

Chemoselective synthesis of substituted pyrazoles through AgOTf-catalyzed cascade propargylic substitution–cyclization–aromatization†

Su-Xia Xu, Lu Hao, Tao Wang, Zong-Cang Ding and Zhuang-Ping Zhan*

Cite this: *Org. Biomol. Chem.*, 2013, **11**, 294Received 4th September 2012,
Accepted 6th November 2012

DOI: 10.1039/c2ob27016a

www.rsc.org/obc

A cascade AgOTf-catalyzed chemoselective approach to 3,5/1,3-disubstituted pyrazoles from propargylic alcohols and *para*-tolylsulfonohydrazide has been developed. Good chemoselectivity is observed depending on the different substituents in the alkyne moiety of the propargylic alcohols, generating two different kinds of products through different aromatization mechanisms. The pyrazolo[5,1-*a*]isoquinoline skeleton can also be effectively constructed by this method through a cascade bicyclization process.

Introduction

Pyrazoles and their derivatives have been recognized as important frameworks in pharmaceutical science,¹ and certain pyrazole derivatives possessing selective COX-2 inhibition, antiobesity activity and selective human NHE-1 inhibition have been developed into clinical drugs (Fig. 1).^{1a-c} Owing to the attractive medicinal properties of pyrazoles, various approaches have been developed for their preparation.² Conventional approaches involve either the construction of two C–N bonds by condensation of hydrazines with 1,3-dicarbonyl compounds or their 1,3-dielectrophilic equivalents, or the generation of one C–N bond and one C–C bond by intermolecular cycloaddition reaction.^{2a} However, these methods have some limitations including multi-step procedures, harsh conditions and poor selectivity. Accordingly, new approaches allowing for efficient assembly of different pyrazole skeletons with diverse substitution patterns are in high demand.

Over the past decade, transition-metal-catalyzed cascade reactions of propargylic alcohols have received considerable attention, since these reactions can directly construct complicated molecules from readily accessible starting materials under mild conditions.³ Recently, our group has developed effective methods for the construction of O- and N-containing heterocycles through consecutive transition metal-catalyzed propargylic substitution reactions and cyclization reactions, both of which were catalyzed by a single catalyst.⁴ It seems plausible that this strategy can be extended to prepare pyrazoles from propargylic alcohols and *para*-tolylsulfonohydrazide. Herein, we wish to report an efficient cascade reaction for the synthesis of pyrazoles from propargylic alcohols and *para*-tolylsulfonohydrazide. Notably, good chemical selectivity is observed in the reaction depending on the different substituents in the alkyne moiety of the propargylic alcohols, generating two different kinds of products through different aromatization mechanisms.

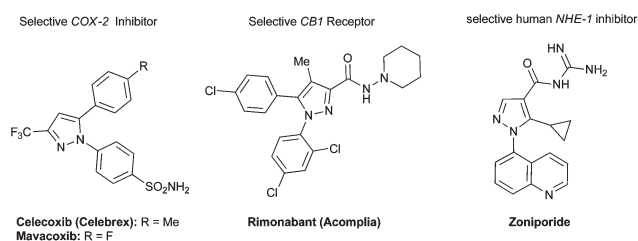


Fig. 1 Selected pyrazole-containing drugs.

Results and discussion

Initially, on the basis of our previous success in FeCl₃-catalyzed propargylic substitution,⁵ we treated the propargylic alcohol **1a** with **2** using 10 mol% FeCl₃ as the catalyst in acetonitrile at reflux. However, no amount of the desired product **4a** was observed under these conditions (Table 1, entry 1). Then, we changed the catalyst to AgOTf, which had been successfully used in our syntheses of pyrrolo[1,2-*a*]indoles.^{4a} To our delight, the target product **4a** was furnished in 42% yield (Table 1, entry 2). Next solvent screening showed that the reaction performed in 1,2-dichloroethane (DCE in abbreviation) at reflux afforded the product in 90% yield (Table 1, entry 8). Consequently, catalyst screening demonstrated that AgOTf was

Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, Fujian, P. R. China. E-mail: zpzhai@xmu.edu.cn;
Fax: +86 (0)592 2180318; Tel: +86 (0)592-2180318

†Electronic supplementary information (ESI) available. See DOI: 10.1039/c2ob27016a

Table 1 Screening of catalysts and solvents^a

Entry	Catalyst	Solvent	Time (h)	Yield ^b (%)
1	FeCl ₃	CH ₃ CN	12	0
2	AgOTf	CH ₃ CN	2	42
3	AgOTf	Toluene	15	79
4	AgOTf	CH ₃ NO ₂	2	50
5	AgOTf	PhCl	2	50
6	AgOTf	DMF	18	Trace
7	AgOTf	1,4-Dioxane	2	45
8	AgOTf	DCE	1	90
9	AgBF ₄	DCE	2	72
10	AgOAc	DCE	4	55
11 ^c	InCl ₃	DCE	3	40
12	In(OTf) ₃	DCE	10	25
13	Zn(OTf) ₂	DCE	3	30
14	Cu(OTf) ₂	DCE	2	65
15 ^d	BiCl ₃	DCE	12	Trace
16 ^d	TFA	DCE	24	0
17 ^d	<i>p</i> -TSA	DCE	24	0
18 ^d	TfOH	DCE	12	0

^a Reaction conditions: **1a** (1.0 mmol), **2** (1.2 mmol), and catalyst (10 mol%) in solvent (5 mL) at reflux for an appropriate time (Tf = triflyl; TFA = trifluoroacetic acid; *p*-TSA = *para*-toluenesulfonic acid; DMF = *N,N*-dimethylformamide; DCE = 1,2-dichloroethane). ^b Isolated yields based on **1a**. ^c About 50% of starting material **1a** was recovered. ^d The majority of the starting material **1a** was recovered.

still the preferential catalyst (Table 1, entries 9–17). The result of the investigation into the effect of counterions of silver salts was very interesting. It was found when adopting AgBF₄ and AgOAc as the catalysts the desired product **4a** could be obtained, but longer reaction time was required and lower yields were given (Table 1, entries 9 and 10). Such results indicated that the nature of the counterions markedly affected the catalytic activity of the silver(i): the trifluoromethanesulfonate anion might be the best counterion to facilitate this cascade reaction.

It is worth mentioning that some groups including Hintermann,^{6a} Hartwig,^{6b} and Mukaiyama^{6c} have reported that the “hidden Brønsted acid” produced from the reaction of AgOTf and DCE at reflux might be responsible for the observed acid-like catalytic activity of transition-metal salts. However, as can be seen from the control experiments in Table 1, the reactions performed under Brønsted acid catalysis gave no desired product (entries 16–18). On the other hand, the reactions carried out under the catalysis of different silver salts indeed afforded the pyrazole in moderate yields (entries 9 and 10). Thus, this cascade reaction is very likely catalyzed by the metal salt rather than Brønsted acid.

Next, the substrate scope was investigated under the optimized conditions (Table 2). We were pleased to find that the reaction of aryl-substituted secondary propargylic alcohols proceeded very well, offering an easy access to 3,5-disubstituted 1*H*-pyrazoles with various substituents. In addition, a wide

Table 2 Cascade synthesis of 3,5-disubstituted 1*H*-pyrazoles^a

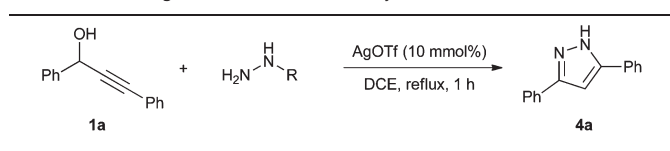
1	2	4

^a Reaction conditions: **1** (1.0 mmol), **2** (1.2 mmol), and AgOTf (10 mol%) in DCE (5 mL) at reflux for an appropriate time. Isolated yields based on **1**. ^b The starting material was recovered. ^c The substitution and cyclization were performed in DCE and PhCl respectively in a one-pot mode.

range of functional groups including F, Cl, Br, MeO, CN and COOMe could be well tolerated, leading to the products in moderate to good yields. Electron-donating functional groups increased the reaction rate and gave good yields (Table 2, **4b** and **4c**), whereas electron-withdrawing substituents slowed the transformation down and provided moderate yields (Table 2, **4d–4g**). Notably, the reaction of propargylic alcohol with an α -furyl group proceeded well, producing the target product in a moderate yield (Table 2, **4h**).

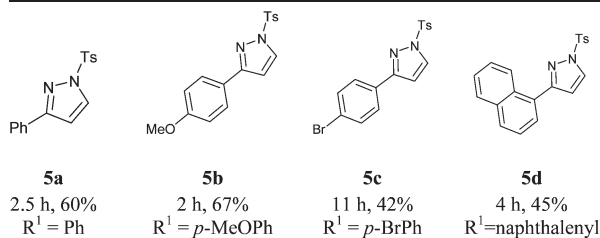
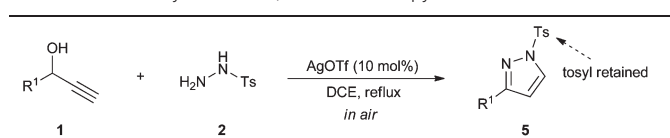
Very interestingly, the next examination into different substituted hydrazines showed that only *p*-tolylsulfonohydrazide worked in the reaction. Reactions with other substituted hydrazines under the standard conditions did not give the pyrazole products (Table 3, entries 2–6). We reasoned that the catalytic activity of AgOTf was suppressed by stronger alkalinity of those substituted hydrazines.

Encouraged by these results, we next examined the reactivity of propargylic alcohols bearing alkyl groups on the alkyne

Table 3 Screening of different substituted hydrazines^a

Entry	Hydrazine	Yield ^b 4a (%)	Recovered ^b 1a (%)
1	TsNHNH ₂	90	0
2	AcNHNH ₂	0	98
3	<i>t</i> -BocNHNH ₂	0	98
4	2,4-Dinitrophenyl-hydrazine	Complex mixture	0
5	PhNHNH ₂	0	97
6	PhCONHNH ₂	0	92

^a Reaction conditions: **1a** (1.0 mmol), hydrazine (1.2 mmol), and AgOTf (10 mol%) in DCE (5 mL) at reflux for one hour. ^b Isolated yields based on **1a**.

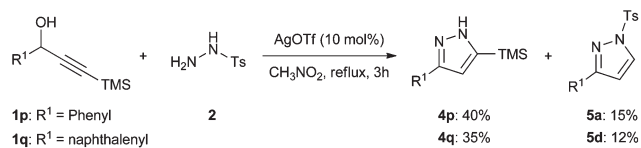
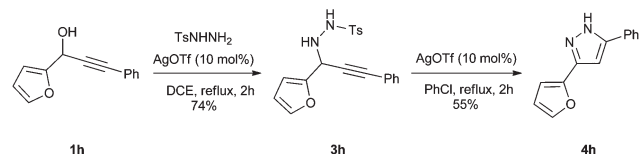
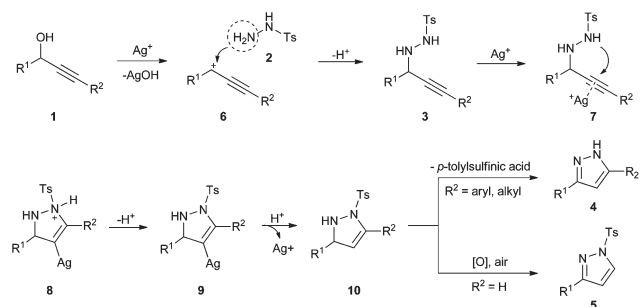
Table 4 Cascade synthesis of 1,3-disubstituted pyrazoles^a

^a Reaction conditions: **1** (1.0 mmol), **2** (1.2 mmol), and AgOTf (10 mol %) in DCE (5 mL) at reflux for an appropriate time. Isolated yields based on **1**.

moiety. Moderate to good yields were obtained (Table 2, **4i–4n**). However, the presence of a strong electron-withdrawing group on the propargylic alcohol had an apparent adverse impact on the conversion (Table 2, **4l** and **4m**). This result could be attributed to the instability of the propargylic cation intermediate formed in the reaction process. Also, we tested the reactivity of alkyl-substituted secondary propargylic alcohol, but it was found no expected product was furnished (Table 2, **4o**).

To further define the generality of this reaction, attention was turned to the reaction of propargylic alcohols with terminal alkyne. Interestingly, we found that the tosyl group was retained in these cases, generating the *N*-tosyl pyrazoles in moderate yields (Table 4). It seemed that the unsaturation degree might come from the oxidation by the oxygen in the air, rather than the elimination of *para*-tolylsulfonic acid.

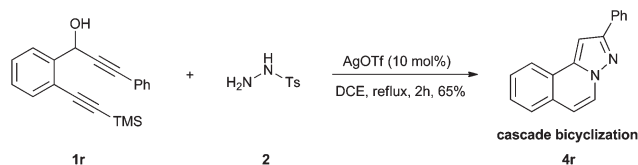
On the other hand, the exploration into the reaction of propargylic alcohols with trimethylsilyl group showed that mixed

**Scheme 1** Cascade reactions of TMS-substituted propargylic alcohols with *para*-tolylsulfonohydride.**Scheme 2** Isolation of the substitution intermediate and AgOTf-catalyzed cyclization.**Scheme 3** Proposed mechanism for the AgOTf-catalyzed cascade synthesis of 3,5- and 1,3-disubstituted pyrazoles.

products were produced (Scheme 1). It was proposed that the trimethylsilyl group had been removed from a certain portion of propargylic alcohols prior to the propargylic substitution, leading to the corresponding propargylic alcohols with terminal alkyne, which would experience the same reaction pathway as shown in Table 2.

To provide preliminary insight into the reaction mechanism for the AgOTf-catalyzed synthesis of pyrazoles, the isolation of the propargylic substitution intermediate was attempted. Indeed, when propargylic alcohol **1h** was subjected to the AgOTf-catalyzed conditions, the propargylic substitution product **3h** was isolated in 74% yield. However, to complete the consecutive AgOTf-catalyzed cyclization, the substitution product **3h** had to be treated at reflux in chlorobenzene instead of 1,2-dichloroethane (Scheme 2).

As a working hypothesis, we proposed the following plausible mechanism for the AgOTf-catalyzed cascade synthesis of pyrazoles (Scheme 3). First, the propargylic alcohol **1** reacts under silver catalysis to yield the propargylic cation intermediate **6**. Next, propargylic substitution occurs by the regioselective attack of the terminal nitrogen atom (–NH₂) of **2**, resulting in the substitution product **3**. Then, through a Ag(I)-mediated triple-bond activation, compound **3** experiences a 5-*endo*-dig cyclization to generate the intermediate **8**. After proton exchange with the metal in **9**, the aromatization of compound



Scheme 4 Synthesis of pyrazolo[5,1-*a*]isoquinoline through AgOTf-catalyzed cascade bicyclization process.

10 can be completed in two ways: one is the elimination of *para*-tolylsulfonic acid, and the other is the oxidation of **10** by the oxygen in the air. The former route leads to the 3,5-disubstituted 1*H*-pyrazoles **4**, while the latter route affords the tosyl-retained products **5** (1,3-disubstituted pyrazoles).

Finally, as a further demonstration, we sought to extend the synthetic utility of the AgOTf-catalyzed cascade sequence. Thus, the *N*-fused heterocyclic skeleton pyrazolo[5,1-*a*]isoquinoline was successfully constructed in 65% yield under the standard reaction conditions through a cascade bicyclization process (Scheme 4), providing an efficient method to access this kind of heterocycles.

Conclusions

In summary, we have developed an efficient AgOTf-catalyzed cascade synthesis of pyrazoles from readily available propargylic alcohols and *para*-tolylsulfonohydrazide. This reaction proceeds through a propargylic substitution–cyclization–aromatization cascade sequence, and a broad range of functional groups are well tolerated. Depending on the different substituents in the alkyne moiety of the propargylic alcohols, two different kinds of products are afforded through different aromatization mechanisms. The heterocyclic skeleton pyrazolo[5,1-*a*]isoquinoline is also effectively constructed by this methodology.

Experimental section

General information

Thin layer chromatography (TLC) was performed on Huanghai pre-coated glass-backed TLC plates and visualized by UV lamp (254 nm). Column chromatography on silica gel (300–400 mesh) was carried out using Technical Grade 60–90 °C petroleum ether (distilled prior to use) and Analytical Grade EtOAc (without further purification). Concentration under reduced pressure was performed by rotary evaporation. Purified compounds were further concentrated under high vacuum (3–5 mmHg). Yields refer to chromatographically purified compounds. ¹H and ¹³C spectra were recorded on a Bruker AV-400 spectrometer. Chemical shifts were reported in ppm. ¹H-NMR spectra were referenced to TMS in CDCl₃ (0 ppm) or d₆-DMSO (2.50 ppm), and ¹³C-NMR spectra were referenced to CDCl₃ (77.0 ppm) or d₆-DMSO (39.5 ppm). All ¹³C-NMR spectra were measured with complete proton

decoupling. HRMS data were obtained *via* Ultra-high Resolution Hybrid Qh-Fourier Transform Mass Spectrometer (En Apex ultra 7.0 FT-MS).

General procedure and representative characterization data

To a flame-dried flask (10 mL) equipped with a magnetic stirring bar, the propargylic alcohol **1** (1.0 mmol, 1.0 equiv.), **2** (1.2 mmol, 1.2 equiv.), and 1,2-dichloroethane (5 mL) were successively added. The mixture was stirred until **2** was dissolved. Subsequently, the catalyst AgOTf (10 mol%, 0.1 mmol) was added. Then, the mixture was heated to reflux for an appropriate time, and monitored periodically by thin-layer chromatography. Upon completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel to afford the products.

3,5-DIPHENYL-1*H*-PYRAZOLE (4A). Prepared according to the general procedure and the reaction was performed for one hour. The product was purified by column chromatography on silica gel (v/v petroleum ether–AcOEt = 15 : 1) to afford a white solid in 90% yield (m.p. 190–192 °C); *R*_f = 0.21 (TLC, v/v petroleum ether–AcOEt = 7 : 1); ¹H-NMR (400 MHz, DMSO): δ 7.17 (s, 1H), 7.31–7.35 (m, 2H), 7.43–7.46 (m, 4H), 7.84 (m, 4H), 13.39 (brs, 1H); ¹³C-NMR (100 MHz, DMSO): δ 99.6, 125.2, 128.8; IR (film): 3417, 3101, 1610 1494 cm⁻¹; ESI-MS: calc. for C₁₅H₁₂N₂ [M + H]⁺: *m/z* = 221.1; found: 221.3.

3-PHENYL-1-TOSYL-1*H*-PYRAZOLE (5A). Prepared according to the general procedure and the reaction was performed for 2.5 hours. The product was purified by column chromatography on silica gel (v/v petroleum ether–AcOEt = 15 : 1) to afford a white solid in 60% yield (m.p. 139–140 °C); *R*_f = 0.20 (TLC, v/v petroleum ether–AcOEt = 5 : 1); ¹H-NMR (400 MHz, CDCl₃): δ 2.41 (s, 3H), 6.73–6.83 (m, 2H), 7.28–7.34 (m, 6H), 7.58 (d, 1H, *J* = 8.4 Hz), 7.86 (d, 2H, *J* = 8.4 Hz); ¹³C-NMR (100 MHz, CDCl₃): δ 21.6, 124.3, 127.0, 127.8, 128.9, 129.1, 129.7, 135.3, 135.5, 139.9, 144.3, 149.8; IR (film): 3180, 1607, 1597 cm⁻¹; ESI-MS: calc. for C₁₆H₁₄N₂O₂S [M + Na + H]⁺: *m/z* (%) = 322.1; found: 322.5.

***N'*-(1-(FURAN-2-YL)-3-PHENYLPROP-2-YNYL)-4-METHYLBENZENE-SULFONOHYDRAZIDE (3H)**. Prepared according to the general procedure and the reaction was performed for 2 hours. The product was purified by column chromatography on silica gel (v/v petroleum ether–AcOEt = 15 : 1) to afford a white solid in 74% yield (m.p. 197–199 °C); *R*_f = 0.22 (TLC, v/v petroleum ether–AcOEt = 7 : 1); ¹H-NMR (400 MHz, CDCl₃): δ 2.41 (s, 3H), 4.03 (d, 1H, *J* = 8.8 Hz), 4.88 (d, 1H, *J* = 8.8 Hz), 6.17 (d, 1H, *J* = 2.0 Hz), 6.32 (dd, 1H, *J* = 3.2, 2.0 Hz), 6.39 (d, 1H, *J* = 3.2 Hz), 7.28–7.36 (m, 4H), 7.42–7.44 (m, 3H), 7.85 (d, 2H, *J* = 8.4 Hz); ¹³C-NMR (100 MHz, CDCl₃): δ 21.6, 50.8, 83.4, 86.1, 109.3, 110.4, 121.2, 128.2, 128.3, 128.8, 129.5, 131.9, 135.3, 143.2, 144.0, 149.4; IR (film): 3256, 2232 (weak), 1597, 1493 cm⁻¹; HRMS(ESI): calc. for C₂₀H₁₈N₂O₃S [M + Na]⁺: *m/z* = 389.0936; found: 389.0935.

3-PHENYL-5-(TRIMETHYLSILYL)-1*H*-PYRAZOLE (4P). Prepared according to the general procedure and the reaction was performed in nitromethane for 3 hours. The product was purified by

column chromatography on silica gel (v/v petroleum ether–AcOEt = 15 : 1) to afford **4p** (a yellow oil; TLC: R_f = 0.32, v/v petroleum ether–AcOEt = 7 : 1) and **5a** in 40% and 15% yields respectively. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 0.34 (s, 9H), 6.74 (s, 1H), 7.26–7.33 (m, 1H), 7.38–7.42 (m, 2H), 7.83–7.85 (m, 2H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ –1.2, 109.8, 125.9, 127.6, 128.6, 133.3, 152.0; IR (film): 3164, 3007, 1607 1513 cm^{-1} ; HRMS (ESI): calc. for $\text{C}_{12}\text{H}_{16}\text{N}_2\text{Si}$ $[\text{M} + \text{H}]^+$: m/z (%) = 217.1161; found: 217.1156.

2-PHENYLPYRAZOLO[5,1-*A*]ISOQUINOLINE (**4r**). Prepared according to the general procedure and the reaction was performed for 2 hours. The product was purified by column chromatography on silica gel (v/v petroleum ether–AcOEt = 15 : 1) to afford a white solid in 65% yield (m.p. 115–116 °C); R_f = 0.25 (TLC, v/v petroleum ether–AcOEt = 7 : 1); $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.99 (d, 1H, J = 7.6 Hz), 7.29 (d, 1H, J = 0.8 Hz), 7.46–7.60 (m, 2H), 7.52–7.60 (m, 2H), 7.72 (dd, 1H, J = 7.6, 1.2 Hz), 8.00–8.02 (m, 2H), 8.13 (dt, 1H, J = 7.6, 0.8 Hz), 8.27 (dd, 1H, J = 8.0, 0.8 Hz); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 94.8, 112.2, 123.8, 124.6, 126.5, 127.4, 127.8, 128.0, 128.5, 128.9, 129.0, 133.3, 140.0, 153.2; IR (film): 3188, 1602, 1501 cm^{-1} ; ESI-MS: calc. for $\text{C}_{17}\text{H}_{12}\text{N}_2$ $[\text{M} + \text{H}]^+$: m/z (%) = 245.1; found: 245.4.

Acknowledgements

We thank the *National Natural Science Foundation of China* (Nos. 21072159 and 21272190), the *973 Projects* (No. 2011CB935901), Xiamen Science and Technology Bureau (No. 3502Z20103006) and the NFFTBS (No. J1030415) for financial support of this project.

Notes and references

- (a) W. G. Bensen, *Pain*, 2003, 515; (b) H. H. Seltzman, *Drug Dev. Res.*, 2009, 70, 601; (c) A. Guzman-Perez, R. T. Wester, M. C. Allen, J. A. Brown, A. R. Buchholz, E. R. Cook, W. W. Day, E. S. Hamanaka, S. P. Kennedy, D. R. Knight, P. J. Kowalczyk, R. B. Marala, C. J. Mularski, W. A. Novomisle, R. B. Ruggeri, W. R. Tracey and R. J. Hill, *Bioorg. Med. Chem. Lett.*, 2001, 11, 803; (d) C. Wasyluk, H. Zheng, C. Castell, L. Debussche, M.-C. Multon and B. Wasyluk, *Cancer Res.*, 2008, 68, 1275; (e) G. Menozzi, L. Mosti, P. Fossa, F. Mattioli and M. Ghia, *J. Heterocycl. Chem.*, 1997, 34, 963; (f) C. M. Park and D. J. Jeon, *Org. Biomol. Chem.*, 2012, 10, 2613.
- For reviews and recent examples, see: (a) S. Fustero, M. Sánchez-Rosellé, P. Barrio and A. Simén-Fuentes, *Chem. Rev.*, 2011, 111, 6984; (b) A. R. Katritzky, C. A. Ramsden, E. F. V. Scriven and R. J. K. Taylor, *Comprehensive Heterocyclic Chemistry*, ed. J. Joule, Elsevier, Amsterdam, 1st edn, 2008, vol. 4, ch. 1, pp. 1–142; (c) Y. M. Janin, *Chem. Rev.*, 2012, 112, 3924; (d) D. Verma, S. Mobin and I. N. N. Namboothiri, *J. Org. Chem.*, 2011, 76, 4764; (e) M. Zora and A. Kivrak, *J. Org. Chem.*, 2011, 76, 9379; (f) D. J. Babinski, H. R. Aguilar, R. Still and D. E. Frantz, *J. Org. Chem.*, 2011, 76, 5915; (g) J. Qian, Y. Liu, J. Zhu, B. Jiang and Z. Xu, *Org. Lett.*, 2011, 13, 4220; (h) S. Gang, P. Liu and Y. Rao, *Org. Lett.*, 2011, 13, 1746; (i) D. A. Borokin, M. Puscau, A. Carlson, A. Solan, K. A. Wheeler, B. Török and R. Dembinski, *Org. Biomol. Chem.*, 2012, 10, 4505; (j) T. Okitsu, K. Sato and A. Wada, *Org. Lett.*, 2010, 12, 3506; (k) O. Jackowski, T. Lecourt and L. Micouin, *Org. Lett.*, 2011, 13, 5664; (l) Y. Wang, X. Bi, W.-Q. Li, D. Li, Q. Zhang, Q. Liu and B. S. Ondon, *Org. Lett.*, 2011, 13, 1722; (m) B. Willy and T. J. Müller, *Org. Lett.*, 2011, 13, 2082.
- For representative examples and reviews, see: (a) C. Ding and X.-L. Hou, *Chem. Rev.*, 2011, 111, 1914; (b) L. Hao and Z.-P. Zhan, *Curr. Org. Chem.*, 2011, 15, 1625; (c) N. Ljungdahl and N. Kann, *Angew. Chem.*, 2009, 121, 652, (*Angew. Chem., Int. Ed.*, 2009, 48, 642); (d) R. J. Detz, H. Hiemstra and J. H. van Maarseveen, *Eur. J. Org. Chem.*, 2009, 6263; (e) R. Sanz, A. Martínez, D. Miguel and J. M. Álvarez-Gutiérrez, *Org. Lett.*, 2007, 9, 727; (f) Z.-P. Zhan, W.-Z. Yang, R.-F. Yang, J.-L. Yu, J.-P. Li and H.-J. Liu, *Chem. Commun.*, 2006, 3352; (g) H.-H. Hui, Q. Zhao, M.-Y. Yang, D. B. She, M. Chen and G.-S. Huang, *Synthesis*, 2008, 191; (h) T. T. Haug, T. Harschneck, A. Duschek, C.-U. Lee, J. T. Binder, H. Menz and S. F. Kirsch, *J. Organomet. Chem.*, 2009, 694, 510.
- (a) L. Hao, Y.-M. Pan, T. Wang, M. Lin, L. Chen and Z.-P. Zhan, *Adv. Synth. Catal.*, 2010, 352, 3215; (b) X.-T. Liu, L. Hao, M. Lin, L. Chen and Z.-P. Zhan, *Org. Biomol. Chem.*, 2010, 8, 3064; (c) T. Wang, X.-L. Chen, L. Chen and Z.-P. Zhan, *Org. Lett.*, 2011, 13, 3324; (d) X. Gao, Y.-M. Pan, M. Lin, L. Chen and Z.-P. Zhan, *Org. Biomol. Chem.*, 2010, 8, 3259.
- Z.-P. Zhan, J.-L. Yu, H.-J. Liu, Y.-Y. Cui, R.-F. Yang, W.-Z. Yang and J.-P. Li, *J. Org. Chem.*, 2006, 71, 8298.
- (a) T. T. Dang, F. Boeck and L. Hintermann, *J. Org. Chem.*, 2011, 76, 9353; (b) D. C. Rosenfeld, S. Shekhar, A. Takemiya, M. Utsunomiya and J. F. Hartwig, *Org. Lett.*, 2006, 8, 4179; (c) H. Jona, H. Mandai, W. Chavasiri, K. Takeuchi and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, 2002, 75, 291.