RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

RSC Advances

PAPER

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/advances

Regioselective synthesis of triazoles *via* base-promoted oxidative cycloaddition of chalcones with azides in aqueous solution

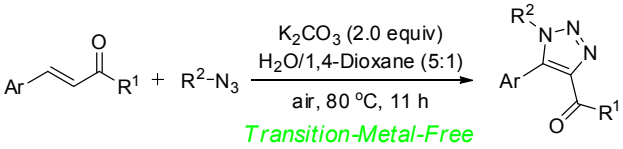
Wenchao Yang,[a] Tao Miao,*[a] Pinhua Li,[a] and Lei Wang*[a,b]

A base-promoted oxidative cycloaddition of chalcones with azides in aqueous solution has been developed under transition-metal-free conditions, which provides a green method for the regioselective synthesis of trisubstituted triazoles in good yields.

Introduction

Triazole represents a unique building block for organic synthesis, and as a key skeleton has been found in many bioactive compounds and synthetic drugs.[1,2] As we known, the classic method for the synthesis of triazoles is Huisgen 1,3-dipolar cycloaddition of organic azides with terminal alkynes.[3] However, this reaction suffered from poor regioselectivity and harsh reaction conditions. Subsequently, the advent of click chemistry has been proven to be the most straightforward and powerful approach for the preparation of triazole derivatives, in which the terminal alkynes are necessary and restrict the scope of Cu- or Ru-catalyzed cycloaddition reactions.[4] Recently, some alternative methods have been established for the synthesis of triazole derivatives including the reactions of azides with alkenes or ketones.[5] For example, Chen and co-workers disclosed a CuO-promoted oxidative cycloaddition of sodium azides with chalcones and further arylation of *N*–H under mild reaction conditions.[5f] Yao et al have also reported a copper(I)-catalyzed aerobic oxidative azide-alkene cycloaddition for the preparation of substituted 1,2,3-triazoles.[5g] More recently, Zhang group described a novel Cu-mediated synthesis of 1,2,3-triazoles from *N*-tosylhydrazones and anilines.[5h] It was found that most of these methods often utilized significant amount of toxic transition metal catalysts, which are not ideal for the biological applications in view of their toxicity. Therefore, a simple and green protocol is still highly desirable for the construction of trizaole and its derivatives.

To address this issue, transition-metal-free strategies have been developed for the preparation of specific 1,2,3-triazoles, such as an organocatalytic enamine-mediated amino acid or amine catalyzed [3+2] cycloaddition of different carbonyl compounds (enones, ketones, β-keto esters and enals) with organic azides,[6] an enaminone-azide multicomponent cascade reaction of aldehydes, nitroalkanes, and organic azides,[7] a TsOH-catalyzed nitroolefin-azide cycloaddition[8] and a condensation of *N*-tosylhydrazones with primary amines.[9] Although these eco-friendly approaches to triazoles were achieved, we considered exploring the alternative transition-metal-free cycloaddition is essential in the preparation of triazoles. In continuation of our interest in developing green synthetic methods in organic synthesis,[10] herein we have reported a novel and simple protocol for the synthesis of 1,2,3-triazoles from the cycloaddition reactions of chalcones with azides under transition-metal-free conditions (Scheme 1).



Scheme 1. Transition-metal-free synthesis of triazoles.

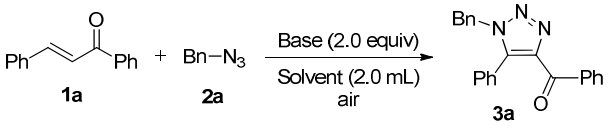
Results and discussion

As shown in Table 1, our efforts to accomplish such a transformation by employing the simple chalcone (**1a**) and BnN_3 (**2a**) as the standard substrates. The reaction of **1a** with **2a** was carried out in the mixture of H_2O/dioxane (5:1), with Et_3N (2.0 equiv) as a base. To our delight, the desired triazole **3a** was isolated in 45% yield (Table 1, entry 1). The structure of **3a** was characterized by ^1H, ^{13}C NMR spectroscopy, and confirmed by single-crystal X-ray diffraction analysis.[11] The addition of piperidine instead of Et_3N led to a comparable yield of **3a** (Table 1, entry 2). Subsequently, inorganic bases, such as NaOAc, KOAc, *t*-BuOLi and *t*-BuOK were found to be ineffective in the cycloaddition of **1a** with **2a**, and poor yields of **3a** were obtained (Table 1, entries 3–6). However, an enhanced yield (61%) of **3a** was achieved when Na_2CO_3 was

[a] Department of Chemistry, Huaibei Normal University, Huaibei, Anhui 235000, P R China; E-mail: leiwang@chnu.edu.cn.
Tel.: +86-561-380-2069; fax: +86-561-309-0518
[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P R China.

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Table 1 Optimization of base and solvent [a]

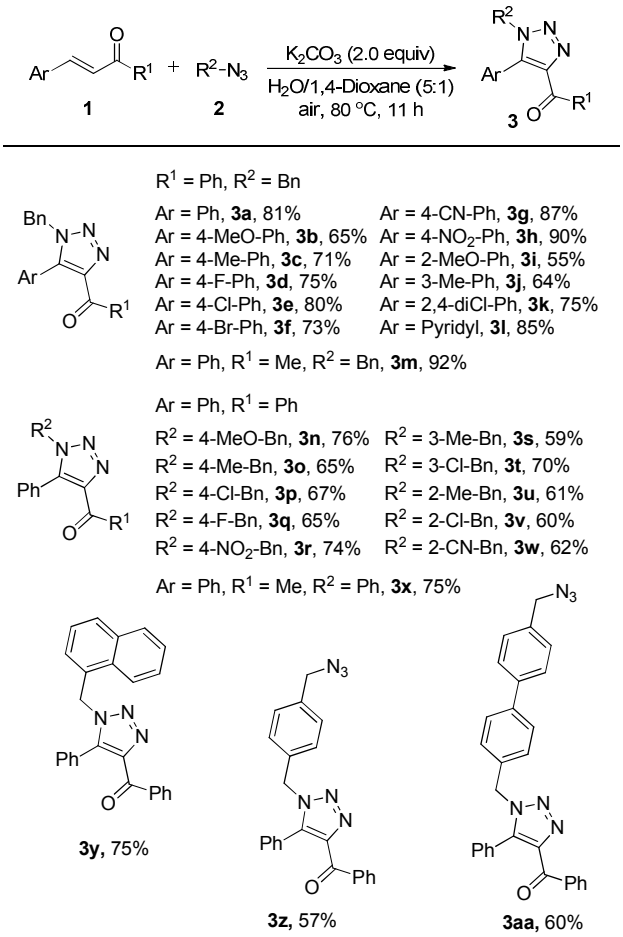


Entry	Base (equiv)	Solvent	Yield (%)[b]
1	Et_3N (2.0)	H_2O:dioxane (5:1)	45
2	piperidine (2.0)	H_2O:dioxane (5:1)	42
3	NaOAc (2.0)	H_2O:dioxane (5:1)	47
4	KOAc (2.0)	H_2O:dioxane (5:1)	24
5	*t*-BuOLi (2.0)	H_2O:dioxane (5:1)	26
6	*t*-BuOK (2.0)	H_2O:dioxane (5:1)	21
7	Na_2CO_3 (2.0)	H_2O:dioxane (5:1)	61
8	K_2CO_3 (2.0)	H_2O:dioxane (5:1)	81
9[c]	K_2CO_3 (2.0)	H_2O:dioxane (5:1)	41
10[d]	K_2CO_3 (2.0)	H_2O:dioxane (5:1)	80
11[e]	K_2CO_3 (2.0)	H_2O:dioxane (5:1)	50
12[f]	K_2CO_3 (2.0)	H_2O:dioxane (5:1)	76
13	K_2CO_3 (1.0)	H_2O:dioxane (5:1)	61
14	K_2CO_3 (3.0)	H_2O:dioxane (5:1)	74
15	–	H_2O:dioxane (5:1)	0
16[g]	K_2CO_3 (2.0)	H_2O:dioxane (5:1)	80
17[h]	K_2CO_3 (2.0)	H_2O:dioxane (5:1)	trace
18	K_2CO_3 (2.0)	DMF	14
19	K_2CO_3 (2.0)	DMSO	34
20	K_2CO_3 (2.0)	toluene	11
21	K_2CO_3 (2.0)	dioxane	33
22	K_2CO_3 (2.0)	THF	12
23	K_2CO_3 (2.0)	CH_3CN	34
24	K_2CO_3 (2.0)	ethanol	38
25	K_2CO_3 (2.0)	H_2O	46
26	K_2CO_3 (2.0)	H_2O:dioxane (3:1)	54
27	K_2CO_3 (2.0)	H_2O:dioxane (6:1)	60
28	K_2CO_3 (2.0)	H_2O: DMF (5:1)	47
29	K_2CO_3 (2.0)	H_2O: CH_3CN (5:1)	44
30	K_2CO_3 (2.0)	H_2O: ethanol (5:1)	40

[a] Reaction conditions: chalcone (**1a**, 0.30 mmol), BnN_3 (**2a**, 0.60 mmol), base (0.60 mmol), solvent (2.0 mL), at 80 ℃, 11 hours. [b] Isolated yield. [c] Reaction time is 5 hours. [d] Reaction time is 24 hours. [e] Reaction temperature is 60 ℃. [f] Reaction temperature is 100 ℃. [g] Under oxygen atmosphere. [h] Under nitrogen atmosphere.

used as a base (Table 1, entry 7). To our delight, K_2CO_3 was the most effective base among the tested bases and the desired product **3a** was obtained in 81% yield (Table 1, entry 8). Employing a shorter reaction time of 5 hours resulted in an isolated yield of 41% (Table 1, entry 9). Prolonging reaction time to 24 hours did not improve this transformation (Table 1, entry 10). We also found that reaction temperature and the amount of K_2CO_3 could dramatically affect the formation of the product **3a** (Table 1, entries 11−14). Especially, the reaction did not proceed in absence of K_2CO_3 (Table 1, entry 15). Moreover, we performed the model reaction in the presence of an oxygen atmosphere, the reaction furnished the desired product (**3a**) in 80% yield (Table 1, entry 16). However, this reaction has been almost prohibited under a nitrogen atmosphere (Table 1, entry 17), which probably indicated that oxidative process was involved in this transformation. The optimization of solvent was also carried out under above reaction conditions. When DMF and DMSO were used as solvent in the reaction of **1a** with **2a**, 14% and 34% yields of **3a** were isolated, respectively (Table 1, entries 18 and 19). The use of toluene as reaction medium could result into lower yield of the corresponding product **3a** (Table 1, entry 20). Changing the solvent from toluene to dioxane increased the yield from 11% to 33% (Table 1, entry 20 *vs* 21). Then, experiments with THF, CH_3CN and ethanol as solvent had no good yield of **3a** (Table 1, entries 22−24). An increased yield of **3a** was obtained when H_2O was used as solvent (Table 1, entry 25). The ratio of dioxane and H_2O have obvious effect to this reaction, and decreased yields were observed when the dioxane/H_2O ratio was changed from 1:5 to 1:3 and 1:6 (Table 1, entries 26 and 27). Other reaction media such as the mixtures of DMF, CH_3CN and ethanol with H_2O showed poor performance of the reaction (Table 1, entries 28−30).

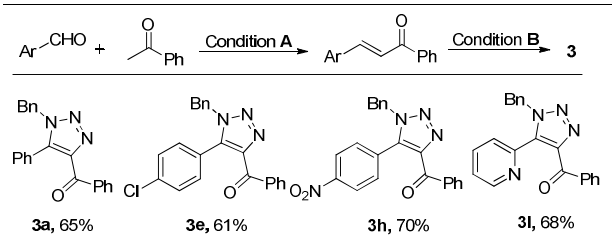
Having the optimized reaction conditions in our hand, the scope and limitation of this reaction with respect to the chalcones and benzyl azides were investigated. As shown in Scheme 2, a series of substituted chalcones containing electron-donating groups (methoxy and methyl), electron-withdrawing groups (cyano and nitro) and halogens (F, Cl, Br) were synthesized and evaluated in this transformation. Generally, chalcones with electron-donating groups provided the desired products in moderate to good yields. In contrast, the presence of electron-donating groups including cyano and nitro groups efficiently accelerated this transformation and better results were obtained (**3g** and **3h**). Moreover, the reaction of benzalacetone with benzyl azide generated the corresponding product **3m** in excellent yield (92%). However, the reactions of methyl acrylate, ethyl acrylate, methyl vinyl ketone and benzoquinone with benzyl azide failed to the corresponding 1,4-disubstituted 1,2,3-triazole products. Benzyl azides bearing methyl, methoxy, fluoro, chloro, cyano and nitro groups on the aromatic rings reacted with chalcone (**1a)** smoothly to afford the corresponding products (**3n–3w**) in 59–76% yields. Phenyl azide was also suitable substrate, and reacted with benzalacetone to give the expected 1,2,3-triazole product **3x** in



Scheme 2 Substrate scope of chalcones and azides [*Reaction conditions:* chalcone (**1**, 0.30 mmol), BnN_3 (**2**, 0.60 mmol), K_2CO_3 (0.60 mmol), H_2O/dioxane (5:1, 2.0 mL), 80 °C for 11 h.]

75% yield. Notably, This reaction was tolerant with halogen substituents, such as fluoro, chloro and bromo groups on the aromatic rings of chalcones and benzyl azides, providing good yields of substituted triazoles, which are the potential substrates for the further transition-metal-catalyzed functionalization. Furthermore, a sight steric effect was found in this cycloaddition reactions (**3b** *vs* **3i**, **3p** *vs* **3t** and **3v**). When more bulky 1-(azidomethyl)naphthalene was used to react with chalcone (**1a**), good yield of product **3y** was obtained. It should be noted that the reaction of 1,4-bis(azidomethyl)benzene with chalcone (**1a**) could selectively generate the corresponding triazole **3z**, with one azide unit retained in the product. The similar result was also observed when 4,4'-bis(azidomethyl)-1,1'-biphenyl was used to react with **1a**, providing **3aa** in 60% yield.

In order to simplify the construction of triazole, a one-pot strategy was examined, as described in Scheme 3. Firstly, benzaldehyde reacted with acetophenone to give the chalcone in H_2O/1,4-dioxane (5:1) in the presence of K_2CO_3 as a base. After 14 hours, benzylazide and K_2CO_3 were successively added into the above reaction system, and the reaction proceeded to generate the corresponding triazoles in the acceptable yields (**3a**, **3e**, **3h** and **3l**, Scheme 3).

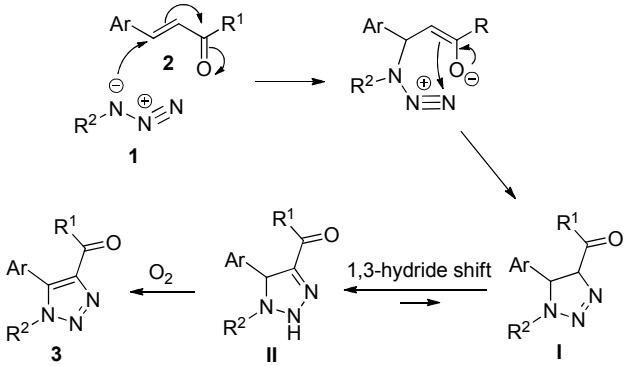


Condition **A**: ArCHO (0.30 mmol), $PhCOCH_3$ (0.30 mmol), K_2CO_3 (2.0 equiv), H_2O/1,4-dioxane (5: 1), room temperature, 14 h.

Condition **B**: BnN_3 (**2a**, 0.6 mmol), K_2CO_3 (2.0 equiv), 80 °C for 11 h.

Scheme 3 One-pot synthesis of triazole derivatives

Although exact mechanism of the reaction is still not clear, on the basis of above observations and the previous literature,[5h-i,6b-c,9c] a possible mechanism for the regioselective synthesis of triazole from **1** and **2** is illustrated in Scheme 4. Initially, a stepwise 1,3-dipolar cycloaddition reaction of chalcone **1** and azide **2** might be involved in this transformation, producing triazoline intermediate **I** in presence of an inorganic base (K_2CO_3). Subsequently, triazoline intermediate **I** would be underwent 1,3-hydride shift to generate intermediate **II**. Finally, the oxidation of intermediate **II** led to the formation of product **3** in the presence of oxidant (O_2).[9c]



Scheme 4 Proposed reaction mechanism.

Conclusion

In summary, we have successively developed a transition-metal-free oxidative cycloaddition reaction of chalcones with azides, which provides an alternative approach to a broad scope of triazoles in good yields. With the growing interest in green chemistry, further mechanistic studies of this process and application of this strategy to construct other useful compounds is currently under investigation in our laboratory.

Acknowledgements

This work was financially supported by the National Science Foundation of China (Nos. 21172092 and 20102039).

Experimental Section

General

All the chemicals and solvents were purchased from commercial suppliers and used without further purification. ^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance NMR spectrometer (400 MHz and 100 MHz, respectively) with $CDCl_3$ as solvent and recorded in ppm relative to internal tetramethylsilane standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopy data of the product were collected on a Waters Micromass GCT instrument. or an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS using ESI.

Typical procedure for K_2CO_3-promoted synthesis of trisubstituted triazoles

Under air atmosphere, a 10 mL oven-dried sealable reaction vessel equipped with a magnetic stir bar charged with (*E*)-chalcone (**1a**, 62.5 mg, 0.30 mmol), K_2CO_3 (83 mg, 0.60 mmol), solvent (H_2O:dioxane = 5:1, 2.0 mL) and benzyl azide (**2a**, 80 mg, 0.60 mmol) were added to the sealed vessel in one-portion. The rubber septum was then replaced by a Teflon-coated screw cap, and the reaction vessel placed in an oil bath at 80 °C for 11 h. After the reaction was completed, it was cooled to room temperature and diluted with ethyl acetate. Then the resulting solution was extracted with EtOAc (25 mL x 3). The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluant: petroleum ether/ethyl acetate = 5:1 to 7:1, V/V) to obtain the desired pure product, (1-benzyl-5-phenyl-1*H*-1,2,3-triazol-4-yl)(phenyl) methanone (**3a**).

Typical procedure for the one-pot synthesis of trisubstituted triazoles

Under air atmosphere, to a solution of benzaldehyde (32 mg, 0.30 mmol) in H_2O/1,4-dioxane (5:1, 2.0 mL) were added K_2CO_3 (83 mg, 0.60 mmol) and acetophenone (36 mg, 0.30 mmol), then the reaction mixture was stirred at room temperature for 14 h. Subsequently, benzylazide (80 mg, 0.60 mmol) and K_2CO_3 (83 mg, 0.60 mmol) were added to the above system, and stirred at 80 °C for 11 h. After reaction completion, the mixture was then extracted with EtOAc (15 mL x 3). The organic layers were dried with anhydrous $MgSO_4$, filtered and concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1 to 7:1, V/V) to give the desired product.

(1-Benzyl-5-phenyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methanone, 3a.[5j] Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 7.6 Hz, 2H), 7.60–7.57 (m, 1H), 7.50–7.44 (m, 5H), 7.31–7.27 (m, 5H), 7.09–7.07 (m, 2H), 5.49 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.2, 143.7, 141.7, 137.0, 134.5, 132.8, 130.5, 129.9, 129.6, 128.7, 128.5, 128.3, 128.0, 127.5, 126.2, 51.9.

(1-Benzyl-5-(4-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)(phenyl) methanone, 3b.[5j] Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 7.6 Hz, 2H), 7.60–7.56 (m, 1H), 7.50–7.46 (m, 2H), 7.32–7.30 (m, 3H), 7.23–7.21 (m, 2H), 7.12–7.11 (m, 2H), 6.98–6.96 (m, 2H), 5.49 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.3, 160.7, 143.5, 141.6, 137.1, 134.7, 132.8, 131.1, 130.5, 128.7, 128.3, 128.0, 127.4, 117.9, 114.0, 55.2, 51.7.

(1-Benzyl-5-(*p*-tolyl)-1*H*-1,2,3-triazol-4-yl)(phenyl)methanone, 3c. Yellow solid, m.p. 77–79 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 7.6 Hz, 2H), 7.60–7.56 (m, 1H), 7.50–7.46 (m, 2H), 7.32–7.30 (m, 3H), 7.28–7.26 (m, 2H), 7.19–7.17 (m, 2H), 7.12–7.11 (m, 2H), 5.48 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.2, 143.6, 141.8, 140.1, 137.1, 134.7, 132.8, 130.5, 129.5, 129.2, 128.7, 128.3, 128.0, 127.5, 123.1, 51.7, 21.3. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{23}H_{20}N_3O$: 354.1606, Found: 354.1603.

(1-Benzyl-5-(4-fluorophenyl)-1*H*-1,2,3-triazol-4-yl)(phenyl) methanone, 3d.[12] Yellow solid, m.p. 241–243 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 7.6 Hz, 2H), 7.61–7.58 (m, 1H), 7.51–7.47 (m, 2H), 7.32–7.30 (m, 3H), 7.27–7.24 (m, 2H), 7.16–7.12 (m, 2H), 7.08–7.06 (m, 2H), 5.48 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.2, 163.5 (d, J_{CF} = 251.7 Hz), 143.8, 140.7, 136.8, 134.4, 133.0, 131.8 (d, J_{CF} = 8.6 Hz), 130.5, 128.8, 128.4, 128.1, 127.4, 122.1 (d, J_{CF} = 3.7 Hz), 115.8 (d, J_{CF} = 22.2 Hz), 52.0.

(1-Benzyl-5-(4-chlorophenyl)-1*H*-1,2,3-triazol-4-yl)(phenyl) methanone, 3e.[5j] Yellow solid, m.p. 142–143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 7.6 Hz, 2H), 7.62–7.58 (m, 1H), 7.52–7.48 (m, 2H), 7.44–7.42 (m, 2H), 7.32–7.31 (m, 3H), 7.22–7.20 (m, 2H), 7.09–7.08 (m, 2H), 5.48 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.1, 143.8, 140.6, 136.8, 136.3, 134.3, 133.0, 131.1, 130.6, 128.9, 128.8, 128.5, 128.1, 127.4, 124.6, 52.0.

(1-Benzyl-5-(4-bromophenyl)-1*H*-1,2,3-triazol-4-yl)(phenyl) methanone, **3f.** White solid, m.p. 137–139 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 8.0 Hz, 2H), 7.62–7.58 (m, 3H), 7.52–7.48 (m, 2H), 7.32–7.31 (m, 3H), 7.15–7.13 (m, 2H), 7.09–7.08 (m, 2H), 5.48 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.0, 143.8, 140.6, 136.8, 134.3, 133.0, 131.8, 131.2, 130.6, 128.8, 128.5, 128.1, 127.4, 125.2, 124.6, 52.0. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{22}H_{17}BrN_3O$: 418.0555, Found: 418.0552.

4-(4-Benzoyl-1-benzyl-1*H*-1,2,3-triazol-5-yl)benzonitrile, 3g.[12] Yellow solid, m.p. 165–177 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 7.6 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.64–7.60 (m, 1H), 7.53–7.49 (m, 2H), 7.37–7.27 (m, 5H), 7.03–7.02 (m, 2H), 5.49 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.8, 144.2, 139.8, 136.4, 133.9, 133.3, 132.1, 131.2, 130.6, 130.5, 128.9, 128.7, 128.2, 127.3, 117.8, 113.8, 52.3.

(1-Benzyl-5-(4-nitrophenyl)-1*H*-1,2,3-triazol-4-yl)(phenyl) methanone, 3h.[12] Yellow solid, m.p. 159–162 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 7.6 Hz, 2H), 8.28 (d, *J* = 8.8 Hz, 2H), 7.63–7.60 (m, 1H), 7.52–7.49 (m, 2H), 7.44–7.42 (m, 2H), 7.30–7.27 (m, 3H), 7.04–7.03 (m, 2H), 5.51 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.7, 148.5, 144.3, 139.6, 136.4, 133.9, 133.3, 133.1, 130.9, 130.6, 128.9, 128.7, 128.2, 127.3, 123.5, 52.4.

(1-Benzyl-5-(2-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)(phenyl) methanone, 3i. Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 7.6 Hz, 2H), 7.57–7.53 (m, 1H), 7.47–7.43 (m, 3H), 7.26–7.24 (m, 3H), 7.12–7.10 (m, 1H), 7.05–7.00 (m, 3H),

6.98–6.94 (m, 1H), 5.43 (s, 2H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.3, 156.6, 144.3, 138.5, 137.1, 134.5, 132.6, 131.6, 131.3, 130.4, 128.4, 128.0, 127.9, 127.7, 120.6, 115.3, 111.0, 55.2, 52.1. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{23}H_{20}N_3O_2$: 370.1556, Found: 370.1552.

(1-Benzyl-5-(*m*-tolyl)-1*H*-1,2,3-triazol-4-yl)(phenyl)methanone, 3j. Yellow solid, m.p. 93–96 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 7.6 Hz, 2H), 7.60–7.57 (m, 1H), 7.51–7.47 (m, 2H), 7.37–7.31 (m, 5H), 7.10 (br, 3H), 7.02 (s, 1H), 5.47 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.3, 143.6, 141.9, 138.3, 137.0, 134.7, 132.9, 130.7, 130.5, 130.2, 128.7, 128.4, 128.3, 128.1, 127.6, 126.7, 126.0, 51.9, 21.2. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{23}H_{20}N_3O$: 354.1606, Found: 354.1602.

(1-Benzyl-5-(2,4-dichlorophenyl)-1*H*-1,2,3-triazol-4-yl)(phenyl) methanone, 3k. Yellow solid, m.p. 161–163 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, *J* = 8.0 Hz, 2H), 7.61–7.58 (m, 1H), 7.52–7.47 (m, 3H), 7.29–7.25 (m, 4H), 7.02–6.99 (m, 3H), 5.60 (d, *J* = 14.8 Hz, 1H), 5.30 (d, *J* = 14.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.6, 144.9, 137.8, 136.9, 136.5, 134.7, 133.6, 133.1, 132.2, 130.5, 129.7, 128.7, 128.6, 128.2, 127.8, 127.3, 124.7, 52.6. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{22}H_{16}Cl_2N_3O$: 408.0670, Found: 408.0665.

(1-Benzyl-5-(pyridin-2-yl)-1*H*-1,2,3-triazol-4-yl)(phenyl) methanone, 3l. Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78–8.77 (m, 1H), 8.24 (d, *J* = 8.0 Hz, 2H), 7.74–7.70 (m, 1H), 7.62–7.57 (m, 2H), 7.50–7.46 (m, 2H), 7.38–7.35 (m, 1H), 7.21–7.20 (m, 3H), 7.05–7.04 (m, 2H), 5.88 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.8, 149.3, 146.2, 143.7, 139.1, 136.9, 136.4, 134.6, 133.0, 130.6, 128.5, 128.1, 128.1, 127.8, 126.9, 124.1, 52.6. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{21}H_{17}N_4O$: 341.1402, Found: 341.1400.

1-(1-Benzyl-5-phenyl-1*H*-1,2,3-triazol-4-yl)ethanone, 3m.[5g] Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.42 (m, 3H), 7.28-7.27 (m, 3H), 7.22-7.20 (m, 2H), 7.04-7.03 (m, 2H), 5.43 (s, 2H), 2.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.6, 143.7, 139.4, 134.5, 129.9, 129.5, 128.7, 128.5, 128.3, 127.4, 125.9, 51.8, 27.8.

(1-(4-methoxybenzyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)(phenyl) methanone, 3n.[12] White solid, m.p. 114–117 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 7.6 Hz, 2H), 7.59–7.56 (m, 1H), 7.51–7.46 (m, 5H), 7.30–7.28 (m, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 5.42 (s, 2H) 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.2, 159.5, 143.7, 141.4, 137.0, 132.8, 130.5, 129.8, 129.7, 129.1, 128.5, 128.0, 126.5, 126.4, 114.0, 55.1, 51.4.

(1-(4-Methylbenzyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)(phenyl) methanone, 3o. White solid, m.p. 123–124 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 7.6 Hz, 2H), 7.60–7.57 (m, 1H), 7.50-7.45 (m, 5H), 7.31–7.27 (m, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 5.45(s, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.3, 143.6, 141.6, 138.2, 137.0, 132.9, 131.5, 130.6, 129.9, 129.7, 129.4, 128.5, 128.1, 127.5, 126.3, 51.7, 21.0. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{23}H_{20}N_3O$: 354.1606, Found: 354.1602.

(1-(4-Chlorobenzyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)(phenyl) methanone, 3p. Yellow solid, m.p. 222–225 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 7.6 Hz, 2H), 7.60–7.56 (m, 1H), 7.51–7.45 (m, 5H), 7.28–7.25 (m, 4H), 7.01 (d, *J* = 8.4 Hz, 2H), 5.44 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.1, 143.7, 141.6, 136.9, 134.4, 132.9, 130.5, 130.0, 129.6, 129.0, 128.9, 128.6, 128.1, 126.1, 51.2. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{22}H_{17}ClN_3O$: 374.1060, Found: 374.1054.

(1-(4-Fluorobenzyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)(phenyl) methanone, 3q. Yellow solid, m.p. 287–288 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 7.6 Hz, 2H), 7.60–7.56 (m, 1H), 7.53–7.45 (m, 5H), 7.28–7.26 (m, 2H), 7.07–7.03 (m, 2H), 6.99–6.95 (m, 2H), 5.45 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.1, 162.5 (d, J_{CF} = 248.1 Hz), 143.7, 141.5, 136.9, 132.9, 130.5, 130.3 (d, J_{CF} = 3.3 Hz), 129.9, 129.6, 129.5, 128.6, 128.1, 126.2, 115.7 (d, J_{CF} = 21.7 Hz), 51.2. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{22}H_{17}FN_3O$: 358.1356, Found: 358.1350.

(1-(4-Nitrobenzyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)(phenyl) methanone, 3r. Yellow solid, m.p. 234–236 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, *J* = 8.0 Hz, 2H), 8.15 (d, *J* = 8.4 Hz, 2H), 7.61–7.57 (m, 1H), 7.53–7.44 (m, 5H), 7.26–7.22 (m, 4H), 5.58 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.0, 147.8, 143.8, 141.8, 141.3, 136.7, 133.1, 130.5, 130.2, 129.4, 128.8, 128.4, 128.1, 125.7, 123.9, 51.0. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{22}H_{17}N_4O_3$: 385.1301, Found: 385.1296.

(1-(3-Methylbenzyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)(phenyl) methanone, 3s. Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 7.6 Hz, 2H), 7.60–7.57 (m, 1H), 7.51–7.44 (m, 5H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.20–7.16 (m, 1H), 7.12–7.10 (m, 1H), 6.90–6.85 (m, 2H), 5.45 (s, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.2, 143.6, 141.7, 138.5, 137.0, 134.4, 132.9, 130.6, 129.9, 129.7, 129.1, 128.6, 128.5, 128.3, 128.1, 126.3, 124.6, 51.9, 21.2. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{23}H_{20}N_3O$: 354.1606, Found: 354.1603.

(1-(3-Chlorobenzyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)(phenyl) methanone, 3t. Yellow solid, m.p. 99–101 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 7.6 Hz, 2H), 7.61–7.57 (m, 1H), 7.52-7.46 (m, 5H), 7.29–7.21 (m, 5H), 7.05 (s, 1H), 6.96–6.94 (m, 1H), 5.45 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.1, 143.7, 141.7, 136.9, 136.3, 134.6, 132.9, 130.5, 130.1, 130.0, 129.5, 128.7, 128.6, 128.1, 127.8, 126.0, 125.7, 51.2. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{22}H_{17}ClN_3O$: 374.1060, Found: 374.1052.

(1-(2-Methylbenzyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)(phenyl) methanone, 3u. White solid, m.p. 270–272 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 7.6 Hz, 2H), 7.61–7.57 (m, 1H), 7.51–7.42 (m, 5H), 7.28–7.27 (m, 2H), 7.20–7.18 (m, 1H), 7.15–7.08 (m, 2H), 6.78–6.76 (m, 1H), 5.49 (s, 2H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.2, 143.6, 141.8, 137.0, 135.5, 132.9, 132.8, 130.6, 130.4, 129.8, 129.5, 128.5, 128.3, 128.1, 127.7, 126.3, 126.3, 49.6, 18.9. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{23}H_{20}N_3O$: 354.1606, Found: 354.1601.

(1-(2-Chlorobenzyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)(phenyl) methanone, 3v. Yellow solid, m.p. 142–146 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 7.6 Hz, 2H), 7.61–7.58 (m, 1H), 7.52–7.42 (m, 5H), 7.37–7.35 (m, 1H), 7.30–7.26 (m, 2H), 7.24–7.21 (m, 2H), 6.95–6.93 (m, 1H), 5.62 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$):

δ 186.2, 143.5, 142.1, 136.9, 132.9, 132.5, 130.6, 130.0, 129.5, 129.5, 129.4, 128.7, 128.6, 128.1, 127.2, 126.3, 125.9, 49.2. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{22}H_{17}ClN_3O$: 374.1060, Found: 374.1050.

2-((4-Benzoyl-5-phenyl-1*H*-1,2,3-triazol-1-yl)methyl) benzonitrile, 3w. Yellow solid, m.p. 209–212 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 7.6 Hz, 2H), 7.62–7.54 (m, 3H), 7.50–7.41 (m, 6H), 7.28–7.26 (m, 2H), 7.15–7.13 (m, 1H), 5.72 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.0, 143.7, 142.1, 137.9, 136.8, 133.3, 133.0, 132.8, 130.5, 130.2, 129.3, 128.8, 128.8, 128.2, 128.1, 125.5, 116.2, 111.3, 49.6. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{23}H_{17}N_4O$: 365.1402, Found: 365.1395.

1-(1,5-diphenyl-1H-1,2,3-triazol-4-yl)ethanone, 3x.[6i] Yellow solid, m.p. 103–106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.34 (m, 6H), 7.30–7.26 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.8, 143.5, 139.0, 135.8, 130.2, 129.9, 129.4, 129.3, 128.3, 125.7, 125.2, 28.3.

(1-(Naphthalen-1-ylmethyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl) (phenyl)methanone, 3y. Yellow solid, m.p. 213–216 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 7.6 Hz, 2H), 8.00–7.98 (m, 1H), 7.89–7.87 (m, 1H), 7.83–7.81 (m, 1H), 7.61–7.58 (m, 1H), 7.53–7.48 (m, 6H), 7.43–7.41 (m, 2H), 7.31–7.27 (m, 2H), 6.84–6.83 (m, 1H), 5.99 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.2, 143.6, 142.1, 137.0, 133.5, 132.9, 130.6, 130.4, 130.0, 129.9, 129.5, 129.2, 128.8, 128.6, 128.1, 126.8, 126.4, 126.3, 126.0, 125.0, 122.6, 50.0. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{26}H_{20}N_3O$: 390.1606, Found: 390.1604.

(1-(4-(Azidomethyl)benzyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl) (phenyl)methanone, 3z. Yellow solid, m.p. 158–160 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 7.6 Hz, 2H), 7.60–7.56 (m, 1H), 7.50–7.43 (m, 5H), 7.27–7.23 (m, 4H), 7.08 (d, *J* = 8.0 Hz, 2H), 5.48 (s, 2H), 4.31 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.2, 143.7, 141.7, 136.9, 135.6, 134.6, 132.9, 130.5, 130.0, 129.6, 128.6, 128.5, 128.1, 128.0, 126.1, 54.0, 51.5. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{23}H_{19}N_6O$: 395.1620, Found: 395.1616.

(1-((4'-(Azidomethyl)-[1,1'-biphenyl]-4-yl)methyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methanone, 3aa. Yellow solid, m.p. 99–101 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 7.6 Hz, 2H), 7.59–7.57 (m, 3H), 7.54–7.48 (m, 7H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 7.2 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.53 (s, 2H), 4.38 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.2, 143.7, 141.7, 140.5, 140.1, 137.0, 134.6, 133.7, 132.9, 130.6, 130.0, 129.7, 128.6, 128.6, 128.1, 127.4, 127.3, 126.2, 54.3, 51.6. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{29}H_{23}N_6O$: 471.1933, Found: 471.1929.

Notes and References

1 (*a*) H. C. Kolb and K. B. Sharpless, *Drug Discovery Today*, 2003, **8**, 1128; (*b*) P. Wu, A. K. Feldman, A. K. Nugent, C. J. Hawker, A. Scheel, B. Voit, J. Pyun, J. M. J. Frechet, K. B. Sharpless and V. V. Fokin, *Angew. Chem., Int. Ed.*, 2004, **43**, 3928; (*c*) N. J. Agard, J. A. Prescher and C. R.Bertozzi, *J. Am. Chem. Soc.*, 2004, **126**, 15046; (*d*) M. I. Garcia-Moreno, D. Rodriguez-Lucena, C. O. Mellet and J. M. G. Fernandez, *J. Org. Chem.*, 2004, **69**, 3578; (*e*) M. Meldal and C. W. Tornoe, *Chem. Rev.*, 2008, **108**, 2952; (*f*) S. Wacharasindhu, S. Bardhan, Z.-K. Wan, K. Tabei and T. S. Mansour, *J. Am. Chem. Soc.*, 2009, **131**, 4174; (*g*) C.-B. Yim, I. Dijkgraaf, R. Merkx, C. Versluis, A. Eek, G. E. Mulder, D. T. S. Rijkers, O. C. Boerman and R. M. J. Liskamp, *J. Med. Chem.*, 2010, **53**, 3944; (*h*) R. P. Tripathi, A. K. Yadav, A. Ajay, S. S. Bisht, V. Chaturvedi and S. K. Sinha, *Eur. J. Med. Chem.*, 2010, **45**, 142.

2 (*a*) R. Manetsch, A. Krasiski, Z. Radi, J. Raushel, P. Taylor, K. B. Sharpless and H. C. Kolb, *J. Am. Chem. Soc.*, 2004, **126**, 12809; (*b*) J. Wang, G. Sui, V. P. Mocharla, R. J. Lin, M. E. Phelps, H. C. Kolb and H.-R. Tseng, *Angew. Chem., Int. Ed.*, 2006, **45**, 5276; (*c*) A. Sugawara, T. Sunazuka, T. Hirose, K. Nagai, Y. Yamaguchi, H. Hanaki, K. B. Sharpless and S. Omura, *Bioorg. Med. Chem. Lett.*, 2007, **17**, 6340; (*d*) H. Chen, J. L. Taylor and S. R. Abrams, *Bioorg. Med. Chem. Lett.*, 2007, **17**, 1979; (*e*) V. D. Bock, D. Speijer, H. Hiemstra and J. H. Van Maarseveen, *Org. Biomol. Chem.*, 2007, **5**, 971.

3 (*a*) A. Michael, *J. Prakt. Chem.*, 1893, **48**, 94; (*b*) R. Huisgen, *Angew. Chem., Int. Ed.*, 1963, **2**, 565; (*c*) R. Huisgen, *Angew. Chem., Int. Ed.,* 1963, **2**, 633.

4 (*a*) V. V. Rostovtsev, L. G. Green, V. V. Fokin and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2002, **41**, 2596; (*b*) H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2001, **40**, 2004; (*c*) A. E. Cohrt, J. F. Jensen and T. E. Nielsen, *Org. Lett.*, 2011, **12**, 5414; (*d*) P. Wu and V. V. Fokin, *Aldrichimica Acta*, 2007, **40**, 7; (e) L. Zhang, X. G. Chen, P. Xue, H. H. Y. Sun, I. D. Williams, K. B. Sharpless, V. V. Fokin and G. C. Jia, *J. Am. Chem. Soc.,* 2005, **127**, 15998; (f) M. M. Majireck and S. M. Weinreb, *J. Org. Chem.,* 2006, **71**, 8680; (g) A. Tam, U. Arnold, M. B. Soellner and R. T. Raines, *J. Am. Chem. Soc.,* 2007, **129**, 12670.

5 (*a*) Y. Tanaka and S. I. Miller, *J. Org. Chem.*, 1972, **37**, 3370; (*b*) V. R. Kamalraj, S. Senthil and P. Kannan, *J. Mol. Struct.*, 2008, **892**, 210; (*c*) J. E. Hein, J. Tripp, L. Krasnova, K. B. Sharpless and V. V. Fokin, *Angew. Chem., Int. Ed.*, 2009, **48**, 8018; (*d*) T. J. Donohoe, J. F. Bower, D. B. Baker, J. A. Basutto, L. K. Chan and P. Gallagher, *Chem. Commun.,* 2011, **47**, 10611; (*e*) J. Zhang, J. Wu, L. Shen, G. Jin and S. Cao, *Adv. Synth. Catal.*, 2011, **353**, 580; (*f*) Y. Zhang, X. Li, J. Li, J. Chen, X. Meng, M. Zhao and B. Chen, *Org. Lett.*, 2012, **14**, 26; (*g*) D. Janreddy, V. Kavala, C.-W. Kuo, W.-C. Chen, C. Ramesh, T. Kotipalli, T.-S. Kuo, M.-L. Chen, C.-H. He and C.-F. Yao, *Adv. Synth. Catal.*, 2013, **355**, 2918; (*h*) Z. Chen, Q. Yan, Z. Liu, Y. Xu and Y. Zhang, *Angew. Chem., Int. Ed.*, 2013, **52**, 13324; (i) J. Zhang and C.-W. T. Chang, *J. Org. Chem.*, 2009, **74**, 685. (j) Y.-C. Wang, Y.-Y. Xie, H.-E. Qu, H.-S. Wang, Y.-M. Pan and F.-P. Huang, *J. Org. Chem.*, 2014, **79**, 4463.

6. (a) D. B. Ramachary, K. Ramakumar and V. V. Narayana, *Chem. Eur. J.*, 2008, **14**, 9143; (b) L. J. T. Danence, Y. Gao, M. Li, Y. Huang and J. Wang, *Chem. Eur. J.*, 2011, **17**, 3584; (c) S. Zeghada, G. Bentabed-Ababsa, A. Derdour, S. Abdelmounim, L. R. Domingo, J. A. Sáez, T. Roisnel, E. Nassare and F. Mongin, *Org. Biomol. Chem.*, 2011, **9**, 4295; (d) M. Belkheira, D. E. Abed, J.-M. Pons and C. Bressy, *Chem. Eur. J.*, 2011, **17**, 12917; (e) L. Wang, S. Peng, L. J. T. Danence, Y. Gao and J. Wang, *Chem. Eur. J.*, 2012, **18**, 6088; (f) N. Seus, L. C. Goncalves, A. M. Deobald, L. Savegnago, D. Alves and M.W. Paixao, *Tetrahedron*, 2012, **68**, 10456; (g) D. B. Ramachary and A. B. Shashank, *Chem. Eur. J.*, 2013, **19**, 13175; (h) W. Li, Q. Jia, Z. Du and J. Wang, *Chem. Commun.*, 2013, **49**, 10187. (i) L. Li and J. Wang, *Angew. Chem., Int. Ed.*, 2014, **53**, 14186.

(7) J. Thomas, J. John, N. Parekh and W. Dehaen, *Angew. Chem., Int. Ed.*, 2014, **53**, 10155.

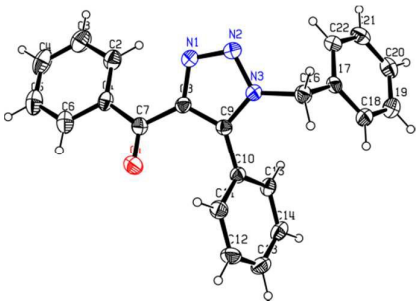
(8) X.-J. Quan, Z.-H. Ren, Y.-Y. Wang and Z.-H. Guan, *Org. Lett.*, 2014, **16**, 5728.

(9) (a) S. S. Berkel, S. Brauch, L. Gabriel, M. Henze, S. Stark, D. Vasilev, L. A. Wessjohann, M. Abbas and B. Westermann, *Angew. Chem., Int. Ed.*, 2012, **51**, 5343; (b) Z.-J. Cai, X.-M. Lu, Y. Zi, C. Yang, L.-J. Shen, J. Li, S.-Y. Wang and S.-J. Ji, *Org. Lett.*, 2014, **16**, 5108; (c) H.-W. Bai, Z.-J. Cai, S.-Y. Wang and S.-J. Ji, *Org. Lett.*, 2015, **17**, 2898.

10 (*a*) X. Sun, P. Li, X. Zhang and L. Wang, *Org. Lett.*, 2014, **16**, 2126; (*b*)X. Sun, P. Li, X. Zhang and L. Wang, *Green Chem.*, 2013, **15**, 3289; (*c*) J. Liu, P. Li, W, Chen and L. Wang, *Chem. Commun.*, 2012, **48**, 10052; (*d*) X. Zhang and L. Wang, *Green Chem.*, 2012, **14**, 2141; (*e*) S. Wang, P. Li, L. Yu and L. Wang, *Org. Lett.*, 2011, **13**, 5968; (*f*) T. He, L.

Yu, L. Zhang and L. Wang, *Org. Lett.*, 2011, **13**, 5016; (*g*) T. He, H. Li, P. Li and L. Wang, *Chem. Commun.*, 2011, **47**, 8946.

11 X-Ray single crystal structure of **3a** (CCDC 1431855).



12 Y.-Y. Xie, Y.-C. Wang, H.-E. Qu, X.-C. Tan, H.-S. Wang and Y.-M. Pan, *Adv. Synth. Catal.*, 2014, **356**, 3347.