Tetrahedron 65 (2009) 4639–4643

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Synthesis and structure characterization of unsymmetrical oxacalix[2]benzene[2]pyrazines

Mei Li, Ming-Liang Ma, Xiao-Yan Li, Ke Wen *

Division of Supramolecular Chemistry and Medicinal Chemistry, Key Laboratory of Brain Functional Genomics, MOE & STCSM, Shanghai Institute of Brain Functional Genomics, East China Normal University, Shanghai 200062, China

ARTICLE INFO

Article history:
Received 16 January 2009
Received in revised form 8 April 2009
Accepted 10 April 2009
Available online 17 April 2009

ABSTRACT

The synthesis of two unsymmetrically linked oxacalix[2]benzene[2]pyrazines (**1** and **2**) is described. X-ray single crystal structure analysis revealed a highly distorted 1,3-alternate conformation of compound **1** (containing *ortho*- and *meta*-diphenol components) and a distorted boat conformation of compound **2** (containing *meta*- and *para*-diphenol components). Oxacalix[2]benzene[2]pyrazine containing both *ortho*- and *para*-diphenol components was not obtained via similar synthetic strategy.

1. Introduction

Calix[4]arenes are an interesting class of macrocyclic compounds, which can adopt four different conformations. Among them, cone and 1,3-alternate conformations present high level of molecular symmetry.[1] Due to their interesting conformational and cavity structures, they have been widely used as molecular platforms and hosts in supramolecular chemistry.[2] Heterocalixaromatics,[3] in which the methylene linkages between the aromatic units in calixarenes are replaced by heteroatoms, such as sulfur,[4] oxygen,[5] and nitrogen,[6] have attracted much attention recently because of their synthetic availability, tunable cavities, and potential applications in supramolecular chemistry. Katz et al.[7] and Wang and Yang[8] have successfully incorporated nitrogen containing heterocycles into the oxacalix[4]arene systems via nucleophilic aromatic substitution (S_NAr) reactions, conformationally, these compounds are all oxacalix[4]arene analogues with cage-like structures and high molecular symmetry. Post-synthetic functionalization of oxacalix[2]- arene[2]hetarenes have been demonstrated by Dehaen[9] and Wang[10] et al. Oxacalix[*n*]arene[*n*]hetarenes have already found their applications in recognition of neutral and ionic species.[7b,10b,11]

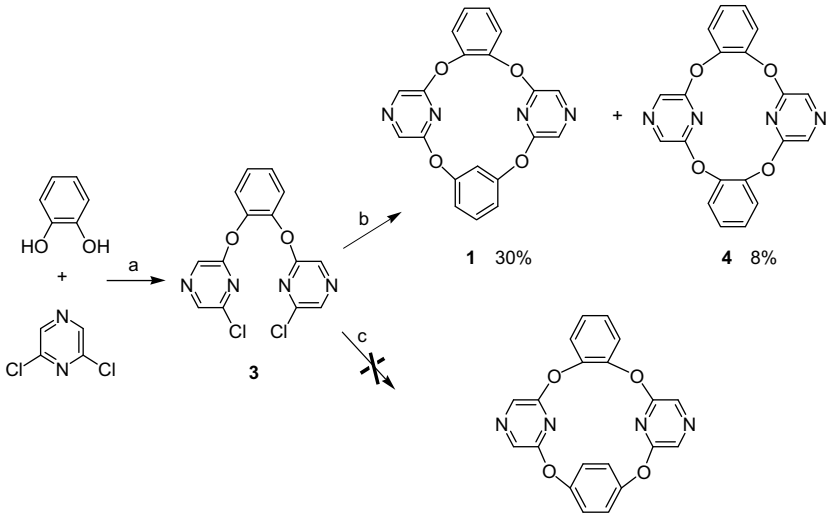
Recently, we became interested in the synthesis, structures, and conformations of oxacalix[*n*]benzene[*n*]hetarene analogues with novel cavity scaffolds, which resulted in the development of some new macrocyclic structures.[12] In extension of our work on the synthesis and structures of oxacalix[*n*]benzene[*n*]hetarene analogues, we are now focusing on the synthesis and structure characterization of unsymmetrical oxacalix[2]benzene[2]hetarenes. During our literature search, we found that calixarenes and heteracalixarenes with their aromatic units being linked via *ortho*-, or *para*-, or unsymmetrical fashion, rather than the regular symmetrical *meta*-linkage were much less studied,[13] possibly due to their synthetic difficulties. We envisioned that the introduction of unsymmetrical linkage between the aromatic units of the calixarenes or heteracalixarenes could increase not only the molecular diversities and functionalities of this class of macrocycles, but also new conformations with unsymmetrical cavities. Host molecules of such would potentially offer us new opportunity to study molecular recognition toward specific unsymmetrical guests. Calixarenes are usually synthesized under hash reaction conditions, and it is still a challenge to introduce unsymmetrical linkage into calixarene systems. However, oxacalix[*n*]arene[*n*]hetarenes were mostly synthesized under milder reaction conditions, and they could also be constructed via fragment coupling strategies. The synthetic convenience of oxacalix[*n*]arene[*n*]hetarenes would thus allow us to introduce unsymmetrical linkage into this class of macrocycles and study their structural and conformational properties. Herein we wish to report the synthesis and X-ray single crystal structures of unsymmetrical oxacalix[2]benzene[2]pyrazines **1** and **2** (see Schemes 1 and 2). To our knowledge, this is the first attempt to address the synthesis as well as structures and conformations of unsymmetrical oxacalix[2]benzene[2]hetarenes.

2. Results and discussion

The synthesis of the unsymmetrical oxacalix[2]benzene[2]pyrazines (**1** and **2**) involves the fragment coupling of 2,6-dichloropyrazine with two different diphenols (*ortho*-, *meta*-, and *para*-diphenols) in two-step reaction sequences (Schemes 1 and 2).

* Corresponding author. Tel.: +86 21 62237102; fax: +86 21 62601953.
E-mail address: kwen@brain.ecnu.edu.cn (K. Wen).

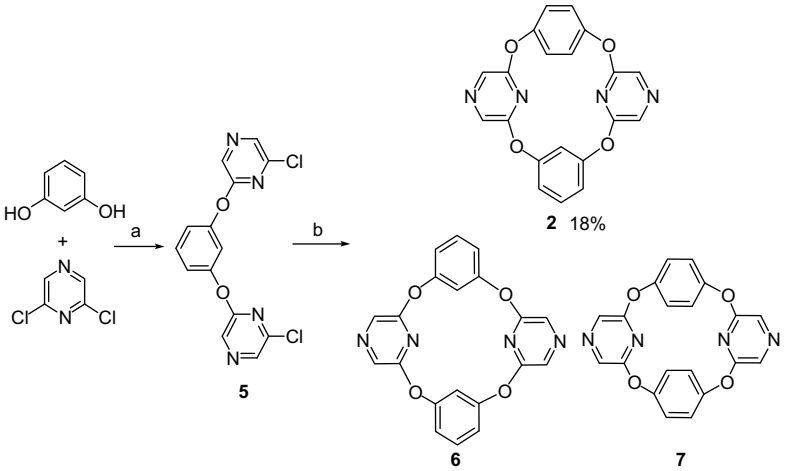
0040-4020/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2009.04.045



Scheme 1. Synthesis of compound **1**. (a) K_2CO_3, DMF, rt; (b) *m*-diphenol, Cs_2CO_3, DMSO, 80 °C; (c) *p*-diphenol, Cs_2CO_3, DMSO, 80 °C.

As shown in Scheme 1, compound **3**[12] was first prepared in 80% yield by the reaction of *ortho*-diphenol with 2,6-dichloropyrazine (1:2 ratio) in the presence of K_2CO_3 in DMF at room temperature. After screening the bases (Na_2CO_3, K_2CO_3, Cs_2CO_3, NaH) and solvents (DMSO, DMF, THF, and CH_3CN), the optimized reaction condition for cyclocondensation of *meta*-diphenol with **3** was set in DMSO at 80 °C for 24 h with Cs_2CO_3 as a base. The yield for the desired product **1** was 30%. In the reaction mixture, symmetrical product, *ortho*-linked oxacalix[2]benzene[2]pyrazine (**4**),[12] was obtained in 8% yield, and other unknown species were also present as by-products due to the bridging C–O bond breaking and reformation in the reaction process.[7a] Prolonged reaction time or high temperature resulted in diminished yield of the desired product **1** and increased yield of by-product **4**. Compound **1** could also be obtained in 21% yield by reaction of compound **5** with *ortho*-diphenol under similar reaction conditions. Attempts to synthesize unsymmetrical oxacalix[2]benzene[2]pyrazine with *ortho*- and *para*-diphenol components via similar strategy by employing compound **3** as intermediate were unsuccessful (Scheme 1). We believe that the high molecular strain of the proposed structure is responsible for the failure. Symmetrical compound **4** was the only isolated product (23%) in this reaction. Compound **2** was prepared in 18% yield (Scheme 2). In this protocol, symmetrical by-products **6** and **7** were obtained as the result of the bridging C–O bond breaking and reformation in the reaction process. Structure of the compound similar to **6** (oxacalix[2]arene[2]pyrazine) has been described by Katz et al.,[7a] while the structure of compound **7** has not been precedented.

Oxacalix[4]arenes and related oxacyclophanes with four oxygen atom bridges appeared in the literature all adopt 1,3-alternate conformations.[3] In our previous report, *ortho*-linked oxacalix[2]-benzene[2]pyrazine (**4**) was found to adopt an 1,3-alternate conformation, and 1,3,5-alternate, core conformations were found for *ortho*-linked oxacalix[3]benzene[3]pyrazine and oxacalix[3]-benzene[3]pyrimidine, respectively.[12] In order to determine the conformational characters of the unsymmetrical oxacalix[2]-benzene[2]pyrazines (**1** and **2**) in the solid state, single crystals of compounds **1** and **2** with X-ray diffraction quality were grown by slow evaporation from sample solution in ethyl acetate. As shown in Figure 1 (top), compound **1** adopts a highly distorted 1,3-alternate conformation, the pair of the opposite pyrazine rings are arranged in an unparalleled face-to-face orientation with a dihedral angle of 96.8°, and a centroid–centroid distance of 5.498 Å. The transannular N···N distances of two upper rim nitrogen atoms are 6.810 Å and 3.732 Å for the two lower rim nitrogen atoms. The two benzene planes (*ortho*-linked and *meta*-linked) are also arranged in a distorted face-to-face orientation with a dihedral angle of 48.4°, and a centroid–centroid distance of 5.638 Å. The bridging oxygen atoms are partially conjugated to the pyrazine rings (average C–O length 1.36 Å), while no conjugation exists between the bridging



Scheme 2. Synthesis of compound **2**. (a) K_2CO_3, DMF, rt; (b) *p*-diphenol, Cs_2CO_3, DMSO, 80 °C.

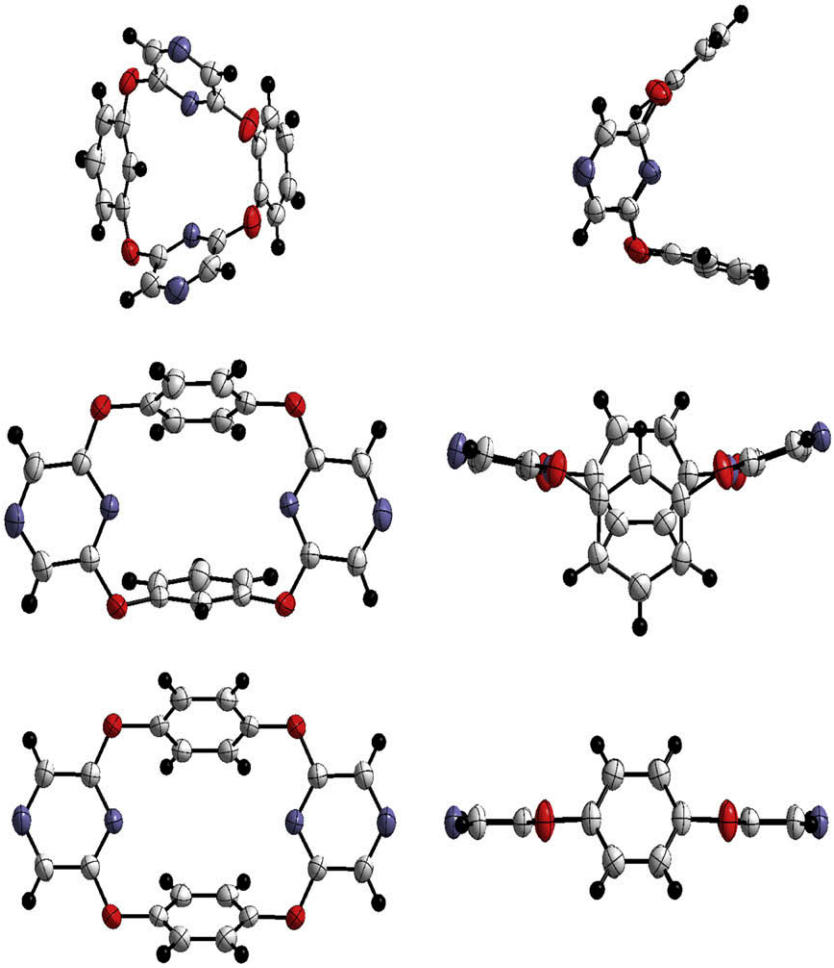


Figure 1. X-ray crystal structures of compound **1** (top left, top view; top right, side view), **2** (middle left, top view; middle right, side view), and **7** (bottom left, top view; bottom right, side view). Color codes: oxygen=red, nitrogen=purple, carbon=gray, hydrogen=black.

oxygen atoms and the benzene planes (average C–O length 1.395 Å). In the solid state, the benzene rings are in close contact with the concave surface of another molecule via weak π–π stacking interaction. π–π Stacking interactions exist between the pyrazine rings in the solid state (Supplementary data, Fig. S1). Also shown in Figure 1 (middle), compound **2** adopts a distorted 'boat' conformation with the two pyrazine rings approach coplanarity (154.5° between the ring planes). The two benzene planes are positioned in opposite side of the 'boat' with a dihedral angle of 33.5° and a centroid–centroid distance of 4.610 Å. Partial conjugation between the bridged oxygen atoms and pyrazine rings were observed (average C–O length 1.364 Å) while no conjugation exists between the bridging oxygen atoms and the benzene planes (average C–O length 1.408 Å). π–π Stacking interactions were also observed between the pyrazine rings in the solid state (Supplementary data, Fig. S2). By-product **7**, *para*-linked oxacalix[2]benzene[2]pyrazine (Fig. 1, bottom) adopts a boat conformation with very high molecular symmetry. The two pyrazine rings are arranged in coplanarity (179.7°), while the two benzene planes are arranged in a face-to-face orientation with a dihedral angle of 57.4° and a centroid-to-centroid distance of 4.645 Å. Similarly, the bridging oxygen atoms in compound **7** only conjugate with the pyrazine rings (average C–O length 1.359 Å) but not the benzene planes (average C–O length 1.409 Å). In the solid state, compound **7** packs in a layered fashion with all the pyrazine rings participated in the strong π–π stacking interactions (Supplementary data, Fig. S3). Crystalline material of **7** has poor solubility in any of organic (such as DMF and DMSO) or inorganic solvents (even in high temperature), which could be caused by the strong intermolecular interaction (π–π stacking interaction) that prevents the liberation of compound **7** from its crystal lattice.

3. Conclusions

In conclusion, unsymmetrical oxacalix[2]benzene[2]pyrazines (**1** and **2**) have been synthesized by nucleophilic aromatic substitution of 2,6-dichloropyrazine with two different diphenols (*ortho*- and *meta*-, or *meta*- and *para*-) via fragment coupling strategies. The hydroxyl substitution pattern of the two diphenols employed in the assembly of the cyclotetramers is responsible for the conformations of the unsymmetrical products. As a result, compound **1** was found to adopt a distorted 1,3-alternate conformation in the solid state, and compound **2**, a distorted boat conformation. Our continuous efforts on the synthesis, structures, properties, as well as searching specific applications of these unsymmetrical oxacalix[*n*]benzene[*n*]hetarenes will be reported in due course.

4. Experimental section

4.1. General

All chemicals were used as received without further purification. Chemical reactions were performed in oven-dried glassware under an atmosphere of nitrogen. Classic column chromatography was performed using Merck 60 (70–230 mesh) silica gel. ^{1}H and ^{13}C NMR spectra were recorded at Bruker Avance 500 spectrometer in

$CDCl_3$ or DMSO-d_6. Chemical shifts are reported in parts per million versus tetramethylsilane. Mass spectra were recorded on a Bruker micrOTOF-Q spectrometer (LC/MS). Single crystal X-ray diffraction data were collected on a Bruker SMART APEX 2 X-ray diffractometer equipped with a normal focus Mo-target X-ray tube (λ=0.71073 Å).

4.2. Synthesis of compound 1

To a stirred solution of cesium carbonate (3.01 g, 9.2 mmol) in DMSO (100 mL) was added dropwise a solution of resorcinol (0.46 g, 4.2 mmol) in 100 mL DMSO and a solution of compound **3**[12] (1.41 g, 4.2 mmol) in 100 mL DMSO at the same rate during 6 h (achieving high dilution). The reaction mixture was stirred for another 24 h at 80 °C and then poured into 500 mL of water, extracted with ethyl acetate for three times. The combined organic layers were washed with water, brine, and dried over Na_2SO_4. The solvent was evaporated and the crude product was purified by chromatograph on a silica gel column (petroleum ether/ethyl acetate 4:1). Compound **1** (0.47 g, 30%) was obtained as white solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ=8.37 (s, 2H), 8.21 (s, 2H), 7.26 (t, J=8.15, 1H), 7.13 (m, 4H), 6.86 (dd, J_1=2.3, J_2=8.15, 2H), 6.78 (t, J=2.25, 1H); ^{13}C NMR (500 MHz, DMSO-d_6): δ=157.52, 156.57, 153.31, 145.01, 129.94, 128.84, 128.24, 126.49, 124.28, 114.89, 112.49; HRMS (ESI): m/z calcd for $C_{20}H_{13}N_4O_4^+$ [M+H$^+$]: 373.0931; found: 373.0929. Compound **4**[12] was obtained in 8% yield.

4.3. Synthesis of compound 2

By replacing catechol with resorcinol, compound **5** was obtained (82.7%) as white solid by using a similar protocol as in the synthesis of compound **3**.[12] ^{1}H NMR (500 MHz, DMSO-d_6): δ=8.58 (s, 2H), 8.55 (s, 2H), 7.57 (t, J=8.25, 1H), 7.31 (t, J=2.2, 1H), 7.23 (dd, J_1=8.2, J_2=2.25, 2H); ^{13}C NMR (500 MHz, DMSO-d_6): δ=157.92, 153.31, 144.37, 137.88, 133.72, 130.98, 118.29, 114.39; HRMS (ESI): m/z calcd for $C_{14}H_9Cl_2N_4O_2^+$ [M+H$^+$]: 335.0097; found 335.0092. In the second step, replacing **3** with **5** as in the synthesis of **1**, compound **2** was isolated as white solid in 18% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.16 (s, 2H), 8.13 (s, 2H) 7.29 (m, 1H), 6.80 (s, 4H), 6.70 (m, 2H), 6.67 (d, J=7.0, 1H); ^{13}C NMR (500 MHz, $CDCl_3$): δ=159.1, 158.6, 154.5, 150.2, 129.9, 126.8, 126.7, 123.5, 119.5, 118.0; HRMS (ESI): m/z calcd for $C_{20}H_{13}N_4O_4^+$ [M+H$^+$]: 373.0931; found: 373.0939. Compounds **6** and **7** were also isolated during the column chromatography in less than 5% yields. ^{1}H NMR (500 MHz, $CDCl_3$) for compound **6**: δ=8.12 (s, 4H), 7.25 (t, J=8.0, 2H), 6.82 (q, J_1=2.5, J_2=6.0, 4H), 6.60 (t, J=2.0, 2H); ^{13}C NMR (500 MHz, $CDCl_3$): δ=157.93, 153.14, 130.24, 127.19, 118.76, 115.94. HRMS (ESI): m/z calcd for $C_{20}H_{13}N_4O_4^+$ [M+H$^+$]: 373.0931; found: 373.0926. ^{1}H NMR (500 MHz, DMSO-d_6) for compound **7**: δ=8.22 (s, 4H), 7.00 (s, 8H); ^{13}C NMR (500 MHz, DMSO-d_6): δ=157.79, 149.08, 126.14, 123.07. HRMS (ESI): m/z calcd for $C_{20}H_{13}N_4O_4^+$ [M+H$^+$]: 373.0931; found: 373.0936.

4.4. Crystallographic data for compound 1

[$C_{20}H_{12}N_4O_4$]; M_r=372.34; monoclinic; space group $P2_1/c$; a=13.8804(7); b=12.8192(7); c=19.5735(10) Å; α=90°; β=105.8030(10)°; γ=90°; V=3351.2(3) Å^3; ρ_{calcd}=1.476 g cm^{-3}; T=296(2) K; 27,609 independent measured reflections; F^2 refinement; R_1=0.0333; wR_2=0.0737. This data was deposited in the Cambridge Crystallographic data centre, CCDC 709284.

4.5. Crystallographic data for compound 2

[$C_{20}H_{12}N_4O_4$]; M_r=372.34; monoclinic; space group $C2/c$; a=18.8314(5); b=10.7633(3); c=18.2294(5) Å; α=90; β=112.0020(10); γ=90°; V=3425.78(16) Å^3; ρ_{calcd}=1.444 g cm^{-3}; T=296(2) K; 19,405 independent measured reflections; F^2 refinement; R_1=0.0292; wR_2=0.0731. This data was deposited in the Cambridge Crystallographic data centre, CCDC 709285.

4.6. Crystallographic data for compound 7

[$C_{20}H_{12}N_4O_4$]; M_r=372.34; orthorhombic; space group $Cmca$; a=17.3725(4); b=13.5070(3); c=14.1108(4) Å; ρ_{calcd}=1.494 g cm^{-3}; T=296(2) K; 18,344 independent measured reflections; F^2 refinement; R_1=0.0297; wR_2=0.0876. This data was deposited in the Cambridge Crystallographic data centre, CCDC 709286.

Acknowledgements

The authors thank Shanghai Commission for Science and Technology (06Pj14034, 06DZ19002), Ministry of Education (106078), and Ministry of Science and Technology of China (973 Project, 2003CB716600) for financial support. We think Dr. Xiao-Li Zhao of Shanghai Key Laboratory of Green Chemistry and Chemical Processes and Department of Chemistry of East China Normal University for performing the X-ray crystallographic study.

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.04.045.

References and notes

1. (a) Gutsche, C. D. *Calixarenes*; Royal Society of Chemistry: Cambridge, UK, 1989; (b) Gutsche, C. D. *Calixarenes Revisited*; Royal Society of Chemistry: London, 2000.
2. (a) Böhmer, V. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 713–745; (b) Ikeda, A.; Shinkai, S. *Chem. Rev.* **1997**, *97*, 1713–1734; (c) Rebek, J., Jr. *Acc. Chem. Res.* **1999**, *32*, 278–286; (d) Hof, F.; Craig, S. L.; Nuckolls, C.; Rebek, J., Jr. *Angew. Chem., Int. Ed.* **2002**, *41*, 1488–1508; (e) Cram, D. J.; Cram, J. M. *Container Molecules and their Guests*; Royal Society of Chemistry: Cambridge, 1994; (f) Biros, S. M.; Ullrich, E. C.; Hof, F.; Trembleau, L.; Rebek, J., Jr. *J. Am. Chem. Soc.* **2004**, *126*, 2870–2876; (g) Colasson, B.; Reinaud, O. *J. Am. Chem. Soc.* **2008**, *130*, 15226–15227; (h) Nishimura, N.; Kobayashi, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 6255–6258; (i) Srinivasan, K.; Gibb, B. C. *Chem. Commun.* **2008**, 4640–4642; (j) Liu, S.; Gibb, B. C. *Chem. Commun.* **2008**, 3709–3716.
3. Recent reviews see: (a) Wang, M.-X. *Chem. Commun.* **2008**, 4541–4551; (b) Maes, W.; Dehaen, W. *Chem. Soc. Rev.* **2008**, *37*, 2393–2402.
4. Lhotak, P. *Eur. J. Org. Chem.* **2004**, 1675–1692.
5. (a) Sommer, N.; Staab, H. A. *Tetrahedron Lett.* **1966**, *7*, 2837–2841; (b) Chambers, R. D.; Hoskin, P. R.; Khalil, A.; Richmond, P.; Sandford, G.; Yufit, D. S.; Howard, J. A. K. *J. Fluorine Chem.* **2002**, *116*, 19–22; (c) Li, X.-H.; Upton, T. G.; Gibb, C. L. D.; Gibb, B. C. *J. Am. Chem. Soc.* **2003**, *125*, 650–651; (d) Yang, F.; Yan, L.; Ma, K.; Yang, L.; Li, J.; Chen, L.; You, J. *Eur. J. Org. Chem.* **2006**, 1109–1112; (e) Katz, J. L.; Feldman, M. B.; Conry, R. R. *Org. Lett.* **2005**, *7*, 91–94; (f) Katz, J. L.; Selby, K. J.; Conry, R. R. *Org. Lett.* **2005**, *7*, 3505–3507; (g) Konishi, H.; Tanaka, K.; Teshima, Y.; Mita, T.; Morikawa, O.; Kobayashi, K. *Tetrahedron Lett.* **2006**, *47*, 4041–4044; (h) Konishi, H.; Mita, T.; Morikawa, O.; Kobayashi, K. *Tetrahedron Lett.* **2007**, *48*, 3029–3032; (i) Hao, E.; Fronczek, F. R.; Vicente, M. G. H. *J. Org. Chem.* **2006**, *71*, 1233–1236; (j) Konishi, H.; Mita, T.; Yasukawa, Y.; Morikawa, O.; Kobayashi, K. *Tetrahedron Lett.* **2008**, *49*, 6831–6834.
6. (a) Ito, A.; Ono, Y.; Tanaka, K. *J. Org. Chem.* **1999**, *64*, 8236–8241; (b) Miyazaki, Y.; Kanbara, T.; Yamamoto, T. *Tetrahedron Lett.* **2002**, *43*, 7945–7948; (c) Wang, M.-X.; Zhang, X.-H.; Zheng, Q.-Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 838–842; (d) Wang, Q.-Q.; Wang, D.-X.; Ma, H.-W.; Wang, M.-X. *Org. Lett.* **2006**, *8*, 5967–5970; (e) Liu, S.-Q.; Wang, D.-X.; Zheng, Q.-Y.; Wang, M.-X. *Chem. Commun.* **2007**, 3856–3858; (f) Gong, H.-Y.; Zhang, X.-H.; Wang, D.-X.; Ma, H.-W.; Zheng, Q.-Y.; Wang, M.-X. *Chem.—Eur. J.* **2006**, *12*, 9262–9275; (g) Gong, H.-Y.; Wang, D.-X.; Xiang, J.-F.; Zheng, Q.-Y.; Wang, M.-X. *Chem.—Eur. J.* **2007**, *13*, 7791–7802; (h) Vale, M.; Pink, M.; Rajca, S.; Rajca, A. *J. Org. Chem.* **2008**, *73*, 27–35; (i) Tsue, H.; Matsui, K.; Ishibashi, K.; Takahashi, H.; Tokita, S.; Ono, K.; Tamura, R. *J. Org. Chem.* **2008**, *73*, 7748–7755; (j) Touil, M.; Lachkar, M.; Siri, O. *Tetrahedron Lett.* **2008**, *49*, 7250–7252.
7. (a) Katz, J. L.; Geller, B. J.; Conry, R. R. *Org. Lett.* **2006**, *8*, 2755–2758; (b) Katz, J. L.; Geller, B. J.; Foster, P. D. *Chem. Commun.* **2007**, 1026–1028.
8. Wang, M.-X.; Yang, H.-B. *J. Am. Chem. Soc.* **2004**, *126*, 15412–15422.
9. (a) Maes, W.; Van Rossom, W.; Van Hecke, K.; Van Meervelt, L.; Debaen, W. *Org. Lett.* **2006**, *8*, 4161–4164; (b) Van Rossom, W.; Maes, W.; Kishore, L.; Ovaere, M.; Van Meervelt, L.; Dehaen, W. *Org. Lett.* **2008**, *10*, 585–588.

10. (a) Wang, Q.-Q.; Wang, D.-X.; Zheng, Q.-Y.; Wang, M.-X. *Org. Lett.* **2007**, *9*, 2847–2850; (b) Yang, H.-B.; Wang, D.-X.; Wang, Q.-Q.; Wang, M.-X. *J. Org. Chem.* **2007**, *72*, 3757–3763; (c) Hou, B.-Y.; Zheng, Q.-Y.; Wang, D.-X.; Wang, M.-X. *Tetrahedron* **2007**, *63*, 10801–10808; (d) Hou, B.-Y.; Zheng, Q.-Y.; Wang, D.-X.; Huang, Z.-T.; Wang, M.-X. *Chem. Commun.* **2008**, 3864–3866.
11. (a) Hou, B.-Y.; Wang, D.-X.; Yang, H.-B.; Zheng, Q.-Y.; Wang, M.-X. *J. Org. Chem.* **2007**, *72*, 5218–5226; (b) Wang, D.-X.; Zheng, Q.-Y.; Wang, Q.-Q.; Wang, M.-X. *Angew. Chem., Int. Ed.* **2008**, *47*, 7485–7488.
12. Ma, M.-L.; Wang, H.-X.; Li, X.-Y.; Liu, L.-Q.; Jin, H.-S.; Wen, K. *Tetrahedron* **2009**, *65*, 300–304.
13. (a) Lehmann, F. P. A. *Tetrahedron* **1974**, *30*, 727-–733; (b) Gilbert, E. E. *J. Heterocycl. Chem.* **1974**, *11*, 899–904; (c) Bottino, F.; Foti, S.; Pappalardo, S. *Tetrahedron* **1976**, *32*, 2567–2570; (d) Kime, D. E.; Norymberski, J. K. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1048–1052; (e) Boros, E. E.; Andrews, C. W.; Davis, A. O. *J. Org. Chem.* **1996**, *61*, 2553–2555; (f) Ogoshi, T.; Kanai, S.; Fujinami, S.; Yamagishi, T.; Nakamoto, Y. *J. Am. Chem. Soc.* **2008**, *130*, 5022–5023.