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C–H Acylation

Regioselective *ortho*-Acylation of *N*-Aryl-1,2,3-triazoles with Alcohols in Water

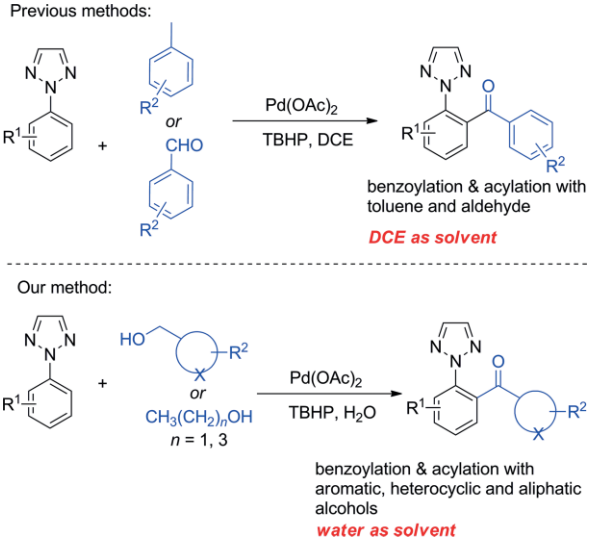
Chanchal Premi,[a] Shyam Sunder Patel,[a] and Nidhi Jain*[a]

Abstract: A palladium-catalyzed regioselective *ortho*-acylation of *N*-aryl-1,2,3-triazoles has been achieved under aqueous conditions without the assistance of surfactants or additives. The reaction takes place by using benzylic, heterocyclic, and aliphatic alcohols as the acylating reagents and *tert*-butyl hydroperoxide (TBHP) as the oxidant and provides an alternative route for the synthesis of triazole-substituted aryl, heteroaryl, and aliphatic ketones in moderate to excellent yields.

Introduction

Palladium-catalyzed and directing-group-assisted C–H functionalizations have led to new synthetic organic chemistry strategies for the direct conversion of carbon–hydrogen bonds into carbon–carbon and carbon–heteroatom bonds.[1] Among the various ligand-assisted C–H activation methods, *ortho*-functionalization is the most promising approach because of its capacity for excellent regioselectivity and reactivity.[2] Recently, a fair amount of literature regarding Pd-catalyzed acylations of aromatic C–H bonds with the assistance of directing groups such as those of 2-phenylpyridine,[3] acetanilide,[4] aryl ketone oximes,[5] azobenzene,[6] and *N*-nitrosoanilines[7] has been reported. Acylating reagents, including α-oxo carboxylic acids,[8] toluene,[9] benzaldehyde,[10] benzyl alcohols,[11] and aniline[12] have been employed for this purpose. Amongst the various directing groups, the 1,2,3-triazole ring system is one of the least explored in a regioselective C–H bond activation.[13] Most of the studies that involve *N*-aryl-1,2,3-triazole functionalizations, including alkoxylations,[14] halogenations,[15] and arylations[16] have been reported by the Kuang group. Recently, the same group also reported the acylation of these triazoles by using toluene and benzaldehyde as the acylating reagents along with 1,2-dichloroethane (DCE) as the solvent.[17]

Although Pd-catalyzed acylations in organic media have been explored, there are few reports in which the reaction was achieved in water.[11c,18] Water can serve as an ideal green solvent in terms of its availability, cost, and nontoxicity, and it has been successfully employed in various C–H bond transformations in the past few years.[19] Although reactions in water can suffer from the low solubility of the organic substrates, this drawback has, to an extent, been overcome by using phase-transfer catalysts and surfactants. In our endeavor towards the development of water as a green reaction medium, we attempted the synthesis of triazole-substituted aryl ketones in water by employing a Pd-catalyzed C–H functionalization strategy (Scheme 1). We chose to examine 1,2,3-triazoles because of their synthetic utility as building blocks in medicinal and materials chemistry.[20,21] To the best of our knowledge, there are no prior reports of the acylation of *N*-arylriazoles in water.



Scheme 1. Comparisons between approaches for the palladium-catalyzed acylation of *N*-aryl-1,2,3-triazoles. TBHP = *tert*-butyl hydroperoxide.

Results and Discussion

Our investigation began with the reaction of *N*-phenyl-1,2,3-triazole (**1a**) with benzyl alcohol (**2a**) in the presence of palladium acetate and *tert*-butyl hydroperoxide (70 % in water) under air at 80 °C for 24 h. We were pleased to see that a regioselective *ortho*-acylation of **1a** occurred to give (phenyl)[2-(2*H*-1,2,3-triazol-2-yl)phenyl]methanone (**3a**) as the only product in 34 % yield (Table 1, Entry 1). To improve the reaction, we pursued extensive optimization studies with regard to the catalyst, solvent, oxidant, temperature, and time by using **1a** and **2a** as the model substrates (Table 1). To examine the role of palla-

[a] *Department of Chemistry, Indian Institute of Technology, New Delhi 110016 India*
E-mail: njain@chemistry.iitd.ac.in
http://web.iitd.ac.in/~njain/#/home

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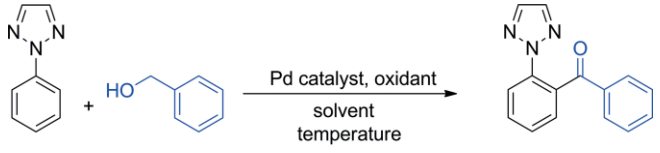
dium as the catalyst, we varied the catalytic loading of palladium acetate and found that increasing the amount of catalyst from 5 to 10 mol-% improved the yield of **3a** to 71 % (Table 1, Entry 2). A further increase, however, in the amount of $Pd(OAc)_2$ to 15 mol-% did not influence product yield (Table 1, Entry 3). As expected, in the absence of the Pd catalyst, the desired product **3a** did not form (Table 1, Entry 4). The screening of other palladium salts such as $PdCl_2$ and $Pd(CH_3CN)_2$ showed them to be less effective catalysts than $Pd(OAc)_2$ (Table 1, Entries 5 and 6).

Table 1. Optimization of the reaction conditions for the acylation of *N*-aryl-1,2,3-triazole.[a]



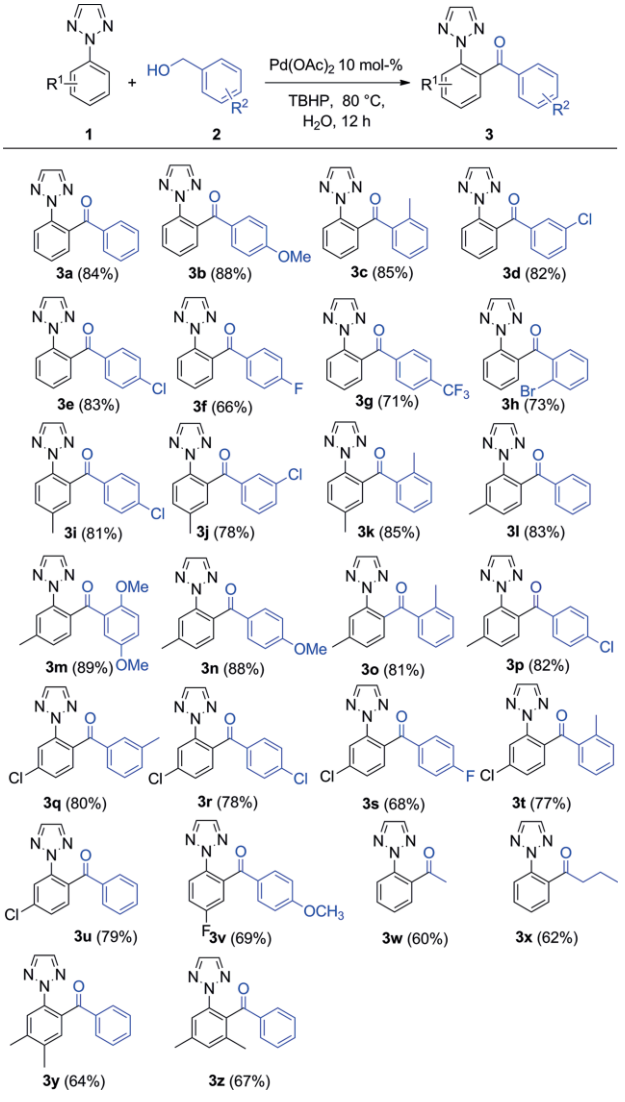
1a **2a** **3a**

Entry	Catalyst (mol-%)	Oxidant (equiv.)	Solvent	*T* [°C]	Yield[b] [%]
1	$Pd(OAc)_2$ (5)	TBHP (4)	–	80	34
2	$Pd(OAc)_2$ (10)	TBHP (4)	–	80	71, 0[c]
3	$Pd(OAc)_2$ (15)	TBHP (4)	–	80	72
4	–	TBHP (4)	–	80	–
5	$PdCl_2$ (10)	TBHP (4)	–	80	51
6	$Pd(CH_3CN)_2$ (10)	TBHP (4)	–	80	63
7	$Pd(OAc)_2$ (10)	TBHP (4)	DCE	80	47
8	$Pd(OAc)_2$ (10)	TBHP (4)	dioxane	80	55
9	$Pd(OAc)_2$ (10)	TBHP (4)	DMF	80	trace
10	$Pd(OAc)_2$ (10)	TBHP (4)	DMSO	80	trace
11	$Pd(OAc)_2$ (10)	TBHP (4)	H_2O	80	84
12	$Pd(OAc)_2$ (10)	H_2O_2 (4)	–	80	trace
13	$Pd(OAc)_2$ (10)	$K_2S_2O_8$ (4)	–	80	–
14	$Pd(OAc)_2$ (10)	O_2	–	80	–
15	$Pd(OAc)_2$ (10)	TBHP (1)	–	80	15
16	$Pd(OAc)_2$ (10)	TBHP (10)	–	80	80[d]
17	$Pd(OAc)_2$ (10)	TBHP (4)	H_2O	60	59
18	$Pd(OAc)_2$ (10)	TBHP (4)	H_2O	110	45
19	$Pd(OAc)_2$ (10)	TBHP (4)	H_2O	80	49[e], 85[f]

[a] Reagents and conditions: **1a** (0.344 mmol), **2a** (0.689 mmol), Pd catalyst, and oxidant (1.376 mmol) in H_2O (0.5 mL) were heated for 12 h. [b] Isolated yields are reported. [c] Tetra-*n*-butylammonium bromide (TBAB) was used as phase-transfer catalyst (PTC). [d] Yield of diacylated product. [e] Reaction time was 7 h. [f] Reaction time was 24 h.

Next we carried out the optimization experiments with respect to the solvent. The employment of solvents such as DCE and 1,4-dioxane decreased the product yields to 47 and 55 %, respectively (Table 1, Entries 7 and 8), whereas the use of *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) had a much stronger effect on the result of the reaction, and no product could be isolated in either case (Table 1, Entries 9 and 10). The addition of water, however, had a favorable effect and substantially enhanced the yield of **3a** to 84 % (Table 1, Entry 11). This suggests that water is an ideal choice as a "green" solvent for this reaction. The screenings of other oxidants such as H_2O_2, $K_2S_2O_8$, and O_2 were then carried out, but all were found to be ineffective, as the desired product was not obtained (Table 1, Entries 12–14). Next, we optimized the reaction for the amount of TBHP (70 % in H_2O). It was found that decreasing the amount of TBHP to 1 equiv. resulted in a decreased yield of 15 % (Table 1, Entry 15), whereas increasing the amount to 10 equiv. resulted in the formation of a diacylated product (Table 1, Entry 16). A variation in the reaction temperature revealed that lowering it to 60 °C reduced the product yield, and increasing the temperature to 110 °C gave equally unfavorable results, as a large amount of unidentified impurities were formed (Table 1, Entries 17 and 18). In addition, decreasing the reaction time afforded a lower product yield, whereas extending the time did not have an influence (Table 1, Entry 19 vs. 11). Notably, no trace amounts of the diacylated product were observed after a reaction time of 24 h. Thus, the optimized conditions included 10 mol-% of $Pd(OAc)_2$ and 4.0 equiv. of TBHP in H_2O at 80 °C for 12 h (Table 1, Entry 11).

With the optimized conditions in hand, we investigated the scope of reaction by varying the benzyl alcohol and *N*-aryl-1,2,3-triazole substrates (Scheme 2). It was found that the reaction was quite general, and a variety of benzyl alcohols were

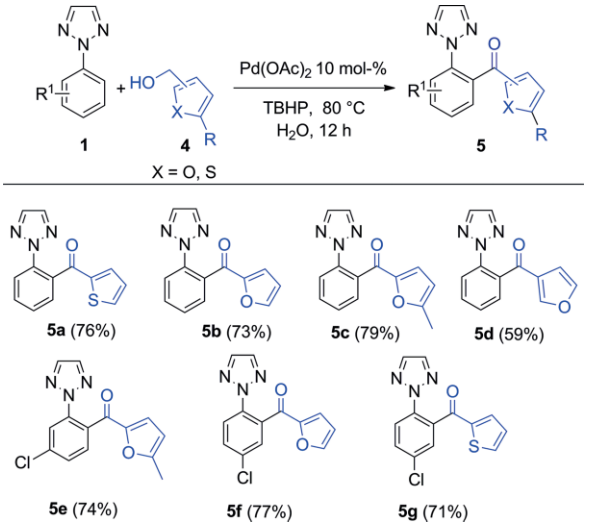


Scheme 2. Examination of the scope of the benzyl alcohol and triazole substrates. Reagents and conditions: **1** (1 equiv.), **2** (2 equiv.), $Pd(OAc)_2$ (10 mol-%), and TBHP (4 equiv.) in H_2O (0.5 mL) at 80 °C for 12 h. The isolated yields are reported.

well tolerated. Those benzyl alcohols that contain electron-donating groups (i.e., OMe, Me), irrespective of whether they are at the *ortho*, *meta*, or *para* position, gave excellent yields of the corresponding products (e.g., **3b**, **3c**, **3m**–**3o**). Those that contain electron-withdrawing groups such as F, Cl, Br, and CF_3 were also compatible under the reaction conditions and also afforded reasonable product yields (e.g., **3d**–**3h**). The *N*-aryl-1,2,3-triazoles that have methyl, Cl, and F substituents at different positions also showed a high level of regioselectivity, and the acylations were found to occur at the sterically less hindered *ortho*-C–H bond of the substituted *N*-aryl-1,2,3-triazoles (e.g., to give **3i**–**3k**, **3l**–**3p**, and **3q**–**3v**). The lowest yields were also observed by using fluoro-substituted substrates, both in the case of the benzyl alcohol as well as the triazole (e.g., to give **3f**, **3s**, and **3v**). The scope of the substrates was further extended to aliphatic alcohols. In this case, acylation took place smoothly irrespective of the chain length to yield **3w** and **3x**, albeit in moderate yields. These lower yields may be attributed to the reduced stability of the acyl radical, relative to a benzoyl radical that is generated during the reaction. Unsaturated aliphatic alcohols, however, did not yield an acylated product. *N*-Aryltriazoles that contain 3,5- and 4,5-disubstituted aryl rings were also examined and found to afford the desired C-2-benzoylated products **3y** and **3z** in 64 and 67 % yield, respectively.

In addition, methyl alcohols that are substituted with heteroaromatic units such as a furan or thiophene moiety also tolerated the reaction conditions. In these cases, the corresponding heteroaryl ketone derivatives **5a**–**5g** were afforded in moderate yields (Scheme 3). An *N*-aryl-1,2,3-triazole that is substituted with a chloro group at either the *meta* or *para* position showed a high level of regioselectivity, and acylation took place at the sterically less hindered *ortho* position (i.e., to give **5e**, **5f**, and **5g**), as was also observed with the benzyl alcohols. A slightly lower yield was obtained when furan-3-ylmethanol was used as the substrate (i.e., to give **5d**). When pyridin-3-ylmethanol was used as the substrate, no reaction took place. The structure of **5f** was confirmed by X-ray crystal structure analysis (Figure 1).

Next, this strategy was applied to the synthesis of triazole-substituted fluorenone, which is known to be a core structural unit of many biologically potent compounds. Traditional strategies for the synthesis of fluorenone employ Friedel–Crafts ring-closing reactions of biarylcarboxylic acids,[22] the carbonylation of *o*-halobiaryls,[23] and the palladium-catalyzed cyclization of *o*-iodobenzophenones.[24] By using our method, (2-bromophenyl)[5-methyl-2-(2*H*-1,2,3-triazol-2-yl)phenyl]methanone (**8**) was prepared, which upon treatment with $Pd(OAc)_2$ and K_2CO_3 in *N*,*N*-dimethylacetamide (DMA) as the solvent at 100 °C



Scheme 3. Scope of heteroaryl alcohols as substrates. Reagents and conditions: **1** (1.0 equiv.), **4** (2.0 equiv.), $Pd(OAc)_2$ (10 mol-%), and TBHP (4.0 equiv.), in H_2O (0.5 mL) at 80 °C for 12 h. Isolated yields are reported.

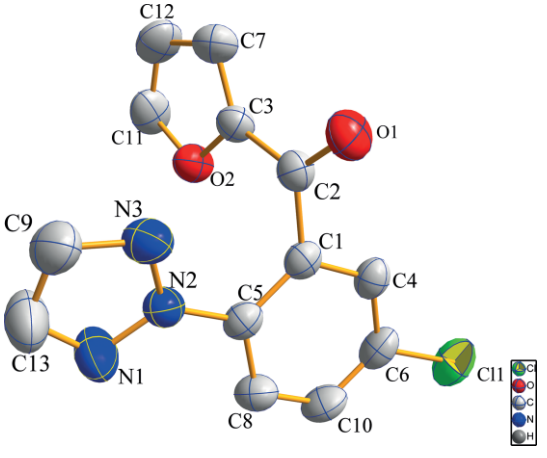
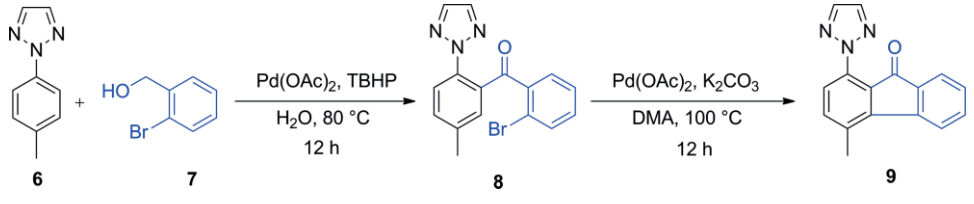


Figure 1. Single crystal X-ray structure of **5f**.

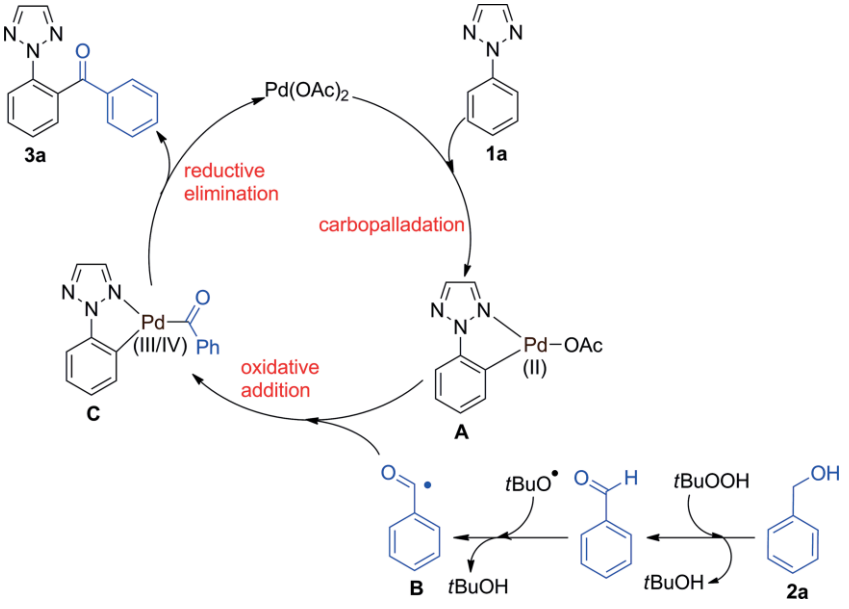
yielded 4-methyl-1-(2*H*-1,2,3-triazol-2-yl)-9*H*-fluoren-9-one (**9**) in 78 % yield (Scheme 4). The reaction was also performed on a gram scale (2 g) to afford 1.20 g of the desired product (Supporting Information).

Mechanism

On the basis of reports in the literature[17,11a] and control experiments, we have proposed a plausible mechanism (Scheme 5).



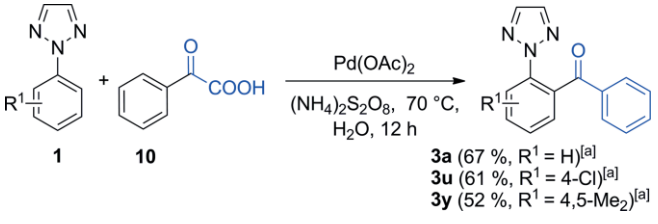
Scheme 4. Synthesis of 1,2,3-triazole-substituted fluorenone.



Scheme 5. Proposed Mechanism.

The reaction is initiated through an *ortho*-carbopalladation of 2-aryl-1,2,3-triazole (**1a**) with $Pd(OAc)_2$ to form the intermediate **A**,[25] which undergoes a reaction with acyl radical **B** that is generated in situ from benzyl alcohol under oxidizing conditions. Acyl radical **B** undergoes an oxidative addition to then give intermediate **C**. Finally, a reductive elimination releases the desired acylated product **3a** along with the regeneration of the active Pd^{II} catalyst. The in situ formation of benzaldehyde as an intermediate was confirmed by ^1H NMR analysis of the reaction mixture after 6 h of reaction time and showed the characteristic aldehyde proton peak at δ = 9.8 ppm.

Interestingly, we also found that a decarboxylative acylation of *N*-aryl-1,2,3-triazoles could be achieved with α-oxo acid **10** in water. After a few optimization experiments, we successfully obtained the desired products **3a**, **3u**, and **3y** in moderate yields by using ammonium peroxodisulfate as the oxidant (Scheme 6).[26]



Scheme 6. Acylation of *N*-aryl-1,2,3-triazole with oxocarboxylic acid. Reagents and conditions: **1** (1.0 equiv.), **10** (1.5 equiv.), $Pd(OAc)_2$ (10 mol-%), and $(NH_4)_2S_2O_8$ (2.5 equiv.), in H_2O (0.5 mL) at 70 °C for 12 h. [a] Isolated yields.

Conclusions

We have developed an efficient and mild method for the acylation of triazoles that have pharmaceutical potential. The reaction uses readily available benzylic, heterocyclic, and aliphatic alcohols with $Pd(OAc)_2$ and TBHP in water to yield *N*-aryl-1,2,3-triazole-substituted aryl, heteroaryl, and aliphatic ketones, respectively, in moderate to high yields with excellent regioselectivity. The reaction is effective in the absence of a PTC or surfactant. The procedure involves an easy workup process that employs a minimal amount of organic solvent to extract the product from the aqueous reaction mixture, thus making the overall method highly economical and environmentally friendly.

Experimental Section

General Methods: All reactions were carried out under air in an oven-dried round-bottomed flask that was sealed with a septum or a sealed tube. All of the solvents were purchased from Aldrich or Spectrochem and used as received. Palladium(II) acetate was purchased from Alfa-Aesar (98 % purity). For column chromatography, silica gel (230–400 mesh) from SRL Co. was used. A gradient elution (ethyl acetate/hexane) was used for TLC, which was performed on Merck aluminium sheets (silica gel 60F254). All of the isolated compounds were characterized by ^1H and ^{13}C NMR spectroscopy along with HRMS. The ^1H and ^{13}C NMR spectroscopic data were recorded with a Bruker DPX-300 MHz spectrometer at 300 and 75 MHz, respectively. $CDCl_3$ and $[D_6]$DMSO were used as the NMR solvents with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts are reported in δ (ppm) values relative to that of TMS (δ = 0.00 ppm), and the coupling constants (*J*) are reported in Hz. High-resolution mass spectra were recorded with a Q-TOF (Q = quadrupole) instrument by using electrospray ionization.

General Procedure for the Preparation of Glyoxalbis(*N*-arylosazones): The glyoxalbis(*N*-arylosazones) were prepared by using a literature method.[27] To a 40 % aqueous solution of glyoxal (5 mmol) was added phenylhydrazine (10 mmol) in ethanol (40 mL) as the mixture was stirred and cooled in an ice bath. A yellow solid formed instantaneously, and this yellow suspension was stirred at room temperature for 1 h. The reaction mixture was extracted with dichloromethane, and the organic layer was concentrated and then dried with a vacuum pump for 45 min. The crude glyoxalbis(*N*-phenyl)osazone was used directly in the next step.

Preparation of *N*-Aryl-1,2,3-Triazoles: All of the triazoles were synthesized by using a reported procedure.[27] An oven-dried two-neck round-bottomed flask was charged with a mixture of the glyoxalbis(*N*-phenylosazone) (1 g, 0.042 mmol) and copper triflate (0.05 g, 0.14 mmol) in dry toluene (10 mL). The contents were stirred and heated at reflux under a stream of nitrogen at 110 °C for 12 h. After this, the reaction mixture was cooled to room temperature, and the solvent was evaporated under reduced pressure. The oily residue was purified by chromatography on a silica gel column (hexane/ethyl acetate, 98:2) to yield the desired compound.

Typical Procedure for the *ortho*-Acylation of *N*-Aryl-1,2,3-triazoles To Yield 3a–3z and 5a–5g: An oven-dried reaction vessel was charged with a mixture of *N*-aryl-1,2,3-triazole (**1**, 0.34 mmol), the benzyl alcohol (**2**, 0.68 mmol, 2 equiv.), $Pd(OAc)_2$ (0.0344 mmol, 10 mol-%), TBHP (1.36 mmol, 4 equiv.), and H_2O (0.5 mL) at room temperature, and the system was sealed with a Teflon cap. The contents were stirred at 80 °C for 12 h and then cooled to room temperature. A slurry was made by adding silica gel directly into the reaction mixture. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate, 93:7) to yield the *ortho*-acylated 2-aryl-1,2,3-triazole as the product.

Procedure for the *ortho*-Acylation of *N*-Aryl-1,2,3-triazoles by α-Oxocarboxylic Acid To Yield 3a, 3u, and 3y: An oven-dried reaction vessel was charged with a mixture of *N*-aryl-1,2,3-triazole (**1**, 0.34 mmol), 2-oxo-2-phenylacetic acid (**10**, 0.51 mmol, 1.5 equiv.), $Pd(OAc)_2$ (0.0344 mmol, 10 mol-%), ammonium peroxodisulfate $(NH_4)_2S_2O_8$ (0.85 mmol, 2.5 equiv.), and H_2O (0.5 mL) at room temperature, and the system was sealed with a Teflon cap. The contents were stirred at 80 °C for 12 h and then cooled to room temperature. A slurry was made by adding silica gel directly into the reaction mixture. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate, 93:7) to yield the *ortho*-acylated 2-aryl-1,2,3-triazoles as the product.

Synthesis of 4-Methyl-1-(2*H*-1,2,3-triazol-2-yl)-9*H*-fluoren-9-one (9):[28] To a 15 mL vial that contained (2-bromophenyl)[5-methyl-2-(2*H*-1,2,3-triazol-2-yl)phenyl]methanone (**8**, 5.86 mmol), $Pd(OAc)_2$ (3 mol-%), 2,2′-bis(diphenylphosphino)-1,1′-binaphthalene (BINAP, 10 mol-%), K_2CO_3 (3 equiv.), and trimethylacetic acid (0.5 mmol) was added DMA (5 mL). The resulting mixture was heated at 120 °C for 8 h. After cooling to room temperature, water was added, and the product was extracted with ethyl acetate (6 × 20 mL). The organic layer was concentrated under reduced pressure. Column chromatography on silica gel (hexane/ethyl acetate, 95:5) gave the desired product.

Spectral Data

(Phenyl)[2-(2*H*-1,2,3-triazol-2-yl)phenyl]methanone (3a):[17b] Yellowish brown solid (70 mg, 84 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90 (d, J = 8.1 Hz, 1 H), 7.55 (d, J = 7.2 Hz, 3 H), 7.41 (d, 4 H, d = 8.7 Hz), 7.32 (d, J = 7.5 Hz, 1 H), 7.18 (t, J = 7.5 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.16, 137.70, 137.02, 135.83, 132.86, 132.68, 131.07, 129.56, 128.98, 128.27, 128.22 ppm. ESI-MS: calcd. for $C_{15}H_{11}N_3OH^+$ 250.0975; found 250.0367.

(4-Methoxyphenyl)[2-(2*H*-1,2,3-triazol-2-yl)phenyl]methanone (3b): Brown solid (80 mg, 88 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00 (d, J = 7.5 Hz, 1 H), 7.62 (d, J = 7.5 Hz, 1 H), 7.55 (s, 4 H), 7.33 (s, 1 H), 7.11 (m, 2 H), 7.00 (d, J = 7.2 Hz, 1 H), 3.8 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.34, 159.57, 138.36, 135.82, 132.69, 131.04, 129.55, 129.21, 128.15, 122.27, 122.08, 119.78, 112.65, 55.37 ppm. ESI-MS: calcd. for $C_{16}H_{13}N_3O_2H^+$ 280.1081; found 280.0275.

(*o*-Tolyl)[2-(2*H*-1,2,3-triazol-2-yl)phenyl]methanone (3c):[17a] Pale yellow solid (85 mg, 85 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88 (s, 1 H), 7.62 (m, 2 H), 7.50 (d, J = 9 Hz, 2 H), 7.21 (dd, J_1 = 12 Hz, J_2 = 15 Hz, 3 H), 7.14 (dd, J_1 = 12 Hz, J_2 = 15 Hz, 1 H), 6.94 (t, J = 6 Hz, 1 H), 2.63 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.82, 139.76, 138.11, 137.00, 135.81, 134.54, 132.94, 132.01, 131.62, 131.43, 130.17, 128.48, 125.96, 125.09, 123.08, 21.16 ppm. ESI-MS: calcd. for $C_{16}H_{13}N_3O$ 263.0950; found 263.09211.

(3-Chlorophenyl)[2-(2*H*-1,2,3-triazol-2-yl)phenyl]methanone (3d): Brown solid (82 mg, 82 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, J = 8.1 Hz, 1 H), 7.70 (m, 2 H), 7.56 (s, J = 8.1 Hz, 4 H), 7.47 (d, J = 6 Hz, 1 H), 7.41 (dd, J = 5.1 Hz, 1 H), 7.24 (dd, J_1 = 7.5 Hz, J_2 = 13.2 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.78, 138.71, 137.63, 135.94, 134.60, 132.74, 131.87, 131.43, 129.56, 129.53, 128.75, 128.29, 127.07, 122.30 ppm. ESI-MS: calcd. for $C_{15}H_{10}ClN_3ONa$ 306.0404; found 306.0406.

(4-Chlorophenyl)[2-(2*H*-1,2,3-triazol-2-yl)phenyl]methanone (3e):[17b] Pale yellow liquid (83 mg, 83 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, J = 6.0 Hz, 1 H), 7.66 (ddd, J_1 = 1.8 Hz, J_2 = 5.1 Hz, J_3 = 11.4 Hz, 1 H), 7.60 (d, J = 6.6 Hz, 2 H), 7.55 (d, J = 3.3 Hz, 4 H), 7.28 (d, J = 6.6 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.92, 139.20, 137.59, 135.93, 135.79, 135.52, 131.28, 130.27, 129.56, 128.98, 128.60, 128.24, 122.28 ppm. ESI-MS: calcd. for $C_{15}H_{10}ClN_3O$ 283.0512; found 283.0833.

(4-Fluorophenyl)[2-(2*H*-1,2,3-triazol-2-yl)phenyl]methanone (3f):[17b] Brown solid (66 mg, 66 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (dd, J_1 = 5.1 Hz, J_2 = 5.7 Hz, 1 H), 7.99 (d, J = 6 Hz, 1 H), 7.65 (m, 3 H), 7.54 (d, J = 1.8 Hz, 2 H), 7.13 (t, J = 6.3 Hz, 1 H), 6.94 (t, J = 1.5 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.67, 167.18 ($^1J_{C,F}$ = 250.5 Hz), 137.59, 135.89, 133.52, 132.89, 132.35, 131.60, 131.20, 129.48, 128.30, 122.37, 115.57 ($^2J_{C,F}$ = 21.7 Hz) ppm. ESI-MS: calcd. for $C_{15}H_{10}FN_3OH^+$ 268.0881; found 268.0147.

[2-(2*H*-1,2,3-Triazol-2-yl)phenyl][4-(trifluoromethyl)phenyl]-methanone (3g):[17b] White solid (71 mg, 71 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, J = 6 Hz, 1 H), 7.76 (d, J = 6 Hz, 2 H), 7.68 (dt, J = 6 Hz, 1 H), 7.56 (s, 3 H), 7.53 (d, J = 4.8 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.95, 139.95, 137.69, 135.97, 134.61 ($^2J_{C,F}$ = 32.4 Hz), 131.57, 129.57, 129.08, 128.35, 125.30 ($^3J_{C,F}$ = 3.8 Hz), 122.26 ($^1J_{C,F}$ = 271.5 Hz) ppm. ESI-MS: calcd. for $C_{16}H_{10}F_3N_3O$ 317.0776; found 317.0864.

(2-Bromophenyl)[2-(2*H*-1,2,3-triazol-2-yl)phenyl]methanone (3h):[17b] Pale yellow solid (81 mg, 73 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, J = 6 Hz, 1 H), 7.63 (dd, J_1 = 5.7 Hz, J_2 = 8.7 Hz, 2 H), 7.49 (d, J = 3.3 Hz, 3 H), 7.46 (d, J = 5.1 Hz, 1 H), 7.18 (dd, J_1 = 1.5 Hz, J_2 = 5.4 Hz, 1 H), 7.08 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.67, 138.36, 138.19, 135.90, 134.33, 133.68, 132.19, 132.07, 131.03, 130.67, 130.19, 128.84, 126.57, 123.33, 121.68 ppm. ESI-MS: calcd. for $C_{15}H_{10}BrN_3O$ 327.0007; found 327.1589.

(4-Chlorophenyl)[5-methyl-2-(2*H*-1,2,3-triazol-2-yl)phenyl]-methanone (3i): White solid (75 mg, 81 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, J = 6.3 Hz, 1 H), 7.55 (d, J = 5.1 Hz, 2 H), 7.50 (s, 2 H), 7.46 (dd, J_1 = 0.9 Hz, J_2 = 6.3 Hz, 1 H), 7.33 (1 H), 7.25 (d, J = 5.1 Hz, 2 H), 2.44 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.13, 139.12, 138.65, 135.68, 135.54, 135.48, 132.00, 131.92, 130.24, 129.83, 128.55, 122.24, 21.02 ppm. ESI-MS: calcd. for $C_{16}H_{12}ClN_3O$ 297.0669; found 297.0478.

(3-Chlorophenyl)[5-methyl-2-(2*H*-1,2,3-triazol-2-yl)phenyl]-methanone (3j): Reddish brown liquid (78 mg, 78 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90 (d, J = 7.5 Hz, 1 H), 7.70 (s, 1 H), 7.54 (s, 2 H), 7.51 (t, J = 7.2 Hz, 2 H), 7.39 (t, J = 6 Hz, 1 H), 7.28 (dd, J_1 = 8.1 Hz, J_2 = 16.8 Hz, 2 H), 2.49 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.01, 138.76, 136.61, 135.67, 134.54, 132.66, 132.06, 131.78, 131.10, 129.86, 129.50, 128.71, 127.02, 122.25, 119.14,

21.03 ppm. ESI-MS: calcd. for $C_{16}H_{12}ClN_3O$ 297.0669; found 297.0148.

[5-Methyl-2-(2*H*-1,2,3-triazol-2-yl)phenyl](*o*-tolyl)methanone (3k): Brown solid (85 mg, 85 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, J = 8.7 Hz, 1 H), 7.39 (s, 2 H), 7.35 (s, 2 H), 7.15 (dd, J_1 = 7.5 Hz, J_2 = 15.6 Hz, 1 H), 7.03 (t, J = 8.1 Hz, 2 H), 6.86 (t, J = 7.2 Hz, 1 H), 2.54 (s, 3 H), 2.38 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.82, 139.57, 138.61, 137.00, 135.94, 135.37, 134.37, 131.85, 131.41, 131.36, 130.34, 130.07, 124.89, 122.95, 21.03, 20.95 ppm. HRMS: calcd. for $C_{17}H_{15}N_3NaO$ 300.1107; found 300.1109.

[4-Methyl-2-(2*H*-1,2,3-triazol-2-yl)phenyl](phenyl)methanone (3l): Brown solid (83 mg, 83 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (s, 1 H), 7.65 (d, J = 5.4 Hz, 2 H), 7.51 (s, 2 H), 7.49 (d, J = 6 Hz, 1 H), 7.43 (t, J = 5.4 Hz, 1 H), 7.34 (d, J = 5.7 Hz, 1 H), 7.27 (t, J = 5.7 Hz, 2 H), 2.52 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.35, 141.94, 137.78, 137.23, 135.70, 133.61, 132.69, 130.15, 129.72, 128.93, 128.44, 128.17, 122.95, 21.39 ppm. HRMS: calcd. for $C_{16}H_{13}N_3NaO$ 286.0950; found 286.0949.

(2,5-Dimethoxyphenyl)[4-methyl-2-(2*H*-1,2,3-triazol-2-yl)phenyl]methanone (3m): White solid (88 mg, 89 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (s, 1 H), 7.56 (s, 2 H), 7.48 (dd, J_1 = 5.7 Hz, J_2 = 9.3 Hz, 2 H), 7.33 (d, J = 5.4 Hz, 1 H), 7.09 (dd, J_1 = 3 Hz, J_2 = 6 Hz, 1 H), 6.67 (d, J = 6.3 Hz, 1 H), 3.88 (s, 3 H), 3.86 (s, 3 H), 2.51 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.02, 153.06, 148.86, 141.53, 137.67, 135.69, 135.47, 130.37, 129.60, 128.92, 124.49, 124.31, 123.00, 121.81 110.63, 109.71, 55.94, 21.35 ppm. HRMS: calcd. for $C_{18}H_{17}N_3NaO_3$ 346.1153; found 346.1154.

(4-Methoxyphenyl)[4-methyl-2-(2*H*-1,2,3-triazol-2-yl)phenyl]methanone (3n): Brown liquid (87 mg, 88 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (s, 1 H), 7.65 (d, J = 6.6 Hz, 2 H), 7.55 (s, 2 H), 7.44 (d, J = 5.7 Hz, 1 H), 7.32 (d, J = 5.7 Hz, 1 H), 6.78 (d, J = 6.6 Hz, 2 H), 3.80 (s, 3 H), 2.51 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.04, 163.26, 141.44, 137.68, 135.62, 131.34, 130.52, 130.34, 129.50, 128.88, 122.97, 113.47, 55.37, 21.34 ppm. HRMS: calcd. for $C_{17}H_{15}N_3NaO_2$ 316.1055; found 316.1056.

[4-Methyl-2-(2*H*-1,2,3-triazol-2-yl)phenyl](*o*-tolyl)methanone (3o): Pale yellow solid (80 mg, 81 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59 (s, 1 H), 7.46 (d, J = 7.8 Hz, 1 H), 7.41 (d, J = 6 Hz, 2 H), 7.27 (d, J = 7.5 Hz, 1 H), 7.12 (d, J = 6.9 Hz, 1 H), 7.06 (dd, J_1 = 7.2 Hz, J_2 = 11.1 Hz, 2 H), 6.86 (t, J = 7.2 Hz, 1 H), 2.51 (s, 3 H), 2.43 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.76, 143.89, 142.20, 139.40, 138.15, 137.51, 135.51, 131.91, 131.34, 130.19, 129.82, 129.10, 124.85, 123.67, 21.37, 20.86 ppm. ESI-MS: calcd. for $C_{17}H_{15}N_3O$ 277.1215; found 277.1470.

(4-Chlorophenyl)[4-methyl-2-(2*H*-1,2,3-triazol-2-yl)phenyl]methanone (3p): Pale yellow solid (81 mg, 82 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80 (s, 1 H), 7.54 (t, J = 6 Hz, 4 H), 7.46 (d, J = 7.8 Hz, 1 H), 7.33 (d, J = 7.5 Hz, 1 H), 7.27 (d, J = 8.4 Hz, 2 H), 2.52 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.97, 142.18, 138.98, 137.66, 135.80, 133.61, 131.51, 130.18, 129.62, 129.07, 128.81, 128.49, 122.88, 21.39 ppm. HRMS: calcd. for $C_{16}H_{12}ClN_3ONa$ 320.0558; found 320.0559.

[4-Chloro-2-(2*H*-1,2,3-triazol-2-yl)phenyl](*m*-tolyl)methanone (3q): Pale yellow solid (80 mg, 80 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71 (s, 1 H), 7.58 (m, 2 H), 7.45 (s, 2 H), 7.40 (d, J = 7.8 Hz, 1 H), 7.27 (d, J = 7.8 Hz, 1 H), 6.87 (t, J = 8.4 Hz, 2 H), 2.44 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.68, 167.07, 163.69, 142.04, 137.70, 135.73, 133.77, 131.49, 131.37, 129.80, 129.59, 129.05, 122.96, 115.45, 115.16, 21.37 ppm. HRMS: calcd. for $C_{16}H_{12}ClN_3NaO$ 320.0556; found 320.0561.

[4-Chloro-2-(2*H*-1,2,3-triazol-2-yl)phenyl](4-chlorophenyl)methanone (3r): Light yellow liquid (78 mg, 78 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.982 (s, 1 H), 7.52 (d, J = 8.4 Hz, 4 H), 7.41 (s, 2 H), 7.22 (d, J = 8.4 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.90, 139.46, 138.28, 137.16, 136.31, 135.33, 130.68, 130.20, 128.71, 128.31, 123.60, 122.35 ppm. ESI-MS: calcd. for $C_{15}H_9Cl_2N_3O$, 317.0123; found 317.1543.

[4-Chloro-2-(2*H*-1,2,3-triazol-2-yl)phenyl](4-fluorophenyl)methanone (3s): Brown solid (68 mg, 68 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (s, 1 H), 7.68 (dd, J_1 = 3.9 Hz, J_2 = 5.7 Hz, 2 H), 7.65 (s, 2 H), 7.49 (s, 2 H), 6.98 (t, J = 6.3 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.60, 167.29 (d, $J_{C,F}$ = 253.7 Hz), 163.90, 138.29, 137.06, 136.27, 133.32, 131.57, 130.67, 128.30, 122.42, 115.70 (d, $J_{C,F}$ = 21.9 Hz) ppm. HRMS: calcd. for $C_{15}H_9ClFN_3NaO$ 324.03102; found 324.03103.

[4-Chloro-2-(2*H*-1,2,3-triazol-2-yl)phenyl](*o*-tolyl)methanone (3t): Pale yellow liquid (77 mg, 77 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (s, 1 H), 7.43 (m, 4 H), 7.61 (t, J = 9 Hz, 1 H), 7.09 (d, J = 7.2 Hz, 1 H), 7.02 (d, J = 7.5 Hz, 1 H), 6.89 (t, J = 7.5 Hz, 1 H), 2.56 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.60, 139.79, 138.67, 137.07, 136.64, 136.03, 132.54, 131.66, 131.59, 131.21, 129.94, 128.34, 125.02, 123.06, 20.98 ppm. ESI-MS: calcd. for $C_{16}H_{12}ClN_3O$ 297.0669; found 297.0478.

[4-Chloro-2-(2*H*-1,2,3-triazol-2-yl)phenyl](phenyl)methanone (3u): Pale yellow solid (78 mg, 79 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (s, 1 H), 7.63 (d, J = 8.4 Hz, 2 H), 7.53 (s, 2 H), 7.49 (s, 2 H), 7.44 (d, J = 7.2 Hz, 1 H), 7.33 (d, J = 7.8 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.15, 138.39, 136.88, 136.84, 136.20, 133.03, 130.78, 128.94, 128.36, 128.22, 122.36 ppm. HRMS: calcd. for $C_{15}H_{10}ClKN_3O$ 322.0143; found 322.0143.

[5-Fluoro-2-(2*H*-1,2,3-triazol-2-yl)phenyl](4-methoxyphenyl)methanone (3v): Pale yellow solid (69 mg, 69 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (dd, J_1 = 3.6 Hz, J_2 = 6.9 Hz, 1 H), 7.66 (d, J = 5.4 Hz, 2 H), 7.56 (s, 2 H), 7.33 (dt, J = 2.1 Hz, 1 H), 7.25 (dd, J_1 = 2.1 Hz, J_2 = 6 Hz, 1 H), 6.81 (d, J = 6.6 Hz, 2 H), 3.81 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.20, 163.65, 163.37 (d, $J_{C,F}$ = 250.72), 135.83, 135.07, 133.88, 133.88, 131.47, 129.41, 124.64, 117.80, 116.52 (d, $J_{C,F}$ = 24.15 Hz), 113.69, 55.43 ppm. ESI-MS: calcd. for $C_{16}H_{12}FN_3O_2$ 297.0914; found 298.0807.

1-[2-(2*H*-1,2,3-Triazol-2-yl)phenyl]ethanone (3w):[17b] Brown liquid (60 mg, 60 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (t, J = 3 Hz, 3 H), 7.54 (dd, J_1 = 8.4 Hz, J_2 = 6.3 Hz, 2 H), 7.45 (d, J = 1.8 Hz, 1 H), 2.19 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.89, 136.43, 136.16, 134.27, 133.03, 130.97, 127.90, 127.20, 30.10 ppm. ESI-MS: calcd. for $C_{10}H_8N_3NaO$ 209.0565; found 209.0240.

1-[2-(2*H*-1,2,3-Triazol-2-yl)phenyl]butan-1-one (3x): Yellow solid (62 mg, 62 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90 (d, J = 8.7 Hz, 1 H), 7.83 (s, 2 H), 7.534 (dd, J_1 = 2.1 Hz, J_2 = 2.4 Hz, 2 H), 7.40 (d, J = 2.1 Hz, 1 H), 2.42 (t, J = 7.2 Hz, 2 H), 1.68 (q, J_1 = 7.2 Hz, J_2 = 10.2 Hz, 2 H), 0.89 (t, J = 5.4 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.77, 136.25, 134.99, 134.07, 133.60, 127.80, 123.77, 44.85, 29.70, 17.57, 13.63 ppm. ESI-MS: calcd. for $C_{12}H_{13}N_3NaO$ 238.0956; found 238.2899.

[4,5-Dimethyl-2-(2*H*-1,2,3-triazol-2-yl)phenyl](phenyl)methanone (3y): White solid (64 mg, 64 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74 (s, 1 H), 7.69 (d, J = 7.2, 2 H), 7.53 (s, 2 H), 7.44 (t, J = 7.2 Hz, 1 H), 7.36 (s, 1 H), 7.28 (t, J = 7.8 Hz, 2 H), 2.43 (s, 3 H), 2.38 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.36, 140.37, 137.35, 137.21, 135.81, 135.42, 132.55, 130.58, 130.27, 128.89, 128.39, 128.10, 123.38, 19.82, 19.34 ppm. HRMS: calcd. for $C_{17}H_{15}N_3NaO$ 300.1107; found 300.1108.

[2,4-Dimethyl-6-(2*H*-1,2,3-triazol-2-yl)phenyl](phenyl)methanone (3z): Pale yellow liquid (67 mg, 67 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70 (d, J = 4.8 Hz, 1 H), 7.50 (s, 2 H), 7.44 (t, J_1 = 6 Hz, 1 H), 7.33 (dd, J_1 = 7.8 Hz, J_2 = 15 Hz, 2 H), 7.14 (s, 1 H), 2.53 (s, 3 H), 2.27 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.35, 140.15, 137.68, 137.38, 137.25, 135.29, 132.84, 131.09, 129.18, 128.72, 128.34, 119.98, 19.81, 19.34 ppm. HRMS: calcd. for $C_{17}H_{15}N_3NaO$ 300.1101; found 300.1102.

(Thiophen-2-yl)[2-(2*H*-1,2,3-triazol-2-yl)phenyl]methanone (5a): Brown solid (76 mg, 76 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, J = 6.3 Hz, 1 H), 7.64 (m, 4 H), 7.53 (t, J = 5.4 Hz, 1 H), 7.44 (s, 1 H), 6.83 (d, J = 2.1 Hz, 1 H), 6.36 (d, J = 1.5 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 182.38, 152.45, 146.84, 137.73, 135.86, 131.78, 131.44, 129.60, 128.08, 122.49, 118.45, 112.09 ppm. HRMS: calcd. for $C_{13}H_9N_3NaOS$ 278.0358; found 278.0335.

(Furan-2-yl)[2-(2*H*-1,2,3-triazol-2-yl)phenyl]methanone (5b): Brown solid (72 mg, 73 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, J = 6.3 Hz, 1 H), 7.57 (m, 4 H), 7.44 (ddd, J_1 = 0.6 Hz, J_2 = 5.7 Hz, J_3 = 11.1 Hz, 1 H), 7.36 (s, 1 H), 6.75 (d, J = 2.7 Hz, 1 H), 6.30 (dd, J_1 = 1.2 Hz, J_2 = 2.7 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 182.37, 152.44, 146.84, 137.73, 135.85, 131.77, 131.43, 129.59, 128.08, 124.58, 122.48, 118.47, 112.09 ppm. HRMS: calcd. for $C_{13}H_9N_3NaO_2$ 262.0586; found 262.0584.

(5-Methylfuran-2-yl)[2-(2*H*-1,2,3-triazol-2-yl)phenyl]methanone (5c): Yellow solid (78 mg, 79 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, J = 6.6 Hz, 1 H), 7.66 (s, 2 H), 7.59 (d, J = 1.8 Hz, 2 H), 7.58 (s, J = 2.7 Hz, 2 H), 6.77 (s, 1 H), 6.03 (d, J = 2.1 Hz, 1 H), 2.27 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 180.02, 158.86, 150.69, 136.18, 136.02, 133.93, 133.10, 131.18, 129.58, 123.94, 121.40, 109.25, 13.99 ppm. HRMS: calcd. for $C_{14}H_{11}N_3NaO_2$ 276.0851; found 276.0853.

(Furan-3-yl)[2-(2*H*-1,2,3-triazol-2-yl)phenyl]methanone (5d): Yellow solid (48 mg, 59 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, J = 1.2 Hz, 1 H), 7.70 (s, 2 H), 7.48 (m, 4 H), 7.34 (t, J = 1.2 Hz, 1 H), 6.70 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.61, 148.27, 144.27, 137.02, 136.41, 135.94, 131.59, 130.26, 128.30, 127.82 123.01, 108.74 ppm. ESI-MS: calcd. for $C_{13}H_9N_3NaO_2$ 262.0592; found 262.0584.

[4-Chloro-2-(2*H*-1,2,3-triazol-2-yl)phenyl](5-methylfuran-2-yl)-methanone (5e): Brown solid (73 mg, 74 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (s, 1 H), 7.91 (d, J = 6.3 Hz, 1 H), 7.64 (s, 2 H), 7.56 (d, J = 6.3 Hz, 1 H), 6.75 (s, 1 H), 5.01 (d, J = 2.1 Hz, 1 H), 2.25 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 180.05, 150.68, 149.04, 144.06, 136.03, 133.95, 133.09, 131.20, 129.58, 123.96, 109.89, 109.28, 13.98 ppm. HRMS: calcd. for $C_{14}H_{10}ClN_3NaO_2$ 310.0128; found 310.0129.

[5-Chloro-2-(2*H*-1,2,3-triazol-2-yl)phenyl](furan-2-yl)methanone (5f): White solid (76 mg, 77 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, J = 6.6 Hz, 1 H), 7.64 (s, J = 9.3 Hz, 3 H), 7.45 (ddd, J_1 = 1.8 Hz, J_2 = 6.6 Hz, J_3 = 13.2 Hz, 1 H), 7.44 (s, 1 H), 6.90 (d, J = 2.4 Hz, 1 H), 6.41 (dd, J_1 = 1.5 Hz, J_2 = 2.7 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 180.75, 152.06, 147.12, 136.08, 133.95, 132.80, 131.34, 129.45, 123.69, 118.79, 112.30 ppm. HRMS: calcd. for $C_{13}H_8ClN_3NaO_2$ 296.0191; found 296.0190.

[5-Chloro-2-(2*H*-1,2,3-triazol-2-yl)phenyl](thiophen-2-yl)methanone (5g): White solid (71 mg, 71 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, J = 6.6 Hz, 1 H), 7.65 (s, 3 H), 7.58 (ddd, J_1 = 1.8 Hz, J_2 = 6.3 Hz, J_3 = 13.5 Hz, 1 H), 7.44 (s, 1 H), 6.89 (d, J = 2.7 Hz, 1 H), 6.40 (dd, J_1 = 1.2 Hz, J_2 = 2.7 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 180.76, 152.06, 147.12, 136.07, 133.96, 132.80, 131.34, 129.46, 123.69, 118.79, 112.29 ppm. HRMS: calcd. for $C_{13}H_8ClN_3NaOS$ 311.9968; found 311.9983.

4-Methyl-1-(2*H*-1,2,3-triazol-2-yl)-9*H*-fluoren-9-one (9): Yellow solid (1.20 g, 78 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.91 (s, 1 H), 7.71 (dd, J_1 = 7.8 Hz, J_2 = 13.2 Hz, 2 H), 7.55 (s, J = 7.5 Hz, 1 H), 7.38 (d, J = 2.7 Hz, 2 H), 7.34 (s, J = 8.1 Hz, 1 H), 2.67 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.93, 143.79, 143.52, 137.89, 135.64, 134.66, 134.51, 134.33, 129.11, 126.87, 125.88, 124.60, 123.55, 20.45 ppm. HRMS: calcd. for $C_{16}H_{11}N_3NaO$ 284.0794; found 284.0792.

Supporting Information (see footnote on the first page of this article): Spectroscopic (^{1}H NMR and ^{13}C NMR) and EI-MS data for the synthesized compounds.

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Keywords: Acylation · Nitrogen heterocycles · C–H activation · Regioselectivity · Palladium

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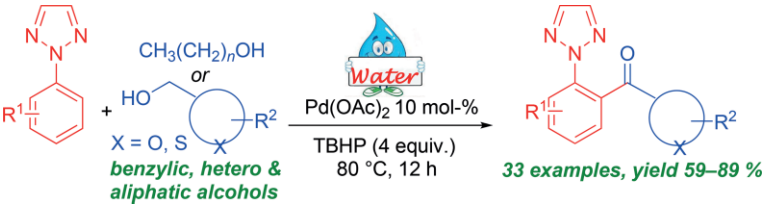
C–H Acylation

*C. Premi, S. S. Patel, N. Jain** 1–9

Regioselective *ortho*-Acylation of *N*-Aryl-1,2,3-triazoles with Alcohols in Water



A palladium-catalyzed regioselective *ortho*-acylation of *N*-aryl-1,2,3-triazoles with benzylic, heterocyclic, and aliphatic alcohols has been achieved under aqueous conditions to give the corresponding triazole-substituted ketones in moderate to high yields. TBHP = *tert*-butyl hydroperoxide.

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