

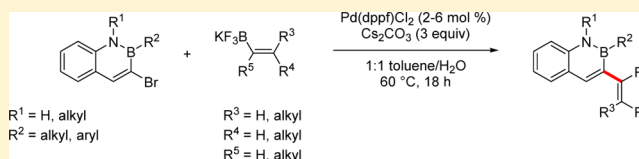
# Suzuki–Miyaura Cross-Coupling of Brominated 2,1-Borazonaphthalenes with Potassium Alkenyltrifluoroborates

Gary A. Molander,\* Steven R. Wisniewski, and Elham Etemadi-Davan

Roy and Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, 231 South 34th Street, Philadelphia, Pennsylvania 19104-6323, United States

## Supporting Information

**ABSTRACT:** Conditions have been developed for the palladium-catalyzed cross-coupling of 3-bromo-2,1-borazonaphthalenes with potassium alkenyltrifluoroborates. Twenty-seven alkenyl-substituted azaborines have been synthesized through this method, providing access to a family of 2,1-borazonaphthalenes with alkenyl substitution at the C3 position.



## INTRODUCTION

2,1-Borazonaphthalenes serve as versatile isosteres of all-carbon naphthalene substructures, which allows facile emplacement of a variety of substituents about the ring in an efficient and selective manner. Because of electronic desymmetrization brought about by the incorporation of a B—N bond in these aromatic systems, borazines have proven to be far more easily elaborated than naphthalenes themselves. Previous studies have focused on decorating these ring systems by utilizing arylation reactions. Alkenylation reactions are herein examined as a means to elaborate brominated 2,1-borazonaphthalenes.

2-Alkenylnaphthalenes can be synthesized through a variety of transition-metal-catalyzed transformations, including Heck,<sup>1</sup> Mizoroki–Heck,<sup>2</sup> Hiyama,<sup>3</sup> and Suzuki–Miyaura<sup>4</sup> reactions. However, installation of an alkenyl substituent on a functionalized naphthalene is more challenging and often requires four or five steps.<sup>5</sup> One method to afford alkenyl-substituted naphthalenes is to perform free-radical bromination of a methyl-substituted derivative followed by a Wittig olefination.<sup>6</sup> Aside from the generation of a stoichiometric amount of difficult-to-remove phosphine oxide waste, additional substitution on the naphthalene can affect regiochemical control of free-radical bromination. Similarly, titanium-mediated carbonylation with dichloromethyl methyl ether followed by Wittig olefination afforded 2-alkyl-3-alkenylnaphthalene in moderate yield over two steps.<sup>7</sup> In addition to the drawbacks described above, the use of a strong Lewis acid limits functional group tolerability in this approach. Further, there is only one example demonstrating the installation of an alkenyl substituent on a 2-arylnaphthalene through the cross-coupling of naphthyl iodide and alkenylboronic acid, which provides 2-aryl-3-alkenylnaphthalene in good yield.<sup>8</sup> The naphthyl iodide in this case was synthesized through gold-catalyzed cyclization/iodination, which required preparation of the requisite starting material (1-arylalka-2,3-dienyl acetate). Additionally, to the best of our knowledge, installation of an alkenyl substituent at the C3 position of a 1,2-disubstituted naphthalene has not been reported.

Accessing 2,1-borazonaphthalenes, a class of azaborines<sup>9</sup> that are BN-isosteres of naphthalene, with alkenyl substituents

at the C3 position under mild reaction conditions would therefore serve as an example of how functionalized azaborines could be prepared more efficiently than their corresponding all-carbon analogues. Recently, we reported the bromination of 2,1-borazonaphthalenes in high yield under mild reaction conditions with complete regiochemical control.<sup>10</sup> Because of the inherent reactivity of azaborine, bromination occurs selectively at the C3 position of the azaborine in the presence of alkyl/aryl substituents on boron and nitrogen. We therefore envisioned these brominated azaborines as prefucionalized electrophilic components in Suzuki–Miyaura cross-coupling reactions<sup>11</sup> with potassium alkenyltrifluoroborates<sup>12</sup> as a route to C3-alkenyl-substituted 2,1-borazonaphthalenes, a compound class that has not been previously reported.

## RESULTS AND DISCUSSION

Optimization of the reaction of 3-bromo-2-methyl-2,1-borazonaphthalene **1** with functionalized alkenyltrifluoroborate **2** was carried out by screening palladium sources, solvents, and bases. Side products represent the sum of homocoupling of the azaborine, protodebromination of the azaborine, and unidentified side products. Conditions for the cross-coupling of potassium aryltrifluoroborates with brominated 2,1-borazonaphthalenes did not afford the desired product in appreciable yield (Table 1, entry 1). Therefore, several other ligands were screened in this reaction (entries 2–4 and 7). Of the ligands tested, triphenylphosphine (PPh<sub>3</sub>) and 1,1'-bis(diphenylphosphino)ferrocene (dppf) provided the highest conversions to products. Several solvents/ratios were tested for these ligands, and the best result was obtained using toluene as the cosolvent and Pd(dppf)Cl<sub>2</sub> as the palladium source (entry 7). Attempts to lower palladium loading resulted in incomplete conversion of the starting material.

A representative set of potassium alkenyltrifluoroborates were subjected to the developed reaction conditions with

Received: October 2, 2014

Published: October 30, 2014

**Table 1. Optimization of Cross-Coupling with Potassium Alkenyltrifluoroborates**

entry	palladium source (loading)	base	solvent	P:SP <sup>a</sup>
1	XPhos-Pd-G2 (4 mol %)	Cs <sub>2</sub> CO <sub>3</sub>	1:1 CPME/H <sub>2</sub> O	trace product
2	SPhos-Pd-G2 (4 mol %)	K <sub>2</sub> CO <sub>3</sub>	1:1 CPME/H <sub>2</sub> O	trace product
3	Pd <sub>2</sub> dba <sub>3</sub> /cataCXium A (4 mol %)	Cs <sub>2</sub> CO <sub>3</sub>	1:1 CPME/H <sub>2</sub> O	0.50:1.0
4	(Ph <sub>3</sub> P) <sub>2</sub> PdCl <sub>2</sub> (6 mol %)	Cs <sub>2</sub> CO <sub>3</sub>	1:1 CPME/H <sub>2</sub> O	2.57:1.0
5	(Ph <sub>3</sub> P) <sub>2</sub> PdCl <sub>2</sub> (6 mol %)	Cs <sub>2</sub> CO <sub>3</sub>	1:1 toluene/H <sub>2</sub> O	2.00:1.0
6	(Ph <sub>3</sub> P) <sub>2</sub> PdCl <sub>2</sub> (6 mol %)	Cs <sub>2</sub> CO <sub>3</sub>	9:1 toluene/H <sub>2</sub> O	2.50:1.0
7	Pd(dppf)Cl <sub>2</sub> (6 mol %)	Cs <sub>2</sub> CO <sub>3</sub>	1:1 toluene/H <sub>2</sub> O	3.10:1.0
8	Pd(dppf)Cl <sub>2</sub> (6 mol %)	Cs <sub>2</sub> CO <sub>3</sub>	1:1 CPME/H <sub>2</sub> O	1.85:1.0

<sup>a</sup>Product:side products.

3-bromo-2-methyl-2,1-borazonaphthalene as the electrophilic partner (Table 2). Cyclic alkenyltrifluoroborates were successful nucleophiles in the reaction by providing the desired product in yields up to 90% (entries 5, 6, 8, and 10). Alkenyltrifluoroborates with alkyl substituents afforded the desired product in high yields (entries 2, 3, and 9). Vinyltrifluoroborate was a suitable nucleophile for the reaction because the azaborine was obtained in 70% yield (entry 7). Most importantly, *cis*-1-propenyltrifluoroborate was successfully employed in the reaction, affording the product in high yield without isomerization of the alkene (entry 3). The scalable nature of the cross-coupling reaction was demonstrated by performing the coupling on a 4.5 mmol scale

(1 g of azaborine) with one-third palladium loading (2 mol %), which provided the desired product in similar yield (entry 8).

The developed reaction conditions were extended to cross-coupling of 3-bromo-2-phenyl-2,1-borazonaphthalene with an array of potassium alkenyltrifluoroborates to demonstrate that azaborine can also be substituted with an aryl group on the boron. Six different alkenyltrifluoroborates were employed in the coupling and provided the desired product in yields up to 90%. The mild reaction conditions of the coupling were demonstrated in the successful coupling of an alkenyltrifluoroborate with an alkyl chloride substituent, affording the desired product in 90% yield (Table 3, entry 2). Cyclic alkenyltrifluoroborates were successfully engaged in the reaction as the desired products were obtained in high yields (entries 3, 4, and 6).

To demonstrate the versatility of this method, an array of brominated 2,1-borazonaphthalenes were synthesized and subjected to the developed reaction conditions with 1-decenyltrifluoroborate as the nucleophile in the reaction. The cross-coupled products were obtained with secondary cyclic and acyclic groups on boron in yields up to 90% (Table 4, entries 1 and 2). Azaborines with various substitution patterns on the arene of boron were suitable electrophiles for coupling as the cross-coupled products were isolated in high yield (entries 3–5). Substitution on the nitrogen of the 2,1-borazonaphthalenes did not affect the coupling as reactions with both *N*-allyl and *N*-benzyl substituents provided the desired product in high yields (entries 6 and 7).

To demonstrate that the developed reaction conditions can be directly applied to the functionalization of other azaborines, 6-bromo-2-methyl-3-phenyl-2,1-borazonaphthalene was subjected to the reaction (eq 1). The desired product was obtained

**Table 2. Scope of the Cross-Coupling with Potassium Alkenyltrifluoroborates<sup>c</sup>**

entry	product	entry	product	entry	product	entry	product
1		4		7		10	
2		5		8		11	
3		6		9			

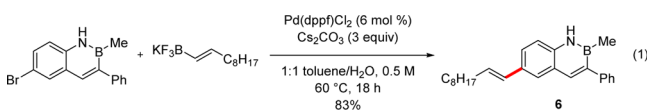
<sup>a</sup>Alkenyltrifluoroborate ratio of 94:6 *cis*/*trans* employed in this reaction. <sup>b</sup>Reaction completed on a 4.5 mmol scale with 2.0 mol % Pd(dppf)Cl<sub>2</sub>. <sup>c</sup>Reaction conditions (unless otherwise noted): 1.0 equiv of 3-bromo-2-methyl-2,1-borazonaphthalene, 1.1 equiv of potassium alkenyltrifluoroborate, 6.0 mol % Pd(dppf)Cl<sub>2</sub>, 3.0 equiv of base, 1:1 toluene/H<sub>2</sub>O, and 60 °C for 18 h.

Table 3. Scope of the Cross-Coupling of Brominated B-Phenyl 2,1-Borazonaphthalenes<sup>a</sup>

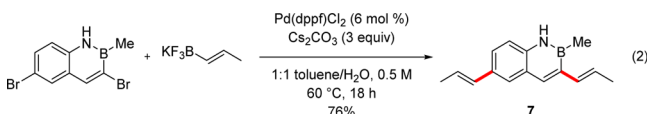
$\text{B-Phenyl 2,1-Borazonaphthalene} + \text{Kf}_3\text{B-alkenyl} \xrightarrow[\text{1:1 toluene/H}_2\text{O, 0.5 M, 60 }^\circ\text{C, 18 h}]{\text{Pd(dppf)Cl}_2 \text{ (6 mol \%), Cs}_2\text{CO}_3 \text{ (3 equiv)}} \text{Product}$	
entry	product
1	<b>4a</b> , 73%
2	<b>4b</b> , 90%
3	<b>4c</b> , 79%
4	<b>4d</b> , 86%
5	<b>4e</b> , 76%
6	<b>4f</b> , 81%

<sup>a</sup>Reaction conditions (unless otherwise noted): 1.0 equiv of 3-bromo-2-phenyl-2,1-borazonaphthalene, 1.1 equiv of potassium alkenyltrifluoroborate, 6.0 mol % Pd(dppf)Cl<sub>2</sub>, 3.0 equiv of base, 1:1 toluene/H<sub>2</sub>O, and 60 °C for 18 h.

in 83% yield to afford C6-alkenyl-substituted 2,1-borazonaphthalenes, examples of which are absent in the literature.



The reaction conditions were then extended to cross-coupling of 3,6-dibrominated 2,1-borazonaphthalene. The addition of 2.2 equiv of 1-propenyltrifluoroborate provides a doubly cross-coupled product in 76% yield (eq 2).



In conclusion, a general method for Suzuki–Miyaura cross-coupling of brominated 2,1-borazonaphthalenes with potassium alkenyltrifluoroborates has been developed. Azaborines with alkyl and aryl groups on boron and with or without substitution on nitrogen are suitable reagents for the coupling. Through this route, functionalized 2,1-borazonaphthalenes with alkenyl substituents can be easily accessed for the first time.

## EXPERIMENTAL SECTION

**General Considerations.** Toluene was dried over activated alumina. Standard benchtop techniques were employed for handling air-sensitive reagents. Melting points (°C) are uncorrected. NMR spectra were recorded on a 400 or 500 MHz spectrometer. <sup>11</sup>B NMR

Table 4. Scope of the Cross-Coupling with Various Brominated 2,1-Borazonaphthalenes<sup>a</sup>

$\text{Brominated 2,1-Borazonaphthalene} + \text{Kf}_3\text{B-alkenyl} \xrightarrow[\text{1:1 toluene/H}_2\text{O, 0.5 M, 60 }^\circ\text{C, 18 h}]{\text{Pd(dppf)Cl}_2 \text{ (6 mol \%), Cs}_2\text{CO}_3 \text{ (3 equiv)}} \text{Product}$	
entry	product
1	<b>5a</b> , 81%
2	<b>5b</b> , 90%
3	<b>5c</b> , 88%
4	<b>5d</b> , 81%
5	<b>5e</b> , 83%
6	<b>5f</b> , 62%
7	<b>5g</b> , 90%
8	<b>5h</b> , 80%

<sup>a</sup>Reaction conditions (unless otherwise noted): 1.0 equiv of 3-bromo-2,1-borazonaphthalene, 1.1 equiv of potassium alkenyltrifluoroborate, 6.0 mol % Pd(dppf)Cl<sub>2</sub>, 3.0 equiv of base, 1:1 toluene/H<sub>2</sub>O, and 60 °C for 18 h.

spectra were obtained on a spectrometer equipped with the appropriate decoupling accessories. All <sup>11</sup>B NMR chemical shifts were referenced to external BF<sub>3</sub>·OEt<sub>2</sub> (0.0 ppm) with a negative sign indicating an upfield shift. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, br = broad), coupling constant *J* (Hz), and integration. Analytical thin-layer chromatography (TLC) was performed on TLC silica gel plates (0.25 mm) precoated with a fluorescent indicator. Visualization of the TLC plates was effected with ultraviolet light. Standard flash chromatography procedures were followed using 100–200 mesh silica gel. HRMS data were obtained by either ESI or CI using a TOF mass spectrometer.

**Spectral Information of 2,1-Borazonaphthalenes.** 2,1-Borazonaphthalenes were synthesized<sup>13</sup> and brominated<sup>10</sup> according to methods previously described in the literature.

**3-Bromo-2-(4-trifluoromethylphenyl)-2,1-borazonaphthalene.** The title compound was obtained as a white solid in 90% yield (1.0 mmol scale, 316.7 mg): mp 98–103 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.49 (s, 1H), 8.07 (s, 1H), 7.98 (d, *J* = 7.8 Hz, 2H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.51–7.49 (m, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.30–7.27 (m, 1H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 147.3, 139.0, 133.6, 131.2 (d, *J* = 32.5 Hz), 129.7, 129.2, 126.5 (q, *J* = 27.5 Hz), 125.3, 124.6 (q, *J* = 3.6 Hz), 122.5, 118.4; <sup>11</sup>B NMR (128.38 MHz, CDCl<sub>3</sub>) δ 32.9; IR (neat) 3367, 2923, 1556, 1427, 1120, 1070 cm<sup>−1</sup>; HRMS (CI) *m/z* [M + H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>11</sub>BNF<sub>3</sub>Br 352.9825, found 352.9802.

**General Procedure for the Palladium-Catalyzed Cross-Coupling Reaction of Potassium Alkenyltrifluoroborates with Brominated 2,1-Borazonaphthalenes.** To a Biotage 10 mL microwave vial equipped with a magnetic stir bar were added 3-bromo-2,1-alkenyltrifluoroborate (1.1 mmol, 1.1 equiv), Cs<sub>2</sub>CO<sub>3</sub> (3.0 mmol, 977 mg), Pd(dppf)Cl<sub>2</sub> (6.0 mol %, 42 mg), and potassium alkenyltrifluoroborate



(1.0 mmol, 1.0 equiv). The vial was sealed with a cap, lined with a Teflon septum, and evacuated and purged with argon gas three times. Anhydrous degassed toluene (1.0 mL) and deionized H<sub>2</sub>O (1.0 mL) were added under argon gas. The reaction mixture was heated at 60 °C for 18 h. After cooling to rt, the reaction mixture was extracted with EtOAc (3 × 10 mL) and dried (MgSO<sub>4</sub>). After being concentrated in vacuo, the product was isolated by flash column chromatography and eluted with a gradient of EtOAc in hexanes (0 to 10% EtOAc).

**N-(3-(2-Methyl-2,1-borazonaphth-2-yl)allyl)morpholine (3a).** The title compound was obtained as a yellow solid in 88% yield (235.8 mg): mp 89–93 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.79 (s, 1H), 7.72 (s, 1H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.34–7.37 (m, 1H), 7.18 (d, *J* = 8.1 Hz, 1H), 7.15–7.12 (m, 1H), 5.24–5.23 (m, 1H), 5.12 (d, *J* = 2.5 Hz, 1H), 3.67 (t, *J* = 4.6 Hz, 4H), 3.31 (s, 2H), 2.48 (br, 4H), 0.79 (s, 3H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 149.0, 140.1, 129.6, 128.1, 125.0, 121.0, 117.4, 114.2, 67.3, 64.8, 53.9; <sup>11</sup>B NMR (128.38 MHz, CDCl<sub>3</sub>) δ 36.7; IR (neat) 3319, 2928, 1566, 1434, 1109, 891 cm<sup>-1</sup>; HRMS (ESI+) *m/z* [M + H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>22</sub>BN<sub>2</sub>O 269.1825, found 269.1820.

**2-Methyl-3-((E)-1-propen-1-yl)-2,1-borazonaphthalene (3b).** The title compound was obtained as a yellow solid in 98% yield (179.3 mg): mp 69–75 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.76 (s, 1H), 7.65 (s, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.36–7.29 (m, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.13–7.10 (m, 1H), 6.59 (d, *J* = 15.6 Hz, 1H), 6.19–6.12 (m, 1H), 1.91 (dd, *J* = 6.6, 1.5 Hz, 3H), 0.85 (s, 3H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 139.5, 138.7, 134.8, 129.3, 127.6, 126.5, 125.6, 121.0, 117.4, 19.4; <sup>11</sup>B NMR (128.38 MHz, CDCl<sub>3</sub>) δ 37.2; IR (neat) 3364, 2924, 1614, 1457, 1343 cm<sup>-1</sup>; HRMS (CI) *m/z* [M]<sup>+</sup> calcd for C<sub>12</sub>H<sub>14</sub>BN 183.1219, found 183.1216.

**2-Methyl-3-((Z)-1-propen-1-yl)-2,1-borazonaphthalene (3c).** The title compound was obtained as a brown solid in 87% yield (159.2 mg): mp 98–103 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.42 (s, 1H), 7.68 (s, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.37–7.34 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.18–7.13 (m, 1H), 6.57–6.54 (m, 1H), 5.72–5.79 (m, 1H), 1.85 (dd, *J* = 7.0, 1.8 Hz, 3H), 0.74 (s, 3H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 140.8, 139.6, 132.1, 129.4, 127.8, 125.3, 125.0, 121.0, 117.6, 14.8; <sup>11</sup>B NMR (128.38 MHz, CDCl<sub>3</sub>) δ 37.3; IR (neat) 3364, 2925, 1611, 1560, 1454 cm<sup>-1</sup>; HRMS (CI) *m/z* [M]<sup>+</sup> calcd for C<sub>12</sub>H<sub>14</sub>BN 183.1219, found 183.1213.

**3-(Isopropen-1-yl)-2-methyl-2,1-borazonaphthalene (3d).** The title compound was obtained as a yellow oil in 69% yield (126.2 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.80 (s, 1H), 7.68 (s, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.39–7.36 (m, 1H), 7.19–7.15 (m, 2H), 5.21–5.11 (m, 1H), 5.07 (d, *J* = 1.9 Hz, 1H), 2.16 (s, 3H), 0.87 (s, 3H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 148.4, 139.6, 139.2, 129.6, 128.0, 125.1, 121.0, 117.4, 113.0, 23.9; <sup>11</sup>B NMR (128.38 MHz, CDCl<sub>3</sub>) δ 36.9; IR (neat) 3368, 2933, 1567, 1462, 1453 cm<sup>-1</sup>; HRMS (CI) *m/z* [M]<sup>+</sup> calcd for C<sub>12</sub>H<sub>14</sub>BN 183.1219, found 183.1220.

**4-(2-Methyl-2,1-borazonaphthyl)-3,6-dihydro-2H-pyran (3e).** The title compound was obtained as a yellow oil in 82% yield (184.5 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.75 (s, 1H), 7.73 (s, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.34–7.38 (m, 1H), 7.18 (d, *J* = 8.1 Hz, 1H), 7.16–7.13 (m, 1H), 5.83–5.82 (m, 1H), 4.36–4.35 (m, 2H), 3.97 (t, *J* = 5.4 Hz, 2H), 2.52–2.49 (m, 2H), 0.84 (s, 3H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 138.6, 137.6, 137.5, 128.5, 127.0, 124.1, 121.9, 120.1, 116.4, 65.2, 63.9, 28.1; <sup>11</sup>B NMR (128.38 MHz, CDCl<sub>3</sub>) δ 36.7; IR (neat) 3325, 2923, 1572, 1458, 1032 cm<sup>-1</sup>; HRMS (CI) *m/z* [M]<sup>+</sup> calcd for C<sub>14</sub>H<sub>16</sub>BNO 225.1325, found 225.1336.

**8-[3-(2-Methyl-2,1-borazonaphthyl)]-1,4-dioxaspiro[4.5]-dec-7-ene (3f).** The title compound was obtained as a white solid in 81% yield (227.6 mg): mp 83–88 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.73 (s, 1H), 7.69 (s, 1H), 7.54–7.56 (m, 1H), 7.32–7.35 (m, 1H), 7.16 (d, *J* = 8 Hz, 1H), 7.13–7.10 (m, 1H), 5.66–5.65 (m, 1H), 4.05–4.02 (m, 4H), 2.63–2.59 (m, 2H), 2.50–2.49 (m, 2H), 1.93 (t, *J* = 6.5 Hz, 2H), 0.81 (s, 3H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 140.9, 139.5, 138.7, 129.4, 127.8, 125.2, 121.1, 120.9, 117.3, 108.3, 64.7, 36.5, 31.8, 28.7; <sup>11</sup>B NMR (128.38 MHz, CDCl<sub>3</sub>) δ 37.0; IR (neat) 3308, 2927, 1609, 1460, 1047 cm<sup>-1</sup>; HRMS (CI) *m/z* [M]<sup>+</sup> calcd for C<sub>17</sub>H<sub>20</sub>BNO<sub>2</sub> 281.1587, found 281.1593.

**2-Methyl-3-vinyl-2,1-borazonaphthalene (3g).** The title compound was obtained as a light yellow solid in 70% yield (118.3 mg): mp 52–56 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.70 (s, 1H), 7.64 (s, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.33–7.30 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.10–7.08 (m, 1H), 6.73–6.66 (m, 1H), 5.87–5.85 (m, 1H), 5.74–5.71 (m, 1H), 0.70 (s, 3H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 140.7, 140.3, 139.9, 129.6, 128.2, 125.3, 121.2, 117.5, 114.8; <sup>11</sup>B NMR (128.38 MHz, CDCl<sub>3</sub>) δ 37.2; IR (neat) 3365, 2927, 1610, 1457 cm<sup>-1</sup>; HRMS (CI) *m/z* [M]<sup>+</sup> calcd for C<sub>11</sub>H<sub>12</sub>BN 169.1063, found 169.1063.

**3-(4,4-Difluoro-1-cyclohexen-1-yl)-2-methyl-2,1-borazonaphthalene (3h).** The title compound was obtained as a white solid in 90% yield (233.1 mg): mp 72–76 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.73 (s, 1H), 7.69 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.41–7.37 (m, 1H), 7.20–7.15 (m, 2H), 5.59–5.56 (m, 1H), 2.78–2.72 (m, 2H), 2.67–2.64 (m, 2H), 2.25–2.17 (m, 2H), 0.82 (s, 3H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 140.8, 139.5, 139.1, 129.4, 128.0, 124.9, 123.3 (t, *J* = 239.6 Hz), 121.0, 118.2 (t, *J* = 4.9 Hz), 117.3, 35.3 (t, *J* = 26.4 Hz), 31.0 (t, *J* = 24.4 Hz), 27.8 (t, *J* = 5.2 Hz); <sup>11</sup>B NMR (128.38 MHz, CDCl<sub>3</sub>) δ 36.2; IR (neat) 3397, 2936, 1613, 1560, 1425, 1058, cm<sup>-1</sup>; HRMS (CI) *m/z* [M]<sup>+</sup> calcd for C<sub>15</sub>H<sub>16</sub>BNF<sub>2</sub> 259.1344, found 259.1327.

**3-[(E)-1-Decen-1-yl]-2-methyl-2,1-borazonaphthalene (3i).** The title compound was obtained as a yellow solid in 75% yield (210.7 mg): mp 58–62 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.79 (s, 1H), 7.65 (s, 1H), 7.57 (d, *J* = 7.75 Hz, 1H), 7.34–7.31 (m, 1H), 7.16–7.11 (m, 2H), 6.58 (d, *J* = 15.5 Hz, 1H), 6.18–6.12 (m, 1H), 2.26–2.22 (m, 2H), 1.53–1.47 (m, 2H), 1.40–1.28 (m, 10H), 0.92 (t, *J* = 6.9 Hz, 3H), 0.86 (s, 3H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 139.5, 138.8, 133.4, 132.2, 129.3, 127.6, 125.6, 121.0, 117.4, 34.0, 32.2, 30.0, 29.9, 29.7, 29.6, 23.0, 14.4; <sup>11</sup>B NMR (128.38 MHz, CDCl<sub>3</sub>) δ 37.1; IR (neat) 3366, 2921, 1556, 1463, 977 cm<sup>-1</sup>; HRMS (CI) *m/z* [M]<sup>+</sup> calcd for C<sub>19</sub>H<sub>28</sub>BN 281.2315, found 281.2328.

**tert-Butyl-4-[3-(2-methyl-2,1-borazonaphthyl)]-3,6-dihydropyridine-1-(2H)-carboxylate (3j).** The title compound was obtained as a white solid in 65% yield (210.6 mg): mp 83–87 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.75 (s, 1H), 7.69 (s, 1H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.36–7.33 (m, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.14–7.11 (m, 1H), 5.71 (br, 1H), 4.07 (br, 2H), 3.64 (t, *J* = 5.5 Hz, 2H), 4.47 (br, 2H), 1.52 (s, 9H), 0.80 (s, 3H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 155.3, 139.9, 139.6, 138.7, 129.5, 128.0, 125.1, 121.1, 120.7, 117.4, 79.7, 44.3, 40.1, 34.9, 29.4, 28.8; <sup>11</sup>B NMR (128.38 MHz, CDCl<sub>3</sub>) δ 32.0; IR (neat) 3327, 2975, 1677, 1563, 1423, 1163 cm<sup>-1</sup>; HRMS (CI) *m/z* [M + H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>26</sub>BN<sub>2</sub>O<sub>2</sub> 325.2087, found 325.2080.

**2-Methyl-3-[(Z)-4-phenyl-1-buten-1-yl]-2,1-borazonaphthalene (3k).** The title compound was obtained as a yellow solid in 83% yield (226.5 mg): mp 74–77 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.66 (s, 1H), 7.59 (s, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.38–7.36 (m, 1H), 7.35–7.31 (m, 2H), 7.22–7.13 (m, 5H), 6.58 (dd, *J* = 11.5, 1.4 Hz, 1H), 5.69 (dt, *J* = 11.5, 7.2 Hz, 1H), 2.79 (t, *J* = 7.7 Hz, 2H), 2.70–2.45 (m, 2H), 0.73 (s, 3H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 142.3, 140.6, 139.7, 132.1, 129.9, 129.5, 128.9, 128.6, 127.9, 126.1, 125.3, 121.0, 117.5, 36.7, 30.6; <sup>11</sup>B NMR (128.38 MHz, CDCl<sub>3</sub>) δ 37.4; IR (neat) 3373, 2925, 1556, 1452, 746, 703 cm<sup>-1</sup>; HRMS (CI) *m/z* [M]<sup>+</sup> calcd for C<sub>19</sub>H<sub>20</sub>BN 273.1689, found 273.1683.

**3-[(E)-1-Decen-1-yl]-2-phenyl-2,1-borazonaphthalene (4a).** The title compound was obtained as a white oil in 73% yield (250.3 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.05 (s, 1H), 7.91 (s, 1H), 7.77–7.75 (m, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.51–7.47 (m, 3H), 7.42–7.39 (s, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 15.5 Hz, 1H), 6.07 (dt, *J* = 15.4, 7.0 Hz, 1H), 2.21 (q, *J* = 7.0 Hz, 2H), 1.50–1.45 (m, 2H), 1.40–1.35 (m, 10H), 0.96 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 139.8, 139.6, 133.2, 132.7, 132.3, 129.5, 128.8, 128.2, 128.0, 125.9, 121.0, 118.0, 33.7, 32.2, 29.9, 29.8, 29.7, 29.6, 23.0, 14.4; <sup>11</sup>B NMR (128.38 MHz, CDCl<sub>3</sub>) δ 34.4; IR (neat) 3370, 2923, 2852, 1421, 749 cm<sup>-1</sup>; HRMS (CI) *m/z* [M + Na]<sup>+</sup> calcd for C<sub>24</sub>H<sub>30</sub>BNNa 366.2369, found 366.2375.

**3-(6-Chloro-1-hexen-1-yl)-2-phenyl-2,1-borazonaphthalene (4b).** The title compound was obtained as a brown oil in 90% yield (288.9 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.03 (s, 1H), 7.92

(s, 1H), 7.72 (dd,  $J = 7.25, 1.5$  Hz, 2H), 7.68 (d,  $J = 7.5$  Hz, 1H), 7.50–7.46 (m, 3H), 7.42–7.39 (m, 1H), 7.26 (d,  $J = 8$  Hz, 1H), 7.23–7.20 (m, 1H), 6.68 (d,  $J = 15.5$  Hz, 1H), 6.00 (dt,  $J = 15.4, 7.0$  Hz, 1H), 3.57 (t,  $J = 6.5$  Hz, 2H), 2.23–2.19 (m, 2H), 1.86–1.83 (m, 2H), 1.62–1.58 (m, 2H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  140.1, 139.6, 133.4, 133.1, 131.1, 129.5, 128.8, 128.2, 128.1, 125.7, 121.7, 118.0, 45.3, 32.7, 32.3, 27.0;  $^{11}\text{B}$  NMR (128.38 MHz,  $\text{CDCl}_3$ )  $\delta$  35.0; IR (neat) 3373, 2933, 1558, 1421, 969, 752  $\text{cm}^{-1}$ ; HRMS (CI)  $m/z$   $[\text{M}]^+$  calcd for  $\text{C}_{20}\text{H}_{21}\text{BNCl}$  321.1456, found 321.1463.

**3-(1-Cyclohexen-1-yl)-2-phenyl-2,1-borazonaphthalene (4c).** The title compound was obtained as a yellow solid in 79% yield (225.1 mg): mp 88–92 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (s, 1H), 7.85 (s, 1H), 7.79–7.78 (m, 2H), 7.66 (d,  $J = 7.5$  Hz, 1H), 7.45–7.39 (m, 4H), 7.28 (d,  $J = 8.1$  Hz, 1H), 7.22–7.19 (m, 1H), 5.73–5.71 (m, 1H), 2.19–2.13 (m, 4H), 1.66–1.65 (m, 4H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  142.3, 140.5, 139.6, 132.8, 129.5, 128.9, 128.1, 128.0, 125.6, 124.2, 121.5, 117.9, 29.9, 26.1, 23.5, 22.6;  $^{11}\text{B}$  NMR (128.38 MHz,  $\text{CDCl}_3$ )  $\delta$  34.0; IR (neat) 3375, 2920, 1558, 1451, 751  $\text{cm}^{-1}$ ; HRMS (CI)  $m/z$   $[\text{M}]^+$  calcd for  $\text{C}_{20}\text{H}_{20}\text{BN}$  285.1689, found 285.1705.

**4-(2-Phenyl-2,1-borazonaphthyl)-3,6-dihydro-2H-pyran (4d).** The title compound was obtained as a white solid in 86% yield (246.8 mg): mp 112–115 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (s, 1H), 7.91 (s, 1H), 7.76–7.68 (m, 2H), 7.69 (d,  $J = 7.5$  Hz, 1H), 7.47–7.42 (m, 4H), 7.29 (d,  $J = 8.1$  Hz, 1H), 7.24–7.21 (m, 1H), 5.75–5.73 (m, 1H), 4.31–4.29 (m, 2H), 3.84 (t,  $J = 5.5$  Hz, 2H), 2.30 (td,  $J = 5.3, 2.7$  Hz, 2H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  140.9, 139.7, 139.4, 132.7, 129.6, 128.9, 128.4, 128.2, 125.3, 122.8, 121.7, 118.0, 66.2, 64.9, 29.5;  $^{11}\text{B}$  NMR (128.38 MHz,  $\text{CDCl}_3$ )  $\delta$  34.0; IR (neat) 3287, 2930, 1564, 1455, 1229, 758  $\text{cm}^{-1}$ ; HRMS (CI)  $m/z$   $[\text{M}]^+$  calcd for  $\text{C}_{19}\text{H}_{18}\text{BNO}$  287.1481, found 287.1487.

**2-Phenyl-3-(isopropen-1-yl)-2,1-borazonaphthalene (4e).** The title compound was obtained as a brown oil in 76% yield (186.2 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (br, 2H), 7.92–7.81 (m, 2H), 7.70 (d,  $J = 7.5$  Hz, 1H), 7.47–7.43 (m, 4H), 7.29 (d,  $J = 8.0$  Hz, 1H), 7.25–7.22 (m, 1H), 5.06–5.02 (m, 2H), 1.99 (s, 3H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  149.2, 140.9, 139.5, 132.6, 129.5, 128.7, 128.2, 128.0, 125.2, 121.5, 117.8, 113.0, 24.1;  $^{11}\text{B}$  NMR (128.38 MHz,  $\text{CDCl}_3$ )  $\delta$  33.6; IR (neat) 3367, 2925, 1573, 1463, 757  $\text{cm}^{-1}$ ; HRMS (CI)  $m/z$   $[\text{M}]^+$  calcd for  $\text{C}_{17}\text{H}_{16}\text{BN}$  245.1376, found 245.1377.

**8-(2-Phenyl-2,1-borazonaphthyl)-1,4-dioxaspiro[4.5]dec-7-ene (4f).** The title compound was obtained as a white solid in 81% yield (277.8 mg): mp 108–112 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (s, 1H), 7.90 (s, 1H), 7.80–7.78 (m, 2H), 7.65 (d,  $J = 7.5$  Hz, 1H), 7.45–7.39 (m, 4H), 7.28 (d,  $J = 8.0$  Hz, 1H), 7.21–7.18 (m, 1H), 6.62–5.60 (m, 1H), 4.05–3.98 (m, 4H), 2.47–2.46 (m, 2H), 2.38 (td,  $J = 6.3, 1.6$  Hz, 2H), 1.79 (t,  $J = 6.5$  Hz, 2H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  141.9, 141.1, 139.6, 132.7, 129.4, 128.9, 128.1, 125.3, 121.5, 121.1, 117.8, 108.2, 64.5, 36.4, 31.6, 29.0;  $^{11}\text{B}$  NMR (128.38 MHz,  $\text{CDCl}_3$ )  $\delta$  34.4; IR (neat) 3326, 1560, 1421, 1112, 755  $\text{cm}^{-1}$ ; HRMS (CI)  $m/z$   $[\text{M}]^+$  calcd for  $\text{C}_{22}\text{H}_{22}\text{BNO}_2$  343.1744, found 343.1756.

**2-Isopropyl-3-[(E)-1-decen-1-yl]-2,1-borazonaphthalene (5a).** The title compound was obtained as a colorless oil in 81% yield (247.8 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (s, 1H), 7.67 (s, 1H), 7.62 (d,  $J = 7.8$  Hz, 1H), 7.39–7.35 (m, 1H), 7.24 (d,  $J = 8.0$  Hz, 1H), 7.18–7.15 (m, 1H), 6.69 (dd,  $J = 15.6, 0.4$  Hz, 1H), 6.13–6.18 (m, 1H), 2.31–2.26 (m, 2H), 1.96–1.92 (m, 1H), 1.57–1.54 (m, 2H), 1.43–1.35 (m, 10H), 1.23 (d,  $J = 7.3$  Hz, 6H), 0.97 (t,  $J = 6.9$  Hz, 3H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  139.6, 138.4, 132.2, 131.1, 129.3, 127.6, 125.7, 121.2, 117.7, 33.8, 32.2, 30.0, 29.9, 29.7, 29.6, 23.0, 19.6, 14.4;  $^{11}\text{B}$  NMR (128.38 MHz,  $\text{CDCl}_3$ )  $\delta$  38.8; IR (neat) 3424, 2924, 1560, 1427, 969  $\text{cm}^{-1}$ ; HRMS (CI)  $m/z$   $[\text{M}]^+$  calcd for  $\text{C}_{21}\text{H}_{32}\text{BN}$  309.2628, found 309.2633.

**2-Cyclopropyl-3-[(E)-1-decen-1-yl]-2,1-borazonaphthalene (5b).** The title compound was obtained as a yellow solid in 90% yield (276.3 mg): mp 51–55 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (s, 1H), 7.56 (d,  $J = 7.7$  Hz, 1H), 7.32–7.29 (m, 1H), 7.18 (s, 1H), 7.11 (t,  $J = 7.9$  Hz, 2H), 6.69 (d,  $J = 15.6$  Hz, 1H), 6.38–6.24 (m, 1H), 2.25 (q,  $J = 7.2$  Hz, 2H), 1.52–1.48 (m, 2H), 1.39–1.28 (m, 10H),

0.92–0.89 (m, 5H), 0.66–0.55 (m, 3H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  139.5, 138.5, 132.8, 132.4, 129.3, 127.6, 125.5, 121.0, 117.4, 34.0, 32.2, 30.0, 29.9, 29.7, 29.6, 23.0, 14.4, 6.0;  $^{11}\text{B}$  NMR (128.38 MHz,  $\text{CDCl}_3$ )  $\delta$  37.1; IR (neat) 3374, 3010, 2920, 1557, 1428, 1105  $\text{cm}^{-1}$ ; HRMS (CI)  $m/z$   $[\text{M}]^+$  calcd for  $\text{C}_{21}\text{H}_{30}\text{BN}$  307.2471, found 307.2484.

**3-[(E)-1-Decen-1-yl]-2-(4-fluorophenyl)-2,1-borazonaphthalene (5c).** The title compound was obtained as a yellow oil in 88% yield (317.6 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (s, 1H), 7.85 (s, 1H), 7.71–7.65 (m, 3H), 7.41–7.37 (m, 1H), 7.25 (d,  $J = 8.5$  Hz, 1H), 7.22–7.19 (m, 1H), 7.17–7.14 (m, 2H), 6.62 (dd,  $J = 15.6, 0.7$  Hz, 1H), 6.01 (dt,  $J = 15.5, 7.0$  Hz, 1H), 2.17 (qd,  $J = 7.3, 1.3$  Hz, 2H), 1.48–1.49 (m, 2H), 1.36–1.29 (m, 10H), 0.92 (t,  $J = 7.0$  Hz, 3H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  163.6 (d,  $J = 252$  Hz), 139.8, 139.3, 134.9 (d,  $J = 7.4$  Hz), 132.4, 132.3, 129.3, 127.9, 125.7, 121.6, 117.8, 115.1 (d,  $J = 19.6$  Hz), 33.5, 32.0, 29.7, 29.6, 29.5, 29.4, 22.8, 14.2;  $^{11}\text{B}$  NMR (128.38 MHz,  $\text{CDCl}_3$ )  $\delta$  33.9; IR (neat) 3375, 2923, 1595, 1224, 832  $\text{cm}^{-1}$ ; HRMS (CI)  $m/z$   $[\text{M}]^+$  calcd for  $\text{C}_{24}\text{H}_{29}\text{BNF}$  361.2377, found 361.2368.

**3-[(E)-1-Decen-1-yl]-2-(3-methoxyphenyl)-2,1-borazonaphthalene (5d).** The title compound was obtained as a colorless oil in 81% yield (302.1 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (s, 1H), 7.94 (s, 1H), 7.68 (d,  $J = 7.7$  Hz, 1H), 7.43–7.40 (m, 2H), 7.32 (d,  $J = 7.2$  Hz, 1H), 7.29–7.27 (m, 2H), 7.22 (t,  $J = 7.5$  Hz, 1H), 7.01 (dd,  $J = 8.2, 2.7$  Hz, 1H), 6.68 (d,  $J = 15.6$  Hz, 1H), 6.10–6.04 (m, 1H), 3.89 (s, 3H), 2.21–2.16 (m, 2H), 1.47–1.43 (m, 2H), 1.36–1.28 (m, 10H), 0.93 (t,  $J = 6.9$  Hz, 3H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  159.4, 139.8, 139.5, 132.5, 132.3, 129.5, 129.4, 128.0, 125.9, 125.5, 121.7, 118.3, 118.0, 114.4, 55.4, 33.7, 32.2, 29.9, 29.8, 29.6, 29.6, 23.0, 14.4;  $^{11}\text{B}$  NMR (128.38 MHz,  $\text{CDCl}_3$ )  $\delta$  34.8; IR (neat) 3366, 2924, 1558, 1451, 1236, 971, 761  $\text{cm}^{-1}$ ; HRMS (CI)  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{25}\text{H}_{33}\text{BNO}$  374.2655, found 374.2661.

**3-[(E)-1-Decen-1-yl]-2-(4-trifluorophenyl)-2,1-borazonaphthalene (5e).** The title compound was obtained as a light brown oil in 83% yield (341.3 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (s, 1H), 7.91 (s, 1H), 7.80 (d,  $J = 7.7$  Hz, 2H), 7.70–7.68 (m, 3H), 7.42–7.39 (m, 1H), 7.27 (d,  $J = 8.1$  Hz, 1H), 7.22–7.21 (m, 1H), 6.56 (dd,  $J = 15.6, 1.0$  Hz, 1H), 5.60–5.94 (m, 1H), 2.14 (m, 2H), 1.42–1.39 (m, 2H), 1.27–1.32 (m, 10H), 0.90 (t,  $J = 5.1$  Hz, 3H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  140.1, 139.1, 133.1, 132.8, 131.9, 130.4 (d,  $J = 32.3$  Hz), 129.4, 128.1, 126.3 (q,  $J = 272.2$  Hz), 125.8, 124.6 (q,  $J = 3.7$  Hz), 121.9, 117.9, 33.5, 32.0, 29.6, 29.5, 29.3, 22.8, 14.2;  $^{11}\text{B}$  NMR (128.38 MHz,  $\text{CDCl}_3$ )  $\delta$  34.5; IR (neat) 3395, 2924, 1559, 1323, 969, 836  $\text{cm}^{-1}$ ; HRMS (CI)  $m/z$   $[\text{M}]^+$  calcd for  $\text{C}_{25}\text{H}_{29}\text{BNF}_3$  411.2345, found 411.2353.

**1-Allyl-3-[(E)-1-decen-1-yl]-2-methyl-2,1-borazonaphthalene (5f).** The title compound was obtained as a light yellow oil in 62% yield (199.0 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (s, 1H), 7.61 (d,  $J = 7.0$  Hz, 1H), 7.39 (dd,  $J = 4.7, 1.2$  Hz, 2H), 7.17–7.13 (m, 1H), 6.66 (dd,  $J = 15.5, 1.0$  Hz, 1H), 6.10–6.01 (m, 2H), 5.15 (dd,  $J = 10.5, 1.4$  Hz, 1H), 4.99 (dd,  $J = 17.2, 1.3$  Hz, 1H), 4.72 (dd,  $J = 4.1, 2.0$  Hz, 2H), 2.27–2.22 (m, 2H), 1.54–1.49 (m, 2H), 1.41–1.27 (m, 10H), 0.93–0.89 (m, 6H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  141.2, 137.7, 134.7, 132.7, 131.3, 130.2, 127.8, 126.7, 120.8, 115.9, 115.5, 49.8, 33.8, 32.2, 30.1, 29.9, 29.7, 29.6, 23.0, 14.4;  $^{11}\text{B}$  NMR (128.38 MHz,  $\text{CDCl}_3$ )  $\delta$  38.7; IR (neat) 2923, 1556, 1405, 1212, 968  $\text{cm}^{-1}$ ; HRMS (CI)  $m/z$   $[\text{M}]^+$  calcd for  $\text{C}_{22}\text{H}_{32}\text{BN}$  321.2628, found 321.2633.

**1-Benzyl-3-[(E)-1-decen-1-yl]-2-methyl-2,1-borazonaphthalene (5g).** The title compound was obtained as a light brown oil in 90% yield (333.9 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (s, 1H), 7.68 (d,  $J = 7.0$  Hz, 1H), 7.35–7.27 (m, 5H), 7.19–7.16 (m, 3H), 6.78 (dd,  $J = 15.6, 0.6$  Hz, 1H), 6.19 (dt,  $J = 15.5, 6.9$  Hz, 1H), 5.38 (s, 2H), 2.36–2.37 (m, 2H), 1.63–1.57 (m, 2H), 1.50–1.39 (m, 10H), 1.00–0.98 (m, 6H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  141.3, 138.8, 138.02, 132.7, 131.4, 130.2, 129.0, 127.9, 127.1, 126.9, 126.1, 120.9, 115.9, 51.4, 33.8, 32.2, 30.1, 29.9, 29.8, 29.7, 23.0, 14.4;  $^{11}\text{B}$  NMR (128.38 MHz,  $\text{CDCl}_3$ )  $\delta$  39.0; IR (neat) 2924, 2853, 1610, 1492, 1402, 1360, 967  $\text{cm}^{-1}$ ; HRMS (CI)  $m/z$   $[\text{M}]^+$  calcd for  $\text{C}_{26}\text{H}_{34}\text{BN}$  371.2784, found 371.2791.

**3-[(E)-1-Decen-1-yl]-2-(4-methylphenyl)-2,1-borazonaphthalene (5h).** The title compound was obtained as a light yellow oil in 80% yield (285.6 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (s, 1H), 7.91 (s, 1H), 7.68 (d,  $J$  = 7.5 Hz, 1H), 7.57–7.52 (m, 2H), 7.42–7.37 (m, 2H), 7.29–7.25 (m, 2H), 7.21 (t,  $J$  = 7.5 Hz, 1H), 6.68 (d,  $J$  = 15.5 Hz, 1H), 6.07 (dt,  $J$  = 15.4, 7.0 Hz, 1H), 2.47 (s, 3H), 2.20 (q,  $J$  = 6.9 Hz, 2H), 1.49–1.46 (m, 2H), 1.39–1.33 (m, 10H), 0.94 (t,  $J$  = 6.9 Hz, 3H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  139.7, 137.5, 133.9, 132.7, 132.2, 130.3, 129.5, 128.1, 128.0, 125.9, 121.6, 117.9, 33.7, 32.2, 30.0, 29.9, 29.7, 29.6, 23.0, 21.9, 14.4;  $^{11}\text{B}$  NMR (128.38 MHz,  $\text{CDCl}_3$ )  $\delta$  34.7; IR (neat) 3369, 2923, 2852, 1612, 1557, 1450, 969  $\text{cm}^{-1}$ ; HRMS (CI)  $m/z$  [M] $^+$  calcd for  $\text{C}_{25}\text{H}_{32}\text{BN}$  357.2628, found 357.2632.

**6-[(E)-1-Decen-1-yl]-2-methyl-3-phenyl-2,1-borazonaphthalene (6).** The title compound was obtained as a brown oil in 83% yield (296.3 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (s, 1H), 7.77 (s, 1H), 7.57 (d,  $J$  = 1.5 Hz, 1H), 7.47–7.41 (m, 5H), 7.33–7.31 (m, 1H), 7.16 (d,  $J$  = 8.5 Hz, 1H), 6.46 (d,  $J$  = 16.0 Hz, 1H), 6.23 (dt,  $J$  = 15.7, 6.9 Hz, 1H), 2.27–2.22 (m, 2H), 1.52–1.48 (m, 2H), 1.39–1.28 (m, 10H), 0.92 (t,  $J$  = 7.0 Hz, 3H), 0.83 (s, 3H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  145.1, 141.8, 139.0, 131.3, 130.0, 129.6, 128.5, 128.4, 127.2, 126.3, 126.0, 125.3, 117.7, 33.4, 32.2, 29.8, 29.8, 29.6, 29.6, 23.0, 14.4;  $^{11}\text{B}$  NMR (128.38 MHz,  $\text{CDCl}_3$ )  $\delta$  36.4; IR (neat) 3372, 2924, 2853, 1617, 1577, 1456, 962, 762  $\text{cm}^{-1}$ ; HRMS (CI)  $m/z$  [M] $^+$  calcd for  $\text{C}_{25}\text{H}_{32}\text{BN}$  357.2628, found 357.2621.

**2-Methyl-3,6-di[(E)-1-propen-1-yl]-2,1-borazonaphthalene (7).** The title compound was obtained as a yellow solid in 76% yield (169.4 mg): mp 106–110  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (s, 1H), 7.60 (s, 1H), 7.48 (d,  $J$  = 1.5 Hz, 1H), 7.38 (dd,  $J$  = 8.3, 1.9 Hz, 1H), 7.07 (d,  $J$  = 8.4 Hz, 1H), 6.62 (dd,  $J$  = 15.7, 0.7 Hz, 1H), 6.48 (dd,  $J$  = 15.7, 1.5 Hz, 1H), 6.26–6.14 (m, 2H), 1.95–1.93 (m, 6H), 0.86 (s, 3H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  137.4, 137.6, 133.9, 130.1, 130.0, 125.7, 125.4, 124.5, 124.3, 123.1, 116.6, 18.3, 17.8;  $^{11}\text{B}$  NMR (128.38 MHz,  $\text{CDCl}_3$ )  $\delta$  37.2; IR (neat) 3371, 2957, 2910, 1610, 1557, 1436  $\text{cm}^{-1}$ ; HRMS (CI)  $m/z$  [M] $^+$  calcd for  $\text{C}_{15}\text{H}_{18}\text{BN}$  223.1532, found 223.1532.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Copies of  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{11}\text{B}$  NMR spectra for all compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [gmlandr@sas.upenn.edu](mailto:gmlandr@sas.upenn.edu).

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This research was supported by the NIGMS (R01 GM-081376) and Eli Lilly. Frontier Scientific is acknowledged for their generous donation of potassium organotrifluoroborates. Frontier Scientific and Johnson Matthey are acknowledged for their donation of palladium salts. Dr. Rakesh Kohli (University of Pennsylvania) is acknowledged for obtaining the HRMS data.

## ■ REFERENCES

- (1) Ehle, A. R.; Zhou, Q.; Watson, M. P. *Org. Lett.* **2012**, *14*, 1202.
- (2) Martinez, R.; Voica, F.; Genet, J.-P.; Darses, S. *Org. Lett.* **2007**, *9*, 3213.
- (3) Gorrane, A.; Garcia, H.; Corma, A. *J. Catal.* **2013**, *302*, 49.
- (4) Kuroda, J.; Inamoto, K.; Hiroya, K.; Doi, T. *Eur. J. Org. Chem.* **2009**, 2251.
- (5) (a) Green, I. R.; Hugo, V. I.; Oosthuizen, G.; Giles, R. G. F. *Synth. Commun.* **1996**, *26*, 867. (b) Giles, R. G. F.; Green, I. R.; Hugo,

V. I.; Mitchell, P. R. K.; Yorke, S. C. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2383.

(6) (a) Sun, Y.-P.; Sears, D. F., Jr.; Saltiel, J.; Mallory, F. B.; Mallory, C. W.; Buser, C. A. *J. Am. Chem. Soc.* **1988**, *110*, 6974. (b) Saltiel, J.; Choi, J.-O.; Sears, D. F., Jr.; Eaker, D. W.; Mallory, F. B.; Mallory, C. W. *J. Phys. Chem.* **1994**, *98*, 13162.

(7) Ito, T.; Ikemoto, T.; Yamano, T.; Mizuno, Y.; Tomimatsu, K. *Tetrahedron: Asymmetry* **2013**, *14*, 3525.

(8) Kong, W.; Fu, C.; Ma, S. *Eur. J. Org. Chem.* **2010**, 6545.

(9) For recent reviews of azaborines, see: (a) Liu, Z.; Marder, T. B. *Angew. Chem., Int. Ed.* **2008**, *47*, 242. (b) Campbell, P. G.; Marwitz, A. J. V.; Liu, S.-Y. *Angew. Chem., Int. Ed.* **2012**, *51*, 6074. (c) Bosdet, M. J. D.; Piers, W. E. *Can. J. Chem.* **2009**, *87*, 8.

(10) Molander, G. A.; Wisniewski, S. R. *J. Org. Chem.* **2014**, *79*, 6663.

(11) For reviews of the Suzuki–Miyaura reaction, see: (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (b) Bellina, F.; Carpita, A.; Rossi, R. *Synthesis* **2004**, 2419. (c) Kotha, S.; Lahiri, K.; Kashinath, D. *Tetrahedron* **2002**, *58*, 9633. (d) Sandrock, D. L. *Alkylboron Reagents. In Science of Synthesis, Cross Coupling and Heck-Type Reactions 1*; Molander, G. A., Ed.; Georg Thieme Verlag: Stuttgart, Germany, 2013; Vol. 1. (e) Miyaura, N. *Metal-Catalyzed Cross-Coupling Reactions of Organoboron Compounds with Organic Halides. In Metal-Catalyzed Cross-Coupling Reactions*; de Meijere, A.; Diederich, F., Eds.; Wiley-VCH: Weinheim, Germany, 2003; Vol. 1. (f) *Boronic Acids*; Hall, D. G., Ed.; Wiley-VCH: Weinheim, Germany, 2005. (g) Molander, G. A.; Canturk, B. C. *Angew. Chem., Int. Ed.* **2009**, *48*, 9240.

(12) For reviews of potassium organotrifluoroborates, see: (a) Molander, G. A.; Figueroa, R. *Aldrichimica Acta* **2005**, *38*, 49. (b) Molander, G. A.; Ellis, N. *Acc. Chem. Res.* **2007**, *40*, 275. (c) Stefani, H. A.; Cella, R.; Vieira, A. S. *Tetrahedron* **2007**, *63*, 3623. (d) Darses, S.; Genet, J. P. *Chem. Rev.* **2008**, *108*, 288. (e) Molander, G. A.; Jean-Gerard, L. *Organotrifluoroborates: Organoboron Reagents for the Twenty-First Century. In Boronic Acids: Preparation and Applications in Organic Synthesis, Medicine and Materials*; Hall, D. G., Ed.; Wiley-VCH: Weinheim, Germany, 2011; Vol. 2, pp 507–550. (f) Molander, G. A.; Jean-Gerard, L. *Cross-Coupling Reactions of Organotrifluoroborate Salts. In Organic Reactions*; Denmark, S. E., Ed.; John Wiley & Sons, Inc.: New York, 2013; Vol. 79, pp 1–316.

(13) Wisniewski, S. R.; Guenther, C. G.; Argintaru, O. A.; Molander, G. A. *J. Org. Chem.* **2014**, *79*, 365–378.