B,N Heterocycles

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BN-Dibenzo[*a*,*o*]picenes: Analogues of an Unknown Polycyclic Aromatic Hydrocarbon**

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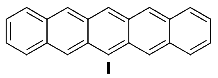
Dedicated to Professor Ernst-Ulrich Würthwein on the occasion of his 65th birthday

Polycyclic aromatic hydrocarbons (PAHs), and particularly the linear acenes, have garnered considerable interest owing to their potential as organic semiconducting materials.[1] These fused aromatic compounds have been used to fabricate electronic transistor[2] and light-emitting diode[3] devices, while substituted derivatives of the pentacene framework (**I**) have been explored as the acceptor material in bulk heterojunction solar cells.[4] These studies not only demonstrated that these molecules perform efficiently, but that their electronic properties can be tuned by the position of the substituent groups. It has also been shown that the pentacene isomer picene (**II**) displays superconductive properties when doped with alkali metals.[5]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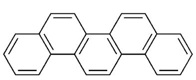
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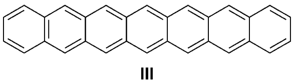
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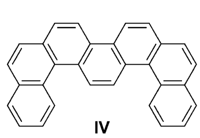
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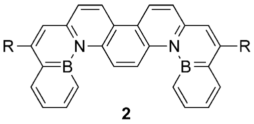

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The favorable set of properties of the acenes is motivation for the development of methods for more efficient, scalable syntheses and the preparation of acenes with more extended conjugation.[6] However, the accessibility of higher acenes is limited owing to their reduced light and oxygen stability and their low solubility.[7] For example, unsubstituted heptacene **III** persists only in a PMMA matrix[8] at ambient temperature and requires stabilization by bulky protecting groups.[9] This requirement can restrict the performance of higher acenes in electronic devices.

Another approach to modifying the properties of acenes is to incorporate main group elements into the acene framework. This strategy can both modify[10] and enhance[11] their photophysical properties, while leading to increased stability and ease of synthesis. Particularly, the transposition of carbon–carbon units for the isoelectonic boron–nitrogen elements in the all-carbon frameworks is thought to introduce new, appealing properties without disturbing the electronic structure significantly.[12] While more polarized, the BN unit in these compounds is stabilized by aromaticity and the planarity enforced by the unsaturated ring system.[13] For example, in comparison to pyrene, the analogue where the internal C$-$C unit is replaced by B$-$N exhibits red-shifted green emission while retaining moisture and air stability.[14] Similar properties are exhibited by BN phenanthrenes.[15] The methodologies we developed for preparing these smaller BN aromatics are adaptable to the preparation of higher non-linear acenes and it is anticipated that incorporation of BN moieties into these structures should impart higher stability while maintaining favorable optical and electronic properties.

Accordingly we report herein the synthesis and characterization of several derivatives of the BN containing dibenzo[*a*,*o*]picene **2** (BN-DBP). The parent hydrocarbon **IV** is structural isomer of heptacene that has not been reported, although intriguing structural and electronic properties for this PAH have been predicted.[16] Along with the parent compound (**2b**, R = H), we synthesized a number of substituted derivatives (R = Ar) and investigated their photophysical properties. These compounds are highly stable as solids undergoing only slow decomposition upon exposure to oxygen; they are completely tolerant of water. The structural, optical and redox properties of the compounds were fully probed using experimental and computational techniques.

All BN-DBP derivatives **2** were prepared in moderate to good yields (Scheme 1). The 3,8-dibromo-4,7-phenanthroline starting material was prepared in excellent overall yield using a modification of a reported procedure,[17] and used to generate the 3,8-diethynyl-4,7-phenanthroline precursors **1** by Sonogashira coupling.[18] Although these coupling reactions proceed with essentially full conversions, the purification of the resulting bis(acetylide) compounds **1** was made difficult by their generally poor solubility. The derivative **1c** was characterized by X-ray crystallography and exhibited extensive π-stacking interactions in the crystal lattice (see the Supporting Information for details). While all dialkynes **1** were weakly fluorescent, their emissive properties were not probed in detail. Treatment of the dialkynes with a slight excess of the known boracycle[19] (Scheme 1) presum-

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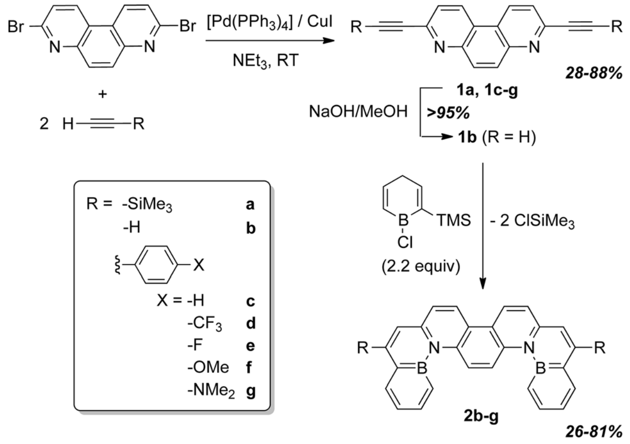


Scheme 1. Synthesis of precursors 3,8-diethynyl-4,7-phenanthrolines **1a**–**g** and BN-DBP compounds **2b**–**g**. For an X-ray structural analysis of **1c**, see the Supporting Information, Figure S14.

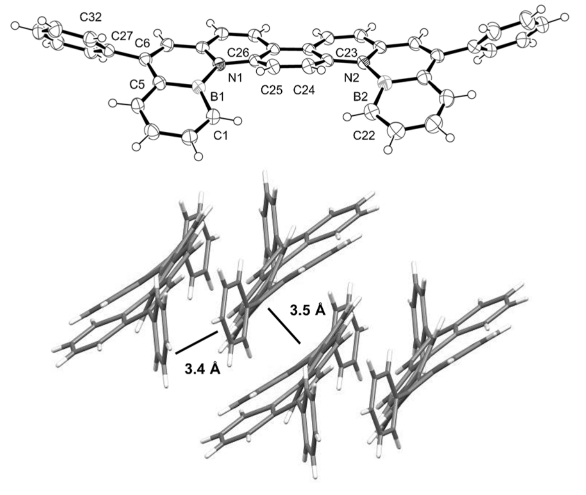


Figure 2. Top: ORTEP diagrams (ellipsoids set at 50% probability) of the molecular structure of **2c**. Selected bond lengths [Å] and angles [°]: N1–B1 1.4862(18), N2–B2 1.4890(18), B1–C1 1.5194(19), B2–C22 1.519(2), N1–C26 1.4138(15), N2–C23 1.4180(16); C26-N1-B1 123.35(10), C23-N2-B2 123.93(11), C26-N1-B1-C1 15.96(19), B1-N1-C26-C25 26.16(17), C5-C6-C27-C32 51.95(17). Bottom: Packing of **2c**.

ably results in pyridine–borabenzene derivatives by elimination of Me_3SiCl; these intermediates were not characterized but rather allowed to undergo cycloisomerization of the pendant alkyne[15] over the course of 2 days at room temperature. Orange to dark red solids were isolated by filtration; several washes of the filtrate with hexanes and dichloromethane gave the pure BN-DBPs **2c**–**g** in good yields (46–81%; Supporting Information). The only exception was the parent compound **2b**, which was obtained only in 26% yield. We suspect that side reactions involving Diels–Alder reactions between the terminal alkyne and an isomer of the boracycle in which the diene is conjugated[20] or a borabenzene intermediate[21] are competitive with cycloisomerization. Unfortunately, treatment of the TMS substituted dialkyne **1a** with boracycle gave incomplete conversion into **2a** and so the yield of unsubstituted BN-DBP **2b** could not be improved by desilation of **2a**. In the case of OMe substituted **2f**, a second unidentified unsymmetrical product is observed in small amounts (ca. 5%; Supporting Information, Figure S12b–d).

Single crystals of compounds **2b**, **2c**, **2d**, and **2f** were obtained and analyzed by X-ray diffraction. Figure 1 and 2 depict the molecular structures and packing interactions for derivatives **2b** and **2c**, respectively; similar depictions of the structures of **2d** and **2f** are given in the Supporting Information. The seven annulated rings of the core framework are non-planar, with the flanking BN rings twisted out of the plane roughly defined by the central 4,7-phenanthroline unit. In all four structures, these BN "wings" are oriented on the same side of the central rings plane, lending the frameworks C_s symmetry. In **2b**, the C1-B1-N1-C26 dihedral angle is 33.4°, while in **2c** this twist is slightly smaller (26.2°). The B–N bond distances of about 1.48–1.49 Å are similar to those found in the parent B,N phenanthrenes,[15] and the C–C distances are indicative of π delocalization throughout the 7 rings. The curvature in the molecular structures does not preclude π-stacking motifs in the crystal lattice, as also shown in Figure 1 and Figure 2. Interactions between the phenanthroline cores on different molecules are apparent, and the boracyclic parts of two molecules stack in a ladder-like fashion with a distance of about 3.1 Å.

Conjugation throughout the molecular framework is also demonstrated by the substantial aromaticity found for each ring by NICS computations (Table 1, B3LYP/6-311+G(d,p))[22] on the parent **2b** and the unknown all-carbon analogue **IV**. NICS(1), (0), and −(1) values indicate each unique ring a–d exhibits strong aromaticity, with the central ring d showing the highest and the nitrogen containing ring the lowest. Interestingly, the NICS(1) values for rings c and d

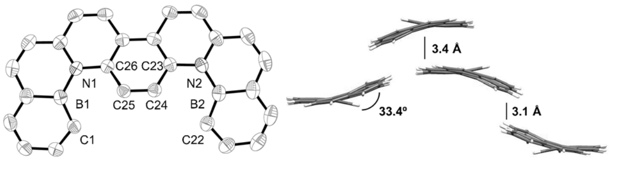
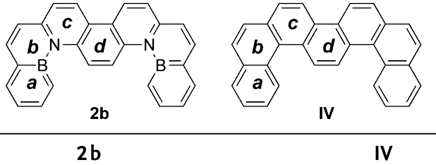


Figure 1. Left: ORTEP diagrams (ellipsoids set at 50% probability) of the molecular structure of **2b**. Selected bond lengths [Å] and angles [°]: N1–B1 1.488(2), N2–B2 1.492(2), B1–C1 1.517(2), B2–C22 1.515(2), N1–C26 1.4167(17), N2–C23 1.4147(17); C26-N1-B1 123.24(11), C23-N2-B2 123.15(11), C26-N1-B1-C1 13.0(2), B1-N1-C26-C25 23.46(19). Right: π-stacking interactions in **2b**.

Table 1: NICS(1/0/−1) values for **2b** and the all-carbon analogue **IV**.



Ring	2b	IV
a	−7.6/−6.1/−9.3	−9.6/−8.6/−11.6
b	−8.7/−7.4/−9.6	−8.2/−6.0/−9.0
c	−5.5/−2.3/−4.9	−9.6/−6.8/−8.9
d	−11.8/−8.5/−7.7	−10.6/−6.4/−6.9

are slightly higher than those determined for NICS(−1); the situation is reversed for rings a and b. This is presumably due to the static dihelical structure preserved in these computations. The NICS values for all-carbon species **IV** shows the same trends, indicating again that the BN analogues are suitable stand-ins for less accessible PAH derivatives.

In solution, the C_s symmetry of parent BN-DBP **2b** is apparently maintained, although fluxional interchange with a C_2 symmetric structure in which the BN wings are on opposite sides of the central phenanthroline plane cannot be ruled out (Supporting Information, Figure S25). Resonances for the protons appear between $\delta = 9.22$ and 7.10 ppm, with the lowest field resonance at 9.22 from the protons of the central ring d. They are significantly deshielded ($\Delta\delta = 1.04$ ppm) relative to the shift found for the dialkyne starting material **1b**, as they are now influenced by the flanking aromatic boracycles. In the ^{11}B NMR spectrum, a broad resonance at about $\delta = 30.4$ ppm, is comparable to the shift found for the BN-phenanthrenes.[15] Compounds **2c**–**g** display similar NMR spectroscopic characteristics.

Under an argon atmosphere, compounds **2b**–**f** are indefinitely stable in the solid state and exhibit good photostability under irradiation with 320 nm light. The BN-DBPs could be heated up to 220 °C in a tube for 10 h without decomposition. The compounds are poorly soluble in aromatic hydrocarbons, CH_2Cl_2, and THF, but dissolve sufficiently in bromobenzene. The BN-DBPs are stable in solution for weeks, also in the presence of water. Exposure to oxygen leads to slow decomposition (hours); this process is faster in solution than in the solid state. The nature of the decomposition products is not known, but Diels–Alder type addition of O_2 to the borabenzene rings is a likely reaction path.[21]

All compounds **2b**–**f** are yellow to orange in CH_2Cl_2 and display strong green emission in solution. UV/Vis and emission spectra of compounds **2** can be seen in the Supporting Information (Figures S19,20), while photophysical data are summarized in Table 2. The strongest absorptions are usually found at about 490, 470, and 300–310 nm. An exception is the *para*-methoxy-substituted compound **2f**, which shows a more intense absorption (in comparison to the band at 300 nm) at 382 nm. According to TD-DFT calculations, this absorption has contributions from the p-orbital on the methoxy oxygen of **2f** (Supporting Information). The BN-DBPs show emission maxima at about 515 and 540 nm with medium to high quantum yields. In comparison to the parent BN-phenanthrenes[15] the emission maxima are significantly red-shifted (by about 65 nm). The Stokes shifts of 20–23 nm are larger than those observed in the phenanthrenes (4 nm).[15]

Table 2: Photophysical data for BN-DBPs **2**.

BN-DBP	R	λ_{abs} [nm][a]	λ_{em} [nm][b]	Φ_f[c]
2b	H	492, 466, 296	542, 514	0.41
2c	Ph	493, 469, 305	544, 515	0.62
2d	4-$CF_3C_6H_4$	495, 471, 304	545, 517	0.38
2e	4-FC_6H_4	494, 469, 305	544, 517	0.44
2f	4-$MeOC_6H_4$	492, 469, 382	541, 514	0.90
2g	4-$Me_2NC_6H_4$	493, 470, 301	542, 513	0.48

[a] Most significant absorptions. [b] Excitation wavelength corresponds to the longest absorption maximum. [c] Determined using a calibrated sphere.

With the exception of **2f**, the absorption and emission properties of the compounds do not change substantially with changing substituents on the aryl group. TD-DFT calculations (B3LYP/6-31+G(d)) were performed for the phenyl substituted **2c** and show that the lowest energy transition (493 nm) can be attributed to a transition from HOMO to LUMO (calcd: 484 nm, $f = 0.204$), whereas another strong transition (calcd. 426 nm, $f = 0.233$) can be attributed to a transition from HOMO−1 to LUMO+1 (Figure 3). Both transitions are $\pi \rightarrow \pi^*$ in character and do not involve contributions from the (nearly orthogonal) aryl substituent. The strong absorption at 305 nm, however, is a transition from HOMO−5 (which is partially distributed on the phenyl substituents) to LUMO (calcd 316 nm, $f = 0.479$); there is some variation in the position of this absorption as the aryl group changes. The HOMO–LUMO gap of 3 eV in **2b** is smaller than that calculated for **IV** (4 eV), which is consistent with previous assessments of the effect of BN for CC substitution[23] but substantially larger than that of 1.38 eV found for linear heptacenes.[24]

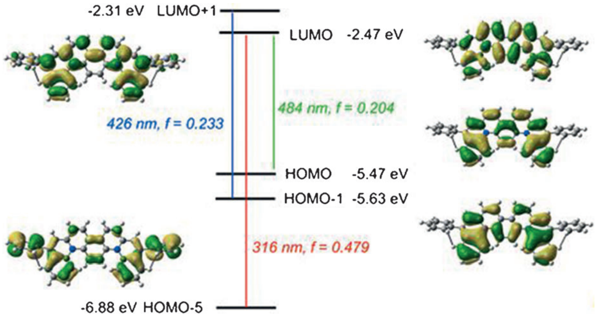


Figure 3. Calculated molecular orbitals (HOMO−5, HOMO, LUMO, LUMO+1) of compound **2c**, oscillator strength, absorption and transition energies (TD-DFT, B3LYP/6-31+G(d)).

Cyclic voltammetry measurements on **2b**–**f** show that each compound undergoes two reversible reductions (Table 3), suggesting that mono and dianionic derivatives may be accessible. The reversibility was also maintained at higher scan rates of 0.2 Vs^{-1}, which points to a fast redox process in solution. Oxidation is irreversible, which is

Table 3: Electrochemical data for compounds **2**.[a]

BN-DBP	R	E_{pc}[b] [V]	$E_{1/2}$[c] [V]
2b	H	−2.01/−2.25	−2.06/−2.27
2c	Ph	−1.89/−2.12	−1.93/−2.16
2d	4-$CF_3C_6H_4$	−1.72/−1.93	−1.73/−1.97
2e	4-FC_6H_4	−2.05/−2.30	−2.10/−2.34
2f	4-$MeOC_6H_4$	−1.83/−2.06	−1.93/−2.12
2g	4-$Me_2NC_6H_4$	−2.10/−2.34	−2.15/−2.38

[a] In THF with $nBu_4N^+PF_6^-$, scan rate 100 mVs^{-1} [b] Cathodic peak potential vs Fc/Fc^+ [c] Reduction potentials versus Fc/Fc^+.

consistent with the high-lying HOMO orbital and disruption of aromaticity.

In summary, we have described the synthesis of several BN-dibenzo[*a*,*o*]picenes **2**, isoelectronic analogues of an isomer of heptacene. The all-carbon species are not known and the reactivity reported herein shows that synthesis developed for the preparation of BN isosteres can allow for the assessment of all-carbon PAH structural motifs not easily accessed by current synthetic methods. Indeed, the comparative photophysical properties of B–N versus C–C structures show that the BN analogues may also be more suitable for device applications.

Experimental Section

General experimental details, full characterization of all new compounds, and computational details are included in the Supporting Information. Supplementary crystallographic data for CCDC 932450 (**1c**), CCDC 932451 (**2b**), CCDC 932453 (**2c**), CCDC 932452 (**2d**), and CCDC 932454 (**2f**) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Representative example for the synthesis of BN-dibenzo-[*a*,*o*]picenes **2**: In a two-necked round bottom flask with an attached swivel frit apparatus, dialkyne **1b** (105 mg, 0.46 mmol) was dissolved in toluene (20 mL). A solution of boracycle (187 mg, 1.01 mmol, 2.2 equiv) in dichloromethane (3 mL) was added to the stirring mixture. After 2 days volatiles were removed under vacuum and 10 mL of fresh dichloromethane were added. The mixture was sonicated and filtered through the frit. Volatiles were removed under reduced pressure. The orange–brown solid was dissolved in dichloromethane and filtered through a pad of aluminum oxide with dichloromethane as eluent to give an orange solid. Recrystallization from dichloromethane/hexanes gave **2b** in 26 % yield (46 mg, 12.00 mmol) as orange needles. ^{1}H NMR (CD$_2$Cl$_2$, 400.14 MHz): $\delta = 9.22$ (s, 2H), 8.62 (d, $J = 8.5$ Hz, 2H), 8.52 (d, $J = 8.5$ Hz, 2H), 8.10–8.08 (m, 4H), 7.94–7.91 (m, 4H), 7.45 (d, $J = 8.5$ Hz, 2H), 7.22–7.19 ppm (m, 2H). ^{13}C [^{1}H] NMR (CD$_2$Cl$_2$, 100.64 MHz): $\delta = 145.5$, 142.9, 141.2, 139.2, 132.7, 129.3, 127.4, 124.1, 122.7, 122.4, 114.1 ppm. ^{11}B NMR (CD$_2$Cl$_2$): $\delta = 30.4$ ppm (broad). HRMS: Calcd for C$_{26}$H$_{18}$B$_2$N$_2$ ([M^+]) 380.1656, Observed: 380.1646.

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[1] a) J. E. Anthony, *Chem. Rev.* **2006**, *106*, 5028; b) C. Wang, H. Dong, W. Hu, Y. Liu, D. Zhu, *Chem. Rev.* **2011**, *111*, 2208.

[2] a) M. M. Payne, S. R. Parkin, J. E. Anthony, C.-C. Kuo, T. N. Jackson, *J. Am. Chem. Soc.* **2005**, *127*, 4986; b) G. S. Tulevski, C. Nuckolls, A. Afzali, T. O. Graham, C. R. Kagan, *Appl. Phys. Lett.* **2006**, *89*, 183101.

[3] M. A. Wolak, J. Delcamp, C. A. Landis, P. A. Lane, J. Anthony, Z. Kafafi, *Adv. Funct. Mater.* **2006**, *16*, 1943.

[4] a) Y. Shu, Y.-F. Lim, Z. Li, B. Purushothaman, R. Hallani, J. E. Kim, S. R. Parkin, G. G. Malliaras, J. E. Anthony, *Chem. Sci.* **2011**, *2*, 363; b) A. A. Gorodetsky, M. Cox, N. J. Tremblay, I. Kymissis, C. Nuckolls, *Chem. Mater.* **2009**, *21*, 4090.

[5] R. Mitsuhashi, Y. Suzuki, Y. Yamanari, H. Mitamura, T. Kambe, N. Ikeda, H. Okamoto, A. Fujiwara, M. Yamaji, N. Kawasaki, Y. Maniwa, Y. Kubozono, *Nature* **2010**, *464*, 76.

[6] a) J. Xiao, H. M. Duong, Y. Liu, W. Shi, L. Ji, G. Li, S. Li, X.-W. Liu, J. Ma, F. Wudl, Q. Zhang, *Angew. Chem.* **2012**, *124*, 6198; *Angew. Chem. Int. Ed.* **2012**, *51*, 6094; b) C. Tönshoff, H. F. Bettinger, *Angew. Chem.* **2010**, *122*, 4219; *Angew. Chem. Int. Ed.* **2010**, *49*, 4125.

[7] a) S. S. Zade, M. Bendikov, *Angew. Chem.* **2010**, *122*, 4104; *Angew. Chem. Int. Ed.* **2010**, *49*, 4012; b) R. Mondal, C. Tönshoff, D. Khon, D. C. Neckers, H. F. Bettinger, *J. Am. Chem. Soc.* **2009**, *131*, 14281.

[8] R. Mondal, B. K. Shah, D. C. Neckers, *J. Am. Chem. Soc.* **2006**, *128*, 9612.

[9] M. M. Payne, S. R. Parkin, J. E. Anthony, *J. Am. Chem. Soc.* **2005**, *127*, 8028.

[10] a) T. K. Wood, W. E. Piers, B. A. Keay, M. Parvez, *Angew. Chem.* **2009**, *121*, 4069; *Angew. Chem. Int. Ed.* **2009**, *48*, 4009; b) T. K. Wood, W. E. Piers, B. A. Keay, M. Parvez, *Chem. Eur. J.* **2010**, *16*, 12199.

[11] Q. Miao, T.-Q. Nguyen, T. Someya, G. B. Blanchet, C. Nuckolls, *J. Am. Chem. Soc.* **2003**, *125*, 10284.

[12] a) Z. Q. Liu, T. B. Marder, *Angew. Chem.* **2008**, *120*, 248; *Angew. Chem. Int. Ed.* **2008**, *47*, 242; b) M. J. D. Bosdet, W. E. Piers, *Can. J. Chem.* **2009**, *87*, 8; c) P. G. Campbell, A. J. V. Marwitz, S.-Y. Liu, *Angew. Chem.* **2012**, *124*, 6178; *Angew. Chem. Int. Ed.* **2012**, *51*, 6074; d) J.-S. Lu, S.-B. Ko, N. R. Walters, Y. Kang, F. Sauriol, S. Wang, *Angew. Chem. Int. Ed.* **2013**, *52*, 4544.

[13] a) J. F. Araneda, B. Neue, W. E. Piers, *Angew. Chem.* **2012**, *124*, 10117; *Angew. Chem. Int. Ed.* **2012**, *51*, 9977; b) S. Saito, K. Matsuo, S. Yamaguchi, *J. Am. Chem. Soc.* **2012**, *134*, 9130; c) Z. Zhou, A. Wakamiya, T. Kushida, S. Yamaguchi, *J. Am. Chem. Soc.* **2012**, *134*, 4529.

[14] M. J. D. Bosdet, W. E. Piers, T. S. Sorensen, M. Parvez, *Angew. Chem.* **2007**, *119*, 5028; *Angew. Chem. Int. Ed.* **2007**, *46*, 4940.

[15] M. J. D. Bosdet, C. A. Jaska, W. E. Piers, T. S. Sorensen, M. Parvez, *Org. Lett.* **2007**, *9*, 1395.

[16] a) O. V. Serdyuk, A. V. Gulevskaya, A. F. Pozharskii, V. E. Avakyan, *J. Heterocycl. Chem.* **2008**, *45*, 195; b) A. V. Gulevskaya, O. V. Serduke, A. F. Pozharskii, D. V. Besedin, *Tetrahedron* **2003**, *59*, 7669.

[17] P. N. W. Baxter, R. G. Khoury, J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **2000**, *6*, 4140.

[18] K. A. Bunten, A. K. Kakkar, *Macromolecules* **1996**, *29*, 2885.

[19] D. A. Hoic, J. R. Wolf, W. M. Davis, G. C. Fu, *Organometallics* **1996**, *15*, 1315.

[20] C. A. Jaska, W. E. Piers, R. McDonald, M. Parvez, *J. Org. Chem.* **2007**, *72*, 5234.

[21] T. K. Wood, W. E. Piers, B. A. Keay, M. Parvez, *Org. Lett.* **2006**, *8*, 2875.

[22] Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, *Chem. Rev.* **2005**, *105*, 3842.

[23] S. Yamaguchi, K. Tamao, *Chem. Lett.* **2005**, *34*, 2.

[24] D. Chun, Y. Cheng, F. Wudl, *Angew. Chem.* **2008**, *120*, 8508; *Angew. Chem. Int. Ed.* **2008**, *47*, 8380.