Organic & Biomolecular Chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: Z. Dzambaski and B. Bondži, *Org. Biomol. Chem.*, 2019, DOI: 10.1039/C9OB01090D.

ROYAL SOCIETY OF CHEMISTRY

rsc.li/obc

View Article Online
DOI: 10.1039/C9OB01090D

Dehydrogenative C(sp^3)–H Bond Functionalization of Tetrahydroisoquinolines Mediated by Organic Oxidants under Mild Conditions

Zdravko Džambaski, Bojan P. Bondžić*

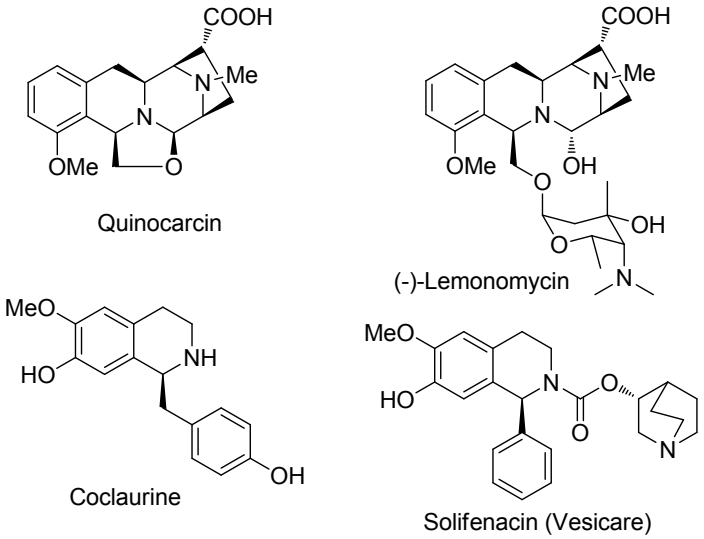
Dr. Z. Džambaski, Dr. B. P. Bondžić*
Center for Chemistry, ICTM institute, University of Belgrade,
Njegoševa 12, 11 000 Belgrade, Serbia
E-mail: bbondzic@chem.bg.ac.rs

Abstract

Organocatalyzed Mannich reaction of unsubstituted and N-Aryl-substituted tetrahydroisoquinolines (THIQs) and Strecker reaction of several N-aryl-substituted THIQs through dehydrogenative C(sp3)–H bond functionalization (cross-dehydrogenative coupling) promoted by organic single electron oxidants DDQ and IBX is presented. Oxidative C-H functionalization/Mannich reaction of less reactive N-aryl substituted pyrrolidines is achieved via metal catalyzed photoredox catalysis. Operationally simple procedures provide desired products in effective and time preserving manner.

Tetrahydroisoquinoline (THIQ) ring system is present in numerous natural and synthetic organic compounds, many of which display useful and interesting biological activities (Figure 1).[1] Covering a wide range of structural types, they are very attractive targets for synthesis and have stimulated the development of new synthetic approaches and methodologies. Recently cross-dehydrogenative coupling (CDC) reactions emerged as effective tool for functionalization of THIQs.

Figure 1. Selected examples of bioactive molecules containing THIQ motif



View Article Online
DOI: 10.1039/C9OB01090D

Since the seminal studies on cross-dehydrogenative coupling by Murahashi and Li through the activation of the α-C(sp^3)–H bond of tertiary amines,[2] tremendous progress has been made in the THIQ functionalizations mostly employing high-valent transition-metal catalysts combined with co-oxidants such as *tert*-butyl hydroperoxide (TBHP), H_2O_2, molecular oxygen, etc.[3,4] or utilizing visible light photoredox catalysis with transition metal complexes as catalysts.[5]
However, the use of organic oxidants possessing a high activity for C–H oxidation would be more desirable from the viewpoint of green and sustainable chemistry.[6] Moreover, metal impurities can be detrimental in pharmaceutically important intermediates and final products.[7] Hence, significant efforts have been made to accomplish CDC reactions in the absence of metal catalysts. Visible light photoredox catalysis in the presence of organic photosenzitizers such as Eritrozine B[8], eosin Y,[9] or carbon nitride[10] has proven to be very effective tool for the functionalization of THIQs. Among organic oxidants, elemental Iodine, [11] 2-iodoxybenzoic acid (IBX)[12] and hipervalent iodine (III)[13] reagents are notable examples in the oxidations and functionalizations of THIQs.

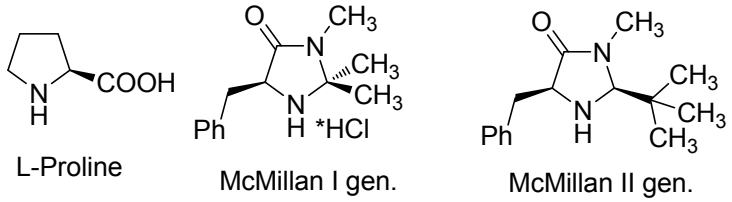
2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as an organic oxidant with high oxidation potential has been extensively used in benzylic oxidation reactions and subsequent coupling reactions with various nucleophiles in the presence or in the absence of metal catalysts.[14] Stoichiometric DDQ had been used in tertiary amine C-H oxidations and the subsequent synthesis of vicinal diamines,[15] in the THIQ arylations,[16] Mukaiama/Manich type reactions of *N*-aryl pyrrolidines and silyl enol ethers [17] and in the intramolecular aza-Prins-type cyclizations.[18] Catalytic DDQ in the presence of catalytic amounts of AIBN was used in THIQ functionaizations by Prabhu group, using oxygen as stoichiometric oxidant.[19] Single example of oxidative carbon–carbon bond-forming reaction of THIQ and acetone catalyzed by DDQ in the presence of organocatalyst proceeding via an isolable iminium ion has been shown previously.[20]

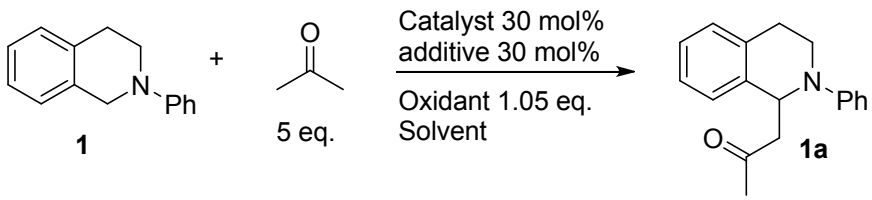
Our aim was to develop a domino organocatalyzed Mannich reaction coupled with an organic oxidant promoted C-H oxidation of THIQs. As the single reported example[20] is limited to acetone as a nucleophile, systematic investigation about the reactivity, selectivity and substrate scope in these reactions are needed. Mannich products such as β-amino ketones and aldehydes are versatile synthetic intermediates for numerous pharmaceuticals and natural products and can be easily converted to 1,3-amino alcohols by reduction, or to Michael acceptors by elimination of amine functionality.[21]

In order to make the reaction more practical and operationally simple it is essential to activate ketones to their enolate form since ketones are less reactive pronucleophiles. Adding catalytic amount of organocatalyst increases reaction rate and ads to operational simplicity since organocatalysts are neither water nor oxygen sensitive. Herein we report a Mannich-type reaction of THIQs with ketones by employing organic oxidants and catalytic amount of amine catalyst. Short studies on Strecker reaction of THIQs employing organic oxidants and metal complex promoted photoredox oxidation of *N*-aryl pyrrolidines are also shown.

Table1. Optimization of *N*-aryl substituted THIQ oxidation/organocatalyzed Mannich reaction[a]

View Article Online
DOI: 10.1039/C9OB01090D





Entry	Catalyst	Time (h)	Oxidant	Additive	Solvent	Yield (%)[b]
1	/	48	DDQ	/	CH_3CN	<10
2	L-Proline	48	DDQ	/	CH_3CN	65
3	L-Proline	2	DDQ	TFA	CH_3CN	78
4	L-Proline	2	DDQ	TFA	Acetone	72
5	L-Proline	4	DDQ	PTSA	CH_3CN	57
6	L-Proline	4	DDQ	AcOH	CH_3CN	61
7	L-Proline	4	Chloranil	TFA	CH_3CN	63
8	L-Proline	24	IBX	/	DMSO	<10
9	L-Proline	24	PIDA	/	CH_3CN	<10
11	L-Proline	24	PIFA	/	CH_3CN	/
12	L-Proline	24	NHPI	/	CH_3CN	/
13	L-Proline	24	mCPBA	/	CH_3CN	/
14	McMillan I gen.	4	DDQ	/	CH_3CN	65
15	McMillan II gen.	4	DDQ	TFA	CH_3CN	68
16	pyrrolidine	12	DDQ	TFA	CH_3CN	48
17	benzylamine	16	DDQ	TFA	CH_3CN	34

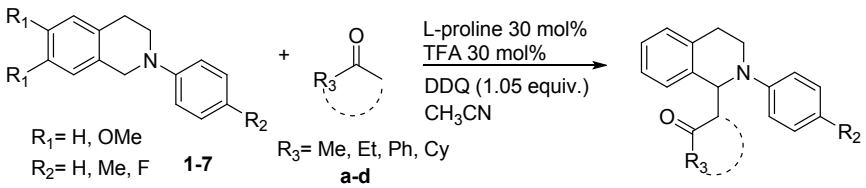
[a] Reaction conditions unless otherwise noted: Tetrahydroisoquinoline (0.25 mmol, 1 equiv.), Oxidant (0.263 mmol, 1.05 equiv.), L-proline (0.075 mmol, 0.3 equiv.) and acetone (10 equiv.) were added to solvent (2 mL) and stirred for designated period of time; [b] Isolated yield after column chromatography.
IBX= 2-Iodoxybenzoic acid; PIDA = phenyliododiacetate; PIFA= (bis(trifluoroacetoxy)iodo)benzene; NHPI = *N*-hydroxyphthalimide; mCPBA = *meta*-chloroperoxybenzoic acid.

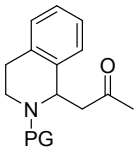
Our investigation started by testing various organic oxidants in our envisaged reaction setup. Firstly, we tested DDQ as an oxidant of *N*-Phenyl-tetrahydroisoquinoline **1** in the presence of 5 equivalents of acetone as a nucleophile in CH_3CN as a solvent. Reaction proceeds sluggishly to yield 10% of desired target material after 48h (Table 1, Entry 1). Addition of the 30 mol% of L-proline tremendously improved the reaction yield and 65% of desired product was obtained after 48h (Table 1, Entry 2). It is known that acidic additives can increase the reaction rate of organocatalyzed reactions by increasing the rate of enamine formation and hydrolysis. Upon addition of 30 mol% of TFA as an additive, reaction rate is dramatically increased, reaction is finished in 2 hours, and the yield is improved to 78% (Table 1, Entry 3). If reaction was performed in acetone as a solvent slightly lower yield of the product is obtained (Table 1, Entry 4). Several

View Article Online
DOI: 10.1039/C9OB01090D

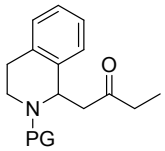
acidic additives such as AcOH and PTSA were tested but did not perform as good as TFA (Table 1, Entries 5 and 6). Using Chloranil as an oxidant gave slightly lower yield of 63% of final product (Table 1, Entry 7). Hypervalent iodine reagents did not give any product under optimized conditions (Table 1, Entries 8-11). NHPI and mCPBA also did not promote oxidation step in this reaction (Table 1, Entries 12 and 13). In the presence of McMillan type organocatalysts I and II with DDQ as an oxidant reaction proceeds to give 65% and 68% yield of desired product respectively (Table 1, Entries 14 and 15). It is worth noting that 5-10% ee in final product was observed with L-proline and McMillan type catalysts. Achiral secondary and primary amines such as pyrrolidine and benzylamine in the presence of TFA also give rise to desired product, in 48% and 34% yield respectively (Table 1, Entries 16 and 17), in absence of TFA reaction doesn't proceed.

Scheme 1. Organocatalyzed, DDQ promoted, THIQ oxidation /Mannich reaction

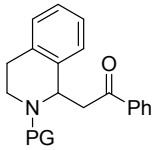




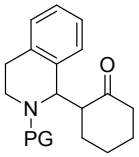
Compd.	PG	Yield(%)
1a	Ph	78
2a	*p*-F-C_6H_4	73
3a	*p*-Me-C_6H_4	71
4a	*o*-Me-C_6H_4	52



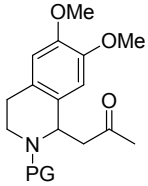
Compd.	PG	Yield(%)
1b	Ph	62
2b	*p*-F-C_6H_4	54
3b	*p*-Me-C_6H_4	55



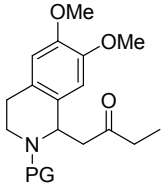
Compd.	PG	Yield(%)
1c	Ph	60
2c	*p*-F-C_6H_4	61
3c	*p*-Me-C_6H_4	57



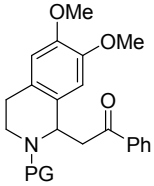
Compd.	PG	Yield(%)
1d	Ph	48
2d	*p*-F-C_6H_4	57



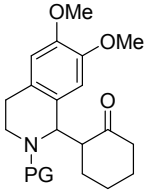
Compd.	PG	Yield(%)
5a	Ph	71
6a	*p*-F-C_6H_4	65
7a	*p*-Me-C_6H_4	70



Compd.	PG	Yield(%)
5b	Ph	61
6b	*p*-F-C_6H_4	55
7b	*p*-Me-C_6H_4	58



Compd.	PG	Yield(%)
5c	Ph	60
6c	*p*-F-C_6H_4	71



Compd.	PG	Yield(%)
6d	*p*-F-C_6H_4	55
7d	*p*-Me-C_6H_4	44

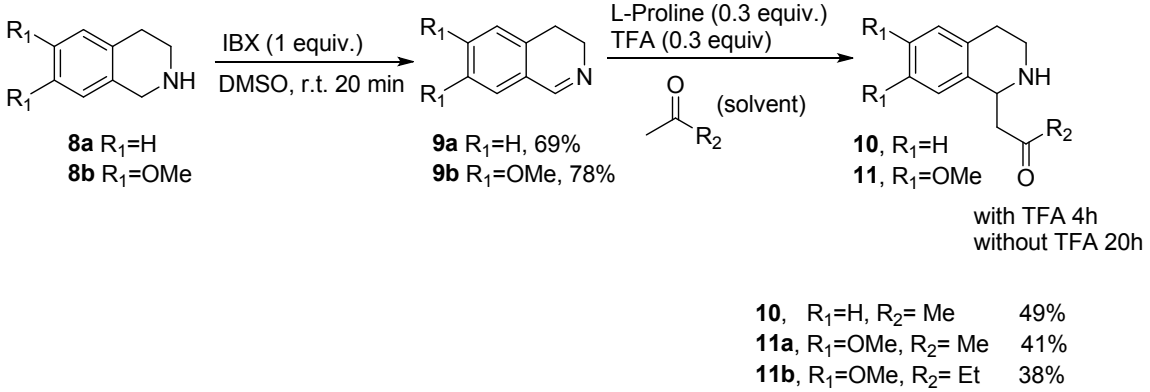
View Article Online
DOI: 10.1039/C9OB01090D

After the optimal conditions were found, scope of the reaction was investigated. *N*-phenyl, *N*-*p*-tolyl, *N*-*p*-C_6H_4-F- or *N*-*o*-tolyl substituted THIQs were tested. *N*-aryl groups stabilize reactive intermediates in cross-dehydrogenative couplings,[22] and these tertiary substituted substrates proved to be the best choice in this reaction setup.

As the nucleophilic partners several ketones were tested: acetone, ethyl methyl ketone, acetophenone and cyclohexanone (Scheme 1). In all cases good yields were obtained, reactions with acetone proceeded most efficiently giving the best yields among tested ketones. Ethyl methyl ketone having two enolizable positions reacts exclusively at the less substituted side of the molecule to give products in very good yields (Scheme 1, products **1-3b** and **5-7b)**. Acetophenone reacts efficiently as well giving very good yields of products in all cases (Scheme 1, products **1-3c** and **5,6c)**. Cyclohexanone reacts a bit slower compared to other tested ketones giving desired products **1,2d** and **6,7d** in approximately 1:1.3 diastereomeric ratio (see Scheme 1 and Supporting information). *o*-Tolyl substituted THIQ reacted only with acetone (product **4a**, Scheme 1) and did not react with any other nucleophile under optimized conditions, most probably due to the increased sterical hindrance close to the reaction center. All the aryl substituted tertiary THIQs reacted very efficiently, however, it is often required to remove the protecting group of the amine to have unsubstituted secondary amine for the synthetic or biomedical purposes.

Unprotected THIQ **8a** did not react under optimized conditions using DDQ as an oxidant. After oxidant screening tests it was found that IBX is effective oxidant of unprotected THIQs in DMSO as a solvent. It was possible to isolate intermediary imines **9a** and **9b** under these conditions in 69% and 78% respectively. Isolated imines from both, tetrahydroisoquinoline **8a** and 6,7-dimethoxy-tetrahydroisoquinoline **8b** reacted with ketones under Mannich reaction conditions (enamine formed from ketone and catalytic amount of L-proline) to give moderate yields of desired products **10a** and **11a,b** (Scheme 2). One pot reaction was attempted but did not proceed at all: upon addition of ketone, catalyst and additive to DMSO solution of imine formed *in situ* from THIQ **8a** and IBX, Mannich reaction did not take place. Oxidation of **8a** with IBX also proceeds in MeOH at 60 °C, to give iminium ion **9a**. Upon addition of acetone, L-proline and additive to this reaction mixture no reaction occurs. Optimization of this reaction and making it a one pot or tandem process is the subject of our continued interest, as it is known that tandem reaction could be far more effective and time saving omitting isolation of intermediates.

Scheme 2. C-H Oxidation/Mannich reaction of unprotected THIQs



8a R_1=H
8b R_1=OMe

9a R_1=H, 69%
9b R_1=OMe, 78%

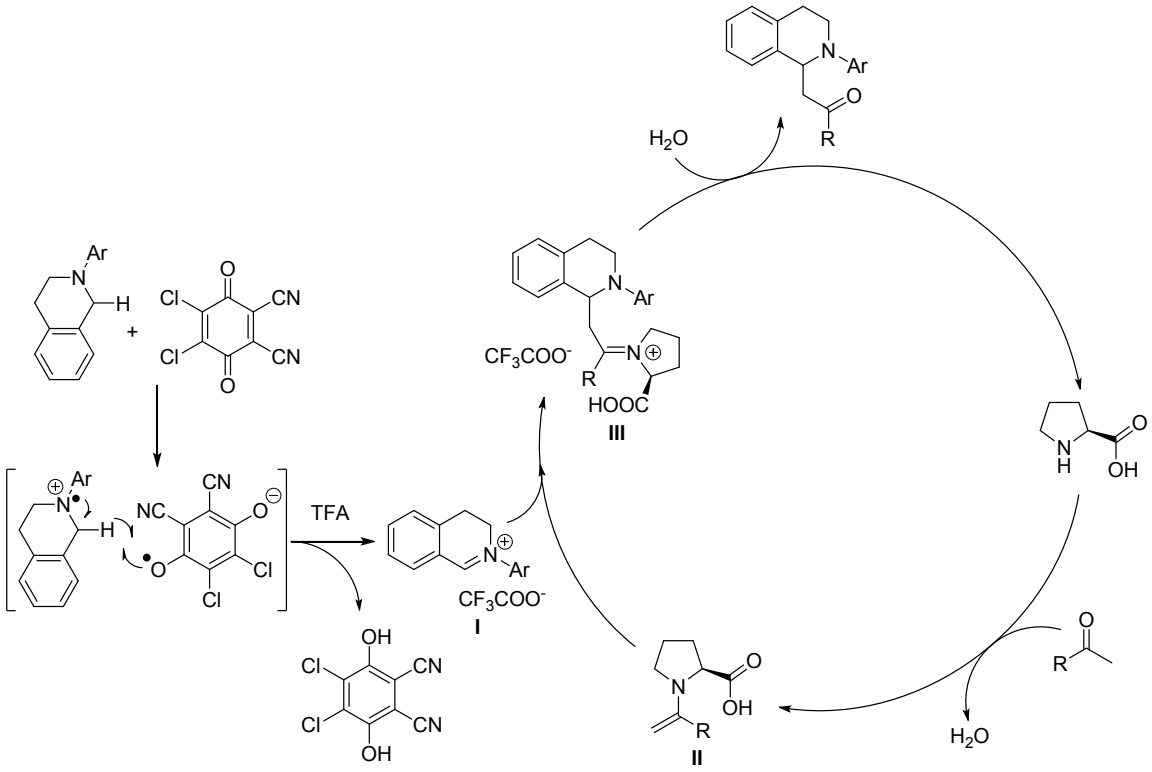
10, R_1=H
11, R_1=OMe

10, R_1=H, R_2= Me 49%
11a, R_1=OMe, R_2= Me 41%
11b, R_1=OMe, R_2= Et 38%

View Article Online
DOI: 10.1039/C9OB01090D

Plausible mechanism of THIQ C-H oxidation/Mannich reaction is shown in Scheme 3. DDQ promoted oxidations are thought to begin with single electron oxidation of tertiaty amines. [23] In the next step upon hydride abstraction iminium ion is formed. Counterion exchange with TFA may take place giving iminium ion **I** which undergoes nucleophilic attack from enamine **II** formed from ketone and L-proline. Mannich adduct **III** undergoes hydrolysis with water to give desired product, recovering L-proline catalyst, which enters the next cycle (Scheme 3).

Scheme 3. Plausible mechanism of DDQ promoted C-H oxidation/L-proline catalyzed Mannich reaction



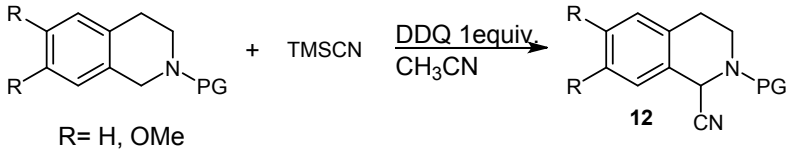
DDQ promoted C-H oxidation of THIQs/Strecker reaction

As the extension of the methodology of using organic oxidants for CDC functionalizations of THIQs we also tested DDQ as an oxidant in C-H oxidation/Strecker reaction using TMSCN as the source of CN^- ion. α-Cyanations of THIQs using 2,2,6,6-tetramethylpiperidine *N*-oxide fluoroborate salt as an oxidant are known[24] while DDQ has been used as an oxidant in the α-cyanation of allyl ethers.[25]

DDQ oxidation of *N*-aryl substituted THIQs proceeded very efficiently providing imine *in situ*, upon imine formation completion as confirmed by TLC, TMSCN is added to reaction mixture to provide Strecker product in good yields (Scheme 4). Reduction of Strecker adducts might provide vicinal diamines, potentially pharmaceutically important compounds.

View Article Online
DOI: 10.1039/C9OB01090D

Scheme 4. DDQ promoted C-H oxidation/Strecker reaction of *N*-aryl substituted THIQs



R= H, OMe

12a R= H, PG=Ph, 75%
12b R= H, PG= p-F-C_6H_4, 58%
12c R= OMe, PG= p-F-C_6H_4, 67%
12d R= OMe, PG= p-Me-C_6H_4, 62%

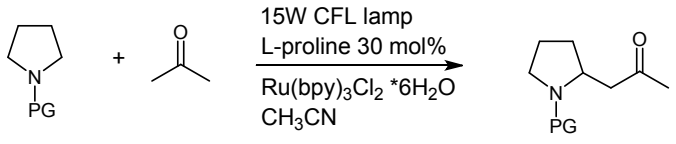
CDC coupling of pyrrolidines

Most of CDC coupling methodologies (vide supra) are still limited to activated amines such as tetrahydroisoquinolines or benzylamines, and only a few examples have been reported using pyrrolidine or piperidine derivatives.[17,26] Thus, it is very challenging to develop an oxidative Mannich reaction of nonactivated tertiary amines. *N*-aryl substituted pyrrolidines or piperidines did not react under optimized conditions of DDQ or IBX promoted C-H oxidation/Mannich reaction. No reaction was observed also when other organic oxidants: mCPBA, PIDA, PIFA or NHPI were tested. Under conditions of metal catalyzed photoredox catalysis, using $[Ru(bpy)_3]Cl_2$ in the presence of L-proline and irradiating with 15W CFL lamp reaction with acetone proceeded to give products in low yields after few days of reaction time (See supporting information) (Scheme 4). Yields up to 36% were obtained, main issue being loss of activity of catalyst after 12-24h. $[Ru(bpz)_3][PF6]_2$ catalyst was tested as well but did not provide better yields of the product **13a** compared to $[Ru(bpy)_3]Cl_2$ catalyst. 8W CFL lamp didn't provide better yields and **13a** was isolated in 15% yield after 4 days of reaction. Mechanism of this type of reaction is very well known and has been previously described.[5b] Reaction proceeds via single electron transfer (SET) from the *N*-aryl substituted tertiary amine to $Ru(bpy)_3^{2+}$* species formed upon irradiation of $Ru(bpy)_3^{2+}$ catalyst. Amine radical cation that is formed looses hydride to give iminium ion that undergoes nucleophilic attack by enamine species present in the reaction mixture and formed from ketone and secondary amine catalyst. Ru^+ species are reoxidized by molecular oxygen *in situ* to reenter catalytic cycle.

A number of substrates possessing different aryl groups have also been tested but in all cases desired reaction was not observed (See Supporting information, Scheme S1). We are currently working on the further improvements of this reaction and we will report results in due course.

Scheme 4. Visible-light-promoted asymmetric cross-dehydrogenative coupling of tertiary amines to ketones

View Article Online
DOI: 10.1039/C9OB01090D



(2)

13a PG = *p*-MeO-C_6H_4- 34%
13b PG = 3,4,5-tri-MeO-C_6H_2- 18%
13c PG = 3,4-di-Me-C_6H_3- 36%
13d PG = *p*-Cl-C_6H_4- 13%

Conclusion

We have shown that organic oxidants, DDQ and IBX can be successfully used in the C(sp3)−H bond oxidation/organocatalyzed Mannich reaction of tertiary N-Aryl-substituted and N-unsubstituted THIQs in the effective manner. Use of organocatalyst and acidic additive in the Mannich reaction of in situ formed iminium ions and ketones tremendously improved the reaction times and yields of this domino process. Besides Mannich reaction, Strecker type addition of TMSCN to iminium ion (formed in situ) can also be performed with tertiary aryl substituted THIQs using DDQ as an oxidant. Less reactive N-aryl pyrrolidines did not undergo oxidation reaction with organic oxidants. However, under conditions of metal complex catalyzed photoredox reactions, C-H oxidation and subsequent organocatalyzed Mannich reaction take place. These procedures represent a powerful method to form new carbon−carbon bonds directly from two different C−H bonds under oxidative conditions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgement

This work was supported by the Ministry of Education, Science and Technology of the Republic of Serbia (Grant No. 172020). We gratefully acknowledge COST action CA15106: C-H Activation in Organic Synthesis (CHAOS) for support.

View Article Online
DOI: 10.1039/C9OB01090D

Notes and references

1 (a) A. W. Kahsai, J. Cui, H. U. Kaniskan, P. P. Garner, G. Fenteany, *J. Biol. Chem*. 2008, **283**, 24534; (b) S. Kumar, V. K. Eyunni, M.Gangapuram, K. K Redda, *Lett. Drug. Des. Discov.* 2014, **11**, 428; (c) M. R. Bennett, M. L. Thompson, S. A. Shepherd, M. S. Dunstan, A. J. Herbert, D. R. M. Smith, V. A. Cronin, B. R. K. Menon, C. Levy, J. Micklefield, *Angew. Chem. Int. Ed.* 2018, **57**, 10600.

2 (a) S.-I. Murahashi, *Angew. Chem., Int. Ed.* 1995, **34**, 2443; (b) C.-J. Li, *Acc. Chem. Res.* 2009, **42**, 335.

3 For selected reviews on CDC reactions, see: (a) S.-I. Murahashi, D. Zhang, *Chem. Soc. Rev.*, 2008, **37**, 1490; (b) C. J. Scheuermann, *Chem. Asian. J.* 2010, **5**, 436; (c) A. E. Wendlandt, A. M. Suess, S. S. Stahl, *Angew. Chem., Int. Ed.* 2011, **50**, 11062; (d) C. Liu, H. Zhang, W. Shi, A. Lei, *Chem. Rev.* 2011, **111**, 1780; (e) C. S. Yeung, V. M. Dong, *Chem. Rev.* 2011, **111**, 1215; (f) S. A. Girard, T. Knauber, C.-J. Li, *Angew. Chem., Int. Ed.* 2014, **53**, 74.

4 (a) B. Schweitzer-Chaput, M. Klussmann, *Eur. J. Org. Chem*. 2013, 666; (b) H. Ueda, K. Yoshida, H. Tokuyama, *Org. Lett*. 2014, **16**, 4194; (c) T. Nobuta, N. Tada, A. Fujiya, A. Kariya, T. Miura, A. Itoh, *Org. Lett*. 2013, **15**, 574; (d) A. Sud, D. Sureshkumar, M. Klussmann, *Chem. Commun*. 2009, 3169; (e) O. Basle, C.-J. Li, *Org. Lett.* 2008, **10**, 3661; (f) H. Richter, O. G. Mancheño, *Eur. J. Org. Chem.* 2010, 4460.

5 (a) A. G. Condie, J. C. González-Gómez, C. R. J. Stephenson, *J. Am. Chem. Soc.* 2010, **132**, 1464; (b) M. Rueping, C. Vila, R.M. Koenigs, K. Poscharny, D. C. Fabry, *Chem. Commun.* 2011, **47**, 2360; (c) P. Querard, I. Perepichka, E. Zysman-Colman, C.-J. Li, *Beilstein J.Org. Chem.* 2016, **12**, 2636; (d) G. Q. Xu, J. T. Xu, Z. T. Feng, H. Liang, Z. Y. Wang, Y. Qin, P. F. Xu, *Angew. Chem. Int. Ed.* 2018, **57**, 5110; (e) M. Neumann, K. Zeitler, *Org. Lett.* 2012, **14**, 2658; (f) Q. Yang, L. Zhang, C. Ye, S. Luo, L.-Z. Wu, C.-H. Tung, *Angew. Chem. Int. Ed*. 2017, **56**, 3694; (g) H. Hou, S. Zhu, I. Atodiresei, M. Rueping, *Eur. J. Org. Chem.* 2018, 1277.

6 P. T. Anastas, N. Eghbali, *Chem. Soc. Rev*. 2010, **39**, 301.

7 (a) S. Ahuja, Impurities Evaluation of Pharmaceuticals, Marcel Dekker, New York, 1998; (b) F. Qiu, D. L. Norwood, *J. Liq. Chromatogr. Relat. Technol*. 2007, **30**, 877.

8 L. Ren, H. Cong, *Org. Lett.*, 2018, **20**, 3225.

9 D. P. Hari, B. Konig, *Org. Lett*. 2011, **13**, 3852.

10 L. Mçhlmann, M. Baar, J. Rieß, M. Antonietti, X. Wang, S. Blechert, *Adv. Synth. Catal*. 2012, **354**, 1909.

11 J. Dhineshkumar, M. Lamani, K. Alagiri, K. R. Prabhu, *Org. Lett*. 2013, **15**, 1092-1095.

12 (a) K. C. Nicolaou, C. J. N. Mathison, T. Montagnon *J. Am. Chem. Soc.* 2004, **126**, 5192; (b) C. de Graaff, L. Bensch, M. J. van Lint, E. Ruijter, R. V. A. Orru, *Org. Biomol. Chem*. 2015, **13**, 10108.

13 (a) W. Muramatsu, K. Nakano, C.-J. Li,*Org. Biomol. Chem*. 2014, **12**, 2189; (b) Z. Peng, Z. Yu, D.-H. Chen, S. Liang, L. Zhang, D. Zhao, L. Song, C. Jiang, *Synlett*, 2017, **28**, 1835.

14 (a) W. Tu, L. Lei, P. E. Floreancig, *Angew. Chem. Int. Ed*. 2008, **47**, 4184; (b) Y.-C. Xu, D. T. Kohlman, S. X. Liang, C. Erikkson, *Org. Lett*. 1999, **1**, 1599; (c) Y. Zhang, C.-J. Li, *Angew. Chem., Int. Ed*. 2006, **45**, 1949; (d) Y. Zhang, C.-J. Li, *J. Am. Chem. Soc.* 2006, **128**, 4242; (e) B. A. Snider, *Chem. Rev*. 1996, **96**, 339; (f) H. H. Jung, P. E. Floreancig, *Tetrahedron* 2009, **65**, 10830; (g) L. Liu, P. E. Floreancig, *Org. Lett.,* 2010, **12**, 4686.

15 A. S.-K, Tsang, M. H. Todd, *Tetrahedron Lett*. 2009, **50**, 1199.

16 W. Muramatsu, K. Nakano, C.-J. Li**,** *Org. Lett*. 2013, **15**, 3650.

17 H. Jo, A. H. E. Hassan, S. Y. Jung, J. K. Lee, Y. S. Cho, S.-J. Min, *Org.Lett*. 2018, **20**, 1175.

18 Y. W. Son, T. H. Kwon, J. K. Lee, A. N. Pae, J. Y. Lee, Y. S. Cho, S.-J. Min, *Org. Lett*, 2011, **13**, 6500**.**

19 K. Alagiri, P. Devadig, K. R. Prabhu, *Chem.-Eur. J.* 2012, **18**, 5160.

20 A. S.-K. Tsang, P. Jensen, J. M. Hook, A. S. K. Hashmi, M. H. Todd, *Pure Appl. Chem.* 2011, **83**, 655.

21 M. Arend, B. Westermann, N. Risch, Angew. Chem. Int. Ed. 1998, **37**, 1044 and references therein.

22 A. S.-K. Tsang, A. S. K. Hashmi, P. Comba, M. Kerscher, B. Chan, M. H. Todd, *Chem. -Eur. J.* 2017, **23**, 9313.

23 (a) D. Cheng, W. Bao, *Adv. Synth. Catal*. 2008, **350**, 1263; (b) P. C. Montevecchi, M. L. Navacchia, *J. Org. Chem.* 1998, **63**, 8035; (c) Y. Zhang,C.-J. Li, *J. Am. Chem. Soc.* 2006, **128**, 4242; (d) B.-P. Ying, B. G. Trogden, D. T. Kohlman, S. X.Liang, Y.-C. Xu, *Org. Lett.* 2004, **6**, 1523.

24 C. Yan, Y. Liu, Q. Wang, *RSC Advances*, 2014, **4**, 60075.

25 Y. Hayashi, T. Mukaiyama, *Chem. Lett.* 1987, 1811

26 (a) L. Zhao, C.-J. Li, *Angew. Chem., Int. Ed*. 2008, **47**, 7075; (b) W. Chen, D. Seidel, *Org. Lett*. 2014, **16**, 3158; (c) G. Kumaraswamy, A. N. Murthy, A. Pitchaiah, *J. Org. Chem*. 2010, **75**, 3916; (d) M. M. D. Pramanik, S. B.

View Article Online
DOI: 10.1039/C9OB01090D

Nagode, R. Kant, N. Rastogi, *Org. Biomol. Chem*. 2017, **15**, 7369; (e) D. Sureshkumar, A. Sud, M. Klussmann, *Synlett*, 2009, **10**, 1558