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Cascade Dehydrogenative Hydroboration for the Synthesis of Azaborabenzofulvenes

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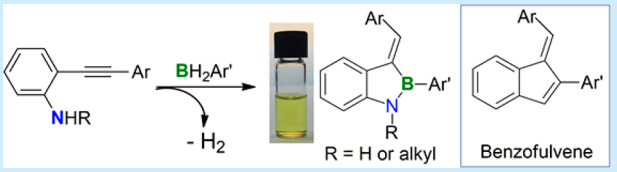
Supporting Information

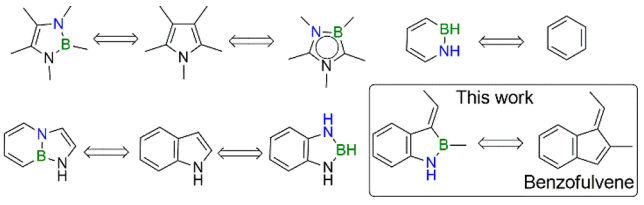
ABSTRACT: Tandem dehydrogenative hydroboration has been established to be highly effective in the synthesis of BN isosteres of benzofulvene and derivatives. The scope of this synthetic method is applicable to a variety of substrates. Spectroscopic and computational studies indicate that the new azaborabenzofulvenes have similar electronic properties as their carbonaceous analogues.



Molecules or fragments with the same number of atoms and the same number and same arrangement of electrons are known as isosteres, which play important roles in drug design, medicinal chemistry, and materials science. The replacement of a CC unit with a BN unit in aromatic molecules (BN arenes), for example, has been demonstrated to be a highly effective approach in creating new molecules or materials with distinctively different photophysical/chemical properties from their all carbon analogues.[1] One class of BN arenes is azaborines and derivatives, pioneered by Dewar and co-workers.[2] Rapid advances in azaborine/BN arene chemistry and applications have been achieved in the past decade.[3−10] BN arene based materials have often been found to perform better in optoelectronic devices, compared to their carbon analogues.[10a] Liu et al. demonstrated that isosteric substitution of a C=C unit with a BN unit is a promising strategy for the development of new pharmaceutical reagents.[4]

Another class of conjugated BN heterocycles that also attracts much interest is azaboroles and derivatives, in which a CC unit in a five-membered ring is replaced by a BN unit.[11] Examples of azaboroles include 1,3,2-diazaborole, 1,4,2-diazaborole, 1,2,4,3-triazaborole, etc. (Scheme 1),[12−15] some of which have been demonstrated to serve as a cyclopentadienyl-like ligands for transition metals.[11] In addition, BN isosteres of indacenes and pentalene have also been successfully generated.[16,17] CC replacement by BN in these systems have also been found to have a great impact on electronic properties.

Scheme 1. Selected Examples of BN-Containing Heterocycles along with Their Carbonaceous Counterpart



Benzofulvene and derivatives are important scaffolds/substrates for pharmaceutical reagents and materials.[18,19] The typical preparation of benzofulvenes mainly involves cyclization of alkenes/alkynes mediated by transition-metal catalysts, Lewis acid, and organotin compounds,[20] which often generate mixtures of both *E* and *Z* isomers.[20d,f] The synthesis of BN isosteres of benzofulvenes has not been explored. During our recent study of internal donor-assisted hydroboration of alkynes, we discovered that dehydrogenative hydroboration is a highly effective method for accessing a class of previously unknown azaborabenzofulvenes shown in Scheme 1. The details are presented herein.

Dehydrogenative coupling of amine−borane with the aid of a catalyst has been extensively investigated previously for generating hydrogen storage materials and hybrid inorganic−organic polymers.[21] Catalyst-free dehydrogenative coupling of amine−borane is much less explored as it is generally considered to be a kinetically unfavorable process at room temperature.[21] Recently, Bertrand and we reported facile, catalyst-free dehydrogenation reactions between primary arylamines and 9-BBN at room temperature.[22] Such transformations could serve as a facile approach for constructing a BN covalent bond. We envisioned that by replacing 9-BBN with monosubstituted boranes BH_2Ar such as $BH_2(Mes)$, it may be possible to generate a B−N and a B−C bond in a one-pot manner by taking advantage of sequential dehydrogenation and hydroboration of alkynyl arylamines.

Based on this consideration, we first examined the reaction 2-(phenylethynyl)aniline with $BH_2(Mes)$ by NMR spectroscopy. As shown in Figure S2, an amine−borane adduct formed immediately upon mixing the two reactants (~0.1 mmol, 1:1, in 1.0 mL of C_6D_6) at ambient temperature that has a characteristic four-coordinate boron chemical shift at ~ −4 ppm in the ^{11}B NMR spectrum. The adduct was gradually consumed as H_2 was produced, as shown by ^1H NMR spectroscopy. A new ^{11}B chemical shift at ~45 ppm appeared,

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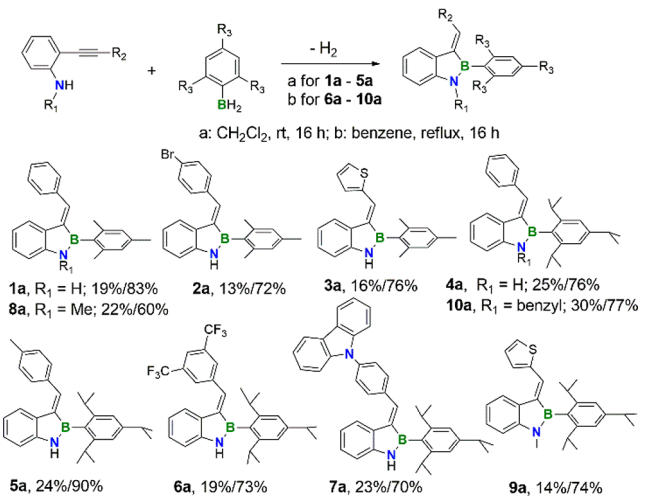
which is characteristic of a B═N unit.[24] The reaction reached completion with a relatively clean formation of the product **1a** (~80% yield) after 20 h (Figure S1). The same reaction was also performed on a synthetic scale using CH_2Cl_2 as the solvent at ambient temperature. Chromatography and recrystallization under air afforded **1a** as a yellow solid in 19% yield. The low isolated yield of **1a** was caused by its poor stability on chromatography. NMR spectroscopic analyses established that **1a** is (*Z*)-3-benzylidene-2-mesityl-2,3-dihydro-1*H*-benzo[*d*]-[1,2]-azaborole, an analogue of benzofulvene, as shown in Scheme 2. Changing the substrate to *p*-Br-phenyl- or 1-thienyl-

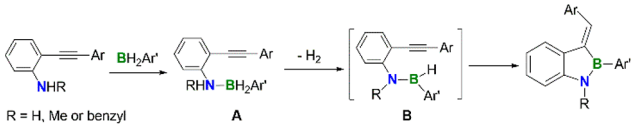
Scheme 2. Dehydrogenative Hydroboration of Alkynyl Arylamines Showing Isolated/NMR Yields



substituted alkyne and using the same solvent and reaction conditions, compounds **2a** and **3a** were isolated in 13% and 16% yields, respectively. Again, the slow decomposition of the BN-benzofulvenes on the silica gel column led to the low isolated yields of these compounds. To enhance the stability of the product, the Mes group in borane was replaced with a bulkier 2,4,6-triisopropylphenyl (Tip) group, which did improve the isolated yield of **4a** from the reaction of 2-(phenylethynyl)aniline with BH_2(Tip) to 25%. Nonetheless, slow decomposition of **4a** on column was still observed. Using BH_2(Tip), compound **5a** was also prepared and isolated in 24% yield. Compounds **6a** and **7a** that contain an electron-donating carbazolyl and the electron-withdrawing CF_3 group, respectively, were also synthesized using the same method, except that benzene was used as the solvent and heating was necessary to improve the solubility of the substrates for these two molecules. NMR data showed that alkyl analogues (R_2 = *n*-Bu, Mes, or Tip-borane) could also be obtained; however, efforts to purify/isolate the product failed (see Figure S45a–d). Compounds **1a**–**7a** were fully characterized by NMR and HRMS analyses. These examples show the applicability of the dehydrogenative hydroboration to different substrates.

A key mechanistic question concerning the BN-benzofulvene formation is the sequence of dehydrogenation and hydroboration after the formation of the adduct **A** (Scheme 3). For compound **1a**, no intermediate between **A** and the final product was observed in the NMR tracking experiments. Hydroboration of diarylalkynes normally requires elevated temperatures, while most of the transformations studied here can readily proceed at room temperature. Furthermore, previously we have shown

Scheme 3. Proposed Mechanism for the Dehydrogenative Hydroboration of Alkynyl Arylamines



that mixing primary anilines with 9-BBN gave a dehydrogenated product exclusively,[22b] which is an analogue of **B** shown in Scheme 3. Thus, it is possible that in the formation of BN-benzofulvenes dehydrogenation occurs first. On the other hand, the internal donor group could act as a directing group to promote hydroboration under mild conditions.[23] To probe the possibility of amino-directed hydroboration, the reactions of BH_2Ar with secondary 2-alkynylanilines for **8a**–**10a** were examined. If donor-directed hydroboration occurs first, the reaction of *N*-methyl-2-(phenylethynyl)aniline with BH_2(Mes) for **8a** should have a comparable rate to that of 2-(phenylethynyl)aniline for **1a**. However, NMR tracking for **8a** showed only the formation of the adduct **A** after 3 h at ambient temperature with a small amount of H_2 formation, and no hydroboration was observed (Figures S3 and S4). In contrast, the reaction for **1a** under the same conditions produced the dehydrogenative hydroboration product **1a** in ~50% yield after 3 h and reached completion after 20 h. For the synthesis of **8a**, the reaction requires several days to complete at ambient temperature. A similarly slow reaction was also observed for the second amine substrates used for **9a** and **10a** at rt. Upon heating the reaction mixture involving secondary amines to 80 °C, the dehydrogenative hydroboration proceeded smoothly and generated the desired product within a few hours with isolated/NMR yields comparable to those of primary alkynylarylamines (see Scheme 2). On the basis of these observations, a plausible reaction mechanism is proposed and shown in Scheme 3. In the dehydrogenative hydroboration reaction, following adduct **A** formation, dehydrogenation occurs first, forming the intermediate **B**, which presumably undergoes a rapid *cis*-hydroboration, forming the final product.

The crystal structures of **2a**, **8a**, and **10a** were examined by single-crystal X-ray diffraction analyses with those of **8a** and **10a** shown in Figure 1 (That of **2a** is provided in the Supporting Information). All three molecules have a benzene-fused B,N heterocycle with an *exo* C═C bond that has a typical C═C bond length, confirming their isosteric relationship with

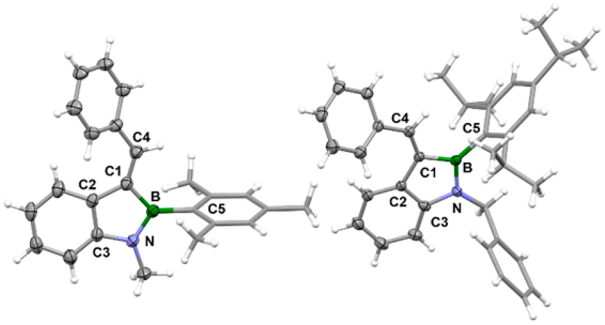


Figure 1. Crystal structures of **8a** (left) and **10a** (right). Important bond lengths (Å), **8a**/**10a**: B–N 1.421(4)/1.418(3), B–C1 1.557(4)/1.564(3), B–C5 1.568(4)/1.573(3), C1–C2 1.476(4) /1.475(3), C2–C3 1.416(4)/1.412(3), N–C3 1.407(3)/1.422(3), C1–C4 1.351(4)/1.347(3).

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benzofulvene. The *Z* configuration of the *exo* alkene unit is consistent with *cis*-hydroboration. In all three structures, the azaborole ring is planar. The B−N bond lengths in all three structures are similar (1.40−1.42 Å) and consistent with the previously reported values of B−N double bonds.[4b,24] In the crystal lattice of **2a**, the molecules have an extended 1D structure facilitated by intermolecular NH···π, π···π stacking, and Br···π interactions. Like benzofulvenes, which are known to have a yellow color,[20e,f] all BN-benzofulvenes reported here have a yellow or light yellow color in solution and the solid state as shown in Figure 2.

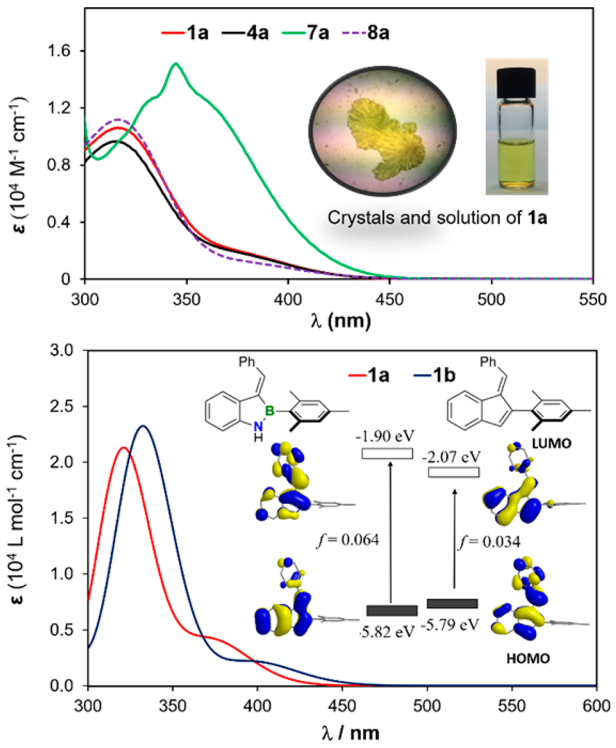

Figure 2. (Top) Absorption spectra of **1a**, **4a**, **7a**, and **8a** in CH_2Cl_2 (10^{-5} M) with photographs showing the colors of **1a**. (Bottom) TD-DFT[B3LYP/6-31G(d)]-calculated UV−vis absorption spectra and HOMO and LUMO energies/diagrams of **1a** and its carbon analogue **1b**.

UV−vis spectra are shown in Figure 2. Compounds **1a**, **4a**, and **8a** have very similar absorption profiles with a major absorption band at 320 nm and a weak band at ∼390 nm. DFT and TD-DFT studies indicate that the first absorption band of these molecules is mainly from π−π* transitions of the azaborabenzofulvene core and the styryl fragment. Adding a carbazolyl to the pendant phenyl group on alkene (**7a**) leads to the appearance of a strong absorption band at λ_{max} = ∼350 nm, which can be attributed to the carbazolyl domination in the HOMO of **7a**, and a great charge transfer character in the $S_0 \rightarrow S_1$ vertical excitation (HOMO to LUMO), with a very high oscillator strength (0.350), based on TD-DFT data (Table S7). To compare the electronic properties of **1a** with its carbonaceous analogue **1b**, DFT and TD-DFT calculations were also performed for **1b**. The HOMO and LUMO orbitals of **1a** and **1b** are depicted in Figure 2. BN substitution results in a greater HOMO−LUMO gap by ∼0.2 eV mostly due to destabilization of the LUMO. TD-DFT-calculated UV−vis spectra for **1a** and **1b** are similar except that the spectrum of **1a** is blue-shifted relative to that of **1b**. These data support the notion that **1a** and **1b** share similar electronic properties. Nonetheless, DFT data show that the H atom bound to the N atom in **1a** possesses a positive charge character (Figure S10), similar to that in 1,2-dihydro-1,2-azaborine,[4c] and the latter was shown to be important for interactions with proteins via hydrogen bonds.[4g] H−D exchange of **1a** in CD_3OD was examined, and the rate constant k_{HD} was determined to be $1.7(1) \times 10^{-6}$ M^{-1} s^{-1} (Figure S5). The H−D exchange rate of **1a** was about two times faster than that of 1,2-dihydro-1,2-azaborine.[4c]

Photolysis of benzene vapor with a mercury resonance lamp is known to give fulvene as the major product, and fulvene to benzene photoisomerization was also reported previously.[25] Bettinger and Liu showed that 1,2-dihydro-1,2-azaborine displays a distinct photochemical reactivity.[26] These motivated us to examine the possible photo-conversion of BN-benzofulvene **6a** to benzoazaborine.[27] However, only *E*/*Z* isomerization was observed after 30 min irradiation at 360 nm with a 1:2 *E*/*Z* ratio at the photostationary state (Figure S6). This observation is consistent with the photoreactivity of the benzofulvene system reported previously.[20f]

In summary, a facile dehydrogenative hydroboration method has been established and demonstrated for the synthesis of various BN-benzofulvenes. The scope of this reaction is general for a variety of substrates. Computational studies indicate that the BN-benzofulvenes show electronic properties similar to those of their all-carbon analogues. The BN unit in BN-benzofulvenes widens the HOMO−LUMO gap and introduces a polar N−H bond, which may be useful for applications in functional materials and pharmaceutical reagents.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b00363.

Experimental details, synthesis, characterization data, computational results and single-crystal data, and NMR spectra (PDF)

Accession Codes

CCDC 1821087−1821089 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Liu, Z.; Marder, T. B. *Angew. Chem., Int. Ed.* **2008**, *47*, 242. (b) Bosdet, M. J. D.; Piers, W. E. *Can. J. Chem.* **2009**, *87*, 8. (c) Campbell, P. G.; Marwitz, A. J. V.; Liu, S.-Y. *Angew. Chem., Int. Ed.* **2012**, *51*, 6074. (d) Wang, X.-Y.; Wang, J.-Y.; Pei, J. *Chem. - Eur. J.* **2015**, *21*, 3528. (e) Helten, H. *Chem. - Eur. J.* **2016**, *22*, 12972. (f) Bélanger-Chabot, G.; Braunschweig, H.; Roy, D. K. *Eur. J. Inorg. Chem.* **2017**, *2017*, 4353. (g) Giustra, Z. X.; Liu, S.-Y. *J. Am. Chem. Soc.* **2018**, *140*, 1184.

(2) Dewar, M. J. S.; Kubba, V. P.; Pettit, R. *J. Chem. Soc.* **1958**, 3073.

(3) Ashe, A. J.; Fang, X. *Org. Lett.* **2000**, *2*, 2089.

(4) (a) Marwitz, A. J. V.; Abbey, E. R.; Jenkins, J. T.; Zakharov, L. N.; Liu, S.-Y. *Org. Lett.* **2007**, *9*, 4905. (b) Abbey, E. R.; Zakharov, L. N.; Liu, S.-Y. *J. Am. Chem. Soc.* **2008**, *130*, 7250. (c) Liu, L.; Marwitz, A. J. V.; Matthews, B. W.; Liu, S.-Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 6817. (d) Marwitz, A. J. V.; Matus, M. H.; Zakharov, L. N.; Dixon, D. A.; Liu, S.-Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 973. (e) Knack, D. H.; Marshall, J. L.; Harlow, G. P.; Dudzik, A.; Szaleniec, M. I.; Liu, S.-Y.; Heider, J. *Angew. Chem., Int. Ed.* **2013**, *52*, 2599. (f) Zhao, P.; Nettleton, D. O.; Karki, R. G.; Zécri, F. J.; Liu, S.-Y. *ChemMedChem* **2017**, *12*, 358. (g) Lee, H.; Fischer, M.; Shoichet, B. K.; Liu, S.-Y. *J. Am. Chem. Soc.* **2016**, *138*, 12021. (h) Rombouts, F. J. R.; Tovar, F.; Austin, N.; Tresadern, G.; Trabanco, A. A. *J. Med. Chem.* **2015**, *58*, 9287. (i) Vlasceanu, A.; Jessing, M.; Kilburn, J. P. *Bioorg. Med. Chem.* **2015**, *23*, 4453.

(5) (a) Emslie, D. J. H.; Piers, W. E. P.; Parvez, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 1252. (b) Neue, B.; Araneda, J. F.; Piers, W. E.; Parvez, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 9966.

(6) (a) Braunschweig, H.; Geetharani, K.; Jimenez-Halla, J. O. C.; Schäfer, M. *Angew. Chem., Int. Ed.* **2014**, *53*, 3500. (b) Braunschweig, H.; Celik, M. A.; Hupp, F.; Krummenacher, I.; Mailänder, L. *Angew. Chem., Int. Ed.* **2015**, *54*, 6347.

(7) (a) Fingerle, M.; Maichle-Mössmer, C.; Schundelmeier, S.; Speiser, B.; Bettinger, H. F. *Org. Lett.* **2017**, *19*, 4428. (b) Müller, M.; Maichle-Mössmer, C.; Bettinger, H. F. *Angew. Chem., Int. Ed.* **2014**, *53*, 9380. (c) Biswas, S.; Maichle-Mössmer, C.; Bettinger, H. F. *Chem. Commun.* **2012**, *48*, 4564.

(8) (a) Wisniewski, S. R.; Guenther, C. L.; Andreea Argintaru, O.; Molander, G. A. *J. Org. Chem.* **2014**, *79*, 365. (b) Jouffroy, M.; Davies, G. H. M.; Molander, G. A. *Org. Lett.* **2016**, *18*, 1606. (c) Liu, X.; Wu, P.; Li, J.; Cui, C. *J. Org. Chem.* **2015**, *80*, 3737.

(9) Taniguchi, T.; Yamaguchi, S. *Organometallics* **2010**, *29*, 5732.

(10) (a) Hatakeyama, T.; Hashimoto, S.; Seki, S.; Nakamura, M. *J. Am. Chem. Soc.* **2011**, *133*, 18614. (b) Wang, X.-Y.; Lin, H.-R.; Lei, T.; Yang, D.-C.; Zhuang, F.-D.; Wang, J.-Y.; Yuan, S.-C.; Pei, J. *Angew. Chem., Int. Ed.* **2013**, *52*, 3117. (c) Zhuang, F.-D.; Han, J.-M.; Tang, S.; Yang, J.-H.; Chen, Q.-R.; Wang, J.-Y.; Pei, J. *Organometallics* **2017**, *36*, 2479. (d) Zhang, W.; Zhang, F.; Tang, R.; Fu, Y.; Wang, X.; Zhuang, X.; He, G.; Feng, X. *Org. Lett.* **2016**, *18*, 3618.

(11) Su, B.; Kinjo, R. *Synthesis* **2017**, *49*, 2985.

(12) (a) Weber, L.; Böhling, L. *Coord. Chem. Rev.* **2015**, *284*, 236. (b) Weber, L.; Eickhoff, D.; Marder, T. B.; Fox, M. A.; Low, P. J.; Dwyer, A. D.; Tozer, D. J.; Schwedler, S.; Brockhinke, A.; Stammler, H. G.; Neumann, B. *Chem. - Eur. J.* **2012**, *18*, 1369.

(13) Su, B.; Li, Y.; Ganguly, R.; Lim, J.; Kinjo, R. *J. Am. Chem. Soc.* **2015**, *137*, 11274.

(14) (a) Su, B.; Li, Y.; Ganguly, R.; Lim, J.; Kinjo, R. *J. Am. Chem. Soc.* **2015**, *137*, 11274. (b) Loh, Y. K.; Chong, C. C.; Ganguly, R.; Li, Y.; Vidovic, D.; Kinjo, R. *Chem. Commun.* **2014**, *50*, 8561.

(15) (a) Abbey, E. R.; Zakharov, L. N.; Liu, S. Y. *J. Am. Chem. Soc.* **2010**, *132*, 16340. (b) Abbey, E. R.; Zakharov, L. N.; Liu, S. Y. *J. Am. Chem. Soc.* **2011**, *133*, 11508.

(16) Morgan, M. M.; Patrick, E. A.; Rautiainen, J. M.; Tuononen, H. M.; Piers, W. E.; Spasyuk, D. M. *Organometallics* **2017**, *36*, 2541.

(17) (a) Wang, X. Y.; Narita, A.; Feng, X.; Müllen, K. *J. Am. Chem. Soc.* **2015**, *137*, 7668. (b) Ma, C.; Zhang, J.; Li, J.; Cui, C. *Chem. Commun.* **2015**, *51*, 5732.

(18) (a) Felts, A. S.; Siegel, B. S.; Young, S. M.; Moth, C. W.; Lybrand, T. P.; Dannenberg, A. J.; Marnett, L. J.; Subbaramaiah, K. *J. Med. Chem.* **2008**, *51*, 4911. (b) Walters, M. J.; Blobaum, A. L.; Kingsley, P. J.; Felts, A. S.; Sulikowski, G. A.; Marnett, L. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 3271. (c) Alcalde, E.; Mesquida, N.; Frigola, J.; López-Pérez, S.; Mercè, R. *Org. Biomol. Chem.* **2008**, *6*, 3795.

(19) (a) Barberá, J.; Rakitin, O. A.; Ros, M. B.; Torroba, T. *Angew. Chem., Int. Ed.* **1998**, *37*, 296. (b) Kosaka, Y.; Kawauchi, S.; Goseki, R.; Ishizone, T. *Macromolecules* **2015**, *48*, 4421.

(20) (a) Cordier, P.; Aubert, C.; Malacria, M.; Lacôte, E.; Gandon, V. *Angew. Chem., Int. Ed.* **2009**, *48*, 8757. (b) Hashmi, A. S. K.; Braun, I.; Nösel, P.; Schädlich, J.; Wieteck, M.; Rudolph, M.; Rominger, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 4456. (c) Bryan, C. S.; Lautens, M. *Org. Lett.* **2010**, *12*, 2754. (d) Martinelli, C.; Cardone, A.; Pinto, V.; Mastropasqua Talamo, M.; D'arienzo, M. L.; Mesto, E.; Schingaro, E.; Scordari, F.; Naso, F.; Musio, R.; Farinola, G. M. *Org. Lett.* **2014**, *16*, 3424. (e) Kovalenko, S. V.; Peabody, S.; Manoharan, M.; Clark, R. J.; Alabugin, I. V. *Org. Lett.* **2004**, *6*, 2457. (f) Mohamed, R. K.; Mondal, S.; Jorner, K.; Delgado, T. F.; Lobodin, V. V.; Ottosson, H.; Alabugin, I. V. *J. Am. Chem. Soc.* **2015**, *137*, 15441.

(21) (a) Staubitz, A.; Robertson, A. P. M.; Manners, I. *Chem. Rev.* **2010**, *110*, 4079. (b) Alcaraz, G.; Sabo-Etienne, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 7170. (c) Lorenz, T.; Lik, A.; Plamper, F. A.; Helten, H. *Angew. Chem., Int. Ed.* **2016**, *55*, 7236. (d) Helten, H.; Robertson, A. P. M.; Staubitz, A.; Vance, J. R.; Haddow, M. F.; Manners, I. *Chem. - Eur. J.* **2012**, *18*, 4665.

(22) (a) Romero, E. A.; Peltier, J. L.; Jazzar, R.; Bertrand, G. *Chem. Commun.* **2016**, *52*, 10563. (b) Yuan, K.; Wang, S. *Org. Lett.* **2017**, *19*, 1462.

(23) (a) Yuan, K.; Suzuki, N.; Mellerup, S. K.; Wang, X.; Yamaguchi, S.; Wang, S. *Org. Lett.* **2016**, *18*, 720. (b) Nagai, A.; Murakami, T.; Nagata, Y.; Kokado, K.; Chujo, Y. *Macromolecules* **2009**, *42*, 7217.

(24) Rao, Y. L.; Amarne, H.; Chen, L. D.; Brown, M. L.; Mosey, N. J.; Wang, S. *J. Am. Chem. Soc.* **2013**, *135*, 3407.

(25) (a) Kaplan, L.; Wilzbach, K. E. *J. Am. Chem. Soc.* **1967**, *89*, 1030. (b) Ward, H. R.; Wishnok, J. S. *J. Am. Chem. Soc.* **1968**, *90*, 5353.

(26) Brough, S. A.; Lamm, A. N.; Liu, S.-Y.; Bettinger, H. F. *Angew. Chem., Int. Ed.* **2012**, *51*, 10880.

(27) Scott, L. T.; Schultz, T. H.; Hashemi, M. M.; Wallace, M. B. *J. Am. Chem. Soc.* **1991**, *113*, 9692.

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