EurJOC European Journal of Organic Chemistry

SHORT COMMUNICATION

DOI: 10.1002/ejoc.201402490

Lewis Acid Catalyzed [3+2] Coupling of Indoles with Quinone Monoacetals or Quinone Imine Ketal

Chang Shu,[a,b] Li-Hua Liao,[a,b] Yi-Jun Liao,[a,b] Xiao-Yan Hu,[a,b] Yong-Hong Zhang,[a,b] Wei-Cheng Yuan,[a] and Xiao-Mei Zhang*[a]

Keywords: Nitrogen heterocycles / Fused-ring systems / C–C coupling / Lewis acids / Acetals

The one-pot synthesis of benzofuroindolines and tetrahydroindolo[2,3-*b*]indoles was accomplished through a mild and concise [3+2] coupling of indoles and quinone monoacetals or quinone imine ketal promoted by a Lewis acid. A wide variety of benzofuroindolines and tetrahydroindolo[2,3-*b*]indoles were prepared in moderate to good yields.

Introduction

Fused indolines are important building blocks for a large number of natural products and pharmaceuticals.[1] As a consequence, the synthesis of fused indolines such as pyrroloindolines,[2] furoindolines,[2c,2d,2j,2q,3] benzofuroindolines,[4] tetrahydroindolo [2,3-*b*]indoles,[5] and other types of fused indolines[6] has attracted considerable attention, and diverse strategies for their synthesis have been developed. The benzofuroindoline core is a unique motif found in many important natural alkaloids,[1e,1g,4] such as diazonamides[4a–4d] and azonazine[4e,4f] (Figure 1). Given that diazonamide A has been found to be a very potent anticancer agent owing to its high antitumor activity (IC_{50} < 5 nm),[4a,4b] it has received considerable attention from chemists to synthesize these benzofuroindoline skeletons.[4g–4l] The prevalence of these indole-derived heterocyclic frameworks continues to inspire the development of new reactions for their construction.

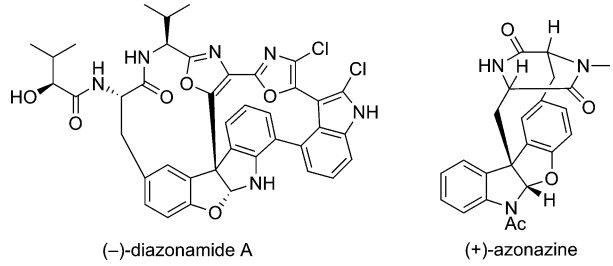


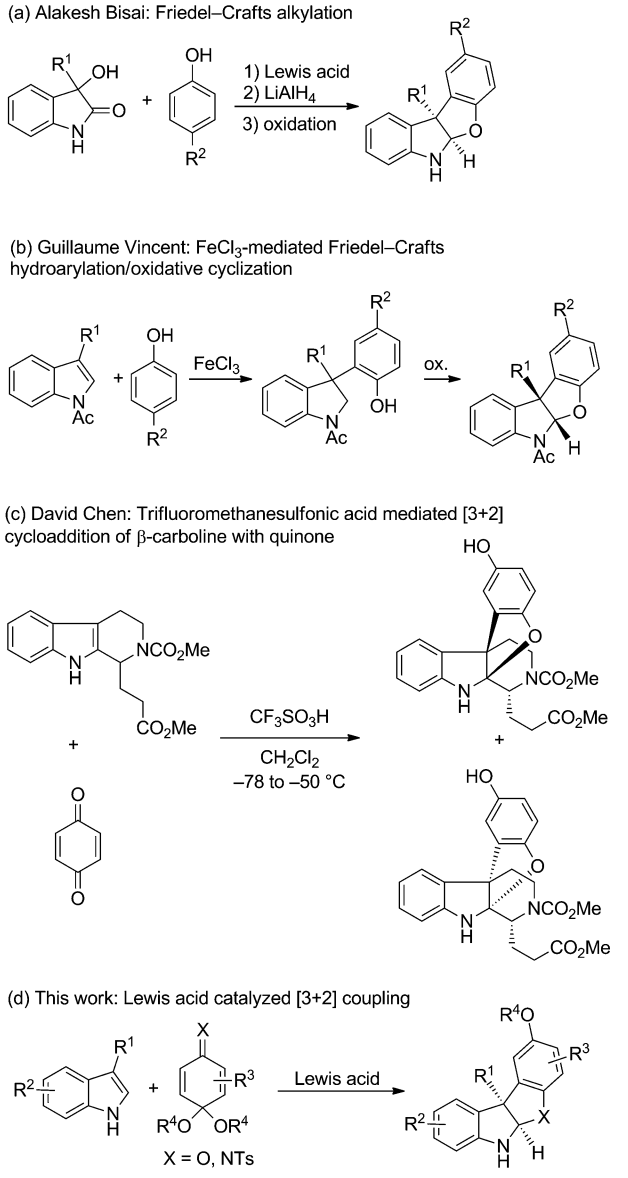
Figure 1. Representative benzofuroindoline natural products.

In 2012, Bisai et al.[4m] reported the Lewis acid catalyzed Friedel–Crafts alkylation of 3-hydroxy-2-oxindole that provides access to benzofuroindolines in three steps (Scheme 1, a). Soon after, Vincent[4n] and co-workers reported $FeCl_3$-mediated Friedel–Crafts hydroarylation with electrophilic *N*-acetylindoles and phenols to afford 3,3-disubstituted indolines, followed by oxidation to yield the desired benzofuroindolines (Scheme 1, b). Furthermore, the direct construction of benzofuroindolines through the [3+2] coupling of 3-substituted indoles with quinones was also documented by several groups.[4o–4w] For example, in 2011, Chen and co-workers employed a Brønsted acid catalyzed direct [3+2] coupling of β-carbolines with quinones as a key strategy in the formal synthesis of (+)-haplophytine (Scheme 1, c).[4w]

Quinone monoacetals and quinone imine ketals have attracted much attention owing to their particular reactivities and broad utilities in organic synthesis.[7,8] In 1994, Swenton et al. employed acetic acid to catalyze the [3+2] couplings of quinone monoacetals with vinyl thiol.[8a] Recently, Kita et al. presented the [3+2] couplings of quinone monoacetals with various alkenes promoted by Brønsted acids.[8b,8c] Inspired by these reports and the work of Chen[4w] on the [3+2] coupling of β-carbolines with quinones, we envisioned that, through dearomatization,[9] 3-substituted indoles might undergo [3+2] coupling with quinone monoacetals or quinone imine ketals to generate benzofuroindolines and tetrahydroindolo[2,3-*b*]indoles in one pot. Herein, we present the Lewis acid promoted [3+2] coupling of 3-substituted indoles with quinone monoacetals or quinone imine ketals. Through this mild and concise transformation, a wide variety of benzofuroindolines and tetrahydroindolo[2,3-*b*]indoles were prepared in moderate to good yields (Scheme 1, d), which thus provides a good extension of the work of Chen and co-workers.

[a] Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences,
Chengdu 610041, China
E-mail: xmzhang@cioc.ac.cn
http://www.cioc.ac.cn
[b] University of Chinese Academy of Sciences,
Beijing 100049, China

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201402490.

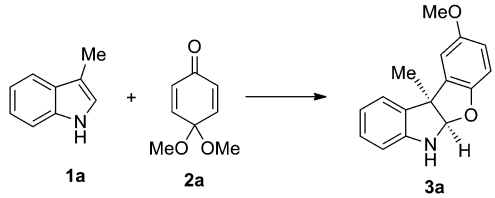


Scheme 1. Strategies for the formation of benzofuroindolines.

Results and Discussion

First, we initiated the reaction of 3-methylindole (**1a**) with 4,4-dimethoxycyclohexa-2,5-dienone (**2a**) in toluene at 25 °C for 24 h. If the reaction was conducted in the absence of catalyst, no product was generated (Table 1, entry 1). In the presence of Brønsted acids, such as acetic acid, trifluoroacetic acid, and pentafluorobenzoic acid, quinone monoacetal **2a** decomposed completely and no desired product was detected (Table 1, entry 2–4). Afterwards, various Lewis acids were evaluated in the reaction. Several metal chlorides were found to exhibit poor reactivity in the reaction (Table 1, entries 5–7). To our delight, upon using some metal triflates better yields were observed (Table 1, entries 8–10); zinc trifluoromethanesulfonate [$Zn(OTf)_2$] gave the desired product in the highest yield of 86% (Table 1, entry 8). Thus, $Zn(OTf)_2$ was determined to be the optimal Lewis acid in the reaction and it was used in the following investigations. Then, several other solvents were screened. However, they all delivered lower yields than toluene (Table 1, entries 11–14). Hence, toluene was identified as the most favorable solvent for the reaction. Upon conducting the reaction at 50 °C, a lower yield of the product was obtained (Table 1, entry 15), because quinone monoacetal decomposed quickly at that higher temperature. If the reaction was conducted at 0 °C, only a trace amount of the product was observed.

Table 1. The [3+2] coupling of 3-methylindole (**1a**) with 4,4-dimethoxycyclohexa-2,5-dienone (**2a**) promoted by Lewis acids.[a]



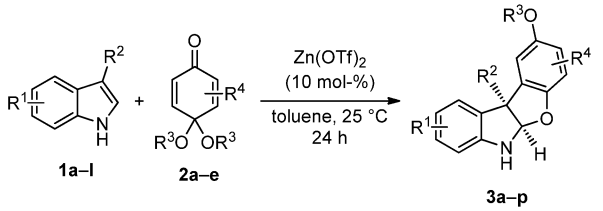
Entry	Catalyst	Solvent	*T* [°C]	Yield[b] [%]
1	none	toluene	25	n.r.
2	CF_3CO_2H	toluene	25	n.d.
3	CF_3SO_3H	toluene	25	n.d.
4	$C_6F_5CO_2H$	toluene	25	n.d.
5	$AlCl_3$	toluene	25	30
6	$FeCl_3$	toluene	25	trace
7	$SnCl_4$	toluene	25	33
8	$Zn(OTf)_2$	toluene	25	86
9	$Cu(OTf)_2$	toluene	25	67
10	$Sc(OTf)_2$	toluene	25	47
11	$Zn(OTf)_2$	CH_2Cl_2	25	62
12	$Zn(OTf)_2$	ether	25	0
13	$Zn(OTf)_2$	THF	25	19
14	$Zn(OTf)_2$	CH_3CN	25	66
15	$Zn(OTf)_2$	toluene	50	55
16	$Zn(OTf)_2$	toluene	0	trace

[a] Unless otherwise specified, the reaction was performed with **1a** (0.20 mmol), **2a** (0.30 mmol), and acid (0.02 mmol) in solvent (2 mL) for 24 h. [b] Yield of isolated product based on **1a**; n.r.: no reaction, n.d.: not determined.

With the optimized reaction conditions in hand, the scope of the reaction was investigated. In the presence of $Zn(OTf)_2$ (10 mol-%), various 3-substituted indoles and quinone monoacetals were subjected to the [3+2] coupling. The results are summarized in Table 2. Substituents on the benzene ring of the indole clearly affected the results. 3-Methyl-5-fluoroindole (**1b**) gave only a trace amount of the product, perhaps as a result of the strong electron-withdrawing nature of the fluoro group, which reduced the nucleophilicity of the indole (Table 2, entry 2). Nonetheless, the 5-chloro-, 5-bromo-, and 5-methylindole derivatives underwent the reaction smoothly to generate the corresponding products in good yields (Table 2, entries 3–5). A stronger electronic effect was observed with 3-methyl-6-fluoroindole (**1f**) and 3-methyl-6-bromoindole (**1g**), which did not afford any products (Table 2, entries 6 and 7). Reactions of indoles with bulkier substituents in the 3-position gave inferior yields of the products (Table 2, entries 8–11). No reaction was observed with 3-phenylindole (**1l**; Table 2,

entry 12). Afterwards, several other quinone monoacetals bearing different substituents were also subjected to the reaction. They all reacted with 3-methylindole smoothly to generate the products in moderate to good yields (Table 2, entries 13–16). Notably, bulkier substrate **2d** gave product **3o** in good yield after a prolonged reaction time (Table 2, entry 15).

Table 2. The [3+2] coupling of 3-substituted indoles **1a**–**l** and quinone monoacetals **2a**–**e** promoted by $Zn(OTf)_2$.[a]



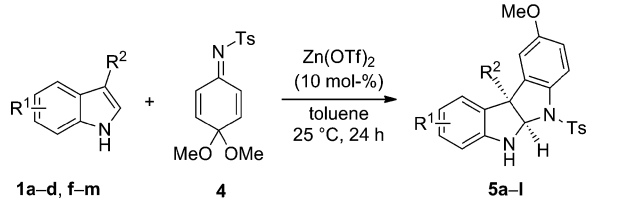
1a–l 2a–e 3a–p

Entry	3	Yield[b] [%]
1	**3a**: R^1 = H, R^2 = Me	86
2	**3b**: R^1 = 5-F, R^2 = Me	trace
3	**3c**: R^1 = 5-Cl, R^2 = Me	89
4	**3d**: R^1 = 5-Br, R^2 = Me	89
5	**3e**: R^1 = 5-Me, R^2 = Me	86
6	**3f**: R^1 = 6-F, R^2 = Me	0
7	**3g**: R^1 = 6-Br, R^2 = Me	0
8	**3h**: R^1 = H, R^2 = Et	77
9	**3i**: R^1 = H, R^2 = cyclohexyl	62
10	**3j**: R^1 = H, R^2 = CH_2CH_2OTBS	67
11	**3k**: R^1 = H, R^2 = CH_2CH_2NPhth	72
12	**3l**: R^1 = H, R^2 = Ph	0
13	**3m**: R^3 = Me, R^4 = 6-Br	58
14	**3n**: R^3 = Me, R^4 = 5-Me	62
15[c]	**3o**: R^3 = Me, R^4 = 3,5-Me_2	84
16	**3p**: R^3 = Et, R^4 = H	60

[a] Unless otherwise specified, the reaction was performed with **1** (0.20 mmol), **2** (0.30 mmol), and $Zn(OTf)_2$ (0.02 mmol) in toluene (2 mL) for 24 h; TBS = *tert*-butyldimethylsilyl, Phth = phthalyl. [b] Yield of isolated product based on **1**. [c] The reaction was performed for 48 h.

Besides, this reaction protocol was also effective for quinone imine ketal **4**. We found that **4** was more reactive than quinone monoacetal **2**. Under the optimal reaction conditions, indoles bearing many sorts of substituents were tolerable in the reaction with **4** to afford the corresponding tetrahydroindolo[2,3-*b*]indoles **5** in moderate to good yields. Even indoles **1b**, **1f**, and **1g**, which failed to provide the products in the reaction with quinone monoacetal **2a**, partook in the reaction to afford the products in fairly good yields (Table 3, entries 2, 5, and 6). Only 3-phenylindole (**1l**) was still inactive in this case (Table 3, entry 11).

Table 3. The [3+2] coupling of 3-substituted indoles **1** and quinone imine ketal **4** promoted by $Zn(OTf)_2$.[a]



1a–d, f–m 4 5a–l

Entry	5	Yield[b] [%]
1	**5a**: R^1 = H, R^2 = Me	86
2	**5b**: R^1 = 5-F, R^2 = Me	76
3	**5c**: R^1 = 5-Cl, R^2 = Me	72
4	**5d**: R^1 = 5-Br, R^2 = Me	57
5	**5e**: R^1 = 6-F, R^2 = Me	68
6	**5f**: R^1 = 6-Br, R^2 = Me	75
7	**5g**: R^1 = H, R^2 = Et	67
8	**5h**: R^1 = H, R^2 = cyclohexyl	46
9	**5i**: R^1 = H, R^2 = CH_2CH_2OTBS	76
10	**5j**: R^1 = H, R^2 = CH_2CH_2NPhth	60
11	**5k**: R^1 = H, R^2 = Ph	0
12	**5l**: R^1 = H, R^2 = cyclopentyl	42

[a] Unless otherwise specified, the reaction was performed with **1** (0.20 mmol), **4** (0.30 mmol), and $Zn(OTf)_2$ (0.02 mmol) in toluene (2 mL) for 24 h. [b] Yield of isolated product based on **1**.

The relative configuration of fused indoline **5d** was determined to be *cis* by X-ray crystal structure analysis[10] (Figure 2). All other fused indolines were assigned relative configurations by analogy.

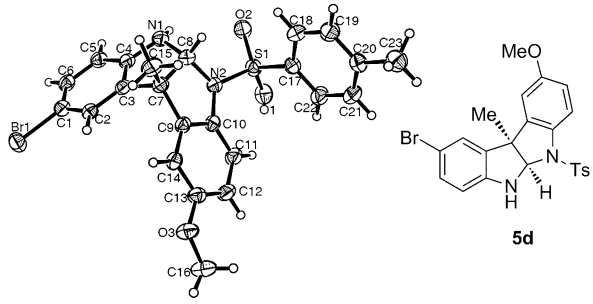
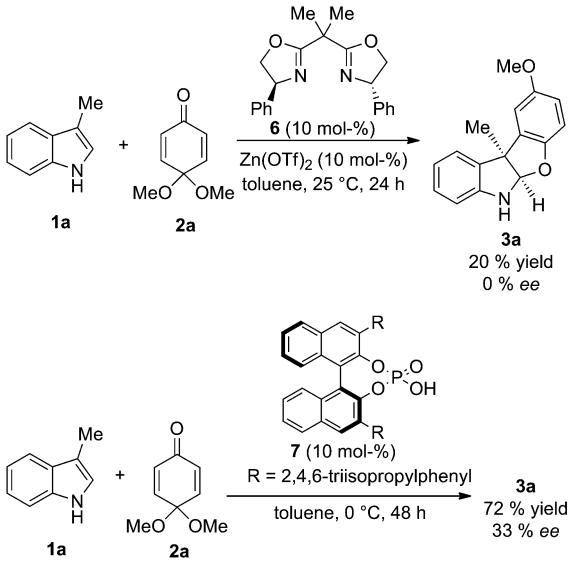


Figure 2. X-ray crystal structure of *cis*-fused indoline **5d**.

Furthermore, we also attempted to employ chiral catalysts in the reaction (Scheme 2). However, a poor yield of the racemic product was obtained with chiral $Zn(OTf)_2$-Box (**6**). Several chiral phosphoric acids were also tested in which R-TRIP (**7**) provided the product in moderate yield with the highest enantiomeric excess value of 33%.

To study the mechanism of the reaction, in situ MS analysis was performed. As can be seen in Figure 3, a trace amount of quinone oxonium was detected in the solution of quinone monoacetal **2a** in toluene (Figure 3a). After the addition of $Zn(OTf)_2$, the peak for quinone oxonium increased remarkably (Figure 3, b). After 3-methylindole was added, the peak for quinone oxonium decreased and the peak for product **3a** emerged (Figure 3, c).

On the basis of the above MS (ESI) analysis, we propose the reaction pathway shown in Scheme 3. In the presence



Scheme 2. Catalytic asymmetric variant of this process.

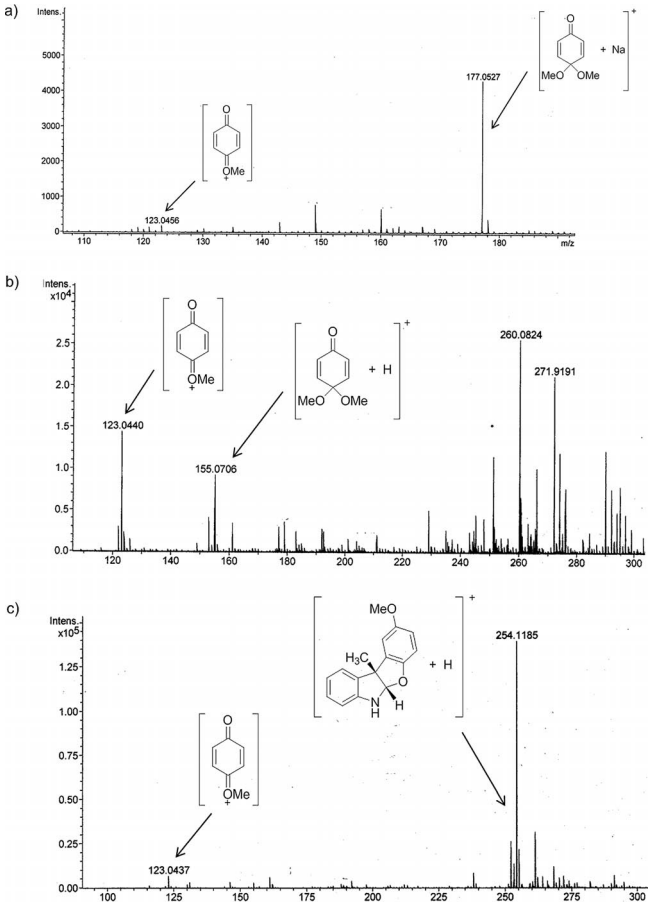
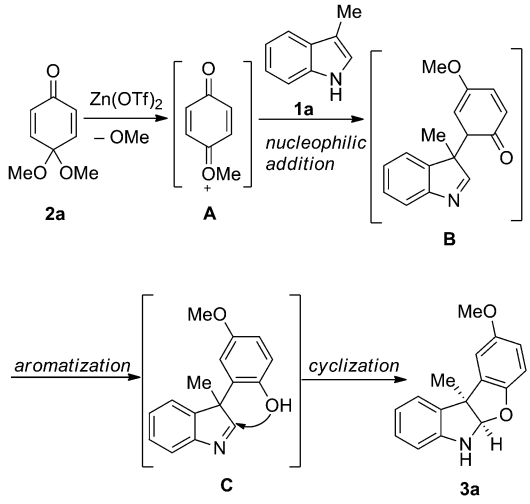


Figure 3. MS (ESI) was performed with the standard procedure for MS detection. (a) **2a** in toluene, (b) **2a** and $Zn(OTf)_2$ (10 mol-%) in toluene stirred for 30 min, (c) 3-methylindole (**1a**) was added.

of the $Zn(OTf)_2$ Lewis acid, one of the methoxy groups of quinone monoacetal **2a** is removed and quinone oxonium **A** is generated. Then, 3-methylindole attacks the highly reactive quinone oxonium to give intermediate **B**, which undergoes aromatization immediately to give phenol intermediate **C**. Finally, spontaneous cyclization affords benzofuroindoline **3a**.



Scheme 3. Plausible reaction pathway.

Conclusions

In conclusion, we developed a mild and concise [3+2] coupling of indoles and quinone monoacetals or quinone imine ketal promoted by a Lewis acid. Through this transformation, a series of structurally unique benzofuroindolines and tetrahydroindolo[2,3-*b*]indoles were synthesized in moderate to good yields. The relative configuration of one product was determined to be *cis* on the basis of X-ray crystal structure analysis. Afterwards, in situ MS (ESI) analysis was performed and a key quinone oxonium intermediate was detected. Accordingly, a plausible reaction pathway was proposed.

Experimental Section

General Procedure for the [3+2] Coupling of 3-Substituted Indoles 1 with Quinone Monoacetal 2 or Quinone Imine Ketal 4: 3-Substituted indole **1** (0.20 mmol) and quinone monoacetal **2** (0.30 mmol) or quinone imine ketal **4** (0.30 mmol) were added to a flame-dried vial equipped with a magnetic stirring bar. Then, toluene (2 mL) was added to dissolve the mixture. Afterwards, $Zn(OTf)_2$ (10.8 mg, 0.02 mmol) was added. The mixture was stirred at 25 °C for 24 h. The solvent was evaporated, and the residue was subjected to chromatography (silica gel, petroleum ether/EtOAc 20:1 to 10:1) to afford desired product **3** or **5**.

Supporting Information (see footnote on the first page of this article): Experimental procedures and spectral and analytical data for the benzofuroindolines and tetrahydroindolo[2,3-*b*]indoles; HPLC chromatograms for chiral benzofuroindoline **3a**.

Acknowledgments

The authors are grateful for financial support from the National Basic Research Program of China (973 Program, 2010CB833300) and the National Sciences Foundation of China (NSFC) (grant numbers 21372218 and 21172217).

[1] For reviews, see: a) L. M. Repka, S. E. Reisman, *J. Org. Chem.* **2013**, *78*, 12314–12320; b) C. C. J. Loh, D. Enders, *Angew. Chem. Int. Ed.* **2012**, *51*, 46–48; *Angew. Chem.* **2012**, *124*, 46–49; c) D. Zhang, H. Song, Y. Qin, *Acc. Chem. Res.* **2011**, *44*, 447–457; d) J. Kim, M. Movassaghi, *Chem. Soc. Rev.* **2009**, *38*, 3035–3050; e) M. Lachia, C. J. Moody, *Nat. Prod. Rep.* **2008**, *25*, 227–253; f) A. Steven, L. E. Overman, *Angew. Chem. Int. Ed.* **2007**, *46*, 5488–5508; *Angew. Chem.* **2007**, *119*, 5584–5605; g) T. Ritter, E. M. Carreira, *Angew. Chem. Int. Ed.* **2002**, *41*, 2489–2494; *Angew. Chem.* **2002**, *114*, 2601–2606.

[2] For selected recent examples, see: a) M. E. Kieffer, K. V. Chuang, S. E. Reisman, *J. Am. Chem. Soc.* **2013**, *135*, 5557–5560; b) A. Coste, J. Kim, T. C. Adams, M. Movassaghi, *Chem. Sci.* **2013**, *4*, 3191–3197; c) W. C. Chen, W. G. Yang, L. Yan, C. H. Tan, Z. Y. Jiang, *Chem. Commun.* **2013**, *49*, 9854–9856; d) A. J. Lin, J. Yang, M. Hashim, *Org. Lett.* **2013**, *15*, 1950–1953; e) Z. H. Zhang, J. C. Antilla, *Angew. Chem. Int. Ed.* **2012**, *51*, 11778–11782; *Angew. Chem.* **2012**, *124*, 11948–11952; f) S. Zhu, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2012**, *134*, 10815–10818; g) M. E. Kieffer, K. V. Chuang, S. E. Reisman, *Chem. Sci.* **2012**, *3*, 3170–3174; h) F. Fan, W. Q. Xie, D. W. Ma, *Chem. Commun.* **2012**, *48*, 7571–7573; i) Q. Cai, C. Liu, X. W. Liang, S. L. You, *Org. Lett.* **2012**, *14*, 4588–4590; j) O. Lozano, G. Bessley, T. M. Del Campo, A. L. Thompson, G. T. Giuffredi, M. Bettati, M. Walker, R. Borman, V. Gouverneur, *Angew. Chem. Int. Ed.* **2011**, *50*, 8105–8109; *Angew. Chem.* **2011**, *123*, 8255–8259; k) T. Benkovics, I. A. Guzei, T. P. Yoon, *Angew. Chem. Int. Ed.* **2010**, *49*, 9153–9157; *Angew. Chem.* **2010**, *122*, 9339–9343; l) V. R. Espejo, X. B. Li, J. D. Rainier, *J. Am. Chem. Soc.* **2010**, *132*, 8282–8284; m) H. X. Wu, F. Xue, X. Xiao, Y. Qin, *J. Am. Chem. Soc.* **2010**, *132*, 14052–14054; n) H. X. Wu, F. Xue, X. Xiao, Y. Qin, *J. Am. Chem. Soc.* **2010**, *132*, 14052–14054; o) L. M. Repka, J. Ni, S. E. Reisman, *J. Am. Chem. Soc.* **2010**, *132*, 14418–11420; p) X. Li, S. Z. Luo, J. P. Cheng, *Chem. Eur. J.* **2010**, *16*, 14290–14294; q) A. W. Schammel, B. W. Boal, L. S. Zu, T. Mesganaw, N. K. Garg, *Tetrahedron* **2010**, *66*, 4687–4695.

[3] For selected recent examples, see: a) B. H. Shupe, E. E. Allen, J. P. MacDonald, S. O. Wilson, A. K. Franz, *Org. Lett.* **2013**, *15*, 3218–3221; b) C. Liu, W. Zhang, L. X. Dai, S. L. You, *Org. Lett.* **2012**, *14*, 4525–4527; c) G. Cera, M. Chiarucci, A. Mazzanti, M. Mancinelli, M. Bandini, *Org. Lett.* **2012**, *14*, 1350–1353; d) C. Liu, W. Zhang, L. X. Dai, S. L. You, *Org. Biomol. Chem.* **2012**, *10*, 7177–7183; e) M. B. Calvert, J. Sperry, *Tetrahedron Lett.* **2012**, *53*, 5426–5429; f) L. S. Zu, B. W. Boal, N. K. Garg, *J. Am. Chem. Soc.* **2011**, *133*, 8877–8879; g) G. Cera, P. Crispino, M. Monari, M. Bandini, *Chem. Commun.* **2011**, *47*, 7803–7805.

[4] For selected examples, see: a) G. L. Wang, L. B. Shang, A. W. G. Burgett, P. G. Harran, X. D. Wang, *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 2068–2073; b) N. S. Williams, A. W. G. Burgett, A. S. Atkins, X. D. Wang, P. G. Harran, S. L. McKnight, *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 2074–2079; c) J. Li, A. W. Burgett, L. Esser, C. Amezscusa, P. G. Harran, *Angew. Chem. Int. Ed.* **2001**, *40*, 4770–4773; *Angew. Chem.* **2001**, *113*, 4906–4909; d) N. Lindquist, W. Fenical, G. D. Vanduyne, J. Clardy, *J. Am. Chem. Soc.* **1991**, *113*, 2303–2304; e) Q. X. Wu, M. S. Crews, M. Draskovic, J. Sohn, T. A. Johnson, K. Tenney, F. A. Valeriote, X. J. Yao, L. F. Bjeldanes, P. Crews, *Org. Lett.* **2010**, *12*, 4458–4461; f) J. C. Zhao, S. M. Yu, Y. Liu, Z. J. Yao, *Org. Lett.* **2013**, *15*, 4300–4303; g) C. M. Cheung, F. W. Goldberg, P. Magnus, C. J. Russell, R. Turnbull, V. Lynch, *J. Am. Chem. Soc.* **2007**, *129*, 12320–12327; h) K. C. Nicolaou, P. Bheema Rao, J. Hao, M. V. Reddy, G. Rassias, X. Huang, D. Y.-K. Chen, S. A. Snyder, *Angew. Chem. Int. Ed.* **2003**, *42*, 1753–1758; *Angew. Chem.* **2003**, *115*, 1795–1800; i) R. Shintani, G. C. Fu, *Angew. Chem. Int. Ed.* **2003**, *42*, 4082–4085; *Angew. Chem.* **2003**, *115*, 4216–4219; j) A. W. G. Burgett, Q. Y. Li, Q. Wei, P. G. Harran, *Angew. Chem. Int. Ed.* **2003**, *42*, 4961–4966; *Angew. Chem.* **2003**, *115*, 5111–5116; k) T. Sawada, D. E. Fuerst, J. L. Wood, *Tetrahedron Lett.* **2003**, *44*, 4919–4921; l) K. C. Nicolaou, M. Bella, D. Y. K. Chen, X. H. Huang, T. T. Ling, S. A. Snyder, *Angew. Chem. Int. Ed.* **2002**, *41*, 3495–3499; *Angew. Chem.* **2002**, *114*, 3645–3649; m) S. Ghosh, L. K. Kinthada, S. Bhunia, A. Bisai, *Chem. Commun.* **2012**, *48*, 10132–10134; n) R. Beaud, R. Guillot, C. Kouklovsky, G. Vincent, *Angew. Chem. Int. Ed.* **2012**, *51*, 12546–12550; *Angew. Chem.* **2012**, *124*, 12714–12718; o) W. E. Noland, F. J. Baude, *J. Org. Chem.* **1966**, *31*, 3321–3337; p) K. C. Joshi, V. N. Pathak, R. Gupta, *J. Fluorine Chem.* **1988**, *38*, 153–161; q) M. G. Corradini, C. Costantini, G. Prota, T. M. Schultz, *Gazz. Chim. Ital.* **1989**, *119*, 153–156; r) J. C. Henrion, B. Jacquet, M. Hocquaux, C. Lion, M. Hedayatullah, *Bull. Soc. Chim. Belg.* **1996**, *105*, 403–407; s) J. S. Yadav, B. V. S. Reddy, T. Swamy, *Tetrahedron Lett.* **2003**, *44*, 9121–9124; t) C. Chan, C. Li, F. Zhang, S. J. Danishefsky, *Tetrahedron Lett.* **2006**, *47*, 4839–4841; u) K. C. Nicolaou, U. Majumder, S. P. Roche, D. Y.-K. Chen, *Angew. Chem. Int. Ed.* **2007**, *46*, 4715–4718; *Angew. Chem.* **2007**, *119*, 4799–4802; v) K. C. Nicolaou, S. M. Dalby, S. L. Li, T. Suzuki, D. Y. K. Chen, *Angew. Chem. Int. Ed.* **2009**, *48*, 7616–7620; *Angew. Chem.* **2009**, *121*, 7752–7756; w) W. Tian, L. R. Chennamaneni, T. Suzuki, D. Y.-K. Chen, *Eur. J. Org. Chem.* **2011**, 1027–1031; x) R. R. Knowles, J. Carpenter, S. B. Blakey, A. Kayano, I. K. Mangion, C. J. Sinz, D. W. C. MacMillan, *Chem. Sci.* **2011**, *2*, 308–311.

[5] a) R. B. Bedford, N. Fey, M. F. Haddow, R. F. Sankey, *Chem. Commun.* **2011**, *47*, 3649–3651; b) P. Magnus, R. Turnbull, *Org. Lett.* **2006**, *8*, 3497–3499.

[6] For selected recent examples, see: a) Q. Peng, S. Luo, X. Xia, L. Liu, P. Huang, *Chem. Commun.* **2014**, *50*, 1986–1988; b) H. G. Cheng, L. Q. Lu, T. Wang, Q. Q. Yang, X. P. Liu, Y. Li, Q. H. Deng, J. R. Chen, W. J. Xiao, *Angew. Chem. Int. Ed.* **2013**, *52*, 3250–3254; *Angew. Chem.* **2013**, *125*, 3332–3336; c) H. Xiong, H. Xu, S. H. Liao, Z. W. Xie, Y. Tang, *J. Am. Chem. Soc.* **2013**, *135*, 7851–7854; d) Y. L. Zhang, X. H. Liu, X. H. Zhao, J. L. Zhang, L. Zhou, L. L. Lin, X. M. Feng, *Chem. Commun.* **2013**, *49*, 11311–11313; e) G. Cera, M. Chiarucci, A. Mazzanti, M. Mancinelli, M. Bandini, *Org. Lett.* **2012**, *14*, 1350–1353; f) L. Zhao, Z. Y. Li, L. Chang, J. Y. Xu, H. Q. Yao, X. M. Wu, *Org. Lett.* **2012**, *14*, 2066–2069; g) Q. Cai, C. Zheng, J.-W. Zhang, S.-L. You, *Angew. Chem. Int. Ed.* **2011**, *50*, 8665–8669; *Angew. Chem.* **2011**, *123*, 8824–8828; h) B. Han, Y. C. Xiao, Y. A. Yao, Y. C. Chen, *Angew. Chem. Int. Ed.* **2010**, *49*, 10189–10191; *Angew. Chem.* **2010**, *122*, 10387–10389; i) Z. W. Zuo, W. Q. Xie, D. W. Ma, *J. Am. Chem. Soc.* **2010**, *132*, 13226–13228; j) Y. Lian, H. M. L. Davies, *J. Am. Chem. Soc.* **2010**, *132*, 440–441.

[7] For reviews, see: a) D. Magdziak, S. J. Meek, T. R. R. Pettus, *Chem. Rev.* **2004**, *104*, 1383–1429; b) C. C. Liao, R. K. Peddinti, *Acc. Chem. Res.* **2002**, *35*, 856–866.

[8] For selected examples, see: a) M. L. Kerns, S. M. Conroy, J. S. Swenton, *Tetrahedron Lett.* **1994**, *35*, 7529–7532; b) T. Dohi, Y. J. Hu, T. Kamitanaka, Y. Kita, *Tetrahedron* **2012**, *68*, 8424–8430; c) T. Dohi, Y. J. Hu, T. Kamitanaka, N. Washimi, Y. Kita, *Org. Lett.* **2011**, *13*, 4814–4817; d) T. Hashimoto, H. Nakatsu, Y. Takiguchi, K. Maruoka, *J. Am. Chem. Soc.* **2013**, *135*, 16010–16013.

[9] For a recent review, see: C. X. Zhuo, W. Zhang, S. L. You, *Angew. Chem. Int. Ed.* **2012**, *51*, 12662–12686; *Angew. Chem.* **2012**, *124*, 12834–12858.

[10] CCDC-983833 (for **5d**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: April 25, 2014
Published Online: June 16, 2014

