## Green Chemistry

Cite this: Green Chem., 2012, 14, 3269

www.rsc.org/greenchem

## COMMUNICATION

# Cascade [4 + 1] annulation *via* more environmentally friendly nitrogen ylides in water: synthesis of bicyclic and tricyclic fused dihydrofurans<sup>†</sup>

Atul Kumar,\* Suman Srivastava and Garima Gupta

*Received 12th August 2012, Accepted 3rd October 2012* DOI: 10.1039/c2gc36276g

A novel imidazolium ylide activated [4 + 1] annulation approach is described for the diastereoselective synthesis of bicyclic and tricyclic fused dihydrofurans in water. This cascade annulation presumably proceeds *via* a Michael reaction triggered zwitterion enolate followed by concomitant intramolecular cyclization. The methodology has distinction of being the first report on imidazolium ylide mediated [4 + 1] annulation in water as a unified greener approach involving an *in situ* base regeneration system and an alternative to pyridine ylide.

Five-membered oxygen-containing heterocycles are valuable synthetic intermediates in a diverse range of naturally occurring and pharmacologically active molecules.<sup>1</sup> Annulated dihydro-furan motifs such as furopyranone, furochromenone and tetra-hydrobenzofuran are versatile intermediates in numerous natural products and therapeutic agents such as plicadin,<sup>2</sup> neo-tanshinlactone,<sup>3</sup> medicagol,<sup>4</sup> psoralidin,<sup>5</sup> wedelolactone,<sup>6</sup> myco-rrhizin A,<sup>7</sup> evodone,<sup>8</sup> coumestan and coumestrol<sup>9</sup> (Fig. 1).

Their broad occurrence in natural or synthetic bioactive substances has stimulated significant interest in the development of new, efficient preparation methods. Among numerous known synthetic methods, cascade [4 + 1] annulation with a twoelectron, one-carbon fragment which features both C–C and C–O bond formation in one step represents the particularly attractive transformation for these subunits.<sup>10</sup>



Fig. 1 Natural product containing furan motifs.

†Electronic supplementary information (ESI) available: Experimental procedures and spectral data for all the compounds. See DOI: 10.1039/c2gc36276g



Scheme 1 Imidazolium ylide mediated cascade [4 + 1] annulation.

In this perspective carbon monoxide,<sup>11</sup> isocyanides,<sup>12</sup> diazo reagents,<sup>13</sup> nucleophilic carbenes,<sup>14</sup> *N*-heterocyclic carbenes<sup>15</sup> (NHCs) are used as a typical one carbon unit source. Ylides such as nitrogen,<sup>16</sup> phosphorous<sup>17</sup> and sulphur<sup>18</sup> have been developed as functional two-electron, one-carbon units, and now considered as a powerful tool for annulations. Nitrogen ylides in particular have been widely employed for the construction of heterocycles.<sup>19</sup> However, pyridine is the most extensively used nitrogen ylide in synthetic chemistry,<sup>20</sup> but the use of pyridine has generated some limitations due to toxicity and cumbersome work-up procedures. Recently, Tang and co-workers have tried to reduce quantity of pyridine for the synthesis of dihydrofuran by using pyridine and Fe(Tcpp)Cl combination.<sup>21</sup>

We wish to report here imidazolium ylide, a novel greener nitrogen ylide mediated cascade [4 + 1] annulation for the synthesis of bicyclic and tricyclic fused dihydrofurans in water (Scheme 1). This approach involves a green alternative to pyridinium ylide chemistry.

The growing importance of green chemistry has lighted the search for transformations that are capable of promoting two or more distinct transformations sequentially in one pot with eco-friendly conditions or under aqueous conditions.<sup>22</sup> Cascade reactions<sup>23</sup> constituting an attractive branch of organic chemistry thus considered to fall under the category of "green chemistry due to the undeniable benefits of atom economy, as well as economies of time, resource management, and waste generation".

As part of our plan we aimed at developing new ecofriendly synthesis of biologically important heterocycles,<sup>24</sup> as well as synthesis of natural product tryptanthrin in water,<sup>25</sup> which inspired us to investigate the environment friendly conditions for the synthesis of dihydrofuran derivatives.

Despite the existence of various elegant stepwise methods for building fused dihydrofuran ring systems,<sup>26</sup> green and efficient processes are extremely scarce. Herein we report imidazolium ylide mediated [4 + 1] annulation for the highly efficient and diastereoselective construction of functionalized dihydrofuran in

Medicinal and Process Chemistry Division, CSIR-Central Drug Research Institute, Lucknow, 226001, India. E-mail: dratulsax@gmail.com, dratulkumarlab@gmail.com



Scheme 2 Imidazolium ylide mediated [4 + 1] cascade annulation with an *in situ* base regeneration system.

water, and it is observed that imidazolium ylide acts as a twoelectron, one-carbon fragment in a cascade [4 + 1] annulation approach, having an advantage of *in situ* base regeneration systems (Scheme 2). In this approach *N*-methyl imidazole acts as a base for deprotonation and Knoevenagel condensation. Subsequently *N*-methyl imidazole acts as a good leaving group to finish the intramolecular substitution reaction. This *in situ* generated *N*-methyl imidazole also acts as a base for the rest of the reaction, hence minimises the amount of the base required for the reaction.

The imidazolium ylide, 5, was generated in situ from N-methyl-3-phenacylimidazolium bromide 3 by its deprotonation with the use of a base, 3 in turn can be synthesized by the reaction of phenacyl bromide and N-methyl imidazole in ether. 3-Benzylidene-6-methyl-2H-pyran-2,4(3H)-dione, 4, was easily synthesized in situ from 4-hydroxy-6-methyl-2H-pyran-2-one and aldehyde via Knoevenagel condensation catalyzed by a base as illustrated in Scheme 2. N-Methyl-3-phenacylimidazolium bromide, 3, would react with benzylidene-6-methyl-2H-pyran-2,4(3H)-dione, 4, via [4 + 1] annulation leading to the corresponding 2-benzoyl-6-methyl-3-phenyl-2H-furo[3,2-c]pyran-4(3H)one, 6. A series of experiments were performed by varying solvents and base to arrive at the best optimal reaction conditions and establish the superiority of water as a solvent compared to commonly utilized organic solvents. The results are summarised in Table 1. In search for a greener solvent, the reaction was performed in water, CH<sub>3</sub>CN, DMF, THF, toluene and ethanol (entries 1–11). Delightfully, we found that the reaction in water furnished the maximum yield of the product (95%) in only 2 h (entry 1), and hence all subsequent experiments were performed in this medium. The model reaction was also investigated employing different bases, viz. DBU, Et<sub>3</sub>N, K<sub>2</sub>CO<sub>3</sub>, N-methyl imidazole, and the results show that the N-methyl imidazole is ideal for the reaction.

With the optimum conditions in hand, we began to explore the substrate scope of this imidazolium ylide mediated cascade [4 + 1] annulation. As highlighted in Schemes 3–5 this strategy proved to be tolerant of a wide range of diketones such as 4-hydroxy-6-methyl-2*H*-pyran-2-one, 4-hydroxy coumarin, cyclohexane 1,3-dione and dimidone, the corresponding furopyranone, furochromenone and tetrahydrobenzofuranone were obtained in moderate to excellent yields (80–95%) with high diastereoselectivity.

 Table 1
 Optimisation of solvent and base<sup>a</sup>

Entry	Solvent	Base	Time (h)	$\mathrm{Yield}^{e}(\%)$
1	Water <sup>b</sup>	N-Methyl imidazole	2	95
2	Water <sup>b</sup>	N-Methyl imidazole <sup><math>c</math></sup>	10	67
3	Water <sup>b</sup>	N-Methyl imidazole <sup>d</sup>	10	58
4	EtOH	N-Methyl imidazole	2	40
5	Toluene	N-Methyl imidazole	2	50
6	THF	N-Methyl imidazole	2	30
7	$DMF^{b}$	N-Methyl imidazole	2	68
8	CH <sub>3</sub> CN	N-Methyl imidazole	3	80
9	Water <sup>b</sup>	DBU (5 mmol)	6	60
10	Water <sup>b</sup>	$Et_3N$ (5 mmol)	8	67
11	Water <sup>b</sup>	$K_2CO_3$ (5 mmol)	12	20

<sup>*a*</sup> Reaction conditions: 1-methyl-3-phenacylimidazolium bromide (1 mmol), 4-hydroxy-6-methyl-2*H*-pyran-2-one (1 mmol) and benzaldehyde (1 mmol), *N*-methyl imidazole (0.5 mmol) in solvent (5 mL) at reflux temperature. <sup>*b*</sup> 100 °C. <sup>*c*</sup> *N*-Methyl imidazole (0.2 mmol). <sup>*d*</sup> *N*-Methyl imidazole (0.1 mmol). <sup>*e*</sup> Isolated yield.



<sup>a</sup>Reaction condition: Aldehyde (1 mmol), *N*-methyl imidazolium salt (1 mmol), 4-hydroxy-6-methyl-2*H*-pyran-2-one (1 mmol) and *N*- methyl imidazole (0.5 mmol), 100 °C, 2h in water. <sup>b</sup>Isolated yield.

Scheme 3 Synthesis of furopyranone.<sup>a</sup>



Entry	Compounds	$\mathbb{R}^1$	R	Yield <sup>b</sup> (%)
9	8a	Н	Isopropyl	92
10	8b	$OCH_3$	Ph	87
11	8c	Br	2,4 Cl Ph	89
12	8d	$OCH_3$	Fc	88

<sup>*a*</sup>Reaction condition: Aldehyde (1 mmol), *N*-methyl imidazolium salt (1 mmol), 4-hydroxy coumarin (1 mmol) and *N*-methylimidazole (0.5 mmol), 100 °C, 2h in water. <sup>*b*</sup>Isolated yield.

Scheme 4 Synthesis of furochromenone.<sup>a</sup>

	$\sim$ Br $\sim$ R <sup>2</sup> R <sup>2</sup>	O O	100 °	$P_{C_{2h}}^{N-} \xrightarrow{Q}_{R^2}^{O}$	
R <sup>1</sup> 3		9		10	<b>)a-j</b> R <sup>1</sup>
Entry	Compounds	$\mathbb{R}^2$	$\mathbb{R}^1$	R	Yield <sup>b</sup> (%)
13	10a	Η	Н	3-NO <sub>2</sub> Ph	88
14	10b	Н	Н	$4- \operatorname{OCH}_3 \operatorname{Ph}$	85
15	10c	Н	Н	4- Cl Ph	89
16	10d	Н	Н	Biphenyl	82
17	10e	$\mathrm{CH}_3$	Η	Propyl	94
18	10f	$\mathrm{CH}_3$	4-Br	2,5-OCH <sub>3</sub> Ph	87
19	10g	$\mathrm{CH}_3$	Н	Napthyl	84
20	10h	$\mathrm{CH}_3$	Н	3-NO <sub>2</sub> Ph	86
21	10i	Η	Н	Fc	88
22	10j	$\mathrm{CH}_3$	OCH <sub>3</sub>	Fc	87

<sup>a</sup>Reaction condition: Aldehyde (1 mmol), *N*-methyl imidazolium salt (1 mmol), cyclohexane 1, 3-dione / dimidone (1 mmol) and *N*-15 methylimidazole (0.5 mmol), 100 °C, 2h in water. <sup>b</sup>Isolated yield.

Scheme 5 Synthesis of tetrahydrobenzofuranone.<sup>a</sup>



Fig. 2 Key COSY correlations of compound 8c.

Electronic and steric variations of imidazolium ylides were accommodated with good yields. To expand the scope of the [4 + 1] annulation, several aromatic, aliphatic, heteroaromatic as well as organometallic aldehydes were investigated. Products **6a–h**, **8a–d**, **10a–j** were well characterized by NMR spectroscopy. The relative configuration of the products was established by coupling constants (*J*) of <sup>1</sup>H NMR.

The structures of all the compounds were established from one-dimensional (<sup>1</sup>H NMR and <sup>13</sup>C NMR) and two-dimensional (COSY, HSQC, and HMBC) NMR spectral data. Compound **8c** was chosen as a representative example. H-2 and H-3 occur as doublets at 6.07 (J = 5.1 Hz) and 5.45 (J = 5.0 Hz) ppm respectively and among these two protons an H, H-COSY correlation was observed (Fig. 2). The doublet at 6.07 ppm is assigned to H-2, and has HSQ correlation with 90.70 ppm. The H-2 proton shows HMB correlation with C1', C3, C3a, C9b (Fig. 3), and H-3 shows an HMB correlation with C1', C2, C2', C1'', C3a, C9b (Fig. 3).

A mechanism that could explain the aforementioned reactions is proposed in Fig. 4. The Michael addition of imidazolium ylides with enones affords the zwitterionic intermediate I. Tautomerisation of zwitterionic intermediate I affords resonancestabilized zwitterion enolate intermediate II. The zwitterion



Fig. 3 Key HMBC correlations of compound 8c.



Fig. 4 Plausible reaction mechanism for an imidazolium ylide activated zwitterion mediated [4 + 1] annulation approach.

enolate II subsequently undergoes annulation *via* displacement of *N*-methyl imidazole to give the product.

The last step is a typical intramolecular  $S_N 2$  substitution reaction. The stereochemistry of the  $S_N 2$  reaction necessitated nucleophilic enolate attack from the back side of the electrophilic carbon atom bearing the leaving imidazolium group, which subsequently assumes 2-benzoyl and 3-aryl groups in a stereochemical opposite position for the sake of steric hindrance in carbanion and transition states. Thus, only *trans* isomeric 2,3-dihydrofuran is obtained as a sole product.

#### Conclusions

In summary, we have developed a green nitrogen ylide mediated [4 + 1] annulation approach *via* an imidazolium ylide for the synthesis of diastereoselective fused dihydrofurans in water. This is the first approach involving an *in situ* base regeneration system, therefore minimizing the amount of the base. Further expansion of this green nitrogen ylide activated approach is in progress.

#### Experimental

#### Typical procedure for the preparation of 1-methyl-3phenacylimidazoliumbromide (3)

A solution of 8.2 g (0.1 mol) of *N*-methylimidazole and 20.0 g (0.1 mol) of phenacyl bromide in 300 mL of ether was allowed to stand at room temperature for 16 h. The solids, which separated, were collected and then recrystallized from acetonitrile to afford 27.0 g (95%) of 1-methyl-3-phenacylimidazolium bromide as a white powder.

### Representative one pot procedure for the synthesis of 6a–h, 8a–d, and 10a–j

A mixture of substituted aldehyde (1 mmol), 4-hydroxy coumarin/5,5 dimethyl,1,3-cyclohexanedione/1,3-cyclohexanedione/ 4-hydroxy-6-methyl-2*H*-pyran-2-one (1 mmol) and *N*-methyl imidazole (0.5 mmol) in water (5 mL) was allowed to reflux for 1 h at 100 °C. After that 1-methyl-3-phenacylimidazolium bromide (1 mmol) was added and stirring was continued for 1 h at 100 °C. After completion of the reaction as indicated on TLC, the reaction mixture was extracted with ethyl acetate and water. The organic layer was dried over anhydrous sodium sulphate and concentrated *in vacuo*. The crude product was chromatographed on a silica gel column with a hexane–ethyl acetate mixture to afford dihydrofuran derivatives **6a–h**, **8a–d**, and **10a–j** in good to excellent yields.

#### Acknowledgements

SS and GG are thankful to CSIR-UGC for the financial assistance. SAIF-CDRI was acknowledged for providing the spectral data. CSIR-CDRI Communication Number 8335.

#### Notes and references

- (a) M. C. Elliott and E. Williams, J. Chem. Soc., Perkin Trans. 1, 2001, 2303–2340; (b) M. C. Elliott, J. Chem. Soc., Perkin Trans. 1, 2000, 1291–1318; (c) M. L. King, C. C. Chiang, H. C. Ling, E. Fujita, M. Ochiai and A. T. McPhail, J. Chem. Soc., Chem. Commun., 1982, 1150; (d) B. Y. Hwang, B.-N. Su, H. Chai, Q. Mi, L. B. S. Kardono, J. J. Afriastini, S. Riswan, B. D. Santarsiero, A. D. Mesecar, R. Wild, C. R. Fairchild, G. D. Vite, W. C. Rose, N. R. Farnsworth, G. A. Cordell, J. M. Pezzuto, S. M. Swanson and A. D. Kinghorn, J. Org. Chem., 2004, 69, 3350.
- 2 B. A. Chauder, A. V. Kalinin, N. J. Taylor and V. Snieckus, Angew. Chem., Int. Ed., 1999, 38, 1435–1438.
- 3 (a) X. Wang, K. F. Bastow, C.-M. Sun, Y.-L. Lin, H.-J. Yu, M.-J. Don, T.-S. Wu, S. Nakamura and K.-K. Lee, *J. Med. Chem.*, 2004, **47**, 5816– 5819; (b) X. Wang, K. Nakagawa-Goto, K. F. Bastow, M.-J. Don, Y.-L. Lin, T.-S. Wu and K.-H. Lee, *J. Med. Chem.*, 2006, **49**, 5631–5634.
- 4 (a) R. T. Scannell and R. Stevenson, J. Heterocycl. Chem., 1980, 17, 1727–1728; (b) A. L. Livingston, S. C. Witt, R. E. Lundin and E. M. Bickoff, J. Org. Chem., 1965, 30, 2353–2355.
- 5 P. Pahari and J. Rohr, J. Org. Chem., 2009, 74, 2750-2754.
- 6 C. C. Li, Z. X. Xie, Y. D. Zhang, J. H. Chen and Z. Yang, J. Org. Chem., 2003, 68, 8500–8504.
- 7 (a) J. Trofast and B. Wickberg, *Tetrahedron*, 1977, 33, 875; (b) B. Yu,
   T. Jiang, W. Quan, J. Li, X. Pan and X. She, *Org. Lett.*, 2009, 11, 629–632.
- R. R. Juo and W. Herz, J. Org. Chem., 1985, 50, 700–703;
   (b) P. A. Jacobi, D. G. Walker and I. M. A. Odeh, J. Org. Chem., 1981, 46, 2065–2069; (c) M. Aso, A. Ojida, G. Yang, O. J. Cha, E. Osawa and K. Kanematsu, J. Org. Chem., 1993, 58, 3960–3968.
- 9 (a) G. A. Kraus and N. Zhang, J. Org. Chem., 2000, 65, 5644–5646; (b) T. Yao, D. Yue and R. C. Larock, J. Org. Chem., 2005, 70, 9985–9989.
- 10 (a) K. C. Nicolaou, D. J. Edmonds and P. G. Bulger, Angew. Chem., Int. Ed., 2006, 45, 7134–7186; (b) X. Fang, K. Jiang, C. Xing, L. Hao and Y. R. Chi, Angew. Chem., Int. Ed., 2011, 50, 1910–1913.
- 11 (a) T. Mandai, J. Tsuji, Y. Tsujiguchi and S. Saito, J. Am. Chem. Soc., 1993, 115, 5865; (b) M. Murakami, K. Itami and Y. Ito, Angew. Chem.,

1995, **107**, 2943, (Angew. Chem., Int. Ed. Engl., 1995, **34**, 2691); (c) M. S. Sigman and B. E. Eaton, J. Am. Chem. Soc., 1996, **118**, 11783.

- 12 M. Oshita, K. Yamashita, M. Tobisu and N. Chatani, J. Am. Chem. Soc., 2005, 127, 761–766.
- 13 L.-B. Zhao, Z.-H. Guan, Y. Han, Y.-X. Xie, S. He and Y.-M. Liang, J. Org. Chem., 2007, 72, 10276–10278.
- 14 (a) J. H. Rigby and W. Dong, Org. Lett., 2002, 2, 1673; (b) C. Spino,
  H. Rezaei, K. Dupont-Gaudet and F. B. langer, J. Am. Chem. Soc., 2004,
  126, 9926; (c) L. Boisvert, F. Beaumier and C. Spino, Org. Lett., 2007, 9,
  5361.
- 15 (a) F.-g. Sun and S. Ye, Org. Biomol. Chem., 2011, 9, 3632; (b) C. Ma and Y. Yang, Org. Lett., 2005, 7, 1343–1345.
- 16 Z. Shi, B. Tan, W. Wen, Y. Leong, X. Zeng, M. Lu and G. Zhong, Org. Lett., 2010, 12, 5402–5405.
- 17 (a) J. Tian, R. Zhou, H. Sun, H. Song and Z. He, J. Org. Chem., 2011, 76, 2374–2378; (b) Y. Du, X. Lu and C. Zhang, Angew. Chem., 2003, 115, 1065–1067.
- 18 (a) A. M. Bernard, A. Frongia, P. P. Piras, F. Secci and M. Spiga, Org. Lett., 2005, 7, 4565–4568; (b) J.-C. Zheng, C.-Y. Zhu, X.-L. Sun and Y. Tang, J. Org. Chem., 2008, 73, 6909–6912; (c) L.-Q. Lu, J.-J. Zhang, F. Li, Y. Cheng, J. An, J.-R. Chen and W.-J. Xiao, Angew. Chem., Int. Ed., 2010, 49, 4495–4498; (d) L.-Q. Lu, F. Li, J. An, Y. Cheng, J.-R. Chen and W.-J. Xiao, Chem.–Eur. J., 2012, 18, 4073–4079.
- 19 (a) J. A. Vanecko and F. G. West, Org. Lett., 2002, 4, 2813–2816; (b) E. Vedejs, D. W. Piotrowski and F. C. Tucci, J. Org. Chem., 2000, 65, 5498–5505.
- 20 (a) C. P. Chuang and A. I. Tsai, *Synthesis*, 2006, 675–674; (b) Q. F. Wang, H. Hou, L. Hui and C. G. Yan, *J. Org. Chem.*, 2009, 74, 7403–7408; (c) Y. Han, H. He, R. Yao, Q. Fu and C. G. Yan, *Synthesis*, 2010, 4061–4067.
- 21 C.-R. Liu, B.-H. Zhu, J.-C. Zheng, X.-L. Sun, Z. Xieb and Y. Tang, *Chem. Commun.*, 2011, 47, 1342–1344.
- 22 (a) R. T. Baker and W. Tumas, Science, 1999, 284, 1477; (b) P. T. Anastas and J. C. Warner, Green Chemistry: Theory and Practice, Oxford University Press, Oxford, 1998; (c) P. Anastas and T. Williamson, Green Chemistry, Frontiers in Benign Chemical Synthesis and Procedures, Oxford Science Publications, Oxford, 1998; (d) S. Kobayashi and K. Manabe, Acc. Chem. Res., 2002, 35, 209; (e) U. K. Lindström, Chem. Rev., 2002, 102, 2751; (f) C. J. Li, Chem. Rev., 2005, 105, 3095; (g) U. M. Lindstrom, Organic Reactions in Water, Blackwell Publishing, Oxford, UK, 2007; (h) V. K. Ahluwalia and R. S. Varma, Green Solvents for Organic Synthesis, Alpha Science International, Abingdon, UK, 2009; (i) C. J. Li, Chem. Rev., 1993, 93, 2023.
- 23 For selected reviews on the cascade reactions that involve dipole type intermediates to construct heterocycles, see: (a) A. Padwa and S. K. Bur, *Tetrahedron*, 2007, 63, 5341; (b) A. Padwa, *Progr. Heterocycl. Chem.*, 2009, 20, 20; (c) J. D. Weaver, A. Recio III, A. J. Grenning and J. A. Tunge, *Chem. Rev.*, 2011, 111, 1846; (d) C. Wang and J. A. Tunge, *J. Am. Chem. Soc.*, 2008, 130, 8118; (e) R. Shintani, M. Murakami, T. Tsuji, H. Tanno and T. Hayashi, *Org. Lett.*, 2009, 11, 5642; (f) B. M. Trost and S. M. Silverman, *J. Am. Chem. Soc.*, 2010, 132, 8238; (g) Q. Zhang, L. Yang and X. Tong, *J. Am. Chem. Soc.*, 2010, 132, 2550, and references therein.
- 24 (a) A. Kumar and S. Sharma, Green Chem., 2011, 13, 2017–2020;
  (b) A. Kumar, G. Gupta and S. Srivastava, Green Chem., 2011, 13, 2459–2463;
  (c) A. Kumar, M. Kumar and M. K. Gupta, Green Chem., 2012, 14, 2677–2681;
  (d) A. Kumar, M. Kumar, M. Kumar, M. K. Gupta and L. P. Gupta, RSC Advances, 2012, 2, 8277–8280;
  (e) A. Kumar, M. K. Gupta and M. Kumar, Green Chem., 2012, 14, 290;
  (f) A. Kumar, M. K. Gupta and M. Kumar, RSC Advances, 2012, 2, 7371–7376.
- 25 A. Kumar, V. D. Tripathi and P. Kumar, *Green Chem.*, 2011, **13**, 51–54.
- 26 (a) L.-P. Fan, P. Li, X.-S. Li, D.-C. Xu, M.-M. Ge, W.-D. Zhu and J.-W. Xie, J. Org. Chem., 2010, 75, 8716–8719; (b) Y. Ye, L. Wang and R. Fan, J. Org. Chem., 2010, 75, 1760–1763; (c) J. L. Garrido, I. Alonso and J. C. Carretero, J. Org. Chem., 1998, 63, 9406–9413; (d) M. P. Doyle, D. C. Forbes, M. N. Protopopova, S. A. Stanley, M. M. Vasbinder and K. R. Xavier, J. Org. Chem., 1997, 62, 7210–7215.