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[3+2] Cycloadditions of α -acyl ketene dithioacetals with propargylamines: pyrrole synthesis in water

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ABSTRACT

A series of 2,3,4-trisubstituted and 1,2,3,4-tetrasubstituted pyrroles were synthesized via [3+2] cycloaddition of α -acyl ketene dithioacetals (or related substrates) with commercially available propargylamines as 1,3-dipoles in water. Most of the reactions can be performed in the absence of an external base. The reaction of secondary amine (*N*-methylprop-2-yn-1-amine) with α -acyl ketene dithioacetals showed different reaction behaviours depending on the addition or absence of an external base.

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Increased environmental awareness within the synthetic organic chemistry community has lately pushed green chemistry technologies to the fore and led to the development of cleaner and relatively benign chemical processes.¹ The use of water as solvent has attracted increasing interest in recent years.² Indeed, water is an environmentally benign, non-flammable liquid over a wide temperature range and possesses a high heat capacity making it inherently safe. Furthermore, the insolubility of organic compounds in water causes them to react on its surface and often exhibits unique reactivity and selectivity that cannot be attained with conventional organic solvents.² Consequently, the design of novel methods to prepare the privileged heterocyclic scaffolds that combine the synthetic efficiency of domino protocols and the use of water as the reaction medium constitutes a very important challenge in green chemistry.³

As one of the most important classes of heterocycles, pyrroles are not only the key subunits in numerous natural products,⁴ pharmaceutical substances⁵ and organic materials,⁶ but are also useful and versatile building blocks in organic synthesis.⁷ As a consequence, much attention has been paid to the synthesis of pyrrole derivatives either by classic methods such as the Paal–Knorr,⁸ Hantzsch,⁹ Barton–Zard and Van Leusen^{7b,10} or by transition metal-catalysed cyclization¹¹ and multicomponent reaction.¹² However, most of these methods require the use of organic solvents which are harmful to the environment. Therefore, the efficient

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construction of substituted pyrroles in aqueous media is important, in particular, those performed under metal-free conditions.¹³ During our research on the synthesis of carbocyclic¹⁴ and heterocyclic compounds^{15–17} by domino reactions, very recently, we developed a new synthetic strategy for the direct synthesis of 2,3,4-trisubstituted and 1,2,3,4-tetrasubstituted pyrroles via the [3+2] cycloaddition strategy in DMF solvent with propargylamines as 1,3-dipoles.¹⁷ The concept of green chemistry and our continuing interest in organic reaction in aqueous media¹⁸ prompted us to explore the feasibility of the [3+2] cycloaddition in water. As a result, it was found that water is not only an efficient green solvent for the [3+2] cycloaddition of propargylamines with polarized α -acyl ketene dithioacetals or vinylogous thiolesters as the dipolarophiles, but allows a wider choice of products of the reaction. Herein, we wish to letter a recent development in the use of propargylamines as 1.3-dipoles for the synthesis of polysubstituted pyrroles in water.

Initially, the reaction of α , α -diacetyl ketene dithioacetal **1a** with propargylamine **2a** was employed as a model reaction in water. It was found that, in the presence of K₂CO₃ or DBU (1,8-diazabicy-clo[5.4.0]undec-7-ene), the desired product 2,3,4-trisubstituted pyrrole **4a** was produced only in moderate to good yields (45–70%) by treating **1a** (0.5 mmol) with **2a** (0.5 mmol) in H₂O (5 mL) at 100 °C for 12–20 h (Table 1, entries 1–4). In these cases, the deacylative product **3a** was also obtained and the yield of **3a** increased with increasing the amount of base. Interestingly, under identical conditions but in the absence of an external base, **4a** was produced in higher yield (Table 1, entry 5). To our delight, the yield of **4a** raised to 93% by increasing the amount of **2a** to 2.0 equiv without the addition of an external base (Table 1, entry





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Table 1Optimization of reaction conditions^a



 Entry	2a (equiv)	Base (equiv)	Solvent	Time (h)	Yield ^b (%) 4a 3a 1a
1	1.0	DBU (1.0)	H ₂ O	12	45 38 0
2	1.0	DBU (0.5)	H_2O	20	60 20 0
3	1.0	DBU (0.3)	H_2O	20	70 10 0
4	1.0	K_2CO_3 (1.0)	H_2O	12	65 25 0
5	1.0	-	H_2O	16	80 0 11
6	2.0	-	H_2O	12	93 0 0

^a All reactions were carried out in open air.

^b Isolated yield.

6). This result suggested that propargylamine **2a** plays a dual role as both a base and a nucleophile in the above deacylative [3+2] cycloaddition reaction. In comparison, α -acetyl ketene dithioacetal **3a** failed to react with **2a** in H₂O either in the presence or absence of K₂CO₃ (1.0 equiv) with intact substrate **3a** recovered, which indicates that **3a** would not be involved in the formation of **4a** since **3a** (having only one EWG; EWG = electron-withdrawing group) is much less reactive than **1a** (having two EWGs) for S_NV reaction.¹⁹

Obviously, the above result provides a clean and efficient route to highly substituted pyrroles from easily available substrates in water under transition-metal-free conditions in a single operation. With this viable protocol in hand, the scope of the reaction was then investigated by the reactions of propargylamine 2a with α -acyl ketene dithioacetals **1** under optimal conditions (Table 1, entry 6) and the results are summarized in Table 2. It was found that the [3+2] cvcloaddition is not sensitive to the nature of the EWG of substrates **1** and exhibits good flexibility. All the reactions of **2a** with acvl ketene dithioacetals **1a**-**n** bearing the EWG as acetyl, propionyl, ethoxycarbonyl, benzoyl, and N-arylcarbamoyl with either electron-neutral, electron-deficient or electron-rich group on the benzene ring, nitro and cyano group, obtained the desired 2,3,4-trisubstituted pyrroles 4a-n in high to excellent yields (Table 2, entries 1–14). The above results mean that an acetyl, propionyl, ethoxycarbonyl, benzoyl, N-arylcarbamoyl, nitro or cyano group can be introduced regiospecifically in the 3-position of 2,3,4-trisubstituted pyrroles 4 accomplished by chemoselective deacylation (Table 2, entries 1–14). Notably, under otherwise identical conditions as above, the [3+2] cycloaddition of 1a with 3-phenylprop-2-yn-1-aminium chloride 2b also proceeded smoothly to give the desired product 40 in 72% yield in the presence of 2.0 equiv of K₂CO₃ (Table 2, entry 15). The successful synthesis of 40 shows that the deacylative [3+2] cycloaddition is applicable to the synthesis of a wide variety of 2,3,4-trisubstituted pyrroles bearing variable substituents at the 4-position.

To further extend the scope of the deacylative [3+2] cycloaddition in water, the reactions of propargylamine **2a** with selected 3-(ethylthio(aryl)methylene)pentane-2,4-diones **5** were then examined. As a result, 2,3,4-trisubstituted pyrroles **4p**–**r** were prepared in high yields from the reaction of **2a** (1.0 mmol) with the corresponding **5** (0.5 mmol) in H₂O at 100 °C for 30–33 h (Scheme 1). These results offer further enhancement of the efficiency of the deacylative [3+2] cycloaddition using water as the solvent.

Furthermore, to evaluate the efficiency of secondary propargylamine in the [3+2] cycloaddition, the reactions of α -acyl ketene dithioacetals **1** with *N*-methylprop-2-yn-1-amine **2c** were examined. It was found that, under otherwise identical conditions as

Table 2

Synthesis of 2,3,4-trisubstituted pyrroles 4a-o^a



Entry	1	R	EWG	R ¹	Time (h)	Product	Yield ^b (%)
1	1a	Me	MeCO	Н	12	4a	93
2	1b	Et	EtCO	Н	12	4b	90
3	1c	Me	CO ₂ Et	Н	12	4c	90
4 ^c	1d	Ph	COPh	Н	16	4d	70
5	1e	Me	C ₆ H ₅ NHCO	Н	20	4e	90
6	1f	Me	4-ClC ₆ H ₄ NHCO	Н	20	4f	89
7	1g	Me	2-ClC ₆ H ₄ NHCO	Н	20	4g	88
8	1h	Me	4-MeOC ₆ H ₄ NHCO	Н	30	4h	86
9	1i	Me	2-MeOC ₆ H ₄ NHCO	Н	30	4 i	87
10	1j	Me	4-MeC ₆ H ₄ NHCO	Н	30	4j	85
11	1k	Me	2-MeC ₆ H ₄ NHCO	Н	30	4k	82
12	11	Me	2,4-Me ₂ C ₆ H ₃ NHCO	Н	30	41	80
13	lm	Me	NO ₂	Н	8	4m	87
14	ln	Me	CN	Н	12	4n	71
15 ^d	1a	Me	MeCO	Ph	16	40	72

^a Reaction conditions: **1** (0.5 mmol), **2a** (1.0 mmol), H₂O (5.0 mL), 100 °C, 8–30 h.

^b Isolated yield.

1.0 equiv K₂CO₂ was used.

^d 2.0 equiv K₂CO₃ was used.

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 ${\bf 4p}\colon$ Ar = Ph, 30 h, 85% yield; ${\bf 4q}\colon$ Ar = 4-MeO-C_6H_4, 33 h, 88% yield; ${\bf 4r}\colon$ Ar = 4-Cl-C_6H_4, 30 h, 80% yield



above, all selected acetyl ketene dithioacetals **1** with a variety of electron-withdrawing groups at the α -position, including acetyl, ethoxycarbonyl, cyano and *N*-arylcarbamoyl with either electron-neutral, electron-deficient or electron-rich group on the benzene ring (Table 3, entries 1–6), could react with **2c** smoothly to give the desired 1,2,3,4-tetrasubstituted pyrroles **4s**–**x** in high yields. However, no reaction was detectable for substrate **10** bearing a phenyl group at the α -position under identical conditions (Table 3, entry 7). As a comparison, 1,2,3,4-tetrasubstituted pyrroles **4s**–**x** cannot be obtained from the same reaction by using DMF as the solvent.¹⁷

Interestingly, under identical conditions as above but in the presence of an external K_2CO_3 (0.5 equiv), the 1,2,3,4-tetrasubstituted pyrrole **60** bearing a acetyl group at the C2 of the pyrrole core could be obtained in 63% yield (Table 4, entry 4). Similarly, the corresponding 1,2,3,4-tetrasubstituted pyrroles **6c**, **6d**, **6n** and **6p** were synthesized in good to high yields from reactions of **2c** with **1c**, **1d**, **1n** and **1p**, respectively (Table 4, entries 1–3 and 5), which indicated that 1,2,3,4-tetrasubstituted pyrroles **6** could be prepared from reactions of **2c** with suitable substrates **1** in water (5.0 mL) in the presence of K_2CO_3 (0.5 equiv).

On the basis of the above experimental results together with related letters,^{17,20} the possible mechanisms for the formation of **4** and **6** (Tables 2–4 and Scheme 1) are proposed in Scheme 2 (with α -acetyl ketene dithioacetals **1** as an example). In the case of the reaction of **1** and **2** in the absence of an external base, the

Table 3

Synthesis of 1,2,3,4-tetrasubstituted pyrroles 4s-x from 1 and 2c^a



Entry	1	R	EWG	Time (h)	Product	Yield ^b (%)
1	1a	Me	MeCO	16	4 s	85
2	1c	Me	CO ₂ Et	16	4t	83
3 ^c	1e	Me	C ₆ H ₅ NHCO	30	4u	80
4 ^c	1f	Me	4-ClC ₆ H ₄ NHCO	30	4v	82
5 ^c	1h	Me	4-MeOC ₆ H ₄ NHCO	30	4w	75
6	ln	Me	CN	16	4x	73
7 ^d	10	C_6H_5	CO ₂ Et	30	4y	0

 a Reaction conditions: 1 (0.5 mmol), 2c (1.0 mmol), H_2O (5.0 mL), 100 °C, 16–30 h.

^b Isolated yield.

^c 5.0 equiv of **2c** was used.

^d With recovery of 96% of **10**.

Table 4

Synthesis of 1,2,3,4-tetrasubstituted pyrroles 6^a



 a Reaction conditions: 1 (0.5 mmol), 2c (1.0 mmol), K_2CO_3 (0.25 mmol), H_2O (5.0 mL), 100 °C, 10–16 h.

^b Isolated yield.

N,S-acetal intermediate A could be formed via the acetyl enhanced addition-elimination $(S_N V)$ of propargylamines 2 to enones 1.^{14b,19} Subsequently, in the presence of amine 2 as a base, intermediate A would undergo a sequential tautomerization and 5-exo-dig cyclization to give intermediate C. Finally, the 2,3,4-trisubstituted or 1,2,3,4-tetrasubstituted pyrroles **4** are produced via deacetylation and subsequent isomerization (Scheme 2). However, under identical conditions but in the presence of an external base (K_2CO_3), the reaction of 1 with secondary amine 2c (Table 4) seems to favour the formation of intermediate **D** from the intermolecular Michael addition of N-methylprop-2-yn-1-amine 2c to α -acetyl ketene dithioacetals 1. Then the methylene pyrrolidine intermediate E, generated via an intramolecular 5-exo-dig cyclization of intermediate **D**, undergoes a sequential ethylthio elimination and 1,2-acetyl migration to generate intermediate **F**, which is followed by elimination of the second ethylthio group and subsequent aromatization leading to 1,2,3,4-tetrasubstituted pyrroles 6 (Scheme 2).^{17,20c}

In conclusion, a series of 2,3,4-trisubstituted and 1,2,3,4-tetrasubstituted pyrroles were synthesized in a single-step in good to excellent yields via the [3+2] cycloaddition of α -acyl ketene dithioacetals (or related substrates) with commercially available propargylamines as 1,3-dipoles by using water as the solvent. The reaction of secondary amine (*N*-methylprop-2-yn-1-amine) with α -acyl ketene dithioacetals showed different reaction behaviours depending on the addition or absence of an external base. In the absence of an external base, polysubstituted pyrroles bearing an



Scheme 2. Proposed mechanisms for formation of 4 and 6.

ethylthio group at the C2-position were obtained. Whereas polysubstituted pyrroles bearing an acetyl group at the C2-position were obtained when an external base (K_2CO_3) was added. These results showed the crucial role of water in organic reactions. Further studies are in progress.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013. 01.020.

References and notes

- (a) Anastas, P.; Eghbali, N. Chem. Soc. Rev. 2010, 39, 301; (b) Ahluwalia, V. K.; Varma, R. S. Green Solvents for Organic Synthesis; Alpha Science, Oxford, U.K., 2009.
- (a) Simon, M.-O.; Li, C.-J. Chem. Soc. Rev. 2012, 41, 1415; (b) Butler, R. N.; Coyne, A. G. Chem. Rev. 2010, 110, 6302; (c) Chanda, A.; Fokin, V. V. Chem. Rev. 2009, 109, 725; (d) Li, C.-J.; Chen, L. Chem. Soc. Rev. 2006, 35, 68; (e) Li, C.-J. Chem. Rev. 2005, 105, 3095; (f) Li, C.-J.; Chan, T.-H. Comprehensive Organic Reactions in Aqueous Media; Wiley: New York, 2007; (g) Lindström, U. M. Chem. Rev. 2002, 102, 2751; (h) Lubineau, A.; Augé, J.; Queneau, Y. Synthesis 1994, 741.
- For selected recent examples, see: (a) Sarrafi, Y.; Sadatshahabi, M.; Alimohammadi, K.; Tajbakhsh, M. Green Chem. 2011, 13, 2851; (b) Moseley, J. D.; Kappe, C. O. Green Chem. 2011, 13, 794; (c) Ke, F.; Qu, Y.; Jiang, Z.; Li, Z.; Wu, D.; Zhou, X. Org. Lett. 2011, 13, 454; (d) De, S.; Dutta, S.; Saha, B. Green Chem. 2011, 13, 2859; (e) Carvalho, L. C. R.; Fernandes, E.; Marques, M. M. B. Chem.-Eur. J. 2011, 17, 12544; (f) Jung, E. J.; Park, B. H.; Lee, Y. R. Green Chem. 2010, 12, 2003; (g) Ma, N.; Jiang, B.; Zhang, G.; Tu, S.-J.; Wever, W.; Li, G. Green Chem. 2010, 12, 1357; (h) Ding, Q.; Cao, B.; Liu, X.; Zong, Z.; Peng, Y.-Y. Green Chem. 2010, 12, 1607; (i) Zhou, Y.; Zhai, Y.; Li, J.; Ye, D.; Jiang, H.; Liu, H. Green Chem. 2010, 12, 1397; (j) Kumaravel, K.; Vasuki, G. Green Chem. 2009, 11, 1945.
- For reviews, see: (a) Fan, H.; Peng, J.; Hamann, M. T.; Hu, J.-F. Chem. Rev. 2008, 108, 264; (b) Fürstner, A. Angew. Chem., Int. Ed. 2003, 42, 3582; (c) Agarwal, S.; Cämmerer, S.; Filali, S.; Fröhner, W.; Knöll, J.; Krahl, M. P.; Reddy, K. R.; Knölker, H.-J. Curr. Org. Chem. 2005, 9, 1601; (d) Hoffmann, H.; Lindel, T. Synthesis 2003, 1753; (e) Walsh, C. T.; Garneau-Tsodikova, S.; Howard-Jones, A. R. Nat. Prod. Rep. 2006, 23, 517.

- (a) Bellina, F.; Rossi, R. Tetrahedron 2006, 62, 7213; (b) Huffman, J. W.; Padgett, L. W. Curr. Med. Chem. 2005, 12, 1395; (c) Huffman, J. W. Curr. Med. Chem. 1999, 6, 705.
- For reviews, see: (a) Guernion, N. J. L.; Hayes, W. Curr. Org. Chem. 2004, 8, 637;
 (b) Novák, P.; Müller, K.; Santhanam, K. S. V.; Haas, O. Chem. Rev. 1997, 97, 207;
 (c) Curran, D.; Grimshaw, J.; Perera, S. D. Chem. Soc. Rev. 1991, 20, 391.
- (a) Jolicoeur, B.; Chapman, E. E.; Thompson, A.; Lubell, W. D. Tetrahedron 2006, 62, 11531; (b) Ono, N. Heterocycles 2008, 75, 243.
- (a) Pall, C. Ber. Dtsch. Chem. Ges. 1885, 18, 367; (b) Banik, B. K.; Samajdar, S.; Banik, I. J. Org. Chem. 2004, 69, 213; (c) Minetto, G.; Raveglia, L. F.; Sega, A.; Taddei, M. Eur. J. Org. Chem. 2005, 24, 5277.
- (a) Hantzsch, A. Ber. Dtsch. Chem. Ges. 1890, 23, 1474; (b) Palacios, F.; Aparicio, D.; De los Santos, J. M.; Vicario, J. Tetrahedron 2001, 57, 1961.
- 10. For reviews, see: Van Leusen, D.; Van Leusen, A. M. Org. React. 2001, 57, 417.
- (a) Jiang, Y.; Chan, W. C.; Park, C.-M. J. Am. Chem. Soc. 2012, 134, 4104; (b) Trost, B. M.; Lumb, J.-P.; Azzarelli, J. M. J. Am. Chem. Soc. 2011, 133, 740; (c) Rakshit, S.; Patureau, F. W.; Glorius, F. J. Am. Chem. Soc. 2010, 132, 9585; (d) Mizuno, A.; Kusama, H.; Iwasawa, N. Angew. Chem., Int. Ed. 2009, 48, 8318; (e) Larionov, O. V.; de Meijere, A. Angew. Chem., Int. Ed. 2005, 44, 5664; (f) Kim, J. T.; Kelin, A. V.; Gevorgyan, V. Angew. Chem., Int. Ed. 2003, 42, 98; (g) Kamijo, S.; Kanazawa, C.; Yamamoto, Y. J. Am. Chem. Soc. 2005, 127, 9260; (h) Dhawan, R.; Arndtsen, B. A. J. Am. Chem. Soc. 2004, 126, 468; (i) Tejedor, D.; González-Cruz, D.; García-Tellado, F.; Marrero-Tellado, J. J.; Rodríguez, M. L. J. Am. Chem. Soc. 2004, 126, 8390; (j) Barber, D. M.; Sanganee, H.; Dixon, D. J. Chem. Commun. 2011, 47, 4379; (k) Kramer, S.; Madsen, J. L. H.; Rottländer, M.; Skrydstrup, T. Org. Lett. 2010, 12, 2758; (l) Ackermann, L.; Sandmann, R.; Kaspar, T. Org. Lett. 2009, 11, 2031; (m) Merkul, E.; Boersch, C.; Frank, W.; Müller, T. J. J. Org. Lett. 2009, 11, 2269; (n) Wang, Y.-F.; Toh, K. K.; Chiba, S.; Narasaka, K. Org. Lett. 2008, 10, 5019.
- (a) Balme, G. Angew. Chem., Int. Ed. 2004, 43, 6238; (b) Estévez, V.; Villacampa, M.; Menéndez, J. C. Chem. Soc. Rev. 2010, 39, 4402; (c) Frolova, L. V.; Evdokimov, N. M.; Hayden, K.; Malik, I.; Rogelj, S.; Kornienko, A.; Magedov, I. V. Org. Lett. 2011, 13, 1118; (d) Maiti, S.; Biswas, S.; Jana, U. J. Org. Chem. 2010, 75, 1674; (e) St. Cyr, D. J.; Martin, N.; Arndtsen, B. A. Org. Lett. 2007, 9, 449; (f) Bharadwaj, A.

R.; Scheidt, K. A. Org. Lett. 2004, 6, 2465; (g) Cadierno, V.; Gimeno, J.; Nebra, N. Chem. Eur. J. 2007, 13, 9973.

- 13. (a) Rueping, M.; Parra, A. Org. Lett. **2010**, *12*, 5281 (from (*E*)bromonitrostyrenes and enaminones); (b) Khalili, B.; Jajarmi, P.; Eftekhari-Sis, B.; Hashemi, M. M. J. Org. Chem. **2008**, 73, 2090 (three-component reaction of β -dicarbonyl compounds with arylglyoxals in the presence of ammonium acetate).
- For selected recent letters, see: (a) Han, X.-D.; Zhao, Y.-L.; Meng, J.; Ren, C.-Q.; Liu, Q. J. Org. Chem. 2012, 77, 5173; (b) Zhao, Y.-L.; Yang, S.-C.; Di, C.-H.; Han, X.-D.; Liu, Q. Chem. Commun. 2010, 46, 7614; (c) Zhao, Y.-L.; Chen, L.; Yang, S.-C.; Tian, C.; Liu, Q. J. Org. Chem. 2009, 74, 5622; (d) Bi, X.; Dong, D.; Liu, Q.; Pan, W.; Zhao, L.; Li, B. J. Am. Chem. Soc. 2005, 127, 4578.
- For selected recent letters, see: (a) Li, Y.; Xu, X.; Tan, J.; Xia, C.; Zhang, D.; Liu, Q. J. Am. Chem. Soc. 2011, 133, 1775; (b) Tan, J.; Xu, X.; Zhang, L.; Li, Y.; Liu, Q. Angew. Chem., Int. Ed. 2009, 48, 2868; (c) Wang, H.; Zhao, Y.-L.; Ren, C.-Q.; Diallo, A.; Liu, Q. Chem. Commun. 2011, 47, 1236; (d) Meng, J.; Zhao, Y.-L.; Ren, C.-Q.; Li, Y.; Li, Z.; Liu, Q. Chem. Eur. J. 2009, 15, 1830; (e) Zhao, Y.-L.; Li, D.-Z.; Han, X.-D.; Chen, L.; Liu, Q. Adv. Synth. Catal. 2008, 350, 1537; (f) Zhao, Y.-L.; Zhang, W.; Wang, S.; Liu, Q. J. Org. Chem. 2007, 72, 4985; (g) Chen, L.; Zhao, Y.-L.; Liu, Q.; Chen, C.; Piao, C.-R. J. Org. Chem. 2007, 72, 9259.
- Jon Grenning, A. J.; Tunge, A. Angew. Chem., Int. Ed. 2011, 50, 1688; (b) Yuan, H.; Wang, M.; Liu, Y.; Wang, L.; Liu, J.; Liu, Q. Chem. Eur. J. 2010, 16, 13450.
- 17. Zhao, Y.-L; Di, C.-H.; Liu, S.-D.; Meng, J.; Liu, Q. Adv. Synth. Catal. 2012, 354, 3545.
- (a) Ouyang, Y.; Dong, D.; Yu, H.; Liang, Y.; Liu, Q. Adv. Synth. Catal. 2006, 348, 206; (b) Dong, D.; Ouyang, Y.; Yu, H.; Liu, Q.; Liu, J.; Wang, M.; Zhu, J. J. Org. Chem. 2005, 70, 4535.
- For reviews, see: (a) Dieter, R. K. *Tetrahedron* **1986**, 42, 3029; (b) Junjappa, H.; Ila, H.; Asokan, C. V. *Tetrahedron* **1990**, 46, 5423.
- (a) Xin, X.; Wang, D.; Li, X.; Wan, B. Angew. Chem., Int. Ed. 2012, 51, 1693; (b) Cacchi, S.; Fabrizi, G.; Filisti, E. Org. Lett. 2008, 10, 2629; (c) Mo, D.-L.; Ding, C.-H.; Dai, L.-X.; Hou, X.-L. Chem. Asian J. 2011, 6, 3200; (d) Misra, N. C.; Panda, K.; Ila, H.; Junjappa, H. J. Org. Chem. 2007, 72, 1246.