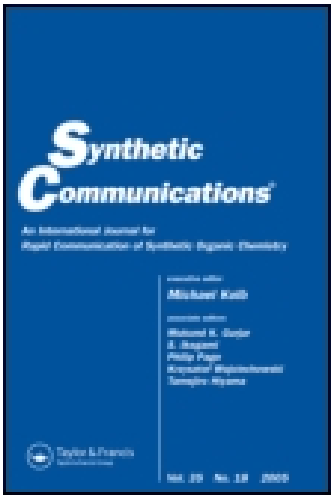

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Convenient Preparation of Cycloalkenyl Boronic Acid Pinacol Esters

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Convenient Preparation of Cycloalkenyl Boronic Acid Pinacol Esters

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Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada

Abstract: A practical method for the preparation of cycloalkenyl boronic acid pinacol esters is described. These important synthetic intermediates are typically made using more expensive methods like transition metal-catalyzed borylation of alkenyl halides or triflates. In this work, they are obtained from the simple corresponding cycloalkanones, which are subjected to Shapiro reaction conditions followed by trapping with a borate ester. The requisite products are obtained in very good to excellent yields, and the reactions can be scaled up to multigram amounts. By providing a simple alternative to common methods that make use of expensive transition-metal catalysts and formation of sensitive intermediates, this convenient method will be useful for the synthesis of ring-containing partners for Suzuki–Miyaura cross-coupling and other reactions employing boronic esters as substrates.

Keywords: Boronic acid, boronic esters, Shapiro reaction, Suzuki–Miyaura cross-coupling

The Suzuki–Miyaura cross-coupling of aryl or alkenyl boronic acids and esters is one of the most important reactions in organic synthesis,[1] and it has been tremendously utilized in the synthesis of natural products and bioactive molecules.[2] In this context, the analogous cycloalkenyl boronic acids and esters are also important coupling partners to access novel, polysubstituted alkenes. These boronic esters can, however, be forbiddingly expensive. (For example, the 2007 Aldrich price for 1 g of

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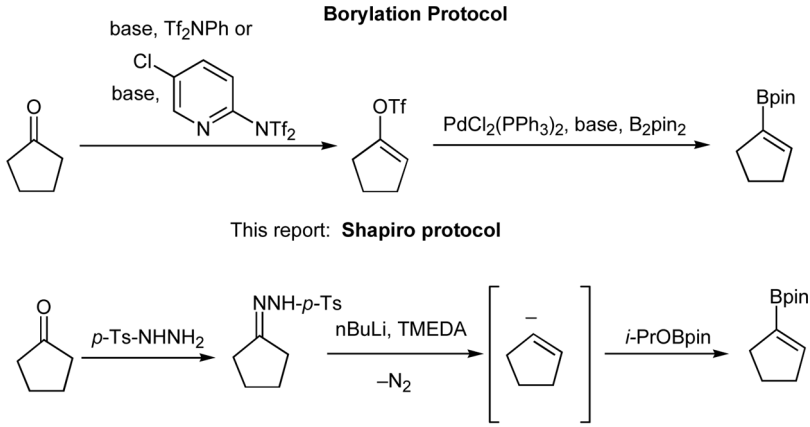
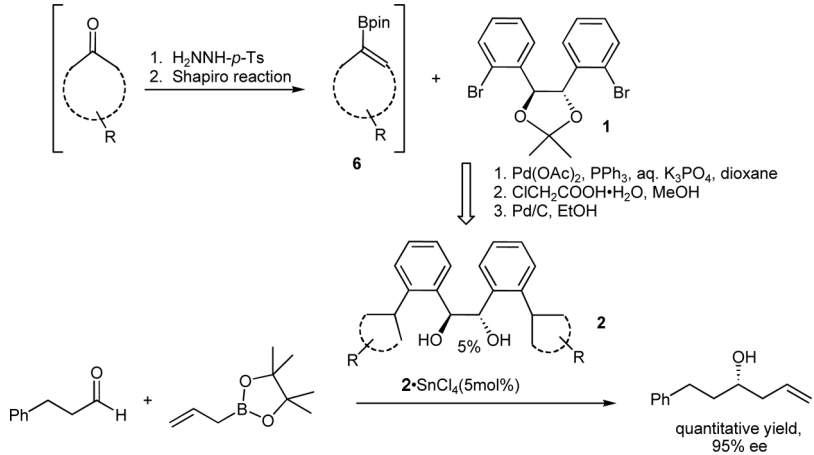


Scheme 1. General approaches to cycloalkenyl boronic esters.

cyclohexenyl boronic acid pinacol ester is CDN$ 285) In general, cycloalkenyl boronates are accessed by Miyaura borylation of cycloalkenyl triflates or halides (Scheme 1).[3] The sensitive cycloalkenyl triflates are in turn obtained from the parent cycloalkanones using deprotonation and enolate quenching with expensive triflating agents.[4] Herein, we report a very convenient preparation and isolation of various cycloalkenyl boronic esters using the Shapiro reaction[5] of cycloalkylhydrazones and isolation of the corresponding cycloalkenyl boronic acids as their pinacol esters. Aside from one example where the organoboron product was not isolated, this appears to be the first report of preparation of cycloalkenyl boronic acid pinacol esters using a Shapiro protocol.[6] The current methodology provides the requisite cycloalkenyl boronic esters in 65–90% overall yield for a two-step sequence.[7]

While working on the modification of the diol scaffold utilized in the **2** · $SnCl_4$-catalyzed allylboration of aldehyde substrates (Scheme 2), we noticed that introduction of cycloalkyl groups in the ortho-position of the hydrobenzoin skeleton was crucial for obtaining homoallyl alcohol products in high enantioselectivities.[8] During our optimization efforts to generate various ring sizes on the diol catalyst **2**, we required a rapid preparation of the corresponding cycloalkenyl boronic esters. The latter would serve to install various cycloalkyl rings at the ortho-position of the protected hydrobenzoin **1** by a Suzuki–Miyaura cross-coupling process.

A general preparation of cycloalkenyl boronic esters had to be economical and efficient. As such, we envisioned a cycloalkenyl anion capture of a boron-containing electrophile. To this end, we explored a Shapiro reaction of the cycloalkyl hydrazones to generate cycloalkenyl

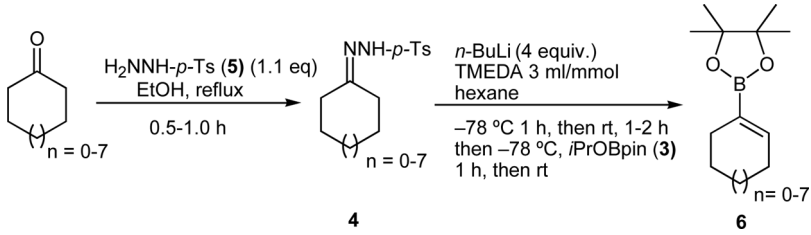


Scheme 2. Preparation and application of cycloalkenyl boronic esters for the preparation of ortho-cycloalkyl substituted diol **2**.

anions. We anticipated that quenching of the generated anions with commercially available isopropoxy pinacol borate would allow for easier handling and for proper purification and characterization of the products as stable pinacol esters.

In the event, as shown in Scheme 3, cycloalkylhydrazones **4** were readily obtained as crystalline solids in almost quantitative yields by a simple addition/dehydration reaction with inexpensive hydrazide reagent **5** in refluxing absolute ethanol. The majority of cycloalkyl hydrazone substrates started to precipitate out when the reaction reached completion, after which the reaction mixture was cooled in an ice bath to allow for completion of crystallization. The freshly obtained cycloalkyl hydrazones **4** were suspended in hexanes followed by addition of *N,N*-tetramethylethylenediamine (TMEDA) (3 ml/mmol of hydrazone) and cooled to −78 °C. This mixture was treated with 4 equivalents of *n*- BuLi, after which dinitrogen was extruded at room temperature during 1 to 2 h. The resulting orange to red-brown solutions containing the corresponding cycloalkenyl anion equivalents were cooled to −78 °C and treated with isopropoxypinacol borate **3** (Scheme 3), and the resulting products were easily purified by flash chromatography over silica gel.

The resulting cycloalkenyl boronate products **6** are robust and can be stored for weeks without any observable decomposition. Table 1 illustrates the scope of this protocol. The majority of the products were obtained in good to excellent yields, and this chemistry appears to be general for the preparation of various ring sizes of cycloalkenyl boronic esters from the corresponding cycloalkanones.



Scheme 3. Preparation of cycloalkenyl pinacol boronate esters.

CONCLUSION

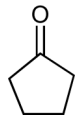
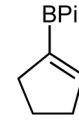
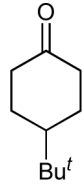
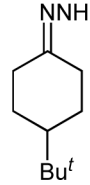
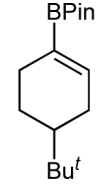
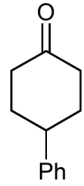
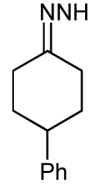
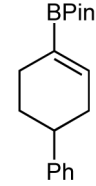
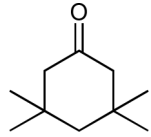
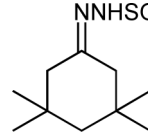
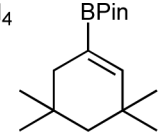
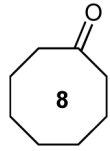
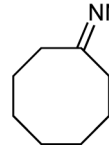
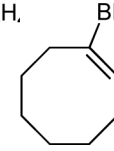
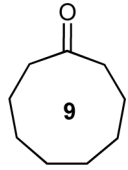
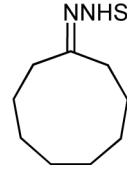
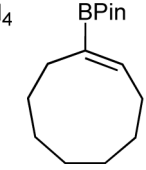
We have described a two-step sequence that provides easy access to cycloalkenyl boronic esters in good to excellent yields, and this methodology is readily scalable to multigram quantities. The intermediates are robust and can be stored for months without any observable degradation. Accordingly, expensive reagents including palladium catalyst, bis(pinacolato)diboron, and activating agents are avoided. As such, this method should find widespread application in the preparation of cycloalkenylboronic acid pinacol esters and their application in several types of cross-coupling reactions.

EXPERIMENTAL

General

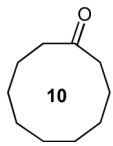
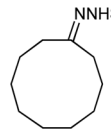
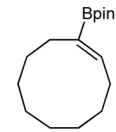
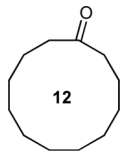
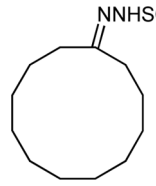
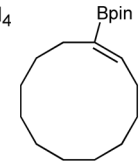
All cycloalkanones were purchased from Aldrich or TCI America. TMEDA was purchased from Acros Organics in 2.5-L containers. Unless otherwise noted, all reactions were performed under an argon atmosphere using flame-dried glassware. TMEDA and hexane were distilled over CaH_2. Thin-layer chromatography (TLC) was performed on silica-gel 60 F254 plates and were visualized with UV light and $KMnO_4$ stain. NMR spectra were recorded on 300-, 400-, or 500-MHz instruments. The residual solvent protons (^1H) or the solvent carbons (^{13C} H) were used as internal standards. ^1H NMR data are presented as follows: chemical shift in parts per million downfield from tetramethylsilane (multiplicity, coupling constant, integration). The following abbreviations are used in reporting NMR data: s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; qt, quartet of triplets; dd, doublet of doublets; dt, doublet of triplets; AB, AB quartet; m, multiplet. High-resolution mass spectra were recorded by the University of Alberta Mass Spectrometry Services Laboratory using

Table 1. Preparation of cycloalkenyl pinacol boronic esters. Yields (%) are for the two-step sequence

Entry	Cycloalkanone	Cyclohydrazone	Product	Yield (%) of **6**, two steps
1		 (**4a**)	 (**6a**)	80
2		 (**4b**)	 (**6b**)	70
3		 (**4c**)	 (**6c**)	65
4		 (**4d**)	 (**6d**)	90
5		 (**4f**)	 (**6e**)	80
6		 (**4g**)	 (**6f**)	70

(*Continued*)

Table 1. Continued

Entry	Cycloalkanone	Cyclohydrazone	Product	Yield (%) of **6**, two steps
7		 (**4h**)	 (**6g**)	88
8		 (**4i**)	 (**6h**)	95

either electron impact (EI) or electrospray (ES) ionization techniques. Infrared spectra and optical rotations were recorded by the University of Alberta Department of Chemistry Spectral Services.

Compound 4a

p-Tolylsulfonylhydrazine (90.0 g, 0.48 mol) was added to a 250-mL flask equipped with a magnetic stirbar, and this white solid was suspended in 60 ml of absolute ethanol. Cyclopentanone (40.7 g, 0.48 mol) was added to this suspension, and the reaction mixture was heated to reflux at 100 °C. After heating for 20 min, the mixture dissolved, and after another 20 min, a white solid corresponding to the hydrazone started crashing out. After heating for 1 h, the reaction mixture was cooled using an ice-water bath to precipitate out the majority of the hydrazone. The resulting solid was collected by filtration and was washed thoroughly with ice-cold ethanol. Air drying under reduced pressure for 1 h afforded 114 g of the required hydrazone in near quantitative yield as a white solid with identical spectral properties compared to literature.[9]

Compound 6a

To a flame-dried 500-ml round-bottom flask equipped with a magnetic stirbar and rubber septum, cyclopentanone *p*-tolylsulfonylhydrazone

(6.48 g, 27.15 mmol) was added followed by 80 mL of anhydrous hexanes. To this mixture 80 ml of anhydrous TMEDA (~3 mL/mmol of hydrazone) were added, and the reaction mixture was cooled to −78 °C and maintained at this temperature for 15 min, after which 43 ml (107.5 mmol, 4.0 equiv.) of 2.5 M *n*-BuLi was added over 15 min. The reaction mixture was then stirred for 1 h at −78 °C and then brought to room temperature and stirred for 1.5 h. Nitrogen was extruded from the reaction, and at the end of the period, the reaction mixture was then brought to −78 °C and maintained for another 15 min, after which 20.1 g (108.6 mmol, 4 equiv.) of pinacol isopropyl borate were added. The reaction mixture was stirred for another hour at −78 °C and then brought to room temperature and stirred for 3 h. The reaction was quenched with the addition of saturated NH_4Cl and then extracted three times with ether. The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was subjected to flash chromatography (2% EtOAc/hexanes) to afford 4.19 g (80%) of **6a** as a light yellow oil. IR (neat) 2979, 1615, 1374, 1318, 1146 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.54 (t, $J = 2.0$ Hz, 1 H), 2.48–2.31 (m, 4 H), 1.88–1.74 (m, 2 H), 1.27 (s, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 83.0, 34.8, 34.5, 24.8, 23.9. HRMS (EI) calcd. for $C_{11}H_{19}O_2$ ^{11}B: 194.1478. Found: 194.1482.

Compound 4b

Following the general procedure described for **4a**, the product was obtained in 90% yield as a white solid. IR (cast film) 3221, 2955, 2868, 1643, 1598, 1395, 1327, 1164 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, $J = 8.4$ Hz, 2H), 7.36 (brs, 1H), 7.31 (d, $J = 8.4$ Hz, 2H), 2.68–2.72 (m, 1H), 2.44–2.49 (m, 1H), 2.43 (s, 3H), 2.06 (ddd, $J = 4.8$, 12.4, 12.4 Hz, 1H), 1.87–1.92 (m, 2H), 1.75 (ddd, $J = 5.2$, 13.6, 13.6, 1H), 1.03–1.23 (m, 3H), 0.84 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.80, 145.20, 143.88, 135.44, 129.51, 128.46, 128.09, 126.62, 126.37, 43.14, 34.99, 33.87, 32.76, 26.65, 21.57. HRMS (m/z calcd. for $C_{17}H_{27}N_2O_2S$: 323.17878. Found: 323.17876.

Compound 6b

Following the general procedure described for **6a**, **6b** was obtained in 77% yield as a pale yellow solid. IR (cast film) 3026, 2978, 2924, 1633, 1387, 1340, 1314, 1146 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.19–7.344

(m, 5H), 6.7–6.72 (m, 1H), 2.77–2.85 (m, 1H), 2.37–2.48 (m, 2H), 2.21–2.34 (m, 2H), 1.97–2.01 (m, 1H), 1.68–1.83 (m, 1H), 1.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.24, 146.26, 128.37, 126.86, 125.97, 83.12, 39.81, 34.93, 29.82, 27.06, 24.88, 24.85. HRMS (EI) calcd. for $C_{19}H_{25}O_2{}^{11}B$: 284.19476. Found: 284.19481.

Compound 4c

Following the general procedure described for **4a**, the requisite hydrazone was obtained in 95% yield as a white solid. IR (cast film) 3219, 3061, 2930, 1325, 1185, 1164 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, $J = 8.4$ Hz, 2 H), 7.53 (brs, 1 H), 7.34 (d, $J = 8.4$ Hz, 2H), 7.14–7.31 (m, 5H), 2.80–2.85 (m, 1H), 2.76 (dddd, $J = 4.0$, 4.0, 12.4, 12.4 Hz, 1H), 2.55–2.60 (m, 1H), 2.45 (s, 3H), 2.26 (ddd, $J = 4.8$, 14, 14 Hz, 1H), 2.03–2.07 (m, 2H), 1.98 (ddd, $J = 5.6$, 14.8, 14.8 Hz, 1H), 1.68 (dddd, $J = 4$, 13.2, 13.2, 13.2 Hz, 1H), 1.58 (dddd, $J = 4.4$, 13, 13, 13 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.20, 143.85, 135.56, 129.51, 128.13, 47.08, 34.94, 32.48, 27.48, 27.40, 26.72, 26.39, 21.62. HRMS (ESI), m/z calcd. for $C_{19}H_{23}N_2O_2S$: 343.14748. Found: 343.14738.

Compound 6c

Following the general procedure described for **6a**, the product was obtained in 68% yield as a light yellow oil that crystallizes upon standing. IR (cast film) 2962, 2916, 2870, 1636, 1388, 1331, 1145 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.59 (t, $J = 2$ Hz, 1H), 2.26–2.36 (m, 1H), 1.97–2.14 (m, 2H), 1.77–1.90 (m, 2H), 1.24 (s, 12H), 1.03–1.15 (m, 1H), 0.83–0.92 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.43, 83.01, 43.81, 32.27, 28.47, 27.85, 27.14, 24.87, 24.82, 23.98. HRMS (EI) calcd. for $C_{16}H_{29}O_2{}^{11}B$: 264.21126. Found: 264.22607.

Compound 4d

Following the general procedure described for **4a**, the product was obtained in quantitative yield as a white solid. IR (cast film) 3228, 2953, 2897, 1641, 1598, 1458, 1339, 1163 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, $J = 8.4$ Hz, 2H), 7.27 (d, $J = 8$ Hz, 2H), 2.39 (s, 3H), 1.99 (d, $J = 4.8$ Hz, 4 H), 1.28 (s, 2H), 0.82 (s, 6H), 0.81 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.23, 143.77, 135.40, 129.41, 127.98, 52.22, 47.87, 39.43, 35.01, 34.66, 30.63, 30.59, 21.54. HRMS (EI) calcd. for $C_{17}H_{26}N_2O_2S$: 322.17151. Found 322.17151.

Compound 6d

Following the general procedure described for **6a**, the product was obtained in 90% yield as a pale yellow solid. IR (cast film) 2978, 2951, 2899, 1633, 1387, 1328, 1147 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.27 (t, $J = 2.4$ Hz, 1H), 8.85 (d, $J = 2.8$ Hz, 2H), 1.32 (s, 2H), 1.27 (s, 12H), 1.01 (s, 6H), 0.92 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.26, 82.94, 49.81, 39.63, 33.28, 30.99, 29.93, 29.79, 24.80. HRMS (EI) calcd. for $C_{16}H_{29}O_2{}^{11}B$: 264.21126. Found 264.23635.

Compound 4e

Following the general procedure described for **4a**, the product was isolated in quantitative yield as a white solid. IR (neat) 3214, 2926, 1330, 1160 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, $J = 8.4$ Hz, 2H), 7.88–7.56 (s, 1 H), 7.28 (d, $J = 8.4$ Hz, 2 H), 2.40 (s, 3 H), 2.28 (t, $J = 6.4$ Hz, 2 H), 2.22 (t, $J = 6.4$ Hz, 2 H), 1.70–1.60 (m, 4 H), 1.42–1.31 (m, 4 H), 1.21–1.12 (m, 2 H). HRMS (EI) calcd. for $C_{15}H_{23}N_2O_2S$: 295.1475. Found: 295.1475. Anal. calcd. for $C_{15}H_{23}N_2O_2S$: C, 61.02; H, 7.80; N, 9.49. Found: C, 61.11; H, 7.62; N, 9.53. For ^{13}C NMR, see Ref. 9b.

Compound 6e

Following the general procedure described for **6a**, the product was isolated in 80% yield as a pale yellow oil. IR (cast film) 2925, 1630, 1381, 1148 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.58 (t, $J = 8.0$ Hz, 1 H), 2.32–2.28 (m, 2 H), 2.28–2.19 (m, 2 H), 1.56–1.41 (m, 8 H), 1.26 (s, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 114.3, 82.9, 29.6, 28.8, 27.1, 26.4, 26.2, 25.9, 24.7. HRMS (EI) calcd. for $C_{14}H_{25}O_2{}^{11}B$: 236.1948. Found: 236.1948.

Compound 4f

Following the general procedure described for **4a**, the product was isolated in quantitative yield as a white solid. IR (cast film) 3224, 2924, 2865, 1338, 1185, 1167 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, $J = 8.4$ Hz, 2H), 1.29 (d, $J = 8$ Hz, 2H), 2.41 (s, 3H), 2.28–2.31 (m, 2H), 2.20–2.23 (m, 2H), 1.60–1.72 (m, 4H), 1.49–1.55 (m, 2H), 1.41–1.47 (m, 2H), 1.16–1.22 (m, 2H), 1.03–1.08 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.90, 143.89, 135.85, 129.42, 127.92, 35.50, 30.46, 28.34, 27.57, 27.49,

24.52, 23.48, 22.93, 21.54; HRMS (EI) calcd. for $C_{16}H_{24}N_2O_2S$: 308.15585. Found: 308.15596.

Compound 6f

Following the general procedure described for **6a**, the product was isolated in 70% yield as a colorless oil. IR (cast film) 2977, 2928, 2857, 1629, 1379, 1146 1167 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.48 (t, $J = 8.4$ Hz), 2.20–2.29 (m, 4H), 1.43–1.49 (m, 10H), 1.25 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.94, 82.90, 27.36, 26.85, 26.50, 25.78, 25.58, 25.38, 24.78, 24.71, 24.67; HRMS (EI) calcd. for $C_{15}H_{27}O_2{}^{11}B$: 250.21041. Found: 250.11952.

Compound 4g

Following the general procedure described for **4a**, the product was isolated in quantitative yield as a white solid. IR (cast film) 3219, 2927, 2869, 1598, 1335, 1167 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, $J = 8.4$ Hz, 2H), 7.46 (brs, 1H), 7.30 (d, $J = 8.4$ Hz, 2H), 2.41 (s, 3H), 2.34 (appt, $J = 6.3$ Hz, 2H), 2.21 (appt, $J = 6.6$ Hz, 2H), 1.62–1.70 (m, 4H), 1.08–1.32 (m, 8H), 1.01–1.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.29, 143.81, 135.69, 129.40, 128.17, 41.97, 34.97, 30.08, 25.51, 25.24, 24.02, 23.82, 23.34, 22.79, 22.56; HRMS (m/z) calcd. for $C_{17}H_{27}N_2O_2S$: 323.17878. Found: 323.17850.

Compound 6g

Following the general procedure described for **6a**, the product was isolated in 88% yield as a colorless oil. IR (cast film) 2978, 2926, 2852, 1626, 1475, 1380, 1348, 1302, 1146 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.33 (t, $J = 8.8$ Hz), 2.31–2.35 (m, 4H), 1.57–1.60 (m, 4H), 1.37–1.40 (m, 8H), 1.25 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.91, 82.79, 26.97, 26.95, 26.78, 26.44, 25.63, 24.78, 24.67, 21.40, 20.79. HRMS (EI) calcd. for $C_{16}H_{29}O_2{}^{11}B$: 264.22606. Found: 264.22591.

Compound 4h

Following the general procedure described for **4a**, the product was isolated in quantitative yield as a white solid. IR (cast film) 2978, 2929, 2860, 1625,

1468, 1409, 1147 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, $J = 8.8$ Hz, 2H), 7.47 (brs, 1H), 7.28 (d, $J = 8.8$ Hz, 2H), 2.40 (s, 3H), 2.21 (appt, $J = 8$ Hz, 2H), 2.12 (appt, $J = 8.8$ Hz, 2H), 1.57–1.65 (m, 2), 1.41–1.49 (m, 2H), 1.08–1.15 (m, 8H), 0.8–0.95 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.44, 143.81, 135.71, 129.52, 128.16, 31.31, 28.80, 25.98, 25.88, 23.67, 23.23, 22.96, 22.73, 22.66, 21.88, 21.62, 21.49. HRMS (EI) calcd. for $C_{19}H_{30}N_2O_2S$: 350.20280. Found: 350.20289.

Compound 6h

Following the general procedure described for **6a**, the product was isolated in 95% yield as a colorless oil. IR (cast film) 2977, 2928, 2859, 1625, 1468, 1408, 1379, 1344, 1301, 1147 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.28 (t, $J = 6$ Hz, 1H), 2.16–2.22 (m, 4H), 1.47–1.54 (m, 4H), 1.34–1.41 (m, 8H), 1.29–1.30 (m, 4H), 1.26 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.70, 132.56, 82.88, 34.63, 31.71, 27.35, 26.46, 25.53, 24.89, 24.17, 22.67, 22.48, 14.00, 10.95. HRMS (EI) calcd. for $C_{18}H_{33}O_2{}^{11}B$: 292.25736. Found: 292.25804.

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