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Regioselective synthesis of branched alkenylborons via copper-catalyzed protoborylation of 1,4-diynes

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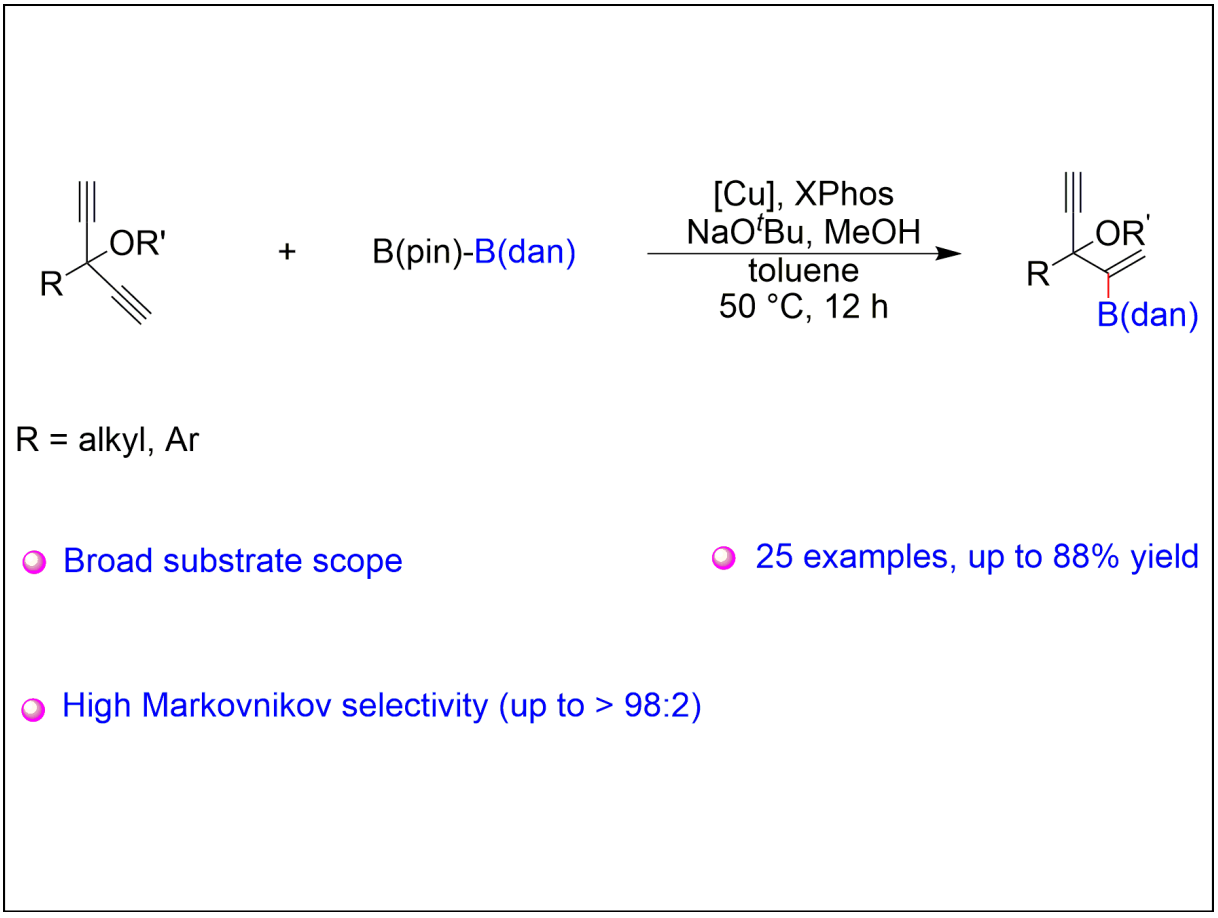
Graphical abstract



Regioselective synthesis of branched alkenylborons via copper-catalyzed protoborylation of 1,4-diynes.

Public summary

- A copper-catalyzed protoborylation reaction of 1,4-diynes was developed.
- The mono-phosphine ligand XPhos supported the formation of branched alkenylboron products in high yields and regioselectivities.
- This reaction provides an efficient approach for the synthesis of multifunctionalized α-vinylborons.

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SI Supporting Information

Abstract: A copper-catalyzed highly regioselective protoborylation of 1,4-diynes for the synthesis of alkenylboramide compounds was reported. Various (hetero)aryl and alkyl substituted terminal 1,4-diynes afforded the corresponding products in high yields and regioselectivities. The utility of alkenyl-B(dan) products was proven by their convenient derivatizations.

Keywords: 1, 4-diynes; copper catalysis; protoborylation; regioselectivity; α-alkenylborons

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1 Introduction

1,4-Enynes are important structural units in many natural products and biologically active compounds[1–4] and are versatile reagents in modern synthetic organic chemistry because of their multiple active sites to be further functionalized through a series of transformations[5–8]. On the other hand, alkenylboron compounds are widely employed in a range of C–C bond-forming reactions because they are generally nontoxic and have high reactivity in cross-coupling reactions[9–15]. Hydro and protoborylation of alkynes with boron-containing reagents represent straightforward and practical methods for the synthesis of this kind of compound (Scheme 1a)[16–20]. Over the past few years, great progress has been made in the transition-metal catalyzed borylation of terminal alkynes[21–37]. In particular, borylation reactions with copper catalysts, where Cu-B species are generated with diboron reagents, have been the mainstay[38]. A vast majority of these borylations furnished the corresponding linear alkenylboron products with high β-selectivity. However, the methods for the synthesis of α-borylated products are more limited, and only a few examples have been reported[39–44]. The seminal method for the selective protoborylation of terminal alkynes to produce α-alkenylboronates was reported by Hoveyda in 2011[39] by employing NHC-Cu complexes as catalysts. In 2013, Carretero and coworkers reported a copper-catalyzed borylation strategy that can achieve high Markovnikov selectivity[40]. However, only substrates with directing groups at the propargyl position, such as amine, hydroxyl or 2-$PySO_2$ groups, were allowed in this strategy. Later, Yoshida developed an α-selective protoborylation of terminal alkynes by using a masked diboron B(pin)–B(dan) as a borylation reagent in the presence of a copper catalyst[41]. Subsequently, the same group also reported a borylation reaction using an anthranilamide-substituted boron moiety B(aam), which enabled α-regioselectivity because of its much lower Lewis acidity (Scheme 1b)[44]. Herein, we report the protoborylation of 1,4-diynes with high regioselectivity by the use of a bulky ligand XPhos with a copper catalyst (Scheme 1c).

2 Results and discussion

2.1 Screening of reaction conditions

Initially, (3-(benzyloxy)penta-1,4-diyn-3-yl)benzene (**1a**) was selected to react with diboron B(pin)–B(dan). In the presence of $Cu(OTf)_2$ (5 mol%) and NaO^tBu (10 mol%), we initially chose L_1 (DPEphos) as the ligand, and the desired protoborylation products **3a** and **4a** were obtained in high yield but with poor regioselectivity (Table 1, entry 1). When the reaction was run in the presence of L_3 (Xantphos), the reverse regioselectivity of the protoborylation product was observed (entry 3). Due to the unsatisfactory regioselectivities given by bisphosphine ligands, we turned our attention to monophosphine ligands. When L_5 (PCy_3) was employed, **3a** and **4a** were obtained in 71% yield with moderate regioselectivity (**3a**:**4a** = 80:20, entry 5).

To further improve the regioselectivity of the product, different mono-phosphine ligands were investigated (entries 6–10). Then, bulky and electron-rich L_{10} (XPhos) was identified as the best ligand, which delivered desired product **3a** in a moderate yield and with good regioselectivity (**3a**:**4a** = 92:8, entry 10). Next, we explored the reactive performance of XPhos with other solvents. Toluene was found to give the product in high yield and regioselectivity, while other solvents afforded inferior results. It was found that toluene gave higher regioselectivity up to 95:5 (entry 14). Subsequently, we explored the catalytic activity of other copper salts in the presence of XPhos, and $Cu(OAc)_2$ gave a higher regioselectivity of up to 97:3 (entry 15). Finally, to exclude the background reaction that may be promoted by the copper salt and B(pin)-B(dan), we tried a control reaction, without

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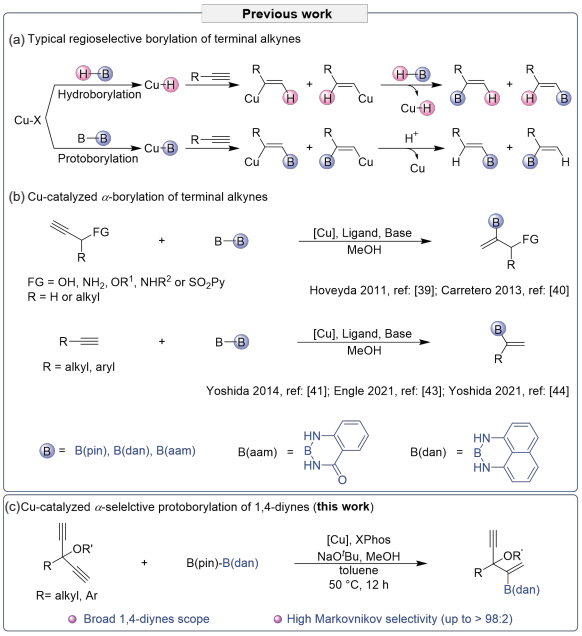


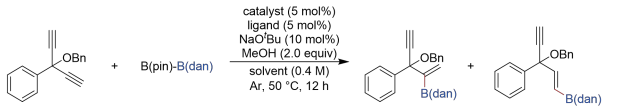
Scheme 1. Copper-catalyzed borylation reactions.

the addition of XPhos, the protoborylation reaction did not occur, and 98% of substrate **1a** remained (entry 16). Therefore, the optimized reaction conditions were determined as follows (entry 15): a mixture of **1a** and **2** in toluene was stirred at 50 °C for 12 h in the presence of 5 mol% $Cu(OAc)_2$ as the catalyst, 5 mol% XPhos as the ligand, 2.0 equivalents of MeOH as the additive and 10 mol% NaO^{t}Bu as the base.

2.2 Substrate scope of 1,4-diynes

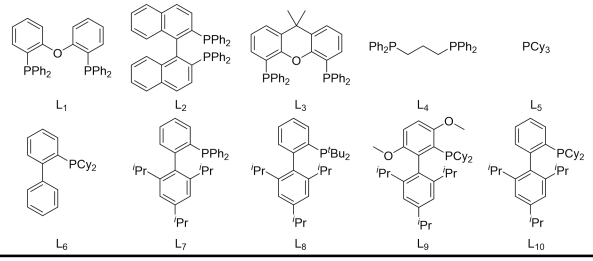
With the optimized conditions in hand, we examined the substrate scope of the protoborylation using a variety of 1,4-diynes **1a**–**1y** bearing various functionalities. The results are summarized in Scheme 2. Various aryl-substituted 1,4-diynes with B(pin)–B(dan) were tested, and the substrates bearing electron-withdrawing groups, such as trifluoromethyl (**1b**) and halogens (**1c**–**1e**), or electron-donating groups, such as methoxy (**1f**), tert-butyl (**1g**), methyl (**1h**, **1i**, **1k**) and acetal group (**1m**), could give the vinylboron products in good yield with high α-selectivities. Polycyclic hydrocarbon-substituted 1,4-diynes such as **1j**, **1l** and **1p** were competent during the protoborylation process. Moreover, the reaction proceeded smoothly for thienyl- and furyl-substituted 1,4-diynes **1n** and **1o**, giving corresponding products **3n** and **3o** in 79% and 66% yields, respectively. In addition to aromatic substituted terminal alkynes, this protoborylation reaction was also applied to diverse aliphatic substituted alkynes. The corresponding desired products were also obtained in satisfactory yields and with excellent regioselectivities (**3q**–**3u**). Most notably, substrate **1v**–**1x,** containing a highly reactive double bond, afforded corresponding products **3v**–**3x** in high yield and with excellent chemo- and regioselectivities. For cyclopropyl group-substituted 1,4-diyne (**1t**), no open ring product was found. Finally, the reactivity of the internal alkynes was also examined. Phenyl substituted internal alkyne **1z** only gave desired product **3z** in 13% yield. *n*-C_5H_{11} substituted internal alkyne **1aa** was tested for this reaction, and a similar poor result was observed. We speculate that the large steric hindrance

Table 1. Optimization of the reaction conditions.[a]



1a 2 3a 4a

Entry	[Cu]	Ligand	Solvent	Yield (%)[b] (**3a**+**4a**)	(**3a**:**4a**)[c]
1	$Cu(OTf)_2$	L_1	MTBE	77	62:38
2	$Cu(OTf)_2$	L_2	MTBE	71	65:35
3	$Cu(OTf)_2$	L_3	MTBE	86	23:77
4	$Cu(OTf)_2$	L_4	MTBE	49	84:16
5	$Cu(OTf)_2$	L_5	MTBE	71	80:20
6	$Cu(OTf)_2$	L_6	MTBE	70	84:16
7	$Cu(OTf)_2$	L_7	MTBE	42	86:14
8	$Cu(OTf)_2$	L_8	MTBE	54	74:26
9	$Cu(OTf)_2$	L_9	MTBE	80	86:14
10	$Cu(OTf)_2$	L_{10}	MTBE	88	92:8
11	$Cu(OTf)_2$	L_{10}	dioxane	77	84:16
12	$Cu(OTf)_2$	L_{10}	THF	86	87:13
13	$Cu(OTf)_2$	L_{10}	PhCl	77	95:5
14	$Cu(OTf)_2$	L_{10}	toluene	80	95:5
15	$Cu(OAc)_2$	L_{10}	toluene	89 (86)[d]	97:3
16[e]	$Cu(OAc)_2$	-	toluene	0	-



[a]Reaction conditions unless otherwise specified: The mixture of **1a** (0.2 mmol, 1.0 equiv), **2** (0.2 mmol, 1.0 equiv), copper catalyst (5 mol%), ligand (5 mol%), NaO^{t}Bu (10 mol%) and MeOH (2.0 equiv) in extra dry solvent (0.4 mol/L) was stirred at 50 °C for 12 h under argon atmosphere. [b]Yield of (**3a**+**4a**) was determined by ^{1}H NMR with mesitylene as an internal standard. [c]Ratio of **3a**/**4a** was determined by crude ^{1}H NMR analysis. [d]Isolated yield of **3a** is given in parentheses. [e]Without the addition of XPhos.

of the internal alkyne leads to poor reactivity. In addition, the structure of **3j** was determined by X-ray single crystal diffraction (CCDC NO. 2150379).

We then studied the catalytic synthesis of optically active vinylboron compounds. After careful screening of various chiral ligands, unfortunately, we only obtained 20% enantiomeric excess value of product **3a'** in the presence of 5 mol% $Cu(OTf)_2$ as the catalyst and 5 mol% (*R*,*R*)-Ph-BPE as the chiral ligand (Scheme 3). To demonstrate the utility of the current strategy, a gram-scale reaction between **1a** and B(pin)–B(dan) was carried out. Desired product **3a** was obtained in 83% isolated yield (1.38 g) with 85:15 regioselectivity (Scheme 4).

Product **3a** generated from the protoborylation reaction

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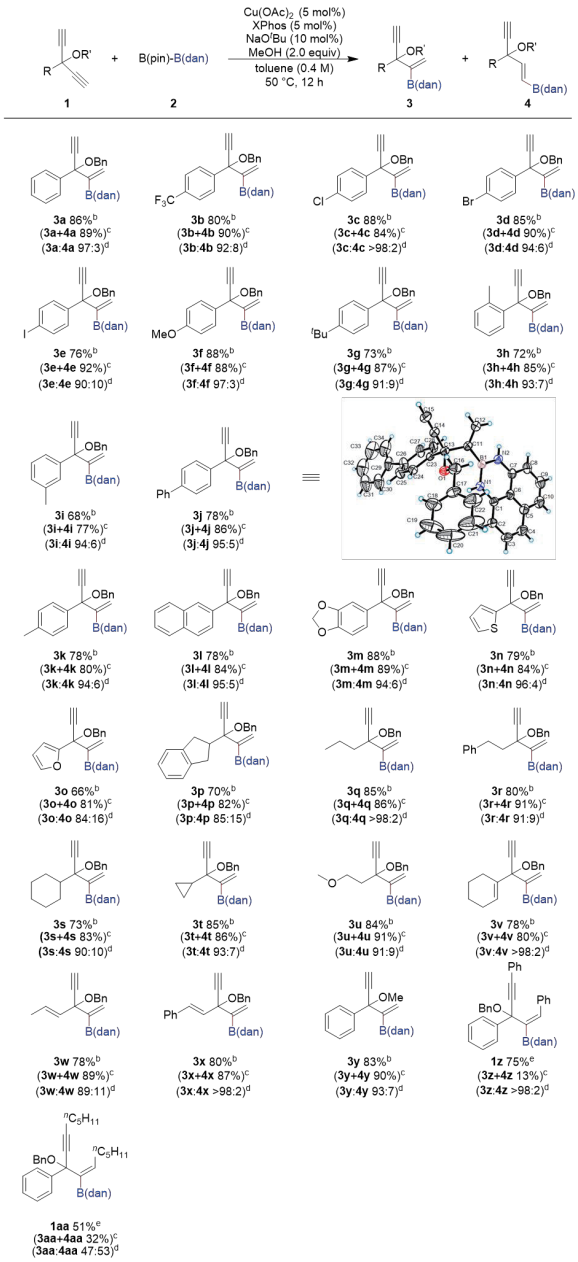
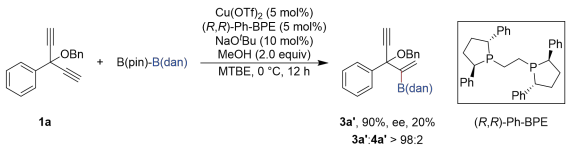


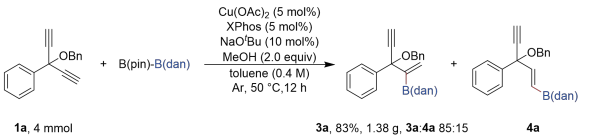
[a]The mixture of 1 (0.2 mmol, 1.0 equiv), 2 (0.2 mmol, 1.0 equiv), $Cu(OAc)_2$ (5 mol%), XPhos (5 mol%), NaO^{t}Bu (10 mol%) and MeOH (2.0 equiv) in extra dry toluene (0.4 mol/L) was stirred at 50 °C for 12 h under argon atmosphere. [b]Isolated yield of 3. [c]Yield of (3+4) was determined by ^{1}H NMR analysis with mesitylene as internal standard. [d]Ratio of 3/4 was determined by crude ^{1}H NMR analysis. [e]The amount of substrate 1 was determined by crude ^{1}H NMR analysis.

Scheme 2. Substrate scope of 1,4-diynes.[a]

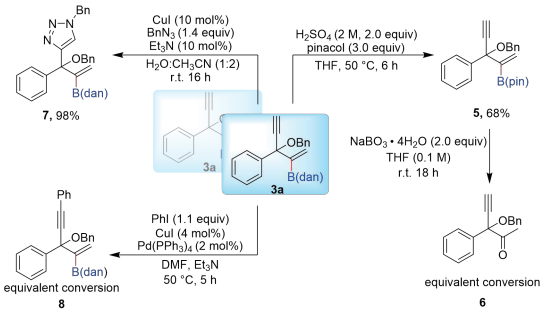
contains a vinyl-B(dan) group that can undergo various transformations. As shown in Scheme 5, product **5** was obtained in 68% yield by treating the B(dan) moiety of **3a** with pinacol under acidic condition[41] and further reacting with $NaBO_3$•$4H_2O$ to obtain methyl ketone **6** in quantitative yield[45]. The other alkynyl group of alkenylboron compound **3a** can also undergo a variety of transformations. For example, Cu-catalyzed [3+2]-cycloaddition of **3a** with BnN_3 afforded triazole **7** in 98% yield[46]. Additionally, Pd-catalyzed Sonogashira coupling of **3a** with iodobenzene gave



Scheme 3. Optimization of the reaction conditions for the synthesis of enantioenriched alkenylboron compound **3a'**.



Scheme 4. Gram-scale synthesis of alkenylboron product **3a**.



Scheme 5. Transformation of alkenylboron product **3a**.

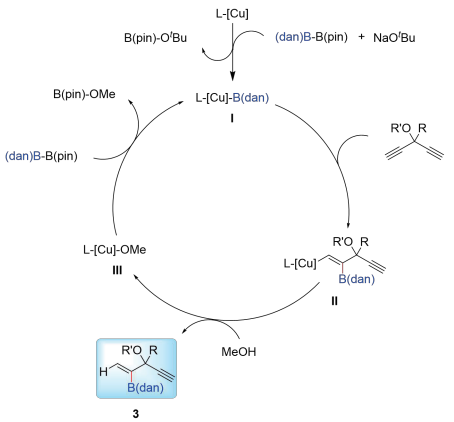
product **8** in a quantitative yield[47].

2.3 Mechanistic pathway

A possible mechanistic pathway for the protoborylation of 1,4-diynes is shown in Scheme 6. First, Cu-B species **I** could be generated from B(pin)–B(dan) with the help of a copper catalyst and NaO^{t}Bu, and then the insertion of alkynyl into the Cu–B bond, which generated alkenylcopper species **II** followed by protonation with MeOH, provided products **3** and regenerated species **III**. The released copper species **III** would be delivered to the next catalyst cycle. The B(dan) moiety is more easily added to the internal carbon of alkynyl due to the steric repulsion between the substituent on the 1,4-diynes and the bulkier copper species.

3 Conclusions

In summary, we have developed a copper-catalyzed proto-



Scheme 6. Proposed mechanistic pathway.

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borylation of 1,4-diynes. It was found that the employment of a mono-phosphine ligand XPhos facilitated the synthesis of a series of branched alkenylboron products in high yields and with good regioselectivities. The current catalytic system was compatible with various substrates, including aliphatic and aromatic substituted alkynes. This reaction provides an attractive and efficient approach for the synthesis of multifunctionalized α-vinylborons.

4 Experimental section

4.1 General procedure

General procedure A: An oven-dried 10 mL Schlenk tube equipped with a magnetic stirring bar was charged with $Cu(OAc)_2$ (1.8 mg, 0.01 mmol, 5 mol%), XPhos (4.8 mg, 0.01 mmol, 5 mol%) and NaO^{t}Bu (1.9 mg, 0.02 mmol, 10 mol%). Then, the tube was sealed and removed from the glove box. Subsequently, toluene (0.5 mL), B(pin)-B(dan) (58.8 mg, 0.2 mmol, 1.0 equiv), 1,4-pentadiyne **1** (0.2 mmol, 1.0 equiv) and MeOH (12.8 mg, 0.4 mmol, 2.0 equiv) were added under an argon atmosphere. The reaction mixture was stirred at 50 °C for 12 h. After cooling to room temperature, the reaction mixture was filtered through celite and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as the eluent to give target product **3**.

4 mmol scale experiment for the preparation of 3a: An oven-dried 50 mL Schlenk tube equipped with a magnetic stirring bar was charged with $Cu(OAc)_2$ (36.3 mg, 0.2 mmol, 5 mol%), XPhos (95.3 mg, 0.2 mmol, 5 mol%) and NaO^{t}Bu (38.4 mg, 0.4 mmol, 10 mol%). Then, the tube was sealed and removed from the glove box. Subsequently, toluene (10 mL), B(pin)-B(dan) (1.18 g, 4.0 mmol, 1.0 equiv), substrate **1a** (0.99 g, 4.0 mmol, 1.0 equiv) and MeOH (0.26 g, 8.0 mmol, 2.0 equiv) were added under an argon atmosphere. The reaction mixture was stirred at 50 °C for 12 h. After cooling to room temperature, the reaction mixture was filtered through celite and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1) to give **3a** as a yellow oil (1.38 g, 3.32 mmol, 83%).

Procedure B for the synthesis of 3a': An oven-dried 10 mL Schlenk tube equipped with a magnetic stirrer was charged with $Cu(OTf)_2$ (3.6 mg, 0.01 mmol, 5 mol%), (*R*,*R*)-Ph-BPE (5.1 mg, 0.01 mmol, 5 mol%) and NaO^{t}Bu (1.9 mg, 0.02 mmol, 10 mol%). Then, the tube was sealed and removed from the glove box. Subsequently, MTBE (0.5 mL) was added under an argon atmosphere, and the mixture was stirred at room temperature for 30 min. Then, B(pin)-B(dan) (58.8 mg, 0.2 mmol, 1.0 equiv), **1a** (49.3 mg, 0.2 mmol, 1.0 equiv) and MeOH (12.8 mg, 0.4 mmol, 2.0 equiv) were added under an argon atmosphere. The reaction mixture was stirred at 0 °C for 12 h. The reaction mixture was filtered through celite and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give target product **3a'** (20% ee, 90%) as a yellow oil. The ee value of **3a'** was determined by chiral HPLC analysis, which was performed on an Agilent 1260 Infinity equipped with a Daicel Chiralcel AD column. Conditions: hexane/isopropanol = 90/10, flow rate = 0.50 mL/min, column temperature = 25 °C, UV-Vis detection at λ = 230 nm. Retention times: t_{R1} (major) = 17.89 min, t_{R2} (minor) = 19.10 min.

Procedure C for the synthesis of 5: Under an air atmosphere, a 10 mL Schlenk tube equipped with a magnetic stirring bar was charged with **3a** (82.9 mg, 0.2 mmol, 1.0 equiv), pinacol (70.9 mg, 0.6 mmol, 3.0 equiv), tetrahydrofuran (0.75 mL) and 2.0 mol/L H_2SO_4 aqueous solution (0.2 mL, 0.4 mmol of H_2SO_4, 2.0 equiv) before the mixture was stirred at 50 °C for 6 h. Then, the mixture was diluted with ethyl acetate and filtered through celite. The organic solution was washed with saturated $NaHCO_3$ aqueous solution, and the aqueous phase was extracted with ethyl acetate (10 mL×3). The combined organic phases were dried over anhydrous Na_2SO_4. After filtration and concentration, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1). Product **5** was obtained as a yellow oil (50.9 mg, 0.136 mmol, 68%).

Procedure D for the synthesis of 6: To a 10 mL Schlenk tube equipped with a magnetic stirring bar, **5** (74.9 mg, 0.2 mmol, 1.0 equiv) and tetrahydrofuran (2.0 mL) were added. An aqueous solution of $NaBO_3$•$4H_2O$ (0.4 mmol, 2.0 equiv in 2.0 mL water) was added. The reaction mixture was stirred at 25 °C for 6 h. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (10 mL×3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1) to give product **6** as a yellow oil (52.8 mg, 0.2 mmol, 100%).

Procedure E for the synthesis of 7: Under an argon atmosphere, an oven-dried 10 mL Schlenk tube equipped with a magnetic stirring bar was charged with **3a** (82.9 mg, 0.2 mmol, 1.0 equiv) and benzyl azide (37.3 mg, 0.28 mmol, 1.4 equiv). Then, H_2O (0.5 mL) and CH_3CN (1.0 mL) were added under an argon atmosphere. Following the addition of Et_3N (2.0 mg, 0.02 mmol, 10 mol%) and CuI (3.8 mg, 0.02 mmol, 10 mol%), the reaction mixture was stirred at 25 °C for 16 h. The reaction mixture was diluted with saturated $NaHCO_3$ aqueous solution (2 mL) and extracted with ethyl acetate (10 mL×3). The combined organic phases were dried over anhydrous Na_2SO_4. After filtration and concentration, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to give product **7** as a white solid (106.8 mg, 0.195 mmol, 98%).

Procedure F for the synthesis of 8: An oven-dried 10 mL Schlenk tube equipped with a magnetic stirring bar was charged with $Pd(PPh_3)_4$ (4.6 mg, 0.004 mmol, 2 mol%) and CuI (1.5 mg, 0.008 mmol, 4 mol%). Then, the tube was sealed and removed from the glove box. Subsequently, **3a** (82.9 mg, 0.2 mmol, 1.0 equiv), iodobenzene (44.9 mg, 0.22 mmol, 1.1 equiv), Et_3N (0.21 mL) and DMF (0.16 mL) were added under argon atmosphere. The reaction mixture was stirred at 50 °C for 5 h. After cooling to room temperature, the reaction mixture was filtered through celite and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1) to give product **8** as a colorless oil (97.6 mg, 0.199 mmol, 100%).

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4.2 Characterization data for products

2-(3-(benzyloxy)-3-phenylpent-1-en-4-yn-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1, 3, 2]diazaborinine (3a):This compound was prepared according to general procedure A described above and obtained as a colorless oil in 86% yield (71.3 mg). R_f = 0.35 (petroleum ether/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.60 (m, 2H), 7.45 – 7.41 (m, 2H), 7.40 – 7.31 (m, 5H), 7.29 – 7.27 (m, 1H), 7.00 (dd, *J* = 8.2, 7.6 Hz, 2H), 6.93 (dd, *J* = 8.4, 0.8 Hz, 2H), 6.05 – 6.02 (m, 3H), 6.02 (s, 2H), 5.82 (d, *J* = 1.6 Hz, 1H), 4.64 (d, *J* = 10.8 Hz, 1H), 4.55 (d, *J* = 10.4 Hz, 1H), 2.92 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.27, 141.16, 138.19, 136.36, 128.72, 128.60, 128.38, 128.27, 127.96, 127.62, 126.69, 126.13, 120.04, 117.49, 105.83, 82.52, 82.47, 78.97, 67.19.^{11}B NMR (128 MHz, $CDCl_3$) δ 28.23. HRMS (ESI) *m*/*z* calculated for $C_{28}H_{24}BN_2O$ $[M+H]^+$: 415.1982, found: 415.1985.

2-(3-(benzyloxy)-3-(4-(trifluoromethyl)phenyl)pent-1-en-4-yn-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1, 3, 2]diazaborinine (3b): This compound was prepared according to general procedure A described above and obtained as a white solid in 80% yield (77.3 mg). R_f = 0.35 (petroleum ether/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.50 – 7.29 (m, 5H), 7.01 (dd, *J* = 8.0, 7.2 Hz, 2H), 6.95 (dd, *J* = 8.3, 1.2 Hz, 2H), 6.09 (d, *J* = 1.2 Hz, 1H), 6.07 – 6.01 (m, 4H), 5.88 (d, *J* = 1.6 Hz, 1H), 4.64 (d, *J* = 10.4 Hz, 1H), 4.59 (d, *J* = 10.8 Hz, 1H), 2.97 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.56, 140.92, 137.69, 136.35, 130.41 (q, *J* = 32.4 Hz), 128.84, 128.49, 128.22, 127.64, 127.18, 127.00, 125.60 (q, *J* = 3.8 Hz), 124.14 (q, *J* = 273.2 Hz), 120.05, 117.73, 105.94, 82.33, 81.71, 79.74, 67.47. ^{11}B NMR (128 MHz, $CDCl_3$) δ 27.62. ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.47. HRMS (ESI) *m*/*z* calculated for $C_{29}H_{23}BF_3N_2O$ $[M+H]^+$: 483.1856, found: 483.1860.

2-(3-(benzyloxy)-3-(4-chlorophenyl)pent-1-en-4-yn-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1, 3, 2]diazaborinine (3c): This compound was prepared according to general procedure A described above and obtained as a white solid in 88% yield (79.2 mg). R_f = 0.55 (petroleum ether/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 2H), δ 7.45 – 7.30 (m, 7H), 7.01 (dd, *J* = 8.2, 7.4 Hz, 2H), 6.94 (dd, *J* = 8.2, 1.1 Hz, 2H), 6.09 – 6.00 (m, 5H), 5.83 (d, *J* = 1.5 Hz, 1H), 4.62 (d, *J* = 10.6 Hz, 1H), 4.55 (d, *J* = 10.6 Hz, 1H), 2.94 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.99, 140.06, 137.85, 136.35, 134.15, 128.78, 128.76, 128.44, 128.11, 128.08, 127.62, 126.69, 120.02, 117.64, 105.89, 82.11, 81.99, 79.35, 67.31. ^{11}B NMR (128 MHz, $CDCl_3$) δ 27.55. HRMS (ESI) *m*/*z* calculated for $C_{28}H_{23}BClN_2O$ $[M+H]^+$: 449.1592, found: 449.1587.

2-(3-(benzyloxy)-3-(4-bromophenyl)pent-1-en-4-yn-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1, 3, 2]diazaborinine (3d): This compound was prepared according to general procedure A described above and obtained as a yellow oil in 85% yield (83.8 mg). R_f = 0.30 (petroleum ether/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 4H), 7.44 – 7.29 (m, 5H), 7.01 (dd, *J* = 8.4, 7.2 Hz, 2H), 6.94 (dd, *J* = 8.4, 1.2 Hz, 2H), 6.07 – 6.04 (m, 3H), 6.03 (s, 2H), 5.83 (d, *J* = 1.6 Hz, 1H), 4.61 (d, *J* = 10.8 Hz, 1H), 4.55 (d, *J* = 10.8 Hz, 1H), 2.94 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.97, 140.60, 137.82, 136.33, 131.70, 128.78, 128.43, 128.40, 128.11, 127.62, 126.72, 122.39, 120.01, 117.64, 105.89, 82.16, 81.90, 79.38, 67.31. ^{11}B NMR (128 MHz, $CDCl_3$) δ 27.48. HRMS (ESI) *m*/*z* calculated for $C_{28}H_{23}BBrN_2O$ $[M+H]^+$: 493.1087, found: 493.1085.

2-(3-(benzyloxy)-3-(4-iodophenyl)pent-1-en-4-yn-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1, 3, 2]diazaborinine (3e): This compound was prepared according to general procedure A described above and obtained as a yellow oil in 76% yield (82.5 mg). R_f = 0.65 (petroleum ether/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.65 (m, 2H), 7.44 – 7.33 (m, 7H), 7.01 (dd, *J* = 8.4, 7.2 Hz, 2H), 6.94 (dd, *J* = 8.3, 1.1 Hz, 2H), 6.07 – 6.04 (m, 3H), 6.03 (s, 2H), 5.83 (d, *J* = 1.5 Hz, 1H), 4.61 (d, *J* = 10.8 Hz, 1H), 4.55 (d, *J* = 10.8 Hz, 1H), 2.94 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.31, 140.97, 137.81, 137.68, 136.33, 128.78, 128.61, 128.43, 128.11, 127.62, 126.75, 120.01, 117.63, 105.89, 94.24, 82.24, 81.86, 79.38, 67.31. ^{11}B NMR (128 MHz, $CDCl_3$) δ 27.88. HRMS (ESI) *m*/*z* calculated for $C_{28}H_{23}BIN_2O$ $[M+H]^+$: 541.0948, found: 541.0952.

2-(3-(benzyloxy)-3-(4-methoxyphenyl)pent-1-en-4-yn-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1, 3, 2]diazaborinine (3f): This compound was prepared according to general procedure A described above and obtained as a colorless oil in 88% yield (77.8 mg). R_f = 0.40 (petroleum ether/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 2H), 7.45 – 7.41 (m, 2H), 7.41 – 7.29 (m, 3H), 7.01 (dd, *J* = 8.2, 7.4 Hz, 2H), 6.94 (dd, *J* = 8.4, 0.8 Hz, 2H), 6.91 – 6.85 (m, 2H), 6.09 – 6.03 (m, 4H), 6.02 (d, *J* = 1.6 Hz, 1H), 5.79 (d, *J* = 1.6 Hz, 1H), 4.62 (d, *J* = 10.8 Hz, 1H), 4.52 (d, *J* = 10.8 Hz, 1H), 3.78 (s, 3H), 2.93 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.51, 141.19, 138.28, 136.37, 133.28, 128.69, 128.36, 128.02, 127.91, 127.62, 125.81, 120.03, 117.46, 113.92, 105.82, 82.67, 82.15, 78.71, 67.08, 55.39. ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.13. HRMS (ESI) *m*/*z* calculated for $C_{29}H_{26}BN_2O_2$ $[M+H]^+$: 445.2087, found: 445.2085.

2-(3-(benzyloxy)-3-(4-(*tert*-butyl)phenyl)pent-1-en-4-yn-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1, 3, 2]diazaborinine (3g): This compound was prepared according to general procedure A described above and obtained as a white solid in 73% yield (68.7 mg). R_f = 0.50 (petroleum ether/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 2H), 7.47 – 7.42 (m, 2H), 7.41 – 7.35 (m, 4H), 7.35 – 7.30 (m, 1H), 7.01 (dd, *J* = 8.3, 7.2 Hz, 2H), 6.94 (dd, *J* = 8.4, 0.8 Hz, 2H), 6.07 (d, *J* = 1.6 Hz, 1H), 6.06 – 6.01 (m, 4H), 5.80 (d, *J* = 1.6 Hz, 1H), 4.64 (d, *J* = 10.4 Hz, 1H), 4.57 (d, *J* = 10.8 Hz, 1H), 2.93 (s, 1H), 1.31 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.16, 141.25, 138.32, 138.11, 136.36, 128.69, 128.35, 127.90, 127.64, 126.36, 125.93, 125.53, 120.05, 117.43, 105.80, 82.68, 82.48, 78.74, 67.13, 34.69, 31.48. ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.75. HRMS (ESI) *m*/*z* calculated for $C_{32}H_{32}BN_2O$ $[M+H]^+$: 471.2608, found: 471.2611.

2-(3-(benzyloxy)-3-(*o*-tolyl)pent-1-en-4-yn-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1, 3, 2]diazaborinine (3h): This compound was prepared according to general procedure A described above and obtained as a white solid in 72% yield (61.4 mg). R_f = 0.65 (petroleum ether/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 7.4, 1.8 Hz, 1H),

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7.45 – 7.28 (m, 5H), 7.28 – 7.20 (m, 2H), 7.20 – 7.16 (m, 1H), 7.01 (dd, J = 8.4, 7.2 Hz, 2H), 6.94 (dd, J = 8.3, 0.9 Hz, 2H), 6.10 – 6.01 (m, 4H), 5.81 (d, J = 1.6 Hz, 1H), 5.78 (d, J = 1.6 Hz, 1H), 4.64 (d, J = 10.8 Hz, 1H), 4.37 (d, J = 10.8 Hz, 1H), 2.93 (s, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.23, 138.24, 137.69, 137.21, 136.37, 132.60, 128.69, 128.59, 128.39, 127.88, 127.62, 126.31, 125.73, 120.03, 117.43, 105.81, 83.09, 82.40, 78.83, 66.73, 21.57. ^{11}B NMR (128 MHz, $CDCl_3$) δ 27.73. HRMS (ESI) *m*/*z* calculated for $C_{29}H_{26}BN_2O$ $[M+H]^+$: 429.2138, found: 429.2141.

2-(3-(benzyloxy)-3-(*m*-tolyl)pent-1-en-4-yn-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1, 3, 2]diazaborinine (3i):This compound was prepared according to general procedure A described above and obtained as a yellow oil in 68% yield (58.5 mg). R_f = 0.45 (petroleum ether/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 4H), 7.40 – 7.31 (m, 3H), 7.27 – 7.22 (m, 1H), 7.10 (d, J = 7.3 Hz, 1H), 7.00 (dd, J = 8.4, 7.2 Hz, 2H), 6.93 (dd, J = 8.4, 1.2 Hz, 2H), 6.06 – 6.01 (m, 3H), 6.01 (s, 2H), 5.80 (d, J = 1.7 Hz, 1H), 4.63 (d, J = 10.4 Hz, 1H), 4.55 (d, J = 10.8 Hz, 1H), 2.91 (s, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.18, 141.12, 138.25, 138.23, 136.35, 129.05, 128.68, 128.45, 128.37, 127.91, 127.61, 127.35, 126.05, 123.73, 120.02, 117.45, 105.80, 82.62, 82.43, 78.80, 67.15, 21.76. ^{11}B NMR (128 MHz, $CDCl_3$) δ 27.75. HRMS (ESI) *m*/*z* calculated for $C_{29}H_{26}BN_2O$ $[M+H]^+$: 429.2138, found: 429.2138.

2-(3-([1,1'-biphenyl]-4-yl)-3-(benzyloxy)pent-1-en-4-yn-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1, 3, 2]diazaborinine (3j): This compound was prepared according to general procedure A described above and obtained as a white solid in 78% yield (76.8 mg). R_f = 0.65 (petroleum ether/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 2H), 7.64 – 7.55 (m, 4H), 7.48 – 7.44 (m, 2H), 7.44 – 7.37 (m, 4H), 7.37 – 7.29 (m, 2H), 7.01 (dd, J = 8.3, 7.3 Hz, 2H), 6.94 (dd, J = 8.4, 0.8 Hz, 2H), 6.11 (d, J = 1.6 Hz, 1H), 6.09 – 6.03 (m, 4H), 5.84 (d, J = 1.6 Hz, 1H), 4.67 (d, J = 10.4 Hz, 1H), 4.60 (d, J = 10.8 Hz, 1H), 2.97 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.15, 141.11, 140.66, 140.32, 138.16, 136.37, 128.89, 128.74, 128.43, 128.00, 127.63, 127.54, 127.34, 127.26, 127.11, 126.29, 120.05, 117.52, 105.86, 82.47, 82.44, 79.07, 67.26. ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.76. HRMS (ESI) *m*/*z* calculated for $C_{34}H_{28}BN_2O$ $[M+H]^+$: 491.2295, found: 491.2293.

2-(3-(benzyloxy)-3-(*p*-tolyl)pent-1-en-4-yn-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1, 3, 2]diazaborinine (3k): This compound was prepared according to general procedure A described above and obtained as a white solid in 78% yield (66.8 mg). R_f = 0.55 (petroleum ether/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 2H), 7.45 – 7.42 (m, 2H), 7.40 – 7.31 (m, 3H), 7.18 – 7.14 (m, 2H), 7.01 (dd, J = 8.4, 7.2 Hz, 2H), 6.93 (dd, J = 8.4, 0.8 Hz, 2H), 6.07 – 6.00 (m, 5H), 5.80 (d, J = 1.6 Hz, 1H), 4.63 (d, J = 10.8 Hz, 1H), 4.54 (d, J = 10.8 Hz, 1H), 2.92 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.20, 138.32, 138.28, 138.01, 136.36, 129.30, 128.69, 128.36, 127.91, 127.62, 126.59, 125.91, 120.03, 117.45, 105.80, 82.63, 82.39, 78.76, 67.10, 21.24. ^{11}B NMR (128 MHz, $CDCl_3$) δ 27.71. HRMS (ESI) *m*/*z* calculated for $C_{29}H_{26}BN_2O$ $[M+H]^+$: 429.2138, found: 429.2130.

2-(3-(benzyloxy)-3-(naphthalen-2-yl)pent-1-en-4-yn-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1, 3, 2]diazaborinine (3l): This compound was prepared according to general procedure A described above and obtained as a colorless oil in 78% yield (72.6 mg). R_f = 0.75 (petroleum ether/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 1.6 Hz, 1H), 7.91 – 7.76 (m, 3H), 7.67 (dd, J = 8.6, 1.9 Hz, 1H), 7.51 – 7.43 (m, 4H), 7.42 – 7.30 (m, 3H), 6.99 (dd, J = 8.3, 7.4 Hz, 2H), 6.92 (dd, J = 8.2, 1.0 Hz, 2H), 6.09 (s, 2H), 6.03 (dd, J = 7.2, 1.2 Hz, 2H), 6.01 (d, J = 1.6 Hz, 1H), 5.83 (d, J = 2.0 Hz, 1H), 4.70 (d, J = 10.4 Hz, 1H), 4.53 (d, J = 10.4 Hz, 1H), 2.99 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.13, 138.44, 138.16, 136.34, 133.21, 133.12, 128.74, 128.54, 128.44, 128.00, 127.73, 127.60, 126.57, 126.44, 126.42, 126.00, 124.57, 120.03, 117.49, 105.83, 82.73, 82.51, 79.18, 67.35. ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.46. HRMS (ESI) *m*/*z* calculated for $C_{32}H_{26}BN_2O$ $[M+H]^+$: 465.2138, found: 465.2145.

2-(3-(benzo[*d*][1, 3]dioxol-5-yl)-3-(benzyloxy)pent-1-en-4-yn-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1, 3, 2]diazaborinine (3m): This compound was prepared according to general procedure A described above and obtained as a white solid in 88% yield (81.1 mg). R_f = 0.45 (petroleum ether/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.28 (m, 5H), 7.13 (dd, J = 8.2, 1.8 Hz, 1H), 7.09 (d, J = 1.6 Hz, 1H), 7.01 (dd, J = 8.2, 7.4 Hz, 2H), 6.94 (dd, J = 8.2, 1.0 Hz, 2H), 6.77 (d, J = 8.4 Hz, 1H), 6.10 – 6.03 (m, 5H), 5.93 (s, 2H), 5.82 (d, J = 2.0 Hz, 1H), 4.60 (d, J = 10.8 Hz, 1H), 4.56 (d, J = 10.4 Hz, 1H), 2.92 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.98, 147.54, 141.12, 138.08, 136.33, 135.35, 128.70, 128.37, 127.96, 127.62, 126.23, 120.20, 120.01, 117.49, 108.04, 107.38, 105.84, 101.36, 82.43, 82.07, 78.83, 67.10. ^{11}B NMR (128 MHz, $CDCl_3$) δ 27.47. HRMS (ESI) *m*/*z* calculated for $C_{29}H_{24}BN_2O_3$ $[M+H]^+$: 459.1880, found: 459.1873.

2-(3-(benzyloxy)-3-(thiophen-2-yl)pent-1-en-4-yn-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1, 3, 2]diazaborinine (3n): This compound was prepared according to general procedure A described above and obtained as a yellow oil in 79% yield (66.8 mg). R_f = 0.75 (petroleum ether/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_2$) δ 7.45 – 7.40 (m, 2H), 7.39 – 7.30 (m, 3H), 7.26 (dd, J = 4.8, 1.2 Hz, 1H), 7.21 (dd, J = 3.6, 1.2 Hz, 1H), 7.02 (dd, J = 8.4, 7.2 Hz, 2H), 6.98 – 6.90 (m, 3H), 6.13 (d, J = 1.2 Hz, 1H), 6.11 (s, 2H), 6.07 (dd, J = 7.2, 0.8 Hz, 2H), 5.79 (d, J = 1.2 Hz, 1H), 4.66 (d, J = 10.8 Hz, 1H), 4.60 (d, J = 10.8 Hz, 1H), 2.95 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.02, 141.14, 137.84, 136.37, 128.69, 128.41, 128.01, 127.63, 126.71, 126.57, 126.49, 126.10, 120.07, 117.53, 105.89, 81.69, 80.08, 78.54, 67.33. ^{11}B NMR (128 MHz, $CDCl_3$) δ 27.90. HRMS (ESI) *m*/*z* calculated for $C_{26}H_{21}BN_2NaOS$ $[M+Na]^+$: 443.1365, found: 443.1365.

2-(3-(benzyloxy)-3-(furan-2-yl)pent-1-en-4-yn-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3o): This compound was prepared according to general procedure A described above and obtained as a yellow oil in 66% yield (53.6 mg). R_f = 0.55 (petroleum ether/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, J = 2.0, 0.8 Hz, 1H), 7.43 – 7.29 (m, 5H), 7.04 (dd, J = 8.0, 7.2 Hz, 2H), 6.97 (dd, J = 8.2, 1.0 Hz, 2H), 6.61 (dd, J = 3.4, 1.0 Hz, 1H), 6.35 (dd, J = 3.4, 1.8 Hz, 1H), 6.19 (s, 2H), 6.10 (dd, J = 7.2, 1.2 Hz, 2H), 6.04 (d, J = 1.4 Hz, 1H), 5.82 (d, J = 1.4 Hz, 1H), 4.68

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(d, J = 10.8 Hz, 1H), 4.45 (d, J = 10.4 Hz, 1H), 2.91 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.68, 143.54, 141.31, 137.79, 136.39, 128.70, 128.52, 128.05, 127.66, 126.71, 120.09, 117.44, 110.41, 110.14, 105.84, 80.57, 78.26, 77.86, 67.51. ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.16. HRMS (ESI) m/z calculated for $C_{26}H_{22}BN_2O_2$ $[M+H]^+$: 405.1774, found: 405.1770.

2-(3-(benzyloxy)-3-(2,3-dihydro-1*H*-inden-2-yl)pent-1-en-4-yn-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3p): This compound was prepared according to general procedure A described above and obtained as a white solid in 70% yield (63.2 mg). R_f = 0.75 (petroleum ether/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.31 (m, 5H), 7.18 – 7.15 (m, 1H), 7.13 – 7.06 (m, 3H), 7.03 (dd, J = 8.4, 7.2 Hz, 2H), 6.96 (dd, J = 8.4, 1.2 Hz, 2H), 6.34 (d, J = 1.6 Hz, 1H), 6.23 (s, 2H), 6.10 (dd, J = 7.0, 1.0 Hz, 2H), 5.93 (d, J = 1.6 Hz, 1H), 4.81 (d, J = 10.8 Hz, 1H), 4.36 (d, J = 10.4 Hz, 1H), 3.46 – 3.29 (m, 1H), 3.25 – 3.08 (m, 2H), 2.89 – 2.69 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.25, 142.25, 140.92, 138.21, 136.37, 128.73, 128.36, 128.25, 127.97, 127.64, 126.37, 126.21, 124.49, 124.33, 120.10, 117.72, 106.02, 85.97, 80.57, 79.76, 67.17, 48.45, 35.65. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.00. HRMS (ESI) m/z calculated for $C_{31}H_{28}BN_2O$ $[M+H]^+$: 455.2295, found: 455.2311.

2-(3-(benzyloxy)-3-ethynylhex-1-en-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1, 3, 2]diazaborinine (3q): This compound was prepared according to general procedure A described above and obtained as a yellow oil in 85% yield (64.4 mg). R_f = 0.65 (petroleum ether/ethyl acetate = 20/1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 4H), 7.35 – 7.29 (m, 1H), 7.05 (dd, J = 8.4, 7.2 Hz, 2H), 6.98 (dd, J = 8.2, 1.0 Hz, 2H), 6.24 (s, 2H), 6.23 (d, J = 1.6 Hz, 1H), 6.12 (dd, J = 7.4, 1.0 Hz, 2H), 5.87 (d, J = 2.0 Hz, 1H), 4.74 (d, J = 10.8 Hz, 1H), 4.33 (d, J = 10.4 Hz, 1H), 2.78 (s, 1H), 2.01 (ddd, J = 13.2, 12.0, 4.6 Hz, 1H), 1.80 (ddd, J = 13.2, 12.0, 4.6 Hz, 1H), 1.64 – 1.52 (m, 1H), 1.45 – 1.30 (m, 1H), 0.91 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.09, 138.21, 136.43, 128.72, 128.56, 127.96, 127.69, 127.64, 120.15, 117.65, 105.99, 82.59, 82.04, 77.96, 67.03, 43.62, 18.23, 14.25. ^{11}B NMR (128 MHz, $CDCl_3$) δ 27.98. HRMS (ESI) m/z calculated for $C_{25}H_{26}BN_2O$ $[M+H]^+$: 381.2138, found: 381.2135.

2-(3-(benzyloxy)-3-phenethylpent-1-en-4-yn-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1, 3, 2]diazaborinine (3r):This compound was prepared according to general procedure A described above and obtained as a colorless oil in 80% yield (71.2 mg). R_f = 0.40 (petroleum ether/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.29 (m, 5H), 7.25 – 7.20 (m, 2H), 7.17 – 7.10 (m, 3H), 7.04 (dd, J = 8.4, 7.2 Hz, 2H), 6.98 (dd, J = 8.2, 1.0 Hz, 2H), 6.29 (d, J = 2.0 Hz, 1H), 6.21 (s, 2H), 6.10 (dd, J = 7.2, 1.2 Hz, 2H), 5.90 (d, J = 2.0 Hz, 1H), 4.78 (d, J = 10.8 Hz, 1H), 4.36 (d, J = 10.8 Hz, 1H), 2.92 (ddd, J = 13.7, 12.0, 4.9 Hz, 1H), 2.86 (s, 1H), 2.73 (ddd, J = 13.9, 11.9, 5.1 Hz, 1H), 2.38 (ddd, J = 13.5, 11.9, 4.9 Hz, 1H), 2.12 (ddd, J = 13.4, 12.0, 5.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.69, 140.97, 138.02, 136.36, 128.74, 128.60, 128.52, 128.44, 128.10, 128.01, 127.66, 125.93, 120.12, 117.67, 106.02, 82.33, 81.60, 78.57, 67.14, 43.02, 31.28. ^{11}B NMR (128 MHz, $CDCl_3$) δ 27.51. HRMS (ESI) m/z calculated for $C_{30}H_{28}BN_2O$ $[M+H]^+$: 443.2295, found: 443.2295.

2-(3-(benzyloxy)-3-cyclohexylpent-1-en-4-yn-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1, 3, 2]diazaborinine (3s): This compound was prepared according to general procedure A described above and obtained as a white solid in 73% yield (61.5 mg). R_f = 0.70 (petroleum ether/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 5H), 7.04 (dd, J = 8.4, 7.2 Hz, 2H), 6.97 (dd, J = 8.4, 1.2 Hz, 2H), 6.25 – 6.17 (m, 3H), 6.09 (dd, J = 7.2, 1.2 Hz, 2H), 5.90 (d, J = 2.4 Hz, 1H), 4.74 (d, J = 10.4 Hz, 1H), 4.29 (d, J = 10.8 Hz, 1H), 2.75 (s, 1H), 2.33 – 2.21 (m, 1H), 1.87 – 1.74 (m, 2H), 1.71 – 1.59 (m, 2H), 1.48 – 1.31 (m, 2H), 1.21 – 1.03 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.15, 138.43, 136.39, 128.67, 128.42, 128.29, 127.86, 127.68, 120.12, 117.57, 105.96, 86.25, 80.46, 78.97, 66.79, 46.20, 28.39, 27.78, 26.57, 26.34, 26.14. ^{11}B NMR (128 MHz, $CDCl_3$) δ 27.58. HRMS (ESI) m/z calculated for $C_{28}H_{30}BN_2O$ $[M+H]^+$: 421.2451, found: 421.2451.

2-(3-(benzyloxy)-3-cyclopropylpent-1-en-4-yn-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1, 3, 2]diazaborinine (3t): This compound was prepared according to general procedure A described above and obtained as a yellow oil in 85% yield (64.3 mg). R_f = 0.65 (petroleum ether/ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.23 (m, 5H), 7.04 (dd, J = 8.0, 7.2 Hz, 2H), 6.97 (dd, J = 8.4, 1.2 Hz, 2H), 6.29 (s, 2H), 6.16 – 6.09 (m, 3H), 5.76 (d, J = 1.6 Hz, 1H), 4.78 (d, J = 10.4 Hz, 1H), 4.46 (d, J = 10.4 Hz, 1H), 2.67 (s, 1H), 1.45 – 1.35 (m, 1H), 0.99 – 0.88 (m, 1H), 0.69 – 0.59 (m, 1H), 0.52 – 0.41 (m, 1H), 0.40 – 0.31 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.15, 138.23, 136.40, 128.74, 128.62, 127.98, 127.68, 125.69, 120.10, 117.55, 105.90, 84.35, 79.03, 78.13, 67.26, 19.16, 4.21, 2.16. ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.00. HRMS (ESI) m/z calculated for $C_{25}H_{24}BN_2O$ $[M+H]^+$: 379.1982, found: 379.1985.

2-(3-(benzyloxy)-3-(2-methoxyethyl)pent-1-en-4-yn-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1, 3, 2]diazaborinine (3u): This compound was prepared according to general procedure A described above and obtained as a yellow oil in 84% yield (66.3 mg). R_f = 0.20 (petroleum ether/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.29 (m, 5H), 7.04 (t, J = 7.7 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 6.24 (s, 3H), 6.12 (d, J = 7.2 Hz, 2H), 5.86 (s, 1H), 4.72 (d, J = 10.4 Hz, 1H), 4.33 (d, J = 10.4 Hz, 1H), 3.73 – 3.60 (m, 1H), 3.59 – 3.48 (m, 1H), 3.28 (s, 3H), 2.82 (s, 1H), 2.46 – 2.30 (m, 1H), 2.25 – 2.09 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.01, 137.91, 136.38, 128.73, 128.51, 128.02, 127.65, 127.62, 120.11, 117.66, 105.99, 81.38, 80.41, 78.40, 69.06, 66.92, 58.63, 40.91. ^{11}B NMR (128 MHz, $CDCl_3$) δ 27.38. HRMS (ESI) m/z calculated for $C_{25}H_{26}BN_2O_2$ $[M+H]^+$: 397.2087, found: 397.2090.

2-(3-(benzyloxy)-3-(cyclohex-1-en-1-yl)pent-1-en-4-yn-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1, 3, 2]diazaborinine (3v): This compound was prepared according to general procedure A described above and obtained as a yellow oil in 78% yield (65.0 mg). R_f = 0.65 (petroleum ether/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.26 (m, 5H), 7.04 (dd, J = 8.4, 7.2 Hz, 2H), 6.96 (dd, J = 8.2, 1.0 Hz, 2H), 6.26 (t, J = 3.8 Hz, 1H), 6.17 (s, 2H), 6.16 – 6.09 (m, 3H),

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5.81 (d, J = 1.9 Hz, 1H), 4.54 (s, 2H), 2.79 (s, 1H), 2.19 – 1.90 (m, 4H), 1.71 – 1.52 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.30, 138.47, 136.82, 136.38, 128.58, 128.14, 127.72, 127.65, 126.33, 125.86, 120.02, 117.38, 105.76, 83.29, 82.14, 77.76, 66.56, 25.40, 24.33, 22.90, 22.38. ^{11}B NMR (128 MHz, $CDCl_3$) δ 27.69. HRMS (ESI) m/z calculated for $C_{28}H_{28}BN_2O$ $[M+H]^+$: 419.2295, found: 419.2303.

(*E*)-2-(3-(benzyloxy)-3-ethynylhexa-1,4-dien-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1, 3, 2]diazaborinine (3w): This compound was prepared according to general procedure A described above and obtained as a yellow oil in 78% yield (59.2 mg). R_f = 0.50 (petroleum ether/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.29 (m, 5H), 7.05 (dd, J = 8.2, 7.4 Hz, 2H), 6.97 (dd, J = 8.2, 1.0 Hz, 2H), 6.23 (s, 2H), 6.18 – 6.07 (m, 4H), 5.76 (d, J = 1.6 Hz, 1H), 5.68 (dq, J = 15.3, 1.6 Hz, 1H), 4.63 (d, J = 10.8 Hz, 1H), 4.52 (d, J = 10.8 Hz, 1H), 2.88 (s, 1H), 1.76 (dd, J = 6.4, 1.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.20, 138.20, 136.40, 131.65, 129.18, 128.71, 128.55, 127.95, 127.66, 125.75, 120.09, 117.52, 105.87, 81.49, 81.14, 78.77, 66.92, 17.75. ^{11}B NMR (128 MHz, $CDCl_3$) δ 27.99. HRMS (ESI) m/z calculated for $C_{25}H_{24}BN_2O$ $[M+H]^+$: 379.1982, found: 379.1984.

(*E*)-2-(3-(benzyloxy)-3-ethynyl-5-phenylpenta-1,4-dien-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1, 3, 2]diazaborinine (3x): This compound was prepared according to general procedure A described above and obtained as a white solid in 80% yield (70.4 mg). R_f = 0.45 (petroleum ether/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.21 (m, 10H), 7.09 – 6.94 (m, 5H), 6.35 (d, J = 16.0 Hz, 1H), 6.26 (s, 2H), 6.21 (d, J = 1.6 Hz, 1H), 6.12 (dd, J = 7.2, 0.8 Hz, 2H), 5.81 (d, J = 1.6 Hz, 1H), 4.68 (d, J = 10.8 Hz, 1H), 4.62 (d, J = 10.8 Hz, 1H), 2.98 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.13, 138.06, 136.37, 135.97, 132.60, 129.72, 128.75, 128.74, 128.56, 128.35, 128.03, 127.65, 127.06, 126.12, 120.11, 117.57, 105.93, 81.72, 80.78, 79.34, 67.20. ^{11}B NMR (128 MHz, $CDCl_3$) δ 27.81. HRMS (ESI) m/z calculated for $C_{30}H_{26}BN_2O$ $[M+H]^+$: 441.2138, found: 441.2136.

2-(3-methoxy-3-phenylpent-1-en-4-yn-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1, 3, 2]diazaborinine (3y): This compound was prepared according to general procedure A described above and obtained as a yellow oil in 83% yield (56.4 mg). R_f = 0.45 (petroleum ether/ethyl acetate = 20/1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.51 (m, 2H), 7.39 – 7.31 (m, 2H), 7.31 – 7.24 (m, 1H), 7.02 (dd, J = 8.4, 7.2 Hz, 2H), 6.95 (dd, J = 8.4, 1.2 Hz, 2H), 6.18 (dd, J = 6.8, 1.0 Hz, 2H), 6.07 (d, J = 1.6 Hz, 1H), 5.89 (s, 2H), 5.80 (d, J = 1.6 Hz, 1H), 3.39 (s, 3H), 2.86 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.28, 141.11, 136.37, 128.53, 128.20, 127.61, 126.55, 126.02, 119.99, 117.55, 105.90, 82.43, 82.24, 78.60, 52.32. ^{11}B NMR (128 MHz, $CDCl_3$) δ 27.89. HRMS (ESI) m/z calculated for $C_{22}H_{20}BN_2O$ $[M+H]^+$: 339.1669, found: 339.1675.

2-(3-(benzyloxy)-3-phenylpent-1-en-4-yn-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5): This compound was prepared according to procedure C described above. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.62 (m, 2H), 7.48 – 7.41 (m, 2H), 7.36 – 7.26 (m, 4H), 7.29 – 7.18 (m, 2H), 6.25 (d, J = 2.4 Hz, 1H), 5.99 (d, J = 2.4 Hz, 1H), 4.65 (d, J = 11.2 Hz, 1H), 4.42 (d, J = 11.6 Hz, 1H), 2.82 (s, 1H), 1.10 (d, J = 3.2 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.66, 139.14, 129.33, 128.14, 127.88, 127.76, 127.61, 127.20, 127.14, 83.46, 82.79, 80.64, 77.50, 66.57, 24.66, 24.56. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.80. HRMS (ESI) m/z calculated for $C_{24}H_{28}BO_3$ $[M+H]^+$: 375.2132, found: 375.2132.

3-(benzyloxy)-3-phenylpent-4-yn-2-one (6): This compound was prepared according to procedure D described above. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 2H), 7.36 – 7.16 (m, 8H), 4.62 (d, J = 10.8 Hz, 1H), 4.39 (d, J = 11.2 Hz, 1H), 2.84 (s, 1H), 2.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.74, 137.76, 136.58, 129.10, 128.79, 128.43, 127.78, 127.76, 126.94, 85.10, 79.46, 79.31, 67.84, 24.62. HRMS (ESI) m/z calculated for $C_{18}H_{17}O_2$ $[M+H]^+$: 265.1229, found: 265.1232.

2-(3-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-3-(benzyloxy)-3-phenylprop-1-en-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1, 3, 2]diazaborinine (7): This compound was prepared according to procedure E described above. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.48 (m, 2H), 7.36 – 7.22 (m, 11H), 7.18 – 7.16 (m, 1H), 7.15 – 7.09 (m, 2H), 6.98 (t, J = 7.6 Hz, 2H), 6.90 (d, J = 8.0, 2H), 6.17 (s, 2H), 6.03 (d, J = 7.2 Hz, 2H), 5.90 (s, 1H), 5.79 (s, 1H), 5.50 – 5.31 (m, 2H), 4.61 (d, J = 11.6 Hz, 1H), 4.56 (d, J = 11.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.12, 142.09, 141.22, 138.75, 136.25, 134.64, 129.09, 128.66, 128.49, 128.29, 127.86, 127.82, 127.77, 127.63, 127.53, 127.47, 127.03, 123.81, 119.85, 117.21, 105.73, 83.48, 66.66, 54.03. ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.01. HRMS (ESI) m/z calculated for $C_{35}H_{31}BN_5O$ $[M+H]^+$: 548.2622, found: 548.2631.

2-(3-(benzyloxy)-3,5-diphenylpent-1-en-4-yn-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1, 3, 2]diazaborinine (8):

This compound was prepared according to procedure F described above. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, J = 8.4, 1.4 Hz, 2H), 7.53 – 7.43 (m, 4H), 7.42 – 7.33 (m, 4H), 7.36 – 7.24 (m, 5H), 7.01 (dd, J = 8.2, 7.2 Hz, 2H), 6.93 (dd, J = 8.2, 1.0 Hz, 2H), 6.11 (d, J = 2.0 Hz, 1H), 6.08 (s, 2H), 6.05 (dd, J = 7.2, 1.2 Hz, 2H), 5.81 (d, J = 2.0 Hz, 1H), 4.73 (d, J = 10.8 Hz, 1H), 4.63 (d, J = 11.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.74, 141.19, 138.42, 136.33, 131.88, 128.86, 128.68, 128.56, 128.50, 128.30, 128.13, 127.87, 127.61, 126.79, 125.75, 122.39, 120.01, 117.42, 105.78, 90.93, 87.99, 83.06, 67.21. ^{11}B NMR (128 MHz, $CDCl_3$) δ 27.32. HRMS (ESI) m/z calculated for $C_{34}H_{28}BN_2O$ $[M+H]^+$: 491.2295, found: 491.2297.

Supporting information

The supporting information for this article can be found online at https://doi.org/10.52396/JUSTC-2022-0074.

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Conflict of interest

The authors declare that they have no conflict of interest.

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