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Investigating the reactivity of 9-phenyl-9-borafluorene with N–H, O–H, P–H, and S–H bonds

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ABSTRACT

The reactions of 9-phenyl-9-borafluorene with N–H, P–H, O–H, and S–H containing substrates were investigated. Protodeborylation reactions were observed for phenol, water, aniline, and para-bromothiophenol. In the water reaction, both O–H bonds reacted with 9-phenyl-9-borafluorene to furnish the oxygen bridged diborane whereas only one of the N–H bonds in aniline reacted. Phenylphosphine coordinated to the boron center to give an adduct that did not react further. The results were compared to the corresponding reactions with the same substrates and pentaphenylborole.

1. Introduction

9-Borafluorenes have garnered attention in recent years due to their potential utility in electronic materials such as organic light emitting diodes (OLEDs) and organic photovoltaic devices [1–7]. The sp^2 hybridized boron atom with a vacant p_z orbital in the 9-position enables conjugation throughout the planar ring system [8–10]. This alters the electronic structure in comparison to its' carbonaceous analogue, fluorene, which bears a sp^3 carbon that disrupts conjugation. Although promising photophysical properties have been reported for 9-borafluorenes, the incorporation of the boron center results in more reactive species, and correspondingly, decreased stability [11–15].

Only a few reports exist in the literature alluding to the relative stability of 9-borafluorenes as manipulations are typically performed in an inert atmosphere. 9-Borafluorenes with bulky aryl substituents on boron have been reported to be air-stable and can even be subjected to flash column chromatography for purification (**A**-**C**, Fig. 1) [11,13,16–20]. In terms of reactivity, Lewis bases readily coordinate to boron [16,19–30] and unsaturated organic molecules can undergo insertion into the endocyclic B–C bond of the central BC_4 ring to give 6- and 7-membered boracycles [31–36].

Although limited, examples exploring the reactivity of 9-borafluorenes with protic sources have been reported. 9-Chloro or 9-bromo-9-borafluorenes (**D**) react with amines and alcohols to furnish the corresponding amino and alkoxy species (**E**) by dehydrohalogen coupling reactions (Fig. 2) [37,38]. In regard to 9-aryl-9-borafluorenes, Rupar and co-workers found that a polymeric variant of **B** reversibly binds ammonia [19]. Hydrolysis studies on the bidentate perfluorinated 9-borafluorene (**F**) indicated that the endocyclic B–C bonds in each is cleaved to generate the boron anhydride **G** [29,39]. Bettinger and coworkers reported the isolation of boroxine **I** from the hydrolysis of 9-azido-9-borafluorene (**H**) [38,40]. Despite the interest in 9-borafluorenes, the literature lacks a study on the reactivity of protic substrates with a 9-borafluorene. In this context, we herein investigate the reactions of 9-phenyl-9-borafluorene with substrates containing E–H bonds (E = N, O, P, and S) as an indicator of the relative stability and reactivity of this species.

2. Results and discussion

The stoichiometric reaction of phenol with 9-phenyl-9-borafluorene (**1**) in CH_2Cl_2 led to an immediate color change from yellow to colorless (Scheme 1) and *in situ* $^{11}B\{^1H\}$ NMR spectroscopy revealed a new signal at 46.0 ppm shifted upfield from **1** (65.0 ppm) [42]. After work up, the FT-IR spectrum of the isolated solid lacked an O-H stretch and the ^1H NMR spectrum in $CDCl_3$ had no

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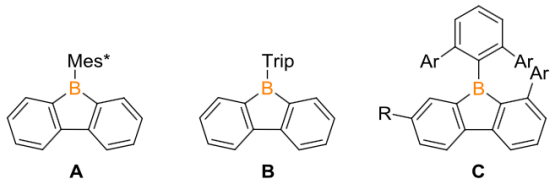


Fig. 1. Air-stable 9-borafluorenes **A-C**. Mes* = 2,4,6-tri(tert-butyl)phenyl; Trip = 2,4,6-triisopropylphenyl; Ar = 4-tertbutylphenyl, R = t-butyl.

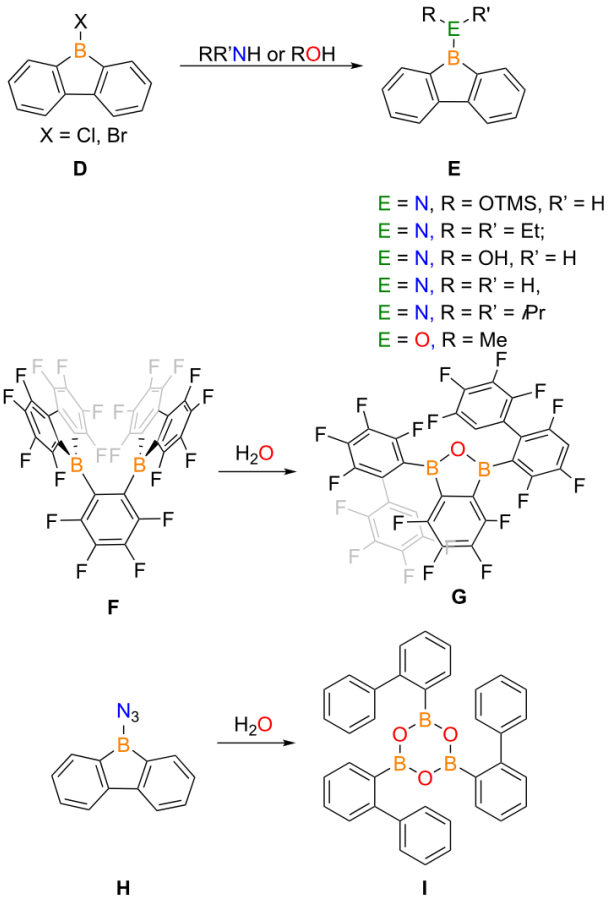
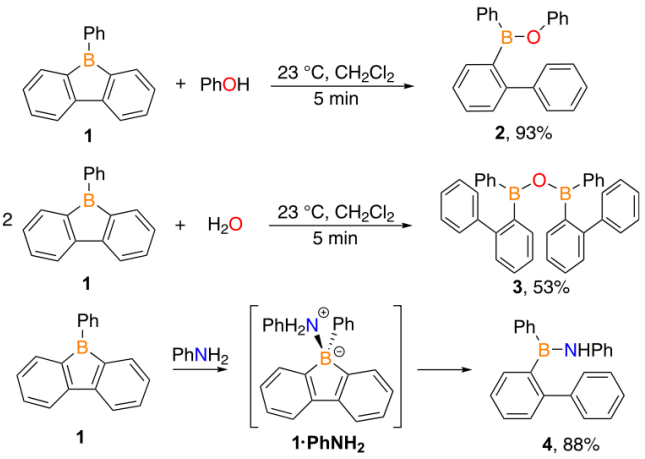


Fig. 2. Reported reactions of 9-X-9-borafluorenes (**D**, X = Cl, Br) with amines and alcohols as well as the hydrolysis of the perfluorinated bidentate 9-borafluorene (**F**) and 9-azido-9-borafluorene (**H**).



Scheme 1. Reactions of **1** with phenol, water, and aniline. Reaction conditions for **4**: 23 °C, CH_2Cl_2, 4 d.

signal corresponding to the O-H moiety of phenol at 5.35 ppm. X-ray diffraction studies corroborated this and identified the compound as the ring opened protodeborylation product (**2**, Fig. 3).

Given the observed protodeborylation with phenol, one equivalent of H_2O was added to two equivalents of **1** in CH_2Cl_2 at room temperature resulting in the instantaneous loss of the characteristic yellow color of **1**. Acquiring an *in situ* $^{11}B\{^1H\}$ NMR spectrum showed a single broad resonance at 46.2 ppm consistent with a three-coordinate boron center and after workup, an FT-IR spectrum of the isolated white solid lacked an O-H stretch (Fig. S-6). The identity of the compound was assigned as diboroxane (**3**) based on single crystal X-ray diffraction, resulting from the protodeborylation of two molecules of **1**. An *in situ* ^1H NMR spectroscopy experiment on the 1:1 reaction of H_2O and **1** in $CDCl_3$ under the same conditions showed only resonances corresponding to diboroxane **3** and excess H_2O with no evidence of a product from only one of the O–H bonds reacting (Fig. S-7).

To examine the reactivity of N–H bonds, the 1:1 reaction of aniline with **1** in $CDCl_3$ was carried out which generated a white slurry (Scheme 1). *In situ* $^{11}B\{^1H\}$ NMR spectroscopy revealed a four-coordinate resonance at 0.4 ppm that converts to a peak in the three-coordinate region at 42.4 ppm after 4 days. The ^1H NMR spectrum showed the disappearance of the NH_2 signal at 3.55 ppm and emergence of a broad singlet at 6.56 ppm (the product is fluxional on the NMR time scale at 27 °C and variable temperature NMR spectroscopy was utilized to resolve the spectrum at −50 °C). The FT-IR spectrum of the isolated solids displayed a peak for an N-H stretch at 3360 cm^{-1} and X-ray diffraction studies confirmed the product as the ring-opened aminoborane (**4**). The observed four-coordinate intermediate at 0.4 ppm by $^{11}B\{^1H\}$ NMR spectroscopy is in the range for reported adducts of **1** (24.6 to −19.1 ppm) [16,21–28]. Therefore, a mechanism is proposed by initial coordination of the nitrogen lone pair to the boron center forming **1·PhNH₂**. Conversion to the three-coordinate peak at 42.4 ppm is rationalized by the nucleophilic endocyclic B–C bond scavenging an acidic proton on the coordinated aniline resulting in ring opening to **4**. The second N–H bond did not react with an additional equivalent of **1** at 23 °C in $CDCl_3$ or at 100 °C in toluene as the $^{11}B\{^1H\}$ and ^1H NMR spectra were consistent with **4** and free **1**.

The reaction of 1-naphthalenethiol with **1** in toluene had no evidence of reaction even after heating to 100 °C for 5 days based on ^1H or $^{11}B\{^1H\}$ NMR spectroscopy (Scheme 2). Monitoring the room temperature reaction with 4-bromothiophenol in $CDCl_3$ by *in situ* ^1H NMR spectroscopy indicated consumption of the S-H resonance (3.44 ppm) after 36 hours. The $^{11}B\{^1H\}$ NMR spectra showed a slight shift from the starting material at 65.0 ppm to 66.0 ppm with no intermediates through the course of the reaction. The FT-IR spectrum lacked the S-H stretch [43] for 4-bromothiophenol at 2600 cm^{-1} and the product was identified as the ring opened species (**5**) (see Table 2 for metrical parameters).

Given that the endocyclic B–C bond in **1** can be cleaved by O–H, N–H, and S–H bonds, this prompted investigation of a P–H bond. The reaction of phenylphosphine and **1** in CH_2Cl_2 led to the instantaneous formation of a white slurry in CH_2Cl_2 (Scheme 2). $^{11}B\{^1H\}$ NMR spectroscopy displayed a resonance at −10.1 ppm, indicative of a four-coordinate center and the ^1H NMR spectrum of the isolated product redissolved in $CDCl_3$ has a doublet at 4.42 ppm ($J_{P\text{-}H}$ = 364 Hz) shifted downfield from the free species

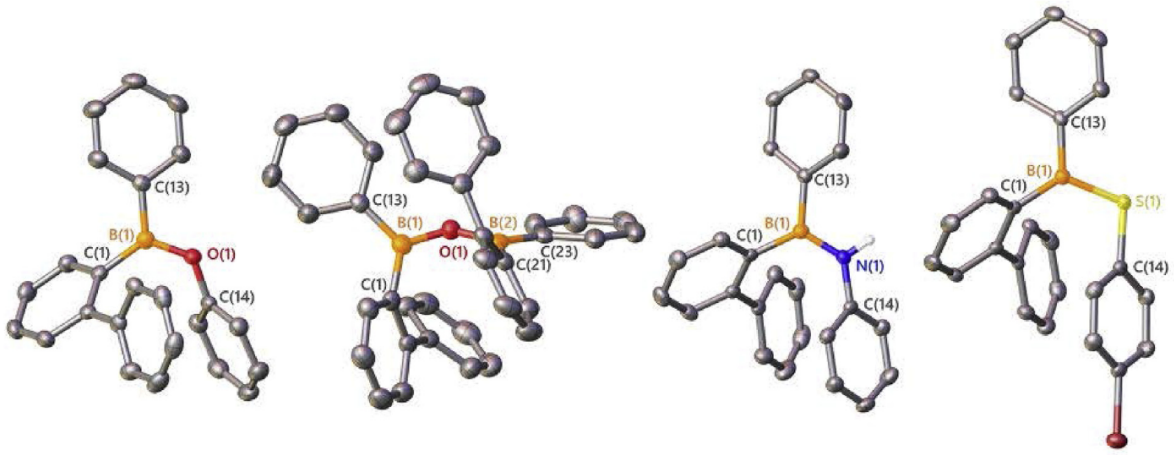
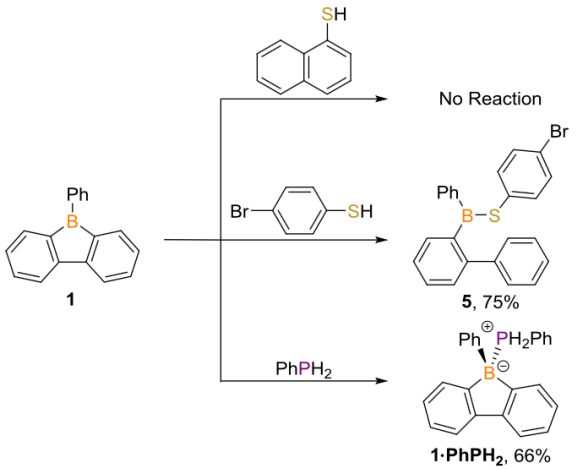


Fig. 3. Solid-state structures of **2**, **3**, **4**, and **5** (left to right). Hydrogen atoms are omitted for clarity and ellipsoids are drawn at the 50% probability level. **2** crystallizes with two molecules in the asymmetric unit, and one representative molecule is shown and discussed as the metrical parameters are comparable.



Scheme 2. Reaction of 1-naphthalenethiol, 4-bromothiophenol, and phenylphosphine with **1**. Reaction conditions for 1-naphthalenethiol: 100 °C, PhMe, 5 d. Reaction conditions for **5**: 23 °C, CH_2Cl_2, 36 h. Reaction conditions for **1·PhPH$_2$**: 23 °C, CH_2Cl_2, 5 min.

Table 1
Bond lengths (Å) and angles (deg) of the borafluorene moiety of **1·PhPH$_2$** and **1**.

Entry	**1·PhPH$_2$**	**1**[3]
B(1)-C(1)	1.618(5)	1.580(10)
C(1)-C(6)	1.413(5)	1.430(10)
C(6)-C(7)	1.477(5)	1.512(11)
C(7)-C(12)	1.409(5)	1.430(9)
C(12)-B(1)	1.625(5)	1.592(10)
B(1)-C(13)	1.614(5)	1.572(9)
C(12)-B(1)-C(1)	99.5(3)	104.2(6)
B(1)-C(1)-C(6)	109.6(3)	108.1(6)
C(1)-C(6)-C(7)	110.5(3)	109.7(6)
C(6)-C(7)-C(12)	110.0(3)	110.8(6)
C(7)-C(12)-B(1)	109.3(3)	107.1(6)

($PhPH_2$ = 3.93 ppm). The lone peak in the ^{31}P NMR spectrum is a triplet at −47.0 ppm, shifted downfield from free phenylphosphine (−122.0 ppm) and has an identical coupling constant of 364 Hz that is comparable to known $PhPH_2$ borane adducts (cf. J = 360–380 Hz) [44–46]. The product was crystallized from a saturated *n*-pentane solution at −33 °C confirming the identity as adduct **1·PhPH$_2$**. Heating a solution of **1·PhPH$_2$** to 100 °C for 24 h in toluene did not induce further reactivity by $^{11}B\{^1H\}$, ^{31}P, or ^1H NMR spectroscopy Fig. 4.

All four of the ring opened compounds exhibit boron-heteroatom bond lengths consistent with pi-delocalization of the lone pair to boron [**2**: B-O = 1.365(3) Å, **3**: B-O = 1.371(3)/1.375(3) Å, **4**: B-N = 1.404(2)Å, and **5**: B-S = 1.800(2) Å] [46–56] and have a trigonal planar boron center with the sum of the angles about boron ranging between 359.60(14)° to 360.0(3)°. The diphenyl torsional angles of the biphenyl moiety range from 42.8(3)° to 48.3(2)° with the twisting caused by the presence of the protons ortho to the ipso-carbon. The framework of **1** persists in adduct **1·PhPH$_2$** and thus can be compared to the free species [3] (Table 1). In the central BC_4 ring the B–C bonds lengthen [B(1)-C(1) 1.618(5) Å and B(1)-C(12) 1.625(5) Å vs. 1.580(10) Å and 1.592(10)Å] due to the boron undergoing a change in hybridization from sp^2 to sp^3 and the C–C bonds shorten [C(1)-C(6) 1.413(5) Å, C(6)-C(7) 1.477(5) Å, C(7)-C(12) 1.409(5) Å vs. C(1)-C(6) 1.430(9) Å, C(6)-C(7) 1.512(11) Å, C(7)-C(12) 1.430(9) Å] from the disruption of the anti-aromaticity in the BC_4 ring [3,32].

9-Borafluorenes are relatives to boroles with the notable difference being a biphenyl backbone in place of the 1,3-butadiene framework in the central BC_4 ring. This decreases the anti-aromatic character of the molecule, Lewis acidity, and reactivity. Comparing the reactions described herein with **6** indicate there are many similarities, yet some striking differences. Phenol reacts rapidly with **6** to give the protodeborylated borabutadiene product akin to **2** [47]. Both boracycles react instantly in a 2:1 stoichiometry with water to give the diboroxane species [46]. For the 1:1 reaction with water, the product from reaction of only one O–H bond was isolated with **6,** but not observed with **1**. Phenylphosphine readily formed coordination complexes with **1** and **6** with both reactions complete within the minimum time required to obtain NMR spectra [46]. In the reaction of **1** with $PhNH_2$, the adduct intermediate could be observed by $^{11}B\{^1H\}$ NMR spectroscopy at room temperature, while cooling to low temperature (−40 °C) was necessary to retard the reaction of **6** sufficiently to observe the intermediate. The slower reactivity with aniline is further supported by the lengthened reaction time for the non-benzofused borole at room temperature (4 d vs. < 5 min) and longer reaction times have also been observed in the insertion chemistry of these boracycles [32,34,57–64].

Table 2
Bond lengths (Å) and angles (deg) of the ring-opened products **2**, **3**, **4**, and **5**.

	2	3	4	5
B(1)-E[a]	1.365(3)	1.371(3)/1.375(3)	1.404(2)	1.800(2)
B(1)-E[a]-C(14)	126.13(16)		129.64(13)	108.50(9)
B(1)-E[a]-B(2)		134.9(2)		
$\Sigma_{angles\ at\ B}$	359.95(19)	360.0(3)	359.94(13)	359.60(14)
Diphenyl Torsional Angle	48.2(2)	46.8(3)/42.8(3)	48.2(2)	43.7(2)

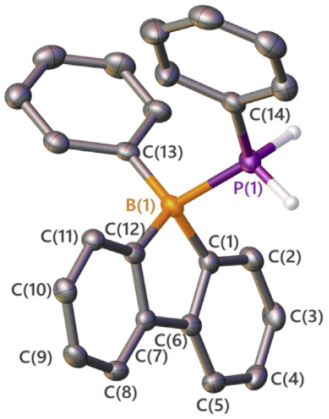


Fig. 4. Solid-state structure of **1·PhPH$_2$**. Hydrogen atoms are omitted for clarity (except those bonded to phosphorus) and ellipsoids are drawn at the 50% probability level. **1·PhPH$_2$** crystallizes with two molecules in the asymmetric unit, and one representative molecule is shown and discussed as the metrical parameters are comparable. Notable bond lengths (Å) and angles (deg): B(1)-P(1) 1.977(4), P(1)-B(1)-C(1) 108.1(2), P(1)-B(1)-C(12) 104.4(2), P(1)-B(1)-C(13) 108.2(2).

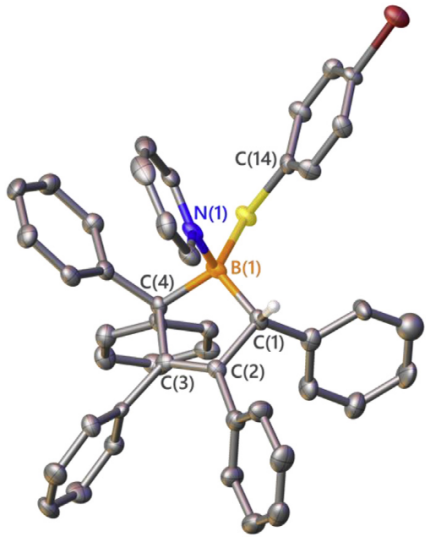
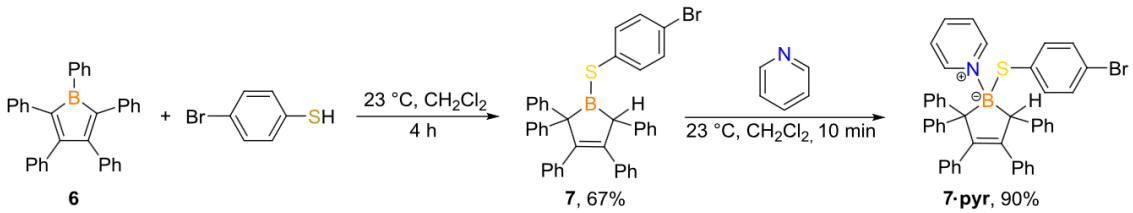


Fig. 5. Solid-state structure of **7·pyr**. Hydrogen atoms are omitted for clarity (except the protons bonded to the quaternary carbon), and ellipsoids are drawn at the 50% probability level. **7·pyr** crystallizes with two molecules in the asymmetric unit, only one molecule is shown and discussed as the metrical parameters are comparable for both molecules. Selected bond lengths (Å): B(1)-N(1) 1.650(8), B(1)-S(1) 1.937(7), B(1)-C(1) 1.696(9), C(1)-C(2) 1.542(8), C(2)-C(3) 1.353(9), B(1)-C(4) 1.629(10).

The largest difference in reactivity between **1** and **6** is with the two thiols. 1-Naphthalenethiol did not react at all with **1** whereas **6** reacted to produce a 1-bora-cyclopent-3-ene in which the sulfur is bound to boron and the phenyl group and the S-H proton migrated to the carbon atom adjacent to boron [46]. 4-Bromothiophenol reacted with **1** to generate the ring opened thioborane and the corresponding reaction was conducted with **6** to determine if the substituent influenced the reactivity (Scheme 3). The product was identified as the analogous 1-bora-cyclopent-3-ene **7** by obtaining an X-ray diffraction structure of its' pyridine adduct, **7·pyr** (Fig. 5). The $^{11}B\{^1H\}$ signal for the free species at 77.2 ppm is close to other 1-boracyclopent-3-ene systems [41,46,47]. This difference in thiol reactivity from **1** to **6** is due to the latter having a true diene backbone which can undergo a 1,4-addition [65–70] whereas the biphenyl backbone resists addition chemistry.

3. Conclusion

The reactions of water, phenol, aniline and 4-bromothiophenol with 9-phenyl-9-borafluorene resulted in ring opening of the BC_4 ring to generate a biphenyl borane with the heteroatom bound to boron. For water, both O–H bonds reacted with an equivalent of 9-phenyl-9-borafluorene while only one N–H bond of aniline reacted. The corresponding reaction with phenylphosphine generated a coordination complex that did not react further. Comparing the results to pentaphenylborole revealed the same protodeborylation for phenol, water, phenylphosphine, and aniline, albeit with much more sluggish reaction times for the latter. Thiols proved to be the exception as in reactions with pentaphenylborole produced 1-bora-cyclopent-3-ene heterocycles rather than ring opening. These results reveal insight into the stability of 9-borafluorenes for applications in electronic materials as well as the B–C bond cleavage process that is critical for ring insertion chemistry to access unsaturated polycyclic systems.



Scheme 3. Reaction of 4-bromothiophenol with **6**.

4. Experimental section

4.1. General information and methods

All manipulations were performed under an inert atmosphere in a nitrogen-filled MBraun Unilab glove box. Solvents were purchased from commercial sources as anhydrous grade, dried further using a JC Meyer Solvent System with dual columns packed with solvent-appropriate drying agents and stored over molecular sieves. Phenylphosphine was purchased from Strem Chemicals and used as received. 4-Bromothiophenol, pyridine, and phenol were purchased from Sigma-Aldrich and used as received. Aniline was purchased from Sigma-Aldrich and purified by distillation prior to use. In-house deionized water was used without further purification. **1** [42] and **6** [71] were prepared by the literature procedures. $CDCl_3$ for NMR spectroscopy was purchased from Cambridge Isotope Laboratories and dried by stirring for 3 days over CaH_2, distilled, and stored over 4 Å molecular sieves. Multinuclear NMR spectra were recorded on Bruker 400 or 600 MHz spectrometers. FT-IR spectra were recorded on a Bruker Alpha ATR FT-IR spectrometer on solid samples. High resolution mass spectra (HRMS) were obtained in the Baylor University Mass Spectrometry Center on a Thermo Scientific LTQ Orbitrap Discovery spectrometer using +ESI and at the University of Texas at Austin Mass Spectrometry Center on a Micromass Autospec Ultima spectrometer using CI. Melting points were measured with a Thomas Hoover Unimelt capillary melting point apparatus and are uncorrected. Single crystal X-ray diffraction data were collected on a Bruker Apex II-CCD detector using Mo-K_α radiation ($\lambda = 0.71073$ Å). Crystals were selected under paratone oil, mounted on micromounts, and immediately placed in a cold stream of N_2. Structures were solved and refined using SHELXTL [72] and figures were produced using OLEX2 [73]. The crystallographic data for structures **2**–**5**, **1·PhPH$_2$**, and **7·pyr** have been deposited with the Cambridge Crystallographic Data Center (CCDC 1880118–1880123).

4.2. Synthesis and characterization of the compounds

4.2.1. Compound *2*

At room temperature (23 °C), a solution of phenol (39.0 mg, 0.415 mmol) in CH_2Cl_2 (2 mL) was added to a solution of **1** (100.0 mg, 0.415 mmol) in CH_2Cl_2 (3 mL). Upon completion of the addition, the yellow solution became colorless. The mixture was stirred for 5 min and the solvent removed *in vacuo* leaving a white residue. The resultant solid was washed with *n*-pentane (3 × 1 mL) to give **2** as a white powder. Yield: (129.0 mg, 93%); Crystals of **2** suitable for X-ray diffraction studies were grown by storing a saturated *n*-pentane solution at −33 °C for three days. m.p. 74–75 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, J = 6.0 Hz, 2H), 7.57 (t, J = 6.0 Hz, 2H), 7.50–7.42 (m, 3H), 7.39 (t, J = 6.0 Hz, 1H), 7.32 (d, J = 12.0 Hz, 1H), 7.25 (t, J = 6.0 Hz, 1H), 7.20 (t, J = 6.0 Hz, 2H), 7.04 (d, J = 6.0 Hz, 2H), 6.90 (t, J = 6.0 Hz, 2H), 6.85 (t, J = 6.0 Hz, 1H) 6.17 (d, J = 6.0 Hz, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 155.08, 145.90, 143.03, 136.59, 133.85, 132.01, 129.30, 128.56, 128.48, 128.43, 127.95, 127.04, 126.07, 122.69, 120.06; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 46.4 (s), FT-IR (ranked intensity, cm^{-1}) 1592(7), 1489(6), 1435(8), 1271(12), 1241(3), 1070(10), 908(4), 782(13), 740(1), 765(11), 698(15), 689(2), 627(14), 644(9), 507(5); HRMS (ESI+) for $C_{24}H_{19}BONa$ (M+Na), Calcd: 356.1457; Found: 356.1456.

4.2.2. Compound *3*

At room temperature (23 °C), a solution of **1** (195.0 mg, 0.812 mmol) in CH_2Cl_2 (3 mL) was added a solution of degassed water (8.0 mg, 0.444 mmol) in CH_2Cl_2 (1 mL). Upon completion of the addition, the yellow solution became colorless. The mixture was stirred for 5 min and the solvent removed *in vacuo*. The solids were washed with *n*-pentane (3 × 0.5 mL) and dried *in vacuo* to give a white powder. Yield (110.0 mg, 54%); Crystals of **3** for X-ray diffraction studies were grown by vapor diffusion of diethyl ether into hexanes at ambient temperature. m.p. 126–127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.34 (m, 10H), 7.28–7.26 (m, $CDCl_3$, 2H), 7.21–7.16 (m, 10H), 7.11–7.04 (m, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.86, 143.25, 136.29, 132.78, 131.60, 129.10, 128.96, 128.62, 128.47, 127.52, 126.97, 126.02; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 46.2 (br, s); FT-IR (ranked intensity, cm^{-1}) 1592(13), 1435(8), 1339(6), 1271(14), 1240(4), 890(5), 781(10), 740(2), 694(1), 646(3), 615(12), 602(15), 565(11), 542(9), 506(7); HRMS (ESI+) for $C_{36}H_{28}B_2OK$ (M+K), Calcd: 537.1970; Found: 537.1960.

4.2.3. Compound *4*

At room temperature (23 °C), a CH_2Cl_2 (3 mL) solution of aniline (35.0 mg, 0.377 mmol) was added to a solution of **1** (90.0 mg, 0.377 mmol) in CH_2Cl_2 (3 mL). Upon addition, a white precipitate formed and after stirring for 4 d, the solution became colorless. The volatiles were removed *in vacuo* leaving a white residue. The residue was washed with *n*-pentane (3 × 1 mL) and dried *in vacuo* to give a white powder. Yield: (110.0 mg, 88%); Crystals of **4** for X-ray diffraction studies were grown by vapor diffusion of a CH_2Cl_2 solution into toluene at ambient temperature. m.p. 108–110 °C; ^{1}H NMR (400 MHz, $CDCl_3$, -50 °C) δ 7.62 (d, J = 8.0 Hz, 2H), 7.54–7.35 (m, 7H), 7.15–7.03 (m, 5H), 6.98 (t, J = 8.0 Hz, 2H), 6.91 (t, J = 8.0 Hz, 1H), 6.58 (s, *PhNH*, 1H), 6.46 (d, J = 8.0 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, -50 °C) δ 145.83, 142.69, 142.49, 140.09, 139.12, 133.80, 133.55, 130.25, 128.60, 128.52, 128.41, 128.17, 127.86, 127.70, 126.45, 126.29, 122.59, 121.40, 77.37; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 42.4 (s); FT-IR (ranked intensity, cm^{-1}): 3360(13), 1591(6), 1496(4) 1427(3), 1373(7), 1298(10), 1071(15) 913(8) 783(12) 742(1), 693(2), 671(9), 567(14), 540(11), 510(5); HRMS (ESI+) for $C_{24}H_{21}BP$ (M+H), Calcd: 333.1798; Found: 333.1799.

4.2.4. Compound *5*

At room temperature (23 °C), a solution of **1** (99.0 mg, 0.410 mmol) in CH_2Cl_2 (3 mL) was added to a solution of 4-bromothiophenol (78.0 mg, 0.410 mmol) in CH_2Cl_2 (2 mL). After stirring for 36 h, the volatiles were removed *in vacuo*. The resulting residue was washed with *n*-pentane (3 × 1 mL) and dried *in vacuo* to give a white powder. Yield: (133.0 mg, 75%); Crystals of **5** suitable for X-ray diffraction studies were grown by vapor diffusion of a CH_2Cl_2 solution into hexanes at ambient temperature. m.p. 129–130 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (s, 2H), 7.51 (t, J = 6.0 Hz, 1H), 7.43–7.36 (m, 3H), 7.34–7.25 (m, 3H), 7.20 (t, J = 6.0 Hz, 1H), 7.18–7.13 (m, 2H), 7.05 (d, J = 12.0 Hz, 2H), 6.97 (d, J = 6.0 Hz, 2H), 6.47 (d, J = 6.0 Hz, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 145.86, 143.24, 136.29, 135.57, 134.78, 132.79, 132.37, 131.61, 131.21, 129.28, 129.11, 128.99, 128.96, 128.67, 128.62, 128.48, 128.14, 128.06, 127.52, 127.16, 126.97, 126.01, 121.33; ^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ 66.2 (br, s); FT-IR (ranked intensity, cm^{-1}) 1591(13), 1470(9), 1428(11), 1242(3), 1167(14), 1068(8), 1007(4), 911(7), 809(5), 781(10), 741(2), 694(1), 647(12), 600(15), 475(6); HRMS (ESI+) for $C_{24}H_{18}BSBr$ (M+H), Calcd: 428.0515; found: 428.0515.

4.2.5. Compound *1·PhPH$_2$*

At room temperature (23 °C), a solution of phenylphosphine (30.0 mg, 0.995 mmol) in CH_2Cl_2 was added to a solution of **1** (239.0 mg, 0.995 mmol) in CH_2Cl_2 (3 mL) to give a white slurry which was stirred for 5 min. The volatiles were removed *in vacuo* and the residue washed with *n*-pentane (3 × 1 mL) and dried *in vacuo* to give a white powder. Yield: (103.0 mg, 58%); Crystals of **1·PhPH$_2$** for X-ray diffraction studies were grown from a saturated

n-pentane solution at −33 °C. m.p. 98–100 °C; ^{1}H NMR (400 MHz, Toluene-d_8) δ 7.72 (t, J = 8.0 Hz, 4H), 7.67 (d, J = 8.0 Hz, 2H), 7.32–7.14 (m, 7H), 6.81 (t, J = 8.0 Hz, 1H), 6.69 (td, J = 4.0, 8.0 Hz, 2H), 6.62–6.55 (m, 2H), 4.42 (d, $J_{P\text{-}H}$ = 364 Hz, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 149.06, 133.64, 133.38, 133.33, 131.79, 131.73, 131.71, 129.02, 128.95, 128.03, 127.40, 126.39, 126.33, 120.11, 119.19, 118.88; ^{31}P NMR (243 MHz, $CDCl_3$) δ −47.0 (t, $J_{P\text{-}H}$ = 364 Hz); ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$) δ −47.0 (s), ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ −10.1 (s); FT-IR (ranked intensity, cm^{-1}): 1484(14), 1429(6), 1266(15), 1028(11), 893(5), 789(10), 736(1), 701(2), 688(9), 645(3), 617(8), 488(7), 455(12), 438(13), 422(4); HRMS (ESI+) for $C_{24}H_{20}$BPNa (M+Na), Calcd: 373.1285; Found: 373.1280.

4.2.6. Compound **7**

At room temperature (23 °C), a solution of **6** (162.0 mg, 0.365 mmol) in CH_2Cl_2 (3 mL) was added to a solution of 4-bromothiophenol (69.1 mg, 0.365 mmol) in CH_2Cl_2 (2 mL). to give a colorless solution. After stirring for 4 h the volatiles were removed *in vacuo* leaving an off-white residue. The resultant solid was washed with *n*-pentane (3 × 1 mL) and dried *in vacuo* to give a white powder. Yield: (155.0 mg, 67%); d.p. 107–109 °C; ^{1}H NMR (400 MHz, $CDCl_3$, -30 °C) δ 7.57 (d, J = 8.0 Hz, 2H), 7.44–7.30 (m, 7H), 7.22 (t, J = 8.0 Hz, 1H), 7.16 (d, J = 8.0 Hz, 2H), 7.02–6.86 (m, 12H), 6.77 (t, J = 8.0 Hz, 3H), 6.50 (d, J = 4.0 Hz, 2H), 4.20 (s, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 145.95, 144.80, 143.47, 142.38, 139.76, 137.77, 137.59, 135.07, 131.60, 130.95, 130.72, 129.73, 129.31, 128.77, 128.26, 128.10, 127.92, 127.46, 127.26, 126.49, 126.09, 124.83, 122.01, 77.37, 66.60, 51.61; ^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ 77.2; FT-IR (ranked intensity, cm^{-1}) 1597(11), 1488(10), 1468(2), 1440(14), 1133(5), 1066(13), 1029(8), 911(15), 755(9), 741(3), 696(1), 579(7), 548(12), 532(6), 507(4); HRMS (CI+) for $C_{40}H_{30}$BBrS (M+), Calcd: 634.1324; Found: 634.1340.

4.2.7. Compound ***7·pyr***

At room temperature (23 °C), pyridine (22.0 mg, 0.274 mmol) was added to a solution of **7** (239.0 mg, 0.274 mmol) in CH_2Cl_2 (3 mL) and stirred for 10 min. The volatiles were removed *in vacuo* and the white residue was washed with hexanes (3 × 1 mL) and dried *in vacuo* to give a white powder. Yield: (235.0 mg, 90%); Crystals of **7·pyr** for X-ray diffraction studies were grown by vapor diffusion of a CH_2Cl_2 solution of **7·pyr** into toluene at ambient temperature. d.p. 109–111 °C; ^{1}H NMR (400 MHz, Toluene-d_8, 75 °C) δ 8.46 (s, 1H), 7.65 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 8.0, 2H), 7.19 (q, J = 4.0 Hz, 5H), 6.92–6.87 (m, 3H), 6.83–6.66 (m, 19H), 6.47 (d, J = 8.0 Hz, 2H), 4.19 (s, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.80, 138.34, 136.36, 135.10, 131.62, 131.30, 131.04, 129.91, 129.46, 129.29, 128.24, 127.98, 127.54, 127.29, 126.45, 126.02, 125.10, 123.95, 100.14, 77.36; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 10.8 (s); FT-IR (ranked intensity, cm^{-1}): 1596(6), 1489(9), 1471(2), 1440(10), 1154(13), 1070(8), 1031(12), 1007(5), 853(15), 808(7), 761(11), 695(1), 591(14), 551(3), 478(4); HRMS (ESI+) for $C_{45}H_{35}$BNSBrNa (M+Na), calcd: 733.1695; found: 733.1696.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2018.12.034.

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