_{16}H_{12}F_3N_3Na$ 326.0876, found 326.0877.

2-Benzyl-4-(2-chlorophenyl)-1,2,3-triazole (15): From 2-bromochlorobenzene (0.191 g, 1 mmol), 2-benzyl-1,2,3-triazole (0.318 g, 2 mmol) and KOAc (0.196 g, 2 mmol), product **15** was obtained in 78% yield (0.210 g) as a white solid: mp 50–52 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.90 (dd, J = 7.8, 2.0 Hz, 1H), 7.47 (dd, J = 7.8, 1.6 Hz, 1H), 7.40-7.32 (m, 7H), 5.66 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 135.3, 134.7, 132.2, 130.5, 129.5, 129.4, 128.9, 128.5, 128.1, 127.1, 58.9. HRMS calcd for $[M+Na]^+$ $C_{15}H_{12}ClN_3Na$ 292.0612, found 292.0613.

2-Benzyl-4-(3,5-bis(trifluoromethyl)phenyl)-1,2,3-triazole (16): From 3,5-bis(trifluoromethyl)bromobenzene (0.293 g, 1 mmol), 2-benzyl-1,2,3-triazole (0.318 g, 2 mmol) and KOAc (0.196 g, 2 mmol), product **16** was obtained in 44% yield (0.163 g) as a white solid: mp 111–113 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 2H), 7.97 (s, 1H), 7.84 (s, 1H), 7.40–7.32 (m, 5H), 5.65 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.6, 134.9, 132.8, 132.4 (q, J = 32.5 Hz), 131.9, 129.0, 128.7, 128.2, 125.9, 123.5 (q, J = 272.5 Hz), 121.9 (q, J = 3.8 Hz), 59.2. HRMS calcd for $[M+Na]^+$ $C_{17}H_{11}F_6N_3Na$ 394.0749, found 394.0750.

2-Benzyl-4-(naphthalen-2-yl)-1,2,3-triazole (17): From 2-bromonaphthalene (0.207 g, 1 mmol), 2-benzyl-1,2,3-triazole (0.318 g, 2 mmol) and KOAc (0.196 g, 2 mmol), product **17** was obtained in 55% yield (0.157 g) as a white solid: mp 91–93 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 1H), 8.00 (s, 1H), 7.95–7.82 (m, 4H), 7.55–7.45 (m, 2H), 7.42–7.32 (m, 5H), 5.68 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2, 135.4, 133.6, 133.4, 131.8, 128.9, 128.7, 128.4, 128.3, 128.1, 127.9, 127.8, 126.6, 126.4, 124.9, 124.1, 58.9. HRMS calcd for $[M+Na]^+$ $C_{19}H_{15}N_3Na$ 308.1158, found 308.1159.

2-Benzyl-4-(naphthalen-1-yl)-1,2,3-triazole (18): From 1-bromonaphthalene (0.207 g, 1 mmol), 2-benzyl-1,2,3-triazole (0.318 g, 2 mmol) and KOAc (0.196 g, 2 mmol), product **18** was obtained in 74% yield (0.211 g) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (m, 1H), 7.92 (s, 1H), 7.91–7.57 (m, 2H), 7.69 (d, J = 7.8 Hz, 1H), 7.58–7.49 (m, 3H), 7.45–7.32 (m, 5H), 5.73 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5, 135.5, 134.5, 134.1, 129.2, 129.0, 128.6, 128.5, 128.2, 128.0, 127.4, 126.9, 126.2, 125.6, 125.4, 59.0. HRMS calcd for $[M+Na]^+$ $C_{19}H_{15}N_3Na$ 308.1158, found 308.1158.

4-(Anthracen-9-yl)-2-benzyl-1,2,3-triazole (19): From 9-bromoanthracene (0.257 g, 1 mmol), 2-benzyl-1,2,3-triazole (0.318 g, 2 mmol) and KOAc (0.196 g, 2 mmol), product **19** was obtained in 57% yield (0.191 g) as a yellow solid: mp 100–102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (s, 1H), 8.06 (d, J = 8.2 Hz, 2H), 7.92 (s, 1H), 7.85 (d, J = 8.2 Hz, 2H), 7.55–7.36 (m, 9H), 5.85 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 136.8, 135.5, 131.3, 131.2, 129.0, 128.6, 128.5, 128.4, 128.2, 126.3, 125.9, 125.3, 124.6, 59.0. HRMS calcd for $[M+Na]^+$ $C_{23}H_{17}N_3Na$ 358.1315, found 358.1320.

3-(2-Benzyl-1,2,3-triazol-4-yl)pyridine (20): From 3-bromopyridine (0.158 g, 1 mmol), 2-benzyl-1,2,3-triazole (0.318 g, 2 mmol) and KOAc (0.196 g, 2 mmol), product **20** was obtained in 54% yield (0.127 g) as a white solid: mp 74–76 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.04 (bs, 1H), 8.60 (bs, 1H), 8.09 (d, J = 8.2 Hz, 1H), 7.91 (s, 1H), 7.38–7.32 (m, 6H), 5.64 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 147.2, 145.2, 135.1, 133.5, 131.7, 129.0, 128.6, 128.2, 126.8, 123.9, 59.0. HRMS calcd for $[M+Na]^+$ $C_{14}H_{12}N_4Na$ 259.0954, found 259.0958.

4-(2-Benzyl-1,2,3-triazol-4-yl)pyridine (21): From 4-bromopyridine hydrochloride (0.194 g, 1 mmol), 2-benzyl-1,2,3-triazole (0.318 g, 2 mmol) and KOAc (0.294 g, 3 mmol), product **21** was obtained in 51% yield (0.120 g) as a white solid: mp 79–81 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (bs, 2H), 7.96 (s, 1H), 7.68 (d, J = 4.8 Hz, 2H), 7.36—7.29 (m, 5H), 5.64 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6, 145.7, 137.9, 134.9, 132.4, 129.0, 128.7, 128.2, 120.4, 59.2. HRMS calcd for $[M+Na]^+$ $C_{14}H_{12}N_4Na$ 259.0954, found 259.0952.

3-(2-Benzyl-1,2,3-triazol-4-yl)quinoline (22): From 3-bromoquinoline (0.208 g, 1 mmol), 2-benzyl-1,2,3-triazole (0.318 g, 2 mmol) and KOAc (0.196 g, 2 mmol), product **22** was obtained in 56% yield (0.160 g) as a white solid: mp 65–67 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.35 (bs, 1H), 8.51 (s, 1H), 8.13 (d, J = 8.4 Hz, 1H), 8.04 (s, 1H), 7.87 (d, J = 8.2 Hz, 1H), 7.72 (t, J = 7.8 Hz, 1H), 7.57 (t, J = 7.8 Hz, 1H), 7.42–7.26 (m, 5H), 5.69 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.6, 148.1, 145.5, 135.1, 132.3, 131.9, 129.9, 129.6, 129.0, 128.6, 128.2, 128.1, 127.3, 59.1. HRMS calcd for $[M+Na]^+$ $C_{18}H_{14}N_4Na$ 309.1111, found 309.1112.

4-(2-Benzyl-1,2,3-triazol-4-yl)isoquinoline (23): From 4-bromoisoquinoline (0.208 g, (0.182 g, 1 mmol), 2-benzyl-1,2,3-triazole (0.318 g, 2 mmol) and KOAc (0.196 g, 2 mmol), product **23** was obtained in 78% yield (0.223 g) as a white solid: mp 127–129 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.26 (bs, 1H), 8.76 (bs, 1H), 8.49 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 8.2 Hz, 1H), 7.97 (s, 1H), 7.75 (t, J = 7.8 Hz, 1H), 7.64 (t, J = 7.8 Hz, 1H), 7.45–7.30 (m, 5H), 5.73 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2, 144.8, 143.1, 135.2, 134.2, 133.4, 131.2, 128.9, 128.5, 128.2, 128.1, 127.5, 124.8, 121.7, 59.1. HRMS calcd for $[M+Na]^+$ $C_{18}H_{14}N_4^{Na}$ 309.1111, found 309.1111.

General procedure for palladium-catalyzed direct C5-arylations of 2-benzyl-4-aryl-1,2,3-triazole: products 24–29

The reaction of the aryl bromide (2 mmol), 2-benzyl-4-aryl-1,2,3-triazole (1 mmol), KOAc (0.196 g, 2 mmol) in the presence of $Pd(OAc)_2$ (2.4 mg, 0.02 mmol) in DMA (4 mL) at 150 °C during 16 h, under argon affords the coupling products **24**–**29** after evaporation of the solvent and purification on silica gel. Eluent heptane:diethyl ether 4:1 for compounds **24** and **28**; heptane:diethyl ether 9:1 for compound **25**; heptane:diethyl ether 19:1 for compounds **26** and **29**; heptane:diethyl ether 7:3 for compound **27**.

4-(2-Benzyl-5-phenyl-1,2,3-triazol-4-yl)benzonitrile (24): From 4-bromobenzonitrile (0.364 g, 2 mmol), 2-benzyl-4-phenyl-1,2,3-triazole **7** (0.235 g, 1 mmol) and KOAc (0.196 g, 2 mmol), product **24** was obtained in 68% yield (0.228 g) as a white solid: mp 97–99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 8.5 Hz, 2H), 7.52–7.32 (m, 10H), 5.65 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 143.0, 135.8, 135.0, 132.4, 130.5, 129.1, 129.0, 128.9, 128.7, 128.6, 128.4, 118.8, 111.9, 59.2. HRMS calcd for $[M+Na]^+$ $C_{22}H_{16}N_4Na$ 359.1267, found 359.1270.

2-Benzyl-4-(4-chlorophenyl)-5-phenyl-1,2,3-triazole (25):[15] From 4-bromochlorobenzene (0.382 g, 2 mmol), 2-benzyl-4-phenyl-1,2,3-triazole **7** (0.235 g, 1 mmol) and KOAc (0.196 g, 2 mmol), product **25** was obtained in 51% yield (0.176 g) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55–7.47 (m, 4H), 7.44 (d, J = 8.5 Hz, 2H), 7.40–7.31 (m, 8H), 5.64 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.0, 143.8,

135.3, 134.4, 130.9, 129.7, 129.0, 128.9, 128.8, 128.6, 128.5, 128.4, 128.3, 59.0. HRMS calcd for $[M+Na]^+$ $C_{21}H_{16}ClN_3Na$ 368.0925, found 368.0928.

2-Benzyl-4-(4-(*tert*-butyl)phenyl)-5-(4-chlorophenyl)-1,2,3-triazole (26): From 4-bromochlorobenzene (0.382 g, 2 mmol), 2-benzyl-4-(4-(*tert*-butyl)phenyl)-1,2,3-triazole **8** (0.291 g, 1 mmol) and KOAc (0.196 g, 2 mmol), product **26** was obtained in 42% yield (0.168 g) as a white solid: mp 113–115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 8.4 Hz, 2H), 7.48–7.31 (m, 11H), 5.63 (s, 2H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 145.0, 143.7, 135.4, 134.3, 129.9, 129.7, 128.9, 128.8, 128.5, 128.3, 128.0, 127.9, 125.7, 58.9, 34.8, 31.4. HRMS calcd for $[M+Na]^+$ $C_{25}H_{24}ClN_3Na$ 424.1551, found 424.1552.

4-(2-Benzyl-5-(4-methoxyphenyl)-1,2,3-triazol-4-yl)benzonitrile (27): From 4-bromobenzonitrile (0.364 g, 2 mmol), 2-benzyl-4-(4-methoxyphenyl)-1,2,3-triazole **9** (0.265 g, 1 mmol) and KOAc (0.196 g, 2 mmol), product **27** was obtained in 40% yield (0.146 g) as a white solid: mp 70–72 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.46–7.32 (m, 7H), 6.92 (d, J = 8.4 Hz, 2H), 5.63 (s, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 145.6, 142.6, 136.0, 135.1, 132.4, 129.9, 129.0, 128.6, 128.5, 128.4, 122.8, 118.9, 114.4, 111.8, 59.1, 55.5. HRMS calcd for $[M+Na]^+$ $C_{23}H_{18}N_4ONa$ 389.1373, found 389.1377.

2-Benzyl-4-(4-methoxyphenyl)-5-(4-(trifluoromethyl)phenyl)-1,2,3-triazole (28): From 4-bromobenzotrifluoride (0.450 g, 2 mmol), 2-benzyl-4-(4-methoxyphenyl)-1,2,3-triazole **9** (0.265 g, 1 mmol) and KOAc (0.196 g, 2 mmol), product **28** was obtained in 53% yield (0.217 g) as a white solid: mp 97–99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.3 Hz, 4H), 7.41-7.32 (m, 3H), 6.92 (d, J = 8.4 Hz, 2H), 5.64 (s, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 145.3, 143.1, 135.2, 135.0, 130.1 (q, J = 32.5 Hz), 129.8, 128.9, 128.5, 128.4, 128.3, 125.6 (q, J = 3.8 Hz), 124.2 (q, J = 272.0 Hz), 123.1, 114.3, 59.0, 55.4. HRMS calcd for $[M+Na]^+$ $C_{23}H_{18}F_3N_3ONa$ 432.1294, found 432.1293.

2-Benzyl-4-(3,5-bis(trifluoromethyl)phenyl)-5-phenyl-1,2,3-triazole (29) From 3,5-bis(trifluoromethyl)bromobenzene (0.586 g, 2 mmol), 2-benzyl-4-phenyl-1,2,3-triazole **7** (0.235 g, 1 mmol) and KOAc (0.196 g, 2 mmol), product **29** was obtained in 60% yield (0.268 g) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 2H), 7.85 (s, 1H), 7.55–7.50 (m, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.45–7.36 (m, 6H), 5.69 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.8, 142.0, 134.9, 133.4, 132.1 (q, J = 32.5 Hz), 130.1, 129.3, 129.1, 129.0, 128.7, 128.5, 128.4, 128.1, 123.1 (q, J = 272.5 Hz), 121.8 (q, J = 3.8 Hz), 59.2. HRMS calcd for $[M+Na]^+$ $C_{23}H_{15}F_6N_3Na$ 470.1062, found 470.1061.

General procedure for palladium-catalyzed direct C4,C5-diarylations of 2-benzyl-1,2,3-triazole: products 30 and 31

The reaction of the aryl bromide (3 mmol), 2-benzyl-1,2,3-triazole (0.159 g, 1 mmol), KOAc (0.294 g, 3 mmol) in the presence of $Pd(OAc)_2$ (2.4 mg, 0.02 mmol) in DMA (4 mL) at 150 °C during 16 h, under argon affords the coupling products **30** and **31** after evaporation of the solvent and purification on silica gel. Eluent heptane:diethyl ether 19:1.

2-Benzyl-4,5-bis(4-(trifluoromethyl)phenyl)-1,2,3-triazole (30): From 4-bromobenzotrifluoride (0.675 g, 3 mmol), 2-benzyl-1,2,3-triazole (0.159 g, 1 mmol) and KOAc (0.196 g, 2 mmol), product **30** was obtained in 43% yield (0.192 g) as a white solid: mp 61–63 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 8.4 Hz, 4H), 7.64 (d, J = 8.4 Hz, 4H), 7.47 (d, J = 8.4 Hz, 2H), 7.42–7.33 (m, 3H), 5.67 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 134.9, 134.4, 130.7 (q, J = 32.5 Hz), 129.0, 128.8, 128.7, 128.4, 125.8 (q, J = 3.8 Hz), 124.1 (q, J = 272.0 Hz), 59.3. HRMS calcd for $[M+Na]^+$ $C_{23}H_{15}F_6N_3Na$ 470.1062, found 470.1061.

2-Benzyl-4,5-bis(3,5-bis(trifluoromethyl)phenyl)-1,2,3-triazole (31): From 3,5-bis(trifluoromethyl)bromobenzene (0.879 g, 3 mmol), 2-benzyl-1,2,3-triazole (0.159 g, 1 mmol) and KOAc (0.294 g, 3 mmol), product **31** was obtained in 52% yield (0.303 g) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (s, 4H), 7.93 (s, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.45-7.32 (m, 3H), 5.71 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.6, 134.4, 132.6 (q, J = 32.5 Hz), 129.2, 129.0, 128.5, 128.2, 123.1 (q, J = 272.5 Hz), 122.7 (q, J = 3.8 Hz), 59.6. HRMS calcd for $[M+Na]^+$ $C_{25}H_{13}F_{12}N_3Na$ 606.0810, found 606.0817.

General procedure for palladium-catalyzed direct C5-arylations followed by intramolecular reaction of 2-benzyl-4-aryl-1,2,3-triazoles: products 32–35

The reaction of the aryl dihalide (2 mmol), 2-benzyl-4-aryl-1,2,3-triazole (1 mmol), KOPiv (0.280 g, 2 mmol) in the presence of PdCl(C_3H_5)(dppb) (0.122 g, 0.2 mmol) in DMA (4 mL) at 150 °C during 16 h, under argon affords the coupling products **32–35** after evaporation of the solvent and purification on silica gel. Eluent heptane:diethyl ether 9:1 for compound **32**; heptane:diethyl ether 19:1 for compounds **33–35**.

2-Benzyl-6-(trifluoromethyl)-phenanthro[9,10-*d*][1,2,3]triazole (32): From 1,2-dibromobenzene (0.472 g, 2 mmol), 2-benzyl-4-(4-(trifluoromethyl)phenyl)-1,2,3-triazole **4** (0.303 g, 1 mmol) and KOPiv (0.280 g, 2 mmol), product **32** was obtained in 54% yield (0.203 g) as a yellow solid: mp 118–120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (s, 1H), 8.56 (d, J = 8.3 Hz, 1H), 8.53–8.46 (m, 2H), 7.82 (d, J = 8.3 Hz, 1H), 7.68-7.63 (m, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.42-7.33 (m, 3H), 5.91 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1, 140.6, 135.2, 130.3, 129.7, 129.5 (q, J = 32.5 Hz), 129.0, 128.7, 128.5, 128.3, 128.1, 127.1, 125.0, 124.6 (q, J = 272.0 Hz), 124.5, 123.9, 123.8 (m), 121.0 (q, J = 4.0 Hz), 60.0. HRMS calcd for $[M+Na]^+$ $C_{22}H_{14}F_3N_3Na$ 400.1032, found 400.1031.

2-Benzyl-5,7-bis(trifluoromethyl)-phenanthro[9,10-*d*][1,2,3]triazole (33): From 1,2-dibromobenzene (0.472 g, 2 mmol), 2-benzyl-4-(3,5-bis(trifluoromethyl)phenyl)-1,2,3-triazole **16** (0.371 g, 1 mmol) and KOPiv (0.280 g, 2 mmol), product **33** was obtained in 42% yield (0.187 g) as a white solid: mp 147–149 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.01 (s, 1H), 8.63 (d, J = 8.3 Hz, 1H), 8.56 (d, J = 8.0 Hz, 1H), 8.27 (s, 1H), 7.75 (t, J = 7.9 Hz, 1H), 7.64 (t, J = 7.9 Hz, 1H), 7.46 (d, J = 8.4 Hz, 2H), 7.43–7.32 (m, 3H), 5.91 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.8, 140.6, 135.0, 132.2, 130.0 (q, J = 32.5 Hz), 129.7, 129.1, 128.8, 128.3, 127.9, 127.3, 126.4, 124.8 (q, J = 272.5 Hz), 124.5 (m), 123.6, 123.5 (q, J = 272.5 Hz), 60.2. HRMS calcd for $[M+Na]^+$ $C_{23}H_{13}F_6N_3Na$ 468.0906, found 468.0904.

2-Benzyl-6-chloro-9-(trifluoromethyl)-phenanthro[9,10-*d*][1,2,3]triazole (34): From 2-bromo-4-chloro-1-iodobenzene (0.634 g, 2 mmol), 2-benzyl-4-(4-(trifluoromethyl)phenyl)-1,2,3-triazole **4** (0.303 g, 1 mmol) and KOPiv (0.280 g, 2 mmol), product **34** was obtained in 45% yield (0.185 g) as a white solid: mp 179–181 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (s, 1H), 8.59 (d, J = 8.3 Hz, 1H), 8.49 (d, J = 2.0 Hz, 1H), 8.43 (d, J = 8.3 Hz, 1H), 7.87 (d, J = 8.3 Hz, 1H), 7.63 (dd, J = 8.3, 2.0 Hz, 1H), 7.46 (d, J = 8.4 Hz, 2H), 7.42-7.33 (m, 3H), 5.91 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.6, 140.5, 135.0, 134.4, 131.1, 129.7 (q, J = 32.5 Hz), 129.3, 129.0, 128.9, 128.8, 128.3, 127.5, 125.4, 124.7, 124.5 (q, J = 3.7 Hz), 124.4 (q, J = 272.0 Hz), 123.8, 123.4, 121.1 (q, J = 3.7 Hz), 60.1. HRMS calcd for $[M+Na]^+$ $C_{22}H_{13}ClF_3N_3Na$ 434.0642, found 434.0646.

2-Benzyl-6,9-bis(trifluoromethyl)-phenanthro[9,10-*d*][1,2,3]triazole (35): From 2-bromo-1-iodo-4-(trifluoromethyl)benzene (0.351 g, 2 mmol), 2-benzyl-4-(4-(trifluoromethyl)phenyl)-1,2,3-

triazole **4** (0.303 g, 1 mmol) and KOPiv (0.280 g, 2 mmol), product **35** was obtained in 36% yield (0.160 g) as a white solid: mp 192–194 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (s, 2H), 8.66 (d, J = 8.3 Hz, 2H), 7.94 (d, J = 8.3 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.42–7.33 (m, 3H), 5.96 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 134.9, 130.1 (q, J = 32.5 Hz), 129.6, 129.1, 128.8, 128.4, 127.5, 124.8, 124.7 (q, J = 3.7 Hz), 124.2 (q, J = 272.0 Hz), 121.1 (q, J = 3.9 Hz), 60.3. HRMS calcd for $[M+Na]^+$ $C_{23}H_{13}F_6N_3Na$ 468.0906, found 468.0902.

4-Phenyl-1,2,3-triazole (36): 2-Benzyl-4-phenyl-1,2,3-triazole **7** (0.118 g, 0.5 mmol), *t*BuOK (0.280 g, 2.5 mmol) under O_2 bubbling were reacted in DMSO at 60 °C during 2 h. The reaction was quenched with saturated ammonium chloride. The product was extracted three times with EtOAc. The organics were combined, dried over Na_2SO_4 and concentrated. The crude mixture was purified on silica gel to afford the product **36** in 93% (0.067 g) yield as a white solid: mp 141–143 °C. Eluent heptane:diethyl ether 7:3. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.27 (bs, 1H), 7.99 (s, 1H), 7.83 (d, J = 8.3 Hz, 2H), 7.49 (t, J = 7.9 Hz, 2H), 7.38 (t, J = 7.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5, 130.0, 129.1, 128.9, 126.3. HRMS calcd for $[M+Na]^+$ $C_8H_7N_3Na$ 168.0532, found 168.0534.

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Conflict of Interest

The authors declare no conflict of interest.

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