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Hypervalent iodine(III)-promoted *N*-incorporation into *N*-aryl vinylogous carbamates to quinoxaline diesters: access to 1,4,5,8-tetraazaphenanthrene†

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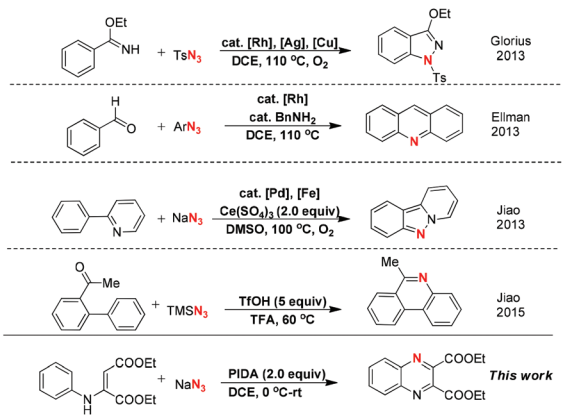
A novel oxidative *N*-incorporation strategy for synthesis of quinoxaline diesters under metal-free conditions is described for the first time. The mild reaction conditions allow for this transformation *via* the formation of two C(sp^2)–N bonds utilizing cheaply available NaN_3 as the N-atom source. *N*-Aryl vinylogous carbamates in this study undergo azidation at enamino C(sp^2)–H selectively. The robustness of this strategy is further demonstrated by the synthesis of a valuable 1,4,5,8-tetraazaphenanthrene derivative using a mild and convenient approach.

Introduction

Of all the C–N bond formation reactions, aromatic C–N bond forming methods under oxidative conditions are the most fascinating approaches and highly explored in recent years,[1] due to the wide occurrence of azaheterocycles in natural products, biologically active molecules and materials science.[2] Over the past few decades, most of the literature procedures and conventional methods seem to suggest that a substrate with nitrogen functionality is essential for aromatic C–N bond formation for the synthesis of azaheterocycles.[3] Such procedures often require multisteps to bring nitrogen functionality into the substrate and have limited generality. On the other hand, most of the aromatic C–N bond transformations have been achieved *via* toxic and expensive metal-based catalysts.[4]

Though cheap and environmentally benign catalytic systems based on Cu and Fe have also been used for C–N bond formation in heterocyclic synthesis,[4f–h] recently chemists have mainly directed their efforts towards designing green economy strategies for expeditious synthesis of azaheterocycles from nitrogen functionality free substrates under metal-free conditions[5] which is highly challenging and desirable. C–N bond forming reactions on arenes involving easily accessible azides are of great importance for the synthesis of azaheterocycles.[6] Despite numerous methods for construction of aromatic C–N bonds which lead to azaheterocycles being reported,[7] methods *via* incorporation of the N-atom into arene molecules using azides as the N-source under metal-free conditions are rare.[8] However a few research groups like Glorius, Ellman and Jiao *et al.* have developed prominent reactions for the synthesis of azaheterocycles *via* *N*-incorporation into arene molecules by using azides and employing transition metal catalysts (Scheme 1).[9] More recently, a new approach was described by Yu's group for oxidative *N*-incorporation into *N*-arylenamines under copper catalysis.[10] However, these *N*-incorporation strategies utilized transition metal catalysts and organic azides as the N-source.[9,10] Recently, Jiao *et al.* have developed a metal-free expeditious nitrogenation of 2-acetylbiphenyls leading to phenanthridines under acidic conditions (Scheme 1).[8] Our interests in the development of metal-free protocols for the synthesis of heterocyclic scaffolds,[11] persuaded us to design a strategy for the synthesis of azaheterocycles *via* *N*-incorporation from nitrogen functionality free substrates. Herein, we



Scheme 1 Intermolecular nitrogen incorporation strategies to synthesize azaheterocycles.

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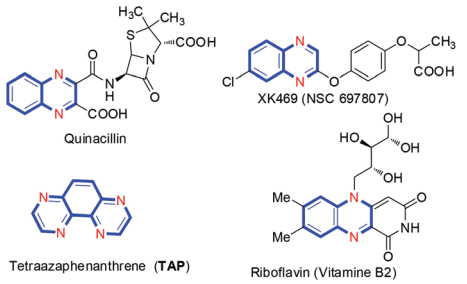


Fig. 1 Biologically important compounds and TAP containing a quinoxaline core.

are delighted to report for the first time an unprecedented metal-free hypervalent iodine(III) promoted dehydrogenative nitrogenation of *N*-aryl vinylogous carbamates using sodium azides as the N-source *via* the formation of two C(sp^2)–N bonds leading to quinoxalines in a cascade fashion.

Hypervalent iodine(III) derivatives have been recognized as very promising reagents for metal-free oxidative dehydrogenative transformations in synthetic organic chemistry,[12] due to their low toxicity, environmentally friendly nature and easy handling.

Among azaheterocycles, quinoxaline containing compounds have found use as potential anticancer,[13] antiviral, antibiotic and anti-inflammatory agents[14] (Fig. 1) and applications in diverse areas of materials science. In particular, a quinoxaline core bearing ester functionalities is a key structural unit of n-type semiconductors (Fig. 1).[15] Not surprisingly, many efforts have been directed for the efficient synthesis of quinoxalines. Generally, the most common strategy to build up quinoxaline rings relies on the condensation of *o*-phenylenediamine with 1,2-dicarbonyls or their equivalents.[16] However, these methods have some drawbacks such as generality and multisteps with a narrow substrate scope. Owing to this, we aimed to develop a metal-free protocol for the synthesis of quinoxalines *via* a dehydrogenative *N*-incorporation strategy using azides as the N-source with hypervalent iodine(III).

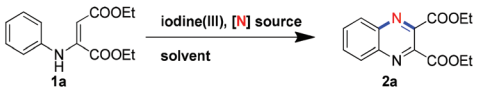
Results and discussion

Having been inspired by the very recent applications of dehydrogenative nitrogenation reactions involving azides as the source of the N-atom in the synthesis of natural products and biologically active compounds,[9] we have selected the intermolecular cyclization reaction between diethyl 2-(phenylamino)maleate **1a** and azides as the target for the formation of two C(sp^2)–N bonds with hypervalent iodine reagents, which lead to quinoxalines.

Accordingly, we started our study with the readily prepared diethyl 2-(phenylamino)maleate **1a** (see the ESI†) to probe the feasibility of the reaction. Initially, the nitrogenation of **1a** was investigated by using 1 equiv. of sodium azide (NaN_3) as the N-source and 1 equiv. of bis(trifluoroacetate) (PIFA) in 1,2-dichloroethane (DCE) as the solvent at 0 °C to room temperature (27 °C) for 6 h. We were delighted to find that the desired product diethyl quinoxaline-2,3-dicarboxylate **2a** was indeed observed in 21% yield (Table 1, entry 1). This interesting result motivated us to improve the yield of the desired product **2a**. On switching from PIFA to less potent PIDA, the yield of the product increased to 38% (Table 1, entry 2). Next, we screened the reaction by varying the equivalents of PIDA and NaN_3 (Table 1, entries 3–11). We were pleased to find quinoxaline **2a** in 78% yield with 2 equiv. of PIDA and 2 equiv. of NaN_3 in DCE solvent (Table 1, entry 6). Among the various solvents tested, DCE was found to be effective (Table 1, entry 6). Our attempts to further improve the yield by replacing NaN_3 with other N-sources were shown to be unsuccessful (Table 1, entries 13 & 14). Continuing our zest, we screened other oxidant sources, unfortunately our attempts were in vain (Table 1, entries 15 & 16).

Under the optimal reaction conditions (Table 1, entry 6), the scope of the nitrogenation reaction of *N*-aryl vinylogous carbamates bearing electron-donating substituents (–Me, –OMe) provided the desired products in very good yields (Table 2, **2a–2j**). Electron-donating substituents at any position of the ring were well tolerated, whereas weak electron-donating groups like halogens on the aryl ring of vinylogous carbamate derivatives greatly affected the reactivity (Table 3). When we employed our standard conditions to *ortho* halo substituted *N*-aryl vinylogous carbamates, we observed alkyl *N*-aryloxamate as the byproduct in 18% yield (see the ESI,† Table 1, **2k-2**, entry 1) along with our desired product **2k-1**.

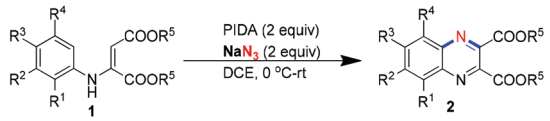
Table 1 Optimization of the reaction conditions for the synthesis of diethyl quinoxaline-2,3-dicarboxylate (**2a**)[a]



Entry	Iodine(III) (equiv.)	[N] source	Solvent	Yield[b] (%)
1	PIFA (1.0)	NaN_3 (1.0)	DCE	21
2	PIDA (1.0)	NaN_3 (1.0)	DCE	38
3	PIDA (1.5)	NaN_3 (1.0)	DCE	50
4	PIDA (1.5)	NaN_3 (1.5)	DCE	52[c]
5	PIDA (2.0)	NaN_3 (1.5)	DCE	68
6	**PIDA (2.0)**	**NaN_3 (2.0)**	**DCE**	**78**
7	PIDA (2.0)	NaN_3 (2.0)	DCM	75
8	PIDA (2.0)	NaN_3 (2.0)	HFIP	13
9	PIDA (2.0)	NaN_3 (2.0)	DMF	63
10	PIDA (2.0)	NaN_3 (2.0)	CH_3CN	50
11	PIDA (2.0)	NaN_3 (2.0)	THF	17
13	PIDA (2.0)	$TMSN_3$ (2.0)	DCE	22
14	—	IBA-N_3	DCE	ND
15	PhIO	NaN_3 (2.0)	TFE	ND
16	PhI(OH)(OTs)	NaN_3 (2.0)	DCE	ND

[a] Reaction conditions **1a** (0.19 mmol), PIDA (0.38 mmol), NaN_3 (0.38 mmol), DCE (3 mL), 0 °C–27 °C, 6 h. [b] Yield of the isolated product after column chromatography. [c] Reaction was carried out at 40 °C, IBA-N_3 = 1-azido-1,2-benziodoxol-3-(1*H*)-one, $TMSN_3$ = trimethylsilyl azide, HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol, TFE = 2,2,2-triflouroethanol, ND = not detected.

Table 2 Nitrogenation reaction of *N*-aryl vinylogous carbamates bearing electron donating groups[a,b]

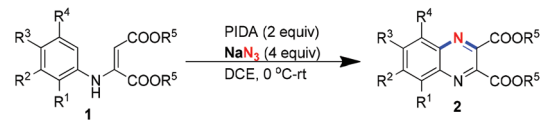


1 2

R^1	R^2	R^3	R^4	R^5	2	Yield (%)
H	H	H	H	Et	**2a**	78
H	H	H	H	Me	**2b**	72
H	H	OMe	H	Me	**2c**	67
H	Me	OMe	H	Et	**2d**	80
H	Me	OMe	H	Me	**2e**	75
Me	H	H	Me	Me	**2f**	65
Me	H	Me	H	Me	**2g**	68
Me	H	Me	H	Et	**2h**	64[c]
Me	H	H	H	Et	**2i**	62
Me	H	H	H	Me	**2j**	61

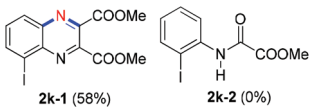
[a] Reaction conditions **1a** (0.19 mmol), PIDA (0.38 mmol), NaN_3 (0.38 mmol), DCE (3 mL), 0 °C–27 °C, 4–6 h. [b] Yield of the isolated product after column chromatography. [c] Compound **2h** (CCDC 1453940) was further confirmed by single crystal XRD (see the ESI).

Table 3 Nitrogenation reaction of *N*-aryl vinylogous carbamates bearing halogens[a,b]



1 2

R^1	R^2	R^3	R^4	R^5	2		Yield (%)
I	H	H	H	Me	**2k-1**	**2k-2**	58, 0
I	H	H	H	Et	**2l**		59
Br	H	H	H	Et	**2m**		61
Br	H	H	H	Me	**2n**		58
F	H	H	H	Et	**2o**		57
H	H	I	H	Et	**2p**		61
H	H	Br	H	Et	**2q**		64
H	H	Br	H	Me	**2r-1**	**2r-2**	51[c], 4[c]
H	H	Cl	H	Et	**2s**		61
Cl	H	H	H	Me	**2t-1**	**2t-2**	60, 10
H	H	F	H	Et	**2u**		62
H	H	F	H	Me	**2v**		64
Br	H	H	Br	Me	**2w-1**	**2w-2**	54[c], 3[c]
Br	H	Me	H	Et	**2x-1**	**2x-2**	48[c], 5[c]



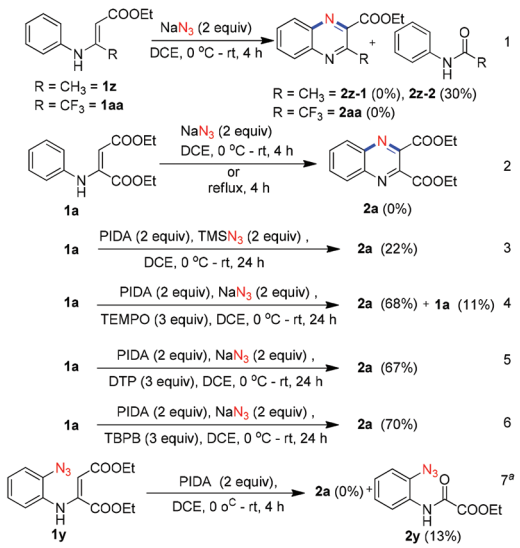
2k-1 (58%) **2k-2** (0%)

[a] Reaction conditions **1a** (0.19 mmol), PIDA (0.38 mmol), NaN_3 (0.76 mmol), DCE (4 mL), 0 °C–27 °C, 4–6 h. [b] Yield of the isolated product after column chromatography. [c] Ratio was determined by ^{1}H NMR.

In order to reduce the formation of by-products, we screened the reaction with different equivalents of NaN_3, we found 4 equivalents of NaN_3 were furnishing the quinoxaline **2k-1** selectively (Table 3, **2k-2**). When we extended these conditions to **1l-1x**, we obtained the desired quinoxalines **2l–2q**, **2r-1**, **2s**, **2t-1**, **2u**, **2v**, **2w-1** and **2x-1** in moderate yields, except in four cases (**2r-2**, **2t-2**, **2w-2** & **2x-2**) where the formation of the byproduct was identified, albeit in negligible yields (Table 3). To test the scope of this method, we performed a control experiment wherein we replaced α-ester functionality in vinylogous carbamate **1a** with $-CH_3$ (**1z**) and $-CF_3$ (**1aa**) and subjected it to standard conditions, unfortunately this failed to give the desired products rather compound **1z** yielded the byproduct *N*-phenylacetamide (**2z-2**) in 30% yield (Table 4, eqn (1)).

To probe the mechanism of this dehydrogenative nitrogenation, preliminary control experiments were conducted (Table 4). No nitrogenation product **2a** was observed in the absence of PIDA as an oxidant even under thermal conditions (Table 4, eqn (2)), which indicates the key role played by PIDA in the dehydrogenative nitrogenation. To obtain more insight into the mechanism, we performed the reaction in the presence of organic azide $TMSN_3$ resulting in **2a** (22%), thus indicating the low reactivity of $TMSN_3$ (Table 4, eqn (3)). To probe whether the reaction proceeds through a radical pathway, we performed the standard reaction in the presence of radical scavengers like 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO), di-*tert*-butyl peroxide (DTP) and *tert*-butyl peroxybenzoate (TBPB) (Table 4, eqn (4)–(6)), which showed no significant decrease in the yield of the product **2a**, thus confirming the ionic mechanism for the reaction. Accordingly, we envisioned that the enamine C(sp^2)–H azidation product may serve as the key intermediate **III** in this transformation. To verify this possibility, we conducted another control experiment with *ortho* azido *N*-acyl vinylogous carbamate **1y** in the absence of NaN_3

Table 4 Test on the scope of the method and control experiments



[a] Trace amount of **2a** was observed in TLC.

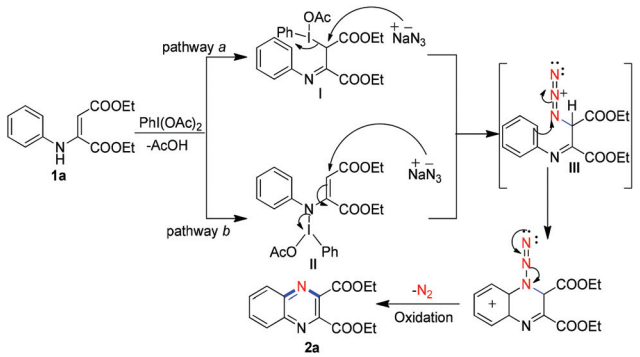
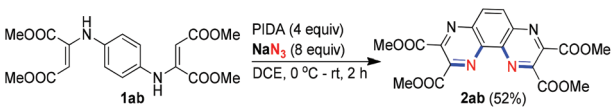


Fig. 2 Plausible reaction mechanism for **2**.



Scheme 2 Synthesis of tetramethyl pyrazino[2,3-*f*]quinoxaline-2,3,8,9-tetracarboxylate (**2ab**).

which resulted in **2a** in a trace amount and the corresponding alkyl *N*-aryl oxamate **2y** in 13% yield (Table 4, eqn (7)).

Together, these observations indicated that an ionic mechanism may be involved in this transformation. Based on these experiments, we have proposed a plausible mechanism as shown in Fig. 2, where the intermolecular reaction of **1a** and PIDA generated the intermediates **I** (pathway a) and **II** (pathway b) by the loss of acetic acid. Afterwards, the azide intermediate **III** formed by either cleavage of C–I or N–I bonds would undergo the Friedel–Crafts reaction followed by aromatization leading to the product **2a**.

After having successfully synthesized the quinoxalines, to check further applicability of our protocol, the reaction was extended to synthesize tetramethyl pyrazino[2,3-*f*]quinoxaline-2,3,8,9-tetracarboxylate (**2ab**) from bis *N*-aryl vinylogous carbamates (**1ab**) which afforded **2ab**, albeit in moderate yield (52%) under standard conditions in a single step (Scheme 2). It is worth mentioning here that, this straightforward method is highly superior to what is found in the literature report[17] for the synthesis of such a valuable scaffold, since it avoids multiple steps, metal-catalysts and harsh conditions.

Conclusions

In conclusion, we have presented an unprecedented metal-free hypervalent iodine(III)-promoted dehydrogenative *N*-incorporation into *N*-aryl vinylogous carbamates for synthesis of quinoxaline diesters. This protocol involves mild reaction conditions for *N*-incorporation *via* the formation of two C(sp^2)–N bonds in a cascade fashion utilizing cheaply available azide as the N-source. The robustness of this strategy is demonstrated by the synthesis of a tetraazaphenanthrene (TAP) derivative involving the formation of four new C–N bonds and two rings in a single step. Further investigations on the more detailed mechanism and applications of the present protocol are currently underway in our lab.

Acknowledgements

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Notes and references

1 For selected reviews on C–N bond formation, see: (*a*) C. Sambiagio, S. P. Marsden, A. J. Blacker and P. C. Mc Gowan, *Chem. Soc. Rev.*, 2014, **43**, 3525; (*b*) G. Y. Song, F. Wang and X. W. Li, *Chem. Soc. Rev.*, 2012, **41**, 3651; (*c*) T. A. Ramirez, B. G. Zhao and Y. Shi, *Chem. Soc. Rev.*, 2012, **41**, 931; (*d*) Y. Zhang, X. Yang, Q. Yao and D. Ma, *Org. Lett.*, 2012, **14**, 3056; (*e*) C. Fischer and B. Koenig, *Beilstein J. Org. Chem.*, 2011, **7**, 59; (*f*) D. S. Surry and S. L. Buchwald, *Chem. Sci.*, 2011, **2**, 27; (*g*) F. Monnier and M. Taillefer, *Angew. Chem., Int. Ed.*, 2009, **48**, 6954.

2 (*a*) T. Henkel, R. M. Brunne, H. Müller and F. Reichel, *Angew. Chem., Int. Ed.*, 1999, **111**, 688; (*b*) F. Fache, E. Schulz, M. L. Tommasino and M. Lemaire, *Chem. Rev.*, 2000, **100**, 2159; (*c*) M. Feher and J. M. Schmidt, *J. Chem. Inf. Comput. Sci.*, 2002, **43**, 218; (*d*) R. Hili and A. K. Yudin, *Nat. Chem. Biol.*, 2006, **2**, 284; (*e*) N. Ramkumar and R. Nagarajan, *J. Org. Chem.*, 2014, **79**, 736; (*f*) D. B. Ramachary and J. Sangeeta, *Org. Biomol. Chem.*, 2011, **9**, 1277; (*g*) M. Bakthadoss, D. Kannan, J. Srinivasan and V. Vinayagam, *Org. Biomol. Chem.*, 2015, **13**, 2870.

3 (*a*) C. Venkatesh, B. Singh, P. K. Mahata, H. Ila and H. Junjappa, *Org. Lett.*, 2005, **7**, 2169; (*b*) Y. Kikugawa, A. Nagashima, T. Sakamoto, E. Miyazawa and M. Shiiya, *J. Org. Chem.*, 2003, **68**, 6739; (*c*) X. Ban, Y. Pan, Y. Lin, S. Wang, Y. Du and K. Zhao, *Org. Biomol. Chem.*, 2012, **10**, 3606.

4 (*a*) K. Shin, H. Kim and S. Chang, *Acc. Chem. Res.*, 2015, **48**, 1040; (*b*) M. A. Mcgowan, J. L. Henderson and S. L. Buchwald, *Org. Lett.*, 2012, **14**, 1432; (*c*) C.-L. Sun and Z.-J. Shi, *Chem. Rev.*, 2014, **114**, 9219; (*d*) A. F. Larsen and T. Ulven, *Chem. Commun.*, 2014, **50**, 4997; (*e*) S. Ueda and S. L. Buchwald, *Angew. Chem., Int. Ed.*, 2012, **51**, 10364; (*f*) X.-X. Guo, D.-W. Gu, Z. Wu and W. Zhang, *Chem. Rev.*, 2015, **115**, 1622; (*g*) F. S. Melkonyan, D. E. Kuznetsov, M. A. Yurovskaya and A. V. Karchava, *RSC Adv.*, 2013, **3**, 8388; (*h*) A. Sh. El-Etrawy and A. A.-H. Abdel-Rahman, *Chem. Heterocycl. Compd.*, 2010, **46**, 1033.

5 R. Samanta, K. Matcha and A. P. Antonchick, *Eur. J. Org. Chem.*, 2013, 5769.

6 *Organic Azides: Syntheses and Applications*, ed. S. Bräse and K. Banert, Wiley & Sons, 2010.
7 (*a*) K. Seth, M. Nautiyal, P. Purohit, N. Parikh and A. K. Chakraborti, *Chem. Commun.*, 2015, **51**, 191; (*b*) F. Collet, R. H. Dodd and P. Dauban, *Chem. Commun.*, 2009, **45**, 5061; (*c*) J. Y. Kim, S. H. Park, J. Ryu, S. H. Cho, S. H. Kim and S. Chang, *J. Am. Chem. Soc.*, 2012, **134**, 9110.
8 C. Tang, Y. Yuan and N. Jiao, *Org. Lett.*, 2015, **17**, 2206.
9 (*a*) D.-G. Yu, M. Suri and F. Glorius, *J. Am. Chem. Soc.*, 2013, **135**, 8802; (*b*) Y. Lian, J. R. Hummel, R. G. Bergman and J. A. Ellman, *J. Am. Chem. Soc.*, 2013, **135**, 12548; (*c*) Q.-Z. Zheng, P. Feng, Y.-P. Liang and N. Jiao, *Org. Lett.*, 2013, **15**, 4262.
10 H. Ma, D. Li and W. Yu, *Org. Lett.*, 2016, **18**, 868.
11 (*a*) S. Vidyacharan, A. Sagar, N. C. Chaitra and D. S. Sharada, *RSC Adv.*, 2014, **4**, 34232; (*b*) S. Vidyacharan, N. C. Chaitra, A. Sagar and D. S. Sharada, *Synth. Commun.*, 2015, **45**, 898; (*c*) S. Vidyacharan, A. Sagar and D. S. Sharada, *Org. Biomol. Chem.*, 2015, **13**, 7614; (*d*) S. Vidyacharan, A. H. Shinde, B. Satpathi and D. S. Sharada, *Green Chem.*, 2014, **16**, 1168; (*e*) A. H. Shinde, S. Vidyacharan and D. S. Sharada, *Tetrahedron Lett.*, 2014, **55**, 3064; (*f*) A. Sagar, V. N. Babu and D. S. Sharada, *RSC Adv.*, 2015, **5**, 29066; (*g*) A. Sagar, V. N. Babu and D. S. Sharada, *Tetrahedron Lett.*, 2015, **56**, 2710.
12 (*a*) Z. Zheng, S. Ma, L. Tang, D. Zhang-Negrerie, Y. Du and K. Zhao, *J. Org. Chem.*, 2014, **79**, 4687; (*b*) V. V. Zhdankin and P. J. Stang, *Chem. Rev.*, 2002, **102**, 2523; (*c*) H. Tohma and Y. Kita, *Adv. Synth. Catal.*, 2004, **346**, 111; (*d*) V. V. Zhdankin and P. J. Stang, *Chem. Rev.*, 2008, **108**, 5299; (*e*) T. Dohi and Y. Kita, *Chem. Commun.*, 2009, 2073; (*f*) J. P. Brand, D. F. Gonzalez, S. Nicolai and J. Waser, *Chem. Commun.*, 2011, **47**, 102; (*g*) Y. He, J. Huang, D. Liang, L. Liu and Q. Zhu, *Chem. Commun.*, 2013, **49**, 7352; (*h*) F. Zhao, X. Liu, R. Qi, D. Zhang-Negrerie, J. Huang, Y. Du and K. Zhao, *J. Org. Chem.*, 2011, **76**, 10338; (*i*) A. Yoshimura and V. V. Zhdankin, *Chem. Rev.*, 2016, **116**, 3328.
13 (*a*) L. Marcus, N. Kingi and J. Bergman, *J. Med. Chem.*, 2008, **51**, 7744.
14 (*a*) J. K. Landquist, in *Comprehensive Heterocyclic Chemistry*, ed. A. R. Katritzky and C. W. Rees, Pergamon, Oxford, 1984, vol. 1, p. 166; (*b*) L. E. Seitz, W. J. Suling and R. C. Reynolds, *J. Med. Chem.*, 2002, **45**, 5604; (*c*) Y. B. Kim, Y. H. Kim, J. Y. Park and S. K. Kim, *Bioorg. Med. Chem. Lett.*, 2004, **14**, 541; (*d*) W. He, M. R. Meyers, B. Hanney, A. Spada, G. Blider, H. Galzeinski, D. Amin, S. Needle, K. Page, Z. Jayyosi and H. Perrone, *Bioorg. Med. Chem. Lett.*, 2003, **13**, 3097; (*e*) C. W. Lindsley, Z. Zhao, W. H. Leister, R. G. Robinson, S. F. Barnett, D. Defeo-Jones, R. E. Jones, G. D. Hartman, J. R. Huff, H. E. Huber and M. E. Duggan, *Bioorg. Med. Chem. Lett.*, 2005, **15**, 761.
15 (*a*) P. Gawrys, T. Marszalek, E. Bartnik, M. Kucinska, J. Ulanski and M. Zagorska, *Org. Lett.*, 2011, **13**, 6091.
16 (*a*) S. Okumura, Y. Takeda, K. Kiyokawa and S. Minakata, *Chem. Commun.*, 2013, **49**, 9266; (*b*) Z.-J. Yang, C.-Z. Liu, B.-L. Hu, C.-L. Deng and X.-G. Zhang, *Chem. Commun.*, 2014, **50**, 14554; (*c*) S. Shi, T. Wang, W. Tang, M. Ruldoph and A. S. Hashmi, *Chem. – Eur. J.*, 2013, **19**, 6576.
17 (*a*) S. C. Shim and S. K. Lee, *Synthesis*, 1980, **2**, 116; (*b*) R. N. Hinkens, M. B. Vamos and D. Maetens, *J. Heterocycl. Chem.*, 1980, **17**, 873.