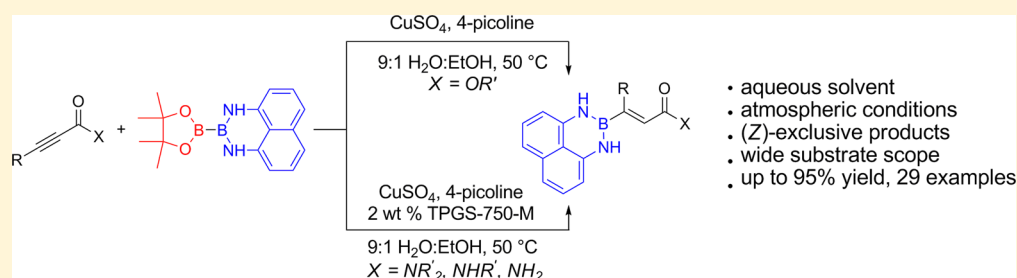


Chemo-, Regio-, and Stereoselective Copper(II)-Catalyzed Boron Addition to Acetylenic Esters and Amides in Aqueous Media

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Supporting Information



ABSTRACT: Aqueous conditions were developed for conducting an open-to-air, copper(II)-catalyzed addition of pinBBdan to alkynoates and alkynamides. The simple and mild β -borylation protocol proceeds in a remarkably chemo-, regio-, and stereoselective fashion to afford 1,8-diaminonaphthalene protected (Z)- β -boryl enoates and primary, secondary, and tertiary enamides in good to excellent yields. These reactions demonstrate a high tolerance toward a variety of alkyl, aryl, and heteroatom functional groups and provide convenient access to a diverse range of vinylboronic acid derivatives.

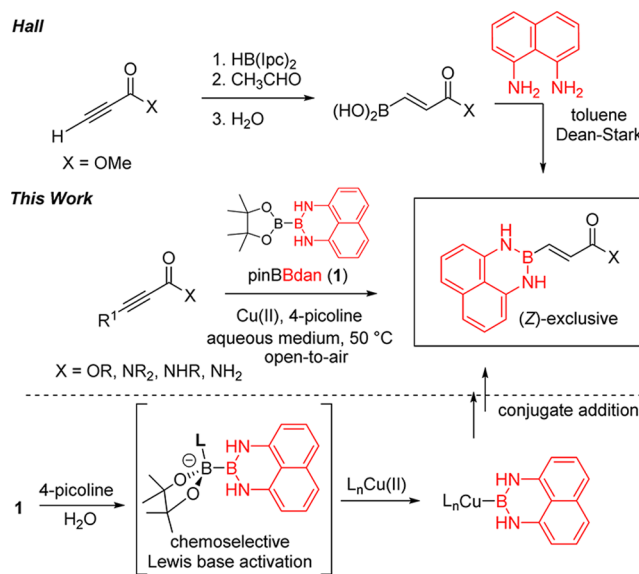
INTRODUCTION

Vinylboronic acids and their derivatives serve as valuable intermediates in organic synthesis, particularly with Suzuki–Miyaura cross-coupling reactions to form carbon–carbon bonds.¹ As a consequence, efficient and economical methods for their preparation are essential. Access to these derivatives via borylation of alkynes with boron sources such as HBpin and bis(pinacolato)diboron (B_2pin_2) is well established including uncatalyzed,² transition metal-catalyzed,³ and base/acid catalyzed⁴ processes.⁵ However, some have disadvantages such as the use of organic solvents and precious transition metals such as platinum or palladium, and the production of toxic byproducts. Among the class of vinylboronic acid derivatives, routes to conjugated vinylboronates bearing carbonyl groups is severely limited, and methods toward primary and secondary amides are nonexistent.⁶ Because of the utility of vinylboronic acids, the development of simple, efficient, and sustainable methods for their installation is important.

Among the myriad of protecting groups for boron, the pinacol (pin) moiety is a standout, popular choice because of its compatibility with numerous reaction conditions. However, the 1,8-diaminonaphthyl group (dan), an alternative boron ligand, is emerging as an orthogonal protecting group.⁷ This moiety is attractive because of its robustness and compatibility, and it allows fine-tuning of the reactivity of the boron center. For example, chemoselective transformations of Bpin derivatives occur in the presence of the Bdan group.^{7e,8} Therefore, novel methods to introduce Bdan into organic substrates efficiently are valuable. A differentially protected diboron reagent, pinBBdan (**1**),^{8e} has been particularly useful for the incorporation of the Bdan substituent.^{8e,g,9} For example,

elegant work by Fernandez and co-workers reported the organocatalytic addition of **1** to α,β -unsaturated carbonyls.^{9a} Further, Hall and co-workers pioneered a method to incorporate Bdan on the vinylic β -carbon of esters (Scheme 1).^{7c,10} The multistep procedure, however, was limited to esters

Scheme 1. Approaches to Bdan Vinylboronates



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containing no substituents on the β -carbon.¹⁰ Regardless, the copper-catalyzed enantioselective conjugate borylation,^{8f} alkylation,^{7c} and reduction¹¹ reactions developed demonstrate the utility of these compounds as synthetic intermediates.

Given our interest in developing sustainable methods for the borylation of activated carbon–carbon bonds¹² and the paucity of borylation reactions in water,¹³ we set out to contribute a simple, efficient, and environmentally friendly process for the addition of Bdan to acetylenic carbonyl groups. Water is a notably enticing solvent choice partly due to its cost-effectiveness, but moreover because it is not flammable or toxic. Further, we wanted to capitalize on our initial finding that earth abundant and air stable Cu(II) efficiently catalyzes the borylation of α,β -unsaturated carbonyls, affording an environmentally and user-friendly method.^{12a,14} The seminal work of Marder and co-workers,¹⁵ outlining the Pt-catalyzed borylation of α,β -unsaturated ketones, propelled other transition metal-catalyzed and metal-free investigations on β -borylation reactions.¹⁶ Inspired by these contributions, we report the development of an efficient and aqueous-based method for generating structurally diverse 1,8-diaminonaphthalene protected β -boryl- α,β -unsaturated carbonyl compounds, including primary and secondary amides (Scheme 1). In this strategy, we capitalize on the chemoselective activation of the more Lewis acidic boron of Bpin by activating it with a Lewis base (either water or 4-picoline) to form an sp^2 – sp^3 diboron intermediate, thereby facilitating the efficient transfer of Bdan.^{12a,17}

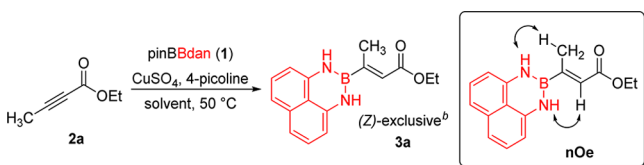
RESULTS AND DISCUSSION

Preliminary studies utilized commercially available 2-butyne (2a) and the previously established aqueous borylation protocol of alkynoates with B₂(pin)₂.¹⁸ Under these conditions, no reaction was observed, likely due to the insolubility of the pinBBdan diboron reagent in water (Table 1, entry 1). Addition

of an environmentally benign alcohol, such as ethanol or 2-propanol, promoted solubility (entry 2–7). As such, the reaction proceeds smoothly to provide the (Z)- β -boryl- α,β -unsaturated ester 3a as a single regio- and stereoisomer, which was verified by nuclear Overhauser effect (NOE) experiments. The expected chemoselective transfer of Bdan to the β carbon was observed as a consequence of the differential in Lewis acidity of each boron center, allowing the conjugate addition of the 1,8-diaminonaphthyl boryl–copper complex (Scheme 1). The optimal percentage of alcohol in the aqueous solvent system was determined by monitoring the percent conversion over time (entries 2–5). We observed a high conversion after 6 h with 5% ethanol (entry 2). However, complete conversion was achieved in a shorter period of time when the ethanol additive was increased to 10% (entry 3). Higher percentages of the ethanol additive had a negative effect on the rate of conversion, requiring 6 h to reach completion (entries 4–5). Unlike the copper(I)-catalyzed borylation reaction developed by Yun et al.,¹⁹ in which a methanol additive increased the rate of the reaction, no reaction was observed in this case (entry 6). Under these conditions, pinBBdan was insoluble and unable to participate in the reaction. 2-Propanol, on the other hand, was an adequate additive (entry 7). Next, we explored the use of a nanomicellar surfactant, 2 wt % TPGS-750-M,²⁰ as an alternative aqueous reaction media and found these conditions to be similar to those for the 10% ethanol mixture (entries 8–9). In comparison, no improvement to the yield was observed with the addition of the surfactant to the EtOH/H₂O mixture. As expected, copper(II) and 4-picoline were needed for the efficient conversion to product (entries 10–11). We opted to utilize copper(II) instead of copper(I) sources such as CuCl because of solubility issues in water and oxidation to copper(II) upon exposure to air.^{12a} Therefore, the simpler conditions were determined to be optimal (entries 3 and 9).

Under these optimized conditions, the functional group tolerance and scope of the reaction was examined (Table 2). Overall, the borylation reaction rapidly installed the Bdan functional unit onto the β -carbon regio- and stereoselectively, providing the (Z)-stereoisomer in all cases. Various alkyl chains ranging from methyl to heptyl substituents on the R¹ position provided the products in high yields with short reaction times (3a–d). The more sterically hindered *tert*-butyl substituent affected neither the yield nor the selectivity of the product (3e). Next, we examined various cyclic rings and obtained high yields for the cyclopropyl (3f) and cyclohexyl (3h) substituents. Unfortunately, the borylated product for ethyl 3-cyclopentyl-propionate (3g) was only obtained in 48% yield. Regioselectivity for β -borylation was demonstrated by applying the reaction conditions to the conjugated cyclohex-3-en-1-yne ester (2i) to give the (Z)- $\alpha,\beta,\gamma,\delta$ -unsaturated diene in a 78% yield. When R¹ contained an ether substituent, the borylation proceeded smoothly to give 3j in a 77% yield. Next, we probed substituent tolerance in the R² position and found that substrates containing sterically bulky substituents, such as a phenyl ring and branched isobutyl group, are readily borylated to provide good yields of the respective (Z)- β -boryl- α,β -unsaturated esters (3k–l). Finally, we demonstrated the chemoselectivity of this reaction by examining unsaturation at the R² position. The borylation of hexynoate derivatives bearing allyl (2m) and propargyl (2n) groups resulted in high yields of the β -borylated products, thus verifying that the reaction occurs exclusively at the more activated alkyne.

Table 1. Optimization of Reaction Conditions^a



entry	solvent	time (h)	conversion, ^c % (yield, %)
1	H ₂ O	6	0
2	5% EtOH/H ₂ O	6	93
3	10% EtOH/H ₂ O	4	100 (86)
4	15% EtOH/H ₂ O	6	100
5	20% EtOH/H ₂ O	6	100
6	10% MeOH/H ₂ O	6	0
7	10% ⁱ PrOH/H ₂ O	4	100 (85)
8	2 wt % TPGS-750-M/H ₂ O	6	94
9	10% EtOH/H ₂ O, 2 wt % TPGS-750-M	6	100 (86)
10	10% EtOH/H ₂ O ^d	1	0
11	10% EtOH/H ₂ O ^e	1	0

^aReaction conditions: pinBBdan (0.52 mmol), 2-butyne 2a (0.625 mmol), 4-picoline (5 mol %), CuSO₄ (1 mol %). ^bExclusive stereoselectivity was obtained, as determined by GC-MS of the crude material and confirmed by NOE of the isolated product. ^cConversion determined by monitoring the consumption of pinBBdan using GC-MS. ^dWithout copper. ^eWithout 4-picoline.

Table 2. Boryl Conjugate Addition to Substituted Alkynoates^a

$ \begin{array}{c} \text{R}^1 \\ \\ \text{C} \equiv \text{C} \\ \\ \text{C}(\text{OR}^2) \\ \text{2a-n} \end{array} \xrightarrow[50^\circ\text{C, 4-8 h}]{\begin{array}{c} \text{pinBBdan} \\ 1 \text{ mol \% CuSO}_4 \\ 5 \text{ mol \% 4-picoline} \\ 10 \% \text{ EtOH/H}_2\text{O} \end{array}} \begin{array}{c} \text{R}^1 \\ \\ \text{danB} - \text{C} = \text{C} \\ \\ \text{C}(\text{OR}^2) \\ \text{3a-n} \end{array} \quad \text{(Z)-exclusive}^b $					
entry	substrate	product		time (h)	yield ^c %
1			3a	4	86
2			3b	4	79
3			3c	4	88
4			3d	4	82
5			3e	6	81
6			3f	4	83
7			3g	8	48
8			3h	4	72
9			3i	8	78
10			3j	4	77
11			3k	4	79
12			3l	8	85
13			3m	6	82
14			3n	6	73

^aReaction conditions: pinBBdan (0.52 mmol), alkynoate **2** (0.625 mmol), 4-picoline (5 mol %), and CuSO₄ (1 mol %). ^bExclusive stereoselectivity was obtained, as determined by GC-MS of the crude material and confirmed by NOE of the isolated product. ^cAveraged from two or more experiments.

Prompted by the great success of the alkynoate substrates, we sought to expand the substrate scope to include acetylenic

amide derivatives. Amides have received minimal attention as substrates due to their inherently low reactivity toward 1,4-conjugate additions.²¹ In fact, methods to access (Z)-β-boryl-α,β-unsaturated amides directly are not available. However, it has been suggested that acetylenic amides and esters undergo 3,4-syn addition reactions.^{21d} Gratifyingly, Weinreb amide **4a** reacted readily under our 10% ethanol aqueous conditions to provide the desired product **5a** in an 82% yield (Table 3, entry

Table 3. Screening of Solvent System for the Borylation of Weinreb Amide^a

$ \begin{array}{c} \text{O} \\ \\ \text{C}_6\text{H}_{13} - \text{C} \equiv \text{C} - \text{N}(\text{OMe})\text{Me} \\ \text{4a} \end{array} \xrightarrow[5 \text{ mol \% 4-picoline solvent, } 50^\circ\text{C, 4 h}]{\begin{array}{c} \text{pinBBdan (2.1 equiv)} \\ 1 \text{ mol \% CuSO}_4 \end{array}} \begin{array}{c} \text{H}_{13}\text{C}_6 \\ \\ \text{danB} - \text{C} = \text{C} \\ \\ \text{NH} - \text{N}(\text{OMe})\text{Me} \\ \text{5a} \end{array} \quad \text{(Z)-exclusive}^b $			
entry	solvent		yield (%)
1	10% EtOH/H ₂ O		82
2	2 wt % TPGS-750-M/H ₂ O		61
3	10% EtOH/H ₂ O, 2 wt % TPGS-750-M		91

^aReaction conditions: pinBBdan (0.625 mmol), alkynamide **4** (0.520 mmol), 4-picoline (5 mol %), and CuSO₄ (1 mol %). ^bDetermined by ¹H NMR of the crude material and confirmed by NOE of the isolated product.

1). We re-examined the use of a surfactant to pursue an increase in the reaction yield. When ethanol was replaced by the 2 wt % TPGS-750-M surfactant, a drastically lower yield was obtained (entry 2). However, in contrast to the alkynoate optimization results, when ethanol was employed in conjunction with the surfactant, an excellent yield of **5a** was obtained (91%, entry 3). As expected, the reaction remained stereoselective for the (Z)-isomer.

As the addition of the 2 wt % TPGS-750-M surfactant improved the yield, we continued to use this aqueous-based media to explore the scope and limitations of alkynamide substrates (Table 4). A comparable, but slightly lower, yield was obtained when the alkyl chain of the Weinreb amide was reduced from a hexyl (**5a**) to a methyl substituent (**5b**).

A series of *N,N*-dimethyl amide substrates were synthesized to explore further the effects of substitutions on the alkyne. Substrates with aliphatic substituents on the R¹ position, such as propyl (**4c**) or hexyl (**4d**) groups, undergo β-borylations in good yields. The branched *tert*-butyl derivative also gave the desired product **5e** stereoselectively. Although this reaction does not reach completion after 48 h, a good yield (71%) is still obtained. Additionally, the borylation of amides containing cyclic R¹ substituents proceeded smoothly and provided the desired products in excellent yields (**5f–h**). Even 3-cyclopentyl-*N,N*-dimethylpropionamide (**4f**) afforded the borylation product in an 89% yield, which was surprising given that the ester equivalent was low yielding. The conjugated cyclohex-3-en-1-yne substituted *N,N*-dimethylpropionamide (**4h**) was regioselectively borylated at the β-position, providing the (Z)-α,β,γ,δ-unsaturated diene, **5h**, in a 79% yield. Borylation of the methylene phenyl ether (**4i**) also proceeded smoothly. Finally, we demonstrated that the steric bulk of the tertiary amide was well tolerated with an alkynamide derivative of *D*-proline (**4j**). This substrate readily undergoes β-borylation to give the desired product in excellent yield (92%) and without racemization of the chiral center.

Table 4. Boryl Conjugate Addition to Weinreb Amides and Substituted Alkynamides^a

entry	Substrate	product	time (h)	yield ^c %	
1			5a	4	88
2			5b	10	85
3			5c	15	76
4			5d	10	86
5			5e	48	71
6			5f	12	89
7			5g	15	93
8			5h	28	79
9			5i	15	82
10			5j	9	92
11			5k	12	76
12			5l	12	96
13			5m	15	41
14			5n	16	90
15			5o	9	93

^aReaction conditions: pinBBdan (0.625 mmol), alkynamide 4 (0.520 mmol), 4-picoline (5 mol %), and CuSO₄ (1 mol %). ^bDetermined by ¹H NMR of the crude material and confirmed by NOE of the isolated product. ^cAveraged from two or more experiments.

The acidic hydrogen of the amide functional group is also tolerated under these mild conditions, as evidenced by **5k–o**. To the best of our knowledge, borylation of secondary and primary amides have never been reported.²² The secondary amides were regio- and stereoselectively borylated in good to

excellent yields (**5k–l**). When the steric demand of the amide substituent was increased from a methyl to a benzyl group, the borylation of **4l** proceeded nearly quantitatively (96%, **5l**). Gratifyingly, the less reactive carboxamides readily undergo borylation as well (**4m–o**). Excellent yields were obtained when the R¹ position was substituted with a propyl (**5n**) or hexyl (**5o**) alkyl chain while a modest yield was obtained for a methyl substituent (**5m**). Interestingly, a trend of increasing product yield as the R¹ substituent became larger was observed, presumably as a consequence of the solubility of the starting material.

CONCLUSIONS

In summary, we have developed a mild and efficient copper(II)-catalyzed β -borylation of alkynoates and alkynamides using an unsymmetrical diboron reagent, pinBBdan. We demonstrate the chemoselective transfer of the less Lewis acidic Bdan moiety, and notably borylated inherently unreactive secondary and primary amides. The reaction is carried out under environmentally friendly conditions, which are open-to-air and employ an aqueous media. Catalytic amounts of an inexpensive, air stable copper(II) catalyst and a commercially available amine base also makes this approach cost-effective.

EXPERIMENTAL SECTION

General Information. All borylation reactions were carried out open-to-air and performed at least in duplicate. Milli-Q water was obtained using a UV water system. Deionized water was used straight from the house DI water tap and was not degassed or further purified. Dry THF and DCM were obtained from a solvent purification system. Copper sulfate pentahydrate, 4-picoline, TPGS-750-M, and other commercially available reagents and substrates (**2a–c**) were purchased and used as received. CuSO₄ stock solutions were prepared by dissolving 2.6 mg of CuSO₄ in 1 mL of Milli-Q water or 2 wt % TPGS-750-M. The unsymmetrical diboron reagent, pinBBdan, was synthesized according to the literature.^{8e} TLC analyses were performed using silica gel MF₂₅₄ plates or Silicycle aluminum backed silica gel F-254 plates, and spots were visualized with UV light and KMnO₄ stain.

Instrumentation. ¹H NMR spectra were recorded on either a 500 or 400 MHz spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl₃: 7.26 ppm, (CD₃)₂SO: 2.50 ppm, (CD₃)₂CO: 2.05 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, br = broad), coupling constants (Hz), and integration. ¹³C{¹H}NMR spectra were recorded on a 600, 500, or 400 MHz spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl₃: 77.16 ppm, (CD₃)₂SO: 39.51 ppm, (CD₃)₂CO: 206.68 ppm). The carbon directly attached to boron may not be observed, except for three examples, due to quadrupolar relaxation. ¹¹B NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts are reported in ppm using boron trifluoride diethyl etherate as an external standard (BF₃O(C₂H₅)₂: 0 ppm). High resolution mass spectra (HRMS) were performed on an LC-ESI-TOF. Gas chromatography (GC) analyses were performed on a GC system coupled to a mass selective detector and autosampler. Optical rotation was determined using a polarimeter. Melting and boiling points were measured on a melting point apparatus and uncorrected.

General Procedure 1. Dry THF (6.58 mL, 0.612 M) and non-1-yne (0.500 g, 4.02 mmol, 1.0 equiv) were added to an oven-dried nitrogen purged flask. The flask was cooled to –78 °C using a dry ice–acetone cold bath. Next, *n*-butyllithium (1.690 mL of 2.5 M in hexanes, 4.23 mmol, 1.05 equiv) was added dropwise to the flask and allowed to stir for 30 min. To the flask, ethyl chloroformate (0.450 g, 4.02 mmol, 1.0 equiv) was then slowly added dropwise. The reaction

temperature was held at -78°C for 8–9 h and allowed to warm to room temperature overnight. The reaction was quenched with saturated aqueous ammonium chloride (30 mL) and extracted with hexanes ($3 \times 5\text{ mL}$). The organic layer was then washed with DI water ($5 \times 10\text{ mL}$), dried over sodium sulfate, filtered, and concentrated *in vacuo*. Column chromatography was used to purify the product, eluting with hexanes and ethyl acetate.

General Procedure 2. Dry THF (8.6 mL, 0.612 M) and pent-1-yne (0.50 mL, 5.27 mmol, 1.0 equiv) were added to an oven-dried nitrogen purged flask. The flask was cooled to -78°C using a dry ice–acetone cold bath. Next, *n*-butyllithium (2.11 mL of 2.5 M in hexanes, 5.27 mmol, 1.0 equiv) was added dropwise to the flask and allowed to stir for 30 min. To the flask, phenyl chloroformate (643 μL , 5.27 mmol, 1.0 equiv) was slowly added dropwise. The reaction temperature was held at -78°C for 8–9 h and allowed to warm to room temperature overnight. The reaction was quenched with saturated aqueous ammonium chloride (30 mL) and extracted with hexanes ($3 \times 5\text{ mL}$). The organic layer was then washed with DI water ($5 \times 10\text{ mL}$), dried over sodium sulfate, filtered, and concentrated *in vacuo*. Column chromatography was used to purify the product, eluting with hexanes and ethyl acetate.

General Procedure 3.^{20a} Dry THF (27.2 mL, 0.2 M), methyl non-2-ynoate **3c** (1.0 mL, 5.44 mmol, 1.0 equiv), and *N,O*-dimethylhydroxylamine (997 mg, 16.32 mmol, 3.0 equiv) were added to an oven-dried nitrogen purged flask. The flask was cooled to -20°C using a sodium chloride ice bath and kept cold for 1 h prior to the dropwise addition of *sec*-butylmagnesium chloride (12.0 mL of 2 M in diethyl ether, 24.0 mmol, 4.4 equiv). The consumption of the starting material was monitored by TLC. The reaction was quenched with saturated aqueous ammonium chloride (20 mL). The mixture was extracted with diethyl ether ($3 \times 10\text{ mL}$). The combined extracts were washed with brine, dried over sodium sulfate, filtered, and concentrated *in vacuo*. The product was purified using column chromatography, eluting with hexanes and ethyl acetate.

General Procedure 4.^{20a} Dry THF (10 mL, 0.5 M) and oct-1-yne (500 mg, 4.54 mmol, 1.0 equiv) were added to an oven-dried nitrogen purged flask. The flask was cooled to -78°C using a dry ice–acetone cold bath. Next, *n*-butyllithium (1.8 mL of 2.5 M in hexanes, 4.54 mmol, 1.0 equiv) was added dropwise to the flask and allowed to stir for 30 min. This solution was transferred dropwise via cannula to a separate nitrogen dried flask containing dry THF (10 mL) and dimethylcarbamic chloride (0.84 mL, 9.07 mmol, 2.0 equiv). The reaction temperature was held at -78°C for 6 h and allowed to warm to room temperature overnight. The reaction was quenched with DI water (10 mL) and extracted with hexanes ($10 \times 3\text{ mL}$). The organic layer was then washed with DI water ($5 \times 15\text{ mL}$), dried over sodium sulfate, filtered, and concentrated *in vacuo*. Column chromatography was used to purify the product, eluting with hexanes and diethyl ether (**4c**) or hexanes and ethyl acetate (**4d–i**).

General Procedure 5. Dry DCM (45.3 mL, 0.1 M) and hexynoic acid (0.50 mL, 4.53 mmol, 1.0 equiv) were added to an oven-dried nitrogen purged flask and cooled to 0°C . Triethylamine (0.63 mL, 4.53 mmol, 1.0 equiv) was added dropwise to the flask and allowed to stir for 15 min before the dropwise addition of pivaloyl chloride (0.61 mL, 4.98 mmol, 1.1 equiv). The consumption of starting material was monitored by TLC. Triethylamine (917 mg, 9.06 mmol, 2.0 equiv) was added dropwise to a separate nitrogen dried flask containing dry DCM (45.3 mL, 0.1 M) and *D*-proline methyl ester hydrochloride (585 mg, 4.53 mmol, 1.0 equiv). The solution was stirred at room temperature for 1 h prior to being added dropwise to the initial flask via cannula. The reaction mixture was allowed to warm to room temperature overnight. DI water (15 mL) was used to quench the reaction. Subsequently, the product was extracted with DCM ($3 \times 10\text{ mL}$). The organic layer was then washed with DI water ($2 \times 10\text{ mL}$), 10% NaOH ($3 \times 10\text{ mL}$), and brine. The extract was dried over sodium sulfate, filtered, and concentrated *in vacuo*. Column chromatography was used to purify the product, eluting with hexane and ethyl acetate. The resulting product was >97% pure and used as is for the β -borylation reaction.

General Procedure 6.^{20a} Methyl non-2-ynoate **3c** (600 mg, 3.57 mmol, 1.0 equiv) and MeOH (28.5 mL, 0.1 M) were added to an oven-dried nitrogen purged flask. To the reaction mixture, an excess of 28–30% ammonium hydroxide (36.8 mL, 267 mmol, 75 equiv) was added dropwise and allowed to stir at room temperature for 6 h (**4m–n**) or 17 h (**4o**). The consumption of the starting material was monitored by TLC. The aqueous based solvent from the crude reaction mixture was concentrated *in vacuo* to provide an off-white colored solid. The mixture was dissolved in ethyl acetate and rinsed with DI water ($3 \times 10\text{ mL}$). The combined extracts were washed with brine, dried over sodium sulfate, filtered, and concentrated *in vacuo*. The solid was solubilized in a minimal amount of diethyl ether at room temperature, and then hexanes solvent was added slowly until the solution became cloudy. The crude solution was sealed with parafilm and stored at 5°C overnight. The precipitate was filtered, and the obtained crystals were washed with cold hexanes. After being dried on high vacuum, the final product was obtained as white crystals.

General Procedure 7: β -Borylation of Alkynoates with pinBBdan (3a–n**).** In a 2 dram vial were added pinBBdan **1** (153 mg, 0.520 mmol, 1.0 equiv), 4-picoline (2.55 μL , 0.026 mmol, 0.05 equiv), and ethyl but-2-ynoate **2a** (66 μL , 0.625 mmol, 1.2 equiv). Then, 0.5 mL of 2.6 mg/mL CuSO_4 stock solution (prepared with Milli-Q water), 0.4 mL of Milli-Q water, and 0.1 mL 200 of proof ethanol (9:1 ratio, 0.52 M) were added down the sides of the reaction vessel. Care was taken to ensure that solid reagents were not splashed on the sides of the vial. The reaction mixture was heated to 50°C and stirred vigorously. The reaction was monitored for completion by TLC. In many cases, the product and borylating reagent exhibited the same R_f ; therefore, GC-MS was used to determine complete consumption of the borylating reagent in these cases. After the reaction was found to be complete, 2 mL of ethyl acetate were added to quench the reaction. The product was extracted using ethyl acetate ($3 \times 10\text{ mL}$). The combined extracts were then washed with DI water ($5 \times 10\text{ mL}$) and brine. The organic layer was dried over sodium sulfate, filtered, and concentrated *in vacuo*. Column chromatography was used to purify the borylated product, eluting with hexanes and ethyl acetate.

General Procedure 8: β -Borylation of Alkynamides with pinBBdan (5a–o**).** In a 2 dram vial were added pinBBdan **1** (183 mg, 0.624 mmol, 1.2 equiv), 4-picoline (2.55 μL , 0.026 mmol, 0.05 equiv), and *N*-methoxy-*N*-methylnon-2-ynamide **4a** (103 mg, 0.520 mmol, 1.0 equiv). Then, 0.5 mL of 2.6 mg/mL CuSO_4 stock solution (prepared with aqueous 2 wt % TPGS-750-M), 0.4 mL of aqueous 2 wt % TPGS-750-M, and 0.1 mL of 200 proof ethanol (9:1 ratio, 0.52 M) were added down the sides of the reaction vessel. Care was taken to ensure that solid reagents were not splashed on the sides of the vial. The reaction mixture was heated to 50°C and stirred vigorously. The reaction was monitored for completion by TLC. In some cases, the product and acetylenic amide exhibited the same R_f ; therefore, GC-MS was used to determine the complete consumption of the starting material in these cases. After the reaction was found to be complete, 2 mL of ethyl acetate were added to quench the reaction. The product was extracted using ethyl acetate ($3 \times 10\text{ mL}$). The combined extracts were then washed with DI water ($5 \times 10\text{ mL}$) and brine. The organic layer was dried over sodium sulfate, filtered, and concentrated *in vacuo*. Column chromatography was used to purify the borylated product, eluting with hexanes and ethyl acetate (**5a–l**) or diethyl ether and ethyl acetate (**5m–o**).

Ethyl Dec-2-ynoate (2d**).** Synthesized according to general procedure 1. The title compound was isolated in a 96% yield (758 mg) as a yellow liquid. TLC $R_f = 0.33$ in 100% hexanes. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR are consistent with literature.^{12b}

Ethyl 4,4-Dimethylpent-2-ynoate (2e**).** Synthesized according to general procedure 1 (4.77 mmol scale). The title compound was isolated in a 66% yield (485 mg) as a colorless liquid (bp 182.7°C). TLC $R_f = 0.31$ in 100% hexanes. ^1H NMR (400 MHz, CDCl_3) δ 4.20 (q, $J = 7.1\text{ Hz}$, 2H), 1.29 (t, $J = 7.1\text{ Hz}$, 3H), 1.27 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 154.3 (C), 96.5 (C), 72.0 (C), 61.9 (CH_2), 30.1 (CH_3), 27.6 (C), 14.2 (CH_3). HRMS (APCI+): calcd for $\text{C}_9\text{H}_{14}\text{O}_2$ $[\text{M} + \text{H}]^+$, 155.1067; found, 155.1059.

Ethyl 3-Cyclopropylpropiolate (2f). Synthesized according to general procedure 1 (2.36 mmol scale). The title compound was isolated in an 87% yield (285 mg) as a yellow liquid (bp 148.9 °C). TLC R_f = 0.35 in 19:1 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 4.15 (q, J = 7.1 Hz, 2H), 1.39–1.28 (m, 1H), 1.25 (t, J = 7.1 Hz, 3H), 0.93–0.81 (m, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 153.9 (C), 93.1 (C), 68.6 (C), 61.8 (CH_2), 14.1 (CH_3), 9.3 (CH_2), –0.5 (CH). HRMS (APCI+): calcd for $\text{C}_8\text{H}_{11}\text{O}_2$ [$\text{M} + \text{H}$] $^+$, 139.0754; found, 139.0753.

Ethyl 3-Cyclopentylpropiolate (2g). Synthesized according to general procedure 1 (3.39 mmol scale). The title compound was isolated in a 70% yield (396 mg) as a colorless liquid (bp 207.1 °C). TLC R_f = 0.41 in 19:1 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 4.18 (q, J = 7.1 Hz, 2H), 2.74–2.67 (m, 1H), 1.94–1.89 (m, 2H), 1.75–1.61 (m, 4H), 1.60–1.49 (m, 2H), 1.27 (t, J = 7.1 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 154.1 (C), 93.4 (C), 72.8 (C), 61.8 (CH_2), 33.1 (CH_2), 29.8 (CH), 25.3 (CH_2), 14.2 (CH_3). HRMS (APCI+): calcd for $\text{C}_{10}\text{H}_{15}\text{O}_2$ [$\text{M} + \text{H}$] $^+$, 167.1067; found, 167.1065.

Ethyl 3-Cyclohexylpropiolate (2h). Synthesized according to general procedure 1 (4.59 mmol scale). The title compound was isolated in a 55% (434 mg) yield as a colorless oil (bp 249.8 °C). TLC R_f = 0.58 in 9:1 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 4.21 (q, J = 7.1 Hz, 2H), 2.55–2.46 (m, 1H), 1.88–1.80 (m, 2H), 1.76–1.67 (m, 2H), 1.55–1.46 (m, 3H), 1.35–1.27 (m, 3H), 1.30 (t, J = 7.1 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 154.2 (C), 93.0 (C), 73.2 (C), 61.9 (CH_2), 31.6 (CH_2), 29.0 (CH), 25.7 (CH_2), 24.8 (CH_2), 14.2 (CH_3). HRMS (ESI+): calcd for $\text{C}_{11}\text{H}_{17}\text{O}_2$ [$\text{M} + \text{H}$] $^+$, 181.1223; found, 181.1223.

Ethyl 3-(Cyclohex-1-en-1-yl)propiolate (2i). Synthesized according to general procedure 1 (4.71 mmol scale). The title compound was isolated in a 78% yield (656 mg) as a yellow liquid. TLC R_f = 0.44 in 19:1 hexanes/EtOAc. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR are consistent with literature.^{12b}

Ethyl 4-Phenoxybut-2-ynoate (2j). Synthesized according to general procedure 1 (3.90 mmol scale). The title compound was isolated in a 55% yield (438 mg) as a white solid. TLC R_f = 0.46 in 9:1 hexanes/EtOAc. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR are consistent with literature.^{21d}

Phenyl Hex-2-ynoate (2k). Synthesized according to general procedure 2. The title compound was isolated in a 75% yield (739 mg) as a pale yellow liquid (bp 283.9 °C). TLC R_f = 0.36 in 19:1 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 7.42–7.36 (m, 2H), 7.30–7.23 (m, 1H), 7.15–7.12 (m, 2H), 2.38 (t, J = 7.1 Hz, 2H), 1.71–1.60 (m, 2H), 1.05 (t, J = 7.4 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 152.2 (C), 150.3 (C), 129.6 (CH), 126.4 (CH), 121.6 (CH), 92.3 (C), 73.0 (C), 21.2 (CH_2), 20.9 (CH_2), 13.6 (CH_3). HRMS (APCI+): calcd for $\text{C}_{12}\text{H}_{13}\text{O}_2$ [$\text{M} + \text{H}$] $^+$, 189.0910; found, 189.0902.

Isobutyl Hex-2-ynoate (2l). Synthesized according to general procedure 2. The title compound was isolated in an 86% yield (763 mg) as a pale yellow liquid (bp 219.1 °C). TLC R_f = 0.48 in 19:1 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 3.93 (d, J = 6.8 Hz, 2H), 2.31 (t, J = 7.1 Hz, 2H), 2.02–1.92 (m, 1H), 1.66–1.55 (m, 2H), 1.00 (t, J = 7.4 Hz, 3H), 0.94 (d, J = 6.8 Hz, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 154.2 (C), 89.4 (C), 73.4 (C), 71.9 (CH_2), 27.7 (CH), 21.2 (CH_2), 20.8 (CH_2), 19.2 (CH_3), 13.6 (CH_3). HRMS (APCI+): calcd for $\text{C}_{10}\text{H}_{17}\text{O}_2$ [$\text{M} + \text{H}$] $^+$, 169.1223; found, 169.1217.

Allyl Hex-2-ynoate (2m). Synthesized according to general procedure 2. The title compound was isolated in a 67% yield (539 mg) as a yellow liquid (bp 208.9 °C). TLC R_f = 0.42 in 19:1 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 5.98–5.87 (m, 1H), 5.30–5.25 (m, 1H), 5.39–5.32 (m, 1H), 4.65 (dt, J = 5.9, 1.3 Hz, 2H), 2.31 (t, J = 7.1 Hz, 2H), 1.67–1.56 (m, 2H), 1.0 (t, J = 7.4 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 153.7 (C), 131.4 (CH), 119.3 (CH_2), 90.0 (C), 73.2 (C), 66.4 (CH_2), 21.2 (CH_2), 20.8 (CH_2), 13.6 (CH_3). HRMS (APCI+): calcd for $\text{C}_9\text{H}_{13}\text{O}_2$ [$\text{M} + \text{H}$] $^+$, 153.0910; found, 153.0901.

But-2-yn-1-yl Hex-2-ynoate (2n). To a mixture of hex-2-ynoic acid (500 mg, 4.46 mmol, 1.3 equiv) in DCM (32.4 mL, 0.1 M), but-2-yn-1-ol (0.26 mL, 3.43 mmol, 1.0 equiv) was added followed by the solution of DMAP (41.9 mg, 0.343 mmol, 0.1 equiv) in DCM (1.8

mL, 0.2 M). The solution was cooled to 0 °C and stirred for 15 min prior to the addition of DCC (0.751 mL, 4.80 mmol, 1.4 equiv). The consumption of the starting material was monitored by TLC. After 6 h, the reaction mixture was filtered through a short plug of silica, which was rinsed with hexanes (3 $\times$ 10 mL). The filtrate was concentrated *in vacuo* to provide the final product **2n** as a colorless liquid in a 93% yield (522 mg) (bp >235 °C (decomp)). TLC R_f = 0.38 in 19:1 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 4.71 (q, J = 2.4 Hz, 2H), 2.31 (t, J = 7.1 Hz, 2H), 1.85 (t, J = 2.4 Hz, 3H), 1.66–1.55 (m, 2H), 1.01 (t, J = 7.4 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 153.4 (C), 90.9 (C), 84.3 (C), 73.0 (C), 72.7 (C), 54.2 (CH_2), 21.3 (CH_2), 21.0 (CH_2), 13.8 (CH_3), 4.0 (CH_3). HRMS (APCI+): calcd for $\text{C}_{10}\text{H}_{13}\text{O}_2$ [$\text{M} + \text{H}$] $^+$, 165.0910; found, 165.0907.

N-Methoxy-N-methylnon-2-ynamide (4a). Synthesized according to general procedure 3. The title compound was isolated in a 90% yield (966 mg) as a pale yellow oil. TLC R_f = 0.40 in 4:1 hexanes/EtOAc. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR are consistent with the literature.²³

N-Methoxy-N-methylbut-2-ynamide (4b). Synthesized according to general procedure 3. The title compound was isolated in a 55% yield (380 mg) as a colorless oil. TLC R_f = 0.34 in 3:2 hexanes/EtOAc. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR are consistent with the literature.²⁴

N,N-Dimethylhex-2-ynamide (4c). Synthesized according to general procedure 4. The title compound was isolated in a 91% yield (575 mg) as a pale yellow oil (bp >210 °C (decomp)). TLC R_f = 0.26 in 7:3 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 3.19 (s, 3H), 2.95 (s, 3H), 2.33 (t, J = 7.1 Hz, 2H), 1.60 (m, 2H), 1.01 (t, J = 7.3 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 155.0 (C), 93.1 (C), 74.3 (C), 38.5 (CH_3), 34.2 (CH_3), 21.5 (CH_2), 21.0 (CH_2), 13.7 (CH_3). HRMS (ESI+): calcd for $\text{C}_8\text{H}_{14}\text{NO}$ [$\text{M} + \text{H}$] $^+$, 140.1070; found, 140.1075.

N,N-Dimethylnon-2-ynamide (4d). Synthesized according to general procedure 4. The title compound was isolated in a 78% yield (642 mg) as a yellow oil. TLC R_f = 0.18 in 1:1 hexanes/EtOAc. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR are consistent with the literature.^{20a}

N,N-4,4-Tetramethylpent-2-ynamide (4e). Synthesized according to general procedure 4. The title compound was isolated in a 68% yield (473 mg) as an off-white solid (mp 64.0–64.8 °C). TLC R_f = 0.39 in 3:2 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 3.17 (s, 3H), 2.94 (s, 3H), 1.27 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 155.0 (C), 100.3 (C), 72.7 (C), 38.5 (CH_3), 34.2 (CH_3), 30.3 (CH_3), 27.8 (C). HRMS (ESI+): calcd for $\text{C}_9\text{H}_{16}\text{NO}$ [$\text{M} + \text{H}$] $^+$, 154.1226; found, 154.1222.

3-Cyclopentyl-N,N-dimethylpropiolamide (4f). Synthesized according to general procedure 4. The title compound was isolated in an 85% yield (638 mg) as a light brown liquid (bp >250 °C (decomp)). TLC R_f = 0.34 in 3:2 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 3.16 (s, 3H), 2.93 (s, 3H), 2.75 (p, J = 7.3 Hz, 1H), 2.00–1.88 (m, 2H), 1.77–1.62 (m, 4H), 1.61–1.53 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 155.0 (C), 97.1 (C), 73.6 (C), 38.4 (CH_3), 34.1 (CH_3), 33.3 (CH_2), 30.1 (CH), 25.1 (CH_2). HRMS (ESI+): calcd for $\text{C}_{10}\text{H}_{16}\text{NO}$ [$\text{M} + \text{H}$] $^+$, 166.1226; found, 166.1227.

3-Cyclohexyl-N,N-dimethylpropiolamide (4g). Synthesized according to general procedure 4. The title compound was isolated in a 64% yield (521 mg) as a white solid (mp 51.0–51.8 °C). TLC R_f = 0.35 in 3:2 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 3.19 (s, 3H), 2.96 (s, 3H), 2.61–2.49 (m, 1H), 1.89–1.64 (m, 4H), 1.57–1.30 (m, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 155.0 (C), 96.7 (C), 74.0 (C), 38.5 (CH_3), 34.1 (CH_3), 31.8 (CH_2), 29.2 (CH), 25.8 (CH_2), 24.8 (CH_2). HRMS (ESI+): calcd for $\text{C}_{11}\text{H}_{18}\text{NO}$ [$\text{M} + \text{H}$] $^+$, 180.1383; found, 180.1387.

3-(Cyclohex-1-en-1-yl)-N,N-dimethylpropiolamide (4h). Synthesized according to general procedure 4 (9.1 mmol scale). The title compound was isolated in a 94% yield (1.56 g) as an off-white solid (mp 41.6–42.6 °C). TLC R_f = 0.36 in 3:2 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 6.36–6.31 (m, 1H), 3.18 (s, 3H), 2.97 (s, 3H), 2.18–2.09 (m, 4H), 1.68–1.54 (m, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 155.1 (C), 139.8 (CH), 119.2 (C), 92.4 (C), 79.5 (C), 38.5 (CH_3), 34.2 (CH_3), 28.5 (CH_2), 26.0 (CH_2), 22.1 (CH_2), 21.3 (CH_2). HRMS (ESI+): calcd for $\text{C}_{11}\text{H}_{13}\text{NO}$ [$\text{M} + \text{H}$] $^+$, 178.1226; found, 178.1224.

***N,N*-Dimethyl-4-phenoxybut-2-ynamide (4i).** Synthesized according to general procedure 4. The title compound was isolated in a 21% yield (194 mg) as a yellow oil (bp >180 °C (decomp)). TLC R_f = 0.41 in 1:1 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 7.33–7.27 (m, 2H), 7.03–6.95 (m, 2H), 4.85 (s, 2H), 3.07 (s, 3H), 2.94 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 157.4 (C), 153.7 (C), 129.7 (CH), 122.0 (CH), 115.1 (CH), 86.0 (C), 79.9 (C), 55.9 (CH_2), 38.3 (CH_3), 34.2 (CH_3). HRMS (ESI+): calcd for $\text{C}_{12}\text{H}_{14}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$, 204.1019; found, 204.1023.

Methyl Hex-2-ynoate (4j). Synthesized according to general procedure 5. The title compound was isolated in a 64% yield (645 mg, 1:1 mixture of rotamers) as a colorless viscous oil (bp >235 °C (decomp)). TLC R_f = 0.44 in 3:2 hexanes/EtOAc. In the NMR spectra, the second rotamer is designated by * and the overlapping rotamer peaks are designated by † . ^1H NMR (400 MHz, CDCl_3) δ 4.63 (dd, J = 8.7, 3.2 Hz, 1H), 4.50* (dd, J = 8.7, 3.8 Hz, 1H), 3.84–3.54 † (m, 10H), 2.33 (t, J = 7.0 Hz, 2H), 2.28* (t, J = 7.0 Hz, 2H), 2.25–2.19 (m, 1H), 2.14–1.89 † (m, 7H), 1.66–1.51 † (m, 4H), 1.02 (t, J = 7.3 Hz, 3H), 0.98* (t, J = 7.3 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 172.4 (C), 172.0* (C), 153.1 (C), 152.9* (C), 92.3 (C), 92.1* (C), 74.8 (C), 74.7* (C), 60.7 (CH), 57.9* (CH), 52.3 (CH_3), 52.2* (CH_3), 48.4 (CH_2), 45.7* (CH_2), 30.6 (CH_2), 29.7* (CH_2), 24.1 (CH_2), 23.1* (CH_2), 21.2 (CH_2), 21.1* (CH_2), 20.7 (CH_2), 20.6* (CH_2), 13.4 (CH_3), 13.3* (CH_3). HRMS (ESI+): calcd for $\text{C}_{12}\text{H}_{18}\text{NO}_3$ [$\text{M} + \text{H}$] $^+$, 224.1281; found, 224.1297.

***N*-Methylhex-2-ynamide (4k).** Synthesized according to general procedure 5. The title compound was isolated in a 68% yield (386 mg, 9:1 mixture of rotamers) as a white solid. TLC R_f = 0.41 in 3:2 hexanes/EtOAc. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR are consistent with the literature.⁷

***N*-Benzylhex-2-ynamide (4l).** Synthesized according to general procedure 5. The title compound was isolated in a 53% yield (483 mg, 9:1 mixture of rotamers) as a white solid (mp 44.2–45.1 °C). TLC R_f = 0.29 in 4:1 hexanes/EtOAc. In the NMR spectra, the minor rotamer is designated by * and the overlapping rotamer peaks are designated by † . ^1H NMR (400 MHz, CDCl_3) δ 7.39–7.26 † (m, 10H), 6.06 (br s, 1H), 6.00* (br s, 1H), 4.60* (d, J = 6.6 Hz, 2H), 4.47 (d, J = 5.9 Hz, 2H), 2.33* (t, J = 7.1 Hz, 2H), 2.26 (t, J = 7.1 Hz, 2H), 1.57 † (m, 4H), 0.99 (t, J = 7.3 Hz, 3H), 0.98* (t, J = 7.3 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 153.6 † (C), 137.7* (C), 137.5 (C), 128.9* (CH), 128.8 (CH), 128.0 (CH), 127.9* (CH), 127.8 (CH), 127.2* (CH), 87.9 † (C), 75.6 † (C), 47.4* (CH_2), 43.9 (CH_2), 21.4 (CH_2), 21.3* (CH_2), 21.0* (CH_2), 20.7 (CH_2), 13.7 (CH_3), 13.6* (CH_3). HRMS (ESI+): calcd for $\text{C}_{13}\text{H}_{16}\text{NO}$ [$\text{M} + \text{H}$] $^+$, 202.1226; found, 202.1234.

But-2-ynamide (4m). Synthesized according to general procedure 6. The title compound was isolated in a 65% yield (193 mg) as off-white crystals. TLC R_f = 0.48 in 1:1 hexanes/EtOAc. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR are consistent with the literature.²⁵

Hex-2-ynamide (4n). Synthesized according to general procedure 6. The title compound was isolated in a 43% yield (170 mg) as white crystals (mp 80.5–81.5 °C). TLC R_f = 0.28 in 1:1 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 6.33 (br s, 1H), 5.80 (br s, 1H), 2.29–2.23 (m, 2H), 1.63–1.51 (m, 2H), 1.02–0.95 (m, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 155.3 (C), 89.0 (C), 75.1 (C), 21.3 (CH_2), 20.7 (CH_2), 13.6 (CH_3). HRMS (ESI+): calcd for $\text{C}_6\text{H}_{10}\text{NO}$ [$\text{M} + \text{H}$] $^+$, 112.0757; found, 112.0755.

Non-2-ynamide (4o). Synthesized according to general procedure 6. The title compound was isolated in an 81% yield (443 mg) as white crystals. TLC R_f = 0.40 in 1:1 hexanes/EtOAc. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR are consistent with the literature.^{20a}

Ethyl (Z)-3-(1*H*-Naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)but-2-enoate (3a). Synthesized according to general procedure 7. The title compound was isolated in 80–89% yields (116 mg, 126 mg, and 130 mg) as a yellow solid (mp 85.7–87.2 °C). TLC R_f = 0.34 in 9:1 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 7.11 (dd, J = 8.2, 7.4 Hz, 2H), 7.04 (dd, J = 8.2 Hz, 4J = 1.0 Hz, 2H), 6.35 (dd, J = 7.4 Hz, 4J = 1.0 Hz, 2H), 6.22 (q, 4J = 1.7 Hz, 1H), 5.80 (br s, 2H), 4.22 (q, J = 7.2 Hz, 2H), 2.30 (d, 4J = 1.7 Hz, 3H), 1.33 (t, J = 7.2 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 166.2 (C), 140.7 (C), 136.4 (C), 127.7 (CH), 125.7 (CH), 120.2 (C), 118.3 (CH), 106.3 (CH),

60.1 (CH_2), 16.6 (CH_3), 14.5 (CH_3); ^{11}B NMR (128 MHz, CDCl_3) δ 28.58. HRMS (ESI+): calcd for $\text{C}_{16}\text{H}_{18}\text{BN}_2\text{O}_2$ [$\text{M} + \text{H}$] $^+$, 281.1456; found, 281.1450.

Ethyl (Z)-3-(1*H*-Naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)hex-2-enoate (3b). Synthesized according to general procedure 7. The title compound was isolated in 78–80% yields (124 mg and 129 mg) as a yellow solid (mp 102.5–104 °C). TLC R_f = 0.44 in 9:1 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 7.12 (dd, J = 8.3, 7.2 Hz, 2H), 7.05 (dd, J = 8.3 Hz, 4J = 1.0 Hz, 2H), 6.35 (dd, J = 7.2 Hz, 4J = 1.0 Hz, 2H), 6.19 (t, 4J = 0.7 Hz, 1H), 5.78 (br s, 2H), 4.22 (q, J = 7.2 Hz, 2H), 2.80–2.72 (m, 2H), 1.58–1.47 (m, 2H), 1.33 (t, J = 7.2 Hz, 3H), 0.99 (t, J = 7.3 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 166.0 (C), 140.7 (C), 136.4 (C), 127.7 (CH), 125.2 (CH), 120.1 (C), 118.2 (CH), 106.3 (CH), 60.1 (CH_2), 32.4 (CH_2), 23.2 (CH_2), 14.5 (CH_3), 14.4 (CH_3); ^{11}B NMR (128 MHz, CDCl_3) δ 28.86. HRMS (ESI+): calcd for $\text{C}_{18}\text{H}_{22}\text{BN}_2\text{O}_2$ [$\text{M} + \text{H}$] $^+$, 309.1769; found, 309.1759.

Methyl (Z)-3-(1*H*-Naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)non-2-enoate (3c). Synthesized according to general procedure 7. The title compound was isolated in 84–92% yields (147 mg, 152 mg, and 162 mg) as a yellow solid (mp 75.1–76.3 °C). TLC R_f = 0.44 in 9:1 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 7.14 (dd, J = 8.3, 7.3 Hz, 2H), 7.07 (dd, J = 8.3 Hz, 4J = 1.0 Hz, 2H), 6.36 (dd, J = 7.3 Hz, 4J = 1.0 Hz, 2H), 6.19 (t, 4J = 0.7 Hz, 1H), 5.83 (br s, 2H), 3.78 (s, 3H), 2.83–2.76 (m, 2H), 1.54–1.28 (m, 8H), 0.94–0.88 (m, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 166.4 (C), 140.6 (C), 136.3 (C), 127.6 (CH), 124.3 (CH), 120.1 (C), 118.1 (CH), 106.3 (CH), 51.2 (CH_3), 31.7 (CH_2), 30.5 (CH_2), 29.9 (CH_2), 29.7 (CH_2), 22.7 (CH_2), 14.2 (CH_3); ^{11}B NMR (128 MHz, CDCl_3) δ 28.85. HRMS (ESI+): calcd for $\text{C}_{20}\text{H}_{26}\text{BN}_2\text{O}_2$ [$\text{M} + \text{H}$] $^+$, 337.2082; found, 337.2078.

Ethyl (Z)-3-(1*H*-Naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)dec-2-enoate (3d). Synthesized according to general procedure 7. The title compound was isolated in 78–88% yields (141 mg, 152 mg, and 168 mg) as a yellow solid (mp 40–41 °C). TLC R_f = 0.55 in 9:1 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 7.12 (dd, J = 8.3, 7.3 Hz, 2H), 7.05 (dd, J = 8.3 Hz, 4J = 1.0 Hz, 2H), 6.35 (dd, J = 7.3 Hz, 4J = 1.0 Hz, 2H), 6.17 (t, 4J = 0.7 Hz, 1H), 5.79 (br s, 2H), 4.22 (q, J = 7.2 Hz, 2H), 2.80–2.73 (m, 2H), 1.55–1.22 (m, 13H), 0.91–0.86 (m, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 166.0 (C), 140.7 (C), 136.4 (C), 127.7 (CH), 125.0 (CH), 120.2 (C), 118.2 (CH), 106.3 (CH), 60.1 (CH_2), 31.9 (CH_2), 30.5 (CH_2), 30.1 (CH_2), 30.0 (CH_2), 29.3 (CH_2), 22.8 (CH_2), 14.4 (CH_3), 14.2 (CH_3); ^{11}B NMR (128 MHz, CDCl_3) δ 28.90. HRMS (ESI+): calcd for $\text{C}_{22}\text{H}_{30}\text{BN}_2\text{O}_2$ [$\text{M} + \text{H}$] $^+$, 365.2395; found, 365.2382.

Ethyl (Z)-4,4-Dimethyl-3-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)pent-2-enoate (3e). Synthesized according to general procedure 7. The title compound was isolated in 73–89% yields (122 mg and 149 mg) as a white solid (mp 102.3–103.3 °C). TLC R_f = 0.51 in 9:1 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 7.13 (dd, J = 8.4, 7.3 Hz, 2H), 7.06 (dd, J = 8.4 Hz, 4J = 1.0 Hz, 2H), 6.33 (dd, J = 7.3 Hz, 4J = 1.0 Hz, 2H), 5.95 (s, 1H), 5.66 (br s, 2H), 4.23 (q, J = 7.2 Hz, 2H), 1.34 (t, J = 7.2 Hz, 3H), 1.30 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 168.2 (C), 140.7 (C), 136.3 (C), 127.7 (CH), 124.0 (CH), 119.7 (C), 118.0 (CH), 106.1 (CH), 60.7 (CH_2), 36.1 (C), 30.7 (CH_3), 14.3 (CH_3); ^{11}B NMR (128 MHz, CDCl_3) δ 29.76. HRMS (ESI+): calcd for $\text{C}_{19}\text{H}_{24}\text{BN}_2\text{O}_2$ [$\text{M} + \text{H}$] $^+$, 323.1925; found, 323.1927.

Ethyl (Z)-3-Cyclopropyl-3-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)acrylate (3f). Synthesized according to general procedure 7. The title compound was isolated in 80–87% yields (128 mg, 132 mg, and 139 mg) as a white solid (mp 125.7–127.2 °C). TLC R_f = 0.37 in 9:1 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 7.10 (dd, J = 8.3, 7.2 Hz, 2H), 7.04 (dd, J = 8.3 Hz, 4J = 1.0 Hz, 2H), 6.31 (dd, J = 7.2 Hz, 4J = 1.0 Hz, 2H), 6.03 (d, 4J = 0.9 Hz, 1H), 5.62 (br s, 2H), 4.21 (q, J = 7.1 Hz, 2H), 3.04–2.96 (m, 1H), 1.31 (t, J = 7.1 Hz, 3H), 1.03–0.97 (m, 2H), 0.72–0.67 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 166.6 (C), 140.4 (C), 136.3 (C), 127.7 (CH), 123.6 (CH), 120.0 (C), 118.3 (CH), 106.3 (CH), 60.0 (CH_2), 14.5 (CH_3), 13.6 (CH), 8.7 (CH_2); ^{11}B NMR (128 MHz, CDCl_3) δ 28.75. HRMS (ESI+): calcd for $\text{C}_{18}\text{H}_{20}\text{BN}_2\text{O}_2$ [$\text{M} + \text{H}$] $^+$, 307.1612; found, 307.1599.

Ethyl (Z)-3-Cyclopentyl-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)acrylate (3g). Synthesized according to general procedure 7. The title compound was isolated in 45–51% yields (88 mg and 79 mg) as a white solid (mp 112.5–113.2 °C). TLC R_f = 0.47 in 9:1 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 7.12 (dd, J = 8.3, 7.2 Hz, 2H), 7.05 (dd, J = 8.3 Hz, 4J = 1.0 Hz, 2H), 6.33 (dd, J = 7.2 Hz, 4J = 1.0 Hz, 2H), 6.03 (d, 4J = 1.0 Hz, 1H), 5.66 (br s, 2H), 4.20 (q, J = 7.1 Hz, 2H), 3.93–3.81 (m, 1H), 2.04–1.94 (m, 2H), 1.80–1.63 (m, 4H), 1.52–1.39 (m, 2H), 1.32 (t, J = 7.1 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 166.1 (C), 140.5 (C), 136.3 (C), 127.7 (CH), 124.2 (CH), 119.9 (C), 118.2 (CH), 106.2 (CH), 60.0 (CH_2), 41.6 (CH), 33.4 (CH_2), 25.9 (CH_2), 14.4 (CH_3); ^{11}B NMR (128 MHz, CDCl_3) δ 29.55. HRMS (ESI $^+$): calcd for $\text{C}_{20}\text{H}_{24}\text{BN}_2\text{O}_2$ [$\text{M} + \text{H}$] $^+$, 335.1925; found, 335.1922.

Ethyl (Z)-3-Cyclohexyl-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)acrylate (3h). Synthesized according to general procedure 7. The title compound was isolated in 69–75% yields (125 mg, 130 mg, 132 mg, and 136 mg) as a white solid (mp 137.1–137.6 °C). TLC R_f = 0.50 in 9:1 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 7.12 (dd, J = 8.3, 7.2 Hz, 2H), 7.05 (dd, J = 8.3 Hz, 4J = 1.0 Hz, 2H), 6.33 (dd, J = 7.2 Hz, 4J = 1.0 Hz, 2H), 5.96 (d, 4J = 0.9 Hz, 1H), 5.63 (br s, 2H), 4.20 (q, J = 7.2 Hz, 2H), 3.57–3.45 (m, 1H), 1.82–1.67 (m, 5H), 1.46–1.12 (m, 8H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 166.0 (C), 140.5 (C), 136.3 (C), 127.7 (CH), 123.2 (CH), 119.9 (C), 118.1 (CH), 106.2 (CH), 60.0 (CH_2), 40.5 (CH), 33.0 (CH_2), 26.3 (CH_2), 26.1 (CH_2), 14.4 (CH_3); ^{11}B NMR (128 MHz, CDCl_3) δ 29.35. HRMS (ESI $^+$): calcd for $\text{C}_{21}\text{H}_{26}\text{BN}_2\text{O}_2$ [$\text{M} + \text{H}$] $^+$, 349.2082; found, 349.2068.

Ethyl (Z)-3-(Cyclohex-1-en-1-yl)-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)acrylate (3i). Synthesized according to general procedure 7. The title compound was isolated in 75–82% yields (136 mg and 147 mg) as a dark yellow solid (mp 120–121.5 °C). TLC R_f = 0.45 in 9:1 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 7.11 (dd, J = 8.3, 7.3 Hz, 2H), 7.03 (dd, J = 8.3 Hz, 4J = 1.0 Hz, 2H), 6.34 (dd, J = 7.3 Hz, 4J = 1.0 Hz, 2H), 6.11 (s, 1H), 5.81 (br s, 2H), 5.42 (m, 1H), 4.19 (q, J = 7.2 Hz, 2H), 2.20–2.06 (m, 4H), 1.78–1.64 (m, 4H), 1.30 (t, J = 7.2 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 156.9 (C), 140.8 (C), 138.1 (C), 136.5 (C), 127.7 (CH), 125.0 (CH), 122.4 (CH), 120.2 (C), 118.2 (CH), 106.3 (CH), 60.3 (CH_2), 28.6 (CH_2), 25.3 (CH_2), 23.0 (CH_2), 22.2 (CH_2), 14.5 (CH_3); ^{11}B NMR (128 MHz, CDCl_3) δ 27.95. HRMS (ESI $^+$): calcd for $\text{C}_{21}\text{H}_{24}\text{BN}_2\text{O}_2$ [$\text{M} + \text{H}$] $^+$, 347.1925; found, 347.1915.

Ethyl (Z)-3-(1H-Naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-4-phenoxybut-2-enoate (3j). Synthesized according to general procedure 7. The title compound was isolated in 67–86% yields (131 mg and 167 mg) as a yellow solid (mp 114.5–116 °C). TLC R_f = 0.36 in 9:1 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 7.34–7.22 (m, 2H), 7.11 (dd, J = 8.3, 7.2 Hz, 2H), 7.03 (dd, J = 8.3 Hz, 4J = 1.0 Hz, 2H), 7.01–6.96 (m, 3H), 6.32 (dd, J = 7.2 Hz, 4J = 1.0 Hz, 2H), 6.30 (t, 4J = 2.1 Hz, 1H), 6.14 (br s, 2H), 5.41 (d, 4J = 2.1 Hz, 2H), 4.25 (q, J = 7.2 Hz, 2H), 1.35 (t, J = 7.2 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 165.6 (C), 158.3 (C), 140.8 (C), 136.4 (C), 129.8 (CH), 127.7 (CH), 126.1 (CH), 121.5 (CH), 120.3 (C), 118.1 (CH), 114.8 (CH), 106.2 (CH), 68.3 (CH_2), 60.7 (CH_2), 14.4 (CH_3); ^{11}B NMR (128 MHz, CDCl_3) δ 28.33. HRMS (ESI $^+$): calcd for $\text{C}_{22}\text{H}_{22}\text{BN}_2\text{O}_3$ [$\text{M} + \text{H}$] $^+$, 373.1718; found, 372.1716.

Phenyl (Z)-3-(1H-Naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)hex-2-enoate (3k). Synthesized according to general procedure 7. The title compound was isolated in 74–83% yields (136 mg and 154 mg) as an orange solid (mp 116.3–116.8 °C). TLC R_f = 0.47 in 9:1 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 7.44–7.38 (m, 2H), 7.28–7.22 (m, 1H), 7.16–7.11 (m, 4H), 7.07 (dd, J = 8.3 Hz, 4J = 1.0 Hz, 2H), 6.41 (t, 4J = 0.8 Hz, 1H), 6.38 (dd, J = 7.2 Hz, 4J = 1.0 Hz, 2H), 5.82 (br s, 2H), 2.85–2.79 (m, 2H), 1.61–1.50 (m, 2H), 1.00 (t, J = 7.3 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 164.1 (C), 150.6 (C), 140.6 (C), 136.4 (C), 129.6 (CH), 127.7 (CH), 125.9 (CH), 124.1 (CH), 121.8 (CH), 120.2 (C), 118.4 (CH), 106.4 (CH), 32.7 (CH_2), 23.2 (CH_2), 14.5 (CH_3); ^{11}B NMR (128 MHz, CDCl_3) δ 28.97. HRMS (ESI $^+$): calcd for $\text{C}_{22}\text{H}_{22}\text{BN}_2\text{O}_2$ [$\text{M} + \text{H}$] $^+$, 357.1769; found, 357.1768.

Isobutyl (Z)-3-(1H-Naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)hex-2-enoate (3l). Synthesized according to general procedure 7. The title compound was isolated in 83–86% yields (145 mg and 150 mg) as a yellow solid (mp 86.9–88.1 °C). TLC R_f = 0.57 in 9:1 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 7.12 (dd, J = 8.3, 7.3 Hz, 2H), 7.05 (dd, J = 8.3 Hz, 4J = 1.0 Hz, 2H), 6.36 (dd, J = 7.3 Hz, 4J = 1.0 Hz, 2H), 6.20 (s, 1H), 5.77 (br s, 2H), 3.94 (dd, J = 6.6, 0.6 Hz, 2H), 2.79–2.71 (m, 2H), 2.05–1.93 (m, 1H), 1.58–1.46 (m, 2H), 1.02–0.96 (m, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 166.2 (C), 140.7 (C), 136.4 (C), 127.7 (CH), 125.2 (CH), 120.1 (C), 118.2 (CH), 106.3 (CH), 70.4 (CH_2), 32.4 (CH_2), 27.9 (CH), 23.3 (CH_2), 19.3 (CH_3), 14.5 (CH_3); ^{11}B NMR (128 MHz, CDCl_3) δ 28.89. HRMS (ESI $^+$): calcd for $\text{C}_{20}\text{H}_{26}\text{BN}_2\text{O}_2$ [$\text{M} + \text{H}$] $^+$, 337.2082; found, 337.2084.

Allyl (Z)-3-(1H-Naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)hex-2-enoate (3m). Synthesized according to general procedure 7. The title compound was isolated in 81–83% yields (135 mg and 139 mg) as a yellow solid (mp 65.0–65.9 °C). TLC R_f = 0.39 in 19:1 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 7.13 (dd, J = 8.3, 7.3 Hz, 2H), 7.06 (dd, J = 8.3 Hz, 4J = 1.0 Hz, 2H), 6.35 (dd, J = 7.3 Hz, 4J = 1.0 Hz, 2H), 6.23 (s, 1H), 6.05–5.94 (m, 1H), 5.80 (br s, 2H), 5.42–5.36 (m, 1H), 5.32–5.27 (m, 1H), 4.70–4.66 (m, 2H), 2.81–2.74 (m, 2H), 1.59–1.48 (m, 2H), 1.00 (t, J = 7.4 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 165.5 (C), 140.6 (C), 136.4 (C), 132.3 (CH), 127.7 (CH), 124.7 (CH), 120.1 (C), 118.5 (CH_2), 118.2 (CH), 106.3 (CH), 64.9 (CH_2), 32.4 (CH_2), 23.2 (CH_2), 14.4 (CH_3); ^{11}B NMR (128 MHz, CDCl_3) δ 28.92. HRMS (ESI $^+$): calcd for $\text{C}_{19}\text{H}_{22}\text{BN}_2\text{O}_2$ [$\text{M} + \text{H}$] $^+$, 321.1769; found, 321.1768.

But-2-yn-1-yl (Z)-3-(1H-Naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)hex-2-enoate (3n). Synthesized according to general procedure 7. The title compound was isolated in 72–74% yields (125 mg and 128 mg) as a yellow solid (mp 132.8–133.5 °C). TLC R_f = 0.35 in 19:1 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 7.11 (dd, J = 8.3, 7.3 Hz, 2H), 7.04 (dd, J = 8.3 Hz, 4J = 1.0 Hz, 2H), 6.35 (dd, J = 7.3 Hz, 4J = 1.0 Hz, 2H), 6.21 (t, 4J = 0.9 Hz, 1H), 5.75 (br s, 2H), 4.72 (q, 5J = 2.4 Hz, 2H), 2.80–2.74 (m, 2H), 1.88 (t, 5J = 2.4 Hz, 3H), 1.57–1.46 (m, 2H), 0.99 (t, J = 7.3 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 165.0 (C), 140.6 (C), 136.4 (C), 127.7 (CH), 124.2 (CH), 120.2 (C), 118.3 (CH), 106.3 (CH), 83.3 (C), 73.3 (C), 52.5 (CH_2), 32.4 (CH_2), 23.2 (CH_2), 14.4 (CH_3), 3.8 (CH_3); ^{11}B NMR (128 MHz, CDCl_3) δ 28.91. HRMS (ESI $^+$): calcd for $\text{C}_{20}\text{H}_{22}\text{BN}_2\text{O}_2$ [$\text{M} + \text{H}$] $^+$, 333.1769; found, 333.1770.

(Z)-N-Methoxy-N-methyl-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)non-2-enamide (5a). Note: β -carbon observed with 3 s delay. Synthesized according to general procedure 8. The title compound was isolated in 85–91% yields (161 mg, 163 mg, 170 mg, and 174 mg) as a yellow solid (mp 85.6–86.5 °C). TLC R_f = 0.39 in 3:2 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 7.12 (dd, J = 8.3, 7.2 Hz, 2H), 7.04 (dd, J = 8.3 Hz, 4J = 1.0 Hz, 2H), 6.57 (br s, 1H), 6.37 (dd, J = 7.2 Hz, 4J = 1.0 Hz, 2H), 5.79 (br s, 2H), 3.71 (s, 3H), 3.26 (s, 3H), 2.67–2.60 (m, 2H), 1.54–1.44 (m, 2H), 1.42–1.35 (m, 2H), 1.33–1.25 (m, 4H), 0.89–0.84 (m, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 167.6 (C, br), 153.4 (C–B, br), 140.8 (C), 136.5 (C), 127.7 (CH), 124.6 (CH, br), 120.1 (C), 118.1 (CH), 106.2 (CH), 61.7 (CH_2), 32.3 (CH_3 , br), 31.9 (CH_2), 31.0 (CH_2), 30.1 (CH_2), 29.8 (CH_2), 22.8 (CH_2), 14.2 (CH_3); ^{11}B NMR (128 MHz, CDCl_3) δ 28.98. HRMS (ESI $^+$): calcd for $\text{C}_{21}\text{H}_{29}\text{BN}_2\text{O}_2$ [$\text{M} + \text{H}$] $^+$, 366.2347; found, 366.2361.

(Z)-N-Methoxy-N-methyl-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)but-2-enamide (5b). Note: β -carbon observed with 3 s delay. Synthesized according to general procedure 8. The title compound was isolated in 82–87% yields (126 and 135 mg) as a yellow solid (mp 99.2–100.1 °C). TLC R_f = 0.24 in 3:2 hexanes/EtOAc. ^1H NMR (400 MHz, CDCl_3) δ 7.12 (dd, J = 8.3, 7.3 Hz, 2H), 7.04 (dd, J = 8.3 Hz, 4J = 1.0 Hz, 2H), 6.63 (br s, 1H), 6.37 (dd, J = 7.3 Hz, 4J = 1.0 Hz, 2H), 5.86 (br s, 2H), 3.71 (s, 3H), 3.27 (s, 3H), 2.20 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 167.6 (C, br), 147.3 (C–B, br), 140.8 (C), 136.4 (C), 127.7 (CH), 125.5 (CH, br), 120.1 (C), 118.1 (CH), 106.2 (CH), 61.8 (CH_3), 32.2 (CH_3 , br), 16.7

(CH₃); ¹¹B NMR (128 MHz, CDCl₃) δ 28.69. HRMS (ESI⁺): calcd for C₁₆H₁₉BN₃O₂ [M + H]⁺, 296.1565; found, 296.1562.

(Z)-N,N-Dimethyl-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)hex-2-enamide (5c). Synthesized according to general procedure 8. The title compound was isolated in 75–77% yields (122 and 127 mg) as a beige solid (mp 197.3–198.3 °C). TLC R_f = 0.33 in 1:1 hexanes/EtOAc. ¹H NMR (400 MHz, (CD₃)₂CO) δ 7.37 (br s, 2H), 7.05 (dd, J = 8.3, 7.4 Hz, 2H), 6.94 (dd, J = 8.3 Hz, ⁴J = 1.0 Hz, 2H), 6.54 (s, 1H), 6.50 (dd, J = 7.4 Hz, ⁴J = 1.0 Hz, 2H), 3.04 (s, 3H), 2.93 (s, 3H), 2.43–2.37 (m, 2H), 1.53–1.42 (m, 2H), 0.88 (t, J = 7.4 Hz, 3H); ¹³C{¹H}NMR (101 MHz, (CD₃)₂CO) δ 168.8 (C), 143.0 (C), 137.4 (C), 131.4 (CH), 128.4 (CH), 121.1 (C), 117.7 (CH), 106.6 (CH), 37.7 (CH₃), 34.2 (CH₃), 33.3 (CH₂), 23.7 (CH₂), 14.5 (CH₃); ¹¹B NMR (128 MHz, (CD₃)₂CO) δ 28.94. HRMS (ESI⁺): calcd for C₁₈H₂₃BN₃O [M + H]⁺, 309.1929; found, 309.1938.

(Z)-N,N-Dimethyl-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)non-2-enamide (5d). Synthesized according to general procedure 8. The title compound was isolated in 80–88% yields (143 mg, 156 mg, 159 mg, and 160 mg) as a beige solid (mp 50.4–51.2 °C). TLC R_f = 0.28 in 3:2 hexanes/EtOAc. ¹H NMR (400 MHz, CDCl₃) δ 7.11 (dd, J = 8.3, 7.3 Hz, 2H), 7.03 (dd, J = 8.3 Hz, ⁴J = 1.0 Hz, 2H), 6.37–6.33 (m, 3H), 5.76 (br s, 2H), 3.04 (s, 3H), 3.02 (s, 3H), 2.35–2.29 (m, 2H), 1.50–1.39 (m, 2H), 1.37–1.23 (m, 6H), 0.89–0.83 (m, 3H); ¹³C{¹H}NMR (101 MHz, CDCl₃) δ 168.9 (C), 140.9 (C), 136.4 (C), 129.6 (CH), 127.7 (CH), 120.0 (C), 117.9 (CH), 106.1 (CH), 38.0 (CH₃), 34.5 (CH₃), 31.8 (CH₂), 31.5 (CH₂), 29.8 (CH₂), 29.7 (CH₂), 22.7 (CH₂), 14.2 (CH₃); ¹¹B NMR (128 MHz, CDCl₃) δ 28.92. HRMS (ESI⁺): calcd for C₂₁H₂₉BN₃O [M + H]⁺, 350.2398; found, 350.2420.

(Z)-N,N-4,4-Tetramethyl-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)pent-2-enamide (5e). Synthesized according to general procedure 8. The title compound was isolated in 69–74% yields (115 mg, 119 mg, and 124 mg) as a beige solid (mp >195 °C (decomp)). TLC R_f = 0.23 in 1:1 hexanes/EtOAc. ¹H NMR (400 MHz, CDCl₃) δ 7.11 (dd, J = 8.3, 7.2 Hz, 2H), 7.03 (dd, J = 8.3 Hz, ⁴J = 1.0 Hz, 2H), 6.32 (dd, J = 7.2 Hz, ⁴J = 1.0 Hz, 2H), 5.97 (s, 1H), 5.68 (br s, 2H), 3.07 (s, 3H), 2.97 (s, 3H), 1.22 (s, 9H); ¹³C{¹H}NMR (101 MHz, CDCl₃) δ 170.8 (C), 140.9 (C), 136.3 (C), 127.7 (CH), 127.0 (CH), 119.7 (C), 117.9 (CH), 106.0 (CH), 38.5 (CH₃), 36.6 (C), 34.3 (CH₃), 30.6 (CH₃); ¹¹B NMR (128 MHz, CDCl₃) δ 29.67. HRMS (ESI⁺): calcd for C₁₉H₂₅BN₃O [M + H]⁺, 322.2085; found, 322.2081.

(Z)-3-Cyclopentyl-N,N-dimethyl-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)acrylamide (5f). Synthesized according to general procedure 8. The title compound was isolated in 89% yields (154 mg and 154 mg) as a beige solid (mp >185 °C (decomp)). TLC R_f = 0.25 in 1:1 hexanes/EtOAc. ¹H NMR (400 MHz, CDCl₃) δ 7.11 (dd, J = 8.3, 7.3 Hz, 2H), 7.03 (dd, J = 8.3 Hz, ⁴J = 0.9 Hz, 2H), 6.32 (dd, J = 7.3 Hz, ⁴J = 0.9 Hz, 2H), 6.20 (s, 1H), 5.75 (br s, 2H), 3.05 (s, 3H), 3.01 (s, 3H), 3.00–2.90 (m, 1H), 1.99–1.85 (m, 2H), 1.76–1.55 (m, 4H), 1.51–1.39 (m, 2H); ¹³C{¹H}NMR (101 MHz, CDCl₃) δ 169.1 (C), 140.8 (C), 136.3 (C), 128.7 (CH), 127.7 (CH), 119.9 (C), 118.0 (CH), 106.1 (CH), 43.0 (CH), 38.3 (CH₃), 34.5 (CH₃), 33.3 (CH₂), 25.8 (CH₂); ¹¹B NMR (128 MHz, CDCl₃) δ 29.35. HRMS (ESI⁺): calcd for C₂₀H₂₅BN₃O [M + H]⁺, 334.2085; found, 334.2086.

(Z)-3-Cyclohexyl-N,N-dimethyl-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)acrylamide (5g). Synthesized according to general procedure 8. The title compound was isolated in 93% yields (168 mg and 168 mg) as a white solid (mp 175.2–177.5 °C). TLC R_f = 0.43 in 1:1 hexanes/EtOAc. ¹H NMR (400 MHz, CDCl₃) δ 7.11 (dd, J = 8.3, 7.3 Hz, 2H), 7.03 (dd, J = 8.3 Hz, ⁴J = 1.0 Hz, 2H), 6.33 (dd, J = 7.3 Hz, ⁴J = 1.0 Hz, 2H), 6.13 (s, 1H), 5.68 (br s, 2H), 3.05 (s, 3H), 3.01 (s, 3H), 2.66–2.56 (m, 1H), 1.80–1.64 (m, 5H), 1.40–1.11 (m, 5H); ¹³C{¹H}NMR (101 MHz, CDCl₃) δ 168.8 (C), 140.8 (C), 136.4 (C), 127.6₆ (CH), 127.6₇ (CH), 119.8 (C), 118.0 (CH), 106.0 (CH), 42.2 (CH), 38.2 (CH₃), 34.5 (CH₃), 33.1 (CH₂), 26.3 (CH₂), 26.1 (CH₂); ¹¹B NMR (128 MHz, CDCl₃) δ 29.45. HRMS (ESI⁺): calcd for C₂₁H₂₇BN₃O [M + H]⁺, 348.2242; found, 348.2247.

(Z)-3-(Cyclohex-1-en-1-yl)-N,N-dimethyl-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)acrylamide (5h). Synthesized according to general procedure 8. The title compound was isolated in 77–81% yields (138 mg and 145 mg) as a light brown solid (mp >155 °C (decomp)). TLC R_f = 0.21 in 1:1 hexanes/EtOAc. ¹H NMR (400 MHz, CDCl₃) δ 7.11 (dd, J = 8.3, 7.3 Hz, 2H), 7.02 (dd, J = 8.3 Hz, ⁴J = 1.0 Hz, 2H), 6.33 (dd, J = 7.3 Hz, ⁴J = 1.0 Hz, 2H), 6.21 (s, 1H), 5.78 (br s, 2H), 5.63 (p, J = 1.8 Hz, 1H), 3.02 (s, 3H), 2.98 (s, 3H), 2.15–2.08 (m, 4H), 1.71–1.59 (m, 4H); ¹³C{¹H}NMR (101 MHz, CDCl₃) δ 169.5 (C), 141.0 (C), 137.7 (C), 136.4 (C), 128.3 (CH), 127.7 (CH), 126.6 (CH), 120.0 (C), 117.9 (CH), 106.1 (CH), 38.2 (CH₃), 34.4 (CH₃), 28.3 (CH₂), 25.7 (CH₂), 23.0 (CH₂), 22.1 (CH₂); ¹¹B NMR (128 MHz, CDCl₃) δ 28.66. HRMS (ESI⁺): calcd for C₂₁H₂₅BN₃O [M + H]⁺, 346.2085; found, 346.2090.

(Z)-N,N-Dimethyl-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-4-phenoxybut-2-enamide (5i). Synthesized according to general procedure 8. The title compound was isolated in 80–83% yields (156 mg, 159 mg, and 160 mg) as a beige solid (mp >153 °C (decomp)). TLC R_f = 0.29 in 20:1 Et₂O/EtOAc. ¹H NMR (400 MHz, CDCl₃) δ 7.31–7.24 (m, 2H), 7.11 (dd, J = 8.3, 7.3 Hz, 2H), 7.03 (dd, J = 8.3 Hz, ⁴J = 1.0 Hz, 2H), 7.00–6.94 (m, 1H), 6.94–6.89 (m, 2H), 6.65 (t, ⁴J = 1.3 Hz, 1H), 6.38 (br s, 2H), 6.35 (dd, J = 7.3 Hz, ⁴J = 1.0 Hz, 2H), 4.94 (d, ⁴J = 1.3 Hz, 2H), 3.03 (s, 6H); ¹³C{¹H}NMR (101 MHz, CDCl₃) δ 167.7 (C), 158.3 (C), 141.0 (C), 136.5 (C), 132.2 (CH), 129.8 (CH), 127.7 (CH), 121.4 (CH), 120.2 (C), 117.9 (CH), 114.8 (CH), 106.2 (CH), 68.4 (CH₂), 38.1 (CH₃), 34.8 (CH₃); ¹¹B NMR (128 MHz, CDCl₃) δ 28.42. HRMS (ESI⁺): calcd for C₂₂H₂₃BN₃O₂ [M + H]⁺, 372.1878; found, 372.1886.

Methyl (Z)-3-(1H-Naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)hex-2-enoyl-D-prolinate (5j). Note: β-carbon observed with 3 s delay. Synthesized according to general procedure 8. The title compound was isolated in 92% yields (187 mg and 196 mg), (76:24 mixture of rotamers) as a yellow solid (mp 149.9–151.4 °C). TLC R_f = 0.40 in 1:1 hexanes/EtOAc. [α]_D²⁵ +35.7 (c 0.038 $\bar{c}$, CH₃OH). In the NMR spectra, minor rotamer is designated by * and the overlapping rotamer peaks are designated by †. ¹H NMR (400 MHz, CDCl₃) δ 7.11[†] (dd, J = 8.3, 7.3 Hz, 4H), 7.03[†] (dd, J = 8.3 Hz, ⁴J = 0.8 Hz, 4H), 6.38–6.33 (m, 5H), 6.20* (s, 1H), 5.79 (br s, 2H), 5.77* (br s, 2H), 4.57 (dd, J = 8.4, 4.0 Hz, 1H), 4.42* (dd, J = 8.4, 3.5 Hz, 1H), 3.75–3.60[†] (m, 8H), 3.57–3.45[†] (m, 2H), 2.57–1.92[†] (m, 12H), 1.57–1.44[†] (m, 4H), 0.98–0.92[†] (m, 6H); ¹³C{¹H}NMR (126 MHz, CDCl₃) δ 173.1* (C), 172.9 (C), 166.9* (C), 166.6 (C), 150.3[†] (C–B, br), 140.9 (C), 140.9* (C), 136.4[†] (C), 128.4* (CH), 128.2 (CH), 127.7[†] (CH), 120.1[†] (C), 118.0* (CH), 117.9 (CH), 106.2* (CH), 106.1 (CH), 60.1* (CH), 58.5 (CH), 52.7* (CH₃), 52.3 (CH₃), 47.7 (CH₂), 46.1* (CH₂), 33.1* (CH₂), 32.9 (CH₂), 31.5* (CH₂), 29.4 (CH₂), 25.0 (CH₂), 23.2 (CH₂), 23.1* (CH₂), 23.0* (CH₂), 14.5* (CH₃), 14.4 (CH₃); ¹¹B NMR (128 MHz, CDCl₃) δ 29.79. HRMS (ESI⁺): calcd for C₂₂H₂₇BN₃O₃ [M + H]⁺, 392.2140; found, 392.2149.

(Z)-N-Methyl-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)hex-2-enamide (5k). Synthesized according to general procedure 8. The title compound was isolated in 71–81% yields (108 and 123 mg) as a yellow solid (mp >157 °C (decomp)). TLC R_f = 0.27 in 1:1 hexanes/EtOAc. ¹H NMR (400 MHz, CDCl₃) δ 7.11 (dd, J = 8.3, 7.3 Hz, 2H), 7.03 (dd, J = 8.3 Hz, ⁴J = 0.8 Hz, 2H), 6.34 (dd, J = 7.3 Hz, ⁴J = 0.8 Hz, 2H), 6.11 (s, 1H), 5.76 (br s, 2H), 5.60 (br d, J = 4.9 Hz, 1H), 2.88 (d, J = 4.9 Hz, 3H), 2.72–2.65 (m, 2H), 1.56–1.45 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H); ¹³C{¹H}NMR (101 MHz, CDCl₃) δ 167.5 (C), 140.8 (C), 136.3 (C), 128.3 (CH), 127.7 (CH), 120.0 (C), 118.0 (CH), 106.2 (CH), 32.2 (CH₂), 26.2 (CH₃), 23.4 (CH₂), 14.4 (CH₃); ¹¹B NMR (128 MHz, CDCl₃) δ 28.83. HRMS (ESI⁺): calcd for C₁₇H₂₁BN₃O [M + H]⁺, 294.1772; found, 294.1778.

(Z)-N-Benzyl-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)hex-2-enamide (5l). Synthesized according to general procedure 8. The title compound was isolated in 95–98% yields (183 mg, 183 mg, and 188 mg) as a yellow solid (mp 113.5–114.8 °C). TLC R_f = 0.18 in 4:1 hexanes/EtOAc. ¹H NMR (400 MHz, CDCl₃) δ 7.26–7.39 (m, 5H), 7.10 (dd, J = 8.3, 7.3 Hz, 2H), 7.03 (dd, J = 8.3 Hz, ⁴J = 0.8 Hz, 2H), 6.33 (dd, J = 7.3 Hz, ⁴J = 0.8 Hz, 2H), 6.13 (s, 1H), 5.88 (t, J = 5.7 Hz, 1H), 5.76 (br s, 2H), 4.50 (d, J = 5.7

H₂, 2H), 2.74–2.69 (m, 2H), 1.58–1.46 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H); ¹³C{¹H}NMR (101 MHz, CDCl₃) δ 166.4 (C), 140.8 (C), 138.3 (C), 136.4 (C), 128.9 (CH), 128.1 (CH), 128.0 (CH), 127.7₂ (CH), 127.7₁ (CH), 120.1 (C), 118.1 (CH), 106.2 (CH), 43.6 (CH₂), 32.4 (CH₂), 23.5 (CH₂), 14.5 (CH₃); ¹¹B NMR (128 MHz, CDCl₃) δ 29.14. HRMS (ESI⁺): calcd for C₂₃H₂₅BN₃O [M + H]⁺, 370.2085; found, 370.2086.

(Z)-3-(1*H*-Naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)but-2-enamide (5m). Synthesized according to general procedure 8. The title compound was isolated in 35–46% yields (46 mg, 59 mg, and 60 mg) as a yellow solid (mp 164.8–165.6 °C). TLC *R*_f = 0.47 in 1:1 Et₂O/EtOAc. ¹H NMR (400 MHz, (CD₃)₂SO) δ 7.89 (s, 2H), 7.31 (s, 1H), 7.04 (dd, *J* = 8.3, 7.4 Hz, 2H), 6.97–6.93 (s, 1H), 6.87 (dd, *J* = 8.3 Hz, ⁴*J* = 0.9 Hz, 2H), 6.50 (dd, *J* = 7.4 Hz, ⁴*J* = 0.9 Hz, 2H), 6.34 (q, ⁴*J* = 1.6 Hz, 1H), 2.16 (d, ⁴*J* = 1.6 Hz, 3H); ¹³C{¹H}NMR (101 MHz, (CD₃)₂SO) δ 168.4 (C), 142.2 (CH), 135.9 (C), 130.4 (C), 127.6 (CH), 119.8 (C), 116.3 (CH), 105.6 (CH), 16.2 (CH₃); ¹¹B NMR (128 MHz, (CD₃)₂SO) δ 30.04. HRMS (ESI⁺): calcd for C₁₄H₁₅BN₃O [M + H]⁺, 252.1303; found, 252.1291.

(Z)-3-(1*H*-Naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)hex-2-enamide (5n). Synthesized according to general procedure 8. The title compound was isolated in 85–95% yields (123 mg, 132 mg, and 138 mg) as a yellow solid (mp 133.5–134.3 °C). TLC *R*_f = 0.23 in 2:1 Et₂O/EtOAc. ¹H NMR (400 MHz, CDCl₃) δ 7.12 (dd, *J* = 8.3, 7.3 Hz, 2H), 7.04 (dd, *J* = 8.3 Hz, ⁴*J* = 1.0 Hz, 2H), 6.35 (dd, *J* = 7.3 Hz, ⁴*J* = 1.0 Hz, 2H), 6.18 (t, ⁴*J* = 0.9 Hz, 1H), 5.78 (s, 2H), 5.63 (br s, 1H), 5.55 (br s, 1H), 2.72–2.68 (m, 2H), 1.57–1.45 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H); ¹³C{¹H}NMR (101 MHz, CDCl₃) δ 168.3 (C), 140.7 (C), 136.4 (C), 127.7 (CH), 127.2 (CH), 120.1 (C), 118.2 (CH), 106.3 (CH), 32.4 (CH₂), 23.3 (CH₂), 14.5 (CH₃); ¹¹B NMR (128 MHz, CDCl₃) δ 29.07. HRMS (ESI⁺): calcd for C₁₆H₁₉BN₃O [M + H]⁺, 280.1616; found, 280.1621.

(Z)-3-(1*H*-Naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)non-2-enamide (5o). Synthesized according to general procedure 8. The title compound was isolated in 89–99% yields (149 mg, 153 mg, and 167 mg) as a yellow solid (mp 98.6–99.3 °C). TLC *R*_f = 0.33 in 2:1 Et₂O/EtOAc. ¹H NMR (400 MHz, CDCl₃) δ 7.12 (dd, *J* = 8.3, 7.2 Hz, 2H), 7.04 (dd, *J* = 8.3 Hz, ⁴*J* = 1.0 Hz, 2H), 6.35 (dd, *J* = 7.2 Hz, ⁴*J* = 1.0 Hz, 2H), 6.16 (t, ⁴*J* = 0.93 Hz, 1H), 5.80 (br s, 2H), 5.70 (br s, 1H), 5.57 (br s, 1H), 2.74–2.69 (m, 2H), 1.51–1.22 (m, 8H), 0.90–0.83 (m, 3H); ¹³C{¹H}NMR (101 MHz, CDCl₃) δ 168.7 (C), 140.8 (C), 136.4 (C), 127.7 (CH), 127.0 (CH), 120.1 (C), 118.1 (CH), 106.2 (CH), 31.8 (CH₂), 30.4 (CH₂), 30.1 (CH₂), 29.7 (CH₂), 22.7 (CH₂), 14.2 (CH₃); ¹¹B NMR (128 MHz, CDCl₃) δ 28.97. HRMS (ESI⁺): calcd for C₁₉H₂₅BN₃O [M + H]⁺, 322.2085; found, 322.2080.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00648.

Copies of ¹H NMR, ¹³C NMR, ¹¹B and NOE spectra for all products (PDF)

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Notes

The authors declare no competing financial interest.

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