J. Chem. Sci. (2019) 131:55
https://doi.org/10.1007/s12039-019-1631-8

REGULAR ARTICLE

Metal-free selective aryl C–H formylation co-controlled by 1,2,3-triazole and hydroxyl using DMSO as formyl source

XINYUAN MA[a], WEIGEN DU[a], WEI LIU[b], YAOWEN LIU[a], TIEBO XIAO[a,*] and YUBO JIANG[a,*]

[a]Faculty of Science, Kunming University of Science and Technology, Kunming 650500, China
[b]School of Pharmacy, Nantong University, Nantong 226001, China
E-mail: xiaotb@kmust.edu.cn; ybjiang@kmust.edu.cn

MS received 12 February 2019; revised 5 April 2019; accepted 16 April 2019; published online 21 June 2019

Abstract. A facile and efficient method for direct C–H formylation of phenolated 1,4-disubstituted 1,2,3-triazoles using DMSO as the formyl source has been developed. The reaction proceeded smoothly under metal-free conditions with good functional group tolerance and high selectivity co-controlled by the triazole ring and hydroxyl group.

Keywords. 1,4-disubstituted 1,2,3-triazoles; metal-free; C–H formylation; site-selective; DMSO.

1. Introduction

The formylation reaction is an important transformation in organic synthesis.[1,2] Due to the remarkable application value in chemistry, formylation of arene has attracted much interest of organic chemists. Traditionally, the most classical methods include Vilsmeier–Haack,[3–5] Duff reaction,[6–8] Reimer Tiemann,[9,10] Rieche[11] and Friedel–Crafts acylations.[12,13] Nevertheless, these reactions generally require excess strong bases or acids in workup processes and are unfriendly to the environment. Therefore, the development of a facile and mild formylation method is a challenge for synthetic organic chemists. In recent years, dimethyl sulfoxide (DMSO) has been widely used as an important carbon source which has provided new transformations for the formation of carbon-carbon bonds to prepare formyl heteroarene molecules.[14] The Pummerer reaction in which DMSO is involved can deliver the formylation product with acidic activators.[15] In 2013, Cheng group reported the ammonium-promoted formylation of indoles by DMSO and H_2O.[16] Dimethyl sulfoxide participated oxidation/α-formylation reaction of substituted 2,3-dihydropyrroles under air and protonic acid-free condition *via* iron-mediated cascade reaction was developed by Zhang.[17] Cao and other coworkers reported selective C(3)-formylation of imidazo[1, 2-*a*]pyridine C–H bonds with DMSO using molecular oxygen and Cu-catalyst.[18] Based on these developments, focus on highly efficient formylation of varied substrates is worthy of further exploration using DMSO as a carbonyl reagent.

Over the last few decades, 1,2,3-triazoles[19,20] have been found as an important and most useful class of five-membered heterocycles which possess a plethora of applications in broad fields such as materials chemistry,[21] biological science,[22] food-additive studies,[23] and organic synthesis[24] owing to their structural characteristics. Research shows that the 1,2,3-triazoles, as an important structural motif, possess extensive biological activities and potential medical values, such as *anti*-Alzheimer's, *anti*-diabetic, *anti*-cancer and *anti*-HIV activities.[25–28] On the other hand, the broad range of applications has accelerated the development for the construction of various 1,2,3-triazoles, especially with complicated structures. Meanwhile, transition metal-catalyzed C–H bond functionalization has emerged as a powerful strategy for the straightforward elaboration of 1,2,3-triazoles. Ackermann and some other researchers had demonstrated regioselective arylations on the C(5) position of 1,4-disubstituted 1,2,3-triazoles via Cu/Pd-catalyzed procedures.[29] At a similar time,

*For correspondence

Electronic supplementary material: The online version of this article (https://doi.org/10.1007/s12039-019-1631-8) contains supplementary material, which is available to authorized users.

Table 1. Selected optimization of the reaction conditions.[a,b]

1a **2a**

Entry	Catalyst	Acid	Temp. (°C)	Time (h)	Yield (%)
1	$Cu(OAc)_2$	PivOH	140	12	13
2	CuI	PivOH	140	12	16
3	$CuCl_2$	PivOH	140	12	18
4	CuSCN	PivOH	140	12	21
5	CuCl	PivOH	140	12	24
6	CuO	PivOH	140	12	25
7	$Cu(OTf)_2$	PivOH	140	12	26
8	–	PivOH	140	12	32
9	–	AcOH	140	12	23
10	–	CF_3COOH	140	12	29
11	–	CF_3SO_3H	140	12	23
12	–	$C_6F_{13}COOH$	140	12	21
13	–	–	140	12	39
14	–	–	140	24	44
15	–	–	140	60	67
16	–	–	140	48	78
17	–	–	120	48	32
18	–	–	160	48	43
19[c]	–	–	140	48	54
20[d]	–	–	140	48	27

[a] Reaction conditions unless noted: 2-(4-(*p*-tolyl)-1*H*-1,2,3-triazol-1-yl)phenol (**1a**, 0.5 mmol) was added to the DMSO (3 mL) and then heated for 48 h. [b] Isolated yields. [c] O_2. [d] N_2.

the Rh- and Ru-catalyzed alkenylation of *ortho* C–H bonds on C(1) or C(4) aryl positions of 1,4-disubstituted 1,2,3-triazoles were also explored.[30,31] Additionally, our group are interested in Pd-catalyzed sp^2 C–H activation reaction and have reported selective arylation, nitration, alkoxylation, acetoxylation, acylation, chlorination and cyclization of 1,4-disubstituted 1,2,3-triazoles with good to excellent yields.[32] As far as we know, although a great deal of work has been done on the triazole modification, there is no report about the selective C–H formylation under metal-free condition. Herein, we present a convenient metal-free C–H bond functionalization approach for the selective formylation of phenolated 1,4-disubstituted 1,2,3-triazoles using DMSO as a formyl source.

2. Experimental

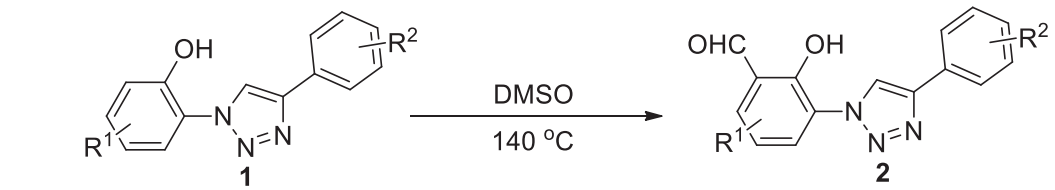
2.1 *Materials and methods*

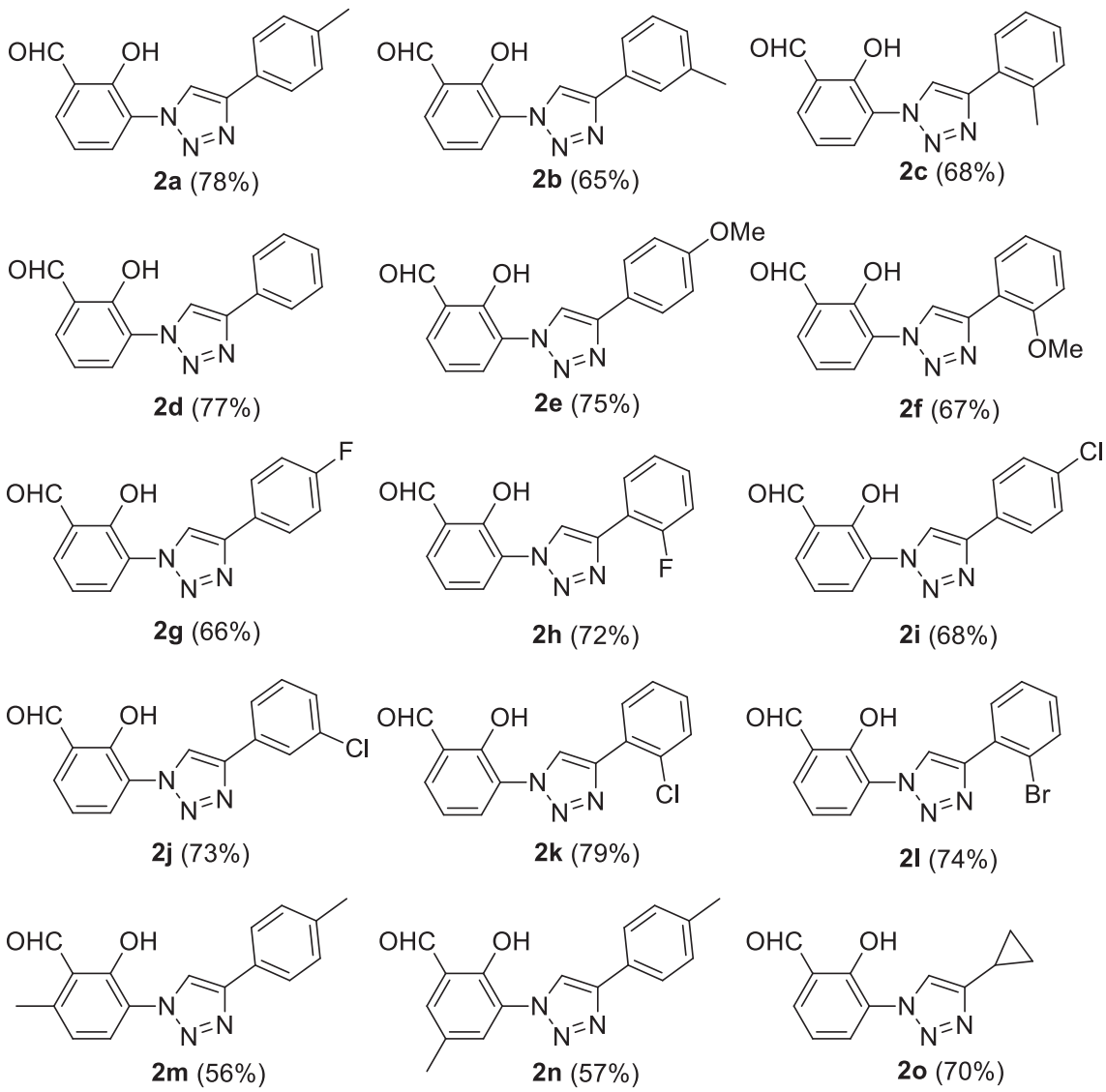
All solvents and reagents were purchased from the suppliers and used without further purification. ^1H NMR and ^{13}C NMR were recorded in $CDCl_3$ at room temperature on Bruker spectrometer (500 MHz or 600 MHz). The chemical-shifts scale is based on internal TMS. All reactions were monitored by TLC with Huanghai GF 254 silica gel coated plates. Column chromatography was carried out using 300–400 mesh silica gel at medium pressure. Infrared spectra were taken on a Bruker Vertex Series FTIR (KBr) and are reported in reciprocal centimetres (cm^{-1}).

2.2 *General synthetic procedures*

2-(4-(*p*-Tolyl)-1*H*-1,2,3-triazol-1-yl)phenol **1a** (0.5 mmol) and DMSO (3 mL) were sequentially added to a 15 mL pressure tube. Then the tube was sealed and stirred at 140 °C for 48 h. After consumption of the 1,4-disubstituted 1,2,3-triazoles monitored by TLC analysis, H_2O (15 mL) was added to the mixture and extracted with EtOAc in 3 times (3 x 15 mL). The combined organic layers were washed with brine (3 x 5 mL), dried with Na_2SO_4, and concentrated under reduced pressure to afford the crude product. Purification by column chromatography on silica gel with EtOAc-PE (1:8) afforded the desired product **2a**.

Table 2. Substrates scope of 1,4-disubstituted 1, 2, 3-triazoles.[a,b]





[a] Reaction conditions: 0.5 mmol of **1** was added to DMSO (3 mL) and then stirred at 140 °C for 48 h. [b] Yield of isolated product after column chromatography.

3. Results and Discussion

Initially, we tested the reaction of 2-(4-(*p*-tolyl)-1*H* -1, 2,3-triazol-1-yl)phenol (**1a**) as a model to compose 2-hydroxy-3-(4-(*p*-tolyl)- 1*H*-1,2,3- triazol-1-yl) benzaldehyde (**2a**). The treatment of **1a** (1.0 equiv.) in the presence of $Cu(OAc)_2$ (20 mol%) and pivalic acid (PivOH, 1.0 equiv.) at 140 °C for 12 h generated the formylation product **2a** in 13% yield (Table 1, entry 1). Intrigued by this experimental observation, we decided to optimize the conditions. The results from the optimization studies are summarized in Table 1. Starting from the conditions in entry 1, we screened various catalysts and found that other catalysts including CuI, $CuCl_2$, CuCl, etc., are less effective than the catalyst-free conditions (Table 1, entries 2–8). As for acids tested, others such as AcOH, CF_3COOH, CF_3SO_3H and $C_6F_{13}COOH$ were inconspicuous in this procedure

(Table 1, entries 9–12). To our delight, **2a** was still generated in a higher yield of 39% without any acid (Table 1, entry 13). Reaction time also had a significant effect on the formylation reaction and the product was obtained in 78% yield at 48 h (Table 1, entries 14–16). Additional optimization revealed that the yield decreased gradually upon increasing or decreasing the temperature (Table 1, entries 17–18). When using O_2 or N_2 instead of air, there was no significant improvement in the yield of **2a** (Table 1, entries 19–20). These preliminary experiments clearly revealed that the best way to proceed with the formylation of 2-(4-(*p*-tolyl)-1*H*-1,2,3-triazol-1-yl)phenol is using DMSO as the solvent at 140 °C for 48 h.

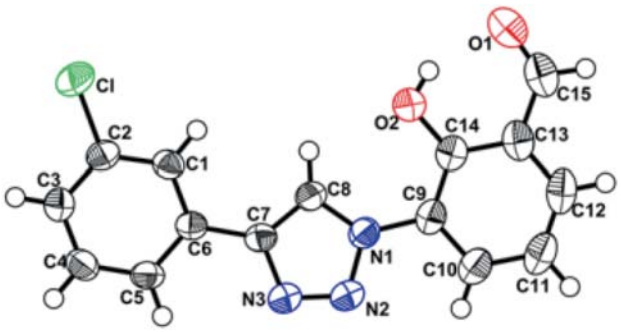
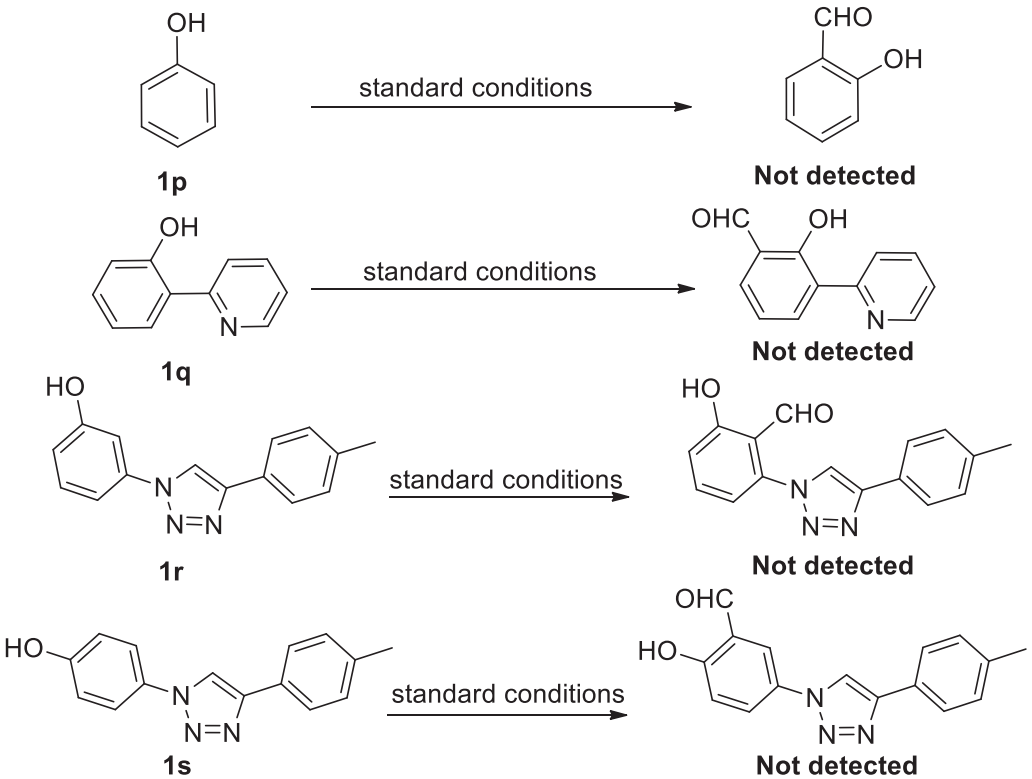
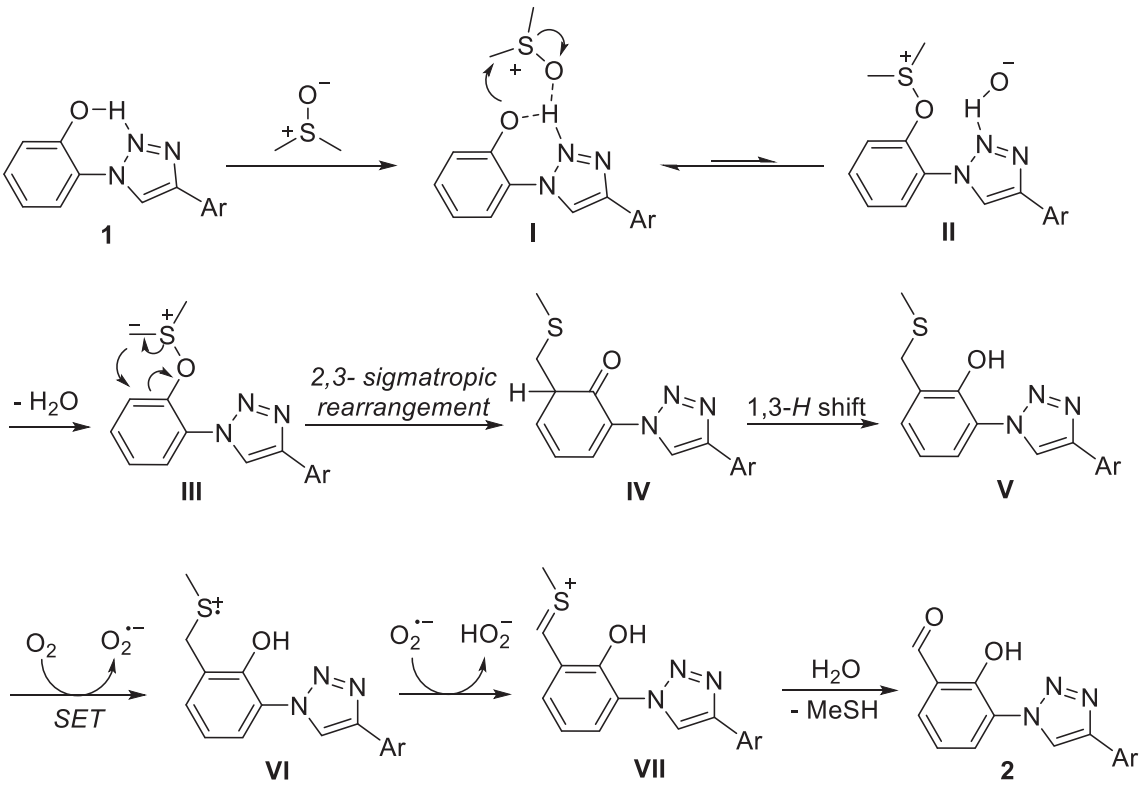


Figure 1. X-ray structure of compound **2j**.

With the optimized reaction conditions in hand, we proceeded to survey the scope of the reaction (Table 2). In general, both electron-donating and electron-withdrawing groups on the aromatic moiety were tolerated well under this procedure (Table 2, **2a**–**2o**). 1,2,3-triazoles with electron-donating groups on C(4) aryl are applicable and gave the corresponding products in 65–78% isolated yields (Table 2, **2a**–**2c** and **2e**–**2f**). By comparison, it is found that the yields of substrates with an electron donor group in the *para* position of C(4) aryl were higher than those of other cases (Table 2, **2a** *vs.* **2b** and **2c**; **2e** *vs.* **2f**). Notably, fluoro, chloro and bromo functional groups could all survive well under the standard procedures, offering handles for further functionalization (Table 2, **2g**–**2l**). Interestingly, contrary to the cases of compounds with an electron-donating group, the yields of substrates with a halogen in the*ortho* or *meta* position of C(4) aryl were higher (Table 2, **2h** *vs.* **2g**; **2k** and **2j** *vs.* **2i**). While molecules with –Cl at the *ortho*-position of C(4) aryl resulted in a higher yield than those bearing -F or -Br (Table 2, **2k** *vs.* **2h** and **2l**). The substrates contained -CH_3 group on the N(1) aryl of the 1, 2, 3-triazole could deliver the desired products in moderate yields, although the C(4) aryl group of the heterocycle had an electron-donating group (Table 2, **2m** and **2n**). Regrettably, the reaction proved to be incompatible with phenol ring equipped with groups such as



Scheme 1. Control experiments.



Scheme 2. Plausible mechanism.

mate-$COOCH_3$, *mate*-Cl or *ortho*-Cl. To our delight, except 4-aryl 1,2,3-triazoles, 4-cyclopropyl substrate could also go smoothly under the standard conditions and deliver the target molecule in 70% yield (Table 2, **2o**). In addition, the C(4) aromatic ring of 1,2,3-triazoles bearing NO_2 or OH, and C(4) pyridine, thiophene substituted 1,2,3-triazoles were also examined, but there were no target products detected under the standard conditions.

To confirm the site-selectivity and target structure, we further tested the X-ray single diffraction of corresponding product **2j** (CCDC reference number 1884642)[33] except the NMR data analysis, which approved the product unambiguously (Figure 1).

In order to shed light on the co-controlling role of the triazole ring and hydroxyl group in the effect of site-selectivity, several control reactions were conducted (Scheme 1). When we chose phenol or 2-(pyridin-2-yl)phenol as the substrate (Scheme 1, **1p** and **1q**), there were no formylation products observed under the optimal conditions, indicating that the 1,2,3-triazole ring is indispensable for the transformation. In addition, if the hydroxyl was fixed at *meta*- or *para*- other than *ortho*-position of N(1) aryl of the substrates (Scheme 1, **1r** and **1s**), no target molecules were detected in the system, which states that the adjacent hydroxyl group of the heterocycle is another key factor for the formylation process.

On the basis of all the experimental results described above together with literature reports,[34] a reasonable mechanism of this transformation is proposed in Scheme 2. First, compound **1**, which has an intramolecular hydrogen bond, could react with solvent DMSO to form intermediate **I**, thus enhancing the nucleophilicity of phenoxy atom. Nucleophilic substitution between phenoxy atom and DMSO gave intermediate **II**, which can lose a molecule of water to afford intermediate **III**. Intermediate **III** subsequently underwent [2,3]-sigmatropic rearrangement to intermediate **IV** that can readily convert to intermediate **V** through 1,3-*H* migration. Single electron oxidation of intermediate **V** by oxygen generated intermediate **VI** and oxygen radical anion, which can undergo hydrogen abstraction to provide **VII**. Intermediate**VII** is ultimately hydrolyzed to yield the desired formylated product **2**.

4. Conclusions

In conclusion, we have developed a regioselective efficient metal-free protocol for formylation of phenolated 1,4-disubstituted substrates using DMSO as both solvent and formyl carbon donor without any other additives, generating a broad range of formylated 1,2,3-triazole derivatives. Under the co-controlling effect, the clean system provides facile access to highly

functionalized 1,2,3-triazole derivatives bearing both formyl and hydroxyl groups on N(1) aryl, which may have a wide range of potential application values.

Supplementary Information (SI)

All the spectra are available at www.ias.ac.in/chemsci.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (Nos. 21662020 and 21801101) and the Analysis and Testing Fund of Kunming University of Science and Technology (No. 2017M20162111052).

References

1. Olah G A, Ohannesianm L and Arvanaghi M 1987 Formylating agents *Chem. Rev.* **87** 671
2. Zhu C, Pinkert T, Greßies S and Glorius F 2018 One-pot C–H formylation enabled by relay catalysis of manganese(I) and iron(III) *ACS Catal.* **8** 10036
3. Lauchli R and Shea K J 2006 A synthesis of the welwistatin core *Org. Lett.* **8** 5287
4. Roudias M, Vallée F, Martel J and Paquin J -F 2018 Use of XtalFluor-E as an alternative to $POCl_3$ in the Vilsmeier-Haack formylation of C-2-glycals *J. Org. Chem.* **83** 8731
5. Zaman A, Ahmad I, Pervaiz M, Ahmad S, Kiran S, Khan M A, Gulzar T and Kamal T 2019 A novel synthetic approach for the synthesis of pyrano[3, 2-c] quinolone-3carbaldehydes by using modified Vilsmeier Haack reaction, as potent antimicrobial agents *J. Mol. Struct.* **1180** 227
6. Duff J C and Bills E J 1932 Reactions between hexamethylenetetramine and phenolic compounds. Part I. A new method for the preparation of 3- and 5-aldehydosalicylic acids *J. Chem. Soc.* 1987
7. Grimblat N, Sarotti A M, Kaufman T S and Simonetti S O 2016 A theoretical study of the Duff reaction: insights into its selectivity *Org. Biomol. Chem.* **14** 10496
8. Weclawski M K, Deperasińska I, Leniak A, Banasiewicz M, Kozankiewicz B and Gryko D T 2016 Unexpected formation of π-expanded isoquinoline from anthracene possessing four electron-donating groups via the Duff reaction *Org. Biomol. Chem.* **14** 7046
9. Yamabe S and Fukuda T 2011 A significant role of alkaline cations on the Reimer-Tiemann reaction *Org. Biomol. Chem.* **9** 5109
10. Ren S, Wu Z, Guo Q and Shen B 2015 Zeolites as shape-selective catalysts: highly selective synthesis of vanillin from Reimer–Tiemann reaction of guaiacol and chloroform *Catal. Lett.* **145** 712
11. Kolanowska A, Kuziel A, Li Y, Jurczykb S and Boncel S 2017 Rieche formylation of carbon nanotubes—one-step and versatile functionalization route *RSC Adv.* **7** 51374
12. Katritzky A R, Suzuki K, Singh S K and He H -Y 2003 Regiospecific *C*-acylation of pyrroles and indoles using *N*-acylbenzotriazoles *J. Org. Chem.* **68** 5720
13. Chakiri A B and Hodge P 2017 Synthesis of isopropyl-substituted anthraquinones via Friedel–Crafts acylations: migration of isopropyl groups *R. Soc. Open Sci.* **4** 170451
14. (a) Qian J, Zhang Z, Liu Q, Liu T and Zhang G 2014 Dimethyl sulfoxide participating in copper(I) iodide-catalyzed cascade oxidation/formylation reactions: the synthesis of *a*-formylpyrroles from 2, 3-dihydro-1*H*-pyrroles *Adv. Synth. Catal.* **356** 3119; (b) Cui X, Zhang Y, Deng Y and Shi F 2014 Amine formylation via carbon dioxide recycling catalyzed by a simple and efficient heterogeneous palladium catalyst *Chem. Commun.* **50** 189
15. (a) Pummerer R 1909 Uber phenyl-sulfoxyessigsaure *Ber. Dtsch. Chem. Ges.* **42** 2282; (b) Bur S K and Padwa A 2004 The Pummerer reaction: methodology and strategy for the synthesis of heterocyclic compounds *Chem. Rev.* **104** 2401; (c) Hu G, Xu J and Li P 2018 Synthesis of *N*-alkylated 2-pyridones through Pummerer type reactions of activated sulfoxides and 2-fluoropyridine derivatives *Org. Biomol. Chem.* **16** 4151
16. Parnes R, Reiss H and Pappo D 2018 $Cu(OTf)_2$-catalyzed Pummerer coupling of β-ketosulfoxides *J. Org. Chem.* **83** 723
17. Zhang Z, Tian Q, Qian J, Liu Q, Liu T, Shi L and Zhang G 2014 Dimethyl sulfoxide participant iron-mediated cascade oxidation/α-formylation reaction of substituted 2, 3-dihydropyrroles under air and protonic acid free condition *J. Org. Chem.* **79** 8182
18. Cao H, Lei S, Li N, Chen L, Liu J, Cai H, Qiu S and Tan J 2015 Cu-catalyzed selective C_3-formylation of imidazo[1, 2-*a*]pyridine C–H bonds with DMSO using molecular oxygen *Chem. Commun.* **51** 1823
19. (a) Rostovtsev V V, Green L G, Fokin V V and Sharpless B K 2002 A stepwise huisgen cycloaddition process: copper(I)-catalyzed regioselective "ligation" of azides and terminal alkynes *Angew. Chem. Int. Ed.* **41** 2596; (b) Deraedt C, Pinaud N and Astruc D 2014 Recyclable catalytic dendrimer nanoreactor for part-per-million CuI catalysis of "click" chemistry in water *J. Am. Chem. Soc.* **136** 12092; (c) Song W and Zheng N 2017 Iridium-catalyzed highly regioselective azide-ynamide cycloaddition to access 5-amido fully substituted 1, 2, 3-triazoles under mild, air, aqueous, and bioorthogonal conditions *Org. Lett.* **19** 6200; (d) Luo G, Sun C, Li Y, Li X and Zhao Z 2018 N_2-Selective alkylation of NH-1, 2, 3-triazoles with vinyl ethers via gold catalysis *RSC Adv.* **8** 27610
20. (a) Yu X, Huang Z, Liu W, Shi S and Kuang C 2015 Palladium-catalyzed oxidative C–H/C–H cross-coupling of 1-substituted 1, 2, 3-triazoles with furans and thiophenes *Org. Biomol. Chem.* **13** 4459; (b) He P, Tian Q and Kuang C 2015 Palladium-catalyzed *ortho*-C–H alkenylation of 2-benzyl-1, 2, 3-triazoles *Org. Biomol. Chem.* **13** 7146
21. (a) He C and Shreeve J M 2015 Energetic materials with promising properties: synthesis and characterization of 4, 4'-bis(5-nitro-1, 2, 3-2*H*-triazole) derivatives *Angew. Chem. Int. Ed.* **54** 6260; (b) Johansson J R, Beke-Somfai T, Stalsmeden A S and Kann N 2016 Ruthenium-catalyzed azide alkyne cycloaddition reaction: scope, mechanism, and applications *Chem. Rev.* **116** 14726
22. (a) Emileh A, Duffy C, Holmes A P, Bastian A R, Aneja R, Tuzer F, Rajagopal S, Li H, Abrams C F and Chaiken I M 2014 Covalent conjugation of a peptide triazole to

HIV1 gp120 enables intramolecular binding site occupancy *Biochemistry* **53** 3403; (b) Kuntala N, Telu J R, Banothu V, Nallapati S B, Anireddy J S and Pal S 2015 Novel benzoxepine-1, 2, 3-triazole hybrids: synthesis and pharmacological evaluation as potential antibacterial and anticancer agents *Med. Chem. Comm.* **6** 1612

23. (a) Kumar P, Joshi C, Srivastava A K, Gupta P, Boukherroub R and Jain S L 2016 Visible light assisted photocatalytic [3 + 2] azide–alkyne "click" reaction for the synthesis of 1, 4-substituted 1, 2, 3-triazoles using a novel bimetallic Ru–Mn complex *ACS Sustain. Chem. Eng.* **4** 69; (b) Rostovskii N V, Ruvinskaya J O, Novikov M S, Khlebnikov A F, Smetanin I A and Agafonova A V 2017 Switchable synthesis of pyrroles and pyrazines via Rh(II)-catalyzed reaction of 1, 2, 3-triazoles with isoxazoles: experimental and DFT evidence for the 1, 4-diazahexatriene intermediate *J. Org. Chem.* **82** 256
24. (a) Lal K, Yadav P and Kumar A 2016 Synthesis, characterization and antimicrobial activity of 4-((1-benzyl/phenyl-1*H*-1, 2, 3-triazol-4-yl)methoxy) benzaldehyde analogues *Med. Chem. Res.* **25** 644; (b) Dhamodharan P, Sathya K and Dhandapani M 2017 Studies on synthesis, structural, luminescent and thermal properties of a new non-linear optical crystal: 4-amino-4*H*-1, 2, 4-triazol-1-ium-3-hydroxy-2, 4, 6-trinitrophenolate *Physica B.* **508** 33; (c) Radhakrishna L, Pandey M K and Balakrishna M S 2018 1, 2, 3-Triazole based bisphosphine, 5-(diphenylphosphanyl)-1-(2-(diphenylphosphanyl)-phenyl)-4-phenyl-1*H*-1, 2, 3-triazole: an ambidentate ligand with switchable coordination modes *RSC Adv.* **8** 25704
25. Rastegari A, Nadri H, Mahdavi M, Moradi A, Mirfazli S S, Edraki N, Moghadam F H, Larijani B, Akbarzadeh T and Saeedi M 2019 Design, synthesis and *anti*-Alzheimer's activity of novel 1, 2, 3-triazole-chromenone carboxamide derivatives *Bioorg. Chem.* **83** 391
26. Saeedi M, Mohammadi-Khanaposhtani M, Pourrabia P, Razzaghi N, Ghadimi R, Imanparast S, Faramarzi M A, Bandarian F, Esfahani E N, Safavi M, Rastegar H, Larijani B, Mahdavi M and Akbarzadeh T 2019 Design and synthesis of novel quinazolinone-1, 2, 3-triazole hybrids as new *anti*-diabetic agents: in vitro α-glucosidase inhibition, kinetic, and docking study *Bioorg. Chem.* **83** 161
27. (a) Pagliai F, Pirali T, Grosso E D, Brisco R D, Tron G C, Sorba G and Genazzani A A 2006 Rapid synthesis of triazole-modified resveratrol analogues via click chemistry *J. Med. Chem.* **49** 467; (b) Aouad M R, Soliman M A, Alharbi M O, Bardaweel S K, Sahu P K, Ali A A, Messali M, Rezki N and Al-Soud Y A 2018 Design, synthesis and anticancer screening of novel benzothiazole-piperazine-1, 2, 3-triazole hybrids *Molecules* **23** 2788
28. (a) Jana S, Iram S, Thomas J, Hayat M Q, Pannecouque C and Dehaen W 2017 Application of the triazolization reaction to afford dihydroartemisinin derivatives with *anti*-HIV activity *Molecules* **22** 303; (b) Pribut N, Veale C G L, Basson A E, van Otterlo W A L and Pelly S C 2016 Application of the Huisgen cycloaddition and 'click' reaction toward various 1, 2, 3-triazoles as HIV non-nucleoside reverse transcriptase inhibitors *Bioorg. Med. Chem. Lett.* **26** 3700
29. (a) Ackermann L, Althammer A and Fenner S 2009 Palladium-catalyzed direct arylations of heteroarenes with tosylates and mesylates *Angew. Chem. Int. Ed.* **48** 201; (b) Ackermann L, Jeyachandran R, Potukuchi H, Novak P and Buttner L 2010 Palladium-catalyzed dehydrogenative direct arylations of 1, 2, 3-triazoles *Org. Lett.* **12** 2056; (c) Tirler C and Ackermann L 2015 Ruthenium(II)-catalyzed cross-dehydrogenative C–H alkenylations by triazole assistance *Tetrahedron* **71** 4543; (d) Ackermann L, Vicente R and Born R 2008 Palladium-catalyzed direct arylations of 1, 2, 3-triazoles with aryl chlorides using conventional heating *Adv. Synth. Catal.* **350** 741
30. Li X, Liu K, Zou G and Liu P 2014 Ruthenium-catalyzed alkenylation of arenes with alkynes or alkenes by 1, 2, 3-triazole-directed C–H activation *Eur. J. Org. Chem.* 7878
31. Zhao S, Yu R, Chen W, Liu M and Wu H 2015 Efficient approach to mesoionic triazolo[5, 1-*a*]isoquinolium through rhodium-catalyzed annulation of triazoles and internal alkynes *Org. Lett.* **17** 2828
32. (a) Zhao F, Chen Z, Huang S and Jiang Y 2016 Palladium-catalyzed nitration of arenes by 1, 2, 3-triazole-directed C–H activation *Synthesis* **48** 2105; (b) Zhao F, Chen Z, Liu Y, Xie K and Jiang Y 2016 Palladium-catalyzed acylation of arenes by 1, 2, 3-triazole-directed C–H activation *Eur. J. Org. Chem.* 5971; (c) Zhao F, Liu Y, Yang S, Xie K and Jiang Y 2017 Pd-catalyzed selective N(3)-*ortho* C–H arylation of 1, 4-disubstituted 1, 2, 3-triazoles *Org. Chem. Front.* **4** 1112; (d) Zhao F, Chen Z, Ma X, Huang S and Jiang Y 2017 Palladium-catalyzed acetoxylation of arenes by 1, 2, 3-triazole-directed C–H activation *Tetrahedron Lett.* **58** 614; (e) Liu Y, Zhang W, Xie K and Jiang Y 2017 Silver-catalyzed intramolecular C(5)–H acyloxylation of 1, 4-disubstituted 1, 2, 3-triazoles *Synlett* **28** 1496; (f) Ma X, Huang H, Yang J, Feng X and Xie K 2018 Pd-catalyzed decarboxylative N(3)-*ortho* C–H acylation of 1, 4-disubstituted 1, 2, 3-triazoles with α-oxocarboxylic acids *Synthesis* **50** 2567; (g) Ma X, Mo Q, Chang J and Xie K 2018 Pd-catalyzed regioselective C–H chlorination of disubstituted 1, 2, 3-triazoles *Synth. Commun.* **48** 1403; (h) Ma X, Liu Y, Xie K and Jiang Y 2018 Pd-catalyzed selective decarboxylation/C–H activation coupling of aryl acid with thiazole and oxazole directed by 1, 2, 3-triazole *Tetrahedron Lett.* **59** 3624; (i) Yang J, Zhao F, Liu Y, Luo F, Cheng H and Jiang Y 2018 Selective diacetoxylation of disubstituted 1, 2, 3-triazoles through palladium-catalyzed C–H activation *Synlett* **29** 1373
33. CCDC 1884642 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk
34. Burdon M G and Moffatt J G 1966 Sulfoxide-carbodiimide reactions. IV. acid-catalyzed reactions of phenols with sulfoxides and carbodiimides *J. Am. Chem. Soc.* **88** 5855