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Functionalized Dibenzoborepins as Components of Small Molecule and Polymeric π-Conjugated Electronic Materials

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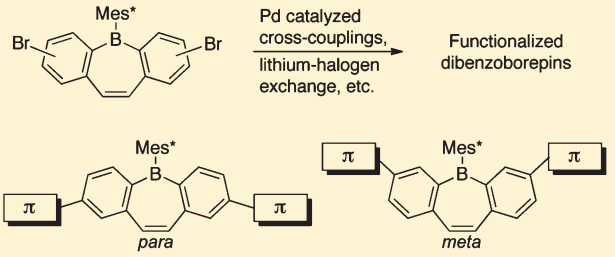
Supporting Information

ABSTRACT: We present the synthesis and characterization of dibenzo[*b*,*f*]borepins (DBBs) functionalized at the *para* and *meta* position with respect to the boron center in order to understand how regiochemical issues influence photophysical and electrochemical properties. An expanded synthetic repertoire is presented, using palladium catalysis (to perform Stille, Suzuki, Buchwald–Hartwig, and Sonogashira cross-coupling reactions) and lithium–halogen exchange to synthesize a series of extended π-conjugated DBBs. These chemistries are enabled by the use of a sterically bulky Mes* (2,4,6-tri-*tert*-butylphenyl) group on boron and the inclusion of reactive bromide handles on the DBB core. Photophysical, electrochemical, and computational analyses of these compounds indicate that relative to the protio-DBB the installation of groups at the *meta* positions decreases the optical band gap while *para* substitution raises the electron affinity of the system. Thus, both the HOMO–LUMO gap and specific frontier molecular orbital levels can be tuned by the installation of different conjugated substituents.



INTRODUCTION

Boron-containing π-conjugated materials have received considerable attention in recent years due to their unique optical and structural properties that result from the vacant p-orbital of the boron center.[1] The tricoordinate organoborane center is inherently electron-deficient, which makes these boron-containing materials amenable for use as electron-accepting units for donor–acceptor nonlinear optical (NLO) materials.[2] The Lewis acidity of the vacant p-orbital makes boron an ideal material for sensor applications;[3] in fact, Gabbaï and Müllen have used organoboranes to selectively bind fluoride and cyanide anions. These properties, along with the planar geometry of the boron center, make organoboranes desirable components for constructing tunable π-conjugated materials[4] such as components for a diverse array of colored organic light-emitting diodes (OLEDs).[5]

The majority of organoborane systems used in these applications incorporate tricoordinate boron into the π-system formally as triaryl boranes through either direct main-chain conjugation,[6−8] lateral substitution,[5a,b,9] or as an end-capping unit[3b,10] (Figure 1). The former includes synthetic methodology employed by Chujo such as hydroboration polymerization between a dihydroborane and a suitable diyne forming poly(*p*-arylene-borane)s[11] where the boron center is directly incorporated into the main π-conjugation pathway. More recently, Jäkle has synthesized poly(fluorenyl *B*-bromoborane)s via the highly selective tin–boron exchange between a bis(trimethylstannyl)fluorene and bis(dibromoboryl)fluorene followed by post-polymerization modification by quenching with a variety of aryl nucleophiles to construct electronically diverse triaryl boranes within the polymer chain.[6]

Lateral substitutions have been achieved by tin/silicon–boron exchange or by addition reactions between aryl lithiates and dimesitylboron fluoride to form both small molecules and side-borylated polymers such as Yamaguchi's oligophenylene ethynylenes[12] that feature dimesitylborane side groups and Jäkle's oligo- and polythiophenes bearing the same.[9] End-capped molecules have been prepared through similar chemistry to incorporate boron–boron or boron–donor electronic interactions such as Shirota's dimesitylborane-capped oligothiophenes[13] and Müllen's donor–acceptor ladder-type oligofluorenes.[3b]

In addition to incorporation through triaryl borane connectivities, boron has also been included as part of polycyclic aromatic frameworks such as azabora-,[14] borata-,[15] and bora-annulenes[16] (Figure 2). Azabora-annulenes are annulenes where one pair of adjacent π-conjugated carbon centers is replaced with a boron–nitrogen double bond with the most basic example being azaborine (**I**), which is isoelectronic with benzene. Dewar initially synthesized derivatives of azaborine in 1962;[17] however, sufficient characterization was difficult to obtain until the experimental studies of Ashe[18] and more recently Liu[19] investigated the aromaticity, reactivity, and optoelectronic properties. In recent years, strong synthetic efforts out of the Piers laboratory led to the construction of a variety of more complex polycyclic aromatics such as B=N variants of phenanthrene, pyrene, and triphenylene.[14b−d] Borata-annulenes are anionic molecules in which one sp^2 hybridized carbon is replaced by an anionic boron center; such is the

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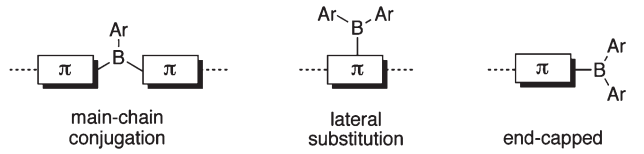


Figure 1. Different tricoordinate triarylborane architectures.

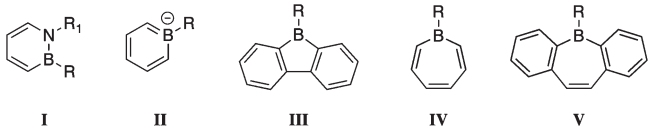


Figure 2. Boron-based heteroaromatics: 1,2-azaborine (**I**), boratabenzene (**II**), 9-borafluorene (dibenzo[*b*,*d*]borole) (**III**), borepin (**IV**), and dibenzo[*b*,*f*]borepin (**V**).

case for boratabenzene (**II**), which was first synthesized by Herberich in 1970 and shown to be a suitable ligand for transition metal complexes.[20] Since the seminal publication on borataannulenes, Bazan, Ashe, and others have synthesized a variety of larger systems including borataanthracene[21] and boratanapthalene[22] and explored their application to coordination chemistry. Boraannulenes are conjugated heterocycles where one carbon is replaced with a neutral boron center as exemplified by the 4π-electron formally anti-aromatic borole ring first synthesized by Eisch and co-workers in 1969, which is isoelectronic with the cyclopentadienyl cation. The unsubstituted borole ring is unstable; however, the perarylation or incorporation into larger polycyclic aromatics such as 9-borafluorene (dibenzoborole, **III**) allow for further functionalization and manipulation.[23] In contrast to its carbon and nitrogen analogues (fluorene and carbazole, respectively), dibenzoborole has the potential of being an electron-transporting material due to the electron deficiency of the boron center.

One class of less-utilized boron-based building blocks for π-electronic materials investigation is the borepins (**IV**), seven-membered, 6π-electron neutral aromatic heterocycles that are isoelectronic with the tropylium cation. Vol'pin initially suggested that borepins would be Hückel-type aromatic compounds,[24] and in the nearly 50 years following, various *B*-substituted borepins and benzoborepins were studied theoretically[25,26] and experimentally.[27−29] Ashe evaluated the aromaticity of the borepin ring by X-ray crystal analysis, NMR and UV−vis spectroscopy and determined that they are indeed aromatic as predicted. Some years later, Schleyer as well as Schulman and Disch performed extensive theoretical studies of borepin and its benzo-annulated analogues spurring much interest in their design and synthesis. Unfortunately, the air and moisture sensitivity of these molecules due to the unshielded vacant p-orbital on the boron center hindered the investigation and application of borepin-based materials, and their preparative chemistry has been restricted to small molecule analogues rather than for elaboration into extended π-conjugated systems unlike the other boron-based examples described above.

To overcome these limitations, Piers[30] and we[31] independently described the synthesis and characterization of a variety of more robust molecules containing different flavors of the dibenzo[*b*,*f*]borepin ring system (DBB, **V**) in an effort to better understand the local aromaticity of the central borepin ring and its involvement in the overall π-conjugated network. Piers reported a series of different benzo- and napthoborepins that utilized mesityl (1,3,5-trimethylbenzene) as the boron substituent, which imparted enough stability to enable purification and exposure to ambient environments. These molecules exhibited blue photoluminescence with rather high quantum yields in some cases suggesting potential application as light-emitting components in OLEDs. In an associated paper,[32] they describe the synthesis and electronic characterization of new silepin molecules as potential precursors to formation of borepins via tin−silicon exchanges.

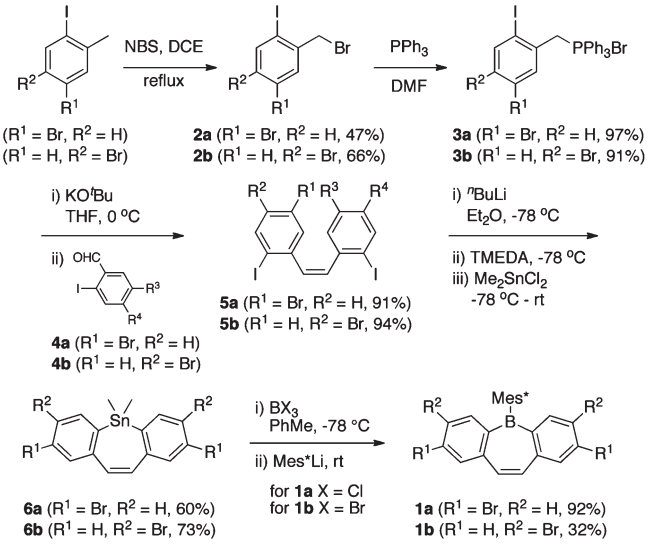
We extended the DBB conjugation pathway through the vacant boron p-orbital by transition-metal-catalyzed cross-coupling reactions onto chlorides placed *para* to the boron center. Due to the rather low reactivity of the chlorides, installation of π-electron groups onto the DBB core under even highly active palladium catalysis was unsuccessful; however, nickel-catalyzed Kumada cross-couplings with aryl Grignards led to aryl-coupled DBBs. The kinetic protection afforded by the *B*-Mes* groups (2,4,6-tri-*tert*-butylphenyl)[33,23c] allowed these molecules to withstand treatment with aggressive transmetalation reagents necessary for doing Kumada-type cross-coupling chemistry. Despite these initial advances in elaboration of the DBB scaffold, it will be important for future materials development to have a more general and reactive platform through which to do a diverse array of chemical modifications for electronic property tuning. Herein, we report the synthesis of brominated DBBs as well as the design, synthesis, and characterization of functionalized DBBs via expanded synthetic manipulations now available with these borepin aryl bromides.

RESULTS AND DISCUSSION

Design Considerations. In designing functionalized DBB molecules there were two apparent positions where π-electron groups could be installed that could lead to extended intramolecular delocalization, *meta* or *para* to the boron center. The *meta* isomer could facilitate the delocalization of π-electrons through the stilbene-like carbon moiety by essentially isolating the boron and precluding it from participating in charge delocalization. However, installation of functional groups *para* to the boron could make the boron center a more integral part of the π-conjugation pathway. In order to better understand these electronic issues, we synthesized brominated DBBs that allowed us to prepare a series of π-conjugated *para* and *meta* isomers to compare the effect of electron delocalization through the boron center or the stilbene-like olefin.

Synthesis of *para* and *meta* Brominated DBBs. Brominated DBBs **1a**−**b** were targeted to allow for more facile cross-coupling reactions due to the anticipated enhanced reativities of aryl bromides under palladium catalyzed cross-coupling chemistries. The syntheses of the brominated DBBs are shown in Scheme 1. The common bromoiodobenzylbromide precursors **2a**−**b** were used to prepare phosphonium salts **3a**−**b** via Arbuzov chemistry, and *N*-methylmorpholine *N*-oxide mediated oxidations furnished benzaldehydes **4a**−**b**. The stilbenes were assembled by

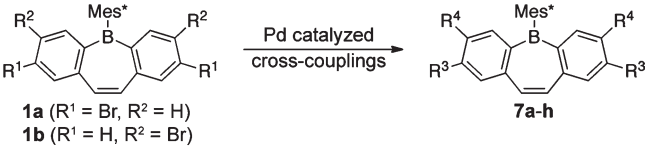
Scheme 1. Synthesis of Dibenzo[*b*,*f*]borepins with *para* and *meta* Bromides for Further Functionalization

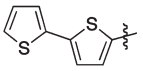
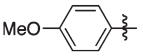
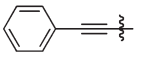
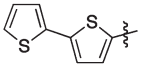
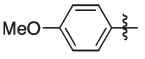
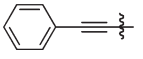


Wittig reactions between **3** and **4** to form stilbenes **5a**−**b** with a *Z*:*E* selectivity of greater than 82%.[34] Subsequently, chemoselective lithium−halogen exchange at the iodides of **5** followed by *in situ* treatment of the dilithio species with dimethyltin dichloride resulted in formation of the brominated stannepins **6a**−**b**. Tin−boron exchange proved to be very capricious and highly sensitive to any trace air and/or moisture present especially in the toluene. Tin−boron exchange between stannepin **6a** and boron trichloride furnished a *B*-chloro DBB that was treated *in situ* with Mes*Li[35] to form the *para* brominated *B*-Mes* DBB **1a** in 92% yield; however, utilizing this procedure for the synthesis of the *meta*-DBB **1b** resulted in yields ranging from 6% to 14% with the remainder of the material being *B*-hydroxy DBB formed through unavoidable oxidation of the intermediate *B*-chloro DBB species. Since a large excess (5 equiv) of Mes*Li was added, we presumed the *B*-chloro DBB intermediate formed from **6b** was not as reactive as that from **6a** possibly due to the electronics of the *meta*-brominated ring system. As a result, boron tribromide was chosen for the tin−boron exchange with **6b** followed by the addition of Mes*Li at room temperature. These alterations increased the yield of **1b** to 32%. Installation of the Mes* group at the boron center rendered the DBBs stable against air, moisture, and even nucleophiles such as fluoride, thus allowing for standard synthetic manipulation and purification by column chromatography under ambient conditions.

Pd-Mediated Cross-Couplings. The *meta* and *para* brominated DBBs were subjected to a variety of palladium-catalyzed cross-coupling reactions in order to tune electronic properties (e.g., Stille, Suzuki, and Sonogashira; see Chart 1). These coupling methods required a broad range of cross-coupling partners and reaction conditions, thus showing the robustness of the borepin core. Stille couplings of stannylated thiophene and bithiophene with **1a**−**b** (in dimethyl formamide at 80 °C) led to coupled products **7a**,**e** and **7b**,**f** respectively. The Suzuki coupling of 4-methoxyphenyl boronic acid with **1b** (in biphasic toluene/aqueous potassium bicarbonate at reflux) led to the corresponding aryl coupled product **7g**, whereas Sonogashira couplings of **1a**−**b** with phenylacetylene (in toluene and diisopropylamine at 75 °C) furnished products **7d**,**h**. The borepin

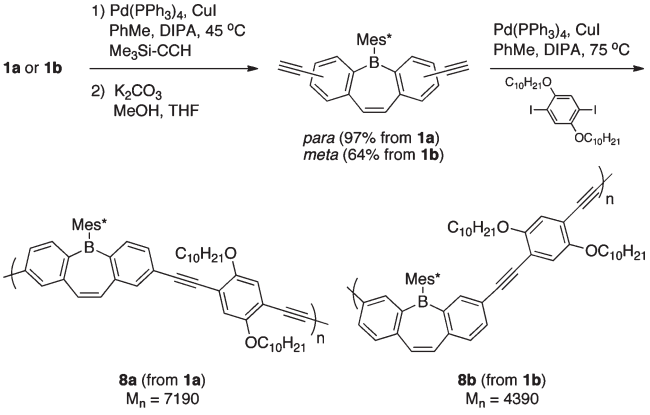
Chart 1. *B*-Mes* Dibenzo[*b*,*f*]borepins Functionalized by Stille (7a−b,e,f), Suzuki (7g), and Sonogashira (7d,h) Cross-Coupling Reactions



DBB	product	R^3	R^4	yield
1a	**7a**		H	53%
1a	**7b**		H	73%
1a	**7c**		H	[a]
1a	**7d**		H	56%
1b	**7e**	H		quant.
1b	**7f**	H		56%
1b	**7g**	H		79%
1b	**7h**	H		33%[b]

[a] **7c** was previously synthesized in our lab by Kumada cross-coupling.[31] [b] Yield determined by ^{1}H NMR.

Scheme 2. Synthesis of *para* (8a) and *meta* (8b) DBB polymers via Sonogashira polymerizations



core survived all of these chemical exposures, and all coupling products were handled and purified under ambient conditions. These compounds also exhibited stability toward thermal decomposition as seen by the heating of **7b** to 130 °C for 45 min without noticeable decomposition apparent by ^{1}H NMR (see Figure 13 in the Supporting Information).

Sonogashira coupling between the DBBs and trimethylsilyl acetylene under standard conditions yielded *para* and *meta* TMS-protected diethynyl DBBs in 97% and 64% yields, respectively

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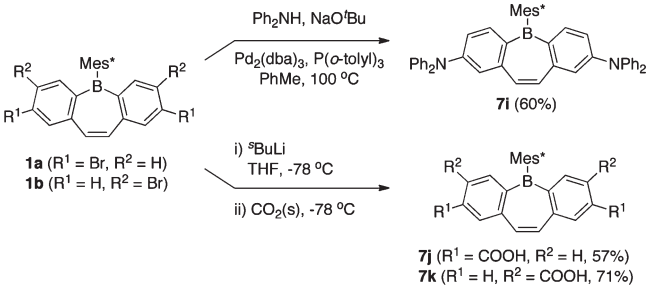
(Scheme 2). Subsequent TMS deprotection with methanol and potassium carbonate in THF gave terminal *para* and *meta* acetylenes that were then polymerized under Sonogashira cross-coupling conditions with 1,4-bis(decyloxy)-2,5-diiodobenzene[36] to form poly(arylene)ethynylene polymers **8a** and **8b**, respectively (Scheme 2). Molecular weight determination of the polymers by gel permeation chromatography (GPC) revealed reasonable polydispersity indexes of 2.45 (**8a**) and 1.93 (**8b**); furthermore, both polymers are readily soluble in common organic solvents (i.e., chloroform, toluene), which could enable solution processing.

In order to further explore the stability of the DBBs toward even more aggressive reaction conditions, *para*-DBB **1a** was subjected to Buchwald−Hartwig amination conditions. This cross-coupling installed diphenylamine onto the DBB core by palladium catalysis in the presence of sodium *tert*-butoxide in toluene at 100 °C in 60% yield with no sign of borepin decomposition (Scheme 3). Attempts to synthesize the *meta* bis(diphenylamino) DBB from **1b** resulted in protio-DBB and starting materials suggesting that the proximity of the Mes* and the *meta* bromides precluded the insertion of the diphenylamine moiety due to steric restraints. DBB **7i** has the general structure of D-π-A-π-D, where D is an electron donor, π is a π-conjugated bridge, and A is an acceptor, which has been shown to be an efficient chromophore motif useful for two-photon absorption processes.[37] It might also be possible to use boron or nitrogen centered redox activity to control intramolecular charge-transfer processes within molecules such as **7i** and analogues of the same design.

Scheme 3. Exposure of Brominated DBBs to Aggressive Reaction Conditions: Buchwald−Harwig Amination (leading to 7i) and Lithium−Halogen Exchange (leading to 7j,k)



Lithium−Halogen Exchange. We also demonstrated that DBBs **1a**−**b** could undergo lithium−halogen exchange with *s*-BuLi in THF at −78 °C followed by quenching with an electrophile, in this case solid carbon dioxide, to form diacid DBBs **7j**−**k** in 57% and 71% yields respectively (Scheme 3). This general procedure should be applicable to install other functional groups including aldehydes, which could then be used to synthesize polymers or extended systems that incorporate arylene vinylene motifs through Wittig or Horner−Wadsworth−Emmons olefinations.

Frontier Molecular Orbtial Calculations. We carried out density functional theory (B3LYP/6-31G*) calculations for the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the DBB systems (using *B*-2,6-dimethylphenyl rather than *B*-Mes*, Figure 3) with substituents attached at the *meta* and *para* positions to gain insight into the effect of site-specific functionalization on the frontier molecular orbital densities. These calculations revealed a node in the HOMO located at the boron center for DBBs **7a**−**c** and **7e**−**g** when functionalization was at the *para* position, effectively dividing the HOMO in half, while the HOMO of the *meta* substituted DBBs were continuous and fully delocalized onto the substituents (representative surfaces shown in Figure 3). Only the phenylacetylene functionalized DBBs **7d, h** did not follow

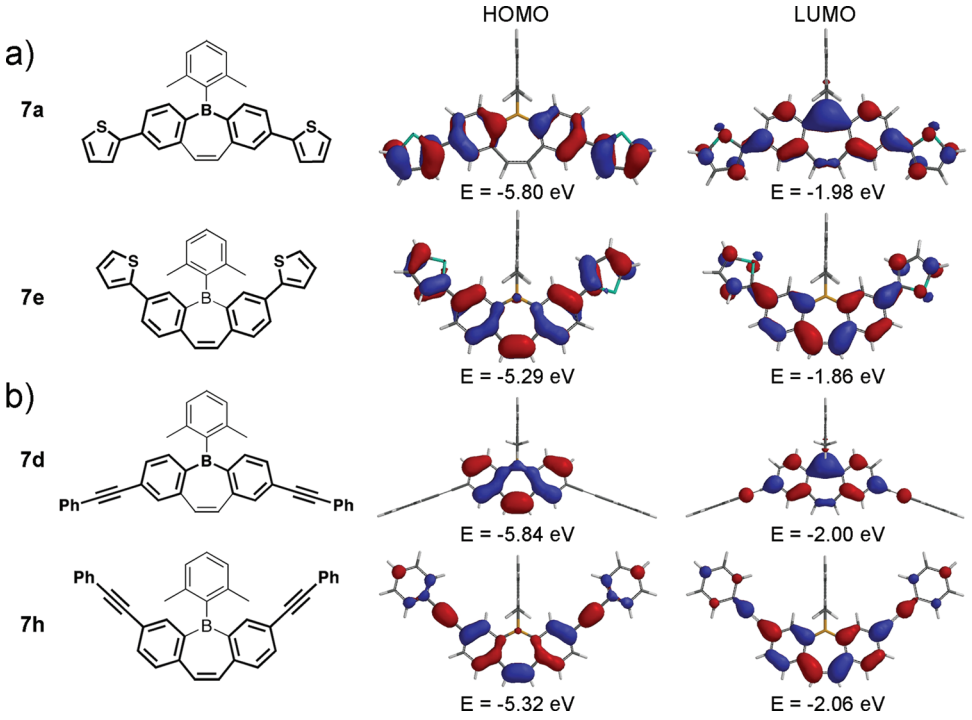


Figure 3. Structures (left) and DFT (B3LYP/6-31G*) Calculations Depicting the HOMO (center) and LUMO (right) Wave Functions of (a) *para* **7a** and *meta* **7e** and (b) *para* **7d** and *meta* **7h**.

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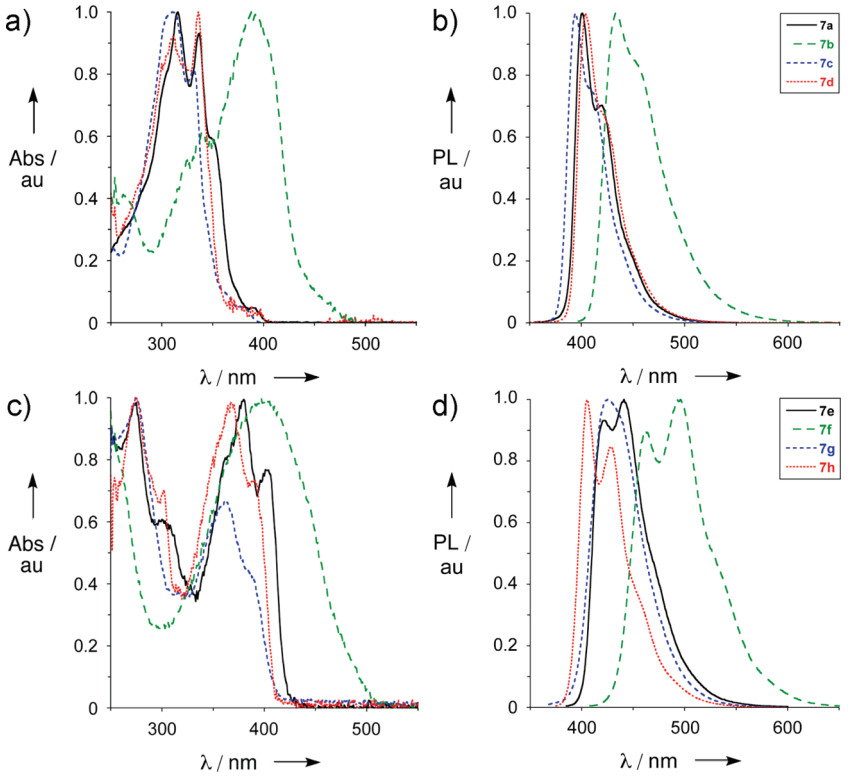

Figure 4. Normalized UV−vis data for (a) *para* substituted DBBs **7a**−**d** and (c) *meta* substituted DBBs **7e**−**h** and normalized photoluminescence data for (b) *para* substituted DBBs **7a**−**d** and (d) *meta* substituted DBBs **7e**−**h**. UV−vis and PL spectra were acquired in $CHCl_3$ at room temperature. The legends for panels a and b are shown in panel b, and those for panels c and d are shown in panel d.

this trend due to the phenyl group of the substituent being rotated orthogonal to the DBB core; however, DFT calculations done on the *para* 4-ethynylanisole-substituted DBBs exhibited similar frontier molecular orbital surfaces as **7a**−**c**. This suggests that electron rich substituents might lead to more planar molecules to optimize the charge-transfer interaction to the boron center as evident in the large wave function densities located on boron in the LUMO.

Optical Characterization. Solution-phase absorption, photoluminescence (PL), and lifetime data were measured to observe how different substituents and conjugation paths through the DBBs affected electronic properties. Figure 4 shows the optical characterization data for the *para* and *meta* functionalized DBBs **7a**−**h** which have also been compiled numerically in Table 1. Representatively, the *para*-DBB **7a** had a weak low-energy charge-transfer band at 389 nm and more intense higher energy $\pi-\pi^*$ signature centered at 315 nm. In contrast, the absorption profile of the *meta*-DBB **7e** did not show the weak charge-transfer band and the $\pi-\pi^*$ transitions were red-shifted by over 50 nm. The photoluminescence maximum observed at 401 nm (with a shoulder at 419 nm) for **7a** was sharp and at higher energy than that of **7e**, which exhibited a bimodal emission with maxima centered at 422 and 441 nm. The *para*-DBB **7a** had an average weighted photoluminescence lifetime ($<\tau>$) of 5.63 ns compared to 2.75 ns for the *meta*-DBB **7e**. The rest of the DBBs followed the same trend (see Table 1) with red-shifted absorption and emission profiles and shorter $<\tau>$ upon going from the *para*- to *meta*-DBBs with a particular substituent; however, there were no notable trends in the radiative (k_r) and nonradiative (k_{nr}) rate processes among the isomeric compounds surveyed. Regardless of the regiochemistry of the substitution, all of the substituted DBBs had red-shifted absorption and emission profiles with respect to the protio-DBB. Unlike the Piers silepins, we observed no significant solvatochromism (that is, no greater than 10 nm shifts) for the corresponding borepins except for the strongly donating diphenylamine substituted DBB **7i** (see Figure 5 and Table S1 in the Supporting Information), which showed a fluorescence λ_{max} red-shift of 65 nm on going from a nonpolar solvent (cyclohexane) to a polar solvent (acetonitrile). While we found negligible solvatochromism for the anisole functionalized DBB **7c**, the analogous silepin in the associated paper (***p*-1-PhOMe**)[32] showed a 25 nm fluorescence red-shift in moving to more polar solvents. This is not unexpected because the wave functions for the borepin HOMOs and LUMOs are much more equally distributed throughout the molecular core when compared to the silepins.

The *para* polymer **8a** had an onset of absorption at 449 nm and a more intense band centered at 397 nm with higher energy vibrational fine structure, whereas the *meta* polymer **8b** onset was red-shifted by 24 nm. The photoluminescence spectra for both polymers were intense with quantum yields near 70% with the maximum for *meta* polymer **8b** observed at 462 nm being red-shifted by 20 nm compared to that of the *para* polymer **8a**. Additionally, *para* polymer **8a** had a $<\tau>$ of 0.92 ns, and *meta* polymer **8b** had a $<\tau>$ of 0.89 ns. It was suprising that both polymers had near identical quantum yields and lifetimes. Otherwise, these polymers exhibited the same photophysical trends (Figure 6) as all of the previously discussed substituted DBBs with the *meta* isomer having red-shifted absorption and photoluminescence spectra with respect to the *para* isomer.

Electrochemical Characterization. Cyclic voltammetry (CV) performed on the DBBs revealed reversible one-electron reduction

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peaks presumed to originate from the vacant p-orbitals of the boron centers. Figure 7 shows representative CVs for the reversible reduction of **7a** ($E_{1/2}$ = −2.15 V) and **7e** ($E_{1/2}$ = −2.26 V), which shows that the reduction half-wave potential ($E_{1/2}$) for the *para*-substituted DBB was 110 mV less negative than the *meta*-DBB (data compiled numerically in Table 2). This difference can be rationalized by the fact that the *para*-DBB **7a** includes the boron center in the π-electron delocalization pathway resulting in a more facile reduction, whereas the *meta*-DBB **7e** extends linear conjugation through the carbon−carbon double bond moiety. In general, the reduction potentials for all of the *para*-DBBs were less negative than those for the corresponding *meta*-DBBs (see Table 2) with exception of the phenyl acetylene substituted DBBs, which showed identical reduction potentials as a result of the π-conjugating phenyl groups being orthogonal to the DBB cores. Furthermore, all substituted DBBs had more positive reduction potentials than the protio-DBB ($E_{1/2}$ = −2.54 V) suggesting that any substitution on the ring regardless of regiochemistry helps to make the system more reducible.

Table 1. Optical Properties of Functionalized *B*-Mes* Dibenzo[*b*,*f*]borepins[a]

compound	abs λ, nm (log ε)	PL λ, nm	Φ_F, %	$\langle\tau\rangle$, ns	k_r, 10^9 ns^{-1}	k_{nr},10^9 ns^{-1}
protio-DBB[12]	357 (3.56) 340 (3.76) 321 (4.29) 309 (4.36)	384	36	na	na	na
7a	350 (5.41) 337 (5.60) 315 (5.64)	401, 419	35	5.5	0.0636	0.118
7b	388 (4.87) 339 (4.66)	434, 454	45	0.63*	0.714	0.873
7c[12]	381 (3.55) 363 (3.84) 331 (4.77) 310 (4.86)	395, 411	38	7.2	0.0528	0.0861
7d	389 (3.46) 371 (3.63) 336 (4.81) 311 (4.77)	403, 423	43	7.1	0.0606	0.0803
7e	402 (4.12) 380 (4.23) 303 (4.01) 273 (4.23)	422, 441	39	2.8*	0.139	0.218
7f	399 (4.35)	462, 496	33	0.71*	0.465	0.944
7g	385 (4.32) 361 (4.51) 274 (4.68)	425	60	5.7*	0.105	0.0701
7h	390 (3.79) 367 (3.92) 274 (3.93)	405. 428	99.8	1.6*	0.624	0.00125
7i	380 (4.42) 319 (3.59)	437	23	5.1	0.0451	0.151
8a	397 (na) 339 (na) 304 (na)	442, 470	69	0.92	0.750	0.337
8b	410 (na)	462, 491	64	0.89	0.720	0.404

[a] All lifetime data were fit to single exponential decays except for those marked with an asterisk (*), which were double exponential.

With repeated cycles to ca. +900 mV in the CV experiment, monomer **7b** eventually polymerized due to oxidation of the bithiophene segment and subsequent follow-up oligomerization. Under comparably positive applied potentials, monomers **7a**, **e**, and **f** appeared to oxidize irreversibly but did not polymerize or otherwise deposit on the working electrode. The CVs recorded during the polymerization of **7b** and the subsequent polymer CV of poly(**7b**) recorded in monomer-free electrolyte are shown in Figure 8. Poly(**7b**) showed a reversible reduction with an $E_{1/2}$ of −2.12 V (vs −2.10 for the monomer) and an anodic peak potential (E_{pa}) of 0.81 V. This indicates that the borepin cores remain electronically isolated along the polymer; furthermore, anodic polymerization is a fairly destructive technique compared to chemical cross-coupling methods, and the borepin appears to be no more susceptible to oxidative damage than do typical electropolymerizable monomers. Attempts to chemically polymerize **7b** via iron(III) chloride oxidation were unsuccessful in our hands; however, it should be noted that the failed attempts resulted in recovery of the monomer, testifying to the stability of the DBB core under oxidizing conditions.

Comparison to Dibenzo[*b*,*f*]silepins. Boron and silicon are emerging as two attractive constituents for main-group functional π-conjugated electronic materials. In an associated paper, Mercier et al.[32] present the synthesis of a variety of *para* and *meta* functionalized dibenzo[*b*,*f*]silepins in parallel for comparison to the DBBs reported here. The syntheses of their silicon-containing compounds utilized Wittig chemistry to form halogenated *cis*-stilbene precursors that could be converted into the silepins by quenching the appropriate dilithio stilbene with dimethylsilicon dichloride. Similar to the DBBs, the silepin cores withstood a variety of palladium-catalyzed cross-coupling conditions. The Piers

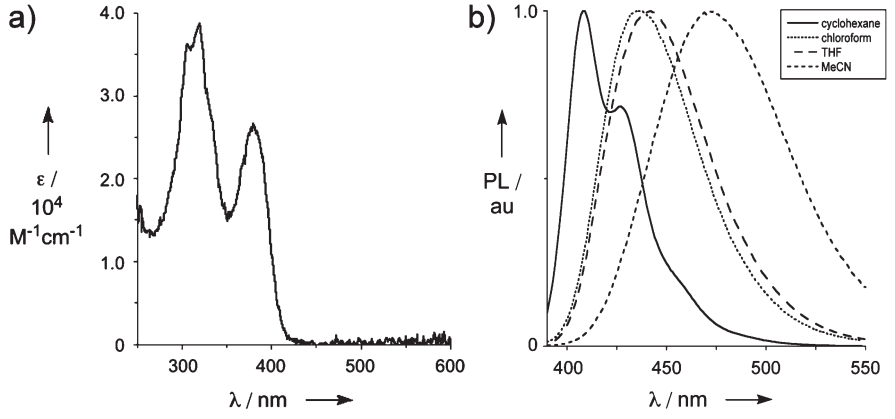

Figure 5. UV−vis (a) and photoluminescence (b) data for **7i**. UV−vis was acquired in $CHCl_3$, and PL spectra were acquired in cyclohexane, $CHCl_3$, THF, and MeCN at room temperature, with excitation at 379.

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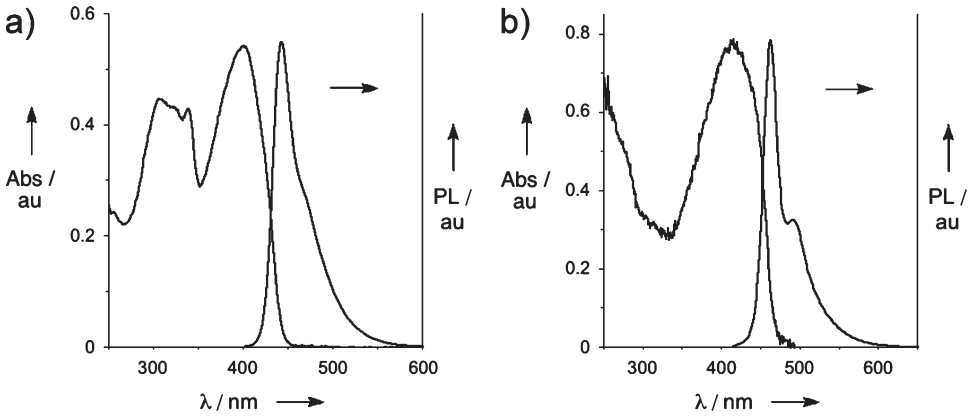


Figure 6. UV−vis and photoluminescence data for **8a** (a) and **8b** (b). UV−vis and PL spectra were acquired in $CHCl_3$ at room temperature, with excitation at 397 nm (a) and 410 nm (b).

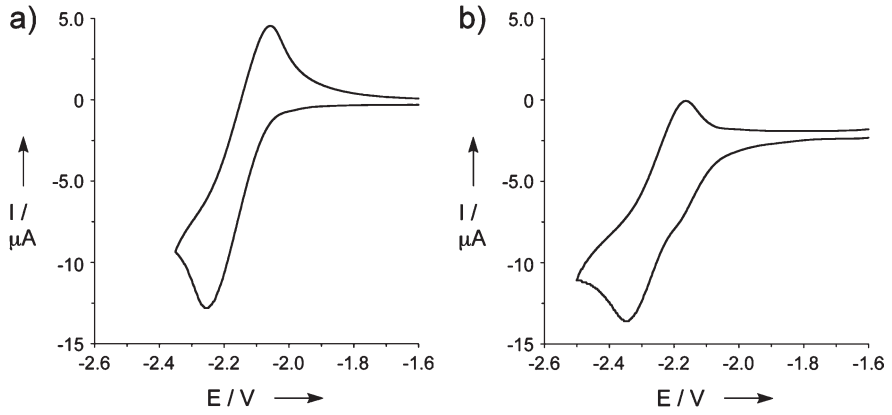


Figure 7. Cyclic voltammetry of **7a** (a) and **7e** (b). CVs were acquired in 2.5 mM solutions of analyte in 0.1 M nBu$_4$NPF$_6$/THF and are reported relative to Ag/Ag$^+$.

Table 2. Electrochemical Properties of Functionalized *B*-Mes* Dibenzo[*b*,*f*]borepins[a]

compound	abs λ_{onset}, nm	E_g, eV	$E_{1/2}$, V	E_{red}, eV
protio-DBB[12]	358	3.46	−2.54	−3.47
7a	400	3.10	−2.15	−3.06
7b	491	2.53	−2.10	−2.99
7c[12]	392	3.16	−2.23	−3.12
7d	400	3.10	−2.10	−3.09
7e	426	2.91	−2.26	−3.14
7f	510	2.43	−2.19	−2.98
7g	416	2.98	−2.40	−3.24
7h	412	3.01	−2.10	−3.09
7i	418	2.97	−2.23	−3.32
8a	449	2.76	na	na
8b	473	2.62	na	na

[a] E_g values were calculated from λ_{onset}, and E_{red} values were calculated from onset of the reduction wave and referenced to the energy level of Fc/Fc$^+$ taken as −4.8 eV.

strategy was to use these functionalized silepins as substrates for borepin formation via silicon−boron exchange, and they demonstrated one example of this transformation. In comparing the photophysical properties, the *para*- and *meta*-DBBs all had smaller HOMO−LUMO energy gaps than the corresponding silepins, which is evidenced by the red-shifted absorption profiles. This suggests that the tricoordinate boron center is crucial for complete electron delocalization in the *para*-DBBs and imparts a more planar geometry relative to the boat-shaped silepin cores. In the *meta*-DBBs and silepins, the boron and silicon centers are not intimately involved in the conjugation pathway; however, they act to planarize the stilbene portion of the molecule, which the trigonal planar boron does more effectively than the tetrahedral silicon as witnessed by the red-shifted onsets of absorption. The *meta*-silepins were more easily reduced than the corresponding *para*-silepins; however, this trend was opposite for the borepins indicating that π-conjugation to the vacant p-orbital stabilizes the LUMOs.

■ CONCLUSION

We have reported a synthetic approach that enables the formation of extended DBB systems through a variety of palladium-catalyzed cross-coupling reactions including Suzuki, Stille, Buchwald−Hartwig, and Sonogashira chemistries, as well as the ability to install electrophiles after lithium−halogen exchange. This has been made possible by the installation of bromides on robust *B*-Mes* DBB cores and has led to the rapid diversification with aryl, heteroaromatic, alkynyl, and carbonyl substituents from common core scaffolds. These molecules could

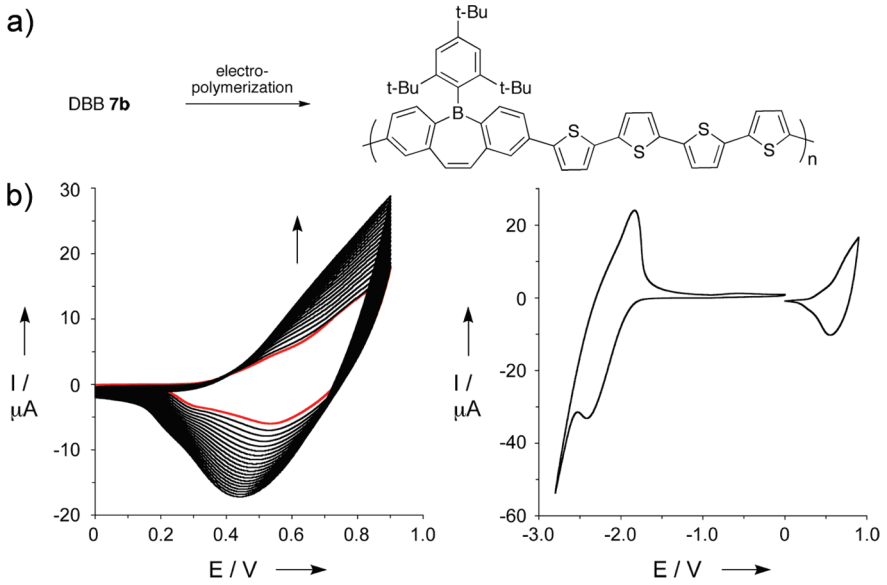


Figure 8. Electrochemical polymerization data for poly(**7b**). (a) Growth curve showing multiple CV traces of monomer **7b** and (b) cyclic voltammagram of the resulting polymer. CVs were obtained in 0.1 M nBu$_4$NPF$_6$/THF with polymer growth done in a 2.5 mM solution of **7b**. All potentials are reported relative to Ag/Ag$^+$.

also be included in π-conjugated polymer architectures through chemical or even electrochemical polymerization techniques. These synthetic investigations have allowed us to study how the substitution patterns influence photophysical and electrochemical properties. We found that *meta*-substitution decreases the optical band gap, whereas *para*-substitution raises the electron affinity of the system. This enables the selective tuning of the HOMO and LUMO energy levels and wave functions of the DBB system by altering the substituent and/or its location around the DBB core. The ability to functionalize the DBB core from a common dibromo DBB scaffold under a variety of reaction conditions, which leads to a diverse array of functional groups, makes it an exciting new π-conjugated building block for application-specific electronic fine-tuning in future studies.

EXPERIMENTAL SECTION

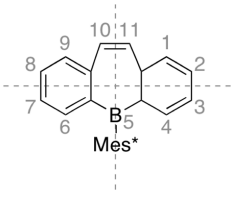
General. All reaction manipulations were carried out under an atmosphere of prepurified nitrogen or argon using Schlenk techniques. Nonaqueous solvents were degassed by sparging with nitrogen for 15 min prior to use, and toluene, diethyl ether, and THF were distilled over sodium/benzophenone ketyl. Tetrakis(triphenylphosphine) palladium was obtained from Strem Chemicals, and 32−63 μm silica gel was used. ^{1}H NMR and ^{13}C NMR spectra were obtained in deuterated chloroform (the signal for residual protio solvent was set at 7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR), deuterated methylene chloride (the signal for residual protio solvent was set at 5.32 ppm for ^{1}H NMR and 54 ppm for ^{13}C NMR), or deuterated dimethyl sulfoxide (the signal for residual protio solvent was set at 2.50 ppm for ^{1}H NMR and 39.52 ppm for ^{13}C NMR) using a 400 MHz FT-NMR spectrometer. All efforts to obtain ^{13}C NMR were unsuccessful due to the low solubility of the functionalized DBBs (overnight scans did not result in spectra with reasonable signal-to-noise ratios) and quadrupolar relaxation of boron. Mass spectra were obtained with EI and FAB ionization (matrix for FAB was 3-nitrobenzyl alcohol), and GPC analyses were done by Aurora Analytics, LLC, Baltimore, MD.

Photophysical Considerations. Spectroscopic measurements were conducted in $CHCl_3$ solution at room temperature. UV−vis absorption spectra were recorded on a UV−vis spectrophotometer. Photoluminescence spectra were recorded on a fluorometer with a 75 W xenon lamp, maintaining optical densities below 0.1 au, and lifetime data were collected on a generic LED system. Quantum yields were determined relative to quinine sulfate in 0.1 N H_2SO_4 (55%).

Electrochemical Considerations. Cyclic voltammetry was performed in a one-chamber, three-electrode cell using a potentiostat. A 2 mm^2 Pt button electrode was used as the working electrode with a platinum wire counter electrode relative to a quasi-internal Ag wire reference electrode submersed in 0.01 M $AgNO_3$/0.1 M n-Bu$_4$NPF$_6$ in anhydrous acetonitrile. Measurements were taken on millimolar analyte concentrations in 0.1 M n-Bu$_4$PF$_6$ (in THF) electrolyte solutions recorded at a scan rate of 100 mV/s. Potentials are reported relative to the Ag/Ag$^+$ couple with which the Fc/Fc$^+$ couple was found to be 205 mV.

Computational Considerations. Molecular orbital calculations were performed at the DFT level (B3LYP/6-31G*) on equilibrium geometries using Spartan '04 (Wave Function Inc., Irvine, CA).

For reference, we used the numbering scheme for dibenzo-[*b,f*]borepins as shown below.



*2,8-Dibromo-5-(2,4,6-tri-tert-butylphenyl)dibenzo[b,f]borepin (**1a**).* A solution of stannepin **6a** (102 mg, 0.209 mmol) in toluene (2 mL) was cooled to −78 °C in a dried 25 mL Schlenk tube under nitrogen. A solution of BCl_3 in hexane (1.0 M, 0.23 mL, 0.23 mmol) was added dropwise with stirring after which the reaction mixture was allowed to slowly warm to room temperature over 1 h. A solution of Mes*Li (265 mg, 1.05 mmol) in toluene (3 mL) was added dropwise, and the resulting mixture was left stirring at room temperature for 18 h. The reaction mix was partitioned between 1:1 water/diethyl ether, and the organic phase was washed with brine (2×). The aqueous layer was removed and extracted with diethyl ether (2×), the combined organics were dried with $MgSO_4$ and filtered,

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and the solvent was removed under reduced pressure to a yellow oil that was further purified by column chromatography (SiO_2, hexane) to yield 114 mg (0.193 mmol, 92%) of **1a** as an off-white solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.84 (m, 4H), 7.50 (s, 2H), 7.47 (dd, 2H, J = 8.3, 2.0 Hz), 7.11 (s, 2H), 1.42 (s, 9H), 0.94 (s, 18H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 151.1, 149.1, 143.9, 143.3, 139.2, 135.4, 134.1, 130.7, 130.5, 126.7, 123.5, 38.7, 35.3, 31.5, 30.1; HRMS (FAB) m/z calcd for $C_{32}H_{37}BBr_2$ [M^+] 590.1355, found 590.1314.

*3,7-Dibromo-5-(2,4,6-tri-tert-butylphenyl)dibenzo[b,f]borepin (**1b**).* A solution of stannepin **6b** (80.4 mg, 0.166 mmol) in toluene (2 mL) was cooled to −78 °C in a dried 25 mL Schlenk tube under nitrogen. A solution of BBr_3 in hexane (1.0 M, 0.18 mL, 0.18 mmol) was added dropwise with stirring after which the reaction mixture was allowed to slowly warm to room temperature over 1 h. A solution of Mes*Li (209 mg, 0.829 mmol) in toluene (2 mL) was added dropwise, and the resulting mixture was left stirring at room temperature for 18 h. The reaction mix was partitioned between 1:1 water/diethyl ether, and the organic phase was washed with brine (2×). The aqueous layer was removed and extracted with diethyl ether (2×), the combined organics were dried with $MgSO_4$ and filtered, and the solvent was removed under reduced pressure to an off-white solid that was further purified by column chromatography (SiO_2, hexane) to yield 31.5 mg (0.053 mmol, 32%) of **1b** as an off-white solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.06 (d, 2H, J = 2.3 Hz), 7.70 (dd, 2H, J = 8.3, 2.3 Hz), 7.54 (m, 4H), 7.16 (s, 2H), 1.45 (s, 9H), 0.97 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 149.1, 145.7, 145.64, 145.62, 144.1, 140.2, 134.6, 134.5, 133.5, 132.0, 128.2, 123.2, 121.8, 38.6, 35.3, 31.6, 29.9; HRMS (FAB) m/z calcd for $C_{32}H_{37}BBr_2$ [M^+] 590.1355, found 590.1363.

4-Bromo-2-iodotoluene. A solution of acetic acid (100 mL) and acetic anhydride (50 mL) was cooled to 0 °C in a 500 mL 3-neck round-bottom under nitrogen with stirring. $NaIO_4$ (15.4 g, 71.9 mmol) and I_2 (12.2 g, 48.1 mmol) were added portionwise at 0 °C after which H_2SO_4 (21 mL) was added dropwise while maintaining a temperature of 0−5 °C. Bromotoluene (23.1 g, 135 mmol) was added portionwise at 0 °C, and after 2 h the resulting mixture was allowed to warm to room temperature and stir overnight. The reaction mixture was poured into 10% $NaHCO_3$ (aq) (200 mL) and ice (250 g) and extracted with methylene chloride (3×). The combined organics were washed with water (3×), dried with $MgSO_4$, and filtered, and the solvent was removed under reduced pressure to provide a reddish oil that was further purified by vacuum distillation (92 °C at 1 mmHg) yielding 30 g (10 mmol, 66%) of 4-bromo-2-iodotoluene as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 2H), 7.34 (d, 2H, J = 8.1 Hz), 7.08 (d, 2H, J = 8.1 Hz), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 131.3, 130.8, 119.6, 101.5, 27.8; HRMS (EI) m/z calcd for C_7H_6BrI [M^+] 295.8698, found 295.8696

*5-Bromo-1-(bromomethyl)-2-iodobenzene (**2a**).* A solution of 5-bromo-2-iodotoluene (6.75 g, 22.7 mmol) and 1,2-dichloroethane (25 mL) was stirred at room temperature in a 50 mL two neck round-bottom under nitrogen. Benzoyl peroxide (281 mg, 1.14 mmol) and NBS (4.5 g, 25 mmol) were added at once, and the resulting mixture was heated to reflux and irradiated with a 250 W incandescent flood lamp (12 in away from round-bottom) for 5 h. The reaction mixture was allowed to cool to room temperature after which precipitates were filtered off and rinsed with hexane. The filtrate was dried with $MgSO_4$ and filtered, and the solvent was removed under reduced pressure to provide an orange solid that was then rinsed with cold methanol, yielding 3.99 g (10.6 mmol, 47%) of an off-white solid that was used without further purification. Characterization data matched that found in literature.[38]

*4-Bromo-1-(bromomethyl)-2-iodobenzene (**2b**).* A solution of 4-bromo-2-iodotoluene (3.94 g, 13.3 mmol) and 1,2-dichloroethane (19 mL) was stirred at room temperature in a 50 mL two neck round-bottom under nitrogen. Benzoyl peroxide (164 mg, 0.663 mmol) and NBS (2.63 g, 14.6 mmol) were added at once, and the resulting mixture was heated to reflux for 5 h. The reaction mixture was allowed to cool to room temperature after which precipitates were filtered off and washed with hexane. The filtrate was dried with $MgSO_4$ and filtered, and the solvent was removed under reduced pressure to provide an orange solid that was then rinsed with cold methanol, yielding 3.27 g (8.75 mmol, 66%) of an off-white solid that was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, 1H, J = 2.0 Hz), 7.47 (dd, 1H, J = 8.3, 2.0 Hz), 7.33 (d, 1H, J = 8.3 Hz), 4.54 (s, 2H); HRMS (EI) m/z calcd for $C_7H_5Br_2I$ [M^+] 377.7762, found 377.7759.

*5-Bromo-2-iodobenzyltriphenylphosphonium Bromide (**3a**).* A solution of benzyl bromide **2a** (3.74 g, 9.96 mmol) in DMF (10 mL) was stirred at room temperature in a dried 25 mL round-bottom under nitrogen. Triphenyl phosphine (2.9 g, 11 mmol) was added portionwise at room temperature, and the resulting reaction mixture was allowed to stir overnight. After 18 h, the reaction mixture was poured into toluene and the resulting suspension was filtered. The solid was added to diethyl ether rinsing with a minimal amount of DCM as necessary. The resulting suspension was filtered yielding 6.18 g (9.68 mmol, 97%) of **3a** as an off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (m, 15H), 7.53 (m, 2H), 7.10 (dt, 1H, J = 8.4, 2.4 Hz), 5.84 (d, 2H, J = 14.5 Hz); HRMS (FAB) m/z calcd for $C_{25}H_{20}BrIP$ [M^+-^{79}Br] 556.9531, found 556.9527.

*4-Bromo-2-iodobenzyltriphenylphosphonium Bromide (**3b**).* A solution of benzyl bromide **2b** (2.42 g, 6.45 mmol) in DMF (6 mL) was stirred at room temperature in a dried 25 mL round-bottom under nitrogen. Triphenyl phosphine (1.9 g, 7.1 mmol) was added portionwise at room temperature, and the resulting reaction mixture was allowed to stir overnight. After 18 h, the reaction mixture was poured into toluene, and the resulting suspension was filtered. The solid was added to diethyl ether, rinsing with a minimal amount of DCM as necessary. The resulting suspension was filtered, yielding 3.73 g (5.85 mmol, 91%) of **3b** as an off-white solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.87 (m, 4H), 7.69 (m, 12H), 7.37 (m, 2H), 5.55 (d, 2H, J = 14.3 Hz); HRMS (FAB) m/z calcd for $C_{25}H_{20}BrIP$ [M^+ − ^{79}Br] 556.9531, found 556.9535.

*5-Bromo-2-iodobenzaldehyde (**4a**).* A solution of *N*-methyl morpholine-*N*-oxide (870 mg, 7.2 mmol) and 4 Å sieves (5.8 g) in acetonitrile (18 mL) in a dried 250 mL Schlenk flask under nitrogen was cooled to 0 °C, and benzyl bromide **2a** (880 mg, 2.3 mmol) was added at once. The reaction mixture was held at 0 °C for 2 h before warming to room temperature. The reaction mixture was then filtered through a short plug (SiO_2, hexane) to yield 761 mg (2.44 mmol, 99%) of **4a** as an off-white solid. Characterization data matches that found in literature.[39]

*4-Bromo-2-iodobenzaldehyde (**4b**).* A solution of *N*-methyl morpholine-*N*-oxide (2.81 g, 23.2 mmol) and 4 Å sieves (19 g) in acetonitrile (60 mL) in a dried 250 mL Schlenk flask under nitrogen was cooled to 0 °C, and benzyl bromide **2b** (2.9 g, 7.7 mmol) was added at once. The reaction mixture was held at 0 °C for 2 h before warming to room temperature. The reaction mixture was then filtered through a short plug (SiO_2, hexane) to yield 2.15 g (6.92 mmol, 90%) of **4b** as an off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.13 (d, 1H, J = 0.8 Hz), 7.73 (dd, 1H, J = 8.3, 0.8 Hz), 7.61 (dd, 1H, J = 8.3, 0.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 142.8, 134.1, 132.3, 131.1, 130.2, 100.9; HRMS (EI) m/z calcd for C_7H_4BrIO [M^+] 309.8490, found 309.8489.

*(Z)-1,2-Bis(5-bromo-2-iodophenyl)ethene (**5a**).* A solution of phosphonium salt **3a** (3.84 g, 6.02 mmol) in THF (60 mL) was cooled to 0 °C in a 250 mL Schlenk flask under nitrogen with stirring. Potassium *tert*-butoxide (815 mg, 7.12 mmol) was added portionwise, and the resulting mixture was held at 0 °C for 30 min. A solution of benzaldehyde **4a** (1.7 g, 5.5 mmol) in THF (60 mL) was added dropwise at 0 °C, and the reaction was allowed to warm to room temperature and left stirring for 24 h. The reaction mix was partitioned between 1:1 water/diethyl ether. The aqueous layer was removed and extracted with diethyl ether (3×), the organics were dried with $MgSO_4$ and filtered, and the solvent was removed under reduced pressure to provide an off-white solid that

was further purified by a short plug (SiO_2, 10% ethyl acetate in hexane) to yield 2.95 g (4.99 mmol, 91%) 82:18 *Z*:*E* of **5a** as an off-white solid that was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, 2H, J = 8.4 Hz), 7.05 (dd, 2H, J = 8.4, 2.4 Hz), 7.02 (d, 2H, J = 2.4 Hz), 6.58 (s, 2H); HRMS (FAB) m/z calcd for $C_{14}H_8Br_2I_2$ [M^+] 587.7082, found 587.7067.

*(Z)-1,2-Bis(4-bromo-2-iodophenyl)ethene (**5b**).* A solution of phosphonium salt **3b** (2.96 g, 4.64 mmol) in THF (42 mL) was cooled to 0 °C in a 100 mL Schlenk flask under nitrogen with stirring. Potassium *tert*-butoxide (628 mg, 5.49 mmol) was added portionwise, and the resulting mixture was held at 0 °C for 30 min. A solution of benzaldehyde **4b** (1.31 g, 4.22 mmol) in THF (40 mL) was added dropwise at 0 °C, and the reaction was allowed to warm to room temperature and left stirring for 24 h. The reaction mix was partitioned between 1:1 water/diethyl ether. The aqueous layer was removed and extracted with diethyl ether (3×), the organics were dried with $MgSO_4$ and filtered, and the solvent was removed under reduced pressure to provide an off-white solid that was further purified by a short plug (SiO_2, 5% ethyl acetate in hexane) to yield 2.34 g (3.98 mmol, 94%) 85:15 *Z*:*E* of **5b** as an off-white solid that was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, 2H, J = 2.0 Hz), 7.21 (dd, 2H, J = 8.3, 2.0 Hz), 6.73 (d, 2H, J = 8.3 Hz), 6.55 (s, 2H); HRMS (FAB) m/z calcd for $C_{14}H_8Br_2I_2$ [M^+] 587.7082, found 587.7087.

*2,8-Dibromo-5,5-dimethyldibenzo[b,f]stannepin (**6a**).* A solution of **5a** (1.51 g, 2.05 mmol) in diethyl ether (70 mL) was cooled to −78 °C in a 200 mL Schlenk flask under nitrogen with stirring. A solution of *n*-butyl lithium in hexanes (1.73 M, 2.61 mL, 4.52 mmol) was added dropwise, and the resulting mixture was held at −78 °C for 10 min followed by the addition of TMEDA (525 mg, 4.52 mmol). The reaction mixture was held at −78 °C for 2 h after which a solution of dimethyltin dichloride (451 mg, 2.05 mmol) in THF (5 mL) was added dropwise. The resulting mixture was allowed to warm to room temperature and left to stir for 18 h. The reaction mixture was partitioned between 1:1 water/diethyl ether. The aqueous layer was removed and extracted with diethyl ether (3×), and the organics were washed with 0.2 M HCl (1×) and water (1×). The combined organics were dried with $MgSO_4$ and filtered, and the solvent was removed under reduced pressure to provide a yellow oil that was further purified by column chromatography (SiO_2, hexane) to yield 476 mg (0.982 mmol, 60%) of **6a** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, 2H, J = 1.7 Hz), 7.38 (dd, 2H, J = 7.8, 1.7 Hz), 7.29 (d, 2H, J = 7.8 Hz), 6.84 (s, 2H), 0.51 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 140.3, 136.1, 134.0, 131.9, 130.3, 123.3, −11.3; HRMS (FAB) m/z calcd for $C_{16}H_{15}Br_2Sn$ [MH^+] 484.8536, found 484.8553.

*3,7-Dibromo-5,5-dimethyldibenzo[b,f]stannepin (**6b**).* A solution of **5b** (501 mg, 0.848 mmol) in diethyl ether (42 mL) was cooled to −78 °C in a 100 mL Schlenk flask under nitrogen with stirring. A solution of *n*-butyl lithium in hexanes (1.73 M, 1.1 mL, 1.9 mmol) was added dropwise, and the resulting mixture was held at −78 °C for 10 min followed by the addition of TMEDA (0.217 mg, 1.86 mmol). The reaction mixture was held at −78 °C for 2 h after which a solution of dimethyltin dichloride (187 mg, 0.848 mmol) in THF (5 mL) was added dropwise. The resulting mixture was allowed to warm to room temperature and left to stir for 18 h. The reaction mixture was partitioned between 1:1 water/diethyl ether. The aqueous layer was removed and extracted with diethyl ether (3×), and the organics were washed with 0.2 M HCl (1×) and water (1×). The combined organics were dried with $MgSO_4$ and filtered, and the solvent was removed under reduced pressure to provide a yellow oil that was further purified by column chromatography (SiO_2, hexane) to yield 254 mg (0.525 mmol, 73%) of **6b** as a white solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.56 (d, 2H, J = 2.2 Hz), 7.41 (dd, 2H, J = 8.3, 2.2 Hz), 7.19 (d, 2H, 8.3 Hz), 6.86 (s, 2H), 0.54 (s, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 145.0, 142.4, 137.5, 134.1, 131.9, 131.3, 123.1, −11.0; HRMS (FAB) m/z calcd for $C_{16}H_{15}Br_2Sn$ [MH^+] 484.8536, found 484.8526.

*2,8-Di(thiophen-2-yl)-5-(2,4,6-tri-tert-butylphenyl)dibenzo[b,f]borepin (**7a**).* A solution of borepin **1a** (28 mg, 0.047 mmol) and $Pd(PPh_3)_4$ (3.0 mg, 0.026 mmol) in DMF (1.5 mL) was stirred in a dry 25 mL Schlenk tube under nitrogen. 2-Tributylstannyl thiophene (55 mg, 0.14 mmol) was added dropwise, and the resulting mixture was heated to 80 °C for 18 h. Upon cooling, the reaction was diluted with diethyl ether and stirred vigorously with KF (2×). The filtered organic layer was then partitioned between 1:1 water/diethyl ether. The aqueous layer was removed and extracted with diethyl ether (3×), and the organics were washed with brine (2×). The combined organics were dried with $MgSO_4$ and filtered, and the solvent was removed under reduced pressure to provide a yellow oil that was further purified by column chromatography (SiO_2, 1% ethyl acetate in hexane) to yield 15 mg (0.025 mmol, 53%) of **7a** as an off-white solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.99 (d, 2H, J = 7.9 Hz), 7.92 (d, 2H, J = 1.6 Hz), 7.61 (dd, 2H, J = 8.2, 1.9 Hz), 7.52 (m, 4H), 7.39 (dd, 2H, J = 5.1, 1.0 Hz), 7.27 (s, 2H), 7.14 (m, 2H), 1.45 (s, 9H), 1.00 (s, 18H); MS (FAB) m/z calcd for $C_{40}H_{43}BS_2$ [M^+] 598.3, found 598.3.

*2,8-Di([2,2′-bithiophen]-5-yl)-5-(2,4,6-tri-tert-butylphenyl)dibenzo-[b,f]borepin (**7b**).* A solution of borepin **1a** (32.8 mg, 0.0554 mmol) and $Pd(PPh_3)_4$ (3.2 mg, 0.0028 mmol) in DMF (1.5 mL) was stirred in a dry 25 mL Schlenk tube under nitrogen. 2-Tributylstannyl thiophene (73 mg, 0.16 mmol) was added dropwise, and the resulting mixture was heated to 80 °C for 18 h. Upon cooling, the reaction was diluted with diethyl ether and stirred vigorously with KF (2×). The filtered organic layer was then partitioned between 1:1 water/diethyl ether. The aqueous layer was removed and extracted with diethyl ether (3×), and the organics were washed with brine (2×). The combined organics were dried with $MgSO_4$ and filtered, and the solvent was removed under reduced pressure to provide an orange solid that was further purified by rinsing with methanol to yield 31 mg (0.041 mmol, 73%) of **7b** as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, 2H, J = 8.1 Hz), 7.87 (d, 2H, J = 1.8 Hz), 7.60 (dd, 2H, J = 8.1, 1.8 Hz), 7.52 (s, 2H), 7.41 (d, 2H, J = 3.8 Hz), 7.25 (m, 4H), 7.21 (d, 2H, J = 3.8 Hz), 7.08 (m, 4H), 1.47 (s, 9H), 1.02 (s, 18H); HRMS (FAB) m/z calcd for $C_{48}H_{47}BS_4$ [M^+] 762.2654, found 762.2674.

*2,8-Bis(phenylethynyl)-5-(2,4,6-tri-tert-butylphenyl)dibenzo[b,f]-borepin (**7d**).* A solution of borepin **1a** (30 mg, 0.05 mmol), CuI (1 mg, 0.005 mmol) and $Pd(PPh_3)_4$ (2.9 mg, 0.0025 mmol) in toluene (1 mL) and DIPA (0.2 mL) was stirred in a dried 25 mL Schlenk flask under nitrogen. Phenyl acetylene (14 mg, 0.13 mmol) was added dropwise at room temperature, and the resulting reaction mixture was heated to 75 °C for 18 h. The reaction mixture was allowed to cool to room temperature after which it was partitioned between water and diethyl ether and washed with NH_4Cl (2×) and brine (2×). The aqueous layer was removed and extracted with diethyl ether (3×), the combined organics were dried with $MgSO_4$ and filtered, and the solvent was removed under reduced pressure to provide a brown solid that was further purified by column chromatography (SiO_2, 1% ethyl acetate in hexane) to yield 18.2 mg (0.0287 mmol, 56%) of **7d** as an off-white solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.99 (d, 2H, J = 8.0 Hz), 7.85 (s, 2H), 7.58 (m, 4H), 7.54 (s, 2H), 7.49 (d, 2H, J = 8.0 Hz), 7.39 (m, 6H), 7.21 (s, 2H), 1.45 (s, 9H), 0.99 (s, 18H); HRMS (FAB) m/z calcd for $C_{48}H_{47}B$ [M^+] 634.3771, found 634.3784.

*3,7-Di(thiophen-2-yl)-5-(2,4,6-tri-tert-butylphenyl)dibenzo[b,f]-borepin (**7e**).* A solution of borepin **1b** (7.8 mg, 0.013 mmol) and $Pd(PPh_3)_4$ (1.0 mg, 0.0009 mmol) in DMF (1 mL) was stirred in a dry 25 mL Schlenk tube under nitrogen. 2-Tributylstannyl thiophene (21 mg, 0.056 mmol) was added dropwise, and the resulting mixture was heated to 80 °C for 18 h. Upon cooling, the reaction was diluted with diethyl ether and stirred vigorously with KF (2×). The filtered organic layer was then partitioned between 1:1 water/diethyl ether. The aqueous layer was removed and extracted with diethyl ether (3×), and the organics were washed with brine (2×). The combined organics were

dried with $MgSO_4$ and filtered, and the solvent was removed under reduced pressure to provide a yellow solid that was further purified by column chromatography (SiO_2, 5% ethyl acetate in hexane) to yield 7.9 mg (0.013 mmol, quant) of **7e** as an off-white solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.30 (d, 2H, J = 2.2 Hz), 7.85 (dd, 2H, J = 8.2, 2.2 Hz), 7.68 (d, 2H, J = 8.2 Hz), 7.58 (s, 2H), 7.24 (dd, 2H, J = 5.1, 1.1 Hz), 7.20 (m, 4H), 7.03 (dd, 2H, J = 5.1, 3.6 Hz), 1.48 (s, 9H), 0.97 (s, 18H); HRMS (FAB) m/z calcd for $C_{40}H_{43}BS_2$ [M^+] 598.2899, found 598.2906.

*3,7-Di([2,2′-bithiophen]-5-yl)-5-(2,4,6-tri-tert-butylphenyl)dibenzo-[b,f]borepin (**7f**).* A solution of borepin **1a** (11.2 mg, 0.0189 mmol) and $Pd(PPh_3)_4$ (1.5 mg, 0.051 mmol) in DMF (1 mL) was stirred in a dry 25 mL Schlenk tube under nitrogen. 2-Tributylstannyl thiophene (38 mg, 0.083 mmol) was added dropwise, and the resulting mixture was heated to 80 °C for 18 h. Upon cooling, the reaction was diluted with diethyl ether and stirred vigorously with KF (2×). The filtered organic layer was then partitioned between 1:1 water/diethyl ether. The aqueous layer was removed and extracted with diethyl ether (3×), and the organics were washed with brine (2×). The combined organics were dried with $MgSO_4$ and filtered, and the solvent was removed under reduced pressure to provide an orange solid that was further purified by rinsing with methanol to yield 8.0 mg (0.01 mmol, 56%) of **7f** as an orange solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.29 (d, 2H, J = 2.1 Hz), 7.84 (dd, 2H, J = 8.2, 2.1 Hz), 7.70 (d, 2H, J = 8.2 Hz), 7.61 (s, 2H), 7.152 (m, 12H), 1.51 (s, 9H), 1.01 (s, 18H); HRMS (FAB) m/z calcd for $C_{48}H_{47}BS_4$ [M^+] 762.2654, found 762.2670.

*3,7-Bis(4-methoxyphenyl)-5-(2,4,6-tri-tert-butylphenyl)dibenzo-[b,f]borepin (**7g**).* A solution of borepin **1b** (13.2 mg, 0.0223 mmol), 4-methoxyphenyl boronic acid (11 mg, 0.072 mmol), Na_2CO_3 (24.4 mg, 0.231 mmol) and $Pd(PPh_3)_4$ (1.6 mg, 0.0014 mmol) in toluene (1 mL), water (0.3 mL) and ethanol (0.3 mL) was stirred in a 5 mL round-bottom equipped with a reflux condenser under nitrogen. The resulting mixture was heated to reflux for 18 h after which it was allowed to cool to room temperature. The reaction mixture was partitioned between water and diethyl ether and washed with NH_4Cl (2×) and brine (2×). The aqueous layer was removed and extracted with diethyl ether (3×), the combined organics were dried with $MgSO_4$ and filtered, and the solvent was removed under reduced pressure to provide a brown solid that was further purified by column chromatography (SiO_2, 5% ethyl acetate in hexane) to yield 11.3 mg (0.0175 mmol, 79%) of **7g** as an off-white solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.25 (d, 2H, J = 2.1 Hz), 7.84 (dd, 2H, J = 8.2, 2.1 Hz), 7.73 (d, 2H, J = 8.2 Hz), 7.55 (s, 2H), 7.41 (d, 4H, J = 8.8 Hz), 7.23 (s, 2H), 6.89 (d, 4H, J = 8.8 Hz), 1.46 (s, 9H), 0.98 (s, 18H); HRMS (FAB) m/z calcd for $C_{46}H_{51}BO_2$ [M^+] 646.3982, found 646.4002.

*3,7-Bis(phenylethynyl)-5-(2,4,6-tri-tert-butylphenyl)dibenzo[b, f]borepin (**7h**).* A solution of borepin **1b** (40.2 mg, 0.0679 mmol), CuI (1.3 mg, 0.0068 mmol) and $Pd(PPh_3)_4$ (3.9 mg, 0.0034 mmol) in toluene (1.5 mL) and DIPA (0.3 mL) was stirred in a dried 25 mL Schlenk flask under nitrogen. Phenyl acetylene (15.2 mg, 0.149 mmol) was added dropwise at room temperature, and the resulting reaction mixture was heated to 75 °C for 18 h. The reaction mixture was allowed to cool to room temperature after which it was partitioned between water and diethyl ether and washed with NH_4Cl (2×) and brine (2×). The aqueous layer was removed and extracted with diethyl ether (3×), the combined organics were dried with $MgSO_4$ and filtered, and the solvent was removed under reduced pressure to provide a brown oil/solid that was purified by column chromatography (SiO_2, 2% ethyl acetate in hexane) to yield **7h** (0.022 mmol, 33% by NMR) and stannepin **6b** as an off-white solid. The mixture was further purified by dissolving in toluene (1 mL) and treating with dichlorophenylborane (0.05 mL) followed by repeating the aqueous workup. The resulting residue was purified by column chromatography (SiO_2, hexane) to yield 5.1 mg of **7h** (0.008 mmol, 11%) as an off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, 2H, J = 1.7 Hz), 7.69 (dd, 2H, J = 8.1, 1.7 Hz), 7.61 (d, 2H, J = 8.1 Hz), 7.53 (s, 2H), 7.46 (m, 4H), 7.32 (m, 6H), 7.18 (s, 2H), 1.46 (s, 9H), 1.00 (s, 18H); HRMS (FAB) m/z calcd for $C_{48}H_{47}B$ [M^+] 634.3771, found 634.3780.

*2,8-Bis(diphenylamino)-5-(2,4,6-tri-tert-butylphenyl)dibenzo[b,f]-borepin (**7i**).* A solution of borepin **1a** (19.4 mg, 0.0328 mmol), diphenylamine (13.6 mg, 0.0786 mmol), NaO^tBu (9.1 mg, 0.092 mmol), $Pd_2(dba)_3$ (0.95 mg, 0.0016 mmol) and P(*o*-tolyl)$_3$ (1.1 mg, 0.0033 mmol) in toluene (1 mL) was stirred in a dried 25 mL Schlenk flask under nitrogen, and the resulting reaction mixture was heated to 100 °C for 18 h. The reaction mixture was allowed to cool to room temperature after which it was partitioned between water and diethyl ether and washed with brine (2×). The aqueous layer was removed and extracted with diethyl ether (3×), the combined organics were dried with $MgSO_4$ and filtered, and the solvent was removed under reduced pressure to provide a orange solid that was further purified by rinsing with MeOH to yield 15 mg (0.019 mmol, 60%) of **7i** as tan solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.72 (d, 2H, J = 8.6 Hz), 7.45 (s, 2H), 7.30 (t, 8H, J = 7.8 Hz), 7.14 (m, 16H), 6.91 (dd, 2H, J = 8.6, 2.3 Hz), 6.79 (s, 2H), 1.37 (s, 9H), 1.02 (s, 18H); HRMS (FAB) m/z calcd for $C_{56}H_{57}BN_2$ [M^+] 768.4615, found 768.4616.

*2,8-Dicarboxylic Acid-5-(2,4,6-tri-tert-butylphenyl)dibenzo[b,f]borepin (**7j**).* A solution of **1a** (41.9 mg, 0.0601 mmol) in THF (1 mL) was cooled to −78 °C in a 25 mL Schlenk flask under nitrogen with stirring. A solution of *sec*-butyl lithium in hexanes (1.4 M, 0.152 mL, 0.213 mmol) was added dropwise, and the resulting mixture was held at −78 °C for 30 min after which excess solid CO_2 was added. The resulting mixture was allowed to warm to room temperature and left to stir for 18 h. The reaction mixture was diluted with hexane and filtered, rinsing with copious amounts of hexane to yield 18 mg (0.034 mmol, 57%) of **7j** as an off-white solid. ^{1}H NMR (400 MHz, DMSO) δ 13.3 (s, 2H), 8.35 (d, 2H, J = 1.1 Hz), 8.00 (d, 2H, J = 1.1 Hz), 7.93 (dd, 2H, J = 8.1, 1.1 Hz), 7.51 (s, 2H), 7.44 (s, 2H), 1.40 (s, 9H), 0.91 (s, 18H); HRMS (FAB) m/z calcd for $C_{34}H_{39}BO_4$ [M^+] 522.2941, found 522.2951.

*3,7-Dicarboxylic Acid-5-(2,4,6-tri-tert-butylphenyl)dibenzo[b,f]borepin (**7k**).* A solution of **1b** (12.1 mg, 0.0204 mmol) in THF (1 mL) was cooled to −78 °C in a 25 mL Schlenk flask under nitrogen with stirring. A solution of *sec*-butyl lithium in hexanes (1.4 M, 0.05 mL, 0.07 mmol) was added dropwise and the resulting mixture was held at −78 °C for 30 min after which excess solid CO_2 was added. The resulting mixture was allowed to warm to room temperature and left to stir for 18 h. The reaction mixture was diluted with hexane and filtered, rinsing with copious amounts of hexane to yield 7.6 mg (0.014 mmol, 71%) of **7k** as an off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, 2H, J = 1.3 Hz), 8.03 (dd, 2H, J = 7.5, 1.1 Hz), 7.57 (d, 2H, J = 8.5 Hz), 7.44 (s, 2H), 7.22 (s, 2H), 1.40 (s, 9H), 0.96 (s, 18H); MS (FAB) m/z calcd for $C_{34}H_{39}BO_4$ [M^+] 522.3, found 522.3.

*2,8-Bis(trimethylsilylethynyl)-5-(2,4,6-tri-tert-butylphenyl)dibenzo-[b,f]borepin (**para bis(TMS acetylene) DBB**).* A solution of borepin **1a** (125 mg, 0.179 mmol), CuI (3.4 mg, 0.018 mmol) and $Pd(PPh_3)_4$ (10 mg, 0.009 mmol) in toluene (2 mL) and DIPA (0.4 mL) was stirred in a dried 25 mL Schlenk flask under nitrogen. TMS acetylene (39.6 mg, 0.395 mmol) was added dropwise at room temperature, and the resulting reaction mixture was heated to 45 °C for 18 h. The reaction mixture was allowed to cool to room temperature after which it was partitioned between water and diethyl ether and washed with NH_4Cl (2×) and brine (2×). The aqueous layer was removed and extracted with diethyl ether (3×), the combined organics were dried with $MgSO_4$ and filtered, and the solvent was removed under reduced pressure to provide a brown oil that was further purified by column chromatography (SiO_2, hexane) to yield 109 mg (0.175 mmol, 56%) of ***para* bis(TMS acetylene) DBB** as an off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, 2H, J = 8.0 Hz), 7.73 (s, 2H), 7.47 (s, 2H), 7.38 (d, 2H, J = 8.0 Hz), 7.09 (s, 2H), 1.43 (s, 9H), 0.92 (s, 18H), 0.27 (s, 18H); HRMS (FAB) m/z calcd for $C_{42}H_{55}BSi_2$ [M^+] 626.3935, found 626.3927.

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*3,7-Bis(trimethylsilylethynyl)-5-(2,4,6-tri-tert-butylphenyl)dibenzo-[b,f]borepin (**meta bis(TMS acetylene) DBB**).* A solution of borepin **1a** (34 mg, 0.057 mmol), CuI (1.1 mg, 0.0057 mmol) and $Pd(PPh_3)_4$ (3.3 mg, 0.0029 mmol) in toluene (1.5 mL) and DIPA (0.3 mL) was stirred in a dried 25 mL Schlenk flask under nitrogen. TMS acetylene (12.7 mg, 0.126 mmol) was added dropwise at room temperature, and the resulting reaction mixture was heated to 45 °C for 18 h. The reaction mixture was allowed to cool to room temperature after which it was partitioned between water and diethyl ether and washed with NH_4Cl (2×) and brine (2×). The aqueous layer was removed and extracted with diethyl ether (3×), the combined organics were dried with $MgSO_4$ and filtered, and the solvent was removed under reduced pressure to provide a brown oil that was further purified by column chromatography (SiO_2, hexane) to yield 23 mg (0.037 mmol, 64%) of ***meta* bis(TMS acetylene) DBB** as an off-white solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.04 (d, 2H, J = 1.6 Hz), 7.59 (m, 6H), 7.19 (s, 2H), 1.47 (s, 9H), 0.98 (s, 18H), 0.19 (s, 18H); HRMS (FAB) m/z calcd for $C_{42}H_{55}BSi_2$ [M^+] 626.3935, found 626.3927.

*2,8-Diethynyl-5-(2,4,6-tri-tert-butylphenyl)dibenzo[b,f]borepin (**para diethynyl DBB**).* A solution of borepin ***para* bis(TMS acetylene) DBB** (103 mg, 0.165 mmol) and potassium carbonate (91 mg, 0.66 mmol) in 3 mL of a 1:1 methanol/THF solution was stirred at room temperature for 4 h. The reaction mixture was partitioned between NH_4Cl and diethyl ether and washed with NH_4Cl (1×), brine (2×). The aqueous layer was removed and extracted with diethyl ether (2×), the combined organics were dried with $MgSO_4$ and filtered, and the solvent was removed under reduced pressure to yield 79 mg (0.165 mmol, quant) of the ***para* diethynyl DBB** as a pale yellow solid that was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, 2H, J = 8.0 Hz), 7.76 (d, 2H, J = 1.6 Hz), 7.47 (s, 2H), 7.40 (s, 2H), 7.11 (s, 2H), 3.20 (s, 2H), 1.43 (s, 9H), 0.93 (s, 18H).

*3,7-Diethynyl-5-(2,4,6-tri-tert-butylphenyl)dibenzo[b,f]borepin (**meta diethynyl DBB**).* A solution of borepin ***meta* bis(TMS acetylene) DBB** (22 mg, 0.035 mmol) and potassium carbonate (19 mg, 0.14 mmol) in 2 mL of a 1:1 methanol: THF solution was stirred at room temperature for 4 h. The reaction mixture was partitioned between NH_4Cl and diethyl ether and washed with NH_4Cl (1×), brine (2×). The aqueous layer was removed and extracted with diethyl ether (2×), the combined organics were dried with $MgSO_4$ and filtered, and the solvent was removed under reduced pressure to yield 17 mg (0.035 mmol, quant) of the ***meta* diethynyl DBB** as a pale yellow solid that was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, 2H, J = 1.7 Hz), 7.65 (dd, 2H, J = 8.0, 1.7 Hz), 7.57 (d, 2H, J = 8.0), 7.48 (s, 2H), 7.16 (s, 2H), 3.06 (s, 2H), 1.44 (s, 9H), 0.97 (s, 18H).

*para Polymer (**8a**).* A solution of 1,4-bis(decyloxy)-2,5-diiodobenzene (106.5 mg, 0.165 mmol), CuI (3.2 mg, 0.017 mmol) and $Pd(PPh_3)_4$ (9.6 mg, 0.0083 mmol) in toluene (1 mL) and DIPA (0.4 mL) was stirred in a dried 25 mL Schlenk flask under nitrogen. The ***para* diethynyl DBB** (prepared above, 79 mg, 0.165 mmol) in toluene (1 mL) was added dropwise at room temperature and the resulting reaction mixture was heated to 75 °C for 18 h. The reaction mixture was allowed to cool to room temperature after which it was precipitated into 30 mL of stirring methanol. The resulting solid was collected by vacuum filtration and rinsed with methanol to yield 136 mg (0.156 mmol, 94%) of **8a** as an orange solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.98 (m, 2H), 7.80 (m, 2H), 7.50 (d, 2H, J = 1.7 Hz), 7.47 (m, 2H), 7.14 (d, 2H, J = 3.0 Hz), 7.05 (s, 2H), 4.03 (m, 4H), 1.86 (m, 4H), 1.45 (s, 9H), 1.39 (m, 4H), 1.25 (m, 24H), 0.97 (s, 18H), 0.85 (s, 6H). M_n = 7190.

*meta Polymer (**8b**).* A solution of 1,4-bis(decyloxy)-2,5-diiodobenzene (22.6 mg, 0.0352 mmol), CuI (0.7 mg, 0.0035 mmol) and $Pd(PPh_3)_4$ (2.0 mg, 0.002 mmol) in toluene (0.5 mL) and DIPA (0.3 mL) was stirred in a dried 25 mL Schlenk flask under nitrogen. The ***meta* diethynyl DBB** (prepared above, 17 mg, 0.0352 mmol) in toluene (1 mL) was added dropwise at room temperature and the resulting reaction mixture was heated to 75 °C for 18 h. The reaction mixture was allowed to cool to room temperature after which it was precipitated into 30 mL of stirring methanol. The resulting solid was collected by vacuum filtration and rinsed with methanol to yield 27 mg (0.031 mmol, 88%) of **8b** as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 2H), 7.69 (m, 2H), 7.59 (dd, 2H, J = 8.0, 1.3 Hz), 7.51 (m, 2H), 7.18 (m, 2H), 6.89 (m, 2H), 3.94 (m, 4H), 1.77 (m, 4H), 1.45 (m, 13H), 1.25 (m, 24H), 1.02 (s, 18H), 0.87 (m, 6H). M_n = 4390.

■ ASSOCIATED CONTENT

Supporting Information. ^{1}H and ^{13}C NMR spectra for all new compounds, UV−vis and PL spectra, CV data and molecular orbital calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) Wade, C. R.; Broomsgrove, A. E. J.; Aldridge, S.; Gabbaï, F. P. *Chem. Rev.* **2010**, *110*, 3958–84. (b) Jäkle, F. *Chem. Rev.* **2010**, *110*, 3985–4022.

(2) (a) Matsumi, N.; Chujo, Y. *Polym. J.* **2008**, *40*, 77–89. (b) Lin, N.; Zhao, X.; Cheng, X.; Jiang, M. *J. Mol. Struct.: THEOCHEM* **2007**, *820*, 98–106. (c) Entwistle, C. D.; Marder, T. B. *Chem. Mater.* **2004**, *16*, 4574–4585.

(3) (a) Hudnall, T. W.; Chiu, C.-W.; Gabbaï, F. P. *Acc. Chem. Res.* **2009**, *42*, 388–97. (b) Zhou, G.; Baumgarten, M.; Müllen, K. *J. Am. Chem. Soc.* **2008**, *130*, 12477–12484. (c) Hudnall, T. W.; Gabbaï, F. P. *J. Am. Chem. Soc.* **2007**, *129*, 11978–11986.

(4) Yamaguchi, S.; Wakamiya, A. *Pure Appl. Chem.* **2006**, *78*, 1413–1424.

(5) (a) Nagai, A.; Kokado, K.; Nagata, Y.; Chujo, Y. *Macromolecules* **2008**, *41*, 8295. (b) Wakamiya, A.; Mori, K.; Yamaguchi, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 4273–4276. (c) Qin, Y.; Kiburu, I.; Shah, S.; Jäkle, F. *Org. Lett.* **2006**, *8*, 5227–30.

(6) Li, H.; Jäkle, F. *Angew. Chem., Int. Ed.* **2009**, *48*, 2313–2316.

(7) Lorbach, A.; Bolte, M.; Li, H.; Lerner, H-W; Holthausen, M. C.; Jäkle, F.; Wagner, M. *Angew. Chem., Int. Ed.* **2009**, *121*, 4654–4658.

(8) Matsumi, N.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **1998**, *120*, 10776–10777.

(9) Li, H; Sundararaman, A.; Venkatasubbaiah, K; Jäkle, F. *J. Am. Chem. Soc.* **2007**, *129* (18), 5792–5793. (b) Jäkle, F. *J. Inorg. Organomet. Polym. Mater.* **2005**, *15* (3), 293–307.

(10) Liu, X. Y.; Bai, D. R.; Wang, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 5475–5478.

(11) Matsumi, N.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **1998**, *120*, 5112–5113.

(12) Zhao, C. H.; Wakamiya, A.; Inukai, Y.; Yamaguchi, S. *J. Am. Chem. Soc.* **2006**, *128*, 15934–15935.

(13) Noda, T.; Ogawa, H.; Shirota, Y. *Adv. Mater.* **1999**, *11*, 283–285.

(14) (a) Lepeltier, M.; Lukoyanova, O.; Jacobson, A.; Jeeva, S.; Perepichka, D. F. *Chem. Commun* **2010**, *46*, 7007–7009. (b) Bosdet, M. J. D.; Jaska, C. A.; Piers, W. E.; Sorensen, T. S.; Parvez, M. *Org. Lett.* **2007**, *9*, 1395–1398. (c) Bosdet, M. J. D.; Piers, W. E.; Sorensen, T. S.; Parvez, M. *Angew. Chem., Int. Ed.* **2007**, *46* (26), 4940. (d) Jaska, C. A.; Emslie, D. J. H.; Bosdet, M. J. D.; Piers, W. E.; Sorensen, T. S.; Parvez, M. *J. Am. Chem. Soc.* **2006**, *128*, 10885–96.

(15) (a) Rogers, J. S.; Bu, X.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 730–731. (b) Lee, B. Y.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 8577–8578. (c) Hoic, D. A.; DiMare, M.; Fu, G. C. *J. Am. Chem. Soc.* **1997**, *119*, 7155–7156.

(16) (a) Wood, T. K.; Piers, W. E.; Keay, B. A.; Parvez, M. *Chem. Eur. J.* **2010**, *16*, 12199–12206. (b) Metz, M. V.; Schwartz, D. J.; Stern, C. L.; Nickias, P. N.; Marks, T. J. *Angew. Chem., Int. Ed.* **2000**, *39* (7), 1312–1316. (c) Ashe, A. J., III; Fang, X.; Kampf, J. W. *Organometallics* **1999**, *18*, 466–473.

(17) Dewar, M. J. S.; Marr, P. A. *J. Am. Chem. Soc.* **1962**, *84*, 3782.

(18) Ashe, A. J., III; Fang, X.; Fang, X.; Kampf, J. W. *Organometallics* **2001**, *20*, 5413–5418.

(19) (a) Daly, A.; Tanjaroon, C.; Marwitz, A. J. V.; Liu, S.-Y.; Kukolich, S. *J. Am. Chem. Soc.* **2010**, *132*, 5501–5506. (b) Abbey, E. R.; Zakharov, L. N.; Liu, S.-Y. *J. Am. Chem. Soc.* **2008**, *130*, 7250–7252.

(20) Herberich, G. E.; Greiss, G.; Heil, H. F. *Angew. Chem., Int. Ed.* **1970**, *9*, 805–806.

(21) Lee, R. A.; Lachicotte, R. J.; Bazan, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 6037–6046.

(22) Ashe, A. J., III; Fang, X.; Kampf, J. W. *Organometallics* **1999**, *18*, 466–473.

(23) (a) Fan, C.; Piers, W. E.; Parvez, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 2955–2958. (b) Braunschweig, H.; Kupfer, T. *Chem. Commun* **2008**, 4487. (c) Wakamiya, A.; Mishima, K.; Ekawa, K.; Yamaguchi, S. *Chem. Commun* **2008**, 579–581. (d) Yamaguchi, S.; Shirasaka, T.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.* **2002**, *124*, 8816–8817.

(24) Vol'pin, M. E. *Russ. Chem. Rev.* **1960**, *29*, 129–160.

(25) Schulman, J. M.; Disch, R. L. *Organometallics.* **2000**, *19*, 2932–2936.

(26) Subramanian, G.; Schleyer, P. v R.; Jiao, H. *Organometallics* **1997**, *16*, 2362–2369.

(27) Tamelen, E. E. v.; Brieger, G.; Untch, K. G. *Tetrahedron Lett.* **1960**, *8*, 14–15.

(28) Leusink, A. J.; Drenth, W.; Noltes, J. G.; Kerk, G. J. M. v. d. *Tetetrahedron Lett.* **1967**, *14*, 1263–1266.

(29) (a) Ashe, A. J., III; Kampf, J. W.; Nakadaira, Y.; Pace, J. M. *Angew. Chem., Int. Ed.* **1992**, *31* (9), 1255–1258. (b) Ashe, A. J., III; Klein, W.; Rousseau, R. *Organometallics* **1993**, *12*, 3224–3231.

(30) Mercier, L. G.; Piers, W. E.; Parvez, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 6108–6111.

(31) Caruso, A., Jr.; Siegler, M. A.; Tovar, J. D. *Angew. Chem., Int. Ed.* **2010**, *49* (25), 4213–4217.

(32) Mercier, L. G.; Furukawa, S.; Piers, W. G.; Wakamiya, A.; Yamaguchi, S.; Parvez, M.; Harrington, R. W.; Clegg, W. *Organometallics* **2011**, DOI is 10.1021/om2000597.

(33) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587–4589.

(34) Dunne, E. C.; Coyne, E. J.; Crowley, P. B.; Gilheany, D. G. *Tetrahedron Lett.* **2002**, *43*, 2449–2453.

(35) Šterk, D.; Modec, B.; Mohar, B. *J. Org. Chem.* **2007**, *72*, 8010–8018.

(36) Swager, T.; Gil, C. J.; Wrighton, M. S. *J. Phys. Chem.* **1995**, *99*, 4886–4893.

(37) Albota, M.; Beljonne, D.; Brédas, J.-L.; Ehrlich, J. E.; Fu, J.-Y.; Heikal, A. A.; Hess, S. E.; Kogej, T.; Levin, M. D.; Marder, S. R.; McCord-Maughon, D.; Perry, J. W.; Rockel, H.; Rumi, M.; Subramaniam, G.; Webb, W. W.; W. X-L.; Xu, C. *Science* **1998**, *281*, 1653.

(38) Amijs, C. H. M.; Van Klink, G. P. M.; Van Koten, G. *Green Chem.* **2003**, *5*, 470–474.

(39) Zhou, N.; Wang, L.; Thompson, D. W.; Zhao, Y. *Org. Lett.* **2008**, *10*, 3001–3004.