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One-Step Access to Luminescent Pentaaryldiazaboroles via C−C Double Bond Formation from Imidoylstannanes

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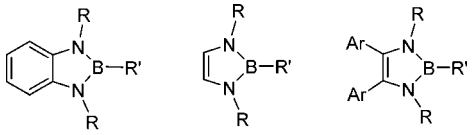
Supporting Information

ABSTRACT: A series of pentaaryl-substituted diazaboroles have been prepared for the first time by a novel strategy based on the C−C double bond formation from imidoylstannane reagents in the presence of dibromophenylboranes. The aryl substituents on the 4,5-position of the planar C_2N_2B core have substantial effects on their electronic structures. All the new diazaboroles are luminescent both in solution and in the solid state. DFT calculations indicate the 4,5-*C*-aryl substituents have significant contributions to the LUMOs.

Peripheral aryl-substituted aromatic systems, such as hexaarylbenzenes and pentaarylpyrroles, have potential applications in molecular electronics and nanotechnology because of their restricted intramolecular rotations of the periphery aryl rings and unique photophysical properties.[1] BN-containing aromatic systems, where a C=C bond is substituted by an isoelectronic B−N unit in aromatic hydrocarbons, have been one of the recent focuses in main group chemistry due to their potential applications as optoelectronic materials.[2] Therefore, many efforts have been devoted to the synthesis of their derivatives.

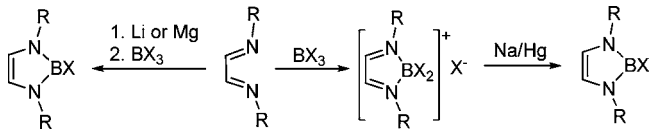
1,3,2-Diazaboroles, isoelectronic with pyrroles, are important aromatic boracycles that have been studied for decades since the first synthesis in 1973.[3] The primary concerns on the molecules have been centered on their aromaticity and electronic properties in comparison to pyrroles,[4] and synthesis of N-heterocyclic boryl anions.[5] However, the study of diazaboroles was to a great extent limited to 1,3,2-benzodiazaboroles (Chart 1, **A**)[6] and 1,3-N- and B-substituted

Chart 1



derivatives (**B**); the 4,5-*C*-aryl derivatives (**C**) are extremely rare, probably due to the lack of synthetic approaches.[7] The widely employed methods to synthesize diazaboroles developed by Weber and Schmid require suitable α-diimines, which must be reduced by highly active metals in the processes (Scheme 1).[4a,b] Although several synthetic routes to α-diimine ligands based on aldimine coupling reactions mediated by lanthanide

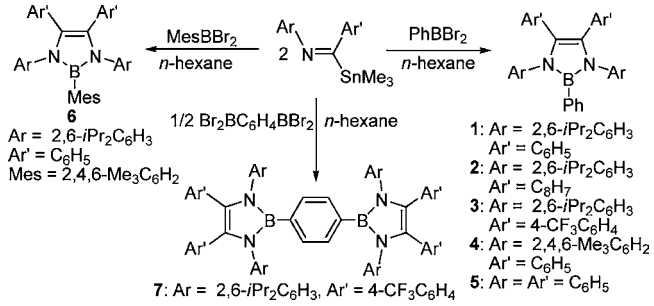
Scheme 1. Normal Routes to Diazaboroles



metals and cyanide ions have been recently developed,[8] tetraaryl-substituted α-diimines with bulky aryl substituents that are required, in some cases, for the protection of a low-coordinate central atom are still not accessible by these methodologies. Inspired by the unique electronic properties of peripheral aryl-substituted aromatic compounds and significant electronic effects of the 4,5-*C*-substituents on N-heterocyclic carbenes,[9] we became interested in pentaaryldiazaboroles. Surprisingly, such boracycles have not been reported so far.

We report here a facile one-step strategy for the synthesis of the first pentaaryldiazaboroles based on a novel C−C double bond formation reaction from imidoylstannane reagents (Scheme 2) in the presence of a dibromophenylborane. The

Scheme 2. New Strategy for the Synthesis of the Peripheral Aryl-Substituted Diazaboroles 1−7



overall reaction leads to the one-step coupling of the two imines and the borane, with the formation of a C−C double bond and the five-membered ring closure. To the best our knowledge, this type of coupling reaction has not been applied for the synthesis of α-diimine-derived main group and transition metal complexes. This protocol allows direct access to a series of peripheral aryl-substituted diazaboroles and does not need α-diimine ligands. Interestingly, the resulting pentaaryldiazaboroles are luminescent both in solution and in

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the solid state, in contrast to well-documented benzodiazaboroles.[6]

The desired imidoylstannane reagents were obtained in excellent yields by reactions of different aryl-substituted imidazoyl chlorides with Me_3SnLi. Subsequent reaction of the imidoylstannane reagents with $PhBBr_2$ or $MesBBr_2$ (Mes = 2,4,6-$Me_3C_6H_2$) in refluxing *n*-hexane directly yielded the expected pentaaryldiazaboroles **1**–**6** in modest yield (Scheme 2). The phenyl-linked bis-diazaborole **7** can be obtained with 1,4-$(BBr_2)_2C_6H_4$ by the same strategy.

These new compounds were isolated as pale yellow or yellow crystals and have been fully characterized by ^1H, ^{11}B, and ^{13}C NMR and EI mass spectroscopy and elemental analysis. The molecular structures of **2** and **3** have been determined by single-crystal X-ray analysis and are shown in Figure 1. The

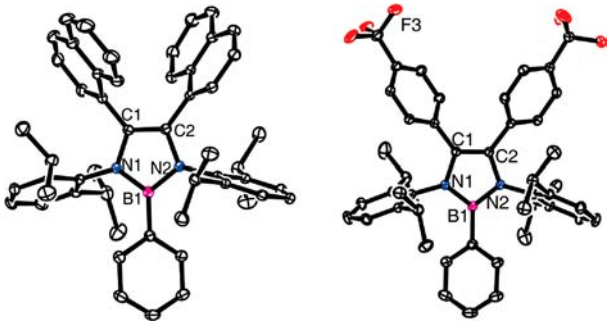
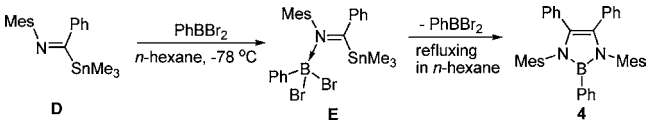


Figure 1. ORTEP drawings of **2** (left) and **3** (right) with 30% ellipsoid probability. Selected bond length and angles (deg): for **2**, B1–N2 1.436(2), B1–N1 1.438(2), N1–C1 1.4224(18), N2–C2 1.4198(18); for **3**, B1–N2 1.4358(19), B1–N1 1.4375(19), N1–C1 1.4118(16), N2–C2 1.4062(17).

planar central C_2N_2B cores of **2** and **3** are surrounded by the propeller-like twisted aryl rings with torsion angles of 29.8°(B), 80.7°(N), 57.4°(C), 66.1°(C), and 72.2°(N) in **2** and 32.1°(B), 76.2°(N), 49.6°(C), 43.9°(C), and 80.2°(N) in **3**, respectively. No intermolecular π–π interactions have been observed in the solid state. This structural feature resembles those observed in their isoelectronic pentaphenylpyrroles.[1j]

The mechanism of the C–C double bond formation has not been fully established. However, it is quite possible that the first step involves the formation of a donor–acceptor complex between an imidoylstannane and $PhBBr_2$. This complex, upon heating, eliminates Me_3SnBr to generate a carbene intermediate, Ar(PhBrB)N-C(Ar′), which subsequently dimerizes to form the C=C bond with the elimination of $PhBBr_2$ and formation of the five-membered ring system. The isolation of the donor–acceptor complex **E** (Scheme 3) at low temperature and its subsequent transformation to **4** by heating strongly support this mechanism. The intermediate **E** has been characterized by ^1H, ^{11}B, and ^{13}C NMR spectroscopy. The ^1H NMR spectrum clearly shows a singlet at δ 0.45 ppm with tin satellites ($^2J_{Sn-H}$ = 56 Hz), indicating the presence of Me_3Sn group. The ^{11}B NMR spectrum of **E** shows the resonance at

Scheme 3. Synthesis of the Intermediate E



δ6.46 ppm, which falls in the range for four-coordinate boron species.[10] However, the donor–acceptor complex is not stable in solution and slowly eliminates Me_3SnBr at ambient temperature. Furthermore, it was found that reaction of the aminodibromoborane $(iPr)_2NBBr_2$ with an ArN=CAr′($SnMe_3$) directly led to the elimination of Me_3SnBr with the formation of the corresponding boryl-substituted imine ArN=C(Ph)[BBrN(iPr_2)],[11] while the C–C coupling product has not been observed, indicating that relatively strongly Lewis acidic boranes such as $PhBBr_2$ are required for the coupling.

The most prominent and interesting features of these diazaboroles can be seen in their UV–vis and emission spectra (Figure 2). The diazaboroles **1**–**7** are fluorescent both in

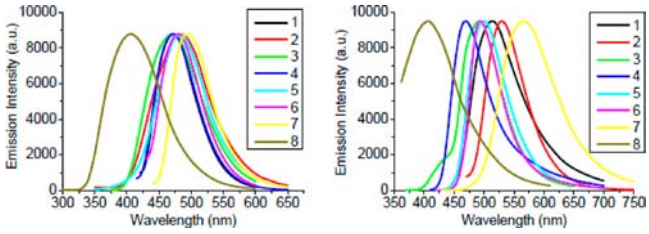


Figure 2. Luminescent spectra of **1**–**8** in THF (left) and in the solid state (right).

solution and in the solid state. For comparison, the absorption and luminescence properties of the diazaborole $(CHNAr)_2BC_6H_5$ (**8**, Ar = 2,6-$iPr_2C_6H_3$),[5b] without aryl substituents on the 4,5-position, have also been investigated. The absorption and luminescence maxima measured in THF are listed in Table 1. The absorption and fluorescence

Table 1. Absorption and Emission Data for Compounds 1–8 in THF and in the Solid State (in Parentheses)

compd	λ_{abs} (nm)[a]	λ_{ex} (nm)[b]	λ_{em} (nm)[c]	Stokes shifts (cm^{-1})	Φ_F[d]
1	406 (407)[e]	415 (367)	471 (513)	3400 (5080)	0.82 (0.04)
2	344 (452)	317 (432)	484 (528)	8410 (3180)	0.16 (0.40)
3	346 (380)	363 (366)	471 (491)	7670 (5950)	0.61 (0.15)
4	388 (393)	403 (364)	472 (469)	4950 (4120)	0.59 (0.03)
5	398 (407)	416 (427)	481 (499)	4340 (4530)	0.06 (0.03)
6	411 (409)	422 (367)	480 (494)	3500 (4210)	0.90 (0.04)
7	439 (440)	432 (362)	495 (566)	2580 (5060)	0.90 (0.01)
8	280 (355)	323 (333)	406 (407)	11080 (3600)	0.76 (0.22)

[a]Absorption maximum. [b]Wavelengths for excitation. [c]Emission maximum. [d]Absolute quantum yield determined by a calibrated integrating sphere system within ±3% errors. [e]Data in parentheses refer to the solid-state data (the solid samples were obtained by grinding crystals).

properties were also investigated in *n*-hexane and dichloromethane (Table S4). The results indicated that the absorption and fluorescence properties of these compounds were only slightly affected by solvent polarity. Notably, it can be seen from Table 1 and Figure 2 that introduction of aryl groups to the 4,5-positions of the C_2N_2B core results in the apparent red

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shifts of the absorption and emission maxima compared to those of the 4,5-dihydro derivative **8**. The absorption maxima for these compounds range from 344 to 439 nm, while the emission maxima shift from violet to blue, and even to green in comparison to that of **8**. The absorption maxima of **1**, **4**, **5**, and **6** are red-shifted relative to the other compounds since the small C_6H_5 groups on the 4,5-position in these compounds would result in their relatively small torsion angles and thus the enhanced π-conjunction with the central core. The fluorescence maxima of **1**−**7** are within the narrow range from 471 to 495 nm, indicating that the substituents of the aryl rings on the central core have a limited effect on their emission maxima. However, the quantum yields (Φ_F) of these compounds are apparently affected by the steric hindrance of the aryl group on the boron and nitrogen atoms. The highest Φ_F values (0.90) are observed for **6** and **7**. The boron atom is efficiently protected by the Mes group in **6**, while the extended π system in **7** may electronically stabilize the boron center. For the four 4,5-C_6H_5-substituted derivatives **1**, **4**, **5**, and **6**, the quantum yields decrease [**6** (0.90) > **1** (0.71) > **4** (0.59) > **5** (0.06)] with the decrease of the steric hindrance around the boron atom. The very low Φ_F observed for **5** is most likely due to the poor protection for the three-coordinate boron center from the attack by solvent molecules.[12] Compounds **1**, **3**, and **8** have similar steric effects around the boron atoms, and relatively high quantum yields (0.82, 0.61, and 0.76) have been observed for these compounds, indicating the necessity of bulky groups around the boron atom. The relatively low Φ_F (0.16) of **2** may result from the fact that the ideal planar geometry for the excited state can hardly be approached by the big naphthyl groups.

Compounds **1**−**8** are also luminescent in the solid state. Red-shifts of the emission maxima and relatively large Stokes shifts in the solid state compared to their THF solutions (Figure 2) are generally observed, except for **8**. The large red-shift of the absorption maximum found for **2** in the solid state in comparison to that in solution (Table 1) may be attributed to the increased π−π interactions between the two naphthyl rings due to the relatively large torsion angles between the naphthyl rings and the C_2N_2B ring observed in the solid state. Notably, the quantum yields in the solid state appear to be related to the 4,5-substituents of the central ring. Low quantum yields have been observed for **1** (0.04), **4** (0.03), **5** (0.03), and **6** (0.04), featuring the same C_6H_5 groups in the 4,5-positions. In contrast, **2**, featuring 4,5-naphthyl groups, has the highest Φ_F (0.40) in the solid state, presumably due to the fact that rotation of the naphthyl rings is restricted in the solid state. Furthermore, the weak intermolecular CH···π interactions between the naphthyl rings (Figure S7) observed in the structure of **2** may restrict the rotations of the naphthyl rings, leading to the enhanced emission in the solid state compared to that in solution (aggregation-induced emission enhancement).[13] A relatively high Φ_F (0.15) is also observed for **3**, in which the strong electron-withdrawing CF_3 group may result in a small degree of the π bonding character between the 4,5-carbon atoms and the neighboring carbon atoms of the phenyl rings, thus suppressing the molecular motion in the solid state. It is noted that the luminescence properties for diazaborole derivatives in the solid state have only been reported very recently.[14] However, a fair number of boron fluorophores have been reported to be luminescent in the solid state.[15]

To have an insight on the effects of the 4,5-substituents, preliminary DFT calculations were performed on **1**−**3** at the B3LYP/6-31G(d,p) level.[16] The calculated bond parameters are well correlated to those determined by single-crystal X-ray analysis (see Tables S2 and S3). The HOMO and LUMO of **3** are shown in Figure 3, while those of **1** and **2** are shown in Figures S2 and S4. The HOMOs of **1**−**3** are located in the core ring with noticeable contributions from the B-aryl and 4,5-C-aryl rings, while the LUMOs mainly correspond to the two 4,5-aryl rings, indicating the significant contribution of the 4,5-aryl rings to the LUMOs of **1**−**3**. In addition, the LUMO is delocalized over the 4,5-aryl rings and central C_2N_2 segment. These orbital interactions may decrease the LUMO level, resulting in the red-shifted absorption and emission of these compounds. The calculated LUMO levels disclosed the order of **1** (−0.64) > **2** (−1.11) > **3** (−1.36 eV) (Table S5), indicating that the LUMOs are significantly stabilized by electron-withdrawing groups on the 4,5-phenyl rings.

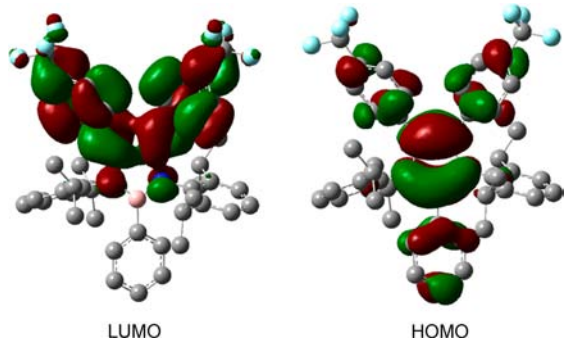

Figure 3. Calculated frontier orbitals for **3**.

In summary, the first series of pentaaryldiazaboroles have been prepared by a novel one-step strategy based on the C−C double bond formation from imidoylstannane reagents in the presence of a dibromophenylborane. The preliminary photophysical studies indicated that these diazaboroles are luminescent both in solution and in the solid state and are distinct from other diazaboroles in their electronic structures. DFT calculations disclosed significant contributions of the 4,5-C-aryl rings to the LUMOs. In addition, the present studies allowed facile access to peripheral aryl-substituted aromatic diazaboroles in one step. This strategy is promising for the one-pot synthesis of other main group N-heterocyclic systems. Further studies on the ring systems are currently in progress.

■ ASSOCIATED CONTENT

Supporting Information

Synthesis and characterization of the new compounds in this paper, DFT calculations for **3**, and CIF files for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) For selected references, see: (a) Gagnon, E.; Maris, T.; Arseneault, P.-M.; Maly, K. E.; Wuest, J. D. *Cryst. Growth Des.* **2010**, *10*, 648. (b) Tsuzuki, S.; Fujii, A. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2584. (c) Nishio, M. *CrystEngComm* **2004**, *6*, 130. (d) Medintz, I. L.; Uyeda, H. T.; Goldman, E. R.; Mattoussi, H. *Nat. Mater.* **2005**, *4*, 435. (e) Peczuh, M. W.; Hamilton, A. D. *Chem. Rev.* **2000**, *100*, 2479. (f) Tse, W. C.; Boger, D. L. *Acc. Chem. Res.* **2004**, *37*, 61. (g) Mutai, T.; Tomoda, H.; Ohkawa, T.; Yabe, Y.; Araki, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 9522. (h) Roncali, J.; Leriche, P.; Cravino, A. *Adv. Mater.* **2007**, *19*, 2045. (i) Forrest, S. R. *Nature* **2004**, *428*, 911. (j) Feng, X.; Tong, B.; Shen, J.; Shi, J.; Han, T.; Chen, L.; Zhi, J.; Lu, P.; Ma, Y.; Dong, Y. *J. Phys. Chem. B* **2010**, *114*, 16731.

(2) For reviews, see: (a) Piers, W. E.; Bosdet, M. J. D. *Can. J. Chem.* **2009**, *87*, 8. (b) Campbell, P. G.; Marwitz, A. J. V.; Liu, S.-Y. *Angew. Chem., Int. Ed.* **2012**, *51*, 6074.

(3) Merrian, J. S.; Niedenzu, K. *J. Organomet. Chem.* **1973**, *51*, 21.

(4) For reviews on diazaboroles, see: (a) Weber, L. *Coord. Chem. Rev.* **2001**, *215*, 39. (b) Weber, L. *Coord. Chem. Rev.* **2008**, *252*, 1. (d) Asay, M.; Jones, C.; Driess, M. *Chem. Rev.* **2011**, *111*, 354. (e) Jäkle, F. *Chem. Rev.* **2010**, *110*, 3985.

(5) (a) Segawa, Y.; Yamashita, M.; Nozaki, K. *Science* **2006**, *314*, 113. (b) Segawa, Y.; Suzuki, Y.; Yamashita, M.; Nozaki, K. *J. Am. Chem. Soc.* **2008**, *130*, 16069. (c) Yamashita, M.; Nozaki, K. *Pure Appl. Chem.* **2008**, *80*, 1187. (d) Yamashita, M.; Nozaki, K. *Bull. Chem. Soc. Jpn.* **2008**, *81*, 1377.

(6) For recent leading references on 1,3,2-benzodiazaboroles, see: (a) Weber, L.; Werner, V.; Fox, M. A.; Marder, T. B.; Schwedler, S.; Brockhinke, A.; Stammler, H.-G.; Neumann, B. *Dalton Trans.* **2009**, 1339. (b) Weber, L.; Werner, V.; Fox, M. A.; Marder, T. B.; Schwedler, S.; Brockhinke, A.; Stammler, H.-G.; Neumann, B. *Dalton Trans.* **2009**, 2823. (c) Weber, L.; Halama, J.; Böhling, L.; Chrostowska, A.; Dargelos, A.; Stammler, H.-G.; Neumann, B. *Eur. J. Inorg. Chem.* **2011**, 3091. (d) Chrostowska, A.; Maciejczyk, M.; Dargelos, A.; Baylère, P.; Weber, L.; Werner, V.; Eickhoff, D.; Stammler, H. G.; Neumann, B. *Organometallics* **2010**, *29*, 5192. (e) Nishida, J.; Fujiata, T.; Fujisaki, Y.; Tokito, S.; Yamashita, Y. *J. Mater. Chem.* **2011**, *21*, 16442. (f) Weber, L.; Eickhoff, D.; Werner, V.; Boehling, L.; Schwedler, S.; Chrostowska, A.; Dargelos, A.; Maciejczyk, M.; Stammler, H.-G.; Neumann, B. *Dalton Trans.* **2011**, 4434.

(7) Hinchliffe, A.; Mair, F. S.; McInnes, E. J. L.; Pritchard, R. G.; Warren, J. E. *Dalton Trans.* **2008**, 222.

(8) Jin, W.; Makioka, Y.; Kitamara, T.; Fujiwara, Y. *J. Org. Chem.* **2001**, *66*, 514. (b) Ogle, J. W.; Zhang, J.; Relbenspies, J. H.; Abboud, K. A.; Miller, S. A. *Org. Lett.* **2008**, *10*, 3677. (c) Powell, A. B.; Brown, J. R.; Vasudevan, K. V.; Cowley, A. H. *Dalton Trans.* **2009**, 2521.

(9) (a) Leuthäußer, S.; Schmidts, V. C.; Thiele, M.; Plenio, H. *Chem.-Eur. J.* **2008**, *14*, 5465. (b) Ogle, J. W.; Miller, S. A. *Chem. Commun.* **2009**, 5728.

(10) Wang, Y.; Hu, H.; Zhang, J.; Cui, C. *Angew. Chem., Int. Ed.* **2011**, *50*, 2816.

(11) Tian, D.; Cui, C. *Zhongguo Keji Lunwen Zaixian* **2010**, *5*, 458.

(12) (a) Cao, D. X.; Liu, Z. Q.; Fang, Q.; Xu, G. B.; Xue, G.; Liu, G. Q.; Yu, W. T. *J. Organomet. Chem.* **2004**, *689*, 2201. (b) Wade, C.; Broomsgrove, A.; Aldridge, S.; Gabbaï, F. *Chem. Rev.* **2010**, *110*, 3958. (c) Shirota, Y. *J. Mater. Chem.* **2005**, *15*, 75. (d) Qin, Y.; Cheng, G. L.; Achara, O.; Parab, K.; Jäkle, F. *Macromolecules* **2004**, *37*, 7123. (e) Qin, Y.; Cheng, G. L.; Sundararaman, A.; Jäkle, F. *J. Am. Chem. Soc.* **2002**, *124*, 12672.

(13) An, B.-K.; Kwon, S.-K.; Jung, S.-D.; Park, S. Y. *J. Am. Chem. Soc.* **2002**, *124*, 14410. (b) Zeng, Q.; Dong, Y.; Di, C.; Qin, A.; Hong, Y.; Ji, L.; Zhu, Z.; Jim, C. K. W.; Yu, G.; Li, Q.; Li, Z.; Liu, Y.; Qin, J.; Tang, B.-Z. *Chem. Commun.* **2007**, 70.

(14) Weber, L.; Kahlert, J.; Brockhinke, R.; Böhling, L.; Brockhinke, A.; Stammler, H.-G.; Neumann, B.; Harder, R. A.; Fox, M. A. *Chem.—Eur. J.* **2012**, *18*, 8347.

(15) (a) Shimizu, M.; Takeda, Y.; Higashi, M.; Hiyama, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 3653. (b) Zhao, C.-H.; Zhao, Y.-H.; Pan, H.; Fu, G.-L. *Chem. Commun.* **2011**, *47*, 5518. (c) Fu, G.−L.; Zhang, H.-Y.; Yan, Y.-Q.; Zhao, C.-H. *J. Org. Chem.* **2012**, *77*, 1983. (d) Fu, G.-L.; Pan, H.; Zhao, Y.-H.; Zhao, C.-H. *Org. Biomol. Chem.* **2011**, *9*, 8141. (e) Ozdemir, T.; Atilgan, S.; Kutuk, I. L.; Yildirim, T.; Tulek, A.; Bayindir, M.; Akkaya, E. U. *Org. Lett.* **2009**, *11*, 2105. (f) Zhang, D.; Wen, Y.; Xiao, Y.; Yu, G.; Liu, Y.; Qian, X. *Chem. Commun.* **2008**, 4777. (g) Zhang, G.; Lu, J.; Sabat, M.; Fraser, C. L. *J. Am. Chem. Soc.* **2010**, *132*, 2160. (h) Wakamiya, A.; Mori, K.; Yamaguchi, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 4273.

(16) See Supporting Information for the calculation details.